Chiral Phosphine-Catalyzed Asymmetric Transformations of Allenoates and Alkynoates and Photoinduced, Copper-Catalyzed C–N Couplings with Aromatic Nitrogen Heterocycles

by

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B.S., Chemistry and Mathematics, 2009
Gettysburg College

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY
IN ORGANIC CHEMISTRY

at the
Massachusetts Institute of Technology

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Chiral Phosphine-Catalyzed Asymmetric Transformations of Allenoates and Alkynoates and Photoinduced, Copper-Catalyzed C–N Couplings with Aromatic Nitrogen Heterocycles

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Submitted to the Department of Chemistry on January 22, 2015
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ABSTRACT

Chapter 1 describes the development of chiral biphenyl-derived phosphines and their application as catalysts for an asymmetric [4 + 1] annulation to form functionalized cyclopentenes bearing a non-spirocyclic quaternary stereocenter. Additional studies demonstrate the synthetic utility of the cyclopentene products for further stereoselective functionalization and provide insight into the mechanism of the reaction.

Chapter 2 describes the development of photoinduced, copper-catalyzed C–N couplings between aromatic nitrogen heterocycles (i.e., indole, benzimidazole, imidazole, and carbazole) and aryl, alkenyl, and alkynyl halides. These reactions utilize an inexpensive catalyst (Cul, without an additional ligand) and proceed at unusually low temperature for Ullmann coupling processes with these heterocycles (room temperature). Additional studies probe the selectivity of the reaction with respect to both the nucleophilic and the electrophilic coupling partner.

Chapter 3 details progress towards developing a method for asymmetric, intermolecular γ additions of oxygen nucleophiles to alkynoates using a chiral phosphine catalyst. Conditions are presented that effectively couple alkynoates bearing an aryl substituent at the γ position with a variety of alcohols in good yield and high ee. Future efforts will be focused on expanding the scope of this process and conducting experiments to gain insight into the reaction mechanism.

Thesis Supervisor: Professor Gregory C. Fu
Title: Altair Professor of Chemistry, California Institute of Technology
PREFACE

Portions of this thesis have appeared in the following publications:

**A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles and Electrophiles for Photoinduced, Copper-Catalyzed Processes**

**Biphenyl-Derived Phosphepines as Chiral Nucleophilic Catalysts: Enantioselective [4 + 1] Annulations to Form Functionalized Cyclopentenes**
ACKNOWLEDGMENTS

Reflecting on my five years in the Fu group, I am amazed by how many people have helped me reach this milestone. First and foremost, I would like to thank my advisor, Professor Greg Fu. Greg’s mentorship has been invaluable to me, and I am grateful for his constant support, both in my graduate work and in the pursuit of my career goals. Ever since I took his physical organic chemistry course during my first semester at MIT, I have appreciated his clear, calculated approach to explaining chemistry. I have learned so much from him, and I hope to emulate his example in my own teaching. It has been a true honor to work with such a great chemist, teacher, and advisor.

In addition, I thank my thesis committee chair Professor Mo Movassaghi. I always looked forward to my annual meetings with Mo and am very appreciative of his support and constructive feedback. Professor Tim Jamison deserves acknowledgment for serving on my thesis committee. I enjoyed my interactions with Tim both as a student in his class and as his teaching assistant. I owe many thanks to my undergraduate research advisor Professor Tim Funk. Tim inspired me to pursue graduate studies in organic chemistry and has never hesitated to support me during my time at Gettysburg College and beyond.

Group members dictate the lab environment, and I have been fortunate to work with talented, enthusiastic colleagues. Everyone who I have had the privilege to work with in the Fu group has had an impact on me and my research, and I thank them all for their support, encouragement, and feedback. In particular, I would like to acknowledge Alex Bissember, Ash Wilsily, Craig Smith, and Nathan Schley. I greatly appreciate their guidance, helpful discussions, and friendship. Yuji Fujiwara deserves a special thanks for his patience in helping me when I first began in the lab. He is a model of efficiency and helped me tremendously.

I have been especially lucky to overlap with excellent graduate students in the Fu group. From the very beginning at the MIT visiting weekend, I seemed destined to spend my graduate school career with Sarah Yunmi Lee. Sharing the challenges and successes of graduate school with a close friend has been a blessing, and the Fu group would not have been the same without her. My graduate school experience was positively affected by another great friend, Junwon Choi. I could always direct my obvious questions to Junwon, and I am thankful for his helpfulness around the lab. Along with Junwon, Shoshana Bachman and Crystal Chu helped create an all-star office area where there was never a shortage of entertainment. I appreciate their friendship and look forward to many more good times to come at Caltech. Additionally, I thank Sue Zultanski, Yufan Liang, Nick Bencivenga, and Joe Ahn for their contributions.

Outside of the lab, I have to thank Erik Townsend for being a great roommate and an even better friend.

Of course I never could have made it this far without the unwavering support of my family. Thanks to Mom and Dad for believing in me and for providing a constant source of love and encouragement. I could not have asked for more supportive parents. I owe a special thanks to Andy whose support helped me get through my first few years in Boston. Derek deserves recognition for his support and intellectual contributions that helped me get into MIT in the first place. Last, and most importantly, thanks to my amazing wife Andrea. I am forever grateful for the sacrifices you have made so that I could achieve this goal. I know that this journey together has not been easy, but without your love, patience, and support, none of this would have been possible. This thesis is dedicated to you.
TABLE OF CONTENTS

Abstract 3
Preface 4
Acknowledgments 5

CHAPTER 1. Biphenyl-Derived Phosphepines as Chiral Nucleophilic Catalysts: Enantioselective [4 + 1] Annulations to Form Functionalized Cyclopentenes

A. Introduction 11
B. Results and Discussion 15
C. Conclusion 23
D. Experimental (with $^1$H NMR Spectra) 25

CHAPTER 2. A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles and Electrophiles for Photoinduced, Copper-Catalyzed Processes

A. Introduction 171
B. Results and Discussion 174
C. Conclusion/Recent Developments 185
D. Experimental (with $^1$H NMR Spectra) 187

CHAPTER 3. Catalytic Asymmetric C–O Bond Formation: Phosphine-Catalyzed Intermolecular $\gamma$ Additions of Alcohols to Aryl-Substituted Alkynoates

A. Introduction 249
B. Results and Discussion 253
C. Conclusion/Future Work 259
D. Experimental (with $^1$H NMR Spectra) 261

Curriculum Vitae 303
CHAPTER 1

Biphenyl-Derived Phosphepines as Chiral Nucleophilic Catalyts: Enantioselective [4 + 1] Annulations to Form Functionalized Cyclo pentenes
A. Introduction

As part of an ongoing effort to demonstrate the versatility of asymmetric nucleophilic catalysis, our group became interested in exploring chiral tertiary phosphines as catalysts. Few examples of highly enantioselective phosphine-catalyzed processes had been reported at the point that this program was initiated. However, due to efforts from our group and from others, chiral tertiary phosphines have since emerged as powerful nucleophilic catalysts for a variety of asymmetric transformations. In particular, axially chiral 1,1′-binaphthyl-derived phosphines (e.g., 1a), originally reported as chiral ligands for transition-metal complexes, have proven to be effective catalysts for a diverse array of interesting enantioselective processes, including [4 + 2] annihilations between α-substituted allenates and imines, [3 + 2] cycloadditions of electron-deficient allenes with electron-poor olefins, and γ-additions of various nucleophiles to electron-deficient allenes. The steric and electronic properties of these phosphines can be tuned by altering the substituents at the 3,3′-positions (R′) and the substituent bound to phosphorus (R2) in order to optimize the reactivity and selectivity of the catalyst. Modifications to the catalyst backbone can also affect reactivity and selectivity; however, to the best of our knowledge, there have been no applications of axially chiral biphenyl-derived phosphines (e.g., 1b) as asymmetric nucleophilic catalysts.

8 We are aware of only one report of an axially chiral biphenyl-derived phosphine used in asymmetric catalysis (as a chiral ligand for transition metals): Alberico, E.; Karandikar, S.; Gladiali, S. ChemCatChem 2010, 2, 1395–1398.
The use of phosphines as nucleophilic catalysts for the synthesis of 5-membered carbocycles,\(^9\) which are commonly found subunits in a wide range of bioactive compounds,\(^{10}\) has been extensively investigated. Due in part to the advantages of a convergent synthetic route, much of this effort has focused on the development of both racemic and asymmetric variants of Lu’s powerful phosphine-catalyzed [3 + 2] annulations.\(^{11,12}\) In Lu’s pioneering reports, two strategies for accessing a reactive three-carbon intermediate were demonstrated (Scheme 1.1); the first approach utilizes an electron-deficient allene, whereas the second method exploits a Morita–Baylis–Hillman derivative.


\(^{12}\) For early examples of enantioselective variants, see: (a) Reference 1b. (b) Reference 5a.
An allenolate as the three-carbon annulation partner:

![Diagram of allenolate annulation]

A Morita-Baylis-Hillman adduct as the three-carbon annulation partner:

![Diagram of Morita-Baylis-Hillman annulation]

**Scheme 1.1.** Synthesis of Cyclopentenes via Phosphine-Catalyzed [3 + 2] Annulations

While significant progress has been made towards controlling the enantioselectivity and diastereoselectivity of these [3 + 2] cycloaddition reactions, these processes often suffer from the formation of an undesired regioisomer (especially when R₁ = H (Scheme 1.1)), and few examples for the enantioselective construction of cyclopentenes with a non-spirocyclic quaternary stereocenter have been reported. In 2010, Tong described a complementary [4 + 1] annulation that combines the structural features of the three-carbon partners in Lu’s [3 + 2] reactions.

---


(allenoates and Morita–Baylis–Hillman derivatives) in a four-carbon component (eq 1.1). Such an approach obviates the formation of regioisomeric products. In addition, Tong demonstrated an array of nucleophiles that generate cyclopentenes containing a non-spirocyclic quaternary stereocenter. Therefore, we set out to develop an asymmetric variant of this valuable transformation.

At the point that we began our investigation, no progress towards this objective had been reported. However, as we neared the completion of our study, Lu described an asymmetric [4 + 1] annulation between α-substituted allenoates and pyrazolones that utilizes an amino acid-derived, bifunctional chiral phosphine (1c) to generate cyclopentenes with a spirocyclic quaternary stereocenter in good ee (eq 1.2). To the best of our knowledge, there have been no other reports of asymmetric [4 + 1] annulations with similar α-substituted allenoates.

B. Results and Discussion

For our initial investigations, we chose to examine \(\alpha\)-cyano carbonyl compounds as nucleophiles since \(\alpha\)-cyano ketones and esters proved to be effective in Tong’s racemic \([4 + 1]\) annulations.\(^{18}\) In our model reaction, coupling benzoylecetonitrile with a benzhydryl ester allenoate, we determined that a series of chiral \(1,1’\)-binaphthyl-derived phosphines that have been shown to be useful for a variety of nucleophile-catalyzed processes were not effective for this transformation (Table 1.1, entries 1–3). Either insufficient enantioselectivity and/or low yield were observed. Therefore, we decided to explore biphenyl-derived phosphines as catalysts and were pleased to determine that new phosphines \(1d\) and \(1e\) catalyze the \([4 + 1]\) annulation in high ee and good yield (entries 4 and 5).\(^{19}\) Lowering the catalyst loading to 5% led to incomplete conversion over 24 hours as did running the reaction without cesium carbonate or replacing cesium carbonate with the more soluble base 2,6-lutidine (entries 6–8). A moderate decrease in enantioselectivity was observed when the reaction was run at room temperature or when the ester substituent was changed to a benzyl group (entries 9 and 10). Although the addition of two equivalents of water had a deleterious effect on the reaction, adventitious moisture and oxygen had little impact on enantioselectivity and yield (entries 11 and 12).

\(^{18}\) Preliminary studies, which were mostly focused on the effect of catalyst structure, were conducted by Lorena Riesgo

\(^{19}\) Although systematic studies of \(3,3’\)-substituted biphenyl-derived phosphines have not been carried out, investigations with binaphthyl-based phosphines suggest that the \(3,3’\)-substituents may play a significant role in improving enantioselectivity.
Table 1.1. Phosphepine-Catalyzed Enantioselective [4 + 1] Annulation: Effect of Reaction Parameters

<table>
<thead>
<tr>
<th>entry</th>
<th>change from the <em>standard conditions</em></th>
<th>ee (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(R)-1f, instead of (R)-1d</td>
<td>-38</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>(R)-1g, instead of (R)-1d</td>
<td>6</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>(R)-1h, instead of (R)-1d</td>
<td>76</td>
<td>&gt;95</td>
</tr>
<tr>
<td>4</td>
<td>none</td>
<td>94</td>
<td>&gt;95</td>
</tr>
<tr>
<td>5</td>
<td>(R)-1e, instead of (R)-1d</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>5% (R)-1d</td>
<td>93</td>
<td>64</td>
</tr>
<tr>
<td>7</td>
<td>no Cs&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>92</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>2,6-lutidine, instead of Cs&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>92</td>
<td>56</td>
</tr>
<tr>
<td>9</td>
<td>r.t.</td>
<td>89</td>
<td>&gt;95</td>
</tr>
<tr>
<td>10</td>
<td>R = Bn, instead of CHPH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>89</td>
<td>88</td>
</tr>
<tr>
<td>11</td>
<td>2.0 equiv of added water</td>
<td>82</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>under air, instead of nitrogen</td>
<td>93</td>
<td>90</td>
</tr>
</tbody>
</table>

All data are the average of two experiments.  

<sup>a</sup>A negative ee value signifies that the major product of the reaction is the (R) enantiomer.  

<sup>b</sup>The yield was determined by °H NMR spectroscopy with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

Phosphepines 1d and 1e were synthesized from 3-methoxy-2-nitrobenzoic acid via a common late-stage phosphine-oxide intermediate that could be resolved by chiral HPLC (Scheme 1.2). Suzuki cross-coupling between the enantiopure intermediate and the appropriate boronic acid followed by reduction of the phosphine-oxide product with trichlorosilane yielded phosphepines 1d and 1e in 30% and 25% overall yield, respectively, over 10 steps. This synthetic pathway was established by Yuji Fujiwara during his time in the Fu group. These phosphepines are relatively stable towards oxidation as solids under air; essentially no phosphine oxide (<5%).
was observed by \(^{31}\)P NMR spectroscopy after 21 days. However, they are more readily oxidized as a solution in toluene; exposure to air for 8 days led to approximately 10% phosphine oxide formation for phosphepine 1d and approximately 55% phosphine oxide formation for phosphepine 1e (monitored by \(^{31}\)P NMR spectroscopy).

Scheme 1.2. Synthesis of Phosphepines 1d and 1e from 3-Methoxy-2-nitrobenzoic Acid.

With optimized conditions established for an asymmetric [4 + 1] annulation with benzoyleacetonitrile as the nucleophile, we next investigated the scope of the reaction with related nucleophilic coupling partners in order to enantioselectively synthesize a variety of cyclopentenes that bear an all-carbon quaternary stereocenter (Table 1.2). Phenyl ketones with an electron-donating or an electron-withdrawing group on the phenyl substituent can be tolerated (entries 2 and 3). Similarly, a thienyl ketone reacts in good ee and yield; the reaction was run at 0 °C instead
of −10 °C to achieve full conversion (entry 4). Alkyl ketones with alkyl groups that range in size from an n-alkyl group to a t-butyl group react with similar enantioselectivities (entries 5–7). In addition to α-cyano ketones, various α-cyano amides are also suitable nucleophiles for this transformation, including a diphenyl amide and a Weinreb amide (entries 8–11). An α-cyano ester reacts in good ee although an increase in catalyst loading is required to obtain a useful yield (entry 12). On a gram scale with benzoylacetonitrile as the nucleophile, the reaction proceeds in 93% ee and 76% yield (1.12 g), and the catalyst could be recovered after the reaction as the phosphine oxide (88% recovery; the catalyst was oxidized with t-BuOOH to quench the reaction).
Table 1.2. α-Cyano Ketones, Amides, and Esters as Nucleophiles in Phosphepine-Catalyzed Enantioselective [4 + 1] Annulations

<table>
<thead>
<tr>
<th>entry</th>
<th>ee (%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>94</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>94</td>
<td>83</td>
</tr>
<tr>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>90</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>93</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>93</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>94</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>91</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>86</td>
<td>73</td>
</tr>
<tr>
<td>11</td>
<td>88</td>
<td>86</td>
</tr>
<tr>
<td>12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>82</td>
<td>61</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup> Yield of purified product. <sup>b</sup> Reaction was run at 0 °C. <sup>c</sup> Reaction was run with 20% (R)-1d.

Unfortunately, when we applied this method with an α-cyano sulfone (phenylsulfonylacetonitrile) as the nucleophile for the synthesis of a cyclopentene containing a fully-substituted heteroatom-bearing stereocenter, the cyclopentene product was generated with moderate enantioselectivity (54% ee). In an effort to expand the scope of this process, we determined that, with a related biphenyl-derived phosphepine (1e) as the catalyst, enantioenriched...
α-cyano sulfones can be efficiently synthesized in improved ee as can an α-cyano phosphine oxide and an α-cyano phosphonate (Table 1.3).20

**Table 1.3.** α-Cyano Sulfones, Phosphine Oxides, and Phosphonates as Nucleophiles in Phosphepine-Catalyzed Enantioselective [4 + 1] Annulations

<table>
<thead>
<tr>
<th>entry</th>
<th>ee (%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>94</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>87</td>
<td>88</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup> Yield of purified product.

The cyclopentene products of this [4 + 1] annulation are well-poised for further stereoselective functionalization. The electron-deficient olefin in particular provides a convenient handle to install additional stereocenters around the cyclopentane ring. For example, a dihydroxylation (eq 1.3) and an epoxidation (eq 1.4) of the illustrated α-cyano sulfone product proceed in good yield to form two new stereocenters with high diastereoselectivity.

![Reaction Scheme](image)

**Equation 1.3**

Under the standard reaction conditions, n-hexylsulfonylacetonitrile reacts in 78% ee and 94% yield (determined by <sup>1</sup>H NMR spectroscopy with CH<sub>2</sub>Br<sub>2</sub> as an internal standard).

20 Under the standard reaction conditions, n-hexylsulfonylacetonitrile reacts in 78% ee and 94% yield (determined by <sup>1</sup>H NMR spectroscopy with CH<sub>2</sub>Br<sub>2</sub> as an internal standard).
The ability to include a substituent at the β'-position of the allenoate for enantioselective [4 + 1] annulations would represent a significant expansion in the scope of this chemistry as cyclopentenes with contiguous quaternary and tertiary stereocenters on the ring could be formed. In his original report, Tong reported a single example of a diastereoselective [4 + 1] annulation between benzoyleacetonitrile and an ethyl β'-substituted allenoate. The reaction, catalyzed by PPh₃, proceeded in good yield but only 2:1 dr.¹⁵ In addition, Lu reported one example of an enantioselective [4 + 1] annulation with a phenyl β'-substituted allenoate and a pyrazolone nucleophile. Amino acid-derived phosphine 1c catalyzes the reaction with good enantioselectivity (81% ee) and high diastereoselectivity (>20:1).¹⁶ In contrast to Lu’s result, we obtained a promising lead with an alkyl β'-substituted allenoate using an α-cyano sulfone as the nucleophile (eq 1.5).²¹

While some precedent for enantioselective and diastereoselective [4 + 1] annulations of β'-substituted allenoates already existed, to the best of our knowledge, no examples of Tong’s [4 + 1] annulation have previously been described with γ-substituted allenoates. We were therefore pleased that such an allenoate reacts with an α-cyano sulfone under our standard conditions to yield the target cyclopentene with high enantioselectivity, diastereoselectivity, and yield (eq 1.6).

²¹ (a) The minor diastereomer is formed in 28% ee. (b) The impact of the ester substituent on ee and dr was not investigated for reactions with β'-substituted allenoates and γ-substituted allenoates.
As originally proposed by Tong, phosphine-catalyzed [4 + 1] annulations may proceed through the pathway illustrated in Scheme 1.3. Attack of the phosphine at the β-position of the allenoate generates an enolate that can eliminate acetate to form a doubly activated diene phosphonium intermediate. Next, the deprotonated nucleophile attacks at the γ-position of the diene (attack at the β'-position of the diene is also possible). After a proton transfer, the resulting intermediate cyclizes to complete the cyclopentane ring and form another enolate intermediate. This time, the enolate eliminates the phosphine to furnish the cyclopentene product and regenerate the free catalyst.

Scheme 1.3. Outline of a Possible Pathway for Phosphine-Catalyzed [4 + 1] Annulations

In order to gain insight into the mechanism of this coupling, we determined the rate law using benzoylacetonitrile and a benzhydryl ester allenoate with phosphine 1d as a model system (the coupling illustrated in Table 1.1). This study was conducted at room temperature without cesium carbonate due to the poor solubility of cesium carbonate in toluene; at room temperature,
identical results are observed with and without cesium carbonate (89% ee and >95% yield). The reaction was determined to be first order in catalyst and zeroth order in nucleophile and allenoate. Furthermore, $^{31}$P NMR spectroscopy experiments indicate that the primary resting state of the catalyst is a phosphonium intermediate, not the free phosphine itself. Taken together, these data suggest that Step 1 and Step 3 (Scheme 3.1) are unlikely to be turnover-limiting.

C. Conclusion

In summary, we have synthesized new axially chiral biphenyl-derived phosphines and demonstrated the first use of this class of phosphines as enantioselective nucleophilic catalysts. Specifically, we applied these phosphines to enantioselective [4 + 1] annulations for the synthesis of cyclopentenes with a fully-substituted stereocenter (either all-carbon or heteroatom-substituted) in good ee and yield. Furthermore, the synthesis of more highly substituted and stereochemically rich products can be achieved through the use of substituted allenoates or through diastereoselective functionalizations of the cyclopentene products. Finally, preliminary investigations into the reaction mechanism (rate law and catalyst resting state) suggest that neither addition of the phosphine to the allenoate nor addition of the nucleophile to an allenoate adduct is the turnover-limiting step. This reaction complements the existing chiral phosphine-catalyzed asymmetric [3 + 2] annulation methods particularly by eliminating the formation of undesired regioisomeric products.
D. Experimental

I. General Information 25
II. Synthesis of Allenoates 26
III. Synthesis of Phosphepine Catalysts 29
IV. Catalytic Enantioselective [4+1] Annulations 36
V. Stereoselective Functionalization 53
VI. Mechanistic Studies 55
VII. X-Ray Crystallographic Data, inc. Determination of Stereochemistry 59
VIII. $^1$H NMR Spectra 135

I. General Information

The following reagents and solvents were purchased and used as received, unless otherwise specified: benzoylacetonitrile (Alfa Aesar), 4-methoxybenzoylacetonitrile (Aldrich), methyl 4-(cyanoacetyl)benzoate (Aldrich), 3-oxo-3-(2-thienyl)propionitrile (Alfa Aesar), pivaloylacetonitrile (TCI), $N,N$-dimethylcyanoacetamide (Alfa Aesar), 4-(cyanoacetyl)morpholine (Alfa Aesar), methyl cyanoacetate (Alfa Aesar; distilled), phenylsulfonylacetonitrile (Oakwood), tert-butylsulfonylacetonitrile (Alfa Aesar), Cs$_2$CO$_3$ (Aldrich), toluene (Aldrich, anhydrous), RuCl$_3$ (Aldrich), and NaIO$_4$ (Aldrich). All other nucleophiles have previously been reported and were synthesized according to literature procedures.

$^1$H, $^{13}$C, and $^{31}$P NMR spectroscopic data were collected on a Varian 500 MHz spectrometer at ambient temperature. $^{13}$C NMR spectroscopic data for all phosphorus-containing compounds were collected on a Varian 600 MHz spectrometer at ambient temperature with $^1$H and $^{31}$P decoupling. HPLC analyses were carried out using an Agilent 1100 Series system with Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 25.0 cm, particle size 5 μm). The resolution of the catalyst was carried out using a Gilson PLC 2020 Personal Purification System with a Daicel CHIRALPAK® IC column (internal diameter 2.0 cm, column length 25.0 cm, particle size 5 μm).
II. Synthesis of Allenoates

The yields have not been optimized.

\[
\text{MsO} \quad \equiv \quad \text{O} \quad \text{THP}
\]

4-((Tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-yl methanesulfonate [110284-14-5].

To an oven-dried 500-mL round-bottom flask with a stir bar was added 4-((tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-ol\(^{22}\) (9.80 g, 57.6 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles). Then, CH\(_2\)Cl\(_2\) (150 mL; anhydrous) and Et\(_3\)N (12.0 mL, 86.4 mmol) were added in turn. The reaction mixture was cooled to 0 °C in an ice bath, and then MsCl (5.4 mL, 69.1 mmol) was added dropwise over 5 min. The reaction mixture was stirred for ~2 h, at which time TLC analysis showed that the reaction was complete. Next, the reaction was diluted with water (150 mL), the organic layer was separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic extracts were dried over MgSO\(_4\) and concentrated, and the residue was purified by column chromatography (30% EtOAc/hexanes), which furnished the title compound (11.7 g, 86%) as a colorless oil.

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OH}
\end{array}
\]

Benzhydryl 2-(hydroxymethyl)buta-2,3-dienoate. To an oven-dried 1-L round-bottom flask with a stir bar was added 4-((tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-yl methanesulfonate (8.00 g, 34.1 mmol) and THF (350 mL; anhydrous). Next, Pd(PPh\(_3\))\(_4\) (1.98 g, 1.71 mmol) and benzhydrol (31.4 g, 170.5 mmol) were added in turn to the reaction mixture. The flask was evacuated and backfilled with nitrogen (3 cycles), and then 2,6-lutidine (9.9 mL, 85.3 mmol) was added via syringe. Next, the flask was evacuated and backfilled with CO via balloon (3 cycles). The reaction was stirred for ~2 h, at which time TLC analysis showed that the reaction was complete. The reaction mixture was concentrated, and the residue was purified by column chromatography (10% EtOAc/hexanes), which furnished a mixture of product and benzhydrol.

The mixture was dissolved in MeOH (250 mL), and pyridinium p-toluenesulfonate (897 mg, 3.57 mmol) was added. The reaction was stirred for ~16 h, at which time TLC analysis showed that the reaction was complete. The reaction mixture was concentrated, and the residue was purified by column chromatography on silica gel (30% EtOAc/hexanes), which furnished the title compound (3.24 g, 34% over two steps) as a colorless oil.

\[ \text{H NMR (500 MHz, CDCl}_3\delta \] 7.39–7.26 (m, 1OH), 6.95–6.92 (m, 1H), 5.34 (t, 2H, \( J = 2.0 \) Hz), 4.37–4.34 (m, 2H), 2.70–2.20 (br s, 1H).

\[ \text{C NMR (126 MHz, CDCl}_3\delta \] 213.6, 166.0, 140.2, 128.7, 128.1, 127.1, 100.0, 80.2, 77.7, 61.1.

FT-IR (neat) 3418, 3088, 3063, 3031, 2988, 2933, 2875, 1965, 1940, 1809, 1721, 1716, 1699, 1694, 1683, 1600, 1586, 1549, 1495, 1455, 1423, 1386, 1354, 1259, 1187, 1158, 1106, 1081, 1026, 974, 913, 890, 853, 812, 782, 744 cm\(^{-1}\).

MS (ESI) \( m/z \) (M–H) calcd for C\(_{18}\)H\(_{15}\)O\(_3\): 279, found: 279.

\[ \text{Benzhydryl 2-(acetoxyethyl)buta-2,3-dienoate} \text{. To an oven-dried 200-mL round-bottom flask with a stir bar was added benzhydryl 2-(hydroxymethyl)buta-2,3-dienoate (3.24 g, 11.6 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles), and then CH}_2\text{Cl}_2 (60 mL; anhydrous) and 2,6-lutidine (2.03 mL, 17.4 mmol) were added in turn via syringe. The reaction mixture was stirred, and a solution of acetyl chloride (1.24 mL, 17.4 mmol) in CH}_2\text{Cl}_2 (5 mL; anhydrous) was added dropwise to the reaction mixture. After ~2 h, at which time TLC analysis showed that the reaction was complete, the reaction mixture was directly filtered through a large plug of silica gel (20% EtOAc/hexanes; monitored by TLC) to afford the title compound (3.31 g, 89%) as a viscous, colorless oil.}

\[ \text{H NMR (500 MHz, CDCl}_3\delta \] 7.38–7.26 (m, 1OH), 6.95 (s, 1H), 5.37 (t, 2H, \( J = 2.5 \) Hz), 4.82 (t, 2H, \( J = 2.5 \) Hz), 2.04 (s, 3H).

\[ \text{C NMR (126 MHz, CDCl}_3\delta \] 215.3, 170.7, 164.4, 140.2, 128.7, 128.1, 127.1, 97.2, 80.7, 77.7, 61.0, 21.0.
FT-IR (neat) 3065, 3032, 2989, 1968, 1714, 1716, 1699, 1652, 1600, 1586, 1495, 1426, 1377, 1361, 1224, 1122, 1028, 972, 916, 857, 779, 744 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C₂₀H₁₈O₄: 322.1205, found: 322.1205.

\[
\begin{align*}
&\text{O} \\
&\text{Et} \\
&\text{OAc} \\
&\text{BnO} \\
&\text{II}
\end{align*}
\]

**Benzyl 3-acetoxy-2-vinylidenepentanoate.** The product was synthesized according to a literature procedure from benzyl buta-2,3-dienoate, propionaldehyde, and acetyl chloride.²³

\(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.39–7.28 (m, 5H), 5.54 (tdd, 1H, \(J = 2.0, 5.5, 7.5\) Hz), 5.32 (d, 2H, \(J = 2.0\) Hz), 5.22 (d, 1H, \(J = 12.5\) Hz), 5.18 (d, 1H, \(J = 12.5\) Hz), 2.02 (s, 3H), 1.86–1.70 (m, 2H), 0.92 (t, 3H, \(J = 7.5\) Hz).

\(^1^3\)C NMR (126 MHz, CDCl₃) \(\delta\) 213.7, 170.3, 165.3, 136.0, 128.6, 128.3, 128.1, 101.5, 81.7, 71.4, 66.8, 26.6, 21.2, 9.9.

FT-IR (neat) 3066, 2972, 2938, 2880, 1741, 1713, 1498, 1456, 1372, 1233, 1144, 1020, 968, 857, 782 cm⁻¹.

MS (FAB) m/z (M⁺+H) calcd for C₁₆H₁₉O₄: 275.1283, found: 275.1284.

\[
\begin{align*}
&\text{t-BuO} \\
&\text{O} \\
&\text{OAc} \\
&\text{Me} \\
&\text{II}
\end{align*}
\]

**t-Butyl 2-(acetoxymethyl)penta-2,3-dienoate.** The title compound was synthesized from 5-((tetrahydro-2H-pyran-2-yl)oxy)pent-3-yn-2-ol through the same synthetic pathway as for benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate.

\(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 5.61 (q, 1H, \(J = 7.5\) Hz), 4.74 (d, 1H, \(J = 12.5\) Hz), 4.70 (d, 1H, \(J = 12.5\) Hz), 2.06 (s, 3H), 1.78 (d, 3H, \(J = 7.0\) Hz), 1.47 (s, 9H).

\(^1^3\)C NMR (126 MHz, CDCl₃) \(\delta\) 211.3, 170.6, 165.0, 98.2, 91.1, 81.4, 61.6, 28.3, 21.0, 12.9.

III. Synthesis of Phosphepine Catalysts

(3,3'-Dibromo-6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dimethanol. To a 200-mL round-bottom flask with a stir bar was added (6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dimethanol24 (4.7 g, 17.2 mmol). This solid was dissolved in DMF (35 mL; anhydrous), and the resulting solution was cooled to 0 °C in an ice bath. Next, 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione (4.32 g, 15.1 mmol) was added portion-wise to the reaction mixture. After the addition was complete, the ice bath was removed, and the reaction mixture was stirred for 1 h while it warmed to r.t. Additional 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione (480 mg, 1.7 mmol) was added, and then the reaction mixture was stirred for ~20 h at r.t. Next, water (160 mL) was added, resulting in the formation of a white precipitate. The precipitate was collected by filtration and purified by two recrystallizations from hot toluene to yield the title compound (5.56 g, 75%) as a white solid.

^1H NMR (500 MHz, CDCl₃) δ 7.60 (d, 2H, J = 9.0 Hz), 6.82 (d, 2H, J = 9.0 Hz), 4.58 (d, 2H, J = 12.0 Hz), 4.10 (d, 2H, J = 12.0 Hz), 3.67 (s, 6H), 3.16 (br s, 2H).

^13C NMR (126 MHz, CDCl₃) δ 156.4, 139.3, 133.4, 127.2, 116.6, 112.2, 62.3, 56.2.

FT-IR (neat) 3233, 1569, 1474, 1459, 1430, 1289, 1263, 1235, 1204, 1134, 1077, 1036, 1015, 970, 920, 803, 781, 738 cm⁻¹.

MS (FAB) m/z (M⁺) calcd for C₁₆H₁₆Br₃BrO₄: 431.9395, found 431.9383.

3,3'-Dibromo-2,2'-bis(chloromethyl)-6,6'-dimethoxy-1,1'-biphenyl. To an oven-dried 250-mL round-bottom flask with a stir bar was added (3,3'-dibromo-6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dimethanol (5.56 g, 12.9 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles), and CH₂Cl₂ (130 mL; anhydrous) was added. Then, (i-Pr)₂EtN (9.0 mL, 51.6 mmol) was added, and the reaction mixture was cooled to 0 °C in an ice bath. MsCl (3.0 mL, 38.7 mmol) was added dropwise to the reaction mixture over ~20 min. After the addition was complete, the reaction was warmed to r.t. and stirred for 1 h. Next, water (150 mL) was added. The organic layer was separated from the aqueous layer and sequentially washed with 1 M HCl (150 mL x 2) and water (100 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated to afford the impure product, which was used in the next step without further purification.

The impure product was transferred to a 100-mL round-bottom flask with a stir bar. Then, LiCl (11.5 g, 271 mmol) was added, and the mixture was dissolved in DMA (21.0 mL; anhydrous). The reaction mixture was heated to 70 °C for ~14 h. Next, water (90 mL) was added, and the resulting solids were collected by filtration, dissolved in CH₂Cl₂, and purified by column chromatography on silica gel (33→50% CH₂Cl₂/hexanes), which furnished the title compound (5.75 g, 95%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, 2H, J = 9.0 Hz), 6.88 (d, 2H, J = 9.0 Hz), 4.35 (d, 2H, J = 11.0 Hz), 4.30 (d, 2H, J = 11.0 Hz), 3.70 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 156.6, 136.2, 134.0, 126.9, 116.2, 112.9, 56.1, 44.5.

FT-IR (neat) 2936, 2837, 1568, 1558, 1461, 1435, 1288, 1271, 1260, 1235, 1218, 1162, 1138, 1127, 1072, 1033, 940, 913, 894, 809, 778, 737 cm⁻¹.

MS (FAB) m/z (M⁺) calcd for C₁₆H₁₄Br₈BrCl₂O₂: 467.8717, found: 467.8736.
(11aR)-4,8-Dibromo-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[ce]phosphepine 6-oxide. An oven-dried 1-L round-bottom flask with a stir bar was charged with 3,3'-dibromo-2,2'-bis(chloromethyl)-6,6'-dimethoxy-1,1'-biphenyl (5.28 g, 11.3 mmol) and sodium hydride (678 mg, 28.3 mmol; 95%). Then, the flask was evacuated and backfilled with nitrogen (3 cycles). THF (428 mL; anhydrous) was added, and after all of the dichloride had dissolved, phenylphosphine (1.37 mL, 12.4 mmol) was added via syringe. The reaction was heated to 65 °C and stirred for 72 h. Next, the reaction mixture was concentrated to ~50 mL and then cooled to 0 °C in an ice bath. Then, water (100 mL) was carefully added, followed by tert-butylhydroperoxide (5 mL; 70% in water). The reaction was stirred for 1 h to ensure that all of the phosphine was oxidized to the phosphine oxide. The solution was then treated with aqueous Na₂S₂O₃ (50 mL; 10% by weight) and extracted with CH₂Cl₂ (150 mL x 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated, and the residue was purified by column chromatography on silica gel (15% EtOAc/CH₂Cl₂), which furnished the title compound (4.38 g, 74%) as a white solid.

The product was resolved by preparatory HPLC (CHIRALPAK® IC column, 2.0 cm x 25.0 cm, 8% 2-PrOH/CH₂Cl₂), which provided each enantiomer in >99% ee (2.11 g of the (R)-product (fast-eluting enantiomer), 2.06 g of the (S)-product (slow-eluting enantiomer)).

¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, 1H, J = 9.0 Hz), 7.57–7.51 (m, 2H), 7.50–7.45 (m, 2H), 7.44–7.38 (m, 2H), 6.85 (td, 2H, J = 2.5, 9.0 Hz), 3.89–3.73 (m, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.16 (dd, 1H, J = 8.5, 14.0 Hz), 3.10 (dd, 1H, J = 14.0, 22.0 Hz).

¹³C NMR (126 MHz, CDCl₃) δ 156.7, 156.4, 133.6, 133.2, 132.7, 132.3, 131.9, 131.1, 131.0, 128.6, 126.04, 126.01, 116.4, 115.9, 111.7, 111.6, 56.2, 35.8, 34.1.

FT-IR (neat) 3435, 3054, 2936, 2837, 1563, 1471, 1463, 1436, 1418, 1398, 1270, 1225, 1210, 1171, 1103, 1066, 1028, 999, 940, 860, 828, 806, 746, 728 cm⁻¹.

MS (FAB) m/z (M⁺+H) calc for C₂₂H₂₀Br₈BrO₃P: 522.9496, found: 522.9503.

[α]²⁵_D = −212° (c = 1.00, CHCl₃).
(11aR)-4,8-Di([1,1':3',1"'-terphenyl]-5'-yl)-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[c,e]phosphepine 6-oxide. To an oven-dried 100-mL round-bottom flask was added enantiopure (11aR)-4,8-dibromo-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[c,e]phosphepine 6-oxide (1.08 g, 2.1 mmol), Pd₂dba₃/HP(t-Bu)₃BF₄ (1:1.2) (340 mg, 0.21 mmol), 3,5-diphenylboronic acid (2.88 g, 10.5 mmol), and potassium fluoride dihydrate (1.58 g, 16.8 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles), and then THF (21.0 mL; anhydrous) was added. The reaction was stirred at r.t. for ~14 h. Next, the reaction mixture was diluted with Et₂O and filtered through a pad of silica gel, washing successively with Et₂O and toluene. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (25% EtOAc/hexanes), which furnished the title compound (1.62 g, 93%) as a white solid.

The absolute configuration of the product was determined by X-ray crystallography.

¹H NMR (500 MHz, CDCl₃) δ 7.96–7.64 (br, 5H), 7.59 (t, 1H, J = 2.0 Hz), 7.51–7.28 (m, 18H), 7.20–7.14 (m, 2H), 7.12–7.01 (m, 5H), 3.91 (s, 3H), 3.89 (s, 3H), 3.72 (t, 1H, J = 15.5 Hz), 3.46 (t, 1H, J = 15.5 Hz), 3.36 (dd, 1H, J = 14.0, 22.0 Hz), 3.22 (dd, 1H, J = 8.5, 14.0 Hz).

¹³C NMR (126 MHz, CDCl₃) δ 157.1, 156.8, 141.8, 141.4, 141.3, 140.9, 135.8, 135.0, 131.72, 131.66, 131.3, 131.1, 130.8, 130.5, 130.1, 128.8, 128.7, 128.2, 127.5, 127.41, 127.37, 125.3, 124.4, 124.3, 110.8, 109.9, 109.8, 56.2, 56.1, 33.2, 31.1.

FT-IR 3057, 3034, 2935, 2834, 2216, 1593, 1497, 1484, 1460, 1436, 1410, 1349, 1268, 1232, 1217, 1201, 1185, 1167, 1153, 1102, 1078, 1029, 945, 909, 883, 845, 813, 759, 733 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₅₈H₄₆O₃P: 821.3185, found 821.3167.

[α]25° = -98.3° (c = 1.00, CHCl₃).
(11aR)-4,8-Di[(1,1′:3′,1″-terphenyl]-5″-yl]-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[c,e]phosphepine ((R)-1d). To an oven-dried 100-mL round-bottom flask with a stir bar was added enantiopure (11aR)-4,8-di[(1,1′:3′,1″-terphenyl]-5″-yl]-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[c,e]phosphepine 6-oxide (1.62 g, 1.97 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles), and then toluene (39.4 mL; anhydrous), Et₃N (1.92 mL, 13.8 mmol), and HSiCl₃ (0.99 mL, 9.85 mmol) were added sequentially via syringe. The reaction was heated to 75 °C and stirred for ~14 h. Next, the reaction mixture was diluted with degassed water (40 mL), and NaOH (6 M) was added dropwise until the aqueous layer became clear. The organic layer was separated, and the aqueous layer was extracted with degassed toluene (20 mL x 3). The combined organic extracts were dried over MgSO₄, filtered through a pad of celite with toluene, and concentrated to afford the title compound (1.43 g, 90%) as a white solid.

$^1$H NMR (500 MHz, CDCl₃) δ 7.96–7.82 (br, 2H), 7.78 (t, 1H, J = 2.0 Hz), 7.74–7.68 (m, 4H), 7.65 (t, 1H, J = 1.5 Hz), 7.62–7.51 (br, 4H), 7.50–7.40 (m, 9H), 7.40–7.31 (m, 4H), 7.24 (d, 1H, J = 8.5 Hz), 7.04 (dd, 1H, J = 1.0, 8.5 Hz), 6.98 (d, 1H, J = 8.0 Hz), 6.91–6.83 (m, 4H), 6.71–6.64 (m, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.42 (dd, 1H, J = 4.0, 14.5 Hz), 2.98 (dd, 1H, J = 12.0, 14.5 Hz), 2.92–2.79 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl₃) δ 156.5, 156.2, 142.6, 142.4, 141.4, 141.12, 141.09, 136.2, 134.7, 134.2, 134.1, 133.6, 131.7, 130.6, 130.5, 128.9, 128.5, 127.9, 127.8, 127.7, 127.44, 127.37, 125.3, 124.9, 124.4, 123.6, 110.7, 109.3, 108.7, 56.2, 56.1, 27.9, 26.2.

FT-IR 3056, 3033, 2953, 2934, 2832, 1593, 1496, 1484, 1461, 1432, 1411, 1264, 1182, 1156, 1079, 1028, 944, 909, 882, 837, 807, 758, 737, 713, 697 cm⁻¹.

MS (ESI) $m/z$ (M$^+$+H) calcd for C₅₈H₄₆O₂P: 805.3235, found 805.3231.

$[\alpha]_{D}^{25} = -97.7°$ (c = 1.00, CHCl₃).
(11aR)-4,8-Bis(3,5-di-tert-butylphenyl)-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzol[c,e]phosphepine 6-oxide. To an oven-dried 100-mL round-bottom flask was added enantiopure (11aR)-4,8-dibromo-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzol[c,e]phosphepine 6-oxide (500 mg, 0.96 mmol), Pd2(dba)3/HP(t-Bu)3BF4 (156 mg, 0.096 mmol), 3,5-di-tert-boronic acid (899 mg, 3.84 mmol), and potassium fluoride dihydrate (723 mg, 7.68 mmol). The flask was evacuated and backfilled with nitrogen (3 cycles), and then THF (10.0 mL; anhydrous) was added. The reaction was stirred at r.t. for ~14 h. Next, the reaction mixture was diluted with Et2O and filtered through a pad of silica gel, washing successively with Et2O and toluene. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (12% EtOAc/hexanes), which furnished the title compound (513 mg, 72%) as a white solid.

1H NMR (500 MHz, CDCl3) δ 8.42–7.72 (br, 1H), 7.42 (d, 1H, J = 8.5 Hz), 7.40–7.34 (m, 2H), 7.30 (dd, 1H, J = 1.0, 8.5 Hz), 7.27–7.15 (m, 6H), 7.05 (t, 1H, J = 2.0 Hz), 7.03 (t, 1H, J = 2.0 Hz), 6.96–6.42 (br, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 3.75 (t, 1H, J = 15.0 Hz), 3.45–3.31 (m, 2H), 3.01 (dd, 1H, J = 8.5, 14.5 Hz), 1.36 (s, 18H), 1.18 (br s, 18H).

13C NMR (126 MHz, CDCl3) δ 156.8, 156.6, 150.4, 139.9, 139.6, 136.9, 136.5, 132.6, 131.7, 131.4, 131.2, 131.1, 130.6, 130.0, 128.2, 125.5, 125.2, 120.8, 120.4, 109.8, 109.7, 56.3, 56.2, 35.2, 34.8, 32.8, 32.6, 31.7, 31.5.

FT-IR 3060, 2961, 2866, 2200, 1593, 1484, 1464, 1393, 1362, 1395, 1285, 1268, 1248, 1218, 1202, 1167, 1151, 1100, 1077, 1050, 926, 910, 879, 862, 829, 811, 731 cm⁻¹.

MS (ESI) m/z (M+H) calcd for C50H62O3P: 741.4437, found 741.4438.

[α]25D = −173° (c = 1.00, CHCl3).
(11aR)-4,8-Bis(3,5-di-tert-butylphenyl)-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[\(c,e\)]phosphepine ((\(R\))-1e). To an oven-dried 20-mL vial with a stir bar was added enantiopure (11aR)-4,8-bis(3,5-di-tert-butylphenyl)-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[\(c,e\)]phosphepine 6-oxide (513 mg, 0.69 mmol). The vial was capped with a PTFE-lined septum cap and evacuated and backfilled with nitrogen (3 cycles). Then, toluene (13.8 mL; anhydrous), Et\(\text{3}N\) (675 \(\mu\)L, 4.84 mmol), and HSiCl\(_3\) (349 \(\mu\)L, 3.46 mmol) were added sequentially via syringe. The vial was detached from the nitrogen manifold, and the septum cap was covered with vacuum grease. The reaction was heated to 75 °C and stirred for \(~\)14 h. Next, the reaction mixture was diluted with degassed water (14 mL), and then NaOH (6 M) was added dropwise until the aqueous layer became clear. The organic layer was separated, and the aqueous layer was extracted with degassed toluene (10 mL x 3). The combined organic extracts were dried over MgSO\(_4\), filtered through a pad of celite with toluene, and concentrated to afford the title compound (491 mg, 98%) as a white solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53 (br, 2H), 7.38–7.33 (m, 2H), 7.23–7.18 (m, 2H), 7.15 (t, 1H, \(J = 7.5\) Hz), 7.04 (t, 2H, \(J = 7.5\) Hz), 7.00 (dd, 1H, \(J = 1.0, 8.5\) Hz), 6.96 (d, 1H, \(J = 8.5\) Hz), 6.90 (t, 2H, \(J = 7.0\) Hz), 6.95–6.40 (br, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.50 (dd, 1H, \(J = 3.5, 14.5\) Hz), 2.93–2.82 (m, 2H), 2.75 (dd, 1H, \(J = 4.0, 11.5\) Hz), 1.35 (s, 18H), 1.24 (br s, 18H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 156.3, 155.9, 150.2, 140.7, 140.6, 137.4, 135.7, 135.2, 134.8, 133.7, 132.4, 130.9, 130.6, 128.8, 127.9, 125.4, 125.1, 124.6, 120.4, 120.2, 110.9, 109.2, 108.7, 56.24, 56.19, 35.1, 34.9, 31.8, 31.6, 28.4, 26.9.

FT-IR 2962, 2903, 2866, 2832, 1593, 1484, 1432, 1393, 1362, 1287, 1265, 1203, 1153, 1079, 878, 808, 740 cm\(^{-1}\).

MS (ESI) \(m/z\) (M\(^{+}\)+H) calcd for C\(_{50}\)H\(_{42}\)O\(_2\)P: 725.4487, found 725.4488.
IV. Catalytic Enantioselective [4+1] Annulations

**General Procedure** (for a glovebox-free procedure, see the following paragraph). In a glovebox, an oven-dried 20-mL vial with a stir bar was charged with catalyst (0.040 mmol), nucleophile (0.48 mmol), Cs$_2$CO$_3$ (169 mg, 0.52 mmol), and toluene (3.2 mL; anhydrous). A separate oven-dried 20-mL vial was charged with allenolate (0.41 mmol) and toluene (3.3 mL; anhydrous). Both vials were capped with PTFE-lined septum caps, the joints were covered with electrical tape, and the vials were removed from the glovebox and fitted with a nitrogen-filled balloon. The catalyst solution was cooled to –10 °C and stirred (adequate stirring is necessary to achieve full conversion). Next, the allenolate solution (3.2 mL) was added to the catalyst solution via syringe. The nitrogen-filled balloon was detached, the septum cap was covered with vacuum grease, and the reaction mixture was stirred at –10 °C for 24 h. Next, a solution of t-BuOOH (100 μL; 5.0–6.0 M in decane) was added. The reaction mixture was allowed to warm to r.t., and then it was treated with an aqueous solution of Na$_2$S$_2$O$_3$ (10 mL; 10% by weight). The organic layer was separated, and the aqueous layer was washed with EtOAc (10 mL x 3). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$ and then concentrated, and the residue was purified by column chromatography.

**Glovebox-Free Procedure.** An oven-dried 20-mL vial with a stir bar was charged with catalyst (0.040 mmol), nucleophile (0.480 mmol), and Cs$_2$CO$_3$ (169 mg, 0.520 mmol). The vial was capped with a PTFE-lined septum cap, taped, and evacuated and backfilled with nitrogen (3 cycles). Next, toluene (3.2 mL; anhydrous) was added via syringe, and the reaction mixture was stirred. A separate oven-dried 20-mL vial was charged with allenolate (0.41 mmol), capped with a PTFE-lined septum cap, taped, and evacuated and backfilled with nitrogen (3 cycles). Then, the allenolate was dissolved in toluene (3.3 mL; anhydrous). Both vials were fitted with a nitrogen-filled balloon and detached from the nitrogen manifold. The catalyst solution was cooled to –10 °C and stirred (adequate stirring is necessary to achieve full conversion). Next, the allenolate solution (3.2 mL) was added to the catalyst solution via syringe. The nitrogen-filled balloon was detached, the septum cap was covered with vacuum grease, and the reaction mixture was stirred at –10 °C for 24 h. Then, a solution of t-BuOOH (100 μL; 5.0–6.0 M in decane) was
added. The reaction mixture was allowed to warm to r.t., and then it was treated with an aqueous solution of Na$_2$S$_2$O$_3$ (10 mL; 10% by weight). The organic layer was separated, and the aqueous layer was washed with EtOAc (10 mL x 3). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$ and then concentrated, and the residue was purified by column chromatography.

![Chemical structure](image)

**(S)-Benzhydryl 4-benzoyl-4-cyanocyclopent-1-enecarboxylate (Table 1.2, Entry 1).** The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxyethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), benzoylecetonitrile (69.7 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (5→10% EtOAc/hexanes). Pale-yellow solid. First run: 142 mg (87% yield), 94% ee. Second run ((S)-catalyst 1d): 136 mg (83% yield), 93% ee.

**Glovebox-Free Procedure:** ((R)-catalyst 1d): 126 mg (78% yield), 93% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 7% 2-PrOH/hexanes; 1.0 mL/min; retention times: 47.1 min (major), 53.4 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.14–8.10 (m, 2H), 7.66 (tt, 1H, J = 1.5, 7.5 Hz), 7.56–7.51 (m, 2H), 7.38–7.27 (m, 10H), 6.94 (s, 1H), 6.83 (quintet, 1H, J = 2.5 Hz), 3.70 (qd, 1H, J = 2.5, 19.0 Hz), 3.62–3.51 (m, 2H), 3.34–3.27 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 190.2, 162.3, 139.9, 139.5, 134.5, 133.0, 132.4, 129.9, 129.1, 128.7, 128.2, 127.25, 127.22, 122.1, 77.5, 48.0, 43.6, 42.8.

FT-IR (neat) 3081, 3063, 3030, 2960, 2924, 2240, 1717, 1694, 1640, 1595, 1580, 1495, 1448, 1424, 1368, 1344, 1319, 1307, 1261, 1241, 1187, 1171, 1099, 1063, 1030, 1000, 935, 906, 865, 840, 804, 795, 775, 743 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$+Na) calcd for C$_{27}$H$_{21}$NNaO$_3$: 430, found: 430.

$[\alpha]^{25}_D = -41.7^\circ$ (c = 1.00, CHCl$_3$).
(S)-Benzhydryl 4-cyano-4-(4-methoxybenzoyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 2). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 4-methoxybenzoylacetonitrile (84.1 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (7 → 15% EtOAc/hexanes). White solid. First run: 177 mg (101% yield), 93% ee. Second run ((S)-catalyst 1d): 165 mg (94% yield), 94% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 15% 2-PrOH/hexanes; 1.0 mL/min; retention times: 48.2 min (minor), 52.3 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14–8.09 (m, 2H), 7.38–7.27 (m, 10H), 7.02–6.97 (m, 2H), 6.94 (s, 1H), 6.82 (quintet, 1H, $J$ = 2.0 Hz), 3.90 (s, 3H), 3.71 (qd, 1H, $J$ = 2.5, 19.0 Hz), 3.61–3.49 (m, 2H), 3.28 (qd, 1H, $J$ = 2.5, 19.0 Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 188.4, 164.5, 162.4, 139.9, 139.7, 132.9, 132.4, 128.7, 128.2, 127.23, 127.21, 125.1, 122.4, 114.3, 77.4, 55.8, 47.7, 43.5, 42.9.

FT-IR (neat) 3064, 3031, 2935, 2841, 2235, 1716, 1683, 1644, 1600, 1575, 1511, 1495, 1455, 1422, 1367, 1315, 1261, 1241, 1176, 1099, 1064, 1029, 991, 965, 911, 842, 812, 777, 760, 738 cm$^{-1}$.

MS (El) $m/z$ (M$^+$) calcd for C$_{28}$H$_{23}$NO$_4$: 437.1627, found 437.1622.

$[\alpha]^{25}_D = -45.6^\circ$ (c = 1.00, CHCl$_3$).

(S)-Methyl 4-(3-((benzhydryloxy)carbonyl)-1-cyanocyclopent-3-ene carboxyl)benzoate (Table 1.2, Entry 3). The title compound was synthesized according to
the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), methyl 4-(cyanoacetyl)benzoate (97.5 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol), except that the reaction was run for 48 h. The product was purified by column chromatography on silica gel (7–15% EtOAc/hexanes). White solid. First run: 154 mg (83% yield), 94% ee. Second run ((S)-catalyst 1d): 153 mg (82% yield), 95% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 29.6 min (minor), 35.9 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20–8.15 (m, 4H), 7.37–7.27 (m, 10H), 6.94 (s, 1H), 6.83 (quintet, 1H, $J$ = 2.0 Hz), 3.97 (s, 3H), 3.68 (qd, 1H, $J$ = 2.5, 19.0 Hz), 3.58–3.54 (m, 2H), 3.32 (qd, 1H, $J$ = 2.0, 19.0 Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 189.9, 165.9, 162.2, 139.9, 139.4, 135.8, 135.1, 133.0, 130.2, 129.8, 128.7, 128.3, 127.25, 127.22, 121.7, 77.6, 52.8, 48.2, 43.5, 42.7.

FT-IR (neat) 3088, 3064, 3031, 2952, 2850, 2237, 1727, 1643, 1609, 1586, 1573, 1496, 1455, 1436, 1406, 1367, 1347, 1283, 1242, 1190, 1111, 1065, 1030, 992, 964, 912, 868, 829, 789, 725 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{29}$H$_{23}$NO$_5$: 465.1576, found 465.1560.

[$\alpha$]$^D_{25}$ = $-40.3^\circ$ (c = 1.00, CHCl$_3$).

(S)-Benzhydryl 4-cyano-4-(thiophene-2-carbonyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 4). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 3-oxo-3-(2-thienyl)propionitrile (72.6 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol), except that the reaction was run in 12.8 mL of toluene at 0 °C for 48 h. The product was purified by column chromatography on silica gel (7–12% EtOAc/hexanes). Pale-yellow solid. First run: 145 mg (88% yield), 90% ee. Second run ((S)-catalyst 1d): 145 mg (88% yield), 90% ee.
HPLC analysis: Daicel CHIRALPAK® AD column; 7% 2-PrOH/hexanes; 1.0 mL/min; retention times: 32.7 min (major), 40.3 min (minor).

The absolute configuration of the product was determined by X-ray crystallography.

^1^H NMR (500 MHz, CDCl₃) δ 8.11 (dd, 1H, J = 1.0, 4.0 Hz), 7.79 (dd, 1H, J = 1.0, 4.5 Hz), 7.38–7.27 (m, 10H), 7.22 (dd, 1H, J = 4.0, 5.0 Hz), 6.94 (s, 1H), 6.82 (quintet, 1H, J = 2.0 Hz), 3.68 (qd, 1H, J = 2.5, 19.0 Hz), 3.62–3.47 (m, 2H), 3.31–3.23 (m, 1H).

^1^C NMR (126 MHz, CDCl₃) δ 183.2, 162.3, 139.9, 139.5, 139.3, 136.4, 134.5, 133.0, 128.9, 128.7, 128.2, 127.22, 127.21, 122.1, 77.5, 48.5, 43.4, 43.0.

FT-IR (neat) 3089, 3031, 2926, 2237, 1717, 1668, 1600, 1586, 1516, 1495, 1455, 1409, 1367, 1354, 1308, 1262, 1241, 1188, 1100, 1068, 1051, 989, 964, 910, 838, 863, 729 cm⁻¹.

MS (El) m/z (M⁺) calced for C₂₅H₁₉NO₃S: 413.1086, found: 413.1097.

[α]₂⁵° = -26.9° (c = 1.00, CHCl₃).

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(S)-Benzhydryl 4-cyano-4-heptanoylcylopent-1-enecarboxylate (Table 1.2, Entry 5).

The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 3-oxononanenitrile (73.5 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (5→10% EtOAc/hexanes). White solid. First run: 151 mg (91% yield), 93% ee. Second run ((S)-catalyst 1d): 146 mg (88% yield), 93% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 5% 2-PrOH/hexanes; 1.0 mL/min; retention times: 18.3 min (major), 23.3 min (minor).

^1^H NMR (500 MHz, CDCl₃) δ 7.40–7.27 (m, 1H), 6.93 (s, 1H), 6.79–6.75 (m, 1H), 3.33–3.20 (m, 3H), 3.12–3.04 (m, 1H), 2.89–2.77 (m, 2H), 1.69–1.60 (m, 2H), 1.36–1.24 (m, 6H), 0.89 (t, 3H, J = 6.5 Hz).

^1^C NMR (126 MHz, CDCl₃) δ 201.2, 162.2, 139.9, 139.5, 133.0, 128.7, 128.2, 127.2, 121.6, 77.5 50.7, 42.4, 41.7, 39.6, 31.6, 28.7, 23.8, 22.6, 14.1.
(S)-Benzhydryl 4-cyano-4-(cyclohexanecarbonyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 6). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 3-cyclohexyl-3-oxopropanenitrile (72.6 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by flash chromatography on silica gel (5→10% EtOAc/hexanes). White solid. First run: 162 mg (98% yield), 93% ee. Second run ((S)-catalyst 1d): 154 mg (93% yield), 93% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 5% 2-PrOH/hexanes; 1.0 mL/min; retention times: 22.0 min (major), 24.9 min (minor).

The absolute configuration of the product was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.37–7.28 (m, 1OH), 6.93 (s, 1H), 6.76 (quintet, 1H, $J = 2.0$ Hz), 3.32–3.21 (m, 3H), 3.13–3.04 (m, 1H), 3.00 (tt, 1H, $J = 3.5$, 11.5 Hz), 1.99–1.88 (m, 2H), 1.86–1.78 (m, 2H), 1.76–1.68 (m, 1H), 1.52–1.30 (m, 4H), 1.29–1.18 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 204.4, 162.3, 139.9, 139.5, 133.0, 128.7, 128.2, 127.23, 127.20, 121.7, 77.4, 50.3, 48.7, 42.9, 42.0, 29.7, 29.6, 25.6, 25.42, 25.40.

FT-IR (neat) 3064, 3031, 2855, 2237, 1721, 1641, 1600, 1495, 1450, 1367, 1309, 1260, 1241, 1188, 1149, 1127, 1093, 1030, 987, 905, 851, 740 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{27}$H$_{29}$NO$_3$: 415.2147, found: 415.2159.

$[\alpha]^{25}_D = -21.5^\circ$ (c = 1.00, CHCl$_3$).

FT-IR (neat) 3064, 3032, 2955, 2929, 2858, 2238, 1721, 1641, 1600, 1586, 1495, 1455, 1402, 1366, 1308, 1260, 1241, 1188, 1140, 1091, 1031, 1002, 984, 914, 864, 758, 741 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{27}$H$_{29}$NO$_3$: 415.2147, found: 415.2159.

$[\alpha]^{25}_D = -21.5^\circ$ (c = 1.00, CHCl$_3$).
(S)-Benzhydryl 4-cyano-4-pivaloylcyclopent-1-enecarboxylate (Table 1.2, Entry 7). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), pivaloylacetonitrile (60.1 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (4→10% EtOAc/hexanes). White solid. First run: 114 mg (74% yield), 94% ee. Second run ((S)-catalyst 1d): 118 mg (76% yield), 95% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 5% 2-PrOH/hexanes; 1.0 mL/min; retention times: 26.8 min (minor), 29.0 min (major).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.41–7.27 (m, 10H), 6.94 (s, 1H), 6.79–6.76 (m, 1H), 3.39–3.28 (m, 2H), 3.27–3.20 (m, 1H), 3.17–3.09 (m, 1H), 1.40 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 205.9, 162.4, 139.9, 139.3, 132.7, 128.7, 128.2, 127.25, 127.23, 122.8, 77.4, 47.6, 46.0, 45.2, 44.0, 27.3.

FT-IR (neat) 3064, 3032, 2971, 2235, 1720, 1716, 1644, 1600, 1586, 1495, 1480, 1455, 1428, 1398, 1368, 1307, 1261, 1242, 1188, 1092, 1030, 1002, 987, 961, 915, 863, 758, 742 cm\(^{-1}\).

MS (EI) \(m/z\) (M\(^+\)) calcd for C\(_{25}\)H\(_{25}\)NO\(_3\): 387.1834, found: 387.1837.

\([\alpha]\)\(^{25}\)\(_D\) = \(-33.4^\circ\) (c = 1.00, CHCl\(_3\)).

(S)-Benzhydryl 4-cyano-4-(dimethylcarbamoyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 8). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), \(N,N\)-dimethylcyanoacetamide (53.8 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (25→30% EtOAc/hexanes).
White solid. First run: 110 mg (73% yield), 83% ee. Second run ((S)-catalyst 1d): 110 mg (73% yield), 83% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 18.9 min (major), 22.9 min (minor).

^1H NMR (500 MHz, CDCl₃) δ 7.37–7.27 (m, 1OH), 6.93 (s, 1H), 6.82 (quintet, 1H, J = 2.5 Hz), 3.74 (qd, 1H, J = 2.5, 19.0 Hz), 3.45–3.36 (m, 2H), 3.26 (s, 3H), 3.19 (qd, 1H, J = 2.5, 19.0 Hz), 3.03 (s, 3H).

^13C NMR (126 MHz, CDCl₃) δ 165.3, 162.4, 139.9, 132.5, 128.7, 128.2, 127.2, 121.3, 77.4, 44.3, 43.7, 42.8, 38.8, 37.7.

FT-IR (neat) 3063, 3032, 2930, 2234, 1716, 1661, 1652, 1586, 1495, 1455, 1390, 1367, 1309, 1243, 1188, 1154, 1097, 1052, 1030, 992, 966, 913, 861, 741 cm⁻¹.

MS (El) m/z (M⁺) calcd for C₂₃H₂₂N₂O₃: 374.1630, found: 374.1628.

[α]²⁵ D = −43.6° (c = 1.00, CHCl₃).

(S)-Benzhydryl 4-cyano-4-(diphenylcarbamoyl)cyclopent-1-ene carboxylate (Table 1.2, Entry 9). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 2-cyano-N,N-diphenylacetamide (113 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (10→20% EtOAc/hexanes). White solid. First run: 186 mg (93% yield), 91% ee. Second run ((S)-catalyst 1d): 184 mg (92% yield), 91% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 45.1 min (major), 58.0 min (minor).

^1H NMR (500 MHz, CDCl₃) δ 7.47–7.26 (m, 20H), 6.90 (s, 1H), 6.79–6.75 (m, 1H), 3.66 (qd, 1H, J = 2.5, 19.0 Hz), 3.50 (qd, 1H, J = 2.5, 16.5 Hz), 3.07–3.04 (m, 1H), 3.04–3.00 (m, 1H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.7, 162.4, 140.0, 139.5, 132.8, 129.8, 128.7, 128.2, 127.2, 121.3, 77.4, 47.3, 46.2, 44.5.

FT-IR (neat) 3063, 3032, 2928, 2854, 2251, 2235, 1716, 1674, 1595, 1492, 1454, 1432, 1342, 1305, 1241, 1186, 1098, 1030, 990, 959, 911, 865, 841, 757, 730 cm$^{-1}$.

MS (El) m/z (M') calcd for C$_{33}$H$_{26}$N$_2$O$_3$: 498.1944, found: 498.1949.

$[\alpha]_{25}^D = -60.2^\circ$ (c = 1.00, CHCl$_3$).

(S)-Benzhydryl 4-cyano-4-(methoxy(methyl)carbamoyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 10). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 2-cyano-N-methoxy-N-methylacetamide (61.5 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol), except that the reaction was run in 12.8 mL of toluene for 48 h. The product was purified by column chromatography on silica gel (17$\rightarrow$25% EtOAc/hexanes), followed by column chromatography on reverse-phase C-18 silica gel (5$\rightarrow$100% acetonitrile/water). White solid. First run: 119 mg (76% yield), 86% ee. Second run ((S)-catalyst 1d): 109 mg (70% yield), 86% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 25% 2-PrOH/hexanes; 1.0 mL/min; retention times: 12.6 min (major), 13.9 min (minor).

The absolute configuration of the product was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.37–7.27 (m, 10H), 6.93 (s, 1H), 6.79 (quintet, 1H, $J = 2.5$ Hz), 3.87 (s, 3H), 3.50 (qd, 1H, $J = 3.0$, 19.0 Hz), 3.44–3.33 (m, 2H), 3.27 (s, 3H), 3.22–3.14 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.1, 162.5, 140.0, 139.6, 133.0, 128.7, 128.2, 127.2, 121.6, 77.4, 41.0, 44.0, 43.3, 42.1, 33.6.

FT-IR (neat) 3030, 2942, 2239, 1717, 1674, 1496, 1455, 1368, 1308, 1242, 1175, 1095, 1049, 1030, 977, 907, 861, 741, 726 cm$^{-1}$.
MS (FAB) $m/z$ (M$^+$−H) calcd for C$_{23}$H$_{21}$N$_2$O$_4$: 389.1501, found: 389.1516.

$[\alpha]^{25}_D = -45.7^\circ$ (c = 1.00, CHCl$_3$).

(S)-Benzhydryl 4-cyano-4-(morpholine-4-carbonyl)cyclopent-1-enecarboxylate

(Table 1.2, Entry 11). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 4-(cyanoacetyl)morpholine (74.0 mg, 0.48 mmol), and (R)-catalyst 1d (32.2 mg, 0.040 mmol).

The product was purified by column chromatography on silica gel (25→35% EtOAc/hexanes).

White solid. First run: 143 mg (86% yield), 88% ee. Second run ((S)-catalyst 1d): 142 mg (85% yield), 88% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 37.2 min (major), 42.1 (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.38–7.27 (m, 10H), 6.93 (s, 1H), 6.82 (quintet, 1H, $J = 2.5$ Hz), 3.86–3.55 (m, 9H), 3.44–3.33 (m, 2H), 3.18 (qd, 1H, $J = 2.5$, 19.0 Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.4, 162.3, 139.9, 139.8, 132.5, 128.7, 128.2, 127.22, 127.21, 121.3, 77.5, 66.8, 66.0, 47.8, 44.2, 44.1, 43.4, 42.7.

FT-IR (neat) 3064, 3031, 2965, 2923, 2857, 2234, 1717, 1658, 1496, 1455, 1427, 1366, 1303, 1272, 1242, 1188, 1112, 1098, 1030, 991, 965, 910, 863, 841, 730 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$+Na) calcd for C$_{25}$H$_{24}$N$_2$NaO$_4$: 439, found: 439.

$[\alpha]^{25}_D = -52.9^\circ$ (c = 1.00, CHCl$_3$).
(S)-3-Benzhydryl 1-methyl 1-cyanocyclopent-3-ene-1,3-dicarboxylate (Table 1.2, Entry 12). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), methyl cyanoacetate (47.6 mg, 0.48 mmol), and (R)-catalyst 1d (64.4 mg, 0.080 mmol), except that the reaction was run in 12.8 mL of toluene for 48 h. The product was purified by column chromatography on silica gel (7→15% EtOAc/hexanes). White solid. First run: 86 mg (59% yield), 82% ee. Second run ((S)-catalyst 1d): 90 mg (62% yield), 82% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 4% 2-PrOH/hexanes; 1.0 mL/min; retention times: 34.9 min (major), 41.3 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.38–7.27 (m, 10H), 6.94 (s, 1H), 6.79 (quintet, 1H, $J = 2.5$ Hz), 3.87 (s, 3H), 3.45–3.33 (m, 3H), 3.27–3.19 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 168.9, 162.2, 139.9, 139.2, 133.5, 128.7, 128.2, 127.2, 120.2, 77.5, 54.3, 45.4, 44.1, 42.8.

FT-IR (neat) 3064, 3031, 2955, 2246, 1748, 1717, 1641, 1600, 1568, 1496, 1455, 1435, 1367, 1279, 1259, 1241, 1187, 1097, 1062, 1030, 988, 962, 906, 839, 741 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{22}$H$_{19}$NO$_4$: 361.1314, found: 361.1321.

$[\alpha]_{D}^{25} = -12.0^\circ$ (c = 1.00, CHCl$_3$).

(R)-Benzhydryl 4-cyano-4-(phenylsulfonyl)cyclopent-1-enecarboxylate (Table 1.3, Entry 1). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), phenylsulfonylacetonitrile (87.0 mg, 0.48 mmol), and (R)-catalyst 1e (29.0 mg, 0.040 mmol). The product was purified by
column chromatography on silica gel (10→15% EtOAc/hexanes). White solid. First run: 167 mg (94% yield), 90% ee. Second run ((S)-catalyst 1e): 173 mg (98% yield), 88% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 7% 2-PrOH/hexanes; 1.0 mL/min; retention times: 57.0 min (major), 62.1 min (minor).

The absolute configuration of the product (with (S)-catalyst 1e) was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.08–8.03 (m, 2H), 7.79 (tt, 1H, $J = 1.5, 7.5$ Hz), 7.69–7.63 (m, 2H), 7.39–7.28 (m, 10H), 6.93 (s, 1H), 6.78 (quintet, 1H, $J = 2.0$ Hz), 3.65–3.55 (m, 2H), 3.25–3.14 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.7, 139.7, 138.3, 135.7, 134.2, 133.3, 130.6, 129.8, 128.8, 128.3, 127.23, 127.21, 118.2, 77.8, 64.1, 41.3, 40.2.

FT-IR (neat) 3064, 3031, 2925, 2243, 1718, 1643, 1600, 1583, 1496, 1479, 1448, 1430, 1369, 1331, 1312, 1262, 1243, 1182, 1155, 1099, 1085, 1047, 1030, 988, 963, 911, 864, 723 cm$^{-1}$.

MS (EI) $\text{m/}z$ (M$^+$) calcd for C$_{26}$H$_{21}$NO$_4$S: 443.1191, found: 443.1207.

$[\alpha]_{D}^{25} = +25.1^\circ$ (c = 1.00, CHCl$_3$).

(R)-Benzhydryl 4-cyano-4-(cyclohexylsulfonyl)cyclopent-1-enecarboxylate (Table 1.3, Entry 2). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 2-(cyclohexylsulfonyl)acetonitrile (89.9 mg, 0.48 mmol), and (R)-catalyst 1e (29.0 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (7→12% EtOAc/hexanes), followed by column chromatography on reverse-phase C-18 silica gel (5→100% acetonitrile/water). White solid. First run: 156 mg (87% yield), 87% ee. Second run ((S)-catalyst 1e): 162 mg (90% yield), 86% ee.
HPLC analysis: Daicel CHIRALPAK® AD column; 15% 2-PrOH/hexanes; 1.0 mL/min; retention times: 17.8 min (minor), 24.1 min (major).

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.39–7.28 (m, 10H), 6.95 (s, 1H), 6.79 (quintet, 1H, J = 2.5 Hz), 3.65–3.60 (m, 1H), 3.60–3.56 (m, 1H), 3.50 (tt, 1H, J = 3.5, 12.0 Hz), 3.42–3.35 (m, 1H), 3.31-3.23 (m, 1H), 2.34–2.23 (m, 2H), 2.02–1.93 (m, 2H), 1.79–1.65 (m, 3H), 1.44–1.33 (m, 2H), 1.32–1.21 (m, 1H).

\(^{13}\)C NMR (126 MHz, CDCl₃) δ 161.8, 139.7, 138.1, 133.1, 128.7, 128.3, 127.2, 118.5, 77.8, 61.8, 61.6, 42.0, 40.8, 25.91, 25.86, 25.1, 24.9.

FT-IR (neat) 3064, 3032, 2938, 2859, 2241, 1717, 1645, 1600, 1586, 1495, 1454, 1429, 1368, 1319, 1263, 1242, 1184, 1139, 1098, 1042, 1031, 990, 912, 849, 818, 738 cm⁻¹.

MS (El) m/z (M⁺) calcd for C₂₆H₂₇NO₄S: 449.1661, found: 449.1655.

\([\alpha]^{25}_D = +11.9^\circ\) (c = 1.00, CHCl₃).

(R)-Benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate (Table 1.3, Entry 3). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), tert-butylsulfonylacetonitrile (77.4 mg, 0.48 mmol), and (R)-catalyst le (29.0 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (10→15% EtOAc/hexanes). White solid. First run: 162 mg (96% yield), 95% ee. Second run ((S)-catalyst 1e): 166 mg (98% yield), 94% ee.

Glovebox-Free Procedure: (R)-catalyst 1e): 166 mg (98% yield), 95% ee.

HPLC analysis: Daicel CHIRALCELL® OD column; 15% 2-PrOH/hexanes; 1.0 mL/min; retention times: 11.9 (minor), 14.9 (major).

The absolute configuration of the product (with (S)-catalyst 1e) was determined by X-ray crystallography.
(R)-Benzhydryl 4-cyano-4-(diphenylphosphoryl)cyclopent-1-enecarboxylate (Table 1.3, Entry 4). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), 2-(diphenylphosphoryl)acetonitrile (116 mg, 0.48 mmol), and (R)-catalyst 1e (29.0 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (35→45% EtOAc/hexanes). White solid. First run: 177 mg (88% yield), 84% ee. Second run ((S)-catalyst 1e): 170 mg (84% yield), 83% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 31.1 min (major), 39.4 (minor).

The product (with (S)-catalyst 1e) was enriched to higher ee by preparatory HPLC (CHIRALPAK® IB column, 2.0 cm x 25.0 cm, 14% 2-PrOH/hexanes), which yielded the product in 95% ee. After dihydroxylation of the enantioenriched compound, the absolute configuration was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.09–7.99 (m, 4H), 7.67–7.61 (m, 2H), 7.59–7.53 (m, 4H), 7.37–7.27 (m, 10H), 6.92 (s, 1H), 6.81–6.78 (m, 1H), 3.62–3.48 (m, 2H), 3.16–3.08 (m, 1H), 3.02–2.92 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.8, 139.70, 139.68, 137.9, 133.0, 128.7, 128.3, 127.2, 119.2, 77.7, 67.1, 61.5, 43.4, 41.8, 25.5.

FT-IR (neat) 3067, 3032, 2980, 2938, 2241, 1716, 1636, 1586, 1496, 1465, 1455, 1430, 1399, 1367, 1348, 1308, 1261, 1242, 1187, 1120, 1099, 1047, 1031, 1018, 985, 966, 911, 863, 775, 757, 738 cm$^{-1}$.

MS (FAB) $m/z$ (M–H) calcd for C$_{24}$H$_{24}$NO$_4$S: 422.1426, found: 422.1407.

$[\alpha]^{25}_{D} = +13.3^\circ$ (c = 1.00, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38–7.28 (m, 10H), 6.95 (s, 1H), 6.82–6.78 (m, 1H), 3.68–3.64 (m, 1H), 3.64–3.60 (in, 1H), 3.44–3.37 (in, 1H), 3.33–3.25 (in, 1H), 1.65 (s, 9H).
\[^{13}\text{C} \text{NMR} \ (126 \ \text{MHz}, \ \text{CDCl}_3) \ \delta \ 162.3, \ 139.8, \ 139.4, \ 134.0, \ 133.3, \ 133.2, \ 132.1, \ 132.0, \ 129.2, \ 129.1, \ 128.7, \ 128.2, \ 127.3, \ 127.2, \ 122.5, \ 77.5, \ 41.3, \ 40.3, \ 39.6. \]

FT-IR (neat) 3062, 3031, 2925, 2852, 2232, 1716, 1641, 1589, 1495, 1485, 1455, 1438, 1366, 1346, 1307, 1261, 1240, 1203, 1118, 1093, 1029, 997, 985, 911, 862, 726 cm\(^{-1}\).

MS (FAB) \(m/z\) (M\(^+\)+H) calcd for C\(_{32}\)H\(_{27}\)NO\(_3\)P: 504.1729, found: 504.1705.

\([\alpha]^{25}_D = +18.5^\circ \ \text{(c} = 1.00, \ \text{CHCl}_3\)).

(R)-Benzhydryl 4-cyano-4-(diphenoxophosphoryl)cyclopent-1-enecarboxylate (Table 1.3, Entry 5). The title compound was synthesized according to the General Procedure from benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (129 mg, 0.40 mmol), diphenyl (cyanomethyl)phosphonate (131 mg, 0.48 mmol), and (R)-catalyst 1e (29.0 mg, 0.040 mmol). The product was purified by flash chromatography on silica gel (20->25% EtOAc/hexanes). Colorless oil. First run: 184 mg (86% yield), 86% ee. Second run ((S)-catalyst 1e): 194 mg (91% yield), 88% ee.

HPLC analysis: Daicel CHIRALPAK\(^\text{®}\) AD column; 20% 2-ProOH/hexanes: 1.0 mL/min; retention times: 30.6 min (minor), 40.3 min (major).

\(^1\text{H} \text{NMR} \ (500 \ \text{MHz}, \ \text{CDCl}_3) \ \delta \ 7.39-7.28 \ (m, \ 14H), \ 7.25-7.19 \ (m, \ 6H), \ 6.94 \ (s, \ 1H), \ 6.85-6.81 \ (m, \ 1H), \ 3.61-3.43 \ (m, \ 2H), \ 3.42-3.34 \ (m, \ 1H), \ 3.30-3.21 \ (m, \ 1H).

\(^{13}\text{C} \text{NMR} \ (126 \ \text{MHz}, \ \text{CDCl}_3) \ \delta \ 161.9, \ 149.89, \ 149.86, \ 139.71, \ 139.70, \ 139.0, \ 133.9, \ 130.0, \ 128.6, \ 128.1, \ 127.1, \ 126.0, \ 120.4, \ 119.7, \ 77.5, \ 41.7, \ 40.1, \ 38.5.

FT-IR (neat) 3064, 3031, 2926, 2238, 1719, 1643, 1589, 1488, 1456, 1366, 1308, 1284, 1241, 1206, 1182, 1161, 1095, 1071, 1025, 1009, 985, 953, 828, 762 cm\(^{-1}\).

MS (FAB) \(m/z\) (M\(^+\)+Na) calcd for C\(_{32}\)H\(_{26}\)NNaO\(_3\)P: 558.1446, found: 558.1447.

\([\alpha]^{25}_D = +1.2^\circ \ \text{(c} = 1.00, \ \text{CHCl}_3\)).
(4S,5S)-Benzyl 4-(tert-butylsulfonyl)-4-cyano-5-ethylcyclopent-1-enecarboxylate (eq 1.5). The title compound was synthesized according to the General Procedure from benzyl 3-acetoxy-2-vinylidenepentanoate (110 mg, 0.40 mmol), tert-butylsulfonylacetonitrile (77.4 mg, 0.48 mmol), and (S)-catalyst 1d (32.2 mg, 0.040 mmol), except that the reaction was run for 72 h. The product was purified by column chromatography on silica gel (12% EtOAc/hexanes). White solid. First run: 125 mg (83% yield), 82% ee, 6.0:1 dr. Second run ((R)-catalyst 1d): 130 mg (87% yield), 82% ee, 5.7:1 dr.

The dr of the reaction was determined through analysis of the unpurified reaction mixture by $^1$H NMR spectroscopy.

HPLC analysis: Daicel CHIRALCEL® OD column; 10% 2-PrOH/hexanes; 1.0 mL/min; retention times: 15.1 min (minor), 25.4 min (major).

The product was enriched to higher ee by preparatory HPLC (CHIRALPAK® IC column, 2.0 cm x 25.0 cm, 12.5% 2-PrOH/hexanes), which furnished the major diastereomer in >99% ee. The absolute configuration of the enantioenriched compound was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.40–7.31 (m, 5H), 6.68 (dd, 1H, $J = 1.5, 2.5$ Hz), 5.21 (d, 1H, $J = 12.0$ Hz), 5.17 (d, 1H, $J = 12.0$ Hz), 4.05–3.98 (m, 1H), 3.68 (ddd, 1H, $J = 0.5, 3.0, 19.5$ Hz), 3.22 (td, 1H, $J = 2.5, 20.0$ Hz), 2.15–1.98 (m, 2H), 1.67 (s, 9H), 1.01 (t, 3H, $J = 7.5$ Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.9, 138.2, 136.6, 135.6, 128.8, 128.5, 128.3, 117.5, 68.7, 66.8, 66.6, 51.3, 43.5, 26.0, 24.3, 10.8.

FT-IR (neat) 3066, 3033, 2971, 2938, 2880, 2238, 1716, 1649, 1498, 1478, 1456, 1385, 1340, 1307, 1240, 1184, 1118, 1091, 1065, 1015, 992, 970, 917, 793, 770, 739 cm$^{-1}$. 

MS (FAB) m/z (M$^+$/H) calcd for C$_{20}$H$_{26}$NO$_4$S: 376.1582, found: 376.1577.

[$\alpha$]$^2_{D} = +12.2^\circ$ (c = 1.00, CHCl$_3$).
(3R,4R)-tert-Butyl 4-(tert-butylsulfonyl)-4-cyano-3-methylcyclopent-1-enecarboxylate (eq 1.6). The title compound was synthesized according to the General Procedure from tert-butyl 2-(acetoxymethyl)penta-2,3-dienoate (45.3 mg, 0.20 mmol), tert-butylsulfonylacetonitrile (38.7 mg, 0.24 mmol), and (S)-catalyst 1d (16.1 mg, 0.02 mmol). The product was purified by column chromatography on silica gel (10% EtOAc/hexanes). White solid. First run: 65.7 mg (100% yield), 96% ee, >20:1 dr. Second run ((R)-catalyst 1d): 64.5 mg (98% yield), 96% ee, >20:1 dr.

The dr of the reaction was determined through analysis of the unpurified reaction mixture by $^1$H NMR spectroscopy.

HPLC analysis: Daicel CHIRALCEL® OD column; 8% 2-PrOH/hexanes; 1.0 mL/min; retention times: 7.8 min (minor), 16.7 min (major).

The absolute configuration of the product was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.40–6.36 (m, 1H), 3.99–3.92 (m, 1H), 3.49 (td, 1H, $J$ = 3.0, 17.0 Hz), 3.32 (td, 1H, $J$ = 1.5, 17.0 Hz), 1.64 (s, 9H), 3.10 (d, 3H, $J$ = 7.5 Hz), 1.49 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.5, 141.8, 132.8, 117.0, 81.8, 67.6, 46.9, 43.0, 28.2, 25.5, 17.4.

FT-IR (neat) 2978, 2937, 2237, 1709, 1647, 1478, 1458, 1394, 1369, 1356, 1306, 1275, 1260, 1171, 1120, 1093, 933, 847, 794, 751 cm$^{-1}$.

MS (FAB) $m/z$ (M$^+$+H) calcd for C$_{16}$H$_{26}$NO$_4$S: 328.1582, found: 328.1579.

[α]$^{25}_D$ = +70.1° (c = 1.00, CHCl$_3$).
V. Stereoselective Functionalization

(1S,2R,4R)-Benzhydryl 4-(tert-butylsulfonfyl)-4-cyano-1,2-dihydroxycyclopentane carboxylate (eq 1.3). The title compound was synthesized, according to a literature procedure for dihydroxylation, from (R)-benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate (127 mg, 0.30 mmol, 95% ee), NaIO$_4$ (96.3 mg, 0.45 mmol), and RuCl$_3$ (3 small crystals). The reaction was run at 0 °C for 10 min (in the case of longer reaction times, decomposition of the product is observed). The product was purified by column chromatography on silica gel (33% EtOAc/hexanes). White solid. First run: 111 mg (81% yield), 96% ee, >20:1 dr. Second run ((S)-benzhydryl 4-(tert-butylsulfonfyl)-4-cyanocyclopent-1-enecarboxylate, 0.20 mmol, 94% ee): 70.2 mg (77% yield), 95% ee, >20:1 dr.

The dr of the reaction was determined through analysis of the unpurified reaction mixture by $^1$H NMR spectroscopy.

HPLC analysis: Daicel CHIRALCEL® OD column; 20% 2-PrOH/hexanes; 1.0 mL/min; retention times: 15.7 min (minor), 18.3 min (major).

The relative stereochemistry of the product was determined by X-ray crystallography.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.39–7.28 (m, 10H), 6.93 (s, 1H), 4.59 (q, 1H, $J$ = 8.5 Hz), 3.82 (s, 1H), 3.18 (dd, 1H, $J$ = 8.0, 14.5 Hz), 3.15 (d, 1H, $J$ = 14.0 Hz), 2.65 (d, 1H, $J$ = 14.5 Hz), 2.52–2.44 (m, 2H), 1.63 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.2, 139.0, 138.9, 129.0, 128.9, 128.7, 128.6, 127.1, 126.9, 119.1, 80.7, 79.9, 75.6, 67.7, 59.8, 43.6, 40.9, 25.8.

FT-IR (neat) 3477, 3064, 3032, 2976, 2242, 1738, 1600, 1586, 1496, 1478, 1454, 1401, 1367, 1306, 1256, 1202, 1187, 1146, 1118, 1083, 1030, 1002, 959, 911, 796, 738 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{24}$H$_{27}$NO$_6$S: 457.1559, found: 457.1578.

$[\alpha]^D_{25} = +3.7^\circ$ (c = 1.00, CHCl$_3$).
(1S,3R,5R)-Benzhydryl 3-(tert-butylsulfonyl)-3-cyano-6-oxabicyclo[3.1.0]hexane-1-carboxylate (eq 1.4). MCPBA (89.8 mg, 0.400 mmol; based on 77% purity) was added to an oven-dried 4-mL vial with a stir bar. The vial was capped, purged with nitrogen, and 1,2-dichloroethane (0.25 mL; anhydrous) was added. Then, (R)-benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate (24.2 mg, 0.050 mmol; 88% ee) was added as a solution in 1,2-dichloroethane (0.25 mL). The cap of the vial was covered with vacuum grease, and the reaction mixture was heated to 50 °C. After 48 h, the reaction was quenched with a 1:1 mixture of 10% Na₂S₂O₃ and saturated NaHCO₃ (1.6 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2 mL x 3). The combined organic extracts were concentrated, and the product was purified by column chromatography on silica gel (5→25% EtOAc/hexanes). White solid. First run: 12.5 mg (57% yield), 12:1 dr. Second run: 11.7 mg (53% yield), 12:1 dr. Note: The yield of the reaction depends on the scale of the reaction.

The dr of the reaction was determined through analysis of the unpurified reaction mixture by ¹H NMR spectroscopy.

The relative stereochemistry of the product was determined by X-ray crystallography.

¹H NMR (500 MHz, CDCl₃) δ 7.39–7.28 (m, 1OH), 6.94 (s, 1H), 4.03 (s, 1H), 3.19 (d, 1H, J = 14.5 Hz), 2.97 (d, 1H, J = 14.5 Hz), 2.85–2.79 (m, 2H), 2.85 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 165.6, 139.1, 139.0, 128.9, 128.8, 128.6, 128.4, 127.4, 127.0, 118.8, 78.9, 67.7, 62.0, 61.1, 58.9, 37.0, 36.6, 25.5.

FT-IR (neat) 2922, 2242, 1738, 1496, 1455, 1409, 1308, 1261, 1187, 1120, 1014, 956, 915, 887, 791, 746 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₄H₂₃NNaO₃S: 462, found: 462.

[α]²⁵D = +21.4° (c = 1.00, CHCl₃).
VI. Mechanistic Studies

**Determination of the Rate Law.** Due to the limited solubility of Cs₂CO₃ in toluene, the rate law was determined in the absence of Cs₂CO₃. At room temperature, the same yield and ee are observed when the reaction is run with Cs₂CO₃ and without Cs₂CO₃ (>95% yield and 89% ee).

**Representative Procedure.** In a glovebox, an oven-dried 20-mL vial with a stir bar was charged with a solution of catalyst 1d in toluene (0.8 mL, 0.025 M) and a solution of benzoylacetonitrile in toluene (0.8 mL, 0.30 M). The vial was capped with a PTFE-lined septum cap and stirred at r.t. until the reaction mixture was homogeneous. Then, a solution of benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate and dibenzyl ether (internal standard) in toluene (1.6 mL, 0.125 M in allenolate, 0.0625 M in dibenzyl ether) was added via syringe. Next, the reaction mixture was stirred, and aliquots (0.5 mL) were taken every 2 min over a 10-min period. Each aliquot was immediately subjected to t-BuOOH (100 μL; 5.0–6.0 M in decane) to quench the reaction. The aliquots were removed from the glovebox, filtered through a plug of silica gel with Et₂O, and concentrated. The extent of product formation was determined by ¹H NMR spectroscopic analysis. The initial rate was measured by plotting product concentration (mM) over the course of the first 10 min of the reaction.
Order in Allenoate:

Table S1.1 Observed Initial Rates.

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<th>allenoate (mM)</th>
<th>$k_{\text{obs}}$ (mM/min)</th>
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<td>93.8</td>
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Figure S1.1

Order in Allenoate
Order in Benzoylacetonitrile:

Table S1.2. Observed Initial Rates.

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<th>$k_{\text{obs}}$ (mM/min)</th>
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Figure S1.2.

Order in Benzoylacetonitrile

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<th>Benzoylacetonitrile Concentration (mM)</th>
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Order in Catalyst:

Table S1.3. Observed Initial Rates.

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<td>12.50</td>
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Determination of the Resting State of the Catalyst. In a glovebox, an oven-dried 4-mL vial with a stir bar was charged with catalyst 1d (10.0 mg, 0.012 mmol) and benzoylacetonitrile (21.8 mg, 0.15 mmol). Then, toluene-d₈ (0.5 mL) was added, and the mixture was stirred at r.t. After the reaction mixture had become homogenous, the solution (0.4 mL) was transferred to an oven-dried NMR tube. A second 4-mL vial was charged with benzhydryl 2-(acetoxyethyl)buta-2,3-dienoate (40.3 mg, 0.125 mmol) and toluene-d₈ (0.5 mL). The NMR tube and the vial that contained the allenoate were capped, taped, and removed from the glovebox. The solution of the allenoate (0.4 mL) was injected via syringe into the NMR tube, and the NMR tube was shaken to ensure complete mixing of the solution. Then, the resting state of the catalyst was determined by coupled ³¹P NMR spectroscopy, beginning 6 min after the addition of the allenoate solution to the reaction mixture (64 scans, experiment time = 2 min). One major peak was observed in the ³¹P NMR spectrum (δ 35.6), and essentially no free phosphine was detected (δ 0.8; <5%).
VII. X-Ray Crystallographic Data, including Determination of Stereochemistry

(11aR)-4,8-Di[(1,1':3',1'"-terphenyl)-5'-yl]-1,11-dimethoxy-6-phenyl-6,7-dihydro-5H-dibenzo[c,e]phosphepine 6-oxide. The absolute stereochemistry of the title compound was determined using the product derived from the fast-eluting enantiomer of the dibromide intermediate (see details in Section III). Crystals suitable for X-ray crystallography were grown by dissolving the compound in a hot 5:1 mixture of CH$_3$CN and MeOH. Crystals grew upon cooling to room temperature.

Solvent omitted.
A suitable crystal of C$_{58}$H$_{45}$O$_5$P·(CH$_3$OH)$_2$·(CH$_3$CN) was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.4. Crystal data and structure refinement for crystal_01.

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Table S1.5. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($A^2 x 10^3$) for crystal_01. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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C(5)-C(6)-C(13) 118.84(18)
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C(8)-C(7)-C(6)  120.44(18)
C(12)-C(7)-C(6)  120.77(17)
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C(10)-C(9)-C(8)  120.46(19)
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O(2)-C(24)-C(25)  115.69(17)
C(23)-C(24)-C(25)  120.45(18)
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O(3)-C(28)-C(29)  124.57(18)
C(29)-C(28)-C(26)  120.50(18)
(S)-Benzhydryl 4-cyano-4-(thiophene-2-carbonyl)cyclopent-1-ene carboxylate (Table 1.2, Entry 4). The title compound was synthesized through the use of (R)-catalyst 1d. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH₂Cl₂, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

One of two molecules in the asymmetric unit is shown.

A suitable crystal of C₂₅H₁₉NO₃S was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.7. Crystal data and structure refinement for crystal_02.

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Table S1.8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (\(\text{Å}^2\times 10^3\)) for crystal_02. U(eq) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

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(S)-Benzhydryl 4-cyano-4-(cyclohexanecarbonyl)cyclopent-1-enecarboxylate (Table 1.2, Entry 6). The title compound was synthesized through the use of \((R)\)-catalyst 1d. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH\(_2\)Cl\(_2\), diluting with 10\% 2-PrOH/hexanes, and crystallizing by slow evaporation.

One of two molecules in the asymmetric unit is shown.

A suitable crystal of C\(_{27}\)H\(_{27}\)NO\(_3\) was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-K\(\alpha\) radiation at a temperature of 120 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. Two-site disorder in the cyclohexyl substituent in one of the two molecules in the asymmetric unit was modeled using similarity restraints placed on appropriate atoms and atom pairs. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.10. Crystal data and structure refinement for crystal_03.

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Table S1.11. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for crystal_03. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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C(3A)-C(4A)-H(4AB)  106.7
H(4AA)-C(4A)-H(4AB) 106.6
C(5A)-C(4A)-C(3A)   122.7(11)
C(5A)-C(4A)-H(4AA)  106.7
C(5A)-C(4A)-H(4AB)  106.7
C(4A)-C(5A)-H(5AA)  112.6
C(4A)-C(5A)-H(5AB)  112.6
H(5AA)-C(5A)-H(5AB) 110.1
C(6A)-C(5A)-C(4A)   95.7(11)
C(6A)-C(5A)-H(5AA)  112.6
C(6A)-C(5A)-H(5AB)  112.6
C(5A)-C(6A)-H(6AA)  104.7
C(5A)-C(6A)-H(6AB)  104.7
H(6AA)-C(6A)-H(6AB) 105.7
C(7A)-C(6A)-C(5A)   130.3(11)
C(7A)-C(6A)-H(6AA)  104.7
C(7A)-C(6A)-H(6AB)  104.7
C(6A)-C(7A)-H(7AA)  110.2
C(6A)-C(7A)-H(7AB)  110.2
C(6A)-C(7A)-C(2A)   107.7(17)
H(7AA)-C(7A)-H(7AB) 108.5
C(2A)-C(7A)-H(7AA)  110.2
C(2A)-C(7A)-H(7AB)  110.2
C(1)-C(2A)-C(3A)    107.1(18)
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C(1)-C(2A)-H(2A)    111.1
C(3A)-C(2A)-C(7A)   109.2(14)
C(3A)-C(2A)-H(2A)   111.1
C(7A)-C(2A)-H(2A)   111.1
(S)-Benzhydryl 4-cyano-4-(methoxy(methyl)carbamoyl)cyclopent-1-enecarboxylate

*(Table 1.2, Entry 10).* The title compound was synthesized through the use of *(R)-catalyst 1d.* Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH₂Cl₂, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

One of two molecules in the asymmetric unit is shown.

A suitable crystal of C₂₃H₂₂N₂O₄ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-Kα radiation at a temperature of 120 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.13. Crystal data and structure refinement for crystal_04.

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Table S1.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal_04. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

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C(36)-C(37)-C(38) 120.2(3)
C(37)-C(38)-C(39) 119.4(3)
C(38)-C(39)-C(40) 120.3(3)
C(35)-C(40)-C(39) 120.3(3)
C(42)-C(41)-C(34) 120.2(3)
C(46)-C(41)-C(34) 120.2(3)
C(46)-C(41)-C(42) 119.7(3)
C(43)-C(42)-C(41) 119.6(4)
C(44)-C(43)-C(42) 120.8(4)
C(43)-C(44)-C(45) 120.1(3)
C(44)-C(45)-C(46) 119.4(4)
C(41)-C(46)-C(45) 120.5(4)
(S)-Benzhydryl 4-cyano-4-(phenylsulfonyl)cyclopent-1-ene carboxylate (Table 1.3, Entry 1). The title compound was synthesized through the use of (S)-catalyst \textit{1e}. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH$_2$Cl$_2$, diluting with 10\% 2-PrOH/hexanes, and crystallizing by slow evaporation.

A suitable crystal of C$_{26}$H$_{21}$NO$_4$S was selected for analysis. All measurements were made on a Bruker SMART CCD with filtered Mo-K$\alpha$ radiation at a temperature of 100 K. Using Olex2 \cite{1}, the structure was solved with the ShelXS \cite{2} structure solution program using Direct Methods and refined with the ShelXL \cite{2} refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.


\cite{2} Sheldrick, G. M. \textit{Acta Crystallogr. A 2008, 64, 112}.
Table S1.16. Crystal data and structure refinement for crystal_05.

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Table S1.17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal_05. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

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Table S1.18. Bond lengths [Å] and angles [°] for crystal_05.

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(S)-Benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate (Table 1.3, Entry 3). The title compound was synthesized through the use of (S)-catalyst 1e. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH₂Cl₂, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

A suitable crystal of C₂₄H₂₅NO₄S was selected for analysis. All measurements were made on a Bruker SMART CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.19. Crystal data and structure refinement for crystal_06.

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Table S1.20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for crystal_06. $U(eq)$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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(1R,2S,4S)-Benzhydryl 4-cyano-4-(diphenylphosphoryl)-1,2-
dihydroxycyclopentane-carboxylate. The title compound was synthesized through the use of
(S)-benzhydryl 4-cyano-4-(diphenylphosphoryl)cyclopent-1-enecarboxylate (Table 1.3, Entry 5),
which was prepared using (S)-catalyst 1e and enriched to higher ee by preparatory HPLC (95% ee; see Section IV). A literature procedure for the dihydroxylation of a cyclopentene was
followed, with the exception that the aqueous solutions of OsO₄ and NMO were prepared from
the corresponding solids instead of using solutions purchased from commercial sources (the
product was obtained in low yield; unoptimized). Crystals suitable for X-ray crystallography
were grown by dissolving the compound in a minimal amount of CH₂Cl₂, diluting with 10% 2-
PrOH/hexanes, and crystallizing by slow evaporation.

Solvent omitted.

A suitable crystal of C$_{32}$H$_{28}$NO$_2$P$\cdot$0.19(H$_2$O) was selected for analysis. All measurements were made on a Bruker SMART CCD with filtered Mo-K$_\alpha$ radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The partially occupied (0.19) water molecule was refined as a rigid body. The absolute stereochemistry was determined on the basis of the absolute structure parameter.


Table S1.22. Crystal data and structure refinement for crystal_07.

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| Unit cell dimensions| a = 9.4976(6) Å  \(\alpha = 90^\circ\)  
b = 15.3682(10) Å  \(\beta = 90^\circ\)  
c = 18.6904(12) Å  \(\gamma = 90^\circ\) |
| Volume              | 2728.1(3) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.317 Mg/m³ |
| Absorption coefficient | 0.144 mm⁻¹ |
| F(000)              | 1136 |
| Crystal size        | 0.4 x 0.3 x 0.25 mm³ |
| Theta range for data collection | 2.179 to 27.601° |
| Index ranges        | -12<=h<=12, -20<=k<=20, -24<=l<=24 |
| Reflections collected| 52409 |
| Independent reflections | 6299 [R(int) = 0.0343] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.6685 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 6299 / 0 / 367 |
| Goodness-of-fit on F² | 1.074 |
| Final R indices [l>2sigma(l)] | R₁ = 0.0307, wR₂ = 0.0716 |
| R indices (all data) | R₁ = 0.0348, wR₂ = 0.0745 |
| Absolute structure parameter | 0.01(2) |
| Largest diff. peak and hole | 0.314 and -0.208 e/Å⁻³ |
Table S1.23. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for crystal_07. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table S1.24. Bond lengths [Å] and angles [°] for crystal_07.

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(4S,5S)-Benzyl 4-(tert-butylsulfonyl)-4-cyano-5-ethylcyclopent-1-enecarboxylate (eq 1.5). The title compound was synthesized through the use of (S)-catalyst 1d. The product was enriched to higher ee by preparatory HPLC, which yielded a single diastereomer in >99% ee (see Section IV). Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH₂Cl₂, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

A suitable crystal of C₂₀H₂₅NO₄S was selected for analysis. All measurements were made on a Bruker SMART CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.25. Crystal data and structure refinement for crystal_08.

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<tr>
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<tr>
<td></td>
<td>b = 5.8842(2) Å</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>(a = 90^\circ).</td>
</tr>
<tr>
<td></td>
<td>(\beta = 96.87^\circ).</td>
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<tr>
<td></td>
<td>(\gamma = 90^\circ).</td>
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<td>Absorption correction</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>Data / restraints / parameters</td>
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<td>Largest diff. peak and hole</td>
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Table S1.26. Atomic coordinates ($x\times10^4$) and equivalent isotropic displacement parameters ($\AA^2$ x $10^3$) for crystal_08. U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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Table S1.27. Bond lengths [Å] and angles [°] for crystal_08.

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(1S,2R,4R)-Benzhydryl 4-(tert-butylsulfonyl)-4-cyano-1,2-dihydroxycyclopentanecarboxylate (eq 1.3). The title compound was synthesized from (R)-benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH$_2$Cl$_2$, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

A suitable crystal of C$_{24}$H$_{27}$NO$_6$S was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-K$_\alpha$ radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.28. Crystal data and structure refinement for crystal_09.

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Table S1.29. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for crystal_09. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table S1.30. Bond lengths [Å] and angles [°] for crystal_09.

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(3S,4S)-tert-Butyl 4-(tert-butylsulfonyl)-4-cyano-3-methylocyclopent-1-enecarboxylate (eq 1.6). The title compound was synthesized through the use of (S)-catalyst 1d. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a minimal amount of CH$_2$Cl$_2$, diluting with 10% 2-PrOH/hexanes, and crystallizing by slow evaporation.

A suitable crystal of C$_{16}$H$_{25}$NO$_4$S was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-K$_\alpha$ radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.31. Crystal data and structure refinement for crystal_10.

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Table S1.32. Atomic coordinates \( (x \times 10^4) \) and equivalent isotropic displacement parameters \( (\text{Å}^2 \times 10^3) \) for crystal_10. \( U(\text{eq}) \) is defined as one third of the trace of the orthogonalized \( U^T \) tensor.

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(1S,3R,5R)-Benzhydryl 3-(tert-butylsulfonyl)-3-cyano-6-oxabicyclo[3.1.0]hexane-1-carboxylate (eq 1.4). The title compound was synthesized from (R)-benzhydryl 4-(tert-butylsulfonyl)-4-cyanocyclopent-1-enecarboxylate. Crystals suitable for X-ray crystallography were grown by dissolving the compound in a small amount of CH$_2$Cl$_2$, carefully adding a similar amount of 10% 2-PrOH/hexanes, and crystallizing by slow diffusion of the 2-PrOH/hexanes layer into the CH$_2$Cl$_2$ layer.

A suitable crystal of C$_{24}$H$_{25}$NO$_5$S was selected for analysis. All measurements were made on a Bruker Photon CMOS with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S1.34. Crystal data and structure refinement for crystal_11.

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Table S1.35. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal_11. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table S1.36. Bond lengths [Å] and angles [°] for crystal_11.

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C(4)-C(1)-C(2)  110.85(15)
C(4)-C(1)-C(3)  111.46(15)
C(6)-C(5)-S(1)  105.47(10)
C(9)-C(5)-S(1)  114.23(10)
C(9)-C(5)-C(6)  105.57(12)
C(10)-C(5)-S(1)  109.16(11)
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C(10)-C(5)-C(9)  112.49(13)
C(7)-C(6)-C(5)  103.44(12)
O(3)-C(7)-C(6)  113.25(13)
O(3)-C(7)-C(8)  59.53(9)
O(3)-C(7)-C(11)  118.52(12)
C(8)-C(7)-C(6)  110.00(12)
C(8)-C(7)-C(11)  123.25(13)
C(11)-C(7)-C(6)  118.65(13)
O(3)-C(8)-C(7)  59.07(10)
O(3)-C(8)-C(9)  112.82(12)
C(7)-C(8)-C(9)  109.33(12)
C(8)-C(9)-C(5)  104.06(12)
N(1)-C(10)-C(5)  178.14(18)
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O(4)-C(11)-C(7)  122.19(14)
O(5)-C(11)-C(7)  111.52(13)
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C(13)-C(12)-C(19)  114.20(13)
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C(16)-C(15)-C(14)  120.39(17)
C(15)-C(16)-C(17)  119.85(17)
C(16)-C(17)-C(18)  120.02(17)
C(13)-C(18)-C(17)  120.31(16)
C(20)-C(19)-C(12)  121.86(14)
C(20)-C(19)-C(24)  119.09(15)
C(24)-C(19)-C(12)  119.04(14)
C(21)-C(20)-C(19)  120.21(16)
C(22)-C(21)-C(20)  120.13(17)
C(23)-C(22)-C(21)  119.93(17)
C(22)-C(23)-C(24)  120.24(17)
C(23)-C(24)-C(19)  120.36(17)
VIII. $^1$H NMR Spectra
**Sample**: PRESATURATION

- **Date**: Aug 3 2013
- **Saturation Mode**: n
- **Solvent**: CDCl3 wet n
- **File**: /indy/dziegle/special/r/vnmrsys/data/DZ-05-088-1-Purified
- **Temp**: not used
- **File Gain**: 32

**Acquisition**
- **HST**: 0.008
- **SW**: 8000.0
- **PW**: 9.900
- **AT**: 3.000
- **ALFA**: 10.000
- **NP**: 48000

**Flags**
- **FB**: not used
- **BS**: 32
- **DI**: 1.000
- **NT**: 32
- **CT**: 32

**Processing**
- **Transmitter**: 1b
- **TN**: not used
- **SFREQ**: 499.698
- **TOF**: 499.7
- **TPWR**: 61
- **PW**: 4.950
- **RF**: 4632.1

**Decoupler**
- **C13**: -83.5
- **DOP**: -71.4
- **DM**: 32

**DecWave**
- **W40_autox7**: 250
- **SC**: 0
- **DPWR**: 41
- **M1**: 30
- **DAF**: 32258

The spectrum shows the peaks at 7.46, 3.07, 2.20, and 1.00 ppm, which correspond to the chemical shifts of the Ph, OH, and other functional groups in the molecule.
B-Substituted-Allenoate

exp37 PROTON

SAMPLE     PRESATURATION
date Sep 16 2013  satmode  n
solvent cdc13  wet  n
file /indy/dziegle-r/vnmrsys/data/DZ-
      05-B-Substituted-A-
      llineoate/PRONON1.~
fid  hst  0.006
      pwr0  9.900
ACQUISITION
sw  8000.0  alfa  10.000
at  3.000  n
fb  48000  n
bs  32  n
di  1.000  n
nt  32  n
ct  32  n
TRANSMITTER
transmitter H1
sfrq  499.698  sp  -0.1
tof  498.7  wp  4986.8
twpr  61  rfi  4632.1
pw  4.950  rfp  3627.8
DECODER
dn  0  n
decwave W40_auto7  n
decov  250  n
pwr  4i  n
pwr  50  n
fcomp  32528  al  cdc  ph

[Chemical structure and spectrum image]

BnO OAc

[peaks and ppm values]
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<td>EXP49 PROTON</td>
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<td>File</td>
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<tr>
<td>Acquisition</td>
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<tr>
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**Diagram:**

[Diagram showing a spectroscopy spectrum with peaks at various ppm values.]
(Table 1.2, Entry 1)
DZ-03-218-1-Purified
exp10 PROTON

SAMPLE
date Apr 30 2013
solvent cdc13
file /indy/dziegle-r/vnmrsys/data/DZ--03-218-1-Purified-
PROTON01.fid
ACQUISITION
sw 8000.0
at 3.000
np 40000
fb not used
bs 32
nt 16
ct 16
TRANSMITTER
ln H1
tof 499.7
pw 4.950
dn C13
dm nnn
DECcoupler rfp 3627.8

PRESATURATION
satmode n
SATURATION temp not used
SPs 20
hst 0.000
sw 8000.0
at 3.000
np 40000
fb not used
bs 32
nt 16
ct 16
TRANSMITTER
ln H1
TOFs 499.7
DISPLAY -0.1
pw 4.950
rfi 4630.1
DECcoupler rfp 3627.8

PLOT
250
2.04 9.95
2.05 0.95
3.20 2.14
1.10 1.06

MeO
\(\text{CN}\)

(C13 0)

Ph

Table 1.2, Entry 2)
DZ-03-230-1-Purified

Experiment PROTON

SAMPLE

date Apr 30 2013
solvent cdc13 wet
file /indy/dziegielewski/vnmrsys/data/DZ--~
03-230-1-Purified/PROTON01.fid
ACQUISITION
sw 8000.0
at 3.000
np 48000
fb not used
bs 32
sl 1.000
tn 16
ct 16

TRANSMITTER

TN

DECcoupler
dn

DELTA

dm

decwave

dmf

MeO2C

PH

(C) - 0.20

DISPLAY

PLOT

(cdc ph

9 3 2

1.08 1.06

Table 1.2, Entry 3)
Table 1.2, Entry 4

8 7 6 5 4 3 1 ppm

1.00 1.02 1.00
0.92 0.96 1.08 1.08
1.09 2.19
Table 1.2, Entry 5

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<td>3.22</td>
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<td>6.87</td>
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**Note:** The table above is extracted from the provided image. The chemical structure and additional details are not included in the image.
(Table 1,2, Entry 7)
Me \text{N} \text{O} \text{CN}

Me

Me

(\text{Table 1.2, Entry 8})
DZ-03-228-1-Purified

Sample: PROTON
Date: May 1, 2013
Solvent: CDCl3
File: /indy/dziegler/vnmrsys/data/DZ-03-228-1-Purified/PROTON01.fid

Acquisition:
- SW: 8000.0 Hz
- AT: 3.000 Hz
- NP: 48000
- FB: not used
- BS: 32 in
- DI: 1.000 dp
- NT: 16 hs
- CT: 16

Transmitter:
- TN: H1
- SFRE: 499.708 Hz
- TOF: 499.7 Hz
- PW: 4.950 Hz
- DECOUPLER: C13
- DOF: 0
- DM: nnn
- DECWAVE: W40

Presaturation:
- SATMODE: n
- WET: n

Special:
- Gain: 32
- Spin: 20
- HS: 0.008

Processing:
- LB: 0.20
- FN: not used
- DISPLAY: sp -0.1

Plot:
- WC: 250
- SC: 0
- VS: 80
- TH: 34
- CDC: 34

Ph N
O
O

Ph

Ph

Ph

Ph

Ph

Ph

(Tab 1.2, Entry 9)
Table 1.2, Entry 10

MeO -N -C=O

Me

Me

Ph

Ph

$^{13}C$ and $^1H$ NMR Spectra

Table 1.2, Entry 10

MeO -N -C=O

Me

Me

Ph

Ph

$^{13}C$ and $^1H$ NMR Spectra
Table 1.2, Entry 11
DZ-03-278-1-Purified
exp23 PROTON

SAMPLE PRESATURATION
date May 1 2013 satmode n
solvent cdc13 wet n
file /indy/dziegle- r:/vmrsys/data/DZ--
03-278-1-Purified/-PROTON01.fid

ACQUISITION
sw 8000.0 at 3.000
np 48000 fb not used
bs 32 ln n
dl 1.000 dp y
nt 16 hs
ct 16

TRANSMITTER
tn H1 fn not used
sfra 499.708 DISPLAY
tof 499.7 sp -9.1
tpwr 61 wp 4999.8
pw 4.950 rf1 4835.1
decoupler rf1 3627.9
dn C13 dp -27.0
dof 0 lp -72.6
dm nnn decwave W40_autox7 wc 250
decwave 991 sc 0
dpwr 41 vs 22
dmf 32258 th

MeO-CN

Ph

P.0 2.6

MeO-CN

Ph

(Table 1.2, Entry 12)
DZ-03-272-1-Purified

**SAMPLE**
- **date**: May 1 2013
- **solvent**: cdc13
- **file**: /indy/dziegle-r/vnmrsys/data/DZ-03-272-1-Purified/PROTON01.fid

**ACQUISITION**
- **sw**: 8000.0
- **at**: 3.000
- **np**: 48000
- **fb**: not used
- **bs**: 32
- **dl**: 1.000
- **nt**: 16
- **ct**: 16
- **TRANSMITTER**: H1
- **tn**: 499.708
- **tof**: -0.1
- **tpwr**: 61
- **pw**: 4.950
- **DECOUPLER**: C13
- **dof**: 0
- **dm**: nnn
- **deccwave**: W40_autox7
- **decwave**: 250

**DECOUPLER**
- **dn**: C13
- **rfi**: 4630.1
- **pdf**: 3627.9
- **dp**: -7.0
- **dmf**: 32250
- **ai**: cdc
- **ph**: 43

**(Table 1.3, Entry 1)**

- [Chemical Structure Image]
DZ-03-298-1-Purified
exp23 PROTON

SAMPLE  PRESATURATION  SPECIAL
date  May 1 2013  satmode  n  temp  not used
solvent  cdc13  wet  n  gain  32
file  /indy/dziegle-
\r/vnmrsys/data/DZ--
03-298-1-Purified/-
PROTON01.fid  spin  20
ACQUISITION  hst  0.000
sw  8000.0  pw90  6.500
at  3.000  alfa  10.000
np  48000  FLAGS
fb  not used  t1  n
bs  32  ln  n
d1  1.000  dp  y
nt  16  hs  nn
tc  16  PROCESSING
TRANSMITTER  lb  0.20
fn  not used
sfrq  499.708  DISPLAY
tpw  61  wp  4996.0
tpw  4.950  rf1  4630.1
DECOUPLER  rfp  3627.8
dn  28.8  C13
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(Table 1.3, Entry 2)
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fn not used
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dn C13

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dpr 41

dw 41

PLOT
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Table 1.3, Entry 3

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T J 1.07 2.13 1.06

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ppm
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- bs: 32
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- nt: 16
- ct: 16

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- tof 499.7
- tpwr 61
- pw 4.950
- dn C13
- df 0
- dm 0

**DECOUPLER**
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- dpw r 41
- def 32258

**PRESATURATION**
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- wet n

**SPECIAL**
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- gain 32
- alfa 10.000
- flags
- hst 0.008
- dm 0
- spin 20
- presaturation

**PROCESSING**
- lb 0.20
- fn not used
- display
- wc 250
- sc 0
- vs 85
- ph

**PLOT**
- w 14.47
- r 5.96
- f 1.00

**Display**
- PhO-P..CN
- PhO-P..CN

(Table 1.3, Entry 5)
exp19 PROTON

SAMPLE

date Jul 8 2013 satmode n
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file /indy/dziegle-r/vnmrsys/data/DZ--05-050-1-Resolved/ PROTON1.fid

ACQUISITION

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np 48000
fb not used
bs 32
dt 1.000
nt 16
ct 16

TRANSMITTER

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lpwr 61 wp 4996.0
pw 4.950 rf1 4630.7
dn C13 rp 13.9
dof 0 lp -73.4
dm nnn

decwave W40_autox7- wc 250
decwave 991 sc 0
dpwr 41 vs 15
dmf 32258

PRESATURATION

satmode n
wet n

gain 32

SPECIAL

temp not used
gain 32
tmp 5

FLAGS

il n in n
hs
lp
fn
sp
wp
rfl
rfp
rp
Ip
wc
sc
vs
th

PROCESSING

0.20 not used

DISPLAY

-0.1

PLOT

cdc ph
DZ-06-074-2-Purified

exp43 PROTON

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at 3.000 alfa 10.000
np 48000 FLAGS n
bs 32 ln n
d1 2.000 dp y
nt 16 hs nn
c0 16 PROCESSING

TRANSMITTER lb 0.20

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tpw 81 wp 4966.8
pw 4.950 rf1 4635.7

DECoupler rfp 3627.7

dn C13 rp -171.4
dof 0 lp -72.7
dm nnn PLOT 250

decwave W40_autox7- wc 591 sc 0
dpw 41 wc 22

dmf 32258 th a1 cdc ph 9

(eq 1.6)
DZ-05-176-1-Purified

exp34 PROTON

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(eq 1.3)

\[ \text{t-Bu-SO}_2\text{CN} \]

\[ \text{HO}\text{HO}\text{O} \]

\[ \text{Ph} \text{Ph} \]

\[ \text{1 ppm} \]

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DZ-06-112-1-Purified

exp2 PROTON

SIMPLE PRESATURATION

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temp not used

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TRANSMITTER lb 0.20
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DISPLAY

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dof 0 lp -73.7

ddm nnm

PLOT

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991 sc 0

dpw 41 vs 20
daf 32258 th 13

dt ai cdcc ph

\[ \text{eq 1.4} \]
CHAPTER 2

A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles and Electrophiles for Photoinduced, Copper-Catalyzed Processes
A. Introduction

Due to the prevalence of aromatic nitrogen heterocycles in bioactive compounds, methods for their functionalization have substantial importance. With regard to \( \text{Caryl-N} \) bond formation, powerful methods (e.g., Ullmann couplings and Buchwald–Hartwig reactions) have been developed with a variety of transition metals, but low cost and low toxicity make copper catalysts particularly attractive. However, copper-catalyzed N-arylations of aromatic nitrogen heterocycles almost always require elevated temperature. Even with recent advances in catalyst design and ligand structure, temperatures greater than 100 °C can be required depending on the nitrogen heterocycle.

In 2012, based on a previous study on the photophysical properties of a copper–carbazolide complex, Fu and Peters reported the photoinduced, copper-catalyzed N-arylation of lithium carbazolide with iodobenzene at unusually low temperature. By irradiating the reaction mixture with a 100-watt mercury lamp, moderate yield could be achieved at temperatures as low as -40 °C (eq 2.1).

In this report, Fu and Peters showed that the reaction likely proceeds through a single-electron transfer (SET) pathway as opposed to a concerted oxidative addition pathway (Scheme

---

2.1). A variety of experimental evidence was provided to support this conclusion. For example, a deuterium-labeled olefin substrate undergoes cyclization prior to C–N bond formation resulting in a 1:1 mixture of diastereomers (eq 2.2). This result is fully consistent with a radical cyclization step and, therefore, a radical intermediate. Furthermore, in a competition experiment between 1-bromonaphthalene and 4-chlorobenzonitrile, product 2c, derived from 4-chlorobenzonitrile, is preferentially formed, which supports an SET mechanism (eq 2.3). Product 2b would be expected to predominate if a concerted oxidative addition pathway is operative, but due to the favorable reduction potential of 4-chlorobenzonitrile compared to 1-bromonaphthalene (−2.03 V compared to −2.17 V versus SCE in DMF), product 2c should predominate if an SET pathway is operative.

Scheme 2.1. Two Possible Pathways for Ullmann Couplings with an Aryl Halide

![Scheme 2.1](image)

Assuming the hypothesis that this reaction proceeds via an SET pathway is correct, it was anticipated that this reaction platform should be viable for coupling carbazoles with alkyl halides since alkyl halides are typically more susceptible to one-electron reduction than aryl halides. Through optimization of the appropriate reaction parameters, conditions were developed with Cul as the catalyst under which carbazole couples with alkyl iodides and bromides to generate the desired N-alkylated products in good yield (eq 2.4). This process is effective for secondary and hindered primary alkyl halides, substrates that are challenging electrophiles for simple SN₂ reactions.

Mechanistic investigations into this process revealed that copper bis(carbazolide) complex [Cu(carbazolide)₂]Li is present during the reaction (observed by electrospray mass spectroscopy). This complex was independently synthesized and characterized and was shown to be chemically competent in the photoinduced Ullmann coupling reaction. This data is consistent with the hypothesis that [Cu(carbazolide)₂]Li is an intermediate in the catalytic cycle and supports the catalytic cycle depicted in Scheme 2.2.

Scheme 2.2. Possible Catalytic Cycle for Photoinduced, Cu-Catalyzed C–N Bond Formation

Changes to the amido ligand in copper complexes of the type (Ph₃P)₂Cu(NAr₂) have been shown to have a substantial impact on the photoluminescence properties of the complex (e.g., NAr₂ = carbazole versus NPh₂). Similarly, we suspected that modifications to the carbazolide ligand in [Cu(carbazolide)₂]Li (or a related catalytically active species) could impact the photophysics of the complex. Therefore, if these photoinduced, C–N bond-forming processes proceed through initial photoexcitation of a copper–carbazolide complex as predicted (Scheme 2.2), it was unclear whether other aromatic nitrogen heterocycles could form a copper complex capable of undergoing the desired photoexcitation/electron-transfer process. As a result, we decided to investigate other aromatic nitrogen heterocycles as nucleophiles for this mild, photoinduced, Ullmann coupling reaction with the goal of developing a unified set of reaction conditions for a variety of nitrogen nucleophiles. Much of this investigation was conducted in collaboration with Dr. Junwon Choi.

B. Results and Discussion

The structural resemblance of indole to carbazole made indole a logical nucleophile to begin our investigation. In addition, indoles are a common subunit found in natural products and bioactive compounds. When the conditions developed for the arylation of lithium carbazolide

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with iodobenzene using a catalytic amount of Cul were applied to lithium indolide, the reaction proceeded in low yield (eq 2.5).

\[
\text{\begin{align}
\mathrm{Li}^+ & \quad \text{I-Ph} \\
& \quad 1.2 \text{ equiv} \\
\stackrel{10\% \text{ Cul}}{\text{hv}} \quad (100\text{-watt Hg lamp}) \quad \mathrm{r.t.}, \mathrm{CH}_3\mathrm{CN} \\
& \quad \rightarrow \\
\mathrm{Ph} & \quad \text{N-Ph} \\
& \quad <20\% \text{ yield}
\end{align}}
\]

An investigation of various reaction parameters revealed that the wavelength of light is critical to achieving optimal C–N bond formation. By irradiating the reaction at 254 nm rather than 350 nm, N-phenylindole could be formed in good yield (Table 2.1, entry 1). Note that the active copper–nucleophile complex was generated in situ from Cul, indole, and LiOt-Bu (similar to the carbazole alkylation conditions). This reaction could be performed on a gram scale with only a minor decrease in yield (1.3 g of product, 65% yield). In addition, the reaction tolerates small amounts of water; doping the reaction with 10 mol% water led to a minimal decrease in yield (<10%). However, poor yield is observed when the reaction is performed under air instead of nitrogen. Switching to a shorter wavelength of light requires the use of quartz glass for the reaction vessel since borosilicate glass filters out much of the 254 nm radiation. For example, when the reaction was performed under the optimized conditions with a borosilicate test tube rather than a quartz test tube, the reaction efficiency decreased dramatically (<10% yield).
Table 2.1. N-Arylation of Indoles at Room Temperature

Under the optimized conditions, a variety of substituted indoles, including a sterically hindered indole, efficiently undergo C–N bond formation with iodobenzene (Table 2.1, entries 4, 6, 8, and 9). In addition, an ortho-substituted aryl iodide and an electron-rich aryl iodide are suitable electrophiles for this reaction (entries 5 and 7). An iodothiophene, an iodoaniline, and an iodo-substituted aryl ester proved to be poor coupling partners for this transformation as did an electron-deficient indole.

In an effort to expand this methodology to include a variety of aromatic nitrogen heterocycles, we determined that a second family of nucleophiles, benzimidazoles, react well under the established reaction conditions. Like indoles, benzimidazoles are a privileged scaffold in medicines and bioactive compounds. Benzimidazole reacts with iodobenzene as well as an

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electron-rich aryl iodide and an electron-poor aryl iodide in high yield although a solvent mixture (3:1 CH₃CN/t-BuOH) is required presumably to increase solubility (Table 2.2, entries 1–3). This solvent mixture was only observed to be advantageous when benzimidazole itself was employed as the nucleophile. Under the standard reaction conditions, a 5-substituted benzimidazole undergoes the desired cross-coupling with iodobenzene in high yield. However, arylation could occur at either nitrogen leading to approximately a 1:1 mixture of regioisomers (entry 4). This ratio of regioisomers is consistent with literature examples. Finally, a sterically hindered benzimidazole, 2-methylbenzimidazole, couples with iodobenzene, an ortho-substituted aryl iodide, and even a heteroaryl iodide in good yield (entries 5–7).

**Table 2.2. N-Arylation of Benzimidazoles at Room Temperature**

<table>
<thead>
<tr>
<th>entry</th>
<th>benzimidazole</th>
<th>Ar</th>
<th>yield (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Ph</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>4-CN-C₆H₄</td>
<td>4-CN-C₆H₄</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>p-anisyl</td>
<td>p-anisyl</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>Ph</td>
<td>83^b</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>o-tolyl</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>3-pyridyl</td>
<td>3-pyridyl</td>
<td>76</td>
</tr>
</tbody>
</table>

^a Yield of purified product (average of two experiments).

^b 1.1:1 mixture of isomers.

Since imidazoles closely resemble benzimidazoles and represent a third family of bioactive nitrogen heterocycles, we were interested in applying our photoinduced, Ullmann coupling conditions to this class of nucleophiles. Imidazole couples with iodobenzene and an ortho-substituted aryl iodide with moderate efficiency (Table 2.3, entries 1 and 2). However, while a sterically demanding electrophile is tolerated, the reaction with a sterically demanding imidazole

proceeds in just modest yield with iodobenzene as the electrophile (entry 3). Similar to benzimidazole, a solvent mixture is necessary to achieve efficient C–N bond formation with unsubstituted imidazole as the nucleophile.

**Table 2.3. N-Arylation of Imidazoles at Room Temperature**

<table>
<thead>
<tr>
<th>entry</th>
<th>imidazole</th>
<th>Ar</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>Ph</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>o-tolyl</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Ph</td>
<td>46</td>
</tr>
</tbody>
</table>

* Yield of purified product (average of two experiments).

In the initial paper on photoinduced Ullmann couplings between a copper–carbazolide and iodobenzene, the arylation of lithium carbazolide with iodobenzene was reported to proceed in 58% isolated yield under catalytic conditions. We were pleased to observe that, under our newly developed conditions, the same overall transformation could be achieved with a substantial improvement in yield (Table 2.4, entry 1). This method could be applied for the arylation of carbazole with a variety of other aryl iodides including an electron-rich aryl iodide, an electron-deficient aryl iodide, an *ortho*-substituted aryl iodide, and a heteroaryl iodide (entries 2–5). In addition, a carbazole with an electron-donating substituent and a carbazole with an electron-withdrawing substituent cross-couple with a sterically hindered aryl iodide in good yield (entries 6 and 7).
Table 2.4. N-Arylation of Carbazoles at Room Temperature

<table>
<thead>
<tr>
<th>entry</th>
<th>carbazole</th>
<th>Ar</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td>Ph</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>4-CN-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>p-anisyl</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>o-tolyl</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>3-pyridyl</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>o-tolyl</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>o-tolyl</td>
<td>74</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yield of purified product (average of two experiments).

In previous studies, the stoichiometric coupling of a preformed copper-carbazolide complex was demonstrated with aryl iodides, bromides, and chlorides.<sup>31</sup> However, only aryl iodides were shown to be suitable electrophiles for copper-catalyzed processes. Therefore, we were pleased to determine that an aryl bromide and an activated aryl chloride undergo cross-coupling with various aromatic nitrogen heterocycles under our newly developed reaction conditions (Table 2.5).
Table 2.5. An Unactivated Aryl Bromide and an Activated Aryl Chloride as Electrophiles

<table>
<thead>
<tr>
<th>entry</th>
<th>nucleophile</th>
<th>electrophile</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Nucleophile 1" /></td>
<td><img src="image2" alt="Electrophile 1" /></td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Nucleophile 2" /></td>
<td><img src="image4" alt="Electrophile 2" /></td>
<td>62</td>
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<tr>
<td>3</td>
<td><img src="image5" alt="Nucleophile 3" /></td>
<td><img src="image6" alt="Electrophile 3" /></td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="Nucleophile 4" /></td>
<td><img src="image8" alt="Electrophile 4" /></td>
<td>61</td>
</tr>
</tbody>
</table>

* Yield of purified product (average of two experiments).

As the established reaction conditions are effective for a variety of aromatic nitrogen heterocycles as well as aryl iodides, bromides, and chlorides, we were interested in exploring the selectivity of the reaction with respect to the nucleophile and the electrophile. Nucleophile competition experiments revealed that good-to-excellent selectivity can be obtained with one equivalent of LiOt-Bu relative to one of the nucleophiles (Table 2.6). The more acidic aromatic nitrogen heterocycle tends to be selectively arylated.\(^{39}\) However, the level of selectivity is difficult to predict on pK\(_a\) alone as it could be complicated by factors such as differences in the photophysical properties of the corresponding copper complexes and the formation of mixed complexes (copper complexes with two different aromatic nitrogen heterocycles as ligands). These experiments were performed in a solvent mixture (3:1 CH\(_3\)CN/t-BuOH) as these conditions are the most general conditions for the four nucleophiles.

Table 2.6. Relative Reactivity of Nucleophilic Coupling Partners

<table>
<thead>
<tr>
<th>Nu$^1$—H</th>
<th>Nu$^2$—H</th>
<th>$\frac{\text{Nu}^1\text{—Ph}}{\text{Nu}^2\text{—Ph}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 equiv</td>
<td>1.0 equiv</td>
<td>10% Cul hv (254 nm)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nu$^1$—H</th>
<th>Nu$^2$—H</th>
<th>(Nu$^1$—Ph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>imidazole (14.4)</td>
<td>carbazole (19.9)</td>
<td>13</td>
</tr>
<tr>
<td>imidazole (14.4)</td>
<td>indole (21.0)</td>
<td>&gt;50</td>
</tr>
<tr>
<td>benzimidazole (16.4)</td>
<td>carbazole (19.9)</td>
<td>&gt;50</td>
</tr>
<tr>
<td>benzimidazole (16.4)</td>
<td>indole (21.0)</td>
<td>&gt;50</td>
</tr>
<tr>
<td>carbazole (19.9)</td>
<td>indole (21.0)</td>
<td>6</td>
</tr>
</tbody>
</table>

All ratios are the average of two experiments. $pK_a$ values (DMSO) are provided in parentheses.

With regard to the electrophile, we have observed in competition experiments with indole as the nucleophile that an aryl bromide and an aryl chloride are considerably less reactive than an aryl iodide (eq 2.6). The observed trend is consistent with the susceptibility of the aryl halide to one-electron reduction but also the propensity of the C–X bond to undergo concerted oxidative addition.

\[
\begin{align*}
\text{N} & \xrightarrow{1.4 \text{ equiv}} \text{Et} \\
\text{I} & \xrightarrow{10\% \text{ Cul} \ \text{hv (254 nm)}} \text{P (iodide) Et} \\
\text{Ph} & \xrightarrow{1.0 \text{ LiO}t/-\text{BuOH}} \text{Me} \\
\text{X} & \xrightarrow{1.4 \text{ LiO}t/-\text{BuOH} \ \text{CH}_3\text{CN}} \text{P (X) Me} \\
\hline
\text{X} & \text{P (iodide) / P (X)} \\
\text{Br} & 7 \\
\text{Cl} & 18
\end{align*}
\]

181
In Tables 2.1–2.4, we have demonstrated that the reaction conditions are compatible with a variety of functional groups. The cross-coupling proceeds in the presence of an ether, a nitrile, a pyridine, and an aryl fluoride. In addition, various successful substrates contain relatively weak C–H bonds that could potentially react with an intermediate aryl radical (e.g., benzylic or α to oxygen). In order to further probe the functional group compatibility of the reaction, we performed the reaction between indole and iodobenzene in the presence of an array of stoichiometric additives (Table 2.7). In these experiments, an ester, amide, ketone, secondary amine, primary amine, aryl chloride, trans-alkene, cis-alkene, and alkyne remain largely intact at the end of the reaction, and at most, a modest decrease in reaction efficiency is observed. This decrease in reaction efficiency can be partly offset by increasing the reaction time. For example, irradiating the reaction for 48 hours instead of 24 hours increases the yield from 58% to 66% with cyclohexylamine as the additive.
Table 2.7. Functional-Group Tolerance

<table>
<thead>
<tr>
<th>Additive</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Recovery of Additive (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
<td>79</td>
<td>-</td>
</tr>
<tr>
<td>n-Bu&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;O&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;Me</td>
<td>69</td>
<td>&gt;95</td>
</tr>
<tr>
<td>NMe</td>
<td>72</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;Me</td>
<td>62</td>
<td>85</td>
</tr>
<tr>
<td>Cy&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;N&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;H</td>
<td>73</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Cy&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>58</td>
<td>82</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;Cl</td>
<td>72</td>
<td>90</td>
</tr>
<tr>
<td>n-Bu&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;-&lt;br&gt;n-Bu</td>
<td>66</td>
<td>&gt;95</td>
</tr>
<tr>
<td>n-Bu&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;-&lt;br&gt;n-Bu</td>
<td>73</td>
<td>&gt;95</td>
</tr>
<tr>
<td>n-Bu&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;-&lt;br&gt;n-Bu</td>
<td>74</td>
<td>&gt;95</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup> Yield and recovery of additive were determined by GC analysis with the aid of a calibrated internal standard.

In order to confirm that copper and light are required to achieve efficient C–N bond formation, a series of control experiments were conducted. Reactions were run omitting light, Cul, and light and Cul for a representative example from each family of nucleophiles. In each reaction, no C–N bond formation was observed (<2%). Furthermore, we wondered if a photoredox catalyst, which shuttles electrons but is not directly involved in inner-sphere bond forming processes, could serve as a replacement for Cul. However, employing [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> as the photoredox catalyst resulted in no product formation under our standard conditions and under related conditions (eq 2.7).
Having achieved our objective of demonstrating a range of aromatic nitrogen heterocycles as nucleophiles for photoinduced Ullmann couplings, we were interested in expanding the electrophile scope of the process beyond aryl and alkyl halides. With minimal optimization, Dr. José María Muñoz-Molina was able to demonstrate that alkenyl iodides, an alkenyl bromide, and an alkynyl bromide react with an assortment of nucleophiles in good yield (Table 2.8).

**Table 2.8. New Families of Electrophiles: Alkenyl and Alkynyl Halides**

<table>
<thead>
<tr>
<th>entry</th>
<th>nucleophile</th>
<th>electrophile</th>
<th>yield (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="nucleophile1" /></td>
<td><img src="image2" alt="electrophile1" /></td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="nucleophile2" /></td>
<td><img src="image4" alt="electrophile2" /></td>
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<tr>
<td>3</td>
<td><img src="image5" alt="nucleophile3" /></td>
<td><img src="image6" alt="electrophile3" /></td>
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<tr>
<td>4</td>
<td><img src="image7" alt="nucleophile4" /></td>
<td><img src="image8" alt="electrophile4" /></td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9" alt="nucleophile5" /></td>
<td><img src="image10" alt="electrophile5" /></td>
<td>63</td>
</tr>
</tbody>
</table>

^a Yield of purified product (average of two experiments).
C. Conclusion/Recent Developments

In summary, we have demonstrated for the first time that nitrogen nucleophiles other than carbazoles are suitable for photoinduced Ullmann coupling processes. A common procedure has been developed for the coupling of indoles, benzimidazoles, imidazoles, and carbazoles with aryl halides. These reactions proceed at room temperature, an unusually mild temperature for the copper-catalyzed arylation of aromatic nitrogen heterocycles; other copper-catalyzed methods usually require elevated temperatures (greater than 100 °C for some nitrogen heterocycles). In addition, the described method utilizes an inexpensive catalyst and tolerates an array of functional groups. High levels of selectivity could be achieved in competition experiments with respect to both the nucleophilic and the electrophilic coupling partner. Finally, the electrophile scope for photoinduced, copper-catalyzed C–N couplings has also been expanded to include aryl bromides and chlorides as well as alkenyl and alkynyl halides.

Since the completion of this investigation, further progress in photoinduced, Ullmann coupling chemistry has been accomplished. In a concurrent study, aryl thiols were shown to be viable nucleophiles for arylation reactions. Furthermore, C–O bond formation could be achieved by coupling phenols and aryl iodides. Lastly, a new family of nitrogen nucleophiles, amides, have been shown to be effective coupling partners for photoinduced, copper-catalyzed alkylations with alkyl iodides, bromides, and chlorides. Similar to the findings reported herein for the arylation of various aromatic nitrogen heterocycles, 254 nm light was required to achieve optimal yield when phenols or amides were employed as the nucleophilic coupling partner.

I. General Information

The following reagents were purchased and used as received unless otherwise specified: indole (Aldrich), 6-methoxyindole (AstaTech), 3-methylindole (Aldrich), 2-methylindole (Alfa Aesar), 7-methylindole (Aldrich), benzimidazole (Alfa Aesar), 5-methoxybenzimidazole (Aldrich), 2-methylbenzimidazole (Aldrich), imidazole (Alfa Aesar), 2-methylimidazole (Aldrich), carbazole (Aldrich; recrystallized), 3-methoxycarbazole (Matrix Scientific), iodobenzene (Aldrich), 4-iodotoluene (Aldrich), 2-iodotoluene (Aldrich), 4-iodoanisole (Aldrich), 4-iodobenzonitrile (Aldrich), 3-iodopyridine (Aldrich), bromobenzene (Avocado), 4-chlorobenzonitrile (Avocado), 1-ethyl-4-iodobenzene (Avocado), 4-bromotoluene (Aldrich), 4-chlorotoluene (Aldrich), benzylacetone (Aldrich), dicyclohexylamine (Aldrich), cyclohexylamine (Aldrich), chlorobenzene (Aldrich), trans-5-decene (Aldrich), cis-5-decene (TCI), 5-decyne (Lancaster), dibenzyl ether (Alfa Aesar), bromomethylenecyclohexane (Aldrich), Cul (Aldrich), LiOt-Bu (Alfa Aesar), and t-BuOH (Aldrich; anhydrous). CH3CN was deoxygenated and dried by sparging with nitrogen followed by passage through an activated alumina column (S. G. Water) prior to use.

All coupling reactions were carried out using a Luzchem LZC-4V photoreactor at 254 nm (UVC). $^1$H NMR data and $^{13}$C NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. GC analyses were carried out on an Agilent 6890 series system with a DB-1 column (length 30 m, I.D. 0.25 mm) or an HP-5 column (length 30 m, I.D. 0.25 mm) or on an Agilent 6850 series system with a BETA DEX 120 column (length 30 m, I.D. 0.25 mm).
II. Photoinduced, Cu-Catalyzed N-Arylations

**General Procedure.** The nitrogen heterocycle (1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), and CuI (19.0 mg, 0.10 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The test tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the test tube was evacuated and backfilled with nitrogen (three cycles). Then, CH$_3$CN (4.0 mL) and the aryl iodide (1.40 mmol; if the aryl iodide is a solid, then it was added immediately after the addition of CuI) were added in turn via syringe. The test tube was detached from the nitrogen manifold, and the puncture holes in the septum were covered with vacuum grease. The resulting mixture was stirred for 5 min, and then the test tube was transferred to a Luzchem LZC-4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). Next, the mixture was passed through a long plug of silica gel (monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

Notes: (a) A Honeywell ultraviolet air treatment system (model #RUVLAMP1), available for ~$110 from retail outlets such as Amazon or The Home Depot, furnishes a comparable result: indole and iodobenzene couple in 63% yield (calibrated GC analysis) after 48 h. (b) Use of a borosilicate, rather than a quartz, test tube leads to a low yield of the C–N coupling product.

![1-Phenyl-1H-indole](image)

1-Phenyl-1H-indole (Table 2.1, Entry 1) [16096-33-6]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography (hexanes). A $^1$H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Pale-yellow oil. First run: 142 mg (73% yield). Second run: 148 mg (77% yield).
1-(p-Tolyl)-1H-indole (Table 2.1, Entry 2) [167283-32-1]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% EtOAc/hexanes). A 1H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Colorless oil. First run: 140 mg (68%). Second run: 143 mg (69%).

2-(4-(1H-Indol-1-yl)phenyl)propan-2-ol (Table 2.1, Entry 3). The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-(4-iodophenyl)propan-2-ol (367 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% EtOAc/hexanes) and purified by column chromatography on silica gel (7.5% EtOAc/hexanes→15% EtOAc/hexanes). Pale-orange solid. First run: 144 mg (57%). Second run: 143 mg (57%).

1H NMR (500 MHz, CDCl3) δ 7.71–7.69 (m, 1H), 7.67–7.62 (m, 2H), 7.60–7.56 (m, 1H), 7.51–7.46 (m, 2H), 7.34 (d, 1H, J = 3.0 Hz), 7.23 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 7.18 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 6.69 (dd, 1H, J = 3.0, 1.0 Hz), 6.81 (br s, 1H), 1.66 (s, 6H).

13C NMR (126 MHz, CDCl3) δ 147.5, 138.5, 136.0, 129.4, 128.1, 125.9, 124.2, 122.4, 121.2, 120.5, 110.7, 103.6, 72.6, 32.0.
FT-IR (neat) 3541, 3399, 3103, 3049, 2974, 2927, 2868, 1606, 1582, 1570, 1519, 1457, 1412, 1363, 1347, 1334, 1317, 1298, 1281, 1256, 1234, 1213, 1170, 1137, 1114, 1094, 1066, 1015, 955, 883, 862, 840, 770, 762, 742, 720 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₁₇H₁₈NO: 252, found: 252.

**6-Methoxy-1-phenyl-1H-indole (Table 2.1, Entry 4)** [487058-34-4]. The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et₂O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). A ¹H NMR spectrum was collected and compared to literature values to confirm the structure of the product. White solid. First run: 147 mg (66%). Second run: 150 mg (67%).

**6-Methoxy-1-(o-tolyl)-1H-indole (Table 2.1, Entry 5).** The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et₂O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). Yellow oil. First run: 154 mg (65% yield). Second run: 165 mg (70% yield).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56 (d, 1H, $J = 8.5$ Hz), 7.40–7.36 (m, 2H), 7.35–7.31 (m, 2H), 7.06 (d, 1H, $J = 3.2$ Hz), 6.82 (dd, 1H, $J = 8.5$, 2.2 Hz), 6.59 (d, 1H, $J = 3.2$ Hz), 6.50 (s, 1H), 3.76 (s, 3H), 2.09 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.8, 138.5, 137.8, 136.0, 131.4, 128.3, 128.2, 127.8, 127.0, 122.6, 121.5, 110.1, 102.5, 94.0, 55.8, 17.8.

FT-IR (neat) 3102, 3026, 2994, 2952, 2831, 1621, 1603, 1573, 1513, 1487, 1459, 1380, 1340, 1324, 1292, 1279, 1225, 1205, 1177, 1121, 1095, 1031, 927, 806, 769, 746, 720 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$+H) calcd for C$_{16}$H$_{16}$NO: 238, found: 238.

3-Methyl-1-phenyl-$1H$-indole (Table 2.1, Entry 6) [112817-88-6]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes$\rightarrow$1% Et$_2$O/hexanes). A $^1$H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Colorless oil. First run: 152 mg (73%). Second run: 145 mg (70%).

1-(4-Methoxyphenyl)-3-methyl-$1H$-indole (Table 2.1, Entry 7) [876337-56-3]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10%
EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→2% 
Et₂O/hexanes). A ¹H NMR spectrum was collected and compared to literature values to confirm 
the structure of the product. Colorless oil. First run: 138 mg (58%). Second run: 138 mg (58%).

2-Methyl-1-phenyl-1H-indole (Table 2.1, Entry 8) [16176-77-5]. The title compound 
was synthesized according to the General Procedure from 2-methylindole (131 mg, 1.00 mmol), 
LiOt-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 
mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and 
purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). A ¹H NMR 
spectrum was collected and compared to literature values to confirm the structure of the product. 
Colorless oil. First run: 122 mg (59%). Second run: 124 mg (60%).

7-Methyl-1-phenyl-1H-indole (Table 2.1, Entry 9) [473918-43-3]. The title compound 
was synthesized according to the General Procedure from 7-methylindole (131 mg, 1.00 mmol), 
LiOt-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 
mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and 
purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). A ¹H NMR 
spectrum was collected and compared to literature values to confirm the structure of the product. 
White solid. First run: 139 mg (67%). Second run: 133 mg (64%).
1-Phenyl-1\(H\)-benzo[d]imidazole (Table 2.2, Entry 1) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol), except that a mixture of \(t\)-BuOH (1.0 mL) and CH\(_3\)CN (3.0 mL) was used as the solvent (\(t\)-BuOH and CH\(_3\)CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH\(_3\)CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH\(_2\)Cl\(_2\)) and purified by column chromatography on silica gel (0.75% MeOH/CH\(_2\)Cl\(_2\), then 15%→25% EtOAc/hexanes). A \(^1\)H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow oil. First run: 158 mg (81%). Second run: 165 mg (85%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

4-(1\(H\)-Benzo[d]imidazol-1-yl)benzonitrile (Table 2.2, Entry 2) [25699-95-0]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321 mg, 1.40 mmol), except that a mixture of \(t\)-BuOH (1.0 mL) and CH\(_3\)CN (3.0 mL) was used as the solvent (\(t\)-BuOH and CH\(_3\)CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH\(_3\)CN. The product was filtered through a plug of silica gel (5% MeOH/CH\(_2\)Cl\(_2\)) and purified by column chromatography on silica gel (1% MeOH/CH\(_2\)Cl\(_2\), then 40%→55% EtOAc/hexanes). A \(^1\)H NMR spectrum was collected and compared to literature
values to confirm the structure of the product. Yellow solid. First run: 185 mg (84%). Second run: 180 mg (82%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

\[
\begin{align*}
\text{OMe} & \\
1-(4\text{-Methoxyphenyl})-1H\text{-benzo}[d]\text{imidazole (Table 2.2, Entry 3) [2622-61-9]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuL (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH}_3\text{CN (3.0 mL) was used as the solvent (t-BuOH and CH}_3\text{CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH}_3\text{CN. The reaction mixture was filtered through a plug of silica gel (5\% MeOH/CH}_2\text{Cl}_2) and purified by column chromatography on silica gel (1\% MeOH/CH}_2\text{Cl}_2, then 30\%-50\% EtOAc/hexanes). A }^1\text{H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 177 mg (79\%). Second run: 164 mg (73\%).} \\
\text{Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} & \\
1\text{-}(4\text{-Methoxyphenyl})-1H\text{-benzo}[d]\text{imidazole (Table 2.2, Entry 3) [2622-61-9]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuL (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH}_3\text{CN (3.0 mL) was used as the solvent (t-BuOH and CH}_3\text{CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH}_3\text{CN. The reaction mixture was filtered through a plug of silica gel (5\% MeOH/CH}_2\text{Cl}_2) and purified by column chromatography on silica gel (1\% MeOH/CH}_2\text{Cl}_2, then 30\%-50\% EtOAc/hexanes). A }^1\text{H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 177 mg (79\%). Second run: 164 mg (73\%).} \\
\text{Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.}
\end{align*}
\]

\[
\begin{align*}
\text{OMe} & \\
6\text{-Methoxy-1-phenyl-1H-benzo}[d]\text{imidazole (Table 2.2, Entry 4) [69445-55-2]. The title compound was synthesized according to the General Procedure from 5-}
\end{align*}
\]
methoxybenzimidazole (148 mg, 1.00 mmol), LiOr-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH2Cl2) and purified by column chromatography (1%→5% MeOH/CH2Cl2, then 20%→35% EtOAc/hexanes). A 1H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 182 mg (81%, 6-methoxy-1-phenyl-1H-benzo[de]imidazole/5-methoxy-1-phenyl-1H-benzo[de]imidazole = 1.0:1). Second run: 190 mg (85%, 6-methoxy-1-phenyl-1H-benzo[de]imidazole/5-methoxy-1-phenyl-1H-benzo[de]imidazole = 1.1:1).

2-Methyl-1-phenyl-1H-benzo[de]imidazole (Table 2.2, Entry 5) [1484-39-5]. The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiOr-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH2Cl2) and purified by column chromatography on silica gel (1%→5% MeOH/CH2Cl2, then 20%→35% ethyl acetate/hexanes). A 1H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 169 mg (81%). Second run: 175 mg (84%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

2-Methyl-1-(o-tolyl)-1H-benzo[de]imidazole (Table 2.2, Entry 6) [68874-09-9]. The title compound was synthesized according to the General Procedure from 2-
methylbenzimidazole (132 mg, 1.00 mmol), LiOtt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH2Cl2) and purified by column chromatography (1% MeOH/CH2Cl2, then 20% EtOAc/hexanes). A 1H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 170 mg (76%). Second run: 166 mg (75%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

2-Methyl-1-(pyridin-3-yl)-1H-benzo[d]imidazole (Table 2.2, Entry 7). The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiOtt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH2Cl2) and purified by column chromatography on silica gel (2% MeOH/CH2Cl2). Yellow solid. First run: 139 mg (66%). Second run: 140 mg (67%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

1H NMR (500 MHz, CDCl3) δ 8.78 (d, 1H, J = 3.2 Hz), 8.70 (s, 1H), 7.45 (apparent t, 2H, J = 3.2 Hz), 7.55 (dd, 1H, J = 7.9, 5.1 Hz), 7.28 (t, 1H, J = 7.8 Hz), 7.21 (t, 1H, J = 7.8 Hz), 7.10 (d, 1H, J = 8.0 Hz), 2.52 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 151.4, 150.1, 148.3, 142.8, 136.3, 134.6, 133.0, 124.5, 123.2, 123.0, 119.4, 109.6, 14.6.

FT-IR (neat) 3391, 3053, 2927, 2851, 1615, 1587, 1575, 1524, 1486, 1456, 1427, 1393, 1372, 1314, 1287, 1249, 1187, 1149, 1105, 1050, 1029, 1015, 999, 929, 878, 810, 765, 745, 712 cm⁻¹.
MS (ESI) \( m/z \) (M\(^{+}\)H) calcd for C\(_{13}\)H\(_{12}\)N\(_{3}\): 210, found: 210.

1-Phenyl-1\(H\)-imidazole (Table 2.3, Entry 1) [7164-98-9]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), Cul (28.6 mg, 0.15 mmol), and iodobenzene (428 mg, 2.10 mmol), except that a mixture of \( t \)-BuOH (1.5 mL) and CH\(_{3}\)CN (4.5 mL) was used as the solvent (\( t \)-BuOH and CH\(_{3}\)CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH\(_{3}\)CN. The reaction mixture was filtered through a plug of silica gel (1% MeOH/CH\(_{2}\)Cl\(_{2}\)) and purified by column chromatography (1% MeOH/CH\(_{2}\)Cl\(_{2}\), then 40%-50% EtOAc/hexanes). A \( ^{1} \)H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Pale-yellow oil. First run: 150 mg (69%). Second run: 148 mg (68%).

1-(o-Tolyl)-1\(H\)-imidazole (Table 2.3, Entry 2) [25371-93-1]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), Cul (28.6 mg, 0.15 mmol), and 2-iodotoluene (458 mg, 2.10 mmol), except that a mixture of \( t \)-BuOH (1.5 mL) and CH\(_{3}\)CN (4.5 mL) was used as the solvent (\( t \)-BuOH and CH\(_{3}\)CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH\(_{3}\)CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH\(_{2}\)Cl\(_{2}\)) and purified by column chromatography (1%-3% MeOH/CH\(_{2}\)Cl\(_{2}\), then 30%-50% EtOAc/hexanes). A \( ^{1} \)H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow oil. First run: 154 mg (65%). Second run: 161 mg (68%).
2-Methyl-1-phenyl-1H-imidazole (Table 2.3, Entry 3) [60053-07-8]. The title compound was synthesized according to the General Procedure from 2-methylimidazole (123 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and iodobenzene (428 mg, 2.10 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH₂Cl₂) and purified by column chromatography (2% MeOH/CH₂Cl₂, then 40% → 50% EtOAc/hexanes). A ¹H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow oil. First run: 106 mg (45%). Second run: 109 mg (46%).

9-Phenyl-9H-carbazole (Table 2.4, Entry 1) [1150-62-5]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes → 1% Et₂O/hexanes). A ¹H NMR spectrum was collected and compared to literature values to confirm the structure of the product. White solid. First run: 212 mg (87%). Second run: 206 mg (85%).

4-(9H-Carbazol-9-yl)benzonitrile (Table 2.4, Entry 2) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321
mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% 
EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→2% 
Et2O/hexanes). A \(^1\)H NMR spectrum was collected and compared to literature values to confirm 
the structure of the product. Yellow solid. First run: 203 mg (76%). Second run: 209 mg 
(78%).

\[
\text{NOMe} \\
\text{9-(4-Methoxyphenyl)-9H-carbazole (Table 2.4, Entry 3) [19264-74-5]}.
\]
The title 
compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 
mmol), LiOr-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 
1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% 
EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% 
Et2O/hexanes). A \(^1\)H NMR spectrum was collected and compared to literature values to confirm 
the structure of the product. White solid. First run: 215 mg (79%). Second run: 196 mg 
(72%).

\[
\text{9-(o-Tolyl)-9H-carbazole (Table 2.4, Entry 4) [19155-50-1]}.
\]
The title compound was 
synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOr-Bu 
(112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The 
reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by 
column chromatography on silica gel (hexanes→1% Et2O/hexanes). A \(^1\)H NMR spectrum was 
collected and compared to literature values to confirm the structure of the product. White solid. 
First run: 213 mg (83%). Second run: 204 mg (79%).
9-(Pyridin-3-yl)-9H-carbazole (Table 2.4, Entry 5) [168127-56-8]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), Cul (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (50% EtOAc/hexanes) and purified by column chromatography on silica gel (10% EtOAc/hexanes). A $^1$H NMR spectrum was collected and compared to literature values to confirm the structure of the product. White solid. First run: 154 mg (63%). Second run: 166 mg (68%).

3-Methoxy-9-(o-tolyl)-9H-carbazole (Table 2.4, Entry 6). The title compound was synthesized according to the General Procedure from 3-methoxycarbazole (100 mg, 0.51 mmol), LiOt-Bu (56.8 mg, 0.71 mmol), Cul (9.7 mg, 0.051 mmol), and 2-iodotoluene (155 mg, 0.71 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et$_2$O/hexanes). Colorless oil. First run: 110 mg (76%). Second run: 110 mg (76%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (d, 1H, $J = 7.5$ Hz), 7.65 (d, 1H, $J = 2.0$ Hz), 7.50–7.33 (m, 5H), 7.27–7.23 (m, 1H), 7.06–7.01 (m, 2H), 6.96 (d, 1H, $J = 9.0$ Hz), 3.96 (s, 3H), 1.97 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.2, 141.8, 137.5, 136.4, 136.3, 131.6, 129.4, 128.8, 127.4, 126.0, 123.5, 123.0, 120.4, 119.2, 115.1, 110.7, 110.0, 103.4, 56.3, 17.7.

FT-IR (neat) 3050, 2993, 2932, 2830, 1627, 1600, 1580, 1498, 1485, 1462, 1438, 1381, 1359, 1329, 1285, 1254, 1236, 1206, 1179, 1167, 1149, 1119, 1098, 1035, 943, 912, 860, 847, 806, 764, 746, 720 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$) calcd for C$_{20}$H$_{17}$NO: 287, found: 287.
1-Fluoro-9-(o-tolyl)-9H-carbazole (Table 2.4, Entry 7). The title compound was synthesized according to the General Procedure from 1-fluorocarbazole (100 mg, 0.54 mmol), LiOt-Bu (60.5 mg, 0.76 mmol), CuI (10.3 mg, 0.054 mmol), and 2-iodotoluene (165 mg, 0.76 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et2O/hexanes). Pale-yellow oil. First run: 111 mg (75%). Second run: 110 mg (74%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14 (d, 1H, $J = 8.0$ Hz), 7.93 (d, 1H, $J = 7.5$ Hz), 7.47–7.34 (m, 5H), 7.30 (t, 1H, $J = 7.5$ Hz), 7.18 (td, 1H, $J = 8.0, 4.0$ Hz), 7.10 (dd, 1H, $J = 12.0, 7.5$ Hz), 7.01 (d, 1H, $J = 8.5$ Hz), 2.01 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 149.6 (d, $J_{CF} = 245.8$ Hz), 141.9, 137.4, 137.3, 131.1, 129.0, 128.9, 128.7 (d, $J_{CF} = 8.7$ Hz), 127.0 (d, $J_{CF} = 4.8$ Hz), 126.9, 126.7, 123.0 (d, $J_{CF} = 2.9$ Hz), 120.5, 120.2, 119.8 (d, $J_{CF} = 6.8$ Hz), 116.2 (d, $J_{CF} = 3.9$ Hz), 112.1 (d, $J_{CF} = 17.3$ Hz), 110.3, 17.5.

FT-IR (neat) 3058, 2955, 2924, 1635, 1602, 1577, 1498, 1455, 1435, 1381, 1354, 1339, 1316, 1290, 1248, 1226, 1184, 1154, 1116, 1081, 1053, 1014, 951, 925, 884, 787, 745, 733, 722 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{14}$FN: 275, found: 275.

1-Phenyl-1H-indole (Table 2.5, Entry 1) [16096-33-6]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography (hexanes). A $^1$H NMR spectrum was collected and compared to
literature values to confirm the structure of the product. Pale-yellow oil. First run: 115 mg (60% yield). Second run: 122 mg (63% yield).

\[ \text{N} \]

1-Phenyl-1H-benzo[d]imidazole (Table 2.5, Entry 2) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), \( \text{LiO}t-\text{Bu} \) (112 mg, 1.40 mmol), \( \text{CuI} \) (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol), except that a mixture of \( \text{t-BuOH} \) (1.0 mL) and \( \text{CH}_3\text{CN} \) (3.0 mL) was used as the solvent (\( \text{t-BuOH} \) and \( \text{CH}_3\text{CN} \) were added in turn via syringe), due to the poor solubility of the heterocycle in neat \( \text{CH}_3\text{CN} \). Reaction time: 48 h. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by normal-phase column chromatography on silica gel (0.75% MeOH/CH₂Cl₂) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). A \(^1\text{H}\) NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow oil. First run: 118 mg (61%). Second run: 125 mg (64%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

\[ \text{N} \]

4-(9H-Carbazol-9-yl)benzonitrile (Table 2.5, Entry 3) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), \( \text{LiO}t-\text{Bu} \) (112 mg, 1.40 mmol), \( \text{CuI} \) (19.0 mg, 0.10 mmol), and 4-chlorobenzonitrile (193 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel.
(hexanes→2% Et₂O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). A ¹H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 192 mg (72%). Second run: 194 mg (72%).

![Chemical Structure](image)

4-(1H-Benzimidazol-1-yl)benzonitrile (Table 2.5, Entry 4) [25699-95-0]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-chlorobenzonitrile (193 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. Reaction time: 48 h. The product was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by column chromatography on silica gel (1% MeOH/CH₂Cl₂, then 40%→55% EtOAc/hexanes). A ¹H NMR spectrum was collected and compared to literature values to confirm the structure of the product. Yellow solid. First run: 131 mg (60%). Second run: 135 mg (62%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

### III. Nucleophile Competition Experiments

**Procedure.** Both of the nitrogen heterocycles (0.40 mmol each) and LiOt-Bu (32.0 mg, 0.40 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where t-BuOH (0.40 mL) and CH₃CN (0.40 mL) were added. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH₃CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl
ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 2 h. Note: Reactions with benzimidazole were quickly transferred to the photoreactor before they became heterogeneous.

IV. Electrophile Competition Experiments

Procedure. Indole (46.9 mg, 0.40 mmol) and LiOr-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where CH$_3$CN (0.80 mL), 1-ethyl-4-iodobenzene (130 mg, 0.56 mmol), and the aryl bromide or chloride (0.56 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH$_3$CN (0.80 mL, 0.050 M) was added, followed by dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 1 h.

V. Functional-Group Tolerance Experiments

Procedure. Indole (46.9 mg, 0.40 mmol) and LiOr-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz test tube was transferred to a glovebox, where CH$_3$CN (0.80 mL) and the additive (0.40 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH$_3$CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The reaction mixture was stirred for 3 min, and then an aliquot was taken for a t = 0 time point. Next, the quartz test tube was capped with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). The yield of product and the percent recovery of the additive were determined by GC analysis.
VI. Photoinduced, Cu-Catalyzed N-Alkenylations/Alkynylations

**General Procedure.** The nitrogen heterocycle (0.50 mmol) and LiOt-Bu (83.0 mg, 1.04 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The quartz tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was evacuated and backfilled with nitrogen (3 cycles). Then, CH$_3$CN (4.0 mL) was added, and the mixture was stirred for 10 min. Next, a solution of CuI in CH$_3$CN (500 µL, 0.10 M) was added via syringe, and the mixture was stirred for 10 min. A 4-mL oven-dried vial was charged with the alkenyl iodide (0.85 mmol), closed with a septum cap, and evacuated and backfilled with nitrogen (3 cycles). The alkenyl iodide was transferred to the quartz tube via syringe. The vial was rinsed with CH$_3$CN (0.50 mL), and the washing was transferred to the quartz tube. The test tube was detached from the nitrogen manifold, and the puncture holes in the septum were covered with vacuum grease. The mixture was stirred for 10 min, and then the test tube was transferred to a Luzchem LZC-4V photoreactor, where it was irradiated at 254 nm for 12 h (adequate stirring is important). Next, the reaction mixture was passed through a plug of silica gel (10% EtOAc/hexanes; monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

Note: For the N-alkynylation process (Table 2.8, entry 5), the same procedure was employed, except that the reaction mixture was irradiated for 24 h.

![t-Bu](image)

**9-((4-(tert-Butyl)cyclohexylidene)methyl)-9H-carbazole (Table 2.8, Entry 1).** The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 1-(iodomethylidene)-4-tert-butyl-cyclohexane (237 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 138 mg (87%). Second run: 131 mg (83%).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.11 (d, 2H, $J = 7.7$ Hz), 7.46 (t, 2H, $J = 7.7$ Hz), 7.40–7.21 (m, 4H), 6.45 (s, 1H), 2.75–2.62 (m, 1H), 2.36–2.25 (m, 2H), 2.11–2.03 (m, 1H), 1.89–1.70 (m, 2H), 1.35–1.20 (m, 2H), 1.08–0.96 (m, 1H), 0.89 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.6, 140.9, 125.6, 122.9, 120.1, 119.3, 114.1, 110.0, 48.1, 33.2, 32.5, 29.2, 28.9, 28.1, 27.6.

FT-IR (neat) 3054, 2986, 2305, 1479, 1457, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{23}$H$_{27}$N: 317, found: 317.

![Diagram](image1)

9-(4-(tert-Butyl)cyclohex-1-en-1-yl)-9$^H$-carbazole (Table 2.8, Entry 2). The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 4-tert-butyl-1-iodo-1-cyclohexene (225 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 114 mg (75%). Second run: 114 mg (75%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.11 (d, 2H, $J = 7.7$ Hz), 7.46–7.36 (m, 4H), 7.28–7.19 (m, 2H), 6.10–6.06 (m, 1H), 2.50–2.36 (m, 3H), 2.24–2.12 (m, 1H), 2.11–2.00 (m, 1H), 1.65–1.50 (m, 2H), 1.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.4, 134.3, 128.3, 125.6, 122.9, 120.2, 119.1, 109.8, 44.0, 32.4, 28.5, 27.3, 26.6, 24.4.

FT-IR (neat) 3054, 2987, 2305, 1452, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{22}$H$_{25}$N: 303, found: 303.

![Diagram](image2)

1-((4-(tert-Butyl)cyclohexylidene)methyl)-1$^H$-indole (Table 2.8, Entry 3). The title compound was synthesized according to the General Procedure from indole (59 mg, 0.50 mmol) and 1-(iodomethylidene)-4-tert-butyl-cyclohexane (237 mg, 0.85 mmol). The product was
purified by column chromatography (hexanes). White solid. First run: 100 mg (75%). Second run: 99 mg (74%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, 1H, $J = 7.8$ Hz), 7.32 (d, 1H, $J = 8.3$ Hz), 7.27–7.21 (m, 1H), 7.18–7.12 (m, 1H), 7.11–7.08 (m, 1H), 6.58–6.53 (m, 2H), 2.66–2.48 (m, 2H), 2.26–2.15 (m, 1H), 2.05–1.97 (m, 1H), 1.91–1.79 (m, 2H), 1.31–1.15 (m, 2H), 1.10–0.97 (m, 1H), 0.89 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.7, 136.6, 128.5, 128.1, 121.7, 120.7, 119.7, 116.4, 110.3, 101.8, 48.1, 33.4, 32.5, 29.0, 28.4, 28.2, 27.6.

FT-IR (neat) 3054, 2986, 2305, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{25}$N: 267, found: 267.

1-(Cyclohexylidenemethyl)-1H-indole (Table 2.8, Entry 4). The title compound was synthesized according to the General Procedure from indole (59 mg, 0.50 mmol) and bromomethylenecyclohexane (155 mg, 0.85 mmol). Reaction time: 48 h. The product was purified by column chromatography (hexanes). Colorless oil. First run: 58 mg (55%). Second run: 60 mg (57%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (d, 1H, $J = 7.8$ Hz), 7.34 (d, 1H, $J = 8.2$ Hz), 7.29–7.23 (m, 1H), 7.20–7.15 (m, 1H), 7.13–7.09 (m, 1H), 6.61–6.57 (m, 2H), 2.38–2.32 (m, 2H), 2.24–2.18 (m, 2H), 1.78–1.70 (m, 2H), 1.70–1.63 (m, 2H), 1.60–1.52 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.1, 136.6, 128.5, 128.1, 121.7, 120.7, 119.7, 116.8, 110.3, 101.8, 33.4, 28.5, 28.3, 27.4, 26.5.

FT-IR (neat) 2934, 2956, 2253, 1674, 1511, 1475, 1462, 1377, 1319, 1234, 1088, 907 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{15}$H$_{17}$N: 211, found: 211.
9-((Triisopropylsilyl)ethynyl)-9H-carbazole (Table 2.8, Entry 5). The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 2-bromo-1-triisopropylsilyl acetylene (222 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 109 mg (63%). Second run: 107 mg (62%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.02 (d, 2H, $J = 7.7$ Hz), 7.64 (d, 2H, $J = 8.1$ Hz), 7.53 (t, 2H, $J = 7.7$ Hz), 7.34 (t, 2H, $J = 7.7$ Hz), 1.31–1.14 (m, 21H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.5, 126.7, 123.3, 122.0, 120.3, 111.4, 92.6, 72.8, 18.8, 11.4.

FT-IR (neat) 3054, 2986, 2305, 2178, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{23}$H$_{29}$NSi: 347, found: 347.
VII. $^1$H NMR Spectra
(Table 2.1, Entry 1)
DZ-04-292-1-Purified

PROTON

Sample: April 2, 2013
Solvent: CDCl3
File: /indy/dziegle-r/vnmrsys/data/DZ-04-292-1-Purified/PROTON01.fid

Acquisition:
- SW: 8000.0 Hz
- AT: 3.000 ppm
- NP: 48000
- FB: Not used
- BS: 32
- DS: 1.000 ap y
- NT: 18 hs
- CT: 16

Transmitter:
- TN: H1
- SFreq: 499.708 Hz
- TPwr: 61
- PW: 4.950

Decoupler:
- DN: C13
- DPW: 0
- DM: nnn
- DECWAVE: W40_eutox7

Presaturation:
- SATMODE: Wet
- SAT: 0.008

Special:
- Temp: Not used
- Gain: 32
- Spin Hst: 0.0
- PW90: 9.8
- ALFA: 10.0

Flags:
- IL: In
- DP: Hs

Processing:
- LB: 0.20
- FN: Not used

Display:
- SP: -0.1
- WP: 4996
- RFL: 4630
- RP: 3627
- IP: -73

Plot:
- WC: 2
- SC: 18
- TH: 108

(Table 2.1, Entry 2)
DZ-05-082-1-Purified

exp25 PROTON

SAMPLE

DATE: Jul 26 2013

SOLVENT: cdc13

FILE: /indy/dziegle-r/vnmrsys/data/DZ-05-082-1-Purified/PROTON01.fid

ACQUISITION

sw: 8000.0
at: 3.000
np: 48000
fb: not used
bs: 32

di: 1.000
dp: y

nt: 32
ct: 32

TRANSMITTER

tn: 0.20
tf: 499.698
tof: 499.7
tpw: 61

DECOUPLER

dn: C13
dof: 0

dc: 84

decwave W40_aurox7-

dpwr: 41

dmf: 32258

PRESATURATION

satmode: wet

SPECIAL

temp: not used
gain: 32

FLAGs

il: in
dp: hs

PROCESSING

0.20

DISPLAY

PLOT

cdc: ph

(Table 2.1, Entry 3)
MeO

(Entry 4)

(Table 2.1, Entry 4)
(Table 2.1, Entry 5)
(Table 2.1, Entry 7)
DZ-04-266-2-Purified
exp20 PROTON

SAMPLE
date Mar 20 2013
solvent cdcl3
file /indy/dziegle~r/vnmrsys/data/DZ--04-266-2-Purified/

PRE-SATURATION
satmode n
satmode wet n

ACQUISITION
gen 30
sw 8000.0
at 3.000
np 48000
fb not used

TRANSMITTER
H1
sfrq 499.708

DECOUPLER
C13
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doer 0

dm nnn

decwave g

dgwr 35

dmr 32250

(ACS 2.1, Entry 8)

Table 2.1, Entry 8

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3.19 3.20 1.00
Table 2.1, Entry 9

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- 1.95
- 0.94

0.87 1.95 0.94
4.93 1.00 3.24
DZ-04-270-1-Purified

exp20 PROTON

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date Mar 26 2013 satmode n
solvent cdc13 wet n
file /indy/dziegle= SPECIAL n
r/vnmrsys/data/DZ-- temp not used
04-270-1-Purified/- gain 32
PROTON01_fid spin 0
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sw 6000.0 pw90 4.300
at 3.000 alpha 10.000
np 48000lags
fo not used 11 n
bs 32 in n
dt 1.000 dp y
nt 16 hs n
ct 16 PROCESSING

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fn not used
sfrq 449.708 DISPLAY
of 499.7 sp -0.1
tpwr 61 wp 4496.8
pw 4.350 rfi 4629.9
DECoupler rfp 3827.9
dn C13 rp 24.7
dof 0 1p -72.1
dm nnn PLot
decwave W40_autox7/ wc 250
991 sc 0
dpwr 41 vs 135
dmf 3250 th 4
al cdc ph

(Table 2.2, Entry 2)
**DZ-04-268-3-Purified**

**SAMPLE**

- Date: Apr 2 2013
- Solvent: CDCl3
- File: /indy/dziegle-r/vnmrsys/data/DZ-04-268-3-Purified/PROTON02.fid

**ACQUISITION**

- SW: 8000.0
- AT: 3.000
- NP: 48000
- BS: 32
- DL: 1.000
- NT: 16
- CT: 16

**TRANSMITTER**

- TN: H1
- SFREQ: 499.700
- TOR: 0.1
- PW: 6.950
- DC: 0.0
- DM: -79.4

**DECOUPLER**

- DWAVE: 490_autox7-250
- DPWR: -25
- DMF: 3225

**PRESATURATION**

- SATMODE: N
- WET: N
- TEMP: not used
- GAIN: 32
- SPIN: 20

**PROCESSING**

- 0.20

**DISPLAY**

- -0.1

**PLOT**

- 250

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(Table 2.2, Entry 3)
(Table 2.2, Entry 4)
(Table 2.2, Entry 4)
Sample: 1H CDC13

Date: Mar 21 2013
Solvent: CDCl3

File: /indy/jwchoi/vnmrsys/data/JC9291H_1HCDCl3/PROTON02.fid

Acquisition:
- SW: 8000.0
- AT: 3.000
- NP: 48000
- FB: not used
- BS: 32
- D1: 2.000
- NT: 16
- CT: 16

Transmitter:
- TN: H1
- SFREQ: 499.708
- TOF: 499.7
- TPWR: 61

Decoupler:
- DN: C13
- DOF: 0
- DM: nnn
- DMF: 32258

Presaturation:
- SATMODE: n
- SAT: not used

Special:
- TEMP: not used
- GAIN: 30
- SPIN: 20

Flags:
- IL: n
- DP: n

Processing:
- LB: 0
- FN: not used

Display:
- SP: -
- WP: 499
- RFL: 463
- RFP: 362
- RP: 4
- LP: -6

Plot:
- WC: sc
- VS: th
- NH: cdc

(Table 2.2, Entry 5)
(Table 2.2, Entry 6)
Table 2.2, Entry 7

N(Tal 2Me):N

(Table 2.2, Entry 7)
DZ-Ph-imidazole 1H CDC13

**exp10 PROTON**

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| at      | 3.000         |
| np      | 48000         |
| fb      | not used      |
| bs      | 32            |
| dt      | 2.000         |
| nt      | 16            |
| ct      | 16            |
| TRANSFER |            |
| bn      | H1            |
| tof     | 499.7         |
| tpwr    | 61            |
| pw      | 4.950         |
| DECOUPLER | rfp 3627.9 |
| dn      | 1C13          |
| dof     | 0             |
| dm      | nnn           |
| decwave | w40_autox7-  |
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(Table 2.3, Entry 1)
(Table 2.3, Entry 2)
(Table 2.3, Entry 3)
DZ-04-230-3-Purified

exp20 PROTON

SAMPLE
DZ-04-230-3-Purified

PRESATURATION
date Mar 18 2013
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solvent cdc13 wet n
file /indy/dziegle-
r/vnmrsys/data/DZ--
04-230-3-Purified/
satmode

ACQUISITION
acq 0.008

sw 8000.0 pw90

at 3.000

np 48000

fb not used

bs 32

di 1.000

nt 16

cf 16

TRANSIMITER
lb 0.20

fn not used

sfrq 499.708

display -0.1

sw 4.850

decoupler

rfl 3627.8

rfl 4630.1

dof 0.5

dp 35

ct 16

PROCESSING

transmitter 1b

decoupler

(2.4, Entry 1)

TABLE 2.4, ENTRY 1

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exp20 PROTON

Table 2.4, Entry 2

(CL3283 IN CDCl3

SAMPLE

date Mar 17 2013
solvent cdcl3
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3_1H_CDCl3/PROTON-
1.fid

ACQUISITION

sw 8000.0
at 3.000
np 40000
fb not used
bs 32
nl 2.000
t 16
ct 16

TRANSMITTER

tn H1
sf 499.700
tof 499.7
tpwr 61
pw 4.850

DECOUPLER
dn C13
dof 0

dm w

decwave g

dpwr 35

dmf 32558

DISPLAY

sp -
wp -
rf 499

PROCESSING

lb 0
fn not used

dp 0
hs 0

PLOT

wc 9
sc -
th 0

al cd c ph

(CN)2

N

(Table 2.4, Entry 2)
(Table 2.4, Entry 3)
Me

(Table 2.4, Entry 4)
(Table 2.4, Entry 5)
(Table 2.4, Entry 6)
JMM1250
exp10 PROTON

SAMPLE
DATE Apr 27 2013
Solvent cdc13 wet
File /indy/jmmolin-
1250/PROTON01.fid

PRESATURATION
Gain 20
Spin 20
Acquisition Spin 0.0
Satmode n
Temp not used

Acquisition
Sw 8000.0
At 3.000
Pw90 9.000
Sp 16
Dp n
Nt 16
Bn 16

Spin
Sw 8000.0
At 3.000
Pw90 9.000
Sp 16
Dp n
Nt 16
Bn 16

Transmitter Processing
Tn H1 nb 0.20
Sfqa 499.700 fn not used
Tof 499.7 DISPLAY
Tpw 61 sp -0.0
Pw 4.950 wp 4996.8

Decoupler
Dn C13 rfp 0
Dof 0 rp 24.3
Dm 1.

Decwave W42_autox7-
S91 wc 250
Dpw 41 sc 0
Dmf 32258 vs 101
Th 31

(Colour 2.5, Entry 2)
exp10 PROTON

SAMPLE

date Apr 27 2013 satmode n
solvent cdc13 wet n
file /indy/jwchoi/

vnmrsys/data/JC100-
05_1H_CDC13/PROTON-
02.fid spin 32

ACQUISITION

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at 3.000 alfa 10.000
np 48000 flags
fb not used
bs 32

at 2.000 dp
nt 16 hs
ct 16 processing

TRANSMITTER

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fn not used
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tpw 61 wp 4996.8
pw 4.950 rfp 4630.1
decoupler rfp 3627.5
dn C13 rp 17.3
dof 0 lp -64.2
dm nnn

dcwave w40_autox7 wc 250

991 sc 0
gpw 41 vo 97
dmf 32258 th al cdc ph 33

(Table 2.5, Entry 3)
DZ-05-034-1-Purified

exp10 PROTON

SAMPLE          PRESATURATION
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solvent  cdcl3      wet n
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         r/vnmrsys/data/DZ--
file    05-034-1-Purified/
gain32  PROTON01.fid  spin 20

ACQUISITION
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at     3.000   alfa  10.000
np     48000   FLAGS
fb     not used 11  n
bs     32 1n
di     1.000   dp  y

nt     16  hs  nn
ct     16  PROCESSING

TRANSMITTER
lb     0.20
fn     not used

sfrq  499.708

DISPLAY

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tpwr  61  wp  4999.0

pw     4.950  rf1  4630.1

DECOUPLER

rfp    3627.8
dn     C13  rp  15.6
dof    0  lp  -72.5
dm     nnn

decwave W40_autox7- wc  250

dpwr  41  vs  100
dmf   32258

0.96  2.02  1.97
2.88  1.00

(Table 2.5, Entry 4)
(Table 2.8, Entry 1)
(Table 2.8, Entry 2)
Table 2.8, Entry 3:

![N-t-Bu](image)

分子结构图

(JMM1193, Exp10 PROTON)

- **SAMPLE**: Date Mar 26 2013
- **Solvent**: CDCl3
- **File**: /indy/jmmolin/a/vnmrsys/data/JMM-1193/PROTON01.fid

**ACQUISITION**:
- **SW**: 8000.0 Hz
- **At**: 3.000 ppm
- **NP**: 40000
- **FB**: Not used
- **BS**: 32
- **DL**: 1.000 s
- **NT**: 16
- **CT**: 16

**TRANSMITTER**:
- **TN**: 499.7 Hz
- **SFRQ**: 499.7 Hz
- **TOF**: 499.7 Hz
- **TPWR**: 61 sp
- **PW**: 4.950 Hz
- **DECOPPER**: C13, rfp 0
- **DOF**: 0
- **DM**: nnn 1p
- **DECWAVE**: W40, autox7

**PROCESSING**:
- **LB**: 0.008
- **HS**: 0.089
- **PW90**: 2.00
- **ALPHA**: 10.000
- **FLAGS**: il, in, dp, y

**DISPLAY**:
- **SP**: -0.0
- **WP**: 4996.8 Hz
- **RFL**: 250
- **RFP**: 0
- **RP**: 26.0
- **LP**: -70.8
- **WC**: 250
- **SC**: 0
- **VS**: 45
- **TH**: 13
- **AL**: cdc, ph

N-t-Bu (Table 2.8, Entry 3)
(Table 2.8, Entry 4)
JMM1202

exp10 PROTON

SAMPLE

date Mar 26 2013
solvent cdc13
file /indy/jmmolin-
a/vnmrsys/data/JMM-
1202/PROTON01.fid

ACQUISITION

sw 8000.0
at 3.000
np 48000
fb not used
bs 32
nt 16
ct 16

TRANSmitter

tn H1
sref 499.708
ctof 499.7
tpwr 61
pw 4.550

dn C13
df 0

decwave W40_auton7

dpwr 41

dm 32258

PRESaturation

satmode n

SPECIAL

temp not used

FLAGS

11

DISPLAY

0.20

0.0

1001.7

0

-25.5

-71.9

0

250

3

N

N

= TIPS

(Table 2.8, Entry 5)
CHAPTER 3

Catalytic Asymmetric C–O Bond Formation: Phosphine-Catalyzed Intermolecular γ Additions of Alcohols to Aryl-Substituted Alkynoates
A. Introduction

Methods for the asymmetric functionalization of carbonyl compounds at the $\alpha$ position and at the $\beta$ position have been extensively investigated.\textsuperscript{43,44} In contrast, there are relatively few methods for the asymmetric functionalization of carbonyl compounds at the $\gamma$ position.\textsuperscript{45} The emergence of phosphines as nucleophilic catalysts has sparked the development of a mode of reactivity that accomplishes this challenging objective.

In 1992, Trost reported that phosphines can catalyze the isomerization of electron-deficient allenes and alkynes to the corresponding 1,3-dienes (eq 3.1).\textsuperscript{46} In subsequent reports, both Trost and Lu demonstrated that this reactivity can be exploited to add nucleophiles to the $\gamma$ position of the carbonyl starting material by intercepting intermediate 3a to form a stabilized phosphorus ylide as shown in the catalytic cycle depicted in Scheme 3.1.\textsuperscript{47} However, this methodology was limited to allene and alkyne starting materials that lack $\delta$ hydrogens and, therefore, cannot undergo isomerization to the corresponding 1,3-dienes (eq 3.2). A variety of nucleophiles including carbon, nitrogen, and oxygen-based nucleophiles were shown to be effective for this reaction.

\begin{equation}
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{X}
\end{array}
\end{array}
\xrightarrow{\text{cat. PR}_3, \text{toluene, } \Delta}
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{X}
\end{array}
\end{array}
\end{equation}

\text{via}

(3.1)

\text{3a}


Scheme 3.1. Outline of a Possible Catalytic Cycle for Phosphine-Catalyzed γ-Addition Reactions

The ability to employ substrates with γ substituents (other than OBn) would significantly increase the utility of the reaction, as a product with a stereocenter at the γ position could be generated. Trost demonstrated the first examples of γ additions with such substrates in a racemic, intramolecular oxygen γ-addition reaction.47b Later, our group reported that the same transformation could be accomplished asymmetrically by utilizing chiral phosphine 3b as the catalyst (eq 3.3).48 This report marked the first example of a chiral phosphine-catalyzed

asymmetric $\gamma$-addition reaction to electron-deficient allenes or alkynes to form a $\gamma$ stereocenter. In both reports, including an acid additive proved to be critical to overcoming the competing isomerization pathway, a trend that has continued in subsequent investigations.

In order to realize the full potential of this promising mode of reactivity, further studies aimed at developing conditions under which $\gamma$-substituted substrates react with nucleophiles in an intermolecular fashion were necessary. Such processes would significantly expand the scope of the transformation with respect to the allene or alkyne starting material. To this end, our group reported the first example of an asymmetric, intermolecular $\gamma$ addition of a nucleophile to an isomerizable allene (eq 3.4). With chiral phosphine 3c as a catalyst, nitromethane was demonstrated to add to allenamides with an array of $\gamma$ substituents in good yield and high ee.


Building on this result, our group has since reported chiral phosphine-catalyzed asymmetric $\gamma$ additions of a variety of nucleophiles to electron-deficient allenes and alkynes, most of which utilize either chiral binaphthyl-derived phosphines similar to $3c$ or chiral phosphine $3b$ as the catalyst. With regard to carbon nucleophiles, the scope has been expanded to include intermolecular $\gamma$ additions of malonate esters. In addition, both alkyl and aryl thiols have been shown to be effective nucleophiles for intermolecular $\gamma$ additions. Lastly, the asymmetric $\gamma$ addition of nitrogen nucleophiles has been demonstrated in both an intramolecular and an intermolecular fashion.

Despite this success with carbon, sulfur, and nitrogen nucleophiles, the asymmetric, intermolecular $\gamma$ addition of oxygen nucleophiles has remained elusive. To the best of our knowledge, the only example of a phosphine-catalyzed intermolecular oxygen $\gamma$ addition to a $\gamma$-substituted allene or alkyn was reported by Trost in 1994 (eq 3.5), and no examples exist where a stereocenter is formed at the $\gamma$ position. However, several oxygen nucleophiles have been shown to add to $\gamma$-unsubstituted allenoates and alkynoates (eq 3.6). In addition to the alcohols originally reported by Trost and Lu (methanol, benzyl alcohol, and cholesterol), Alvarez-Ibarra has demonstrated that carboxylates can be utilized as nucleophiles for this transformation.

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54 (a) For the $\gamma$ addition of alkyl thiols, see: Sun, J.; Fu, G. C. J. Am. Chem. Soc. 2010, 132, 4568-4569. (b) For the $\gamma$ addition of aryl thiols, see: Fujisawa, Y.; Sun, J.; Fu, G. C. Chem. Sci. 2011, 2, 2196-2198.
The products of an asymmetric, intermolecular oxygen γ-addition reaction with a γ-substituted starting material, α,β-unsaturated carbonyl compounds with an oxygen-substituted γ stereocenter, have proven to be useful intermediates for the synthesis of biologically active natural products. Therefore, encouraged by the variety of nucleophiles that have already been utilized in chiral phosphine-catalyzed, asymmetric γ-addition reactions (including the asymmetric, intramolecular γ addition of oxygen nucleophiles) and by previous examples of alcohols and carboxylates as nucleophiles for intermolecular γ additions to γ-unsubstituted allenoates and alkynoates, we decided to pursue chiral phosphine-catalyzed asymmetric, intermolecular γ additions with oxygen nucleophiles. Such a method would provide a concise route to a useful class of synthetic intermediates.

**B. Results and Discussion**

For our initial investigations, we chose to study the reaction between an allenoate with a general n-alkyl γ substituent and a variety of oxygen nucleophiles including p-methoxybenzyl alcohol, phenol, acetic acid, benzoic acid, and a 1:1 mixture of benzoic acid and sodium benzoate. Unfortunately, after extensive screening including evaluations of catalyst structure, acid additives, solvent, and temperature, γ-addition product was only observed with p-methoxybenzyl alcohol as the nucleophile, and at best, only moderate yield could be obtained (eq 3.7). The isomerization pathway to the corresponding 1,3-diene was predominant in these reactions. Phosphepine 3d proved to be the optimal catalyst in terms of the ratio of γ-addition product to isomerization product. However, high enantioselectivity was observed with chiral phosphine 3b as the catalyst.

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Since isomerization to the 1,3-diene could not be overcome by the addition of an acid additive as in other phosphine-catalyzed $\gamma$-addition reactions, we decided to investigate $\gamma$-substituted allenoates that lack $\delta$ hydrogens and, therefore, cannot undergo the isomerization reaction. To the best of our knowledge, there have been no examples of phosphine-catalyzed $\gamma$ additions with allenoates or alkynoates bearing aryl substituents at the $\gamma$ position, so we were interested if these substrates could undergo the desired $\gamma$-addition reaction. When $p$-methoxyphenyl-substituted allenolate 3e was employed as the substrate, we were pleased to observe that the reaction proceeds in good yield and high ee with phosphine 3b as the catalyst (eq 3.8). However, aryl-substituted allenoates are relatively unstable, rendering them difficult to purify and inconvenient to store. For instance, significant decomposition of allenolate 3e was observed after 72 hours at $-40\, ^\circ\text{C}$.

As a result of this instability, we wondered if the corresponding alkynoate (3f) would display similar reactivity and perhaps be more stable and easier to purify. When this alkynoate was exposed to the same reaction conditions, the desired $\gamma$-addition product was formed in improved yield with the same level of enantioselectivity (eq 3.9). Additionally, alkynoate 3f is significantly more stable as no decomposition was observed after months at $-40\, ^\circ\text{C}$ (significant decomposition was observed over the course of a week at room temperature). Therefore, subsequent investigations were carried out with aryl-substituted alkynoates rather than allenoates.
Both the allenoate and the alkynoate are readily available substrates as they can be synthesized in a single step from commercially available starting materials (Scheme 3.2). The allenoate can be prepared via an olefination reaction between the appropriate phosphorane and acid chloride, and the alkynoate can be prepared via a copper-mediated coupling between t-butyl propiolate and the corresponding benzylic chloride. The accessibility of these substrates is a significant advantage when considering the potential utility of this method.

Scheme 3.2. Synthesis of Aryl-Substituted Allenoate and Alkynoate Starting Materials

With a promising result in hand, we were interested in exploring the scope of this process with respect to the aryl substituent on the alkynoate. When we applied our conditions to a 2-thienyl-substituted alkynoate, the reaction proceeded in low yield (eq 3.10). We hypothesized that this decrease in yield could be the result of phosphine-catalyzed oligomerization of the alkyne starting material, and therefore, slow addition of the alkynoate to a solution of catalyst and alcohol could be advantageous. Indeed, adding the alkynoate as a solution in toluene over 16 hours led to a drastic increase in yield with high enantioselectivity.

For a study on the synthesis of alkynoates with an aryl substituent at the γ position, see: Davies, K. A.; Abel, R. C.; Wulff, J. E. J. Org. Chem. 2009, 74, 3997–4000.
In order to maximize the generality of the reaction, we chose to optimize the reaction conditions and study the effect of various reaction parameters using this challenging 2-thienyl-substituted alkynoate (Table 3.1). Under the optimized conditions, a high yield can be achieved with 5% phosphine 3b as long as the nucleophile loading is increased to 4.0 equivalents (entry 1). Several chiral phosphines that have been shown to be effective in other asymmetric γ-addition and/or cycloaddition reactions catalyze the reaction in substantially lower ee and yield (entries 2–4). Further lowering the catalyst loading results in a significant decrease in yield as does lowering the equivalents of nucleophile (entries 5–7). As previously observed, normal addition of the alkynoate solution dramatically reduces the reaction efficiency (entry 8). Finally, the reaction tolerates water reasonably well (entry 9), but running the reaction under air rather than nitrogen results in a poor yield potentially due to catalyst deactivation via oxidation to the phosphine oxide (entry 10).
Table 3.1. Phosphine-Catalyzed Asymmetric Oxygen γ Addition: Effect of Reaction Parameters

<table>
<thead>
<tr>
<th>entry</th>
<th>change from the &quot;standard conditions&quot;</th>
<th>ee (%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>(S)-3d, instead of (R)-3b</td>
<td>58</td>
<td>41</td>
</tr>
<tr>
<td>3</td>
<td>(S)-3g, instead of (R)-3b</td>
<td>26</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>(R)-3h, instead of (R)-3b</td>
<td>26</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>2% (R)-3b</td>
<td>92</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>2.0 equiv of alcohol</td>
<td>92</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>1.2 equiv of alcohol</td>
<td>90</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>normal addition</td>
<td>92</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>2.0 equiv of added water</td>
<td>92</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>under air, instead of nitrogen</td>
<td>92</td>
<td>42</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup>The yield was determined by <sup>1</sup>H NMR spectroscopy with benzyl acetate as an internal standard.

With optimized reaction conditions established, we focused our efforts on further exploring the scope of this process. First, the reaction conditions were applied to alkynoates with an array of aryl substituents at the γ position (Table 3.2). A phenyl-substituted alkynoate reacts with high ee and yield (entry 1), and an electron-donating and an electron-withdrawing group at the para position of the phenyl substituent are well-tolerated (entries 2 and 3). Furthermore, the reaction proceeds with good ee when alkynoates with more sterically hindered ortho-substituted phenyl groups are employed (entries 4 and 5). However, an increased catalyst loading is required to achieve a good yield with these substrates. A 2-naphthyl-substituted alkynoate provides high ee and yield under the reaction conditions (entry 6). Lastly, alkynoates containing an aromatic heterocycle as a substituent, including a thiophene and an indole, are also effective substrates for this chemistry (entries 7 and 8).
Table 3.2. Aryl-Substituted Alkynoates in Phosphine-Catalyzed Asymmetric Oxygen γ Additions

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>ee (%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>96</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>OMe</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>96</td>
<td>84</td>
</tr>
<tr>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>OMe</td>
<td>88</td>
<td>76</td>
</tr>
<tr>
<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Me</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>94</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>92</td>
<td>89</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup>Yield of purified product. <sup>b</sup>Reaction was run with 10% (S)-3b.

In addition to varying the alkynoate structure, we were interested in determining the outcome of the reaction with nucleophiles other than p-methoxybenzyl alcohol (Table 3.3). Like p-methoxybenzyl alcohol, benzyl alcohol reacts with alkynoate 3f in high ee and yield (entry 1). Another alcohol with an unsaturated substituent, allyl alcohol, proved to be an effective nucleophile as well (entry 2). However, when an aliphatic alcohol is employed as the nucleophile, an increase to 10% catalyst loading is required to achieve good yield (entry 3). Similarly, TMS-ethanol, which should be able to be deprotected to yield the free γ-hydroxy carbonyl product, reacts in high ee and synthetically useful yield (entry 4). The reaction tolerates a branched, primary aliphatic alcohol (entry 5), but reactions with secondary alcohols (i.e., cyclohexanol and cyclopentanol) proceed in low yield (<20%).
Table 3.3. Alcohols as Nucleophiles in Phosphine-Catalyzed Asymmetric Oxygen γ Additions

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>ROH</th>
<th>ee (%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>Me-&lt;sup&gt;OH&lt;/sup&gt;</td>
<td>96</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>TMS-&lt;sup&gt;OH&lt;/sup&gt;</td>
<td>96</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>OH</td>
<td>96</td>
<td>75</td>
</tr>
</tbody>
</table>

All data are the average of two experiments. <sup>a</sup> Yield of purified product.

C. Conclusion/Future Work

In summary, we have demonstrated the first examples of chiral phosphine-catalyzed asymmetric, intermolecular γ-additions with oxygen nucleophiles. Additionally, these reactions represent the first examples of allen- and alkynoates with aryl substituents at the γ position as substrates in phosphine-catalyzed γ-addition chemistry. An array of aryl-substituted alkynoates react in high ee and yield under the established reaction conditions, and a variety of primary alcohols are effective nucleophiles. The products of this reaction are α,β-unsaturated carbonyl compounds with an oxygen-substituted stereocenter at the γ position, substrates that are well-poised for further stereoselective elaboration at the α and β positions. Compounds of this type have been shown to be key intermediates for the synthesis of biologically active natural products. Future work will focus on further exploring the scope of this process by varying the electron-withdrawing group on the alkyne starting material (e.g., amides, sulfones, and phosphonates). We will also conduct nucleophile competition experiments and determine the rate law of the reaction and the resting state of the catalyst. These experiments should provide insight into the mechanism of this process.

259
D. Experimental

I. General Information

The following reagents were purchased and used as received, unless otherwise specified: CuI (Aldrich, 98%), n-Bu₄NI (Aldrich), K₂CO₃ (Amresco, anhydrous), t-butylpropiolate (TCI America), 4-methoxybenzyl chloride (Aldrich), benzyl chloride (Aldrich), 4-chlorobenzyl chloride (Aldrich), 2-methylbenzyl chloride (Aldrich), 2-(chloromethyl)naphthalene (Alfa Aesar), 4-methoxybenzyl alcohol (Aldrich), benzyl alcohol (Aldrich), allyl alcohol (Aldrich), propargyl alcohol (Aldrich), 1-pentanol (Aldrich), 2-(trimethylsilyl)ethanol (Aldrich), cyclohexanemethanol (Aldrich), (R)-SITCP (3b, Strem, >99% ee), and (S)-SITCP (3b, Strem, >99% ee). The remaining benzylic chlorides for alkyne synthesis have previously been reported and were synthesized according to literature procedures. Toluene was deoxygenated and dried by sparging with nitrogen followed by passage through an activated alumina column (S. G. Water) prior to use.

¹H and ¹³C spectroscopic data were collected on a Varian 500 MHz spectrometer at ambient temperature. HPLC analyses were carried out using an Agilent 1100 Series system with Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 25.0 cm, particle size 5 µm).
II. Synthesis of Alkynoates

The alkynoates were synthesized according to a procedure modified from a literature procedure for the synthesis of similar compounds.58 The yields have not been optimized.

Procedure A. An oven-dried round-bottom flask with a stir bar was charged with CuI (1.00 equiv) and K₂CO₃ (2.00 equiv). The flask was filled with an atmosphere of nitrogen, and then anhydrous acetonitrile was added (0.2 M) via syringe. Next, the benzyl chloride (1.00 equiv) was added via syringe followed by tert-butyl propiolate (2.00 equiv). If the benzyl chloride was a solid, it was added before the flask was put under nitrogen. The reaction was stirred for 48 hours at room temperature and then quenched with enough saturated aqueous NH₄Cl to double the volume of the reaction mixture. The reaction mixture was extracted twice with Et₂O. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated. The resulting residue was purified by column chromatography.

Procedure B. An oven-dried round-bottom flask with a stir bar was charged with CuI (1.00 equiv), K₂CO₃ (1.00 equiv), and n-Bu₄NI (1.00 equiv). The flask was filled with an atmosphere of nitrogen, and then anhydrous acetonitrile was added (0.2 M) via syringe. Next, the benzyl chloride (1.00 equiv) was added via syringe followed by tert-butyl propiolate (2.00 equiv). If the benzyl chloride was a solid, it was added before the flask was put under nitrogen. The reaction was heated to 40 °C, stirred for 48, and then quenched with enough saturated aqueous NH₄Cl to double the volume of the reaction mixture. The reaction mixture was extracted twice with Et₂O. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated. The resulting residue was purified by column chromatography.

*tert-Butyl 4-phenylbut-2-ynoate.* The title compound was synthesized according to Procedure B from *tert*-butyl propiolate (1.40 g, 11.1 mmol), benzyl chloride (700 mg, 5.53 mmol), CuI (1.05 g, 5.53 mmol), K₂CO₃ (764 mg, 5.53 mmol), and n-Bu₄NI (2.04 g, 5.53 mmol).
mmol). The product was purified by column chromatography on silica gel (2→4% Et₂O/hexanes), which furnished the title compound (928 mg, 78%) as a pale-yellow oil.

1H NMR (500 MHz, CDCl₃) δ 7.36–7.24 (m, 5H), 3.72 (s, 2H), 1.50 (s, 9H).

13C NMR (126 MHz, CDCl₃) δ 152.9, 134.5, 128.9, 128.2, 127.2, 84.0, 83.4, 76.2, 28.1, 25.1.

FT-IR (neat) 2980, 2242, 1706, 1477, 1454, 1419, 1394, 1369, 1279, 1258, 1159, 1079, 1066, 1032, 844, 754, 732 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₁₁H₁₃O₂: 217.1, found: 217.1.

**tert-Butyl 4-(4-methoxyphenyl)but-2-ynoate.** The title compound was synthesized according to Procedure A from tert-butyl propiolate (3.22 g, 25.6 mmol), 4-methoxybenzyl chloride (2.00 g, 12.8 mmol), CuI (2.44 g, 12.8 mmol), and K₂CO₃ (3.54 g, 25.6 mmol). The product was purified by column chromatography on silica gel (7.5→10% Et₂O/hexanes), which furnished the title compound (2.88 g, 91%) as a yellow oil.

1H NMR (500 MHz, CDCl₃) δ 7.25–7.21 (m, 2H), 6.89–6.84 (m, 2H), 3.80 (s, 3H), 3.65 (s, 2H), 1.50 (s, 9H).

13C NMR (126 MHz, CDCl₃) δ 158.8, 153.0, 129.2, 126.5, 114.3, 84.5, 83.3, 76.0, 55.5, 28.1, 24.3.

FT-IR (neat) 2980, 2935, 2837, 2241, 1703, 1699, 1612, 1587, 1514, 1463, 1456, 1422, 1394, 1370, 1250, 1159, 1069, 1034, 844, 812, 755 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₁₀H₁₈O₃: 247.1, found: 247.1.

**tert-Butyl 4-(4-chlorophenyl)but-2-ynoate.** The title compound was synthesized according to Procedure B from tert-butyl propiolate (785 mg, 6.22 mmol), 4-chlorobenzyl chloride (500 mg, 3.11 mmol), CuI (592 mg, 3.11 mmol), K₂CO₃ (430 mg, 3.11 mmol), and n-
Bu₄NI (1.15 g, 3.11 mmol). The product was purified by column chromatography on silica gel (2.5% Et₂O/hexanes), which furnished the title compound (593 mg, 76%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.31 (d, 2H, J = 7.5 Hz), 7.26 (d, 2H, J = 6.5 Hz), 3.68 (s, 2H), 1.50 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 152.8, 133.2, 132.9, 129.5, 129.0, 83.6, 83.2, 76.5, 28.1, 24.6.

FT-IR (neat) 2980, 2241, 1735, 1492, 1457, 1408, 1395, 1369, 1280, 1257, 1158, 1092, 1069, 1016, 844, 796, 754 cm⁻¹.

MS (FAB) m/z (M⁺+H) calcd for C₁₄H₁₆C₁₀₂: 251.1, found: 251.1.

 tert-Butyl 4-(2-methoxyphenyl)but-2-ynoate. The title compound was synthesized according to Procedure B from tert-butyl propiolate (1.61 g, 12.8 mmol), 2-methoxybenzyl chloride (1.00 g, 6.40 mmol), CuI (1.22 g, 6.40 mmol), K₂CO₃ (885 mg, 6.40 mmol), and n-Bu₄NI (2.36 g, 6.40 mmol). The product was purified by column chromatography on silica gel (5 → 8% Et₂O/hexanes), which furnished the title compound (1.38 g, 88%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.45–7.41 (m, 1H), 7.25 (dt, 1H, J = 1.5, 8.0 Hz), 6.96 (dt, 1H, J = 1.0, 7.5 Hz), 6.85 (dd, 1H, J = 0.5, 8.0 Hz), 3.84 (s, 3H), 3.68 (s, 2H), 1.50 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 156.8, 153.0, 129.2, 128.5, 122.9, 120.7, 110.2, 84.4, 83.2, 76.1, 55.5, 28.2, 19.6.

FT-IR (neat) 3003, 2979, 2937, 2838, 2241, 1703, 1699, 1601, 1591, 1495, 1464, 1439, 1394, 1369, 1282, 1249, 1158, 1108, 1069, 1050, 1029, 845, 753 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₁₅H₁₈NaO₃: 269.1, found: 269.1.

 tert-Butyl 4-(o-tolyl)but-2-ynoate. The title compound was synthesized according to Procedure B from tert-butyl propiolate (1.26 g, 9.96 mmol), 2-methylbenzyl chloride (700 mg, 4.98 mmol), CuI (948 mg, 4.98 mmol), K₂CO₃ (688 mg, 4.98 mmol), and n-Bu₄NI (1.84 g, 4.98 mmol).
mmol). The product was purified by column chromatography on silica gel (3→5%
Et₂O/hexanes), followed by column chromatography on reverse-phase C-18 silica gel (5→100%
acetonitrile/water), which furnished the title compound (1.09 g, 95%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.39–7.34 (m, 1H), 7.22–7.14 (m, 3H), 3.64 (s, 2H), 2.33
(s, 3H), 1.50 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 152.9, 136.2, 132.8, 130.4, 128.7, 127.5, 126.5, 83.7,
83.3, 76.3, 28.1, 23.3, 19.5.

FT-IR (neat) 2980, 2239, 1705, 1494, 1478, 1463, 1394, 1369, 1278, 1258, 1157, 1105,
1069, 1033, 844, 754, 740 cm⁻¹.

MS (ESI) m/z (M⁺H) calcd for C₁₅H₂₀O₂: 231.1, found: 231.1.

tert-Butyl 4-(naphthalen-2-yl)but-2-ynoate. The title compound was synthesized
according to Procedure B from tert-butyl propiolate (1.07 g, 8.50 mmol), 2-
(chloromethyl)naphthalene (750 mg, 4.25 mmol), CuI (809 mg, 4.25 mmol), K₂CO₃ (587 mg,
4.25 mmol), and n-Bu₄NI (1.57 g, 4.25 mmol). The product was purified by column
chromatography on silica gel (2→5% Et₂O/hexanes), which furnished the title compound (861
mg, 76%) as a pale-yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.85–7.78 (m, 4H), 7.52–7.44 (m, 2H), 7.42 (dd, 1H, J =
1.5, 8.5 Hz), 3.88 (s, 2H), 1.52 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 152.9, 133.6, 132.6, 131.9, 128.6, 127.8, 126.7, 126.5,
126.4, 126.0, 83.9, 83.4, 76.5, 28.2, 25.3.

FT-IR (neat) 3055, 2979, 2933, 2240, 1702, 1636, 1601, 1509, 1477, 1457, 1412, 1394,
1369, 1277, 1159, 1125, 1069, 1033, 844, 813, 754 cm⁻¹.

MS (ESI) m/z (M⁺Na) calcd for C₁₈H₁₈NaO₂: 289.1, found: 289.1.
**tert-Butyl 4-(thiophen-2-yl)but-2-ynoate.** The title compound was synthesized according to Procedure B from tert-butyl propiolate (997 mg, 7.90 mmol), 2-(chloromethyl)thiophene (524 mg, 3.95 mmol), CuI (752 mg, 3.95 mmol), K$_2$CO$_3$ (546 mg, 3.95 mmol), and $n$-Bu$_4$NI (1.46 g, 3.95 mmol). The product was purified by column chromatography on silica gel (2.5% Et$_2$O/hexanes), which furnished the title compound (684 mg, 78%) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.20 (dd, 1H, $J = 1.0$, 5.0 Hz), 7.01–6.97 (m, 1H), 6.95 (dd, 1H, $J = 3.5$, 5.0 Hz), 3.88 (d, 2H, $J = 1.0$ Hz), 1.50 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 152.7, 136.4, 127.2, 126.1, 124.9, 83.5, 82.7, 75.8, 28.1, 20.0.

FT-IR (neat) 3109, 2980, 2933, 2244, 1705, 1478, 1458, 1437, 1414, 1394, 1369, 1280, 1258, 1159, 1113, 1079, 1065, 1033, 845, 754, 700 cm$^{-1}$.

MS (FAB) $m/z$ (M$^+$+H) calcd for C$_{12}$H$_{15}$O$_2$S: 223.1, found: 223.1.

**tert-Butyl 4-(1-tosyl-1H-indol-5-yl)but-2-ynoate.** The title compound was synthesized according to Procedure B from tert-butyl propiolate (1.03 g, 8.13 mmol), 5-(chloromethyl)-1-tosyl-1H-indole (1.30 g, 4.06 mmol), CuI (773 mg, 4.06 mmol), K$_2$CO$_3$ (561 mg, 4.06 mmol), and $n$-Bu$_4$NI (1.50 g, 4.06 mmol) except the reaction was heated to 60 °C and run for 24 hours. The product was purified by column chromatography on silica gel (10–15% EtOAc/hexanes) followed by a second column on silica gel (85% CH$_2$Cl$_2$/hexanes), which furnished the title compound (1.31 g, 79%) as a pale-yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.93 (d, 1H, $J = 8.5$ Hz), 7.77–7.72 (m, 2H), 7.56 (d, 1H, $J = 3.5$ Hz), 7.48 (q, 1H, $J = 1.0$ Hz), 7.25–7.20 (m, 3H), 6.62 (dd, 1H, $J = 1.0$, 3.5 Hz), 3.75 (s, 2H), 2.34 (s, 3H), 1.49 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 152.9, 145.1, 135.3, 134.0, 131.3, 130.1, 129.5, 127.1, 126.9, 124.9, 120.8, 113.8, 109.0, 84.2, 83.4, 76.2, 28.1, 25.0, 21.7.
FT-IR (neat) 3143, 3116, 2980, 2931, 2241, 1703, 1596, 1460, 1446, 1394, 1370, 1306, 1275, 1219, 1188, 1173, 1139, 1093, 995, 844, 813, 797, 762, 725 cm\(^{-1}\).

MS (ESI) \(m/z\) \((M^++Na)\) calcd for C\(_{23}\)H\(_{23}\)NNaO\(_4\)S: 432.1, found: 432.1.

III. Phosphine-Catalyzed Asymmetric Oxygen \(\gamma\)-Additions

**General Procedure.** An oven-dried 4-mL vial with a stir bar was charged with catalyst 3b (0.020 mmol). The vial was capped with a PTFE-lined septum cap, taped, and evacuated and backfilled with nitrogen (3 cycles). Next, alcohol (1.60 mmol) and toluene (0.40 mL; anhydrous) were added via syringe, and the reaction mixture was stirred. Then, a solution of alkyne (0.40 mmol) in toluene (1.20 mL; anhydrous) was added over 16 hours via syringe pump. The tip of the needle was positioned against the wall of the vial to ensure that the solution was added continuously rather than dropwise. After the addition was complete, the reaction mixture was stirred for an additional 8 hours and then quenched with a solution of \(t\)-BuOOH (50 \(\mu\)L; 5.0–6.0 M in decane). The reaction mixture was stirred for 5 minutes, and then added to an aqueous solution of Na\(_2\)S\(_2\)O\(_3\) (4 mL; 10% by weight). The organic layer was separated, and the aqueous layer was washed with EtOAc (4 mL x 5). The combined organic extracts were dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated. The resulting residue was purified by column chromatography.

\((E)\)-\(t\)-Butyl 4-((4-methoxybenzyl)oxy)-4-phenylbut-2-enoate (Table 3.2, Entry 1).

The title compound was synthesized according to the General Procedure from \(t\)-butyl 4-phenylbut-2-ynoate (86.5 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 \(\mu\)L, 1.60 mmol), and \((S)\)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (7.5→10% Et\(_2\)O/hexanes). Colorless oil. First run: 133 mg (94% yield), 96% ee. Second run ((\(R\))-catalyst 3b): 134 mg (95% yield), 96% ee.
HPLC analysis: Daicel CHIRALPAK® AS column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 8.0 min (minor), 9.5 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41–7.29 (m, 5H), 7.27–7.24 (m, 2H), 6.91–6.85 (m, 3H), 6.00 (dd, 1H, $J = 1.5$, 16.0 Hz), 4.94 (dd, 1H, $J = 1.5$, 5.5 Hz), 4.46 (d, 1H, $J = 11.5$ Hz), 4.39 (d, 1H, $J = 11.5$ Hz), 3.81 (s, 3H), 1.46 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.8, 159.4, 146.4, 139.4, 130.1, 129.5, 128.9, 128.3, 127.4, 123.0, 114.0, 80.6, 79.6, 70.2, 55.4, 28.2.

FT-IR (neat) 3062, 3029, 2977, 2932, 2866, 2836, 1713, 1655, 1612, 1586, 1514, 1492, 1455, 1422, 1392, 1367, 1303, 1250, 1152, 1110, 1036, 981, 850, 822, 757 cm$^{-1}$.

MS (ESI) m/z (M$^+$+Na) calcd for C$_{22}$H$_{26}$NaO$_4$: 377.2, found: 377.2.

$[\alpha]_{25}^D = -37.8^\circ$ (c = 1.00, CHCl$_3$).

(\textit{E})-\textit{tert}-Butyl 4-((4-methoxybenzyl)oxy)-4-(4-methoxyphenyl)but-2-enoate (Table 3.2, Entry 2). The title compound was synthesized according to the General Procedure from \textit{tert}-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 $\mu$L, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (10→17.5% Et$_2$O/hexanes). Colorless oil. First run: 142 mg (92% yield), 96% ee. Second run ((R)-catalyst 3b): 137 mg (89% yield), XX% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 16.1 min (major), 18.3 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27–7.21 (m, 4H), 6.93–6.84 (m, 5H), 5.97 (dd, 1H, $J = 1.5$, 15.5 Hz), 4.89 (dd, 1H, $J = 1.5$, 5.5 Hz), 4.43 (d, 1H, $J = 11.5$ Hz), 4.35 (d, 1H, $J = 11.5$ Hz), 3.82 (s, 3H), 3.81 (s, 3H), 1.46 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.9, 159.7, 159.3, 146.7, 131.4, 130.2, 129.5, 128.8, 122.8, 114.2, 113.9, 80.6, 79.1, 69.9, 55.5, 55.4, 28.2.
FT-IR (neat) 3001, 2976, 2865, 2836, 1711, 1653, 1611, 1586, 1513, 1457, 1442, 1420, 1392, 1368, 1337, 1303, 1249, 1171, 1152, 1111, 1098, 1035, 981, 832, 758 cm⁻¹.

MS (ESI) m/z (M⁺Na) calcd for C₂₂H₂₅ClNaO₄: 411.1, found: 411.1.

[α]²⁵_D = -41.0° (c = 1.00, CHCl₃).

(E)-tert-Butyl 4-(4-chlorophenyl)-4-((4-methoxybenzyl)oxy)but-2-enoate (Table 3.2, Entry 3). The title compound was synthesized according to the General Procedure from tert-butyl 4-(4-chlorophenyl)but-2-ynoate (100 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 µL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (7.5–10% Et₂O/hexanes). Pale-yellow oil. First run: 131 mg (84% yield), 97% ee. Second run ((R)-catalyst 3b): 129 mg (83% yield), 95% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 1% 2-PrOH/hexanes; 1.0 mL/min; retention times: 9.1 min (major), 11.4 min (minor).

¹H NMR (500 MHz, CDCl₃) δ 7.37–7.32 (m, 2H), 7.29–7.25 (m, 2H), 7.25–7.21 (m, 2H), 6.91–6.86 (m, 2H), 6.82 (dd, 1H, J = 5.5, 16.0 Hz), 5.98 (dd, 1H, J = 1.5, 15.5 Hz), 4.91 (dd, 1H, J = 1.0, 5.5 Hz), 4.44 (d, 1H, J = 11.5 Hz), 4.38 (d, 1H, J = 11.5 Hz), 3.81 (s, 3H), 1.46 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 165.6, 159.5, 145.8, 138.0, 134.1, 129.8, 129.5, 129.1, 128.8, 123.4, 114.0, 80.8, 78.8, 70.3, 55.4, 28.2.

FT-IR (neat) 2977, 2933, 2867, 2836, 1713, 1656, 1612, 1586, 1514, 1489, 1456, 1392, 1368, 1338, 1303, 1250, 1153, 1111, 1089, 1036, 1015, 981, 824, 758 cm⁻¹.

MS (ESI) m/z (M⁺Na) calcd for C₂₂H₂₅ClNaO₄: 411.1, found: 411.1.

[α]²⁵_D = -41.0° (c = 1.00, CHCl₃).
(E)-tert-Butyl 4-((4-methoxybenzyl)oxy)-4-(2-methoxyphenyl)but-2-enoate (Table 3.2, Entry 4). The title compound was synthesized according to the General Procedure from tert-butyl 4-(2-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 µL, 1.60 mmol), and (S)-catalyst 3b (14.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (7.5→10% Et₂O/hexanes). Colorless oil. First run: 115 mg (75% yield), 89% ee. Second run ((R)-catalyst 3b): 119 mg (77% yield), 88% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 9.7 min (major), 11.0 min (minor).

1H NMR (500 MHz, CDCl₃) δ 7.44 (dd, 1H, J = 2.0, 8.0 Hz), 7.31–7.24 (m, 3H), 7.00 (dt, 1H, J = 1.0, 7.0 Hz), 6.93–6.85 (m, 4H), 6.01 (dd, 1H, J = 1.5, 15.5 Hz), 5.47 (dd, 1H, J = 1.5, 5.0 Hz), 4.48 (d, 1H, J = 11.5 Hz), 4.41 (11.5 Hz), 3.83 (s, 3H), 3.82 (s, 3H), 1.46 (s, 9H).

13C NMR (126 MHz, CDCl₃) δ 166.2, 159.3, 156.8, 146.3, 130.5, 129.4, 129.0, 127.7, 127.4, 122.0, 121.1, 113.9, 110.6, 80.4, 73.6, 70.5, 55.5, 55.4, 28.2.

FT-IR (neat) 3002, 2976, 2934, 2837, 1713, 1653, 1612, 1600, 1587, 1514, 1489, 1464, 1392, 1367, 1340, 1302, 1287, 1247, 1152, 1093, 1032, 982, 850, 823, 756 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₃H₂₈NaO₅: 407.2, found: 407.2.

[α]D²⁵ = −57.7° (c = 1.00, CHCl₃).
(E)-tert-Butyl 4-((4-methoxybenzyl)oxy)-4-(o-tolyl)but-2-enoate (Table 3.2, Entry 5).

The title compound was synthesized according to the General Procedure from tert-butyl 4-(o-tolyl)but-2-yne-1-olate (92.1 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 μL, 1.60 mmol), and (S)-catalyst 3b (14.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (7.5→10% Et2O/hexanes). Colorless oil. First run: 128 mg (87% yield), 87% ee.

Second run ((R)-catalyst 3b): 127 mg (86% yield), 85% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 8.4 min (major), 9.7 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.44–7.39 (m, 1H), 7.28–7.19 (m, 4H), 7.18–7.13 (m, 1H), 6.91–6.84 (m, 3H), 5.94 (dd, 1H, $J = 1.5$, 15.5 Hz), 5.16 (dd, 1H, $J = 1.5$, 5.0 Hz), 4.47 (d, 1H, $J = 11.5$ Hz), 4.36 (11.5 Hz), 3.82 (s, 3H), 2.28 (s, 3H), 1.47 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 159.4, 145.7, 137.2, 136.1, 130.8, 130.1, 129.5, 128.1, 127.5, 126.6, 123.0, 114.0, 80.6, 76.7, 70.2, 55.4, 28.2, 19.4.

FT-IR (neat) 3064, 3002, 2976, 2932, 2867, 2836, 1713, 1655, 1612, 1586, 1515, 1487, 1463, 1420, 1392, 1367, 1339, 1302, 1249, 1210, 1152, 1111, 1090, 1036, 980, 850, 824, 751, 728 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$+Na) calcd for C$_{23}$H$_{28}$NaO$_4$: 391.2, found: 391.2.

$[\alpha]^{25}_D = -42.3^\circ$ (c = 1.00, CHCl$_3$).

271
(E)-tert-Butyl 4-((4-methoxybenzyl)oxy)-4-(naphthalen-2-yl)but-2-enoate (Table 3.2, Entry 6). The title compound was synthesized according to the General Procedure from tert-butyl 4-(naphthalen-2-yl)but-2-ynoate (107 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 µL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (7.5 → 10% Et₂O/hexanes). Pale-yellow oil. First run: 158 mg (98% yield), 95% ee. Second run ((R)-catalyst 3b): 156 mg (96% yield), 94% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 14.1 min (minor), 16.2 min (major).

¹H NMR (500 MHz, CDCl₃)  δ 7.89–7.82 (m, 3H), 7.79 (s, 1H), 7.54–7.45 (m, 3H), 7.29–7.24 (m, 2H), 6.96 (dd, 1H, J = 5.5, 15.5 Hz), 6.91–6.87 (m, 2H), 6.04 (dd, 1H, J = 1.5, 15.5 Hz), 5.12 (dd, 1H, J = 1.5, 5.5 Hz), 4.51 (d, 1H, J = 11.0 Hz), 4.43 (d, 1H, J = 11.5 Hz), 3.82 (s, 3H), 1.47 (s, 9H).

¹³C NMR (126 MHz, CDCl₃)  δ 165.8, 159.4, 146.3, 136.8, 133.4, 130.1, 129.5, 128.8, 128.1, 127.9, 126.6, 126.5, 126.4, 125.0, 123.2, 114.0, 110.1, 80.7, 79.7, 70.2, 55.4, 28.2.

FT-IR (neat) 3056, 2976, 2931, 2865, 1711, 1653, 1612, 1586, 1513, 1456, 1392, 1367, 1303, 1249, 1151, 1123, 1105, 1035, 981, 897, 856, 821, 752 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₆H₂₈NaO₄: 427.2, found: 427.2.

[α]₂⁰D = −61.2° (c = 1.00, CHCl₃).
(E)-tert-Butyl 4-((4-methoxybenzyl)oxy)-4-(thiophen-2-yl)but-2-enoate (Table 3.2, Entry 7). The title compound was synthesized according to the General Procedure from tert-butyl 4-(thiophen-2-yl)but-2-ynoate (88.9 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 μL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (7.5% Et₂O/hexanes). Pale-yellow oil. First run: 136 mg (94% yield), 93% ee. Second run ((R)-catalyst 3b): 133 mg (92% yield), 92% ee.

HPLC analysis: Daicel CHIRALPAK® AS column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 9.5 min (minor), 12.2 min (major).

¹H NMR (500 MHz, CDCl₃) δ 7.34–7.31 (m, 1H), 7.28–7.24 (m, 2H), 7.01–6.98 (m, 2H), 6.94–6.86 (m, 2H), 6.01 (dd, 1H, J = 1.5, 15.5 Hz), 5.19 (dd, 1H, J = 1.5, 5.5 Hz), 4.52 (d, 1H, J = 11.5 Hz), 4.44 (d, 1H, J = 11.5 Hz), 3.81 (s, 3H), 1.48 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 165.6, 159.5, 145.3, 143.0, 129.7, 129.6, 126.9, 126.2, 126.0, 123.7, 114.0, 80.8, 74.9, 70.2, 55.4, 28.2.

FT-IR (neat) 3105, 3071, 2977, 2933, 2866, 2836, 1712, 1654, 1612, 1586, 1514, 1457, 1440, 1392, 1368, 1302, 1251, 1153, 1097, 1036, 980, 873, 848, 824, 762, 706 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₀H₂₄NaO₄S: 383.1, found: 383.1.

[α]²⁵D = −20.8° (c = 1.00, CHCl₃).
(E)-tert-Butyl 4-((4-methoxybenzyl)oxy)-4-(1-tosyl-1H-indol-5-yl)but-2-enoate

(Table 3.2, Entry 8). The title compound was synthesized according to the General Procedure from tert-butyl 4-(1-tosyl-1H-indol-5-yl)but-2-ynoate (164 mg, 0.40 mmol), 4-methoxybenzyl alcohol (199 µL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (15% EtOAc/hexanes). White solid. First run: 198 mg (90% yield), 92% ee. Second run ((R)-catalyst 3b): 192 mg (88% yield), 91% ee.

HPLC analysis: Daicel CHIRALPAK® AD column; 7% 2-PrOH/hexanes; 1.0 mL/min; retention times: 29.5 min (major), 36.6 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.96 (d, 1H, $J = 8.5$ Hz), 7.79–7.75 (m, 2H), 7.58 (d, 1H, $J = 3.5$ Hz), 7.49 (d, 1H, $J = 1.5$ Hz), 7.28–7.20 (m, 5H), 6.89–6.83 (m, 3H), 6.64 (dd, 1H, $J = 0.5$, 3.5 Hz), 5.98 (dd, 1H, $J = 1.5$, 15.5 Hz), 4.99 (dd, 1H, $J = 1.5$, 5.5 Hz), 4.43 (d, 1H, $J = 11.5$ Hz), 4.37 (d, 1H, $J = 12.0$ Hz), 3.80 (s, 3H), 2.35 (s, 3H), 1.45 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8, 159.4, 146.6, 145.2, 135.3, 134.7, 134.5, 131.1, 130.1, 130.0, 129.5, 127.02, 127.00, 124.0, 122.8, 120.3, 114.0, 113.9, 109.0, 80.7, 79.6, 70.1, 55.4, 28.2, 21.7.

FT-IR (neat) 3142, 3114, 2977, 2932, 2867, 2837, 1713, 1652, 1612, 1596, 1514, 1456, 1372, 1303, 1248, 1218, 1173, 1126, 1035, 995, 910, 849, 813, 768, 730 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$+Na) calcd for C$_{31}$H$_{33}$NNaO$_6$S: 570.2, found: 570.2.

$[\alpha]^{25}_D = -42.6^\circ$ (c = 1.00, CHCl$_3$).
(E)-tert-Butyl 4-(benzyloxy)-4-(4-methoxyphenyl)but-2-enoate (Table 3.3, Entry 1).

The title compound was synthesized according to the General Procedure from tert-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), benzyl alcohol (166 µL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on silica gel (7.5% Et2O/hexanes). Colorless oil. First run: 124 mg (87% yield), 94% ee. Second run ((R)-catalyst 3b): 126 mg (89% yield), 94% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 10.8 min (major), 12.3 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.38–7.23 (m, 7H), 6.94–6.86 (m, 3H), 6.00 (dd, 1H, $J = 1.5, 15.5$ Hz), 4.92 (dd, 1H, $J = 1.5, 5.5$ Hz), 4.50 (d, 1H, $J = 12.0$ Hz), 4.43 (d, 1H, $J = 12.0$ Hz), 3.82 (s, 3H), 1.47 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 159.7, 146.5, 138.2, 131.3, 128.8, 128.5, 127.81, 127.79, 122.8, 114.2, 80.6, 79.5, 70.3, 55.4, 28.2.

FT-IR (neat) 3064, 3031, 2977, 2932, 2836, 1713, 1652, 1609, 1586, 1511, 1393, 1367, 1304, 1250, 1151, 1099, 1035, 981, 833, 736 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$/Na) calcd for C$_{22}$H$_{26}$NaO$_4$: 377.2, found: 377.2.

$[\alpha]^{25}_D = -52.0^\circ$ (c = 1.00, CHCl$_3$).

(E)-tert-Butyl 4-(allyloxy)-4-(4-methoxyphenyl)but-2-enoate (Table 3.3, Entry 2).

The title compound was synthesized according to the General Procedure from tert-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), allyl alcohol (109 µL, 1.60 mmol), and (S)-catalyst 3b (7.1 mg, 0.020 mmol). The product was purified by column chromatography on...
silica gel (7.5% Et$_2$O/hexanes). Colorless oil. First run: 105 mg (86% yield), 94% ee. Second run (($R$)-catalyst 3b): 108 mg (89% yield), 93% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 6.4 min (major), 7.2 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.24 (m, 2H), 6.91–6.83 (m, 3H), 5.97 (dd, 1H, J = 1.5, 15.5 Hz), 5.90 (tdd, 1H, J = 5.5, 10.5, 17.5 Hz), 5.27 (qd, 1H, J = 1.5, 17.0 Hz), 5.18 (qd, 1H, J = 1.5, 10.5 Hz), 4.89 (dd, 1H, J = 1.5, 5.5 Hz), 3.98–3.88 (m, 2H), 3.80 (s, 3H), 1.46 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8, 159.7, 146.5, 134.6, 131.4, 128.6, 122.7, 117.3, 114.2, 80.6, 79.6, 69.4, 55.4, 28.2.

FT-IR (neat) 3078, 2978, 2933, 2836, 1711, 1654, 1648, 1610, 1586, 1512, 1457, 1420, 1392, 1368, 1336, 1304, 1250, 1152, 1100, 1036, 982, 926, 833 cm$^{-1}$.

MS (ESI) m/z (M$^+$+Na) calcld for C$_{18}$H$_{24}$NaO$_4$: 327.2, found: 327.2.

$[^{[\alpha]}_D] = -57.3^\circ$ (c = 1.00, CHCl$_3$).

(\textit{E})-\textit{tert}-Butyl 4-(4-methoxyphenyl)-4-(pentyloxy)but-2-enoate (Table 3.3, Entry 3).

The title compound was synthesized according to the General Procedure from \textit{tert}-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), 1-pentanol (174 µL, 1.60 mmol), and (S)-catalyst 3b (14.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (5→10% Et$_2$O/hexanes). Colorless oil. First run: 108 mg (81% yield), 97% ee.

Second run ((\textit{R})-catalyst 3b): 111 mg (83% yield), 95% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 1% 2-PrOH/hexanes; 0.8 mL/min; retention times: 6.2 min (major), 7.2 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.25–7.20 (m, 2H), 6.91–6.86 (m, 2H), 6.85 (dd, 1H, J = 6.0, 16.0 Hz), 5.95 (dd, 1H, J = 1.5, 16.0 Hz), 4.80 (dd, 1H, J = 1.5, 5.5 Hz), 3.80 (s, 3H), 3.41–3.30 (m, 2H), 1.68–1.54 (m, 2H), 1.46 (s, 9H), 1.38–1.24 (m, 4H), 0.88 (t, 3H, 7.0 Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 159.5, 147.0, 131.9, 128.5, 122.5, 114.1, 80.6, 80.5, 69.0, 55.4, 29.6, 28.5, 28.2, 22.6, 14.1.
FT-IR (neat) 2956, 2933, 2860, 1713, 1655, 1511, 1457, 1392, 1367, 1338, 1303, 1250, 1152, 1103, 1036, 981, 832 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₀H₃₂NaO₄: 357.2, found: 357.2.

\[ \alpha \]²⁵ D = -50.5° (c = 1.00, CHCl₃).

(E)-tert-Butyl 4-(4-methoxyphenyl)-4-(2-(trimethylsilyl)ethoxy)but-2-enoate (Table 3.3, Entry 4). The title compound was synthesized according to the General Procedure from tert-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), TMS-ethanol (229 µL, 1.60 mmol), and (S)-catalyst 3b (14.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (5→7.5% Et₂O/hexanes). Colorless oil. First run: 92.4 mg (63% yield), 95% ee. Second run ((R)-catalyst 3b): 96.2 mg (66% yield), 96% ee.

HPLC analysis: Daicel CHIRALPAK® OD column; 0.3% 2-PrOH/hexanes; 0.8 mL/min; retention times: 6.5 min (major), 8.4 min (minor).

¹H NMR (500 MHz, CDCl₃) δ 7.25–7.20 (m, 2H), 6.91–6.86 (m, 2H), 6.84 (dd, 1H, J = 5.5, 15.5 Hz), 5.94 (dd, 1H, J = 1.0, 15.5 Hz), 4.81 (dd, 1H, J = 1.0, 5.5 Hz), 3.80 (s, 3H), 3.51–3.41 (m, 2H), 1.46 (s, 9H), 1.02–0.86 (m, 2H), -0.02 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 165.9, 159.5, 147.0, 131.9, 128.5, 122.5, 114.1, 80.5, 80.3, 66.2, 55.4, 28.2, 18.4, -1.2.

FT-IR (neat) 2953, 2837, 1714, 1653, 1610, 1586, 1511, 1442, 1419, 1392, 1368, 1336, 1249, 1152, 1101, 1036, 981, 942, 858, 835, 755 cm⁻¹.

MS (ESI) m/z (M⁺+Na) calcd for C₂₀H₃₂NaO₄Si: 387.2, found: 387.2.

\[ \alpha \]²⁵ D = -51.9° (c = 1.00, CHCl₃).

277
(E)-tert-Butyl 4-(cyclohexylmethoxy)-4-(4-methoxyphenyl)but-2-enoate (Table 3.3, Entry 5). The title compound was synthesized according to the General Procedure from tert-butyl 4-(4-methoxyphenyl)but-2-ynoate (98.5 mg, 0.40 mmol), cyclohexanemethanol (197 µL, 1.60 mmol), and (S)-catalyst 3b (14.2 mg, 0.040 mmol). The product was purified by column chromatography on silica gel (5→10% Et2O/hexanes). Colorless oil. First run: 110 mg (75% yield), 96% ee. Second run ((R)-catalyst 3b): 109 mg (75% yield), 96% ee.

HPLC analysis: Daicel CHIRALCEL® OD column; 0.3% 2-PrOH/hexanes; 0.8 mL/min; retention times: 6.5 min (major), 7.1 min (minor).

\[ ^1H \text{ NMR (500 MHz, CDCl}_3) \delta 7.24-7.19 (m, 2H), 6.91-6.86 (m, 2H), 6.83 (dd, 1H, } J = 5.5, 15.5 \text{ Hz}), 5.95 (dd, 1H, } J = 1.5, 16.0 \text{ Hz}), 4.77 (dd, 1H, } J = 1.5, 5.0 \text{ Hz}), 3.80 (s, 3H), 3.21-3.11 (m, 2H), 1.82-1.54 (m, 6H), 1.46 (s, 9H), 1.30-1.08 (m, 3H), 0.98-0.83 (m, 2H). \]

\[ ^13C \text{ NMR (126 MHz, CDCl}_3) \delta 166.0, 159.5, 147.1, 132.0, 128.5, 122.3, 114.1, 80.6, 80.5, 74.7, 55.4, 83.3, 30.25, 30.20, 28.2, 26.7, 26.02, 25.99. \]

FT-IR (neat) 2977, 2924, 2852, 1713, 1656, 1586, 1511, 1450, 1420, 1392, 1367, 1338, 1303, 1249, 1151, 1118, 1072, 1037, 981, 891, 832 cm\(^{-1}\).

MS (ESI) \text{ } m/z (M^+Na) \text{ } \text{calcd for C}_{22}\text{H}_{32}\text{NaO}_4: 383.2, \text{ found: 383.2.} \]

\[ \alpha]_{D}^{25} = -46.4^\circ \text{ (c = 1.00, CHCl}_3). \]
IV. $^1$H NMR Spectra
DZ-06-190-1-Purified

exp75 PROTON

SAMPLE

date Sep 29 2014 setamode n
solvent cdc13 wet n
file /indy/dziegle=
06-190-1-Purified/ SPECIAL
PROTON.M1.fid spin 20
ACQUISITION hst 0.008
sv 8000.0 pw50 8.800
at 3.000 alfa 10.000
np 40000
fb not used t1 n
bs 32 in y
dl 2.000 dp n
nt 16 hs n
ct 16

TRANSMITTER

tn H1 fn not used
strq 409.609 DISPLAY
tof 489.7 sp -0.2
tpwr 61 wp 4936.8
pw 4.950 rfl 4635.7
DECOUPLER

dn C13 rp -173.6
dof 0 lp -72.0
dm nnn

decwave 40_autox7_wc 234

dpwr 41 vs s
dwf 32250 th 11

PROCESSING

0.20 not used

DISPLAY

PLOT

10 9 8 7 6 5 4 3 2 1 ppm

5.14 2.00 9.62
DZ-06-212-2-Purified

exp75 PROTON

SAMPLE PRESATURATION
date Dec 18 2014 satmode n
solvent cdc13 wet n
file /indy/dziegle-r/vnmrsys/data/DZ--
06-212-2-Purified/ gain 34
PROTON01.fld spin 20
ACQUISITION hst 0.000
sw 8000.0 pw90 9.900
at 3.000 alfa 10.000
np 40000 Flags
fb not used 11 n
bs 32 in n
d1 2.000 dp y
nt 16 hs nn
c1 16 PROCESSING
tr TRANSMITTER lb 0.20
ln H1 fn not used
sfrq 499.678 DISPLAY
tof 499.7 sp -8.0
tpwr 61 wp 4996.6
pw 4.950 rf1 4636.0
DECOPPLER rfp 3627.6
dn C13 rp 8.4
dof 0 lp -73.3
dw nnn PLOT 234
decwave W40_autox7- wc 32258 th 22
al cdc ph

10 9 8 7 6 5 4 3 2 1 ppm

1.82 1.84 3.02 2.00 9.25
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<th>file</th>
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<th>np</th>
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<td>sat mode n</td>
<td>cdc13 w</td>
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<td>48000</td>
<td>not used</td>
<td>32</td>
<td>2.000</td>
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<td>16</td>
<td>H1</td>
<td>not used</td>
</tr>
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<td>wet n</td>
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<td>wet n</td>
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</table>

**Chemical Structure**

- t-BuO
- Cl

**NMR Spectra**

- ppm values: 4.26, 2.00, 9.95
**SAMPLE**

- **PRESATURATION**
  - `date`: Oct 21 2014
  - `satmode`: n
- **solvent**
  - `cdcl3`
- **file**
  - `/indy/dziegel-r/vrnrsys/data/DZ-06-216-1-Purified/PROTON01.fid`

---

**ACQUISITION**

- `sw`: 8000.0
- `at`: 3.000
- `np`: 48000
- `fb`: not used
- `bs`: 32
- `dl`: 2.000
- `nt`: 16
- `ct`: 16

---

**TRANSMITTER**

- `tn`: H1
- `sfrq`: 499.689
- `tof`: 499.7
- `pw`: 61
- `pw`: 4.950
- `dn`: C13
- `dor`: 0
- `dm`: nnn
- `decuwave`: W40_autox7

---

**DECOUPLER**

- `decw`: W40

---

**PRESATURATION**

- `satmode`: wet
- `SPECIAL` temp: 25.0

---

**ACQUISITION**

- `hst`: 0.000
- `sw`: 8000.0
- `at`: 3.000
- `np`: 48000
- `fb`: not used
- `bs`: 32
- `dl`: 2.000
- `nt`: 16
- `ct`: 16

---

**DISPLAY**

- `sp`: -
- `wp`: 4996
- `rfl`: 1001
- `rp`: -175
- `lp`: -72.4

---

**PLOT**

- `sc`: 0.20
- `vs`: 3.2
- `th`: 5.8
- `ph`: 234
- `al`: cdc

---

**Diagram**

- Molecular structure with chemical shifts: 0.90, 0.93, 1.32, 0.83, 2.99, 5.29, 2.00.
### Sample Information

**Sample:** DZ-06-178-1-Purified

**Date:** Dec 21 2014

**Solvent:** CDCl₃

**File:** /indy/dziegle-r/vnmrsys/data/DZ-06-178-1-Purified/PROTON03.fid

### Acquisition Parameters

- **SW:** 8000.0 Hz
- **AT:** 5.000 Hz
- **NP:** 48000
- **FB:** Not used
- **BS:** 32
- **DI:** 2.000
- **NT:** 16
- **CT:** 16

### Transmitter Parameters

- **TN:** H1
- **SF:** 499.678 Hz
- **TOF:** 499.7 Hz
- **TPWR:** 61
- **PW:** 4.950

### Decoupler Parameters

- **DN:** 13
- **DOF:** 0
- **DAE:** 0
- **DACWAVE:** W40_autoX7
- **DECWAVE:** 234

### Processing Parameters

- **DISPLAY:** 0.20
- **PLOT:** 1

### Chemical Shifts

- **8.89 ppm**
- **2.70 ppm**
- **2.00 ppm**
- **2.92 ppm**
- **3.31 ppm**
DZ-06-168-1-Purified

exp75 PROTON

SAMPLE

date: Dec 21 2014
solvent: cdcl3
file: /indy/dziegle-r/vnursys/data/DZ-06-168-1-Purified~

ACQUISITION

sw: 8000
at: 3.000
np: 48000
fb: not used
bs: 2
ct: 16

TRANSMITTER

tn: H1
sfreq: 499.678
lp

DECOUPLER
dn: C13
dof: 0

DECWAVE

decwave: W40_autox

DISPLAY

sp

PROCESSING

lb

dp

PLOT

wc

dpw

dwf

1.0

2.00

3.64

8.51

10

9

8

7

6

5

4

3

2

1

ppm

1.94

0.84

0.84

0.84
exp75 PROTON

SAMPLE PRESATURATION
date Dec 8 2014 satmode n
solvent cdc13 wet n
file /indy/dziegle-
EXP/PROTON02.fid spin 20
06-200-1-Purified/- gain 32
ACQUISITION hst 0.008
sw 8000.0 pw90 9.900
t 3.000 a1fa 10.000
np 48000 FLAGS
fb not used f1 n
bs 32 ln n
d1 2.000 dp y
nt 16 hs nn
cr 16 PROCESSING
TRANSMITTER lb 0.20
fn not used
sfrq 499.676 DISPLAY
tof 499.7 sp -0.0
tpwr 61 wp 4836.0
pw 4.950 rfl 4636.0
DECOUPLER rfp 3827.6
dn C13 rp 33.6
dof 0 1p -72.8
dm nnn PLOT 234
decwave W40_autox7 wc 234
dpw 41 ve 8
dmr 32258 th el cdc ph

t-BuO

PLOT 234
(Table 3.2, Entry 1)
(Table 3.2, Entry 2)
DZ-06-272-1-Purified

exp75 PROTON

SAMPLE
PRESATURATION
date Dec 19 2014 satmode n
solvent cdc13 wet n
file /indy/dziegle-
      r,vnmrsys/data/DZ--
temp 25.0
06-272-1-Purified/~
gain 34

ACQUISITION
prot 20

ACQUISITION
hst 0.000

sw 8000.0

at 3.000

sp 20

Ac 10.000

np 48000

fs not used

bs 32

di 2.000

dp y

nt 16

ct 16

TRANSMITTER

lb 0.20

tn H1 fn not used

stf 499.678

tof 499.7 sp -0.0

tpw 61

pw 4.950

rf 4636.0

rfp 3627.6

rr 11.9

da 0

r 1

dc 6

dm 234

decwave W40_autox7

PLOT

dw 234

dc 8

dw 13

dw 15

(Table 3.2, Entry 3)
DZ-06-284-1-Purified
exp77 PROTON

SAMPLE
file /indy/dziegle-/vnmrsys/data/DZ-~
PROTON01.fid

PRESATURATION
satmode n

SPECIAL
temp 25.0

ACQUISITION
spin 20

sw 8000.0
at 3.000
fb not used
bs 32
hi

d1 2.000
nt 16

dn C13

tn 16

TRANSMITTER
fn not used

DISPLAY
-6.2

DECOUPLER

DECWAVE W40_autox7= wc

PLOT

process 0

PROCESSING

TABLE 3.2, Entry 4

MeO

O

MeO

OMe

r-BuO

(Table 3.2, Entry 4)
exp77 PROTON

DZ-06-278-1-Purified

SAMPLE PRESATURATION
Date Jan 20 2015 satmode n
Solvent cdc13 wet n
File /indy/dziegle=r\nmr\sys\data\DZ--
06-278-1-Purified/s
gain 34
Acquisition hst 0.008

Acq

Gain 1.00

Spin

Spin

Pw 90 9.000
At 3.000 alfa 10.000
Np 48000
Fb not used 11 n
Bs 32 ln n
Di 2.000 dp y
Tt 16 hs mn
Gb 16

Ttl 0.20

Transmitter

Freq 499.678
Display -0.2
Gpwr 4998.8
Sp -0.2
Spwr 4.950
Rf 1001.5

Decoupler

Rf 0

Decwave

W40_autox5 wc 234

Display

Sc 8

Decpwr 41 vs 15

Decpwr 32258 th 44

Al cdc ph

(Table 3.2, Entry 5)

OMe

t-BuO

Me

1.05 1.05
4.91 3.10
1.00 1.00
1.06 1.06
3.16 3.16
3.10 3.10
9.31
Table 3.2, Entry 6

- Measured at 499.678 ppm.
DZ-06-258-2-Purified

**exp75 PROTON**

**SAMPLE**
- Date: Dec 10, 2014
- Mode: sat
- Solvent: cdc13 wet
- File: /indy/dziegle=special
- Room temp: 25.0
- Gain: 34

**ACQUISITION**
- HST: 0.008
- SW: 8000.0
- PW: 9.900
- ALFA: 10.000
- NP: 48000
- BS: 32
- DI: 2.000
- NT: 16
- CS: 16

**TRANSMITTER**
- LB: 0.20
- SFTR: 499.678
- TOF: 499.7
- TPWR: 61
- PW: 4.950
- RFP: 4636.0
- RP: 13.4
- LP: -72.2
- WC: 234
- SC: 8
- VS: 12
- TH: 44

**DECOUPLER**
- C14: 3627.6
- Rf: 13.8

**PLOT**
- 10 9 8 7 6 5 4 3 2 1 ppm
- 0.96 1.99 2.76 3.08 1.00 1.05 1.07 3.21 9.77

(Table 3.2, Entry 7)
(Table 3.2, Entry B)
(Table 3.3, Entry 1)
DZ-06-266-1-Purified

exp75 PROTON

SAMPLE

PRESATURATION

date Dec 15 2014
solvent cdcl3
file /indy/dziegle=r/vnmrsys/data/DZ-
06-266-1-Purified/-
PROTON01.fid

ACQUISITION

sw 8000.0
at 3.000
np 40000
fb not used
bs 32
sl 2.000
nt 16
ct 16

TRANSMITTER

tn 11
sfreq 499.678

DECOUPLER

dn C13
dof 0

dm nnn

decwave W40_autom7- wc 234

dpw 41

dwf 32256

PROCESSING

lb 0

DISPLAY

sp wp 499
rfp 3637.6

TABLE 3.3, ENTRY 2

(MeO)

(1-BuO)
DZ-06-268-1-Purified

exp75 PROTON

SAMPLE PRESATURATION
date Dec 16 2014 satmode n
solvent cdc13 wet n
file /indy/dziegle-r/vnmrsys/data/DZ-- temp 25.0
06-268-1-Purified/ gain 32
PROTON01.fid spin 20

ACQUISITION hst 0.008
sw 8000.0 pm99 9.300
at 3.000 alfa 10.000
tp 48000
fb not used il n
bs 32 ln n
dl 2.000 dp y
nt 16 hs nm
cd 16

TRANSMITTER

tn 10.000

sfrq 499.678

DISPLAY
tof 499.7 sp
tpwr 61 wp 4996.6

DECOUPLER
dn C13 rp

dnf 0.000

dn mm

decwave W40_autox7

dcwrp 991 sc

dcwrp 41 vs 15

dcwrp 32258 th

al cdc ph

Table 3.3, Entry 3)
Sample: \textit{diz}e
g

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Entry & Signal & ppm & Assignment \\
\hline
1 & 1.96 & 2.11 & 1.00 & 1.07 & 3.34 & 2.17 & 9.39 & 2.15 & 8.62 \\
\hline
Table 3.3, Entry 4
\end{tabular}
\end{table}

\textbf{Table 3.3, Entry 4}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{NMR Spectrum of Sample}
\end{figure}
(Table 3.3, Entry 5)
Daniel T. Ziegler  
Department of Chemistry and Chemical Engineering, California Institute of Technology  
1200 E. California Blvd, MC 101-20  
Pasadena, CA 91125  
(626) 395-3634, dziegler@caltech.edu

EDUCATION:

2009 – 2015  Ph.D., Organic Chemistry, Massachusetts Institute of Technology
2005 – 2009  B.S., Chemistry and Mathematics, Gettysburg College  
summa cum laude, with honors in chemistry

RESEARCH EXPERIENCE:

2009 – 2015  Graduate Research Assistant  
Advisor: Prof. Gregory C. Fu  
Massachusetts Institute of Technology (2009 – 2012)  
California Institute of Technology (2012 – 2015)  
Investigated photoinduced, copper-catalyzed reactions and chiral phosphine-catalyzed  
asymmetric transformations of electron-deficient allenes and alkynes

2008 – 2009  Undergraduate Research Assistant  
Advisor: Prof. Timothy W. Funk  
Gettysburg College  
Developed an iridium-catalyzed cyclopropanol ring-opening reaction for the synthesis of  
α-methyl ketones

TEACHING EXPERIENCE:

2014  Research Mentor: Summer Undergraduate Research Program (SURF), Caltech
2014  Teaching Assistant: Ch41c, Organic Chemistry (3rd term), Caltech
2014  Teaching Assistant: Ch41b, Organic Chemistry (2nd term), Caltech
2010  Head Teaching Assistant: 5.12, Organic Chemistry I, MIT
2009  Teaching Assistant: 5.36, Organic Chemistry Lab, MIT

HONORS/AWARDS:

2010  EMD Serono Summer Fellowship
2009  Moore Fellowship
2009  Salutatorian of Gettysburg College Class of 2009
2009  Stine Chemistry Prize
2009  Society for Analytical Chemists of Pittsburgh Award
2009  American Chemical Society Undergraduate Award in Inorganic Chemistry
2009  Earl E. Ziegler Senior Math Award
2008  Phi Beta Kappa – early induction and member of the nominating committee
2008  American Chemical Society Undergraduate Award in Analytical Chemistry
2008  Glenn S. Weiland Summer Research Scholarship
2008  Earl E. Ziegler Junior Math Award
2006  CRC Freshman Achievement Award in Chemistry
PUBLICATIONS:


PRESENTATIONS:

