Electronic Supplementary Information for

S–H Rotamerization *via* Tunneling in a Thiol Form of Thioacetamide

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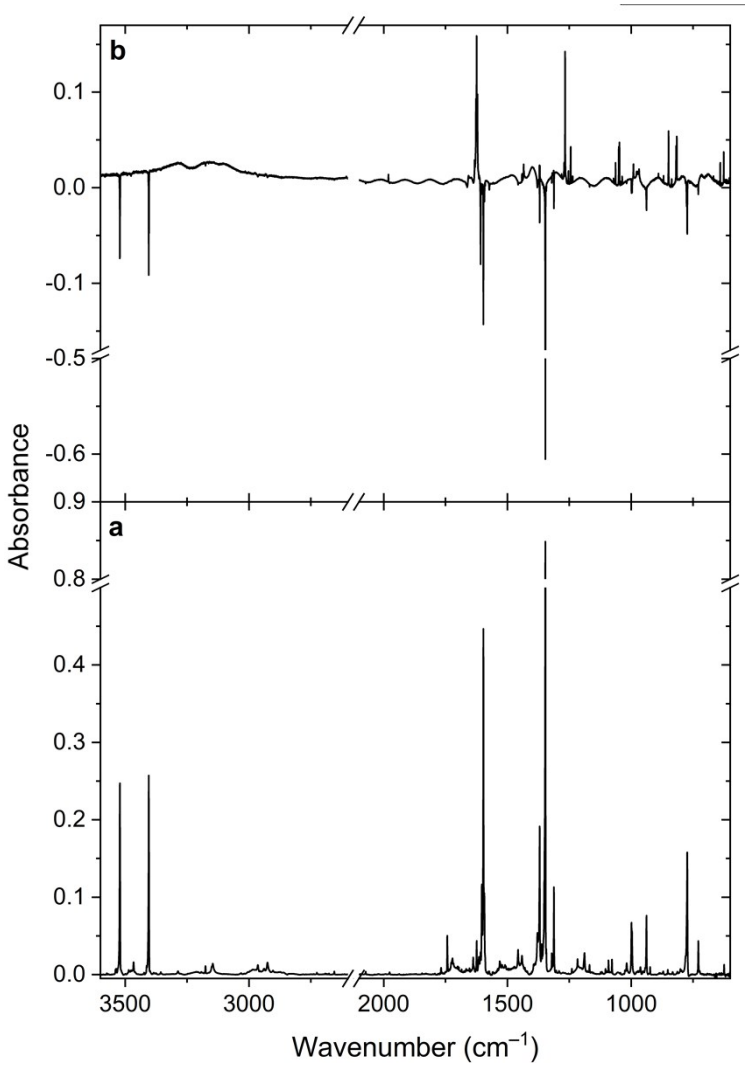

Figure S1. (**a**) Mid-IR spectrum of the thioacetamide monomers isolated in an Ar matrix at 11 K, collected immediately after the deposition of the sample. (**b**) Changes in the mid-IR spectrum of matrix-isolated thioacetamide upon UV irradiation ($\lambda = 269$ nm for 3 min). Positive bands grow upon the irradiation.

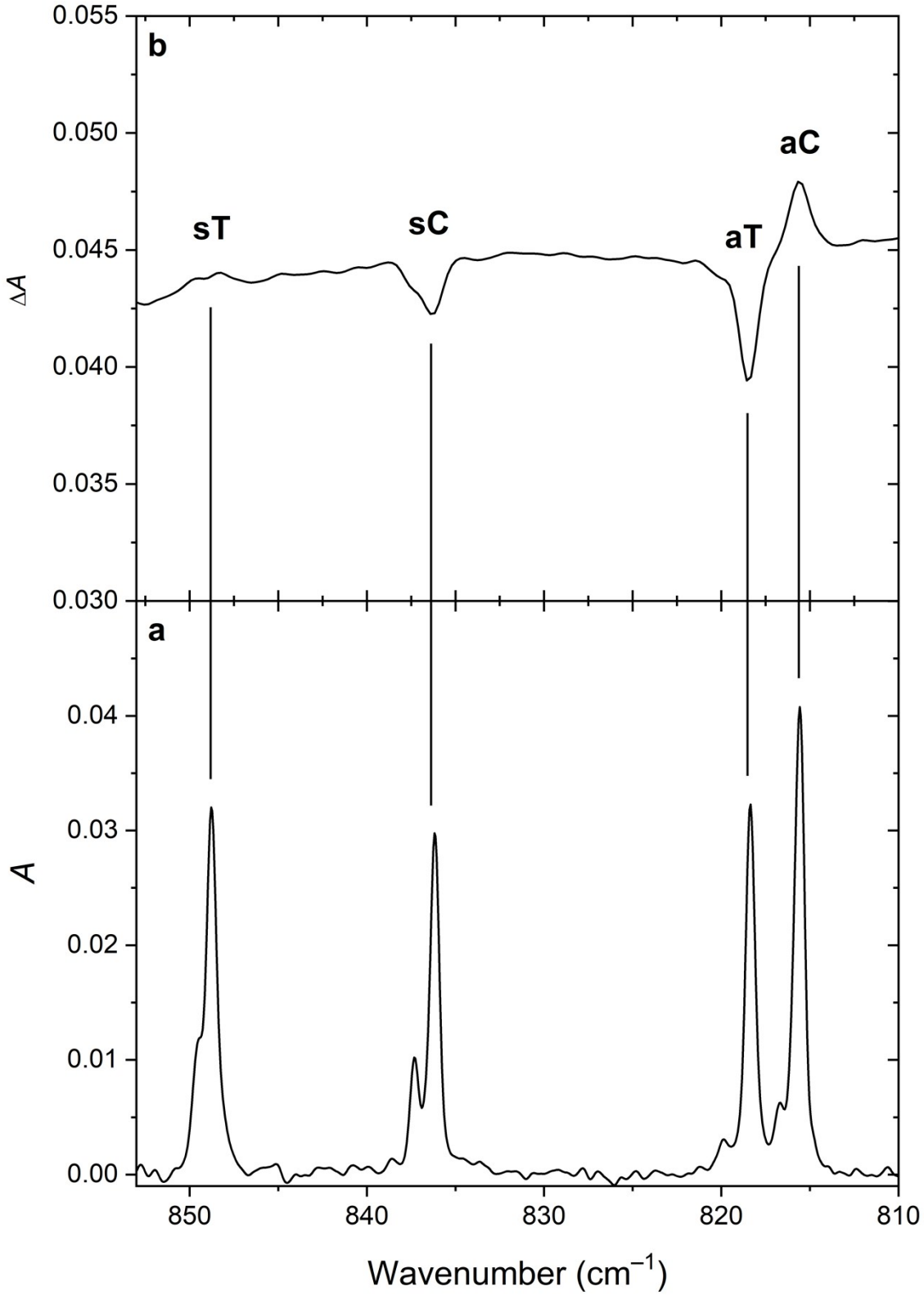

Figure S2. (**a**) Fragment of the Mid-IR spectrum (855–810 cm^{-1} region) of the thioacetamide monomers isolated in an Ar matrix at 11 K immediately after UV irradiation. (**b**) Changes in the mid-IR spectrum of matrix-isolated thioacetamide when no filter was used during the collection of spectra after exposing the sample to the spectrometer beam source for 217 min.

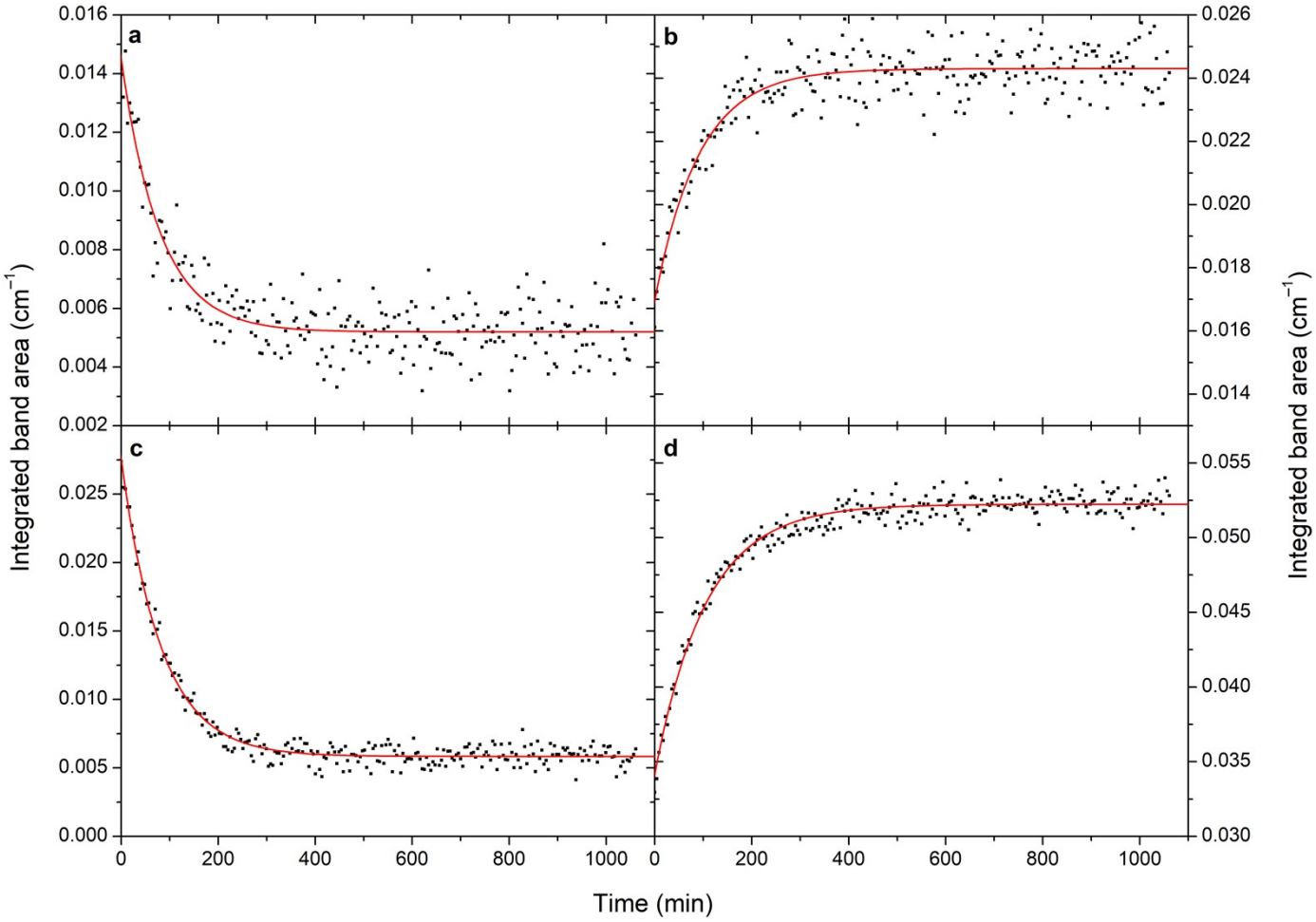

Figure S3. (**a**) Kinetic decay curve of the band at 623 cm^{-1} (**sC**), (**b**) kinetic growth curve of the band at 626 cm^{-1} (**sT**), (**c**) kinetic decay curve of the band at 836 cm^{-1} (**sC**), (**d**) kinetic growth curve of the band at 849 cm^{-1} (**sC**). The spectra were recorded using the longpass filter with a cut-off wavenumber of 870 cm^{-1} (experiment **1a**, at 11 K).

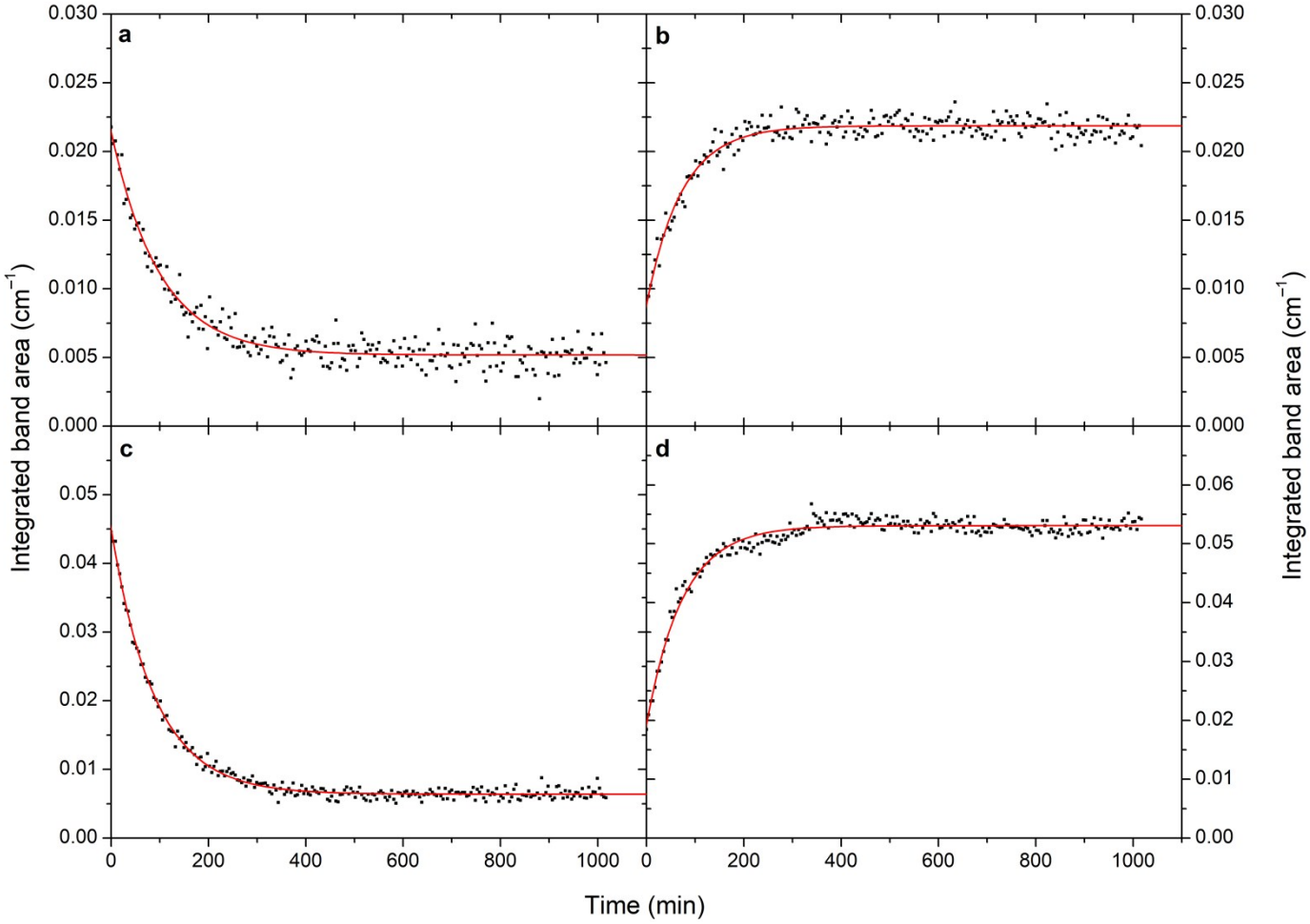

Figure S4. (**a**) Kinetic decay curve of the band at 620 cm^{-1} (**sC**), (**b**) kinetic growth curve of the band at 623 cm^{-1} (**sT**), (**c**) kinetic decay curve of the band at 835 cm^{-1} (**sC**), (**d**) kinetic growth curve of the band at 848 cm^{-1} (**sT**), in Ar matrix at 20 K. The spectra were recorded using the longpass filter with the cut-off wavenumber of 870 cm^{-1} (experiment **1b**).

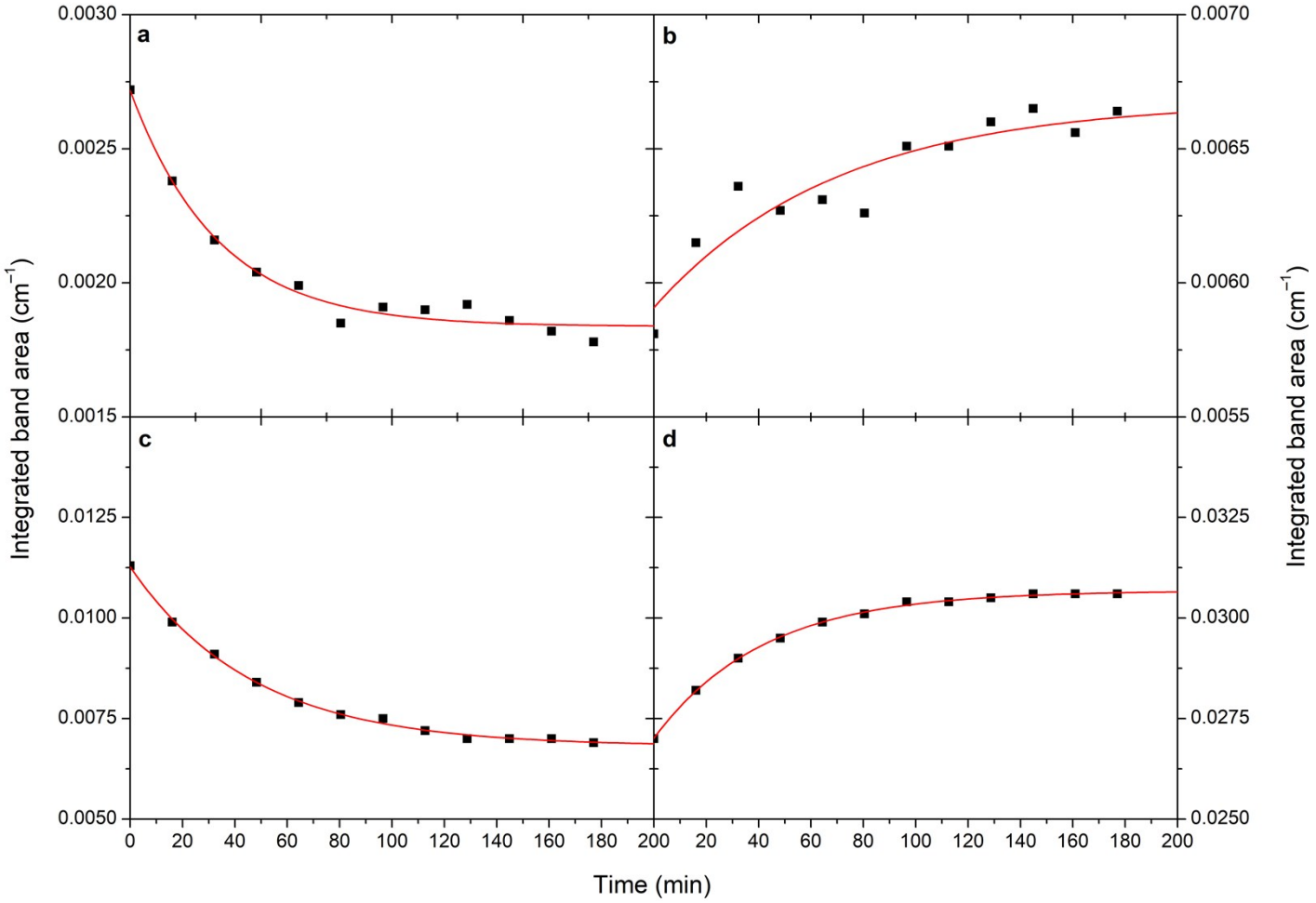

Figure S5. (**a**) Kinetic decay curve of the band at 623 cm^{-1} (**sC**), (**b**) kinetic growth curve of the band at 626 cm^{-1} (**sT**), (**c**) kinetic decay curve of the band at 836 cm^{-1} (**sC**), (**d**) kinetic growth curve of the band at 849 cm^{-1} (**sT**), in Xe matrix at 11 K. The spectra were recorded using the longpass filter with the cut-off wavenumber of 870 cm^{-1} (experiment **3**).

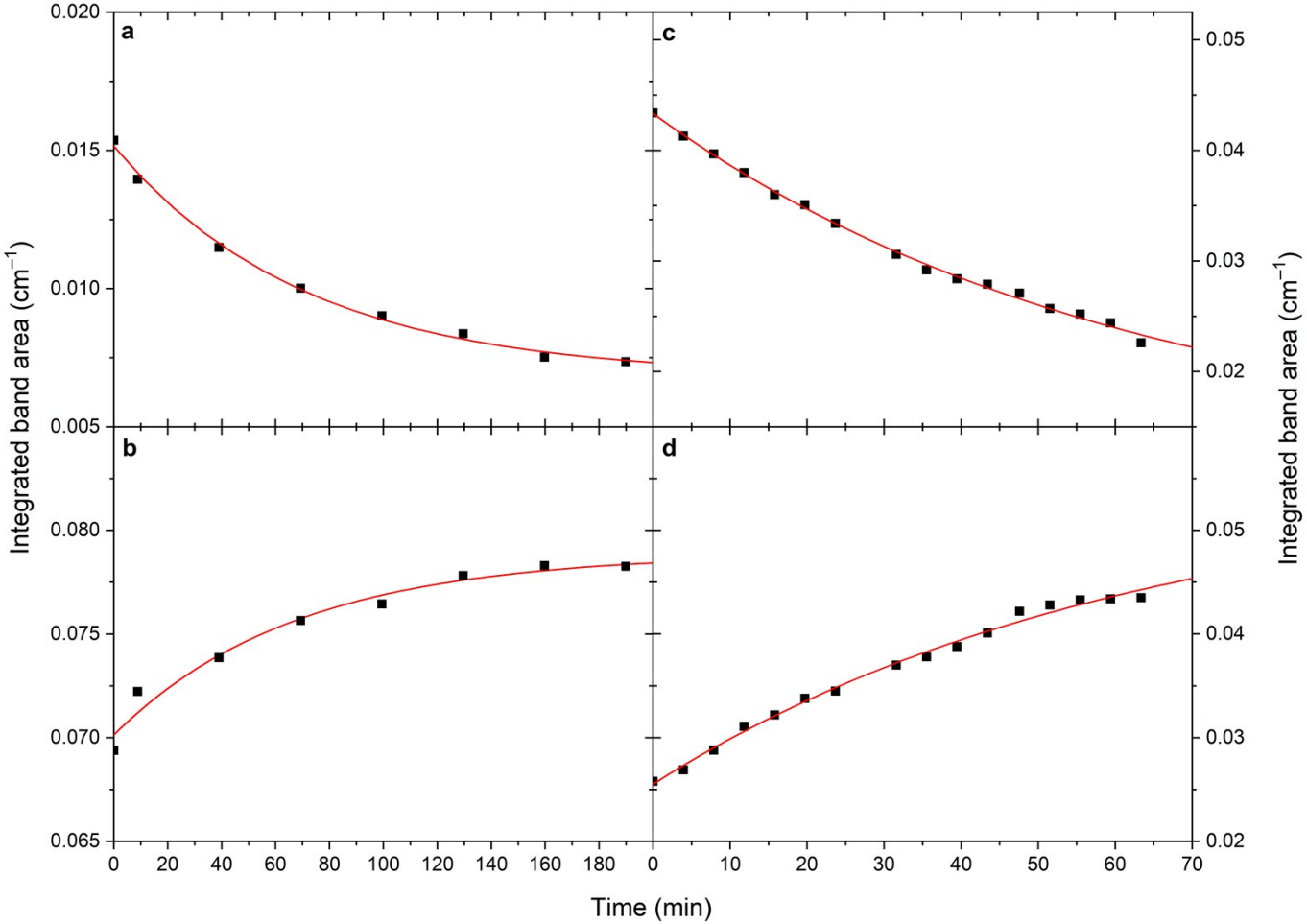

Figure S6. (**a**) Kinetic decay curve of the band at 836 cm^{-1} (**sC**), (**b**) kinetic growth curve of the band at 849 cm^{-1} (**sT**), in Ar matrix at 11 K. The spectra were recorded using the longpass filter with the cut-off wavenumber of 1960 cm^{-1} (experiment **4a**). (**c, d**) plots the curves of the same bands when the measurement was repeated during the same experiment.

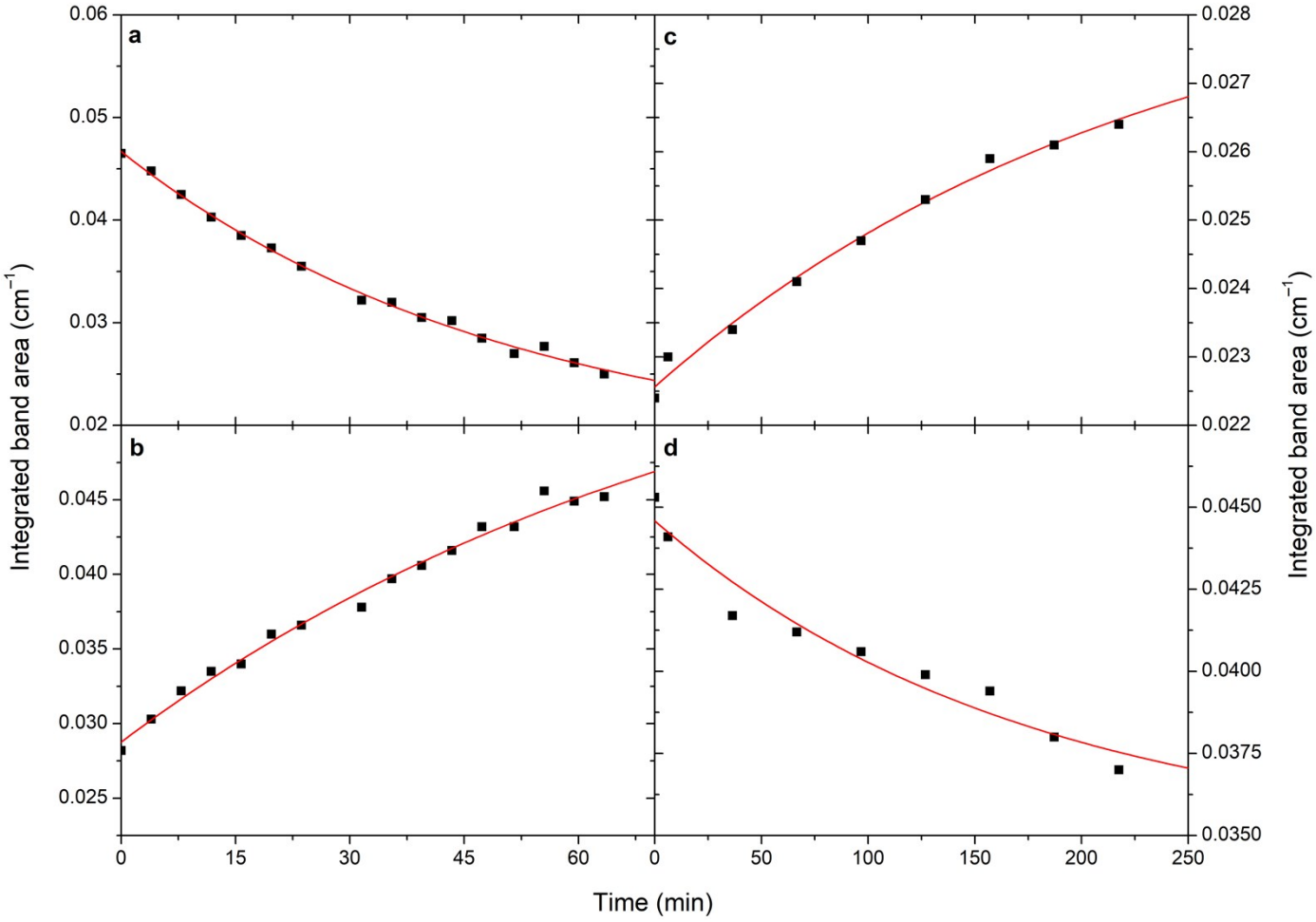

Figure S7. (**a**) Kinetic decay curve of the band at 836 cm^{-1} (**sC**), (**b**) kinetic growth curve of the band at 849 cm^{-1} (**sT**), (**c**) kinetic growth curve of the band at 816 cm^{-1} (**aC**), (**d**) kinetic decay curve of the band at 818 cm^{-1} (**aT**), in Ar matrix at 11 K. The spectra were recorded without using any filter (experiment **4b**).

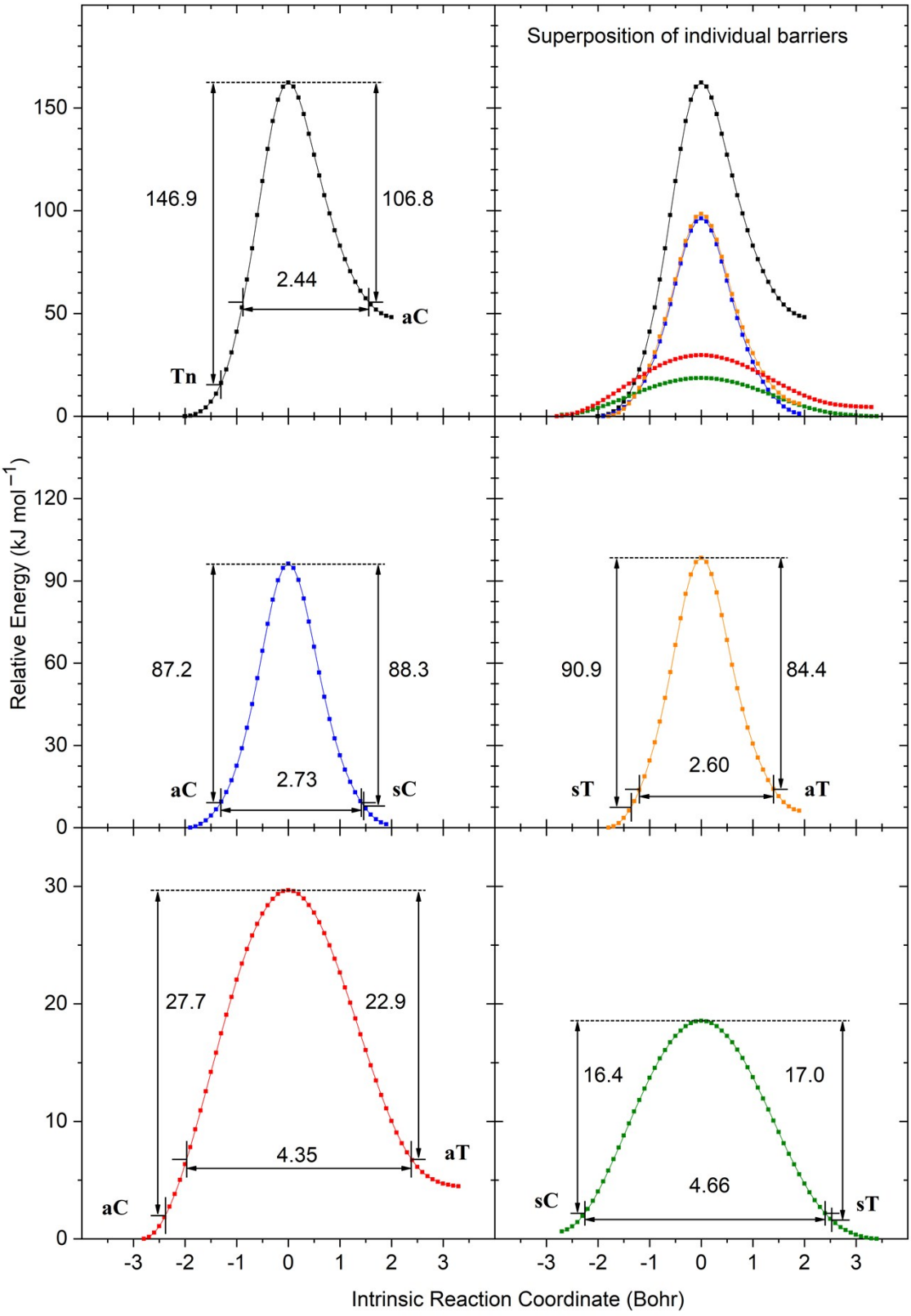

Figure S8. IRC pathways between the thioacetamide isomers as calculated at the B3LYP/6-311++G(3df,3pd) level of theory. The colors in the top-right panel displaying the superimposed profiles all correspond to those of each individual profile in the rest of the panels.

Table S1. Cartesian coordinates (in Å) of the **Tn** tautomer as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.283881	0.000000
S	-0.168012	-1.358478	0.000000
N	-1.057753	1.116049	0.000000
H	-1.987466	0.731082	0.000000
H	-0.947449	2.116062	0.000000
C	1.337009	0.980343	0.000000
H	1.432099	1.618176	0.882142
H	2.141122	0.254466	0.000000
H	1.432099	1.618176	-0.882142

Table S2. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **Tn** tautomer as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3694.4179	37.2886
2	3564.7349	42.0762
3	3166.2241	1.5240
4	3071.6932	8.2463
5	3021.3099	18.8524
6	1637.5680	154.9839
7	1488.0402	8.2178
8	1481.5459	10.3812
9	1403.8862	38.2732
10	1376.5186	244.9253
11	1322.2294	40.7817
12	1037.6401	0.2203
13	1021.8841	24.1543
14	987.7281	16.0086
15	732.4758	7.6178
16	612.9309	5.3280
17	518.0586	3.7582
18	427.2914	1.1822
19	378.2104	1.9831
20	337.2837	157.3861
21	31.7943	0.0078

Table S3. Cartesian coordinates (in Å) of the **aC** isomer as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.476229	0.000000
S	-0.340048	-1.273389	0.000000
N	-0.955276	1.305784	0.000000
H	-0.610233	2.264863	0.000000
C	1.476471	0.781276	0.000000
H	1.957092	0.350525	0.879350
H	1.957092	0.350525	-0.879350
H	1.640109	1.857275	0.000000
H	-1.675181	-1.134480	0.000000

Table S4. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aC** isomer as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3455.0698	1.5990
2	3118.9390	11.7739
3	3095.0491	4.1593
4	3035.0141	5.5051
5	2686.1431	1.3681
6	1680.8891	149.3842
7	1482.4249	22.6937
8	1472.7704	11.5825
9	1406.1832	14.0646
10	1299.3493	69.2782
11	1070.3380	52.2207
12	1063.9286	5.1831
13	996.4669	53.5051
14	851.8389	13.7590
15	828.7418	53.9772
16	636.6275	49.1557
17	501.3818	0.0755
18	449.8539	6.9078
19	339.8745	18.0836
20	325.2994	4.3443
21	97.8543	0.4673

Table S5. Cartesian coordinates (in Å) of the **aT** isomer as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.479605	0.000000
S	-0.502335	-1.232590	0.000000
N	-0.937876	1.328045	0.000000
H	-0.578649	2.280874	0.000000
C	1.480764	0.759055	0.000000
H	1.954708	0.323926	0.880650
H	1.954708	0.323926	-0.880650
H	1.659551	1.833381	0.000000
H	0.727594	-1.768943	0.000000

Table S6. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aT** isomer as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3469.6854	2.8136
2	3112.0676	14.5335
3	3095.9082	4.6867
4	3032.6044	6.8796
5	2687.7799	1.1906
6	1682.4660	166.0005
7	1482.8715	17.6961
8	1475.2210	11.4980
9	1403.4970	12.1004
10	1300.0307	61.0301
11	1065.6938	65.2176
12	1064.8786	5.2834
13	1011.4560	50.2947
14	896.7393	12.7192
15	831.9264	58.2396
16	638.0009	48.3015
17	506.9022	0.9946
18	433.6786	3.0692
19	340.0875	0.7125
20	245.1554	4.9926
21	164.2887	0.0976

Table S7. Cartesian coordinates (in Å) of the **sC** isomer as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.500945	0.000000
S	-0.302135	-1.274433	0.000000
N	-0.862430	1.423716	0.000000
H	-1.823152	1.089375	0.000000
C	1.470814	0.812772	0.000000
H	1.953845	0.385691	0.879943
H	1.953845	0.385691	-0.879943
H	1.604685	1.890715	0.000000
H	-1.642929	-1.208857	0.000000

Table S8. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **sC** isomer as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3481.3760	5.0620
2	3143.3598	4.6651
3	3093.4306	5.4264
4	3038.7526	5.4430
5	2679.1971	1.1441
6	1693.5949	134.0084
7	1478.6504	12.1570
8	1473.9888	11.8748
9	1405.6028	13.7739
10	1266.4270	233.9674
11	1078.9905	25.8644
12	1069.5359	3.9606
13	996.4691	9.0763
14	867.4159	12.8501
15	855.4898	54.3986
16	616.2180	42.3314
17	493.4231	2.5792
18	442.8079	13.4119
19	328.2438	2.8180
20	278.6584	8.0265
21	105.6295	1.3377

Table S9. Cartesian coordinates (in Å) of the **sT** isomer as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.499620	0.000000
S	-0.446990	-1.241737	0.000000
N	-0.871789	1.414649	0.000000
H	-1.829281	1.067159	0.000000
C	1.466086	0.824168	0.000000
H	1.953124	0.404140	0.881033
H	1.953124	0.404140	-0.881033
H	1.588921	1.904043	0.000000
H	0.791964	-1.756953	0.000000

Table S10. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **sT** isomer as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3466.4948	4.6467
2	3136.9600	6.4429
3	3093.3999	6.1605
4	3036.9686	6.3858
5	2684.1467	0.3138
6	1690.3755	139.1256
7	1481.1225	11.9684
8	1474.5135	8.1855
9	1403.8575	12.3466
10	1283.2580	229.8708
11	1076.7845	23.9269
12	1070.8868	4.5367
13	995.9720	7.2725
14	875.5497	7.7667
15	870.3081	49.8493
16	621.8946	33.4617
17	497.0180	3.8761
18	421.1523	14.4722
19	334.5616	0.9257
20	203.5083	16.5083
21	170.3821	0.0001

Table S11. Cartesian coordinates (in Å) of the **Tn–aC** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.399719	0.000000
S	-0.013254	-1.326561	0.000000
N	-1.239201	0.791533	0.000000
H	-1.488376	-0.573544	0.000000
H	-1.470280	1.783067	0.000000
C	1.210035	1.272362	0.000000
H	1.820856	1.057319	0.876566
H	1.820856	1.057319	-0.876566
H	0.943203	2.327593	0.000000

Table S12. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **Tn–aC** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3458.6054	1.5593
2	3121.1513	9.7801
3	3106.6354	1.2513
4	3044.2682	3.6541
5	1786.7239	2.4690
6	1571.9781	183.6614
7	1474.1668	56.4747
8	1471.1220	12.1202
9	1408.1544	20.3981
10	1321.6629	97.2727
11	1093.8859	52.5734
12	1050.8489	1.8023
13	978.3773	36.0427
14	909.3064	2.3538
15	705.8478	27.1584
16	620.8459	82.0744
17	600.3002	8.6235
18	462.9283	15.1006
19	334.2143	1.9633
20	105.8606	0.6240
21	i 1709.4957	1017.7205

Table S13. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **Tn–aC** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.06183	-2.00567
2	-0.06183	-1.99732
3	-0.06173	-1.89747
4	-0.06144	-1.79779
5	-0.06094	-1.69820
6	-0.06020	-1.59862
7	-0.05914	-1.49894
8	-0.05766	-1.39915
9	-0.05570	-1.29930
10	-0.05317	-1.19941
11	-0.05001	-1.09949
12	-0.04619	-0.99956
13	-0.04169	-0.89962
14	-0.03652	-0.79968
15	-0.03076	-0.69975
16	-0.02458	-0.59981
17	-0.01828	-0.49986
18	-0.01231	-0.39990
19	-0.00714	-0.29993
20	-0.00321	-0.19996
21	-0.00080	-0.10000
22	0.00000	0.00000
23	-0.00075	0.10000
24	-0.00281	0.19996
25	-0.00586	0.29992
26	-0.00951	0.39987
27	-0.01340	0.49980
28	-0.01725	0.59972
29	-0.02090	0.69964
30	-0.02429	0.79958
31	-0.02741	0.89955
32	-0.03023	0.99952
33	-0.03275	1.09950
34	-0.03499	1.19948
35	-0.03694	1.29945
36	-0.03861	1.39942
37	-0.04002	1.49939
38	-0.04117	1.59936
39	-0.04208	1.69932
40	-0.04276	1.79927
41	-0.04322	1.89921
42	-0.04349	1.99908

Table S14. Cartesian coordinates (in Å) of the **aC–sC** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.529086	0.000000
S	-0.324365	-1.298204	0.000000
N	-0.879365	1.374982	0.000000
H	-1.567603	2.084164	0.000000
C	1.496028	0.768415	0.000000
H	1.696360	1.836364	0.000000
H	1.949945	0.309975	0.879571
H	1.949945	0.309975	-0.879571
H	-1.659417	-1.179089	0.000000

Table S15. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aC–sC** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3916.1249	418.0402
2	3138.2645	10.2968
3	3096.7924	4.6549
4	3036.7417	4.6778
5	2696.4242	0.3645
6	1831.7974	382.4181
7	1475.5256	12.1439
8	1473.8936	12.5558
9	1388.9953	13.1302
10	1105.1410	72.7234
11	1027.9604	0.0764
12	983.1959	42.2648
13	810.7488	19.4350
14	573.0857	80.5509
15	497.4386	0.0006
16	411.5041	25.9257
17	407.3064	101.2074
18	325.5971	2.6200
19	316.5144	15.3248
20	31.5039	1.3730
21	i 1061.0271	190.2959

Table S16. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **aC–sC** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.03667	-1.89740
2	-0.03650	-1.79771
3	-0.03617	-1.69784
4	-0.03567	-1.59794
5	-0.03499	-1.49806
6	-0.03413	-1.39822
7	-0.03306	-1.29844
8	-0.03173	-1.19867
9	-0.03009	-1.09888
10	-0.02808	-0.99905
11	-0.02566	-0.89919
12	-0.02280	-0.79932
13	-0.01953	-0.69945
14	-0.01591	-0.59957
15	-0.01212	-0.49966
16	-0.00838	-0.39974
17	-0.00501	-0.29980
18	-0.00232	-0.19987
19	-0.00059	-0.09994
20	0.00000	0.00000
21	-0.00059	0.09994
22	-0.00227	0.19986
23	-0.00484	0.29980
24	-0.00804	0.39973
25	-0.01156	0.49965
26	-0.01512	0.59955
27	-0.01851	0.69944
28	-0.02159	0.79930
29	-0.02429	0.89915
30	-0.02662	0.99898
31	-0.02862	1.09882
32	-0.03032	1.19868
33	-0.03178	1.29856
34	-0.03301	1.39847
35	-0.03403	1.49839
36	-0.03486	1.59832
37	-0.03550	1.69826
38	-0.03594	1.79820
39	-0.03620	1.89809

Table S17. Cartesian coordinates (in Å) of the **aT–sT** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.000000	0.526379	0.000000
S	-0.478441	-1.257524	0.000000
N	-0.874387	1.378837	0.000000
H	-1.555235	2.095033	0.000000
C	1.497109	0.761759	0.000000
H	1.952410	0.307582	0.880723
H	1.952410	0.307582	-0.880723
H	1.693900	1.830980	0.000000
H	0.749627	-1.801473	0.000000

Table S18. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aT–sT** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3917.1777	426.1651
2	3132.0206	12.9326
3	3098.7171	5.4092
4	3036.0112	6.1218
5	2673.8088	2.7127
6	1824.0915	393.3831
7	1478.6402	11.8557
8	1474.7083	8.9388
9	1387.0935	12.0539
10	1108.0083	78.6323
11	1028.0540	0.1060
12	990.7994	25.1901
13	811.5325	16.4502
14	579.1038	70.3325
15	504.9365	0.1058
16	423.4183	111.9626
17	394.5879	24.3527
18	335.3085	1.3952
19	281.1091	4.5880
20	141.0180	0.0924
21	i 1059.1018	196.1595

Table S19. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **aT–sT** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.03749	-1.79671
2	-0.03731	-1.69831
3	-0.03686	-1.59850
4	-0.03614	-1.49859
5	-0.03513	-1.39866
6	-0.03384	-1.29872
7	-0.03226	-1.19879
8	-0.03037	-1.09887
9	-0.02817	-0.99897
10	-0.02564	-0.89910
11	-0.02275	-0.79926
12	-0.01949	-0.69941
13	-0.01591	-0.59955
14	-0.01213	-0.49965
15	-0.00841	-0.39974
16	-0.00503	-0.29980
17	-0.00233	-0.19987
18	-0.00060	-0.09994
19	0.00000	0.00000
20	-0.00059	0.09994
21	-0.00227	0.19986
22	-0.00483	0.29980
23	-0.00799	0.39973
24	-0.01144	0.49964
25	-0.01488	0.59953
26	-0.01812	0.69940
27	-0.02104	0.79924
28	-0.02361	0.89908
29	-0.02584	0.99892
30	-0.02777	1.09878
31	-0.02945	1.19868
32	-0.03090	1.29859
33	-0.03213	1.39853
34	-0.03314	1.49848
35	-0.03395	1.59843
36	-0.03456	1.69838
37	-0.03495	1.79827
38	-0.03514	1.89762

Table S20. Cartesian coordinates (in Å) of the **aC–aT–1** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	-0.462740	0.186761	-0.002754
S	1.344097	-0.096880	-0.082413
N	-0.871789	1.377816	-0.000971
H	-1.893059	1.414874	0.026486
C	-1.295537	-1.065186	0.006943
H	-1.070818	-1.670823	-0.871831
H	-1.049537	-1.675024	0.877140
H	-2.359796	-0.829687	0.020106
H	1.519847	-0.063414	1.248374

Table S21. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aC–aT–1** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3417.5437	2.7100
2	3106.4106	16.8175
3	3094.3163	3.9879
4	3029.1417	9.1358
5	2677.2106	0.2730
6	1699.3629	113.0216
7	1475.8492	21.3621
8	1467.1849	12.0581
9	1406.2600	14.6614
10	1289.6114	79.1920
11	1081.7431	4.9567
12	1060.6450	50.3230
13	961.2260	33.8080
14	945.6359	46.0589
15	807.2731	8.8102
16	615.6612	35.9479
17	450.3261	2.2303
18	442.7899	4.2036
19	337.4697	1.3791
20	190.5629	0.1046
21	i 314.5118	12.2108

Table S22. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **aC–aT–1** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.01130	-2.79872
2	-0.01124	-2.69882
3	-0.01110	-2.59887
4	-0.01089	-2.49892
5	-0.01060	-2.39896
6	-0.01026	-2.29901
7	-0.00985	-2.19905
8	-0.00939	-2.09909
9	-0.00888	-1.99913
10	-0.00833	-1.89917
11	-0.00775	-1.79921
12	-0.00714	-1.69925
13	-0.00652	-1.59929
14	-0.00589	-1.49933
15	-0.00527	-1.39937
16	-0.00464	-1.29941
17	-0.00404	-1.19945
18	-0.00346	-1.09949
19	-0.00290	-0.99954
20	-0.00238	-0.89958
21	-0.00191	-0.79962
22	-0.00147	-0.69967
23	-0.00109	-0.59971
24	-0.00076	-0.49976
25	-0.00049	-0.39981
26	-0.00028	-0.29986
27	-0.00012	-0.19991
28	-0.00003	-0.09997
29	0.00000	0.00000
30	-0.00003	0.09997
31	-0.00012	0.19991
32	-0.00027	0.29986
33	-0.00048	0.39981
34	-0.00073	0.49977
35	-0.00104	0.59972
36	-0.00139	0.69968
37	-0.00179	0.79963
38	-0.00222	0.89959
39	-0.00267	0.99955
40	-0.00315	1.09951
41	-0.00365	1.19947
42	-0.00416	1.29943
43	-0.00467	1.39939
44	-0.00518	1.49935

45	-0.00568	1.59931
46	-0.00617	1.69927
47	-0.00664	1.79923
48	-0.00707	1.89919
49	-0.00748	1.99914
50	-0.00786	2.09910
51	-0.00820	2.19904
52	-0.00850	2.29898
53	-0.00875	2.39891
54	-0.00897	2.49882
55	-0.00914	2.59868
56	-0.00927	2.69843
57	-0.00937	2.79799
58	-0.00945	2.89740
59	-0.00951	2.99697
60	-0.00955	3.09680
61	-0.00958	3.19675
62	-0.00960	3.29673

Table S23. Cartesian coordinates (in Å) of the **aC–aT–2** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.462740	0.186761	-0.002754
S	-1.344097	-0.096880	-0.082413
N	0.871789	1.377816	-0.000971
H	1.893059	1.414874	0.026486
C	1.295537	-1.065186	0.006943
H	1.049537	-1.675023	0.877140
H	1.070818	-1.670823	-0.871831
H	2.359796	-0.829687	0.020106
H	-1.519847	-0.063414	1.248374

Table S24. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **aC–aT–2** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3417.5437	2.7100
2	3106.4114	16.8175
3	3094.3190	3.9876
4	3029.1432	9.1361
5	2677.2106	0.2730
6	1699.3629	113.0217
7	1475.8488	21.3620
8	1467.1849	12.0581
9	1406.2596	14.6615
10	1289.6114	79.1920
11	1081.7429	4.9566
12	1060.6447	50.3232
13	961.2260	33.8079
14	945.6359	46.0588
15	807.2729	8.8102
16	615.6611	35.9479
17	450.3258	2.2303
18	442.7899	4.2036
19	337.4696	1.3791
20	190.5592	0.1046
21	i 314.5118	12.2108

Table S25. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **aC–aT–2** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.01130	-2.79872
2	-0.01124	-2.69882
3	-0.01110	-2.59887
4	-0.01089	-2.49892
5	-0.01060	-2.39896
6	-0.01026	-2.29901
7	-0.00985	-2.19905
8	-0.00939	-2.09909
9	-0.00888	-1.99913
10	-0.00833	-1.89917
11	-0.00775	-1.79921
12	-0.00714	-1.69925
13	-0.00652	-1.59929
14	-0.00589	-1.49933

15	-0.00527	-1.39937
16	-0.00464	-1.29941
17	-0.00404	-1.19945
18	-0.00346	-1.09949
19	-0.00290	-0.99954
20	-0.00238	-0.89958
21	-0.00191	-0.79962
22	-0.00147	-0.69967
23	-0.00109	-0.59971
24	-0.00076	-0.49976
25	-0.00049	-0.39981
26	-0.00028	-0.29986
27	-0.00012	-0.19991
28	-0.00003	-0.09997
29	0.00000	0.00000
30	-0.00003	0.09997
31	-0.00012	0.19991
32	-0.00027	0.29986
33	-0.00048	0.39981
34	-0.00073	0.49977
35	-0.00104	0.59972
36	-0.00139	0.69968
37	-0.00179	0.79963
38	-0.00222	0.89959
39	-0.00267	0.99955
40	-0.00315	1.09951
41	-0.00365	1.19947
42	-0.00416	1.29943
43	-0.00467	1.39939
44	-0.00518	1.49935
45	-0.00568	1.59931
46	-0.00617	1.69927
47	-0.00664	1.79923
48	-0.00707	1.89919
49	-0.00748	1.99914
50	-0.00786	2.09910
51	-0.00820	2.19904
52	-0.00850	2.29898
53	-0.00875	2.39891
54	-0.00897	2.49882
55	-0.00914	2.59868
56	-0.00927	2.69843
57	-0.00937	2.79799
58	-0.00945	2.89740
59	-0.00951	2.99697
60	-0.00955	3.09680
61	-0.00958	3.19675
62	-0.00960	3.29673

Table S26. Cartesian coordinates (in Å) of the **sC–sT–1** transition state as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	-0.485141	0.197122	-0.002898
S	1.325433	-0.173667	-0.082062
N	-0.941534	1.368774	0.002535
H	-0.206514	2.072046	-0.030442
C	-1.375223	-1.007065	0.010397
H	-1.179711	-1.626848	-0.865870
H	-1.162980	-1.624521	0.884239
H	-2.417779	-0.697906	0.019063
H	1.512975	-0.065859	1.243270

Table S27. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **sC–sT–1** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3481.8849	8.0624
2	3132.2536	10.0013
3	3091.2503	5.1258
4	3036.3809	4.1867
5	2676.7449	0.3486
6	1714.3638	98.2039
7	1473.3079	12.6672
8	1468.1598	11.7926
9	1406.8222	12.6509
10	1271.2975	219.6149
11	1082.5516	7.7944
12	1068.8798	24.4776
13	969.4112	20.1411
14	955.3992	18.6825
15	801.9698	42.3205
16	599.5039	31.3815
17	447.7564	1.8226
18	423.9754	9.9576
19	330.6039	0.5676
20	193.3952	0.4257
21	i 254.5597	12.7224

Table S28. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **sC–sT–1** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.00683	-2.69867
2	-0.00677	-2.59877
3	-0.00667	-2.49883
4	-0.00653	-2.39888
5	-0.00633	-2.29893
6	-0.00610	-2.19898
7	-0.00584	-2.09903
8	-0.00554	-1.99907
9	-0.00521	-1.89912
10	-0.00486	-1.79917
11	-0.00449	-1.69921
12	-0.00411	-1.59926
13	-0.00372	-1.49930
14	-0.00333	-1.39935
15	-0.00294	-1.29939
16	-0.00257	-1.19944
17	-0.00220	-1.09948
18	-0.00185	-0.99953
19	-0.00153	-0.89957
20	-0.00122	-0.79962
21	-0.00095	-0.69966
22	-0.00070	-0.59971
23	-0.00049	-0.49976
24	-0.00032	-0.39981
25	-0.00018	-0.29986
26	-0.00008	-0.19991
27	-0.00002	-0.09997
28	0.00000	0.00000
29	-0.00002	0.09997
30	-0.00008	0.19991
31	-0.00018	0.29986
32	-0.00032	0.39982
33	-0.00049	0.49977
34	-0.00070	0.59972
35	-0.00094	0.69968
36	-0.00121	0.79964
37	-0.00151	0.89960
38	-0.00183	0.99955
39	-0.00217	1.09951
40	-0.00252	1.19947
41	-0.00288	1.29943
42	-0.00324	1.39939
43	-0.00361	1.49935
44	-0.00397	1.59931

45	-0.00432	1.69927
46	-0.00466	1.79922
47	-0.00498	1.89918
48	-0.00528	1.99913
49	-0.00556	2.09908
50	-0.00582	2.19902
51	-0.00604	2.29896
52	-0.00624	2.39888
53	-0.00642	2.49878
54	-0.00656	2.59865
55	-0.00669	2.69848
56	-0.00679	2.79828
57	-0.00687	2.89805
58	-0.00694	2.99784
59	-0.00699	3.09769
60	-0.00703	3.19759
61	-0.00706	3.29754
62	-0.00707	3.39752

Table S29. Cartesian coordinates (in Å) of the **sC–sT–2** transition states as optimized at the B3LYP/6-311++G(3df,3pd) level of theory.

Atom	X	Y	Z
C	0.485141	0.197122	-0.002898
S	-1.325433	-0.173667	-0.082062
N	0.941534	1.368774	0.002535
H	0.206514	2.072046	-0.030442
C	1.375223	-1.007065	0.010397
H	1.162980	-1.624521	0.884239
H	1.179711	-1.626848	-0.865870
H	2.417779	-0.697906	0.019063
H	-1.512975	-0.065859	1.243270

Table S30. Unscaled harmonic vibrational frequencies (E_{harm}, in cm^{-1}) and absolute IR intensities (I, in km mol^{-1}) of the **sC–sT–2** transition state as calculated at the B3LYP/6-311+G(d,p) level of theory.

Mode number	E_{harm}	I
1	3481.8849	8.0624
2	3132.2536	10.0013
3	3091.2503	5.1258
4	3036.3809	4.1867
5	2676.7449	0.3486
6	1714.3638	98.2039
7	1473.3079	12.6672
8	1468.1598	11.7925
9	1406.8222	12.6509
10	1271.2975	219.6149
11	1082.5516	7.7944
12	1068.8798	24.4776
13	969.4112	20.1411
14	955.3992	18.6825
15	801.9698	42.3205
16	599.5039	31.3815
17	447.7564	1.8226
18	423.9754	9.9576
19	330.6039	0.5676
20	193.3952	0.4257
21	i 254.5597	12.7224

Table S31. Relative energies (ΔE, in hartree) for the minimum-energy path along the intrinsic reaction coordinate (IRC, in bohr) originating from the **sC–sT–2** transition state (IRC = 0) as calculated at the B3LYP/6-311++G(3df,3pd) level of theory.

	ΔE	IRC
1	-0.00683	-2.69867
2	-0.00677	-2.59877
3	-0.00667	-2.49883
4	-0.00653	-2.39888
5	-0.00633	-2.29893
6	-0.00610	-2.19898
7	-0.00584	-2.09903
8	-0.00554	-1.99907
9	-0.00521	-1.89912
10	-0.00486	-1.79917
11	-0.00449	-1.69921
12	-0.00411	-1.59926
13	-0.00372	-1.49930
14	-0.00333	-1.39935

15	-0.00294	-1.29939
16	-0.00257	-1.19944
17	-0.00220	-1.09948
18	-0.00185	-0.99953
19	-0.00153	-0.89957
20	-0.00122	-0.79962
21	-0.00095	-0.69966
22	-0.00070	-0.59971
23	-0.00049	-0.49976
24	-0.00032	-0.39981
25	-0.00018	-0.29986
26	-0.00008	-0.19991
27	-0.00002	-0.09997
28	0.00000	0.00000
29	-0.00002	0.09997
30	-0.00008	0.19991
31	-0.00018	0.29986
32	-0.00032	0.39982
33	-0.00049	0.49977
34	-0.00070	0.59972
35	-0.00094	0.69968
36	-0.00121	0.79964
37	-0.00151	0.89960
38	-0.00183	0.99955
39	-0.00217	1.09951
40	-0.00252	1.19947
41	-0.00288	1.29943
42	-0.00324	1.39939
43	-0.00361	1.49935
44	-0.00397	1.59931
45	-0.00432	1.69927
46	-0.00466	1.79922
47	-0.00498	1.89918
48	-0.00528	1.99913
49	-0.00556	2.09908
50	-0.00582	2.19902
51	-0.00604	2.29896
52	-0.00624	2.39888
53	-0.00642	2.49878
54	-0.00656	2.59865
55	-0.00669	2.69848
56	-0.00679	2.79828
57	-0.00687	2.89805
58	-0.00694	2.99784
59	-0.00699	3.09769
60	-0.00703	3.19759
61	-0.00706	3.29754
62	-0.00707	3.39752

Table S32. Cartesian coordinates (in Å) of the **Tn** tautomer as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	-0.277532	-0.060914	0.000000
S	1.370023	0.119162	0.000000
N	-0.872014	-1.269617	0.000000
H	-0.298082	-2.098419	0.000000
H	-1.874853	-1.372436	0.000000
C	-1.239175	1.105289	0.000000
H	-1.883474	1.065535	0.884940
H	-0.694315	2.044495	0.000000
H	-1.883474	1.065535	-0.884940

Table S33. Cartesian coordinates (in Å) of the **aC** isomer as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.483375	0.000000
S	-0.335705	-1.282054	0.000000
N	-0.967297	1.299720	0.000000
H	-0.624559	2.262682	0.000000
C	1.478816	0.795602	0.000000
H	1.963392	0.367560	0.881777
H	1.963392	0.367560	-0.881777
H	1.637922	1.875413	0.000000
H	-1.670680	-1.132257	0.000000

Table S34. Cartesian coordinates (in Å) of the **aT** isomer as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.486527	0.000000
S	-0.498333	-1.240743	0.000000
N	-0.949868	1.322251	0.000000
H	-0.593023	2.278935	0.000000
C	1.483583	0.773315	0.000000
H	1.961966	0.341596	0.883197
H	1.961966	0.341596	-0.883197
H	1.656830	1.851640	0.000000
H	0.733157	-1.776689	0.000000

Table S35. Cartesian coordinates (in Å) of the **sC** isomer as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.507464	0.000000
S	-0.302955	-1.284087	0.000000
N	-0.864041	1.429016	0.000000
H	-1.823519	1.083678	0.000000
C	1.473915	0.821169	0.000000
H	1.960312	0.397230	0.882823
H	1.960312	0.397230	-0.882823
H	1.599383	1.902762	0.000000
H	-1.644411	-1.210424	0.000000

Table S36. Cartesian coordinates (in Å) of the **sT** isomer as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.506587	0.000000
S	-0.449644	-1.250654	0.000000
N	-0.871071	1.422248	0.000000
H	-1.828002	1.065912	0.000000
C	1.470395	0.829694	0.000000
H	1.960184	0.412154	0.883943
H	1.960184	0.412154	-0.883943
H	1.586484	1.912879	0.000000
H	0.790576	-1.766051	0.000000

Table S37. Cartesian coordinates (in Å) of the **Tn–aC** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.404923	0.000000
S	-0.019184	-1.332313	0.000000
N	-1.238284	0.798980	0.000000
H	-1.490915	-0.574639	0.000000
H	-1.463923	1.794322	0.000000
C	1.218737	1.272575	0.000000
H	1.829284	1.053449	0.878925
H	1.829284	1.053449	-0.878925
H	0.958785	2.332578	0.000000

Table S38. Cartesian coordinates (in Å) of the **aC–sC** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.541427	0.000000
S	-0.321659	-1.313520	0.000000
N	-0.887339	1.377355	0.000000
H	-1.578234	2.085424	0.000000
C	1.498224	0.784742	0.000000
H	1.693068	1.856762	0.000000
H	1.955090	0.328096	0.882190
H	1.955090	0.328096	-0.882190
H	-1.656440	-1.180561	0.000000

Table S39. Cartesian coordinates (in Å) of the **aT–sT** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.000000	0.537329	0.000000
S	-0.475570	-1.270127	0.000000
N	-0.883058	1.379514	0.000000
H	-1.566681	2.094586	0.000000
C	1.499728	0.777381	0.000000
H	1.958607	0.325610	0.883343
H	1.958607	0.325610	-0.883343
H	1.689698	1.850793	0.000000
H	0.751931	-1.819423	0.000000

Table S40. Cartesian coordinates (in Å) of the **aC–aT–1** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	-0.468378	0.189811	-0.002012
S	1.348572	-0.098188	-0.082500
N	-0.872073	1.384431	-0.001167
H	-1.896733	1.411381	0.026264
C	-1.298973	-1.068842	0.006712
H	-1.072067	-1.675655	-0.873868
H	-1.055000	-1.680118	0.879804
H	-2.367199	-0.836418	0.017822
H	1.522469	-0.065011	1.249940

Table S41. Cartesian coordinates (in Å) of the **aC–aT–2** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.468378	0.189811	-0.002012
S	-1.348572	-0.098188	-0.082500
N	0.872073	1.384431	-0.001167
H	1.896733	1.411381	0.026264
C	1.298973	-1.068842	0.006712
H	1.055000	-1.680118	0.879803
H	1.072068	-1.675655	-0.873869
H	2.367199	-0.836419	0.017823
H	-1.522469	-0.065011	1.249940

Table S42. Cartesian coordinates (in Å) of the **sC–sT–1** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	-0.489970	0.198587	-0.002294
S	1.332517	-0.176179	-0.081667
N	-0.947908	1.370907	0.000240
H	-0.205007	2.069405	-0.037837
C	-1.380465	-1.010179	0.012235
H	-1.184045	-1.634381	-0.863880
H	-1.175072	-1.625989	0.892040
H	-2.423829	-0.694167	0.015137
H	1.525644	-0.022800	1.239887

Table S43. Cartesian coordinates (in Å) of the **sC–sT–2** transition state as optimized by the CBS-QB3 method.

Atom	X	Y	Z
C	0.489970	0.198587	-0.002294
S	-1.332517	-0.176179	-0.081667
N	0.947908	1.370907	0.000240
H	0.205007	2.069405	-0.037837
C	1.380465	-1.010179	0.012235
H	1.175071	-1.625989	0.892040
H	1.184045	-1.634381	-0.863880
H	2.423829	-0.694167	0.015137
H	-1.525644	-0.022799	1.239887

Table S44. Relative zero-point corrected energies (ΔE_{ZPE})[a] of the thioacetamide isomers (minima) and the first-order transition states (TSs) computed by the CBS-QB3 method, as well as conformationally-relevant dihedral angles (φ_1 and φ_2).[b]

Structures	φ_1	φ_2	ΔE_{ZPE}	$\Delta\Delta E^{\#}(\rightarrow)$	$\Delta\Delta E^{\#}(\leftarrow)$
minima					
Tn	–	–	–37.6	–	–
aC	180.0	0.0	1.7	–	–
aT	180.0	180.0	6.1	–	–
sC	0.0	0.0	1.1	–	–
sT	0.0	180.0	0.0	–	–
TSs					
Tn–aC	180.0	0.0	111.1	148.8	109.4
aC–sC	180.0	0.0	98.6	96.9	97.5
aT–sT	180.0	–180.0	100.2	94.2	100.2
aC–aT–1	178.8	88.7	27.3	25.6	21.2
aC–aT–2	–178.8	–88.7	27.3	25.6	21.2
sC–sT–1	–0.5	83.3	15.7	14.6	15.7
sC–sT–2	0.5	–83.3	15.7	14.6	15.7

[a] All energies in kJ mol^{-1}, the energy of isomer **sT** was chosen as the relative zero.

[b] In degrees, φ_1 = H–N=C–S, φ_2 = H–S–C=N, see also Figure 1.

Table S45. Cartesian coordinates (in Å) of the **Tn** tautomer as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.284491	0.000000
S	-0.170425	-1.361902	0.000000
N	-1.056858	1.117483	0.000000
H	-1.987275	0.731314	0.000000
H	-0.948017	2.118744	0.000000
C	1.340122	0.984014	0.000000
H	1.435928	1.625629	0.884316
H	2.147511	0.255699	0.000000
H	1.435928	1.625629	-0.884316

Table S46. Cartesian coordinates (in Å) of the **aC** isomer as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.480764	0.000000
S	-0.339336	-1.277191	0.000000
N	-0.962649	1.305814	0.000000
H	-0.609061	2.265340	0.000000
C	1.479975	0.784788	0.000000
H	1.964454	0.352804	0.881761
H	1.964454	0.352804	-0.881761
H	1.645785	1.864848	0.000000
H	-1.677565	-1.134746	0.000000

Table S47. Cartesian coordinates (in Å) of the **aT** isomer as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.484742	0.000000
S	-0.505229	-1.235283	0.000000
N	-0.940844	1.333673	0.000000
H	-0.568638	2.284991	0.000000
C	1.485716	0.756307	0.000000
H	1.961858	0.317942	0.883104
H	1.961858	0.317942	-0.883104
H	1.671814	1.833805	0.000000
H	0.728384	-1.772156	0.000000

Table S48. Cartesian coordinates (in Å) of the **sC** isomer as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.504965	0.000000
S	-0.305771	-1.278389	0.000000
N	-0.860554	1.432427	0.000000
H	-1.822118	1.092128	0.000000
C	1.475851	0.810373	0.000000
H	1.960235	0.380268	0.882649
H	1.960235	0.380268	-0.882649
H	1.612792	1.892051	0.000000
H	-1.650045	-1.209502	0.000000

Table S49. Cartesian coordinates (in Å) of the **sT** isomer as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.504520	0.000000
S	-0.451613	-1.244590	0.000000
N	-0.869283	1.424776	0.000000
H	-1.827168	1.070059	0.000000
C	1.471777	0.819507	0.000000
H	1.959618	0.395465	0.883697
H	1.959618	0.395465	-0.883697
H	1.600070	1.902860	0.000000
H	0.787983	-1.768014	0.000000

Table S50. Cartesian coordinates (in Å) of the **Tn–aC** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.403298	0.000000
S	-0.015309	-1.330644	0.000000
N	-1.241004	0.791698	0.000000
H	-1.480505	-0.578951	0.000000
H	-1.469696	1.785971	0.000000
C	1.213424	1.276917	0.000000
H	1.827135	1.061645	0.879520
H	1.827135	1.061645	-0.879520
H	0.947355	2.336828	0.000000

Table S51. Cartesian coordinates (in Å) of the **aC–sC** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.540205	0.000000
S	-0.327101	-1.306229	0.000000
N	-0.880198	1.382048	0.000000
H	-1.562947	2.094103	0.000000
C	1.500837	0.769823	0.000000
H	1.710384	1.840457	0.000000
H	1.953879	0.306095	0.882154
H	1.953879	0.306095	-0.882154
H	-1.665218	-1.181591	0.000000

Table S52. Cartesian coordinates (in Å) of the **aT–sT** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	0.000000	0.537161	0.000000
S	-0.484106	-1.263544	0.000000
N	-0.871650	1.389267	0.000000
H	-1.543565	2.111540	0.000000
C	1.503217	0.757727	0.000000
H	1.956895	0.297265	0.883300
H	1.956895	0.297265	-0.883300
H	1.711997	1.829095	0.000000
H	0.745716	-1.812650	0.000000

Table S53. Cartesian coordinates (in Å) of the **aC–aT–1** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	-0.464627	0.188443	-0.003571
S	1.345778	-0.098237	-0.082553
N	-0.870939	1.384485	-0.000992
H	-1.895864	1.410645	0.028137
C	-1.297448	-1.067714	0.007142
H	-1.074417	-1.676792	-0.874817
H	-1.051236	-1.681525	0.879783
H	-2.366313	-0.832978	0.021979
H	1.524409	-0.063330	1.251279

Table S54. Cartesian coordinates (in Å) of the **aC–aT–2** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	0.464627	0.188443	-0.003571
S	-1.345778	-0.098237	-0.082553
N	0.870939	1.384485	-0.000992
H	1.895864	1.410645	0.028137
C	1.297448	-1.067714	0.007142
H	1.051235	-1.681525	0.879782
H	1.074417	-1.676792	-0.874818
H	2.366313	-0.832978	0.021980
H	-1.524409	-0.063330	1.251279

Table S55. Cartesian coordinates (in Å) of the **sC–sT–1** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	-0.486954	0.198362	-0.003709
S	1.328981	-0.172686	-0.082164
N	-0.948537	1.371346	0.002686
H	-0.207635	2.072605	-0.032191
C	-1.375236	-1.012013	0.010835
H	-1.180203	-1.633658	-0.869136
H	-1.160597	-1.632380	0.887055
H	-2.422136	-0.702919	0.021688
H	1.519779	-0.058191	1.245647

Table S56. Cartesian coordinates (in Å) of the **sC–sT–2** transition state as optimized by the G4 method.

Atom	X	Y	Z
C	0.486954	0.198362	-0.003709
S	-1.328981	-0.172686	-0.082164
N	0.948537	1.371346	0.002686
H	0.207635	2.072605	-0.032191
C	1.375236	-1.012013	0.010835
H	1.160597	-1.632380	0.887055
H	1.180203	-1.633658	-0.869136
H	2.422136	-0.702919	0.021688
H	-1.519779	-0.058191	1.245647

Table S57. Relative zero-point corrected energies (ΔE_{ZPE})[a] of the thioacetamide isomers (minima) and the first-order transition states (TSs) computed by the G4 method, as well as conformationally-relevant dihedral angles (φ_1 and φ_2).[b]

Structures	φ_1	φ_2	ΔE_{ZPE}	$\Delta\Delta E^{\#}(\rightarrow)$	$\Delta\Delta E^{\#}(\leftarrow)$
minima					
Tn	–	–	–36.6	–	–
aC	180.0	0.0	1.3	–	–
aT	180.0	180.0	5.9	–	–
sC	0.0	0.0	1.0	–	–
sT	0.0	180.0	0.0	–	–
TSs					
Tn–aC	180.0	0.0	111.7	148.2	110.4
aC–sC	180.0	0.0	101.5	100.2	100.5
aT–sT	180.0	–180.0	103.1	97.2	103.1
aC–aT–1	179.0	88.5	27.1	25.9	21.2
aC–aT–2	–179.0	–88.5	27.1	25.9	21.2
sC–sT–1	–0.5	84.8	15.7	14.7	15.7
sC–sT–2	0.5	–84.8	15.7	14.7	15.7

[a] All energies in kJ mol^{-1}, the energy of isomer **sT** was chosen as the relative zero.

[b] In degrees, φ_1 = H–N=C–S, φ_2 = H–S–C=N, see also Figure 1.