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Construction of Enantioenriched Cyclic Compounds by Asymmetric Allylic Alkylation and Ring-Closing Metathesis

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A new approach to highly enantioenriched cyclic compounds (up to 98 % *ee*) has been developed by using ω-ethylenic allylic substrates in a one-pot asymmetric allylic alkylation and ring-closing metathesis sequence. The starting compounds are synthetic equivalents of cyclic allylic substrates. The method is exemplified with both Cu and Ir catalysts, and chiral phosphoramidite ligands.

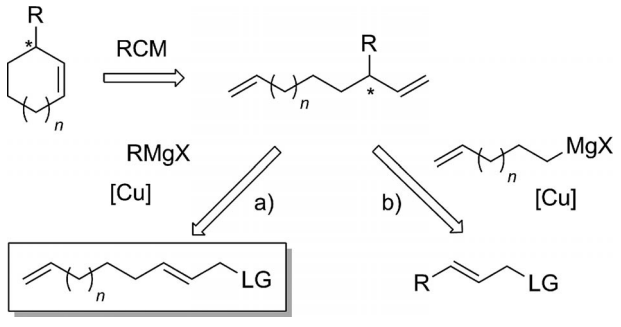
Introduction

Asymmetric allylic alkylation is one of the most used and versatile transformations for the generation of new C–C bonds in asymmetric synthesis.[1] A wide range of metals have been employed for this reaction and among them Pd, Ir, Mo, Ni, Rh, and Ru are the most representative examples.[2] In particular, palladium has been extensively reviewed in recent years, and preferentially used in combination with symmetrical substrates and stabilized nucleophiles, such as malonate carbanions, showing excellent results.[3]

Copper can be considered complementary to palladium because it is highly γ regioselective with unsymmetrical or monosubstituted allylic substrates, and allows the introduction of alkyl groups in the form of organometallic species, including organozinc, lithium, magnesium, and aluminium reagents.[4] However, despite the diverse applications that have been found in recent years, there are still some limitations in the copper-catalyzed asymmetric allylic alkylation of cyclic compounds. Notably, the main feature of the allylic alkylation mechanism using copper as the metal source is the S_N2' *anti* displacement, which occurs in oxidative addition with excellent chirality transfer.[4,5] The S_N2' *anti* displacement can be over-ruled by using a *syn*-directing leaving group.[6] However, when starting from a racemic mixture of a cyclic allylic substrate, the stereogenic center of the substrate, not the chiral catalyst, dictates the course of the reaction, thus both possible diastereomeric σ-allyl intermediates would be formed, generating both possible products in equal amounts. Only recently have we been able to partly circumvent this problem and elucidate the mechanistic pathway.[7] In contrast, palladium has been widely employed for the formation of enantioenriched cyclic compounds because the choice of an appropriate chiral ligand allows the discrimination of the two enantiotopic termini of the *meso* π-allyl species formed upon ionization.

A different situation arises when a linear monosubstituted (or non-symmetrical) allylic substrate is used in the copper-catalyzed allylic alkylation. The leaving group stands at an achiral center and thus the chiral ligand plays the main role in controlling the selectivity during the oxidative addition step.

Because of these observations, we envisaged creating enantioenriched cyclic compounds through a copper-catalyzed allylic alkylation followed by ring-closing metathesis. Our strategy relies on the use of an aliphatic allylic compound containing a terminal double bond as synthetic equivalent of a cyclic allylic substrate. This ω-ethylenic allylic substrate can undergo copper-catalyzed asymmetric allylic alkylation and bears a convenient functionality to be cyclized through ring-closing metathesis (pathway a, Scheme 1). This approach is not entirely new, but complementary to the one already developed in our laboratory in



Scheme 1. Strategies for the enantioselective construction of cyclic compounds.

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which this functionality is introduced through the allylic alkylation step from the nucleophile (pathway b, Scheme 1).[8]

Results and Discussion

We started our investigation by considering the simple unsubstituted allylic chloride **1a**, which contains four methylene units in between the two double bonds, producing after the process a seven-membered ring product. Copper-catalyzed asymmetric allylic alkylation was performed by using 3 mol-% of copper thiophenecarboxylate (CuTC), 3.3 mol-% of a chiral ligand (Figure 1), and 1.3 equiv. of Grignard reagent in dichloromethane at –78 °C. Grubbs I catalyst[9] was used for the subsequent ring-closure step.

For this initial screening, phenethylmagnesium bromide and cyclohexylmagnesium chloride were used as representative primary and secondary Grignard reagents, respectively. A preliminary screening of different chiral ligands, including phosphoramidite-type,[10] ferrocenyl-based,[11] and SimplePhos ligands,[12] was performed to evaluate their efficiency. The results are shown in Table 1.

High regioselectivity, up to 99%, was observed in all cases. Concerning the enantioselectivity, in the case of phenethyl addition, up to 85% enantiomeric excess was achieved with phosphoramidite ligand **L1**. Similarly, ligand **L2**, containing two naphthyl substituents on the amine moiety, gave a good *ee* of 78%. A matched/mismatched effect was observed when using ligand **L5** as only 40% *ee* was obtained, and, in addition, the opposite enantiomer was formed, which suggests that the chiral binaphthol moiety dictates the enantioselective outcome of the reaction. Surprisingly, the orientation of the substituent is significant, as only 30% *ee* was obtained when ligand **L7** was used (entry 7 vs. 2). Biphenol-derived ligands **L3** and **L6** were not efficient as only moderate-to-low selectivities were observed (entries 3 and 6). Bidentate ferrocenyl-based ligands **L8** and **L9** were also tested and appeared to be ineffective for this transformation, although the γ adduct was favored in the process. Similarly to the ferrocenyl-based ligands, SimplePhos ligand **L11** behaved well, as excellent regioselectivity was observed, but low enantioselectivity. Lower enantiomeric excesses were generally observed when using a secondary Grignard reagent. Ligand **L3** was the most efficient for promoting the formation of adduct **4b**, giving 80% *ee*, whereas only 67% *ee* was obtained with ligand **L1**. These results suggest that the more hindered nucleophile requires the more flexible biphenol-derived ligand. Better enantioselectivities were not achieved with the other phosphoramidites tested. Indeed, almost racemic mixtures were

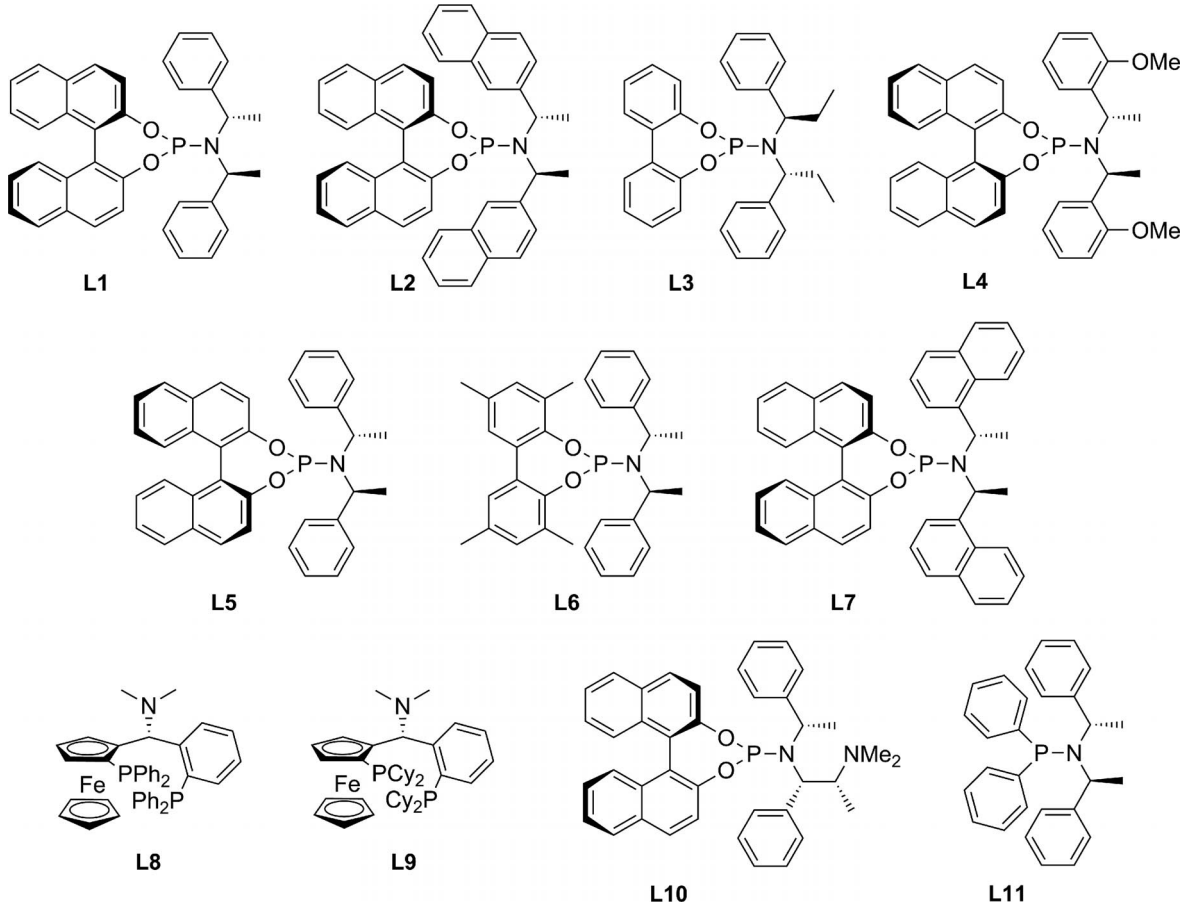
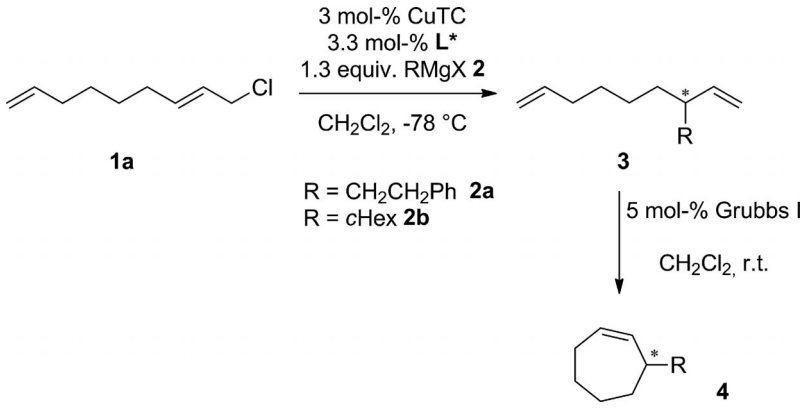


Figure 1. Chiral ligands used in this work.

Table 1. Screening of chiral ligands for the Cu-AAA/RCM of allylic chloride **1a**.[a]



Entry	R	L*	γ/α[b]	Product	*ee* [%], config.[c]
1	**2a**	**L1**	>99:1	**4a**	85, *R*
2	**2a**	**L2**	98:2	**4a**	78, *R*
3	**2a**	**L3**	90:10	**4a**	58, *S*
4	**2a**	**L4**	95:5	**4a**	50, *S*
5	**2a**	**L5**	98:2	**4a**	40, *S*
6	**2a**	**L6**	87:13	**4a**	18, *R*
7	**2a**	**L7**	91:9	**4a**	30, *R*
8	**2a**	**L8**	98:2	**4a**	2, *R*
9	**2a**	**L9**	93:7	**4a**	16, *R*
10	**2a**	**L10**	89:11	**4a**	0
11	**2a**	**L11**	>99:1	**4a**	27, *R*
12	**2b**	**L1**	98:2	**4b**	67, *R*
13	**2b**	**L2**	88:12	**4b**	48, *R*
14	**2b**	**L3**	>99:1	**4b**	80, *S*
15	**2b**	**L5**	91:9	**4b**	53, *S*
16	**2b**	**L6**	90:10	**4b**	36, *R*
17	**2b**	**L7**	>99:1	**4b**	46, *R*
18	**2b**	**L8**	>99:1	**4b**	2, *R*
19	**2b**	**L9**	97:3	**4b**	6, *S*
20	**2b**	**L10**	90:10	**4b**	2, *R*

[a] General reagents and conditions: 3 mol-% CuTC, 3.3 mol-% **L***, 1.3 equiv. RMgX in CH_2Cl_2 at –78 °C. [b] Determined by ^1H NMR or GC–MS analysis. [c] Determined by chiral GC or SFC analysis.

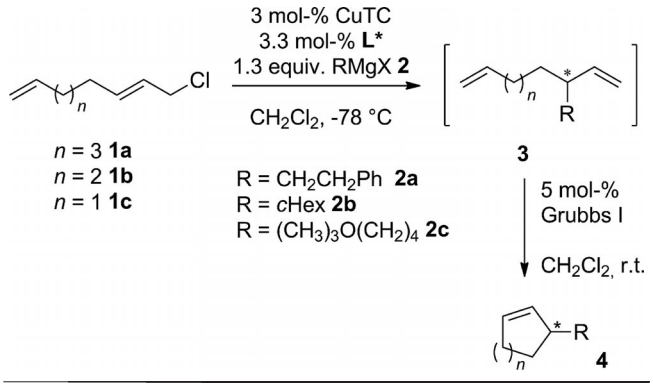
obtained with ferrocenyl-based ligands **L8** and **L9**, although these ligands were highly regioselective (entries 18 and 19).

We continued our study on the formation of enantioenriched cyclic compounds by synthesizing two other allylic substrates to give access to six- and five-membered ring adducts. For the following screening we used a selection of chiral phosphoramidite ligands and increased the scope of the reaction to show the versatility of our methodology by introducing other nucleophiles. As a key feature of our strategy, we performed the copper-catalyzed asymmetric allylic alkylation and ring-closing metathesis in one pot, which means that the Grubbs catalyst was added to the reaction mixture after the allylic alkylation step without quenching the reaction. The results are summarized in Table 2.

Excellent S_N2' selectivity was observed in all instances. Ligand **L2** gave the best enantioselectivity for the construction of a six-membered ring with a primary substituent as up to 86 and 93% *ee* were obtained for the introduction of a phenethyl and 4-*tert*-butoxybutyl moiety, respectively (entries 3 and 5). Up to 74% enantiomeric excess was observed for the cyclohexyl-substituted adduct with ligand **L1** (entry 4), which was also the best ligand for the formation of the five-membered ring with a phenethyl moiety (86% *ee*, entry 6). A good enantioselectivity of 82% was also achieved with ligand **L3** for the introduction of the more sterically demanding cyclohexyl group (entry 7). In these two latter instances, it was possible to determine the enantiomeric excess after the alkylation process, thus showing that no loss of enantioselectivity takes place during the ring closure. Finally, up to 73% *ee* was obtained with ligand **L4** in the case of the 4-*tert*-butoxybutyl-substituted five-membered adduct.

We then considered the reactivity of β-substituted allylic substrates, which have been scarcely documented over the years, although we have reported a few examples in which an inversion of the matched/mismatched effect was observed.[13] In this study we prepared two β-methyl-substituted ω-ethylenic allylic chlorides, which were subjected to a one-pot copper-catalyzed asymmetric allylic alkylation and

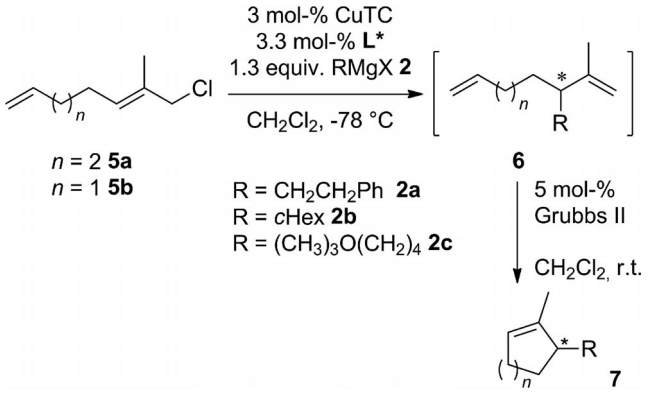
Table 2. Cu-AAA/RCM of allylic chlorides **1a**–**c**.



Entry	Substr.	R	L*	γ/α[a]	*ee* of 3[b] [%]	4	Yield[c] [%]	*ee* [%], config.[b]
1[d]	**1a**	**2a**	**L1**	>99:1	–	**4a**	62[e]	85, *R*
2[d]	**1a**	**2b**	**L3**	>99:1	–	**4b**	55[e]	80, *S*
3	**1b**	**2a**	**L2**	>99:1	–	**4c**	66	86, *R*
4	**1b**	**2b**	**L1**	94:6	–	**4d**	68	74, *R*
5	**1b**	**2c**	**L2**	>99:1	–	**4e**	68	93, *R*
6	**1c**	**2a**	**L1**	92:8	87, *R*	**4f**	62	86, *R*
7	**1c**	**2b**	**L3**	>99:1	82, *S*	**4g**	74	82, *S*
8	**1c**	**2c**	**L4**	>99:1	–	**4h**	52	73, *R*

[a] Determined by ^{1}H NMR or GC–MS analysis. [b] Determined by chiral GC or SFC analysis. [c] Yield of the isolated product after flash column chromatography on SiO_2. [d] Reaction performed in a two-pot procedure. [e] Overall yield.

Table 3. Cu-AAA/RCM of β-methyl-substituted allylic chlorides **5a**,**b**.



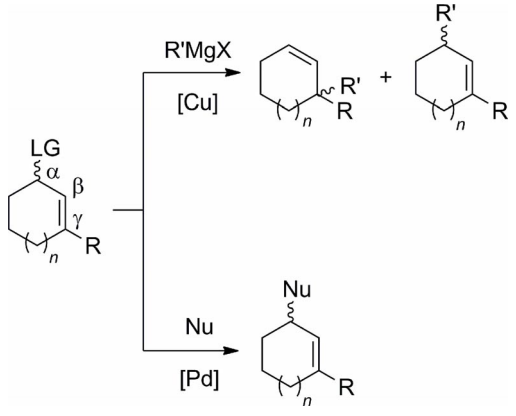
Entry	Substr.	R	L*	γ/α[a]	7	Yield[b] [%]	*ee* [%], config.[c]
1	**5a**	**2a**	**L5**	93:7	**7a**	62	82, *S*
2	**5a**	**2b**	***ent*-L1**	83:17	**7b**	–	40, (+)
3	**5a**	**2c**	**L2**	91:9	**7c**	65	82, (+)
4[d]	**5b**	**2a**	**L5**	95:5	**7d**	–	66, *S*
5[d]	**5b**	**2b**	***ent*-L1**	90:10	**7e**	–	30, (–)

[a] Determined by ^{1}H NMR or GC–MS analysis. [b] Yield of the isolated product after flash column chromatography on SiO_2. [c] Determined by chiral GC or SFC analysis. [d] Reaction performed in a two-pot procedure.

ring-closing metathesis by using the same conditions as reported previously and replacing the Grubbs I catalyst with the more active Grubbs II catalyst[14] (Table 3).

Moderate-to-good regioselectivities were obtained. Mismatched ligand **L5** was effective for the addition of the phenethyl moiety in the synthesis of both the six- and five-membered rings, however, lower enantioselectivity was obtained in the latter case (82 and 66%, respectively, entries 1 and 4). Conversely, the more bulky phosphoramidite ligand **L2** was the most efficient in the case of the introduction of the 4-*tert*-butoxybutyl moiety. The addition of a secondary Grignard reagent was also explored, and in both cases low enantiomeric excess was observed, up to 40% for the six-membered adduct and 30% for the five-membered product (entries 2 and 5).

We then turned our attention to a challenging class of allylic substrates that contain a substituent in the γ position. Direct asymmetric allylic alkylation of this type of cyclic system would not generate the alkylated cyclic product in a highly selective manner. In fact, limitations in regio- and enantiocontrol would arise from either a copper- or palladium-catalyzed transformation. As discussed earlier for the copper-catalyzed allylic alkylation, both possible diastereomeric species would be formed with excellent chirality transfer after oxidative addition when starting from a racemic mixture of the unsubstituted allylic cyclic substrate, thus eventually producing a homogeneous mixture of the possible products, that is, a racemate. Furthermore, in the presence of a substituent in the γ position, a mixture of regioisomers would be expected because of the steric hindrance at this site. In palladium chemistry it is well known that this catalyst is usually regioselective for the less hindered position. However, the presence of a substituent in the γ position generates a non-*meso* π-allyl intermediate, preventing deracemization of the substrate and leading to the formation of a mixture of enantiomers (Scheme 2).



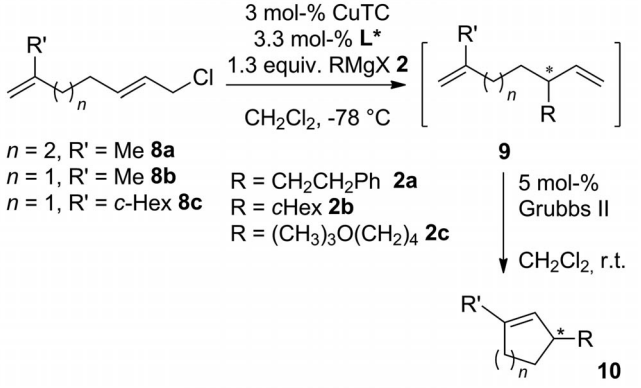
Scheme 2. Allylic alkylation of γ-substituted cyclic systems.

To circumvent these problems we wished to apply our strategy, thereby forming enantioenriched cyclic compounds through an asymmetric allylic alkylation and ring-closing metathesis. For this unprecedented reaction sequence leading to γ-substituted cycloalkenes, we decided to use both nonstabilized and stabilized nucleophiles. We synthesized the corresponding substituted ethylenic allylic

chloride for the copper-catalyzed transformation and the substituted allylic carbonate for the iridium-catalyzed process. The choice of iridium as metal catalyst instead of palladium is a result of the recent and rapid growth of iridium-mediated allylic substitution reactions, which have shown high selectivities in favor of the branched product.[15]

Table 4 shows the results obtained for the one-pot copper-catalyzed asymmetric allylic alkylation and ring-closing metathesis reactions of allylic chlorides **8a** and **8b**. All reactions proceeded in a highly regioselective manner. Ligand **L4** gave the best enantiomeric excess of 67% for the formation of a six-membered ring with a phenethyl group. Phosphoramidite ligand **L3** was reasonably efficient with both **8a** and **8b** for the cyclohexyl alkylation with a maximum of 74% *ee* in the case of the five-membered adduct (entry 4), whereas ligand **L1** (or ***ent*-L1**) gave moderate enantioselectivity for the introduction of the 4-*tert*-butoxybutyl group with a maximum of 70% *ee* in the case of the more sterically demanding cyclohexyl substituent on the ethylenic double bond in **8c** (entry 6).

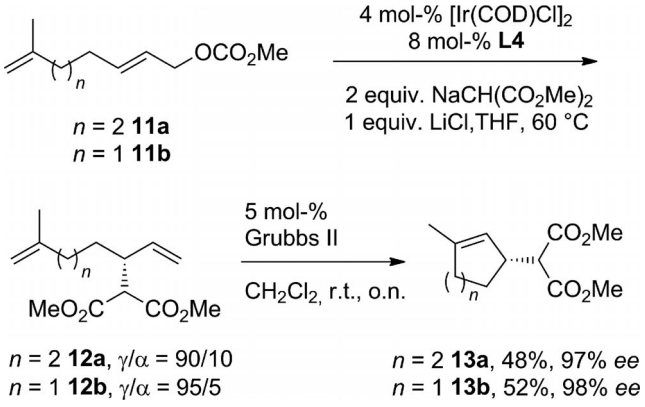
Table 4. Cu-AAA/RCM of allylic chlorides **8a**,**b**.



Entry	Substr.	R′	R	L*	γ/α[a]	10	Yield[b] [%]	*ee* [%], config.[c]
1[d]	**8a**	Me	**2a**	**L4**	92:8	**10a**	62[e]	67, S
2	**8a**	Me	**2b**	**L3**	>99:1	**10b**	70	64, *S*
3	**8a**	Me	**2c**	***ent*-L1**	>99:1	**10c**	78	62, *S*
4	**8b**	Me	**2b**	**L3**	>99:1	**10d**	55	74, *S*
5	**8b**	Me	**2c**	**L1**	>99:1	**10e**	60	68, *S*
6[d]	**8c**	*c*Hex	**2c**	***ent*-L1**	96:4	**10f**	–	70, (+)

[a] Determined by ^{1}H NMR or GC–MS analysis. [b] Yield of the isolated product after flash column chromatography on SiO_2. [c] Determined by chiral GC or SFC analysis. [d] Reaction performed in a two-pot procedure. [e] Overall yield.

The iridium-catalyzed asymmetric allylic alkylation and ring-closing metathesis were then studied, and the results are reported in Scheme 3. The optimum conditions required 4 mol-% of $[Ir(cod)Cl]_2$ and 8 mol-% of a chiral ligand. Only π-accepting ligand **L4** was employed because its efficiency has already been described with similar substrates.[16] Note that because of the incompatibility of the reaction conditions (i.e., different reaction solvents), the whole process was performed in a two-step procedure. Excellent regioselectivity was observed with both substrates as well as high enantioselectivities of up to 98% *ee*.

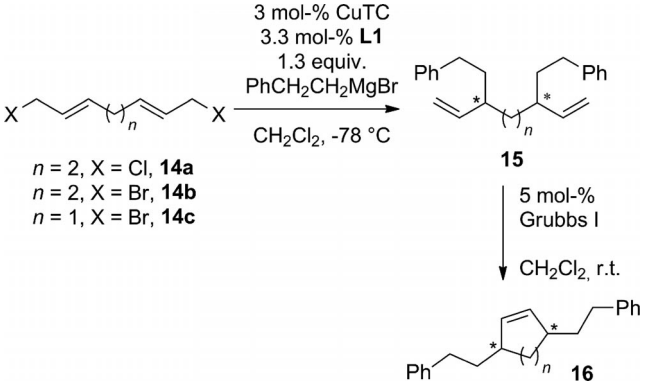


Scheme 3. Ir-AAA/RCM of allylic carbonates **11a**,**b**.

In view of the results obtained with monosubstituted allylic olefins, we studied the reactivity of a double allylic substrate to generate enantioenriched disubstituted cycloalkenes. This class of electrophile contains two reactive sites that can sequentially undergo allylic alkylation to produce two terminal vinyl groups that can be subjected to intramolecular metathesis. The advantage of this approach is that essentially complete enantio- and diastereoselectivity can be achieved as a result of double stereoselection or double asymmetric induction. The double asymmetric synthesis plays a decisive role in the stereochemical control of a variety of transformations,[17] and a few examples have already been reported for the allylic substitution reaction.[18]

We prepared the corresponding double allylic substrates by using either a bromide or chloride as the leaving group. Copper-catalyzed asymmetric allylic alkylation was carried out by using our standard conditions employing chiral ligand **L1**, which was the best ligand for the alkylation of

Table 5. Double Cu-AAA/RCM of allylic chlorides **14a**–**c**.



Entry	Substr.	**15**	Yield[a] [%]	γ,γ/γ,α (or α,α)[b]	**16**	Yield[a] [%]	*dr* [c] [%]	*ee*[c] [%]
1	**14a**	**15a**	88	>99:1	**16a**	64	83:17	96
2	**14b**	**15a**	82	>99:1	**16a**	100[e]	84:16	97
3[d]	**14c**	**15b**	100[e]	88:12	**16b**	100[e]	85:15	97

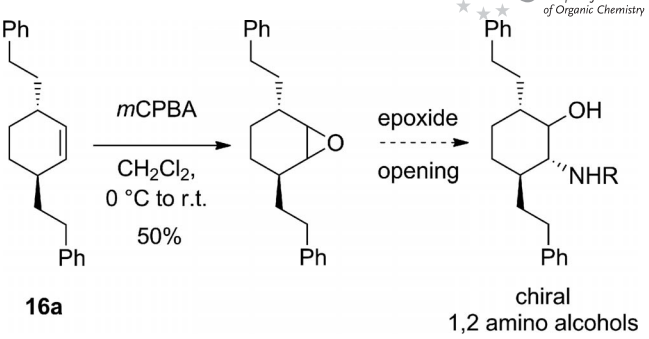
[a] Yield of the isolated product after flash column chromatography on SiO_2. [b] Determined by ^{1}H NMR or GC–MS analysis. [c] Determined by chiral GC or SFC analysis. [d] Hoveyda–Grubbs II catalyst was used in the RCM step. [e] Conversion.

allylic substrate **1c**, and by using phenethylmagnesium bromide as the alkylating agent. The results are shown in Table 5.

The double allylic alkylation reactions of substrates **14a** and **14b** were highly regioselective in favor of the γ adduct, whereas the regioselectivity was moderately good in the case of double allylic chloride **14c**, which has only one carbon atom between the two reactive sites, which results in some steric hindrance between the two substituents at the γ positions. Concerning the diastereoselectivity, up to 85:15 was achieved with the latter substrate. The synergic effect of the catalyst and the substrate in controlling the outcome of the reaction could be responsible for this result. As expected, high enantioselectivities were achieved for this transformation with *ee* values of up to 97%.

We envisaged a possible derivatization of the highly enantioenriched dialkylated products by transformation of the double bond (Scheme 4). Cycloalkene **16a** was converted into the corresponding epoxide under classical reaction conditions.[19] No matter how the oxidation proceeds (from the top or the bottom face), the same C_2-symmetrical compound should be obtained. This compound should be able to undergo a desymmetrization reaction. Indeed, the opening of the epoxide with a nucleophile, such as an amine, for example, would generate a chiral 1,2-amino alcohol. This class of compound has largely been used in asymmetric synthesis either as chiral auxiliaries[20] or as chiral building blocks for natural product synthesis.[21]

The methodology presented herein represents an alternative approach to the construction of enantioenriched cyclic compounds through an asymmetric allylic alkylation combined with ring-closing metathesis (Scheme 1). By this approach, different alkyl-substituted cycloalkenes were obtained because a broad range of alkyl Grignard reagents can be employed as alkylating partners for the chiral copper complex in the allylic substitution reaction. When an aromatic group is needed as a substituent in the cyclic unit the complementary approach is perhaps more advantageous as the asymmetric allylic arylation remains challenging for aliphatic allylic substrates, despite the progress achieved in this

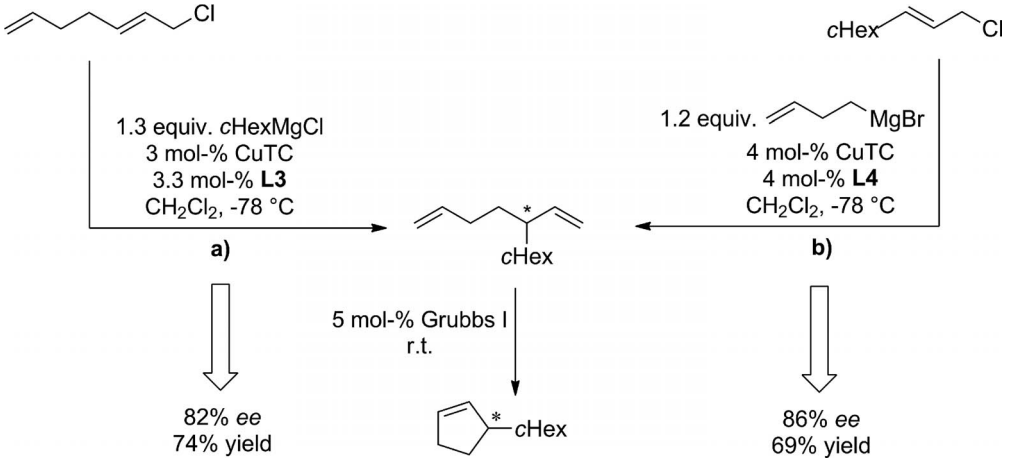


Scheme 4. Possible derivatization of product **16a**.

field with copper as catalyst.[22] On the other hand, to introduce a 4-*tert*-butoxybutyl moiety, for example, the first approach is maybe more desirable because of the easier preparation of the starting materials. Scheme 5 shows two specific examples of these complementary methodologies that can be used to synthesize the same product. Similar selectivities were achieved, slightly better in the case of method b, although the advantage of method a is the ease of preparation of the starting material and the availability of the Grignard reagent.

In view of the results obtained with the different ω-ethylenic allylic substrates, we have gained more insight into some mechanistic aspects of the process. First, we considered the effect of the substituent in the β position of the allylic olefin because the presence of this substituent could cause hindrance in the system and modify the chiral environment. From a direct comparison of the results obtained with the unsubstituted allylic chlorides **1b** and **1c**, and the β-methyl-substituted allylic chlorides **5a** and **5b**, a general decrease in the enantioselectivity was observed for the latter substrates, accentuated in the case of the addition of the cyclohexyl group for the construction of both the six- and five-membered rings. This shows that, as mentioned above, the methyl group is generally detrimental to the reaction.

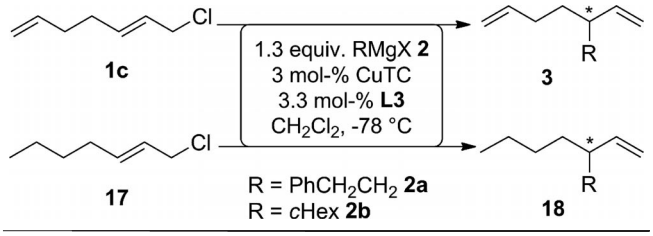
Then we questioned whether the terminal double bond of the ω-ethylenic allylic chlorides used in this study could play a role in the allylic alkylation reaction, and at which



Scheme 5. Complementary strategy for the formation of a cyclohexyl-substituted ring.

stage, as this olefin could take part in the catalytic cycle as a ligand coordinated to the copper(III) complex formed upon the oxidative addition, or prior to this step. This intramolecular coordination could eventually change the chiral environment around the reactive center, and therefore the terminal double bond could influence the outcome of the reaction. To demonstrate this hypothesis we prepared the saturated analogue **17** of allylic chloride **1c**. This compound does not contain the terminal double bond, consequently it should show a different reactivity in the copper-catalyzed asymmetric allylic alkylation reaction. For a direct comparison of the reactivity of the two allylic chlorides, we performed the copper-catalyzed allylic alkylation with two nucleophilic species employed before in our investigations, phenethylmagnesium bromide and cyclohexylmagnesium chloride (Table 6).

Table 6. Asymmetric allylic alkylation of unsaturated and saturated allylic substrates.



Entry	Substr.	R	L*	γ/α[a]	Product	*ee* [%], config.[b]
1	**1c**	**2a**	**L1**	92:8	**3a**	87, *R*
2	**17**	**2a**	**L1**	98:2	**18a**	95, *R*
3	**1c**	**2b**	**L3**	>99:1	**3b**	82, *R*
4	**17**	**2b**	**L3**	>99:1	**18b**	38, *R*

[a] Determined by ^{1}H NMR or GC–MS analysis. [b] Determined by chiral GC or SFC analysis.

Divergent results were obtained for the primary and secondary Grignard reagents. Better regio- and enantioselectivities were obtained for the phenethyl alkylation of the saturated analogue **17** than for the unsaturated substrate **1c**, whereas only 38% *ee* was observed for the saturated cyclohexyl-substituted adduct **18b** instead of the 82% *ee* determined for the unsaturated product **3b**. This suggests that in the latter instance (cyclohexyl alkylation), there is a positive effect of the terminal double bond coordinated to the metal center, although we do not have any experimental evidence of this coordination. In contrast, the presence of this double bond has a slight negative impact on the outcome of the reaction with the primary phenethylmagnesium bromide reagent because the intramolecular coordination of the double bond to copper modifies the chiral pocket.

We also investigated the reactivity of ω-ethylenic olefins having a methyl substituent on the terminal double bond. In this instance, the presence of the methyl group could cause a decrease in the coordinating ability of the olefin through steric hindrance such that maybe the reactivity of this substrate becomes more similar to its saturated analogue, or, alternatively, there could be a significant modification of the chiral environment around the reactive center. From a comparison of the results obtained with the substituted substrates **8a**,**b** and the unsubstituted analogues **1b**,**c**, a decrease in enantioselectivity was again observed in the case of the substituted alkylated adducts in the phenethyl, cyclohexyl, or *tert*-butoxybutyl substitution. In particular, in the case of the cyclohexyl-substituted five-membered system, we did not observe such a strong decrease in enantioselectivity as was noted when using the saturated allylic substrate **17**. Thus, we can speculate that in this instance, the positive effect of the coordinated double bond is weaker. On the contrary, especially for the formation of six-membered substituted rings, the substantial loss of enantiocontrol could result from the steric hindrance generated by the methyl group. We have also reported one example with the more sterically demanding cyclohexyl group as substituent on the terminal olefin to gain more insight into the role of this substituent. Surprisingly, the copper-catalyzed allylic alkylation of substrate **8c** proceeded with a selectivity of 70%, similar to the values observed with the other substrates, which suggests that the cyclohexyl group exhibits steric hindrance comparable to that of the methyl group.

Conclusions

We have described an efficient enantioselective process for the construction of enantioenriched cyclic compounds by coupling the powerful asymmetric allylic alkylation and ring-closing metathesis reactions. For this approach, ω-ethylenic allylic substrates were employed as synthetic equivalents of cyclic allylic compounds.[23]

With simple unsubstituted ω-ethylenic allylic chlorides, five-, six-, and seven-membered rings could be generated with enantiomeric excesses of up to 86, 93 and 85%, respectively. We also studied the reactivity of β-methyl-substituted ω-ethylenic allylic chlorides to access five- and six-membered cycloalkenes with a methyl group in the β position, achieving an enantioselectivity of up to 82%. Next, we illustrated the formation by this methodology of challenging enantioenriched rings not easily accessible by direct asymmetric allylic alkylation of cyclic substrates. In this instance we used both copper and iridium as metal sources for the asymmetric allylic alkylation step, achieving the γ-methyl-substituted cyclopentenes and -hexenes in up to 98% *ee*. Finally, the insertion of a second allylic leaving group into the allylic substrate allowed a highly enantioselective double asymmetric allylic alkylation to obtain interesting synthons that could be further elaborated for synthetic purposes.

We also tried to elucidate the effect of the ethylenic double bond during the allylic alkylation step. Even though the role of this terminal olefin has not been totally clarified in the catalytic cycle, proof of its intervention has been documented with some extra experimental data, and further investigations need to be carried out for a better understanding of the effect of this second double bond.

Experimental Section

General: All reactions were conducted under an inert atmosphere. Unless otherwise stated, all reagents were purchased from commer-

cial suppliers and used without further purification. All solvents employed in the reactions were dried by passage through alumina columns and degassed prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^{1}H (300 or 400 MHz) and ^{13}C (75 or 101 MHz) NMR spectra were recorded in $CDCl_3$, and chemical shifts (δ) are given in ppm relative to residual $CHCl_3$. The reactions were monitored by GC–MS using a Hewlett-Packard (EI mode) HP6890-5973 instrument. Optical rotations were measured at 20 °C in a 1 cm cell in the stated solvent. $[\alpha]_D$ values are given in 10^{-1} °C m^2 g^{-1} (concentration c given as g per 100 mL). Enantiomeric excesses were determined by chiral GC (capillary column, 10 psi H_2). Temperature programs are described as follows: initial temperature (°C)–initial time (min)–temperature gradient (°C min^{-1})–final temperature (°C); retention times (t_R) are given in min. All Grignard reagents except for cyclohexylmagnesium chloride (Aldrich) were synthesized in diethyl ether by addition of the corresponding bromide to magnesium. Flash chromatography was performed on silica gel (32–63 μm, 60 Å). The synthesis of the starting substrates is described in the Supporting Information.

Typical Procedure for the One-Pot Copper-Catalyzed Enantioselective Allylic Alkylation/Ring-Closing Metathesis: A flame-dried Schlenk tube was charged with the copper salt (3 mol-%) and the chiral ligand (3.3 mol-%). Dichloromethane (2 mL) was added and the mixture was stirred at room temperature for 20 min. The allylic chloride (0.5 mmol) dissolved in dichloromethane (1 mL) was introduced dropwise and the reaction mixture was stirred for a further 5 min before being cooled to –78 °C. The Grignard reagent (1–2 M in diethyl ether, 1.3 equiv.) in dichloromethane (up to 1 mL) was added over 60 min through a syringe pump. Once the addition was complete, the reaction mixture was left at –78 °C for a further 60 min until GC–MS analysis of an aliquot showed that all the starting material had been converted. At this point the reaction mixture was warmed to room temperature and Grubbs catalyst (first or second generation, 5 mol-%) was added. The reaction mixture was stirred at room temperature until GC–MS analysis of an aliquot showed that all of the S_N2' product had been converted. The reaction was then quenched by the addition of aqueous hydrochloride acid (1 N, 2 mL). Diethyl ether (5 mL) was added and the aqueous phase was separated and extracted with diethyl ether (3 × 3 mL). The combined organic fractions were washed with brine (5 mL), dried with anhydrous sodium sulfate, filtered, and reduced in vacuo. The oily residue was purified by flash column chromatography to yield the metathesis product. Analysis by GC or SFC on a chiral stationary phase showed the enantiomeric excess.

Typical Procedure for the Enantioselective Iridium-Catalyzed Allylic Alkylation: A flame-dried Schlenk tube was charged with $[Ir(cod)Cl]_2$ (4 mol-%), the chiral ligand (8 mol-%), and lithium chloride (1 equiv.). Tetrahydrofuran (0.5 mL) was added and the mixture was stirred at room temperature for 20 min. The allylic carbonate (0.5 mmol) and a solution of freshly prepared sodium malonate were added, and the reaction mixture was stirred at 60 °C for 16 h. The reaction mixture was hydrolyzed with water, extracted with diethyl ether, and dried with magnesium sulfate. The oily residue was purified by flash column chromatography to yield the product as a mixture of S_N2' and S_N2 regioisomers. Sodium malonate was prepared as follows: A flame-dried flask was charged with sodium hydride (1 mmol), which was washed with pentane (3 × 5 mL) and tetrahydrofuran (5 mL). Tetrahydrofuran (1.5 mL) was then added followed by dimethyl malonate (1 mmol).

Typical Procedure for the Intramolecular Ring-Closing Metathesis: The substrate was placed together with the Grubbs catalyst (first or second generation, 5 mol-%) in a dried Schlenk tube and dissolved in dichloromethane (2 mL). The reaction mixture was left at room temperature until complete conversion (by GC–MS analysis) at which point the solvent was evaporated. The oily residue was purified by flash column chromatography to yield the metathesis product. GC or SFC analysis on a chiral stationary phase showed the enantiomeric excess.

(*R*)-(3-Vinylnon-8-enyl)benzene (3a): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.21 (m, 5 H), 5.93–5.79 (m, 1 H), 5.70–5.57 (m, 1 H), 5.11–4.97 (m, 4 H), 2.76–2.66 (m, 1 H), 2.62–2.52, (m, 1 H), 2.11–2.00 (m, 3 H), 1.81–1.68 (m, 1 H), 1.67–1.54 (m, 1 H), 1.49–1.24 (m, 6 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.2, 143.0, 139.3, 128.6 (2 C), 128.4 (2 C), 125.7, 114.9, 114.3, 43.9, 37.0, 35.0, 33.9, 33.7, 29.2, 26.7 ppm. HRMS (EI): calcd. for $C_{17}H_{24}$ [M]$^+$ 228.1878; found 228.1882. Enantiomeric excess was measured on the metathesis product **4a**.

(–)-(*R*)-3-Phenethylcyclohept-1-ene (4a):[7a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.20 (m, 5 H), 5.90–5.81 (m, 1 H), 5.72–5.65 (m, 1 H), 2.77–2.16 (m, 2 H), 2.09–1.95 (m, 3 H), 1.81–1.55 (m, 4 H), 1.44–1.24 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.0, 137.9, 131.6, 128.6 (2 C), 128.4 (2 C), 125.7, 39.3, 39.0, 33.8, 33.6, 30.7, 28.9, 27.1 ppm. $[\alpha]_D^{25}$ = –25.5 (c = 1.0, $CHCl_3$) for 85% *ee* {ref.:[7a] $[\alpha]_D^{25}$ = –18 (c = 1.0, $CHCl_3$, 38% *ee*, (*R*) enantiomer}. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OB column, method: MeOH 0%–2–1–15, 5 °C): t_R = 4.26 (–), 4.72 (+) min.

(*R*)-Nona-1,8-dien-3-ylcyclohexane (3b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.74 (m, 1 H), 5.61–5.47 (m, 1 H), 5.02–4.85 (m, 4 H), 2.08–1.96 (m, 2 H), 1.90–0.88 (m, 18 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.8, 139.4, 114.9, 114.2, 50.2, 41.9, 33.9, 31.7, 31.3, 29.8, 29.2, 27.2, 27.0, 26.9, 26.8 ppm. HRMS (EI): calcd. for $C_{15}H_{26}$ [M]$^+$ 206.2035; found 206.2034. Enantiomeric excess was measured on the metathesis product **4b**.

(+)-(*S*)-3-Cyclohexylcyclohept-1-ene (4b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81–5.72 (m, 1 H), 5.69–5.61 (m, 1 H), 2.16–1.90 (m, 3 H), 1.80–0.95 (m, 17 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 136.9, 131.1, 45.3, 43.7, 31.0, 30.4, 30.2, 29.8, 28.7, 27.2, 27.0, 26.9, 26.8 ppm. HRMS (EI): calcd. for $C_{13}H_{22}$ [M]$^+$ 178.1722; found 178.1723. $[\alpha]_D^{25}$ = +11.4 (c = 0.4, $CHCl_3$) for 80% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 70–80–1–170–0, 50 cm s^{-1}): t_R = 28.65 (+), 28.95 (–) min.

(*R*)-(3-Vinyloct-7-enyl)benzene (3c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.18 (m, 5 H), 5.95–5.76 (m, 1 H), 5.71–5.55 (m, 1 H), 5.14–4.93 (m, 4 H), 2.77–2.50 (m, 2 H), 2.17–1.96 (m, 3 H), 1.82–1.20 (m, 6 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 142.9, 142.8, 139.0, 128.4 (2 C), 128.3 (2 C), 125.6, 114.8, 114.3, 43.7, 36.8, 34.5, 33.9, 33.5, 26.6, 26.5 ppm. HRMS (EI): calcd. for $C_{16}H_{22}$ [M]$^+$ 214.1722; found 214.1719. Enantiomeric excess was measured on the metathesis product **4c**.

(–)-(*R*)-[2-(Cyclohex-2-enyl)ethyl]benzene (4c):[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.27 (m, 5 H), 5.82–5.63 (m, 2 H), 2.72 (t, J = 8.3 Hz, 2 H), 2.25–1.42 (m, 9 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.0, 131.9, 128.5 (2 C), 128.4 (2 C), 127.3, 125.8, 38.4, 34.9, 33.4, 29.1, 25.5, 21.6 ppm. $[\alpha]_D^{25}$ = –65.2 (c = 1.0, $CHCl_3$) for 86% *ee* {ref.:[23] $[\alpha]_D^{25}$ = –104.4 (c = 1.2, $CHCl_3$, 92% *ee*) (*R*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-3P column, method: 60–30–1–170–0, 50 cm s^{-1}): t_R = 104.2 (+), 104.7 (–) min.

(*S*)-Octa-1,7-dien-3-ylcyclohexane (3d): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.72 (m, 1 H), 5.62–5.47 (m, 1 H), 5.04–4.85 (m,

4 H), 2.12–1.92 (m, 3 H), 1.82–1.58 (m, 5 H), 1.52–0.81 (m, 10 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 141.6, 139.2, 114.9, 114.2, 50.1, 41.8, 33.9, 31.2, 29.7, 26.9, 26.8 (2 C), 26.7 (2 C) ppm. Enantiomeric excess was measured on the metathesis product **4d**.

(–)-(*R*)-3-Cyclohexylcyclohex-1-ene (4d):[23] ^1H NMR (400 MHz, $CDCl_3$): δ = 5.74–5.51 (m, 2 H), 2.07–1.82 (m, 3 H), 1.80–1.42 (m, 8 H), 1.40–0.91 (m, 7 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 131.1, 127.2, 42.7, 40.9, 30.3, 29.9, 26.8 (2 C), 25.8 (2 C), 25.5, 22.3 ppm. $[\alpha]_D^{25}$ = –38.6 (*c* = 1.1, $CHCl_3$) for 74% *ee* {ref.[23] $[\alpha]_D^{25}$ = –42 (*c* = 1.0, $CHCl_3$, 70% *ee*) (*R*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (CHIRALDEX B-TA column, method: 70–120–15–170–5, 50 cm s^{-1}): t_R = 90.27 (+), 92.31(–) min.

(*R*)-10-*tert*-Butoxy-6-vinyldec-1-ene (3e): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.70 (m, 1 H), 5.60–5.41 (m, 1 H), 5.07–4.87 (m, 4 H), 3.31 (t, *J* = 6.8 Hz, 2 H), 2.11–1.87 (m, 3 H), 1.56–1.20 (m, 10 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.3, 139.1, 114.2, 114.1, 72.4, 61.6, 43.9, 34.9, 34.4, 33.9, 30.8, 27.6 (3 C), 26.5, 23.7 ppm. HRMS (EI): calcd. for $C_{16}H_{30}ONa$ [M + Na]$^+$ 261.2189; found 261.2187. The enantiomeric excess was measured on the metathesis product **4e**.

(–)-(*R*)-3-(4-*tert*-Butoxybutyl)cyclohex-1-ene (4e):[23] ^1H NMR (300 MHz, $CDCl_3$): δ = 5.74–5.58 (m, 2 H), 3.38 (t, *J* = 6.6 Hz, 2 H), 2.14–1.97 (m, 3 H), 1.90–1.88 (m, 2 H), 1.86–1.12 (m, 8 H), 1.20 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 132.3, 126.7, 72.5, 61.6, 36.3, 35.2, 30.9, 29.1, 27.6 (3C), 25.4, 23.7, 21.6 ppm. $[\alpha]_D^{25}$ = –40.7 (*c* = 1.0, $CHCl_3$) for 93% *ee* {ref.[23] $[\alpha]_D^{25}$ = –145.8 (*c* = 1.8, $CHCl_3$, 90% *ee*) (*R*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 68.44 (–), 68.90 (+) min.

(–)-(*R*)-[2-(Cyclopent-2-enyl)ethyl]benzene (4f):[23] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.14 (m 5 H), 5.84–5.69 (m, 2 H), 2.82–2.60 (m, 2 H), 2.50–2.25 (m, 2 H), 2.21–2.03 (m, 1 H), 1.88–1.42 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 142.9, 135.0, 130.6, 128.5 (2 C), 128.4 (2 C), 125.7, 45.3, 38.1, 34.4, 32.1, 29.9 ppm. $[\alpha]_D^{25}$ = –36.7 (*c* = 0.4, $CHCl_3$) for 86% *ee* {ref.[23] $[\alpha]_D^{25}$ = –117 (*c* = 1.5, $CHCl_3$, 44% *ee*) (*R*) enantiomer}. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OJ column, method: MeOH 0%–2–1–15, 5 °C): t_R = 11.21 (–), 11.53 (+) min.

(+)-(*S*)-Hepta-1,6-dien-3-ylcyclohexane (3g):[24] ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87–5.64 (m, 1 H), 5.60–5.41 (m, 1 H), 5.40–4.78 (m, 4 H), 2.12–1.97 (m, 1 H), 2.11–1.41 (m, 8 H), 1.38–0.74 (m, 7 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 141.4, 139.4, 115.4, 114.3, 49.7, 41.9, 31.9, 31.3, 31.0, 29.8, 26.9, 26.8 (2 C) ppm. $[\alpha]_D^{25}$ = +3.4 (*c* = 0.76, $CHCl_3$) for 82% *ee* {ref.[24] $[\alpha]_D^{25}$ = +3.4 (*c* = 0.98, $CHCl_3$, 73% *ee*) (*S*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (Chirasil DEX-CB column, method: 70–90–0.5–75–20–0.5–80–2–15–170–0, 30 cm s^{-1}): t_R = 108.24 (–), 110.49 (+) min.

(+)-(*S*)-Cyclopent-2-enylcyclohexane (4g):[24] ^1H NMR (400 MHz, $CDCl_3$): δ = 5.76–5.70 (m, 2 H), 2.49–2.40 (m, 1 H), 2.33–2.18 (m, 2 H), 1.99–1.88 (m, 1 H), 1.78–1.59 (m, 5 H), 1.53–1.43 (m, 1 H), 1.28–1.09 (m, 4 H), 1.02–0.87 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 133.6, 130.7, 51.9, 43.1, 32.4, 31.3, 31.2, 29.9, 27.5, 26.9, 26.7 ppm. $[\alpha]_D^{25}$ = +38.5 (*c* = 0.4, $CHCl_3$) for 82% *ee* {ref.[24] $[\alpha]_D^{25}$ = –88.2 (*c* = 1.03, $CHCl_3$, 73% *ee*) (*R*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-3P column, method: 60–0–1–170–0, 50 cm s^{-1}): t_R = 32.27 (+), 32.92 (–) min.

(*R*)-9-*tert*-Butoxy-5-vinylnon-1-ene (3h): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.71 (m, 1 H), 5.58–5.43 (m, 1 H), 5.04–4.88 (m, 4 H), 3.31 (t, *J* = 6.8 Hz, 2 H), 2.18–1.90 (m, 3 H), 1.56–1.21 (m, 8 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.0, 139.1, 114.4, 114.2, 72.4, 61.6, 43.5, 34.8, 34.1, 31.4, 30.8, 27.6 (3 C), 23.8 ppm. HRMS (EI): calcd. for $C_{15}H_{28}ONa$ [M + Na]$^+$ 247.2032; found 247.2030. The enantiomeric excess was measured on the metathesis product **4h**.

(+)-(*R*)-3-(4-*tert*-Butoxybutyl)cyclopent-1-ene (4h): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.79–5.70 (m, 2 H), 3.38 (t, *J* = 6.7 Hz, 2 H), 2.75–2.61 (m, 1 H), 2.43–2.22 (m, 2 H), 2.18–1.98 (m, 2 H), 1.65–1.29 (m, 6 H), 1.23 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 135.4, 130.1, 72.4, 61.6, 45.6, 36.0, 32.0, 31.0, 29.9, 27.6 (3 C), 24.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{24}ONa$ [M + Na]$^+$ 219.1719; found 219.1719. $[\alpha]_D^{25}$ = +1.7 (*c* = 1.0, $CHCl_3$) for 73% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-3P column, method: 60–0–1–170–0, 45 cm s^{-1}): t_R = 45.09 (+), 45.44 (–) min.

(*S*)-[3-(Prop-1-en-2-yl)oct-7-enyl]benzene (6a): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.14 (m, 5 H), 5.90–5.73 (m, 1 H), 5.07–4.91 (m, 2 H), 4.82 (s, 1 H), 4.74 (s, 1 H), 2.86–2.42 (m, 2 H), 2.15–1.98 (m, 3 H), 1.72–1.60 (m, 2 H), 1.65 (s, 3 H), 1.42–1.27 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 147.2, 142.9, 139.1, 128.4 (2 C), 128.3 (2 C), 125.6, 114.4, 112.1, 46.9, 35.4, 33.9, 33.8, 32.9, 26.8, 17.9 ppm. HRMS (EI): calcd. for $C_{17}H_{24}$ [M]$^+$ 228.1878; found 228.1877. The enantiomeric excess was determined on the metathesis product **7a**.

(–)-(*S*)-[2-(2-Methylcyclohex-2-enyl)ethyl]benzene (7a):[23] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.14 (m, 5 H), 5.44 (br. s, 1 H), 2.66 (m, 1 H), 2.64–2.48 (m, 1 H), 2.12–1.83 (m, 3 H), 1.68 (s, 3 H), 1.82–1.44 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.0, 136.9, 128.4 (2 C), 128.3 (2 C), 125.6, 122.7, 38.3, 34.6, 33.6, 27.4, 25.6, 22.2, 19.8 ppm. HRMS (EI): calcd. for $C_{15}H_{20}$ [M]$^+$ 200.1565; found 200.1567. $[\alpha]_D^{25}$ = –37.3 (*c* = 1.05, $CHCl_3$) for 82% *ee* {ref.[23] $[\alpha]_D^{25}$ = –7.5 (*c* = 1.25, $CHCl_3$, 18% *ee*) (*S*) enantiomer}. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 84.51 (–), 86.75 (+) min.

(2-Methylocta-1,7-dien-3-yl)cyclohexane (6b): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.88–5.73 (m, 1 H), 5.03–4.89 (m, 2 H), 4.75 (s, 1 H), 4.61 (s, 1 H), 2.12–1.31 (m, 2 H), 1.90–1.80 (m, 1 H), 1.78–1.48 (m, 5 H), 1.56 (s, 3 H), 1.28–1.07 (m, 6 H), 0.91–0.74 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 146.8, 139.3, 114.2, 112.2, 53.4, 39.7, 33.9, 33.3, 31.8, 31.1, 28.9, 27.1, 26.8, 26.6, 18.7 ppm. HRMS (EI): calcd. for $C_{15}H_{26}$ [M]$^+$ 206.2035; found 206.2033. The enantiomeric excess was determined on the metathesis product **7b**.

(+)-6-Cyclohexyl-1-methylcyclohex-1-ene (7b): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.49 (br. s, 1 H), 2.03–1.58 (m, 3 H), 1.68 (s, 3 H), 1.85–1.55 (m, 7 H), 1.51–0.80 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 136.2, 124.1, 44.0, 39.4, 31.6, 27.4, 27.2, 27.0, 26.9, 25.6, 23.9, 22.2, 22.1 ppm. HRMS (EI): calcd. for $C_{13}H_{22}$ [M]$^+$ 178.1722; found 178.1720. $[\alpha]_D^{25}$ = +8.7 (*c* = 1.04, $CHCl_3$) for 40% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 56.74 (+), 58.27 (–) min.

10-*tert*-Butoxy-6-(prop-1-en-2-yl)dec-1-ene (6c): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.86–5.72 (m, 1 H), 5.04–4.89 (m, 2 H), 4.75 (s, 1 H), 4.64 (s, 1 H), 3.30 (t, *J* = 6.8 Hz, 2 H), 2.10–1.94 (m, 3 H), 1.57 (s, 3 H), 1.55–1.46 (m, 4 H), 1.35–1.22 (m, 6 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 147.7, 139.1, 114.2,

111.4, 72.4, 61.6, 47.2, 33.9, 33.4, 32.9, 30.8, 27.6 (3 C), 26.8, 24.1, 17.9 ppm. HRMS (EI): calcd. for $C_{17}H_{32}O$ $[M]^+$ 252.2453; found 252.2457. The enantiomeric excess was determined on the metathesis product **7c**.

(+)-6-(4-*tert*-Butoxybutyl)-1-methylcyclohex-1-ene (7c): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.40 (br. s, 1 H), 3.33 (t, J = 6.8 Hz, 2 H), 2.03–1.85 (m, 3 H), 1.68 (s, 3 H), 1.66–1.38 (m, 6 H), 1.35–1.20 (m, 4 H), 1.19 (m, 9 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 137.5, 122.2, 72.5, 61.6, 38.5, 32.5, 30.9, 27.6 (3 C), 27.3, 25.6, 23.9, 22.3, 19.7 ppm. HRMS (ESI): calcd. for $C_{15}H_{28}NaO$ $[M + Na]^+$ 247.20324; found 247.20350. $[\alpha]_D^{25}$ = +16.2 (c = 1.08, $CHCl_3$) for 82% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (Chirasil DEX-CB column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 75.04 (–), 77.04 (+) min.

(+)-(*S*)-[3-(Prop-1-en-2-yl)hept-6-enyl]benzene (6d): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.10 (m, 5 H), 5.96–5.77 (m, 1 H), 5.08–4.96 (m, 2 H), 4.91–4.87 (m, 1 H), 4.79 (d, J = 2.3 Hz, 1 H), 2.66–2.48 (m, 2 H), 2.22–1.93 (m, 3 H), 1.83–1.58 (m, 2 H), 1.70 (s, 3 H), 1.53–1.45 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 146.9, 142.9, 139.1, 128.6, 128.5, 128.4, 125.7, 114.6, 114.4, 112.5, 46.7, 35.4, 33.9, 32.7, 31.8, 19.4 ppm. HRMS (EI): calcd. for $C_{16}H_{22}$ $[M]^+$ 214.1722; found 214.1725. $[\alpha]_D^{25}$ = +0.8 (c = 1.04, $CHCl_3$) for 65% *ee*. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OJ column, method: MeOH 2%–2–1–15): t_R = 3.90 (+), 4.13 (–) min.

(–)-(*S*)-[2-(2-Methylcyclopent-2-enyl)ethyl]benzene (7d): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.20 (m, 5 H), 5.46–5.38 (m, 1 H), 2.82–2.69 (m, 1 H), 2.68–2.50 (m, 2 H), 2.42–2.08 (m, 3 H), 2.06–1.94 (m, 1 H), 1.71 (s, 3 H), 1.70–1.57 (m, 1 H), 1.56–1.42 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 143.1, 143.0, 128.4 (2 C), 128.3 (2 C), 125.7, 124.8, 47.8, 35.6, 33.9, 30.9, 30.2, 14.9 ppm. HRMS (EI): calcd. for $C_{14}H_{18}$ $[M]^+$ 186.1409; found 186.1407. $[\alpha]_D^{25}$ = –17.1 (c = 1.08, $CHCl_3$) for 66% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 70.61 (–), 71.74 (+) min.

(+)-(2-Methylhepta-1,6-dien-3-yl)cyclohexane (6e): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87–5.74 (m, 1 H), 5.10–4.88 (m, 2 H), 4.77–4.75 (m, 1 H), 4.73 (d, J = 2.3 Hz, 1 H), 2.10–2.05 (m, 1 H), 2.04–1.94 (m, 2 H), 1.90–1.55 (m, 7 H), 1.56 (s, 3 H), 1.30–1.10 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 146.6, 139.5, 114.2, 112.6, 39.7, 32.1, 31.9, 31.2, 30.3, 28.9, 27.0, 26.9, 26.7, 18.8 ppm. HRMS (EI): calcd. for $C_{14}H_{24}$ $[M]^+$ 192.1878; found 192.1881. $[\alpha]_D^{25}$ = +7.9 (c = 1.05, $CHCl_3$) for 30% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-3P column, method: 60–0–1–170–0, 45 cm s^{-1}): t_R = 40.35 (+), 40.96 (–) min.

(–)-(2-Methylcyclopent-2-enyl)cyclohexane (7e): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.38 (br. s, 1 H), 2.53–2.45 (m, 1 H), 2.27–2.19 (m, 2 H), 1.92–1.53 (m, 7 H), 1.65 (s, 3 H), 1.38–0.80 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 141.8, 125.2, 53.7, 39.3, 32.2, 31.6, 27.1, 26.9, 26.7, 26.4, 25.0, 15.2 ppm. HRMS (EI): calcd. for $C_{12}H_{20}$ $[M]^+$ 164.1565; found 164.1563. $[\alpha]_D^{25}$ = –5.8 (c = 0.61, $CHCl_3$) for 30% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (Chirasil DEX-CB column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 35.94 (–), 36.24 (+) min.

(*R*)-(7-Methyl-3-vinyloct-7-enyl)benzene (9a): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.19 (m, 5 H), 5.71–5.58 (m, 1 H), 5.17–5.01 (m, 2 H), 4.74 (s, 1 H), 4.70 (s, 1 H), 2.78–2.65 (m, 1 H), 2.63–2.52 (m, 1 H), 2.18–1.97 (m, 3 H), 1.75 (s, 3 H), 1.68–1.27 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 146.1, 142.9, 142.9, 128.4 (2 C), 128.3 (2 C), 125.6, 114.8, 109.8, 43.7, 37.9, 36.9, 34.6, 33.6, 25.1, 22.4 ppm. HRMS (EI): calcd. for $C_{17}H_{24}$ $[M]^+$ 228.1878; found 228.1881. The enantiomeric excess was determined on the metathesis product **10a**.

(–)-(*S*)-[2-(3-Methylcyclohex-2-enyl)ethyl]benzene (10a):[25] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.11 (m, 5 H), 5.34 (br. s, 1 H), 2.65 (t, J = 8.2 Hz, 2 H), 2.12–1.90 (m, 2 H), 1.94–1.85 (m, 3 H), 1.67 (s, 3 H), 1.83–1.68 (m, 2 H), 1.66–1.42 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.0, 134.2, 128.4 (2 C), 128.3 (2 C), 125.9, 125.6, 38.5, 35.0, 33.4, 30.3, 28.9, 24.9, 21.9 ppm. HRMS (EI): calcd. for $C_{15}H_{20}$ $[M]^+$ 200.1565; found 200.1564. $[\alpha]_D^{25}$ = –24.7 (c = 1.0, $CHCl_3$) for 49% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 50 cm s^{-1}): t_R = 87.56 (–), 88.50 (+) min.

(*R*)-(7-Methylocta-1,7-dien-3-yl)cyclohexane (9b): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.62–5.49 (m, 1 H), 5.03–4.86 (m, 2 H), 4.70 (s, 1 H), 4.68 (s, 1 H), 2.07–1.90 (m, 2 H), 1.83–1.59 (m, 6 H), 1.70 (s, 3 H), 1.52–1.37 (m, 2 H), 1.35–0.83 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 146.2, 141.7, 114.9, 109.7, 50.1, 41.9, 37.9, 34.7, 31.3, 31.2, 29.7, 26.8, 26.7, 25.5, 22.4 ppm. HRMS (EI): calcd. for $C_{15}H_{26}$ $[M]^+$ 206.2035; found 206.2036. The enantiomeric excess was determined on the metathesis product **10b**.

(+)-(*S*)-3-Cyclohexyl-1-methylcyclohex-1-ene (10b): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.31 (br. s, 1 H), 2.10–1.86 (m, 3 H), 1.85–1.42 (m, 8 H), 1.70 (s, 3 H), 1.40–0.80 (m, 7 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 134.2, 125.3, 43.0, 41.3, 30.5 (2 C), 30.4, 30.1, 26.9 (2 C), 25.7, 24.2, 22.7 ppm. HRMS (EI): calcd. for $C_{13}H_{22}$ $[M]^+$ 178.1722; found 178.1719. $[\alpha]_D^{25}$ = +2.4 (c = 0.5, $CHCl_3$) for 64% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (Chirasil DEX-CB column, method: 60–0–1–170–5, 50 cm s^{-1}): t_R = 57.29 (–), 57.73 (+) min.

(*R*)-10-*tert*-Butoxy-2-methyl-6-vinyldec-1-ene (9c): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.59–5.44 (m, 1 H), 5.00–4.89 (m, 2 H), 4.69 (s, 1 H), 4.64 (s, 1 H), 3.31 (t, J = 6.6 Hz, 2 H), 2.08–1.90 (m, 2 H), 1.69 (s, 3 H), 1.55–1.12 (m, 11 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 146.2, 143.4, 114.1, 109.7, 72.5, 61.6, 44.0, 37.9, 34.9, 34.6, 30.8, 27.6 (3 C), 25.2, 23.8, 22.9 ppm. HRMS (EI): calcd. for $C_{17}H_{32}NaO$ $[M + Na]^+$ 275.23454; found 275.23462. The enantiomeric excess was determined on the metathesis product **10c**.

(–)-(*S*)-3-(4-*tert*-Butoxybutyl)-1-methylcyclohex-1-ene (10c): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.36–5.31 (br. s, 1 H), 3.38 (t, J = 6.7 Hz, 2 H), 2.11–1.85 (m, 3 H), 1.82–1.71 (m, 2 H), 1.68 (s, 3 H), 1.60–1.25 (m, 8 H), 1.24 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 132.1, 126.5, 72.5, 61.6, 36.6, 35.5, 31.0, 30.3, 28.9, 27.6 (3 C), 24.0, 23.7, 22.0 ppm. HRMS (EI): calcd. for $C_{15}H_{28}O$ $[M - C_4H_9]^+$ 167.1436; found 167.1433. $[\alpha]_D^{25}$ = –9.4 (c = 1.0, $CHCl_3$) for 61% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 50 cm s^{-1}): t_R = 76.94 (–), 77.44 (+) min.

(*R*)-(6-Methylhepta-1,6-dien-3-yl)cyclohexane (9d): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.63–5.47 (m, 1 H), 5.06–4.86 (m, 2 H), 4.73 (s, 1 H), 4.71 (s, 1 H), 2.10–1.52 (m, 8 H), 1.76 (s, 3 H), 1.42–0.81 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 146.6, 141.5, 115.4, 109.6, 49.9, 42.0, 35.8, 31.3, 29.9, 29.7, 26.9, 26.9, 26.8, 22.8 ppm. HRMS (EI): calcd. for $C_{14}H_{24}$ $[M]^+$ 192.1878; found 192.1876. The enantiomeric excess was measured on the metathesis product **10d**.

(+)-(*S*)-(3-Methylcyclopent-2-enyl)cyclohexane (10d): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.34–5.30 (m, 1 H), 2.45–2.36 (m, 1 H),

2.21–2.13 (m, 2 H), 2.02–1.91 (m, 1 H), 1.71 (s, 3 H), 1.77–1.58 (m, 1 H), 1.57–1.47 (m, 5 H), 1.26–1.04 (m, 4 H), 0.91–0.83 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 140.4, 127.2, 52.0, 43.4, 36.6, 31.2, 31.1, 28.4, 26.8, 26.6, 26.5, 16.8 ppm. HRMS (EI): calcd. for $C_{12}H_{20}$ $[M]^+$ 164.1565; found 164.1564. $[\alpha]_D^{25}$ = +64.3 (*c* = 1.0, $CHCl_3$) for 74% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 40.21 (+), 41.03 (–) min.

(*S*)-9-*tert*-Butoxy-2-methyl-5-vinylnon-1-ene (9e): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.61–5.45 (m, 1 H), 5.30–4.90 (m, 2 H), 4.73 (s, 1 H), 4.70 (s, 1 H), 3.31 (t, *J* = 6.7 Hz, 2 H), 2.10–1.86 (m, 3 H), 1.70 (s, 3 H), 1.57–1.22 (m, 8 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 146.4, 143.2, 114.6, 109.7, 72.6, 61.7, 43.9, 35.5, 35.0, 33.0, 30.9, 27.6 (3 C), 23.9, 22.7 ppm. HRMS (EI): calcd. for $C_{16}H_{30}ONa$ $[M + Na]^+$ 261.2189; found 261.2187. The enantiomeric excess was measured on the metathesis product **10e**.

(–)-(*S*)-3-(4-*tert*-Butoxybutyl)-1-methylcyclopent-1-ene (10e): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.35–5.28 (m, 1 H), 3.37 (t, *J* = 6.8 Hz, 2 H), 2.71–2.58 (m, 1 H), 2.30–1.98 (m, 4 H), 1.75 (s, 3 H), 1.60–1.27 (m, 6 H), 1.23 (m, 9 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 139.9, 129.1, 72.4, 61.7, 45.9, 36.4, 36.3, 30.9, 30.8, 27.6 (3 C), 24.6, 16.7 ppm. HRMS (EI): calcd. for $C_{14}H_{26}O$ $[M]^+$ 210.1984; found 210.1981. $[\alpha]_D^{25}$ = –32.4 (*c* = 0.6, $CHCl_3$) for 68% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 58.75 (+), 59.13 (–) min.

(9-*tert*-Butoxy-5-vinylnon-1-en-2-yl)cyclohexane (9f): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.58–5.47 (m, 1 H), 5.03–4.90 (m, 2 H), 4.65 (s, 1 H), 4.69 (s, 1 H), 3.31 (t, *J* = 6.8 Hz, 2 H), 2.10–1.85 (m, 3 H), 1.83–1.62 (m, 6 H), 1.56–1.43 (m, 3 H), 1.41–1.03 (m, 10 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 153.7, 143.3, 114.4, 106.5, 72.5, 61.6, 44.4, 44.0, 34.9, 33.5, 32.6, 32.5 (2 C), 30.8, 27.6 (3 C), 26.9, 26.8, 26.5, 23.8 ppm. HRMS (EI): calcd. for $C_{21}H_{38}NaO$ $[M + Na]^+$ 329.28149; found 329.28181. The enantiomeric excess was determined on the metathesis product **10f**.

(+)-[3-(4-*tert*-Butoxybutyl)cyclopent-1-enyl]cyclohexane (10f): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.25 (br. s, 1 H), 3.32 (t, *J* = 6.5 Hz, 2 H), 2.65–2.50 (m, 1 H), 2.31–2.12 (m, 2 H), 2.09–1.87 (m, 2 H), 1.80–1.65 (m, 7 H), 1.55–1.02 (m, 10 H), 1.18 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.6, 125.8, 72.4, 61.7, 45.4, 39.8, 36.4, 32.8, 32.1, 32.0 (2 C), 31.0, 30.3, 27.6 (3 C), 26.5 (2 C), 24.6 ppm. HRMS (EI): calcd. for $C_{15}H_{25}O$ $[M - C_4H_9]^+$ 221.1905; found 221.1905. $[\alpha]_D^{25}$ = +30.2 (*c* = 1.0, $CHCl_3$) for 70% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-3P column, method: 60–30–1–170–0, 50 cm s^{-1}): t_R = 102.50 (–), 102.71 (+) min.

Dimethyl (*R*)-2-(7-Methylocta-1,7-dien-3-yl)malonate (12a): ^1H NMR (400 MHz, $CDCl_3$): δ = 5.68–5.56 (m, 1 H), 5.13–5.04 (m, 2 H), 4.69 (s, 1 H), 4.65 (s, 1 H), 3.73 (s, 3 H), 3. 68 (s, 3 H), 3.38 (d, *J* = 8.9 Hz, 1 H), 2.82–2.72 (m, 1 H), 2.07–1.89 (m, 2 H), 1.68 (s, 3 H), 1.54–1.23 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 168.8 (2 C), 137.9, 125.4, 117.7, 110.0, 56.9, 52.4, 52.3, 44.2, 37.4, 31.9, 24.9, 22.4 ppm. HRMS (ESI): calcd. for $C_{14}H_{22}O_4$ $[M]^+$ 254.1518; found 254.1522. The enantiomeric excess was measured on the metathesis product **13a**.

Dimethyl (+)-(*R*)-2-(3-Methylcyclohex-2-enyl)malonate (13a):[26] ^1H NMR (300 MHz, $CDCl_3$): δ = 5.27 (br. s, 1 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.29 (d, *J* = 10.5 Hz, 1 H), 3.00–2.85 (m, 1 H), 1.98–1.90 (m, 2 H), 1.82–1.58 (m, 2 H), 1.68 (s, 3 H), 1.41–1.24 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 169.1 (2 C), 137.1, 121.5, 57.3, 52.4 (2 C), 35.8, 29.9, 26.5, 24.1, 21.3 ppm. HRMS (ESI): calcd. for $C_{12}H_{18}O_4$ $[M]^+$ 226.1205; found 226.1208. $[\alpha]_D^{25}$ = +15.3 (*c* = 0.9, $CHCl_3$) for 97% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 72.91 (–), 75.02 (+) min.

Dimethyl (*R*)-2-(6-Methylhepta-1,6-dien-3-yl)malonate (12b): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.70–5.54 (m, 1 H), 5.17–5.05 (m, 2 H), 4.71 (s, 1 H), 4.65 (s, 1 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.40 (d, *J* = 8.9 Hz, 1 H), 2.84–2.70 (m, 1 H), 2.20–1.88 (m, 4 H), 1.69 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 168.7, 168.7, 145.1, 137.9, 118.1, 110.5, 57.0, 52.6, 52.4, 43.8, 35.1, 30.2, 22.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}O_4$ $[M]^+$ 240.1362; found 240.1364. The enantiomeric excess was measured on the metathesis product **13b**.

Dimethyl (+)-(*R*)-2-(3-Methylcyclopent-2-enyl)malonate (13b): ^1H NMR (300 MHz, $CDCl_3$): δ = 5.22 (br. s, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.40–3.28 (m, 1 H), 3.24 (d, *J* = 9.8 Hz, 1 H), 2.28–2.05 (m, 2 H), 1.70 (s, 3 H), 1.65–1.52 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 169.3 (2 C), 143.2, 125.1, 57.2, 52.3 (2 C), 45.7, 36.0, 28.7, 16.7 ppm. HRMS (ESI): calcd. for $C_{11}H_{16}O_4$ $[M]^+$ 212.1049; found 212.1051. $[\alpha]_D^{25}$ = +59.1 (*c* = 1.0, $CHCl_3$) for 98% *ee*. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60–0–1–170–5, 45 cm s^{-1}): t_R = 56.07 (–), 56.46 (+) min.

(3,6-Divinyloctane-1,8-diyl)dibenzene (15a): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.16 (m, 10 H), 5.69–5.58 (m, 2 H), 5.14–4.95 (m, 4 H), 2.77–2.67 (m, 4 H), 2.66–2.48 (m, 2 H), 2.18–1.92 (m, 4 H), 1.80–1.67 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 143.1, 143.0, 142.9 (2 C), 128.5 (4 C), 128.4 (4 C), 125.7 (2 C), 115.0, 114.9, 44.1, 43.8, 37.0, 36.8, 33.6 (2 C), 32.6, 32.5 ppm. HRMS (EI): calcd. for $C_{24}H_{30}$ $[M]^+$ 318.2348; found 318.2343. The enantiomeric excess was determined on the metathesis product **16a**.

(–)-3,6-Diphenethylcyclohex-1-ene (16a): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.18 (m, 10 H), 5.72 (s, 2 H), 2.68 (t, *J* = 7.9 Hz, 4 H), 2.90–2.19 (m, 2 H), 1.80–1.48 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 142.8, 131.8 (2 C), 131.5 (2 C), 128.4 (4 C), 128.3 (4 C), 125.7, 38.4, 37.9, 35.4, 34.6, 33.6, 33.2, 29.1, 26.1 ppm. HRMS (EI): calcd. for $C_{22}H_{26}$ $[M]^+$ 290.2035; found 290.2033. $[\alpha]_D^{25}$ = –92.8 (*c* = 1.0, $CHCl_3$) for 96% *ee*. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OB column, method: MeOH 2%–2–1–15): t_R = 12.31 (+), 13.35 (–) min.

(+)-(3,5-Divinylheptane-1,7-diyl)dibenzene (15b): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.10 (m, 10 H), 5.80–5.37 (m, 2 H), 5.23–4.95 (m, 4 H), 2.82–2.45 (m, 4 H), 2.30–2.02 (m, 2 H), 1.90–1.23 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.0, 142.9, 142.8, 142.7, 128.5 (2 C), 128.4 (2 C), 128.3 (4 C), 125.6 (2 C), 115.4, 114.6, 41.5, 40.8, 40.5, 37.7, 36.2, 33.6, 33.4 ppm. HRMS (EI): calcd. for $C_{23}H_{28}$ $[M]^+$ 304.2191; found 304.2194. $[\alpha]_D^{25}$ = +0.6 (*c* = 1.03, $CHCl_3$) for 95% *ee*. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OJ column, method: MeOH 2%–2–1–15). t_R = 9.09 (+), 11.03 (–) min.

(–)-3,5-Diphenethylcyclopent-1-ene (16b): ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.13 (m, 10 H), 5.76 (s, 2 H), 2.83–2.58 (m, 6 H), 1.82–1.53 (m, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 142.8 (2 C), 134.6 (2 C), 128.4 (4 C), 128.3 (4 C), 125.6 (2 C), 44.4, 37.9 (2 C), 36.5 (2 C), 34.3 (2 C) ppm. HRMS (EI): calcd. for $C_{21}H_{24}$ $[M]^+$ 276.1878; found 276.1874. $[\alpha]_D^{25}$ = –85.9 (*c* = 1.07, $CHCl_3$) for 97% *ee*. The enantiomeric excess was determined by SFC on a chiral stationary phase (Chiralcel OD column, method: MeOH 2%–2–1–15): t_R = 7.29 (–), 8.64 (+) min.

Supporting Information (see footnote on the first page of this article): Full experimental details, NMR spectra, and all chromatograms for the chiral GC or SFC.

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