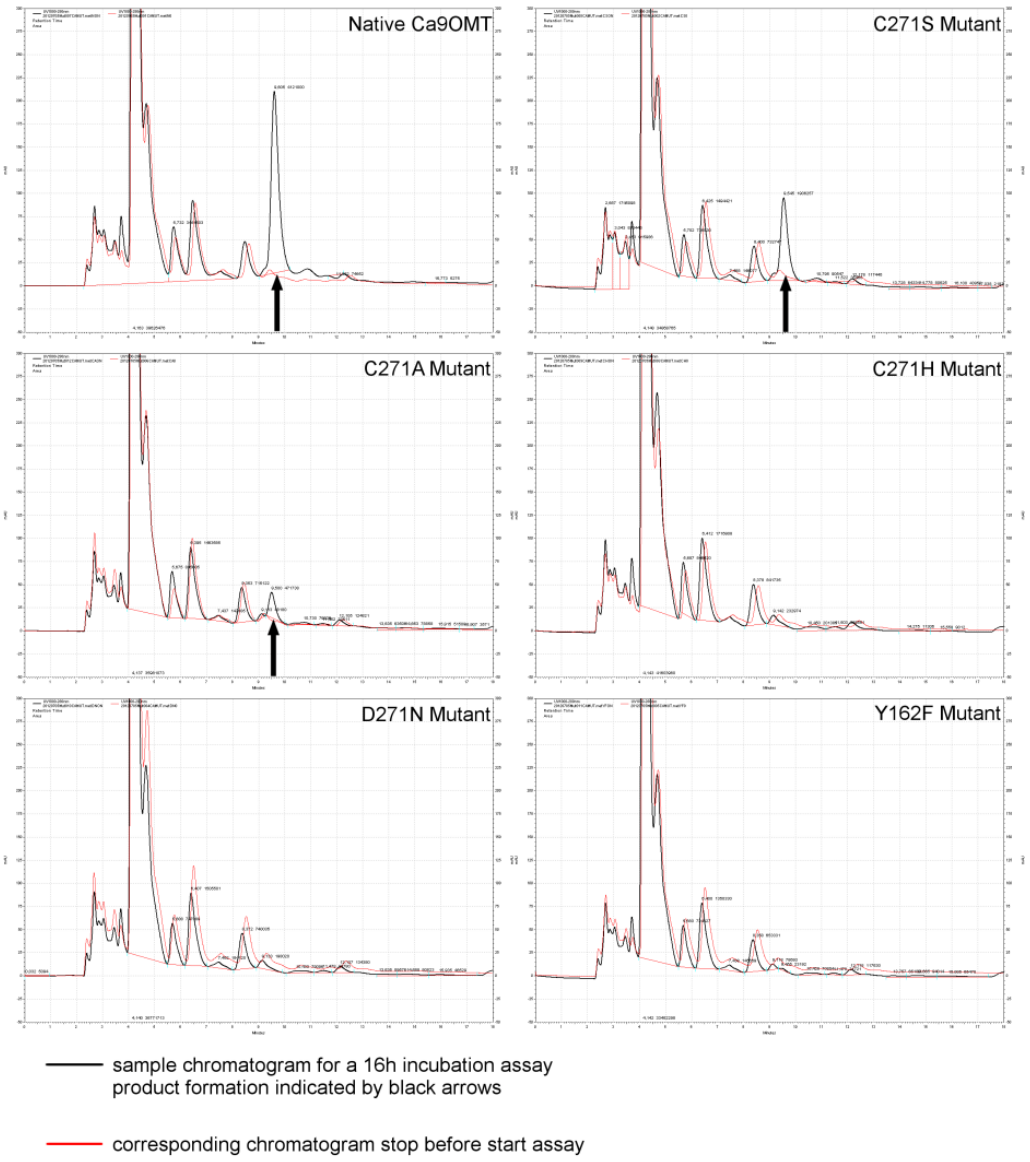
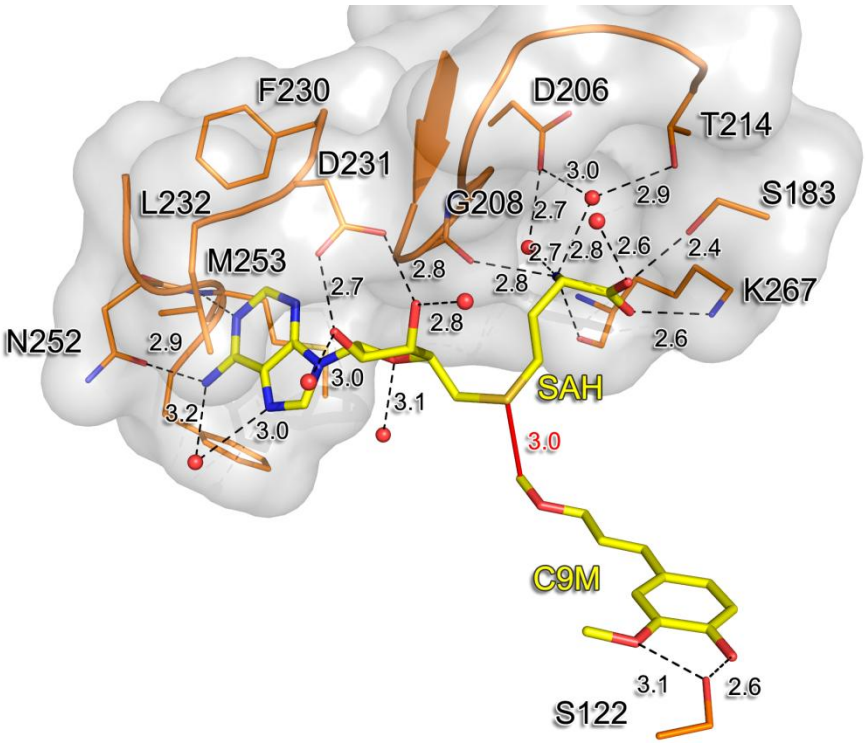
Supplementary Material



Supplementary Figure S1. Representative chromatograms.



Supplementary Figure S2. SAM binding mode.

Supplementary Table S1. SAM interactions.

Residues complexing the purine ring system of SAM/SAH
Y162: non-polar cavity
L232: non-polar cavity
N252: H-bond between side chain and purine ring amino function(N6)2.9 Å
M253: non-polar cavity
Residues complexing the ribose ring of SAM/SAH
D231: two direct H-bond interactions between side chain and ribose hydroxyl functions 2.8 Å and 2.7 Å
S176: bridged H-bond via HOH586A,distance S176 HOH586A: 3.0 Å distance HOH586A and hydroxyl function of SAM(O3): 2.8 Å
H234: bridged H-bond via HOH586A distance H234 HOH586A: 3.1 Å distance HOH586A and hydroxyl function of SAM(O2): 3.0 Å
D272: bridged H-bond via HOH568A distance D272 HOH568A: 2.9 Å distance HOH568A and ring bound oxygen(O4) of SAM: 3.1 Å
W273: bridged H-bond via HOH568A distance W273 HOH568A: 2.9 Å distance HOH568A and ring bound oxygen(O4) of SAM: 3.1 Å
Residues complexing the thioether function of SAM
V205-T214: several non-polar interactions
Residues complexing the methionine carboxyl and amino functions
S183: H-bond between side chain and SAM carboxyl function (O) 2.4 Å
G208: H-bond between backbone oxygen and SAM amino function (N) 2.8 Å
K267: H-bond between side chain and SAM carboxyl function(O): 2.6 Å H-bond between backbone oxygen and SAM amino function 2.7 Å

Supplementary Table S2: Results of isothermal titration calorimetry measurements (ITC) all values derived from three independent measurements. Error ranges indicate the estimated standard deviations from triplicate measurements.

Combination of Ligand and Protein	**N [sites]**	**K_b [M^{-1}]**	**K_d [µM]**	**ΔH^0 [kj/mol]**	**$-T\Delta S^0$ [kj/mol/ deg]**
A:experimental setup 1 **sample cell:** Ca9OMT **syringe**: coniferyl alcohol	0.779 ±0.212	$1.95 \cdot 10^5$ $\pm 0.38 \cdot 10^5$	5.26 ±1.02	-43.7 ±5.7	13.0 ±5.3
B:experimental setup 2 **sample cell:** Ca9OMT+coniferyl alcohol **syringe:** SAM	0.525 ±0.057	$2.45 \cdot 10^6$ $\pm 0.85 \cdot 10^6$	0.45 ±0.16	-55.1 ±3.5	18.2 ±4.4
C:experimental setup 3 **sample cell:** Ca9OMT **syringe:** SAM	n.d.	n.d.	n.d.	n.d.	n.d.
D:experimental setup 4 **sample cell:** Ca9OMT+SAM **syringe:** coniferyl alcohol	0.865 ±0.046	$3.96 \cdot 10^5$ $\pm 1.95 \cdot 10^5$	2.94 ±1.29	-62.2 ±4.0	29.9 ±5.3