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Tetrahedron 60 (2004) 1803–1816
Tetrahedron

# An efficient and general method for resolving cyclopropene carboxylic acids☆

Lian-an Liao, Fan Zhang, Ni Yan, James A. Golen† and Joseph M. Fox*

*Brown Laboratories, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA*

Received 10 November 2003; revised 15 December 2003; accepted 15 December 2003

**Abstract**—A general method is described for the resolution of cycloprop-2-ene carboxylic acids via diastereomeric *N*-acyloxazolidines prepared from enantiomerically pure oxazolidinones. Although a number of oxazolidinones were shown to resolve cyclopropene carboxylic acids, the oxazolidinones of *S*-phenylalaninol, *S*-phenylglycine and (1*S*,2*R*)-*cis*-1-amino-2-indanol are optimal in terms of resolving power and cost effectiveness. Separations were performed using simple flash chromatography, and because there is typically a large difference in $R_f$ values it is possible to separate gram quantities of pure diastereomers in a single chromatogram. The cycloprop-2-ene carboxylic acids that can be resolved include those that are substituted at the 1-position by H, Ph, α-naphthyl, $CO_2Me$, $CH_2OMOM$, and trans-styryl; alkene substituents include Me, *n*-alkyl, Ph and tethered alkynes. Remarkably, 2-methyl-3-propylcycloprop-2-ene carboxylic acid can also be resolved with ease. The relative configurations of four diastereomerically pure oxazolidines were determined by X-ray crystallography. Reduction of the *N*-acyloxazolidinones with $LiBH_4$ give enantiomerically pure derivatives of 3-hydroxymethylcyclopropene that react with either MeMgCl or vinylMgCl and catalytic CuI to give enantiomerically pure products of *syn*-addition.


## 1. Introduction

Although the unusual reactivity of cyclopropenes makes them interesting tools for synthesis,[1–7] methods that produce enantiomerically enriched cyclopropenes are rare.[8–18] Racemic cyclopropenecarboxylic esters[19,20] can be prepared easily and in quantity by the reactions of stabilized diazo compounds with alkynes,[21] and the groups of Doyle and Müller have described enantioselective versions of the process using chiral-catalysts.[9–14,17,22,23] For intermolecular catalytic asymmetric cyclopropenation reactions, excellent enantioselectivities have been obtained for the reactions of propargylethers (≥94% ee) acetals (88–95% ee) and amines (≥97% ee) with diazoacetates or *N*,*N*-dimethyldiazoacetamide using $[MEPY]_4Rh_2$.[9,10,17] High selectivity could also be achieved in the enantioselective cyclopropenation of *t*-butylacetylene (89% ee) or the diastereoselective cyclopropenation of 1-hexyne (86% de with *d*-menthyldiazoacetate).[9]

Although the Doyle/Müller system for enantioselective cyclopropenation represents a significant advance, there are a number of challenges that must be addressed before cyclopropene carboxylic acids can be generally useful as chirons.[24] Most importantly, the enantioselective reactions that have been described so far have been restricted to those that utilize unsubstituted diazoacetates or *N*,*N*-dimethyldiazoacetamide. Reactions that produce enantiomerically enriched cyclopropenes with quaternary centers are unknown. Furthermore, when applied to internal alkynes the chiral catalysts produce cyclopropenes with very low enantiomeric excess.[9] Because of renewed interest in the development of stereoselective reactions of cyclopropenes,[6,25–29] including that of our own group,[30] we sought to develop a simple and inexpensive procedure for obtaining numerous derivatives of cyclopropene carboxylic acids in enantiomerically pure form. For example, facially selective carbometallation (Scheme 1)[30] and hydrometallation reactions[27] are powerful new methods for preparing diverse types of cyclopropane products from common chiral precursors. The multicomponent nature of such reactions makes them attractive for complex molecule synthesis and drug discovery. However, before the present work was undertaken, there was no general method for obtaining the enantiomerically pure starting materials. We show here that a variety of cycloprop-2-ene carboxylic acids can be resolved through conversion to diastereomeric *N*-acyloxazolidinones and separated by column chromatography to provide gram quantities of diastereomerically pure cyclopropenes. The method is notably general and reliable, and it significantly enhances the value of the processes in

☆ Supplementary data associated with this article can be found in the online version at doi: 10.1016/S0040-4020(03)02036-2

*Keywords*: Cyclopropene; Enantiomerically pure oxazolidione.
* Corresponding author. Tel.: +1-302-831-0191; fax: +1-302-831-6335; e-mail address: jmfox@udel.edu
† To whom inquires regarding X-ray crystallography should be addressed. Current Address: Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747-2300, USA.

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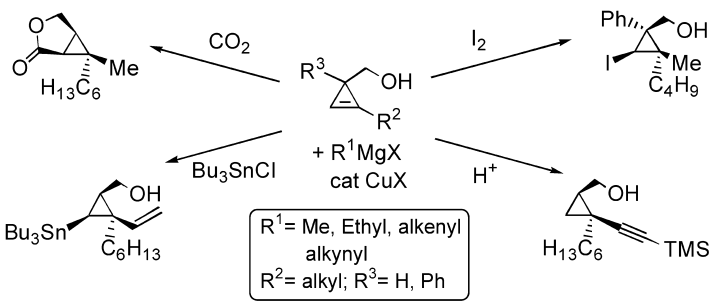
doi:10.1016/j.tet.2003.12.042




**Scheme 1.**

Scheme 1 and new reactions of chiral cyclopropenes that are under development.

## 2. Results and discussion

A rational starting point for the resolution of cyclopropene carboxylic acids was via diastereomeric esters, because Kass and co-workers had previously shown that diastereomeric-*l*-menthyl 2-phenyl-3-*t*-butyl-1-trimethylsilyl-cyclopropene carboxylates were separable by MPLC.[18] Accordingly, we reacted a number of enantiomerically pure alcohols with acid chloride **1**, but disappointingly none of the diastereomeric esters were separable by TLC (Fig. 1).

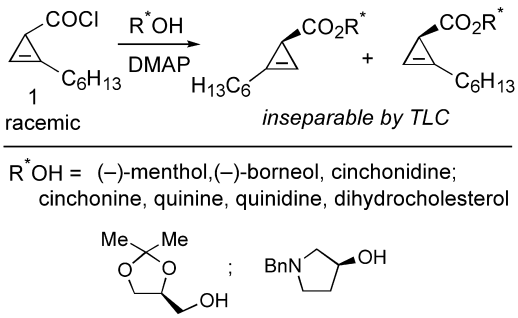



**Figure 1.** Attempted resolution of diastereomeric esters.

Given the lack of success in these screening efforts, further work was preceded by computational screening of various auxilaries using molecular mechanics. Based on these models, it was surmised that chiral oxazolidinones would be excellent resolving groups for cyclopropene carboxylic acids because of the difference in the relative orientations of the alkene and oxazolidinone substituents for the diastereomers (Fig. 2). The models assumed that the preferred conformations of the *N*-acyloxazolidinones would place the carbonyls in an *anti* orientation,[31] and that like other cyclopropylcarbonyl compounds[32] the cyclopropene and the attached carbonyl would align in an *s-cis* conformation. Another possibility is that materials would separate readily because the carbonyl oxygens of the acyloxazolidinone

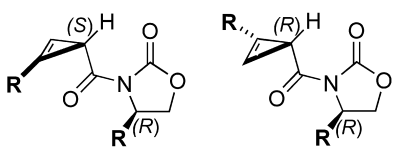
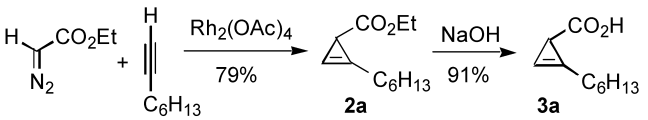


**Figure 2.** Conformations of diastereomeric oxazolidinones.

**Table 1**. Synthesis of cyclopropene carboxylic acids

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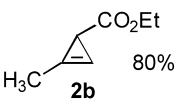
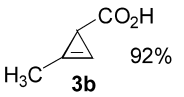
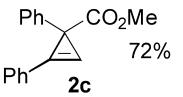
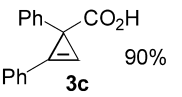
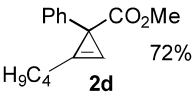
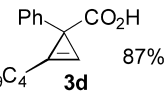
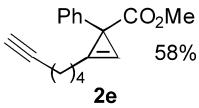
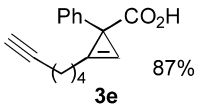
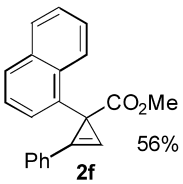
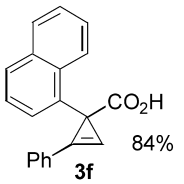
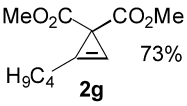
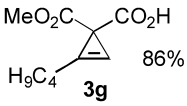
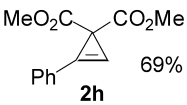
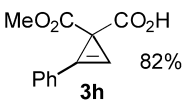
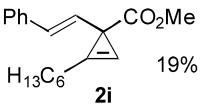
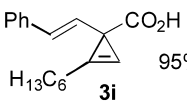
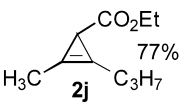
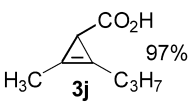
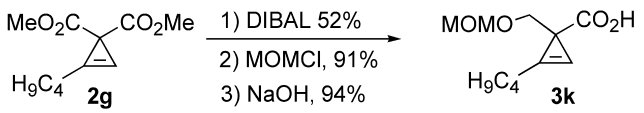
|  **2b** 80% |  **3b** 92% |
|  **2c** 72% |  **3c** 90% |
|  **2d** 72% |  **3d** 87% |
|  **2e** 58% |  **3e** 87% |
|  **2f** 56% |  **3f** 84% |
|  **2g** 73% |  **3g** 86% |
|  **2h** 69% |  **3h** 82% |
|  **2i** 19% |  **3i** 95% |
|  **2j** 77% |  **3j** 97% |

could chelate to the hydrated surface of silica. Again, because the carbonyls would be held in the same plane, the diastereomers would have distinct shapes and should separate readily.

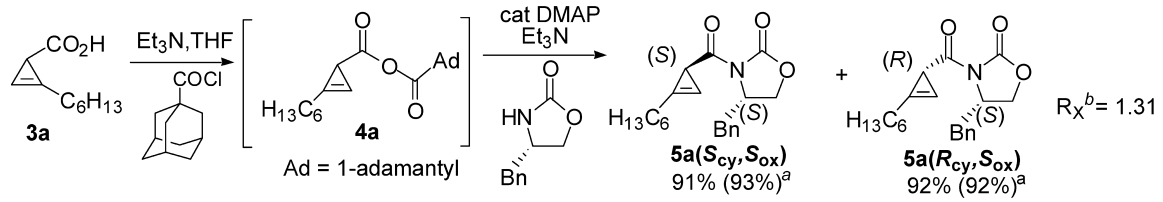


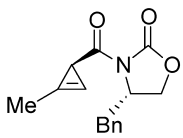

**Scheme 2.**

Cycloprop-2-ene carboxylic acids were synthesized by $Rh_2(OAc)_4$ catalyzed reaction of appropriate diazo compounds with alkynes[20] followed by saponification[33] (Table 1). All but one of the cyclopropenes in Table 1 was easily prepared and purified in good yield and in multigram quantities. The exception was **2i**, which could still be made easily on a 0.5 g scale even though it was produced in only 19% yield. For the cyclopropenes that were derived from malonate, hydrolysis was selective and gave monoacids[34] **3g** and **3h** in 86 and 82% yields, respectively. DIBAL reduction of **2g** was less selective but still gave the monoalcohol in 52% yield (Scheme 2). Of the commercially available oxazolidinones that were surveyed, the best auxilaries in terms of resolving ability and cost effectiveness are those from (*S*)-phenylalaninol, (*S*)-phenylglycinol and (1*R*,2*S*)-1-amino-2-indanol (Table 2). Regarding the use of stoichiometric quantities of these auxilaries, we note that all three oxazolidinones are commercially available and inexpensive if purchased in quantity. (*S*)-Benzyloxazolidinone and (*S*)-phenyloxazolidinone cost ca. 85 cents/gram when purchased in bulk, and (1*R*,2*S*)-1-amino-2-indanol can be purchased for ca. $2.50 per gram.[35] We also note that large scale preparations have been reported for all three oxazolidinones.[36–39]

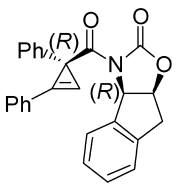
In the optimized procedures for preparing the *N*-acyloxazolidinones, the cycloprop-2-ene carboxylic acid was allowed to react with either pivaloyl chloride or adamantoyl chloride, and the resulting mixed anhydride was combined either with the oxazolidinone and $Et_3N$/LiCl[40]/cat. DMAP[41]

**Table 2**. Resolution of cyclopropene carboxylic acids

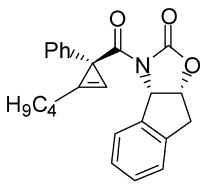


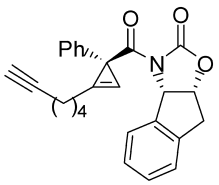

**5b(fast**[c]**)** 88%
**5b(slow**[c]**)** 88%
$R_X$=1.06



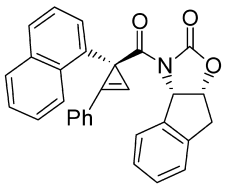

**5c($S_{cy}$,$R_{ox}$)** 91%
**5c($R_{cy}$,$R_{ox}$)** 90%
$R_X$=1.25



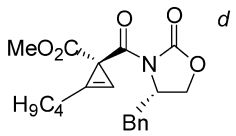

**5d(fast)** 88% (90%)[a]
**5d(slow)** 89% (88%)[a]
$R_X$=1.14



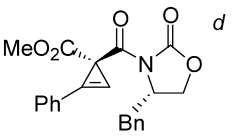

**5e(fast)** 90%
**5e(slow)** 89%
$R_X$=1.15



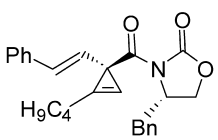

**5f(fast)** 90% (87%)[a]
**5f(slow)** 88% (85%)[a]
$R_X$=1.22



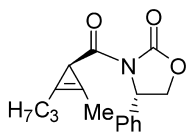

**5g(fast)** 93%
**5g(slow)** 92%
$R_X$=1.50



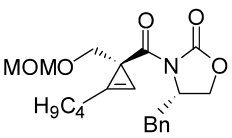

**5h(fast)** 86%
**5h(slow)** 89%
$R_X$=1.58




**5i(fast)** 73%
**5i(slow)** 73%
$R_X$=1.19




**5j(fast)** 93%
**5j(slow)** 92%
$R_X$=1.33



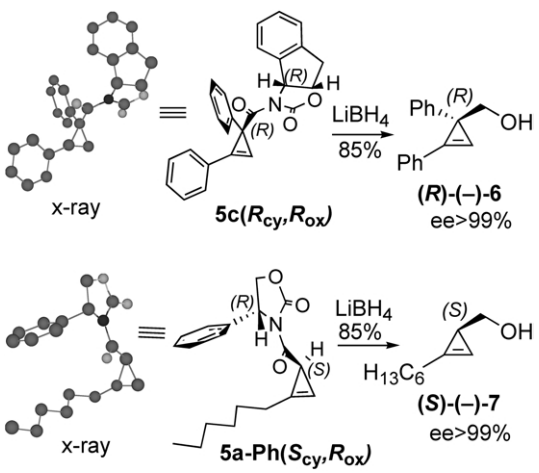

**5k(fast)** 86%
**5k(slow)** 86%
$R_X$=1.50

[a] Yields in parentheses refer to those obtained using (*S*)-phenyloxazolidine as the resolving group.
[b] $R_x$=$R_f$(fast)/$R_f$(slow).
[c] For compounds with unassigned absolute stereochemistry, the designations 'fast' and 'slow' refer to the relative speed with which the diastereomers elute by chromatography.
[d] For these examples, the lithium salt of the oxazolidinone was used instead of $Et_3N$/DMAP.

or directly with the lithium salt of the oxazolidinone.[42,43] 1-Adamantoyl chloride has not been used previously for the synthesis of *N*-acyloxazolidinones. In most cases, we found adamantoyl chloride to be superior to pivaloyl chloride because minor amounts of *N*-pivaloyloxazolidinones were usually formed with the latter reagent. The use of slightly more hindered adamantoyl chloride ameliorates the selectivity issue. The addition of a catalytic amount of DMAP was necessary in order to obtain both diastereomeric products in good yield. For example, although mixed anhydride **4c** (formed in situ) reacts cleanly at rt to give **5c($R_{cy}$,$R_{ox}$)** in the absence of DMAP, **5c($S_{cy}$,$R_{ox}$)** is formed in less than 10% yield. Both diastereomers were formed at equal rates when DMAP was added.[41] Obviously, the former process of distinguishing the enantiomers of **4a–k** by kinetic resolution is of interest—optimization of that process is underway and will be the subject of a future manuscript.

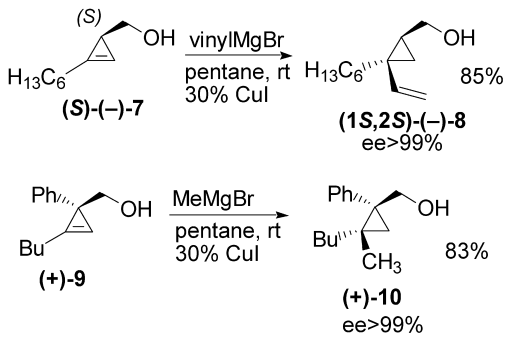
The notable feature about using oxazolidinones to resolve cycloprop-2-ene carboxylic acids is the generality of the method for structurally varied cyclopropenes. This is true even when the alkene substituents are very similar in terms of sterics (example **5j** of Table 2). For the 11 pairs of diastereomers **5a–k**, it was never necessary to test more than two auxilaries in order to find a suitable resolving agent. Furthermore, the syntheses are straightforward and separations were carried out using simple flash chromatography to provide significant amounts of diastereomerically pure material. For example, a single chromatograph (column diameter=1.5″) afforded 1.5 g of **5a($S_{cy}$,$S_{ox}$)** and an equal amount of **5a($R_{cy}$,$S_{ox}$)**. Using this as a calibration point with respect to the amount of material that can be purified quickly, it is useful to quantitatively compare the resolving abilities of oxazolidinone auxilaries toward different cyclopropene carboxylic acids via their $R_x$ values.[44] As shown in Table 2, the separations for most of the *N*-acyloxazolidinones is excellent ($R_f$ difference >15%), and even in the worst case (**5b**), 0.7 g of each pure diastereomer was obtained after two chromatograms (first column diameter=1.5″; second column diameter=1″).

X-ray crystallography revealed the absolute configurations of four of the diastereomers from Table 2. Two of those structures are displayed in Scheme 3; their diastereomers **5c($S_{cy}$,$R_{ox}$)** and **5a-Ph($R_{cy}$,$R_{ox}$)** are displayed in the Supporting Information. The reduction of the *N*-acyloxazolidinones in Scheme 3 gave 3-hydroxymethylcyclopropenes (*R*)-(−)-**6** and (*S*)-(−)-**7** that were enantiomerically pure within the detection limits (ee >99%) of our analysis by chiral HPLC.




**Scheme 3.**

The enantiomerically pure 3-hydroxymethylcyclopropenes that were prepared in this manner were subjected to facially selective Cu-catalyzed additions of Grignard reagents as shown in Scheme 4.[30] In each case, the addition occurred with high facial selectivity and with complete preservation of enantiomeric purity.




**Scheme 4.**

## 3. Conclusions

A method has been described for the resolution of cycloprop-2-ene-carboxylic acids via diastereomeric *N*-acyloxazolidines prepared from enantiomerically pure oxazolidinones. The method is remarkably general, and can be used to resolve significant quantities of cyclopropenes even when the alkene substituents are very similar. The relative configurations of four diastereomerically pure oxazolidines were established by X-ray crystallography. Reduction of the *N*-acyloxazolidinones with $LiBH_4$ give enantiomerically pure derivatives of 3-hydroxymethylcyclopropene that react with either MeMgCl or vinylMgCl and catalytic CuI to give enantiomerically pure products of *syn*-addition.

## 4. Experimental

### 4.1. General

All reactions were carried out in nitrogen atmosphere in glassware that was flame-dried under vacuum and cooled under nitrogen. GC analyses were performed using either an HP5 or HP1 column and a FID detector. Pentane, toluene, THF, ether and $CH_2Cl_2$ were dried with columns packed with activated neutral alumina. Alternatively, solvents were distilled from Na/benzophenone or $CaH_2$ (for $CH_2Cl_2$). Triethylamine was distilled from $CaH_2$. Copper(I)iodide (98%) was purchased from Acros. Ethyl diazoacetate (90% purity), Propyne, 1,7-Octadiyne, phenylacetylene, 1-hexyne, 1-octyne, Pivaloyl chloride and 1-adamantoyl chloride were purchased from Aldrich (we recommend that the purity of 1-adamantoyl chloride be verified by $^{13}C$ NMR

prior to use). (*S*)-phenyloxazolidione, (*S*)-benzyloxazolidinone and (1*S*,2*R*)-1-amino-2-indanol were purchased from Chemicrea Inc., Tokyo, JAPAN. (3a*S*)-*cis*-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one was prepared according to the literature precedent[39] from (1*S*,2*R*)-1-amino-2-indanol, and (3a*R*)-*cis*-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one was purchased from Aldrich. $Rh_2(OAc)_4$ was purchased from Pressure Chemical Co. Chromatography was performed on silica gel (ICN SiliTech 32-62D, 60 Å). For $^1H$ NMR, the abbreviation 'app' stands for apparent (e.g., 'app d'= apparent doublet). For $^{13}C$ NMR, multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons 'down' (dn). Exceptions are methine carbons of alkynes and cyclopropenes, which usually have the same phase as 'normal' methylenes and quaternary carbons.[45] Yields in this paper refer to isolated yields (average of 2 runs) of compounds estimated to be >95% pure by $^1H$, $^{13}C$ NMR. Diastereomer purities were determined using normal phase silica HPLC columns, and enantiomeric excesses were determined by HPLC using CHIRACEL OD, OJ or AD columns, or by GC using Chiraldex G-TA or B-PH columns. All HPLC runs were preformed at a rate of 1.0 mL/min.

The synthesis of **2a** has been reported previously.[30,46]

**4.1.1. Ethyl 2-methylcycloprop-2-ene-1-carboxylate (2b).** A 250 mL 3-neck flask was charged with $Rh_2(OAc)_4$ (256 mg, 0.58 mmol) and 100 mL $CH_2Cl_2$. The flask was sealed with three rubber septa, connected to an oil bubbler, and purged with $N_2$. The solution was then sparged (using a long needle) with propyne gas for 10 min. The addition of propyne was then ceased and the outlet to the oil bubbler was removed and replaced by a balloon filled with propyne. A solution of ethyl diazoacetate (6 mL, 90% purity (Aldrich), 51.3 mmol) in 4 mL $CH_2Cl_2$ was added over the course of 7 h via syringe pump. About once an hour, the balloon was emptied and refilled with propyne. After the addition was complete, the mixture was filtered through a pad of silica gel, concentrated (care should be taken not to distil away the product), and then chromatographed on silica gel (5% ether in pentane). Not all of the solvent from the chromatography was removed because of the volatility of the product. $^1H$ NMR analysis of the colorless solution (9.03 g) indicated that it contained ca. 5.3 g (42.0 mmol, 82%) of **2b**, 2.6 g of ether and 1.2 g of pentane. This solution was used for the preparation of **3b** without further purification. A similar experiment gave **2b** in 77% yield. $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 6.34 (m, $J$=1.3 Hz, 1H), 4.12–4.15 (m, 2H), 2.16–2.17 (d, $J$=1.3 Hz, 3H), 2.11–2.12 (d, $J$=1.6 Hz, 1H), 1.26 (t, $J$=7.2 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 90 MHz, $\delta$): 176.5 (u), 111.6(u), 94.6(u), 60.1(u), 20.0(dn), 14.3(dn), 10.5(dn); IR (neat, $cm^{-1}$): 3135, 2975, 1809, 1729, 1251, 1186; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_7H_{11}O_2$, 127.0759; found, 127.0753.

### 4.2. General procedures for cyclopropenation

A solution of the diazoacetate (10 mmol) in 20 mL $CH_2Cl_2$ was added at rt via syringe pump (0.5–1.0 mL/h) to a stirred mixture of $Rh_2(OAc)_4$ (0.10 mmol) and alkyne (30 mmol). After the syringe pump addition was complete, the mixture was allowed to stir for 1 h and then filtered through celite, concentrated, and chromatographed (eluting with 3–10% ethyl acetate in hexane) to give the corresponding cyclopropene derivative.

**4.2.1. Methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (2c).** The general procudure for cyclopropenation with methyl phenyldiazoacetate[47] (1.76 g, 10 mmol) and phenylacetylene (3.06 g, 30 mmol) gave 1.85 g (7.40 mmol, 73%) of **2c**, a pale yellow oil. A similar experiment that started with 5.0 g methyl phenyldiazoacetate gave **2c** in 71% yield. $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.62–7.59 (m, 2H), 7.41–7.35 (m, 5H), 7.30–7.26 (m, 2H), 7.20 (m, 2H), 3.70 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 175.1(u), 140.9(u), 130.1(dn), 130.0(dn), 128.9(dn), 128.3(dn), 128.1(dn), 125.6(dn), 125.4(u), 117.3(u), 100.4(u), 52.3(dn), 33.6(u); IR (DCM, $cm^{-1}$): 3211, 2916, 1766, 1721, 1506, 1213; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{17}H_{14}O_2$, 250.0630; found, 250.0643.

**4.2.2. Methyl 2-butyl-1-phenylcycloprop-2-ene-1-carboxylate (2d).**[48] The general procedure for cyclopropenation with methyl phenyldiazoacetate[47] (1.76 g, 10 mmol) and 1-hexyne (2.46 g, 30 mmol) gave 1.64 g (7.1 mmol, 71%) of **2d**, a colorless oil. A similar experment that started with 3.0 g of methyl phenyldiazoacetate gave **2d** in 72% yield. $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.25–7.28 (m, 4H), 7.16–7.21 (m, 1H), 6.64 (t, $J$=1.5 Hz, 1H), 3.66 (s, 3H), 2.54 (app dt, $J$=7.4, 1.4 Hz, 2H), 1.58–1.53 (app quintet, $J$=7.4 Hz, 2H), 1.37–1.31 (m, 2H), 0.89–0.85 (t, $J$=7.4 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 176.1(u), 141.8(u), 128.3(dn), 128.1(dn), 126.3(dn), 121.0(u), 97.0(u), 52.0(dn), 33.1(u), 28.9(u), 24.2(u), 22.3(u), 13.8(dn); IR (neat, $cm^{-1}$): 3131, 2959, 1719, 1494, 1222, 1023; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{15}H_{19}O_2$, 231.1385; found, 231.1396.

**4.2.3. Methyl 1-phenyl-2-(hexyn-5-yl)-cycloprop-2-ene-1-carboxylate (2e).** A 100 mL flask was charged with $Rh_2(OAc)_4$ (22 mg, 0.05 mmol), 50 mL $CH_2Cl_2$ and 1,7-octadiyne (2.00 g, 2.50 mL, 18.46 mmol). A solution of methyl phenyldiazoacetate (1.62 g, 9.23 mmol) in 10 mL $CH_2Cl_2$ was added via syringe pump at a rate of 0.7 mL/h at rt. The crude mixture was filtered through a pad of silica, concentrated and then chromatographed (the eluent was 5% ethyl acetate in hexane) to give 1.37 g (5.39 mmol, 58%) of the title compound as a colorless oil. A similar experiment also gave **2e** in 58% yield. $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.31–7.24 (m, 4H), 7.22–7.18 (m, 1H), 6.71 (t, $J$=1.4 Hz, 1H), 3.68 (s, 3H), 2.58 (dt, $J$=7.3, 1.4 Hz, 2H), 2.14–2.18 (app dt, $J$=7.0, 2.7 Hz, 2H), 1.93 (t, $J$=2.7 Hz, 1H), 1.76–1.65 (m, 2H), 1.60–1.51 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 90 MHz, $\delta$): 175.9(u), 141.6(u), 128.2(dn), 128.0(dn), 126.3(dn), 120.6(u), 97.4(u), 84.0(u), 68.6(u), 52.0(dn), 33.0(u), 27.7(u), 25.8(u), 24.0(u), 18.0(u); IR (neat, $cm^{-1}$): 3289, 2947, 1718, 1224, 1021, 701, 647; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{17}H_{19}O_2$, 255.1385; found, 255.1391.

**4.2.4. Methyl 2-phenyl-1-(α-naphthyl)cycloprop-2-ene-1-carboxylate (2f).** The general procudure for cyclopropenation with methyl (α-naphthyl)diazoacetate[49] (1.13 g, 5.0 mmol) and phenylacetylene (1.53 g, 15 mmol) gave 843 mg (2.81 mmol, 56%) of **2f**, a pale yellow oil. A similar experiment with 2.0 g of (α-naphthyl)diazoacetate gave a

55% yield of **2f**. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 8.17 (dd, $J$=7.9, 0.6 Hz, 1H), 7.86 (dd, $J$=7.5, 0.5 Hz, 1H), 7.77–7.74 (m, 3H), 7.56–7.42 (m, 7H), 7.36–7.32 (m, 1H), 3.66 (s, 3H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 176.5(u), 139.3(u), 134.2 (u, 2 carbons), 132.9(u), 130.5(dn), 130.3(dn), 129.5(dn), 129.4(dn), 128.4(dn), 126.6(dn), 126.3(u), 126.2(dn), 126.1(dn), 125.1(dn), 118.9(u), 104.0(u), 53.0(dn), 33.2(u); IR ($CH_2Cl_2$, cm$^{-1}$): 3065, 2951, 1720, 1596, 1506, 1222, 1093; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{21}H_{16}O_2$, 300.1150; found, 300.1130.

**4.2.5. Dimethyl 2-butylcycloprop-2-ene-1,1-dicarboxylate (2g).**[26] The general procudure for cyclopropenation with dimethyl diazomalonate (3.33 g, 21.08 mmol) and a solution of $Rh_2(OAc)_4$ (56 mg, 0.13 mmol) and 1-hexyne (6.93 g, 84.3 mmol) in $CH_2Cl_2$ (20 mL) gave 3.2 g (15.10 mmol, 72%) of the title compound as pale yellow oil. The spectral data were in accord those reported previously.[26] $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.35 (t, $J$=1.4 Hz, 1H), 3.72 (s, 6H), 2.55 (dt, $J$=1.4, 7.3 Hz, 2H), 1.58 (m, 2H), 1.39 (m, 2H), 0.92 (t, $J$=7.3 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 172.3 (u), 114.9 (u), 93.8 (u), 52.6 (dn), 32.8 (u), 28.8 (u), 24.1 (u), 22.6 (u), 14.1 (dn).

**4.2.6. Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (2h).** The general procudure for cyclopropenation with dimethyl diazomalonate(6.64 g, 40.0 mmol) and a solution of $Rh_2(OAc)_4$ (106 mg, 0.24 mmol) and phenylacetylene (21.4 g, 210.0 mmol) in $CH_2Cl_2$ (80 mL) gave 6.5 g (28.0 mmol, 67%) of the title compound as pale yellow solid, mp 70.5–71.5 (lit[50] 67–70°). The spectral data were in accord with those reported previously.[50] $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.64 (m, 2H), 7.45 (m, 3H), 6.90 (s, 1H), 3.72 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 171.2, 130.6, 130.4, 128.9, 123.9, 112.2, 95.2, 52.4, 32.8.

**4.2.7. Methyl 2-hexyl-1-*trans*-styrylcycloprop-2-ene-1-carboxylate (2i).** The general procedure for cyclopropenation with methyl (*E*)-2-diazo-4-phenyl butenoate[51] (2.12 g, 10.5 mmol), 1-octyne (4.63 g, 42 mmol) and $Rh_2(OAc)_4$ (28 mg, 0.063 mmol) gave 0.54 g (20%) of the title compound as pale yellow oil. A similar experiment that started with 240 mg of methyl (*E*)-2-diazo-4-phenyl butenoate gave **2i** in 18% yield. $^1$H NMR ($CDCl_3$, 360 MHz, $\delta$): 7.40–7.17 (m, 6H), 6.33 (t, $J$=1.2 Hz, 1H), 6.05 (d, $J$=16.2 Hz, 1H), 3.73 (s, 3H), 2.52 (app dt, $J$=7.2, 1.1 Hz, 2H), 1.61 (m, 2H), 1.30–1.60 (m, 6H), 0.90 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 176.1 (u), 137.7 (u), 131.8 (dn), 128.4 (dn), 127.9 (dn), 127.1 (dn), 126.8 (dn), 116.9 (u), 93.3 (u), 52.1(dn), 31.6 (u), 30.6 (u), 29.0 (u), 27.1 (u), 23.7 (u), 22.7 (u), 14.2 (dn); IR ($CCl_4$, cm$^{-1}$): 3025, 2952, 2931, 2360, 2336, 1722, 1244, 1226, 1060, 964, 765; HRMS-CI ($NH_3$) *m/z*: [M+H] calcd for $C_{19}H_{24}O_2$, 285.1854; found, 285.1849.

**4.2.8. Ethyl 2-propyl-3-methyl-cycloprop-2-ene-1-carboxylate (2j).** The general procedure for cyclopropenation with ethyl diazoacetate (2.53 g, 2.3 mL, 20 mmol) in 2.7 mL $CH_2Cl_2$ and a solution of 2-hexyne (2.46 g, 3.4 mL, 30 mmol) and $Rh_2(OAc)_4$ (88 mg, 0.2 mmol) in 150 mL $CH_2Cl_2$ gave 2.60 g (15.5 mmol, 78%) of the title compound as a colorless oil. A similar experiment gave **2j** in 76% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 4.10–4.15 (q, $J$=7.1 Hz, 2H), 2.41–2.37 (m, 2H), 2.06 (t, $J$=1.5 Hz, 3H), 2.03 (s, 1H), 1.62–1.56 (m, 2H), 1.26 (t, $J$=7.1 Hz, 3H), 0.95–0.99 (t, $J$=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.4(u), 106.6(u), 102.2(u), 60.2(u), 26.8(u), 23.1(dn), 20.7(u), 14.8(dn), 14.2(dn), 10.2(dn); IR (neat, cm$^{-1}$): 2961, 2935, 1721, 1457, 1367, 1335, 1241, 1179, 1179, 1044; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{10}H_{17}O_2$, 169.1229; found, 169.1236.

### 4.3. General procedures for ester saponification

Aqueous KOH (30 mL of an 8.5% solution) was added to a 100 mL round bottomed flask that contained the cycloprop-2-ene-1-carboxylate (17.8 mmol), and 30 mL MeOH. The mixture was stirred overnight at the indicated temperature, concentrated to remove the bulk of the MeOH, acidified to pH 1–3 with conc. HCl, extracted (4×30 mL $CH_2Cl_2$), dried ($Na_2SO_4$) filtered, and concentrated. The residue was chromatographed on silica gel (20–40% ethyl acetate in hexane) to provide the cycloprop-2-ene-1-carboxylic acid.

**4.3.1. 2-Hexylcycloprop-2-ene-1-carboxylic acid (3a).** The general procedure for ester saponification conducted at rt with **2a** (3.2 g, 16.4 mmol) gave 2.55 g (15.1 mmol, 92%) of **3a** as a clear oil. A similar experiment with 1.0 g of **2a** gave **3a** in 90% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.31 (m, 1H), 2.48–2.52 (m, 2H), 2.12 (d, $J$=1.5 Hz, 1H), 1.61–1.55 (m, 2H), 1.38–1.25 (m, 6H), 0.88 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 183.7(u), 115.4(u), 93.6(u), 31.6(u), 28.9(u), 26.7(u), 25.1(u), 22.7(u), 19.7(dn), 14.2(dn); IR (neat, cm$^{-1}$): 3510, 2973, 1698, 1425, 1273, 1125; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{10}H_{17}O_2$, 169.1229; found, 169.1230.

**4.3.2. 2-Methyl-cycloprop-2-ene-1-carboxylic acid (3b).** The general procedure for ester saponification with **2b** [1.50 g (2.55 g of a ~59% mixture in $Et_2O$/pentane), 11.9 mmol] was conducted at 0 °C during the addition of KOH and subsequently at rt. The yield was 1.08 g (110 mmol, 92%) of **3b**, a colorless oil. A similar experiment gave **3b** in 91% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.34 (m, 1H), 2.17 (d, $J$=1.3 Hz, 3H), 2.11 (d, $J$=1.5 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 183.1(u), 111.2(u), 94.2(u), 19.8(dn), 10.4(dn); IR (neat, cm$^{-1}$): 2977, 1813, 1700, 1423, 1283, 1248, 1121, 711; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_5H_7O_2$, 99.0446; found, 99.0451.

**4.3.3. 1,2-Diphenylcycloprop-2-ene-2-carboxylic acid (3c).** The general procedure for ester saponification conducted at 35 °C with **2c** (3.0 g, 12.0 mmol) gave 2.58 g (10.9 mmol, 91%) of **3c** as a white solid, mp 136–138 °C. A similar experiment with 730 mg of **2c** gave **3c** in 88% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.63–7.59 (m, 2H), 7.43–7.36 (m, 5H), 7.28–7.24 (m, 2H), 7.19–7.15 (m, 2H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 180.6(u), 140.4(u), 130.6(dn), 130.4(dn), 129.3(dn),128.8(dn), 128.5(dn), 127.1(dn), 125.4(u), 117.3(u), 100.2(u), 33.5(u); IR (KBr, cm$^{-1}$): 3589, 3033, 2868, 1787, 1664, 1496, 1409, 1222, 1099; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{16}H_{12}O_2$, 236.0837; found, 236.0833.

**4.3.4. 2-Butyl-1-phenylcycloprop-2-ene-1-carboxylic acid (3d).** The general procedure for ester saponification

conducted at rt with **2d** (3.0 g, 13.0 mmol) gave 2.48 g (11.5 mmol, 88%) of **3d** as a clear oil. A similar experiment with 520 mg of **2d** gave **3d** in 85% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.30–7.19 (m, 5H), 6.64 (app t, $J$=1.6 Hz, 1H), 2.56–2.52 (m, 2H), 1.59–1.56 (m, 2H), 1.32–1.30 (m, 2H), 0.86 (t, $J$=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 181.9(u), 140.8(u), 128.8(dn), 128.3(dn), 126.4(dn), 120.7(u), 96.3(u), 29.2(u), 28.7(u), 24.2(u), 22.2(u), 13.7(dn); IR (neat, cm$^{-1}$): 3513, 2953, 1696, 1605, 1506, 1245, 1046; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{14}H_{17}O_2$, 217.1229; found, 217.1229.

**4.3.5. 1-Phenyl-2-(5-hexynyl)-cycloprop-2-ene-1-carboxylic acid (3e).** The general procedure for ester saponification with **2e** (1.29 g, 5.10 mmol) was conducted at 0 °C during the addition of KOH and subsequently at rt. The yield was 1.06 g (4.42 mmol, 87%) of **3e**, a colorless oil. A similar experiment also gave **3e** in 87% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.30–7.27 (m, 4H), 7.23–7.18 (m, 1H), 6.70 (t, $J$=1.5 Hz, 1H), 2.59 (app dt, $J$=7.3 Hz, 1.5 Hz, 2H), 2.16 (app dt, $J$=6.9 Hz, 2.6 Hz, 2H), 1.93 (t, $J$=2.7 Hz, 1H), 1.77–1.70 (m, 2H), 1.61–1.50 (m, 2H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 182.0(u), 140.7(u), 128.4(dn), 128.0(dn), 126.5(dn), 120.2(u), 96.7(u), 83.9(u), 68.6(u), 32.7(u), 27.7(u), 25.7(u), 24.0(u), 18.0(u); IR (neat, cm$^{-1}$): 3312, 2944, 1688, 1254, 804, 744, 696, 633; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{16}H_{17}O_2$, 241.1229; found, 241.1226.

**4.3.6. 2-Phenyl-1-(α-naphthyl)cycloprop-2-ene-1-carboxylic acid (3f).** The general procedure for ester saponification conducted at 50 °C with **2f** (3.00 g, 10.0 mmol) gave 2.38 g (8.32 mmol, 83%) of **3f** as a pale yellow solid, mp 126–129 °C. A similar experiment with 1.20 g of **2f** gave **3f** in 85% yield. $^1$H NMR ($CDCl_3$, 360 MHz, $\delta$): 8.22 (app d, $J$=8.3 Hz, 1H), 7.90–7.86 (app dd, $J$=8.3, 1.1 Hz, 1H), 7.78–7.76 (m, 3H), 7.58–7.45 (m, 7H), 7.34 (dd, $J$=8.3, 7.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 181.6(u), 138.0(u), 133.8(u), 132.1(u), 130.1(dn), 129.9(dn), 129.0(dn), 128.8(dn), 128.1(dn),126.1(dn), 125.9(dn), 125.8(u), 125.7(dn), 125.5(dn), 124.6(dn), 118.1(u), 102.9(u), 32.3(u); IR (KBr, cm$^{-1}$): 3556, 3036, 2928, 1703, 1600, 1503, 1247, 1019; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{20}H_{14}O_2$, 286.0994; found, 286.0984.

**4.3.7. 2-Butylcycloprop-2-ene-1,1-dioic acid monomethyl ester (3g).** A solution of **2g** (5.04 g, 23.8 mmol) in 50 mL methanol was added dropwise to a solution of KOH (1.33 g, 23.8 mmol) in 15 mL water that was cooled in an ice bath. The reaction mixture was allowed to stir rt for 2 d, at which point it was concentrated to remove MeOH and diluted with 20 mL water. Three extractions with ether (3×10 mL) removed unchanged **2g** (0.82 g, 16%). The remaining aqueous layer was acidified with 10% HCl (aq) and extracted with ether (3×20 mL). The organics were combined, sequentially washed with water and brine, dried ($Na_2SO_4$), filtered and concentrated to give **3g** (3.90 g, 83%) as a pale yellow oil. A similar experiment that started with 1.27 g of **2g** gave **3g** in 88% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.17 (app t, $J$=1.5 Hz, 1H), 3.76 (s, 3H), 2.52 (m, 2H), 1.58 (m, 2H), 1.40 (m, 2H), 0.92 (t, $J$=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 178.1 (u), 173.2 (u), 110.6(u), 89.9(u), 53.6 (dn), 31.2 (u), 28.7 (u), 23.7 (u), 22.5 (u), 14.0 (dn); IR (neat, cm$^{-1}$): 3147, 2955, 2874, 2360, 2095, 1749, 1668, 1435, 1315, 1065, 850; HRMS-CI *m/z* [M+H] calcd for $C_{10}H_{15}O_4$, 199.0970; found, 199.0963.

**4.3.8. 2-Phenylcycloprop-2-ene-1,1-dioic acid monomethyl ester (3h).** The procedure was identical to that used to prepare **3g**, except that **2h** (4.00 g, 17.25 mmol), KOH (0.97 g, 17.25 mmol), MeOH (40 mL), water (10 mL) were used. The protocol gave 3.14 g (83%) of the title compound as a pale yellow solid, mp 88–89 °C. Additionally, unchanged **2h** (0.40 g, 10%) was recovered. A similar experiment that started with 9.5 g of **2h** gave **3h** in 85% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.52–7.46 (m, 5H), 6.75 (s, 1H), 3.75 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.2 (u), 172.5 (u), 131.5 (dn), 130.8 (dn), 129.5 (dn), 122.9 (u), 108.6 (u), 92.4 (u), 53.9 (dn), 31.3 (u); IR (neat, cm$^{-1}$): 3164, 3054, 2987, 2958, 2685, 2361, 2055, 1756, 1675, 1441, 1420, 1317, 1264, 1071, 705; Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.76; H, 4.60.

**4.3.9. 2-Hexyl-1-*trans*-styrylcycloprop-2-ene-1-carboxylic acid (3i).** A mixture of **2i** (0.42 g, 1.48 mmol), MeOH (4 mL) and 2 N KOH (aq) (6 mL) was stirred at 50 °C for 3 h. The mixture was extracted with ether (3×5 mL), and the aqueous layer was acidified with 10% HCl (aq) and extracted with ether (3×10 mL). The organics were combined, washed with water and brine, dried ($Na_2SO_4$), filtered and concentrated to give 370 mg (93%) of **3i** as a pale yellow oil. A similar experiment that started with 0.58 g of **2i** gave **3i** in 96% yield. $^1$H NMR ($CDCl_3$, 400 Hz, $\delta$): 7.37–7.18 (m, 6H), 6.31 (app t, $J$=1.4 Hz, 1H), 6.03 (d, $J$=16.1 Hz, 1H), 2.52 (app dt, $J$=7.3, 1.4 Hz, 2H), 1.61 (m, 2H), 1.40–1.26 (m, 6H), 0.87 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 182.7 (u), 137.8 (u), 131.1 (dn), 128.9 (dn), 128.3 (dn), 127.4 (dn), 126.5 (dn), 116.6 (u), 92.8 (u), 31.9 (u), 30.6 (u), 29.3 (u), 27.3 (u), 23.9 (u), 23.0 (u), 14.5 (dn); IR ($CCl_4$, cm$^{-1}$): 3026, 2957, 2931, 2860, 2360, 2335, 1686, 1419, 1289, 1264, 964, 803, 746; HRMS-CI, *m/z*: [M] calcd for $C_{18}H_{22}O_2$, 270.1620; found, 270.1614.

**4.3.10. 2-Propyl-3-methyl-cycloprop-2-ene-1-carboxylic acid (3j).** The general procedure for ester saponification with **2j** (0.888 g, 5.28 mmol) was conducted at 0 °C during the addition of KOH and subsequently at rt. The procedure gave 0.711 g (5.08 mmol, 96%) of **3j** as a colorless oil. A similar experiment gave **3j** in 98% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 2.41–2.37 (m, 2H), 2.06 (app t, $J$=1.5 Hz, 3H), 2.02 (s, 1H), 1.64–1.55 (m, 2H), 0.96 (t, $J$=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 184.4(u), 106.2(u), 101.8(u), 26.8(u), 22.9(dn), 20.7(u), 14.2(dn), 10.1(dn); IR (neat, cm$^{-1}$): 2962, 2628, 1691, 1420, 1286, 1236, 1123; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_8H_{13}O_2$, 141.0916; found, 141.0920.

**4.3.11. Methyl 2-butyl-1-hydroxymethylcycloprop-2-ene-1-carboxylate.** A 250 mL round bottomed flask containing a solution of **2g** (3.27 g, 15.4 mmol) in 40 mL THF was cooled in an ice bath, and a solution of DIBAL (30.3 mmol; 60.6 mL of a 0.5 M solution in pentane) was added dropwise via an additional funnel. The mixture was stirred for 1 h and then quenched with water, acidified with

10% HCl (aq) and extracted with ether (3×20 mL). The organic phase was washed with water and brine, dried over $Na_2SO_4$, filtered, and concentrated. Chromatography (10% ethyl acetate in hexanes) gave 1.48 g (8.04 mmol, 56%) of the title compound, a colorless oil. Additionally, 0.84 g of **2g** (26%) was recovered. A similar experiment with 5.50 g of **2g** gave the title compound in 57% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.43 (t, $J$=1.2 Hz, 1H), 3.74 (m, 2H), 3.63 (s, 3H), 2.52 (bs, 1H), 2.48 (app dt, $J$=1.2, 7.1 Hz, 2H), 1.53 (m, 2H), 1.36 (m, 2H), 0.88 (t, $J$=7.4 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 176.8 (u), 119.9 (u), 97.3 (u), 67.3 (u), 51.8 (dn), 31.1 (u), 29.0 (u), 24.6 (u), 22.3 (u), 13.8 (dn); IR ($CH_2Cl_2$, cm$^{-1}$): 2958, 2934, 2873, 1703, 1458, 1436, 1387, 1288, 1190, 1162, 1087, 1020, 975, 832, 791; HRMS-CI, *m/z*: [M] calcd for $C_{10}H_{16}O_3$, 184.1099; found, 184.1096.

**4.3.12. Methyl 2-butyl-1-(methoxymethoxymethyl)cycloprop-2-ene-1-carboxylate.** To a dry 25 mL round bottomed flask was added methyl 2-butyl-1-hydroxymethylcycloprop-2-ene-1-carboxylate (1.48 g, 8.04 mmol), *N*,*N*-diisopropylethylamine (1.25 g, 9.65 mmol), and $CH_2Cl_2$ (15 mL). The flask was swept with nitrogen and then cooled in an ice bath. Methyl chloromethylether (970 mg, 12.06 mmol) was added via syringe, and the ice bath was removed. The mixture was allowed to stir at rt for 5 h. Concentration and chromatography (20% ethyl acetate in hexanes) gave 1.64 g (91%) of the title compound, a pale yellow oil. A similar experiment that started with 0.41 g of the starting alcohol gave the title compound in 90% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.43 (app t, $J$=1.3 Hz), 4.60 (s, 2H), 3.84 (d, $J$=10.3 Hz, 1H), 3.67 (d, $J$=10.3 Hz, 1H), 3.63 (s, 3H), 3.33 (s, 3H), 2.48 (app dt, $J$=7.4, 1.5 Hz), 1.54 (m, 2H), 1.36 (m, 2H), 0.89 (t, $J$=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 176.3 (u), 119.5 (u), 97.5 (u), 96.7 (u), 71.9 (u), 55.4 (dn), 52.2 (dn), 29.5 (u), 29.3 (u), 24.9 (u), 22.6 (u), 14.1 (dn); IR ($CH_2Cl_2$, cm$^{-1}$): 2952, 2934, 2874, 1715, 1466, 1288, 1243, 1149, 1104, 1046, 799; HRMS-CI *m/z*: [M−OMe] calcd for $C_{12}H_{20}O_4$, calcd, 197.1178; found, 197.1169.

**4.3.13. 1-Methoxymethoxymethyl-2-butylcycloprop-2-ene-1-carboxylic acid (3k).** A mixture of methyl 2-butyl-1-(methoxymethoxymethyl)cycloprop-2-ene-1-carboxylate (1.64 g, 7.20 mmol), MeOH (8 mL) and 2 N KOH (aq) (10 mL) was stirred at 50 °C under nitrogen for 3 h. The mixture was extracted with ether (3×5 mL). The aqueous phase was acidified with 10% HCl (aq) and extracted with ether (3×10 mL). The combined organics were washed with water and brine, dried over $Na_2SO_4$, filtered, and concentrated to give 1.44 g (94%) of the title compound as a pale yellow oil. A similar experiment that started with 420 mg of the ester gave the title compound in 96% yield. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 6.45 (app t, $J$=1.3 Hz, 1H), 4.63 (s, 1H), 3.85 (d, $J$=10.4 Hz, 1H), 3.69 (d, $J$=10.4 Hz, 1H), 3.35 (s, 3H), 2.52 (app dt, $J$=1.6, 7.3 Hz, 2H), 1.57 (m, 2H), 1.40 (m, 2H), 0.92 (t, $J$=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 182.6 (u), 119.0(u), 97.0 (u), 96.7(u), 71.5 (u), 55.5(dn), 29.3 (u), 29.2(u), 24.8(u), 22.6(u), 14.1(dn); IR (neat, cm$^{-1}$): 3135, 2934, 2875, 2572, 2059, 1803, 1585, 1415, 1295, 1150, 1105, 917; Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.45; H, 8.58.

## 4.4. General procedures for resolution

A stirred solution of the cycloprop-2-ene-1-carboxylic acid (1 equiv.) in THF (50 mL/mmol acid) was cooled to −30 °C. Triethylamine (3.5 equiv.) and adamantoyl chloride (1.05 equiv.) were added sequentially and stirring was continued at −30 °C for 1 h. Lithium chloride (5.0 equiv.), the appropriate oxazolidinone (1.1 equiv.) and DMAP (0.1 equiv.) were then added and the cold bath was removed. The mixture was allowed to gradually rise to rt while stirring continued overnight. The solvents were removed and the residue was partitioned between ether and water. The aqueous layer was extracted twice with ether, and the combined organics were dried ($Na_2SO_4$), filtered, and concentrated. Chromatography separated the diastereomeric products.

**4.4.1. (4*S*)-4-Benzyl-3-[(1*R*)-2-hexylcycloprop-2-en-1-oyl]-oxazolidinone [5a($R_{cy}$,$S_{ox}$)] and (4*S*)-4-benzyl-3-[(1*S*)-2-hexylcycloprop-2-en-1-oyl]oxazolidinone [*5a*($S_{cy}$,$S_{ox}$)].** The general procedure for resolution using (*S*)-benzyl-oxazolidinone (390 mg, 2.2 mmol) and **3a** (336 mg 2.0 mmol) gave 298 mg (0.91 mmol, 91%) of **5a($S_{cy}$,$S_{ox}$)** and 301 mg (0.92 mmol, 92%) of **5a($R_{cy}$,$S_{ox}$)** after chromatography with a gradient (5–15%) of ethyl acetate in hexane. **5a($S_{cy}$,$S_{ox}$)** eluted first. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 27%. A similar experiment with 890 mg of **3a** gave **5a($S_{cy}$,$S_{ox}$)** in 92% yield and **5a($R_{cy}$,$S_{ox}$)** in 90% yield.

The absolute configuration of **5a($S_{cy}$,$S_{ox}$)** was determined by reduction with $LiBH_4$, which gave (*S*)-(−)-**7** in 85% yield. The same alcohol was obtained in 81% yield from $LiBH_4$ reduction of crystallographically characterized **5a-Ph($S_{cy}$,$R_{ox}$)**.

Similarly, the absolute configuration of **5a($R_{cy}$,$S_{ox}$)** was determined by reduction with $LiBH_4$, which gave (*R*)-(+)-**7** in 75% yield. The same alcohol was obtained in 83% yield from $LiBH_4$ reduction of crystallographically characterized **5a-Ph($R_{cy}$,$R_{ox}$)**.

**5a($S_{cy}$,$S_{ox}$)**: A semisolid. $[\alpha]_D^{23}$=+105° (*c* 1.00, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.18–7.32 (m, 5H), 6.28 (m, 1H), 4.67–4.62 (m, 1H), 4.22–4.13 (m, 2H), 3.43 (d, $J$=1.1 Hz, 1H), 3.29 (dd, $J$=10.1, 3.2 Hz, 1H), 2.73 (dd, $J$=9.8, 3.5 Hz, 1H), 2.52–2.47 (m, 2H), 1.62–1.55 (m, 2H), 1.38–1.23 (m, 6H), 0.88–0.85 (t, $J$=6.7 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.5(u), 154.5(u), 136.0(u), 129.9(dn), 129.3(dn), 127.6(dn), 114.6(u), 92.6(u), 66.7 (u), 56.1(dn), 38.5 (u), 31.9 (u), 29.2 (u), 27.2(u), 25.3 (u), 22.9 (u), 20.4(dn), 14.5(dn); IR ($CCl_4$, cm$^{-1}$): 3031, 2958, 1777, 1688, 1363, 1209; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{20}H_{25}NO_3$, 327.1834; found, 327.1826.

**5a($R_{cy}$,$S_{ox}$)**: A semisolid. $[\alpha]_D^{23}$=+46° (*c* 1.03, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.33–7.18 (m, 5H), 6.26 (m, 1H), 4.67–4.62 (m, 1H), 4.22–4.13 (m, 2H), 3.43 (d, $J$=1.4 Hz, 1H), 3.27 (dd, $J$=10.0, 3.3 Hz, 1H), 2.77 (dd, $J$=9.6, 3.7 Hz, 1H), 2.55–2.51(m, 2H), 1.62–1.57(m, 2H), 1.38–1.26(m, 6H), 0.86 (t, $J$=5.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.0(u), 154.0(u), 135.5(u), 129.4(dn), 128.9(dn), 127.2(dn), 113.9(u), 92.4(u), 66.3(u), 55.7(dn),

38.0(u), 31.5(u), 28.8(u), 26.8(u), 24.9(u), 22.5(u), 20.0(dn), 14.0(dn); IR ($CCl_4$, $cm^{-1}$): 3051, 2957, 1784, 1590, 1361, 1205; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{20}H_{25}NO_3$, 327.1834; found, 327.1826.

**4.4.2. (4*R*)-3-[(1*S*)-2-Hexylcycloprop-2-en-1-oyl]-4-phenyloxazolidinone [5a-Ph($S_{cy}$,$R_{ox}$)] and (4*R*)-3-[(1*R*)-2-hexylcycloprop-2-en-1-oyl]-4-phenyloxazolidinone [5a-Ph($R_{cy}$,$R_{ox}$)].** The general procedure for resolution using (*R*)-phenyloxazolidinone (1.44 g, 8.8 mmol) and **3a** (1.35 g, 8.0 mmol) gave 1.165 g (3.72 mmol, 93%) of **5a-Ph($R_{cy}$, $R_{ox}$)** and 1.153 g (3.68 mmol, 92%) of **5a-Ph($S_{cy}$,$R_{ox}$)** after chromatography with a gradient of 5–15% ethyl acetate in hexane. **5a-Ph($R_{cy}$,$R_{ox}$)** eluted first. Relative configurations for both diastereomers were determined by X-ray crystallography of crystals that were grown from ethyl acetate/hexane. A similar experiment with 356 mg of **3a** gave **5a-Ph($R_{cy}$,$R_{ox}$)** in 92% yield and **5a-Ph($S_{cy}$,$R_{ox}$)** in 92% yield.

**5a-Ph($R_{cy}$,$R_{ox}$)**: White needles, mp 50.5–52.5 °C. $[\alpha]_D^{23}=-168°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.34–7.28 (m, 5H), 6.13 (m, 1H), 5.42 (dd, *J*=4.7, 4.0 Hz, 1H), 4.68 (app t, *J*=8.7 Hz, 1H), 4.27 (dd, *J*=4.8, 4.1 Hz, 1H), 3.41 (d, *J*=1.5 Hz, 1H), 2.45–2.43 (m, 2H), 1.55–1.53 (m, 2H), 1.32–1.24 (m, 6H), 0.86 (t, *J*=6.9 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 176.9(u), 154.7(u), 139.7(u), 129.5(dn), 129.0(dn), 126.5(dn), 114.4(u), 92.5(u), 70.5(u), 58.4(dn), 31.9(u), 29.2(u), 27.1(u), 25.3(u), 22.9(u), 20.6(dn), 14.5(dn); IR ($CCl_4$, $cm^{-1}$): 3056, 2931, 1766, 1695, 1363, 1241, 1204, 1071; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{19}H_{24}NO_3$, 314.1756; found, 314.1762.

**5a-Ph($S_{cy}$,$R_{ox}$)**: White needles, mp 83–86 °C. $[\alpha]_D^{23}=-73°$ (*c* 1.05, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.34–7.27 (m, 5H), 6.19 (m, 1H), 5.42 (dd, *J*=4.8, 3.8 Hz, 1H), 4.68 (app t, *J*=8.8 Hz, 1H), 4.26 (dd, *J*=5.0, 3.8 Hz, 1H), 3.43 (d, *J*=1.6 Hz, 1H), 2.39–2.34 (m, 2H), 1.39–1.37 (m, 2H), 1.24–1.16(m, 6H), 0.84 (t, *J*=6.8 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 176.8(u), 154.7(u), 139.8(u), 129.5(dn), 128.9(dn), 126.3(dn), 114.2(u), 92.5(u), 70.5(u), 58.4(dn), 31.8(u), 29.1(u), 27.0(u), 25.2(u), 22.9(u), 20.4(dn), 14.5(dn); IR ($CCl_4$, $cm^{-1}$): 3021, 2926, 1775, 1692, 1382, 1195; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{19}H_{23}NO_3$, 313.1834; found, 313.1826.

**4.4.3. Diastereomers of (4*S*)-4-benzyl-3-(2-methylcycloprop-2-en-1-oyl)oxazolidinone: 5b(fast) and 5b(slow).** The general procedure for resolution using (*S*)-benzyloxazolidinone (1.38 g, 7.80 mmol) and **3b** (0.637 g, 6.5 mmol) gave 0.732 g (2.85 mmol, 88%) of **5b(fast)** (the diastereomer that elutes more quickly) and 0.740 g (2.88 mmol, 89%) of **5b(slow)** (the diastereomer that elutes more slowly). The chromatography eluent was 1:1:1:8 MTBE:$CH_2Cl_2$:toluene:hexane. A second chromatograph of the 'mixed' fractions was required. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 6%. A similar experiment gave **5b(fast)** in 89% yield and **5b(slow)** in 86% yield.

**5b(fast)**: White solid, mp=96–98.5 °C. $[\alpha]_D^{23}=+201°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.31–7.19 (m, 5H), 6.30 (m, 1H), 4.65–4.62 (m, 1H), 4.20–4.14 (m, 2H), 3.44 (d, *J*=1.4 Hz, 1H), 3.29 (dd, *J*=10.1, 3.2 Hz, 1H), 2.77–2.71 (m, 1H), 2.18 (d, *J*=1.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 177.3(u), 154.5(u), 136.0(u), 129.9(dn), 129.3(dn), 127.7(dn), 110.5(u), 93.4(u), 66.8(u), 56.1(dn), 38.5(u), 20.7(dn), 10.8(dn); IR (KBr, $cm^{-1}$): 3140, 2921, 1762, 1687, 1491, 1357, 1214, 1103, 769, 714; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{15}H_{16}NO_3$, 258.1130; found, 258.1118.

**5b(slow)**: White solid, mp=73–75 °C. $[\alpha]_D=+112°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.31–7.18(m, 5H), 6.28 (m, 1H), 4.65–4.64 (m, 1H), 4.20–4.14 (m, 2H), 3.43 (d, *J*=1.6 Hz, 1H), 3.27 (dd, *J*=10.0, 3.3 Hz, 1H), 2.81–2.75 (m, 1H), 2.19 (d, *J*=1.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 177.3(u), 154.5(u), 136.0(u), 129.9(dn), 129.3(dn), 127.7(dn), 110.2(u), 93.8(u), 66.8(u), 56.1(dn), 38.5(u), 20.7(dn), 10.9(dn); IR (KBr, $cm^{-1}$): 3135, 2975, 1772, 1679, 1375, 1189, 736, 701; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{15}H_{16}NO_3$, 258.1130; found, 258.1143.

**4.4.4. Preparation of *5c($R_{cy}$,$R_{ox}$)* and *5c($S_{cy}$,$R_{ox}$)*.** The general procedure for resolution using (3a*R*)-*cis*-tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (385 mg, 2.20 mmol) and **3c** (472 mg, 2.0 mmol) gave two diastereomers after chromatography with a gradient of 10–20% ethyl acetate in hexane. **5c($S_{cy}$,$R_{ox}$)** (353 mg, 0.90 mmol, 90%) eluted first, followed by **5c($R_{cy}$,$R_{ox}$)** (358 mg, 0.91 mmol, 91%). Relative configurations for both diastereomers were determined by X-ray crystallography of crystals that were grown from acetone/hexane. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 22%. A similar experiment that started with 95 mg of **3c** gave **5c($S_{cy}$,$R_{ox}$)** in 90% yield and **5c($R_{cy}$,$R_{ox}$)** in 93% yield.

**5c($S_{cy}$,$R_{ox}$)**: White crystals, mp 73–75 °C. $[\alpha]_D^{23}=-378°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.78–7.75 (m, 2H), 7.65–7.63 (m, 1H), 7.43–7.30 (m, 4H), 7.27–7.17(m, 8H), 5.99 (d, *J*=6.8 Hz, 1H), 5.26–5.23 (m, 1H), 3.35–3.30 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 174.5(u), 151.9(u), 141.5(u), 140.0(u), 139.5(u), 130.6(dn), 130.3(dn), 130.2(dn), 129.5(dn), 129.2(dn), 128.6(dn), 128.5(dn), 127.8(dn), 126.8(dn), 126.5(u), 125.6(dn), 121.8(u), 101.5(u), 78.5(dn), 63.8(dn), 38.4(u), 37.3(u); IR (KBr, $cm^{-1}$): 3057, 2921, 1782, 1768, 1595, 1192; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{26}H_{19}NO_3$, 393.1365; found, 393.1352.

**5c($R_{cy}$,$R_{ox}$)**: White crystals, mp 96–98 °C. $[\alpha]_D^{23}=+44°$ (*c* 1.03, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.89–7.86 (m, 1H), 7.80–7.77(m, 2H), 7.43–7.34 (m, 4H), 7.29–7.13 (m, 8H), 5.97 (d, *J*=7.0 Hz, 1H), 5.29–5.26 (m, 1H), 3.37–3.35 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 174.2(u), 152.0(u), 141.4(u), 140.1(u), 139.5(u), 130.6(dn), 130.4(dn), 130.3(dn), 129.2(dn), 128.6(dn), 128.5(dn), 127.7(dn), 126.6(dn), 126.5(dn), 126.3(u), 125.7(dn), 122.3(u), 101.1(u), 78.6(dn), 63.6(dn), 38.5(u), 36.6(u); IR (KBr, $cm^{-1}$): 3037, 2906, 1787, 1760, 1595, 1195; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{26}H_{19}NO_3$, 393.1365; found, 393.1352.

**4.4.5. Preparation of 5d(fast) and 5d(slow).** The general procedure for resolution using (3a*S*)-*cis*-tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (385 mg, 2.20 mmol) and **3d**

(432 mg, 2.00 mmol) gave 328 mg (0.88 mmol, 88%) of **5d(fast)** (the diastereomer that elutes more quickly) and 332 mg (0.89 mmol, 89%) of **5d(slow)** (the diastereomer that elutes more slowly). Chromatography was performed with a gradient of 10–20% ethyl acetate in hexane. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 11%.

**5d(fast)**: A semisolid. $[\alpha]_D^{23}=-171°$ (*c* 1.0, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.70 (d, *J*=7.6 Hz, 1H), 7.34–7.12 (m, 6H), 7.05–7.02 (m, 2H), 6.76 (t, *J*=1.5 Hz, 1H), 5.95–5.90 (d, *J*=6.9 Hz, 1H), 5.22–5.21 (m, 1H), 3.34–3.31 (m, 2H), 2.62–2.60 (m, 2H), 1.57–1.56 (m, 2H), 1.36–1.34 (m, 2H), 0.87 (t, *J*=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 175.5(u), 151.8(u), 142.8(u), 140.1(u), 139.5(u), 130.2(dn), 128.4(dn), 128.4(dn), 127.8(dn), 126.4(dn), 126.3(dn), 125.6(dn), 124.0(u), 100.7(u), 78.4(dn), 63.5(dn), 38.5(u), 36.2(u), 29.5(u), 24.9(u), 22.7(u), 14.2(dn); IR (KBr, $cm^{-1}$): 3054, 2912, 1789, 1695, 1267; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{24}H_{23}NO_3$, 373.1678; found, 373.1674.

**5d(slow)**: A semisolid. $[\alpha]_D=-10.4°$ (*c* 1.01, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.79 (dd, *J*=7.0, 1.1 Hz, 1H), 7.36–7.33 (m, 2H), 7.26 (d, *J*=7.1 Hz, 1H), 7.19–7.15 (m, 2H), 7.12–7.10 (m, 1H), 7.03–7.01(m, 2H), 6.79 (t, *J*=1.3 Hz, 1H), 5.96 (d, *J*=7.0 Hz, 1H), 5.25–5.22 (m, 1H), 3.34–3.31 (m, 2H), 2.65–2.61 (m, 2H), 1.57–1.53 (m, 2H), 1.35–1.29 (m, 2H), 0.84 (t, *J*=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 175.4(u), 151.9(u), 142.8(u), 140.1(u), 139.6(u), 130.2(dn), 128.5(dn), 128.4(dn), 127.6(dn), 126.3(dn), 126.2(dn), 125.6(dn), 124.4(u), 100.4(u), 78.4(dn), 63.4(dn), 38.5(u), 36.0(u), 29.4(u), 24.7(u), 22.7(u), 14.1(dn); IR (KBr, $cm^{-1}$): 3055, 2933, 1786, 1693, 1202; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{24}H_{23}NO_3$, 373.1678; found, 373.1674.

**4.4.6. Preparation of 5e(fast) and 5e(slow).** The general procedure for resolution was followed using (3a*S*)-*cis*-tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (84 mg, 0.48 mmol), **3e** (96 mg, 0.40 mmol), triethylamine (142 mg, 0.2 mL, 1.4 mmol), 1-adamantoyl chloride (98 mg, 0.44 mmol), LiCl (84 mg, 2.0 mmol) and DMAP (5 mg, 0.04 mmol). Chromatography (the eluent was 5% ethyl acetate in hexane) gave 70 mg (0.18 mmol, 88%) of **5e(fast)** (the diastereomer that elutes more quickly) and 68 mg (0.17 mmol, 86%) of **5e(slow)** (the diastereomer that elutes more slowly). A similar experiment gave **5e(fast)** in 92% yield and **5e(slow)** in 92% yield. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 14%.

**5e(fast)**: A semisolid. $[\alpha]_D^{23}=+188°$ (*c* 0.98, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.72 (d, *J*=7.4 Hz, 1H), 7.36–7.26 (m, 3H), 7.23–7.19 (m, 2H), 7.16–7.14 (m, 1H), 7.06–7.04 (m, 2H), 6.82 (app s, 1H), 5.95 (d, *J*=6.9 Hz, 1H), 5.25–5.21(m, 1H), 3.40–3.28 (m, 2H), 2.66 (t, *J*=7.2 Hz, 2H), 2.18 (app dt, *J*=7.0, 2.6 Hz, 2H), 1.95–1.94 (m, 1H), 1.77–1.73 (m, 2H), 1.61–1.55 (m, 2H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 174.9(u), 151.4(u), 142.2(u), 139.7(u), 139.0(u), 129.8(dn), 128.1(2 carbons, dn), 127.3(dn), 126.0(2 carbons, dn), 125.2(dn), 123.2(u), 100.7(u), 84.1(u), 78.0(dn), 68.5(u), 63.1(dn), 38.0(u), 35.8(u), 27.9(u), 26.0(u), 24.3(u), 18.1(u); IR ($CCl_4$, $cm^{-1}$): 3313, 2933, 1793, 1683, 1359, 1297, 1190, 767, 697; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{26}H_{24}NO_3$, 398.1756; found, 398.1769.

**5e(slow)**: A semisolid. $[\alpha]_D^{23}=+14.8°$ (*c* 1.00, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.78 (d, *J*=7.4 Hz, 1H), 7.37–7.32 (m, 2H), 7.28–7.26 (m, 1H), 7.19–7.15 (m, 2H), 7.13–7.10 (m, 1H), 7.03–7.01 (m, 2H), 6.83 (app t, *J*=1.3 Hz, 1H), 5.96 (d, *J*=7.0 Hz, 1H), 5.27–5.23 (m, 1H), 3.40–3.28 (m, 2H), 2.68–2.64 (m, 2H), 2.12 (app dt, *J*=7.1, 2.8 Hz, 2H), 1.91 (t, *J*=2.7 Hz, 1H), 1.72–1.68 (m, 2H), 1.68–1.51 (m, 2H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 174.8(u), 151.4(u), 142.2(u), 139.6(u), 139.1(u), 129.8(dn), 128.1(dn), 128.0(dn), 127.1(dn), 125.9(dn), 125.8(dn), 125.2(dn), 123.6(u), 100.4(u), 84.1(u), 78.0(dn), 68.4(u), 63.0(dn), 38.1(u), 35.5(u), 27.8(u), 26.0(u), 24.1(u), 18.0(u); IR ($CCl_4$, $cm^{-1}$): 3313, 2931, 1792, 1684, 1359, 1191, 810, 735, 634; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{26}H_{24}NO_3$, 398.1756; found, 398.1776.

**4.4.7. Preparation of 5f(fast) and 5f(slow).** The general procedure for resolution using (3a*S*)-*cis*-tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (385 mg, 2.20 mmol) and **3f** (572 mg, 2.0 mmol) gave 399 mg (0.90 mmol, 90%) of **5f(fast)** (the diastereomer that elutes more quickly) and 390 mg (0.88 mmol, 88%) of **5f(slow)** (the diastereomer that elutes more slowly). Chromatography was performed with a gradient of 10–20% ethyl acetate in hexane. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 20%. A similar experiment that started with 115 mg of **3f** gave **5f(fast)** in 89% yield and **5f(slow)** in 90% yield.

**5f(fast)**: A pale yellow semisolid. $[\alpha]_D^{23}=+38.7°$ (*c* 0.95, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 8.38–8.35 (m, 1H), 7.81–7.75 (m, 3H), 7.72–7.69 (m, 2H), 7.54 (s, 1H), 7.50 (dd, *J*=6.0, 1.2 Hz, 1H), 7.41–7.35 (m, 6H), 7.26–7.24 (m, 1H), 7.17–7.11 (m, 2H), 5.80 (d, *J*=7.0 Hz, 1H), 5.03–4.99 (m, 1H), 3.22 (dd, *J*=17.7, 6.6 Hz, 1H), 3.06 (app d, *J*=17.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.4(u), 152.2(u), 140.3(u), 138.7(u), 138.0(u), 134.0(u), 132.6(u), 130.3(2 carbons, dn), 130.2(dn), 129.3(dn), 129.2(dn), 128.7(dn), 128.3(dn), 128.2(dn), 128.2(dn), 126.8(u), 126.5(dn), 126.0(dn), 125.7(dn), 125.4(dn), 124.4(dn), 121.8(u), 104.1(u), 78.7(dn), 64.4(dn), 38.4(u), 37.5(u); IR ($CH_2Cl_2$, $cm^{-1}$): 3029, 2926, 1784, 1676, 1362, 1265, 1190; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{30}H_{21}NO_3$, 443.1521; found, 443.1503.

**5f(slow)**: A pale yellow solid, mp 78–80 °C. $[\alpha]_D^{23}=+8.7°$ (*c* 1.07, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 8.27 (d, *J*=8.4 Hz, 1H), 7.90–7.87 (m, 2H), 7.78–7.81(m, 1H), 7.74–7.76(d, *J*=7.6 Hz, 1H), 7.69–7.71(d, *J*=8.1 Hz, 1H), 7.62(s, 1H), 7.51–7.53(dd, *J*=6.1, 1.1 Hz, 1H), 7.32–7.41(m, 5H), 7.26–7.28(m, 1H), 7.15–7.21(m, 2H), 5.74–5.75(d, *J*=6.6 Hz, 1H), 4.94–4.98(m, 1H), 3.10–3.23(m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 177.1(u), 152.1(u), 140.1(u), 139.0(u), 138.3(u), 134.0(u), 132.4(u), 130.39 (dn), 130.33(dn), 130.2(dn), 129.3(dn), 129.3(dn), 128.7(dn), 128.4(dn), 128.4(dn), 128.2(dn), 126.9(u), 126.5(dn), 125.9(dn), 125.7(dn), 125.4(dn), 124.3(dn), 120.2(u), 105.5(u), 79.1(dn), 65.1(dn), 38.0(u), 37.2(u); IR ($CCl_4$, $cm^{-1}$): 3029, 2924, 1785, 1680, 1362, 1262, 1190; HRMS-CI($NH_3$) *m/z*: [M+], calcd for $C_{30}H_{21}NO_3$, 443.1521; found, 443.1503.

**4.4.8. Diastereomers of (4*S*)-4-benzyl-3-(2-butyl-1-methoxycarbonyl-cycloprop-2-en-1-oyl)oxazolidinone:**

**5g(fast) and 5g(slow).** A solution of **3g** (204 mg, 1.03 mmol) and triethylamine (1.42 mmol) in 10 mL THF was stirred in a 25 mL flask and cooled in a bath of dry ice/acetone. Pivaloyl chloride (124 mg, 1.03 mmol) was added via syringe, and the solution was stirred at −78 °C for 5 min and then warmed to 0 °C for 1 h. The mixture was once again cooled in the dry ice/acetone bath.

In a separate 10 mL flask, a solution of (*S*)-benzyloxazolidinone (273 mg, 1.55 mmol) in 4 mL THF, cooled in a bath of dry ice/acetone. n-BuLi (1.5 mL of a 2.5 M solution in hexanes, 1.55 mmol) was added dropwise. This solution was stirred at −78 °C for 0.5 h, and then transferred via cannula to the 25 mL flask that contained the mixed anhydride. The reaction mixture was stirred at −78 °C for 5 min then warmed to 0 °C for 0.5 h. The reaction was carefully quenched with water, and 2 mL of 1% HCl was added. Three extracts with ether (3×20 mL) were combined and washed with water and brine, dried ($Na_2SO_4$), filtered and concentrated. Chromatography (20% MTBE in petroleum ether) gave **5g(fast)** (171 mg, 0.48 mmol, 93%) and **5g(slow)** (169 mg, 0.47 mmol, 92%). The $R_f$ difference in MTBE:petroleum ether (4:6) was 40%. A similar experiment with 1.00 g of **3g** gave **5g(fast)** in 92% yield and **5g(slow)** in 91% yield.

**5g(fast)**: Colorless oil. $[\alpha]_D^{23}=+48.6°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.36–7.21 (m, 5H), 6.53 (app t, *J*=1.4 Hz, 1H), 4.68 (m, 1H), 4.24–4.19 (m, 2H), 3.69 (s, 3H), 3.38 (dd, *J*=13.5, 3.4 Hz, 1H), 2.80 (dd, *J*=13.5, 9.8 Hz, 1H), 2.61 (m, 2H), 1.63 (m, 2H), 1.41 (m, 2H), 0.93 (t, *J*=7.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 172.7 (u), 171.7 (u), 153.8 (u), 135.7 (u), 129.9 (dn), 129.3 (dn), 127.7 (dn), 117.3 (u), 95.4 (u), 66.8 (u), 55.5 (dn), 52.6 (dn), 38.0 (u), 35.7 (u), 29.1 (u), 24.5 (u), 22.6 (u), 14.1 (dn); IR ($CCl_4$, $cm^{-1}$): 3153, 3055, 2958, 2933, 2873, 2359, 2332, 1785, 1734, 1716, 1695, 1436, 1387, 1310, 1261, 1214, 789, 756, 703; HRMS-CI *m/z* [M] calcd for $C_{20}H_{23}NO_5$, 357.1576; found, 357.1580.

**5g(slow)**: Colorless oil. $[\alpha]_D^{23}=+56.8°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.34–7.21 (m, 5H), 6.52 (t, *J*=1.1 Hz, 1H), 4.67 (m, 1H), 4.25–4.19 (m, 2H), 3.68 (s, 3H), 3.32 (dd, *J*=13.5, 3.2 Hz, 1H), 2.83 (dd, *J*=13.5, 9.5 Hz, 1H), 2.62 (m, 2H), 1.66 (m, 2H), 1.43 (m, 2H), 0.94 (t, *J*=7.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 172.7 (u), 171.6 (u), 153.8 (u), 135.7 (u), 129.9 (dn), 129.3 (dn), 127.7 (dn), 117.2 (u), 95.6 (u), 66.8 (u), 55.5 (dn), 52.6 (dn), 37.9 (u), 35.6 (u), 29.0 (u), 24.4 (u), 22.6 (u), 14.1 (dn); IR ($CCl_4$, $cm^{-1}$): 3153, 3058, 2958, 2933, 2873, 2363, 2321, 1785, 1734, 1717, 1693, 1436, 1387, 1312, 1251, 1213, 701; HRMS-CI *m/z* [M] calcd for $C_{20}H_{23}NO_5$, 357.1576; found, 357.1561.

**4.4.9. Diastereomers of (4*S*)-4-benzyl-3-(2-phenyl-1-methoxycarbonyl-cycloprop-2-en-1-oyl)oxazolidinone: 5h(fast) and 5h(slow).** The procedure was identical to that used to resolve **3g**, except that adamantoyl chloride (99 mg, 0.5 mmol) was used in place of pivaloyl chloride. The other materials were used in the following quantities: **3h** (109 mg, 0.5 mmol), $Et_3N$ (61 mg, 0.084 mL, 0.6 mmol), THF (7 mL), (*S*)-benzyloxazolidinone (233 mg, 0.75 mmol), n-BuLi (0.3 mL of a 2.5 M solution in hexane, 0.75 mmol). Chromatography (20% MTBE in Petroleum Ether) gave **5h(fast)** (81 mg, 0.21 mmo1, 86%) and **5h(slow)** (84 mg, 0.22 mmo1, 89%). The $R_f$ difference in MTBE:petroleum ether (1:1) was 45%. A similar experiment with 1.62 g of **3h** gave **5h(fast)** in 81% yield and **5h(slow)** in 79% yield.

**5h(fast)**: A semisolid. $[\alpha]_D^{23}=+137.9$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.76 (m, 2H), 7.45(m, 3H), 7.32–7.18 (m, 5H), 7.00 (s, 1H), 4.71 (m, 1H), 4.30–4.21 (m, 1H), 3.70 (s, 3H), 3.35 (dd, *J*=13.4, 3.2 Hz, 1H), 2.81 (dd, *J*=13.4, 9.7 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 172.0 (u), 170.8 (u), 154.0 (u), 135.6 (u), 131.04 (dn), 130.97 (dn), 129.9(dn), 129.37 (dn), 129.32(dn), 127.8, (dn), 124.9 (u), 114.5 (u), 97.0 (u), 67.0 (u), 55.7 (dn), 52.9 (dn), 38.0 (u), 36.6(u); IR ($CH_2Cl_2$, $cm^{-1}$): 3154, 3066, 3031, 2953, 2359, 2338, 2274, 1784, 1739, 1718, 1695, 1387, 1354, 1312, 1214, 1111, 1083, 766; HRMS-CI *m/z* [M] calcd for $C_{22}H_{19}NO_5$, 377.1263; found, 377.1259.

**5h(slow)**: A semisolid. $[\alpha]_D^{23}=-22.2$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.78 (m, 2H), 7.45(m, 3H), 7.24–7.17 (m, 5H), 7.00 (s, 1H), 4.68 (m, 1H), 4.26–4.20 (m, 2H), 3.71 (s, 3H), 3.35 (dd, *J*=13.6, 3.3 Hz, 1H), 2.91 (dd, *J*=13.6, 9.1 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 172.0 (u), 170.7 (u), 154.0 (u), 135.6 (u), 131.04 (dn), 131.02 (dn), 129.95(dn), 129.34 (dn), 129.31(dn), 127.7 (dn), 124.9 (u), 114.4 (u), 97.1 (u), 67.0 (u), 55.7 (dn), 52.9 (dn), 37.9 (u), 36.5(u); IR ($CH_2Cl_2$, $cm^{-1}$): 3154, 3065, 3031, 2953, 2359, 2322, 2283, 1784, 1739, 1719, 1694, 1390, 1355, 1311, 1214, 1112, 1083, 768; HRMS-CI *m/z* [M] calcd for $C_{22}H_{19}NO_5$, 377.1263; found, 377.1256.

**4.4.10. Diastereomers of (4*S*)-4-benzyl-3-(2-hexyl-1-*trans*-styryl-cycloprop-2-en-1-oyl)oxazolidinone: 5i(fast) and 5i(slow).** The general procedure for resolution was followed using **3i** (108 mg, 0.4 mmol), 1-adamantoyl-chloride (84 mg, 0.42 mmol), $Et_3N$ (202 mg, 2.0 mmol), LiCl (85 mg, 2.0 mmol), DMAP (5 mg, 0.04 mmol), (*S*)-benzyloxazolidione (75 mg, 0.42 mmol) and THF (30 mL). Chromatography (10% MTBE in Petroleum Ether) gave **5i(fast)** (64 mg, 0.15 mmol, 73%) and **5i(slow)** (63 mg, 0.15 mmol, 73%) of the title compounds as pale yellow oils. The purities of **5i(fast)** and **5i(slow)** were estimated by $^1H$ NMR to be >95 and >96%, respectively. The $R_f$ difference in toluene:MTBE:petroleum ether (2:1:2) was 17%. A similar experiment with 1.62 g of **3i** gave **5i(fast)** in 73% yield and **5i(slow)** in 73% yield.

**5i(fast)**: A pale yellow oil. $[\alpha]_D^{23}=+32.3°$ (*c* 1.00, THF). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 7.32–7.16 (m, 10H), 6.71 (t, *J*=1.3 Hz, 1H), 6.55 (d, *J*=16.0 Hz, 1H), 6.18 (d, *J*=16.0 Hz, 1H), 4.73 (m, 1H), 4.23–4.15 (m, 2H), 3.34 (dd, *J*=13.4, 3.3 Hz, 1H), 2.79 (dd, *J*=13.4, 9.3 Hz, 1H), 2.58 (m, 2H), 1.64 (m, 2H), 1.40–1.26 (m, 6H), 0.87 (t, *J*=7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, $\delta$): 176.1 (u), 153.0 (u), 137.7 (u), 135.6 (u), 132.7 (dn), 129.9 (dn), 129.4 (dn), 128.9 (dn), 128.3 (dn), 127.8 (dn), 127.4 (dn), 126.5 (dn), 123.0 (u), 98.6 (u), 66.8 (u), 55.6 (dn), 38.2 (u), 35.1 (u), 31.9 (u), 29.3 (u), 27.4 (u), 25.1 (u), 23.0 (u), 14.5 (dn); IR ($CH_2Cl_2$, $cm^{-1}$): 3054, 2957, 2931, 2859, 2305, 1786, 1687, 1600, 1448, 1388, 1351, 1259, 1215, 1076, 959, 896, 757, 713; HRMS-CI, *m/z*: [M+Na]: calcd for $C_{28}H_{31}NO_3$, 452.2226; found, 452.2218.

**5i(slow)**: A pale yellow oil. $[\alpha]_D^{23}$=+42.6 (*c* 1.00, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.31–7.16 (m, 10H), 6.68 (app s, 1H), 6.45 (d, *J*=16.1 Hz, 1H), 6.20 (d, *J*=16.1 Hz, 1H), 4.62 (m, 1H), 4.18–4.13 (m, 2H), 3.37 (dd, *J*=13.3, 3.1 Hz, 1H), 2.84 (dd, 1H), 2.62 (app t, *J*=7.2 Hz, 2H), 1.64 (m, 2H), 1.40–1.26 (m, 6H), 0.88 (t, *J*=6.7 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 175.6 (u), 152.8 (u), 137.8 (u), 135.8 (u), 132.9 (dn), 130.0 (dn), 129.4 (dn), 128.9 (dn), 128.4 (dn), 127.8 (dn), 127.5 (dn), 126.5 (dn), 123.1 (up), 99.7 (u), 66.7 (u), 56.1 (dn), 38.1 (u), 34.7 (u), 32.0 (u), 29.4 (u), 27.4 (u), 25.1 (u), 23.1 (u), 14.6 (dn); IR ($CH_2Cl_2$, $cm^{-1}$): 3054, 2958, 2931, 2858, 2305, 1788, 1686, 1600, 1385, 1350, 1270, 1076, 959, 909, 756, 710; HRMS-CI, *m/z*: [M+Na]: calcd for $C_{28}H_{31}NO_3$, 452.2226; found, 452.2187.

**4.4.11. Diastereomers of (4*S*)-4-phenyl-3-[2-methyl-3-propylcycloprop-2-en-1-oyl]oxazolidinone: 5j(fast) and 5j(slow).** The general procedure for resolution was followed using **3j** (400 mg, 2.86 mmol), 1-adamantoylchloride (622 mg, 3.14 mmol), $Et_3N$ (1.01 g, 1.4 mL, 10 mmol), LiCl (600 mg, 14.3 mmol), DMAP (5 mg, 0.04 mmol), (*S*)-phenyloxazolidinone (75 mg, 0.42 mmol) and THF (30 mL). Chromatography (10% MTBE in hexane) gave **5j(fast)** (378 mg, 1.33 mmol, 93%) and **5j(slow)** (0.375 g, 1.32 mmol, 92%). A similar experiment gave **5j(fast)** in 92% yield and **5j(slow)** in 93% yield. The $R_f$ difference in MTBE:toluene:hexane (1:1:2) was 28%.

**5j(fast)**: White solid, 66.5–68 °C. $[\alpha]_D^{25}$=+143° (*c* 1.0, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.37–7.29 (m, 5H), 5.44 (dd, *J*=8.7, 4.0 Hz, 1H), 4.69 (app t, *J*=8.7 Hz, 1H), 4.26 (dd, *J*=8.8, 3.9 Hz, 1H), 3.35 (s, 1H), 2.39–2.34 (m, 2H), 1.95 (m, 3H), 1.61–1.54 (m, 2H), 0.95 (t, *J*=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 177.2(u), 154.9(u), 140.0(u), 129.5 (dn), 128.9(dn), 126.3(dn), 105.3(u), 100.7(u), 70.4(u), 58.4(dn), 26.8(u), 23.5(dn), 20.9(u), 14.3(dn), 10.0(dn); IR (KBr, $cm^{-1}$): 3034, 2964, 1907, 1775, 1686, 1453, 1375, 1305, 1189, 1093, 765, 699; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{17}H_{20}NO_3$, 286.1443; found, 286.1453.

**5j(slow)**: White solid, 43–46.5 °C. $[\alpha]_D$=+132° (*c* 1.0, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.36–7.26 (m, 5H), 5.45 (dd, *J*=8.7, 3.9 Hz, 1H), 4.69 (app t, *J*=8.8 Hz, 1H), 4.26 (dd, *J*=8.8, 4.0 Hz, 1H), 3.35 (s, 1H), 2.29–2.25 (m, 2H), 2.03–2.04 (t, *J*=1.5 Hz, 3H), 1.43–1.37 (m, 2H), 0.83 (t, *J*=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 90 MHz, $\delta$): 176.7(u), 154.4(u), 139.5(u), 129.0(dn), 128.4(dn), 125.9(dn), 104.8(u), 100.1(u), 70.0(u), 58.0(dn), 26.1(u), 23.0(dn), 20.3(u), 13.7(dn), 9.6(dn); IR (KBr, $cm^{-1}$): 3030, 2960, 1772, 1685, 1451, 1376, 1303, 1182, 1106, 166, 705; HRMS-CI($NH_3$) *m/z*: [M+H], calcd for $C_{17}H_{20}NO_3$, 286.1443; found, 286.1453.

**4.4.12. Diastereomers of (4*S*)-4-benzyl-3-(2-butyl-1-methoxymethoxymethyl-cycloprop-2-en-1-oyl)oxazolidinone: 5k(fast) and 5k(slow).** The general procedure for resolution was followed using **3k** (86 mg, 0.4 mmol), 1-adamantoylchloride (83 mg, 0.42 mmol), $Et_3N$ (202 mg, 0.28 mL, 2.0 mmol), LiCl (85 mg, 2.0 mmol), DMAP (5 mg, 0.04 mmol), (*S*)-benzyloxazolidinone (75 mg, 0.42 mmol) and THF (30 mL). Chromatography (20% MTBE in petroleum ether) gave **5k(fast)** (64 mg, 0.17 mmol, 86%) and **5k(slow)** (65 mg, 0.17 mmol, 86%). The $R_f$ difference in MTBE:petroleum ether (4:6) was 40%. A similar experiment gave **5k(fast)** in 91% yield and **5k(slow)** in 90% yield.

**5k(fast)**: A pale yellow oil. $[\alpha]_D$=+10.9 (*c* 1.0, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.34–7.20 (m, 5H), 6.78 (app t, *J*=1.2 Hz, 1H), 4.65–4.60 (m, 1H), 4.63 (s, 2H), 4.21 (m, 1H), 4.14 (m, 1H), 4.06 (d, *J*=11.3 Hz, 1H), 3.57 (d, *J*=11.3 Hz, 1H), 3.36 (m, 1H), 3.34 (s, 3H), 2.71 (dd, *J*=13.3, 9.7 Hz, 1H), 2.55 (app dt, *J*=1.0, 7.4 Hz, 2H), 1.60 (m 2H), 1.39 (m, 2H), 0.92 (t, *J*=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 176.1 (u), 153.6 (u), 135.8 (u), 129.8 (dn), 129.3 (dn), 127.7 (dn), 123.3 (u), 100.1 (u), 96.4 (u), 72.9 (u), 67.0 (u), 55.67 (dn), 55.66(dn), 38.3 (u), 33.5 (u), 29.4 (u), 25.5 (u), 22.7 (u), 14.2 (dn); IR ($CCl_4$, $cm^{-1}$): 2956, 2930, 2875, 2228, 1784, 1691, 1605, 1454, 1386, 1350, 1215, 1150, 971; Anal. Calcd for $C_{21}H_{27}NO_5$: C, 67.54; H, 7.29; N, 3.75. Found: C, 67.26; H, 7.27; N, 3.68.

**5k(slow)**: A pale yellow oil. $[\alpha]_D$=+31.5 (*c* 1.0, THF). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.32–7.20 (m, 5H), 6.72 (app t, *J*=1.2 Hz, 1H), 4.63 (s, 2H), 4.63–4.60 (m, 1H), 4.21 (m, 1H), 4.16 (m, 1H), 3.80 (s, 2H), 3.34 (s, 3H), 3.34 (dd, *J*=13.4, 3.2 Hz, 1H), 2.80 (dd, *J*=13.4, 9.5 Hz, 1H), 2.62 (m, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.94 (t, *J*=7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 175.6 (u), 153.4 (u), 135.8 (u), 129.9 (dn), 129.3 (dn), 127.7 (dn), 123.9 (u), 101.5 (u), 96.4 (u), 73.1 (u), 67.0 (u), 56.1 (dn), 55.7(dn), 38.1 (u), 33.0 (u), 29.5 (u), 25.5 (u), 22.7 (u), 14.2 (dn); IR ($CCl_4$, $cm^{-1}$): 2957, 2930, 2874, 2232, 1787, 1690, 1604, 1454, 1386, 1350, 1213, 1150, 971; Anal. Calcd for $C_{21}H_{27}NO_5$: C, 67.54; H, 7.29; N, 3.75. Found: C, 67.67; H, 7.47; N, 3.76.

### 4.5. General procedures for reduction

A solution of the cycloprop-2-en-1-oyl oxazolidinone (1.0 mmol) in THF (30 mL) was cooled in an ice bath. Methanol (32 mg, 40 μL, 1.0 mmol) and $LiBH_4$(4.0 mmol, 2.0 mL of a 2.0 M solution in THF) were added sequentially. The ice bath was removed, and stirring was continued for 4 h while the mixture warmed to rt. The reaction was quenched by $NH_4Cl$ (aq) and extracted with ether (3×30 mL). The organics were combined, dried ($Na_2SO_4$), filtered, concentrated, and chromatographed (10–30% ethyl acetate in hexane) to provide the 3-hydroxymethyl-cycloprop-1-ene.

**4.5.1. (3*S*)-(−)-1-Hexyl-3-hydroxymethylcycloprop-1-ene [*S*-(−)-7].** The general procedure for reduction with **5a($S_{cy}$,$S_{ox}$)** (327 mg, 1.0 mmol) gave 131 mg (0.85 mmol, 85%). The general procedure with **5a-Ph($S_{cy}$,$R_{ox}$)** (313 mg, 1.0 mmol) gave 131 mg product, 85%. A similar experiment with 800 mg of **5a($S_{cy}$,$S_{ox}$)** gave *S*-(−)-**7** in 86% yield. The specific rotation of the colorless oil was $[\alpha]_D$=−34.3° (*c* 1.03, THF). Analysis by HPLC (CHIRACEL OD using 15% IPA in hexane) showed the material to be of >99% ee. Other spectral data were identical to those reported for the racemate.[30]

**4.5.2. (3*R*)-1,3-Diphenyl-3-hydroxymethylcycloprop-1-ene [*R*-(−)-6] and (3*S*)-1,3-diphenyl-3-hydroxymethyl-cycloprop-1-ene [*S*-(+)-6].** The general procedure for

reduction with **5c($R_{cy}$,$R_{ox}$)** (320 mg, 0.81 mmol) gave 163 mg (91%) of *R*-(−)-**6**, a semisolid, $[\alpha]_D=-18.9°$ (*c* 1.1, THF). A similar experiment with 250 mg of **5c($R_{cy}$,$R_{ox}$)** gave *R*-(−)-**6** in 86% yield. Analysis by HPLC (CHIRACEL OD using 15% IPA in hexane) showed the material to be of >99% ee. $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.58–7.56 (m, 2H), 7.39–7.26 (m, 8H), 7.19–7.21(m, 1H), 4.29–4.33(m, 1H), 4.21–4.25(m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 145.2(u), 130.1(dn), 129.9(dn), 129.3(dn), 128.7(dn), 127.6(u), 126.9(dn), 126.3(dn), 123.0(u), 105.4(u), 68.1(u), 32.8(u); IR ($CCl_4$, $cm^{-1}$): 3595, 3282, 2875, 1717, 1508, 1265, 1065; HRMS-CI($NH_3$) *m*/*z*: [M+H] calcd for $C_{16}H_{13}O$, 221.0966; found, 221.0960.

Similarly, reduction of **5c($S_{cy}$,$R_{ox}$)** (320 mg, 0.81 mmol) gave 160 mg (89%) of *S*-(+)-**6**, $[\alpha]_D=+18.7°$ (*c* 1.0, THF), >99% ee. A similar experiment with 200 mg of **5c($S_{cy}$,$R_{ox}$)** gave *R*-(+)-**6** in 85% yield

**4.5.3. (+)-1-Butyl-3-hydroxymethyl-3-phenylcycloprop-1-ene [(+)-9].** The general procedure for reduction with **5d(fast)** (373 mg, 1.0 mmol) gave 167 mg (0.83 mmol, 83%) of (+)-**9**, a colorless oil. A similar experiment that started with 500 mg of **5d(fast)** gave (+)-**9** in 82% yield. Analysis by HPLC (CHIRACEL OD using 15% IPA in hexane) showed the material to be of >99% ee. $[\alpha]_D=+23.1°$ (*c* 1.0, THF). Other spectral data were identical to those reported for the racemate.[30]

**4.5.4. (1*S*,2*S*)-(−)-1-Hexyl-2-hydroxymethyl-1-vinylcyclopropane [(1*S*,2*S*)-(−)-8] was prepared from (*S*)-(−)-7 in the same way as the racemate.**[30] Gas Chromatography on a Chiraldex B-PH column showed the material to be of >99% ee. The injection temperature for the GC was 120 °C. The GC oven temperature was increased from 70° to 90° at a rate of 1.0 °C/min, from 90 °C to 110 °C at 0.2 °C/min, and then from 110 °C to 150 °C at 5.0 °C/min. The product is a clear oil, $[\alpha]_D=-3.0°$ (*c* 1.0, THF). Other spectral data were identical to those reported for the racemate.[30]

**4.5.5. (+)-1α-Butyl-2β-hydroxymethyl-1β-methyl-2α-phenylcyclopropane (+)-10].** Was prepared from (+)-(**9**) in the same way as the racemate.[30] Gas Chromatography with a Chiraldex B-PH column showed the material to be of >99% ee. The injection temperature for the GC was 120 °C. The GC oven temperature was increased from 90° to 110° at a rate of 1.0 °C/min, from 110 °C to 140 °C at 0.5 °C/min, and then from 140 °C to 150 °C at 1.0 °C/min. The product is a clear oil, $[\alpha]_D=+7.8°$ (*c* 1.0, THF). Other spectral data were identical to those reported for the racemate.[30]

## Acknowledgements

The project described was supported by NIH Grant Number P20 RR017716-01 from the COBRE Program of the National Center for Research Resources.

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