Supplementary Information for manuscript:

"A high-throughput, multiplexed assay for superfamily-wide profiling of enzyme activity"

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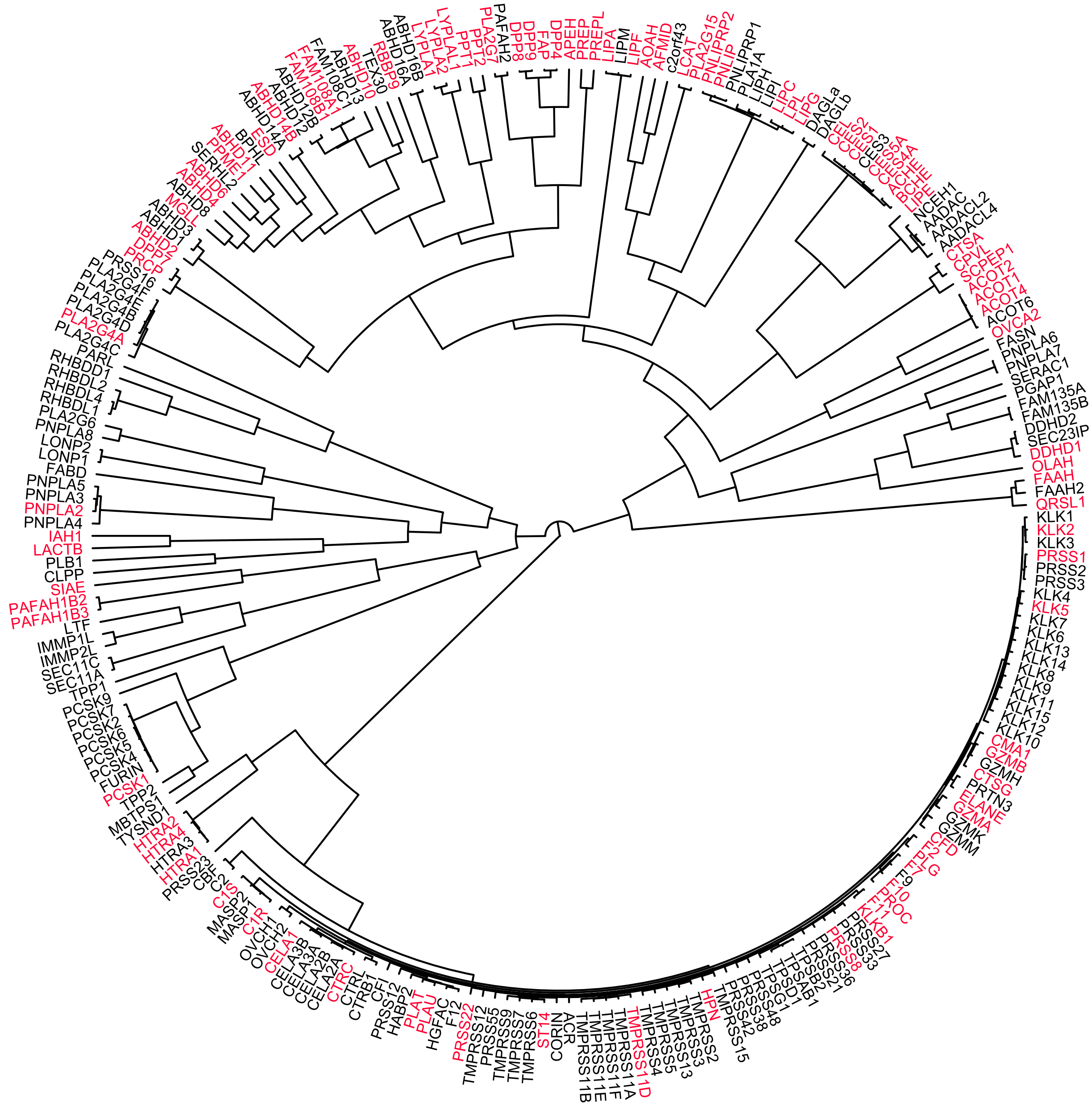
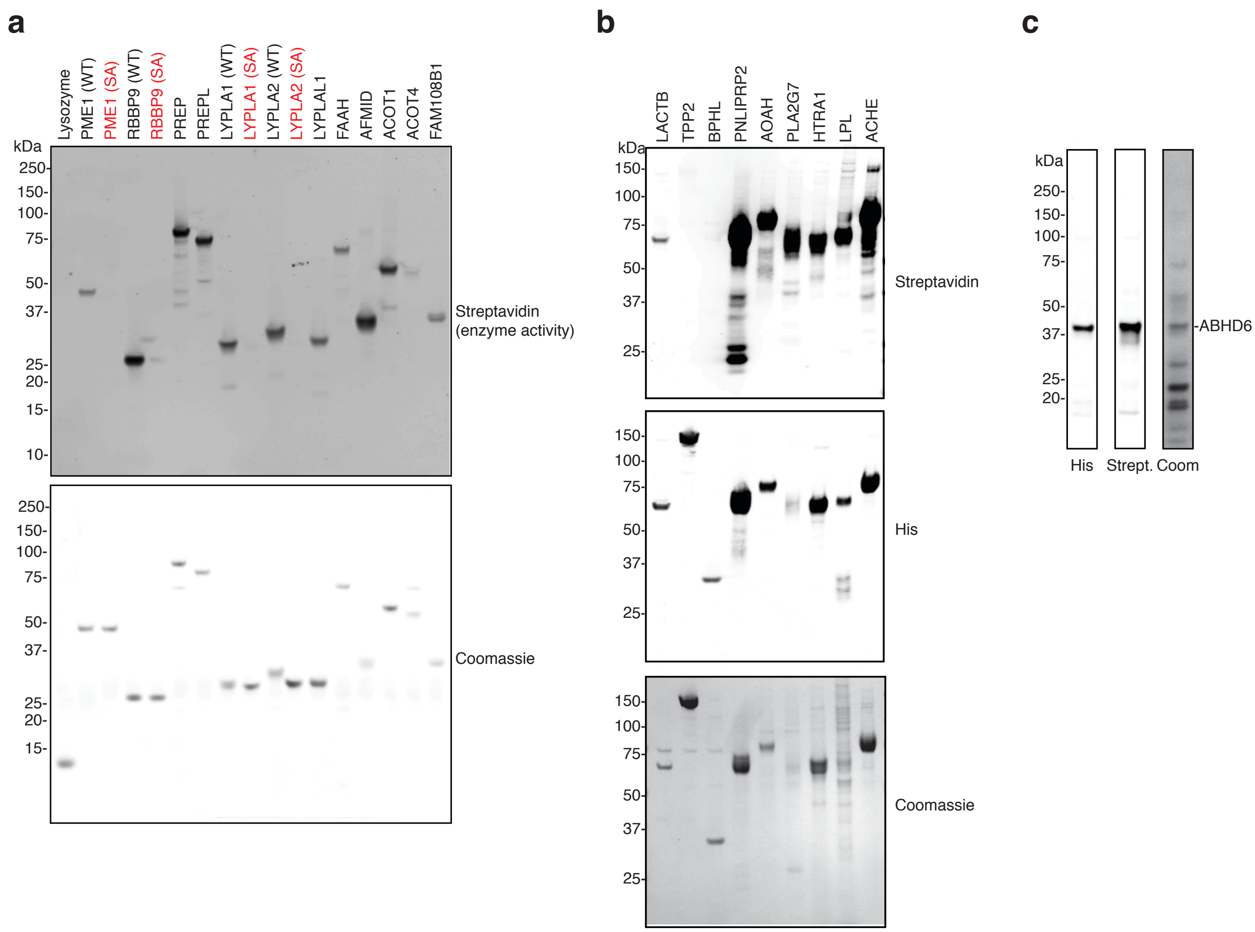
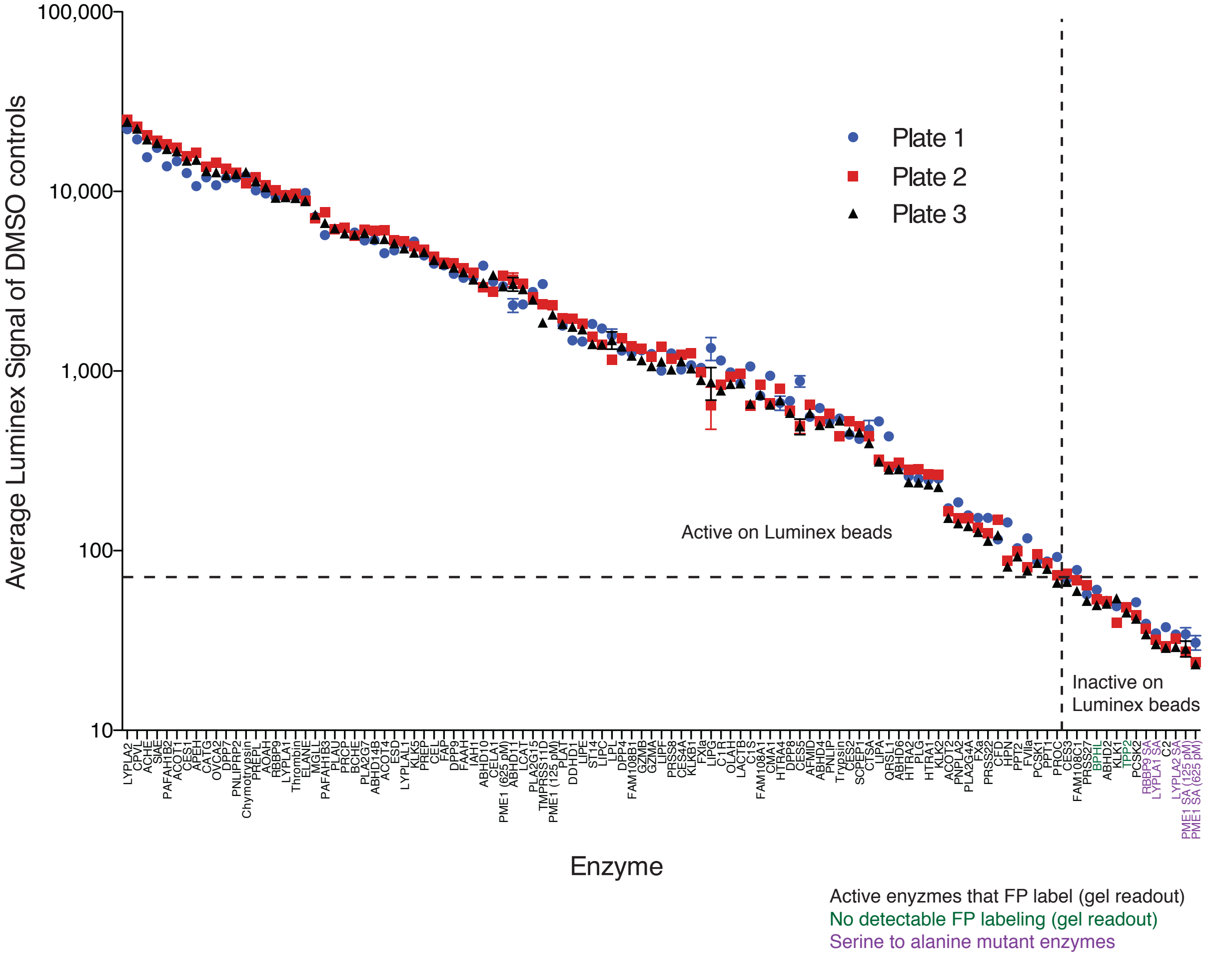
Supplementary Results



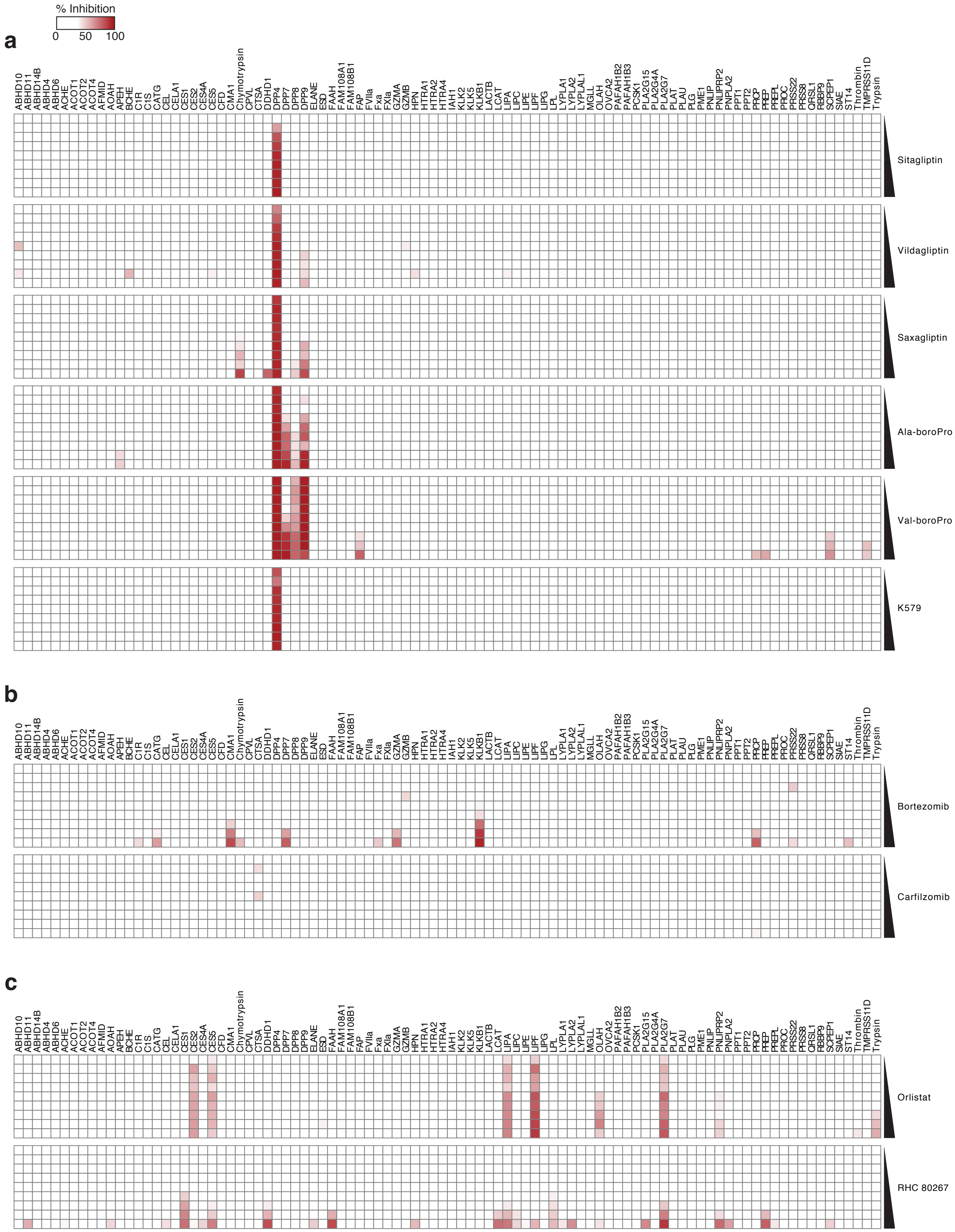
Supplementary Figure 1 The diverse serine hydrolase panel screened in this study. The dendrogram depicts the ~240 human serine hydrolases with branch lengths corresponding to sequence relatedness. The 94 enzymes colored red were included in the initial EnPlex assay.



Supplementary Figure 2 Representative analyses of protein purity and activity. Enzymes purified from (**a**) *E. coli* or (**b**) HEK 293T cells were labeled with FP-biotin (1 μM), separated by SDS-PAGE, and analyzed by Western blotting with a streptavidin-conjugated infrared dye to confirm activity (the appearance of a band in the streptavidin blot indicates an active enzyme). Note that the catalytically inactivated proteins (colored red) and lysozyme do not label with the FP-probe. Similarly, we saw no labeling for two purified serine hydrolases, TPP2 and BPHL, indicating that these enzymes were either inactive or do not react with the FP-probe. (**c**) A few proteins, including His-tagged ABHD6, were difficult to purify to homogeneity. Here, co-migration of the His band and the streptavidin band indicates that ABHD6 is the only active hydrolase in the sample, even though it is <25% pure by Coomassie staining. The EnPlex assay only requires purity from other FP-sensitive enzymes, as shown here for ABHD6, and not from all cellular proteins.



Supplementary Figure 3 EnPlex assay reproducibility. Bead mixtures (frozen aliquots thawed one time) were evaluated on separate days on separate plates. Enzymes were considered active that gave signals >2-fold higher than that observed with catalytically inactivated enzymes (corresponding to a Luminex signal of 75). The median Luminex signal reflects both enzyme abundance and rate of reactivity with the FP-probe. The reason several FP-sensitive enzymes appear inactive on the beads is unclear, but is potentially due to immobilization impairing catalytic activity. Error bars represent s.e.m.


% Inhibition
0
50
100
a
b
c
ABHD10 ABHD11 ABHD14B ABHD4 ABHD6 ACHE ACOT1 ACOT2 ACOT4 AFMID AOAH APEH BCHE C1R C1S CATG CEL CELA1 CES1 CES2 CES4A CES5 CFD CMA1 Chymotrypsin CPVL CTSA DDHD1 DPP4 DPP7 DPP8 DPP9 ELANE ESD FAAH FAM108A1 FAM108B1 FAP FVIIa Fxa FXIa GZMA GZMB HPN HTRA1 HTRA2 HTRA4 IAH1 KLK2 KLK5 KLKB1 LACTB LCAT LIPA LIPC LIPE LIPF LIPG LPL LYPLA1 LYPLA2 LYPLAL1 MGLL OLAH OVCA2 PAFAH1B2 PAFAH1B3 PCSK1 PLA2G15 PLA2G4A PLA2G7 PLAT PLAU PLG PME1 PNLIP PNLIPRP2 PNPLA2 PPT1 PPT2 PRCP PREP PREPL PROC PRSS22 PRSS8 QRSL1 RBBP9 SCPEP1 SIAE ST14 Thrombin TMPRSS11D Trypsin
Sitagliptin
Vildagliptin
Saxagliptin
Ala-boroPro
Val-boroPro
K579
Bortezomib
Carfilzomib
Orlistat
RHC 80267

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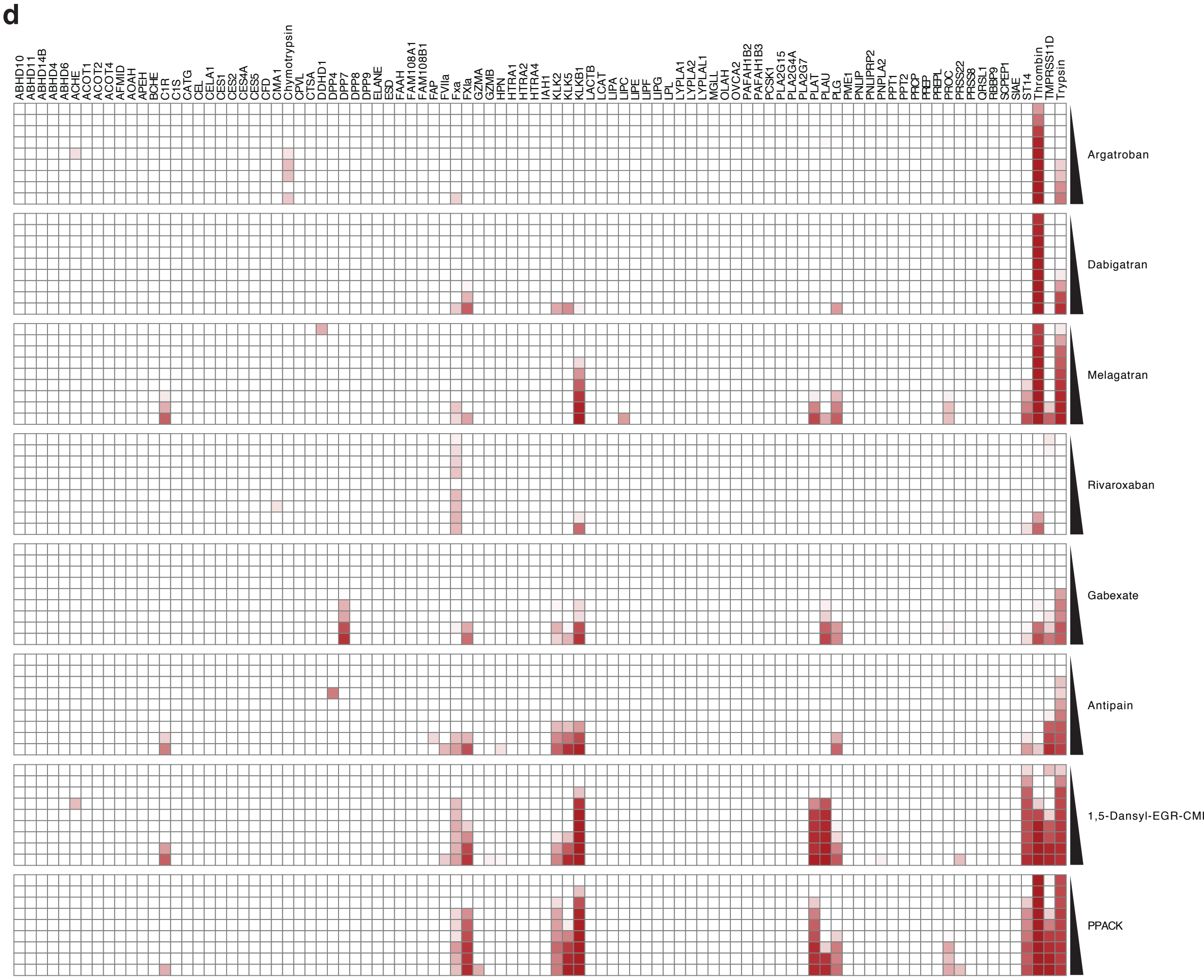
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Melagatran
Rivaroxaban
Gabexate
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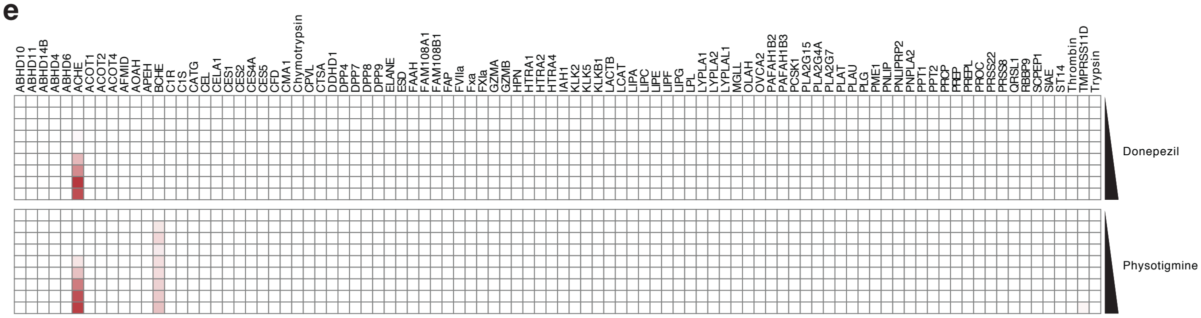
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Donepezil
Physotigmine

f


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ABHD11
ABHD14B
ABHD4
ABHD6
ACHE
ACOT1
ACOT2
ACOT4
AFMID
AOAH
APEH
BCHE
C1R
C1S
CATG
CEL
CELA1
CES1
CES2
CES4A
CES5
CFD
CMA1
Chymotrypsin
CPVL
CTSA
DDHD1
DPP4
DPP7
DPP8
DPP9
ELANE
ESD
FAAH
FAM108A1
FAM108B1
FAP
FVIIa
FXa
FXIa
GZMA
GZMB
HPN
HTRA1
HTRA2
HTRA4
IAH1
KLK2
KLK5
KLKB1
LACTB
LCAT
LIPA
LIPC
LIPE
LIPF
LIPG
LPL
LYPLA1
LYPLA2
LYPLAL1
MGLL
OLAH
OVCA2
PAFAH1B2
PAFAH1B3
PCSK1
PLA2G15
PLA2G4A
PLA2G7
PLAT
PLAU
PLG
PME1
PNLIP
PNLIPRP2
PNPLA2
PPT1
PPT2
PRCP
PREP
PREPL
PROC
PRSS22
PRSS8
QRSL1
RBBP9
SCPEP1
SIAE
ST14
Thrombin
TMPRSS11D
Trypsin
Arachidonyl TFMK
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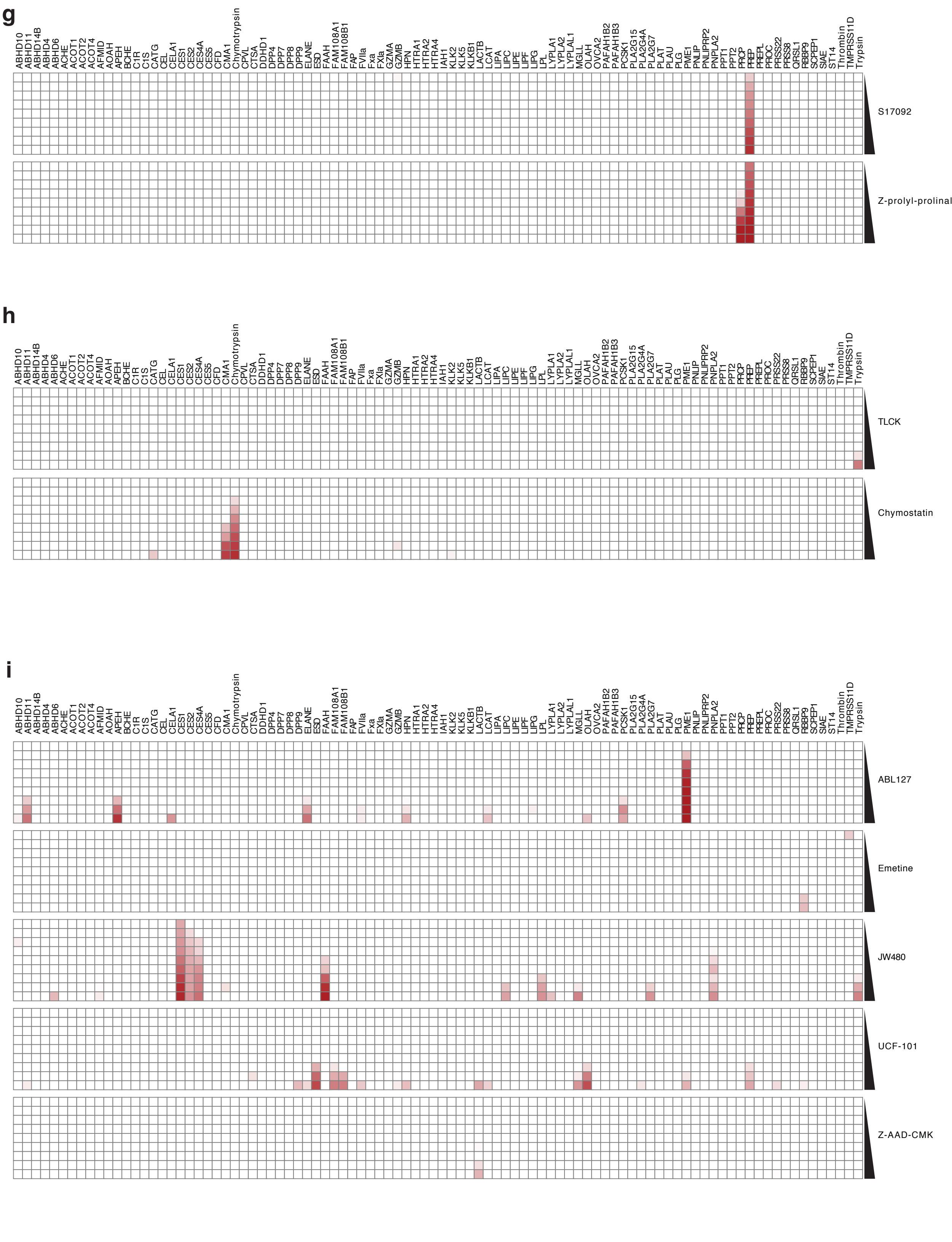
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Z-prolyl-prolinal
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ABHD10 ABHD11 ABHD14B ABHD4 ABHD6 ACHE ACOT1 ACOT2 ACOT4 AFMID AOAH APEH BCHE C1R C1S CATG CEL CELA1 CES1 CES2 CES4A CES5 CFD CMA1 Chymotrypsin CPVL CTSA DDHD1 DPP4 DPP7 DPP8 DPP9 ELANE ESD FAAH FAM108A1 FAM108B1 FAP FVIIa FXa FXIa GZMA GZMB HPN HTRA1 HTRA2 HTRA4 IAH1 KLK2 KLK5 KLKB1 LACTB LCAT LIPA LIPC LIPE LIPF LIPG LPL LYPLA1 LYPLA2 LYPLAL1 MGLL OLAH OVCA2 PAFAH1B2 PAFAH1B3 PCSK1 PLA2G15 PLA2G4A PLA2G7 PLAT PLAU PLG PME1 PNLIP PNLIPRP2 PNPLA2 PPT1 PPT2 PRCP PREP PREPL PROC PRSS22 PRSS8 QRSL1 RBBP9 SCPEP1 SIAE ST14 Thrombin TMPRSS11D Trypsin
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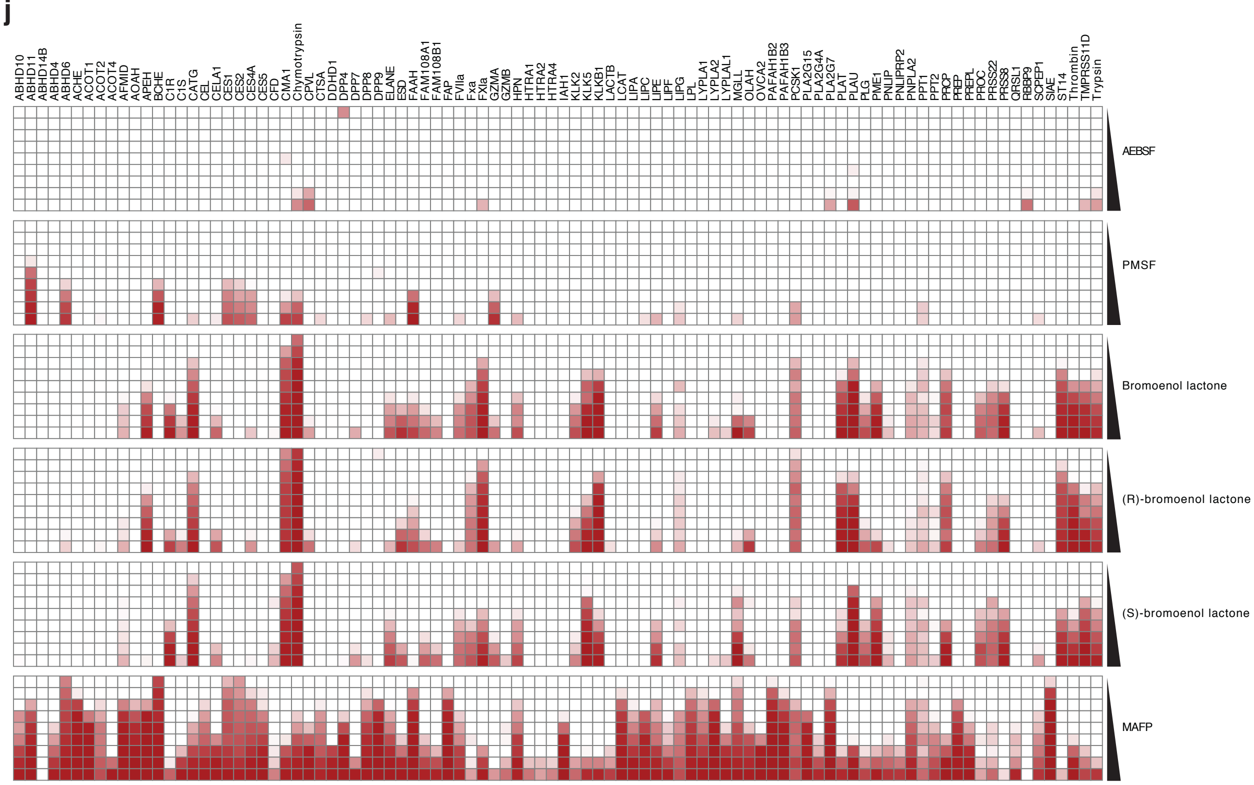
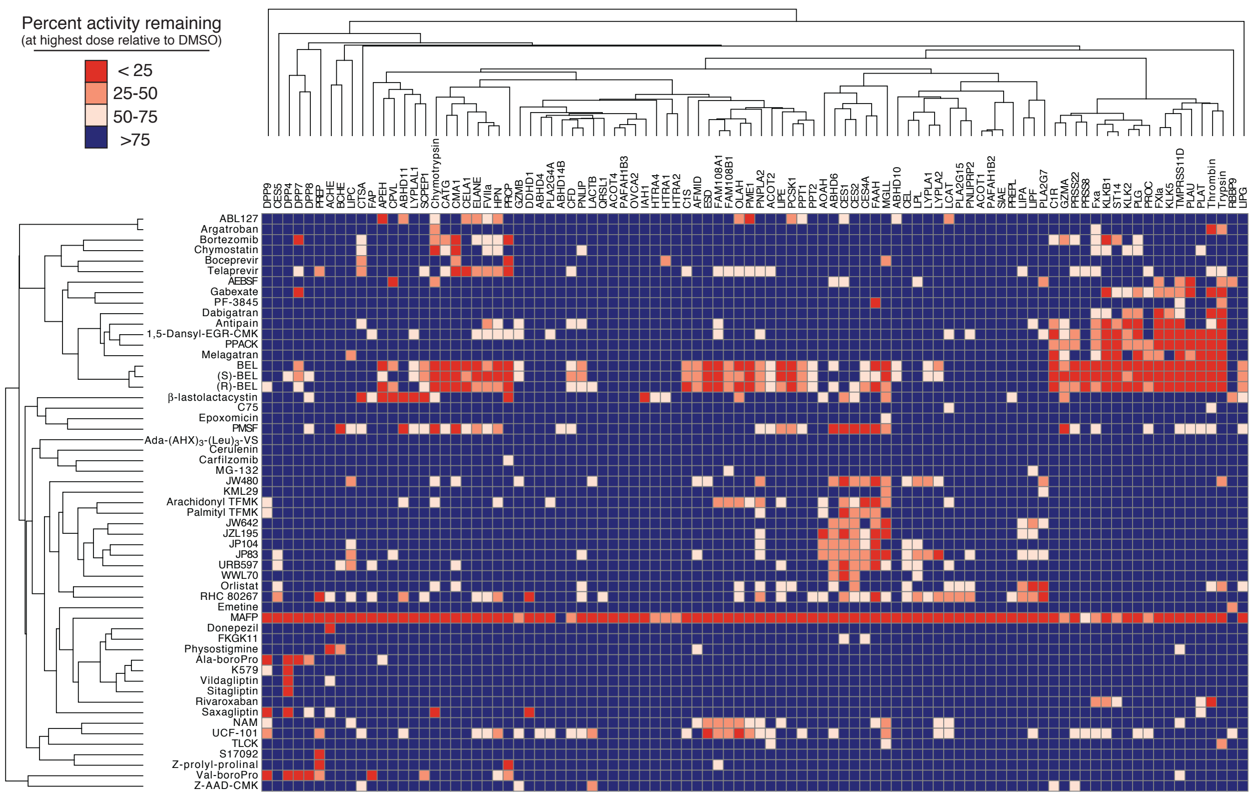
ABHD10 ABHD11 ABHD14B ABHD4 ABHD6 ACHE ACOT1 ACOT2 ACOT4 AFMID AOAH APEH BCHE C1R C1S CATG CEL CELA1 CES1 CES2 CES4A CES5 CFD CMA1 Chymotrypsin CPVL CTSA DDHD1 DPP4 DPP7 DPP8 DPP9 ELANE ESD FAAH FAM108A1 FAM108B1 FAP FVIIa FXa FXIa GZMA GZMB HPN HTRA1 HTRA2 HTRA4 IAH1 KLK2 KLK5 KLKB1 LACTB LCAT LIPA LIPC LIPE LIPF LIPG LPL LYPLA1 LYPLA2 LYPLAL1 MGLL OLAH OVCA2 PAFAH1B2 PAFAH1B3 PCSK1 PLA2G15 PLA2G4A PLA2G7 PLAT PLAU PLG PME1 PNLIP PNLIPRP2 PNPLA2 PPT1 PPT2 PRCP PREP PREPL PROC PRSS22 PRSS8 QRSL1 RBBP9 SCPEP1 SIAE ST14 Thrombin TMPRSS11D Trypsin
ABL127
Emetine
JW480
UCF-101
Z-AAD-CMK

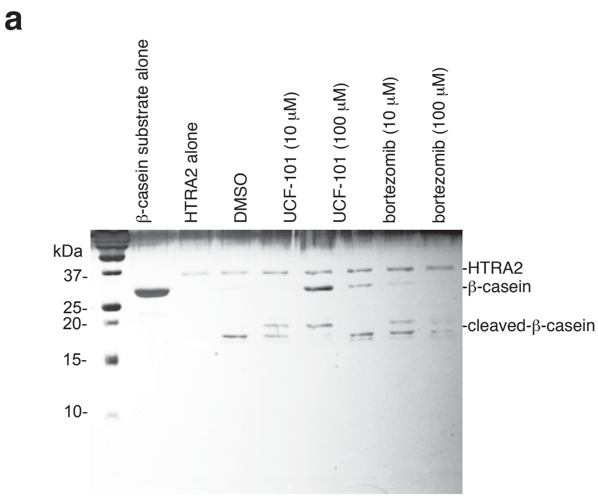
j

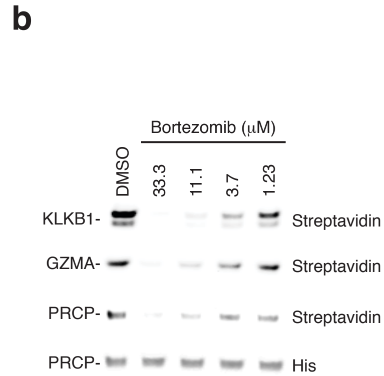


Supplementary Figure 4 Complete EnPlex profiles for the 55 widely used inhibitors with at least one target in the enzyme panel. Inhibitors were grouped according their intended target(s): (**a**) dipeptidyl peptidases, (**b**) proteasome, (**c**) DAG lipase (and assorted other lipases), (**d**) enzymes involved in blood clotting, (**e**) ACHE, (**f**) FAAH, MGLL, and ABHD6, (**g**) PREP, (**h**) trypsin/chymotrypsin, (**i**) other, and (**j**) non-selective.

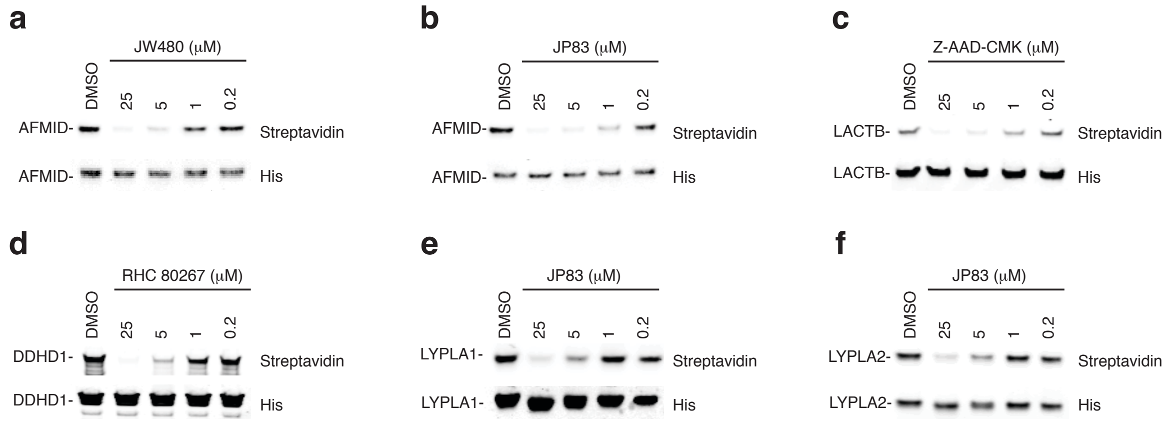


Supplementary Figure 5 Two-dimensional hierarchical clustering of all interactions at the highest compound concentration for the 55 widely used inhibitors (33 μM for all compounds except for Ada-(AHX)$_3$-(Leu)$_3$-VS and epoxomicin, which were screened at 16.7 μM). The percent activity remaining relative to DMSO controls is shown. Clustering was performed based on the Pearson correlation.

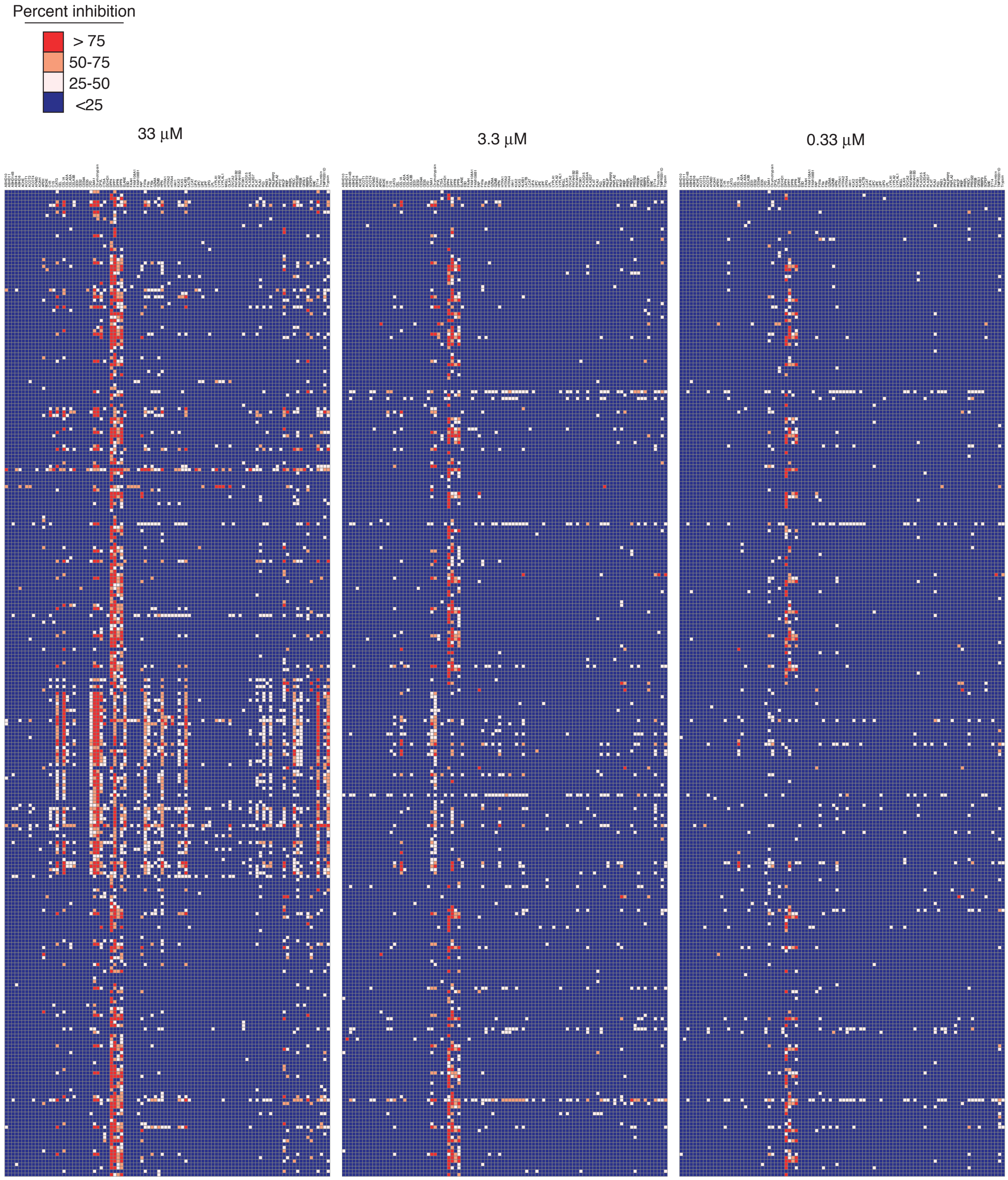




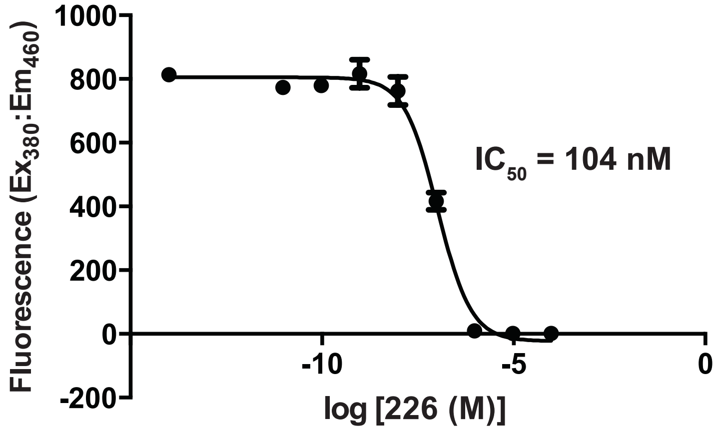
Supplementary Figure 6 Validation of bortezomib off-targets. (**a**) HTRA2 (0.02 mg/mL) was incubated with its substrate β-casein (0.02 mg/mL) for 1 h in the presence of bortezomib or the HTRA2 inhibitor UCF-101 before being quenched, separated by SDS-PAGE, and analyzed by silver staining. This shows that bortezomib, even at 100 μM, does not significantly inhibit HTRA2. (**b**) Gel-based competitive ABPP confirms bortezomib inhibits KLKB1, GZMA, and PRCP. Full gel images are shown in **Supplementary Figure 11**.



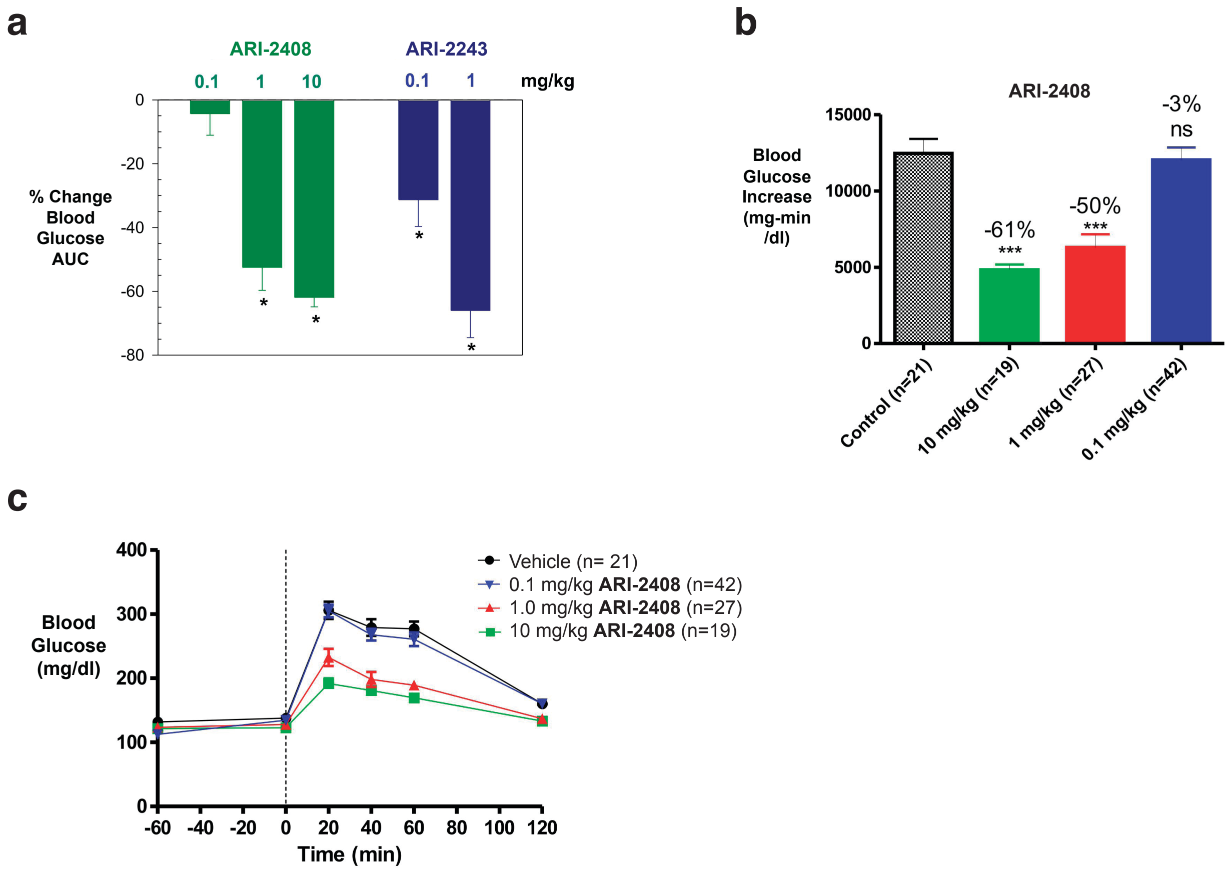
Supplementary Figure 7 Validation of lead inhibitor candidates identified in the EnPlex screen from the 55 widely used inhibitor library. The interactions between (**a**) JW480 and AFMID, (**b**) JP83 and AFMID, (**c**) Z-AAD-CMK and LACTB, (**d**) RHC 80267 and DDHD1, (**e**) JP83 and LYPLA1, and (**f**) JP83 and LYPLA2 were confirmed by gel-based competitive ABPP. Full gel images are shown in **Supplementary Figure 11**.



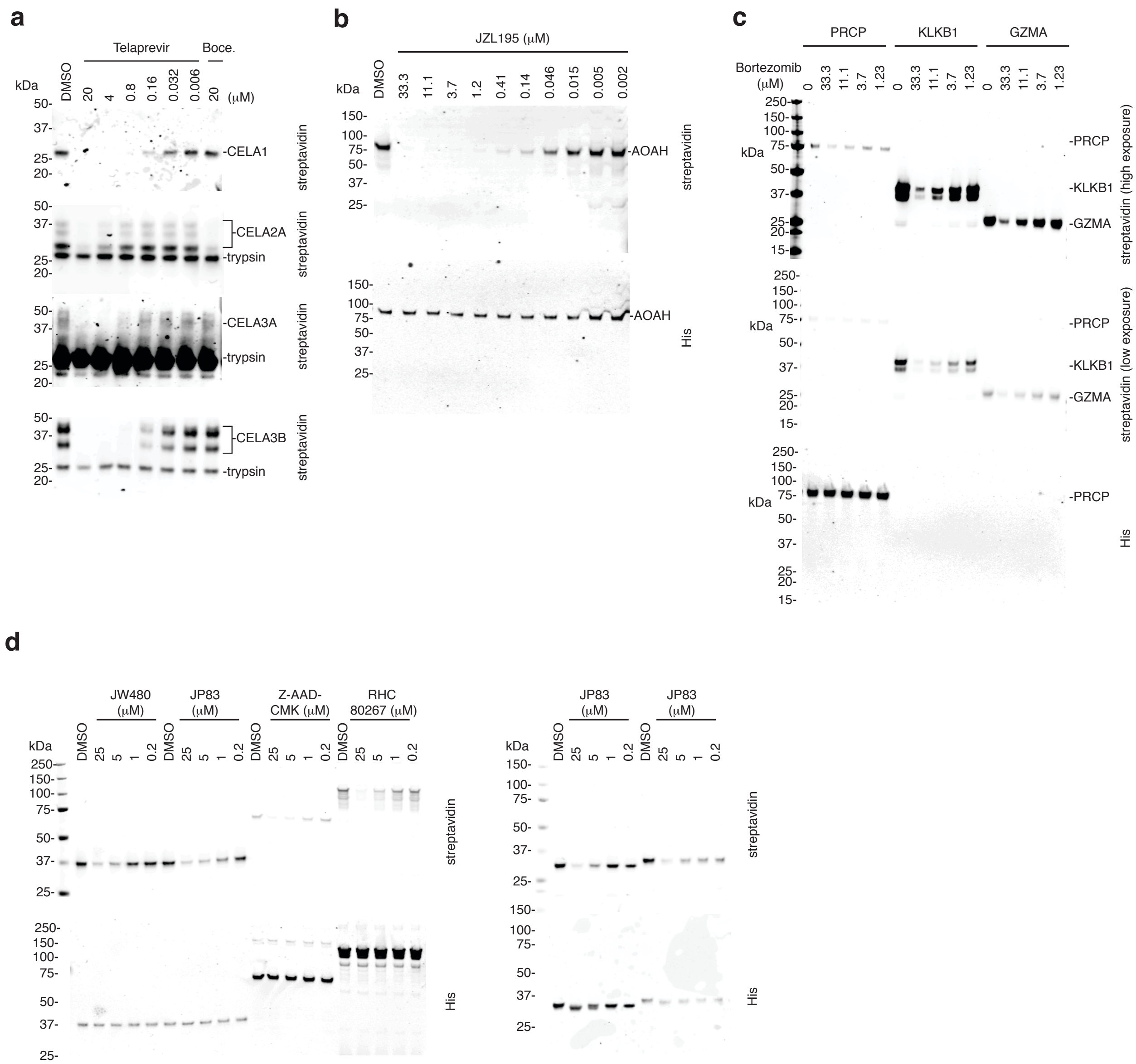
Supplementary Figure 8 Heatmaps of the boronic acid and nitrile screening data. The percent inhibition of each enzyme (columns) relative to DMSO controls is shown. The compound numbers (rows) correspond to **Supplementary Table 6**.



Supplementary Figure 9 Compound **226** inhibits APEH with an IC_{50} = 104 nM in a substrate (Ac-Ala-AMC) assay. Data are means ± s.e.m of three independent experiments.



Supplementary Figure 10 ARI-2408 and ARI-2243 have potent antiglycemic activity in mice in an oral glucose tolerance test. (**a**) The percent change in blood glucose AUC for both compounds. n = 7 mice/group for ARI-2243; n =19, 27, and 42 mice/group for ARI-2408 at 10, 1 and 0.1 mg/kg, respectively. (**b**) The blood glucose increase (mg-min/dL) and (**c**) complete time course for ARI-2408. *$p < 0.01$ versus vehicle control; *** $p < 0.001$ versus vehicle control. Error bars represent s.e.m.



Supplementary Figure 11 Full gel images for those cropped in the paper figures. (**a**) Gel from **Figure 3c**. Note that trypsin was used to activate CEL2A, 3A, and 3B and was not removed prior to resolving these experiments. (**b**) Full gel from **Figure 4b**. (**c**) Full gel from **Supplementary Figure 6b**. Note that only PRCP is His-tagged. (**d**) Full gels from **Supplementary Figure 7.**

Supplementary Table 1 Comparison of competitive ABPP screening methods for serine hydrolases.

	ABPP-MudPIT	**Gel-based ABPP**	**Fluopol-ABPP**	**EnPlex**
Readout	Mass spectrometry	SDS-PAGE	Fluorescence polarization	Luminex
Enzymes	30-40	10-20	1	100s
Compounds	3-5	hundreds	thousands	thousands
Major limitation(s)	• Low throughput • Expensive • Selectivity information limited to active enzymes in specific cell lysates/tissues	• Low throughput • Limited selectivity information (due to gel resolution and sensitivity)	• Requires large amounts of purified protein • No selectivity information	• Requires purified protein, but only small amounts

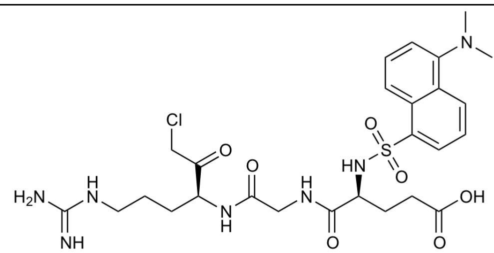
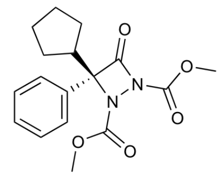
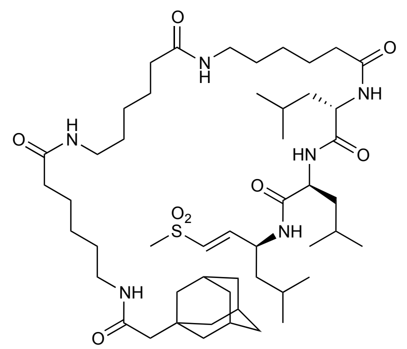
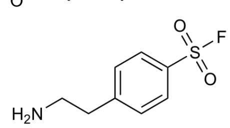
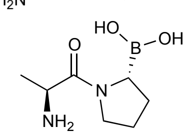
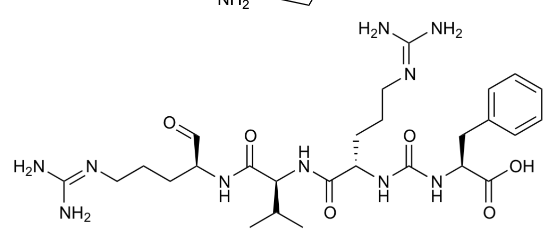
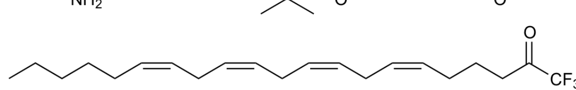
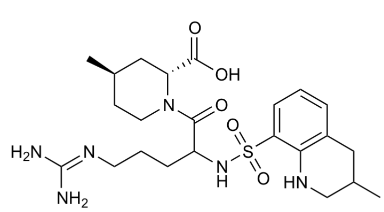
Supplementary Table 2 Enzyme panel assembled in this study.

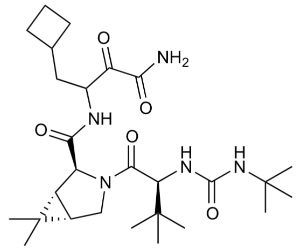
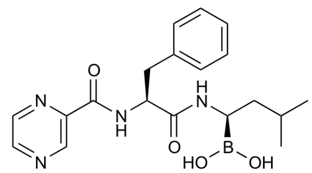
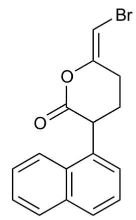
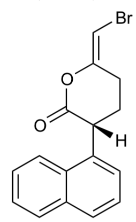
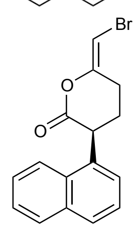
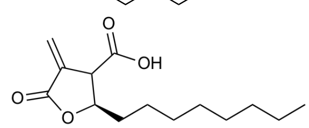
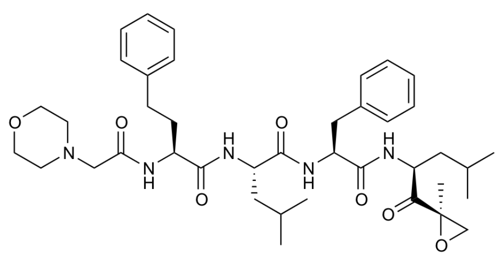
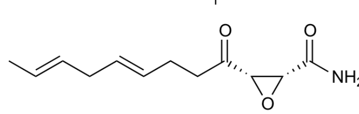
Gene Symbol	Preferred Protein Name	NCBI Gene ID	Genbank Accession number	Species	Expression system	clone	Tag	Vendor, if applicable
ABHD2	Abhydrolase domain-containing protein 2	11057	NP_008942.3	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
ABHD4	Abhydrolase domain-containing protein 4	63874	NP_071343.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
ABHD6	Monoacylglycerol lipase ABHD6	57406	NP_065727.4	*Homo sapiens*	E. coli	aa 29-end	C-terminal His/V5	
ABHD10	Mycophenolic acid acyl-glucuronide esterase, mitochondrial	55347	NP_060864.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
ABHD11	Abhydrolase domain-containing protein 11	83451	NP_683710.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
ABHD14B	Abhydrolase domain-containing protein 14B	84836	NP_001139786.1	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
ACHE	Acetylcholinesterase	11423	NP_033729.1	*Mus musculus*	HEK293T	full-length	C-terminal FLAG/His	
ACOT1	Acyl-coenzyme A thioesterase 1	641371	NP_001032238.1	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
ACOT2	Acyl-coenzyme A thioesterase 2	10965	NP_006812.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
ACOT4	Acyl-coenzyme A thioesterase 4	122970	NP_689544.3	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
AFMID	Kynurenine formamidase	125061	NP_001138998.1	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
AOAH	Acyloxyacyl hydrolase	313	NP_001628.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
APEH	Acylamino-acid-releasing enzyme	327	NP_001631.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
BCHE	Cholinesterase	590	NP_000046.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
BPHL	Valacyclovir hydrolase	670	NP_004323.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
C1R	Complement C1r subcomponent	715	NP_001724.3	*Homo sapiens*	Mouse myeloma cells	full-length	C-terminal His	R&D Systems
C1S	Complement C1s subcomponent	716	NP_958850.1	*Homo sapiens*	Mouse myeloma cells	full-length	C-terminal His	R&D Systems
C2	Complement C2	717	NP_000054.2	*Homo sapiens*	Mouse myeloma cells	aa 21-752	C-terminal His	R&D Systems
CEL	Bile salt-activated lipase	1056	NP_001798.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CELA1	Chymotrypsin-like elastase family member 1	396766	NP_998988.1	*Sus scrofa*	Porcine pancreas	aa 27-264	none	abcam
CELA2A	Chymotrypsin-like elastase family member 2A	63036	NP_254275.1	*Homo sapiens*	HEK293T	active enzyme	C-terminal FLAG/His	
CELA3A	Chymotrypsin-like elastase family member 3A	10136	NP_005738.4	*Homo sapiens*	HEK293T	active enzyme	C-terminal FLAG/His	
CELA3B	Chymotrypsin-like elastase family member 3B	23436	NP_031378.1	*Homo sapiens*	HEK293T	active enzyme	C-terminal FLAG/His	
CES1	Liver carboxylesterase 1	1066	NP_001020366.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CES2	Cocaine esterase	8824	NP_003860.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CES3	Carboxylesterase 3	23491	NP_079198.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CES4A	Carboxylesterase 4A	283848	NP_776176.5	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CES5	Carboxylesterase 5A	234673	NP_766347	*Mus musculus*	Mouse myeloma cells	full-length	C-terminal His	R&D Systems
CFD	Complement factor D	1675	NP_001919.2	*Homo sapiens*	Mouse myeloma cells	aa 26-253	C-terminal His	R&D Systems
CMA1	Chymase	1215	NP_001827.1	*Homo sapiens*	Human skin	active enyzme	none	Enzo
CPVL	Probable serine carboxypeptidase CPVL	54504	NP_112601.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CTRC	Chymotrypsin-C	514047	NP_001092435.1	*Bos taurus*	Bovine pancreas	active enyme	none	Promega
CTSA	Lysosomal protective protein	5476	NP_000299.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
CTSG	Cathepsin G	1511	NP_001902.1	*Homo sapiens*	Human neutrophils	active enzyme	none	Enzo
DDHD1	Phospholipase DDHD1	80821	NP_085140.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
DPP4	Dipeptidyl peptidase 4	1803	NP_001926.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
DPP7	Dipeptidyl peptidase 7	29952	NP_037511.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
DPP8	Dipeptidyl peptidase 8	54878	NP_569118.1	*Homo sapiens*	Insect cells	full-length	N-terminal His	Enzo

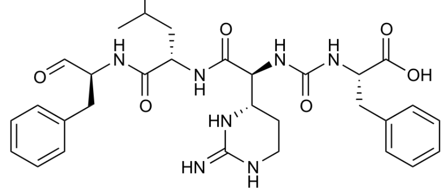
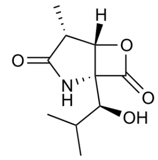
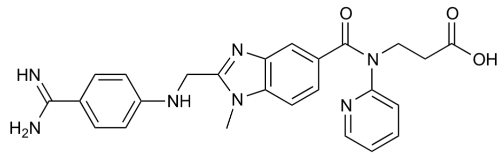
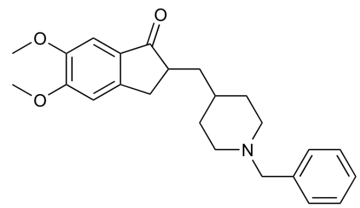
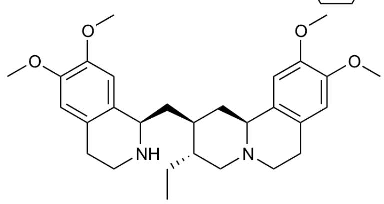
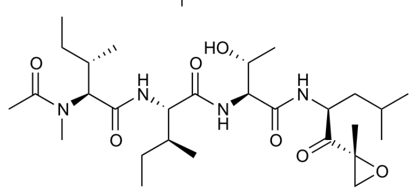
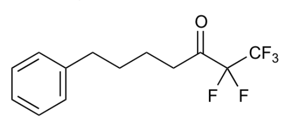
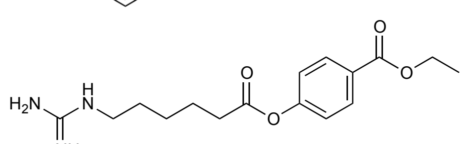
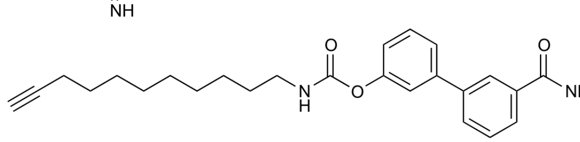
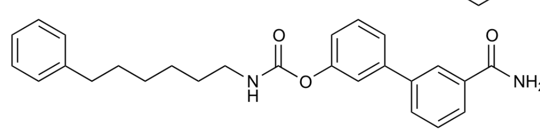
DPP9	Dipeptidyl peptidase 9	91039	NP_631898.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
ELANE	Neutrophil elastase	1991	NP_001963.1	*Homo sapiens*	Human neutrophils	active enzyme	none	Enzo
ESD	S-formylglutathione hydrolase	2098	NP_001975.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
F2	Prothrombin	2147	NP_000497.1	*Homo sapiens*	Human plasma	active enzyme	none	Enzo
F7	Coagulation factor VII	2155	NP_000122.1	*Homo sapiens*	Human plasma	active enzyme	none	Enzo
F10	Coagulation factor X	2159	NP_000495.1	*Homo sapiens*	Human plasma	active enzyme	none	Enzo
F11	Coagulation factor XI	2160	NP_000119.1	*Homo sapiens*	Human plasma	active enzyme	none	abcam
FAAH	Fatty-acid amide hydrolase 1	29347	NP_077046.1	*Rattus novegicus*	E. coli	aa 30-end	N-terminal His	
FAM108A1	Abhydrolase domain-containing protein 17A	81926	NP_112490.3	*Homo sapiens*	E. coli	aa 21-end	C-terminal His/V5	
FAM108B1	Abhydrolase domain-containing protein 17B	51104	NP_057098.2	*Homo sapiens*	E. coli	aa 20-end	C-terminal His/V5	
FAM108C1	Abhydrolase domain-containing protein 17C	58489	NP_067037.1	*Homo sapiens*	HEK293T	aa 27-end	C-terminal FLAG/His	
FAP	Seprase	2191	NP_004451.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
GZMA	Granzyme A	3001	NP_006135.1	*Homo sapiens*	E. coli	full-length	not specified	Enzo
GZMB	Granzyme B	3002	NP_004122.2	*Homo sapiens*	E. coli	full-length	not specified	Enzo
HPN	Serine protease hepsin	3249	NP_892028.1	*Homo sapiens*	Schneider 2 cells	active enzyme	C-terminal His/V5	Enzo
HTRA1	Serine protease HTRA1	56213	NP_062510.2	*Mus musculus*	HEK293T	full-length	C-terminal FLAG/His	
HTRA2	Serine protease HTRA2, mitochondrial	27429	NP_037379.1	*Homo sapiens*	E. coli	aa 234-458	C-terminal His	R&D Systems
HTRA4	Serine protease HTRA4	203100	NP_710159.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
IAH1	Isoamyl acetate-hydrolyzing esterase 1 homolog	285148	NP_001034702.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
KLK1	Kallikrein-1	3816	NP_002248.1	*Homo sapiens*	Yeast	full-length	not specified	Abcam
KLK2	Kallikrein-2	3817	NP_005542.1	*Homo sapiens*	Mouse myeloma cells	aa 67-293	C-terminal His	R&D Systems
KLK5	Kallikrein-5	25818	NP_036559.1	*Homo sapiens*	Mouse myeloma cells	full-length	C-terminal His	R&D Systems
KLKB1	Plasma kallikrein	3818	NP_000883.2	*Homo sapiens*	Human plasma	full-length	none	Abcam
LACTB	Serine beta-lactamase-like protein LACTB, mitochondrial	114294	NP_116246.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LCAT	Group XV phospholipase A2	3931	NP_000220.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LIPA	Lysosomal acid lipase/cholesteryl ester hydrolase	3988	NP_001121077.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LIPC	Hepatic triacylglycerol lipase	3990	NP_000227.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LIPE	Hormone-sensitive lipase	3991	NP_005348.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LIPF	Gastric triacylglycerol lipase	8513	NP_001185758.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LIPG	Endothelial lipase	9388	NP_006024.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LPL	Lipoprotein lipase	4023	NP_000228.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
LYPLA1	Acyl-protein thioesterase 1	10434	NP_006321.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
LYPLA1 (S119A)	Acyl-protein thioesterase 1 (S119A)	10434	NP_006321.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
LYPLA2	Acyl-protein thioesterase 2	11313	NP_009191.1	*Homo sapiens*	E. coli	full-length	C-terminal His/V5	
LYPLA2 (S122A)	Acyl-protein thioesterase 2 (S122A)	11313	NP_009191.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
LYPLAL1	Lysophospholipase-like protein 1	127018	NP_620149.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
MGLL	Monoglyceride lipase	11343	NP_009214.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
OLAH	S-acyl fatty acid synthase thioesterase, medium chain	55301	NP_060794.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
OVCA2	Ovarian cancer-associated gene 2 protein	124641	NP_543012.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
PAFAH1B2	Platelet-activating factor acetylhydrolase IB subunit beta	5049	NP_002563.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	
PAFAH1B3	Platelet-activating factor acetylhydrolase IB subunit gamma	5050	NP_001139411.1	*Homo sapiens*	E. coli	full-length	C-terminal His/myc	

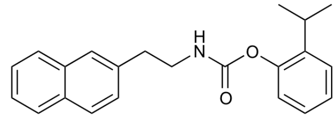
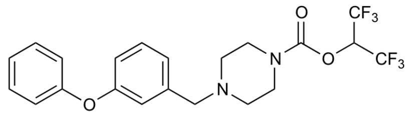
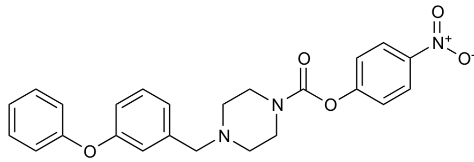
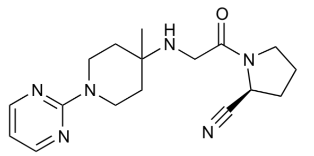
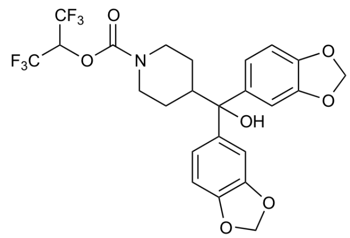
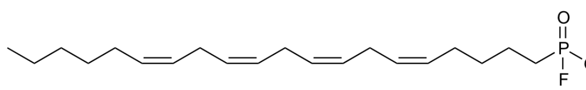
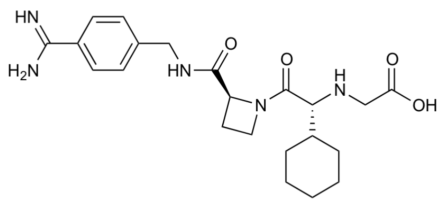
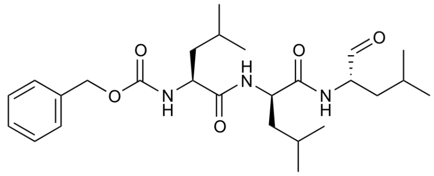
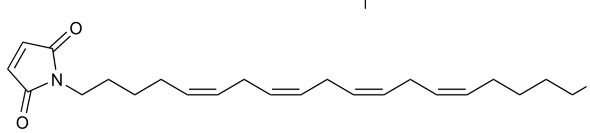
PCSK1	Neuroendocrine convertase 1	5122	NP_000430.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PCSK2	Neuroendocrine convertase 2	5126	NP_002585.2	*Homo sapiens*	CHO cells	aa 110-end	C-terminal His	R&D Systems
PLA2G15	Group XV phospholipase A2	23659	NP_036452.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PLA2G4A	Cytosolic phospholipase A2	5321	NP_077734.1	*Homo sapiens*	Spodoptera frugiperda	full-length	C-terminal His	R&D Systems
PLA2G7	Platelet-activating factor acetylhydrolase	7941	NP_005075.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PLAT	Tissue-type plasminogen activator	5327	NP_000921.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PLAU	Urokinase-type plasminogen activator	5328	NP_002649.1	*Homo sapiens*	Mouse myeloma cells	full-length	C-terminal His	R&D Systems
PLG	Plasminogen	5340	NP_000292.1	*Homo sapiens*	Human plasma	active enyzme	none	Abcam
PNLIP	Pancreatic triacylglycerol lipase	5406	NP_000927.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PNLIPRP2	Pancreatic lipase-related protein 2	5408	NP_005387.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PNPLA2	Patatin-like phospholipase domain-containing protein 2	57104	NP_065109.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PPME1	Protein phosphatase methylesterase 1	51400	NP_057231.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
PPME1 (S156A)	Protein phosphatase methylesterase 1 (S156A)	51400	NP_057231.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
PPT1	Palmitoyl-protein thioesterase 1	9374	NP_001191032.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PPT2	Lysosomal thioesterase PPT2	9374	NP_005146.4	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PRCP	Lysosomal Pro-X carboxypeptidase	5547	NP_005031.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
PREP	Prolyl endopeptidase	5550	NP_002717.3	*Homo sapiens*	E. coli	full-length	N-terminal His	
PREPL	Prolyl endopeptidase-like	9581	NP_001165074.1	*Homo sapiens*	E. coli	full-length	N-terminal His	
PROC	Vitamin K-dependent protein C	5624	NP_000303.1	*Homo sapiens*	CHO cells	aa 43-461		
PRSS1	Trypsin-1	615237	NP_001107199.1	*Bos taurus*	Bovine	active enzyme	none	Promega
PRSS8	Prostasin	5652	NP_002764.1	*Homo sapiens*	CHO cells	aa 33-319	C-terminal His	R&D Systems
PRSS22	Brain-specific serine protease 4	64063	NP_071402.1	*Homo sapiens*	Mouse myeloma cells	aa 33-317	C-terminal His	R&D Systems
PRSS27	Serine protease 27	83886	NP_114154.1	*Homo sapiens*	Mouse myeloma cells	aa 23-290	C-terminal His	R&D Systems
QRSL1	Glutamyl-tRNA(Gln) amidotransferase subunit A, mitochondrial	55278	NP_060762.3	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
RBBP9	Putative hydrolase RBBP9	10741	NP_006597.2	*Homo sapiens*	E. coli	full-length	N-terminal His	
RBBP9 (S75A)	Putative hydrolase RBBP9 (S75A)	10741	NP_006597.2	*Homo sapiens*	E. coli	full-length	N-terminal His	
SCPEP1	Retinoid-inducible serine carboxypeptidase	59342	NP_067639.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
SIAE	Sialate O-acetylesterase	54414	NP_733746.1	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	
ST14	Suppressor of tumorigenicity 14 protein	6768	NP_068813.1	*Homo sapiens*	E. coli	aa 596-855	N-terminal His	R&D Systems
TMPRSS11D	Transmembrane protease serine 11D	9407	NP_004253.1	*Homo sapiens*	Mouse myeloma cells	aa 72-418	N-terminal His	R&D Systems
TPP2	Tripeptidyl-peptidase 2	7174	NP_003282.2	*Homo sapiens*	HEK293T	full-length	C-terminal FLAG/His	

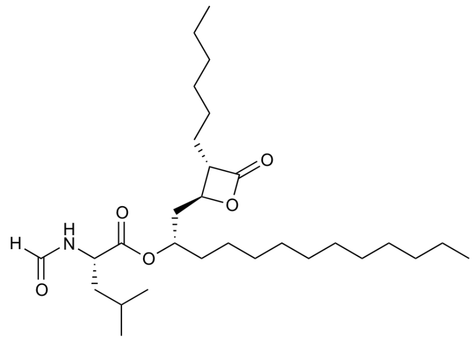
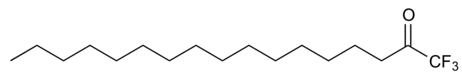
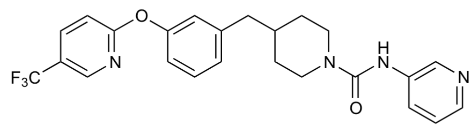
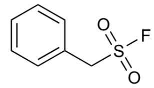
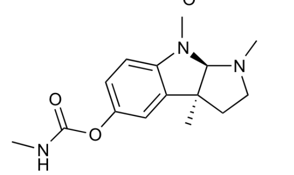
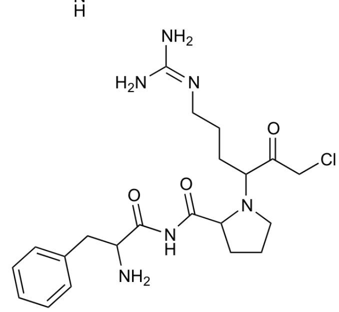
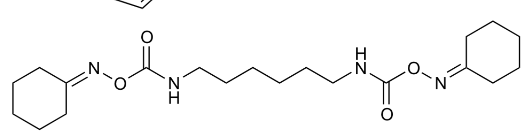
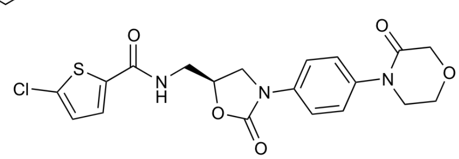
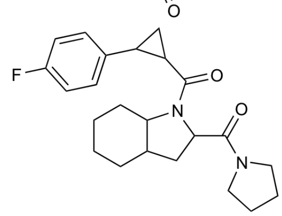
Supplementary Table 3 55 widely used inhibitors profiled in this study. These compounds were obtained from the indicated source and used without further confirmation of their purity or specific activity.

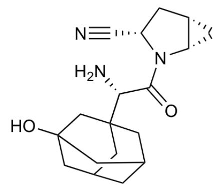
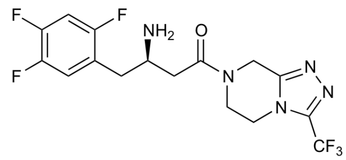
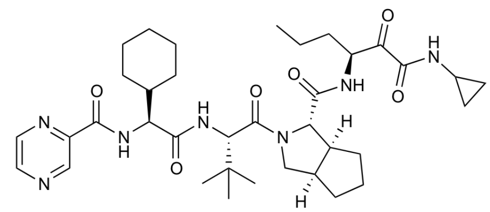
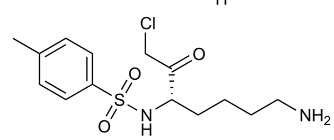
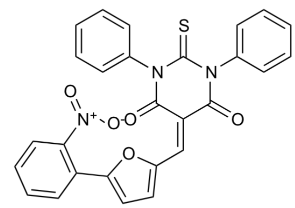
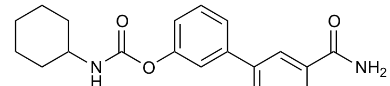
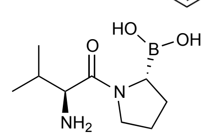
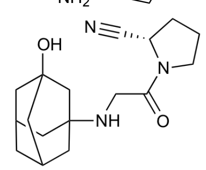
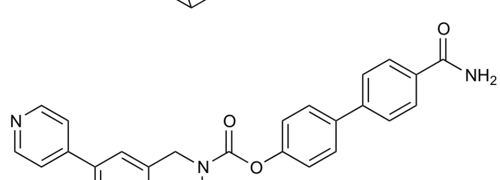
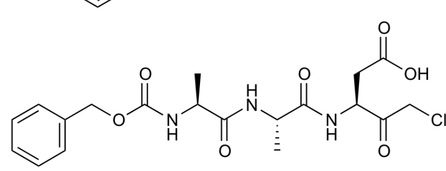
Inhibitor	Source	Structure	Primary Target(s)
1,5-Dansyl-Glu-Gly-Arg chloromethyl ketone (1,5-Dansyl-EGR-CMK)	CalBioChem		PLAU, FXa
ABL127	Sigma		PME1
Ada-(Ahx)$_3$-(Leu)$_3$-vinyl sulfone	Enzo		20S proteasome
AEBSF	Sigma		pan-serine protease inhibitor
Ala-boroPro	W. Bachovchin (Tufts Univ.)		Dipeptidyl peptidases
Antipain	Santa Cruz		many serine and cysteine proteases
Arachidonyl trifluoromethyl ketone (Arachidonyl TFMK)	Cayman Chemical		Cytosolic and calcium-independent PLA2 enzymes, FAAH
Argatroban	Sigma		Thrombin

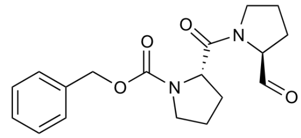
Boceprevir (Victrelis)	TRC		HCV NS3 protease
Bortezomib (Velcade)	LC Laboratories		20S proteasome
Bromoenol lactone (BEL)	Cayman Chemical		Calcium-independent PLA2 enzymes, chymotrypsin
(R)-bromoenol lactone [(R)-BEL]	Cayman Chemical		Calcium-independent PLA2 enzymes
(S)-bromoenol lactone [(S)-BEL]	Cayman Chemical		Calcium-independent PLA2 enzymes
C75	Cayman Chemical		FASN
Carfilzomib (Kyprolis)	ChemieTek		20S proteasome
Cerulenin	Cayman Chemical		FASN

Chymostatin	Santa Cruz		Chymotrypsin-like serine proteases, chymases, cysteine proteases
Clasto-Lactacystin β-lactone (active metabolite of lactacystin; also called β-clastolactacystin)	Cayman Chemical		20S proteasome
Dabigatran (active metabolite of Pradaxa)	TRC		Thrombin
Donepezil (Aricept)	Selleckchem		ACHE
Emetine	Sigma		RBBP9 (also inhibits translation *via* unknown target)
Epoxomicin	Sigma		20S proteasome
FKGK11	Cayman Chemical		Calcium-independent phospholipases
Gabexate mesylate	Enzo		Tryptase, thrombin, PLAU, PLG, FXa
JP104	Cayman		FAAH
JP83	Cayman Chemical		FAAH

JW480	Cayman Chemical		NCEH1
JW642	Cayman Chemical		MGLL
JZL195	Cayman Chemical		MGLL, FAAH
K579	Santa Cruz		DPP4
KML29	Cayman Chemical		MGLL
MAFP	Cayman Chemical		pan-serine hydolase inhibitor
Melagatran (active metabolite of Ximelagatran)	Santa Cruz		Thrombin
MG-132	Peptides International		20S proteasome
N-arachidonyl maleimide (NAM)	Santa cruz		MGLL

Orlistat (Xenical/Alli)	Cayman Chemical		Gastric/pancreatic lipases
Palmityl trifluoromethyl ketone (Palmityl TFMK)	Cayman Chemical		Calcium-independent and cytosolic PLA2 enzymes
PF-3845	Cayman Chemical		FAAH
Phenylmethanesulfonyl fluoride (PMSF)	Sigma		pan-serine protease inhibitor
Physostigmine	Enzo		ACHE, BCHE
PPACK	Santa Cruz		Thrombin
RHC 80267	Sigma		DAG lipases
Rivaroxaban (Xarelto)	Fisher		Factor Xa
S17092	Sigma		PREP

Saxagliptin (Onglyza)	TRC		DPP4
Sitagliptin (Januvia)	Sigma		DPP4
Telaprevir (Incivek/Incivo)	Selleckchem		HCV NS3 protease
TLCK	Cayman Chemical		Tryspin-like serine proteases
UCF-101	Calbiochem		HTRA2
URB597	Cayman Chemical		FAAH
Val-boroPro (Talabostat)	W. Bachovchin (Tufts Univ.)		Dipeptidyl peptidases
Vildagliptin (Zomelis)	TSZ Chem		DPP4
WWL70	Cayman Chemical		ABHD6
Z-AAD-CMK	Calbiochem		GZMB

Z-prolyl-prolinal	Santa Cruz		PREP

Supplementary Table 4 Comparison of IC_{50} values determined by EnPlex with published values. An asterisk (*) indicates that enzymes from different species were used to obtain the two values shown. Because the lowest dose evaluated by EnPlex was 5 nM, compounds inhibiting enzyme activity > 50% at that dose were assigned a value of "< 5".

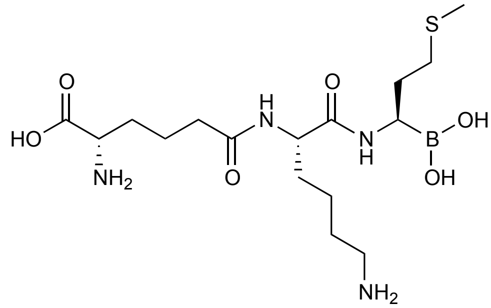
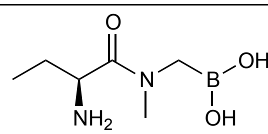
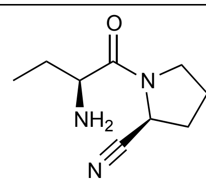
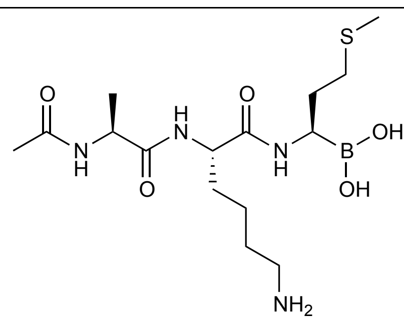
Compound	**Enzyme**	**IC_{50}**	**Published $IC_{50}/K_i/K_d$ (nM)**	**Reference**
ABL127	PME1	12.2	4.2	[1]
Ala-boroPro	DPP4	<5	2	[2]
Ala-boroPro	DPP8	1034	13	[3]
Ala-boroPro	DPP9	189.1	2.8	[3]
Antipain	Trypsin	187.8	430	[4]
Antipain	Plasmin	8167	6600	[5]
Arachidonyl TFMK	FAAH	3984	550	[6]
Arachidonyl TFMK	MGLL*	267.7	2900	[6]
Boceprevir	CMA1	4517	32	[7]
Argatroban	Thrombin	<5	12	[8]
Bortezomib	CMA1	4650	280	[9]
Bortezomib	DPP7	8512	8700	[9]
Chymostatin	Chymotrypsin*	128.8	94	[10]
Chymostatin	CMA1	1085	420	[10]
Dabigatran	Thrombin	<5	4.5	[11]
Dabigatran	FXa	28109	3760	[11]
Dabigatran	Trypsin*	1611	50.3	[11]
Donepezil	ACHE*	278.6	5.7	[12]
Emetine	RBBP9	6008	7800	[13]
Gabexate	PLAU	1348	1300	[14]
Gabexate	PLG	364.4	1600	[15]
Gabexate	KLKB1	488.2	200	[15]
Gabexate	Thrombin	1487	970	[15]
JP104	FAAH	< 5	7.3	[16]
JP83	FAAH	< 5	1.6	[16]
JW642	MGLL	53.7	3.7	[17]
JW642	FAAH	4742	14000	[17]
JW642	ABHD6*	51.3	107	[17]
JZL195	MGLL*	350.8	19	[18]
JZL195	FAAH*	12.1	13	[18]
JZL195	ABHD6*	55	50	[18]
K579	DPP4	< 5	5	[19]
KML29	MGLL	22	5.9	[17]
MAFP	FAAH	5.1	2.5	[20]
Melagatran	Thrombin	< 5	2	[21]
Melagatran	Trypsin*	15.75	4	[22]
Melagatran	PLG	2874	1400	[22]
Melagatran	KLKB1	363	690	[22]
Melagatran	FXa	2398	9400	[22]
N-arachidonyl maleimide	MGLL	194.1	140	[23]
Orlistat	PLA2G7	260	50	[24]
Palmityl TFMK	FAAH	3967	73	[6]
PPACK	Thrombin	<5	18	[25]
PF-3845	FAAH	<5	18	[26]
Physostigmine	ACHE*	1236	70	[27]
Physostigmine	BCHE	5	35	[27]
RHC 80267	PLA2G7	7438.5	23000	[24]

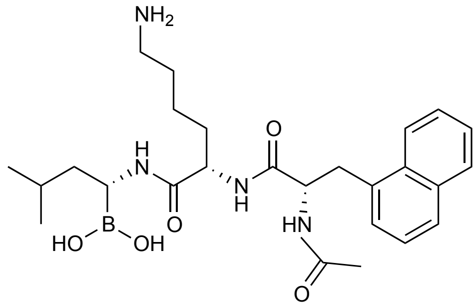
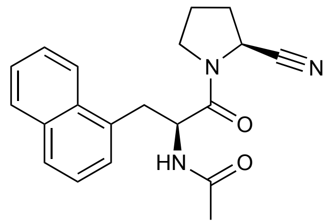
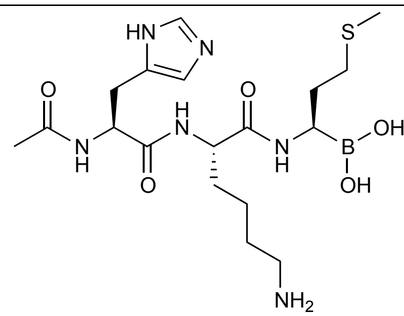
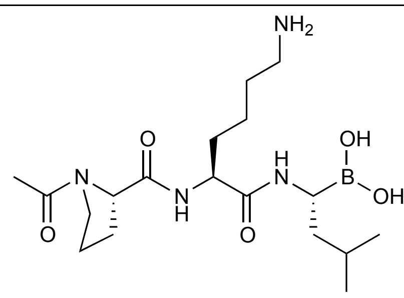
RHC 80267	FAAH	8106	10000	[24]
Rivaroxaban	FXa	<5	0.7	[28]
S17092	PREP	<5	0.9	[29]
Saxagliptin	DPP4	<5	1.3	[30]
Saxagliptin	DPP8	5323	508	[30]
Saxagliptin	DPP9	583.9	98	[30]
Sitagliptin	DPP4	7.1	18	[30]
Telaprevir	CMA1	725.2	26	[7]
Telaprevir	CELA1	221.8	30	[7]
URB597	FAAH	27.98	45	[16]
Val-boroPro	DPP4	<5	0.18	[31]
Val-boroPro	DPP8	<5	1.5	[31]
Val-boroPro	DPP9	<5	0.76	[31]
Vildagliptin	DPP4	<5	13	[30]
Vildagliptin	DPP9	219.2	258	[30]
WWL70	ABHD6*	25.23	70	[32]
Z-prolyl-prolinal	PREP	<5	14	[33]

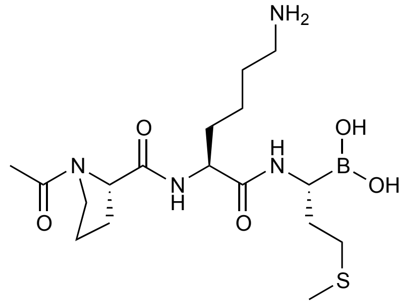
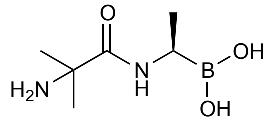
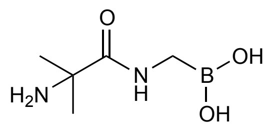
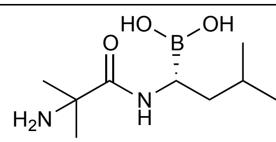
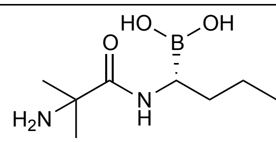
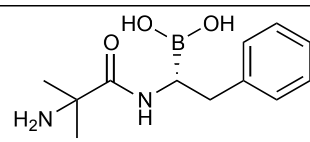
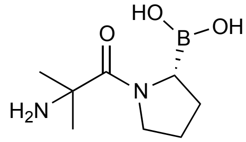
Supplementary Table 5 The serine hydrolase targets of bortezomib. An asterisk (*) indicates that enzymes from different species were used to obtain the two values shown. Published values are from ref. 9. New targets were defined as enzymes inhibited >40% at 33 μM in the EnPlex assay. ND, not determined.

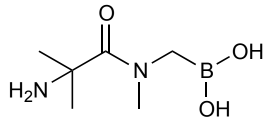
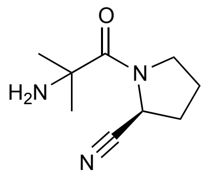
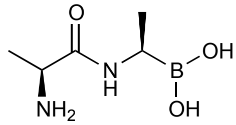
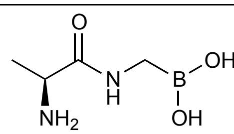
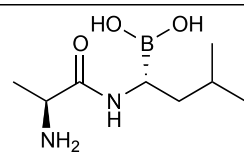
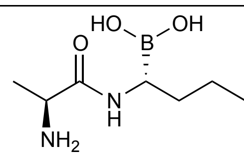
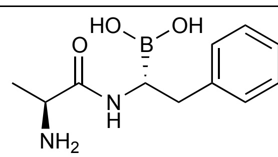
			Published values		EnPlex	
	Enzyme	**Initial Target Identification Method**	IC_{50} (μM)	% inhibition (at 10 μM)	IC_{50} (μM)	% inhibition (at 33 μM)
Previously known targets	Chymotrypsin*	Enzyme panel	ND	95	> 33	53
	CMA1	Enzyme panel	0.28	95	4.7	84.2
	CTSA	MS-ABPP	2.5	ND	> 33	32.4
	CTSG	Enzyme panel; MS-ABPP	0.95	95	36	61.8
	DPP7	MS-ABPP	8.7	ND	8.5	78.7
	ELANE	Enzyme panel	ND	40	> 33	36.1
	HTRA2	*In silico* database mining	0.003	ND	> 33	< 5
Previously unknown targets	C1R	EnPlex	-	-	>33	44.5
	FXa	EnPlex	-	-	>33	48.8
	GZMA	EnPlex	-	-	11.9	72.4
	KLKB1	EnPlex	-	-	2.0	94.2
	PRCP	EnPlex	-	-	12.4	77.9
	PRSS22	EnPlex	-	-	>33	44.4
	ST14	EnPlex	-	-	>33	51.5

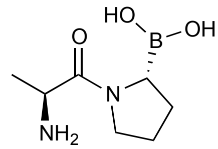
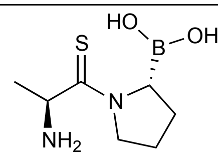
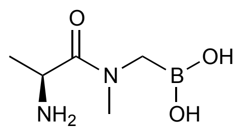
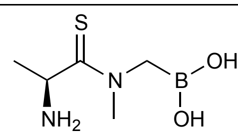
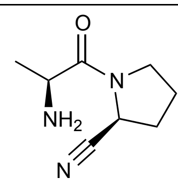
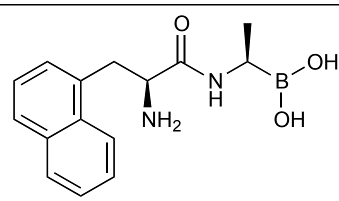
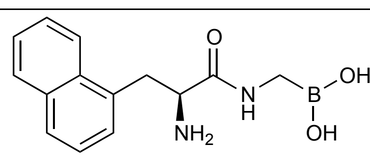
Supplementary Table 6 Numbers, names, structures, and chemical characterization of the boronic acid and nitrile library. The compound number (left column) corresponds to the compound numbers in **Figure 5** and **Supplementary Figure 8**.

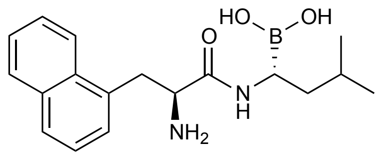
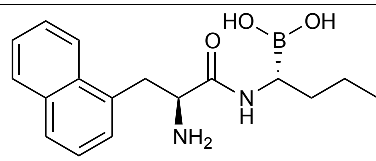
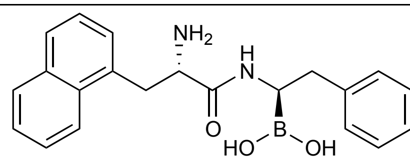
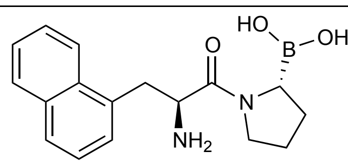
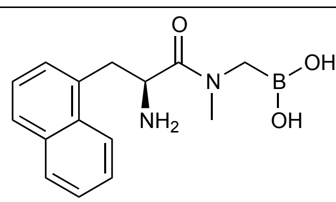
Compound Number	Compound Name	Compound Structure	Characterization or Reference
1	Aad(Lys-boroMet)		^{1}H NMR (D_2O) δ 4.44 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.91(dd, *J* = 6.1, 5.8 Hz, 1H), 3.01 (dd, *J* = 7.8, 7.1 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 1H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 2.00 - 1.60 (m, 10H), 1.50 - 1.40 (m, 2H). MS (ESI$^+$) *m/z* (rel intensity): 202.1 ([[M - H_2O]/2 + H]$^+$, 100), 403.3 ([M - H_2O + H]$^+$, 60).
2	Abu-boroSar		^{1}H NMR (D_2O) δ 4.79 (t, *J* = 6.6 Hz, 1H), 3.21 (s, 3H), 2.53 (s, 2H), 2.01 - 1.96 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (D_2O) δ 174.39, 47.50, 47.01, 38.44, 17.57. MS (ESI$^+$) *m/z* (rel intensity): 157.2 ([M - H_2O + H]$^+$, 100).
3	Abu-Pro-CN		^{1}H NMR (D_2O) δ 4.86 (dd, *J* = 7.5, 5.4 Hz, 1H), 4.32 (t, *J* = 6.0 Hz, 1H), 3.79 - 3.65 (m, 2H), 2.42 - 2.33 (m, 2H), 2.25 - 2.13 (m, 2H), 2.05 - 1.96 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 182.1 ([M + H]$^+$, 100).
4	Ac-Ala-Lys-boroMet		^{1}H NMR (D_2O) δ 4.46 (dd, *J* = 8.7, 6.0 Hz, 1H), 4.24 (q, *J* = 4.8 Hz, 1H) 2.99 (t, *J* = 7.5 Hz, 2H), 2.76 (m, 1H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.10 (s, 3H), 2.01 (s, 3H), 1.67 - 1.85 (m, 6H), 1.44 - 1.47 (m, 2H), 1.37 (d, *J* = 7.2 Hz, 1H). MS (ESI$^+$) *m/z* (rel intensity): 373.1 ([M - H_2O + H]$^+$, 100).

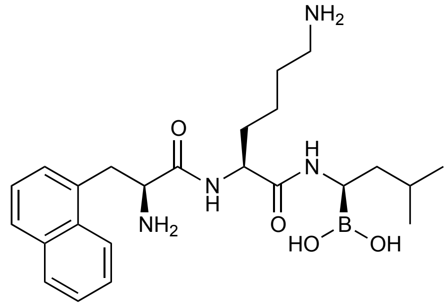
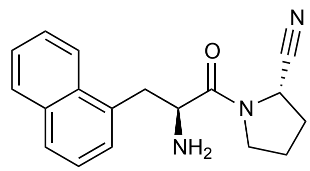
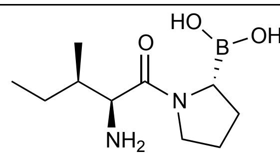
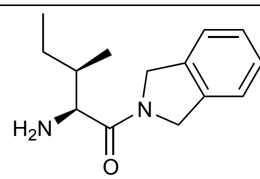
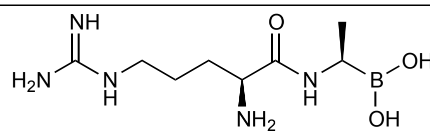
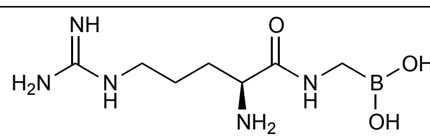
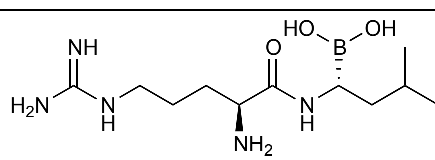
5	Ac-Ala(1-naph)-Lys-boroLeu		^{1}H NMR (D_2O) δ 8.10 (d, *J* = 7.8 Hz, 1H), 8.0 (d, *J* = 7.3 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.65 - 7.42 (m, 4H), 4.67 (m, 1H), 4.31 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.60 - 3.50 (m, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 1H), 1.94 (s, 3H), 1.62 - 1.51 (m, 5H), 1.33 -1.24 (m, 4H), 0.92 (d, *J* = 4.1 Hz, 3H), 0.90 (d, *J* = 4.0 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 481.3 ([M - H_2O + H]$^+$, 100).
6	Ac-Ala(1-naph)-Pro-CN		^{1}H NMR (D_2O) δ 8.21 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.77 - 7.59 (m, 2H), 7.51 - 7.40 (m, 2H), 5.00 - 4.80 (m, 1H), 4.65 - 4.60 (m, 1H), 3.78 (dd, *J* = 13.1, 4.9 Hz, 1H), 3.39 (t, *J* = 11.1 Hz, 2H), 3.20 (dd, *J* = 16.8, 8.0 Hz, 1H), 2.02 - 1.90 (m, 5H), 1.71 - 1.60 (m, 1H), 1.41 - 1.34 (m, 1H). MS (ESI$^+$) *m/z* (rel intensity): 358.1 ([M + Na]$^+$, 71), 336.1 ([M + H]$^+$, 100).
7	Ac-His-Lys-boroMet		^{1}H NMR (D_2O) δ 8.63 (s, 1H), 7.31 (s, 1H), 4.67 (dd, *J* = 7.5, 6.6 Hz, 1H), 4.44 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.42 - 3.15 (m, 3H), 2.98 (t, *J* = 7.6 Hz, 3H), 2.80 - 2.60 (m, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.99 (s, 3H), 1.98 (br, 1H), 1.84 - 1.68 (m, 8H), 1.50 - 1.30 (m, 4H). MS (ESI$^+$) *m/z* (rel intensity): 439.2 ([M - H_2O + H]$^+$, 100).
8	Ac-Pro-Lys-boroLeu		^{1}H NMR (D_2O) δ 4.46 - 4.35 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.0 (dd, *J* = 7.4, 7.0 Hz, 1H), 2.77 (dd, *J* = 9.0, 6.3 Hz, 1H), 2.34 - 2.29 (m, 1H), 2.11 (s, 3H), 2.00 - 1.30 (m, 15H), 0.90 (d, *J* = 3.9 Hz, 3H), 0.88 (d, *J* = 3.7 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 381.2 ([M - H_2O + H]$^+$, 100).

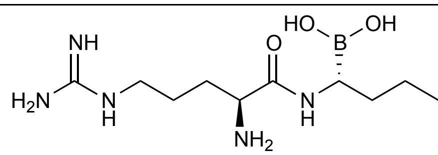
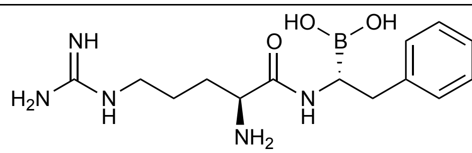
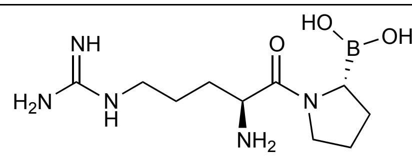
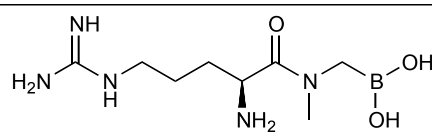
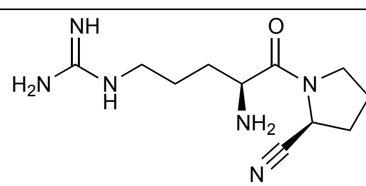
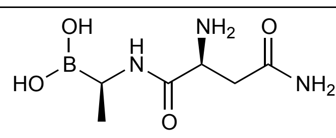
9	Ac-Pro-Lys-boroMet		^{1}H NMR (D_2O) δ 4.48 - 4.43 (m, 1H), 4.40 - 4.35(m, 1H), 3.64 (t, J = 6.6 Hz, 2H), 3.0 (t, J = 7.3Hz, 2H), 2.78 - 2.73 (m, 1H), 2.55 (dd, J = 7.5, 7.2 Hz, 2H), 2.35 - 2.25 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.00 - 1.64 (m, 10H), 1.55 - 1.35 (m, 2H). MS (ESI$^+$) *m/z* (rel intensity): 399.2 ([M - H_2O + H]$^+$, 100).
10	Aib-boroAla		^{1}H NMR (D_2O) δ 2.78 (q, J = 7.4 Hz, 1H), 1.56 (s, 3H), 1.55 (s, 3H), 1.08 (d, J = 7.4 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 313.2 ([2 × (M - H_2O) + H]$^+$, 100), 157.3 ([M - H_2O + H]$^+$, 18).
11	Aib-boroGly		^{1}H NMR (D_2O) 2.68 (s, 2H), 1.59 (s, 6H). MS (ESI+) *m/z*, (rel Intensity): 143.2 ([M - H_2O + H]$^+$, 70), 285.2 ([2 x (M - H_2O) + H]$^+$, 100).
12	Aib-boroLeu		^{1}H NMR (D_2O) δ 2.93 (dd, J = 8.0, 7.4 Hz, 1H), 1.60 (s, 6H), 1.50 (m, 1H), 1.45 - 1.30 (m, 2H), 0.90 (t, J = 4.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 199.2 ([M - H_2O + H]$^+$, 100), 397.3 ([2 x (M - H_2O) + H]$^+$, 50).
13	Aib-boroNva		^{1}H NMR (D_2O): δ 2.83 (t, J = 7.5 Hz, 1H), 1.63 (s, 6H), 1.56 - 1.47 (m, 2H), 1.40 - 1.28 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 553.4 ([3 × (M - H_2O) + H]$^+$, 4), 369.3 ([2 × (M - H_2O) + H]$^+$, 100), 185.2 ([M - H_2O + H]$^+$, 16).
14	Aib-boroPhe		^{1}H NMR (D_2O) δ 7.55 - 7.25 (m, 5H), 3.42 - 3.35 (m, 1H), 3.30 - 3.14 (dd, J = 10.2, 5.9 Hz, 1H), 2.98 (dd, J = 13.7, 5.9 Hz, 1H), 2.80 (dd, J = 13.7, 10.2 Hz, 1H), 1.55 (s, 3H), 1.50 (s, 3H). MS (ESI+) *m/z*, (rel Intensity): 245.1 ([M - H_2O + H]$^+$, 100), 263.1 ([M + H]$^+$, 40).
15	Aib-boroPro		

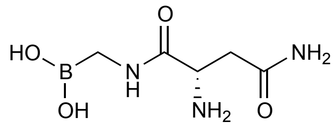
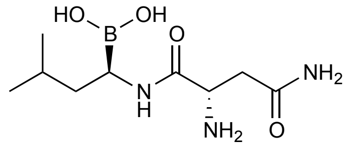
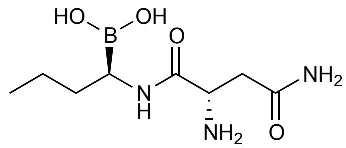
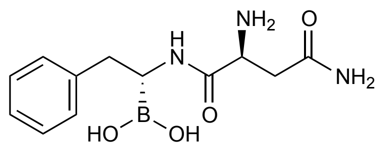
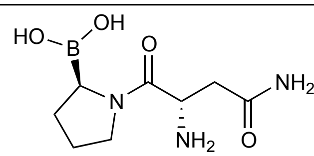
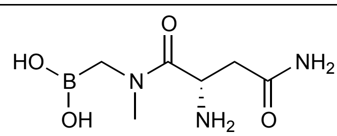
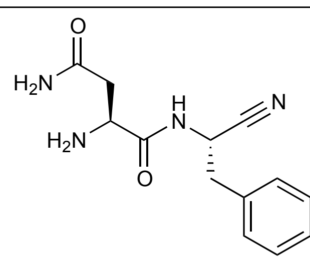
16	Aib-boroSar		^{1}H NMR (D_2O) δ 3.31 (s, 3H), 2.57 (s, 2H), 1.76 (s, 6H). ^{13}C NMR (D_2O) δ 175.92, 57.79, 50.89, 40.09, 24.64. MS (ESI^{+}) *m/z* (rel intensity): 157.1 ($[M - H_2O + H]^{+}$, 100).
17	Aib-Pro-CN		^{1}H NMR (D_2O): δ 3.93 - 3.85 (m, 2H), 3.78 - 3.69 (m, 1H), 2.34 - 2.14 (m, 4H), 1.73 (s, 3H), 1.69 (s, 3H). MS (ESI^{+}) *m/z* (rel intensity): 182.1 ($[M + H]^{+}$, 100).
18	Ala-boroAla		^{1}H NMR (D_2O) δ 4.10 (q, *J* = 6.4 Hz, 1H), 2.92 (q, *J* = 7.5 Hz, 1H), 1.53 (d, *J* = 6.4 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 3H). MS (ESI^{+}) *m/z* (rel intensity): 285.2 ($[2 \times (M - H_2O) + H]^{+}$, 100), 143.2 ($[M - H_2O + H]^{+}$, 26).
19	Ala-boroGly		^{1}H NMR (D_2O): δ 4.06 (q, *J* = 6.9 Hz, 1H), 2.78 (d, *J* = 16.9 Hz, 1H), 2.70 (d, *J* = 16.9 Hz, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). MS (ESI^{+}) *m/z* (rel intensity): 257.1 ($[2 \text{ x } (M - H_2O) + H]^{+}$, 100), 129.1 ($[M - H_2O + H]^{+}$, 73).
20	Ala-boroLeu		35
21	Ala-boroNva		^{1}H NMR (D_2O): δ 4.08 (q, *J* = 7.1 Hz, 1H), 2.86 (t, *J* = 7.5 Hz, 1H), 1.56 - 1.48 (m, 5H), 1.37 - 1.26 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI^{+}) *m/z* (rel intensity): 511.3 ($[3 \times (M - H_2O) + H]^{+}$, 32), 341.2 ($[2 \times (M - H_2O) + H]^{+}$, 100), 171.1 ($[M - H_2O + H]^{+}$, 38).
22	Ala-boroPhe		^{1}H NMR (D_2O) δ 7.55 - 7.25 (m, 5H), 4.0 (q, *J* = 7.0 Hz, 1H), 3.42 - 3.35 (m, 1H), 3.00 - 2.90 (m, 1H), 2.85 - 2.60 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H). MS (ESI+) *m/z* (rel Intensity): 219.1 ($[M - H_2O + H]^{+}$, 100), 437.2 ($[2 \text{ x } (M - H_2O) + H]^{+}$, 40).

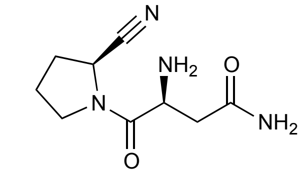
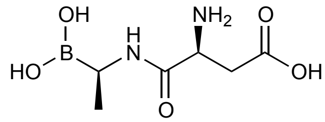
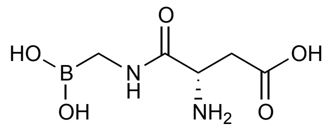
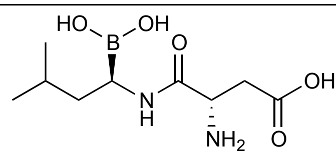
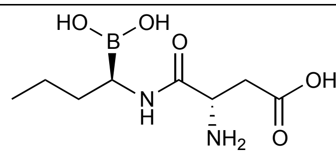
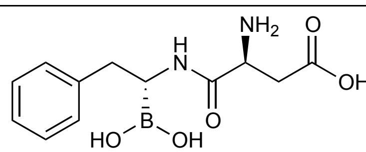
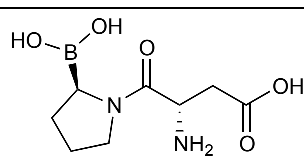
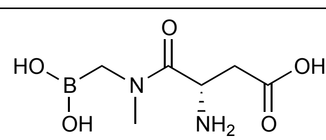
23	Ala-boroPro		34
24	Ala-boroPro thioxoamide (ARI-2243)		See **Supplementary Note 2**
25	Ala-boroSar		^{1}H NMR (D_2O) δ 4.63 (q, *J* = 6.4 Hz, 1H), 3.19 (s, 3H), 2.53 (s, 2H), 1.56 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (D_2O) δ 174.39, 47.01, 38.44, 17.57. MS (ESI$^+$) *m/z* (rel intensity): 143.1 ([M - H_2O + H]$^+$, 100).
26	Ala-boroSar thioxoamide		^{1}H NMR (D_2O) δ 4.69 (q, *J* = 6.7 Hz, 1H), 3.50 - 3.30 (m, 5H), 1.48 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (D_2O) δ 197.77, 53.23, 51.94, 44.72, 20.30. MS (ESI$^+$) *m/z* (rel intensity): 317.1 ([2 x (M - H_2O) + H]$^+$, 25), 177.1 ([M + H]$^+$, 52), 159.0 ([M - H_2O + H]$^+$, 100).
27	Ala-Pro-CN		36
28	Ala(1-naph)-boroAla		^{1}H NMR (D_2O) δ 8.07 - 7.93 (m, 3H), 7.66 - 7.47 (m, 4H), 4.28 (dd, *J* = 6.6, 9.4 Hz, 1H), 3.75 - 3.59 (m, 2H), 2.61 (q, *J* = 7.5 Hz, 1H), 0.75 (d, *J* = 7.5 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 537.3 ([2 × (M - H_2O) + H]$^+$, 25), 269.2 ([M - H_2O + H]$^+$, 100).
29	Ala(1-naph)-boroGly		^{1}H NMR (D_2O) δ 8.07 - 7.93 (m, 3H), 7.71 - 7.45 (m, 4H), 4.29 (dd, *J* = 8.4, 7.1 Hz, 1H), 3.73 - 3.60 (m, 2H), 2.51 (d, *J* = 17.0 Hz, 1H), 2.31 (d, *J* = 17.0 Hz, 1H). MS (ESI+) *m/z* (rel Intensity): 255.1 ([M - H_2O + H]$^+$, 100), 273.2 ([M + H]$^+$, 40).

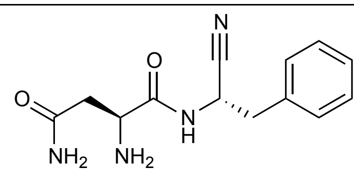
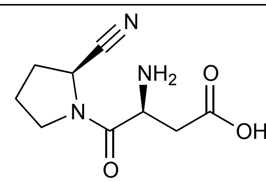
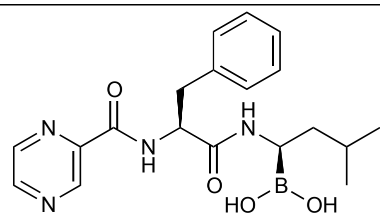
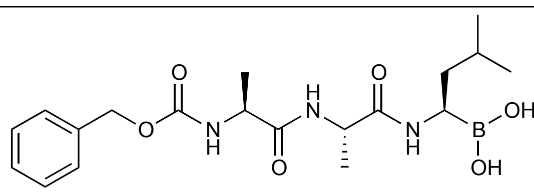
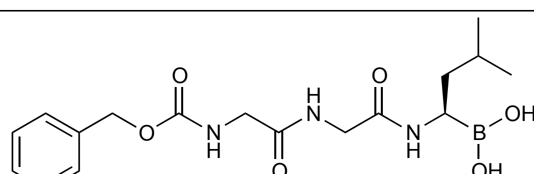
30	Ala(1-naph)-boroLeu		^{1}H NMR (D_2O) δ 8.02 -7.80 (m, 3H), 7.62 - 7.38 (m, 4H), 4.33 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.72 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.55 (dd, *J* = 13.8, 10.5 Hz, 1H), 2.52 (dd, *J* = 10.0, 5.2 Hz, 1H), 1.00 - 0.55 (m, 9H). MS (ESI$^+$) *m/z* (rel intensity): 311.2 ([M - H_2O + H]$^+$, 100).
31	Ala(1-naph)-boroNva		^{1}H NMR (D_2O): δ 8.05 - 7.90 (m, 3H), 7.65 - 7.40 (m, 4H), 4.33 (dd, *J* = 10.2, 6.1 Hz, 1H), 3.80 - 3.65 (m, 1H), 3.65 - 3.50 (m, 1H), 2.50 - 2.47 (m, 1H), 1.10 -1.00 (m, 1H), 0.90 - 0.65 (m, 6H). MS (ESI$^+$) *m/z* (rel intensity): 593.3 ([2 × (M - H_2O) + H]$^+$, 13), 337.1 ([M + Na]$^+$, 12), 297.2 ([M - H_2O + H]$^+$, 100).
32	Ala(1-naph)-boroPhe		^{1}H NMR (D_2O) δ 8.09 - 7.98 (m, 3H), 7.75 - 7.45 (m, 5H), 7.18 (m, 3H), 6.73 (m, 2H), 4.32 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.78 (dd, *J* = 13.6, 6.3 Hz, 1H), 3.70 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.85 (dd, *J* = 10.0, 5.3 Hz, 1H), 2.65 (dd, *J* = 13.9, 5.3 Hz, 1H), 2.12 (dd, *J* = 13.9, 10.5 Hz, 1H). MS (ESI$^+$) *m/z* (rel Intensity): 345.1 ([M - H_2O + H]$^+$, 100), 689.3 ([2 x (M - H_2O) + H]$^+$, 40).
33	Ala(1-naph)-boroPro		See **Supplementary Note 2**
34	Ala(1-naph)-boroSar		^{1}H NMR (D_2O) δ 8.13 - 7.97 (m, 3H), 7.73 - 7.43 (m, 4H), 4.91 (dd, *J* = 5.4, 10.9 Hz, 1H), 3.91 (dd, *J* = 13.7, 5.4 Hz, 1H), 3.60 (dd, *J* = 10.9, 13.7 Hz, 1H), 2.25 (d, *J* = 14.9 Hz, 1H), 2.16 (d, *J* = 14.9 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (D_2O) δ 172.71, 136.08, 133.67, 131.72, 131.20, 131.13, 129.87, 129.02, 128.39, 124.96, 50.52, 47.36, 37.87, 36.15. MS (ESI$^+$) *m/z* (rel intensity): 269.2 ([M - H_2O + H]$^+$, 100).

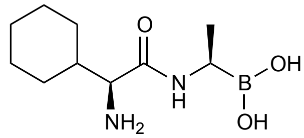
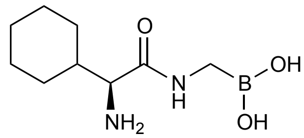
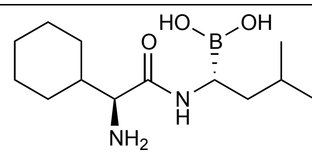
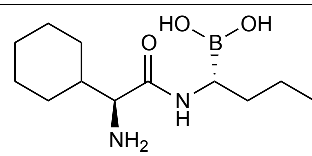
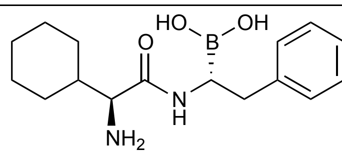
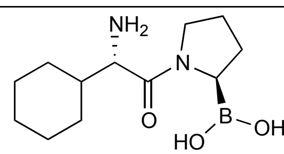
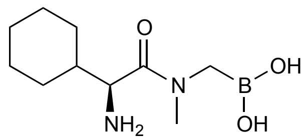
35	Ala(1-naph)-Lys-boroLeu		^{1}H NMR (D_2O) δ 8.0 (d, J = 6.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.65 - 7.42 (m, 4H), 4.31 (dd, J = 8.0, 7.6 Hz, 1H), 4.08 (t, J = 7.0 Hz, 1H), 3.68 - 3.58 (m, 2H), 2.86 (dd, J = 8.0, 7.5 Hz, 2H), 2.59 (t, J = 8.0 Hz, 1H), 1.60 - 1.48 (m, 5H), 1.31 - 1.16 (m, 4H), 0.90 (d, J = 4.7 Hz, 3H), 0.88 (d, J = 4.7 Hz, 3H). MS (ESI^{+}) m/z (rel intensity): 220.2 ([[M - H_2O]/2 + H]$^{+}$, 100), 439.2 ([M - H_2O + H]$^{+}$, 75).
36	Ala(1-naph)-Pro-CN		See **Supplementary Note 2**
37	allo-Ile-boroPro		^{1}H NMR (D_2O) δ 4.20 (t, J = 3.8 Hz, 1H), 3.67 (t, J = 9.1 Hz, 1H), 3.47 - 3.38 (m, 1H), 3.02 (dd, J = 11.4, 6.9 Hz, 1H), 2.11 - 1.87 (m, 4H), 1.70 - 1.55 (m, 1H), 1.47 - 1.31 (m, 2H), 0.95 - 0.88 (m, 6H). MS (ESI^{+}) m/z (rel intensity): 229.2 ([M + H]$^{+}$, 20), 211.2 ([M - H_2O + H]$^{+}$, 100).
38	Allo-Ile-Isoindoline		37
39	Arg-boroAla		^{1}H NMR (D_2O) δ 4.01 (t, J = 6.6 Hz, 1H), 3.23 (t, J = 6.8 Hz, 2H), 2.96 (q, J = 7.5 Hz, 1H), 1.94 - 1.88 (m, 2H), 1.68 - 1.62 (m, 2H), 1.17 (d, J = 7.5 Hz, 3H). MS (ESI^{+}) m/z (rel intensity): 246.1 ([M + H]$^{+}$, 100).
40	Arg-boroGly		^{1}H NMR (D_2O) δ 4.00 (t, J = 6.6 Hz, 1H), 3.22 (t, J = 6.8 Hz, 2H), 2.81 (d, J = 16.9 Hz, 1H), 2.73 (d, J = 16.9 Hz, 1H), 2.07 - 1.80 (m, 2H), 1.75 - 1.59 (m, 2H). MS (ESI^{+}) m/z (rel Intensity): 232.1 ([M + H]$^{+}$, 100).
41	Arg-boroLeu		^{1}H NMR (D_2O) δ 4.0 (t, J = 6.6 Hz, 1H), 3.21 (t, J = 6.8 Hz, 2H), 2.97 (dd, J = 9.4, 6.3 Hz, 1H), 1.95 - 1.86 (m, 2H), 1.67 - 1.34 (m, 5H), 0.90 (d, J = 5.8 Hz, 3H), 0.88 (d, J = 5.3 Hz, 3H).

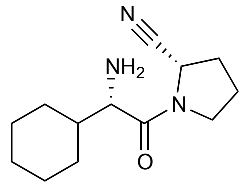
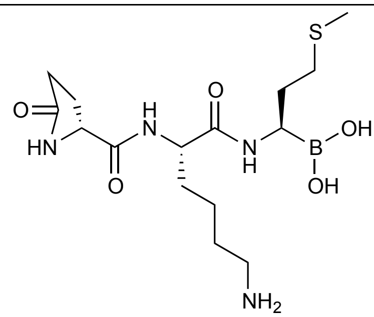
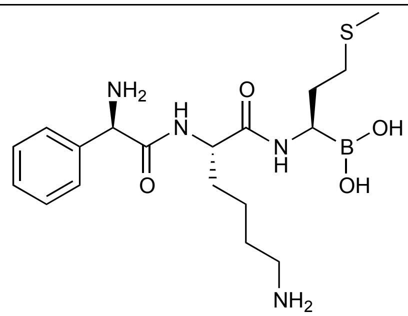
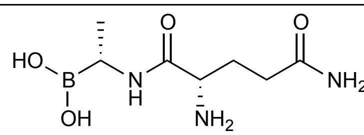
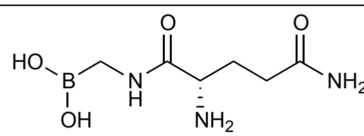
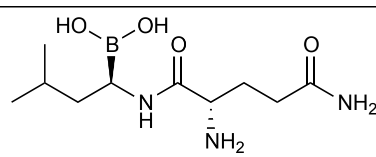
			MS (ESI$^+$) *m/z* (rel intensity): 270.2 ([M - H_2O + H]$^+$, 10), 288.2 ([M + H]$^+$, 100).
42	Arg-boroNva		^{1}H NMR (D_2O): δ 4.01 (t, *J* = 6.6 Hz), 3.22 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 1H), 1.95 - 1.87 (m, 2H), 1.66 - 1.61 (m, 2H), 1.56 - 1.49 (m, 2H), 1.37 - 1.29 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 274.2 ([M + H]$^+$, 100), 256.1 ([M - H_2O + H]$^+$, 9).
43	Arg-boroPhe		^{1}H NMR (D_2O) δ 7.50 - 7.25 (m, 5H), 3.91 (t, *J* = 6.7 Hz, 1H), 3.30 - 3.12 (m, 3H), 3.10 - 2.85 (m, 2H), 1.88 - 1.77 (m, 2H), 1.56 - 1.48 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 322.1 ([M + H]$^+$, 100).
44	Arg-boroPro		^{1}H NMR (D_2O) δ 4.34 (t, *J* = 6.1 Hz 1H), 3.74 (t, *J* = 8.3 Hz, 1H), 3.50 - 3.41 (m, 1H), 3.23 (t, *J* = 6.9 Hz, 2H), 3.10 (dd, *J* = 10.8, 7.0 Hz, 1H), 2.15 - 2.07 (m, 2H), 2.00 - 1.85 (m, 3H), 1.75 - 1.60 (m, 3H). MS (ESI$^+$) *m/z* (rel intensity): 272.2 ([M + H]$^+$, 50), 254.2 ([M - H_2O + H]$^+$, 100).
45	Arg-boroSar		^{1}H NMR (D_2O) δ 4.66 (t, *J* = 6.5 Hz 1H), 3.25 (t, *J* = 6.7 Hz, 2H), 3.22 (s, 3H), 2.57 (s, 2H), 2.04 - 1.96 (m, 2H), 1.76 - 1.64 (m, 2H). ^{13}C NMR (D_2O) δ 173.38, 159.27, 50.10, 49.65, 47.51, 42.83, 38.89, 29.69, 25.89. MS (ESI$^+$) *m/z* (rel intensity): 228.1 ([M - H_2O + H]$^+$, 100).
46	Arg-Pro-CN		
47	Asn-boroAla		^{1}H NMR (D_2O) δ 4.32 (t, *J* = 5.9 Hz, 1H), 3.04 - 2.86 (m, 3H), 1.16 (d, *J* = 7.5 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 371.2 ([2 × (M - H_2O) + H]$^+$, 63), 226.1 ([M + Na]$^+$, 34), 186.2 ([M - H_2O + H]$^+$, 100).

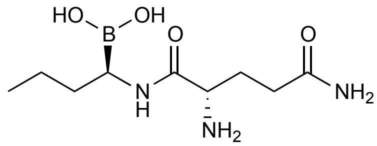
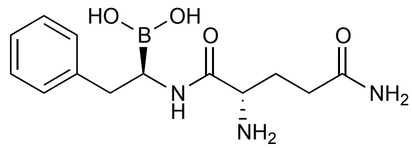
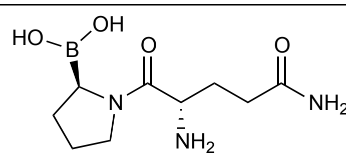
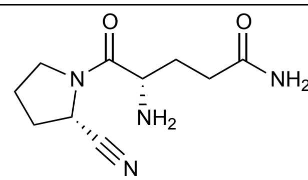
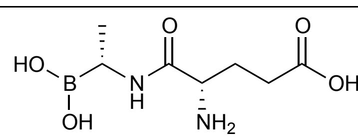
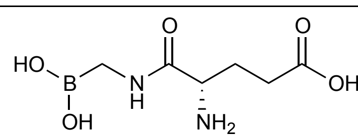
48	Asn-boroGly		^{1}H NMR (D_2O) δ 4.33 (dd, *J* = 6.9, 6.1 Hz, 1H), 3.02 - 2.89 (m, 2H), 2.82 (d, *J* = 17.1 Hz, 1H), 2.75 (d, *J* = 17.1 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 172.0 ($[M - H_2O + H]^+$, 100), 343.1 ($[2 \times (M - H_2O) + H]^+$, 50).
49	Asn-boroLeu		
50	Asn-boroNva		^{1}H NMR (D_2O): δ 4.34 (t, *J* = 6.5Hz, 1H), 3.02 - 2.88 (m, 3H), 1.59 -1.51 (m, 2H), 1.43 - 1.23 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 427.3 ($[2 \times (M - H_2O) + H]^+$, 100), 214.1 ($[M - H_2O + H]^+$, 67).
51	Asn-boroPhe		See **Supplementary Note 2**
52	Asn-boroPro		^{1}H NMR (D_2O) δ 4.10 - 4.05 (m, 1H), 3.75 - 3.70 (m, 1H), 3.55 - 3.35 (m, 1H), 3.15 - 3.05 (m, 1H), 3.00 - 2.75 (m, 2H), 2.20 - 2.05 (m, 2H), 2.02 - 1.85 (m, 1H), 1.80 - 1.65 (m, 1H). MS (ESI^+) *m/z* (rel intensity): 212.1 ($[M - H_2O + H]^+$, 100).
53	Asn-boroSar		The obtained sample was a mixture of **Asn-boroSar** (- $^6/_7$) and **Asp-boroSar** (-1/7). For **Asn-boroSar,** ^{1}H NMR (D_2O) δ 4.90 (dd, *J* = 6.0, 7.4 Hz, 1H), 3.21 (s, 3H), 3.00 - 2.93 (m, 2H), 2.58 (s, 2H). MS (ESI^+) *m/z* (rel intensity): 186.1 ($[M - H_2O + H]^+$, 100).
54	Asn-Phe-CN		^{1}H NMR (D_2O): δ 7.45 - 7.30 (m, 5H), 5.03 (t, *J* = 7.6 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 1H), 3.33 - 3.09 (m, 2H), 2.86 (d, *J* = 6.2 Hz, 2H). MS (ESI^+) *m/z* (rel intensity): 261.1 ($[M + H]^+$, 100).

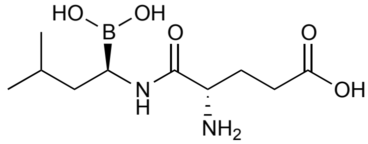
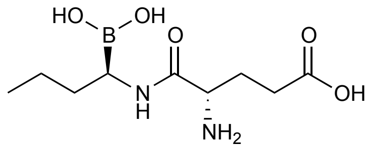
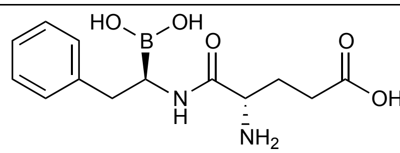
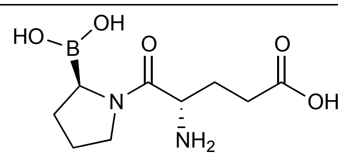
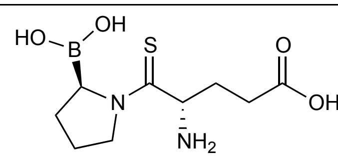
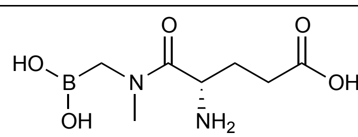
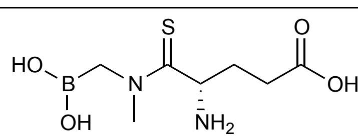
55	Asn-Pro-CN		^{1}H NMR (D_2O): δ 4.86 (dd, *J* = 7.2, 5.4 Hz, 1H), 4.63 (dd, *J* = 7.7, 5.4 Hz, 1H), 3.79 - 3.65 (m, 2H), 3.05 - 2.85 (m, 2H), 2.43 - 2.30 (m, 2H), 2.25 - 2.10 (m, 2H). MS (ESI^+) *m/z* (rel intensity): 211.1 ($[M + H]^+$, 100).
56	Asp-boroAla		^{1}H NMR (D_2O) δ 4.35 (dd, *J* = 7.0, 5.6 Hz, 1H), 3.15 - 2.90 (m, 3H), 1.18 (d, *J* = 7.5 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 373.2 ($[2 \times (M - H_2O) + H]^+$, 44), 187.1 ($[M - H_2O + H]^+$, 100).
57	Asp-boroGly		^{1}H NMR (D_2O) δ 4.33 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.15 - 2.91 (m, 3H), 2.90 - 2.70 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 173.1 ($[M - H_2O + H]^+$, 100).
58	Asp-boroLeu		^{1}H NMR (D_2O) δ 4.34 (dd, *J* = 6.3, 6.0 Hz, 1H), 3.11 - 2.96 (m, 3H), 1.60 - 1.44 (m, 2H), 1.38 - 1.21 (m, 1H), 0.89 (d, *J* = 4.9 Hz, 3H), 0.88 (d, *J* = 4.9 Hz, 3H). LCMS (ESI^+) m/z (rel intensity): 229.1 ($[M - H_2O + H]^+$, 100), 457.3 ($[2 \times (M - H_2O) + H]^+$, 55).
59	Asp-boroNva		^{1}H NMR (D_2O): δ 4.35 (dd, *J* = 6.9, 1.3 Hz, 1H), 3.06 - 3.02 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 1H), 1.57 - 1.49 (m, 2H), 1.36 - 1.28 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 429.2 ($[2 \times (M - H_2O) + H]^+$, 89), 215.1 ($[M - H_2O + H]^+$, 100).
60	Asp-boroPhe		See **Supplementary Note 2**
61	Asp-boroPro		
62	Asp-boroSar		^{1}H NMR (D_2O) major isomer (~ $^2/_3$) δ 4.28 (d, *J* = 7.2 Hz, 1H), 3.05 (d, *J* = 18.3 Hz, 1H), 2.94 (s, 3H), 2.79 (d, *J* = 18.3 Hz, 1H), 2.63 (d, *J* = 14.5 Hz, 1H), 2.45 (d, *J* = 14.5 Hz, 1H); minor

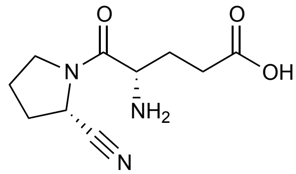
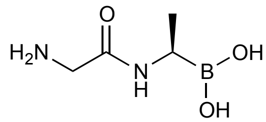
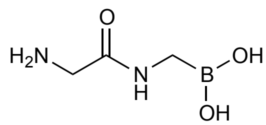
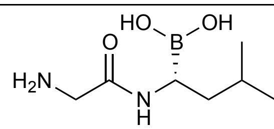
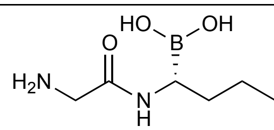
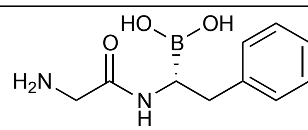
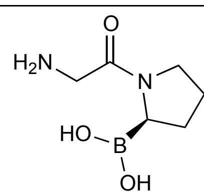
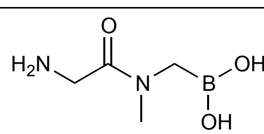
			isomer (~ $^{1}/_{3}$) δ 4.91 (dd, *J* = 5.5, 7.9 Hz, 0.5H), 3.45 (s, 1.5H), 3.20 - 3.00 (m, 1H), 2.58 (s, 1H). ^{13}C NMR (D_2O) major isomer δ 174.30, 172.20, 47.07, 38.95, 36.29; minor isomer δ 174.71, 172.20, 52.89, 48.57, 39.89, 35.55. MS (ESI^+) *m/z* (rel intensity): 187.0 ($[M - H_2O + H]^+$, 100).
63	Asp-Phe-CN		^{1}H NMR (D_2O) δ 7.43 - 7.28 (m, 5H), 5.02 (t, *J* = 7.8 Hz, 1H), 4.26 - 4.20 (m, 1H), 3.30 - 3.10 (m, 2H), 2.91 (d, *J* = 6.2 Hz, 2H). MS (ESI^+) *m/z* (rel intensity): 262.2 ($[M - H_2O + H]^+$, 100), 523.2 ($[2 \times (M - H_2O) + H]^+$, 30).
64	Asp-Pro-CN		^{1}H NMR (D_2O) δ 4.86 (dd, *J* = 6.9, 5.1 Hz, 1H), 4.64 (dd, *J* = 7.9, 5.1 Hz, 1H), 3.79 - 3.68 (m, 2H), 3.14 (dd, *J* = 17.7, 5.4 Hz, 1H), 3.0 (dd, *J* = 17.7, 8.1 Hz, 1H), 2.42 - 2.30 (m, 2H), 2.25 - 2.10 (m, 2H). MS (ESI^+) *m/z* (rel intensity): 212.2 ($[M + H]^+$, 100), 422.9 ($[2M + H]^+$, 50).
65	Bortezomib		40
66	Cbz-ala-ala-boroLeu		^{1}H NMR (D_2O) δ 7.62 (s, 5H), 5.32 (s, 2H), 4.58 (q, *J* = 7.2 Hz, 1H), 4.24 (q, *J* = 6.9 Hz, 1H), 2.93 (dd, *J* = 8.0, 6.9 Hz, 1H), 1.77 (m, 3H), 1.60 - 1.41 (m, 8H), 1.07 (t, *J* = 4.8 Hz, 6H). LCMS (ESI^+) m/z (rel intensity): 390.1 ($[M - H_2O + H]^+$, 100), 779.2 ($[2 \times (M - H_2O) + H]^+$, 50).
67	Cbz-Gly-Gly-boroLeu		^{1}H NMR (D_2O) δ 7.65 (s, 5H), 5.32 (s, 2H), 4.16 (s, 2H), 4.05 (s, 2H), 3.23 - 3.08 (m, H), 1.84 - 1.35(m, 3H), 1.07 (t, *J* = 4.8 Hz, 6H). MS (ESI^+) *m/z* (rel intensity): 362.2 ($[M - H_2O + H]^+$, 100), 723.1 ($[2 \times (M - H_2O) + H]^+$, 90).

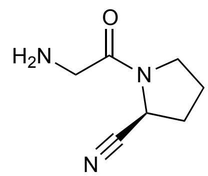
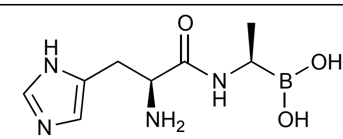
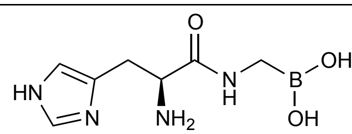
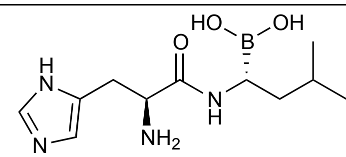
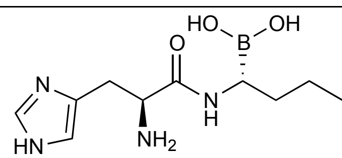
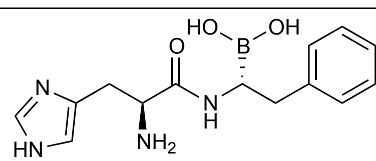
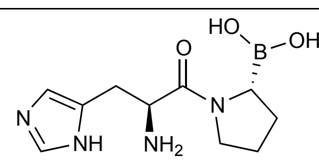
68	Chg-boroAla		[1]H NMR (D_2O) δ 3.76 (d, J = 6.6 Hz, 1H), 2.87 (q, J = 7.4 Hz, 1H), 1.90 - 1.60 (m, 6H), 1.30 - 1.05 (m, 8H). MS (ESI^+) m/z (rel intensity): 421.3 ([2 × (M - H_2O) + H]$^+$, 86), 211.2 ([M - H_2O + H]$^+$, 100).
69	Chg-boroGly		[1]H NMR (D_2O) δ 3.74 (d, J = 6.7 Hz, 1H), 2.80 (d, J = 16.9 Hz, 1H), 2.68 (d, J = 16.9 Hz, 1H), 1.86 - 1.63 (m, 7H), 1.27 - 1.03 (m, 6H). MS (ESI^+) m/z (rel Intensity): 197.2 ([M - H_2O + H]$^+$, 100), 393.3 ([2 x (M-H_2O) + H]$^+$, 70).
70	Chg-boroLeu		35
71	Chg-boroNva		[1]H NMR (D_2O): δ 3.80 (d, J = 6.4 Hz, 1H), 2.82 (t, J = 7.6 Hz, 1H), 1.80 - 1.05 (m, 15H), 0.90 (t, J = 7.2 Hz, 3H). MS (ESI^+) m/z (rel intensity): 477.4 ([2 × (M - H_2O) + H]$^+$, 26), 239.2 ([M - H_2O + H]$^+$, 100).
72	Chg-boroPhe		[1]H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.75 (d, J = 5.6 Hz, 1H), 3.18 (dd, J = 10.3, 5.4 Hz, 1H), 2.99 (dd, J = 14.2, 5.4 Hz, 1H), 2.82 (dd, J = 14.2, 10.3 Hz, 1H), 1.80 - 1.64 (m, 6H), 1.30 - 0.95 (m, 5H). MS (ESI^+) m/z (rel Intensity): 287.2 ([M - H_2O + H]$^+$, 100), 573.3 ([2 x (M - H_2O) + H]$^+$, 40).
73	Chg-boroPro		[1]H NMR (D_2O) δ 4.05 (d, J = 5.6 Hz, 1H), 3.66 (dd, J = 9.1, 8.5 Hz, 1H), 3.44 (dd, J = 6.9, 6.6 Hz, 1H), 3.00 (dd, J = 7.2, 6.0 Hz, 1H), 2.06 - 1.58 (m, 9H), 1.18 - 1.04 (m, 5H). MS (ESI^+) m/z (rel intensity): 237.2 ([M - H_2O + H]$^+$, 100).
74	Chg-boroSar		[1]H NMR (D_2O) δ 4.40 (d, J = 6.8 Hz, 1H), 3.23 (s, 3H), 2.51(d, J = 14.9 Hz, 2H), 2.00 - 1.08 (m, 11H). [13]C NMR (D_2O) δ 173.45, 54.70, 47.93, 41.84, 39.11, 30.65, 30.14, 27.76, 27.62. MS (ESI^+) m/z (rel intensity): 421.3 ([2 ×

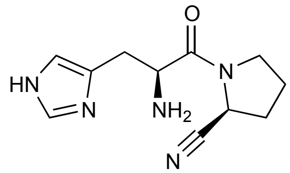
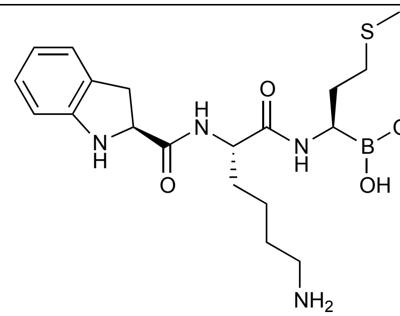
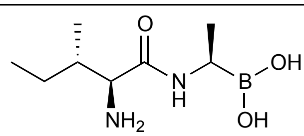
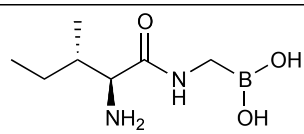
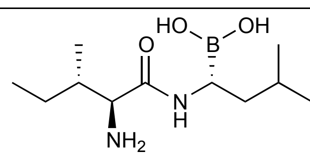
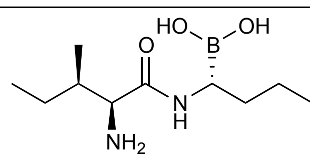
			(M - H_2O) + H]$^+$, 100), 211.1 ([M - H_2O + H]$^+$, 16).
75	Chg-Pro-CN		41
76	D-pGlu-Lys-boroMet		^{1}H NMR (D_2O) δ 4.46 (dd, J = 7.1, 7.0 Hz, 1H), 4.37 (dd, J = 8.3, 4.5 Hz, 1H), 2.96 (t, J = 7.3 Hz, 2H), 2.77 (dd, J = 8.3, 6.9 Hz, 1H), 2.65 - 2.48 (m, 3H), 2.42 (dd, J = 8.3, 7.0 Hz, 2H), 2.09 (s, 3H), 2.08 - 2.00 (m, 2H), 1.95 - 1.55 (m, 6H), 1.50 - 1.40 (m, 2H). MS(ESI$^+$) m/z (rel intensity): 373.3 ([M - H_2O + H]$^+$, 100).
77	D-Phg-Lys-boroMet		^{1}H NMR (D_2O) δ 7.26 (m, 5H), 4.92 (s, 1H), 4.28 (dd, J = 9.3, 5.3 Hz, 1H), 2.49 (m, 3H), 2.31 (dd, J = 7.2, 6.9 Hz, 2H), 1.84 (s, 3H), 1.58 - 1.35 (m, 4H), 1.25 - 1.15 (m, 2H), 0.95 - 0.80 (m, 2H). MS (ESI$^+$) m/z (rel intensity): 393.2 ([M - H_2O + H]$^+$, 100).
78	Gln-boroAla		31
79	Gln-boroGly		^{1}H NMR (D_2O) δ 4.03 (t, J = 6.6 Hz, 1H), 2.82 (d, J = 16.9 Hz, 1H), 2.73 (d, J = 16.9 Hz, 1H), 2.52 - 2.32 (m, 2H), 2.15 (dd, J = 7.3, 7.1 Hz, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 186.1 ([M - H_2O + H]$^+$, 100).
80	Gln-boroLeu		^{1}H NMR (D_2O) δ 4.44 (dd, J = 9.0, 4.9 Hz, 1H), 2.81 (dd, J = 8.4, 7.2 Hz, 1H), 2.60 - 2.40 (m, 3H), 2.15 - 2.08 (m, 1H), 1.61 - 1.56 (m, 1H), 1.41 - 1.38 (m, 1H), 1.37 - 1.29 (m, 1H), 0.89 (t, J = 4.2 Hz, 6H). MS (ESI$^+$) *m/z* (rel intensity): 225.1 ([M - H_2O + H]$^+$, 100), 449.3 ([2 x (M - H_2O) + H]$^+$, 90).

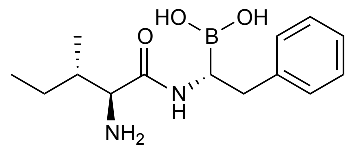
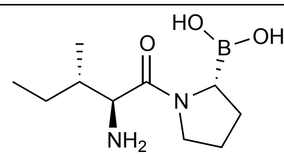
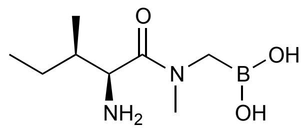
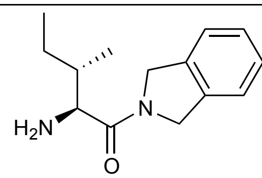
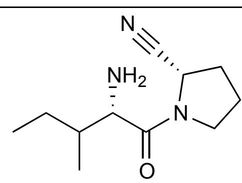
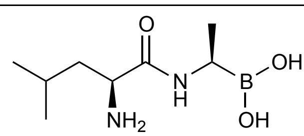
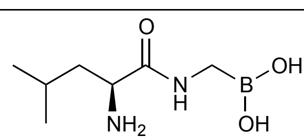
81	Gln-boroNva		^{1}H NMR (D_2O): δ 4.05 (t, *J* = 6.6 Hz, 1H), 2.93 (t, *J* = 7.4 Hz, 1H), 2.50 - 2.41 (m, 2H), 2.19 - 2.12 (m, 2H), 1.58 - 1.51 (m, 2H), 1.40 - 1.28 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 455.4 ([2 × (M - H_2O) + H]$^+$, 65), 268.2 ([M + Na]$^+$, 15), 228.2 ([M - H_2O + H]$^+$, 100).
82	Gln-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 4.38 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.12 (dd, *J* = 10.2, 5.6 Hz, 1H), 2.95 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.72 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.55 - 2.35 (m, 3H), 2.05 - 1.95 (m, 1H). MS (ESI$^+$) *m/z* (rel Intensity): 259.1 ([M - H_2O -NH_3 + H]$^+$, 100).
83	Gln-boroPro		^{1}H NMR (D_2O) δ 4.36 (t, *J* = 6.0 Hz, 1H), 3.70 (dt, *J* = 8.3, 2.1 Hz, 1H), 3.52 - 3.42 (m, 1H), 3.09 (dd, *J* = 10.8, 7.0 Hz, 1H), 2.51 - 2.41 (m, 2H), 2.21 - 2.07 (m, 4H), 1.97 - 1.92 (m, 1H), 1.75 - 1.71 (m, 1H). MS (ESI$^+$) *m/z* (rel intensity): 209.1 ([M - H_2O - NH_3 + H]$^+$, 15), 226.1 ([M - H_2O + H]$^+$, 100), 244.1 ([M + H]$^+$, 10).
84	Gln-Pro-CN		^{1}H NMR (D_2O) δ 4.85 (dd, *J* = 7.5, 5.4 Hz, 1H), 4.42 (t, *J* = 5.9 Hz, 1H), 3.80 - 3.64 (m, 2H), 2.63 (t, *J* = 10.8, 7.0 Hz, 2H), 2.43 - 2.12 (m, 6H). MS (ESI$^+$) *m/z* (rel intensity): 208.1 ([M - NH_3 + H]$^+$, 70), 225.1 ([M + H]$^+$, 100).
85	Glu-boroAla		
86	Glu-boroGly		^{1}H NMR (D_2O): δ 4.20 (t, *J* = 6.8 Hz, 1H), 2.81 (d, *J* = 16.9 Hz, 1H), 2.71 (d, *J* = 16.9 Hz, 1H), 2.54 (t, *J* = 7.3 Hz, 2H), 2.14 (dd, *J* = 7.2, 6.7 Hz, 2H). MS (ESI$^+$) *m/z* (rel intensity): 355.1 ([2 x (M - H_2O) - H_2O + H]$^+$, 63), 205.2 ([M + H]$^+$, 34), 187.1 ([M - H_2O + H]$^+$, 100); 169.1 ([M - 2 x H_2O + H]$^+$, 55).

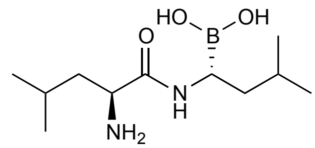
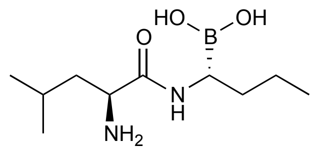
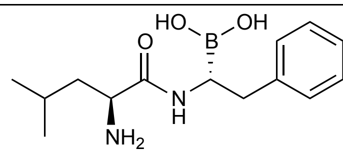
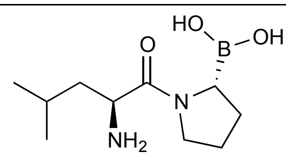
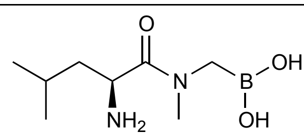
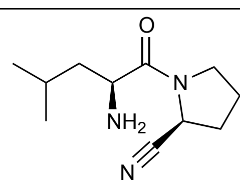
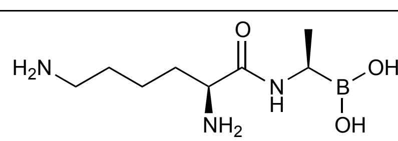
87	Glu-boroLeu		^{1}H NMR (D_2O) δ 4.08 (t, *J* = 6.9 Hz, 1H), 2.98 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.60 - 2.45 (m, 2H), 2.21 - 2.13 (m, 2H), 1.61 - 1.35 (m, 3H), 0.90 (t, *J* = 5.7 Hz, 6H). MS (ESI$^+$) *m/z* (rel intensity): 225.1 ([M - $2H_2O$ + H]$^+$, 25), 243.1 ([M - H_2O + H]$^+$, 100), 467.3 ([2 x (M - H_2O) + H]$^+$, 90).
88	Glu-boroNva		^{1}H NMR (D_2O): δ 4.07 (t, *J* = 6.7 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 1H), 2.57 - 2.51 (m, 2H), 2.20 - 2.13 (m, 2H), 1.57 - 1.50 (m, 2H), 1.38 - 1.30 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 439.2 ([2 × M - 3 × H_2O + H]$^+$, 100), 229.1 ([M - H_2O + H]$^+$, 75).
89	Glu-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.99 (t, *J* = 6.3 Hz, 1H), 3.25 (dd, *J* = 10.1, 6.2 Hz, 1H), 2.98 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.88 (dd, *J* = 14.0, 10.1 Hz, 1H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.08 (dt, *J* = 7.5, 6.3 Hz, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 277.1 ([M - H_2O + H]$^+$, 100), 295.1([M + H]$^+$, 20).
90	Glu-boroPro		
91	Glu-boroPro thioxoamide		^{1}H NMR (D_2O) δ 4.65 (t, *J* = 6.2 Hz, 1H), 4.10 - 3.95 (m, 1H), 3.75 - 3.65 (m, 1H), 3.58 (t, *J* = 8.3 Hz, 1H), 2.63 (t, 2H), 2.30 - 1.85 (m, 6H). MS (ESI$^+$) *m/z* (rel intensity): 261.1 ([M + H]$^+$, 100).
92	Glu-boroSar		^{1}H NMR (D_2O) δ 2.21 (dt, *J* = 6.4, 7.1 Hz, 2H), 2.50 (s, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 3.22 (s, 3H), 4.69 (t, *J* = 6.4 Hz, 1H). ^{13}C NMR (D_2O) δ 178.12, 173.15, 49.61, 47.48, 38.74, 30.96, 27.43. MS (ESI$^+$) *m/z* (rel intensity): 201.1 ([M - H_2O + H]$^+$, 100).
93	Glu-boroSar thioxoamide (ARI-2408)		See **Supplementary Note 2**

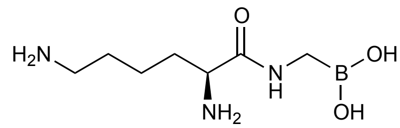
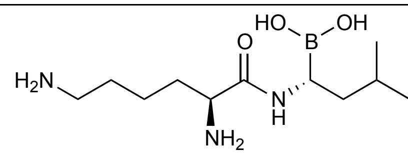
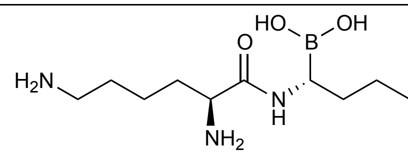
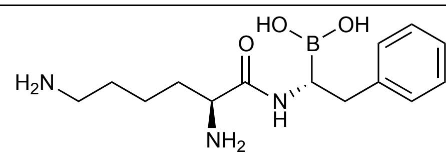
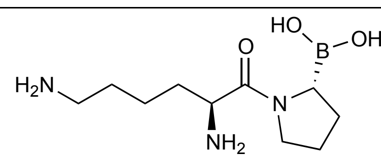
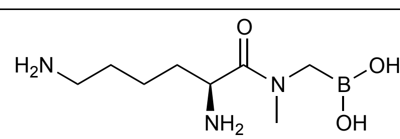
94	Glu-Pro-CN		^{1}H NMR (D_2O) δ 4.85 (dd, J = 7.5, 5.3 Hz, 1H), 4.45 (t, J = 6.0 Hz, 1H), 3.83 - 3.66 (m, 2H), 2.63 (t, J = 10.8, 7.0 Hz, 2H), 2.43 - 2.12 (m, 6H). MS (ESI^+) m/z (rel intensity): 208.1 ($[M - H_2O + H]^+$, 70), 226.1 ($[M + H]^+$, 100).
95	Gly-boroAla		^{1}H NMR (D_2O) δ 3.82 (s, 2H), 2.98 (q, J = 7.5 Hz, 1H), 1.16 (d, J = 7.5 Hz, 3H). MS (ESI^+) m/z (rel intensity): 257.2 ($[2 \times (M - H_2O) + H]^+$, 100), 169.2 ($[M + Na]^+$, 6), 129.3 ($[M - H_2O + H]^+$, 23).
96	Gly-boroGly		^{1}H NMR (D_2O) δ 3.80 (s, 2H), 2.76 (s, 2H). ^{13}C NMR (D_2O) δ 171.19, 47.07, 38.09. MS (ESI^+) m/z (rel intensity): 115.1 ($[M - H_2O + H]^+$, 100).
97	Gly-boroLeu		35
98	Gly-boroNva		^{1}H NMR (D_2O): δ 3.84 (s, 2H), 2.98 (t, J = 7.3 Hz, 1H), 1.59 - 1.51 (m, 2H), 1.39 - 1.29 (m, 2H), 0.90 (t, J = 7.1 Hz, 3H). MS (ESI^+) m/z (rel intensity): 469.3 ($[3 \times (M - H_2O) + H]^+$, 20), 313.2 ($[2 \times (M - H_2O) + H]^+$, 100), 157.1 ($[M - H_2O + H]^+$, 63).
99	Gly-boroPhe		See **Supplementary Note 2**
100	Gly-boroPro		42
101	Gly-boroSar		^{1}H NMR (D_2O) δ 4.18 (s, 2H), 3.10 (s, 3H), 2.55 (s, 2H). ^{13}C NMR (D_2O) δ 171.19, 46.47, 39.84, 38.11. MS (ESI^+) m/z (rel intensity): 129.2 ($[M - H_2O + H]^+$, 100).

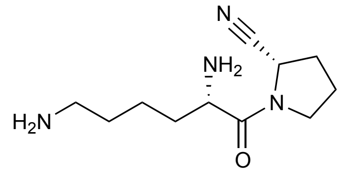
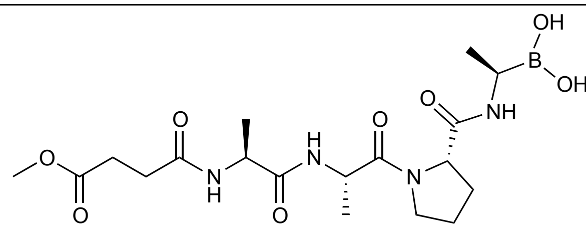
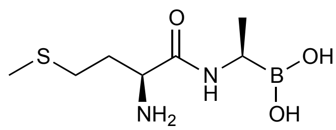
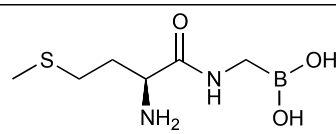
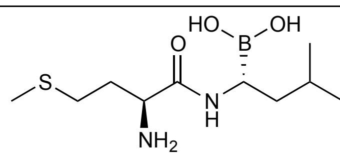
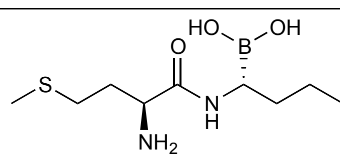
102	Gly-Pro-CN		43
103	His-boroAla		^{1}H NMR (D_2O) 8.70 (s, 1H). 7.44 (s, 1H), 4.23 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.40 - 3.35 (m, 2H), 2.99 (q, *J* = 7.5 Hz, 1H), 1.09 (d, *J* = 7.5 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 417.3 ([2 × (M - H_2O) + H]$^+$, 21), 209.2 ([M - H_2O + H]$^+$, 100).
104	His-boroGly		^{1}H NMR (D_2O) δ 8.70 (s, 1H), 7.44 (s, 1H), 4.26 (t, *J* = 7.1 Hz, 1H), 3.38 (d, *J* = 7.1 Hz, 2H), 2.75 (s, 2H). MS (ESI^+) *m/z* (rel Intensity): 195.0 ([M - H_2O + H]$^+$, 100), 213.0 ([M + H]$^+$, 20).
105	His-boroLeu		35
106	His-boroNva		^{1}H NMR (D_2O): δ 8.72 (s, 1H), 7.45 (s, 1H), 4.25 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.43 - 3.31 (m, 2H), 2.95 (dd, *J* = 8.5, 2.1 Hz, 1H), 1.51 - 1.38 (m, 2H), 1.22 - 1.14 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 473.3 ([2 × (M - H_2O) + H]$^+$, 19), 237.2 ([M - H_2O + H]$^+$, 100).
107	His-boroPhe		^{1}H NMR (D_2O) δ 8.63 (s, 1H), 7.45 - 7.07 (m, 6H), 4.20 (dd, *J* = 7.4, 7.1 Hz, 1H), 3.40 - 3.20 (m, 13H), 2.92 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.79 (dd, *J* = 14.1, 9.6 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 285.1 ([M - H_2O + H^+], 100).
108	His-boroPro		34

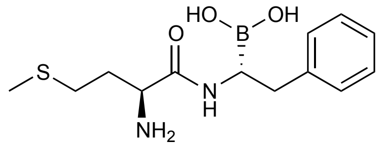
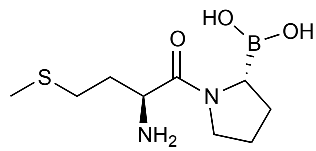
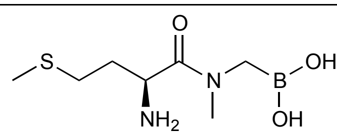
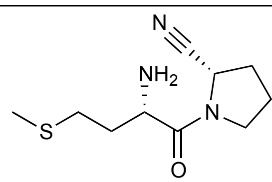
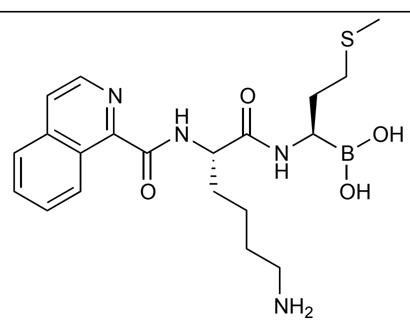
109	His-Pro-CN		^{1}H NMR (D_2O) δ 8.76 (s, 1H), 7.49 (s, 1H), 4.83 (dd, *J* = 7.2, 5.3 Hz, 1H), 4.67 (t, *J* = 6.9 Hz, 1H), 3.74 - 3.65 (m, 1H), 3.51 - 3.41 (m, 3H), 2.37 - 2.27 (m, 2H), 2.14 - 2.06 (m, 2H). MS (ESI^+) *m/z* (rel intensity): 234.1 ($[M + H]^+$, 100).
110	Ica-Lys-boroMet		^{1}H NMR (D_2O) δ 7.42 - 7.25 (m, 4H), 4.78 (br, 1H), 4.50 (t, *J* = 7.3 Hz, 1H), 3.71 (d, *J* = 10.0 Hz, 1H), 3.36 (d, *J* = 6.0 Hz, 1H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.78 (dd, *J* = 8.3, 6.3 Hz, 1H), 2.04 (s, 3H), 1.95 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel intensity): 405.1 ($[M - H_2O + H]^+$, 100).
111	Ile-boroAla		^{1}H NMR (D_2O) δ 3.88 (d, *J* = 6.4 Hz, 1H), 2.89 (q, *J* = 7.5 Hz, 1H), 2.00 - 1.93 (m, 1H), 1.60 -1.19 (m, 2H), 1.16 (d, *J* = 7.5 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 6.7 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 553.3 ($[2 \times (M - H_2O) + H]^+$, 100), 185.2 ($[M - H_2O + H]^+$, 28).
112	Ile-boroGly		^{1}H NMR (D_2O) δ 3.85 (d, *J* = 6.2 Hz, 1H), 2.81 (d, *J* = 16.8 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 1.98 - 1.92 (m, 2H), 1.56 - 1.48 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 171.1 ($[M - H_2O + H]^+$, 100), 341.2 ($[2 x (M - H_2O) + H]^+$, 80).
113	Ile-boroLeu		^{1}H NMR (D_2O) δ 3.90 (d, *J* = 5.8 Hz, 1H), 2.90 (dd, *J* = 9.4, 6.5 Hz, 1H), 2.03 - 1.97 (m, 1H), 1.57 - 1.25 (m, 5H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.98 - 0.88 (m, 9H). MS (ESI^+) *m/z* (rel intensity): 227.1 ($[M - H_2O + H]^+$, 70), 453.3 ($[2 x (M - H_2O) + H]^+$, 100).
114	Ile-boroNva		^{1}H NMR (D_2O): δ 3.88 (d, *J* = 5.9 Hz, 1H), 2.81 (t, *J* = 7.5 Hz, 1H), 1.99 - 1.93 (m, 1H), 1.55 - 1.23 (m, 6H), 1.00 - 0.86 (m, 9H). MS (ESI^+) *m/z* (rel intensity): 637.5 ($[3 \times (M - H_2O) + H]^+$, 4), 425.3 ($[2 \times (M - H_2O) + H]^+$, 100), 213.2 ($[M - H_2O + H]^+$, 29).

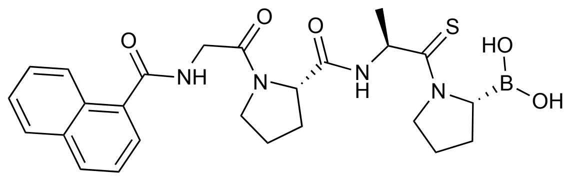
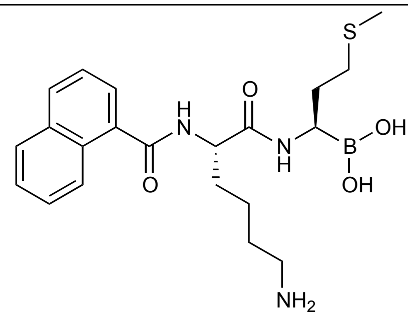
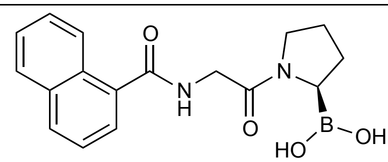
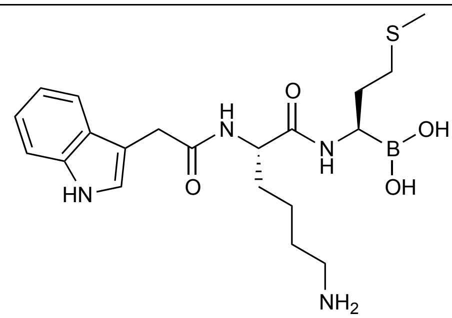
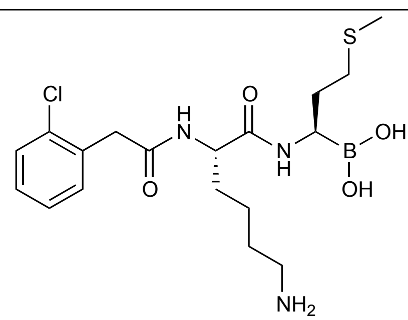
115	Ile-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.76 (m, 1H), 3.10 (m, 1H), 2.95 - 2.92 (m, 1H), 2.79 - 2.73 (m, 1H), 1.88 (m, 1H), 1.21 - 1.10 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 261.1 ($[M - H_2O + H]^+$, 100), 521.3 ($[2 \times (M - H_2O) + H]^+$, 40).
116	Ile-boroPro		[34]
117	Ile-boroSar		^{1}H NMR (D_2O) δ 4.47 (d, *J* = 6.4 Hz, 1H), 3.24 (s, 3H), 2.54 (dd, *J* = 14.9, 7.9 Hz, 2H), 1.60 - 1.21 (m, 2H), 2.12 - 2.07 (m, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (D_2O) δ 173.49, 54.59, 47.85, 39.16, 38.91, 26.34, 16.44, 12.84. MS (ESI^+) *m/z* (rel intensity): 185.1 ($[M - H_2O + H]^+$, 100).
118	Ile-Isoindoline		[44]
119	Ile-Pro-CN		[45]
120	Leu-boroAla		^{1}HNMR (D_2O) δ 3.96 (t, *J* = 7.2 Hz, 1H), 2.82 (q, *J* = 7.5 Hz, 1H), 1.71 - 1.55 (m, 3H), 1.08 (d, *J* = 7.5 Hz, 3H), 0.90 - 0.86 (m, 6H). MS (ESI^+) *m/z* (rel intensity): 369.3 ($[2 \times (M - H_2O) + H]^+$, 100), 185.2 ($[M - H_2O + H]^+$, 57).
121	Leu-boroGly		^{1}H NMR (D_2O) δ 3.99 (dd, *J* = 7.4, 7.1 Hz, 1H), 2.80 (d, *J* = 16.8 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 1.80 - 1.58 (m, 2H), 0.96 - 0.88 (m, 6H). MS (ESI^+) *m/z* (rel Intensity): 171.1 ($[M - H_2O + H]^+$, 100), 341.2 ([2 x (M -

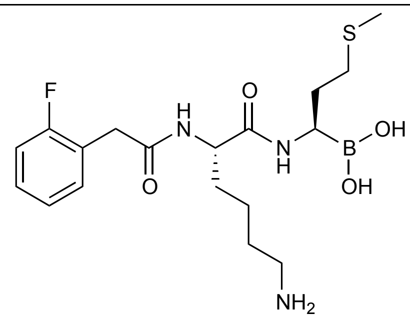
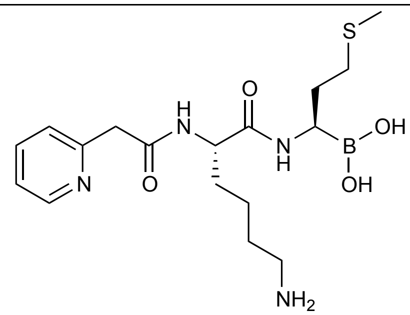
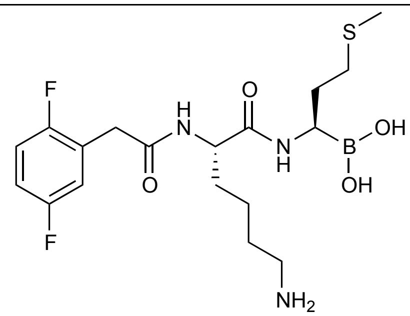
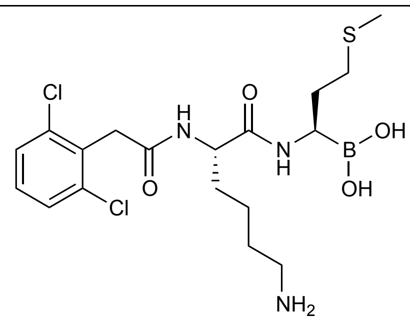
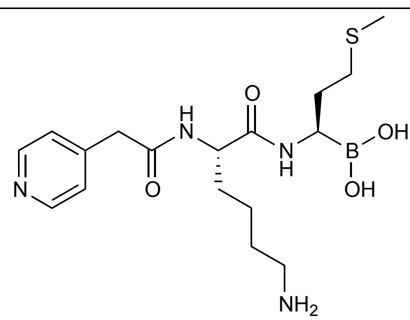
			$H_2O) + H]^+$, 95).
122	Leu-boroLeu		35
123	Leu-boroNva		^{1}H NMR (D_2O): δ 4.03 (t, *J* = 7.0 Hz, 1H), 2.85 (t, *J* = 7.3 Hz, 1H), 1.78 - 1.63 (m, 3H), 1.56 - 1.49 (m, 2H), 1.39 - 1.28 (m, 2H), 0.97 - 0.90 (m, 9H). MS (ESI^+) *m/z* (rel intensity): 637.6 ($[3 \times (M - H_2O) + H]^+$, 3), 425.3 ($[2 \times (M - H_2O) + H]^+$, 100), 213.2 ($[M - H_2O + H]^+$, 57).
124	Leu-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.91 (t, *J* = 7.0 Hz, 1H), 3.16 (dd, *J* = 10.0, 5.7 Hz, 1H), 2.99 (dd, *J* = 14.0, 5.7 Hz, 1H), 2.79 (dd, *J* = 14.0, 10.0 Hz, 1H), 1.50 - 1.30 (m, 3H), 0.95 - 0.91 (m, 6H). MS (ESI^+) *m/z* (rel Intensity): 261.1 ($[M - H_2O + H]^+$, 100), 521.3 ($[2 \text{ x } (M - H_2O) + H]^+$, 40).
125	Leu-boroPro		34
126	Leu-boroSar		^{1}H NMR (D_2O) δ 4.58 (dd, *J* = 5.3, 3.2 Hz, 2H), 3.21 (s, 3H), 2.54 (s, 2H), 1.86 - 1.72 (m, 3H), 0.99 (d, *J* = 5.3 Hz, 6H). ^{13}C NMR (D_2O) δ 174.13, 49.18, 47.55, 41.17, 38.68, 26.27, 24.98, 24.59, 23.10, 22.79. MS (ESI^+) *m/z* (rel intensity): 185.1 ($[M - H_2O + H]^+$, 100).
127	Leu-Pro-CN		^{1}H NMR (D_2O) δ 4.86 (dd, *J* = 7.5, 5.2 Hz, 1H), 4.33 - 4.29 (m, 1H), 3.74 - 3.66 (m, 2H), 2.45 - 2.25 (m, 2H), 2.23 - 2.12 (m, 2H), 2.10 - 1.73 (m, 3H), 1.01 (t, *J* = 2.5 Hz, 6H). MS (ESI^+) *m/z* (rel intensity): 210.2 ($[M + H]^+$, 100).
128	Lys-boroAla		^{1}H NMR (D_2O) δ 4.00 (t, *J* = 6.6 Hz, 1H), 3.02 - 2.92 (m, 3H), 1.96 - 1.88 (m, 2H), 1.76 - 1.66 (m, 2H), 1.50 - 1.40 (m, 2H), 1.18 (d, *J* = 7.5 Hz, 3H).

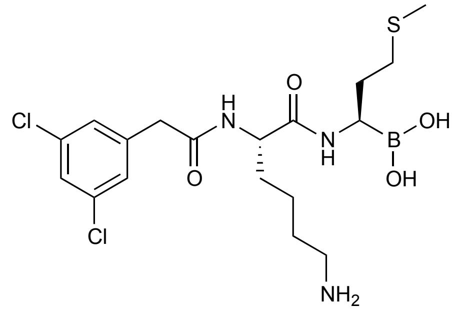
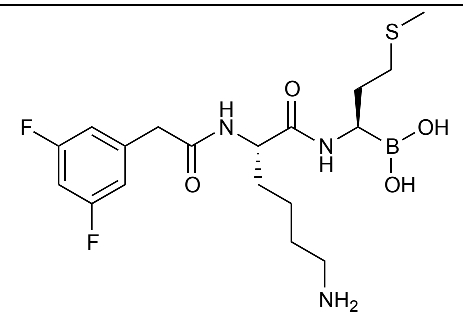
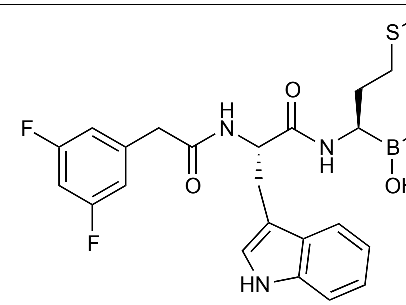
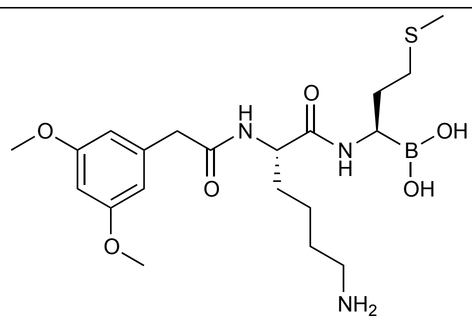
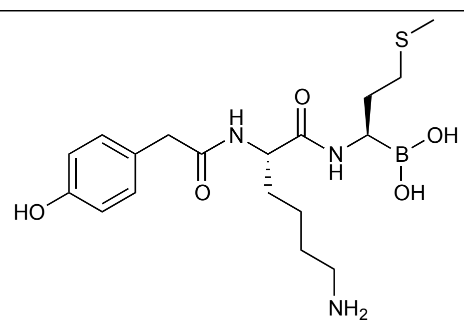
			MS (ESI$^+$) *m/z* (rel intensity): 399.3 ([2 × (M - H_2O) + H]$^+$, 48), 200.2 ([M - H_2O + H]$^+$, 20), 182.2 ([M – 2 × H_2O + H]$^+$, 100).
129	Lys-boroGly		^{1}H NMR (D_2O) δ 3.96 (t, *J* = 6.7 Hz, 1H), 2.98 (t, *J* = 2.6 Hz, 2H), 2.80 (d, *J* = 16.9 Hz, 1H), 2.71 (d, *J* = 16.9 Hz, 1H), 1.98 - 1.80 (m, 2H), 1.74 - 1.63 (m, 2H), 1.48 - 1.37 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 168.2 ([M - 2H_2O + H]$^+$, 100), 186.2 ([M - H_2O + H]$^+$, 65).
130	Lys-boroLeu		^{1}H NMR (D_2O) δ 4.0 (dd, *J* = 6.7, 6.6 Hz, 1H), 2.92 (m, 3H), 1.96 - 1.87 (m, 2H), 1.73 - 1.67 (m, 2H), 1.58 - 1.36 (m, 5H), 0.90 (t, *J* = 6.0 Hz, 6H). MS (ESI$^+$) *m/z* (rel intensity): 242.1 ([M - H_2O + H]$^+$, 100).
131	Lys-boroNva		^{1}H NMR (D_2O): δ 3.99 (t, *J* = 6.6 Hz, 1H), 3.01 - 2.88 (m, 3H), 1.90 - 1.86 (m, 2H), 1.75 - 1.30 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 455.3 ([2 × (M - H_2O) + H]$^+$, 26), 228.2 ([M - H_2O + H]$^+$, 34), 210.2 ([M - 2 × H_2O + H]$^+$, 100).
132	Lys-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.92 (dd, *J* = 6.6, 6.3 Hz, 1H), 3.26 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.10 - 2.85 (m, 4H), 2.10 - 1.61 (m, 4H), 1.42 - 1.31 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 259.2 ([M - H_2O - NH_3 + H]$^+$, 100), 276.2 ([M - H_2O + H]$^+$, 80).
133	Lys-boroPro		34
134	Lys-boroSar		^{1}H NMR (D_2O) δ 4.63 (t, J = 6.6 Hz, 1H), 3.22 (s, 3H), 3.00 (t, J = 7.1 Hz, 2H), 2.50 (s, 2H), 2.03 - 1.94 (m, 2H), 1.77 - 1.66 (m, 2H), 1.56 - 1.43 (m, 2H). ^{13}C NMR (D_2O) δ 173.56, 50.31, 50.23, 47.56, 41.54, 38.87, 32.04, 28.89, 23.58, 23.24. MS (ESI$^+$) *m/z* (rel intensity): 200.1 ([M - 2 × H_2O + H]$^+$, 100).

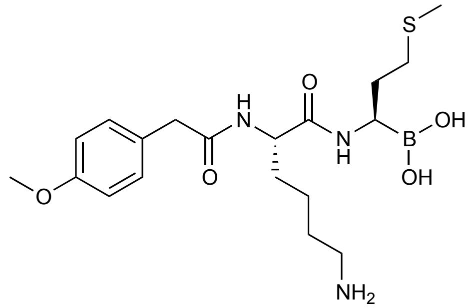
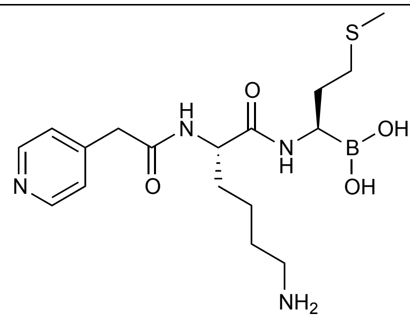
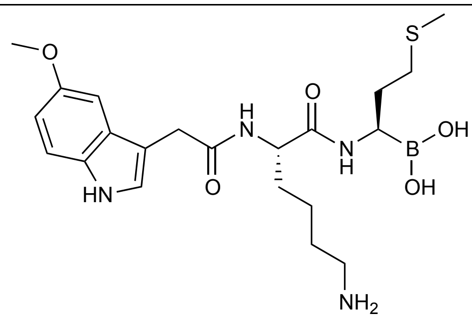
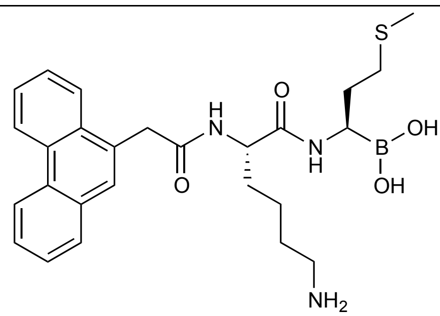
135	Lys-Pro-CN		
136	MeOSu-Ala-Ala-Pro-boroAla		^{1}H NMR (D_2O) δ 4.61 (q, *J* = 7.1 Hz, 1H), 4.52 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.84 - 3.72 (m, 3H), 3.71 (s, 3H), 2.75 - 2.55 (m, 4H), 2.40 - 2.30 (m, 1H), 2.12 - 1.99 (m, 3H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.37 (d, *J* = 7.9 Hz, 3H), 1.07 (d, *J* = 7.7 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 425.2 ([M - H_2O + H]$^+$, 100).
137	Met-boroAla		^{1}H NMR (D_2O) δ 4.11 (t, *J* = 6.7 Hz, 0.7H, *trans*-form), 3.90 - 3.80 (m, 0.2H, *cis*-form), 2.93 (q, *J* = 7.5 Hz, 1H), 2.69 - 2.59 (m, 2H), 2.25 - 2.10 (m, 5H), 1.18 (d, *J* = 7.5 Hz, 2.5H, *trans*-form), 1.08 (d, *J* = 7.3 Hz, 0.6H, *cis*-form). MS (ESI$^+$) *m/z* (rel intensity): 405.2 ([2 × (M - H_2O) + H]$^+$, 100), 203.3 ([M - H_2O + H]$^+$, 24).
138	Met-boroGly		^{1}H NMR (D_2O) δ 4.12 (t, *J* = 6.7 Hz, 1H), 2.83 (t, *J* = 16.9 Hz, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.54 - 2.70 (m, 2H), 2.16 - 2.21 (m, 2H), 2.12 (s, 3H). MS (ESI$^+$) *m/z* (rel Intensity): 189.0 ([M - H_2O + H]$^+$, 100), 207.0 ([M + H]$^+$, 15).
139	Met-boroLeu		^{1}H NMR (D_2O) δ 4.05 (t, *J* = 6.7 Hz, 1H), 2.87 (m, 1H), 2.55 - 2.46 (m, 2H), 2.12 - 2.04 (m, 2H), 2.01 (s, 3H), 1.50 - 1.25 (m, 3H), 0.82 - 0.77 (m, 6H). MS (ESI$^+$) *m/z* (rel intensity): 245.0 ([M - H_2O + H]$^+$, 60), 489.2 ([2 x (M - H_2O) + H]$^+$, 100).
140	Met-boroNva		^{1}H NMR (D_2O): δ 4.14 (t, *J* = 6.7 Hz, 1H), 2.92 (t, *J* = 7.9 Hz, 1H), 2.74 - 2.58 (m, 2H), 2.37 -2.14 (m, 2H), 2.12 (s, 3H), 1.58 - 1.51(m, 2H), 1.39 - 1.29 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 461.3 ([2 ×

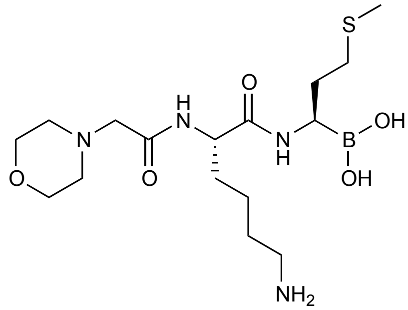
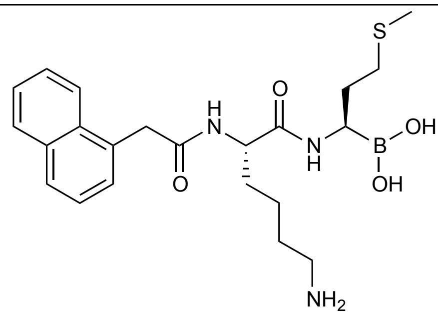
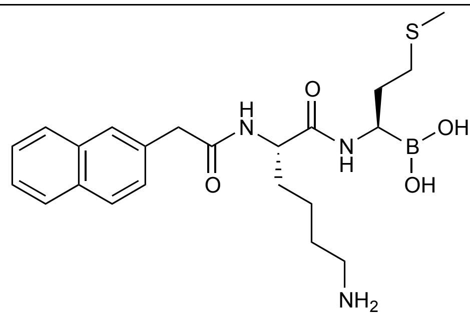
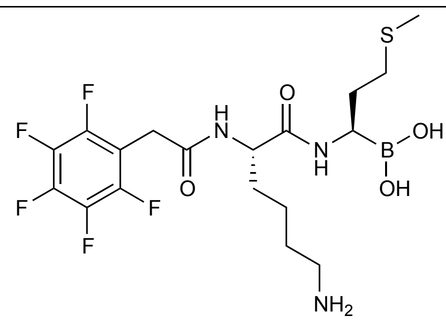
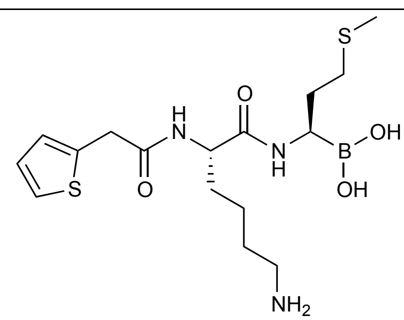
			(M - H_2O) + H]$^+$, 83), 271.1 ([M + Na]$^+$, 4), 231.1 ([M - H_2O + H]$^+$, 100).
141	Met-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 4.03 (m, 1H), 3.24 (m, 1H), 3.02 - 2.80 (m, 2H), 2.52 - 2.47 (m, 2H), 2.13 - 1.90 (m, 5H). MS (ESI$^+$) *m/z* (rel Intensity): 279.1 ([M - H_2O + H]$^+$, 100), 557.2 ([2 x (M - H_2O) + H]$^+$, 40).
142	Met-boroPro		^{1}H NMR (D_2O) δ 4.40 (dd, *J* = 7.0, 5.5 Hz, 1H), 3.69 (t, *J* = 8.8 Hz, 1H), 3.47 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.04 (dd, *J* = 7.7, 6.6 Hz, 1H), 2.67 - 2.59 (m, 2H), 2.20 - 2.14 (m, 2H), 2.12 (s, 3H), 1.74 - 1.60 (m, 2H), 1.45 - 1.30 (m, 2H). MS (ESI$^+$) *m/z* (rel intensity): 229.1 ([M - H_2O + H]$^+$, 40), 457.3 ([2 x (M - H_2O + H]$^+$, 100).
143	Met-boroSar		^{1}H NMR (D_2O) δ 4.76 (br, 1H), 3.24 (s, 3H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.55 (s, 2H), 2.24 (dt, *J* = 6.9, 7.0 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (D_2O) δ 173.19, 50.32, 49.58, 47.43, 38.85, 31.59, 30.58, 16.58. MS (ESI$^+$) *m/z* (rel intensity): 203.1 ([M - H_2O + H]$^+$, 100).
144	Met-Pro-CN		^{1}H NMR (D_2O) δ 4.87 (dd, *J* = 7.5, 5.2 Hz, 1H), 4.48 (dd, *J* = 6.4, 6.0 Hz, 1H), 3.81 - 3.68 (m, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.43 - 2.16 (m, 5H), 2.14 (br, 1H), 2.13 (s, 3H), 1.74 - 1.60 (m, 2H), 1.45 - 1.30 (m, 2H). MS (ESI$^+$) *m/z* (rel intensity): 228.1 ([M + H]$^+$, 100).
145	N-(1-isoquinoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.25 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.95 - 7.83 (m, 2H), 7.70 - 7.50 (m, 2H), 4.60 (m, 1H), 2.78 (dd, *J* = 7.3, 7.2 Hz, 1H), 2.57 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.35 (dd, *J* = 7.5, 7.2 Hz, 2H), 1.85 (s, 3H), 1.80 - 1.30 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 415.2 ([M - H_2O + H]$^+$, 100).

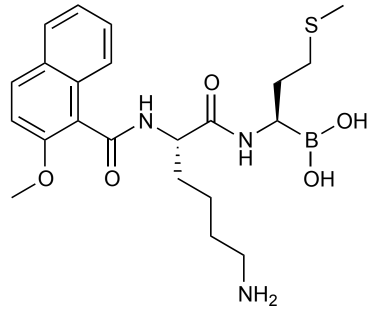
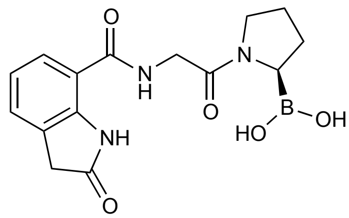
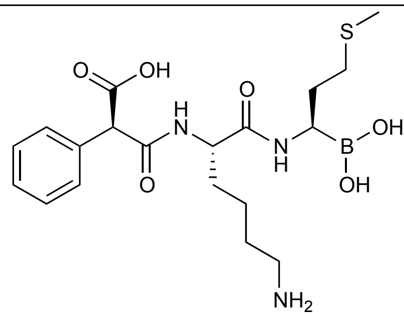
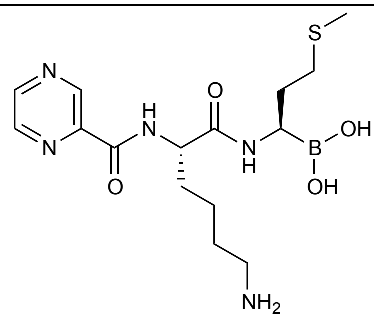
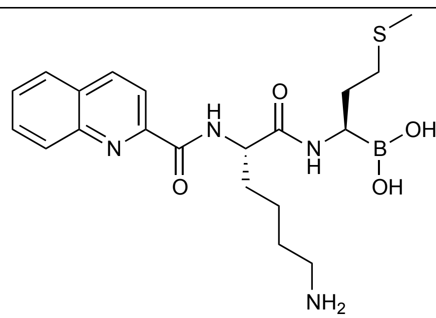
146	N-(1-naphcarbonyl)-Gly-Pro-Ala-boroPro Thioxoamide		[1]H NMR (DMSO-d_6): δ 8.60 - 8.55 (m, 1H), 8.36 - 8.34 (m, 1H), 8.20 - 8.10 (m, 1H), 8.02 - 7.98 (m, 2H), 7.63 - 7.50 (m, 4H), 4.80 - 4.60 (m, 1H), 4.59 - 4.40 (m, 1H), 4.39 - 4.15 (br, 2H), 3.90 - 3.60 (br, 4H), 1.98 - 1.74 (m, 7H), 1.25 (d, 3H, J = 7.2 Hz). MS (ESI^+) m/z (rel intensity): 493.2 ($[M - H_2O + H]^+$, 100).
147	N-(1-naphthoyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.90 - 7.78 (m, 3H), 7.52 - 7.30 (m, 4H), 4.55 (dd, J = 8.1, 5.4 Hz, 1H), 2.81 (t, J = 7.2 Hz, 2H), 2.58 (m, 1H), 2.40 (t, J = 7.2 Hz, 2H), 1.87 (s, 3H), 1.80 - 1.30 (m, 8H). MS (ESI^+) m/z (rel Intensity): 414.2 ($[M - H_2O + H]^+$, 100).
148	N-(1-napthalenecarbonyl)-Gly-boroPro		42
149	N-(2-(1H-indole-3-yl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.65 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.37 (s, 1H), 7.30 (dd, J = 8.0, 7.0 Hz, 1H), 7.21 (dd, J = 7.9, 7.0 Hz, 1H), 4.47 (dd, J = 9.4, 5.5 Hz, 1H), 3.84 (d, J = 4.4 Hz, 2H), 2.85 - 2.65 (m, 3H), 2.45 (t, J = 7.5Hz, 2H), 2.06 (s, 3H), 1.90 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI^+) m/z (rel Intensity): 417.2 ($[M - H_2O + H]^+$, 100).
150	N-(2-(2-chlorophenyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.22 (m, 1H), 7.09 (m, 3H), 4.24 (m, 1H), 3.6 (s, 2H), 2.73 (m, 2H), 2.44 (m, 1H), 2.28 (m, 2H), 1.82 (s, 3H), 1.80 - 1.30 (m, 6H), 1.27 - 1.10 (m, 2H). MS (ESI^+) m/z (rel Intensity): 412.2 ($[M - H_2O + H]^+$, 100).

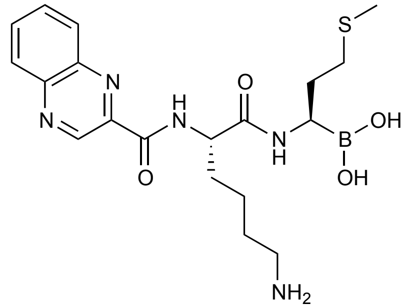
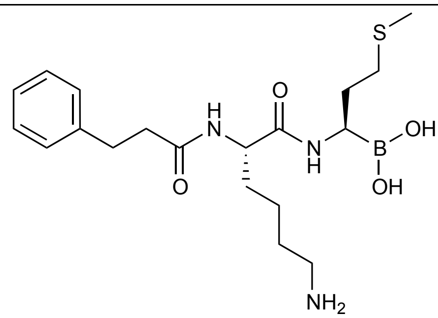
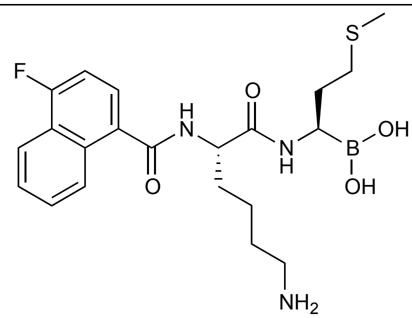
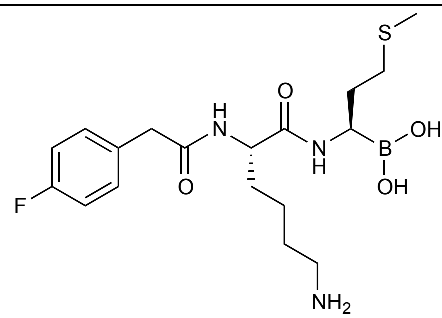
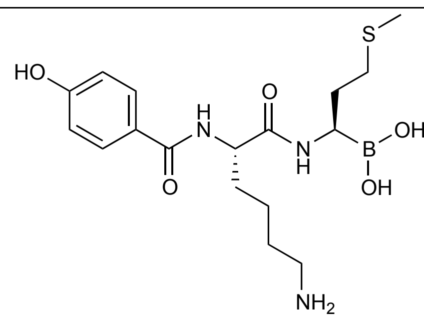
151	N-(2-(2-fluorophenyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.45 - 7.30 (m, 2H), 7.26 - 7.15 (m, 2H), 4.48 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.76 (s, 2H), 3.0 (t, *J* = 7.5 Hz, 2H), 2.75 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.54 (dd, *J* = 7.6, 7.3 Hz, 2H), 2.09 (s, 3H), 1.90 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 396.1 ($[M - H_2O + H]^+$, 100).
152	N-(2-(2-pyridinyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 8.38 (d, *J* = 5.5 Hz, 1H), 8.29 (m, 1H), 7.74 - 7.68 (m, 2H), 4.18 (dd, *J* = 7.3, 7.0 Hz, 1H), 3.73 (s, 2H), 2.71 (dd, *J* = 7.6, 7.4 Hz, 2H), 2.44 (m, 1H), 2.22 (t, *J* = 7.4 Hz, 2H), 1.77 (s, 3H), 1.75 - 1.15 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 190.2 ($[[M - H_2O]/2 + H]^+$, 100), 379.2 ($[M - H_2O + H]^+$, 85).
153	N-(2-(2,5-difluorophenyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.22 - 7.08 (m, 3H), 4.47 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.75 (s, 2H), 3.0 (t, *J* = 7.5 Hz, 2H), 2.76 (dd, *J* = 8.3, 6.3 Hz, 2H), 2.54 (dd, *J* = 7.5, 7.3 Hz, 2H), 2.09 (s, 3H), 1.90 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 414.2 ($[M - H_2O + H]^+$, 100).
154	N-(2-(2,6-dichlorophenyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.20 - 7.15 (m, 2H), 7.05 - 7.01 (m, 1H), 4.24 (m, 1H), 3.86 (s, 2H), 2.75 - 2.70 (m, 2H), 2.45 - 2.41(m, 1H), 2.30 - 2.25 (m, 2H), 1.81 (s, 3H), 1.70 - 1.20 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 446.1 ($[M - H_2O + H]^+$, 100), 448.1 ($[M - H_2O + H]^+$, 60).
155	N-(2-(3-pyridinyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 8.5 (m, 2H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.9, 7.1 Hz, 1H), 4.18 (t, *J* = 6.9 Hz, 1H), 3.73 (s, 2H), 2.73 (dd, *J* = 7.4, 7.0 Hz, 2H), 2.44 (t, *J* = 7.1 Hz, 1H), 2.23 (dd, *J* = 7.2, 7.1 Hz, 2H), 1.78 (s, 3H), 1.75 - 1.30 (m, 6H), 1.25 - 1.10 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 190.2 ($[[M - H_2O]/2 + H^+]$, 100), 379.2 ($[M - H_2O + H]^+$, 60).

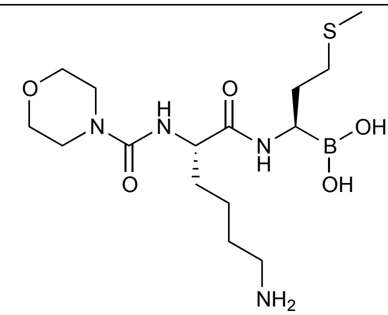
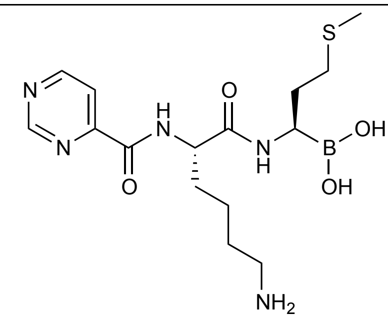
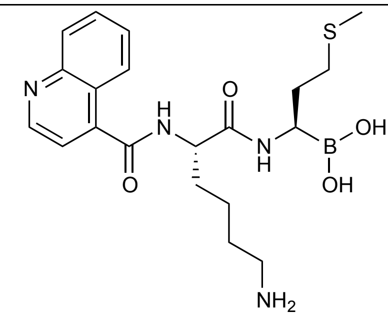
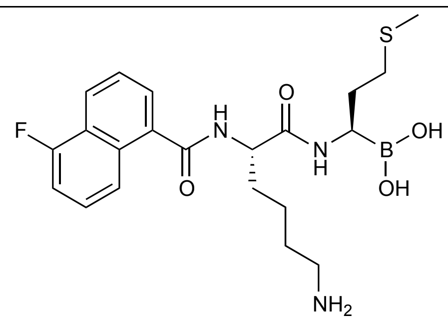
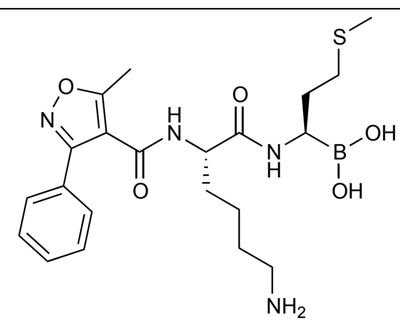
156	N-(2-(3,5-dichlorophenyl) acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.48 (s, 1H), 7.31 (s, 2H), 4.45 (m, 1H), 3.68 (s, 2H), 2.98 (dd, *J* = 7.8, 7.5 Hz, 2H), 2.78 - 2.70 (m, 1H), 2.51 (dd, *J* = 7.5, 7.2 Hz, 1H), 2.07 (s, 3H), 1.85 - 1.60 (m, 4H), 1.46 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 446.1 ($[M - H_2O + H]^+$, 100), 448.1 ($[M - H_2O + H]^+$, 60).
157	N-(2-(3,5-difluorophenyl) acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 6.92 (m, 3H), 4.45 (t, *J* = 6.0 Hz, 1H), 3.68 (s, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.72 (m, 1H), 2.49 (t, *J* = 7.5Hz, 2H), 2.07(s, 3H), 2.00 - 1.60 (m, 6H), 1.46 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 446.1 ($[M - H_2O + H]^+$, 100), 414.2 ($[M - H_2O + H]^+$, 60).
158	N-(2-(3,5-difluorophenyl) acetyl)-Trp-boroMet		^{1}H NMR (D_2O-CD_3CN, 4 : 1) δ 7.68 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.25 - 7.15 (m, 3H), 6.91 (m, 1H), 6.74 (m, 2H), 3.60 (s, 2H), 3.45 - 3.25 (m, 2H), 2.64 (m, 1H), 2.22 (s, 3H), 1.97 - 1.25 (m, 4H). MS (ESI^+) *m/z* (rel Intensity): 472.1 ($[M - H_2O + H]^+$, 100), 512.3 ($[M - H_2O + Na]^+$, 10).
159	N-(2-(3,5-dimethoxyphenyl)acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 6.58 (s, 3H), 4.45 (t, *J* = 5.5 Hz, 1H), 3.85 (s, 6H), 3.62 (s, 2H), 2.96 (dd, *J* = 7.6, 7.5 Hz, 2H), 2.73 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.06 (s, 3H), 2.00 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 438.2 ($[M - H_2O + H]^+$, 100).
160	N-(2-(4-hydroxyphenyl) acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 6.94 (d, *J* = 7.1 Hz, 2H), 6.18 (d, *J* = 7.1 Hz, 2H), 4.17 (m, 1H), 3.31(s, 2H), 2.67 (m, 2H), 2.37 (m, 1H), 2.18 (m, 2H), 1.79 (s, 3H), 1.70 - 1.30 (m, 6H), 1.20 - 1.10 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 394.1 ($[M - H_2O + H]^+$, 100).

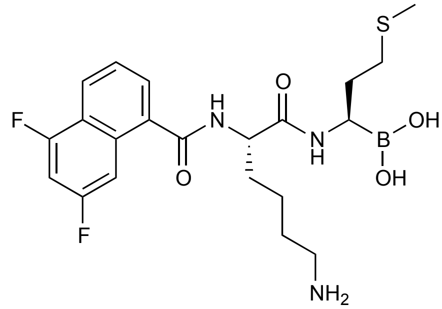
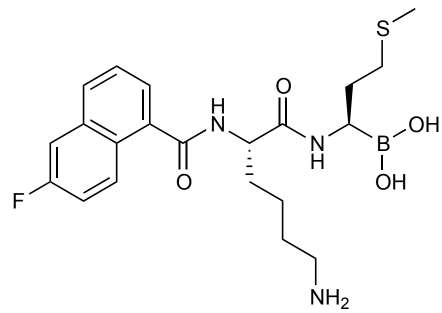
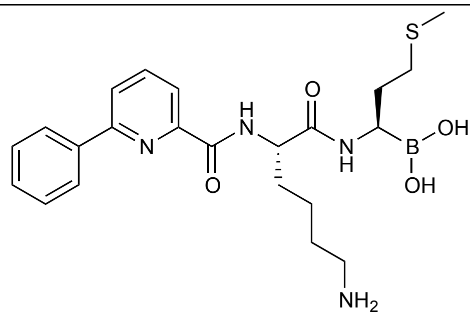
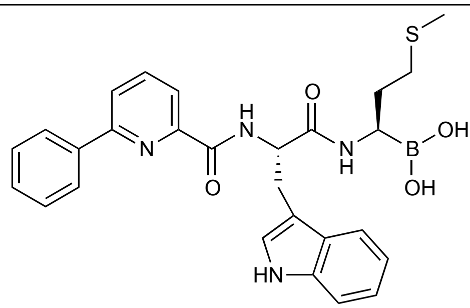
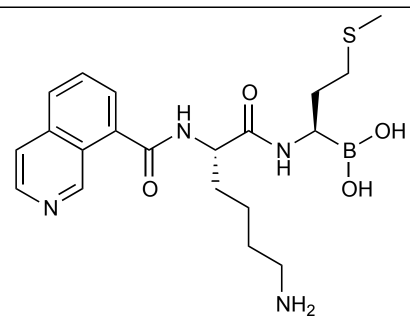
161	N-(2-(4-methoxyphenyl)acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.44 (t, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 3.62 (s, 2H), 2.97 (dd, *J* = 7.8, 7.4 Hz, 2H), 2.72 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.47 (dd, *J* = 7.6, 7.4 Hz, 2H), 2.07 (s, 3H), 2.00 - 1.60 (m, 6H), 1.50 - 1.40 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 408.2 ([M - H_2O + H]$^+$, 100).
162	N-(2-(4-pyridinyl)acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.48 (d, *J* = 5.7 Hz, 2H), 7.72 (d, *J* = 5.7 Hz, 2H), 4.18 (dd, *J* = 6.9, 6.8 Hz, 1H), 3.79 (s, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.78 (dd, *J* = 7.3, 6.8 Hz, 1H), 2.23 (dd, *J* = 7.1, 7.0 Hz, 2H), 1.79 (s, 3H), 1.75 - 1.30 (m, 6H), 1.25 - 1.10 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 190.2 ([[M - H_2O]/2 + H]$^+$, 100), 379.2 ([M - H_2O + H]$^+$, 50).
163	N-(2-(5-methoxyindole-3-yl)acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.47 (d, *J* = 8.9 Hz, 1H), 7.36 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 8.9, 8.0 Hz, 1H), 4.47 (dd, *J* = 5.2, 4.2 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 6.3 Hz, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.05 (s, 3H), 1.90 - 1.50 (m, 6H), 1.35 - 1.20 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 447.2 ([M - H_2O + H]$^+$, 100).
164	N-(2-(9-phenanthryl)acetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.60 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.64 - 7.52 (m, 4H), 4.39 (dd, *J* = 9.3, 5.5 Hz, 1H), 2.85 - 2.80 (m, 2H), 2.63 (m, 1H), 2.33 (dd, *J* = 7.6, 7.4 Hz, 1H), 1.89 (s, 1H), 1.81 - 1.51 (m, 6H), 1.40 - 1.29 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 478.2 ([M - H_2O + H]$^+$, 100).

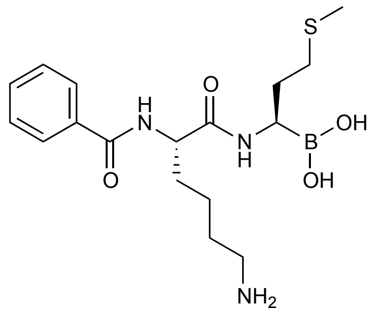
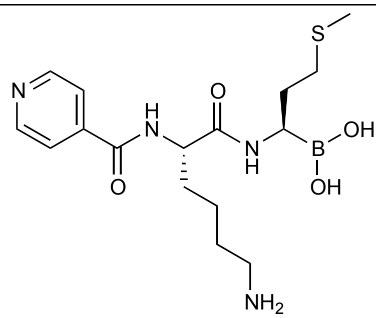
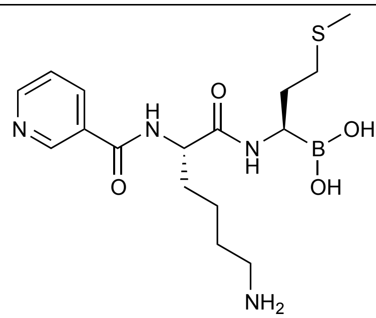
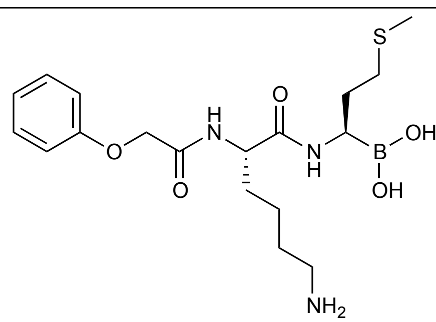
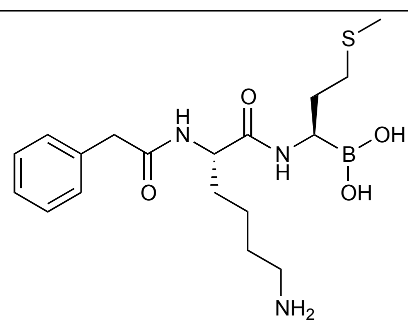
165	N-(2-(morpholin-4-yl)acetyl-Lys-boroMet		[1]H NMR (D_2O) δ 4.48 (dd, *J* = 5.1, 4.5 Hz, 1H), 4.13 (s, 2H), 4.04 (m, 4H), 3.46 (m, 4H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.83 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.58 (dd, *J* = 7.5, 7.2 Hz, 2H), 2.12 (s, 3H), 1.95 - 1.60 (m, 6H), 1.50 - 1.30 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 194.2 ($[[M - H_2O]/2 + H]^+$, 100), 387.2 ($[M - H_2O + H]^+$, 98).
166	N-(2-(naphthalen-1-yl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.72 - 7.70 (m, 3H), 7.40 - 7.10 (m, 4H), 4.21 (m, 1H), 3.93 (s, 2H), 2.79 (m, 2H), 2.58 (m, 1H), 2.19 (m, 2H), 1.76 (s, 3H), 1.75 - 1.30 (m, 6H), 1.06 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 428.2 ($[M - H_2O + H]^+$, 100).
167	N-(2-(naphthalene-2-yl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.71 - 7.68 (m, 3H), 7.60 (s, 1H), 7.33 - 7.29 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 4.20 (m, 1H), 3.58 (s, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.40 (m, 1H), 2.11 (t, *J* = 7.2 Hz, 2H), 1.71 (s, 3H), 1.70 - 1.30 (m, 6H), 1.10 - 0.96 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 428.2 ($[M - H_2O + H]^+$, 100).
168	N-(2-(pentafluorophenyl)acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 4.48 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.88 (s, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.77 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.55 (dd, *J* = 7.6, 7.3 Hz, 2H), 2.10 (s, 3H), 1.95 - 1.60 (m, 6H), 1.55 - 1.40 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 408.1 ($[M - H_2O + H]^+$, 100).
169	N-(2-(thiophen-2-acetyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.10 (d, *J* = 4.8 Hz, 1H), 6.80 - 6.70 (m, 2H), 4.20 (dd, *J* = 5.7, 5.4 Hz, 1H), 3.63 (s, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.42 (dd, *J* = 7.2, 6.7 Hz, 1H), 2.25 (t, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 1.60 - 1.35 (m, 6H), 1.39 - 1.16 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 384.1 ($[M - H_2O + H]^+$, 100).

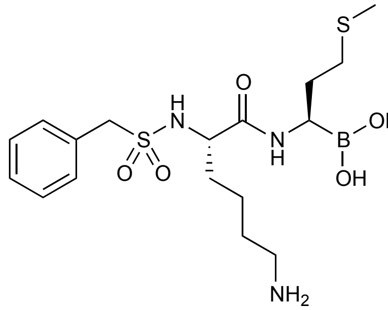
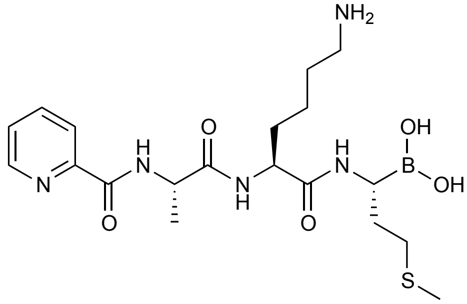
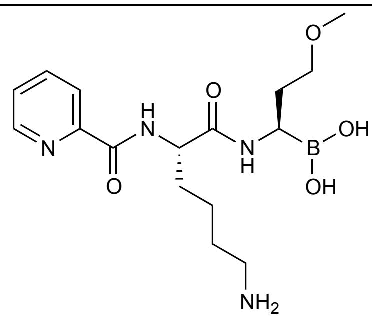
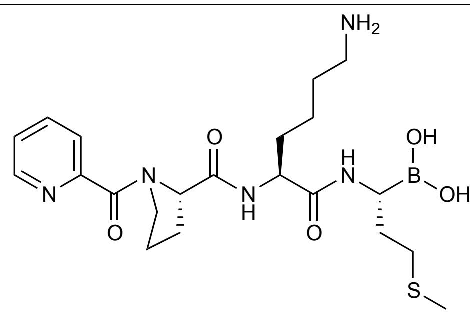
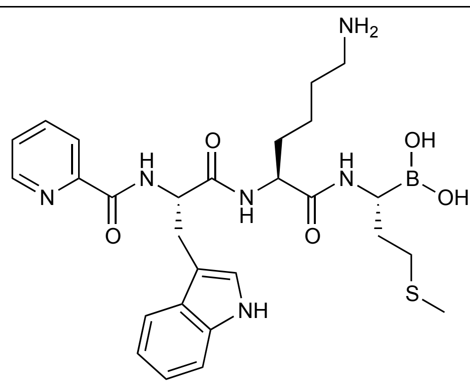
170	N-(2-methoxy-1-napthoyl)-Lys-boroMet		[1]H NMR (D_2O) δ 8.08 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.45 (m, 3H), 4.01 (s, 3H), 3.03 (t, *J* = 7.5Hz, 2H), 2.89 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.63 (m, 2H), 2.10 (s, 3H), 2.05 - 1.50 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 444.2 ($[M - H_2O + H]^+$, 100).
171	N-(2-oxoindoline-7-carbonyl)-Gly-boroPro		[1]H NMR (D_2O) δ 7.57 (d, *J* = 6.9 Hz, 1H), 7.46 (d, *J* = 6.4 Hz, 1H), 7.15 (dd, *J* = 6.9, 6.4 Hz, 1H), 4.20 (s, 2H), 3.64 (br, 1H), 3.60 (s, 2H), 3.54 - 3.50 (m, 1H), 3.08 - 3.04 (m, 1H), 2.20 - 2.00 (m, 3H), 1.75 - 1.70 (m, 1H). MS (ESI^+) *m/z* (rel intensity): 314.2 ($[M - H_2O + H]^+$, 100), 617.2 ($[2 x (M - H_2O) + H]^+$, 60).
172	N-(2-phenyl-2-hydroxycarbonyl)acetyl-Lys-boroMet		[1]H NMR (D_2O) δ 7.20 - 7.11 (m, 5H), 4.60 (s, 1H), 4.23 (dd, *J* = 9.1, 4.8 Hz, 1H), 2.60 - 2.55 (m, 2H), 2.46 (dd, *J* = 7.8, 7.2 Hz, 2H), 2.40 - 2.20 (m, 2H), 1.84 (s, 3H), 1.55 - 1.50 (m, 1H), 1.49 - 1.41 (m, 4H), 1.35 - 1.25 (m, 2H), 1.10 - 1.03 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 422.2 ($[M - H_2O + H]^+$, 100).
173	N-(2-pyrazinecarbonyl)-Lys-boroMet		[1]H NMR (D_2O) δ 9.20 (d, *J* = 1.3 Hz, 1H), 8.85 (d, *J* = 2.5Hz, 1H), 8.78 (dd, *J* = 2.5, 1.3 Hz, 1H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.82 (dd, *J* = 8.2, 6.4 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 2.06 - 2.02 (m, 2H), 1.90 - 1.70 (m, 4H), 1.60 - 1.50 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 366.1 ($[M - H_2O + H]^+$, 100).
174	N-(2-quinolinecarbonyl)-Lys-boroMet		[1]H NMR (D_2O) δ 8.61 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.97 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.81 (dd, *J* = 8.7, 7.2 Hz, 1H) 3.04 (dd, *J* = 7.5, 7.3 Hz, 2H), 2.82 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.10 - 2.05 (m, 2H), 2.03 (s, 3H), 1.90 - 1.20 (m, 6H). MS (ESI^+) *m/z* (rel Intensity): 208.0 ([$[M - H_2O]/2$ +

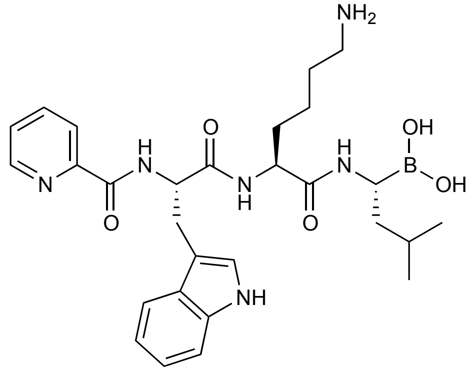
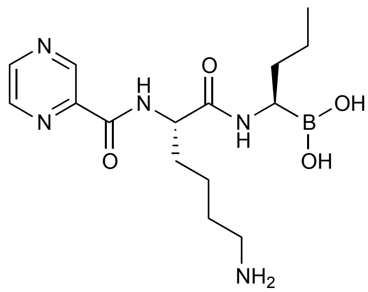
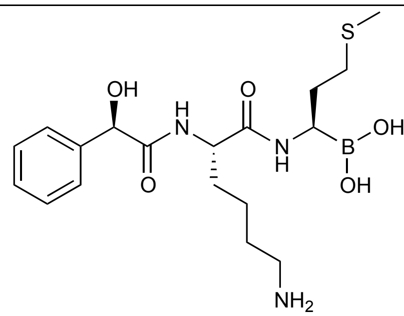
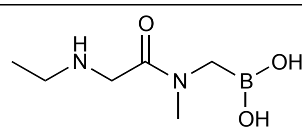
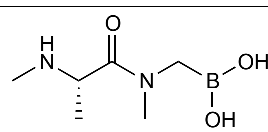
			H]+, 100), 415.1 ([M - H_2O + H]+, 90).
175	N-(2-quinoxalinecarbonyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.43 - 7.25 (m, 5H), 4.50 (t, *J* = 7.3 Hz, 1H), 3.70 (m, 1H), 3.36 (m, 1H), 2.98 (m, 2H), 2.78 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.04 (s, 3H), 1.95 - 1.65 (m, 6H), 1.60 - 1.50 (m, 2H). MS (ESI+) *m/z* (rel Intensity): 416.2 ([M - H_2O + H]+, 100).
176	N-(3-phenyl)propanoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.15 - 6.99 (m, 5H), 4.03 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.71 - 2.57 (m, 4H), 2.43 - 2.37 (m, 3H), 1.83 (s, 3H), 1.50 - 1.20 (m, 6H), 1.00 - 0.80 (m, 2H). MS (ESI+) *m/z* (rel Intensity): 392.2 ([M - H_2O + H]+, 100).
177	N-(4-fluoro-1-naphthoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.99 (d, *J* = 6.5 Hz, 1H), 7.89 (d, *J* = 6.7 Hz, 1H), 7.37 (m, 3H), 7.04 (dd, *J* = 9.3, 8.5 Hz, 1H), 4.50 (m, 1H), 2.78 (m, 2H), 2.55 (dd, *J* = 7.7, 6.2 Hz, 1H), 2.36 (m, 2H), 1.84 (s, 3H), 1.80 - 1.25 (m, 8H). MS (ESI+) *m/z* (rel Intensity): 432.2 ([M - H_2O + H]+, 100).
178	N-(4-fluorophenylacetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.02 (m, 2H), 6.87 (m, 2H), 4.20 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.41 (s, 2H), 2.70 (m, 2H), 2.45 - 2.40 (m, 1H), 2.24 (t, *J* = 7.3 Hz, 2H), 1.82 (s, 3H), 1.80 - 1.29 (m, 6H), 1.20 - 1.10 (m, 2H). MS (ESI+) *m/z* (rel Intensity): 396.1 ([M - H_2O + H]+, 100).
179	N-(4-hydroxybenzoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.78 (d, *J* = 8.7 Hz, 2H), 7.0 (d, *J* = 8.7 Hz, 2H), 4.71 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.03 (dd, *J* = 7.6, 7.4 Hz, 2H), 2.77 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.06 (s, 3H), 2.00 - 1.500 (m, 8H). MS (ESI+) *m/z* (rel Intensity): 380.1 ([M - H_2O + H]+, 100).

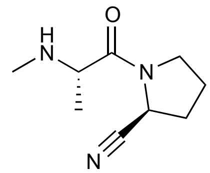
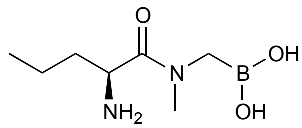
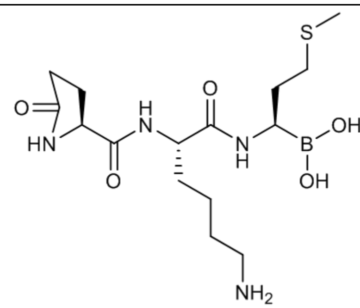
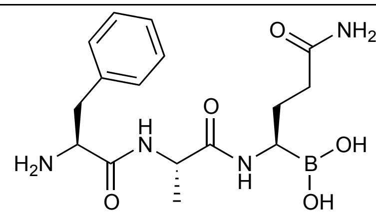
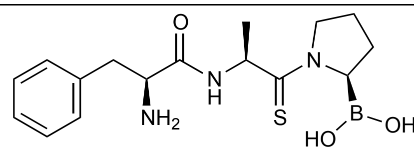
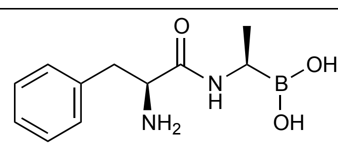
180	N-(4-morpholinylcarbonyl)-Lys-boroMet		[1]H NMR (D_2O) δ 4.83 (m, 1H), 4.13 (dd, *J* = 7.8, 7.0 Hz, 1H), 3.48 (m, 4H), 3.20 (m, 4H), 2.74 (dd, *J* = 6.8, 6.7 Hz, 2H), 2.44 - 2.25 (m, 3H), 1.84 (s, 3H), 1.61 - 1.20 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 373.2 ($[M - H_2O + H]^+$, 100).
181	N-(4-pyrimidinoyl)-Lys-boroMet		[1]H NMR (D_2O) δ 9.26 (s, 1H), 9.02 (d, *J* = 5.1 Hz, 1H), 8.06 (d, *J* = 5.1Hz, 1H), 4.68 (br, 1H), 2.97 (dd, *J* = 8.4, 5.5 Hz, 2H), 2.79 (dd, *J* = 8.9, 7.2 Hz, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.01 (s, 3H), 2.00 - 1.45 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 366.1 ($[M - H_2O + H]^+$, 100).
182	N-(4-quinolinoyl)-Lys-boroMet		[1]H NMR (D_2O) δ 9.20 (d, *J* = 5.5 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 2H), 8.19 (dd, *J* = 8.3, 7.4 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.02 (dd, *J* = 8.0, 7.4 Hz, 1H), 3.03 - 2.90 (m, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 2.00 - 1.50 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 208.1 ($[[M - H_2O]/2 + H]^+$, 100), 415.2 ($[M - H_2O + H]^+$, 90).
183	N-(5-fluoro-1-naphthoyl)-Lys-boroMet		[1]H NMR (D_2O) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.43 - 7.30 (m, 2H), 7.08 (dd, *J* = 9.8, 8.6 Hz, 1H), 4.51 (dd, *J* = 7.4, 6.9 Hz, 1H), 2.78 (dd, *J* = 7.4, 7.0 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 1H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.84 (s, 3H), 1.75 - 1.25 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 432.2 ($[M - H_2O + H]^+$, 100).
184	N-(5-methyl-3-phenyl-isoxazole-4-carbonyl)-Lys-boroMet		[1]H NMR (D_2O) δ 7.15 (m, 5H), 4.30 (m, 1H), 2.67 (m, 2H), 2.53 (m, 1H), 2.34 (m, 5H), 1.85 (s, 3H), 1.70 - 0.90 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 445.2 ($[M - H_2O + H]^+$, 100).

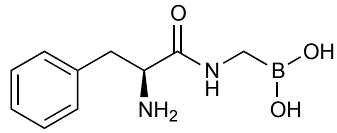
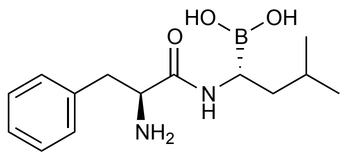
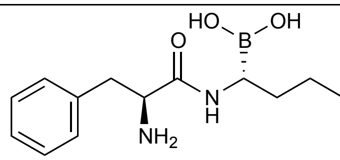
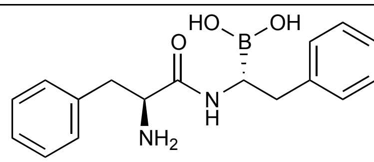
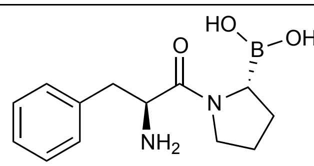
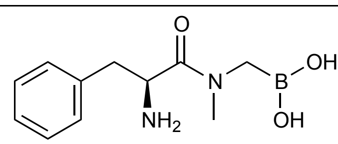
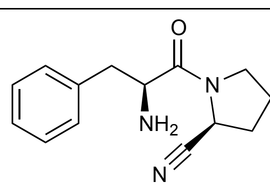
185	N-(5,7-difluoro-1-naphthoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 6.5Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 8.9 Hz, 1H), 4.51 (m, 1H), 2.78 (m, 2H), 2.37 (dd, *J* = 7.6, 6.6 Hz, 1H), 2.34 (t, *J* = 6.7 Hz, 2H), 1.83 (s, 3H), 1.80 - 1.25 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 450.1 ([M - H_2O + H]$^+$, 100).
186	N-(6-fluoro-1-naphthoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.87 (m, 1H), 7.8 (d, *J* = 9.8 Hz, 1H), 7.45 - 7.30 (m, 3H), 7.24 - 7.18 (m, 1H), 4.50 (m, 1H), 2.78 (m, 2H), 2.56 (m,1H), 2.40 - 2.30 (m, 2H), 1.83 (s, 3H), 1.80 - 1.30 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 432.2 ([M - H_2O + H]$^+$, 100).
187	N-(6-phenylpicolinoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.45 - 8.00 (m, 5H), 7.65 - 7.50 (m, 3H), 2.99 (dd, *J* = 7.5, 7.2 Hz, 2H), 2.78 (dd, *J* = 7.8, 6.8 Hz, 1H), 2.53 (dd, *J* = 7.3, 7.1 Hz, 2H), 2.02 (s, 3H), 2.00 - 1.50 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 441.3 ([M - H_2O + H]$^+$, 100).
188	N-(6-phenylpicolinoyl)-Trp-boroMet		^{1}H NMR (D_2O-CD_3CN, 4 : 1) δ 8.27 - 8.18 (m, 3H), 8.07 - 8.03 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 - 7.72 (m, 4H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.53 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.18 (m, 1H), 3.67 (d, *J* = 7.1Hz, 1H), 3.01 (m, 1H), 2.52 - 2.38 (m, 2H), 2.06 (s, 3H), 1.57 - 1.40 (m, 4H). MS (ESI$^+$) *m/z* (rel Intensity): 499.1 ([M - H_2O + H]$^+$, 100), 539.1 ([M - H_2O + Na^+], 20).
189	N-(8-isoquinolinoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 9.83 (s, 1H), 8.55 (d, *J* = 6.6 Hz, 1H), 8.48 (d, *J* = 6.4 Hz, 1H), 8.38 (dd, *J* = 7.2, 6.0 Hz, 1H), 8.22 - 8.17 (m, 2H), 2.98 (dd, *J* = 7.5, 7.4 Hz, 2H), 2.84 (m, 1H), 2.55 (t, *J* = 7.3 Hz, 2H), 2.04 (s, 3H), 2.00 - 1.52 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 208.0 ([[M - H_2O]/2 + H]$^+$, 100),

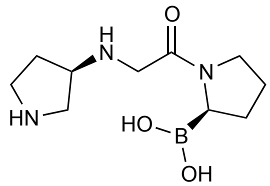
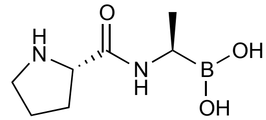
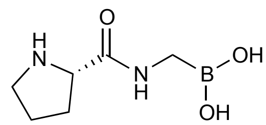
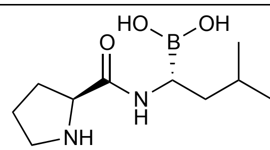
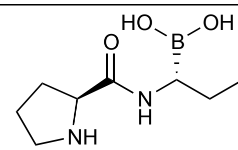
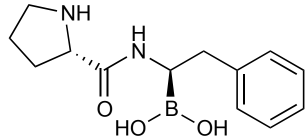
			415.2 ([M - H_2O + H]$^+$, 50).
190	N-(benzoyl)-lys-boroMet		^{1}H NMR (D_2O) δ 7.90 - 7.40 (m, 5H), 4.66 (dd, *J* = 8.7, 5.8 Hz, 1H), 2.98 (dd, *J* = 7.5, 7.3 Hz, 2H), 2.79 (m, 1H), 2.55 (dd, *J* = 7.3, 7.0 Hz, 2H), 2.06 (s, 3H), 2.00 - 1.50 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 364.2 ([M - H_2O + H]$^+$, 100).
191	N-(isonicotinoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 8.97 (d, *J* = 6.5 Hz, 2H), 8.37 (d, *J* = 6.5 Hz, 2H), 4.72 (br, 1H), 3.0 (dd, *J* = 7.5, 7.3 Hz, 2H), 2.80 (m, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 2.00 - 1.50 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 183.1 ([[M - H_2O]/2 + H$^+$], 100), 415.2 ([M - H_2O + H]$^+$, 90).
192	N-(nicotinoyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 9.22 (s, 1H), 8.97 (d, *J* = 6.7 Hz, 2H), 8.21 (t, *J* = 6.7 Hz, 1H), 3.0 (dd, *J* = 7.5, 7.3 Hz, 2H), 2.80 (m, 1H), 2.56 (dd, *J* = 7.3, 7.1 Hz, 2H), 2.08 (s, 3H), 2.05 - 1.50 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 183.1 ([[M - H_2O]/2 + H]$^+$, 90), 415.2 ([M - H_2O + H]$^+$, 100).
193	N-(phenoxyacetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.25 - 7.08 (m, 2H), 6.85 - 6.70 (m, 3H), 4.48 (s, 2H), 4.29 (m, 1H), 2.60 (m, 2H), 2.41 (t, *J* = 6.6 Hz, 1H), 2.25 (t, *J* = 7.0 Hz, 2H), 1.80 (s, 3H), 1.70 - 1.00 (m, 6H). MS (ESI$^+$) *m/z* (rel Intensity): 394.2 ([M - H_2O + H]$^+$, 100).
194	N-(phenylacetyl)-Lys-boroMet		^{1}H NMR (D_2O) δ 7.20 - 7.07 (m, 5H), 4.21 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.42 (s, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.42 (m, 1H), 2.22 (t, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 1.80 - 1.35 (m, 6H), 1.30 - 1.10 (m, 2H). MS (ESI$^+$) *m/z* (rel Intensity): 378.2 ([M - H_2O + H]$^+$, 100).

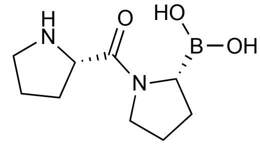
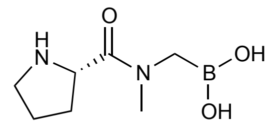
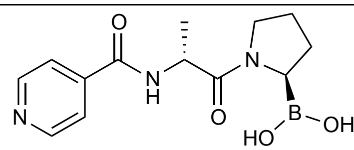
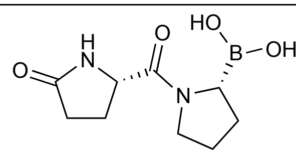
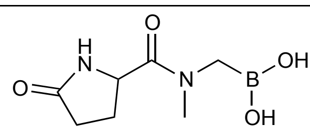
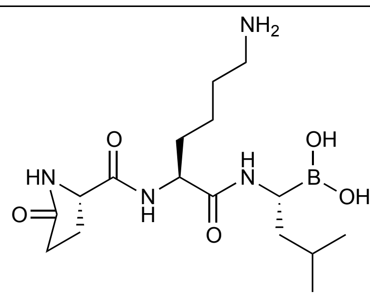
195	N-(phenylmethanesulfonyl-Lys-boroMet		[1]H NMR (D_2O) δ 7.48 (s, 5H), 4.52 (s, 2H), 3.85 (m, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.79 (m, 1H), 2.56 (dd, *J* = 8.1, 7.0 Hz, 1H), 2.10 (s, 3H), 1.90 - 1.30 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 414.2 ($[M - H_2O + H]^+$, 100).
196	N-(picolinoyl)-Ala-Lys-boroMet		[1]H NMR (D_2O) δ 8.66 (d, *J* = 4.2Hz, 1H), 8.07 (m, 2H), 7.69 (d, *J* = 4.5Hz, 1H), 4.51 (m, 1H), 3.0 (m, 2H), 2.80 (m, 1H), 2.55 (dd, *J* = 7.4, 6.3 Hz, 2H), 2.08 (s, 3H), 2.00 - 1.40 (m, 11H). MS (ESI$^+$) *m/z* (rel Intensity): 436.2 ($[M - H_2O + H]^+$, 100).
197	N-(picolinoyl)-Lys-boroMet (O)		[1]H NMR (D_2O) δ 8.83 (d, *J* = 5.1 Hz, 1H), 8.58 (dd, *J* = 7.8, 5.1 Hz, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.10 (m, 1H), 4.67 (br, 1H), 3.45 (t, *J* = 6.1 Hz, 2H), 3.25(s, 3H), 2.95(t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 1H), 2.05 - 1.40 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 175.1 ($[[M - H2O]/2 + H]^+$, 100), 349.2 ($[M - H_2O + H]^+$, 95).
198	N-(picolinoyl)-Pro-Lys-boroMet		[1]H NMR (D_2O) δ 8.72 - 8.50 (m, 1H), 8.30 - 8.00 (m, 1H), 7.95 - 7.60 (m, 2H), 4.70 - 4.51 (m, 1H), 3.80 - 3.65 (m, 2H), 3.0 (t, *J* = 7.5 Hz, 2H), 2.80 (m, 1H), 2.55 - 2.40 (m, 3H), 2.10 - 1.40 (m, 11H). MS (ESI$^+$) *m/z* (rel Intensity): 462.2 ($[M - H_2O + H]^+$, 100).
199	N-(picolinoyl)-Trp-Lys-boroMet		[1]H NMR (D_2O) δ 8.95 (s, 1H), 8.02 (m, 2H), 7.67 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.35 (s, 1H), 7.24 (t, 1H, *J* = 7.0 Hz), 7.15 (m, 1H), 4.31 (m, 1H), 3.44 (d, *J* = 6.6 Hz, 2H), 2.86 (m, 2H), 2.65 (m, 1H), 2.52 (m, 2H), 2.08 (s, 3H), 2.00 - 1.30 (m, 8H). MS (ESI$^+$) *m/z* (rel Intensity): 551.2($[M - H_2O + H]^+$, 100).

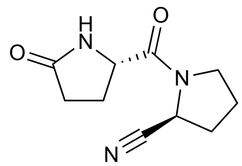
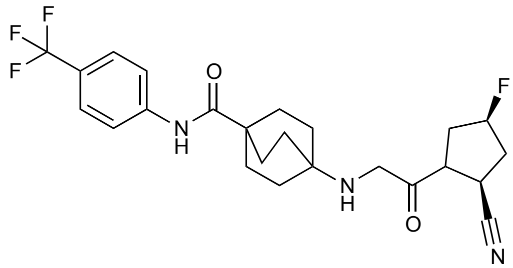
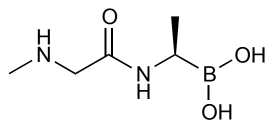
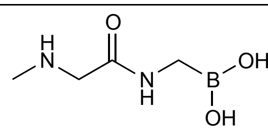
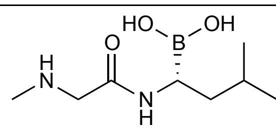
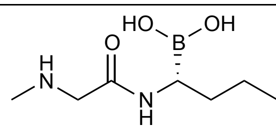
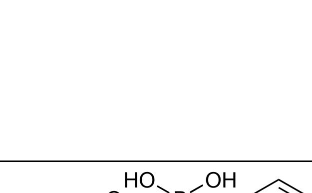
200	N-(picolinoyl)-Trp-Lys-boroLeu		[1]H NMR (D_2O) δ 8.63 (d, *J* = 7.5 Hz, 1H), 8.04 - 8.00 (m, 2H), 7.68 - 7.62 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.25 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.80 (m, 1H), 4.30 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.44 (d, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 7.5Hz, 2H), 2.68 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.70 - 1.24 (m, 10H), 0.89 (d, *J* = 2.7 Hz, 3H), 0.87 (d, *J* = 2.7Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 267.1 ($[M - H_2O + H]^+$, 100), 533.3 ($[2 \times (M - H_2O) + H]^+$, 95).
201	N-(pyrazinoyl)-Lys-boroNva		[1]H NMR (D_2O) δ 9.20 (s, 1H), 8.82 (s, 1H), 8.75 (s, 1H), 4.70 (br, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 1H), 2.05 - 1.90 (m, 3H), 1.72 (t, *J* = 7.5 Hz, 2H), 1.53 - 1.41 (m, 4H), 1.29 (dt, *J* = 7.2, 7.0 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H),. MS (ESI^+) *m/z* (rel Intensity): 334.3 ($[M - H_2O + H]^+$, 100).
202	N-(R-2-hydroxy-2-phenyl)acetyl-Lys-boroMet		[1]H NMR (D_2O) δ 7.48 (s, 5H), 5.26 (s, 1H), 4.51 (dd, *J* = 8.4, 5.1 Hz, 1H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 6.6 Hz, 1H), 2.48 (dd, *J* = 7.7, 7.3 Hz, 2H), 2.07 (s, 3H), 2.00 - 1.55 (m, 6H), 1.40 - 1.30 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 394.2 ($[M - H_2O + H]^+$, 100).
203	N(Et)Gly-boroSar		[1]H NMR (D_2O) δ 4.26 (s, 2H), 3.20(q, *J* = 7.3 Hz, 2H), 3.09 (s, 3H), 2.57 (s, 2H), 1.32 (t, *J* = 7.3 Hz, 3H). [13]C NMR (D_2O) δ 170.41, 46.48, 46.22, 45.95, 38.10, 12.87. MS (ESI^+) *m/z* (rel intensity): 157.1 ($[M - H_2O + H]^+$, 100).
204	N(Me)Ala-boroSar		[1]H NMR (D_2O) δ 4.54 (q, 1H, *J* = 7.0Hz, 1H), 3.19 (s, 3H), 2.74 (s, 3H), 2.56 (s, 2H), 1.57 (d, *J* = 7.0 Hz, 3H). [13]C NMR (D_2O) δ 173.38, 54.87, 47.24, 38.63, 33.91, 16.45. MS (ESI^+) *m/z* (rel intensity): 157.1 ($[M - H_2O + H]^+$, 100).

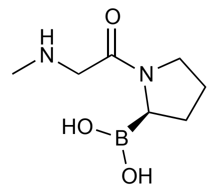
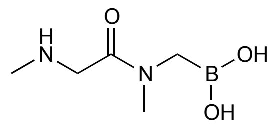
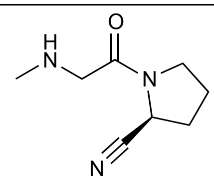
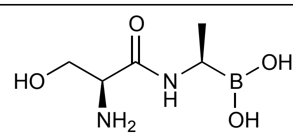
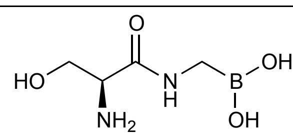
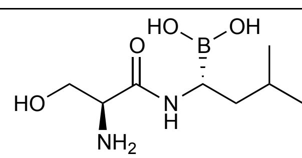
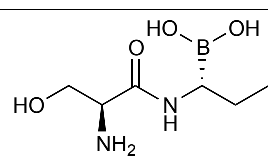
205	N(Me)Ala-Pro-CN		^{1}H NMR (D_2O) δ 4.87 (dd, *J* = 6.3, 5.7 Hz, 1H), 4.23 (q, *J* = 6.9 Hz, 1H), 3.76 - 3.62 (m, 2H), 2.73 (s, 3H), 2.40 - 2.12 (m, 4H), 1.57 (d, *J* = 6.9 Hz, 3H). MS (ESI^{+}) *m/z* (rel Intensity): 182.1 ([M + H]$^{+}$, 100).
206	Nva-boroSar		^{1}H NMR (D_2O) δ 4.58 (t, *J* = 6.7 Hz, 1H), 3.20 (s, 3H), 2.53 (s, 1H), 1.89 (dt, *J* = 7.0, 8.8 Hz, 2H), 1.46 - 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (D_2O) δ 173.97, 50.49, 47.64, 38.70, 34.47, 20.01, 15.32. MS (ESI^{+}) *m/z* (rel intensity): 171.1 ([M - H_2O + H]$^{+}$, 100).
207	pGlu-Lys-boroMet		^{1}H NMR (D_2O) δ 4.46 (t, *J* = 7.2 Hz, 1H), 4.37 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.77 (dd, *J* = 7.8, 6.9 Hz, 1H), 2.55 (t, *J* = 7.2 Hz, 1H), 2.42 (dd, *J* = 8.3, 6.9 Hz, 2H), 2.08 (s, 3H), 1.95 - 1.55 (m, 6H), 1.50 - 1.30 (m, 2H). MS (ESI^{+}) *m/z* (rel Intensity): 371.2 ([M - H_2O + H]$^{+}$, 100).
208	Phe-Ala-boroGln		^{1}H NMR (D_2O) δ 7.45 - 7.31 (m, 5H), 4.56 (m, 1H), 4.29 (dd, *J*= 7.2, 6.7 Hz, 1H), 3.34 - 3.14 (m, 2H), 3.00 - 2.80 (m, 1H), 2.50 - 2.28 (m, 2H), 2.00 - 1.80 (m, 2H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.37 - 1.33 (m, 1H). MS (ESI^{+}) *m/z* (rel Intensity): 347.3 ([M - H_2O + H]$^{+}$, 100).
209	Phe-Ala-S-boroPro		^{1}H NMR (D_2O) δ 7.45 - 7.21 (m, 5H), 4.95 (q, *J* = 6.7 Hz, 1H), 4.29 (t, *J* = 7.2Hz, 1H), 3.99 - 3.95 (m, 1H), 3.71 - 3.66 (m, 1H), 3.50 - 3.43(m, 1H), 3.34 - 3.09 (m, 2H), 2.21 - 2.15(m, 3H), 1.90 - 1.85 (m, 1H), 1.39 (d, *J* = 6.7 Hz, 3H). MS (ESI^{+}) *m/z* (rel Intensity): 332.4 ([M - H_2O + H]$^{+}$, 100).
210	Phe-boroAla		^{1}H NMR (D_2O) δ 7.52 - 7.35 (m, 5H), 4.27 (t, *J* = 7.6 Hz, 1H), 3.26 (d, *J* = 8.0Hz, 2H), 2.90 (q, *J* = 7.5 Hz, 1H), 1.07 (d, *J* = 7.5 Hz, 3H). MS (ESI^{+}) *m/z* (rel intensity): 437.3 ([2 × (M - H_2O) + H]$^{+}$, 65), 219.2 ([M - H_2O + H]$^{+}$, 100).

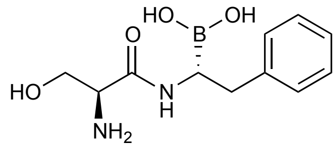
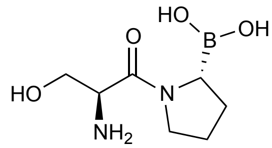
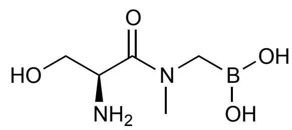
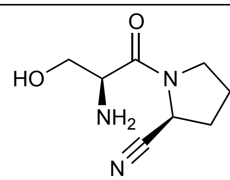
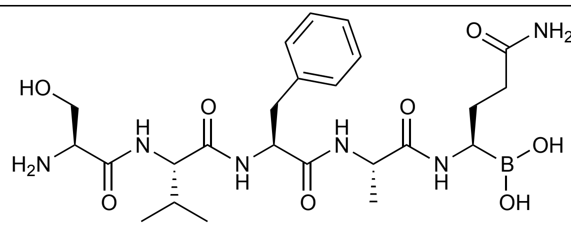
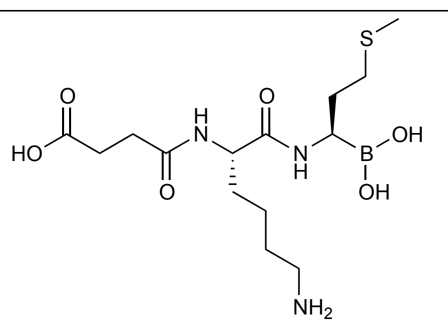
211	Phe-boroGly		^{1}H NMR (D_2O) δ 7.45 - 7.28 (m, 5H), 4.20 (t, *J* = 7.4 Hz, 1H), 3.20 (d, *J* = 7.4 Hz, 2H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.55 (d, *J* = 16.9 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 205.2 ($[M - H_2O + H]^+$, 100), 409.2 ($[2 \times (M - H_2O) + H]^+$, 60).
212	Phe-boroLeu		35
213	Phe-boroNva		^{1}H NMR (D_2O): δ 7.50 - 7.35 (m, 3H), 7.35 - 7.20 (m, 2H), 4.21 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.26 - 3.11 (m, 2H), 2.72 (dd, *J* = 8.5, 6.2 Hz, 1H), 1.38 - 1.24 (m, 2H), 1.09-1.01 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 493.3 ($[2 \times (M - H_2O) + H]^+$, 93), 287.1 ($[M + Na]^+$, 4), 247.1 ($[M - H_2O + H]^+$, 100).
214	Phe-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 8H), 7.15 - 7.05 (m, 2H), 4.19 (t, *J* = 7.7 Hz, 1H), 3.22 - 3.05 (m, 3H), 2.87 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.59 (dd, *J* = 13.9, 10.2 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 295.1 ($[M - H_2O + H]^+$, 100), 589.3 ($[2 \times (M - H_2O) + H]^+$, 30).
215	Phe-boroPro		34
216	Phe-boroSar		^{1}H NMR (D_2O) δ 7.42 - 7.30 (m, 5H), 4.77 (br, 1H), 3.35 - 3.17 (m, 2H), 2.65 (s, 3H), 2.42 (s, 2H). ^{13}C NMR (D_2O) δ 172.77, 135.31, 132.13, 131.92, 130.99, 51.68, 47.46, 39.91, 38.24. MS (ESI^+) *m/z* (rel Intensity): 219.1 ($[M - H_2O + H]^+$, 100).
217	Phe-Pro-CN		See **Supplementary Note 2**

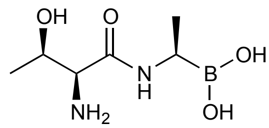
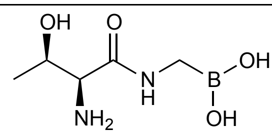
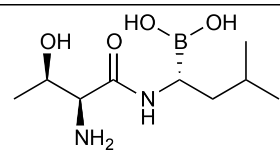
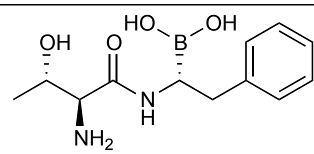
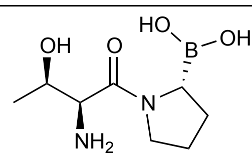
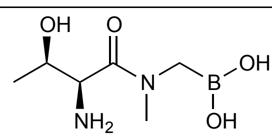
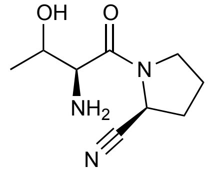
218	PHX1149		[1]H NMR (D_2O) δ 4.21 (t, *J* = 7.5 Hz, 1H), 4.13 (s, 2H), 3.85 (dd, *J* = 14.5, 8.1 Hz, 1H), 3.64 - 3.40 (m, 5H), 3.10 (t, *J* = 8.1 Hz, 1H), 2.65 - 2.59 (m, 1H), 2.33 - 2.26 (m, 1H), 2.13 - 1.90 (m, 3H), 1.80 - 1.75 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 224.5 ($[M - H_2O + H]^+$, 70), 242.5 ($[M + H]^+$, 100).
219	Pro-boroAla		[1]H NMR (D_2O) δ 4.41 (t, *J* = 7.1 Hz, 1H), 3.55 - 3.40 (m, 2H), 3.04 (q, *J* = 7.5 Hz, 1H), 2.54 - 2.41 (m, 1H), 2.24 - 2.07 (m, 3H), 1.23 (d, *J* = 7.5 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 337.2 ($[2 \times (M - H_2O) + H]^+$, 100), 169.2 ($[M - H_2O + H]^+$, 43).
220	Pro-boroGly		[1]H NMR (D_2O) δ 4.36 (dd, *J* = 7.6, 7.14 Hz, 1H), 3.50 - 3.30 (m, 2H), 2.47 (d, *J* = 16.9 Hz, 1H) 2.40 (d, *J* = 16.9 Hz, 1H), 2.82 - 2.37 (m, 3H), 2.11 - 1.83 (m, 2H). MS (ESI^+) *m/z* (rel Intensity): 155.1 ($[M - H_2O + H]^+$, 100), 173.2 ($[M + H]^+$, 75).
221	Pro-boroLeu		[1]H NMR (D_2O) δ 4.28 (dd, *J* = 7.8, 6.9 Hz, 1H), 3.38 - 3.28 (m, 2H), 2.90 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.35 (m, 1H), 2.03 - 1.90 (m, 3H), 1.53 - 1.25 (m, 3H), 0.85 - 0.79 (m, 7H). MS (ESI^+) *m/z* (rel intensity): 211.0 ($[M - H_2O + H]^+$, 80), 421.2 ($[2 \times (M - H_2O) + H]^+$, 100).
222	Pro-boroNva		[1]H NMR (D_2O): δ 4.35 (t, *J* = 7.7 Hz, 1H), 3.43 - 3.35 (m, 2H), 2.91 (t, *J* = 7.5 Hz, 1H), 2.43 - 2.04 (m, 4H), 1.57 - 1.49 (m, 2H), 1.37 - 1.26 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 589.5 ($[3 \times (M - H_2O) + H]^+$, 3), 393.3 ($[2 \times (M - H_2O) + H]^+$, 56), 197.2 ($[M - H_2O + H]^+$, 100).
223	Pro-boroPhe		[1]H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 4.28 (dd, *J* = 8.1, 7.2 Hz, 1H), 3.45 - 3.36 (m, 2H), 3.23 (dd, *J* = 10.1, 6.2 Hz, 1H), 2.97 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.85 (dd, *J* = 14.0, 10.1 Hz, 1H), 2.36 - 2.20 (m,1H) 2.06 - 1.90 (m,

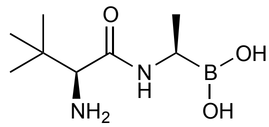
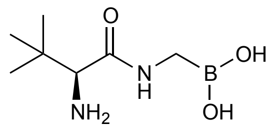
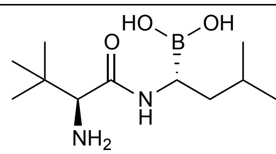
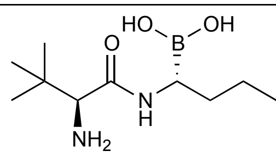
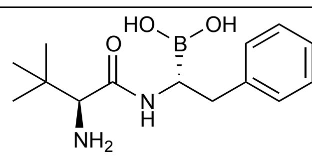
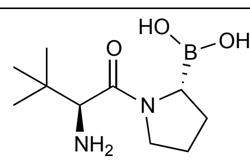
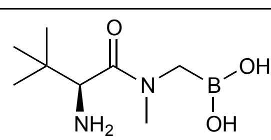
			3H). MS (ESI^+) *m/z* (rel Intensity): 245.1 ($[M - H_2O + H]^+$, 100), 263.1 ($[M + H]^+$, 40).
224	Pro-boroPro		34
225	Pro-boroSar		^1H NMR (D_2O) δ 4.85 (br, 1H), 3.51 - 3.40 (m, 2H), 3.16 (s, 3H), 2.58 (s, 2H), 2.57 - 2.04 (m, 4H). ^{13}C NMR (D_2O) δ 173.06, 58.48, 49.23, 46.49, 38.68, 31.06, 26.20. MS (ESI^+) *m/z* (rel intensity): 169.2 ($[M - H_2O + H]^+$, 100).
226	Py(D)AlaboroPro		42
227	pyro-Glu-boroPro		^1H NMR (D_2O) δ 4.63 (dd, *J* = 8.4, 5.6 Hz, 1H), 4.39 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.70 (dd, *J* = 9.2, 8.2 Hz, 1H), 3.46 - 3.38 (m, 2H), 2.97 (dd, *J* = 10.7, 6.7 Hz, 1H), 2.52 - 2.45 (m, 1H), 2.42 - 2.36 (m, 3H), 2.04 - 1.83 (m, 6H), 1.67 - 1.60 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 209.1 ($[M - H_2O + H]^+$, 90), 227.1 ($[M + H]^+$, 25), 417.2 ($[2 x (M - H_2O) + H]^+$, 100).
228	PyroGlu-boroSar		^1H NMR (D_2O) δ 4.18 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.12 (s, 3H), 2.60 - 2.37 (m, 5H), 2.12 - 2.06 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 182.2 ($[M - H_2O + H]^+$, 100).
229	PyroGlu-Lys-boroLeu		^1H NMR (D_2O) δ 4.44 (t, *J* = 7.2 Hz, 1H), 4.38 (dd, *J* = 4.8, 8.9 Hz, 1H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.77 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.57 - 2.50 (m, 1H), 2.43 (dd, *J* = 8.1, 7.3 Hz, 2H), 2.10 - 1.99 (m, 1H), 1.87 - 1.29 (m, 10H), 0.90 (d, *J* = 4.0 Hz, 3H), 0.88 (d, 3H, *J* = 4.0 Hz). MS (ESI^+) *m/z* (rel intensity): 353.2 ($[M - H_2O + H]^+$, 100).

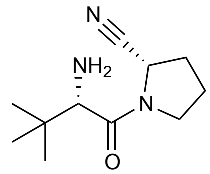
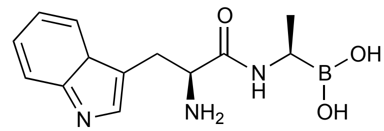
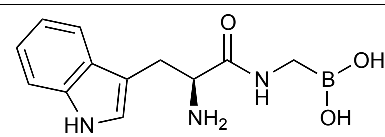
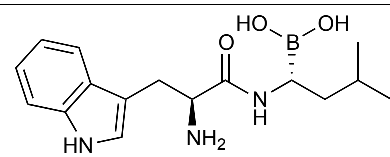
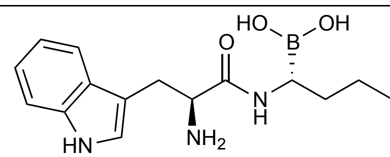
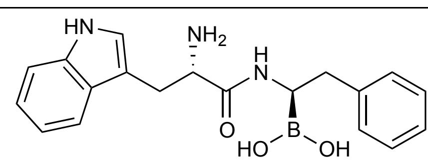
230	PyroGlu-Pro-CN		[1]H NMR (D_2O) δ 4.83 (br, 1H), 4.67 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.76 - 3.61 (m, 2H), 2.67 - 2.64 (m, 1H), 2.52 - 2.45 (m, 2H), 2.38 - 2.30 (m, 2H), 2.24 - 2.11 (m, 3H). MS (ESI^+) *m/z* (rel Intensity): 208.0 ($[M + H]^+$, 75), 415.0 ($[2M + H]^+$, 100).
231	R-Gly-Pro-CN		46
232	Sar-boroAla		[1]H NMR (D_2O) δ 3.88 (s, 2H), 3.00 (q, *J* = 7.5 Hz, 1H), 2.76 (s, 3H), 1.18 (d, *J* = 7.5 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 285.1 ($[2 \times (M - H_2O) + H]^+$, 100), 143.1 ($[M - H_2O + H]^+$, 16).
233	Sar-boroGly		[1]H NMR (D_2O) δ 3.87 (s, 2H), 2.38 (s, 2H), 2.76 (s, 3H). MS (ESI^+) *m/z* (rel Intensity): 129.1 ($[M - H_2O + H]^+$, 100), 147.1 ($[M + H]^+$, 90).
234	Sar-boroLeu		35
235	Sar-boroNva		[1]H NMR (D_2O) δ 4.01 (t, *J* = 6.4 Hz, 1H), 3.90 (s, 2H), 3.01 (t, *J* = 7.3 Hz, 1H), 2.77(s, 3H), 1.62 (br, 1H), 1.53 (m, 1H), 1.40 - 1.29 (m, 2H), 0.90 (dd, *J* = 4.8, 4.6 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 171.0 ($[M - H_2O + H]^+$, 90), 189.0 ($[M + H]^+$, 50), 341.3 ($[2 x (M - H_2O) + H]^+$, 100).
236	Sar-boroPhe		[1]H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.82 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.41 (dd, *J* = 9.9, 7.0 Hz, 1H), 2.96 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.84 (dd, *J* = 13.8, 9.9 Hz, 1H), 2.57 (s, 3H). MS (ESI^+) *m/z* (rel Intensity): 219.1 ($[M - H_2O + H]^+$, 100), 237.1 ($[M + H]^+$, 30).

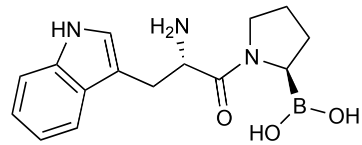
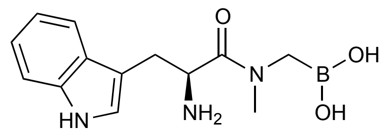
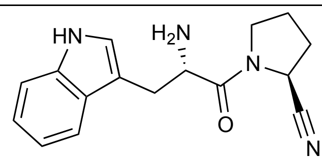
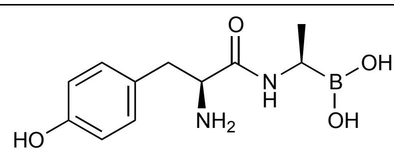
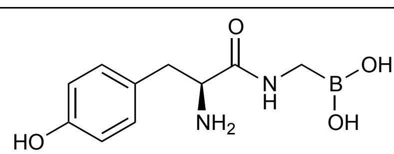
237	Sar-boroPro		^{1}H NMR (D_2O) δ 4.00 (s, 2H), 3.45 - 3.35 (m, 1H), 3.12 - 3.05 (m, 1H), 2.78 (s, 2H), 2.14 - 1.94 (m, 3H), 1.76 - 1.70 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 169.1 ([M - H_2O + H]$^+$, 100).
238	Sar-boroSar		^{1}H NMR (D_2O) δ 4.25 (s, 2H), 3.08 (s, 3H), 2.81 (s, 3H), 2.56 (s, 2H). ^{13}C NMR (D2O) δ 170.23, 48.52, 46.17, 38.19, 35.72. MS (ESI^+) *m/z* (rel intensity): 143.1 ([M - H_2O + H]$^+$, 100).
239	Sar-Pro-CN		^{1}H NMR (D_2O) δ 4.83 (dd, *J* = 6.7, 4.8 Hz, 1H), 4.08 (s, 2H), 3.70 - 3.62 (m, 1H), 3.54 - 3.45 (m, m, 1H), 2.82 (s, 3H), 2.37 - 2.13 (m, 4H). MS (ESI^+) *m/z* (rel Intensity): 168.1 ([M + H]$^+$, 100), 335.2 ([2M + H]$^+$, 25).
240	Ser-boroAla		^{1}H NMR (D_2O) δ 4.00 - 3.95 (m, 1H), 3.85 - 3.70 (m, 2H), 2.85 - 2.75 (m, 1H), 1.05 - 0.95 (m, 3H). MS (ESI^+) *m/z* (rel intensity): 317.2 ([2 × (M - H_2O) + H]$^+$, 100), 159.2 ([M - H_2O + H]$^+$, 39).
241	Ser-boroGly		^{1}H NMR (D_2O) δ 4.14 (dd, *J* = 5.0, 4.8 Hz, 1H), 3.90 - 4.03 (m, 2H), 2.83 (d, *J* = 16.9 Hz, 1H), 2.76 (d, *J* = 16.9 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 145.1 ([M - H_2O + H]$^+$, 100), 289.2 ([2 x (M - H_2O) + H]$^+$, 50).
242	Ser-boroLeu		35
243	Ser-boroNva		^{1}H NMR (D_2O): δ 4.14 (dd, *J* = 5.9, 4.4Hz, 1H), 3.96 (ddd, *J* = 22.5, 12.3, 4.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 1H), 1.59 - 1.51 (m, 2H), 1.41 - 1.27 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 541.3 ([3 × (M - H_2O) - H_2O + H]$^+$, 4), 373.2 ([2 × (M - H_2O) + H]$^+$, 100), 187.3 ([M - H_2O + H]$^+$, 30).

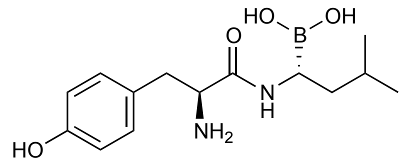
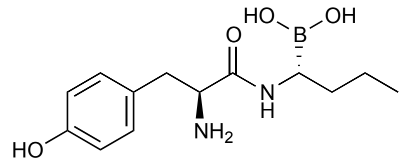
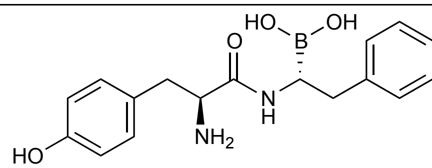
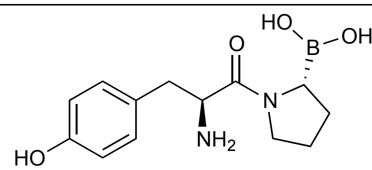
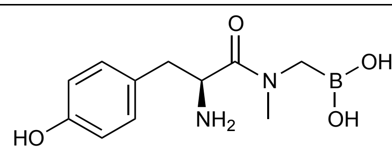
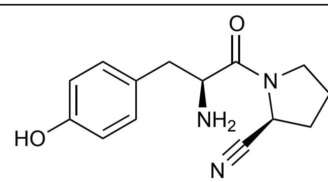
244	Ser-boroPhe		See **Supplementary Note 2**
245	Ser-boroPro		^{1}H NMR (D_2O) δ 4.34 (dd, *J* = 6.7, 4.8 Hz, 1H), 4.0 (dd, *J* = 12.5, 4.1 Hz, 1H), 3.82 (dd, *J* = 12.5, 7.0 Hz, 1H), 3.67 - 3.60 (m, 1H), 3.49 - 3.42 (m, 1H), 3.05 (dd, *J* = 11.2, 6.9 Hz, 1H), 2.10 - 1.89 (m, 3H), 1.72 - 1.62 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 185.1 ($[M - H_2O + H]^+$, 100), 369.2 ($[2 x (M - H_2O) + H]^+$, 60).
246	Ser-boroSar		^{1}H NMR (D_2O) δ 4.71 (dd, J = 5.6, 5.0 Hz, 1H), 4.0 (m, 2H), 3.22 (s, 3H), 2.51 (s, 2H). ^{13}C NMR (D_2O) δ 171.90, 61.46, 52.65, 47.35, 38.81. MS (ESI^+) *m/z* (rel intensity): 159.0 ($[M - H_2O + H]^+$, 100).
247	Ser-Pro-CN		^{1}H NMR (D_2O) δ 4.87 (dd, *J* = 7.5, 5.3 Hz, 1H), 4.45 (dd, *J* = 5.3, 4.5 Hz, 1H), 4.10 - 3.97 (m, 2H), 3.79 - 3.69 (m, 2H), 2.43 - 2.12 (m, 4H). MS (ESI^+) *m/z* (rel Intensity): 184.1 ($[M + H]^+$, 100), 367.2 ($[2M + H]^+$, 30).
248	Ser-Val-Phe-Ala-boroGln		^{1}H NMR (D_2O) δ 7.41 - 7.27 (m, 5H), 4.77 (m, 1H), 4.64 (m, 1H), 4.50 (m, 1H), 4.17 (dd, *J* = 6.9, 6.6 Hz, 2H), 3.92 - 3.88 (m, 2H), 3.13 - 3.03 (m, 2H), 2.33 (m, 1H), 2.03 - 2.00 (m, 1H), 1.85 (m, 2H), 1.41 (d, *J*= 6.9 Hz, 3H), 0.87(d, *J* = 6.5 Hz, 6H). LCMS (ESI+) *m/z*, (rel Intensity): 533.1 ($[M + H]^+$, 100).
249	Suc-Lys-boroMet		^{1}H NMR (D_2O) δ 4.48 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 1H), 2.68 - 2.50 (m, 6H), 2.12 (s, 3H), 1.95 - 1.35 (m, 8H). MS (ESI^+) *m/z* (rel Intensity): 360.1 ($[M - H_2O + H]^+$, 100).

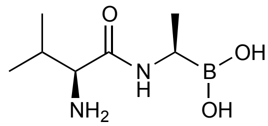
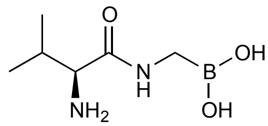
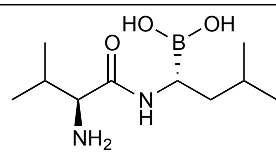
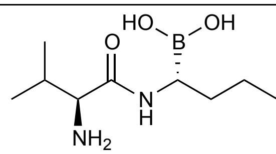
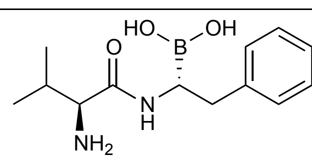
250	Thr-boroAla		^{1}H NMR (D_2O) δ 4.11 - 4.17 (m, 1H), 3.84 (d, *J* = 6.5 Hz, 1H), 2.97 (q, *J* = 7.4 Hz, 1H), 1.30 (d, *J* = 6.5 Hz, 3H), 1.18 (d, *J* = 7.4 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 345.2 ($[2 \times (M - H_2O) + H]^+$, 100), 173.5 ($[M - H_2O + H]^+$, 5).
251	Thr-boroGly		^{1}H NMR (D_2O) δ 4.14 (q, *J* = 6.4 Hz, 1H), 3.83 (d, *J* = 6.4 Hz, 1H), 2.83 (d, *J* = 16.9 Hz, 1H), 2.76 (d, *J* = 16.9 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 159.1 ($[M - H_2O + H]^+$, 100), 317.2 ($[2 \times (M - H_2O) + H]^+$, 75).
252	Thr-boroLeu		[35]
253	Thr-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 4.11 (q, *J* = 6.4 Hz, 1H), 3.80 (d, *J* = 6.2 Hz, 1H), 3.26 (dd, *J* = 9.8, 6.3 Hz, 1H), 2.98 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.86 (dd, *J* = 13.8, 9.8 Hz, 1H), 1.26 (d, *J* = 6.4 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 249.1 ($[M - H_2O + H]^+$, 100), 497.2 ($[2 \times (M - H_2O) + H]^+$, 50).
254	Thr-boroPro		[34]
255	Thr-boroSar		^{1}H NMR (D_2O) δ 4.53 (d, *J* = 5.8 Hz, 1H), 4.26 (dt, *J* = 5.8, 6.5 Hz, 1H), 3.26 (s, 3H), 2.57 (d, *J* = 5.2 Hz, 2H), 1.32 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (D_2O) δ 172.01, 68.42, 55.64, 47.66, 39.20, 20.92. MS (ESI^+) *m/z* (rel intensity): 173.1 ($[M - H_2O + H]^+$, 100).
256	Thr-Pro-CN		^{1}H NMR (D_2O) δ 4.87 (dd, *J* = 7.5, 5.4 Hz, 1H), 4.39 - 4.27 (m, 2H), 3.85 - 3.69 (m, 2H), 2.44 - 2.10 (m, 4H), 1.35 (d, *J* = 6.0 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 198.1 ($[M + H]^+$, 100).

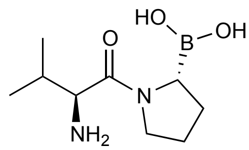
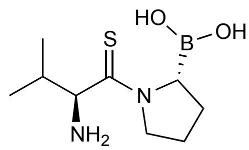
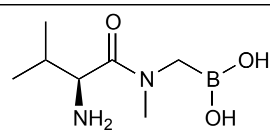
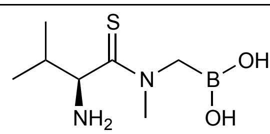
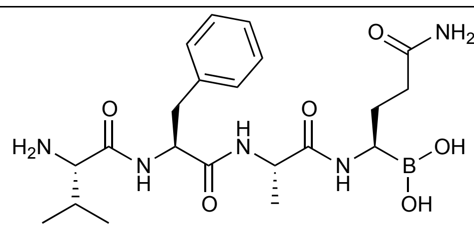
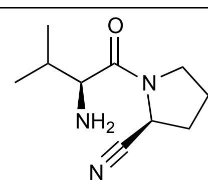
257	Tle-boroAla		[1]H NMR (D_2O) δ 3.81 (s, 1H), 2.96 (q, *J* = 7.5 Hz, 1H), 1.23 (d, *J* = 7.5 Hz, 3H), 1.15 (s, 9H). MS (ESI^+) *m/z* (rel intensity): 369.2 ($[2 \times (M - H_2O) + H]^+$, 100), 185.2 ($[M - H_2O + H]^+$, 69).
258	Tle-boroGly		[1]H NMR (D_2O) δ 3.70 (s, 1H), 2.77 (d, *J* = 16.7 Hz, 1H), 2.67 (d, *J* = 16.7 Hz, 1H), 1.05 (s, 9H). MS (ESI^+) *m/z* (rel Intensity): 171.2 ($[M - H_2O + H]^+$, 100), 313.2 ($[2 x (M - H_2O) + H]^+$, 50).
259	Tle-boroLeu		35
260	Tle-boroNva		[1]H NMR (D_2O): δ 3.75 (s, 1H), 2.79 (t, *J* = 7.6 Hz, 1H), 1.54 - 1.47 (m, 2H), 1.39 - 1.28 (m, 2H), 1.07 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 425.3 ($[2 \times (M - H_2O) + H]^+$, 100), 213.2 ($[M - H_2O + H]^+$, 46).
261	Tle-boroPhe		[1]H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.70 (s, 1H), 3.15 (dd, *J* = 10.6, 6.0 Hz, 1H), 2.97 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.78 (dd, *J* = 14.1, 10.6 Hz, 1H), 1.05 (s, 9H). MS (ESI^+) *m/z* (rel Intensity): 261.1 ($[M - H_2O + H]^+$, 100), 521.3 ($[2 x (M - H_2O) + H]^+$, 50).
262	Tle-boroPro		34
263	Tle-boroSar		[1]H NMR (D_2O) δ 4.39 (s, 1H), 3.24 (s, 3H), 2.46 (d, *J* = 14.9 Hz, 2H), 1.09 (s, 9H). [13]C NMR (D_2O) δ 172.91, 57.65, 48.09, 39.87, 37.60, 27.96. MS (ESI^+) *m/z* (rel intensity): 185.2 ($[M - H_2O + H]^+$, 100).

264	Tle-Pro-CN		47
265	Trp-boroAla		^{1}H NMR (D_2O) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.32 - 7.15 (m, 3H), 4.26 (t, *J* = 7.6 Hz, 1H), 3.38 (d, *J* = 7.6 Hz, 2H), 2.76 (q, *J* = 7.4 Hz, 1H), 0.90 (d, *J* = 7.4 Hz, 3H). MS (ESI^{+}) *m/z* (rel intensity): 515.3 ([2 × (M - H_2O) + H]$^{+}$, 37), 258.1 ([M - H_2O + H]$^{+}$, 100).
266	Trp-boroGly		^{1}H NMR (D_2O) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.32 - 7.18 (m, 3H), 4.26 (t, *J* = 7.1 Hz, 1H), 3.39 (d, *J* = 7.1 Hz, 2H) 2.68 (d, *J* = 17.0 Hz, 1H), 2.54 (d, *J* = 17.0 Hz, 1H). MS (ESI^{+}) *m/z* (rel Intensity): 244.1 ([M - H_2O + H]$^{+}$, 100), 261.1 ([M + H]$^{+}$, 20).
267	Trp-boroLeu		35
268	Trp-boroNva		^{1}H NMR (D_2O): δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.30 - 7.10 (m, 3H), 4.29 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.45 - 3.31 (m, 2H), 2.63 (t, *J* = 5.9 Hz, 1H), 1.23 - 0.85 (m, 4H), 0.74 (t, *J* = 7.3 Hz, 3H). MS (ESI+) *m/z* (rel intensity): 571.3 ([2 × (M - H_2O) + H]$^{+}$, 23), 326.2 ([M + Na]$^{+}$, 6), 286.2 ([M - H_2O + H]$^{+}$, 100).
269	Trp-boroPhe		^{1}H NMR (D_2O) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.45 - 7.19 (m, 6H), 6.90 - 6.80 (m, 2H), 4.25 (dd, *J* = 8.5, 7.1 Hz, 1H), 3.45 - 3.30 (m, 2H), 2.94 (dd, *J* = 10.4, 5.1 Hz, 1H), 2.67 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.30 (dd, *J* = 13.8, 10.4 Hz, 1H). MS (ESI^{+}) *m/z* (rel Intensity): 334.1 ([M - H_2O + H]$^{+}$, 100), 667.3 ([2 x (M - H_2O) + H]$^{+}$, 40).

270	Trp-boroPro		^{1}H NMR (D_2O) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.1Hz, 1H), 7.36 (s, 1H), 7.30 - 7.20 (m, 2H), 4.55 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.80 - 3.75 (m, 1H), 3.49 (dd, *J* = 15.1, 5.6 Hz, 1H), 3.38 - 3.06 (m, 3H), 2.09 - 2.01 (m, 3H), 1.73 - 1.68 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 284.2 ($[M - H_2O + H]^+$, 70), 302.2 ($[M + H]^+$, 100).
271	Trp-boroSar		^{1}H NMR (D_2O) δ 7.64 - 7.20 (m, 5H), 4.84 (dd, J = 6.6, 8.2 Hz, 1H), 3.55 - 3.38 (m, 2H), 2.63 (s, 3H), 2.30 (s, 2H). ^{13}C NMR (D_2O) δ 173.25, 138.80, 128.99, 128.08, 124.91, 122.34, 120.37 114.79, 108.03, 51.04, 47.60, 38.28, 28.83. MS (ESI^+) *m/z* (rel intensity): 258.1 ($[M - H_2O + H]^+$, 100).
272	Trp-Pro-CN		^{1}H NMR (D_2O) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.33 - 7.18 (m, 2H), 4.59 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.56 - 3.34 (m, 3H), 2.76 - 2.71 (m, 1H), 2.22 - 2.13 (m, 2H), 1.88 - 1.83 (m, 1H), 1.68 - 1.64 (m, 1H). MS (ESI^+) *m/z* (rel Intensity): 283.1 ($[M + H]^+$, 100), 305.1 ($[M + Na]^+$, 35).
273	Tyr-boroAla		^{1}H NMR (D_2O) δ 7.17 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.15 (t, *J* = 7.3 Hz, 1H), 3.14 - 3.10 (m, 2H), 2.83 (q, *J* = 7.4 Hz, 1H), 1.01 (d, *J* = 7.4 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 469.2 ($[2 \times (M - H_2O) + H]^+$, 67), 235.2 ($[M - H_2O + H]^+$, 100).
274	Tyr-boroGly		^{1}H NMR (D_2O) δ 7.15 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 4.14 (t, *J* = 7.3 Hz, 1H), 3.10 (d, *J* = 7.3 Hz, 2H), 2.73 (d, *J* = 16.9 Hz, 1H), 2.60 (d, *J* = 16.9 Hz, 1H). MS (ESI^+) *m/z* (rel Intensity): 221.1 ($[M - H_2O + H]^+$, 100), 441.2 ($[2 x (M - H_2O) + H]^+$, 60).

275	Tyr-boroLeu		35
276	Tyr-boroNva		[1]H NMR (D_2O): δ 7.15 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.15 (dd, J = 9.3, 6.4 Hz, 1H), 3.12 (ddd, J = 42.0, 13.7, 6.4 Hz, 2H), 2.66 (dd, J = 9.3, 5.5 Hz, 1H), 1.33 - 1.18 (m, 2H), 1.04 - 0.94 (m, 2H), 0.80 (t, J = 7.1 Hz, 3H). MS (ESI^+) m/z (rel intensity): 525.3 ($[2 \times (M - H_2O) + H]^+$, 65), 263.2 ($[M - H_2O + H]^+$, 100).
277	Tyr-boroPhe		[1]H NMR (D_2O) δ 7.31 - 7.20 (m, 3H), 7.17 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 6.9 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.13 (dd, J = 8.8, 6.9 Hz, 1H), 3.20 - 3.00 (m, 3H), 2.84 (dd, J = 13.9, 5.2 Hz, 1H), 2.51 (dd, J = 13.9, 10.7 Hz, 1H). MS (ESI^+) m/z (rel Intensity): 311.1 ($[M - H_2O + H]^+$, 100).
278	Tyr-boroPro		34
279	Tyr-boroSar		[1]H NMR (D_2O) δ 7.17 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 4.72 (dd, J = 6.6, 9.4 Hz, 1H), 3.29 - 3.09 (m, 2H), 2.69 (s, 3H), 2.42 (s, 2H). [13]C NMR (D_2O) δ 172.81, 158.05, 133.59, 127.08, 118.57, 51.77, 47.55, 38.20. MS (ESI^+) m/z (rel intensity): 235.2 ($[M - H_2O + H]^+$, 100).
280	Tyr-Pro-CN		[1]H NMR (D_2O) δ 7.21 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.46 (dd, J = 9.3, 5.4 Hz, 1H), 3.42 - 3.25 (m, 2H), 3.10 (dd, J = 13.5, 9.7 Hz, 1H), 2.72 - 2.69 (m, 1H), 2.25 - 2.17 (m, 2H), 1.97 - 1.92 (m, 1H), 1.79 - 1.73 (m, 1H). MS (ESI^+) m/z (rel Intensity): 260.1 ($[M + H]^+$, 100), 519.2 ($[2M + H]^+$, 75).

281	Val-boroAla		
282	Val-boroGly		^{1}H NMR (D_2O): δ 3.73 (d, *J* = 6.5 Hz, 1H), 2.77 (d, *J* = 16.7 Hz, 1H), 2.66 (d, *J* = 16.7 Hz, 1H), 2.15 (dt, *J* = 6.6, 6.5 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (D_2O) δ 172.36, 61.30, 32.55, 30.90, 20.19, 19.68. MS (ESI^+) *m/z* (rel intensity): 313.2 ([2 x (M - H_2O) + H]$^+$, 59), 157.2 ([M - H_2O + H]$^+$, 100).
283	Val-boroLeu		^{1}H NMR (D_2O) δ 3.82 (d, *J* = 6.2 Hz, 1H), 2.90 (dd, *J* = 9.1, 6.7 Hz, 1H), 2.28 - 2.17 (m, 1H), 1.62 - 1.33 (m, 3H), 1.04 (d, *J*= 2.8 Hz, 3H), 1.02 (d, *J* = 2.8 Hz, 3H), 0.91 (d, *J* = 4.0 Hz, 3H), 0.89 (d, *J* = 4.0 Hz, 3H). LCMS (ESI^+) m/z (rel intensity): 213.1 ([M - H_2O + H]$^+$, 90), 425.2 ([2 x (M - H_2O) + H]$^+$, 100). 637.4 ([3 x (M - H_2O) + H]$^+$, 60).
284	Val-boroNva		^{1}H NMR (D_2O): δ 3.81 (d, *J* = 6.2 Hz, 1H), 2.83 (t, *J* = 7.5 Hz, 1H), 2.25 - 2.16 (m, 1H), 1.56 - 1.48 (m, 2H), 1.41 - 1.28 (m, 2H), 1.04 - 1.00 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 3H). MS (ESI^+) *m/z* (rel intensity): 595.5 ([3 × (M - H_2O) + H]$^+$, 6), 397.3 ([2 × (M - H_2O) + H]$^+$, 100), 199.2 ([M - H_2O + H]$^+$, 25).
285	Val-boroPhe		^{1}H NMR (D_2O) δ 7.45 - 7.25 (m, 5H), 3.71 (d, *J* = 5.6 Hz, 1H), 3.15 (dd, *J* = 10.8, 6.1 Hz, 1H), 2.98 (dd, *J* = 14.1, 6.1 Hz, 1H), 2.78 (dd, *J* = 14.1, 10.8 Hz, 1H), 2.13 (q, *J* = 6.6 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H). MS (ESI^+) *m/z* (rel Intensity): 247.1 ([M - H_2O + H]$^+$, 100), 493.2 ([2 x (M - H_2O) + H]$^+$, 50).

286	Val-boroPro		34
287	Val-boroPro thioxoamide		^{1}H NMR (D_2O) δ 4.25 (d, *J* = 7.1 Hz, 1H), 4.05 - 3.95 (m, 1H), 3.70 - 3.60 (m, 1H), 3.55 - 3.45 (m, 1H), 2.35 - 1.80 (m, 5H), 1.07 - 1.00 (m, 6H). MS (ESI$^+$) *m/z* (rel intensity): 231.1 ([M + H]$^+$, 100).
288	Val-boroSar		^{1}H NMR (D_2O) δ 4.42 (d, *J* = 6.5 Hz, 2H), 3.23 (s, 3H), 2.57 (d, *J* = 14.8 Hz, 1H), 2.50 (d, *J* = 14.8 Hz, 1H), 2.32 (dq, *J* = 6.9, 6.5 Hz, 1H), 1.05 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (D_2O) δ 173.75, 51.59, 47.62, 38.74, 26.13, 10.76. MS (ESI$^+$) *m/z* (rel intensity): 171.1 ([M - H_2O + H]$^+$, 100).
289	Val-boroSar thioxoamide		^{1}H NMR (D_2O) δ 4.45 (d, *J* = 7.4 Hz, 2H), 3.55 - 3.30 (m, 5H), 2.30 - 2.20 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H). MS (ESI$^+$) *m/z* (rel intensity): 205.2 ([M + H]$^+$, 36), 187.1 ([M - H_2O + H]$^+$, 100).
290	Val-Phe-Ala-boroGln		^{1}H NMR (D_2O) δ 7.43 - 7.30 (m, 5H), 4.70 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = 5.7 Hz, 1H), 3.13 - 2.80 (m, 3H), 2.60 - 2.40 (m, 1H), 2.31 - 2.15 (m, 2H), 1.90 - 1.85 (m, 1H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.0 (d, *J* = 3.9 Hz, 3H), 0.98 (d, *J* = 3.9 Hz, 3H). MS (ESI$^+$) *m/z* (rel Intensity): 446.3 ([M - H_2O + H]$^+$, 100).
291	Val-Pro-CN		49

Supplementary Table 7 Evaluation of boronic acid-based ARI-2408 and ARI-2243 compared with clinically used DPP4 inhibitors in enzyme substrate assays for DPP4, DPP8, and DPP9**.** Monkey toxicity data for ARI-2408 and ARI-2243 is described in detail in **Supplementary Note 1**. The selectivity (for DPP4 over DPP8 and DPP9) and safety of compound ARI-2408, but not compound ARI-2243 or the clinically used drugs vildagliptin and saxagliptin, compares well to sitagliptin.

		IC_{50}			***Fold Selectivity***		**Monkey Adverse Events**
Compound	***Ki (DPP IV)***	***DPPIV***	***DPP8***	***DPP9***	**DPP8**	**DPP9**	
ARI-2408	0.9 nM	1.7 nM	12 μM	11 μM	**7,000X**	**6,500X**	**No**
ARI-2243	27 pM	0.7 nM	3.8 nM	8.4 nM	5.4X	12X	Yes
Vildagliptin	27 nM	58 nM	140 nM	110 nM	2.4X	1.9X	Yes
Sitagliptin	9 nM	18 nM	48 mM	10 mM	2,700X	560X	No
Saxagliptin	1.3 nM	1.0 nM	197 nM	54 nM	200X	60X	Yes

Supplementary Table 8 Safety profile of ARI-2408 and ARI-2243 compared to sitagliptin (Januvia) in monkeys. *Januvia NDA (21-995) Review, 2006; Section 2.6.6.8: pp. 104-111

Proportion of Animals with observed Adverse Events (e.g., skin lesions, edema, or death)				
Dose	ARI-2243	ARI-2408		Sitagliptin
(mg/kg)	Single	Single	Repeat	Repeat*
0.3	5/12	-	-	
1.0	11/12	-	-	-
3.0	9/12	-	-	-
90.0	-	-	-	-
100.0	-	0/4	0/4	0/6
300.0	-	0/6	-	-
500.0	-	-	-	-

Supplementary Note 1

Detailed compound ARI-2408 monkey toxicity conclusions:

Treatment with a single dose of compound ARI-2408 at 300 mg/kg or seven consecutive days of dosing at 100 mg/kg, did not result in any test article-related alterations in clinical observations or measured clinical chemistry parameters. Absolute neutrophil counts (ANE) and white blood cell (WBC) counts were increased in most animals at both doses at 24 hours postdose. The extent of the increase at 24 hours was similar between doses. Altered hematology parameters had returned to predose levels by Day 7. Notably, ARI-2408 exposure under both dosing regimens did not result in clinical observations of edema or swelling of the extremities in any animal, including four animals which had previously been dosed with compound ARI-2243 and observed to have edema and swelling.

Detailed compound ARI-2243 monkey toxicity conclusions:

This study evaluated the toxicity of compound ARI-2243 when administered as daily oral doses to cynomolgous monkeys for two days at dose levels of 0 (vehicle control), 0.3, 1.0 and 3.0 mg/kg/day. Parameters which were evaluated in all animals to examine test article-related effects were: daily and detailed clinical observations, body weights/body weight change, food consumption, hematology, coagulation, and clinical chemistry. Physical examinations, ophthalmic examination, urinalysis, and electrocardiograms were performed pretest, but these parameters were not evaluated following dosing and so cannot be used to determine test article-related toxicity (except *ad hoc* physical examinations in one monkey when it was in poor health). In addition, plasma samples were collected for determination of whole blood concentrations of compound ARI-2243. Monkeys tolerated two daily doses of compound ARI-2243 at 0.3

mg/kg/day, but one monkey died after a single dose at 1 mg/kg and another was euthanized due to toxicity 10 days after a single dose at 3 mg/kg. Toxicity occurred at all dose levels and was manifested chiefly by clinical signs of edema and/or erythema of the skin of the extremities and peri-oral region, ulceration (noted as abrasions, crusts, sores, or sloughing) of the skin of the feet and tail, and increased lactate dehydrogenase (LDH), aspartate aminotransferase (AST), and creatine kinase (CK) activities. Postmortem findings in the euthanized monkey suggested that the clinical signs and changes in clinical chemistry parameters reflected tissue damage from drug-related skeletal muscle degeneration, vasculitis and thrombosis of dermal and submucosal blood vessels, and subsequent infarction of overlying skin and mucosa. When the study ended 12 days after dosing stopped, clinical chemistry changes had resolved completely but skin lesions were still present in some monkeys.

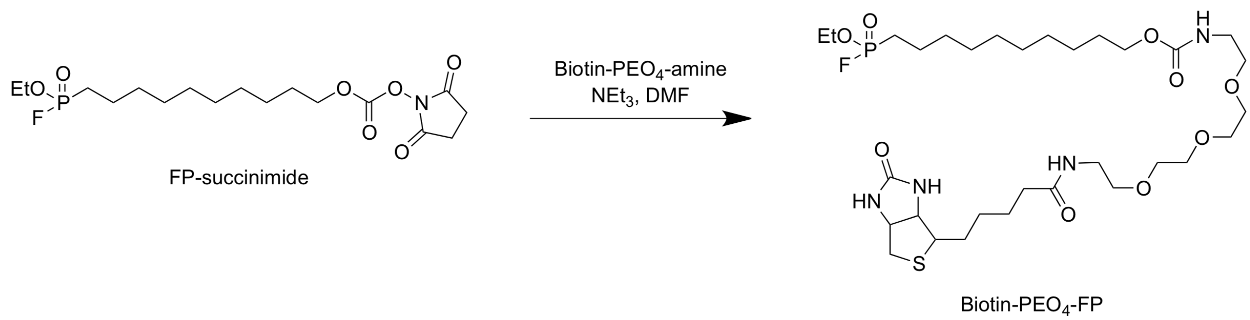
Based on these results, a no-observed-adverse-effect level was not identified. At the lowest dose level of 0.3 mg/kg/day, toxicity was limited to skin lesions on the feet of one monkey (incidence = 8%) and increased LDH, AST, and/or CK activities in three monkeys (incidence = 25%).

Supplementary Note 2

Synthetic Methods

Synthesis of Biotin-PEO$_4$-FP ("FP-biotin"):

Scheme 1.



A solution of FP-succinimide [50] (41 mg, 0.1 mmol) in DMF (2.0 ml) was treated with Et_3N (20.2 mg, 0.2 mmol) and biotin-PEO$_4$-amine (50 mg, 0.12 mmol, purchased from ChemPep Inc. CAS No. 359860-27-8) at room temperature. The reaction mixture was stirred for 5 hrs and then concentrated *in vacuo*. The residue was partitioned into water and ethyl acetate. The organic phase was isolated and the aqueous phase was extracted with more ethyl acetate. All organic phases were combined and washed with water, then brine, dried over Na_2SO_4 and concentrated under reduced pressure. Anhydrous Et_2O (10 ml) was added to the residue and the mixture was ultrasonicated. The desired compound Biotin-PEO$_4$-FP was precipitated out and the solvent was removed using pipette. This procedure was repeated for 3 times to give Biotin-PEO$_4$-FP as a pale gray powder (30 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (br, 1H), 6.47 (br, 1H), 5.49 (br, 1H), 5.36 (br, 1H), 4.55 - 4.45 (m, 1H), 4.30 - 4.20 (m, 3H), 4.05 - 3.95 (m, 2H), 3.65 - 3.59 (m, 8H), 3.59 - 3.52 (m, 4H), 3.45 - 3.30 (m, 4H), 3.15 - 3.05 (m, 1H), 2.95 - 2.85 (m, 1H), 2.80 - 2.70 (m, 1H), 2.22 - 2.19 (m, 2H), 1.90 - 1.75 (m, 2H), 1.75 - 1.57 (m, 8H), 1.45 - 1.27 (m, 17H). LC-MS (ESI$^+$) *m/z* (rel intensity), 713.3 ($(M + H)^+$, 100), 357.2 (32); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 176.00, 166.71, 159.59, 73.05, 72.88, 72.75, 72.66, 67.69, 65.72 (J=7.5 Hz), 64.43, 62.88, 58.29, 43.41, 43.20, 41.80, 38.63, 33.06, 32.84, 32.11, 31.90, 31.74, 31.62, 30.89, 30.78, 28.51, 28.30, 28.06, 27.77, 26.17, 25.87, 24.58 (J=5.2 Hz), 19.05 (J=6.0 Hz); tr = 9.6 min (Column: Agilent Eclipse Plus C18 4.6 x 50 mm, 1.8 μm particle size; Flow rate: 0.5 mL/min; Eluent gradient 2% B for the first 3 min, then from 2% to 98% B over 6 min and kept 98% B for 5 min; Solvent A, 0.1 % TFA in water; Solvent B, 0.08 % TFA in acetonitrile); Purity >98.5% (a/a). HRMS calcd for $C_{31}H_{59}FN_4O_9PS$ $[M + H]^+$, 713.3719 ; found, 713.3716.

Synthesis of the boronic acid- and nitrile-based compounds. Syntheses were performed using the previously described synthetic methods[34, 42, 45, 51]. All the target compounds were purified by RP-HPLC using Varian semi-preparative system with a Discovery C18 569226-U RP-HPLC column. The mobile phase was typically made by mixing water (0.1% TFA) with acetonitrile (0.08% TFA) in gradient concentration. Purities determined by HPLC analysis were greater than 95%. HRMS were performed by Technical Services of University of Michigan. Chemical characterization for numbered compounds not shown below is included in **Supplementary Table 6**.

Compound 24. Ala-boroPro thioxoamide or ARI-2243

^{1}H NMR (300 MHz, D_2O): δ 4.55 (q, *J* = 6.6 Hz, 1H), 4.00-3.92 (m, 1H), 3.69 - 3.62 (m, 1H), 3.56 - 3.50 (m, 1H), 2.25 - 2.08 (m, 3H), 1.90 - 1.83 (m, 1H), 1.51 (d, *J* = 6.7 Hz). ^{13}C NMR (300 MHz, D_2O): δ 194.51, 60.36, 54.48, 54.38, 29.30, 28.78, 20.22. HRMS Calcd for $C_7H_{16}BN_2O_2S$ $[M + H]^+$, 203.1026; found 203.1030.

Compound 33. Ala-(1-naph)-boroPro

^{1}H NMR (300 MHz, D_2O): δ 8.10 – 7.46 (m, 7H), 4.65 - 4.55 (m, 1H), 2.78 - 3.75 (m, 5H), 1.99 - 1.4 (m, 4H). ^{13}C NMR (300 MHz, D_2O): δ 169.44, 136.28, 133.78, 132.01, 131.82, 131.65, 131.50, 129.73, 129.00, 128.52, 125.26, 54.37, 51.46, 49.98, 35.93, 29.17. HRMS Calcd for $C_{17}H_{22}BN_2O_3$ [M + H]$^+$, 313.1718; found 313.1727.

Compound 36. Ala-(1-naph)-Pro-CN

^{1}H NMR (300 MHz, D_2O): δ 8.16 – 7.99 (m, 3H). 7.76 - 7.46 (m, 4H), 4.80 - 4.64 (m, 2H), 4.00 - 3.50 (m, 3H), 3.10 - 3.04 (m, 1H), 2.11 – 3.31 (m, 4H). ^{13}C NMR (300 MHz, D_2O): δ 171.02, 136.11, 133.88, 131.77, 131.57, 131.44, 130.08, 129.11, 128.67, 125.22, 120.54, 54.01, 49.40, 49.23, 36.88, 31.67, 26.98. HRMS Calcd for $C_{18}H_{20}N_3O$ [M + H]$^+$, 294.1601; found 294.1611.

Compound 51. Asn-boroPhe

^{1}H NMR (300 MHz, D_2O): δ 7.42 - 7.27 (m, 5H), 4.27 (t, J = 6.2 Hz, 1H), 3.26 - 3.20 (m, 1H), 3.00 - 2.75 (m, 4H). ^{13}C NMR (300 MHz, D_2O): δ 175.13, 171.72, 142.10, 131.57, 131.32, 129.21, 51.42, 46.32, 38.24, 37.43. HRMS Calcd for $C_{12}H_{17}BN_3O_3$ [M - H2O + H]$^+$, 262.1357; found 262.1368.

Compound 60. Asp-boroPhe

^{1}H NMR (300 MHz, D_2O): δ 7.42 - 7.25 (m, 5H), 4.30 - 4.20 (m, 1H), 3.21 - 3.11 (m, 1H), 3.05 – 2.77 (m, 4H). ^{13}C NMR (300 MHz, D_2O): δ 175.75, 171.66, 142.14, 131.57, 131.33, 129.21, 51.36, 46.38, 38.22, 37.77. HRMS Calcd for $C_{12}H_{16}BN_2O_4$ [M - H2O + H]$^+$, 263.1198; found 263.1210.

Compound 93. Glu-boroSar thioxoamide or ARI-2408

^{1}H NMR (300 MHz, D_2O): δ 4.65 (t, J = 6.4 Hz, 1H), 3.15 (s, 3H), 2.53 (t, J = 7.1 Hz, 2H), 2.47 (s, 2H) 2.25 -2.05 (m, 2H). ^{13}C NMR (300 MHz, D_2O): δ 195.96, 178.82, 55.57, 52.00, 45.06, 31.03, 30.10. HRMS Calcd for $C_7H_{14}BN_2O_4$ [M - H2O + H]$^+$, 201.1047; found 201.1043.

Compound 99. Gly-boroPhe

^{1}H NMR (300 MHz, D_2O): δ 7.57 - 7.04 (m, 5H), 3.72 (s, 2H), 3.33 - 3.27 (m, 1H), 3.00 - 2.58 (m, 2H). ^{13}C NMR (300 MHz, D_2O): δ 169.89, 142.08, 131.57, 131.28, 129.21, 46.19, 42.10, 38.38. HRMS Calcd for $C_{10}H_{14}BN_2O_2$ [M - H2O + H]$^+$, 205.1143; found 205.1142.

Compound 217. Phe-Pro-CN

^{1}H NMR (300 MHz, D_2O): δ 7.48 - 7.33 (m, 5H) 4.52 (dd, J = 5.5 Hz, 1H), 3.43 - 3.33 (m, 2H), 3.24 - 3.16 (m, 1H), 2.71 - 2.68 (m, 1H), 2.24 - 1.53 (m, 4H). ^{13}C NMR (300 MHz, D_2O): δ 170.87, 135.83, 132.92, 132.41, 130.92, 120.89, 55.58, 49.69, 49.50, 39.61, 27.33, 24.64. HRMS Calcd for $C_{14}H_{18}N_3O$ [M + H]$^+$, 244.1444; found 244.1452.

Compound 226. Py(D)Ala-boroPro

Previously characterized in ref. 42.

Compound 244. Ser-boroPhe

^{1}H NMR (300 MHz, D_2O): δ 7.40 - 7.25 (m, 5H), 4.15 - 4.05 (m, 1H), 3.95 - 3.80 (m, 2H), 3.30 - 3.20 (m, 1H), 3.00 – 2.75 (m, 2H). ^{13}C NMR (300 MHz, D_2O): δ 170.69, 142.09, 131.60, 131.29, 129.22, 62.78, 56.24, 46.37, 38.36. HRMS Calcd for $C_{11}H_{16}BN_2O_3$ [M - H2O + H]$^+$, 235.1248; found 235.1256.

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