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Redox-Neutral Synthesis of β-Amino Aldehydes from Imines by an Alkynylation/Hydration Sequence

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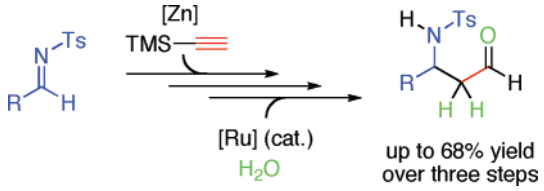

N-Protected β-amino aldehydes have been prepared starting from imines through a sequence involving a Zn-mediated direct alkynylation followed by a Ru-catalyzed anti-Markovnikov alkyne hydration. The rate and the efficiency of the latter reaction are enhanced by the use of microwave irradiation. The possibility to carry out a one-pot Ru-catalyzed hydration/oxidation process from a terminal alkyne to a carboxylic acid was demonstrated, which provided direct access to a *N*-protected β-amino acid from the corresponding terminal alkyne.

Introduction

β-Amino carbonyl compounds are useful building blocks for the synthesis of complex bioactive molecules[1] and can be used as precursors of important classes of substances, such as β-amino acids[2] and 1,3-amino alcohols.[3] In addition, the β-amino carbonyl functional motif is found in several natural products.[2]

Within this class of compounds, β-amino aldehydes are particularly valuable because of the versatility of the formyl group, which can be easily reduced or oxidized and can react with many nucleophiles. On the other hand, access to β-amino aldehydes can be difficult, mostly because of the instability of these compounds under the conditions used for their preparation. In particular, β-amino aldehydes are known to undergo polymerization, self-condensation, or elimination of the β-amino group.[4]

To date, the most common approaches used for the synthesis of β-amino aldehydes are based either on a Mannich reaction[5] between an imine and an ester with subsequent reduction of the carboxylic group to the aldehyde[6] (often carried out after conversion into the corresponding Weinreb amide[7]) or on the homologation of *N*-protected α-amino acid derivatives, followed also in this case by a reduction step.[4a,c,8] Furthermore, synthetic routes have been described which feature the conjugate addition of nitrogen nucleophiles to α,β-unsaturated aldehydes or amides as the key step.[4a,d,9,10] Recently, the first organocatalytic enantioselective Mannich reactions between imines and unmodified aldehydes as donors have been reported, which afforded β-amino aldehydes with high enantiomeric excess in a single step.[11,12]

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Following our interest in the field of organozinc additions to carbon−heteroatom double bonds,[13] we recently developed the first dimethylzinc-mediated direct alkynylation of imines, providing access to a large array of *N*-substituted propargylic amines.[14,15] In addition, highly active in situ catalysts for the Ru-catalyzed anti-Markovnikov hydration of terminal alkynes have been introduced, which allow the straightforward conversion of functionalized acetylenes into the corresponding aldehydes.[16−19]

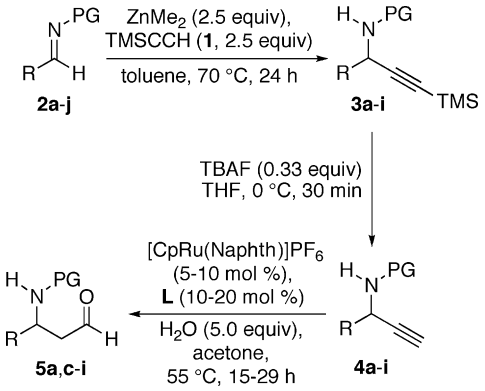
We anticipated that addition of (trimethylsilyl)acetylene (**1**) to *N*-protected imines **2**, followed by removal of the silyl group, could be used to generate terminal secondary propargylic amines **4**, which might be directly converted to β-amino aldehydes by means of the catalytic hydration reaction, avoiding a wasteful reduction/oxidation sequence. Herein, we report the results of our studies concerning the aforementioned synthetic route (Scheme 1). To the best of our knowledge, this is the first time that β-amino aldehydes have been generated from imines by such an alkynylation/hydration sequence.[20] In addition, the first Ru-catalyzed anti-Markovnikov hydration of terminal alkynes under microwave irradiation will be described, as well as a Ru-catalyzed one-pot hydration/oxidation protocol for the direct conversion of propargylic amines into β-amino acids.

TABLE 1. $ZnMe_2$-Mediated Synthesis of Propargylic Amines and Subsequent Desilylation (from 2 to 4 in Scheme 1)

entry	substrate	R	PG	yield of **3**[a,b] (%)	yield of **4**[b,c] (%)
1	**2a**	Ph	Ts	60	85
2	**2b**	Ph	$P(O)Ph_2$	78	55
3	**2c**	4-MePh	Ts	81	90
4	**2d**	4-MeOPh	Ts	76	79
5	**2e**	2-BrPh	Ts	77	94
6	**2f**	2-Naphthyl	Ts	70	41
7	**2g**	2-Furyl	Ts	61	85
8	**2h**	c-Hex	Ts	74	90
9	**2i**	*t*-Bu	Ts	81	99
10	**2j**	(*E*)-PhCH═CH	Ts	0	

[a] Conditions: Imines **2a**−**j** were added under argon to a mixture of $ZnMe_2$ and **1** (2.5 equiv each) in toluene. The reaction mixture was stirred for 24 h at 70 °C. For a general procedure, see the Supporting Information. [b] After column chromatography. [c] Conditions: A mixture of compounds **3a**−**i** and 0.33 equiv of TBAF in THF was stirred for 30 min at 0 °C. For a general procedure, see the Supporting Information.

SCHEME 1. Synthesis of β-Amino Aldehydes by Means of an Alkynylation/Anti-Markovnikov Hydration Sequence



Results and Discussion

Initially, we focused our attention on the conversion of various *N*-protected imines **2a**−**j** into acetylenes **3**. This transformation was effected by reacting the substrates with 2.5 equiv of a mixture of dimethylzinc and (trimethylsilyl)ethyne (**1**) in toluene at 70 °C for 24 h. Desilylation of the resulting 1-trimethylsilyl-substituted alkynes **3** by treatment with a substoichiometric quantity of tetrabutylammonium fluoride in THF at 0 °C yielded propargylamines **4** (Table 1). Although some of the compounds presented in Table 1 had already been known, except for **4a**[14a] none of them had been prepared via direct alkynylation of the corresponding imine prior to this study.

The alkynylation of aromatic *N*-sulfonyl and *N*-phosphinoyl aldimines **2a**−**g** proceeded smoothly (entries 1−7), affording the resulting *N*-protected amines **3a**−**g** in 61−81% yield. Noteworthy, imines **2h**−**i** bearing α-branched alkyl groups such as cyclohexyl or *tert*-butyl were also good substrates for the reaction (entries 8 and 9).[21] Unfortunately, the *N*-tosylimine derived from (*E*)-cinnamic aldehyde **2j** failed to provide the desired product, but gave a complex mixture.

Upon treatment with TBAF, all TMS-protected alkynes **3a**−**i** afforded the desired terminal acetylenes **4a**−**i**, generally with satisfactory yields (79−99%). Only compounds **3b** and **3f**

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(21) As reported in ref 14a, imines derived from linear aliphatic aldehydes are not suitable for the alkynylation reaction with phenylacetylene under analogous conditions.

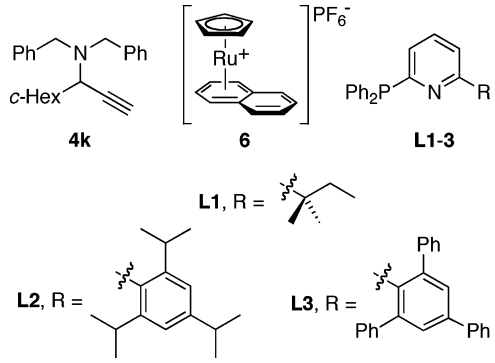

FIGURE 1. Amine **4k** and catalyst precursors used in this study.

TABLE 2. Ruthenium-Catalyzed Anti-Markovnikov Hydration of Alkynes 4[a]

entry	substrate	ligand	[Ru] (mol %)	time (h)	yield of **5**[b] (%)
1	**4a**	**L2**	10	17	83
2	**4b**	**L1** or **L2**	10	>130	nd[c]
3	**4c**	**L2**	10	29	83
4	**4d**	**L2**	10	15	83
5	**4e**	**L2**	10	17	84
6	**4f**	**L3**	10	19	85
7	**4g**	**L1**	10	22	90
8	**4h**	**L1**	10	15	91
9	**4i**	**L2**	10	20	85
10	**4i**	**L3**	10	12	92
11	**4k**	**L1** or **L2**	10	>130	0
12	**4a**	**L2**	5	90	48
13	**4d**	**L2**	5	40	78
14	**4i**	**L2**	5	90	77

[a] Conditions: The catalyst was generated from **L1**−**3** (10 or 20 mol %) and **6** (5 or 10 mol %) in MeCN for 0.5−6 h at 60 °C followed by evaporation. Hydration of the substrates was carried out with water (5 equiv) in acetone under argon. For a general procedure, see the Supporting Information. [b] After column chromatography. [c] Not determined. The substrate was completely converted, but did not provide the desired compound.

furnished the corresponding products with diminished yields of 55% and 41%, respectively (entries 2 and 6).

To assess the use of a compound bearing a Lewis basic nitrogen atom in the following hydration reaction, the known terminal propargylamine **4k**, having two benzyl groups on the nitrogen, was prepared according to a procedure reported by Knochel (Figure 1).[22]

With compounds **4a**−**i,k** in hand, we next turned our attention to the Ru-catalyzed anti-Markovnikov hydration reaction (Scheme 1). According to our previously published protocol,[18a] the catalysts were generated in situ by mixing the air-stable precursor [CpRu(η^6-naphthalene)]PF_6[23] (**6**) with 2 equiv of a 6-substituted 2-(diphenylphosphino)pyridine (**L1**, **L2**, or **L3**; Figure 1).

The results obtained in the hydration reaction, using **L1**−**3** as ligands, are presented in Table 2. Noteworthy, all aldehydes were solids which could be easily purified by standard flash column chromatography on silica gel. Moreover, they could be stored for several weeks at room temperature without decomposition, an observation in sharp contrast with the previously reported instability of various other β-amino aldehydes.[4]

All substrates bearing a *N*-tosyl group reacted smoothly under the influence of the ruthenium catalyst (entries 1 and 3−10),

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TABLE 3. Ruthenium-Catalyzed Hydration of Alkynes 4 under MW Irradiation[a]

entry	substrate	[Ru] (mol %)	*P* (W)/ *T* (°C)	time (min)	yield of **5**[b] (%)
1	**4c**		75/120	120	0
2	**4c**	10	50/90	5	92
3	**4c**	5	50/90	30	94
4	**4c**	2.5	75/120	120	traces
5	**4e**	5	75/100	15	79
6	**4f**	5	75/115	20	76
7	**4g**	10	50/90	30	88
8	**4h**	5	75/100	30	92
9	**4i**	5	75/100	15	73

[a] Conditions: as described in footnote *a* of Table 2; use of **L3** (2 equiv) under MW irradiation. For a general procedure, see the Supporting Information. [b] After column chromatography.

and the corresponding terminal aldehydes were afforded in high yields (83−92%). Unfortunately, although alkyne **4b** bearing the diphenylphosphinoyl protecting group was completely converted under standard reaction conditions, it failed to provide the expected product **5b** (entry 2). *N*,*N*-Dibenzylpropargylamine **4k** did not react at all and was recovered unchanged even after more than 5 days (entry 11). Interestingly, use of only 5 mol % ruthenium catalyst still allowed protected β-amino aldehydes to be obtained in moderate to good yields (48−78%, entries 12−14). However, under those conditions the reaction time had to be prolonged substantially (≥40 h).

Although the current protocol for the catalytic hydration reaction led to β-amino aldehydes in high yields, it still required heating of the reaction mixture at 55 °C for a prolonged time. Microwave (MW) irradiaton is known to be a useful tool for shortening reaction times, and often it improves efficiencies of thermally induced reactions.[24] We therefore decided to examine its effect on the Ru-catalyzed anti-Markovnikov alkyne hydration, employing complex **6** and phosphine **L3** as catalyst precursors. To the best of our knowledge, this is the first time that such a reaction has been performed under MW irradiation. The results obtained are presented in Table 3.

First, it was ensured that in the absence of the catalyst no hydration occurred and that the reaction was not induced by simple MW irradiation (entry 1). To our delight, in the presence of 10 mol % catalyst a very fast reaction was observed, and starting from **4c** the expected product was formed after only 5 min in high yield. Reducing the catalyst loading to 5 mol % required a longer reaction time (30 min), but led to approximately the same yield of **5c** (entry 3). Use of less catalyst proved inefficient. Under the above conditions, various *N*-tosylpropargylamines afforded the corresponding aldehydes in good to high yields (73−92%), often requiring a smaller amount of catalyst in comparison with that of the thermal reaction. Noteworthy, the reaction time never exceeded 30 min (entries 4−9).

Having found a reliable procedure for the transformation of *N*-tosyl alkynes **4** into the corresponding aldehydes **5**, we next explored ways to further elaborate the latter compounds. Guided by various protocols for the oxidation of aldehydes into carboxylic acids using $RuCl_3$ as a catalyst in the presence of a

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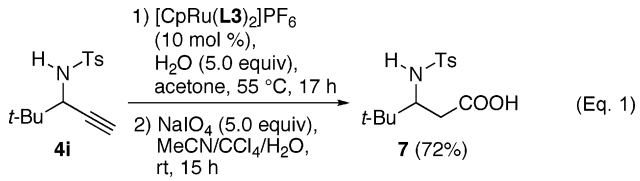
stoichiometric oxidant,[25] we were intrigued by the possibility of directly converting amines **4** into β-amino acids by means of a Ru-catalyzed one-pot hydration/oxidation procedure. Proof-of-principle was demonstrated by the hydration of propargylamine **4i** with the **L3**/Ru catalyst under standard conditions, followed by replacement of acetone with the typical MeCN/CCl_4/H_2O solvent mixture for the oxidation and addition of sodium periodate, which led to the formation of β-amino acid **7** in good yield (eq 1).



(Eq. 1)

Conclusion

In conclusion, we have described the synthesis of *N*-protected β-amino aldehydes by a novel alkynylation/hydration strategy. Key steps are the $ZnMe_2$-mediated addition of **1** to aryl and alkyl imines and, after desilylation of the resulting propargylamines, a Ru-catalyzed anti-Markovnikov hydration reaction. The latter process could be conducted under MW irradiation, leading to a shortening of the reaction times from several hours to minutes. Furthermore, a novel one-pot hydration/oxidation process has been developed, which warrants direct access to β-amino acid **7** from terminal alkyne **4i** in good overall yield.

Experimental Section

Aromatic *N*-tosyl imines **2a**,**c**−**g** were prepared using a modified version of the method reported by Kim and co-workers,[26] employing 1,2-dichloroethane as the solvent instead of CH_2Cl_2 and heating at reflux for 48 h instead of 12 h. *N*-Tosyl imine *N*-benzylidenediphenylphosphinamide (**2b**) was prepared according to the procedure reported by Jennings and Lovely[27] using an extended reaction time of 16 h. *N*-Tosyl imines derived respectively from cyclohexanecarbaldehyde (**2h**)[28] and 2,2-dimethylpropanal (**2i**)[29] were prepared following literature procedures. The *N*-tosylimine derived from (*E*)-cinnamic aldehyde was prepared according to the method described by Masquelin and Obrecht.[30] *N*,*N*-Dibenzylpropargylamine **4k** was prepared following the procedure described by Gommermann and Knochel.[22]

Typical Procedure for the Addition of 1 to Imines 2a−j. In an oven-dried Schlenk flask under an inert atmosphere of argon, **1** (0.491 g, 5.0 mmol, 2.5 equiv) was dissolved in anhydrous toluene (17.5 mL). A 2.0 M solution of dimethylzinc in toluene (2.5 mL, 5.0 mmol, 2.5 equiv) was then carefully added, and the resulting mixture was stirred at room temperature for 30 min. The appropriate imine **2** (2.0 mmol) was then added in one portion, and the temperature was increased to 70 °C. The resulting solution was then stirred for 24 h, after which a white precipitate appeared in some cases. The reaction was allowed to cool to rt, and it was quenched with water (40 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL), and the organic phase was washed with brine (100 mL) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure furnished the crude product **3a**−**i** typically as a solid, which was purified by flash column chromatography and/or by recrystallization (see the Supporting Information for details).

***N*-(*p*-Toluensulfonyl)-3-amino-3-phenyl-1-(trimethylsilyl)-prop-1-yne (3a). 3a** was purified by flash column chromatography (ethyl acetate/*n*-pentane, 1:6): yield 0.429 g (1.20 mmol, 60%); colorless solid; mp 139−140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 9H), 2.43 (s, 3H), 4.86 (d, J = 9.2 Hz, 1H), 5.34 (d, J = 9.2 Hz, 1H), 7.25−7.36 (m, 5H), 7.45−7.52 (m, 2H), 7.76−7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.3, 21.6, 49.7, 91.6, 101.4, 127.2, 127.4, 128.3, 128.5, 129.5, 137.2, 137.3, 143.3; MS (EI, 70 eV) m/z = 356 $[M - 1]^+$, 260, 234, 218, 202 $[M - Ts]^+$, 159, 91.

Typical Procedure for the Desilylation Reaction of Amines 3a−i. In an oven-dried Schlenk flask under an inert atmosphere of argon, a solution of the appropriate 1-(trimethylsilyl)propargylamine **3** (1.00−1.56 mmol) in dry THF (5.0−7.8 mL) was prepared. The resulting clear solution was cooled to 0 °C with an ice bath, and a 1.0 M solution of tetrabutylammonium fluoride in THF (0.33−0.52 mL, 0.33−0.52 mmol, 0.33 equiv) was added dropwise during ca. 1 min. The reaction mixture was stirred at 0 °C for 30 min, and the reaction was subsequently quenched with 20 mL of water. The aqueous layer was washed with Et_2O (3 × 25 mL), and the combined organic layers were dried over Na_2SO_4. Removal of the solvent by rotary evaporation afforded crude terminal alkynes **4a**−**i**, which were subsequently purified by flash column chromatography (see the Supporting Information for details).

***N*-(*p*-Toluensulfonyl)-1-amino-1-phenylprop-2-yne (4a). 4a** was prepared from **3a** (0.358 g, 1.0 mmol) and purified by flash column chromatography (ethyl acetate/*n*-pentane, 1:6): yield 0.240 g (0.85 mmol, 85%); colorless solid; mp 129−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (dd, J = 2.5, 0.8 Hz, 1H), 2.43 (s, 3H), 4.97 (d, J = 8.8 Hz, 1H), 5.32 (dd, J = 8.7, 2.1 Hz, 1H), 7.26−7.36 (m, 5H), 7.42−7.49 (m, 2H), 7.74−7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 49.0, 74.7, 80.4, 127.1, 127.4, 128.4, 128.6, 129.4, 136.8, 137.1, 143.5; IR (KBr) 3253, 2923, 2862, 1598, 1493, 1435, 1325, 1159, 1093, 1042 cm^{-1}; MS (EI, 70 eV) m/z = 260 $[M - C_2H]^+$, 220, 194 $[M - C_7H_7]^+$, 155 $[Ts]^+$, 130 $[M - Ts]^+$, 115 $[M - C_7H_8NO_2S]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$. Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.34; H, 5.29; N, 4.94.

General Procedure for the Anti-Markovnikov Hydration of Propargylic Amines 4a−i under Thermal Conditions. Under an inert atmosphere of argon, a flame-dried Schlenk flask was charged with **6** (5−10 mol %), a pyridylphosphane ligand, **L** (10−20 mol %, 2.0 equiv relative to **6**), and degassed CH_3CN (1 mL/10 mg of **6**). The mixture was heated to 60 °C for 1−6 h (1 h for **L1**, 6 h for **L2** and **L3**), and then the solvent was removed in vacuo to afford a yellow powder or resin. A solution of the appropriate propargylic amide **4** and water (5.0 equiv relative to **6**) in acetone (1−4 mL/mmol of substrate) was subsequently added, and the resulting mixture was heated at 55−60 °C. After completion of the reaction (15−90 h, according to TLC), the solution was allowed to cool to room temperature, and *tert*-butylmethyl ether (10 mL) was added. The organic layer was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4. The solvent was then removed under vacuum to afford the crude aldehydes **5a,c**−**i**, which were purified by flash column chromatography (see the Supporting Information for details).

General Procedure for the Anti-Markovnikov Hydration of Propargylic Amines 4 under Microwave Irradiation. Under an inert atmosphere of argon, a flame-dried vial was placed in a Schlenk flask. The vial was charged with **6** (5−10 mol %), pyridylphosphane **L3** (10−20 mol %, 2.0 equiv relative to **6**), and degassed CH_3CN (1 mL/10 mg of **6**), and the in situ catalyst was generated as described above. After removal of the solvent, a solution of the adequate propargylic amine **4** and water (5.0 equiv relative to **6**) in acetone (1−4 mL/mmol of substrate) was

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subsequently added. The vial was sealed with a septum, removed from the Schlenk flask, and placed in the cavity of the microwave reactor, which was then locked with the pressure device. The microwave source was then turned on. Constant microwave irradiation of 50−75 W as well as simultaneous air cooling (1.4−4.0 bar, 20−58 psi) was used during the entire reaction time (5−30 min), so that the temperature was kept at 90−120 °C. After cooling to room temperature, the products were isolated as described above for the thermal reaction.

***N*-Tosyl-1-amino-1-phenylpropanal (5a). 5a** was prepared from propargylic amine **4a** (0.120 g, 0.42 mmol) and purified by flash column chromatography (ethyl acetate/*n*-pentane, 1:2): yield 0.075 g (0.247 mmol, 83%); light orange solid; mp 88−89 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 2.88−2.97 (m, 1H, A part of an AB system), 3.00−3.09 (m, 1H, B part of an AB system), 4.80 (q, J = 6.9 Hz, 1H), 5.47 (br s, 1H), 7.04−7.11 (m, 2H), 7.14−7.21 (m, 5H), 7.56−7.62 (m, 2H), 9.63 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 50.1, 53.2, 126.4, 127.0, 127.8, 128.6, 129.4, 136.9, 139.1, 143.3, 199.4; IR (KBr) 3520, 3254, 3051, 2823, 1727, 1598, 1455, 1315, 1159, 1082 cm^{-1}; MS (CI, CH_4, 70 eV) m/z = 304 $[M + 1]^+$, 260 $[M - C_2H_3O]^+$, 200, 172, 155 $[Ts]^+$, 148 $[M - Ts]^+$, 133 $[M - C_7H_8NO_2S]^+$, 104, 91 $[C_7H_7]^+$. Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.42; H, 5.83; N, 4.62.

One-Pot Anti-Markovnikov Hydration/Oxidation of Propargylic Amine 4i. Under an inert atmosphere of argon, a flame-dried Schlenk flask was charged with **6** (10 mol %), pyridylphosphane **L3** (20 mol %, 2.0 equiv relative to **6**), and degassed CH_3CN (1 mL/10 mg of **6**). The mixture was heated to 60 °C for 6 h, and the solvent was then removed in vacuo to afford a yellow powder. A solution of propargylic amide **4i** (1 equiv) and water (5.0 equiv relative to **6**) in acetone (1 mL/0.1 mmol of substrate) was subsequently added, and the resulting mixture was heated at 55 °C. After completion of the reaction (17 h, according to TLC), the solution was allowed to cool to rt. Evaporation of the solvent under reduced pressure furnished crude aldehyde **5i**, which was successively dissolved in a $MeCN/CCl_4/H_2O$ (2:2:4) mixture. $NaIO_4$ (99%, 4 equiv relative to **4i**) was then added in one portion, and the resulting solution was stirred for 15 h at room temperature. The solvent was evaporated and the residue taken up in water. After acidification to pH 2 with 2 N HCl, the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was then removed under vacuum to afford crude β-amino acid **7**, which was purified by flash column chromatography (silica gel).

***N*-Tosyl-1-amino-1-(2-*tert*-butyl)propanoic Acid (7). 7** was prepared from propargylic amine **4i** (40 mg, 0.15 mmol) and purified by flash column chromatography (ethyl acetate/*n*-pentane/acetic acid, 80:20:1): yield 32 mg (0.11 mmol, 72%); white solid; mp 169 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (s, 9 H), 2.35−2.39 (m, 2 H, AB system), 2.41 (s, 3 H), 3.43 (dt, J = 9.6, 5.4 Hz, 1 H), 5.26 (d, J = 9.4 Hz, 1 H), 7.28 (dd, J = 8.6, 0.7 Hz, 2 H), 7.76 (dt, J = 8.1, 1.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 26.4, 35.3, 58.9, 127.1, 127.6, 129.6, 137.7, 143.4, 177.0; IR (KBr) 3276, 2971, 1716, 1447, 1314, 1150, 1087 cm^{-1}; MS (EI, 70 eV) m/z = 300 $[M^+]$, 242 $[M - C_2H_3O]^+$, 224 $[M - C_4H_9]^+$, 198, 155 $[Ts]^+$, 91 $[C_7H_7]^+$. Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.16; H, 7.07; N, 4.68. Found: C, 56.09; H, 7.17; N, 4.60.

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Supporting Information Available: General experimental procedures, analytical data of compounds **3a**−**i**, complete characterization of compounds **4a**−**i**, **5a**,**c**−**i**, and **7**, and ^{1}H NMR and ^{13}C NMR spectra of compounds **3a**−**i**, **4a**−**i**, **5a**,**c**−**i**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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