Advancing the Reactivity of Dimethylcyclopropane-1,1-dicarboxylates via Cross Metathesis

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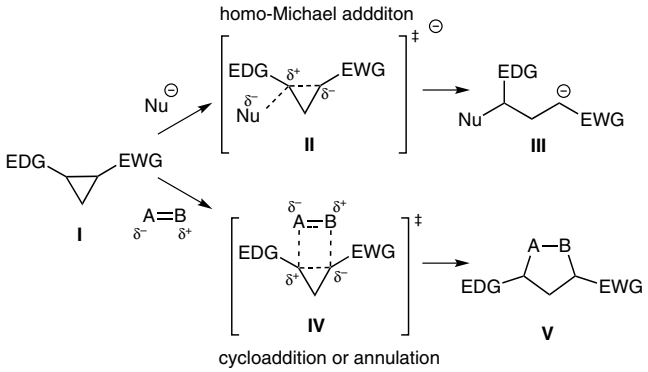
Abstract: Cross metathesis of the readily available dimethyl 2-vinylcycloropane-1,1-dicarboxylate with a variety of olefins gave divergent access to new donor–acceptor cyclopropanes bearing a π-donor alkenyl substituent. The synthetic utility of these cyclopropanes was shown by their participation in cycloaddition reactions with nitrones to yield the anticipated tetrahydro-1,2-oxazines. Hydrogenation yielded the alkyl-substituted adducts which would be more difficult to access via other means.

Key words: heterocycles, cycloaddition, cyclopropanes, metathesis, ruthenium

Advances in the synthetic utility of donor–acceptor cyclopropanes are appearing at an ever increasing rate.[1] The importance of these seemingly simple molecules is evident by their use in complex natural product synthesis.[2] Useful reactions of these molecules **I**, include both nucleophilic ring opening as well as cycloaddition (or annulation) processes to yield **III** or **V**, respectively (Scheme 1). Both types of transformations require an acceptor moiety and a donor moiety vicinally disposed. The 'donor' group can be any functional group capable of stabilizing a developing positive charge in the transitions states (**II** or **IV**) in the ring opening event. Our research group has a longstanding interest in cyclopropane-1,1-dicarboxylates **1** (*vide infra*) as tools for synthesis. The substrates which behave the best by far are those bearing an aryl or vinyl group vicinal to the geminal diester. While simple alkyl moieties at this position are tolerated, the reaction times are longer and the yields are typically lower.



Scheme 1 Donor-acceptor cyclopropanes in addition and cycloaddition reactions

One strategy to circumvent the lack of reactivity of cyclopropanes bearing a simple alkyl substituent[3] is to employ the corresponding alkenyl cyclopropane **1** (Scheme 2) and to saturate the double bond in **2** post-cycloaddition to yield **3**. This would obviate the use of the less reactive cyclopropane **4**. While this is certainly a good strategy, the requisite cyclopropanes **1** bearing a variety of alkenyl groups may be difficult to prepare using typical cyclopropanation methods (Corey–Chaykovsky[4] or carbenoid insertion[5]). The simple parent 2-vinyl cyclopropane-1,1-dicarboxylate (**1**; R = H) is, on the other hand very readily available in large quantities and in racemic[6] or enantioenriched[7] form. Herein we present a divergent strategy involving cross metathesis for the synthesis of a wide variety of dimethyl 2-alkenylcyclopropane-1,1-dicarboxylates from simple starting materials and their use in circumventing difficulties in cycloaddition chemistry.

The literature is surprisingly sparse in examples[8,9] of the cross metathesis of vinyl cyclopropanes and to our knowledge, there are no examples using donor–acceptor cyclopropanes. Our initial investigations (shown in Table 1) into the cross metathesis of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**5**) and 1-hexene focused on determining the appropriate catalyst and conditions for this reaction. Grubbs 1st, 2nd and Grubbs–Hoveyda 2nd generation catalysts[10] were all screened and it was determined that Grubbs 2nd generation catalyst was required to ensure complete conversion of starting materials for the desired metathesis product **6a** (Table 1, entries 1–5). Although both Grubbs 1st and Grubb–Hoveyda 2nd generation catalysts did promote the formation of product, the transformation never reached completion even with extended reaction times and increased catalytic loading. The use of 2nd generation Grubbs catalyst allowed for lower catalyst loadings while giving comparable yields of isolated product at 70% and 67% for both 5 mol% and 1 mol%, respectively (entries 1 and 2). In the hope of increasing the overall yield of the metathesis, the stoichiometry of 1-hexene was varied (entries 6 and 7). It was quickly observed that lowering the excess of 1-hexene from 1.4 equivalents to 1.2 equivalents greatly decreased the yield of the desired metathesis product while promoting a large increase in both cyclopropane and hexene dimerization by-products. In contrast, increasing the excess of 1-hexene to 2.0 equivalents showed no additional increase in product yield. Interestingly, when the temperature was decreased to room temperature and then to 0 °C (entries 8 and 9) the *E*/*Z* product ratio also decreased, along with an

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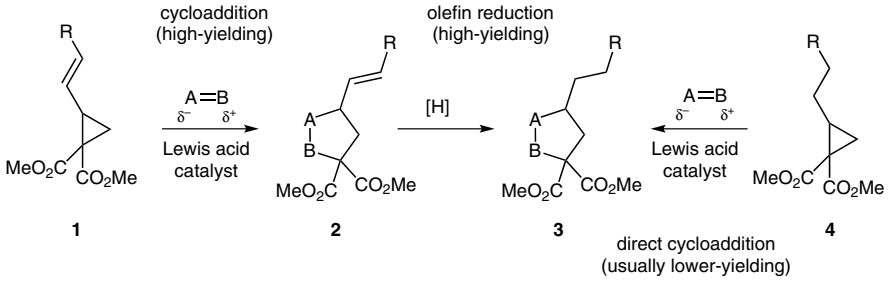
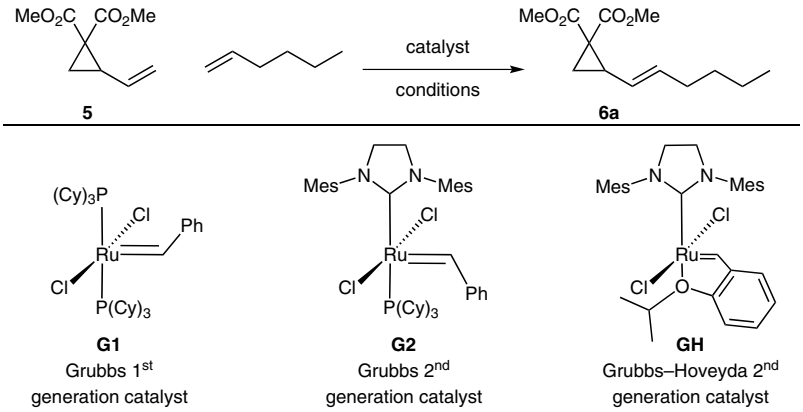


Scheme 2 Two cycloaddition strategies to adduct **3**

overall decrease in yield and increase in reaction time. Finally, diethyl ether was employed[11] in order to help solubilize any unwanted dimer products formed, so that they remained active product-forming entities (entry 10). Although dimer formation was minimized, the reaction was sluggish and led to incomplete product conversion even under extended reaction times.

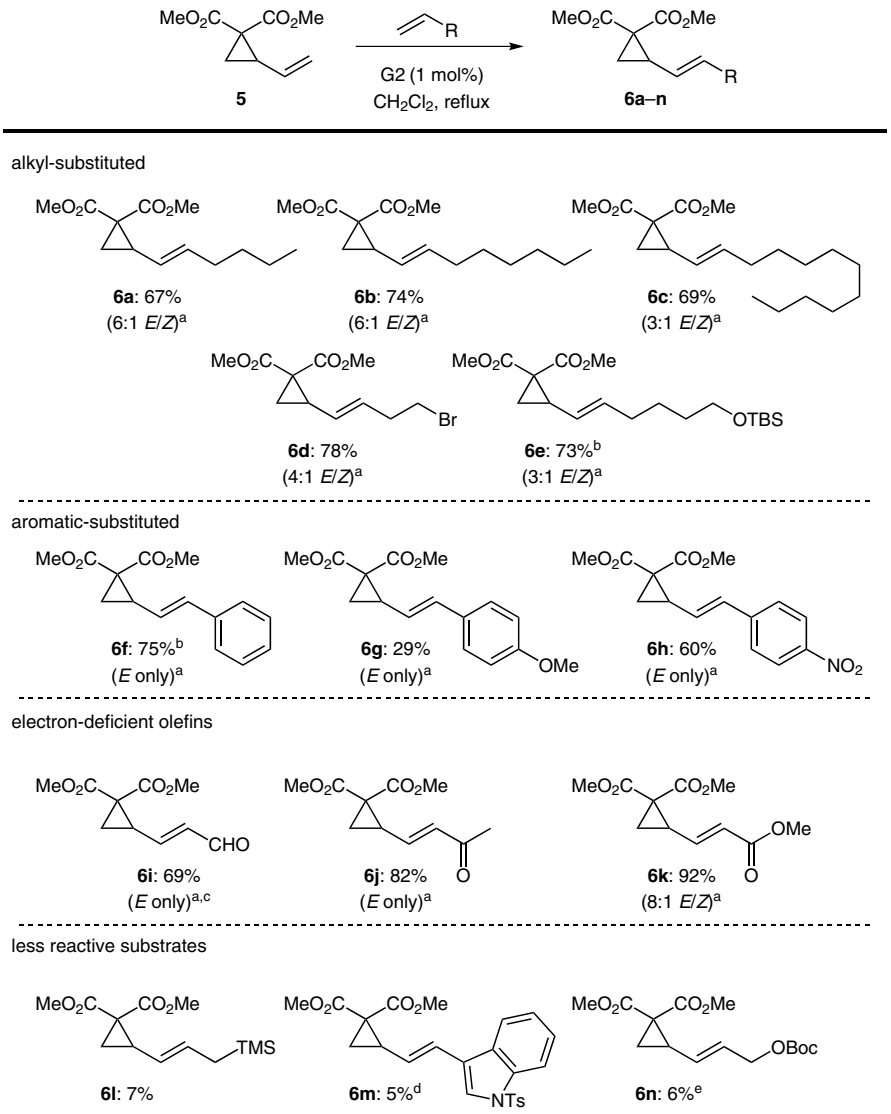
With our best cross-metathesis conditions in hand (Table 1, entry 2), we examined the scope of olefins that would undergo metathesis with dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**5**). We first studied the use of readily available alkyl-substituted olefins (Scheme 3). Gratifyingly, 1-hexene, 1-octene, and 1-dodecene underwent the cross metathesis smoothly giving vinyl cyclopropanes **6a**, **6b**, and **6c** in 67%, 74%, and 69% yields, respectively with little or no observed dimerization products isolated. It is noteworthy to mention that with a much longer alkyl chain (product **6c**), the *E*/*Z* ratio was reduced to 3:1. More functionalized olefins also underwent the metathesis efficiently, allowing access to **6d** and **6e** in good yields. In the case of **6e**, a higher catalyst loading was required to drive the reaction to completion. Disubstituted alkyl olefins, including 2,4,4-trimethylpent-1-ene, were also subjected to

Table 1 Optimization of Cross Metathesis



Entry	1-Hexene (equiv)	Catalyst (mol%)	Solvent/temp (°C)	Time	Yield (%) (*E*/*Z*)[a]
1	1.4	G2 (5%)	CH_2Cl_2/reflux	2 h	70% (6:1)[a]
2	1.4	G2 (1%)	CH_2Cl_2/reflux	3 h	67% (6:1)[a]
3	1.4	G1 (1%)	CH_2Cl_2/reflux	24 h	IC[b]
4	1.4	G1 (10%)	CH_2Cl_2/reflux	24 h	IC[b]
5	1.4	GH (1%)	CH_2Cl_2/reflux	24 h	IC[b]
6	1.2	G2 (1%)	CH_2Cl_2/reflux	2 h	53% (6:1)[a]
7	2.0	G2 (1%)	CH_2Cl_2/reflux	2 h	67% (6:1)[a]
8	1.4	G2 (1%)	CH_2Cl_2/r.t.	24 h	50% (2:1)[a]
9	1.4	G2 (1%)	CH_2Cl_2/0 °C	72 h	IC[b]
10	1.4	G2 (1%)[c]	Et_2O/reflux	40 h	IC[b]

[a] *E*/*Z* ratio determined by ^{1}H NMR.
[b] IC = incomplete reaction.
[c] CuI (3 mol%) was also added.



Scheme 3 Metathesis scope. [a] *E*/*Z* ratio was determined by ^{1}H NMR. [b] Increased catalyst loading was required to promote product conversion. [c] (*E*)-But-2-enal was used as the metathesis partner. [d] Isolated as an inseparable mixture of product and indole dimer. [e] Isolated as an inseparable mixture of product and cyclopropane dimer.

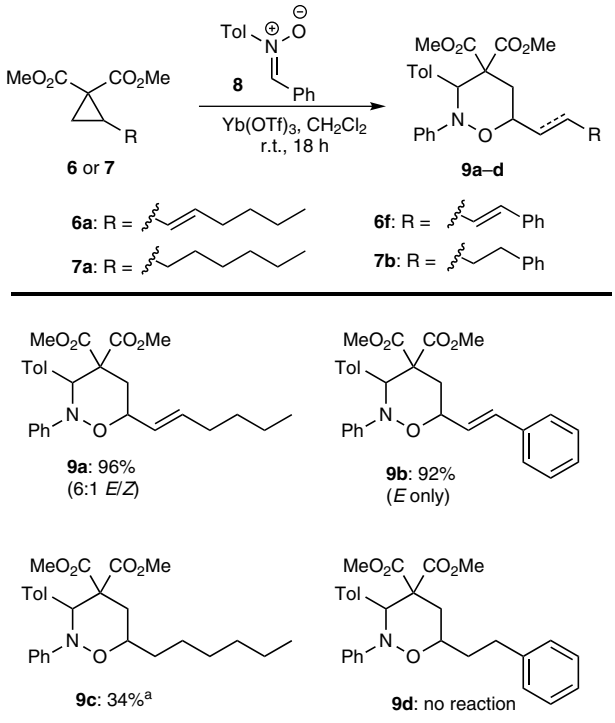
the reaction conditions, however only cyclopropane dimer was isolated.

We next examined the effects of styrenes as participants in the cross-metathesis reaction. The reaction of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**5**) and styrene proved to be difficult due to the increased reactivity of the starting material towards dimerization as well as polymerization.[12] After several attempts at modifying the reaction conditions, it was determined that the required metathesis product **6f** could be isolated in good yield (75%) when 3 equivalents of styrene and 2.5 mol% of catalyst were used. Additionally, the reaction had to be monitored scrupulously by TLC until the cyclopropane starting material was consumed. If the reaction was left longer, styrene dimer would form rapidly, making purification extremely difficult. When *p*-methoxystyrene was subjected to the reaction conditions, the styrene dimer proved to be the major product allowing for isolation of **6g** in only 29% yield. Many modifications were made to increase the yield of **6g** however the *p*-methoxystyrene proved to be too reactive and in all cases the dimer was the major isolated product. Finally, electron-withdrawing *p*-nitrostyrene underwent the metathesis with success giving **6h** in 60% yield, a result that could be attributed to the lowered reactivity of the olefin towards dimerization under these conditions.

A variety of electron-deficient α,β-unsaturated olefins were explored as cross-metathesis partners. The initial metathesis between **5** and acrolein led to the desired product **6i**, however in a low yield of 33% with significant decomposition of acrolein. To avoid the decomposition of acrolein, (*E*)-but-2-enal was used as a substitute and **6i** was isolated in 69% yield. Interestingly, methyl vinyl ketone underwent the reaction giving **6j** as the sole product in 82% yield with no sign of starting material decomposition. Methyl acrylate also showed great success towards the metathesis allowing access to **6k** in 92% yield.

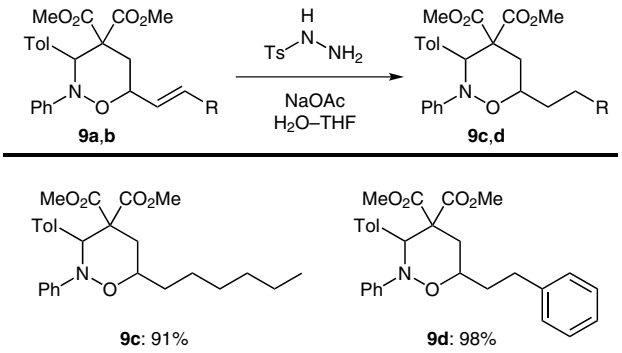
Although a range of olefins were able to undergo the metathesis successfully in modest to excellent yields, there were a few substrates that gave poor results. Allyl trimethylsilane proved to be very unreactive towards the metathesis allowing for only 7% yield of product **6l** under the reaction conditions, even when increased reaction times and catalyst loadings were employed. 1-Tosyl-3-vinylindole and allyl *tert*-butyl carbonate both showed limited success undergoing the metathesis in 5% and 6% yields, respectively (**6m** and **6n**); however the products were inseparable from the corresponding dimers.

With adducts such as **6** in hand we set forth to compare the reactivity of these cyclopropanes against their saturated counterparts. In order to secure the corresponding alkyl-substituted cyclopropanes **7a** and **7b** (Scheme 4), vinyl cyclopropanes **6a** and **6f** were reduced using mild hydrazine transfer hydrogenation conditions.[13] To test the reactivity of each cyclopropane, a fundamental and well-studied nitrone cycloaddition reaction was performed.[14] Each cyclopropane was subjected to nitrone **8** and catalytic $Yb(OTf)_3$ in CH_2Cl_2 for an extended reaction period of 18 hours. Both alkenyl-substituted cyclopropanes **6a** and **6f** gave excellent conversions to the corresponding tetrahydro-1,2-oxazines (**9a** and **9b**) in 96% and 92% yields, respectively. In contrast, saturated cyclopropane **7a** produced tetrahydro-1,2-oxazine **9c** in a 34% (based on recovered starting material) yield as an inseparable mixture of product and starting cyclopropane. Saturated cyclopropane **7b** did not react under the standard reaction conditions and only starting material was recovered. If the reaction conditions were made more severe [20 mol% $Yb(OTf)_3$ in refluxing 1,2-dichloroethane], it was possible to convert **7a** and **7b** into their corresponding oxazine products **9c** and **9d** in isolated yields of 44% and 25%, respectively.[15]



Scheme 4 Comparative nitrone cycloaddition reactions. [a] Isolated as an inseparable mixture of product and cyclopropane starting material.

Finally, the tetrahydro-1,2-oxazines were reduced in order to access the alkyl-substituted derivative. Due to the sensitivity of the tetrahydro-1,2-oxazines N–O bond, a mild tosylhydrazine/sodium acetate reduction was utilized (Scheme 5). Reduction of **9a** and **9b** was successful leading to isolations of tetrahydro-1,2-oxazines **9c** and **9d** in 91% and 98% yield, respectively.



Scheme 5 Vinyl tetrahydro-1,2-oxazine reduction

In conclusion, we have produced a variety of alkenyl-substituted cyclopropanes via a cross-metathesis procedure that utilizes moderately low loadings of Grubbs 2nd generation catalyst and is applicable to a wide series of olefins.[16] Additionally, we have shown that alkenyl-substituted cyclopropanes can serve as surrogates to access products which would normally be formed from alkyl-substituted cyclopropanes, allowing for a significant increase in yield for a given cycloaddition reaction. Mild olefin reduction conditions allow for quick access to alkyl-substituted cycloadducts with high overall yields.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(15) Product **9d** was isolated as an inseparable mixture with starting cyclopropane.

(16) **General Experimental Procedure for the Synthesis of Substituted Vinyl Cyclopropane 6a–k**: Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**5**; 1 equiv) and olefin (1.4–5.0 equiv) were dissolved in anhyd CH_2Cl_2. Grubbs 2nd generation catalyst (G2; 0.01 equiv) was then added and a reflux condenser was attached. The reaction vessel was then purged with argon and the reaction was brought to reflux. Upon completion by TLC analysis the solvent was removed and the residue was purified by flash chromatography (EtOAc–hexanes) to yield the desired cyclopropanes **6a–k**.
Analytical Data for Selected Compounds:
Dimethyl 2-(Hex-1-enyl)cyclopropane-1,1-dicarboxylate (6a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 (dt, *J* = 15.3, 7.0 Hz, 1 H), 5.35 (ddt, *J* = 15.2, 8.2, 1.2 Hz, 1 H), 3.72 (s, 6 H), 2.54 (q, *J* = 8.2 Hz, 1 H), 1.99 (q, *J* = 7.0 Hz, 2 H), 1.68 (dd, *J* = 7.4, 4.7 Hz, 1 H), 1.55 (dd, *J* = 9.4, 4.7 Hz, 1 H), 1.25–1.31 (m, 4 H), 0.86 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 168.0, 135.6, 124.2, 52.6, 35.6, 32.1, 31.2, 27.5, 27.0, 22.0, 20.8, 13.9. IR (thin film): 3000, 2955, 2929, 2857, 1730, 1437, 1332, 1280, 1260, 1210, 1131 cm^{-1}. HRMS: *m*/*z* calcd for $C_{13}H_{20}O_4$: 240.1362; found: 240.1368 (6:1 *trans* to *cis*).
Dimethyl 2-Styrylcyclopropane-1,1-dicarboxylate (6f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.32 (m, 4 H), 7.20–7.26 (m, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 5.81 (dd, *J* = 16.0, 9.0 Hz, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 2.76 (q, *J* = 8.2 Hz, 1 H), 1.85 (dd, *J* = 7.8, 5.1 Hz, 1 H), 1.70 (dd, *J* = 9.0, 5.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 167.9, 136.7, 133.9, 128.6, 127.6, 126.1, 124.5, 52.8, 52.7, 36.0, 31.7, 21.3. IR (thin film): 3027, 2953, 2847, 1731, 1494, 1437, 1283, 1252, 1207, 1128, 964, 770, 744, 694 cm^{-1}. HRMS: *m*/*z* calcd for $C_{15}H_{16}O_4$: 260.1049; found: 260.1049 (only *E*-olefin observed by ^{1}H NMR).
Dimethyl 2-(3-Oxobut-1-enyl)cyclopropane-1,1-dicarboxylate (6j): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.23–6.30 (m, 2 H), 3.71 (s, 6 H), 2.56–2.65 (m, 1 H), 2.15 (s, 3 H), 1.78 (dd, *J* = 7.6, 5.3 Hz, 1 H), 1.72 (dd, *J* = 8.8, 4.7 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.0, 169.0, 167.2, 142.1, 133.3, 52.9, 52.8, 36.5, 29.8, 27.0, 21.5. IR (thin film): 3007, 2956, 2856, 1731, 1674, 1625, 1438, 1333, 1291, 1253, 1212, 1131, 983 cm^{-1}. HRMS: *m*/*z* calcd for $C_{11}H_{14}O_5$: 226.0841; found: 226.0831 (only *E*-olefin observed by ^{1}H NMR).
General Experimental Procedure for the Synthesis of Tetrahydro-1,2-oxazines 9a–d: $Yb(OTf)_3 \cdot xH_2O$ (5–20 mol %) was added to a solution of cyclopropane **6a**, **6f**, and **7a**,**b** (1 equiv) and nitrone **8** (1.2 equiv) in CH_2Cl_2 or 1,2-dichloroethane. Reactions in CH_2Cl_2 were performed at r.t., while reactions in 1,2-dichloroethane were refluxed for 18 h. The reaction mixture was wet loaded and purified by flash chromatography (EtOAc–hexanes) to yield the desired tetrahydro-1,2-oxazine **9a–d**.
Analytical Data for Selected Compounds:
Dimethyl 6-(Hex-1-enyl)-2-phenyl-3-*p*-tolylmorpholine-4,4-dicarboxylate (9a): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49–7.56 (m, 2 H), 7.14–7.21 (m, 3 H), 6.91–6.98 (m, 4 H), 5.88–5.97 (m, 1 H), 5.64–5.76 (m, 1 H), 5.62 (s, 1 H), 4.40–4.47 (m, 1 H), 3.88 (s, 3 H), 3.45 (s, 3 H), 2.44–2.61 (m, 2 H), 2.05–2.11 (m, 5 H), 1.33–1.49 (m, 4 H), 0.95 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.1, 168.4, 146.3, 135.2, 135.0, 130.8, 130.5, 129.0, 127.9, 127.8, 127.7, 116.0, 77.2, 65.9, 59.2, 53.3, 52.5, 32.2, 30.8, 22.3, 22.2, 20.5, 13.9. IR (thin film): 3028, 2954, 2927, 2859, 1742, 1509, 1453, 1434, 1235, 1177, 1149, 1082, 967, 821, 755, 702 cm^{-1}. HRMS: *m*/*z* calcd for $C_{27}H_{33}NO_5$: 451.2359; found: 451.2354. (6:1 *trans* to *cis*).
General Experimental Procedure for Olefin Reduction to Tetrahydro-1,2-oxazines 9c–d: Vinyl tetrahydro-1,2-oxazines **9a** and **9b** (1 equiv) were dissolved in THF–H_2O (1:1). Tosylhydrazine (10 equiv) and NaOAc (13 equiv) were added and the reaction mixture was heated to reflux for 24 h. H_2O was added to the reaction and the aqueous layer was extracted with Et_2O (4 ×). The organic phases were combined and dried with $MgSO_4$, filtered, and the solvent was removed. The residue was purified by flash chromatography (EtOAc–hexanes) to yield the desired tetrahydro-1,2-oxazines (**9c** and **9d**).
Analytical Data for Selected Compounds:
Dimethyl 6-Phenethyl-2-phenyl-3-*p*-tolylmorpholine-4,4-dicarboxylate (9d): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52–7.56 (m, 2 H), 7.30–7.34 (m, 2 H), 7.26–7.29 (m, 2 H), 7.17–7.24 (m, 4 H), 6.94–7.00 (m, 4 H), 5.67 (s, 1 H), 3.98–4.07 (m, 1 H), 3.85 (s, 3 H), 3.46 (s, 3 H), 2.96–3.04 (m, 1 H), 2.83–2.91 (m, 1 H), 2.46–2.52 (m, 2 H), 2.13–2.23 (m, 4 H), 1.97–2.06 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 168.5, 146.4, 141.6, 135.2, 130.7, 130.5, 129.1, 128.4, 128.0, 127.9, 126.0, 115.7, 76.5, 66.0, 59.2, 53.3, 52.5, 36.4, 31.9, 31.0, 20.6 (one carbon missing presumably due to overlap in the aromatic region). IR (thin film): 3027, 2951, 2924, 2857, 1741, 1509, 1453, 1434, 1236, 1166, 1090, 820, 753, 701 cm^{-1}. HRMS: *m*/*z* calcd for $C_{29}H_{31}NO_5$: 473.2202; found: 473.2191.

