Supporting Information for

Synthesis of Enantioenriched gem-Disubstituted 4-Imidazolidinones by Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation

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Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching or KMnO₄ staining. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ¹H NMR spectra were recorded on Varian Inova 500 MHz, Varian 400 MHz, and Bruker 400 MHz spectrometers and are reported relative to residual CHCl₃ (δ 7.26 ppm). ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz), a Varian 400 MHz spectrometer (100 MHz), and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to CHCl₃ (δ 77.16 ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ¹³C NMR are reported in terms of chemical shifts (δ ppm) Some reported spectra include minor solvent impurities of water (δ 1.56 ppm), ethyl acetate (δ 4.12, 2.05, 1.26 ppm), methylene chloride (δ 5.30 ppm), acetone (δ 2.17 ppm), grease (δ 1.26, 0.86 ppm), and/or silicon grease (δ 0.07 ppm), which do not impact product assignments. Most NMR spectra are complicated by rotational isomerism about amide bonds. IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl or KBr plates and reported in frequency of absorption (cm⁻¹). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. Analytical SFC was performed with a Mettler SFC supercritical CO₂ analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source, or an Agilent 6230 TOF, in electrospray ionization (ESI⁺), atmospheric pressure chemical ionization (APCI⁺), or mixed ionization mode (MM: ESI-APCI⁺), or from the Caltech Mass Spectrometry Laboratory using a JMS-600H High
Resolution Mass Spectrometer in fast atom bombardment (FAB+) mode. Absolute stereochemistry is assigned by analogy to previous results by our group.²

Reagents were purchased from commercial sources and used as received unless otherwise stated. The ligand (S)-(CF₃)₃-t-BuPHOX was prepared according to a literature procedure.³

**List of Abbreviations:**

- ee – enantiomeric excess
- SFC – supercritical fluid chromatography
- TLC – thin-layer chromatography
- IPA – isopropanol

**General Procedure for Pd-Catalyzed Allylic Alkylation Reactions**

In a N₂ filled glovebox, Pd₂(dba)₃ (4 mol %) or Pd₂(pmdba)₃ (4 mol %) and (S)-(CF₃)₃-t-BuPHOX (10 mol %) were suspended in 2:1 hexanes:PhMe (2 mL) in a 20 mL glass vial. After stirring for 20 minutes at 25 °C, the appropriate imidazolidinone (1.0 equiv) and 2:1 hexanes:PhMe (5.1 mL, total substrate concentration 0.014 M) were added to the pre-stirred catalyst solution. The vial was then sealed and heated to the appropriate temperature in a heating block. After full consumption of starting material, as monitored by TLC, the reaction mixture was exposed to air. The crude reaction mixture was loaded directly onto a flash column and the product was isolated by silica gel flash chromatography.

**tert-butyl (R)-5-allyl-3-benzoyl-5-benzyl-4-oxoimidazolidine-1-carboxylate (8a)**
Prepared according to the general procedure with allyl ester 7a (49.0 mg, 0.105 mmol, 1.0 equiv), Pd₂(pmdba)₃ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF₃)₃-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 40 °C for 50 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide benzyl imidazolidinone 8a as a colorless oil (33.7 mg, 0.0801 mmol, 76% yield, 92% ee); 'H NMR (400 MHz, CDCl₃; compound exists as a 2:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.52 (dt, J = 9.6, 6.5, 2.5 Hz, 1H), 7.44 – 7.30 (m, 4H), 7.31 – 7.23 (m, 3H), 7.12 (ddt, J = 8.8, 7.2, 2.0 Hz, 2H), 5.77 – 5.56 (m, 1H), 5.27 – 5.13 (m, 2H), 4.93 (d, J = 7.6 Hz, 1H*), 4.85 (d, J = 7.4 Hz, 1H*), 4.31 (d, J = 7.6 Hz, 1H*), 4.18 (d, J = 7.4 Hz, 1H*), 3.62 (d, J = 7.6 Hz, 1H*), 3.40 (d, J = 13.5 Hz, 1H*), 3.27 (dd, J = 13.6, 7.7 Hz, 1H*), 3.02 (dd, J = 13.8, 7.4 Hz, 1H*), 2.95 (dd, J = 13.5, 4.4 Hz, 1H), 2.69 – 2.52 (m, 1H), 1.65 (s, 9H*), 1.54 (s, 9H*); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 171.4, 168.4, 168.1, 152.6, 151.9, 135.9, 135.3, 133.3, 133.3, 132.6, 132.5, 131.9, 131.5, 130.0, 129.9, 128.9, 128.9, 128.8, 128.6, 127.9, 127.9, 127.8, 127.6, 126.0, 120.5, 82.2, 81.3, 71.5, 71.1, 61.3, 61.3, 41.7, 40.9, 40.6, 39.7, 28.8, 28.5; IR (Neat Film, NaCl) 2927, 1758, 1707, 1390, 1368, 1295, 1167, 702, 660 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₅H₂₉N₂O₄ [M+H]^+: 421.2122, found 421.2108; [α]D²¹.⁷ +19.50 (c 1.0, CHCl₃); SFC (AD-H, IPA/CO₂ = 7/93, flow rate = 2.5 mL/min, λ = 210 nm) tₚ = 5.13 min (major), 6.29 min (minor).
tert-butyl (R)-5-allyl-3-benzoyl-4-oxo-5-(4-(trifluoromethyl)benzyl)imidazolidine-1-carboxylate (8b)

Prepared according to the general procedure with allyl ester 7b (53.8 mg, 0.101 mmol, 1.0 equiv), Pd$_2$(pmdba)$_3$ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF$_3$)$_3$-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 60 °C for 23 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide 4-trifluorobenzyl imidazolidinone 8b as a colorless oil (37.7 mg, 0.0772 mmol, 76% yield, 89% ee); $^1$H NMR (400 MHz, CDCl$_3$; compound exists as a 3:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by $^*$, and the minor rotamer by $^\#$) δ 7.60 – 7.52 (m, 3H), 7.47 – 7.37 (m, 3H), 7.36 – 7.22 (m, 3H), 5.82 – 5.59 (m, 1H), 5.31 – 5.19 (m, 2H), 4.96 (d, $J = 7.7$ Hz, 1H$^\#$), 4.89 (d, $J = 7.5$ Hz, 1H$^*$), 4.42 (d, $J = 7.7$ Hz, 1H$^\#$), 4.34 (d, $J = 7.5$ Hz, 1H$^*$), 3.72 (d, $J = 13.4$ Hz, 1H$^*$), 3.48 (d, $J = 13.5$ Hz, 1H$^\#$), 3.29 (ddt, $J = 13.7$, 7.8, 1.0 Hz, 1H), 3.05 (dd, $J = 13.3$, 1.8 Hz, 1H), 2.72 – 2.55 (m, 1H), 1.67 (s, 9H$^\#$), 1.56 (s, 9H$^*$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.1, 171.1, 168.3, 168.0, 152.5, 152.0, 140.2, 139.6, 133.1, 133.1, 132.8, 132.8, 131.5, 131.1, 130.4, 130.4, 130.0, 129.7, 128.9, 128.0, 128.0, 125.7, 125.7, 125.6, 125.5, 125.5, 125.4, 125.4, 122.9, 121.1, 121.0, 82.5, 81.7, 71.3, 70.9, 61.4, 61.4, 41.4, 41.1, 40.3, 39.9, 28.8, 28.5; IR (Neat Film, NaCl) 2977, 1754, 1707, 1391, 1369, 1326, 1294, 1263, 1226, 1165, 1126, 1068, 1019, 858, 700, 662 cm$^{-1}$; HRMS (MM: ESI-APCI): m/z calc’d for C$_{26}$H$_{31}$F$_3$N$_3$O$_4$ [M+NH$_4$]$^+$: 506.2261, found 506.2254; [α]$_D^{21.5}$ +25.45 (c 1.0, CHCl$_3$); SFC (OJ-H, IPA/CO$_2$ = 10/90, flow rate = 2.5 mL/min, λ = 254 nm) $t_R$ = 1.55 min (major), 1.71 min (minor).
tert-butyl (S)-5-allyl-3-benzoyl-5-methyl-4-oxoimidazolidine-1-carboxylate (8c)

Prepared according to the general procedure with allyl ester 7c (40.7 mg, 0.105 mmol, 1.0 equiv), Pd₂(pmdba)₃ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF₃)₃-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 60 °C for 19 h. Purified by silica gel flash chromatography (15% EtOAc/hexanes) to provide methyl imidazolidinone 8c as a colorless oil (31.3 mg, 0.0909 mmol, 88% yield, 86% ee); ¹H NMR (400 MHz, CDCl₃; compound exists as a 4:3 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.65 – 7.50 (m, 3H), 7.43 (t, J = 7.6 Hz, 2H), 5.70 (ddt, J = 17.3, 9.9, 7.5 Hz, 1H), 5.25 – 5.13 (m, 3H), 5.07 (dd, J = 13.8, 7.7 Hz, 1H), 3.16 (dd, J = 13.7, 7.8 Hz, 1H*), 2.90 (dd, J = 13.8, 7.2 Hz, 1H#), 2.56 – 2.38 (m, 1H), 1.63 – 1.48 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 168.8, 168.6, 152.8, 151.7, 133.3, 132.7, 132.1, 131.9, 129.1, 128.1, 120.5, 81.8, 81.3, 66.2, 65.8, 60.9, 60.8, 41.3, 40.0, 28.6, 28.5, 23.6, 22.7; IR (Neat Film, NaCl) 3076, 2977, 2931, 1759, 1702, 1602, 1477, 1450, 1388, 1368, 1297, 1263, 1227, 1168, 1124, 1059, 998, 965, 928, 906, 879, 859, 823, 792, 774, 733, 704, 662, 614 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₁₉H₂₅N₂O₄ [M+H]: 345.1809, found 345.1805; [α]D₂¹⁺ +4.82 (c 1.0, CHCl₃); SFC (AD-H, IPA/CO₂ = 7/93, flow rate = 2.5 mL/min, λ = 210 nm) tₐ = 3.40 min (major), 3.04 min (minor).
**tert-butyl (R)-5-allyl-3-benzoyl-5-(3-methylbut-2-en-1-yl)-4-oxoimidazolidine-1-carboxylate** (8d)

Prepared according to the general procedure with allyl ester 7d (42.2 mg, 0.0954 mmol, 1.0 equiv), Pd$_2$(pmdba)$_3$ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF$_3$)$_3$-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 60 °C for 24 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide prenyl imidazolidinone 8d as a colorless oil (30.3 mg, 0.0760 mmol, 80% yield, 80% ee); $^1$H NMR (400 MHz, CDCl$_3$; compound exists as a 3:2 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) \( \delta 7.62 - 7.50 \) (m, 3H), \( 7.42 \) (td, \( J = 7.7, 4.8 \) Hz, 2H), \( 5.75 - 5.58 \) (m, 1H), \( 5.24 - 4.96 \) (m, 5H), \( 3.17 \) (dd, \( J = 13.6, 7.8 \) Hz, 1H*), \( 3.06 \) (dd, \( J = 14.3, 7.9 \) Hz, 1H*), \( 2.90 \) (dd, \( J = 13.8, 7.2 \) Hz, 1H#), \( 2.78 \) (dd, \( J = 14.4, 6.9 \) Hz, 1H#), \( 2.58 - 2.36 \) (m, 2H), \( 1.73 \) (d, \( J = 1.5 \) Hz, 3H), \( 1.64 \) (d, \( J = 1.4 \) Hz, 3H), \( 1.56 \) (s, 3H), \( 1.54 \) (s, 3H), \( 1.50 \) (s, 3H).
1.56 (s, 9H*), 1.51 (s, 9H*); $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) δ 172.1, 168.7, 168.5, 152.7, 151.7, 137.3, 137.2, 133.3, 132.7, 132.7, 132.1, 131.7, 129.1, 129.1, 128.0, 128.0, 120.4, 120.3, 117.3, 117.0, 81.8, 81.2, 70.4, 70.0, 61.7, 61.6, 40.6, 39.4, 35.3, 34.3, 28.6, 28.5, 26.4, 26.3, 18.3, 18.2; IR (Neat Film, NaCl) 2976, 1758, 1702, 1449, 1396, 1368, 1305, 1264, 1233, 1168, 1143, 924, 858, 772, 702, 665 cm$^{-1}$; HRMS (MM: ESI-APCI): $m/z$ calc’d for C$_{23}$H$_{30}$N$_2$O$_4$ [M+H]$^+$: 399.2278, found 399.2275; $[\alpha]_D^{21.7}$ – 3.75 (c 1.0, CHCl$_3$); SFC (OJ-H, IPA/CO$_2$ = 1/99, flow rate = 2.5 mL/min, λ = 254 nm) $t_R$ = 2.98 min (major), 3.34 min (minor).

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![chart]

**tert-butyl (R)-5-allyl-3-benzoyl-5-cinnamyl-4-oxoimidazolidine-1-carboxylate (8e)**

Prepared according to the general procedure with allyl ester 7e (47.6 mg, 0.0970 mmol, 1.0 equiv), Pd$_2$(pmdba)$_3$ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF$_3$)$_3$-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 40 °C for 48 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide cinnamyl imidazolidinone 8e as a colorless oil (41.9 mg, 0.0938
mmol, 97% yield, 85% ee); \(^1\)H NMR (400 MHz, CDCl\(_3\); compound exists as a 1.8:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) \(\delta\) 7.61 – 7.48 (m, 3H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 4H), 7.25 (ddt, \(J = 6.6, 3.5, 1.5\) Hz, 1H), 6.60 – 6.48 (m, 1H), 6.14 – 6.00 (m, 1H), 5.79 – 5.64 (m, 1H), 5.27 – 5.17 (m, 2H), 5.17 – 4.99 (m, 2H), 3.30 (ddd, \(J = 13.7, 7.6, 1.3\) Hz, 1H*), 3.18 (dd, \(J = 13.6, 7.8\) Hz, 1H*), 3.05 (ddd, \(J = 13.8, 6.8, 1.4\) Hz, 1H\#), 2.93 (dd, \(J = 13.8, 7.4\) Hz, 1H\#), 2.71 – 2.45 (m, 2H), 1.62 (s, 9H\#), 1.53 (s, 9H*); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.8, 168.6, 168.4, 152.7, 151.8, 137.0, 136.7, 135.6, 135.5, 133.2, 132.8, 132.7, 131.8, 131.4, 129.1, 129.1, 128.9, 128.8, 128.0, 128.0, 127.9, 126.4, 126.3, 122.8, 122.3, 120.8, 120.7, 82.0, 81.4, 70.4, 70.0, 61.6, 61.6, 40.7, 40.1, 39.5, 38.9, 28.7, 28.5; IR (Neat Film, NaCl) 2974, 1755, 1703, 1398, 1296, 1172, 703 cm\(^{-1}\); HRMS (MM: ESI-APCI): \(m/z\) calc’d for C\(_{27}\)H\(_{34}\)N\(_3\)O\(_4\) [M+NH\(_4\)]\(^+\): 464.2544, found 464.2521; \([\alpha]_D^{21.6}\) +30.48 (c 1.0, CHCl\(_3\)); SFC (AD-H, IPA/CO\(_2\) = 10/90, flow rate = 2.5 mL/min, \(\lambda = 210\) nm) \(t_R = 5.15\) min (major), 4.77 min (minor).
**tert-butyl (R)-5-allyl-3-benzoyl-4-oxo-5-(prop-2-yn-1-yl)imidazolidine-1-carboxylate (8f)**

Prepared according to the general procedure with allyl ester 7f (43.8 mg, 0.106 mmol, 1.0 equiv), Pd$_2$(pmdba)$_3$ (4.7 mg, 0.00425 mmol, 4 mol %), and (S)-(CF$_3$)$_3$-t-BuPHOX (6.3 mg, 0.0106 mmol, 10 mol %) at 60 °C for 45 h. Purified by silica gel flash chromatography (20% EtOAc/hexanes) to provide propargyl imidazolidinone 8f as a colorless oil (18.1 mg, 0.0491 mmol, 46% yield, 91% ee); $^1$H NMR (400 MHz, CDCl$_3$; compound exists as a 1.8:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.75 – 7.61 (m, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 5.81 – 5.59 (m, 1H), 5.32 – 5.03 (m, 4H), 3.39 – 2.75 (m, 2H), 2.66 (dd, $J = 16.7$, 2.6 Hz, 1H*), 2.59 (dd, $J = 16.7$, 2.6 Hz, 1H*), 2.52 – 2.36 (m, 1H), 2.09 (t, $J = 2.6$ Hz, 1H*), 2.06 (t, $J = 2.6$ Hz, 1H*), 1.57 (s, 9H*), 1.53 (s, 9H*); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.0, 170.9, 168.6, 168.4, 152.4, 151.8, 133.1, 132.8, 132.8, 131.4, 131.1, 129.3, 129.2, 128.1, 128.1, 121.0, 120.9, 116.2, 82.2, 81.7, 79.1, 78.3, 72.0, 71.3, 69.6, 69.1, 62.2, 62.1, 40.1, 39.9, 38.7, 38.6, 28.6, 28.5, 28.5, 27.2, 25.9; IR (Neat Film, NaCl) 3276, 2980, 2930, 1760, 1704, 1642, 1602, 1478, 1449, 1392, 1369, 1266, 1228, 1172, 1091, 1015, 928, 878, 857, 768, 739, 704, 664 cm$^{-1}$; HRMS (MM: ESI-APCI): $m/z$ calc’d for C$_{21}$H$_{28}$N$_3$O$_4$ [M$+$NH$_4$]$^+$: 386.2074, found 386.2066; [α]$_D$$^{21.4}$ = –14.43 (c 1.0, CHCl$_3$); SFC (OJ-H, IPA/CO$_2$ = 7/93, flow rate = 2.5 mL/min, λ = 210 nm) $t_R$ = 2.43 min (major), 2.11 min (minor).
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tert-butyl (R)-3-benzoyl-5-benzyl-5-(2-methylallyl)-4-oxoimidazolidine-1-carboxylate (8g)

Prepared according to the general procedure with allyl ester 7g (48.1 mg, 0.101 mmol, 1.0 equiv), Pd₂(pmdba)₃ (4.4 mg, 0.004 mmol, 4 mol %), and (S)-(CF₃)₃-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 60 °C for 26 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide benzyl imidazolidinone 8g as a colorless oil (36.4 mg, 0.0838 mmol, 83% yield, 89% ee); ¹H NMR (400 MHz, CDCl₃; compound exists as a 2.5:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.57 – 7.48 (m, 1H), 7.40 (d, J = 4.4 Hz, 3H), 7.35 – 7.22 (m, 4H), 7.16 – 7.08 (m, 2H), 4.98 – 4.75 (m, 3H), 4.36 (d, J = 7.7 Hz, 1H#), 4.21 (d, J = 7.5 Hz, 1H*), 3.66 (d, J = 13.3 Hz, 1H*), 3.45 (d, J = 13.4 Hz, 1H#), 3.22 (d, J = 13.5 Hz, 1H*), 3.01 – 2.88 (m, 1H), 2.62 (d, J = 13.7 Hz, 1H#), 2.56 (d, J = 13.5 Hz, 1H*), 1.72 (s, 3H), 1.66 (s, 9H#), 1.54 (s, 9H*); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 171.3, 168.5, 168.2, 152.6, 152.0, 140.7, 140.3, 135.8, 135.2, 133.5, 133.4, 132.5, 132.5, 130.0, 128.9, 128.8, 128.6, 127.9, 127.9, 127.8, 127.6, 116.6, 116.4, 82.3, 81.3, 71.6, 71.1, 61.2, 61.1, 43.6, 42.5, 42.2, 41.1, 28.8, 28.6, 23.9, 23.8; IR (Neat Film, NaCl) 2974, 1755, 1708, 1450, 1397, 1368, 1295, 1216, 1171, 1141, 1076, 901, 703 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₆H₃₀N₂NaO₄ [M+Na]⁺: 457.2098, found 457.2083; [α]D²¹.⁸ +26.68 (c 1.5, CHCl₃); SFC (OD-H, IPA/CO₂ = 10/90, flow rate = 2.5 mL/min, λ = 254 nm) tₘ = 3.79 min (major), 3.47 min (minor).
tert-buty 1(R)-5-allyl-3-benzoyl-5-(2-chloroallyl)-4-oximidazolidine-1-carboxylate (8h)

Prepared according to the general procedure with allyl ester 7h (44.6 mg, 0.0994 mmol, 1.0 equiv), Pd\(_2\)(pmdba)\(_3\) (4.4 mg, 0.004 mmol, 4 mol%), and (S)-(CF\(_3\))\(_3\)-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol%) at 40 °C for 5.5 h. Purified by silica gel flash chromatography (10% EtOAc/hexanes) to provide alkenyl chloride 8h as a colorless oil (37.4 mg, 0.0924 mmol, 93% yield, 86% ee); \(^1\)H NMR (400 MHz, CDCl\(_3\); compound exists as a 2.7:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) \(\delta\) 7.64 (ddt, \(J = 8.5, 2.9, 1.7\) Hz, 2H), 7.55 (ddt, \(J = 7.6, 6.9, 1.3\) Hz, 1H), 7.46 – 7.38 (m, 2H), 5.75 – 5.60 (m, 1H), 5.38 – 5.28 (m, 2H), 5.27 – 5.08 (m, 4H), 3.40 (d, \(J = 14.3\) Hz, 1H), 3.20 – 3.06 (m, 1H), 2.94 – 2.76 (m, 1H), 2.54 – 2.38 (m, 1H), 1.57 (s, 9H*)), 1.50 (s, 9H*); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.9, 170.9, 168.4, 168.1, 152.2, 151.6, 136.7, 136.7, 133.2, 133.2, 132.6, 132.6, 131.1, 130.7, 129.0, 129.0, 127.9, 121.1, 121.0, 117.9, 117.8, 82.0, 81.3, 68.8, 68.6, 61.6, 61.5, 44.8, 44.1, 41.0, 39.6, 28.5, 28.3; IR (Neat Film, NaCl) 2976, 1758, 1707, 1394, 1368, 1295,
1266, 1140, 704 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₁H₂₉ClN₃O₄ [M+NH₄]⁺: 422.1841, found 422.1825. [α]D²¹.⁷ –3.52 (c 1.0, CHCl₃); SFC (OJ-H, IPA/CO₂ = 7/93, flow rate = 2.5 mL/min, λ = 210 nm) tᵣ = 2.19 min (major), 1.99 min (minor).

Prepared according to the general procedure with allyl ester 7i (53.7 mg, 0.0100 mmol, 1.0 equiv), Pd₂(dba)₃ (3.7 mg, 0.004 mmol, 4 mol %), and (S)-(CF₃)₃-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 40 °C for 22 h. Purified by silica gel flash chromatography (25% EtOAc/hexanes) to provide carbamate 8i as a colorless foam (37.2 mg, 0.0754 mmol, 75% yield, 85% ee); ¹H NMR (400 MHz, CDCl₃; compound exists as a 2:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.73 – 7.59 (m, 2H), 7.55 (td, J = 7.3, 1.4 Hz, 1H), 7.42 (q, J = 7.4 Hz, 2H), 7.36 – 7.27 (m, 5H), 5.75 – 5.55 (m, 1H), 5.26 – 4.97 (m, 6H), 3.80 – 3.62 (m, 2H), 3.02 (dd, J = 13.5, 8.0 Hz, 1H*), 2.85 (dd, J =
13.7, 7.3 Hz, 1H\textsuperscript{\textcircled{a}}), 2.51 (dd, J = 13.8, 7.5 Hz, 1H\textsuperscript{\textcircled{b}}), 2.41 (dd, J = 13.5, 7.0 Hz, 1H\textsuperscript{\textcircled{b}}), 1.58 (s, 9H\textsuperscript{\textcircled{a}}), 1.50 (s, 9H\textsuperscript{\textcircled{b}}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 171.2, 170.8, 168.5, 168.2, 156.4, 156.3, 152.4, 152.2, 136.5, 136.2, 133.1, 133.0, 132.8, 132.7, 131.0, 130.7, 129.3, 129.2, 128.7, 128.4, 128.3, 128.0, 121.2, 82.6, 81.8, 69.5, 67.3, 67.2, 61.6, 61.5, 45.7, 45.5, 37.9, 37.1, 28.6, 28.4; IR (Neat Film, NaCl) 3347, 2977, 1704, 1519, 1449, 1392, 1369, 1304, 1166, 1073, 927, 858, 733, 698, 662 cm\textsuperscript{-1}; HRMS (MM: ESI-APCI): m/z calc’d for C\textsubscript{27}H\textsubscript{31}N\textsubscript{3}NaO\textsubscript{6} [M+Na]\textsuperscript{+}: 516.2105, found 516.2087; [\textgreek{a}]\textsubscript{D}\textsuperscript{21.8} = -18.93 (c 1.0, CHCl\textsubscript{3}); SFC (AD-H, IPA/CO\textsubscript{2} = 20/80, flow rate = 2.5 mL/min, λ = 210 nm) t\textsubscript{R} = 6.15 min (major), 3.52 min (minor).

\textit{tert-butyl (S)-5-allyl-3-benzoyl-5-(2-cyanoethyl)-4-oxoimidazolidine-1-carboxylate (8j)}

Prepared according to the general procedure with allyl ester 7j (41.4 mg, 0.0970 mmol, 1.0 equiv), Pd\textsubscript{2}(dba)\textsubscript{3} (3.7 mg, 0.004 mmol, 4 mol %), and (S)-(CF\textsubscript{3})\textsubscript{3}-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 40 °C for 22 h. Purified by silica gel flash chromatography (20%
EtOAc/hexanes) to provide nitrile 8j as a colorless oil (37.2 mg, 0.0970 mmol, >99% yield, 95% ee); \(^1\)H NMR (400 MHz, CDCl\(_3\)); compound exists as a 2.5:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by 

δ 7.69 – 7.61 (m, 2H), 7.61 – 7.54 (m, 1H), 7.49 – 7.38 (m, 2H), 5.74 – 5.60 (m, 1H), 5.30 – 5.18 (m, 3H), 5.17 – 5.06 (m, 1H), 3.11 (dd, \(J = 13.6, 8.1\) Hz, 1H*), 2.86 (dd, \(J = 13.7, 7.4\) Hz, 1H\(^\dagger\)), 2.63 (dt, \(J = 13.8, 6.8\) Hz, 1H\(^\dagger\)), 2.53 – 2.14 (m, 4H), 1.57 (s, 9H\(^\dagger\)), 1.53 (s, 9H*); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 170.7, 170.6, 168.2, 168.0, 152.2, 151.9, 133.0, 132.9, 132.8, 132.7, 130.5, 130.1, 129.0, 129.0, 128.0, 121.7, 121.6, 118.4, 118.2, 82.7, 82.1, 68.6, 68.3, 61.5, 61.5, 41.1, 39.7, 31.6, 30.4, 28.5, 28.3, 12.9, 12.7; IR (Neat Film, NaCl) 2976, 1756, 1705, 1390, 1295, 1164, 704 cm\(^{-1}\); HRMS (MM: ESI-APCI): \(m/z\) calc’d for C\(_{21}\)H\(_{29}\)N\(_4\)O\(_4\) [M+NH\(_4\)]\(^+\): 401.2183, found 401.2182; \([\alpha]\)\(_D\)\(^{21.7}\) –33.24 (c 1.0, CHCl\(_3\)); SFC (IC, IPA/CO\(_2\) = 15/85, flow rate = 2.5 mL/min, \(\lambda = 210\) nm) \(t_R = 5.49\) min (major), 4.78 min (minor).
Prepared according to the general procedure with allyl ester 7k (44.4 mg, 0.010 mmol, 1.0 equiv), Pd\(_2\)(dba)\(_3\) (3.7 mg, 0.004 mmol, 4 mol %), and (S)-(CF\(_3\))\(_3\)-t-BuPHOX (5.9 mg, 0.01 mmol, 10 mol %) at 60 °C for 19 h. Purified by silica gel flash chromatography (25% EtOAc/hexanes) to provide ketone 8k as a colorless oil (31.4 mg, 0.0784 mmol, 79% yield, 93% ee); \(^1\)H NMR (400 MHz, CDCl\(_3\); compound exists as a 1.3:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by \(*\), and the minor rotamer by \#) δ 7.67 – 7.60 (m, 2H), 7.59 – 7.52 (m, 1H), 7.44 (t, \(J = 7.7\) Hz, 2H), 5.76 – 5.60 (m, 1H), 5.25 – 5.17 (m, 2H), 5.13 – 5.02 (m, 2H), 3.15 (dd, \(J = 13.6, 8.0\) Hz, 1H\(*\)), 2.89 (dd, \(J = 13.8, 7.2\) Hz, 1H\#), 2.59 – 2.27 (m, 4H), 2.21 – 2.00 (m, 4H), 1.54 (s, 9H\#), 1.51 (s, 9H\*); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 207.3, 206.6, 171.7, 171.6, 168.6, 168.3, 152.6, 151.7, 133.2, 133.1, 132.8, 132.7, 131.5, 131.2, 129.1, 129.1, 128.1, 121.0, 121.0, 82.3, 81.6, 69.0, 68.7, 61.5, 61.4, 41.2, 39.6, 39.0, 38.2, 30.5, 30.1, 29.6, 28.5, 28.5; IR (Neat Film, NaCl) 2974, 1755, 1708, 1450, 1397, 1368, 1295, 1216, 1171, 1141, 1076, 901, 703 cm\(^{-1}\); HRMS (MM: ESI-APCI): \(m/\)z calc’d for C\(_{22}\)H\(_{32}\)N\(_3\)O\(_5\) [M+NH\(_4\)]\(^+\): 418.2336, found 418.2347; [\(\alpha\)]\(_{D}\)\(^{21.7}\) +3.65 (c 1.0, CHCl\(_3\)); SFC (IC, IPA/CO\(_2\) = 20/80, flow rate = 2.5 mL/min, \(\lambda = 210\) nm) \(t_R = 2.42\) min (major), 3.23 min (minor).
Procedure for the large-scale preparation of compound 8a

In a N₂ filled glovebox, Pd₂(pmdba)₃ (82 mg, 0.0744 mmol, 4 mol %) and (S)-(CF₃)₃-t-BuPHOX (110 mg, 0.186 mmol, 10 mol %) were suspended in 2:1 hexanes:PhMe (45 mL) in a 500 mL Schlenk flask. After stirring for 20 minutes at 25 °C, imidazolidinone 7a (864 mg, 1.86 mmol, 1.0 equiv) and 2:1 hexanes:PhMe (90 mL, total substrate concentration 0.014 M) were added to the pre-stirred catalyst solution. The flask was then sealed and heated at 40 °C in an oil bath for 64 h. The reaction mixture was then cooled to 23 °C and exposed to air. The crude reaction mixture was loaded directly onto a flash column and the product was isolated by silica gel flash chromatography (10% EtOAc/hexanes) to provide 8a as a colorless oil (674 mg, 1.60 mmol, 86% yield, 95% ee); All characterization data matched those reported above for compound 8a; [α]D₂²⁺1 +21.69 (c 1.0, CHCl₃); SFC (AD-H, IPA/CO₂ = 7/93, flow rate = 2.5 mL/min, λ = 210 nm) tR = 5.07 min (major), 6.31 min (minor).
Synthesis of Allylic Alkylation Substrates

*tert*-butyl 4-oxo-2-thioxoimidazolidine-1-carboxylate (2)

Prepared from 2-thiohydantoin according to the literature procedure of Tatibouët under an atmosphere of air. All characterization data matched those reported in the literature.

*tert*-butyl 4-oxoimidazolidine-1-carboxylate (3)

Compound 2 (10.43 g, 48.23 mmol, 1.0 equiv) and anhydrous NiCl₂ (31.25 g, 241.1 mmol, 5.0 equiv) were added to a round-bottom flask, MeOH (dried by distillation over 3 Å molecular sieves, 480 mL, 0.1 M) was added, and the mixture was subjected to rapid magnetic stirring to form a suspension. This suspension was cooled to 0 °C in an ice bath, and NaBH₄ (27.37 g, 723.4 mmol, 15 equiv) was added portionwise. Care should be taken, as this step is highly exothermic and results in the rapid generation of a large volume of hydrogen gas. Following complete addition of NaBH₄, the reaction mixture was removed from the ice bath and allowed to warm to 23 °C. After 1 h of stirring, glacial acetic acid (10 mL) was added, and the reaction mixture was filtered through a plug of celite under pressurized air. A steel rod was periodically used to break up the plug of nickel salts and accelerate filtration. The resulting bright green solution was concentrated under reduced pressure. The resulting solids were dissolved in a mixture of deionized water (500 mL), EtOAc (300 mL), and glacial acetic acid (20 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (4x200 mL). The combined organic phases were washed with a solution of NaHCO₃ and NaCl (100 mL, equal parts saturated NaHCO₃ and NaCl solutions), dried over Na₂SO₄, and concentrated under reduced pressure to afford the title compound as an off-white solid (8.58 g, 46.08 mmol, 96% yield) of sufficient purity for use in the next step; an analytically pure sample could be obtained by silica gel flash chromatography (90% EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.01 (m, 1H), 4.78 (d, J = 11.6 Hz, 2H), 3.89 (d, J = 15.2 Hz, 2H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 155.6 (s), 55.4 (t, J = 11.6 Hz, 2C), 46.4 (s, 2C), 30.3 (s, 9H).
MHZ, CDCl3) δ 172.3, 153.1, 152.7, 81.2, 59.1, 58.9, 47.6, 47.1, 28.4; IR (Neat Film, KBr) 3213, 3120, 2978, 2934, 1714, 1456, 1414, 1366, 1326, 1294, 1257, 1171, 1128, 1080, 898, 855, 771, 700, 575, 491, 461 cm⁻¹; HRMS (FAB+): m/z calc’d for C₈H₁₅N₂O₃ [M+H]+: 187.1083, found 187.1086.

**tert-butyl 3-benzyol-4-oxoimidazolidine-1-carboxylate (4)**

To a solution of 3 (8.58 g, 46.08 mmol, 1.0 equiv) in CH₂Cl₂ (400 mL, 0.12 M) at 23 °C was added Et₃N (11.6 mL, 82.94 mmol, 1.8 equiv) followed by BzCl (8.03 mL, 69.12 mmol, 1.5 equiv). After 9 h of stirring, the reaction mixture was washed with water (200 mL) and brine (100 mL) and the combined aqueous washes were extracted with CH₂Cl₂ (2x50 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (25% EtOAc/hexanes) to afford the title compound as a white solid (7.47 g, 25.73 mmol, 56% yield); ¹H NMR (400 MHz, CDCl3) δ 7.68 – 7.60 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.39 (m, 2H), 5.29 (s, 2H), 4.17 (s, 2H), 1.51 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 167.5, 152.6, 133.1, 132.8, 129.2, 128.1, 81.9, 61.8, 49.9, 49.4, 28.4; IR (Neat Film, NaCl) 2980, 1763, 1708, 1477, 1448, 1411, 1368, 1305, 1212, 1163, 1127, 895, 858, 768, 727, 704, 662 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₁₅H₂₂N₄O₄ [M+NH₄]+: 308.1600, found 308.1605.

**5-allyl 1-(tert-butyl) 3-benzyol-4-oxoimidazolidine-1,5-dicarboxylate (6)**

To a solution of LiHMDS (9.43 g, 56.38 mmol, 2.2 equiv) in THF (150 mL) at −78 °C in a flame-dried round-bottom flask was added allyl ¹H-imidazole-1-carboxylate⁵ (4.68 g, 30.76 mmol, 1.2 equiv) by syringe with rapid stirring. Immediately thereafter, a solution of imidazolidinone 4 (7.44 g, 25.63 mmol, 1.0 equiv) in THF (100 mL, 0.1 M total concentration) was added over 15 min by cannula while stirring at −78 °C. After an additional 13 min of stirring, the reaction mixture was poured into 1 N aqueous HCl (200 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were dried over a mixture of NaHCO₃
and Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (20→35% Et₂O/hexanes) to provide allyl ester 6 as a viscous oil that solidified upon standing to form a white solid (4.80 g, 12.82 mmol, 50% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1.1:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.61 (dd, J = 8.3, 1.3 Hz, 2H), 7.56 (t, J = 7.8 Hz, 2H), 5.98 – 5.80 (m, 1H), 5.43 – 5.18 (m, 4H), 4.96 (s, 1H #), 4.88 (s, 1H *), 4.81 – 4.62 (m, 2H), 1.52 (s, 9H #), 1.46 (s, 9H *); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 168.2, 165.7, 165.6, 163.5, 163.2, 152.1, 151.9, 133.0, 132.6, 131.0, 130.9, 129.2, 128.1, 119.8, 119.2, 82.8, 82.6, 67.2, 63.5, 63.0, 61.5, 28.3, 28.2; IR (Neat Film, NaCl) 2977, 1748, 1716, 1449, 1405, 1369, 1302, 1250, 1167, 1135, 987, 939, 770, 725, 696, 668 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₁₉H₂₆N₃O₆ [M+NH₄]⁺: 392.1816, found 392.1822.

1-(tert-butyl) 5-(2-methylallyl) 3-benzoyl-4-oxoimidazolidine-1,5-dicarboxylate (S1)

To a solution of methallyl 1H-imidazole-1-carboxylate⁶ (286 mg, 1.72 mmol, 2 equiv) in THF (5.2 mL) at −78 °C in a flame-dried round-bottom flask was added LiHMDS solution (1 M in THF, 1.89 mL, 1.89 mmol, 2.2 equiv) by syringe. Immediately thereafter, a solution of imidazolidinone 4 (250 mg, 0.861 mmol, 1.0 equiv) in THF (3.4 mL, 0.1 M total concentration) was added dropwise by syringe with rapid stirring at −78 °C. After an additional 10 min of stirring, the reaction mixture was poured into 1 N aqueous HCl (20 mL) and extracted with ethyl acetate (4 x 15 mL). The combined organic extracts were dried over a mixture of NaHCO₃ and Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (40% Et₂O/hexanes) to provide methallyl ester S1 as a viscous oil that solidified upon standing to form a white solid (149 mg, 0.384 mmol, 45% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1:1 mixture of rotamers. Fully resolved rotamer peaks are denoted by *) δ 7.65 – 7.59 (m, 2H), 7.59 – 7.53 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 5.48 – 5.27 (m, 2H), 5.06 – 4.84 (m, 3H), 4.75 – 4.51 (m, 2H), 1.75 (s, 3H), 1.52 (s, 9H *), 1.46 (s, 9H *); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 168.3, 165.7, 165.6, 163.5, 163.3, 152.1, 151.9, 138.9, 138.8, 133.0, 132.7, 132.7, 129.2, 128.2, 114.5, 114.1, 82.8, 82.7, 69.8, 63.5, 63.1, 61.5, 28.4, 28.3, 19.6, 19.5, 19.5, 19.5; IR (Neat Film, KBr) 3064, 2978, 2934, 1772, 1750, 1716, 1602, 1583,

![Chemical Structure](image-url)

5-allyl 1-(tert-butyl) 3-benzoyl-5-benzyl-4-oxoimidazolidine-1,5-dicarboxylate (7a)

To a solution of lactam 6 (500 mg, 1.34 mmol, 1.0 equiv) in DMF (13.4 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 64 mg, 1.60 mmol, 1.2 equiv). The reaction mixture was stirred for 25 min, resulting in a bright yellow solution. BnBr (477 μL, 4.02 mmol, 3.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 55 min. The reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (4x15 mL). The combined organic extracts were washed with saturated aq. LiCl (2x10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (7.5→15% acetone/hexanes) to provide the title compound as a colorless oil (291 mg, 0.626 mmol, 47% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1.2:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.59 – 7.49 (m, 1H), 7.47 – 7.26 (m, 7H), 7.21 – 7.14 (m, 2H), 6.02 – 5.80 (m, 1H), 5.42 – 5.26 (m, 2H), 5.24 (d, J = 7.1 Hz, 1H*), 5.16 (d, J = 7.0 Hz, 1H#), 4.83 – 4.61 (m, 2H), 4.46 (d, J = 7.2 Hz, 1H#), 4.40 (d, J = 7.0 Hz, 1H*), 3.86 – 3.50 (m, 2H), 1.56 (s, 9H#), 1.56 (s, 9H*); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 168.0, 166.7, 166.6, 166.2, 166.1, 152.0, 151.8, 134.7, 134.1, 132.8, 132.8, 132.6, 132.6, 131.2, 130.9, 130.3, 130.2, 128.9, 128.9, 128.8, 128.9, 128.6, 128.0, 127.9, 127.9, 127.7, 119.7, 119.1, 82.9, 82.4, 72.9, 72.8, 67.2, 67.2, 61.2, 61.2, 38.0, 37.1, 28.4, 28.3; IR (Neat Film, NaCl) 2977, 1771, 1712, 1602, 1450, 1393, 1294, 1230, 1147, 1075, 1010, 768, 701 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₆H₃₂N₃O₆ [M+NH₄]⁺: 482.2286, found 482.2284.
5-allyl 1-(tert-butyl) 3-benzoyl-4-oxo-5-(4-(trifluoromethyl)benzyl)imidazolidine-1,5-dicarboxylate (7b)

To a solution of lactam 6 (128.4 mg, 0.343 mmol, 1.0 equiv) in DMF (3.4 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 16.5 mg, 0.412 mmol, 1.2 equiv). The reaction mixture was stirred for 15 min, resulting in a bright yellow solution. 4-trifluoromethylbenzyl bromide (159 μL, 1.03 mmol, 3.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 35 min. The reaction mixture was poured into water (5 mL) and extracted with ethyl acetate (4x5 mL). The combined organic extracts were washed with saturated aq. LiCl (2x3 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (15% EtOAc/hexanes) to provide the title compound as a colorless oil (122 mg, 0.229 mmol, 67% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.51 (m, 3H), 7.44 – 7.27 (m, 6H), 5.99 – 5.84 (m, 1H), 5.43 – 5.15 (m, 3H), 4.84 – 4.63 (m, 2H), 4.55 (dd, J = 7.2, 2.8 Hz, 1H), 3.92 – 3.59 (m, 2H), 1.56 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 168.3, 168.0, 166.6, 166.5, 165.9, 165.7, 152.4, 152.0, 139.2, 138.6, 133.1, 132.6, 131.2, 130.8, 130.3, 129.9, 129.0, 128.2, 128.1, 125.8, 125.7, 125.6, 125.5, 120.1, 119.5, 83.4, 82.9, 72.8, 72.7, 67.5, 67.5, 61.5, 61.4, 37.8, 37.0, 28.5, 28.4; IR (Neat Film, NaCl) 2977, 1772, 1710, 1389, 1325, 1291, 1228, 1164, 1068, 1019, 857, 697, 665 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₇H₃₁F₃N₃O₆ [M+NH₄⁺]: 550.2159, found 550.2139.

5-allyl 1-(tert-butyl) 3-benzoyl-5-methyl-4-oxoimidazolidine-1,5-dicarboxylate (7c)

To a suspension of NaH (60% dispersion in mineral oil, 32 mg, 0.801 mmol, 1.2 equiv) in THF (6.7 mL, 0.1 M) at −78 °C was added lactam 6 (250 mg, 0.668 mmol, 1.0 equiv). The reaction mixture was warmed to 0 °C and stirred for 45 min, resulting in a bright yellow solution. MeI (208 μL, 3.34 mmol, 5.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 2 h. The reaction mixture was poured into saturated aq. NaHCO₃ (10 mL) and extracted with ethyl acetate (3x6 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by automated silica gel flash chromatography (Telodyne ISCO, 0→50% acetone/hexanes) to provide the title compound as a colorless oil (90 mg, 0.232 mmol, 35% yield); ¹H NMR (400 MHz, CDCl₃; compound exists
as a 1.2:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #\) δ 7.63 – 7.52 (m, 3H), 7.42 (t, J = 7.6 Hz, 2H), 5.96 – 5.80 (m, 1H), 5.41 – 5.19 (m, 4H), 4.75 – 4.57 (m, 2H), 1.83 (s, 3H#), 1.78 (s, 3H*), 1.50 (s, 9H#), 1.46 (s, 9H*); 13C NMR (100 MHz, CDCl3) δ 168.6, 168.4, 167.5, 167.2, 152.3, 152.2, 138.5, 138.4, 133.0, 132.8, 131.4, 131.0, 129.1, 128.1, 119.6, 119.1, 82.6, 82.4, 68.4, 68.2, 67.1, 61.1, 61.0, 28.4, 28.2, 20.5, 19.9; IR (Neat Film, NaCl) 2979, 1773, 1740, 1714, 1602, 1477, 1450, 1386, 1370, 1305, 1244, 1162, 1124, 1067, 913, 859, 770, 732, 702, 667 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C20H28N3O6 [M+H4]⁺: 406.1973, found 406.1975.

5-allyl 1-(tert-butyl) 3-benzoyl-5-(3-methylbut-2-en-1-yl)-4-oxoimidazolidine-1,5-dicarboxylate (7d)

To a solution of lactam 6 (300 mg, 0.801 mmol, 1.0 equiv) in DMF (8 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 38.5 mg, 0.962 mmol, 1.2 equiv). The reaction mixture was stirred for 13 min, resulting in a bright yellow solution. Prenyl bromide (280 μL, 2.40 mmol, 3.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 1 h. The reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (4x15 mL). The combined organic extracts were washed with saturated aq. LiCl (2x10 mL), dried over anhydrous Na2SO4, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (15% EtOAc/hexanes) to provide the title compound as a colorless oil (230 mg, 0.520 mmol, 65% yield); 1H NMR (400 MHz, CDCl3; compound exists as a 1.1:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #\) δ 7.61 – 7.51 (m, 3H), 7.45 – 7.37 (m, 2H), 5.98 – 5.76 (m, 1H), 5.43 – 5.19 (m, 3H), 5.16 – 4.99 (m, 2H), 4.77 – 4.52 (m, 2H), 3.26 – 2.93 (m, 2H), 1.77 (s, 3H), 1.67 (d, J = 1.4 Hz, 3H*), 1.66 (d, J = 1.5 Hz, 3H#), 1.51 (s, 9H#), 1.47 (s, 9H*); 13C NMR (100 MHz, CDCl3) δ 168.6, 168.4, 166.9, 166.9, 166.8, 166.7, 152.1, 152.1, 138.5, 138.4, 133.0, 132.8, 131.4, 131.0, 129.1, 129.1, 128.1, 128.1, 119.6, 119.1, 116.1, 115.8, 82.6, 82.3, 72.1, 72.0, 67.1, 67.0, 61.7, 31.7, 30.8, 28.4, 28.3, 26.4, 26.3, 18.3, 18.2; IR (Neat Film, NaCl) 2978, 2931, 1771, 1746,

5-allyl 1-(tert-butyl) 3-benzoyl-5-cinnamyl-4-oxoimidazolidine-1,5-dicarboxylate (7e)

To a solution of lactam 6 (157.2 mg, 0.420 mmol, 1.0 equiv) in DMF (4.2 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 20.2 mg, 0.504 mmol, 1.2 equiv). The reaction mixture was stirred for 14 min, resulting in a bright yellow solution. Cinnamyl bromide (186 μL, 1.26 mmol, 3.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 20 min. The reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (4x6 mL). The combined organic extracts were washed with saturated aq. LiCl (2x5 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (15% EtOAc/hexanes) to provide the title compound as a colorless oil (154 mg, 0.314 mmol, 75% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1:1:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.55 – 7.49 (m, 3H), 7.41 – 7.30 (m, 6H), 7.28 – 7.24 (m, 1H), 6.61 (dd, J = 15.9, 2.9 Hz, 1H), 6.16 – 6.02 (m, 1H), 5.98 – 5.82 (m, 1H), 5.42 – 5.12 (m, 4H), 4.81 – 4.58 (m, 2H), 3.53 – 3.42 (m, 1H*), 3.29 (ddd, J = 14.3, 6.5, 1.5 Hz, 1H*), 3.23 – 3.10 (m, 1H), 1.54 (s, 9H*), 1.52 (s, 9H*); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 168.3, 166.3, 166.7, 166.7, 166.7, 166.5, 166.2, 152.3, 152.2, 136.5, 136.4, 136.3, 133.0, 133.0, 132.7, 131.3, 131.0, 129.2, 128.9, 128.8, 128.2, 128.1, 128.0, 126.4, 121.7, 121.2, 119.8, 119.2, 82.9, 82.6, 72.3, 72.1, 67.2, 61.7, 36.5, 35.6, 29.8, 28.4, 28.4; IR (Neat Film, NaCl) 2975, 1772, 1709, 1388, 1290, 1226, 1168, 752, 694 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₈H₃₄N₃O₆ [M+NH₄]⁺: 508.2442, found 508.2426.
5-allyl 1-(tert-butyl) 3-benzyol-4-oxo-5-(prop-2-yn-1-yl)imidazolidine-1,5-dicarboxylate (7f)

To a solution of lactam 6 (250 mg, 0.668 mmol, 1.0 equiv) in THF (6.7 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 32 mg, 0.801 mmol, 1.2 equiv). The reaction mixture was stirred for 15 min, resulting in a bright yellow solution. Propargyl bromide (80% in PhMe, 252 μL, 2.67 mmol, 4.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 1 h. The reaction mixture was poured into saturated aq. NaHCO₃ (10 mL) and extracted with ethyl acetate (3x6 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by automated silica gel flash chromatography (Telodyne ISCO, 0→30% acetone/hexanes) to provide the title compound as a colorless oil (158 mg, 0.383 mmol, 57% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1:1 mixture of rotamers. Fully resolved rotamer peaks are denoted by *) δ 7.72 – 7.63 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.37 (m, 2H), 5.96 – 5.75 (m, 1H), 5.44 (d, J = 7.1 Hz, 1H*), 5.40 (d, J = 6.9 Hz, 1H*), 5.36 – 5.20 (m, 3H), 4.76 – 4.53 (m, 2H), 4.36 (dd, J = 17.2, 2.7 Hz, 1H*), 3.27 (dd, J = 17.3, 2.7 Hz, 1H*), 3.23 – 3.15 (m, 1H), 2.12 (dt, J = 5.4, 2.6 Hz, 1H), 1.52 (s, 9H*), 1.47 (s, 9H*); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 168.1, 165.9, 165.8, 165.6, 165.6, 151.9, 151.5, 133.0, 132.5, 131.0, 130.7, 129.2, 128.1, 119.9, 119.3, 82.9, 82.7, 78.2, 77.5, 72.3, 71.8, 71.1, 70.8, 67.3, 67.3, 62.0, 28.3, 28.2, 24.2, 23.3; IR (Neat Film, NaCl) 3280, 2977, 1771, 1747, 1714, 1602, 1450, 1392, 1370, 1296, 1229, 1152, 1059, 1019, 858, 790, 770, 740, 701, 665 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₂H₂₈N₅O₆ [M+NH₄]⁺: 430.1973, found 430.1969.

1-(tert-butyl) 5-(2-methylallyl) 3-benzyol-5-benzyl-4-oximidazolidine-1,5-dicarboxylate (7g)

To a solution of lactam S1 (76.1 mg, 0.196 mmol, 1.0 equiv) in THF (2 mL, 0.1 M) at 23 °C was added NaH (60% dispersion in mineral oil, 9.4 mg, 0.235 mmol, 1.2 equiv). The reaction mixture was stirred for 5 min, resulting in a bright yellow solution. BnBr (93 μL, 0.784 mmol, 4.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 5 h. The reaction mixture was poured into saturated aq. NaHCO₃ (5 mL) and extracted with ethyl acetate (4x3 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced
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5-allyl 1-(tert-butyl) 3-benzoyl-5-(2-chloroallyl)-4-oximidazolidine-1,5-dicarboxylate (7h)

To a vial containing lactam 6 (250 mg, 0.668 mmol, 1.0 equiv), NaH (60% dispersion in mineral oil, 32 mg, 0.802 mmol, 1.2 equiv), and TBAI (25 mg, 0.0668 mmol, 0.1 equiv) was added THF (6.7 mL, 0.1 M) at 23 °C. The reaction mixture was stirred for 20 min, resulting in a bright yellow solution. 2,3-dichloropropene (246 μL, 2.67 mmol, 4.0 equiv) was then added and the reaction mixture was stirred at 23 °C for 27 h. The mixture was then heated to 40 °C using a heating block and stirred for an additional 4 h, then poured into saturated aq. NaHCO₃ (10 mL) and extracted with ethyl acetate (4x5 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (15% EtOAc/hexanes) to provide the title compound as a colorless oil (163.9 mg, 0.365 mmol, 55% yield); ¹H NMR (400 MHz, CDCl₃; compound exists as a 1.2:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.66 – 7.61 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 – 7.39 (m, 2H), 5.97 – 5.80 (m, 1H), 5.48 – 5.19 (m, 6H), 4.81 – 4.56 (m, 2H), 3.67 (d, J = 14.8 Hz, 1H*), 3.43 (d, J = 14.9 Hz, 1H#), 3.36 – 3.23 (m, 1H), 1.50 (s, 9H*), 1.47 (s, 9H#); ¹³C NMR (100 MHz, CDCl₃) δ
168.3, 168.1, 166.5, 166.4, 166.0, 165.8, 151.9, 151.6, 118.4, 82.8, 82.5, 70.6, 70.6, 67.4, 67.3, 61.6, 61.5, 41.5, 41.0, 31.0, 28.2; IR (Neat Film, NaCl) 3062, 2980, 2931, 2909, 2360, 1770, 1747, 1714, 1694, 1651, 1634, 1583, 1477, 1450, 1392, 1370, 1322, 1295, 1231, 1172, 1145, 1099, 1050, 1013, 989, 936, 888, 857, 792, 769, 724, 703, 682, 665, 634 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₂H₂₀Cl₅N₅O₆ [M+NH₄⁺]: 466.1739, found 466.1750.

5-allyl 1-(tert-butyl) 3-benzoyl-5-(((benzyloxy)carbonyl)amino)methyl)-4-oxoimidazolidine-1,5-dicarboxylate (7i)

To a vial containing lactam 6 (199 mg, 0.532 mmol, 1.0 equiv), and benzyl ((phenylsulfonyl)methyl)carbamate⁷ (195 mg, 0.638 mmol, 1.2 equiv) was added CH₂Cl₂ (2.7 mL, 0.2 M). Cs₂CO₃ (433 mg, 1.33 mmol, 2.5 equiv) was then added in a single portion and the reaction mixture was stirred at 23 °C for 4 h. Saturated aq. NH₄Cl (3 mL) was then added, and the resulting mixture was stirred vigorously for 30 min. The layers were then separated, and the aqueous layer was extracted with CH₂Cl₂ (3 x 3 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (20% EtOAc/hexanes) to provide the title compound as a colorless oil (149 mg, 0.341 mmol, 64% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.58 (m, 2H), 7.54 (td, J = 7.0, 1.6 Hz, 1H), 7.40 (q, J = 7.9 Hz, 2H), 7.32 (q, J = 2.3 Hz, 5H), 5.99 – 5.73 (m, 1H), 5.46 – 4.82 (m, 7H), 4.76 – 4.53 (m, 2H), 4.17 – 3.95 (m, 2H), 1.49 (d, J = 5.9 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 168.1, 166.2, 166.1, 165.5, 165.1, 156.8, 156.6, 152.5, 151.8, 136.4, 136.2, 132.9, 132.9, 132.6, 132.5, 131.0, 130.7, 129.4, 129.3, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 120.0, 119.3, 83.1, 82.8, 71.2, 70.7, 67.2, 67.2, 67.1, 61.5, 61.3, 43.2, 43.0, 29.8, 28.3, 28.2; IR (Neat Film, NaCl) 3380, 3066, 2978, 1714, 1601, 1519, 1454, 1393, 1304, 1166, 1068, 989, 941, 855, 737, 698, 666 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C₂₈H₃₁N₅NaO₈ [M+Na⁺]: 560.2003, found 560.1998.
5-allyl 1-((tert-butyl) 3-benzoyl-5-(2-cyanoethyl)-4-oximidazolidine-1,5-dicarboxylate (7j)

To a vial containing lactam 6 (250 mg, 0.668 mmol, 1.0 equiv) and K$_2$CO$_3$ (462 mg, 3.34 mmol, 5 equiv) were added acetone (2.7 mL, 0.25 M) and acrylonitrile (175 µL, 2.67 mmol, 4 equiv). The vial was sealed and the reaction mixture was heated to 50 °C using a heating block, stirred for 20 h, and allowed to cool to 23 °C. The crude mixture was filtered through cotton and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (25% EtOAc/hexanes) to provide the title compound as a colorless oil (94.6 mg, 0.221 mmol, 33% yield); $^1$H NMR (400 MHz, CDCl$_3$; compound exists as a 1.7:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 168.1, 166.4, 165.5, 165.3, 152.9, 152.2, 133.1, 132.6, 130.9, 130.6, 129.3, 128.2, 120.4, 119.7, 118.5, 118.2, 83.7, 83.4, 70.9, 70.8, 67.6, 67.6, 61.8, 61.8, 28.3, 28.3, 27.6, 12.7, 12.5; IR (Neat Film, NaCl) 3065, 2979, 2936, 2343, 2249, 1770, 1745, 1714, 1698, 1651, 1602, 1582, 1477, 1449, 1386, 1372, 1301, 1245, 1225, 1173, 1154, 1114, 1081, 1048, 1028, 994, 939, 894, 858, 845, 793, 781, 770, 733, 701, 672, 664, 621 cm$^{-1}$; HRMS (MM: ESI-APCI): m/z calc’d for C$_{22}$H$_{29}$N$_4$O$_6$ [M+NH$_4$]$^+$: 445.2082, found 445.2085.

5-allyl 1-((tert-butyl) 3-benzoyl-4-oxo-5-(3-oxobutyl)imidazolidine-1,5-dicarboxylate (7k)

To a vial containing lactam 6 (250 mg, 0.668 mmol, 1.0 equiv) and K$_2$CO$_3$ (462 mg, 3.34 mmol, 5 equiv) were added acetone (3 mL, 0.25 M) and methyl vinyl ketone (223 µL, 2.67 mmol, 4 equiv). The vial was sealed, and the reaction mixture was heated to 50 °C using a heating block, stirred for 6 h, and allowed to cool to 23 °C. The crude mixture was filtered through cotton and
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concentrated under reduced pressure. The product was purified by silica gel flash chromatography (33% EtOAc/hexanes) to provide the title compound as a colorless oil (228 mg, 0.513 mmol, 77% yield); 1H NMR (400 MHz, CDCl3; compound exists as a 1.1:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.62 (d, J = 7.7 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.39 (t, J = 7.7 Hz, 2H), 5.95 – 5.75 (m, 1H), 5.41 – 5.05 (m, 4H), 4.73 – 4.52 (m, 2H), 2.75 – 2.35 (m, 4H), 2.11 (d, J = 3.0 Hz, 3H), 1.47 (s, 9H*), 1.43 (s, 9H#); 13C NMR (100 MHz, CDCl3) δ 207.5, 206.7, 168.4, 168.2, 166.9, 166.8, 166.4, 166.2, 152.5, 152.2, 132.8, 132.7, 132.7, 131.1, 130.8, 129.1, 128.0, 119.7, 119.1, 82.9, 82.6, 70.9, 67.1, 67.1, 61.4, 61.3, 38.5, 37.8, 29.8, 29.4, 28.2, 28.1, 27.8, 26.9; IR (Neat Film, NaCl) 3074, 2977, 2931, 1757, 1703, 1642, 1602, 1583, 1478, 1448, 1393, 1368, 1304, 1226, 1168, 1091, 1061, 999, 970, 928, 880, 858, 826, 795, 768, 731, 701, 664 cm⁻¹; HRMS (MM: ESI-APCI): m/z calc’d for C23H32N3O7 [M+NH₄]⁺: 462.2235, found 462.2251.

Derivatization of Allylic Alkylation Products

(R)-5-allyl-3-benzoyl-5-benzylimidazolidin-4-one (9)

To a solution of benzyl imidazolidinone 8a (15 mg, 0.0357 mmol, 1.0 equiv) in CH2Cl2 (0.36 mL, 0.1 M) was added trifluoroacetic acid (41 µL, 0.536 mmol, 15 equiv), and the reaction mixture was stirred in a sealed vial at 23 °C for 22 h. The resulting solution was concentrated under reduced pressure and the residue taken up in Et2O (0.5 mL), washed with 5% aq. K2CO3 (1 mL), dried with Na2SO4, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (33% EtOAc/hexanes) to provide free amine 9 as a white solid (9.3 mg, 0.0290 mmol, 81% yield); 1H NMR (400 MHz, CDCl3) δ 7.58 – 7.49 (m, 3H), 7.46 – 7.40 (m, 2H), 7.38 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 5.85 (dddd, J = 17.0, 10.2, 8.6, 6.2 Hz, 1H), 5.31 – 5.17 (m, 2H), 4.71 (d, J = 9.6 Hz, 1H), 4.32 (d, J = 9.6 Hz, 1H), 3.15 (d, J = 13.6 Hz, 1H), 2.76 (d, J = 13.6 Hz, 1H), 2.63 (ddt, J = 14.0, 6.1, 1.4 Hz, 1H), 2.32 (ddt, J = 13.9, 8.5, 0.9 Hz, 1H), 2.21 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 176.0, 169.7, 135.6, 133.4, 132.5, 132.1, 130.5, 129.3, 128.8, 128.0, 127.6, 120.9, 68.4, 61.9, 42.1, 41.1; IR (Neat Film, NaCl) 2921, 1743, 1674, 1494, 1449, 1380, 1306, 1235, 922, 796, 732, 700 cm⁻¹; HRMS (MM:
ESI-APCI): m/z calc’d for C_{20}H_{21}N_{2}O_{2} [M+H]^+: 321.1598, found 321.1590; [α]_{D}^{21.7} +69.27 (c 0.5, CHCl_{3}).

**tert-butyl (R)-5-allyl-5-benzyl-4-oximidazolidine-1-carboxylate (10)**

To a solution of benzyl imidazolidinone 8a (15 mg, 0.0357 mmol, 1.0 equiv) in 50% MeOH/H_{2}O (0.36 mL, 0.1 M) was added LiOH·H_{2}O (22 mg, 0.536 mmol, 15 equiv) and the reaction mixture was heated with stirring in a sealed vial at 70 °C for 1 h using a heating block. MeOH was removed under reduced pressure and the solution was diluted with H_{2}O (0.5 mL) and extracted with ethyl acetate (4 x 0.5 mL). The combined organic extracts were dried over Na_{2}SO_{4} and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (40% EtOAc/hexanes) to provide free lactam 10 as a colorless film (9.0 mg, 0.0284 mmol, 80% yield); {^1}H NMR (400 MHz, CDCl_{3}; compound exists as a 1:1:1 mixture of rotamers. For fully resolved peaks, the major rotamer is denoted by *, and the minor rotamer by #) δ 7.26 – 7.12 (m, 5H), 6.38 (d, J = 32.9 Hz, 1H), 5.74 – 5.53 (m, 1H), 5.24 – 5.04 (m, 2H), 4.41 (d, J = 5.5 Hz, 1H#), 4.32 (d, J = 5.4 Hz, 1H*), 3.79 (d, J = 5.5 Hz, 1H#), 3.68 (d, J = 5.3 Hz, 1H*), 3.50 (d, J = 13.3 Hz, 1H*), 3.27 (d, J = 13.4 Hz, 1H#), 3.16 (dd, J = 13.6, 8.4 Hz, 1H#), 3.01 (dd, J = 13.3, 1.7 Hz, 1H), 2.93 (dd, J = 13.8, 8.2 Hz, 1H*), 2.71 – 2.54 (m, 1H), 1.64 (s, 9H#), 1.49 (s, 9H*); {^{13}}C NMR (100 MHz, CDCl_{3}) δ 174.4, 174.2, 152.9, 151.9, 136.5, 135.9, 132.4, 132.0, 130.0, 129.9, 128.5, 128.3, 127.1, 126.9, 119.7, 119.6, 81.7, 80.5, 68.6, 68.4, 58.1, 57.9, 41.1, 40.0, 38.8, 28.8, 28.5; IR (Neat Film, NaCl) 3242, 2976, 2930, 1708, 1454, 1402, 1368, 1341, 1174, 1143, 1078, 996, 920, 768, 702 cm\(^{-1}\); HRMS (MM: ESI-APCI): m/z calc’d for C_{18}H_{25}N_{2}O_{3} [M+H]^+: 317.1860, found 317.1852; [α]_{D}^{21.8} –67.38 (c 0.5, CHCl_{3}).

**methyl (R)-2-amino-2-benzylpent-4-enoate (11)**

To a solution of benzyl imidazolidinone 8a (10 mg, 0.0238 mmol, 1.0 equiv) in MeOH (0.4 mL, 0.06 M) was added concentrated H_{2}SO_{4} (85 µL). The reaction vessel was sealed, and the reaction mixture was stirred at 70 °C in a heating block for 3 days. Care should be taken, as gas pressure is generated over the course of the reaction. The crude mixture was then added to saturated aq.
NaHCO₃ (10 mL, gas evolution) and extracted with ethyl acetate (4 x 4 mL). The combined organic extracts were dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (20% EtOAc/hexanes + 0.1% Et₃N) to provide amino ester 11 as a colorless film (1.3 mg, 0.00593 mmol, 25% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 – 7.08 (m, 2H), 5.77 – 5.64 (m, 1H), 5.24 – 5.11 (m, 2H), 3.71 (s, 3H), 3.19 (d, J = 13.2 Hz, 1H), 2.80 (dd, J = 13.2, 6.9 Hz, 1H), 2.73 (ddt, J = 13.3, 6.4, 1.3 Hz, 1H), 2.33 (dd, J = 13.5, 8.4 Hz, 1H). All characterization data matched those reported in the literature.⁸

**Addendum to Table 1 – additional reaction optimization.**⁹

![Reaction scheme](image)

Bisphosphine ligand L₂ was evaluated for the conversion of 7a to 8a by an adaptation of the reported method by Trost and coworkers. This reaction was incomplete after 38 h and provided product 8a in a modest ~43% ee.

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**References**


alkylation cascade for the formation of adjacent quaternary and tertiary stereocentres. 


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$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 8a.
Infrared spectrum (Thin Film, NaCl) of compound 8a.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8a.
$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 8b.
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Infrared spectrum (Thin Film, NaCl) of compound 8b.

\[^{13}\text{C} \text{ NMR (100 MHz, } \text{CDCl}_3\text{)}\text{ of compound 8b.}\]
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$^1$H NMR (400 MHz, CDCl$_3$) of compound 8c.
Infrared spectrum (Thin Film, NaCl) of compound 8c.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8c.
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$\text{BzN} \quad \text{N} \quad \text{Boc}$

H NMR (400 MHz, CDCl$_3$) of compound 8d.

$^1$H NMR (400 MHz, CDCl$_3$) of compound 8d.
Infrared spectrum (Thin Film, NaCl) of compound 8d.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8d.
Infrared spectrum (Thin Film, NaCl) of compound 8e.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8e.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 8f.
Infrared spectrum (Thin Film, NaCl) of compound 8f.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8f.
$^{1}H$ NMR (400 MHz, CDCl$_3$) of compound 8g.
Infrared spectrum (Thin Film, NaCl) of compound 8g.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8g.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 8h.
Infrared spectrum (Thin Film, NaCl) of compound 8h.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8h.
$\text{H NMR (400 MHz, CDCl}_3\text{) of compound } 8i$. 

$\text{BzN} \text{NHCBz}$

$\text{Boc}$
Infrared spectrum (Thin Film, NaCl) of compound 8i.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8i.
1H NMR (400 MHz, CDCl₃) of compound 8j.
Infrared spectrum (Thin Film, NaCl) of compound 8j.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8j.
\[ f_1 (\text{ppm}) \]

\[ \begin{array}{cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc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Infrared spectrum (Thin Film, NaCl) of compound 8k.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 8k.
^1H NMR (400 MHz, CDCl₃) of compound 3.
Infrared spectrum (Thin Film, KBr) of compound 3.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4.
Infrared spectrum (Thin Film, NaCl) of compound 4.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 4.
Supporting Information for Serce, Sun, and Stoltz

\[ \text{H NMR (400 MHz, CDCl}_3\text{) of compound 6.} \]
Infrared spectrum (Thin Film, NaCl) of compound 6.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 6.
$^1$H NMR (400 MHz, CDCl$_3$) of compound S1.
Infrared spectrum (Thin Film, KBr) of compound S1.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound S1.
Supporting Information for Sercel, Sun, and Stoltz

\( \text{H NMR (400 MHz, CDCl}_3 \) of compound 7a.
Infrared spectrum (Thin Film, NaCl) of compound 7a.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7a.
Supporting Information for Sercel, Sun, and Stoltz

$^1$H NMR (400 MHz, CDCl$_3$) of compound 7b.
Supporting Information for Serce, Sun, and Stoltz

Infrared spectrum (Thin Film, NaCl) of compound 7b.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7b.
Supporting Information for Sercel, Sun, and Stoltz

$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 7c.
Infrared spectrum (Thin Film, NaCl) of compound 7c.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7c.
$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 7d.
Infrared spectrum (Thin Film, NaCl) of compound 7d.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7d.
Supporting Information for Sercel, Sun, and Stoltz

$^1$H NMR (400 MHz, CDCl$_3$) of compound 7e.
Infrared spectrum (Thin Film, NaCl) of compound 7e.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7e.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 7f.
Infrared spectrum (Thin Film, NaCl) of compound 7f.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7f.
$^{1}$H NMR (500 MHz, CDCl$_3$) of compound 7g.
Infrared spectrum (Thin Film, NaCl) of compound 7g.

$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 7g.
Supporting Information for Sercel, Sun, and Stoltz

$^1$H NMR (400 MHz, CDCl$_3$) of compound 7h.

Cl
O
BzN
N
Boc

$^7$h

Sf

($p$-$p$)$_{37}$ of compound $^7$h.
Infrared spectrum (Thin Film, NaCl) of compound 7h.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) of compound 7h.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 7i.
Infrared spectrum (Thin Film, NaCl) of compound 7i.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7i.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 7j.
Infrared spectrum (Thin Film, NaCl) of compound 7j.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7j.
\[ \text{BzN} \text{N} \text{Boc} \text{Me} \text{O}\]

**Supporting Information for Serce, Sun, and Stoltz**

\[ \frac{\text{H NMR (400 MHz, CDCl}_3\text{)}}{\text{of compound 7k}}. \]

\[ \frac{1}{\text{H NMR (400 MHz, CDCl}_3\text{) of compound 7k.}} \]
Infrared spectrum (Thin Film, NaCl) of compound 7k.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 7k.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 9.
Infrared spectrum (Thin Film, NaCl) of compound 9.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 9.
Supporting Information for Sercel, Sun, and Shih.

H NMR (400 MHz, CDCl₃) of compound 10.
Infrared spectrum (Thin Film, NaCl) of compound 10.

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 10.
$^{1}$H NMR (500 MHz, CDCl$_3$) of compound 11.