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A new synthesis of highly functionalized cyclohexenes *via* a vinylogous Ferrier-Petasis cyclization reaction

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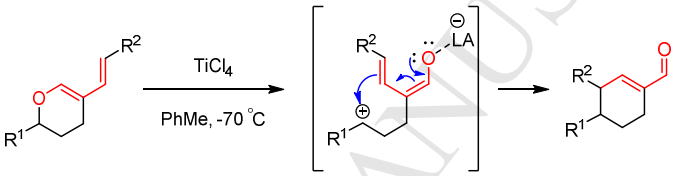
Dedicated to prof. Marek Chmielewski on his 75th Birthday.

Research on the O→C rearrangement reaction shows that alkoxydienes undergo a smooth rearrangement in a vinylogous manner with a catalytic amount of titanium (IV) chloride, which leads to highly substituted cyclohexenes a particularly useful starting material in the synthesis of cyclohexane containing products.

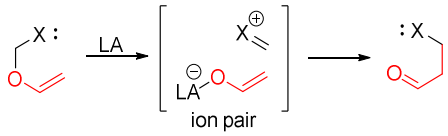


Keywords: Vinylogous Ferrier reaction; 1,5-rearrangement; *O*-1,3-alkoxydienes

INTRODUCTION

Vinylogy can be defined as the transmission of electronic effects through a conjugated system. The SN' reaction is probably the best-known example of a double bond acting as an electron-conducting channel between two reacting termini. Many other polar reactions have been modified in a vinylogous manner, including the Claisen and benzoin condensations, the aldol and Mannich reactions, and the electrophilic addition to double bonds.[1]

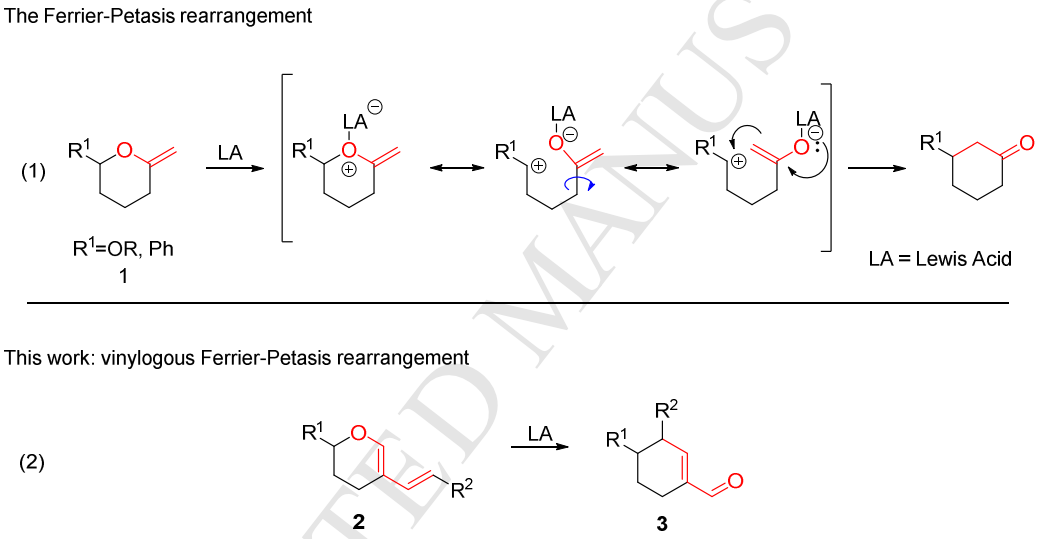
The Lewis acid-promoted [1,3] O-to-C rearrangement of vinyl ethers and acetals is one of the fundamental reactions in organic synthesis.[2] This transformation is believed, in general, to proceed *via* ionic cleavage, forming an ion pair (an enolate and a carbocationic species), followed by their recombination (Scheme 1).[3,4]



Scheme 1. The [1,3] O→C rearrangement of vinyl ethers.

The intramolecular transformation, where cyclic vinyl ethers undergo a

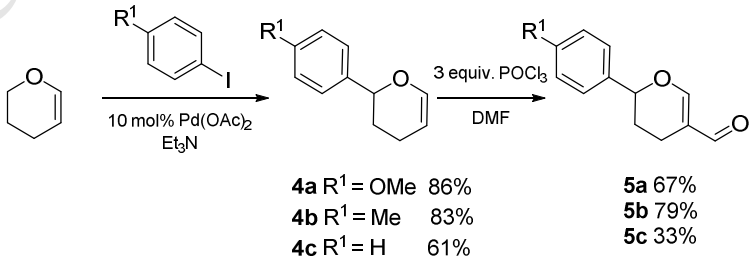
fragmentation/aldol-type recombination sequence, generating a carbocycle, is known as the Ferrier-Petasis rearrangement[5] (Scheme 1, eq 1). Recently, such reactions have found widespread applications in complex natural product synthesis.[6,7] In contrast, little attention has been given to the *O*-1,3-dienyl version of the Ferrier reaction, where regiochemistry could be an issue.[8] Very recently, Tayama[9] has demonstrated that the Ferrier reaction of *O*-1,3-dienyl acetals in the presence of bulky aluminium complexes proceeds with high α-regioselectivity ([1,3] rearrangement) to afford the corresponding α-alkenyl-substituted β-alkoxy aldehydes, whereas the use of other Lewis acids led to the formation of the α- and γ-regioisomers with the former predominant. In the present work, we hypothesized that in *O*-1,3-dienyl ethers **2**,a vinylogous Ferrier-Petasis cyclization to the corresponding 6-membered carbocyclic products *via* a 6 – endo-trig pathway should be preferred as it would proceed via a stabilized carbocation (Scheme 2, eq 2).



Scheme 2. The Ferrier-Petasis reaction of vinyl ethers **1** and *O*-1,3-alkoxydienes **2.**

RESULTS AND DISCUSSION

In order to test our hypothesis, we synthesized a series of three α,β-unsaturated aldehydes with phenyl (**4c**), 4-methylphenyl (**4b**) and 4-methoxyphenyl (**4a**) groups in two steps from 3,4-dihydropyran (DHP) (Scheme 3).

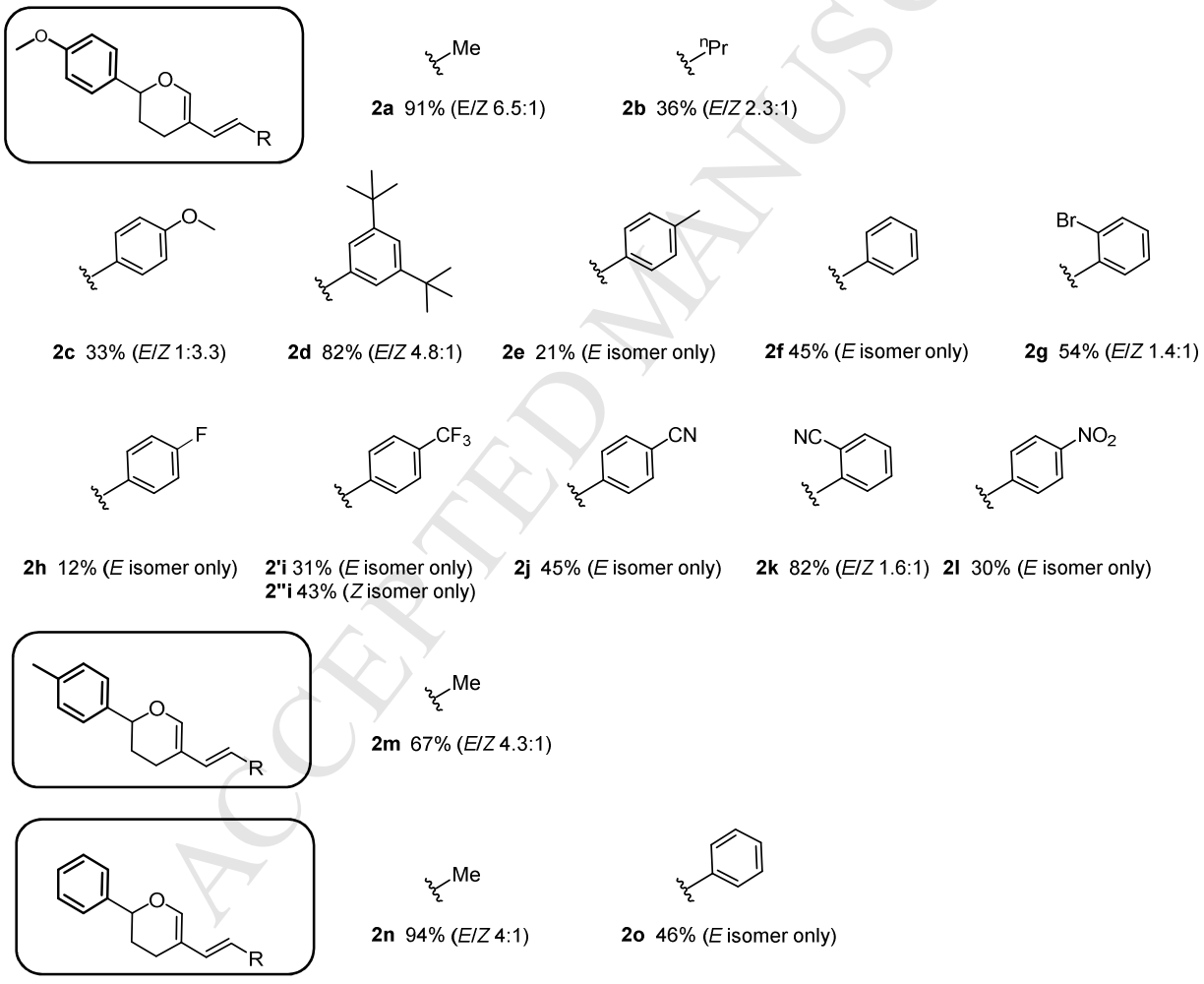


Scheme 3. The synthesis of α,β-unsaturated aldehydes **5**.

The first step was the Heck coupling of aryl iodides with 3,4-dihydro-2*H*-pyran which facilitated the regioselective synthesis of arylated cyclic enol ethers **4a-c**. Good yields were obtained using 10 mol% of $Pd(OAc)_2$ in the presence of Et_3N in DHP at 140 ℃. [10]

The formylation of **4** under the classical Vilsmeier-Haack reaction conditions employing phosphorus oxychloride gave the expected α,β-unsaturated aldehydes **5a-c** selectively[11] We did not observe products of the electron-rich arene formylation. While the synthesis of aldehydes **5** proved to be straightforward, their chromatographic purification was quite difficult, therefore they were used in the next step without further purification.

In the next step, aldehydes **5a-c** were transformed into olefins **2a-p** using the Wittig reaction. The expected olefins were obtained in moderate to good yields after optimization (Scheme 4).[12]

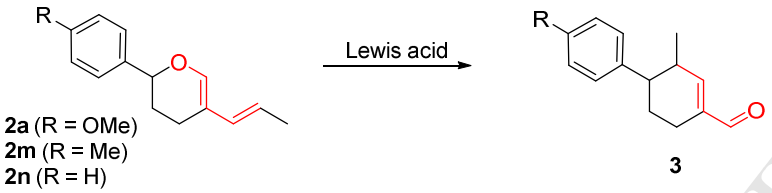


Scheme 4. The Synthesis of *O*-1,3-Alkoxydienes **2**.

With a variety of *O*-dienyl ethers in hand, our interest was directed toward the regio- and stereochemistry in the Lewis acid-promoted Ferrier reaction. Therefore, vinyl ethers **2a**,

2m, **2n** were screened for the initial optimization with various Lewis acids in different solvents and concentrations (Table 1).

Table 1. The Ferrier Rearrangement of *O*-1,3-Alkoxydienes Promoted by Representative Lewis Acids.[a]



2a (R = OMe)
2m (R = Me)
2n (R = H)

3

Entry/Substrate	Catalyst/equiv.	Solvent	Concentration [M]	Temp. [°C]	Time [h]	Yield [%][b]
1/(**2a**)	-	xylene	0.04	120	12	no reaction
2/(**2a** or **2m,** or **2n**)	$BF_3{\cdot}Et_2O$/ 0.1	toluene	0.04	-85	0.25	degradation
3/(**2a**)	$AlCl_3$/ 1	toluene	0.04	-70	12	23
4/(**2a**)	Et_2AlCl/ 2	toluene	0.04	-70	20	32
5/(**2a** or **2m,** or **2n**)	$Al(OTf)_3$/ 0.1	toluene	0.04	RT	12	degradation
6/(**2a** or **2m,** or **2n**)	$Al(OTf)_3$/ 0.1	toluene	0.04	0	3	degradation
7/(**2a** or **2m,** or **2n**)	TMSOTf/ 0.01	CH_2Cl_2	0.04	-70	1	degradation
8/(**2a** or **2m,** or **2n**)	TMSOTf/ 0.05	CH_2Cl_2	0.04	-70	1	degradation
9/(**2a** or **2m,** or **2n**)	$TiCl_4$/ 0.01	toluene	0.04	-70	0.25	<10
10 /(**2a** or **2m,** or **2n**)	$TiCl_4$/ 0.05	toluene	0.04	-70	0.25	<10
11/(**2a**)	$TiCl_4$/ 0.1	toluene	0.04	-70	0.25	28
12/(**2a**)	$TiCl_4$/ 0.8	toluene	0.04	-70	0.17	37
13/(**2a**)	$TiCl_4$/ 0.8	**toluene**	**0.005**	**-70**	**0.17**	**51**
14/(**2m**)	$TiCl_4$/ 0.8	toluene	0.005	-70	0.17	39
15/(**2n**)	$TiCl_4$/ 0.8	toluene	0.005	-70	0.1	degradation
16/(**2a**)	$TiCl_4$/ 0.1	CH_2Cl_2	0.04	-70	0.25	10
17/(**2a**)	$TiCl_4$/ 0.5	CH_2Cl_2	0.04	-70	0.25	24
18/(**2a** or **2m,** or **2n**)	$Cu(OTf)_2$/ 0.1	toluene	0.04	RT	1	degradation

[a] All reactions were carried out with **2a** (0.1 mmol), and catalyst in the indicated solvent, unless otherwise noted.

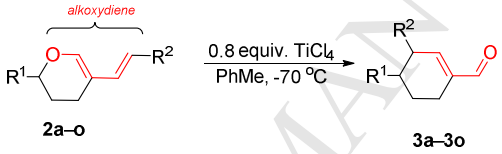
[b] Yield of isolated products.

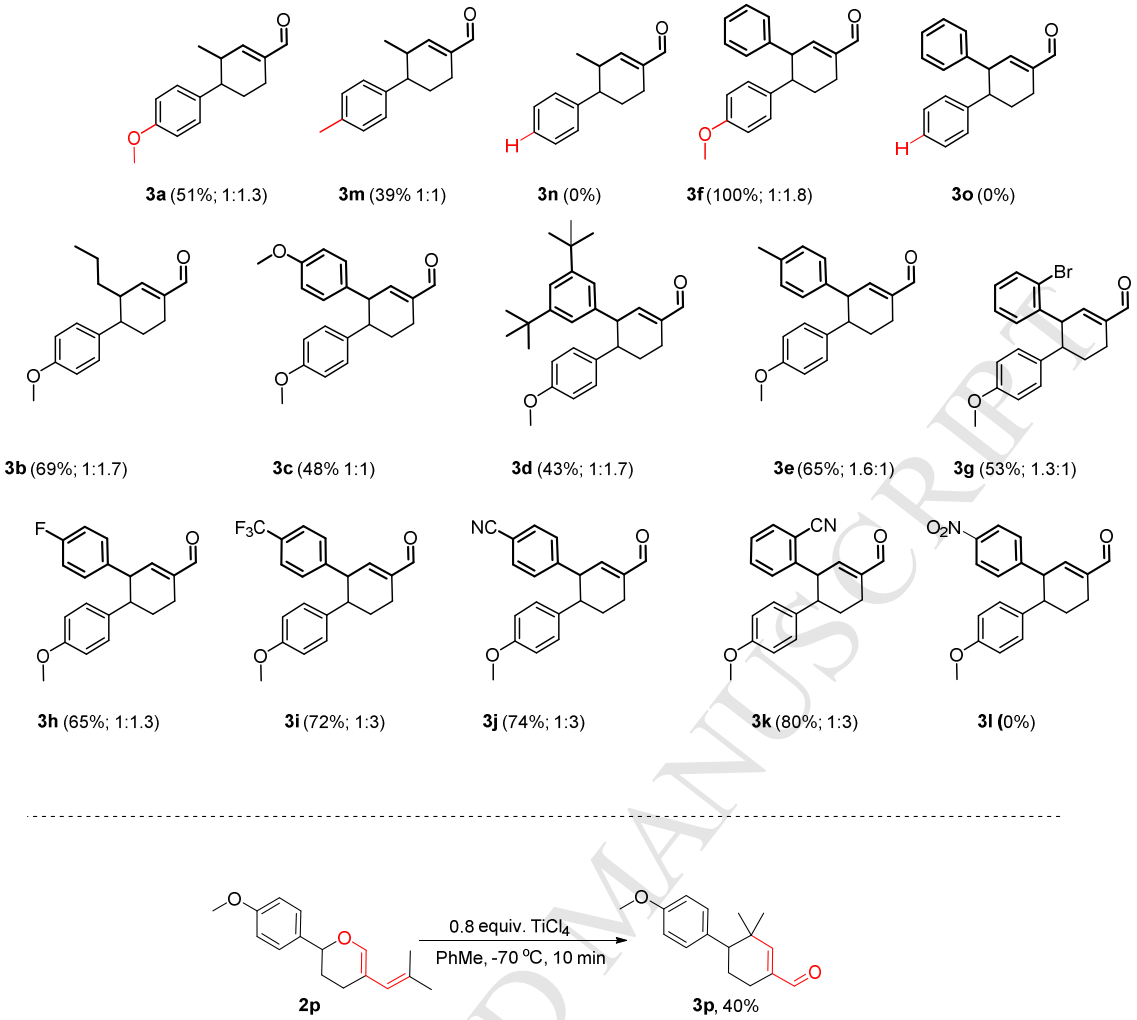
Among the screened catalysts, $TiCl_4$ was the most successful one. Using 0.8 equiv. of titanium (IV) chloride in toluene led to the expected product **3a** in good yield as a single regioisomer (entry 13). It should be mentioned that the formation of unidentified polar impurities was also observed, lowering the yield of the desired product. The rearrangement of 4-methoxyphenyl (**2a**) and 4-methylphenyl (**2m**) ethers to the corresponding cyclohexene

carbaldehydes **3a** and **3m** was observed in 10 min at -70 ℃ with 51 and 39 % isolated yield respectively, whereas with the *O*-dienyl ether with phenyl (**2n**) group, hydrolysis was the sole observed reaction outcome.

This revealed that, analogously to vinyl ethers, the reaction progress with *O*-dienyl ethers was also significantly affected by the stability of the *in situ* generated benzylic carbocation.[13] As far as other Lewis acids are concerned, the use of aluminum compounds also gave the expected substituted cyclohexene **3a** (entries 3 and 4). However, these catalysts were less efficient and furnished the desired product in a lower yield. The use of other Lewis acids, such as $BF_3{\cdot}Et_2O$ or TMSOTf (entries 2 and 7), as well as $Cu(OTf)_2$ (entry 17), was not effective and led to rapid degradation of the substrate, even at low temperatures. In the above reaction, we observed the formation of almost equimolar amounts of *syn/anti* isomers as determined by in NMR spectroscopy.

Using optimized reaction conditions, the scope of the oxygen-to-carbon rearrangement reaction was examined. The obtained results are summarized in Scheme 5.

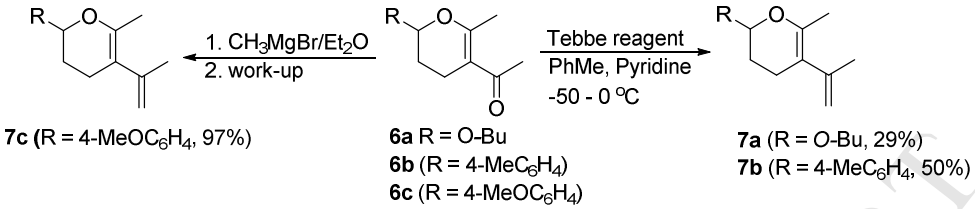




Scheme 5. The substrate scope of the vinylogous Ferrier-Petasis reaction.

Under the optimized conditions, the reaction of different *O*-1,3-dienyl acetals proceeded with moderate to good yields and without noticeable differences when comparing either aromatic (**2c-k**) or aliphatic (**2a-b**) alkoxydienes. However, we noticed that the reaction yield depended on the electronic influence of groups R^2 present on the aromatic ring. In the presence of weakly to moderately electron-donating groups on the aromatic ring, the oxygen-to-carbon rearrangement reaction proceeded with high to excellent yields (**3e-k**). There was no noticeable dependence on the positions of substituents on the aromatic ring (**3j-3k**). It is also worth noting that we performed the comparative experiment with single *E* or *Z* isomers **2i.** Both reactions led to a mixture of *cis/trans* isomers. However, we noticed that the *E* isomer rearranged faster than the *Z* one. Finally, the γ-regioselective Ferrier-Petasis reaction of *O*-dienyl ether **2p** was attempted to form a quaternary carbon stereocenter. In this case, the best result was also obtained by using $TiCl_4$ to afford γ-regioisomer **3p** in 40% yield as a sole product (Scheme 5).

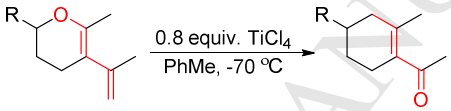
Finally, we performed the rearrangement reaction of more complex *O*-1,3-dienyl ethers **7a-c** prepared from the easily accessible α,β-unsaturated ketones [14] **6a-c** by Tebbe methylenation[15] or through an addition-elimination[16] reaction sequence (Scheme 6).

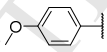


Scheme 6. The synthesis of *O*-1,3-dienyl ethers **7a-c.**

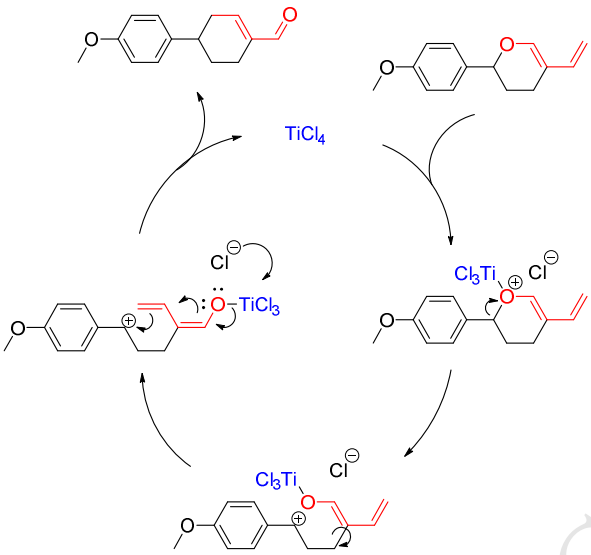
In the presence of 0.8 equiv. of titanium (IV) chloride, compounds **7b-c** gave the expected ketones **8b-c** with good yields comparable to previous examples (Table 2), whereas compound **7a** decomposed rapidly. The use of $BF_3{\cdot}Et_2O$ or $EtAlCl_2$ gave a complex mixture of products. No reaction occurred with DIBAL-H or $HgCl_2$.[17]

Table 2. The vinylogous-type rearrangement of *O*-1,3-dienyl ethers **7.**



Entry	Substrate	R	Product	Time [min]	Yield [%]
1	**7a**	*O*-butyl-	**8a**	5	degradation
2	**7b**		**8b**	30	71
3	**7c**		**8c**	120	54

Based on literature reports, we proposed a catalytic cycle for the investigated reaction (Scheme 7).[18] The activation of the *O*-1,3-dienyl ether with $TiCl_4$ results in the formation of a carboxonium cation. The alkoxydiene oxygen-carbon bond breaking and the following bond rotation leads to the emergence of an intermediate with a stabilized carbocation. Next, the chloride anion present in the reaction mixture restores the catalyst. The corresponding carbonyl compound is formed through the recombination of the nucleophilic and electrophilic components of the molecule.



Scheme 7. Plausible mechanistic pathway for the $TiCl_4$-catalyzed [1,5] O → C rearrangement.

In summary, we observed a novel [1,5] O→C rearrangement of cyclic alkoxydienes, leading to highly substituted cyclohexenes. The rearrangement proceeds readily with substrates bearing an aryl ring substituted with electron-donating groups. The rearrangement could be regarded as a formal vinylogous Ferrier reaction. Efforts to improve the yields, stereoselectivity, and reaction conditions are now in progress.

EXPERIMENTAL

General Remarks.

All reactions involving air- and moisture-sensitive materials were performed under argon in pre-dried glassware. The reagents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals and used without further purification. All solvents were purified by standard techniques. Thin layer chromatography was performed with Silica gel 60 F254 aluminum plates (Merck) with visualization by UV light and charring with Pancaldi reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O). Column chromatography was carried out with Merck silica gel (230 - 400 mesh) or Roth Florisil® (60-100 mesh). NMR analyses were performed using Varian Mercury 400 MHz, Varian VNMRS 500 MHz and 600 MHz spectrometers. Chemical shifts are calibrated using residual solvents signals $CDCl_3$: δ(H) = 7.26, δ(C) = 77.0 or TMS and are reported in parts per million and coupling constants (*J*) were given in Hertz (Hz). Infrared spectra (IR) were recorded on a FT-IR-1600-Perkin Elmer spectrophotometer, FT-IR Jasco 6200 and FT-IR Spectrum 2000 Perkin Elmer spectrophotometer and are reported in frequency of absorption (cm^{-1}). HRMS spectra were recorded on an ESI-TOF Mariner Spectrometer, SYNAPT G2-S HDMS or AMD 604 mass spectrometer and are given in m/z.

Melting points were measured on a Melting Point Meter MPM-H2 apparatus and are uncorrected.

1. **Experimental details and characterization data for 2-aryl-3,4-dihydro-2*H*-pyran 4a-c[9]**

The 2-substituted 3,4-dihydro-2*H*-pyran derivatives were prepared by Heck-type coupling reaction according to a literature procedure[7] from 3,4-dihydro-2*H*-pyran and aryl iodides.

1.1. 2-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyran **4a**

Compound **4a** was obtained according to the general procedure starting with 2.4 g (10.3 mmol) of 4-iodoanisole and purified by column chromatography using 5% of diethyl ether in hexanes; Isolated yield 1.68 g (86 %); yellow oil; TLC R_f = 0.35 (1:9 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 6.94 – 6.85 (m, 2H), 6.51 (d, J = 5.6 Hz, 1H), 4.85 – 4.68 (m, 2H), 3.81 (s, 3H), 2.32 – 2.10 (m, 1H), 2.09 – 1.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 144.3, 134.2, 127.2, 113.8, 100.5, 76.8, 55.3, 30.2, 20.4; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ [$M^{+\bullet}$] 190.0994, found 190.0996; IR (film) ν 3059, 3000, 2952, 2922, 2839, 1649, 1614 cm^{-1}.

1.2. 2-(4-methylphenyl)-3,4-dihydro-2*H*-pyran **4b**

Compound **4b** was obtained according to the general procedure starting with 0.5 g (2.3 mmol)

of 4-iodotoluene and purified by column chromatography using 5% of diethyl ether in hexanes; isolated yield 223 mg (56 %); yellow oil; TLC R_f = 0.70 (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 6.53 (dt, J=6.3, 1.8 Hz, 1H), 4.84 – 4.73 (m, 2H), 2.35 (s, 3H), 2.31 – 2.18 (m, 1H), 2.09 – 1.98 (m, 2H), 1.98 – 1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 139.1, 137.3, 129.0, 125.9, 100.5, 77.0, 30.3, 21.1, 20.4; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O$ [$M^{+\bullet}$] 174.1045, found 174.1046; IR (film) ν 2922, 2848, 1649, 1517, 1241, 1077, 1059, 1038, 811, 732 cm^{-1}.

1.3. 2-phenyl-3,4-dihydro-2H-pyran **4c**

Compound **4c** was obtained according to the general procedure starting with 1.84 g (9.0 mmol) of iodobenzene and purified by column chromatography using 2% of diethyl ether in hexanes; Isolated yield 795 mg (61 %); yellow oil; TLC R_f = 0.70 (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 – 7.21 (m, 2H), 7.17 – 7.09 (m, 2H), 7.09 – 7.00 (m, 1H), 6.51 (d, J = 5.9 Hz, 1H), 4.70 – 4.62 (m, 1H), 4.62 – 4.54 (m, 1H), 1.96 – 1.81 (m, 1H), 1.76 – 1.64 (m, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 144.3, 142.3, 128.2, 127.3, 125.8, 100.2, 76.7, 30.4, 20.1; HRMS (EI) *m/z* calcd for $C_{11}H_{12}O$ [$M^{+\bullet}$] 160.0888, found 160.0886; IR (film) ν 3060, 2032, 2923, 2847, 1650 cm^{-1}.

2. **Experimental details and characterization data for 2-aryl-3,4-dihydro-2*H*-pyran-5-carbaaldehyde[11]**

General procedure for compounds **5 a-c:**

The Vilsmeier reagent was obtained by the addition of $POCl_3$ (3 equiv.) to DMF cooled to 0 °C (4 equiv.). The solution was stirred at 0 °C until it was light orange (about 30 min). To the reagent prepared in this manner, a solution of 2-aryl-3,4-dihydro-2*H*-pyran (1 equiv.) in DMF (30 mL) was added. The reaction mixture was stirred at room temperature until TLC showed the reaction to be complete. The reaction mixture was cooled to 0 °C, quenched by slow addition of saturated $NaHCO_3$ (20 mL), and diluted with diethyl ether (40 mL). The aqueous layer was saturated with sodium chloride and extracted with diethyl ether until TLC showed no presence of product in the water layer. The combined extracts were dried with Na_2SO_4 and concentrated. The crystals were filtered off and washed with hexane.

2.1. 2-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde **5a**

This compound was obtained according to the general procedure starting with 2.08 g (10.9 mmol) of compound **4a**; isolated yield 1.6 g (67 %); white crystals; mp 58-60 ℃; TLC R_f=0.17 (2:8 AcOEt/hexanes); crystallized from diethyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.43 (s, 1H), 7.26 (d, *J*=8.5 Hz, 2H), 6.91 (d, *J*=8.3 Hz, 2H), 4.97 (d, *J*=9.4 Hz, 1H), 3.80 (s, 3H), 2.55 – 2.36 (m, 1H), 2.34 – 2.20 (m, 1H), 2.18 – 2.05 (m, 1H), 1.98 – 1.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 190.4, 165.2, 159.7, 131.6, 127.4, 119.4, 114.0, 80.2, 55.3, 28.1, 17.3; HRMS (ES-TOF) *m/z* calcd for $C_{13}H_{14}O_3Na$ [M+Na$^+$] 241.0841, found 241.0942; IR (film) *v* 2964, 2935, 2935, 2907, 2837, 1664, 1629, 1516, 1251, 1195, 1179, 1161, 1032, 830 cm^{-1}.

2.2. 2-(4-methylphenyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde **5b**

This compound was obtained according to the general procedure starting with 277 mg (1.59 mmol) of compound **4b**; isolated yield 159 mg (79 %); yellow oil; TLC R_f = 0.18 (2:8 AcOEt/hexanes); column chromatography (Roth Florisil®; 1:9 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ 9.11 (s, 1H), 7.12 (s, 8H), 6.93 (s, 4H), 6.72 (s, 1H), 4.40 (dd, *J* = 10.2, 2.7 Hz, 1H), 2.27 (ddd, *J* = 17.1, 4.9, 2.9 Hz, 1H), 2.06 (s, 3H), 2.01 – 1.90 (m, *J* = 17.0, 10.9, 6.0, 1.5 Hz, 1H), 1.52 – 1.44 (m, 1H), 1.41 – 1.31 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 188.60, 163.41, 137.56, 137.09, 128.99, 125.77, 119.50, 79.60, 28.02, 20.68, 17.24; HRMS (EI) *m/z* calcd for $C_{13}H_{14}O_2$ [M$^{+\bullet}$] 202.0994, found 202.0996; IR (film) *v* 2923, 1670, 1629, 1251, 1193, 1224, 1162 cm^{-1}.

2.3. 2-phenyl-3,4-dihydro-2*H*-pyran-5-carbaldehyde **5c**

This compound was obtained according to the general procedure starting with 784 mg (4.9 mmol) of compound **4c**; isolated yield 514 mg (33 %); white crystals; mp 76-78 ℃; TLC R_f= 0.24 (2:8 AcOEt/hexanes); column chromatography (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) *δ* 9.10 (s, 1H), 7.16 – 6.95 (m, 5H), 6.70 (s, 1H), 4.37 (dd, *J* = 10.2, 2.7 Hz, 1H), 2.24 (dddd, *J* = 16.9, 5.2, 3.0, 0.9 Hz, 1H), 1.93 (dddd, *J* = 17.0, 10.8, 6.1, 1.6 Hz, 1H), 1.49 – 1.40 (m, 1H), 1.37 – 1.24 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) *δ* 188.6, 163.3, 140.0, 128.3,

125.7, 119.5, 79.5, 28.0, 17.2; HRMS (EI) *m/z* calcd for $C_{12}H_{12}O_2$ [$M^{+\bullet}$] 188.0837, found 188.0837; IR (film) *v* 3062, 3033, 2929, 2856, 1769, 1673, 1628,1231, 1192, 1171, 1103, 700 cm^{-1}.

3. **Experimental details and characterization data for 1-(6-methyl-3,4-dihydro-2*H*-pyran-5-yl)ethenone[15]**

The 2-substituted 1-(6-methyl-3,4-dihydro-2*H*-pyran-5-yl)ethenone derivatives were prepared by condensation followed by cyclization reaction according to a literature procedure[15] from formaldehyde, acetylacetone and an appropriate vinyl ether.

3.1. 1-(2-butoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-yl)ethanone **6a**

This compound was synthesised according to the general procedure starting with 5 g (0.05 mol) of butyl vinyl ether; isolated yield 4.1 g (39 %); yellow oil; TLC R_f = 0.72 (3:7 AcOEt/hexanes); column chromatography (1:9 Et_2O/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.65 (dd, *J* = 3.8, 2.5 Hz, 1H), 3.65 (ddd, *J* = 9.6, 6.5, 6.5 Hz, 1H), 3.25 (ddd, *J* = 9.6, 6.5, 6.5 Hz, 1H), 2.32 (t, *J* = 1.6 Hz, 3H), 2.26 (m, 1H), 1.93 – 1.79 (m, 4H), 1.58 (dddd, *J* = 13.2, 6.0, 4.5, 3.8 Hz, 1H), 1.45 – 1.33 (m, 3H), 1.29 – 1.16 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 196.7, 159.7, 110.4, 97.3, 68.0, 31.6, 28.8, 26.1, 20.3, 19.2, 18.8, 13.5; HRMS (EI) *m/z* calcd for $C_{12}H_{20}O_3$ [$M^{+\bullet}$] 212.1412, found 212.1409; IR (film) *v* 2959, 2935, 2872, 1677, 1585, 1278, 1379, 1355, 1119, 1064, 1010, 962, 931 cm^{-1}.

3.2. 1-[6-methyl-2-(4-methylphenyl)-3,4-dihydro-2H-pyran-5-yl]ethanone **6b**

This compound was synthesised according to the general procedure starting with 5 g (0.042 mol) of 4-methylstyrene; isolated yield 6.3 g (65 %); white crystals; mp 54-55 ℃; TLC R_f = 0.32 (2:8 AcOEt/hexanes); column chromatography (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 4H), 4.85 (dd, *J* = 10.2, 2.5 Hz, 1H), 2.52 – 2.43 (m, 2H), 2.36 (s, 3H), 2.29 (t, *J* = 1.5 Hz, 3H), 2.23 (s, 3H), 2.19 – 2.10 (m, 1H), 1.97 – 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 164.6, 137.8, 137.6, 129.2, 125.8, 110.1, 77.9, 29.7, 29.3, 23.1, 21.1, 21.1; HRMS (EI) m/z calcd for $C_{15}H_{18}O_2$ [$M^{+\bullet}$] 230.1307, found 230.1297; IR (film) *v* 2952, 2924, 2852, 1673, 1577, 1381, 1359, 1276, 1249 , 1075, 1017, 937, 814 cm^{-1}.

3.3. 1-[2-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2H-pyran-5-yl]ethanone **6c**

This compound was synthesised according to the general procedure starting with 1 g (7.5 mmol) of 4-vinylanisole; isolated yield 1.74 g (92 %); waxy solid; TLC R_f=0.38 (2:8 AcOEt/hexanes); column chromatography (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ 7.07 (m, 2H), 6.77 (m, 2H), 4.44 (dd, J=10.2, 2.6 Hz, 1H), 3.29 (s, 3H), 2.35 (t, J=1.5 Hz, 3H), 2.07 – 1.90 (m, 5H), 1.71 – 1.59 (m, 1H), 1.59 – 1.45 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 196.5, 163.3, 159.6, 133.0, 127.1, 113.8, 109.8, 77.3, 54.5, 29.2, 29.0, 23.0, 20.8; HRMS (ES–TOF) m/z calcd for $C_{15}H_{18}O_3Na$ [M+Na^+] 269.1154, found 269.1149; IR (film) *v* 2954, 2930, 2838, 1671, 1614, 1577, 1516, 1380, 1360, 1277, 1247, 1211, 1176, 1066, 1033, 940, 830 cm^{-1}.

4. **Experimental details and characterization data for alkoxydienes.**

General procedure for compounds **2a-d; 2f-g, 2m-p**[12]:

To a solution of diisopropylamine (1.4 equiv.) in THF (5 mL) cooled to -78 ˚C, n-butyllithium (1.2 equiv., 2.5 M solution in hexane) was added dropwise. The mixture was stirred at 0 ˚C for 30 minutes. To base prepared in this manner, phosphonium salt (1.1 equiv.) was added in three portions. The reaction mixture was stirred at RT until it cleared. It was cooled to 0 ˚C and 2-aryl-3,4-dihydro-2H-pyran-5-carbaldehyde (1 equiv.) was added. The reaction mixture was stirred at RT until TLC showed the reaction to be complete. The solvent was evaporated under reduced pressure. The residue was suspended in diethyl ether and filtered. The filtrate was evaporated under reduced pressure. The product was purified by FCC in the appropriate solvent system.

4.1. 2-(4-methoxyphenyl)-5-(prop-1-en-1-yl)-3,4-dihydro-2*H*-pyran **2a**

This compound was obtained according to the general procedure starting with 1.04 g (4.8 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 6.5:1 ratio was obtained (980 mg, 91 %); TLC R_f = 0.74 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ **signals due to E isomer *inter alia*** 6.59 (s, 1H), 5.98 (d, *J* = 15.5 Hz, 1H), 5.41 (dq, *J* = 15.5, 6.7 Hz, 1H), 4.76 (dd, *J* = 10.8, 2.3 Hz, 1H), 3.80 (s, 3H), 2.34 – 2.26 (m, 1H), 2.24 – 2.18 (m, 1H), 1.75 (dd, *J*=6.7, 1.2 Hz 3H); δ **signals due to Z isomer *inter alia*** δ 6.62 (s, 1H), 5.70 (d, *J* = 11.7 Hz, 1H), 5.32 (dq, *J* = 11.7, 7.3 Hz, 1H), 3.81 (s, 3H), 2.56 – 2.47 (m, 1H), 2.41 – 2.33 (m, 1H), 1.83 (dd, *J* = 7.3, 1.7 Hz 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **signals due to E isomer *inter alia*** 159.2, 143.9, 133.6, 129.5, 118.8, 77.3, 55.3, 29.4, 20.7, 18.3; δ **signals due to Z isomer *inter alia*** 159.1, 145.1, 133.7, 128.1, 121.3, 76.7, 55.2, 29.8, 24.7, 14.8; HRMS (EI) *m/z* calcd for $C_{15}H_{18}O_2$ [$M^{+\bullet}$] 230.1307, found 230.1310; IR (film) *v* 2947, 2930, 2844, 1646, 1614, 1517, 1441, 1245, 1180, 1141, 1032, 967, 830 cm^{-1}.

4.2. 2-(4-methoxyphenyl)-5-(hex-1-en-1-yl)-3,4-dihydro-2*H*-pyran **2b**

This compound was obtained according to the general procedure starting with 37 mg (0.17 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 2.3:1 ratio was obtained (15.8 mg, 36 %); TLC R_f = 0.76 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ **signals due to E isomer *inter alia*** 6.62 (s, 1H), 6.00 (d, *J* = 15.6 Hz, 1H), 5.50 – 5.38 (m, 1H), 4.81 – 4.74 (m, 1H), 3.81 (s, 3H); δ **signals due to Z isomer *inter alia*** 6.62 (s, 1H), 5.72 (d, *J* = 11.7 Hz, 1H), 5.25 (dt, *J* = 11.8, 7.4 Hz, 1H), 4.81 – 4.74 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)δ **signals due to E isomer *inter alia*** 144.1, 35.1, 29.5, 23.0, 20.8, 13.7; δ **signals due to Z isomer *inter alia*** δ 145.0, 31.0, 29.8, 24.8, 23.7, 13.8; HRMS (EI) *m/z* calcd for $C_{17}H_{22}O_2$ [$M^{+\bullet}$] 258.1620,

found 258.1614; IR (film) *v* 2954, 2927, 2870, 2836, 1648, 1614, 1515, 1247, 1179, 1146, 1034, 957 cm^{-1} .

4.3. 2-(4-methoxyphenyl)-5-[2-(4-methoxyphenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2c**

This compound was obtained according to the general procedure starting with 100 mg (0.46 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 1:3.3 ratio was obtained (49 mg, 33 %); TLC R_f = 0.75 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.60 (d, *J* = 15.8 Hz, 1H), 6.36 – 6.29 (m, 1H), 4.69 – 4.60 (m, 1H), 3.32 (s, 3H), 3.28 (s, 3H); δ **signals due to Z isomer *inter alia*** 6.36 – 6.29 (m, 1H), 5.96 (d, *J* = 11.9 Hz, 1H), 4.69 – 4.60 (m, 1H), 3.28 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 159.0, 146.2, 133.4, 131.2, 130.5, 127.3, 126.8, 126.1, 122.1, 114.1, 113.8, 77.6, 55.2, 29.3, 20.7; δ **signals due to Z isomer *inter alia*** δ 159.2, 146.9, 133.6, 131.5, 128.5, 127.4, 126.2, 124.9, 114.1, 112.4, 77.1, 55.3, 29.6, 24.0; HRMS (ES-TOF) *m/z* calcd for $C_{21}H_{22}O_3Na$ [M+Na^+] 345.1467, found 345.1565; IR (film) *v* 2952, 2931, 2915, 2835, 1610, 1511, 1248, 1174, 1124, 1032, 830 cm^{-1}.

4.4. 2-(4-methoxyphenyl)-5-[2-(3,5-diisopropyl)ethenyl]-3,4-dihydro-2*H*-pyran **2d**

This compound was obtained according to the general procedure starting with 92 mg (0.42 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 4.8:1 ratio was obtained (85 mg, 82 %); TLC R_f = 0.76 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.92 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.64 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.28 (s, 3H), 2.17 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.32 (s, 18H); δ **signals due to Z isomer *inter alia*** 7.07 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.44 (d, *J* = 12.0 Hz, 1H), 6.02 (d, *J* = 12.0 Hz, 1H), 4.76 – 4.68 (m, 1H), 3.27 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 159.5, 150.8, 146.7, 138.1, 133.6, 127.5, 123.9, 121.1, 120.7, 120.4, 113.7, 77.4, 54.4, 34.6, 31.3, 29.4, 20.6; δ **signals due to Z isomer *inter alia*** δ 149.8, 147.2, 146.3, 145.6, 143.8, 141.6, 127.2, 126.9, 123.6, 113.7, 76.8, 54.4, 34.5, 31.2, 30.9, 23.6; HRMS (EI) *m/z* calcd for $C_{28}H_{36}O_2$ [$M^{+\bullet}$] 404.2715, found 404.2705; IR (film) *v* 2960, 2904, 2867, 1631, 1614, 1590, 1515, 1248, 1177, 1145, 1036, 829 cm^{-1}.

4.5. 2-(4-methoxyphenyl)-5-[2-phenyl-ethenyl]-3,4-dihydro-2*H*-pyran **2f**

This compound was obtained as a single E isomer according to the general procedure starting with 1 g (4.5 mmol) of compound **5a;** white crystals; mp 159-160℃; isolated yield 555 mg (45 %); TLC R_f = 0.62 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (600 MHz, C_6D_6) δ 7.34 – 7.29 (m, 2H), 7.18 – 7.10 (m, 4H), 7.06 – 7.00 (m, 1H), 6.80 – 6.74 (m, 3H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.60 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.26 (s, 3H), 2.10 – 2.00 (m, 2H), 1.74 (m, 2H); ^{13}C NMR (151 MHz, C_6D_6) δ 159.5, 147.0, 138.5, 133.5, 128.5, 128.2, 127.2, 126.3, 125.8, 122.6, 113.7, 113.6,

77.5, 54.4, 29.4, 20.4; HRMS (ES-TOF) *m/z* calcd for $C_{20}H_{20}O_2Na$ [M+Na$^+$] 315.1361, found 315.1457; IR (film) *v* 2959, 2911, 2840, 1628, 1612, 1513, 1443, 1249, 1178, 1148, 1034, 954, 831, 816, 745 cm^{-1}.

4.6. 2-(4-methoxyphenyl)-5-[2-(2-bromophenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2g**

This compound was obtained according to the general procedure starting with 150 mg (0.69 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 1.4:1 ratio was obtained (139 mg, 54 %); TLC R_f = 0.76 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.54 (d, *J* = 15.9 Hz, 1H), 4.65 – 4.59 (m, 1H), 3.31 (s, 3H), 2.22 – 2.09 (m, 2H), 1.80 – 1.70 (m, 2H); **signals due to Z isomer *inter alia*** 6.25 (d, *J* = 11.9 Hz, 1H), 6.01 (d, *J* = 11.9 Hz, 1H), 4.57 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.28 (s, 3H), 2.02 – 1.87 (m, 1H), 1.69 – 1.59 (m, 1H), 1.54 – 1.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **signals due to E isomer *inter alia*** 159.5, 148.0, 138.1, 133.4 126.0, 123.4, 113.8, 77.7, 54.5, 29.3; δ **signals due to Z isomer *inter alia*** δ 159.4, 148.6, 133.5, 126.2, 123.5, 113.7, 77.1, 54.4, 29.4; HRMS (EI) *m/z* calcd for $C_{20}H_{19}BrO_2$ [M$^{+\bullet}$] 372.0548, found 372.0540; IR (film) *v* 2952, 2930, 2836, 1722, 1624, 1514, 1177, 1147, 1032, 830, 751 cm^{-1}.

4.7. 2-(4-methylphenyl)-5-prop-1-en-1-yl-3,4-dihydro-2*H*-pyran **2m**

This compound was obtained according to the general procedure starting with 208 mg (1.03 mmol) of compound **5b,** an inseparable mixture of E/Z isomers in a 5:1 ratio was obtained (207 mg, 97 %); TLC R_f = 0.71 (2:8 AcOEt/hexanes); crystallized from diethyl ether; ^{1}H NMR (400 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.64 (s, 1H), 5.92 (d, *J* = 15.4 Hz, 1H), 5.38 – 5.24 (m, 1H), 4.70 – 4.58 (m, 1H), 2.08 (s, 3H), 2.04 (d, *J* = 7.9 Hz, 1H), 2.01 – 1.97 (m, 1H), 1.77 – 1.70 (m, 2H), 1.69 (dd, *J* = 6.6, 1.3 Hz, 2H); **signals due to Z isomer *inter alia*** 6.69 (s, 1H), 5.72 (d, *J* = 11.6 Hz, 1H), 5.52 – 5.41 (m, 1H), 2.20 (dd, *J* = 16.8, 7.8 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) **signals due to E isomer *inter alia*** δ 144.07, 136.82, 117.87, 77.27, 29.70, 20.69, 20.58, 18.02; **signals due to Z isomer *inter alia*** δ 145.23, 138.99, 120.63, 113.21, 77.27, 30.00, 24.57, 14.56, HRMS (EI) *m/z* calcd for $C_{15}H_{18}O$ [M$^{+\bullet}$] 214.1358, found 214.1362; IR (film) *v* 2924, 2852, 1625, 1437, 1193, 1146, 1119, 754, 721, 695, 542 cm^{-1}.

4.8. 2-phenyl-5-(prop-1-en-1-yl)-3,4-dihydro-2*H*-pyran **2n**

This compound was obtained according to the general procedure starting with 200 mg (1.1 mmol) of compound **5c**; an inseparable mixture of E/Z isomers in a 4:1 ratio, was obtained (129 mg, 59 %); TLC R_f = 0.82 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 Hz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.36 (s, 1H), 5.66 (d, J=15.4 Hz, 1H), 5.10 – 4.99 (m, 1H), 4.39 – 4.30 (m, 1H); **signals due to Z isomer *inter alia*** 6.41 (s, 1H), 5.45 (d, J=12.3 Hz, 1H), 5.10 – 4.99 (m, 1H), 4.39 – 4.30 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 143.9, 141.9, 130.1,

128.2, 125.8, 118.00, 77.3, 29.7, 20.5, 18.0; δ **signals due to Z isomer *inter alia*** δ 145.1, 141.9, 128.5, 128.2, 125.8, 120.7, 76.7, 30.0, 24.5, 14.6; HRMS (EI) m/z calcd for $C_{14}H_{16}O$ [$M^{+\bullet}$] 200.1201, found 200.1197; IR (film) *v* 2923, 2854, 1724, 1686, 1626, 1451, 1127, 1064, 757, 700 cm^{-1}.

4.9. 2-phenyl-5-[2-phenyl-ethenyl]-3,4-dihydro-2*H*-pyran **2o**

This compound was obtained as single E isomer according to the general procedure starting with 200 mg (1.1 mmol) of compound **5c**; isolated yield 132 mg (46 %); TLC R_f = 0.76 (2:8 AcOEt/hexanes); flash column chromatography (1:9 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ 7.37 (m, 2H), 7.26 – 7.10 (m, 6H), 7.11 – 7.00 (m, 2H), 6.73 (s, 1H), 6.64 (d, J=16.0 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.6 (dd, *J* = 8.9, 4.0 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.77 – 1.64 (m, 2H); δ ^{13}C NMR (101 MHz, C_6D_6) δ 146.8, 141.5, 138.5, 128.5, 128.3, 128.1, 127.6, 126.3, 125.8, 125.8, 122.7, 113.7, 77.6, 29.4, 20.2; HRMS (EI) m/z calcd for $C_{19}H_{18}O$ [$M^{+\bullet}$] 262.1358, found 262.1360; IR (film) *v* 3452, 3061, 3032, 2927, 1723, 1688, 1451, 1266, 1171, 1068, 1027, 754, 699 cm^{-1}.

General procedure for compounds **2e**; **2h – k**; **2p**:

To a solution of diisopropylamine (2 equiv.) in THF (5 mL) cooled to -78 ˚C, n-butyllithium (2 equiv., 2.5 M solution in hexanes) was added dropwise. The mixture was stirred at 0 ˚C for 30 minutes. To base prepared in this manner, phosphonium salt (2 equiv.) was added in three portions. The reaction mixture was stirred at RT until it cleared. It was cooled to 0˚C and 2-aryl-3,4-dihydro-2H-pyran-5-carbaldehyde (1 equiv.) was added. The reaction mixture was stirred at RT until TLC showed the reaction to be complete. The reaction mixture was quenched by slow addition of saturated $NaHCO_3$ and diluted with ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried with Na_2SO_4 and concentrated. The residue was suspended in diethyl ether and filtered. The filtrate was evaporated under reduced pressure. The product was purified by FCC in the appropriate solvent system.

4.10. 2-(4-methoxyphenyl)-5-[2-(4-methylphenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2e**

This compound was obtained as single E isomer according to the general procedure starting with 150 mg (0.69 mmol) of compound **5a**; isolated yield 45 mg (21 %); waxy solid; TLC R_f = 0.52 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 – 7.23 (m, 4H), 7.11 (m, 2H), 6.92 (m, 2H), 6.84 (s, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.30 (d, *J*=16.0 Hz, 1H), 4.85 (dd, *J*=10.5, 2.4 Hz, 1H), 3.82 (s, 3H), 2.51 – 2.30 (m, 5H), 2.16 (ddd, *J* = 1.9, 6.0, 2.8 Hz, 1H), 2.11 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.3, 146.5, 136.1, 135.5, 133.4, 129.3, 127.3, 127.1, 125.6, 122.5, 113.9, 113.7, 77.7, 55.3, 29.3, 21.1, 20.7; HRMS (EI) *m/z* calcd for $C_{21}H_{22}O_2$ [$M^{+\bullet}$] 306.1620, found 306.1617; IR (film) *v* 2952, 2914, 2848, 1628, 1612, 1514, 1250, 1178, 1149, 1035, 956, 832, 817, 767 cm^{-1}.

4.11. 2-(4-methoxyphenyl)-5-[2-(4-fluorphenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2h**

This compound was obtained as single E isomer according to the general procedure starting with 114 mg (0.52 mmol) of compound **5a;** isolated yield 38 mg (22%); waxy solid; TLC R_f= 0.69 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 6.98 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.85 (dd, *J* = 10.5, 2.4 Hz, 1H), 3.81 (s, 3H), 2.53 – 2.28 (m, 2H), 2.23 – 2.12 (m, 1H), 2.11 – 1.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 159.4, 146.9, 134.5, 133.3, 127.8, 127.3, 127.0, 121.3, 115.4, 113.9, 113.5, 77.7, 55.3, 29.2, 20.6; ^{19}F NMR (376MHz, $CDCl_3$) δ -116.23*;* HRMS (ES-TOF) *m/z* calcd for $C_{20}H_{19}FO_2$ [$M^{+\bullet}$] 310.1369, found 310.1375; IR (film) *v* 2955, 2932, 2839, 1631, 1613, 1508, 1250, 1227, 1179, 1156, 1126, 1035, 953, 830 cm^{-1}.

4.12. 2-(4-methoxyphenyl)-5-[2-(4-trifluormethylphenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2i**

This compound was obtained according to the general procedure starting with 70 mg (0.32 mmol) of compound **5a;** a mixture of E/Z isomers in a ratio 1:1.4 was obtained.

2'i Isolated yield of E isomer 35.2 mg (31 %); waxy solid; TLC R_f = 0.70 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.92 (m, 3H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.88 (dd, *J* = 10.5, 2.4 Hz, 1H), 3.82 (s, 3H), 2.54 – 2.32 (m, 2H), 2.25 –2.14 (m, 1H), 2.12 – 1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 148.3, 141.8, 133.0, 130.6, 127.9, 127.3, 125.5, 120.9, 113.9, 113.5, 77.9, 55.3, 29.1, 20.5; ^{19}F NMR (376MHz, $CDCl_3$) δ -62.27;HRMS (EI) *m/z* calcd for $C_{21}H_{19}F_3O_2$ [$M^{+\bullet}$] 360.1367, found 360.1345; IR (film) *v* 2957, 2925, 2840, 1631, 1607, 1516, 1326, 1249, 1199, 1156, 1109, 1067, 1035, 951, 858, 829 cm^{-1}.

2"i Isolated yield of Z isomer 49.7 mg (43 %); waxy solid; TLC R_f = 0.62 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.35 (m, 2H), 7.25 (m, 2H), 6.90 (m, 2H), 6.78 (s, 1H), 6.28 (d, *J* = 12.1 Hz, 1H), 6.12 (d, *J* = 12.1 Hz, 1H), 4.82 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.81 (s, 3H), 2.21 – 2.07 (m, 1H), 1.99 – 1.89 (m, 1H), 1.86 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.3, 142.9, 133.2, 131.1, 129.2, 128.2, 127.1, 124.5, 123.8, 123.2, 113.9, 112.0, 77.3, 55.3, 29.4, 24.1; ^{19}F NMR (376MHz, $CDCl_3$) δ -62.33; HRMS (EI) *m/z* calcd for $C_{21}H_{19}F_3O_2$ [$M^{+\bullet}$] 360.1367, found 360.1345.

4.13. 2-(4-methoxyphenyl)-5-[2-(4-cyanophenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2j**

This compound was obtained as single E isomer according to the general procedure starting with 70 mg (0.32 mmol) of compound **5a**; isolated yield 45.9 mg (45 %); yellow oil; TLC R_f= 0.66 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.42 (m, 2H), 7.30 (m, 2H), 6.95 – 6.88 (m, 3H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.88 (dd, *J* = 10.5, 2.4 Hz, 1H), 3.82 (s, 3H), 2.50 – 2.32 (m, 2H), 2.23 – 2.15 (m, 1H), 2.11 – 1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 149.1, 142.9, 132.8, 132.4, 131.9, 127.3, 125.9, 120.6, 119.3, 113.9, 113.5, 109.1, 78.0, 55.3, 29.0, 20.4; HRMS (EI) *m/z* calcd for $C_{21}H_{19}NO_2$ [$M^{+\bullet}$] 317.1416, found 317.1405; IR (film) *v* 2959, 2919, 2844, 2217, 1619, 1588, 1511, 1242, 1176, 1140, 825 cm^{-1}.

4.14. 2-(4-methoxyphenyl)-5-[2-(2-cyanophenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2k**

This compound was obtained according to the general procedure starting with 150 mg (0.69 mmol) of compound **5a**; an inseparable mixture of E/Z isomers in a 1.6:1 ratio was obtained (176 mg, 82 %); TLC R_f = 0.45 (2:8 AcOEt/hexanes); flash column chromatography (1:9 AcOEt/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ **signals due to E isomer *inter alia*** 6.85 – 6.79 (d, *J* = 15.5 Hz), 6.64 – 6.58 (d, *J* = 15.5 Hz), 4.63 – 4.55 (m, 1H), 3.32 (s, 3H), 2.11 – 1.98 (m, 2H); **signals due to Z isomer *inter alia*** 6.25 (d, *J* = 12.0 Hz, 1H), 5.99 (d, *J* = 12.0 Hz, 1H),), 4.63 – 4.55 (m, 1H), 3.29 (s, 3H), 1.95 – 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **signals due to E isomer *inter alia*** 159.6, 149.3, 117.8, 113.9, 77.9, 54.5, 29.1, 20.1; δ **signals due to Z isomer *inter alia*** δ 159.5, 149.5, 118.0, 113.8, 77.1, 54.4, 29.2, 19.7; HRMS (ES-TOF) *m/z* calcd for $C_{21}H_{19}NO_2Na$ [M+Na^+] 340.1314, found 340.1314; IR (film) *v* 2953, 2929, 2837, 2221, 1624, 1592, 1515, 1249, 1198, 1181, 1151, 1034, 954, 830, 760 cm^{-1}.

4.15. 2-(4-methoxyphenyl)-5-[2-(4-nitrophenyl)ethenyl]-3,4-dihydro-2*H*-pyran **2l**

To a solution of diisopropylamine (1.6 mL, 4 mmol) in THF (10 mL) cooled to -78°C, *n*-butyllithium (0.57 mL, 4 mmol, 2.5M solution in hexanes) was added dropwise. The mixture was stirred at 0 °C for 30 minutes. To base prepared in this manner, phosphonium salt (1.9 g, 4 mmol) was added in three portions. The reaction mixture was stirred at RT until it cleared. It was cooled to 0 °C and 2-aryl-3,4-dihydro-2H-pyran-5-carbaaldehyde (1 equiv.) was added. The reaction mixture was heated to 55°C and stirred at this temperature until TLC showed the reaction to be complete (about 20 h). The reaction mixture was cooled to RT and quenched by slow addition of saturated $NaHCO_3$. It was diluted with ethyl acetate (10 mL). The aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried with Na_2SO_4 and concentrated. The residue was suspended in diethyl ether and filtered. The filtrate was evaporated under reduced pressure. The residue was purified by FCC using 8% ethyl acetate in hexanes as the eluent. Isolated yield 46.3 mg (30 %); waxy solid; TLC R_f = 0.59 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 2H), 7.49 – 7.44 (m, 2H), 7.34 – 7.28 (m, 3H), 6.96 (s, 1H), 6.94 – 6.88 (m, 3H), 6.33 (d, J=15.9 Hz, 1H), 4.90 (dd, *J* = 10.6, 2.4 Hz, 1H), 3.82 (s, 3H), 2.49 – 2.36 (m, 2H), 2.23 – 2.17 (m, 1H), 2.10 – 2.01 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 149.7, 145.7, 145.0, 133.0, 132.7, 130.6, 127.3, 125.7,

124.1, 113.9, 113.6, 78.0, 55.3, 28.9, 20.4; HRMS (EI) m/z calcd for $C_{20}H_{19}NO_4$ [$M^{+\bullet}$] 337.1314, found 337.1313; IR (film) *v* 2955, 2922, 2850, 1622, 1582, 1510, 1338, 1246, 1195, 1180, 1153, 1108, 1032, 952, 861, 833 cm^{-1}.

4.16. 2-(4-methoxyphenyl)-5-(2-methylprop-1-en-1-yl)-3,4-dihydro-2*H*-pyran **2p**

This compound was obtained according to the general procedure starting with 70 mg (0.32 mmol) of compound **5a**; isolated yield 63 mg (90 %); waxy solid; TLC R_f = 0.86 (2:8 AcOEt/hexanes); flash column chromatography (8:92 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.52 (s, 1H), 5.51 (s, 1H), 4.78 (dd, *J* = 10.3, 2.5 Hz, 1H), 3.81 (s, 3H), 2.48 – 2.34 (m, 1H), 2.19 (ddd, *J* = 16.6, 5.6, 2.6 Hz, 1H), 2.11 – 2.02 (m, 1H), 2.01 – 1.88 (m, 1H), 1.82 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 143.4, 133.9, 130.8, 127.2, 123.3, 113.8, 111.9, 76.5, 55.3, 29.9, 27.0, 25.0, 19.6; HRMS (EI) m/z calcd for $C_{16}H_{20}O_2$ [$M^{+\bullet}$] 244.1463, found 244.1472; IR (film) *v* 2951, 2933, 2914, 2835, 1615, 1517, 1442, 1254, 1179, 1156, 1032, 884, 820 cm^{-1}.

General procedure for compounds **7a-b**

These compounds were prepared according to a literature procedure[16] using Tebbe's reagent.

4.17. 4-butoxy-2-methyl-1-(prop-1-en-2-yl)cyclohexene **7a**

This compound was obtained according to the general procedure starting with 200 mg (0.94 mmol) of compound **6a**; isolated yield 50 mg (26 %); yellow oil; TLC R_f = 0.57 (2:8 AcOEt/hexanes); flash column chromatography (2:98 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (dd, *J* = 4.0, 2.7 Hz, 1H), 4.90 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.67 (dd, *J* = 2.7, 0.9 Hz, 1H), 3.78 (ddd, *J* = 9.7, 6.7, 6.7 Hz, 1H), 3.51 (ddd, *J* = 9.7, 6.3, 6.3 Hz, 1H), 2.27 – 2.11 (m, 1H), 2.00 – 1.89 (m, 1H), 1.86 – 1.73 (m, 8H), 1.66 – 1.47 (m, 2H), 1.44 – 1.31 (m, 2H), 0.98 – 0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 142.1, 113.0, 111.5, 96.7, 67.5, 31.8, 27.0, 22.4, 20.9, 19.3, 17.5, 13.8; HRMS (EI) m/z calcd for $C_{13}H_{22}O_2$ [$M^{+\bullet}$] 210.1620, found 210.1627; IR (film) *v* 2958, 2930, 2870, 1671, 1441, 1379, 1237, 1134, 1117, 1065, 1015, 893 cm^{-1}.

4.18. 1-methyl-4-[3-methyl-4-(prop-1-en-2-yl)cyclohex-3-en-1-yl]benzene **7b**

This compound was obtained according to the general procedure starting with 100 mg (0,43 mmol) of compound **6b;** isolated yield 49 mg (50 %); waxy solid; TLC R_f = 0. 34 (2:8 AcOEt/hexanes); column chromatography (2:8 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.96 - 4.93 (m, 1H), 4.81 – 4.71 (m, 2H), 2.35 (s, 3H), 2.31 – 2.20 (m, 1H), 2.15 – 2.01 (m, 2H), 1.97 – 1.86 (m, 4H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 145.1, 139.3, 137.2, 129.0, 125.9, 113.2, 110.8, 76.7, 30.4, 24.9, 22.6, 21.1, 17.9; HRMS (EI) m/z calcd for $C_{16}H_{20}O$ [$M^{+\bullet}$] 228.1514, found 228.1514; IR (film) *v* 2922, 2847, 1663, 1630, 1516, 1435, 1382, 1240, 1205, 1086, 892, 812, 744, 697 cm^{-1}.

4.19. 1-methoxy-4-[3-methyl-4-(prop-1-en-2-yl)cyclohex-3-en-1-yl]benzene **7c**

To a solution of compound **6c** in THF (2 mL) cooled to 0 ˚C, methylmagnesium bromide (4 equiv., 3 M solution in diethyl ether) was added dropwise. The mixture was stirred at RT for 12h and then heated to 60 ˚C until TLC showed the reaction to be complete. The reaction mixture was cooled to 0˚C and quenched by slow addition of saturated $NaHCO_3$ followed by dilution with ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried with Na_2SO_4 and concentrated. The residue was purified by FCC on Florisil® using 2% diethyl ether in hexanes as the eluent. Isolated yield 42.5 mg (87 %).

(**7c**): waxy solid; column chromatography (2:98 Et_2O/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 6.90 (m, 2H), 4.95 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.75 (m, 2H), 3.81 (s, 3H), 2.36 – 2.19 (m, 1H), 2.16 – 2.12 (m, 1H), 2.08 – 1.99 (m, 1H), 1.97 – 1.87 (m, 4H), 1.85 (dd, *J* = 1.4, 0.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 146.2, 145.1, 134.5, 127.3, 113.8, 113.2, 110.7, 76.5, 55.3, 30.3, 25.0, 22.6, 17.9; HRMS (EI) m/z calcd for $C_{16}H_{20}O_2$ [$M^{+\bullet}$] 244.1463, found 244.1453; IR (film) *v* 2946, 2921, 2840, 1660, 1614, 1514, 1244, 1204, 1175, 1084, 1036, 891, 827 cm^{-1}.

5. Experimental details and characterization data of cyclohexenes derivatives 3

General procedure for [1,5] O→C rearrangement reaction of alkoxydienes **2a-2b, 2d, 2f-2g**

To a solution of alkoxydiene **2** (1 equiv., 0.04 M solution in toluene) cooled to -78 ˚C was added dropwise a 0.1 M solution of the Lewis acid (80 mol%) in toluene. The reaction mixture was stirred keeping the temperature below -65˚C until TLC showed the reaction to be complete. The reaction was quenched with triethylamine (2 mL) and saturated $NaHCO_3$. The reaction mixture was diluted with ethyl acetate (5 mL) and the aqueous layer was extracted twice with ethyl acetate (2x5 mL). The combined extracts were dried with Na_2SO_4 and evaporated. The product was purified by FCC in the appropriate solvent system.

5.1. 3-methyl-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3a**

(5.1 mg, 51%) was obtained according to the general procedure starting with 10 mg (0.04 mmol) of compound **2a**; yellow oil; TLC R_f = 0.53 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (400 MHz, C_6D_6) δ ***inter alia*** 9.35 (s, 1H), 9.33 (s, 1.4 H), 6.11 - 6.09 (m, 1H), 5.99 – 5.97 (m, 1H), 3.33 (s, 3.8 H), 3.32 (s, 3H), 0.70 (d, *J* = 7.1 Hz, 3H), 0.48 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ ***inter alia*** 192.6, 192.5, 158.5, 158.3, 154.3, 154.0, 140.1, 140.4, 135.4, 137.0, 113.0, 113.6, 54.4, 54.4, 22.2, 22.1, 21.5, 21.4; HRMS (ES-TOF) m/z calcd for $C_{15}H_{18}O_2Na$ [M+Na^+] 253.1205, found 253.1300; IR (film) *v* 2956, 2931, 2871, 2836, 1684, 1642, 1611, 1513, 1460, 1247, 1177, 1037, 833 cm^{-1}.

5.2. 3-propyl-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3b**

(10.9 mg; 69 %) was obtained according to the general procedure starting with 15.6 mg (0.06 mmol) of compound **2b**; yellow oil; TLC R_f = 0.54 (2:8 AcOEt/hexanes); flash column chromatography (7:93 AcOEt/Hex); ^{1}H NMR (600 MHz, C_6D_6) δ ***inter alia*** 9.13 (s, 1H), 9.11 (s, 1.7 H), 6.07 (d, *J* = 4.5 Hz, 1.8H), 5.96 (m, 1H), 3.04 (s, 8.5H), 2.43 – 2.37 (m, 2H), 1.82 – 1.75 (m, 1H), 1.43 – 1.36 (m, 1H), 1.31 – 1.25 (m, 2H), 0.41 (t, *J* = 7.1 Hz, 3H), 0.36 (t, *J* = 7.0 Hz, 5.5H); ^{13}C NMR (151 MHz, C_6D_6) δ ***inter alia*** 192.6, 192.5, 158.4, 158.3, 152.5, 153.3, 141.0, 140.7, 137.0, 135.0, 128.6, 128.0, 113.9, 113.6, 54.4, 54.3, 45.0, 42.6, 41.9, 40.6, 34.2, 32.2, 30.2, 29.8, 22.0, 21.6, 20.5, 19.2, 13.9, 13.9; HRMS (EI) m/z calcd for $C_{17}H_{22}O_2$ [$M^{+\bullet}$] 258.1620, found 258.1616; IR (film) *v* 2955, 2927, 2855, 1685, 1610, 1512, 1462, 1248, 1177, 1036, 831 cm^{-1}.

5.3. 3-(3,4-diisopropylphenyl)-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3d**

(6.9 mg; 23 %) was obtained according to the general procedure starting with 30 mg (0.07 mmol) of compound **2d**; yellow oil; TLC R_f = (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (600 MHz, C_6D_6) δ ***inter alia*** δ 9.69 (s, 1.7 H), 9.63 (s, 1H), 6.62 – 6.60 (m, 1.7H), 6.65-6.63 (m, 1H), 3.51 (s, 5.7H), 3.55 – 3.52 (m, 1H), 3.49 (s, 3H), 1.44 (s, 15.3H), 1.42 (s, 9H), 1.40 (s, 15.5 H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, C_6D_6) δ ***inter alia*** 192.7, 192.5, 158.3, 158.2, 152.1, 150.6, 150.4, 149.5, 141.8, 141.6, 141.4, 137.0, 136.1, 135.1, 124.6, 124.3, 124.2, 123.9, 122.6, 120.0, 120.0, 113.5, 113.2, 54.3, 54.3, 51.7, 48.6, 48.5, 43.9, 34.9, 34.8, 34.5, 34.3, 31.9, 31.2, 31.2, 31.2, 31.1, 30.1, 22.6, 21.5; HRMS (EI) m/z calcd for $C_{28}H_{36}O_2$ [$M^{+\bullet}$] 404.2715, found 404.2707; IR (film) *v* 2959, 2869, 1688, 1462, 1362, 1277, 1248, 1185, 1081, 1038, 964, 823 cm^{-1}.

5.4. 3-phenyl-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3f**

(100 mg; 100 %) was obtained according to the general procedure starting with 100 mg (0.17 mmol) of compound **2f**; yellow oil; TLC R_f = 0.60; ^{1}H NMR (400 MHz, C_6D_6) δ ***inter alia*** 9.40 (s, 1H), 9.34 (s, 1.8H), 6.22 – 6.19 (m, 1H), 6.18 – 6.15 (m, 1.9H), 3.40 – 3.35 (m, 1H), 3.24 (s, 3H), 3.22 (s, 5.8H), 3.21 – 3.17 (m, 1.7H), 2.76 (ddd, *J* = 12.9, 5.5, 2.5 Hz, 1H), 2.69 – 2.61 (m, 1H), 2.60 – 2.52 (m, 2.1 H), 2.50 – 2.42 (m, 2.1H), 1.46 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ ***inter alia*** 192.7, 192.5, 158.4, 158.3, 151.6, 150.1, 142.5, 142.0, 141.7, 141.2, 140.6, 138.1, 135.9, 134.9, 128.8, 128.3, 128.2, 128.2, 126.5, 124.6, 113.6, 113.2, 54.3, 51.0, 48.2, 48.2, 43.9, 29.4, 22.6, 22.0, 22.0, 21.6; HRMS (EI) m/z calcd for $C_{20}H_{20}O_2$ [$M^{+\bullet}$] 292.1463, found 292.1462; IR (film) *v* 2932, 2835, 1684, 1642, 1610, 1513, 1248, 1178, 1035, 831, 750, 703 cm^{-1}.

5.5. 3-(2-bromophenyl)l-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3g**

(3.8 mg; 53 %) was obtained according to the general procedure starting with 20 mg (0.06 mmol) of compound **2g**; yellow oil; TLC R_f = 0.46 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (600 MHz, C_6D_6) δ ***inter alia*** 9.30 (s, 1.3H), 9.25 (s, 1H), 5.96 – 5.94 (m, 1H), 5.94 – 5.92 (m, 1.4H), 3.18 (s, 3H), 3.19 (s, 3.9H), 2.87

(ddd, *J* = 12.0, 6.2, 3.0 Hz, 1.4H), 2.49 – 2.41 (m, 1H), 2.20 – 2.10 (m, 1H), 2.10 – 2.02 (m, 1.6H), 1.45 – 1.37 (m, 1.6H); ^{13}C NMR (151 MHz, C_6D_6) δ ***inter alia*** 192.6, 192.4, 158.4, 158.4, 150.5, 149.8, 141.5, 141.1, 113.6, 113.0, 54.2, 54.2, 45.1, 43.6, 43.5, 28.7, 23.4, 21.7, 21.6; HRMS (EI) m/z calcd for $C_{20}H_{19}BrO_2$ [$M^{+\bullet}$] 372.0548, found 372.0544; IR (film) *v* 2955, 2932, 2870, 2836, 1686, 1512, 1467, 1248, 1181, 1035, 829, 755 cm^{-1}.

General procedure for [1,5] O→C rearrangement reaction of alkoxydienes **2c, 2e, 2h – 2j, 2m, 2o**

To a solution of alkoxydiene **2** (1 equiv., 0.04 M solution in toluene) cooled to -78 °C was added dropwise a 0.1 M solution of the Lewis acid (80 mol%) in toluene. The reaction mixture was stirred keeping the temperature below -65 °C until TLC showed the reaction to be complete. The reaction was quenched at this temperature with phosphate buffer (1 M solution, pH 7.4). The reaction mixture was diluted with ethyl acetate (5 mL) and the aqueous layer was extracted twice with ethyl acetate (2x5 mL). The combined extracts were dried with Na_2SO_4 and evaporated.

5.6. 3,4-di(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3c**

(9.3 mg , 48%) was obtained according to the general procedure starting with 19.3 mg (0.06 mmol) of compound **2c**; yellow oil; isolated; TLC R_f = 0. 65 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (400 MHz, $CDCl_3$) δ ***inter alia*** 9.62 (s, 1H), 9.55 (s, 1H), 7.29 – 7.22 (m, 2H), 7.19 – 7.14 (m, 2H), 3.75 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.74 (s, 3H), 3.17 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ***inter alia*** 194.27, 194.02, 158.53, 158.37, 158.05, 158.01, 153.74, 152.17, 141.58, 141.20, 113.77, 113.62, 113.23, 112.98, 55.18, 55.16, 48.35, 47.59, 29.70, 29.50, 22.60, 21.98, 21.63, 21.44; HRMS (EI) m/z calcd for $C_{21}H_{22}O_3$ [$M^{+\bullet}$] 322.1569, found 322.1565; IR (film) *v* 3062, 3033, 2929, 2856, 1673, 1628, 1192, 1171, 1103, 758, 700 cm^{-1}.

5.7. 3-(4-methylphenyl)-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3e**

(11.4 mg; 60 %) was obtained according to the general procedure starting with 19 mg (0.06 mmol) of compound **2e**; yellow oil; TLC R_f = 0.50 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AOEt/PhMe); ^{1}H NMR (600 MHz, $CDCl_3$) δ ***inter alia*** 9.54 (s, 1.6H), 9.47 (s, 1H), 3.77 (t, *J* = 4.3 Hz, 1H), 3.11 (ddd, *J* = 12.9, 5.5, 2.7 Hz, 1.7H), 3.60 – 3.53 (m, *J* = 11.2 Hz, 1H), 2.57 – 2.46 (m, *J* = 17.8, 2.2 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 5.5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ***inter alia*** 194.3, 194.1, 157.9, 156.7, 153.7, 152.2, 141.6, 141.1, 139.1, 136.4, 136.3, 136.1, 135.0, 134.5, 130.1, 129.0, 128.8, 128.2, 128.2, 128.1, 113.6, 113.1, 55.2, 55.2, 50.6, 48.1, 48.0, 44.1, 22.7, 22.6, 21.9, 21.7, 21.0, 21.0; HRMS (EI) m/z calcd for $C_{21}H_{22}O_2$ [$M^{+\bullet}$] 306.1620, found 306.1606; IR (film) *v* 2955, 2924, 2852, 1629, 1611, 1512, 1249, 1179, 1148, 1034, 956, 832, 818 cm^{-1}.

5.8. 3-(4-fluorophenyl)-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3h**

(12.1 mg; 65 %) was obtained according to the general procedure starting with 18.6 mg (0.06 mmol) of compound **2h**; an inseparable mixture of syn/anti isomers was obtained; yellow oil; TLC R_f = 0.53 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (600 MHz, $CDCl_3$) δ ***inter alia*** 9.63 (s, 1H), 9.56 (s, 1.3H), 6.94 – 6.91 (m, 1H),6.79 – 6.77 (m, 1.3H), 3.89 – 3.85 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3.8H), 3.66 – 3.61 (m, 1.5H), 3.20 (ddd, *J* = 12.9, 5.7, 2.7 Hz, 1H), 2.65 – 2.58 (m, 1.6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ***inter alia*** 194.1, 193.9, 55.2, 55.2, 50.5, 48.5, 47.5, 44.0, 29.5, 22.5, 22.0, 21.4; HRMS (ES-TOF) m/z calcd for $C_{20}H_{19}FO_2$ [$M^{+\bullet}$] 310.1369, found 310.1364; IR (film) *v* 2928, 2853, 1684, 1608, 1511, 1248, 1178, 1159, 1035, 833 cm^{-1}.

5.9. 3-(4-trifuloromethylphenyl)-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3i**

(7.7 mg; 72 %) was obtained according to the general procedure starting with 8 mg (0.02 mmol) of compound **2i**; yellow oil; TLC R_f = 0.48 (2:8 AcOEt/hexanes); flash column chromatography (1:99 AcOEt/PhMe); ^{1}H NMR (500 MHz, $CDCl_3$) δ ***inter alia*** 9.64 (s, 1H), 9.57 (s, 3H), 6.92 (d, J=4.0 Hz, 1H), 6.77 – 6.74 (m, 3H), 3.96 – 3.92 (m, 1H), 3.76 (s, 9H), 3.75 (s, 3H), 3.75 – 3.71 (m, 3H), 3.31 – 3.23 (m, 1H), 2.68 – 2.60 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ***inter alia***; δ 193.9, 193.7, 158.2, 158.2, 151.6, 150.2, 125.3, 124.4, 113.8, 113.4, 55.2, 55.2, 51.0, 48.3, 48.1, 43.9, 29.5, 22.5, 22.0, 21.5; HRMS (ES- TOF) m/z calcd for $C_{21}H_{19}F_3O_2$ [$M^{+\bullet}$] 360.1337, found 360.1338; IR (film) *v* 2929, 2854, 1686, 1611, 1513, 1326, 1349, 1165, 1123, 1112, 1068, 1036, 1018, 833, 758 cm^{-1}.

5.10. 3-(4-cyanophenyl)-4-(4-methoxyphenyl)cyklohex-1-enecarbaldehyde **3j**

(5.1 mg; 74 %) was obtained according to the general procedure starting with 6.9 mg (0.02 mmol) of compound **2j**; yellow oil; TLC R_f = 0.20 (2:8 AcOEt/hexanes); flash column chromatography (2:8 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 9.65 (s, 1H), 9.58 (s, 3H), 7.50 – 7.47 (m, 6H), 7.40 – 7.37 (m, 2H), 7.00 – 6.97 (m, 6H), 6.90 – 6.87 (m, 1H), 6.86 – 6.82 (m, 6H), 6.70 – 6.67 (m, 2H), 6.65 – 6.62 (m, 2H), 3.78 – 3.77 (m, 1H), 3.77 – 3.75 (m, 12H), 3.74 – 3.70 (m, 3H), 2.79 – 2.72 (m, 1H), 2.72 – 2.60 (m, 7H), 2.35 (m, 6H), 2.13 – 2.06 (m, 3H), 2.03 – 1.93 (m, 5H), 1.86 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 196.3, 192.3, 148.9, 132.0, 131.5, 130.7, 130.4, 127.1, 125.6, 120.5, 118.9, 113.8, 113.7, 113.4, 113.3, 77.7, 54.4, 54.3, 43.4, 31.9, 29.8, 29.0, 20.1, 14.0; HRMS (ES-TOF) *m/z* calcd for $C_{21}H_{19}NO_2$ [$M^{+\bullet}$] 317.1416, found 317.1412; IR (film) *v* 2959, 2919, 2844, 2217, 1619, 1588, 1511, 1242, 1176, 1140, 825 cm^{-1}.

5.11. 3-methyl-4-(4-methylphenyl)cyklohex-1-enecarbaldehyde **3m**

(4.8 mg; 39 %) was obtained according to the general procedure starting with 12.3 mg (0.06 mmol) of compound **2m**; yellow oil; TLC R_f = 0.60 (2:8 AcOEt/ Hex); ^{1}H NMR (400 MHz, C_6D_6) δ ***inter alia*** 9.34 (s, 1H), 9.32 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 6H), 6.08 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 1H), 5.97 (ddd, *J* = 2.2, 1.1 Hz, 1H), 2.13 (s, 5H), 2.12 (s, 4H), 0.70 (s, 2H), 0.68 (s, 3H), 0.48 (s, 2H), 0.46 (s, 2H); ^{13}C NMR (101 MHz, C_6D_6) δ ***inter alia*** 192.68, 192.56,

154.28, 154.08, 135.59, 135.28, 47.91, 42.31, 37.94, 35.81, 29.85, 29.82; HRMS (EI) m/z calcd for $C_{15}H_{18}O$ [$M^{+\bullet}$] 214.1358, found 214.1359; IR (film) *v* 2925, 2853, 1713, 1685, 1514, 1454, 1376, 1262, 1179, 1077, 813 cm^{-1}.

5.12. 4-(4-methoxyphenyl)-3,3-dimethylcyclohex-1-ene-1-carbaldehyde **3p**

This compound was obtained according to the general procedure starting with 40.9 mg (0.17 mmol) of compound **2p;** isolated yield 22.4 mg (40 %); yellow oil; TLC R_f = 0.57 (2:8 AcOEt/hexanes); flash column chromatography (2:98 AcOEt/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ ***inter alia*** 9.48 (s, 1H), 7.10 – 7.06 (m, 2H), 6.54 (dd, *J* = 2.1, 1.1 Hz, 1H), 3.81 (s, 3H), 2.95 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.61 (dd, *J* = 12.7, 2.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ***inter alia*** 194.59, 161.18, 158.15, 138.58, 134.12, 75.02, 37.31, 28.27, 24.72, 22.81, 22.43; LRMS (EI) m/z calcd for $C_{16}H_{20}O_2$ [$M^{+\bullet}$] 244.1, found 244.1; IR (film) *v* 2954, 2938, 1720, 1685, 1611, 1513, 1484, 1248, 1179, 1037, 831 cm^{-1}.

5.13. 1-[2-methyl-4-(4-methylphenyl)cyclohex-1-en-1-yl]ethanone **8b**

This compound was obtained according to the general procedure starting with 38.4 mg (0.17 mmol) of compound **7b**; isolated yield 36 mg (71 %); yellow oil; TLC R_f = 0.57 (2:8 AcOEt/hexanes); flash column chromatography (2:98 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 4H), 2.83 – 2.72 (m, 1H), 2.50 – 2.39 (m, 2H), 2.40 – 2.19 (m, 8H), 2.06 – 1.95 (m, 1H), 1.92 (s, 3H), 1.80 – 1.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.94, 143.00, 140.76, 135.78, 132.84, 129.17, 126.60, 41.30, 39.30, 29.76, 29.49, 27.43, 21.46, 20.96; HRMS (EI) m/z calcd for $C_{16}H_{20}O$ [$M^{+\bullet}$] 228.1514, found 228.1515; IR (film) *v* 2946, 2921, 2840, 1660, 1614, 1514, 1244, 1204, 1175, 1084, 1036, 891, 827 cm^{-1}.

5.14. 1-[4-(4-methoxyphenyl)-2-methylcyclohex-1-en-1-yl]ethanone **8c**

This compound was obtained according to the general procedure starting with 41 mg (0.17 mmol) of compound **7c**; isolated yield 22.2 mg (54 %); yellow oil; TLC R_f = 0.50 (2:8 AcOEt/hexanes); flash column chromatography (1:9 AcOEt/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (m, 2H), 6.86 (m, 2H), 3.80 (s, 3H), 2.76 (s, 1H), 2.50 – 2.16 (m, 5H), 2.04 – 1.81 (m, 4H), 1.67 (s, 2H), 1.37 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.0, 158.0, 140.8, 138.1, 132.8, 127.6, 113.9, 55.3, 41.4, 38.8, 29.8, 29.6, 27.4, 21.5; HRMS (ES-TOF) m/z calcd for $C_{16}H_{20}O_2$ [$M^{+\bullet}$] 244.1463; found 244.1464; IR (film) *v* 2924, 2840, 1613, 1514,1246, 1205, 1177, 1084, 1037, 828 cm^{-1}.

5.15. 3-(2-cyanophenyl)-4-(4-methoxyphenyl)cykloheks-1-enocarbaldehyde **3k**

To a solution of alkoxydiene **2k** (60 mg, 0.17 mmol, 0.04 M solution in toluene) cooled to -78 °C was added Lewis acid (3 equiv., 5.1 mL 0.1 M solution in toluene). The reaction mixture was stirred keeping the temperature below -65 °C until TLC showed the reaction to be complete. The reaction was quenched at this low temperature with phosphate buffer (1 M solution, pH 7.4). The reaction mixture was diluted with ethyl acetate (5 mL) and the aqueous layer was extracted twice with ethyl acetate (2x5 mL). The combined extracts were dried with

Na_2SO_4. and evaporated. The residue was purified by FCC using 20% ethyl acetate in hexanes as the eluent.

(44.2 mg; 80 %) was obtained; yellow oil; TLC R_f = 0.23 (2:8 AcOEt/hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ ***inter alia*** 9.30 (s, 1H), 9.25 (s, 3H), 6.83 (d, 6H), 6.81 – 6.75 (m, 4H), 6.72 (m, 6H), 6.65 (m, 6H), 5.80 – 5.77 (m, 4H), 4.12 (s, 1H), 3.92 (ddd, *J* = 5.8, 3.5, 1.8 Hz, 3H), 3.21 (s, 3H), 3.18 (s, 9H), 2.83 (ddd, *J* = 3.0, 6.3, 3.0 Hz, 1H), 2.57 (dd, *J* = 17.9, 4.8 Hz, 2H), 2.53 – 2.46 (m, 4H), 2.46 – 2.40 (m, 3H), 2.18 – 2.07 (m, 5H), 2.04 – 1.94 (m, 2H), 1.69 – 1.62 (m, 3H), 1.53 – 1.43 (m, 6H), 1.39 – 1.33 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ ^{13}C NMR (126 MHz, C_6C_6) δ ***inter alia*** 192.4, 192.3, 158.7, 158.5, 149.1, 148.2, 146.1, 142.6, 141.9, 141.5, 134.3, 133.0, 132.3, 132.2, 132.0, 131.1, 129.6, 129.2, 128.3, 128.3, 126.7, 117.3, 117.3, 114.7, 113.8, 113.4, 113.2, 54.2, 54.2, 48.6, 47.8, 45.0, 43.4, 29.2, 22.2, 22.1, 21.9; HRMS (ES-TOF) m/z calcd for $C_{21}H_{19}NO_2Na$ [M+Na$^+$] 340.1310, found 340.1412; IR (film) *v* 2932, 2837, 2224, 1685, 1513, 1249, 1179, 1034, 832, 767 cm^{-1}.

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