General Information: The following commercially obtained reagents for the allylic amination reaction were used as received: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)2 (Aldrich or Strem); N,N-diisopropylethylamine (DIPEA, Aldrich), (+)-(S,S)-Cr(salen)Cl (Strem Chemicals), tert-butyl methyl ether (TBME, anhydrous, Aldrich). Dry Solvents tetrahydrofuran (THF), methylene chloride (CH2Cl2), and diethyl ether (Et2O), were purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). All allylic amination reactions were run under air with no precautions taken to exclude moisture. All other reactions were run over a stream of N2 gas with dry solvent in flame-dried glassware unless otherwise stated. Solvents were removed by rotatory evaporation at ca. 40 torr, unless otherwise stated. All products were filtered through a glass wool plug prior to obtaining a final weight. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV, potassium permanganate, ceric ammonium molybdate, and ninhydrin staining. Flash column chromatography was performed as described by Still et al.1 using EM reagent silica gel 60 (230-400 mesh). CDCl3 used to analyze compounds containing epoxide or aldehyde functionality was filtered through basic alumina immediately prior to use. 1H NMR spectra were recorded on a Varian Unity-400 (400 MHz) or Varian Unity-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CHCl3 at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, b = broad, app = apparent; coupling constant(s) in Hz; integration. Proton-decoupled 13C NMR spectra were recorded on a Varian Unity-400 (100 MHz) or Varian Unity-500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl3 at 77.0 ppm). 19F NMR spectra were recorded on a Varian Unity-400 (376 MHz) spectrometer and are reported in ppm using CFCl3 as an external standard (0.00 ppm). IR spectra were recorded as thin films on NaCl plates on a Mattson Galaxy Series FTIR 5000 and are reported in frequency of absorption (cm⁻¹). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Optical rotations were measured using a 1 mL cell with a 1 dm path length or a 0.2 mL cell with a 10 mm path length on a Jasco P-1020 polarimeter. Optical rotations were obtained with a sodium lamp and are reported as follows: [α]D (c = g/100 mL, solvent). Melting points are uncorrected.
Table 1. Exogenous, Catalytic Base Additives for Direct C—H Amination

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>yield(%)</th>
<th>L:B</th>
<th>E:Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>(S,S)-Cr(salen)Cl</td>
<td>2</td>
<td>50</td>
<td>11:1</td>
</tr>
<tr>
<td>3</td>
<td>pyridine</td>
<td>9</td>
<td>12:1</td>
<td>14:1</td>
</tr>
<tr>
<td>4</td>
<td>2,6-di-tert-butylpyridine</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>N-isopropylamine</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>N,N-diisopropylamine</td>
<td>66</td>
<td>12:1</td>
<td>15:1</td>
</tr>
<tr>
<td>7</td>
<td>triethylamine</td>
<td>60</td>
<td>14:1</td>
<td>15:1</td>
</tr>
<tr>
<td>8</td>
<td>N,N-diisopropylethylamine</td>
<td>66</td>
<td>11:1</td>
<td>17:1</td>
</tr>
<tr>
<td>9</td>
<td>MeOC(O)NHTsH-DIPEA</td>
<td>9</td>
<td>6:1</td>
<td>10:1</td>
</tr>
</tbody>
</table>

*isolated yield of linear product. 
*linear/branched ratio determined by HPLC of crude reaction mixture.

determined by 'H NMR after chromatography. 
'1H NMR yield by comparison with internal standard. 
2.0 equiv. of the pre-formed salt was used instead of MeOC(O)NHTs.

Catalytic Base Exploration

Standard Procedure for Table 1, liquid additives. A 1 dram vial was charged with 1-decene (42.1 mg, 0.3 mmol, 1.0 equiv), followed by tert-butyl methyl ether (0.450 mL), 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (15.1 mg, 0.03 mmol, 0.10 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv), and a stir bar were then sequentially added. Liquid additive (0.018 mmol, 0.06 equiv) was added via syringe. The vial was fitted with a Teflon cap, and heated to 45°C (with magnetic stirring) in an oil bath for 72 h. The vial was removed, allowed to cool to room temperature, and thoroughly rinsed into a 125 mL separatory funnel with ether (ca. 30 mL). The organic phase was washed with 5% aq. K2CO3 (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over MgSO4, filtered through a 1:1 mixture of Celite/silica gel, and evaporated to dryness (ca. 30-40°C, 30 torr). The crude product was purified by flash chromatography on silica gel (7% EtOAc/hexanes), and evaporated to dryness. Yields are reported as the amount of linear product (E and Z isomers).

HPLC analysis of L/B ratio. Immediately before workup, the vial was sampled by removing ~5 µL solvent. This small sample was dissolved in a mixture of ether/water (1 mL), mixed by vortex stirring, and the organic layer transferred to a new vial. Ether was removed by passing a gentle stream of nitrogen over the vial (2 min), followed by addition of 2 mL acetonitrile. HPLC analysis (Agilent© Eclipse XDB-C8, 35°C, 35% H2O/MeCN, 1.5 mL/min) was used to determine the linear/branched ratio, tR = 13.5 (linear E & Z), 12.8 min (branched), reported as the average of two injections. Linear products possessing E and Z configuration were not separated by this method.

Procedure for Table 1, solid additives. Reactions with solid additives were run in an analogous way as above by adding the solid additive (0.018 mmol, 0.06 equiv) immediately after the palladium catalyst.

Entry 1: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)2 (15.1 mg, 0.03 mmol, 0.10 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Product yield was determined by comparison to an internal standard (nitrobenzene). Run 1: (1.2% yield); run 2: (1.2% yield); run 3: (1.8% yield). E/Z and L/B were not determined. Average yield: 1%.
Entry 2: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), (S)-NS-Cr(salen)Cl (11.4 mg, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (57.3 mg, 0.156 mmol, 52% yield [11:1 L/B, 21:1 E/Z]); run 2: (52.9 mg, 0.144 mmol, 48% yield [10:1 L/B, 17:1 E/Z]). **Average yield: 50% [11:1 L/B, 19:1 E/Z].** Allylic acetate products were also isolated as a yellow oil. Run 1 (4.7 mg, 0.0237 mmol, 8% yield [2:1 L/B, 12:1 E/Z]); run 2 (7.3 mg, 0.0368 mmol, 12% yield, [1.5:1 L/B, 14:1 E/Z]). **Average allylic acetate yield: 10% [2:1 L/B, 13:1 E/Z].**

Entry 3: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), pyridine (1.45 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (11.0 mg, 0.030 mmol, 10% yield [12:1 L/B, 14:1 E/Z]); run 2: (8.8 mg, 0.0239 mmol, 8% yield [12:1 L/B, 13:1 E/Z]). **Average yield: 9% [12:1 L/B, 14:1 E/Z].**

Entry 4: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), di-tert-butylpyridine (1.67 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (no product detected by HPLC); run 2: (no product detected by HPLC).

Entry 5: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N-isopropylamine (2.07 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (no product detected by HPLC); run 2: (no product detected by HPLC).

Entry 6: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylamine (2.54 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (69.6 mg, 0.189 mmol, 63% yield [11:1 L/B, 16:1 E/Z]); run 2: (75.4 mg, 0.205 mmol, 68% yield [13:1 L/B, 14:1 E/Z]). **Average yield: 66% [12:1 L/B, 15:1 E/Z].**

Entry 7: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), triethylamine (2.51 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (67.0 mg, 0.182 mmol, 61% yield [14:1 L/B, 15:1 E/Z]); run 2: (64.9 mg, 0.177 mmol, 59% yield [14:1 L/B, 15:1 E/Z]). **Average yield: 60% [14:1 L/B, 15:1 E/Z].**

Entry 8: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (73.6 mg, 0.200 mmol, 67% yield [11:1 L/B, 15:1 E/Z]); run 2: (73.0 mg, 0.199 mmol, 66% yield [11:1 L/B, 19:1 E/Z]). **Average yield: 66% [11:1 L/B, 17:1 E/Z].**

Entry 9: Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylaminium methyl tosylcarbamate [215.1 mg, 0.6 mmol, 2.0 equiv, transferred with TBME (2 x 0.150 mL), added last], benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), were used following the standard procedure, except that the initial volume of solvent added with the starting material was 0.150 mL to accommodate the DIPEAH-MeOCNTs transfer volume. Run 1: (7.8 mg, 0.0212 mmol, 7% yield [6:1 L/B, 8:1 E/Z]); run 2: (10.6 mg, 0.0288 mmol, 10% yield [7:1 L/B, 11:1 E/Z]). **Average yield: 9% [7:1 L/B, 10:1 E/Z].**

N,N-diisopropylethylaminium methyltosylcarbamate. To a flame-dried 15 mL flask with Teflon stir bar was added N,N-diisopropylethylamine (0.52 mL, 3.0 mmol, 1.0 equiv) and then cooled to 0°C. A solution of methyl tosylcarbamate (687.8 mg, 3.0 mmol, 1.0 equiv) in dichloromethane (1.5 mL) under N₂ was then transferred dropwise via syringe to the amine base with vigorous stirring. After the addition was completed, the reaction slowly warmed to room temperature over 4 h. Solvent was removed by rotatory evaporation (30°C, 20 torr) to yield a pale yellow, viscous oil.
Exploration of Catalytic DIPEA Loadings. Base loadings at 25 mol% and higher became highly viscous, and required vigorous stirring to achieve reproducible results.

Alternate Procedure for Difficult Stirring Conditions. A 3.0 mL conical Reacti-Vial© (Thermo Scientific, Rockford, IL) was charged with 1-decene (42.1 mg, 0.3 mmol, 1.0 equiv), followed by t-butyl methyl ether (0.450 mL), 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (15.1 mg, 0.03 mmol, 0.10 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), methlytosyl carbamate (137.6 mg, 0.6 mmol, 2.0 equiv), and a spin-vane were then sequentially added. Under vigorous magnetic stirring, DIPEA was added dropwise via syringe at a rate of 1 drop/10 sec. A black, insoluble residue quickly forms on the sides of the vial. The vial was fitted with an open cap containing a Teflon septum, and heated to 45°C (with magnetic stirring) in an oil bath for 72 h. The vial was removed, allowed to cool to room temperature, and thoroughly rinsed into a 125 mL separatory funnel with acetone (2 x 0.5 mL) and ether (ca. 30 mL). The organic phase was washed with 5% aq. K₂CO₃ (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over MgSO₄, filtered through a 1:1 mixture of Celite/silica gel, and evaporated to dryness. Yields were determined by comparison with an internal standard (nitrobenzene).

Run 1: (1.8% yield); run 2: (3.7% yield), run 3: (2.0% yield). Average yield: 3%.

(0 mol%): See Table 1, entry 1.

(1 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (10.0 µL, 0.003 mmol, 0.010 equiv, 0.3M stock solution in TBME), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv), and 0.440 mL TBME were used following the standard procedure. Yields were determined by comparison with an internal standard (nitrobenzene). Run 1: (1.8% yield); run 2: (3.7% yield), run 3: (2.0% yield). Average yield: 3%.
(3 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (1.57 µL, 0.009 mmol, 0.030 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (65.0 mg, 0.177 mmol, 59% yield); run 2: (68.4 mg, 0.186 mmol, 62% yield); run 3: (56.0 mg, 0.152 mmol, 51% yield). **Average yield: 57%**.

(6 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.060 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (73.6 mg, 0.200 mmol, 67% yield); run 2: (73.0 mg, 0.199 mmol, 66% yield); run 3: (71.6 mg, 0.195 mmol, 65% yield). **Average yield: 66%**.

(10 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (13.1 µL, 0.075 mmol, 0.25 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the alternate procedure. Run 1: (30.6 mg, 0.0833 mmol, 28% yield); run 2: (31.4 mg, 0.0854 mmol, 28% yield); run 3: (27.3 mg, 0.0743 mmol, 25% yield); run 4: (28.3 mg, 0.0770 mmol, 26% yield). **Average yield: 27%**.

(25 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (26.1 µL, 0.15 mmol, 0.50 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the alternate procedure. Run 1: (22.7 mg, 0.0618 mmol, 21% yield); run 2: (21.6 mg, 0.0588 mmol, 20% yield); run 3: (23.0 mg, 0.0626 mmol, 21% yield); run 4: (22.7 mg, 0.0618 mmol, 21% yield). **Average yield: 21%**.

(50 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (104.5 µL, 0.6 mmol, 2.0 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the alternate procedure. Run 1: (9.7 mg, 0.0264 mmol, 9% yield); run 2: (12.5 mg, 0.0340 mmol, 11% yield); run 3: (12.7 mg, 0.0346 mmol, 12% yield); run 4: (12.4 mg, 0.0337 mmol, 11% yield). **Average yield: 11%**.

(100 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (52.3 µL, 0.3 mmol, 1.0 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the alternate procedure. Run 1: (9.2 mg, 0.0250 mmol, 8% yield); run 2: (12.5 mg, 0.0340 mmol, 11% yield); run 3: (12.7 mg, 0.0346 mmol, 12% yield); run 4: (12.4 mg, 0.0337 mmol, 11% yield). **Average yield: 11%**.

(200 mol%): Pd[1,2-bis(phenylsulfinyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), N,N-diisopropylethylamine (104.5 µL, 0.6 mmol, 2.0 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the alternate procedure. Run 1: (9.7 mg, 0.0264 mmol, 9% yield); run 2: (8.6 mg, 0.0234 mmol, 8% yield); run 3: (10.4 mg, 0.0283 mmol, 9% yield); run 4: (8.7 mg, 0.0237 mmol, 8% yield). **Average yield: 9%**.
### Table 2. Scope and Comparison of the Brønsted Base vs. Lewis Acid Promoted Allylic C—H Amination

<table>
<thead>
<tr>
<th>entry</th>
<th>allylic amination product</th>
<th>isolated yield</th>
<th>DIPEA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Cr(salen)Cl&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Allylic Amination Product" /></td>
<td>5</td>
<td>61%&lt;sup&gt;e&lt;/sup&gt;</td>
<td>37%&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>2</td>
<td><img src="image" alt="Allylic Amination Product" /></td>
<td>6</td>
<td>R = CHO</td>
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<td>R = CN</td>
<td>79%</td>
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<td>R = H</td>
<td>81%</td>
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<td>5</td>
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<td>89%</td>
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<td>18</td>
<td>R = Fm</td>
<td>55%&lt;sup&gt;f&lt;/sup&gt;</td>
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</table>

<sup>a</sup>Average of at least two runs at 0.3 mmol. Products were isolated as one regio- and olefin isomer (<sup>1</sup>H NMR).<sup>b</sup>18:1 E/Z. <sup>c</sup>13:1 E/Z. <sup>d</sup>Reported in SI ref. 14. <sup>e</sup>48 h reaction time. <sup>f</sup>10 mol% DIPEA, CCl<sub>4</sub> solvent, 24 h reaction time; Fm = 9-fluorenymethyl.

## Substrate Scope

**General DIPEA Procedure.** A 1 dram vial was charged with olefin (0.3 mmol, 1.0 equiv), followed by t-butyl methyl ether (0.450 mL), 1,2-Bis(phenylsulfonyl)ethane palladium(II) acetate (15.1 mg, 0.03 mmol, 0.10 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv), and a stir bar were then sequentially added. N,N-Diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv) was added via
autopipet (or syringe), and the reaction mixture instantly became cloudy. The vial was fitted with a Teflon cap, and heated to 45°C (with magnetic stirring) in an oil bath for 72 h. The vial was removed, allowed to cool to room temperature, and vigorously rinsed into a 125 mL separatory funnel with ether (ca. 30 mL). The organic phase was washed with 5% aq. K₂CO₃ (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over MgSO₄ filtered through a 1:1 mixture of Celite/silica gel, and evaporated to dryness (ca. 30-40°C, 30 torr). The crude product was purified by flash chromatography on silica gel, and evaporated to dryness.

**Comparison to Cr-catalyzed reaction conditions.** Reactions with Cr were run in an analogous way as above by substituting (+)-Cr(salen)Cl (11.4 mg, 0.018 mmol, 0.06 equiv, Strem) for DIPEA. This reagent was added immediately after the palladium catalyst.

(E)-methyl 6-(N-(methoxycarbonyl)-4-methylphenylsulfonamido)hex-5-enoate [5]: Methyl hex-5-enoate (38.5 mg, 0.3 mmol, 1.0 equiv, Aldrich) was reacted following the general procedure. Column chromatography (30% EtOAc/hexanes) yielded the product as a pale yellow oil. Linear/branched ratio was >20:1 after chromatography. Run 1 (66.1 mg, 0.186 mmol, 62% yield, 18:1 E/Z); run 2 (64.0 mg, 0.180 mmol, 60% yield, 17:1 E/Z). **Average yield: 61%, 18:1 E/Z.** Cr conditions: Linear/branched ratio was >20:1 after chromatography, (39.5 mg, 0.111 mmol, 37% yield, 13:1 E/Z).

1H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 16.0 Hz, 1H), 6.38 (dd, J = 6.5, 1.0 Hz, 2H), 3.72 (s, 3H); 13C NMR (500 MHz, CDCl₃) δ 130.1, 129.4, 128.5, 127.7, 127.1, 54.0, 48.6, 21.6; IR (film, cm⁻¹): 3042, 2957, 2226, 1737, 1605, 1495, 1443, 1360, 1318, 1277, 1231, 1169, 1130, 1089, 1018, 971, 912, 881, 815, 768, 733, 676; HRMS (ESI) m/z calc'd for C₁₀H₁₂NO₅S [M+H]+: 356.1168, found 356.1154.

(E)-methyl 3-((4-formylphenyl)allyl(tosyl)carbamate [6]: p-Allylbenzaldehyde (43.9 mg, 0.3 mmol, 1.0 equiv) was reacted according to the standard procedure. Flash chromatography (30% EtOAc/hexanes) afforded off-white crystals. Run 1 (88.5 mg, 0.237 mmol, 79% yield); run 2 (84.1 mg, 0.225 mmol, 75% yield). Only the linear E product was observed by 1H NMR. **Average yield: 77%.** Cr conditions: Only the linear E product was observed by 1H NMR. Run 1 (81.7 mg, 0.219 mmol, 73% yield); run 2 (88.5 mg, 0.237 mmol, 79% yield); Average yield 76%.

1H NMR (500 MHz, CDCl₃) δ 9.99 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 15.8, 6.3 Hz, 1H), 4.65 (dd, J = 6.5, 1.0 Hz, 2H), 3.73 (s, 3H), 2.43 (s, 3H); 13C NMR (500 MHz, CDCl₃) δ 191.7, 152.6, 144.8, 142.2, 136.2, 135.7, 132.6, 130.1, 129.4, 128.5, 127.7, 127.1, 54.0, 48.6, 21.6; IR (film, cm⁻¹): 3039, 2959, 2920, 2861, 2832, 2745, 1739, 1699, 1603, 1569, 1443, 1360, 1309, 1280, 1231, 1213, 1089, 969, 912, 879, 815, 757, 676; HRMS (ESI) m/z calc'd for C₁₀H₂₀NO₅S [M+H]+: 374.1062, found 374.1059.

(E)-methyl 3-((4-cyanophenyl)allyl(tosyl)carbamate [7]: p-Allylbenzonitrile (43.0 mg, 0.3 mmol, 1.0 equiv) was reacted according to the standard procedure. Column chromatography (35% EtOAc/hexanes) led to the isolation of white crystals. Run 1 (89.2 mg, 0.241 mmol, 80% yield); run 2 (86.1 mg, 0.232 mmol, 78% yield). Only the linear E product was observed by 1H NMR. **Average yield: 79%.** Cr conditions: Only the linear E product was observed by 1H NMR. Run 1 (67.0 mg, 0.181 mmol, 60% yield); run 2 (64.6 mg, 0.175, 58% yield); Average yield: 59%.

1H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 16.0, 6.3 Hz, 1H), 4.63 (dd, J = 6.5, 1.0 Hz, 2H), 3.72 (s, 3H), 2.43 (s, 3H); 13C NMR (500 MHz, CDCl₃) δ 152.6, 144.9, 140.7, 136.2, 134.2, 131.9, 129.4, 128.4, 128.0, 127.0, 118.5, 111.2, 54.0, 48.5, 21.6; IR (film, cm⁻¹): 3042, 2957, 2226, 1737, 1605, 1495, 1443, 1360, 1318, 1277, 1231, 1169, 1130, 1089, 1018, 971, 912, 881, 815, 768, 733, 676; HRMS (ESI) m/z calc’d for C₁₀H₁₉N₂O₅S [M+H]+: 371.1066, found 371.1065.
(E)-methyl 2-hydroxy-3-methoxy-5-(3-(N-(methoxycarbonyl)-4-methylphenylsulfonamido)prop-1-enyl)benzoate[8]: Methyl 5-allyl-3-methoxy-salicylate (66.7 mg, 0.3 mmol, 1.0 equiv, Aldrich) was reacted following the general procedure. Column chromatography (30% EtOAc/hexanes) yielded the product as a white solid. Run 1 (104.8 mg, 0.233 mmol, 78% yield); run 2 (112.0 mg, 0.249 mmol, 83% yield). Only the linear E product was observed by H NMR. Average yield: 81%. Cr Conditions: Only the linear E product was observed by H NMR. Run 1 (53.4 mg, 0.119 mmol, 40% yield).

1H NMR (500 MHz, CDCl3) δ 11.01 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.10 (dt, J = 15.5, 6.5 Hz, 1H), 4.57 (d, J = 6.5 Hz, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H); 13C NMR (500 MHz, CDCl3) δ 170.5, 152.6, 151.9, 148.6, 144.6, 136.3, 133.0, 129.2, 128.4, 127.1, 122.4, 119.7, 113.7, 112.2, 56.1, 53.9, 52.4, 48.7, 21.5; IR (film, cm⁻¹): 3066 (broad), 2957, 1737, 1678, 1597, 1482, 1444, 1363, 1291, 1273, 1242, 1203, 1170, 1088, 1070, 964, 874, 794, 754, 669; HRMS (ESI) m/z calc’d for C32H28NO8S [M+H⁺]: 540.1223, found 540.1212.

(E)-methyl 3-methoxy-5-(3-(N-(methoxycarbonyl)-4-methylphenylsulfonamido)prop-1-enyl)-2-(trifluoromethylsulfonyloxy)benzoate[9]: Methyl 5-allyl-3-methoxy-2-(trifluoromethylsulfonyloxy)benzoate[5] (106.3 mg, 0.3 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (35% EtOAc/hexanes) yielded the product as an orange oil. Run 1 (155.3 mg, 0.267 mmol, 89% yield); run 2 (154.1 mg, 0.265 mmol, 88% yield). Only the linear E product was observed by H NMR. Average yield: 89%. Cr Conditions: Only the linear E product was observed by H NMR. Run 1 (62.4 mg, 0.107 mmol, 36% yield). The β-methyl styrene product resulting from olefin isomerization was also isolated as colorless needles (33.3 mg, 0.0940 mmol, 31% yield). Olefin geometry (E/Z ratio) was not determined.

1H NMR (500 MHz, CDCl3) δ 7.81 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 2.0 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.32 (dt, J = 15.8, 6.0 Hz, 1H), 4.61 (d, J = 6.0 Hz, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 3.71 (s, 3H), 2.41 (s, 3H); 13C NMR (500 MHz, CDCl3) δ 164.2, 152.5, 151.7, 144.9, 136.9, 136.7, 136.1, 131.2, 129.4, 128.3, 127.4, 125.4, 121.1, 118.6 (q, J = 319.6 Hz), 114.2, 56.3, 54.0, 52.6, 48.4, 21.5; 19F NMR: (470 MHz, CFCl3) δ -73.9 (s, 3F); IR (film, cm⁻¹): 3021, 2955, 1744, 1549, 1422, 1363, 1333, 1275, 1217, 1171, 1135, 1088, 1066, 968, 904, 879, 815, 736; HRMS (ESI) m/z calc’d for C23H22NO16S2F3 [M+H⁺]: 582.0715, found 582.0696.

(E)-methyl 3-methoxy-5-(prop-1-enyl)-2-(trifluoromethylsulfonyloxy)benzoate[9a]: E/Z ratio was not determined.

1H NMR (500 MHz, CDCl3) δ 7.52 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 6.31-6.41 (m, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 1.93 (d, J = 5.0 Hz, 3H); 19F NMR: (376 MHz, CFCl3) δ -74.0 (s, 3F); IR (film, cm⁻¹): 3042, 2962, 2922, 2854, 1732, 1657, 1591, 1423, 1345, 1303, 1280, 1260, 1247, 1214, 1137, 1067, 1009, 963, 874, 781, 713; HRMS (ESI) m/z calc’d for C13H13O6F3NaS [M+Na⁺]: 737.0290, found 737.0283.

(S)-2-((4-allylphenoxy)methyl)oxirane [(-)-10a]: A 50 mL round bottom flask with stir bar was charged with p-allylphenol[6] (500 mg, 3.7 mmol, 1.0 equiv) and DMF (7 mL). The flask was cooled to 0°C, and NaH (156.3 mg, 3.9 mmol, 1.05 equiv, 60% by weight in mineral oil) was added portionwise. After stirring for 1 h at 0°C (H2 evolution ceased), (S)-oxiran-2-ylmethyl 4-methylbenzenesulfonate (2.35 g, 10.3 mmol, 2.78 equiv, Aldrich) dissolved in DMF (3.5 mL, 1 x 1 mL rinse) was cannulated into the flask. The reaction mixture was then allowed to warm to room temperature, and stirred for 13 h. The reaction was quenched by cooling to 0°C, and adding sat. NH4Cl (5 mL). After transferring to a separatory funnel and diluting with EtOAc (100 mL), the organic layer was washed twice with H2O, dried 30 min over Na2SO4, and the solvent evaporated at 25°C. Column chromatography (15% EtOAc/hexanes) afforded the pure product as a colorless oil (557.2 mg, 2.93 mmol, 79% yield).

1H NMR (500 MHz, CDCl3) δ 7.10 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.90-5.99 (m, 1H), 5.03-5.08 (m, 2H), 4.19 (dd, J = 11.0, 3.0 Hz, 1H), 3.95 (dd, J = 11.0, 6.0 Hz, 1H), 3.32-3.37 (m, 3H), 2.90 (dd, J = 4.8, 4.3 Hz, 1H), 2.75 (dd, J = 5.0, 2.5 Hz, 1H); 13C NMR: (125 MHz, CDCl3) δ 156.8, 137.7, 132.6, 129.5, 115.4, 114.5, 114.3, 112.2, 48.7, 21.5; IR (film, cm⁻¹): 3066 (broad), 2957, 1737, 1678, 1597, 1482, 1444, 1363, 1291, 1273, 1242, 1203, 1170, 1088, 1070, 964, 874, 794, 754, 669; HRMS (ESI) m/z calc’d for C23H22NO16S2F3 [M+H⁺]: 582.0715, found 582.0696.
(S,E)-methyl 3-(4-(oxiran-2-methyloxy)phenyl)allyl(tosyl)carbamate(-10): Compound (-)-10a (57.1 mg, 0.3 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (30% EtOAc/hexanes) yielded the product as a pale orange oil. Run 1 (65.3 mg, 0.157 mmol, 52% yield); run 2 (75.0 mg, 0.180 mmol, 60% yield), run 3 (63.5 mg, 0.152 mmol, 51% yield). Only the linear E product was observed by 1H NMR. **Average yield: 54%.** Cr conditions: no product could be detected by 1H NMR of the crude reaction mixture.

1H NMR (500 MHz, CDCl3) δ 7.82 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 15.5 Hz, 1H), 6.10 (dt, J = 15.8, 6.6 Hz, 1H), 4.59 (d, J = 5.5 Hz, 2H), 4.24 (dd, J = 11.0, 3.0 Hz, 1H), 3.95 (dd, J = 11.0, 5.5 Hz, 1H), 3.71 (s, 3H), 3.37-3.34 (m, 1H), 2.91 (dd, J = 5.0, 4.0 Hz, 1H), 2.76 (dd, J = 5.0, 3.0 Hz, 1H), 2.41 (s, 3H); 13C NMR (500 MHz, CDCl3) δ 158.3, 152.7, 144.5, 136.4, 133.5, 129.5, 129.3, 128.5, 127.8, 121.7, 114.6, 68.7, 53.8, 50.0, 48.9, 44.6, 21.6; IR (film, cm⁻¹): 3440 (broad), 3038, 3008, 2961, 2930, 2877, 1735, 1652, 1607, 1436, 1248, 1126, 1089, 1034, 968, 911, 815, 733, 675; HRMS (ESI) m/z calcd for C₃₂H₂₅NO₅SNa [M+Na]⁺: 440.1144, found 440.1137. [α]D = -0.26° (c = 1.0, CHCl₃).

(R,E)-methyl 4-(oxiran-2-yl)but-2-enyl(tosyl)carbamate (+-11): (-)-(S)-2-(but-3-enyloxirane) (29.4 mg, 0.3 mmol, 1.0 equiv, >99% ee) was reacted according to the standard procedure, except that Na₂SO₄ was used to dry the organic layers following the workup. Column chromatography provided the product as a colorless oil. 48 h reaction time: run 1 (48.1 mg, 0.148 mmol, 49% yield); run 2 (45.8 mg, 0.141 mmol, 47% yield); 24 h reaction time (42.3 mg, 0.130 mmol, 43% yield); 72 h reaction time (48.2 mg, 0.148 mmol, 49% yield). Linear/branched and E/Z isomer ratios were >20:1 by 1H NMR. **Average yield (48 h reaction time) 48%.** Cr conditions: no product could be detected by 1H NMR of the crude reaction mixture.

1H NMR (500 MHz, CDCl3) δ 7.83 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.80 (dt, J = 15.5, 7.0 Hz, 1H), 5.68 (dd, J = 15.0, 6.0 Hz, 1H), 4.43 (d, J = 6.0 Hz, 2H), 3.68 (s, 3H), 3.02-2.98 (m, 1H), 2.77 (dd, J = 5.0, 4.0 Hz, 1H), 2.52 (dd, J = 5.0, 3.0 Hz, 1H), 2.43 (s, 3H), 2.30-2.35 (m, 2H); 13C NMR (500 MHz, CDCl3) δ 152.6, 144.6, 136.4, 129.6, 129.3, 128.5, 127.6, 53.8, 51.0, 48.4, 46.5, 34.9, 21.6; IR (film, cm⁻¹): 2961, 2924, 1732, 1653, 1597, 1443, 1355, 1307, 1272, 1237, 1168, 1128, 1090, 974; HRMS (ESI) m/z calcd for C₂₃H₂₇NO₃SNa [M+Na]⁺: 360.1062, found 360.1051; [α]D = +0.04° (c = 1.09, CHCl₃).

(S)-1-(R)-2-methyloxiran-2-yl)pent-4-en-1-ol (+-12a): This procedure was adapted from a similar report in the literature. A 50 mL round bottom flask with stir bar was charged with (±)-2-methylhepta-1,6-dien-3-ol (504.8 mg, 4.0 mmol, 1.0 equiv), 4Å molecular sieves (500 mg), (+)-diisopropyl tartrate (276 µL, 1.32 mmol, 0.33 equiv, via syringe equipped with a 16 gauge needle), and CH₂Cl₂ (16 mL). The reaction mixture was then cooled to -10°C, and Ti(O-i-Pr)₄ (234 µL, 0.8 mmol, 0.2 equiv) was added dropwise via syringe with stirring for 1 h. The solution was then cooled to -35 °C, and tert-butyl hydrogen peroxide (327 µL, 1.8 mmol, 0.45 equiv, 5.5 M in decane) was added dropwise to the white slurry. After 11 h, 5% aq. HCl (4.4 mL) was added, and the reaction mixture was warmed to room temperature. The mixture was filtered through a fritted funnel filled with celite, and transferred to a separatory funnel with CH₂Cl₂ (20 mL). The organic layer was washed with water (2 × 10 mL), filtering through a fritted glass funnel each time to clear the emulsion. The organic layer was then dried over Na₂SO₄ (1 h), decanted, and concentrated by rotary evaporation at 0°C. Flash chromatography (30% ether/pentane) afforded the epoxide as a single diastereomer (85.3 mg, 0.6 mmol, 15% yield). A small sample was prepared for Mosher ester analysis (**vida infra**).

1H NMR (500 MHz, CDCl3) δ 5.83 (ddt, J = 16.8, 10.3, 7.0 Hz, 1H), 5.05 (dd, J = 17.0, 1.5 Hz, 1H), 4.98 (d, J = 10.5 Hz, 1H), 3.65 (app d, J = 9.0 Hz, 1H), 2.89 (d, J = 5.0 Hz, 1H), 2.60 (d, J = 4.5 Hz, 1H), 2.25-2.32 (m, 1H), 2.13-2.21 (m, 2H), 1.67-1.75 (m, 1H), 1.45-1.53 (m, 1H), 1.33 (s, 3H); 13C NMR: (125 MHz, CDCl3) δ 138.2, 114.9, 71.0, 59.1, 50.2, 32.1, 29.8, 18.0; IR (film, cm⁻¹): 3446 (broad), 3077, 2981, 2930, 2860, 1722, 1641, 1391, 1391, 1273, 1235, 1101, 1066, 994, 911, 816; HRMS (Cl, CH₄) m/z calcd for C₁₀H₁₃O₂ [M+H]⁺: 143.10721, found 143.10715; [α]D = +6.0° (c = 0.42, CHCl₃).
Determination of enantiomeric purity by Mosher ester analysis. The epoxy alcohol described above (10.7 mg, 0.08 mmol, 1.0 equiv) was placed in a 1 dram vial, and diluted with CH₂Cl₂ (0.5 mL). Triethylamine (50 µL, 0.37 mmol, 4.6 equiv), N,N-dimethylaminopyridine (4.0 mg, 0.037 mmol, 0.46 equiv), and (+)-α-methoxytrifluoromethylcarbonyl chloride (30 µL, 0.16 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred with a Teflon cap and refluxed until the reaction was deemed complete by TLC analysis (20 min). The orange solution was treated with (N,N-dimethyl)propylylamine (−0.2 mL) to consume excess acid chloride, and the solvent was removed by blowing with N₂. The thick orange oil was dissolved in 5% EtOAc/hexanes, and passed through a pipet filled with silica gel. The colorless solution was concentrated to dryness and analyzed by ¹H NMR. A racemic standard was also synthesized for comparison using V(O)(acac)₂/7-BuOOH. Average ratio of integral values corresponds to a 96% ee.

¹H NMR (500 MHz, CDCl₃, diagnostic signals) Major diastereomer: δ 4.77 (dd, J = 8.0 Hz, 5.0 Hz, 1H), 2.79 (d, J = 5.0 Hz, 1H), 2.55 (d, J = 5.0 Hz, 1H). Minor diastereomer: δ 4.89 (dd, J = 9.0, 4.0 Hz, 1H), 2.82 (d, J = 5.0 Hz, 1H), 2.59 (d, J = 5.0 Hz, 1H).

((S,E)-5-(N-(methoxycarbonyl)-4-methylphenylsulfonamido)-1-((R)-2-methyloxiran-2-yl)pent-3-enyl acetate(−)-12b): Epoxy alcohol (+)-12a (142 mg, 1.0 mmol, 1.0 equiv) was added to a 25 mL round bottom flask with stir bar, and dissolved in CH₂Cl₂ (10 mL). Triethylamine (0.560 mL, 4.0 mmol, 4.0 equiv) and acetic anhydride (0.189 mL, 2.0 mmol, 2.0 equiv) were added via syringe, and the reaction stirred 3.5 hr at room temperature. Evaporation of the reaction solvent, followed by column chromatography (10% EtOAc/hexanes) provided the epoxy acetate as a colorless oil (131.0 mg, 0.711 mmol, 71% yield).

S-E-4-(N-(methoxycarbonyl)-4-methylphenylsulfonamido)-1-((R)-2-methyloxiran-2-yl)but-2-enyl acetate [−]-12b: Epoxy acetate (-)-12b (55.3 mg, 0.33 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (30% EtOAc/hexanes) yielded the product as a colorless oil (82.4 mg, 0.200 mmol, 67% yield; run 2 (73.7 mg, 0.179 mmol, 60% yield) Linear/branched and E/Z ratios were >20:1 by ¹H NMR. Average yield: 64%. Cr conditions: no product could be detected by ¹H NMR of the crude reaction mixture.

¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.61-5.73 (m, 2H), 4.67 (dd, J = 9.0, 4.0 Hz, 1H), 4.33-4.41 (m, 2H), 3.67 (s, 3H), 2.80 (d, J = 5.0 Hz, 1H), 2.57 (d, J = 4.5 Hz, 1H), 2.42 (s, 3H), 2.35-2.47 (m, 2H), 2.03 (s, 3H), 1.31 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 170.1, 152.6, 144.6, 136.4, 129.7, 129.3, 128.4, 127.9, 74.3, 56.2, 53.8, 53.1, 48.4, 33.4, 21.6, 20.9, 16.9; IR (film, cm⁻¹): 3070, 2924, 2854, 1738, 1634, 1507, 1234, 1066, 1029, 955, 911; HRMS (EI, CH₃) m/z calc’d for C₁₀H₁₀O₂Na [M+Na⁺]: 207.0997, found 207.0990; [α]₀²⁵ = -8.6° (c = 1.08, CHCl₃).

(S)-4,8-dimethyl-1,7-diene[(−)-13a]: A 500 mL round bottom flask was charged with triphenyloxiphosphonium methyl iodide (15.7 g, 38.9 mmol, 2.0 equiv), THF (187 mL), and a stir bar. The flask was cooled to 0°C with stirring, and potassium tert-butoxide (4.36 g, 38.9 mmol, 2.0 equiv) was added portionwise as the slurry turned bright yellow. After 30 minutes at 0°C, (−)-(S)-citronellal (3.53 mL, 19.45 mmol, 1.0equiv, Aldrich, [α]₀²⁵ = -15°, neat) was added dropwise via syringe into the reaction mixture. After stirring an additional 30 min at 0°C, 36 mL sat. aqueous NH₄Cl was added dropwise, and the solution warmed to room temperature. The reaction mixture was diluted with diethyl ether (300 mL) and extracted with ether (2 x 300 mL). The combined ether layers were then washed with water (1 x 500 mL) and brine (1 x 500 mL) before drying over Na₂SO₄ (with stirring, 1 h). Decantation of ether, followed by solvent removal at 0°C produced the crude product as a pale yellow oil. This was filtered through a pad of silica gel with pentane to afford a colorless oil (2.8173 g, 18.52 mmol, 95% yield).

¹H NMR (500 MHz, CDCl₃) δ 5.78 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 5.09-5.12 (m, 1H), 4.97-5.02 (m, 2H), 1.87-2.10 (m, 4H), 1.69 (s, 3H), 1.61 (s, 3H), 1.48-1.54 (m, 1H), 1.32-1.39 (m, 1H), 1.11-1.18 (m, 1H), 0.88 (d, J =
7.0 Hz, 3H). $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ 137.7, 131.1, 124.8, 115.5, 41.3, 36.6, 32.4, 25.7, 25.6, 19.3, 17.6; IR (film, cm$^{-1}$): 3076, 2967, 2914, 1873, 2856, 2729 (weak), 1825 (weak), 1641, 1454, 1440, 1377, 993, 911; HRMS (Cl, CH$_4$) $m/z$ calc’d for C$_{11}$H$_{20}$ [M$^+$]: 152.15650, found 152.15632; $[\alpha]_D^{20} = -2.3^\circ$ (neat).

$(3R,6S)$-2,6-dimethylon-8-ene-2,3-diol(+)13b: To a 500 mL round bottom flask was added ADmix-β (6.44 g, Aldrich), diene (+)13a (1.0 g, 6.57 mmol, 1.0 equiv), methane sulfonamide (812 mg, 8.54 mmol, 1.3 equiv), tert-butanol (81 mL), water (64 mL), and a stir bar. The mixture was stirred for 64 h at room temperature, followed by quenching with solid Na$_2$SO$_3$ (8.1 g) and stirring an additional 30 min until the yellow color faded. After removal of tert-butanol by rotatory evaporation (45°C), followed by dilution with water (480 mL) and extraction with ethyl acetate (3 x 200 mL), the combined organic layers were dried with MgSO$_4$. The solids were filtered and discarded, and the filtrate evaporated to yield the product as a colorless oil (930 mg, 5.0 mmol, 76% yield).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.77 (ddt, $J = 17.3, 10.5, 7.1$ Hz, 1H), 4.97-5.01 (m, 2H), 3.32 (d, $J = 8.5$ Hz, 1H), 2.26 (bs, 1H), 2.06-2.12 (m, 2H), 1.87-1.93 (m, 1H), 1.60-1.67 (m, 1H), 1.49-1.55 (m, 2H), 1.20 (s, 3H), 1.15 (s, 3H), 1.11-1.29 (m, 2H), 0.89 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ 137.4, 115.7, 79.0, 73.2, 41.1, 33.7, 32.9, 29.1, 26.5, 23.1, 19.5; IR (film, cm$^{-1}$): 3400 (broad), 3075, 2975, 2955, 2926, 2871, 1640, 1461, 1439, 1378, 1281, 1228, 1166, 1071, 993, 910, 779; HRMS (ESI) $m/z$ calc’d for C$_{11}$H$_{22}$O$_2$Na [M+Na$^+$]: 209.1517, found 209.1511; $[\alpha]_D^{20} = +1.76^\circ$ (c = 2.0, CHCl$_3$).

**Determination of Diastereoselectivity:** Analysis of Mosher esters by HPLC (Agilent© Eclipse XDB-C8, 35% H$_2$O/McCN, 1.0 mL/min @ 30°C, $t_r = 7.82$, 8.18 min). Major diastereomer (8.18 min), 31:1 dr. The absolute configuration of the resulting diol was assigned by analogy.

$(R)$-2,2-dimethyl-3-((S)-3-methylhex-5-enyl)oxirane(+)13c: Diol (+)13b (552.9 mg, 3.0 mmol, 1.0 equiv) was added to a 100 mL round bottom flask with 0.9 mL of methanol, and pyridine (1.5 mL, 18.6 mmol, 6.2 equiv). The reaction flask was cooled to 0°C, and methanesulfonyl chloride (0.465 mL, 6.0 mmol, 2.0 equiv, freshly distilled) was added dropwise, turning the solution yellow. The reaction was warmed to room temperature and stirred an additional 12 h, before being quenched with N,N-dimethylaminopropylamine (0.42 mL, 3.3 mmol, 1.1 equiv). The now heterogeneous yellow solution was allowed to stir for 10 min, then decanted into a separatory funnel. The solution was washed with 10% aqueous CuSO$_4$ (6 x 20 mL) and sat. NaHCO$_3$ (1 x 60 mL) before drying over Na$_2$SO$_4$. Decantation of the drying agent and removal of solvents left the crude mono mesylate as a colorless liquid; this material was sufficiently pure for the next step.

$^1$H NMR (500 MHz, CDCl$_3$, diagnostic peaks) $\delta$ 5.72-5.81 (m, 1H), 4.98-5.02 (m, 2H), 4.54 (dd, $J = 10.0, 2.5$ Hz, 1H), 3.11 (s, 3H), 2.05-2.10 (m, 1H), 2.02 (bs, 1H), 1.89-1.95 (m, 1H), 1.50-1.71 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H), 0.91 (d, $J = 6.5$ Hz, 3H).

The mesylate obtained above was dissolved in methanol (15 mL), and stirred with solid K$_2$CO$_3$ (450 mg, 3.3 mmol, 1.1 equiv) for 4 h at room temperature. The reaction mixture was then slowly poured into ice cold sat. aqueous NH$_4$Cl (150 mL) and allowed to stand until vigorous bubbling subsided. The solution was extracted with ethyl ether (3 x 100 mL), dried over Na$_2$SO$_4$, and evaporated to dryness at 20°C. Flash chromatography (5% EtOAc/hexanes) isolated the epoxide as a colorless liquid (300.0 mg, 1.78 mmol, 60% yield for 2 steps).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.77 (ddt, $J = 17.0, 10.0, 7.0$ Hz, 1H), 5.00 (d, $J = 17.0$ Hz, 1H), 4.99 (d, $J = 10.0$ Hz, 1H), 2.69 (app t, $J = 6.3$ Hz, 1H), 2.06-2.11 (m, 2H), 1.89-1.95 (m, 1H), 1.24-1.82 (m, 5H), 1.30 (s, 3H), 1.26 (s, 3H), 0.89 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ 137.2, 115.8, 64.6, 58.3, 41.1, 33.0, 32.6, 26.5, 24.9, 19.4, 18.7; IR (film, cm$^{-1}$): 3077, 2979, 2959, 2924, 2873, 1640, 1461, 1378, 1332, 1249, 1122, 994, 910, 869, 793, 738, 679; HRMS (Cl, CH$_4$) $m/z$ calc’d for C$_{11}$H$_{22}$O$_2$ [M+H$^+$]: 169.15925, found 169.15947; $[\alpha]_D^{20} = -1.3^\circ$ (c = 1.08, CHCl$_3$).

methyl (R,E)-6-((S)-3,3-dimethyloxiran-2-yl)-4-methylhex-2-enyl(1H) carbamate(+)13c: Epoxide (-)13c (50.5 mg, 0.3 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (15% EtOAc/hexanes) yielded the product as a colorless oil. Run 1 (70.8 mg, 0.179 mmol, 60% yield); run 2 (69.1 mg, 0.175 mmol, 58% yield). No branched products were observed, and the E/Z ratio was >20:1 by $^1$H NMR. **Average yield: 59%**. Cr conditions: No branched products were observed, and the E/Z ratio was >20:1 by $^1$H NMR. Run 1 (53.1 mg, 0.134 mmol, 45% yield).
\[^1\]H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.83 (d, \(J = 8.5\) Hz, 2H), 7.30 (d, \(J = 8.0\) Hz, 2H); 5.65 (dd, \(J = 15.5, 7.5\) Hz, 1H), 5.51 (dt, \(J = 15.3, 6.5\) Hz, 1H), 4.41 (d, \(J = 6.0\) Hz, 2H), 3.69 (s, 3H), 2.68-2.70 (m, 4H), 2.43 (s, 3H), 2.17-2.21 (m, 1H), 1.35-1.54 (m, 4H), 1.30 (s, 3H), 1.24 (s, 3H), 1.03 (dd, \(J = 7.0\) Hz, 3H); \[^13\]C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 152.6, 144.5, 140.7, 136.4, 129.2, 128.4, 123.2, 64.4, 58.2, 53.7, 48.5, 36.3, 33.3, 26.7, 24.8, 21.6, 20.3, 18.6; IR (film, cm\textsuperscript{-1}): 2956, 2926, 2874, 1737, 1597, 1444, 1360, 1325, 1291, 1271, 1186, 1170, 1121, 1090, 973, 875, 814, 769, 756, 676; HRMS (ESI) m/z calc’d for C\textsubscript{20}H\textsubscript{30}NO\textsubscript{3}S [M+H]\textsuperscript{+}: 396.1845, found 396.1830; \(\alpha\)\textsubscript{D}\textsuperscript{23} = +0.5° (c = 1.08, CHCl\textsubscript{3}).

**Nucleophile Scope**

**Table 2, entry 11:** Allyl cyclohexane (38.8 mg, 96% pure, 0.3 mmol, 1.0 equiv) and methyl tosylcarbamate (157.6 mg, 0.6 mmol, 2.0 equiv, \textit{vide infra}) were reacted following the general procedure. Purification by flash chromatography (70% EtOAc/hexanes) produced a light orange oil. Run 1 (88.4 mg, 0.252 mmol, 84% yield); run 2 (84.9 mg, 0.242 mmol, 81% yield); run 3 (88.2 mg, 0.251 mmol, 84% yield).

**Table 2, entry 12:** Allyl cyclohexane (38.8 mg, 96% pure, 0.3 mmol, 1.0 equiv) and benzyl tosylcarbamate (183.2 mg, 0.6 mmol, 2.0 equiv, \textit{vide infra}) were reacted following the general procedure. Purification by flash chromatography (50% EtOAc/hexanes) produced a light orange oil. Run 1 (109.0 mg, 0.255 mmol, 85% yield); run 2 (111.4 mg, 0.261 mmol, 87% yield); run 3 (113.2 mg, 0.265 mmol, 88% yield). **Average yield: 87%**. The linear (Z) and branched products were not observed by \[^1\]H NMR. Spectroscopic data for the amination product matched which was reported previously.\textsuperscript{12}

**Table 2, entry 13:** Allyl cyclohexane (38.8 mg, 96% pure, 0.3 mmol, 1.0 equiv), BocNHTs (162.8 mg, 0.6 mmol, 2.0 equiv, Aldrich), and DIPEA (5.2 \textmu L, 0.03 mmol, 0.1 equiv, \textit{via syringe}) were reacted according to the general procedure, using carbon tetrachloride as solvent. Flash chromatography (50% EtOAc/hexanes) isolated a colorless oil. Run 1 (81.9 mg, 0.208 mmol, 69% yield); run 2 (81.5 mg, 0.207 mmol, 69% yield); run 3 (84.1 mg, 0.214 mmol, 71% yield); run 4 (84.3 mg, 0.214 mmol, 71% yield); run 5 (79.0 mg, 0.200 mmol, 67% yield). **Average yield: 69%**. Cr conditions: run 1 (7.6 mg, 0.0193 mmol, 6% yield), run 2 (14.1 mg, 0.0358 mmol, 12% yield); run 3 (9.6 mg, 0.0244 mmol, 8% yield). Average yield with Cr: 9%. The linear (Z) and branched products were not observed by \[^1\]H NMR. Spectroscopic data for the amination product matched which was reported previously.\textsuperscript{12}

**Table 2, entry 14:** Allyl cyclohexane (38.8 mg, 96% pure, 0.3 mmol, 1.0 equiv) and FmocNHTs (236.1 mg, 0.6 mmol, 2.0 equiv, \textit{vide infra}) were reacted according to the \textit{modified procedure for difficult stirring}, using carbon tetrachloride as solvent. Flash chromatography (70% EtOAc/hexanes) isolated a light yellow oil. Run 1 (87.0 mg, 0.169 mmol, 56% yield); run 2 (82.5 mg, 0.160 mmol, 53% yield). **Average yield: 55%**. Cr conditions: run 1 (27.1 mg, 0.0526 mmol, 18% yield);
run 2 (22.6 mg, 0.0438 mmol, 15% yield); run 3 (22.7 mg, 0.0440 mmol, 15% yield). Average yield with Cr: 16%. The linear (Z) and branched products were not observed by $^1$H NMR. Spectroscopic data matched that which was reported previously.\textsuperscript{12} Methyl \textit{N}-nosylcarbamate. To a flame-dried 10 mL round bottom flask with stir bar under N$_2$ was added \textit{p}-nitrobenzenesulfonylisocyanate\textsuperscript{13} (342.3 mg, 1.5 mmol, 1.0 equiv) and THF (2.0 mL). After cooling the solution to 0°C, methanol (2.0 mL) was added dropwise over 3 min. The reaction was then allowed to warm to 20°C, and stirred for 10 h. After removal of solvents, the crude product solidified as off-white plates (374.0 mg, 1.437 mmol, 96% yield).\textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 8.41 (d, $J = 8.8$ Hz, 2H), 8.27 (d, $J = 9.2$ Hz, 2H), 7.42 (bs, 1H), 3.74 (s, 3H); $^{13}$C NMR: (125 MHz, CD$_3$CN) $\delta$ 152.1, 151.9, 145.1, 130.5, 125.3, 54.3; IR (film, cm$^{-1}$): 1608, 1533, 1452, 1315, 1240, 1163, 1113, 1012, 950, 881, 852, 795, 771, 741; LRMS (EI, 70 eV) 227.9(2), 227.9 (12), 212.0(2), 202.0(7), 186.0(44), 122.0(26), 78.0(83), 63.0(100).\textit{(E)}-methyl 3-cyclohexylallyl(4-nitrophenylsulfonyl)carbamate: Allyl cyclohexane (38.8 mg, 96% pure, 0.3 mmol, 1.0 equiv) and methyl nosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were reacted following the general procedure. Purification by flash chromatography (15% EtOAc/hexanes) produced off-white crystalline solids (17.8 mg, 0.0465 mmol, 16% yield). Cr conditions: (43.6 mg, 0.0.114 mmol, 38% yield). 10% DIPEA/CCl$_4$ conditions: run 1 (29.2 mg, 0.0763 mmol, 25% yield); run 2 (25.1 mg, 0.0656 mmol, 22% yield). Average yield (10% DIPEA/CCl$_4$ conditions): 24%. The linear (Z) and branched products were not observed by $^1$H NMR.\textsuperscript{1}H NMR (500 MHz, CDCl$_3$) $\delta$ 8.34 (d, $J = 9.0$ Hz, 2H), 8.15 (d, $J = 9.0$ Hz, 2H), 5.78 (dd, $J = 15.5, 6.5$ Hz, 1H), 5.44 (dt, $J = 15.5, 6.5$ Hz, 1H), 4.43 (d, $J = 6.5$ Hz, 2H), 3.72 (s, 3H), 1.96-2.02 (m, 1H), 1.66-1.76 (m, 5H), 1.04-1.32 (m, 5); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ 152.3, 150.4, 144.9, 142.6, 130.0, 123.8, 121.1, 54.1, 49.0, 40.3, 32.6, 26.0, 25.9; IR (film, cm$^{-1}$): 2927, 2854, 1743, 1537, 1446, 1402, 1377, 1348, 1315, 1259, 1240, 1178, 1128, 1090, 1012, 976; HRMS (ESI) $m/z$ calc’d for C$_{17}$H$_{22}$N$_{2}$O$_{6}$NaS [M+Na]$^+$: 405.1096, found 405.1094.
Methyl tosylcarbamate: To a 1 L flame-dried round bottom flask with septum was added dry methanol (500 mL) and a stir bar. The flask was cooled in an ice bath cooled at 0°C, and  p-toluenesulfonylisocyanate (100 mL, 0.657 mol, 1.0 equiv) was added dropwise via syringe with stirring. The reaction was then allowed to warm to room temperature. After stirring 2 h, removal of the solvent in vacuo produced a colorless syrup that crystallized spontaneously. The solids were then triturated with pentane (2 x 50 mL) and ether (1 x 50 mL), followed by drying under high vacuum (0.5 torr) to yield white plates (141 g, 615 mmol, 94% yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.93 (d, \(J = 8.5\) Hz, 2H), 7.86 (bs, 1H), 7.34 (d, \(J = 8.0\) Hz, 2H), 3.69 (s, 3H), 2.44 (s, 3H); mp 103-105 °C [lit.\(^{14}\) 106-107 °C]. This procedure was adapted from Uehara, et. al.,\(^{15}\) and the data is in agreement with that reported previously.

Benzyl tosylcarbamate: To a 1 L round bottom flask was added benzyl alcohol (9.9 mL, 95.0 mmol, 1.0 equiv), dichloromethane (200 mL), and a stir bar. The mixture was cooled to 0°C with an ice bath, p-toluenesulfonylisocyanate (15.2 mL, 99.8 mmol, 1.05 equiv) was added dropwise, and the reaction stirred for 2 h at 20°C. After removal of solvent under reduced pressure, the product was crystallized as white plates from 5:1 ether/CH\(_2\)Cl\(_2\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 8.5\) Hz, 2H), 7.44 (bs, 1H), 7.34 (m, 3H), 7.30 (d, \(J = 8.0\) Hz, 2H), 7.25 (m, 2H), 5.09 (s, 3H), 2.44 (s, 3H); mp 94-95 °C [lit. 103.5-104 °C]. This data is in agreement with that reported previously.\(^{16}\)

(9H-fluoren-9-yl)methyl tosylcarbamate: This compound was prepared in the same manner as benzyltosyl carbamate.

\(^1\)H NMR (500 MHz, acetone-d6) \(\delta\) 7.87 (d, \(J = 8.5\) Hz, 2H), 7.84 (d, \(J = 7.5\) Hz, 2H), 7.63 (d, \(J = 7.5\) Hz, 2H), 7.42 (d, \(J = 8.0\) Hz, 2H), 7.39 (s, \(J = 7.5\) Hz, 2H), 7.26...
(t, J = 7.5 Hz, 2H), 4.37 (d, J = 7.5 Hz, 2H), 4.19 (t, J = 6.5 Hz, 1H), 2.43 (s, 3H); mp 170-172 °C [lit. 170-171 °C]. This data is in agreement with that reported previously.17

\[ \text{N-}((R,E)-4-(benzylloxy)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enyl)-4-methylbenzenesulfonamide} \]

\[ ([\pm]-19]: \text{Compound (+)-14} \quad (43.7 \text{ mg, 0.0893 mmol, 1.0 equiv}) \] was added to a 10 mL flame-dried tear-drop flask with spin-vane stir bar. MeOH (1.3 mL) was added, followed by K₂CO₃ (23.4 mg, 0.169, 1.9 equiv), and the reaction was vigorously stirred for 6.75 h at 25°C. The reaction was then quenched with NH₄Cl (1 mL), and diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (2 x 10 mL), and the organic layers were combined, dried over MgSO₄, filtered through Celite, and evaporated under reduced pressure. The crude colorless oil (39.0 mg, 0.0940 mmol, >99% yield) required no additional purification.

\[ \text{\(1^H\) NMR (500 MHz, CDCl₃) } \delta 7.74 \ (d, J = 8.5 \text{ Hz}, 2H), 7.27-7.34 \ (m, 7H), 5.66 \ (dt, J = 15.7, 5.6 \text{ Hz}, 1H), 5.48 \ (dd, J = 15.0, 7.8 \text{ Hz}, 1H), 4.55 \ (d, J = 12.0 \text{ Hz}, 1H), 4.52 \ (bs, 1H), 4.41 \ (d, J = 12.0 \text{ Hz}, 1H), 4.11 \ (\text{app q}, J = 6.3 \text{ Hz}, 1H), 3.87 \ (dd, J = 8.8, 6.8 \text{ Hz}, 1H), 3.78 \ (\text{app t}, J = 7.0 \text{ Hz}, 1H), 3.66 \ (dd, J = 8.5, 6.5 \text{ Hz}, 1H), 3.53-3.63 \ (m, 2H), 2.41 \ (s, 3H), 1.36 \ (s, 3H), 1.33 \ (s, 3H); \text{\(1^3C\) NMR: (125 MHz, CDCl₃) } \delta 143.9, 138.4, 137.1, 130.4, 129.9, 128.6, 128.0, 127.8, 127.4, 109.9, 79.8, 77.4, 70.9, 65.8, 44.9, 26.7, 25.5, 21.8; \text{IR (film, cm}^{-1}) \]: 3434 (broad), 1639, 1496, 1454, 1369, 1323, 1308, 1290, 1259, 1215, 1159, 1093; HRMS (ESI) m/z calc’d for C_{23}H_{30}NO_{5}S [M+H]⁺: 432.1845, found 432.1855; [\alpha]_D^{25} = +29.5° (c = 2.67, CHCl₃).

\[ \text{(E)-methyl 4-(benzylloxy)-4-(2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enylcarbamate} \]

\[ ([\pm]-20]: \text{Compound (+)-14} \quad (40.2 \text{ mg, 0.082 mmol}) \] was added to 10 mL round bottom flask containing a stir bar. Dimethoxethane (1 mL) was added via syringe, and the flask cooled to -78°C. A dark, forest green solution of sodium naphthalide was slowly added dropwise (via syringe) until the solution became a light forest green color that persisted for 2 min (Note: trace amounts of benzoquinone/dihydroquinone in the starting material can cause a “false” blue-green color that should not be confused with the endpoint. This color will eventually fade to light yellow upon addition of more reducing reagent). After an additional 10 min at -78°C, the solution was diluted with saturated NH₄Cl (4 mL), allowed to warm to room temperature, and diluted with ethyl acetate (10 mL). The layers were separated, and the aqueous layer extracted with ethyl acetate (2 x 10 mL). Organic fractions were combined, dried over MgSO₄, and evaporated at reduced pressure. Flash chromatography (30% EtOAc/hexanes) led to the isolation of a colorless oil (22.6 mg, 0.067 mmol, 82% yield).

\[ \text{\(1^H\) NMR (400 MHz, CDCl₃) } \delta 7.23-7.33 \ (m, 5H), 5.74 \ (dt, J = 15.5, 5.5 \text{ Hz}, 1H), 5.50 \ (dd, J = 15.6, 8.0 \text{ Hz}, 1H), 4.80 \ (bs, 1H), 4.63 \ (d, J = 12.4 \text{ Hz}, 1H), 4.47 \ (d, J = 12.0 \text{ Hz}, 1H), 4.18 \ (\text{app t}, J = 6.4 \text{ Hz}, 1H), 3.93 \ (dd, J = 8.4, 6.8 \text{ Hz}, 1H), 3.82-3.85 \ (3H, m), 3.72 \ (dd, J = 8.4, 6.4 \text{ Hz}, 1H), 3.67 \ (s, 3H), 3.18 \ (s, 3H), 1.35 \ (s, 3H); \text{\(1^3C\) NMR (100 MHz, CDCl₃) } \delta 156.8, 138.2, 132.1, 128.3, 128.7 (22 peaks), 127.5, 109.7, 79.8, 77.4, 70.4, 65.6, 52.2, 42.2, 26.4, 25.2; \text{IR (film, cm}^{-1}) \]: 3347 (broad), 3038, 2988, 2929, 2874, 1723, 1532, 1458, 1381, 1371, 1338, 1253, 1214, 1155, 1068, 976, 853, 778; HRMS (ESI) m/z calc’d for C_{16}H_{20}NO_{2} [M+H]⁺: 336.1811, found 336.1803; [\alpha]_D^{24} = +26.2° (c = 1.07, CHCl₃).

\[ \text{(E)-methyl 4-(benzylloxy)-4-(2,2-dimethyl-1,3-dioxolan-4-yl)but-2-en-1-amine} \]

\[ ([\pm]-21]: \text{Compound (+)-20} \quad (22.6 \text{ mg, 0.067 mmol, 1.0 equiv}) \] was transferred to a sealed tube and diluted with 0.25 mL ethanol, 0.75 mL water, and 0.5 mL of 2N NaOH. The tube was heated to 110°C for 2-4 h, then allowed to cool to room temperature. The water/ethanol mixture was transferred to a 25 mL round bottom flask, the ethanol evaporated, and the mixture diluted with EtOAc (5 mL) and brine (2 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (3 x 5 mL). Organic layers were combined, dried over MgSO₄, filtered, and evaporated to dryness. The crude oil was purified by flash chromatography (10% MeOH/CH₂Cl₂/1% conc. NH₄OH) to afford a pale yellow oil (16.8 mg, 0.061 mmol, 95% yield).

\[ \text{\(1^H\) NMR (500 MHz, CDCl₃) } \delta 7.30-7.35 \ (m, 4H), 7.24-7.28 \ (m, 1H), 5.87 \ (dt, J = 15.5, 5.5 \text{ Hz}, 1H), 5.48 \ (dd, J = 15.5, 8.0 \text{ Hz}, 1H), 4.66 \ (d, J = 12.5 \text{ Hz}, 1H), 4.49 \ (d, J = 12.5 \text{ Hz}, 1H), 4.20 \ (q, J = 6.5 \text{ Hz}, 1H), 3.94 \ (dd, J = 8.5, 6.8 \text{ Hz}, 1H), 3.84 \ (\text{app t}, J = 7.5 \text{ Hz}, 1H), 3.73 \ (dd, J = 8.5, 6.5 \text{ Hz}, 1H), 3.35 \ (bs, 2H), 1.42-1.52 \ (m, 2H), 1.39 \ (s, 3H), 1.35 \ (s, 3H); \text{\(1^3C\) NMR (125 MHz, CDCl₃) } \delta 138.4, 137.3, 128.3, 127.7, 127.4, 125.7, 109.7, 80.3, 77.6, 70.2, 65.8, 43.5, 26.5, 25.3; \text{IR (film, cm}^{-1}) \]: 3367 (broad), 3037, 2992, 2982, 2913, 2866, 1584, 1498, 1455, 1380, 1370,
1330, 1262, 1215, 1157, 1068, 979, 850, 742, 698; HRMS (ESI) m/z calc’d for C₁₆H₂₃NO₃ [M+H]^+: 278.1756, found 278.1756; [α]_D^25 = +30.7° (c = 1.68, CHCl₃).

(R,E)-4-((benzylxoy)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-N-methylbut-2-en-1-amine [(+)-22]: To a flame-dried 25 mL round bottom flask containing a stir bar, under nitrogen, was added lithium aluminum hydride (15.0 mg, 0.396 mmol, 5.5 equiv) and THF (2.0 mL). The flask was placed in a water bath at 20 °C, and a solution of carbamate (+)-20 (24.2 mg, 0.0722 mmol, 1.0 equiv) in THF (1.0 mL, with 2 x 1 mL rinses) was added dropwise via cannula. After the bubbling subsided, a reflux condenser was attached and the reaction was heated to reflux for 5 h. After cooling to room temperature, the flask was placed in an ice bath and quenched with water (~0.1 mL), 15% NaOH (0.5 mL), and vigorously stirred for 8 hr. The reaction was then diluted with ether (15 mL) and dried for 1 hr with Na₂SO₄. The resulting solution was filtered through Celite, concentrated under reduced pressure, and purified by flash chromatography (7% MeOH/CH₂Cl₂/1% conc. NH₄OH) to yield a colorless oil (10.5 mg, 0.0360 mmol, 50% yield).

³H NMR (400 MHz, CDCl₃) δ 7.24-7.33 (m, 5H), 5.81 (dt, J = 15.6, 6.0 Hz, 1H), 5.50 (dd, J = 15.6, 8.0 Hz, 1H), 4.66 (d, J = 12.4 Hz, 1H), 4.47 (d, J = 12.4 Hz, 1H), 4.19 (app q, J = 6.7 Hz, 1H), 3.94 (dd, J = 8.4, 6.8 Hz, 1H), 3.83 (app t, J = 7.2 Hz, 1H), 3.73 (dd, J = 8.6, 6.6 Hz, 1H), 3.24 (d, J = 5.6 Hz, 2H), 2.42 (s, 3H), 1.76 (bs, 1H), 1.39 (s, 3H), 1.35 (s, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 183.8, 134.5, 128.3, 127.6, 127.4, 127.4, 127.6, 127.4, 109.7, 80.3, 77.5, 70.1, 65.8, 53.0, 35.9, 26.5, 25.3; IR (film, cm⁻¹): 3394, 2981, 2960, 2931, 2916, 2895, 2877, 2791, 1604, 1454, 1371, 1259, 1211, 1157, 1065, 977, 852, 739; HRMS (ESI) m/z calc’d for C₁₇H₂₅NO₃ [M+H]^+: 292.1913, found 292.1916; [α]_D^25 = +26.4° (c = 2.44, CHCl₃).

**Figure 4.** Late-Stage Oxidation of Natural Product Derivatives via Direct C—H Allylic Amination

**A. Estrone Derivative**

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**B. Cedrene Derivative**

(a) 1 (10 mol%), DIPEA (6 mol%), TsNHCO₂Me (2.0 equiv.), BQ (2.0 equiv.), 0.66 M TBME, 45°C, 72h.
Acetylated N-tosylcarbamate derivative of estrone [(+)-24]: Allyl estrone acetate (+)-23\textsuperscript{19} (46.8 mg, 0.1 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (15% EtOAc/hexanes) yielded the product as a colorless oil. Run 1 (47.7 mg, 0.0686 mmol, 69% yield); run 2 (52.1 mg, 0.0750 mmol, 75% yield). Only the linear E product was observed by "H NMR. Average yield: 72%.

\[ \text{[\text{+}]-24} \]

\[ \text{[\text{+}]-24} \]

Unprotected steroid derivative [(+)-26]: Allyl estrone alcohol (+)-25\textsuperscript{20} (62.5 mg, 0.2 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (50% EtOAc/hexanes) yielded the product as pale yellow solids. Run 1 (60.0 mg, 0.111 mmol, 56% yield); run 2 (56.9 mg, 0.105 mmol, 53% yield). Only the linear E product was observed by "H NMR. The internal olefin product resulting from starting material isomerization was also obtained as a white solid (16.7 mg, 0.0534 mmol, 27% yield). Average yield: 55%. Cr conditions: Only the linear E product was observed by "H NMR. Run 1 (36.7 mg, 0.0681 mmol, 34% yield, L/B & E/Z > 20:1).

\[ \text{[\text{+}]-26} \]

\[ \text{[\text{+}]-26} \]

(-)-(S)-1-((2R,3aS,4R,6aS)-3a-allyl-1,1,4-trimethyloctahydropentalen-2-y1)ethanol([(-)-27]: This starting material was synthesized in 4 steps from (-)-a-cedrene.

\[ \text{[(-)-27]} \]

\[ \text{[(-)-27]} \]

(-)-methyl(E)-3-((2R,3aS,4R,6aS)-2-((S)-1-hydroxyethyl)-1,1,4-trimethyloctahydropentalen-3a-yl)(tosyl)carbamate([(-)-28]: Alcohol (-)-27 (70.9 mg, 0.3 mmol, 1.0 equiv) was reacted following the general procedure. Column chromatography (30% EtOAc/hexanes) isolated the product as a thick, colorless oil. Run 1 (108.7 mg, 0.234 mmol, 78% yield); run 2 (113.2 mg, 0.244 mmol, 81% yield). Only the linear E product was observed by "H NMR. Average yield: 80%.

\[ \text{[(-)-28]} \]

\[ \text{[(-)-28]} \]
0.79 (d, J = 6.5 Hz, 3H); 13C NMR: (125 MHz, CDCl3) δ 152.7, 144.4, 142.7, 136.6, 129.2, 128.3, 119.8, 69.2, 63.1, 53.6, 53.4, 52.9, 49.0, 47.6, 42.4, 38.6, 33.8, 28.7, 25.6, 24.2, 23.9, 21.5, 15.0; IR (film, cm⁻¹): 3424 (broad), 2951, 1735, 1656, 1599, 1496, 1446, 1366, 1169, 1089, 914, 870, 813; HRMS (ESI) m/z calc’d for C_{23}H_{38}NO_5S [M+H]^+ = 464.2471, found 464.2452; [α]_D^25 = -13.3° (c = 1.20, CHCl₃).

**Mechanism Studies**

**A. Proposed Catalytic Cycle for Base-Catalyzed Allylic C—H Amination**

![Catalytic Cycle](image)

**B. Reaction Promotion by exogenous Acetate Source**

Exogenous Acetate Reaction with TBAOAc: Pd[1,2-bis(phenylsulfynyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), tetra(n-butylammonium)acetate (5.4 mg, 0.018 mmol, 0.06 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (68.5 mg, 0.186 mmol, 62% yield [11:1 L/B, 22:1 E/Z]); run 2: (69.2 mg, 0.188 mmol, 63% yield [14:1 L/B, 19:1 E/Z]). **Average yield: 63% [13:1 L/B, 20:1 E/Z].**

Exogenous Acetate Reaction with (DIPEAH)OAc: Pd[1,2-bis(phenylsulfynyl)ethane](OAc)₂ (15.1 mg, 0.03 mmol, 0.10 equiv), benzoquinone (64.9 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the modified procedure for difficult stirring with the following modifications: only 0.350 mL TBME was added to the vial, and 0.1 mL of a stock solution of DIPEA/AcOH [0.18M; DIPEA (31.35 μL, 0.18 mmol) and AcOH (10.3 μL, 0.18 mmol) in 1.00 mL of TBME] was added instead of DIPEA. Run 1: (73.4 mg, 0.200 mmol, 67% yield [11:1 L/B, 16:1 E/Z]); run 2: (68.6 mg, 0.187 mmol, 62% yield [11:1 L/B, 14:1 E/Z]). **Average yield: 65% [11:1 L/B, 15:1 E/Z].**
Table 3. Effect of Quinone Sterics on Lewis Acid vs. Brønsted Base C—H Amination Systems

<table>
<thead>
<tr>
<th>Entry</th>
<th>Quinone</th>
<th>DIPEA Yield(%)</th>
<th>Cr(salen)Cl Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>66</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>6</td>
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<td>7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Average isolated yield of linear product after at least two runs at 0.3 mmol. <sup>b</sup>BQ (1.0 equiv.) was used.

**Entry 1:** See Table 1, entries 2 (Cr conditions) & 8 (DIPEA conditions).

**Entry 2:** Pd[1,2-bis(phenylsulfinyl)ethane](OAc)<sub>2</sub> (15.1 mg, 0.03 mmol, 0.1 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), benzoquinone (32.4 mg, 0.3 mmol, 1.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (69.7 mg, 0.190 mmol, 63% yield); run 2: (75.5 mg, 0.205 mmol, 68% yield), run 3: (75.8 mg, 0.206 mmol, 69% yield). **Average yield: 67%**. Cr conditions: Run 1: (31.8 mg, 0.0865 mmol, 29% yield); run 2: (36.0 mg, 0.0980 mmol, 33% yield), run 3: (28.8 mg, 0.0784 mmol, 26% yield), run 4: (29.0 mg, 0.0789 mmol, 26% yield). **Average yield (Cr conditions): 28%**.

**Entry 3:** Pd[1,2-bis(phenylsulfinyl)ethane](OAc)<sub>2</sub> (15.1 mg, 0.03 mmol, 0.1 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), methylbenzoquinone (73.3 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (78.3 mg, 0.213 mmol, 71% yield); run 2: (77.2 mg, 0.210 mmol, 70% yield). **Average yield: 71%**. Cr conditions: Run 1: (35.0 mg, 0.0952 mmol, 32% yield); run 2: (40.7 mg, 0.111 mmol, 37% yield). **Average yield (Cr conditions): 35%**.

**Entry 4:** Pd[1,2-bis(phenylsulfinyl)ethane](OAc)<sub>2</sub> (15.1 mg, 0.03 mmol, 0.1 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), 2,3-dimethylbenzoquinone (81.7 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (65.0 mg,
0.177 mmol, 59% yield); run 2: (66.0 mg, 0.180 mmol, 60% yield). **Average yield: 60%**. 
Cr conditions: Run 1: (44.2 mg, 0.120 mmol, 40% yield); run 2: (42.0 mg, 0.114 mmol, 38% yield). **Average yield (Cr conditions): 39%**.

**Entry 5:** Pd[1,2-bis(phenylsulfinyl)ethane](OAc)$_2$ (15.1 mg, 0.03 mmol, 0.1 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), 2,6-dimethylbenzoquinone (81.7 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (66.4 mg, 0.181 mmol, 60% yield); run 2: (65.5 mg, 0.178 mmol, 59% yield). **Average yield:** 60%. 
Cr conditions: Run 1: (11.7 mg, 0.0318 mmol, 11% yield); run 2: (11.8 mg, 0.0321 mmol, 11% yield). **Average yield (Cr conditions): 11%**.

**Entry 6:** Pd[1,2-bis(phenylsulfinyl)ethane](OAc)$_2$ (15.1 mg, 0.03 mmol, 0.1 equiv), N,N-diisopropylethylamine (3.14 µL, 0.018 mmol, 0.06 equiv), 2,5-dimethylbenzoquinone (81.7 mg, 0.6 mmol, 2.0 equiv), and methyl tosylcarbamate (137.6 mg, 0.6 mmol, 2.0 equiv) were used following the standard procedure. Run 1: (82.4 mg, 0.224 mmol, 75% yield); run 2: (82.2 mg, 0.224 mmol, 75% yield). **Average yield:** 75%. 
Cr conditions: Run 1: (9.6 mg, 0.0261 mmol, 9% yield); run 2: (5.9 mg, 0.0161 mmol, 5% yield). **Average yield (Cr conditions): 7%**.

**References**

3. see ref 2.