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Comparison of Electrophilic Amination Reagents for N-Amination of 2-Oxazolidinones and Application to Synthesis of Chiral Hydrazones

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Abstract: Comparison of several hydroxylamine-based electrophilic ammonia equivalents in the N-amination of 2-oxazolidinones revealed that *O*-(*p*-nitrobenzoyl)hydroxylamine ($NbzONH_2$) and sodium hydride in dioxane is a superior reagent combination for this purpose. Practical preparations of a variety of chiral *N*-acylhydrazones by this method gave yields ranging from 45 to 95%. Methods for exchange or removal of the aldehyde component have been developed, making this a general route to chiral *N*-acylhydrazones of interest for asymmetric synthesis applications.

Chiral hydrazones have served prominent roles in the early development of asymmetric synthesis, most notably as chiral auxiliaries for enantioselective α-alkylation of carbonyl compounds[1] and as chiral nitrogen donor auxiliaries for asymmetric amine synthesis via reductive amination[2] or addition of organometallic reagents to the C=N bond.[3] Applications of chiral hydrazones have broadened in recent years; new developments include allene anion additions to SAMP hydrazones,[4] chiral umpolung reactivity[5] and [2 + 2] cycloadditions[6] employing formaldehyde hydrazones, and asymmetric catalysis with phosphine−hydrazone P,N-chelate complexes.[7] In our own studies, we have designed chelating chiral *N*-acylhydrazones for applications in asymmetric amine synthesis including radical addition[8] and allylsilane addition.[9]

Hydrazones for the foregoing synthetic methods are generally derived by condensation of the appropriate hydrazine with an aldehyde or ketone. These hydrazines in turn are often prepared by N-amination of the corresponding amine or amide.[10] Amination of chiral amines is usually achieved via nitrosation and reduction,[11] a procedure accompanied by significant toxicity concerns, or by a multistep procedure involving the Shestakov rearrangement of N-substituted ureas (a type of Hofmann degradation).[12] To our knowledge, the latter procedure has not been successful for preparation of *N*-acylhydrazines (i.e., hydrazides).

An attractive possibility for synthesis of *N*-acylhydrazones is the direct transfer of the unprotected amino group. A number of hydroxylamine derivatives (see Chart 1) are competent electrophilic NH_2^+ equivalents that have been shown to transfer the amino group to various oxygen or nitrogen nucleophiles, including deprotonated amides.[13] Among these, *O*-(mesitylenesulfonyl)hydroxylamine ($MtsONH_2$) was successfully adopted for our initial preparations of (S)-2-amino-4-benzyl-2-oxazolidinone (**1a**)[8a] by N-amination according to the precedent of White and Kim.[14a,15] However, the instability of $MtsONH_2$ proved troublesome, as forewarned by the original literature

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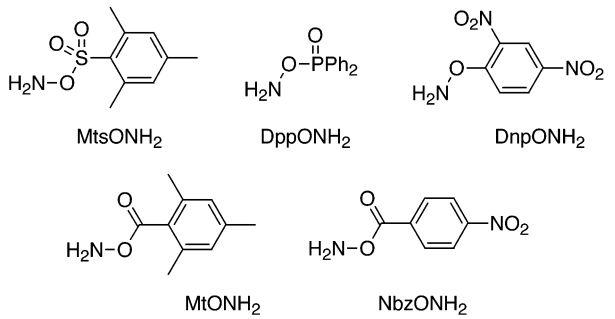
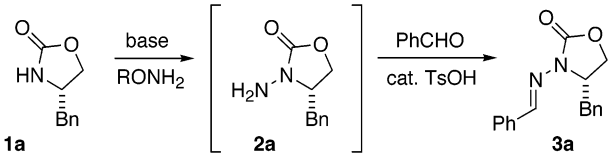
CHART 1



SCHEME 1



reports of its preparation,[13b] so we sought more reliable protocols. Here, we report a study comparing several hydroxylamine-based electrophilic NH_2^+ equivalents for the N-amination of oxazolidinones, revealing *O*-(*p*-nitrobenzoyl)hydroxylamine ($NbzONH_2$) and sodium hydride as a superior reagent combination for this purpose and culminating in practical preparations of a variety of chiral *N*-acylhydrazones.

A survey of amination reagents was carried out first for the N-amination of oxazolidinone **1a** (Scheme 1) in the presence of a base. In all cases, amination of **1a** gave a mixture of *N*-amino-2-oxazolidinone **2a** and small amounts of unreacted **1a**, separable with difficulty. Instead of separating at this stage, the mixture was submitted to condensation with benzaldehyde (toluene, catalytic amount of *p*-toluenesulfonic acid) followed by chromatography to afford the pure hydrazone **3a**. A comparison of $MtsONH_2$ (see Chart 1) with *O*-mesitoylhydroxylamine[13c] ($MtONH_2$), *O*-(diphenylphosphinyl)-hydroxylamine[13d] ($DppONH_2$), *O*-(2,4-dinitrophenyl)-hydroxylamine[13e] ($DnpONH_2$), and *O*-(*p*-nitrobenzoyl)-hydroxylamine[16] ($NbzONH_2$) showed significant differences among these reagents. Because yields in the condensation step are reliably >90% for benzaldehyde,[8,9] the yield of **3a** in each run is indicative of the effectiveness of the amination conditions.

Aminations of **1a** with $DnpONH_2$ were effective using the previously described *n*-BuLi deprotonation conditions (THF, −78 °C),[8a] affording yields slightly inferior to the original report with $MtsONH_2$ (Table 1, entries 1 and 4), while $MtONH_2$, $DppONH_2$, and $NbzONH_2$ exhibited better reactivity with NaH (dioxane, 60 °C) as the base (Table 1, entries 2, 3, and 5). Although $NbzONH_2$ failed to undergo the desired reaction when employing *n*-BuLi (Table 1, entry 5), in conjunction with NaH this reagent gave the best results among all variations attempted in this study. Furthermore, neither $DppONH_2$ nor $NbzONH_2$ has yet shown any tendency to decompose upon storage as dry solids at ca. 0−5 °C, a welcome and practical improvement over $MtsONH_2$ for application to anhydrous reactions. These observations led to our optimized procedure in which deprotonation (NaH), amination (either $DppONH_2$ or $NbzONH_2$), and condensation with an aldehyde were applied in sequence.

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TABLE 1. Comparison of Reagents $RONH_2$ and Bases for N-Amination of Oxazolidinone 1a

		yield of **3a**[a] (%)	
entry	$RONH_2$	*n*-BuLi[b]	NaH[c]
1	$MtsONH_2$	75[d,e]	
2	$MtONH_2$	22	52
3	$DppONH_2$	41[e]	73
4	$DnpONH_2$	66	54
5	$NbzONH_2$	0[f]	80

[a] Yield of benzaldehyde hydrazone unless noted. [b] Conditions A: (1) *n*-BuLi (1.1 equiv), THF, −78 °C, 1 h then add $RONH_2$; (2) PhCHO (1.0−2.5 equiv), cat. *p*-TsOH, toluene, reflux. [c] Conditions B: (1) NaH (1.1 equiv), dioxane, 60 °C, 1 h, then cool to 25 °C and add $RONH_2$; (2) same as A. [d] Reference 8a. [e] Yield of **2a** (step 2 omitted). [f] Decomposition occurred.

SCHEME 2

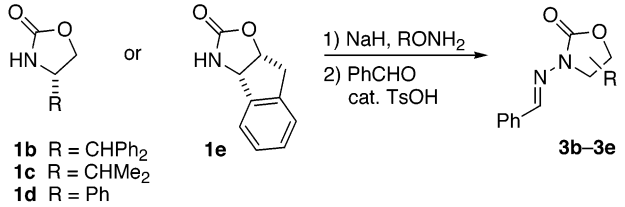


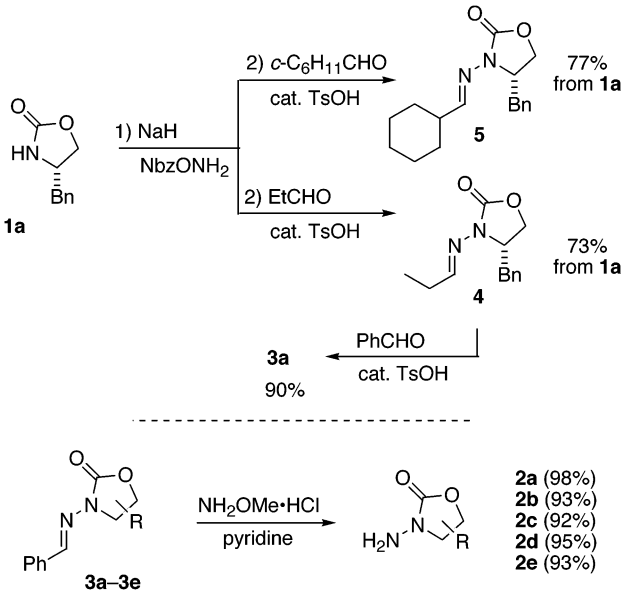
TABLE 2. Preparation of Various Chiral Benzaldehyde *N*-Acylhydrazones

entry	$RONH_2$	substrate	product, yield (%)
1	$DppONH_2$	**1a**	**3a**, 73
2		**1b**	**3b**, 68
3		**1c**	**3c**, 56
4		**1d**	**3d**, 74
5		**1e**	**3e**, 59
6	$NbzONH_2$	**1a**	**3a**, 80
7		**1b**	**3b**, 68
8		**1c**	**3c**, 45
9		**1d**	**3d**, 95
10		**1e**	**3e**, 92

Several commercially available chiral 2-oxazolidinones (Scheme 2) bearing alkyl (**1c**), benzyl (**1a**, **1b**), or aryl (**1d**, **1e**) substituents were next employed to test the scope of these amination conditions (Table 2). Amination with $DppONH_2$ proceeded in moderate to good yields (56−74% after condensation with benzaldehyde). Amination of valine-derived oxazolidinone **1c** was least efficient among these, and the use of $NbzONH_2$ offered no improvement. In contrast, the oxazolidinones with benzylic substituents (**1a**, **1b**) were aminated by $NbzONH_2$ in good yields (68−80%). Interestingly, a dramatic improvement was observed in the cases of aryl oxazolidinones (**1d**, **1e**); hydrazones **3d** and **3e** were obtained in excellent yields (95% and 92%).

The optimized amination procedure also proved reliable for synthesis of other aldehyde hydrazones from **1a** by three strategies (Scheme 3). First, crude amination product **2a** obtained as above was divided into two portions and then condensed with propionaldehyde and cyclohexanecarboxaldehyde to give hydrazones **4** and **5** in very good yields (73% and 77%, respectively, from **1a**). Second, hydrazones readily undergo exchange with al-

SCHEME 3



dehydes. Thus, **4** was converted to **3a** in 90% yield by reaction with PhCHO (3 equiv, cat. TsOH, toluene, reflux), although **3a** could not be converted to **4** in the same way.[17] A third stepwise strategy extends access to an even wider variety of hydrazones. After preparation of **3a**−**e**, these hydrazones were easily converted to **2a**−**e** in 92−98% yield by treatment with $MeONH_2$·HCl in pyridine (Scheme 3). By this route, **2a**−**e** are available in pure form for subsequent condensation with aldehydes of interest. Thus, it is possible to prepare and store one initial hydrazone in large scale, then exchange or remove the aldehyde component as needed. Considering the documented utility of hydrazones derived from **2a**,[8,9] one can expect new *N*-amino-2-oxazolidinones **2b**−**e** to also be useful for a variety of asymmetric synthesis objectives.

In conclusion, a highly reliable and efficient method was developed to prepare chiral *N*-acylhydrazones from various commercially available 4-substituted 2-oxazolidinones. Among hydroxylamine-based amination reagents, *O*-(*p*-nitrobenzoyl)hydroxylamine ($NbzONH_2$) was found to be most effective for *N*-amination of 2-oxazolidinones. This optimized procedure facilitates continuing applications of chiral *N*-acylhydrazones in various asymmetric synthesis objectives.

Experimental Section

Materials and Methods. Reactions employed oven-dried glassware under nitrogen unless otherwise noted. Dioxane and toluene were dried over activated molecular sieves (4 Å). All other materials were used as received or purified by standard procedures. Thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230−400 mesh silica gel as slurry in hexane. Gradient flash chromatography was conducted by adsorption of product mixtures on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Melting points are uncorrected. Combustion analyses were performed by Atlantic Microlab (Norcross, GA).

General Procedure A: Amination of 2-Oxazolidinones. To a solution of 2-oxazolidinone **1** in dioxane (0.2 M) was added NaH (1.0−1.10 equiv). The mixture was stirred at 60 °C for 1 h and then cooled to room temperature. *p*-Nitrobenzoylhydroxylamine ($NbzONH_2$, 1.00−1.05 equiv) was added. After 24 h, the reaction mixture was filtered through Celite and concentrated to afford *N*-amino-2-oxazolidinone **2** as a brown oil. Without purification, **2** was dissolved in toluene (0.5 M), and aldehyde (1.0−2.5 equiv) and $TsOH·H_2O$ (0.02 equiv) were added. The mixture was stirred under reflux. When the reaction was complete (TLC), the mixture was concentrated and purified by gradient flash chromatography (hexane → 2:1 hexane/EtOAc) or recrystallization from ethanol to furnish pure hydrazone.

(*S*)-3-(Benzylidene)amino-4-phenylmethyl-2-oxazolidinone (3a). From **1a** (200 mg, 1.13 mmol), NaH (60%) (47 mg, 1.18 mmol), $NbzONH_2$ (216 mg, 1.19 mmol), and benzaldehyde (0.15 mL, 1.48 mmol) by general procedure A with chromatography was obtained **3a**[8a] (253 mg, 80% yield) as a colorless solid.

Multigram Scale. From **1a** (8.00 g, 45.1 mmol), NaH (60%) (1.81 g, 45.2 mmol), $NbzONH_2$ (8.22 g, 45.1 mmol), and benzaldehyde (4.60 mL, 45.1 mmol) by general procedure A with recrystallization was obtained **3a** (7.40 g) as colorless needlelike crystals. From the mother liquor, additional **3a**[8a] (2.03 g) was obtained by chromatography (total 9.43 g, 74% yield).

(*S*)-3-(Benzylidene)amino-4-diphenylmethyl-2-oxazolidinone (3b). From **1b** (100 mg, 0.395 mmol), NaH (60%) (17 mg, 0.425 mmol), $NbzONH_2$ (76 mg, 0.417 mmol), and benzaldehyde (0.10 mL, 0.984 mmol) by general procedure A with chromatography was obtained **3b** (96 mg, 68% yield) as a colorless solid. Recrystallization from 2-propanol afforded colorless needles: mp 119.5−120 °C; $[\alpha]_D^{25}$ −189.6 (*c* 0.35, $CHCl_3$); IR (film) 3061, 3028, 2914, 1750, 1717, 1598, 1449, 1235, 1214, 1094, 1030, 744, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.50 (m, 2H), 7.34 (m, 7H), 7.25 (m, 4H), 7.16 (m, 2H), 5.07 (ddd, J = 8.6, 5.9, 5.5 Hz, 1H), 4.65 (d, J = 5.9 Hz, 1H), 4.54 (dd, J = 9.1, 8.6 Hz, 1H), 4.27 (dd, J = 9.1, 5.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 151.3, 140.4, 139.0, 134.5, 130.3, 128.9, 128.8, 128.6, 127.5, 127.4, 127.1, 64.7, 60.5, 53.0; MS (CI) *m*/*z* (relative intensity) 357 ($[M + H]^+$, 25). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.34; H, 5.65; N, 7.80.

(*S*)-3-(Benzylidene)amino-4-isopropyl-2-oxazolidinone (3c). From **1c** (100 mg, 0.774 mmol), NaH (60%) (33 mg, 0.825 mmol), $NbzONH_2$ (148 mg, 0.813 mmol), and benzaldehyde (0.10 mL, 0.984 mmol) by general procedure A with chromatography was obtained **3c** (81 mg, 45% yield) as a colorless solid. Recrystallization from ethanol afforded squarelike crystals: mp 92.5−93 °C; $[\alpha]_D^{25}$ −94.8 (*c* 0.31, $CHCl_3$); IR (film) 3062, 3035, 2965, 2916, 1752, 1491, 1413, 1221, 1087, 962, 884 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.72 (m, 2H), 7.40 (m, 3H), 4.39 (m, 1H), 4.21 (dd, J = 10.6, 5.5 Hz, 1H), 4.20 (dd, J = 10.9, 5.5 Hz, 1H), 2.36 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 150.8, 134.5, 130.3, 128.6, 127.3, 62.8, 61.7, 28.5, 17.7, 15.1; MS (CI) *m*/*z* (relative intensity) 233 ($[M + H]^+$, 100). Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.01; H, 6.96; N, 11.95.

(S)-3-(Benzylidene)amino-4-phenyl-2-oxazolidinone (3d). From **1d** (100 mg, 0.613 mmol), NaH (60%) (25 mg, 0.625 mmol), $NbzONH_2$ (117 mg, 0.643 mmol), and benzaldehyde (0.10 mL, 0.984 mmol) by general procedure A with chromatography was obtained **3d** (155 mg, 95% yield) as a colorless solid. Recrystallization from 2-propanol afforded colorless needles: mp 157−158 °C; $[\alpha]_D^{25}$ −128.3 (*c* 0.32, $CHCl_3$); IR (film) 3032, 2920, 1770, 1717, 1652, 1588, 1507, 1457, 1404, 1231, 1026, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.57 (m, 2H), 7.42 (m, 2H), 7.33 (m, 6H), 5.32 (dd, J = 9.0, 5.9 Hz, 1H), 4.80 (dd, J = 9.0, 8.5 Hz, 1H), 4.21 (dd, J = 8.5, 5.9 Hz, 1H); ^{13}C NMR (125

(17) (a) Exchange with excess propionaldehyde (cat. *p*-TsOH) gave **4** in 70% yield from the corresponding formaldehyde hydrazone. Unfortunately, the latter was obtained in only 32% yield from **1a**. (b) For a related example of the exchange reaction of aldehydes with a hydrazone, see: Figueiredo, J. M.; Câmara, C. de A.; Amarante, E. G.; Miranda, A. L. P.; Santos, F. M.; Rodrigues, C. R.; Fraga, C. A. M.; Barreiro, E. J. *Bioorg. Med. Chem.* **2000**, *8*, 2243−2248. (c) For an example of an exchange reaction involving transoximation, see: Clark, M. A.; Wang, Q.; Ganem, B. *Tetrahedron Lett.* **2002**, *43*, 347−349.

MHz, $CDCl_3$) δ 154.5, 147.3, 137.1, 133.8, 130.2, 129.6, 129.0, 128.5, 127.4, 125.9, 69.6, 59.4; MS (CI) *m/z* (relative intensity) 267 ([M + H]$^+$, 100). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.93; H, 5.29; N, 10.42.

(Benzylidene)amino-2-oxazolidinone 3e. From **1e** (100 mg, 0.517 mmol), dioxane (15 mL), NaH (60%) (25 mg, 0.625 mmol), $NbzONH_2$ (110 mg, 0.604 mmol), and benzaldehyde (0.10 mL, 0.984 mmol) by general procedure A with chromatography was obtained **3e** (146 mg, 92% yield) as a colorless solid. Recrystallization from ethanol afforded colorless needles: mp 160−161 °C; $[\alpha]_D^{25}$ +405.1 (*c* 0.32, $CHCl_3$); IR (film) 3065, 3033, 2926, 1773, 1719, 1590, 1459, 1398, 1363, 1200, 1040, 755, 687 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.78 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.44 (m, 3H), 7.40−7.25 (m, 3H), 5.64 (d, *J* = 7.4 Hz, 1H), 5.40 (ddd, *J* = 7.4, 6.0, 1.5 Hz, 1H), 3.48 (dd, *J* = 16.0, 6.0 Hz, 1H), 3.41 (dd, *J* = 16.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 149.6, 140.1, 138.5, 134.6, 130.3, 129.8, 128.7, 127.7, 127.3, 126.1, 125.5, 77.1, 65.6, 38.7; MS (CI) *m/z* (relative intensity) 279 ([M + H]$^+$, 100). Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.41; H, 5.07; N, 10.05.

(*S*)-3-(1-Propylidene)amino-4-phenylmethyl-2-oxazolidinone (4) and (*S*)-3-(Cyclohexylmethylidene)amino-4-phenylmethyl-2-oxazolidinone (5). From **1a** (200 mg, 1.13 mmol), NaH (60%) (47 mg, 1.17 mmol), and $NbzONH_2$ (216 mg, 1.19 mmol) was obtained crude **2a** (257 mg) as described in general procedure A. This sample was divided into two parts for condensation with two different aldehydes as described below.

A mixture of crude **2a** (126 mg), propionaldehyde (0.04 mL, 0.55 mmol), and $TsOH\cdot H_2O$ (2 mg) in toluene (0.5 M) was stirred at reflux. Upon completion (TLC), concentration and gradient flash chromatography (hexane → 2:1 hexane/EtOAc) furnished **4**[8a] (93 mg, 73% yield from **1a**) as a colorless oil.

A mixture of crude **2a** (131 mg), cyclohexane carboxaldehyde (0.07 mL, 0.58 mmol), and $TsOH\cdot H_2O$ (2 mg) in toluene (0.5 M) was stirred at reflux. Upon completion (TLC), concentration and gradient flash chromatography (hexane → 2:1 hexane/EtOAc) furnished **5**[8a] (120 mg, 77% yield from **1a**) as a colorless oil.

General Procedure B: *N*-Amino-2-oxazolidinones from Hydrazones. To a solution of hydrazone **3** in pyridine (0.1−0.3 M) was added methoxylamine hydrochloride (3.0−3.5 equiv). After 2 d at room temperature, concentration and gradient flash chromatography (hexane → 1:2 hexane/EtOAc) afforded hydrazine **2**.

(*S*)-3-Amino-4-phenylmethyl-2-oxazolidinone (2a). From **3a** (30 mg, 0.106 mmol) by general procedure B was obtained **2a**[8a] (20 mg, 98%) as a colorless oil.

(*S*)-3-Amino-4-diphenylmethyl-2-oxazolidinone (2b). From **3b** (30 mg, 0.084 mmol) by general procedure B was obtained **2b** (21 mg, 93%) as a colorless solid; $[\alpha]_D^{25}$ +42.0 (*c* 0.75, $CHCl_3$); IR (film) 3338, 3215, 3028, 2918, 1762, 1617, 1496, 1419, 1222, 1093, 1031 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.30 (m, 4H), 7.28−7.20 (m, 6H), 4.58 (dd, *J* = 15.1, 6.9 Hz, 1H), 4.40−4.35 (m, 2H), 4.08 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.70 (broad s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 140.7, 139.3, 129.0, 128.9, 128.5, 128.3, 127.5, 127.3, 65.5, 61.7, 54.3; MS (CI) *m/z* (relative intensity) 269 ([M + H]$^+$, 100); high-resolution mass spectrum (FAB) *m/z* 269.1283 ([M + H]$^+$), calcd for $C_{16}H_{17}N_2O_2$ 269.1291.

(*S*)-3-Amino-4-isopropyl-2-oxazolidinone (2c). From **3c** (70 mg, 0.301 mmol) by general procedure B was obtained **2c** (39 mg, 90%) as a colorless oil: $[\alpha]_D^{25}$ +10.5 (*c* 0.62, $CHCl_3$); IR (film) 3336, 3215, 2919, 2849, 1751, 1650, 1559, 1458, 1419, 1221, 1118, 1043 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (dd, *J* = 8.9, 8.6 Hz, 1H), 4.01 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.96 (broad s, 2H), 3.69 (ddd, *J* = 8.6, 7.0, 4.1 Hz, 1H), 2.20 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 63.1, 62.6, 28.1, 17.6, 15.4; MS (CI) *m/z* (relative intensity) 145 ([M + H]$^+$, 100); high-resolution mass spectrum (FAB) *m/z* 145.0984 ([M + H]$^+$), calcd for $C_6H_{13}N_2O_2$ 145.0978.

(*S*)-3-Amino-4-phenyl-2-oxazolidinone (2d). From **3d** (79 mg, 0.297 mmol) by general procedure B was obtained **2d** (50 mg, 95%) as a colorless solid: $[\alpha]_D^{25}$ +87.5 (*c* 1.6, $CHCl_3$); IR (film) 3343, 3215, 3188, 2915, 1756, 1627, 1458, 1414, 1215, 1108, 1026, 959 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44−7.36 (m, 3H), 7.33−7.30 (m, 2H), 4.76 (dd, *J* = 8.5, 7.7 Hz, 1H), 4.58 (dd, *J* = 9.2, 8.5 Hz, 1H), 4.09 (dd, *J* = 9.2, 7.7 Hz, 1H), 3.82 (s, broad, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 137.0, 129.2, 129.0, 126.9, 68.7, 63.4; MS (CI) *m/z* (relative intensity) 179 ([M + H]$^+$, 100). Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.50; H, 5.70; N, 15.84.

3-Amino-2-oxazolidinone 2e. From **3e** (102 mg, 0.366 mmol) by general procedure B was obtained **2e** (65 mg, 93%) as a colorless solid: $[\alpha]_D^{25}$ −78.5 (*c* 0.85, $CHCl_3$); IR (film) 3330, 3218, 3043, 2924, 1751, 1635, 1461, 1405, 1329, 1205, 1108, 1033 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.29−7.26 (m, 2H), 5.26 (ddd, *J* = 7.3, 6.9, 1.5 Hz, 1H), 5.12 (d, *J* = 7.5 Hz, 1H), 4.03 (broad s, 2H), 3.41 (dd, *J* = 17.9, 6.9 Hz, 1H), 3.29 (dd, *J* = 17.9, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 140.2, 138.2, 129.6, 127.4, 125.7, 125.5, 76.6, 65.9, 39.1; MS (CI) *m/z* (relative intensity) 191 ([M + H]$^+$, 100). Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.30; N, 14.73. Found: C, 62.93; H, 5.37; N, 14.74.

Hydrazone Interconversion by Exchange of the Aldehyde Component: (*S*)-3-(1-Benzylidene)amino-4-phenylmethyl-2-oxazolidinone (3a). A mixture of **4** (52 mg, 0.240 mmol), benzaldehyde (0.08 mL, 0.79 mmol), and $TsOH\cdot H_2O$ (3 mg) in toluene was heated at reflux for 1 h. Concentration and gradient flash chromatography (hexane → 2:1 hexane/EtOAc) afforded hydrazone **3a**[8a] (61 mg, 90%) as a colorless solid.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **2b**−**e** and **3b**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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