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PAPER

Reductive hydroxyalkylation/alkylation of amines with lactones/esters†

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We have developed a one-pot method for the direct intermolecular reductive hydroxyalkylation or alkylation of amines using lactones or esters as the hydroxyalkylating/alkylating reagents. The method is based on the *in situ* amidation of lactones/esters with DIBAL-H–amine complex (for primary amines) or DIBAL-H–amine hydrochloride salt complex (for secondary amines), followed by reduction of the amides with an excess of DIBAL-H. Different from the reduction of Weinreb amides with DIBAL-H where aldehydes are formed, the reduction of the *in situ* formed Weinreb amides yielded amines. Moreover, this method is not limited to Weinreb amides, instead, it also works for *other* amides in general. A plausible mechanism is suggested to account for the outcome of the reactions.

Introduction

Amines are an important class of compounds in organic chemistry, which constitute a major body of natural products (alkaloids) and pharmaceutical agents.[1] For the preparation of higher order amines, the monoalkylation of primary or secondary amines with halides is a logic but problematic method[2,3] due to the well-known over-alkylation (Scheme 1, route A).[2a] As a result, many indirect methods[4] have been developed for the monoalkylation of amines, which include the classic Gabriel synthesis of primary amines,[5] alkylation involving *N*-protection and deprotection,[6] addition to imines,[7] reductive amination of aldehydes or ketones (Scheme 1, route B),[8] and reduction[9] or reductive alkylation of amides (Scheme 1, route C).[10] On the other hand, lactones and esters are a class of stable, easily available and environmentally friendly starting materials.[11,12] Their uses for amines synthesis are usually related to stepwise procedures.[13] Only a single instance of one-step synthesis[14] has been reported, which involved a low-yield (<35%) intramolecular reductive alkylation of lactam-ester.[14a] In continuation with our endeavor[3b,10a,b,15] to develop step-economical synthetic methods,[16] a one-pot synthesis[17] of hydroxyalkylated amines/amines by reductive (hydroxy)alkylation of amines with lactones/esters (Scheme 1, route D) was undertaken. We now report the results of this investigation. It is worth noting that hydroxyalkyl carbinamines constitutes a group of multi-functionalized compounds of multi-uses.[8b,18]

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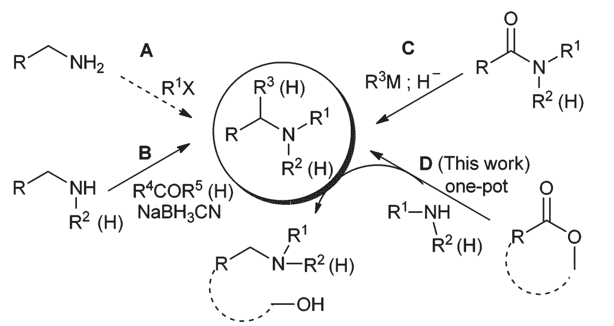
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/c2ob25901j



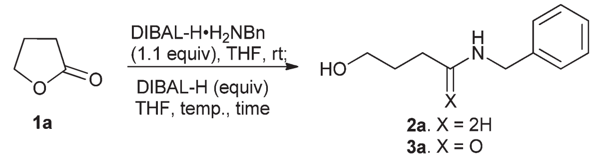
Scheme 1 Typical known (routes A to C) and Present (route D) synthetic approaches to secondary and tertiary amines.

Results and discussion

The investigation stemmed from the amide synthesis developed from our laboratory, namely, the amidation of lactones/esters with DIBAL-H–amine complex or DIBAL-H–amine hydrochloride salt complex.[19] The reductive hydroxyalkylation of benzylamine with lactone **1a** was selected as a model reaction and the results are outlined in Table 1. The optimal protocol was identified as successive treatment of lactone **1a** with 1.1 equiv of DIBAL-H–benzylamine complex in THF at rt, and 5.0 equiv of DIBAL-H at rt (Table 1, entry 4).

With the optimal reaction conditions defined, the reductive alkylations of amines with other lactones were investigated. As outlined in Table 2, the reductive alkylation of primary amines with different lactones gave the corresponding hydroxyalkylated secondary amines in good yields (entries 1–8). For the reductive hydroxyalkylation of allylamine, portion-wise addition of 8.0 equiv of DIBAL-H with prolonged reaction time (48 h) was necessary to ensure a decent yield (Table 2, entries 9, 10). For the reductive alkylation of secondary amines, use of its

Table 1 Investigation on the conditions for the reductive 4-hydroxybutylation of benzylamine with γ-butyrolactone



Entry	DIBAL-H (equiv)	Temp. (°C)	Time (h)	% Yield[a] 2a	3a
1	3.2	0	5	—	—
2	3.2	rt	24	54	32
3	4	rt	24	76	9
4	5	rt	3	90	0
5	5	50	1	87	0

[a] Isolated yield.

hydrochloride salt–DIBAL-H complex was essential in the amidation step,[19] and the subsequent reduction reaction proceeded smoothly to give the corresponding tertiary amines (entries 11–14). Remarkably, in contrast with the reaction of the Weinreb amides and DIBAL-H, which gave aldehydes as the reduction products,[20] reaction of the Weinreb amides, generated *in situ* from lactones **1a**/**1c** and DIBAL-H–*N*-methyl-*N*-methoxyamine hydrochloride salt complex, yielded the reductive hydroxyalkylated amines (entries 13, 14).

In view of future application of this method for the synthesis of natural products, the reaction with chiral and commercially unavailable lactones was envisioned. Among a number of methods available for the synthesis of lactones,[11,12] the SmI_2-mediated[21] one-pot reductive coupling of a ketone with an α,β-unsaturated ester was a straightforward and versatile one.[22] Lactone 1-oxaspiro[4.5]decan-2-one (**1e**) was thus synthesized by SmI_2-mediated one-pot reductive coupling[22b] of cyclohexanone with methyl acrylate (76% yield), and subjected to the reaction with benzylamine to give the desired hydroxyalkylated amine **2o** in 78% yield (entry 15). The reductive hydroxyalkylation of benzylamine with (*R*)-β-methyl-γ-butyrolactone (**1f**), a chiron easily available from degeneration of Tigogenin,[23] led to hydroxyalkylated amine (*R*)-**2p** in 83% yield (entry 16).

This one-pot method can also be applied to the reductive alkylation of amines with esters. As can be seen from entries 17, 18 (Table 2), reductive alkylation of primary or secondary amines gave smoothly the corresponding secondary or tertiary amines in comparable yields. The reaction of diethylamine with enantiomerically pure ester **1h**, another chiron easily available in kilogram scale,[24] produced the desired amine **2s** in 58% yield (entry 19). Finally, reductive alkylation of benzylamine with ester **1i** produced the amine **2t** in 60% yield (entry 20).

A plausible mechanism for the one-pot reductive alkylation of amines with lactones/esters is suggested in Scheme 2. The carbonyl group of the *in situ* formed amide chelates with two molecules of DIBAL-H to form intermediate **A**, which undergoes an intramolecular hydride delivery to yield intermediate **B**. Intermediate **B** is prone to *N*-lone pair assisted elimination to generate an iminium species **C**. Reduction of **C** with a third molecule of DIBAL-H produced complex **D**, which after workup, gave amine product eventually.

Conclusions

In summary, a one-pot method for the intermolecular reductive hydroxyalkylation/alkylation of amines using lactones/esters as the hydroxyalkylating/alkylating reagents has been developed. This method can be used for direct synthesis of either secondary or tertiary amines depending on the starting amines used. Moreover, in view of the current interest in the direct reductive alkylation of amides,[10] the capture of the presumed *in situ* formed iminium ion intermediate **C** (Scheme 2) by a carbon-centered nucleophile would led to a C–C bond formation, and provide a direct method for the synthesis of *sec*-alkylcarbinamines from amines and lactones/esters.

Experimental section

General method

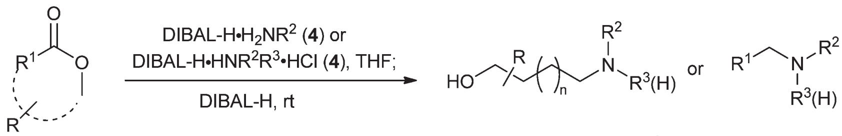
Melting points were uncorrected. HRFABMS spectra were recorded on a 7.0T FT-MS instrument. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm and referenced to residual solvent or solvent signals ($CDCl_3$, 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR; CD_3CN, 1.94 ppm for ^1H NMR and 118.3 ppm for ^{13}C NMR). Silica gel (300–400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with ethyl acetate–hexane mixture. THF was distilled over sodium benzophenone ketyl under N_2.

Typical procedure for the reductive hydroxyalkylation/alkylation of amines using lactones/esters

Under a nitrogen atmosphere, to a solution of γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) in THF (3.5 mL) was added DIBAL-H·H_2NBn complex (1.1 mmol), prepared[19] from DIBAL-H (1 M in hexane, 1.1 mL, 1.1 mmol) and benzylamine (0.12 mL, 1.1 mmol) in THF (0.4 mL) at rt. After being stirred for 30 min, the mixture was cooled to 0 °C, and DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) was added dropwise. The resulting mixture was stirred at rt. After a complete conversion of the amide intermediate as indicated by TLC monitoring (3 h), the reaction was quenched carefully with MeOH (0.5 mL) at 0 °C, and diluted with THF (10 mL). To the mixture was added 5 mL of a saturated aqueous solution of potassium sodium tartrate and stirred vigorously for 3 h before being extracted with Et_2O (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2–MeOH = 10 : 1 containing 1% ammonia) to give 4-hydroxybutylamine **2a**[25a] (162 mg, 90%).

***N*-Benzyl-4-hydroxybutan-1-amine (2a).** Colorless oil. ν/cm^{-1} (film) 3292, 3062, 3028, 2931, 2858, 1645, 1603, 1547, 1495, 1453, 1037, 1058, 1029, 738, 699. δ_H (400 MHz, $CDCl_3$)

Table 2 Reductive ω-hydroxyalkylation/alkylation of amines with ω-lactones/esters



1 **2a-s**

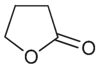
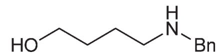
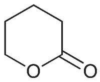
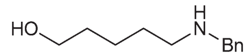
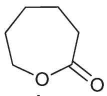
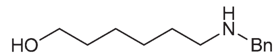
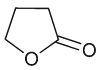
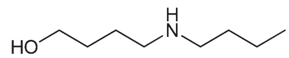
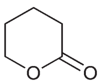
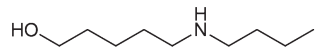
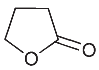
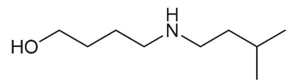
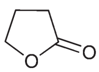
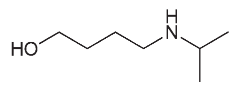
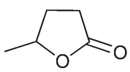
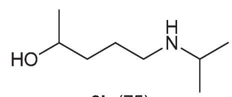
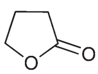
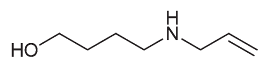
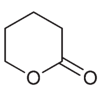
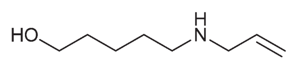
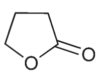
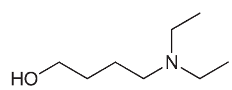
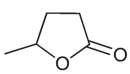
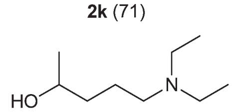
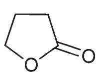
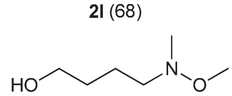
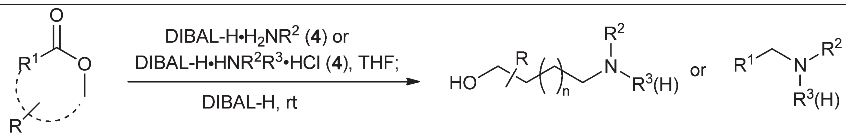
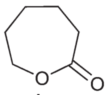
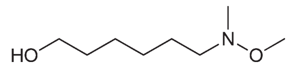
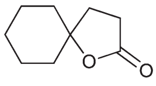
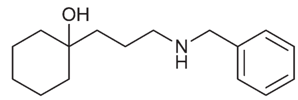
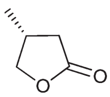
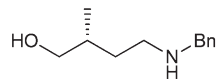
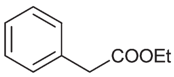
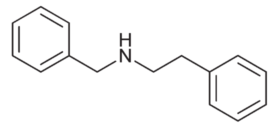
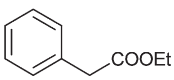
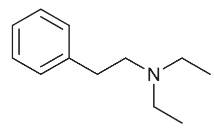
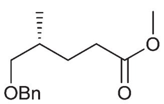
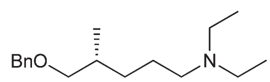
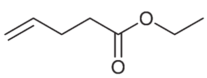
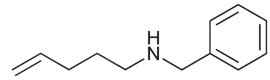
Entry	Ester	**4**/Temp./time (equiv/°C/h)	DIBAL-H/temp./time (equiv/°C/h)	Product **2**[a] (%Yield)
1	 **1a**	1.1/rt/0.5	5/rt/3	 **2a** (90)
2	 **1b**	1.1/rt/0.5	5/rt/4	 **2b** (92)
3	 **1c**	1.1/rt/0.5	7/rt/6	 **2c** (87)
4	 **1a**	2.5/rt/0.5	5/rt/23	 **2d** (83)
5	 **1b**	2.5/rt/0.5	5/rt/24	 **2e** (85)
6	 **1a**	2.5/rt/0.5	6/rt/20	 **2f** (73)
7	 **1a**	2.5/rt/0.5	6/rt/17	 **2g** (81)
8	 **1d**	2.5/rt/0.5	6/rt/17	 **2h** (75)
9	 **1a**	2.5/rt/0.5	8/rt/48	 **2i** (72) + **3b** (13)[b]
10	 **1b**	2.5/rt/0.5	8/rt/48	 **2j** (67) + **3c** (8)[b]
11	 **1a**	2/rt/0.5	5/rt/1	 **2k** (71)
12	 **1d**	2/rt/0.5	5/rt/1	 **2l** (68)
13	 **1a**	2/rt/0.5	4/0/0.5	 **2m** (68)

Table 2 *(Contd.)*



1 **2a-s**

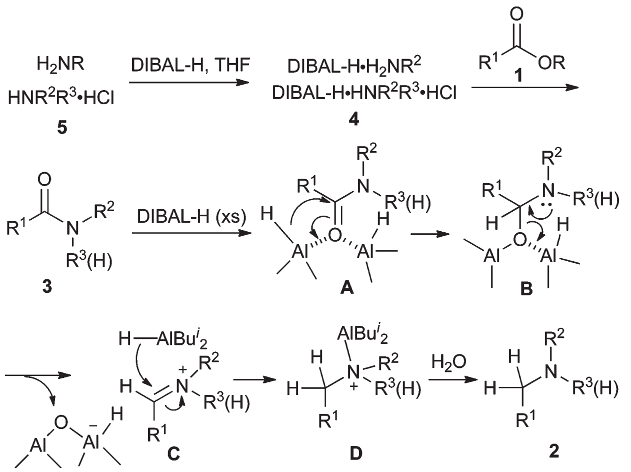
Entry	Ester	**4**/Temp./time (equiv/°C/h)	DIBAL-H/temp./time (equiv/°C/h)	Product **2**[a] (%Yield)
14	 **1c**	2/rt/0.5	4/0/0.5	 **2n** (66) + **6** (22)[c]
15	 **1e**	1.5/rt/0.5	6/rt/5	 **2o** (78)
16	 **1f**	1.2/rt/0.5	5/rt/5	 **2p** (83)
17	 **1g**	5/50/2	6/rt/48	 **2q** (76) + **3d** (10)[b]
18	 **1g**	5/50/2	5/rt/1	 **2r** (66)
19	 **1h**	5/rt/2	6/rt/5	 **2s** (58)
20	 **1i**	2/rt/0.5	6/rt/48	 **2t** (60)

[a] Isolated yield. [b] Yield of the amide intermediate **3**. [c] Yield of side product 1,6-hexanediol **6**.

1.68–1.56 (4H, m, CH_2), 2.65 (2H, t, J = 5.8 Hz, NCH_2), 3.55 (2H, s br, OH and NH), 3.56 (2H, t, J = 6.8 Hz, OCH_2), 3.75 (2H, s, NCH_2Ph), 7.34–7.21 (5H, m, Ph). δ_C (100 MHz, $CDCl_3$), 27.9 (CH_2), 31.8 (CH_2), 49.0 (NCH_2), 53.6 (NCH_2Ph), 62.2 (OCH_2), 127.0, 128.1, 128.3, 139.2. MS (ESI, m/z): 180 (M + H^+). HRMS (ESI, m/z) [M + H^+] Calculated for $C_{11}H_{18}NO_2^+$ 180.1383, found: 180.1378.

***N*-Benzyl-4-hydroxybutanamide (3a).**[19] White solid. mp 73–74 °C. ν/cm^{-1} (film) 3297, 3085, 2921, 2871, 1640, 1549, 1453, 1422, 1379, 1275, 1059, 1015, 731, 696. δ_H (400 MHz, $CDCl_3$) 1.81 (2H, pentet, J = 6.2 Hz, CH_2), 2.31 (2H, t, J = 6.9 Hz, CH_2CO), 3.59 (2H, dd, J = 10.4, 5.4 Hz, CH_2O), 3.74 (1H, t, J = 4.7 Hz, OH), 4.35 (2H, d, J = 5.7 Hz, NCH_2Ph), 6.69 (1H, s br, NH), 7.32–7.20 (5H, m). δ_C (100 MHz, $CDCl_3$) 28.1 (CH_2), 33.5 (CH_2CO), 43.5 (NCH_2Ph), 61.9 (CH_2OH), 127.3, 127.6, 128.6, 138.1, 173.6 (CO). MS (ESI, m/z): 216 (M + Na^+).

***N*-Benzyl-5-hydroxypentan-1-amine (2b).** Following the typical procedure, the reaction of the amide generated *in situ* from ω-valerolactone **1b** (0.095 mL, 1.0 mmol) and DIBAL-H·H_2NBn (1.1 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2b**[25b] (177 mg, 92%) as a colorless oil. ν/cm^{-1} (film) 3350, 3062, 3028, 2931, 2857, 1643, 1602, 1548, 1495, 1453, 1383, 1075, 1054, 745, 699. δ_H (400 MHz, $CDCl_3$) 1.41–1.33 (2H, m, CH_2), 1.52 (4H, pentet, J = 7.1 Hz, CH_2CH_2), 2.61 (2H, t, J = 7.1 Hz, NCH_2), 2.78 (2H, s br, OH and NH), 3.55 (2H, t, J = 6.4 Hz, OCH_2), 3.76 (2H, s,



Scheme 2 Plausible mechanism for the one-pot reductive alkylation of amines with lactones/esters.

NCH_2Ph), 7.32–7.21 (5H, m, Ph). δ_C (100 MHz, $CDCl_3$) 23.3 (CH_2), 29.3 (CH_2), 32.3 (CH_2), 48.9 (NCH_2Ph), 53.7 (NCH_2), 61.9 (OCH_2), 126.9, 128.1, 128.3, 139.6. MS (ESI, *m/z*): 194 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{12}H_{20}NO^+$ 194.1539, found: 194.1533.

***N*-Benzyl-6-hydroxyhexan-1-amine (2c).** Following the typical procedure, the reaction of the amide generated *in situ* from ε-caprolactone **1c** (0.110 mL, 1.0 mmol) and DIBAL-H·H_2NBn (1.1 mmol), with DIBAL-H (1.0 M in hexane, 7.0 mL, 7.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2c**[25c] (179 mg, 87%) as a colorless oil. ν/cm^{-1} (film) 3295, 3062, 3027, 2929, 2855, 1642, 1603, 1581, 1495, 1454, 1380, 1058, 737, 699. δ_H (400 MHz, $CDCl_3$) 1.36–1.29 (4H, m, CH_2CH_2), 1.51 (4H, app. pentet, *J* = 7.1 Hz, CH_2CH_2), 2.60 (2H, t, *J* = 7.3 Hz, NCH_2), 2.87 (2H, s br, OH and NH), 3.53 (2H, t, *J* = 6.6 Hz, OCH_2), 3.76 (2H, s, NCH_2Ph), 7.31–7.20 (5H, m, Ph). δ_C (100 MHz, $CDCl_3$) 25.5 (CH_2), 26.9 (CH_2), 29.5 (CH_2), 32.5 (CH_2), 48.9 (NCH_2), 53.6 (NCH_2Ph), 62.0 (OCH_2), 126.8, 128.0, 128.2, 139.5. MS (ESI, *m/z*): 208 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{13}H_{22}NO^+$ 208.1696, found: 208.1696.

***N*-Butyl-4-hydroxybutan-1-amine (2d).** Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·H_2N*n*-Bu (2.5 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2d**[25d] (120 mg, 83%) as a colorless oil. ν/cm^{-1} (film) 3372, 3286, 2956, 2931, 2871, 1644, 1537, 1466, 1416, 1377, 1309, 1116, 1072. δ_H (400 MHz, $CDCl_3$) 0.83 (3H, t, *J* = 7.3 Hz, CH_3), 1.26 (2H, sextet, *J* = 6.9 Hz, CH_2), 1.41 (2H, pentet, *J* = 6.9 Hz, CH_2), 1.62–1.50 (4H, m, CH_2CH_2), 2.54 (2H, t, *J* = 7.3 Hz, NCH_2), 2.57 (2H, t, *J* = 5.6 Hz, NCH_2), 3.48 (2H, t, *J* = 4.9 Hz, OCH_2), 4.00 (2H, s br, OH and NH). δ_C (100 MHz, $CDCl_3$) 13.7 (CH_3), 20.2 (CH_2), 28.2 (CH_2), 31.5 (CH_2), 32.1 (CH_2), 49.0 (NCH_2), 49.4 (NCH_2), 62.2 (OCH_2). MS (ESI, *m/z*): 146 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_8H_{20}NO^+$ 146.1539, found: 146.1542.

***N*-Butyl-5-hydroxypentan-1-amine (2e).** Following the typical procedure, the reaction of the amide generated *in situ* from ω-valerolactone **1b** (0.095 mL, 1.0 mmol) and DIBAL-H·H_2N*n*-Bu (2.5 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2e**[25e] (135 mg, 85%) as a colorless oil. ν/cm^{-1} (film) 3372, 3286, 2931, 2860, 1634, 1537, 1466, 1414, 1377, 1307, 1117, 1058. δ_H (400 MHz, $CDCl_3$) 0.85 (3H, t, *J* = 7.3 Hz, CH_3), 1.53–1.21 (10H, m, CH_2CH_2), 2.52 (4H, app. q, *J* = 7.0 Hz, NCH_2), 2.71 (2H, s br, OH and NH), 3.50 (2H, t, *J* = 6.5 Hz, OCH_2). δ_C (100 MHz, $CDCl_3$) 13.8 (CH_3), 20.3 (CH_2), 23.4 (CH_2), 29.4 (CH_2), 31.9 (CH_2), 32.4 (CH_2), 49.5 (NCH_2), 49.6 (NCH_2), 61.8 (OCH_2). MS (ESI, *m/z*): 160 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_9H_{22}NO^+$ 160.1696, found: 160.1694.

***N*-(4-Hydroxybutyl)-3-methylbutan-1-amine (2f).** Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·$H_2NCH_2CH_2CH(CH_3)_2$ (2.5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2f** (116 mg, 73%) as a colorless oil. ν/cm^{-1} (film) 3383, 3289, 2955, 2929, 1870, 1644, 1537, 1469, 1416, 1382, 1367, 1307, 1115, 1071. δ_H (400 MHz, $CDCl_3$) 0.85 (6H, d, *J* = 6.6 Hz, CH_3), 1.35 (2H, app. q, *J* = 7.4 Hz, CH_2), 1.66–1.54 (5H, m, CH_2CH_2 and *CH*Me_2), 2.63–2.56 (4H, m, NCH_2), 3.52 (2H, t, *J* = 4.8 Hz, OCH_2), 3.70 (2H, s br, OH and NH). δ_C (100 MHz, $CDCl_3$) 22.5 (Me), 26.0 (*CH*Me_2), 28.7 (CH_2), 32.5 (CH_2), 38.7 (CH_2), 47.6 (NCH_2), 49.7 (NCH_2), 62.4 (OCH_2). MS (ESI, *m/z*): 160 (M + H^+). HRMS (ESI, *m/z*) Calculated for [M + H^+] $C_9H_{22}NO^+$ 160.1695, found: 160.1696.

4-Hydroxy-*N*-isopropylbutan-1-amine (2g). Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·i-PrNH_2 (2.5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2g**[25f] (107 mg, 81%) as a colorless oil. ν/cm^{-1} (film) 3363, 3277, 2965, 2933, 2865, 1644, 1470, 1383, 1364, 1339, 1175, 1134, 1060. δ_H (400 MHz, $CDCl_3$) 1.05 (6H, d, *J* = 6.3 Hz, Me), 1.67–1.59 (4H, m, CH_2CH_2), 2.60 (2H, t, *J* = 5.8 Hz, NCH_2), 2.77 (1H, septet, *J* = 6.3 Hz, NCH), 3.44 (2H, s br, OH and NH), 3.53 (2H, t, *J* = 4.9 Hz, OCH_2). δ_C (100 MHz, $CDCl_3$) 22.5 (Me), 29.1 (CH_2), 32.4 (CH_2), 46.9 (NCH_2), 48.7 (NCH), 62.3 (OCH_2). MS (ESI, *m/z*): 132 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_7H_{18}NO^+$ 132.1383, found: 132.1390.

4-Hydroxy-*N*-isopropylpentan-1-amine (2h). Following the typical procedure, the reaction of the amide generated *in situ* from γ-valerolactone **1d** (0.095 mL, 1.0 mmol) and DIBAL-H·H_2Ni-Pr (2.5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2h**[25g] (109 mg, 75%) as a colorless oil. ν/cm^{-1} (film) 3367, 3277, 2966, 2929, 2868, 1647, 1469, 1383, 1370, 1339, 1174, 1126, 1090. δ_H (400 MHz, $CDCl_3$) 1.03 (3H, d, *J* = 6.3 Hz, NCH*Me*), 1.04 (3H, d, *J* = 6.3 Hz, NCH*Me*), 1.12

(3H, d, J = 6.0 Hz, OCH*Me*), 1.46–1.31 (2H, m, CH_2), 1.78–1.60 (2H, m, CH_2), 2.51–2.43 (1H, m, NCH), 2.78–2.71 (2H, m, NCH_2), 3.71–3.62 (1H, m, OCH), 3.79 (2H, s br, OH and NH). δ_C (100 MHz, $CDCl_3$) 22.2 (NCH*Me*), 22.6 (NCH*Me*), 23.6 (OCH*Me*), 27.8 (CH_2), 39.0 (CH_2), 47.1 (NCH), 48.7 (NCH_2), 67.2 (OCH). MS (ESI, *m*/*z*): 146 (M + H^+). HRMS (ESI, *m*/*z*) [M + H^+] Calculated for $C_8H_{20}NO^+$ 146.1539, found: 146.1541.

***N*-Allyl-4-hydroxybutAN-1-amine (2i).** Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·$H_2NCH_3CH{=}CH_2$ (2.5 mmol), with DIBAL-H (1.0 M in hexane, 8.0 mL, 8.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2i**[25h] (93 mg, 72%), along with 13% of the amide intermediate **3b**. **2i**: yellow oil. ν/cm^{-1} (film) 3372, 3288, 3078, 2933, 2862, 1644, 1548, 1453, 1377, 1187, 1108, 1060, 996, 919. δ_H (400 MHz, $CDCl_3$) 1.62–1.51 (4H, m, CH_2CH_2), 2.58 (2H, t, J = 5.9 Hz, NCH_2), 3.18 (2H, app. dt, J = 6.1, 1.3 Hz, N*CH_2*CH=), 3.50 (2H, t, J = 6.7 Hz, OCH_2), 3.50 (2H, s br, OH and NH), 5.04 (1H, ddd, J = 10.2, 2.7, 1.2 Hz, CH=), 5.11 (1H, ddd, J = 17.2, 3.2, 1.6 Hz,=CH_2), 5.82 (1H, ddt, J = 16.4, 10.2, 6.1 Hz,=CH_2). δ_C (100 MHz, $CDCl_3$) 28.0 (CH_2), 31.9 (CH_2), 48.8 (NCH_2), 51.8 (N*CH_2*CH=), 62.2 (OCH_2), 116.4 (=CH_2), 135.8 (=CH). MS (ESI, *m*/*z*): 130 (M + H^+). HRMS (ESI, *m*/*z*) [M + H^+] Calculated for $C_7H_{16}NO^+$ 130.1226, found: 130.1234.

***N*-Allyl-4-hydroxybutanamide (3b).**[25i] White solid. mp 72–74 °C. δ_H (400 MHz, $CDCl_3$) 1.83 (2H, app. pentet, J = 6.4 Hz, CH_2), 2.33 (2H, t, J = 7.0 Hz, CH_2CO), 3.62 (2H, t, J = 5.8 Hz, NCH_2), 3.69 (1H, s br, OH), 3.81 (2H, app. t, J = 5.6 Hz, OCH_2), 5.06–5.18 (2H, m,=CH_2), 5.84–5.72 (1H, m,=CH), 6.57 (1H, s br, NH). δ_C (100 MHz, $CDCl_3$) 28.2 (CH_2), 33.5 (*CH_2*CO), 41.9 (NCH_2), 61.8 (OCH_2), 116.2 (=CH_2), 134.0 (=CH), 173.6 (CO). ν/cm^{-1} (film) 3299, 3086, 2924, 2872, 1650, 1642, 1552, 1421, 1384, 1261, 1058, 922. MS (ESI, *m*/*z*) 166 (M + Na^+).

***N*-Allyl-5-hydroxypentan-1-amine (2j).** Following the typical procedure, the reaction of the amide generated *in situ* from ω-valerolactone **1b** (0.095 mL, 1.0 mmol) and DIBAL-H·$H_2NCH_3CH{=}CH_2$ (2.5 mmol), with DIBAL-H (1.0 M in hexane, 8.0 mL, 8.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2j** (97 mg, 67%), along with 8% of the amide intermediate **3c**. **2j**: yellow oil. ν/cm^{-1} (film) 3293, 3083, 2930, 2867, 1641, 1548, 1421, 1383, 1262, 1158, 1056, 988, 920. δ_H (400 MHz, $CDCl_3$) 1.37–1.32 (2H, m, CH_2), 1.47 (4H, app. septet, J = 7.1 Hz, CH_2CH_2), 2.53 (2H, t, J = 7.1 Hz, NCH_2), 2.57 (2H, s br, OH and NH), 3.16 (2H, app. dt, J = 6.1, 1.6 Hz, N*CH_2*CH=), 3.51 (2H, t, J = 6.5 Hz, OCH_2), 5.02 (1H, ddd, J = 10.2, 2.6, 1.1 Hz,=CH_2), 5.09 (1H, ddd, J = 17.2, 3.2, 1.5 Hz,=CH_2), 5.82 (1H, ddt, J = 16.4, 10.2, 6.1 Hz, CH). δ_C (100 MHz, $CDCl_3$) 23.4 (CH_2), 29.4 (CH_2), 32.4 (CH_2), 49.0 (NCH_2), 52.2 (N*CH_2*CH=), 61.8 (OCH_2), 116.0 (=CH_2), 136.3 (=CH). MS (ESI, *m*/*z*): 144 (M + H^+). HRMS (ESI, *m*/*z*) [M + H^+] Calculated for $C_8H_{18}NO^+$ 144.1383, found: 144.1385.

***N*-Allyl-5-hydroxypentanamide (3c).**[25i] White solid. mp 68–70 °C. ν/cm^{-1} (film) 3293, 3083, 2930, 2867, 1641, 1548, 1422, 1384, 1261, 1158, 1058, 988, 921. δ_H (400 MHz, $CDCl_3$) 1.55 (2H, app. dt, J = 14.1, 6.1 Hz, CH_2), 1.70 (2H, pentet, J = 7.3 Hz, CH_2), 2.22 (2H, t, J = 7.3 Hz, CH_2CO), 3.19 (1H, s br, OH), 3.59 (2H, t, J = 5.8 Hz, OCH_2), 3.82 (2H, app. tt, J = 5.7, 1.4 Hz, NCH_2), 5.06–5.18 (2H, m,=CH_2), 5.73–5.85 (1H, m,=CH), 6.26 (1H, s br, NH). δ_C (100 MHz, $CDCl_3$) 21.8 (CH_2), 31.8 (CH_2), 35.9 (CH_2CO), 41.8 (NCH_2), 61.7 (OCH_2), 116.2 (=CH_2), 134.2 (=CH), 173.3 (CO). MS (ESI, *m*/*z*) 180 (M + Na^+).

***N*,*N*-Diethyl-4-hydroxybutan-1-amine (2k).** Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·$HNEt_2$·HCl (2 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2k**[25j] (103 mg, 71%) as a colorless oil. ν/cm^{-1} (film) 3388, 2970, 2935, 2872, 2817, 1653, 1469, 1382, 1293, 1199, 1065. δ_H (400 MHz, $CDCl_3$) 1.00 (6H, t, J = 7.2 Hz, Me), 1.63–1.59 (4H, m, CH_2CH_2), 2.39–2.36 (2H, m, NCH_2), 2.51 (4H, q, J = 7.2 Hz, N*CH_2*Me), 3.52–3.49 (2H, m, OCH_2). δ_C (100 MHz, $CDCl_3$) 10.6 (Me), 26.3 (CH_2), 32.7 (CH_2), 46.1 (N*CH_2*Me), 53.3 (NCH_2), 62.5 (OCH_2). MS (ESI, *m*/*z*): 146 (M + H^+). HRMS (ESI, *m*/*z*) [M + H^+] Calculated for $C_8H_{20}NO^+$ 146.1539, found: 146.1541.

***N*,*N*-Diethyl-4-hydroxypentan-1-amine (2l).** Following the typical procedure, the reaction of the amide generated *in situ* from γ-valerolactone **1b** (0.095 mL, 1.0 mmol) and DIBAL-H·$HNEt_2$·HCl (2 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2l**[25k] (108 mg, 68%) as a colorless oil. ν/cm^{-1} (film) 3408, 2975, 2938, 2798, 1648, 1475, 1385, 1190, 1122, 1058. δ_H (400 MHz, $CDCl_3$) 1.02 (6H, t, J = 7.2 Hz, CH_2*Me*), 1.13 (3H, d, J = 6.2 Hz, CH*Me*), 1.39–1.29 (1H, m, CH_2), 1.77–1.52 (3H, m, CH_2), 2.50–2.36 (4H, m, N*CH_2*Me), 2.66–2.57 (2H, m, NCH_2), 3.71–3.63 (1H, m, OCH). δ_C (100 MHz, $CDCl_3$) 10.6 (CH_2*Me*), 23.8 (CH_2), 24.9 (CH*Me*), 39.5 (CH_2), 46.0 (N*CH_2*Me), 53.7 (NCH_2), 67.3 (OCH). MS (ESI, *m*/*z*) 160 (M + H^+). HRMS (ESI, *m*/*z*) [M + H^+] Calculated for $C_8H_{20}NO^+$ 160.1696, found: 160.1699.

4-Hydroxy-*N*-methoxy-*N*-methylbutan-1-amine (2m). Following the typical procedure, the reaction of the amide generated *in situ* from γ-butyrolactone **1a** (0.076 mL, 1.0 mmol) and DIBAL-H·$HN(OCH_3)CH_3$·HCl (2 mmol), with DIBAL-H (1.0 M in hexane, 4.0 mL, 4.0 mmol) produced, after flash column chromatography (eluent: EtOAc–hexane = 5 : 1, v/v), **2m** (91 mg, 68%) as a colorless oil. ν/cm^{-1} (film) 3400, 2941, 2871, 1462, 1383, 1049, 998. δ_H (400 MHz, $CDCl_3$) 1.62 (4H, s, CH_2CH_2), 2.54 (3H, s, NMe), 2.62 (2H, s br, NCH_2), 3.50 (3H, s, OMe), 3.59 (2H, t, J = 5.5 Hz, OCH_2). δ_C (100 MHz, $CDCl_3$) 24.7 (CH_2), 31.4 (CH_2), 44.7 (NMe), 59.6 (OMe), 60.6 (OCH_2), 62.6 (NCH_2). MS (ESI, *m*/*z*) 156 (M + Na^+). HRMS (ESI, *m*/*z*) [M + Na^+] Calculated for $C_6H_{15}NNaO_2^+$ 156.0995, found: 156.0997.

6-Hydroxy-*N*-methoxy-*N*-methylhexan-1-amine (2n). Following the typical procedure, the reaction of the amide generated *in situ* from ε-caprolactone **1c** (0.110 mL, 1.0 mmol) and DIBAL-H·HN(OCH_3)CH_3·HCl (2 mmol), with DIBAL-H (1.0 M in hexane, 4.0 mL, 4.0 mmol) produced, after flash column chromatography (eluent: EtOAc–hexane = 5 : 1, v/v), **2n** (106 mg, 66%), along with 22% of the 1,6-hexanediol **6**. **2n**: colorless oil. ν/cm^{-1} (film) 3369, 2936, 2859, 1647, 1464, 1441, 1379, 1049. δ_H (400 MHz, $CDCl_3$) 1.28–1.38 (4H, m, CH_2CH_2) 1.56–1.46 (4H, m, CH_2CH_2), 2.35 (1H, s br, OH), 2.50 (3H, s, NMe), 2.54 (2H, t, J = 7.8 Hz, NCH_2), 3.45 (3H, s, OMe), 3.56 (2H, t, J = 6.6 Hz, OCH_2). δ_C (100 MHz, $CDCl_3$) 25.3 (CH_2), 25.6 (CH_2), 27.1 (CH_2), 32.5 (CH_2), 45.1 (NMe), 59.9 (OMe), 60.7 (OCH_2), 62.5 (NCH_2). MS (ESI, *m/z*) 162 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_8H_{20}NO_2^+$ 162.1489, found: 162.1488.

***N*-Benzyl-3-(1-hydroxycyclohexyl)pentan-1-amine (2o).** 1-Oxaspiro[4.5]decan-2-one **1e** was synthesized by SmI_2-mediated reductive coupling[22b] of cyclohexanone with methyl acrylate (yield: 76%).

Following the typical procedure, the reaction of the amide generated *in situ* from 1-oxaspiro[4.5]decan-2-one **1e** (154 mg, 1.0 mmol) and DIBAL-H·H_2NBn (1.5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2o** (193 mg, 76%) as a colorless oil. ν/cm^{-1} (film) 3389, 3081, 3062, 3027, 2930, 2855, 1602, 1494, 1452, 1261, 1105, 1028, 969, 737, 698. δ_H (400 MHz, CD_3CN) 1.66–1.22 (14H, m, CH_2CH_2), 2.58 (2H, t, J = 6.4 Hz, NCH_2), 3.30 (2H, s br, OH and NH), 3.73 (2H, s, NCH_2Ph), 7.36–7.24 (5H, m, Ph). δ_C (100 MHz, CD_3CN) 23.2 (CH_2), 24.0 (CH_2), 27.0 (CH_2), 38.6 (CH_2), 50.7 (NCH_2), 54.2 (NCH_2Ph), 70.6 (C), 127.9, 129.3 (2C), 141.2. MS (ESI, *m/z*) 248 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{16}H_{26}NO^+$ 248.2009, found: 248.2008.

(*R*)-*N*-Benzyl-4-hydroxy-3-methylbutan-1-amine (2p). Following the typical procedure, the reaction of the amide generated *in situ* from (*R*)-3-methyl-γ-butyrolactone **1f** (100 mg, 1.0 mmol), easily available from degeneration of Tigogenin,[23] and DIBAL-H·H_2NBn complex (1.2 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 10 : 1, v/v, containing 1% aqueous ammonia), **2p** (159 mg, 83%) as a colorless oil. $[\alpha]_D^{20}$ +16.2 (*c* 1.0 in $CHCl_3$). ν/cm^{-1} (film) 3295, 3087, 3063, 3028, 2924, 2871, 1495, 1455, 1381, 1045, 744, 699. δ_H (400 MHz, $CDCl_3$) 0.87 (3H, d, J = 6.9 Hz, Me), 1.50–1.40 (1H, m, CH), 1.71–1.64 (1H, m, CH_2), 1.81–1.72 (1H, m, CH_2), 2.64 (1H, ddd, J = 12.5, 9.1, 3.8 Hz, NCH_2), 2.86 (1H, ddd, J = 11.9, 6.4, 3.8 Hz, NCH_2), 3.29 (1H, dd, J = 11.3, 8.1 Hz, OCH_2), 3.51 (1H, dd, J = 11.3, 3.6 Hz, OCH_2), 3.80 (1H, d, J = 13.1 Hz, NCH_2Ph), 3.81 (1H, d, J = 13.2 Hz, NCH_2Ph), 4.14 (2H, s br, OH and NH), 7.34–7.26 (5H, m, Ph). δ_C (100 MHz, $CDCl_3$) 17.8 (Me), 35.6 (CH), 36.1 (CH_2), 47.1 (NCH_2), 53.4 (NCH_2Ph), 68.0 (OCH_2), 127.5, 128.5, 128.6, 137.9. MS (ESI, *m/z*) 194 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{12}H_{20}NO^+$ 194.1539, found: 194.1544.

***N*-Benzyl-2-phenylethanamine (2q).** Following the typical procedure, the reaction of the amide generated *in situ* from ethyl 2-phenylacetate **1g** (164 mg, 1.0 mmol) and DIBAL-H·H_2NBn (5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 50 : 1, v/v, containing 1% aqueous ammonia), **2q**[25l] (161 mg, 76%), along with 10% of the amide intermediate **3d**. **2q**: colorless oil. ν/cm^{-1} (film) 3331, 3061, 3026, 2924, 2849, 1661, 1602, 1584, 1495, 1453, 1359, 1118, 1029, 737, 698. δ_H (400 MHz, $CDCl_3$) 1.55 (1H, s br, NH), 2.83 (2H, t, J = 6.6 Hz, CH_2Ph), 2.90 (2H, t, J = 6.6 Hz, NCH_2), 3.80 (2H, s, NCH_2Ph), 7.34–7.17 (10H, m, Ph). δ_C (100 MHz, $CDCl_3$) 36.3 (CH_2Ph), 50.5 (NCH_2), 53.8 (NCH_2Ph), 126.1, 126.9, 128.1, 128.4 (2C), 128.7, 140.0, 140.2. MS (ESI, *m/z*) 212 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{12}H_{20}NO^+$ 212.1434, found: 212.1439.

***N*-Benzyl-2-phenylacetamide (3d).**[25m] White solid. mp 118–119 °C. ν/cm^{-1} (film) 3289, 3083, 3031, 2924, 1640, 1600, 1584, 1552, 1492, 1453, 1432, 1366, 1259, 1081, 1029, 727, 694. δ_H (400 MHz, $CDCl_3$) 3.59 (2H, s, CH_2CO), 4.38 (2H, d, J = 5.8 Hz, NCH_2Ph), 5.87 (1H, s br, NH), 7.36–7.14 (10H, m, Ph). δ_C (100 MHz, $CDCl_3$) 43.5 (CH_2CO), 43.7 (NCH_2Ph), 127.3 (2C), 127.4, 128.6, 129.0, 129.4, 134.8, 138.1, 170.8 (CO). MS (ESI, *m/z*) 248 (M + Na^+).

***N*,*N*-Diethyl-2-phenylethanamine (2r).** Following the typical procedure, the reaction of the amide generated *in situ* from ethyl 2-phenylacetate **1g** (164 mg, 1.0 mmol) and DIBAL-H·HNEt$_2$·HCl (5 mmol), with DIBAL-H (1.0 M in hexane, 5.0 mL, 5.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 50 : 1, v/v, containing 1% aqueous ammonia), **2r**[25j] (117 mg, 66%) as a colorless oil. ν/cm^{-1} (film) 3057, 3026, 2968, 2932, 2871, 2800, 1603, 1581, 1495, 1453, 1383, 1200, 1117, 1067, 741, 698. δ_H (400 MHz, $CDCl_3$) 1.07 (6H, t, J = 7.1 Hz, Me), 2.62 (4H, q, J = 7.1 Hz, CH_2Me), 2.80–2.67 (4H, m, CH_2CH_2), 7.22–7.16 (3H, m, Ph), 7.31–7.24 (2H, m, Ph), δ_C (100 MHz, $CDCl_3$) 11.7 (Me), 33.3 (CH_2Me), 46.8 (CH_2Ph), 54.8 (NCH_2), 125.9, 128.3, 128.6, 140.6. MS (ESI, *m/z*) 178 (M + H^+). HRMS (ESI, *m/z*) [M + H^+] Calculated for $C_{12}H_{20}NO^+$ 178.1590, found: 178.1593.

(*R*)-5-(Benzyloxy)-*N*,*N*-diethyl-4-methylpentan-1-amine (2s). Following the typical procedure, the reaction of the amide generated *in situ* from (*R*)-methyl 5-(benzyloxy)-4-methylpentanoate[24] **1h** (236 mg, 1.0 mmol) and DIBAL-H·HNEt$_2$·HCl (5 mmol), with DIBAL-H (1.0 M in hexane, 6.0 mL, 6.0 mmol) produced, after flash column chromatography (eluent: CH_2Cl_2–MeOH = 50 : 1, v/v, containing 1% aqueous ammonia), **2s** (153.0 mg, 58%) as a colorless oil. $[\alpha]_D^{20}$ +2.8 (*c* 1.0 in $CHCl_3$). ν/cm^{-1} (film) 3087, 3064, 3029, 2967, 2931, 2871, 2796, 1494, 1453, 1376, 1201, 1095, 734, 697. δ_H (400 MHz, $CDCl_3$) 0.94 (3H, d, J = 6.8 Hz, CH*Me*), 1.02 (6H, t, J = 7.2 Hz, CH_2*Me*), 1.15–1.06 (1H, m, CH), 1.55–1.36 (3H, m, CH_2), 1.82–1.73 (1H, m, CH_2), 2.40 (2H, ddd, J = 8.5, 6.2, 1.7 Hz, NCH_2), 2.52 (4H, q, J = 7.2 Hz, NCH_2Me), 3.25 (1H, dd, J = 9.1, 6.4 Hz, OCH_2), 3.32 (1H, dd, J = 9.1, 6.4 Hz, OCH_2), 4.49 (1H, d, J = 12.7 Hz, OCH_2Ph), 4.50 (1H, d, J = 12.7 Hz, OCH_2Ph), 7.35–7.24 (5H, m). δ_C (100 MHz, $CDCl_3$) 11.5 (CH_2*Me*), 17.1 (Me), 24.2 (CH), 31.6 (CH_2), 33.4 (CH_2), 46.8 (NCH_2Me), 53.2 (NCH_2), 73.0 (OCH_2), 75.9 (OCH_2Ph), 127.4, 127.5, 128.3, 138.7. MS (ESI, *m/z*) 264 ($M + H^+$). HRMS (ESI, *m/z*) [$M + H^+$] Calculated for $C_{17}H_{30}NO^+$ 264.2322, found: 264.2318.

***N*-Benzyl-4-pentenylamine (2t).** Following the typical procedure, the reaction of the amide generated *in situ* from ethyl 4-pentenoate **1i** (640 mg, 5.0 mmol) and DIBAL-H·H_2NBn (10 mmol) with DIBAL-H (1.0 M in hexane, 30.0 mL, 30.0 mmol) produced, after fractionated, **2t**[25n] (556 mg, 60%) as a colorless oil. ν/cm^{-1} (film) 3308, 3089, 3064, 3027, 2963, 2929, 2869, 1645, 1498, 1453, 1368, 1088, 998, 907, 733, 698; δ_H (400 MHz, $CDCl_3$) 1.26 (1H, s br, NH), 1.55–1.64 (2H, m, CH_2CH_2NH), 2.04–2.10 (2H, m, $CH_2CH{=}$), 2.61 (2H, t, J = 7.3 Hz, CH_2CH_2NH), 3.76 (2H, s, $NHCH_2Ph$), 4.92–5.05 (2H, m,$=CH_2$), 5.79 (1H, tdd, J = 6.7, 10.2, 17.0 Hz, $CH_2CH{=}$), 7.20–7.35 (5H, m, PhH); δ_C (100 MHz, $CDCl_3$) 29.3 (CH_2), 31.8 (CH_2), 49.0 (CH_2CH_2NH), 54.2 ($NHCH_2Ph$), 115.0 ($CH_2{=}$), 127.3, 128.4, 128.7, 138.6 ($CH_2CH{=}$), 140.3; MS (ESI, *m/z*) 176 ($M + H^+$). HRMS (ESI, *m/z*) [$M + H^+$] Calculated for $C_{17}H_{30}NO^+$ 176.1434, found: 176.1442.

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