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Preparation of *Z*-α,β-Unsaturated Diazoketones from Aldehydes. Application in the Construction of Substituted Dihydropyridin-3-ones

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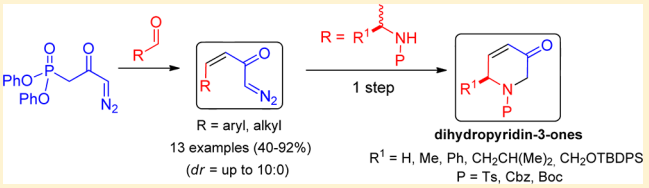
Supporting Information

ABSTRACT: The stereoselective preparation of α,β-unsaturated diazoketones with *Z* geometry is described from aldehydes and a new olefination reagent. When prepared from amino aldehydes, these diazoketones could be converted to substituted dihydropyridin-3-ones in just one step, after an intramolecular N−H insertion reaction. The straightforward synthesis of a natural trihydroxylated piperidine demonstrates the utility of these unsaturated diazoketones for the rapid construction of piperidines.



Diazo compounds are a very interesting class of compounds that can promote a wide range of reactions, such as cyclopropanations, insertion reactions, ylide formation, dimerization and elimination reactions and formation of ketenes by the Wolff rearrangement, among others.[1] An interesting class of these diazo compounds is the α,β-unsaturated diazoketones,[2] which has received little attention when compared to the saturated ones due to the difficulty of its preparation by the usual existing methods.[3] Recently,[2a] we described a methodology for the synthesis of *E*-α,β-unsaturated diazoketones from diazophosphonate **1** and their use as efficient platforms in the synthesis of indolizidines[2b,c] (Scheme 1, chart A). We wondered if we could also extend this method to the synthesis of the rare *Z* isomers after developing new types of Still−Gennari[4] or Ando phosphonates[5] such as **2** or **3** (Scheme 1, chart B). Interestingly, the success in this transformation could also permits the synthesis of γ-amino-unsaturated diazoketones like **4** if amino aldehydes[6] are used. These intermediates would possess the proper *Z* geometry for a direct cyclization to furnish highly functionalized piperidine systems, such as dihydropyridin-3-ones like **5**. Moreover, depending on the amino aldehyde that is employed, not only piperidines but also indolizidine and quinolizidine systems could be achieved.

Herein, we show the development of new Horner−Wadsworth−Emmons (HWE) reagents for the synthesis of α,β-unsaturated diazoketones with *Z* geometry and the conversion of some of them to substituted dihydropyridin-3-ones like **5** in just one step after an intramolecular N−H insertion reaction.[7] Moreover, a three-step synthesis of a natural trihydroxylated piperidine[8] demonstrates the utility of these unsaturated diazoketones for the rapid construction of piperidines. Dihydropyridin-3-ones similar to **5** have already been applied with success in the total syntheses of haouamine,[9,10] paroxetine,[11] and ergolines,[12] and they can also be powerful platforms in the synthesis of many other piperidines. Notwithstanding these applications, straightforward methods to prepare substituted dihydropyridin-3-ones (especially enantiopure ones) are still scarce,[13] being that olefin metathesis[13i,m] is one of the most efficient methods to prepare them.

To investigate our proposal, we started our work by synthesizing new diazophosphonates **6**−**8**[14] (Scheme 2), with the aim of achieving the desired *Z*-α,β-unsaturated diazoketones by an Ando-type HWE reaction.[5] It is worth mentioning that the most useful methodology to prepare diazoketones, involving diazomethane acylation in the presence of acyl chlorides or mixed anhydrides, is generally not good for the synthesis of α,β-unsaturated diazoketones. This is because dipolar cycloaddition to the conjugated double bond rapidly occurs, resulting in the formation of pyrazolines.[15] Diazophosphonates **6**−**8** were prepared by the reaction of diazomethane and the activated 2-(aryloxyphosphoryl)acetic acids;[16] they are stable yellow solids that can be stored for months without decomposition. This stability was also demonstrated after thermogravimetric analysis[17] from diazophosphonate **6**, showing no decomposition in temperatures up to 150 °C.

With a secure and reproducible way to prepare **6**−**8**, we then studied the preparation of the *Z*-unsaturated diazoketones using benzaldehyde as a model in the HWE reaction (Table 1).

As depicted in Table 1, the use of potassium *tert*-butoxide as the base (entry 8) was crucial to guarantee a high yield (92%) and a high level of *Z*-selectivity (*Z*:*E* ratio = 9:1). Employing sodium hydride, a similar yield could be obtained only when 2 equiv of diazophosphonate **6** were used, with the cost of a lower diastereoselectivity (*Z*:*E* ratio = 7:3). The modification of the aromatic ring of the phosphonate (sterically and electronically) did not improve the yield or the *Z*:*E* ratio of the HWE reactions. The use of this best condition for the HWE reaction could also be extended to 4-methoxybenzaldehyde, 4-nitro-

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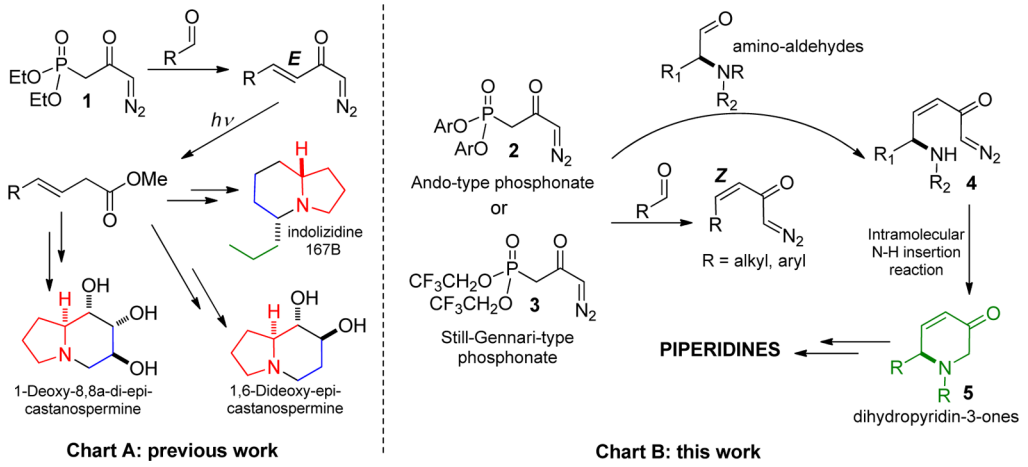
Scheme 1. Unsaturated Diazoketones as Platforms for the Direct Synthesis of Alkaloids



Scheme 2. New Ando-Type Phosphonates

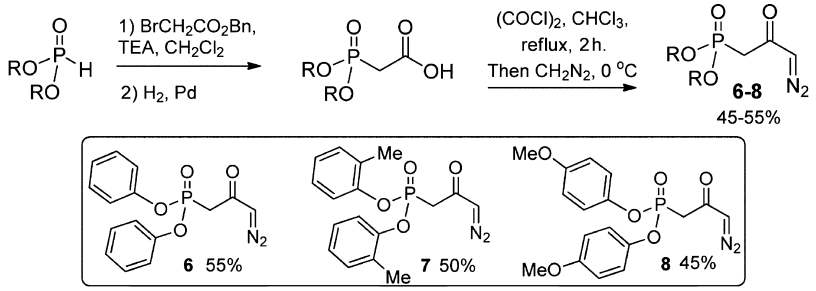
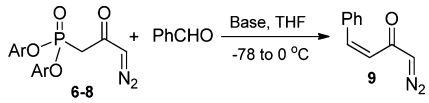


Table 1. Evaluation of the HWE Reaction between Diazophosphonates 6–8 and Benzaldehyde



entry[a]	phosphonate	base	yield[b] (%)	Z/E[c]
1	**6**	NaH	74	7:3
2	**7**	NaH	72	6:4
3	**8**	NaH	70	1:1
4[d]	**6**	NaH	63	7:3
5[e]	**6**	NaH	97	7:3
6	**6**	DIPEA	11	1:1
7	**6**	BuLi	41	6:4
8	**6**	***t*-BuOK**	**92**	**9:1**
9	**7**	*t*-BuOK	75	8:2
10	**8**	*t*-BuOK	82	8:2
11[f]	**6**	*t*-BuOK	80	8:2

[a]Unless otherwise noted, all the reactions were carried out using 0.16 mmol of the aldehyde, 0.16 mmol of the phosphonate, and 0.18 mmol of the base. For the generation of the phosphonate anion, a 0.05 M solution of **6–8** in THF was added to a suspension of the base in THF (0.3 M). [b]Yields (%) for *E* + *Z* after column chromatography purification. [c]Measured by ^{1}H NMR. [d]A 0.3 M solution of the phosphonate was added to the base. [e]2 equiv of the phosphonate anion was employed. [f]3 equiv of 18-crown-6 ether was used as additive.

benzaldehyde, and hexanal, leading to the respective unsaturated diazoketones **10–12** in very good yields and excellent diastereoselectivities (Figure 1).

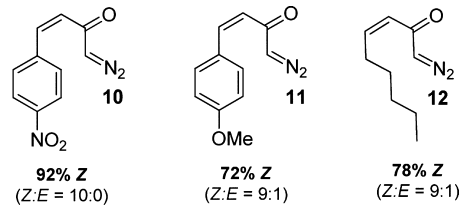


Figure 1. Synthesis of *Z*-α,β-unsaturated diazoketones from aromatic and aliphatic aldehydes.

Aiming for the expedited preparation of dihydropyridin-3-ones as depicted in Scheme 1 (chart B), we then turned our attention to evaluating the scope of this modified HWE reaction in the presence of amino aldehydes (Table 2). Unlike the aromatic and aliphatic aldehydes, amino aldehydes proved to have different behaviors in the HWE reaction with diazophosphonate **6**. For example, depending on the nitrogen protecting group and the size of the substituent alpha to the carbonyl group (R^1), different results[18] were obtained with respect to yields (40–74%) and diastereoselectivities (6:4 to 10:0) (Table 2).

Next, in order to reach the desired dihydropyridin-3-ones, we evaluated the cyclization of the synthesized diazoketones by a metal-catalyzed intramolecular N–H insertion reaction. It is important to note that, although N–H insertion reactions from diazoketones have been well described for decades,[1] no example of this transformation is available in the literature from α,β-unsaturated diazoketones as substrates. For this peculiar case, the presence of the double bond (and the acidic hydrogen in the gamma position) in these unsaturated diazoketones may set a troubled scenario when compared to

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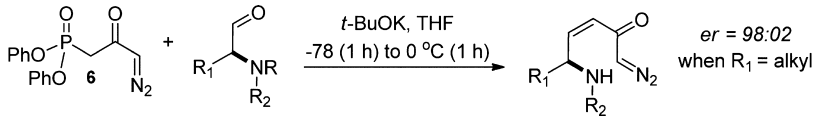
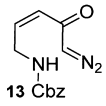
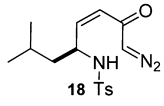
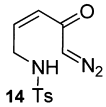
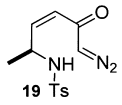
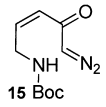
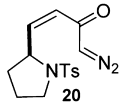
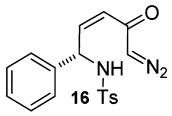
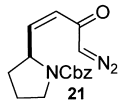
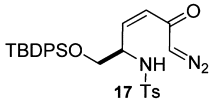
Table 2. Synthesis of Diverse *Z*-α,β-Unsaturated Diazoketones from Amino Aldehydes[19]



diazoketone	Yield *Z*[a]	Yield *E*[a]	*Z*:*E*	diazoketone	Yield *Z*[a]	Yield *E*[a]	*Z*:*E*
 **13** Cbz	68	17	8:2	 **18** Ts	52	13	8:2
 **14** Ts	50	20	7:3	 **19** Ts	50	20	7:3
 **15** Boc	40	26	6:4	 **20**	74	0	10:0
 **16** Ts	73	0	10:0	 **21**	56	14	8:2
 **17** Ts	63	7	9:1				

[a]Isolated yields after column chromatography purification and isomer separation.

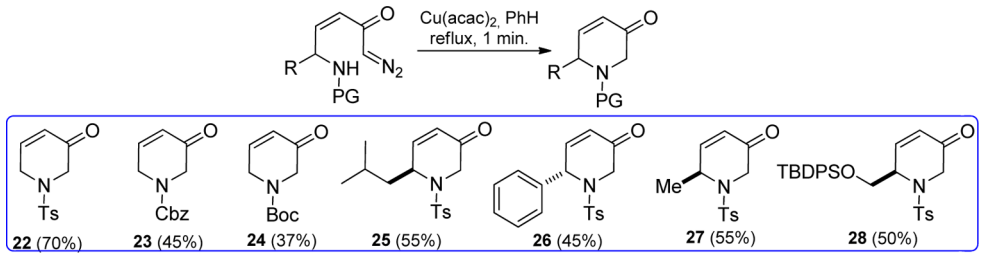


Figure 2. Synthesis of dihydropyridin-3-ones from unsaturated diazoketones **13**–**19**.

the saturated ones, creating the possibility of competing reactions such as cyclopropanation and C–H insertion reactions. To verify this, an exhaustive study was necessary in order to find the best conditions for the desired intramolecular N–H insertion reaction (see the Supporting Information for details). In this study, the simple Cbz-, Ts-, and Boc-protected diazoketones **13**–**15** were employed as a model in the presence of different rhodium and copper salts as catalysts. Based on the pioneering works of Christensen,[7a] Rapoport,[7b] and others[7c–g] for this type of transformation, rhodium catalysts were the first choice. To our surprise, rhodium catalysts were completely nonselective and furnished at 25 °C a complex mixture of products (TLC analysis), probably arising from competing C–H and C=C insertion reactions as mentioned above. We then turned our attention to copper catalysts. Although they were shown to be inactive at 25 °C, reactions carried out at 80 °C led to yields ranging from 30 to 70%. For those catalysts, the tosyl protecting group furnished the best result (Figure 2). In agreement with the literature, the combination of the tosyl protecting group and copper catalysts had been previously claimed by Wang[20] as the best choice for intramolecular N–H insertion reactions, especially when C–H insertions need to be avoided. After finding the suitable conditions for the intramolecular N–H insertion reactions from γ-amino unsaturated diazoketones **13**–**15**, we then extended it to the synthesis of 2-substituted dihydropyridin-3-ones **25**–**28**[21] with different patterns of substitution (Figure 2).

In addition, to illustrate the utility of these dihydropyridin-3-ones in the direct synthesis of hydroxylated piperidines, compound **22** was converted to (±)-(3*R*,5*R*)-piperidine-3,4,5-triol **31**, an α-glycosidadse and β-galactosidase inhibitor isolated from *Eupatorium fortunei TURZ*[22] (Scheme 3). Luche reduction[23] from **22**, followed by a highly selective OsO_4 catalyzed dihydroxylation reaction[24] and tosyl group removal,[25] led to the natural trihydroxylated piperidine **31** after this sequence of three simple steps. All of the spectroscopic data for **31** is in accordance with those published in the literature.[22,26] It is interesting to note that chiral **31** could also be prepared in an analogous sequence just by employing a CBS reduction from dihydropyridin-3-one **22** instead of a Luche reduction.

In conclusion, we have developed a two-step method for easy access to highly functionalized piperidine systems, such as dihydropyridin-3-ones, from aldehydes. This could be accomplished after an unusual type of intramolecular N-H insertion

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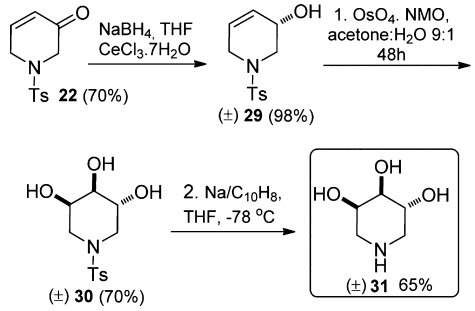
Scheme 3. Dihydropyridin-3-one 22 as an Advanced Intermediate in the Total Synthesis of 3,4,5-Trihydroxypiperidine 31



reaction from *Z*-unsaturated diazoketones. These rare diazoketones could be prepared by employing a new type of olefination reagent and commercially available or easily prepared amino aldehydes. The sequence is direct and permits the expedited synthesis of hydroxylated piperidines, as was demonstrated during the preparation of the natural piperidine **31**. The synthesis of more complex piperidines, such as nojirimycin analogues from chiral dihydropyridin-3-one **28**, is underway in our laboratory.

EXPERIMENTAL SECTION

Diphenyl (3-Diazo-2-oxopropyl)phosphonate (6). 2-(Diphenoxyphosphoryl)acetic acid (4.5 g, 15.4 mmol, 1.0 equiv) was added to a 100 mL flame-dried round-bottom flask followed by the addition of dry toluene (3 × 20 mL) for azeothropic removal of moisture in the rotary evaporator. Next, dry chloroform (38.5 mL) was added and the system cooled to 0 °C. Freshly distilled oxalyl chloride (4.0 mL, 46.2 mmol, 3.0 equiv) was then added dropwise to the reaction vessel and the solution stirred at reflux for 2 h. After this period, the solvent and volatiles were removed on the rotary evaporator, and the resultant residue was dissolved in dry tetrahydrofuran (THF) (14.4 mL) (*Careful: The acid chloride from 2-(diphenoxyphosphoryl)acetic acid is very unstable and care should be exercised during these operations to avoid its hydrolysis.*) To the acid chloride solution, at 0 °C, a cooled and freshly prepared 0.4 M ethereal solution of diazomethane (115 mL) was added and the reaction allowed stirring at 0 °C for 10 min. After that, the solvent was removed in the rotary evaporator (*Careful: Before concentrating on a rotary evaporator, it is important to remove the excess of diazomethane by passing argon through the solution during 5 min*) and the residue was purified by flash column chromatography (diethyl diethyl ether/hexanes 8:2) to furnish the diphenyl (3-diazo-2-oxopropyl)phosphonate (**6**) (2.44 g, 7.70 mmol, 55%) as a yellow solid: mp = 61−63 °C; R_f = 0.33 (silica gel, diethyl ether/hexanes = 8:2); IR (neat) ν_{max} = 3101, 3070, 2970, 2920, 2110, 1636, 1591, 1491, 1362, 1279, 1213, 1188, 1163, 945, 768, 690, 617 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49−7.09 (m, 10H), 5.68 (s, 1H), 3.25 (d, J_{H-P} = 21.8 Hz, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 183.6, 149.8 (d, J_{C-P} = 8.8 Hz), 129.8 (d, J_{C-P} = 0.7 Hz), 125.6 (d, J_{C-P} = 1.2 Hz), 120.6 (d, J_{C-P} = 4.4 Hz), 57.1, 39.8 (d, J_{C-P} = 132.2 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{15}H_{14}N_2O_4P$ [M + H$^+$] 317.0686, found 317.0671.

Di-*o*-tolyl (3-diazo-2-oxopropyl)phosphonate (7): yellow solid (2.60 g, 7.55 mmol, 50%); mp = 59−61 °C; R_f = 0.32 (silica gel, diethyl ether/hexanes = 8:2); IR (neat) ν_{max} = 3084, 3070, 2962, 2922, 2108, 1637, 1585, 1493, 1462, 1358, 1275, 1229, 1169, 1109, 1063, 1051, 951, 845, 806, 762, 708 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.05 (m, 8H), 5.71 (s, 1H), 3.29 (d, J_{H-P} = 21.8 Hz, 2H), 2.24 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 148.7 (d, J_{C-P} = 9.1 Hz), 131.6, 129.5 (d, J_{C-P} = 5.4 Hz), 127.2, 125.5, 120.4, 56.9, 40.4 (d, J_{C-P} = 132.4 Hz), 16.4 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_2O_4P$ [M + H$^+$]: 345.0999, found 345.0984.

Bis(4-methoxyphenyl) (3-diazo-2-oxopropyl)phosphonate (8): yellow solid (2.44 g, 7.70 mmol, 45%); mp = 67−69 °C; R_f = 0.35 (silica gel, diethyl ether/hexanes = 8:2); IR (neat) ν_{max} = 3107, 3078, 3003, 2957, 2941, 2912, 2837, 2110, 1736, 1634, 1502, 1466, 1443, 1360, 1273, 1252, 1207, 1186, 1103, 1034, 947, 835, 810 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18−7.08 (m, 4H), 6.89−6.81 (m, 4H), 5.68 (s, 1H), 3.78 (s, 6H), 3.21 (d, J_{H-P} = 21.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 183.7, 157.1, 143.3 (d, J_{C-P} = 8.9 Hz), 121.5 (d, J_{C-P} = 4.1 Hz), 114.7, 57.0, 55.6, 39.5 (d, J_{C-P} = 132.1 Hz), 30.5 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_2O_6P$ [M + H$^+$] 377.0897, found 377.0918.

General Procedure for the HWE Reaction (*t*-BuOK as Base). *(Z)-1-Diazo-4-phenylbut-3-en-2-one (9).* In a flame-dried round-bottom flask of 10 mL, under argon atmosphere, were added *t*-BuOK (20.1 mg, 0.174 mmol, 1.1 equiv) and dry THF (580 μL). The suspension was cooled to 0 °C, and a solution of diphenyl (3-diazo-2-oxopropyl)phosphonate (**6**) (50.0 mg, 0.158 mmol, 1.0 equiv) in dry THF (3.2 mL) was added. After 10 min, the solution was cooled to −78 °C, and a solution of benzaldehyde (16 μL, 0.158 mmol, 1.0 equiv) in dry THF (790 μL) was added. After 1 h, the temperature was immediately allowed to rise to 0 °C and stirred for an additional 1 h, and then a saturated aqueous NH_4Cl solution (10 mL) was added to the reaction vessel. Next, the aqueous layer was extracted with ethyl acetate (3 × 20 mL), the combined organic layers were washed with water (15 mL) and brine (15 mL), dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, diethyl ether/hexanes = 8:2) to give (*Z*)-1-diazo-4-phenylbut-3-en-2-one (**9**) (22.6 mg, 0.131 mmol, 83% yield) + the *E* isomer (2,8 mg, 0.016 mmol, 9% yield) as yellow oils: R_f = 0.60; IR (neat) ν_{max} = 3099, 3088, 3024, 2096, 1634, 1603, 1493, 1450, 1423, 1391, 1339, 1148, 1103, 1067, 922, 843, 802, 698, 609, 561 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.39−7.33 (m, 3H), 6.87 (d, *J* = 12.6 Hz, 1H), 6.03 (d, *J* = 12.7 Hz, 1H), 5.16 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 139.5, 135.0, 129.7, 129.1, 128.3, 127.2, 57.3 ppm; HRMS (ESI-TOF) calcd for $C_{10}H_9N_2O$ [M + H$^+$] 173.0709, found 173.0798.

*(Z)-1-Diazo-4-(4-nitrophenyl)but-3-en-2-one (**10**):* yellow solid (31.7 mg, 0.146 mmol, 92% yield); mp = 90−91 °C; R_f = 0.37 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3109, 2920, 2853, 2102, 1639, 1591, 1512, 1429, 1335, 1146, 1107, 874, 752, 704, 513 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23−8.15 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 12.4 Hz, 1H), 6.17 (d, *J* = 12.4 Hz, 1H), 5.31 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 183.1, 147.7, 141.5, 137.4, 130.8, 129.1, 123.3, 58.0 ppm, HRMS (ESI) calcd for $C_{10}H_8N_3O_3$ [M + H$^+$] 218.0560, found 218.0562.

*(Z)-1-Diazo-4-(4-methoxyphenyl)but-3-en-2-one (**11**):* yellow solid (23.0 mg, 0.114 mmol, 72% yield); mp = 120−121 °C; R_f = 0.38 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3062, 2090, 1643, 1587, 1512, 1421, 1367, 1551, 1172, 1093, 977, 827 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 2H), 6.90−6.82 (m, 2H), 6.75 (d, *J* = 12.6 Hz, 1H), 5.90 (d, *J* = 11.7 Hz, 1H), 5.23 (s, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 184.4, 161.5, 140.5, 129.9, 129.7, 127.1, 114.4, 55.9, 55.4 ppm, HRMS (ESI) calcd for $C_{11}H_{11}N_2O_2$ [M + H$^+$] 203.0815, found 203.0812.

*(Z)-1-Diazonon-3-en-2-one (**12**):* yellow oil (20.5 mg, 0.123 mmol, 78% yield); R_f = 0.43 (acetone/hexanes 2:8); IR (neat) ν_{max} = 2956, 2927, 2102, 1652, 1367 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (dt, *J* = 11.1, 7.5 Hz, 1H), 5.85 (s, 1H), 5.24 (s, 1H), 2.69 (d, *J* = 7.1 Hz, 2H), 1.47−1.41 (m, 2H), 1.36−1.17 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 148.0, 124.8, 56.7, 31.5, 29.5, 28.9, 22.5, 14.2. ppm; HRMS (ESI) calcd for $C_9H_{15}N_2O$ [M + H$^+$] 167.1179, found 167.1177.

*(Z)-Benzyl (5-diazo-4-oxopent-2-en-1-yl)carbamate (**13**):* yellow oil (28.0 mg, 0.108 mmol, 68% yield); R_f = 0.35 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3414, 3337, 3096, 3063, 3043, 2102, 1713, 1643, 1605, 1524, 1454, 1416, 1346, 1265, 1148, 739 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.34 (m, 3H), 7.33 − 7.30 (m, 2H), 6.13 (s, 1H), 5.92 (d, *J* = 9.2 Hz, 1H), 5.44 (s, 1H), 5.33 (s, 1H), 5.10 (s, 2H), 4.31 (s, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.1, 156.5, 143.6,

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136.5, 128.6, 128.5, 128.1, 126.1, 66.8, 57.4, 39.9, 39.7 ppm; HRMS (ESI) calcd for $C_{13}H_{14}N_3O_3$ [M + H$^+$] 260.1030, found 260.1025.

*(Z)-N-(5-Diazo-4-oxopent-2-en-1-yl)-4-methylbenzenesulfonamide (**14**):* yellow solid (22.0 mg, 0.079 mmol, 50% yield); mp = 97−98 °C; R_f = 0.25 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3157, 3115, 2918, 2885, 2862, 2154, 2098, 1639, 1576, 1418, 1340, 1327, 1165, 1068, 883, 662 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.30 (dd, J = 8.5, 0.6 Hz, 2H), 6.13−6.08 (m, 1H), 5.89 (d, J = 11.2 Hz, 1H), 5.46 (s, 1H), 5.31 (s, 1H), 4.00 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.0, 143.5, 142.0, 136.9, 129.8, 127.1, 126.7, 57.8, 41.7, 21.5 ppm; HRMS (ESI) calcd for $C_{12}H_{14}N_3O_3S$ [M + H$^+$]: 280.0750, found 280.0732.

*(Z)-tert-Butyl (5-diazo-4-oxopent-2-en-1-yl)carbamate (**15**):* yellow oil (14.2 mg, 0.063 mmol, 40% yield); R_f = 0.43 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3352, 3096, 3080, 2976, 2930, 2102, 1699, 1643, 1605, 1514, 1416, 1344, 1275, 1252, 1169, 1070, 862, 783 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.88 (d, J = 9.7 Hz, 1H), 5.33 (s, 1H), 5.15 (s, 1H), 4.35−4.09 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.1, 156.0, 144.4, 125.7, 79.4, 57.2, 39.4, 28.4 ppm; HRMS (ESI) calcd for $C_{10}H_{16}N_3O_3$ [M + H$^+$] 226.1186, found 226.1171.

*(S,Z)-N-(5-Diazo-4-oxo-1-phenylpent-2-en-1-yl)-4-methylbenzenesulfonamide (**16**:).* yellow solid (37.6 mg, 0.115 mmol, 73% yield); mp = 147−149 °C; R_f = 0.15 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3225, 3173, 3097, 3063, 3030, 2980, 2920, 2883, 2745, 2102, 1734, 1707, 1643, 1589, 1493, 1450, 1418, 1350, 1325, 1288, 1265, 1221, 1159, 1119, 1094, 1063, 1047, 939, 816, 700, 557 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.27−7.22 (m, 7H), 6.18 (dd, J = 11.3, 8.8 Hz, 1H), 6.05−5.99 (m, 1H), 5.81 (d, J = 10.6 Hz, 1H), 5.68 (s, 1H), 5.30 (s, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 144.7, 143.4, 138.8, 137.0, 129.6, 128.9, 128.1, 127.4, 127.1, 124.4, 58.0, 55.2, 21.5 ppm; $[\alpha]^{25}_D$ = +165.6 (c 0.82, $CHCl_3$), HRMS (ESI) calcd for $C_{18}H_{18}N_3O_3S$ [M + H$^+$] 356.1063, found356.1065.

*(R,Z)-N-(1-((tert-Butyldiphenylsilyl)oxy)-6-diazo-5-oxohex-3-en-2-yl)-4-methylbenzenesulfonamide (**17**):* yellow solid (51.4 mg, 0.099 mmol, 63% yield); mp = 90−92 °C; R_f = 0.45 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3227, 3117, 3070, 3038, 2947, 2924, 2853, 2108, 1643, 1616, 1593, 1489, 1448, 1423, 1360, 1317, 1232, 1188, 1155, 1111, 1074, 1009, 924, 822, 729, 706, 667, 501, 494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.53 (t, J = 7.5 Hz, 4H), 7.45−7.32 (m, 6H), 7.27−7.20 (m, 2H), 6.01 (dd, J = 11.1, 8.3 Hz, 1H), 5.78 (d, J = 10.8 Hz, 1H), 5.51 (d, J = 4.9 Hz, 1H), 5.26 (s, 1H), 5.01 (s, 1H), 3.76−3.45 (m, 2H), 2.39 (s, 3H), 1.00 (d, J = 14.1 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.2, 144.5, 143.4, 136.9, 135.5, 135.4, 132.6, 129.9, 129.6, 127.8, 127.2, 65.2, 57.4, 53.7, 26.7, 21.5, 19.1 ppm; $[\alpha]^{25}_D$ = −100.4 (c 1.17, $CHCl_3$,), HRMS (ESI) calcd for $C_{29}H_{34}N_3O_4SSi$ [M + H$^+$] 548.2034, found 548.2034.

*(S,Z)-N-(8-Diazo-2-methyl-7-oxooct-5-en-4-yl)-4-methylbenzenesulfonamide (**18**):* yellow solid (25.2 mg, 0.082 mmol, 52% yield); mp = 150−151 °C; R_f = 0.25 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3165, 3088, 2947, 2924, 2866, 2147, 2098, 1649, 1591, 1421, 1367, 1315, 1302, 1169, 1153, 1142, 1097, 1068, 935, 808, 660, 581, 550, 486 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.32−7.22 (m, 2H), 5.86 (dd, J = 11.6, 8.2 Hz, 1H), 5.67 (s, 1H), 5.28 (s, 1H), 4.84−4.65 (m, 1H), 2.41 (s, 3H), 1.68−1.53 (m, 1H), 1.46−1.21 (m, 2H), 0.80 (dd, J = 18.3, 6.5 Hz, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 184.7, 147.3, 143.1, 137.7, 129.4, 127.3, 124.2, 57.9, 50.3, 43.4, 24.4, 23.0, 21.5, 21.2 ppm; $[\alpha]^{25}_D$ = −90.4 (c 1.26, $CHCl_3$); HRMS (ESI) calcd for $C_{16}H_{22}N_3O_3S$ [M + H$^+$] 336.1376, found 336.1373.

*(S,Z)-N-(6-Diazo-5-oxohex-3-en-2-yl)-4-methylbenzenesulfonamide (**19**):* yellow solid (20.9 mg, 0.079 mmol, 50% yield); mp = 136−137 °C; R_f = 0.23 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3159, 3109, 2980, 2964, 2924, 2870, 2106, 1645, 1593, 1462, 1418, 1369, 1353, 1321, 1165, 1074, 978, 804, 579 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.96 (dd, J = 11.5, 8.1 Hz, 1H), 5.71 (d, J = 11.6 Hz, 1H), 5.38 (s, 1H), 5.29 (s, 1H), 4.81 (dd, J = 14.0, 6.8 Hz, 1H), 2.42 (s, 3H), 1.22 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.7, 147.7, 143.3, 137.6, 129.6, 127.2, 124.1, 57.8, 48.2, 21.5, 20.7 ppm; $[\alpha]^{25}_D$ = −94.6 (c 0.82, $CHCl_3$); HRMS (ESI) calcd for $C_{13}H_{16}N_3O_3S$ [M + H$^+$] 294.0907, found 294.0900.

*(S,Z)-1-Diazo-4-(1-tosylpyrrolidin-2-yl)but-3-en-2-one (**20**):* yellow solid (37.3 mg, 0.117 mmol, 74% yield); mp = 109−110 °C; R_f = 0.43 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3080, 2953, 2924, 2856, 2096, 1728, 1649, 1605, 1448, 1420, 1348, 1196, 1157, 1109, 1088, 1032, 986, 824, 795, 723, 660, 584, 546 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.29 (dd, J = 10.9, 8.2 Hz, 1H), 5.87 (d, J = 10.9 Hz, 1H), 5.37 (s, 1H), 5.17 (d, J = 7.1 Hz, 1H), 3.77−3.70 (m, 1H), 3.18 (ddd, J = 10.3, 7.4, 6.1 Hz, 1H), 2.43 (s, 3H), 2.14 (td, J = 13.2, 6.8 Hz, 1H), 1.83−1.75 (m, 1H), 1.68 − 1.54 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 149.1, 143.5, 133.7, 129.0, 127.7, 123.3, 61.9, 58.5, 49.6, 31.7, 24.3, 21.5 ppm; $[\alpha]^{25}_D$ = −8.2 (c 1.21, $CHCl_3$), HRMS (ESI) calcd for $C_{15}H_{18}N_3O_3S$ [M + H$^+$] 320.1063, found 320.1068.

*(S,Z)-Benzyl 2-(4-diazo-3-oxobut-1-en-1-yl)pyrrolidine-1-carboxylate (**21**):* yellow oil (26.6 mg, 0.089 mmol, 56% yield); R_f = 0.42 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 3068, 3032, 2972, 2953, 2878, 2098, 1699, 1645, 1609, 1447, 1414, 1342, 1149, 1119, 1095, 793, 735, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50−7.20 (m, 5H), 6.17−4.91 (m, 5H), 3.74−3.38 (m, 2H), 2.51−2.23 (m, 1H), 2.08−1.60 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 185.2, 155.0, 149.0, 148.1, 136.7, 128.4, 128.2, 127.8, 127.7, 122.8, 66.7, 56.8, 55.9, 47.2, 46.9, 33.2, 32.5, 30.3, 24.6, 24.1 ppm; $[\alpha]^{25}_D$ = −161.9 (c 0.90, $CHCl_3$), HRMS (ESI) calcd for $C_{16}H_{16}N_3O_3$ [M − H$^-$] 298.1197, found 298.1190.

General Procedure for the N−H Insertion Reaction. *1-Tosyl-1,6-dihydropyridin-3(2H)-one (**22**).* In a flame-dried round-bottom flask of 5 mL was added (*Z*)-*N*-(5-diazo-4-oxopent-2-en-1-yl)-4-methylbenzenesulfonamide (**14**) (1.0 equiv, 0.090 mmol, 25 mg) dissolved in distilled benzene (1.8 mL, 0.05 mol/L). The mixture was then warmed to reflux, followed by the addition of copper(II) acetylacetonate (0.1 equiv, 8.95 μmol, 2.3 mg). After 1 min under stirring, the reaction was cooled and the solvent removed under reduced pressure. Next, the crude product was purified by flash column chromatography (hexanes/diethyl ether 2:8) to furnish 1-tosyl-1,6-dihydropyridin-3(2*H*)-one (**22**) (15.7 mg, 0.063 mmol, 70% yield) as a white solid: R_f = 0.60 (silica gel, hexanes/diethyl ether 2:8); mp =101−103 °C; IR (neat) ν_{max} = 3157, 3115, 2918, 2885, 2862, 2154, 2098, 1639, 1576, 1450, 1418, 1340, 1327, 1230, 1165, 1111, 1095, 1068, 1041, 935, 883, 812, 798, 779, 735, 706, 662, 579, 554, 523 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.92 (dt, J = 10.3, 3.7 Hz, 1H), 6.06 (dt, J = 10.3, 2.1 Hz, 1H), 3.97 (s, 2H), 3.81 (s, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 144.9, 144.5, 132.8, 130.1, 128.0, 127.7, 52.8, 44.5, 21.6 ppm; HRMS (ESI) calcd for $C_{12}H_{14}NO_3S$ [M + H$^+$] 252.0689, found 252.0685.

*(S)-6-Isobutyl-1-tosyl-1,6-dihydropyridin-3(2H)-one (**25**):* white solid (10.1 mg, 0.033 mmol, 55% yield); mp = 118−120 °C; R_f = 0.66 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 2959, 2924, 2866, 1701, 1690, 1597, 1468, 1387, 1340, 1259, 1161, 1132, 1090, 1040, 978, 905, 816, 758, 689, 585, 555 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 6.71 (dd, J = 10.5, 4.9 Hz, 1H), 5.65 (d, J = 10.4 Hz, 1H), 4.63 (dt, J = 9.5, 4.8 Hz, 1H), 4.38 (d, J = 18.9 Hz, 1H), 3.87 (d, J = 19.0 Hz, 1H), 2.39 (s, 3H), 1.94−1.86 (m, 1H), 1.63−1.55 (m, 1H), 1.38 (m, 1H), 1.03 (t, J = 8.0 Hz, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.6, 149.5, 143.9, 136.1, 129.9, 129.1, 127.2, 126.4, 122.8, 52.2, 49.1, 40.5, 25.2, 23.0, 21.7, 21.5 ppm; $[\alpha]^{25}_D$ = +19.1 (c 1.80, $CHCl_3$), HRMS (ESI) calcd for $C_{16}H_{22}NO_3S$ [M + H$^+$]: 308.1315, found 308.1308.

*(S)-6-Phenyl-1-tosyl-1,6-dihydropyridin-3(2H)-one (**26**):* white solid (8.3 mg, 0.025 mmol, 45% yield); mp = 146−147 °C; R_f = 0.38 (diethyl ether/hexanes 1:1); IR (neat) ν_{max} = 3059, 3042, 3026, 2970, 2922, 2885, 2854, 1682, 1585, 1491, 1452, 1389, 1346, 1257, 1167, 1090, 1043, 982, 926, 910, 764, 706, 687, 550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.37 (s, 5H), 7.23 (d, J = 8.0 Hz, 2H), 6.96 (dd, J = 10.4, 5.2 Hz, 1H), 5.98 (dd, J = 10.4, 1.2 Hz, 1H), 5.81 (dd, J = 5.1, 1.3 Hz, 1H), 4.31 (d, J = 18.6 Hz, 1H), 3.70 (d, J = 18.6 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$)

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δ 191.4, 163.7, 146.6, 144.1, 136.0, 134.6, 129.9, 129.0, 128.9, 128.3, 128.1, 127.2, 56.3, 49.5, 21.5 ppm; $[\alpha]^{25}_{D} = -105.5$ (c = 0.80, $CHCl_3$); HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ [M + H$^+$] 328.1002, found 328.0997.

*(S)-6-Methyl-1-tosyl-1,6-dihydropyridin-3(2H)-one (**27**):* white solid (9.9 mg, 0.038 mmol, 55% yield); mp = 85−86 °C; R_f = 0.48 (diethyl ether/hexanes 8:2); IR (neat) ν_{max} = 2922, 2867, 2870, 2853, 1695, 1597, 1458, 1391, 1342, 1259, 1192, 1165, 1128, 1092, 999, 922, 814, 781, 708, 687, 555 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.28−7.24 (m, 2H), 6.77 (dd, J = 10.4, 5.0 Hz, 1H), 5.78 (d, J = 10.4 Hz, 1H), 4.79−4.69 (m, 1H), 4.35 (d, J = 18.5 Hz, 1H), 3.87 (d, J = 18.5 Hz, 1H), 2.40 (s, 3H), 1.39 (d, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 150.3, 144.0, 136.2, 130.0, 127.1, 126.2, 49.7, 48.7, 21.5, 17.5 ppm; $[\alpha]^{25}_{D} = -19.8$ (c 1.50, $CHCl_3$); HRMS (ESI) calcd for $C_{13}H_{16}NO_3S$ [M + H$^+$] 266.0845, found 266.0833.

*(R)-6-(((tert-Butyldiphenylsilyl)oxy)methyl)-1-tosyl-1,6-dihydropyridin-3(2H)-one (**28**):* white solid (8.5 mg, 0.016 mmol, 50% yield); R_f = 0.40 (diethyl ether/hexanes 1:1); IR (neat) ν_{max} = 2951, 2928, 2889, 2856, 1693, 1595, 1470, 1427, 1393, 1350, 1261, 1186, 1163, 1111, 1095, 984, 908, 820, 773, 741, 706, 687, 646, 611, 548, 503, 494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.55 (m, 6H), 7.48−7.35 (m, 6H), 7.22 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 10.5, 5.0 Hz, 1H), 5.93 (dd, J = 10.5, 1.3 Hz, 1H), 4.64 (dd, J = 8.2, 3.9 Hz, 1H), 4.35 (d, J = 18.5 Hz, 1H), 4.09 (d, J = 18.5 Hz, 1H), 4.04 (dd, J = 10.6, 4.9 Hz, 1H), 3.83 (dd, J = 10.5, 4.1 Hz, 1H), 2.39 (s, 3H), 1.00 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 146.5, 143.9, 135.7, 135.5, 132.3, 130.0, 129.9, 128.6, 127.9, 127.0, 65.4, 55.0, 51.3, 26.7, 21.5, 19.0 ppm; $[\alpha]^{25}_{D}$ = +120.3 (c 0.6, $CHCl_3$), HRMS (ESI) calcd for $C_{29}H_{34}NO_4SSi$ [M + H$^+$] 520.1972, found 520.1972.

*(±)-1-Tosyl-1,2,3,6-tetrahydropyridin-3-ol (**29**).* Cerium trichloride heptahydrate (0.2 mL of a 0.4 M solution in methanol, 0.08 mmol) was added to a stirred solution of 1-tosyl-1,6-dihydropyridin-3(2H)-one (**32**) (20 mg, 0.080 mmol) in dichloromethane (5 mL) at −78 °C. After 0.25 h, sodium borohydride (45.2 mg, 1.194 mmol) was added, and the resulting solution was stirred for 1 h. After this period, the reaction was warmed to 25 °C and quenched with water (2.7 mL). The layers were separated, and the aqueous portion was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give pure (±)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**38**) as a white solid (24.5 mg, 0.097 mmol, 98% yield): mp = 100−102 °C; R_f = 0.60 (hexanes/ethyl acetate 1:1); IR (neat) ν_{max} = 3063, 3047, 2980, 2885, 2853, 1595, 1493, 1458, 1400, 1335, 1310, 1290, 1259, 1225, 1161, 1138, 1095, 978, 945, 903, 831, 816, 729, 708, 685, 650, 571, 554, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.36 −7.32 (m, 2H), 5.91 (ddt, J = 9.8, 4.1, 2.1 Hz, 1H), 5.81 (dddd, J = 10.1, 3.7, 2.6, 0.8 Hz, 1H), 4.21 (s, 1H), 3.77 (ddd, J = 16.8, 2.2, 1.6 Hz, 1H), 3.40−3.33 (m, 2H), 3.06 (ddd, J = 11.9, 3.7, 0.7 Hz, 1H), 2.44 (s, 3H), δ 2.03 (d, J = 10.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 133.0, 129.8, 128.2, 127.7, 125.8, 63.4, 50.1, 44.9, 21.5. ppm; HRMS (ESI) calcd for $C_{12}H_{16}NO_3S$ [M + H$^+$] 254.0845, found 254.0835.

*(±)-1-Tosylpiperidine-3,4,5-triol (**30**).* In a flame-dried round-bottom flask of 10 mL was added (±)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**29**) (1.0 equiv, 0.059 mmol, 15 mg) dissolved in a mixture of water/acetone (2.1 mL; 9:1). To this mixture was added NMO (2.0 equiv, 0.118 mmol, 13.9 mg) and an aqueous solution of OsO_4 (19.8 μL, 5 mol %, 2.96 μmol). The reaction was stirred at 25 °C for 48 h and then quenched with 270 μL of a saturated solution of sodium bisulfide. Next, the reaction was extracted with ethyl acetate (3 × 10 mL) and the solvent dried over sodium sulfate and removed by reduce pressure. The crude product was purified by flash column chromatography to furnish (±)-1-tosylpiperidine-3,4,5-triol (**30**) (10.5 mg, 0.040 mmol, 70% yield): white solid; mp 158−160 °C; R_f = 0.22 (ethyl acetate 100%); IR (neat) ν_{max} = 3475, 3367, 3233, 2918, 2845, 1599, 1464, 1340, 1228, 1156, 1091, 1073, 1026, 961, 933, 850, 811, 710, 694, 653, 565, 549 cm^{-1}; ^{1}H NMR (400 MHz, MeOD) δ 7.70−7.67 (m, 2H), 7.46 −7.42 (m, 2H), 3.97 (dt, J = 6.9, 3.4 Hz, 1H), 3.83 (td, J = 6.5, 3.6 Hz, 1H), 3.47 (dd, J = 6.5, 3.1 Hz, 1H), 3.33 (dt, J = 3.3, 1.6 Hz, 1H), 3.20 (dd, J = 11.7, 3.3 Hz, 1H), 3.05 (ddd, J = 15.1, 11.6, 5.4 Hz, 2H), 2.83 (dd, J = 11.8, 6.4 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, MeOD) δ 145.26, 134.66, 130.81, 128.80, 73.27, 68.99, 67.60, 49.57, 49.33, 21.46 ppm; HRMS (ESI) calcd for $C_{12}H_{18}NO_5S$ [M + H$^+$] 288.0900, found 288.0901.

*(±)-Piperidine-3,4,5-triol (**31**).* In a 10 mL flask were added sodium metal (0.12 g, 5.0 mmol) and naphthalene (0.72 g, 5.5 mmol) dissolved in dry THF (1.5 mL). The mixture was stirred until the solution became dark green. A further solution was prepared by dissolving the (±)-1-tosylpiperidine-3,4,5-triol (**30**) (1.0 eq., 0.077 mmol, 22 mg) in 320 μL of THF and cooled to −78 °C. Next, the sodium/naphthalene solution was added dropwise into the solution of **39** until the dark green color persisted for 5 min. Then, 2−3 drops of water were added (until the green color disappear), the reaction was diluted with ether (20 mL), dried with Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The product was passed through a column with Dowex and was then purified by flash chromatography (1:1 methanol/ethyl acetate) to give the pure piperidine **30** (6.6 mg, 0.077 mmol, 65% yield): ^{1}H NMR (400 MHz, D_2O, reference acetone δ 2.22) δ 3.99 (m, 1H), 3.77 (m, 1H), 3.57 (dd, J = 8.8, 3.2 Hz, 1H), 3.06 (ddd, J = 13.2, 4.8, 1.2 Hz, 1H), 2.92 (ddd, J = 14.0, 4.0, 1.2 Hz, 1H), 2.69 (dd, J = 14.0, 2.0 Hz, 1H), 2.37 (dd, J = 13.2, 9.6, 1H) ppm; ^{13}C NMR (100 MHz, D_2O; reference acetone δ 215.9) δ 74.0, 68.9, 68.6, 48.8, 48.4. Spectroscopic data is in accordance with those published in the literature.[22,26]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of all new compounds, N−H insertion reaction studies, chiral HPLC studies, and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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