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An Efficient Diastereoselective Route to Differentially Protected *anti*-4-Amino-1-alken-3-ols

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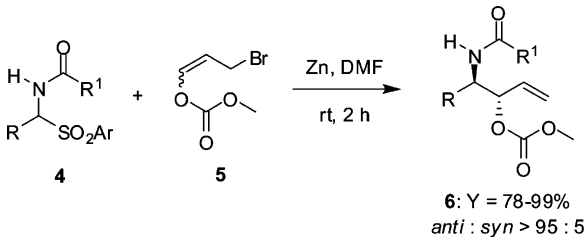
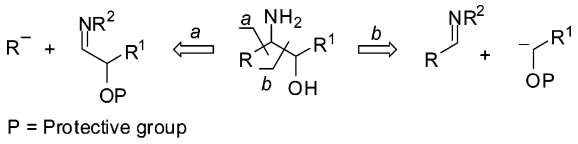


Zinc-promoted hydroxyallylation of α-amidoalkyl arylsulfones **4** using 3-bromo-propenyl methyl carbonate **5** proceeds smoothly in DMF at room temperature to afford high yields of differentially protected *anti*-1,2-amino alcohols **6**.

The everlasting interest in the stereoselective synthesis of 1,2-amino alcohols is largely justified by their widespread occurrence in many bioactive natural products.[1] Enantiomerically enriched vicinal amino alcohols are also profitable starting materials for the synthesis of many chiral catalysts and auxiliaries that are used in several asymmetric processes.[2] Functionalization of alkenes by aminohydroxylation or by nucleophilic ring opening of the corresponding epoxides represents a practical way to introduce these polar groups in a preformed molecular framework.[3] A complementary strategy consists of the assembling of structurally defined compounds by reaction of carbon nucleophiles with electrophilic substrates such as 2-amino aldehydes.[4] Addition of carbanionic systems to azomethine compounds also provides an efficient entry to various functionalized amino derivatives.[5] Thus, 2-alkoxyimines can generate 1,2-amino alcohols by reaction with various carbon nucleophiles following the retrosynthetic path a depicted in Scheme 1.[6] Alternatively, simple imino derivatives can be used as substrates for the same process, providing that α-alkoxy carbanions are used as nucleophiles (Scheme 1, path b).

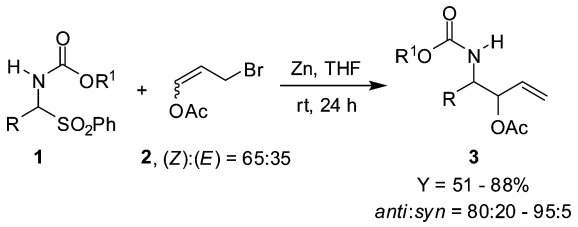
SCHEME 1



Synthetic applications involving the latter strategy have been somewhat limited by the paucity of simple reagents, equivalent to the α-alkoxy carbanion synthon, showing a suitable reactivity with imino derivatives. Indeed, carbanionic reagents endowed with a marked basic character may produce a consistent enolization when reacting with aldimines obtained from aliphatic aldehydes.[7] This drawback could be easily overcome by exploiting less basic carbanionic systems to be used in connection with particularly reactive imino derivatives. The electrophilicity of the azomethine carbon can be suitably tuned by a proper choice of the substituent at the nitrogen atom, and the electron-withdrawing properties of the acyl group makes *N*-acylimines among the more reactive imino derivatives available.[8] An efficient way to access *N*-acylimines is to carry out a base-promoted elimination process involving a good leaving group from *N*-acyl-α-substituted amines such as α-amidoalkyl sulfones **1**.[9] As a carbanionic counterpart, 3-bromo-propenyl acetate **2** when treated with metals such as zinc and indium, has been revealed a profitable equivalent of 1-hydroxy allyl anion synthon in the reaction with various carbonyl derivatives.[10]

The viability of this synthetic approach has been recently demonstrated by reaction of sulfones **1** with allyl bromide **2** that in the presence of zinc gives protected 1,2-amino alcohols in satisfactory yields and *anti* diastereoselections (Scheme 2).[11]

SCHEME 2



Application of this procedure to *N*-arylbenzaldimines using 3-bromo-1-benzoyloxy-1-propene in the presence of zinc metal is also successful in providing the corresponding protected *anti*-

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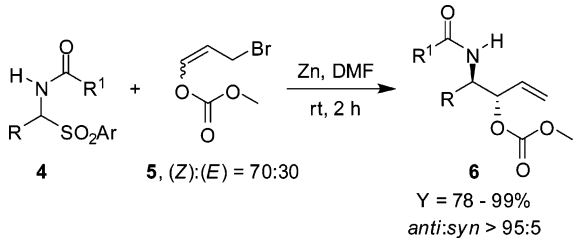
SCHEME 3



1,2-amino alcohols.[12] However, the presence of an amino group having a certain nucleophilic aptitude favors the partial migration of the benzoyl moiety from the ester to the nitrogen atom, leading to a regioisomeric mixture of 1,2-amino alcohol derivatives. This trouble clearly calls for an additional synthetic operation that involves hydrolysis of the benzoyl group from the obtained adducts with consequent loss of the protection at the hydroxy group.

We have recently shown that 3-bromo-propenyl methyl carbonate **5** offer several advantages with respect to **2**, both in terms of preparation and in terms of reactivity. The same zinc- and indium-promoted Barbier-type hydroxyallylations of carbonyl compounds applied to **2**, indeed, did work even better with **5**, in terms of chemical yields, diastereoselectivity, and of lack of internal migration of the carbonate group.[13]

We now report an optimized method of wide applicability for the synthesis of differentially protected 1,2-amino alcohols **6**, based on the zinc-promoted hydroxyallylation of α-amidoalkyl arylsulfones **4** using 3-bromo-propenyl methyl carbonate **5** in DMF at room temperature for 2 h (Scheme 3).

The results collected in Table 1 refer to a representative variety of α-amidoalkyl arylsulfones **4**. The R groups include aromatic, primary and secondary alkyl groups, including functionalized carbon chain (entries 4−9); the $R^1C{=}O$ substituent ranges from classic Boc, Cbz, and ethoxycarbonyl groups to simple formyl. All reactions are characterized by very good yields (78−99%) and, with the exception of entry 9, by excellent simple diastereoselectivity, the minor *syn* isomer being constantly below the sensitivity of the NMR instrumentation. Moreover, the use of DMF as the solvent is not critical, since it can be replaced with THF when **4** displays a poor solubility in DMF, giving good yields in the same reaction times (entries 2 and 7).

Two different synthetic strategies were adopted in order to unambiguously assign the relative *syn* or *anti* stereorelationship of adducts **6**. Adducts **6d,i** were quantitatively transformed to the corresponding aminoalcohols **7d,i** by acidic hydrolysis, and their spectral data were compared with the ones reported in the literature[11,14] (Scheme 4).

All other adducts were quantitatively converted to oxazolidinones by a two-step procedure involving (i) the basic hydrolysis of the methyl carbonate and (ii) NaH-promoted cyclization (Scheme 5). The relative *cis* stereochemistry of the oxazolidinones **8a−c,e−g,j** was unambiguously established by ^{1}H NMR, since it is known that the signals for H4 and H5 protons constantly resonate at lower fields for *cis*-**8** (δ H4 3.80−4.92, δ H5 5.00−5.17) with respect to the corresponding signals for *trans*-**8** (δ H4 3.47−3.85, δ H5 4.48−4.74).[14,15]

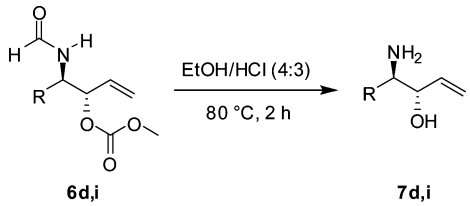
Finally, we tested the zinc-promoted hydroxyallylation of α-amidoalkyl arylsulfones with two chiral substrates. The reaction with chiral α-amidoalkylphenyl sulfone **4k** deriving from D-glyceraldehyde afforded two diasteroisomers in the 85:15 ratio with very good isolated yield (Scheme 6).

TABLE 1. Zinc-Promoted Synthesis of 6

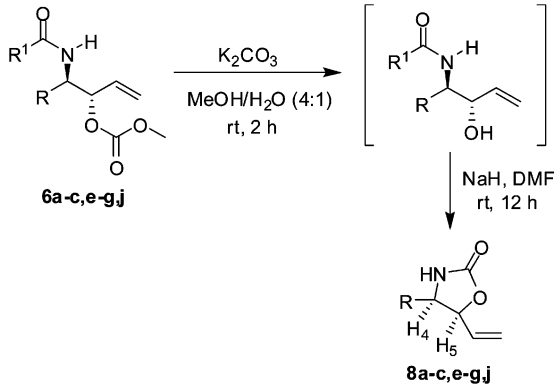
entry	R	R^1	Ar	**6**, yield (%)[a]	**6**, *anti*:*syn*
1	*c*-C_6H_{11}	*t*-BuO	Ph	**6a**, 99	>95:5
2[b]	*n*-C_7H_{15}	*t*-BuO	Ph	**6b**, 87	>95:5
3	*i*-Bu	*t*-BuO	Ph	**6c**, 99	>95:5
4	2-phenyl-ethyl	BnO	Ph	**6d**, 89	>95:5
5[c]	2-phenyl-ethyl	BnO	Ph	**6d**, 91	98:2
6	(*E*)-3-nonenyl	BnO	Ph	**6e**, 80	>95:5
7[b]	5-chloro-pentyl	BnO	Ph	**6f**, 78	>95:5
8	2-phenylsulfonyl-ethyl	BnO	Ph	**6g**, 83	>95:5
9	ethoxycarbonyl	BnO	Tol	**6h**, 98	65:35
10	4-methoxy-phenyl	H	Tol	**6i**, 97	>95:5
11	phenyl	EtO	Tol	**6j**, 99	>95:5

[a] Isolated yields after purification by flash chromatography on silica gel. [b] Reaction in THF. [c] Reaction on 10 mmol scale.

SCHEME 4



SCHEME 5



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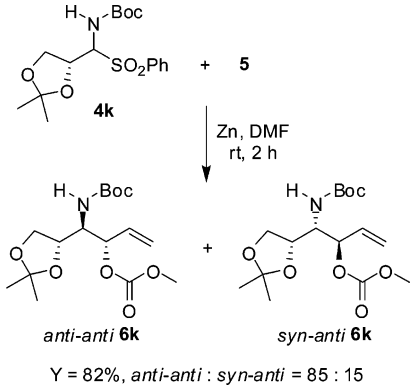
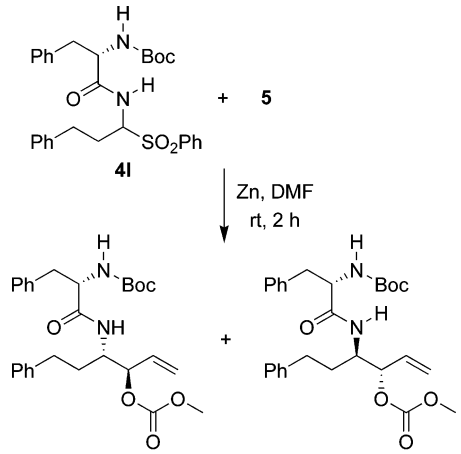
SCHEME 6



Y = 82%, *anti-anti* : *syn-anti* = 85 : 15

SCHEME 7



6l: Y = 92%, d.r. = 60 : 40

The absolute stereochemistry was determined by converting the adducts to the corresponding oxazolidinones (**8k**) and comparing their spectral data with the ones reported in the literature.[16]

The α-amidoalkyl arylsulfones **4l** deriving from *N*-Boc phenylalanine gave again excellent results in terms of overall isolated yield but very poor diastereoselectivity (Scheme 7). These results are in good agreement with the ones obtained in the reaction of the same sulfone with different nucleophiles, such as phenyl magnesium bromide or lithium enolates of acetic acid esters.[17]

In conclusion, a highly efficient synthesis of differentially protected *anti*-4-amino-1-alken-3-ols **6** has been reported, based on the simple zinc-promoted α-hydroxyallylation of α-amidoalkyl arylsulfones **4** with 3-bromo-propenyl methyl carbonate **5**. Products are obtained in very good isolated yields and in most cases with excellent diastereoselectivity. The value of this synthetic protocol was further integrated on one hand by the complete deprotection of **6** to aminoalcohols **7**, and on the other hand by a simple and high yielding two-step synthesis of *cis*-4-substituted-5-vinyl-oxazolidinones **8**, starting from the corresponding protected aminoalcohols **6**.

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Experimental Section

Synthesis of 6. General Procedure. Metallic zinc (0.08 g, 1.2 mmol) was added at 20 °C to a mixture of 3-bromo-propenyl methyl carbonate **5** (0.145 mL, 1.2 mmol) and the appropriate α-amidoalkyl arylsulfone (1 mmol) in DMF (2 mL). The heterogeneous solution was vigorously stirred at the same temperature for 2 h, quenched with saturated NH_4Cl aqueous solution (1 mL), and filtered on a short pad of Celite. The filtered solution was dried on Na_2SO_4 and evaporated at reduced pressure, and the residue was purified by flash chromatography on silica eluting with cyclohexane/ethyl acetate mixtures.

Synthesis of 6d (Table 1, Entry 5). Metallic zinc (0.165 g, 12 mmol) was slowly added added at 0 °C to a mixture of 3-bromo-propenyl methyl carbonate **5** (1.45 mL, 12 mmol) and α-amidoalkyl arylsulfone **4d** (4.095 g, 10 mmol) in DMF (20 mL). The heterogeneous solution was vigorously stirred for 30 min at 0 °C and for 2 h at 20 °C, quenched with saturated NH_4Cl aqueous solution (2 mL), and filtered on a short pad of Celite. The filtered solution was dried on $MgSO_4$ and evaporated at reduced pressure. DMF was removed by distillation at reduced pressure (∼0.2 mmHg), and the residue was purified by flash chromatography on silica eluting with cyclohexane/ethyl acetate 9:1. A first fraction containing a 1:1 mixture of *syn*-**6d** and *anti*-**6d** (0.138 g, 3.6%) was isolated, followed by a fraction containing pure *anti*-**6d** (3.36 g, 88%) as a white solid.

***anti*-2-(*tert*-Butoxycarbonylamino)-1-vinyl-2-cyclohexylethyl Methyl Carbonate (*anti*-6a).** Mp: 99−101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09−1.36 (m, 6H), 1.44 (s, 9H), 1.54−1.86 (m, 5H), 3.79 (s, 3H), 3.65−3.87 (m, 1H), 4.42 (d, J = 10.4 Hz, 1H), 5.18 (t, J = 6.2 Hz, 1H), 5.33 (d, J = 10.6 Hz, 1H), 5.39 (d, J = 17.2 Hz, 1H), 5.82 (ddd, J = 6.5/10.5/17.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.8, 25.9, 26.1, 27.8, 28.2, 29.5, 30.2, 38.3, 54.6, 56.4, 78.1, 79.1, 119.2, 132.3, 154.8, 155.8. GC−MS (70 eV): *m*/*z* (%) 212 (4), 156 (52), 112 (61), 95 (14), 83 (3), 68 (8), 57 (100). Anal. Calcd for $C_{17}H_{29}NO_5$ (327.42): C 62.36, H 8.93, N 4.28. Found: C 62.26, H 8.96, N 4.27

***anti*-2-(*tert*-Butoxycarbonylamino)-1-vinyl-nonyl Carbonate (*anti*-6b).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 7.0 Hz, 3H), 1.21−1.37 (m, 10H), 1.45 (s, 9H), 1.57−1.60 (m, 2H), 3.80 (s, 3H), 3.85 (dt, J = 1.3/4.6 Hz, 1H), 4.46 (d, J = 9.3 Hz, 1H), 5.11−5.18 (m, 1H), 5.31 (dt, J = 1.4/10.5 Hz, 1H), 5.61 (dt, J = 1.4/17.3 Hz, 1H), 5.80 (ddd, J = 6.1/10.6/17.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.5, 25.8, 28.2, 29.0, 29.2, 29.6, 31.6, 52.7, 54.6, 79.2, 80.4, 118.5, 132.6, 155.0, 155.5. GC−MS (70 eV): *m*/*z* (%) 228 (2), 212 (2), 172 (30), 128 (59), 69 (8), 57 (100). Anal. Calcd for $C_{18}H_{33}NO_5$ (343.46): C 62.95, H 9.68, N 4.08. Found: C 62.93, H 9.65, N 4.09

***anti*-2-(*tert*-Butoxycarbonylamino)-1-vinyl-4-methylpentyl Methyl Carbonate (*anti*-6c).** Mp: 52−54 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, J = 6.3 Hz, 3H), 0.93 (d, J = 6.3 Hz, 3H), 1.31 (broad t, J = 7.3 Hz, 2H), 1.45 (s, 9H), 1.62−1.78 (m, 1H), 3.80 (s, 3H), 3.77−3.89 (m, 1H), 4.46 (d, J = 9.5 Hz, 1H), 5.11−5.20 (m, 1H), 5.31 (dt, J = 1.3/10.5 Hz, 1H), 5.35 (dt, J = 1.3/17.3 Hz, 1H), 5.80 (ddd, J = 6.0/10.5/17.3 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.4, 24.6, 28.3, 38.6, 51.1, 54.8, 77.2, 80.8, 118.7, 132.6, 155.1, 155.5. GC−MS (70 eV): *m*/*z* (%) 186 (7), 170 (4), 152 (3), 130 (53), 86 (69), 57 (100). Anal. Calcd for $C_{15}H_{27}NO_5$ (301.19): C 59.78, H 9.03, N 4.65. Found: C 59.82, H 9.01, N 4.67

***anti*-2-(Benzyloxycarbonylamino)-1-vinyl-4-phenylpropyl Methyl Carbonate (*anti*-6d).** Mp: 99−100 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.63−1.85 (m, 1H), 1.85−2.01 (m, 1H), 2.55−2.92 (m, 2H), 3.83 (s, 3H), 3.94−4.14 (m, 1H), 4.85 (d, J = 9.3 Hz, 1H), 5.18 (s, 2H), 5.18−5.28 (m, 1H), 5.29−5.18 (m, 2H), 5.83 (ddd, J = 6.0/10.5/16.8 Hz, 1H), 7.10−7.55 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.6, 32.2, 53.2, 54.7, 66.8, 80.1, 119.0, 125.9, 128.0, 128.2, 128.3, 128.4, 132.1, 136.3, 141.1, 154.9, 156.0. GC−MS (70 eV): *m*/*z* (%) 199 (2), 160 (22), 132 (4), 117 (8), 104

(25), 91 (100), 77 (6), 71 (12), 65 (9), 59 (9). Anal. Calcd for $C_{22}H_{25}NO_5$ (383.44): C 68.91, H 6.57, N 3.65. Found: C 69.10, H 6.55, N 3.64

***anti*-2-(Benzyloxycarbonylamino)-1-vinyl-(*E*)-5-undecyl Methyl Carbonate (*anti*-6e).** ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.89 (t, J = 5.9 Hz, 3H), 1.18−1.40 (m, 6H), 1.40−1.76 (m, 2H), 1.87−2.17 (m, 4H), 3.79 (s, 3H), 3.83−4.04 (m, 1H), 4.72 (d, J = 9.8 Hz, 1H), 5.11 (s, 2H), 5.11−5.23 (m, 1H), 5.25−5.52 (m, 4H), 5.82 (ddd, J = 6.2/10.6/17.0 Hz, 1H), 7.29−7.48 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.5, 28.9, 29.2, 29.7, 31.4, 32.5, 53.0, 54.9, 66.9, 80.3, 119.1, 127.7, 128.1, 128.4, 128.5, 131.8, 132.1, 136.3, 155.0, 156.0. GC−MS (70 eV): *m*/*z* (%) 220 (7), 180 (39), 162 (7), 152 (14), 124 (20), 115 (9), 108 (8), 95 (31), 81(23), 69 (100), 55 (61). Anal. Calcd for $C_{23}H_{33}NO_5$ (403.51): C 68.46, H 8.24, N 3.47. Found: C 68.71, H 8.26, N 3.46

***anti*-2-(Benzyloxycarbonylamino)-1-vinyl-7-chloroepthyl Methyl Carbonate (*anti*-6f).** ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.23−1.54 (m, 6H), 1.64−1.84 (m, 2H), 3.51 (t, J = 6.5 Hz, 2H), 3.79 (s, 3H), 3.84−4.02 (m, 1H), 4.74 (d, J = 9.2 Hz, 1H), 5.11 (s, 2H), 5.11−5.22 (m, 1H), 5.32 (dt, J = 1.4/10.4 Hz, 1H), 5.37 (dt, J = 1.4/16.9 Hz, 1H), 5.80 (ddd, J = 6.1/10.4/16.9 Hz, 1H), 7.34−7.39 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 26.9, 30.0, 32.7, 45.2, 53.6, 55.2, 67.2, 80.5, 119.5, 128.4, 128.5, 128.8, 132.4, 136.6, 155.3, 156.4. GC−MS (70 eV): *m*/*z* (%) 200 (1), 172 (4), 160 (7), 141 (4), 126 (20), 124 (25), 116 (48), 115 (100), 81 (48), 71 (70), 69 (27), 59 (26), 55 (23). Anal. Calcd for $C_{19}H_{26}ClNO_5$ (383.87): C 59.45, H 6.83, N 3.65. Found: C 59.55, H 6.81, N 3.64

***anti*-2-(Benzyloxycarbonylamino)-1-vinyl-4-benzenesulfonylbutyl Methyl Carbonate (*anti*-6g).** Mp: 102−104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79−1.98 (m, 1H), 2.03−2.21 (m, 1H), 3.11−3.22 (m, 2H), 3.79 (s, 3H), 3.88−4.02 (m, 1H), 4.91 (d, J = 9.6 Hz, 1H), 5.08 (s, 2H), 5.10−5.18 m, 1H), 5.34 (dt, J = 1.2/10.6 Hz, 1H), 5.37 (dt, J = 1.2/17.3 Hz, 1H), 5.75 (ddd, J = 6.0/10.6/17.3 Hz, 1H), 7.26−7.44 (m, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.89 (d, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.8, 52.2, 53.0, 54.9, 66.9, 79.5, 119.7, 127.8, 127.9, 128.0, 128.4, 129.2, 131.5, 133.7, 136.0, 138.8, 154.7, 156.0. GC−MS (70 eV): *m*/*z* (%) 281 (2), 207 (5), 197 (9), 153 (6), 143 (13), 142 (11), 126 (15), 125 (18), 112 (41), 95 (100), 77 (81), 68 (62), 57 (21), 51 (35). Anal. Calcd for $C_{22}H_{25}NO_7S$ (447.50): C 59.05, H 5.63, N 3.13. Found: C 58.88, H 5.65, N 3.13

2-(Benzyloxycarbonylamino)-1-vinyl-2-ethoxycarbonylethyl Methyl Carbonate (6h). The title product was obtained in 98% yield as a 65:35 mixture of *syn* and *anti* isomers after flash chromatography on silica. See Supporting Information for copies of ^{1}H and ^{13}C NMR spectra.

***anti*-2-(Formylamino)-1-vinyl-2-(4-methoxyphenyl)ethyl mEthyl Carbonate (*anti*-6i).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (broad s, 6H), 5.28−5.47 (m, 4H), 5.63 (ddd, J = 5.6/10.5/17.3 Hz, 1H), 6.1 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.4, 54.8, 55.1, 79.6, 113.9, 119.7, 128.0, 128.5, 131.5, 154.8, 159.1, 160.6. GC−MS (70 eV): *m*/*z* (%) 247 (8), 164 (100), 147 (15), 137 (22), 136 (25), 121 (18), 115 (11), 109 (21), 91 (16), 77 (21), 65 (8), 51 (8). Anal. Calcd for $C_{14}H_{17}NO_5$ (279.29): C 60.21, H 6.14, N 5.02. Found: C 60.18, H 6.16, N 5.01

***anti*-2-(ethoxycarbonylamino)-1-vinyl-2-phenylethyl methyl carbonate (*anti*-6j).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, J = 7.0 Hz, 3H), 3.80 (s, 3H), 4.11 (q, J = 7.0 Hz, 2H), 4.99−5.10 (m, 1H), 5.24−5.46 (m, 4H), 5.60 (ddd, J = 5.8/10.7/16.6 Hz, 1H), 7.24−7.39 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.4, 54.9, 57.2, 61.1, 79.8, 119.6, 127.2, 127.4, 127.8, 128.5, 131.3, 137.6, 154.9, 155.8. GC−MS (70 eV): *m*/*z* (%) 178 (100), 134 (12), 132 (17), 115 (6), 106 (49), 104 (18), 91 (7), 79 (27), 77 (17), 59 (9). Anal. Calcd for $C_{15}H_{19}NO_5$ (293.32): C 61.42, H 6.53, N 4.78. Found: C 61.37, H 6.52, N 4.79

1-[*tert*-Butoxycarbonylamino-(2,2-dimethyl-1,3-dioxolan-4-yl)-methyl]-allyl Methyl Carbonate (6k). The title product was obtained in 82% yield as a 85:15 mixture of *syn* and *anti* isomers after flash chromatography on silica. The crude reaction mixture was directly cyclized to oxazolidinones **8k**, which can be easily separated by flash chromatography on silica. See Supporting Information for copies of ^{1}H and ^{13}C NMR spectra.

2-(*tert*-Butoxycarbonylamino-3-phenyl-propionylamino)-1-vinyl-4-phenylbutyl Methyl Carbonate (6l). The title product was obtained in 92% yield as a 60:40 mixture of *syn* and *anti* isomers after flash chromatography on silica. See Supporting Information for copies of ^{1}H and ^{13}C NMR spectra.

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Supporting Information Available: Experimental procedures for stereochemical assignment and copies of ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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