

Supporting Information

Tandem Catalytic Allylic Amination and [2,3]-Stevens Rearrangement of Tertiary Amines

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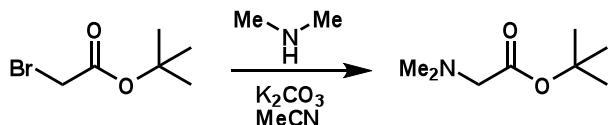
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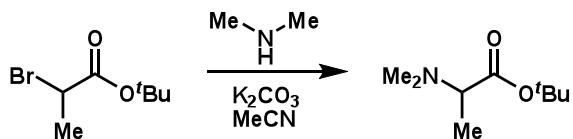
I. Materials and Methods

General Information: All reactions were carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. ¹H and ¹³C NMR spectra were recorded on Varian Inova-400, 500, or 600 spectrometers. Data for ¹H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ¹³C NMR spectra are reported relative to chloroform as an internal standard (77.2 ppm) and are reported in terms of chemical shift (δ ppm). Infrared spectra were recorded on a Perkin-Elmer 1000 series FTIR. GC analyses were performed on an Agilent 7820A System. HRMS data were obtained at The Scripps Center for Mass Spectrometry.

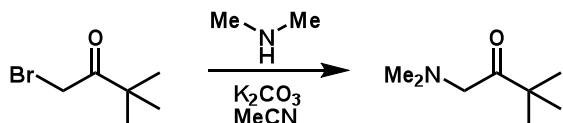
II. Synthesis of Amino Esters



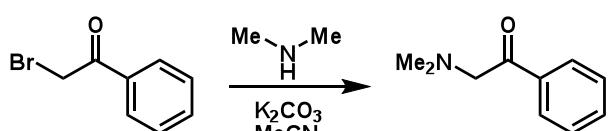
***N,N*-Dimethylglycine *tert*-butyl ester:** In a round bottom flask, a solution of *tert*-butyl bromoacetate (3.59 g, 18.4 mmol) in MeCN (50 mL) was treated sequentially with K_2CO_3 (7.6 g, 55 mmol) and dimethylamine (6.3 mL, 55 mmol, 40 wt%). After stirring overnight at rt, the mixture was charged with aqueous 1N NaOH (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude oil was filtered through a short pad of silica gel (1:1 hexanes: EtOAc eluent) and concentrated under reduced pressure to yield the product as a clear oil (1.63 g, 10.25 mmol, 56%): ^1H NMR (600 MHz, CDCl_3) δ 3.00 (s, 2H), 2.28 (s, 6H), 1.41 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.0, 80.9, 61.3, 45.3, 28.2; IR (film) 2978, 1747, 1368, 1147, 1062, 839 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C8H17NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 160.1, found 160.1.



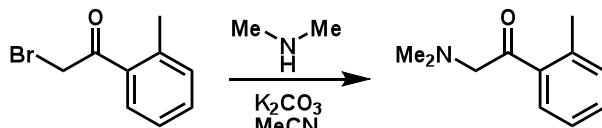
***N,N*-Dimethylalanine *tert*-butyl ester:** Following the typical procedure, the product was obtained as a clear oil (1.64 g, 93%): ^1H NMR (600 MHz, CDCl_3) δ 3.08 (q, $J = 7.0$ Hz, 1H), 2.33 (s, 6H), 1.46 (s, 9H), 1.23 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 172.8, 80.8, 63.7, 41.9, 28.4, 15.6; IR (film) 2979, 1726, 1453, 1368, 1148, 850 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C9H19NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 174.1, found 174.2.



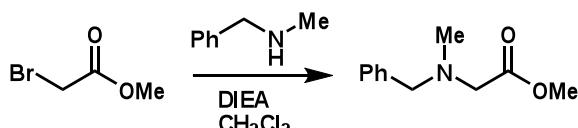
1-Dimethylamino-3,3-dimethyl-2-butanone: Following the typical procedure, the product was obtained as a yellow oil (1.42 g, 84%): ^1H NMR (600 MHz, CDCl_3) δ 3.13 (s, 2H), 2.07 (s, 6H), 0.93 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 211.8, 62.9, 45.3, 43.2, 26.2; IR (film) 2968, 1716, 1480, 1176, 1042, 995, 857, 754 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C8H17NO}]^+([\text{M}+\text{H}]^+)$: m/z 144.1, found 144.2.



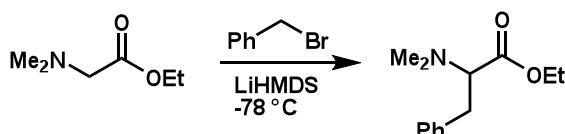
2-(Dimethylamino)-1-phenylethanone: Following the typical procedure, the product was obtained as a yellow oil (1.70 g, 99%): ^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 2H), 3.75 (s, 2H), 2.38 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.5, 135.6, 132.9, 128.3, 127.8, 65.3, 45.5; IR (film) 2832, 1694, 1449, 1286, 1222, 980, 861, 756 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C10H13NO}]^+([\text{M}+\text{H}]^+)$: m/z 164.1, found 164.2.



2-(Dimethylamino)-1-*o*-tolylethanone: Following the typical procedure, purification by flash chromatography (9:1 to 3:7 hexanes:EtOAc gradient eluent) provided the desired product as a yellow oil (485 mg, 56%): ^1H NMR (600 MHz, CDCl_3) δ 7.53 (d, J = 7.0 Hz, 1H), 7.25 (t, J = 7.0 Hz, 2H), 7.13 (t, J = 7.0 Hz, 2H), 4.54 (s, 2H), 2.40 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 201.1, 137.9, 136.8, 131.8, 128.3, 128.1, 125.5, 67.6, 45.6, 20.1; IR (film) 2964, 1681, 1455, 1383, 1217, 979, 757 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C11H15NO}]^+([\text{M}+\text{H}]^+)$: m/z 178.1, found 178.1.

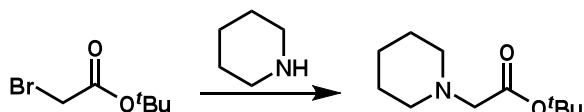


***N*-Methy-*N*-benzylglycine methyl ester:** In a round bottom flask, a solution of methyl bromoacetate (3.0 g, 19.7 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C and charged sequentially with *N*-benzylmethylamine (2.39 g, 19.7 mmol) and DIEA (8.6 mL, 49 mmol). The reaction was allowed to warm to rt and stirred overnight. The mixture was diluted with CH_2Cl_2 (150 mL), washed with saturated aqueous NaHCO_3 (2 x 30 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. Purification by flash chromatography (9:1 to 8:2 hexanes:EtOAc eluent) provided the desired product as a clear oil (3.50 g, 92%): ^1H NMR (600 MHz, CDCl_3) δ 7.31-7.24 (m, 3H), 7.22-7.18 (m, 2H), 3.64 (s, 3H), 3.62 (s, 2H), 3.21 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.3, 138.2, 129.0, 128.3, 127.2, 61.1, 57.4, 51.3, 42.3; IR (film) 2951, 1731, 1454, 1194, 1028, 870, 741 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C11H15NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 194.1, found 194.1.

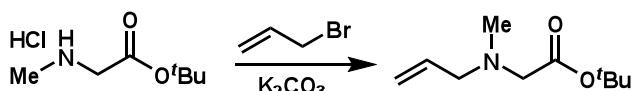


***N,N*-Dimethylphenylalanine ethyl ester:** In a flame-dried round bottom flask, a solution of *N,N*-dimethylglycine ethyl ester (500 mg, 3.82 mmol) in THF (19 mL) was cooled to -78 °C and charged dropwise with a solution of LiHMDS (4.2 mL, 4.2 mmol, 1.0 M THF). After 1 h, benzyl bromide (718 mg, 4.2 mmol) was added, and the reaction was allowed to warm to rt overnight. The mixture was diluted with saturated aqueous NH_4Cl (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. Purification by flash chromatography (9:1 to 6:4 hexanes:EtOAc gradient eluent) provided the desired product as a clear oil (440 mg, 52%): Spectral data were identical to literature values.¹

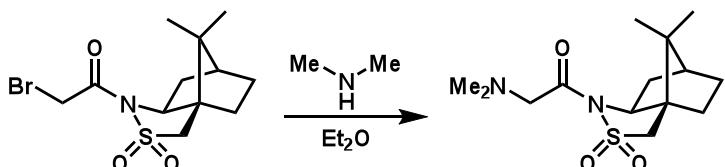
¹ West, F. G.; Glaeske, K. W.; Naidu, B. N. *Synthesis*, **1993**, 10, 977 - 980



***Tert*-butyl 1-piperidineacetate:** Piperidine (1.21 mL, 12.3 mmol) was added dropwise to a solution of *tert*-butyl bromoacetate (1.20 g, 6.15 mmol) in benzene (12 mL) and stirred overnight. The reaction was diluted with Et₂O (150 mL), washed with brine (100 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The crude oil was filtered through a short pad of silica gel (1:1 hexanes:EtOAc eluent) and concentrated under reduced pressure to yield the product as a clear oil (1.20 g, 98%): ¹H NMR (600 MHz, CDCl₃) δ 2.95 (s, 2H), 2.38 (br s, 4H), 1.52-1.47 (m, 4H), 1.34 (s, 9H), 1.34-1.29 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 169.8, 80.6, 60.8, 54.1, 28.1, 25.8, 24.0; IR (film) 2934, 1731, 1367, 1150, 849, 755 cm⁻¹; LCMS (ESI) calc'd for [C11H21NO2]⁺([M+H]⁺): *m/z* 200.2, found 200.2.



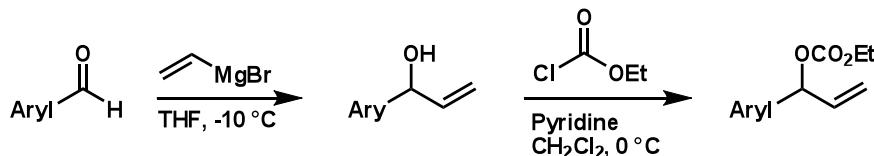
***N*-Methy-*N*-allylglycine *tert*-butyl ester:** Triethylamine (0.79 mL, 5.7 mmol) was added to a solution of sarcosin *tert*-butyl ester hydrochloride (1.03 g, 5.7 mmol) in MeCN (11 mL). After stirring for 5 min, the flask was charged with K₂CO₃ (3.9 g, 28 mmol) and allyl bromide (0.53 mL, 6.3 mmol). After stirring overnight at rt, the reaction was diluted with aqueous 1N NaOH (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography (95:5 to 8:2 hexanes:EtOAc gradient eluent) provided the desired product as a clear oil (456 mg, 43%): ¹H NMR (600 MHz, CDCl₃) δ 5.79-5.70 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 3.01 (s, 4H), 2.23 (s, 3H), 1.34 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 170.1, 153.4, 117.8, 80.7, 60.1, 58.2, 42.1, 28.0; IR (film) 2979, 1735, 1368, 1153, 1055, 920, 841 cm⁻¹; LCMS (ESI) calc'd for [C10H19NO2]⁺([M+H]⁺): *m/z* 186.1, found 186.2.



***N*-[2-(dimethylamino)acetyl]-(1*R*,2*S*)-bornane-10,2-sultam:** The compound was synthesized according to a method reported by Sweeney.² Spectral data were identical to literature values.

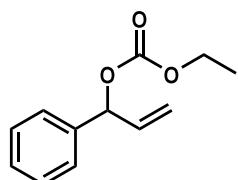
² Workman, J.A.; Garrido, N.P.; Sancion, J.; Roberts, E.; Wessel, H.P.; Sweeney, J.B. *J. Am. Chem. Soc.* **2005**, 127, 1066-1067.

III. Synthesis of Ethyl 1-Arylallyl Carbonates

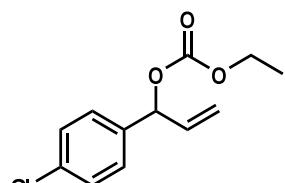


1-Arylprop-2-en-1-ols: A flame-dried flask charged with aldehyde (21.8 mmol) and THF (22 mL) was cooled to -10 °C (acetone/ice). Vinylmagnesium bromide (26 mmol, 1.0 M THF) was added dropwise to the mixture, and the reaction was monitored by TLC. Upon complete conversion (~30 min), the reaction was quenched with saturated aqueous NH₄Cl (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography yielded the desired allylic alcohol.

Ethyl 1-Arylallyl carbonates: The allylic alcohol from the previous step (10.2 mmol) and pyridine (40.8 mmol) were dissolved in CH₂Cl₂ (5.0 mL). The reaction was cooled to 0 °C and charged dropwise with ethyl chloroformate (15.3 mmol). Upon complete addition, the reaction was allowed to warm to rt and monitored by TLC for full conversion. The mixture was diluted with EtOAc (100 mL) and washed with aqueous 1N HCl (2 x 30 mL), saturated aqueous NaHCO₃ (30 mL) and brine (30 mL). The solution was concentrated under reduced pressure. Purification by flash chromatography yielded the desired carbonate.

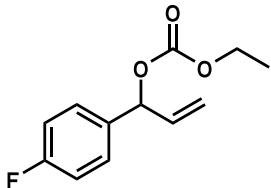


Ethyl 1-phenylallyl carbonates: Following the typical procedure, the product was obtained as a clear oil. Spectral data were identical to literature values.³

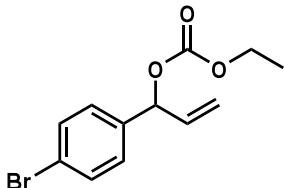


Ethyl 1-(4-chlorophenyl)allyl carbonates: Following the typical procedure, the product was obtained as a clear oil: ¹H NMR (600 MHz, CDCl₃) δ 7.33-7.29 (m, 4H), 6.04 (d, *J* = 6.0 Hz, 1H), 6.02-5.95 (m, 1H), 5.33 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* = 11.0 Hz, 1H), 4.23-4.13 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 154.3, 137.0, 135.5, 134.3, 128.8, 128.6, 117.8, 79.2, 64.3, 14.3; IR (film) 2986, 1747, 1253, 1090, 1008 cm⁻¹. GCMS calc'd for [C₁₂H₁₃ClO₃]⁺([M]⁺): *m/z* 240, found 240.

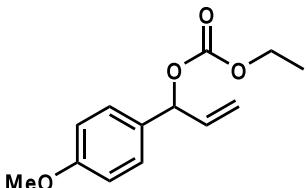
³ Cravoto, G.; Giovenzana, G. B.; Sisti, M.; Palmisano, G. *Tetrahedron*, 1998, 54, 1639-1646



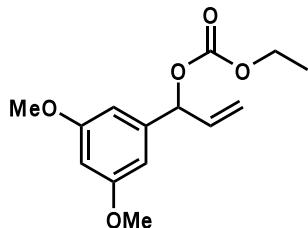
Ethyl 1-(4-fluorophenyl)allyl carbonates: Following the typical procedure, the product was obtained as a clear oil: ^1H NMR (600 MHz, CDCl_3) δ 7.37-7.32 (m, 2H), 7.02 (t, J = 9.0 Hz, 2H), 6.08-6.05 (m, 1H), 6.04-5.96 (m, 1H), 5.32 (d, J = 17.0 Hz, 1H), 5.26 (d, J = 11.0 Hz, 1H), 4.22-4.12 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163 (d, J = 247 Hz, $^1J_{\text{C-F}}$), 154.4, 135.8, 134.3, 129.1 (d, J = 8 Hz, $^2J_{\text{C-F}}$), 117.5, 115.6 (d, J = 21 Hz, $^2J_{\text{C-F}}$), 79.2, 64.2, 14.2; IR (film) 2987, 1744, 1512, 1259, 1009 cm^{-1} . GCMS calc'd for $[\text{C12H13FO}_3]^+([\text{M}]^+)$: m/z 244, found 244.



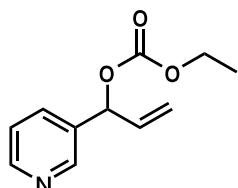
Ethyl 1-(4-bromophenyl)allyl carbonates: Following the typical procedure, the product was obtained as a clear oil: ^1H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.03 (d, J = 7.0 Hz, 1H), 6.01-5.95 (m, 1H), 5.33 (d, J = 17.0 Hz, 1H), 5.27 (d, J = 11.0 Hz, 1H), 4.23-4.13 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 154.4, 137.5, 135.5, 131.8, 128.9, 122.5, 118.0, 79.3, 64.3, 14.3; IR (film) 1985, 1747, 1488, 1248, 1011 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C12H13BrO}_3]^+([\text{M}+\text{Na}]^+)$: m/z 306.994, found 306.9939.



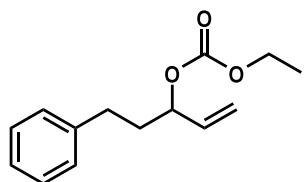
Ethyl 1-(4-methoxyphenyl)allyl carbonates: Following the typical procedure, the product was obtained as a clear oil: ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 16.0 Hz, 1H), 6.19-6.13 (dt, J = 16.0 Hz, J = 7.0 Hz, 1H), 4.75 (d, J = 7.0 Hz, 2H), 4.24-4.18 (m, 2H), 3.79 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 159.8, 155.2, 134.7, 128.1, 127.2, 120.3, 114.1, 68.6, 64.1, 55.4, 14.4; IR (film) 2942, 1746, 1465, 1242, 1057 cm^{-1} . GCMS calc'd for $[\text{C13H16O}_4]^+([\text{M}]^+)$: m/z 236, found 236.



Ethyl 1-(3,5-dimethoxyphenyl)allyl carbonates: Following the typical procedure, the product was obtained as a clear oil: ^1H NMR (600 MHz, CDCl_3) δ 6.52 (s, 2H), 6.39 (s, 1H), 6.03-5.95 (m, 2H), 5.35 (d, J = 15.0 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H), 4.22-4.14 (m, 2H), 3.76 (s, 6H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 161.0, 154.4, 140.8, 135.7, 117.4, 104.9, 100.3, 79.9, 64.1, 55.3, 14.3; IR (film) 2940, 1746, 1613, 1470, 1250, 1067, 940 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}14\text{H}18\text{O}5]^+([\text{M}+\text{H}]^+)$: m/z 267.1227, found 267.1223.



Ethyl 1-(pyridin-3-yl)allyl carbonates: Following the typical procedure, obtained the product was obtained as a clear oil: ^1H NMR (600 MHz, CDCl_3) δ 8.50 (s, 1H), 8.41 (d, J = 5.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.14 (dd, J = 8.0 Hz, J = 5.0 Hz, 1H), 5.98 (d, J = 6.0 Hz, 1H), 5.92-5.84 (m, 1H), 5.23 (d, J = 17.0 Hz, 1H), 5.17 (d, J = 11.0 Hz, 1H), 4.09-3.99 (m, 2H), 1.13 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 154.0, 149.6, 148.7, 134.9, 134.6, 133.9, 123.3, 118.1, 77.4, 64.1, 14.0; IR (film) 2986, 1747, 1257, 1008 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}11\text{H}13\text{NO}3]^+([\text{M}+\text{H}]^+)$: m/z 208.0968, found 208.0973.



Ethyl 5-phenylpent-1-en-3-yl carbonate: Following the typical procedure, the product was obtained as a clear oil. Spectral data were identical to literature values.⁴

⁴ Matsuhashi, H; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T.; *Bull. of the Chem. Soc. of Japan*, **1997**, 70, 1943 - 1952

IV. Table 1 Optimization

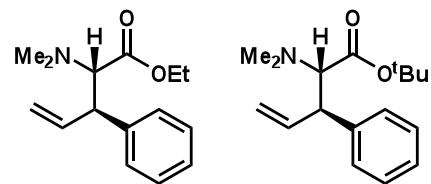
General Information: All reactions were performed on a 0.40 mmol scale in 4 dram screw top vials. GC analyses were performed on an Agilent 7820A System with a Supelco Astec CHIRALDEX™ G-TA Column (30m x 0.25mm x 0.12 μ m). Tridecane was used as a standard.

Retention times:⁵

N,N-dimethylglycine ethyl ester - 3.0 min

N,N-dimethylglycine *tert*-butyl ester - 3.4 min

Tridecane - 5.2 min



Major - 7.8 min
Minor - 8.0 min

Major - 8.1 min
Minor - 8.6 min

Procedure: A vial fitted with a screw cap septum was charged with Pd₂dba₃•CHCl₃ (4 μ mol), P(2-furyl)₃ (16 μ mol), and Cs₂CO₃ (1.2 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This purging procedure was repeated twice. The vial was sequentially charged with MeCN (2.0 mL), cinnamyl carbonate (0.40 mmol), and *N,N*-dimethylglycine ester (0.60 mmol). The mixture was stirred at rt and monitored by GC analysis of aliquots.

⁵ Cinnamyl carbonate was unstable under the GC conditions and no retention peaks were observed.

V. General Procedure for the [2,3]-Stevens Rearrangement

General Information: All reactions were performed on a 0.40 mmol scale in 4 dram screw top vials unless otherwise indicated. The diastereomeric products were separated whenever possible and reported ratios are based on crude ^1H NMR analysis. The spectral data for the major isomer is reported. *The typical procedure is as follows:* a vial fitted with a screw cap septum was charged with $\text{Pd}_2\text{dba}_3\bullet\text{CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), and Cs_2CO_3 (390 mg, 1.2 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This purging procedure was repeated twice. The vial was sequentially charged with MeCN (2.0 mL), ethyl 1-arylallyl carbonate (0.40 mmol), and glycine ester (0.60 mmol). After stirring for 4-16 h at rt, the reaction was filtered through a büchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography provided the desired product.

VI. Table 2 Characterization Data

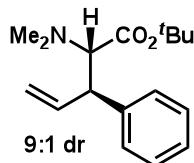


Table 2, Entry 1. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (96 mg, 0.35 mmol, 87%): ^1H NMR (600 MHz, CDCl_3) δ 7.25 (t, J = 7.0 Hz, 2H), 7.21-7.15 (m, 3H), 6.12-6.05 (m, 1H), 5.10 (d, J = 10.0 Hz, 1H), 5.06 (d, J = 17.0 Hz, 1H), 3.67 (dd, J = 12.0 Hz, J = 9.0 Hz, 1H), 3.46 (d, J = 12.0 Hz, 1H), 2.42 (s, 6H), 1.14 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.3, 141.0, 139.5, 128.7, 128.5, 126.9, 116.0, 80.8, 72.3, 50.1, 41.4, 28.3; IR (film) 2977, 1723, 1454, 1367, 1257, 1147, 699 cm^{-1} ; HRMS (ESI-TOF-TOF) calc'd for $[\text{C17H25NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 276.1958, found 276.1965.

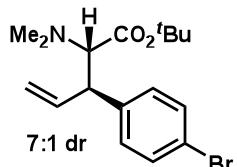


Table 2, Entry 2. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (126 mg, 0.35 mmol, 89%): ^1H NMR (600 MHz, CDCl_3) δ 7.40 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.09-6.02 (m, 1H), 5.11 (d, J = 10.0 Hz, 1H), 5.04 (d, J = 17.0 Hz, 1H), 3.66 (dd, J = 12.0 Hz, J = 9.0 Hz, 1H), 3.39 (d, J = 12.0 Hz, 1H), 2.41 (s, 6H), 1.19 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 160.0, 140.1, 138.9, 131.6, 130.5, 120.7, 116.4, 81.1, 72.2, 49.4, 41.4, 28.2; IR (film) 2977, 2936, 1722, 1367, 1488, 1257, 1147 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C17H24BrNO}_2]^+([\text{M}+\text{H}]^+)$: m/z 354.1063, found 354.1073.

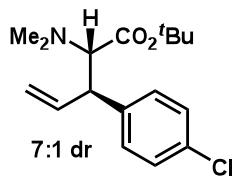


Table 2, Entry 3. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (107 mg, 0.35 mmol, 87%); ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.09-6.02 (m, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 3.67 (dd, *J* = 12.0 Hz, *J* = 9.0 Hz, 1H), 3.40 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 6H), 1.19 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 169.0, 139.6, 139.0, 132.6, 130.1, 128.6, 116.4, 81.1, 72.2, 49.3, 41.4, 28.2; IR (film) 2977, 1720, 1491, 1367, 1257, 1147, 815 cm⁻¹; HRMS (ESI-TOF) calc'd for [C17H24ClNO2]⁺([M+H]⁺): *m/z* 310.1568, found 310.1564.

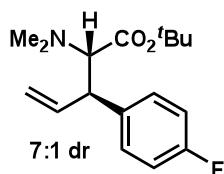


Table 2, Entry 4. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (102 mg, 0.35 mmol, 87%); ¹H NMR (600 MHz, CDCl₃) δ 7.19-7.15 (m, 2H), 6.96 (t, *J* = 9.0 Hz, 2H), 6.11-6.03 (m, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 3.67 (dd, *J* = 12.0 Hz, *J* = 9.0 Hz, 1H), 3.40 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 6H), 1.18 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 169.1, 161.8 (d, *J* = 245 Hz, ¹J_{C-F}), 139.2, 136.8 (d, *J* = 3 Hz, ²J_{C-F}), 130.2 (d, *J* = 8 Hz, ²J_{C-F}), 116.1, 115.3 (d, *J* = 21 Hz, ²J_{C-F}), 81.0, 72.4, 49.2, 41.3, 28.1; IR (film) 2978, 1713, 1510, 1367, 1222, 1149, 826 cm⁻¹; HRMS (ESI-TOF-TOF) calc'd for [C17H24FNO2]⁺([M+H]⁺): *m/z* 294.1864, found 294.1872.

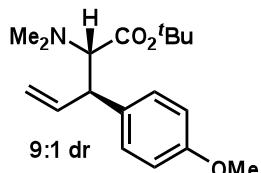


Table 2, Entry 5. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (102 mg, 0.33 mmol, 84%); ¹H NMR (600 MHz, CDCl₃) δ 7.12 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.11-6.03 (m, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 3.76 (s, 3H), 3.64 (dd, *J* = 12.0 Hz, *J* = 9.0 Hz, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 2.42 (s, 6H), 1.18 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 169.3, 158.6, 139.7, 133.2, 129.6, 113.9, 80.8, 72.5, 55.4, 49.2, 41.4, 28.2; IR (film) 2976, 2936, 1720, 1512, 1248, 1147, 1036, 843 cm⁻¹; HRMS (ESI-TOF) calc'd for [C18H27NO3]⁺([M+H]⁺): *m/z* 306.2064, found 306.2059.

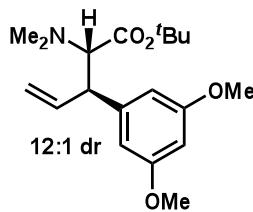


Table 2, entry 6. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 1:1 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (110 mg, 0.33 mmol, 82%): ¹H NMR (600 MHz, CDCl₃) δ 6.37 (d, *J* = 2.0 Hz, 2H), 6.30 (t, *J* = 2.0 Hz, 1H), 6.08-6.01 (m, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 3.75 (s, 6H), 3.61 (dd, *J* = 12.0 Hz, *J* = 9.0 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 6H), 1.21 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 169.2, 160.8, 143.3, 139.1, 116.1, 106.7, 99.0, 80.9, 72.0, 55.4, 50.3, 41.4, 28.2; IR (film) 2976, 2938, 1722, 1597, 1460, 1205, 1154, 1065 cm⁻¹; HRMS (ESI-TOF) calc'd for [C19H29NO4]⁺([M+H]⁺): *m/z* 336.2169, found 336.2179.

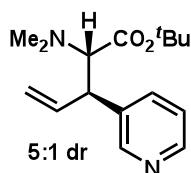


Table 2, Entry 7. A vial fitted with a screw cap septum was charged with Pd₂dba₃•CHCl₃ (4.1 mg, 4 μ mol), P(2-furyl)₃ (3.7 mg, 16 μ mol), and Cs₂CO₃ (390 mg, 1.2 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This procedure was repeated twice. The vial was charged with MeCN (1.2 mL) and *N,N*-dimethylglycine *tert*-butyl ester (95 mg, 0.60 mmol). A solution of 3-pyridyl ethylcarbonate (83 mg, 0.40 mmol) was dissolved in MeCN (0.8 mL) and added to the reaction vial over 4 h via a syringe pump. Upon complete addition of substrate, the reaction was stirred for 20 min at rt. The mixture was filtered through a bÜchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (20:1 to 1:1 CH₂Cl₂:EtOAc gradient eluent) provided the desired product as a white solid (84 mg, 0.30 mmol, 76%): ¹H NMR (600 MHz, CDCl₃) δ 8.46-8.42 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 8.0 Hz, *J* = 5.0 Hz, 1H), 6.11-6.04 (m, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 3.70 (dd, *J* = 12.0 Hz, *J* = 9.0 Hz, 1H), 3.42 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 6H), 1.16 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 168.9, 150.5, 148.3, 138.4, 136.6, 136.0, 123.4, 117.0, 81.4, 72.1, 47.3, 41.4, 28.1; IR (film) 2979, 2828, 2790, 1711, 1368, 1152, 719 cm⁻¹; HRMS (ESI-TOF) calc'd for [C16H24N2O2]⁺([M+H]⁺): *m/z* 277.1910, found 277.1920.

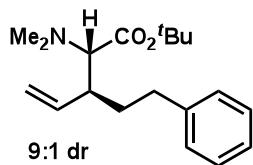


Table 2, Entry 8. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a clear oil (100 mg, 0.33 mmol, 83%): ¹H NMR (600 MHz, CDCl₃): δ 7.27-7.23 (m, 2H), 7.18-7.12 (m, 3H), 5.65-5.58 (m, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 5.12 (d, *J*

= 17.0 Hz, 1H), 2.97 (d, J = 10.0 Hz, 1H), 2.75-2.69 (m, 1H), 2.54-2.46 (m, 2H), 2.31 (s, 6H), 1.69-1.62 (m, 1H), 1.51-1.45 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.2, 142.4, 139.3, 128.6, 128.4, 125.9, 116.8, 81.2, 72.3, 43.9, 41.4, 33.5, 33.3, 28.5; IR (film) 2977, 2933, 1721, 1454, 1367, 1143, 699 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}19\text{H}29\text{NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 304.2271, found 304.2276.

VII. Table 3 Characterization Data

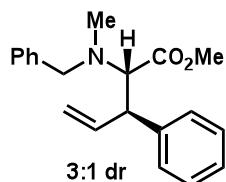


Table 3, Entry 1. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 hexanes:Et₂O eluent) provided the desired product as a clear oil (87 mg, 0.28 mmol, 70%): ^1H NMR (600 MHz, CDCl_3) δ 7.39 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 3H), 7.19 (t, J = 8.0 Hz, 3H), 6.25-6.18 (m, 1H), 5.17 (d, J = 11.0 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 3.92 (d, J = 13.0 Hz, 1H), 3.90-3.86 (m, 1H), 3.70 (d, J = 12.0 Hz, 1H), 3.53 (d, J = 13.0 Hz, 1H), 3.48 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.6, 141.1, 139.5, 139.3, 129.0, 128.7, 128.4, 128.3, 127.2, 127.0, 116.2, 70.5, 58.4, 50.8, 49.7, 38.1; IR (film) 3029, 2948, 1731, 1453, 1163, 699 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}20\text{H}23\text{NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 310.1801, found 310.1811.

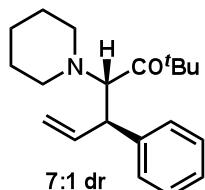


Table 3, Entry 2. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (95:5 hexanes:Et₂O eluent) provided the desired product as a white solid (96 mg, 0.30 mmol, 76%): ^1H NMR (600 MHz, CDCl_3) δ 7.26 (t, J = 8.0 Hz, 2H), 7.21-7.16 (m, 3H), 6.21-6.14 (m, 1H), 5.06 (d, J = 11.0 Hz, 1H), 4.94 (d, J = 17.0 Hz, 1H), 3.77-3.72 (m, 1H), 3.40 (d, J = 12.0 Hz, 1H), 2.78-2.71 (m, 2H), 2.55-2.49 (m, 2H), 1.64-1.57 (m, 2H), 1.54-1.47 (m, 2H), 1.47-1.42 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.3, 141.0, 139.6, 128.8, 128.2, 126.6, 115.3, 80.4, 73.1, 48.7, 28.0, 26.7, 24.8; IR (film) 2934, 1715, 1365, 1255, 1149, 697 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}20\text{H}29\text{NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 316.2271, found 316.2279.



Table 3, Entry 3. A vial fitted with a screw cap septum was charged $\text{Pd}_2\text{dba}_3\bullet\text{CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), Cs_2CO_3 (390 mg, 1.2 mmol), and 1-benzyl-3-piperidone

hydrochloride hydrate (135 mg, 0.60 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This procedure was repeated twice. The vial was charged with MeCN (2.0 mL) and cinnamyl ethylcarbonate (83 mg, 0.40 mmol). After stirring for 4 h at rt, the reaction was filtered through a bÜchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (98 mg, 0.32 mmol, 80%): ¹H NMR (600 MHz, CDCl₃) δ 7.26-7.15 (m, 4H), 7.08-7.00 (m, 4H), 6.71 (d, *J* = 7.0 Hz, 2H), 5.78-5.71 (m, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 3.87 (t, *J* = 10.0 Hz, 1H), 3.56 (d, *J* = 14.0 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H), 2.54-2.47 (m, 1H), 2.36 (d, *J* = 14.0 Hz, 1H), 2.27-2.14 (m, 2H), 2.00-1.94 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 212.3, 141.3, 138.5, 138.0, 128.8, 128.6, 128.3, 128.2, 127.1, 126.7, 116.3, 74.4, 57.5, 49.8, 44.6, 39.1, 26.2; IR (film) 2939, 1710, 1446, 1260, 699 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₂₁H₂₃NO]⁺([M+H]⁺): *m/z* 306.1852, found 306.1853.

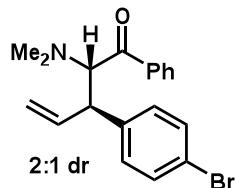


Table 3, Entry 4. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 hexanes:Et₂O eluent) provided the desired product as a yellow solid (133 mg, 0.37 mmol, 93%): ¹H NMR (600 MHz, CDCl₃) 7.68 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.28-6.19 (m, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.02 (t, *J* = 10.0 Hz, 1H), 2.38 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 198.0, 140.4, 139.0, 139.2, 133.0, 131.8, 130.3, 128.7, 127.9, 120.5, 116.7, 69.1, 48.5, 41.5; IR (film) 2936, 2831, 2789, 1672, 1487, 1448, 1199, 1073, 1009, 799, 702 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₁₉H₂₀BrNO]⁺([M+H]⁺): *m/z* 358.0801, found 358.0806.

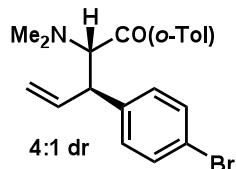


Table 3, Entry 5. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 hexanes:Et₂O eluent) provided the desired product as a off-white solid (139 mg, 0.37 mmol, 93%): ¹H NMR (600 MHz, CDCl₃) 7.34 (d, *J* = 8.0 Hz, 2H), 7.27-7.23 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 4H), 6.25-6.17 (m, 1H), 5.15 (d, *J* = 11.0 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.36 (d, *J* = 11.0 Hz, 1H), 4.02 (dd, *J* = 11.0 Hz, *J* = 9.0 Hz, 1H), 2.40 (s, 6H), 2.28 (d, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 201.8, 140.6, 139.6, 139.1, 137.8, 132.2, 131.8, 131.2, 130.5, 127.9, 125.7, 120.6, 116.6, 72.2, 48.4, 41.5, 20.7; IR (film) 2930, 2790, 1676, 1487, 1252, 1072, 1009, 808, 757, 730, 653 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₂₀H₂₂BrNO]⁺([M+H]⁺): *m/z* 372.0957, found 372.0964.

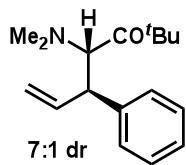


Table 3, Entry 6. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (95:5 hexanes:Et₂O eluent) provided the desired product as a white solid (83 mg, 0.32 mmol, 80%): ¹H NMR (600 MHz, CDCl₃) δ 7.23 (t, *J* = 8.0 Hz, 2H), 7.16-7.10 (m, 3H), 6.28-6.19 (m, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 4.01-3.99 (m, 2H), 2.50 (s, 6H), 0.76 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 211.5, 141.7, 140.1, 129.0, 128.6, 126.6, 116.5, 69.3, 49.5, 43.2, 41.1, 26.6; IR (film) 2966, 1698, 1478, 1454, 1050, 701 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₁₇H₂₅NO]⁺([M+H]⁺): *m/z* 260.2009, found 260.2015.

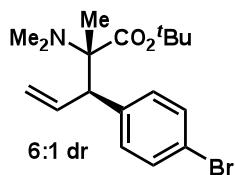


Table 3, Entry 7. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a clear oil (130 mg, 0.35 mmol, 88%): ¹H NMR (600 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.32-6.25 (m, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.17 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 6H), 1.39 (s, 9H), 1.22 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 170.2, 140.5, 137.0, 132.4, 131.0, 120.7, 117.9, 81.6, 68.8, 51.4, 39.9, 28.5, 17.1; IR (film) 2977, 1714, 1488, 1367, 1248, 1168, 1107, 1077, 1011 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₁₈H₂₆BrNO₂]⁺([M+H]⁺): *m/z* 368.1220, found 368.1226.

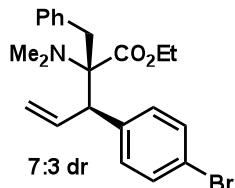


Table 3, Entry 8. Following the typical procedure for the [2,3] Stevens rearrangement (reaction was performed on a 0.80 mmol scale), purification by flash chromatography (9:1 hexanes:Et₂O eluent) provided the desired product as a clear oil (299 mg, 0.72 mmol, 90%): ¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.27-7.24 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.13-6.06 (m, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 17.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.12 (d, *J* = 7.0 Hz, 1H), 3.24 (d, *J* = 15.0 Hz, 1H), 2.86 (d, *J* = 15.0 Hz, 1H), 2.49 (s, 6H), 1.29 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 172.0, 140.4, 139.1, 137.9, 132.3, 131.1, 130.9, 128.1, 126.5, 120.8, 117.0, 72.7, 60.5, 53.0, 41.2, 37.3, 14.7; IR (film) 2981, 1744, 1487, 1257, 1009 cm⁻¹; HRMS (ESI-TOF) calc'd for [C₂₂H₂₆BrNO₂]⁺([M+H]⁺): *m/z* 416.1220, found 416.1217.

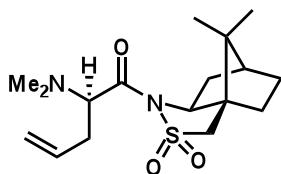


Table 3, Entry 9: Reaction was performed on a 0.20 mmol scale. A vial fitted with a screw cap septum was charged with $\text{Pd}_2\text{dba}_3\text{-CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), Cs_2CO_3 (195 mg, 0.6 mmol), and *N*-(2-(dimethylamino)acetyl)-(1*R*,2*S*)-bornane-10,2-sultam (60 mg, 0.20 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This purging procedure was repeated twice. The vial was sequentially charged with MeCN (1.0 mL) and allyl ethylcarbonate (52 mg, 0.40 mmol). After stirring for 4 h at rt, the reaction was filtered through a Büchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (8:2 to 1:1 hexanes:EtOAc gradient eluent) provided the desired product as a mixture of diastereomers (89% yield, 20:1 dr). The major diastereomer was isolated as a white solid (58 mg, 0.17 mmol, 85%): $[\alpha]_D^{20} +90.0$ (c 0.5, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 5.88-5.78 (m, 1H), 5.10 (d, J = 17.0 Hz, 1H), 5.03 (d, J = 10.0 Hz, 1H), 3.91 (t, J = 7.0 Hz, 1H), 3.86 (t, J = 7.0 Hz, 1H), 3.45 (q, J = 14.0 Hz, 2H), 2.59-2.43 (m, 2H), 2.42 (s, 6H), 2.08-1.99 (m, 2H), 1.92-1.79 (m, 3H), 1.42-1.29 (m, 2H), 1.12 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 134.4, 118.1, 66.5, 65.6, 53.6, 48.6, 48.1, 44.9, 42.3, 38.7, 34.9, 33.3, 26.8, 21.1, 20.3; IR (film) 2958, 1682, 1326, 1221, 1134, 1056, 914, 766 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C17H28N2O3S}]^+([\text{M}+\text{H}]^+)$: m/z 341.2, found 341.2.

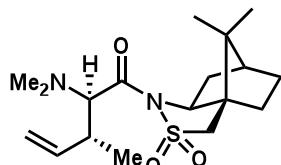


Table 3, Entry 10: Reaction was performed on a 0.20 mmol scale. A vial fitted with a screw cap septum was charged with $\text{Pd}_2\text{dba}_3\text{-CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), Cs_2CO_3 (195 mg, 0.6 mmol), and *N*-(2-(dimethylamino)acetyl)-(1*R*,2*S*)-bornane-10,2-sultam (60 mg, 0.20 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This purging procedure was repeated twice. The vial was sequentially charged with MeCN (1.0 mL) and crotyl ethylcarbonate (60 mg, 0.40 mmol). After stirring for 16 h at rt, the reaction was filtered through a Büchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (95:5 to 8:2 hexanes:EtOAc gradient eluent) provided the desired product as a mixture of diastereomers (97% yield, 20:2:1:0 dr). The major diastereomer was isolated as a white solid (60 mg, 0.17 mmol, 85%): $[\alpha]_D^{20} +71.6$ (c 1, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 5.93-5.84 (m, 1H), 5.09 (d, J = 17.0 Hz, 1H), 5.03 (d, J = 10.0 Hz, 1H), 3.95 (t, J = 7.0 Hz, 1H), 3.71 (d, J = 10.0 Hz, 1H), 3.47 (q, J = 14.0 Hz, 2H), 2.82-2.74 (m, 1H), 2.46 (s, 6H), 2.10 (d, J = 6.0 Hz, 2H), 1.94-1.83 (m, 3H), 1.43-1.31 (m, 2H), 1.13 (s, 3H), 1.03 (d, J = 7.0 Hz, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 141.9, 115.0, 70.2, 65.9, 53.7, 48.3, 48.1, 44.9, 42.2, 39.8, 38.9, 33.5, 26.8, 21.1, 20.4, 17.7; IR (film) 2962, 1686, 1332, 1208, 1132, 1059, 764 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C18H30N2O3S}]^+([\text{M}+\text{H}]^+)$: m/z 355.2, found 355.1.

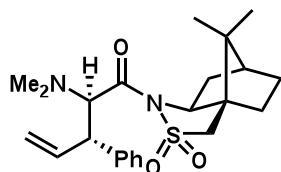
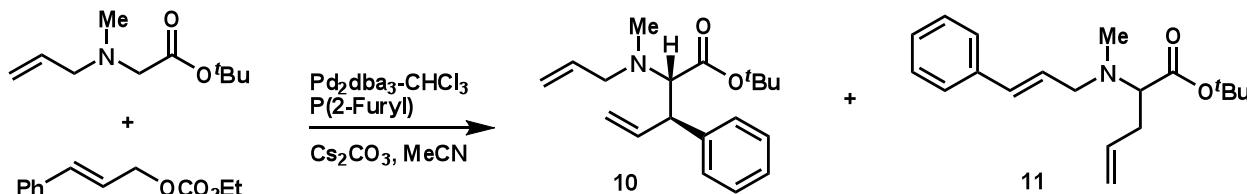


Table 3, Entry 11: Reaction was performed on a 0.40 mmol scale. A vial fitted with a screw cap septum was charged with $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), Cs_2CO_3 (310 mg, 1.2 mmol), and *N*-(2-(dimethylamino)acetyl)-(1*R*,2*S*)-bornane-10,2-sultam (144 mg, 0.48 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This purging procedure was repeated twice. The vial was sequentially charged with MeCN (2.0 mL) and ethyl 1-phenylallyl carbonate (82 mg, 0.40 mmol). After stirring for 14 h at rt, the reaction was filtered through a Büchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (95:5 to 8:2 hexanes:EtOAc gradient eluent) provided the desired product as a mixture of diastereomers (96% yield, 22:2:1:0 dr). The major diastereomer was isolated as a white solid (140 mg, 0.34 mmol, 84%): $[\alpha]_D^{20} +62.5$ (c 0.4, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.13-7.03 (m, 4H), 6.99-6.95 (m, 1H), 6.08-6.00 (m, 1H), 5.00-4.93 (m, 2H), 4.15 (d, $J = 10.0$ Hz, 1H), 3.82 (t, $J = 10.0$ Hz, 1H), 3.17-3.11 (m, 2H), 2.46 (s, 6H), 1.71-1.66 (m, 1H), 1.63-1.58 (m, 2H), 1.45 (br s, 1H), 1.30-1.24 (m, 1H), 1.15-1.02 (m, 3H), 0.63 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 139.9, 139.9, 129.2, 128.6, 127.0, 116.4, 68.5, 65.3, 53.0, 51.5, 47.6, 47.4, 44.4, 41.7, 38.2, 32.9, 26.5, 20.4, 19.9; IR (film) 2957, 1686, 1333, 1207, 1134, 1062, 764, 700 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C}23\text{H}32\text{N}2\text{O}3\text{S}]^+([\text{M}+\text{H}]^+)$: m/z 417.2, found 417.2.

VIII. Mechanistic Experiments

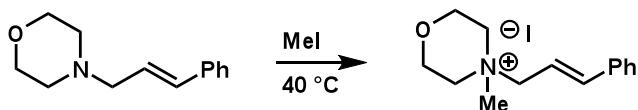


Procedure. Following the typical procedure for the [2,3] Stevens rearrangement, purification by flash chromatography (9:1 / hexanes:Et₂O eluent) provided a mixture of products **10:11** (3.6:1, 94 mg, 0.31 mmol, 78%).

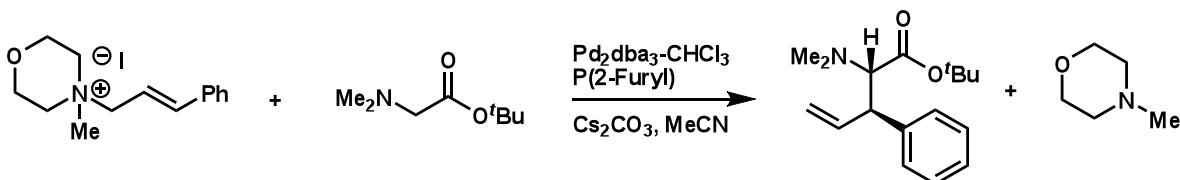
Compound 10: ^1H NMR (600 MHz, CDCl_3) δ 7.297.22 (m, 2H), 7.21-7.14 (m, 3H), 6.14-6.06 (m, 1H), 5.87-5.76 (m, 1H), 5.21 (d, $J = 17.0$ Hz, 1H), 5.13 (d, $J = 10.0$ Hz, 1H), 5.06 (d, $J = 10.0$ Hz, 1H), 5.00 (d, $J = 17.0$ Hz, 1H), 3.71 (dd, $J = 12.0$ Hz, $J = 8.0$ Hz, 1H), 3.54 (d, $J = 12.0$ Hz, 1H), 3.36 (dd, $J = 14.0$ Hz, $J = 5.0$ Hz, 1H), 3.04 (dd, $J = 14.0$ Hz, $J = 7.0$ Hz, 1H), 2.36 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 141.2, 139.7, 136.6, 128.9, 128.5, 126.9, 117.5, 115.9, 80.9, 70.5, 57.4, 49.9, 38.0, 28.1; IR (film) 2978, 1723, 1367, 1256, 1149, 918, 700 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}19\text{H}27\text{NO}2]^+([\text{M}+\text{H}]^+)$: m/z 302.2114, found 302.2121.

Compound 11: ^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, $J = 7.0$ Hz, 2H), 7.31 (t, $J = 7.0$ Hz, 2H), 7.22 (t, $J = 7.0$ Hz, 1H), 6.53 (d, $J = 15.0$ Hz, 1H), 6.20 (dt, $J = 15.0$ Hz, $J = 7.0$ Hz, 1H), 5.85-5.77 (m, 1H), 5.11 (d, $J = 17.0$ Hz, 1H), 5.05 (d, $J = 11.0$ Hz, 1H), 3.41 (dd, $J = 14.0$ Hz, $J = 5.0$ Hz, 1H), 3.31 (t, $J = 7.0$ Hz, 2H), 2.55-2.48 (m, 1H), 2.42-2.36 (m, 1H), 2.37 (s, 3H), 1.49

(s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 137.3, 135.1, 132.6, 128.7, 128.1, 127.5, 126.5, 117.1, 81.2, 66.2, 57.1, 38.2, 34.7, 28.6; IR (film) 2934, 1747, 1495, 1392, 1255, 1150, 996, 791, 748 cm^{-1} ; HRMS (ESI-TOF) calc'd for $[\text{C}19\text{H}27\text{NO}_2]^+([\text{M}+\text{H}]^+)$: m/z 302.2114, found 302.2121.



4-Methyl-4-cinnamylmorpholinium iodide: A screw cap vial was charged with neat 4-cinnamylmorpholine⁶ (406 mg, 2.0 mmol) and iodomethane (1.2 mL, 20 mmol). The vial was then sealed and heated to 40 °C. After 15 min, the reaction was cooled to rt and concentrated under reduced pressure to yield the product as a light brown solid (681 mg, 1.97 mmol, 98%). The crude compound was used without further purification: ^1H NMR (600 MHz, CDCl_3); δ 7.51-7.45 (m, 2H), 7.40-7.28 (m, 3H), 7.25 (d, J = 13.0 Hz, 1H), 6.40-6.30 (m, 1H), 4.84 (d, J = 7.0 Hz, 2H), 4.14-4.00 (m, 4H), 3.74 (br s, 4H), 3.59 (s, 3H).



Procedure: A vial fitted with a screw cap septum was charged $\text{Pd}_2\text{dba}_3\bullet\text{CHCl}_3$ (4.1 mg, 4 μmol), $\text{P}(2\text{-furyl})_3$ (3.7 mg, 16 μmol), Cs_2CO_3 (195 mg, 0.60 mmol), and 4-methyl-4-cinnamylmorpholinium iodide (69 mg, 0.20 mmol). The reaction vial was placed under vacuum for several minutes and then back-filled with nitrogen. This procedure was repeated twice. The vial was charged with MeCN (2.0 mL) and *N,N*-dimethylglycine *tert*-butyl ester (48 mg, 0.30 mmol). After stirring for 3 h at rt, the reaction was filtered through a Büchner funnel under vacuum filtration with EtOAc and then concentrated under reduced pressure. Purification by flash chromatography (9:1 to 8:2 hexanes:Et₂O gradient eluent) provided the desired product as a white solid (46 mg, 0.17 mmol, 84%). Spectral data were identical to the previously reported values (Table 1, Entry 1).

⁶ Li, O.; Law, K.; Ho, C.; Yang, D. *J. Org. Chem.* **2008**, *73*, 8829-8837

IX. Determination of Relative and Absolute Stereochemistry of Products

A. Crystallographic Information

A sample of **6b** was recrystallized from hexanes (slow evaporation). The resulting crystals were suitable for X-ray diffraction and the structure was solved (Figure S01). This structure allowed the assignment of relative configuration as shown. The relative configuration of other similar products was assigned by analogy. We thank Dr. Vincent Lynch (Manager of the X-ray Diffraction Lab at UT Austin) for the X-ray structural analysis. The CIF file is available as a separate file in the supporting information.

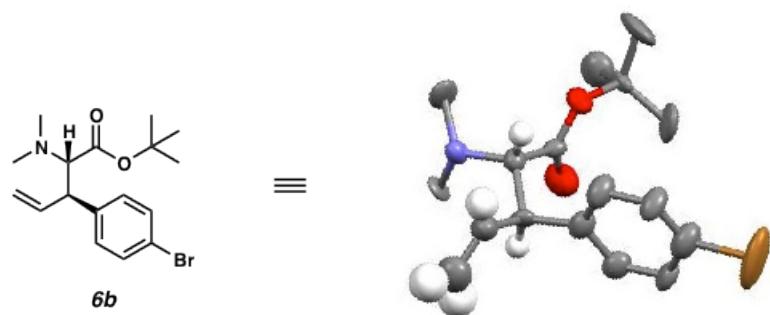


Figure S01

A sample of **6g** was recrystallized from hexanes (slow evaporation). The resulting crystals were suitable for X-ray diffraction and the structure was solved (Figure S02). This structure allowed the assignment of relative configuration as shown. The relative configuration of other similar products was assigned by analogy. We thank Dr. Vincent Lynch (Manager of the X-ray Diffraction Lab at UT Austin) for the X-ray structural analysis. The CIF file is available as a separate file in the supporting information.

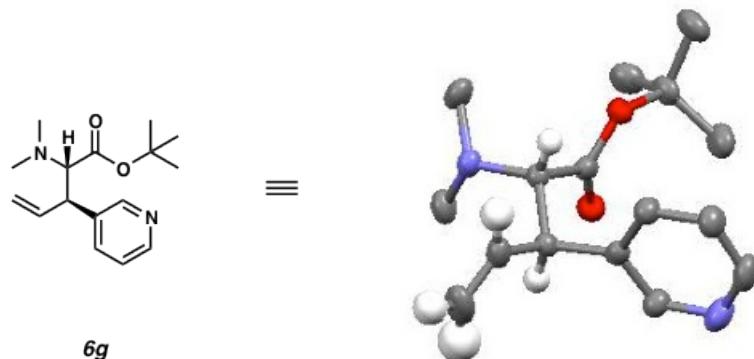
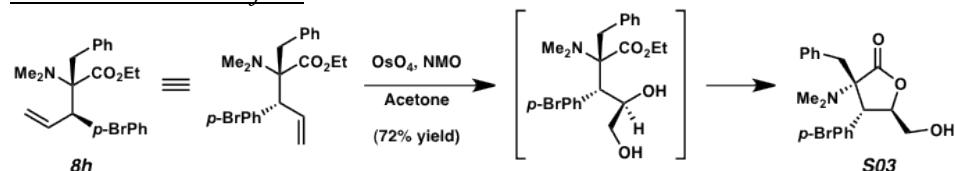
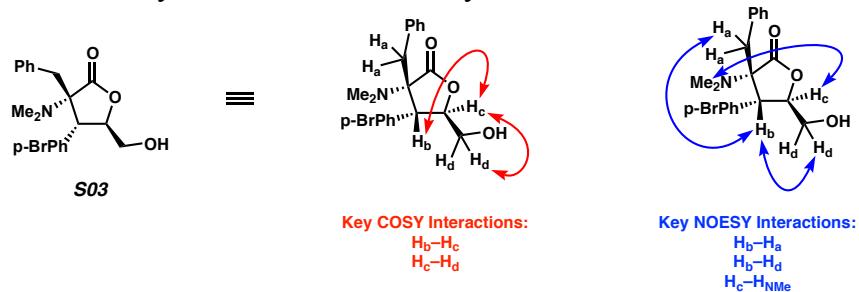


Figure S02

B. Derivatization of 8h

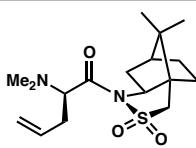
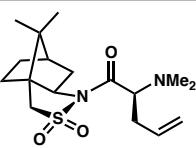
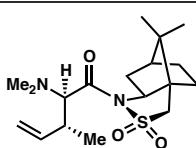
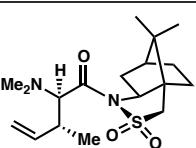
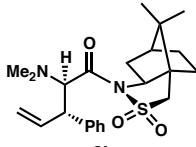


Compound S03: A round bottom flask was charged with compound **8h** (42 mg, 0.10 mmol) and acetone (1.0 ml). The reaction was sequentially charged with 4-methylmorpholine *N*-oxide (18mg, 0.15 mmol) and osmium tetroxide (1.3 mg, 5 μmol , 4 wt% H_2O). After stirring for 15 h at rt, the reaction was diluted with EtOAc (50 ml) and washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. Purification by flash chromatography (9:1 to 7:3 hexanes: EtOAc gradient eluent) provided the desired product as a white solid (28 mg, 0.07 mmol, 72%). ^1H NMR (500 MHz, CDCl_3); δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.37-7.26 (m, 7H), 4.83-4.77 (m, 1H), 3.66 (d, $J = 13.0$ Hz, 1H), 3.60 (d, $J = 14.0$ Hz, 1H), 3.44 (d, $J = 10.0$ Hz, 1H), 3.14 (d, $J = 13.0$ Hz, 1H), 2.95 (d, $J = 14.0$ Hz, 1H), 2.25 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 136.5, 134.0, 131.9, 131.0, 130.7, 129.1, 127.6, 121.8, 82.0, 72.4, 62.9, 44.8, 41.4, 38.1; IR (film) 3422 (br), 2954, 1760, 1492, 1170, 1072, 1009, 909, 703 cm^{-1} ; LCMS (ESI) calc'd for $[\text{C20H22BRNO}_3]^+([\text{M}+\text{H}]^+)$: m/z 404.1, found 404.0. The relative configuration of **S03** was confirmed by detailed 2D NMR analysis:



C. Comparison of Oppolzer Camphorsultam Products with Known Structures

The absolute stereochemistry of compound **8i** was determined by comparing its optical rotation to the optical rotation of its enantiomer, which was reported in the literature.² The absolute stereochemistry of compound **8j** was determined by comparing its reported optical rotation in the literature.² The absolute stereochemistry of **8k** was assigned by analogy.

<i>Our Chemistry</i>	<i>Reference 7</i>
 <p>8i $[\alpha]_D^{20} +90.0$ (c 0.5, CHCl_3)</p>	 <p>$[\alpha]_D^{20} -93.6$ (c 1, CHCl_3)</p>
 <p>8j $[\alpha]_D^{20} +71.6$ (c 1, CHCl_3)</p>	 <p>$[\alpha]_D^{20} +65.4$ (c 1, CHCl_3)</p>
 <p>8k $[\alpha]_D^{20} +62.5$ (c 0.4, CHCl_3)</p>	—

X. ^1H and ^{13}C Spectra

