

Table S1 Thermodynamic properties of species involved in a monomeric pathway for 2,1-HNA

Step	Imaginary frequency (cm <sup>-1</sup> )	Energy of barrier (kcal/mol)	E <sub>total,0K</sub> (Ha)	H <sub>total,298K</sub> (kcal/mol)	H <sub>total,543K</sub> (kcal/mol)	G <sub>total,298K</sub> (kcal/mol)	G <sub>total,543K</sub> (kcal/mol)	S <sub>total,298K</sub> (cal/molK)	S <sub>total,543K</sub> (cal/molK)
IS	-	-	-1241.9885361	103.125	119.582	68.697	34.556	115.472	154.594
TS1	-176.3	28.171	-1241.9436424	100.555	115.935	68.344	36.415	108.036	144.583
IM1	-	-	-1241.9784197	102.976	119.443	67.927	33.255	117.553	156.705
TS2	-128.5	17.692	-1241.9502255	101.912	117.330	69.763	37.895	107.829	144.427
IM2	-	-	-1241.9698583	103.625	119.884	69.244	35.211	115.317	153.952
TS3	-1766.10	48.715	-1241.8922265	98.658	114.471	66.455	34.412	108.007	145.561
FS	-	-	-1242.0228266	103.842	119.778	71.556	39.417	108.285	146.111

Table S2 Thermodynamic properties of species involved in a monomeric pathway for 2,3-HNA

Step	Imaginary frequency (cm <sup>-1</sup> )	Energy of barrier (kcal/mol)	E <sub>total,0K</sub> (Ha)	H <sub>total,298K</sub> (kcal/mol)	H <sub>total,543K</sub> (kcal/mol)	G <sub>total,298K</sub> (kcal/mol)	G <sub>total,543K</sub> (kcal/mol)	S <sub>total,298K</sub> (cal/molK)	S <sub>total,543K</sub> (cal/molK)
IS	-	-	-1241.9877142	101.999	118.065	69.166	36.503	110.121	148.293
TS1	-159.6	32.045	-1241.9366476	101.192	117.020	67.371	33.933	113.434	151.067
IM1	-	-	-1241.9590564	103.129	119.556	69.408	35.871	113.103	152.154
TS2	-71.2	18.680	-1241.9292873	101.632	117.090	69.756	38.107	106.912	143.605
IM2	-	-	-1241.9390928	103.166	119.515	68.815	34.778	115.214	154.067
TS3	-1698.1	37.360	-1241.8795555	99.680	115.947	65.605	31.829	114.290	152.941
FS	-	-	-1242.0232904	104.065	119.995	71.704	39.500	108.542	146.354

Table S3 Thermodynamic properties of species involved in a dimeric pathway for 2,6-HNA

Step	Imaginary frequency (cm <sup>-1</sup> )	Energy of barrier (kcal/mol)	E <sub>total,0K</sub> (Ha)	H <sub>total,298K</sub> (kcal/mol)	H <sub>total,543K</sub> (kcal/mol)	G <sub>total,298K</sub> (kcal/mol)	G <sub>total,543K</sub> (kcal/mol)	S <sub>total,298K</sub> (cal/molK)	S <sub>total,543K</sub> (cal/molK)
IS	-	-	-2296.7446753	196.438	226.247	142.950	88.632	179.398	250.208
TS1	-51.32	39.464	-2296.6817847	192.144	222.311	142.124	90.630	167.766	239.421
IM1	-	-	-2296.7687891	196.113	226.063	145.144	92.908	170.949	242.101
TS2	-532.86	17.431	-2296.7410112	193.239	222.033	145.091	95.619	161.488	229.843
IM2	-	-	-2296.7966537	193.812	223.027	145.102	95.034	163.374	232.715
TS3	-247.58	32.627	-2296.7446587	193.449	221.654	145.741	96.838	160.011	226.939
FS	-		-2296.7453112	194.946	224.558	141.789	87.810	178.291	248.633