Catalytic Enantioselective Amination of Enolsilanes Using C_2-Symmetric Copper(II) Complexes as Chiral Lewis Acids

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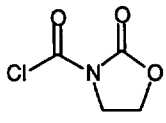
Supporting Information

General Information. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Solvents and reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] $Cu(OTf)_2$ was purchased from Aldrich and stored in an inert atmosphere dry box and used without further purification. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution followed by heating. Melting points were measured with a Büchi SMP-20 melting point apparatus equipped with an Omega Model 450 AET thermocouple and are uncorrected. Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_D^T$ (c g/100 mL, solvent). Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^1H NMR spectra were recorded on a Bruker AM-400 (400 MHz) spectrometer and are reported in ppm using solvent as the internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as: (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; integration; coupling constant(s) in Hz). Where applicable, chemical shifts of rotamers are indicated in parenthesis. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AM-400 (100 MHz) spectrometer and are reported in ppm using solvent as the internal standard ($CDCl_3$ at 77.07 ppm). High resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers in the Harvard University Mass Spectrometry Laboratory. Electrospray mass spectra were obtained using a LCT mass spectrometer (Micromass Instruments, Beverly, MA). Exact mass measurements were obtained by internal calibration with an appropriate lock mass compound. Combustion analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Gas chromatography was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a split-mode capillary injection system and flame ionization detector using the following chiral columns: J&W Scientific CYCLODEX-B (30 m x 0.25 mm), J&W Scientific DB-1701 (30 m x 0.25 mm), and Advanced Separations Technologies Chiraldex GTA (30 m x 0.25 mm). Analytical high performance liquid chromatography (HPLC) was performed on a Hewlett-Packard 1050 Series HPLC equipped with a variable wavelength detector using a Chiralcel AD, OD-H or OJ column (0.46 cm x 25 cm) from Daicel. X-ray crystallographic data was collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. IUPAC names were generated using the Chemistry 4-D Draw program.

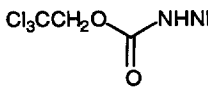
(*S*,*S*)-Bis(*tert*-butyloxazoline) and the corresponding Cu(II) complexes (**1**) were prepared as previously described.[2] The ligand is also commercially available from Aldrich.



2-Oxo-1,3-oxazolidine-3-carbonyl chloride.[3] 3-Trimethylsilyl-2-oxazolidinone[4] (20 mL, 130 mmol) was added to a solution of phosgene (1.93 M in toluene, 140 mL, 270 mmol) at 0 °C. Trimethylsilyl trifluoromethanesulfonate (0.1 mL, 0.5 mmol) was added and the reaction was stirred at 0 °C for 30 min, warmed to room temperature, and stirred an additional 4 h. The solution was concentrated under reduced pressure to give a brown oil which crystallized upon cooling. The product was recrystallized from CH_2Cl_2/hexanes to afford light brown needles (18.4 g, 94%). Analytical data: IR (CH_2Cl_2) 3063, 2996, 2928, 1841, 1806, 1733, 1478, 1384, 1361, 1286, 1189, 1142, 1115, 1044, 991 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.48 (t, 2H, *J* = 7.9 Hz), 4.22 (t, 2H, *J* = 7.9 Hz) ppm; ^{13}C NMR (100 MHz,

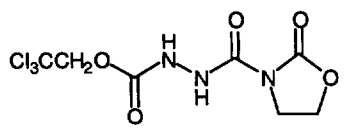
1) Perrin, D. D. and Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pregamon Press, Oxford, 1988.
2) For the preparation of (*S*,*S*)-bis(*tert*-butyloxazoline) and the Cu(II) complexes, see: Evans, D. A.; Peterson, G. S.; Johnson, J. S.; Barnes, D. M.; Campos, K. R.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 4541-4544.
3) Dave Halstead is acknowledged for the initial preparation of this compound.
4) Palomo, C. *Synthesis* **1981**, 809-811.

$CDCl_3$) δ 150.0, 144.9, 61.4, 45.6 ppm; HRMS (EI) 148.9876 (Exact mass calcd for $C_4H_4O_3Cl$ $[M]^+$, 148.9880).

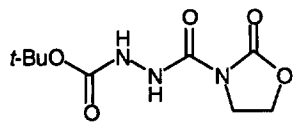


Trichloroethyl carbazate. (II-298) To a mixture of hydrazine (10 mL, 0.32 mol) in $CHCl_3$ (1 L) cooled to -10 °C was added trichloroethylchloroformate (15 mL, 109.0 mmol) as a solution in $CHCl_3$ (150 mL) *via* an addition funnel over 2 h. A white precipitate formed as each drop was added. After the addition was complete, H_2O (400 mL) was added and the precipitate dissolved. The aqueous layer was acidified with 10% aqueous HCl (200 mL) and the layers were separated. The organic layer was washed with 10% aqueous HCl. The organic layer contained diacylated material. The combined aqueous layers were neutralized with solid $NaHCO_3$ and extracted with $CHCl_3$ several times. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated to give a yellow oil (18.5 g, 89.0 mmol, 82%) which was used without purification.

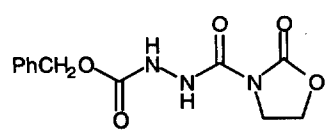
General Procedure for the Preparation of the Hydrazides.
To a solution of the carbazate (1.05 equiv) in CH_2Cl_2 cooled to 0 °C was added pyridine (1.05 equiv). 2-Oxo-1,3-oxazolidine-3-carbonyl chloride (1.0 equiv) was added as a solution in CH_2Cl_2 *via* cannula. The reaction was allowed to warm to room temperature and stir for 2 h. The mixture was diluted with CH_2Cl_2 and poured into H_2O. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with 5% aqueous HCl, H_2O and brine, dried over Na_2SO_4, and concentrated to give a pale yellow fluffy solid.



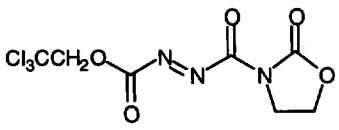
(2-oxo(1,3-oxazolidin-3-yl))-N-[(2,2,2-trichloroethoxy)carbonylamino]carboxamide (2a). Prepared according to the general procedure with trichloroethyl carbazate (12.8 g, 61.7 mmol), pyridine (5.0 mL, 61.7 mmol), CH_2Cl_2 (75 mL) and 2-oxo-1,3-oxazolidine-3-carbonyl chloride (8.8 g, 59.0 mmol in 25 mL CH_2Cl_2). Purification by flash chromatography (20-30% EtOAc/CH_2Cl_2) afforded a white fluffy solid (18.0 g, 56.4 mmol, 96%). Analytical data: mp 133 - 135 °C; IR (film) 3321, 3003, 2960, 2924, 1763, 1721, 1523, 1480, 1403, 1370, 1288, 1204, 1132, 1077, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 6.76 (s, 1H), 4.80 (s, 2H), 4.52 (t, 2H, J = 8 Hz), 4.10 (t, 2H, J = 8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 154.5, 152.0, 94.7, 75.1, 63.2, 42.4 ppm; HRMS (EI) 318.9544 (Exact mass calcd for $C_7H_8N_3O_5Cl_3$ $[M]^+$, 318.9529); Anal. Calcd. for $C_7H_8O_5N_3Cl_3$: C, 26.23; H, 2.52; N, 13.11. Found: C, 26.35; H, 2.53; N, 13.03.



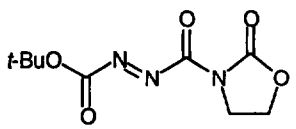
N-[(*tert*-Butoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (2b). (I-139) Prepared according to the general procedure with *tert*-butyl carbazate (4.6 g, 34.8 mmol), pyridine (2.8 mL, 34.8 mmol), CH_2Cl_2 (30 mL) and 2-oxo-1,3-oxazolidine-3-carbonyl chloride (4.9 g, 33.1 mmol in 15 mL CH_2Cl_2). Recrystallization from benzene/petroleum ether (10:1) afforded the product as a white fluffy solid (6.1 g, 24.7 mmol, 75%). Analytical data: mp 126 - 127 °C; IR (film) 3339, 3266, 3034, 2982, 2932, 1751, 1734, 1700, 1539, 1488, 1478, 1453, 1411, 1369, 1303, 1230, 1164, 1093, 1044, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 6.29 (s, 1H), 4.48 (t, 2H, J = 8 Hz), 4.08 (t, 2H, J = 8 Hz), 1.48 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.24, 155.22, 152.3, 81.9, 63.1, 42.4, 28.1 ppm; HRMS (CI, NH_3) 263.1352 (Exact mass calcd for $C_9H_{15}N_3O_5$ $[M + NH_4]^+$, 263.1355); Anal. Calcd. for $C_9H_{15}O_5N_3$: C, 44.08; H, 6.17; N, 17.13. Found: C, 44.16; H, 6.17; N, 17.23.



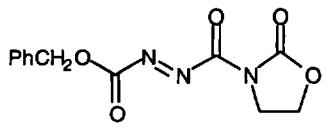
(2-Oxo(1,3-oxazolidin-3-yl))-N-[(phenylmethoxy)carbonylamino]carboxamide (2c). Prepared according to the general procedure with benzyl carbazate (5.81 g, 35.0 mmol), pyridine (2.9 mL, 35.0 mmol), CH_2Cl_2 (30 mL) and 2-oxo-1,3-oxazolidine-3-carbonyl chloride (4.96 g, 33.3 mmol in 15 mL CH_2Cl_2). Purification by flash chromatography (20-30% EtOAc/CH_2Cl_2) afforded a white fluffy solid (8.64 g, 31.0 mmol, 93%). Analytical data: mp 154 - 155 °C; IR (film) 3318, 3032, 2918, 1758, 1716, 1522, 1478, 1456, 1401, 1285, 1215, 1128, 1087, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.36 (m, 5H), 6.55 (bs, 1H), 5.19 (s, 2H), 4.47 (t, 2H, J = 8 Hz), 4.07 (t, 2H, J = 8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.1, 152.2, 135.5, 128.6, 128.5, 128.2, 68.0, 63.1, 42.4 ppm; HRMS (EI) 279.0866 (Exact mass calcd for $C_{12}H_{13}N_3O_5$ $[M]^+$, 279.0855); Anal. Calcd. for $C_{12}H_{13}O_5N_3$: C, 51.61; H, 4.69; N, 15.05. Found: C, 51.69; H, 4.67; N, 15.04.



2,2,2-Trichloroethyl {[(2-oxo-1,3-oxazolidin-3-yl)carbonyl]diazenyl}formate (3a). (II-86) To a solution of **2a** (2.50 g, 7.8 mmol) in $CHCl_3$ (40 mL)[5] cooled to 0 °C was added fuming nitric acid (2.1 mL, 6 equiv)[6] *via* an addition funnel. The reaction was stirred at 0 °C for 2 h and then warmed to room temperature for approximately 8 h. The reaction started to turn orange as it was warmed to room temperature and after about 4 h the flask was filled with an orange gas. The mixture was poured into ice. The layers were separated and the aqueous layer was extracted with $CHCl_3$. The organic layer was washed with saturated aqueous $NaHCO_3$, H_2O (2x) and brine, dried over Na_2SO_4, and concentrated to give an orange oil which solidified *in vacuo*. Recrystallization from CH_2Cl_2/hexane afforded the product **3a** as a fluffy orange solid (1.80 g, 5.65 mmol, 72 %). Analytical data: mp 85 - 88 °C; IR (film) 2969, 2928, 1791, 1731, 1478, 1444, 1392, 1370, 1345, 1279, 1216, 1127, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); 5.06 (s, 2H), 4.63 (t, 2H, J = 8 Hz), 4.24 (t, 2H, J = 8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.0, 151.3, 93.3, 76.7, 63.6, 42.4 ppm; HRMS (CI, NH_3) 334.9705 (Exact mass calcd for $C_7H_6N_3O_5Cl_3$ $[M+NH_4]^+$, 334.9717); Anal. Calcd. for $C_7H_6O_5N_3Cl_3$: C, 26.40; H, 1.90; N, 13.19. Found: C, 26.50; H, 1.93; N, 13.13.

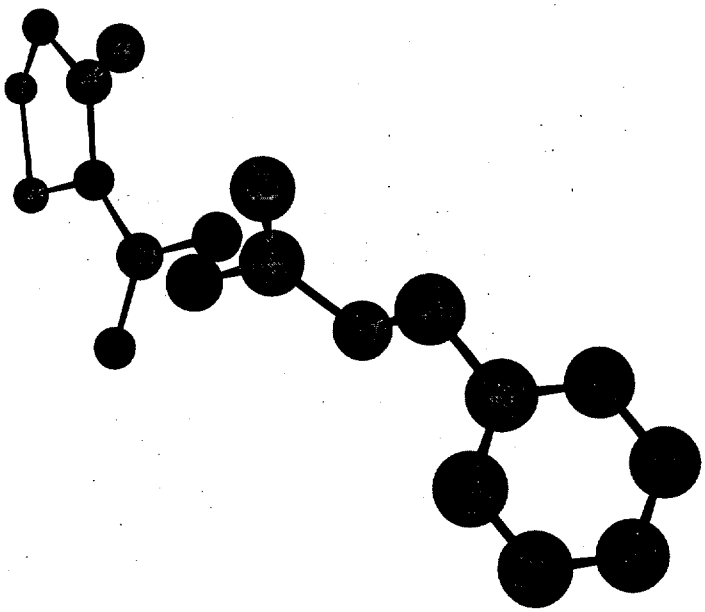


***tert*-Butyl {[(2-oxo-1,3-oxazolidin-3-yl)carbonyl]diazenyl}formate (3b).** (I-21) To a solution of **2b** (2.30 g, 9.38 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C was added pyridine (0.80 mL, 9.85 mmol). N-Bromosuccinimide (1.75 g, 9.85 mmol)[7] was added as a solid over 4 min. The reaction immediately turned orange and was allowed to warm to room temperature and stir for 2 h. The mixture was diluted with CH_2Cl_2 and H_2O was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with 0.5 M aqueous HCl, 10% aqueous K_2CO_3, H_2O and brine, dried over Na_2SO_4, and concentrated to give an orange oil which crystallized overnight *in vacuo*. Recrystallization from benzene/petroleum ether (5:1) afforded the product **3b** as a yellow solid (1.72 g, 7.07 mmol, 72%). Analytical data: mp 99 - 100 °C; IR (film) 2985, 2935, 1798, 1770, 1729, 1478, 1392, 1372, 1345, 1279, 1260, 1221, 1151, 1126, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.60 (t, 2H, J = 8 Hz), 4.20 (t, 2H, J = 8 Hz), 1.64 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 158.3, 151.4, 87.1, 63.5, 42.5, 27.7 ppm; HRMS (CI, NH_3) 261.1201 (Exact mass calcd for $C_9H_{13}N_3O_5$ $[M + NH_4]^+$, 261.1199). Anal. Calcd. for $C_9H_{13}O_5N_3$: C, 44.45; H, 5.39; N, 17.28. Found: C, 44.27; H, 5.34; N, 17.19.

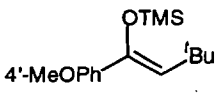


Phenylmethyl {[(2-oxo-1,3-oxazolidin-3-yl)carbonyl]diazenyl}formate (3c). (I-71) To a suspension of **2c** (2.14 g, 7.67 mmol) in CH_2Cl_2 (60 mL) was added pyridine (0.70 mL, 8.43 mmol) and the mixture became homogenous. The solution was cooled to 0 °C and N-bromosuccinimide (1.50 g, 8.43 mmol)[7] was added as a solid over 4 min. The reaction immediately turned orange and was allowed to warm to room temperature and stir for 2 h. The mixture was diluted with CH_2Cl_2 and H_2O was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with 0.5 M aqueous HCl, 10% aqueous K_2CO_3, H_2O and brine, dried over Na_2SO_4, and concentrated to give a yellow solid. Recrystallization from benzene/pentane (20:1) afforded the product **3c** as a yellow solid (1.90 g, 6.86 mmol, 89%). Analytical data: mp 104 - 106 °C; IR (film) 3034, 2990, 2919, 1795, 1771, 1727, 1498, 1477, 1456, 1391, 1369, 1344, 1222, 1126, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.46 (m, 5H), 5.48 (s, 2H), 4.60 (t, 2H, J = 8 Hz), 4.21 (t, 2H, J = 8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.4, 151.2, 70.8, 63.4 42.4 ppm; HRMS (CI) 295.1056 (Exact mass calcd for $C_{12}H_{11}N_3O_5$ $[M+NH_4]^+$, 295.1042).

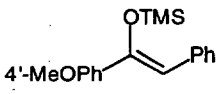
5) Washed with H_2O, dried over $CaCl_2$, and distilled according to ref. 1 to remove EtOH stabilizer. Alternatively, $CDCl_3$ can be used.
6) Little, R. D.; Venegas, M. G. *Org. Synth., Coll. Vol. VII* **1990**, 56-59.
7) (a) Carpino, L. A.; *et. al. Org. Synth., Coll. Vol. V* **1973**, 160-171. (b) Starr, J. T.; Rai, G. S.; Dang, H.; McNelis, B. J. *Synth. Commun.* **1997**, *27*, 3197-3200.



General Procedure for Preparation of the Enolsilanes (4a-g, i and 6a-d). (II-41,287)
To a solution of diisopropylamine (2.26 mL, 17.3 mmol, 1.15 equiv) in THF (20 mL) cooled to 0 °C was added n-BuLi (11.5 mL, 16.5 mmol, 1.44 M in hexanes). After 15 min, the mixture was cooled to -78 °C and the aryl ketone (15.0 mmol, sometimes as a solution in THF) was added. After 20 min, chlorotrimethylsilane (2.28 mL, 18.0 mmol, 1.2 equiv) was added. The solution was stirred at -78 °C for 1 h and then allowed to warm to room temperature and stir for 1-4 h. The reaction mixture was partitioned between pentane and pH 7 phosphate buffer. The organic layer was washed with pH 7 phosphate buffer, 0.5 M aqueous $CuSO_4$ (5x), pH 7 phosphate buffer and brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation (between 150 mtorr and 2 mm Hg) generally afforded the enolsilanes as clear liquids, however some were slightly yellow. Enolsilane **4c** was a tan solid and was used without purification. This procedure did not work for the preparation of **4h** and provided a 4:1 (*Z*:*E*) mixture of enol silane **4j**, so in these cases the procedure below was employed.



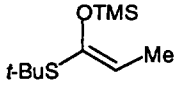
4h



4j

Preparation of the Enolsilanes 4h and 4j. (III-15, 24, II-257) To a solution of sodium bis(trimethylsilyl)amide (8.4 mL, 8.4 mmol, 1.0 M in THF) in THF (1.6 mL) cooled to -78 °C was added DMPU (1 mL) followed by the aryl ketone (1.44 g for **4h** or 1.58 g for **4j**, 7.0 mmol, in 5 mL THF). After 20 min, chlorotrimethylsilane (1.3 mL, 10.5 mmol, in 1 mL THF) was added. The reaction mixture became viscous. After 30 min at -78 °C, the mixture was allowed to warm to room temperature and stirred for 2-4 h. The reaction mixture was partitioned between pentane and pH 7 phosphate buffer. The organic layer was washed with pH 7 phosphate buffer, 5% aqueous cold HCl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The unpurified material was passed through a plug of SiO_2 or Florisil (2 inch, equilibrated first with 100% Et_2O and then the desired solvent system) using 2-5% Et_2O/pentane to give enolsilane **4h** as a clear thick liquid (1.92 g, 6.9 mmol, 98%) and enolsilane **4j** as a clear oil (2.00 g, 6.7 mmol, 96%) which solidified over several months.

General Procedure for the Preparation of Thioester Enolsilanes (8):



(*E*)-1-(*tert*-butylthio)-1-trimethylsilyloxyprop-1-ene.[8] (III-110) To a solution of diisopropylamine (1.31 mL, 10.0 mmol) in THF (10 mL) cooled to 0 °C was added n-BuLi (6.25 mL, 10.0 mmol, 1.6 M in hexanes). After 15 min, the mixture was cooled to -78 °C and HMPA (3.5 mL) was added. Freshly distilled *t*-butylthiopropionate (2.44 mL, 15.0 mmol) was added as a solution in THF (10 mL) and HMPA (3 mL) *via* cannula over 2 min. After 20 min, chlorotrimethylsilane (1.5 mL, 12.0 mmol) was added as a solution in hexanes (5 mL). The solution was stirred at -78 °C for 30 min and then allowed to warm to room temperature and stir for 2h. The reaction mixture was partitioned between pentane and pH 7 phosphate buffer. The organic layer was washed with pH 7 phosphate buffer (3x), 0.5 M aqueous

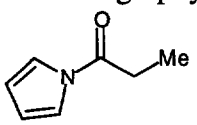
8) (a) Gennari, C.; Beretta, M. G.; Bernardi, A.; Moro, G.; Scolastico, C.; Todeschini, R. *Tetrahedron*, **1986**, *42*, 893-909. (b) Oare, D. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 157-172. (c) Ireland, R. E.; Wipf, P.; Armstrong, J. D. *J. Org. Chem.* **1991**, *56*, 650-657. (d) Otera, J.; Fujita, Y.; Fukuzumi, S. *Synlett* **1994**, 213-214.

$CuSO_4$ (5x), pH 7 phosphate buffer (2x) and brine, dried over $MgSO_4$, and concentrated *in vacuo*. Distillation (62 °C, 8 mm Hg) afforded the (*E*) silylketene acetal as a clear liquid.

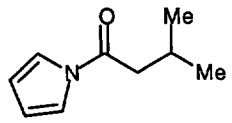
(*Z*)-1-(*tert*-butylthio)-1-trimethylsilyloxyprop-1-ene.[9]

General Procedure for the Preparation of Acylpyrroles.

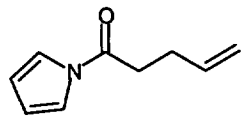
To a solution of freshly distilled pyrrole (7.0 mL, 100 mmol) in THF (100 mL) cooled to 0 °C was added n-BuLi (38.0 mL, 95 mmol, 2.5 M in hexanes). The solution turned anywhere from yellowish-green to dark green depending on the experiment. After 15 min, the solution was cooled to -78 °C and it became a slurry. The acid chloride (95 mmol) was added as a solution in THF (25 mL) quickly *via* cannula and the reaction immediately became homogenous. After 30 min at -78 °C, the reaction was warmed to room temperature and stirred anywhere from 2h to overnight. The reaction was poured into a separatory funnel containing Et_2O and H_2O. The organic layer was washed with H_2O (2x) and brine (2x), dried over $MgSO_4$, and concentrated to give a brown liquid (or brown solid for 3-phenyl-1-pyrrolylpropan-1-one). Purification by distillation (or chromatography/recrystallization for 3-phenyl-1-pyrrolylpropan-1-one) gave the desired acylpyrrole.



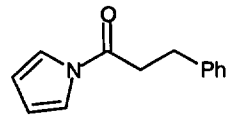
1-pyrrolylpropan-1-one. Distillation (83-85 °C, 16 mm Hg) provided a clear liquid (7.38 g, 60.0 mmol, 63%). Analytical data: IR (neat) 3148, 2985, 2943, 2883, 1722, 1592, 1543, 1471, 1407, 1365, 1321, 1272, 1240, 1125, 1084, 1070, 1015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (bs, 2H), 6.29 (t, 2H, *J* = 2.4 Hz), 2.87 (q, 2H, *J* = 7.4 Hz), 1.29 (t, 3H, *J* = 7.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 118.9, 112.9, 27.9, 8.5 ppm; LRMS (EI) 123 (Exact mass calcd for C_7H_9NO $[M]^+$, 123.0684).



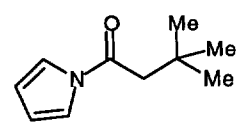
3-methyl-1-pyrrolylbutan-1-one. (III-131) Distillation (68 °C, ca. 2 mm Hg) provided a clear liquid (66%). Analytical data: IR (neat) 3149, 3108, 2961, 2934, 2873, 1718, 1590, 1542, 1469, 1406, 1370, 1346, 1321, 1308, 1259, 1220, 1172, 1139, 1106, 1072, 1053, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (bs, 2H), 6.29 (t, 2H, *J* = 2.1 Hz), 2.69 (d, 2H, *J* = 6.9 Hz), 2.30 (app septet, 1H, *J* = 6.7 Hz), 1.04 (d, 6H, *J* = 6.7 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 119.0, 112.9, 43.4, 25.5, 22.6 ppm; HRMS (EI) 151.1000 (Exact mass calcd for $C_9H_{13}NO$ $[M]^+$, 151.0997).



1-pyrrolylpent-4-en-1-one. (III-145) Distillation (76-78 °C, ca. 2 mm Hg) provided a clear liquid (11.1 g, 74.4 mmol, 78%). Analytical data: IR (neat) 3149, 3108, 3080, 2980, 2919, 1717, 1642, 1593, 1559, 1541, 1471, 1448, 1408, 1370, 1322, 1280, 1244, 1121, 1074 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (bs, 2H), 6.29 (t, 2H, *J* = 2.4 Hz), 5.89 (ddt, 1H, *J* = 16.9, 10.3, 6.5 Hz), 5.12 (ddd, 1H, *J* = 17.1, 1.6, 1.6 Hz), 5.05 (ddd, 1H, *J* = 10.2, 1.3, 1.3 Hz), 2.92 (t, 2H, *J* = 7.4 Hz), 2.53 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 136.2, 118.9, 115.9, 113.0, 33.7, 28.2 ppm; HRMS (EI) 149.0843 (Exact mass calcd for $C_9H_{11}NO$ $[M]^+$, 149.0841).



3-phenyl-1-pyrrolylpropan-1-one. (III-129) This reaction was performed using 75.0 mmol of hydrocinnamoyl chloride. The unpurified product was obtained as a brown solid which was dissolved in CH_2Cl_2 and SiO_2 was added. The solvent was evaporated and the solid was added to the top of a SiO_2 column and eluted with 4% Et_2O/pentane. The resulting solid was recrystallized from hexanes to give a white solid (8.6 g, 43.2 mmol, 58%). Analytical data: IR (neat) 3147, 3062, 3028, 2930, 1718, 1653, 1603, 1559, 1541, 1497, 1470, 1407, 1373, 1324, 1308, 1278, 1246, 1119, 1074, 1060 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.34 (m, 7H), 6.29 (t, 2H, *J* = 2.3 Hz), 3.08-3.18 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 140.2, 128.6, 128.4, 126.4, 118.9, 113.1, 36.4, 30.3 ppm; HRMS (EI) 199.1000 (Exact mass calcd for $C_{13}H_{13}NO$ $[M]^+$, 199.0997).

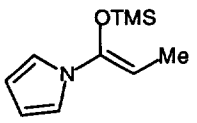


3,3-dimethyl-1-pyrrolylbutan-1-one. (III-130) Distillation (70 °C, ca. 2 mm Hg) provided a clear liquid (87%). Analytical data: IR (neat) 3151, 3108, 2958, 2906, 2870, 1713, 1589, 1542, 1468, 1404, 1366, 1340, 1272, 1230, 1201, 1168, 1115, 1074, 1059, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (bs, 2H), 6.28 (t, 2H, *J* = 2.3 Hz), 2.70 (s, 2H), 1.11 (s, 9H)

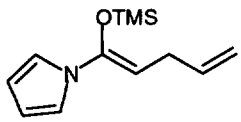
9) Hall, P. L.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9571-9574.

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 119.3, 112.8, 46.6, 31.4, 29.7 ppm; HRMS (EI) 165.1151 (Exact mass calcd for $C_{10}H_{15}NO$ $[M]^+$, 165.1154).

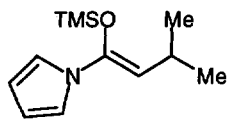
General Procedure for the Preparation of Acylpyrrole Enolsilanes (10).
To a solution of sodium bis(trimethylsilyl)amide (27.5 mL, 27.5 mmol, 1.1 equiv, 1.0 M in THF) in THF (10.0 mL) cooled to -78 °C was added DMPU (4 mL) followed by the acylpyrrole (25.0 mmol, in 7.5 mL THF). After 20 min, chlorotrimethylsilane (4.4 mL, 35.0 mmol, 1.4 equiv) was added. The reaction mixture became viscous. After 30 min at -78 °C, the mixture was allowed to warm to room temperature and stirred anywhere from 2h to overnight. The reaction mixture was partitioned between pentane and pH 7 phosphate buffer. The organic layer was washed with pH 7 phosphate buffer (several times), 0.5 M aqueous $CuSO_4$, pH 7 phosphate buffer and brine, dried over Na_2SO_4, and concentrated *in vacuo.* Distillation (300 mtorr - 2 mm Hg) provided the *Z* enolsilane as a clear thick liquid (the *E* isomer was not detected by NMR).



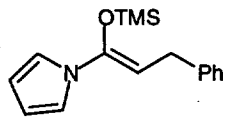
(*Z*)-1-pyrrolyl-1-trimethylsilyloxyprop-1-ene (10a). (III-178) This reaction was performed using 30.0 mmol of 1-pyrrolylpropan-1-one. Distillation (54 °C, ca. 2 mm Hg) provided the enolsilane as a clear liquid (5.57 g, 28.5 mmol, 95%). Analytical data: IR (neat) 3105, 2960, 2919, 2865, 1686, 1558, 1479, 1415, 1386, 1350, 1314, 1297, 1255, 1148, 1089, 1074, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.86 (t, 2H, *J* = 2.2 Hz), 6.17 (t, 2H, *J* = 2.2 Hz), 4.73 (q, 1H, *J* = 6.9 Hz), 1.68 (d, 3H, *J* = 6.9 Hz), 0.17 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 119.0, 108.9, 91.9, 10.6, -0.09 ppm; HRMS (EI) 195.1078 (Exact mass calcd for $C_{10}H_{17}NOSi$ $[M]^+$, 195.1079).



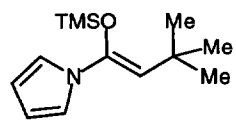
(*Z*)-1-pyrrolyl-1-trimethylsilyloxypenta-1,4-diene (10b). (III-149) Distillation (76-78 °C, ca. 2 mm Hg) provided the enolsilane as a clear liquid (4.15 g, 18.7 mmol, 75%). Analytical data: IR (neat) 3142, 3106, 3080, 3005, 2961, 2900, 1683, 1654, 1640, 1559, 1521, 1479, 1409, 1364, 1313, 1255, 1141, 1102, 1082, 1045, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, 2H, *J* = 2.2 Hz), 6.17 (t, 2H, *J* = 2.2 Hz), 5.86 (ddt, 1H, *J* = 16.1, 10.1, 6.0 Hz), 5.09 (ddd, 1H, *J* = 17.1, 1.8, 1.8 Hz), 5.01 (ddd, 1H, *J* = 10.1, 1.6, 1.6 Hz), 4.70 (t, 1H, *J* = 7.4 Hz), 2.87 (ddd, 2H, *J* = 7.4, 5.9, 1.6 Hz), 0.14 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.0, 119.0, 114.7, 109.0, 94.9, 29.5, -0.15 ppm; HRMS (EI) 221.1227 (Exact mass calcd for $C_{12}H_{19}NOSi$ $[M]^+$, 221.1236).



(*Z*)-3-methyl-1-pyrrolyl-1-trimethylsilyloxybut-1-ene (10c). (III-136) Distillation (69-70 °C, ca. 2 mm Hg) provided the enolsilane as a clear liquid (4.92 g, 22.0 mmol, 88%). Analytical data: IR (neat) 3106, 3019, 2958, 2906, 2870, 1681, 1558, 1519, 1479, 1407, 1384, 1365, 1325, 1312, 1254, 1182, 1158, 1104, 1078, 1043 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.84 (t, 2H, *J* = 2.2 Hz), 6.15 (t, 2H, *J* = 2.2 Hz), 4.52 (d, 1H, *J* = 9.6 Hz), 2.63 (dq, 1H, *J* = 9.6, 6.7 Hz), 1.03 (d, 6H, *J* = 6.7 Hz), 0.14 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 119.1, 108.8, 105.7, 25.1, 23.4, -0.22 ppm; HRMS (EI) 223.1398 (Exact mass calcd for $C_{12}H_{21}NOSi$ $[M]^+$, 223.1392).

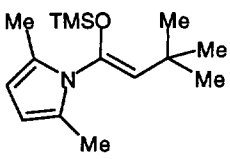


(*Z*)-3-phenyl-1-pyrrolyl-1-trimethylsilyloxyprop-1-ene. (III-157) This reaction was performed using 12.3 mmol of 3-phenyl-1-pyrrolylpropan-1-one. Distillation (92-95 °C, 300 mtorr) provided the enolsilane as a clear thick liquid (2.86 g, 10.5 mmol, 86%). Analytical data: IR (neat) 3105, 3063, 3028, 2960, 2899, 2842, 1681, 1604, 1560, 1494, 1478, 1453, 1410, 1365, 1313, 1256, 1133, 1086, 1074, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.42 (m, 5H), 6.93 (t, 2H, *J* = 2.1 Hz), 6.21 (t, 2H, *J* = 2.1 Hz), 4.92 (t, 1H, *J* = 7.4 Hz), 3.51 (d, 2H, *J* = 7.4 Hz), 0.20 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.1, 128.4, 128.2, 126.0, 119.0, 109.1, 96.3, 31.4, -0.09 ppm; HRMS (EI) 271.1386 (Exact mass calcd for $C_{16}H_{21}NOSi$ $[M]^+$, 271.1392).



(*Z*)-3,3-dimethyl-1-pyrrolyl-1-trimethylsilyloxybut-1-ene (10d). (III-133) Distillation provided the enolsilane as a clear liquid (4.6 g, 19.4 mmol, 78%). Analytical data: IR (neat) 2958, 2905, 2867, 1673, 1559, 1480, 1463, 1394, 1355, 1317, 1298, 1254, 1202, 1119, 1080, 1047 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.76 (t, 2H, *J* = 2.2 Hz), 6.12 (t, 2H, *J* = 2.2 Hz),

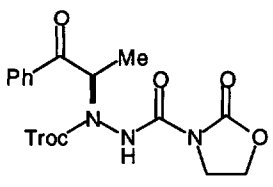
4.55 (s, 1H), 1.52 (s, 9H), 0.09 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 120.4, 111.0, 108.4, 30.7, 30.6, 0.09 ppm; HRMS (EI) 237.1554 (Exact mass calcd for $C_{13}H_{23}NOSi$ [M]$^+$, 237.1549).



(Z)-1-(2,5-dimethylpyrrolyl)-3,3-dimethyl-1-trimethylsilyloxybut-1-ene. (III-153) This reaction was performed using 5.8 mmol of 1-(2,5-dimethylpyrrolyl)propan-1-one. Distillation (52 °C, 600 mtorr) provided the enolsilane as a clear liquid (1.08 g, 4.07 mmol, 70%). Analytical data: IR (neat) 3105, 2956, 2905, 2866, 1674, 1582, 1523, 1478, 1462, 1394, 1339, 1300, 1264, 1254, 1232, 1190, 1090, 1039, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 2H), 4.46 (s, 1H), 2.19 (s, 6H), 1.19 (s, 9H), 0.01 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 127.8, 117.9, 105.6, 30.9, 30.3, 12.5, -0.14 ppm; HRMS (EI) 265.1862 (Exact mass calcd for $C_{15}H_{27}NOSi$ [M]$^+$, 265.1862).

General Procedure for the Amination Reaction Catalyzed by 2-10 mol% *t*-BuBox and 50 mol% Cu(OTf)$_2$. (II-111)
To an oven-dried 10 mL round bottom flask containing a magnetic stirring bar was added the azo compound **3** (63.6 mg, 0.20 mmol) and THF (0.3 mL). The orange solution was cooled to -78 °C and the catalyst solution containing t-BuBox (1.2-5.8 mg, 0.004-0.020 mmol) and $Cu(OTf)_2$ (36.2 mg, 0.10 mmol) in THF (1.0 mL) was added *via* cannula. The enolsilane (0.3 mmol) was added and the reaction was stirred at -78 °C for 24 h. The reaction was diluted with CH_2Cl_2 and saturated aqueous NH_4Cl was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ (2x) and brine, dried over Na_2SO_4, and concentrated. Purification by flash chromatography provided the title compounds as white foams.

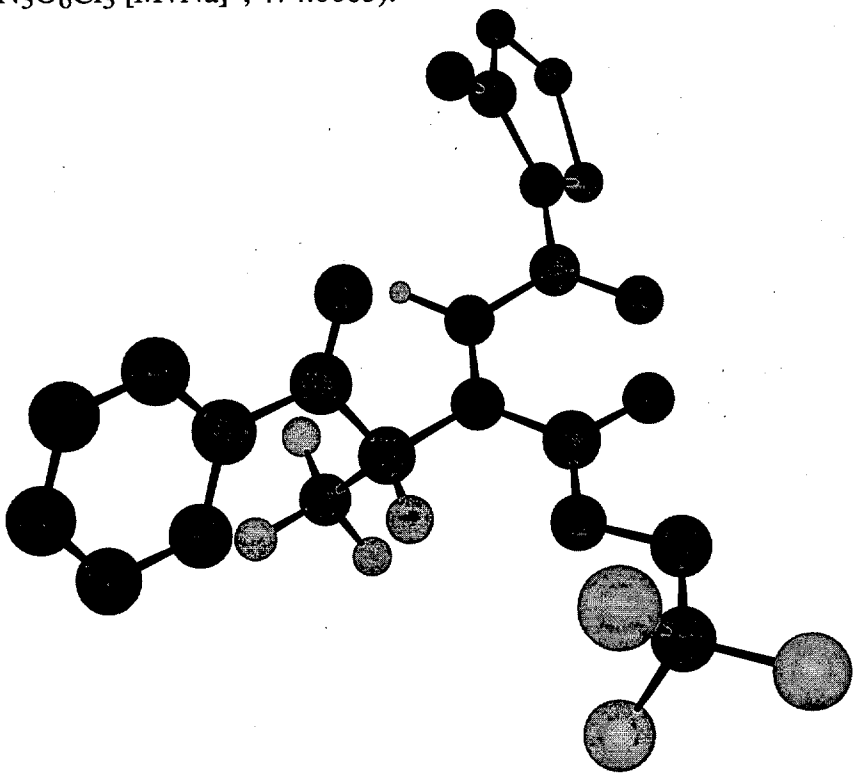
General Procedure for the Amination Reaction with Alcohol Additive.
To an oven-dried 10 mL round bottom flask containing a magnetic stirring bar was added the azo compound **3** (1 equiv) and THF. The orange solution was cooled to the indicated temperature (-20 to -78 °C) and the green catalyst solution **1** (5-10 mol% in THF)[10] was added in one portion or the blue hydrate catalyst **2** (1-5 mol%) was added as a solid in one portion. Trifluoroethanol (1 equiv) was added followed by the enolsilane (1.0-1.5 equiv). The reaction was stirred at this temperature until complete (1 min-24 h). The reaction was diluted with CH_2Cl_2 and saturated aqueous $NaHCO_3$ was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography provided the title compounds as white foams. The racemic samples were prepared by $SnCl_4$ (1 equiv) promoted reaction of the azo compound **3** with enolsilanes (0.2 M, CH_2Cl_2, -78 °C) or using $Cu(OTf)_2$ (0.5 equiv) in the case of some acylpyrrole enolsilanes (0.2 M, THF, -20 °C).

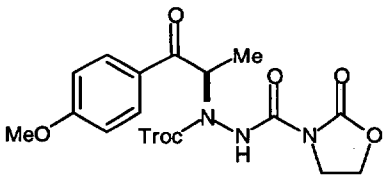


N-((1*R*)-1-methyl-2-oxo-2-phenylethyl)-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5a). (II-205,207,246,248,179) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4a** (150 μL, 0.75 mmol). The reaction was complete in 1 min as seen by infrared spectroscopy. Purification by flash chromatography (50% EtOAc/hexanes) gave **5a** as a white foam (215 mg, 0.475 mmol, 95%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (20% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 22 min; (***S***) enantiomer t_r = 32 min; 99% ee.
Analytical data: IR (film) 3311, 2995, 1762, 1729, 1689, 1596, 1577, 1511, 1481, 1450, 1401, 1313, 1279, 1227, 1149, 1038, 969 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (9.74) (s, 1H), 7.96 (7.94) (d, 2H, *J* = 8 Hz), 7.61 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.7 Hz), 5.88 (q, 1H, *J* = 7.4 Hz), 4.78 (4.81) (d, 1H, *J* = 11.9 Hz), 4.70 (4.68) (d, 1H, *J* = 11.8 Hz), 4.50 (bt, 2H, *J* = 8 Hz), 4.05-4.15 (m, 2H), 1.54 (1.55) (d, 3H, *J* = 7.3 Hz) ppm; ^{1}H NMR (400 MHz, 330 K, $CDCl_3$) δ 9.67 (s, 1H), 7.95 (d, 2H, *J* = 7.5 Hz), 7.58 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 2H, *J* = 7.7 Hz), 5.85 (q, 1H, *J* = 7.3 Hz), 4.78 (d, 1H, *J* = 11.8 Hz), 4.71 (d, 1H, *J* = 11.8 Hz), 4.46 (t, 2H, *J* = 8.0

10) A dry flask with a magnetic stirrer was charged with (*S,S*)-*tert*-Bu-box and $Cu(OTf)_2$ in an inert atmosphere (N_2) glove box. The flask was capped with a rubber septum and removed from the glove box. THF was added *via* syringe and the mixture was stirred for 30 min to give a clear green solution (sometimes appears bluish-green).

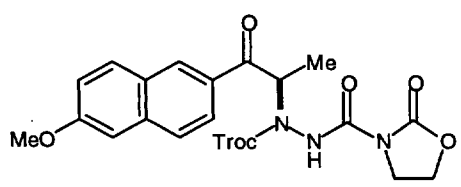
Hz), 4.05 (bt, 2H, J = 8.1 Hz), 1.54 (d, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 155.1, 154.1 (153.7), 152.1, 134.5 (134.2), 133.8 (133.9), 128.9, 128.6 (128.5), 94.8 (94.6), 75.7 (75.9), 63.0, 58.4 (59.3), 42.5, 14.5 (14.9) ppm; ^{13}C NMR (100 MHz, 330 K, $CDCl_3$) δ 198.5, 155.0, 154.1 (b), 152.1, 134.9, 133.6, 128.9, 128.5, 94.8, 76.0, 63.0, 58.5 (b), 42.5, 14.4 (b) ppm; HRMS (FAB, NBA-NaI) 474.0013 (Exact mass calcd for $C_{16}H_{16}N_3O_6Cl_3$ [M+Na]$^+$, 474.0003).





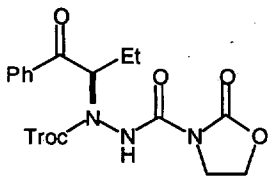
N-[(1*R*)-2-(4-methoxyphenyl)-1-methyl-2-oxoethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5b). (II-267,181) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4b** (150 μL, 0.75 mmol). The reaction was complete in less than 1 min as seen by infrared spectroscopy. Purification by flash chromatography (50-60% EtOAc/hexanes) gave **5b** as a white foam (231 mg, 0.480 mmol, 96%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (40% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 14.9 min; (***S***) enantiomer t_r = 23.7 min; 99% ee.

Analytical data: IR (film) 3312, 2961, 1761, 1728, 1676, 1600, 1573, 1512, 1481, 1400, 1320, 1265, 1233, 1174, 1149, 1036, 971 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (9.77) (s, 1H), 7.94 (7.91) (d, 2H, J = 9-10 Hz), 6.94 (d, 2H, J = 8.8 Hz), 5.82 (q, 1H, J = 7.3 Hz), 4.76 (4.79) (d, 1H, J = 11.8 Hz), 4.68 (4.65) (d, 1H, J = 11.7 Hz), 4.48 (bt, 2H, J = 8.3 Hz), 4.03-4.13 (m, 2H), 3.86 (s, 3H), 1.51 (1.52) (d, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 164.1, 155.0, 154.1 (153.7), 152.0, 131.0 (130.9), 127.2 (127.0), 114.1, 94.8 (94.6), 75.7 (75.9), 63.0, 57.9 (58.9), 55.5, 42.5, 14.7 (15.1) ppm; HRMS (FAB, NBA-NaI) 504.0131 (Exact mass calcd for $C_{17}H_{18}N_3O_7Cl_3$ [M+Na]$^+$, 504.0108).

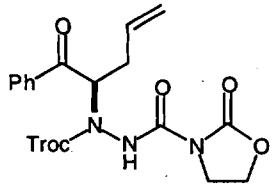


N-[(1*R*)-2-(6-methoxy(2-naphthyl))-1-methyl-2-oxoethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5c). (II-182) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **4c** (85 mg, 0.3 mmol, in 0.5 mL THF). Purification by flash chromatography (50-60% EtOAc/hexanes) gave **5c** as a white foam (103 mg,

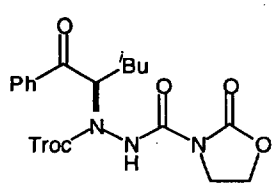
0.193 mmol, 97%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (40% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 19.0 min; (***S***) enantiomer t_r = 28.0 min; 99% ee.
Analytical data: IR (film) 3312, 2938, 1761, 1728, 1678, 1624, 1507, 1481, 1398, 1318, 1270, 1233, 1199, 1148, 1107, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (9.82) (s, 1H), 8.43 (8.39) (s, 1H), 7.95 (t, 1H, *J* = 8 Hz), 7.85 (7.84) (d, 1H, *J* = 9.0 Hz), 7.78 (d, 1H, *J* = 8.6 Hz), 7.20 (7.20) (d, 1H, *J* = 8.9 Hz), 7.14 (s, 1H), 6.01 (q, 1H, *J* = 7.3 Hz), 4.78 (4.80) (d, 1H, *J* = 11.8 Hz), 4.71 (4.68) (d, 1H, *J* = 11.8 Hz), 4.49 (t, 2H, *J* = 8 Hz), 4.05-4.14 (m, 2H), 3.94 (s, 3H), 1.58 (1.59) (d, 3H, *J* = 7.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3 (198.4), 160.1 (160.2), 155.0, 154.2 (153.7), 152.1, 137.7, 131.3 (131.2), 130.4 (130.2), 129.7 (129.5), 127.8, 127.5 (127.5), 124.8 (124.7), 120.0 (121.1), 105.8, 94.8 (94.6), 75.7 (75.9), 63.0, 58.2 (59.1), 55.5, 42.5, 14.8 (15.2) ppm; HRMS (FAB, NBA-NaI) 554.0267 (Exact mass calcd for $C_{21}H_{20}N_3O_7Cl_3$ [M+Na]$^+$, 554.0265).



N-((1*R*)-1-ethyl-2-oxo-2-phenylethyl)-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5d). (II-263,197) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4d** (150 μL, 0.75 mmol). The reaction was complete in 25 min as seen by infrared spectroscopy. Purification by flash chromatography (30-40% EtOAc/hexanes) gave **5d** as a white foam (214 mg, 0.458 mmol, 92%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (20% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 17 min; (***S***) enantiomer t_r = 24 min; 98% ee.
Analytical data: IR (film) 3304, 2967, 1761, 1728, 1687, 1597, 1580, 1508, 1481, 1448, 1399, 1321, 1220, 1147, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (9.83) (s, 1H), 7.96 (7.93) (d, 2H, *J* = 7.4 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.49 (t, 2H, *J* = 7.7 Hz), 5.68 (dd, 1H, *J* = 9.6, 9.6 Hz), 4.78 (4.83) (d, 1H, *J* = 11.8 Hz), 4.74 (4.71) (d, 1H, *J* = 11.8 Hz), 4.48 (m, 2H), 4.03-4.15 (m, 2H), 1.84-1.99 (m, 2H), 1.40 (dd, 3H, *J* = 7.5, 7.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 155.1, 154.7 (154.0), 151.7 (151.6), 135.2 (134.9), 133.8 (133.9), 128.9, 128.5 (128.5), 94.8 (94.6), 75.8 (75.9), 65.0 (63.9), 63.0, 42.5, 22.1 (22.5), 11.2 (11.5) ppm; HRMS (FAB, NBA-NaI) 488.0175 (Exact mass calcd for $C_{17}H_{18}N_3O_6Cl_3$ [M+Na]$^+$, 488.0159).



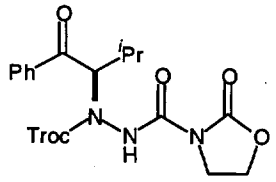
N-[N-((1*R*)-2-oxo-2-phenyl-1-prop-2-enylethyl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (5e). (III-99, 196) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4e** (150 μL, 0.75 mmol). The reaction was complete in 2 h as seen by infrared spectroscopy. Purification by flash chromatography (40% EtOAc/hexanes) gave **5e** as a white foam (220 mg, 0.460 mmol, 92%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (30% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 11.2 min; (***S***) enantiomer t_r = 14.0 min; 97% ee. The reaction was also conducted at -50°C to give **5e** in 99% ee (10 mol% **1**, 4 h).
Analytical data: IR (film) 3304, 2920, 1761, 1733, 1686, 1507, 1480, 1399, 1310, 1232, 1138, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (9.72) (s, 1H), 7.99 (7.95) (d, 2H, *J* = 7.6 Hz), 7.60 (m, 1H), 7.48 (t, 2H, *J* = 7.7 Hz), 5.89-5.97 (m, 1H), 5.79-5.86 (m, 1H), 5.20 (5.19) (bd, 1H, *J* = 17.0 Hz), 5.10 (bd, 1H, *J* = 10.1 Hz), 4.77 (4.84) (d, 1H, *J* = 11.8 Hz), 4.70 (4.73) (d, 1H, *J* = 11.7 Hz), 4.70 (t with rotamer, 2H, *J* = 8 Hz), 4.00-4.13 (m, 2H), 2.60-2.74 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 155.1, 154.3 (153.6), 151.6, 135.1 (134.8), 133.9 (134.0), 133.4, 128.9 (128.9), 128.7 (128.6), 118.4, 94.6 (94.7), 75.8 (76.0), 63.1, 62.7 (61.2), 42.5, 32.7 (33.2) ppm; HRMS (ESI) 478.0361 (Exact mass calcd for $C_{18}H_{18}N_3O_6Cl_3$ [M+H]$^+$, 478.0339).



N-[(1*R*)-1-(2-methylpropyl)-2-oxo-2-phenylethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5f) (II-264,193) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4f** (150 μL, 0.75 mmol). The reaction was complete in 2 h as seen by infrared spectroscopy. Purification by flash

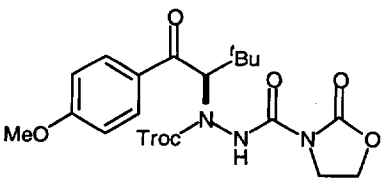
chromatography (20-30% EtOAc/hexanes) gave **5f** as a white foam (227 mg, 0.460 mmol, 92%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 24 min; (***S***) enantiomer t_r = 30 min; 98% ee.

Analytical data: IR (film) 3305, 2959, 2928, 2870, 1763, 1729, 1688, 1597, 1580, 1507, 1481, 1448, 1400, 1369, 1314, 1233, 1138, 1040, 1004 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (9.85), 7.96 (7.93) (d, 2H, *J* = 7.6 Hz), 7.60 (m, 1H), 7.49 (t, 2H, *J* = 7.7 Hz), 5.91 (m, 1H), 4.78 (s, 1H), 4.74 (4.71) (d, 1H, *J* = 11.5 Hz), 4.49 (t with rotamer, 2H), 4.04-4.16 (m, 2H), 2.04 (bm, 1H), 1.82 (m, 1H), 1.58 (m, 1H), 1.11 (1.09) (d, 3H, *J* = 6.3 Hz), 0.92 (0.91) (d, 3H, *J* = 6.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 155.1, 154.6 (153.9), 151.5 (151.3), 135.0 (134.7), 133.8 (133.7), 128.9, 128.6 (128.5), 94.8 (94.6), 75.8 (76.0), 53.0, 61.5 (60.6), 42.5 (42.4), 37.7 (37.3), 24.9 (24.8), 23.3, 21.6 (21.4) ppm; HRMS (FAB, NBA-NaI) 516.0480 (Exact mass calcd for $C_{19}H_{22}N_3O_6Cl_3$ [M+Na]$^+$, 516.0472).



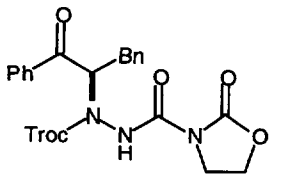
N-[(1*R*)-1-(methylethyl)-2-oxo-2-phenylethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5g) (II-244,201) According to the general procedure, 1.5 mL of a 0.017 M solution of **1** (5 mol%, 0.025 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **4g** (150 μL, 0.75 mmol). The reaction was complete in 3 h as seen by infrared spectroscopy. Purification by flash chromatography (30% EtOAc/hexanes) gave **5g** as a white foam (206 mg, 0.429 mmol, 86%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 25.8 min; (***S***) enantiomer t_r = 34.8 min; 99% ee.

Analytical data: IR (film) 3306, 2964, 2929, 2875, 1763, 1729, 1688, 1597, 1580, 1514, 1481, 1448, 1401, 1370, 1303, 1271, 1222, 1146, 1122, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (9.73) (bs, 1H), 8.04 (8.01) (d, 2H, *J* = 7.7 Hz), 7.58 (m, 1H), 7.47 (t, 2H, *J* = 7.6 Hz), 5.48 (5.46) (d, 1H, *J* = 10 Hz), 4.79 (d, 1H, *J* = 12 Hz), 4.67 (d, 1H, *J* = 11.8 Hz), 4.45 (t, 2H, *J* = 8.2 Hz), 3.95-4.06 (m, 2H), 1.10 (1.13) (d, 3H, *J* = 6.6 Hz), 0.90 (d, 3H, *J* = 6.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 155.2, 154.3 (153.4), 151.1 (151.0), 136.7 (136.5), 133.7 (133.8), 128.8, 128.7, 94.7 (94.6), 75.7 (76.1), 65.6 (64.6), 63.0, 42.4, 27.8 (27.2), 19.6 (19.7), 19.4 (19.3) ppm; HRMS (FAB, NBA-NaI) 502.0321 (Exact mass calcd for $C_{18}H_{20}N_3O_6Cl_3$ [M+Na]$^+$, 502.0316).



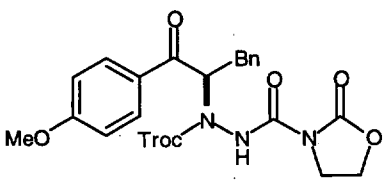
N-[(1*R*)-1-(tert-butyl)-2-(4-methoxyphenyl)-2-oxoethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5h). (III-31,39) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (76 mg, 0.24 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **4h** (56 mg, 60 μL, 0.20 mmol, in 0.1 mL THF). The reaction was worked-up after 6 h. Purification by flash chromatography (30-40% EtOAc/hexanes) gave **5h** as a white foam (88 mg, 0.168 mmol, 84% based on **4h**). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (30% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 10.2 min; (***S***) enantiomer t_r = 15.1 min; 98% ee.

Analytical data: IR (film) 3322, 2961, 1763, 1727, 1681, 1600, 1575, 1512, 1481, 1399, 1369, 1309, 1237, 1173, 1124, 1095, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (bs, 1H), 7.98 (d, 2H, *J* = 8.5 Hz), 6.93 (d with rotamer, 2H, *J* = 8.7 Hz), 5.71 (5.68) (bs, 1H), 4.68-4.88 (m, 2H), 4.45 (bt, 2H, *J* = 8 Hz), 3.98 (bm, 2H), 3.85 (s, 3H), 1.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194 (b), 163.9, 155.2, 154.8 (153.6), 151.0 (150.8), 130.9, 130.8, 114.0, 94.8, 76.0 (76.4), 65.4 (b), 63.0, 55.5, 42.4, 36.0 (b), 27.6 (27.8) ppm; HRMS (FAB, NBA-NaI) 546.0599 (Exact mass calcd for $C_{20}H_{24}N_3O_7Cl_3$ [M+Na]$^+$, 546.0578).

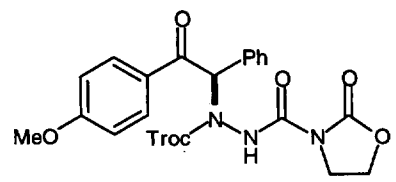


N-[(1*R*)-2-oxo-2-phenyl-1-benzylethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5). (II-255,260) According to the general procedure, 2.0 mL of a 0.125 M solution of **1** (50 mol%, 0.25 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 0.5 mL THF) cooled to -78 °C. Enol silane **4** (200 μL) was added and the reaction was stirred for 8h. Trifluoroethanol (40 μL, 0.50 mmol) was added and the reaction was stirred for another 3h. The reaction was

followed by infrared spectroscopy. The IR stretch at 1764 cm^{-1} increased dramatically and the stretch at 1698 cm^{-1} decreased dramatically when trifluoroethanol was added. Purification by flash chromatography (20-30% EtOAc/hexanes) gave **5** as a white foam (225 mg, 0.426 mmol, 85%). Enantiomeric excess was determined by HPLC with a Chiralcel OJ column (30% EtOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 19 min (variable); (***S***) enantiomer t_r = 29 min (variable); 99% ee. The reaction did not go to completion using 10 mol% **1**. The reaction was also conducted using 50 mol% **1** without the addition of trifluoroethanol and the product was obtained in 83% yield and 99% ee.
Analytical data: IR (film) 3300, 3068, 3021, 2925, 1761, 1733, 1687, 1597, 1520, 1480, 1449, 1399, 1306, 1230, 1126, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.98 (bd, 1H, *J* = 7.1 Hz), 7.91 (d, 1H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.4 Hz), 7.43 (m, 2H), 7.34 (d, 2H, *J* = 7.5 Hz), 7.28 (t, 2H, *J* = 7.5 Hz), 7.20 (m, 1H), 6.10 (6.03) (t, 1H, *J* = 7 Hz), 4.72 (4.83) (d, 1H, *J* = 11.8 Hz), 4.62 (4.56) (d, 1H, *J* = 11.8 Hz), 4.48 (t with rotamer, 2H, *J* = 8 Hz), 3.96-4.10 (m, 2H), 3.31 (3.34) (d, 1H, *J* = 8.0 Hz), 3.24 (3.21) (d, 1H, *J* = 6.6 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 155.2, 153.9 (153.2), 151.5 (151.5), 136.5 (136.7), 135.4 (135.1), 133.7 (133.8), 129.2, 128.7 (large peak - 3 aromatic carbons?), 126.9 (127.0), 94.6 (94.5), 75.6 (76.0), 63.3 (61.5), 63.1, 42.4, 34.7 (34.1) ppm; HRMS (ESI) 528.0522 (Exact mass calcd for $C_{22}H_{20}N_3O_6Cl_3$ $[M+H]^+$, 528.0496).

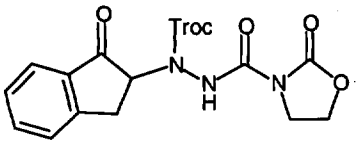


N-[(1*R*)-2-(4-methoxyphenyl)-2-oxo-1-benzylethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5i). (II-289, III-9) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **4i** (90 μL, 0.3 mmol, in 0.2 mL THF). The reaction was worked-up after 12 h. Purification by flash chromatography (40% EtOAc/hexanes) gave **5i** as a white foam (105 mg, 0.188 mmol, 94%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (20% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 32 min; (***S***) enantiomer t_r = 36 min; 99% ee. The reaction was also conducted at -20 °C to give **5i** in 91% ee (5 min, 85% yield).
Analytical data: IR (film) 3302, 2960, 1762, 1733, 1682, 1600, 1576, 1559, 1512, 1480, 1456, 1399, 1308, 1262, 1237, 1172, 1125, 1094, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.67 (9.70) (bs, 1H), 7.97 (bd, 1H, *J* = 7.4 Hz), 7.89 (d, 1H, *J* = 8.6 Hz), 7.33 (d, 2H, *J* = 7.5 Hz), 7.27 (t, 2H, *J* = 7.5 Hz), 7.20 (m, 1H), 6.90 (6.87) (d, 2H, *J* = 8.8 Hz), 6.05 (5.98) (t, 1H, *J* = 7.1 Hz), 4.72 (4.83) (d, 1H, *J* = 11.8 Hz), 4.62 (4.56) (d, 1H, *J* = 11.8 Hz), 4.47 (t with rotamer, 2H, *J* = 8 Hz), 3.96-4.10 (m, 2H), 3.85 (s, 3H), 3.30 (3.33) (d, 1H, *J* = 7.8 Hz), 3.23 (3.20) (d, 1H, *J* = 6.2 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 164.0 (164.1), 155.2, 153.9 (153.2), 151.5 (151.5), 136.9 (136.7), 131.1 (131.1), 129.3, 128.7, 128.3 (128.0), 126.9 (126.9), 114.0, 94.7 (94.5), 75.7 (76.0), 63.1, 61.5 (b), 55.5, 42.4, 34.9 (34.3) ppm; HRMS (ESI) 558.0625 (Exact mass calcd for $C_{23}H_{22}N_3O_7Cl_3$ $[M+H]^+$, 558.0601).

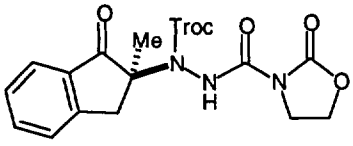


N-[(1*R*)-2-(4-methoxyphenyl)-2-oxo-1-phenylethyl]-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (5j). (III-17-19) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -50 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **4j** (90 mg, 0.3 mmol, in 0.1 mL THF). The reaction was worked-up after 24 h. Purification by flash chromatography (50-60% EtOAc/hexanes) gave **5j** as a white foam (102 mg, 0.187 mmol, 94%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (50% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***R***) enantiomer t_r = 33 min; (***S***) enantiomer t_r = 39 min; 97% ee. The reaction was also conducted at -20 °C to give **5j** in 91% ee (2 h, 95% yield).
Analytical data: IR (film) 3310, 2958, 1761, 1731, 1676, 1599, 1575, 1509, 1480, 1456, 1398, 1316, 1251, 1231, 1170, 1123, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.91 (9.88) (s, 1H), 7.86 (d with rotamer, 2H, *J* = 8.8 Hz), 7.36 (m, 2H), 7.31 (m, 3H), 6.88 (s, 1H), 6.82 (d, 2H, *J* = 8.9 Hz), 4.74-4.82 (m, 2H), 4.30-4.39 (m, 2H), 3.80-3.88 (m, 1H), 3.80 (s, 3H), 3.61-3.67 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 163.9, 154.9, 154.7 (153.6), 150.7, 132.5 (132.0), 131.5 (131.3), 130.6 (130.5), 129.1 (129.2), 128.8 (128.8), 127.2

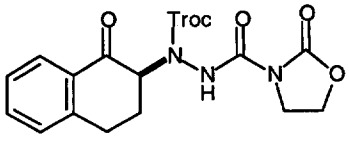
(127.2), 113.9, 94.8 (94.7), 75.8, 67.1 (67.9), 62.8, 55.5, 42.2 (42.1) ppm; HRMS (FAB, NBA-NaI) 566.0267 (Exact mass calcd for $C_{22}H_{20}N_3O_7Cl_3$ [M+Na]$^+$, 566.0265).



N-[N-(1-oxoindan-2-yl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (7a). (II-159, 273,III-92) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **6a** (65 μL, 0.3 mmol). The reaction was worked-up after 12 h. Purification by flash chromatography (10% EtOAc/CH_2Cl_2) gave **7a** as a white foam (81 mg, 0.180 mmol, 90%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (40% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***S***) enantiomer t_r = 19.5 min; (***R***) enantiomer t_r = 28.1 min; 21% ee.
Analytical data: IR (film) 3306, 2951, 1760, 1724, 1610, 1513, 1479, 1400, 1298, 1234, 1205, 1145, 1094, 1038 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (9.70) (s, 1H), 7.77 (d, 1H, *J* = 7.7 Hz), 7.62 (t, 1H, *J* = 7.5 Hz), 7.45 (bd, 1H, *J* = 7.4 Hz), 7.39 (t, 1H, *J* = 7.4 Hz), 4.97 (4.83) (bt, 1H), 4.78 (d, 1H, *J* = 11.8 Hz), 4.69 (4.68) (d, 1H, *J* = 11.8 Hz), 4.41-4.48 (m, 2H), 3.97-4.10 (m, 2H), 3.59 (3.63) (dd, 1H, *J* = 8.4, 17.5 Hz), 3.41 (3.47) (dd, 1H, *J* = 5.6, 17.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0 (199.6), 154.9, 153.5 (153.4), 152.3 (152.0), 151.5 (151.4), 135.8, 134.6 (134.5), 128.0, 126.7, 124.5 (124.7), 94.7 (94.3), 75.8 (76.0), 65.0 (66.1), 63.1, 42.4, 30.6 (31.7) ppm; HRMS (ESI) 450.0008 (Exact mass calcd for $C_{16}H_{14}N_3O_6Cl_3$ [M+H]$^+$, 450.0026).

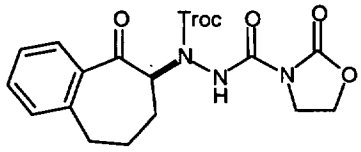


N-[N-((2*S*)-2-methyl-1-oxoindan-2-yl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (7b). (II-280, 284, 285) According to the general procedure, 1.25 mL of a 0.04 M solution of **1** (10 mol%, 0.05 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -78 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by **6b** (160 μL, 0.75 mmol, in 0.25 mL THF). The reaction was complete in 6 h as seen by infrared spectroscopy. Purification by flash chromatography (40-50% EtOAc/hexanes) gave **7b** as a white foam (204 mg, 0.439 mmol, 88%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (30% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***S***) enantiomer t_r = 16.3 min; (***R***) enantiomer t_r = 19.8 min; 96% ee. The reaction at -20 °C was complete in 1 min and afforded **7b** in 86% ee.
Analytical data: IR (film) 3316, 2978, 1762, 1723, 1610, 1513, 1479, 1433, 1398, 1338, 1302, 1286, 1209, 1164, 1130, 1082, 1039, 966 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (9.70) (s, 1H), 7.81 (bd, 1H, *J* = 7.2 Hz), 7.61 (bd with rotamer, 1H, *J* = 7 Hz), 7.40 (bd, 2H, *J* = 7.5 Hz), 4.77 (bd, 1H, *J* = 11.6 Hz), 4.53 (t, 2H, *J* = 8.2 Hz), 4.49 (bd overlapping with peak at 4.53, 1H), 4.09 (t, 2H, *J* = 8 Hz), 3.80 (d, 1H, *J* = 16.7 Hz), 3.19 (3.25) (d, 1H, *J* = 17.2), 1.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 155.1, 152.7 (152.8), 150.4, 135.4, 133.3, 127.7, 126.5, 124.9, 94.7, 75.5, 68.5, 63.2, 42.4, 41.1, 22.4 ppm; HRMS (FAB, NBA-NaI) 486.0011 (Exact mass calcd for $C_{17}H_{16}N_3O_6Cl_3$ [M+Na]$^+$, 486.0002).



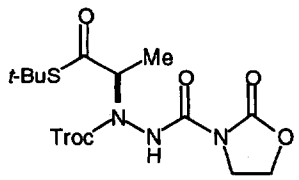
N-[N-((2*S*)-1-oxo(2-2,3,4-trihydronaphthyl))(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (7c). (II-109, 272, 286) According to the general procedure, 1.25 mL of a 0.04 M solution of **1** (10 mol%, 0.05 mmol, in THF) was added to a solution of **3** (159 mg, 0.50 mmol, in 1 mL THF) cooled to -20 °C. Trifluoroethanol (40 μL, 0.50 mmol) was added followed by the triethylsilyl derivative of **6c** (182 mg, 0.70 mmol, in 0.25 mL THF). The reaction was complete in 30 min as seen by infrared spectroscopy. Purification by flash chromatography (CH_2Cl_2 to 15% EtOAc/CH_2Cl_2) gave **7c** as a off-white foam (123 mg, 0.265 mmol, 53%). Enantiomeric excess was determined by HPLC with a Chiralcel OJ column (40% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***S***) enantiomer t_r = 23 min (variable); (***R***) enantiomer t_r = 35 min (variable); 93% ee. The reduced azo compound **2a** was also isolated (40 mg, 0.13 mmol, 26%). The amination of **6c** proceeded in 51% yield and 88% ee (-20 °C, 30 min).
Analytical data: IR (film) 3306, 2926, 1761, 1732, 1691, 1601, 1509, 1481, 1456, 1400, 1339, 1314, 1277, 1230, 1126, 1092, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (9.58) (s, 1H), 8.04 (d with rotamer, 1H, *J* = 7.7 Hz), 7.51 (t, 1H, *J* = 7.5 Hz), 7.32 (t with rotamer, 1H, *J* = 7.5 Hz), 7.25 (d, 1H, *J* = 7 Hz), 5.19 (5.06) (dd, 1H, *J* = 4.5, 14.0 Hz), 4.84 (4.83) (d, 1H, *J* = 11.8 Hz), 4.72 (4.77) (d, 1H, *J* = 11.8 Hz), 4.46 (m, 2H), 3.97-4.14

(m, 2H), 3.20-3.31 (m, 1H), 3.05-3.11 (m, 1H), 2.54-2.63 (m, 1H), 2.27-2.43 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4 (193.0), 154.9, 154.3 (154.1), 152.2 (152.1), 143.5 (143.4), 134.2 (134.2), 131.8 (131.7), 128.8, 128.0 (128.1), 127.0 (127.0), 94.9 (94.7), 75.8 (76.0), 64.8 (66.2), 63.0, 42.5 (42.4), 28.7 (28.9), 27.4 (27.9) ppm; HRMS (FAB, NBA-NaI) 485.9992 (Exact mass calcd for $C_{17}H_{16}N_3O_6Cl_3$ [M+Na]$^+$, 486.0002).



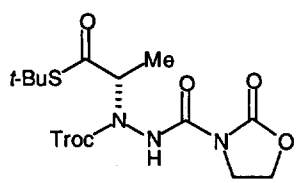
N-[N-((2*S*)-1-oxo(2,3,4,5-tetrahydrobenzo[c][7]annulen-2-yl))(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (7d). (III-46,91) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **6d** (70 μL, 0.3 mmol, in 0.2 mL THF). The reaction was worked-up after stirring overnight. Purification by flash chromatography (50% EtOAc/hexanes) gave **7d** as a white foam (90 mg, 0.188 mmol, 94%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (40% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*S*) enantiomer t_r = 10.6 min; (*R*) enantiomer t_r = 14.6 min; 99% ee. When the reaction was conducted at -40 °C, the product was obtained in 95% ee.

Analytical data: IR (film) 3307, 2953, 2868, 1762, 1729, 1679, 1598, 1509, 1481, 1448, 1400, 1343, 1307, 1276, 1227, 1164, 1142, 1097, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (9.74) (s, 1H), 7.90 (dd with rotamer, 1H, *J* = 1.3, 8 Hz), 7.45 (dt, *J* = 1.3, 7.5 Hz), 7.32 (t, 1H, *J* = 7.5 Hz), 7.23 (d, 1H, *J* = 7.5 Hz), 5.26 (5.21) (dd, 1H, *J* = 4.3, 11.8 Hz), 4.80 (4.81) (d, 1H, *J* = 11.8 Hz), 4.69 (4.64) (d, 1H, *J* = 11.8 Hz), 4.48 (m, 2H), 4.03-4.16 (m, 2H), 3.03-3.13 (m, 1H), 2.93-3.00 (m, 1H), 2.32-2.41 (m, 1H), 2.16-2.27 (m, 1H), 1.91-2.05 (m, 1H), 1.73-1.85 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 155.0, 154.4 (154.1), 152.1, 142.4 (142.1), 135.8 (135.7), 133.1, 130.3, 129.8 (130.0), 126.9 (126.9), 94.8 (94.6), 75.8, 65.8 (67.0), 63.0, 42.5, 33.6 (33.7), 25.6 (26.2), 23.7 (23.9) ppm; HRMS (FAB, NBA-NaI) 500.0139 (Exact mass calcd for $C_{18}H_{18}N_3O_6Cl_3$ [M+Na]$^+$, 500.0159).



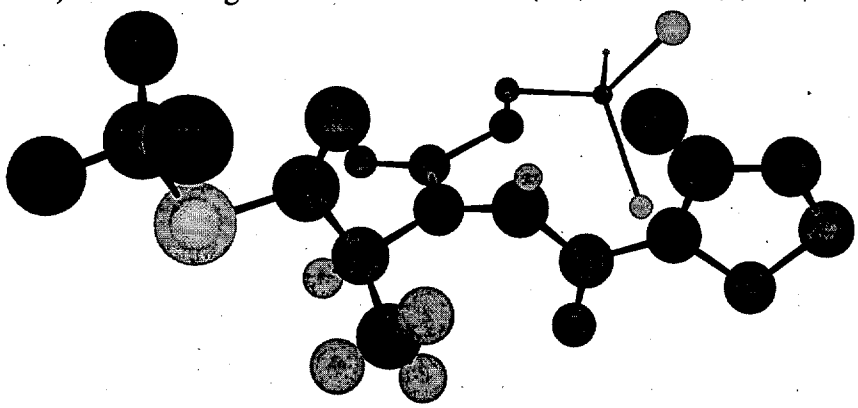
N-{N-[(1*R*)-2-(*tert*-butylthio)-1-methyl-2-oxoethyl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (9). (III-112,113) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by (*E*) **8** (≥98:2, 70 μL, 0.3 mmol). The reaction was worked-up after 2 h. Purification by flash chromatography (30-40% EtOAc/hexanes) gave (*R*) **9** as a white solid (77 mg, mmol, 83%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*R*) enantiomer t_r = 17.2 min; (*S*) enantiomer t_r = 21.6 min; 96% ee. Conducting the reaction at -78 °C (8 h) also afforded (*R*) **9** in 96% ee.

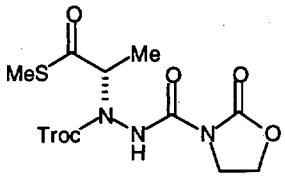
Analytical data: IR (film) 3308, 2964, 2926, 1765, 1733, 1682, 1513, 1481, 1456, 1399, 1366, 1309, 1275, 1234, 1149, 1094, 1039, 953 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (9.54) (s, 1H), 4.97 (4.90) (q, 1H, *J* = 7.2 Hz), 4.88 (4.79) (d, 1H, *J* = 11.8 Hz), 4.70 (4.67) (d, 1H, *J* = 11.7 Hz), 4.49 (t with rotamer, 2H, *J* = 8 Hz), 4.01-4.15 (m, 2H), 1.47 (bd with rotamer under peak at 1.46, 3H), 1.46 (bs, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 155.1, 153.7 (153.5), 152.0, 94.8 (94.6), 75.8 (76.0), 63.4 (64.5), 63.1, 48.8 (48.9), 42.5 (42.4), 29.8, 14.3 (14.9) ppm; HRMS (ESI) 486.0049 (Exact mass calcd for $C_{14}H_{20}N_3O_6SCl_3$ [M+Na]$^+$, 486.0036).



N-{N-[(1*S*)-2-(*tert*-butylthio)-1-methyl-2-oxoethyl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (9). (III-115,60) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by (*Z*) **8** (≥98:2, 70 μL, 0.3 mmol). The reaction was worked-up after stirring overnight. Purification by flash chromatography (30-40% EtOAc/hexanes) gave (*S*) **9** as a white solid (83 mg, 0.179 mmol, 89%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*R*) enantiomer t_r = 16.3 min; (*S*) enantiomer t_r = 20.5 min; 84% ee. The

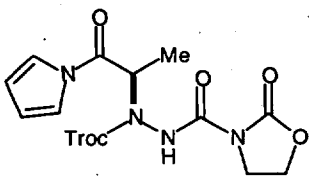
(*S*) adduct was recrystallized (Et_2O, 96% ee) and its absolute configuration was proven by X-ray crystallography (see below). Conducting the reaction at -20 °C (2 h) afforded (*S*) **9** in 63% ee.





N-[N-((1*S*)-1-methyl-2-methylthio-2-oxoethyl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide. (III-116) According to the general procedure, 0.8 mL of a 0.025 M solution of **1** (10 mol%, 0.02 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -78 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by the (*Z*) silylketene acetal (≥98:2, 70 μL, 0.3 mmol). The reaction was worked-up after stirring overnight. It appeared to be complete after 5 min by TLC. Purification by flash chromatography (40-50% EtOAc/hexanes) gave the adduct as a clear oil (81 mg, 0.192 mmol, 96%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*R*) enantiomer t_r = 32.1 min; (*S*) enantiomer t_r = 46.7 min; 59% ee.

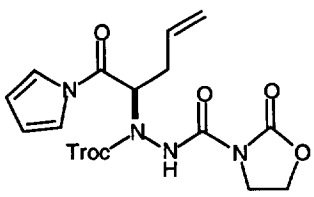
Analytical data: IR (film) 3306, 2995, 1762, 1734, 1684, 1507, 1481, 1399, 1309, 1235, 1149, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.60 (9.56) (s, 1H), 5.09 (5.01) (q, 1H, *J* = 7.2 Hz), 4.78 (4.85) (d, 1H, *J* = 11.8 Hz), 4.73 (d, 1H, *J* = 11.8 Hz), 4.49 (t, 2H, *J* = 8 Hz), 4.06 (4.12) (t, 2H, *J* = 8 Hz), 2.33 (s, 3H), 1.52 (1.53) (d, 3H, *J* = 7.4 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 155.1, 153.7 (153.4), 152.0, 94.7 (94.5), 75.8 (76.0), 63.2 (64.3), 63.1, 42.5, 14.3 (14.9), 11.6 ppm; HRMS (ESI) 421.9726 (Exact mass calcd for $C_{11}H_{14}N_3O_6SCl_3$ $[M+H]^+$, 421.9747).



N-[N-((1*R*)-1-methyl-2-oxo-2-pyrrolylethyl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (11a). (III-126,128,132)

According to the general procedure, 0.6 mL of a 0.017 M solution of **1** (5 mol%, 0.01 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **10a** (70 μL, 0.3 mmol). The reaction was complete as soon as the enolsilane was added. Purification by flash chromatography (55% EtOAc/hexanes) gave **11a** as a white foam (84 mg, 0.190 mmol, 95%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (30% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*S*) enantiomer t_r = 14 min; (*R*) enantiomer t_r = 21 min; 98% ee. The reaction was also conducted with 1 and 2 mol% **1** to give **11a** in 93% and 95% yield, respectively, in 98% ee.

Analytical data: IR (film) 3310, 3148, 2995, 1762, 1721, 1514, 1472, 1400, 1369, 1339, 1316, 1290, 1271, 1234, 1154, 1102, 1076, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.34 (7.30) (bs, 2H), 6.33 (t, 2H, *J* = 2.2 Hz), 5.61 (5.54) (q, 1H, *J* = 7.2 Hz), 4.78 (4.81) (d, 1H, *J* = 11.8 Hz), 4.70 (4.65) (d, 1H, *J* = 11.8 Hz), 4.49 (t, 2H, *J* = 8 Hz), 4.05 (4.11) (t, 2H, *J* = 8 Hz), 1.60 (1.62) (d, 3H, *J* = 7.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 (169.2), 155.0, 153.8 (153.2), 151.9, 119.3 (119.1), 114.0 (114.1), 94.5, 75.8 (75.9), 63.0, 56.5 (55.3), 42.4, 14.8 (15.2) ppm; HRMS (ESI) 441.0128 (Exact mass calcd for $C_{14}H_{15}N_4O_6Cl_3$ $[M+H]^+$, 441.0135).

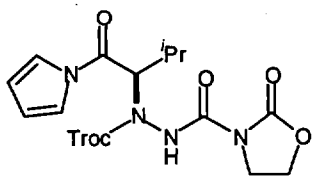


N-[N-((1*R*)-2-oxo-1-prop-2-enyl-2-pyrrolylethyl)(2,2,2-trichloroethoxy)carbonylamino](2-oxo(1,3-oxazolidin-3-yl))carboxamide (11b). (III-151,165,166)

According to the general procedure, 0.6 mL of a 0.017 M solution of **1** (5 mol%, 0.01 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **10b** (75 μL, 0.3 mmol). The reaction was complete within 5 min. In addition to the desired product, a silylated byproduct was formed which was protodesilylated (TFA, CH_2Cl_2) prior to chromatography. Purification by flash chromatography (30-40% EtOAc/hexanes) gave **11b** as a white foam (68 mg, 0.145 mmol, 73%) and **12b** as a white foam (19 mg, 20%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (20% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***S***) enantiomer t_r = 15.7 min; (***R***) enantiomer t_r = 19.8 min; 98% ee.

This reaction was also conducted with hydrate catalyst **2** at room temperature. According to the general procedure, **2** (7 mg, 5 mol%) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 1.0 mL THF) at room temperature and it dissolved to give a green solution. Trifluoroethanol (15 μL, 0.20 mmol) and **10b** (75 μL, 0.3 mmol) were added immediately. There was a slight exotherm and the reaction turned purple after 1 min. After 10 min, 10% aqueous HCl (5 drops) was added and the solution immediately turned yellowish-green. CH_2Cl_2 and saturated $NaHCO_3$ were added and the reaction was worked-up according to the general procedure. Purification was conducted as described above to give **11b** (71 mg, 0.151 mmol, 75% yield, 96% ee) and **12b** (14 mg, 0.031 mmol, 15%). This reaction was also performed at -20 °C to give **11b** in 98% ee (71% yield).

Analytical data: IR (film) 3302, 3149, 2962, 2925, 1762, 1721, 1516, 1472, 1400, 1370, 1317, 1288, 1269, 1245, 1123, 1076, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (9.67) (s, 1H), 7.40 (7.33) (bs, 2H), 6.33 (t, 2H, *J* = 2.3 Hz), 5.81-5.93 (m, 1H), 5.59 (5.50) (dd, 1H, *J* = 5.8, 8.8 Hz), 5.26 (5.23) (bd, 1H, *J* = 17 Hz), 5.15 (bd, 1H, *J* = 10.2 Hz), 4.79 (4.83) (d, 1H, *J* = 11.8 Hz), 4.70 (d, 1H, *J* = 11.8 Hz), 4.47 (t, 2H, *J* = 8.0 Hz), 3.98-4.10 (m, 2H), 2.83 (app pentet, 1H, *J* = 8 Hz), 2.69 (app pentet, 1H, *J* = 6.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.1, 153.9 (153.1), 151.5, 132.2, 119.4 (119.2), 114.0 (114.2) (2 C?), 94.5, 75.9 (76.1), 63.1, 60.1 (58.3), 42.4, 33.0 (33.7) ppm; HRMS (ESI) 467.0309 (Exact mass calcd for $C_{16}H_{17}N_4O_6Cl_3$ $[M+H]^+$, 467.0292).



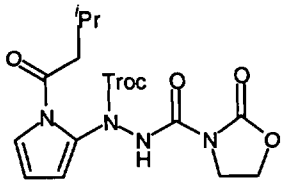
N-{N-[(1*R*)-1-(methylethyl)-2-oxo-2-pyrrolylethyl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (11c). (III-137,162,173)

According to the general procedure, 0.6 mL of a 0.017 M solution of **1** (5 mol%, 0.01 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **10c** (75 μL, 0.3 mmol). The reaction was complete within 5 min. In addition to the desired product, a silylated byproduct was formed which was protodesilylated (TFA, CH_2Cl_2) prior to chromatography. Purification by flash chromatography (40-50% EtOAc/hexanes) gave **11c** as a white foam (60 mg, 0.128 mmol, 64%) and **12c** as a white foam (22 mg, 0.047 mmol, 23%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (10% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (***S***) enantiomer t_r = 18.8 min; (***R***) enantiomer t_r = 23.3 min; 99% ee.

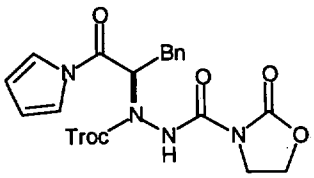
This reaction was also conducted using the hydrate catalyst **2**. According to the general procedure, **2** (7 mg, 5 mol%) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 1.0 mL THF) cooled to -20 °C and it dissolved to give a green solution. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **10c** (75 μL, 0.3 mmol). The reaction became light purple and was complete within 5 min. Purification was conducted as described above to give **11c** (60 mg, 0.128 mmol, 64% yield, 99% ee) and **12c** (20 mg, 0.043 mmol, 21%). This reaction was also performed at room temperature to give **11c** in 99% ee (64% yield).

Analytical data: IR (film) 3304, 3145, 2966, 1762, 1719, 1520, 1471, 1400, 1371, 1310, 1276, 1248, 1117, 1076, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (9.73) (bs, 1H), 7.45 (7.40) (bs, 2H), 6.33 (t, 2H, *J* = 2.3 Hz), 5.14 (5.09) (d, 1H, *J* = 10 Hz), 4.81 (4.89) (d, 1H, *J* = 11.8 Hz), 4.69 (4.78) (d, 1H, *J* = 11.8 Hz), 4.46 (t, 2H, *J* = 8.1 Hz), 3.95-4.08 (m, 2H), 2.50 (bm, 1H), 1.10 (1.16) (bd, 3H), 0.97 (d with rotamer, 3H, *J* = 6.7 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167 (b), 155.2, 154.0 (153.0), 151.1, 119.5 (119.4), 114.1 (113.9), 94.6,

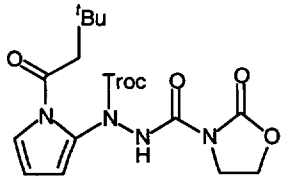
75.8 (76.2), 64.6 (63.5), 63.1, 42.3, 28.2 (27.3), 19.1 ppm; HRMS (ESI) 469.0430 (Exact mass calcd for $C_{16}H_{19}N_4O_6Cl_3$ [M+H]$^+$, 469.0448).



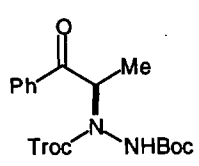
N-{N-[1-(3-methylbutanoyl)pyrrol-2-yl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (12c). Analytical data: IR (film) 3309, 3148, 2960, 2871, 1759, 1719, 1481, 1400, 1313, 1280, 1249, 1214, 1176, 1128, 1105, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (10.22) (s, 1H), 7.06 (d with rotamer, 1H, J = 2.1 Hz), 6.51 (6.54) (m, 1H), 6.21 (m, 1H), 4.78 (4.70, 4.67) (bs, 2H), 4.46 (bt, 2H, J = 7.4 Hz), 4.05 (4.09) (bt, 2H, J = 8 Hz), 2.67 (bd, 2H, J = 6.0 Hz), 2.27 (m, 1H), 1.00 (0.99) (bd, 6H, J = 5.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (171.2), 154.8, 153.5 (153.8), 150.7, 128.3 (128.5), 119.5 (119.7), 114.2, 110.6 (110.7), 94.6, 75.9, 63.0, 44.4 (44.6), 42.4, 25.3 (25.6), 22.6 (22.5) ppm; HRMS (ESI) 469.0470 (Exact mass calcd for $C_{16}H_{19}N_4O_6Cl_3$ [M+H]$^+$, 469.0448).



N-{N-[(1*R*)-2-oxo-1-benzyl-2-pyrrolylethyl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (11). (III-159)
According to the general procedure, 0.6 mL of a 0.017 M solution of **1** (5 mol%, 0.01 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by the enolsilane (75 μL, 0.3 mmol). The reaction was complete within 5 min. In addition to the desired product, a silylated byproduct was formed which was protodesilylated (TFA, CH_2Cl_2) prior to chromatography. Purification by flash chromatography (40-50% EtOAc/hexanes) gave **11** as a white foam (30 mg, 0.058 mmol, 29%) and **12** (50 mg, 0.097 mmol, 48%). Enantiomeric excess was determined by HPLC with a Chiralcel AD column (20% ^{i}PrOH/hexanes, 1 mL/min, 254 nm); (*S*) enantiomer t_r = 18.6 min; (*R*) enantiomer t_r = 20.5 min; 93% ee.
Analytical data: IR (film) 3301, 3144, 2923, 1762, 1719, 1516, 1472, 1399, 1368, 1308, 1285, 1268, 1245, 1122, 1088, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (9.73) (bs, 1H), 7.20-7.36 (m, 7H), 6.27 (6.23) (bs, 2H), 5.82 (5.68) (bt, 1H, J = 7.3 Hz), 4.71 (4.79) (d, 1H, J = 11.8 Hz), 4.57 (bd, 1H, J = 12 Hz), 4.48 (t, 2H, J = 8 Hz), 3.96-4.12 (m, 2H), 3.38 (dd, 1H, J = 8.4, 14.3 Hz), 3.28 (dd, 1H, J = 7.1, 14.3 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (b), 155.2, 153.6 (152.7), 151.5, 135.4, 129.1, 128.9, 127.2 (127.3), 119.5 (119.2), 113.9, 94.4, 75.7 (76.1), 63.1, 61.3 (59.4), 42.3, 34.6 (35.4) ppm; HRMS (ESI) 517.0428 (Exact mass calcd for $C_{20}H_{19}N_4O_6Cl_3$ [M+H]$^+$, 517.0448).

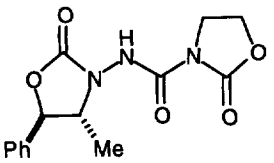


N-{N-[1-(3,3-dimethylbutanoyl)pyrrol-2-yl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (12d). (III-135)
According to the general procedure, 0.6 mL of a 0.017 M solution of **1** (5 mol%, 0.01 mmol, in THF) was added to a solution of **3** (63.6 mg, 0.20 mmol, in 0.3 mL THF) cooled to -20 °C. Trifluoroethanol (15 μL, 0.20 mmol) was added followed by **10d** (75 μL, 0.3 mmol). The reaction was stirred overnight. The only product detected was the enolsilane of the aminated pyrrole which was converted to **12d** upon treatment with TFA in CH_2Cl_2. Analytical data: IR (film) 3308, 3148, 2958, 2871, 1761, 1718, 1481, 1400, 1366, 1328, 1264, 1214, 1178, 1117, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (10.23) (s, 1H), 7.07 (d with rotamer, 1H, J = 2.0 Hz), 6.51 (6.54) (m, 1H), 6.19 (m, 1H), 4.70 (4.78) (s, 2H), 4.46 (bt, 2H, J = 7.8 Hz), 4.06 (bt, 2H, J = 8 Hz), 2.68 (s, 2H), 1.07 (1.05) (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 (170.8), 154.8, 153.5 (153.8), 150.7 (150.7), 128.3 (128.6), 120.2 (120.4), 114.3 (114.4), 110.3 (110.4), 94.6 (94.7), 75.9, 63.0, 47.7 (47.9), 42.3, 31.7 (31.9), 29.8 ppm; HRMS (ESI) 483.0589 (Exact mass calcd for $C_{17}H_{21}N_4O_6Cl_3$ [M+H]$^+$, 483.0605).

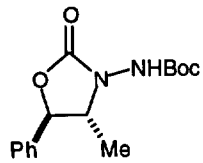


N-((1*R*)-1-methyl-2-oxo-2-phenylethyl)-N-[(*tert*-butoxy)carbonylamino](2,2,2-trichloroethoxy)carboxamide (13). (II-140, 258) To a solution of **5a** (1.12 g, 2.48 mmol) in THF (15 mL) was added 4-dimethylaminopyridine (60 mg, 0.5 mmol, 0.2 equiv) as a solid. Di-*tert*-butyl dicarbonate (1.08 g , 4.96 mmol, 2 equiv) was added as a solution in THF (5 mL) *via* cannula and the reaction was stirred for 3 h. The solvent was removed *in vacuo* and the residue

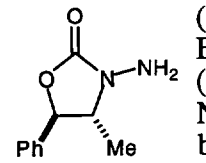
was purified by flash chromatography (30% EtOAc/hexanes) to give a white foam (1.36 g, 2.46 mmol, 99%). The imide was hydrolyzed as follows: To a solution of the Boc-hydrazide (1.37 g, 2.47 mmol) in THF (30 mL) / H_2O (10 mL) cooled to 0 °C was added 30% H_2O_2 (1.25 mL, *ca.* 4 equiv) followed by lithium hydroxide monohydrate (207 mg, 4.94 mmol, 2 equiv). The mixture was stirred at 0 °C for 30 min and then treated with aqueous Na_2SO_3 (1.5 g in 20 mL H_2O). Saturated aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated to give a white foam (1.06 g). Purification by flash chromatography (10% EtOAc/hexanes) afforded **13** as a white foamy solid (0.99 g, 2.25 mmol, 91%).
Analytical data: IR (film) 3328, 3064, 2980, 1746, 1725, 1690, 1597, 1579, 1479, 1450, 1410, 1368, 1331, 1298, 1246, 1225, 1161, 1110, 1090, 1060, 1027, 1002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, 2H, J = 8.8 Hz), 7.58 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.7 Hz), 6.91 (6.81, 6.64) (s, 1H), 5.81 (m, 1H), 4.84 (4.59) (d, 1H, J = 11.8 Hz), 4.73 (s, 1H), 1.50 (1.53) (d, 3H, J = 7.5 Hz), 1.45 (1.47) (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7 (199.4), 155.4, 154.8 (154.4), 134.5 (134.4), 133.8, 128.9, 128.5 (128.4), 94.8 (94.6), 81.4 (81.6), 75.7, 58.7 (59.4), 28.2 (28.1), 14.4 (14.8) ppm; HRMS (ESI) 439.0609 (Exact mass calcd for $C_{17}H_{21}N_2O_5Cl_3$ $[M+H]^+$, 439.0594).



N-((4*R*,5*R*)-4-methyl-2-oxo-5-phenyl(1,3-oxazolidin-3-yl))(2-oxo(1,3-oxazolidin-3-yl))carboxamide. (II-143, III-5) To a solution of **5a** (90 mg, 0.20 mmol) in THF (6 mL) cooled to -78 °C was added L-Selectride (0.27 mL, 0.27 mmol, 1 M in THF, new bottle). After 1 h at -78 °C, the reaction was warmed to room temperature and stirred for 1h. Saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated to give an oil/film. Purification by flash chromatography (20% EtOAc/CH_2Cl_2) afforded the oxazolidinone as a clear oil which became a white foam (56 mg, 0.183 mmol, 92%).
Analytical data: IR (film) 3318, 2978, 2925, 1761, 1715, 1508, 1479, 1458, 1402, 1270, 1240, 1202, 1149, 1124, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.39-7.47 (m, 5H), 4.98 (d, 1H, J = 9.3 Hz), 4.52 (t with rotamer, 2H, J = 8 Hz), 3.98-4.18 (m, 3H), 1.36 (d, 3H, J = 6.1 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.2, 151.0, 136.0, 129.5, 128.9, 126.9, 82.9, 63.3, 61.1, 42.3, 16.1 ppm; HRMS (ESI) 306.1101 (Exact mass calcd for $C_{14}H_{15}N_3O_5$ $[M+H]^+$, 306.1090).

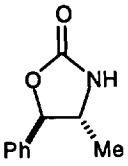


N-((4*R*,5*R*)-4-Methyl-2-oxo-5-phenyl(1,3-oxazolidin-3-yl))(tert-butoxy)carboxamide (14). (III-182) To a solution of **13** (176 mg, 0.40 mmol) in THF (10 mL) cooled to -78 °C was added L-Selectride (0.60 mL, 0.60 mmol, 1 M in THF) slowly. After 1 h at -78 °C, the reaction was warmed to room temperature and stirred for 1h. Saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated to give an oil. Purification by flash chromatography (30% EtOAc/hexanes) afforded **14** as a clear oil/white foam (110 mg, 0.377 mmol, 94%).
Analytical data: IR (film) 3310 (b), 2978, 2933, 1781, 1728, 1495, 1458, 1393, 1369, 1322, 1281, 1249, 1205, 1149, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.47 (m, 5H), 6.45 (bs, 1H), 4.93 (d, 1H, J = 9.3 Hz), 3.99 (bs, 1H), 1.51 (s, 9H), 1.34 (d, 3H, J = 6.1 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 154.4, 136.2, 129.3, 128.9, 126.8, 82.8, 82.4, 60.8, 28.2, 16.0 ppm; HRMS (ESI) 315.1336 (Exact mass calcd for $C_{15}H_{20}N_2O_4$ $[M+Na]^+$, 315.1321).

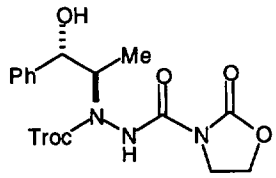


(4*R*,5*R*)-3-Amino-4-methyl-5-phenyl-1,3-oxazolidin-2-one (15). (II-151,162, III-184,194) The Boc-oxazolidinone **14** (50 mg, 0.171 mmol) was dissolved in a solution of 4 M HCl in dioxane (1.0 mL) and stirred at room temperature for 1h. The reaction was concentrated under a stream of N_2. The residue was dissolved in EtOAc and washed with saturated aqueous $NaHCO_3$ (2x) and brine, dried over Na_2SO_4, and concentrated to give a pale yellow solid (31 mg, 0.161 mmol, 94%). This material is used directly in the next reaction or purified by flash chromatography (50% EtOAc/hexanes) to give the amino-oxazolidinone **15** as a white solid.
Analytical data: IR (film) 3340, 3208, 2971, 2931, 1759, 1620, 1500, 1455, 1381, 1348, 1323, 1288, 1212, 1141, 1118, 1076, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.41 (m, 5H), 4.89 (d, 1H, J = 8.7 Hz), 3.93 (s, 2H), 3.58 (dq, 1H, J = 8.6, 6.1 Hz), 1.38 (d, 3H, J = 6.1 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0,

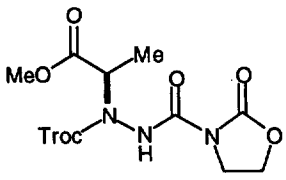
136.6, 129.2, 128.9, 126.3, 82.1, 62.8, 16.6 ppm; HRMS (CI, NH_3) 210.1247 (Exact mass calcd for $C_{10}H_{12}N_2O_2$ $[M+NH_4]^+$, 210.1243).



(4*R*,5*R*)-4-Methyl-5-phenyl-1,3-oxazolidin-2-one (16). (III-195) The amino-oxazolidinone **15** (31 mg, 0.161 mmol) was dissolved in acetone (2 mL). The solution was allowed to sit for 15 min and concentrated. The residue was dissolved in acetic acid (1.5 mL) and zinc dust (150 mg, 2.3 mmol) was added followed by acetone (70 µL, 0.97 mmol). After 2 h, more zinc dust (150 mg) and acetone (70 µL) were added and the slurry was stirred for an additional 16 h. Saturated aqueous $NaHCO_3$ was added slowly until the mixture was slightly basic. The mixture was extracted with EtOAc (3x). The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (50% EtOAc/hexanes) afforded **16** as a white solid (26 mg, 0.147 mmol, 91%). The (*R*, *S*) diastereomer could not be detected by NMR or HPLC (Chiralcel AD column, 10% ^{i}PrOH/hexanes, 1 mL/min, (*R*, *R*) **16** t_r = 11.1min; (*R*, *S*) **16** t_r = 16.3 min). Analytical data: $[\alpha]_D^{24}$ -17.9 (*c* 1.15, $CHCl_3$), lit.[11] $[\alpha]_D^{20}$ -15.9 (*c* 0.38, $CHCl_3$); IR (CH_2Cl_2) 3450, 3055, 2987, 1765, 1422, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.44 (m, 5H), 5.48 (bs, 1H), 5.05 (d, 1H, *J* = 7.4 Hz), 3.84 (dq, 1H, *J* = 6.3, 6.3 Hz), 1.40 (d, 3H, *J* = 6.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 137.7, 129.0, 128.9, 125.9, 85.4, 56.6, 19.9 ppm; HRMS (EI) 177.0796 (Exact mass calcd for $C_{10}H_{11}NO_2$ $[M]^+$, 177.0790).



N-((1*R*,2*S*)-2-Hydroxy-1-methyl-2-phenylethyl)-N-[(2-oxo(1,3-oxazolidin-3-yl))carbonylamino](2,2,2-trichloroethoxy)carboxamide (17). (II-163, III-183) To a solution of **5a** (90 mg, 0.20 mmol) in trifluoroacetic acid (2 mL) cooled to 0 °C was added triethylsilane (64 µL, 0.40 mmol). The reaction was stirred at 0 °C for 2 h. The solution was concentrated and the residual trifluoroacetic acid was removed by azeotroping with toluene. Purification by flash chromatography (40% EtOAc/hexanes) afforded **17** as a clear oil (86 mg, 0.190 mmol, 95%). The (*R*, *R*) diastereomer could not be detected by NMR or HPLC (Chiralcel AD column, 20% ^{i}PrOH/hexanes, 1 mL/min, (*R*, *S*) **17** t_r = 14.4 min; (*R*, *R*) **17** t_r = 18.0 min). Analytical data: IR (film) 3429 (b), 3310, 2995, 1763, 1735, 1518, 1480, 1451, 1401, 1319, 1290, 1233, 1197, 1128, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (bs, 1H), 7.42 (d, 2H, *J* = 7.5 Hz), 7.35 (t, 2H, *J* = 7.5 Hz), 7.27 (d, 1H, *J* = 7.8 Hz), 5.32 (bs, 1H), 4.96 (d, 0.5H, *J* = 11.8 Hz), 4.81 (bs, 1H), 4.68 (d, 0.5H, *J* = 11.6 Hz), 4.52 (t, 2H, *J* = 8.1 Hz), 4.48 (bs, 1H), 4.2-4.4 (bs, 1H), 4.11 (m, 2H), 1.05 (bs, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 153.7 (b), 153.3 (b), 140.6, 128.4, 127.4, 125.8, 95.9, 75.6 (76.1), 74.6 (b), 63.2, 61.1 (b), 42.5, 9.4 (b) ppm; HRMS (ESI) 454.0318 (Exact mass calcd for $C_{16}H_{18}N_3O_6Cl_3$ $[M+H]^+$, 454.0339).



N-{N-[(1*R*)-2-methoxy-1-methyl-2-oxoethyl](2,2,2-trichloroethoxy)carbonylamino}(2-oxo(1,3-oxazolidin-3-yl))carboxamide (18). (II-23,27) & (III-169,185) N-Bromosuccinimide (192 mg, 1.08 mmol, 3 equiv) was added to a solution of the thioester **9** (165 mg, 0.355 mmol) in 6:1 THF (3.4 mL):H_2O (0.6 mL) at room temperature. The reaction was stirred for 24 h. TLC showed that some starting material remained. The solution was poured into 0.2M aqueous $Na_2S_2O_3$ (5 mL) and extracted with EtOAc (3x). The organic layer was washed with 1M HCl, H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in MeOH and an etheral solution of CH_2N_2 was added until a yellow color persisted. After 5 min, the solution was concentrated to give a yellow oil. Purification by flash chromatography (20-40% EtOAc/hexanes) gave recovered thioester (20 mg, 0.043 mmol, 12%) and the desired methyl ester **18** (100 mg, 0.256 mmol, 72%). The thioester can also be hydrolyzed with LiOOH followed by CH_2N_2 treatment to give the methyl ester **18**.

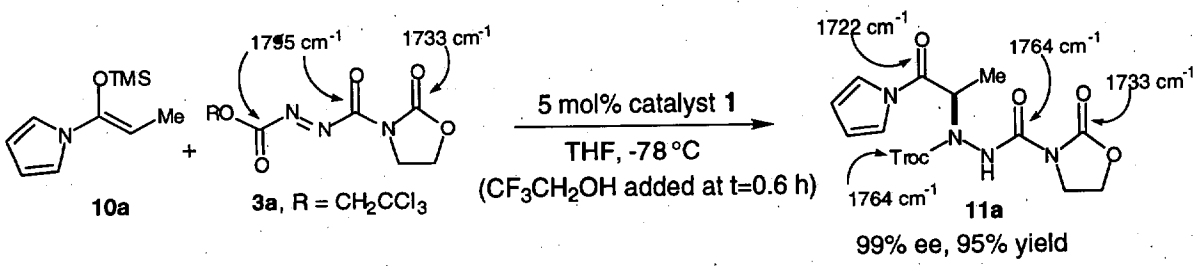
To a solution of acylpyrrole **11a** (84 mg, 0.19 mmol) in MeOH (1.0 mL) was added triethylamine (10 µL) at room temperature. After stirring overnight, the reaction was concentrated and purified by flash chromatography (50% EtOAc/hexanes) to give **18** as an oil/foam (67 mg, 0.172 mmol, 90%).
Analytical data: IR (film) 3306, 3000, 2958, 1760, 1733, 1515, 1482, 1435, 1400, 1313, 1229, 1151, 1098, 1071, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (9.55) (s, 1H), 5.03 (4.96) (q, 1H, *J* = 7.4 Hz), 4.78 (4.88)

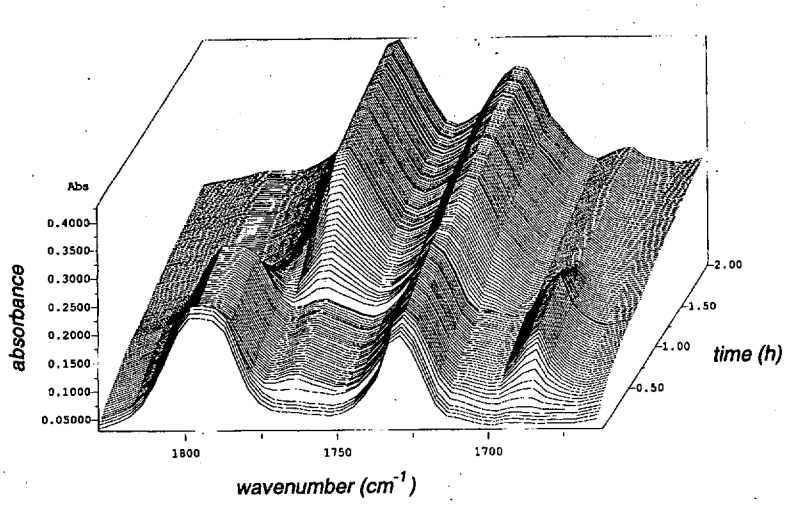
11) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc. Perkin Trans. 1*, **1989**, 1529-1535.

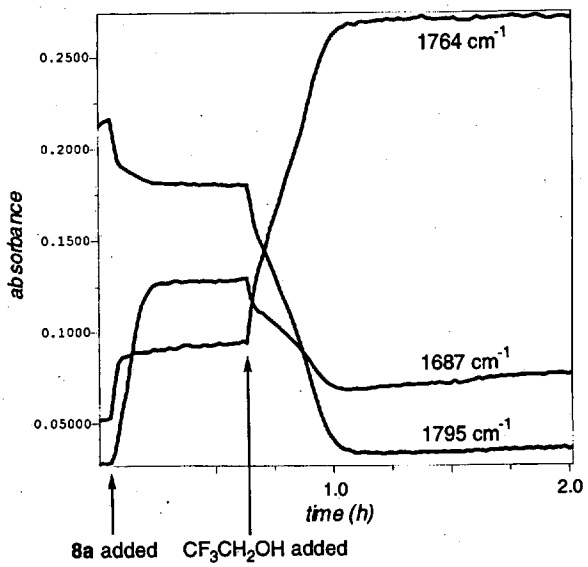
(d, 1H, J = 11.8 Hz), 4.71 (4.70) (d, 1H, J = 11.8 Hz), 4.50 (t, 2H, J = 8 Hz), 4.07 (4.13) (t, 2H, J = 8 Hz), 3.77 (s, 3H), 1.51 (1.53) (d, 3H, J = 7.5 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 155.1, 153.9 (153.6), 152.0, 94.8, 75.8 (75.9), 63.1, 56.4 (57.5), 52.7, 42.5, 14.3 (14.7) ppm; HRMS (ESI) 405.9993 (Exact mass calcd for $C_{11}H_{14}N_3O_7Cl_3$ $[M+H]^+$, 405.9975).

***In situ* IR Spectroscopic Studies.**

Reactions were monitored using a ReactIR 1000 from ASI Applied Systems (Millersville, MD; www.asirxn.com) fitted with an immerscible DiComp ATR probe. The spectra were acquired in 128 scans per spectrum at a gain of 1 and a resolution of 2 using ReactIR 2.1 software. IR spectra were recorded every 1 min over the course of the reaction. A representative example is shown in Figure S1 with the exception that trifluoroethanol was not present at the beginning of the reaction, but was added after 0.6 h.







Possible intermediate (1687 cm^{-1}) prior to addition of the alcohol:

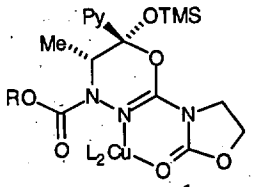


Figure S1. IR reaction profile (1650-1850 cm^{-1}) showing changes in absorbance bands as a function of time (left) and plot of absorbance versus time (right) for the amination of **10a**.