Sterically Biased 3,3-Sigmatropic Rearrangement of Azides: Efficient Preparation of
Non-Racemic α -Amino Acids and Heterocycles.

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Supporting Information

GENERAL INFORMATION	4
Experimental Section	4
Synthesis of (<i>E</i>)- <i>t</i> -butyl-(3-iodoallyloxy)-dimethylsilane 4a :	4
Synthesis of (<i>E</i>)-1-Iodo-3-phenyl-1-propene 4b :	5
Synthesis of (<i>E</i>)-3,3-dimethyl-1-iodo-1-butene 4c :	5
Synthesis of (<i>E</i>)-1-iodo-1-pentene 4d :	6
Synthesis of (<i>E</i>)-3-(2-vinylphenyl)-1-bromo-1-propene 4e :	6
Synthesis of allylic alcohol 5a :	7
Synthesis of allylic alcohol 5b :	8
Synthesis of allylic alcohol 5c :	8
Synthesis of allylic alcohol 5d :	9
Synthesis of allylic alcohol 5e :	9
Synthesis of allylic alcohol 5f :	10
Synthesis of allylic alcohol 6a :	11
Synthesis of allylic alcohol 6b :	12
Synthesis of allylic alcohol 6c :	12
Synthesis of allylic alcohol 6d :	12
Synthesis of allylic alcohol 6e :	13
Synthesis of allylic alcohol 6f :	13
Synthesis of azide 7a	14
Synthesis of azide 7b	14
Synthesis of azide 7c :	15
Synthesis of azide 7d	15
Synthesis of azide 7e :	16
Synthesis of azide 8a	16
Synthesis of azide 8b	16
Synthesis of azide 8c :	17
Synthesis of azide 8d	17
Synthesis of azide 8e :	18
Synthesis of azide 9f or 10f	18
Synthesis of amine 11a :	19
Synthesis of amine 11b (isolated as the hydrochloric salt):	20
Synthesis of amine 11c :	20
Synthesis of amine 11d :	21
Synthesis of amine 11e :	21
Synthesis of Fm-carbamate 12a :	21
Synthesis of Fm-carbamate 12b :	22
Synthesis of Fm-carbamate 12c :	23
Synthesis of Fm-carbamate 12d :	23
Synthesis of amino acid 13a :	24
Synthesis of amino acid 13b :	25

Synthesis of amino acid 13c via the amino aldehyde :	25
Synthesis of amino acid 13d :	26
Synthesis of <i>t</i> -Bu carbamate 14b :	26
Synthesis of <i>t</i> -Bu carbamate 14c :	28
Synthesis of <i>t</i> -Bu carbamate 14d :	29
Synthesis of dehydropiperidine 15b :	30
Dihydropyrrole 15c :	31
Synthesis of dehydropiperidine 15d :	31
Synthesis of <i>t</i> -Bu carbamate 16 :	32
Synthesis of <i>N</i> -Boc amine 17 :	32
Synthesis of <i>t</i> -Bu carbamate 18 :	33
Synthesis of heterocycle 19 :	34
Synthesis of (+)-Boc-coniine:	35
¹ H NMR Spectra	36
Vinyl iodide 4a	36
Vinyl iodide 4c :	37
Vinyl iodide 4d :	38
3-(<i>o</i> -iodophenyl)-1-bromo-1-propene (precursor to vinylbromide 4e):	39
1-(3-Bromoallyl)-2-vinyl-benzene 4e :	40
Allylic alcohol 5a :	41
Allylic alcohol 5b :	42
Allylic alcohol 5c :	43
Allylic alcohol 5d :	44
Allylic alcohol 5e :	45
Propargylic alcohol precursor to 5f :	46
Allylic alcohol 5f :	47
Allylic alcohol 6a :	48
Allylic alcohol 6b :	49
Allylic alcohol 6c :	50
Allylic alcohol 6d :	51
Allylic alcohol 6e :	52
Propargylic alcohol precursor to 6f :	53
Allylic alcohol 6f :	54
Allylic azide 7a :	55
Allylic azide 7b :	56
Allylic azide 7c :	57
Allylic azide 7d :	58
Allylic azide 7e :	59
Allylic azides 9f/10f/7f/8f :	60
Blow-up section of the 1H NMR of allylic azides 9f/10f/7f/8f :	61
Allylic azide 8a :	62
Allylic azide 8b :	63
Allylic azide 8c :	64
Allylic azide 8d :	65
Allylic azide 8e :	66
Allylic azides 10f/9f/8f/7f :	67

Blown-up section of the ^1H NMR of allylic azides 10f/9f/8f/7f :	68
Primary amine 11a :	69
Ammonium salt of primary amine 11b :	70
Primary amine 11c :	71
Primary amine 11d :	72
Primary amine 11e :	73
Fm-carbamate 12a :	74
Fm-carbamate 12b :	75
Fm-carbamate 12c :	76
Fm-carbamate 12d :	77
Amino acid 13a :	78
Amino acid 13b :	79
Amino aldehyde precursor to amino acid 13c :	80
Amino acid 13c :	81
Amino acid 13d :	82
Secondary amine precursor to <i>t</i> -Bu carbamate 14b :	83
<i>t</i> -Bu carbamate 14b :	84
Secondary amine precursor to <i>t</i> -Bu carbamate 14c :	85
<i>t</i> -Bu carbamate 14c :	86
Secondary amine precursor to <i>t</i> -Bu carbamate 14d :	87
<i>t</i> -Bu carbamate 14d :	88
<i>t</i> -Bu carbamate 16 :	89
<i>O</i> -TBDMS- <i>t</i> -Bu carbamate precursor to 18 :	90
<i>t</i> -Bu carbamate-alcohol precursor to 18 :	91
<i>t</i> -Bu carbamate 18 :	92
Dehydropiperidine 15b :	93
Dihydropyrrole 15c :	94
Dehydropiperidine 15d :	95
<i>t</i> -Bu carbamate 17 :	96
Dihydropyran 19 :	97
(+)- <i>N</i> -Boc coniine:	98

GENERAL INFORMATION

All reactions were performed under an inert atmosphere of argon in glassware that had been flame dried. Solvents were distilled from potassium/benzophenone ketyl (Et₂O, THF, benzene, toluene), from calcium hydride (CH₂Cl₂, ClCH₂CH₂Cl, triethylamine) or from potassium hydroxide (*N,N,N,N*-tetramethylethylenediamine) prior to use. Reagents were purchased from Aldrich and used without purification. The synthesis of menthyl carboxaldehyde **1** was previously described. Flash chromatography was performed using Merck silica gel (230-400 Mesh ASTM) with solvents distilled prior to use. NMR spectra were recorded on a Bruker AC-300 spectrometer (¹H NMR at 300MHz, ¹³C NMR at 75.5 MHz). The following abbreviations were used: s, singlet, d, doublet, t, triplet, q, quartet, qi, quintet, sx, sextet, sp, septet. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm (¹H NMR), 77.0 ppm (¹³C NMR); CD₂Cl₂: 5.33 (¹H NMR), 53.1 ppm (¹³C NMR); acetone-*d*₆: 2.09 ppm (¹H NMR)). Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer with a thin layer of the product on a NaCl disk. HPLC analyses were performed on a HP 1100 apparatus; GC analyses were performed on a Agilent 6890 series apparatus; GCMS analyses were performed on a HP 5890 serie II instrument (25 m length, 25μ OD, capillary Stabilwax-DB5 column) coupled with a mass spectrometer (HP 5971). High-resolution spectrometry was performed on a ZAB-1F micromass spectrometer. Optical rotations [α]²⁰_D were measured on a Perkin Elmer 343 polarimeter. Diastereomeric and enantiomeric ratios were determined as specified below for individual compounds.

Experimental Section

Synthesis of (*E*)-*t*-butyl-(3-iodoallyloxy)-dimethylsilane **4a**:

In a 1 L r.b. flask was dissolved Cp₂ZrCl₂ (7.72 g, 26.42 mmol) in THF (193 mL). The yellow solution was cooled to 0 °C and protected from light. Then, LiEt₃BH (1.0 M in THF, 26.40 mL, 26.42 mmol) was added dropwise over a period of 10 min. A white

suspension was obtained and the reaction mixture was stirred at r.t. for 1 h. Then, 3-(*t*-butyldimethylsilyloxy)-1-propyne (3.00 g, 17.61 mmol) was added and the mixture was again stirred 1h at r.t. The reaction mixture was cooled to 0 °C and I₂ (7.82 g, 30.82 mmol) was added by small portions and stirred at r.t. for 15 min. The resulting mixture was again cooled to 0 °C and quenched with a saturated solution of NaHCO₃ (150 mL). The aqueous phase was extracted with 3 portions of Et₂O and the combined organic extracts were washed with 3 portions of water and once with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a yellow oil. The crude product was purified by silica gel column chromatography with 100% pentanes as eluant to afford a colorless oil (4.35 g, 83 %). ¹H NMR (CDCl₃, 300MHz): δ 6.64-6.57 (m, 1H), 6.32-6.25 (m, 1H), 4.11 (dd, 2H, *J* = 5.0, 2.2 Hz), 0.90 (s, 9H), 0.07 (s, 6H). IR (neat, cm⁻¹): 2954, 2930, 2857, 1370, 1256, 1127, 1099, 933. LRMS (m/z, (relative intensity)): 241 ((M-C₄H₉)⁺, 100), 211 (4), 185 (10), 167 (15), 113 (8), 99 (9), 85 (26). HRMS calculated for C₅H₁₀ISiO (M-C₄H₉)⁺: 240.9546, found: 240.9543.

Synthesis of (*E*)-1-Iodo-3-phenyl-1-propene **4b**:

Prepared by the same procedure as per **4a**. The spectral data were identical to the ones found in: J. E. Mulvaney, T.L. Folk, D. J. Newton, *J. Org. Chem.* **1967**, 32, 1674-1675. R. Mathias, P. Weyerstahl, *Chem. Ber.* **1979**, 112, 3041-3053.

Synthesis of (*E*)-3,3-dimethyl-1-iodo-1-butene **4c**:

In 500 mL r.b. flask was dissolved 1-pentyne (2.50 g, 36.70 mmol) in CH₂Cl₂ (25 mL). This solution was cooled to 0 °C and a solution of Br₂BH·SMe₂ (1.0 M in CH₂Cl₂, 40.4 mL, 40.36 mmol) was added dropwise over a period of 10 min. The reaction mixture was stirred at r.t. for 7 h and treated with a 3N aqueous solution of NaOH (61.0 mL, 183.5mmol) dropwise after cooling to 0 °C. A white solid precipitated. This slurry was stirred at r.t. for 2.5 h and then cooled again to 0 °C. Then, iodine (14.00 g, 55.05 mmol)

in CH_2Cl_2 (25 mL) was added in small portions. The resulting reaction mixture was stirred for 2 h at r.t. The aqueous phase was extracted with three portions of Et_2O and the combined organic extracts were washed with one portion of saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$, one portion of water and once with brine, dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a yellowish oil. The crude product was purified on silica gel with 100% pentanes as eluant to afford a colorless oil (6.0 g, 83 %). **^1H NMR** (CDCl_3 , 300MHz): δ 6.55 (d, 1H, $J = 14.3$ Hz), 5.93 (d, 1H, $J = 14.8$ Hz), 1.02 (s, 9H). **IR** (neat, cm^{-1}): 3068, 1461, 1363, 1260, 953, 456. **LRMS** (m/z , (relative intensity)): 210 (M^+ , 20), 119 (13), 86 (86), 84 (100). **HRMS** calculated for $\text{C}_6\text{H}_{11}\text{I}$: 209.9905, found: 209.9901.

Synthesis of (*E*)-1-iodo-1-pentene **4d**:

Prepared by the same procedure as per **4c**. **^1H NMR** (CDCl_3 , 300MHz): δ 6.56-6.46 (m, 1H), 5.97 (dd, 1H, $J = 14.3, 1.65$ Hz), 2.01 (qd, 2H, $J = 7.2, 1.65$ Hz), 1.41 (sext, 2H, $J = 7.2$ Hz), 0.90 (t, 3H, $J = 7.2$ Hz). **IR** (neat, cm^{-1}): 2959, 2929, 2872, 946. **LRMS** (m/z , (relative intensity)): 196 (M^+ , 100), 167 (50), 154 (53), 127(20), 69(10), 41(31). **HRMS** calculated for $\text{C}_5\text{H}_9\text{I}$: 195.9749, found: 195.9755.

Synthesis of (*E*)-3-(2-vinylphenyl)-1-bromo-1-propene **4e**:

Biscyclopentadienylzirconium dichloride (7.25 g, 24.81 mmol) was dissolved in THF (180 mL), and cooled to 0 °C while shielding the reaction from daylight. Lithium triethylborohydride (1.0 M in THF, 25.00 mL, 25.00 mmol) was added dropwise. The mixture was warmed to r.t. and stirred for 1 h while shielding the reaction from daylight. 3-(*o*-Iodophenyl)-1-propyne (4.00 g, 16.52 mmol) in THF (15.0 mL) was added. The solution was stirred for 1 h still shielded from daylight and then *N*-bromosuccinimide (4.71 g, 26.42 mmol) was added in small portions. The mixture was stirred for 1 h at r.t.

The mixture was quenched with a solution of saturated aqueous NaHCO_3 and stirred until the color disappeared. Pentane was added, the two phases were separated and the aqueous phase was extracted twice with pentane. The organic phases were combined, washed with a solution of saturated aqueous sodium thiosulfate, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel, eluting with pentane furnished a clear liquid (3.92 g, 73 %). **^1H NMR** (CDCl_3 , 300 MHz): δ 7.85 (d, 1H, $J = 8.3$ Hz), 7.33-7.19 (m, 2H), 6.93 (t, 1H, $J = 7.7$ Hz), 6.29 (dt, 1H, $J = 13.7, 6.6$ Hz), 6.14 (d, 1H, $J = 13.2$ Hz), 3.49 (d, 2H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3060, 2907, 1619, 1464, 1012, 942, 907, 748, 712. **LRMS** (m/z , (relative intensity)): 322 (M^+ , 30), 243 (20), 116 (100). **HRMS** calculated for $\text{C}_9\text{H}_8\text{BrI}$: 321.8854, found: 321.8858.

(*E*)-3-(*o*-Iodophenyl)-1-bromo-1-propene (2.85 g, 8.82 mmol) was dissolved in toluene (40 mL). The mixture was stirred vigorously during 15 min. Pd_2dba_3 (0.213 g, 0.176 mmol) was added followed by tributylvinyltin (3.08 g, 6.71 mmol). The reaction was stirred at r.t. for 4 days. The reaction mixture was filtered over a pad of silica gel and concentrated under reduced pressure. Flash chromatography on silica gel, eluting with pentane furnished a clear liquid (1.65 g, 84 %). **^1H NMR** (CDCl_3 , 300 MHz): δ 7.52-7.48 (m, 1H), 7.25-7.20 (m, 2H), 7.15-7.12 (m, 1H), 6.90 (dd, 1H, $J = 17.0, 11.0$ Hz), 6.32 (dt, 1H, $J = 13.7, 6.6$ Hz), 5.99 (d, 1H, $J = 13.7$ Hz), 5.62 (d, 1H, $J = 17.0$ Hz), 5.32 (d, 1H, $J = 10.4$ Hz), 3.42 (d, 2H, 6.6 Hz). **IR** (neat, cm^{-1}): 3063, 3017, 2915, 2848, 1623, 1483, 989, 944, 913, 770. **LRMS** (m/z , (relative intensity)): 240 ($(\text{MNH}_4)^+$, 10), 223 (M^+ , 2), 143 (100), 128 (80). **HRMS** calculated for $\text{C}_{11}\text{H}_{12}\text{Br}$ ($\text{M}^+ + \text{H}$): 223.0122, found: 223.0119.

Synthesis of allylic alcohol **5a**:

See the procedure for **5c**. **^1H NMR** (CDCl_3 , 300MHz): δ 5.76-5.73 (m, 2H), 4.45 (br s, 1H), 4.22-4.20 (m, 2H), 2.12 (dqi, 1H), 1.73-1.59 (m, 3H), 1.40-1.23 (m, 4H), 1.12-0.79 (m, 8H), 0.91 (s, 9H), 0.76 (d, 3H, $J = 6.6$ Hz), 0.08 (s, 6H). **IR** (neat, cm^{-1}): 3623-3149,

2960, 2919, 2848, 1486, 1384, 1251, 969. **LRMS** (m/z , (relative intensity)): 358 ((MNH_4)⁺, 6), 340 (($\text{M}-\text{H}_2\text{O}$) NH_4)⁺, 22), 323 (100), 191 (31), 135 (10), 74 (11). **HRMS** calculated for $\text{C}_{20}\text{H}_{44}\text{NO}_2\text{Si}$ (MNH_4)⁺: 358.3141, found: 358.3136. $[\alpha]_{\text{D}}^{20} = -14.7$ (c 2.22, CHCl_3).

Synthesis of allylic alcohol **5b**:

See the procedure for **5c**. **¹H NMR** (CDCl_3 , 300 MHz) : δ 7.33-7.18 (m, 5H), 5.82-5.74 (m, 1H), 5.62 (dd, $J = 15.4, 5.0$ Hz), 4.43 (d, 1H, $J = 4.9$ Hz), 3.41 (d, 2H, $J = 6.6$ Hz), 2.17-2.07 (dqi, 1H, $J = 6.6, 2.8$ Hz), 1.74-1.64 (m, 3H), 1.40-1.24 (m, 4H), 1.11-0.67 (m, 3H), 0.93 (d, 3H, $J = 6.6$ Hz), 0.89 (d, 3H, $J = 6.1$ Hz), 0.76 (d, 3H, $J = 7.2$ Hz). **IR** (neat, cm^{-1}): 4317, 4057, 3582, 3422, 3063, 3028, 2959, 1944, 1666, 1603, 1494, 1460, 1384, 972, 747, 699. **LRMS** (m/z , (relative intensity)): 286 (M^+ , 0.5), 268 (10), 130 (100), 115 (30), 91 (50), 41 (10). **HRMS** calculated for $\text{C}_{20}\text{H}_{30}\text{O}$: 286.2297, found 286.2301. $[\alpha]_{\text{D}}^{20} = -12.9$ (c 3.48, CHCl_3).

Synthesis of allylic alcohol **5c**:

In a 250 mL r.b. flask was dissolved Synthesis of (*E*)-3,3-dimethyl-1-iodo-1-butene **4c** (3.00 g, 14.28 mmol) in Et_2O (45 mL) and this solution was cooled to -78°C and *tert*-butyllithium (1.7 M in pentane, 16.8 mL, 28.56 mmol) was added dropwise. The reaction mixture was stirred at -78°C for 30 min and 2 h at r.t. Then, the mixture was cooled again to -78°C and a solution of AlMe_3 (2.0 M in hexane, 21.4 mL, 42.84 mmol) was added. Then, a solution of *p*-menthane-3-carboxaldehyde **1** (2.00 g, 11.90 mmol) dissolved in Et_2O (15 mL) was added dropwise and the reaction mixture was stirred at -78°C for 3 h. The reaction mixture was then allowed to warm to 0°C and treated with a saturated solution of NaHCO_3 followed by a 1N aqueous solution of HCl until dissolution of the white solid. The aqueous phase was extracted with 3 portions of Et_2O and the combined

organic extracts were washed once with water and once with brine, dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a yellow oil. The crude product was purified on silica gel with 5:95 / EtOAc : hexanes as eluant to afford a white solid (1.69 g, 56 %). m.p.: 49-50 °C. $^1\text{H NMR}$ (CDCl_3 , 300MHz): δ 5.63 (d, 1H, J = 15.9 Hz), 5.43 (dd, 1H, J = 15.9, 6.1 Hz), 4.37 (d, 1H, J = 5.5 Hz), 2.14 (dqi, 1H, J = 7.2, 2.8 Hz), 1.72-1.69 (m, 3H), 1.45 (brs, 1H), 1.36-1.21 (m, 3H), 1.11-0.73 (m, 2H), 1.02 (s, 9H), 0.92 (d, 3H, J = 7.2 Hz), 0.88 (d, 3H, J = 6.6 Hz), 0.76 (d, 3H, J = 7.2 Hz). **IR** (neat, cm^{-1}): 3361, 1386, 1364, 975. **LRMS** (m/z , (relative intensity)): 252 (M^+ , 10), 195 (12), 139 (15), 113 (100), 83 (75). **HRMS** calculated for $\text{C}_{17}\text{H}_{32}\text{O}$: 252.2453, found: 252.2455. $[\alpha]_{\text{D}}^{20} = -20.2$ (c 2.16, CHCl_3).

Synthesis of allylic alcohol **5d**:

Prepared by the same procedure as per **5c**. $^1\text{H NMR}$ (CDCl_3 , 300MHz): δ 5.64-5.49 (m, 2H), 4.37 (d, 1H, J = 5.0 Hz), 2.13 (dqi, 1H, J = 7.2, 1.5 Hz), 2.03 (q, 2H, J = 6.6 Hz), 1.70-1.63 (m, 3H), 1.47-1.26 (m, 3H), 1.01-0.78 (m, 8H), 0.90 (dd, 6H, J = 7.2, 2.2 Hz), 0.76 (d, 3H, J = 6.6 Hz). **IR** (neat, cm^{-1}): 3378 (br), 2954, 2923, 2871, 1640, 1455, 970. **LRMS** (m/z , (relative intensity)): 238 (M^+ , 14), 139 (14), 99 (60), 84 (100). **HRMS** calculated for $\text{C}_{16}\text{H}_{30}\text{O}$: 238.2297, found 238.2303. $[\alpha]_{\text{D}}^{20} = -29.3$ (c 2.87, CHCl_3).

Synthesis of allylic alcohol **5e**:

Prepared by the same procedure as per **5c**. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.51-7.49 (m, 1H), 7.24-7.16 (m, 3H), 6.96 (dd, 1H, J = 17.6, 11.0 Hz), 5.79-5.27 (dt, 1H, J = 15.4, 6.0 Hz), 5.64 (d, 1H, J = 15.9 Hz), 5.46 (dd, 1H, J = 15.4, 5.0 Hz), 5.27 (d, 1H, J = 12.1 Hz), 4.39 (br d, 1H, J = 5.0 Hz), 3.46 (d, 2H, J = 6.0 Hz), 2.18-2.00 (dqi, 1H, J = 6.6, 2.8 Hz), 1.70-1.50 (m, 5H), 1.31-1.21 (m, 3H), 1.05-0.72 (m, 2H), 0.90 (d, 3H, J = 6.6 Hz), 0.88 (d, 3H, J = 6.6 Hz), 0.73 (d, 3H, J = 7.1 Hz). **IR** (neat, cm^{-1}): 3444 (br), 3020, 2953,

2920, 2870, 1452, 974, 769. **LRMS** (m/z , (relative intensity)): 312 (M^+ , 1), 294 (5), 251 (5), 173 (40), 130 (100). **HRMS** calculated for $C_{22}H_{32}O$: 312.2453, found: 312.2447. $[\alpha]_D^{20} = -15.4$ (c 1.07, $CHCl_3$).

Synthesis of allylic alcohol **5f**.

In a 25 mL r.b. flask was dissolved ethynylbenzene (1.45g, 14.28 mmol) in THF (10 mL). This solution was cooled to $-78\text{ }^{\circ}\text{C}$, *n*-butyllithium (1.91M in pentane, 7.44 mL, 14.28 mmol) was added dropwise and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 45 min and then for 2 h at r.t. Then, the mixture was cooled again to $-78\text{ }^{\circ}\text{C}$ and a solution of *p*-menthane-3-carboxaldehyde **1** (1.64 g, 9.75 mmol) in THF (15 mL) was added dropwise and stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h. The reaction mixture was then allowed to warm to $0\text{ }^{\circ}\text{C}$ and treated with a saturated solution of NH_4Cl . The aqueous phase was extracted with three portions of Et_2O and the combined organic extracts were washed once with water and once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give a yellow oil. The crude mixture of propargylic alcohols was purified on silica gel with 100% toluene as eluant to afford a colorless oil (888 mg, (35 %) of the major diastereomer and 700 mg (27 %) of the minor diastereomer (see **6f** below). Major alcohol: **¹H NMR**: (300 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.34-7.30 (m, 3H), 4.88-4.87 (m, 1H), 2.17-2.02 (m, 2H), 1.77-1.54 (m, 3H), 1.48-1.32 (m, 2H), 1.10-0.86 (m, 9H), 0.80 (d, $J = 7.0\text{ Hz}$, 3H). **IR** (neat, cm^{-1}): 3590-3160 (br), 2954, 2197, 755. **LRMS** (m/z , (relative intensity)): 270 (M^+ , 15), 255 (11), 227 (6), 131 (66), 83 (100). **HRMS** calculated for $C_{19}H_{26}O$: 270.1984, found: 270.1982.

In a 25 mL r.b. flask was dissolved the major propargylic alcohol (450 mg, 1.66 mmol) in THF (9.2 mL) and the resulting solution was cooled to $0\text{ }^{\circ}\text{C}$. Red-Al (65% weight, 1.04 g, 3.33 mmol) was added dropwise and the resulting reaction mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 10 min and heated to reflux for a period of 23 h. The reaction mixture was then cooled to $0\text{ }^{\circ}\text{C}$ and a solution of $EtOH/H_2O$ 1:1 was poured, stirred for 1 h at $0\text{ }^{\circ}\text{C}$ and filtered over a celite pad. The mother liquor was concentrated under reduced pressure and the aqueous

phase was extracted with 3 portions of Et₂O (75 mL) and the combined organic extracts were washed once with water and once with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a yellow-brown oil. The crude oil was purified on silica gel with 1: 20 EtOAc/ hexanes as eluant to afford **5f** as clear oil (350 mg, 77 %). **¹H NMR** (300 MHz, CDCl₃) δ 7.42-7.39 (m, 2H), 7.35-7.30 (m, 2H), 7.24-7.21 (m, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.30 (dd, J = 16.0 Hz, 5.0 Hz, 1H), 4.64-4.62 (m, 1H), 2.23-2.13 (m, 1H), 1.75-1.66 (m, 3H), 1.55-1.26 (m, 3H), 1.09-0.77 (m, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H), 0.81 (d, J = 6.5 Hz, 3H). **IR** (neat, cm⁻¹): 3610-3140 (br), 3063, 3027, 2957, 2915, 2870, 1495, 1455, 967, 750. **LRMS** (m/z, (relative intensity)): 272 (M⁺, 18), 229 (4), 167 (12), 133 (100), 115 (30), 91 (48), 83 (70). **HRMS** calculated for C₁₉H₂₈O: 272.2140, found: 272.2134.

Synthesis of allylic alcohol **6a**:

Prepared by the procedure as per **5c** except AlMe₃ was omitted. Mixtures of **5a** and **6a** were obtained and sufficient quantities of **6a** could be isolated pure to carry out the rest of the sequence. Compound **6a** as the sole diastereomer can also be obtained by first oxidizing **5a** and reducing the resulting ketone stereoselectively with Et₃BHLi (see ref. 9b). **¹H NMR** (CDCl₃, 300MHz) : δ 5.76 (d, 2H, J = 3.3 Hz), 4.48-4.44 (m, 1H), 4.20-4.19 (m, 2H), 1.97-1.81 (m, 2H), 1.66-1.57 (m, 3H), 1.47 (br s, 1H), 1.34-1.25 (m, 2H), 1.12-0.59 (m, 8H), 0.91 (s, 9H), 0.79 (d, 3H, J = 7.2 Hz), 0.08 (s, 6H) **IR** (neat, cm⁻¹) : 3623-3149 (br), 2960, 2920, 2849, 1469, 1385, 1252, 970. **LRMS** (m/z, (relative intensity)): 358 ((MNH₄)⁺, 5), 340 ((M-H₂O)NH₄)⁺, 14), 323 (100), 191 (38), 135 (12), 74 (14). **HRMS** calculated for C₂₀H₄₄NO₂Si (MNH₄)⁺: 358.3141, found: 358.3136. [α]_D²⁰ = -23.5 (*c* 2.36, CHCl₃).

Synthesis of allylic alcohol **6b**:

Prepared by the same procedure as per **6a**. **¹H NMR** (CDCl₃, 300 MHz): δ 7.32-7.26 (m, 2H), 7.22-7.16 (m, 3H), 5.82 (dt, 1H, J = 15.4, 7.1 Hz), 5.63 (dd, 1H, J = 15.4, 7.1 Hz), 4.44-4.40 (m, 1H), 3.42 (d, 2H, J = 7.2 Hz), 1.95-1.80 (m, 2H), 1.76-1.52 (m, 3H), 1.39 (d, 1H, J = 3.9 Hz), 1.38-1.25 (m, 1H), 1.10-0.62 (m, 4H), 0.91 (d, 3H, J = 6.1 Hz), 0.85 (d, 3H, J = 7.1 Hz), 0.76 (d, 3H, J = 7.1 Hz). **IR** (neat, cm⁻¹): 3600-3100 (br), 3025, 2954, 2932, 2866, 1492, 1448, 1020, 972, 693. **LRMS** (m/z, (relative intensity)): 286 (M⁺, 10), 243 (5), 195 (45), 147 (70), 129 (95), 91 (80), 83 (100). **HRMS** calculated for C₂₀H₃₀O: 286.2297, found: 286.2292. $[\alpha]_D^{20}$ = -12.0 (c 1.05, CHCl₃).

Synthesis of allylic alcohol **6c**:

Prepared by the same procedure as per **6a**. **¹H NMR** (CDCl₃, 300MHz): δ 5.68 (d, 1H, J = 15.9 Hz), 5.37 (dd, 1H, J = 15.9, 7.7 Hz), 4.35 (dd, 1H, J = 7.7, 3.9 Hz), 2.00-1.86 (m, 2H), 1.73-1.54 (m, 3H), 1.47 (m, 1H), 1.33-1.22 (m, 1H), 1.09-0.60 (m, 3H), 1.01 (s, 9H), 0.89 (d, 3H, J = 6.6 Hz), 0.84 (d, 3H, J = 6.6 Hz), 0.77 (d, 3H, J = 6.6 Hz). **IR** (neat, cm⁻¹): 3361 (br), 2958, 2917, 2869, 1386, 1364, 975. **LRMS** (m/z, (relative intensity)): 252 (M⁺, 12), 195 (14), 139 (22), 113 (84), 95 (55), 83 (100). **HRMS** calculated for C₁₇H₃₂O: 252.2453, found: 252.2455. $[\alpha]_D^{20}$ = -27.4 (c 2.28, CHCl₃).

Synthesis of allylic alcohol **6d**:

Prepared by the same procedure as per **6a**. **¹H NMR** (CDCl₃, 300MHz): δ 5.68-5.60 (m, 1H), 5.49 (dd, 1H, J = 15.4, 7.2 Hz), 4.37 (dd, 1H, J = 7.2, 4.4 Hz), 2.04-1.89 (m, 4H), 1.72-1.62 (m, 3H), 1.44-1.34 (m, 4H), 1.04-0.62 (m, 6H), 0.90 (dd, 6H, J = 2.2, 7.2 Hz), 0.78 (d, 3H, J = 7.2 Hz). **IR** (neat, cm⁻¹): 3358, 1668, 970. **LRMS** (m/z, (relative

intensity)): 238 (M^+ , 4), 220 ($M-H_2O$, 1), 139 (25), 123 (8), 99 (86), 83 (100). **HRMS** calculated for $C_{16}H_{30}O$: 238.2297, found: 238.2291. $[\alpha]_D^{20} = -28.9$ (c 2.21, $CHCl_3$).

Synthesis of allylic alcohol **6e**:

Prepared by the same procedure as per **6a**. **1H NMR** ($CDCl_3$, 300 MHz): δ 7.52-7.49 (m, 1H), 7.27-7.14 (m, 3H), 6.95 (dd, 1H, $J = 17.6, 11.0$ Hz), 5.84-5.73 (dt, 1H, $J = 15.4, 6.6$ Hz), 5.65 (d, 1H, $J = 15.9$ Hz), 5.50 (dd, 1H, $J = 16.0, 6.6$ Hz), 5.28 (d, 1H, $J = 11.0$ Hz), 4.41-4.37 (m, 1H), 3.46 (d, 2H, $J = 6.6$ Hz), 2.11-1.80 (m, 2H), 1.75-1.47 (m, 4H), 1.41-1.22 (m, 2H), 1.11-0.60 (m, 3H), 0.87 (d, 3H, $J = 6.1$ Hz), 0.80 (d, 3H, $J = 7.2$ Hz), 0.75 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3600-3100 (br), 2952, 2870, 1454, 1367, 1020, 973, 771, 757. **LRMS** (m/z , (relative intensity)): 312 (M^+ , 1), 294 ($M-H_2O$, 5), 251 (8), 173 (40), 130 (100), 117 (60), 83 (95). **HRMS** calculated for $C_{22}H_{32}O$: 312.2453, found: 312.2444. $[\alpha]_D^{20} = -18.2$ (c 0.73, $CHCl_3$).

Synthesis of allylic alcohol **6f**:

Prepared by the same procedure as per **5f**. Minor propargyl alcohol, precursor to **6f**: **1H NMR**: (300 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.34-7.30 (m, 3H), 4.88 (d, $J = 4.5$ Hz, 1H), 2.03-1.94 (m, 2H), 1.77-1.65 (m, 3H), 1.45-1.25 (m, 2H), 1.13-0.86 (m, 9H), 0.82 (d, $J = 7.0$ Hz, 3H). **IR** (neat, cm^{-1}): 3600-3150 (br), 2955, 2201, 755. **LRMS** (m/z , (relative intensity)): 270 (M^+ , 5), 255 (15), 252 (10), 227 (18), 131 (100), 83 (80). **HRMS** calculated for $C_{19}H_{26}O$: 270.1984, found: 270.1990. **6f**: **1H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.31 (m, 4H), 7.27-7.22 (m, 1H), 6.60 (d, 1H, $J = 16.0$ Hz), 6.28 (dd, 1H, $J = 16.0$ Hz, 6.5 Hz), 4.64-4.60 (m, 1H), 2.09-1.91 (m, 2H), 1.74-1.63 (m, 3H), 1.41-1.24 (m, 2H), 1.10-0.92 (m, 2H), 0.91-0.68 (m, 7H), 0.83 (d, $J = 7.0$ Hz, 3H). **IR** (neat, cm^{-1}): 3610-3154 (br), 3064, 3027, 2957, 2916, 2870, 1495, 1455, 967, 751. **LRMS** (m/z , (relative

intensity)): 272 (M^+ , 14), 229 (2), 167 (8), 133 (100), 115(26), 91 (41), 83 (55). **HRMS** calculated for $C_{19}H_{28}O$: 272.2140, found: 272.2134.

Synthesis of azide **7a**

In a 50 mL r.b. flask was dissolved allylic alcohol **5a** (865 mg, 2.539 mmol) and triphenylphosphine (1.33 g, 5.079 mmol) in benzene (17.3 mL) and this solution was cooled to 0 °C. Two solutions of hydrazoic acid (3.4 mL, 1.5 M in benzene, 5.079 mmol) and diethylazodicarboxylate (DEAD) (885 mg, 5.079 mmol) were added dropwise simultaneously at 0 °C. The reaction mixture was stirred for 6 h letting the mixture warm slowly to r.t. The resulting reaction mixture was then diluted with hexane and filtered over a pad of celite to remove the undesired triphenylphosphine oxide salts. The mother liquor was washed with two portions of MeOH:H₂O (70:30), once with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a yellow oil. The crude product was purified on silica gel with 5:95 / EtOAc : hexanes as eluant to afford **7a** as a colorless oil (706 mg, 76 %). **¹H NMR** (CDCl₃, 300MHz): δ 5.56 (dd, 1H, $J = 15.4, 9.4$ Hz), 5.33 (dd, 1H, $J = 15.4, 7.7$ Hz), 3.92-3.86 (m, 1H), 3.60 (qd, 2H, $J = 9.9, 4.4$ Hz), 1.99-1.82 (m, 2H), 1.74-1.70 (m, 1H), 1.64-1.55 (m, 3H), 1.42-1.25 (m, 2H), 1.02-0.79 (m, 8H), 0.90 (s, 9H), 0.70 (d, 3H, $J = 6.6$ Hz), 0.08 (s, 6H). **IR** (neat, cm⁻¹) 2955, 2931, 2859, 2105, 1257, 839. **LRMS** (m/z , (relative intensity)): 383 ((MNH_4)⁺, 100), 340 (24), 323 (32), 191 (11), 132 (6). **HRMS** calculated for $C_{20}H_{43}N_4OSi$: 383.3206, found: 383.3194. $[\alpha]_D^{20} = -40.8$ (c 2.15, CHCl₃). > 90% d.e. (HPLC).

Synthesis of azide **7b**

Prepared by the same procedure as per **7a**. **¹H NMR** (CDCl₃, 300 MHz): δ 7.32-7.16 (m, 5H), 5.43-5.34 (m, 2H), 4.04 (q, 1H, $J = 7.1$ Hz), 2.81-2.77 (m, 2H), 1.98-1.15 (m, 6H), 1.10-0.65 (m, 10H), 0.67 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm⁻¹): 3060, 2959, 2870, 2098,

1453, 1240, 972. **LRMS** (m/z, (relative intensity)): 283 ($M^+ - N_2$, 20), 240 (30), 220 (20), 192 (60), 145 (55), 91 (100). **HRMS** calculated for $C_{20}H_{29}N$ ($M^+ - N_2$): 283.2300, found: 283.2295. $[\alpha]_D^{20} = -43.4$ (*c* 1.44, $CHCl_3$). 94% d.e. (HPLC).

Synthesis of azide **7c**

Prepared by the same procedure as per **7a**. **1H NMR** ($CDCl_3$, 300MHz): δ 5.52-5.36 (m, 2H), 3.54 (d, 1H, $J = 8.3$ Hz), 2.02-1.91 (m, 2H), 1.75-1.71 (br d, 1H, $J = 12.1$ Hz), 1.61-1.55 (m, 3H), 1.48-1.32 (m, 1H), 1.05-0.74 (m, 3H), 0.86 (d, 6H, $J = 7.2$ Hz), 0.88 (s, 9H), 0.71 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 2957, 2918, 2871, 2834, 2095, 1386, 1366, 1252, 1241, 975. **LRMS** (m/z, (relative intensity)): 249 ($(M^+ - N_2)$, 3), 234 ($(M^+ - N_2 - CH_3)$, 30), 220 (14), 192 (27), 150 (26), 110(42), 95 (44), 83 (100). **HRMS** calculated for $C_{17}H_{31}N$ ($M^+ - N_2$): 249.2456, found: 249.2447. $[\alpha]_D^{20} = -57.8$ (*c* 2.82, $CHCl_3$). 88% d.e. (GC).

Synthesis of azide **7d**

Prepared by the same procedure as per **7a**. **7d**: **1H NMR**($CDCl_3$, 300MHz): δ 5.48 (dd, 1H, $J = 15.4, 8.8$ Hz), 5.33 (dd, 1H, $J = 15.4, 8.3$ Hz), 3.78 (q, 1H, $J = 7.7$ Hz), 1.93-1.88 (m, 2H), 1.75-1.71 (br d, 1H, $J = 12.1$ Hz), 1.64-1.25 (m, 7H), 1.05-0.83 (m, 7H), 0.87 (dd, 6H, $J = 7.1, 2.8$ Hz), 0.71 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 2957, 2918, 2845, 2094, 1456, 1237, 973. **LRMS** (m/z, (relative intensity)): 235 ($M^+ - N_2$, 6), 220 (29), 206 (9), 192 (74), 109 (52), 95 (86), 83 (100). **HRMS** calculated for $C_{16}H_{33}N_4$: 281.2705, found: 281.2710. $[\alpha]_D^{20} = -41.4$ (*c* 2.50, $CHCl_3$). 84 % d.e. (HPLC).

Synthesis of azide **7e**

Prepared by the same procedure as per **7a**. **¹H NMR** (CDCl₃, 300 MHz): δ 7.48 (br d, 1H, J = 6.6 Hz), 7.26-7.13 (m, 3H), 6.96 (dd, 1H, J = 17.6, 11.0), 5.65 (d, 1H, J = 17.0 Hz), 5.39-5.31 (m, 3H), 4.07-4.01 (m, 1H), 2.92 (dd, 1H, J = 13.7, 7.1 Hz), 2.81 (dd, 1H, J = 13.7, 7.1 Hz), 1.97-1.10 (m, 8H), 1.00-0.61 (m, 8H), 0.68 (d, 3H, J = 7.1 Hz). **IR** (neat, cm⁻¹): 3010, 2955, 2921, 2871, 2098, 1453, 1239, 973, 771. **LRMS** (m/z, (relative intensity)): 355 ((M+NH₄)⁺, 100), 338 (MH⁺, 5), 312 (45), 295 (38), 209 (60). **HRMS** calculated for C₂₂H₃₂N₃ (MH)⁺: 338.2596, found: 338.2588. $[\alpha]_D^{20}$ = -24.1 (*c* 1.16, CHCl₃). 94% d.e. (HPLC).

Synthesis of azide **8a**

Prepared by the same procedure as per **7a** starting from **6a**. **¹H NMR** (CDCl₃, 300MHz): δ 5.56 (dd, 1H, J = 15.4, 9.4 Hz), 5.33 (dd, 1H, J = 15.4, 7.7 Hz), 3.87 (dd, 1H, J = 11.5, 6.6 Hz), 3.60 (m, 2H), 1.95-1.57 (m, 4H), 1.40-1.32 (m, 2H), 1.03-0.78 (m, 7H), 0.87 (d, 3H, J = 6.6 Hz), 0.90 (s, 9H), 0.69 (d, 3H, J = 6.6 Hz), 0.07 (s, 6H). **IR** (neat, cm⁻¹) 2954, 2931, 2859, 2105, 1255. **LRMS** (m/z, (relative intensity)): 383 ((MNH₄)⁺, 100), 340 (10), 323 (10), 191 (8), 132 (3). **HRMS** calculated for C₂₀H₄₃N₄OSi: 383.3206, found: 383.3213. $[\alpha]_D^{20}$ = -41.7 (*c* 2.52, CHCl₃).

Synthesis of azide **8b**

Prepared by the same procedure as per **7a** starting from **6b**. **8b**: **¹H NMR** (CDCl₃, 300 MHz): δ 7.30-7.14 (m, 5H), 5.42-5.28 (m, 2H), 4.05 (dt, 1H, J = 7.7, 6.6 Hz), 2.86 (dd, 1H, J = 13.8, 6.6 Hz), 2.72 (dd, 1H, J = 13.8, 7.7 Hz), 1.95-1.80 (m, 1H), 1.73-1.52 (m,

3H), 1.46-1.26 (m, 2H) 1.00-0.54 (m, 4H) 0.87 (d, 3H, $J = 6.6$ Hz), 0.76 (d, 3H, $J = 7.1$ Hz), 0.62 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3029, 2954, 2919, 2866, 2097, 1448, 1232, 967, 693. **LRMS** (m/z , (relative intensity)): 283 ($(\text{M}^+ - \text{N}_2)$, 10), 240 (20), 192 (25), 91 (100). **HRMS** calculated for $\text{C}_{20}\text{H}_{29}\text{N}$ ($\text{M}^+ - \text{N}_2$): 283.2300, found: 283.2295. $[\alpha]_{\text{D}}^{20} = -73.1$ (c 2.01, CHCl_3).

Synthesis of azide **8c**

Prepared by the same procedure as per **7a** starting from **6c**. **^1H NMR** (CDCl_3 , 300MHz): δ 5.54-5.36 (m, 2H), 3.51 (d, 1H, $J = 8.8$ Hz), 2.02-1.93 (m, 1H), 1.83-1.58 (m, 3H), 1.41-1.25 (m, 1H), 1.05-0.79 (m, 5H), 0.87 (d, 6H, $J = 7.1$ Hz), 0.87 (s, 9H), 0.71 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 2957, 2921, 2872, 2844, 2095, 1386, 1366, 1252, 1241, 975. **LRMS** (m/z , (relative intensity)): 252 ($(\text{M} - \text{N}_2 - \text{CH}_3)^+$, 100), 250 ($(\text{M} - \text{N}_2)\text{H}^+$, 30), 235 (48), 209 (16), 150 (9), 110(9), 83 (5). **HRMS** calculated for $\text{C}_{17}\text{H}_{32}\text{N}$: 250.2535, found: 250.2531. $[\alpha]_{\text{D}}^{20} = -60.4$ (c 2.08, CHCl_3).

Synthesis of azide **8d**

Prepared by the same procedure as per **7a** starting from **6d**. **^1H NMR** (CDCl_3 , 300MHz): δ 5.49 (dd, 1H, $J = 15.4, 9.3$ Hz), 5.31 (dd, 1H, $J = 14.8, 8.2$ Hz), 3.77 (q, 1H, $J = 7.2$ Hz), 2.03-1.87 (m, 1H), 1.86-1.29 (m, 9H), 1.08-0.77 (m, 7H), 0.87 (d, 6H, $J = 7.1$ Hz), 0.71 (d, 3H, $J = 7.2$ Hz). **IR** (neat, cm^{-1}): 2958, 2922, 2869, 2096, 1455, 1237, 973. **LRMS** (m/z , (relative intensity)): 235 ($\text{M} - \text{N}_2^+$, 7), 220 (24), 206 (8), 192 (60), 109 (67), 95 (82), 83 (100). **HRMS** calculated for $\text{C}_{16}\text{H}_{33}\text{N}_4$: 281.2705, found: 281.2710. $[\alpha]_{\text{D}}^{20} = -57.6$ (c 2.06, CHCl_3).

Synthesis of azide **8e**

Prepared by the same procedure as per **7a** starting from **6e**. **¹H NMR** (CDCl₃, 300 MHz): δ 7.47 (d, 1H, J = 6.6 Hz), 7.21-7.08 (m, 3H), 6.96 (dd, 1H, J = 17.6, 11.0), 5.64 (d, 1H, J = 17.0 Hz), 5.34-5.31 (m, 3H), 4.10-3.98 (m, 1H), 2.97 (dd, 1H, J = 13.7, 6.6 Hz), 2.78 (dd, 1H, J = 13.7, 6.6 Hz), 1.97-1.75 (m, 2H), 1.73-1.45 (m, 3H), 1.44-1.16 (m, 3H), 0.99-0.51 (m, 2H), 0.84 (d, 3H, J = 6.6 Hz), 0.73 (d, 3H, J = 6.6 Hz), 0.58 (d, 3H, J = 6.6 Hz). **IR** (neat, cm⁻¹): 2953, 2919, 2868, 2097, 1454, 1236, 971. **LRMS** (m/z, (relative intensity)): 355 (MNH₄⁺, 20), 329 (30), 209 (100), 194 (40). **HRMS** calculated for C₂₂H₃₅N₄: 355.2862, found: 355.2867. $[\alpha]_D^{20}$ = -54.8 (c 1.03, CHCl₃).

Synthesis of azide **9f** or **10f**

7f/8f

9f/10f

Prepared by the same procedure as per **7a** starting from **5f** or **6f**. The ratio of **9f**:**10f** was 3:1 starting from **5f** and 1:3 starting from **6f** (see blown-up portions of NMRs of these compounds in this supporting information). In both cases, the ratio of (**9f**+**10f**):(**7f**+**8f**) was 96:4. **7f**: **¹H NMR** (CDCl₃, 300 MHz): δ 7.61-7.26 (m, 5H), 5.62-5.55 (m, 1H), 5.00 (d, 1H, J = 7.2 Hz), 4.43 (dd, 1H, J = 8.8, 3.9 Hz), 2.13-1.85 (m, 2H), 1.73-1.45 (m, 3H), 1.40-1.25 (m, 2H), 1.10-0.77 (m, 3H), 0.90 (d, 3H, J = 6.6 Hz), 0.87 (d, 3H, J = 6.6 Hz), 0.81 (d, 3H, J = 6.6 Hz). **8f**: **¹H NMR** (CDCl₃, 300 MHz): δ 7.44-7.27 (m, 5H), 5.63-5.56 (m, 1H), 4.99 (d, 1H, J = 7.2 Hz), 4.42 (d, 1H, J = 7.7 Hz), 2.14-1.86 (m, 2H), 1.72-1.68 (m, 3H), 1.55-1.45 (m, 1H), 1.34-1.25 (m, 3H), 1.05-0.67 (m, 3H), 0.97 (d, 3H, J = 7.2 Hz), 0.88 (d, 3H, J = 6.1 Hz), 0.80 (d, 3H, J = 7.2 Hz). **¹³C NMR** (CDCl₃, 75 MHz): δ 136.3 (s), 134.5 (d), 132.7 (d), 128.6 (d), 128.0 (d), 127.9 (d), 126.8 (d), 126.6 (d), 123.5 (d), 65.6 (d), 65.0 (d), 44.3 (d), 43.8 (d), 43.4 (d), 35.0 (t), 34.9 (t), 32.6 (d), 31.6 (t), 26.3 (d), 24.1 (t), 22.7 (q), 21.4 (q), 15.3 (q), 15.1 (q), 14.1 (q). **IR** (neat, cm⁻¹): 3081,

3031, 2951, 2921, 2096, 1496, 1449, 1248, 967. **LRMS** (m/z , (relative intensity)): 315 ($(\text{MNH}_4)^+$, 2), 270 (45), 255 (100), 226 (4), 132(11), 104 (10). **HRMS** calculated for $\text{C}_{19}\text{H}_{31}\text{N}_4$ (MNH_4) $^+$: 315.2549, found: 351.2539. **9f**: $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.61-7.26 (m, 5H), 6.63 (d, 1H, $J = 15.4$ Hz), 6.16 (dd, 1H, $J = 15.4$, 8.3 Hz), 4.43 (dd, 1H, $J = 8.8$, 3.9 Hz), 2.13-1.85 (m, 2H), 1.73-1.45 (m, 3H), 1.40-1.25 (m, 2H), 1.10-0.77 (m, 3H), 0.90 (d, 3H, $J = 6.6$ Hz), 0.87 (d, 3H, $J = 6.6$ Hz), 0.81 (d, 3H, $J = 6.6$ Hz). **10f**: $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.61-7.26 (m, 5H), 6.61 (d, 1H, $J = 15.4$ Hz), 6.27 (dd, 1H, $J = 15.4$, 7.7 Hz), 4.43 (dd, 1H, $J = 8.8$, 3.9 Hz), 2.13-1.85 (m, 2H), 1.73-1.45 (m, 3H), 1.40-1.25 (m, 2H), 1.10-0.77 (m, 3H), 0.90 (d, 3H, $J = 6.6$ Hz), 0.87 (d, 3H, $J = 6.6$ Hz), 0.81 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3066, 3028, 2958, 2870, 2095, 1495, 1451, 1249, 968. **LRMS** (m/z , (relative intensity)): 315 ($(\text{MNH}_4)^+$, 3), 270 (75), 255 (100), 226 (9), 158 (11), 132 (19), 81 (7). **HRMS** calculated for $\text{C}_{19}\text{H}_{31}\text{N}_4$ (MNH_4) $^+$: 315.2549, found: 351.2539.

Synthesis of amine **11a**:

In a 25 mL r.b. flask was dissolved the azide **7a** (420 mg, 1.149 mmol) and triphenylphosphine (301 mg, 1.149 mmol) in THF (4.2 mL). After addition of water (31 mg, 1.724 mmol), the reaction mixture was stirred at r.t. for 17 h and then extracted with 3 portions of Et_2O . The combined organic extracts were washed once with water and once with brine, dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a white oily solid. The crude product was purified on silica gel with 1:4 / EtOAc : hexanes as eluant to afford a colorless oil (370 mg, 95 %). $^1\text{H NMR}$ (CDCl_3 , 300MHz): δ 5.46-5.29 (m, 2H), 3.57 (dd, 1H, $J = 8.3$, 2.8 Hz), 3.44-3.33 (m, 2H), 1.89-1.54 (m, 8H), 1.37-1.26 (m, 1H), 0.97-0.80 (m, 9H), 0.90 (s, 9H), 0.68 (d, 3H, $J = 6.6$ Hz), 0.06 (s, 6H). **IR** (neat, cm^{-1}) 3386, 3311, 2955, 2929, 2857, 1471, 1384. **LRMS** (m/z , (relative intensity)): 339 ($(\text{M})^+$, 1), 324 ($(\text{M}-\text{CH}_3)^+$, 2), 282 (16), 194 (100), 177 (6), 135 (10), 109 (10), 95 (15), 74 (39). **HRMS** calculated for $\text{C}_{20}\text{H}_{41}\text{NOSi}$: 339.2957, found: 339.2948. $[\alpha]_{\text{D}}^{20} = -49.2$ (c 1.80, CHCl_3).

Synthesis of amine **11b** (isolated as the hydrochloric salt):

LiAlH₄ (364 mg, 9.63 mmol) was suspended in THF (40 mL). Allylic azide **7b** (1.90 g, 6.09 mmol) was added over a period of 5 min. The reaction was stirred at r.t for 30 min. The reaction mixture was quenched with water and then washed with 2N HCl. The phases were separated and the aqueous phase was extracted three times with CH₂Cl₂. The organic layers were combined, washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give the ammonium salt of **11b** as white crystalline solid (1.81 g, 92 %). m.p. 239 °C (decomposition). ¹H NMR (CDCl₃, 300 MHz): δ 8.79 (s, 3H), 7.27-7.15 (m, 5H), 5.44-5.38 (m, 2H), 3.93-3.78 (m, 1H), 3.35 (dd, 1H, *J* = 13.2, 4.4 Hz), 2.97 (dd, 1H, *J* = 13.2, 11.0 Hz), 1.88-1.42 (m, 4H), 1.41-1.15 (m, 2H), 0.96-0.55 (m, 4H) 0.84 (d, 3H, *J* = 7.1 Hz), 0.76 (d, 3H, *J* = 6.6 Hz), 0.65 (d, 3H, *J* = 7.1 Hz). IR (neat, cm⁻¹): 3034, 2954, 2913, 1612, 1510, 1453, 1373, 1210. LRMS (*m/z*, (relative intensity)): 284 (M-H(HCl)⁺, 2), 270 (2), 194 (100). HRMS calculated for C₂₀H₃₀N (M-H)⁺: 284.2378, found: 284.2373. [α]_D²⁰ = -1.3 (*c* 1.07, CHCl₃).

Synthesis of amine **11c**:

LiAlH₄ (542 mg, 20.5 mmol) was suspended in THF (80 mL). Allylic azide **7c** (3.81 g, 13.7 mmol) was added over a period of 5 min. The reaction was stirred at r.t for 30 min. The reaction mixture was quenched with water and then washed with 2N HCl. The reaction mixture was basified with 3N NaOH and stirred for 15 min. Phases were separated and the aqueous phase was extracted three times with Et₂O. Organic layers were combined, washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give amine **11c** as a colorless oil (3.27 g, 96 %). ¹H NMR (CDCl₃, 300MHz): δ 5.41 (dd, 1H, *J* = 15.4, 7.2 Hz), 5.29 (dd, 1H, *J* = 15.4, 8.8 Hz), 2.96 (d, 1H, *J* = 7.2 Hz), 1.95-1.80 (m, 2H), 1.73-1.68 (m, 1H), 1.60-1.54 (m, 2H), 1.42-1.30 (m, 1H), 1.08-0.70 (m, 4H), 0.88 (s, 9H), 0.85 (d, 6H, *J* = 6.6 Hz), 0.69 (d, 3H, *J* = 6.6 Hz). IR

(neat, cm^{-1}): 3380, 3314, 3186, 2957, 2869, 1466, 1386, 1363, 974. **LRMS** (m/z , (relative intensity)): 252 ($(\text{MH})^+$, 36), 235 (78), 194 (100), 137 (10), 95 (9). **HRMS** calculated for $\text{C}_{17}\text{H}_{34}\text{N}$: 252.2691, found: 252.2694. $[\alpha]_{\text{D}}^{20} = -38.4$ (c 3.77, CHCl_3).

Synthesis of amine **11d**:

Prepared by the same procedure as per **11c**. **^1H NMR** (CDCl_3 , 300MHz) : δ 5.46-5.31 (m, 2H), 3.36 (q, 1H, $J = 7.2$ Hz), 1.93-1.80 (m, 2H), 1.71 (br d, 1H, $J = 12.7$ Hz), 1.63-1.45 (m, 4H), 1.41-1.27 (m, 3H), 1.02-0.78 (m, 7H), 0.85 (dd, 6H, $J = 7.2, 2.2$ Hz), 0.70 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3367, 3283, 2956, 1575, 970. **LRMS** (m/z , (relative intensity)): 237 ($(\text{M})^+$, 1), 194 (100), 177 (6), 98 (20), 56 (45). **HRMS** calculated for $\text{C}_{16}\text{H}_{31}\text{N}$: 237.2456, found: 237.2451. $[\alpha]_{\text{D}}^{20} = -55.5$ (c 2.77, CHCl_3).

Synthesis of amine **11e**:

Prepared by the same procedure as per **11c**. **^1H NMR** (CDCl_3 , 300 MHz) : δ 7.50 (d, 1H, $J = 8.8$ Hz), 7.20-7.11 (m, 3H), 7.03 (dd, 1H, $J = 17.0$ and 11.0), 5.65 (d, 1H, $J = 17.6$ Hz), 5.44-5.22 (m, 3H), 3.63 (m, 1H), 2.97-2.89 (m, 2H), 1.77-1.14 (m, 8H), 0.98-0.65 (m, 8H), 0.67 (d, 3H, $J = 7.1$ Hz). **IR** (neat, cm^{-1}): 3340, 3064, 2952, 1625, 1453. **LRMS** (m/z , (relative intensity)): 312 ($(\text{MH})^+$, 70), 194 (100). **HRMS** calculated for $\text{C}_{22}\text{H}_{34}\text{N}$ ($(\text{MH})^+$): 312.2691, found: 312.2697. $[\alpha]_{\text{D}}^{20} = -11.9$ (c 1.40, CHCl_3).

Synthesis of Fmoc-carbamate **12a**:

In a 100 mL r.b. flask was dissolved the amine **11a** (610 mg, 1.80 mmol) in dichloromethane (11 mL) and a 10% solution of NaHCO_3 (21 mL) was added. This reaction mixture was cooled to 0 °C and a solution of 9-fluoromethylchloroformate (558

mg, 2.16 mmol) in dichloromethane (10.0mL) was poured into the reaction r.b. flask and stirred at r.t. for 23 h. The aqueous phase was separated and extracted with 2 portions of dichloromethane. The combined organic layers were washed once with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure to give a yellow oily solid. The crude product was purified by flash chromatography on silica gel using 1:9 / EtOAc : hexanes as eluent to obtain a white solid (1.0 g, 100 %). $^1\text{H NMR}$ (CDCl_3 , 300MHz) : δ 7.77 (d, 2H, $J = 7.2$ Hz), 7.60 (d, 2H, $J = 7.7$ Hz), 7.44-7.28 (m, 4H), 5.41 (d, 2H, $J = 3.9$ Hz), 5.08-4.95 (m, 1H), 4.55 (d, 1H, $J = 7.7$ Hz), 4.38 (d, 1H, $J = 6.6$ Hz), 4.33-4.21 (m, 1H), 3.64 (qd, 2H, $J = 10.5, 4.4$ Hz), 1.90-1.81 (m, 2H), 1.73-1.67 (m, 1H), 1.61-1.55 (m, 3H), 1.37-1.26 (m, 2H), 1.01-0.76 (m, 9H), 0.90 (s, 9H), 0.67 (d, 3H, $J = 7.2$ Hz), 0.06 (s, 6H). **LRMS** (m/z , (relative intensity)): 504 ($(\text{M}-\text{C}_4\text{H}_9)^+$, 10), 416 (18), 282 (6), 194 (45), 178 (100), 118 (11), 89 (7), 74 (10). **HRMS** calculated for $\text{C}_{31}\text{H}_{42}\text{NO}_3\text{Si}$ ($\text{M}-\text{C}_4\text{H}_9$) $^+$: 504.2934, found 504.2922.

Synthesis of Fm-carbamate **12b**:

Prepared by the same procedure as per **12a**, except that in this case, the ammonium salt of **11b** (1.07 g, 3.32 mmol) was neutralized prior to being used by adding it to a biphasic mixture of 1N NaOH (50 mL) and Et_2O (50 mL) and then stirring vigorously until complete dissolution of the chloride salt. The phases were then separated and the aqueous phase was extracted three times with Et_2O . The organic layers were combined, washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give the free amine as a colorless oil, which was used in this reaction without further purification. m.p. 123 °C: $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 7.77 (d, 2H, $J = 7.7$ Hz), 7.56 (d, 2H, $J = 7.1$ Hz), 7.41 (t, 2H, $J = 7.4$ Hz), 7.31 (t, 2H, $J = 7.4$ Hz), 7.26-7.12 (m, 5H), 5.45-5.16 (m, 2H), 4.74-4.05 (m, 1H), 4.55-4.31 (m, 3H), 4.21 (t, 1H, $J = 6.6$ Hz), 2.96-2.62 (m, 2H), 1.93-1.78 (m, 1H), 1.78-1.46 (m, 4H), 1.45-1.21 (m, 1H), 1.05-0.65 (m, 3H), 0.85 (d, 3H, $J = 6.6$ Hz), 0.81 (d, 3H, $J = 7.1$ Hz), 0.67 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3327, 3033, 2953, 1706, 1507, 1239, 738. **LRMS** (m/z , (relative intensity)): 508

((MH)⁺, 40), 416 (M⁺-C₇H₇, 60), 178 (100). **HRMS** calculated for C₃₅H₄₂NO₂: 508.3215, found: 508.3222. $[\alpha]_D^{20} = -34.5$ (c 1.00, CHCl₃).

Synthesis of Fm-carbamate **12c**:

Prepared by the same procedure as per **12a**. **¹H NMR**(CDCl₃, 300MHz) : δ 7.76 (d, 2H, $J = 7.2$ Hz), 7.59 (d, 2H, $J = 7.2$ Hz), 7.35 (dt, 4H, $J = 12.1, 7.2$ Hz), 5.44-5.28 (m, 2H), 4.78-4.64 (m, 1H), 4.41 (d, 2H, $J = 7.2$), 4.24 (t, 1H, $J = 7.2$), 3.99-3.86 (m, 1H), 1.96-1.67 (m, 3H), 1.41-1.21 (m, 2H), 1.10-0.82 (m, 5H), 0.89 (s, 9H), 0.85 (d, 6H, $J = 7.2$ Hz), 0.67 (d, 3H, $J = 7.2$ Hz). **LRMS** (m/z, (relative intensity)): 474 ((MH)⁺, 5), 330 (7), 235 (26), 194 (34), 179 (100), 165 (13), 82 (8). **HRMS** calculated for C₃₂H₄₄NO₂: 474.3372, found: 474.3366.

Synthesis of Fm-carbamate **12d**:

Prepared by the same procedure as per **12a**. **¹H NMR** (CDCl₃, 300MHz) : δ 7.77 (d, 2H, $J = 7.7$ Hz), 7.60 (d, 2H, $J = 7.7$ Hz), 7.34 (dt, 4H, $J = 12.1, 7.7$ Hz), 5.41-5.24 (m, 2H), 4.65-4.54 (m, 1H), 4.40 (d, 2H, $J = 6.6$ Hz), 4.23 (t, 1H, $J = 6.6$ Hz), 4.16-4.09 (m, 1H), 1.88-1.23 (m, 10H), 1.08-0.82 (m, 13H), 0.67 (d, 3H, $J = 6.6$ Hz). **LRMS** (m/z, (relative intensity)): 460 ((MH)⁺, 100), 316 (8), 282 (15), 221 (22), 178 (64), 98 (2). **HRMS** calculated for C₃₁H₄₂NO₂: 460.3215, found: 460.3206.

Synthesis of amino acid **13a** :

In a 25 mL 3 necks r.b. flask was dissolved the protected amine **12a** (50 mg, 0.089 mmol) in dichloromethane (1.0 mL) and this solution was cooled to -78 °C and ozone was bubbled through until the reaction mixture turned blue (approx. 5 min) and then nitrogen was bubbled through for 15 min. The resulting mixture was quenched at -78 °C with triphenylphosphine (46.7 mg, 0.178 mmol), was allowed to warm to r.t. over 19 h and concentrated under reduced pressure to give a yellow liquid. The crude aldehyde was dissolved in a 10 mL r.b. flask with 2-methyl-2-butene (0.19 mL, 125 mg, 1.780 mmol) in *tert*-butanol (1.0 mL) at r.t. In a another r.b. flask was stirred NaClO₂ (48.3 mg, 0.534 mmol) and NaH₂PO₄·H₂O (25.2 mg, 20.178 mmol) in water (1.0 mL) and this mixture was added into the first flask containing the aldehyde. After, the reaction mixture was stirred at r.t. for 5 h, the aqueous phase was separated and extracted three times with EtOAc. The combined organic layers were washed once with brine, dried over MgSO₄, filtered and concentrated under reduced pressure to give a light yellow oil. The crude product was purified by flash chromatography on silica gel using 2:3 / EtOAc : hexanes as eluent to produce a white solid (29.5mg, 75 %). m.p. 103 °C. ¹H NMR (CDCl₃, 300MHz) : δ 10.47 (br CO₂H, 1H), 7.77 (d, 2H, *J* = 7.2 Hz), 7.62 (t, 2H, *J* = 6.6 Hz), 7.36 (dt, 4H, *J* = 12.7, 7.7 Hz), 5.64 (d, 1H, *J* = 8.8 Hz), 4.51-4.36 (m, 2H), 4.41 (t, 1H, *J* = 6.6 Hz), 4.26 (t, 1H, *J* = 7.2 Hz), 4.15 (dd, 1H, *J* = 7.7, 2.2 Hz), 3.89 (dd, 1H, 6.6, 3.3 Hz), 0.91 (s, 9H), 0.08 (s, 6H). ¹³C NMR (CDCl₃, 75MHz): 175.5 (s), 156.0 (s), 143.6 (s), 141.2 (s), 127.7 (d), 127.1 (d), 125.1 (d), 120.0 (d), 67.3 (t), 63.3 (t), 55.6 (d), 47.0 (d), 25.7 (q), 18.2 (s), -5.6 (q). IR (neat, cm⁻¹): 3442, 3437, 3281, 3071, 2952, 2929, 2857, 1723, 1512, 1254, 1111, 835, 738. LRMS (m/z, (relative intensity)): 384 ((M-C₄H₉)⁺, 4), 206 (18), 178 (100), 165 (18), 116 (19), 74 (20). HRMS calculated for C₂₀H₂₂NO₅Si (M-C₄H₉)⁺: 384.1267, found: 384.1259. [α]_D²⁰ = +10.7 (c 2.00, CHCl₃). 86% e.e. (HPLC).

Synthesis of amino acid **13b**:

Prepared by the same procedure as per **13a**. See G. Barcelo, J.-P. Senet, G. Sennyey, J. Bensoam, A. Loffet, *Synthesis* **1986**, 8, 627-632. $[\alpha]_D^{20} = +25.6$ (c 1.04, CHCl_3). 95% e.e. (HPLC).

Synthesis of amino acid **13c** via the amino aldehyde :

In a 25 mL r.b. flask was dissolved the protected amine **12c** (370 mg, 0.781 mmol) in dichloromethane (14.8 mL). The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and ozone was bubbled through until the reaction mixture turned blue (approx. 8 min.) and then nitrogen was bubbled for 15 min. The resulting mixture was quenched at $-78\text{ }^{\circ}\text{C}$ with dimethylsulfide (1.15 mL, 970 mg, 15.6 mmol), was allowed to warm to r.t. over 3h and was concentrated under reduced pressure to give a yellow liquid. The crude product was purified by flash chromatography on silica gel using 1:4 / EtOAc : hexanes as eluent to obtain a white oily solid (175 mg , 67 %). **^1H NMR** (CDCl_3 , 300MHz): δ 9.86 (s, 1H), 7.76 (d, 2H, $J = 7.7$ Hz), 7.60 (d, 2H, $J = 7.7$ Hz), 7.36 (dt, 4H, $J = 11.0, 7.7$ Hz), 5.42 (br d, 1H, $J = 8.8$ Hz), 4.43-4.38 (m, 2H), 4.30-4.19 (m, 2H), 1.07(s, 9H). **IR** (neat, cm^{-1}): 3336 (br), 2963, 2866, 1717, 1509, 1325, 1241, 758, 740. **LRMS** (m/z , (relative intensity)): 355 ($(\text{MNH}_4)^+$, 13), 338 ($(\text{MH})^+$, 100), 308 (10), 178 (77), 160 (36), 116 (21). **HRMS** calculated for $\text{C}_{21}\text{H}_{24}\text{NO}_3$: 338.1756, found: 338.1764. $[\alpha]_D^{20} = +2.0$ (c 2.26, CHCl_3).

In a 25 mL r.b. flask was dissolved the amino aldehyde (150 mg, 0.445 mmol) in acetone (6.0 mL). This solution was cooled to $0\text{ }^{\circ}\text{C}$ and a few drops of Jones' reagent were added until the reaction mixture turned orange. The reaction was stirred at r.t. for 4h, quenched with isopropanol and concentrated under reduced pressure. The resulting residue was extracted with 3 portions of dichloromethane. The combined organic layers were washed once with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure to give a yellow liquid. The crude product was purified by flash chromatography on silica

gel using 1:20 / MeOH : CH₂Cl₂ as eluent to obtain a clear glossy solid (66.2 mg, 42 %). m.p. 71 °C. ¹H NMR (CDCl₃, 300MHz): δ 7.76 (d, 2H, *J* = 7.7 Hz), 7.59 (d, 2H, *J* = 7.2 Hz), 7.35 (dt, 4H, *J* = 11.6, 7.7 Hz), 5.32 (d, 1H, *J* = 9.4 Hz), 4.42 (qi, 2H, *J* = 7.1 Hz), 4.25-4.21 (m, 1H), 1.04 (s, 9H). IR (neat, cm⁻¹): 3557-2507 (br), 3066, 2967, 1720, 1708, 1560, 1510, 1218, 1059, 758, 740. LRMS (m/z, (relative intensity)): 371 ((MNH₄)⁺, 88), 354 ((MH)⁺, 15), 327 (31), 310 (27), 178 (100), 132 (50), 86 (12). HRMS calculated for C₂₁H₂₄NO₄: 354.1705, found: 354.1714. [α]_D²⁰ = -8.7 (*c* 1.91, CHCl₃). 88% e.e. (HPLC).

Synthesis of amino acid **13d**:

Prepared by the same procedure as per **13a**, except that the mixture was quenched with dimethylsulfide in lieu of triphenylphosphine. m.p. 54-56 °C. ¹H NMR (CDCl₃, 300MHz): δ 7.76 (d, 2H, *J* = 7.2 Hz), 7.59 (d, 2H, *J* = 6.6 Hz), 7.36 (dt, 4H, *J* = 11.6, 7.2 Hz), 5.20 (d, 1H, *J* = 7.7 Hz), 4.43 (d, 2H, *J* = 6.6 Hz), 4.23 (t, 1H, *J* = 7.2 Hz), 3.56 (m, 2H), 1.92-1.83 (m, 1H), 1.74-1.64 (m, 1H), 1.42 (sext, 2H, *J* = 7.2 Hz), 0.96 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (CDCl₃, 75MHz): 177.6 (s), 156.1 (s), 143.8 (s), 141.3 (s), 127.7 (d), 127.1 (d), 125.1 (d), 120.0 (d), 67.1 (t), 53.6 (d), 47.1 (d), 34.4 (t), 18.5 (t), 13.6 (q). IR (neat, cm⁻¹): 3429, 3320, 3069, 2962, 2872, 2741, 2616, 1734, 1702, 1521, 1448, 1339, 1107. LRMS (m/z, (relative intensity)): 357 ((MNH₄)⁺, 5), 340 ((MH)⁺, 5), 214 (32), 196 (11), 179 (86), 165 (18), 118 (100). HRMS calculated for C₂₀H₂₂NO₄ (MH)⁺: 340.1549, found: 340.1547. [α]_D²⁰ = -1.9 (*c* 2.07, CHCl₃). 84% e.e. (HPLC).

Synthesis of *t*-Bu carbamate **14b**:

The ammonium salt of **11b** (1.81 g, 5.62 mmol) was added to a biphasic mixture of 1N NaOH (50 mL) and Et₂O (50 mL) and then stirred vigorously until the complete dissolution of the chloride salt. The phases were separated and the aqueous phase was extracted three times with Et₂O. The organic layers were combined, washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give the free

amine as a colorless oil (1.62 g, 98%). At r.t., CsOH•H₂O (0.952 g, 5.67 mmol) and MS 4Å (1.80 g) were stirred in DMF (35 mL) during 15 min and then the free amine **11b** (1.62 g, 5.6 mmol) was added. After 30 min, 4-bromobutene (2.30 mL, 22.7 mmol) was added and the reaction mixture was stirred overnight at r.t. for 20 h after which time, additional 4-bromobutene (1.60 mL, 11.3 mmol) was added. After 24 h, the reaction was complete. The reaction mixture was filtered to remove the MS 4Å and the filter paper was rinsed several times with Et₂O (20 mL). The mother liquor was quenched with NaOH 1M (30 mL). The phases were separated and the aqueous phase was extracted three times with Et₂O. The organic layers were combined, washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. The crude product was purified by flash chromatography on silica gel column eluting with Et₂O and hexanes (1:1) to give the alkylated amine as a colorless oil (1.30 g, 68 %). **¹H NMR** (CDCl₃, 300 MHz): δ 7.29-7.15 (m, 5H), 5.66 (ddt, 1H, *J* = 17.0, 10.5, 6.6 Hz), 5.23-5.20 (m, 2H), 4.96 (d, 1H, *J* = 12.1 Hz), 4.92 (d, 1H, *J* = 4.4 Hz), 3.25-3.17 (m, 1H), 2.72 (d, 2H, *J* = 7.2 Hz), 2.68 (dt, 1H, *J* = 11.6, 7.1 Hz), 2.48 (dt, 1H, *J* = 11.6, 6.8 Hz), 2.16 (q, 2H, *J* = 6.8 Hz), 1.92-1.65 (m, 3H), 1.62-1.24 (m, 4H), 1.05-0.70 (m, 4H), 0.85 (d, 3H, *J* = 6.6 Hz), 0.84 (d, 3H, *J* = 7.1 Hz), 0.68 (d, 3H, *J* = 6.6 Hz). **IR** (neat, cm⁻¹): 3700-3100 (br), 3060, 2954, 2866, 1638, 1452, 1118, 967, 693. **LRMS** (*m/z* (relative intensity)): 339 (*M*⁺, 1), 248 (*M*⁺-C₇H₇, 100), 110 (60). **HRMS** calculated for C₁₇H₃₀N (*M*-C₇H₇)⁺: 248.2378, found : 248.2385. [α]_D²⁰ = -45.5 (*c* 1.41, CHCl₃).

This amine (1.05 g, 2.94 mmol) and Et₃N (0.62 mL, 4.42 mmol) were dissolved in DMF (31 mL). Then, (Boc)₂O (965 mg, 4.42 mmol) was added to the reaction mixture. The reaction was stirred at r.t. for 4 h. The reaction mixture was quenched with saturated NH₄Cl and then made basic with 1N NaOH. The organic phase was extracted three times with a mixture of hexanes and Et₂O (1:1), washed twice with water and then with brine, dried over magnesium sulfate and concentrated under reduced pressure to give a colorless oil. The crude product was purified by flash chromatography on a silica gel column eluting with hexanes and Et₂O (9:1) to give *N*-protected amine **14b** as colorless oil (1.24 g, 96 %). **¹H NMR** (CDCl₃, 300 MHz): δ 7.29-7.14 (m, 5H), 5.71 (ddt, 1H, *J* = 17.0, 10.4, 7.0 Hz), 5.47 (dd, 1H, *J* = 15.4, 6.6 Hz), 5.29 (dd, 1H, *J* = 15.4, 8.8 Hz), 5.03-4.96 (m, 2H), 4.70-4.20 (br s, 1H), 3.14-2.90 (m, 2H), 2.95 (dd, 1H, *J* = 13.8, 8.2 Hz), 2.83

(dd, 1H, $J = 13.2, 7.2$ Hz), 2.33-2.05 (m, 2H), 1.86 (dq, 1H, $J = 9.3, 3.8$ Hz), 1.77-1.17 (m, 6H), 1.39 (s, 9H), 1.08-0.58 (m, 3H), 0.85 (d, 3H, $J = 6.6$ Hz), 0.82 (d, 3H, $J = 7.7$ Hz), 0.67 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3065, 3029, 2954, 2866, 1691, 1457, 1404, 1365, 1170. **LRMS** (m/z (relative intensity)): 348 ($\text{M}^+ - \text{C}_7\text{H}_7$, 25), 292 (100), 248 (60), 154 (88). **HRMS** calculated for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{N}$ ($\text{M} - \text{C}_7\text{H}_7$) $^+$: 348.2902, found : 348.2906. $[\alpha]_{\text{D}}^{20} = -59.4$ (c 1.12, CHCl_3).

Synthesis of *t*-Bu carbamate **14c**:

The alkylation was performed as per *N*-Boc amine **14d** starting with 101 mg (0.402 mmol) of amine **11c** to give the desired product as a colorless oil (98.1 mg, 85 %). Except, in this case, the reaction was completed in 3 h. **^1H NMR** (CDCl_3 , 300 MHz): δ 5.94-5.81 (m, 1H), 5.26-5.04 (m, 4H), 3.25 (dd, 1H, $J = 14.3, 5.5$ Hz), 3.03 (dd, 1H, $J = 13.6, 6.6$ Hz), 2.57 (d, 1H, $J = 7.7$ Hz), 2.0-1.86 (m, 1H), 1.74-1.67 (m, 1H), 1.64-1.51 (m, 3H), 1.48-1.16 (m, 2H), 1.05-0.77 (m, 18 H), 0.72 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3082, 2954, 2895, 1645, 1454, 1363, 970, 915. **LRMS** (m/z (relative intensity)): 276 ($\text{M}^+ - \text{CH}_3$, 5), 234 (50), 96 (100). **HRMS** calculated for $\text{C}_{16}\text{H}_{28}\text{N}$ ($\text{M} - \text{C}_4\text{H}_9$) $^+$: 234.2222, found : 234.2224. $[\alpha]_{\text{D}}^{20} = -65.5$ (c 1.60, CHCl_3).

The protection of the resulting alkylated amine was performed as per **14d** starting with 504 mg (1.73 mmol) of the above amine to give *N*-protected amine **14c** as a colorless oil (641 mg, 96 %). However, after 30 h, 562 mg (2.63 mmol) of supplementary $(\text{Boc})_2\text{O}$ and Et_3N (0.360 mL, 2.60 mmol) were added. The reaction was completed in 42 h. **^1H NMR** (CDCl_3 , 300 MHz): δ 5.88-5.67 (m, 1H), 5.52-5.30 (m, 2H), 5.10-4.95 (m, 2H), 4.61-4.17 (m, 1H), 3.97-3.53 (m, 2H), 1.96-1.23 (m, 7H), 1.42 (s, 9H), 1.05-0.74 (m, 9H), 0.90 (s, 9H), 0.69 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3078, 2963, 1812, 1693. **LRMS** (m/z (relative intensity)): 334 ($\text{M}^+ - \text{C}_4\text{H}_6$, 5), 278 (60), 234 (100), 140 (75), 96 (50). **HRMS** calculated for $\text{C}_{21}\text{H}_{36}\text{NO}_2$ ($\text{M} - \text{C}_4\text{H}_9$) $^+$: 334.2746, found : 334.2748. $[\alpha]_{\text{D}}^{20} = -48.3$ (c 1.47, CHCl_3).

Synthesis of *t*-Bu carbamate **14d**:

In a 50 mL r.b. flask was added CsOH monohydrated (202 mg, 1.023 mmol), 4Å molecular sieve (325 mg) and DMF (5.4 mL). The amine **11d** (272 mg, 1.146 mmol) was then added to the suspension and stirred 30 min at r.t. Then, the 4-bromo-1-butene (178 mg, 1.318 mmol) was added and the resulting suspension was stirred at r.t. for 19 h and an excess of 4-bromo-1-butene (0.5 eq.) was added. The resulting mixture was stirred again for another 87 h and was filtered over a silica gel pad, washed with EtOAc and the filtrate was concentrated under reduced pressure. The residue was then diluted with a 1M aqueous solution of NaOH and was extracted with 3 portions of EtOAc. The combined organic extracts were washed once with water and once with brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a yellow oily solid. The crude product was purified on silica gel with 1:1 / Et₂O:Hexanes as eluant to afford a colorless oil (334 mg, 67 %). ¹H NMR (CDCl₃, 300MHz): δ 5.82-5.69 (m, 1H), 5.27 (dd, 1H, *J* = 15.1, 9.1 Hz), 5.13 (d, 1H, *J* = 8.3 Hz), 5.10-5.08 (m, 1H), 5.02 (d, 1H, *J* = 8.8 Hz), 2.94 (dt, 1H, *J* = 13.2, 8.2 Hz), 2.70 (dt, 1H, *J* = 11.6, 7.2 Hz), 2.59-2.49 (m, 1H), 2.24 (q, 2H, *J* = 6.9 Hz), 1.92-1.83 (m, 2H), 1.71 (br d, 1H, *J* = 12.1 Hz), 1.62-1.54 (m, 2H), 1.42-1.20 (m, 6H), 1.02-0.76 (m, 6H), 0.88 (d, 6H, *J* = 7.1 Hz), 0.70 (d, 3H, *J* = 7.2 Hz). IR (neat, cm⁻¹): 3077, 2956, 2925, 2871, 2843, 1640, 1455, 1122, 972, 912. LRMS (*m/z*, (relative intensity)): 248 ((M-C₃H₇)⁺, 100), 137 (11), 110 (41), 81 (13). HRMS calculated for C₁₇H₃₀N (M-C₃H₇)⁺: 248.2378, found 248.2380. [α]_D²⁰ = -70.9 (c 2.26, CHCl₃).

In a 50 mL r.b. flask was dissolved the alkylated amine (113 mg, 0.388 mmol) in DMF (2.25 mL) and this solution was stirred at r.t. for 5 min. Then, triethylamine (59 mg, 0.582 mmol) was added and this solution was stirred for another 5 min at r.t. Di-*tert*-butyldicarbonate (127 mg, 0.582 mmol) was added and the resulting mixture was stirred for 20 min at r.t. and then heated to 60°C during 6 h. The mixture was cooled to r.t. and treated with a saturated aqueous solution of NH₄Cl and the aqueous phase was extracted with 3 portions of EtOAc. The combined organic extracts were washed once with water

and once with brine, dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a yellow oil. The crude product was purified on silica gel with 1:20 / EtOAc:Hexanes as eluant to afford a colorless oil (152 mg, 100 %). **^1H NMR** (CDCl_3 , 300MHz): δ 5.79-5.67 (m, 1H), 5.43-5.32 (m, 2H), 5.00 (dd, 2H, $J = 17.1, 9.9$ Hz), 3.06 (br m, 1H), 2.26 (q, 2H, $J = 7.7$ Hz), 1.86-1.69 (m, 3H), 1.62-1.50 (m, 5H), 1.45 (s, 9H), 1.31-1.25 (m, 4H), 1.02-0.77 (m, 7 H), 0.86 (d, 3H, $J = 6.0$ Hz), 0.85 (d, 3H, $J = 6.6$ Hz), 0.68 (d, 3H, $J = 6.6$ Hz). **LRMS** (m/z, (relative intensity)): 391 (M^+ , 1), 348 ($(\text{M}-\text{C}_3\text{H}_7)^+$, 6), 335 ($(\text{M}-\text{C}_4\text{H}_8)^+$, 6), 292 (100), 248 (42), 221 (46), 154 (70), 81 (26). **HRMS** calculated for $\text{C}_{25}\text{H}_{45}\text{NO}_2$: 391.3450, found 391.3462.

Synthesis of dehydropiperidine **15b**:

N-protected amine **14b** (1.15 g, 2.62 mmol) was dissolved in CH_2Cl_2 (520 mL, concentration = 0.005 M). Argon was bubbled through the mixture for 15 min and then the solution was heated to 40 °C. The reflux was stopped and then the Grubbs-Nolan catalyst (22 mg, 0.026 mmol, 1 mol%) was added to the reaction mixture. The reaction was stirred at 40 °C for 3 h. The solvent was evaporated and the crude product was purified by flash chromatography on a silica gel column eluting with hexanes and Et_2O (9:1) to give dihydropiperidine **15b** as a colorless oil (0.69 g, 96 %) and 3-vinyl-*p*-menthane as a colorless liquid (429 mg, 99 %). **^1H NMR** (CDCl_3 , 300 MHz): δ 7.30-7.19 (m, 5H), 5.85-5.74 (m, 1H), 5.55 (dt, 1H, $J = 9.9, 3.9$ Hz), 4.65-4.42 (m, 1H), 4.28-3.87 (m, 1H), 2.96-2.82 (m, 1H), 2.79 (dd, 1H, $J = 11.5, 3.8$ Hz), 2.75 (dd, 1H, $J = 11.5, 3.8$ Hz), 2.28-2.10 (m, 1H), 2.04-1.83 (m, 1H), 1.38 (s, 9H); **IR** (neat, cm^{-1}): 3034, 2972, 2937, 2857, 1691, 1418, 1170, 693. **LRMS** (m/z (relative intensity)): 273 (M^+ , 1), 200 ($\text{M}^+-\text{OC}_4\text{H}_9$, 10), 126 (98), 82 (100). **HRMS** calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_2$: 273.1729, found : 273.1737. $[\alpha]_{\text{D}}^{20} = +130.2$ (c 1.18, CHCl_3).

Dihydropyrrole **15c**:

The reaction was performed as per compound **15b** starting with 403 mg (1.02 mmol) of *N*-protected amine **14c** to give dihydropyrrole **15c** as a colorless oil (216 mg, 94 %) and 3-vinyl-*p*-menthane as a colorless liquid (162 mg, 96 %). Compound **15b** displayed two sets of signals corresponding to two rotamers of the Boc group. **Rotamer A**: $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 5.95-5.72 (m, 2H), 4.51-4.18 (m, 2H), 3.85 (dd, 1H, J = 16.0 and 4.4 Hz), 1.47 (s, 9H), 0.88 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 156.0 (s), 128.5 (d), 127.0, 79.0 (s), 72.5 (d), 54.9 (t), 37.1 (s), 28.4, 26.5 (q). **Rotamer B**: $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 5.95-5.72 (m, 2H), 4.51-4.18 (m, 2H), 3.85 (dd, 1H, J = 16.0 and 4.4 Hz), 1.52 (s, 9H), 0.88 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 156.0 (s), 128.5 (d), 126.3 (d), 79.7, 72.5 (d), 54.9 (t), 37.1 (s), 27.4 (q), 26.5 (q). **IR** (neat, cm^{-1}): 2970, 2867, 1699, 1379, 1173, 1102. **LRMS** (m/z (relative intensity)): 226 (MH^+ , 50), 187 (60), 126 (100). **HRMS** calculated for $\text{C}_{13}\text{H}_{24}\text{NO}_2$ (MH^+): 226.1807, found: 226.1804. $[\alpha]_{\text{D}}^{20} = +105.8$ (c 1.46, CHCl_3).

Synthesis of dehydropiperidine **15d**:

In a 500 mL r.b. flask was dissolved **14d** (475 mg, 1.213 mmol) in CH_2Cl_2 (245 mL, 0.005 M) and the reaction was refluxed for 10 min. The reflux was stopped, the Grubbs catalyst (10.3 mg, 0.012 mmol) was added in small portions, and the reaction mixture was refluxed for 3 h. The resulting solution was concentrated under reduced pressure and the crude product was purified on silica gel with 1:20 / EtOAc:Hexanes as eluant to afford **15d** as a colorless oil (225 mg, 82 %). $^1\text{H NMR}$ (CDCl_3 , 300MHz): δ 5.81-5.74 (m, 1H), 5.67-5.63 (m, 1H), 4.34 (br s, 1H), 4.11 (br s, 1H), 2.96-2.73 (br m, 1H), 2.28-2.08 (br m, 1H), 1.91 (dt, 1H, J = 12.7, 4.4 Hz), 1.67-1.31 (m, 4H), 1.47 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz). **IR** (neat, cm^{-1}): 3032, 2962, 2931, 2873, 1693, 1416, 1390, 1364, 1250, 1174, 704. **LRMS** (m/z , (relative intensity)): 182 ($(\text{M}-\text{C}_3\text{H}_7)^+$, 22), 126 (100), 82 (92).

HRMS calculated for $C_{10}H_{16}NO_2$ (M- C_3H_7): 182.1181, found 182.1176. $[\alpha]_D^{20} = +138.8$ (*c* 1.73, $CHCl_3$).

Synthesis of *t*-Bu carbamate **16**:

The protection was performed as per amine **14d** starting with 27 mg (0.0867 mmol) of amine **11e** to give *N*-protected amine **16** as a colorless oil (33 mg, 94 %). **¹H NMR** ($CDCl_3$, 300 MHz): δ 7.49 (m, 1H), 7.25-6.98 (m, 4H), 5.65 (d, 1H, $J = 17.6$ Hz), 5.32 (d, 1H, $J = 11.0$ Hz), 5.25-5.15 (m, 2H), 4.65-4.20 (m, 2H), 2.98 (dd, 1H, $J = 13.7$, 6.1 Hz), 2.79 (dd, 1H, $J = 13.7$, 7.7 Hz), 1.90-1.60 (m, 3H), 1.46-1.15 (m, 2H), 1.41 (s, 9H), 0.98-0.70 (m, 5H), 0.83 (d, 3H, $J = 6.6$ Hz), 0.82 (d, 3H, $J = 6.6$ Hz), 0.65 (d, 3H, $J = 6.6$ Hz). **IR** (neat, cm^{-1}): 3333 (br), 2953, 2924, 1702, 1365, 1170. **LRMS** (*m/z* (relative intensity)): 412 (MH^+ , 20), 194 (100). **HRMS** calculated for $C_{27}H_{42}NO_2$ (MH) $^+$: 412.3215, found : 412.3223. $[\alpha]_D^{20} = -32.5$ (*c* 1.08, $CHCl_3$).

Synthesis of *N*-Boc amine **17**:

The reaction was performed as per **15b** starting with 42 mg (0.102 mmol) of *N*-protected amine **16** to give dihydropiperidine **17** as a white solid (26 mg, 100 %) and 3-vinyl-*p*-menthane as a colorless liquid (18 mg, 100 %). m.p. 80 °C. **¹H NMR** ($CDCl_3$, 300 MHz): δ 7.21-7.14 (m, 3H), 7.10-7.06 (m, 1H), 6.54 (d, 1H, $J = 9.3$ Hz), 6.00 (dd, 1H, $J = 9.9$, 4.9 Hz), 4.65-4.52 (m, 1H), 4.51-4.42 (m, 1H), 3.05 (dd, 1H, $J = 15.9$, 6.1 Hz), 2.91 (dd, 1H, $J = 15.9$, 5.5 Hz), 1.43 (s, 9H). **¹³C NMR** ($CDCl_3$, 75 MHz): δ 155.0 (s), 132.9 (s), 132.7 (s), 129.3 (d), 128.5 (d), 128.0 (d), 127.6 (d), 126.9 (d), 126.4 (d), 79.4 (s), 44.3 (d), 34.6 (t), 28.3 (q). **IR** (neat, cm^{-1}): 3344, 2976, 2925, 1695, 1493, 1168.

LRMS (m/z (relative intensity)) : 245 (M^+ , 2), 189 ($M^+ - C_4H_9$, 25) 128 (100). **HRMS** calculated for $C_{15}H_{19}NO_2$: 245.1416, found : 245.1419; $[\alpha]_D^{20} = -136.7$ (c 1.18, $CHCl_3$).

Synthesis of *t*-Bu carbamate **18**:

The protection with Boc was performed as per amine **14d** starting with 500 mg (1.47 mmol) of amine **11a** to give the *N*-protected amine as a colorless oil (650 mg, 100 %). **¹H NMR** ($CDCl_3$, 300 MHz) : δ 5.38 (d, 2H, $J = 4.4$ Hz), 4.77 (br s, 1H), 4.08 (br s, 1H), 3.65 (dd, 1H, $J = 9.9, 4.4$ Hz), 3.58 (dd, 1H, $J = 9.9, 3.9$ Hz), 1.97-1.78 (m, 2H), 1.71 (br d, 1H, $J = 11.5$ Hz), 1.63-1.50 (m, 2H), 1.48-1.21 (m, 2H), 1.44 (s, 9H), 1.00-0.76 (m, 9H), 0.88 (s, 9H), 0.67 (d, 3H, $J = 6.6$ Hz), 0.04 (s, 6H). **IR** (neat, cm^{-1}) : 3354 (br), 2954, 2929, 2859, 1719, 1489, 1173, 837. **LRMS** (m/z (relative intensity)) : 440 (MH^+ , 25), 384 (100), 194 (60). **HRMS** calculated for $C_{25}H_{50}NO_3Si$ (MH^+): 440.3560, found : 440.3564. $[\alpha]_D^{20} = -40.8$ (c 1.14, $CHCl_3$).

Then, the *N*-protected amine (418 mg, 0.951 mmol) was dissolved in THF (4.0 mL) and a mixture (12 mL) of acetic acid and water (5:1) was added. The mixture was stirred 24 h at r.t. Water was added (5.0 mL) and the two phases were separated. The aqueous phase was extracted twice with pentane. The organic phases were combined, washed once with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel, eluting with hexanes and ethyl acetate (7:3) furnished the primary alcohol as a white solid (302 mg, 98 %). m.p. 51 °C. **¹H NMR** ($CDCl_3$, 300 MHz) : δ 5.47 (dd, 1H, $J = 15.4, 8.8$ Hz), 5.32 (dd, 1H, $J = 15.9, 6.0$ Hz), 4.73 (br s, 1H), 4.18 (br s, 1H), 3.66 (dd, 1H, $J = 10.4, 3.8$ Hz), 3.59 (dd, 1H, $J = 11.0, 6.0$ Hz), 1.95-1.22 (m, 7H), 1.45 (s, 9H), 1.03-0.68 (m, 3H), 0.86 (d, 6H, $J = 7.1$ Hz), 0.68 (d, 3H, $J = 7.1$ Hz); **IR** (neat, cm^{-1}) : 3500-3100 (br), 2919, 2872, 1693, 1171; **LRMS** (m/z (relative intensity)) : 326 (MH^+ , 5), 294 (40), 270 (100), 238 (60), 194 (100),

177 (80); **HRMS** calculated for $C_{19}H_{36}NO_3$ (MH)⁺: 326.2695, found : 326.2689; $[\alpha]_D^{20} = -73.1$ (*c* 1.16, $CHCl_3$).

The primary alcohol (300 mg, 0.921 mmol) was dissolved in DMF (3.0 mL) and cooled to 0 °C. NaH 60 % w/w in oil (55 mg, 1.38 mmol) was added and the mixture was stirred 5 min. Allyl bromide (0.095 mL, 1.105 mmol) was added and the reaction mixture was stirred 2 h at 0 °C. The reaction mixture was quenched with a saturated solution of ammonium chloride. Phases were separated and the aqueous phase was extracted twice with Et_2O . Organic phases were combined, washed once with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel, eluting with hexanes and ethyl acetate (9:1) furnished **18** as a clear oil (288 mg, 85 %). **¹H NMR** ($CDCl_3$, 300 MHz) : δ 5.92-5.83 (m, 1H), 5.41-5.39 (m, 2H), 5.25 (dd, 1H, *J* = 17.6, 1.6 Hz), 5.17 (dd, 1H, *J* = 10.4, 1.1 Hz), 4.84 (br s, 1H), 4.18 (br s, 1H), 4.07-3.92 (m, 2H), 3.49 (dd, 1H, *J* = 9.9, 4.4 Hz), 3.40 (dd, 1H, *J* = 9.3, 4.4 Hz), 1.97-1.78 (m, 2H), 1.70 (br d, 1H, *J* = 12.6 Hz), 1.65-1.57 (m, 2H), 1.44 (s, 9H), 1.43-1.18 (m, 2H), 0.99-0.75 (m, 9H), 0.66 (d, 3H, *J* = 6.6 Hz). **IR** (neat, cm^{-1}) : 3400-3100 (br), 2952, 2916, 2864, 1717, 1491, 1172. **LRMS** (*m/z* (relative intensity)) : 366 (MH^+ , 15), 310 (100), 194 (70). **HRMS** calculated for $C_{22}H_{40}NO_3$ (MH)⁺: 366.3008, found : 366.3002; $[\alpha]_D^{20} = -54.8$ (*c* 1.56, $CHCl_3$).

Synthesis of heterocycle **19**:

N-protected amine **18** (40 mg, 0.109 mmol) was dissolved in dichloroethane (50 mL, concentration: 0.0022 M). Argon was bubbled through the mixture for 15 min and then the solution was heated to reflux. The reflux was stopped and then the Grubbs-Nolan catalyst (4.5 mg, 0.0041 mmol, 5 mol%) was added to the reaction mixture. The reaction was stirred at reflux of dichloroethane for 1 h. The solvent was evaporated and the crude product was purified by flash chromatography on a silica gel column eluting with hexanes and ethyl acetate (4:1) to give heterocycle **19** as a white solid (18 mg, 81 %) and 3-vinyl-*p*-menthane as a colorless liquid (15 mg, 84 %). m.p. 66 °C. **¹H NMR** ($CDCl_3$,

300 MHz): δ 5.91-5.80 (m, 2H), 4.86-4.79 (m, 1H), 4.16-4.03 (m, 3H), 3.77-3.71 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 155.1 (s), 129.7 (d), 124.7 (d), 79.5 (s), 69.4 (t), 65.2 (t), 43.9 (d), 28.3 (q). **IR** (neat, cm^{-1}): 3332 (br), 2976, 2925, 1708, 1518, 1244, 1168. **LRMS** (m/z (relative intensity)): 184 (M^+-CH_3 , 2), 169 (M^+-2CH_3 , 30), 113 (100). **HRMS** calculated for $\text{C}_9\text{H}_{14}\text{NO}_3$ ($\text{M}-\text{CH}_3$) $^+$: 184.0974, found : 184.0979; $[\alpha]_{\text{D}}^{20} = -132.1$ (c 1.09, CHCl_3).

Synthesis of (+)-Boc-coniine:

In a 50 mL r.b. flask was dissolved piperidine adduct **15d** (200 mg, 0.888 mmol) in EtOH (10 mL). Raney Nickel/ EtOH (1 g) was added. The reaction mixture was then put under an H_2 atmosphere and stirred at r.t. for 22 h. The reaction was filtered through a celite pad, washed with EtOH and the mother liquor was concentrated under reduced pressure to afford the pure product as a colorless oil (198 mg, 98 %). ^1H NMR (CDCl_3 , 300MHz): δ 4.15 (br s, 1H), 3.90 (br d, 1H, $J = 12.6$ Hz), 2.65 (dt, 1H, $J = 13.5, 2.2$ Hz), 1.66-1.13 (m, 10H), 1.38 (s, 9H), 0.85 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75MHz): 155.0 (s), 78.7 (t), 50.0 (d), 38.5 (t), 31.7 (t), 28.3 (q), 25.6 (t), 19.3 (t), 18.9 (t), 13.9 (q). **IR** (neat, cm^{-1}): 2933, 2866, 1693, 1416, 1390, 1365, 1247, 1173, 1149. **LRMS** (m/z , (relative intensity)): 184 ($(\text{M}-\text{C}_3\text{H}_7)^+$, 12), 154 (15), 128 (100), 84 (78). **HRMS** calculated for $\text{C}_{10}\text{H}_{18}\text{NO}_2$ ($\text{M}-\text{C}_3\text{H}_7$): 184.1337, found 184.1333. $[\alpha]_{\text{D}}^{20} = +14.7$ (c 1.77, CHCl_3).

^1H NMR SpectraVinyl iodide **4a**

SL-161 PUR

Vinyl iodide **4c**:

SL-41 PUR

Vinyl iodide **4d**:

SL - 165 PUR

3-(*o*-iodophenyl)-1-bromo-1-propene (precursor to vinylbromide **4e**):

DGA-2-115GA

1-(3-Bromoallyl)-2-vinyl-benzene **4e**:

DGA-2-117GA

Allylic alcohol **5a**:

SL-179 MAJO

Allylic alcohol **5b**:

DGA-1-85FB

Allylic alcohol **5c**:

Allylic alcohol **5d**:

Alylic alcohol **5e**:

DGA-2-119FB

Propargylic alcohol precursor to **5f**:

<PRIME CDCL₃

Allylic alcohol **5f**:

Allylic alcohol **6a**:

SL-179 MINORITAIRE

Allylic alcohol **6b**:

DGA-1-87FACARA

Allylic alcohol **6c**:

SL-45 MINORITAIRE

Allylic alcohol **6d**:

Alylic alcohol **6e**:

DGA-2-121HC

Propargylic alcohol precursor to **6f**:

CDCl₃:

Allylic alcohol **6f**:

DCL_3

Allylic azide **7a**:

Alylic azide **7b**:

DGA-1-103E

Allylic azide **7c**:

Allylic azide **7d**:

Alylic azide **7e**:

DGA-2-123GA

Allylic azides **9f/10f/7f/8f**:

96 : 4

Blow-up section of the ^1H NMR of allylic azides **9f/10f/7f/8f**:

Allylic azide **8a**:

Alylic azide **8b**:

DGA-1-89FB

Allylic azide **8c**:

Allylic azide **8d**:

Alylic azide **8e**:

DGA-2-125FB

Allylic azides **10f/9f/8f/7f**:

SL-2-115 C2

96 : 4

Blown-up section of the ^1H NMR of allylic azides **10f/9f/8f/7f**:

SL - 2 - 115 C2

Primary amine **11a**:

Ammonium salt of primary amine **11b**:

DGA-1-73S3

Primary amine **11c**:

Primary amine **11d**:

SL-17 SEL

Primary amine **11e**:

DGA-2-127GA

Fm-carbamate **12a**:

Fm-carbamate **12b**:

DGA-2-041GA

Fmoc-carbamate **12c**:

Fm-carbamate **12d**:

Amino acid **13a**:

SL - 2 - 103

Amino acid **13b**:

Amino aldehyde precursor to amino acid **13c**:

Amino acid **13c**:

Amino acid **13d**:

SL-2-107 PUR

Chemical structure of compound 10: A bicyclic molecule with a cyclohexene ring fused to a cyclohexane ring. The cyclohexene ring has a vinyl group at C1 and a 2-benzyl-4-penten-1-yl group at C2. The cyclohexane ring has an isopropyl group at C3.

t-Bu carbamate **14b**:

DGA-1-111F

Secondary amine precursor to *t*-Bu carbamate **14c**:

DGA-2-029GA

t-Bu carbamate **14c**:

DGA-2-0331A

Secondary amine precursor to *t*-Bu carbamate **14d**:

*CDCl*₃

t-Bu carbamate **14d**.

SL-25 PUR

t-Bu carbamate **16**:

DGA-2-129FA

O-TBDMS- *t*-Bu carbamate precursor to **18**:

DGA-2-191B3

t-Bu carbamate-alcohol precursor to **18**:

DGA-2-193FA

t-Bu carbamate **18**:

DGA-2-199FA

Dehydropiperidine **15b**:

DGA-1-133I

Dihydropyrrole **15c**:

DGA-2-39FC

Dehydropiperidine **15d**:

SL-27 PUR

t-Bu carbamate **17**:

DGA-2-133FB

Dihydropyran **19**:

DGA-3-019FC

(+)-*N*-Boc coniine:

SL-29 PUR