

Supplemental Information

The Nitrogen Atom of Vitamin B₆ Is Essential for the Catalysis of Radical Aminomutases

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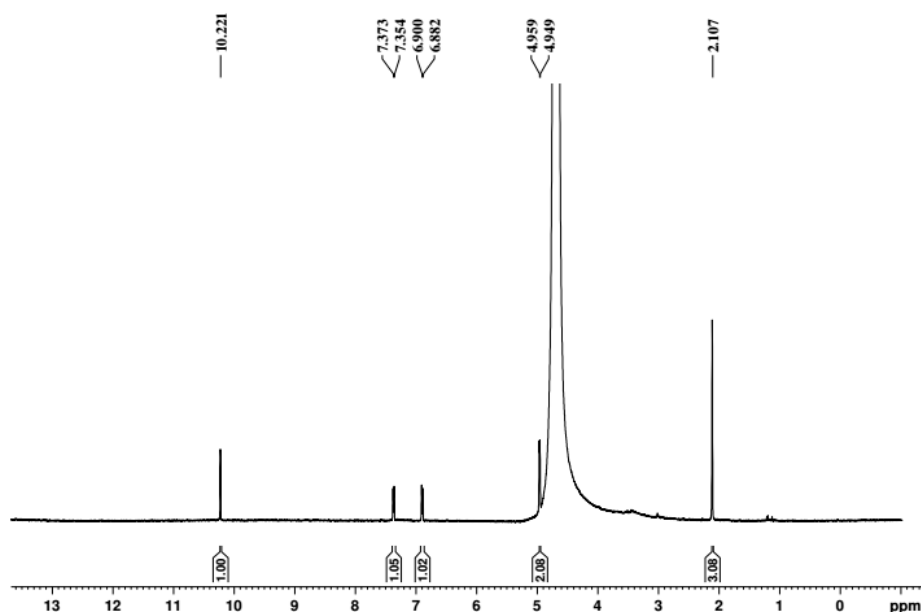


Figure S1. ¹H NMR spectrum of dAPLP in D₂O.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 200.0 PPM / DBE: min = -20.0, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

234 formula(e) evaluated with 53 results within limits (up to 20 closest results for each mass)

Elements Used:

C: 1-100 H: 1-10 O: 1-10 P: 1-3 Na: 0-1

deazaPLP

190215esi01 68 (1.002) Cm (67.70)

1: TOF MS ES-
3.70e+007

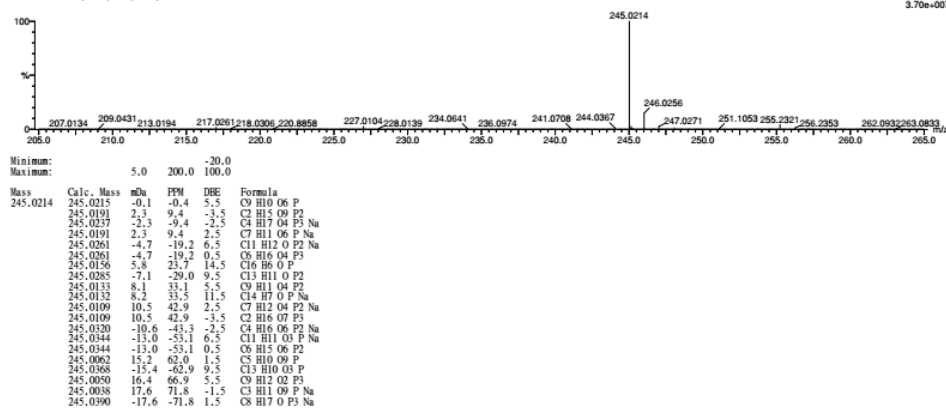


Figure S2. HRESI Mass spectrum of dAPLP in negative ion mode.

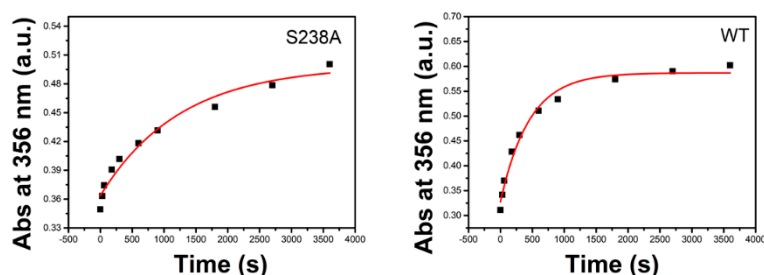


Figure S3. Comparison of rate of suicide inactivation between the S238A variant (left) and WT (right). The rate of hydroxycobalamin formation was followed at 356 nm. The suicide inactivation rates were 3.72×10^{-4} and $1.97 \times 10^{-3} \text{ s}^{-1}$ for S238A and WT, respectively.

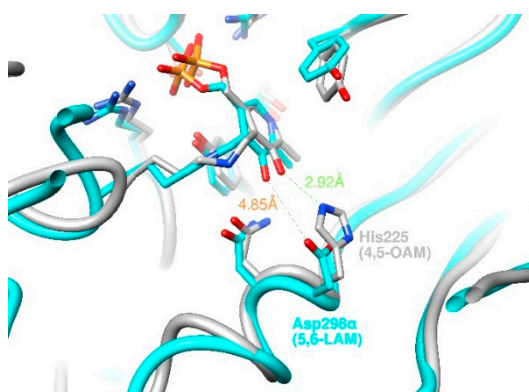


Figure S4. Superimpose of active sites of substrate free crystal structure of 5,6-LAM (cyan) and 4,5-OAM (gray). His225 of 4,5-OAM overlays with Asp298α of 5,6-LAM. His225 makes hydrogen bonding interaction with phenolic hydroxyl group of PLP whereas Asp298α is 4.85 Å away from phenolic hydroxyl group of PLP indicating absence of any interaction between PLP and Asp298α.

Gaussian Archive Entries for the B3LYP/6-31G(d,P) Optimized Geometries

dAPLP

S[•]

1|1|UNPC-DESKTOP-TBQL3NN|SP|ROMP2-FC|GTMP2large|C12H16N1O1(2)|LABPC|12

-Nov-2020|0||# romp2 maxdisk=7840MW geom=connectivity gtmp2large scf=tight||Substrate

(1-aminopropane) radical aldimine with deaza-Pyridoxal model gtmp2 energy||0,2|N,0,-

1.72867794,0.18560711,-0.46479394|C,0,-0.75762252,1.01088273,-0.27282032|H,0,-

0.95496797,2.0895123,-0.23751674|C,0,0.6214819,0.577721,-0.0994531|C,0,0.92614231,-

0.81178441,0.12546005|C,0,2.25148205,1.27022163,0.04213924|C,0,2.96491575,1.0546402
9,0.25648006|C,0,1.66671307,1.52172431,0.09439408|H,0,3.77389137,1.76368079,0.40557
409|O,0,-0.0274474,-1.73743806,-0.30915084|H,0,-0.89850185,1.24687764,0.41260201|
C,0,-3.09470466,0.71232012,-0.59458272|C,0,-3.96067104,0.24391972,0.53537493|H,0,-
3.49810752,0.34772602,-1.54884963|H,0,-3.0783048,1.81362639,-0.63679705|H,0,-
3.86734755,0.76957773,1.4833267|C,0,-4.61036555,-1.09702047,0.52125252|H,0,-
5.4168711,-1.16614057,1.2584419|H,0,-5.02506969,-1.33366834,-0.4666265|H,0,-
3.89257975,-1.9010596,0.75752486|C,0,3.24535171,0.31890375,0.23010278|
H,0,4.27201618,-0.65301965,0.35999696|C,0,2.53221718,2.74917836,0.00963821|
H,0,1.96731351,-3.27699942,0.78576132|H,0,2.22752701,-3.18964634,-0.94608875|H,0
,3.59665046,-2.94837219,0.15953377|C,0,1.39965812,3.01073376,0.12807961|
H,0,0.95453629,3.37283914,-0.80590268|H,0,0.71978523,3.29131727,0.94102453|
H,0,2.33276497,3.558759,0.27909202||Version=IA32W-G09RevD.01|State=2-A|HF=-
593.1802553|MP2=-595.5458377|RMSD=4.902e-009|PG=C01 [X(C12H16N1O1)]||@

TS1: S[•]→ I[•]

1|1|UNPC-DESKTOP-TBQL3NN|SP|ROMP2-FC|GTMP2large|C12H16N1O1(2)|LABPC|01
-Dec-2020|0||# romp2 maxdisk=7840MW geom=connectivity gtmp2large scf=tight||
Transition State gtmp2 energy calculation for the reaction from Substrate (1-aminopropane)
radical to Intermediate radical aldimine with deAzaPyridoxal model||0,2|N,0,-1.90443531,
0.22960755,-0.61807451|C,0,-0.87562587,1.0823896,0.38947797|H,0,1.07947332,
2.15285327,-0.35389212|C,0,0.4609103,0.61811435,0.15991032|C,0,0.78019949,-
0.77520044,-0.22075326|C,0,2.08827298,-1.24141856,0.00193592|C,0,2.79799234,1.0661
1623,0.33511422|C,0,1.51291449,1.54522427,0.12098901|H,0,3.59773889,1.76901271,0.55
139531|O,0,-0.15914195,-1.70641646,-0.50069244|C,0,-3.22119349,0.10076061,
0.65210562|C,0,-3.25105293,0.75626018,-0.67129233|H,0,-3.33677163,1.84756256,-
0.68855523|H,0,-2.93039797,0.71439327,1.49824201|H,0,-3.87140889,0.29022018,-
1.43931774|C,0,-3.69264003,-1.29449341,0.89263277|H,0,-1.01444069,-1.22889812,-

0.65800231|H,0,-4.69282958,-1.29427272,1.35105252|H,0,-3.0247302,-1.83865789,
1.56858536|H,0,-3.7608004,-1.85443497,-0.04465955|C,0,2.36949434,-2.71977706,-
0.0728677|H,0,1.76155695,-3.27810697,0.64758043|H,0,2.12163012,-3.12183408,-1.061494
75|H,0,3.42362211,-2.92701628,0.13043814|C,0,1.24592943,3.03085801,0.19045343|
H,0,0.85859791,3.42526107,-0.75712049|H,0,0.51203845,3.28280541,0.9660077|
H,0,2.16613348,3.57384774,0.42007539|C,0,3.08089421,-0.30526819,0.27924828|
H,0,4.0971459,-0.65005001,0.45266054||Version=IA32W-G09RevD.01|State=2-A|HF=-
593.123119|MP2=-595.5261355|RMSD=3.435e-009|PG=C01 [X(C12H16N1O1)]||@

I*

1|1|UNPC-DESKTOP-TBQL3NN|SP|ROMP2-FC|GTMP2large|C12H16N1O1(2)|LABPC|12
-Nov-2020|0||# romp2 maxdisk=7840MW geom=connectivity gttmp2large scf=t
ight||Intermediate (1-aminopropane) radical aldimine with deaza-Pyrido
xal model gttmp2 energy||0,2|N,0,1.95688415,-0.04691219,0.33330147|C,0,
0.93209136,0.9289386,0.18480405|H,0,1.23910071,1.97287791,0.16322251|C
,0,-0.42507627,0.57066418,0.06574351|C,0,-0.86102723,-0.80262079,0.109
49673|C,0,-2.21599062,-1.14982467,-0.00689688|C,0,-2.75939209,1.218831
67,-0.21354362|C,0,-1.43019588,1.58922569,-0.10150259|H,0,-3.51477689,
1.98970865,-0.33976385|O,0,0.01736149,-1.81850548,0.2677061|C,0,3.2524
4991,0.19438784,-0.34882661|C,0,3.14931236,0.32519207,1.12631392|H,0,3
.1555612,1.32295107,1.56038037|H,0,3.29992888,1.13420508,-0.89981046|H
,0,3.53406319,-0.46075267,1.77191756|C,0,3.90814229,-0.98538424,-1.022
56584|H,0,0.92338307,-1.41872783,0.33693875|H,0,4.97415833,-0.79102032
, -1.18408122|H,0,3.44781298,-1.18493007,-1.99550159|H,0,3.81266502,-1.
88560766,-0.40892347|C,0,-2.6120642,-2.60291073,0.04708349|H,0,-2.1240
5736,-3.17823036,-0.74738659|H,0,-2.30647861,-3.06363355,0.99296362|H,
0,-3.69439259,-2.71636253,-0.0588785|C,0,-1.04508973,3.04723352,-0.155
27697|H,0,-0.5455056,3.37507833,0.76528326|H,0,-0.35809481,3.26082287,

-0.98399468|H,0,-1.93044712,3.67350615,-0.29072039|C,0,-3.15096573,-0.
12853432,-0.16775429|H,0,-4.20316658,-0.38464877,-0.25885356||Version=
IA32W-G09RevD.01|State=2-A|HF=-593.1504092|MP2=-595.5365304|RMSD=4.171
e-009|PG=C01 [X(C12H16N1O1)]||@

TS2: I[•]→ P[•]

1|1|UNPC-DESKTOP-TBQL3NN|SP|ROMP2-FC|GTMP2large|C12H16N1O1(2)|LABPC|15

-Dec-2020|0||# romp2 maxdisk=7840MW geom=connectivity gtmp2large scf=t

ight||Transition State gtmp2 energy calculation for the reaction from

Intermediate radical to Product (2-aminopropane) radical aldimine with

deAzaPyridoxal model||0,2|N,0,1.9064287,-0.13115248,-0.07679024|C,0,0
.96286002,0.84098879,-0.10766726|H,0,1.28537181,1.88218177,-0.14237957
|C,0,-0.43865894,0.54710315,-0.06203408|C,0,-0.91103825,-0.8034791,-0.
04762985|C,0,-2.28552924,-1.10218533,-0.01049003|C,0,-2.75197556,1.290
4007,-0.01675056|C,0,-1.40098056,1.60549246,-0.05127163|H,0,-3.4847318
2,2.0924235,-0.00553462|O,0,-0.06162283,-1.85292747,-0.07647067|C,0,3.
30510047,0.23895522,0.00711349|C,0,3.00721874,-0.2048819,1.38450843|H,
0,2.69257324,0.50987788,2.133539|H,0,3.48198858,1.31648657,-0.09529497
|H,0,3.14588756,-1.23880547,1.67376163|C,0,4.24237064,-0.5878337,-0.85
082906|H,0,0.86091779,-1.49110716,-0.11800227|H,0,5.28235164,-0.404605
51,-0.56211754|H,0,4.12476474,-0.33244304,-1.90828946|H,0,4.03153991,-
1.65464142,-0.73170868|C,0,-2.72868304,-2.54202767,0.00452452|H,0,-2.3
6689918,-3.0780571,-0.87978347|H,0,-2.32483143,-3.07373124,0.87318573|
H,0,-3.8193268,-2.61455978,0.03102912|C,0,-0.96927256,3.05346776,-0.07
406203|H,0,-0.3407276,3.31075776,0.78735221|H,0,-0.3936826,3.29828111,
-0.97525987|H,0,-1.84116752,3.71194409,-0.05290885|C,0,-3.18703146,-0.

04201215,0.00583758|H,0,-4.25232805,-0.25644412,0.03421155||Version=IA

32W-G09RevD.01|State=2-A|HF=-593.123735|MP2=-595.5272649|RMSD=5.630e-0

09|PG=C01 [X(C12H16N1O1)]||@

P•

1|1|UNPC-DESKTOP-TBQL3NN|SP|ROMP2-FC|GTMP2large|C12H16N1O1(2)|LABPC|11

-Dec-2020|0||# romp2 maxdisk=7840MW geom=connectivity gtmp2large scf=t

ight||Product (2-aminopropane) radical aldimine with deaza-Pyridoxal m

odel gtmp2 energy||0,2|N,0,1.81355347,-0.18206599,0.04377741|C,0,0.947

41936,0.77115116,0.03723614|H,0,1.28414324,1.81537706,0.04847353|C,0,-

0.48826363,0.53243319,0.01537358|C,0,-0.97434963,-0.80471483,0.0074753

7|C,0,-2.36060172,-1.07551797,-0.01167813|C,0,-2.76989292,1.33141867,-

0.01577192|C,0,-1.41017691,1.6148484,0.00355949|H,0,-3.48662746,2.1472

5093,-0.02530865|O,0,-0.14252611,-1.85689996,0.01843472|C,0,3.23777009

,0.14438738,0.05924021|C,0,3.8853654,-0.42790886,1.27984741|H,0,3.2919

8392,-0.70600973,2.14252471|H,0,3.35962826,1.24861833,0.06995989|H,0,4

.96700833,-0.47397353,1.34858707|C,0,3.89544506,-0.37521376,-1.2348151

3|H,0,0.79411191,-1.49496313,0.02990999|H,0,4.96799405,-0.15712447,-1.

23066638|H,0,3.76135299,-1.45700776,-1.32031909|H,0,3.44767501,0.10167

955,-2.1115294|C,0,-2.83453948,-2.50463125,-0.01896838|H,0,-2.45030092

, -3.04506613,-0.89095921|H,0,-2.47357481,-3.04624618,0.86217851|H,0,-3

.9265476,-2.55456757,-0.03347373|C,0,-0.94747436,3.05554713,0.01092515

|H,0,-0.35648266,3.2962687,0.90225188|H,0,-0.32983571,3.29664096,-0.86

203823|H,0,-1.80783822,3.72889377,-0.00196525|C,0,-3.23010929,0.006851

56,-0.02301658|H,0,-4.30090745,-0.18201408,-0.03798863||Version=IA32W-

G09RevD.01|State=2-A|HF=-593.1794512|MP2=-595.5469636|RMSD=1.795e-009|

PG=C01 [X(C12H16N1O1)]||@