Supporting Information

Template-controlled synthesis of chiral cyclohexylhemi-cucurbit[8]uril

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1 General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Solvents used for flash chromatography were reagent grade, which were dried and distilled prior to use according to standard procedures. (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** was synthesized[1] starting from (*R*,*R*)-1,2-cylohexanediammonium tartaric salt. The salt was obtained via crystallization[2] from 1,2-cyclohexanediamine *cis-/trans-* and *meso-* mixture with *L*-(+)-tartaric acid.

Flash chromatography was run over Thomar CC Silica Gel 60 (0.04-0.063 mm) stationary phase. Infrared spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer and are reported in wavenumbers. Intensities of the peaks are reported using the following abbreviations: vs-very strong, s- strong, w-weak. Elemental analysis was performed on an Elementar vario MICRO cube instrument in CHNS mode. Optical rotation was measured with an Anton Paar MCP 500 polarimeter. HPLC based reaction rate monitoring was performed on an Agilent 1200 Series HPLC system with a Kinetex C18 column (2.1x100 mm, 2.6 µm) and UV-detection at 210 nm.[3] Identification of reaction products and traces was performed by RP-HPLC-HRMS on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer with a Zorbax Eclipse Plus C18 column (2.1x150 mm, 1.8 µm) and AJ-ESI ionization. 1D ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance III 400 MHz spectrometer. *J* values are given in Hz. Chemical shifts were referenced to the residual solvent signal.

^{1}H diffusion NMR and reaction kinetics experiments were performed on a Bruker Avance III 800 MHz spectrometer using a Bruker PADUL probe equipped with a z-gradient coil and regular 5 mm NMR tubes. Probe temperature was set to 288 K and each sample was allowed to thermally equilibrate in the probe for at least 20 min prior to diffusion measurements. ^{1}H diffusion NMR experiments utilized the standard convection compensated pulse program dstebpgp3s with bipolar rectangular gradient pulses with 1 ms pulse duration, 150 ms diffusion time, 5 ms LED delay and 3 spoil gradients.

^{19}F Diffusion NMR experiments were performed on a Bruker Avance III 400 MHz spectrometer using a Bruker BBO probe equipped with a z-gradient coil and Shigemi tubes. Probe temperature was set to 296 K and each sample was allowed to thermally equilibrate in the probe for at least 20 min prior to diffusion measurements. ^{19}F diffusion NMR experiments utilized the standard pulse program stebpgp1s with rectangular gradient pulses with 0.7 ms pulse duration, 100 ms diffusion time and 1 spoil gradient.

In all diffusion NMR experiments the gradient was varied from 5% to 95% of maximum power linearly in 32 steps. 4 dummy scans and 16 scans were collected at each gradient step. All 32 rows of diffusion datasets were phase and baseline corrected, diffusion coefficients D were calculated with the Bruker TopSpin T1/T2 module and the D dimension of all datasets normalized according to residual solvent peaks. 2D DOSY spectra were generated with Bruker TopSpin DOSY module.

Single crystal X-ray diffraction data was collected on a Rigaku Compact HomeLab diffractometer, equipped with a Saturn 944 HG CCD detector and Oxford Cryostream cooling system, at T = 200.0(1) K using monochromatic Cu-$K\alpha$ radiation (1.54178Å) from a MicroMax^{TM}-003 sealed tube microfocus X-ray source. The strategy of data collection was calculated using Rigaku *CollectionStrategy*[4], the

program package *XDS*[5] was used for data integration, reduction and for applying empirical absorption corrections. The structure was solved using *SHELXD*[6]; and refined against F^2 with *SHELXL-2013*[6] through *OLEX2*[7] program package. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were treated as riding on their parent carbon and oxygen atoms, with $U_{iso}(H) = 1.2U_{iso}(C)$ for CH and CH_2; $U_{iso}(H) = 1.5U_{iso}(C)$ for CH_3 and OH. The contribution of the diffuse solvent to the structure factors was calculated with SQUEEZE procedure[8] of *PLATON*[9], and accounted for in the final refinement cycles.

2 Experimental Procedures and Compound Characterization Data

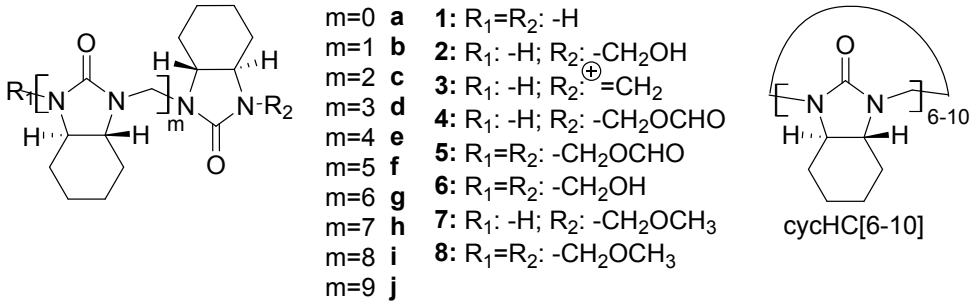
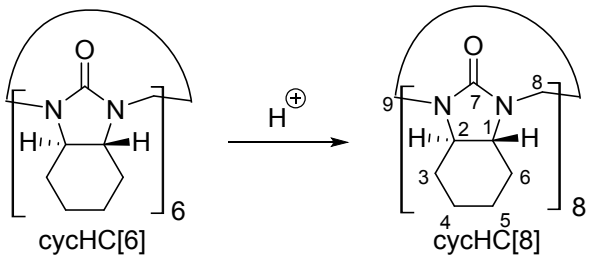


Figure S1. Structures of compounds observed in reaction mixtures by HRMS.

2.1 Synthetic procedures

2.1.1 Screening the conditions for the synthesis of cycHC[8] from cycHC[6]



Acetonitrile or other co-solvent was added to a solution of (*all-R*)-cycHC[6] HCl[10] complex in a carboxylic acid. The resulting 0.04 M solution was stirred at rt or at 100°C for 2 to 72 hours, according to specific conditions, as outlined in Table S1. Reaction progress and cycHC[8]:cycHC[6] ratios were monitored by HPLC-UV and TLC.

Table S1. Screening the reaction conditions for the transformation of cycHC[6] to cycHC[8].

No	cycHC[6] (mg)	Acid (eq.)/ co-solvent	Time (h)	Mixture	Temp. (°C)	Ratio of cycHC[8] to cycHC[6]
1	5	HCOOH (10)/ CH_3CN	24	heterogeneous	rt	No reaction
2	5	HCOOH (10)/ $CHCl_3$	24	homogeneous	rt	50:50
3	20	HCOOH	24	homogeneous	rt	83:17
4	20	HCOOH	24	homogeneous	100	Oligomers
5	20	HCOOH (300)/ H_2O	24	heterogeneous	rt	No reaction
6	20	HCOOH (300)/ $CHCl_3$	24	homogeneous	rt	60:40
			48	homogeneous	rt	80:20
7	20	HCOOH (300)/ CH_3CN	24	homogeneous	rt	90:10
8	5	CF_3COOH (300)/ $CHCl_3$	24	homogeneous	rt	75:25
9	20	CH_3COOH (300)/ CH_3CN	72	homogeneous	rt	Oligomers and cycHC[6]
10	5	CH_3COOH (300)/ $CHCl_3$	48	homogeneous	rt	Oligomers and cycHC[6]
11	5	H_2SO_4 (300)/ CH_3CN	2	homogeneous, yellow	rt	polymerization of CH_3CN
12	5	H_2SO_4(300)/ CH_3COOH	2	homogeneous, yellowish film	rt	decomposition of starting material
13	5	H_2SO_4(50)/ CH_3COOH/ CH_3CN	24	homogeneous, yellow	rt	50:50 and oligomers
14	10	$NaPF_6$(50)/ CH_3COOH/ CH_3CN	24	heterogeneous	rt	99:1

a) Synthesis of cycHC[8] from cycHC[6] with formic acid

To a solution of (*all-R*)-cycHC[6] HCl complex (1.58 g, 1.66 mmol) in HCOOH (20 mL) acetonitrile (20 mL) was added. The resulting clear solution was stirred at rt for 24 hours. Reaction progress was

monitored by HPLC (final cycHC[8]:cycHC[6] ratio 90:10) and TLC. The reaction was quenched by the addition of H_2O (120 mL) and the resulting suspension, was filtered, washed with 3 á 10 mL of H_2O and dried in open air at rt for 2 days. The resulting residue was purified by recrystallization from CH_2Cl_2/acetonitrile mixture (3 mL of CH_2Cl_2, 10 mL of acetonitrile, 20 min. ice bath).

HRMS analysis of reaction mixture showed oligomers with hydrogens on both ends (**1b-h**) and with a methyleneformate group on one end of the oligomers (**4b-h**).

(*all-R*)-cycHC[8] was isolated by crystallization as a white solid (885 mg first crop, >99% purity, 56%), the mother liquor was used for a second crystallization, which gave cycHC[8] in a mixture with cycHC[6**]** (218 mg, 9:1, respectively, by HPLC). The remaining mother liquor contained cycHC[8] and cycHC[6] in a ratio of ~6:4. Overall yield is 71%. Mp 255-260 °C. $[\alpha]_D^{25}$ -78.5° (c 0.59, $CHCl_3$). (Found: C, 62.74; N, 7.95; H, 18.26 for $C_{64}H_{96}N_{16}O_8$: C, 63.13; N, 7.95; H, 18.41%). IR (KBr, cm^{-1}) 3502 w, 2936 s, 2858 s, 1711 (CO) vs, 1435 s, 1359 vs, 1332 s, 1232 vs, 1134 w, 1058 w, 1014 w, 988 w, 919 w, 830 w, 774 s, 667 w, 628 w, 532 w, 516 w, 476 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18–1.05 (1H, m, **H**4ax), 1.23 (1H, qd, *J* = 11.0, 2.9, **H**3ax), 1.29 (1H, qd, *J* = 11.3, 3.3, **H**6ax), 1.47–1.35 (1H, m, **H**5ax), 1.73 (1H, bd, *J* = 12.7, **H**5eq), 1.82 (1H, bd, *J* = 12.5, **H**4eq), 2.30 (1H, dd, *J*= 11.5, 2.7, **H**6eq), 2.49 (1H, td, *J* = 11.0, 2.9, **H**2), 2.62 (1H, dd, *J* = 11.6, 2.7, **H**3eq), 2.83 (1H, td, *J* = 11.1, 3.1, **H**1), 4.59 (1H, s, **H**8), 4.77 (1H, s, **H**9). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.77 (C7), 64.86 (C1), 59.68 (C2), 55.83 (C8), 46.69 (C9), 28.76 (C6), 27.63 (C3), 24.48 (C5), 24.19 (C4). Analytical data is consistent with ref. 3.

b) Synthesis of cycHC[8] from cycHC[6] with trifluoroacetic acid

To a solution of (*all-R*)-cycHC[6**]** HCl complex (108 mg, 0.11 mmol) in CF_3COOH (1.5 mL) acetonitrile (1.5 mL) was added. The resulting clear solution was stirred at rt 2 hours. Reaction progress was monitored by HPLC (final cycHC[8]:cycHC[6] ratio 95:5) and TLC. Reaction was quenched by the addition of H_2O (10 mL) and the resulting suspension, filtered, washed 3 times á 2 mL of H_2O and dried in open air at rt for 2 days. The resulting residue was purified by flash chromatography (1-5% gradient MeOH/CH_2Cl_2).

HRMS analysis of the reaction mixture showed no oligomers. Compound (*all-R*)-cycHC[8] was obtained as a white solid (74 mg, 71%).

c) Synthesis of cycHC[8] from cycHC[6] with sodium hexafluorophosphate ($NaPF_6$)

To a solution of (*all-R*)-cycHC[6**]** HCl complex (15 mg, 0.016 mmol) in CH_3COOH (0.17 mL) and acetonitrile (0.17 mL) $NaPF_6$ (134 mg, 0.8 mmol, 50 eq.) was added. Heterogeneous solution was stirred 24 hours at rt. Reaction progress was controlled by HPLC (final cycHC[8]:cycHC[6] ratio from reaction mixture 99:1) and TLC. Reaction was quenched by addition of H_2O (2 mL). Then, the resulting suspension was filtered and washed 3 times á 1 mL of H_2O and dried in open air at rt for 2 days. The resulting residue was purified by flash chromatography (1-5% gradient MeOH/CH_2Cl_2).

HRMS analysis of reaction mixture showed no oligomers. Compound (*all-R*)-cycHC[8**]** was obtained after purification as a white solid (13 mg, 90%). Isolated cycHC[8] did not contained PF_6 anion, according to ^{19}F-NMR analysis.

2.1.2 ^{13}C labelling

We introduced ^{13}C label to methylene bridges of cycHC[6][10].

To a mixture of (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** (250 mg, 1.8 mmol, 1eq.) and parafolmaldehyde-^{13}C (54 mg, 1.8 mmol, 1 eq.) 4M acid aqueous solution was added (7 mL), reaction mixture was stirred 24 hours at 70^{o} C. Then, the resulting suspension was filtered, washed 3 á 1 ml of H_2O and dried in open air at rt for 2 days. Compound ^{13}C-labelled (*all-R*)-cycHC[6] HCl was obtained as a white solid (173 mg, 61%).

^{13}C-labelled cycHC[6] HCl (5 mg, 5 μmol) and non-labelled cycHC[6] HCl (5 mg, 5 μmol) as an equimolar mixture were dissolved in NMR sample tube in DCO_2D (300 μL) and CD3CN (300 μL) to produce ^{13}C-labelled cycHC[8]. Reaction mixture was analyzed by ^{1}H and ^{13}C NMR and MS.

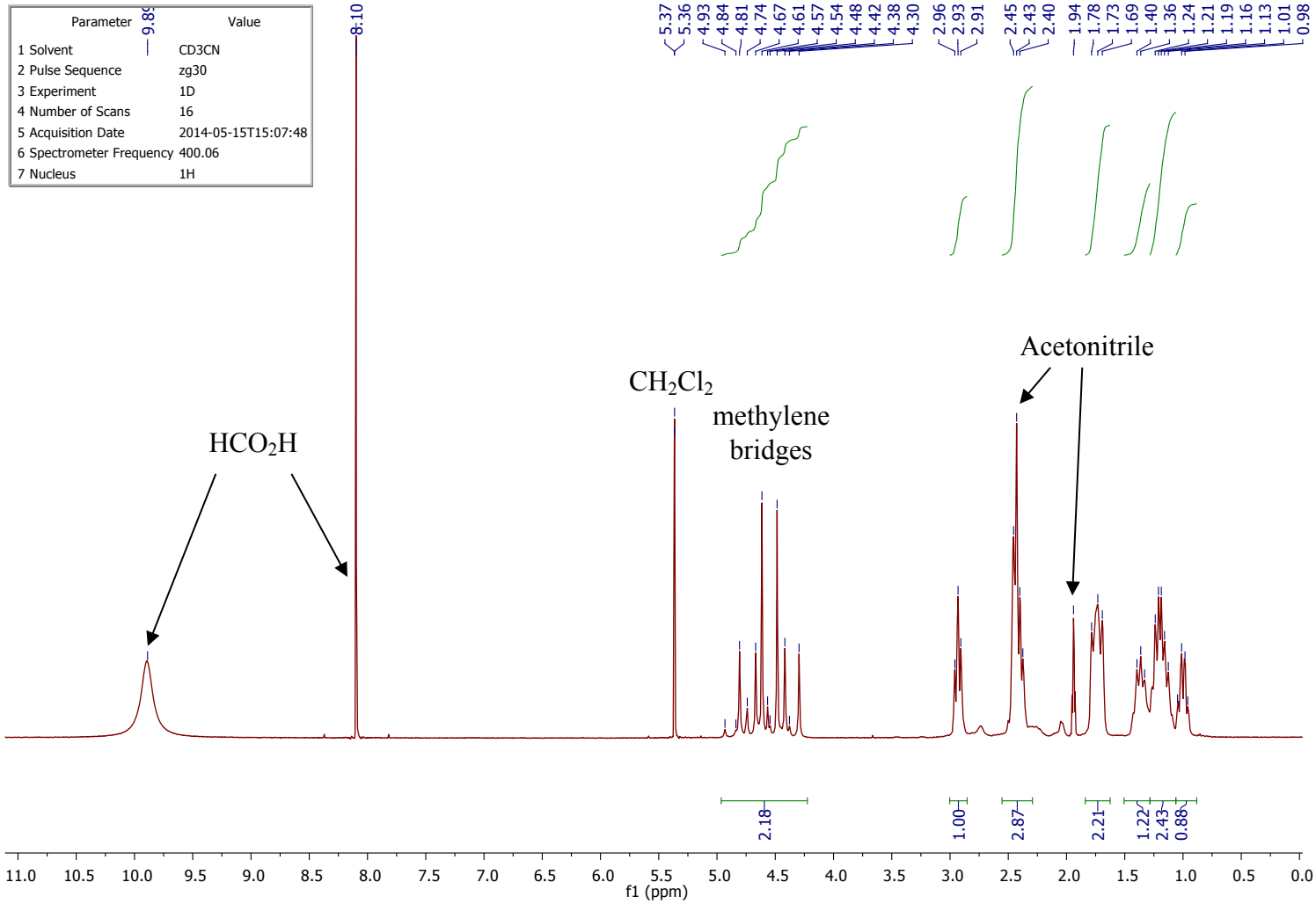


Figure S2. ^{1}H-NMR spectrum recorded at 30 min. from the beginning of the reaction (page S7) in DCO_2D and D_3CCN, mixture contains ^{13}C-labeled cycHC[6] (methylene bridges - peaks number 1, 2, 5, 6) and non-labelled cycHC[6] (methylene bridges - peaks number 3, 4) and minor amount of formed cycHC[8].

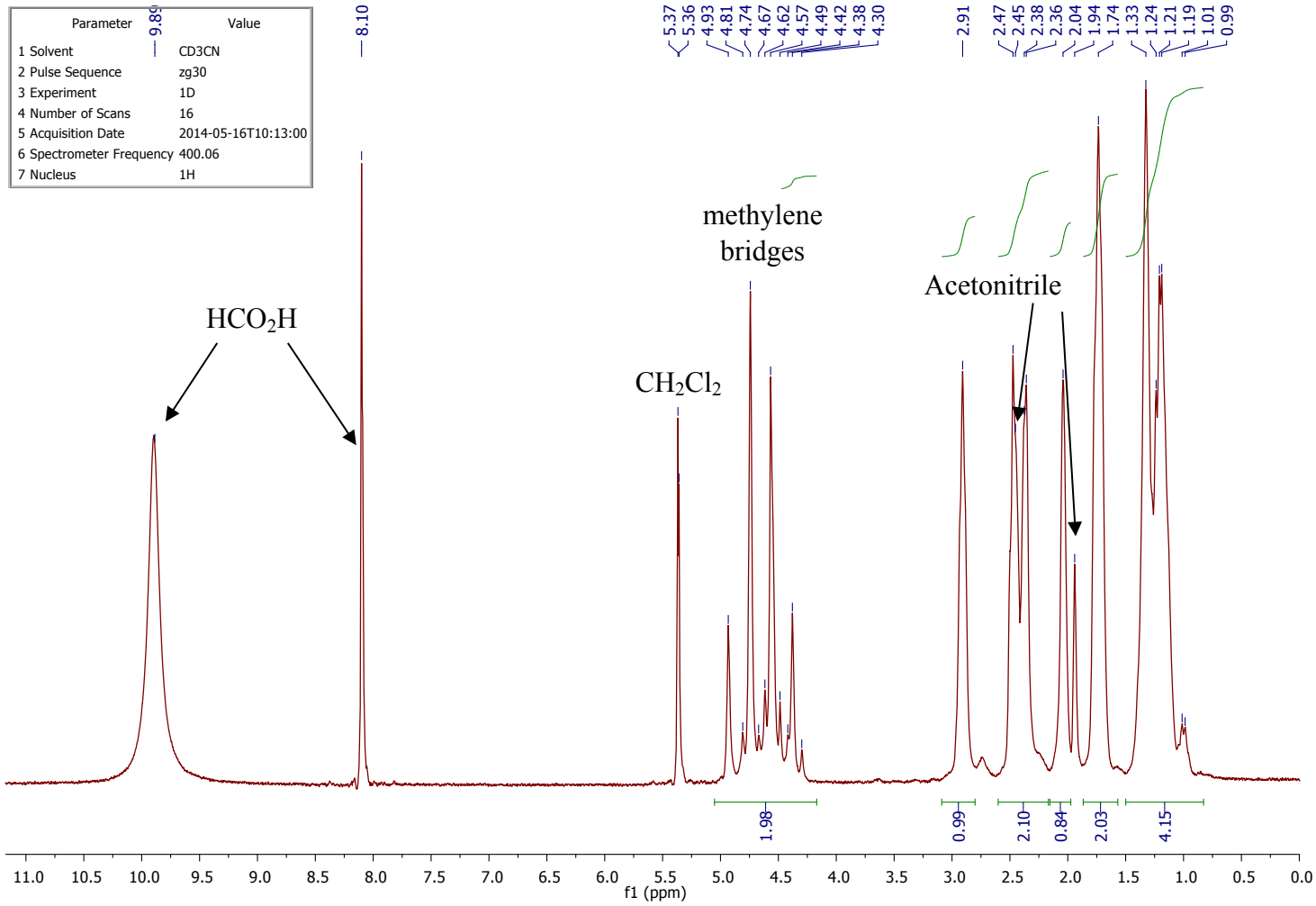


Figure S3. ^{1}H-NMR spectrum recorded at 20h 30 min. from the beginning of the reaction page S7 in DCO_2D and D_3CCN, mixture contains ^{13}C-labelled cycHC[8] in majority and cycHC[6] in minor amount.

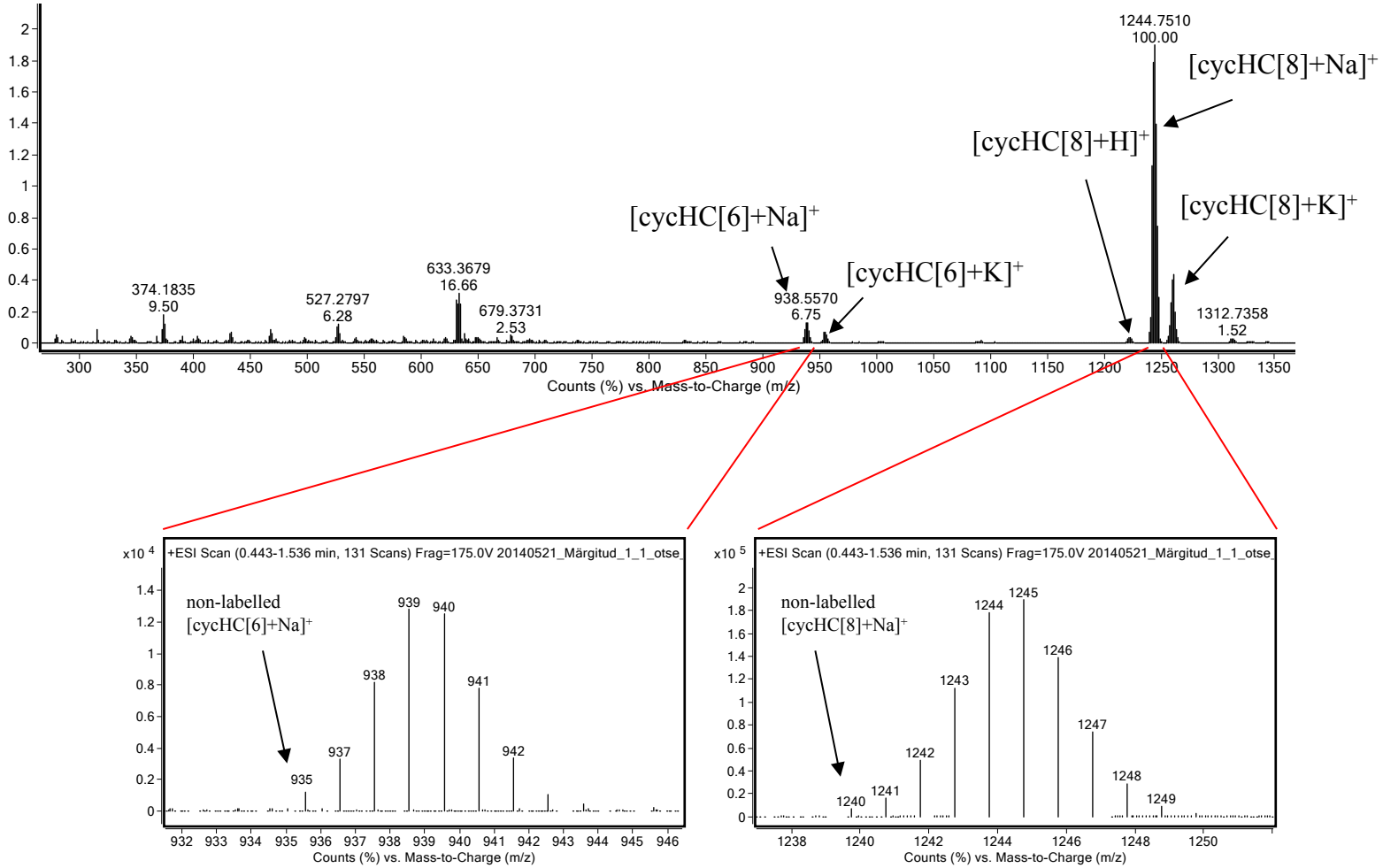
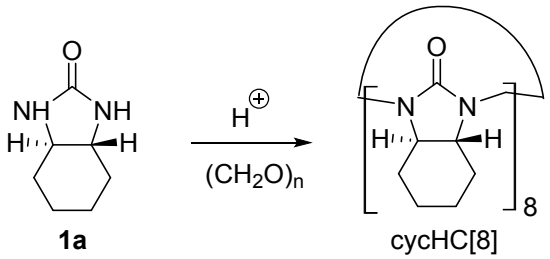


Figure S4. MS spectrum of cycHC[6] (calculated *m/z* for non-labelled [cycHC[6]+Na]$^+$ is 935) and cycHC[8] (calculated *m/z* for non-labelled [cycHC[8]+Na]$^+$ is 1240) from labelling experiment in page S7.

2.1.3 Screening the conditions for the synthesis of cycHC[8] starting from (*R,R,N,N'*)-cyclohex-1,2-diylurea



1a cycHC[8]

Acetonitrile or other co-solvents were added to a mixture of (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** and paraformaldehyde (1 eq) in a carboxylic acid. The resulting 0.25 M reaction mixture was stirred for 1.5 - 120 h at specific conditions, as outlined in Table S2. Reaction progress and cycHC[8]:cycHC[6] ratios were monitored by HPLC and TLC.

Table S2. Screening of reaction conditions for the synthesis of cycHC[8] from **1a**

No	1a (mg)	Acid (eq.)/ co-solvent	Mixture	Time (h)	Temp. (°C)	Ratio of cycHC[8]: cycHC[6]
1	20	HCOOH (300)/ HCl	heterogeneous	24	70	Unidentified by-product
2	20	HCOOH	heterogeneous	24	70	oligomers
3	50	HCOOH (300)/ CH_3CN	heterogeneous	24	RT	92:8 and oligomers
4	50	CH_3COOH	heterogeneous	48	RT	oligomers
5	20	CH_3COOH (300)/ CH_3CN	heterogeneous	120	RT	oligomers
6	20	H_2SO_4(300)/ CH_3CN	homogeneous, yellow	2	RT	Polymerization of CH_3CN
7	157	CF_3COOH (300)/ CH_3CN	heterogeneous	2	RT	96:4

*a) Synthesis of cycHC[8] from **1a** with HCOOH*

To a mixture of (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** (200 mg, 1.4 mmol) and paraformaldehyde (43 mg, 1.4 mmol, 1 eq.), HCOOH (2.7 mL) and acetonitrile (2.7 mL) were added, heterogeneous reaction mixture was stirred 24 hours at rt. Reaction progress was followed by HPLC (cycHC[8]:cycHC[6] ratio from reaction mixture is 92:8) and TLC. To the resulting clear solution H_2O (6 mL) was added and stirred at ice bath 30 min. The crystals were filtered, washed 3 times á 1 mL of H_2O and dried in

open air at rt for 2 days. Purification by flash chromatography was performed (1-5% gradient MeOH/CH_2Cl_2).

For HPLC-MS analysis reaction mixture was diluted in methanol, which gave oligomers **7a-j** and **8a-j**, which were formed from the corresponding iminium oligomers **3a-j** in reaction with methanol. When another aliquot was diluted in acetonitrile and injected directly to the MS, intermediates **1a-g**, **2a-e**, **4a-g**, **5a-g**, **7a-g** and **8a-d** were detected.

Compound (*all-R*)-cycHC[8] was obtained as a white solid (15 mg, 7 %), along with mixture of oligomers (29 mg, 14%).

*b) Synthesis of cycHC[8] from **1a** with CF_3COOH*

To a mixture of (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** (1654 mg, 11.8 mmol) and paraformaldehyde (354 mg, 11.8 mmol, 1 eq.), CF_3COOH (22 mL) and acetonitrile (22 mL) were added, heterogeneous reaction mixture was stirred 2 hours at rt. Reaction progress was followed by TLC. To the resulting clear solution H_2O (60 mL) was added and stirred at ice bath 30 min. The crystals were filtered, washed 3 á 10 mL of H_2O and dried in open air at rt for 2 days. Purification by flash chromatography was performed (1-5% gradient MeOH/CH_2Cl_2).

Mass spectrometric analysis of reaction mixture diluted with methanol revealed oligomers **1a-g** and **7a-g** and **8a-g**.

Compound (*all-R*)-cycHC[8**]** was obtained as a white solid (1303 mg, 73 %).

*c) Synthesis of cycHC[8] from **1a** with $NaPF_6$*

To a mixture of (*R,R,N,N'*)-cyclohex-1,2-diylurea **1a** (10 mg, 0.07 mmol) and paraformaldehyde (2 mg, 0.07 mmol, 1 eq.), CH_3COOH (0.140 mL), acetonitrile (0.140 mL) and $NaPF_6$ (75 mg, 0.45 mmol, 50 eq. towards cycHC[8]) were added. Reaction mixture was stirred 24 hours at rt. Reaction progress was followed by HPLC (cycHC[8]:cycHC[6] ratio from reaction mixture is 95:5) and TLC. To the resulting heterogeneous solution H_2O (1 mL) was added and stirred at ice bath 30 min. The crystals were filtered and washed 3 times á 1 mL of H_2O and dried in open air at rt for 2 days. Purification by flash chromatography was performed (1-5 % gradient MeOH/CH_2Cl_2).

HRMS analysis of reaction mixture showed no oligomers. Compound (*all-R*)-cycHC[8**]** was obtained as a white solid (6 mg, 55 %). Isolated cycHC[8] did not contained PF_6 anion, according to ^{19}F-NMR analysis. Mixture of oligomers (2 mg, 3-10 unit long oligomers) was isolated as the major by-products.

Oligomers were obtained from synthesis of cycHC[8] from **1a** in formic acid (Table S2, entry 3) and separated by flash chromatography. For mass spectrometric analysis the oligomers were dissolved in a chloroform/methanol mixture (1:4) and injected directly to ESI-MS, which showed oligomeric intermediates up to decamers (**1a-j**, **2a-j**, **6b-j**, **7a-j** and **8a-j**).

2.1.4 Screening the conditions for the synthesis of cycHC[8] or cycHC[6] from oligomers or homologues using different templates

Table S3. Reaction conditions for the synthesis 6- and 8-membered homologues of cycHC[*n*] starting from oligomers or cycHC[8].

No	Starting material (mg)	Acid (eq.)/ co-solvent	Mixture	Time (h)	Temp. (°C)	Ratio of cycHC[8]:cycHC[6]
1	Oligomers (8)	HCOOH (300)/ CH_3CN	homogeneous	24	RT	85:15
2	Oligomers (20)	4M HCl_{aq}	heterogeneous	24	70	0:100
3	cycHC[8] (25)	4M HCl_{aq}	heterogeneous	24	70	0:100
4	cycHC[8] (1)	HCOOH (3000)/ CH_3CN	homogeneous	120	RT	70:30

a) Synthesis of cycHC[6] from cycHC[8] with HCl

Heterogeneous mixture of (*all-R*)-cycHC[8] (50 mg, 0.04 mmol) in 4M $HCl_{aq.}$ (1.3 mL) was stirred 24 hours at 70 °C. Reaction progress was followed by TLC and HPLC-UV (fanal cycHC[6]:cycHC[8] ratio of reaction mixture is 95:5). The resulting heterogeneous solution was cooled to rt, filtered and washed 3 á 1 mL of H_2O and dried in open air at rt for 2 days.

(*all-R*)-cycHC[6] HCl complex was obtained as a white solid (37 mg, 71%). Product was identical with previously reported in ref. 10.

b) Synthesis of cycHC[6] from cycHC[8] with NaCl

To a mixture of (*all-R*)-cycHC[8] (65 mg, 0.05 mmol) and NaCl (145 mg, 2.50 mmol, 50 eq) acetic acid (1.7 mL) was added. Heterogeneous reaction mixture was stirred 72 hours at 70 °C. Reaction progress was followed by TLC and HPLC-UV (final cycHC[6]:cycHC[8] ratio of reaction mixture is 60:40). To the resulting heterogeneous solution H_2O (2 mL) was added and stirred at ice bath for 30 min. Then, the resulting suspension was filtered and washed 3 á 1 mL of H_2O and dried in open air at rt for 2 days. Purification by flash chromatography (MeOH:CH_2Cl_2 1-10 % gradient)

Compound (*all-R*)-cycHC[6] HCl complex was obtained as a white solid (6 mg, purity >99%, 9% and 33 mg mixture of cycHC[8] and cycHC[6] with ratio 75:25, overall yield of cycHC[6] 21%). Product was identical with previously reported in ref. 10.

2.2 Chromatographic and mass-spectrometric procedures

For chromatographic analysis 10 µL of reaction mixtures was taken and dissolved in 100 µL chloroform (or acetic acid) and diluted in 400 µL acetonitrile or methanol depending on reaction mixture solubility.

Separation by HPLC-UV was performed with eluents A (acetonitrile) and B (water) in gradient mode from 50A/50B to 100A/0B within 10 min. Column temperature was set at 30°C, flow rate to 0.25 mL/min and injection volume was 5 µL. HPLC-MS analysis was performed using the same gradient mode with eluents C (acetonitrile with 0.1 % formic acid and 1 % water) and D (water with 0.1 % formic acid). Flow rate was 0.4 mL/min, temperature 30 °C and injection volume was varied depending on the concentration of analytes.

3 Qualitative mass-spectrometric analysis of intermediates

Calculated *m/z* values of different oligomers and averaged experimental values of samples along with standard deviations are listed in Table S4. All mass-to-charge ratios are presented for $[M+Na]^+$ adducts (most abundant).

Table S4. Experimental and theoretical *m*/*z* values of oligomeric intermediates

Comp.	Calc. *m*/*z*	Exp. *m*/*z* ± deviation*	Comp.	Calc. *m*/*z*	Exp. *m*/*z* ± deviation*
1a	163.0842	163.0839 ± 0.0003 (*n* = 3)	**6b**	375.2003	375.2005 (*n* = 1)
1b	315.1791	315.1795 ± 0.0005 (*n* = 4)	**6c**	527.2952	527.2956 (*n* = 1)
1c	467.2741	467.2746 ± 0.0005 (*n* = 4)	**6d**	679.3902	679.3905 (*n* = 1)
1d	619.3691	619.3696 ± 0.0002 (*n* = 4)	**6e**	815.4903	815.4910 (*n* =1)
1e	771.4640	771.4654 ± 0.0006 (*n* = 4)	**6f**	983.5801	983.5809 (*n* = 1)
1f	923.5590	923.5598 ± 0.0005 (*n* = 4)	**6g**	1135.6751	1135.6750 (*n* = 1)
1g	1075.6540	1075.654 ± 0.001 (*n* = 4)	**6h**	1287.7701	1287.7700 (*n* = 1)
1h	1227.7489	1227.744 ± 0.004 (*n* = 2)	**6i**	1439.8650	1439.8630 (*n* = 1)
1i	1379.8439	1379.844 (*n* = 1)	**6j**	1591.9600	1591.9580 (*n* = 1)
1j	1531.9389	1531.938 (*n* = 1)	**7a**	207.1104	207.1103 ± 0.0002 (*n* = 4)
2a	193.0947	193.0946 ± 0.0003	**7b**	359.2054	359.2057 ± 0.0001

		(n = 2)			(n = 4)
2b	345.1897	345.1899 ± 0.0000 (n = 2)	**7c**	511.3003	511.3004 ± 0.0003 (n = 4)
2c	497.2847	497.2849 ± 0.0005 (n = 2)	**7d**	663.3953	663.3955 ± 0.0003 (n = 4)
2d	649.3796	649.380 ± 0.001 (n = 2)	**7e**	815.4903	815.4913 ± 0.0005 (n = 4)
2e	801.4746	801.474 ± 0.002 (n = 2)	**7f**	967.5852	967.585 ± 0.001 (n = 4)
2f	953.5696	953.5702 (n = 1)	**7g**	1119.6802	1119.679 ± 0.001 (n = 4)
2g	1105.6645	1105.665 (n = 1)	**7h**	1271.7751	1271.773 ± 0.004 (n = 2)
2h	1257.7595	1257.76 (n = 1)	**7i**	1423.8701	1423.873 ± 0.004 (n = 2)
2i	1409.8545	1409.855 (n = 1)	**7j**	1575.9651	1575.966 ± 0.002 (n = 2)
2j	1561.9494	1561.95 (n = 1)	**8a**	251.1366	251.1363 ± 0.0008 (n = 4)
4a	221.0897	221.0899 (n = 1)	**8b**	403.2316	403.232 ± 0.002 (n = 4)
4b	373.1846	373.187 ± 0.002 (n = 2)	**8c**	555.3265	555.326 ± 0.002 (n = 4)
4c	525.2796	525.2802 ± 0.0001 (n = 2)	**8d**	707.4215	707.421 ± 0.003 (n = 4)
4d	677.3746	677.3754 ± 0.0003 (n = 2)	**8e**	859.5165	859.518 ± 0.002 (n = 3)
4e	829.4695	829.469 ± 0.001 (n = 2)	**8f**	1011.6114	1011.6110 ± 0.0007 (n = 3)
4f	981.5645	981.5645 ± 0.0001 (n = 2)	**8g**	1163.7064	1163.707 ± 0.005 (n = 3)
4g	1133.6594	1133.6590 ± 0.0007 (n = 2)	**8h**	1315.8014	1315.799 ± 0.004 (n = 2)
4h	1285.7544	1285.7400 (n = 1)	**8i**	1467.8963	1467.89 ± 0.01 (n = 2)
5a	279.0951	279.0955 (n = 1)	**8j**	1619.9913	1619.98 ± 0.01 (n = 2)
5b	431.1901	431.1905 (n = 1)	**8e**	859.5165	859.518 ± 0.002 (n = 3)
5c	583.2851	583.2856 (n = 1)	**8f**	1011.6114	1011.6110 ± 0.0007 (n = 3)
5d	735.3800	735.3807 (n = 1)	**8g**	1163.7064	1163.707 ± 0.005 (n = 3)

5e	887.4750	887.4757 (n = 1)	**8h**	1315.8014	1315.799 ± 0.004 (n = 2)
5f	1039.5700	1039.5710 (n = 1)	**8i**	1467.8963	1467.89 ± 0.01 (n = 2)
5g	1191.6649	1191.6660 (n = 1)	**8j**	1619.9913	1619.98 ± 0.01 (n = 2)

*n is number of samples

4 Kinetics studies

Data was obtained by ^{1}H NMR from a sample consisting of 20 mg of (*all-R*)-cycHC[6] dissolved in 0.3 mL of DCOOD and 0.3 mL of CD_3CN. The residual CH_2Cl_2 signal was used as internal reference for analyte signal integration and mass balance. No intermediates were detected during the transformation of cycHC[6] to cycHC[8] in the NMR time scale. Data was analyzed with Sigmaplot 11™.

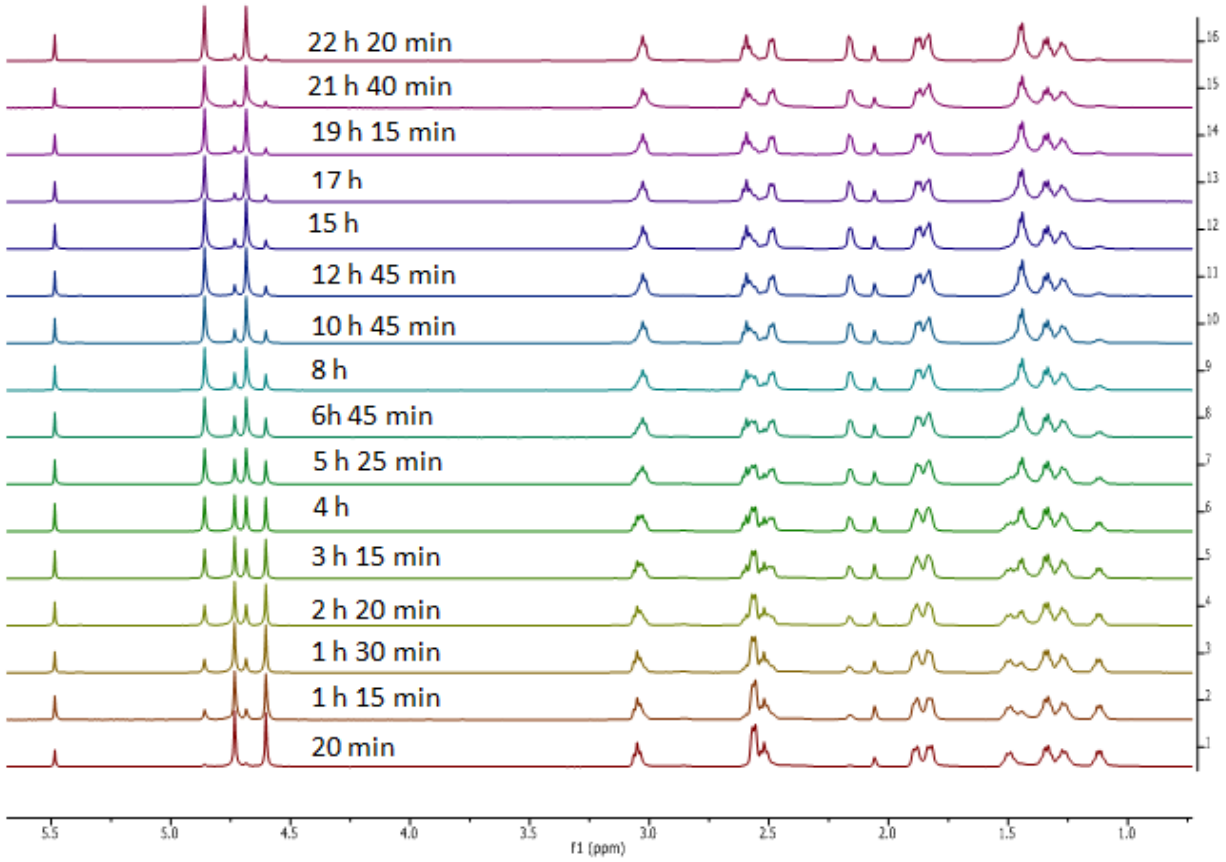


Figure S5. Stacked ^{1}H-NMR spectra recorded during cycHC[6] transformation to cycHC[8]. CH_2Cl_2 (5.5 ppm) integral was used as internal reference and bridge methylene peaks (4.6 ppm for cycHC[6] and 4.8 ppm for cycHC[8]) integrals were used for the collection of kinetic data (see Table S5).

Table S5. ^{1}H-NMR integrals and the concentrations of cycHC[8] and cycHC[6] during cycHC[6] transformation to cycHC[8].

Reaction time	^{1}H-NMR integrals			Conc. (mol/L)		Conc. (mass%)		
	CH_2Cl_2 5.5 ppm*	cycHC[6] (6H) 4.6 ppm	cycHC[8] (8H) 4.8 ppm	cycHC[6]	cycHC[8]	cycHC[6]	cycHC[8]	Sum of mass%.
0				0.0351	0	100	0	100
00:20:46	1.00	5.18	0.27	0.0334	0.0014	95	5	100
01:13:01	1.00	3.01	0.76	0.0194	0.0038	55	14	69
01:31:57	1.00	3.76	1.25	0.0242	0.0063	69	23	92
02:21:17	1.00	2.81	1.63	0.0181	0.0082	52	30	81
03:14:55	1.00	2.36	2.11	0.0152	0.0106	43	39	82
04:03:52	1.00	2.07	2.52	0.0133	0.0127	38	46	84
05:26:44	1.00	1.63	3.02	0.0105	0.0152	30	55	85
06:46:18	1.00	1.35	3.32	0.0087	0.0167	25	61	86
08:05:50	1.00	1.11	3.54	0.0071	0.0178	20	65	85
10:25:54	1.00	0.87	3.84	0.0056	0.0193	16	70	86
12:45:57	1.00	0.68	4.03	0.0044	0.0203	12	74	86
14:53:11	1.00	0.60	4.14	0.0039	0.0208	11	76	87
17:05:09	1.00	0.54	4.63	0.0035	0.0233	10	85	95
19:12:23	1.00	0.48	4.50	0.0031	0.0226	9	83	91
21:37:35	1.00	0.41	4.77	0.0026	0.0240	8	88	95

*CH_2Cl_2 was used as internal reference.

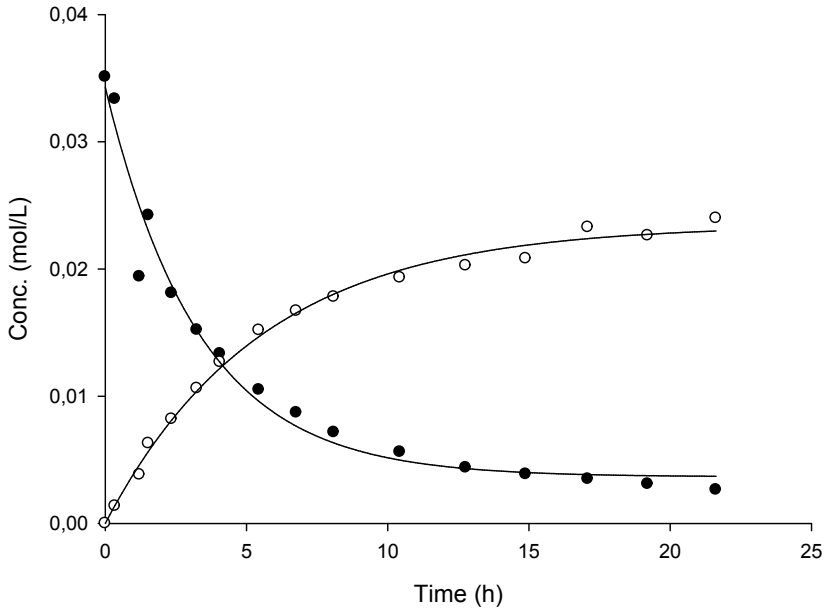


Figure S6. Kinetics plot of cycHC[6] (filled circles) and cycHC[8] (empty circles).

cycHC[6] concentration curve was fitted with the following equation:

$$f = y_0 + a \times e^{-b \times x}$$

,

where y_0 is the residual concentration (mol/L) of cycHC[6], a is cycHC[6] concentration (mol/L) at t_0, b is cycHC[6] consumption reaction rate constant and x is time (h).

For $f = 0.0037(\pm 0.0008) + 0.031(\pm 0.001) \times e^{-0.30(\pm 0.03) \times x}$ the R^2 of fitting was 0.975.

cycHC[8] concentration rise was fitted to the following equation:

$$f = a(1 - e^{-b \times x})$$

,

where a is maximum concentration (mol/L) of cycHC[8], b is cycHC[8] concentration rise rate constant per hour and x is time (h).

For $f = 0.0234(\pm 0.0004)(1 - e^{-0.191(\pm 0.009) \times x})$ the R^2 of fitting was 0.994.

The equilibrium between cycHC[6] and cycHC[8] was studied by evaluating the equilibrium constant (K_{eq}) from experimental data and computationally (page S27).

$4\ cycHC[6] \rightleftharpoons 3\ cycHC[8]$

K_{eq} is calculated at equilibrium, where concentrations of cycHC[8] and cycHC[6] were 0.0240M and 0.0026M, respectively, by the following equation

$$K_{eq} = \frac{[cycHC[8]]^3}{[cycHC[6]]^4} = 3.0 \times 10^5$$

,

corresponding to a difference in Gibbs free energies (ΔG) of -31 kJ/mol in favour of cycHC[8].

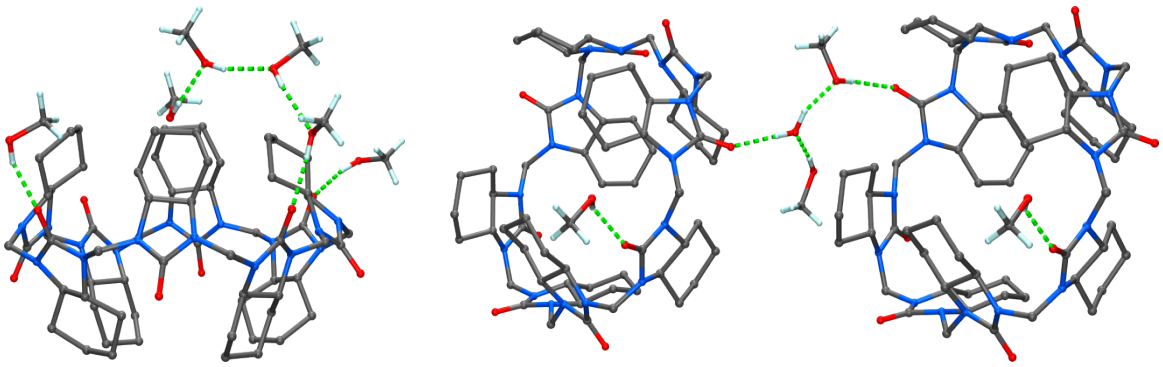
5 Crystal structure data

5.1 Crystallization procedure

Single crystals of the (*all-R*)-cycHC[8]·6.75(CH_4O)·H_2O were obtained from a (1:1) solution of (*all-R*)-cycHC[8] and (*S*)-Mosher acid in MeOH by slow evaporation method. The small colorless needle-like crystals lose solvent quite quickly when removed from mother liquor resulting in crystal deterioration. The compound was found to crystallize in a non-centrosymmetric space group $P2_1$, with two molecules of (*all-R*)-cycHC[8] and a number of solvent molecules in the asymmetric unit. (*S*)-Mosher acid was not incorporated in the crystal structure. Nine methanol molecules (s.o.f ≥ 0.5, U_{iso} < 0.15) and one water molecule were found in the asymmetric unit. Restraints were applied to the geometry of the solvent molecules. The structure also contained some diffuse solvent.

5.2 Crystal data

2($C_{64}H_{96}N_{16}O_8$)·6.75(CH_4O)·H_2O, M_r = 2669.42, Monoclinic, $P2_1$, a =16.510(4) Å, b = 27.312(3) Å, c = 17.957(3) Å, β = 96.33(3)°, V = 8048(3) Å^3, Z = 2, Cu-$K\alpha$ radiation (λ = 1.54178 Å) at T = 200.0(1) K, 84720 reflections measured, of which 27756 unique (23872 with $I>2\sigma(I)$), R_{int} = 0.033, $R_1[F^2>2\sigma(F^2)]$ = 0.059, wR_2 (all data) = 0.167, S = 1.02, Flack x = 0.05(6); absolute structure determined by anomalous diffraction effects using 10228 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$. The crystallographic data is deposited with the Cambridge Crystallographic Data Centre (CCDC 1053111 and can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



a) **b)**

Figure S7. Two symmetrically independent molecules of (*all-R*)-cycHC[8] engage in hydrogen bonding with solvent (methanol, water) molecules, forming either **a)** discrete or **b)** continuous motifs. Hydrogen bonds are shown as dashed green lines.

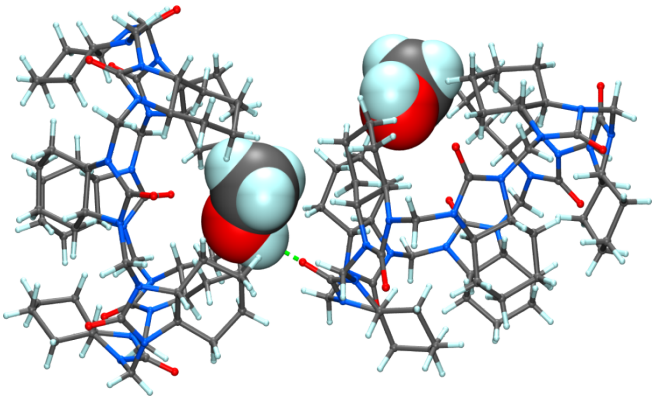


Figure S8. Two symmetrically independent molecules of (*all-R*)-cycHC[8] stack in a side-to-top manner, assisted by hydrogen bonded methanol molecules included in the portals of both moieties. Hydrogen bonds are shown as dashed green lines.

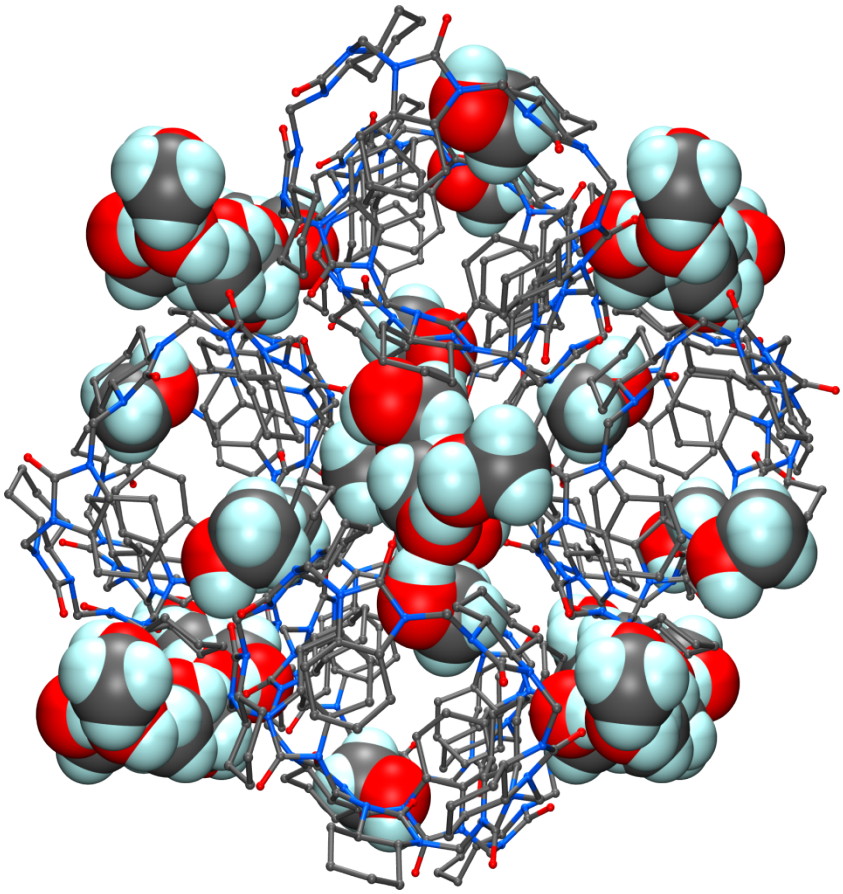


Figure S9. Molecules of (*all-R*)-cycHC[8] pack in columns, whereas the solvent molecules can be seen as being accommodated in the thus formed channels. This might also explain the fast deterioration of the crystals upon removal from mother liquor.

6 Diffusion NMR analysis and evaluation of association constants K_a

6.1 Sample preparation

Diffusion NMR samples were prepared by adding 1 molar equivalent of the appropriate low MW guest compound (as a solution in 0.1 ml of $CDCl_3$) to a solution of (*all-R*)-cycHC[8] (5 mg, 0.004 mmol) in $CDCl_3$ (0.5 ml). Samples were subsequently stored in 5 mm NMR tubes and sealed with tube caps and parafilm to avoid solvent evaporation before and during analysis.

6.2 DOSY spectra

The following 2D DOSY plots illustrate the change in the diffusion coefficient of various tested guest molecules in the presence of cycHC[8] compared to the diffusion coefficient in neat $CDCl_3$. D_{Free} denotes the diffusion coefficient of the free undisturbed guest molecule in neat solvent and D_{Obs} denotes the observed guest molecule's diffusion coefficient in the presence of macrocyclic host compound. D_{Bound} denotes the diffusion coefficient of the macrocyclic host and is equal to the diffusion coefficient of the bound guest compound (binding of the low MW guest has a negligible effect on the hosts's diffusion coefficient).

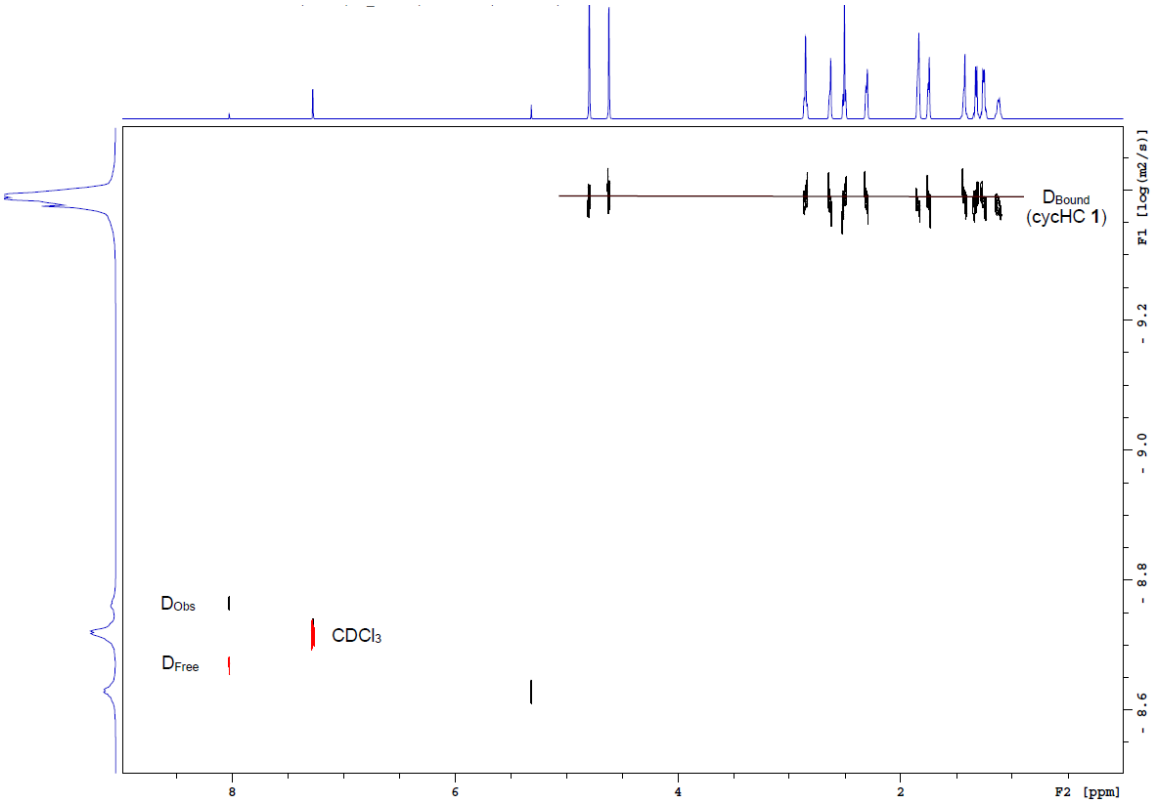


Figure S10. DOSY spectra of HCOOH in pure $CDCl_3$ (red) and in the presence of cycHC[8] (black).

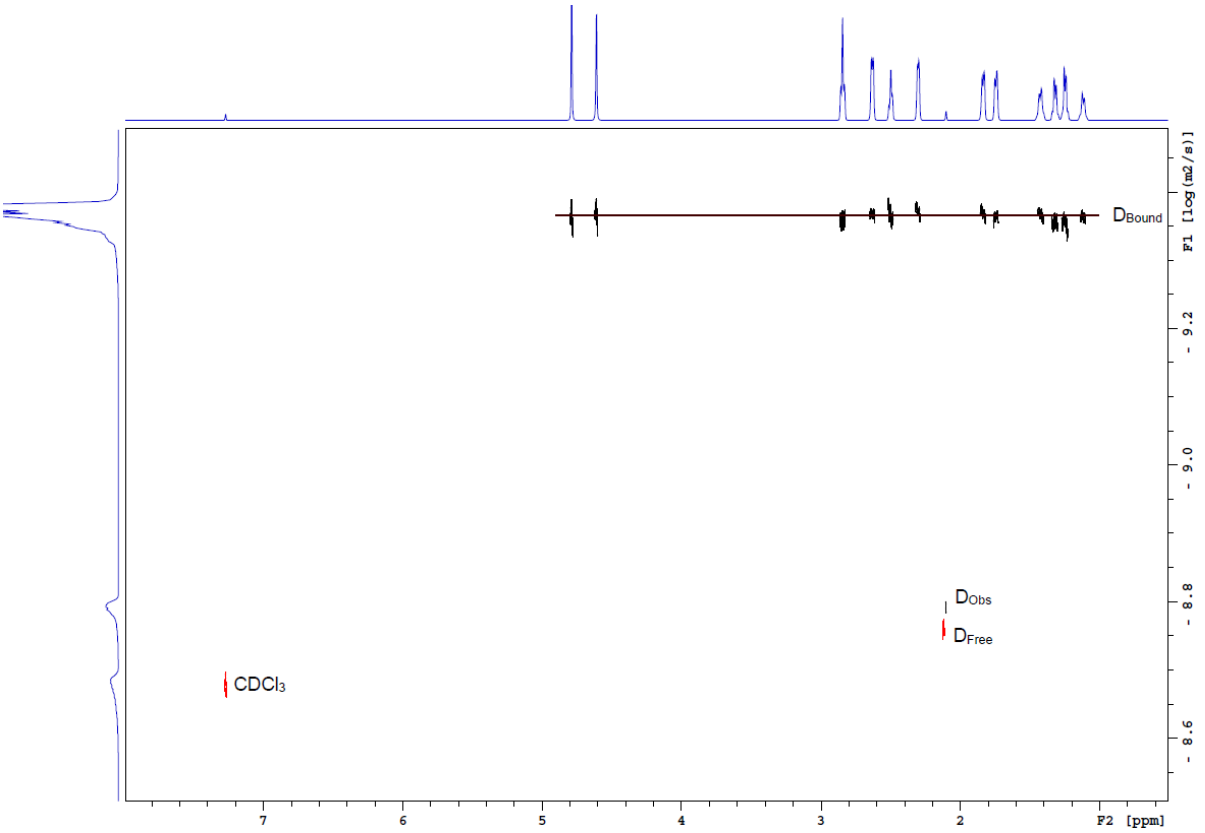


Figure S11. DOSY spectra of CH_3COOH in pure $CDCl_3$ (red) and in the presence of cycHC[8] (black).

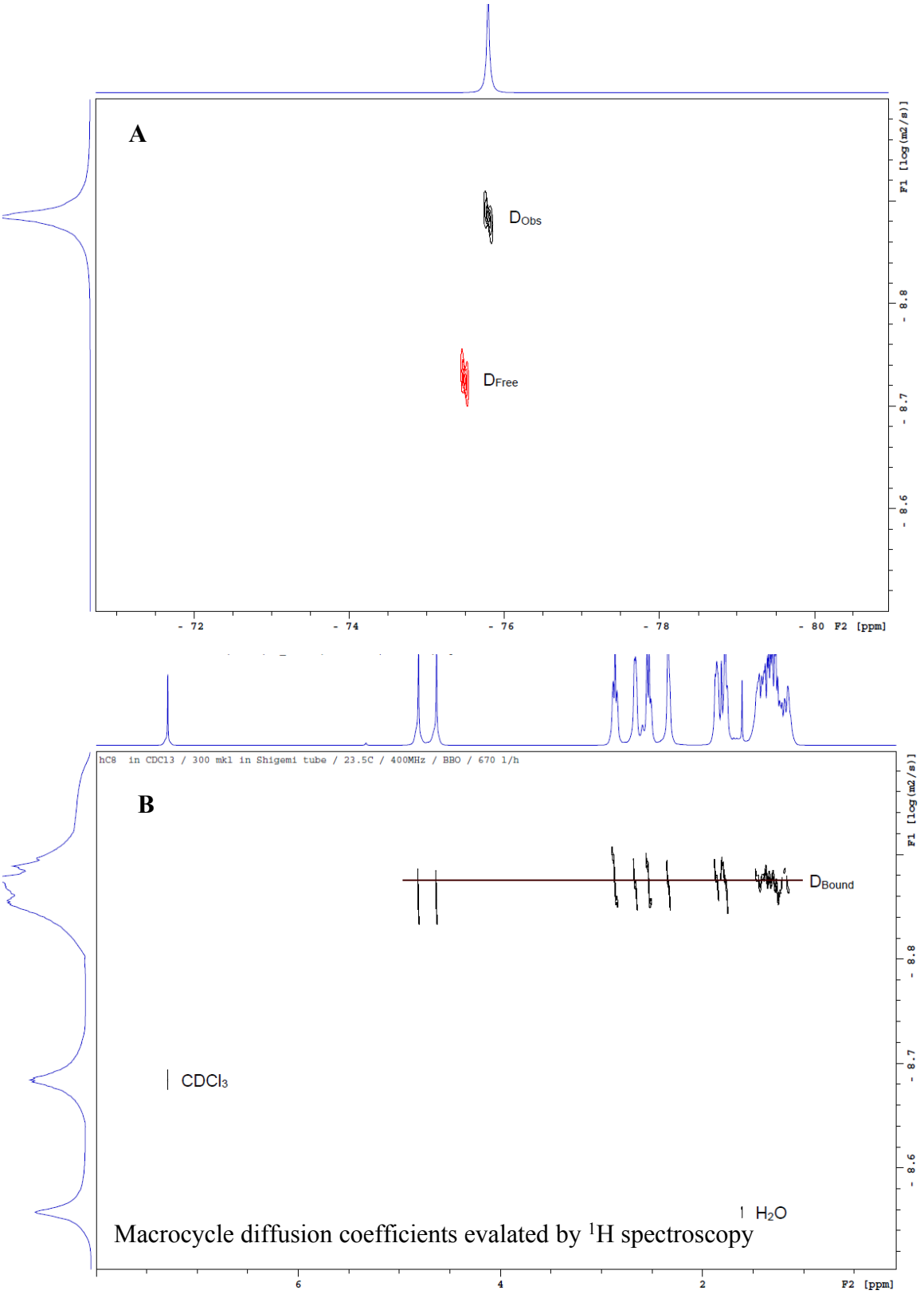


Figure S12. A: ^{19}F DOSY spectra of CF_3COOH in pure $CDCl_3$ (red) and in the presence of cycHC[8] (black); B: ^{1}H-DOSY of cycHC[8]

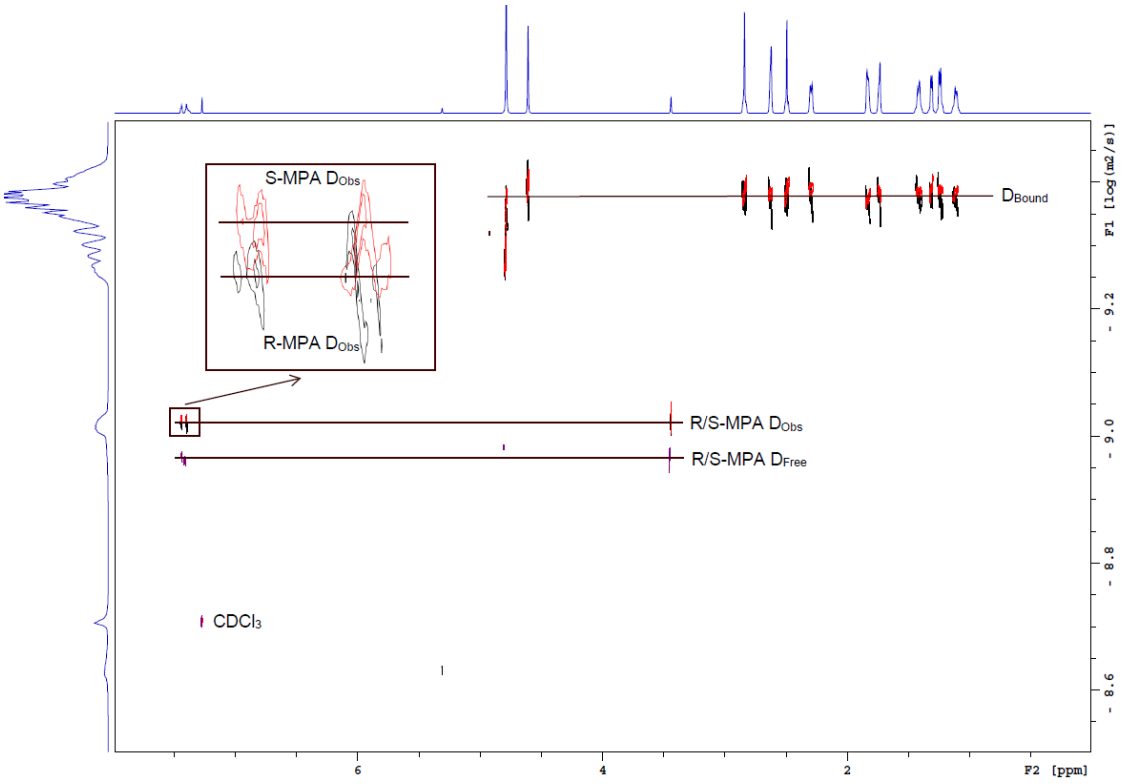


Figure S13. DOSY spectra of (*R*/*S*)-MPA in pure $CDCl_3$ (cyan), (*S*)-MPA (red) and (*R*)-MPA (black) in the presence of cycHC[8].

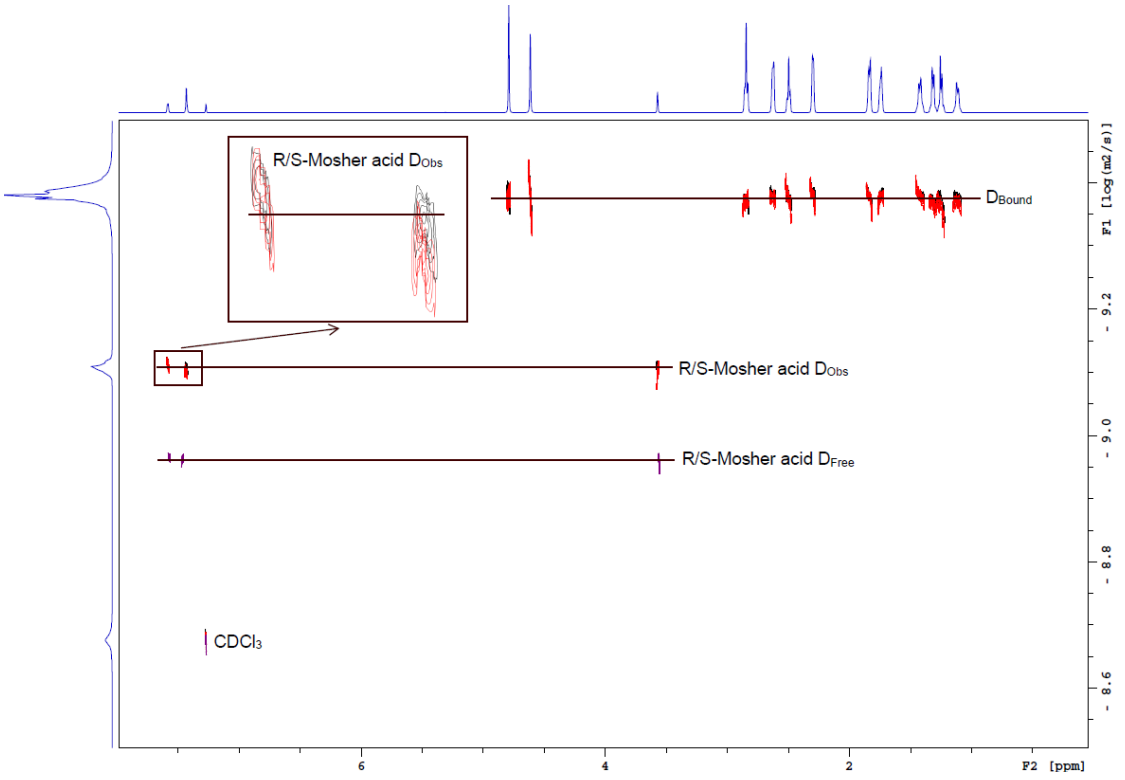


Figure S14. DOSY spectra of (*R*/*S*)-Mosher acid in pure $CDCl_3$ (cyan), (*S*)-Mosher acid ((*S*)-MTPA) (red) and (*R*)-Mosher acid ((*R*)-MTPA) (black) in the presence of cycHC[8].

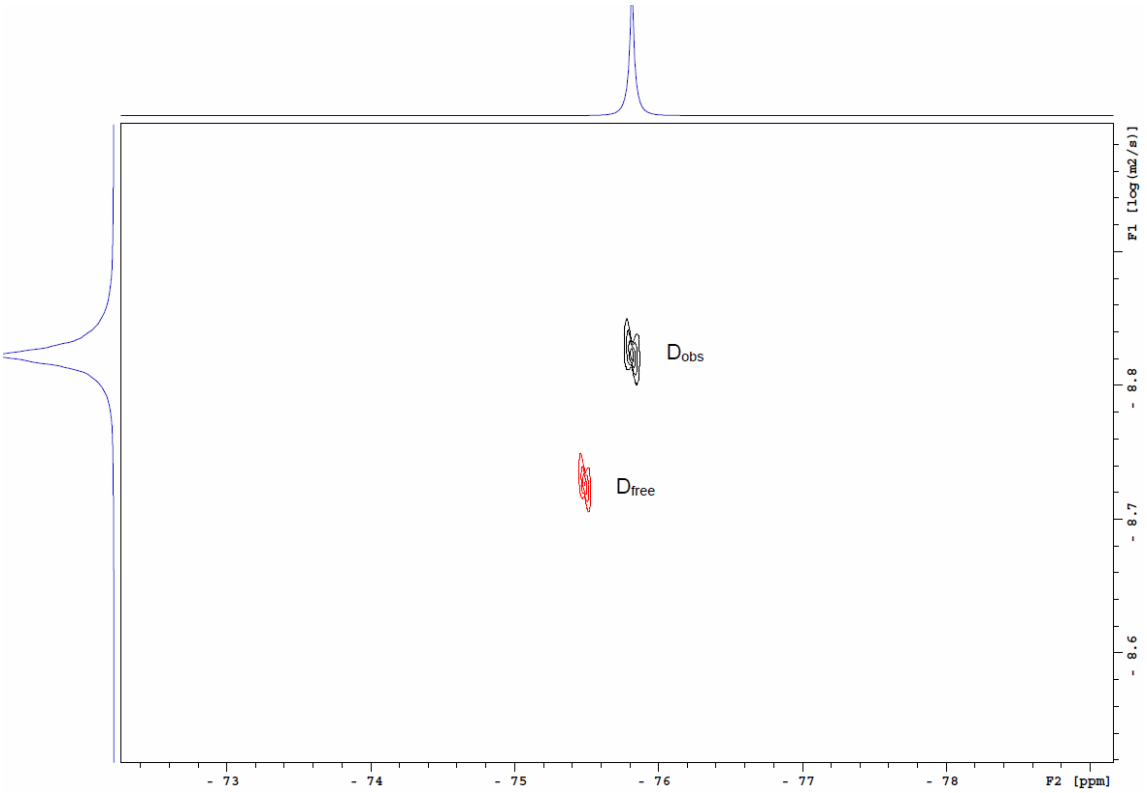


Figure S15. ^{19}F DOSY spectra of CF_3COOH in pure $CDCl_3$ (red) and in the presence of cycHC[6] (black).

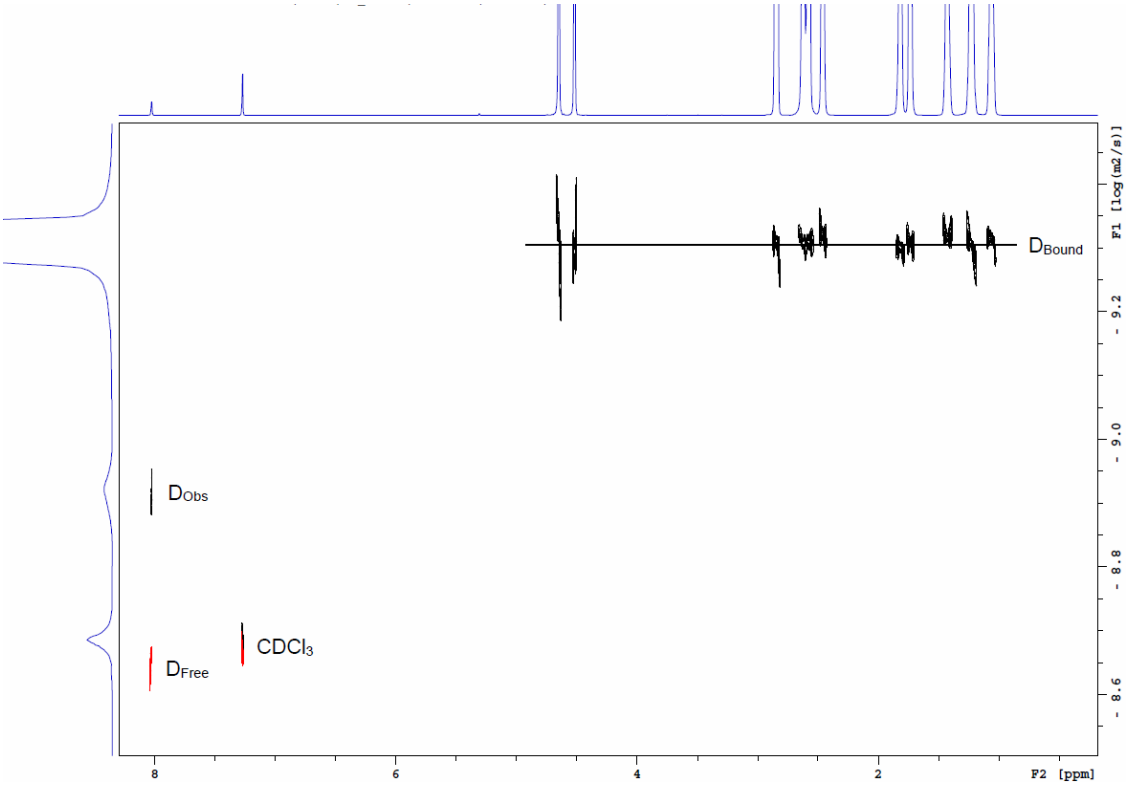


Figure S16. DOSY spectra of HCOOH in pure $CDCl_3$ (red) and in the presence of cycHC[6] (black).

6.3 Diffusion coefficients and calculation of association constants

Each diffusion coefficient *D* results from the fit of 32 data points (peak areas). In order to avoid *D* value distortion by signal overlap, a single peak with clear baseline separation from all other signals was selected for diffusion coefficient assignment for each compound. Errors given are standard errors estimated by the fitting procedure.

Fraction of complexed molecules, *p,* was calculated by

$$p = \frac{D_{free} - D_{obs}}{D_{free} - D_{bound}},$$

where D_{free} denotes the diffusion coefficient of free guest in $CDCl_3$, D_{obs} denotes the diffusion coefficient of guest in the presence of cycHC[8] and D_{bound} denotes the diffusion coefficient of bound guest. The latter was experimentally proven to be equal to the diffusion coefficient of cycHC[8].

Association constants K_a were calculated by

$$K_a = \frac{p}{(1-p)(C_1 - C_{guest})},$$

where C_1 denotes the concentration of cycHC[8] and C_{guest} denotes the concentration of the guest molecule. For more detailed information about the association constants calculation the reader is referred to Rymden *et al.*[11]

Table S7. Diffusion coefficients of the free and bound guest molecules and association constants with cycHC[8]

Guest	D_{free} (10^{-10} m^2s^{-1})	D_{obs} (10^{-10} m^2s^{-1})	D_1, D_{bound} (10^{-10} m^2s^{-1})	***p***	K_a, M^{-1}
CH_3COOH	17.85 (±0.06)	16.55 (±0.03)	4.26 (±0.01)	0.10 (±0.01)	17 (±2)
HCOOH	22.55 (±0.02)	17.72 (±0.01)	4.35 (±0.01)	0.27 (±0.01)	72.6 (±0.5)
[a]CF_3COOH	18.60 (±0.07)	13.57 (±0.08)	13.20 (±0.03)	0.93 (±0.02)	29 (±1)×10^3
(*R*)-MPA	11.23 (±0.01)	10.30 (±0.01)	4.39 (±0.01)	0.14 (±0.01)	29 (±3)
(*S*)-MPA	11.34 (±0.05)	9.82 (±0.01)	4.35 (±0.01)	0.21 (±0.01)	50 (±3)
(*R*)-MTPA	11.15 (±0.07)	7.491 (±0.001)	4.106 (±0.003)	0.52 (±0.01)	3.3 (±0.1)×10^2
(*S*)-MTPA	11.02(±0.07)	7.581 (±0.002)	4.064 (±0.003)	0.51 (±0.01)	3.0 (±0.1) ×10^2

[a]Due to technical limitations, the diffusion coefficients of CF_3COOH were measured by ^{19}F spectroscopy on a different spectrometer, at a slightly higher temperature, with a different pulse program and in a Shigemi tube. It is known that the same compound/solvent can display different diffusion behavior in NMR tubes of different geometry and temperature[12] which explains the discrepancy in *D* values when compared to other entries. This does not affect the relative diffusion rates of dissolved species.

Table S8. Diffusion coefficients of the free and bound guest molecules and association constants with cycHC[6]

Guest	D_{free} (10^{-10} m^{2}s^{-1})	D_{obs} (10^{-10} m^{2}s^{-1})	D_1, D_{bound} (10^{-10} m^{2}s^{-1})	p	K_a, M^{-1}
HCOOH	23.11 (±0.03)	12.47 (±0.02)	5.00 (±0.06)	0.53 (±0.01)	353 (±3)
[a]CF_3COOH	19.0 (±0.1)	14.99 (±0.1)	16.07 (±0.07)	0,92	21 (±3)×10^3

[a] See comment under Table S7.

7 Computational details

7.1 Equilibrium between cycHC[6] and cycHC[8]

The equilibrium between cycHC[6] and cycHC[8] was studied by evaluating the equilibrium constant (K_{eq}) from experimental data (page S18) and computationally. It is suggested that the equilibrium is thermodynamically controlled due to the broad spectrum of observed oligomers during the transformation reaction. Despite the large number, there were no prevailing oligomers in the reaction mixture, thus it is presumed that the equilibria between intermediates do not dictate the equilibrium between cycHC[6] and cycHC[8]. The Jacobson–Stockmayer theory states that the macrocycles produced under thermodynamic control are strainless[13] and their desired size is obtained by the aid of template molecules.[14] We have shown previously that the formate anion can be encapsulated inside cycHC[6] and the formic acid can be bound outside of cycHC[6].[15] To study whether the encapsulation drives the reaction towards cycHC[8], density functional theory calculations were used.

Geometry optimizations for local minima were carried out using the dispersion corrected B97-D functional,[16] along with the def2-SV(P)[17] basis set. Vibrational analysis was performed to ensure that all chosen geometries were at local minima. Additionally a single point calculation at the B97-D[16]/def2-TZVPD[17] level of theory was performed for every stationary point, with inclusion of the solvation model COSMO (ε = 51,1 – formic acid), to refine the energies. The total energies were calculated using the single point energies from the solvent phase calculation and adding the Gibbs free energy correction from the vibrational part of the gas phase calculation[18]. Gibbs free energy was estimated using the temperature 293.15 K and the pressure 0.1 MPa. The calculations were performed using the program package Turbomole 6.5.[19]

Complexation studies (Table 3 from the main text) have shown that cycHC[8] acts as a host for carboxylic acids. According to DFT calculations, the guest location preferences for cycHC[8] remained the same as for cycHC[6][15]. Therefore the theoretical ΔG was calculated for a reaction involving inclusion complex with the formate anion,

$$4(HCOO^- @ cycHC[6]) \rightleftharpoons 3(HCOO^- @ cycHC[8]) + HCOO^-.$$

The computationally derived ΔG is −177 kJ/mol in favour of cycHC[8], indicating that the complexation with formate anion induces a preference towards the formation of cycHC[8]. The calculation gives a qualitative explanation for the equilibrium preference of the system. Based on these findings, it can be proposed that complexation with formate anion may govern

the overall equilibrium between the 6- and 8-membered cycHCs and drive the aforementioned reaction towards the formation of cycHC[8].

Table S9. Calculated energies (in Hartrees) of the studied geometries.

Name	Energy	Gibbs Corr.	Total
cycHC[6]	−2980.157550[a]	1.109313	−2979.048237
$HCOO^-$@ cycHC[6]	−3169.461130[b]	1.127793	−3168.333337
[HCOOH+cycHC[6]]	−3169.948819[b]	1.137799	−3168.811021
cycHC[8]	−3973.535695[a]	1.474656	−3972.061039
$HCOO^-$@cycHC[8]	−4162.866502[b]	1.495944	−4161.370558
$HCOO^-$@cycHC[8]	−4162.788348[a]	1.495944	−4161.292404
[$HCOO^-$+cycHC[8]]	−4162.748669[a]	1.491423	−4161.257246
HCOOH@cycHC[8]	−4163.339071[b]	1.507781	−4161.831289
HCOOH@cycHC[8]	−4163.292729[a]	1.507781	−4161.784948
[HCOOH+cycHC[8]]	−4163.289851[a]	1.503302	−4161.786549
$HCOO^-$	−189.284877[b]	−0.004220	−189.289100

a – calculated energies are in gas phase due to unsuitability of the continuum model for the guest-less cavity
b – COSMO solvation model is included

The energy differences of cycHC[6] and cycHC[8] per monomer were compared to confirm that the Jacobson–Stockmayer theory applies. The difference of ΔGs is 1 kJ/mol in favour of cycHC[6] affirms that both macrocycles are strainless. Formic acid favours to be bound outside the cycHC[8] by 4 kJ/mol as can be seen on Figure S17. Formate anion favours to be bound inside the cycHC[8] by 92 kJ/mol.

The results do not include a basis set superposition error (BSSE) correction due to incompatibility between the continuum solvation model (COSMO) and the counterpoise (CP) approach to BSSE correction. In the CP workflow, COSMO energies of fragments with different cavities would be added, which would lead to physically meaningless results.

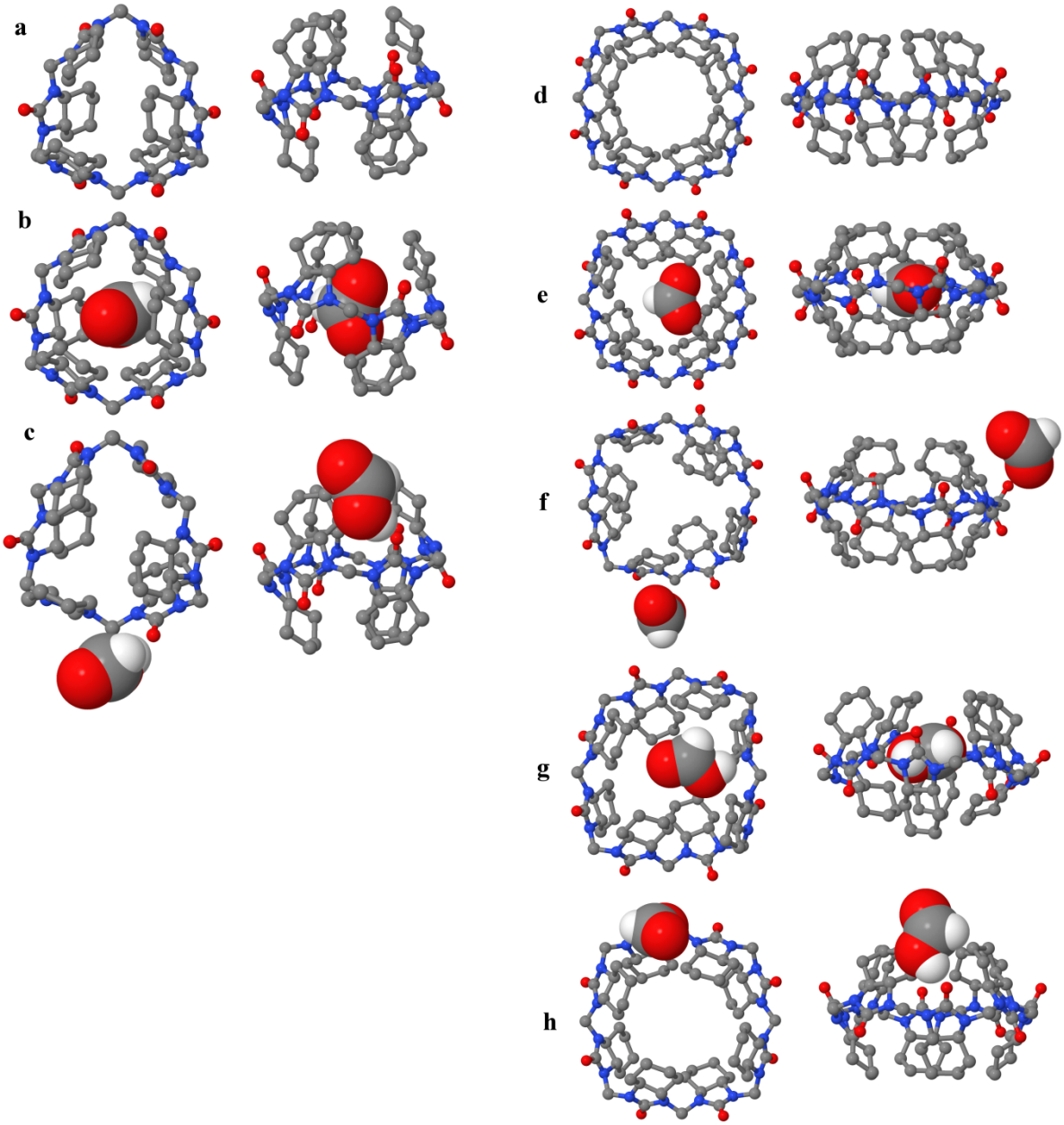


Figure S17. Geometries used in equilibrium calculations: a) cycHC[6], b) $HCOO^-$@cycHC[6] (the anion bound outside the cycHC[6] is unfavoured – ref 15), c) [HCOOH+cycHC[6]] (the formic acid bound inside the cycHC[6] is unfavoured – ref 15), d) cycHC[8], e) $HCOO^-$@cycHC[8], f) [$HCOO^-$@+cycHC[8]], g) HCOOH@cycHC[8] and h) [HCOOH+cycHC[8]]. Image was created using Jmol[20].

7.2 Equilibrium between cycHC[6] and cycHC[8]

To gain detailed insight into the reaction pathways of the transformation of cycHC[6] to cycHC[8], a computational study with model structures was performed. Irrespective of the vast number of possible reaction routes leading to the transformation of cycHC[6] to cycHC[8], they can be conceptually reduced to two basic steps: chain depropagation and chain propagation.

Because of its high efficiency, the density functional BP86[21] in combination with the def2-SV(P)[17] basis set was used to model the reaction pathways. Vibrational analysis was performed to ensure that all chosen geometries were at local minima or at first order saddle points, as appropriate. The transition states were verified using intrinsic reaction coordinate calculations. To refine the energies, a single point calculation at the B97-D/def2-TZVPD[16,17] level of theory was performed for every stationary point, with inclusion of the solvation model COSMO (ε = 51,1 – formic acid). The total energies were calculated using the single point energies from the solvent phase calculation and adding the Gibbs free energy correction from vibrational part of the gas phase calculation[18]. Gibbs free energy was estimated using the temperature 293.15 K and the pressure 0.1 MPa. The calculations were performed using the program package Turbomole 6.5.[19]

Figure S18 shows the relative energies and structures of the intermediates and transition states in the depropagation and propagation reaction. Due to the zig-zag orientation of the monomers in a macrocycle, there are two different types of methylene bridges and thus four different locations for the proton in cycHC[*n*] + H^+. As we have shown in our previous work[15], the protonation from inside of the macrocycle is energetically most favoured.[15] The geometry of the dimer **1bH**$^+$, protonated at the position corresponding to the inner protonation site, was chosen as starting geometry for computational depropagation and propagation studies. After the protonation, the chain depropagation can advance through two different reaction paths, differentiated on the reaction coordinate diagram in Figure S18 by continuous and dotted lines, respectively. The dissociation of the C–N bond (**TS2a** – continuous line) has lower transition state energy (64 kJ/mol) compared to substitution reaction (80 kJ/mol) (**TS2b** – dotted line). The product of dissociation is an iminium cation **3a**, which can be attacked by a formate anion, yielding the formyl-terminated **4a**. The second possible reaction path involves a nucleophilic attack on the methylene bridge by the formate (**TS2b** – dotted line). The energy of transition state of this substitution reaction is higher and the reaction path produces the formyl compound **4a** directly. Considering that the substitution reaction is energetically more demanding, one can suppose that the formation of formylated compounds proceeds through the iminium ion **3a**. All reactions can proceed also in the reverse direction, starting from the right hand side of the energy diagram (Figure S18). In addition, compound **4a** can be converted to iminium **3a** through protonation of the formyl group and subsequent fragmentation where formic acid leaves.

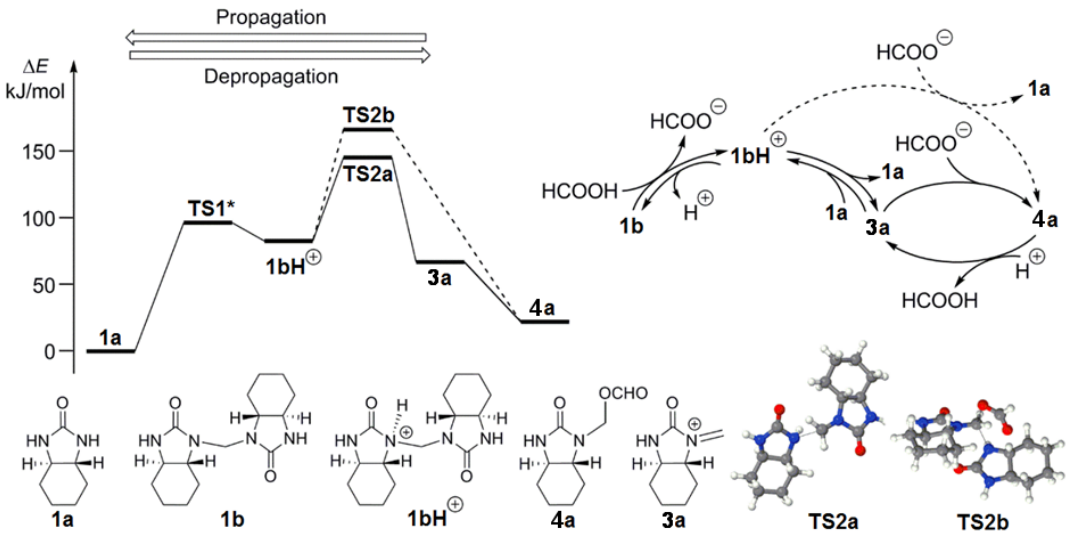


Figure S18. Propagation and depropagation reaction coordinate of the model structures.

Table S10. Calculated energies for the model system. Energies are in Hartrees (except for the last column which has the relative energies in kJ/mol).

Name	Energy	Gibbs correction	Total energy	Energy difference
1b	−955.298024	0.340361	−954.957662	0
TS1	-	-	-	96*
1bH$^+$	−955.728298	0.352470	−955.375828	85
TS2a	−955.709673	0.349975	−955.359698	149
TS2b	−1145.006708	0.366083	−1144.640625	165
3a	−497.104069	0.171000	−496.933069	66
4a	−686.430878	0.191754	−686.239124	22

* - Energy obtained using the Eyring equation

Eyring equation

$$\Delta G = -\ln\left(\frac{kh}{k_B T}\right)RT$$

ΔG – Gibbs free energy
k – reaction rate constant ($5 \cdot 10^{-5}$ s^{-1})
h – Planck's constant
k_B – Boltzmann constant
T – Temperature (293.15 K)
R – Gas Constant

7.3 Geometries for equilibrium of the remacrocyclization reaction

cycHC[6]
138

C	0.5786423	3.6327210	-1.7019190
C	0.1129478	4.1543326	-3.0603004
C	0.1216769	2.9437357	-4.0304662
C	1.4610767	2.1625684	-4.0528719
C	1.9720961	1.7732599	-2.6403673
C	1.9930386	3.0605499	-1.8212270
N	0.7355883	4.5497916	-0.5743914
C	1.7620692	4.0781818	0.2588286
N	2.4161228	3.0510774	-0.4275389
O	2.0402058	4.4916528	1.3797042
C	3.7258334	2.5627679	-0.0451142
C	2.8525462	-0.8939079	3.9916255
C	2.5981772	0.6357841	3.9990444
C	2.3947440	1.2332224	2.5821198
C	3.9639593	-1.3466301	3.0084426
C	3.6220320	-0.7417973	1.6480315
C	3.5930608	0.7848113	1.7508083
N	3.7145456	1.1685843	0.3512050
N	4.5171157	-0.9350080	0.5077049
C	4.7525698	-2.2639348	-0.0366429
C	4.4298845	0.1834265	-0.3352476
O	4.8986392	0.2843782	-1.4643778
C	-0.5750296	2.9308645	4.0138337
C	-1.7628882	1.9345256	4.0392565
C	-2.1964762	1.4552393	2.6287296
C	-0.7632876	4.1168052	3.0315282
C	-1.1305043	3.5131141	1.6771209
C	-2.4299237	2.7145927	1.8003467
N	-2.8452659	2.6239650	0.4073851
N	-1.4337660	4.3812823	0.5400604
C	-0.4129705	5.2525738	-0.0218983
C	-2.3681365	3.7394342	-0.2873614
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C	-2.6757765	0.1793272	-4.0047766
C	-2.6917427	-1.3711189	-3.9863007
C	-3.7179562	-1.9812130	-2.9955082
C	-2.5605945	0.8112829	-2.5927527
C	-3.6718765	0.1895557	-1.7518716
C	-3.4666798	-1.3226951	-1.6407064
N	-4.3167678	-1.6434607	-0.4947684
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C	-4.3959339	-0.5201457	0.3427520
O	-4.8675019	-0.4851913	1.4747792
C	-2.1685380	-1.9827865	4.0516836
C	-0.7155111	-2.5243636	4.0506614
C	-0.1091892	-2.6612595	2.6285462
C	-3.1234752	-2.7333994	3.0865687
C	-2.4424128	-2.7517167	1.7189281
C	-1.1023645	-3.4854784	1.8149296
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C	-2.0626823	-3.9319973	-0.2567455
O	-2.2205060	-4.3994527	-1.3796904
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C	2.4484526	-1.6319980	-4.0374097
C	3.5099332	-2.2128267	-3.0662886

C	0.5217071	-2.6245057	-2.6135593
C	1.6335636	-3.2735249	-1.7935948
C	2.8382114	-2.3344298	-1.6994731
N	3.5637849	-2.9130343	-0.5698525
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H	-0.6859683	2.2546466	-3.7169130
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HCOO-@cycHC[6]
142

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HCOOH@cycHC[6]
143

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C	-4.2702604	0.5935520	-3.3294559
C	-4.3557965	-0.9280384	-3.0462421
C	-3.0333015	-1.5019223	-2.4764678
C	-3.0758482	0.9821907	-4.2386711
C	-1.8150841	0.4098480	-3.5937053
C	-1.9309192	-1.1130686	-3.4604712
N	-0.5184947	-1.4771844	-3.2054765
N	-0.5347701	0.5166757	-4.2958151
C	0.0130518	1.7569741	-4.8395057
C	0.2618566	-0.5710370	-4.0047221
O	1.4117623	-0.7656569	-4.3677723
C	4.1297129	-2.8167912	-1.2618548
C	4.0626865	-3.3580655	0.1883821
C	2.9837399	-4.4549221	0.3794739
C	2.7555832	-2.3446951	-1.8040024
C	1.7774519	-3.5011132	-1.6071364
C	1.6681273	-3.8659521	-0.1229356
N	0.4505953	-4.6804466	-0.1225265
N	0.3585401	-3.3635271	-1.9474622
C	-0.1258225	-2.9033971	-3.2212589
C	-0.3901853	-4.2349309	-1.1460326
O	-1.5615606	-4.5493566	-1.3296783
H	1.4305893	1.5958317	2.0512919
H	3.4288341	2.3478487	4.2638222
H	2.9873623	3.3792605	2.8510369
H	5.0766920	2.0017137	2.3726544
H	3.7293762	1.6455846	1.2590866
H	4.8118668	-0.4796730	1.9393907
H	4.6196948	-0.0741519	3.6672633
H	2.3377181	-0.6671254	1.6655728
H	2.8432336	-1.7004372	3.0359057
H	2.3856542	0.2034425	4.6131275
H	-5.1288449	-3.3047074	1.0470576
H	-3.8015237	-2.4594869	0.2026441
H	-4.5321326	-2.2270194	3.1983904
H	-4.7368877	-0.9672718	1.9527362
H	-2.2418107	-0.7672118	1.7120387
H	-2.6938744	-0.5722576	3.4368096
H	-3.4418082	-4.6467832	2.3701674
H	-3.0847594	-4.7668977	0.6032378
H	-1.5022794	-2.8336592	0.8234782

H -2.3004156 -3.0461597 3.7719935
H -3.5574267 1.0382744 1.8550628
H -4.9441557 2.0890166 2.2281723
H -4.5514958 1.7991297 -0.2631238
H -4.4845771 3.5042971 0.2506419
H -2.0324996 1.7126269 -0.3763103
H -2.6229236 3.1100630 -1.3307770
H -3.3694818 3.9798722 2.8000810
H -2.8975055 2.4925179 3.7055493
H -1.2834161 1.9255101 1.8593310
H -2.3676389 4.5609344 0.7294634
H 4.6188198 3.6750266 -1.9626336
H 4.8237506 2.4465544 -0.6848152
H 5.0995130 1.4838836 -3.0120890
H 3.7654540 0.7069688 -2.1116965
H 3.4235902 2.8702167 -4.3095007
H 3.0070134 1.1168261 -4.4189795
H 2.3376944 2.3157267 -0.3629212
H 2.8581106 4.0210625 -0.2516804
H 2.3418486 4.3153591 -2.6963957
H 1.4843470 1.3877083 -2.4392034
H -4.1588202 1.1325333 -2.3646497
H -5.2179660 0.9449331 -3.7866125
H -5.1834852 -1.1318387 -2.3359251
H -4.6018741 -1.4609567 -3.9913356
H -3.0877369 -2.6013486 -2.3508691
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H -2.9984874 2.0826333 -4.3215346
H -3.2009329 0.5502877 -5.2551680
H -1.7193206 0.8547386 -2.5771686
H -2.2111608 -1.5209318 -4.4613229
H 4.8535696 -1.9768287 -1.3158855
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H 3.8244739 -2.5201272 0.8764349
H 5.0560031 -3.7510525 0.4885676
H 2.9057338 -4.7280560 1.4480007
H 3.2346615 -5.3630287 -0.2106954
H 2.8332523 -2.0628708 -2.8703259
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H 2.1837926 -4.3886197 -2.1519721
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H 0.7518046 5.4312483 -0.6592471
H -0.9305171 5.2033739 -1.3048106
H 0.7183900 -5.8181653 1.6052160
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H -0.7266819 -1.3757497 5.0431386
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H 0.8663822 4.1368937 4.0541229
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H -0.8028797 2.2906249 -5.3574153
C 0.2005183 -0.1669050 0.2066645
O -0.7071216 -0.8740726 -0.4575038
O 1.2154780 0.3058355 -0.2662397
H -0.0829076 -0.0767648 1.2817016
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cycHC[6]-HCOOH-outside
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C	1.8295490	0.3462218	3.6308951
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C	-0.2267797	1.1626199	4.3121126
N	0.4349675	0.0147665	3.9160749
O	-1.3532574	1.2347942	4.8295647
C	0.0540465	-1.3383927	4.2899449
C	-3.9806753	-2.7428111	1.0004029
C	-3.9616950	-1.5534767	1.9956352
C	-2.5324799	-1.0447103	2.3248132
C	-3.0115604	-3.8974169	1.3663463
C	-1.6432119	-3.2617524	1.6049101
C	-1.7335706	-2.2669835	2.7648651
N	-0.3305845	-2.1434056	3.1510790
N	-0.5082012	-4.0874981	2.0140312
C	0.0235461	-5.1072386	1.1214891
C	0.3390798	-3.3337875	2.8333632
O	1.4623057	-3.6495681	3.2128244
C	-4.0068426	2.3386561	1.9651756
C	-4.0220161	2.6479542	0.4454539
C	-2.6087276	2.6811141	-0.1954967
C	-3.0176275	3.2135141	2.7796812
C	-1.6608212	3.1106126	2.0840541
C	-1.7757647	3.6386359	0.6514920
N	-0.3797654	3.9024244	0.3273127
N	-0.5178241	3.8745656	2.5809620
C	0.0432995	3.6028856	3.8918638
C	0.3149348	4.2095440	1.4981936
O	1.4418200	4.6871711	1.5707941
C	4.0324256	2.2374781	-1.5114138
C	4.0019610	1.2908632	-2.7391673
C	3.0094879	1.7279753	-3.8485896
C	2.6249136	2.5454759	-0.9362365
C	1.7795208	3.0387574	-2.1061899
C	1.6583271	1.9448217	-3.1696135
N	0.5123843	2.4233316	-3.9414466
N	0.3826464	3.4047204	-1.9127746
C	0.0011993	4.4342726	-0.9679070
C	-0.3183036	3.1808691	-3.1031944
O	-1.4483210	3.5821112	-3.3615539
C	-4.0412041	0.5427439	-2.8971274
C	-4.0552651	-0.9423039	-2.4513250
C	-2.6390616	-1.5199006	-2.1910298
C	-3.0739991	0.8379431	-4.0734396
C	-1.7111974	0.2732923	-3.6752582
C	-1.8188210	-1.2356740	-3.4450278
N	-0.4205532	-1.6368698	-3.5266108
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C	-0.0426085	1.6228742	-5.0240225
C	0.2588789	-0.7592796	-4.3758509
O	1.3826163	-0.9245659	-4.8393121
C	4.0305834	-2.3344146	-1.2318214
C	4.0292549	-2.9252098	0.2022301
C	3.0574360	-4.1192080	0.3911844
C	2.6103558	-2.0114358	-1.7674393
C	1.7863075	-3.2848113	-1.5985253
C	1.6919689	-3.6595700	-0.1176515
N	0.5598237	-4.5835194	-0.1266890
N	0.3844746	-3.3235189	-1.9923559
C	-0.0228831	-3.0198361	-3.3501800

C	-0.2918689	-4.2500392	-1.1922978
O	-1.4187071	-4.6908887	-1.3902658
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H	3.4298439	2.4285253	4.3860939
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H	5.0695497	2.1255942	2.4964109
H	3.7264158	1.9536700	1.3421272
H	4.6601188	-0.2780146	1.7851427
H	4.5397246	-0.0458128	3.5478223
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H	2.6756539	-1.5125855	2.8509764
H	2.3913261	0.2954421	4.5945771
H	-5.0153768	-3.1337570	0.9192204
H	-3.6964182	-2.3745642	-0.0027980
H	-4.4463261	-1.8613702	2.9450438
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H	-2.0544514	-0.5828804	1.4346304
H	-2.5647715	-0.2819562	3.1245775
H	-3.3413211	-4.4191373	2.2896109
H	-2.9676078	-4.6265185	0.5349384
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H	-3.7187437	1.2797129	2.1089743
H	-5.0319396	2.4489017	2.3757279
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H	-2.3163814	4.6161672	0.6795408
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H	4.6756594	1.7981018	-0.7206250
H	5.0234869	1.2016143	-3.1627208
H	3.7051116	0.2792683	-2.4016457
H	3.3388712	2.6751306	-4.3268840
H	2.9387472	0.9398586	-4.6219016
H	2.1632657	1.6315100	-0.5045527
H	2.6822420	3.3082596	-0.1342253
H	2.3108729	3.9117824	-2.5583675
H	1.3752855	0.9956340	-2.6550573
H	-3.7297000	1.1701028	-2.0388634
H	-5.0698215	0.8584251	-3.1681539
H	-4.6792436	-1.0502032	-1.5406264
H	-4.5372967	-1.5550906	-3.2438559
H	-2.6851051	-2.6064283	-1.9806474
H	-2.1644765	-1.0254526	-1.3162715
H	-3.0134173	1.9285618	-4.2466874
H	-3.4196608	0.3428483	-5.0058640
H	-1.4106315	0.7457417	-2.7095153
H	-2.3636737	-1.6864995	-4.3108998
H	4.6590151	-1.4204579	-1.2553862
H	4.5022597	-3.0645221	-1.9250403
H	3.7291901	-2.1317601	0.9139593
H	5.0596319	-3.2308934	0.4784911
H	3.0061974	-4.3973722	1.4604520
H	3.3920192	-5.0012816	-0.1956840
H	2.6484943	-1.6965574	-2.8285931
H	2.1441423	-1.1867185	-1.1863678
H	2.3241865	-4.1042852	-2.1360684
H	1.4036890	-2.7416942	0.4492520
H	0.8549788	5.1235625	-0.8085271

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H -0.7871339 -5.8109506 0.8632170
H 0.8226746 -3.2172561 -4.0404640
H -0.8765513 -3.6824156 -3.6010370
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H 0.9214245 -1.8308453 4.7730759
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H -0.7453523 3.7247197 4.6552529
H 0.7559477 1.4190082 -5.7590654
H -0.8509251 2.2145076 -5.4887979
H -2.4196423 0.0968646 5.3900460
O -3.0441157 -0.6506638 5.6563442
C -4.3096069 -0.3729735 5.3052900
O -5.2294364 -1.1419584 5.4338469
H -4.4244849 0.6605740 4.8693002

cycHC[8]
184

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C -1.6179959 -2.0593554 -4.7574945
H -2.1905409 -2.3245051 -5.6809141
C -2.6264096 -1.5790702 -3.7149590
H -2.0903768 -1.2769234 -2.7896267
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H -4.0711617 0.0636951 -3.5893696
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C -1.4505487 -0.8988221 5.0405603
H -1.2463535 -0.2856502 4.1282036
C -0.1521082 -0.9690770 5.8435855
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H 1.1040419 -0.8063756 4.0818079
H 1.8829283 -1.6734541 5.4284113
C 0.5123398 -2.8989766 4.2397856
H 0.4852034 -3.6822205 5.0288197
H 1.2816040 -3.2126654 3.5040684
C -0.8794313 -2.8535286 3.5559137
H -0.8662492 -2.1892367 2.6656268
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C -2.8359923 0.8909206 6.2328592
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C -1.1407001 2.4943450 5.3916307
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H -2.6212217 1.2735776 3.3779491
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H	-1.7384262	4.4374553	1.6878567
C	-3.7825077	3.6267604	1.6331573
H	-3.8840173	3.6471504	0.5279979
H	-4.1767480	4.5958799	2.0087547
C	-4.6418129	2.4760645	2.2178092
H	-5.7105587	2.6485173	1.9747057
H	-4.3514619	1.5237064	1.7241826
C	-4.4730300	2.2930825	3.7500797
H	-4.8492250	3.1845763	4.2959709
H	-5.0361414	1.4064102	4.0990057
H	-2.1514823	-4.6648756	-4.7320776
C	0.0615063	4.2602916	4.1407128
H	-0.4165023	5.2615208	4.0959753
C	1.1430332	5.2252438	2.1332998
C	2.0627620	3.2619248	2.9778213
H	2.7775742	3.6454506	3.7475989
C	2.6589252	3.5404165	1.5927336
H	2.0817401	2.9482860	0.8412870
C	4.1070808	3.0564073	1.5396473
H	4.7010082	3.5686845	2.3260845
H	4.5684296	3.2744115	0.5572631
C	4.0641581	1.5255578	1.7937039
H	3.5527668	1.0479265	0.9303129
H	5.0960746	1.1186163	1.8180865
C	3.3200712	1.1358958	3.0972089
H	3.9190344	1.4792487	3.9688617
H	3.2494845	0.0311726	3.1743697
C	1.9045661	1.7599392	3.2072464
H	1.2203060	1.3361456	2.4413747
H	1.4670582	1.5580324	4.2051371
C	2.6706066	5.7128140	0.2407361
H	2.1933443	6.7041106	0.3503692
H	3.7687913	5.8234125	0.1767271
C	3.1132847	4.2792435	-1.7357502
C	0.8685752	4.6712063	-1.2484815
H	0.6320598	3.8228019	-0.5605593
C	0.9897917	4.1135710	-2.6723857
H	0.9751628	4.9757315	-3.3847978
C	-0.2035379	3.2209355	-3.0087722
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H	-2.3792936	3.4793368	-3.0390097
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H	1.7696178	-0.8942508	-3.3697130
C	3.6239237	-1.9073139	-3.7473314
H	4.5975459	-1.7241406	-4.2505852
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C	3.8168792	-2.0536297	-2.2136994
H	2.8390418	-2.3398026	-1.7708283
H	4.5195706	-2.8852392	-2.0001222
C	4.3193632	-0.7576040	-1.5258793
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H	4.3508407	-0.9038097	-0.4261538
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H	2.4429689	0.4040765	-1.4313237
H	3.9313882	1.4063302	-1.4554584
C	1.6554069	-1.0960541	-6.2503224
H	2.3229258	-1.9224104	-6.5566923
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N	0.4425545	-1.7117037	-5.7409516
N	-0.7106515	-3.1550370	-4.4483570
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O	-4.9583249	-0.7383603	5.0963788
O	-0.3173052	2.3428069	6.2873367
O	0.4528709	6.2350837	2.0466166
O	4.3303367	4.2028148	-1.6092800
O	1.5603470	1.8081325	-6.1235331
H	-5.8961710	-3.0180706	1.6914900
H	0.6811025	4.1813181	5.0588096
C	-4.0912429	-3.2084356	3.8361088
C	-1.2268093	-4.4729447	-4.1475465
C	-2.8011876	-5.1493001	-2.3603574
C	-0.5520097	-5.0173953	-1.7809618
H	-0.1760722	-6.0333968	-2.0587714
C	-1.3920534	-5.1517730	-0.5050776
H	-1.5602484	-4.1272053	-0.0909355
C	-0.6209122	-5.9478544	0.5471451
H	-0.3680496	-6.9520020	0.1445628
H	-1.2196177	-6.0824358	1.4681056
C	0.6679022	-5.1376527	0.8491409
H	0.3691321	-4.1887988	1.3451686
H	1.2993179	-5.6917213	1.5739324
C	1.4988677	-4.8031560	-0.4166202
H	1.9284175	-5.7444527	-0.8233541
H	2.3554429	-4.1527462	-0.1426048
C	0.6657837	-4.1287969	-1.5372698
H	0.3316254	-3.1145516	-1.2311261
H	1.2686939	-4.0248621	-2.4608728
C	-3.8129983	-5.9390620	-0.2372269
H	-4.6365620	-6.1811646	-0.9335275
H	-3.5974742	-6.8050012	0.4155929
C	-3.7618998	-4.7933219	1.9621913
C	-4.4520497	-3.4929856	0.1559406
H	-3.4826091	-3.0691742	-0.2033385
C	-4.7098602	-1.2689272	1.3113243
H	-3.6628014	-1.0002150	1.0548827
H	-4.9724330	-0.7560045	2.2578702
C	-5.6852378	-0.8538964	0.1792307
H	-5.1380511	-2.9477108	4.0992036
H	-5.5781670	0.2309189	-0.0294473

H -6.7242919 -1.0077836 0.5439126
C -5.4881928 -1.6627364 -1.1293486
H -3.7858501 -4.1278169 4.3793410
H -6.2689100 -1.3783968 -1.8644147
H -4.5101204 -1.3868742 -1.5795121
C -5.5016332 -3.2005504 -0.9154624
H -6.4990315 -3.5396273 -0.5633368
H -5.2687414 -3.7262163 -1.8612447
H -0.4436335 -5.2064740 -4.4330050
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N -2.6531448 -5.6418043 -1.0585803
N -4.2134733 -4.8521139 0.6385684
N -3.9873231 -3.4913057 2.4210494
O -3.8197630 -5.1733010 -3.0421494
O -3.2618416 -5.7077647 2.6078076

HCOO-@cycHC[8]
188

C 0.5112527 -3.0527345 -5.1935235
C -0.5702972 -0.9892182 -5.1079650
H -0.1942200 -0.5636283 -4.1489598
C -1.5716167 -2.1013932 -4.7721412
H -2.1435267 -2.3509020 -5.7016254
C -2.5770395 -1.6208547 -3.7269522
H -2.0420908 -1.3271988 -2.7989274
H -3.2955978 -2.4238738 -3.4707899
C -3.3186123 -0.4081513 -4.3460704
H -3.9541523 -0.7768495 -5.1816304
H -4.0025301 0.0331540 -3.5917030
C -2.3607517 0.6847200 -4.8849026
H -1.8432336 1.1573820 -4.0261851
H -2.9468711 1.4837035 -5.3848924
C -1.2770489 0.1406767 -5.8549796
H -1.7391787 -0.2563489 -6.7848756
H -0.5674418 0.9434951 -6.1324372
C -4.7373948 -2.7654133 1.4831640
C -3.7229507 -1.1439067 5.0284771
C -1.8111125 -2.3644407 4.4884664
H -1.6824782 -3.0239957 5.3852119
C -1.4080440 -0.9351989 4.8711716
H -1.2962406 -0.3550960 3.9301774
C -0.0506763 -0.9452472 5.5701288
H -0.0909297 -1.5948581 6.4721037
H 0.2457667 0.0726137 5.8903423
C 0.9534080 -1.5037309 4.5273466
H 1.0041592 -0.7812268 3.6895656
H 1.9685657 -1.5676904 4.9715524
C 0.5411266 -2.8829387 3.9541094
H 0.6090486 -3.6490577 4.7597281
H 1.2596832 -3.1828465 3.1628574
C -0.9001962 -2.8916484 3.3804424
H -0.9738838 -2.2238607 2.4980358
H -1.1927946 -3.9200132 3.0867007
C -2.7444051 0.8235048 6.1804715
H -3.8093434 0.9247214 6.4658917
H -2.1037342 0.8847695 7.0807898
C -1.0935147 2.5304905 5.4576523
C -2.8080751 2.0818197 3.9447246
H -2.3431870 1.2910105 3.3160904
C -2.1409345 3.4105416 3.5684441
H -2.7514755 4.2497519 3.9927507
C -2.1059117 3.5728391 2.0492742

H	-1.5362558	2.7349946	1.5992375
H	-1.6171636	4.5255219	1.7646030
C	-3.5825746	3.5656508	1.5764566
H	-3.6190932	3.6074699	0.4690274
H	-4.0812109	4.4878797	1.9523802
C	-4.3720790	2.3284554	2.0714927
H	-5.4321458	2.4018588	1.7489189
H	-3.9407399	1.4276196	1.5917277
C	-4.2958960	2.1285707	3.6078542
H	-4.7800529	2.9758430	4.1416432
H	-4.8105295	1.1946549	3.9080304
H	-2.1254442	-4.7093239	-4.7769476
C	0.1046254	4.3511953	4.2629304
H	-0.3678171	5.3558968	4.2182902
C	1.1557337	5.2712710	2.2067978
C	2.0375210	3.2753003	3.0316814
H	2.8339171	3.6281811	3.7366101
C	2.5268601	3.4894412	1.5945893
H	1.8493081	2.9125573	0.9279152
C	3.9331806	2.9221290	1.4283987
H	4.6262218	3.4017427	2.1546618
H	4.3265875	3.1033253	0.4089882
C	3.8063954	1.4014073	1.7067722
H	3.1633709	0.9650822	0.9164211
H	4.8026973	0.9158574	1.6329752
C	3.1668094	1.0851325	3.0810717
H	3.8628499	1.4099617	3.8874167
H	3.0407964	-0.0112606	3.1860837
C	1.8004880	1.7880889	3.2930900
H	1.0346612	1.4015058	2.5896317
H	1.4424775	1.6223346	4.3286901
C	2.6002399	5.6599452	0.2253650
H	2.1128561	6.6489782	0.3247730
H	3.6977164	5.7853377	0.1505524
C	3.0884484	4.3046426	-1.7956147
C	0.8350890	4.4998602	-1.2359859
H	0.6819002	3.6047465	-0.5953956
C	0.9531718	4.0156411	-2.6862150
H	0.8527138	4.8997212	-3.3676326
C	-0.1766323	3.0393086	-3.0111578
H	-0.1247927	2.1756941	-2.3172328
H	-0.0923594	2.6748137	-4.0549723
C	-1.5029559	3.8204414	-2.8169218
H	-2.3643815	3.1357487	-2.9627912
H	-1.5750342	4.6023290	-3.6068618
C	-1.6108497	4.4937695	-1.4251484
H	-2.5495211	5.0828256	-1.3639502
H	-1.6699039	3.6983447	-0.6564115
C	-0.3935027	5.3926368	-1.0809712
H	-0.3281557	6.2572580	-1.7777715
H	-0.4780327	5.7865014	-0.0493938
C	2.9286098	3.0260324	-3.9129074
H	2.5490792	3.5508776	-4.8157979
H	4.0276770	3.1666555	-3.8297802
C	2.1756149	1.1084283	-5.2956248
C	3.3331856	0.5939139	-3.3396973
H	4.3986199	0.5979546	-3.6843389
C	2.6633689	-0.6766872	-3.8784486
H	1.6966514	-0.8048361	-3.3363689
C	3.5227580	-1.9000741	-3.5655520
H	4.5320864	-1.7730293	-4.0141237
H	3.0747273	-2.8248867	-3.9783403
C	3.6144387	-1.9758516	-2.0177706

H	2.6001298	-2.1959444	-1.6238664
H	4.2663983	-2.8235045	-1.7192883
C	4.1254640	-0.6646874	-1.3685423
H	5.1950620	-0.5243905	-1.6427414
H	4.0848875	-0.7567420	-0.2649046
C	3.3351395	0.5948099	-1.8110394
H	2.2963874	0.5845525	-1.4188448
H	3.8285198	1.5063606	-1.4215429
C	1.7326838	-1.1518626	-6.2153548
H	2.4062126	-1.9870223	-6.4853271
H	1.5186971	-0.5320744	-7.1065904
N	0.5042337	-1.7619332	-5.7321996
N	-0.6770767	-3.2109842	-4.4752113
N	-3.2373009	-2.1954936	4.2487655
N	-2.6165904	-0.4877626	5.5703591
N	-2.3496963	1.9266615	5.3290237
N	-0.9022827	3.3204950	4.3287164
N	0.9297860	4.2187083	3.0879537
N	2.2633443	4.9226704	1.4255823
N	2.1854667	5.0250466	-1.0122987
N	2.3393176	3.5710964	-2.7179062
N	2.6129249	1.6227005	-4.0795270
N	2.3811156	-0.2793276	-5.2575285
O	1.3907533	-3.8988154	-5.3263810
O	-4.9068356	-0.8633718	5.2034760
O	-0.3075428	2.3970480	6.3939103
O	0.5058972	6.3129600	2.1355417
O	4.3141194	4.3119867	-1.7055408
O	1.7022477	1.7474847	-6.2319023
H	-5.8298538	-2.9342890	1.6598967
H	0.7198580	4.2637183	5.1840080
C	-4.0717078	-3.3034196	3.8641058
C	-1.2059724	-4.5235359	-4.1813680
C	-2.8080656	-5.1804847	-2.4108685
C	-0.5644902	-5.0558375	-1.8024671
H	-0.1871196	-6.0762763	-2.0662985
C	-1.4221136	-5.1730577	-0.5369496
H	-1.5797009	-4.1459700	-0.1326344
C	-0.6726634	-5.9670034	0.5317112
H	-0.4241080	-6.9783669	0.1423746
H	-1.2854982	-6.0867001	1.4462409
C	0.6167444	-5.1605341	0.8419980
H	0.3149981	-4.2066810	1.3203193
H	1.2355590	-5.7082991	1.5827519
C	1.4662645	-4.8390108	-0.4142880
H	1.8997496	-5.7839055	-0.8110421
H	2.3175094	-4.1862578	-0.1310831
C	0.6500139	-4.1658553	-1.5475212
H	0.3147793	-3.1513575	-1.2460521
H	1.2666169	-4.0656163	-2.4623360
C	-3.8606868	-5.9223356	-0.2912562
H	-4.6838196	-6.1230143	-1.0023365
H	-3.6837061	-6.8087830	0.3466927
C	-3.8246096	-4.8587295	1.9480632
C	-4.3562264	-3.4529329	0.1657736
H	-3.3504428	-3.0757172	-0.1335010
C	-4.5069264	-1.2568863	1.3899017
H	-3.4336489	-1.0354392	1.2099153
H	-4.7952058	-0.7595275	2.3364325
C	-5.4010090	-0.7440220	0.2300720
H	-5.1136134	-3.0443218	4.1507617
H	-5.2079437	0.3348049	0.0642554
H	-6.4664603	-0.8377426	0.5386195

C	-5.1980488	-1.5177449	-1.0971391
H	-3.7582100	-4.2339271	4.3848980
H	-5.9167713	-1.1523802	-1.8604426
H	-4.1804899	-1.3002421	-1.4837274
C	-5.3331285	-3.0558049	-0.9387876
H	-6.3678371	-3.3319188	-0.6408242
H	-5.0981414	-3.5710433	-1.8904439
H	-0.4229945	-5.2616648	-4.4571635
N	-1.5635748	-4.6700788	-2.7889274
N	-2.6835320	-5.6544474	-1.1010472
N	-4.2273688	-4.8429675	0.6037314
N	-3.9922131	-3.5700416	2.4433082
O	-3.8175523	-5.2088722	-3.1088728
O	-3.4067876	-5.8320461	2.5700182
O	0.2258475	1.2196147	-0.0146775
O	-1.0752862	0.0847676	1.4715493
H	-0.6529989	-0.5771757	-0.4095925
C	-0.4970848	0.2619749	0.3671565

cycHC[8]-HCOO-anion-outside

188

C	0.3810243	-2.9962950	-4.9700610
C	-0.6675297	-0.9101951	-4.8173432
H	-0.2597949	-0.4937315	-3.8575522
C	-1.6730865	-2.0175214	-4.5023388
H	-2.2459349	-2.2563572	-5.4251547
C	-2.6683312	-1.5669599	-3.4428318
H	-2.1465911	-1.3002329	-2.4919890
H	-3.3864902	-2.3833750	-3.2275682
C	-3.4138831	-0.3482703	-4.0475575
H	-3.9900913	-0.7121659	-4.9222298
H	-4.1209246	0.0779082	-3.3007684
C	-2.4498656	0.7570558	-4.5492499
H	-1.9221691	1.2093397	-3.6782240
H	-3.0372781	1.5665946	-5.0318983
C	-1.3883409	0.2225768	-5.5490532
H	-1.9040551	-0.1875837	-6.4406647
H	-0.6891140	1.0301377	-5.8455275
C	-4.8422495	-2.9773206	1.4830761
C	-3.7689392	-1.0849610	4.9587322
C	-1.8341524	-2.3080908	4.5475297
H	-1.7617007	-2.9522533	5.4592532
C	-1.4471373	-0.8779722	4.9437214
H	-1.2750265	-0.2953061	4.0061315
C	-0.1301947	-0.8875110	5.7194508
H	-0.2345994	-1.5228468	6.6250631
H	0.1543959	0.1325807	6.0419695
C	0.9371665	-1.4748635	4.7571742
H	1.0798154	-0.7551655	3.9233118
H	1.9134001	-1.5536455	5.2792166
C	0.5462334	-2.8549429	4.1670161
H	0.5560247	-3.6100104	4.9839240
H	1.3066168	-3.1754139	3.4253158
C	-0.8598630	-2.8672021	3.5120704
H	-0.8808216	-2.2344620	2.6002159
H	-1.1437478	-3.8968114	3.2184050
C	-2.8549175	0.9177288	6.1012742
H	-3.9252097	1.0192432	6.3612752
H	-2.2301582	1.0367937	7.0060031
C	-1.1897100	2.5531234	5.2623264
C	-2.9571087	2.0805441	3.8194213
H	-2.5499296	1.2206860	3.2348435

C	-2.2443351	3.3549409	3.3481518
H	-2.8117618	4.2367231	3.7394373
C	-2.2482213	3.4440854	1.8231938
H	-1.7135661	2.5689851	1.3972565
H	-1.7288253	4.3606040	1.4793280
C	-3.7329136	3.4605623	1.3754960
H	-3.7901801	3.4387646	0.2675954
H	-4.1822434	4.4242508	1.7018665
C	-4.5666909	2.2938515	1.9658782
H	-5.6312160	2.4133442	1.6770468
H	-4.2208720	1.3385924	1.5162199
C	-4.4506962	2.1698282	3.5094191
H	-4.8831418	3.0629045	4.0097629
H	-4.9911651	1.2732399	3.8695466
H	-2.3225637	-4.5284392	-4.6638812
C	-0.0113341	4.3285872	4.0031883
H	-0.5226174	5.3111388	3.9207380
C	1.1351190	5.3059408	2.0388288
C	2.0334665	3.3457716	2.9120919
H	2.7144570	3.7367353	3.7095600
C	2.6799479	3.6311562	1.5511864
H	2.1396098	3.0350332	0.7771278
C	4.1343363	3.1629891	1.5553190
H	4.6908534	3.6843495	2.3634664
H	4.6288059	3.3840871	0.5899074
C	4.0992069	1.6324799	1.8103145
H	3.6278486	1.1488449	0.9291231
H	5.1339909	1.2368451	1.8750480
C	3.3093953	1.2348148	3.0838852
H	3.8684777	1.5856027	3.9794148
H	3.2477637	0.1293919	3.1578324
C	1.8832664	1.8420264	3.1363637
H	1.2365306	1.4093901	2.3439007
H	1.4088833	1.6347813	4.1160395
C	2.7182616	5.7998846	0.1922424
H	2.2261505	6.7859099	0.2839131
H	3.8170844	5.9218051	0.1677255
C	3.2478251	4.3489929	-1.7488169
C	0.9818023	4.7267019	-1.3449219
H	0.7304932	3.8884495	-0.6500920
C	1.1591821	4.1410324	-2.7515073
H	1.1663571	4.9889501	-3.4814790
C	-0.0142633	3.2330072	-3.1148778
H	-0.0771242	2.3926371	-2.3919695
H	0.1131170	2.7995733	-4.1258087
C	-1.2909923	4.1103091	-3.0593580
H	-2.1815940	3.4767945	-3.2425429
H	-1.2435903	4.8462895	-3.8921822
C	-1.4507732	4.8778071	-1.7220036
H	-2.3361604	5.5452610	-1.7762116
H	-1.6513306	4.1463828	-0.9099554
C	-0.1947961	5.7011417	-1.3268698
H	-0.0140716	6.5153125	-2.0609984
H	-0.3250670	6.1561969	-0.3257402
C	3.1302507	2.9722063	-3.8141023
H	2.8369948	3.5067022	-4.7428971
H	4.2295207	3.0418522	-3.6706051
C	2.1972642	1.1195512	-5.1768556
C	3.4387938	0.5275823	-3.2950624
H	4.4867170	0.4992856	-3.6884387
C	2.6933974	-0.7032444	-3.8226630
H	1.7503322	-0.8155327	-3.2365061
C	3.5265389	-1.9616876	-3.5824704

H	4.5148501	-1.8582327	-4.0808183
H	3.0211143	-2.8580247	-3.9909370
C	3.6966288	-2.0782314	-2.0440362
H	2.6967864	-2.2792421	-1.6048151
H	4.3343768	-2.9520633	-1.7966450
C	4.2855864	-0.8017841	-1.3874399
H	5.3436185	-0.6865706	-1.7107061
H	4.2992133	-0.9185100	-0.2830355
C	3.5214429	0.4928122	-1.7692800
H	2.4960116	0.4892060	-1.3425344
H	4.0492047	1.3872543	-1.3806963
C	1.5566389	-1.1116877	-6.0738143
H	2.1814010	-1.9531170	-6.4272953
H	1.2677194	-0.4655941	-6.9243003
N	0.3906675	-1.6870109	-5.4625139
N	-0.7900579	-3.1592780	-4.2394389
N	-3.2415069	-2.1408381	4.2154304
N	-2.6904857	-0.4172951	5.5581847
N	-2.4651578	1.9831501	5.1935986
N	-0.9846597	3.2608075	4.0739724
N	0.8568372	4.2014662	2.8538940
N	2.3372235	5.0421223	1.3747512
N	2.3444176	5.1752947	-1.0603386
N	2.5108529	3.6035502	-2.6641754
N	2.7205122	1.5991106	-3.9618669
N	2.3459786	-0.2665400	-5.1725870
O	1.2632427	-3.8407996	-5.1370165
O	-4.9562038	-0.7966256	5.0702064
O	-0.3930312	2.4579553	6.1909400
O	0.4470540	6.3164010	1.9382283
O	4.4623271	4.2975847	-1.5755186
O	1.7126515	1.8142571	-6.0622915
H	-5.8932577	-3.2423217	1.7614713
H	0.5823839	4.2924989	4.9417533
C	-4.0509074	-3.2850040	3.8476244
C	-1.3782744	-4.4740253	-4.0876747
C	-2.8416104	-5.3608544	-2.2761228
C	-0.5934690	-5.1184092	-1.7642047
H	-0.1789442	-6.1135171	-2.0660030
C	-1.3778331	-5.3066530	-0.4590620
H	-1.5850940	-4.2925173	-0.0337227
C	-0.5348628	-6.0660589	0.5649380
H	-0.2491943	-7.0564395	0.1497650
H	-1.0975911	-6.2293605	1.5046723
C	0.7254455	-5.2011442	0.8272496
H	0.4008582	-4.2651062	1.3324350
H	1.4058981	-5.7256827	1.5312614
C	1.4939022	-4.8305937	-0.4671831
H	1.9409910	-5.7553420	-0.8939959
H	2.3365139	-4.1513872	-0.2214298
C	0.5960547	-4.1817436	-1.5521592
H	0.2327867	-3.1845503	-1.2260406
H	1.1593544	-4.0475638	-2.4957830
C	-3.7470521	-6.1670806	-0.1150550
H	-4.5813398	-6.4557414	-0.7805220
H	-3.4956302	-6.9982775	0.5695265
C	-3.6858274	-4.9220621	2.0306397
C	-4.4874908	-3.7299209	0.1955049
H	-3.5542791	-3.2868422	-0.2265114
C	-4.7959857	-1.4668738	1.2584461
H	-3.7756925	-1.1706820	0.9343117
H	-5.0327591	-0.9200534	2.1935491
C	-5.8418893	-1.1465287	0.1585823

H -5.1017731 -3.0387608 4.1101653
H -5.7875550 -0.0701707 -0.1080381
H -6.8543499 -1.3215386 0.5858184
C -5.6717397 -2.0092451 -1.1184878
H -3.7202774 -4.1792508 4.4178139
H -6.5013438 -1.7989692 -1.8234370
H -4.7375906 -1.7073511 -1.6348664
C -5.5950534 -3.5345625 -0.8395623
H -6.5568599 -3.9113869 -0.4291920
H -5.3705414 -4.0823830 -1.7743229
H -0.6552285 -5.2170834 -4.4842364
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N -4.1700502 -5.0560872 0.7318186
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O -3.8883575 -5.4503268 -2.9028792
O -3.1365795 -5.7855304 2.7100341
O -3.7653150 -1.5958236 -7.1338902
C -3.6533616 -2.8270585 -7.3739728
O -2.9759108 -3.7076807 -6.7847647
H -4.2652022 -3.2066698 -8.2783039

HCOOH@cycHC[8]
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C 0.5370685 -3.2044409 -4.6838355
C -0.3927761 -1.0705379 -4.8240068
H -0.1549973 -0.6447327 -3.8218233
C -1.5136634 -2.0993437 -4.6336434
H -1.9571741 -2.3286299 -5.6350092
C -2.6180003 -1.5180198 -3.7531870
H -2.1913782 -1.2325767 -2.7694284
H -3.4217788 -2.2622255 -3.5849388
C -3.1692748 -0.2723855 -4.4952888
H -3.7034891 -0.6165117 -5.4077738
H -3.9194165 0.2407931 -3.8579747
C -2.0627916 0.7339497 -4.9093321
H -1.6440218 1.1950367 -3.9908827
H -2.5087060 1.5537716 -5.5094120
C -0.8897423 0.0835784 -5.6936144
H -1.2381648 -0.3065434 -6.6733570
H -0.0886026 0.8235687 -5.8856913
C -4.5478768 -2.6167616 1.5216655
C -3.1174614 -1.5053268 5.2301361
C -1.4205546 -2.4732986 3.9659694
H -1.0618884 -3.2893217 4.6418026
C -0.9295288 -1.1293542 4.5233490
H -1.0692234 -0.3580772 3.7291136
C 0.5662131 -1.2050789 4.8308079
H 0.7537093 -2.0065473 5.5768389
H 0.9348002 -0.2474533 5.2463327
C 1.2811760 -1.5206703 3.4892306
H 1.1507292 -0.6476382 2.8197399
H 2.3713747 -1.6389846 3.6627082
C 0.7223084 -2.7732249 2.7682544
H 0.9736271 -3.6814390 3.3588213
H 1.2151286 -2.8841489 1.7791434
C -0.8149902 -2.7152090 2.5820304
H -1.0883019 -1.8872324 1.8980639
H -1.1953889 -3.6566664 2.1432013
C -1.9359352 0.3510979 6.3345672
H -2.8243895 0.3119760 6.9905438
H -1.0166547 0.4536104 6.9387117

C	-0.8423733	2.1568691	5.0546392
C	-3.0383524	1.6638470	4.4439198
H	-2.9249587	0.8225477	3.7210839
C	-2.5970414	2.9555258	3.7489212
H	-2.9610531	3.8183992	4.3592517
C	-3.2431101	3.0624786	2.3686895
H	-2.9698798	2.1765635	1.7608545
H	-2.8965313	3.9714131	1.8329120
C	-4.7758841	3.1194501	2.6074589
H	-5.3086600	3.1159511	1.6343893
H	-5.0152564	4.0855803	3.1037704
C	-5.3009198	1.9553098	3.4889573
H	-6.3763098	2.1160974	3.7092371
H	-5.2317465	1.0109283	2.9103560
C	-4.5184647	1.7668685	4.8161517
H	-4.6693657	2.6374588	5.4894803
H	-4.8628134	0.8534273	5.3357568
H	-2.3322650	-4.5721581	-4.6653518
C	-0.3296951	4.0165154	3.5265129
H	-0.9920098	4.8688370	3.2844686
C	0.6369410	4.9438113	1.4771972
C	1.9163599	3.3522914	2.6201690
H	2.2847704	3.9543635	3.4827842
C	2.6739885	3.8126045	1.3717910
H	2.5212358	3.0671169	0.5568564
C	4.1709792	3.8709969	1.6821645
H	4.3422878	4.5687469	2.5299774
H	4.7415865	4.2249433	0.8042930
C	4.6087369	2.4309877	2.0590080
H	4.5377441	1.8008710	1.1478753
H	5.6754152	2.4353177	2.3633731
C	3.7478390	1.7947432	3.1795760
H	3.9586205	2.3120689	4.1406148
H	4.0357448	0.7319924	3.3160765
C	2.2257560	1.8858966	2.9070031
H	1.9517125	1.2688509	2.0280628
H	1.6564690	1.5248780	3.7820035
C	2.3375346	5.9405992	-0.0355389
H	1.6932203	6.8337964	0.0422535
H	3.3973841	6.2139001	0.1126829
C	3.2047238	4.4958334	-1.8371585
C	0.9140263	4.9116218	-1.8488681
H	0.5460597	4.1121954	-1.1598078
C	1.3102849	4.2377332	-3.1667169
H	1.4516479	5.0312305	-3.9401715
C	0.1937686	3.3140173	-3.6513983
H	0.0038570	2.5229499	-2.8966498
H	0.4750268	2.8153326	-4.5998698
C	-1.0631006	4.2000618	-3.8524740
H	-1.9244014	3.5635641	-4.1368717
H	-0.8714404	4.8848377	-4.7069484
C	-1.4265314	5.0478132	-2.6061462
H	-2.2805396	5.7143142	-2.8448949
H	-1.7667766	4.3710619	-1.7913532
C	-0.2387173	5.8879451	-2.0677541
H	0.0640252	6.6616887	-2.8045936
H	-0.5228149	6.3847404	-1.1207863
C	3.3900407	2.8824254	-3.7199196
H	3.3013942	3.2666844	-4.7575382
H	4.4479855	2.9380308	-3.3881174
C	2.5835405	0.8663603	-4.9156018
C	3.3835512	0.5381876	-2.7473651
H	4.4779737	0.3616893	-2.8947340

C	2.6195556	-0.7109603	-3.2057129
H	1.5781479	-0.6225214	-2.8175259
C	3.2209023	-1.9649984	-2.5747478
H	4.2978909	-2.0432689	-2.8359963
H	2.7143123	-2.8819769	-2.9340127
C	3.0365081	-1.8005664	-1.0406605
H	1.9477178	-1.8283654	-0.8170841
H	3.4966354	-2.6598132	-0.5101652
C	3.6287088	-0.4747380	-0.4911778
H	4.7374502	-0.5182299	-0.5611703
H	3.3785363	-0.3743562	0.5858164
C	3.1427678	0.7835642	-1.2580492
H	2.0601646	0.9490856	-1.0875556
H	3.6887403	1.6845586	-0.9133703
C	2.0289505	-1.4502057	-5.6002508
H	2.6752696	-2.3450200	-5.6801295
H	1.9940751	-0.9249547	-6.5736887
N	0.7106402	-1.9340434	-5.2416973
N	-0.7663279	-3.2664421	-4.1857578
N	-2.8613278	-2.3346306	4.1371448
N	-1.9054139	-0.8933150	5.5883357
N	-2.0113069	1.5304530	5.4787757
N	-1.1429181	2.8872171	3.8912957
N	0.5303762	3.7903722	2.3408657
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N	2.2116826	5.3757958	-1.3622898
N	2.6164611	3.7001643	-2.8110403
N	2.9266986	1.5155029	-3.7256726
N	2.5970785	-0.5056881	-4.6545056
O	1.3712300	-4.1035060	-4.6387248
O	-4.2009164	-1.3420054	5.7778790
O	0.2570275	2.1065951	5.5954628
O	-0.2871348	5.7007948	1.2199244
O	4.3685165	4.4412126	-1.4573787
O	2.3186030	1.4124689	-5.9810847
H	-5.6182012	-2.5492750	1.8391649
H	0.3251740	4.2805603	4.3834158
C	-3.7792679	-3.4027806	3.8063965
C	-1.4359362	-4.5373148	-4.0125404
C	-3.2134674	-5.0757451	-2.3774720
C	-1.0157610	-5.4758670	-1.7184622
H	-0.8022178	-6.4900992	-2.1383026
C	-1.9392772	-5.6416017	-0.5070185
H	-1.9214261	-4.6887108	0.0743652
C	-1.3944666	-6.7449858	0.4012415
H	-1.3216824	-7.6942123	-0.1715429
H	-2.0537714	-6.9081616	1.2738244
C	0.0097026	-6.2756409	0.8721070
H	-0.1280124	-5.4077416	1.5503052
H	0.4885859	-7.0762734	1.4731265
C	0.9574436	-5.8616129	-0.2851918
H	1.2566009	-6.7734844	-0.8470977
H	1.8874820	-5.4254339	0.1355242
C	0.3185379	-4.8667167	-1.2903918
H	0.1404010	-3.8765521	-0.8179994
H	0.9827026	-4.7178042	-2.1650942
C	-4.4788915	-5.8159915	-0.3872299
H	-5.3114128	-5.7791635	-1.1132094
H	-4.5172466	-6.7558344	0.1928341
C	-4.0795450	-4.8726554	1.8564232
C	-4.4888204	-3.3282151	0.1616919
H	-3.4695871	-3.1682439	-0.2665441
C	-4.0127293	-1.1901033	1.3840902

H	-2.9724856	-1.2080123	1.0027104
H	-4.0043555	-0.6733556	2.3618663
C	-4.9368992	-0.4561803	0.3806739
H	-4.7612826	-3.1276681	4.2488968
H	-4.5464770	0.5671718	0.1974019
H	-5.9414354	-0.3413363	0.8441480
C	-5.0808874	-1.2100671	-0.9663479
H	-3.4451977	-4.3727754	4.2338054
H	-5.8148554	-0.6858255	-1.6129818
H	-4.1062900	-1.1793087	-1.4944430
C	-5.4930813	-2.6986155	-0.8035981
H	-6.5172038	-2.7809605	-0.3806675
H	-5.4733770	-3.2108555	-1.7845211
H	-0.7227031	-5.3347865	-4.3078546
N	-1.8787942	-4.7699580	-2.6545731
N	-3.2454800	-5.7635552	-1.1567858
N	-4.6112806	-4.7272989	0.5685797
N	-3.8750153	-3.5884331	2.3750228
O	-4.1777343	-4.7941185	-3.0814498
O	-3.8406541	-5.9276587	2.4311605
O	-0.5581980	1.3528589	1.2616710
O	-0.7600017	0.2871222	-0.7071232
H	-0.0649247	2.2083445	-0.5456925
C	-0.4596229	1.2708770	-0.0689119
H	-0.2434531	2.2525648	1.6032413

cycHC[8]-HCOOH-outside

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C	0.4504757	-3.1054048	-5.2159747
C	-0.6325191	-1.0419227	-5.1903072
H	-0.2882911	-0.6137400	-4.2175997
C	-1.6479368	-2.1511966	-4.8874935
H	-2.1854406	-2.4012848	-5.8361534
C	-2.6919003	-1.6667212	-3.8823627
H	-2.1880428	-1.3749349	-2.9360171
H	-3.4190237	-2.4694804	-3.6493394
C	-3.4080159	-0.4526909	-4.5288455
H	-4.0114851	-0.8217784	-5.3864119
H	-4.1226363	-0.0081627	-3.8045347
C	-2.4302560	0.6378722	-5.0386665
H	-1.9443030	1.1204867	-4.1637423
H	-2.9986969	1.4310201	-5.5669133
C	-1.3116030	0.0872910	-5.9652047
H	-1.7425737	-0.3120239	-6.9077962
H	-0.5931170	0.8887356	-6.2223085
C	-4.7183904	-2.8121889	1.4164283
C	-3.5601160	-1.1486530	4.9499476
C	-1.6545877	-2.3547494	4.3746972
H	-1.5365669	-3.0453193	5.2464301
C	-1.2431866	-0.9462811	4.8230550
H	-1.1227829	-0.3136224	3.9096134
C	0.1135869	-0.9956079	5.5251007
H	0.0578883	-1.6798016	6.3984434
H	0.4159124	0.0052813	5.8880352
C	1.1277042	-1.5256468	4.4759320
H	1.2268321	-0.7605513	3.6761342
H	2.1296420	-1.6315360	4.9401900
C	0.7051720	-2.8732962	3.8349106
H	0.7632336	-3.6712151	4.6071652
H	1.4236637	-3.1504678	3.0358395
C	-0.7365964	-2.8577892	3.2617168
H	-0.8099186	-2.1814173	2.3834668

H	-1.0354040	-3.8734511	2.9350519
C	-2.5773653	0.7747719	6.1700709
H	-3.6257676	0.8533181	6.5126424
H	-1.8894668	0.8348129	7.0335988
C	-0.9761046	2.4647611	5.3117732
C	-2.8562983	2.0865133	3.9893073
H	-2.5045790	1.2638046	3.3198099
C	-2.1758934	3.3872027	3.5436009
H	-2.7056240	4.2424556	4.0320623
C	-2.3008548	3.5720199	2.0326062
H	-1.8131553	2.7194115	1.5131874
H	-1.7985990	4.5044235	1.7055147
C	-3.8171667	3.6267205	1.7103179
H	-3.9666212	3.6756290	0.6114581
H	-4.2266822	4.5703669	2.1315762
C	-4.6119084	2.4299046	2.2945862
H	-5.6952852	2.5733529	2.1030765
H	-4.3126723	1.5043304	1.7577898
C	-4.3697203	2.2032863	3.8112385
H	-4.7503028	3.0625411	4.4036397
H	-4.8875228	1.2871042	4.1542869
H	-2.2460872	-4.7273679	-4.8490570
C	0.1055563	4.3180522	4.0761045
H	-0.4125716	5.2982986	4.0249758
C	1.1334454	5.3016992	2.0477196
C	2.1653482	3.4142918	2.9364054
H	2.8535567	3.8553038	3.6994515
C	2.7498222	3.6962358	1.5477002
H	2.2150986	3.0517600	0.8076875
C	4.2248262	3.3002231	1.5171251
H	4.7828344	3.8737332	2.2873100
H	4.6736503	3.5196132	0.5308904
C	4.2813956	1.7770245	1.8105525
H	3.8140355	1.2438133	0.9558809
H	5.3359147	1.4384743	1.8501050
C	3.5473884	1.3735681	3.1151093
H	4.1136680	1.7713462	3.9853932
H	3.5444162	0.2685893	3.2139353
C	2.0947046	1.9108416	3.1969531
H	1.4480376	1.4306356	2.4320090
H	1.6579855	1.7038621	4.1941553
C	2.6256853	5.8231358	0.1380779
H	2.0978959	6.7906345	0.2181140
H	3.7149589	5.9886036	0.0521513
C	3.0796512	4.3285036	-1.7901279
C	0.8407011	4.6532765	-1.2787458
H	0.6528430	3.8462383	-0.5308704
C	0.9623581	4.0092785	-2.6634806
H	0.9094940	4.8199267	-3.4316929
C	-0.2002972	3.0534990	-2.9240158
H	-0.1956103	2.2414523	-2.1656012
H	-0.1087408	2.5868712	-3.9238548
C	-1.4996231	3.8971631	-2.8355224
H	-2.3829628	3.2326929	-2.9335894
H	-1.5234454	4.5887708	-3.7058947
C	-1.6085271	4.7271307	-1.5307759
H	-2.5124942	5.3688372	-1.5715178
H	-1.7466474	4.0349258	-0.6733183
C	-0.3566010	5.6009505	-1.2460592
H	-0.2360956	6.3818925	-2.0268356
H	-0.4475426	6.0989352	-0.2620748
C	2.9085786	2.8774907	-3.8028964
H	2.5769938	3.4110575	-4.7187294

H	4.0121734	2.9421119	-3.7187540
C	2.0992475	1.0170831	-5.1906544
C	3.1896094	0.4482467	-3.2048124
H	4.2710150	0.5062434	-3.4641763
C	2.5927962	-0.8165096	-3.8365614
H	1.6142335	-1.0315930	-3.3416579
C	3.5130722	-2.0051539	-3.5577657
H	4.5252373	-1.7956539	-3.9640458
H	3.1286051	-2.9303181	-4.0284572
C	3.5606182	-2.1632028	-2.0128172
H	2.5557425	-2.4933172	-1.6763533
H	4.2710600	-2.9708188	-1.7414199
C	3.9386272	-0.8639162	-1.2547677
H	5.0064285	-0.6206613	-1.4329907
H	3.8303960	-1.0308399	-0.1622945
C	3.0902076	0.3615358	-1.6832063
H	2.0250754	0.2430370	-1.3849083
H	3.4844043	1.2790995	-1.2103488
C	1.7083410	-1.2087269	-6.2026381
H	2.3911269	-2.0380340	-6.4635673
H	1.5271083	-0.5711040	-7.0876408
N	0.4626187	-1.8178283	-5.7689803
N	-0.7690403	-3.2604535	-4.5495982
N	-3.0769592	-2.1681380	4.1228761
N	-2.4504067	-0.5198211	5.5267034
N	-2.2552156	1.8993534	5.3084138
N	-0.8632765	3.2479112	4.1573762
N	0.9479849	4.2140902	2.9024609
N	2.3290153	5.0824408	1.3464111
N	2.2081678	5.1448514	-1.0839418
N	2.3373862	3.5152439	-2.6295391
N	2.4848792	1.5024468	-3.9303897
N	2.3267753	-0.3591307	-5.1989809
O	1.3387900	-3.9459085	-5.2979855
O	-4.7389235	-0.8649584	5.1311433
O	-0.1077443	2.3123588	6.1638173
O	0.3889305	6.2692683	1.9345982
O	4.3173845	4.3448849	-1.6834945
O	1.6473284	1.6931914	-6.1084389
H	-5.7878433	-3.0062271	1.6799235
H	0.7297253	4.2703879	4.9931124
C	-3.9169533	-3.2886357	3.7582997
C	-1.3127907	-4.5716985	-4.2685873
C	-2.8953822	-5.2185119	-2.4723469
C	-0.6329774	-5.2122268	-1.9296359
H	-0.3102104	-6.2366138	-2.2403614
C	-1.4560020	-5.3404608	-0.6432019
H	-1.5649399	-4.3214138	-0.1967818
C	-0.7054053	-6.2050217	0.3694132
H	-0.5120198	-7.2080463	-0.0676398
H	-1.2909965	-6.3358368	1.2990795
C	0.6286425	-5.4692074	0.6680959
H	0.3877672	-4.5243399	1.2017753
H	1.2462723	-6.0778385	1.3602010
C	1.4504094	-5.1319702	-0.6027996
H	1.8312220	-6.0773625	-1.0465601
H	2.3388418	-4.5274025	-0.3263039
C	0.6275543	-4.3874569	-1.6854618
H	0.3438175	-3.3701716	-1.3406107
H	1.2165159	-4.2800763	-2.6174748
C	-3.9082255	-5.9928524	-0.3426051
H	-4.7598517	-6.1783546	-1.0224419
H	-3.7274606	-6.8780788	0.2946096

C	-3.7305557	-4.8704966	1.8640335
C	-4.4177496	-3.5237266	0.0915804
H	-3.4417914	-3.1403134	-0.2947504
C	-4.5491776	-1.3005859	1.2713080
H	-3.5010157	-1.0680559	0.9859935
H	-4.7636442	-0.7870812	2.2293698
C	-5.5420441	-0.8378655	0.1733812
H	-4.9520850	-3.0383014	4.0739725
H	-5.4007556	0.2443097	-0.0285924
H	-6.5745282	-0.9562197	0.5686769
C	-5.4164008	-1.6406269	-1.1477825
H	-3.5796967	-4.2103006	4.2784067
H	-6.2071730	-1.3185814	-1.8560740
H	-4.4419853	-1.4008434	-1.6261345
C	-5.4865999	-3.1780050	-0.9443498
H	-6.4857128	-3.4788702	-0.5634987
H	-5.3047628	-3.7051256	-1.9004264
H	-0.5502063	-5.3182807	-4.5742146
N	-1.6413888	-4.7448240	-2.8699509
N	-2.7508070	-5.7499212	-1.1847940
N	-4.2275295	-4.8964691	0.5559162
N	-3.8737198	-3.5602585	2.3374657
O	-3.9255093	-5.1746481	-3.1363210
O	-3.2589940	-5.8136341	2.4885952
O	5.7409302	2.1224152	-1.9158335
O	7.1168074	0.8392889	-0.6871741
H	6.7953396	2.8273033	-0.2914491
C	6.6015355	1.9075369	-0.9111199
H	5.3002019	3.0313354	-1.8588374

Formic Acid

5

C	-2.3734719	1.1282090	-0.1794130
O	-3.3348718	2.0806884	-0.1832355
H	-2.8842189	2.9570272	-0.2045493
O	-1.1852089	1.3274929	-0.1987549
H	-2.8679814	0.1254183	-0.1552168

Formic Acid + H+

4

C	-0.3831958	-0.6035850	1.5592479
O	0.8415822	-0.7845472	1.7561912
O	-0.9976457	0.1356431	0.7546027
H	-1.0893693	-1.2499986	2.2628129

Geometries for the model system

1b

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C	0.221315	0.435915	0.558093
C	1.768264	0.458084	0.598308
C	2.357888	0.097072	1.983994
C	-0.393147	-0.875367	1.108577
C	0.206016	-1.114641	2.493511
C	1.736829	-1.235886	2.400346
N	2.042982	-1.833999	3.698495
N	-0.109150	-2.329436	3.241014
C	0.946712	-2.598603	4.126160
O	0.922381	-3.360807	5.087241
C	3.030665	-0.786542	8.579848
C	4.027042	0.357862	8.886201

C	5.310543	0.309386	8.019290
C	2.691129	-0.927099	7.075792
C	4.018580	-1.030333	6.325262
C	4.872023	0.228221	6.558107
N	5.859621	0.077304	5.492367
N	4.051914	-1.116927	4.866482
C	3.389154	-2.168239	4.119797
C	5.246034	-0.548294	4.395891
O	5.671227	-0.597514	3.246228
H	-0.168719	1.289294	1.161722
H	-0.129363	0.609445	-0.483774
H	2.134448	1.459693	0.281581
H	2.161130	-0.265895	-0.153866
H	3.466680	0.024256	1.933595
H	2.111540	0.880024	2.737461
H	-1.502371	-0.787676	1.157165
H	-0.159862	-1.737132	0.442862
H	-0.021171	-0.212513	3.122716
H	1.974652	-1.984004	1.596588
H	2.096908	-0.633811	9.165248
H	3.463855	-1.750050	8.937130
H	3.519455	1.336134	8.711761
H	4.299289	0.339418	9.964980
H	5.932860	1.213769	8.206043
H	5.934028	-0.577369	8.275789
H	2.058904	-1.824305	6.896842
H	2.119739	-0.042006	6.712701
H	4.577252	-1.908885	6.748646
H	3.307906	-3.085386	4.745719
H	4.025733	-2.374715	3.229490
H	-1.050712	-2.485040	3.612375
H	4.220689	1.118182	6.348566
H	6.507069	0.837757	5.266475

1b-protonated
46

C	-0.776369	-4.268688	2.900418
C	0.676962	-4.333704	2.375582
C	1.519762	-3.080351	2.727136
C	-0.877632	-3.923782	4.407201
C	-0.068823	-2.648228	4.632791
C	1.400393	-2.873591	4.234810
N	2.040703	-1.717569	4.900171
N	0.098440	-2.100790	5.979585
C	1.278715	-1.405329	6.080221
O	1.674692	-0.668309	6.973406
C	3.789287	3.078276	6.114222
C	4.800699	3.807647	5.201931
C	5.852430	2.860733	4.572848
C	3.098924	1.865893	5.436667
C	4.214217	0.987993	4.885838
C	5.088606	1.737368	3.870722
N	5.838124	0.630847	3.262311
N	3.883471	-0.285916	4.140970
C	3.441959	-1.528529	4.954349
C	5.206853	-0.559284	3.285080
O	5.441664	-1.648325	2.837414
H	-1.340997	-3.501911	2.320964
H	-1.283925	-5.237686	2.704026
H	0.671191	-4.479876	1.273787
H	1.183418	-5.229801	2.803354
H	2.577008	-3.235059	2.415280

H	1.136470	-2.183301	2.186274
H	-1.942225	-3.779389	4.695227
H	-0.473870	-4.748569	5.037369
H	-0.490338	-1.853060	3.964211
H	1.754965	-3.805894	4.743680
H	3.010909	3.791714	6.459109
H	4.307168	2.721037	7.034033
H	4.254065	4.330228	4.382986
H	5.321019	4.601386	5.779248
H	6.490236	3.416753	3.850984
H	6.524371	2.433351	5.351729
H	2.483785	1.300716	6.169391
H	2.432975	2.205595	4.608987
H	4.868539	0.650284	5.721099
H	3.780671	-1.337818	5.994380
H	3.995010	-2.373793	4.493299
H	-0.684937	-1.841690	6.585321
H	4.435199	2.200134	3.089967
H	6.687134	0.748351	2.698259
H	3.112473	-0.111077	3.461977

TS2a

46

C	0.532595	-3.466343	5.916669
C	1.618821	-2.371454	5.791963
C	1.536502	-1.544425	4.481330
C	-0.907850	-2.949314	5.668993
C	-0.891237	-2.228624	4.321712
C	0.097003	-1.049750	4.381378
N	-0.368807	-0.208208	3.252687
N	-2.096776	-1.564927	3.814648
C	-1.823657	-0.498292	3.011805
O	-2.506360	0.161907	2.265903
C	0.731413	0.852949	-2.960894
C	2.114110	1.423159	-3.355943
C	2.837668	2.152741	-2.197583
C	0.746495	-0.012382	-1.670919
C	1.438156	0.811337	-0.589596
C	2.872869	1.179511	-1.022941
N	3.428866	1.582201	0.270982
N	1.623718	0.280935	0.789456
C	0.236881	0.782337	2.647602
C	2.866583	0.873389	1.296985
O	3.241166	0.761131	2.454785
H	0.746811	-4.283102	5.188630
H	0.591212	-3.931692	6.923921
H	2.626054	-2.834406	5.866491
H	1.537366	-1.671039	6.655180
H	2.264196	-0.706335	4.499618
H	1.786261	-2.175971	3.598368
H	-1.624127	-3.799872	5.660973
H	-1.230590	-2.251241	6.474585
H	-0.535010	-2.958282	3.552145
H	-0.141400	-0.458532	5.297615
H	0.324052	0.252289	-3.802346
H	0.018244	1.695810	-2.809017
H	2.767262	0.594757	-3.716517
H	1.995470	2.115201	-4.217548
H	3.864253	2.445757	-2.510733
H	2.300150	3.084467	-1.908661
H	-0.293472	-0.27890	-1.380225
H	1.301764	-0.963796	-1.845167

H	0.879054	1.769016	-0.468366
H	-0.394748	1.400588	1.986073
H	1.221117	1.108170	3.024753
H	-3.018886	-2.009737	3.768543
H	3.396872	0.251176	-1.367772
H	4.360857	1.988807	0.395197
H	1.630083	-0.747085	0.874810

TS2b

50

C	1.354362	0.256773	-0.246550
C	2.484114	-0.547007	0.444554
C	2.353515	-0.597409	1.986810
C	-0.074258	-0.159798	0.191695
C	-0.099928	-0.126843	1.718919
C	0.945872	-1.114657	2.258104
N	0.449706	-1.356163	3.626260
N	-1.296265	-0.547825	2.452571
C	-0.970547	-1.066979	3.685063
O	-1.675513	-1.286745	4.652413
C	4.946443	-2.509246	7.495184
C	5.923313	-1.312747	7.398728
C	5.600336	-0.340172	6.235488
C	3.454110	-2.086934	7.527186
C	3.263143	-1.191020	6.312558
C	4.136583	0.070141	6.395328
N	3.480578	0.897351	5.379184
N	1.918577	-0.668558	5.933737
C	1.089362	-1.975734	4.614138
C	2.131719	0.639219	5.306993
O	1.242374	1.304380	4.806576
H	1.487874	1.340659	-0.016615
H	1.447517	0.161215	-1.351206
H	3.469068	-0.113031	0.163279
H	2.484396	-1.594807	0.066578
H	3.114458	-1.274889	2.429596
H	2.485381	0.418180	2.425200
H	-0.825482	0.536717	-0.245180
H	-0.319824	-1.184960	-0.166919
H	0.180656	0.903779	2.051980
H	0.858559	-2.100001	1.745547
H	5.187839	-3.116770	8.395013

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