# **Supplementary Information**

# Iridium-Catalyzed Regiospecific and Stereospecific Allylic Amination for the Syntheses of α,β-Unsaturated γ-Amino Esters and the Bifurcation of the Reaction Pathway Leading to the Formation of Oxazolidin-2-ones

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#### **General Information**

General Methods: Experiments involving moisture- and/or air-sensitive compounds were conducted under an inert atmosphere in an argon-filled drybox or by standard Schlenk techniques. Non-aqueous reagents were transferred by hypodermic syringe under an atmosphere of argon. When necessary, solvents were degassed by purging with argon for at least 15 min just prior to use. Heating was accomplished by silicon oil bath using a temperature controller. Organic solutions were concentrated under reduced pressure using a Büchi rotatory evaporator, unless otherwise noted. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates ( $60-F_{254}$ ) using UV light as a visualizing agent and a KMnO<sub>4</sub> solution or a ceric ammonium molybdate (CAM) solution, and heat as developing agent. Flash chromatography was carried out with ZEOCHEM ZEOprep 60 (particle size 40–63 µm) according to the procedure of Still and coworkers.<sup>[1]</sup> Yields refer to chromatographically and spectroscopically (<sup>1</sup>H NMR) homogeneous (>95%) materials, unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AVANCE III 300 (300 MHz and 75.5 MHz, respectively) spectrometer. Chemical shifts of the <sup>1</sup>H NMR (CDCl<sub>3</sub>: 7.26 ppm) and <sup>13</sup>C NMR (CDCl<sub>3</sub>: 77.0 ppm, C<sub>6</sub>D<sub>6</sub>: 168.02 ppm) spectra were referenced to residual solvent peaks or tetramethylsilane (0.00 ppm) as an internal standard. <sup>1</sup>H NMR spectra are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. When necessary, the multiplicities of the carbons were determined by DEPT (Distortionless Enhancement by Polarization Transfer) experiments. Samples for NOESY experiments were deoxygenated by applying freeze-pump-thaw (3-4 cycles) to a tick-wall NMR tube equipped with a J-Young valve. HPLC analysis was performed on a Young Lin instrument YL9100 HPLC system using chiral stationary phase columns (Daicel Chiralcel OD-H 250 × 4.6 mm ID and Daicel Chiralpak AD-H 250 × 4.6 mm ID). Optical rotations were obtained using a Rudolph Autopol III digital polarimeter and optical rotation data are reported as follows:  $[\alpha]_D^{22}$  (concentration c = g/100 mL, solvent). Melting points were measured using an electrothermal IA9100 digital melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained from the Korea Basic Science Institute, Daegu Center, Daegu, Korea on a JEOL

<sup>[1]</sup> W. C. Still, M, Kahn, A, Mitra J. Org. Chem. 1978, 43, 2923–2925.

JMS700 high-resolution mass spectrometer using the technique of EI (electron impact ionization) or FAB (fast atom bombardment).

Materials: Unless otherwise noted, all reagents were purchased at the highest commercial quality from common commercial suppliers (Sigma Aldrich, TCI, Acros and Strem) and used without further purification. [Ir(cod)Cl]<sub>2</sub> was purchased from Strem and stored in an argon-filled drybox. Phosphoramidite ligand L1 and L2 were prepared according to the literature procedures and stored in an argon-filled drybox.<sup>[2]</sup> (E)-Ethyl 2-hydroxy-4-phenylbut-3-enoate (1") was prepared through the NaBH<sub>4</sub> reduction of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate<sup>[3]</sup> using the literature procedure.<sup>[4]</sup> The Stewart-Grubbs catalyst was purchased from Sigma Aldrich and stored in a desiccator. Tetrahydrofuran (THF), 1,2-dimethoxyethane and 1,4-dioxane were freshly distilled from sodium/benzopheone ketyl under an atmosphere of argon. Nitromethane was refluxed over CaH<sub>2</sub>, fractionally distilled under an atmosphere of argon and stored over 4 Å molecular sieves. Acetonitrile and dichloromethane were freshly distilled from  $CaH_2$  under an atmosphere of argon. Diethyl ether was freshly distilled from LiAlH<sub>4</sub> under an atmosphere of argon. Allylamine was dried with KOH overnight and fractionally distilled from CaCl<sub>2</sub> just prior to use under an atmosphere of argon. Benzylamine (Na), diallylamine (KOH), morpholine (Na) and propylamine (Zn dust) were dried with KOH overnight, fractionally distilled from an appropriate drying agent under an atmosphere of argon and stored over 3 Å molecular sieves. Aniline and N-methylaniline were dried with KOH overnight, fractionally distilled from KOH under reduced pressure and stored over 3 Å molecular sieves. A solution of lithium hexamethyldisilazide (LiHMDS) was freshly prepared by dissolving lithium hexamethyldisilazide (Sigma Aldrich) in anhydrous THF (1.0 M solution) under an inert atmosphere at room temperature just prior to use.

 <sup>[2]</sup> For the preparation of L1, see: a) C. R. Smith, D. J. Mans, T. V. RajanBabu, Org. Synth. 2008, 85, 238–247. For the preparation of L2, see: b) K. Tissot-Croset, D. Polet, A. Alexakis, Angew. Chem. 2004, 116, 2480–2482; Angew. Chem. Int. Ed. 2004, 43, 2426-2428; c) D. Polet, A. Alexakis, K. Tissot-Croset, C. Corminboeuf, K. Ditrich, Chem. Eur. J. 2006, 12, 3596–3509.

<sup>[3]</sup> D. Belmessieri, L. C. Morrill, C. Simal, A. M. Z. Slawin, A. D. Smith, J. Am. Chem. Soc. 2011, 133, 2714–2720 (See Supporting Information).

<sup>[4]</sup> T. Ziegler, F. Bien, C. Jurisch, *Tetrahedron: Asymmetry* **1998**, *9*, 765–768.

#### **Experimental Procedures**



General Procedure for Olefin Cross-Metathesis Reaction: A 100-mL Schlenk-type flask equipped with a magnetic stirring bar and a reflux condenser was charged with the Stewart-Grubbs catalyst (57.2 mg, 0.100 mmol, 2.00 mol%), evacuated and back-filled with argon (3 cycles). A solution of allylic alcohol (5.00 mmol, 1.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL in total) was added to the flask containing the catalyst via double-ended needle. The resultant dark green mixture was treated with an appropriate acrylate (25.0 mmol, 5.00 equiv) and then heated under reflux in a pre-heated oil bath (bath temperature = 53  $^{\circ}$ C) for 24 h. After which the mixture was cooled to room temperature and concentrated to afford a residue, which was purified by flash column chromatography (hexanes/EtOAc) on silica gel to afford the desired (E)- $\alpha$ , $\beta$ -unsaturated  $\gamma$ -hydroxy ester as a single *trans*-diastereomer. When ethyl acrylate or methyl acrylate was employed, the following procedure was adapted to remove an excess amount of the acrylate. Upon completion of the olefin CM reaction, the reaction mixture was cooled to room temperature and the reaction vessel was equipped with a fractional distillation apparatus. Under an atmosphere of argon, the mixture was heated gradually in an oil bath up to 105 °C. During the course of the heating a mixture consisting of acrylates and dichloromethane was distilled off and collected in a pear-shaped flask. Heating was continued until the distillation ceased. The system was then allowed to cool to room temperature and the distillation apparatus was carefully disassembled. The flask containing the crude reaction mixture along with a small amount of acrylates was connected to a high-vacuum line equipped with a cold trap and the mixture was stirred vigorously for 5 min. The flask was then disconnected from the line. All the apparatuses used were washed thoroughly with methanol and the wastes were collected and treated with an aqueous solution of KOH to destroy the acrylates.

**Preparation of (E)-Ethyl 4-Hydroxy-4-phenylbut-2-enoate (1a'):**<sup>[5]</sup> Prepared OH CO<sub>2</sub>Et using 1-phenylprop-2-en-1-ol<sup>[6]</sup> (671 mg, 5.00 mmol, 1.00 equiv) and ethyl acrylate (Caution! Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (E)-ethyl 4-hydroxy-4-phenylbut-2-enoate (842 mg, 82%) was isolated (hexanes/EtOAc =  $4:1 \rightarrow 3.5:1$ ) as a yellow oil. Alternatively, it can be prepared from (E)-ethyl 4-oxobut-2-enoate as follows. To a cold solution of (E)ethyl 4-oxobut-2-enoate (1.28 g, 10.0 mmol, 1.00 equiv) in anhydrous THF (24 mL) at -78 °C was added dropwise phenylmagnesium bromide (1.0 M solution in THF, 12.0 mL, 12.0 mmol, 1.20 equiv) and the mixture was stirred at the same temperature for an additional 10 min. The reaction was quenched with a saturated solution of ammonium chloride (20 mL) and the mixture was extracted with EtOAc ( $3 \times 15$  mL). The combined extract was washed with water and brine (a saturated aqueous solution of NaCl), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc =  $3.8:1 \rightarrow 3.5:1$ ) on silica gel to afford the desired carbinol (1.33 g, 65%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.38–7.26 (m, 5H), 7.02 (dd, J = 15.6, 4.8 Hz, 1H), 6.12 (dd, J = 15.6, 1.5 Hz, 1H), 5.31 (d, J = 3.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.78 (br s, 1H), 1.26 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 166.4, 148.4, 140.9, 128.8, 128.4, 126.6, 120.3, 73.5, 60.5, 14.2; HRMS (EI) exact mass calculated for  $[M]^+$  (C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>) requires m/z 206.0943, found m/z 206.0944.

Preparation of (*E*)-Methyl 4-Hydroxy-4-phenylbut-2-enoate (1e'): Prepared using 1-phenylprop-2-en-1-ol (671 mg, 5.00 mmol, 1.00 equiv) and methyl acrylate (**Caution!** Acrid odor) (2.15 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)methyl 4-hydroxy-4-phenylbut-2-enoate (811 mg, 69%) was isolated (hexanes/EtOAc =  $4:1 \rightarrow 3.5:1 \rightarrow 3:1$ ) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.35–7.25 (m, 5H), 7.00 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.11 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.26 (d, *J* = 4.2 Hz, 1H), 3.68 (s, 3H), 3.16 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  167.0, 149.1, 140.8, 128.7, 128.1, 126.5, 119.4, 73.2, 51.6; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>) requires *m/z* 192.0786, found *m/z* 192.0789.

<sup>[5]</sup> S. Rodriguez, M. Kneeteman, J. Izquierdo, I. Lopez, F. V. Gonzalez, G. Peris, *Tetrahedron* 2006, 62, 11112– 11123.

<sup>[6]</sup> C. J. Brown, G. M. Miller, M. W. Johnson, R.G. Bergman, K. N. Raymond, J. Am. Chem. Soc. 2011, 133, 11964–11966 (See Supporting Information).

Preparation of (*E*)-tert-Butyl 4-Hydroxy-4-phenylbut-2-enoate (1f'): Prepared using 1-phenylprop-2-en-1-ol (671 mg, 5.00 mmol, 1.00 equiv) and tert-butyl acrylate (3.20 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-tert-butyl 4hydroxy-4-phenylbut-2-enoate (983 mg, 88%) was isolated (hexanes/EtOAc = 4:1 $\rightarrow$ 3.5:1) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.38–7.28 (m, 5H), 6.92 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.03 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.29 (t, *J* = 3.6 Hz, 1H), 2.64 (br s, 1H), 1.46 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.8, 147.4, 141.1, 128.7, 128.2, 126.5, 122.0, 80.6, 73.4, 28.0; mp 42–46 °C, HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>) requires *m/z* 234.1256, found *m/z* 234.1255.

Preparation of (*E*)-Ethyl 4-Hydroxy-6-phenylhex-2-enoate (1h'): Prepared using 5-phenylpent-1-en-3-ol<sup>[7]</sup> (811 mg, 5.00 mmol, 1.00 equiv) and ethyl acrylate (**Caution!** Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-hydroxy-6-phenylhex-2-enoate (900 mg, 77%) was isolated (hexanes/EtOAc = 3:1) as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.31–7.26 (m, 2H), 7.21–7.17 (m, 3H), 6.96 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.05 (dd, *J* = 15.6, 1.5 Hz, 1H), 4.35–4.32 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.83–2.67 (m, 2H), 1.99–1.81 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.5, 149.9, 141.2, 128.5, 128.4, 126.0, 120.4, 70.3, 60.5, 37.9, 31.4, 14.2; HRMS (FAB) exact mass calculated for [M+1]<sup>+</sup> (C<sub>14</sub>H<sub>19</sub>O<sub>3</sub>) requires *m*/*z* 235.1334, found *m*/*z* 235.1337.



CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-hydroxy-4-*o*-tolylbut-2-enoate (1.02 g, 93%) was isolated (hexanes/EtOAc = 4:1→3.5:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.38–7.34 (m, 1H), 7.26–7.15 (m, 3H), 7.04 (dd, *J* = 15.6, 4.5 Hz, 1H), 6.14 (dd, *J* = 15.6, 1.8 Hz, 1H), 5.57 (dd, *J* = 3.9, 2.7 Hz, 1H), 4.18 (q, *J* = 7.2 Hz,

<sup>[7]</sup> G. A. Molander, L. Jean-Gérard, J. Org. Chem. 2009, 74, 1297–1303 (See Supporting Information).

<sup>[8]</sup> N. Marion, R. Gealageas, S. P. Nolan, Org. Lett. 2007, 9, 2653–2925 (See Supporting Information).

2H), 2.38 (s, 3H), 2.17 (br d, J = 3.9 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.5, 148.0, 138.8, 135.4, 130.8, 128.2, 126.5, 126.4, 120.4, 70.4, 60.5, 19.1, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>) requires *m/z* 220.1099, found *m/z* 220.1102.

OH Pr CO<sub>2</sub>Et Pr Br

Preparation of (E)-Ethyl 4-(2-Bromophenyl)-4-hydroxybut-2-enoate (1k'):
<sup>t</sup> Prepared using 1-(2-bromophenyl)prop-2-en-1-ol<sup>[9]</sup> (1.07 g, 5.00 mmol, 1.00 equiv) and ethyl acrylate (Caution! Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv)

in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-(2-bromophenyl)-4-hydroxybut-2-enoate (1.37 g, 96%) was isolated (hexanes/EtOAc = 4:1 $\rightarrow$ 3.5:1) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.56–7.46 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.19–7.14 (m, 1H), 7.02 (dd, *J* = 15.6, 7.5 Hz, 1H), 6.20 (dd, *J* = 15.6, 1.8 Hz, 1H), 5.78 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.69 (br s, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.5, 146.9, 140.0, 132.8, 129.6, 128.2, 128.0, 122.4, 120.8, 71.9, 60.6, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>12</sub>H<sub>13</sub>BrO<sub>3</sub>) requires *m/z* 284.0048, found *m/z* 284.0045.



5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-(4-bromophenyl)-4-hydroxybut-2-enoate (1.15 g, 81%) was isolated (hexanes/EtOAc =  $3:1 \rightarrow 2.5:1$ ) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.49 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.98 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.13 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.32 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.37 (br d, *J* = 3.3 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.3, 147.8, 139.8, 131.9, 128.2, 122.2, 120.7, 72.8, 60.6, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>12</sub>H<sub>13</sub>BrO<sub>3</sub>) requires *m/z* 284.0048, found *m/z* 284.0050.

<sup>[9]</sup> H. Muratake, M. Natsume, H. Nakai, *Tetrahedron* 2004, 60, 11783–11803.

<sup>[10]</sup> W. J. Logan, J. S. Parker, M. S. Hallside, J. W. Burton, Org. Lett. 2012, 14, 2940–2943 (See Supporting Information).



**Preparation of** (*E*)-Ethyl 4-Hydroxy-4-(4-methoxyphenyl)but-2enoate (1m<sup>'</sup>): Prepared using 1-(4-methoxyphenyl)prop-2-en-1-ol<sup>[9]</sup> (821 mg, 5.00 mmol, 1.00 equiv) and ethyl acrylate (Caution! Acrid odor)

(2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-hydroxy-4-(4-methoxyphenyl)but-2-enoate (1.37 g, 96%) was isolated (hexanes/EtOAc =  $3:1 \rightarrow 2.5:1$ ) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.27–7.24 (m, 2H), 7.03 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.13 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.29 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.30 (br s, 1 H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.5, 159.6, 148.7, 133.1, 128.0, 120.0, 114.2, 73.1, 60.5, 55.3, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>) requires *m/z* 236.1049, found *m/z* 236.1051.

Preparation of (*E*)-Ethyl 4-(Furan-3-yl)-4-hydroxybut-2-enoate (1n'): Prepared using 1-(furan-3-yl)prop-2-en-1-ol<sup>[11]</sup> (621 mg, 5.00 mmol, 1.00 equiv) and ethyl acrylate (**Caution!** Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-(furan-3-yl)-4-hydroxybut-2-enoate (395 mg, 40%) was isolated (hexanes/EtOAc =  $3:1 \rightarrow 2.5:1$ ) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.42–7.41 (m, 2H), 7.05 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.40 (s, 1H), 6.14 (dd, J = 15.6, 1.5 Hz, 1H), 5.35 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.31 (br s, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.4, 147.6, 143.8, 139.7, 126.0, 120.8, 108.8, 66.0, 60.6, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>) requires *m/z* 196.0736, found *m/z* 196.0738.

BocO  $CO_2Et$  Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)but-2-enoate (1i): Prepared using allyl *tert*-butyl carbonate<sup>[12]</sup> (791 mg, 5.00 mmol, 1.00 equiv) and ethyl acrylate (Caution! Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL), (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)but-2-enoate (976 mg, 77%) was isolated (hexanes/EtOAc = 15:1 $\rightarrow$ 12:1) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.94 (dt, *J* = 15.6, 4.5 Hz, 1H), 6.06 (dt, *J* = 15.9, 1.8 Hz, 1H), 4.73 (dd, *J* = 4.5, 1.8 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5

 <sup>[11]</sup> M. Lafrance, M. Roggen, E. M. Carreira, *Angew. Chem.* 2012, *124*, 3527–3530; *Angew. Chem. Int. Ed.* 2012, *51*, 3470–3473 (See Supporting Information).

<sup>[12]</sup> J. M. Kraus, H. C. Gits, R. B. Silverman, Tetrahedron Lett. 2012, 53, 1319–1322.

MHz)  $\delta$  165.8, 152.9, 140.9, 122.3, 82.7, 64.9, 60.6, 27.7, 14.2; HRMS (EI) exact mass calculated for  $[M+1]^+$  (C<sub>11</sub>H<sub>19</sub>O<sub>5</sub>) requires *m/z* 231.1232, found *m/z* 231.1234.

Preparation of (*E*)-Ethyl 3-(2-oxo-1,3-dioxolan-4-yl)acrylate (10): The reaction of 4-vinyl-1,3-dioxolan-2-one (571 mg, 5.00 mmol, 1.00 equiv) with ethyl acrylate (Caution! Acrid odor) (2.50 g, 25.0 mmol, 5.00 equiv) in dry degassed CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was carried out for 36 h under reflux, (*E*)-ethyl 3-(2-oxo-1,3-dioxolan-4-yl)acrylate (655 mg, 70%) was isolated (hexanes/EtOAc =  $3:1 \rightarrow 2.5:1 \rightarrow 2.3:1 \rightarrow 2:1$ ) as a brown oil along with the corresponding (*Z*)-isomer (143 mg, 15%), which was eluted first.

Characterization data for **10**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.87 (dd, J = 15.6, 5.4 Hz, 1H), 6.21 (d, J = 15.9 Hz, 1H), 5.32 (dd, J = 13.2, 7.2 Hz, 1H), 4.68 (t, J = 8.4 Hz, 1H), 4.28–4.20 (m, 3H), 1.31 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  164.8, 154.0, 139.3, 125.0, 74.6, 68.4, 61.1, 14.1; HRMS (FAB) exact mass calculated for [M+1]<sup>+</sup> (C<sub>8</sub>H<sub>11</sub>O<sub>5</sub>) requires *m/z* 187.0606, found *m/z* 187.0608.

Characterization data for *cis*-isomer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.48 (dd, *J* = 11.4, 6.0 Hz, 1H), 6.07– 5.99 (m, 2H), 4.94 (t, *J* = 9.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.16–4.10 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.3, 154.7, 145.2, 122.8, 74.6, 61.1, 14.0; HRMS (FAB) exact mass calculated for [M+1]<sup>+</sup> (C<sub>8</sub>H<sub>11</sub>O<sub>5</sub>) requires *m*/*z* 187.0606, found *m*/*z* 187.0605.



**Preparation of** (*E*)-Ethyl 4-(Methoxycarbonyloxy)-4-phenylbut-2-enoate (1a) : A mixture of (*E*)-ethyl 4-hydroxy-4-phenylbut-2-enoate (1<sup>'</sup>, 880 mg, 4.27 mmol, 1.00 equiv) and 4-(dimethylamino)pyridine (26.1 mg, 0.213 mmol, 5.00 mol%) in anhydrous dichloromethane (14.0 mL) was treated with dry pyridine (2.02 g, 25.6 mmol, 6.00 equiv). The mixture was cooled in an ice-water bath and methyl chloroformate (1.20 g, 12.8 mmol, 3.00 equiv) was added dropwise. The cooling bath was removed and the mixture was heated under reflux in a pre-heated oil bath (bath temperature = 53 °C) for 15 h. After which the mixture was

cooled to room temperature and extracted with  $CH_2Cl_2$  (3 × 15 mL). The combined extract was washed successively with 1 N HCl, water and brine. The resultant organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc = 10:1) on silica gel to afford the title compound (965 mg, 90%) as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.39–7.34 (m, 5H), 7.01 (dd, *J* = 15.9, 5.1 Hz, 1H), 6.22 (dd, *J* = 5.1, 1.8 Hz, 1H), 6.09 (dd, *J* = 15.9, 1.8 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  165.8, 154.7, 143.8, 136.6, 129.0, 128.9, 127.3, 122.0, 78.0, 60.7, 55.0, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>) requires *m/z* 264.0998, found *m/z* 264.0995.



**Preparation of (***E***)-Ethyl 2-(Methoxycarbonyloxy)-4-phenylbut-3-enoate (1c) :** A mixture of (*E*)-ethyl 2-hydroxy-4-phenylbut-3-enoate<sup>[13]</sup> (1<sup>''</sup>, 700 mg, 3.39 mmol, 1.00 equiv) and pyridine (1.61 g, 20.4 mmol, 6.00 equiv) in anhydrous dichloromethane (14.0 mL) was cooled in an ice-water bath and methyl chloroformate (964 mg, 10.2 mmol, 3.00 equiv) was added dropwise. The cooling bath was removed and the mixture was heated under reflux in a pre-heated oil bath (bath temperature = 53 °C) for 15 h. After which the mixture was cooled to room temperature and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The combined extract was washed successively with 1 N HCl, water and brine. The resultant organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc = 12:1) on silica gel to afford the title compound (662 mg, 78%) as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.39–7.28 (m, 5H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.32– 4.25 (m, 2H), 3.85 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 168.3, 154.8, 135.4, 135.3, 128.6, 128.5, 126.8, 120.2, 75.9, 62.0, 55.3, 14.1; mp 34–36 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>) requires *m/z* 264.0998, found *m/z* 264.1000.

<sup>[13]</sup> T. Ziegler, F. Bien, C. Jurisch, Tetreahedron: Asymmetry 1998, 9, 765–768.



**Preparation of** (*E*)-**Ethyl 2-***tert*-**Butoxycarbonyloxy-4-phenylbut-3-enoate (1d):** A mixture of (*E*)-ethyl 2-hydroxy-4-phenylbut-3-enoate (1<sup>''</sup>, 230 mg, 1.05 mmol, 1.00 equiv), di-*tert*-butyl dicarbonate (230 mg, 1.05 mmol, 1.50 equiv), 4-(dimethylamino)pyridine (4.3 mg, 0.035 mmol, 0.050 equiv) and pyridine (167 mg, 2.11 mmol, 3.00 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL) was heated under reflux in a pre-heated oil bath (bath temperature = 53 °C) for 15 h. After which the mixture was cooled to room temperature and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined extract was washed successively with 1 N HCl, water and brine. The resultant organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc = 12:1) on silica gel to afford the title compound (190 mg, 88%) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.41–7.26 (m, 5H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.31– 4.21 (m, 2H), 1.52 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  168.6, 152.5, 135.6, 135.2, 128.6, 128.5, 126.8, 120.6, 83.2, 75.3, 61.8, 27.6, 14.1; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>) requires *m/z* 306.1467, found *m/z* 306.1464.

$$\mathbb{R}^{1} \xrightarrow{OH} OR^{2} \xrightarrow{1) \text{ LiHMDS, THF, -78 °C, 60 min}} \mathbb{R}^{1} \xrightarrow{OBoc} OR^{2}$$

General Procedure for the Formation of *tert*-Butoxy Carbonates: To a cold solution of carbinol (1.00 equiv) in anhydrous THF (2.50 mL/1.00 mmol) at -78 °C (acetone/dry ice bath) was added dropwise LiHMDS (1.0 M solution in THF, 1.20 equiv) via double-ended needle and the resultant mixture was kept stirring at the same temperature for 60 min. To this mixture was added a solution of di-*tert*-butyl dicarbonate (1.20 equiv) in THF (2.00 mL/1.00 mmol). The system was allowed to slowly warm to 0 °C over several hours. The reaction was then quenched with brine and the mixture was extracted with EtOAc (3 × 15 mL). The combined extract was washed with brine (2 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc) on silica gel column to afford the desired carbonate.

Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-4-phenylbut-2-enoate (1b): Prepared using (*E*)-ethyl 4-hydroxy-4-phenylbut-2-enoate (830 mg, 4.02 mmol, 1.00 equiv), LiHMDS (4.82 mmol, 1.20 equiv) and Boc<sub>2</sub>O (1.05 g, 4.82 mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*butoxycarbonyloxy)-4-phenylbut-2-enoate (996 mg, 81%) was isolated (hexanes/EtOAc =  $12:1 \rightarrow 10:1$ ) as a colorless oil, which was crystallized on standing in a refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.40–7.31 (m, 5H), 7.02 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.17 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.06 (dd, *J* = 15.6, 1.8 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.47 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.9, 152.4, 144.4, 137.0, 128.8, 128.7, 127.3, 121.7, 82.8, 77.0, 60.6, 27.7, 14.2; mp 41–43 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>) requires *m/z* 306.1467, found *m/z* 306.1465.

Preparation of (*E*)-Methyl 4-(*tert*-Butoxycarbonyloxy)-4-phenylbut-2-enoate Ph  $CO_2Me$  (1e): Prepared using (*E*)-methyl 4-hydroxy-4-phenylbut-2-enoate (740 mg, 3.85 mmol, 1.00 equiv), LiHMDS (4.62 mmol, 1.20 equiv) and Boc<sub>2</sub>O (1.01 g, 4.62 mmol, 1.20 equiv), (*E*)methyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1.03 g, 91%) was isolated (hexanes/EtOAc = 12:1 $\rightarrow$ 11:1) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.36–7.31 (m, 5H), 7.03 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.17 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.08 (dd, *J* = 15.6, 1.5 Hz, 1H), 3.73 (s, 3H), 1.47 (s, 9H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75.5 MHz)  $\delta$  165.9, 153.0, 145.1, 137.7, 129.0, 128.8, 127.6, 121.6, 82.1, 77.2, 51.2, 27.6; mp 59– 60 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>) requires *m/z* 292.1311, found *m/z* 292.1314.

Ph Preparation of (*E*)-*tert*-Butyl 4-(*tert*-Butoxycarbonyloxy)-4-phenylbut-2-enoate Ph CO<sub>2</sub>*t*Bu (1f): Prepared using (*E*)-*tert*-butyl 4-hydroxy-4-phenylbut-2-enoate (1.00 g, 4.27 mmol, 1.00 equiv), LiHMDS (4.70 mmol, 1.10 equiv) and Boc<sub>2</sub>O (1.02 g, 4.70 mmol, 1.10 equiv), (*E*)-*tert*butyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (714 mg, 69%) was isolated (hexanes/EtOAc = 20:1→16:1) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.36 (s, 5H), 6.91 (dd, *J* = 15.6, 5.4 Hz, 1H), 6.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 5.97 (dd, *J* = 15.6, 1.5 Hz, 1H), 1.47 (s, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 165.1, 152.4, 143.2, 137.3, 128.8, 128.7, 127.2, 123.7, 82.8, 80.8, 77.1, 28.0, 27.7; mp 112–115 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>26</sub>O<sub>5</sub>) requires *m/z* 334.1780, found *m/z* 334.1782. **Preparation of** (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)pent-2-enoate (1g): Me  $CO_2Et$  Prepared using (*E*)-ethyl 4-hydroxypent-2-enoate<sup>[14]</sup> (721 mg, 5.00 mmol, 1.00 equiv), LiHMDS (6.00 mmol, 1.20 equiv) and Boc<sub>2</sub>O (1.31 g, 6.00 mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*butoxycarbonyloxy)pent-2-enoate (1.05 g, 72%) was isolated (hexanes/EtOAc = 12:1 $\rightarrow$ 10:1) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.89 (dd, *J* = 15.6, 5.1 Hz, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 5.33–5.25 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.49 (s, 9H), 1.40 (d, *J* = 6.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.0, 152.5, 146.0, 121.2, 82.5, 71.6, 60.5, 27.7, 19.7, 14.2; HRMS (FAB) exact mass calculated for [M+1]<sup>+</sup> (C<sub>12</sub>H<sub>21</sub>O<sub>5</sub>) requires *m*/*z* 245.1389, found *m*/*z* 245.1387.

Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-6-phenylhex-2enoate (1h): Prepared using (*E*)-ethyl 4-hydroxy-6-phenylhex-2-enoate (719 mg, 3.07 mmol, 1.00 equiv), LiHMDS (3.68 mmol, 1.20 equiv) and Boc<sub>2</sub>O (803 mg, 3.68 mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-6-phenylhex-2-enoate (840 mg, 82%) was isolated (hexanes/EtOAc =  $12:1 \rightarrow 10:1$ ) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.32–7.16 (m, 5H), 6.87 (dd, *J* = 15.9, 5.7 Hz, 1H), 6.00 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.22–5.16 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.76–2.62 (m, 2H), 2.12–1.90 (m, 2H), 1.50 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.9, 152.7, 144.9, 140.7, 128.5, 128.3, 126.2, 122.0, 82.6, 74.7, 60.6, 35.4, 74.7, 60.6, 35.4, 31.2, 27.7, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>26</sub>O<sub>5</sub>) requires *m/z* 334.1780, found *m/z* 344.1783.



Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-4-*o*-tolylbut-2-enoate (1j): Prepared using (*E*)-ethyl 4-hydroxy-4-o-tolylbut-2-enoate (950 mg, 4.31 mmol, 1.00 equiv), LiHMDS (5.18 mmol, 1.20 equiv) and Boc<sub>2</sub>O (1.13 g, 5.18

mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-*o*-tolylbut-2-enoate (1.14 g, 83%) was isolated (hexanes/EtOAc =  $12:1 \rightarrow 10:1$ ) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.36–7.34 (m, 1H), 7.24–7.16 (m, 3H), 7.01 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.38 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.00 (dd, *J* = 15.6, 1.5 Hz, 1H),

<sup>[14]</sup> S. Lou, G. C. Fu, Org. Synth. 2010, 87, 317–329.

4.18 (q, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.47 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$ 165.9, 152.5, 144.0, 135.5, 135.4, 130.7, 128.6, 127.1, 126.5, 121.7, 82.8, 74.1, 60.6, 27.7, 19.2, 14.2; mp 61–64 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>24</sub>O<sub>5</sub>) requires m/z 320.1624, found m/z320.1620.



Boc<sub>2</sub>O (1.03 g, 4.71 mmol, 1.10 equiv), (*E*)-ethyl 4-(2-bromophenyl)-4-(*tert*-butoxycarbonyloxy)but-2enoate (1.45 g, 87%) was isolated (hexanes/EtOAc =  $12:1 \rightarrow 11:1$ ) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.57 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22–7.17 (m, 1H), 6.99 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.57 (d, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.8, 152.0, 142.8, 136.8, 133.0, 130.0, 128.2, 128.0, 122.5, 122.2, 83.1, 75.6, 60.7, 27.7, 14.2; mp 77–80 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>21</sub>BrO<sub>5</sub>) requires *m/z* 384.0572, found *m/z* 384.0569.



LiHMDS (4.20 mmol, 1.05 equiv) and Boc<sub>2</sub>O (960 mg, 4.40 mmol, 1.10 equiv), (*E*)-ethyl 4-(4-bromophenyl)-4-(*tert*-butoxycarbonyloxy)but-2-enoate (1.12 g, 73%) was isolated (hexanes/EtOAc = 12:1) as a pale yellow oil which was crystallized on standing in a refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.51 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.96 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.45 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.7, 152.2, 143.7, 136.1, 132.0, 128.9, 122.9, 122.2, 83.1, 76.2, 60.7, 27.7, 14.2; mp 66–69 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>21</sub>BrO<sub>5</sub>) requires *m/z* 384.0572, found *m/z* 384.0570.



Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-4-(4methoxyphenyl)but-2-enoate (1m): Prepared using (*E*)-ethyl 4-hydroxy-4-(4-methoxyphenyl)but-2-enoate (810 mg, 3.43 mmol, 1.00 equiv),

LiHMDS (4.11 mmol, 1.20 equiv) and Boc<sub>2</sub>O (898 mg, 4.11 mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-(4-methoxyphenyl)but-2-enoate (992 mg, 86%) was isolated (hexanes/EtOAc = 12:1) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.29 (d, *J* = 8.7 Hz, 2H), 7.01 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.13–6.12 (m, 1H), 6.05 (dd, *J* = 15.6, 1.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 1.46 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.0, 159.9, 152.4, 144.6, 129.0, 128.9, 121.5, 114.1, 82.7, 76.7, 60.6, 55.2, 27.7, 14.2; mp 79–81 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>24</sub>O<sub>6</sub>) requires *m/z* 336.1573, found *m/z* 336.1573.

Preparation of (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-4-(furan-3-yl)but-2-CO<sub>2</sub>Et enoate (1n): Prepared using (*E*)-ethyl 4-(furan-3-yl)-4-hydroxybut-2-enoate (598 mg, 3.05 mmol, 1.00 equiv), LiHMDS (3.66 mmol, 1.20 equiv) and Boc<sub>2</sub>O (798 mg, 3.66 mmol, 1.20 equiv), (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-(furan-3-yl)but-2-enoate (638 mg, 71%) was isolated (hexanes/EtOAc =  $12:1 \rightarrow 11:1$ ) as a pale yellow oil, which was crystallized on standing in a refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.48 (s, 1H), 7.41 (t, *J* = 1.5 Hz, 1H), 7.01 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.41 (d, *J* = 1.2 Hz, 1H), 6.18 (dd, *J* = 5.4, 1.5 Hz, 1H), 6.09 (dd, *J* = 15.6, 1.5 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 165.8, 152.4, 143.7, 143.3, 141.1, 122.4, 122.0, 109.2, 82.9, 69.6, 60.7, 27.7, 14.2; mp 39–43 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>15</sub>H<sub>20</sub>O<sub>6</sub>) requires *m*/z 296.1260, found *m*/z 296.1263.



Preparation of (+)-(R,E)-Ethyl 4-(tert-Butoxycarbonyloxy)-4-phenylbut-2-enoate [(+)-1b]: A 100-mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with the Grubbs 2nd generation catalyst (49.9 mg, 58.8 µmol, 2.0 mol%) and CuI (16.8 mg, 88.3 µmol, 3.0 mol%), evacuated and back-filled with argon (3 cycles).<sup>[15]</sup> To this flask was added a solution of (R)-1-phenylprop-2-en-1-ol<sup>16</sup> (395 mg, 2.94 mmol, 1.00 equiv) in dry Et<sub>2</sub>O (30 mL) via double-ended needle. Ethyl acrylate (Caution! Acrid odor) (1.47 g, 14.7 mmol, 5.00 equiv) was added and the resultant mixture was heated under reflux in a pre-heated oil bath (bath temperature = 40 °C) for 3.5 h. After which the mixture was cooled to room temperature and concentrated. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc=3.8:1) to afford (+)-(R,E)-ethyl 4-hydroxy-4-phenylbut-2-enoate (512 mg, 84%) as a brown oil. HPLC resolution: Chiralcel OD-H column; n-hexane/2-propanol = 96:4; flow rate = 0.7 mL/min; retention time, 28.1 min (major isomer), 33.0 (minor isomer); 92.0% ee;  $\left[\alpha\right]_{D}^{22}$  +89.8 (c 0.84, CHCl<sub>3</sub>). To a solution of (+)-(R,E)-ethyl 4-hydroxy-4-phenylbut-2-enoate (456 mg, 2.21 mmol, 1.00 equiv) in anhydrous THF (6.0 mL) at -78 °C was added dropwise LiHMDS (1.0 M solution in THF, 2.65 mmol, 1.20 equiv) via double-ended needle and the resultant mixture was stirred at the same temperature for 60 min. A solution of Boc<sub>2</sub>O (579 mg, 2.65 mmol, 1.20 equiv) in THF (4.0 mL) was added dropwise and the system was allowed to slowly warm to 0 C over 2 h. The reaction was quenched with brine (10

<sup>[15]</sup> K. Voigtritter, S. Ghorai, B. H. Lipshutz, J. Org. Chem. 2011, 76, 4697–4702.

<sup>[16] (</sup>*R*)-1-phenylprop-2-en-1-ol was obtained from Sigma Aldrich and purified by flash column chromatography (hexanes/EtOAc = 8:1→7:1) on silica gel before use. HPLC resolution: Chiralcel OD-H column; *n*hexane/2-propanol = 99.8:0.2; flow rate = 0.4 mL/min; retention time, 17.1 min (minor isomer), 19.5 min (major isomer); 91.8% ee.

mL) and the mixture was extracted with EtOAc (3 × 10 mL). The combined extract was washed with brine (2 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc =  $12:1 \rightarrow 10:1$ ) to afford (+)-**1b** (540 mg, 78%) as a pale yellow oil. HPLC resolution: Chiralcel OD-H column; *n*-hexane/2-propanol = 99.8:0.2; flow rate = 0.4 mL/min; retention time, 17.1 min (minor isomer), 19.5 min (major isomer); 91.8% ee;  $[\alpha]_D^{22}$  +71.6 (*c* 1.00, CHCl<sub>3</sub>).



General Procedure for the Ir-Catalyzed  $\gamma$ -Amination of Allylic Carbonates: In an argon-filled drybox, a 5-mL screw-capped vial reactor was charged with [Ir(cod)Cl]<sub>2</sub> (6.7 mg, 0.010 mmol, 2.0 mol%) and *rac*-L1 (10.8 mg, 0.020 mmol, 4.0 mol%) and a small magnetic stir bar was added into the vial. The vial was sealed with a cap containing a PTFE septum and removed from the box. Dry degassed THF (0.30 mL) was added under an atmosphere of argon and the resultant reddish mixture was stirred for 10 min at room temperature. Distilled propylamine (0.20 mL) was then added and the resultant mixture was heated at 50 °C in a pre-heated oil bath with stirring for 20 min. After which the mixture was cooled to room temperature and all volatiles were removed *in vacuo*. To the vial reactor containing the activated catalyst was added a solution of substrate 1 (0.500 mmol, 1.00 equiv) in dry degassed nitromethane (0.50 mL) via double-ended needle. The resultant yellow mixture was stirred at room temperature for 10 min before the addition of distilled amine (0.600 mmol, 1.20 equiv or 0.750 mmol, 1.50 equiv) via microsyringe. After stirring for 13 h, the mixture was diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained was analyzed by <sup>1</sup>H NMR and then purified by flash column chromatography (hexanes/EtOAc) on silica gel to afford the desired  $\alpha,\beta$ -unsaturated  $\gamma$ -amino ester **2**.

NHBnPreparation of (E)-Ethyl 4-(Benzylamino)-4-phenylbut-2-enoate (2a): PreparedPhCO2Etusing (E)-ethyl 4-(tert-butoxycarbonyloxy)-4-phenylbut-2-enoate (1b, 153 mg, 0.500

mmol, 1.00 equiv) and distilled benzylamine (64.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(benzylamino)-4-phenylbut-2-enoate (130 mg, 88%) was isolated (hexanes/EtOAc =  $6:1 \rightarrow 5:1$ ) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.38–7.27 (m, 5H), 7.01 (dd, *J* = 15.6, 6.6 Hz, 1H), 6.04 (dd, *J* = 15.9, 0.9 Hz, 1H), 4.37 (d, *J* = 6.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.68 (br s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.4, 149.6, 140.8, 139.9, 128.8, 128.4, 128.1, 127.8, 127.5, 127.1, 121.0, 63.1, 60.4, 51.3, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>) requires *m/z* 295.1572, found *m/z* 295.1569.

Preparation of (*E*)-Ethyl 4-(Diallylamino)-4-phenylbut-2-enoate (2b): Ph CO<sub>2</sub>Et Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1b, 153 mg, 0.500 mmol, 1.00 equiv) and distilled diallylamine (58.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(diallylamino)-4-phenylbut-2-enoate (111 mg, 85%) was isolated (hexanes/EtOAc = 12:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.34–7.24 (m, 5H), 7.06 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.98 (dd, *J* = 15.9, 0.9 Hz, 1H), 5.89–5.76 (m, 2H), 5.20–5.13 (m, 4H), 4.43 (d, *J* = 8.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.10 (d, *J* = 6.3 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 166.2, 147.9, 139.8, 135.5, 128.5, 128.2, 127.5, 123.1, 117.5, 65.6, 60.4, 52.6, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>) requires *m/z* 285.1729, found *m/z* 285.1726.

Preparation of (*E*)-Ethyl 4-Morpholino-4-phenylbut-2-enoate (5c): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (**4b**, 153 mg, 0.500 mmol, 1.00 equiv) and distilled morpholine (52.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-morpholino-4-phenylbut-2-enoate (123 mg, >99%) was isolated (hexanes/EtOAc =  $5:1 \rightarrow 4.5:1$ ) as a yellow oil, which was crystallized on standing in a refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.34–7.25 (m, 5H), 6.99 (dd, *J* = 15.6, 9.0 Hz, 1H), 6.00 (dd, *J* = 15.9, 0.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.79 (d, *J* = 9.0 Hz, 1H), 3.69 (t, *J* = 4.8 Hz, 4H), 2.46–2.34 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.1, 148.7, 139.4, 128.8, 128.2, 127.9, 122.4, 73.2, 67.0, 60.4, 52.0, 14.2; mp 38–40 °C; HRMS (EI) exact mass calculated for  $[M]^+$  (C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>) requires *m/z* 275.1521, found *m/z* 275.1519.

Preparation of (*E*)-Ethyl 4-Phenyl-4-(phenylamino)but-2-enoate (2d): Prepared Ph  $CO_2Et$  using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1b, 153 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (69.8 mg, 0.750 mmol, 1.50 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-phenyl-4-(phenylamino)but-2-enoate (141 mg, >99%) was isolated (hexanes/EtOAc  $= 8:1 \rightarrow 7:1$ ) as an off-white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.39–7.27 (m, 5H), 7.18–7.12 (m, 2H), 7.10 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 6.08 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.05 (t, *J* = 4.5 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.06 (d, *J* = 3.9 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.3, 147.7, 146.6, 139.9, 129.2, 129.0, 128.1, 127.4, 121.8, 118.1, 113.4, 60.5, 59.5, 14.2; mp 79–81 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>) requires *m*/z 281.1416, found *m*/z 281.1412.

**Preparation of (***E***)-Ethyl 4-(Methyl(phenyl)amino)-4-phenylbut-2-enoate (2e):** Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (**1b**, 153 mg, 0.500 mmol, 1.00 equiv) and distilled *N*-methylaniline (64.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(methyl(phenyl)amino)-4-phenylbut-2-enoate (145 mg, 98%) was isolated (hexanes/EtOAc = 12:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.32–7.20 (m, 8H), 6.81–6.74 (m, 3H), 6.00 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.64 (d, *J* = 5.1 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.70 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.1, 149.6, 145.3, 138.6, 129.2, 128.6, 127.9, 127.6, 123.6, 117.4, 113.2, 63.6, 60.5, 33.8, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>) requires *m/z* 295.1572, found *m/z* 295.1569.

NHPh Ph CO<sub>2</sub>Me Preparation of (*E*)-Methyl 4-Phenyl-4-(phenylamino)but-2-enoate (2f): Prepared using (*E*)-methyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1e, 146 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-methyl 4-phenyl-4-(phenylamino)but-2-enoate (111 mg, 83%) was isolated (hexanes/EtOAc = 7:1) as an yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.39–7.28 (m, 5H), 7.18–7.08 (m, 3H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 6.09 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.06 (s, 1H), 4.05 (br s, 1H), 3.71 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.7, 148.0, 146.6, 139.9, 129.2, 129.0, 128.2, 127.4, 121.4, 118.2, 113.5, 59.5, 51.6; mp 59–60 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>) requires *m/z* 267.1259, found *m/z* 267.1257.

NHPh<br/>PhPreparation of (E)-tert-Butyl 4-Phenyl-4-(phenylamino)but-2-enoate (2g):Prepared using (E)-methyl 4-(tert-butoxycarbonyloxy)-4-phenylbut-2-enoate (1f,167 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassednitromethane/THF (v/v = 1:1, 1.0 mL), (E)-tert-butyl 4-phenyl-4-(phenylamino)but-2-enoate (151 mg,98%) was isolated (hexanes/EtOAc = 9:1) as an off-white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.35–7.28(m, 5H), 7.17–7.12 (m, 2H), 7.00 (dd, J = 15.6, 5.7 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 7.8 Hz,2H), 5.98 (dd, J = 15.6, 1.5 Hz, 1H), 5.05–5.02 (m, 1H), 4.06 (br d, J = 3.9 Hz, 1H), 1.46 (s, 9H); <sup>13</sup>C NMR(CDCl<sub>3</sub>, 75.5 MHz) δ 165.6, 146.7, 146.5, 140.2, 129.2, 129.0, 128.0, 127.3, 123.6, 118.0, 113.4, 80.6, 59.5,28.1; mp 102–106 °C; HRMS (EI) exact mass calculated for [M]+ (C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>) requires *m/z* 309.1729,found *m/z* 309.1725.

NHPh Preparation of (*E*)-Ethyl 4-(Phenylamino)pent-2-enoate (2h): Prepared using  $Me^{-1}CO_2Et$  (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)pent-2-enoate (1g, 122 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(phenylamino)pent-2-enoate (101 mg, 92%) was isolated (hexanes/EtOAc = 7:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.15 (d, *J* = 7.8 Hz, 2H), 6.93 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 5.98 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.16 (d, *J* = 7.2 Hz, 2H), 3.72 (br s, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 166.5, 150.5, 146.6, 129.2, 120.5, 117.6, 113.1, 60.3, 49.7, 21.0, 14.1; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>) requires *m/z* 219.1259, found *m/z* 219.1261.

NHPh

Ph $(CO_2Et)$  reaction of (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-6-phenylhex-2-enoate (**1h**, 167 mg, 0.500 mmol, 1.00 equiv) with distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL) was carried out at 30 °C in a pre-heated oil bath for 22 h, (*E*)-ethyl 6-phenyl-4-(phenylamino)hex-2-enoate (149 mg, 97%) was isolated (hexanes/EtOAc = 10:1 $\rightarrow$ 9:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.31–7.12 (m, 7H), 6.90 (dd, *J* = 15.6, 5.4 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 2H), 5.98 (d, *J* = 15.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.99 (s, 1H), 3.69 (s, 1H), 2.77 (d, *J* = 7.5 Hz, 2H), 2.07–1.87 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.4, 149.3, 146.7, 140.9, 129.2, 128.5, 128.4, 126.1, 121.4, 117.7, 113.1, 60.4, 53.7, 36.7, 32.1, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>) requires *m*/*z* 309.1729, found *m*/*z* 309.1727.

Preparation of (E)-Ethyl 6-Phenyl-4-(phenylamino)hex-2-enoate (2i): The

PhHN CO<sub>2</sub>Et Preparation of (*E*)-Ethyl 4-(Phenylamino)but-2-enoate (2j): The reaction of (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)but-2-enoate (1i, 115 mg, 0.500 mmol, 1.00 equiv) with distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL) was carried out at 40 °C in a pre-heated oil bath for 13 h, (*E*)-ethyl 4-(phenylamino)but-2-enoate (61 mg, 60%) was isolated (hexanes/EtOAc = 8:1) as a deep brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.18 (dd, J = 8.4, 7.5 Hz, 2H), 7.06–6.98 (m, 1H), 6.73 (t, J = 7.2 Hz, 1H), 6.59 (t, J = 7.8 Hz, 2H), 6.04 (d, J = 15.6 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.94 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 165.3, 147.2, 145.5, 129.3, 121.7, 117.9, 112.8, 60.4, 44.7, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub>) requires *m/z* 205.1103, found *m/z* 205.1101.



Preparation of (*E*)-Ethyl 4-(Phenylamino)-4-*o*-tolylbut-2-enoate (2k): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-*o*-tolylbut-2-enoate (1j,

160 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol,

1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(phenylamino)-4-o-tolylbut-2-enoate (148 mg, >99%) was isolated (hexanes/EtOAc = 7:1) as a yellow oil, which was crystallized on standing in a

refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.29–7.24 (m, 1H), 7.20–7.10 (m, 6H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 6.07 (d, *J* = 15.6 Hz, 1H), 5.22 (d, *J* = 3.9 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.96 (br s, 1H), 2.35 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.3, 147.3, 146.8, 137.9, 136.1, 130.9, 129.2, 128.0, 126.9, 126.6, 122.1, 117.9, 113.0, 60.4, 55.7, 19.2, 14.1; mp 65–69 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>) requires *m/z* 295.1572, found *m/z* 295.1569.



Preparation of (*E*)-Ethyl 4-(2-Bromophenyl)-4-(phenylamino)but-2-enoate (21): Prepared using (*E*)-ethyl 4-(2-bromophenyl)-4-(*tert*-butoxycarbonyloxy)but-2-enoate (1k, 193 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg,

0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(2-bromophenyl)-4-(phenylamino)but-2-enoate (177 mg, 98%) was isolated (hexanes/EtOAc = 4:1 $\rightarrow$ 3:1) as a yellow oil, which was crystallized on standing in a refrigerator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.60 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.31–7.25 (m, 1H), 7.18–7.05 (m, 4H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 6.02 (d, J = 15.9 Hz, 1H), 5.54–5.51 (m, 1H), 4.22–4.15 (m, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.2, 149.2, 146.0, 138.9, 133.3, 129.5, 129.2, 128.6, 128.1, 123.9, 122.7, 118.3, 113.4, 60.6, 58.1, 14.2; mp 64–66 °C; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>18</sub>BrNO<sub>2</sub>) requires *m/z* 359.0521, found *m/z* 359.0520.



distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(4-bromophenyl)-4-(phenylamino)but-2-enoate (175 mg, 97%) was isolated (hexanes/EtOAc = 8:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.48 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.15 (dd, *J* = 8.1, 7.5 Hz, 2H), 7.05 (dd, *J* = 15.6, 5.7 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 2H), 6.03 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.03 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.04 (br s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.1, 146.9, 146.2, 139.0, 132.1, 129.2, 129.0, 122.4, 122.0, 118.4, 113.6,

60.6, 58.9, 14.2; HRMS (EI) exact mass calculated for  $[M]^+$  (C<sub>18</sub>H<sub>18</sub>BrNO<sub>2</sub>) requires *m*/*z* 359.0521, found *m*/*z* 359.0522.



# Preparation of (E)-Ethyl 4-(4-Methoxyphenyl)-4-(phenylamino)but-2enoate (2n): Prepared using (E)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-(4-

methoxyphenyl)but-2-enoate (**1m**, 168 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(4- methoxyphenyl)-4-(phenylamino)but-2-enoate (153 mg, 98%) was isolated (hexanes/EtOAc = 7:1) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.26 (d, J = 8.7 Hz, 2H), 7.18–7.05 (m, 3H), 6.89 (d, J = 8.7 Hz, 2H), 6.73 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 7.8 Hz, 2H), 6.07 (dd, J = 15.6, 1.5 Hz, 1H), 5.00 (d, J = 4.8 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 4.00 (br s, 1H), 3.80 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 166.4, 159.4, 147.9, 146.7, 132.0, 129.2, 128.6, 121.5, 118.0, 114.4, 113.4, 60.5, 58.9, 55.3, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>) requires *m*/*z* 311.1521, found *m*/*z* 311.1521.

**Preparation of** (*E*)-Ethyl 4-(Furan-3-yl)-4-(phenylamino)but-2-enoate (20): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-(furan-3-yl)but-2-enoate (**1n**, 148 mg, 0.500 mmol, 1.00 equiv) and distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (*E*)-ethyl 4-(furan-3-yl)-4-(phenylamino)but-2-enoate (129 mg, 95%) was isolated (hexanes/EtOAc =  $10:1 \rightarrow 9:1$ ) as a deep brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.42–7.39 (m, 2H), 7.21–7.15 (m, 2H), 7.07 (dd, *J* = 15.6, 5.4 Hz, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 6.39 (s, 1H), 6.11 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.07 (d, *J* = 4.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.93 (br s, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.2, 146.8, 146.4, 143.7, 140.0, 129.2, 124.8, 122.0, 118.2, 113.4, 109.3, 60.5, 51.0, 14.1; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>) requires *m/z* 271.1208, found *m/z* 271.1209.



**Ph Isolation of (Z)-Ethyl 4-(***tert***-Butoxycarbonyloxy)-4-phenylbut-3-enoate [(Z)-4b]: Ph <b>CO**<sub>2</sub>Et When the reaction of (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (**1b**) with benzylamine was conducted in other solvents such as THF, 1,2-dimethoxyethane, 1,4-dioxane, acetonitrile and dichloromethane rather than in nitromethane, a certain amount of isomerized by-product, namely (*Z*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-3-enoate [(*Z*)-**4b**] was observed. The relative configuration of (*Z*)-**4b** was confirmed by NOESY experiments. Thus, NOE was observed between the olefinic proton of the C-3 methylene group and the *ortho*-protons of the phenyl group. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.49–7.45 (m, 2H), 7.38–7.28 (m, 3H), 6.00 (t, *J* = 6.9 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.27 (d, *J* = 6.9 Hz, 2H), 1.48 (s, 9H), 1.28 (t, *J* =7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  170.8, 150.7, 148.1, 134.6, 128.6, 128.5, 124.6, 109.6, 83.5, 60.9, 31.5, 27.5, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>) requires *m*/*z* 306.1467, found *m*/*z* 306.1469.

NHBn Preparation of (+)-(*R*,*E*)-Ethyl 4-(Benzylamino)-4-phenylbut-2-enoate [(+)-(2a)]: Ph  $CO_2Et$  Prepared using (+)-(*R*,*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate [(+)-(1b), 153 mg, 0.500 mmol, 1.00 equiv] and distilled benzylamine (64.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), (+)-(*R*,*E*)-ethyl 4-(benzylamino)-4-phenylbut-2-enoate (124 mg, 84%) was isolated (hexanes/EtOAc = 6:1 $\rightarrow$ 5:1) as a yellow oil. HPLC resolution: Chiralcel OD-H; *n*hexane/2-propanol = 99.5:0.5; flow rate = 1.0 mL/min; retention time, 13.8 min (major isomer), 22.0 min (minor isomer); 92.2% ee;  $[\alpha]_D^{22}$  +18.0 (*c* 1.01, CHCl<sub>3</sub>).

NHPh Preparation of (+)-(R,E)-Ethyl 4-Phenyl-4-(phenylamino)but-2-enoate [(+)-Ph  $CO_2Et$  (2d)]: Prepared using (+)-(R,E)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2enoate [(+)-(**1b**), 91.9 mg, 0.300 mmol, 1.00 equiv] and distilled aniline (33.5 mg, 0.360 mmol, 1.20 equiv) in dry degassed nitromethane (0.30 mL), (+)-(*R*,*E*)-ethyl 4-phenyl-4-(phenylamino)but-2-enoate (78 mg, 93%) was isolated (hexanes/EtOAc =  $8:1 \rightarrow 7:1$ ) as an off-white solid. HPLC resolution: Chiralcel OD-H; *n*-hexane/2-propanol = 98:2; flow rate = 1.0 mL/min; retention time, 31.4 min (major isomer), 37.9 min (minor isomer); 92.6% ee;  $[\alpha]_D^{22}$  +46.6 (*c* 1.02, CHCl<sub>3</sub>).



Confirmation of the Absolute Stereochemistry of (+)-(2a) via the Preparation of (-)-(R,E)-Ethyl 4-(Benzyl(cyanomethyl)amino)-4-phenylbut-2-enoate [(-)-2a']:<sup>[17]</sup> To a solution of (+)-(R,E)-ethyl 4-(benzylamino)-4-phenylbut-2-enoate [(+)-2a, 43.0 mg, 0.146 mmol, 1.00 equiv) in anhydrous acetonitrile (1.0 mL) was added potassium carbonate (101 mg, 0.728 mmol, 5.00 equiv) followed by bromoacetonitrile (52.4 mg, 0.437 mmol, 3.00 equiv). The resultant mixture was then heated under reflux for 2.5 h. After which another portion of bromoacetonitrile (52.4 mg, 0.437 mmol, 3.00 equiv) was added and the mixture was heated under reflux for an additional 2.5 h. At this point the mixture was cooled to room temperature and extracted with dichloromethane ( $3 \times 10$  mL). The combined extract was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc = 6:1) to afford the desired alkylated product 2a' (37 mg, 77%) as a white solid. Spectral data are consistent with previously reported literature values.<sup>[13]</sup> The absolute configuration of (-)-2a' was confirmed by comparison of the specific rotation with the reported value  $[[\alpha]_{D}^{25} - 40 \ (c \ 0.9, \ CHCl_{3})]$ .<sup>[13]</sup> mp 68–71 °C; HRMS (EI) exact mass calculated for  $[M]^{+} (C_{21}H_{22}N_{2}O_{2})$ requires m/z 334.1681, found m/z 334.1678; HPLC resolution: Chiralcel OD-H; n-hexane/2-propanol = 99.5:0.5; flow rate = 1.0 mL/min; retention time, 18.8 min (minor isomer), 26.0 min (major isomer); 93.8% ee;  $[\alpha]_D^{22}$  -31.3 (*c* 1.08, CHCl<sub>3</sub>).

A Gram-Scale Synthesis of (*E*)-Ethyl 4-Phenyl-4-(phenylamino)but-2-enoate (2d): In an argon-filled drybox, a 25-mL Schlenk flask was charged with  $[Ir(cod)Cl]_2$  (26.9 mg, 0.0400 mmol, 1.00 mol%) and

<sup>[17]</sup> H. Bräuner-Osborne, L. Bunch, N. Chopin, F. Couty, G. Evano, A. A. Jensen, M. Kusk, B. Nielsen, N. Rabasso, Org. Biomol. Chem. 2005, 3, 3926–3936. In this paper, the absolute configuration of (–)-2a'was wrongly assigned as Sinister (S).

 $(S_c,S_c,S_a)$ -L1 (43.2 mg, 0.080 mmol, 2.00 mol%) and a magnetic stir bar was added into the flask. The flask was sealed with a rubber septum and removed from the box. Dry degassed THF (1.2 mL) was added under an atmosphere of argon and the resultant reddish mixture was stirred for 10 min at room temperature. Distilled propylamine (0.5 mL) was then added and the resultant mixture was heated at 50 °C in a preheated oil bath with stirring for 20 min. After which the mixture was cooled to room temperature and all volatiles were removed *in vacuo*. To the flask containing the activated catalyst was added a solution of substrate **1b** (1.23 g, 4.00 mmol, 1.00 equiv) in dry degassed nitromethane (4.0 mL) via double-ended needle. The resultant yellow mixture was stirred at room temperature for 10 min before the addition of distilled aniline (447 mg, 4.80 mmol, 1.20 equiv) via syringe. After stirring for 13 h, the mixture was diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained was analyzed by <sup>1</sup>H NMR and then purified by flash column chromatography (hexanes/EtOAc = 9:1→8:1) on silica gel to afford the desired  $\alpha$ , $\beta$ -unsaturated  $\gamma$ -amino ester **2d** (1.00 g, 89%) as a pale yellow solid.



Kinetic Resolution of Racemic (*E*)-Ethyl 4-(*tert*-Butoxycarbonyloxy)-4-phenylbut-2-enoate  $[(\pm)-1b]$  with Aniline: In an argon-filled drybox, a 5-mL screw-capped vial reactor was charged with  $[Ir(cod)Cl]_2$  (3.4 mg, 0.0050 mmol, 2.0 mol%), ( $S_c$ , $S_c$ , $S_a$ )-L2 (6.0 mg, 0.010 mmol, 4.0 mol%) and TBD (2.8 mg, 0.020 mmol, 8.0 mol%). A small magnetic stir bar was added into the vial. The vial was sealed with a cap containing a PTFE septum and removed from the box. Dry degassed nitromethane (0.1 mL) was added under an atmosphere of argon and the resultant mixture was stirred for 10 min at room temperature. A solution of **1b** (76.6 mg, 0.250 mmol, 1.00 equiv) in degassed nitromethane (0.40 mL) was then added via double-ended needle and the reaction mixture was stirred for 10 min before the addition of distilled aniline (10.5 mg, 0.112 mmol, 0.450 equiv). After stirring overnight at room temperature, the mixture was diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained

was purified by flash column chromatography on silica gel (hexanes/EtOAc=7:1) to afford a mixture consisted of the allylic carbonate **1b** and the  $\gamma$ -amination product **2d** as a yellow oil. HPLC resolution for **1b**: Chiralcel OD-H; *n*-hexane/2-propanol = 99.8:0.2, flow rate = 0.4 mL/min; 254 nm; retention time, 19.7 min (minor isomer), 25.0 min (major isomer); 60.2% ee; HPLC resolution for **2d**: Chiralcel OD-H; *n*-hexane/2-propanol = 98:2; flow rate = 1.0 mL/min; 254 nm; retention time, 31.4 min (minor isomer), 37.0 min (major isomer); 43.2% ee. The calculation of conversion (c) and selectivity factor (S) was made using Kagan's methods.<sup>[18]</sup>



**Preparation of** (*E*)-**Ethyl 5-**(*tert*-**Butyldimethylsilyloxy**)-**4-**(**phenylamino**)**pent-2-enoate** (**2p**): In an argon-filled drybox, a 5-mL screw-capped vial reactor was charged with  $[Ir(cod)Cl]_2$  (6.7 mg, 0.010 mmol, 2.0 mol%) and *rac*-**L1** (10.8 mg, 0.020 mmol, 4.0 mol%) and a small magnetic stir bar was added into the vial. The vial was sealed with a cap containing a PTFE septum and removed from the box. Dry degassed THF (0.3 mL) was added under an atmosphere of argon and the resultant reddish mixture was stirred for 10 min at room temperature. Distilled propylamine (0.2 mL) was then added and the resultant mixture was heated at 50 °C in a pre-heated oil bath with stirring for 20 min. After which the mixture was cooled to room temperature and all volatiles were removed *in vacuo*. To the vial reactor containing the activated catalyst was added a solution of (*E*)-ethyl 3-(2-oxo-1,3-dioxolan-4-yl)acrylate (**7**, 91.1 mg, 0.500 mmol, 1.00 equiv) in dry degassed nitromethane (0.50 mL) via double-ended needle. The resultant yellow mixture was stirred at room temperature for 10 min before the addition of distilled aniline (55.9 mg, 0.600 mmol, 1.20 equiv) via microsyringe. The resultant mixture was then heated at 50 °C in a pre-heated oil bath for 13 h. After which the mixture was cooled to room temperature, diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained was analyzed by <sup>1</sup>H NMR. The mixture was placed in a 25-mL round-bottomed flak equipped with a magnetic stirring bar and anhydrous

<sup>[18]</sup> H. B. Kagan, J. C. Fiaud, Top. Stereochem. 1988, 18, 249-330.

DMF (2.0 mL) was added. To this mixture was added imidazole (68.1 mg, 1.00 mmol) followed by *tert*butyldimethylsilyl chloride (75.4 mg, 0.500 mmol). After stirring for 16 h at room temperature, the mixture was diluted with EtOAc and washed with water ( $3 \times 20$  mL). The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude mixture thus obtained was purified by flash column chromatography (hexanes/EtOAc =  $6:1\rightarrow 5:1$ ) on silica gel column to afford the title compound (105 mg, 60%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.19–7.14 (m, 2H), 6.95 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.06 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.25– 4.23 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.07–4.02 (m, 1H), 3.77 (ddd, *J* = 14.7, 10.2, 4.5 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.2, 147.2, 147.0, 129.2, 122.7, 118.0, 113.6, 64.8, 60.4, 56.2, 25.8, 18.3, 14.2, -5.4, -5.5; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>31</sub>NO<sub>6</sub>Si) requires *m*/z 349.2073, found *m*/z 349.2071.



General Procedure for the Formation of Oxazolidin-2-ones (3): In an argon-filled drybox, a 5-mL screw-capped vial reactor was charged with [Ir(cod)Cl]<sub>2</sub> (6.7 mg, 0.010 mmol, 2.0 mol%) and rac-L1 (10.8 mg, 0.020 mmol, 4.0 mol%) and a small magnetic stir bar was added into the vial. The vial was sealed with a cap containing a PTFE septum and removed from the box. Dry degassed THF (0.30 mL) was added under an atmosphere of argon and the resultant reddish mixture was stirred for 10 min at room temperature. Distilled propylamine (0.20 mL) was then added and the resultant mixture was heated at 50 °C in a preheated oil bath with stirring for 20 min. After which the mixture was cooled to room temperature and all volatiles were removed in vacuo. To the vial reactor containing the activated catalyst was added a solution of substrate 1 (0.500 mmol, 1.00 equiv) in dry degassed nitromethane (0.50 mL) via double-ended needle. The resultant vellow mixture was stirred at room temperature for 10 min before the addition of distilled allylamine (0.600 mmol, 1.20 equiv) via microsyringe. After stirring for 13 h, the mixture was diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained was analyzed by <sup>1</sup>H NMR and then purified by flash column chromatography (hexanes/EtOAc =  $4:1 \rightarrow 3:1 \rightarrow 2:1$ ) on silica gel to afford the oxazolidin-2-one **3** as an inseparable mixture of *trans*- and *cis*diastereomers. The structure of **3a** was confirmed by extensive 1D and 2D NMR analyses such as  ${}^{1}H$ ,  ${}^{13}C$ , DEPT-135, DEPT-90, COSY, HSQC and NOESY. The relative configuration of the major trans-isomers were assigned on the basis of the vicinal coupling constants between the C-4 and C-5 protons, whose values are consistent with the ones reported for similar oxazolidin-2-ones,<sup>[19]</sup> and further confirmed by NOESY experiments. For other oxazolidin-2-ones, <sup>1</sup>H, <sup>13</sup>C, COSY and NOESY spectrums are provided.

<sup>[19]</sup> a) B. Lagu, J. M. Wetzel, C. Forray, M. A. Patane, M. G. Bock, *Bioorg. Med. Chem. Lett.* 2000, *10*, 2705–2707;
b) A. Dondoni, D. Perrone, T. Semola, *Synthesis* 1995, 181–186.



Selected nOe cross peaks for oxazolidin-2-one 3a



Preparation of *trans*-Ethyl 2-(3-Allyl-2-oxo-5-phenyloxazolidin-4-yl)acetate (3a):
Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1b, 153 mg, 0.500 mmol, 1.00 equiv) and distilled allylamine (34.3 mg, 0.600 mmol, 1.20 equiv) in

dry degassed nitromethane (0.50 mL), ethyl 2-(3-allyl-2-oxo-5-phenyloxazolidin-4-yl)acetate (120 mg, 83%) was isolated (hexanes/EtOAc = 2:1) as an inseparable 10:1 mixture of *trans*- and *cis*-diastereomers (a pale yellow oil).

Characterization data for the major *trans*-isomer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.45–7.36 (m, 3H), 7.31– 7.26 (m, 2H), 5.74–5.64 (m, 1H), 5.18 (dd, *J* = 9.9, 0.9 Hz, 1H), 5.03 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.69 (q, *J* = 6.3 Hz, 1H), 4.49 (d, *J* = 6.3 Hz, 1H), 4.23–4.17 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.20 (dd, *J* = 15.3, 8.1 Hz, 1H), 2.84 (ABX pattern, dd, *J* = 16.2, 6.6 Hz, 1H), 2.74 (ABX pattern, dd, *J* = 16.2, 6.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  168.9, 157.0, 136.9, 131.2, 129.2, 129.1, 127.2, 119.3, 77.8, 64.2, 61.1, 44.6, 38.6, 14.0; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>) requires *m*/*z* 289.1314, found *m*/*z* 289.1311.



Selected nOe cross peaks for oxazolidin-2-one 3b



Preparation of *trans*-Ethyl 2-(3-Allyl-5-methyl-2-oxooxazolidin-4-yl)acetate (3b): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)pent-2-enoate (1g, 122 mg, 0.500 mmol, 1.00 equiv) and freshly distilled allylamine (34.3 mg, 0.600 mmol, 1.20 equiv)

in dry degassed nitromethane (0.50 mL), ethyl 2-(3-allyl-5-methyl-2-oxooxazolidin-4-yl)acetate (79 mg,

70%) was isolated (hexanes/EtOAc = 2:1) as an inseparable 10:1 mixture of *trans*- and *cis*-diastereomers (a pale yellow oil).

Characterization data for the major *trans*-isomer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  5.77–5.70 (m, 1H), 5.31– 5.33 (m, 2H), 4.43 (q, *J* = 6.3 Hz, 1H), 4.22–4.09 (m, 3H), 3.65–3.53 (m, 2H), 2.78 (ABX pattern, dd, *J* = 16.5, 6.3 Hz, 1H), 2.66 (ABX pattern, dd, *J* = 16.5, 6.9 Hz, 1H), 1.26–1.11 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  169.2, 156.6, 132.0, 118.5, 76.5, 61.0, 55.7, 44.3, 38.7, 17.9, 14.0; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>11</sub>H<sub>17</sub>NO<sub>4</sub>) requires *m/z* 227.1158, found *m/z* 227.1159.



Selected nOe cross peaks for oxazolidin-2-one 3c

**Preparation of** *trans*-Ethyl 2-(3-Allyl-2-oxo-5-phenethyloxazolidin-4yl)acetate (3c): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-6phenylhex-2-enoate (1h, 167 mg, 0.500 mmol, 1.00 equiv) and distilled allylamine (34.3 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), *trans*-ethyl 2-(3allyl-2-oxo-5-phenethyloxazolidin-4-yl)acetate (86 mg, 54%) was isolated (hexanes/EtOAc = 2:1) as a single diastereomer (a pale yellow oil). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.32–7.27 (m, 2H), 7.24–7.16 (m, 3H), 5.83–5.69 (m, 1H), 5.26–5.21 (m, 2H), 4.69–4.62 (m, 1H), 4.22–4.12 (m, 3H), 3.60–3.52 (m, 2H), 2.81–2.61 (m, 4H), 2.08–1.83 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  169.1, 156.6, 140.2, 131.9, 128.5, 128.1, 126.2, 118.8, 74.2, 61.0, 59.0, 44.6, 39.4, 32.8, 29.7, 14.0; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>) requires *m/z* 317.1627, found *m/z* 317.1625.



Selected nOe cross peaks for oxazolidin-2-one 3d

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Preparation of *trans*-Ethyl 2-(2-Oxo-5-phenyl-3-propyloxazolidin-4-yl)acetate (3d) and (*E*)-Ethyl 4-Phenyl-4-(propylamino)but-2-enoate (2q): Prepared using (*E*)-ethyl 4-(*tert*-butoxycarbonyloxy)-4-phenylbut-2-enoate (1b, 153 mg, 0.500 mmol,

1.00 equiv) and distilled propylamine (35.5 mg, 0.600 mmol, 1.20 equiv) in dry degassed nitromethane (0.50 mL), ethyl 2-(2-oxo-5-phenyl-3-propyloxazolidin-4-yl)acetate (44 mg, 36%) was isolated (hexanes/EtOAc =  $8:1 \rightarrow 7:1 \rightarrow 3:1 \rightarrow 2:1$ ) as an inseparable 7:1 mixture of *trans*- and *cis*-diastereomers (a pale yellow oil) along with the corresponding  $\gamma$ -amination product (*E*)-ethyl 4-phenyl-4-(propylamino)but-2-enoate (**2p**, 52 mg, 36%) as a yellow oil.

Characterization data for the major *trans*-**3d**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.44–7.36 (m, 3H), 7.31–7.29 (m, 2H), 4.65 (q, *J* = 6.3 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.45–3.35 (m, 2H), 2.88–2.71 (m, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  169.0, 157.2, 137.2, 129.2, 129.1, 127.0, 77.6, 64.6, 61.1, 43.7, 38.7, 20.1, 14.0, 11.0; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>16</sub>H<sub>21</sub>NO<sub>4</sub>) requires *m/z* 291.1471, found *m/z* 291.1472.

Characterization data for **2q**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.37–7.24 (m, 5H), 6.99 (dd, *J* = 15.6, 6.9 Hz, 1H), 6.01 (dd, *J* = 15.9, 0.9 Hz, 1H), 4.32 (d, *J* = 6.9 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.59–2.43 (m, 2H), 1.56–1.44 (m, 2H), 1.41 (br s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.5, 149.9, 141.2, 128.7, 127.6, 127.4, 120.7, 64.2, 60.3, 49.6, 23.2, 14.2, 11.7; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>15</sub>H<sub>21</sub>NO<sub>2</sub>) requires *m/z* 247.1572, found *m/z* 247.1570.



**Preparation of** (+)-**Ethyl 2-[(4***S***,5***S***)-3-Allyl-2-oxo-5-phenyloxazolidin-4-yl]acetate [(+)-(3a)]: In an argon-filled drybox, a 5-mL screw-capped vial reactor was charged with [Ir(cod)Cl]\_2 (4.0 mg, 6.0 µmol, 2.0 mol%) and** *rac***-L1 (6.5 mg, 0.012 mmol, 4.0 mol%) and a small magnetic stir bar was added into the vial. The vial was sealed with a cap containing a PTFE septum and removed from the box. Dry degassed THF (0.2 mL) was added under an atmosphere of argon and the resultant reddish mixture was stirred for 10 min** 

at room temperature. Distilled propylamine (0.12 mL) was then added and the resultant mixture was heated at 50 °C in a pre-heated oil bath with stirring for 20 min. After which the mixture was cooled to room temperature and all volatiles were removed *in vacuo*. To the vial reactor containing the activated catalyst was added a solution of (+)-**1b** (91.9 mg, 0.300 mmol, 1.00 equiv) in dry degassed nitromethane (0.30 mL) via double-ended needle. The resultant yellow mixture was stirred at room temperature for 10 min before the addition of distilled allylamine (20.6 mg, 0.360 mmol, 1.20 equiv) via microsyringe. After stirring for 13 h at room temperature, the mixture was diluted with EtOAc, filtered through a small pad of silica gel, and concentrated. The crude mixture thus obtained was analyzed by <sup>1</sup>H NMR and then purified by flash column chromatography (hexanes/EtOAc = 4:1→3:1→2:1) on silica gel to afford the desired oxazolidin-2one (+)-(**3a**) as an inseparable 10:1 mixture of *trans*- and *cis*-diastereomers. HPLC resolution: Chiralpak AD-H; *n*-hexane/2-propanol = 99.3:0.7; flow rate = 0.9 mL/min; 211 nm; retention time, 75.8 min (major isomer), 81.6 min (minor isomer); 71.4% ee for *trans*-isomer; [ $\alpha$ ]<sub>D</sub><sup>22</sup> +31.3 (*c* 1.01, CHCl<sub>3</sub>).



**Preparation of** (*E*)-Ethyl 4-(Allylcarbamoyloxy)-4-phenylbut-2-enoate (6): To a cold mixture of carbinol 1' (907 mg, 4.40 mmol, 1.00 equiv), pyridine (475 mg, 6.60 mmol, 1.50 equiv) and 4- (dimethylamino)pyridine (24.4 mg, 0.220 mmol, 5.00 mol%) in anhydrous  $CH_2Cl_2$  (20 mL) at 0 °C was added dropwise phenyl chloroformate (742 mg, 5.28 mmol, 1.20 equiv). The resultant mixture was stirred for 1 h at room temperature and concentrated. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 10:1) on silica gel to afford the mixed carbonate **6'** (1.37 g, 95%) as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.43–7.34 (m, 6H), 7.26–7.14 (m, 3H), 7.07 (dd, *J* = 15.6,

5.1 Hz, 1H), 6.30 (dd, J = 5.1, 1.5 Hz, 1H), 6.16 (dd, J = 15.6, 1.5 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  165.7, 152.7, 151.0, 143.3, 136.2, 129.5, 129.2, 129.0, 127.5, 126.2, 122.4, 120.9, 78.8, 60.8, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>19</sub>H<sub>18</sub>O<sub>5</sub>) requires m/z 326.1154, found m/z 326.1150. A mixture of carbonate **6'** (104 mg, 0.319 mmol, 1.00 equiv) and distilled allylamine (54.6 mg, 0.956 mmol, 3.00 equiv) in dry CHCl<sub>3</sub> (3.2 mL) was heated at 50 °C in a preheated oil bath for 12 h. The reaction mixture was cooled to room temperature and concentrated. The

neared on bath for 12 h. The reaction mixture was cooled to room temperature and concentrated. The residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 6:1) on silica gel to affored the desired carbamate **6** (64 mg, 70%) as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.40–7.30 (m, 5H), 7.03 (dd, *J* = 15.6, 5.1 Hz, 1H), 6.34 (d, *J* = 3.6 Hz, 1H), 6.04 (dd, *J* = 15.6, 1.8 Hz, 1H), 5.89–5.77 (m, 1H), 5.21–5.11 (m, 2H), 4.93 (br s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.83–3.79 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  166.0, 155.0, 145.2, 137.5, 134.1, 128.8, 128.6, 127.3, 121.3, 116.4, 74.7, 60.6, 43.5, 14.2; HRMS (EI) exact mass calculated for [M]<sup>+</sup> (C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>) requires *m*/*z* 289.1314, found *m*/*z* 289.1316.

# HPLC Chromatograms for (*E*)-Ethyl 4-Hydroxy-4-phenylbut-2-enoate (**1a**')



### (1) Racemic sample



Result Table (Uncal - LJHC\_Exp78\_Ph\_OH\_CO2Et\_racemic\_254nm\_ODH\_1\_4% IPA 0.7\_2013-03-08 오후 8\_44\_11 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	27.6	50.0
2	32.1	50.0
	Total	100.0

# (2) Enantioenriched sample



Result Table (Uncal - LJHC\_Exp82\_Ph\_Et\_carbinol\_ODH\_254\_chiral\_1\_4% IPA 0.7\_2013-02-08 오후 9\_11\_44 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	28.1	96.0
2	33.0	4.0
	Total	100.0

# HPLC Chromatograms for (E)-Ethyl 4-(tert-Butoxycarbonyloxy)-4-phenylbut-2-enoate (1b)



# (1) Racemic sample



Result Table (Uncal - LJHC\_Exp79\_Boc\_racemic\_1\_0.2% IPA 0.4\_2012-12-05 오후 6\_54\_53 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	18.4	50.0
2	21.8	50.0
	Total	100.0

# (2) Enantioenriched sample



#### Result Table (Uncal - LJHC\_Exp83\_Boc\_chiral\_1\_0.2% IPA 0.4\_2012-12-05 오후 7\_58\_56 - Channel 1)

	Reten. Time [min]	Area [%]
1	17.1	3.9
2	19.5	96.1
	Total	100.0

# HPLC Chromatograms for (E)-Ethyl 4-(Benzylamino)-4-phenylbut-2-enoate (2a)



### (1) Racemic sample



Result Table (Uncal - LJHC\_Exp90\_amine\_Ph\_BnNH2\_Et\_racemic\_1\_0.5% IPA 1.0\_2012-12-13 오亭 9\_23\_29 - Channel 1)

	Reten. Time [min]	Area [%]
1	13.9	50.2
2	21.4	49.8
	Total	100.0

# (2) Enantioenriched sample



Result Table (Uncal - LJHC\_Exp86\_amine\_Ph\_BnNH2\_Et\_chiral\_substrate\_1\_0.5% IPA 1.0\_2012-12-14 2= 5\_34\_20 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	13.8	96.1
2	22.0	3.9
	Total	100.0

# HPLC Chromatograms for (E)-Ethyl 4-Phenyl-4-(phenylamino)but-2-enoate (2d)



# (1) Racemic sample



Result Table (Uncal - LJHB\_Exp142\_amine\_racemic\_10\_2% IPA 1.0\_2012-11-27 오후 5\_07\_06 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	32.460	49.8
2	39.197	50.2
	Total	100.0

# (2) Enantioenriched sample



Result Table (Uncal - LJHC\_Exp85\_Amine\_chiral\_G2G\_2\_2% IPA 1.0\_2012-12-06 오후 5\_05\_36 - Channel 1)

	Reten. Time [min]	Area [%]
1	31.4	96.3
2	37.7	3.7
	Total	100.0

# HPLC Chromatograms for (E)-Ethyl 4-(Benzyl(cyanomethyl)amino)-4-phenylbut-2-enoate (2a')



## (1) Racemic sample



Result Table (Uncal - LJHC\_Exp106\_amine\_Ph\_PhNCH2CN\_Et\_racemic\_1\_0.5% IPA 0.8\_2012-12-29 오후 2\_44\_35 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	16.7	50.6
2	22.5	49.4
	Total	100.0

# (2) Enantioenriched sample



Result Table (Uncal - LJHC\_Exp108\_amine\_Ph\_PhNCH2CN\_Et\_chiral\_1\_0.5% IPA 0.8\_2013-01-02 오후 9\_30\_56 - Channel 1)

	Reten. Time [min]	Area [%]
1	17.5	3.4
2	23.4	96.6
	Total	100.0

HPLC Chromatograms for trans-Ethyl 2-(3-Allyl-2-oxo-5-phenyloxazolidin-4-yl)acetate (3a)



### (1) Racemic sample



Result Table (Uncal - LJHC\_Exp20\_Ph\_oxazolidinone\_racemic\_ADH\_211nm\_1\_0.7% IPA 0.9 211nm\_2013-03-07 오후 5\_11\_12 - Channel 1)

	Reten. Time [min]	Area [%]
1	75.4	51.3
2	79.6	48.7
	Total	100.0

#### (2) Enantioenriched sample



Result Table (Uncal - LJHC\_Exp129\_Ph\_oxazolidinone\_chiral\_ADH\_211nm\_1\_0.7% IPA 0.9 211nm\_2013-03-08 오후 12\_58\_17 - Channel 1)

	Reten. Time	Area
	[min]	[%]
1	75.8	85.7
2	81.6	14.3
	Total	100.0