### **Supporting Information**

### An Expeditious Route to Sterically Encumbered Nonproteinogenic α-Amino Acid Precursors Using Allylboronic Acids

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#### **Experimental Section:**

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen or argon atmosphere. Chloroform was obtained from Merck India. All other solvents were obtained from Merck India and were dried according to the standard literature procedure. All the required solvents were degassed by purging nitrogen gas through solution under sonication for 2 hours. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light or dipping into KMnO<sub>4</sub> solution. Silica gel (particle size 100-200 mesh) and neutral alumina were purchased from SRL India for performing column chromatography by using mixture of hexanes and ethylacetate eluent. Ethyl glyoxalate (50% in toluene) was purchased from Alfa Aesar Pvt. Ltd and was used as received. The <sup>1</sup>H NMR spectroscopic data were recorded with a Bruker 400, 500 or 600 MHz NMR instruments. <sup>13</sup>C NMR spectra were similarly recorded at 100, 125 or 150 MHz NMR instruments by broadband decoupled mode. The <sup>1</sup>H NMR spectroscopic data are reported relative to either CDCl<sub>3</sub> (7.26) ppm) or DMSO-d<sub>6</sub> (2.50 ppm). Proton and carbon NMR chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual proton signals in CDCl<sub>3</sub> ( $\delta$  = 7.26, 77.16) and DMSO- $d_6$  ( $\delta = 2.50, 39.52$ ). Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, dd: doublet of doublets, dt: doublet of triplets, ddd: doublet of doublets, tt: triplet of triplets, td: triplet of doublets, dtd: doublet of triplet of doublets, m: multiplet, br: broad. Specific rotations were measured on a JASCO polarimeter and have the unit deg cm<sup>3</sup> dm<sup>-1</sup> g<sup>-1</sup>. Concentration in bracket is given in gm/100 mL. Infrared (IR) spectra were recorded by Perkin Elmer ATIR spectrometer, and reported in terms of wave number (cm<sup>-1</sup>). High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method.

#### General Procedure (GP I) for the Synthesis of Imines (1b-1g):



To a solution of corresponding (*L*)-tartarates (1.0 mmol, 1.0 equiv) in dry Et<sub>2</sub>O/THF (1:1, 8.0 mL) at 0 °C under argon, was added periodic acid (1.1 mmol, 1.1 equiv) in two portions. The reaction mixture was allowed to stir for 0.5 to 24 h upon which it was diluted by adding Et<sub>2</sub>O and filtered. The crude mixture was concentrated and re-dissolved in dry DCM and used for next step without further purification.

**GP IA:** A 10 mL sealed tube was charged with (*S*)-2-methyl-2-propanesulfinamide (1.2 mmol) and activated 4 Å molecular sieves (0.1 g/mmol) and 5 mL dry DCM was added. After addition of freshly prepared crude glyoxalate solution in 1 mL of dry DCM and 15  $\mu$ L of pyrrolidine, the resulting mixture was stirred at 60 °C for 6 hours. Upon cooling, reaction mixture was filtered through celite pad and washed with DCM. The crude product was purified by silica gel column chromatography using ethylacetate/ hexane eluent.

**GP IB:** To a solution of (*S*)-2-methyl-2-propanesulfinamide (1.2 mmol) and activated 4 Å molecular sieves (0.1 g/mmol) in dry DCM (5 mL), the corresponding glyoxalate/glyoxamides solution in 1 mL dry DCM was added. The resulting solution was stirred at room temperature under argon atmosphere. Upon completion, as evidenced by the TLC, reaction mixture was filtered through celite pad and washed with DCM. The crude mixture was purified on silica gel column to get the pure imine **1b-1f**.

#### 2,2,2-Trifluoroethyl (*S*,*E*)-2((*tert*-butylsulfinyl)imino)acetate (1b):

 $F_{3}C \longrightarrow 0$ Imine **1b** was synthesized according to **GP IA** and isolated as colourless oil after column chromatography on silica using 8% ethylacetate in hexane as eluent (212 mg, 41% over two stere). 8.05 (s, 1H), 4.72-4.61 (m, 2H), 1.27 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 159.37$ , 153.59, 122.58 (q, J = 277.3 Hz), 61.56 (q, J = 37.4 Hz), 59.62, 22.85 ppm. <sup>19</sup>F NMR: -73.62 ppm. IR (film):  $v_{max} = 1732$ , 1665, 1324, 1245, 1145, 1095 cm<sup>-1</sup>. HRMS-ESI: calculated for  $C_{8}H_{13}F_{3}NO_{3}S$  [M+H]<sup>+</sup> 260.0563; found 260.0561. [a]p<sup>25</sup>: +33.75, (c 0.542, CHCl<sub>3</sub>).

#### Benzyl (*S*,*E*)-2-((*tert*-butylsulfinyl)imino)acetate (1c):

 $\bar{o}$  Imine 1c was synthesized according to GP IB and isolated as colourless oil after column chromatography on silica using 5% ethylacetate in hexane as eluent (133 mg 25% over the single luent (133 mg, 25% over two steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.03$ (s, 1H), 7.40 – 7.32 (m, 5H), 5.33 (s, 2H), 1.25 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 160.93, 155.35, 134.76, 128.75, 128.49, 67.93, 59.02, 22.77 ppm. IR (film): v<sub>max</sub> = 1734, 1639, 1452, 1265, 1131, 1083 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>13</sub>H<sub>17</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 290.0821; found 290.0817. [α]p<sup>25</sup>: +53.21 (c 0.487, CHCl<sub>3</sub>).

#### (S,E)-2-((*tert*-Butylsulfinyl)imino)-*N*-(*o*-tolyl)acetamide (1e):

 $\sqrt{P}$ Imine **1e** was synthesized according to **GP IB** and isolated as colourless oil
  $M^{\sum_{i=1}^{N} + Bu}$  after column chromatography on silica using 12% ethylacetate in hexane as
 eluent (223 mg, 42% over two steps). <sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>):  $\delta =$ 8.62 (s, 1H), 8.10 (d, J = 8.1 Hz, 1H), 8.05 (s, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.31 (s, 3H), 1.30 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 159.31, 158.14, 134.68, 130.69, 127.85, 127.20, 125.56, 121.48, 59.00, 22.83, 17.46$  ppm. **IR (film):**  $v_{max} = 3524$ , 1675, 1652, 1425, 1124, 1091 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{13}H_{19}N_2O_2S [M+H]^+ 267.1162$ ; found 267.1171. [a] $p^{25}$ : +13.25 (c 0.421, CHCl<sub>3</sub>).

#### (S,E)-N-Benzyl-2-((*tert*-butylsulfinyl)imino)acetamide (1f):



(br s, 1H), 4.65 (dd, J = 14.9, 6.4 Hz, 1H), 4.51 (dd, J = 14.9, 5.7 Hz, 1H), 1.24 (s, 9H) ppm.

<sup>13</sup>**C NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta = 160.79$ , 158.80, 137.39, 129.02, 128.00, 127.90, 58.70, 43.63, 22.83 ppm. **IR (film):**  $v_{max} = 3421$ , 1683, 1641, 1412, 1127, 1074 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 267.1162; found 267.1158. [ $\alpha$ ] $p^{25}$ : +56.23 (c 0.254, CHCl<sub>3</sub>).

**General Procedure (GP II): The Synthesis of Peptide Based Imines:** 



To a solution of amino acid methyl esters in dry DMF at 0 °C (ice bath) was added pyridine and it was continued to stir for 10 min. Then tartaric acid and HOBT was added sequentially at 0 °C and stirred for another 20 min. Next, EDC·HCl was added at 0 °C and the reaction mixture was allowed to come to room temperature slowly and stirred further over 24 h. After completion, the reaction was quenched with water and extracted with ethylacetate. The organic layer was washed with saturated aq. citric acid solution followed by 0.5 (N) HCl and *satd*. brine solution. Finally, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, solvent was removed under *vacuo* and purified by silica gel column chromatography to obtain the coupled tartarates **A** in 40-67% yields.

To a solution of tartarate **A** (1.0 mmol) in THF/Et<sub>2</sub>O (1:1, 5 mL) at 0 °C was added H<sub>5</sub>IO<sub>6</sub> (1.0 mmol) under argon atmosphere. The reaction was stirred at the same temperature for 30 min. Then it was diluted with Et<sub>2</sub>O and filtered through celite pad. The solvent was removed under reduced pressure, the crude residue was re-dissolved in 2 mL dry DCM and added to a stirred solution of (*S*)-2-methyl-2-propanesulfiamide (1.00 mmol) containing 4 Å MS in 4 mL dry DCM under argon. Upon completion of the imine formation, the reaction aliquot was filtered through celite, washed with DCM, and purified by silica gel column chromatography to get the pure imines **4b-4e**.

#### Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-tyrosinate (4b):



Imine **4b** was synthesized according to **GP II** and isolated as colourless oil after column chromatography on silica using 25% ethylacetate in hexane as eluent (177 mg, 25% over two steps). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.91$  (s, 1H), 7.29 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 8.1 Hz, 2H), 6.46 (br s, 1H), 4.87

(dt, J = 8.0, 5.7 Hz, 1H), 3.75 (s, 3H), 3.15 (dd, J = 14.1, 5.5 Hz, 1H), 3.08 (dd, J = 14.1, 5.9 Hz, 1H), 1.22 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 171.59, 160.26, 157.96, 155.58, 130.42, 126.74, 115.78, 59.12, 53.44, 52.77, 37.06, 22.78 ppm.$ **IR (film):** $<math>v_{max} = 3421, 1735, 1652, 1354, 1276, 1091$  cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup> 355.1322; found 355.1335. [ $\alpha$ ] $p^{25}$ : +65.20 (c 0.125, CHCl<sub>3</sub>).

#### Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-tryptophanate (4c):



Imine **4c** was synthesized according to **GP II**. *Note: the corresponding* glyoxamide is very unstable in presence of air and show significant decomposition upon exposing to air. After the completion of the first step, the round bottom flask was kept at the 0  $^{\circ}C$  without stirring for

the sedimentation. After 15 min, the top layer was taken in a syringe and added directly to the solution of sulfonamide in DCM without purification for imine synthesis. The imine **4c** was isolated as colourless oil after column chromatography on silica using 30% ethyl acetate in hexane as eluent (150 mg, 20% over two steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.16$  (br s, 1H), 7.92 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 4.98 (dt, *J* = 8.1, 5.4 Hz, 1H), 3.71 (s, 3H), 3.40 (d, *J* = 5.4 Hz, 2H), 1.16 (s, 9H) ppm. <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.77$ , 160.41, 158.11, 136.31, 127.64, 122.91, 122.54, 120.04, 118.67, 111.41, 109.86, 58.85, 53.18, 52.67, 27.76, 22.80 ppm. **IR (film): v**max = 1766, 1652, 1620, 1452, 1254, 1080 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>18</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 378.1842; found 378.1839. [α]p<sup>25</sup>: +12.35 (c 0.253, CHCl<sub>3</sub>).

#### Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-methioninate (4d):

Imine **4d** was synthesized according to **GP II** and isolated as colourless oil after column chromatography on silica using 28% ethyl acetate in hexane as eluent (212 mg, 33% over two steps). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.93$  (s, 1H), 7.53 (d, J = 7.7 Hz, 1H), 4.81 – 4.75 (m,



cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{12}H_{23}N_2O_4S_2$  [M+H]<sup>+</sup> 323.1094; found 323.1089. [a] $p^{25}$ : +56.23 (c 0.268, CHCl<sub>3</sub>).

#### Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-alloisoleucinate (4g):



Imine **4g** was synthesized according to **GP II** and isolated as colourless oil after column chromatography on silica using 25% ethyl acetate in hexane as eluent (75 mg, 12% over two steps). <sup>1</sup>**H NMR** (400 MHz, DMSO- $d_6$ ):  $\delta = 9.20$  (d, J = 7.9 Hz, 1H), 8.08 (s, 1H), 4.33 (t, J = 7.1 Hz, 1H), 3.66 (s, 3H), 1.92 – 1.85 (m, 1H), 1.47

- 1.37 (m, 1H), 1.25 - 1.22 (m, 1H), 1.17 (s, 9H), 0.88 - 0.83 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta = 171.26$ , 160.42, 158.71, 57.74, 56.87, 51.93, 36.15, 24.87, 22.06, 15.42, 11.14 ppm. **IR (film): v**<sub>max</sub> = 2964, 1741, 1680, 1519, 1336, 1092 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>13</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 305.1530; found 305.1515. [ $\alpha$ ]p<sup>25</sup>: +97.25 (c 0.593, CHCl<sub>3</sub>).

#### **General Procedure (GP III): The Synthesis of Peptide Based Imines (4):**



The solution of Boc-protected *N*-terminal serine residue containing oligopeptide **B** (0.3 mmol) in DCM (2.5 mL) was cooled to 0 °C and TFA (0.25 mL) was added dropwise. After 15 min, the reaction mixture was brought to room temperature and stirred for overnight. After complete consumption of the peptide, TFA and DCM was removed under vacuum. The crude mixture was used for the next step without further purification.

The above crude residue was re-dissolved in 4.0 mL of pH = 7 phosphate buffer solution. To it, NaIO<sub>4</sub> (2.0-3.0 equiv) was added at room temperature under dark and stirring was continued for 1 to 4 h. After that the reaction mixture was diluted with water and extracted with ethylacetate thrice. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, solvent was removed under reduced pressure and used for next step without further purification.

The above crude mixture was dissolved in dry DCM (0.5 mL) and was added to a solution to (*S*)-2-methyl-2-propanesulfiamide (0.2 mmol, 24 mg) containing 4 Å MS (100 mg) in dry DCM (2 mL) under argon. The reaction was stirred until all the starting material was consumed as indicated by TLC. Then the reaction mixture was diluted by adding DCM, filtered through celite, filtrate was concentrated under vacuo and the crude residue was purified by silica gel column chromatography to provide pure imine **4**.

Note: for imines **4e**, **4f**, **4h**, and **4i** which are unstable during the purification, was used as crude after removing the solvent, and re-dissolving the crude residue in degassed chloroform for the final allylation step.

Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-phenylalaninate (4a):



Imine **4a** was synthesized according to **GP III** and isolated as colourless oil after column chromatography on silica using 25% ethylacetate in hexane as eluent (36 mg, 36% over three steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.92$  (s, 1H), 7.31 – 7.23 (m, 4H), 7.11 (d, J = 6.7 Hz, 2H), 4.92 (dt, J = 8.3, 5.8 Hz, 1H), 3.75 (s, 3H),

3.23 (dd, J = 13.9, 5.7 Hz, 2H), 3.18 (dd, J = 13.9, 5.9 Hz, 1H), 1.22 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.34$ , 160.22, 157.97, 135.44, 129.30, 128.79, 127.43, 58.87, 53.21, 52.62, 37.85, 22.77 ppm. **IR (film): v**<sub>max</sub> = 3365, 1756, 1685, 1642, 1374, 1074 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 339.1379; found 339.1384. [ $\alpha$ ] $_{D}^{25}$ : +56.81 (c 0.452, CHCl<sub>3</sub>).

#### Methyl ((E)-2-(((S)-tert-butylsulfinyl)imino)acetyl)-L-leucyl-L-phenylalaninate (4j):



Imine **4j** was synthesized according to **GP III** and isolated as colourless oil after column chromatography on silica using 28% ethylacetate in hexane as eluent (38 mg, 28% over three steps). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (s, 1H), 7.28 – 7.22 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.0 Hz,

2H), 6.44 (d, J = 7.8 Hz, 1H), 4.83 (q, J = 6.1 Hz, 1H), 4.53 – 4.48 (m, 1H), 3.74 (s, 3H), 3.15 (dd, J = 13.9, 5.6 Hz, 1H), 3.08 (dd, J = 13.9, 6.3 Hz, 1H), 1.69 – 1.56 (m, 3H), 1.26 (s, 9H), 0.93 (d, J = 5.5 Hz, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 171.65$ , 170.83, 160.47, 158.19, 135.55, 129.34, 128.75, 127.41, 58.93, 53.44, 52.60, 51.66, 41.30, 37.85, 24.86, 22.91, 22.88, 22.25 ppm. **IR (film): v**<sub>max</sub> = 3411, 1747, 1655, 1611, 1254, 1085 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>22</sub>H<sub>34</sub>N<sub>3</sub>O<sub>5</sub>S [M+H]<sup>+</sup> 452.2219; found 452.2231. [ $\alpha$ ] $\rho$ <sup>25</sup>: +47.26 (c 0.635, CHCl<sub>3</sub>).

#### Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-valyl-*L*-alloisoleucinate (4k):

Imine 4k was synthesized according to GP III and isolated 0 Me Me as colourless oil after column chromatography on silica using 30% ethylacetate in hexane as eluent (44 mg, 34% over three MeO<sub>2</sub>C ö steps). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.97$  (s, 1H), 7.37 Me (d, J = 9.0 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 4.58 – 4.55 (m, 1H), 4.36 – 4.33 (m, 1H), 3.75 (s, 3H), 2.23 – 2.16 (m, 1H), 1.95 – 1.85 (m, 1H), 1.44 – 1.39 (m, 2H), 1.26 (s, 9H), 1.02 – 0.99 (m, 6H), 0.93 - 0.88 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.05$ , 170.18, 160.75, 158.25, 58.93, 58.62, 56.75, 52.36, 37.82, 31.50, 25.26, 22.87, 19.25, 18.24, 15.60, 11.69 ppm. **IR (film):**  $v_{max} = 3342$ , 1745, 1702, 1682, 1649, 1064 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{18}H_{34}N_{3}O_{5}S$  [M+H]<sup>+</sup> 404.2219; found 404.2225. [a] $p^{25}$ : +68.42 (c 0.631, CHCl<sub>3</sub>).

# Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-valyl-*L*-alloisoleucyl-*L*-phenylalaninate (4l):



Imine **4I** was synthesized according to **GP III** except 3.0 equiv of NaIO<sub>4</sub> was used at the step II and isolated as white solid after column chromatography on silica using 40% ethyl acetate in hexane as eluent (81 mg,

49% over three steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.16$  (d, J = 6.3 Hz, 1H), 8.11 - 8.03 (m, 1H), 7.24 - 7.19 (m, 3H), 7.11 (d, J = 7.3 Hz, 2H), 7.03 - 6.92 (m, 2H), 4.87 (q, J = 6.6

Hz, 1H), 4.47 - 4.41 (m, 2H), 3.67 (s, 3H), 3.12 - 3.03 (m, 2H), 2.14 - 2.06 (m, 1H), 1.80 - 1.75 (m, 1H), 1.44 - 1.36 (m, 1H), 1.24 (s, 9H), 1.08 - 1.00 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.79 (t, J = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.77$ , 170.82, 170.58, 160.62, 158.72, 136.01, 129.29, 128.64, 127.18, 58.93, 58.81, 57.55, 53.44, 52.31, 38.03, 37.77, 31.60, 24.89, 22.79, 19.31, 18.46, 15.25, 11.21 ppm. **IR (film):**  $\mathbf{v_{max}} = 3262$ , 2964, 1745, 1640, 1548, 1217, 1097 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>27</sub>H<sub>43</sub>N<sub>4</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 551.2903; found 551.2903. **[a]p<sup>25</sup>:** +75.14 (c 0.366, CHCl<sub>3</sub>).

Methyl ((*E*)-2-(((*S*)-*tert*-butylsulfinyl)imino)acetyl)-*L*-leucyl-*L*-phenylalanyl-*L*isoleucinate (4m):



Imine **4m** was synthesized according to **GP III** except 3.0 equiv of NaIO<sub>4</sub> was used at the Step II and isolated as colourless oil after column chromatography on silica using 35% ethylacetate in hexane as eluent (158 mg, 28% over three steps).

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.13$  (s, 1H), 8.01 (br s, 1H), 7.17 – 7.06 (m, 7H), 4.90 (q, *J* = 7.2 Hz, 1H), 4.67 (q, *J* = 7.5, 7.1 Hz, 1H), 4.49 (dd, *J* = 8.4, 5.5 Hz, 1H), 3.68 (s, 3H), 3.03 (dd, *J* = 13.4, 6.6 Hz, 1H), 2.95 (dd, *J* = 13.7, 7.1 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.64 – 1.61 (m, 1H), 1.40 – 1.32 (m, 2H), 1.26 (s, 9H), 1.14 – 1.07 (m, 2H), 0.89 – 0.83 (m, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.81$ , 171.23, 170.65, 160.15, 158.87, 136.28, 129.46, 129.42, 128.53, 126.99, 58.89, 56.77, 54.37, 52.09, 51.88, 41.78, 38.84, 37.81, 25.21, 24.87, 22.87, 22.83, 22.39, 15.42, 11.55 ppm. **IR (film): v**<sub>max</sub> = 3285, 2925, 1742, 1641, 1536, 1205 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>28</sub>H<sub>45</sub>N<sub>4</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 565.3060; found 565.3058. [*α*] $\mathbf{p}^{25}$ : +64.02 (0.587, CHCl<sub>3</sub>).

#### Synthesis of Allylboronic Acids 2:

The following allylboronic acids were synthesized according to the literature reported procedures<sup>[1]</sup> and extracted in CHCl<sub>3</sub> and used immediately for the allylation reaction.



General Procedure (GP IV): The Synthesis of Allylboronic Acids



A 10 mL two neck round bottom flask was charged with allyl alcohol (2.0 mmol) and the flask was backfilled with nitrogen thrice by using Schlenk technique. Then DMSO (1.6 mL) and H<sub>2</sub>O (0.4 mL) were added to it and the reaction mixture was stirred for 2 minutes. Next, freshly prepared H<sub>2</sub>PdCl<sub>4</sub> (0.3 M, 0.34 mL, 0.05 mmol) and diboronic acid (216 mg, 2.4 mmol, 1.2 equiv) were added sequentially and the reaction was stirred at room temperature for another 2 to 24 hours. Upon complete consumption of allyl alcohol as evidenced by TLC (p-anisaldehyde stain), reaction mixture was allowed to settle down over 2 to 3 hours for the complete sedimentation of Pd. Then the reaction mixture was transferred via syringe to a 25 mL round bottom flask under nitrogen (Note: For some boronic acids such as 2v which are unstable under air, the reaction mixture was filtered through HPLC Teflon filter immediately after the complete conversion of allyl alcohols to remove Pd black). Then the filtrate containing crude allyl-boronic acid was diluted with 8 mL degassed chloroform and the resulting solution was washed with degassed 16% aq. NaCl solution (performed four times by stirring the mixture, 8 mL x 4, the aqueous layer was discarded every time. To discard the aqueous layer, first the organic layer was taken away under nitrogen atmosphere using a syringe, after that the aqueous layer was discarded with the help of a syringe and finally the organic layer was pushed back to

the same round bottom flask under nitrogen atmosphere for the second washing with NaCl solution). Finally, the organic layer was taken off by a syringe and transferred into another 25 mL round bottom flask containing anhydrous Na<sub>2</sub>SO<sub>4</sub> under nitrogen with occasional shaking. The resulting crude allylboronic acid solution was used immediately for allylation of sulfinyl imines.

(Note: [a] All the solvents were degassed for 3 hours with 99.999% argon gas under sonication.

[b] For some cases, when allyl alcohols were not completely consumed even after prolonged reaction time, then additional 1 to 2 mol% of  $H_2PdCl_4$  catalyst was added along with 0.2-0.4 equiv of  $B_2(OH)_4$ . The stirring was continued further until complete consumption of allyl alcohols.)

#### General Procedure (GP V): The Allylation of Sulfinyl Imines

A 10 mL Schlenk tube was charged with activated 4 Å molecular sieves (100 mg) and a solution of allyl boronic acid in chloroform (0.39 mmol, 1.3 equiv) was added under argon atmosphere. After stirring at room temperature for 2 minutes, imine **1** (0.3 mmol, 1.0 equiv) was added and the resulting mixture was stirred at room temperature for 4 h. After completion of the reaction as indicated by TLC, reaction was quenched by adding 0.5 ml of methanol. The crude mixture was filtered through celite pad and washed with  $CH_2Cl_2$ . The combined organic fractions were concentrated and purified on a silica gel column to obtain analytically pure homo-allylic amines **3-6**.

#### Ethyl (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoate (3aa):



The compound **3aa** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 12% ethylacetate in hexane as eluent provided the product **3aa** as colourless liquid (73 mg, 71%). <sup>1</sup>**H NMR** 

(600 MHz, CDCl<sub>3</sub>):  $\delta = 5.88$  (dd, J = 17.6, 10.9 Hz, 1H), 5.51 (d, J = 10.8 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.05 (t, J = 6.6 Hz, 1H), 4.21 – 4.16 (m, 3H), 3.49 (d, J = 9.8 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.78 – 1.73 (m, 1H), 1.66 (s, 3H), 1.64 – 1.61 (m, 1H), 1.57 (s, 3H), 1.39 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.67$ , 135.89, 132.36, 123.62, 119.34, 66.59, 65.16, 61.25, 35.39, 34.16, 26.57, 25.73, 22.67, 18.13, 17.76,

14.24. **IR (film):**  $\mathbf{v}_{max} = 3410, 2967, 1732, 1295, 1213, 1098 \text{ cm}^{-1}$ . **HRMS-ESI:** calculated for C<sub>18</sub>H<sub>33</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 366.2073; found 366.2054. **[\alpha]<sub>D</sub><sup>25</sup>: +70.57 (c 0.66, CHCl<sub>3</sub>).** 

#### Ethyl (25,35)-2-(((S)-tert-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoate (3ab):



The compound **3ab** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), neryl boronic acid **2b** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 15% ethylacetate in hexane as eluent provided the product **3ab** as colourless liquid (75 mg, 73%). <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>):  $\delta = 5.99$  (dd, J = 17.6, 10.8 Hz, 1H), 5.59 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 5.08 (t, J = 6.7 Hz, 1H), 4.32 (d, J = 9.8 Hz, 1H), 4.20 – 4.15 (m, 2H), 3.51 (d, J = 9.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.98 – 1.91 (m, 1H), 1.83 (td, J = 12.7, 12.2, 4.7 Hz, 1H), 1.74 (td, J = 12.4, 5.4 Hz, 1H), 1.65 (s, 3H), 1.56 (s, 3H), 1.28 – 1.24 (m, 6H), 0.92 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.68$ , 135.35, 132.41, 123.50, 119.90, 66.25, 65.43, 61.24, 35.97, 35.40, 26.55, 25.70, 22.57, 17.73, 16.69, 14.23 ppm. IR (film): v<sub>max</sub> = 2966, 1733, 1296, 1214, 1158, 1095 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>18</sub>H<sub>33</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 366.2073; found 366.2093. [ $\alpha$ ] $p^{25}$ : +68.43 (c 0.833, CHCl<sub>3</sub>).

### Ethyl (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7,11-trimethyl-3-vinyldodeca-6,10dienoate (3ac):



The compound **3ac** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), farnesyl boronic acid **2c** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 10% ethylacetate in hexane provided the product **3ac** as a colourless oil

(95 mg, 77%) (mixture of *E* and *Z* isomer originated from the commercially available farnesol). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 5.92 - 5.86$  (m, 2H), 5.54 (d, *J* = 10.8 Hz, 2H), 5.31 (d, *J* = 17.6 Hz, 2H), 5.08 (t, *J* = 8.8 Hz, 2H), 4.23 - 4.19 (m, 6H), 3.51 (d, *J* = 9.8 Hz, 2H), 2.06 -2.01 (m, 10H), 1.99 - 1.94 (m, 4H), 1.80 - 1.74 (m, 4H), 1.68 (s, 6H), 1.67 (s, 6H), 1.58 (s, 6H), 1.41 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.94 (s, 18H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.75$ , 136.22, 136.04, 135.80, 135.71, 131.87, 131.57, 124.30, 124.27, 124.23, 123.50, 119.58, 119.51, 66.56, 66.54, 65.18, 65.14, 61.32, 39.76, 35.44, 34.33, 34.12, 32.10, 26.72, 26.63, 26.59, 25.89, 25.83, 23.49, 22.58, 22.46, 18.26, 18.21, 17.82, 17.78, 16.15, 14.29 ppm. **IR (film):**  $v_{max} = 2965$ , 1734, 1216, 1159, 1099, 1022 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>23</sub>H<sub>42</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 412.2880; found 412.2883.

#### Ethyl (S)-2-(((S)-*tert*-butylsulfinyl)amino)-3,3-dimethylpent-4-enoate (3ad):

The compound **3ad** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), prenyl boronic acid **2d** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 10% ethylacetate in hexane as eluent provided the product **3d** as colourless liquid (54 mg, 65%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta =$ 6.03 (dd, J = 17.5, 10.7 Hz, 1H), 5.52 (d, J = 10.8 Hz, 1H), 5.31 (d, J = 17.5 Hz, 1H), 4.25 (d, J = 9.7 Hz, 1H), 4.21 – 4.17 (m, 2H), 3.51 (d, J = 9.8 Hz, 1H), 1.41 (s, 3H), 1.31 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 0.94 (s, 9H) ppm. <sup>13</sup>**C NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.74$ , 136.42, 118.96, 66.30, 61.73, 61.32, 35.43, 26.54, 22.90, 20.51, 14.28 ppm. **IR (film): vmax** = 2964, 1732, 1215, 1158, 1100, 1022 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>13</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 276.1628; found 276.1626. **[a]p<sup>25</sup>**: +169.0 (c 0.5, CHCl<sub>3</sub>)

#### Ethyl (25,35)-2-(((S)-tert-butylsulfinyl)amino)-3-phenylpent-4-enoate (3ae):<sup>[2]</sup>

The compound **3ae** was prepared according to **GP V** by using imine **1a** (61  $HN^{+}T_{Bu}$  mg, 0.3 mmol, 1.0 equiv), cinnamyl boronic acid **2e** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 14% ethylacetate in hexane as eluent provided the product **3ae** as colourless liquid (66 mg, 68%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta =$ 7.29 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 6.8 Hz, 2H), 6.08 – 6.02 (m, 1H), 5.16 – 5.13 (m, 2H), 4.20 – 4.11 (m, 3H), 3.90 (d, J = 9.5 Hz, 1H), 3.67 (t, J = 8.0 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H), 1.05 (s, 9H) ppm. <sup>13</sup>C **NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta =$  172.36, 139.35, 136.99, 128.68, 128.46, 127.29, 117.67, 62.96, 61.74, 56.41, 54.24, 22.57, 14.22 ppm. **IR** (**film**): **v**<sub>max</sub> = 2981, 1732, 1455, 1200, 1178, 1091 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>17</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 324.1628; found 324.1272. [**a**]**p**<sup>20</sup>: + 79.8 (c 0.68, CHCl<sub>3</sub>).

### Ethyl (25,35)-2-(((5)-tert-butylsulfinyl)amino)-3-(2-methoxyphenyl)pent-4-enoate (3af):

The compound **3af** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2f** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 17% ethylacetate in hexane as eluent provided the



product 3af as a colourless oil (79 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.19$  (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.89 (t, J= 7.5 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.11 (dt, J = 17.2, 9.5 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 4.26 (t, *J* = 9.3 Hz, 1H), 4.20 - 4.08 (m, 2H), 4.02 (t, J = 8.7 Hz, 1H), 3.90 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.98 (s, 9H) ppm. <sup>13</sup>C NMR

 $(151 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 173.02, 157.26, 136.23, 129.40, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 128.23, 128.05, 120.73, 117.71, 128.23, 128.05, 128.23, 128.25, 128.$ 110.78, 61.71, 61.42, 56.15, 55.46, 48.59, 22.46, 14.21 ppm. IR (film): v<sub>max</sub> = 2967, 1732, 1493, 1366, 1245, 1096 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{18}H_{28}NO_4S$  [M+H]<sup>+</sup> 354.1734; found 354.1742. [α]<sub>D</sub><sup>25</sup>: +73.80 (c 0.166, CHCl<sub>3</sub>).

#### Ethyl (2S,3S)-2-(((S)-tert-butylsulfinyl)amino)-3-(3-methoxyphenyl)pent-4-enoate (3ag):



The compound **3ag** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), 2g (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (150 mg) at room temperature. Column chromatography on silica using 17% ethylacetate in hexane as eluent provided the product **3ag** as colourless oil (74 mg, 70%). <sup>1</sup>H NMR (600

MHz, CDCl<sub>3</sub>):  $\delta = 7.21$  (t, J = 7.9 Hz, 1H), 6.75 (t, J = 6.6 Hz, 2H), 6.70 (s, 1H), 6.03 (ddd, J = 16.9, 10.2, 8.4 Hz, 1H), 5.16 (d, J = 11.1 Hz, 1H), 5.13 (d, J = 4.0 Hz, 1H), 4.20 - 4.13 (m, 3H), 3.92 (d, J = 9.5 Hz, 1H), 3.77 (s, 3H), 3.65 (t, J = 8.0 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.07 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.33$ , 159.77, 140.82, 136.81, 129.69, 120.75, 117.76, 114.32, 112.38, 62.90, 61.79, 56.44, 55.31, 54.20, 22.59, 14.26 ppm. IR (film):  $v_{max} = 2954, 1732, 1600, 1456, 1261, 1064 \text{ cm}^{-1}$ . HRMS-ESI: calculated for C<sub>18</sub>H<sub>28</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 354.1734; found 354.1747. [α]<sub>D</sub><sup>25</sup>: +114.66 (c 0.133, CHCl<sub>3</sub>).

### Ethyl (25,3S)-2-(((S)-tert-butylsulfinyl)amino)-3-(4-methoxyphenyl)pent-4-enoate (3ah):



The compound **3ah** was prepared according to **GP V** by using imine **1a** (61  $HN^{-S_{+}t}Bu$  mg, 0.3 mmol, 1.0 equiv), **2h** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 17% ethylacetate in hexane as eluent provided the product 3ah as a colourless oil (76 mg, 72%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.12 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 6.09 – 6.02 (m, 1H), 5.18 (d, J = 10.8

Hz, 1H), 5.09 (d, J = 17.2 Hz, 1H), 4.13 – 4.12 (m, 2H), 4.05 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.67 - 3.66 (m, 1H), 1.18 (s, 9H), 1.10 (t, J = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ = 172.43, 158.79, 136.37, 131.48, 129.53, 118.15, 113.94, 62.92, 61.73, 56.50, 55.40, 52.88, 22.82, 14.06 ppm.**IR (film):v**<sub>max</sub> = 2957, 1732, 1613, 1471, 1325, 1082 cm<sup>-1</sup> cm<sup>-1</sup>.**HRMS-ESI:**calculated for C<sub>18</sub>H<sub>28</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 354.1734; found 354.1737.**[α]** $<math>p^{25}$ : +55.87 (c 0.649, CHCl<sub>3</sub>).

# Ethyl (2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(2-((3-methylbut-2-en-1-yl)oxy)phenyl) pent-4-enoate (3ai):



The compound **3ai** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2k** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica (Et<sub>3</sub>N neutralized) using 12% ethylacetate in hexane as eluent provided the product **3ai** as colourless oil (75 mg, 62%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.16 (t, *J* = 7.8 Hz, 1H),

7.11 (d, J = 7.5 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.12 (dt, J = 18.5, 9.5 Hz, 1H), 5.50 (t, J = 5.7 Hz, 1H), 5.16 – 5.09 (m, 2H), 4.57 – 4.49 (m, 2H), 4.28 (t, J = 9.4 Hz, 1H), 4.19 – 4.12 (m, 2H), 4.01 (t, J = 8.8 Hz, 1H), 3.92 (d, J = 10.1 Hz, 1H), 1.80 (s, 3H), 1.75 (s, 3H), 1.24 (t, J = 7.4 Hz, 3H), 0.98 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 173.07, 156.60, 137.56, 136.21, 129.35, 128.39, 128.09, 120.61, 120.06, 117.73, 112.04, 65.27, 61.73, 61.37, 56.14, 48.84, 25.89, 22.45, 18.43, 14.19 ppm. IR (film): v<sub>max</sub> = 2979, 1733, 1491, 1453, 1260, 1079 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>22</sub>H<sub>24</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 408.2203; found 408.2212. [<math>\alpha$ ] $p^{25}$ : +194.2 (c 0.68, CHCl<sub>3</sub>).

#### Ethyl (2S,3S)-3-(2-bromophenyl)-2-(((S)-tert-butylsulfinyl)amino)pent-4-enoate (3aj):



The compound **3aj** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2j** (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 15% ethylacetate in hexane as eluent provided the product **3aj** as colourless oil (101 mg, 84%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.50$  (d, *J* 

= 7.9 Hz, 1H), 7.24 – 7.12 (m, 2H), 7.05 – 7.00 (m, 1H), 5.93 (ddd, J = 17.1, 10.1, 8.6 Hz, 1H), 5.15 (d, J = 13.4 Hz, 1H), 5.12 (d, J = 6.4 Hz, 1H), 4.24 (t, J = 8.7 Hz, 1H), 4.19 – 4.11 (m, 2H), 4.07 (t, J = 9.7 Hz, 1H), 3.93 (d, J = 10.1 Hz, 1H), 1.21 (t, J = 6.3 Hz, 3H), 0.95 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.26, 139.24, 135.34, 133.14, 129.02, 128.49, 127.75, 125.63, 118.80, 63.13, 61.72, 56.24, 52.30, 22.35, 14.14 ppm. IR (film): v<sub>max</sub> = 2980,

1733, 1471, 1305, 1181, 1080 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{17}H_{25}BrNO_3S$  [M+H]<sup>+</sup> 404.2497; found 404.2492. [ $\alpha$ ] $_{D}^{25}$ : +123.0 (c 0.5, CHCl<sub>3</sub>).

#### Ethyl (2S,3S)-3-(4-bromophenyl)-2-(((S)-tert-butylsulfinyl)amino)pent-4-enoate (3ak):<sup>[2]</sup>

The compound **3ak** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2k** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 15% ethylacetate in hexane as eluent provided the product **3ak** as colourless oil (102 mg, 85%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.41$  (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 5.99 (ddd, J = 16.9, 10.3, 8.2 Hz, 1H), 5.16 – 5.10 (m, 2H), 4.19 – 4.11 (m, 3H), 3.92 (d, J = 9.2 Hz, 1H), 3.65 (t, J = 7.8 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H), 1.07 (s, 9H) ppm. <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.03$ , 138.43, 136.45, 131.73, 130.21, 121.16, 118.11, 62.55, 61.86, 56.47, 53.49, 22.59, 14.20 ppm. **IR** (**film**): **v**<sub>max</sub> = 3278, 2968, 1727, 1489, 1178, 1077 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>17</sub>H<sub>24</sub>BrNO<sub>3</sub>SNa [M+Na]<sup>+</sup> 424.0558; found 424.0559. **[a]p<sup>25</sup>:** + 68.0 (c 0.99, CHCl<sub>3</sub>)

#### Ethyl (25,35)-2-(((S)-tert-butylsulfinyl)amino)-3-(naphthalen-1-yl)pent-4-enoate (3al):



The compound **3al** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2l** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (150 mg) at room temperature. Column chromatography on silica using 10% ethyl acetate in hexane as eluent provided the product **3al** as colourless oil (92 mg, 82%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.11$  (d, *J* 

= 8.6 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.18 (ddd, *J* = 17.0, 10.2, 8.3 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 4.57 (t, *J* = 8.3 Hz, 1H), 4.34 (t, *J* = 9.0 Hz, 1H), 4.16 – 4.08 (m, 2H), 3.94 (d, *J* = 9.7 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.66, 136.70, 135.76, 134.14, 132.20, 129.19, 127.75, 126.35, 125.69, 125.37, 125.33, 122.85, 118.17, 62.95, 61.71, 56.27, 48.34, 26.47, 22.35, 14.10 ppm. **IR (film): v**<sub>max</sub> = 2954, 1738, 1452, 1362, 1176, 1085 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>21</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 374.1784; found 374.1793. [*α*]p<sup>25</sup>: +45.23 (c 0.523, CHCl<sub>3</sub>).

#### Ethyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-3-(thiophen-2-yl)pent-4-enoate (3am):

The compound **3am** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2m** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (150 mg) at room temperature.

Column chromatography on silica using 25% ethylacetate in hexane as  $HN^{+}t_{Bu}$  eluent provided the product **3am** as colourless oil (60 mg, 61%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.19$  (d, J = 5.1 Hz, 1H), 6.93 (t, J = 4.2 Hz, 1H), 6.81 (d, J = 3.3 Hz, 1H), 6.06 – 6.00 (m, 1H), 5.20 – 5.18 (m, 2H), 4.22 – 4.15 (m, 5H), 1.25 – 1.22 (m, 12H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta =$ 

171.44, 140.87, 137.31, 126.66, 125.78, 124.98, 117.92, 62.76, 62.04, 56.75, 49.24, 22.82, 14.24 ppm. **IR (film):**  $v_{max} = 2981$ , 1734, 1366, 1283, 1183, 1082 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>15</sub>H<sub>24</sub>NO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> 330.1192; found 330.1177. **[a]** $p^{25}$ : +205.8 (c 0.52, CHCl<sub>3</sub>).

#### Ethyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-3-(furan-2-yl)pent-4-enoate (3an):

The compound **3an** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2n** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **3an** as colourless oil (60 mg, 64%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.32$  (s, 1H),

6.28 (d, J = 5.0 Hz, 1H), 6.07 (d, J = 3.2 Hz, 2H), 5.95 (ddd, J = 17.1, 10.2, 8.5 Hz, 1H), 5.21 (d, J = 5.9 Hz, 1H), 5.19 (d, J = 12.8 Hz, 1H), 4.20 – 4.15 (m, 3H), 4.07 (d, J = 9.1 Hz, 1H), 3.87 (t, J = 7.8 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.16 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 171.75$ , 152.51, 141.95, 134.20, 118.83, 110.35, 107.45, 61.86, 61.42, 56.51, 47.92, 22.71, 14.16 ppm. IR (film): v<sub>max</sub> = 2982, 1734, 1367, 1175, 1094, 1011 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>15</sub>H<sub>24</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 314.1421; found 314.1408. [ $\alpha$ ] $\rho$ <sup>25</sup>: +35.02 (c 0.741, CHCl<sub>3</sub>).

## Ethyl (2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(1-tosyl-1*H*-indol-3-yl)pent-4-enoate (3ao):



EtO<sub>2</sub>C

The compound **3ao** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2o** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 18% ethylacetate in hexane as eluent provided the product **3ao** as gummy solid (113 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.95 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.42 (s, 1H),

7.30 (t, J = 7.4 Hz, 1H), 7.23 – 7.21 (m, 3H), 6.03 (ddd, J = 17.0, 10.2, 7.8 Hz, 1H), 5.19 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 17.0 Hz, 1H), 4.27 (dd, J = 8.4, 6.3 Hz, 1H), 4.11 (dd, J = 7.8, 5.0 Hz, 1H), 4.08 – 3.96 (m, 3H), 2.33 (s, 3H), 1.09 – 1.06 (m, 12H) ppm. <sup>13</sup>C NMR (151 MHz,

 $CDCl_3$ ):  $\delta = 171.83, 145.10, 135.61, 135.38, 135.06, 130.23, 130.03, 126.88, 125.06, 124.04, 125.06, 124.04, 125.06, 124.04, 125.06, 126.08, 126.08, 125.06, 126.08, 126.0$ 123.25, 120.17, 119.70, 118.35, 113.85, 61.93, 61.51, 56.47, 44.91, 22.60, 21.67, 13.99 ppm. **IR (film):**  $v_{max} = 2980, 1732, 1447, 1366, 1173, 1071 cm<sup>-1</sup>$ . **HRMS-ESI:** calculated for  $C_{26}H_{32}N_2NaO_5S_2 [M+Na]^+ 539.1645$ ; found 539.1634. [a] $p^{20}$ : +175.4 (c 0.48, CHCl<sub>3</sub>).

#### Ethyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-3-vinylhexanoate (3ap):



The compound **3ap** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), 2p (0.90 mmol, 3.0 equiv) and 4Å molecular sieves (100 mg) at 60 °C. Column chromatography on silica using 10% ethylacetate in hexane as eluent provided the product **3ap** as colourless oil (55 mg, 64%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 5.60 - 5.54$  (m, 1H), 5.10

(d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.3 Hz, 1H), 4.25 - 4.15 (m, 2H), 4.08 (d, J = 8.3 Hz, 1H),3.81 (t, J = 7.2 Hz, 1H), 2.40 - 2.32 (m, 1H), 1.48 - 1.43 (m, 1H), 1.40 - 1.31 (m, 2H), 1.31 - 1.311.26 (m, 4H), 1.25 (s, 9H), 0.87 (t, J = 6.9 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta =$ 172.64, 137.70, 117.88, 61.83, 61.60, 56.44, 48.41, 32.32, 22.90, 20.15, 14.31, 14.03 ppm. IR (film):  $v_{max} = 2959$ , 1733, 1466, 1366, 1184, 1075, 917 cm<sup>-1</sup>. HRMS-ESI: calculated for  $C_{14}H_{27}NNaO_{3}S [M+H]^{+} 312.1604$ ; found 312.1589. [a] $p^{25}$ : +63.91, (c 0.133, CHCl<sub>3</sub>).

### Ethyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-5-methyl-3-vinylhexanoate (3aq):



The compound 3aq was prepared according to  $HN^{-S_{+}t_{Bu}}$  mg, 0.3 mmol, 1.0 equiv), 2q (0.90 mmol, 3.0 equiv) and 4Å molecular sieves (100 mg) at 60 °C. Column chromatography on silica using 14% The compound **3aq** was prepared according to **GPV** by using imine **1a** (61 colourless oil (61 mg, 67%, dr: 4:1). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.56

(dt, J = 17.1, 9.8 Hz, 1H), 5.10 (d, J = 6.8 Hz, 1H), 5.08 (d, J = 15.3 Hz, 1H), 4.25 - 4.16 (m, 2H), 4.10 (d, J = 8.5 Hz, 1H), 3.80 (dd, J = 8.5, 5.6 Hz, 1H), 2.48 – 2.43 (m, 1H), 1.69 – 1.63 (m, 1H), 1.61 - 1.52 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.25 (s, 9H), 1.21 - 1.17 (m, 1H), 0.89(d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.5 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.61$ , 137.92, 117.74, 62.09, 61.64, 56.47, 46.58, 39.23, 29.84, 25.17, 23.88, 22.92, 21.43, 14.34 ppm. IR (film):  $v_{max} = 2926, 1734, 1467, 1366, 1184, 1083 \text{ cm}^{-1}$ . HRMS-ESI: calculated for C<sub>15</sub>H<sub>19</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 326.1760, found 326.1748. [a]p<sup>25</sup>: +50.00 (c 0.100, CHCl<sub>3</sub>).

### Ethyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-6-methyl-3-vinylhept-5-enoate (3ar):

The compound **3ar** was prepared according to **GP V** by using imine **1a** (41 mg, 0.2 mmol, 1.0 equiv), 2r (0.26 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature.

Column chromatography on silica using 12% ethylacetate in hexane as eluent provided the product **3ar** as colourless oil (49 mg, 78%). <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.61$  (dt, J = 16.8, 9.5 Hz, 1H), 5.09 – 5.03 (m, 3H), 4.18 (q, J = 7.1 Hz, 2H), 4.12 (d, J = 8.2 Hz, 1H), 3.85 (t, J = 10.2 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.27 – 2.21 (m, 1H), 2.06 – 1.99 (m, 1H), 1.67 (s, 3H), 1.57 (s, 3H), 1.29 – 1.19 (m, 12H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.57$ , 137.48, 133.67, 121.16, 117.58, 61.63, 61.07, 56.38, 48.80, 28.93, 25.89, 22.86, 18.06, 14.28 ppm. **IR** (film): **v**<sub>max</sub> = 2979, 1733, 1366, 1271, 1191, 1085 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>16</sub>H<sub>30</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 316.1941; found 316.1952. [**a**]**p**<sup>25</sup>: +60.29 (c 0.933, CHCl<sub>3</sub>).

#### Ethyl (S)-2-(((S)-*tert*-butylsulfinyl)amino)-2-(1-vinylcyclopentyl)acetate (3as):

 $\bar{\rho}$ The compound **3as** was prepared according to **GP V** by using imine **1a** (61<br/>mg, 0.3 mmol, 1.0 equiv), **2s** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves<br/>(100 mg) at room temperature. Column chromatography on silica using 8%<br/>ethylacetate in hexane provided the product **3as** as colourless oil (75 mg,<br/>83%). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 6.08$  (dd, J = 17.5, 10.7 Hz, 1H), 5.54 (d, J = 10.7 Hz,<br/>1H), 5.33 (d, J = 17.5 Hz, 1H), 4.30 (d, J = 9.8 Hz, 1H), 4.20 – 4.16 (m, 2H), 3.50 (d, J = 9.9<br/>Hz, 1H), 2.30 – 2.34 (m, 1H), 1.93 – 1.65 (m, 7H), 1.26 (t, J = 7.0 Hz, 3H), 0.93 (s, 9H) ppm.<br/><sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 134.95, 119.15, 72.93, 66.40, 61.23, 39.69, 35.40,<br/>34.40, 31.26, 26.54, 24.68, 24.10, 14.26 ppm. **IR (film): vmax** = 2959, 1732, 1367, 1296, 1214,<br/>1091 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>15</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 302.1784; found 302.1789.<br/>[**α**] $\mathbf{p}^{25}$ : +76.89 (c 1.06, CHCl<sub>3</sub>).

#### Ethyl (S)-2-(((S)-tert-butylsulfinyl)amino)-2-(1-vinylcyclohexyl)acetate (3at):



The compound **3at** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2t** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 7% ethylacetate in hexane provided the product **3at** as colourless oil (73 mg, 77%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 5.83$  (dd, J = 17.7, 10.9 Hz, 1H),

5.66 (d, J = 10.9 Hz, 1H), 5.35 (d, J = 17.8 Hz, 1H), 4.31 (d, J = 9.7 Hz, 1H), 4.21 – 4.15 (m, 2H), 3.52 (d, J = 9.7 Hz, 1H), 1.95 – 1.87 (m, 2H), 1.84 – 1.80 (m, 1H), 1.77 – 1.71 (m, 1H), 1.66 – 1.61 (m, 2H), 1.58 – 1.54 (m, 1H), 1.52 – 1.38 (m, 2H), 1.38 – 1.31 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 134.85, 120.97, 66.26, 65.54, 61.22, 35.43, 32.45, 29.58, 26.56, 25.72, 22.16, 22.00, 14.26 ppm. IR (film): vmax

= 2954, 1738, 1456, 1385, 1269, 1088 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{16}H_{30}NO_3S [M+H]^+$ 316.1941; found 316.1943. [a] $p^{25}$ : +26.53 (c 0.238, CHCl<sub>3</sub>).

#### Ethyl (2*S*,*3R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-4-methylene-3-propylhexanoate (3au):

<sup>0</sup> <sup>t</sup>Bu<sup>5</sup> NH Et EtO<sub>2</sub>C Me The compound **3au** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2u** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 10% ethylacetate in hexane provided the product **3au** as colourless

oil (72 mg, 76%). <sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 4.87$  (s, 1H), 4.78 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.01 (d, J = 9.3 Hz, 1H), 3.76 (t, J = 8.7 Hz, 1H), 2.34 (ddd, J = 11.2, 8.1, 3.6 Hz, 1H), 2.02 – 1.98 (m, 2H), 1.57 – 1.51 (m, 1H), 1.44 – 1.37 (m, 1H), 1.32 – 1.27 (m, 1H), 1.24 (s, 9H), 1.15 – 1.09 (m, 1H), 1.03 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 173.43$ , 148.59, 111.88, 61.71, 61.46, 56.44, 50.85, 30.99, 25.69, 22.90, 20.17, 14.21, 11.91 ppm. IR (film): v<sub>max</sub> = 2928, 1735, 1342, 1287, 1174, 1075 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>16</sub>H<sub>31</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 340.1917; found 340.1905. [ $\alpha$ ]p<sup>25</sup>: +49.17 (c 0.9, CHCl<sub>3</sub>).

#### Ethyl (S)-2-(((S)-*tert*-butylsulfinyl)amino)-4-phenylpent-4-enoate (3av):

The compound **3av** was prepared according to **GP V** by using imine **1a** (61  $_{HN}$ ,  $_{F}$ ,  $_{Bu}$  mg, 0.3 mmol, 1.0 equiv), **2v** (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 18% ethylacetate in hexane provided the product **3av** as colourless oil (68 mg, 70%). **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.36 - 7.32$  (m, 4H), 7.29 - 7.26 (m, 1H), 5.34 (s, 1H), 5.12 (s, 1H), 4.16 - 4.05 (m, 2H), 4.03 - 3.97 (m, 2H), 3.03 (dd, J = 14.2, 5.0 Hz, 1H), 2.85 (dd, J = 14.2, 7.2 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  173.02, 143.83, 140.28, 128.61, 127.95, 126.54, 116.68, 61.80, 57.01, 56.26, 40.54, 22.72, 14.21 ppm. **IR (film): v**<sub>max</sub> = 2925, 1733, 1342, 1225, 1142, 1094 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>17</sub>H<sub>25</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup> 346.1447; found 346.1437. [ $\alpha$ ] $_{p}$ <sup>25</sup>: +50.43 (c 0.233, CHCl<sub>3</sub>).

# 1-Ethyl 6-methyl (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-methyl-3-vinylhexanedioate (3aw):

The compound **3aw** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2w** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature.



Column chromatography on silica using 12% ethylacetate in hexane as eluent provided the product **3aw** as colourless oil (82 mg, 79%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 5.86$  (dd, J = 17.6, 10.9 Hz, 1H), 5.57 (d, J = 10.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 4.24 (d, J = 9.7 Hz, 1H), 4.22 - 4.16 (m, 2H), 3.67 (s, 3H), 3.51 (d, J = 9.8 Hz, 1H), 2.40 - 2.35 (m, 2H), 2.19 - 2.14 (m, 1H), 2.01 - 1.96 (m, 1H), 1.38 (s, 3H), 1.27 (t, J =

7.1 Hz, 3H), 0.95 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 173.41$ , 172.63, 134.88, 120.25, 66.62, 64.50, 61.38, 51.97, 35.45, 29.07, 29.00, 26.59, 18.04, 14.29 ppm. IR (film): **v**<sub>max</sub> = 2955, 1740, 1728, 1355, 1248, 1072 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>16</sub>H<sub>29</sub>NNaO<sub>5</sub>S [M+Na]<sup>+</sup> 370.1659; found 370.1662. [ $\alpha$ ] $p^{25}$ : +65.79 (c 0.266, CHCl<sub>3</sub>).

### Ethyl (2*S*,3*R*,*E*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-8-(phenylthio)-3-vinyloct-6-enoate (3ax):



The compound **3ax** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2x** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 7% ethylacetate in hexane as eluent provided the product **3ax** as colourless oil (57 mg, 42%). <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.37 – 7.30 (m, 2H), 7.27 – 7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.85 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.52 (d, *J* = 10.8 Hz, 1H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.15 (t, *J* = 6.3 Hz, 1H), 4.21 – 4.19 (m, 3H), 3.51 – 3.47 (m, 3H), 2.04 – 1.94 (m, 2H), 1.72 (s, 3H), 1.58 – 1.50 (m, 2H), 1.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.69, 136.41, 135.83, 131.41, 130.92, 128.80, 127.91, 126.55, 119.44, 66.61, 65.07, 61.34, 44.38, 35.44, 33.73, 26.63, 22.76, 18.03, 15.38, 14.29 ppm. IR (film): v<sub>max</sub> = 2933, 1730, 1354, 1222, 1174, 1075 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>24</sub>H<sub>38</sub>NO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> 452.2288; found 452.2307. [*α*]*p*<sup>25</sup>: +48.75 (c 0.2, CHCl<sub>3</sub>).

### Ethyl (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-6-((4-methoxybenzyl)oxy)-3vinylhexanoate (3ay):



The compound **3ay** was prepared according to **GP V** by using imine **1a** (61 mg, 0.3 mmol, 1.0 equiv), **2y** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **3ay** as colourless oil (126 mg, 99%).

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.23$  (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.56 (dt, *J* = 16.9, 9.7 Hz, 1H), 5.12 – 5.05 (m, 2H), 4.40 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.06 (d, *J* = 8.8 Hz, 1H), 3.82 – 3.79 (m, 4H), 3.41 (t, *J* = 6.0 Hz, 2H), 2.38 – 2.32 (m, 1H), 1.68 – 1.59 (m, 2H), 1.54 – 1.43 (m, 1H), 1.40 – 1.32 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 9H) ppm. <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.51$ , 159.30, 137.37, 130.79, 129.29, 118.27, 113.90, 72.65, 69.81, 61.83, 61.61, 56.42, 55.41, 48.62, 27.37, 26.89, 22.87, 14.29 ppm. **IR** (film): **v**<sub>max</sub> = 2926, 1733, 1613, 1513, 1247, 1080 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>22</sub>H<sub>36</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 426.2309; found 426.2311. [*α*]**p**<sup>25</sup>: +61.75 (c 0.166, CHCl<sub>3</sub>).

### Ethyl (2*S*,3*R*)-3-(2-((*N*-benzyl-4-methylphenyl)sulfonamido)ethyl)-2-(((*S*)-tertbutylsulfinyl)amino)pent-4-enoate (3az):

The compound **3az** was prepared according to **GP V** by using imine **1a** (61 <sup>t</sup>Bu mg, 0.3 mmol, 1.0 equiv), 2z (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica EtO<sub>2</sub>C using 35% ethylacetate in hexane as eluent provided the product 3az as colourless oil (140 mg, 87%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.70 (d, J Ts<sup>∕N</sup> Bn = 8.1 Hz, 2H), 7.33 - 7.25 (m, 7H), 5.34 (dt, J = 16.8, 9.6 Hz, 1H), 5.06 (d, J = 10.2 Hz, 1H), 4.95 (d, J = 17.0 Hz, 1H), 4.35 (d, J = 14.7 Hz, 1H), 4.17 (d, J = 14.8 Hz, 1H), 4.14 - 4.08 (m, J = 14.8 Hz, 1H), 4.14 + 4.08 (m, J = 14.8 Hz, 1H), 4.14 + 4.08 (m, J = 14.82H), 3.94 (d, J = 8.7 Hz, 1H), 3.61 (dd, J = 8.6, 5.9 Hz, 1H), 3.08 – 2.93 (m, 2H), 2.44 (s, 3H), 2.21 - 2.14 (m, 1H), 1.69 - 1.61 (m, 1H), 1.30 - 1.18 (m, 13H) ppm. <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ ):  $\delta = 171.90, 143.39, 136.55, 136.36, 136.11, 129.78, 128.62, 128.37, 127.92, 127.20, 127.20, 127.20, 127.20, 128.42, 128.4$ 118.91, 61.60, 61.33, 56.30, 52.62, 46.49, 45.97, 28.96, 22.70, 21.54, 14.14 ppm. IR (film):  $\mathbf{v}_{max} = 2980, 1732, 1456, 1338, 1151, 1077 \text{ cm}^{-1}$ . **HRMS-ESI:** calculated for C<sub>27</sub>H<sub>39</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub> [M+H]<sup>+</sup> 535.2295; found 535.2303. [a]p<sup>25</sup>: +37.03 (c 1.33, CHCl<sub>3</sub>).

### 2,2,2-Trifluoroethyl (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6enoate (3ba):



The compound **3ba** was prepared according to **GP V** by using imine **1b** (78 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica (Et<sub>3</sub>N neutralized) using 6% ethylacetate in hexane as eluent provided the product **3ba** 

as colourless oil (78 mg, 66%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta = 5.88$  (dd, J = 17.6, 10.9 Hz, 1H), 5.56 (d, J = 10.9 Hz, 1H), 5.32 (d, J = 17.6 Hz, 1H), 5.06 (t, J = 7.0 Hz, 2H), 4.71 – 4.65

(m, 1H), 4.39 - 4.32 (m, 1H), 4.17 (d, J = 10.5 Hz, 1H), 3.62 (d, J = 10.5 Hz, 1H), 2.06 - 2.00 (m, 2H), 1.77 - 1.72 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.42 (s, 3H), 0.97 (s, 9H) ppm. <sup>13</sup>C **NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta = 171.38$ , 135.53, 132.61, 123.64 (q, J = 265 Hz), 123.47, 119.82, 66.48, 65.28, 60.85 (q, J = 36 Hz), 35.52, 34.02, 26.40, 25.82, 22.66, 18.38, 17.84 ppm. **IR** (film): **v**<sub>max</sub> = 2968, 1756, 1277, 1162, 1090 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>18</sub>H<sub>31</sub>F<sub>3</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 398.1971, found 398.1984. [ $\alpha$ ] $p^{25}$ : +85.36 (c 1.45, CHCl<sub>3</sub>).

#### Benzyl (2S,3R)-2-(((S)-tert-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoate (3ca):



The compound **3ca** was prepared according to **GP V** by using imine **1c** (80 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 7% ethylacetate in hexane as eluent provided the product **3ca** as colourless oil (87 mg, 72%). <sup>1</sup>**H NMR** (600

MHz, CDCl<sub>3</sub>):  $\delta = 7.37 - 7.31$  (m, 5H), 5.90 (dd, J = 17.6, 10.9 Hz, 1H), 5.52 (d, J = 10.9 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 5.20 (d, J = 12.3 Hz, 1H), 5.11 (d, J = 12.2 Hz, 1H), 5.06 (t, J = 7.0 Hz, 1H), 4.25 (d, J = 9.9 Hz, 1H), 3.58 (d, J = 10.0 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.79 – 1.74 (m, 1H), 1.68 – 1.64 (m, 4H), 1.58 (s, 3H), 1.41 (s, 3H), 0.92 (s, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 172.62$ , 135.80, 135.43, 132.41, 128.72, 128.63, 128.47, 123.59, 119.49, 67.26, 66.57, 65.21, 35.57, 34.11, 26.57, 25.76, 22.67, 18.23, 17.79 ppm. IR (film): v<sub>max</sub> = 2965, 1733, 1291, 1210, 1165, 1083 cm<sup>-1.</sup> HRMS-ESI: calculated for C<sub>23</sub>H<sub>35</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup> 428.2235; found 428.2233. [α]<sub>D</sub><sup>25</sup>: +165.8 (c 0.48, CHCl<sub>3</sub>).

#### (2S,3R)-2-(((S)-tert-Butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoic acid (3da):



The compound **3da** was prepared according to **GP V** by using imine **1d** (added as a crude), geranyl boronic acid **2a** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at -30°C. Column chromatography on silica using 0.5% MeOH in DCM provided the product **3da** as colourless oil (62 mg, 65% over two steps from glyoxalic acid). <sup>1</sup>H **NMR** (500 MHz,

CDCl<sub>3</sub>):  $\delta = 5.86$  (dd, J = 17.5, 10.8 Hz, 1H), 5.26 (d, J = 10.8 Hz, 1H), 5.10 (d, J = 17.6 Hz, 1H), 5.05 (t, J = 7.5 Hz, 1H), 4.04 (d, J = 9.2 Hz, 1H), 3.77 (d, J = 9.2 Hz, 1H), 2.04 – 1.96 (m, 1H), 1.91 – 1.85 (m, 1H), 1.66 (s, 3H), 1.60 – 1.53 (m, 4H), 1.44 – 1.37 (m, 1H), 1.25 (s, 3H), 1.19 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 174.49$ , 141.21, 131.83, 124.24, 116.85, 65.46, 57.16, 43.89, 38.00, 29.83, 25.80, 22.92, 22.61, 19.29, 17.77 ppm. **IR (film): v**<sub>max</sub> =

3402, 1721, 1461,1375, 1275, 1091 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>16</sub>H<sub>30</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 316.1941; found 314.1952. **[α]D**<sup>25</sup>: +96.20 (c 0.586, CHCl<sub>3</sub>).

## (2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-*N*-(*o*-tolyl)-3-vinyloct-6-enamide (3ea):



The compound **3ea** was prepared according to **GP V** by using imine **1e** (80 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.39 mmol, 1.3 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **3ea** as

colourless oil (94 mg, 77%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.10$  ( br s, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.04 – 6.99 (m, 2H), 5.97 (dd, J = 17.5, 10.8 Hz, 1H), 5.22 (d, J = 10.9 Hz, 1H), 5.10 – 5.04 (m, 2H), 4.61 (d, J = 8.3 Hz, 1H), 3.85 (d, J = 8.3 Hz, 1H), 2.21 (s, 3H), 1.92 (q, J = 8.0 Hz, 2H), 1.67 (s, 3H), 1.63 (s, 3H), 1.61 – 1.58 (m, 1H), 1.53 – 1.46 (m, 1H), 1.31 (s, 9H), 1.11 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 169.69$ , 142.45, 135.40, 131.70, 130.53, 130.43, 126.51, 125.50, 124.45, 123.99, 115.75, 66.37, 56.80, 45.00, 38.43, 25.79, 23.14, 22.84, 18.26, 17.83 ppm. IR (film):  $v_{max} = 3325$ , 1657, 1324, 1211, 1185, 1094 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>23</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 405.2570; found 405.2587. [*a*] $p^{25}$ : +54.12 (c 0.259, CHCl<sub>3</sub>).

### (2*S*,3*R*)-*N*-Benzyl-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enamide (3fa):



The compound **3fa** was prepared according to **GP V** by using imine **1f** (80 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **3fa** as colourless oil (102 mg, 84%). <sup>1</sup>**H NMR** 

(600 MHz, CDCl<sub>3</sub>):  $\delta = 7.30 - 7.21$  (m, 5H), 6.95 (s, 1H), 5.81 (dd, J = 17.5, 10.8 Hz, 1H), 5.07 (d, J = 10.8 Hz, 1H), 4.97 – 4.92 (m, 2H), 4.55 – 4.50 (m, 2H), 4.19 (dd, J = 14.6, 4.2 Hz, 1H), 3.54 (d, J = 8.4 Hz, 1H), 1.84 – 1.79 (m, 2H), 1.63 (s, 3H), 1.51 (s, 3H), 1.45 – 1.40 (m, 1H), 1.36 – 1.30 (m, 1H), 1.23 (s, 9H), 0.99 (s, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  170.92, 142.29, 138.09, 131.55, 128.61, 128.30, 127.41, 124.45, 115.38, 65.91, 56.70, 44.83, 43.90, 38.24, 25.79, 23.06, 22.69, 18.17, 17.76 ppm. IR (film):  $v_{max} = 3452$ , 1666, 1452, 1375,

1215, 1094 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{23}H_{37}N_2O_2S$  [M+H]<sup>+</sup> 405.2570; found 405.2587. **[a]** $p^{25}$ : +97.21 (c 0.496, CHCl<sub>3</sub>).

#### Ethyl (2S,3R)-3,7-dimethyl-2-(((S)-p-tolylsulfinyl)amino)-3-vinyloct-6-enoate (3ga):



The compound **3ga** was prepared according to **GP V** by using imine **1g** (72 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid **2a** (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 8% ethylacetate in hexane as eluent provided the product **3ga** as colourless oil (63 mg, 56%). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 5.82 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.18 (d, *J* = 10.8 Hz, 1H), 5.06 – 5.01 (m, 2H), 4.64 (d, *J* = 9.5 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.74 (d, *J* = 9.7 Hz, 1H), 2.41 (s, 3H), 2.00 – 1.88 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.54 – 1.46 (m, 1H), 1.36 – 1.28 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 171.95, 141.83, 141.57, 141.38, 131.78, 129.60, 125.61, 124.18, 115.76, 62.61, 61.05, 43.84, 38.18, 25.76, 22.67, 21.44, 18.47, 17.74, 14.09 ppm. IR (film): **v**<sub>max</sub> = 2975, 1732, 1446, 1185, 1070, 810 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>21</sub>H<sub>32</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 378.2097; found 378.2082. [α]p<sup>25</sup>: +32.50 (c 0.1, CHCl<sub>3</sub>).

## Ethyl (2*R*,3*S*)-2-(((*R*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoate (*ent*-3aa):



The compound *ent*-3aa was prepared according to GP V by using imine *ent*-1a (61 mg, 0.3 mmol, 1.0 equiv), geranyl boronic acid 2a (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 7% ethylacetate in hexane as eluent provided the product *ent*-3aa as colourless oil (73 mg, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.87 (dd, J = 17.6, 10.9 Hz,

1H), 5.51 (d, J = 10.9 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.04 (t, J = 7.1 Hz, 1H), 4.21 – 4.15 (m, 3H), 3.49 (d, J = 9.8 Hz, 1H), 2.03 – 1.97 (m, 2H), 1.77 – 1.71 (m, 1H), 1.66 (s, 3H), 1.64 – 1.61 (m, 1H), 1.56 (s, 3H), 1.38 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 132.35, 123.61, 119.34, 66.57, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 132.35, 123.61, 119.34, 66.57, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 132.35, 123.61, 119.34, 66.57, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 132.35, 123.61, 119.34, 66.57, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.66$ , 135.87, 132.35, 123.61, 119.34, 66.57, 65.14, 61.24, 35.39, 34.14, 26.56, 25.73, 22.66, 18.12, 17.76, 14.23 ppm. **IR** (film): **v**<sub>max</sub> = 2966, 1733, 1369, 1294, 1213, 1081 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>18</sub>H<sub>34</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 344.2259; found 344.2265. [**a**]**p**<sup>25</sup>: -66.44 (c 0.66, CHCl<sub>3</sub>).

## Ethyl (2*R*,3*R*)-2-((*R*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoate (*ent*-3ab):



The compound *ent*-**3ab** was prepared according to **GP V** by using imine *ent*-**1a** (61 mg, 0.3 mmol, 1.0 equiv), neryl boronic acid **2b** (0.45 mmol, 1.5 equiv) and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 7% ethylacetate in hexane as eluent provided the product *ent*-**3ab** as colourless oil (75 mg, 73%). <sup>1</sup>H

NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 6.00$  (dd, J = 17.6, 10.8 Hz, 1H), 5.59 (d, J = 10.8 Hz, 1H), 5.31 (d, J = 17.6 Hz, 1H), 5.09 (t, J = 7.1 Hz, 1H), 4.32 (d, J = 9.8 Hz, 1H), 4.21 – 4.15 (m, 2H), 3.51 (d, J = 9.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.99 – 1.91 (m, 1H), 1.83 (td, J = 12.6, 11.6, 4.9 Hz, 1H), 1.75 (ddd, J = 13.5, 11.5, 5.6 Hz, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.28 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 0.93 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.67$ , 135.44, 132.41, 123.54, 119.83, 66.28, 65.44, 61.23, 35.99, 35.41, 26.57, 25.71, 22.59, 17.74, 16.72, 14.25 ppm. IR (film): v<sub>max</sub> = 2966, 1733, 1368, 1295, 1213, 1090 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>18</sub>H<sub>33</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup> 366.2079; found 366.2079. [α]p<sup>25</sup>: -149.62 (c 0.533, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-phenylalaninate (5aa):



The compound **5aa** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 22% ethylacetate in hexane as eluent provided the product **5aa** as

colourless oil (39 mg, 83%). <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.29$  (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.1 Hz, 2H), 6.34 (d, J = 7.3 Hz, 1H), 5.75 (dd, J = 17.5, 10.8 Hz, 1H), 5.06 (d, J = 10.9 Hz, 1H), 5.01 – 4.97 (m, 2H), 4.81 (q, J = 6.3 Hz, 1H), 4.50 (d, J = 8.2 Hz, 1H), 3.68 (s, 3H), 3.48 (d, J = 8.3 Hz, 1H), 3.15 (dd, J = 13.8, 4.9 Hz, 1H), 3.07 (dd, J = 13.8, 6.4 Hz, 1H), 1.85 – 1.81 (m, 2H), 1.64 (s, 3H), 1.54 (s, 3H), 1.49 – 1.43 (m, 2H), 1.27 (s, 9H), 0.99 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.62$ , 170.58, 142.39, 135.80, 131.59, 129.66, 128.76, 127.21, 124.42, 115.88, 65.95, 56.75, 53.56, 52.23, 44.75, 38.04, 37.72, 25.75, 23.08, 22.69, 18.06, 17.77 ppm. IR (film): v<sub>max</sub> = 3247, 2958, 737, 1652, 1527, 1082 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>26</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 477.2782; found 477.2891. [**a**]**p**<sup>25</sup>: + 123.0 (c 0.52, CHCl<sub>3</sub>).

Methyl ((2S,3S)-2-(((S)-tert-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-Lphenylalaninate (5ab):



The compound **5ab** was synthesized according to **GP V** by using imine 4a (34 mg, 0.1 mmol), nervl boronic acid 2b (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 20% ethylacetate in hexane as eluent provided the product 5ab as

foamy solid (47 mg, 87%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.16 (d, J = 7.1 Hz, 1H), 6.45 – 6.41 (m, 1H), 5.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.09 (d, J = 10.9 Hz, 1H), 5.03 – 4.98 (m, 2H), 4.83 (q, J = 6.3 Hz, 1H), 4.43 (d, J = 8.1 Hz, 1H), 3.68 (s, 3H), 3.49 (d, J = 8.1 Hz, 1H), 3.16 (dd, J = 13.8, 5.1 Hz, 1H), 3.08 (dd, J = 13.8, 6.4 Hz, 1H), 1.87 – 1.81 (m, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.47 – 1.42 (m, 1H), 1.39 – 1.34 (m, 1H), 1.26 (s, 9H), 1.05 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.70, 170.54,$ 143.20, 135.82, 131.56, 129.64, 128.77, 127.21, 124.52, 115.18, 66.40, 56.78, 53.65, 52.25, 44.30, 37.71, 36.19, 25.75, 23.08, 22.71, 20.01, 17.77 ppm. IR (film): v<sub>max</sub> = 3261, 2964, 1748, 1671, 1548, 1050 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{26}H_{41}N_2O_4S$  [M+H]<sup>+</sup> 477.2782; found 477.2808. [α]p<sup>20</sup>: +161.7 (c 0.4, CHCl<sub>3</sub>).

#### Methyl ((2S)-2-(((S)-tert-butylsulfinyl)amino)-3,3-dimethylpent-4-enoyl)-Lphenylalaninate (5ac):



The compound **5ac** was synthesized according to **GP V** by using  $HN \xrightarrow{S} t_{Bu}$  imine **4a** (34 mg, 0.1 mmol), prenyl boronic acid **2d** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 Column chromatography on silica using 18% ethylacetate in hexane

as eluent provided the product **5ac** as foamy solid (42 mg, 83%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.30$  (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 6.17 (d, J = 7.4Hz, 1H), 6.06 (dd, J = 17.5, 10.8 Hz, 1H), 5.51 (d, J = 10.7 Hz, 1H), 5.32 (d, J = 17.5 Hz, 1H), 4.87 (q, J = 6.3 Hz, 1H), 4.51 (d, J = 8.6 Hz, 1H), 3.69 (s, 3H), 3.30 (d, J = 8.7 Hz, 1H), 3.17 (dd, J = 13.8, 4.8 Hz, 1H), 3.08 (dd, J = 13.8, 6.3 Hz, 1H), 1.44 (s, 3H), 1.34 (s, 3H), 0.93 (s,9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.81$ , 170.94, 136.64, 135.74, 129.71, 128.80, 127.23, 118.86, 67.39, 61.96, 53.36, 52.30, 37.83, 35.67, 26.64, 22.77, 20.68 ppm. IR (film):  $v_{max} = 3268, 2958, 1747, 1671, 1210, 1051 \text{ cm}^{-1}$ . HRMS-ESI: calculated for C<sub>21</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 409.2156; found 409.2170. [a]p<sup>25</sup>: +53.24 (c 0.693, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-phenylpent-4-enoyl)-*L*-phenylalaninate (5ad):



The compound **5ad** was synthesized according to **GP V** by using imine **9a** (34 mg, 0.1 mmol), cinnamyl boronic acid **2e** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at -50 °C. Column chromatography on silica using 28% ethylacetate in hexane as eluent provided the product **5ad** as foamy solid (40 mg, 88%). <sup>1</sup>H

**NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.35$  (d, J = 7.1 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.23 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 7.0 Hz, 2H), 7.15 – 7.14 (m, 3H), 6.92 – 6.90 (m, 2H), 6.07 (ddd, J = 17.7, 10.4, 7.6 Hz, 1H), 5.18 – 5.13 (m, 2H), 4.75 (q, J = 6.6 Hz, 1H), 4.21 – 4.19 (m, 1H), 4.13 (dd, J = 9.9, 4.9 Hz, 1H), 3.70 (s, 3H), 3.59 (d, J = 10.0 Hz, 1H), 3.05 – 2.97 (m, 2H), 1.10 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.63$ , 171.01, 139.07, 137.30, 136.17, 129.38, 129.16, 128.68, 128.52, 127.36, 127.00, 117.49, 64.23, 56.93, 54.03, 52.38, 51.26, 37.68, 22.69 ppm. **IR (film): v**<sub>max</sub> = 3279, 1744, 1658, 1542, 1204, 1046 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>SNa [M+Na]<sup>+</sup> 479.1980; found 479.1981 **.** [α]p<sup>20</sup>: +48.2 (c 0.14, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*S*)-3-(2-bromophenyl)-2-(((*S*)-*tert*-butylsulfinyl)amino)pent-4-enoyl)-*L*-phenylalaninate (5ae):



The compound **5ae** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2j** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ae** as foamy solid (40 mg, 75%). <sup>1</sup>H

**NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.54$  (d, J = 7.9 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.17 – 7.15 (m, 2H), 7.08 – 7.04 (m, 1H), 6.54 (d, J = 7.2 Hz, 1H), 5.98 (ddd, J = 17.0, 10.3, 8.3 Hz, 1H), 5.14 – 5.09 (m, 2H), 4.85 – 4.81 (m, 1H), 4.25 (t, J = 8.4 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 4.02 (t, J = 8.9 Hz, 1H), 3.70 (s, 3H), 3.16 – 3.08 (m, 2H), 1.01 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.62$ , 170.49, 139.67, 135.98, 135.40, 133.28, 129.88, 129.67, 128.74, 128.47, 127.62, 127.18, 125.69, 119.14, 63.40, 56.35, 53.65, 52.59, 52.37, 37.98, 22.52 ppm. IR (film):  $v_{max} = 3292$ , 1745, 1672, 1546, 1219, 1050 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>BrS [M+H]<sup>+</sup> 535.1266; found 535.1259. [ $\alpha$ ] $\sigma^{25}$ : +13.75 (c 0.4, CHCl<sub>3</sub>).

Methyl ((2*S*,3*S*)-3-(4-bromophenyl)-2-(((*S*)-*tert*-butylsulfinyl)amino)pent-4-enoyl)-*L*-phenylalaninate (5af):



The compound **5af** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2k** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 27% ethylacetate in hexane as eluent provided the product **5af** as yellow foamy solid (42 mg, 79%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.43$  (d, J = 7.4 Hz, 1H),

7.36 (d, J = 8.4 Hz, 2H), 7.20 – 7.14 (m, 3H), 7.03 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 6.8 Hz, 2H), 6.00 (ddd, J = 17.5, 10.4, 7.4 Hz, 1H), 5.18 (d, J = 10.4 Hz, 1H), 5.14 (d, J = 17.2 Hz, 1H), 4.71 (q, J = 7.4 Hz, 1H), 4.19 – 4.17 (m, 1H), 4.12 (dd, J = 10.1, 4.5 Hz, 1H), 3.72 (s, 3H), 3.41 (d, J = 10.1 Hz, 1H), 3.09 (dd, J = 13.9, 5.6 Hz, 1H), 2.96 (dd, J = 13.9, 7.5 Hz, 1H), 1.14 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.61$ , 170.72, 137.99, 136.87, 136.16, 131.68, 130.92, 129.31, 128.55, 127.12, 121.34, 117.85, 64.02, 57.03, 54.06, 52.46, 50.32, 37.61, 22.73 ppm. IR (film): v<sub>max</sub> = 3286, 2924, 1743, 1660, 1488, 1042 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>25</sub>H<sub>31</sub>BrN<sub>2</sub>O<sub>4</sub>S [M+Na]<sup>+</sup> 557.1086; found 557.1083. [ $\alpha$ ] $p^{25}$ : +26.25 (c 0.2, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(1-tosyl-1*H*-indol-3-yl)pent-4-enoyl)-*L*-phenylalaninate (5ag):



The compound **5ag** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2o** (0.25 mmol, 2.5 equiv), 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ag** as colourless oil (56 mg, 86%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.98$  (d, J = 8.3 Hz, 1H), 7.76

(d, J = 8.3 Hz, 2H), 7.64 (d, J = 7.9 Hz, 1H), 7.40 (s, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.11 (d, J = 7.3 Hz, 1H), 7.08 (d, J = 7.3 Hz, 1H), 7.02 (t, J = 7.3 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 6.05 (ddd, J = 17.3, 10.4, 7.4 Hz, 1H), 5.19 – 5.12 (m, 2H), 4.65 (q, J = 6.6 Hz, 1H), 4.38 – 4.35 (m, 1H), 4.19 (dd, J = 9.5, 4.5 Hz, 1H), 3.75 (d, J = 9.5 Hz, 1H), 3.69 (s, 3H), 2.85 (d, J = 6.3 Hz, 2H), 2.32 (s, 3H), 1.09 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 171.50$ , 170.40, 145.18, 136.24, 135.65, 135.35, 135.12, 130.06, 129.90, 129.05, 128.43, 127.09, 126.97, 125.16, 124.74, 123.32, 120.84, 120.09, 117.80, 113.67, 62.61, 56.89, 53.74,

52.44, 43.53, 37.48, 22.62, 21.67 ppm. **IR (film):**  $v_{max} = 1743$ , 1689, 1447, 1365, 1175, 1122 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>34</sub>H<sub>40</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub> [M+H]<sup>+</sup> 650.2353; found 650.2362. [a]D<sup>25</sup>: +64.4 (c 0.26, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(thiophen-2-yl)pent-4-enoyl)-*L*-phenylalaninate (5ah):



The compound **5ah** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2m** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ah** as foamy solid (16 mg, 35%). <sup>1</sup>H **NMR** (500 MHz,

CDCl<sub>3</sub>):  $\delta = 7.75$  (d, J = 7.2 Hz, 1H), 7.18 – 7.15 (m, 3H), 7.10 (t, J = 7.7 Hz, 1H), 6.95 – 6.90 (m, 3H), 6.79 (d, J = 3.4 Hz, 1H), 6.03 (ddd, J = 17.3, 10.3, 7.8 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.20 (d, J = 10.3 Hz, 1H), 4.77 – 4.73 (m, 1H), 4.65 (dd, J = 7.6, 2.8 Hz, 1H), 4.12 (dd, J = 10.5, 3.2 Hz, 1H), 3.72 (s, 3H), 3.60 (d, J = 10.5 Hz, 1H), 3.08 (dd, J = 13.9, 5.6 Hz, 1H), 2.97 (dd, J = 13.9, 7.5 Hz, 1H), 1.19 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.59$ , 170.59, 141.14, 137.40, 136.41, 129.37, 128.51, 127.12, 126.97, 126.51, 124.84, 117.74, 64.90, 57.23, 54.23, 52.42, 46.52, 37.64, 22.79 ppm. IR (film):  $v_{max} = 3288$ , 2926, 1742, 1671, 1258, 1029 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 463.1725; found 463.1772. [*a*] $p^{25}$ : +22.73 (c 0.33, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(furan-2-yl)pent-4-enoyl)-*L*-phenylalaninate (5ai):



The compound **5ai** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2n** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ai** as colourless liquid (19 mg, 42%). <sup>1</sup>**H NMR** (500 MHz,

CDCl<sub>3</sub>):  $\delta = 7.53$  (d, J = 7.2 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.10 – 7.08 (m, 3H), 6.25 (dd, J = 3.1, 1.9 Hz, 1H), 6.03 (d, J = 3.2 Hz, 1H), 5.93 (ddd, J = 17.7, 10.3, 7.8 Hz, 1H), 5.19 (d, J = 10.3 Hz, 1H), 5.16 (d, J = 17.1 Hz, 1H), 4.75 – 4.70 (m, 1H), 4.29 (dd, J = 7.7, 3.9 Hz, 1H), 4.13 (dd, J = 9.9, 4.1 Hz, 1H), 3.91 (d, J = 10.0 Hz, 1H), 3.70 (s, 3H), 3.10 (dd, J = 13.8, 5.6 Hz, 1H), 2.99 (dd, J = 14.0, 7.5 Hz, 1H), 1.19 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.61, 170.61, 152.86, 142.00, 136.48, 135.01, 129.47, 128.58, 127.02, 118.54, 110.60, 126 MHz$ 

108.29, 63.61, 57.01, 54.16, 52.39, 45.91, 37.74, 22.73 ppm. **IR (film): v**<sub>max</sub> = 3296, 2927, 1746, 1658, 1214, 1051 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{23}H_{31}N_2O_5SNa$  [M+Na]<sup>+</sup> 469.1773; found 469.1772. [a]p<sup>20</sup>: +13.9 (c 0.2, CHCl<sub>3</sub>).

#### Methyl ((2S)-2-(((S)-tert-butylsulfinyl)amino)-2-(1-vinylcyclohexyl)acetyl)-Lphenylalaninate (5aj):

MeO<sub>2</sub>C

The compound 5aj was synthesized according to GP V by using imine 4a (34 mg, 0.1 mmol), 2t (0.25 mmol, 2.5 equiv), and 4Å molecular sieves at room temperature. Column chromatography on silica using 20% ethylacetate in hexane as eluent provided the product **5aj** as colourless oil (34 mg, 73%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.30$  (t, J = 7.3Hz, 1H), 7.26 - 7.22 (m, 2H), 7.16 (d, J = 7.3 Hz, 2H), 6.22 (d, J = 7.0 Hz, 1H), 5.58 (dd, J = 7.0 Hz, 1H), 17.9, 11.0 Hz, 1H), 5.21 (d, J = 11.0 Hz, 1H), 5.04 (d, J = 17.8 Hz, 1H), 4.85 (q, J = 5.9 Hz, 1H), 4.40 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 3H), 3.41 (d, *J* = 8.5 Hz, 1H), 3.17 (dd, *J* = 13.9, 5.1 Hz, 1H), 3.09 (dd, J = 13.8, 6.2 Hz, 1H), 1.73 - 1.68 (m, 1H), 1.54 - 1.45 (m, 4H), 1.41 - 1.31 (m, 1H), 1.54 - 1.45 (m, 2H), 1.41 - 1.31 (m, 2H)

5H), 1.28 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.80$ , 170.50, 142.03, 135.85, 129.68, 128.82, 127.26, 117.12, 56.84, 53.51, 52.32, 44.64, 37.79, 33.52, 31.31, 26.25, 23.14, 22.17, 21.87 ppm. IR (film): v<sub>max</sub> = 3261, 2926, 1748, 1673, 1456, 1052 cm<sup>-1</sup>. HRMS-ESI: calculated for  $C_{24}H_{37}N_2O_4S$  [M+H]<sup>+</sup> 449.2469; found 449.2489 . [a] $p^{25}$ : +63.25 (0.152, CHCl<sub>3</sub>).

#### Methyl ((2S)-2-(((S)-tert-butylsulfinyl)amino)-2-((S)-cyclohex-2-en-1-yl)acetyl)-Lphenylalaninate (5ak):

HN\_\_+\_Bu MeO<sub>2</sub>

The compound **5ak** was synthesized according to **GP V** by using imine 4a (34 mg, 0.1 mmol), 2aa (0.25 mmol, 2.5 equiv), and 4Å molecular sieves at 60 °C. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ak** as

colourless liquid (10 mg, 28%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.43$  (d, J = 7.8 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 5.78 – 5.75 (m, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.85 (td, J = 8.0, 5.7 Hz, 1H), 3.82 (d, J = 8.8 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 8.8, 3.8 Hz, 1H), 3.22 (dd, *J* = 13.9, 5.6 Hz, 1H), 3.03 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.92 - 2.84 (m, 1H), 1.99 - 1.92 (m, 1H), 1.91 - 1.86 (m, 1H), 1.76 - 1.68 (m, 2H), 1.66 - 1.57 (m, 2H), 1.25 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.83$ , 171.59, 136.51, 132.05, 129.54, 128.69, 127.12, 125.80, 63.17, 56.88, 53.86, 52.44, 39.04, 37.97, 25.83, 25.16, 22.91, 21.83 ppm. **IR (film):**  $v_{max} = 3266, 2925, 1745, 1667, 1205, 1050 \text{ cm}^{-1}$ . **HRMS-ESI:** calculated for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>SNa [M+Na]<sup>+</sup> 443.1980; found 443.1982. [ $\alpha$ ] $p^{25}$ : -10.0 (c 0.12, CHCl<sub>3</sub>).

## Methyl ((2S)-2-(((S)-*tert*-butylsulfinyl)amino)-2-((R)-2-methylenecyclohexyl)acetyl)-L-phenylalaninate (5al):



The compound **5al** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2ab** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 24% ethylacetate in hexane as eluent provided the

product **5al** as colourless oil (23 mg, 53%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.28$  (t, *J* = 7.3 Hz, 2H), 7.23 – 7.19 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.79 (q, *J* = 7.3 Hz, 1H), 4.66 (s, 1H), 4.54 (s, 1H), 4.04 (dd, *J* = 9.9, 5.9 Hz, 1H), 3.81 (d, *J* = 9.8 Hz, 1H), 3.71 (s, 3H), 3.20 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.05 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.67 – 2.63 (m, 1H), 2.21 – 2.16 (m, 1H), 2.10 – 2.04 (m, 1H), 1.60 – 1.56 (m, 2H), 1.46 – 1.42 (m, 2H), 1.40 – 1.35 (m, 2H), 1.26 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.06$ , 171.79, 148.22, 136.47, 129.67, 128.63, 127.07, 108.58, 60.73, 56.94, 53.88, 52.38, 45.73, 37.99, 35.09, 28.14, 27.92, 23.94, 22.96 ppm. **IR (film): v**<sub>max</sub> = 3263, 2925, 1749, 1641, 1556, 1058 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>23</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 435.2318; found 435.2332. **[α]p<sup>25</sup>:** +61.16 (c 0.233, CHCl<sub>3</sub>).

# Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-ethyl-4-methylpent-4-enoyl)-*L*-phenylalaninate (5am):

### Methyl ((2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-(4-chlorophenyl)-4-methylpent-4enoyl)-*L*-phenylalaninate (5an):



The compound **5an** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2ad** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 23% ethylacetate in hexane as eluent provided the product **5an** as foamy solid (39 mg, 78%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.71$  (d, J = 7.3 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.17

- 7.14 (m, 3H), 7.05 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 7.0 Hz, 2H), 4.97 (s, 1H), 4.93 (s, 1H), 4.72 (q, J = 7.6 Hz, 1H), 4.38 (dd, J = 10.4, 4.7 Hz, 1H), 4.16 (d, J = 4.6 Hz, 1H), 3.72 (s, 3H), 3.22 (d, J = 10.4 Hz, 1H), 3.12 (dd, J = 14.0, 5.5 Hz, 1H), 2.97 (dd, J = 13.9, 7.9 Hz, 1H), 1.60 (s, 3H), 1.08 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.67$ , 171.45, 144.75, 136.40, 133.19, 131.11, 129.34, 128.59, 128.48, 127.03, 112.26, 62.34, 57.10, 54.29, 52.42, 52.33, 37.62, 22.93, 22.68 ppm. IR (film): v<sub>max</sub> = 3268, 2926, 1744, 1663, 1218, 1051 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>26</sub>H<sub>34</sub>ClN<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 505.1922; found 505.1949. [α]p<sup>25</sup>: -76.7 (c 0.16, CHCl<sub>3</sub>).

Methyl ((2S)-2-(((S)-*tert*-butylsulfinyl)amino)-4-phenylpent-4-enoyl)-*L*-phenylalaninate (5ao):

The compound **5ao** was synthesized according to **GP V** by using  $MeO_2C_{Ph}$   $H_{Ph}$   $F_{Bu}$  imine **4a** (34 mg, 0.1 mmol), **2v** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 27% ethylacetate in hexane as eluent provided the product **5ao** as gummy solid (36 mg, 79%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.43$  (d, J = 7.3Hz, 1H), 7.29 – 7.26 (m, 3H), 7.26 – 7.20 (m, 5H), 7.14 – 7.12 (m, 2H), 5.25 (s, 1H), 5.02 (s, 1H), 4.64 (td, J = 7.7, 5.7 Hz, 1H), 3.83 (td, J = 8.6, 5.0 Hz, 1H), 3.66 (s, 3H), 3.60 (d, J = 9.0Hz, 1H), 3.18 (dd, J = 15.0, 5.4 Hz, 1H), 3.10 (dd, J = 13.9, 5.6 Hz, 1H), 2.94 (dd, J = 13.9, 7.9 Hz, 1H), 2.66 (dd, J = 14.7, 8.3 Hz, 1H), 1.09 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.97, 171.77, 144.38, 139.98, 136.52, 129.53, 128.79, 128.65, 128.09, 127.11, 126.46, 116.67, 58.93, 56.73, 54.21, 52.41, 39.59, 37.77, 22.62 ppm. IR (film): vmax = 3273, 2927, 1743, 1668, 1213, 1045 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>25</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 456.2161; found 456.2160. 1999. [$ **a** $]<math>p^{25}$ : +86.75, (c 0.366, CHCl<sub>3</sub>). Methyl (*R*)-4-((*S*)-1-(((*S*)-*tert*-butylsulfinyl)amino)-2-(((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)-4-methylhex-5-enoate (5ap):



The compound **5ap** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2w** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 23% ethylacetate in hexane as eluent provided the product **5ap** as colourless oil (29 mg, 62%).

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.30$  (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.0 Hz, 1H), 7.15 (d, J = 7.5 Hz, 2H), 6.31 (d, J = 7.3 Hz, 1H), 5.69 (dd, J = 17.5, 10.8 Hz, 1H), 5.08 (d, J = 10.8 Hz, 1H), 5.01 (d, J = 17.6 Hz, 1H), 4.82 (q, J = 6.0 Hz, 1H), 4.54 (d, J = 8.1 Hz, 1H), 3.70 (s, 3H), 3.63 (s, 3H), 3.48 (d, J = 8.1 Hz, 1H), 3.16 (dd, J = 13.8, 4.8 Hz, 1H), 3.08 (dd, J = 13.8, 6.2 Hz, 1H), 2.19 (t, J = 8.1 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.76 – 1.70 (m, 1H), 1.28 (s, 9H), 0.96 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 174.14$ , 171.61, 170.22, 141.62, 135.74, 129.67, 128.83, 127.29, 116.82, 66.04, 56.84, 53.58, 52.33, 51.71, 44.46, 37.70, 32.57, 29.23, 23.08, 17.51 ppm. IR (film): v<sub>max</sub> = 3273, 2925, 1732, 1632, 1201, 1052 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>24</sub>H<sub>37</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 481.2372; found 481.2379. [α]p<sup>25</sup>: +64.15 (0.125, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-6-((4-methoxybenzyl)oxy)-3vinylhexanoyl)-*L*-phenylalaninate (5aq):



The compound **5aq** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2y** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **5aq** as colourless oil (45 mg, 82%). <sup>1</sup>**H NMR** (500 MHz,

CDCl<sub>3</sub>):  $\delta = 7.27 - 7.21$  (m, 6H), 7.19 - 7.17 (m, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.50 (ddd, J = 16.2, 10.9, 9.0 Hz, 1H), 5.05 - 5.02 (m, 2H), 4.79 (q, J = 7.5 Hz, 1H), 4.39 (s, 2H), 3.83 - 3.79 (m, 4H), 3.74 (dd, J = 9.5, 4.4 Hz, 1H), 3.70 (s, 3H), 3.39 - 3.33 (m, 2H), 3.18 (dd, J = 13.9, 5.8 Hz, 1H), 3.03 (dd, J = 13.9, 7.5 Hz, 1H), 2.54 - 2.49 (m, 1H), 1.78 - 1.66 (m, 1H), 1.63 - 1.54 (m, 1H), 1.45 - 1.34 (m, 2H), 1.23 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.80$ , 171.15, 159.33, 138.13, 136.42, 130.89, 129.55, 129.34, 128.65, 127.13, 117.87, 113.94, 72.62, 69.91, 63.58, 56.86, 55.43, 53.82, 52.39, 47.47, 37.88, 27.60, 26.28, 22.85 ppm. IR (film): v<sub>max</sub> = 3266, 2927, 1745, 1672, 1513, 1240, 1045 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>30</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup> 581.2661; found 581.2664. [ $\alpha$ ]p<sup>25</sup>: +25.0 (c 0.3, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*R*)-3-(2-((*N*-benzyl-4-methylphenyl)sulfonamido)ethyl)-2-(((*S*)-tertbutylsulfinyl)amino)pent-4-enoyl)-*L*-phenylalaninate (5ar):



The compound **5ar** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2z** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at room temperature. Column chromatography on silica using 35% ethylacetate in hexane as eluent provided the product **5ar** as colourless oil (52 mg, 79%). <sup>1</sup>**H NMR** (500 MHz,

CDCl<sub>3</sub>):  $\delta = 7.67$  (d, J = 8.2 Hz, 2H), 7.29 – 7.26 (m, 4H), 7.26 – 7.21 (m, 7H), 7.17 (d, J = 6.9 Hz, 2H), 5.30 (dt, J = 17.2, 9.8 Hz, 1H), 4.97 (d, J = 10.2 Hz, 1H), 4.90 (d, J = 17.1 Hz, 1H), 4.71 (q, J = 7.4 Hz, 1H), 4.35 (d, J = 14.8 Hz, 1H), 4.11 (d, J = 14.9 Hz, 1H), 3.73 – 3.69 (m, 4H), 3.55 (dd, J = 9.7, 4.3 Hz, 1H), 3.14 (dd, J = 13.9, 5.9 Hz, 1H), 3.04 – 2.95 (m, 3H), 2.42 (s, 3H), 2.34 (tt, J = 9.2, 4.2 Hz, 1H), 1.56 – 1.50 (m, 1H), 1.20 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.77$ , 170.92, 143.38, 137.19, 136.93, 136.75, 136.37, 129.84, 129.51, 128.69, 128.60, 127.95, 127.37, 127.19, 118.42, 63.02, 56.86, 53.97, 52.53, 52.40, 46.77, 44.71, 37.79, 28.71, 22.85, 21.62 ppm. **IR (film): v**<sub>max</sub> = 3263, 2925, 1744, 1673, 1137, 1052 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>35</sub>H<sub>46</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub> [M+H]<sup>+</sup> 668.2828; found 668.2850. [ $\alpha$ ]p<sup>25</sup>: +21.2 (c 0.24, CHCl<sub>3</sub>).

# Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-methylpent-4-enoyl)-*L*-phenylalaninate (5as):

The compound **5as** was synthesized according to **GP** V by using imine **4a** (34 mg, 0.1 mmol), **2ae** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at 60 °C. Column chromatography on silica using 24% ethylacetate in hexane as eluent provided the product **5as** as colourless oil (27 mg, 68%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.30 - 7.27$  (m, 3H), 7.23 (d, J = 7.1 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 5.70 (ddd, J = 17.4, 10.4, 7.1 Hz, 1H), 5.05 - 5.01 (m, 2H), 4.81 (q, J = 7.1 Hz, 1H), 3.82 - 3.75 (m, 2H), 3.72 (s, 3H), 3.20 (dd, J = 13.9, 5.8 Hz, 1H), 3.05 (dd, J = 13.9, 7.5 Hz, 1H), 2.81 - 2.76 (m, 1H), 1.24 (s, 9H), 0.85 (d, J = 6.8 Hz, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.84$ , 171.22, 140.06, 136.38, 129.52, 128.65, 127.14, 115.77, 63.79, 56.93, 53.84, 52.42, 40.57, 37.83, 22.85, 14.05 ppm. **IR (film): v**max = 3261, 2961, 1745, 1672, 1209, 1048 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>SNa [M+Na]<sup>+</sup> 417.1824; found 417.1822. **[a]p<sup>25</sup>**: +45.11 (c 0.266, CHCl<sub>3</sub>).
## Methyl ((2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3-methylpent-4-enoyl)-*L*-phenylalaninate (5at):



The compound **5at** was synthesized according to **GP V** by using imine **4a** (34 mg, 0.1 mmol), **2af** (0.25 mmol, 2.5 equiv) and 4Å molecular sieves at 60 °C. Column chromatography on silica using 20% ethylacetate in hexane as eluent provided the product **5at** as colourless oil (20 mg, 51%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.30

- 7.23 (m, 4H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.69 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.04 – 5.01 (m, 2H), 4.82 (q, *J* = 7.0 Hz, 1H), 3.81 (d, *J* = 9.0 Hz, 1H), 3.76 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H), 3.21 (dd, *J* = 13.9, 5.6 Hz, 1H), 3.05 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.80 – 2.76 (m, 1H), 1.24 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 171.83, 171.22, 140.08, 136.41, 129.53, 128.73, 128.66, 127.14, 115.77, 63.83, 56.94, 53.84, 52.41, 40.58, 37.87, 22.87, 14.11 ppm. IR (film): v<sub>max</sub> = 3267, 2926, 1744, 1661, 1543, 1212, 1050 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>SNa [M+Na]<sup>+</sup> 417.1824; found 417.1825. [*α*]p<sup>25</sup>: +33.33 (c 0.33, CHCl<sub>3</sub>).

### Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*tyrosinate (5ba):



The compound **5ba** was synthesized according to **GP V** by using imine **4b** (34 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **5ba** as white solid (35 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 

= 6.93 (d, *J* = 8.3 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 7.4 Hz, 1H), 5.77 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.12 (d, *J* = 10.9 Hz, 1H), 5.03 – 4.99 (m, 2H), 4.73 (dt, *J* = 7.3, 5.5 Hz, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 3H), 3.48 (d, *J* = 8.1 Hz, 1H), 3.01 (dd, *J* = 14.0, 4.9 Hz, 1H), 2.95 (dd, *J* = 14.0, 6.1 Hz, 1H), 1.84 (q, *J* = 7.7 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.49 – 1.43 (m, 1H), 1.42 – 1.36 (m, 1H), 1.29 (s, 9H), 0.99 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 171.83, 170.41, 155.73, 142.34, 131.68, 130.68, 126.93, 124.40, 116.07, 115.80, 65.97, 56.93, 53.78, 52.28, 44.82, 38.04, 36.96, 25.77, 23.13, 22.70, 17.95, 17.80 ppm. IR (film): v<sub>max</sub> = 3367, 2956, 1762, 1682, 1527, 1059 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>26</sub>H<sub>41</sub>N<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup> 493.2731; found 491.2758. [*α*]*p*<sup>25</sup>: +84.30 (c 0.433, CHCl<sub>3</sub>).

# Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-tryptophanate (5ca):



The compound **5ca** was synthesized according to **GP V** by using imine **4c** (38 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product

**5ca** as gummy solid (43 mg, 84%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.35$  (br s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.10 (d, J = 7.2 Hz, 2H), 6.28 (d, J = 7.4 Hz, 1H), 5.69 (dd, J = 17.4, 10.9 Hz, 1H), 5.00 – 4.84 (m, 4H), 4.60 (d, J = 8.2 Hz, 1H), 3.66 (s, 3H), 3.42 (d, J = 8.2 Hz, 1H), 3.33 – 3.27 (m, 2H), 1.83 – 1.77 (m, 2H), 1.64 (s, 3H), 1.53 (s, 3H), 1.44 – 1.33 (m, 2H), 1.29 (s, 9H), 0.97 (s, 3H) ppm. <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta = 171.99$ , 170.41, 142.20, 136.22, 131.61, 127.70, 124.42, 124.35, 122.07, 119.68, 118.65, 115.83, 111.37, 109.27, 66.18, 56.77, 53.08, 52.42, 44.76, 37.92, 27.26, 25.78, 23.13, 22.65, 17.94, 17.79 ppm. **IR (film): v**<sub>max</sub> = 3258, 2956, 1744, 1684, 1482, 1052 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>28</sub>H<sub>42</sub>N<sub>3</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 516.2891; found 516.2896. [α]p<sup>25</sup>: +143.0 (c 0.5, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-methioninate (5da):



The compound **5da** was synthesized according to **GP V** by using imine **4d** (32 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5da** 

as colourless oil (37 mg, 82%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.90$  (d, J = 6.5 Hz, 1H), 5.87 (dd, J = 17.5, 10.8 Hz, 1H), 5.18 (d, J = 10.8 Hz, 1H), 5.05 – 5.01 (m, 2H), 4.63 (td, J = 7.2, 5.2 Hz, 1H), 4.43 (d, J = 8.6 Hz, 1H), 3.72 (s, 3H), 3.49 (d, J = 8.6 Hz, 1H), 2.55 (t, J = 7.1 Hz, 2H), 2.17 – 2.09 (m, 4H), 2.03 – 1.96 (m, 1H), 1.90 – 1.83 (m, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.51 – 1.45 (m, 1H), 1.25 (s, 9H), 1.04 (s, 3H). ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.15$ , 171.02, 142.25, 131.58, 124.49, 115.68, 66.22, 56.66, 52.44, 51.94, 44.68, 37.80, 31.36, 29.97, 25.78, 23.04, 22.74, 18.37, 17.79, 15.58 ppm. **IR (film):** vmax = 3269, 2965, 1748 1671, 1551,

1053 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{22}H_{41}N_2O_4S_2$  [M+H]<sup>+</sup> 461.2502; found 461.2513. [a] $p^{25}$ : +69.82 (c 0.333, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-valinate (5ea):



The compound **5ea** was synthesized according to **GP V** on 0.3 mmol scale by using imine **4e**, geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 20% ethylacetate in hexane as eluent provided the product **5ea** as

colourless oil (77 mg, 60% over four steps from parent peptide). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.56$  (d, J = 7.4 Hz, 1H), 5.86 (dd, J = 17.5, 10.8 Hz, 1H), 5.18 (d, J = 10.8 Hz, 1H), 5.06 - 5.01 (m, 2H), 4.47 (d, J = 8.3 Hz, 1H), 4.40 (dd, J = 8.0, 5.0 Hz, 1H), 3.70 (s, 3H), 3.55 (d, J = 8.3 Hz, 1H), 2.16 - 2.08 (m, 1H), 1.89 - 1.83 (m, 2H), 1.64 (s, 3H), 1.54 (s, 3H), 1.50 - 1.47(m, 1H), 1.43 - 1.37 (m, 1H), 1.25 (s, 9H), 1.02 (s, 3H), 0.93 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.06$ , 171.06, 142.41, 131.55, 124.47, 115.67, 66.02, 57.80, 56.63, 52.04, 44.74, 37.88, 31.26, 25.77, 23.03, 22.71, 18.91, 18.15, 18.11, 17.77 ppm. IR (film):  $v_{max} = 3264$ , 2962, 1751, 1667, 1548, 1042 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>22</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 429.2787; found 429.2804. [ $\alpha$ ] $p^{25}$ : +55.45 (c 1.33, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-leucinate (5fa):



The compound **5fa** was synthesized according to **GP V** on 0.3 mmol scale from imine **4f**, geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 22% ethylacetate in hexane as eluent provided the product **5fa** as

colourless oil (102 mg, 76% over four steps) along with its minor diastereomer (11 mg, 8%); *dr*: 9:1. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.67$  (d, J = 7.2 Hz, 1H), 5.85 (dd, J = 17.5, 10.8 Hz, 1H), 5.17 (d, J = 10.9 Hz, 1H), 5.05 – 5.01 (m, 2H), 4.50 – 4.42 (m, 2H), 3.68 (s, 3H), 3.53 (d, J = 8.0 Hz, 1H), 1.87 – 1.82 (m, 1H), 1.66 – 1.62 (m, 4H), 1.59 – 1.55 (m, 1H), 1.53 (s, 3H), 1.49 – 1.39 (m, 3H), 1.24 (s, 9H), 1.01 (s, 3H), 0.90 (d, J = 4.6 Hz, 3H), 0.89 (d, J = 4.6 Hz, 3H) ppm. <sup>13</sup>C **NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta = 173.02$ , 170.79, 142.47, 131.47, 124.50, 115.62, 65.57, 56.63, 52.11, 51.44, 44.79, 41.20, 37.69, 25.75, 24.83, 23.01, 22.69, 22.63, 22.35, 18.17, 17.75 ppm. **IR (film):**  $\mathbf{v}_{max} = 3266, 2959, 1748, 1671, 1548, 1051 \text{ cm}^{-1}$ . **HRMS-ESI:** calculated for C<sub>23</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 443.2938; found 443.2943.  $[\alpha]_D^{25}$ : +63.13 (c 0.8, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-alloisoleucinate (5ga):



The compound **5ga** was synthesized according to **GP V** by using imine **4g** (30 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 25% ethylacetate in hexane as eluent provided the product **5ga** 

as gummy solid (34 mg, 77%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.25$  (d, J = 8.5 Hz, 1H), 5.88 (dd, J = 17.6, 10.9 Hz, 1H), 5.22 (d, J = 10.7 Hz, 1H), 5.10 – 5.02 (m, 2H), 4.53 (dd, J = 7.9, 4.7 Hz, 1H), 4.48 (d, J = 8.4 Hz, 1H), 3.72 (s, 3H), 3.50 (d, J = 8.3 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.52 – 1.47 (m, 1H), 1.45 – 1.36 (m, 3H), 1.26 (s, 9H), 1.23 – 1.15 (m, 1H), 1.03 (s, 3H), 0.92 – 0.89 (m, 6H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.08$ , 170.93, 142.60, 131.67, 124.49, 115.88, 66.26, 56.90, 56.72, 52.07, 44.81, 38.13, 37.98, 25.79, 25.40, 23.10, 22.76, 18.21, 17.81, 15.64, 11.75 ppm. IR (film): v<sub>max</sub> = 3256, 2964, 1745, 1671, 1544, 1202, 1051 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>23</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>SNa [M+Na]<sup>+</sup> 465.2763; found 465.2759. [a]p<sup>25</sup>: +84.52 (c 0.253, CHCl<sub>3</sub>).

## Dimethyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-glutamate (5ha):



The compound **5ha** was synthesized according to **GP V** by using imine **4h**, geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **5ha** as colourless oil (70 mg, 57%)

over four steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 6.79$  (br s, 1H), 5.87 (dd, J = 17.5, 10.8 Hz, 1H), 5.19 (d, J = 10.8 Hz, 1H), 5.05 – 5.02 (m, 2H), 4.55 (q, J = 7.3 Hz, 1H), 4.43 (d, J = 8.7 Hz, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 3.48 (d, J = 8.6 Hz, 1H), 2.48 – 2.44 (m, 2H), 2.22 – 2.15 (m, 1H), 2.01 – 1.96 (m, 1H), 1.90 – 1.83 (m, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.52 – 1.43 (m, 2H), 1.25 (s, 9H), 1.04 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 173.95$ , 172.02, 171.25, 142.26, 131.61, 124.52, 115.72, 66.40, 56.74, 52.45, 52.16, 51.94, 44.67, 37.89, 30.05, 29.83, 27.10, 25.77, 23.07, 22.76, 18.40, 17.78 ppm. **IR (film): v**<sub>max</sub> = 2924, 1739, 1668, 1336, 1205,

1045 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{23}H_{40}N_2NaO_6S$  [M+Na]<sup>+</sup> 495.2505; found 495.2504. [a] $p^{25}$ : +33.47 (c 0.366, CHCl<sub>3</sub>).

## Dimethyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-aspartate (5ia):



The compound **5ia** was synthesized according to **GP V** by using imine **4i**, geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 35% ethylacetate in hexane as eluent provided the product **5ia** as colourless oil (55 mg, 40%

over four steps). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 6.91$  (d, J = 8.3 Hz, 1H), 5.89 (dd, J = 17.5, 10.8 Hz, 1H), 5.24 (d, J = 10.9 Hz, 1H), 5.08 – 5.05 (m, 2H), 4.90 – 4.87 (m, 1H), 4.45 (d, J = 8.8 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.46 (d, J = 8.8 Hz, 1H), 3.01 (dd, J = 17.4, 4.2 Hz, 1H), 2.83 (dd, J = 17.3, 4.6 Hz, 1H), 1.91 – 1.86 (m, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.51 – 1.44 (m, 2H), 1.25 (s, 9H), 1.06 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.07$ , 170.99, 170.96, 142.13, 131.63, 124.49, 116.00, 66.41, 56.74, 52.68, 52.17, 48.60, 44.65, 37.95, 35.78, 25.77, 23.05, 22.77, 18.51, 17.78 ppm. IR (film):  $v_{max} = 3272$ , 2924, 1737, 1666, 1439, 1368, 1051 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>22</sub>H<sub>39</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 459.2523; found 459.2505. [ $\alpha$ ] $p^{25}$ : +72.07 (c 0.333, CHCl<sub>3</sub>).

## Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-leucyl-*L*-phenylalaninate (6a):



The compound **6a** was prepared according to **GP V** by using imine **4j** (45 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), and 4 Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 28% ethylacetate in hexane as eluent

provided the product **6a** as colourless oil (38 mg, 64%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.30 – 7.22 (m, 3H), 7.15 – 7.13 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 5.81 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 5.06 – 5.01 (m, 2H), 4.79 (dt, *J* = 7.9, 6.3 Hz, 1H), 4.35 (td, *J* = 8.3, 5.7 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 3.50 (d, *J* = 8.8 Hz, 1H), 3.09 (dd, *J* = 6.3, 2.2 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.63 (s, 3H), 1.62 – 1.57 (m, 2H), 1.54 (s, 3H), 1.52 – 1.45 (m, 2H), 1.42 – 1.35 (m, 1H), 1.26 (s, 9H), 1.03 (s, 3H), 0.89 (d, *J* = 6.0 Hz, 3H), 0.86 (d, *J* = 6.0 Hz, 3H) ppm. <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 171.83,

171.44, 170.74, 142.41, 136.25, 131.76, 129.42, 128.69, 127.16, 124.32, 116.11, 66.38, 56.87, 53.52, 52.55, 52.36, 44.72, 41.23, 38.15, 37.90, 25.77, 24.82, 22.99, 22.87, 22.72, 22.17, 18.53, 17.79 ppm. **IR (film):**  $\mathbf{v}_{max} = 3289, 2959, 1739, 1646, 1524, 1055 \text{ cm}^{-1}$ . **HRMS-ESI:** calculated for C<sub>32</sub>H<sub>52</sub>N<sub>3</sub>O<sub>5</sub>S [M+H]<sup>+</sup> 590.3622; found 590.3647. **[a]p<sup>25</sup>:** +80.7 (c 0.24, CHCl<sub>3</sub>).

# Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-valyl-*L*-alloisoleucinate (6b):



The compound **6b** was synthesized according to **GP V** by using imine **4k** (40 mg, 0.1 mmol), geranyl boronic acid **2a** (0.25 mmol, 2.5 equiv), 4 Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 30% ethylacetate in hexane as eluent provided the product **6b** as a gummy oil (38 mg, 71 %, dr: 6:1). <sup>1</sup>H

NMR (400 MHz, *major diastereomer*, CDCl<sub>3</sub>):  $\delta = 6.46$  (d, J = 8.4 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 5.84 (dd, J = 17.5, 10.8 Hz, 1H), 5.18 (d, J = 10.8 Hz, 1H), 5.05 – 5.00 (m, 2H), 4.56 (dd, J = 8.5, 4.9 Hz, 1H), 4.31 (d, J = 9.0 Hz, 1H), 4.21 (t, J = 5.6 Hz, 1H), 3.73 (s, 3H), 3.50 (d, J = 9.0 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.90 – 1.82 (m, 2H), 1.80 – 1.70 (m, 2H), 1.64 (s, 3H), 1.55 (s, 3H), 1.50 – 1.44 (m, 1H), 1.40 – 1.34 (m, 2H), 1.26 (s, 9H), 1.03 (s, 3H), 0.97 – 0.95 (m, 6H), 0.90 – 0.88 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.16$ , 171.00, 170.75, 142.25, 131.66, 124.36, 115.84, 66.64, 59.04, 56.79, 56.62, 52.26, 44.72, 38.05, 37.80, 31.62, 25.80, 25.24, 23.02, 22.71, 19.26, 18.34, 18.32, 17.81, 15.63, 11.68 ppm. IR (film): v<sub>max</sub> = 3032, 2964, 1743, 1647, 1543, 1203, 1050 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>28</sub>H<sub>52</sub>N<sub>3</sub>O<sub>5</sub>S [M+H]<sup>+</sup> 542.3622; found 542.3629. [α]p<sup>25</sup>: +34.84 (c 0.366, CHCl<sub>3</sub>).

# Methyl ((2*S*,3*R*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-3,7-dimethyl-3-vinyloct-6-enoyl)-*L*-valyl-*L*-alloisoleucyl-*L*-phenylalaninate (6c):



The compound **6c** was synthesized according to **GP V** using imine **4l** (31 mg, 0.057 mmol), **2a** (0.14 mmol, 2.5 equiv), 4 Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 40% ethylacetate

in hexane as eluent provided the product **11k** as a white solid (36 mg, 92%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.61$  (br s, 1H), 7.40 (br s, 1H), 7.23 – 7.18 (m, 3H), 7.11 (d, J = 7.2 Hz, 2H), 6.80 (d, J = 8.2 Hz, 1H), 5.84 (dd, J = 17.4, 10.8 Hz, 1H), 5.09 (d, J = 10.8 Hz, 1H), 5.01

-4.95 (m, 2H), 4.83 (q, *J* = 6.7 Hz, 1H), 4.50 (t, *J* = 8.6 Hz, 1H), 4.39 (d, *J* = 8.6 Hz, 1H), 4.26 (t, *J* = 7.9 Hz, 1H), 3.77 (d, *J* = 8.6 Hz, 1H), 3.65 (s, 3H), 3.09 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.01 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.95 – 1.91 (m, 1H), 1.85 – 1.76 (m, 3H), 1.62 (s, 3H), 1.52 – 1.46 (m, 4H), 1.36 – 1.30 (m, 1H), 1.26 (s, 9H), 1.09 – 1.05 (m, 1H), 1.02 (s, 3H), 0.90 – 0.81 (m, 12H) ppm. <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.14, 171.21, 171.13, 171.10, 142.59, 136.35, 131.40, 129.21, 128.61, 127.04, 124.57, 115.02, 66.23, 58.89, 57.68, 56.65, 53.61, 52.29, 44.76, 38.13, 37.73, 37.65, 32.27, 29.79, 25.71, 25.12, 23.08, 22.73, 19.45, 18.67, 17.73, 15.30, 11.47 ppm. **IR (film): v**max = 3293, 2963, 1745, 1647, 1542, 1218, 1048 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>37</sub>H<sub>61</sub>N<sub>4</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 689.4306; found 689.4304. [*α*]**p**<sup>25</sup>: +53.26 (c 0.168, CHCl<sub>3</sub>).

# Methyl ((2S)-2-(((S)-*tert*-butylsulfinyl)amino)-4-phenylpent-4-enoyl)-*L*-leucyl-*L*-phenylalanyl-*L*-isoleucinate (6d):



The compound **6d** was synthesized according to **GP V** by using imine **4m** (21 mg, 0.057 mmol), **2v** (0.14 mmol, 2.5 equiv), 4 Å molecular sieves (100 mg) at room temperature. Column chromatography on silica using 40% ethylacetate in hexane as eluent provided

the product **6d** as a white solid (23 mg, 60%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.40 - 7.35$  (m, 5H), 7.33 - 7.32 (m, 1H), 7.22 - 7.20 (m, 5H), 7.14 - 7.11 (m, 1H), 6.72 (d, J = 8.3 Hz, 1H), 5.38 (s, 1H), 5.14 (s, 1H), 4.64 (td, J = 8.5, 6.0 Hz, 1H), 4.47 (dd, J = 8.4, 5.4 Hz, 1H), 4.28 (td, J = 8.9, 4.8 Hz, 1H), 3.83 (td, J = 8.6, 4.5 Hz, 1H), 3.72 (d, J = 8.7 Hz, 1H), 3.68 (s, 3H), 3.29 (dd, J = 14.5, 4.3 Hz, 1H), 3.19 (dd, J = 14.1, 5.7 Hz, 1H), 3.01 (dd, J = 14.1, 8.9 Hz, 1H), 2.78 (dd, J = 14.6, 8.7 Hz, 1H), 1.88 - 1.82 (m, 1H), 1.52 - 1.44 (m, 2H), 1.39 - 1.25 (m, 3H), 1.14 (s, 9H), 0.88 - 0.82 (m, 12H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 172.33$ , 171.94, 171.91, 170.99, 144.26, 139.75, 137.54, 129.50, 128.98, 128.55, 128.45, 126.74, 126.47, 117.00, 59.87, 56.88, 56.86, 54.79, 53.23, 52.07, 40.79, 39.26, 37.78, 36.98, 25.24, 25.08, 22.99, 22.49, 22.01, 15.54, 11.62 ppm. **IR (film):** v<sub>max</sub> = 3972, 2967, 1755, 1642, 1230, 1058 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>37</sub>H<sub>55</sub>N<sub>4</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 683.3837; found 683.3836. [**a**]**p**<sup>25</sup>: -20.35 (c 0.086, CHCl<sub>3</sub>).

#### Comparison of data of 5aa obtained from allylation of imine and peptide coupling:



To a solution of carboxylic acid **3da** (157 mg, 0.5 mmol, 1.0 equiv) and (L)-phenylalanine-Meester·HCl salt (140 mg, 0.65 mmol, 1.3 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N (0.174 mL) and HBTU (246 mg, 0.65 mmol, 1.3 equiv) were added at room temperature under N<sub>2</sub> atmosphere. The reaction was stirred overnight. Next morning, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated brine solution ( $2 \times 5$  mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified on silica gel column using 20% ethylacetate in hexane as eluent to give **5aa** as colourless oil (42 mg, 18% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.28$  (t, J =7.6 Hz, 2H), 7.22 (t, J = 7.0 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 6.42 (d, J = 7.0 Hz, 1H), 5.76 (dd, J = 17.5, 10.8 Hz, 1H), 5.06 (d, J = 10.8 Hz, 1H), 5.00 - 4.97 (m, 2H), 4.80 (q, J = 6.5 Hz),1H), 4.51 (d, J = 8.2 Hz, 1H), 3.67 (s, 3H), 3.50 (d, J = 8.2 Hz, 1H), 3.15 (dd, J = 13.8, 4.8 Hz, 1H), 3.07 (dd, J = 13.8, 6.4 Hz, 1H), 1.86 – 1.81 (m, 2H), 1.64 (s, 3H), 1.54 (s, 3H), 1.49 – 1.43 (m, 1H), 1.40 – 1.36 (m, 1H), 1.27 (s, 9H), 0.99 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz,  $CDCl_3$ ):  $\delta = 171.61, 170.60, 142.38, 135.84, 131.53, 129.63, 128.72, 127.16, 124.45, 115.78, 129.63, 128.72, 127.16, 124.45, 115.78, 129.63, 129.6$ 65.91, 56.73, 53.62, 52.17, 44.74, 37.99, 37.71, 25.72, 23.06, 22.69, 18.10, 17.75 ppm. IR (film):  $v_{max} = 3273$ , 2966, 1747, 1699, 1545, 1207, 1053 cm<sup>-1</sup>. HRMS-ESI: calculated for  $C_{26}H_{40}N_2NaO_4S$  [M+Na]<sup>+</sup> 499.2601; found 499.2597. [ $\alpha$ ] $p^{25}$ : +122.7 (c 0.52, CHCl<sub>3</sub>).

### Comparison of <sup>1</sup>H NMR data of 5aa (500 MHz, CDCl<sub>3</sub>):

$\begin{array}{c} \overline{} \overline{}$	$\begin{array}{c} \overline{} \overline{}$
7.29 (t, <i>J</i> = 7.3 Hz, 2H)	7.28 (t, <i>J</i> = 7.6 Hz, 2H)
7.23 (t, $J = 7.3$ Hz, 1H)	7.22 (t, $J = 7.0$ Hz, 1H)
7.15 (d, <i>J</i> = 7.1 Hz, 2H)	7.16 (d, <i>J</i> = 7.6 Hz, 2H)

6.34 (d, <i>J</i> = 7.3 Hz, 1H)	6.42 (d, <i>J</i> = 7.0 Hz, 1H)
5.75 (dd, <i>J</i> = 17.5, 10.8 Hz, 1H)	5.76 (dd, <i>J</i> = 17.5, 10.8 Hz, 1H)
5.06 (d, <i>J</i> = 10.9 Hz, 1H)	5.06 (d, <i>J</i> = 10.8 Hz, 1H)
5.01 – 4.97 (m, 2H)	5.00 – 4.97 (m, 2H)
4.81 (q, <i>J</i> = 6.3 Hz, 1H)	4.80 (q, <i>J</i> = 6.5 Hz, 1H)
4.50 (d, <i>J</i> = 8.2 Hz, 1H)	4.51 (d, <i>J</i> = 8.2 Hz, 1H)
3.68 (s, 3H)	3.67 (s, 3H)
3.48 (d, <i>J</i> = 8.3 Hz, 1H)	3.50 (d, J = 8.2 Hz, 1H)
3.15 (dd, <i>J</i> = 13.8, 4.9 Hz, 1H)	3.15 (dd, <i>J</i> = 13.8, 4.8 Hz, 1H)
3.07 (dd, <i>J</i> = 13.8, 6.4 Hz, 1H)	3.07 (dd, <i>J</i> = 13.8, 6.4 Hz, 1H)
1.85 – 1.81 (m, 2H)	1.86 – 1.81 (m, 2H)
1.64 (s, 3H)	1.64 (s, 3H)
1.54 (s, 3H)	1.54 (s, 3H)
1.49 – 1.43 (m, 2H)	1.49 – 1.43 (m, 1H)
	1.40 – 1.36 (m, 1H),
1.27 (s, 9H)	1.27 (s, 9H)
0.99 (s. 3H)	0.99 (s. 3H)
0.99 (5, 511).	0.55 (5, 511)
Comparison of <sup>13</sup> C NMR Data of 5aa (126 ]	MHz, CDCl <sub>3</sub> ):
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I 5aa (Obtained from the allylation of 4a)	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling)
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I 5aa (Obtained from the allylation of 4a) 171.6	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I 5aa (Obtained from the allylation of 4a) 171.6 170.6	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6
Comparison of <sup>13</sup> C NMR Data of 5aa (126 1) 5aa (Obtained from the allylation of 4a) 171.6 170.6 142.4	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8 131.5
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8 131.5 129.6
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8 131.5 129.6 128.7
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I         5aa (Obtained from the allylation of 4a)         171.6         170.6         142.4         135.8         131.6         129.7         128.8         127.2	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8 131.5 129.6 128.7 127.2
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I         5aa (Obtained from the allylation of 4a)         171.6         170.6         142.4         135.8         131.6         129.7         128.8         127.2         124.4	<b>MHz, CDCl3): 5aa</b> (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         124.4
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8           127.2           124.4           115.9	MHz, CDCl <sub>3</sub> ): 5aa (from peptide coupling) 171.6 170.6 142.4 135.8 131.5 129.6 128.7 127.2 124.4 115.8
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I         5aa (Obtained from the allylation of 4a)         171.6         170.6         142.4         135.8         131.6         129.7         128.8         127.2         124.4         115.9         65.9	<b>MHz, CDCl3): 5aa</b> (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I         5aa (Obtained from the allylation of 4a)         171.6         170.6         142.4         135.8         131.6         129.7         128.8         127.2         124.4         15.9         65.9         56.7	<b>MHz, CDCl3): 5aa</b> (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I         5aa (Obtained from the allylation of 4a)         171.6         170.6         142.4         135.8         131.6         129.7         128.8         127.2         124.4         15.9         65.9         56.7         53.6	<b>MHz, CDCl3):</b> 5aa (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7         53.6
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8           127.2           124.4           15.9           65.9           56.7           53.6           52.2	<b>MHz, CDCl3):</b> 5aa (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7         53.6         52.2
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8           127.2           124.4           15.9           65.9           56.7           53.6           52.2           44.7	<b>MHz, CDCl3): 5aa</b> (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7         53.6         52.2         44.7
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8           127.2           124.4           15.9           65.9           56.7           53.6           52.2           44.7           38.0	MHz, CDCl <sub>3</sub> ):         5aa (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7         53.6         52.2         44.7         38.0
Comparison of <sup>13</sup> C NMR Data of 5aa (126 I           5aa (Obtained from the allylation of 4a)           171.6           170.6           142.4           135.8           131.6           129.7           128.8           127.2           124.4           15.9           65.9           56.7           53.6           52.2           44.7           38.0           37.7	MHz, CDCl <sub>3</sub> ):         5aa (from peptide coupling)         171.6         170.6         142.4         135.8         131.5         129.6         128.7         127.2         124.4         115.8         65.9         56.7         53.6         52.2         44.7         38.0         37.7

23.1	23.1
22.7	22.7
18.1	18.1
17.8	17.7

### **Comparison of NMR Data for the compound 3ae:**

Literature Reported Data for <b>3ae</b>	Experimental Data for <b>3ae</b>	Difference
(Ref: Lin et al. Chem. Commun., 2010, 46,		
8460-8462)		
7.32-7.15 (m, 5H)	7.29 (t, <i>J</i> = 7.6 Hz, 2H), 7.21	0.00
	(t, J = 7.4  Hz, 1H), 7.15 (d, J =	
	6.8 Hz, 2H),	
6.12-6.00 (m, 1H)	6.08 – 6.02 (m, 1H)	0.02
5.18-5.13 (m, 2H)	5.16 – 5.13 (m, 2H)	0.00
4.22-4.13 (m, 3H)	4.20 – 4.11 (m, 3H)	0.02
3.92 (d, 1H, J = 9.6 Hz)	3.90 (d, J = 9.5 Hz, 1H)	0.02
3.69 (t, 1H, J = 8.1 Hz)	3.67 (t, J = 8.0  Hz, 1H)	0.02
1.25 (t, 3H, J = 7.2 Hz)	1.25 (t, J = 7.2 Hz, 3H)	0.00
1.05 (s, 9H)	1.05 (s, 9H)	0.00
13C Data Comparison (After calibr	rating the CDCl <sub>3</sub> peak at $\delta = 77.0$	0 <b>3 ppm</b> )
172.2	172.2	0.0
139.2	139.2	0.0
136.8	136.8	0.0
128.5	128.5	0.0
128.3	128.3	0.0
127.1	127.1	0.0
117.5	117.5	0.0
62.8	62.8	0.0
61.6	61.6	0.0
56.2	56.3	0.1
54.1	54.1	0.0
22.4	22.4	0.0
14.0	14.1	0.1

### Comparison of NMR Data for the compound 3ak:

Literature Reported Data for <b>3ak</b>	Experimental Data for <b>3ak</b>	Difference
(Ref: Lin et al. Chem. Commun., 2010, 46,		
8460-8462)		
7.43 (d, 2H, <i>J</i> = 8.4 Hz)	7.41 (d, <i>J</i> = 8.4 Hz, 2H)	0.02
7.04 (d, 2H, $J = 8.1$ Hz)	7.03 (d, $J = 8.4$ Hz, 2H)	0.01
6.07-5.95 (m, 1H)	5.99 (ddd, <i>J</i> = 16.9, 10.3, 8.2	0.04
	Hz, 1H)	
5.18 (d, 1H, $J = 4.5$ Hz)	5.16 – 5.10 (m, 2H)	0.03
5.13 (d, 1H, <i>J</i> = 11.4 Hz)		
4.22-4.12 (m, 3H)	4.19 – 4.11 (m, 3H)	0.01
3.93 (d, 1H, $J = 9.3$ Hz)	3.92 (d, J = 9.2 Hz, 1H)	0.01
3.67 (t, 1H, J = 8.0 Hz)	3.65 (t, J = 7.8 Hz, 1H),	0.02
1.26 (t, 3H, J = 7.2 Hz)	1.24 (t, J = 7.2 Hz, 3H),	0.02
1.09 (s, 9H)	1.07 (s, 9H)	0.02

13C Data Comparison (After Calibrating the CDCl <sub>3</sub> peak at $\delta$ = 77.018 ppm)			
171.9	171.9	0.0	
138.3	138.3	0.0	
136.4	136.3	0.1	
131.6	131.6	0.0	
130.1	130.1	0.0	
121.1	121.0	0.1	
118.0	118.0	0.0	
62.4	62.4	0.0	
61.8	61.7	0.1	
56.4	56.3	0.1	
53.4	53.4	0.0	
22.5	22.5	0.0	
14.1	14.1	0.0	

### N-Sulfinyl amide deprotection and determination of the absolute configuration:



Synthesis of 7: To an ice-cooled solution of (*tert*-butoxycarbonyl)-*L*-isoleucine (578 mg, 2.5 mmol, 1.0 equiv) and methyl *L*-phenylalaninate hydrochloride (700 mg, 3.24 mmol, 1.3 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL), DIPEA (807 mg, 1.08 mL, 6.25 mmol. 2.5 equiv) and HOBT (496 mg, 3.24 mmol, 1.3 equiv) were added. After stirring for 30 min at 0 °C, EDC·HCl (620 mg, 3.24 mmol, 1.3 equiv) was added to the reaction mixture and the reaction was slowly allowed to come to room temperature and stirring was continued for further 18 h. After complete consumption of starting material, reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, and washed with 2×30 mL 10% aq. citric acid solution, 1 M HCl, and brine solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified on silica gel column using 12% ethylacetate in hexane as eluent to get dipeptide 7 as white solid (510 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.29 - 7.26$  (m, 2H), 7.25 - 7.19 (m, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.48 (d, J = 7.5 Hz, 1H),

5.10 – 5.06 (m, 1H), 4.87 (q, J = 6.4 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.69 (s, 3H), 3.13 (dd, J = 13.8, 5.7 Hz, 1H), 3.07 (dd, J = 13.8, 6.1 Hz, 1H), 1.85 – 1.79 (m, 1H), 1.46 – 1.42 (m, 10H), 1.10 – 1.05 (m, 1H), 0.89 – 0.85 (m, 6H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.77$ , 171.42, 155.74, 135.88, 129.33, 128.65, 127.19, 79.90, 59.34, 53.22, 52.27, 38.10, 37.29, 28.39, 24.75, 15.50, 11.42 ppm. **IR (film):**  $v_{max} = 2969$ , 1659, 1499, 1367, 1216, 1166 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>21</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> 415.2209; found 415.2190. [ $\alpha$ ] $\rho^{25}$ : +18.48 (c 1.11, CHCl<sub>3</sub>).

### Synthesis of 7 from 5at:

**Step I**: To a solution of **5at** (150 mg, 0.38 mmol) in MeOH, 4 (N) HCl in dioxane (1.14 mmol, 0.285 mL) was added at room temperature. The reaction was stirred for 30 min, until all the starting material was consumed. Then, MeOH was removed under reduced pressure by using rotary evaporator and the residue was dissolved in 1 (N) NaOH and extracted with ethylacetate (4×8 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and the crude product was used for next step.

**Step II:** The crude material obtained from step I was dissolved in anhydrous  $CH_2Cl_2$  (6 mL), and to it was sequentially added  $Et_3N$  (96 mg, 0.95 mmol, 2.5 equiv), Boc<sub>2</sub>O (100 mg, 0.45 mmol, 1.2 equiv), and DMAP (~2-3 mg) at 0 °C (ice-bath). The reaction was allowed to slowly come to room temperature and stirred overnight. Next, it was diluted with  $CH_2Cl_2$  and washed with saturated brine solution (3×10 mL). The combined organic layer was dried, concentrated and used for next step.

**Step III:** The crude mixture was dissolved in EtOH (8 mL) and to it was added Pd/C (50 mg) under hydrogen atmosphere (using hydrogen balloon) at room temperature. The reaction was stirred for 24 hours, then diluted with  $CH_2Cl_2$  (15 mL), and filtered through cellite. The crude mixture was concentrated and purified on silica gel column using 12% ethylacetate in hexane as eluent to give **7** (38 mg, 26% over three steps) as white solid.

<sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.29 - 7.26$  (m, 2H), 7.24 - 7.21 (m, 1H), 7.12 (d, J = 7.5 Hz, 2H), 6.45 (d, J = 6.9 Hz, 1H), 5.08 (d, J = 8.5 Hz, 1H), 4.87 (q, J = 6.3 Hz, 1H), 3.97 - 3.91 (m, 1H), 3.70 (s, 3H), 3.13 (dd, J = 13.8, 5.6 Hz, 1H), 3.08 (dd, J = 13.7, 6.0 Hz, 1H), 1.85 - 1.79 (m, 1H), 1.46 - 1.42 (m, 10H), 1.12 - 1.04 (m, 1H), 0.89 - 0.85 (m, 6H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 171.78$ , 171.45, 155.79, 135.87, 129.35, 128.69, 127.23, 79.97, 59.36, 53.24, 52.32, 38.12, 37.30, 28.41, 24.78, 15.52, 11.45 ppm. IR (film): v<sub>max</sub> = 2952,

1678, 1507, 1375, 1242, 1141 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{21}H_{32}N_2NaO_5$  [M+Na]<sup>+</sup> 415.2203; found 415.2187. [ $\alpha$ ] $_{D}^{25}$ : +18.18 (c 1.11, CHCl<sub>3</sub>).

Comparison	of NMR	Data for	r the cor	npound 7:
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<sup>1</sup> H NMR Data for <b>7</b> (obtained by	<sup>1</sup> H NMR Data for <b>7</b> (obtained from	Difference
direct peptide coupling)	5at)	
		0.0
7.29 – 7.26 (m, 2H)	7.29 – 7.26 (m, 2H)	0.0
7.25 – 7.19 (m, 1H)	7.24 – 7.21 (m, 1H)	0.01
7.12 (d, $J = 7.4$ Hz, 2H)	7.12 (d, $J = 7.5$ Hz, 2H),	0.0
6.48 (d, <i>J</i> = 7.5 Hz, 1H)	6.45 (d, <i>J</i> = 6.9 Hz, 1H)	0.03
5.10 – 5.06 (m, 1H)	5.08 (d, J = 8.5 Hz, 1H)	0.02
4.87 (q, <i>J</i> = 6.4 Hz, 1H)	4.87 (q, J = 6.3 Hz, 1H)	0.0
3.97 – 3.92 (m, 1H)	3.97 – 3.91 (m, 1H)	0.0
3.69 (s, 3H)	3.70 (s, 3H)	0.01
3.13 (dd, <i>J</i> = 13.8, 5.7 Hz, 1H)	3.13 (dd, <i>J</i> = 13.8, 5.6 Hz, 1H)	0.0
3.07 (dd, <i>J</i> = 13.8, 6.1 Hz, 1H),	3.08 (dd, <i>J</i> = 13.7, 6.0 Hz, 1H)	0.01
1.85 – 1.79 (m, 1H)	1.85 – 1.79 (m, 1H)	0.0
1.46 – 1.42 (m, 10H)	1.46 – 1.42 (m, 10H),	0.0
1.10 – 1.05 (m, 1H)	1.12 – 1.04 (m, 1H)	0.02
0.89 – 0.85 (m, 6H)	0.89 – 0.85 (m, 6H)	0.0
Comparison of <sup>13</sup> C NMR Data		
171.8	171.8	0.0
171.4	171.4	0.0
155.7	155.8	0.1
135.9	135.9	0.0
129.3	129.3	0.0
128.6	128.7	0.1
127.2	127.2	0.0
79.9	80.0	0.1
59.3	59.4	0.1
53.2	53.2	0.0
52.3	52.3	0.0
38.1	38.1	0.0
37.3	37.3	0.0
28.4	28.4	0.0
24.7	24.8	0.1
15.5	15.5	0.0
11.4	11.4	0.0

### Synthetic Modifications of Homoallyl Amino Esters:

# (*S*)-N-((2*S*,3*R*)-1-hydroxy-3,7-dimethyl-3-vinyloct-6-en-2-yl)-2-methylpropane-2-sulfinamide (8):



In a 25 ml two-necked round bottom flask containing  $LiAlH_4$  (57 mg, 1.5 mmol, 1.5 equiv) was added dry THF under nitrogen at 0 °C. Then the solution of **3aa** (344 mg, 1.0 mmol) in THF (2 mL) was added to it dropwise.

Then the reaction mixture was stirred for 0.5 h, until all the starting material was consumed. After completion of the reaction as indicated by TLC, reaction was quenched by adding aq. NH<sub>4</sub>Cl solution. The crude mixture was filtered through celite pad and washed with EtOAc. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified on silica gel column using 20% ethylacetate in hexane as eluent to give **8** as colourless oil (187 mg, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.88$  (dd, *J* = 17.6, 10.8 Hz, 1H), 5.55 (d, *J* = 10.8 Hz, 1H), 5.31 (d, *J* = 17.6 Hz, 1H), 5.07 – 5.03 (m, 1H), 3.87 – 3.86 (m, 2H), 3.41 – 3.34 (m, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 2.97 (t, *J* = 9.6 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.81 – 1.77 (m, 1H), 1.75 – 1.70 (m, 1H), 1.68 (s, 3H), 1.58 (s, 3H), 1.45 (s, 3H), 0.92 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 135.54$ , 132.63, 123.37, 119.96, 69.47, 65.07, 63.11, 34.67, 34.05, 27.17, 25.81, 22.61, 18.94, 17.85 ppm. IR (film): v<sub>max</sub> = 3406, 2963, 1465, 1366, 1127, 1024 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>16</sub>H<sub>32</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 302.2148; found 302.2133. [*a*]*p*<sup>25</sup>: +93.35 (c 0.23, CHCl<sub>3</sub>).

# Ethyl (4*R*,5*R*,*E*)-4-(((*S*)-*tert*-butylsulfinyl)amino)-5,9-dimethyl-5-vinyldeca-2,8-dienoate (9):



To a solution of **8** (151 mg, 0.5 mmol, 1.0 equiv) in dry  $CH_2Cl_2$  (5 mL) was added Dess Martin periodinane (276 mg, 0.65 mmol, 1.3 equiv) at rt. The reaction was stirred at rt for 0.5 h. After completion of the reaction, it was quenched with saturated solution of  $Na_2S_2O_3$  (10 mL). The organic layer diluted with  $CH_2Cl_2$  and

washed with brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and used for next step without further purification.

A 25 mL two neck round bottom flask was charged with NaH (26 mg, 0.65 mmol, 1.3 equiv) and backfilled three times with nitrogen. Then 5 mL dry THF was added and the reaction mixture was cooled to 0  $^{\circ}$ C (ice-bath). Then triethylphosphonoacetate (145 mg, 1.3 equiv, 0.13 mL) was added dropwise. The reaction mixture was stirred at 0  $^{\circ}$ C for 15 min. Then, a solution

of the crude aldehyde in 3 mL THF was added slowly at 0 °C. The reaction mixture was stirred at rt for 1 h and subsequently quenched with saturated brine solution. The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified on silica using 8% ethylacetate in hexane as eluent to get **9** as colourless oil (98 mg, 53% over two steps). <sup>1</sup>H **NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta = 6.95$  (dd, J = 15.6, 7.5 Hz, 1H), 6.01 (d, J = 16.6 Hz, 1H), 5.89 (dd, J = 17.6, 10.8 Hz, 1H), 5.52 (d, J = 10.9 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.06 (t, J = 7.1 Hz, 1H), 4.21 – 4.14 (m, 2H), 3.56 (t, J = 9.0 Hz, 1H), 3.43 (d, J = 9.7 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.76 – 1.70 (m, 1H), 1.68 (s, 3H), 1.65 – 1.61 (m, 1H), 1.59 (s, 3H), 1.40 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 0.92 (s, 9H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 166.15$ , 146.23, 136.21, 132.47, 123.94, 123.63, 119.35, 67.08, 65.78, 60.60, 35.99, 34.18, 26.77, 25.78, 22.71, 18.34, 17.83, 14.35 ppm. IR (film): v<sub>max</sub> = 2968, 2930, 1737, 1368, 1255, 1023 cm<sup>-1</sup>. HRMS-ESI: calculated for C<sub>20</sub>H<sub>36</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 370.2410; found 370.2397. [*a*]*p*<sup>25</sup>: +143.78 (c 0.23, CHCl<sub>3</sub>).

### (S)-4-((S)-1-phenylallyl) oxazolidin-2-one (10):



To a slurry of LiAlH<sub>4</sub> (28 mg, 0.75 mmol, 1.5 equiv) in dry THF (3 mL) at 0 <sup>o</sup>C was dropwisely added a solution of **3ae** (161 mg, 0.5 mmol, 1.0 equiv) in 3 mL THF. The reaction mixture was stirred at rt for 0.5 h and quenched with saturated aq. Na<sub>2</sub>SO<sub>4</sub> solution. The reaction mixture was diluted with EtOAc,

filtered through celite, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and used for next step.

The amino alcohol was dissolved in MeOH (3 mL) and cooled to 0 °C (ice-bath). Then 4 N HCl-dioxane (0.37 mL, 1.5 mmol, 3.0 equiv) was added to it. After 15 min at 0 °C, the reaction was brought to rt and stirred for 3 h. After complete consumption of the starting material, MeOH was concentrated, and the residue was dissolved in ethylacetate. The organic layer was washed with 2(M) aq. Na<sub>2</sub>CO<sub>3</sub> solution. The organic layer was dried using Na<sub>2</sub>SO<sub>4</sub>, concentrated, and redissolved in dry CH<sub>2</sub>Cl<sub>2</sub>. Then 1,1'-carbonyldiimidazole (48 mg, 0.3 mmol, 0.6 equiv) was added to it and the reaction was stirred overnight. The crude reaction mixture was concentrated and purified on silica using 25% ethylacetate in hexane as eluent to get **10** as whitish solid (40 mg, 40% over three steps). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.21 – 7.19 (m, 2H), 5.94 – 5.87 (m, 1H), 5.24 – 5.18 (m, 2H), 4.86 – 4.78 (m, 1H), 4.53 – 4.49 (m, 1H), 4.27 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.35 (t, *J* = 8.9 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.80, 139.33, 135.98, 129.42, 127.96, 127.86, 118.44, 68.92, 55.97, 55.56 ppm. **IR (film): v**max = 3244, 1758, 1685, 1404,

1237, 931 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{12}H_{14}NO_2$  [M+H]<sup>+</sup> 204.1019; found 204.1003. [a] $p^{25}$ : -100.00 (c 0.1, CHCl<sub>3</sub>).

#### Ethyl (2*S*,3*S*)-2-(((*S*)-*tert*-butylsulfinyl)amino)-5-hydroxy-3-phenylpentanoate (11):

HN<sup>S-t</sup>Bu In a 25 ml two-necked round bottom flask containing homoallylic amino ester 3ae (33 mg, 0.1 mmol, 1.0 equiv) was dissolved in 6 mL THF and cooled at -78 °C. BH<sub>3</sub>·SMe<sub>2</sub> (0.25 mmol, 2.5 equiv, 25 µL) EtO<sub>2</sub>C was added dropwise to the reaction mixture. The reaction mixture was stirred at this temperature for 1 h, then allowed to warm to room temperature and stirred for additional 1 h. Then the reaction was cooled at 0 °C and NaOAc (42 mg, 0.5 mmol, 5.0 equiv) solution in 2 mL of water mixed with 0.1 mL of H<sub>2</sub>O<sub>2</sub> (30% in H<sub>2</sub>O) was added dropwise into the reaction mixture. The reaction was then allowed to warm to room temperature and stirred overnight. The aqueous layer was extracted with EtOAc  $(3 \times 5 \text{ mL})$  and dried over anhydrous  $Na_2SO_4$ . The crude reaction mixture was purified on silica using 70% ethylacetate in hexane as eluent to give 11 as colourless oil (11 mg, 31%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.30 - 100$ 7.23 (m, 3H), 7.13 (d, J = 7.2 Hz, 2H), 4.20 – 4.12 (m, 3H), 4.00 (d, J = 8.8 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.50 – 3.44 (m, 1H), 3.35 – 3.30 (m, 1H), 2.05 – 1.96 (m, 3H), 1.28 – 1.25 (m, 3H), 1.16 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.38$ , 139.19, 128.65, 127.49, 62.60, 61.90, 60.46, 56.47, 45.81, 35.20, 22.78, 14.25 ppm. **IR (film):** v<sub>max</sub> = 2927, 1733, 1445, 1366, 1178, 1044 cm<sup>-1</sup>. **HRMS-ESI:** calculated for  $C_{17}H_{28}NO_4S$  [M+H]<sup>+</sup> 342.1734; found 342.1719.  $[\alpha]_{D^{25}}$ : +9.17 (c 0.3, CHCl<sub>3</sub>)

### Ethyl (S)-2-((1,1-dimethylethyl)sulfonamido)-4-phenylpent-4-enoate (12):

To a solution of **3av** (162 mg, 0.5 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added *m*-CPBA (130 mg, 0.75 mmol, 1.5 equiv), and the reaction mixture was stirred at room temperature for 1 h. Upon completion, 10% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 mL) and saturated aqueous NaHCO<sub>3</sub> (2 mL) were added to the reaction vessel. Then the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated brine solution (2×5 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified on silica gel column using 10% ethylacetate in hexane as eluent to give **12** as colourless oil (138 mg, 81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 5.42 (s, 1H), 5.19 (s, 1H), 4.54 (d, *J* = 10.1 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.07 – 3.93 (m, 2H), 3.01 (d, *J* = 6.5 Hz, 2H), 1.26 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.10, 142.97, 139.48, 128.62, 128.15, 126.45, 117.34, 61.70, 60.25, 56.33, 39.98, 24.05, 14.12 ppm. **IR (film):**  $\mathbf{v}_{max} = 2975$ , 1732, 1445, 1301, 1185, 1070 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>17</sub>H<sub>26</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 340.1577; found 340.1580. **[\alpha]\mathbf{p}^{25}: -60.15 (c 0.13, CHCl<sub>3</sub>).** 

### Ethyl (S)-2-((1,1-dimethylethyl)sulfonamido)-4-oxo-4-phenylbutanoate (13):

In a 10 mL oven-dried Schlenk tube containing alkene **12** (80 mg, 0.2 mmol, HN, Bu 1.0 equiv) in CH<sub>3</sub>NO<sub>2</sub> (1 mL) were added AIBN (9 mg, 0.05 mmol, 0.25 equiv). Then the tube was evacuated and filled with oxygen (this procedure was repeated three times). The mixture was stirred at 60 °C for 8 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc concentrated, and purified by silica gel column using 12% ethylacetate in hexane as eluent to give **13** as colourless oil (50 mg, 74% yield). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 5.17 (d, *J* = 9.6 Hz, 1H), 4.47 – 4.43 (m, 1H), 4.28 – 4.19 (m, 2H), 3.83 (dd, *J* = 18.2, 3.7 Hz, 1H), 3.59 (dd, *J* = 18.2, 4.1 Hz, 1H), 1.43 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.70, 171.15, 136.14, 134.02, 128.93, 128.34, 62.21, 60.64, 53.54, 43.35, 24.29, 14.19 ppm. **IR (film): v**max = 3297, 2927, 1740, 1683, 1450, 1317, 1136 cm<sup>-1</sup>. **HRMS-ESI:** calculated for C<sub>16</sub>H<sub>24</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 342.1370; found 342.1355. **[a]p<sup>25</sup>:** -15.00 (c 0.1, CHCl<sub>3</sub>).

### **Computational Details:**

All density functional theory (DFT) calculations were performed within the Gaussian 09 suite of quantum chemical package.<sup>3</sup> Geometries of all the stationary points were optimized in the solvent phase with the B3LYP functional <sup>4</sup> in conjunction with Pople's 6-31G(d,p) double- $\zeta$ split valence basis set on all atoms.<sup>5</sup> Solvent effect was introduced by utilizing conductor-like polarizable continuum (CPCM) solvation model<sup>6</sup> employing the dielectric parameters of chloroform as solvent ( $\epsilon$ =4.7113). Harmonic vibrational frequencies were computed at the same level of theory, to distinguish transition states (with one negative Hessian index) from minima (with all positive Hessian index). The non-thermal zero-point energy (ZPE) correction and the thermal corrections to enthalpy and Gibbs free energy were obtained from the frequency calculations, using standard approximations at 298.15 K and 1 atm pressure. Furthermore, the electronic energies were refined by single point calculations at B3LYP functional overlayed with Grimme's empirical dispersion D3(BJ) correction term,<sup>7</sup> employing the IOp(3/124=40) keyword with the larger triple- $\zeta$  6-311+G(d,p) basis set. This approach has been recently successful in evaluating boronic acid assisted stereo-isomerism of imines.<sup>8</sup>



**Figure S1.** Relative Gibbs free energy profile at B3LYP-D3BJ(CPCM)/6-311+G(d,p) for C-C coupling reaction step. Distances shown are in units of Å.

Initially, the reaction is thought to be undergoing through a chelation assisted monocationic six-membered transition state (TS4) in which both the imine nitrogen and the carbonyl moiety co-ordinate to the boron atom. The intrinsic barrier for TS4 with respect to the preceding reactant complex **RC4** is exceedingly low (~ 6 kcal/mol, Figure S1). However, formation of **RC4** itself is a predominantly high endoergic process (61.1 kcal) starting from the reactants and hence the free energy barrier for TS4 turns out to be 67.0 kcal/mol. Therefore, the C(imine)-C(allyl) coupling step is not possible though this mechanism. Similarly, another monocationic six-membered transition state (TS5) featuring coordination of the imine nitrogen and sulfinyl oxygen to the boron centre and shows even higher free energetic expense at 83.4 kcal/mol ruling out the possibility of C(imine)-C(allyl) coupling through the positively charged transition states. Thereby, we hypothesized neutral transition states starting from the reactant complex **RC2-3** where one OH<sup>-</sup> and one H<sup>+</sup> released from the allyl boronic acid forms a water molecule which is coordinated to the remaining boronic acid through H-bonding. Here two situations are envisaged: TS2 where there is no coordination of the ester oxygen to the boron centre and **TS3** where an explicit B-O(ester) bond is formed. Although, free energy barrier for TS2 (38.8 kcal/mol) and TS3 (45.6 kcal/mol) are significantly lower as compared to the

monocationic transition states, they are too high to occur at the experimental conditions. Instead, we predict a concerted mechanism of B-C bond cleavage and C-C coupling through the neutral **TS1** (17.4 kcal/mol) which is further assisted by chelating H-bonding interactions, as reported in the main text. **TS1** is followed by **INT1** (-15.1 kcal/mol) which is a highly exoergic intermediate with respect to the reactants (**1** and **2**), presumably due to the chelating H-bonding interactions. **INT1** can further undergo hydrolysis to generate the desired product **3ae**.

### **XYZ** coordinates

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IN B C C C C	<b>T1</b> -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000
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IN B C C C C C N H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.188854000 0.447036000 -1.186856000
IN B C C C C C N H H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.188854000 0.447036000 -1.186856000 1.327306000
IN B C C C C N H H H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.188854000 0.447036000 -1.186856000 -1.28656000 -1.485360000
IN B C C C C C N H H H H C	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.18854000 0.447036000 -1.186856000 1.327306000 -1.485360000 1.314979000
IN B C C C C C N H H H H C O	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.188854000 0.447036000 -1.186856000 1.327306000 -1.485360000 1.314979000 2.428807000
<b>IN</b> B C C C C C N H H H H C O O	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.109296000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000 \end{array}$
IN B C C C C C N H H H H C O O C	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.109296000 1.783710000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.168276000\end{array}$
IN B C C C C C N H H H H C O O C H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.487463000 0.570550000 0.579812000 1.109296000 1.783710000 1.043348000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.168276000\\ 2.946536000\end{array}$
IN B C C C C N H H H H C O O C H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.109296000 1.783710000 1.043348000 2.531621000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.168276000\\ 2.946536000\\ 2.576009000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.109296000 1.783710000 1.043348000 2.531621000 2.404275000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 2.428807000\\ 2.168276000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.109296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 2.428807000\\ 2.428807000\\ 2.68276000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 2.428807000\\ 2.428807000\\ 2.68276000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C H H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 1.062566000\\ 2.168276000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000 \end{array}$
IN B C C C C N H H H H C O O C H H C H H H O	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C H H H O S	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.4470366000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 2.428807000\\ 2.428807000\\ 2.68276000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\end{array}$
IN B C C C C N H H H H C O O C H H C H H H O S O	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -1.570910000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.4470366000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\end{array}$
IN B C C C C N H H H H C O O C H H C H H H O S O H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -1.570910000 -3.439988000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ \end{array}$
IN B C C C C N H H H H C O O C H H C H H H O S O H C	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.487463000 0.570550000 0.579812000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -1.570910000 -3.439988000 -3.143010000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.4470366000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 2.428807000\\ 2.428807000\\ 2.6650000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ -0.578248000\end{array}$
IN B C C C C N H H H H C O O C H H C H H H O S O H C C	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.570550000 0.579812000 1.09296000 1.09296000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -3.439988000 -3.143010000 -3.760969000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.809934000\\ \end{array}$
IN B C C C C N H H H H H C O O C H H C H H H O S O H C C H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.487463000 0.570550000 0.579812000 1.09296000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -3.760969000 -3.143010000 -3.760969000 -4.476938000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 0.128340000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.4470366000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 1.314979000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.834224000\\ 0.834224000\\ \end{array}$
<b>IN</b> BCCCCNHHHHCOOCHHCHHHOSOHCCHH	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.570550000 0.579812000 1.09296000 1.09296000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -3.760969000 -4.476938000 -4.302234000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.45800000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -2.171735000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.186356000\\ 2.428807000\\ 1.062566000\\ 2.48807000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.834224000\\ 1.082103000\\ \end{array}$
<b>IN</b> B C C C C N H H H H H C O O C H H C H H H O S O H C C H H H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.570550000 0.579812000 1.09296000 1.09296000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -3.760969000 -4.476938000 -4.302234000 -2.997629000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.45800000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -2.171735000 -1.079948000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.186356000\\ 2.428807000\\ 1.062566000\\ 2.48807000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.834224000\\ 1.082103000\\ 1.571236000\\ \end{array}$
<b>N</b> BCCCCNHHHHCOOCHHCHHHOSOHCCHHHC	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.673239000 0.487463000 0.487463000 0.570550000 0.579812000 1.09296000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -2.441941000 -3.439988000 -3.143010000 -3.760969000 -4.476938000 -4.92233000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.45800000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -1.71735000 -1.722567000	$\begin{array}{c} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ -1.186856000\\ -1.186856000\\ -1.18656000\\ -1.485360000\\ -1.485360000\\ 2.428807000\\ 1.062566000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 0.831833000\\ 1.195590000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ -0.578248000\\ 0.834224000\\ 1.082103000\\ 1.571236000\\ -1.636544000\\ \end{array}$
<b>IN</b> B C C C C N H H H H H C O O C H H C H H H O S O H C C H H H H C H	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -3.107744000 -3.439988000 -3.143010000 -3.439988000 -3.143010000 -3.760969000 -4.476938000 -4.302234000 -2.997629000 -4.222933000 -3.787319000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.45827000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -1.71735000 -1.722567000 -1.805524000	$\begin{array}{l} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.485360000\\ 2.428807000\\ 1.062566000\\ 2.48807000\\ 2.48807000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.834224000\\ 1.082103000\\ 1.571236000\\ -1.636544000\\ -2.636113000\\ \end{array}$
<b>N</b> BCCCCNHHHHCOOCHHCHHHOSOHCCHHHCHH	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -3.107744000 -3.439988000 -3.143010000 -3.439988000 -3.143010000 -3.439988000 -3.143010000 -3.439988000 -3.143010000 -3.760969000 -4.76938000 -3.787319000 -4.718529000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -1.560779000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -1.71735000 -1.722567000 -1.805524000 -2.670006000	$\begin{array}{l} 1.121047000\\ -0.168710000\\ 0.300735000\\ -0.525218000\\ 0.045494000\\ 0.188854000\\ 0.447036000\\ -1.186856000\\ 1.327306000\\ -1.18656000\\ 2.428807000\\ 1.062566000\\ 2.48807000\\ 2.48807000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.946536000\\ 2.576009000\\ 1.613392000\\ 0.831833000\\ 1.195590000\\ 2.417170000\\ 0.852663000\\ -1.124485000\\ -2.327815000\\ -0.042513000\\ 0.834224000\\ 1.082103000\\ 1.571236000\\ -1.636544000\\ -2.636113000\\ -1.400899000\\ \end{array}$
<b>N</b> BCCCCNHHHHCOOCHHCHHHOSOHCCHHHCHHH	T1 -1.928092000 0.623598000 0.991098000 0.952607000 0.003413000 -1.390898000 0.673239000 0.262723000 1.341017000 0.487463000 0.570550000 0.579812000 1.09296000 1.783710000 1.043348000 2.531621000 2.404275000 3.132216000 1.641169000 2.920231000 -3.107744000 -3.439988000 -3.439988000 -3.439988000 -3.760969000 -4.476938000 -4.987870000 -4.987870000	1.704059000 3.833511000 2.639818000 1.378886000 0.252617000 0.694705000 4.726731000 3.960285000 2.558982000 1.625743000 -0.383136000 0.128340000 -1.572833000 -2.245427000 -2.448600000 -3.510894000 -3.510894000 -3.276708000 -4.173424000 -4.044226000 2.357507000 0.234014000 -0.058439000 2.220359000 -1.440634000 -1.259264000 -0.430705000 -1.772567000 -1.722567000 -1.805524000 -2.670006000 -0.939063000	1.121047000 -0.168710000 0.300735000 -0.525218000 0.045494000 0.188854000 -1.186856000 1.327306000 -1.18656000 2.428807000 1.062566000 2.946536000 2.946536000 2.576009000 1.613392000 0.831833000 1.195590000 2.417170000 0.852663000 -1.124485000 -2.327815000 -0.042513000 -0.578248000 0.834224000 1.082103000 1.571236000 -1.636544000 -2.636113000 -1.400899000 -1.652528000

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TS3 B C	-1.367493000 -0.401555000	1.522164000 1.219262000	-0.368752000 -1.949044000
<b>TS3</b> B C C	-1.367493000 -0.401555000 0.946476000	1.522164000 1.219262000 0.826541000	-0.368752000 -1.949044000 -1.680730000
<b>TS3</b> B C C C	-1.367493000 -0.401555000 0.946476000 1.354743000	1.522164000 1.219262000 0.826541000 -0.459334000	-0.368752000 -1.949044000 -1.680730000 -1.401184000
TS3 B C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 1.363300000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000
<b>TS3</b> B C C C C N H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000
TS3 B C C C C N H H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000
TS3 B C C C C N H H H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000 \end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000
TS3 B C C C C N H H H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000
TS3 B C C C C N H H H C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000 \end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000
TS3 B C C C C C N H H H C O	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000\\ 1.979910000\end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000
<b>TS3</b> B C C C C C C N H H H C O O	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000\\ 1.979910000\\ 0.920959000 \end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000
<b>TS3</b> B C C C C C C N H H H C O O C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000\\ 1.979910000\\ 0.920959000\\ 2.211733000 \end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000
<b>TS3</b> B C C C C C C C N H H H C O O C C H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000\\ 1.979910000\\ 0.920959000\\ 2.211733000\\ 2.804401000\end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000
<b>TS3</b> B C C C C C C C N H H H H H C O O C C H H H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000	$\begin{array}{c} 1.522164000\\ 1.219262000\\ 0.826541000\\ -0.459334000\\ -0.296055000\\ 0.013017000\\ 2.218760000\\ 0.478698000\\ 1.632335000\\ -1.265035000\\ 0.933303000\\ 1.979910000\\ 0.920959000\\ 2.211733000\\ 2.804401000\\ 2.721367000\\ \end{array}$	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000
<b>TS3</b> B C C C C C C C N H H H H H C C O O C C H H H C C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.918835000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.858097000
<b>TS3</b> B C C C C C C C C N H H H H H C C O O C C H H H H H H C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 4.142112000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.918835000 1.307938000 1.307938000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.858097000 2.258157000
<b>TS3</b> B C C C C C C C C C N H H H H H C C O C C C C C H H H H H H H	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 4.142112000 3.249259000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.918835000 1.307938000 1.396433000 2.86282000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.858097000 2.258157000 3.794396000
TS3 B C C C C C C C C C N H H H H H H C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.249259000 3.961773000 2.397702000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.918835000 1.307938000 1.307938000 1.396433000 2.862583000 2.87342000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.258157000 3.095488000 -0.484784000
TS3 B C C C C C C C C N H H H H H C C O C C C C C N H H H H H H C C C C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.249259000 3.961773000 -2.397202000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.918835000 1.307938000 1.307938000 1.396433000 2.862583000 2.287342000 -1.325077000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.258157000 3.095488000 -0.484784000 -0.532565000
TS3 B C C C C C C C C C N H H H H H H C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 0.447148000 0.447148000 2.156882000 2.156882000 2.375670000 3.462529000 3.961773000 -2.397202000 -2.315290000 -1.543904000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 2.862583000 2.87342000 -1.325077000 -2.581782000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.677690000 2.487649000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000
TS3 B C C C C C C C C C N H H H H H H C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 0.447148000 1.556882000 2.156882000 2.375670000 3.462529000 3.249259000 3.249259000 -2.315290000 -2.315290000 -2.24583000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 2.862583000 2.87342000 -1.325077000 -2.581782000 3.481573000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000
TS3 B C C C C C C C C N H H H H H C C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 0.447148000 1.556882000 2.188484000 1.477287000 3.462529000 3.462529000 3.249259000 3.249259000 -2.315290000 -1.543904000 -2.224583000 -3.791499000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.307938000 1.307938000 1.396433000 2.862583000 2.287342000 -1.325077000 -2.581782000 3.481573000 -1.263822000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 1.558575000 1.108587000 0.662981000 1.801074000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 1.662953000 0.660484000
TS3 B C C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 3.462529000 3.249259000 3.249259000 -2.315290000 -2.315290000 -2.24583000 -3.791499000 -4.575128000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.307938000 1.307938000 1.307938000 1.396433000 2.862583000 2.287342000 -1.325077000 -2.581782000 3.481573000 -1.263822000 -2.538112000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.677690000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532555000 -0.218418000 -1.662953000 0.660484000 0.308473000
TS3 B C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 4.142112000 3.249259000 4.1542000 -2.315290000 -2.315290000 -2.315290000 -1.543904000 -2.224583000 -3.791499000 -4.575128000 -3.996235000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.307938000 1.307938000 1.307938000 1.307938000 1.325077000 -2.581782000 3.481573000 -1.263822000 -2.538112000 -3.438812000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.677690000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.660484000 0.308473000 0.526764000
TS3 B C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.440148000 -0.11411000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 4.142112000 3.249259000 4.142112000 3.249259000 -2.315290000 -2.315290000 -1.543904000 -2.224583000 -3.791499000 -4.575128000 -3.996235000 -5.488804000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.307938000 1.307938000 1.307938000 1.307938000 1.325077000 -2.581782000 3.481573000 -1.263822000 -2.538112000 -3.438812000 -2.559486000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.660484000 0.308473000 0.526764000 0.911028000
TS3 B C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 4.142112000 3.249259000 4.142112000 3.29259000 -2.315290000 -2.315290000 -2.315290000 -3.791499000 -4.575128000 -3.996235000 -5.488804000 -4.872025000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 1.396433000 2.862583000 2.287342000 -1.325077000 -2.581782000 3.481573000 -1.263822000 -2.538112000 -3.438812000 -2.559486000 -2.556815000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 1.801074000 2.096615000 2.677690000 1.148749000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.660484000 0.308473000 0.526764000 0.911028000 -0.745599000
TS3 B C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 -0.114111000 1.556882000 2.188484000 1.477287000 2.375670000 3.462529000 3.462529000 3.245259000 -2.31529000 -2.31529000 -2.31529000 -2.31529000 -3.791499000 -4.575128000 -3.996235000 -5.488804000 -4.872025000 -3.295001000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 2.862583000 2.87342000 -1.325077000 -2.581782000 3.481573000 -1.263822000 -2.559486000 -2.559486000 -2.559486000 -2.556815000 -1.302694000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 2.677690000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.660484000 0.308473000 0.526764000 0.911028000 -0.745599000 2.104979000
TS3 B C C C C C C C N H H H H H C O O C C H H H H H C C C C C	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 0.447148000 2.188484000 1.477287000 2.375670000 3.462529000 3.462529000 3.462529000 3.462529000 3.961773000 -2.397202000 -2.315290000 -1.543904000 -2.24583000 -3.791499000 -4.575128000 -3.996235000 -5.488804000 -4.872025000 -3.295001000 -2.814404000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 2.862583000 2.87342000 -1.325077000 -2.581782000 3.481573000 -1.263822000 -2.558112000 -3.438812000 -2.559486000 -2.556815000 -1.302694000 -0.365696000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 2.677690000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.526764000 0.308473000 0.526764000 0.51028000 -0.745599000 2.104979000 2.395326000
TS3 BCCCCCNHHHHCOOCHHCHHHOSOHCCHHHHCHHH	-1.367493000 -0.401555000 0.946476000 1.354743000 -0.235939000 -1.363300000 -0.538605000 -1.027134000 1.667987000 0.640108000 0.447148000 0.447148000 2.188484000 1.477287000 2.375670000 3.462529000 3.462529000 3.462529000 3.462529000 3.249259000 -2.31529000 -2.31529000 -2.31529000 -1.543904000 -2.24583000 -3.791499000 -4.575128000 -3.996235000 -5.488804000 -4.872025000 -3.295001000 -2.814404000 -2.814404000 -2.2814404000 -3.295001000 -2.814404000	1.522164000 1.219262000 0.826541000 -0.459334000 -0.296055000 0.013017000 2.218760000 0.478698000 1.632335000 -1.265035000 0.933303000 1.979910000 0.920959000 2.211733000 2.804401000 2.721367000 1.396433000 2.862583000 2.87342000 -1.325077000 -2.581782000 3.481573000 -1.263822000 -2.558112000 -3.438812000 -2.559486000 -2.559486000 -1.302694000 -0.365696000 -1.462975000	-0.368752000 -1.949044000 -1.680730000 -1.401184000 0.778617000 0.168334000 -2.361700000 -2.448734000 -1.554317000 -1.558575000 1.108587000 0.662981000 2.677690000 2.677690000 2.677690000 2.258157000 3.794396000 3.095488000 -0.484784000 -0.532565000 -0.218418000 -1.662953000 0.526764000 0.308473000 0.526764000 0.526764000 0.5104979000 2.395326000 2.767144000

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B C C C C C	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000
B C C C C C N	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000
B C C C C N H	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000
B C C C C C N H H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000
B C C C C C N H H H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 0.897986000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000
B C C C C C N H H H H	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000 \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 0.897986000 -1.468593000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000
B C C C C C N H H H H C	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000
B C C C C C N H H H H C O	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000 2.532178000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000
B C C C C C C N H H H H C O O	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000 2.532178000 1.581040000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000
B C C C C C C N H H H H C O C C C C C C C C C C C C C C	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000
B C C C C C C N H H H H C O C C H	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000 -1.522224000
B C C C C C C N H H H H C O O C H H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -2.546131000 -2.672793000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000 -1.522224000 0.046471000
B C C C C C C N H H H H C O C C H H C C C C C H H H C C C C	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000 -1.522224000 0.046471000 -1.687982000
B C C C C C N H H H H C O O C H H C H C H C C C C C H H H H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -2.672793000 -3.848231000 -4.478060000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.550355000 -0.796380000 -0.796380000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.258826000 3.286801000 2.662089000 1.967294000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000
B C C C C N H H H H C O C C H H C H H H H H C H C H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000 -4.478060000 -3.676590000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.286801000 2.662089000 1.967294000 2.266715000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000
IN B C C C C N H H H H H C O C C H H C H H H H H H H C O C C H H H H	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ -2.672793000\\ -3.848231000\\ -4.478060000\\ -3.676590000\\ -4.378079000 \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.78470000
B C C C C C N H H H H C O O C H H C H H H H H O O C H H C H H H H	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.676590000 -4.378079000 2.137203000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000
IN BCCCCNHHHHCOOCHHCHHHOS	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ -2.672793000\\ -3.848231000\\ -4.478060000\\ -3.676590000\\ -4.378079000\\ 2.137203000\\ 2.766245000\end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.677108000 0.570355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000
I B C C C C N H H H H C O O C H H C H H H O S O	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000 -4.478060000 -3.676590000 2.137203000 2.766245000 2.320637000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000
IB CCCCNHHHHCOOCHHCHHHOSOH	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.074628000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ -2.672793000\\ -3.848231000\\ -4.478060000\\ -3.676590000\\ -4.378079000\\ 2.137203000\\ 2.766245000\\ 2.320637000\\ 2.995647000\\ \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.677000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.61343000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.223635000
IBCCCCNHHHHCOOCHHCHHHOSOHC	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -3.676590000 -3.676590000 -3.378079000 2.137203000 2.766245000 2.320637000 2.995647000 3.389586000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.823897000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.223635000 -1.092897000
IBCCCCNHHHHCOOCHHCHHHOSOHCC	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -3.676590000 -3.676590000 -3.378079000 2.137203000 2.766245000 2.320637000 2.995647000 3.389586000 4 748422000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.823897000 -1.461545000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.611840000 1.318422000 1.223635000 -1.092897000 -0.746488000
IBCCCCNHHHHCOOCHHCHHHOSOHCCH	$\begin{array}{c} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ -2.672793000\\ -2.672793000\\ -3.848231000\\ -4.478060000\\ -3.676590000\\ -4.378079000\\ 2.137203000\\ 2.766245000\\ 2.320637000\\ 2.995647000\\ 3.389586000\\ 4.748422000\\ 4.626818000\\ \end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.823897000 -1.461545000 -2.341395000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.218422000 1.223635000 -1.092897000 -0.746488000 -0.109403000
IBCCCCNHHHHCOOCHHCHHHOSOHCCHH	$\begin{array}{r} 1.297586000\\ -0.074628000\\ -0.848578000\\ -0.848578000\\ -0.706163000\\ 0.006411000\\ 1.347629000\\ -0.209456000\\ 0.712683000\\ -1.619428000\\ 0.020752000\\ -0.697575000\\ -0.028826000\\ -1.864263000\\ -2.546131000\\ -1.860540000\\ -2.672793000\\ -3.848231000\\ -4.478060000\\ -3.676590000\\ -4.378079000\\ 2.137203000\\ 2.766245000\\ 2.320637000\\ 2.995647000\\ 3.389586000\\ 4.748422000\\ 4.626818000\\ 5.233512000\end{array}$	2.075890000 -0.047684000 0.128622000 -0.672118000 0.677108000 0.570355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.823897000 -1.461545000 -2.341395000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.223635000 -1.092897000 -0.746488000 -0.109403000 -1.675033000
IBCCCCNHHHHCOOCHHCHHHOSOHCCHHH	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000 -4.478060000 -3.676590000 -4.378079000 2.137203000 2.766245000 2.320637000 2.3995647000 3.389586000 4.748422000 4.626818000 5.233512000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.677108000 0.570355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.823897000 -1.461545000 -1.777435000 -1.777435000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.318422000 1.318422000 1.318422000 -0.746488000 -0.109403000 -1.675033000 -0.244856000
IBCCCCNHHHHCOOCHHCHHHOSOHCCHHHC	1.297586000 -0.074628000 -0.848578000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000 -4.478060000 -3.676590000 -4.378079000 2.137203000 2.766245000 2.320637000 2.3995647000 3.389586000 4.748422000 4.626818000 5.233512000 5.415808000 2.447167000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.677108000 0.570355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.278465000 -1.461545000 -1.461545000 -2.341395000 -1.777435000 -0.753082000 -1.857242000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.318422000 1.318422000 1.223635000 -1.092897000 -0.746488000 -0.109403000 -1.675033000 -0.244856000 -1.709487000
I B C C C C N H H H H C O O C H H C H H H O S O H C C H H H C H	1.297586000 -0.074628000 -0.848578000 -0.706163000 0.006411000 1.347629000 -0.209456000 0.712683000 -1.619428000 0.020752000 -0.697575000 -0.028826000 -1.864263000 -2.546131000 -1.860540000 -2.672793000 -3.848231000 -4.478060000 -3.676590000 -4.378079000 2.137203000 2.766245000 2.320637000 2.3995647000 3.389586000 4.748422000 4.626818000 5.233512000 5.415808000 2.447167000	2.075890000 -0.047684000 0.128622000 -0.672118000 0.187108000 0.57000000 0.550355000 -0.796380000 0.897986000 -1.468593000 1.497114000 2.532178000 1.581040000 2.914731000 3.558826000 3.286801000 2.662089000 1.967294000 2.266715000 3.614674000 3.002573000 -0.278465000 -1.531351000 2.681343000 -0.278465000 -1.531351000 2.681343000 -0.273082000 -1.777435000 -1.777435000 -1.857242000 -1.857242000	0.458955000 3.349607000 2.276786000 1.005941000 -0.138625000 0.222058000 4.245938000 3.363721000 2.306254000 1.183799000 -0.356392000 0.035148000 -0.840398000 -0.970891000 -1.522224000 0.046471000 -1.687982000 -1.127923000 -2.691708000 -1.778470000 0.917025000 0.611840000 1.318422000 1.223635000 -1.092897000 -0.746488000 -0.746488000 -0.746488000 -0.79487000 -1.79487000 -2.140008000
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### <sup>1</sup>H and <sup>13</sup>C NMR Spectra of All Compounds:
























































S88

































S104

















































































































S161





























S175







S178

















































































































