Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hydrogen-atom-assisted processes on thioacetamide in *para*-H_2 matrix – Formation of thiol tautomers

Supporting Information

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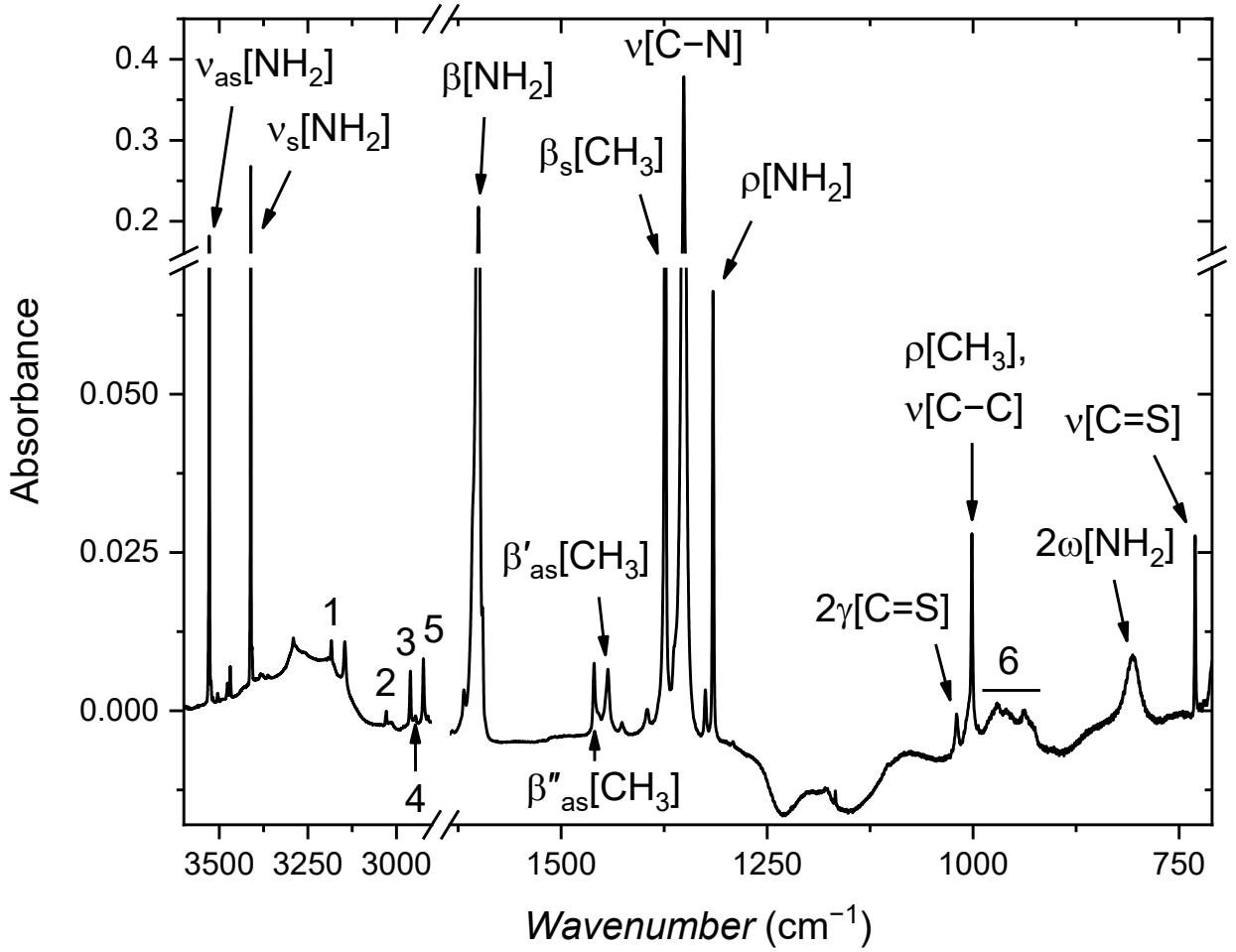

Figure S1 MIR spectrum of the newly deposited TA as obtained in *para*-H_2 matrix, the labels show the most important assigned vibrational modes. Numbers denote the following modes: 1: $2\beta[NH_2]$, 2: $\nu_{as}[CH_3] + \tau[CH_3]$, 3: $\nu'_{as}[CH_3]$, 4: $\nu''_{as}[CH_3]$, 5: $\nu_s[CH_3]$, 6: $\omega[NH_2] + \tau[NH_2]$. The vibrational assignment is based on Table S1.

Table S1 Vibrational assignment of the thione tautomeric form of TA as obtained by this study and compared with an earlier Ar-matrix study.

Wavenumber (cm^{-1})			Approximate
para-H_2[a]	Ar[b]	*I*[c]	description[d]
3528.2	3521	67	$\nu_{as}[NH_2]$
3411.1	3413sh, 3405	59	$\nu_{s}[NH_2]$
3183.7	3176	2.1	$2\beta[NH_2]$
3028.8	3030	0.6	$\nu'_{as}[CH_3]$
2960.9	2964	3.3	?
2946.3	2941	0.9	$\nu''_{as}[CH_3]$
2924.2	2925	7.2	$\nu_{s}[CH_3]$
1600.3	1597	140	$\beta[NH_2]$
1460.0	1457	4.4	$\beta''_{as}[CH_3]$
1443.3	1441	7.8	$\beta'_{as}[CH_3]$
1373.6	1369	49	$\beta_{s}[CH_3]$
1351.2	1346	183	ν[C−N]
1315.6	1312	21	ν[C−C]
1020.1	1018	3.2	$\rho''[CH_3]$
1001.5	999 997	14 10	$\rho'[CH_3]$
970b, 938b	944, 939sh, 938	19	$\rho[NH_2]$
806b	780sh, 776sh, 774	56	$2\omega[NH_2]$?
730.5	729	13	ν[C=S]

[a] Isolated in *para*-H_2 at 3.1 K; sh: shoulder; b: broad

[b] Isolated in Ar matrix at 11 K; see Ref. 1

[c] Normalized experimental band areas as taken from Ref 1.

[d] Re-evaluated, based on Ref. 4; ν: stretching, β: in-plane bending, ρ: rocking, ω: wagging, s: symmetric, as: antisymmetric vibrations.

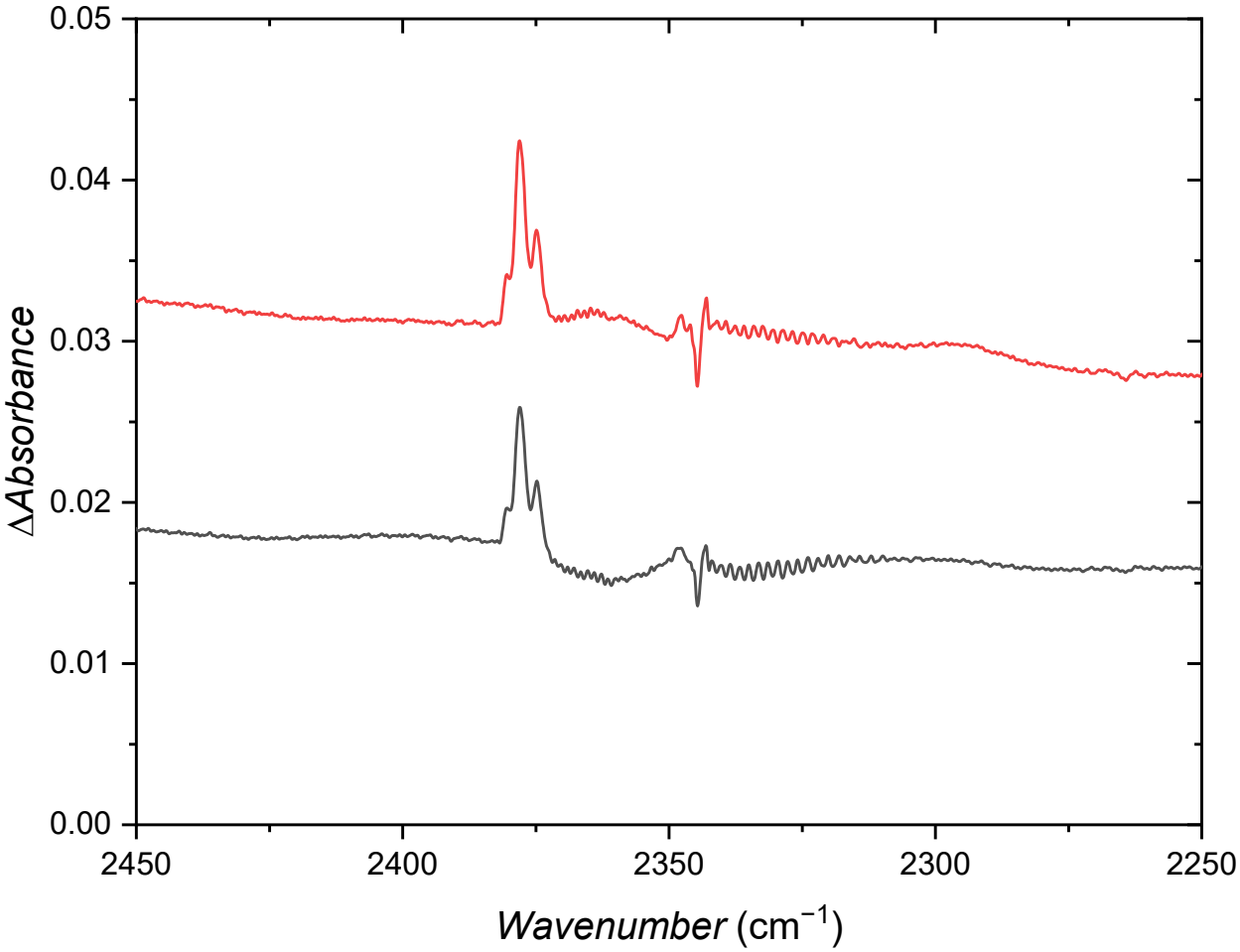

Figure S2 Section of the MIR difference spectra of TA in *para*-H_2 matrix after the first (dark grey trace) and second (red) H-atom generations showing the band that is tentatively assigned to the $H_3C–C(–SH)–NH_2$ radical. The spectra are offset for clarity.

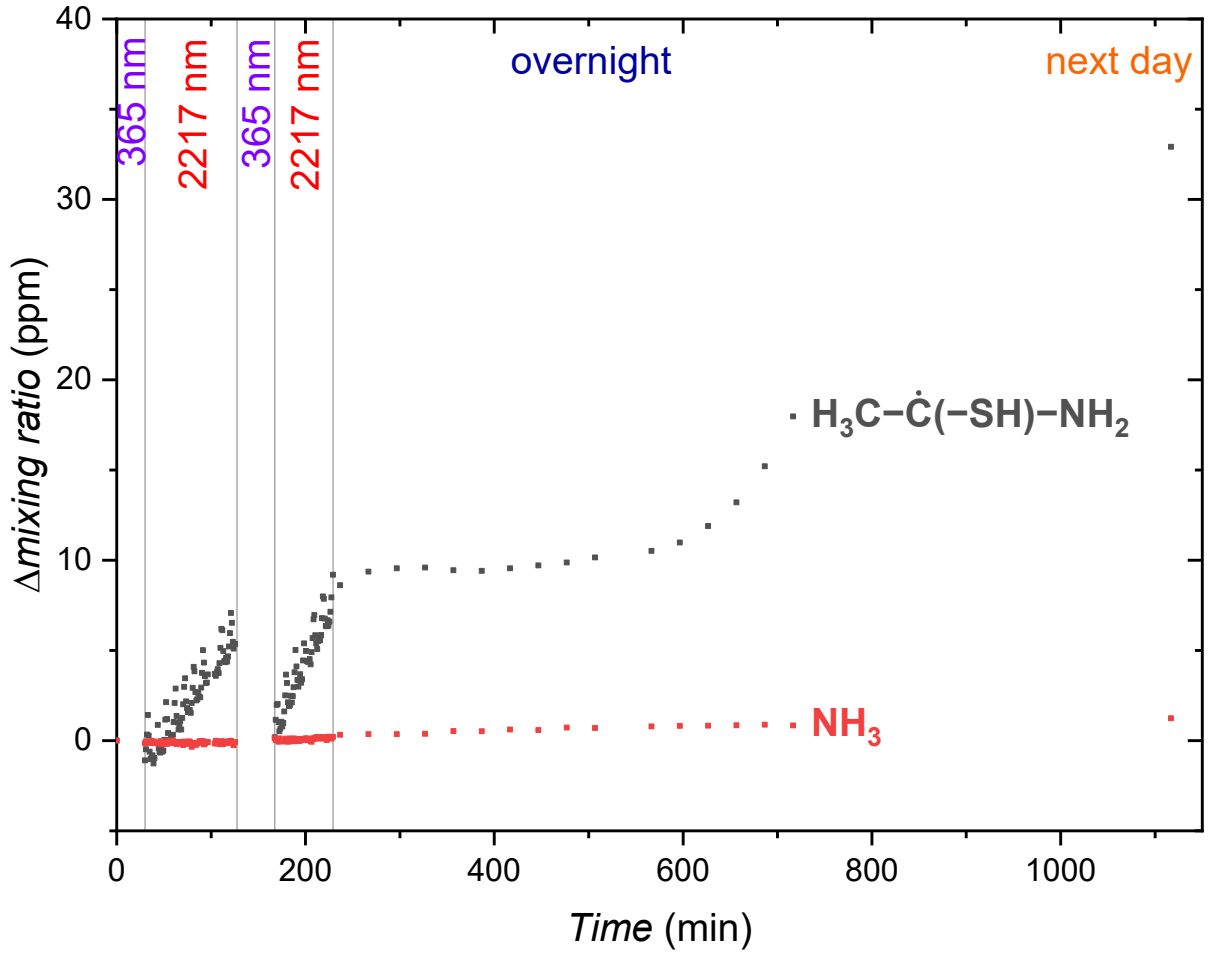

Figure S3 Kinetic curves of the $H_3C–C(–SH)–NH_2$ radical (dark grey trace) as well as NH_3 (red) during and after H atom generation.

C_2H_5NS isomers

Table S2 Cartesian coordinates (Å) of the thioacetamide (TA) thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.364124	-0.118680	-0.000021
C	0.277535	0.059534	0.000235
C	1.237546	-1.103297	0.000022
H	0.694480	-2.040985	0.005511
H	1.877405	-1.066653	-0.885510
H	1.886123	-1.060794	0.878906
N	0.872040	1.266819	0.000179
H	0.300516	2.094536	-0.000876
H	1.872688	1.367622	-0.000494

Table S3 Cartesian coordinates (Å) of the TA *a,c*-thiol rotamer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-0.461120	0.195991	0.000000
C	-1.331283	-1.028214	0.000000
H	-2.373551	-0.718913	-0.000001
H	-1.135035	-1.641241	-0.881082
H	-1.135036	-1.641240	0.881083
S	1.319221	-0.073158	0.000000
H	1.309466	-1.414607	-0.000001
N	-0.964626	1.354679	0.000000
H	-0.266582	2.097113	0.000000

Table S4 Cartesian coordinates (Å) of the TA *a,t*-thiol rotamer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-0.444241	0.187534	-0.000002
C	-1.273416	-1.070812	-0.000003
H	-2.334226	-0.822045	0.000363
H	-1.054824	-1.676647	-0.880690
H	-1.054345	-1.677054	0.880286
S	1.332035	-0.015440	-0.000005
H	1.345700	-1.356948	0.000092
N	-0.861322	1.380870	0.000011
H	-1.879669	1.413310	-0.000017

Table S5 Cartesian coordinates (Å) of the TA *s,c*-thiol rotamer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-0.457262	0.207092	-0.000004
C	-1.345913	-1.006240	-0.000053
H	-2.383495	-0.683570	-0.000224
H	-1.155819	-1.622941	-0.879938
H	-1.156227	-1.622702	0.880132
S	1.287412	-0.249028	0.000049
H	1.776485	1.000888	-0.000698
N	-0.945475	1.371530	0.000017
H	-0.242161	2.106953	0.000174

Table S6 Cartesian coordinates (Å) of the TA *s,t*-thiol rotamer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.4368640	0.1941450	-0.0000240
C	1.3136570	-1.0324940	-0.0000020
H	2.3643740	-0.7467750	0.0002620
H	1.1146370	-1.6472790	0.8792400
H	1.1148620	-1.6470890	-0.8793620
S	-1.3027970	-0.2063320	-0.0000090
H	-1.7135100	1.0712390	0.0002100
N	0.8054750	1.4040160	-0.0000090
H	1.8229440	1.4731950	0.0000110

Table S7 Cartesian coordinates (Å) of the $H_2C{=}C(-SH)-NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.308016	0.069717	-0.061124
C	0.473523	0.066008	0.011541
C	1.128233	1.231424	0.037888
H	2.205519	1.264903	-0.060148
H	0.597555	2.162107	0.145138
N	1.076999	-1.180991	-0.100687
H	0.493773	-1.980453	0.073279
H	1.997544	-1.257241	0.302142
H	-1.515659	-0.822444	0.925813

Table S8 Cartesian coordinates (Å) of the $H_2C{=}C(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.310504	-0.067559	-0.042212
C	0.469778	0.076270	0.003814
C	1.128740	1.237853	-0.000226
H	2.207418	1.255164	0.084610
H	0.618494	2.180168	-0.114159
N	1.056691	-1.184220	-0.059411
H	0.655284	-1.874043	0.558247
H	2.064946	-1.174542	-0.024664
H	-1.566025	1.098998	0.565703

Table S9 Cartesian coordinates (Å) of the $H_2C{=}C(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.309235	0.081704	-0.056200
C	0.469946	0.067355	0.011733
C	1.146066	1.219493	0.014166
H	2.223859	1.229450	-0.083958
H	0.639330	2.163330	0.129344
N	1.035500	-1.204537	0.060754
H	0.599529	-1.880427	-0.548976
H	2.042291	-1.210499	-0.022660
H	-1.501826	-0.898447	0.844786

N.B.: The fourth $H_2C{=}C(-SH)-NH_2$ rotamer transformed into the enantiomer of rotamer #2 upon geometry optimization (not a real minimum on the PES).

C_2H_6NS isomers

Table S10 Cartesian coordinates (Å) of the $H_3C-C(-SH)-NH_2$ radical rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.354230	0.048321	-0.093405
C	0.391636	-0.041699	0.214788
C	1.267769	1.140559	-0.045343
H	0.819933	2.051575	0.348156
H	2.241808	1.010984	0.436085
H	1.448080	1.300220	-1.117944
N	0.932160	-1.298665	-0.078910
H	0.423176	-2.078560	0.312089
H	1.925233	-1.374579	0.087187
H	-1.672098	0.814712	0.964604

Table S11 Cartesian coordinates (Å) of the $H_3C-C(-SH)-NH_2$ radical rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.354591	-0.125865	-0.071312
C	0.382946	0.047773	-0.157197
C	1.296615	-1.117100	0.031441
H	0.865329	-2.019445	-0.395688
H	2.264632	-0.940817	-0.448114
H	1.494624	-1.314396	1.095070
N	0.906805	1.311509	0.101636
H	0.315240	2.082347	-0.169433
H	1.871410	1.446341	-0.168215
H	-1.562783	-0.004793	1.270450

Table S12 Cartesian coordinates (Å) of the $H_3C-C(-SH)-NH_2$ radical rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.357571	-0.130280	-0.064144
C	0.376732	0.043681	-0.132490
C	1.305862	-1.110743	0.030846
H	0.842773	-2.034331	-0.307975
H	2.224172	-0.956320	-0.542900
H	1.600311	-1.258347	1.081825
N	0.923643	1.317893	-0.057159
H	1.805474	1.417060	0.424950
H	0.280033	2.074306	0.107422
H	-1.592687	0.019240	1.272966

Table S13 Cartesian coordinates (Å) of the $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.403303	-0.061297	-0.057599
C	0.355382	0.048766	0.336955
C	1.144084	-1.184712	-0.104689
H	0.724375	-2.090138	0.328110
H	1.133195	-1.267416	-1.190515
H	2.184301	-1.094065	0.217155
N	0.967795	1.251450	-0.207724
H	0.427939	2.074075	0.027842
H	1.906580	1.370781	0.156929
H	0.305090	0.043042	1.442534

Table S14 Cartesian coordinates (Å) of the $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.384091	-0.017270	-0.051936
C	-0.375692	-0.051335	0.392295
C	-1.004748	1.255107	-0.129991
H	-0.538518	2.136519	0.309939
H	-0.920612	1.319476	-1.215682
H	-2.065788	1.261141	0.129073
N	-0.999518	-1.281659	-0.075962
H	-1.984995	-1.291121	0.167173
H	-0.925739	-1.353873	-1.084513
H	-0.430541	-0.046845	1.482894

Table S15 Cartesian coordinates (Å) of the $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.333802	-0.273659	-0.062359
C	0.400688	0.052076	0.423433
C	1.399347	-0.946344	-0.128130
H	1.191703	-1.944561	0.255376
H	1.340916	-0.986662	-1.216540
H	2.412468	-0.661638	0.162942
N	0.647167	1.389294	-0.098870
H	0.553476	1.424291	-1.108050
H	0.041983	2.087306	0.315983
H	0.469911	0.100352	1.508311

C_2H_7NS isomers

Table S16 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.359409	-0.008794	-0.127379
C	-0.420187	0.030115	0.391468
C	-1.201895	-1.163125	-0.133182
H	-0.781454	-2.097711	0.234364
H	-2.243025	-1.107686	0.19964
H	-1.183226	-1.176061	-1.222282
N	-0.949189	1.260408	-0.174119
H	-0.564680	2.073892	0.289087
H	-1.957668	1.290367	-0.088316
H	1.771674	-0.879828	0.808558
H	-0.415343	0.012944	1.486124

Table S17 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.382763	-0.081424	-0.016707
C	0.414874	0.044140	-0.381302
C	1.204881	-1.158714	0.113761
H	0.812896	-2.082116	-0.307788
H	2.254749	-1.066462	-0.178915
H	1.160811	-1.218960	1.201091
N	0.947548	1.264412	0.211113
H	0.452292	2.076815	-0.135008
H	1.928841	1.372038	-0.023300
H	-1.256844	0.011510	1.317883
H	0.420095	0.046517	-1.479207

Table S18 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.351503	-0.120632	-0.110912
C	-0.415587	0.064673	0.380602
C	-1.165261	-1.180463	-0.073225
H	-0.769178	-2.074588	0.405273
H	-2.221680	-1.091322	0.188765
H	-1.096453	-1.291507	-1.155440
N	-1.000948	1.243305	-0.248989
H	-0.505116	2.084257	0.019027
H	-1.965316	1.351247	0.049636
H	1.838829	0.839190	0.691612
H	-0.413407	0.104439	1.474369

Table S19 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.365719	-0.052741	-0.056902
C	0.430833	-0.034608	0.393071
C	1.144048	1.206992	-0.134173
H	0.731979	2.123872	0.290059
H	2.203325	1.160749	0.131549
H	1.062145	1.265136	-1.220406
N	0.944308	-1.307154	-0.088284
H	1.854572	-1.499253	0.311727
H	1.037969	-1.298328	-1.097496
H	-1.587672	1.264459	0.078741
H	0.489738	-0.056997	1.480861

Table S20 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #5 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.386376	-0.016786	-0.021339
C	-0.417590	-0.052275	-0.381673
C	-1.108638	1.224150	0.098546
H	-0.652592	2.115134	-0.332253
H	-2.163775	1.204877	-0.185134
H	-1.057584	1.302976	1.186687
N	-1.008676	-1.299441	0.093733
H	-1.997127	-1.323918	-0.137183
H	-0.933034	-1.366632	1.102499
H	1.285466	0.481875	1.222087
H	-0.445271	-0.080907	-1.472651

Table S21 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.348918	0.127812	-0.077617
C	0.422904	-0.058189	0.391651
C	1.160482	1.186665	-0.103838
H	0.747438	2.099538	0.327644
H	2.213085	1.123999	0.178174
H	1.102242	1.262668	-1.191010
N	0.926504	-1.331582	-0.103568
H	1.888027	-1.466271	0.192733
H	0.910623	-1.345085	-1.117674
H	-1.734190	-1.077015	0.370103
H	0.469620	-0.092607	1.480001

Table S22 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.400931	-0.038202	-0.011519
C	0.439271	0.060150	-0.385760
C	1.166268	-1.190631	0.085496
H	0.703314	-2.088281	-0.317491
H	2.209493	-1.149365	-0.230383
H	1.145623	-1.260763	1.175529
N	1.111677	1.244160	0.087773
H	1.168521	1.249752	1.099624
H	0.617490	2.082200	-0.190976
H	-1.274021	-0.237924	1.311035
H	0.429503	0.089377	-1.475859

Table S23 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.367003	-0.011944	-0.100113
C	0.449222	-0.038702	0.399093
C	1.189970	1.176468	-0.131459
H	0.744537	2.100613	0.233835
H	2.232081	1.136871	0.190207
H	1.160742	1.197879	-1.221750
N	1.069058	-1.255686	-0.057839
H	1.063601	-1.316753	-1.069384
H	0.604575	-2.076680	0.308786
H	-1.712165	1.154406	0.471942
H	0.460119	-0.042030	1.487235

Table S24 Cartesian coordinates (Å) of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #9 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.362868	-0.128196	-0.099607

C	-0.446086	0.074336	0.390741
C	-1.160891	-1.188003	-0.069371
H	-0.707399	-2.078480	0.362745
H	-2.207079	-1.138662	0.230605
H	-1.122010	-1.279239	-1.156738
N	-1.105294	1.248120	-0.118975
H	-1.067277	1.274201	-1.131548
H	-0.674176	2.097545	0.222106
H	1.801485	0.993168	0.493747
H	-0.450507	0.127767	1.477399

C_2H_4NS isomers

Table S25 Cartesian coordinates (Å) of the $H_3C{-}C(-S^{\cdot}){-}NH$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.460092	0.269221	-0.000046
C	1.420219	-0.901558	0.000002
H	2.443769	-0.535113	-0.000081
H	1.256911	-1.515833	0.885588
H	1.256820	-1.515980	-0.885466
S	-1.309895	-0.086620	0.000071
H	-1.178240	-1.421912	0.000184
N	0.842457	1.452683	-0.000156

Table S26 Cartesian coordinates (Å) of the $H_3C{-}C(-S^{\cdot}){-}NH$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.460549	0.274682	-0.000043
C	1.472075	-0.847478	0.000007
H	2.477844	-0.435737	-0.000073
H	1.334601	-1.470372	0.884126
H	1.334522	-1.470522	-0.883995
S	-1.260961	-0.281930	0.000079
H	-1.794924	0.949838	0.000000
N	0.746799	1.482064	-0.000158

Table S27 Cartesian coordinates (Å) of the $H_3C{-}C(-SH){=}N^{\cdot}$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	1.303168	-0.264564	0.000000
C	-0.391539	0.182761	0.000001
H	-1.431866	-0.891484	0.000000

H	-1.323183	-1.526566	-0.880429
H	-1.323189	-1.526569	0.880428
S	-2.419642	-0.433815	-0.000001
H	-0.704624	1.416015	0.000000
N	0.088121	2.060212	-0.000001

Table S28 Cartesian coordinates (Å) of the $H_3C{-}C(-SH){=}N^{\cdot}$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-1.344349	-0.127400	-0.000007
C	0.399978	0.185621	0.000013
H	1.265215	-1.046006	0.000004
H	1.064373	-1.657954	0.880766
H	1.064367	-1.657949	-0.880759
S	2.318394	-0.763000	0.000001
H	0.756975	1.398299	0.000001
N	1.772463	1.491527	-0.000003

TSs of hydrogenation / dehydrogenation processes starting from C_2H_5NS isomers

Table S29 Cartesian coordinates (Å) of the transition state (TS) during the H-atom addition on the C atom of the TA thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.372498	-0.115297	-0.058241
C	0.297045	0.067070	0.033264
C	1.251212	-1.096188	-0.075082
H	0.789172	-2.000683	0.303285
H	1.491811	-1.244544	-1.130866
H	2.181034	-0.909817	0.465094
N	0.871337	1.277224	-0.059852
H	0.286482	2.095306	-0.022906
H	1.863747	1.393306	0.058888
H	-0.041190	-0.254677	1.928240

Table S30 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-NH_2$ group of the TA thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.404981	-0.046829	0.019262
C	-0.240687	-0.034024	-0.086692
C	-1.128778	-1.237404	0.020638
H	-0.549629	-2.147653	-0.088749
H	-1.613085	-1.246722	1.004391
H	-1.923570	-1.228002	-0.731069
N	-0.934128	1.166237	-0.077506
H	-0.363090	1.968213	-0.313134
H	-1.433785	1.695372	1.286907
H	-1.840846	1.172966	-0.527668

Table S31 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring the $-CH_3$ group of the TA thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.399565	-0.432100	0.000000
C	-0.087030	0.218201	0.000000
C	-1.633743	-0.803710	-0.000001
H	-1.124577	-1.754169	0.000032
H	-2.002575	-0.401451	0.935923
H	-2.002542	-0.401499	-0.935957
N	-0.420009	1.506623	-0.000002
H	0.292485	2.221113	0.000003
H	-1.383748	1.798189	0.000012
H	-2.907386	-1.581890	0.000004

Table S32 Cartesian coordinates (Å) of the TS during the H9 atom abstraction from the $-NH_2$ group of the TA thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.435659	-0.032176	-0.046425
C	-0.229375	0.023656	0.021580
C	-1.027865	1.295175	0.020742
H	-0.394471	2.146761	-0.201896
H	-1.835801	1.236845	-0.711301
H	-1.487749	1.439037	1.000141
N	-0.907519	-1.111499	0.187385
H	-0.387513	-1.966099	0.013742
H	-2.046506	-1.182753	-0.201682
H	-2.922438	-1.291475	-0.721833

N.B.: The abstraction of H8 of the TA thione tautomer resulted in the barrierless addition on the S atom.

Table S33 Cartesian coordinates (Å) of the TS during the H5 or H6 atom abstraction from the $-CH_3$ group of the TA thione tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.404497	-0.219247	0.056194
C	-0.213471	0.115490	-0.073925
C	-1.223413	-0.949403	-0.248818
H	-0.794743	-1.936080	-0.364948
H	-1.888359	-1.017749	0.807398
H	-1.985948	-0.730527	-0.996455
N	-0.703021	1.369212	-0.015420
H	-0.069386	2.136539	0.127859
H	-1.688569	1.558870	-0.077020
H	-2.502495	-1.084113	1.648464

N.B.: The abstraction of H4 of the TA thione tautomer resulted in the barrierless addition on the S atom.

Table S34 Cartesian coordinates (Å) of the TS during the H-atom addition on the C atom of the TA *a*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.367694	-0.085608	0.040095
C	-0.419535	-0.075081	-0.078601
C	-1.110931	1.253303	-0.003937
H	-0.771746	1.913699	-0.803565
H	-2.183397	1.100216	-0.094431
H	-0.895374	1.744424	0.946707
N	-1.088161	-1.150604	-0.188633
H	-2.270203	-1.650043	1.228939
H	-0.519715	-1.994643	-0.209015
H	1.557253	1.240980	0.105502

Table S35 Cartesian coordinates (Å) of the TS during the H-atom addition on the =NH group of the TA *a*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.367692	0.085617	0.040097
C	-0.419537	0.075080	-0.078603
C	-1.110917	-1.253311	-0.003935
H	-0.895362	-1.744421	0.946715
H	-2.183383	-1.100240	-0.094443
H	-0.771712	-1.913710	-0.803554
N	-1.088172	1.150597	-0.188636
H	-2.270215	1.650045	1.228947
H	-0.519733	1.994640	-0.209019
H	1.557254	-1.240973	0.105488

Table S36 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-CH_3$ group of the TA *a*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.244517	0.400789	0.000002

C	1.672306	-0.737879	0.000000
H	2.371104	0.088994	0.000008
H	1.412497	-1.225960	0.932485
H	1.412500	-1.225947	-0.932493
S	-1.361808	-0.373807	-0.000001
H	-0.918193	-1.640933	0.000017
N	0.496830	1.622106	0.000000
H	-0.313760	2.241305	0.000000
H	2.846030	-1.588751	-0.000009

Table S37 Cartesian coordinates (Å) of the TS during the H-atom addition on the C atom of the TA *a*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.351489	0.019758	-0.056212
C	0.435820	-0.175885	0.068026
C	1.269591	1.079715	-0.089112
H	0.923854	1.888394	0.551879
H	2.311447	0.866283	0.149040
H	1.205451	1.417116	-1.125468
N	0.853583	-1.381864	-0.083128
H	1.872204	-1.404489	-0.126818
H	-1.394557	1.314421	0.292279
H	0.497872	-0.147782	1.866900

Table S38 Cartesian coordinates (Å) of the TS during the H-atom addition on the =NH group of the TA *a*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.343988	-0.006920	-0.016750
C	-0.431355	0.090503	-0.061086
C	-1.202387	-1.194966	0.076984
H	-0.980924	-1.674118	1.032643
H	-2.272924	-1.000189	0.023982
H	-0.933316	-1.895853	-0.714342
N	-0.916602	1.257079	-0.195165
H	-0.592873	2.590747	1.226781
H	-1.934041	1.249793	-0.201197
H	1.428938	-1.332433	0.170907

Table S39 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-CH_3$ group of the TA *a*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.244517	0.400789	0.000002
C	1.672306	-0.737879	0.000000
H	2.371104	0.088994	0.000008

H	1.412497	-1.225960	0.932485
H	1.412500	-1.225947	-0.932493
S	-1.361808	-0.373807	-0.000001
H	-0.918193	-1.640933	0.000017
N	0.496830	1.622106	0.000000
H	-0.313760	2.241305	0.000000
H	2.846030	-1.588751	-0.000009

Table S40 Cartesian coordinates (Å) of the TS during the H-atom addition on the C atom of the TA *s*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.313063	-0.240208	-0.030593
C	-0.452984	0.195808	0.057546
C	-1.322986	-1.033412	-0.070413
H	-0.976606	-1.847004	0.564350
H	-2.346376	-0.774099	0.187567
H	-1.296687	-1.374155	-1.107514
N	-0.962440	1.361252	-0.109908
H	-0.265027	2.102237	-0.134523
H	1.781318	1.017388	-0.022182
H	-0.512736	0.215823	1.848352

Table S41 Cartesian coordinates (Å) of the TS during the H-atom addition on the =NH group of the TA *s*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.362038	-0.094357	0.047894
C	-0.417839	0.085575	-0.079846
C	-1.130025	-1.233935	-0.004845
H	-0.753218	-1.925371	-0.759904
H	-0.972356	-1.695157	0.972060
H	-2.193584	-1.072929	-0.157773
N	-1.071224	1.169613	-0.188543
H	-0.496376	2.007618	-0.204043
H	-2.251058	1.685384	1.221121
H	1.659745	1.213039	-0.009818

Table S42 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-CH_3$ group of the TA *s*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.244517	0.400789	0.000002
C	1.672306	-0.737879	0.000000
H	2.371104	0.088994	0.000008
H	1.412497	-1.225960	0.932485
H	1.412500	-1.225947	-0.932493

S	-1.361808	-0.373807	-0.000001
H	-0.918193	-1.640933	0.000017
N	0.496830	1.622106	0.000000
H	-0.313760	2.241305	0.000000
H	2.846030	-1.588751	-0.000009

Table S43 Cartesian coordinates (Å) of the TS during the H-atom addition on the C atom of the TA *s*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.325093	-0.203263	-0.025773
C	-0.429323	0.183459	0.060977
C	-1.297484	-1.051967	-0.075425
H	-0.921176	-1.882655	0.519360
H	-2.318033	-0.831048	0.233254
H	-1.304441	-1.360545	-1.122823
N	-0.808310	1.401459	-0.106806
H	-1.827504	1.455947	-0.122545
H	1.717771	1.077188	-0.108087
H	-0.529098	0.194156	1.847537

Table S44 Cartesian coordinates (Å) of the TS during the H-atom addition on the =NH group of the TA *s*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.318420	-0.219163	0.002373
C	-0.426020	0.103417	-0.062579
C	-1.265881	-1.138779	0.078368
H	-1.001906	-1.874979	-0.682045
H	-1.099322	-1.601625	1.053147
H	-2.322606	-0.895487	-0.018655
N	-0.844940	1.296029	-0.196416
H	-0.424694	2.608203	1.207599
H	-1.862190	1.343651	-0.198076
H	1.681984	1.066806	-0.119755

Table S45 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-CH_3$ group of the TA *s*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.244517	0.400789	0.000002
C	1.672306	-0.737879	0.000000
H	2.371104	0.088994	0.000008
H	1.412497	-1.225960	0.932485
H	1.412500	-1.225947	-0.932493
S	-1.361808	-0.373807	-0.000001
H	-0.918193	-1.640933	0.000017

N	0.496830	1.622106	0.000000
H	-0.313760	2.241305	0.000000
H	2.846030	-1.588751	-0.000009

Table S46 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the =NH group of the TA *a*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.453660	0.185651	0.000015
C	1.472068	-0.926712	0.000040
H	2.472258	-0.501375	0.000076
H	1.345040	-1.554031	0.883115
H	1.345098	-1.554017	-0.883054
S	-1.275316	-0.294827	-0.000040
H	-1.066869	-1.621029	-0.000039
N	0.834293	1.386377	0.000032
H	-0.077258	2.131538	0.000008
H	-1.007636	2.557867	-0.000018

Table S47 Cartesian coordinates (Å) of the TS during the H4 or H5 atom abstraction from the $-CH_3$ group of the TA *a*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.392381	0.291901	-0.063539
C	1.383037	-0.781329	-0.265391
H	2.380216	-0.392770	-0.443884
H	1.498917	-1.411877	0.842445
H	1.094484	-1.571802	-0.951286
S	-1.341306	-0.178564	0.009617
H	-1.190737	-1.500239	-0.162413
N	0.772207	1.494406	0.087599
H	0.000956	2.142979	0.237956
H	1.619106	-1.933542	1.683694

N.B.: The abstraction of H3 of the TA *a*,*c*-thiol tautomer resulted in the barrierless addition on the =NH group.

Table S48 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the =NH group of the TA *a*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-0.391036	-0.109496	-0.000026
C	-1.060246	1.241348	0.000161
H	-2.140508	1.119963	0.000118
H	-0.760930	1.809467	0.881603
H	-0.760890	1.809731	-0.881097
S	1.407031	-0.117651	0.000015

H	1.563678	1.215169	0.000214
N	-0.928803	-1.247542	-0.000208
H	-2.097452	-1.178977	-0.000225
H	-3.107084	-0.951266	-0.000214

Table S49 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the $-CH_3$ group of the TA *a*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.384782	0.278959	-0.054129
C	1.325638	-0.841235	-0.266628
H	2.354792	-0.522283	-0.411885
H	1.375506	-1.524420	0.816883
H	1.014885	-1.586887	-0.992968
S	-1.358542	-0.101276	0.009122
H	-1.248341	-1.424799	-0.177862
N	0.690016	1.500787	0.118462
H	1.699233	1.636450	0.080517
H	1.447957	-2.089493	1.634681

Table S50 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the =NH group of the TA *s*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.444712	0.187545	-0.000031
C	1.481165	-0.911928	-0.000043
H	2.475281	-0.473918	-0.000114
H	1.359398	-1.541318	0.882341
H	1.359303	-1.541388	-0.882364
S	-1.225148	-0.463040	0.000082
H	-1.837810	0.731521	0.000069
N	0.816409	1.390876	-0.000096
H	-0.065224	2.160495	-0.000079
H	-0.958703	2.683418	-0.000052

Table S51 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the $-CH_3$ group of the TA *s*,*c*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.382373	0.297120	-0.069715
C	1.379478	-0.773717	-0.267367
H	2.347795	-0.390501	-0.570020
H	1.610366	-1.292296	0.872855
H	1.046384	-1.628668	-0.848567
S	-1.297828	-0.348970	-0.008399
H	-1.900609	0.815540	0.276506
N	0.753867	1.502732	0.066474

H	-0.016600	2.150396	0.213327
H	1.829747	-1.730491	1.747447

Table S52 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the =NH group of the TA *s*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	-0.389254	-0.107783	-0.000007
C	-1.100386	1.220532	-0.000005
H	-2.176171	1.068410	-0.000034
H	-0.815667	1.798674	0.879975
H	-0.815625	1.798703	-0.879951
S	1.398356	0.067618	0.000020
H	1.651089	-1.250533	0.000011
N	-0.880190	-1.266360	-0.000024
H	-2.037694	-1.244646	-0.000036
H	-3.080455	-1.064468	-0.000043

Table S53 Cartesian coordinates (Å) of the TS during the H-atom abstraction from the $-CH_3$ group of the TA *s*,*t*-thiol tautomer as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
C	0.366963	0.280789	-0.065428
C	1.348609	-0.806406	-0.272676
H	2.333762	-0.456485	-0.568492
H	1.560219	-1.356943	0.858461
H	1.004411	-1.643017	-0.874685
S	-1.318312	-0.298420	-0.006663
H	-1.842072	0.907736	0.260163
N	0.621381	1.515682	0.098008
H	1.625459	1.689350	0.052138
H	1.768113	-1.822000	1.721593

Table S54 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-NH_2$ group of the $H_2C{=}CH(-SH)-NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.352299	-0.026755	0.101972
C	-0.392662	0.146648	-0.157884
C	-1.008840	1.348386	-0.004971
H	-2.086425	1.419451	0.054343
H	-0.437580	2.260791	0.015722
N	-1.154451	-1.055140	-0.006212
H	-0.622047	-1.887966	-0.230160
H	-2.004317	-1.042646	-0.559019
H	1.673621	-0.579114	-1.083105
H	-1.669868	-1.326656	1.191272

N.B.: The same addition process of rotamer #2 resulted in the same TS after a reorientation of the −SH group (second-order TS).

Table S55 Cartesian coordinates (Å) of the TS during the H-atom addition on the C atom of the H_2C=CH(−SH)−NH_2 rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.333677	0.049671	0.034044
C	-0.466720	0.050673	0.039563
C	-1.158280	1.211736	-0.120594
H	-2.240591	1.212555	-0.124939
H	-0.643057	2.155982	-0.156664
N	-1.030135	-1.207961	-0.118070
H	-0.557140	-1.940252	0.388507
H	-2.032396	-1.241211	0.003451
H	1.454629	-0.410081	-1.227182
H	-0.359337	0.309537	1.884804

N.B.: The same addition processes of rotamers #1 and #2 resulted in the same TS after a reorientation of the −SH group (second-order TSs).

Table S56 Cartesian coordinates (Å) of the TS during the S_H2 reaction occurring on the $-NH_2$ group of the $H_2C=CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.354084	-0.065133	-0.064725
C	0.400816	0.152615	-0.125326
C	1.017316	1.349161	0.023309
H	2.096430	1.424286	0.051758
H	0.445501	2.260535	0.066732
N	1.134760	-1.060012	-0.020587
H	0.612824	-1.861963	-0.354103
H	2.039749	-1.020563	-0.475682
H	-1.524036	0.091184	1.269183
H	1.542769	-1.441920	1.233930

Table S57 Cartesian coordinates (Å) of the TS during the H7 atom abstraction from the $-NH_2$ group of the $H_2C=CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.325375	-0.105551	-0.055784
C	0.434497	0.155389	-0.037803
C	1.014980	1.368678	0.105296
H	2.090656	1.447241	0.188248
H	0.442076	2.282377	0.097807
N	1.115826	-1.007355	-0.282296
H	0.875614	-1.862726	0.493301
H	2.122103	-0.861928	-0.253613
H	-1.647757	1.029253	0.581278
H	0.815661	-2.438324	1.356641

N.B.: The same abstraction process of rotamer #1 or that of H8 of rotamer #2 did not result in meaningful TSs.

Table S58 Cartesian coordinates (Å) of the TS during the H7 atom abstraction from the $=CH_2$ group of the $H_2C=CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.331381	-0.069987	0.033916
C	0.439957	-0.142845	-0.048532
C	1.063756	-1.334600	0.095713
H	2.139483	-1.379986	0.196694
H	0.515412	-2.263418	0.082131
N	1.075873	1.047962	-0.283105
H	0.790402	1.883803	0.497895
H	2.087573	0.940480	-0.239425
H	-1.463981	1.016298	-0.743692
H	0.679817	2.451557	1.362392

N.B.: The same abstraction process of H8 of rotamer #2 did not result in a meaningful TS.

Table S59 Cartesian coordinates (Å) of the TS during the H8 atom abstraction from the $=CH_2$ group of the $H_2C=CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.305005	-0.025999	-0.068670
C	0.478104	-0.010494	-0.003954
C	1.137327	1.133628	-0.076856
H	2.193633	1.346070	-0.131356
H	0.371331	2.416304	0.177106
N	1.057781	-1.282236	0.110493
H	0.657190	-1.967651	-0.515699
H	2.067103	-1.272770	0.056738
H	-1.465357	-0.987603	0.857969
H	-0.040874	3.118475	0.365368

N.B.: The same abstraction processes of rotamers #1 and #2 as well as that of H7 of rotamer #3 did not result in meaningful TSs or led to H-addition on the $=CH_2$ group.

TSs of hydrogenation / dehydrogenation processes starting from C_2H_7NS isomers

Table S60 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.401876	-0.003385	-0.068758
C	-0.456291	-0.030959	0.412595
C	-1.180630	-1.233383	-0.148319
H	-0.681144	-2.146736	0.185544
H	-2.221458	-1.275541	0.179814
H	-1.152406	-1.225084	-1.239378
N	-0.953303	1.256151	-0.090598
H	-1.606544	1.716567	0.538387
H	-1.369205	1.176047	-1.015438
H	1.471591	-1.331631	0.262676
H	-0.509681	0.002271	1.497149
H	0.133474	1.931257	-0.260093

Table S61 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.432003	-0.039546	-0.024370
C	-0.354223	0.036522	-0.360161
C	-1.043085	1.311992	0.096638
H	-0.539402	2.174565	-0.339867
H	-2.085528	1.296961	-0.230838
H	-1.025062	1.407783	1.182585
N	-1.113884	-1.158247	0.128533
H	-1.282629	-1.104206	1.151256
H	-0.593771	-2.029066	-0.059921
H	1.347247	0.168069	1.301600
H	-0.414102	-0.038625	-1.449509
H	-2.137768	-1.226100	-0.483976

Table S62 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.386955	-0.077269	-0.105328
C	0.363365	0.056568	0.379963
C	1.067562	1.294689	-0.147513
H	0.574507	2.185486	0.244238
H	2.110467	1.301006	0.173210
H	1.026251	1.332634	-1.236608
N	1.059665	-1.173241	-0.090355
H	1.216117	-1.152260	-1.105642
H	0.507205	-2.012199	0.124358
H	-1.827455	0.925799	0.714424
H	0.438877	0.017243	1.470130
H	2.142090	-1.256268	0.538925

N.B.: $H_3C-CH(-SH)-NH_2$ rotamers #1 and #5 transform into TSs #4 and #7, respectively, following the realignment of the $-NH_2$ group , whereas #3 and #9 suffer a reorientation of the $-SH$ group (all of them are second-order TSs). In rotamers #2 and #6, H-abstraction from the adjacent $-SH$ group occurs instead of the S_H2 reaction.

Table S63 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.382940	-0.331172	-0.150113
C	-0.222903	0.250824	0.434078
C	-1.603724	-0.880248	-0.074561
H	-1.204091	-1.768200	0.395358
H	-2.371011	-0.315090	0.443213
H	-1.442068	-0.719479	-1.131875
N	-0.498565	1.503947	-0.202807
H	0.156122	2.228681	0.067753
H	-1.438561	1.823748	-0.006704
H	1.619190	-1.176876	0.865504
H	-0.263550	0.218978	1.525731
H	-2.733342	-1.744095	-0.494631

Table S64 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.387692	-0.406538	-0.002914
C	0.219997	0.269541	-0.421188
C	1.604379	-0.870104	0.059613
H	1.218180	-1.739091	-0.454886
H	2.378444	-0.277897	-0.414102
H	1.432780	-0.753071	1.121212
N	0.483886	1.515653	0.237180
H	-0.280115	2.172304	0.128698
H	1.334944	1.946598	-0.104208
H	-1.220376	-0.360075	1.331213
H	0.273932	0.260304	-1.513719
H	2.731826	-1.750658	0.461608

Table S65 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.284688	-0.502604	-0.101166
C	-0.225762	0.325388	0.419480
C	-1.584801	-0.863287	-0.046050
H	-1.247847	-1.687579	0.568644
H	-2.376722	-0.223166	0.316311
H	-1.359115	-0.847350	-1.103232
N	-0.464151	1.564797	-0.249453
H	0.374874	2.012926	-0.587842
H	-1.003589	2.214043	0.306999
H	2.165896	0.282303	0.548068
H	-0.303109	0.355194	1.505702
H	-2.692955	-1.790895	-0.430406

Table S66 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.388789	-0.333804	-0.067486
C	-0.238742	0.306434	0.424582
C	-1.575905	-0.894210	-0.068759
H	-1.249163	-1.715480	0.555732
H	-2.385146	-0.264609	0.277639
H	-1.328609	-0.904392	-1.121396
N	-0.399910	1.599078	-0.132445
H	-1.202176	2.093834	0.231903
H	-0.412645	1.599713	-1.144332
H	1.084451	-1.638087	0.028398
H	-0.343403	0.347905	1.506217
H	-2.696675	-1.844901	-0.462200

Table S67 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #5 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.402869	-0.334313	-0.003963
C	0.234395	0.317139	-0.409352
C	1.523751	-0.954241	0.035790
H	1.096055	-1.768164	-0.532828
H	2.356358	-0.400085	-0.376852
H	1.350704	-0.910790	1.103330
N	0.492943	1.600246	0.145058
H	1.399050	1.966102	-0.120408
H	0.394473	1.625819	1.151499
H	-1.057862	-0.923507	1.155658
H	0.312505	0.351731	-1.493375
H	2.595142	-1.971204	0.402356

Table S68 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.294153	-0.501241	-0.082921
C	-0.224304	0.335048	0.426204
C	-1.577049	-0.876886	-0.050013
H	-1.223117	-1.701178	0.554773
H	-2.376765	-0.254149	0.326400
H	-1.360807	-0.868846	-1.109707
N	-0.364752	1.622026	-0.147682
H	-1.199556	2.104830	0.160479
H	-0.320884	1.609378	-1.158819
H	2.153481	0.478793	0.250998
H	-0.323969	0.382284	1.507299
H	-2.693454	-1.834403	-0.428060

Table S69 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.417897	-0.359025	0.000678
C	0.246122	0.296715	-0.410114
C	1.553739	-0.936788	0.031901
H	1.121010	-1.759001	-0.521424
H	2.345381	-0.338065	-0.399736
H	1.381157	-0.884867	1.100446
N	0.658898	1.545480	0.136582
H	0.602234	1.553050	1.147787
H	0.101248	2.318417	-0.208348
H	-1.181732	-0.575896	1.306752
H	0.275032	0.327727	-1.496194
H	2.630571	-1.874883	0.373078

Table S70 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.388991	-0.340952	-0.101502
C	-0.251565	0.291372	0.428262
C	-1.593099	-0.882522	-0.069988
H	-1.242695	-1.722442	0.515978
H	-2.371269	-0.239174	0.320268
H	-1.360964	-0.856670	-1.126569
N	-0.563176	1.562168	-0.123233
H	-0.393673	1.607188	-1.120313
H	-0.080292	2.328654	0.328082
H	1.264616	-1.596998	0.360644
H	-0.319261	0.320450	1.511536
H	-2.710099	-1.774058	-0.452606

Table S71 Cartesian coordinates (Å) of the first-order TS during the S_H2 reaction occurring on the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #9 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.311821	-0.491632	-0.091964
C	-0.245876	0.336801	0.416840
C	-1.563644	-0.897893	-0.034474
H	-1.180769	-1.702842	0.579958
H	-2.354707	-0.260053	0.335020
H	-1.345268	-0.899342	-1.094850
N	-0.568385	1.582348	-0.175490
H	-0.317373	1.623444	-1.154614
H	-0.163069	2.375955	0.304183
H	2.165965	0.465251	0.314316
H	-0.313161	0.396517	1.498171
H	-2.644951	-1.842697	-0.376524

Table S72 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.394464	-0.093486	-0.010982
C	-0.410966	0.047497	0.276009
C	-1.212302	-1.139370	-0.230635
H	-0.843307	-2.065851	0.203446
H	-2.265122	-1.027552	0.042543
H	-1.146716	-1.206399	-1.317052
N	-0.910812	1.280541	-0.265670
H	-0.412627	2.084283	0.092924
H	-1.903011	1.394319	-0.094759
H	1.329532	0.049303	-1.346098
H	-0.444483	0.008554	1.427466
H	-0.510398	-0.153422	2.754683

Table S73 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.384531	-0.038652	-0.043461
C	0.405660	-0.037263	0.257064
C	1.132320	1.205737	-0.232291
H	0.740811	2.111653	0.232051
H	2.191794	1.129129	0.021395
H	1.042276	1.303771	-1.316173
N	0.897720	-1.315556	-0.188764
H	1.843741	-1.472768	0.136813
H	0.882490	-1.390576	-1.199729
H	-1.569012	1.288992	0.026747
H	0.578009	-0.056138	1.457536
H	0.930464	-0.097582	2.509438

Table S74 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.364003	-0.152911	-0.075900
C	-0.402779	0.057402	0.261600
C	-1.169949	-1.173262	-0.204280
H	-0.782581	-2.083302	0.254937
H	-2.220123	-1.073677	0.074668
H	-1.112635	-1.277860	-1.289984
N	-0.869226	1.342155	-0.192115
H	-1.863327	1.448264	-0.022326
H	-0.691209	1.471767	-1.181687
H	1.730609	1.058178	0.372698
H	-0.539044	0.079708	1.460192
H	-0.824790	0.123567	2.546781

Table S75 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.408244	-0.076827	-0.023545
C	-0.417116	0.055712	0.270120
C	-1.206526	-1.146308	-0.201554
H	-0.794497	-2.064982	0.208248
H	-2.247328	-1.052387	0.112944
H	-1.181484	-1.221643	-1.292431
N	-1.025994	1.279305	-0.104137
H	-1.459815	1.256393	-1.017475
H	-0.412127	2.076439	-0.024612
H	1.344463	-0.043199	-1.366945
H	-0.410953	-0.009811	1.493034
H	-0.446345	-0.123139	2.581524

Table S76 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.384270	-0.003839	-0.135015
C	-0.420619	0.039230	0.279304
C	-1.198625	-1.148920	-0.243955
H	-0.771522	-2.084062	0.113285
H	-2.234178	-1.084782	0.093742
H	-1.183249	-1.168054	-1.335909
N	-1.019320	1.274791	-0.093704
H	-1.270583	1.315627	-1.073184
H	-0.460940	2.080753	0.151340
H	1.706814	-1.093772	0.582403
H	-0.459409	-0.028878	1.476514
H	-0.624549	-0.140814	2.595870

Table S77 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the C atom of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #9 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.381157	-0.138695	-0.113994
C	-0.418703	0.072378	0.262254
C	-1.155368	-1.188009	-0.137525
H	-0.703070	-2.068555	0.315076
H	-2.193204	-1.115987	0.185550
H	-1.142389	-1.317622	-1.223043
N	-1.070607	1.246901	-0.208754
H	-1.224452	1.222672	-1.210425
H	-0.566579	2.093229	0.018539
H	1.779639	1.027561	0.418654
H	-0.471936	0.132821	1.487761
H	-0.637848	0.210475	2.544694

N.B.: The H-abstraction from C atom is found to be barrierless in the case of the $H_3C{-}CH(-SH){-}NH_2$ rotamers #1 and #3. In rotamer #5, reorientation of the −SH group (*i.e.*, transformation into #4) occurs (second-order TS).

Table S78 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction the H8 atom of the $-NH_2$ group of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.375475	0.002789	-0.129570
C	-0.409997	-0.020502	0.349090
C	-1.105079	-1.323586	-0.041991
H	-0.615112	-2.173218	0.431645
H	-2.149246	-1.308423	0.282341
H	-1.072364	-1.463070	-1.121373
N	-1.021742	1.089883	-0.361235
H	-0.673821	2.167513	0.209030
H	-2.022900	1.080517	-0.152886
H	1.787951	-0.844188	0.827202
H	-0.450855	0.101529	1.434180
H	-0.568596	2.830063	0.849037

Table S79 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.397787	-0.087286	-0.011174
C	0.405522	-0.000970	-0.348016
C	1.139460	-1.292601	0.021599
H	0.682363	-2.141984	-0.482107
H	2.188994	-1.234170	-0.277344
H	1.098046	-1.460996	1.097296
N	1.006714	1.108929	0.376642
H	0.554619	2.196294	-0.116852
H	1.990237	1.168160	0.096341
H	-1.282041	-0.136108	1.326083
H	0.444939	0.128136	-1.434296
H	0.370544	2.876162	-0.708319

Table S80 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.449821	-0.078365	-0.049310
C	-0.367901	0.034398	-0.355813
C	-0.976482	1.344236	0.114992
H	-0.486972	2.192916	-0.358360
H	-2.039072	1.369567	-0.135828
H	-0.882113	1.439197	1.196577
N	-0.981667	-1.092669	0.322645
H	-0.631314	-1.954748	-0.096833
H	-2.174896	-1.135995	0.015570
H	1.364967	-0.014051	1.289948
H	-0.418507	-0.031804	-1.447825
H	-2.991255	-1.234351	-0.487881

Table S81 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.362649	-0.173744	-0.096126
C	-0.411287	0.013116	0.352450
C	-1.129381	-1.287417	-0.011540
H	-0.677449	-2.129648	0.510989
H	-2.180201	-1.228677	0.276307
H	-1.075922	-1.465465	-1.084915
N	-1.023471	1.114203	-0.379697
H	-0.519285	2.191261	0.034148
H	-1.983297	1.214971	-0.033801
H	1.766335	1.004214	0.405269
H	-0.455505	0.152955	1.434475
H	-0.268752	2.886691	0.607957

Table S82 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #3 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.428485	-0.022791	-0.079587
C	0.370527	0.016092	0.358512
C	0.944975	1.353261	-0.081447
H	0.464217	2.177611	0.442211
H	2.013535	1.378612	0.135980
H	0.816856	1.488426	-1.155472
N	1.017976	-1.071253	-0.357484
H	0.682470	-1.959915	0.016878
H	2.199912	-1.105583	-0.013569
H	-1.764994	-1.042341	0.727051
H	0.423443	-0.078325	1.444661
H	3.001471	-1.211171	0.515652

Table S83 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #5 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.453096	-0.131628	-0.043946
C	-0.362603	0.017307	-0.367922
C	-0.921986	1.354629	0.104283
H	-0.391665	2.187888	-0.354925
H	-1.979417	1.422673	-0.155825
H	-0.835273	1.448254	1.188980
N	-0.995556	-1.172315	0.171584
H	-2.161814	-1.199256	-0.200834
H	-1.096510	-1.060509	1.183030
H	1.415145	0.319273	1.221186
H	-0.420431	-0.045765	-1.455305
H	-3.103144	-0.991922	-0.342429

Table S84 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #5 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.419200	-0.028031	-0.007426
C	-0.363649	0.053402	-0.443702
C	-1.059306	1.274572	0.159547
H	-0.555306	2.194131	-0.133495
H	-2.096978	1.323874	-0.179457
H	-1.063401	1.211446	1.247960
N	-1.019053	-1.226395	-0.212014
H	-2.019174	-1.101862	-0.397567
H	-1.029984	-1.445830	1.032481
H	1.252099	0.080428	1.320941
H	-0.332040	0.172221	-1.533478
H	-1.191326	-1.368988	1.950455

Table S85 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.427665	-0.014919	-0.063639
C	0.369753	0.018020	0.382563
C	0.944767	1.345220	-0.104903
H	0.441133	2.190716	0.364179
H	2.005002	1.390634	0.143973
H	0.842246	1.438986	-1.187501
N	0.953006	-1.184264	-0.173610
H	2.130409	-1.253140	0.183594
H	1.033199	-1.068432	-1.186205
H	-1.680748	-1.221824	0.465638
H	0.439877	-0.043137	1.467307
H	3.073363	-1.084683	0.316559

Table S86 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.383601	0.073265	0.107856
C	-0.367492	0.036211	-0.452620
C	-1.081560	1.259718	0.124765
H	-0.598940	2.183081	-0.195931
H	-2.117348	1.278974	-0.218268
H	-1.081139	1.223208	1.213780
N	-0.968672	-1.253962	-0.173043
H	-1.960013	-1.199556	-0.425187
H	-1.038168	-1.392733	1.090761
H	1.730241	-1.093595	-0.456732
H	-0.353642	0.122253	-1.544804
H	-1.243592	-1.291710	1.989118

Table S87 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.395988	-0.048979	-0.005905
C	0.430699	0.009447	-0.358395
C	1.110162	-1.312179	0.009553
H	0.614181	-2.142574	-0.489799
H	2.157821	-1.284324	-0.288933
H	1.067927	-1.483115	1.086518
N	1.172836	1.098660	0.239135
H	0.887585	1.203439	1.214656
H	0.754695	2.189385	-0.253888
H	-1.298768	-0.620476	1.206176
H	0.462631	0.139302	-1.440434
H	0.234720	2.907796	-0.520711

Table S88 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.377214	0.018921	0.105932
C	0.412078	-0.069185	-0.444249
C	1.162685	-1.222278	0.200188
H	0.691558	-2.175845	-0.033147
H	2.190525	-1.237983	-0.165749
H	1.179169	-1.106550	1.283545
N	1.090314	1.181136	-0.224190
H	1.061850	1.433280	1.023161
H	0.514585	1.942518	-0.588743
H	-1.803052	-1.083229	-0.534073
H	0.362108	-0.205288	-1.528686
H	0.757911	1.611192	1.882479

Table S89 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H9 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.356241	-0.103614	-0.087998
C	-0.446334	0.017430	0.384751
C	-1.227086	-1.216086	-0.068774
H	-0.829250	-2.113712	0.404338
H	-2.274579	-1.107942	0.213533
H	-1.163552	-1.339721	-1.149680
N	-1.054079	1.197546	-0.182105
H	-0.807382	1.252857	-1.173771
H	-0.453612	2.223152	0.280720
H	1.540099	-1.392489	0.243186
H	-0.490763	0.106224	1.468718
H	0.198254	2.838569	0.499796

Table S90 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H8 atom of the $-NH_2$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #9 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.383720	0.083897	0.129008
C	-0.392843	0.028562	-0.452409
C	-1.100932	1.255132	0.106475
H	-0.620571	2.171812	-0.230308
H	-2.138460	1.253244	-0.225591
H	-1.092535	1.240232	1.197068
N	-1.139313	-1.171992	-0.172742
H	-1.231459	-1.302019	1.094895
H	-0.569008	-1.988170	-0.397515
H	1.834098	-0.899710	-0.666427
H	-0.335453	0.101949	-1.542739
H	-1.048297	-1.417904	1.991283

N.B.: $H_3C-CH(-SH)-NH_2$ rotamer #1 (H9 abstraction) transforms into TS #3 (H9 abstraction) following the reorientation of the $-SH$ group. The same occurs for #4 (H8 abstraction) leading to TS #5 (H8 abstraction; thus both of them are second-order TSs). In the case of rotamers #4 (H9 abstraction), #7 (H8 abstraction), and #9 (H9 abstraction), no TSs were found.

Table S91 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H4 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.359888	-0.023416	-0.130346
C	0.422117	-0.095602	0.370578
C	1.238236	1.002663	-0.250943
H	0.723674	2.196518	0.224781
H	2.266342	1.067002	0.102878
H	1.137121	1.099847	-1.326907
N	0.887801	-1.394233	-0.108850
H	0.447224	-2.145267	0.409982
H	1.890813	-1.476933	0.004685
H	-1.703946	0.983927	0.688660
H	0.443416	0.003322	1.460407
H	0.376829	2.963509	0.565187

Table S92 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #1 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.445426	-0.095934	-0.098333
C	-0.355990	0.074366	0.370298
C	-1.152349	-1.048653	-0.213780
H	-0.933303	-2.030611	0.193389
H	-2.423781	-0.851153	0.168614
H	-1.210783	-1.036654	-1.298436
N	-0.775552	1.343991	-0.191207
H	-0.349363	2.120481	0.297895
H	-1.782060	1.442106	-0.135077
H	1.755639	-1.008301	0.837656
H	-0.384251	0.030417	1.463131
H	-3.320023	-0.693560	0.445500

Table S93 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H4 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.380056	0.119561	-0.002639
C	-0.407755	-0.115060	-0.359153
C	-1.280199	0.943028	0.261827
H	-0.889800	2.162401	-0.284016
H	-2.326410	0.904447	-0.037016
H	-1.145651	1.089607	1.328793
N	-0.824910	-1.432499	0.122198
H	-0.238612	-2.154697	-0.280801
H	-1.784699	-1.619353	-0.148573
H	1.286226	-0.162327	1.307937
H	-0.442324	-0.014388	-1.451321
H	-0.637517	2.941018	-0.664207

Table S94 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.460307	-0.169391	-0.045566
C	0.348364	0.083435	-0.358982
C	1.154209	-1.049597	0.197323
H	0.941935	-2.021771	-0.234681
H	2.423030	-0.828233	-0.177182
H	1.221461	-1.061045	1.281884
N	0.775372	1.343526	0.225794
H	0.254286	2.117167	-0.167341
H	1.761061	1.498978	0.041556
H	-1.381574	-0.007251	1.285736
H	0.387813	0.055991	-1.455380
H	3.313859	-0.651285	-0.456145

Table S95 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #2 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.402823	-0.100764	-0.019049
C	0.371817	0.161025	-0.438515
C	1.216638	-1.058879	-0.206241
H	0.861394	-1.963484	-0.687033
H	2.287735	-0.902291	-0.322391
H	1.129187	-1.364557	1.140344
N	0.895253	1.300733	0.299701
H	0.346199	2.129771	0.111266
H	1.855339	1.490015	0.032395
H	-1.207288	-0.262695	1.299953
H	0.308629	0.330888	-1.525947
H	1.066468	-1.563434	2.026819

Table S96 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H4 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.370073	-0.088496	-0.065919
C	0.422208	-0.091651	0.380219
C	1.180317	1.045240	-0.252955
H	0.671041	2.216215	0.218176
H	2.220417	1.114598	0.062839
H	1.053929	1.138326	-1.328881
N	0.902816	-1.415479	-0.009504
H	1.822746	-1.589566	0.377541
H	0.963806	-1.491851	-1.018660
H	-1.556730	1.237600	0.030774
H	0.495003	-0.031901	1.465510
H	0.316100	3.009328	0.550356

Table S97 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.454005	-0.058481	0.036681
C	0.364161	0.082581	-0.372333
C	1.126221	-1.070825	0.213483
H	0.909613	-2.049704	-0.207764
H	2.412696	-0.880886	-0.142799
H	1.169051	-1.082964	1.300024
N	0.742378	1.403127	0.094267
H	1.636691	1.673270	-0.296111
H	0.820941	1.421464	1.104453
H	-1.576645	-1.376083	-0.191917
H	0.444519	0.079063	-1.458013
H	3.308269	-0.740900	-0.401529

Table S98 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #4 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.391673	-0.007572	0.073854
C	-0.379614	-0.140183	-0.457438
C	-1.177387	1.106160	-0.173788
H	-0.780490	2.038584	-0.566521
H	-2.245646	0.995841	-0.351814
H	-1.137016	1.308259	1.196357
N	-0.868563	-1.362474	0.158037
H	-1.736379	-1.659495	-0.270457
H	-1.031218	-1.225858	1.148642
H	1.559534	1.291927	-0.219224
H	-0.364621	-0.310388	-1.537753
H	-1.108978	1.423737	2.100210

Table S99 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #5 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.410870	0.007016	-0.012977
C	-0.373494	-0.166403	-0.438554
C	-1.126148	1.124913	-0.225965
H	-0.694326	2.010469	-0.682564
H	-2.202429	1.047684	-0.368886
H	-1.057592	1.403552	1.120406
N	-0.950320	-1.347254	0.192124
H	-1.916573	-1.460827	-0.097279
H	-0.944573	-1.250324	1.200920
H	1.227278	0.619526	1.167779
H	-0.333047	-0.366747	-1.515299
H	-1.002566	1.564133	2.024796

Table S100 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.427032	-0.233045	0.049278
C	0.352175	0.098690	-0.361304
C	1.148659	-1.055142	0.191293
H	0.940232	-2.030796	-0.240151
H	2.430810	-0.830945	-0.204741
H	1.237155	-1.077322	1.274786
N	0.721340	1.420878	0.116632
H	1.679874	1.630118	-0.143225
H	0.655303	1.463372	1.127606
H	-1.891478	0.920300	-0.459882
H	0.429542	0.105369	-1.448267
H	3.296690	-0.658806	-0.490923

Table S101 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #6 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.362022	0.147843	0.069477
C	-0.381020	-0.192357	-0.452115
C	-1.173843	1.066780	-0.303967
H	-0.801113	1.980908	-0.749718
H	-2.250126	0.968333	-0.232577
H	-1.002040	1.533496	1.312643
N	-0.890547	-1.366577	0.242506
H	-1.823627	-1.591710	-0.087396
H	-0.947034	-1.186859	1.238582
H	1.839306	-1.049089	-0.304983
H	-0.324364	-0.446999	-1.516708
H	-0.920351	1.745923	2.067478

Table S102 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H4 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.402311	0.063318	-0.000759
C	-0.429550	-0.120661	-0.351744
C	-1.229059	0.995976	0.266431
H	-0.841065	2.166809	-0.357319
H	-2.290433	0.955914	0.036808
H	-1.022061	1.210997	1.311114
N	-1.012359	-1.401551	-0.015460
H	-1.003941	-1.553724	0.986160
H	-0.489575	-2.157787	-0.441424
H	1.296047	0.030050	1.338212
H	-0.452941	-0.024338	-1.438717
H	-0.594832	2.917962	-0.802585

Table S103 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.500133	-0.176849	-0.065014
C	0.397562	0.112253	-0.338915
C	1.119946	-1.025982	0.252153
H	0.920216	-2.015177	-0.132689
H	2.686462	-0.907137	-0.372858
H	1.411187	-0.964214	1.294343
N	0.891071	1.379051	0.105479
H	0.895364	1.446917	1.115610
H	0.337862	2.143628	-0.257460
H	-1.430735	-0.249466	1.273933
H	0.425028	0.075984	-1.427860
H	3.414202	-0.871941	-0.670576

Table S104 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #7 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.426087	-0.062992	0.001003
C	0.387633	0.170607	-0.449591
C	1.172490	-1.091183	-0.233975
H	0.723501	-1.995460	-0.627464
H	2.235437	-0.992520	-0.436785
H	1.169559	-1.322134	1.116845
N	1.055667	1.295400	0.154255
H	1.169360	1.157534	1.151550
H	0.526349	2.147495	0.022456
H	-1.214167	-0.451106	1.268988
H	0.304113	0.362629	-1.523779
H	1.152839	-1.442915	2.033746

Table S105 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H4 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.368942	-0.044519	-0.103263
C	0.446574	-0.101982	0.370758
C	1.221578	1.020524	-0.259889
H	0.712288	2.194813	0.261562
H	2.262833	1.069121	0.048341
H	1.069832	1.155164	-1.326821
N	1.019237	-1.378915	0.009399
H	0.952238	-1.545532	-0.987710
H	0.557010	-2.142229	0.488974
H	-1.644760	1.192886	0.343453
H	0.485782	-0.017758	1.455660
H	0.364278	2.946993	0.637738

Table S106 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.481519	-0.114548	-0.061679
C	-0.410373	0.095817	0.361463
C	-1.130572	-1.020098	-0.265612
H	-0.970576	-2.016344	0.122470
H	-2.720312	-0.868523	0.291524
H	-1.359190	-0.951828	-1.322168
N	-0.861595	1.379747	-0.073470
H	-0.834033	1.473696	-1.081055
H	-0.326683	2.132678	0.337800
H	1.685404	-1.277587	0.579375
H	-0.439863	0.048393	1.446595
H	-3.462219	-0.820253	0.551507

Table S107 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H6 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #8 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	-1.392215	-0.038710	0.132009
C	0.387586	0.131966	-0.470461
C	1.207291	-1.086550	-0.167321
H	0.768230	-2.036703	-0.451030
H	2.257066	-0.988658	-0.431680
H	1.258536	-1.185891	1.207271
N	1.002744	1.312127	0.076743
H	1.093300	1.249694	1.083717
H	0.477512	2.147592	-0.145766
H	-1.756589	-1.065530	-0.655158
H	0.307120	0.261416	-1.552025
H	1.281791	-1.219951	2.122024

Table S108 Cartesian coordinates (Å) of the first-order TS during the H-atom abstraction from the H5 atom of the $-CH_3$ group of the $H_3C-CH(-SH)-NH_2$ rotamer #9 as optimized at the B3LYP/cc-pV(T+d)Z level of theory.

Atom	X	Y	Z
S	1.462909	-0.258257	-0.055761
C	-0.392640	0.120079	0.313629
C	-1.157053	-1.003650	-0.267866
H	-0.928407	-2.007793	0.058993
H	-2.646396	-0.904622	0.523548
H	-1.564162	-0.892528	-1.264586
N	-0.863738	1.393849	-0.142406
H	-0.758181	1.487299	-1.145500
H	-0.361330	2.156635	0.291076
H	1.960739	0.610149	0.842269
H	-0.433584	0.093446	1.401556
H	-3.330902	-0.865996	0.907086

N.B.: No TSs were found for $H_3C-CH(-SH)-NH_2$ rotamers #1 (H6 abstraction), #3 (H4–H6), #5 (H4, H5), #6 (H4), #9 (H4, H6), even though they are expected to exist.

Barrier heights of hydrogenation / dehydrogenation processes starting from C_2H_5NS isomers

Table S109 Zero-point vibrational energy (ZPVE, in kJ mol^{-1}) corrected energy difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the thione TA form as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial thione TA form is -532.190235 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
S	0	$H_3C-C(-SH)-NH_2$ #1	-100.5
		$H_3C-C(-SH)-NH_2$ #2	-106.7
		$H_3C-C(-SH)-NH_2$ #3	-103.5
C	17.4	$H_3C-CH(-S)-NH_2$ #1	-97.3
		$H_3C-CH(-S)-NH_2$ #2	-94.3
		$H_3C-CH(-S)-NH_2$ #3	-111.7
$-NH_2$	30.2	$H_3C-C=S\cdots NH_3$ adduct	-20.6
$-CH_3$	123.7	$H_2N-C=S + CH_4$	-110.0
H abstraction			
$-NH_2$	22.3	$H_3C-C(-S)=NH$ #1 + H_2	-54.8
$-CH_3$	11.7	$H_2C-C(=S)-NH_2 + H_2$	-69.5

N.B.: The ZPVE-corrected energies of the H atom and the H_2 molecule are -0.502260 and -1.180024 hartree at the applied level of theory.

Table S110 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the *a,c*-thiol TA form as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial *a,c*-thiol TA form is -532.175595 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	*t*-$H_3C-C=NH + H_2S$	-88.2
C	31.3	$H_3C-CH(-SH)-NH$ #1	-97.8
		$H_3C-CH(-SH)-NH$ #2	-91.8
		$H_3C-CH(-SH)-NH$ #3	-91.5
=NH	3.2	$H_3C-C(-SH)-NH2$ #1	-139.0
		$H_3C-C(-SH)-NH2$ #2	-145.1
		$H_3C-C(-SH)-NH2$ #3	-142.0
$-CH_3$	126.4	*a,c*-$HN=C-SH + CH_4$	-89.6
H abstraction			
−SH	0	$H_3C-C(-S)=NH$ #1 + H_2	-93.3

=NH	2.4	$H_3C-C(-SH)=N$ #1 + H_2	-62.9
		a,c-H_2 $C-C(-SH)=NH$ +	-56.2
$-CH_3$	17.9	H_2	

Table S111 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the *a,t*-thiol TA form as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial *a,t*-thiol TA form is -532.172731 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	*c*-H_3C− C=NH + H_2S	-79.1
		H_3C−CH(−SH)− NH #1	-105.3
C	30.9	H_3C−CH(−SH)− NH #2	-99.3
		H_3C−CH(−SH)− NH #3	-99.0
		H_3C− C(−SH)−NH2 #1	-146.5
=NH	2.1	H_3C− C(−SH)−NH2 #2	-152.6
		H_3C− C(−SH)−NH2 #3	-149.5
−CH_3	119.5	*a,t*-HN= C−SH + CH_4	-109.5
H abstraction			
−SH	0	H_3C−C(−S)=NH #2 + H_2	-84.3
=NH	1.4	H_3C−C(−SH)= N #1 + H_2	-70.4
		a,t-H_2 C−C(−SH)=NH +	-57.2
−CH_3	17.5	H_2	

Table S112 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the *s,c*-thiol TA form as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial *s,c*-thiol TA form is -532.175499 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	*t*-H_3C− C=NH + H_2S	-88.5
		H_3C−CH(−SH)− NH #1	-98.0
C	31.7	H_3C−CH(−SH)− NH #2	-92.1
		H_3C−CH(−SH)− NH #3	-91.7
		H_3C− C(−SH)−NH2 #1	-139.2
=NH	3.0	H_3C− C(−SH)−NH2 #2	-145.4
		H_3C− C(−SH)−NH2 #3	-142.2
−CH_3	N/A[a]	*a,c*-HN= C−SH + CH_4	-83.1
H abstraction			
−SH	0	H_3C−C(−S)=NH #1 + H_2	-93.5
=NH	1.8	H_3C−C(−SH)= N #2 + H_2	-71.9
		s,c-H_2 C−C(−SH)=NH +	-56.7
−CH_3	17.3	H_2	

[a] Vibrational frequencies of TS could not be obtained.

Table S113 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the *s,t*-thiol TA form as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial *s,t*-thiol TA form is -532.175037 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	*c*-H_3C− C=NH + H_2S	-73.0
		H_3C−CH(−SH)− NH #1	-99.3
C	31.7	H_3C−CH(−SH)− NH #2	-93.3
		H_3C−CH(−SH)− NH #3	-93.0
		H_3C− C(−SH)−NH2 #1	-140.4
=NH	2.1	H_3C− C(−SH)−NH2 #2	-146.6
		H_3C− C(−SH)−NH2 #3	-143.4
$-CH_3$	123.6	*s,t*-HN= C−SH + CH_4	-99.2
H abstraction			
−SH	0	H_3C−C(−S)=NH #2 + H_2	-78.3
=NH	-0.1	H_3C−C(−SH)= N #2 + H_2	-73.1
$-CH_3$	17.4	*s,t*-H_2 C−C(−SH)=NH + H_2	-57.5

Table S114 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the H_2C=C(−SH)−NH_2 rotamer #1 as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial H_2C=C(−SH)−NH_2 rotamer #1 is -532.162670 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	H_2C= C−NH_2 + H_2S	-64.7
C	17.1	H_2C −CH(−SH)−NH_2 #2	-120.8
$-NH_2$	41.8	H_2C= C(−SH)…NH_3 adduct #1	33.8
$=CH_2$	0	H_3C− C(−SH)−NH_2 #1	-172.9
H abstraction			
−SH	0	H_2C=C(−S)−NH_2 + H_2	-141.9
$-NH_2$	N/A[a]	N/A	N/A
$=CH_2$	N/A[a]	H addition	N/A

[a] Intended processes did not occur.

Table S115 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the H_2C=C(−SH)−NH_2 rotamer #2 as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial H_2C=C(−SH)−NH_2 rotamer #2 is -532.163213 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	H_2C= C−NH_2 + H_2S	-63.2
C	0	H_2C −CH(−SH)−NH_2 #2	-119.4
−NH_2	38.4	H_2C= C(−SH)…NH_3 adduct #1	35.2
=CH_2	0	H_3C− C(−SH)−NH_2 #2	-177.6
H abstraction			
−SH	0	H_2C=C(−S)−NH_2 + H_2	-140.4
−NH_2	N/A[a]	*a,t*-H_2C=C(−SH)− NH + H_2	-82.2
	7.1[b]	*a,c*-H_2C=C(−SH)− NH + H_2	-88.7
=CH_2	N/A[c]	N/A	N/A

[a] No TS could be found for the H7 abstraction process.

[b] TS of the H8 abstraction process.

[c] Intended process did not occur.

Table S116 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the H_2C=C(−SH)−NH_2 rotamer #3 as obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial H_2C=C(−SH)−NH_2 rotamer #3 is -532.164720 hartree. The * symbol marks the enantiomeric form.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	H_2C= C−NH_2 + H_2S	-59.3
C	6.9	H_2C −CH(−SH)−NH_2 #2*	-115.4
−NH_2	42.1	H_2C= C(−SH)…NH_3 adduct #2	28.1
=CH_2	0	H_3C− C(−SH)−NH_2 #2*	-173.7
H abstraction			
−SH	0	H_2C=C(−S)−NH_2 + H_2	-136.5
−NH_2	6.9[a]	*s,t*-H_2C=C(−SH)− NH + H_2	-84.6
	N/A[b]	*s,c*-H_2C=C(−SH)− NH + H_2	-85.0
=CH_2	54.0[c]	HC =C(−SH)−NH_2 + H_2	28.4

[a] TS of the H7 abstraction process.

[b] No TS could be found for the H8 abstraction process.

[c] TS of the H5 abstraction process; H4 abstraction process could not be determined.

Table S117 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the H_3C- C(−SH)−NH_2 radical rotamer #1 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial H_3C- C(−SH)−NH_2 radical rotamer #1 is -532.730791 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	H_3C-:C−NH_2 + H_2S	-192.1
C	0	H_3C−CH(−SH)−NH_2 #1	-344.4
−NH_2	N/A[a]	H-abstraction process	N/A
−CH_3	N/A[a]	H-abstraction process	N/A
H abstraction			
−SH	0	thione + H_2	-333.8
−NH_2	0	*a,t*-thiol + H_2	-287.9
	0	*a,c*-thiol + H_2	-295.4
−CH_3	0	H_2C=C(−SH)−NH_2 #2 + H_2	-262.8

[a] First-order TS could not be obtained.

Table S118 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the H_3C- C(−SH)−NH_2 radical rotamer #2 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial H_3C- C(−SH)−NH_2 radical rotamer #2 is -532.733125 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	H_3C-:C−NH_2 + H_2S	-186.0
C	0	H_3C−CH(−SH)−NH_2 #2	-343.0
−NH_2	N/A[a]	H-abstraction process	N/A
−CH_3	N/A[a]	H-abstraction process	N/A
H abstraction			
−SH	0	thione + H_2	-327.7
−NH_2	0[b]	*s,c*-thiol + H_2	-289.0
−CH_3	0	H_2C=C(−SH)−NH_2 #3 + H_2	-260.7

[a] First-order TS could not be obtained.

[b] Only the H9 abstraction occurs, the H8 abstraction results in the abstraction from the –SH group instead.

Table S119 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C-C(-SH)-NH_2$ radical rotamer #3 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C-C(-SH)-NH_2$ radical rotamer #3 is -532.731926 hartree. The * symbol marks the enantiomeric form.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	$H_3C-:C-NH_2 + H_2S$	-189.2
C	0	$H_3C-CH(-SH)-NH_2$ #5	-337.8
$-NH_2$	N/A[a]	H-abstraction process	N/A
$-CH_3$	N/A[a]	H-abstraction process	N/A
H abstraction			
−SH	0	thione + H_2	-330.8
$-NH_2$	0[b]	*a,c*-thiol + H_2	-292.4
		s,c-thiol + H_2	-292.1
$-CH_3$	0	$H_2C=C(-SH)-NH_2$ #2* + H_2	-259.9

[a] First-order TS could not be obtained.

[b] Only the H8 abstraction occurs, the H9 abstraction results in the abstraction from the –SH group instead.

Table S120 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C-CH(-S^{\cdot})-NH_2$ radical rotamer #1 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C-CH(-S^{\cdot})-NH_2$ radical rotamer #1 is -532.729546 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-S^{\cdot}$	0	$H_3C-CH(-SH)-NH_2$ #1	-347.7
		$H_3C-CH(-SH)-NH_2$ #2	-352.4
		$H_3C-CH(-SH)-NH_2$ #3	-345.5
$-NH_2$	N/A[a]	H-addition on $-S^{\cdot}$ occurs	N/A
$-CH_3$	0	$H_2N-C(H)=S + CH_4$	-380.5
H abstraction			
C	0	thione + H_2	-337.1
$-NH_2$	0[b]	$H_3C-[(H)CSN(H)] + H_2$	-193.3
$-CH_3$	0[c]	$[(H_2)CSC(H)]-NH_2$ #1+ H_2	-249.2

[a] First-order TS could not be obtained.

[b] Only the H9 abstraction occurs, the H8 abstraction results in the addition on the $-S^{\cdot}$ instead.

[c] Only the H6 abstraction occurs, the H4 and H5 abstractions result in the addition on the $-S^{\cdot}$ instead.

Table S121 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #2 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #2 is -532.728404 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-S^{\bullet}$	0	$H_3C{-}CH(-SH){-}NH_2$ #4	-349.2
		$H_3C{-}CH(-SH){-}NH_2$ #5	-347.1
		$H_3C{-}CH(-SH){-}NH_2$ #6	-354.2
$-NH_2$	N/A[a]	H-addition on $-S^{\bullet}$ occurs	N/A
$-CH_3$	0	$H_2N{-}C(H)=S + CH_4$	-383.5
H abstraction			
C	0	thione + H_2	-340.1
$-NH_2$	0[b]	$H_3C{-}[(H)CSN(H)] + H_2$	-196.3
$-CH_3$	0[c]	$[(H_2)CSC(H)]{-}NH_2$ #2 + H_2	-237.1

[a] First-order TS could not be obtained.

[b] Only the H9 abstraction occurs, the H8 abstraction results in the addition on the $-S^{\bullet}$ instead.

[c] Only the H6 abstraction occurs, the H4 and H5 abstractions result in the addition on the $-S^{\bullet}$ instead.

Table S122 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #3 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-S^{\bullet}){-}NH_2$ radical rotamer #3 is -532.735040 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-S^{\bullet}$	0	$H_3C{-}CH(-SH){-}NH_2$ #7	-343.8
		$H_3C{-}CH(-SH){-}NH_2$ #8	-342.9
		$H_3C{-}CH(-SH){-}NH_2$ #9	-344.4
$-NH_2$	0	$H_3C{-}CH(-S^{\bullet})\ldots NH_3$ adduct	-236.3
$-CH_3$	N/A[a]	H-abstraction process	N/A
H abstraction			
C	0	thione + H_2	-322.7
$-NH_2$	N/A[a]	$H_3C{-}[(H)CSN(H)] + H_2$	-178.8
$-CH_3$	0[b]	$[(H_2)CSC(H)]{-}NH_2$ #1 + H_2	-234.8

[a] First-order TS could not be obtained.

[b] Only the H6 abstraction occurs, the H4 and H5 abstractions result in the addition on the $-S^{\bullet}$ instead.

Table S123 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #1 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #1 is -533.364228 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction / S_H2 reaction			
$-SH$	0	$H_3C{-}{\cdot}CH{-}NH_2$ #1+ H_2S	-132.5
$-NH_2$	40.0	$H_3C{-}{\cdot}CH{-}SH\ldots NH_3$ adduct #1	40.8
$-CH_3$	120.9	$H_2N{-}{\cdot}CH{-}SH$ #1 + CH_4	-142.0
H abstraction			
$-SH$	0	$H_3C{-}CH(-S{\cdot}){-}NH_2$ #1 + H_2	-86.7
C	0	$H_3C{-}{\cdot}C(-SH){-}NH_2$ #1 + H_2	-90.0
$-NH_2$	20.2[a]	$H_3C{-}CH(-SH)-$ NH #4 + H_2	-30.6
$-CH_3$	29.1 / 18.3[b]	$H_2C{\cdot}{-}CH(-SH){-}NH_2$ #1 + H_2	-33.3

[a] TS of H8 abstraction was found only; H9 abstraction resulted in –SH rotamerization as well.
[b] TSs of the H4 / H5 abstraction processes.

Table S124 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #2 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #2 is -533.366019 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-SH$	0	$H_3C{-}{\cdot}CH{-}NH_2$ + H_2S	-127.8
$-NH_2$	N/A[a]	H abstraction process	N/A
$-CH_3$	119.3	$H_2N{-}{\cdot}CH{-}SH$ #2 + CH_4	-139.0
H abstraction			
$-SH$	0	$H_3C{-}CH(-S{\cdot}){-}NH_2$ #1 + H_2	-82.0
C	-1.7	$H_3C{-}{\cdot}C(-SH){-}NH_2$ #2 + H_2	-91.4
$-NH_2$	21.0 / 10.7[b]	$H_3C{-}CH(-SH)-$ NH #1 + H_2	-44.1
$-CH_3$	30.9 / 18.4 / 28.1[c]	$H_2C{\cdot}{-}CH(-SH){-}NH_2$ #2+ H_2	-33.2

[a] No TS could be found (abstraction from –SH occurred instead)
[b] TSs of the H8 / H9 abstraction processes.
[c] TSs of the H4 / H5 / H6 abstraction processes.

Table S125 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #3 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #3 is -533.363402 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2$+ H_2S	-134.6
$-NH_2$	N/A[a]	$H_3C{-}^{\cdot}CH{-}SH\ldots NH_3$ adduct #1	38.6
$-CH_3$	118.3	$H_2N{-}^{\cdot}CH{-}SH$ #1 + CH_4	-144.2
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #1 + H_2	-88.9
C	N/A[b]	N/A	N/A
$-NH_2$	16.9[c]	$H_3C{-}CH(-SH){-}$ NH #5 + H_2	-36.0
	10.2[d]	$H_3C{-}CH(-SH){-}$ NH #2 + H_2	-44.9
$-CH_3$	N/A[e]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ + H_2	N/A

[a] No first-order TS could be found; reorientation of the –SH group occurs during the process.
[b] TS could not be determined.
[c] TS of the H8 abstraction process.
[d] TS of the H9 abstraction process.
[e] No first-order TS could be found: reorientation of –SH occurs for the H5 abstraction process; whereas addition on the –SH (H4 abstraction) or $–NH_2$ (H6 abstraction) occurs in the two other cases

Table S126 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #4 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #4 is -533.363655 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2$+ H_2S	-134.0
$-NH_2$	39.5	$H_3C{-}^{\cdot}CH{-}SH\ldots NH_3$ adduct #1	39.2
$-CH_3$	110.2	$H_2N{-}^{\cdot}CH{-}SH$ #1 + CH_4	-143.5
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #1 + H_2	-85.2
C	1.6	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #3 + H_2	-94.4
$-NH_2$	11.9[a]	$H_3C{-}CH(-SH){-}$ NH #3 + H_2	-44.0
$-CH_3$	23.1 / 19.8 / 28.0[b]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ #1 + H_2	-34.8

[a] TS of the H8 abstraction process; the H9 abstraction process did not occur.
[b] TSs of the H4 / H5 / H6 abstraction processes.

Table S127 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #5 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #5 is -533.362865 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2 + H_2S$	-136.0
$-NH_2$	44.3	H atom abstraction	N/A[a]
$-CH_3$	109.3	$H_2N{-}^{\cdot}CH{-}SH$ #1 + CH_4	-145.6
H abstraction			
−SH	N/A[b]	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #1 + H_2	-87.3
C	-0.5	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #3 + H_2	-96.5
$-NH_2$	9.8[c]	$H_3C{-}CH(-SH){-}$ NH #3 + H_2	-46.0
	17.5[d]	$H_3C{-}CH(-SH){-}$ NH #1 + H_2	-52.3
$-CH_3$	25.9[e]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ #3 + H_2	-33.7

[a] Structure optimization ends up in H_2 elimination.
[b] Process could not be determined.
[c] TS of the H8 abstraction process
[d] TS of the H9 abstraction process
[e] TS of the H6 abstraction process; TS of H4 abstraction could not be determined, whereas H5-abstraction results in the reorientation of the –SH group yielding TS #4.

Table S128 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #6 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #6 is -533.365583 hartree. The * symbol marks the enantiomeric form.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2 + H_2S$	-128.9
$-NH_2$	38.7	H atom abstraction	N/A[a]
$-CH_3$	112.2	$H_2N{-}^{\cdot}CH{-}SH$ #2* + CH_4	-140.2
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #2 + H_2	-80.1
C	1.5	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #2* + H_2	-92.5
$-NH_2$	10.8[b]	$H_3C{-}CH(-SH){-}$ NH #7 + H_2	-43.7
	19.7[c]	$H_3C{-}CH(-SH){-}$ NH #6 + H_2	-30.3
$-CH_3$	23.0 / 17.2[d]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ #1 + H_2	N/A[e]

[a] Structure optimization ends up in H_2 elimination.
[b] TS of the H8 abstraction process
[c] TS of the H9 abstraction process
[d] TSs of the H5 and H6 abstraction processes; H4 abstraction does not yield a proper TS.
[e] No minima could be determined.

Table S129 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #7 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #7 is -533.368242 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2$+ H_2S	-121.9
$-NH_2$	N/A[a]	H atom abstraction	N/A
$-CH_3$	122.0	$H_2N{-}^{\cdot}CH{-}SH$ #2 + CH_4	-133.2
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #3 + H_2	-90.6
C	6.0	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #3 + H_2	-82.4
$-NH_2$	24.1[b]	$H_3C{-}CH(-SH)-$ NH #4 + H_2	-31.9
$-CH_3$	30.8 / 7.7 / 25.1[c]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ + H_2	-31.7

[a] No TS of H addition could be determined.
[b] TS of the H9 abstraction process; TS of the H8 abstraction process could not be determined.
[c] TSs of the H4, H5, and H6 abstraction processes.

Table S130 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #8 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #8 is -533.367887 hartree. The * symbol marks the enantiomeric form.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2$+ H_2S	-122.9
$-NH_2$	50.4	$H_3C{-}^{\cdot}CH{-}SH\ldots NH_3$ adduct #1	50.4
$-CH_3$	121.5	$H_2N{-}^{\cdot}CH{-}SH$ #2 + CH_4	-134.1
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #3 + H_2	-91.5
C	2.6	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #2* + H_2	-86.5
$-NH_2$	20.9[a]	$H_3C{-}CH(-SH)-$ NH #2 + H_2	-33.2
	23.1[b]	$H_3C{-}CH(-SH)-$ NH #3 + H_2	-32.9
$-CH_3$	28.4 / 8.1 / 27.2[c]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ #6 + H_2	-30.5

[a] TS of H8 abstraction.
[b] TS of H9 abstraction.
[c] TSs of H4, H5, and H6 abstraction processes.

Table S131 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the / dehydrogenation products of the $H_3C{-}CH(-SH){-}NH_2$ rotamer #9 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}CH(-SH){-}NH_2$ rotamer #9 is -533.368465 hartree. The * symbol marks the enantiomeric form.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition / S_H2 reaction			
−SH	0	$H_3C{-}^{\cdot}CH{-}NH_2$+ H_2S	-121.3
$-NH_2$	51.9	$H_3C{-}^{\cdot}CH{-}SH\ldots NH_3$ adduct #1	51.9
$-CH_3$	123.3	$H_2N{-}^{\cdot}CH{-}SH$ #1 + CH_4	-130.9
H abstraction			
−SH	0	$H_3C{-}CH(-S^{\cdot}){-}NH_2$ #3 + H_2	-90.0
C	4.2	$H_3C{-}^{\cdot}C(-SH){-}NH_2$ #2* + H_2	-85.0
$-NH_2$	23.2[a]	$H_3C{-}CH(-SH)-$ NH #2 + H_2	-31.7
$-CH_3$	12.4[b]	$H_2C^{\cdot}{-}CH(-SH){-}NH_2$ #6 + H_2	-27.4

[a] TS of H8 abstraction; TS of H9 abstraction could not be determined.

[c] TSs of H5 abstraction; no TS for H5, and H6 abstraction processes could be determined.

Table S132 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}C(-S^{\cdot})=NH$ rotamer #1 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}C(-S^{\cdot})=NH$ rotamer #1 is -531.543414 hartree.

Process	Δ*E* (TS)	Product(s)	Δ*E*
H addition			
$-S^{\cdot}$	0	*a,c*-thiol	-341.1
		s,c-thiol	-340.1
=NH	0	thione	-379.5
$-CH_3$	N/A[a]	H abstraction	N/A
H abstraction			
=NH	N/A[b]	H addition	N/A
$-CH_3$	0[c]	$[(H_2)CSC]=NH$ #1 + H_2	-190.4

[a] No TS could be determined, H abstraction occurs on the $-CH_3$ group instead.

[b] H addition on $-S^{\cdot}$ occurs instead.

[c] Only H6 abstraction could be determined; H4 and H5 results in the addition on the $-S^{\cdot}$ instead.

Table S133 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}C(-S^{\bullet})=NH$ rotamer #2 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}C(-S^{\bullet})=NH$ rotamer #2 is -531.537144 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-S^{\bullet}$	0	*a,t*-thiol	-350.1
$=NH$	N/A[a]	H addition on $-S^{\bullet}$	N/A
$-CH_3$	0	HNCS + CH_4	-385.2
H abstraction			
$=NH$	0	$H_3C{-}[CSN]$ + H_2	-156.6
$-CH_3$	0[b]	$[(H_2)CSC]=NH$ #2 + H_2	-197.5

[a] Addition on the $-S^{\bullet}$ occurs instead.

[b] Only H6 abstraction could be determined; H4 and H5 results in the addition on the $-S^{\bullet}$ instead.

Table S134 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}C(-SH)=N^{\bullet}$ rotamer #1 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}C(-SH)=N^{\bullet}$ rotamer #1 is -531.531863 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
$-SH$	0	$H_3C{-}C{\equiv}N$ + H_2S	-381.7
$=N^{\bullet}$	0	*a,c*-thiol	-371.4
		a,t-thiol	-363.9
$-CH_3$	0	HSCN + CH_4	-351.4
H abstraction			
$-SH$	N/A[a]	H addition	N/A
$-CH_3$	0[b]	$[(H_2)CNC]{-}SH$ #1 + H_2	-151.1

[a] Addition on the $-SH$ occurs instead.

[b] TSs of H4 and H5 abstractions; H3 abstraction results in an addition on the $=N^{\bullet}$ instead.

Table S135 Zero-point corrected vibrational energy (ZPVE, in kJ mol^{-1}) difference of the first-order TS (if exists) as well as that of the hydrogenation / dehydrogenation products of the $H_3C{-}C(-SH){=}N^{\cdot}$ rotamer #2 is obtained at the B3LYP/cc-pV(T+d)Z level of theory. The ZPVE-corrected energy of the initial $H_3C{-}C(-SH){=}N^{\cdot}$ rotamer #2 is -531.535192 hartree.

Process	ΔE (TS)	Product(s)	ΔE
H addition / S_H2 reaction			
−SH	0	$H_3C{-}C{\equiv}N + H_2S$	-373.0
$=N^{\cdot}$	0	*s,c*-thiol	-362.4
		s,t-thiol	-361.2
$-CH_3$	0	$HSCN + CH_4$	-342.7
H abstraction			
−SH	N/A[a]	H addition	N/A
$-CH_3$	0[b]	$[(H_2)CNC]{-}SH$ #2 + H_2	-145.2

[a] Addition on the $=N^{\cdot}$ occurs instead.

[b] TSs of H4 and H5 abstractions; H3 abstraction results in an addition on the $=N^{\cdot}$ instead.