

Supporting Information

Asymmetric Transfer Hydrogenation of Imines in Water/Methanol Co-Solvent System and Mechanistic Investigation by DFT Study

Vaishali S. Shende^a, *Savita K. Shingote*^a, *Sudhindra H. Deshpande*^a, *Nishamol Kuriakose*^b,
Kumar Vanka^{b*}, *Ashutosh A. Kelkar*^{a*}

^aChemical Engineering & Process Development, National Chemical Laboratory,

^bPhysical and Materials Chemistry Division, National Chemical Laboratory,

Pune 411008, India

Corresponding Author: E-mail: aa.kelkar@ncl.res.in , Fax: +91 20 25902621

E-mail: k.vanka@ncl.res.in , Fax: +91 20 25902636

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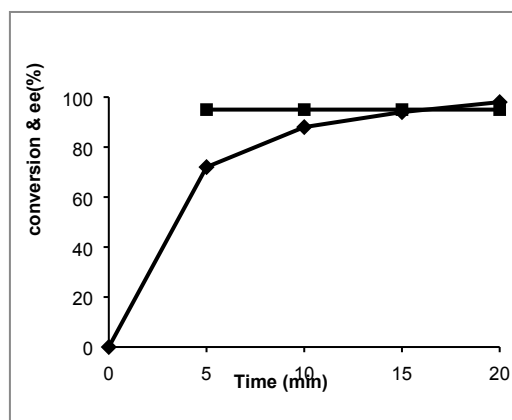
1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. Imine derivatives were synthesized by literature procedure.¹ Water was distilled prior to use. NMR spectra were recorded on a Bruker 200 Hz NMR spectrometer with TMS as the internal standard. Gas chromatographic analysis was carried out on a Agilent 6850 GC equipped with a HP1 column and an FID detector (75 psi Helium gas, 75 psi hydrogen gas, and 220 °C injector and 250 °C detector temperature). HPLC analysis was performed on Perkin Elmer Series 200 equipped with Chiralcel OD-H column purchased from Daicel Chemical Industries. The catalyst $[\text{Cp}^*\text{RhCl}_2]_2$ used was prepared according to the literature² and the racemic products were prepared using racemic TsDPEN and $[\text{Cp}^*\text{RhCl}_2]_2$ as pre-catalyst under the optimized conditions. The configurations of the products were assigned by comparison of their HPLC retention times with those reported (see below) or by analogy.

2. General Procedure for asymmetric transfer hydrogenation of imines

Round bottom flask containing a magnetic stirring bar, and $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$ (1.55 mg, 0.0025 mmol) and (1S, 2S)-TsDPEN (2.75 mg, 0.0075 mmol) in distilled water (1 ml) was stirred for 1 h at 40°C to generate the pre-catalyst. To the above pre-catalyst solution imine substrate (0.5 mmol), HCOONa (0.170 g, 2.5 mmol) and MeOH (1 ml) was added. The reaction mixture was stirred at 40°C for the time indicated, then cooled to room temperature and extracted with DCM (3ml x 2). Organic phase was dried over Na_2SO_4 and solvent was removed under reduced pressure. Conversion was determined by GC and enantioselectivity was determined by Chiral HPLC

3. C-T (Conversion Vs Time) profile for ATH of 1a



Reaction conditions: 1a (0.5 mmol), [Rh(Cp^{*})Cl₂]₂ (0.0025 mmol), (1S, 2S)-TsDPEN (0.0075 mmol), HCOONa (2.5 mmol), 40°C, solvent (2 ml), H₂O/ MeOH (v/v, 1:1); Conv (*), ee (O) **Figure S1:** C-T (Conversion Vs Time) profile for ATH of 1a

4. Co-solvent screening of ATH of imine 1a

Table S1: Co-solvent screening for ATH of imine 1a, conversions at 30 min reaction time

Entry	Co-solvent	Conv (%)	ee (%)
1	MeOH ^a	98	94
2	EtOH ^a	98	94
3	n-PrOH	93	91
4	n-BuOH	94	92
5	IPA	94	92
6	Ethylene glycol	95	80
7	DMF	88	93
8	DMSO	95	89
9	NMP	95	84
10	1,4-dioxane	95	83
11	THF	25	92

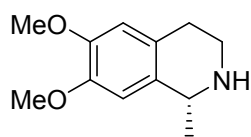
Reaction conditions: 1a (0.5 mmol), [Rh(Cp^{*})Cl₂]₂ (0.0025 mmol), (1S, 2S)-TsDPEN (0.0075 mmol), HCOONa (2.5 mmol), 40°C, solvent (2 ml), H₂O/ co-solvent (v/v, 1:1), Time:30min, ^a Time: 20min

Table S2: Co-solvent screening for ATH of imine **1a**, conversions at 20 min reaction time

Entry	Co-solvents	Conv (%)
1	MeOH	98
2	EtOH	98
3	n-PrOH	70
4	n-BuOH	71
5	IPA	89
6	Ethylene glycol	80
7	DMF	77
8	DMSO	89
9	NMP	76
10	1,4-dioxane	72
11	THF	16

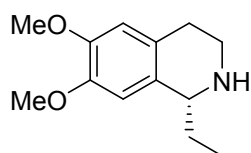
Reaction conditions: 1a (0.5 mmol), [Rh(Cp*)Cl₂]₂ (0.0025 mmol), (1S, 2S)-TsDPEN (0.0075 mmol), HCOONa (2.5 mmol), 40°C, solvent (2 ml), H₂O/ co-solvent (v/v, 1:1), Time: 20min

5. Analytic data of products



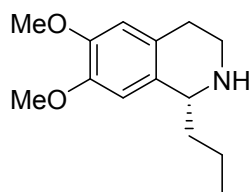
2a

(R)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline³ : 97% yield, 95% ee. ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 1.44 (d, *J* = 6.7 Hz, 3H), 2.19 (br, 1H), 2.10(m, 2H), 2.90-3.03 (m, 1H), 3.17-3.28 (m, 1H), 3.83 (s, 6H), 3.97-4.07 (q, *J* = 6.7 Hz, 1 H), 6.55 (s, 1H), 6.60 (s, 1H); ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 22.70, 29.36, 41.67, 51.14, 55.79, 55.93, 109.05, 111.75, 126.67, 132.22, 147.22, 147.31, HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 1 mL/min, 254 nm): t_S = 11.76min (minor), t_R = 14.86 min (major).



2b

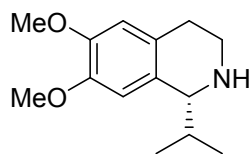
(R)-6,7-Dimethoxy-1-ethyl-1,2,3,4-tetrahydroisoquinoline³ : 95 % yield, 94% ee ; ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 1.01-1.03 (t, *J* = 7.3 Hz, 3H), 1.66-1.77 (m, 1H), 1.86-1.97(m, 1H), 2.0 (br, 1H), 2.63-2.70 (dt, 5.0 Hz, 16.0 Hz, 1H), 2.72-2.79 (dt, *J* = 5.0 Hz, 16.0 Hz, 1H), 2.93-3.0 (m, 1H), 3.20-3.26 (m, 1H), 3.85 (s, 6H), 3.92 (d, *J* = 2.75 Hz, 1 H), 6.57 (s, 1H), 6.62 (s, 1H); ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 10.17, 28.66, 29.07, 40.76, 55.45, 55.61, 56.35, 108.83, 111.33, 126.81, 130.79, 146.79, 146.87 HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 80:20:0.1, flow rate 1mL/min, 280 nm): t_S = 9.91 min (minor), t_R = 12.50 min (major).



2c

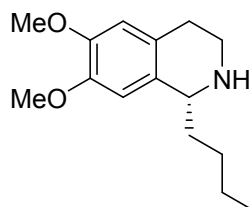
(R)-6,7-Dimethoxy-1-propyl-1,2,3,4-tetrahydroisoquinoline: 94 % yield , 96% ee. ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 0.90-0.93 (t, *J* = 7.3 Hz, 3H), 1.33-1.49 (m, 2H), 1.56-1.66(m, 1H), 1.68-1.76(m, 1H), 1.63 (br, 1H), 2.56-2.63 (dt, 5.5 Hz, 16.0 Hz, 1H), 2.65-2.72 (m, 1H), 2.87-2.92 (dt, 5.0Hz, 12.3 Hz,1H), 3.12-3.18 (m, 1H), 3.78 (s, 3H), 3.79(s, 3H), 3.82-3.85 (dd, *J* = 3.2Hz, 5.0 Hz, 1 H), 6.49 (s, 1H), 6.54 (s, 1H); ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 14.21, 19.38, 29.31, 38.69, 40.98, 55.18, 55.80, 55.98, 109.17, 111.68,

126.95, 131.30, 147.14, 147.21, HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 1 mL/min, 280 nm): tS = 10.16 min (minor), tR = 12.66 min (major).



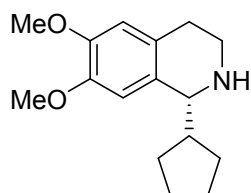
2d

(R)-6,7-Dimethoxy-1-isopropyl -1,2,3,4-tetrahydroisoquinoline⁴: 94 % yield , 99% ee; ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 0.73-0.77 (d, *J* = 6.8 Hz, 3H), 1.11-1.15 (d, *J* = 6.8 Hz, 3H), 1.85 (br, 1H), 2.23-2.38 (m, 1H), 2.52-2.67 (m, 1H), 2.74-2.82 (m, 1H), 2.72-2.97 (m, 2H), 3.26-3.35 (m, 1H), 3.85(s, 7H, Overlapped with CH), 6.57 (s, 1H), 6.65 (s, 1H); ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 16.0, 20.6, 30.3, 32.8, 43.1, 56.2, 56.4, 61.0, 109.4, 112.1, 128.8, 131.0, 147.4, 147.6, HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 0.5 mL/min, 280 nm): tS = 15.41 min (minor), tR = 17.47 min (major).



2e

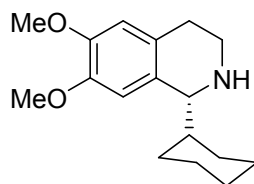
(R)-6,7-Dimethoxy-1-butyl -1,2,3,4-tetrahydroisoquinoline: 94% yield, 93% ee; ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 0.88-0.95, t, 7.07 Hz, 3H; 1.29-1.49, m, 2H; 1.69-1.84, m, 2H; 2.63-2.83, m, 2H; 2.92-3.04, m, 2H; 3.18-3.30, dt, 1H; 5.30Hz, 10.99Hz, 1H; 3.82-3.83, s, 6H; 3.88-3.96, m, 1H; 6.55, s, 1H; 6.59, s, 1H; ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 14.01, 22.80, 28.23, 28.91, 35.94, 40.85, 55.35, 55.80, 55.99, 109.29, 111.74, 126.74, 130.66, 147.27, 147.40 HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 1 mL/min, 280 nm): tS = 9.06 min (minor), tR = 11.51 min (major).



2f

(R)-6,7-Dimethoxy-1-cyclopentyl-1,2,3,4-tetrahydroisoquinoline: 95 % yield , 97% ee; ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 1.23-1.76, m, 9H; 2.26-2.43, m, 1H; 2.71-2.78, m, 1H; 2.94-3.06, m, 1H; 3.24-3.35, m, 1H, 3.82, s, 6H; 3.88-3.91, d, 6.90Hz, 1H; 6.54, s, 1H; 6.65, s, 1H; ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 24.94, 25.70, 28.30, 30.37, 40.46, 45.04, 55.75, 55.98, 58.61, 109.99, 115.55, 126.64, 129.68, 146.92, 147.48; HPLC (Chiralcel OD-H,

hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 1 mL/min, 280 nm): tS = 11.67 min (minor), tR = 14.41 min (major).



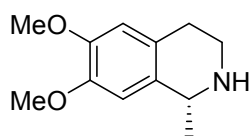
2g

(R)-6,7-Dimethoxy-1-cyclohexyl-1,2,3,4-tetrahydroisoquinoline: 94 % yield , 99% ee; ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 1.17-1.41 (m, 6H), 1.71-1.87 (m, 5H), 2.59-2.73 (dt, *J* = 3.7.0 Hz, 15.4 Hz, 1H), 2.87-2.99 (m, 2H), 3.36-3.44 (m, 1H), 3.86-3.92 (s, 7H, overlapped with NCH), 3.98-3.99 (d, 3.79Hz, 1H), 6.58 (s, 1H), 6.63 (s, 1H); ¹³C NMR (CDCl₃, 200 MHz) δ (ppm): 25.75, 26.51, 26.65, 27.01, 29.47, 30.84, 42.29, 43.21, 55.80, 56.09, 60.31, 109.37, 111.70, 128.15, 129.71, 147.03, 147.17, HPLC (Chiralcel OD-H, hexane:isopropanol: diethylamine = 90:10:0.1, flow rate 1 mL/min, 274 nm): tS = 8.74 min (minor), tR = 9.60 min (major).

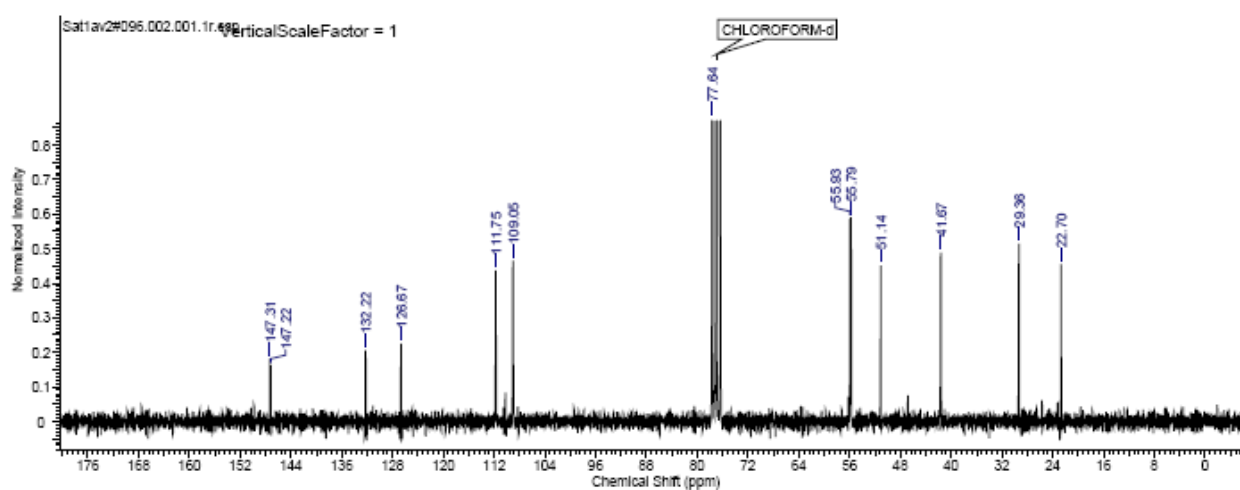
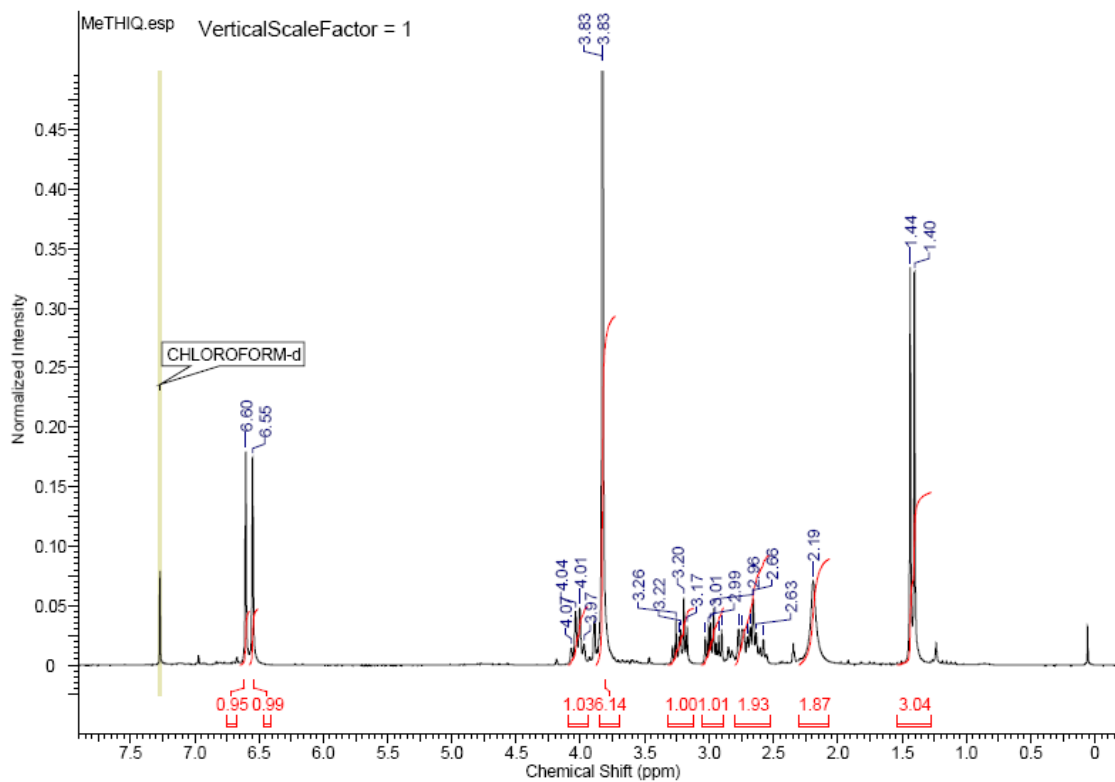
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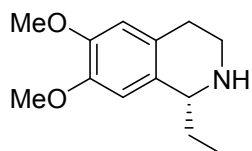
1. Craig P. N.; Nabenhauer F. P.; Williams P. M.; Macko E.; Toner J., *J. Am. Chem. Soc.*, 1952, **74**, 1316-1317.
2. Koelle, U.; Kossakowski, J.; Grumbine, D.; Tilley, T. D., *Inorganic Syntheses*, John Wiley & Sons, Inc.: 2007; pp 225-228
3. Li, C.; Xiao, J., *J. Am. Chem. Soc.* 2008, **130** , 13208-13209
4. Polniaszek, R. P.; Kaufman, C. R., *J. Am. Chem. Soc.* 1989, **111**, 4859-4863

6. ^1H and ^{13}C NMR spectra of products

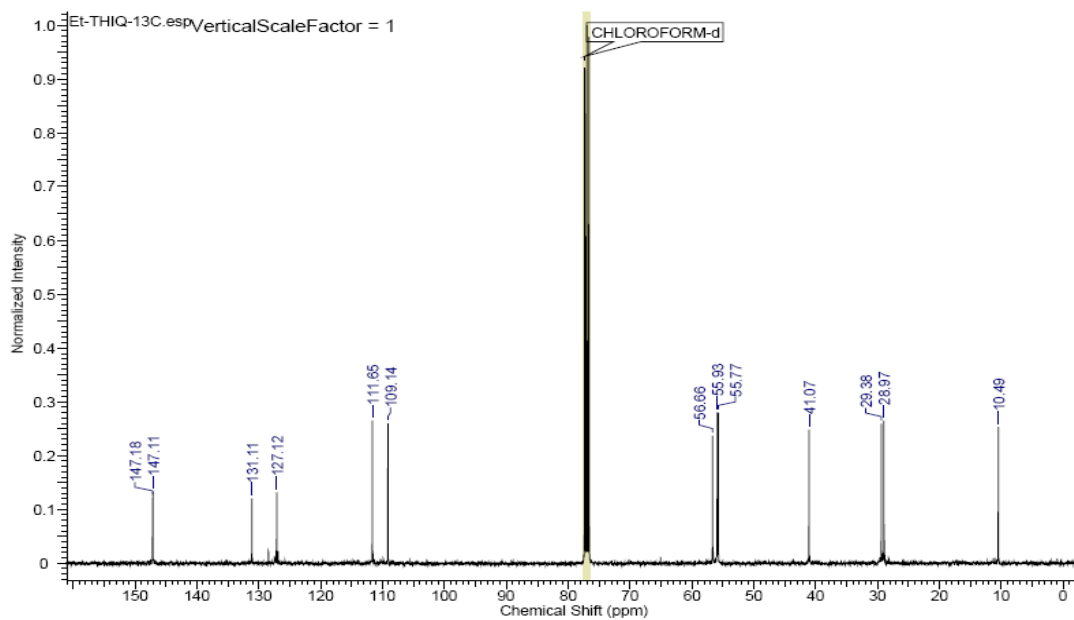
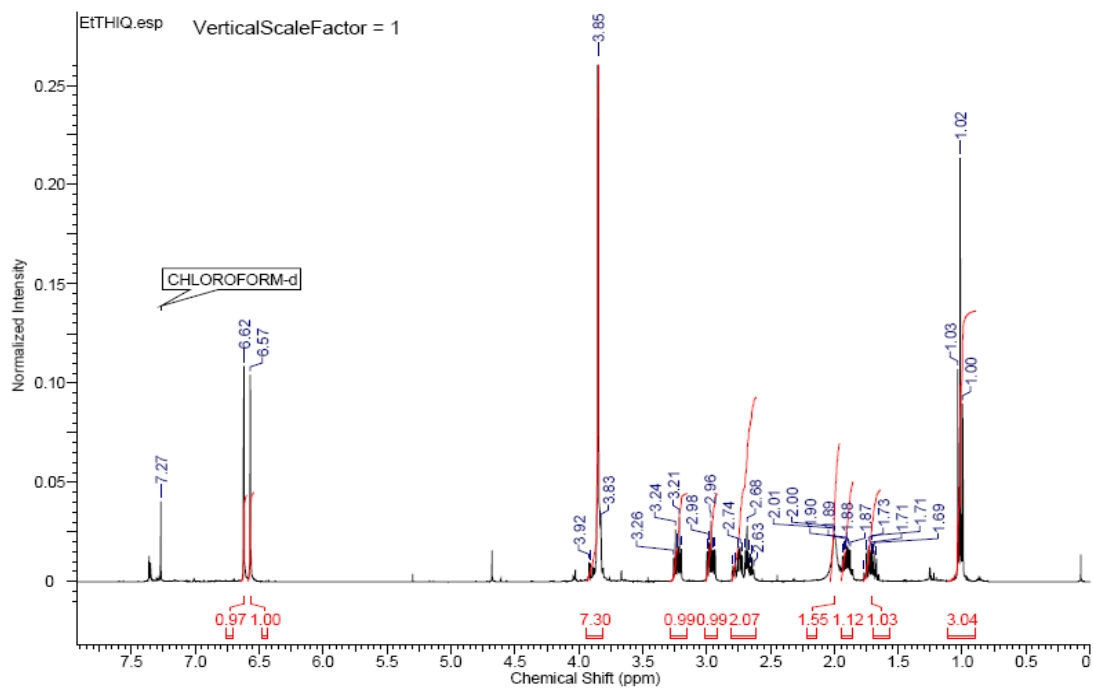


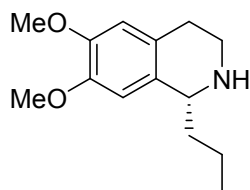
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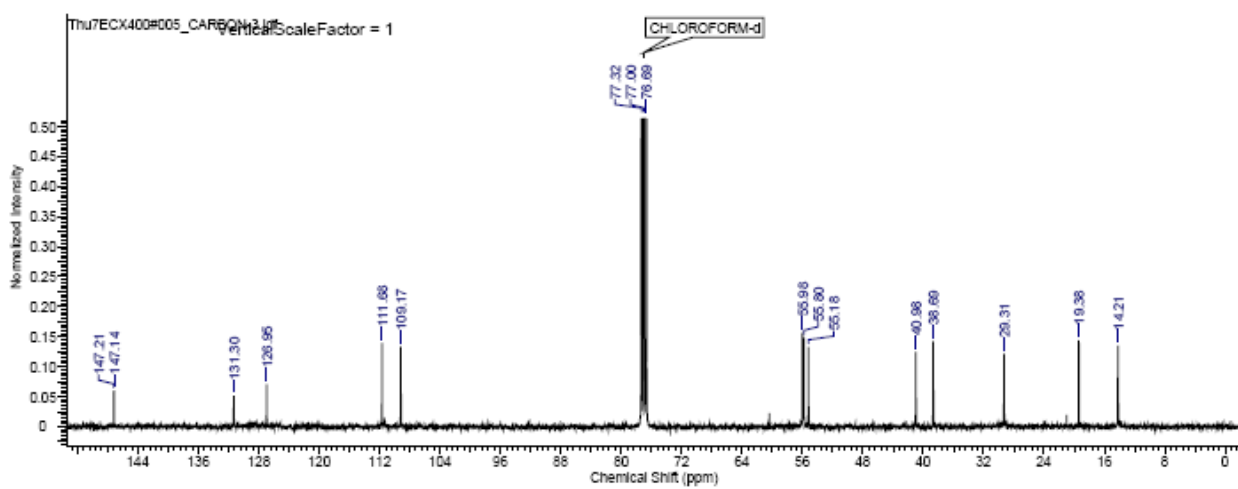
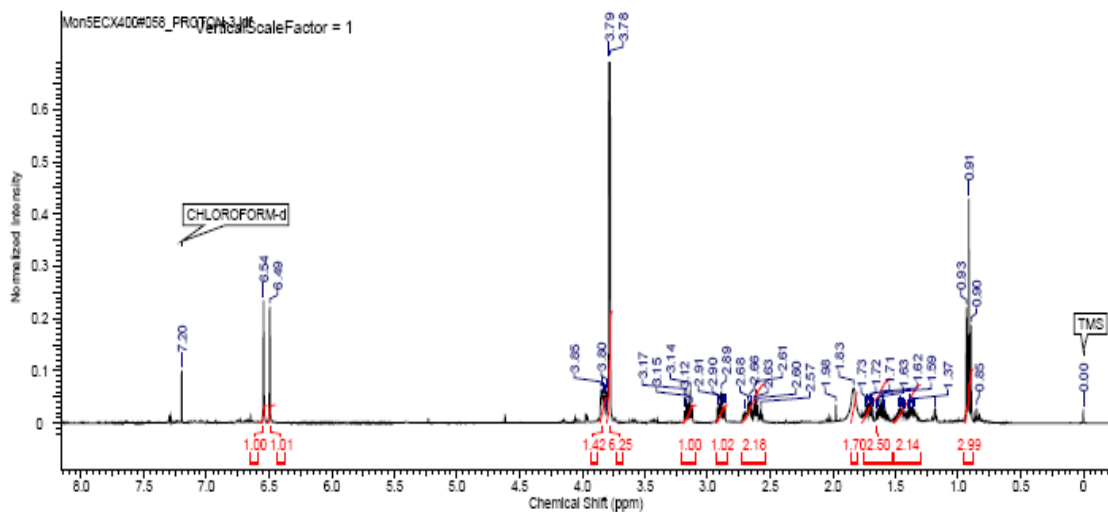


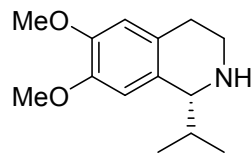
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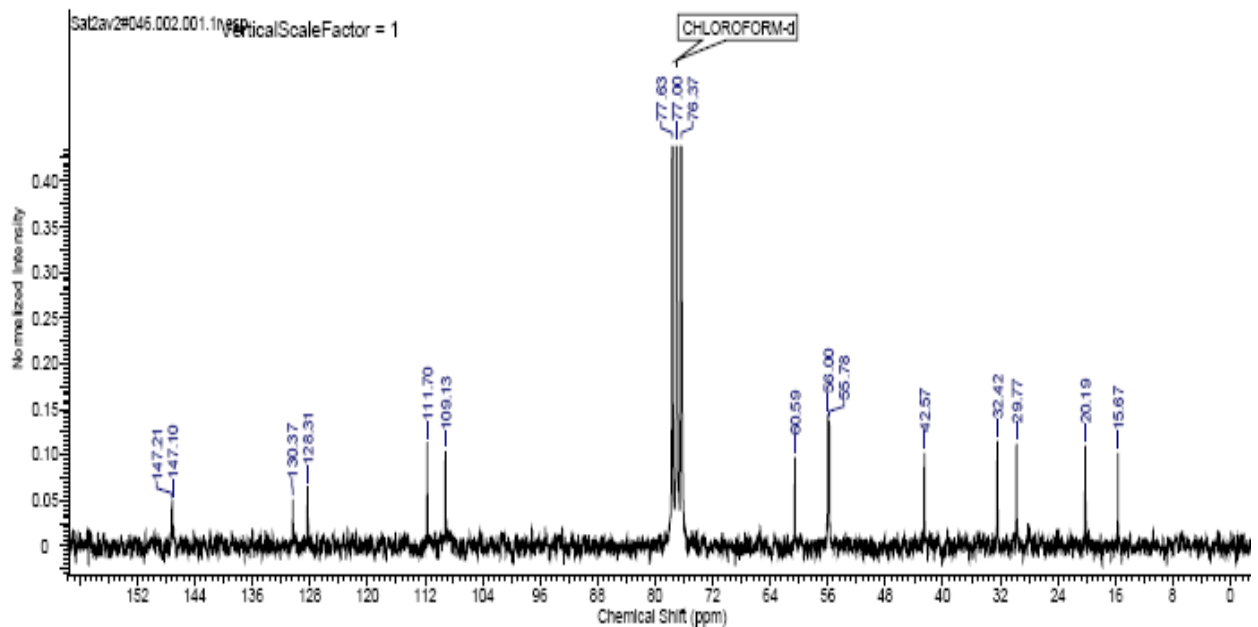
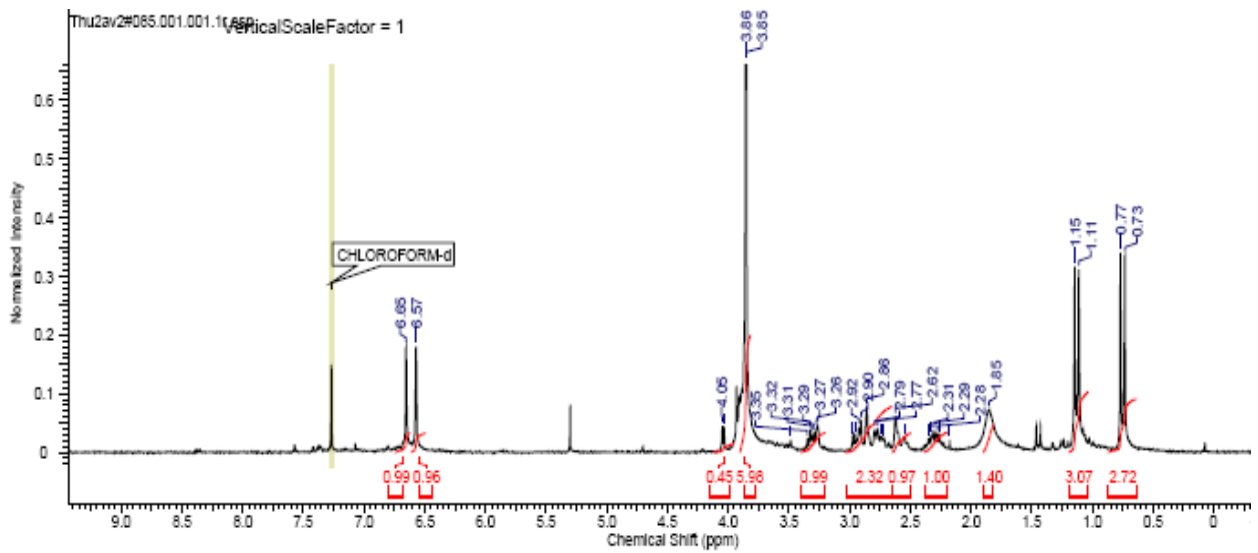


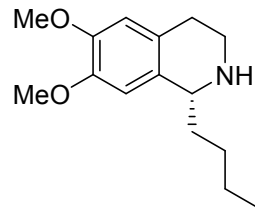
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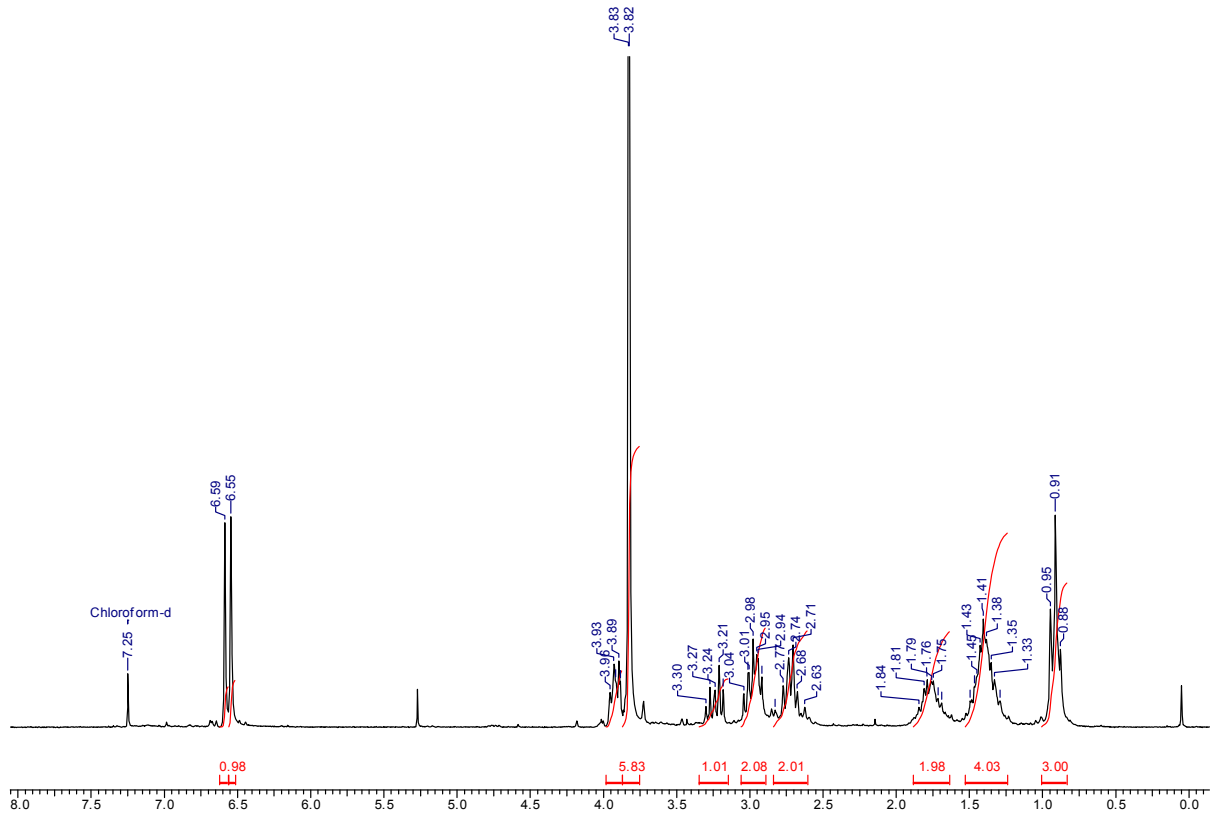


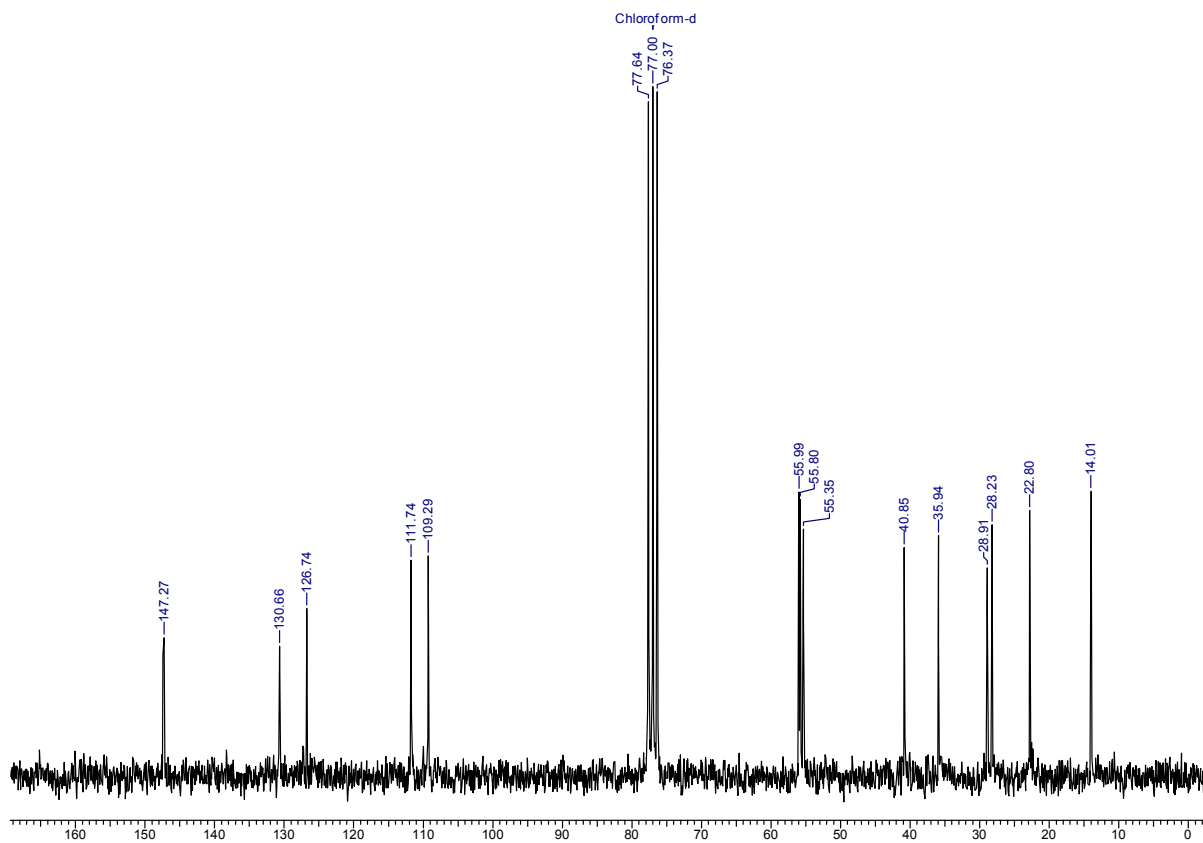
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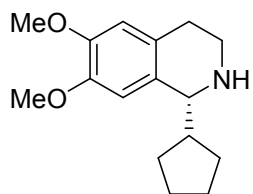




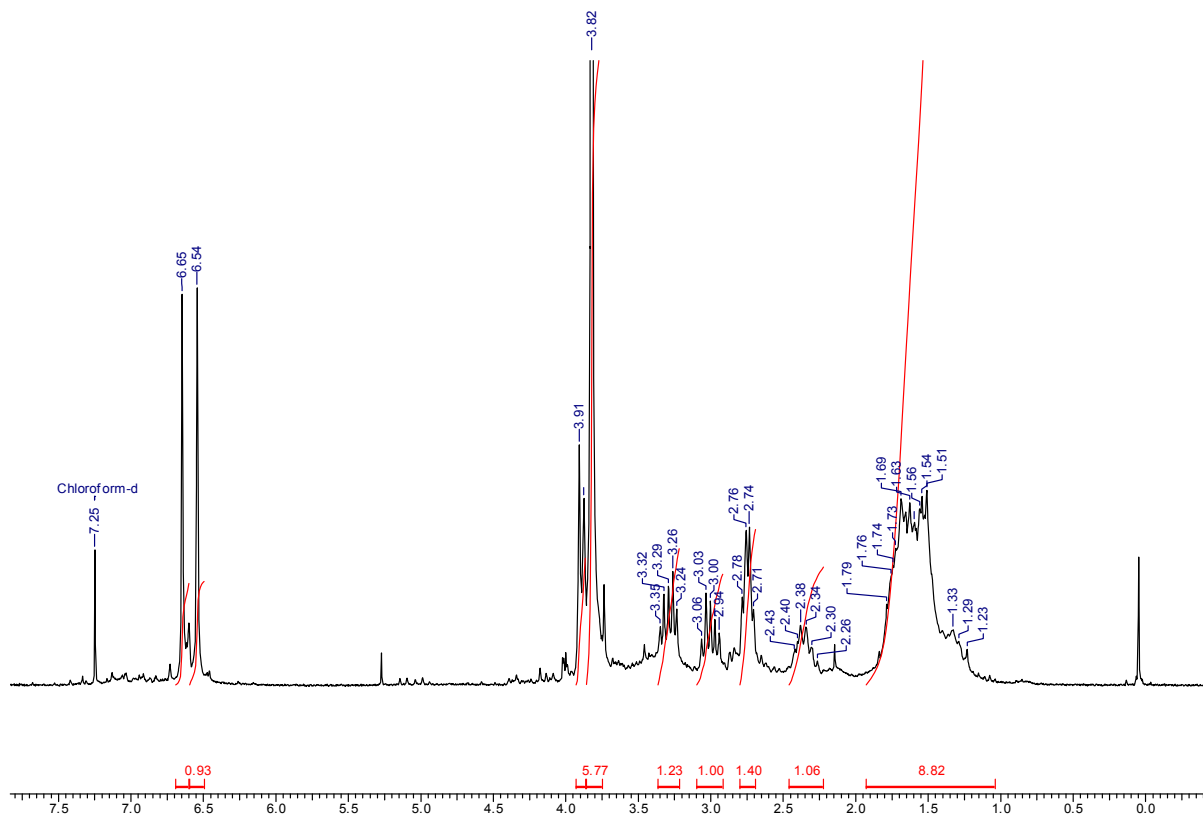
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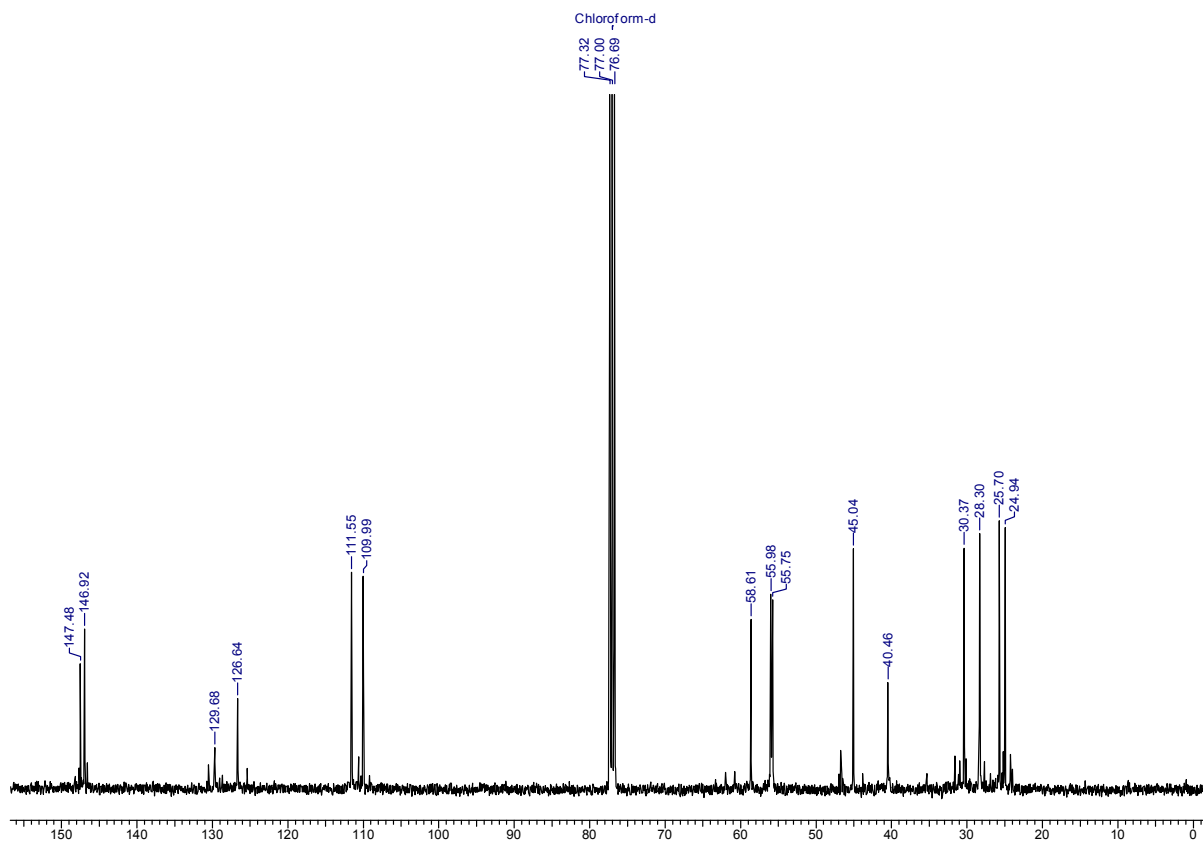


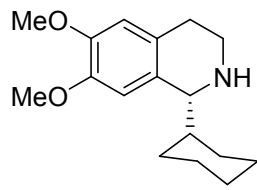




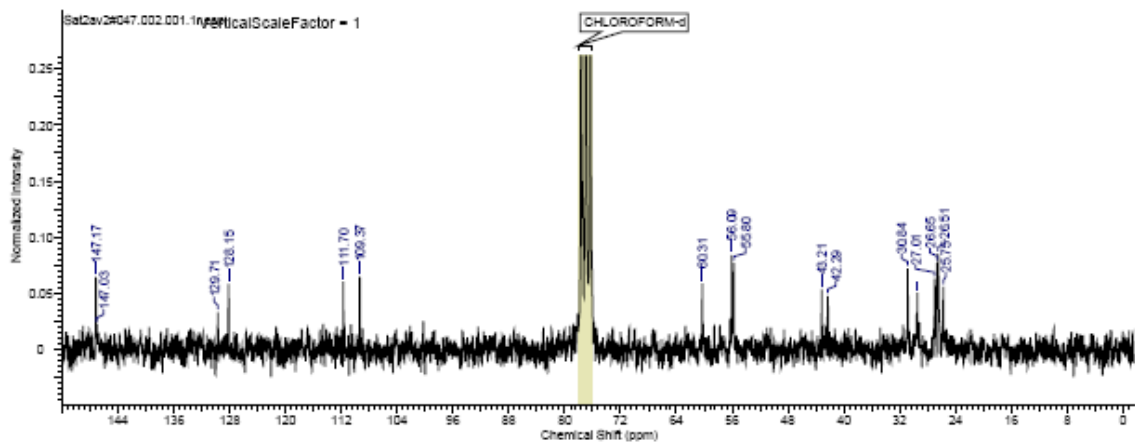
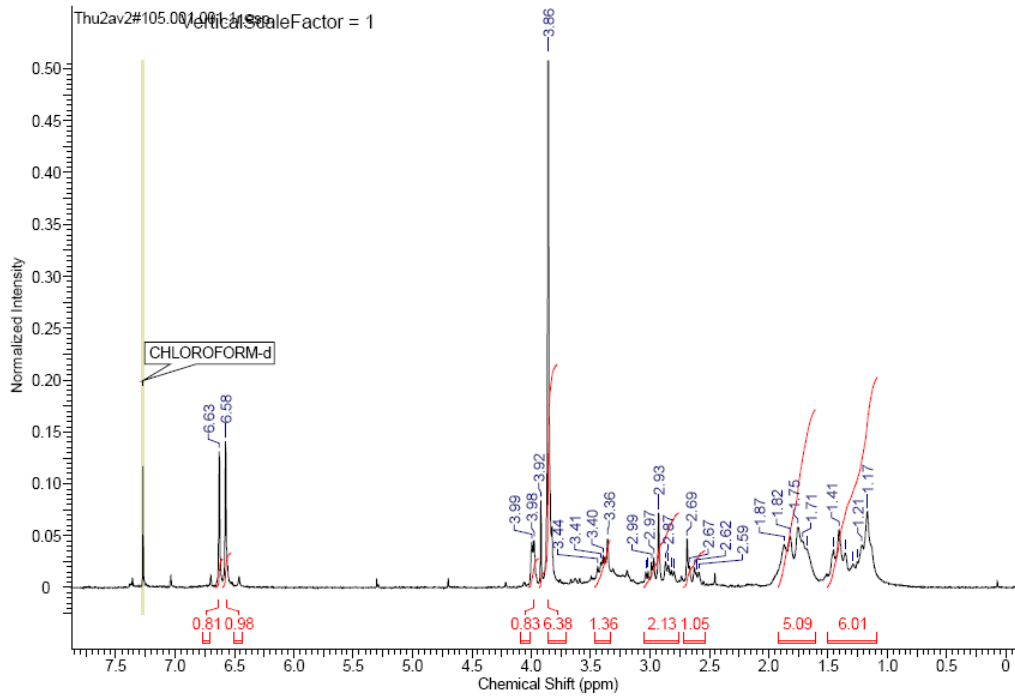
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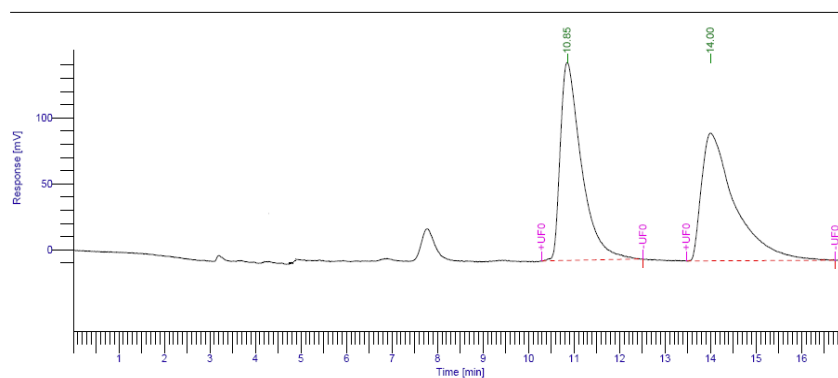
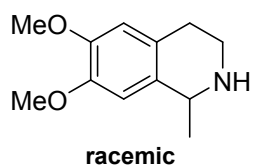




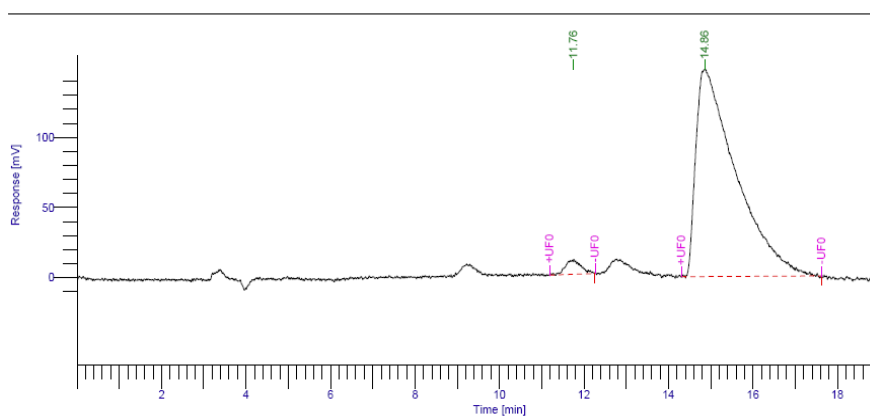
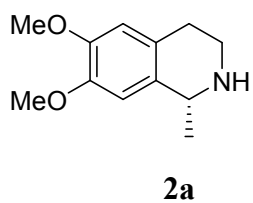
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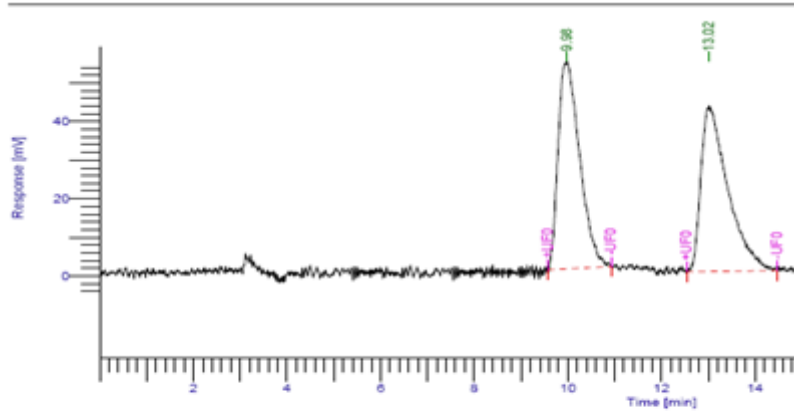
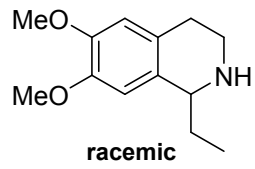
7. HPLC traces of products



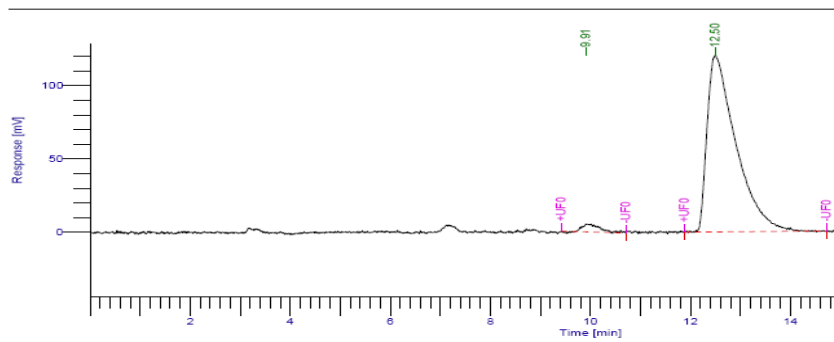
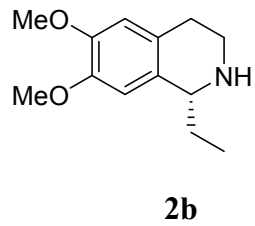
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2	14.00	4911421.26	50.29
		9766381.29	100.00



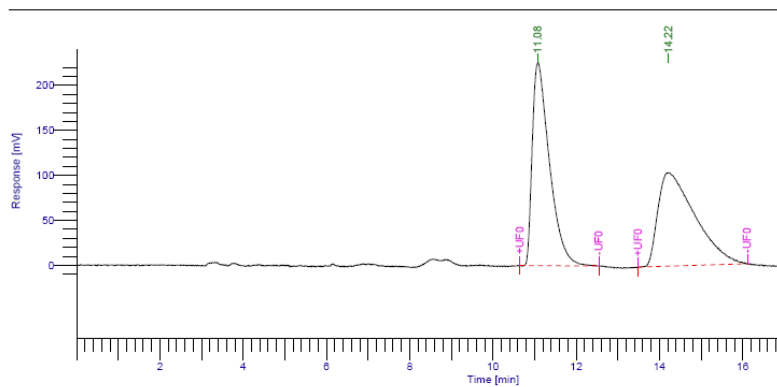
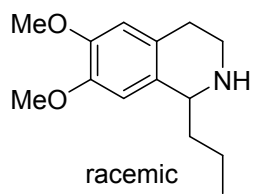
Peak #	Time [min]	Area [uV*sec]	Area [%]
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		10026583.88	100.00



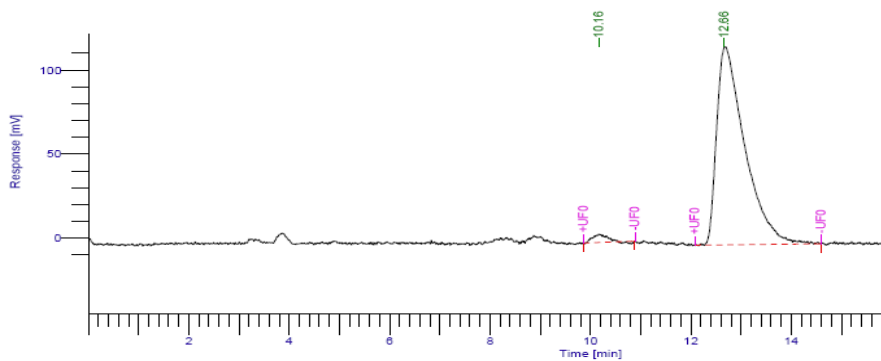
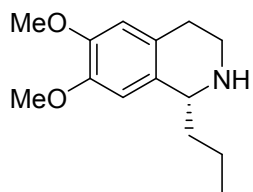
Peak #	Time [min]	Area [uV*sec]	Area [%]
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		3431606.09	100.00



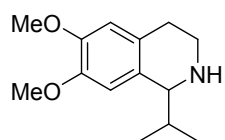
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		4941291.78	100.00



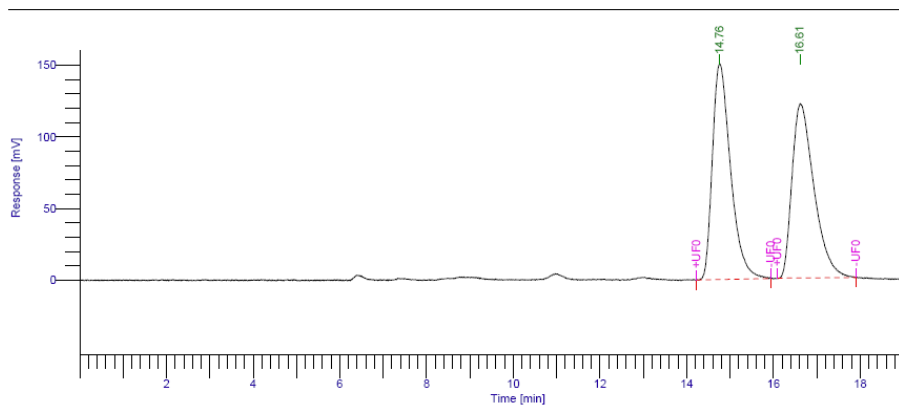
Peak #	Time [min]	Area [uV*sec]	Area [%]
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		12881756.15	100.00



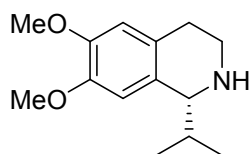
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	10.16	99738.32	2.13
2	12.66	4575720.36	97.87
		4675458.68	100.00



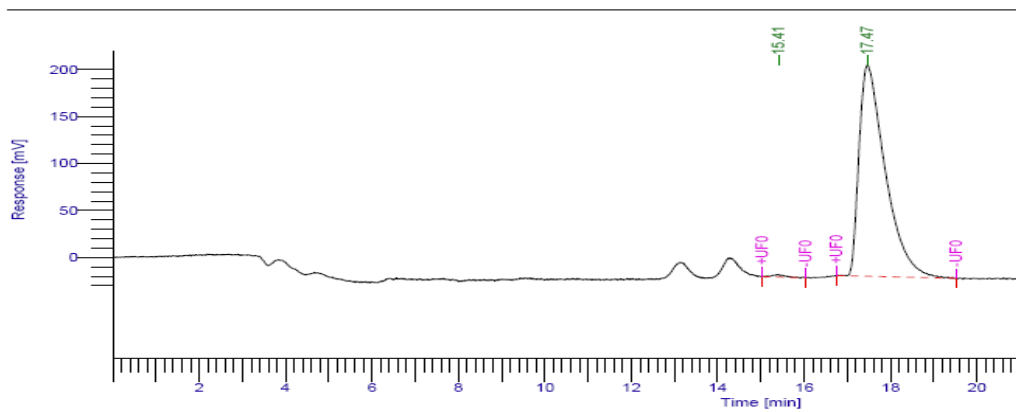
racemic



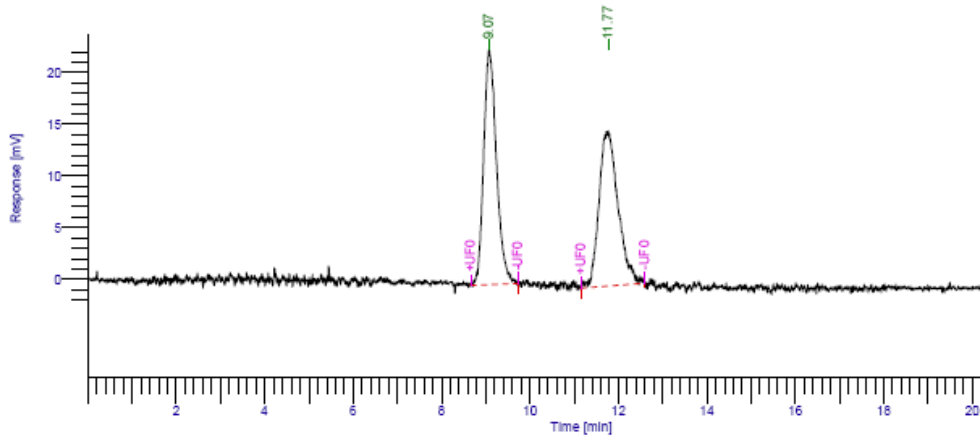
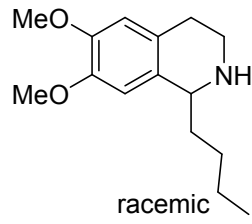
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	14.76	4374205.56	50.62
2	16.61	4267132.56	49.38
		8641338.11	100.00



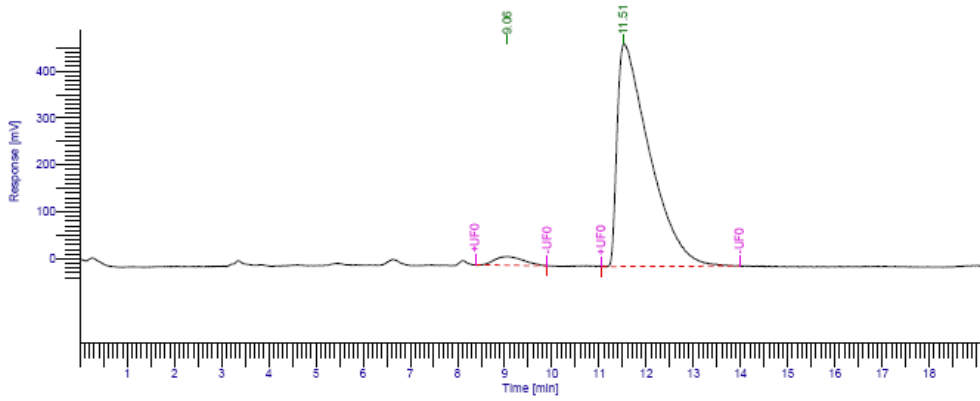
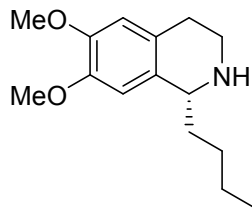
2d



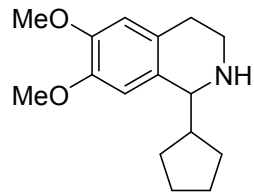
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	15.41	57075.21	0.60
2	17.47	9457054.30	99.40
		9514129.52	100.00



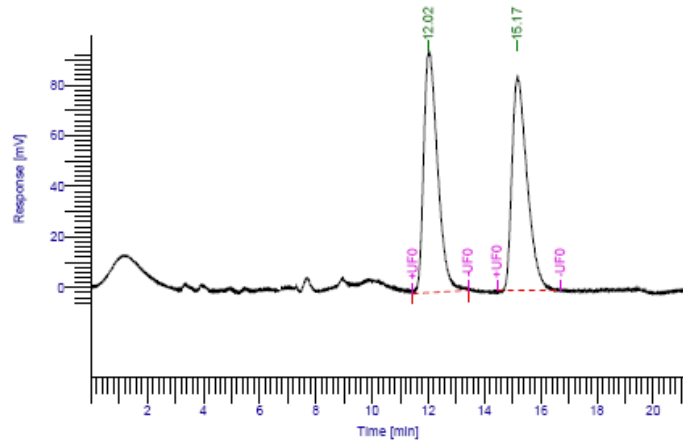
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	9.07	456100.80	50.44
2	11.77	448096.44	49.56
		904197.04	100.00



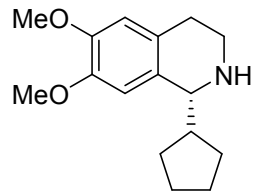
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	9.06	775940.76	3.33
2	11.51	22568180.87	96.67
		23334101.63	100.00



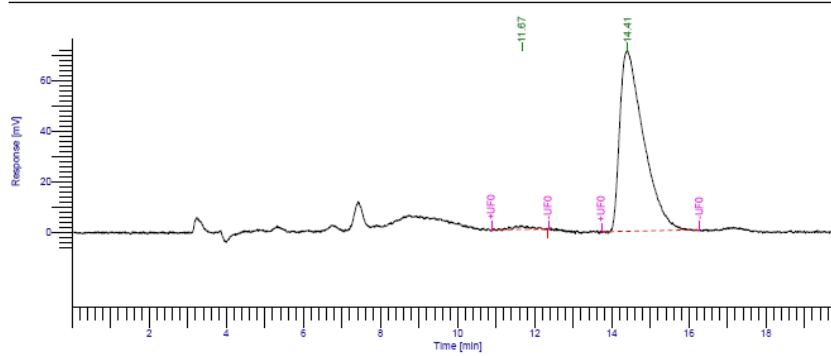
racemic



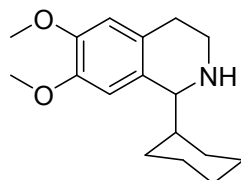
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	12.02	3286224.92	51.01
2	15.17	3156888.41	48.99
		6442913.33	100.00



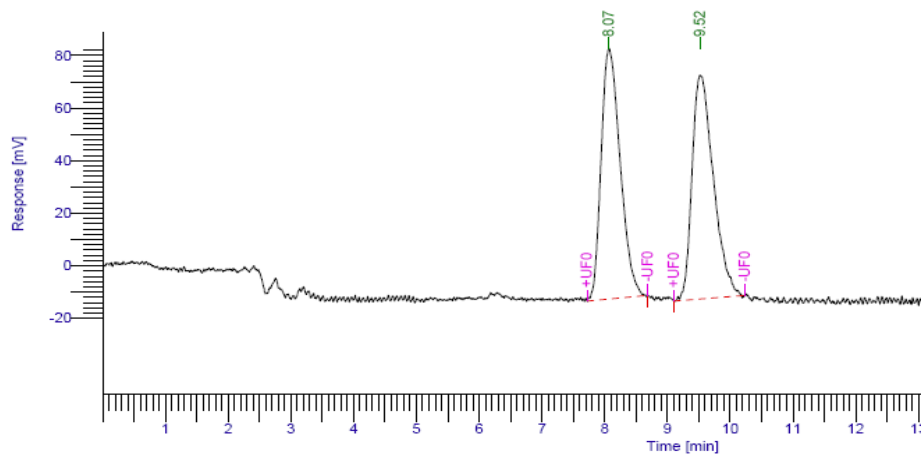
2f



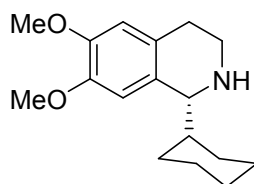
Peak #	Time [min]	Area [uV*sec]	Area [%]
1	11.87	45547.86	1.47
2	14.41	3053557.62	98.53
		3099105.48	100.00



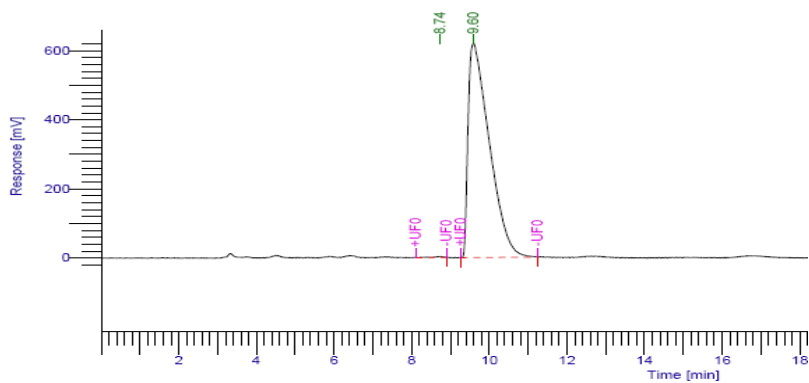
racemic



Peak #	Time [min]	Area [uV*sec]	Area [%]
1	8.07	2004681.47	49.90
2	9.52	2012926.76	50.10
		4017608.23	100.00



2g



Peak #	Time [min]	Area [uV*sec]	Area [%]
1	8.74	61367.00	0.26
2	9.60	23516979.83	99.74
		23578346.82	100.00

8. Computational Details

All the calculations have been done with Turbomole 6.4,¹ using the TZVP basis set² and the PBE functional.³ Furthermore, in order to obtain more reliable energies, single point calculations have been done with the B3LYP⁴ functional. Dispersion corrections⁵ have also been included with single point calculations. For the dispersion correction calculation, a modified empirical dispersion correction, DFT-D3 proposed by Grimme^{5,6} has been employed. The resolution of identity (RI)⁷, along with the multipole accelerated resolution of identity (marij)⁸ approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. The values reported are ΔG values, with zero point energy, internal energy and entropic contributions included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. All the obtained transition states were confirmed to have only a single negative frequency corresponding to the correct normal mode. In addition, intrinsic reaction coordinate (IRC)⁹ calculations were done with all the transition states in order to further confirm that they were the correct transition states, yielding the correct reactant and product structures.

Calculation of relative rate of reaction employing equation $\Delta G = -RT \ln K$

$$K = RT \ln K$$

$$\frac{K_1}{K_2} = e^{-(\Delta G_1 - \Delta G_2)/RT}$$

$$\frac{K_{TS C}}{K_{TS A}} = e^{-(7.1)/RT} \quad K_{TS A} = 1294 K_{TS C}$$

$$\frac{K_{TS C}}{K_{TS B}} = e^{-(4.3)/RT} \quad K_{TS B} = 137600 K_{TS C}$$

DFT Calculations

Table S3. The relative free energy at different temperatures; values are given in (au) and in kcal/mol.

System	Relative Free Energy (T=298.15)		Relative Free Energy (T=313.15)	
	au	kcal/mol	au	kcal/mol
Pathway (i) with H₂O				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.053	-32.952	-0.052	-32.116
TS B	-0.01	-6.362	-0.010	-5.381
Product complex	-0.04	-24.996	-0.040	-24.221
3a product + 2a + H ₂ O	-0.032	-20.017	-0.032	-20.143
Pathway (ii) with CH₃OH				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.059	-37.196	-0.059	-36.357
TS C	-0.013	-8.077	-0.013	-7.113
Product complex	-0.043	-26.799	-0.043	-26.027
3a product + 2a + CH ₃ OH	-0.032	-20.017	-0.032	-20.143
Pathway (iii) without solvent				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.048	-30.088	-0.048	-29.830
TS A	-0.009	-5.5919	-0.009	-5.102
Product complex	-0.029	-18.188	-0.029	-17.791
3a product + 2a	-0.032	-20.017	-0.032	-20.143
Hydrogen Bonding Energy Differences				
TS B	0.000	0.000	0.000	0.000
TS B 8M	0.011	6.822	0.011	6.990
TS C	0.000	0.000	0.000	0.000
TS C 8M	0.010	6.506	0.010	6.707
(A) N-H of product 2a hydrogen bonding only with methanol (Fig. 4)	0.000	0.000	0.000	0.000
(B) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand (Fig. 4)	0.005	2.989	0.005	3.112
(C) N-H of product 2a hydrogen bonding only with water (Fig. 4)	0.000	0.000	0.000	0.000
(D) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand; energy difference in kcal/ mol (Fig. 4)	0.002	1.325	0.002	1.343

Table S4. The free energy at different temperatures; values are given in (au) and in kcal/mol.

System	Free Energy (T=298.15)		Free Energy (T=313.15)	
	au	kcal/mol	au	kcal/mol
Pathway (i) with H₂O				
3a	-1971.307134	-1236995.226	-1971.3129	-1236998.826
1a	-671.0869262	-421107.0462	-671.08965	-421108.7525
Reactant complex	-2718.867855	-1706089.579	-2718.8761	-1706094.781
TS B	-2718.825481	-1706062.989	-2718.8335	-1706068.046
Product complex	-2718.855176	-1706081.623	-2718.8636	-1706086.886
3a product	-1970.123603	-1236252.561	-1970.1236	-1236256.14
2a	-672.3023562	-421869.7285	-672.30237	-421871.5819
H ₂ O	-76.42128197	-47954.35443	-76.422448	-47955.08612
Pathway (ii) with CH₃OH				
3a	-1971.307134	-1236995.226	-1971.3129	-1236998.826
1a	-671.0869262	-421107.0462	-671.08965	-421108.7525
Reactant complex	-2758.131003	-1730727.204	-2758.1395	-1730732.541
TS C	-2758.084598	-1730698.085	-2758.0929	-1730703.296
Product complex	-2758.114434	-1730716.807	-2758.123	-1730722.211
3a product	-1970.123603	-1236252.561	-1970.1236	-1236256.14
2a	-672.3023562	-421869.7285	-672.30237	-421871.5819
CH ₃ OH	-115.6776661	-72587.73549	-115.67905	-72588.60511
Pathway (iii) without solvent				
3a	-1971.307134	-1236995.226	-1971.3129	-1236998.826
1a	-671.0869262	-421107.0462	-671.08965	-421108.7525
Reactant complex	-2642.44201	-1658132.361	-2642.4501	-1658137.409
TS A	-2642.402971	-1658107.865	-2642.4106	-1658112.681
Product complex	-2642.423045	-1658120.461	-2642.4309	-1658125.37
3a product	-1970.123603	-1236252.561	-1970.1236	-1236256.14
2a	-672.3023562	-421869.7285	-672.30237	-421871.5819
TS B	-2718.825481	-1706062.989	-2718.8335	-1706068.046
TS B 8M	-2718.814608	-1706056.167	-2718.8224	-1706061.056
TS C	-2758.084598	-1730698.085	-2758.0929	-1730703.296
TS C 8M	-2758.07423	-1730691.579	-2758.0822	-1730696.59
(A) N-H of product 2a hydrogen bonding only with methanol (Fig. 4)	-2758.114434	-1730716.807	-2758.1230	-1730722.211
(B) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand (Fig. 4)	-2758.10967	-1730713.818	-2758.1181	-1730719.098
(C) N-H of product 2a hydrogen bonding only with water (Fig. 4)	-2718.855176	-1706081.623	-2718.8636	-1706086.886
(D) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand; energy difference in kcal/ mol (Fig. 4)	-2718.853064	-1706080.297	-2718.8614	-1706085.543

Table S5. The relative electronic energy and the relative free energy in (au) and in kcal/mol.

System	Relative Electronic Energy		Relative Free Energy	
	au	kcal/mol	au	kcal/mol
Pathway (i) with H₂O				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.084	-52.961	-0.053	-32.952
TS B	-0.042	-26.528	-0.01	-6.362
Product complex	-0.074	-46.483	-0.04	-24.996
3a product + 2a+ H ₂ O	-0.034	-21.338	-0.032	-20.017
Pathway (ii) with CH₃OH				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.093	-58.56	-0.059	-37.196
TS C	-0.045	-28.418	-0.013	-8.077
Product complex	-0.078	-48.783	-0.043	-26.799
3a product + 2a+ CH ₃ OH	-0.034	-21.338	-0.032	-20.017
Pathway (iii) without solvent				
3a + 1a	0.000	0.000	0.000	0.000
Reactant complex	-0.061	-38.189	-0.048	-30.088
TS A	-0.024	-14.943	-0.009	-5.5919
Product complex	-0.047	-29.663	-0.029	-18.188
3a product + 2a	-0.034	-21.338	-0.032	-20.017
TS B				
TS B	0.000	0.000	0.000	0.000
TS B 8M	0.006	3.972	0.011	6.822
TS C				
TS C	0.000	0.000	0.000	0.000
TS C 8M	0.006	4.039	0.010	6.506
(A) N-H of product 2a hydrogen bonding only with methanol (Fig. 4)				
(A) N-H of product 2a hydrogen bonding only with methanol (Fig. 4)	0.000	0.000	0.000	0.000
(B) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand (Fig. 4)				
(B) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand (Fig. 4)	0.002	1.481	0.005	2.989
(C) N-H of product 2a hydrogen bonding only with water (Fig. 4)				
(C) N-H of product 2a hydrogen bonding only with water (Fig. 4)	0.000	0.000	0.000	0.000
(D) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand;energy difference in kcal/ mol (Fig. 4)				
(D) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand;energy difference in kcal/ mol (Fig. 4)	0.002	1.196	0.002	1.325

Table S6. The electronic energy and free energy in (au) and in kcal/mol.

System	Electronic Energy		Free Energy	
	au	kcal/mol	au	kcal/mol
Pathway (i) with H₂O				
3a	-1971.82	-1237319.116	-1971.307134	-1236995.226
1a	-671.288	-421233.0252	-671.0869262	-421107.0462
Reactant complex	-2719.62	-1706560.801	-2718.867855	-1706089.579
TS B	-2719.58	-1706534.369	-2718.825481	-1706062.989
Product complex	-2719.61	-1706554.324	-2718.855176	-1706081.623
3a product	-1970.62	-1236563.555	-1970.123603	-47954.35443
2a	-672.526	-422009.9239	-672.3023562	-72587.73549
H ₂ O	-76.4234	-47955.69902	-76.42128197	-47954.35443
Pathway (ii) with CH₃OH				
3a	-1971.82	-1237319.116	-1971.307134	-1236995.226
1a	-671.288	-421233.0252	-671.0869262	-421107.0462
Reactant complex	-2758.91	-1731214.795	-2758.131003	-1730727.204
TS C	-2758.86	-1731184.653	-2758.084598	-1730698.085
Product complex	-2758.89	-1731205.019	-2758.114434	-1730716.807
3a product	-1970.62	-1236563.555	-1970.123603	-47954.35443
2a	-672.526	-422009.9239	-672.3023562	-72587.73549
CH ₃ OH	-115.704	-72604.09386	-115.6776661	-72587.73549
Pathway (iii) without solvent				
3a	-1971.82	-1237319.116	-1971.307134	-1236995.226
1a	-671.288	-421233.0252	-671.0869262	-421107.0462
Reactant complex	-2643.17	-1658590.331	-2642.44201	-1658132.361
TS A	-2643.13	-1658567.085	-2642.402971	-1658107.865
Product complex	-2643.16	-1658581.804	-2642.423045	-1658120.461
3a product	-1970.62	-1236563.555	-1970.123603	-47954.35443
2a	-672.526	-422009.9239	-672.3023562	-72587.73549
TS B	-2719.58	-1706534.369	-2718.825481	-1706062.989
TS B 8M	-2719.57	-1706530.396	-2718.814608	-1706056.167
TS C	-2758.86	-1731184.653	-2758.084598	-1730698.085
TS C 8M	-2758.85	-1731180.614	-2758.07423	-1730691.579
(A) N-H of product 2a hydrogen bonding only with methanol (Fig. 4)	-2758.91	-1731214.795	-2758.114434	-1730716.807
(B) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand (Fig. 4)	-2758.89	-1731203.538	-2758.10967	-1730713.818
(C) N-H of product 2a hydrogen bonding only with water (Fig. 4)	-2719.62	-1706560.801	-2718.855176	-1706081.623
(D) N-H of product 2a hydrogen bonding with sulfonyl oxygen of the TsDPEN ligand; energy difference in kcal/ mol (Fig. 4)	-2719.61	-1706553.128	-2718.853064	-1706080.297

The xyz coordinates of all the structures discussed in the manuscript.

3a_real_system

C 1.464 0.847 2.780
C 2.784 1.371 3.033
C 2.660 2.426 4.047
C 1.318 2.483 4.468
C 0.568 1.457 3.727
Rh 2.056 0.259 4.787
N 1.013 -0.395 6.538
C 1.836 -1.317 7.406
C 1.616 -2.766 7.015
C 0.679 -3.503 7.761
C 0.400 -4.837 7.459
C 1.068 -5.463 6.403
C 2.009 -4.744 5.660
C 2.281 -3.406 5.956
C 3.289 -0.771 7.389
C 3.393 0.377 8.399
C 3.330 1.720 8.004
C 3.380 2.748 8.951
C 3.506 2.449 10.310
C 3.588 1.112 10.715
C 3.529 0.088 9.766
N 3.666 -0.391 6.022
S 5.075 -1.063 5.440
O 4.893 -1.489 4.018
C 6.322 0.275 5.385
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C 7.582 2.008 6.493
C 8.348 2.225 5.334
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C 7.074 0.464 4.225
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O 5.619 -2.050 6.434
C 1.090 -0.083 1.668
C -0.918 1.278 3.779
C 0.710 3.427 5.458
C 3.796 3.289 4.496
C 3.998 1.115 2.196
H 3.946 -1.584 7.740
H 3.269 1.942 6.937
H 3.331 3.790 8.626
H 3.553 3.251 11.050
H 3.709 0.867 11.772
H 3.607 -0.953 10.089
H 1.459 -1.217 8.438
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H -0.327 -5.390 8.055
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H 0.771 0.439 7.083
H 6.869 -0.156 3.352
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H 5.993 0.889 7.434
H 9.160 4.160 5.873
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H 3.528 3.901 5.368
H 4.679 2.689 4.761

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H 4.914 1.408 2.723
H 4.096 0.051 1.946
H 0.858 0.489 0.753
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H 0.209 -0.688 1.917
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H -1.216 0.286 3.413
H -1.311 1.391 4.801
H 0.149 4.229 4.948
H -0.003 2.921 6.127
H 1.471 3.906 6.089

1a

C 0.056 0.005 -0.026
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C 2.533 0.004 1.408
C 2.538 0.007 -0.016
C 1.279 0.010 -0.667
C -1.247 -0.002 2.105
H 1.310 0.005 3.131
O 3.517 -0.004 2.382
O 3.527 0.004 -0.979
H 1.325 0.013 -1.759
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C -2.514 -0.014 0.074
N -2.397 -0.011 1.528
C -1.241 -0.000 3.615
H -2.277 -0.003 3.973
H -0.720 -0.884 4.014
H -0.726 0.888 4.014
H -1.253 0.877 -1.472
H -1.238 -0.878 -1.475
H -3.152 0.849 -0.175
H -3.132 -0.893 -0.172
C 4.931 0.002 -0.807
H 5.334 0.000 -1.828
H 5.295 0.904 -0.290
H 5.293 -0.899 -0.288
C 4.921 0.001 2.213
H 5.323 0.000 3.234
H 5.290 -0.898 1.694
H 5.283 0.905 1.697

Pathway (i) reactant complex

C -1.283 3.341 4.793
C -2.125 2.377 4.256
C -1.595 1.112 3.912
C -0.227 0.870 4.101
C 0.629 1.846 4.619
C 0.094 3.112 4.970
C -2.506 0.092 3.362
N -3.652 0.394 2.830
C -4.041 1.809 2.797
C -3.601 2.581 4.042
C -2.104 -1.355 3.402
O 1.952 1.570 4.884
C 2.735 1.071 3.779
O 0.777 4.153 5.522
C 2.187 4.320 5.291
O -4.383 -1.162 0.693

N -1.617 -0.958 -0.279
C -1.340 -0.259 -1.562
C -2.024 1.093 -1.653
C -2.950 1.351 -2.673
C -3.595 2.588 -2.761
C -3.325 3.587 -1.823
C -2.402 3.341 -0.800
C -1.757 2.106 -0.717
C 0.202 -0.177 -1.725
C 0.557 0.175 -3.163
C 0.469 -0.790 -4.176
C 0.760 -0.463 -5.502
C 1.147 0.838 -5.836
C 1.240 1.807 -4.835
C 0.945 1.475 -3.509
N 0.809 -1.464 -1.278
Rh -0.578 -2.806 -0.333
C -0.958 -4.476 -1.940
C -2.136 -4.279 -1.179
C -1.832 -4.509 0.232
C -0.437 -4.882 0.318
C 0.121 -4.790 -1.005
S 2.151 -1.193 -0.296
O 1.913 -0.145 0.767
C 3.389 -0.463 -1.420
C 3.811 -1.187 -2.538
C 4.774 -0.640 -3.382
C 5.330 0.625 -3.129
C 4.897 1.325 -1.995
C 3.930 0.790 -1.140
C 6.346 1.220 -4.070
O 2.691 -2.515 0.137
C 0.292 -5.355 1.538
C -2.855 -4.592 1.323
C -3.498 -3.941 -1.700
C -0.822 -4.458 -3.429
C 1.519 -5.144 -1.398
H 0.537 0.654 -1.078
H 0.197 -1.811 -3.907
H 0.690 -1.229 -6.278
H 1.379 1.093 -6.872
H 1.548 2.824 -5.084
H 1.025 2.236 -2.728
H -1.736 -0.910 -2.356
H -3.161 0.574 -3.412
H -4.308 2.772 -3.567
H -3.825 4.555 -1.890
H -2.179 4.119 -0.066
H -1.030 1.936 0.081
H -1.218 -0.415 0.493
H 0.000 -2.313 1.040
H -2.637 -1.040 -0.097
H 3.381 -2.169 -2.742
H 5.104 -1.206 -4.258
H 5.325 2.307 -1.774
H 3.591 1.330 -0.255
H 5.855 1.645 -4.961
H 6.914 2.028 -3.588
H 7.060 0.463 -4.424
H 3.683 0.732 4.210
H 2.252 0.240 3.248
H 2.925 1.879 3.051
H 2.782 3.605 5.873
H 2.429 4.213 4.221

H 2.404 5.346 5.612
H 0.195 -0.102 3.850
H -1.665 4.326 5.071
H -4.161 2.205 4.918
H -3.845 3.649 3.940
H -3.603 2.268 1.890
H -5.135 1.853 2.680
H -1.818 -1.649 4.423
H -2.936 -1.983 3.066
H -1.237 -1.563 2.751
H -4.243 -0.628 1.543
H -5.169 -0.774 0.276
H -0.888 -5.480 -3.844
H -1.610 -3.861 -3.909
H 0.149 -4.051 -3.741
H 1.585 -6.212 -1.672
H 1.849 -4.556 -2.265
H 2.226 -4.942 -0.585
H -4.117 -4.850 -1.785
H -4.025 -3.251 -1.024
H -3.452 -3.481 -2.697
H -3.380 -5.564 1.299
H -2.390 -4.495 2.314
H -3.613 -3.801 1.228
H 0.296 -6.457 1.582
H 1.333 -5.009 1.534
H -0.179 -4.985 2.458

TS B

C 0.739 -5.926 2.791
C 0.267 -4.851 3.551
C 0.344 -3.549 3.027
C 0.925 -3.352 1.770
C 1.425 -4.417 1.026
C 1.306 -5.731 1.529
C -0.271 -2.394 3.789
N -0.499 -2.569 5.174
C 0.068 -3.781 5.761
C -0.287 -5.022 4.940
C -1.530 -1.887 3.067
O 2.030 -4.170 -0.196
C 3.471 -4.161 -0.112
O 1.814 -6.829 0.863
C 1.231 -7.085 -0.427
N 0.629 -0.348 5.887
C 1.766 -0.256 6.838
C 1.388 -0.619 8.264
C 1.293 0.399 9.224
C 0.917 0.121 10.540
C 0.629 -1.191 10.919
C 0.725 -2.218 9.975
C 1.101 -1.933 8.661
C 2.929 -1.060 6.220
C 4.202 -0.873 7.037
C 4.950 0.309 6.950
C 6.087 0.496 7.738
C 6.495 -0.501 8.630
C 5.761 -1.686 8.721
C 4.624 -1.868 7.928
N 3.042 -0.596 4.811
Rh 1.268 0.338 4.061
C 1.791 2.449 3.920
C 0.353 2.320 4.060
C -0.150 1.621 2.911
C 0.982 1.315 2.043
C 2.161 1.839 2.650

S 3.782 -1.730 3.807
O 3.470 -3.138 4.221
C 5.584 -1.547 4.044
C 6.258 -0.465 3.476
C 7.636 -0.347 3.650
C 8.360 -1.300 4.386
C 7.661 -2.389 4.927
C 6.281 -2.520 4.761
C 9.843 -1.144 4.605
O 3.510 -1.309 2.393
O -2.325 -0.688 6.145
C 0.920 0.669 0.696
C -1.598 1.485 2.564
C -0.481 2.885 5.166
C 2.703 3.211 4.824
C 3.521 1.864 2.034
H 2.659 -2.132 6.253
H 4.647 1.072 6.230
H 6.662 1.421 7.653
H 7.386 -0.357 9.246
H 6.076 -2.474 9.408
H 4.057 -2.800 7.997
H 2.091 0.799 6.858
H 1.528 1.428 8.934
H 0.853 0.930 11.271
H 0.336 -1.415 11.947
H 0.508 -3.248 10.265
H 1.179 -2.746 7.938
H 0.137 -1.465 5.693
H 0.516 -1.455 3.659
H -0.178 0.167 6.262
H 5.708 0.269 2.889
H 8.164 0.496 3.198
H 8.206 -3.152 5.488
H 5.741 -3.374 5.170
H 10.045 -0.563 5.520
H 10.337 -2.119 4.722
H 10.321 -0.614 3.770
H 3.834 -3.952 -1.127
H 3.812 -3.373 0.576
H 3.853 -5.139 0.222
H 0.154 -7.302 -0.326
H 1.374 -6.237 -1.111
H 1.744 -7.973 -0.817
H 1.062 -2.345 1.372
H 0.688 -6.946 3.179
H -1.386 -5.140 4.917
H 0.127 -5.927 5.410
H 1.177 -3.735 5.826
H -0.326 -3.873 6.785
H -2.253 -2.715 3.000
H -1.996 -1.068 3.626
H -1.296 -1.557 2.045
H -1.842 -1.519 5.845
H -3.035 -0.999 6.729
H -1.968 2.438 2.148
H -1.773 0.707 1.812
H -2.212 1.247 3.444
H 0.888 1.435 -0.098
H 1.802 0.038 0.522
H 0.026 0.043 0.584
H 3.578 2.668 1.279
H 4.296 2.062 2.784
H 3.752 0.908 1.546
H 2.772 4.266 4.508
H 2.346 3.203 5.863
H 3.718 2.794 4.812

H -0.847 3.889 4.893
H -1.358 2.257 5.374
H 0.092 2.989 6.098

Pathway (i) product complex

C -1.410 3.311 4.308
C -2.205 2.279 3.787
C -1.603 1.045 3.485
C -0.226 0.884 3.694
C 0.566 1.916 4.192
C -0.040 3.149 4.524
C -2.422 -0.108 2.929
N -3.660 0.354 2.252
C -4.446 1.256 3.115
C -3.677 2.525 3.512
C -2.754 -1.141 4.018
O 1.921 1.719 4.380
C 2.724 2.115 3.245
O 0.682 4.233 4.975
C 1.369 4.041 6.226
O -4.386 -1.821 0.682
N -1.533 -1.256 -0.686
C -1.218 -0.216 -1.657
C -2.087 1.023 -1.496
C -3.071 1.312 -2.451
C -3.888 2.441 -2.331
C -3.724 3.309 -1.249
C -2.745 3.034 -0.288
C -1.940 1.897 -0.405
C 0.295 0.081 -1.545
C 0.778 0.822 -2.782
C 0.942 0.157 -4.006
C 1.334 0.854 -5.150
C 1.566 2.232 -5.089
C 1.407 2.904 -3.876
C 1.018 2.202 -2.731
N 0.970 -1.224 -1.307
Rh -0.294 -2.749 -0.614
C -0.411 -4.713 -1.504
C -1.556 -4.503 -0.630
C -1.045 -4.303 0.694
C 0.414 -4.467 0.654
C 0.788 -4.749 -0.689
S 2.500 -1.037 -0.628
O 2.566 0.193 0.229
C 3.655 -0.744 -2.009
C 3.967 -1.794 -2.875
C 4.856 -1.572 -3.926
C 5.441 -0.311 -4.130
C 5.122 0.719 -3.234
C 4.234 0.512 -2.176
C 6.367 -0.066 -5.293
O 2.909 -2.347 -0.036
C 1.329 -4.426 1.833
C -1.866 -4.108 1.925
C -2.997 -4.534 -1.031
C -0.476 -5.000 -2.968
C 2.155 -5.104 -1.176
H 0.455 0.731 -0.669
H 0.785 -0.923 -4.046
H 1.465 0.319 -6.094
H 1.874 2.777 -5.984
H 1.589 3.980 -3.817
H 0.902 2.729 -1.781
H -1.396 -0.590 -2.688
H -3.188 0.645 -3.310

H -4.645 2.648 -3.090
H -4.348 4.201 -1.159
H -2.594 3.717 0.551
H -1.176 1.698 0.349
H -3.367 0.888 1.423
H -1.828 -0.611 2.147
H -2.541 -1.402 -0.544
H 3.527 -2.779 -2.717
H 5.106 -2.395 -4.601
H 5.575 1.705 -3.366
H 3.989 1.312 -1.478
H 5.815 0.344 -6.154
H 7.153 0.657 -5.035
H 6.851 -0.995 -5.627
H 3.766 1.935 3.536
H 2.486 1.508 2.358
H 2.583 3.186 3.022
H 0.646 3.841 7.035
H 2.094 3.216 6.166
H 1.890 4.984 6.431
H 0.266 -0.056 3.433
H -1.851 4.280 4.557
H -4.153 2.989 4.393
H -3.764 3.268 2.699
H -5.373 1.522 2.586
H -4.746 0.690 4.009
H -3.286 -0.683 4.864
H -3.373 -1.950 3.605
H -1.827 -1.574 4.419
H -4.257 -1.049 1.321
H -5.289 -1.711 0.344
H 2.331 -6.185 -1.044
H 2.271 -4.885 -2.246
H 2.929 -4.551 -0.632
H 1.551 -5.449 2.182
H 2.273 -3.930 1.575
H 0.878 -3.881 2.674
H -2.107 -5.085 2.379
H -1.326 -3.520 2.679
H -2.811 -3.595 1.699
H -0.551 -6.087 -3.143
H -1.351 -4.527 -3.434
H 0.421 -4.641 -3.490
H -3.398 -5.558 -0.941
H -3.603 -3.870 -0.398
H -3.130 -4.219 -2.075

TS B 8M

C -0.180 -4.990 1.907
C -0.254 -4.153 3.020
C -0.004 -2.785 2.899
C 0.342 -2.259 1.654
C 0.446 -3.083 0.521
C 0.169 -4.450 0.668
S -0.714 -4.850 4.643
O -1.597 -3.829 5.293
C 0.861 -2.516 -0.811
N 0.700 -4.926 5.548
Rh 0.545 -4.436 7.653
C 0.511 -2.200 7.559
C 1.879 -2.683 7.647
C 2.011 -3.382 8.905
C 0.747 -3.325 9.599
C -0.174 -2.590 8.751
C 2.965 -2.385 6.670
C 3.252 -3.988 9.473

C 0.569 -3.738 11.024
C -1.552 -2.132 9.105
C -0.047 -1.303 6.504
C 1.498 -6.150 5.268
C 2.339 -6.091 3.999
C 3.129 -4.973 3.694
C 3.941 -4.960 2.559
C 3.976 -6.069 1.707
C 3.189 -7.185 1.997
C 2.376 -7.193 3.134
C 2.392 -6.389 6.513
C 3.198 -7.674 6.465
C 4.597 -7.625 6.540
C 5.360 -8.795 6.518
C 4.731 -10.038 6.421
C 3.337 -10.102 6.341
C 2.579 -8.929 6.361
N 1.478 -6.312 7.675
O -1.276 -6.212 4.345
O 1.436 -6.692 10.297
H 1.827 -7.391 10.846
N -0.793 -7.429 9.346
C -1.607 -6.493 8.736
C -2.625 -7.042 7.761
C -2.910 -8.423 7.744
C -2.092 -9.357 8.599
C -0.699 -8.763 8.780
C -3.368 -6.181 6.942
C -4.395 -6.656 6.130
C -4.724 -8.030 6.162
C -3.960 -8.893 6.949
O -5.078 -5.761 5.329
C -4.818 -5.928 3.917
O -5.725 -8.579 5.387
C -7.044 -8.052 5.624
C -2.242 -5.520 9.734
H 0.830 -7.029 5.177
H 3.084 -4.100 4.346
H 4.548 -4.080 2.335
H 4.612 -6.060 0.819
H 3.204 -8.054 1.335
H 1.756 -8.065 3.354
H 3.094 -5.545 6.596
H 5.095 -6.655 6.614
H 6.449 -8.735 6.577
H 5.324 -10.955 6.405
H 2.836 -11.069 6.262
H 1.491 -8.999 6.286
H -0.872 -5.633 8.035
H 1.849 -6.508 8.659
H -0.104 -2.136 3.768
H 0.528 -1.186 1.558
H 0.227 -5.107 -0.202
H -0.404 -6.051 2.018
H 1.956 -2.560 -0.932
H 0.419 -3.080 -1.644
H 0.563 -1.463 -0.912
H -5.337 -5.100 3.418
H -3.738 -5.869 3.719
H -5.211 -6.890 3.549
H -7.357 -8.254 6.662
H -7.091 -6.970 5.432
H -7.708 -8.587 4.935
H -3.113 -5.122 6.865
H -4.212 -9.956 6.936
H -2.561 -9.487 9.590
H -2.032 -10.353 8.132

H -0.193 -8.787 7.789
H -0.082 -9.367 9.462
H -3.032 -6.050 10.286
H -1.490 -5.169 10.446
H -2.691 -4.666 9.213
H 0.177 -7.081 9.914
H 0.735 -7.010 7.552
H 3.737 -3.271 10.159
H 3.007 -4.899 10.042
H 3.986 -4.238 8.694
H 3.380 -1.377 6.843
H 3.796 -3.099 6.752
H 2.586 -2.417 5.640
H -0.221 -0.295 6.918
H 0.648 -1.199 5.663
H -0.997 -1.691 6.115
H -1.526 -1.058 9.359
H -2.248 -2.252 8.263
H -1.958 -2.666 9.971
H 1.223 -3.125 11.668
H -0.460 -3.585 11.373
H 0.853 -4.799 11.161

Pathway (ii) reactant complex

C 3.982 -0.680 1.011
C 3.416 0.555 1.318
C 3.836 1.274 2.439
C 4.825 0.739 3.260
C 5.409 -0.509 2.981
C 4.976 -1.203 1.843
S 2.150 1.271 0.217
O 2.645 2.622 -0.184
C 6.453 -1.092 3.896
N 0.798 1.475 1.198
Rh -0.631 2.776 0.263
C -0.025 4.716 1.143
C -1.231 4.363 1.876
C -2.273 4.214 0.916
C -1.756 4.530 -0.408
C -0.357 4.876 -0.251
C 0.237 0.161 1.626
C 0.614 -0.202 3.056
C 0.542 0.753 4.079
C 0.847 0.412 5.397
C 1.233 -0.894 5.715
C 1.314 -1.852 4.702
C 1.005 -1.507 3.383
C -1.308 0.200 1.476
C -1.951 -1.172 1.573
C -2.846 -1.461 2.611
C -3.448 -2.719 2.712
C -3.164 -3.708 1.766
C -2.273 -3.431 0.724
C -1.671 -2.174 0.629
N -1.613 0.895 0.197
O 1.946 0.242 -0.872
O -4.364 1.004 -0.846
C -5.559 0.476 -0.276
N -3.512 -0.520 -2.965
C -2.342 -0.203 -3.430
C -1.347 -1.216 -3.836
C -1.798 -2.520 -4.121
C -3.279 -2.774 -4.025
C -3.855 -1.945 -2.877
C 0.024 -0.916 -3.918
C 0.958 -1.892 -4.280

C 0.501 -3.210 -4.556
 C -0.867 -3.491 -4.487
 O 2.296 -1.660 -4.414
 C 2.780 -0.342 -4.104
 O 1.315 -4.232 -4.967
 C 2.504 -4.510 -4.203
 C -1.995 1.256 -3.531
 C 0.566 5.394 -1.310
 C -2.586 4.691 -1.644
 C -3.699 3.858 1.201
 C -1.358 4.275 3.365
 C 1.307 4.999 1.755
 H 0.591 -0.648 0.962
 H 0.270 1.778 3.821
 H 0.789 1.170 6.182
 H 1.476 -1.160 6.745
 H 1.622 -2.873 4.937
 H 1.074 -2.260 2.594
 H -1.714 0.838 2.276
 H -3.066 -0.693 3.357
 H -4.137 -2.927 3.532
 H -3.630 -4.692 1.843
 H -2.039 -4.199 -0.015
 H -0.968 -1.980 -0.185
 H -1.196 0.371 -0.578
 H -0.043 2.312 -1.120
 H -2.635 0.944 0.011
 H 3.387 2.243 2.663
 H 5.154 1.300 4.139
 H 5.424 -2.170 1.600
 H 3.645 -1.216 0.122
 H 5.985 -1.566 4.775
 H 7.050 -1.861 3.386
 H 7.138 -0.319 4.272
 H 3.864 -0.391 -4.254
 H 2.354 0.403 -4.797
 H 2.558 -0.064 -3.061
 H 3.261 -3.726 -4.324
 H 2.260 -4.623 -3.134
 H 2.880 -5.464 -4.591
 H 0.372 0.086 -3.676
 H -1.181 -4.511 -4.716
 H -3.774 -2.480 -4.969
 H -3.490 -3.843 -3.872
 H -3.483 -2.330 -1.908
 H -4.952 -2.024 -2.851
 H -1.636 1.498 -4.543
 H -2.878 1.865 -3.305
 H -1.195 1.543 -2.826
 H -4.167 0.500 -1.701
 H -5.804 1.075 0.612
 H -6.411 0.541 -0.975
 H -5.444 -0.576 0.041
 H -4.320 4.769 1.244
 H -4.115 3.211 0.415
 H -3.805 3.342 2.165
 H -1.592 5.261 3.805
 H -2.158 3.586 3.672
 H -0.424 3.932 3.831
 H 1.381 6.061 2.046
 H 1.467 4.395 2.659
 H 2.120 4.767 1.056
 H 0.630 6.495 -1.267
 H 1.576 4.984 -1.185
 H 0.217 5.118 -2.314
 H -3.045 5.695 -1.684
 H -1.982 4.567 -2.553

H -3.401 3.954 -1.680
TS C
 C 6.268 -2.536 4.964
 C 5.603 -1.586 4.189
 C 6.304 -0.529 3.605
 C 7.677 -0.415 3.820
 C 8.368 -1.345 4.614
 C 7.643 -2.408 5.171
 S 3.809 -1.761 3.898
 O 3.589 -1.390 2.462
 C 9.844 -1.192 4.876
 N 3.055 -0.579 4.835
 Rh 1.327 0.366 3.989
 C 2.276 1.789 2.522
 C 1.957 2.446 3.782
 C 0.518 2.392 3.950
 C -0.040 1.685 2.828
 C 1.062 1.310 1.948
 C 2.879 -0.996 6.253
 C 4.118 -0.803 7.118
 C 4.890 0.363 7.033
 C 5.992 0.554 7.869
 C 6.342 -0.423 8.806
 C 5.583 -1.593 8.896
 C 4.482 -1.780 8.056
 C 1.702 -0.158 6.795
 C 1.262 -0.470 8.216
 C 1.192 0.570 9.153
 C 0.760 0.336 10.461
 C 0.389 -0.951 10.854
 C 0.459 -1.999 9.931
 C 0.893 -1.760 8.625
 N 0.606 -0.274 5.801
 O 3.466 -3.148 4.353
 N -0.475 -2.518 5.091
 C -0.231 -2.338 3.711
 C 0.382 -3.494 2.949
 C 0.307 -4.796 3.473
 C -0.248 -4.970 4.861
 C 0.097 -3.727 5.683
 C 0.969 -3.295 1.695
 C 1.473 -4.358 0.951
 C 1.350 -5.673 1.451
 C 0.780 -5.870 2.712
 O 2.085 -4.105 -0.266
 C 3.526 -4.135 -0.182
 O 1.855 -6.771 0.782
 C 1.273 -7.020 -0.509
 C -1.474 -1.805 2.980
 O -2.384 -0.722 6.075
 C -3.312 -1.162 7.057
 C 0.946 0.650 0.613
 C -1.499 1.601 2.512
 C -0.265 3.033 5.050
 C 2.921 3.179 4.654
 C 3.622 1.735 1.877
 H 2.590 -2.062 6.309
 H 4.633 1.110 6.280
 H 6.586 1.467 7.785
 H 7.205 -0.276 9.459
 H 5.852 -2.366 9.619
 H 3.895 -2.699 8.124
 H 2.039 0.894 6.795
 H 1.489 1.579 8.853
 H 0.716 1.162 11.175

H 0.051 -1.139 11.875
 H 0.178 -3.010 10.231
 H 0.950 -2.589 7.920
 H 0.124 -1.407 5.612
 H 0.575 -1.408 3.592
 H -0.216 0.249 6.131
 H 5.779 0.186 2.973
 H 8.226 0.408 3.356
 H 8.163 -3.154 5.778
 H 5.707 -3.370 5.386
 H 10.022 -0.569 5.768
 H 10.324 -2.164 5.055
 H 10.356 -0.707 4.032
 H 3.894 -3.906 -1.190
 H 3.885 -3.375 0.529
 H 3.884 -5.131 0.124
 H 0.195 -7.233 -0.411
 H 1.420 -6.170 -1.191
 H 1.783 -7.909 -0.902
 H 1.106 -2.288 1.299
 H 0.729 -6.891 3.097
 H -1.346 -5.096 4.835
 H 0.172 -5.872 5.332
 H 1.205 -3.674 5.756
 H -0.307 -3.824 6.703
 H -2.210 -2.619 2.902
 H -1.931 -0.981 3.541
 H -1.224 -1.471 1.964
 H -1.852 -1.513 5.757
 H -3.920 -0.297 7.360
 H -3.998 -1.938 6.669
 H -2.815 -1.561 7.962
 H 3.050 4.219 4.306
 H 2.577 3.222 5.697
 H 3.910 2.701 4.645
 H 3.676 2.465 1.052
 H 4.417 1.987 2.591
 H 3.830 0.735 1.476
 H 0.910 1.409 -0.187
 H 1.807 -0.002 0.417
 H 0.033 0.046 0.531
 H -1.844 2.561 2.091
 H -1.717 0.820 1.774
 H -2.104 1.396 3.406
 H -0.555 4.058 4.764
 H -1.189 2.479 5.268
 H 0.315 3.105 5.979

Pathway (ii) product complex

C 2.910 -0.546 1.217
 C 2.310 0.676 1.506
 C 2.972 1.636 2.275
 C 4.244 1.354 2.768
 C 4.873 0.126 2.500
 C 4.187 -0.812 1.717
 S 0.685 1.091 0.794
 O 0.884 2.416 0.133
 C 6.240 -0.177 3.057
 N -0.395 1.285 2.061
 Rh -1.758 2.901 2.060
 C -0.776 4.865 1.508
 C -1.553 4.946 2.735
 C -2.940 4.666 2.416
 C -2.995 4.328 1.015
 C -1.653 4.481 0.451
 C -1.001 -0.011 2.492

C -0.038 -0.984 3.152
C 0.770 -0.586 4.228
C 1.606 -1.503 4.866
C 1.643 -2.836 4.442
C 0.841 -3.242 3.373
C 0.009 -2.319 2.733
C -2.155 0.339 3.460
C -3.131 -0.814 3.629
C -3.148 -1.577 4.803
C -4.043 -2.642 4.951
C -4.937 -2.953 3.924
C -4.931 -2.194 2.748
C -4.034 -1.134 2.602
N -2.800 1.530 2.939
O 0.308 -0.083 -0.074
N -1.426 -0.039 -2.564
C -0.522 0.234 -3.705
C 0.380 -0.943 -4.071
C 0.164 -2.231 -3.551
C -0.945 -2.485 -2.555
C -2.011 -1.390 -2.613
C 1.458 -0.736 -4.945
C 2.312 -1.771 -5.321
C 2.060 -3.076 -4.843
C 1.006 -3.278 -3.954
O 3.353 -1.494 -6.192
C 4.663 -1.652 -5.616
O 2.861 -4.154 -5.183
C 2.804 -4.520 -6.574
C -1.325 0.727 -4.920
O -3.443 1.859 -2.274
C -4.584 1.428 -2.996
C -1.320 4.362 -0.998
C -4.214 3.989 0.224
C -4.100 4.755 3.357
C -1.034 5.390 4.063
C 0.666 5.230 1.379
H -1.446 -0.510 1.614
H 0.759 0.458 4.546
H 2.236 -1.177 5.697
H 2.297 -3.554 4.942
H 0.864 -4.280 3.034
H -0.613 -2.635 1.892
H -1.703 0.543 4.454
H -2.447 -1.337 5.606
H -4.042 -3.228 5.873
H -5.639 -3.781 4.039
H -5.630 -2.430 1.942
H -4.034 -0.532 1.690
H -0.874 0.031 -1.696
H 0.126 1.062 -3.374
H -3.686 1.733 3.406
H 2.496 2.597 2.478
H 4.768 2.107 3.363
H 4.661 -1.770 1.489
H 2.380 -1.274 0.602
H 6.167 -0.609 4.069
H 6.777 -0.903 2.431
H 6.855 0.730 3.134
H 5.377 -1.413 -6.414
H 4.804 -0.948 -4.778
H 4.828 -2.681 -5.262
H 1.782 -4.831 -6.850
H 3.122 -3.691 -7.224
H 3.487 -5.370 -6.692
H 1.671 0.260 -5.339
H 0.841 -4.293 -3.582

H -1.396 -3.475 -2.734
H -0.517 -2.510 -1.537
H -2.714 -1.490 -1.772
H -2.603 -1.483 -3.538
H -2.029 -0.042 -5.268
H -1.892 1.631 -4.655
H -0.657 0.965 -5.760
H -2.710 1.170 -2.383
H -5.377 2.180 -2.863
H -4.393 1.334 -4.083
H -4.977 0.457 -2.636
H -4.588 4.894 -0.285
H -3.993 3.236 -0.547
H -5.021 3.612 0.866
H -1.403 5.352 -1.480
H -0.297 3.993 -1.136
H -2.009 3.680 -1.516
H 0.762 6.301 1.130
H 1.211 5.063 2.319
H 1.155 4.640 0.596
H -1.050 6.492 4.129
H -1.644 4.999 4.888
H 0.001 5.064 4.221
H -4.515 5.776 3.367
H -4.912 4.077 3.062
H -3.808 4.506 4.387

TS C 8M

C -0.210 -4.996 1.883
C -0.235 -4.190 3.025
C 0.061 -2.816 2.904
C 0.426 -2.305 1.652
C 0.483 -3.118 0.522
C 0.121 -4.480 0.629
C -0.123 -1.899 4.098
N -0.233 -2.530 5.330
C 0.159 -3.923 5.440
C -0.566 -4.754 4.383
C -1.269 -0.906 3.862
O 0.880 -2.563 -0.680
C 2.181 -3.011 -1.121
O 0.159 -5.352 -0.439
C -0.699 -5.008 -1.542
O 0.085 -1.135 7.405
C -0.458 -1.702 8.571
N 2.389 -1.315 6.067
C 3.837 -1.549 6.283
C 4.121 -2.635 7.307
C 4.754 -2.304 8.513
C 5.009 -3.278 9.482
C 4.630 -4.603 9.258
C 3.998 -4.946 8.059
C 3.749 -3.971 7.092
C 4.437 -1.818 4.879
C 5.955 -1.922 4.953
C 6.755 -0.779 5.092
C 8.142 -0.887 5.207
C 8.753 -2.145 5.186
C 7.965 -3.291 5.043
C 6.577 -3.177 4.926
N 3.940 -0.736 3.988
Rh 2.172 0.265 4.714
C 3.078 2.190 5.276
C 1.995 1.874 6.181
C 0.763 1.845 5.433
C 1.095 2.133 4.046

C 2.506 2.349 3.950
S 3.946 -1.164 2.362
O 3.711 -2.634 2.162
C 5.634 -0.860 1.739
C 6.048 0.443 1.457
C 7.334 0.663 0.967
C 8.224 -0.402 0.754
C 7.775 -1.703 1.027
C 6.489 -1.939 1.516
C 9.626 -0.154 0.261
O 3.064 -0.182 1.652
C 0.141 2.334 2.914
C -0.586 1.754 6.066
C 2.085 1.689 7.661
C 4.499 2.455 5.645
C 3.222 2.821 2.727
H 4.051 -2.799 4.541
H 6.279 0.201 5.077
H 8.750 0.013 5.308
H 9.838 -2.231 5.274
H 8.433 -4.277 5.018
H 5.967 -4.075 4.807
H 4.261 -0.606 6.658
H 5.056 -1.269 8.692
H 5.506 -3.000 10.413
H 4.826 -5.366 10.013
H 3.700 -5.980 7.874
H 3.265 -4.261 6.156
H 0.896 -1.096 4.094
H 1.767 -1.170 6.914
H 5.356 1.273 1.595
H 7.654 1.682 0.735
H 8.443 -2.550 0.851
H 6.138 -2.952 1.716
H 10.320 -0.018 1.106
H 9.999 -0.999 -0.333
H 9.681 0.752 -0.356
H 2.412 -2.425 -2.019
H 2.934 -2.819 -0.342
H 2.171 -4.085 -1.368
H -1.754 -5.008 -1.221
H -0.446 -4.026 -1.966
H -0.550 -5.793 -2.294
H 0.747 -1.267 1.543
H -0.453 -6.060 1.951
H -1.653 -4.711 4.575
H -0.264 -5.812 4.442
H 1.251 -4.087 5.293
H -0.078 -4.260 6.460
H -2.185 -1.480 3.653
H -1.435 -0.303 4.759
H -1.061 -0.257 3.004
H -0.190 -1.861 6.343
H 1.972 -2.141 5.618
H -1.461 -2.146 8.394
H 0.177 -2.507 9.003
H -0.587 -0.940 9.366
H 1.848 2.637 8.174
H 1.366 0.928 7.999
H 3.094 1.391 7.979
H 4.659 3.534 5.821
H 4.789 1.929 6.565
H 5.184 2.143 4.846
H 2.932 3.860 2.496
H 4.310 2.807 2.872
H 2.987 2.191 1.859
H 0.052 3.411 2.690

H 0.493 1.838 2.000
H -0.862 1.961 3.150
H -0.743 2.619 6.733
H -1.391 1.768 5.321
H -0.668 0.835 6.676

Pathway (iii) reactant complex

C 4.908 -0.650 2.485
C 4.002 -1.253 1.609
C 3.864 -2.639 1.572
C 4.634 -3.426 2.432
C 5.541 -2.848 3.330
C 5.669 -1.448 3.336
S 3.059 -0.217 0.438
O 4.065 0.702 -0.174
C 6.344 -3.699 4.280
N 2.016 0.720 1.379
Rh 1.414 2.535 0.395
C 0.949 4.688 0.754
C 1.546 4.503 -0.554
C 2.885 3.992 -0.344
C 3.084 3.877 1.084
C 1.911 4.352 1.771
C 0.871 -0.075 1.897
C 1.158 -0.750 3.233
C 1.795 -0.047 4.265
C 2.000 -0.640 5.511
C 1.574 -1.952 5.744
C 0.945 -2.664 4.720
C 0.740 -2.065 3.474
C -0.328 0.887 2.064
C -1.612 0.205 2.499
C -2.166 0.491 3.755
C -3.348 -0.124 4.175
C -3.996 -1.036 3.340
C -3.454 -1.328 2.084
C -2.272 -0.714 1.667
N -0.468 1.652 0.793
O 2.334 -1.191 -0.454
N -1.366 0.192 -1.715
C -0.241 -0.363 -2.482
C -0.638 -1.544 -3.363
C -1.826 -1.176 -4.211
C -2.774 -0.292 -3.648
C -2.528 0.227 -2.282
C -3.907 0.066 -4.397
C -4.115 -0.435 -5.681
C -3.194 -1.363 -6.218
C -2.054 -1.703 -5.481
O -5.248 -0.041 -6.370
C -4.981 0.755 -7.541
O -3.340 -1.908 -7.475
C -4.519 -2.717 -7.664
C -3.677 0.846 -1.526
C 3.934 3.770 -1.388
C 0.955 4.935 -1.861
C -0.417 5.245 1.003
C 1.753 4.526 3.249
C 4.350 3.423 1.735
H 0.567 -0.853 1.171
H 2.156 0.964 4.066
H 2.503 -0.081 6.304
H 1.737 -2.419 6.718
H 0.617 -3.692 4.889
H 0.248 -2.625 2.675
H -0.048 1.623 2.834

H -1.654 1.195 4.416
H -3.761 0.107 5.159
H -4.919 -1.520 3.666
H -3.955 -2.042 1.426
H -1.862 -0.944 0.680
H -0.771 1.053 -0.008
H 1.342 1.706 -0.939
H -1.193 2.367 0.908
H 5.021 0.434 2.487
H 6.382 -0.977 4.018
H 4.529 -4.514 2.401
H 3.167 -3.086 0.863
H 5.891 -3.701 5.285
H 6.397 -4.742 3.940
H 7.372 -3.322 4.389
H -5.958 0.982 -7.982
H -4.479 1.696 -7.260
H -4.359 0.212 -8.269
H -4.490 -3.593 -6.996
H -5.440 -2.145 -7.480
H -4.487 -3.054 -8.706
H -4.647 0.767 -4.008
H -1.348 -2.408 -5.926
H -0.897 -2.407 -2.721
H 0.211 -1.858 -3.985
H 0.168 0.456 -3.103
H 0.556 -0.644 -1.781
H -4.548 0.174 -1.498
H -3.371 1.073 -0.499
H -4.006 1.780 -2.009
H 2.131 5.507 3.588
H 0.699 4.465 3.559
H 2.306 3.758 3.808
H 5.037 4.276 1.874
H 4.158 2.987 2.726
H 4.853 2.666 1.121
H 4.639 4.619 -1.424
H 4.500 2.852 -1.185
H 3.487 3.665 -2.386
H -0.377 6.343 1.098
H -1.106 5.018 0.176
H -0.856 4.858 1.934
H 1.189 5.994 -2.069
H 1.349 4.338 -2.694
H -0.138 4.830 -1.870

TS A

C 6.705 -1.092 4.748
C 5.926 -2.151 5.219
C 6.476 -3.116 6.062
C 7.811 -3.001 6.454
C 8.610 -1.935 6.015
C 8.037 -0.991 5.147
S 4.181 -2.290 4.694
O 4.159 -1.900 3.250
C 10.038 -1.795 6.477
N 3.338 -1.119 5.562
Rh 1.844 0.022 4.541
C 1.506 2.223 4.740
C 0.773 1.714 3.595
C 1.752 1.230 2.639
C 3.055 1.409 3.194
C 2.904 2.026 4.503
C 2.912 -1.577 6.912
C 4.020 -1.559 7.953
C 4.891 -0.467 8.072

C 5.870 -0.438 9.066
C 5.994 -1.505 9.963
C 5.134 -2.600 9.851
C 4.157 -2.625 8.852
C 1.736 -0.651 7.324
C 1.091 -1.025 8.652
C 1.542 -0.426 9.839
C 0.974 -0.751 11.073
C -0.069 -1.679 11.142
C -0.536 -2.273 9.967
C 0.038 -1.949 8.735
N 0.790 -0.639 6.196
O 3.777 -3.693 5.067
N -0.088 -2.910 5.112
C 0.592 -4.128 5.574
C 0.285 -5.282 4.627
C 0.714 -4.895 3.235
C 0.604 -3.538 2.858
C 0.033 -2.562 3.813
C 1.043 -3.145 1.585
C 1.590 -4.059 0.692
C 1.621 -5.431 1.037
C 1.197 -5.821 2.312
O 2.097 -3.595 -0.508
C 3.542 -3.620 -0.550
O 2.135 -6.402 0.210
C 1.546 -6.494 -1.102
C -1.023 -1.609 3.302
C 1.483 0.772 1.241
C -0.683 1.940 3.336
C 0.896 2.914 5.920
C 4.033 2.444 5.388
C 4.345 1.179 2.472
H 2.513 -2.606 6.875
H 4.811 0.350 7.354
H 6.545 0.417 9.140
H 6.761 -1.485 10.739
H 5.225 -3.441 10.543
H 3.487 -3.484 8.766
H 2.177 0.357 7.458
H 2.359 0.297 9.793
H 1.345 -0.275 11.982
H -0.519 -1.932 12.104
H -1.357 -2.993 10.008
H -0.352 -2.408 7.826
H 0.101 -1.999 5.747
H 1.252 -1.389 3.854
H 0.047 0.029 6.431
H 6.274 -0.368 4.056
H 8.649 -0.166 4.771
H 8.239 -3.757 7.117
H 5.858 -3.949 6.397
H 10.094 -1.210 7.410
H 10.493 -2.775 6.680
H 10.655 -1.278 5.729
H 3.825 -3.164 -1.507
H 3.961 -3.036 0.284
H 3.926 -4.651 -0.503
H 0.472 -6.730 -1.021
H 1.674 -5.564 -1.674
H 2.063 -7.321 -1.601
H 1.046 -2.094 1.297
H 1.268 -6.880 2.571
H -0.795 -5.513 4.646
H 0.819 -6.186 4.954
H 1.686 -3.983 5.606
H 0.233 -4.344 6.591

H -1.932 -2.193 3.081
H -1.266 -0.859 4.064
H -0.710 -1.101 2.384
H 1.585 1.617 0.537
H 2.195 -0.002 0.929
H 0.466 0.375 1.121
H -0.858 2.965 2.965
H -1.078 1.250 2.579
H -1.289 1.818 4.245
H 0.810 3.998 5.733
H -0.116 2.544 6.133
H 1.499 2.785 6.829
H 4.502 3.372 5.017
H 3.695 2.633 6.416
H 4.812 1.669 5.428
H 4.417 1.840 1.591
H 5.204 1.404 3.118
H 4.442 0.137 2.139

Pathway (iii) product complex

C 2.633 -1.073 -0.371
C 2.223 -0.665 0.901
C 3.147 -0.512 1.932
C 4.498 -0.773 1.681
C 4.938 -1.192 0.417
C 3.983 -1.333 -0.603
S 0.437 -0.393 1.174
O -0.005 0.461 0.017
C 6.389 -1.513 0.164
N 0.269 0.450 2.591
Rh 0.431 2.496 2.828
C 1.214 4.486 3.146
C 0.004 4.559 2.376
C 0.236 3.842 1.122
C 1.608 3.393 1.105
C 2.200 3.741 2.360
C -0.271 -0.303 3.761
C 0.828 -0.906 4.625
C 1.609 -0.134 5.503
C 2.619 -0.726 6.265
C 2.867 -2.099 6.165
C 2.096 -2.876 5.297
C 1.085 -2.282 4.535
C -1.191 0.675 4.530
C -2.658 0.594 4.124
C -3.617 0.183 5.060
C -4.969 0.097 4.713
C -5.378 0.419 3.417
C -4.428 0.828 2.474
C -3.081 0.925 2.825
N -0.644 2.022 4.367
O -0.189 -1.749 1.293
N -1.674 -1.328 -2.187
C -0.924 -2.555 -2.423
C -1.454 -3.202 -3.699
C -1.452 -2.209 -4.839
C -1.413 -0.824 -4.585
C -1.378 -0.276 -3.162
C -1.343 0.057 -5.674
C -1.338 -0.393 -6.993
C -1.436 -1.777 -7.247
C -1.472 -2.658 -6.168
O -1.281 0.540 -8.018
C -0.059 0.503 -8.774
O -1.426 -2.294 -8.533
C -2.586 -1.958 -9.316

C -2.367 0.874 -2.939
C -0.732 3.713 -0.004
C -1.244 5.297 2.736
C 1.471 5.124 4.474
C 3.612 3.483 2.774
C 2.298 2.760 -0.059
H -0.884 -1.135 3.388
H 1.417 0.938 5.585
H 3.212 -0.114 6.949
H 3.654 -2.561 6.764
H 2.279 -3.949 5.212
H 0.492 -2.887 3.845
H -1.141 0.391 5.599
H -3.298 -0.079 6.072
H -5.703 -0.223 5.456
H -6.432 0.348 3.139
H -4.740 1.069 1.455
H -2.341 1.242 2.087
H -1.466 -0.966 -1.253
H -0.348 0.128 -3.004
H -1.188 2.720 4.880
H 1.902 -1.180 -1.175
H 4.302 -1.652 -1.599
H 5.223 -0.655 2.491
H 2.813 -0.192 2.920
H 7.046 -0.998 0.879
H 6.574 -2.594 0.267
H 6.694 -1.227 -0.851
H -0.157 1.270 -9.552
H 0.802 0.747 -8.130
H 0.100 -0.480 -9.240
H -3.500 -2.361 -8.847
H -2.690 -0.869 -9.442
H -2.441 -2.434 -10.294
H -1.272 1.136 -5.517
H -1.515 -3.729 -6.386
H -2.481 -3.559 -3.514
H -0.847 -4.081 -3.971
H 0.172 -2.379 -2.534
H -1.059 -3.220 -1.558
H -3.392 0.537 -3.146
H -2.315 1.204 -1.891
H -2.141 1.741 -3.577
H 2.629 3.542 -0.763
H 3.184 2.191 0.248
H 1.629 2.075 -0.595
H 4.251 4.345 2.514
H 3.693 3.327 3.858
H 4.022 2.599 2.272
H 1.939 6.114 4.343
H 0.543 5.270 5.042
H 2.148 4.516 5.089
H -1.246 6.298 2.273
H -2.140 4.768 2.387
H -1.337 5.437 3.821
H -0.543 4.496 -0.759
H -0.633 2.733 -0.489
H -1.769 3.825 0.339

2a

C -3.186 2.695 1.167
C -2.835 2.151 -0.078
C -1.797 2.750 -0.809
C -1.108 3.842 -0.250
C -1.445 4.362 1.001
C -2.526 3.790 1.715

C -3.562 0.934 -0.604
C -2.740 0.241 -1.687
N -2.353 1.248 -2.673
C -1.359 2.200 -2.164
C -1.157 3.290 -3.222
O -0.783 5.396 1.617
C 0.359 5.934 0.957
O -2.887 4.209 2.978
C -3.368 5.559 3.075
H -1.985 0.805 -3.517
H -0.376 1.696 -1.997
H -0.277 4.281 -0.801
H -3.993 2.250 1.754
H -3.771 0.237 0.223
H -4.535 1.231 -1.032
H -1.864 -0.264 -1.222
H -3.341 -0.531 -2.189
H -0.888 2.832 -4.188
H -2.084 3.863 -3.359
H -0.347 3.981 -2.953
H 1.135 5.166 0.801
H 0.095 6.386 -0.013
H 0.748 6.713 1.624
H -3.674 5.694 4.120
H -2.587 6.290 2.822
H -4.243 5.709 2.419

3a_product

C 6.298 -3.533 2.622
C 7.339 -2.684 3.013
C 7.856 -1.740 2.128
C 7.322 -1.648 0.839
C 6.283 -2.489 0.417
C 5.779 -3.430 1.333
S 8.016 -2.890 4.699
O 8.914 -4.088 4.654
C 5.734 -2.409 -0.983
N 8.902 -1.524 5.044
C 10.387 -1.668 5.057
C 11.012 -1.305 3.715
C 11.173 0.026 3.293
C 11.725 0.314 2.042
C 12.126 -0.721 1.191
C 11.973 -2.047 1.602
C 11.423 -2.334 2.855
C 10.908 -0.803 6.231
C 11.081 -1.570 7.537
C 12.362 -1.729 8.087
C 12.550 -2.427 9.284
C 11.452 -2.982 9.946
C 10.170 -2.832 9.405
C 9.983 -2.126 8.215
N 10.008 0.340 6.373
Rh 8.162 0.248 5.787
C 7.304 2.229 5.932
C 7.022 1.490 7.130
C 6.209 0.332 6.754
C 5.942 0.410 5.336
C 6.649 1.540 4.817
O 6.814 -2.946 5.593
C 7.416 1.857 8.525
C 8.055 3.517 5.826
C 6.647 2.009 3.399
C 5.016 -0.483 4.578
C 5.642 -0.683 7.686
H 10.635 -2.719 5.259

H	10.859	0.836	3.955
H	11.850	1.354	1.731
H	12.559	-0.493	0.214
H	12.285	-2.863	0.947
H	11.290	-3.372	3.170
H	11.913	-0.440	5.941
H	13.224	-1.302	7.565
H	13.554	-2.540	9.697
H	11.594	-3.532	10.878
H	9.309	-3.273	9.912
H	8.982	-2.014	7.792
H	10.301	0.967	7.126
H	5.894	-4.260	3.329
H	4.965	-4.094	1.029
H	7.730	-0.908	0.145
H	8.666	-1.082	2.446
H	6.015	-1.466	-1.472
H	6.120	-3.232	-1.606
H	4.636	-2.486	-0.992
H	7.592	2.500	3.133
H	6.488	1.176	2.701
H	5.836	2.741	3.238
H	5.244	-0.493	3.505
H	5.073	-1.516	4.943
H	3.978	-0.127	4.697
H	5.660	-1.680	7.228
H	6.205	-0.726	8.627
H	4.595	-0.431	7.934
H	8.300	2.509	8.540
H	6.597	2.398	9.029
H	7.646	0.967	9.126
H	8.633	3.571	4.894
H	7.359	4.373	5.836
H	8.755	3.652	6.661

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