Electronic Supplementary Information

Half-Sandwich Complexes of Rhodium Containing Cysteine-derived ligands

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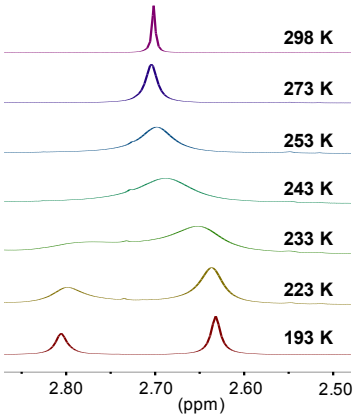
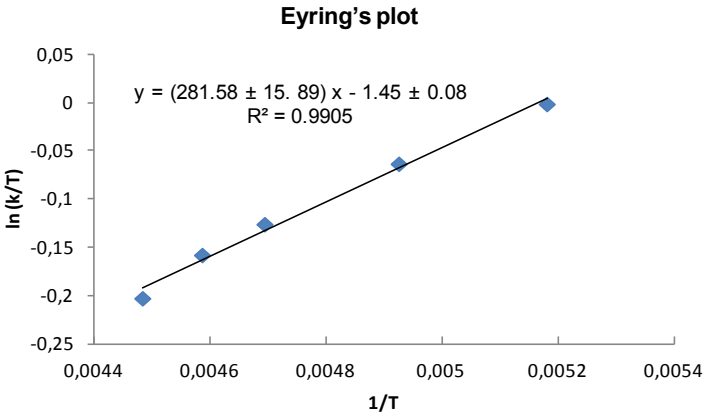
1- Kinetic studies for the epimerization of complex 9

[**9**] = 24.06 mM; solvent = CD_3OD

T (K)	k (s^{-1})
193	192,8292
203	190,6314
213	187,8786
218	186,2358
223	182,1510



ln (k/T)	1/T
-0,000885366	0,005181347
-0,062864258	0,004926108
-0,125496156	0,004694836
-0,157481450	0,004587156
-0,202335758	0,004484305



$\Delta G^{\neq}$ = 12.43 ± 1.62 kcal·mol^{-1}

$\Delta H^{\neq}$ = – 0.56 ± 0.03 kcal·mol^{-1}

$\Delta S^{\neq}$ = – 44.3 ± 5.6 cal·mol^{-1}·K^{-1}

2- Metallacycles characterization for complexes 6Sb, 7Sb and 9

Table S1. Ring puckering parameters characterizing the five- and six-membered metallacycles, according to Cremer and Pople.[1]

Rh-O(1)-C(11)-C(12)-N

	6Sb	**7Sb-A**	**7Sb-B**	**9**
q (Å)	0.573(5)	0.53(2)	0.527(19)	0.513(5)
φ (º)	153.3(5)	150(2)	152(2)	147.1(5)
conformation	$^5E/^5T_1$	$^5E/^5T_1$	$^5E/^5T_1$	^5E

Rh-S-C(13)-C(12)-N

	6Sb	**7Sb-A**	**7Sb-B**	**9**
q (Å)	0.634(4)	0.61(2)	0.62(2)	0.662(4)
φ (º)	-42.9(3)º	-36(2)	-43.0(18)	-34.0(4)
conformation	E_5	E_5	E_5	E_5

Rh-S-C(13)-C(12)-C(11)-O(1)

	6Sb	**7Sb-A**	**7Sb-B**	**9**
q (Å)	1.263(3)	1.244(18)	1.256(15)	1.248(3)
φ (º)	-169.2(2)	-172.5(10)	-169.7(10)	-173.8(2)
θ (º)	102.6(2)	100.4(10)	102.4(9)	101.4(2)
conformation	$B_{4,1}$	$B_{4,1}$	$B_{4,1}$	$B_{4,1}$

(1) D. Cremer and J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354-1358.

3- Hydrogen bond interactions in 6Sb and 7Sb

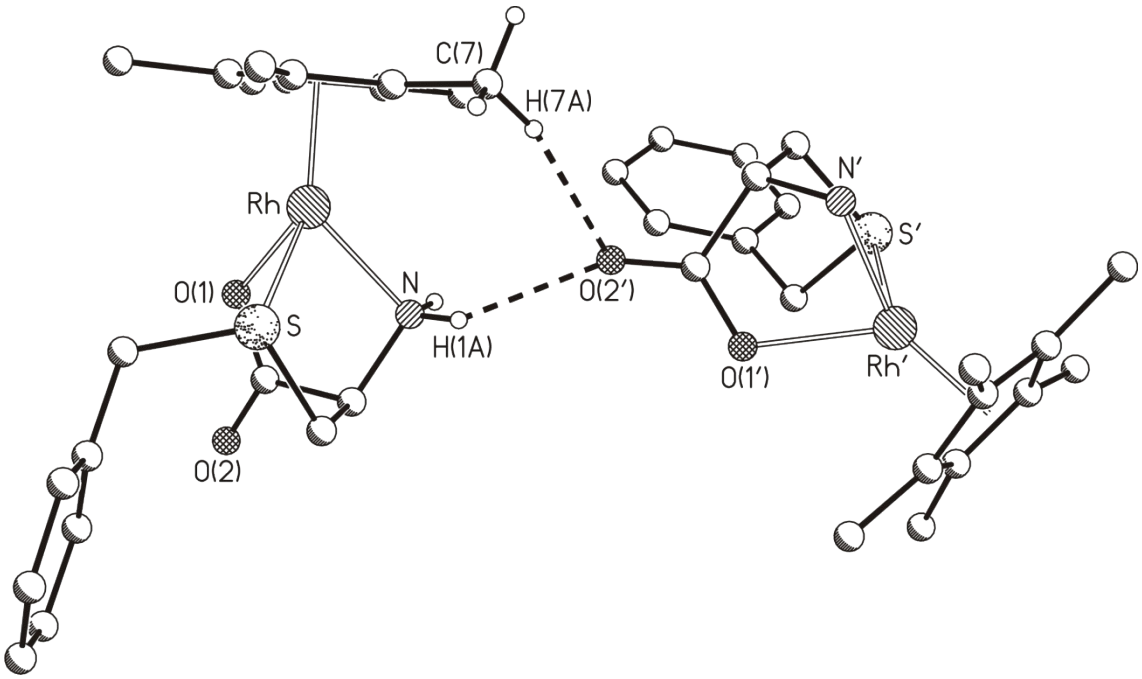


Figure S1. H-bonds of **6Sb** complex

Table S2. Complex **6Sb**. Hydrogen bonds. Geometrical parameters (Å, °)

	D-H	D···A	H···A	D-H···A
C(7)-H(7A)···O(2')	0.98	3.462(7)	2.50	166.5
N-H(1A)··· O(2')	0.87	2.939(6)	2.32	127.1

Symmetry operation: 1-*x*, *y*-1/2, 1/2-*z*.

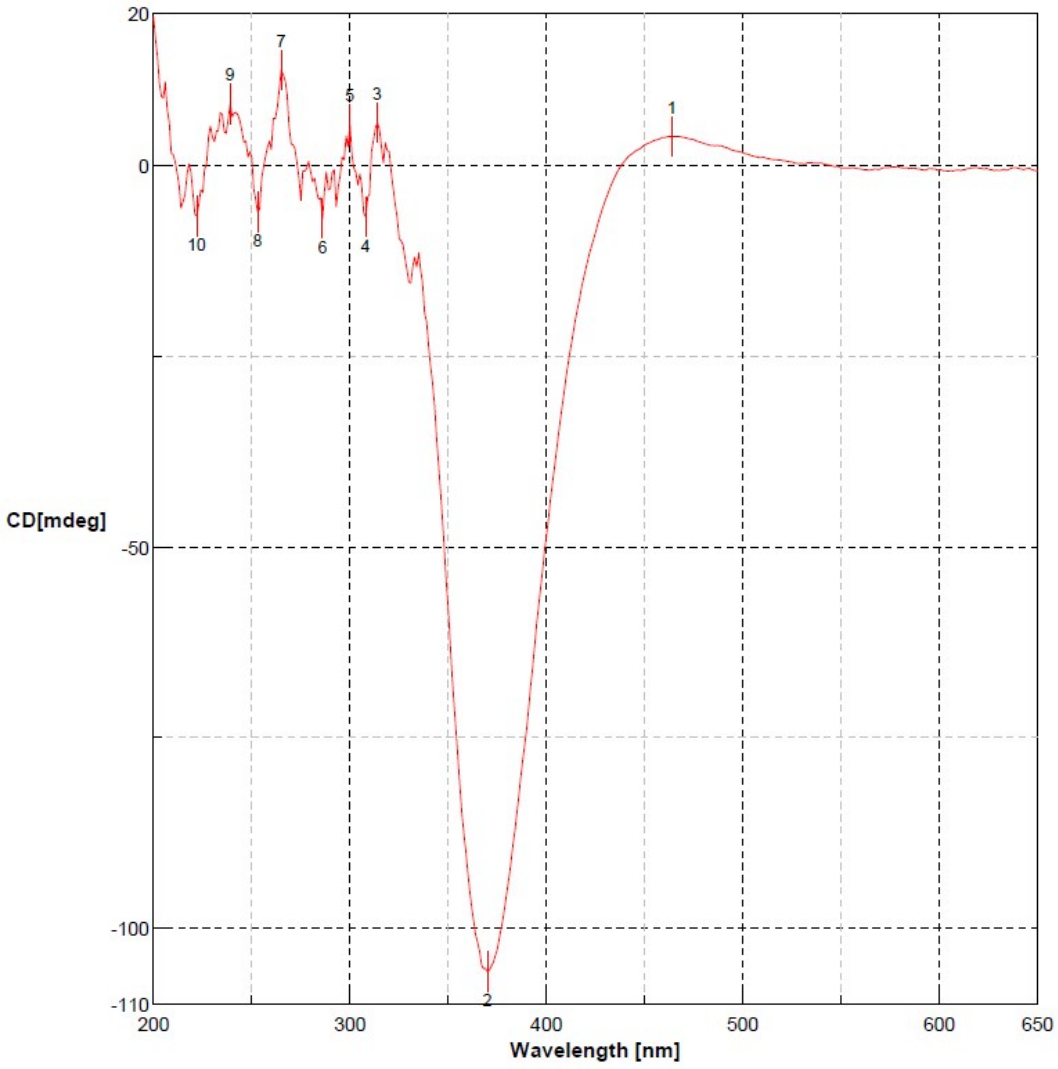
Table S3. Complex **7Sb**. Hydrogen bonds. Geometrical parameters (Å, °)

	D-H	D···A	H···A	D-H···A
N(1)-H(1B)···O(52')	0.910(14)	2.80(3)	1.907(16)	168.8(10)
C(21)-H(21C)···O(51')	0.98(2)	3.54(3)	2.667(16)	148.6(15)
N(51)-H(51B)···O(2')	0.91(2)	2.81(3)	1.900(17)	174.3(14)
C(71)-H(71C)···O(1')	0.98(2)	3.54(3)	2.686(16)	145.6(14)

Symmetry operation: -*x*, *y*+1/2, 1-*z*.

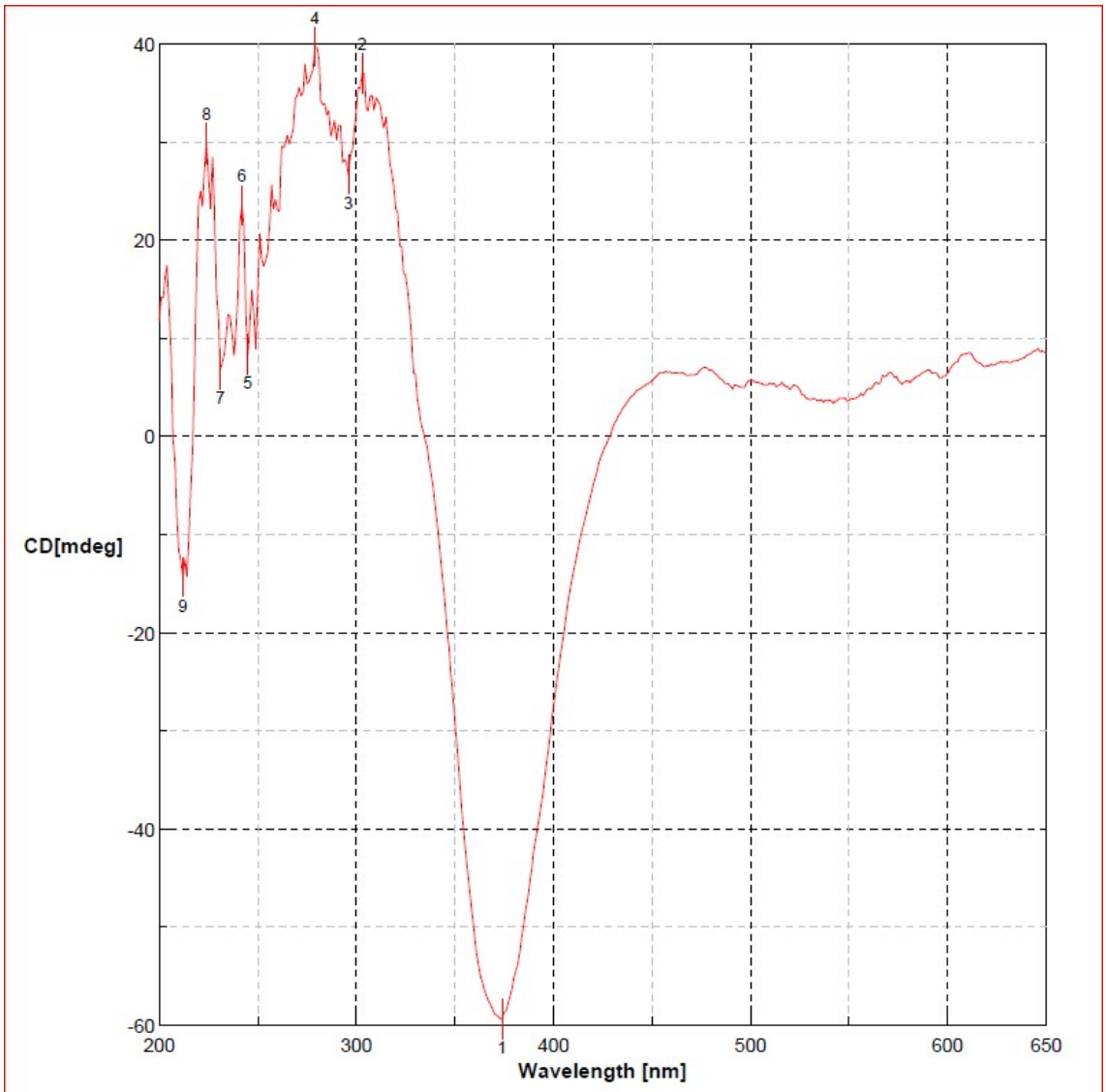
4- Circular dichroism spectra

Circular Dichroism Spectrum for 6Sb



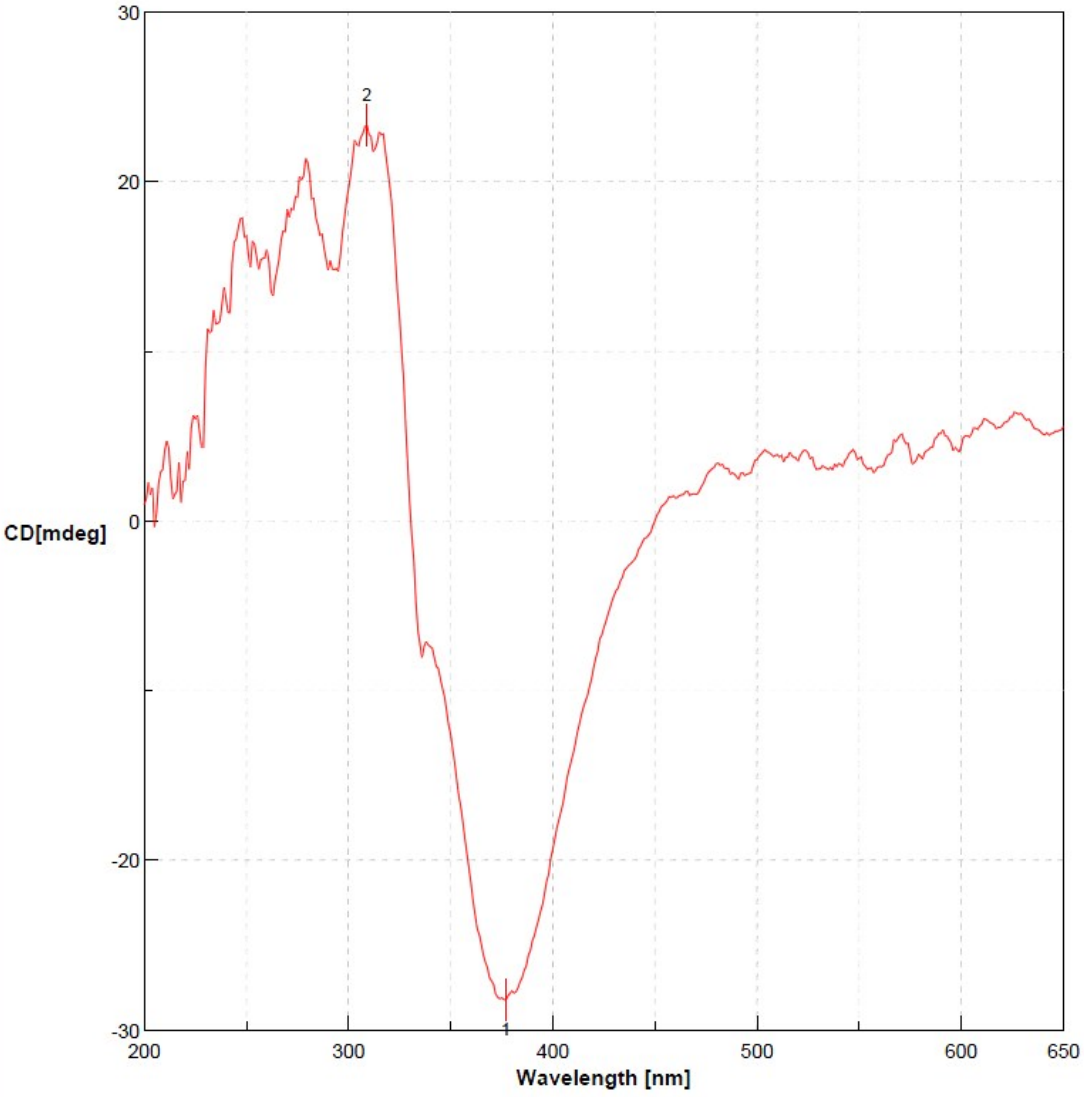
No.	nm	CD[mdeg]	No.	nm	CD[mdeg]	No.	nm	CD[mdeg]
1	464	3.83625	2	370	-105.814	3	314	5.65618
4	308	-6.68981	5	300	5.38149	6	286	-6.87769
7	265	12.5565	8	253	-6.01917	9	239	8.16381
10	222	-6.54476						

Circular Dichroism Spectrum for 7Sb



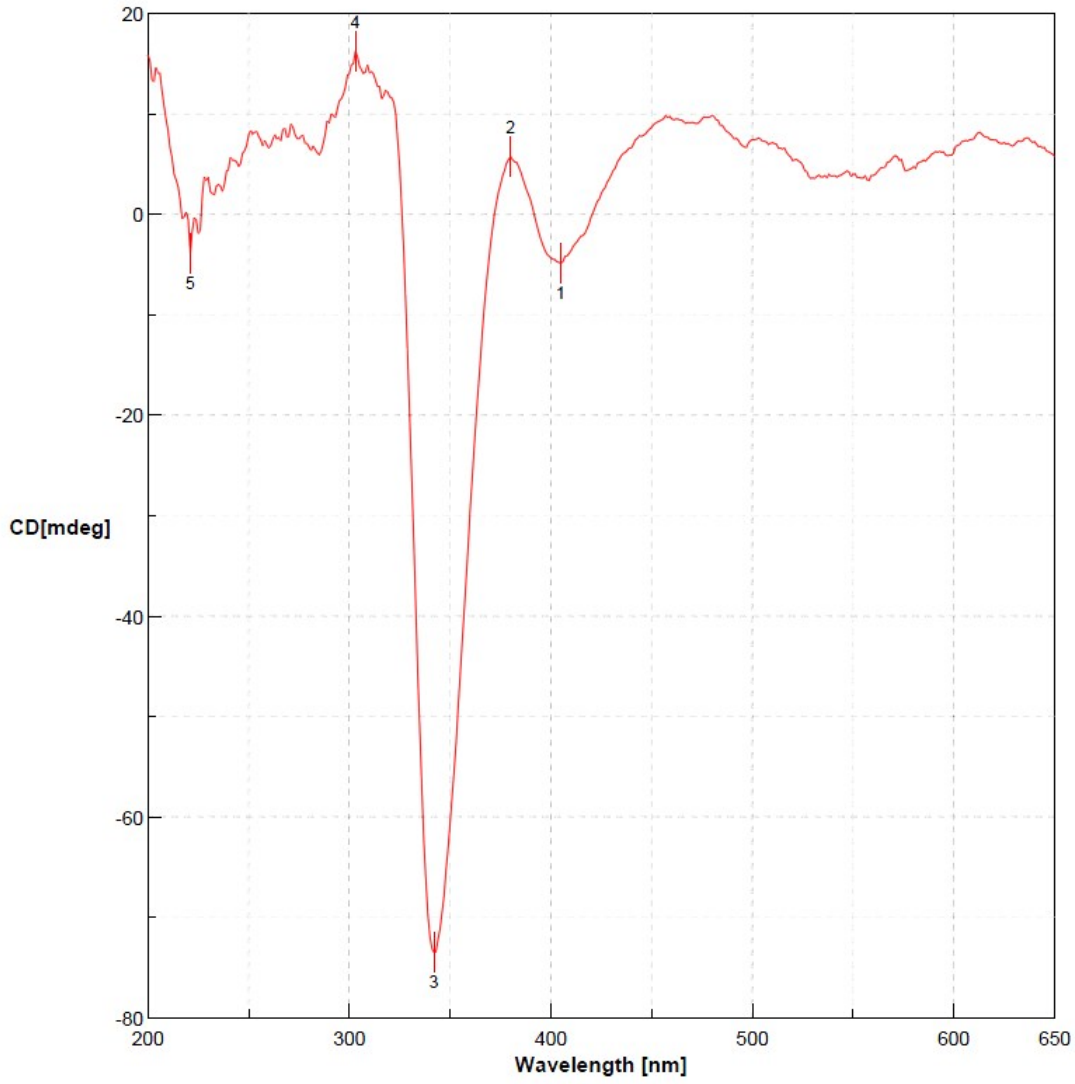
No.	nm	CD[mdeg]	No.	nm	CD[mdeg]	No.	nm	CD[mdeg]
1	374	-59.4394	2	303	37.051	3	296	26.735
4	279	39.7229	5	245	8.36244	6	242	23.5522
7	231	6.81597	8	224	29.9358	9	212	-14.3534

Circular Dichroism Spectrum for 8Sb



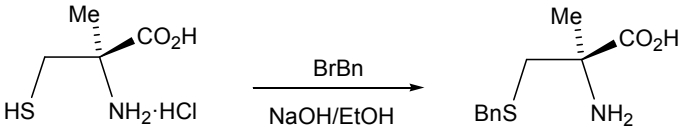
No.	nm	CD[mdeg]	No.	nm	CD[mdeg]
1	377	-28.2154	2	309	23.3423

Circular Dichroism Spectrum for 9



No.	nm	CD[mdeg]	No.	nm	CD[mdeg]	No.	nm	CD[mdeg]
1	405	-4.87482	2	380	5.7619	3	342	-73.4614
4	303	16.2585	5	221	-3.88699			

5- Preparation of HL2 by *S*-benzylation of IV



IV **HL2**

To a solution of 500.0 mg (2.91 mmol) of **IV** in EtOH (13.5 mL) 0.40 mL (2.91 mmol) of benzyl bromide were added. Then, at 5 ºC, to the resulting solution, 6 mL of an ethanolic solution of 2M NaOH were added dropwise. The precipitation of a white solid was observed. The resulting suspension was stirred for 1 h, at RT. After that time, 0.48 mL of 12M HCl was added dropwise until the pH was 6-7. The resulting suspension was filtered and the white precipitate washed consecutively with H_2O, EtOH and Et_2O and vacuum-dried to afford a white solid. Yield: 75%. M. p.: 230-232 ºC. IR (solid, cm^{-1}): 2987, 1606, 1578, 1269, 1231. $[\alpha]_D^{24}$: +62.4 (c = 1.075; HCl(aq) 1M). HRMS (ESI) $C_{11}H_{15}NO_2S$ $[M+H]^+$: Calcd. 226.0896, found 226.0920.

HL2·HCl. *^{1}H NMR (300.13 MHz, D_2O, 298 K, ppm)*: δ 7.38 (m, 5H, H_{Ar}), 3.82 (s, 2H, CH_2Ph), 3.09 (AB system, J_{AB} = 14.8 Hz, 2H, CH_2C^*), 1.57 (s, 3H, Me). *$^{13}C\{^1H\}$ NMR (125.8 MHz, D_2O, 298 K, ppm)*: δ 172.55 (COOH), 137.77, 129.01, 128.84, 127.58 (6C, C_{Ar}), 60.14 (C*), 36.85 (CH_2C^*), 36.37 (CH_2Ph), 21.52 (Me).

6- Frequency list of all ground and transition states

Lower six vibrational frequencies (cm^{-1}) of the optimized (gas-phase) ground and transition states:

Ss-9: 20.3726, 29.6229, 33.9547, 39.1739, 43.6297, 59.5091

m1: 11.9918, 17.3250, 25.5487, 31.8023, 41.8288, 45.6620

ts12: -32.0562, 16.0029, 23.5724, 26.8081, 33.2382, 36.1267

m2: 16.4815, 21.9066, 24.2463, 30.6018, 41.4461, 48.9321

ts23: -27.8106, 11.2387, 18.5158, 25.4118, 28.5932, 36.7650

m3: 17.0428, 19.1337, 26.6523, 30.3397, 37.4974, 47.2798

ts34: -39.9604, 17.7155, 21.0395, 31.2317, 37.5675, 50.1233

m4: 15.3394, 17.7230, 28.2531, 30.8391, 40.0504, 44.0046

Rs-9: 18.7156, 28.5640, 30.7907, 37.0432, 42.7645, 50.6374

MeOH: 336.6882, 1061.1532, 1094.0672, 1179.0483, 1384.9756, 1499.3493