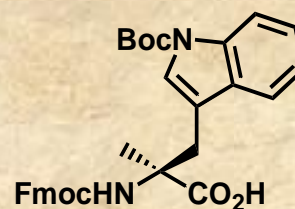
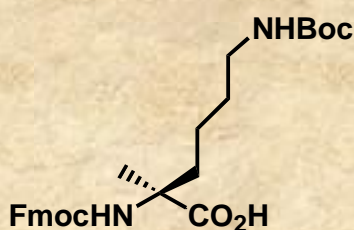
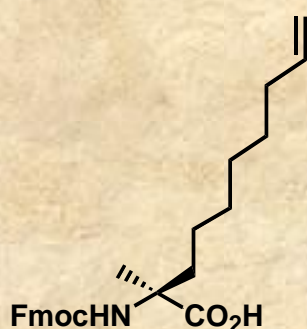
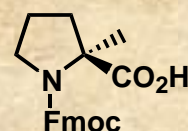
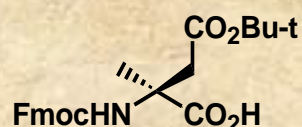
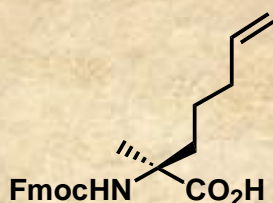
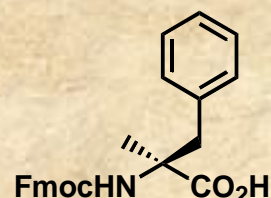
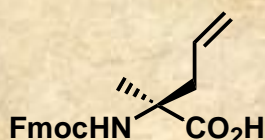


# Nagase's Library of Unnatural Amino Acids

June 2013 Ver.18 revised

**Nagase** provides unique  $\alpha$ -mono substituted and  $\alpha,\alpha$ -disubstituted unnatural amino acids which open new avenues for designing drug candidates and streamlining the production of drugs in the pipeline, which can be supplied in multi-kg and greater quantities via stereoselective alkylation of glycine or alanine and which contain no metal so are safe for API production and environmentally friendly.



**NAGASE**

## New Service!

### Di-Peptides synthesized from our Unnatural Amino Acids

Nagase is developing a range di-peptides which are composed of a natural amino acid connected to N-terminal of our unnatural, alpha, alpha-di-alkylated amino acids.

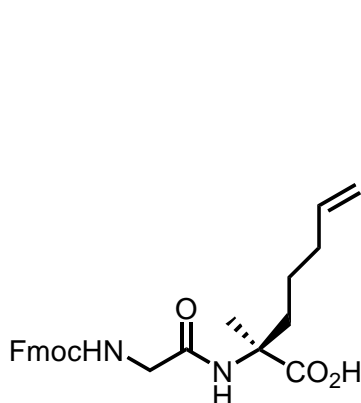


Usually alpha, alpha-di-alkylated amino acids are not so reactive with other natural amino acids at the N-terminal position because of their steric hindrance around the chiral carbon center.

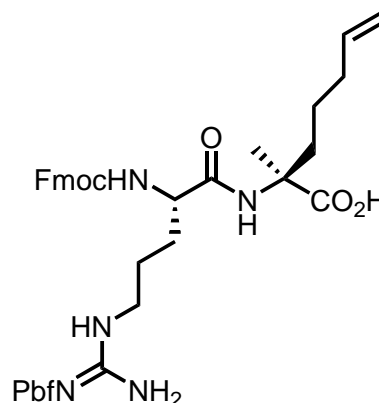
That is the reason why you may have obtained a peptide in low yield as a result of incomplete conjugation of the amino acid adjacent to the dialkylated amino acid.

As a result Nagase commissioned certain peptide custom synthesis companies in Japan and China to provide N-Fmoc-protected di-peptide which is composed of a natural amino acid and alpha, alpha-di-alkylated amino acid and can be used in solid phase peptide synthesis

## Examples



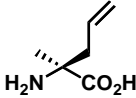
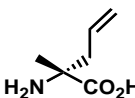
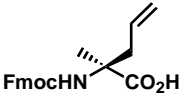
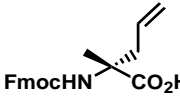
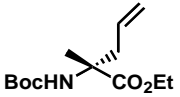
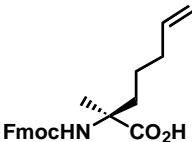
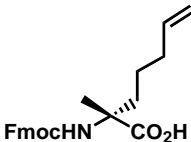
Fmoc-Gly-(S)-Ala(4-Pte)-OH



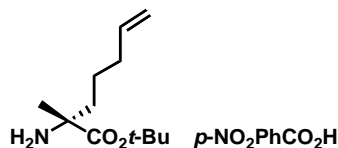
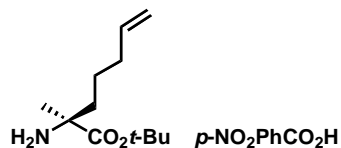
Fmoc-Arg(Pbf)-(S)-Ala(4-Pte)-OH

## Reactive Amino Acids ( $\alpha$ -Alkenyl or $\alpha$ -Alkynyl Glycines and Alanines )

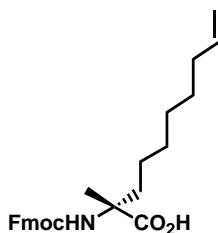
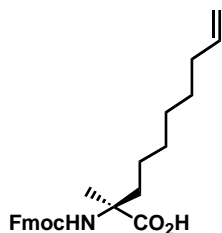
### $\alpha$ -AlkenylAla

335438	<b>(S)-<math>\alpha</math>-Allylalanine-H<sub>2</sub>O</b> (≥ 98.0%, ≥ 98.0%ee) [CAS No.96886-55-4]      C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub> ·H <sub>2</sub> O = 147.17	1g	\$ 300	
335437	<b>(R)-<math>\alpha</math>-Allylalanine-H<sub>2</sub>O</b> (≥ 98.0%, ≥ 98.0%ee) [CAS No.96886-56-5]      C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub> ·H <sub>2</sub> O = 147.17	1g	\$ 300	
				
358028	<b>(S)-N-Fmoc-<math>\alpha</math>-Allylalanine</b> (≥ 98.0%, ≥ 98.0%ee)      (refrigerated transport) [CAS No.288617-71-0]      C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub> = 351.40 containing 20-50% Methyl <i>tert</i> -butyl ether	(NET) 1g	\$ 760(*)	
358027	<b>(R)-N-Fmoc-<math>\alpha</math>-Allylalanine</b> (≥ 98.0%, ≥ 98.0%ee)      (refrigerated transport) [CAS No.288617-76-5]      C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub> = 351.40 containing 20-50% Methyl <i>tert</i> -butyl ether	(NET) 1g	\$ 760(*)	
				
354283	<b>(R)-N-Boc-<math>\alpha</math>-Allylalanine Ethyl ester</b> (≥ 98.0%, ≥ 98.0%ee) [CAS No.1263046-12-3]      C <sub>13</sub> H <sub>23</sub> NO <sub>4</sub> = 257.33	1g	\$ 600	
				
365023	<b>(S)-N-Fmoc-<math>\alpha</math>-(4-Pentenyl)alanine</b> (≥ 98.0%, ≥ 98.0%ee) [CAS No.288617-73-2]      C <sub>23</sub> H <sub>25</sub> NO <sub>4</sub> = 379.46 containing 20-50% of Methyl <i>tert</i> -Butyl ether      (refrigerated transport)	(NET) 1g	\$ 500(*)	
364440	<b>(R)-N-Fmoc-<math>\alpha</math>-(4-Pentenyl)alanine</b> (≥ 98.0%, ≥ 98.0%ee) [CAS No.288617-77-6]      C <sub>23</sub> H <sub>25</sub> NO <sub>4</sub> = 379.46 containing 20-50% of Methyl <i>tert</i> -Butyl ether      (refrigerated transport)	(NET) 5g	\$ 1,800(*)	
		(NET) 1g	\$ 500(*)	
		(NET) 5g	\$ 1,800(*)	
				

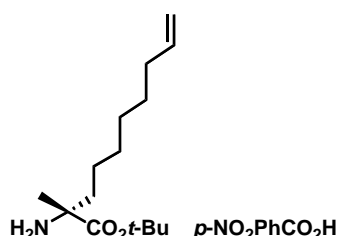
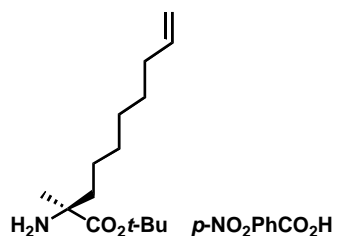
<b>411751</b>	<b>(S)-<math>\alpha</math>-(4-Pentenyl)alanine <i>tert</i>-Butyl ester <i>p</i>-Nitrobenzoate</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)		
	[CAS No.1323987-70-7]	$C_{12}H_{23}NO_2 \cdot C_7H_5NO_4 = 380.44$	1g	\$ 350
			5g	\$ 1,400
<b>411752</b>	<b>(R)-<math>\alpha</math>-(4-Pentenyl)alanine <i>tert</i>-Butyl ester <i>p</i>-Nitrobenzoate</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)		
	[CAS No.1323987-68-3]	$C_{12}H_{23}NO_2 \cdot C_7H_5NO_4 = 380.44$	1g	\$ 350
			5g	\$ 1,400



<b>364441</b>	<b>(S)-N-Fmoc-<math>\alpha</math>-(7-Octenyl)alanine</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 1g	\$ 1,000(*)
	[CAS No.288617-75-4]	$C_{26}H_{31}NO_4 = 421.54$	(NET) 5g	\$ 1,900(*)
	Containing 10-40% of Methyl <i>tert</i> -butyl ether (refrigerated transport)			
<b>363955</b>	<b>(R)-N-Fmoc-<math>\alpha</math>-(7-Octenyl)alanine</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 1g	\$ 1,000(*)
	[CAS No.945212-26-0]	$C_{26}H_{31}NO_4 = 421.54$	(NET) 5g	\$ 1,900(*)
	Containing 10-40% of Methyl <i>tert</i> -butyl ether (refrigerated transport)			



<b>411915</b>	<b>(S)-<math>\alpha</math>-(7-Octenyl)alanine <i>tert</i>-Butyl ester <i>p</i>-Nitrobenzoate</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)		
	[CAS No.1375908-92-1]	$C_{15}H_{29}NO_2 \cdot C_7H_5NO_4 = 422.52$	1g	\$ 700
			5g	\$ 1,500
<b>388630</b>	<b>(R)-<math>\alpha</math>-(7-Octenyl)alanine <i>tert</i>-Butyl ester <i>p</i>-Nitrobenzoate</b>	( $\geq 98.0\%$ , $\geq 98.0\%$ ee)		
	[CAS No.1375904-22-5]	$C_{15}H_{29}NO_2 \cdot C_7H_5NO_4 = 422.52$	1g	\$ 700
			5g	\$ 1,500



Hydrocarbon-stapling of natural peptides enhances helicity, protease resistance, and cell-permeability as well as improves pharmacologic properties.

C. E. Schafmeister, *et. al. J. Am.Chem.Soc.* **2000**, 122, 5891-5892.

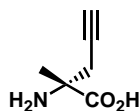
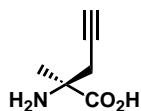
L. D . Walensky, *et. al. Science* **2004**, 305, 1466-1470.

Young-Woo Kim *et. al. Org. Lett.* **2010**, 12, 3046-3049.

### ***α-AlkynylAla***

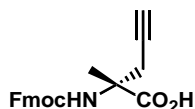
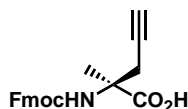
339271 (S)-**α-Propargylalanine** (≥ 98.0%, ≥ 98.0%ee) 1g \$ 300  
[CAS No.1231709-27-5] C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> = 127.14

339270 (R)-**α-Propargylalanine** (≥ 98.0%, ≥ 98.0%ee) 1g \$ 300  
[CAS No.403519-98-2] C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> = 127.14



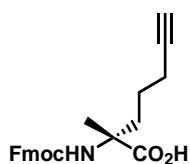
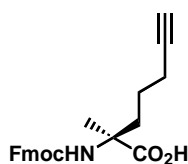
358026 (S)-**N-Fmoc-α-Propargylalanine** (≥ 98.0%, ≥ 98.0%ee) (NET) 1g \$ 500(\*)  
[CAS No.1198791-58-0] C<sub>21</sub>H<sub>19</sub>NO<sub>4</sub> = 349.39  
containing 20-50% Methyl *tert*-butyl ether (refrigerated transport)

358029 (R)-**N-Fmoc-α-Propargylalanine** (≥ 98.0%, ≥ 98.0%ee) (NET) 1g \$ 500(\*)  
[CAS No.1198791-65-9] C<sub>21</sub>H<sub>19</sub>NO<sub>4</sub> = 349.39  
containing 20-50% Methyl *tert*-butyl ether (refrigerated transport)



385412 (S)-**N-Fmoc-α-(4-Pentynyl)alanine** (≥ 98.0%, ≥ 98.0%ee) (NET) 1g \$ 800(\*)  
[CAS No.1050501-65-9] C<sub>23</sub>H<sub>23</sub>NO<sub>4</sub> = 377.44 (NET) 5g \$ 2,400(\*)  
containing 20-50% of Methyl *tert*-butyl ether (refrigerated transport)

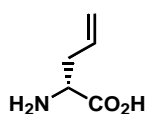
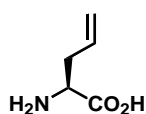
385411 (R)-**N-Fmoc-α-(4-Pentynyl)alanine** (≥ 98.0%, ≥ 98.0%ee) (NET) 1g \$ 800(\*)  
[CAS No.1198791-56-8] C<sub>23</sub>H<sub>23</sub>NO<sub>4</sub> = 377.44 (NET) 5g \$ 2,400(\*)  
containing 20-50% of Methyl *tert*-butyl ether (refrigerated transport)



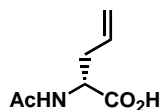
### ***α-AlkenylGly***

345277 (S)-**α-Allylglycine** (≥ 98.0%, ≥ 98.0%ee) 5g \$ 500  
[CAS No.16338-48-0] C<sub>5</sub>H<sub>9</sub>NO<sub>2</sub> = 115.13

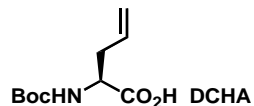
345276 (R)-**α-Allylglycine** (≥ 98.0%, ≥ 98.0%ee) 5g \$ 500  
[CAS No.54594-06-8] C<sub>5</sub>H<sub>9</sub>NO<sub>2</sub> = 115.13



354273 (R)-N-Acetyl- $\alpha$ -allylglycine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 500  
 [CAS No.121786-40-1]  $C_7H_{11}NO_3 = 157.17$



358025 (S)-N-Boc- $\alpha$ -Allylglycine Dicyclohexylamine salt ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 25g \$ 800  
 [CAS No.143979-15-1]  $C_{22}H_{40}N_2O_4 = 396.57$  100g \$ 2,500

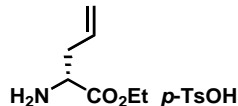
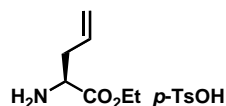


363068 (S)- $\alpha$ -Allylglycine Ethyl ester *p*-Toluenesulfonate ( $\geq 97.0\%$ ,  $\geq 98.0\%$ ee) 5g \$ 200  
 [CAS No.1231709-21-9]  $C_{14}H_{21}NO_5S = 315.39$  25g \$ 800

100g \$ 2,500

413726 (R)- $\alpha$ -Allylglycine Ethyl ester *p*-Toluenesulfonate ( $\geq 97.0\%$ ,  $\geq 98.0\%$ ee) 5g \$ 200  
 [CAS No.1432914-51-6]  $C_{14}H_{21}NO_5S = 315.39$  25g \$ 800

100g \$ 2,500



Application of Allylglycine as the building block for intermediate of pharmaceutical compounds.

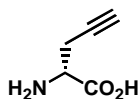
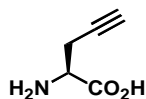
Rutjes, F. P. J. T. *et al. Org. Biomol. Chem.* **2005**, 3, 3435.

Rutjes, F. P. J. T. *et al. J. Chem. Soc. Perkin Trans. 1*, **2000**, 4197.

### $\alpha$ -AlkynylGly

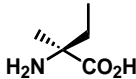
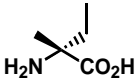
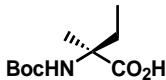
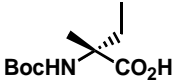

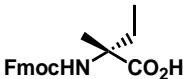
345279 (S)- $\alpha$ -Propargylglycine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 250  
 [CAS No.23235-01-0]  $C_5H_7NO_2 = 113.12$

345278 (R)- $\alpha$ -Propargylglycine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 250  
 [CAS No.23235-03-2]  $C_5H_7NO_2 = 113.12$

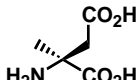
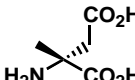


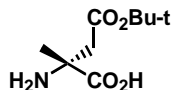
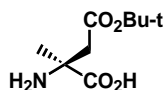
## ***α-Methyl or α-Ethyl derivatives of natural Amino Acids***

### ***Alanine (Ala)***

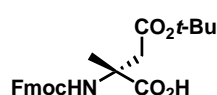
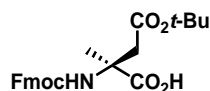
328959	<b>(S)-α-Ethylalanine-H<sub>2</sub>O</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 250
	[CAS No.595-40-4]	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> ·H <sub>2</sub> O = 135.16	5g	\$ 800
328962	<b>(R)-α-Ethylalanine-H<sub>2</sub>O</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 250
	[CAS No.3059-97-0]	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> ·H <sub>2</sub> O = 135.16	5g	\$ 800
				
358835	<b>(S)-N-Boc-α-Ethylalanine</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 300
	[CAS No.151171-11-8]	C <sub>10</sub> H <sub>19</sub> NO <sub>4</sub> = 217.27	5g	\$ 900
395454	<b>(R)-N-Boc-α-Ethylalanine</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 300
	[CAS No.123254-58-0]	C <sub>10</sub> H <sub>19</sub> NO <sub>4</sub> = 217.27	5g	\$ 900
				
354274	<b>(S)-N-Fmoc-α-Ethylalanine</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 400(*)
	[CAS No.857478-30-9]	C <sub>20</sub> H <sub>21</sub> NO <sub>4</sub> = 339.39	5g	\$ 1,600(*)
	(refrigerated transport)			
354275	<b>(R)-N-Fmoc-α-Ethylalanine</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 400(*)
	[CAS No.1231709-22-0]	C <sub>20</sub> H <sub>21</sub> NO <sub>4</sub> = 339.39	5g	\$ 1,600(*)
	(refrigerated transport)			
				

### ***Aspartic acid (Asp)***

346838	<b>(S)-α-Methylaspartic acid</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 400
	[CAS No.3227-17-6]	C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub> = 147.13		
346839	<b>(R)-α-Methylaspartic acid</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 400
	[CAS No.14603-76-0]	C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub> = 147.13		
				
357392	<b>(S)-α-Methylaspartic acid-4-tert-butyl ester</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 230
	[CAS No.1217977-71-3]	C <sub>9</sub> H <sub>17</sub> NO <sub>4</sub> = 203.24	5g	\$ 650
359455	<b>(R)-α-Methylaspartic acid-4-tert-butyl ester</b>	(≥ 98.0%, ≥ 98.0%ee)	1g	\$ 230
	[CAS No.1231709-25-3]	C <sub>9</sub> H <sub>17</sub> NO <sub>4</sub> = 203.24	5g	\$ 650

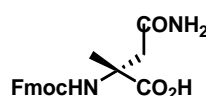
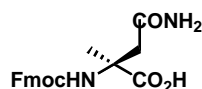


357393	<b>(S)-N-Fmoc-<math>\alpha</math>-Methylaspartic acid-4-<i>tert</i>-butyl ester</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 1g	\$ 600(*)
	[CAS No.1072845-47-6] $C_{24}H_{27}NO_6 = 425.48$	(NET) 5g	\$ 1,400(*)
	containing $\leq 10\%$ Methyl <i>tert</i> -butyl ether (refrigerated transport)		
359457	<b>(R)-N-Fmoc-<math>\alpha</math>-Methylaspartic acid-4-<i>tert</i>-butyl ester</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 1g	\$ 600(*)
	[CAS No.1231709-26-4] $C_{24}H_{27}NO_6 = 425.48$	(NET) 5g	\$ 1,400(*)
	containing $\leq 10\%$ Methyl <i>tert</i> -butyl ether (refrigerated transport)		



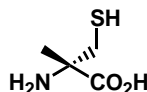
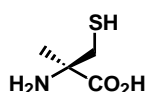
### Asparagine(Asn)

412813	<b>(S)-N-Fmoc-<math>\alpha</math>-Methylasparagine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 600
<b>NEW</b>	[CAS No.1403590-49-7] $C_{20}H_{20}N_2O_5 = 368.39$	5g	\$ 1,800
412814	<b>(R)-N-Fmoc-<math>\alpha</math>-Methylasparagine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 600
<b>NEW</b>	[CAS No.1403590-50-0] $C_{20}H_{20}N_2O_5 = 368.39$	5g	\$ 1,800



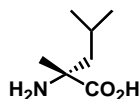
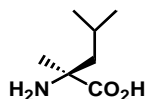
### Cysteine (Cys)

369043	<b>(R)-L-<math>\alpha</math>-Methylcysteine-HCl</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 400
	[CAS No. 148766-37-4] $C_4H_9NO_2S \cdot HCl = 171.65$	5g	\$ 1,600
388254	<b>(S)-D-<math>\alpha</math>-Methylcysteine-HCl</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 1,500
	[CAS No.151062-55-4] $C_4H_9NO_2S \cdot HCl = 171.65$		



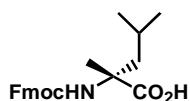
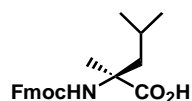
### Leucine (Leu)

328961	<b>(S)-<math>\alpha</math>-Methylleucin</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 250
	[CAS No.105743-53-1] $C_7H_{15}NO_2 = 145.20$		
328960	<b>(R)-<math>\alpha</math>-Methylleucine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 250
	[CAS No.29589-03-5] $C_7H_{15}NO_2 = 145.20$		



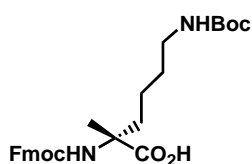
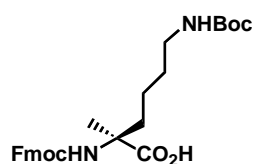


357394	<b>(S)-N-Fmoc-<math>\alpha</math>-Methyleucine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700(*)
	[CAS No.312624-65-0] $C_{22}H_{25}NO_4 = 367.45$ (refrigerated transport)		
357395	<b>(R)-N-Fmoc-<math>\alpha</math>-Methyleucine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700(*)
	[CAS No.1231709-23-1] $C_{22}H_{25}NO_4 = 367.45$ (refrigerated transport)		



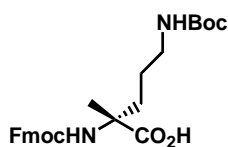
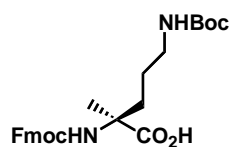
### **Lysine (Lys)**

369412	<b>(S)-N<math>_{\alpha}</math>-Fmoc- N<math>_{\omega}</math>-Boc-<math>\alpha</math>-Methyllysine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700(*)
	[CAS No.1202003-49-3] $C_{27}H_{34}N_2O_6 = 482.58$ (refrigerated transport)	5g	\$ 2,400(*)
369414	<b>(R)-N<math>_{\alpha}</math>-Fmoc- N<math>_{\omega}</math>-Boc-<math>\alpha</math>-Methyllysine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700(*)
	[CAS No.1315449-94-5] $C_{27}H_{34}N_2O_6 = 482.58$ (refrigerated transport)	5g	\$ 2,400(*)



### **Ornithine (Orn)**

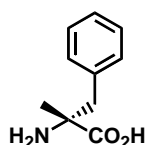
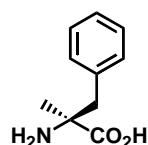
369026	<b>(S)-N<math>_{\alpha}</math>-Fmoc- N<math>_{\omega}</math>-Boc-<math>\alpha</math>-Methylornithine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 600(*)
	[CAS No.1315449-95-6] $C_{26}H_{32}N_2O_6 = 468.55$ (refrigerated transport)	5g	\$ 2,000(*)
369413	<b>(R)-N<math>_{\alpha}</math>-Fmoc- N<math>_{\omega}</math>-Boc-<math>\alpha</math>-Methylornithine</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 600(*)
	[CAS No.171860-40-5] $C_{26}H_{32}N_2O_6 = 468.55$ (refrigerated transport)	5g	\$ 2,000(*)



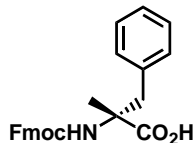
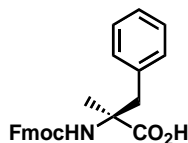
### **Phenylalanine (Phe)**

**Substituted benzene ring derivatives are shown in pp. 10-11**

322901	<b>(S)-<math>\alpha</math>-Methylphenylalanine·H<math>_2</math>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No. 23239-35-2] $C_{10}H_{13}NO_2 \cdot H_2O = 197.23$	5g	\$ 900
322898	<b>(R)-<math>\alpha</math>-Methylphenylalanine·H<math>_2</math>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No. 17350-84-4] $C_{10}H_{13}NO_2 \cdot H_2O = 197.23$	5g	\$ 900

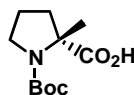
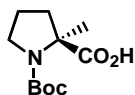


<b>366011</b>	<b>(S)-N-Fmoc-<math>\alpha</math>-Methylphenylalanine-3/2H<sub>2</sub>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No. 135944-05-7]      C <sub>25</sub> H <sub>23</sub> NO <sub>4</sub> · 3/2H <sub>2</sub> O = 428.48	5g	\$ 900
<b>366012</b>	<b>(R)-N-Fmoc-<math>\alpha</math>-Methylphenylalanine-3/2H<sub>2</sub>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No. 152436-04-9]      C <sub>25</sub> H <sub>23</sub> NO <sub>4</sub> · 3/2H <sub>2</sub> O = 428.48	5g	\$ 900

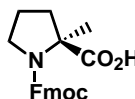


### **Proline (Pro)**

<b>363402</b>	<b>(S)-N-Boc-<math>\alpha</math>-Methylproline</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 400
	[CAS No. 103336-06-7]      C <sub>11</sub> H <sub>19</sub> NO <sub>4</sub> = 229.28	5g	\$ 1,200
<b>363401</b>	<b>(R)-N-Boc-<math>\alpha</math>-Methylproline</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 400
	[CAS No. 166170-15-6]      C <sub>11</sub> H <sub>19</sub> NO <sub>4</sub> = 229.28	5g	\$ 1,200

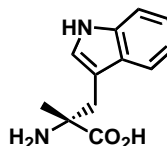
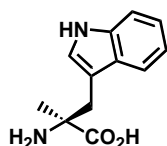


<b>386844</b>	<b>(S)-N-Fmoc-<math>\alpha</math>-Methylproline</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 500
	[CAS No. 167275-47-0]      C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub> = 351.40	5g	\$ 1,500
<b>386843</b>	<b>(R)-N-Fmoc-<math>\alpha</math>-Methylproline</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 500
	[CAS No. 1286768-33-9]      C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub> = 351.40	5g	\$ 1,500

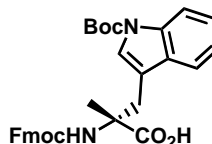
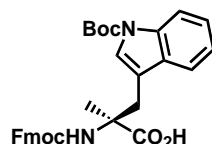


### **Tryptophan (Trp)**

<b>350920</b>	<b>(S)-<math>\alpha</math>-Methyltryptophan-1/2H<sub>2</sub>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700
	[CAS No. 16709-25-4]      C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · 1/2H <sub>2</sub> O = 227.26		
<b>350921</b>	<b>(R)-<math>\alpha</math>-Methyltryptophan-1/2H<sub>2</sub>O</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 700
	[CAS No. 56452-52-9]      C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · 1/2H <sub>2</sub> O = 227.26		



<b>359456</b>	<b>(S)-N-Fmoc-N'-Boc-<math>\alpha</math>-Methyltryptophan</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 200mg	\$ 600(*)
	[CAS No. 1315449-98-9]      C <sub>32</sub> H <sub>32</sub> N <sub>2</sub> O <sub>6</sub> = 540.62	(NET) 1g	\$ 1,200(*)
	containing 5% <i>n</i> -Heptane      (refrigerated transport)		
<b>365299</b>	<b>(R)-N-Fmoc-N'-Boc-<math>\alpha</math>-Methyltryptophan</b> ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	(NET) 200mg	\$ 600(*)
	[CAS No. 220155-72-6]      C <sub>32</sub> H <sub>32</sub> N <sub>2</sub> O <sub>6</sub> = 540.62	(NET) 1g	\$ 1,200(*)
	containing 5% <i>n</i> -Heptane      (refrigerated transport)		



Boyle, S. *et al. Bioorganic & Medicinal Chemistry* **1994**, 2, 357.

van Megen, H. J. *et al. Psychopharmacology (Berlin)* **1997**, 129, 243.

Dethlof, L. A. *et al. Food Chem. Toxicol.* **1998**, 36, 61.

Valerie, A. *et al. J. Med. Chem.* **2001**, 44, 2276.

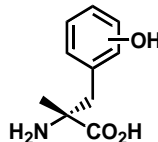
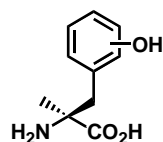
### **Tyrosine (Tyr)**

**339269 (S)- $\alpha$ -Methyl-4-hydroxyphenylalanine** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 250

(S)- $\alpha$ -Methyltyrosine [CAS No.672-87-7]  $C_{10}H_{13}NO_3 = 195.22$

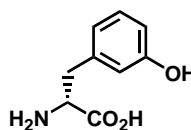
**339268 (R)- $\alpha$ -Methyl-4-hydroxyphenylalanine** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 250

(R)- $\alpha$ -Methyltyrosine [CAS No.672-86-6]  $C_{10}H_{13}NO_3 = 195.22$



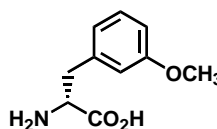
**387902 (R)-D-m-Tyrosine** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 500

[CAS No.32140-49-1]  $C_9H_{11}NO_3 = 181.19$



**387901 (R)-3-Methoxyphenylalanine monohydrate** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 700

[CAS No.145306-65-6]  $C_{10}H_{13}NO_3 \cdot H_2O = 213.23$



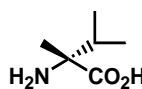
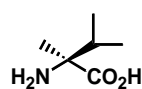
### **Valine (Val)**

**333444 (S)- $\alpha$ -Methylvaline** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 300

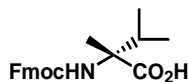
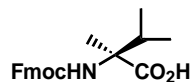
[CAS No.53940-83-3]  $C_6H_{13}NO_2 = 131.18$

**333443 (R)- $\alpha$ -Methylvaline** ( $\geq 98.0\%$ ,  $\geq 98.0\%ee$ ) 1g \$ 300

[CAS No.53940-82-2]  $C_6H_{13}NO_2 = 131.18$



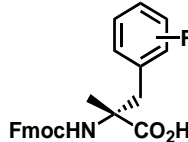
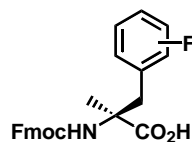
<b>358030</b>	<b>(S)-N-Fmoc-<math>\alpha</math>-Methylvaline</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	(NET)1g	\$ 400(*)
	[CAS No.169566-81-8] $C_{21}H_{23}NO_4 = 353.42$		
	containing $\leq 10\%$ Methyl <i>tert</i> -butyl ether (refrigerated transport)		
<b>358031</b>	<b>(R)-N-Fmoc-<math>\alpha</math>-Methylvaline</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	(NET) 1g	\$ 400(*)
	[CAS No.616867-28-8] $C_{21}H_{23}NO_4 = 353.42$		
	containing $\leq 10\%$ Methyl <i>tert</i> -butyl ether (refrigerated transport)		



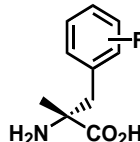
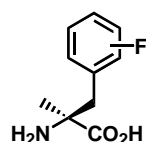
### ***$\alpha$ -Methyl-substituted-phenylalanines***

#### ***F-Phe***

<b>365442</b>	<b>(S)- N-Fmoc-<math>\alpha</math>-Methyl-2-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 300
	[CAS No.1172127-44-4] $C_{25}H_{22}FNO_4 = 419.45$		
<b>364680</b>	<b>(R)- N-Fmoc-<math>\alpha</math>-Methyl-2-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 300
	[CAS No.1315449-93-4] $C_{25}H_{22}FNO_4 = 419.45$		

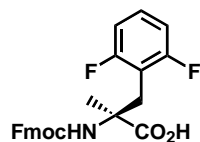


<b>410325</b>	<b>(S)-<math>\alpha</math>-Methyl-3-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 400
	[CAS No.130855-56-0] $C_{10}H_{12}FNO_2 = 197.21$	5g	\$ 1,200
<b>411825</b>	<b>(R)-<math>\alpha</math>-Methyl-3-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 400
	[CAS No. 1270184-80-9] $C_{10}H_{12}FNO_2 = 197.21$	5g	\$ 1,200
<b>410133</b>	<b>(S)-<math>\alpha</math>-Methyl-4-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 300
	[CAS No.130855-57-1] $C_{10}H_{12}FNO_2 = 197.21$	5g	\$ 900
<b>410132</b>	<b>(R)-<math>\alpha</math>-Methyl-4-fluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 300
	[CAS No. 422568-68-1] $C_{10}H_{12}FNO_2 = 197.21$	5g	\$ 900

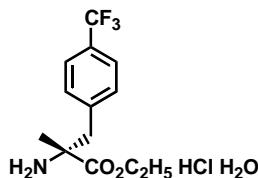


<b>386761</b>	<b>(S)- N-Fmoc-<math>\alpha</math>-Methyl-2,6-difluorophenylalanine</b> ( $\geq 98.0\%$ , $\geq 98.0\%ee$ )	1g	\$ 400
	[CAS No.1223105-51-8] $C_{25}H_{21}F_2NO_4 = 437.44$		

Mapelli C. *et. al. J. Med. Chem.* **2009**, *52*, 7788 – 7799.

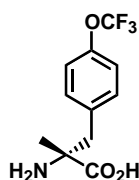
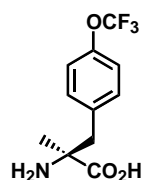


387097 (R)- $\alpha$ -Methyl-4-trifluoromethylphenylalanine ethyl ester hydrochloride monohydrate ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee)  
 [CAS No.1315449-99-0]  $C_{13}H_{16}F_3NO_2 \cdot HCl \cdot H_2O = 329.75$  1g \$ 600



411843 (S)- $\alpha$ -Methyl-4-trifluoromethoxyphenylalanine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 800  
 [CAS No. 1269926-90-0]  $C_{11}H_{12}F_3NO_3 = 263.22$  5g \$ 3,200

410538 (R)- $\alpha$ -Methyl-4-trifluoromethoxyphenylalanine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 800  
 [CAS No.1269835-58-6]  $C_{11}H_{12}F_3NO_3 = 263.22$  5g \$ 3,200



### **Br-Phe**

322899 (S)- $\alpha$ -Methyl-2-bromophenylalanine- $H_2O$  ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 450  
 [CAS No.1212180-27-2]  $C_{10}H_{12}BrNO_2 \cdot H_2O = 276.13$

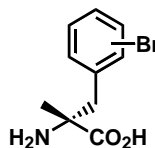
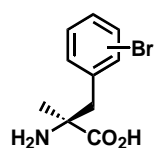
322894 (R)- $\alpha$ -Methyl-2-bromophenylalanine- $H_2O$  ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 450  
 [CAS No.1212307-90-8]  $C_{10}H_{12}BrNO_2 \cdot H_2O = 276.13$

328956 (S)- $\alpha$ -Methyl-3-bromophenylalanine- $H_2O$  ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 300  
 [CAS No.1212117-73-1]  $C_{10}H_{12}BrNO_2 \cdot H_2O = 276.13$

328957 (R)- $\alpha$ -Methyl-3-bromophenylalanine- $H_2O$  ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 300  
 [CAS No.1212321-90-8]  $C_{10}H_{12}BrNO_2 \cdot H_2O = 276.13$

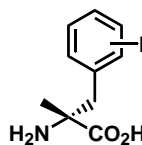
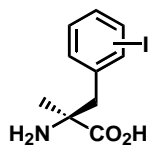
322900 (S)- $\alpha$ -Methyl-4-bromophenylalanine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 400  
 [CAS No.747397-27-9]  $C_{10}H_{12}BrNO_2 = 258.11$

322897 (R)- $\alpha$ -Methyl-4-bromophenylalanine ( $\geq 98.0\%$ ,  $\geq 98.0\%$ ee) 1g \$ 400  
 [CAS No.752971-41-8]  $C_{10}H_{12}BrNO_2 = 258.11$



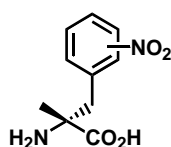
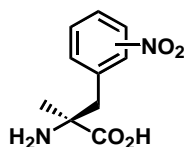
### I-Phe

329205	(S)- $\alpha$ -Methyl-3-iodophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 350
	[CAS No.457653-01-9] C <sub>10</sub> H <sub>12</sub> INO <sub>2</sub> ·H <sub>2</sub> O = 323.13		
329207	(R)- $\alpha$ -Methyl-3-iodophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 350
	[CAS No.457652-83-4] C <sub>10</sub> H <sub>12</sub> INO <sub>2</sub> ·H <sub>2</sub> O = 323.13		
329206	(S)- $\alpha$ -Methyl-4-iodophenylalanine ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No.1215092-16-2] C <sub>10</sub> H <sub>12</sub> INO <sub>2</sub> = 305.11		
329204	(R)- $\alpha$ -Methyl-4-iodophenylalanine ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No.213203-06-6] C <sub>10</sub> H <sub>12</sub> INO <sub>2</sub> = 305.11		



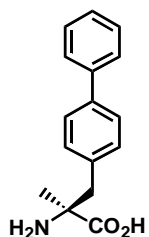
### NO<sub>2</sub>-Phe

333075	(S)- $\alpha$ -Methyl-2-nitrophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 200
	[CAS No.1241680-71-6] C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O = 242.23		
333080	(R)- $\alpha$ -Methyl-2-nitrophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 200
	[CAS No.1241680-73-8] C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O = 242.23		
333078	(S)- $\alpha$ -Methyl-3-nitrophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 200
	[CAS No.1215092-14-0] C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O = 242.23		
333076	(R)- $\alpha$ -Methyl-3-nitrophenylalanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 200
	[CAS No. 1215092-13-9] C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O = 242.23		



### 4-Ph-Phe

335436	(S)- $\alpha$ -Methyl- $\beta$ -(4-biphenyl)alanine-H <sub>2</sub> O ( $\geq 98.0\%$ , $\geq 98.0\%$ ee)	1g	\$ 300
	[CAS No.1231709-24-2] C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub> ·H <sub>2</sub> O = 273.33		

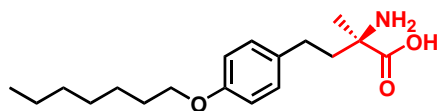


## Application of Unnatural Amino Acids for Pharmaceuticals

Replacement of the  $\alpha$ -hydrogen atom of L- $\alpha$ -Amino acids with an alkyl substituent, which results in  $\alpha,\alpha$ -disubstituted amino acids, has been reported. The modification changes the properties of amino acids as follows: 1) increased chemical stability, 2) increased hydrophobicity, 3) restriction of conformational freedom of side chains in amino acids, 4) restriction of conformational freedom of their peptides, 5) metabolic stability of their peptides.

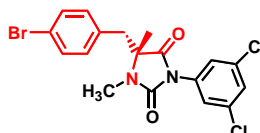
Tanaka, M. *Chem. Pharm. Bull.* **2007**, *55*, 349-358.

Examples of investigational API's including  $\alpha,\alpha$ -disubstituted amino acids.



Chiral Analogue of Single S1P Receptor

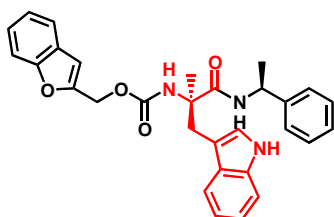
Albert, R. *et al. J. Med. Chem.* **2005**, *48*, 5373-5377.



Integrin  $\alpha$ -2 (LFA-1) Antagonist

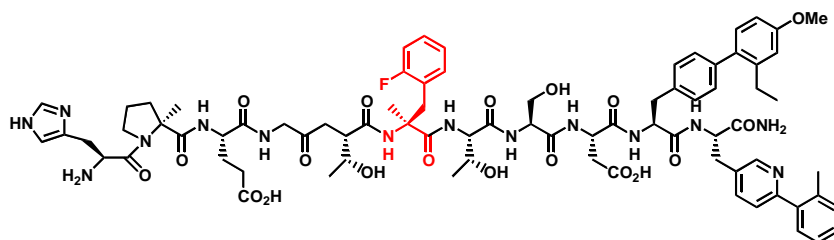
LFA-1/ICAM-1 Interaction Inhibitors

Kelly, T.A. *et al. J. Immunol.* **1999**, *163*, 5173-5177



NK1 Receptor Antagonist

Boyle, S. *et al. Bioorganic & Medicinal Chemistry* **1994**, *2*, 357.

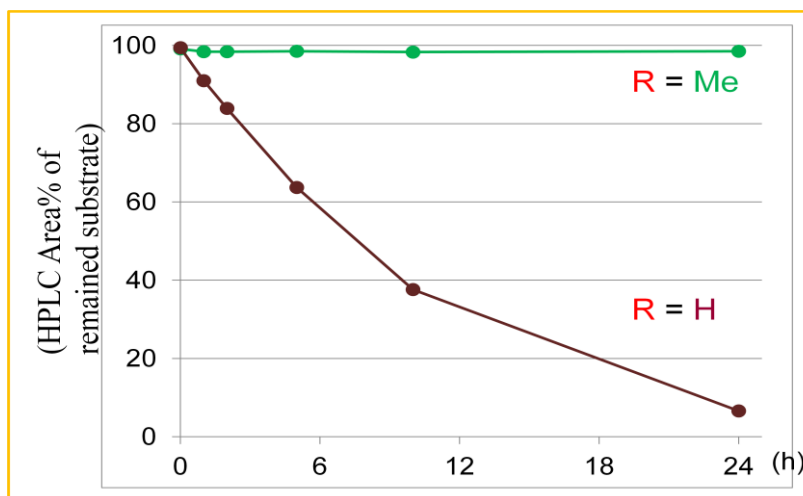
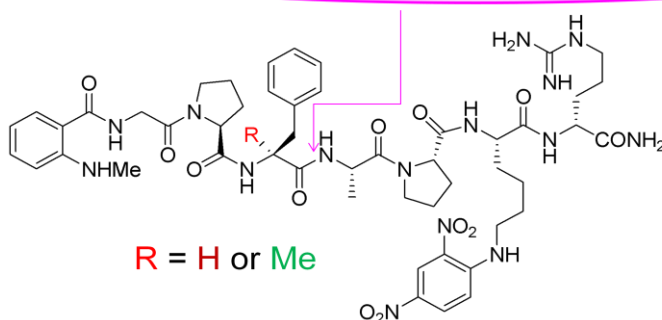


Glucagon-like Peptide-1 Receptor Agonist with Antidiabetic Activity

Mapelli, C. *et al. J. Med. Chem.* **2009**, *52*, 7788 – 7799.

## Resistance of a Peptide with $\alpha,\alpha$ -disubstituted Amino Acid against Protease

$\alpha$ -Chymotrypsin Type:VII From Bovine Pancreas



Incubated at 30 deg in 10% DMSO/0.1 M Pi buffer (pH=8.0) solution

A tryptic digestion assay of  $\alpha$ -methyl phenylalanine-containing peptide was carried out to investigate the effect of  $\alpha,\alpha$ -dialkylamino acid residue on the protease resistance. The introduction of  $\alpha,\alpha$ -dialkylamino acid residue (alpha-Methylphenylalanine) to the peptide backbone exhibited higher protease resistance in 24 hours than the peptide with  $\alpha$ -monoalkyl amino acid (phenylalanine). The peptide with the  $\alpha,\alpha$ -dialkylamino acid residue resulted in complete resistance.

### Reference:

Matsuyama, K.; Yamamoto, K.; Murakami, S.; Anzai, K. Construction of an unnatural amino acids library through asymmetric alkylation of glycine or alanine ester Schiff-base utilizing Maruoka Catalyst®.

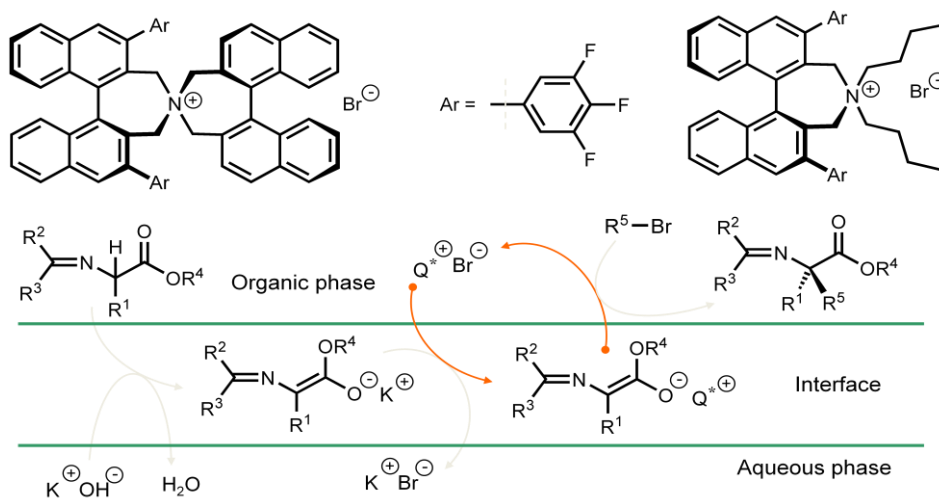
Presented at the 5th International Peptide Symposium, Kyoto, Japan, December 4-9, 2010; P2-204.





## Asymmetric Phase-Transfer Reaction with Maruoka Catalyst<sup>®</sup> to Synthesize

### $\alpha$ - Monosubstituted and $\alpha, \alpha$ -Disubstituted Amino Acids.



Ikunaka, M. and Maruoka, K. 'Asymmetric Phase-Transfer Catalysts for the Production of Non-Proteinogenic  $\alpha$ -Amino Acids' in *Asymmetric Catalysis on Industrial Scale 2<sup>nd</sup> edition*, Blaser, H-U. and Federsel, H.-J. eds. Wiley-VCH Verlag GmbH & Co. KGaA (2010)

According to the Maruoka interfacial mechanism, protected  $\alpha$ -amino acid is converted into the potassium *E*-enolate. And because of the lipophilic nature of the quaternary ammonium salt, it can move more easily and frequently into the interface layer where cation exchange takes place with the potassium *E*-enolate. And as the *si* face of the *E*-enolate is shielded by the molecular cavity of the catalyst, an alkyl halide is only allowed to approach the *re* face of the enolate.

This is the reason why Maruoka Catalyst<sup>®</sup> shows high reactivity and selectivity.

#### Reference:

Ooi, T., Kameda, M., and Maruoka, K. *J. Am. Chem. Soc.*, **2003**, 125, 5139-5151.

Ooi, T., Kameda, M., Tannai, H., and Maruoka, K. *Tetrahedron Lett.*, **2000**, 41, 8339-8342.

Ooi, T., Takeuchi, M., and Maruoka, K. *Synthesis* **2001**, 1716-1718.

Maruoka, K. *Org. Process Research & Development* **2008**, 12, 679-687.

#### Patents:

USP 6,340,753; 6,441,231; 7,928,224; 8,252,962

JP 4,217,085; 4,502,293; 4,605,606; 5,106,562; 5,108,777; 5,108,888

SG 139,249

IN 252,017

CN ZL200680027800.6

#### Trade mark

**Maruoka Catalyst** is the registered trade mark in US, EU.

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