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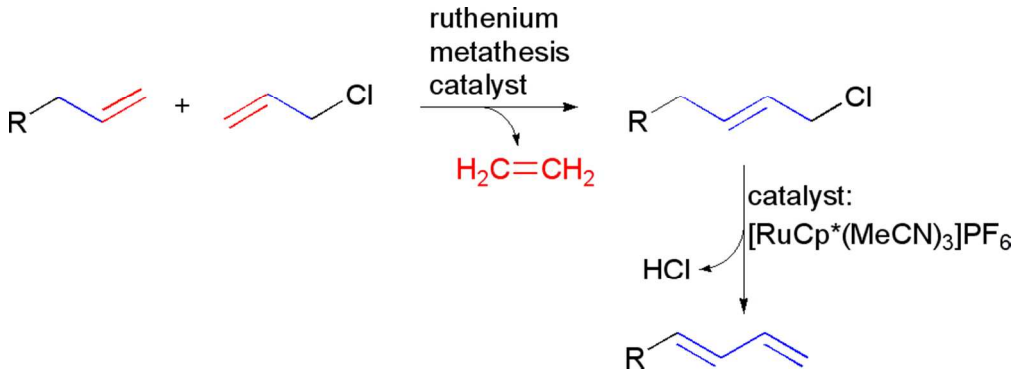

Two step synthesis of terminal 1,3-dienes catalyzed by two different ruthenium complexes
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ARTICLE TYPE

Terminal conjugated dienes *via* a ruthenium-catalyzed cross-metathesis/elimination sequence: application to renewable resources

Hallouma Bilel,[a,b] Naceur Hamdi,[a] Fethi Zagrouba,[a] Cédric Fischmeister,[b] Christian Bruneau[b]

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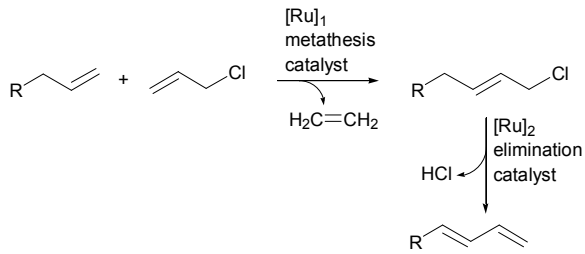
We report a sequence of two ruthenium-catalyzed transformations, namely olefin cross-metathesis with allylic chlorides followed by elimination, which gives a straightforward access to terminal 1,3-dienes from natural products.

Introduction

Catalytic reactions that make possible straightforward transformations of natural compounds into high added-value products have potential in the perspective of the utilization of renewable feedstock for fine chemistry.[1] In this respect, olefin cross-metathesis has already been investigated with the aim of producing polyfunctional products from various unsaturated renewable sources such as unsaturated fats and oils,[2] terpenes,[3] and phenylpropenoids.[4] Natural products featuring a conjugated diene motive are scarce. Among them, some compounds with a branched arrangement as in myrcene[5] or some others with internal conjugated unsaturated structures such as carotenes and retinol,[6] a few C18:3 fatty acid derivatives,[7] conjugated linoleic acid,[8] and other polyfunctional natural products can be found.[9] However, only 1,2-bis(11,13-tetradecadienoyl)-sn-glycero-3-phosphonylcholine present in some lipid membranes as lipid contains a terminal linear 1,3-diene motive.[10] Besides classical cycloaddition reactions, terminal conjugated dienes have recently been used in useful transformations such as rhodium-catalyzed enantioselective [4+2] cycloaddition,[11] [4+3] cycloaddition with vinylcarbenoids,[12] cobalt-catalyzed hydrovinylation,[13] regioselective palladium-catalyzed hydroarylation,[14] and addition to aldehydes[15] and diene isomerization[16] catalyzed by ruthenium hydride complexes.

Many methods for the synthesis of dienes exist. Terminal 1,3-dienes have thus been obtained via elimination reactions,[17] olefination via aldehydes,[18] cross coupling of two olefinic moieties,[19] and olefin metathesis.[20]

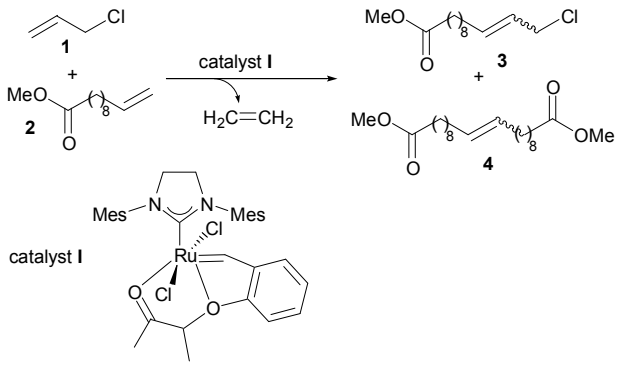
Here we describe a sequence of two ruthenium-catalyzed reactions, which leads to terminal dienes from unsaturated natural products and allylic chlorides via olefin cross-metathesis followed by HCl elimination according to Scheme 1. In the overall transformation the natural product has been formally rearranged and homologated by one $=CH_2$ group.



Scheme 1. Two step ruthenium-catalyzed formation of conjugated dienes

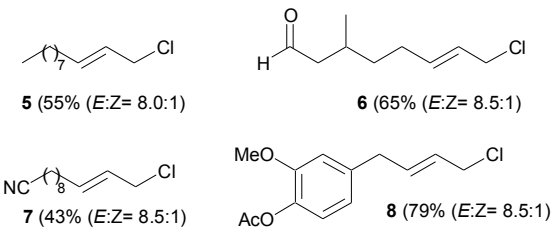
Results and discussion

Based on the pioneering works by M. A. R. Meier,[21] the reaction conditions of the cross-metathesis of allyl chloride **1** with natural products were first optimized using the ruthenium catalyst **I** (Umicore M51) and methyl 10-undecenoate **2** as substrate (Scheme 2).



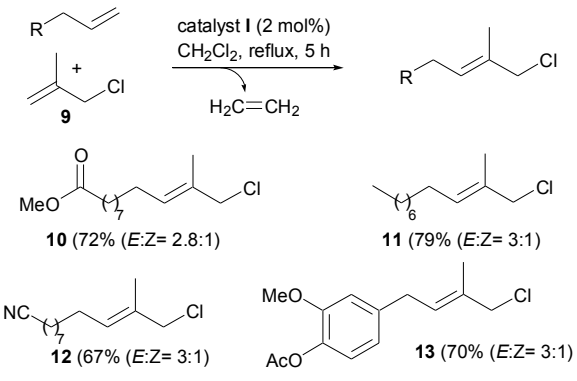
Scheme 2. Cross-metathesis of methyl 10-undecenoate **2** with allyl chloride **1**

Using 6 equivalents of allyl chloride **1** with respect to methyl 10-undecenoate **2** in the presence of 2 mol% of catalyst **I** in refluxing dichloromethane ([**1**]= 0.25 mol.L^{-1}] for 5 h led to the best results. The conversion of **2** was complete and the formation of its self-metathesis product **4** was limited to only trace amounts due to the presence of an excess of allyl chloride **1**. The cross-metathesis product **3** was isolated in 80% yield and the ^{1}H NMR analysis indicated that the *E*-isomer was the major product in a 8.5:1 (*E*/*Z*) molar ratio. Even though these catalytic conditions are different from Meier's ones (neat conditions, different ruthenium catalyst, low catalyst loading), the production of **3** was comparable. Under similar conditions, the cross-metathesis of allyl chloride with 1-decene arising from ethenolysis of methyl oleate[22] and citronellal gave high conversion and the products **5** and **6** were isolated in 55 and 65% yield, respectively. With undecenenitrile readily available from castor oil,[23] the conversion was completed after 5 h and the product **7** was isolated in a moderate 43% yield. Starting from eugenol acetate and allyl chloride, complete conversion was obtained in 5 h and no carbon-carbon double bond isomerisation took place prior and after cross-metathesis, which allowed the isolation of **8** in 79% yield. Satisfactory analyses for compounds **3**, **5**-**8** were obtained and they all resulted from stereoselective formation of the *E*-isomer with a *E*:*Z* ratio in the range 8-8.5:1 (Scheme 3).



Scheme 3. Various allylic products **5**-**8** arising from cross-metathesis of allyl chloride with natural products

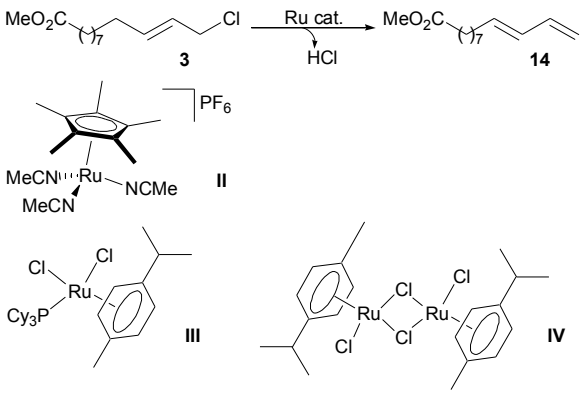
To enlarge the scope of our method, other allylic chlorides were prepared *via* cross-metathesis of 2-methylprop-2-enyl chloride **9** with the same bio-sourced products according to Scheme 4. Under the previous experimental conditions, total conversions of the substrates were observed and the chloromethallyl derivatives **10**-**13** were isolated in good yields.



Scheme 4. Preparation of allylic substrates **10**-**13** via cross-metathesis with methallyl chloride

Again a stereoselective cross-metathesis took place and the (*E*/*Z*) isomer ratio was around 3:1. It is noteworthy that the cross-metathesis of **9** with the trisubstituted double bond of citronellal was not possible in these conditions and even at 80 °C under neat conditions.

We have recently shown that elimination took place from dienic allylic carbonates in the presence of [ruthenium(cyclopentadienyl)(MeCN)(bipyridine)]PF_6 as catalyst at 90 °C to generate dendralenes.[24] The possibility of preparing conjugated dienes from aliphatic allylic chlorides with ruthenium catalysts was thus explored. The elimination reaction starting from methyl 12-chlorododec-10-enoate **3** was studied in detail in the presence of 5 mol% of [ruthenium(pentamethylcyclopentadienyl)$(MeCN)_3$]PF_6 **II** in acetonitrile (Scheme 5, Table 1).



Scheme 5. Ruthenium-catalyzed formation of 1,3-dienes from **3**

The presence of a base was necessary to obtain a good conversion of **3** as only 60% conversion was reached after 17 h of reaction at 90 °C without any base, whereas full conversion was obtained in the presence of 1.2 equivalent of Cs_2CO_3 (entries 1, 2). The temperature could be decreased down to room temperature and complete conversion was obtained in 5 h. The experiments were initially carried out in the presence of molecular sieves that had a beneficial influence in the elimination from allylic carbonates,[24] but starting from the allylic chloride **3**, there was no interest using this water trap. Lower amounts of catalysts led to lower conversions (entries 7, 8). The best solvent was the coordinating acetonitrile whereas very low conversion was obtained in dichloromethane, the solvent of the cross-metathesis reaction (entry 9). Potassium carbonate and triethylamine were also evaluated as bases but they led to incomplete conversion even after 17 h reaction (entries 10, 11). The ruthenium(arene) complexes **III** and **IV** tested under our best conditions were not active (entries 12, 13). Finally, HCl elimination was also attempted with palladium catalysts, which have also shown good activities in some elimination reactions from allylic substrates.[25] Again, the reaction required the presence of a base but efficient reactions could not be performed at room temperature (entries 14, 15). Finally in the absence of ruthenium catalyst, no elimination took place and the starting allylic chloride was recovered. It is noteworthy that both *E* and *Z* isomers of **3** were converted into the diene **14**. The ^{1}H and ^{13}C NMR analysis of **14** indicated that

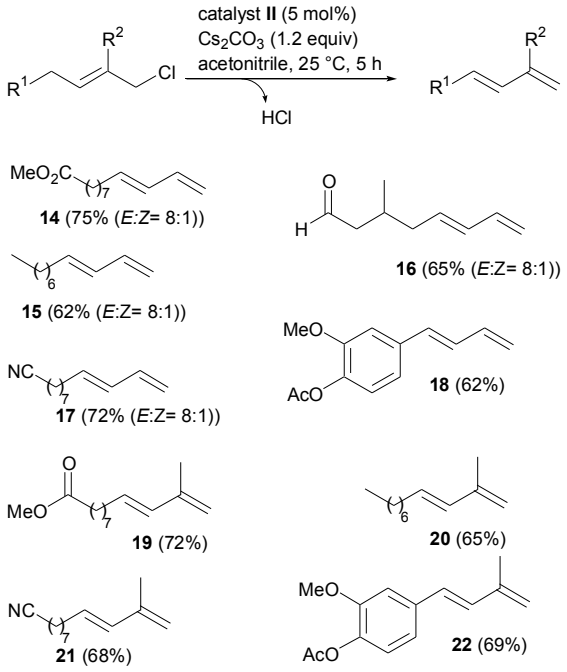
the *E*-stereochemistry of the internal double bond was highly favoured with a *E*/*Z* molar ratio of 8:1, the respective ^{3}J coupling constants being 15.2 and 10.4 Hz. The proton chemical shifts and coupling constants are perfectly in line with previous results of the literature with comparable aliphatic terminal 1,3-dienes.[17,18a, 26] The mechanism of this elimination reaction involves allylic activation by complex **II** to form [RuClCp*(allyl)(MeCN)]PF_6 intermediate as was shown under stoichiometric conditions.[27] In the presence of a non-nucleophilic base, a proton abstraction takes place to give the diene.[24,25,27]

Table 1 Ruthenium-catalyzed elimination of HCl from substrate **3**

Entry	Catalyst	Temp. (°C)	Time (h)	Conversion (%)	Yield in **4** (%)
1[b]	**II** (5 mol%)	90	17	60	n.d.
2	**II** (5 mol%)	90	17	100	68%
3	**II** (5 mol%)	50	17	100	71%
4	**II** (5 mol%)	25	17	100	73%
5[c]	**II** (5 mol%)	25	17	100	71%
6[c]	**II** (5 mol%)	25	5	100	75%
7[c]	**II** (3 mol%)	25	5	40	n.d.
8[c]	**II** (1 mol%)	50	5	20	n.d.
9[d]	**II** (5 mol%)	25	17	15	n.d.
10[e]	**II** (5 mol%)	25	17	86	n.d.
11[f]	**II** (5 mol%)	25	17	80	n.d.
12[c]	**III** (5 mol%)	25	5	2	n.d.
13	**IV** (5 mol%)	90	17	0	-
11[b]	$Pd(OAc)_2$ (5 mol%)	90	17	0	-
14	$Pd(OAc)_2$ (5 mol%) PPh_3 (10 mol%)	90	17	100	75%
15[c]	$Pd(OAc)_2$ (5 mol%) PPh_3 (10 mol%)	25	5	10	n.d.
16	no catalyst	50	17	0	-

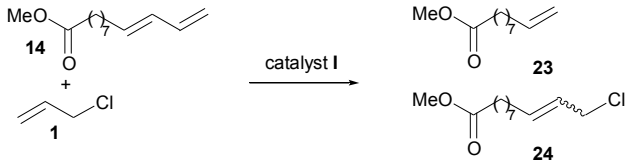
[a] General conditions: **3** (0.5 mmol), catalyst (5 mol%), acetonitrile (3 mL), Cs_2CO_3 (1.2 equiv.), 4 Å molecular sieves (250 mg), conversion determined by GC, isolated yield, n.d. not determined ;
[b] no base; [c] no molecular sieve; [d] CH_2Cl_2 as solvent; [e] K_2CO_3 as a base; [f] Et_3N as a base.

We then applied this ruthenium-based catalyst under the conditions of entry 6 to synthesize dienes from the previously prepared allylic chlorides (Scheme 6). From the less substituted allylic chlorides **5**, **6**, **8**, complete conversion was observed after 5 h and satisfactory amounts of products **15**, **16**, **18** were isolated (62-65% yield). Only the nitrile **7** was converted to only 85% after 5 h at 25 °C but **17** could be isolated in a good yield of 72%. The elimination from the allylic chlorides **10**-**13** required a prolonged heating period to 17 h and a slightly higher reaction temperature of 50 °C to reach complete conversion. Again, under these conditions, a conversion of only 95% was obtained from **12**. The final 2-methyl-1,3-butadiene derivatives were isolated in 65-72% yields. The lower reactivity of **7** and **12** was probably due to the presence of the coordinating nitrile group competing with the acetonitrile as ligand in transient coordination to the metal centre. The formation of the internal double bond of the purely aliphatic dienes **14**-**17** was stereoselective leading to the formation of the *E*-isomer as major product in a *E*/*Z* ratio of 8:1 as detected by ^{1}H and ^{13}C NMR analyses. The best stereoselectivity was obtained during elimination from the aromatic eugenol derivative **8** giving the diene **18** as the sole *E*-isomer with a J^3 coupling constant of 15.6 Hz for the olefinic protons. A perfect stereoselectivity was also observed during elimination from he substituted allylic chlorides **10**-**13**, which led to the (*E*)-dienes **19**-**22** without detection of any trace of the (*Z*)-isomer by NMR. It is also noteworthy that the elimination took place with the two stereoisomers of the allylic substrates, which increases the potential of the reaction.



Scheme 6. Formation of terminal dienes from allylic chlorides: scope of the reaction

Attempts to prepare conjugated terminal trienes using the same sequence from terminal dienes failed. Indeed, the cross-metathesis of the diene **14** with allyl chloride in the presence of a catalytic amount of catalyst **I** led to selective cross-metathesis involving the internal double bond of the diene and formation of methyl decenoate **23** and methyl 11-chloroundec-9-enoate **24**[21] as fatty esters (Scheme 7).



Scheme 7. Cross-metathesis of the diene **14** with allyl chloride

Experimental Section

General remarks: All the reactions were conducted under an inert

atmosphere of argon using standard Schlenk tube techniques. Solvents were dried using MBraun solvent purification system. Allyl chloride and 3-chloro-2-methylpropene were distilled under atmospheric pressure and stored under argon over activated 3Å molecular sieves. Methyl 10-undecenaote and undecylenic nitrile were distilled under reduced pressure and stored under argon. Eugenyl acetate was prepared as described in the literature.[4a] Citronellal was purchased from Acros Organics and used as received (93%). 1-Decene was purchased from Acros Organics and used as received (95%). Cesium carbonate was purchased from Sigma Aldrich and used as received (99%). 4 Å molecular sieves powder <50 µm was purchased from Acros Organics and activated at 150 °C under vacuum for 16 h). ^{1}H (300 MHz) and ^{13}C (100 MHz) spectra were recorded in $CDCl_3$ solutions.

Procedure for cross-metathesis reactions with allyl chloride

Methyl 12-chlorododec-10-enoate (3)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of methyl 10-undecenoate (0.5 mmol), 6.6 mg of Umicore M51 catalyst **I** (0.01 mmol, 2 mol%), 244 µl of allyl chloride (3 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 80%; *E/Z*= 8.5:1

NMR data were consistent with reported data.[21]

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.20-1.32 (br s, 8 H, CH_2), 1.32-1.42 (br s, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 2.04 (m, 2 H, CH_2), 2.29 (t, 7.6 Hz, 2 H, CH_2), 3.66 (s, 3 H, CO_2CH_3), 4.02 (d, 7.2 Hz, CH_2Cl-*E*), 4.08 (d, 6.0 Hz, CH_2Cl-*Z*), 5.55-5.65 (m, 1 H, =CH), 5.70-5.90 (m, 1 H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 24.8 (*E*), 26.9 (*Z*), 28.6 (*E*), 28.9 (*E*), 29.0 (*E*), 29.05 (*E*), 29.1 (*E*), 31.9 (*E*), 34.0 (*E*), 39.4 (*Z*), 45.4 (*E*), 51.3, 125.1 (*Z*), 125.8 (*E*), 135.3 (*Z*), 136.1 (*E*), 174.1. LRMS: $[M\text{-}Cl]^+$ m/z: 210.

1-Chloroundec-2-ene (5)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of 1-decene (0.72 mmol), 9.5 mg of Umicore M51 catalyst **I** (0.014 mmol, 2 mol%), 351 µl of allyl chloride (4.32 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 55%; *E/Z*= 8/1

NMR data were consistent with reported data.[21,9b]

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.88 (t, 6.0 Hz, 3 H, CH_3), 1.20-1.32 (br s, 10 H, CH_2), 1.32-1.42 (br s, 2 H, CH_2), 2.05 (m, CH_2-*E*), 2.11 (m, CH_2-*Z*), 4.03 (d, 7.2 Hz, CH_2Cl-*E*), 4.09 (d, 5.2 Hz, CH_2Cl-*Z*), 5.55-5.65 (m, 1H, CH), 5.71-5.85 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.6 (*E*), 27.1 (*Z*), 28.8 (*E*), 29.1 (*E*), 29.2 (*E*), 29.4 (*E*), 31.8 (*E*), 32.0 (*E*), 39.5 (*Z*), 45.5 (*E*), 125.1 (*Z*), 125.8 (*E*), 135.6 (*Z*), 136.3 (*E*). LRMS: m/z 100%: 55; $[M]^+$ m/z: 188.

8-Chloro-3-methyloct-6-enal (6)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of citronellal (0.65 mmol), 8.5 mg of Umicore M51 catalyst **I** (0.013 mmol, 2 mol%), 316 µl of allyl chloride (3.9 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 65%; *E/Z*: 8.5/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.96 (d, 6.8 Hz, 3 H, CH_3), 1.27-1.40 (m, 1 H, CH_2), 1.40-1.50 (m, 1 H, CH_2), 2.02-2.20 (m, 3 H, CH, CH_2), 2.21- 2.30 (m, 1 H, CH_2), 2.35-2.44 (m, 1 H, CH_2), 4.01 (d, 6.8 Hz, CH_2Cl-*E*), 4.08 (d, 7.2 Hz, CH_2Cl-*Z*), 5.56-5.67 (m, 1 H, CH), 5.70-5.80 (m, 1 H, CH), 9.75 (s, 1 H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.7, 24.5 (*Z*), 27.5 (*E*), 29.4 (*E*), 35.8 (*E*), 36.2 (*Z*), 39.2 (*Z*), 45.2 (*E*), 50.9 (*E*), 125.5 (*Z*), 126.3 (*E*), 134.8 (*Z*), 135.3 (*E*), 202.5. LRMS: m/z 100%: 94; $[M\text{-}Cl]^{+\cdot}$ m/z: 141. Elemental analysis: calcd (%) for $C_9H_{15}ClO$ (174.667): C 61.89, H 8.66; found: C 61.94, H 8.71.

12-Chlorododec-10-enenitrile (7)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of undecylenic nitrile (0.61 mmol), 8 mg of Umicore M51 catalyst **I** (0.0122 mmol, 2 mol%), 298 µl of allyl chloride (3.66 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 43%; E/Z: 8.5/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.28-1.33 (m, 6 H, CH_2), 1.35-1.50 (m, 4 H, CH_2), 1.60-1.70 (p, J= 7.4 Hz, 2 H, CH_2), 2.05 (dt, 7.0 Hz, 7.0 Hz, 2 H, CH_2), 2.33 (t, 7.2 Hz, 2 H, CH_2), 4.03 (d, 7.2 Hz, CH_2Cl-*E*), 4.09 (d, 6.4 Hz, CH_2Cl-*Z*), 5.55-5.66 (m, 1 H, CH), 5.72-5.82 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 17.0 (*E*), 25.3 (*E*), 26.9 (*Z*), 28.5 (*E*), 28.6 (*E*), 28.6 (*E*), 28.8 (*E*), 29.0 (*E*), 31.9 (*E*), 39.4 (*Z*), 45.4 (*E*), 119.7, 125.1 (*Z*), 125.9 (*E*), 135.3 (*Z*), 136.0 (*E*). LRMS: $[M\text{-}Cl]^{+\cdot}$ m/z: 178. Elemental analysis: calcd (%) for $C_{12}H_{20}ClN$ (213.747): C 67.43, H 9.43, N 6.55.; found: C 67.44, H 9.41, N 6.57.

4-(4-Chlorobut-2-enyl)-2-methoxyphenyl acetate (8)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenyl acetate (0.49 mmol), 6.4 mg of Umicore M51 catalyst **I** (0.0097 mmol, 2 mol%), 236 µl of allyl chloride (2.94 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 79%; E/Z: 8.5/1

^{1}H RMN (400 MHz, $CDCl_3$, δ ppm): 2.30 (s, 3H, CH_3), 3.38 (d, 6.4 Hz, CH_2-*E*), 3.46 (d, 4.8 Hz, CH_2-*Z*), 3.81 (s, 3 H, CH_3), 4.06 (d, 6.8 Hz, CH_2Cl-*E*), 4.19 (d, 5.6 Hz, CH_2Cl- *Z*), 5.65-5.75 (m, 1 H, CH-*E*), 5.78-5.83 (m, CH-*Z*), 5.86-5.96 (m, CH-*E*), 6.72-6.81 (m, 2 H, CH_{ar}), 6.95 (d, 8.0 Hz, 1 H, CH_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 20.6 (*E*), 33.1 (*Z*), 38.2 (*E*), 39.0 (*Z*), 44.8 (*E*), 55.8 (*E*), 112.7 (*E*), 120.4 (*Z*), 120.6 (CH_{ar}-*E*), 122.6 (CH_{ar}-*E*), 126.1 (CH-*Z*), 127.5 (CH-*E*), 133.0 (CH-*Z*), 133.9 (*E*), 138.1 (*E*), 138.2 (*E*), 150.9, 169.1. LRMS: $[M]^{+\cdot}$ m/z: 254. Elemental analysis: calcd (%) for $C_{13}H_{15}ClO_3$ (254.709): C 61.30, H 5.94; found: C 61.34, H 5.91.

General procedure for the cross-metathesis reactions with 3-chloro-2-methylpropene

Methyl 12-chloro-11-methyldodec-10-enoate (10)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of methyl 10-undecenaote (0.5 mmol), 6.6 mg of Umicore M51 catalyst **I** (0.010 mmol, 2 mol%), 294 µl of 3-chloro-2-methylpropene (3 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 72% ; *E/Z*: 3/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.25-1.40 (m, 10 H, CH_2), 1.57-1.65 (m, 2 H, CH_2), 1.72 (s, CH_3-*E*), 1.82 (s, CH_3 -*Z*), 1.97-2.07 (m, 2 H, CH_2), 2.29 (t, 7.4 Hz, 2 H, CH_2), 3.66 (s, 3 H, CO_2CH_3), 4.01 (s, CH_2Cl-*E*), 4.06 (s, CH_2Cl-*Z*), 5.37 (t, 7.4 Hz, CH-*Z*), 5.52 (t, 7.2 Hz, CH-*E)*. ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0 (*E*), 21.4 (*Z*), 24.8 (*E*), 27.9 (*E*), 29.0 (*E*), 29.0 (*E*), 29.1 (*E*), 29.1 (*E*), 29.2 (*E*), 34.0 (*E*), 43.6 (*Z*), 51.3 (*E*), 52.5 (*E*), 131.07 (*Z*), 131.11 (*E*), 131.43 (*Z*), 131.47 (*E*),174.2. LRMS: $[M\text{-}Cl]^{+\cdot}$ m/z: 224. Elemental analysis: calcd (%) for $C_{14}H_{25}ClO_2$ (260.800): C 64.47, H 9.66; found: C 64.84, H 9.68

1-Chloro-2-methyldodec-2-ene (11)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of 1-decene (0.72 mmol), 9.5 mg of Umicore M51 catalyst **I** (0.0144 mmol, 2 mol%), 422 µl of 3-chloro-2-methylpropene (4.32 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 79%; E/Z: 3/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.88 (t, 6.8 Hz, 3 H, CH_3), 1.25-1.38 (br s, 12 H, CH_2), 1.73 (s, CH_3-*E*), 1.81 (s, CH_3-*Z*), 1.98-2.09 (m, 2 H, CH_2), 4.02 (s, CH_2Cl-*E*), 4.06 (s, CH_2Cl-*Z*), 5.38 (t, 7.0 Hz, CH-*Z*), 5.53 (t, 7.2 Hz, CH-*E*). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0 (*E*), 14.0 (*E*), 21.4 (*Z*), 22.6 (*E*), 27.8 (*Z*), 28.0 (*E*), 29.1 (*E*), 29.2 (*E*), 29.2 (*E*), 29.4 (*E*), 31.8 (*E*), 43.7 (*Z*), 52.6 (*E*), 131.0 (*Z*), 131.3 (*E*), 131.4 (*E*), 131.6 (*Z*). LRMS: $[M]^{+\cdot}$ m/z: 202. Elemental analysis: calcd (%) for $C_{12}H_{23}Cl$ (202.764): C 71.08, H 11.43; found: C 71.12, H 11.37.

12-Chloro-11-methyldodec-10-enenitrile (12)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of undecylenic nitrile (0.61 mmol), 8 mg of Umicore M51 catalyst **I** (0.0122 mmol, 2 mol%), 358 µl 3-chloro-2-methylpropene (3.66 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel a pentane/Et_2O mixture as eluent.

Isolated yield: 67%; E/Z: 3/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.25-1.40 (m, 8 H, CH_2), 1.41-1.49 (m, 2 H, CH_2), 1.61-1.69 (m, 2 H, CH_2), 1.73 (s, CH_3-*E*), 1.82 (s, CH_3-*Z*), 2.00-2.10 (m, 2 H, CH_2), 2.33 (t, 7.0 Hz, 2 H, CH_2), 4.02 (s, CH_2Cl-*E*), 4.06 (s, CH_2Cl-*Z*), 5.38 (t, 7.6 Hz, CH-*Z*), 5.52 (t, 7.2 Hz, CH-*E*). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0 (*E*), 17.0 (*E*), 21.5 (*Z*), 25.3 (*E*), 27.7 (*Z*), 27.9 (*E*), 28.5 (*E*), 28.6 (*E*), 29.0 (*E*), 29.0(*E*), 29.0(*E*), 29.4 (*Z*), 43.7 (*Z*), 52.5 (*E*), 119.7, 131.0 (*E*), 131.2 (*Z*), 131.4 (*Z*), 131.6 (*E*). LRMS: $[M\text{-}Cl]^{+\cdot}$ m/z: 192. Elemental analysis: calcd (%) for $C_{13}H_{22}ClN$ (227.773): C 68.55, H 9.74, N 6.15; found: C 68.60, H 9.76, N 6.17.

4-(4-Chloro-3-methylbut-2-enyl)-2-methoxyphenyl acetate (13)

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenyl acetate (0.49 mmol), 6.4 mg of Umicore M51 catalyst **I** (0.0097 mmol, 2 mol%), 287 µl of 3-chloro-2-methylpropene (2.94 mmol, 6 equiv.) and 2 mL of dichloromethane. The reaction was refluxed at 50 °C during 5 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Isolated yield: 70%; E/Z: 3/1

^{1}H RMN (400 MHz, $CDCl_3$, δ ppm): 1.85 (s, CH_3-*E*), 1.89 (s, CH_3-*Z*), 2.30 (s, 3 H, CH_3), 3.38 (d, 7.6 Hz, CH_2- *E*), 3.20-3.42 (m, CH_2- *Z*), 3.81 (s, 3 H, CH_3), 4.06 (s, CH_2Cl-*E*), 4.16 (s, CH_2Cl-*Z*), 5.55 (t, 7.0 Hz, CH-*Z*), 5.73 (t, 7.2 Hz, CH-*E*), 6.71-6.78 (m, 2 H, CH_{ar}), 6.94 (d, 8.0 Hz, 1 H, CH_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.2 (*E*), 20.6 (*E*), 21.6 (*Z*), 34.0 (*E*), 43,4 (*Z*), 52.0 (*E*), 55.7 (*E*), 112.4 (*E*), 112.6 (*Z*), 120.4 (*E*), 122.6 (*E*), 128.8 (*E*), 129.1 (*Z*), 132.4 (*Z*), 133.1 (*E*),138.0, 139.0, 150.9, 169.2. LRMS: $[M]^{+\cdot}$ m/z: 268. Elemental analysis: calcd (%) for $C_{14}H_{17}ClO_3$ (268.736): C 62.57, H 6.38; found: C 62.86, H 6.30.

General procedure for the elimination reactions of allyl chloride derivatives

A dry and degassed Schlenk tube was loaded under argon with 0.5 mmol of allyl chloride derivative, $Cp^*Ru(CNCH)_3PF_6$ catalyst **II** (5 mol%), and 1.2 equiv. of cesium carbonate in 3 mL of acetonitrile. The reaction was stirred under the mentioned conditions. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

Methyl dodeca-9,11-dienoate (14)

Isolated yield: 75%; E/Z: 8/1

NMR data were consistent with reported data.[17]

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.25-1.39 (m, 8 H, CH_2), 1.57-1.63 (m, 2 H, CH_2), 2.06 (dt, J= 7.0 Hz, J= 7 Hz, CH_2 -*E*), 2.17 (dt, J= 7.0 Hz, J= 7.0 Hz, CH_2 -*Z*), 2.29 (t, 7.4 Hz, 2 H, CH_2), 3.66 (s, 3 H, CO_2CH_3), 4.94 (d, 10.0 Hz, CH-*E*), 5.08 (d, 16.8 Hz, CH- *E*), 5.17 (d, 16.0 Hz, CH- *Z*), 5.40-5.48 (m, CH- *Z*), 5.70 (dt, J= 15.2 Hz, J= 7.2 Hz, CH- *E*), 6.04 (dd, J= 15.2 Hz, J= 7.8 Hz, CH-*E*), 6.30 (ddd, J= 17.2 Hz, J= 10.0, J= 10.0 Hz, CH-*E*), 6.650- 6.69 (m, CH- *Z*). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 24.9 (*E*), 27.7 (*Z*), 28.9 (*E*), 29.0 (*E*), 29.0 (*E*), 32.5 (*E*), 34.1 (*E*), 51.4 (*E*), 114.6 (*E*), 116.7 (*Z*), 129.2 (*Z*), 130.9 (*E*), 132.3 (*Z*), 132.9 (*Z*), 135.4 (*E*), 137.3 (*E*), 174.3. LRMS: $[M]^{+\cdot}$ m/z: 210.

Undeca-1,3-diene (15)

Isolated yield: 62%; E/Z: 8/1

NMR data were consistent with reported data.[26,30]

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.88 (t, 6.8 Hz, 3 H, CH_3),

1.21-1.33 (m, 8 H, CH_2), 1.37-1.45 (m, 2 H, CH_2), 2.07 (dt, J= 7.1 Hz, J= 7.1 Hz, CH_2-*E*), 2.18 (dt, J= 7.0 Hz, J= 7.0 Hz, CH_2-*Z*), 4.95 (d, 10.4 Hz, CH-*E*), 5.09 (d, 16.4 Hz, CH-*E*), 5.17 (d, 16.4 Hz, CH-*Z*), 5.42-5.49 (m, CH-*Z*), 5.71 (dt, J= 15.2 Hz, J= 7.0 Hz, CH-*E*), 6.18 (dd, J= 15.2 Hz, J= 10.4 Hz, CH-*E*), 6.26-6.35 (ddd, J= 17.2 Hz, J= 10.4 Hz, J= 10.4 Hz, CH-*E*), 6.59-6.69 (m, CH-*Z*). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1 (*E*), 22.6 (*E*), 27.7 (*Z*), 29.1 (*E*), 29.2 (*E*), 29.6 (*Z*), 31.8 (*E*), 32.5 (*E*), 114.5 (*E*), 116.6 (*Z*), 129.1 (*Z*), 130.8 (*E*), 132.3 (*Z*), 133.1 (*Z*), 135.6 (*E*), 137.3 (*E*). LRMS: $[M]^{+\cdot}$ m/z: 152.

3-Methylocta-5,7-dienal (16)

Isolated yield: 65%; E/Z: 8/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.98 (d, 6.4 Hz, 3 H, CH_3), 2.08-2.10 (br s, 2 H, CH_2), 2.13-2.30 (m, 2 H, CH_2), 2.40-2.47 (m, 1 H, CH), 4.99 (d, 10.0 Hz, CH-*E*), 5.12 (d, 16.8 Hz, CH- *E*), 5.21 (d, 15.6 Hz, CH- *Z*), 5.39-5.46 (m, CH- *Z*), 5.58-5.70 (m, 1 H, CH- *E*), 6.00- 6.10 (m, 1 H, CH- *E*), 6.20- 6.38 (m, 1 H, CH-*E*), 6.54- 6.65 (m, 1 H, CH- *Z*), 9.76 (s, 1 H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.9, 28.3 (*E*), 29.7 (*Z*), 34.6 (*Z*), 39.8 (*E*), 50.3 (*E*), 115.6 (*E*), 117.7 (*Z*), 129.7 (*Z*), 131.1 (*Z*), 131.9 (*Z*), 132.1 (*E*), 133.2 (*E*), 136.8 (*E*), 202.6. LRMS: $[M]^{+\cdot}$ m/z: 138. Elemental analysis: calcd (%) for $C_9H_{14}O$ (138.207): C 78.21, H 10.21; found: C 78.52, H 10.09.

Dodeca-9,11-dienenitrile (17)

Isolated yield: 72%; E/Z: 8/1

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.25-1.50 (m, 8 H, CH_2), 1.60-1.70 (m, 2 H, CH_2), 2.04-2.12 (m, CH_2-*E*), 2.18-2.25 (m, CH_2-*Z*), 2.32 (t, 7.0 Hz, 2 H, CH_2), 4.95 (d, 10.0 Hz, C*H*H-*Z*), 5.08 (d, 16.4 Hz, C*H*H-*E*), 5.18 (d, 15.6 Hz, C*H*H-*Z*), 5.40-5.48 (m, CH-*Z*), 5.69 (dt, J= 15.2 Hz, J= 7.4 Hz, CH-*E*), 6.04 (dd, J= 15.2 Hz, J= 10.4 Hz, CH-*E*), 6.32 (dt, J= 17.2 Hz, J= 10.4 Hz, 1H, CH-*E*), 6.60-6.67 (m, 1 H, CH-*Z*). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 17.1 (*E*), 25.3 (*E*), 27.5 (*Z*), 28.5 (*E*), 28.8 (*E*), 28.9 (*E*), 29.3 (*Z*), 32.4 (*E*), 114.7 (*E*), 116.8 (*Z*), 119.8, 129.3 (*Z*), 131.0 (*E*), 132.2 (*Z*), 132.6 (*Z*), 135.2 (*E*), 137.2 (*E*). LRMS: $[M]^{+\cdot}$ m/z: 177. Elemental analysis: calcd (%) for $C_{12}H_{19}N$ (177.286): C 81.30, H 10.80, N 7.90; found: C 81.05, H 10.70, N 7.81.

(*E*)-4-(Buta-1,3-dienyl)-2-methoxyphenyl acetate (18)

Isolated yield: 62%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.31 (s, 3 H, CH_3), 3.86 (s, 3 H, CH_3), 5.18 (d, 10.4 Hz, 1 H, CH), 5.34 (d, 17.2 Hz, 1 H, CH), 6.44-6.60 (m, 2 H, CH_2), 6.72 (dd, J= 15.6 Hz, J= 10.4 Hz, 1 H, CH), 6.90-7.10 (m, 3 H, CH_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 20.6, 55.8, 109.9, 117.8, 119.1, 122.8, 129.8, 132.1, 136.2, 136.9, 139.2, 151.1 (C), 169.0. LRMS: m/z 100%: 176; $[M]^{+\cdot}$ m/z: 218. Elemental analysis: calcd (%) for $C_{13}H_{14}O_3$ (218.248): C 71.54, H 6.47; found: C 71.70, H 6.43.

General procedure for the elimination reactions of 3-chloro-2-methylpropene derivatives

A dry and degassed Schlenk tube was loaded under argon with 0.5 mmol of 3-chloro-2-methylpropene derivative, $Cp^*Ru(CNCH)_3PF_6$ catalyst **II** (5 mol%) and 1.2 equiv. of cesium carbonate in 3 mL of acetonitrile. The reaction was stirred at 50 °C during 17 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a pentane/Et_2O mixture as eluent.

(*E*)-Methyl 11-methyldodeca-9,11-dienoate (19)

Isolated yield: 72%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.25-1.45 (br s, 8 H, CH_2), 1.55-1.67 (m, 2 H, CH_2), 1.83 (s, 3 H, CH_3), 2.09 (q, 7.1 Hz, 2 H, CH_2), 2.30 (t, 7.4 Hz, 2 H, CH_2), 3.66 (s, 3 H, CO_2CH_3), 4.85 (s, 2 H, CH_2), 5.60-5.70 (m, 1 H, CH), 6.12 (d, 15.6 Hz, 1 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 18.7, 24.9, 29.0, 29.1, 29.3, 32.7, 34.1, 51.4, 114.1, 130.9, 132.7, 142.2, 174.3. LRMS: $[M]^{+\cdot}$ m/z: 224. Elemental analysis: calcd (%) for $C_{14}H_{24}O_2$ (224.339): C 74.95, H 10.78; found: C 74.85, H 10.86.

(*E*)-2-Methylundeca-1,3-diene (20)

Isolated yield: 65%

NMR data were consistent with reported data.[31]

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.89 (t, 6.8 Hz, 3 H, CH_3), 1.22-1.35 (br s, 8 H, CH_2), 1.36-1.44 (m, 2 H, CH_2), 1.84 (s, 3 H, CH_3), 2.10 (q, 7.1 Hz, 2 H, CH_2), 4.86 (s, 2 H, CH_2), 5.60-5.80 (m, 1 H, CH), 6.14 (d, 15.2 Hz, 1 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 18.7, 22.6, 29.1, 29.2, 29.4, 31.8, 32.7, 114.0, 131.1, 132.7, 142.2. LRMS: $[M]^{+\cdot}$ m/z: 166.

(*E*)-11-Methyldodeca-9,11-dienenitrile (21)

Isolated yield: 68%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.28-1.33 (m, 4 H, CH_2), 1.37-1.50 (m, 4 H, CH_2), 1.60-1.70 (m, 2 H, CH_2), 1.83 (s, 3 H, CH_3), 2.10 (dt, J= 6.8 Hz, J= 6.8 Hz, 2 H, CH_2), 2.33 (t, 7.2 Hz, 2 H, CH_2), 4.85 (s, 2 H, CH_2), 5.60-5.67 (m, 1 H, CH), 6.13 (d, 15.6 Hz, 1 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 17.1, 18.6, 25.3, 28.5 (CH_2), 28.6, 28.8, 29.2, 32.6, 114.2, 119.8, 130.7, 132.9, 142.1. LRMS: m/z 100%: 95; $[M]^{+\cdot}$ m/z: 191. Elemental analysis: calcd (%) for $C_{13}H_{21}N$ (191.313): C 81.61, H 11.06, N 7.32; found: C 81.49, H 11.12, N 7.26.

(*E*)-2-Methoxy-4-(3-methylbuta-1,3-dienyl)phenyl acetate (22)

Isolated yield: 69%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.97 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.86 (s, 3 H, CH_3), 5.09 (s, 1 H, CH*H*), 5.12 (s, 1 H, C*H*H) 6.49 (d, 16.0 Hz, 1 H, CH), 6.81 (d, 16.0 Hz, 1 H, CH), 6.99-7.02 (m, 3 H, CH_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 18.5, 20.6, 55.8, 110.0, 117.5, 119.1, 122.8, 128.0, 131.9, 136.4, 139.1, 141.8, 151.0, 169.0. LRMS: $[M]^{+\cdot}$ m/z: 232. Elemental analysis: calcd (%) for $C_{14}H_{16}O_3$ (232.275): C 72.39, H 6.94; found: C 72.70, H 6.80.

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Conclusions

In conclusion, we propose a sequence of two ruthenium-catalyzed reactions, olefin cross-metathesis and elimination, which provides an easy access to functional terminal conjugated dienes arising from natural products in various families including fatty acid, terpene, and phenylpropenoid derivatives. The cross-metathesis and the elimination reactions are stereoselective in favour of the formation of (*E*)-isomers. Both reactions tolerate a variety of functional groups such as ester, ether, aldehyde, nitrile. This strategy is not specific of natural products and can be applied as a general protocol to prepare terminal conjugated dienes under mild conditions.

Notes and references

[a]*University of Carthage, Higher Institute of Sciences and Technology of Environment of Borj Cedria, B.P. 1003, 2050, Hammam-Lif, Tunisia. e-mail: naceur.hamdi@isste.rnu.tn*
[b]*UMR6226: CNRS-Université de Rennes1, Institut des Sciences Chimiques, Organometallics : Materials and Catalysis, Centre for Catalysis and Green Chemistry, Campus de Beaulieu, 35042 Rennes Cedex, France. e-mail : christian.bruneau@univ-rennes1.fr*

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