Palladium(II)-Assisted Dialkylation and Alkylation/Acylation of Optically Active Ene Carbamates via Trialkylorganostannane Cross-Coupling and Carbonylative Coupling Processes

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Alkylation of benzyl vinyl carbamate and propene with the anions of diethyl methylmalonate or dimethyl malonate in the presence of palladium(II) chloride, followed by cross-coupling or carbonylative cross-coupling with organostannanes, effected an overall dialkylation or alkylation/acylation of the monoolefin substrate. Complete control of stereochemistry in this palladium(II)-assisted reaction was observed using optically active ene carbamates affording β-amino-unsaturated keto esters in good chemical yields and excellent optical purity.

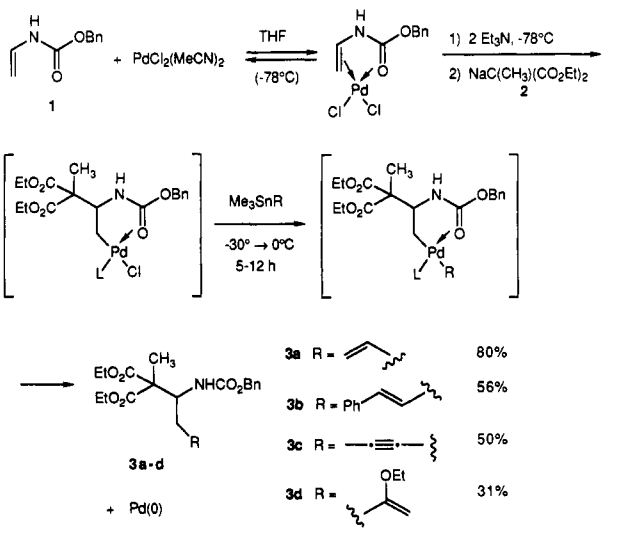
Introduction

Palladium-catalyzed cross-coupling and carbonylative coupling of trialkylorganostannanes with organic halides and triflates is among the most useful of transition-metal-catalyzed carbon–carbon bond forming reactions[1] and is finding increased use in organic synthesis.[2] The key steps in this process are the transfer of an alkyl group from tin to a σ-alkyl- or σ-acyl–palladium(II) complex, formed by oxidative addition of the substrate to the Pd(0) catalyst, followed by reductive elimination to form the carbon–carbon bond. σ-Alkyl–palladium(II) complexes, although quite unstable to β-hydrogen elimination, are also easily generated by the attack of nucleophiles on π-olefin–palladium(II) complexes.[3] Treatment of *these* with trialkylorganostannanes should, in principal, also result in coupling via transmetalation/reductive elimination. The palladium(II) assisted alkylation and carboacylation of optically active ene carbamates and its use in the synthesis of a key relay to (+)-thienamycin[5] have recently been developed in these laboratories. Herein we report the results of combining these reactions to produce σ-alkyl- and σ-acyl–palladium(II) complexes, followed by transmetalation from tin, to effect an overall dialkylation or alkylation/acylation of monoolefins and ene carbamates.

Results and Discussion

The alkene substrate and nucleophile initially chosen for these studies were benzyl vinyl carbamate (1) and the sodium salt of diethyl methylmalonate **2**, since these reagents combine efficiently in the palladium(II)-assisted alkylation of olefins at low temperatures.[4-6] (Trimethyl)(vinyl)tin coupled in good yields while the corresponding (tributyl)(vinyl)tin coupled in only low yield under these same conditions. Other trimethyltin reagents also coupled, albeit in lower yields (eq 1). The vinyl ether **3d** was isolated as the methyl ketone since purification of the vinyl ether was difficult.

(Eq. 1)



The reaction was somewhat temperature sensitive and clearly must proceed in a stepwise manner. If insufficient time for the first alkylation step was allowed, homocoupled products from the reaction of 2 equiv of the organotin reagent with $PdCl_2L_2$ resulted.[7] Regardless of the conditions, β-elimination products were never observed, although reaction at ambient temperature produced only low yields of the coupled product. This is consonant with earlier observations that σ-complexes resulting from the alkylation of enamides were resistant to β-hydride elimination, probably because of stabilization by chelation to the carbamate carbonyl group.[5]

Insertion of carbon monoxide into σ-alkyl palladium(II) complexes occurs readily at about −20 °C, and carbonylative couplings with tin reagents are often more efficient than straightforward alkylative couplings.[8] This proved to be the case here, as well. Treatment of the σ-complex, resulting from alkylation of 1 with the sodium anion of dimethyl malonate, with 1 atm of carbon monoxide for 2 h at −20 °C, followed by addition of the tin reagent, produced carbonylative coupled products in good yield (eq 2). At temperatures below −20 °C, mixtures of coupled and carbonylatively coupled products were obtained, again indicating the requisite stepwise nature of the process.

When propene was used as the olefin substrate in eq 1, competitive β-hydrogen elimination occurred, giving mixtures of mono- and dialkylation products. However, under

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(4) Wieber, G. M.; Hegedus, L. S.; Åkermark, B.; Michalson, E. T. *J. Org. Chem.* **1989**, *54*, 4649.
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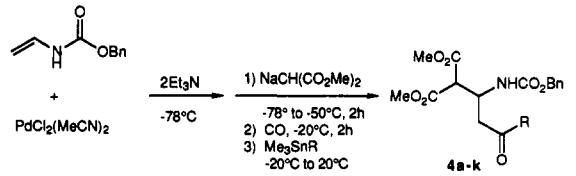
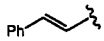
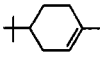
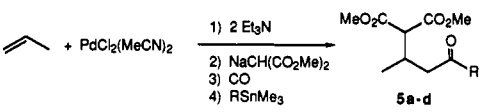
(Eq. 2)



4	R	Yield, %	4	R	Yield, %
a		79	g	pMeOPh	93
b		72	h	pClPh	59
c		74	i		59
d		70	j		62
e	Ph	77	k		69
f	pMePh	95			

carbonylative coupling conditions a clean reaction ensued (eq 3), indicating that CO insertion went more readily than

(Eq. 3)



5a R =  73%

5b R = Ph 75%

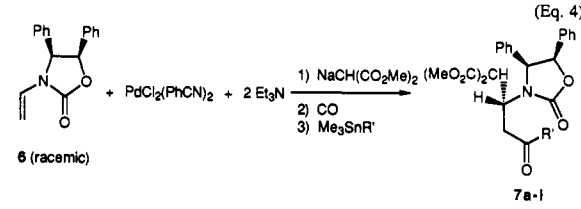
5c R =  63%

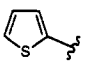
5d R = Ph—≡— 65%

either β-elimination or transmetalation.

Previous studies in these laboratories[5] showed that chiral (both racemic and optically active) ene carbamates afforded a high degree of asymmetric induction in the Pd(II)-assisted carboacylation of these substrates. Similar results were obtained in the carbonylative coupling reactions studied in eqs 4 and 5. With syn (racemic) ene

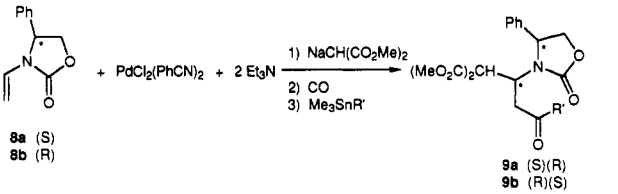
(Eq. 4)



7	R'	Yield, %	7	R'	Yield, %
a		88	f		65
b		70	g		68
c	pMePh	69	h		71
d	Ph	37	i	Ph—≡—	90
e	pClPh	25			

carbamate **6** a *single* (racemic) diastereoisomer of carbonylative coupling product was obtained with a range of vinyl-, alkynyl-, and aryltin reagents. With optically active ene carbamate **8**, again very high diastereoselectivity was observed. The relative and absolute stereochemistries were

(Eq. 5)



9a	R'	Yield, %	$[\alpha]_D$	9b	Yield, %	$[\alpha]_D$
a^1		65	+54°	b^1	68	-57°
a^2		76	+32°	b^2	83	-32°
a^3	Ph—≡—	69	+3°	b^3	76	-3°

assigned by analogy to previous studies.[5] The products derived from (*R*)-**8** and (*S*)-**8** had equal but opposite rotations, indicating that they were indeed enantiomeric.

The above chemistry permits the synthesis of highly functionalized, optically active compounds in a one-pot procedure, in high yield and with excellent stereoselectivity. Because the process must proceed in a stepwise fashion, stoichiometric quantities of palladium are required, but the palladium can be recovered as the metal and recycled. Studies to utilize the β-amino-unsaturated keto esters in total synthesis are in progress.

Experimental Section

General. General instrumental and experimental data are identical with that previously reported.[5] The following were prepared according to literature procedures: *O*-benzyl-*N*-vinylcarbamate,[4] (*S*)-phenylglycinol,[9] (*R*)-phenylglycinol,[9] (±)-*syn*-1,2-diphenylethanolamine,[10] 3-ethenyl-(*S*)-4-phenyl-2-oxazolidinone,[5] 3-ethenyl-(*R*)-4-phenyl-2-oxazolidinone,[5] $PdCl_2(MeCN)_2$,[11] $PdCl_2(PhCN)_2$,[12] trimethylvinylstannane,[13] tributylvinylstannane,[13] (*E*)-β-styryltrimethylstannane,[14] isobutenyltrimethylstannane,[15] (4-*tert*-butylcyclohexenyl)trimethylstannane,[16] (1-ethoxyvinyl)-trimethylstannane,[17] phenyltrimethylstannane,[18] (*p*-methoxyphenyl)trimethylstannane,[18] (*p*-tolyl)trimethylstannane,[18] (*p*-chlorophenyl)trimethylstannane,[18] (1-propynyl)trimethylstannane,[19] (phenylethynyl)trimethylstannane,[19] 2-(trimethylstannyl)furan,[20] 2-(trimethylstannyl)thiophene.[20]

Preparation of (±)-*syn*-4,5-Diphenyl-3-vinyl-2-oxazolidinone (6). From 3.87 g (17.6 mmol) of $Cr(CO)_6$ was prepared 5.73 g (76%) of (±)-[(1,2-*syn*-diphenylethanolamine)(methyl)-carbene]pentacarbonylchromium(0) according to literature procedures.[5]

To a solution of 5.73 g (13.3 mmol) of (±)-[(1,2-*syn*-diphenylethanolamine)(methyl)carbene]pentacarbonylchromium(0) in 50 mL of THF at room temperature was added 0.73 g (50% in oil, 15.0 mmol) of sodium hydride. After evolution of H_2(g),

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the homogeneous amber red solution was transferred slowly (0.75 h) via cannula to a slurry of 0.75 g (50% in oil, 15.5 mmol) of sodium hydride and 9.60 g (45.0 mmol) of diphenyl carbonate in 350 mL of THF. After complete addition, the red-brown mixture was stirred for 4.0 h. The resulting solution was saturated with air (12 h) and filtered through Celite, and the solvent was removed in vacuo. The residue was taken up in 250 mL of 1:1 hexane/ethyl acetate, saturated with air, and placed in a light box (18 h) equipped with six 20-W Vitalite fluorescent lamps.[5] Filtration of the resulting mixture through Celite followed by removal of the solvent in vacuo afforded the crude reaction mixture. The yellow oil was taken up in 200 mL of ether and washed successively with 75 mL of 10% NaOH (2×), 100 mL of H_2O, and 100 mL of brine and dried ($MgSO_4$). Removal of the solvent in vacuo and purification of the crude material by column chromatography (SiO_2; 4:1 hexane/EtOAc; R_f = 0.34) afforded 2.80 g (81%; 61% from $Cr(CO)_6$) of the ene carbamate as a white solid (mp 161–163 °C). Spectroscopic data was identical with reported values.[5]

General Procedure: Preparation of 3a–d. To a stirred solution containing 130 mg (0.50 mmol) of $PdCl_2(MeCN)_2$ in 10 mL of THF at room temperature was added 105 mg (0.60 mmol) of *O*-benzyl-*N*-vinylcarbamate. After 5 min, the amber red solution was cooled to −78 °C and treated with 100 mg (1.00 mmol) of triethylamine and 1.30 mL (0.50 M solution in THF, 0.65 mmol) of the sodium anion of diethyl methylmalonate. The mixture was allowed to warm to −60 °C and was stirred for 1.5 h. The resulting solution was then treated with a −30 °C solution (0 °C for **3a**) of the trimethylorganostannane (1.00 ± 0.02 mmol; **a–d**) in 5 mL of DMF. The mixture was *slowly* warmed to room temperature and stirred for 15–18 h. The resulting black solution was filtered through a pad of silica gel using ether as the eluent. The filtrate was washed successively with 30 mL of H_2O (2×) and 30 mL of brine and dried ($MgSO_4$). Removal of solvent in vacuo and purification of the crude mixture by column chromatography (SiO_2) afforded the products **3a–d**.

3a. Purification by column chromatography (9:1 hexane/EtOAc; R_f = 0.39) afforded 145 mg (80%) of ethyl 3-[(benzyloxycarbonyl)amino]-2-(ethoxycarbonyl)-2-methyl-5-hexenoate (clear oil): ^{1}H NMR (300 MHz) δ 7.30 (s, 5 H, CH_2Ph), 5.75 (m, 1 H, CH=CH_2), 5.49 (d, 1 H, J = 10.8 Hz, NH), 5.04 (s, 2 H, CH_2Ph), 5.03 (m, 2 H, CH=CH_2), 4.19 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 4.18 (m, 1 H, CHNH), 4.09 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 2.39 (m, 1 H, CH_2), 2.17 (m, 1 H, CH_2), 1.47 (s, 3 H, CH_3), 1.25 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 1.17 (t, 3 H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (75.5 MHz) δ 170.9 ($CO_2CH_2CH_3$), 170.8 ($CO_2CH_2CH_3$), 156.0 ($NHCO_2CH_2Ph$), 136.6 (CH=CH_2), 134.2, 128.3, 127.9, 117.6 (CH=CH_2), 66.5 (OCH_2Ph), 61.5 (OCH_2CH_3), 58.1 (OCH_2CH_3), 55.1, 36.0, 19.3 ($CH_3(CO_2CH_2CH_3)_2$), 13.9 (OCH_2CH_3), 13.8 (OCH_2CH_3); IR (neat) 3365, 1733, 1643 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.69; H, 7.12; N, 3.67. Found: C, 63.65; H, 7.21; N, 3.71.

3b. Purification by column chromatography (9:1 hexane/EtOAc; R_f = 0.11) afforded 122 mg (56%) of ethyl 3-[(benzyloxycarbonyl)amino]-2-(ethoxycarbonyl)-2-methyl-6-phenyl-5-hexenoate (white solid): ^{1}H NMR (300 MHz) δ 7.24 (m, 10 H, 2Ph), 6.39 (d, 1 H, J = 15.8 Hz, =CHPh), 6.12 (ddd, 1 H, J = 5.7, 8.4, 15.8 Hz, CH=CHPh), 5.57 (d, 1 H, J = 10.8 Hz, NH), 5.02 (d, 1 H, J = 12.3 Hz, CH_2Ph), 4.93 (d, 1 H, J = 12.3 Hz, CH_2Ph), 4.29 (dt, 1 H, J = 3.4, 10.6 Hz, CHNH), 4.19 (q, 2 H, J = 7.1 Hz, OCH_2CH_3), 4.11 (q, 2 H, J = 7.1 Hz, OCH_2CH_3), 2.58 (m, 1 H, CH_2), 2.35 (m, 1 H, CH_2), 1.52 (s, 3 H, CH_3), 1.25 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 1.19 (t, 3 H, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (75.5 MHz) δ 171.0 ($CO_2CH_2CH_3$), 170.9 ($CO_2CH_2CH_3$), 156.1 ($NHCO_2CH_2Ph$), 137.3, 136.6, 132.7, 128.5, 128.4, 127.9, 127.1, 126.2, 126.1, 66.6 (OCH_2Ph), 61.7, 58.1, 55.4, 35.5, 19.5 ($CH_3(CO_2CH_2CH_3)_2$), 14.0 (OCH_2CH_3), 13.9 (OCH_2CH_3); IR (neat) 3352, 1731 cm^{-1}; mp 78–80 °C. Anal. Calcd for $C_{26}H_{31}NO_6$: C, 68.86; H, 6.89; N, 3.09. Found: C, 68.68; H, 6.78; N, 2.98.

3c. Purification by column chromatography (9:1 hexane/EtOAc; R_f = 0.14) afforded 97 mg (50%) of ethyl 3-[(benzyloxycarbonyl)amino]-2-(ethoxycarbonyl)-2-methyl-5-heptynoate (yellow oil): ^{1}H NMR (300 MHz) δ 7.32 (m, 5 H, Ph), 5.63 (d, 1 H, J = 10.5 Hz, NH), 5.13 (d, 1 H, J = 12.3 Hz, CH_2Ph), 5.04 (d, 1 H, J = 12.3 Hz, CH_2Ph), 4.33 (ddd, 1 H, J = 5.4, 7.6, 10.6 Hz, CHNH), 4.17 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 4.09 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 2.47 (m, 2 H, CH_2), 1.65 (t, 3 H, J = 2.4 Hz, CH_3), 1.47 (s, 3 H, CH_3), 1.25 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 1.18 (t, 3 H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (75.5 MHz) δ 170.7 ($CO_2CH_2CH_3$), 170.5 ($CO_2CH_2CH_3$), 156.0 ($NHCO_2CH_2Ph$), 136.7, 128.3, 128.0, 127.9, 78.1 ($CCCH_3$), 74.6 ($CCCH_3$), 66.6, 61.6, 57.6, 54.2, 22.0, 19.3, 13.9 (OCH_2CH_3), 13.8 (OCH_2CH_3), 3.4 ($CCCH_3$); IR (neat) 3438, 3364, 2235, 1733 cm^{-1}. Anal. Calcd for $C_{21}H_{27}NO_6$: C, 64.77; H, 6.99; N, 3.60. Found: C, 64.88; H, 7.14; N, 3.53.

3d. Treatment of the resulting black solution with 10 mL of 1.0 M HCl and 15 mL of ether at rt for 12 h followed by the usual workup and purification by column chromatography (4:1 hexane/EtOAc; R_f = 0.10) afforded 59 mg (31%) of ethyl 3-[(benzyloxycarbonyl)amino]-2-(ethoxycarbonyl)-2-methyl-5-hexanone (white solid): ^{1}H NMR (300 MHz) δ 7.30 (s, 5 H, Ph), 5.54 (d, 1 H, J = 10.4 Hz, NH), 5.06 (d, 1 H, J = 12.3 Hz, CH_2Ph), 5.00 (d, 1 H, J = 12.3 Hz, CH_2Ph), 4.65 (ddd, 1 H, J = 4.7, 7.9, 10.3 Hz, CHNH), 4.15 (q, 3 H, J = 7.1 Hz, OCH_2CH_3), 4.09 (q, 3 H, J = 7.1 Hz, OCH_2CH_3), 2.72 (m, 2 H, CH_2), 2.15 (s, 3 H, acyl-CH_3), 1.45 (s, 3 H, CH_3), 1.23 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 1.18 (t, 3 H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (75.5 MHz) δ 205.7 (CO-CH_3), 170.6 ($CO_2CH_2CH_3$), 170.5 ($CO_2CH_2CH_3$), 155.7 ($NHCO_2CH_2Ph$), 136.4, 128.4, 128.1, 66.8, 61.8 (OCH_2CH_3), 61.7 (OCH_2CH_3), 58.1, 51.6, 46.0, 29.8, 19.1, 13.88 (OCH_2CH_3), 13.86 (OCH_2CH_3); IR (neat) 3928, 1732, 1716, 1690 cm^{-1}; mp 76–77 °C. Anal. Calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.20; H, 7.12; N, 3.54.

General Procedure: Preparation of 4a–k. To a stirred solution containing 65 mg (0.25 mmol) of $PdCl_2(MeCN)_2$ in 5 mL THF at room temperature was added 50 mg (0.28 mmol) of *O*-benzyl-*N*-vinylcarbamate. After 5 min, the amber red homogeneous solution was cooled to −78 °C and treated with 50 mg (0.50 mmol) of triethylamine and 1.60 mL (0.20 M solution in THF, 0.32 mmol) of the sodium anion of dimethyl malonate. The mixture was allowed to warm to −50 °C and was stirred for 2.0 h. The reaction vessel was evacuated (2×) and the atmosphere replaced with carbon monoxide (1 atm). The mixture was allowed to warm to −20 °C and was stirred for 2.0 h. The resulting black slurry was treated with the corresponding trimethylorganostannanes (0.51 ± 0.02 mmol; **a–k**). The mixture was *slowly* warmed to room temperature and stirred 15–18 h. Filtration of the mixture through a pad of silica gel using ether or ethyl acetate as the eluent and removal of solvent in vacuo afforded the crude reaction mixture, which upon purification by radial-layer chromatography (1 mm; SiO_2) afforded the products **4a–k**.

4a. Purification by radial-layer chromatography (4:1 hexane/EtOAc; R_f = 0.18) afforded 72 mg (79%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-6-heptenoate (clear oil): ^{1}H NMR (300 MHz) δ 7.31 (s, 5 H, CH_2Ph), 6.26 (m, 2 H, =CH), 5.87 (dd, 1 H, J = 2.2, 9.2 Hz, =CH), 5.77 (d, 1 H, J = 9.7 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.71 (m, 1 H, CHNH), 3.96 (d, 1 H, J = 5.5 Hz, $CH(CO_2CH_3)_2$), 3.70 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.11 (dd, 1 H, J = 5.7, 17.4 Hz, CH_2), 2.90 (dd, 1 H, J = 7.0, 17.4 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 197.8 ($COCH$=CH_2), 168.4 (CO_2CH_3), 167.9 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 136.4, 136.2, 129.3, 128.5, 128.1, 128.0, 66.8, 53.7, 52.7 (OCH_3), 52.6 (OCH_3), 47.1, 41.7; IR (neat) 3377, 1736, 1613 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_7$: C, 59.50; H, 5.83; N, 3.85. Found: C, 59.35; H, 5.85; N, 4.00.

4b. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.32) afforded 79 mg (72%) of (*E*)-methyl-3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-7-phenyl-6-heptenoate (clear oil): ^{1}H NMR (300 MHz) δ 7.45 (m, 6 H, =CHPh, =CHPh), 7.32 (s, 5 H, CH_2Ph), 6.68 (d, 1 H, J = 16.3 Hz, CH=CHPh), 5.84 (d, 1 H, J = 9.6 Hz, NH), 5.06 (s, 2 H, CH_2Ph), 4.77 (m, 1 H, CHNH), 4.02 (d, 1 H, J = 5.6 Hz, $CH(CO_2CH_3)_2$), 3.71 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.20 (dd, 1 H, J = 5.7, 17.2 Hz, CH_2), 2.99 (dd, 1 H, J = 6.9, 17.2 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 197.3 ($COCH$=CHPh), 168.4 (CO_2CH_3), 167.9 (CO_2CH_3), 155.4 ($NHCO_2CH_2Ph$), 143.7, 136.3, 134.0, 130.7, 128.9, 128.4, 128.0, 127.9, 125.7, 66.7, 53.6, 52.7 (OCH_3), 52.6 (OCH_3), 47.2, 42.6; IR (neat) 3366, 1736, 1654, 1610 cm^{-1}. Anal. Calcd for $C_{24}H_{25}NO_7$: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.34; H, 5.71; N, 3.14.

4c. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.36) afforded 72 mg (74%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-7-methyl-5-oxo-6-octenoate (clear oil): ^{1}H NMR (300 MHz) δ 7.31 (s, 5 H,

CH_2Ph), 6.00 (s, 1 H, CH=$C(Me)_2$), 5.82 (d, 1 H, J = 9.7 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.68 (m, 1 H, CHNH), 3.96 (d, 1 H, J = 5.5 Hz, $CH(CO_2CH_3)_2$), 3.69 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 2.88 (dd, 1 H, J = 5.5, 17.4 Hz, CH_2), 2.71 (dd, 1 H, J = 7.1, 17.4 Hz, CH_2), 2.11 (d, 3 H, J = 1.1 Hz, CH_3), 1.85 (d, 3 H, J = 1.1 Hz, CH_3); ^{13}C NMR (75.5 MHz) δ 197.5 ($COCH$=$C(CH_3)_2$), 168.5 (CO_2CH_3), 168.0 (CO_2CH_3), 157.2, 155.5, 136.5, 128.4, 128.1, 128.0, 123.2, 66.7, 53.8, 52.6 (OCH_3), 52.5 (OCH_3), 47.2, 46.0, 27.7 (C-H=$C(CH_3)_2$), 20.9 (CH=$C(CH_3)_2$); IR (neat) 3368, 1733, 1618 cm^{-1}. Anal. Calcd for $C_{20}H_{25}NO_7$: C, 61.37; H, 6.44; N, 3.58. Found: C, 61.50; H, 6.50; N, 3.54.

4d. Purification by radial-layer chromatography (4:1 hexane/EtOAc; R_f = 0.23) afforded 82 mg (70%) of methyl 3-[(benzyloxycarbonyl)amino]-6-(4-*tert*-butylcyclohexenyl)-2-(methoxycarbonyl)-5-oxopentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.31 (s, 5 H, CH_2Ph), 6.91 (d, 1 H, J = 5.0 Hz, =$CHCH_2$), 5.82 (d, 1 H, J = 9.6 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.70 (m, 1 H, CHNH), 3.96 (d, 1 H, J = 4.8 Hz, $CH(CO_2CH_3)_2$), 3.69 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.14 (m, 1 H, $COCH_2$), 2.90 (m, 1 H, $COCH_2$), 2.48 (m, 1 H, CH_2), 2.27 (m, 1 H, CH_2), 1.92 (m, 3 H, $CHC(CH_3)_3$, CH_2), 1.21 (m, 1 H, CH_2), 1.02 (m, 1 H, CH_2), 0.85 (s, 9 H, $CHC(CH_3)_3$); ^{13}C NMR (75.5 MHz) δ 198.2 (COC=CH), 168.6 (CO_2CH_3), 168.1 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 141.9, 141.8, 139.0, 136.4, 128.4, 128.0, 127.9, 66.7, 53.7, 52.7 (OCH_3), 52.6 (OCH_3), 47.6, 43.3, 39.4, 32.1, 27.9, 27.0, 24.4, 24.3, 23.3; IR (neat) 3370, 1736, 1662, 1643 cm^{-1}. Anal. Calcd for $C_{26}H_{35}NO_7$: C, 65.94; H, 7.45; N, 2.96. Found: C, 65.71; H, 7.40; N, 2.95.

4e. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.42) afforded 79 mg (77%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-5-phenylpentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.92 (d, 2 H, J = 7.5 Hz, o-COPh), 7.56 (m, 1 H, p-COPh), 7.44 (m, 2 H, m-COPh), 7.32 (s, 5 H, CH_2Ph), 5.88 (d, 1 H, J = 9.4 Hz, NH), 5.06 (s, 2 H, CH_2Ph), 4.86 (m, 1 H, CHNH), 4.07 (d, 1 H, J = 5.6 Hz, $CH(CO_2CH_3)_2$), 3.70 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.52 (dd, 1 H, J = 5.3, 17.6 Hz, CH_2), 3.30 (dd, 1 H, J = 7.1, 17.6 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 197.5 ($COPh$), 168.6 (CO_2CH_3), 168.0 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 136.43, 136.40, 133.6, 128.7, 128.5, 128.13, 128.07, 128.0, 66.8, 53.7, 52.7 (OCH_3), 52.6 (OCH_3), 47.4, 40.9; IR (neat) 3378, 1736, 1681 cm^{-1}. Anal. Calcd for $C_{22}H_{23}NO_7$: C, 63.92; H, 5.61; N, 3.39. Found: C, 64.18; H, 5.81; N, 3.45.

4f. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.27) afforded 102 mg (95%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-5-(*p*-tolyl)-pentanoate (clear oil): ^{1}H NMR (300 MHz; Me_4Si, 0 ppm) δ 7.83 (d, 2 H, J = 8.1 Hz, o-COAr), 7.31 (s, 5 H, CH_2Ph), 7.24 (d, 2 H, J = 8.1 Hz, m-COAr), 5.92 (d, 1 H, J = 9.5 Hz, NH), 5.07 (s, 2 H, CH_2Ph), 4.87 (m, 1 H, CHNH), 4.09 (d, 1 H, J = 5.6 Hz, $CH(CO_2CH_3)_2$), 3.71 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.50 (dd, 1 H, J = 5.4, 17.5 Hz, CH_2), 3.26 (dd, 1 H, J = 7.1, 17.5 Hz, CH_2), 2.40 (s, 3 H, $ArCH_3$); ^{13}C NMR (75.5 MHz) δ 197.0 ($COAr$), 168.5 (CO_2CH_3), 168.0 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 144.4, 136.3, 133.9, 129.3, 128.4, 128.2, 128.0, 127.9, 66.7, 53.7, 52.7 (OCH_3), 52.6 (OCH_3), 47.3, 40.7, 21.6 ($ArCH_3$); IR (neat) 3374, 1732, 1678, 1606 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_7$: C, 64.63; H, 5.90; N, 3.28. Found: C, 64.61; H, 6.01; N, 3.32.

4g. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.36) afforded 103 mg (93%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-5-(*p*-methoxyphenyl)pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.89 (d, 2 H, J = 8.9 Hz, o-COAr), 7.30 (s, 5 H, CH_2Ph), 6.90 (d, 2 H, J = 8.9 Hz, m-COAr), 5.93 (d, 1 H, J = 9.6 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.84 (m, 1 H, CHNH), 4.07 (d, 1 H, J = 5.6 Hz, $CH(CO_2CH_3)_2$), 3.83 (s, 3 H, $ArOCH_3$), 3.69 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.45 (dd, 1 H, J = 5.4, 17.3 Hz, CH_2), 3.21 (dd, 1 H, J = 7.1, 17.3 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 195.9 ($COAr$), 168.6 (CO_2CH_3), 168.0 (CO_2CH_3), 163.8, 155.5 ($NHCO_2CH_2Ph$), 136.3, 130.4, 129.4, 128.44, 128.39, 128.0, 127.9, 113.8, 66.7, 55.4, 53.6, 52.7 (OCH_3), 52.6 (OCH_3), 47.4, 40.4; IR (neat) 3370, 1736, 1674 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_8$: C, 62.30; H, 5.68; N, 3.16. Found: C, 62.09; H, 5.70; N, 3.17.

4h. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.28) afforded 66 mg (59%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-5-(*p*-chlorophenyl)pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.86 (d, 1 H, J = 8.5 Hz, o-COAr), 7.41 (d, 1 H, J = 8.5 Hz, m-COAr), 7.31 (s, 5 H, CH_2Ph), 5.84 (d, 1 H, J = 9.4 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.82 (m, 1 H, CHNH), 4.04 (d, 1 H, J = 5.5 Hz, $CH(CO_2CH_3)_2$), 3.70 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.48 (dd, 1 H, J = 5.6, 17.4 Hz, CH_2), 3.24 (dd, 1 H, J = 6.9, 17.4 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 196.3 ($COAr$), 168.5 (CO_2CH_3), 167.9 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 140.1, 136.3, 134.7, 129.5, 129.0, 128.5, 128.1, 128.0, 66.8, 53.7, 52.8 (OCH_3), 52.7 (OCH_3), 47.3, 40.8; IR (neat) 3377, 1735 cm^{-1}. Anal. Calcd for $C_{22}H_{22}NO_7Cl$: C, 59.00; H, 4.95; N, 3.13. Found: C, 58.86; H, 5.22; N, 3.13.

4i. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.27) afforded 59 mg (59%) of methyl 3-[(benzyloxycarbonyl)amino]-5-(2-furanyl)-2-(methoxycarbonyl)-5-oxopentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.56 (m, 1 H, CH=CHO), 7.30 (s, 5 H, CH_2Ph), 7.22 (d, 1 H, J = 3.4 Hz, β-$CHCH$=CHO), 6.51 (dd, 1 H, J = 1.6, 3.5 Hz, γ-CH=CHO), 5.83 (d, 1 H, J = 9.4 Hz, NH), 5.05 (s, 2 H, CH_2Ph), 4.81 (m, 1 H, CHNH), 4.00 (d, 1 H, J = 5.4 Hz, $CH(CO_2CH_3)_2$), 3.71 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.35 (dd, 1 H, J = 6.0, 16.9 Hz, CH_2), 3.11 (dd, 1 H, J = 6.8, 16.9 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 186.1 (CO furan), 168.4 (CO_2CH_3), 167.8 (CO_2CH_3), 155.4 ($NHCO_2CH_2Ph$), 152.3, 146.8, 136.3, 128.4, 128.03, 127.97, 117.9, 112.4, 66.8, 53.8, 52.7 (OCH_3), 52.6 (OCH_3), 47.3, 40.8; IR (neat) 3366, 1733, 1673 cm^{-1}. Anal. Calcd for $C_{20}H_{21}NO_8$: C, 59.55; H, 5.25; N, 3.47. Found: C, 59.69; H, 5.25; N, 3.56.

4j. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.38) afforded 65 mg (62%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-5-(2-thiophene-yl)pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.74 (d, 1 H, J = 3.4 Hz, CH=CHS), 7.64 (dd, 1 H, J = 1.1, 5.0 Hz, β-$CHCH$=CHS), 7.31 (s, 5 H, CH_2Ph), 7.11 (m, 1 H, γ-CH=CHS), 5.86 (d, 1 H, J = 9.6 Hz, NH), 5.06 (s, 2 H, CH_2Ph), 4.81 (m, 1 H, CHNH), 4.04 (d, 1 H, J = 5.6 Hz, $CH(CO_2CH_3)_2$), 3.71 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.45 (dd, 1 H, J = 5.7, 16.7 Hz, CH_2), 3.21 (dd, 1 H, J = 7.0, 16.7 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 190.3 (CO thiophene), 168.5 (CO_2CH_3, 167.9 (CO_2CH_3), 155.5 ($NHCO_2CH_2Ph$), 143.7, 136.4, 134.4, 132.7, 128.5, 128.3, 128.1, 128.0, 66.8, 53.7, 52.8 (OCH_3), 52.7 (OCH_3), 47.6, 41.5; IR (neat) 3364, 1732, 1659 cm^{-1}. Anal. Calcd for $C_{20}H_{21}NO_7S$: C, 57.27; H, 5.05; N, 3.34. Found: C, 57.30; H, 5.10; N, 3.57.

4k. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.36) afforded 64 mg (69%) of methyl 3-[(benzyloxycarbonyl)amino]-2-(methoxycarbonyl)-5-oxo-6-octynoate (yellow oil): ^{1}H NMR (300 MHz) δ 7.32 (s, 5 H, CH_2Ph), 5.68 (d, 1 H, J = 9.6 Hz, NH), 5.06 (s, 2 H, CH_2Ph), 4.76 (m, 1 H, CHNH), 3.88 (d, 1 H, J = 5.2 Hz, $CH(CO_2CH_3)_2$), 3.71 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.03 (dd, 1 H, J = 6.5, 17.5 Hz, CH_2), 2.85 (dd, 1 H, J = 6.6, 17.5 Hz, CH_2), 1.98 (s, 3 H, CH_3); ^{13}C NMR (75.5 MHz) δ 184.4 ($COCCCH_3$), 168.2 (CO_2CH_3), 167.7 (CO_2CH_3), 155.4 ($NHCO_2CH_2Ph$), 136.4, 128.5, 128.1, 128.0, 91.9 ($COCCCH_3$), 79.9 ($COCCCH_3$), 66.9, 53.7, 52.8 (OCH_3), 52.7 (OCH_3), 47.6, 46.9, 4.1 ($COCCCH_3$); IR (neat) 3335, 2221, 1735, 1670 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_7$: C, 60.80; H, 5.64; N, 3.73. Found: C, 60.61; H, 5.70; N, 3.55.

General Procedure: Preparation of 5a–d. A balloon of propene was attached to the side arm of a flask containing 130 mg (0.50 mmol) of $PdCl_2(MeCN)_2$ in 7 mL of THF at room temperature. After an amber red homogeneous solution resulted, the mixture was cooled to −78 °C and treated with 100 mg (1.00 mmol) of triethylamine and 3.00 mL (0.20 M solution in THF, 0.60 mmol) of the sodium anion of dimethyl malonate. The mixture was warmed to −60 °C and was stirred for 2.0 h. The reaction vessel was evacuated (2×), the atmosphere replaced with carbon monoxide (1 atm), and the mixture was allowed to warm to −30 °C and was stirred for 2.0 h. The resulting black slurry was treated with the corresponding trimethylorganostannane (0.80 ± 0.01 mmol; **a–d**), *slowly* allowed to warm to room temperature, and stirred 15–18 h. Filtration of the mixture through a pad of silica gel using ether as eluent and removal of solvent in vacuo afforded the crude reaction mixture, which upon purification by radial-layer chromatography (1 mm; SiO_2) afforded products **5a–d**.

5a. Purification by radial-layer chromatography (4:1 hexane/Et_2O; R_f = 0.19) afforded 93 mg (73%) of methyl 2-(methoxycarbonyl)-3,7-dimethyl-5-oxo-6-octenoate (clear oil): ^{1}H NMR (300 MHz) δ 6.04 (m, 1 H, CH=$C(CH_3)_2$), 3.70 (s, 6 H, $2OCH_3$),

3.41 (d, 1 H, J = 6.8 Hz, CH(CO_2CH_3)$_2$), 2.78 (m, 1 H, CHCH$_3$), 2.62 (dd, 1 H, J = 4.8, 16.4 Hz, CH_2), 2.33 (dd, 1 H, J = 8.5, 16.4 Hz, CH_2), 2.12 (d, 3 H, J = 1.1 Hz, CH=C(CH_3)$_2$), 1.71 (d, 3 H, J = 1.1 Hz, CH=C(CH_3)$_2$), 0.99 (d, 3 H, J = 6.8 Hz, CHCH_3); ^{13}C NMR (75.5 MHz) δ 199.0 (COCH=C(CH$_3$)$_2$), 169.1 (CO_2CH_3), 169.0 (CO_2CH_3), 155.6 (CH=C(CH$_3$)$_2$), 123.8 (CH=C(CH$_3$)$_2$), 56.2, 52.3, 48.2, 29.5, 27.6, 20.7, 17.6; IR (neat) 1751, 1736, 1686 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 61.09; H, 7.73.

5b. Purification by radial-layer chromatography (4:1 hexane/Et_2O; R_f = 0.18) afforded 104 mg (75%) of methyl 2-(methoxycarbonyl)-3-methyl-5-oxo-5-phenylpentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.96 (m, 2 H, o-COPh), 7.54 (m, 1 H, p-COPh), 7.44 (m, 2 H, m-COPh), 3.73 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.51 (d, 1 H, J = 6.4 Hz, CH(CO_2CH_3)$_2$), 3.25 (dd, 1 H, J = 3.6, 15.6 Hz, CH_2), 2.93 (m, 2 H, CH_2, CHCH$_3$), 1.07 (d, 3 H, J = 6.7 Hz, CHCH_3); ^{13}C NMR (75.5 MHz) δ 198.7 (COPh), 169.1 (CO_2CH_3), 169.0 (CO_2CH_3), 137.0, 133.1, 128.6, 128.1, 56.2, 52.35 (OCH_3), 52.32 (OCH_3), 42.6, 29.6, 17.8; IR (neat) 1751, 1734, 1684 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.64; H, 6.61.

5c. Purification by radial-layer chromatography (4:1 hexane/Et_2O; R_f = 0.08) afforded 85 mg (63%) of methyl 5-(2-furanyl)-2-(methoxycarbonyl)-3-methyl-5-oxopentanoate (clear oil): ^{1}H NMR (300 MHz; Me_4Si, 0 ppm) δ 7.59 (dd, 1 H, J = 0.8, 1.7 Hz, CH=CH-O), 7.26 (dd, 1 H, J = 0.8, 3.6 Hz, β-CHCH=CHO), 6.54 (dd, 1 H, J = 1.7, 3.6 Hz, γ-CH=CHO), 3.75 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.50 (d, 1 H, J = 6.7 Hz, CH-(CO_2CH_3)$_2$), 3.08 (dd, 1 H, J = 4.5, 15.8 Hz, CH_2), 2.94 (m, 1 H, CHCH$_3$), 2.80 (dd, 1 H, J = 8.4, 15.7 Hz, CH_2), 1.09 (d, 3 H, J = 6.7 Hz, CHCH_3); ^{13}C NMR (75.5 MHz) δ 187.6 (COfuran), 169.0 (CO_2CH_3), 168.9 (CO_2CH_3), 152.7, 146.4, 117.4, 112.2, 56.1, 52.4 (OCH_3), 52.3 (OCH_3), 42.4, 29.7, 17.7; IR (neat) 1752, 1734, 1675 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 57.98; H, 6.03.

5d. Purification by radial-layer chromatography (4:1 hexane/Et_2O; R_f = 0.17) afforded 98 mg (65%) of methyl 2-(methoxycarbonyl)-3-methyl-5-oxo-7-phenyl-6-heptynoate (yellow oil): ^{1}H NMR (300 MHz) δ 7.55 (m, 2 H, Ph), 7.38 (m, 3 H, Ph), 3.73 (s, 6 H, 2OCH_3), 3.45 (d, 1 H, J = 6.6 Hz, CH(CO_2CH_3)$_2$), 2.91 (m, 2 H, CHCH$_3$, CH_2), 2.66 (dd, 1 H, J = 9.5, 17.7 Hz, CH_2), 1.07 (d, 3 H, J = 6.8 Hz, CHCH_3); ^{13}C NMR (75.5 MHz) δ 185.9 (COCCPh), 168.8 (CO_2CH_3), 133.1 130.8, 128.6, 119.8, 91.0 (COCCPh), 87.8 (COCCPh), 55.9, 52.4 (OCH$_3$), 49.5, 29.4, 17.6; IR (neat) 2202, 1732, 1682, 1668, 1652 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.64; H, 6.11.

General Procedure: Preparation of 7a–i and 9a$^{1-3}$–b$^{1-3}$. To a stirred solution containing 77 mg (0.20 mmol) of $PdCl_2(PhCN)_2$ in 5 mL of THF at room temperature was added 75 mg (0.28 mmol) of (±)-*syn*-4,5-diphenyl-3-vinyl-2-oxazolidinone (**6**) or 50 mg (0.26 mmol) of (*S*)- or (*R*)-3-ethenyl-4-phenyl-2-oxazolidinone (**8a** or **8b**). After 5 min, the amber-red homogeneous solution was cooled to −78 °C, treated with 40 mg (0.40 mmol) of triethylamine and 1.40 mL (0.20 M solution in THF, 0.28 mmol) of the sodium anion of dimethyl malonate, and was stirred for 2.5 h (5.0 h for **7a–i**). The reaction vessel was evacuated (2×), the atmosphere replaced with carbon monoxide (1 atm), and the mixture was *slowly* allowed to warm to −20 °C. The black slurry was treated with the corresponding trimethylorganostannanes (0.41 ± 0.02 mmol), slowly allowed to warm to room temperature, and stirred 15–18 h. Filtration of the mixture through a pad of silica gel using ether as the eluent and removal of solvent in vacuo afforded the crude reaction mixture, which upon purification by radial-layer chromatography (1 mm; SiO_2) afforded the products **7a–i** and **9a$^{1-3}$–b$^{1-3}$**.

7a. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.20) afforded 79 mg (88%) of methyl 2-(methoxycarbonyl)-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-6-heptenoate (clear oil): ^{1}H NMR (300 MHz) δ 6.95 (m, 10 H, 2Ph), 6.11 (m, 2 H, CH=CH_2), 5.80 (d, 1 H, J = 8.2 Hz, PhCHO), 5.76 (dd, 1 H, J = 4.7, 6.8 Hz, CH=CH$_2$), 5.26 (d, 1 H, J = 8.2 Hz, PhCHN), 4.43 (dt, 1 H, J = 4.7, 7.8 Hz, CHN), 4.06 (d, 1 H, J = 6.4 Hz, CH(CO_2CH_3)$_2$), 3.77 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 3.54 (dd, 1 H, J = 7.8, 17.9 Hz, CH_2), 2.99 (dd, 1 H, J = 4.7, 17.9 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 196.4 (COCH=CH$_2$), 168.0 (CO_2CH_3), 167.6 (CO_2CH_3), 157.2 (CO oxa), 135.6, 134.6, 134.3, 129.0, 128.4, 128.3, 128.2, 127.8, 127.6, 125.6, 80.0, 67.1, 53.9, 52.9 (OCH_3), 52.7 (OCH_3), 49.4, 41.1; IR (neat) 1755, 1676, 1615 cm^{-1}. Anal. Calcd for $C_{25}H_{25}NO_7$: C, 66.51; H, 5.58; N, 3.10. Found: C, 66.39; H, 5.73; N, 2.91.

7b. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.20) afforded 67 mg (70%) of methyl 2-(methoxycarbonyl)-7-methyl-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-6-octenoate (clear oil): ^{1}H NMR (300 MHz) δ 7.00 (m, 10 H, 2Ph), 5.87 (m, 1 H, CH=C(Me)$_2$), 5.80 (d, 1 H, J = 8.2 Hz, PhCHO), 5.28 (d, 1 H, J = 8.2 Hz, PhCHN), 4.43 (dt, 1 H, J = 4.5, 7.8 Hz, CHN), 4.00 (d, 1 H, J = 7.7 Hz, CH(CO_2CH_3)$_2$), 3.77 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.35 (dd, 1 H, J = 7.9, 17.7 Hz, CH_2), 2.81 (dd, 1 H, J = 4.7, 17.7 Hz, CH_2), 1.95 (d, 3 H, J = 1.0 Hz, CH_3), 1.80 (d, 3 H, J = 1.2 Hz, CH_3); ^{13}C NMR (75.5 MHz) δ 196.1 (COCH=C(CH$_3$)$_2$), 168.1 (CO_2CH_3), 167.8 (CO_2CH_3), 157.3, 157.0, 134.9, 134.5, 128.33, 128.27, 128.18, 127.8, 127.6, 125.7, 122.8, 80.1, 67.0, 54.1, 52.9 (OCH_3), 52.7 (OCH_3), 49.5, 45.5, 27.7 (CH=C(CH_3)$_2$), 20.8 (CH=C(CH_3)$_2$); IR (neat) 1756, 1686, 1619 cm^{-1}. Anal. Calcd for $C_{27}H_{29}NO_7$: C, 67.63; H, 6.10; N, 2.92. Found: C, 67.56; H, 6.11; N, 2.79.

7c. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.21) afforded 68 mg (66%) of methyl 2-(methoxycarbonyl)-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-5-(*p*-tolyl)pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.69 (d, 2 H, J = 8.1 Hz, o-COAr), 7.19 (d, 2 H, J = 8.1 Hz, m-COAr), 7.00 (m, 10 H, 2Ph), 5.83 (d, 1 H, J = 8.2 Hz, PhCHO), 5.32 (d, 1 H, J = 8.2 Hz, PhCHN), 4.59 (dt, 1 H, J = 4.1, 7.8 Hz, CHN), 4.14 (d, 1 H, J = 7.6 Hz, CH(CO_2CH_3)$_2$), 3.98 (dd, 1 H, J = 8.2, 18.0 Hz, CH_2), 3.80 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3), 3.30 (dd, 1 H, J = 4.3, 18.0 Hz, CH_2), 2.37 (s, 3 H, ArCH_3); ^{13}C NMR (75.5 MHz) δ 195.8 (COAr), 168.2 (CO_2CH_3), 167.9 (CO_2CH_3), 157.4 (CO oxa), 134.8, 134.5, 133.6, 129.3, 128.5, 128.3, 128.2, 127.9, 127.7, 125.8, 80.2, 67.4, 54.1, 52.9 (OCH_3), 52.8 (OCH_3), 49.9, 40.2, 21.7 (ArCH_3); IR (neat) 1755, 1680, 1607 cm^{-1}. Anal. Calcd for $C_{30}H_{29}NO_7$: C, 69.89; H, 5.67; N, 2.72. Found: C, 69.65; H, 5.87; N, 2.55.

7d. Purification by radial-layer chromatography (1:1 hexane/Et_2O; R_f = 0.18) afforded 37 mg (37%) of methyl 2-(methoxycarbonyl)-5-oxo-5-phenyl-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.79 (m, 2 H, o-COPh), 7.53 (m, 1 H, p-COPh), 7.39 (m, 2 H, m-COPh), 7.00 (m, 10 H, 2Ph), 5.83 (d, 1 H, J = 8.2 Hz, PhCHO), 5.32 (d, 1 H, J = 8.2 Hz, PhCHN), 4.60 (dt, 1 H, J = 4.4, 7.8 Hz, CHN), 4.16 (d, 1 H, J = 4.4 Hz, CH(CO_2CH_3)$_2$), 3.98 (dd, 1 H, J = 8.0, 18.0 Hz, CH_2), 3.81 (s, 3 H, OCH_3), 3.58 (s, 3 H, OCH_3), 3.36 (dd, 1 H, J = 4.4, 18.0 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 196.2 (COPh), 168.2 (CO_2CH_3), 167.8, (CO_2CH_3), 157.4 (CO oxa), 134.8, 134.5, 133.3, 128.6, 128.5, 128.34, 128.30, 128.1, 127.9, 127.7, 125.8, 80.2, 67.4, 54.1, 52.9 (OCH_3), 52.8 (OCH_3), 49.9, 40.3; IR (neat) 1755, 1684 cm^{-1}. Anal. Calcd for $C_{29}H_{27}NO_7$: C, 69.45; H, 5.43; N, 2.79. Found: C, 69.38; H, 5.40; N, 2.97.

7e. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.24) afforded 27 mg (25%) of methyl 2-(methoxycarbonyl)-5-oxo-5-(*p*-chlorophenyl)-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.71 (d, 1 H, J = 8.7 Hz, o-COAr), 7.36 (d, 1 H, J = 8.7 Hz, m-COAr), 7.00 (m, 10 H, 2Ph), 5.83 (d, 1 H, J = 8.2 Hz, PhCHO), 5.29 (d, 1 H, J = 8.2 Hz, PhCHN), 4.56 (dt, 1 H, J = 4.6, 7.8 Hz, CHN), 4.16 (d, 1 H, J = 7.9 Hz, CH(CO_2CH_3)$_2$), 3.89 (dd, 1 H, J = 7.8, 17.9 Hz, CH_2), 3.81 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3), 3.34 (dd, 1 H, J = 4.6, 17.9 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 195.0 (COAr), 168.1 (CO_2CH_3), 157.3 (CO oxa), 134.7, 134.4, 129.6, 128.9, 128.6, 128.4, 128.3, 127.9, 125.8, 80.2, 67.4, 54.0, 53.0 (OCH$_3$), 52.8 (OCH_3), 49.9, 40.3; IR (neat) 1755, 1682, 1589 cm^{-1}. Anal. Calcd for $C_{29}H_{26}NO_7Cl$: C, 64.99; H, 4.89; N, 2.61. Found: C, 64.90; H, 4.69; N, 2.69.

7f. Purification by radial-layer chromatography (7:3 hexane/EtOAc; R_f = 0.19) afforded 64 mg (65%) of methyl 5-(2-furanyl)-2-(methoxycarbonyl)-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]pentanoate (clear oil): ^{1}H NMR (300 MHz) δ 7.52 (dd, 1 H, J = 0.7, 1.7 Hz, OCH=CH), 7.05 (m, 11 H, 2Ph, β-CHCH=CHO), 6.47 (dd, 1 H, J = 1.7, 3.6 Hz, γ-CH=CHO), 5.82 (d, 1 H, J = 8.2 Hz, PhCHO), 5.28 (d, 1 H, J = 8.2 Hz, PhCHN), 4.54 (dt, 1 H, J = 5.5, 8.0 Hz, CHN), 4.15 (d, 1 H, J = 8.1 Hz, CH(CO_2CH_3)$_2$), 3.80 (s, 3 H, OCH_3), 3.66 (dd, 1 H, J = 7.3, 17.3 Hz, CH_2), 3.60 (s, 3 H, OCH_3), 3.32 (dd, 1 H, J = 5.5,

17.3 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 184.9 (CO furan), 168.0 (CO_2CH_3), 167.7 (CO_2CH_3), 146.6 (CO oxa), 134.6, 134.5, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 125.8, 117.8, 112.3, 80.2, 67.2, 54.0, 52.9 (OCH_3), 52.8 (OCH_3), 49.8, 40.0; IR (neat) 1755, 1673 cm^{-1}. Anal. Calcd for $C_{27}H_{25}NO_6$: C, 65.98; H, 5.13; N, 2.85. Found: C, 65.76; H, 5.28; N, 2.76.

7g. Purification by radial-layer chromatography (2:3 hexane/Et_2O; R_f = 0.29) afforded 69 mg (68%) of methyl 2-(methoxycarbonyl)-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-5-(2-thiophene-yl)pentanoate (clear oil): ^1H NMR (300 MHz) δ 7.64 (dd, 1 H, *J* = 1.1, 3.8 Hz, CHS), 7.59 (dd, 1 H, *J* = 1.0, 5.0 Hz, β-CHCH=CHS), 7.00 (m, 11 H, 2*Ph*, γ-CH=CHS), 5.82 (d, 1 H, *J* = 8.2 Hz, PhCHO), 5.30 (d, 1 H, *J* = 8.2 Hz, PhCHN), 4.56 (dt, 1 H, *J* = 5.3, 7.6 Hz, CHN), 4.15 (d, 1 H, *J* = 7.8 Hz, CH(CO_2CH_3)$_2$), 3.79 (s, 3 H, OCH_3), 3.78 (dd, 1 H, *J* = 7.5, 17.1 Hz, CH_2), 3.59 (s, 3 H, OCH_3), 3.39 (dd, 1 H, *J* = 5.3, 17.1 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 189.0 (CO thiophene), 168.0 (CO_2CH_3), 167.7 (CO_2CH_3), 157.3 (CO oxa), 143.5, 134.6, 134.4, 134.1, 132.4, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 125.8, 80.2, 67.2, 54.0, 52.9 (OCH_3), 52.8 (OCH_3), 50.1, 40.7; IR (neat) 1756, 1670 cm^{-1}. Anal. Calcd for $C_{27}H_{25}NO_7S$: C, 63.77; H, 5.15; N, 2.75. Found: C, 63.78; H, 5.18; N, 2.69.

7h. Purification by radial-layer chromatography (7:3 hexane/EtOAC; R_f = 0.18) afforded 66 mg (71%) of methyl 2-(methoxycarbonyl)-5-oxo-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-6-octynoate (yellow oil): ^1H NMR (300 MHz) δ 7.00 (m, 10 H, 2*Ph*), 5.79 (d, 1 H, *J* = 8.2 Hz, PhCHO), 5.22 (d, 1 H, *J* = 8.2 Hz, PhCHN), 4.44 (dt, 1 H, *J* = 4.9, 7.7 Hz, CHN), 4.05 (d, 1 H, *J* = 8.2 Hz, CH(CO_2CH_3)$_2$), 3.78 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.43 (dd, 1 H, *J* = 7.5, 18.2 Hz, CH_2), 3.02 (dd, 1 H, *J* = 4.9, 18.2 Hz, CH_2), 1.91 (s, 3 H, CH_3); ^{13}C NMR (75.5 MHz) δ 183.4 ($COCCCH_3$), 167.9 (CO_2CH_3), 167.4 (CO_2CH_3), 157.1 (CO oxa), 134.5, 134.3, 128.5, 128.3, 127.8, 127.7, 125.7, 91.8 ($COCCCH_3$), 80.1 ($COCCCH_3$), 79.3, 67.0, 53.8, 52.9 (OCH_3), 52.8 (OCH_3), 49.1, 47.0, 4.1 ($COCCCH_3$); IR (neat) 2222, 1756, 1672 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_7$: C, 67.38; H, 5.44; N, 3.02. Found: C, 67.23; H, 5.54; N, 2.86.

7i. Purification by radial-layer chromatography (4:1 hexane/EtOAc; R_f = 0.10) afforded 95 mg (90%) of methyl 2-(methoxycarbonyl)-5-oxo-7-phenyl-3-*N*-[(±)-*syn*-4,5-diphenyl-2-oxazolidinonyl]-6-heptynoate (light yellow oil): ^1H NMR (300 MHz) δ 7.40 (m, 5 H, *Ph*), 7.00 (m, 10 H, 2*Ph*), 5.81 (d, 1 H, *J* = 8.2 Hz, PhCHO), 5.26 (d, 1 H, *J* = 8.2 Hz, PhCHN), 4.53 (dt, 1 H, *J* = 5.0, 7.2 Hz, CHN), 4.14 (d, 1 H, *J* = 8.2 Hz, CH(CO_2CH_3)$_2$), 3.80 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.56 (dd, 1 H, *J* = 7.2, 18.2 Hz, CH_2), 3.22 (dd, 1 H, *J* = 5.0, 18.2 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 183.1 (COCCPh), 167.9 (CO_2CH_3), 167.5 (CO_2CH_3), 157.1 (CO oxa), 134.5, 134.3, 133.2, 130.9, 128.6, 128.5, 128.3, 127.8, 127.7, 125.7, 119.5, 92.1 (COCCPh), 87.1 (COCCPh), 80.2, 67.2, 53.8, 52.9 (OCH_3), 52.8 (OCH_3), 49.3, 47.0; IR (neat) 2202, 1756, 1670 cm^{-1}. Anal. Calcd for $C_{31}H_{27}NO_7$: C, 70.85; H, 5.18; N, 2.67. Found: C, 70.63; H, 5.42; N, 2.54.

9a[1] and 9b[1]. Purification by radial-layer chromatography (2:1 hexane/Et_2O; R_f = 0.12) afforded 49 mg (65%; $[\alpha]_D$ 54.0 (*c* −0.40, CH_2Cl_2)) of (+)-methyl 2-(methoxycarbonyl)-5-oxo-3-(*R*)-*N*-[4-(*S*)-phenyl-2-oxazolidinonyl]-6-heptenoate (**9a[1]**) and 51 mg (68%; $[\alpha]_D$ −56.8 (*c* 1.20, CH_2Cl_2)) of (−)-methyl 2-(methoxycarbonyl)-5-oxo-3-(*S*)-*N*-[4-(*R*)-phenyl-2-oxazolidinonyl]-6-heptenoate (**9b[1]**) (clear oils): ^1H NMR (300 MHz) δ 7.35 (m, 5 H, *Ph*), 6.08 (dd, 2 H, *J* = 5.8, 0.5 Hz, CH=CH_2), 5.74 (t, 1 H, *J* = 5.8 Hz, CH=CH_2), 4.96 (dd, 1 H, *J* = 6.1, 8.9 Hz, OCH_2CHN), 4.55 (t, 1 H, *J* = 8.8 Hz, OCH_2CHN), 4.32 (ddd, 1 H, *J* = 5.5, 7.2, 8.4 Hz, CHN), 4.20 (dd, 1 H, *J* = 6.1, 8.8 Hz, OCH_2CHN), 4.04 (d, 1 H, *J* = 8.4 Hz, CH(CO_2CH_3)$_2$), 3.75 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.35 (dd, 1 H, *J* = 7.2, 17.3 Hz, CH_2), 2.89 (dd, 1 H, *J* = 5.5, 17.3 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 196.5 (COCH=CH_2), 168.0 (CO_2CH_3), 167.6 (CO_2CH_3), 157.3 (CO oxa), 137.8, 135.7, 129.3, 129.2, 129.0, 127.8, 70.2, 61.7, 53.4, 52.9 (OCH_3), 52.8 (OCH_3), 48.8, 40.9; IR (neat) 1747, 1732, 1708 cm^{-1}; mass spectrum *m/e* CI(NH_3) 376 (M + 1)$^+$. Anal. Calcd for $C_{19}H_{21}NO_7$: C, 60.79; H, 5.63; N, 3.73. Found: C, 60.62; H, 5.59; N, 3.60.

9a[2] and 9b[2]. Purification by radial-layer chromatography (1:1 hexane/Et_2O; R_f = 0.32) afforded 61 mg (76%; $[\alpha]_D$ 31.6 (*c* 1.10, CH_2Cl_2)) of (+)-methyl 2-(methoxycarbonyl)-7-methyl-5-oxo-3-(*R*)-*N*-[4-(*S*)-phenyl-2-oxazolidinonyl]-6-octenoate (**9a[2]**) and 67 mg (83%; $[\alpha]_D$ −32.4 (*c* 1.20, CH_2Cl_2)) of (−)-methyl 2-(methoxycarbonyl)-7-methyl-5-oxo-3-(*S*)-*N*-[4-(*R*)-phenyl-2-oxazolidinonyl]-6-octenoate (**9b[2]**) (clear oils): ^1H NMR (300 MHz) δ 7.34 (m, 5 H, *Ph*), 5.83 (m, 1 H, CH=$C(CH_3)_2$), 4.98 (dd, 1 H, *J* = 6.1, 8.9 Hz, OCH_2CHN), 4.54 (t, 1 H, *J* = 8.9 Hz, OCH_2CHN), 4.33 (dt, 1 H, *J* = 5.3, 7.9 Hz, CHN), 4.16 (dd, 1 H, *J* = 6.1, 8.7 Hz, OCH_2CHN), 3.94 (d, 1 H, *J* = 8.2 Hz, CH(CO_2CH_3)$_2$), 3.73 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 3.18 (dd, 1 H, 7.6, 17.3 Hz, CH_2), 2.66 (dd, 1 H, *J* = 5.3, 17.3 Hz, CH_2), 1.98 (d, 3 H, *J* = 1.0 Hz, CH=$C(CH_3)_2$), 1.79 (d, 3 H, *J* = 1.1 Hz, CH=$C(CH_3)_2$); ^{13}C NMR (75.5 MHz) δ 196.0 (COCH=$C(CH_3)_2$), 168.0 (CO_2CH_3), 167.7 (CO_2CH_3), 157.4, 156.7, 138.3, 129.2, 129.1, 127.7, 122.9, 70.3, 61.6, 53.7, 52.8 (OCH_3), 52.7 (OCH_3), 48.9, 45.5, 27.7 (CH=$C(CH_3)_2$), 20.8 (CH=$C(CH_3)_2$); IR (neat) 1760–1730, 1660 cm^{-1}; mass spectrum *m/e* (relative intensity) EI 403 (1, M$^+$). Anal. Calcd for $C_{21}H_{25}NO_7$: C, 62.52; H, 6.24; N, 3.47. Found: C, 62.41; H, 6.20; N, 3.34.

9a[3] and 9b[3]. Purification by radial-layer chromatography (3:2 hexane/EtOAc; R_f = 0.28) afforded 62 mg (69%; $[\alpha]_D$ 2.9, (*c* 1.60, CH_2Cl_2)) of (+)-methyl 2-(methoxycarbonyl)-5-oxo-7-phenyl-3-(*R*)-*N*-[4-(*S*)-phenyl-2-oxazolidinonyl]-6-heptynoate (**9a[3]**) and 68 mg (76%; $[\alpha]_D$ −3.0 (*c* 1.40, CH_2Cl_2)) of (−)-methyl 2-(methoxycarbonyl)-5-oxo-7-phenyl-3-(*S*)-*N*-[4-(*R*)-phenyl-2-oxazolidinonyl]-6-heptynoate (**9b[3]**) (light yellow oils): ^1H NMR (300 MHz) δ 7.39 (m, 10 H, 2*Ph*), 4.96 (dd, 1 H, *J* = 6.4, 8.9 Hz, OCH_2CHN), 4.56 (t, 1 H, *J* = 8.9 Hz, OCH_2CHN), 4.41 (ddd, 1 H, *J* = 5.9, 6.6, 8.7 Hz, CHN), 4.22 (dd, 1 H, *J* = 6.5, 8.9 Hz, OCH_2CHN), 4.11 (d, 1 H, *J* = 8.7 Hz, CH(CO_2CH_3)$_2$), 3.78 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.35 (dd, 1 H, *J* = 6.6, 17.6 Hz, CH_2), 3.10 (dd, 1 H, *J* = 5.9, 17.6 Hz, CH_2); ^{13}C NMR (75.5 MHz) δ 183.2 (COCCPh), 167.9 (CO_2CH_3), 167.5 (CO_2CH_3), 157.2 (CO oxa), 137.5, 133.3, 131.0, 129.5, 129.4, 128.6, 127.9, 119.6, 92.1 (COCCPh), 87.1 (COCCPh), 70.3, 61.8, 53.3, 53.0, 52.9, 48.6, 46.9; IR (neat) 2203, 1755, 1670 cm^{-1}; mass spectrum *m/e* CI(NH_3) 449 (M$^+$). Anal. Calcd for $C_{25}H_{23}NO_7$: C, 66.80; H, 5.15; N, 3.11. Found: C, 67.03; H, 5.35; N, 2.96.

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