Catalyzed Reactions of Enol Ethers with S_N1 Active Groups: A Novel Method for the Preparation of α-Alkylated Ketones

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Abstract: The performance of *tert*-alkylations, alkoxyalkylations, and aldehyde enolate allylations proceeding with low catalyst loading (0.1 mol % – 5 mol %) is described. The reactions are complete within short times and can even be performed without solvent and under ambient conditions. The mechanism of the reaction was investigated by deuterium labeling and cross-over studies.

Keywords: alkylation; boron; catalysis; copper; enolates; Lewis acids; ketones

Introduction

The alkylation of ketone enolates constitutes one of the central reactions for the formation of carbon-carbon bonds in chemistry. To achieve this transformation enolates are usually generated under strongly basic conditions and are further reacted with an alkylating reagent.[1] More recently, these transformations have been achieved in the presence of catalysts.[2] In spite of intense efforts a drawback of these procedures is that high regio- and stereoselectivity of enolate generation is not always easy to achieve, especially in the case of ketones with sterically similar substituents. Also, the atom economy of the overall process is usually low.[3] A different concept developed by Reetz allows for the reaction of S_N1 active electrophiles with silyl enol ethers in the presence of stoichiometric amounts of Lewis acids.[4] However, a general reaction catalytically generating an alkylating reagent for a suitable enolate or enol derivative has remained elusive.

We decided to address exactly these issues by employing enol ethers as enolate equivalents that can be cleaved in an S_N1 manner as precursors for this type of transformation. The method is based on reports that many simple ethers can be cleaved in the presence of Lewis acids.[5] A less general concept has been realized in Ferrier-type rearrangements.[6] To the best of our knowledge, a catalytic or enantioselective variation of these systems has, as yet, not been described. The general idea of the reaction is depicted in Figure 1.

Efficient and well established methods for the synthesis of enol ethers are olefinations of esters and isomerizations of allyl ethers either by transition metal complexes or base.[7] The necessary starting materials are thus readily available.

Results and Discussion

We reasoned that useful precursors for the planned transformation would be *p*-methoxybenzyl (PMB) enol ethers, adamantyl enol ethers, enol ethers of acetals, and allyl enol ethers in reactions with protic acids or strong Lewis acids as potential catalysts. All compounds would, after acid-induced cleavage of the oxygen-carbon bond, lead to enolates and stabilized cations.[8]

Initial Optimization of the Reaction Conditions

The results of our exploratory studies with substrates **1**, **2**, and **3** are summarized in Table 1.

When **1**, that was used as 78:22 mixture of (*Z*) and (*E*) isomers, was exposed to $BF_3 \cdot Et_2O$, $Cu(OTf)_2$,[9] or $B(C_6F_5)_3$,[10] the desired product **4** could be obtained in good yield (75 – 84%) with low catalyst loading (entries 1 – 3). The reactions were run at high concentration (1 M).

In the case of starting material **2** the same Lewis acids also lead to satisfactory results in CH_2Cl_2 at 1 M to 3 M concentration and room temperature. It is interesting to note that for both $B(C_6F_5)_3$ and $Cu(OTf)_2$ a reduction in catalysts loading to 0.1 and 0.25 mol % (entries 4 and 5)

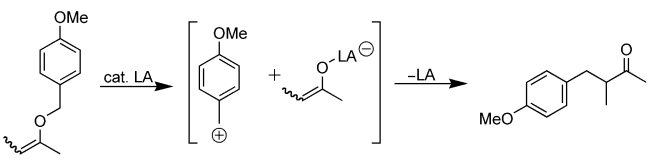

Figure 1. Concept for the Lewis acid-catalyzed alkylation of enolates.

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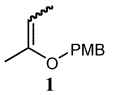
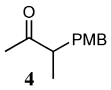
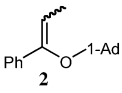
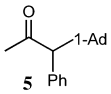
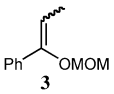
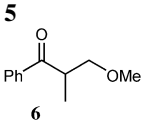
Table 1. Lewis acid catalyzed reaction of enol ethers in CH_2Cl_2.

Entry	Substrate	Product	Catalyst	Yield [%]
1	 **1**	 **4**	$B(C_6F_5)_3$, 1 mol %	84[a]
2	**1**	**4**	$Cu(OTf)_2$, 5 mol %	77[a]
3	**1**	**4**	$BF_3 \cdot Et_2O$, 5 mol %	75[a]
4	 **2**	 **5**	$B(C_6F_5)_3$, 0.1 mol %	84[b]
5	**2**	**5**	$Cu(OTf)_2$, 0.25 mol %	87[b]
6	**2**	**5**	$BF_3 \cdot Et_2O$, 5 mol %	86[c]
7	**2**	**5**	Bu_2BOTf, 1 mol %	85
8	 **3**	 **6**	$B(C_6F_5)_3$, 0.1 mol %	54 : 40[d] (**6**/PhCOEt)
9	**3**	**6**	$Cu(OTf)_2$, 0.25 mol %	81[e]
10	**3**	**6**	$BF_3 \cdot Et_2O$, 5 mol %	73[e]
11	**3**	**6**	Bu_2BOTf, 1 mol %	83[f]

[a] **1**: $Z/E = 78:22$; 1 M.
[b] **2**: $Z/E = 80:20$; 3 M.
[c] **2**: $Z/E = 80:20$; 1 M.
[d] By GC-analysis of the crude mixture.
[e] **3**: $Z/E = 84:16$; 2 M.
[f] **3**: $Z/E = 84:16$; 1 M.

led to a small but noticeable increase in the yield (84% and 87%) of **5** compared to reactions performed with 1 or 5 mol % catalyst (79% and 68% yield). It should be noted that Bu_2BOTf was a suitable catalyst for the rearrangement reaction, also. An 85% yield of **5** could be obtained with a low catalyst loading of 1 mol % (entry 7).

A different outcome was observed with substrate **3**. In this case $Cu(OTf)_2$ (83%, 1 mol %, 5 min, entry 9), $BF_3 \cdot Et_2O$ (73%, 5 mol %, entry 10), and Bu_2BOTf (83%, 1 mol %, entry 11) led to satisfactory results in CH_2Cl_2 (1 M). With $B(C_6F_5)_3$ a 54 : 40 mixture of **6** and propiophenone was obtained (entry 8). A possible reason for this failure of the reaction could be deactivation of the sterically demanding catalyst by complexation of the ether group present in **6**.

We also tested some protic acids (TfOH, aqueous HCl, HOAc, 10-CSA, BOC-proline, and TFA) as catalysts in reactions with **3**. Of these reagents, only TfOH (*ca.* 10 mol %) led to appreciable amounts of desired product (72% **6** and 15% propiophenone) as judged by GC analysis of the reaction mixture.

In the case of the readily accessible allyl enol ethers, care has to be taken in distinguishing the desired enolate allylation from a concerted [3,3]-Claisen rearrangement. We chose substrate **7** shown in Figure 2 to address this possible mechanistic ambiguity.

Because of the formation of an unsymmetrically substituted allyl cation it was assumed that the alkylation would deliver the product resulting from attack at the least hindered site of the cation. Formally, this would result in the product of a [1,3]-rearrangement.[11,12] As demonstrated in Table 2 this regioselectivity was indeed exclusively observed and only the [1,3]-product was obtained.

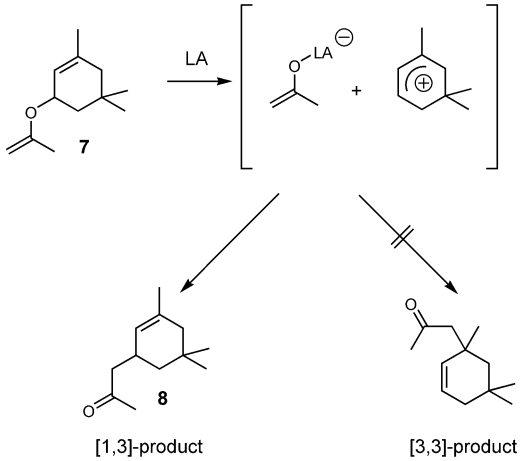


Figure 2. Ionic pathway for the synthesis of [1,3]-Claisen products.

As in the case of **3** it turned out that the use of both $BF_3 \cdot Et_2O$ (entry 1) and $Cu(OTf)_2$ (entry 2) resulted in efficient catalytic turn-over and 72% and 60% isolated yields of **8**. With $BF_3 \cdot Et_2O$ lowering the reaction

temperature to $-78\,^{\circ}C$ resulted in a decreased yield of 55% (entry 1, see footnote). $B(C_6F_5)_3$ performed distinctly inferior to give **8** in only 30% yield. However, analysis of the crude reaction mixture revealed complete consumption of the starting material. This result could be explained by an elimination reaction of a proton from the allyl cation by the enolate. We were unable to isolate the diene, however. Because of the high steric bulk of $B(C_6F_5)_3$ this side reaction should be more relevant than for the less hindered reagents $BF_3 \cdot Et_2O$ and $Cu(OTf)_2$. This point will be discussed more thoroughly, later (see Table 4).

Scope and Limitation of the Lewis Acid-Catalyzed Rearrangement

With a set of reliable reaction conditions in hand we turned our attention to the scope and limitation of the reaction next.

The results with some enol ethers leading to stabilized saturated cations are summarized in Table 3.

It turned out that for all cases with the PMB enol ethers examined the yields were reasonable to high and that $B(C_6F_5)_3$ was slightly superior to $Cu(OTf)_2$. Reaction times were extremely short (< 5 min). Lowering of the reaction temperature to $-30\,^{\circ}C$ still resulted in a very fast reaction (< 5 min) and essentially the same yield (entry 4b). Entry 4 also demonstrates the specific usefulness of our enol ether method. 3-Nonanone, the starting material for enolate alkylation under basic conditions, cannot be deprotonated regioselectively in the presence of bases.[13] Performing the reaction under an atmosphere of air in undistilled and undried solvent was possible (entries 2 and 3) with just a slight reduction in yield.

The importance of the stabilization of the cation was manifested by the observation that exposure of the corresponding benzyl ethers to the Lewis acids did not give any of the desired products. Instead, intractable mixtures of products containing varying amounts of the ketones resulting from protic cleavage were obtained.

We also investigated the possibility of performing the reaction in the absence of solvent. The reaction of **3** proceeded smoothly to give **5** in 72% isolated yield in the presence of 0.1 mol % $Cu(OTf)_2$. The reaction of **15**, possessing an additional methoxy group also proceeded eventlessly with $Cu(OTf)_2$ and $BF_3 \cdot Et_2O$ (entry 7 and footnotes) indicating that both Lewis acids are not prone to product inhibition by ethers.

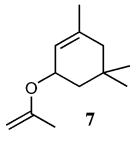
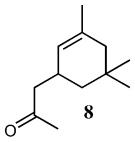
In the case of tertiary cations that are not stabilized by conjugation it is important to note the difference between the 1-adamantyl and *tert*-butyl enol ethers. Because the 1-adamantyl cation is relatively stable towards elimination, the strained bridgehead olefin adamantene[14] would be formed, excellent results can be obtained. In contrast, from the *tert*-butyl cation a proton can be readily eliminated to yield 2-methylpropene by the strongly basic enolate. It therefore came as no surprise that the attempted *tert*-alkylation using **19** gave a mixture of the desired product **20** in 32% yield and propiophenone in 40% yield (entry 9). So far it has been impossible to generate secondary cations under our reaction conditions.

The Lewis acid-catalyzed rearrangement of allyl enol ethers also proved to be fairly general as summarized in Table 4.

As shown in entries 1 and 2 enol ethers **21** and **23** could be rearranged in reasonable to high yields with low catalyst loadings. A proof for the non-concerted mechanism of formation of **24** will be presented in the following paragraph. It should be noted that catalysis of the [3,3]-rearrangement of **23** by Yamamoto' s excellent bulky aluminum reagents gave inferior results in his hands concerning both yield and catalyst loading (10 mol %, 45% yield after 13 h).[12c]

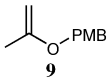
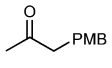
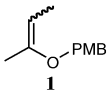
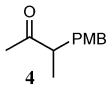
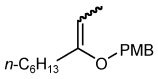
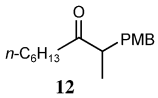
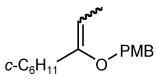
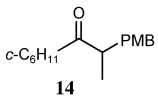
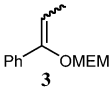
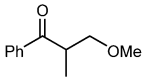
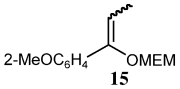
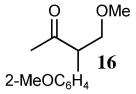
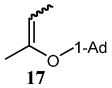
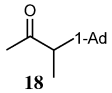
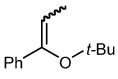
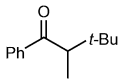
Increasing the steric bulk compared to our initial substrate **7** by introduction of a *tert*-butyl group (substrate **25**, entry 3) resulted in a slight reduction in yield (63%).When the double bond carried an additional terminal methyl substituent (entries 4 and 5) the yields again deteriorated slightly. The reaction of the propiophenone-derived enol ether **31** is interesting with regard to the mechanism of the reaction. The reduction in the

Table 2. Lewis acid catalyzed reaction of allyl enol ethers in CH_2Cl_2.

Entry	Substrate	Product	Catalyst	Yield [%]
1	 **7**	 **8**	$BF_3 \cdot Et_2O$, 7 mol %	72[a]
2	**7**	**8**	$Cu(OTf)_2$, 5 mol %	60[b]
3	**7**	**8**	$B(C_6F_5)_3$, 1 mol %	30[c]

[a] 0.1 M; $-78\,^{\circ}C$ 55%.
[b] 1 M; $-55\,^{\circ}C$.
[c] 1 M.

Table 3. Lewis acid-catalyzed reaction of allyl vinyl ethers in CH_2Cl_2 (1 M).

Entry	Substrate	Product	Catalyst	Yield [%]
1	 **9**	 **10**	$B(C_6F_5)_3$, 1 mol %	78[a]
2	**9**	**10**	$B(C_6F_5)_3$, 1 mol % in air	67[b, c]
3	 **1**	 **4**	$B(C_6F_5)_3$, 1 mol % in air	80[d]
4	 **11**	 **12**	$B(C_6F_5)_3$, 1 mol %	71[b, c]
5	 **13**	 **14**	$B(C_6F_5)_3$, 1 mol %	71[e]
6	 **3**	 **6**	$Cu(OTf)_2$, 0.1 mol %, neat	72
7	 **15**	 **16**	$Cu(OTf)_2$, 1 mol %	71[f]
8	 **17**	 **18**	$B(C_6F_5)_3$, 1 mol %, 3 M	69[g]
9	 **19**	 **20**	$BF_3 \cdot Et_2O$, 5 mol %	32[h]

[a] 1 mol % $Cu(OTf)_2$ 64%.
[b] **9**: $Z/E = 88:12$; $-30\,^{\circ}C$ 66%.
[c] 1 mol % $Cu(OTf)_2$ 70%.
[d] **1**: $Z/E = 78:22$, 5 mol % $BF_3 \cdot Et_2O$ 65%.
[e] 1 mol % $Cu(OTf)_2$ 71%.
[e] **13**: $Z/E = 80:20$.
[f] **15**: $Z/E = 80:20$.
[g] **17**: $Z/E = 83:17$; 1 mol % $Cu(OTf)_2$ 70%.
[h] **19**: $Z/E = 80:20$; 1 M, $-78\,^{\circ}C$ to rt.

basicity of the enolate through conjugation with the aromatic ring results in good to reasonable yields of **32** for all three catalysts investigated. Only minor amounts of propiophenone were obtained. This observation lends support to our hypothesis of base-induced eliminations as undesired side reactions.

The reaction could also be successfully performed with allyl and methallyl enol ethers as described in entries 7 and 8. In the case of the allyl enol ether a 54% yield of **34** could be obtained at $-40\,^{\circ}C$. At lower temperature no rearrangement was observed. Increasing the temperature led to substantial reductions of the isolated yield, e.g., 26% at room temperature. The corresponding methallyl enol ether **35** could already be cleaved at $-65\,^{\circ}C$ to give the desired product **36** in 75% yield. At $-15\,^{\circ}C$ a 62% yield of **36** was obtained.

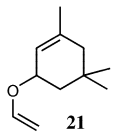
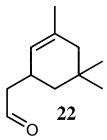
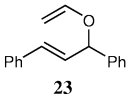
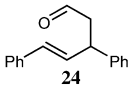
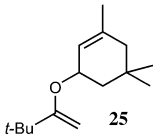
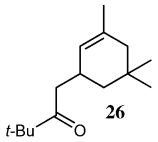
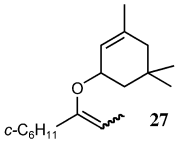
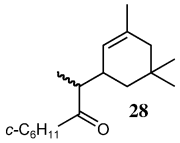
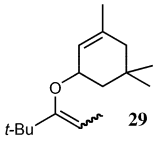
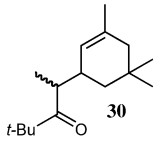
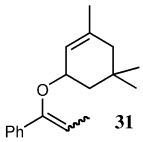
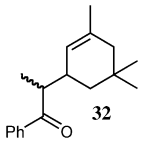
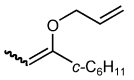
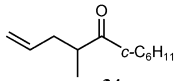
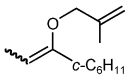
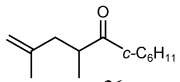
The ease of cleavage of **35** and increased yields of **36**, especially at low temperatures, constitutes a reflection of the increased stability of the methallyl cation. For a proof of the non-concerted nature of the reaction see the following mechanistic discussion.

Our method is therefore superior to the method introduced by Grieco that uses the highly polar 5 M solutions of $LiClO_4$ in Et_2O to induce [1,3]-rearrangements.[15] With this reagent only tri- or tetrasubstituted allyl cations could be generated. Therefore, the Lewis acidity of the $LiClO_4$ system must be considered as substantially lower than our systems. Moreover, it has been reported that the $LiClO_4$/diethyl ether reagent is potentially hazardous.[16]

Mechanistic Considerations

In our initial mechanistic studies we were concerned with a proof of the non-concerted pathway for the

Table 4. Lewis acid-catalyzed reaction of allyl vinyl ethers in CH_2Cl_2 (1 M).

Entry	Substrate	Product	Catalyst	Yield [%]
1	 **21**	 **22**	$BF_3 \cdot Et_2O$, 5 mol %, 0.01 M	84[a]
2	 **23**	 **24**	$B(C_6F_5)_3$, 0.25 mol %	82[b]
3	 **25**	 **26**	$BF_3 \cdot Et_2O$, 5 mol %, 0.1 M	63
4	 **27**	 **28**	$Cu(OTf)_2$, 5 mol %, $-15\,^{\circ}C$	59[c]
5	 **29**	 **30**	$BF_3 \cdot Et_2O$, 5 mol %, 0.1 M	59[d]
6	 **31**	 **32**	$Cu(OTf)_2$, 5 mol %, $-40\,^{\circ}C$	77[e]
7	 **33**	 **34**	$Cu(OTf)_2$, 5 mol %, $-40\,^{\circ}C$	54
8	 **35**	 **36**	$Cu(OTf)_2$, 5 mol %, $-65\,^{\circ}C$	75

[a] 1 mol % $Cu(OTf)_2$ 64%; 1 mol % $B(C_6F_5)_3$, 0.1 M, 72%.
[b] 5 mol % $Cu(OTf)_2$, 67%.
[c] 1 mol % $Cu(OTf)_2$, 0.5 M, $-15\,^{\circ}C$, 59%, dr = 69 : 31.
[d] 5 mol % $Cu(OTf)_2$ 40%, dr = 64 : 36.
[e] **31**: *Z*/*E* = 91 : 9, 5 mol % $BF_3 \cdot Et_2O$, 0.1 M, 83%, 1 mol % $B(C_6F_5)_3$, 0.1 M, 54%.

symmetrical allyl cations (Table 4, entries 2, 7, and 8). As shown in Figure 3 it was demonstrated by deuterium labeling studies in two of the three cases that attack of the enolate on the allyl cation occurred without regioselectivity. This would not have been the case in a concerted [3,3]-Claisen rearrangement. We did not investigate the allyl enol ether because of the volatility of deuterated allyl alcohol necessary for the synthesis of labeled **33**.

A question of general importance for the mechanism of the reaction concerns the problem of attack of the cation on either the generated enolate or on a second enol ether. The latter situation is depicted in Figure 4. In the former case a reagent-controlled course of the alkylation should become possible by ligand variation of the catalyst. In the latter case a chain mechanism would be operating with the usual consequence of a substrate-controlled transformation.

This course of events seems unlikely when considering the results of Tables 1 – 4. Once a cation is generated the further progress of the transformation should be independent of the potential initiator and should also be general within a series of similar substrates. This was not observed, however. Especially in the case of the $B(C_6F_5)_3$-catalyzed enolate allylations the less basic enolates (Table 4, entry 6 and footnotes) give reason-

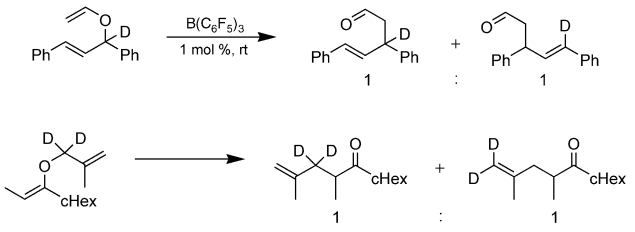


Figure 3. Deuterium labeling studies as proof of a non-concerted mechanism.

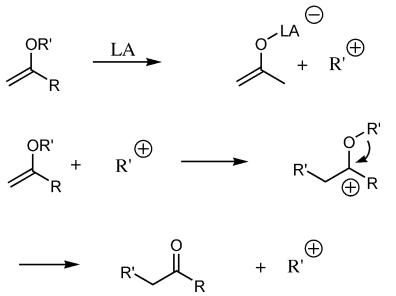


Figure 4. Addition to enol ethers *via* a chain mechanism as alternative to enolate alkylation.

able results, whereas the other more basic enolates essentially result in the failure of the reaction. Besides, the presence of the ketones arising from protonation of the enol ether moiety cannot be readily explained by the chain mechanism. Thus, our reactions did in deed seem to proceed *via* the reaction of enolates with cations.

Another question of mechanistic interest is concerned with the persistence of the ions generated under the reaction conditions. This problem can be addressed experimentally by cross-over studies. The result of a typical experiment is summarized in Figure 5.

All possible products were observed in the GC analysis of the crude reaction mixture in substantial amounts. It should be noted that the numbers refer to the intensities of the corresponding GC signals and do not represent isolated yields. It was impossible to separate the four products.

Thus, the ions generated under our conditions were able to diffuse freely before recombination and should not be considered as contact ion pairs according to the Winstein nomenclature.[17]

Conclusion

In conclusion, we have devised an efficient catalytic system for the alkylation and allylation of enolates based on the Lewis acid-catalyzed cleavage of enol ethers. We anticipate that the mild reaction conditions, insensitivity to ambient exposure, low catalyst loading, and high to excellent turnover frequencies of our system meet the demands for efficient synthesis and will thus lead to considerable use in organic synthesis.

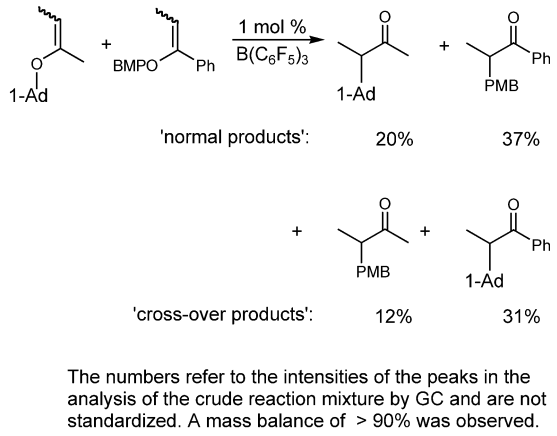


Figure 5. Cross-over study as evidence for long-lived ionic intermediates.

Experimental Section

Typical Experimental Procedures for the Syntheses of Enol Ethers

General Procedure A – Olefination of Esters[18]: Under an argon atmosphere a 1.0 M solution of $TiCl_4$ (4 equiv.) in CH_2Cl_2 was added at 0 °C to dry THF. After the resulting yellow suspension was warmed to room temperature TMEDA (8 equiv.) was added and the brown solution was stirred for 10 min. Zinc (9 equiv.) was added and after the color of the suspension had changed from brown to dark greenish blue (*ca.* 30 min) the 1,1-dibromoalkanes (2.2 equiv.) and the ester (1 equiv.) were added simultaneously and the mixture was stirred overnight. After ice-cooled hydrolysis by a saturated K_2CO_3 solution the complete reaction mixture was filtered through a short column of alumina (Merck, aluminum oxide 90 standardized) using diethyl ether as eluent. The solvent was removed under reduced pressure and the residue purified by column chromatography on alumina to yield the corresponding enol ether.

General Procedure B – Mercury-Catalyzed Vinylation of Allylic Alcohols[19]: Mercury(II) acetate (0.2 equiv) was dried prior to the reaction by gentle heating under vacuum and dissolved under an argon atmosphere in freshly distilled ethyl vinyl ether. To this solution the allylic alcohol (1 equiv) was added and the mixture was stirred for 5 days at ambient temperature. The resulting solution was washed 3 times with H_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was isolated by filtration through a short column of alumina (Merck, aluminum oxide 90, standardized) using pentane as a solvent to yield the corresponding allyl vinyl ether.

Typical Experimental Procedures for the Rearrangement Reactions

General Procedure C: The solid catalyst $B(C_6F_5)_3$ or $Cu(OTf)_2$ was dried by gentle heating (1 min) under vacuum and was dissolved under an argon atmosphere in CH_2Cl_2 at the indicated temperature. After addition of the enol ether stirring

was continued for the declared time. The conversion of the starting material was monitored by TLC and GC analysis. After quenching by addition of 3 drops of triethylamine the solvent was removed and the residue purified immediately by SiO_2 chromatography to give the desired ketone.

General Procedure D: Under an argon atmosphere the enol ether was dissolved in dichloromethane at the indicated temperature. After the addition of the liquid catalyst $BF_3 \cdot OEt_2$ or *n*-Bu_2BOTf (1.0 M in CH_2Cl_2) the solution was stirred until complete conversion of the starting material was monitored by TLC and GC analysis. The catalyst was quenched by addition of 3 drops of NEt_3. After removal of the solvent the crude product was purified immediately by SiO_2 chromatography to yield the desired ketone.

1-Methoxy-4-(1-methylpropenyloxymethyl)-benzene (1)

According to the General Procedure A: $TiCl_4$ (20 mL (1.0 M in CH_2Cl_2), 20 mmol) in THF (150 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), and acetic acid 4-methoxybenzylic ester (0.90 g, 5 mmol). The reaction mixture was stirred over night. Standard work-up followed by column chromatography (Al_2O_3, PE:Et_2O, 95:5) afforded **1** as a colorless oil; yield: 0.54 g (2.8 mmol, 60%); *Z/E* = 78:22; R_f (PE, Al_2O_3): 0.2; ^{1}H NMR (300 MHz, C_6D_6): AA'XX' system with signals at δ = 7.31 and 6.89 (4H)**, 4.67 (s, 2H), 4.65* (s, 2H), 4.62 (m, 1H), 3.42 (s, 3H)**, 1.92* (s, 3H), 1.84 (d, *J* = 6.7 Hz, 3H), 1.79 (t, *J* = 1.3 Hz, 3H), 1.66* (dd, *J* = 6.8 Hz, 0.8 Hz, 3H). ^{13}C-NMR (75 MHz, C_6D_6): δ = 159.7, 153.2*, 150.9, 131.0*, 130.3, 129.2*, 129.0, 114.0, 103.8, 91.4*, 69.4, 68.5, 54.7, 18.2, 16.1*, 12.0*, 10.5; HRMS (EI, 70 eV): calcd. for (M^+): 192.1150; found: 192.1151; IR (neat): ν = 2915, 1685, 1615, 1550, 1465, 1380, 1305, 1250, 1175, 1100, 1035, 820 cm^{-1}. *signals of the minor isomer, ** signals of minor and major isomer not separated.

1-(1-Phenylpropenyloxy)-adamantane (2)

According to the General Procedure A: $TiCl_4$ (40 mL (1.0 M in CH_2Cl_2), 40 mmol) in THF (150 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete 1,1-dibromoethane (2.7 mL, 22 mmol), and 1-adamantyl benzoate (2.56 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **2** as a colorless oil; yield: 2.5 g (9.3 mmol, 93%). *Z/E* = 80:20; R_f (PE, Al_2O_3): 0.6; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.59–7.49** (m, 2H), 7.19–7.11** (m, 2H), 7.09–7.03** (m, 1H), 5.46* (q, *J* = 7.3 Hz, 1H), 5.37 (q, *J* = 6.8 Hz, 1H), 1.93–1.83** (m, 10H), 1.41* (m_c, 2H), 1.34 (m_c, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 151.9, 150.2*, 142.8, 139.9*, 129.0, 128.1*, 127.3, 126.4*, 113.9, 113.3*, 78.4, 76.8*, 44.0, 43.7*, 36.5, 36.4*, 31.3, 31.2*, 13.3, 13.0*; HRMS (EI, 70 eV): calcd. for (M^+): 268.1827; found: 268.1822; IR (neat), ν = 2910, 2850, 1445, 1355, 1325, 1300, 1100, 1065, 780, 700 cm^{-1}. * signals of the minor isomer; ** signals of minor and major isomer not separated.

(1-Methoxymethoxypropenyl)-benzene (3)[20]

According to the General Procedure A: $TiCl_4$ (40 mL (1.0 M in CH_2Cl_2), 40 mmol) in THF (150 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete 1,1-dibromoethane (2.70 mL, 22 mmol), and benzoic acid methoxymethyl ester (1.66 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **3** as a colorless oil; yield: 1.10 g (6.2 mmol, 62%). *Z/E* = 83:17; R_f (PE, Al_2O_3): 0.2. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.48–7.39** (m, 2H), 7.13–7.09** (m, 2H), 7.08–7.01** (m, 1H), 5.26 * (m, 1H), 5.24 (q, *J* = 6.9 Hz, 1H), 4.80* (s, 2H), 4.70 (s, 2H), 3.24 (s, 3H), 3.21* (s, 3H), 1.80 (d, *J* = 6.8 Hz, 3H), 1.60 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 153.4, 137.2, 136.1*, 128.5, 127.9, 126.5, 110.2, 101.3*, 95.9, 94.3*, 56.6, 55.6*, 13.0*, 11.4; HRMS (EI, 70 eV): calcd. for (M^+): 178.0994; found: 178.0997; IR (neat): ν = 2920, 1660, 1495, 1445, 1315, 1260, 1210, 1155, 1095, 1020 cm^{-1}. * signals of the minor isomer ** signals of minor and major isomer not separated.

4-(4-Methoxyphenyl)-3-methylbutan-2-one (4)[21]

Table 1: Entry 1: According to the General Procedure C: $B(C_6F_5)_3$ (5.8 mg, 10 μmol) in CH_2Cl_2 (1 mL) at room temperature, **1** (195 mg, 1 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10) afforded **4** as a colorless oil; yield: 165 mg (0.8 mmol, 84%).

Table 1: Entry 2: According to the General Procedure C: $Cu(OTf)_2$ (18.0 mg, 50 μmol) in CH_2Cl_2 (1 mL) at room temperature, **1** (196 mg, 1 mmol). After 10 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O = 90:10) afforded **4** as a colorless oil; yield: 151 mg (0.9 mmol, 77%).

Table 1: Entry 3: According to the General Procedure D: **1** (187 mg, 0.9 mmol) in CH_2Cl_2 (1 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~5 mol %). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10) afforded **4** as a colorless oil; yield: 141 mg (0.8 mmol, 75%).

Table 3: Entry 3: According to the General Procedure C, but in air: $B(C_6F_5)_3$ (2.7 mg, 5 μmol) in non-dried CH_2Cl_2 (1 mL) at room temperature, 1 (110 mg, 0.6 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10) afforded **4** as a colorless oil; yield: 88 mg (0.4 mmol, 80%). R_f (PE:Et_2O, 90:10, SiO_2): 0.3; ^{1}H NMR (300 MHz, $CDCl_3$): AA'XX' system with signals at δ = 6.97 and 6.72 (4H), 3.70 (s, 3H), AB signal (δ_A = 2.82, δ_B = 2.41, $J_{A,B}$ = 13.4 Hz, additionally split by *J* = 6.8 Hz/7.3 Hz, 2H), 2.68 (m, 1H), 1.98 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.2, 158.0, 131.6, 129.7, 113.7, 55.1, 48.9, 38.0, 28.8, 16.1; HRMS (EI, 70 eV): calcd. for (M^+): 192.1150; found: 192.1154; IR (neat): ν = 2935, 2835, 1710, 1610, 1515, 1460, 1360, 1300, 1250, 1180, 1115, 1035, 815 cm^{-1}.

2-Adamantan-1-yl-1-phenyl-propan-1-one (5)[22]

Table 1: Entry 4: According to the General Procedure C: $B(C_6F_5)_3$ (1.5 mg, 3 μmol) in CH_2Cl_2 (1 mL) at room temper-

ature, **2** (804 mg, 3 mmol). After 20 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, CH:EE, 99:1) afforded **5** as a colorless oil; yield: 680 mg (2.5 mmol, 84%).

Table 1: Entry 5: According to the General Procedure C: $Cu(OTf)_2$ (2.7 mg, 7.5 μmol) in CH_2Cl_2 (1 mL) at room temperature, **2** (804 mg, 3 mmol). After 20 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, CH:EE, 99:1) afforded **5** as a colorless oil; yield: 699 mg (2.6 mmol, 87%).

Table 1: Entry 6: According to the General Procedure D: **2** (278 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~5 mol %). After 4 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 98:2) afforded **5** as a colorless oil; yield: 240 mg (0.9 mmol, 86%).

Table 1: Entry 7: According to the General Procedure D: **2** (1.23 g, 4.6 mmol) in CH_2Cl_2 (5 mL) at room temperature, *n*-Bu_2BOTf (0.05 mL, 1.0 M in CH_2Cl_2, 50 μmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 98:2) afforded **5** as a colorless oil; yield: 1.05 g (3.9 mmol, 85%). R_f (PE:Et_2O, 98:2): 0.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 – 7.80 (m, 2H), 7.51 – 7.43 (m, 1H), 7.41 – 7.31 (m, 2H), 3.24 (q, *J* = 7.0 Hz, 1H), 1.87 (bs, 3H), 1.74 – 1.37 (m, 12H), 1.02 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.2, 139.2, 132.6, 128.5, 128.2, 49.3, 40.2, 37.0, 35.9, 28.7, 11.5; HR-MS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 268.1827; found: 268.1823; IR (neat): ν = 2905, 2850, 1675, 1595, 1445, 1355, 1210, 960, 720, 695 cm^{-1}.

3-Methoxy-2-methyl-1-phenylpropan-1-one (6)[23]

Table 1: Entry 8: According to the General Procedure C: $B(C_6F_5)_3$ (15.5 mg, 50 μmol) in CH_2Cl_2 (1 mL) at room temperature, **3** (178 mg, 1 mmol). After 24 h the reaction was quenched by addition of NEt_3. GC analysis indicated full conversion but a mixture of **6** (54%) and propiophenone (40%). No attempts were made to isolate **6** from the mixture.

Table 1: Entry 9: According to the General Procedure C: $Cu(OTf)_2$ (2.2 mg, 6 μmol) in CH_2Cl_2 (1 mL) at room temperature, **3** (445 mg, 2.5 mmol). After 20 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **6** as a colorless oil; yield: 360 mg (2.0 mmol, 81%).

Table 1: Entry 10: According to the General Procedure D: **3** (178 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~5 mol %). After 2 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2, 96:4) afforded **6** as a colorless oil; yield: 130 mg (0.7 mmol, 73%).

Table 1: Entry 11: According to the General Procedure D: **3** (720 mg, 4.0 mmol) in CH_2Cl_2 (4 mL) at room temperature, *n*-Bu_2BOTf (0.04 mL, 1.0 M in CH_2Cl_2, 40 μmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **6** as a colorless oil; yield: 595 mg (3.3 mmol, 83%).

Table 3: Entry 8: According to the General Procedure C: $Cu(OTf)_2$ (1.8 mg, 4 μmol) neat at room temperature, **3** (712 mg, 4 mmol). After 18 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **6** as a colorless oil; yield: 515 mg (2.9 mmol, 72%). R_f (PE:Et_2O, 96:4, SiO_2): 0.1; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 7.9 Hz, 1.6 Hz, 2H), 7.13 – 7.01 (m, 3H), 3.63 (dd, *J* = 8.5 Hz, 7.2 Hz, 1H), 3.55 (dquintet, *J* = 5.9 Hz, 6.8 Hz, 1H), 3.24 (dd, *J* = 8.2 Hz, 5.7 Hz, 1H), 3.01 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.7, 137.5, 132.6, 2 x 128.6, 75.4, 58.7, 41.4, 14.7; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 178.0994; found: 178.0996; IR (neat): ν = 2975, 2880, 1680, 1595, 1580, 1450, 1385, 1220, 1110, 980, 945 cm^{-1}.

3-Isopropenyloxy-1,5,5-trimethylcyclohexene (7)

According to the General Procedure A: $TiCl_4$ (40 mL, 1.0 M in CH_2Cl_2, 40 mmol) in THF (150 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete dibromomethane (1.52 mL, 22 mmol), and acetic acid 3,5,5-trimethylcyclohex-2-enyl ester (1.82 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **7** as a colorless oil; yield: 970 mg (5.3 mmol, 54%). R_f (PE, Al_2O_3): 0.9; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.42 (bs, 1H), 4.46 (bs, 1H), 3.80 (s, 1H), 3.77 (s, 1H), 1.78 (d, *J* = 17.5 Hz, 1H), 1.70 (s, 3H), 1.67 (dd, *J* = 13.2 Hz, 6.5 Hz, 1H), 1.58 (s, 3H), 1.60 – 1.54 (m, 1H), 1.31 (dd, *J* = 12.5 Hz, 8.6 Hz, 1H), 0.89 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 137.4, 119.8, 81.8, 71.3, 44.3, 40.8, 31.0, 30.8, 26.8, 23.8, 21.8; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 180.1529; found: 180.1514; IR (neat), ν = 3115, 2950, 2825, 1650, 1380, 1370, 1275, 1055, 995, 790 cm^{-1}.

1-(3,5,5-Trimethylcyclohex-2-enyl)propan-2-one (8)[24]

Table 2: Entry 1: According to the General Procedure D: **7** (150 mg, 0.8 mmol) in CH_2Cl_2 (5 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~7 mol %). After 20 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **8** as a colorless oil; yield: 108 mg (0.6 mmol, 72%).

Table 2: Entry 2: According to the General Procedure C: $Cu(OTf)_2$ (18.0 mg, 50 μmol) in CH_2Cl_2 (1 mL) at −55 °C, **7** (180 mg, 1.0 mmol). After 1 h slowly warming up to −20 °C, after 4 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **8** as a colorless oil; yield: 109 mg (0.6 mmol, 60%).

Table 2: Entry 3: According to the General Procedure C: $B(C_6F_5)_3$ (15.5 mg, 50 μmol) in CH_2Cl_2 (1 mL) at room temperature, **7** (180 mg, 1 mmol). After 5 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **8** as a colorless oil; yield: 54 mg (0.3 mmol, 30%). R_f (PE:Et_2O, 98:2, SiO_2): 0.1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.13 (s, 1H), 2.61 (m_c, 1H), AB-signal (δ_A = 2.39, δ_B = 2.32, J_{AB} = 16.0 Hz, additionally split by *J* = 7.1 Hz/7.3 Hz; 2H), 2.14 (s, 3H), AB-signal (δ_A = 1.77, δ_B = 1.54, J_{AB} = 17.2 Hz, 2H), 1.61 (s, 3H), 1.39 (dd, *J* = 12.4 Hz, 5.0 Hz, 1H), 0.93 (s, 3H), 0.87 (s, 3H), 0.99 – 0.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.9, 133.9, 123.0, 50.6, 44.2, 42.7, 31.9, 30.7, 30.1, 30.0, 25.4, 23.9; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 180.1529; found: 180.1522; anal. calcd. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 79.73, H 11.01; IR (neat): ν = 2950, 1715, 1435, 1360, 1255, 1155, 820 cm^{-1}.

1-Isoprenyloxymethyl-4-methoxybenzene (9)

According to the General Procedure A: $TiCl_4$ (40 mL, 1.0 M in CH_2Cl_2, 40 mmol) in THF (250 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete 1,1-dibromomethane (1.52 mL, 22 mmol), acetic acid 4-methoxybenzylic ester (1.80 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE:Et_2O, 95:5) afforded **9** as a colorless oil; yield: 0.67 g (3.8 mmol, 38%). R_f (PE:Et_2O, 96:4, Al_2O_3): 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): AA'XX'-system with signals at δ = 7.13 and 6.74 (4H), 4.53 (s, 2H), 3.95 (t, J = 0.9 Hz, 2H), 3.38 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 159.8, 129.7, 129.4, 114.0, 82.1, 69.4, 54.7, 21.1; HRMS (EI, 70 eV): calcd. for (M^+): 178.0994; found: 178.0990; IR (neat): ν = 2995, 2955, 2835, 1655, 1615, 1515, 1465, 1365, 1280, 1250, 1175, 1060, 1035, 990, 825 cm^{-1}.

4-(4-Methoxyphenyl)-butan-2-one (10)[25]

Table 3: Entry 1: According to the General Procedure C: $B(C_6F_5)_3$ (4.9 mg, 10 μmol) in CH_2Cl_2 (1 mL) at room temperature, **9** (162 mg, 0.9 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10) afforded **10** as a colorless oil; yield: 126 mg (0.7 mmol, 78%).

Table 3: Entry 2: According to the General Procedure C, but in air: $B(C_6F_5)_3$ (5.1 mg, 10 μmol) in non-dried CH_2Cl_2 (1 mL) at room temperature, **9** (178 mg, 1.0 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10) afforded **10** as a colorless oil; yield: 119 mg (0.7 mmol, 67%). R_f (PE:Et_2O, 96:4, SiO_2): 0.3; ^{1}H NMR (300 MHz, $CDCl_3$): AA'XX'-system with signals at δ = 7.09 and 6.82 (4 H), 3.28 (s, 3 H), AA'XX'-system with signals at δ = 2.80 and 2.71 (4H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.0, 157.9, 132.9, 129.1, 113.8, 55.1, 45.3, 30.0, 28.8; HRMS (EI, 70 eV): calcd. for (M^+): 178.0994; found: 178.0996; IR (neat): ν = 2955, 2835, 1610, 1515, 1440, 1365, 1300, 1245, 1180, 1035, 820, 740 cm^{-1}.

1-(1-Hexylpropenyloxymethyl)-4-methoxybenzene (11)

According to the General Procedure A: $TiCl_4$ (20 mL (1.0 M in CH_2Cl_2), 20 mmol) in THF (150 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), heptanoic acid-4-methoxybenzylic ester (1.25 g, 5 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE:Et_2O, 95:5) afforded **11** as a colorless oil; yield: 1.00 g (3.8 mmol, 76%). Z/E = 78:22; R_f (PE:Et_2O = 96:4, Al_2O_3): 0.6; ^{1}H NMR (400 MHz, C_6D_6): AA'XX' system with signals at δ = 7.26 and 6.79 (4H), 7.22* (part of an AA'XX' system, 2H), 4.65 (q, J = 6.7 Hz, 1H), 4.61 (s, 2H), 4.55* (s, 2H), 4.47* (q, J = 6.9 Hz, 1H), 3.32 (s, 3H), 3.30′* (s, 3H), 2.28* (t, J = 7.5 Hz, 2H), 2.11 (t, J = 7.3 Hz, 2H), 1.72 (dt, J = 6.7 Hz, 1.1 Hz, 3H), 0.80 – 2.00 (m, 11H); ^{13}C NMR (100 MHz, C_6D_6): δ = 159.7, 159.7*, 157.1*, 155.2, 131.0, 130.5*, 129.2*, 129.1, 114.0, 104.8, 91.3*, 70.1, 68.5*, 54.7, 32.5, 32.1 32.0*, 30.4*, 29.3*, 29.2, 27.8, 27.6*, 23.0, 22.9, 14.2, 11.9*, 10.7; HRMS (EI, 70 eV): calcd. for M^+: 262.1933; found: 262.1930; IR (neat): ν = 2930, 2860, 1680, 1615, 1585, 1515, 1465, 1300, 1250, 1170, 1040, 820 cm^{-1}. *signals of the minor isomer

1-(4-Methoxy-phenyl)-2-methylnonan-3-one (12)

Table 3: Entry 4: According to the General Procedure C: $B(C_6F_5)_3$ (5.8 mg, 10 μmol) in CH_2Cl_2 (1 mL) at room temperature, **11** (258 mg, 1.0 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 98:2) afforded **12** as a colorless oil; yield: 182 mg (0.7 mmol, 71%). R_f (PE: Et_2O, 96:4, SiO_2): 0.5; ^{1}H NMR (300 MHz, $CDCl_3$): AA'XX' system with signals at δ = 7.05 and 6.80 (4 H), 3.78 (s, 3 H), AB signal (δ_A = 2.90, δ_B = 2.50, J_{AB} = 13.3 Hz, additionally split by J = 7.3 Hz/7.0 Hz, 2H), 2.78 (ddq, J = 7.0 Hz, 7.0 Hz, 7.0 Hz, 1H), AB signal (δ_A = 2.37, δ_B = 2.24, J_{AB} = 16.8 Hz, additionally split by J = 7.3 Hz, 2H), 1.10 – 1.60 (m, 8H), 1.06 (d, J = 6.8 Hz, 3H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 214.4, 158.0, 131.8, 129.8, 113.7, 55.1, 48.2, 42.0, 38.3, 31.5, 28.8, 23.4, 22.4, 16.5, 13.9; HRMS (EI, 70 eV): calcd. for (M^+): 262.1923; found: 262.1928; IR (neat): ν = 2930, 2855, 1715, 1610, 1515, 1460, 1300, 1245, 1180, 1035, 820 cm^{-1}.

1-(1-Cyclohexyl-propenyloxymethyl)-4-methoxybenzene (13)

According to the General Procedure A: $TiCl_4$ (20 mL, 1.0 M in CH_2Cl_2, 20 mmol) in THF (150 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), cyclohexanecarboxylic acid 4-methoxybenzylic ester (1.24 g, 5 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE:Et_2O, 95:5) afforded **13** as a colorless oil; yield: 1.02 g (3.9 mmol, 78%). R_f (PE, Al_2O_3): 0.3; ^{1}H NMR (300 MHz, $CDCl_3$): AA'XX' system with signals at δ = 7.29 (4H) and 6.81 (4H), 4.71 (qd, J = 6.8 Hz, 0.9 Hz, 1H), 4.62 (s, 2H), 3.33 (s, 3H), 2.11 (m, 1H), 1.69 (dd, J = 6.8 Hz, 1.3 Hz, 1H), 2.00 – 1.00 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8, 159.7, 131.2, 129.2, 114.0, 103.6, 71.6, 54.7, 41.1, 31.8, 26.8, 26.7, 11.9; HRMS (EI, 70 eV): calcd. for (M^+): 260.1776; found: 260.1779; IR (neat): ν = 2925, 2850, 1675, 1615, 1515, 1450, 1300, 1250, 1170, 1035 cm^{-1}.

1-Cyclohexyl-3-(4-methoxyphenyl)-2-methylpropan-1-one (14)

Table 3: Entry 5: According to the General Procedure C: $B(C_6F_5)_3$ (3.5 mg, 7 μmol) in CH_2Cl_2 (1 mL) at room temperature, 13 (183 mg, 0.7 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 95:5) afforded **14** as a colorless oil; yield: 131 mg (0.7 mmol, 71%). R_f (PE:Et_2O, 96:4, SiO_2): 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): AA'XX'system with signals at δ = 7.03 and 6.77 (4H), 3.77 (s, 3H), 2.86 (m, 2H), 2.45 (m, 1H), 2.25 (tt, J = 10.9 Hz, 3.0 Hz, 1H), 1.80 – 1.10 (m, 10H), 1.01 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 217.0, 157.9, 132.0, 129.9, 113.7, 55.2, 50.2, 46.7, 38.4, 28.2, 27.9,

25.6, 25.5, 16.9; HRMS (EI, 70 eV): calcd. for (M^+): 260.1776; found: 260.1776; IR (neat): $\nu = 2930$, 2855, 1705, 1610, 1510, 1450, 1245, 1180, 1035, 990, 810 cm^{-1}.

1-Methoxy-2-(1-methoxymethoxypropenyl)-benzene (15)

According to the General Procedure A: $TiCl_4$ (40 mL, 1.0 M in CH_2Cl_2, 40 mmol) in THF (150 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete 1,1-dibromoethane (2.70 mL, 22 mmol), and 2-methoxybenzoic acid methoxymethyl ester (1.96 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE:Et_2O, 95:5) afforded **15** as a colorless oil; yield: 1.17 g (5.6 mmol, 56%). *Z/E* = 80:20; R_f (PE, Al_2O_3): 0.2; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.47$ (dd, $J = 7.5$ Hz, 1.8 Hz, 1H), 7.39* (dd, $J = 7.4$ Hz, 1.8 Hz, 1H), 7.14* (ddd, $J = 8.1$ Hz, 7.3 Hz, 1.8 Hz, 1H), 7.10 (ddd, $J = 8.2$ Hz, 7.4 Hz, 1.8 Hz, 1H), 6.88* (td, $J = 7.6$ Hz, 1.2 Hz, 1H), 6.85 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 6.61* (dd, $J = 8.0$ Hz, 0.6 Hz, 1H), 6.55 (dd, $J = 8.3$ Hz, 0.9 Hz, 1H), 5.42* (q, $J = 7.0$ Hz, 1H), 5.22 (q, $J = 6.8$ Hz, 1H), 4.89* (s, 2H), 4.75 (s, 2H), 3.31* (s, 3H), 3.28 (s, 3H), 3.26* (s, 3H), 3.24 (s, 3H), 1.93 (d, $J = 6.8$ Hz, 3H), 1.56* (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 158.3$*, 158.2, 151.5*, 151.1, 132.3*, 131.8, 130.1*, 129.8, 126.3*, 125.7, 121.1, 120.8*, 111.8*, 111.5, 110.4, 102.5*, 94.8, 94.6*, 56.4, 55.8*, 55.4*, 55.3, 13.2*, 11.5; HRMS (EI, 70 eV): calcd. for (M^+): 208.1111; found: 208.1083. *signals of the minor isomer

3-Methoxy-1-(2-methoxyphenyl)-2-methylpropan-1-one (16)

Table 3: Entry 7: According to the General Procedure C: $Cu(OTf)_2$ (3.6 mg, 10 μmol) in CH_2Cl_2 (1 mL) at room temperature, 15 (208 mg, 1.0 mmol). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, CH:EE, 2% EE) afforded **16** as a colorless oil; yield: 148 mg (0.7 mmol, 71%). R_f (CH:EE = 98:2, SiO_2): 0.1; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.77$ (dd, $J = 7.6$ Hz, 1.8 Hz, 1H), 7.05 (ddd, $J = 8.3$ Hz, 7.3 Hz, 1.8 Hz, 1H), 6.74 (td, $J = 7.5$ Hz, 0.9 Hz, 1H), 6.41 (d, $J = 8.3$ Hz, 1H), 3.82 (sextet, $J = 6.6$ Hz, 1H), 3.73 (dd, $J = 8.8$ Hz, 6.2 Hz, 1H), 3.37 (dd, $J = 8.8$ Hz, 6.3 Hz, 1H), 3.16 (s, 3H), 3.06 (s, 3H), 1.27 (d, $J = 6.8$ Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 204.3$, 158.1, 132.6, 130.8, 130.1, 121.0, 111.6, 75.3, 58.7, 54.9, 46.5, 14.3; HRMS (EI, 70 eV): calcd. for (M^+): 208.1111; found: 208.1086; anal. calcd for $C_{12}H_{16}O_3$ (208.25): C 79.94, H 11.18; found: C 79.73, H 11.01; IR (neat): $\nu = 2950$, 1715, 1435, 1360, 1255, 1160, 820 cm^{-1}.

1-(1-Methylpropenyloxy)-adamantane (17)

According to the General Procedure A: $TiCl_4$ (40 mL (1.0 M in CH_2Cl_2), 40 mmol) in THF (150 mL), TMEDA (12 mL, 80 mmol), Zn (6.00 g, 90 mmol), after the change of color is complete 1,1-dibromoethane (2.70 mL, 22 mmol), and acetic acid adamantan-1-yl ester (1.94 g, 10 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **17** as a colorless oil; yield: 1.83 g (8.9 mmol, 89%). *Z/E* = 80:20; R_f (PE, Al_2O_3): 0.6, 0.5*; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.80$ (qq, $J = 6.6$ Hz, 0.7 Hz, 1H), 1.97 (bs, 3H), 1.87 (bs, 6H), 1.76 (quintet, $J = 1.3$ Hz, 3H), 1.68 (dq, $J = 6.5$ Hz, 1.2 Hz, 3H), 1.45 (s, 6H); ^{1}H NMR* (400 MHz, C_6D_6): $\delta = 5.06$ (qq, $J = 6.9$ Hz, 1.0 Hz, 1H), 1.96 (bs, 3H), 1.88 – 1.82 (m, 6H), 1.74 (quintet, $J = 1.0$ Hz, 3H), 1.50 (dq, $J = 6.6$ Hz, 1.1 Hz, 3H), 1.49 – 1.45 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 149.5$, 110.6, 76.3, 44.2, 36.9, 31.7, 24.6, 12.6; ^{13}C-NMR* (100 MHz, C_6D_6): $\delta = 148.9$, 109.5, 75.9, 43.9, 37.0, 31.6, 19.4, 12.9; HRMS (EI, 70 eV): calcd. for (M^+): 206.1687; found: 206.1667; IR (neat): $\nu = 2910$, 2850, 1675, 1450, 1350, 1325, 1300, 1190, 1070, 980 cm^{-1}. * spectra of minor isomer.

3-Adamantan-1-ylbutan-2-one (18)

Table 3: Entry 8: According to the General Procedure C: $B(C_6F_5)_3$ (5.1 mg, 10 μmol) in CH_2Cl_2 (1 mL) at room temperature, **17** (206 mg, 1 mmol). After 15 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 97:3) afforded **18** as a colorless oil; yield; 142 mg (0.7 mmol, 69%). R_f (PE: Et_2O, 97:3, SiO_2): 0.4; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.30$ (q, $J = 7.0$ Hz, 1H), 2.13 (s, 3H), 1.96 (m_c, 3H), 1.56 (m_c, 9H), 1.49, (ddd, $J = 12.2$ Hz, 4.9 Hz, 2.7 Hz, 3H), 0.97 (d, $J = 7.2$ Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 213.8$, 56.9, 40.0, 37.1, 35.5, 32.8, 28.7, 10.7; HRMS (EI, 70 eV): calcd. for (M^+): 206.1687; found: 206.1673; anal. calcd. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.44, H 10.86; IR (neat): $\nu = 3380$, 2900, 2850, 2675, 1700, 1450, 1420, 1355, 1165, 1065, 955, 815 cm^{-1}.

(1-*tert*-Butoxypropenyl)-benzene (19)[18]

According to the General Procedure A: $TiCl_4$ (60 mL, 1.0 M in CH_2Cl_2, 60 mmol) in THF (250 mL), TMEDA (18 mL, 120 mmol), Zn (9.00 g, 135 mmol), after the change of color is complete 1,1-dibromoethane (4.04 mL, 16.5 mmol), and benzoic acid *tert*-butyl ester (2.66 g, 15 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **19** as a colorless oil; yield: 2.48 g (13.1 mmol, 87%). *Z/E* = 80:20; R_f (PE, Al_2O_3): 0.7; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39 - 7.30$** (m, 2H), 7.27 – 7.10** (m, 3H), 5.30 (q, $J = 6.7$ Hz, 1H), 5.28* (q, $J = 7.4$ Hz, 1H), 1.70 (d, $J = 6.8$ Hz, 3H), 1.62* (d, $J = 7.3$ Hz, 3H), 1.13 (s, 9H), 1.08 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.0$, 150.6*, 141.6, 138.8*, 128.8*, 127.9, 127.7*, 127.3*, 127.1, 126.3, 114.2, 112.9*, 79.3, 77.8*, 29.6, 29.2*, 13.2*, 12.6; HRMS (EI, 70 eV): calcd. for (M^+): 190.1371; found: 190.1354; IR (neat): $\nu = 2975$, 2930, 1650, 1365, 1320, 1170, 1050, 1020, 780, 730, 700 cm^{-1}. *signals of the minor isomer, ** signals of major and minor isomer not separated.

2,3,3-Trimethyl-1-phenylbutan-1-one (20)[26]

Table 3: Entry 9: According to the General Procedure D: 19 (190 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) at $-78\,^\circ$C, $BF_3 \cdot OEt_2$ (1 drop, ~ 5 mol %). After 2 h warming up to room temperature the reaction and quenching by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O,

98:2) afforded **20** as a colorless oil; yield: 61 mg (0.3 mmol, 32%). R_f (PE:Et_2O, 98:2, SiO_2): 0.3; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (m, 2H), 7.43 (dddd, J = 8.2 Hz, 6.5 Hz, 2.3 Hz, 1.1 Hz, 1H), 7.34 (m, 2H), 3.34 (q, J = 7.0 Hz, 1H), 1.06 (d, J = 7.0 Hz, 3H); 0.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.5, 139.1, 132.7, 128.6, 128.3, 48.4, 33.9, 28.1, 13.5; HRMS (EI, 70 eV): calcd. for (M^+): 190.1371; found: 190.1367; IR (neat): ν = 3060, 2960, 1680, 1595, 1445, 1395, 1225, 1180, 1000, 965 cm^{-1}.

1,5,5-Trimethyl-3-vinyloxycyclohexene (21)[27]

According to the General Procedure B: mercury(II) acetate (3.2 g, 10 mmol) in ethyl vinyl ether (500 mL), 3,5,5-trimethyl-2-cyclohexen-1-ol (7.0 g, 50 mmol). After 5 d stirring at room temperature standard work-up followed by column chromatography through a short column (Al_2O_3, pentane) afforded **21** as a colorless oil; yield: 7.1 g (43 mmol, 86%). R_f (PE, Al_2O_3): 0.8. ^1H NMR (400 MHz, C_6D_6): δ = 6.22 (dd, J = 14.3 Hz, 6.6 Hz, 1H), 5.44 (bs, 1H), 4.34 (dd, J = 14.3 Hz, 1.2 Hz, 1H), 4.19 (m_c, 1H), 3.93 (dd, J = 6.6 Hz, 1.2 Hz, 1H), 1.50 – 1.42 (m, 2H), 1.36 (s, 3H), 1.33 (dd, J = 12.8 Hz, 8.6 Hz, 1H), 1.24 (d, J = 17.7 Hz, 1H), 0.73 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 151.2, 136.8, 120.7, 88.0, 74.2, 44.2, 41.4, 30.7, 30.6, 26.8, 23.6; IR (neat): ν = 3115, 2955, 1630, 1455, 1325, 1195, 1050, 985, 945, 820 cm^{-1}.

(3,5,5-Trimethylcyclohex-2-enyl)-acetaldehyde (22)

Table 4: Entry 1: According to the General Procedure D: **21** (166 mg, 1.0 mmol) in CH_2Cl_2 (100 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~5 mol %). After 18 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, pentane:Et_2O, 98:2) afforded **22** as a colorless oil; yield: 140 mg (0.8 mmol, 84%). R_f (PE:Et_2O = 98:2, SiO_2): 0.2; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.72 (t, J = 2.2 Hz, 1H), 5.12 (bs, 1H), 2.62 (bs, 1H), AB signal (δ_A = 2.34, δ_B =2.27, J_{AB} = 16.2 Hz, additionally split by J = 6.7 Hz/7.1 Hz, 2.2 Hz, 2H), AB signal (δ_A = 1.74, δ_B = 1.51, J_{AB} = 17.2 Hz, 2H), 1.57 (s, 3H), 1.45 (dd, J = 12.8 Hz, 5.7 Hz, 1H), 0.95 (m, 1H), 0.88 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.0, 134.5, 122.4, 50.3, 43.9, 42.4, 31.7, 30.0, 28.9, 25.3, 23.9; HRMS (EI, 70 eV): calcd. for (M^+): 166.1358; found: 166.1359; anal. calcd for $C_{11}H_{18}O$ (166.1): C 79.47, H 10.91; found: C 79.48, H 10.96; IR (neat): ν = 2950, 2715, 1725, 1455, 1365, 1135, 1065, 865, 820 cm^{-1}.

1,3-Diphenyl-1-vinyloxyprop-2-ene (23)[12c]

According to the General Procedure B: Mercury(II) acetate (0.64 g, 2 mmol) in ethyl vinyl ether (250 mL), *trans*-1,3-diphenyl-2-propen-1-ol (1.05 g, 5 mmol). After 5 d stirring at room temperature standard work-up followed by column chromatography through a short column (Al_2O_3, pentane) afforded **23** as a colorless oil; yield: 0.48 g (2.0 mmol, 40%). ^1H NMR (300 MHz, C_6D_6): δ = 7.53 – 6.79 (m, 10H), 6.52 (d, J = 16.0 Hz, 1H), 6.38 (dd, J = 14.0 Hz, 6.6 Hz, 1H), 6.25 (dd, J = 15.9 Hz, 6.5 Hz, 1H), 5.18 (d, J = 6.4 Hz, 1H), 4.53 (dd, J = 14.2 Hz, 1.6 Hz, 1H), 4.07 (dd, J = 6.5 Hz, 1.6 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 150.6, 140.8, 136.8, 131.9, 129.7, 128.84, 128.80, 128.1, 127.1, 90.0, 82.3; HRMS (EI, 70 eV): calcd. for (M^+): 236.1201; found: 236.1202; IR (neat): ν = 3030, 2825, 2725, 1720, 1600, 1495, 1450, 1405, 1180, 1030 cm^{-1}.

(*E*)-3,5-Diphenyl-4-pentenal (24)[12c]

Table 4: Entry 2: According to the General Procedure C: $B(C_6F_5)_3$ (1.9 mg, 4 μmol) in CH_2Cl_2 (15 mL) at room temperature, **23** (370 mg, 15 mmol). After 5 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 90:10, SiO_2) afforded **24** as a white solid; yield: 305 mg (1.3 mmol, 82%). R_f (PE:Et_2O, 98:2): 0.1; ^1H NMR (300 MHz, $CDCl_3$): δ = 9.67 (t, J = 2.0 Hz, 1H), 7.33 – 7.07 (m, 10H), 6.35 (d, J = 16.0 Hz, 1H), 6.25 (dd, J = 16.0 Hz, 6.6 Hz, 1H), 4.04 (q, J = 7.2 Hz, 1H), AB signal (δ_A = 2.88, δ_B = 2.82, J_{AB} = 16.8 Hz, additionally split by J = 7.5 Hz/7.3 Hz, 2.2 Hz/1.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.4, 142.8, 137.3, 132.2, 130.8, 129.2, 128.0, 127.9, 127.3, 126.7, 49.4, 43.3; HRMS (EI, 70 eV): calcd. for M^+: 236.1201; found: 236.1199; anal. calcd for $C_{17}H_{16}O$ (236.1): C 86.41, H 6.82; found: C 086.25, H 6.86; IR (neat): ν = 3025, 2840, 2740, 1715, 1595, 1490, 1445, 1410, 1050, 1015, 965, 765, 750, 695 cm^{-1}.

3-(1-*tert*-Butylvinyloxy)-1,5,5-trimethylcyclohexene (25)

According to the General Procedure A: $TiCl_4$ (20 mL, 1.0 M in CH_2Cl_2, 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete dibromomethane (0.76 mL, 11 mmol), and 2,2-dimethylpropionic acid 3,5,5-trimethylcyclohex-2-enyl ester (1.07 g, 4.8 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **25** as a light yellow oil; yield: 0.26 g (1.1 mmol, 23%). R_f (PE, Al_2O_3): 0.9; ^1H NMR (400 MHz, C_6D_6): δ = 5.68 (s, 1H), 4.61 (bs, 1H), 4.15 (s, 1H), 3.97 (s, 1H), 1.70 – 1.36 (m, 4H), 1.54 (bs, 3H), 1.22 (s, 9H), 0.91 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 136.7, 120.9, 78.4, 71.3, 44.7, 41.3, 36.5, 30.9, 30.7, 29.1, 27.8, 24.1; HRMS (EI, 70 eV): calcd. for (M^+): 222.2003; found: 222.1988.

3,3-Dimethyl-1-(3,5,5-trimethylcyclohex-2-enyl)-butan-2-one (26)[24]

Table 4: Entry 3: According to the General Procedure D: **25** (222 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) at −78 °C, $BF_3 \cdot OEt_2$ (1 drop, ~5 mol %). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, CH:EE, 99:1) afforded **26** as a colorless oil; yield: 139 mg (0.6 mmol, 63%). R_f (PE:Et_2O = 98:2, SiO_2): 0.3; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.10 (s, 1H), 2.67 (m_c, 1H), 2.48 – 2.33 (m, 2H), AB signal (δ_A = 1.77, δ_B = 1.53, J_{AB} = 17.2 Hz, 2H), 1.40 (dd, J = 12.3 Hz, 5.4 Hz, 1H), 1.11 (s, 9H), 0.92 (s, 3H), 0.87 (s, 3H), 0.81 (t, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.3, 133.6, 123.8, 44.3, 44.2, 43.4, 42.5, 32.0, 30.1, 29.6, 26.4, 25.4, 24.0; HRMS (EI, 70 eV):

calcd. for ($M^{+\cdot}$): 222.2003; found: 222.1982; IR (neat): $\nu = 2950$, 1705, 1475, 1365, 1270, 1135, 1070, 990, 820 cm^{-1}.

3-(1-Cyclohexylpropenyloxy)-1,5,5-trimethylcyclohexene (27)

According to the General Procedure A: $TiCl_4$ (20 mL (1.0 M in CH_2Cl_2), 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), cyclohexanecarboxylic acid 3,5,5-trimethylcyclohex-2-enyl ester (1.25 g, 5.0 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **27** as a colorless oil; yield: 0.97 g (3.7 mmol, 74%). *Z/E* => 99:<1, R_f (PE, Al_2O_3): 0.8; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.68$ (s, 1H), 4.77 (qd, $J =$ 6.6 Hz, 0.9 Hz, 1H), 4.50 (m_c, 1H), 2.25–2.00 (m, 3H), 1.78 (dd, $J = 6.6$ Hz, 1.2 Hz, 3H), 1.86–1.49 (m, 6H), 1.69 (d, $J =$ 15.3 Hz, 1H), 1.56 (s, 3H), 1.31–1.04 (m, 6H), 0.93 (s, 3H), 0.82 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 159.6$, 135.8, 122.7, 103.6, 72.6, 44.7, 43.1, 40.9, 32.5, 32.4, 31.6, 31.2, 27.27, 27.26, 27.23, 27.0, 24.0, 11.7; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 262.2319; found: 262.2301; IR (neat), $\nu = 2925$, 2855, 1670, 1450, 1360, 1315, 1170, 1130, 1040, 950 cm^{-1}.

1-Cyclohexyl-2-(3,5,5-trimethylcyclohex-2-enyl)-propan-1-one (28)

Table 4: Entry 4: According to the General Procedure C: $Cu(OTf)_2$ (1.6 mg, 4 μmol) in CH_2Cl_2 (1 mL) at -15 °C, **27** (131 mg, 0.5 mmol). After 5 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 96:4) afforded **28** as a colorless oil; yield: 77 mg (0.3 mmol, 59%). dr = 69:31; R_f (PE:Et_2O = 98:2, SiO_2): 0.2; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.14$* (s, 1H), 4.90 (s, 1H); 2.45 (quintet, $J = 7.1$ Hz, 1H), 1.50 (s, 3H), 0.91* (d, $J = 6.9$ Hz, 1H), 0.63 (d, $J = 6.9$ Hz, 1H), 0.81 (s, 3H), 0.73 (s, 3H), 2.45–0.71 (m); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 217.9$, 217.6*, 134.7*, 134.1, 122.8, 120.7*, 50.8*, 50.4, 49.9, 48.9*, 44.3*, 44.1, 40.7*, 38.7, 36.2*, 36.1, 32.2, 32.1*, 30.1*, 30.0, 29.0*, 28.9, 28.3*, 28.0, 26.1, 26.0*, 25.9, 25.8*, 25.7*, 25.3, 25.24*, 24.22*, 24.1, 13.7*, 13.3; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 262.2319; found: 262.2293; anal. calcd. for $C_{18}H_{30}O$ (262.43): C 82.38, H 11.20; found: C 82.40, H 11.33; IR (neat): $\nu = 2930$, 1705, 1450, 1375, 1145, 990, 905, 820 cm^{-1}. *signals of the minor diastereomer.

3-(1-*tert*-Butylpropenyloxy)-1,5,5-trimethylcyclohexene (29)

According to the General Procedure A: $TiCl_4$ (20 mL (1.0 M in CH_2Cl_2), 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), cyclohexanecarboxylic acid 3,5,5-trimethylcyclohex-2-enyl ester (1.07 g, 4.8 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **29** as a colorless oil; yield: 1.03 g (4.3 mmol, 91%). *Z/E* => 99: <1; R_f (PE, Al_2O_3): 0.9; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.77$ (bs, 1H), 4.74* (q, $J =$ 7.0 Hz; 1H), 4.74* (s, 1H), 1.82 (dd, $J = 12.6$ Hz, 5.9 Hz, 1H), 1.69 (d, $J = 7.1$ Hz, 3H), 1.63–1.69 (m, 1H), 1.57 (dd, $J =$ 12.1 Hz, 8.6 Hz, 1H), 1.55 (s, 3H), 1.40 (d, $J = 17.2$ Hz, 1H), 1.20 (s, 9H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 163.9$, 135.7, 123.0, 99.2, 75.3, 44.7, 43.5, 37.1, 31.7, 31.4, 29.9, 26.8, 24.1, 13.1; MS (EI, 70 eV): *m/z* (%) = 236 ($M^{+\cdot}$, 0.2), 123 (100), 107 (3), 81 (11); IR (neat), $\nu = 2955$, 2825, 1655, 1455, 1390, 1325, 1300, 1130, 1000, 970 cm^{-1}.

2,2-Dimethyl-4-(3,5,5-trimethylcyclohex-2-enyl)-entan-3-one (30)

Table 4: Entry 5: According to the General Procedure D: **29** (472 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) at room temperature, $BF_3 \cdot OEt_2$ (1 drop, ~2.5 mol %). After 5 min the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 99:1) afforded **30** as a colorless oil;: yield: 277 mg (1.1 mmol, 59%). dr = 64:36; R_f (PE:Et_2O, 98:2; SiO_2): 0.3; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 5.32* (s, 1H), 4.86 (s, 1H), 2.71 (dq, $J = 8.3$ Hz, 6.8 Hz, 1H), 2.67* (dq, $J = 15.9$ Hz, 6.8 Hz, 1H), 2.37–2.15** (m, 2H), 1.68 (d, J =17.3 Hz, 1H), 1.55* (s, 3H), 1.48 (s, 3H), 1.40 (d, $J =$ 17.1 Hz, 1H), 1.33 (dt, $J = 5.6$ Hz, 1.5 Hz, 1H), 1.29 (dt, $J =$ 5.5 Hz, 1.5 Hz, 1H), 1.05 (s, 9H), 1.03* (s, 9H), 0.95* (d, $J =$ 6.8 Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.85 (s, 3H), 0.80* (s, 3H), 0.72** (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 219.9$, 219.4*, 134.4*, 133.7, 123.2, 120.8*, 45.5, 44.8*, 44.7*, 44.4, 44.3*, 44.2, 41.6*, 39.4, 37.2, 36.8*, 32.2, 32.1*, 30.1, 30.0*, 26.7, 26.6*, 25.4, 25.1*, 24.3*, 24.0, 15.9*, 15.8; HRMS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 236.2161; found: 236.2135; anal. calcd. for $C_{16}H_{28}O$ (236.39): C 81.29, H 11.94; found: C 81.05, H 11.94; IR (neat): $\nu = 2950$, 1700, 1480, 1365, 1060, 990, 960, 905, 825 cm^{-1}. *signals of minor diastereomer; ** signals of major and minor diastereomer not separated.

[1-(3,5,5-Trimethylcyclohexenyloxy)-propenyl]-benzene (31)

According to the General Procedure A: $TiCl_4$ (20 mL, 1.0 M in CH_2Cl_2, 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), benzoic acid 3,5,5-trimethyl-cyclohex-2-enyl ester (1.22 g, 5.0 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, PE) afforded **31** as a colorless oil; yield: 1.03 g (4.0 mmol, 80%). *Z/E* = 91:9; R_f (PE, Al_2O_3): 0.7; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$–7.28** (m, 2H), 7.25–7.20** (m, 2H), 7.18–7.12** (m, 1H), 5.49* (bs, 1H), 5.43 (bs, 1H), 5.25 (q, $J = 6.9$ Hz, 1H), 4.93* (q, $J = 7.5$ Hz, 1H), 4.38* (m_c, 1H), 4.13 (m_c, 1H), AB signal ($\delta_A =$ 1.82, $\delta_B = 1.51$. $J_{AB} = 17.5$ Hz, 2H), 1.72 (d, $J = 6.6$ Hz, 3H), 1.61 (bs, 3H), 1.64–1.61 (m, 1H), 1.42 (dd, $J = 12.6$ Hz, 8.9 Hz, 1H), 0.96** (s, 3H), 0. 68** (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.2$, 137.3, 136.4, 127.9, 127.5, 126.1, 120.8, 120.3*, 110.2, 99.4*, 73.6, 71.4*, 44.2, 41.8, 41.2*, 31.2, 31.0, 26.4, 23.7, 13.0*, 11.7; HR-MS (EI, 70 eV): calcd. for ($M^{+\cdot}$): 256.1827; found: 256.1831; IR (neat): $\nu = 3030$, 2950, 2825, 1655, 1490, 1445, 1365, 1320, 1260, 1175, 1050, 970, 945, 810, 775, 750, 700,

645 cm^{-1}. * signals of minor isomer, **signals of major and minor isomer not separated.

1-Phenyl-2-(3,5,5-trimethylcyclohex-2-enyl)-propan-1-one (32)

Table 4: Entry 6: According to the General Procedure C: $Cu(OTf)_2$ (15.5 mg, 50 μmol) in CH_2Cl_2 (1 mL) at $-40\,^{\circ}C$, **31** (256 mg, 1.0 mmol). After 3 h at $-30\,^{\circ}C$ the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 99:1) afforded **32** as a white solid; yield: 197 mg (0.8 mmol, 77%). dr = 57:43, R_f (PE:Et_2O, 98:2, SiO_2): 0.3; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.82** (m, 2H), 7.53–7.34** (m, 3H), 5.30 (s, 1H), 5.09* (s, 1H), 3.33* (dq, *J* = 7.0 Hz, 7.0 Hz, 1H), 3.26 (dq, *J* = 6.6 Hz, 6.7 Hz, 1H), 2.64–2.42** (m, 1H), 1.73** (d, *J* = 17.1 Hz, 2H), 1.57 (s, 3H), 1.51* (s, 3H), 1.46** (d, *J* = 17.1 Hz, 2H), 1.30 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 1.23* (dd, *J* = 12.9 Hz, 5.5 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.05* (d, *J* = 7.0 Hz, 3H), 0.97** (dd, *J* = 12.0 Hz, 11.9 Hz, 2H), 0.88* (s, 3H), 0.84 (s, 3H), 0.76 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.9, 204.6*, 137.6, 137.6*, 135.1, 134.5*, 133.1, 128.9, 128.7, 128.6*, 123.0, 120.6*, 46.1, 45.2*, 44.6, 44.5*, 40.8, 38.7, 37.0, 37.0*, 32.4, 32.3*, 30.4, 30.3*, 25.6, 25.5*, 24.4, 24.3*, 14.1, 14.0*; HR-MS (EI, 70 eV): calcd. for $C_{18}H_{24}O$ ($M^{+\cdot}$): 256.1827; found: 256.1827; anal. calcd for $C_{18}H_{24}O$ (256.2): C 84.32, H 9.43; found: C 84.45, H, 9.59; IR (film): ν = 2950, 1680, 1595, 1365, 1250, 1210, 970, 750, 690, cm^{-1}.

[1-(2-Methylallyloxy)-propenyl]-cyclohexane (33)

According to the General Procedure A: $TiCl_4$ (20 mL, 1.0 M in CH_2Cl_2, 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), cyclohexanecarboxylic acid allylic ester (0.84 g, 5.0 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, pentane) afforded **33** as a colorless oil (single isomer); yield: 0.37 g (2.0 mmol, 41%). R_f (PE, Al_2O_3): 0.8; ^1H NMR (400 MHz, C_6D_6): δ = 6.00–5.90 (m, 1H), 5.31–5.47 (m, 1H), 5.18–5.07 (m, 1H), 4.74 (qd, *J* = 6.9 Hz, 1.0 Hz, 1H), 4.16 (dt, *J* = 5.7 Hz, 1.6 Hz, 2H), 1.67 (dd, *J* = 6.7 Hz, 1.1 Hz, 3H), 0.80–2.20 (m, 11H); ^{13}C NMR (100 MHz, C_6D_6): δ = 160.8, 135.4, 115.6, 103.3, 70.7, 41.0, 31.6, 26.7, 26.7, 10.8; HRMS (EI, 70 eV): calcd. for (M^+): 180.1514; found: 180.1514; IR (film): ν = 2925, 2855, 1710, 1675, 1450, 1315, 1170, 1050, 990, 920, cm^{-1}.

1-Cyclohexyl-2-methylpent-4-en-1-one (34)

Table 4: Entry 7: According to the General Procedure C: $Cu(OTf)_2$ (18.4 mg, 50 μmol) in CH_2Cl_2 (1 mL) at $-40\,^{\circ}C$, **33** (194 mg, 1.1 mmol). After 48 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 98:2) afforded **34** as a colorless liquid; yield: 105 mg (0.5 mmol, 54%). R_f (PE:Et_2O, 96:4, SiO_2): 0.3; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.58 (dddd, *J* = 17.1 Hz, 10.0 Hz, 7.1 Hz, 7.1 Hz, 1H), 4.91 (dd, *J* = 16.9 Hz, 1.6 Hz, 1H), 4.92–4.85 (m, *J* = 9.8 Hz, 1H), 2.62 (ddq, *J* = 6.9 Hz, 6.9 Hz, 6.9 Hz, 1H), 2.38–2.30 (m, 1H), 2.26 (dddt, *J* = 13.7 Hz, 6.9 Hz, 6.9 Hz, 0.8 Hz, 1H), 1.93 (ddd, *J* = 14.0 Hz, 7.1 Hz, 7.1 Hz, 1H), 1.00–1.90 (m, 10H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.9, 135.9, 116.5, 49.8, 44.1, 37.2, 28.4, 28.2, 25.8, 16.4; HRMS (EI, 70 eV): calcd. for (M^+): 180.1514; found: 180.1519; IR (neat): ν = 2930, 2855, 1705, 1640, 1450, 1375, 1145, 995, 915 cm^{-1}.

[1-(2-Methylallyloxy)-prop-(*Z*)-enyl]-cyclohexane (35)

According to the General Procedure A: $TiCl_4$ (20 mL, 1.0 M in CH_2Cl_2, 20 mmol) in THF (125 mL), TMEDA (6 mL, 40 mmol), Zn (3.00 g, 45 mmol), after the change of color is complete 1,1-dibromoethane (1.35 mL, 11 mmol), cyclohexanecarboxylic acid 2-methyl-allylic ester (0.93 g, 5.0 mmol). The reaction mixture was stirred overnight. Standard work-up followed by column chromatography (Al_2O_3, pentane) afforded **35** as a colorless oil; yield: 0.70 g (3.6 mmol, 71%). R_f (PE, Al_2O_3): 0.5; ^1H NMR (400 MHz, C_6D_6): δ = 5.30 (d, *J* = 0.7; 1 H), 4.99 (d, *J* = 0.7; 1 H), 4.77 (qd, *J* = 6.9, 0.7; 1 H), 4.12 (s, 2 H), 2.15 (m, 1 H), 1.81 (dd, *J* = 6.8, 1.1; 3 H), 1.79 (s, 3 H), 0.90–2.00 (m, 10 H); ^{13}C NMR (100 MHz, C_6D_6): δ = 160.9, 142.7, 111.4, 103.1, 73.6, 41.1, 31.7, 26.8, 26.7, 19.6, 10.8; HRMS (EI, 70 eV): calcd. for (M^+): 194.1671; found: 194.1679; IR (neat): ν = 2925, 2855, 1675, 1450, 1375, 1315, 1190, 1170, 1050, 895, 805 cm^{-1}.

1-Cyclohexyl-2,4-dimethylpent-4-en-1-one (36)

Table 4: Entry 8: According to the General Procedure C: $Cu(OTf)_2$ (89.2 mg, 250 μmol) in CH_2Cl_2 (5 mL) at $-65\,^{\circ}C$, **35** (1.007 g, 5.2 mmol). After 3 h the reaction was quenched by addition of NEt_3. Standard work-up followed by column chromatography (SiO_2, PE:Et_2O, 98:2) afforded **36** as a colorless liquid; yield: 751 mg (3.9 mmol, 75%). R_f (PE:Et_2O, 96:4, SiO_2): 0.3; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.72 (s, 1H), 4.63 (d, *J* = 0.7 Hz, 1H), 2.83 (m, 1H), 2.43 (tt, *J* = 11.0 Hz, 2.9 Hz, 1H), 2.32 (dd, *J* = 14.0 Hz, 6.4 Hz, 1H), 1.91 (dd, *J* = 14.0 Hz, 7.9 Hz, 1H), 1.67 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.80–1.10 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.1, 143.0, 112.3, 49.9, 42.4, 41.0, 28.5, 28.3, 25.8, 25.7, 25.6, 22.3, 16.4; HRMS (EI, 70 eV): calcd. for (M^+): 194.1671; found: 194.1674; IR (neat): ν = 2930, 2855, 1705, 1650, 1450, 1375, 1145, 1060, 995, 890 cm^{-1}.

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References and Notes

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