ELECTRONIC SUPPLEMENTARY INFORMATION

Pseudopeptidic Macrocycles as Cooperative Minimalistic Synzyme Systems for the Remarkable Activation and Conversion of CO_2 in the Presence of Chloride Anion

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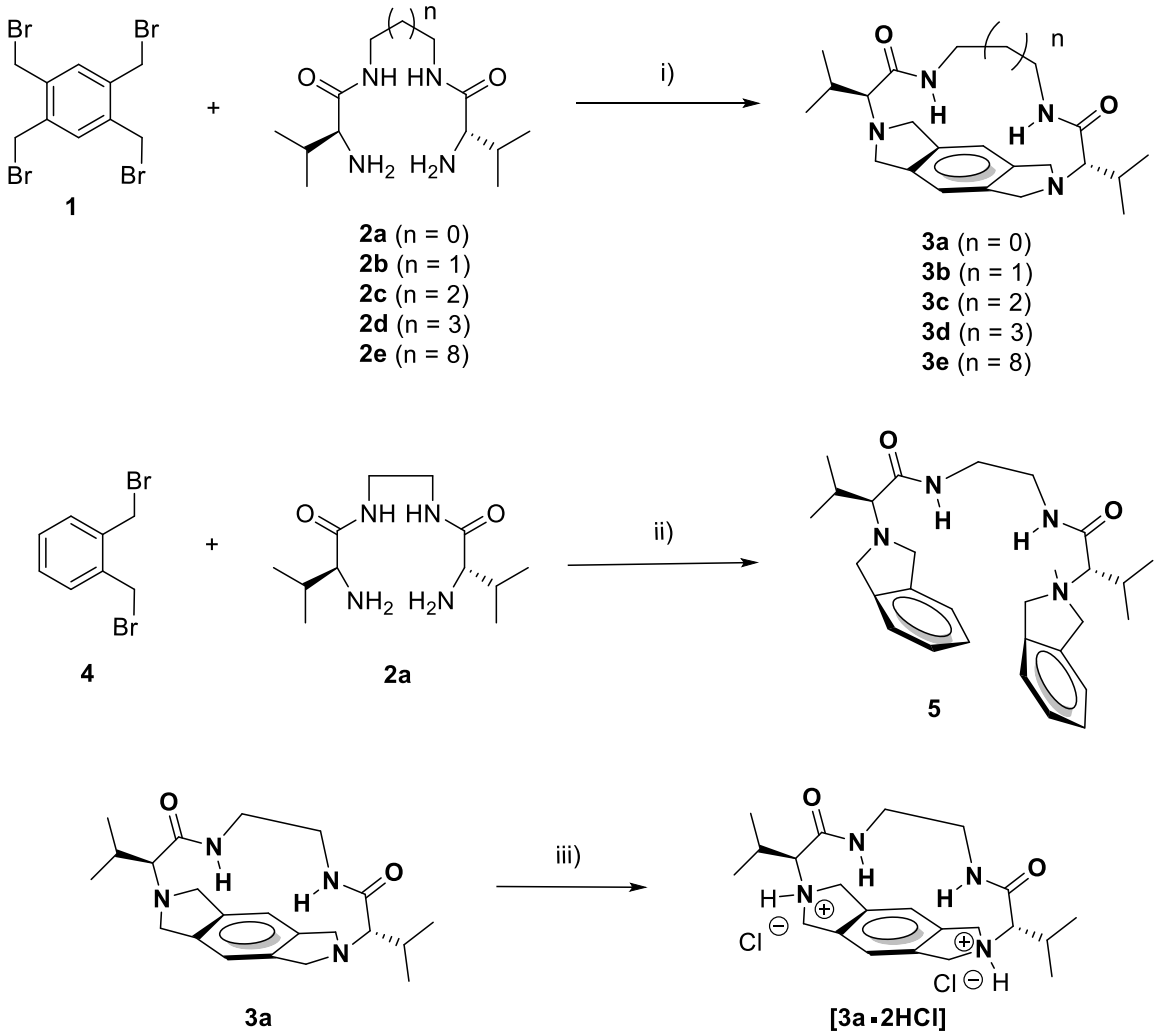
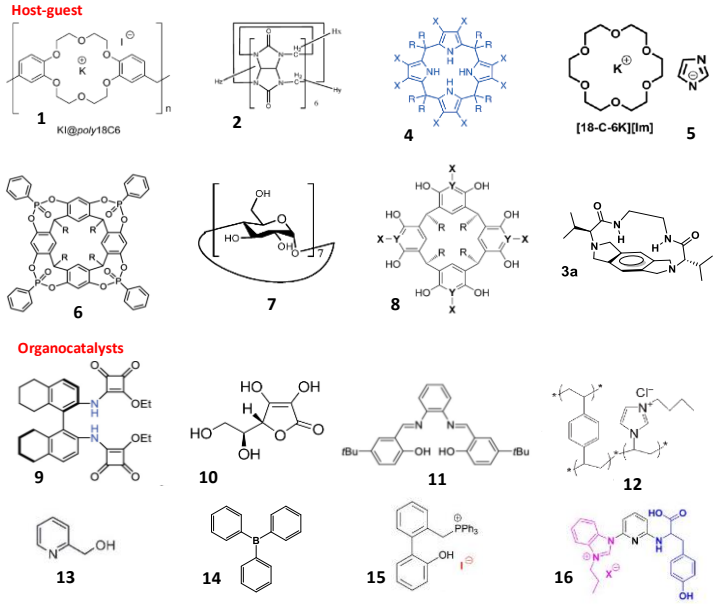


Scheme S1. Synthesis of macrocyclic systems and related analogues. i) CH_3CN, 2-3 h, 90 ºC. ii) CH_3CN, 5 h, 90 ºC. iii) CH_3OH, 1 h, 25 ºC.

Table S1. Comparation of the results in this work with some selected organocatalytic/supramolecular examples for the reaction between styrene oxide (**6**) and CO_2 to afford **7**.



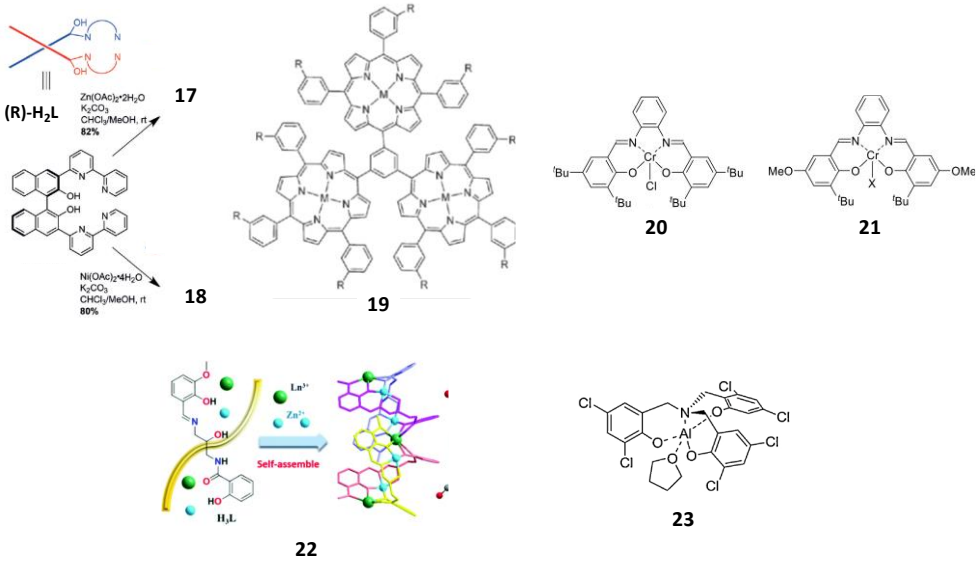
Entry	Ref.	Catalyst	T (°C)	P (bar)	% cat	Time (h)	Conv. (%)	TON	TOF
1	1	Polycrown ether 18C6 (**1**) - KI	100	10	2	3	89	44.5	14.8
2	2	curcurbit[6]uril (**2**) - KI	120	40	1.5 KI 0.1 g CB[6]	5	95	63.3	12.7
3	3	calix[4]pyrrole (R= CH3- X= H) (**4**) - Bu_4NI	100	17	1	15	98	98	6.5
4	4	IL+crown ether [18-C-6-K][Im] (**5**)	100	10	1	6	93	93.5	15.6
5	5	Tetraphosphonate Cavitand (R = C3H7) (**6**) - Bu_4NCl	100	1	1 (**6**) - 1 co-cat	24	85	85	3.5
		Tetraphosphonate Cavitand (R = C3H7) (**6**) - Me_4NCl					25	25	1
		Tetraphosphonate Cavitand (R = C3H7) (**6**) - Me_4NBr					58	58	2.4
		Tetraphosphonate Cavitand (R = C3H7) (**6**) - Me_4NI					92	92	3.8
6	6	β-CD (**7**) - KI	120	60	2.5 KI	12	94	37.6	3.1
7	7	Cavitand-Based Polyphenols (**8**) - Bu_4NI	50	10	1.5 (**8**) - 5 Bu_4NI (MEK)	18	93	62	3.4
		1,2-Epoxyhexane instead of **6** (solventless)	80	10	0.01 (**8**) - 1.6 Bu_4NI	18	74	7400	411
8	This work	Macrocycle **3a**- Bu_4NCl	100	10	0.01 of **3a** - 0.1 Cl	5	76	7600	1525
			80	1	0.01 of **3a** - 1 Cl (ACN)	3	39	3900	1300
9	8	Hemisquaramide (**9**) - Bu_4NI	30	1	2 (**9**) - 5 Bu_4NI	24	92	18.4	0.8
10	9	Ascorbic acid (**10**) - Bu_4NI	60	1	2 (**10**) - 4 Bu_4NI	23	96	48	2.1
11	10	Salophens (**11**)	120	10	10	24	100	10	0.4
					5 (2-MeTHF)	24	90	18	0.8
12	11	PILs (**12**)	110	60	0.526	7	79	150	21.5
13	12	2-Pyridinemethanol (**13**)	25	1	8 (**13**) + 8 Bu_4NI	18	91	11.4	0.6
14	13	Triarylboranes (**14**) Propylene oxide instead of **6**	100	1	0.025 (**14**) + 0.1 PPNCl	24	31	1240	52
		Glycidyl chloride instead of **6**	100	20	0.025 (**14**) + 0.1 PPNCl	3	76	3040	1013
15	14	Phosphonium salts (**15**)	60	1	1	24	92	92	3.8
16	15	Organic pincers (**16**)	25	1	4	24	62	15.5	0.65

References

1: T. Werner and coworkers, *ChemSuschem*, 2015, **8**, 3815-3822; **2:** B. Han and coworkers, *Pure Appl. Chem.*, 2013, **85**, 1633-1641; **3:** T. Ema and coworkers, *Cat. Sci. Technol.*, 2018, **8**, 4193-4198; **4:** H. Jing and coworkers, *Org. Chem Front.*, 2018, **5**, 741-748; **5:** J.-P. Dutasta, V. Dufaud and coworkers, *ACS Catal*., 2015, **5**, 11, 6748-6752; **6:** B. Han and coworkers, *Green Chem.*, 2008, **10**, 1337–1341, **7:** A. W. Kleij and coworkers, *ChemSusChem*, 2016, **9**, 749-755; **8:** T. Ema and coworkers, *Org. Lett.,* 2019, **21**, 1397-1401; **9:** V. D'Elia and coworkers, *ACS Sustainable Chem. Eng*., 2017, **5**, 6392-6397; **10:** M. North and coworkers**,** *ACS Catal.,* 2019, **9**, 1895-1906; **11:** B. Han and coworkers, *Angew. Chem. Int. Ed*., 2007, **46**, 7255-7258; **12:** T. Hirose and coworkers, *Green Chem*., 2016, **18**, 1229-1233; **13:** F. M. Kerton and coworkers, *ACS Catal.*, 2019, **9**, 1799-1809; **14:** S. Shirakawa and coworkers, *Green Chem*., 2016, **18**, 4611-4615; **15:** N. Liu and coworkers, *ACS Catal.,* 2018, **8**, 9945-9957.

Table S2. Selected metal-based catalytic systems for the reaction between styrene oxide (**6**) and CO_2 to afford **7**.

Organometallic



Entry	Ref.	Catalyst	T (°C)	P (bar)	% cat	Time (h)	Conv. (%)	TON	TOF
1	16	Multinuclear complexes **17** (Zn) **18** (Ni)	120 120	150 150	0.1 0.1	24 24	70 97	700 970	29 40
2	17	Trimer Porphyrin Platforms (**19**) (Zn, R = $O(CH_2)_6NBu_3Br$)	120	250	0.002	9	96	48000	5333
3	18	Cr(salophen) **20** - Bu_4NBr	25		2.5 (**16**) - 5 Bu_4NBr	6	65	25.8	4.3
		21 (X = Br) - Bu_4NBr			2.5 (**17**) - 5 Bu_4NBr	6	71	28.2	4.7
4	19	$Zn_3[Co(CN)_6]_2$ - Bu_4NCl	100	3.4	0.1 (Zn) - 1 Bu_4NCl	6	43	430	71.7
5	20	heterometallic helicate complex (**22**) - Bu_4NBr	120	10	0.025 (**18**) – 0.75 Bu_4NBr	1	96	3840	3840
					0.0025 (**18**) – 0.5 Bu_4NBr	1	67	26800	26800
6	21	Al-complex (**23**) – Bu_4NI (4-Fluorostyrene oxide)	70	10	0.05 (**19**) - 0.25 Bu_4NI	18	93	1860	103
		1,2-epoxyhexane instead of **6**			0.0005 (**19**) - 0.5 Bu_4NI	2	24	48000	24000
					0.0005 (**19**) - 0.5 Bu_4NI	18	56	112000	6222

References

16: T. Ema and coworkers, *Angew. Chem. Int. Ed*., 2019, **58**, 9984-9988; **17:** T. Ema and coworkers, *Angew. Chem. Int. Ed*., 2015, **54**, 134-138; **18:** M. North and coworkers, *ACS Catal*., 2016, **6**, 5012-5025; **19**: D.-W. Park and coworkers, *Green Chem*., 2009, **11**, 1754-1757; **20:** W. Liu and coworkers, *Chem. Commun*., 2018, **54**, 2212-2215; **21:** A. W. Kleij and coworkers, *J. Am. Chem. Soc*., 2013, **135**, 1228-1231.

Table S3. Effect of the nature of the alkyl group in the **3a** : R_4NCl catalytic system for the reaction between styrene oxide (**6**) and CO_2 to afford **7**.[a]

Entry	R_4NCl (mol%)	**3a** (mol%)	Conversion[b] (%)	TON (**3a**)
1	X = Bu, (1)	-	65	-
2	X = Et, (1)	-	54	-
3	X = Me, (1)	-	0	-
4	X = Bu, (1)	0.1	93	930
5	X = Et, (1)	0.1	80	800
6	X = Me, (1)	0.1	0	0

[a] Reaction conditions: 1 mL epoxide **6** (8.7 mmol), $p(CO_2)$=1 bar (CO_2 balloon), 5 h, 100 ºC. [b] Conversions determined by ^{1}H NMR; selectivity for **7** was >99.9 %.

Table S4. Effect of the solvent for the reaction between styrene oxide (**6**) and CO_2 to afford **7**.[a]

Entry	Bu_4NCl (mol%)	**3a** (mol%)	Solvent	Time (h)	Conversion[b] (%)	TON (Bu_4NCl)	TON (**3a**)
1	1	-	MeTHF	1	3	3	-
2	1	0.1	MeTHF	1	3	3	30
3	1	-	ACN	1	9	9	-
4	1	0.1	ACN	1	25	25	250
5	1	-	ACN	3	18	18	-
6	1	0.1	ACN	3	59	59	590
7	1	0.01	ACN	3	39	39	3900

[a] Reaction conditions: 80 ºC, 2.4 M of **6** in the solvent, $p(CO_2)$=1 bar. [b] Conversions determined by ^{1}H NMR; selectivity for **7** was >99.9 %.

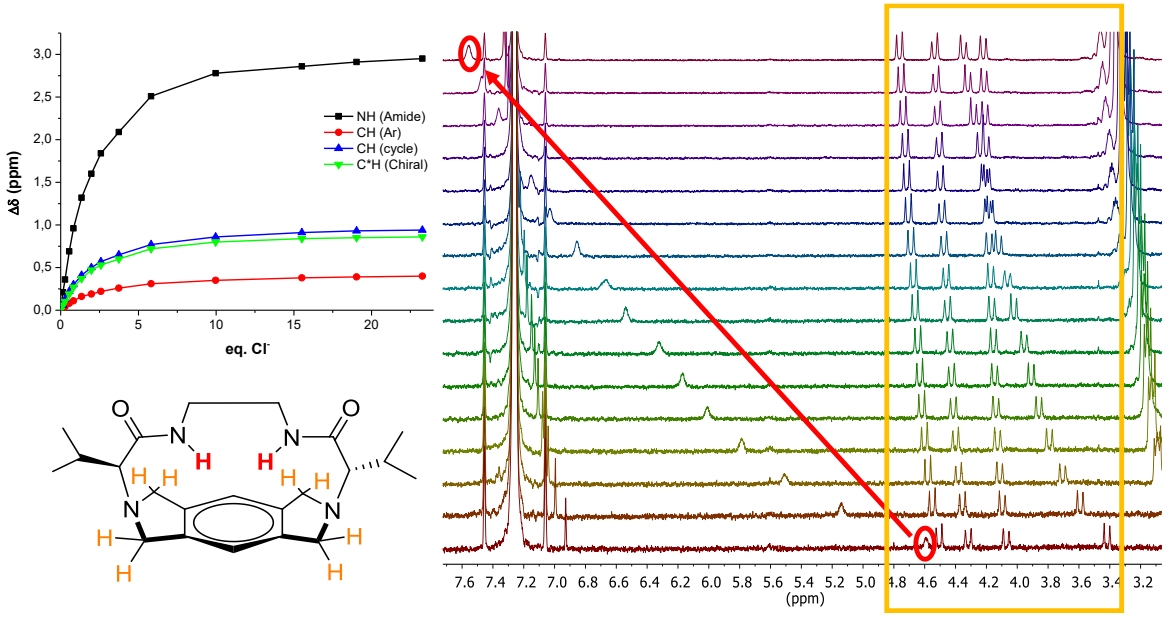


Figure S1. Partial ^{1}H NMR spectra for the titration of **3a** with Bu_4NCl. The downfield shift highlighted in red corresponds to the NH_{amide} signal. Solvent: benzene-d_6 (0.5 mM).

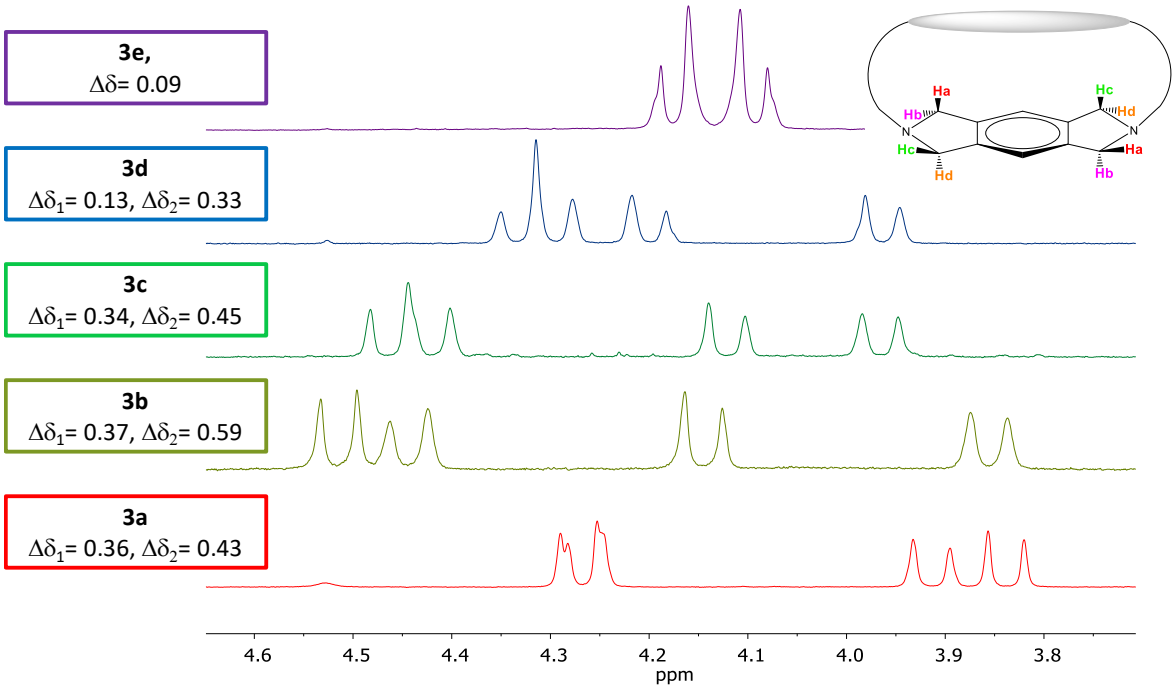


Figure S2. Partial ^{1}H NMR (400 MHz) spectra (signals for the isoindolinic protons) of the macrocyclic pseudopeptides **3a-e**, 6 mM in CD_3OD. $\Delta\delta_1$ and $\Delta\delta_2$ correspond to the difference in chemical shifts between Ha and Hb and/or Hc and Hd.

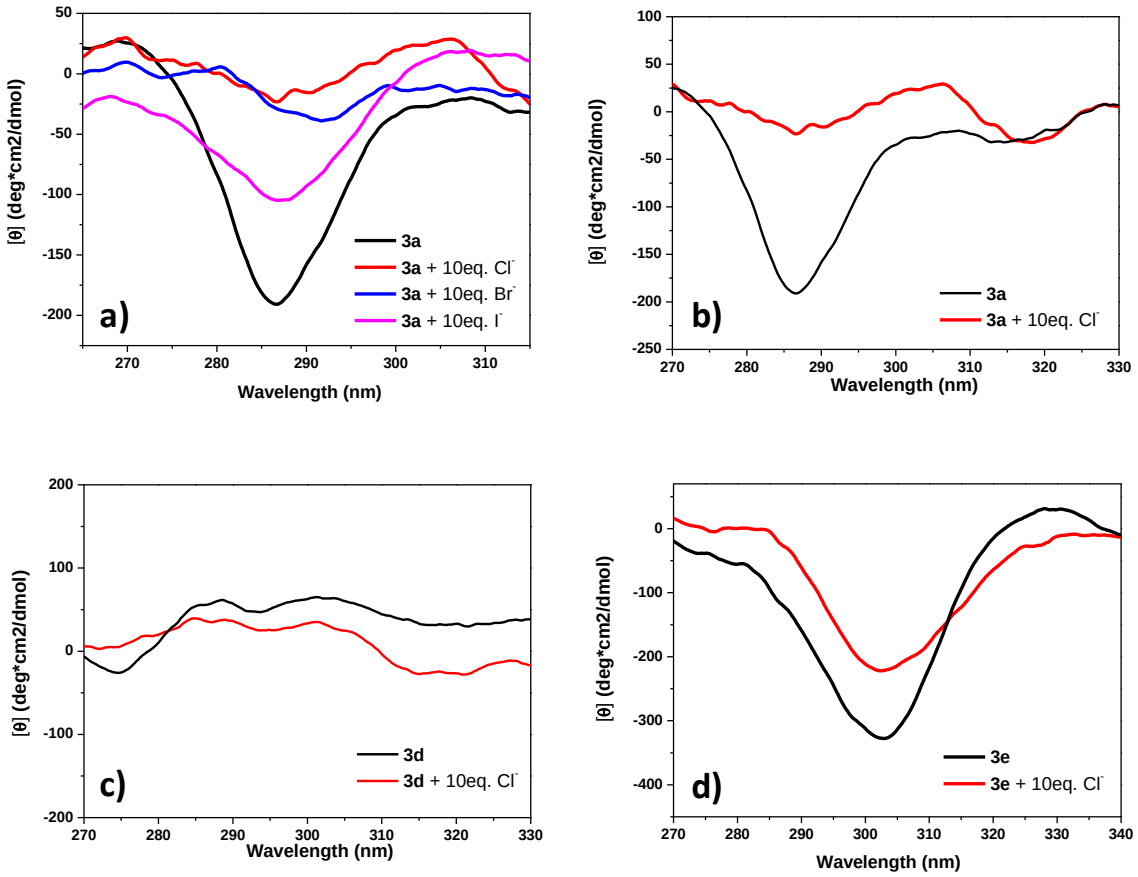


Figure S3. a) CD spectra of **3a** in the presence of 10 eq. of Bu_4NX; b)-d) CD spectra of **3a**, **3d** and **3e** in the absence and presence of 10 eq. of chloride anion.

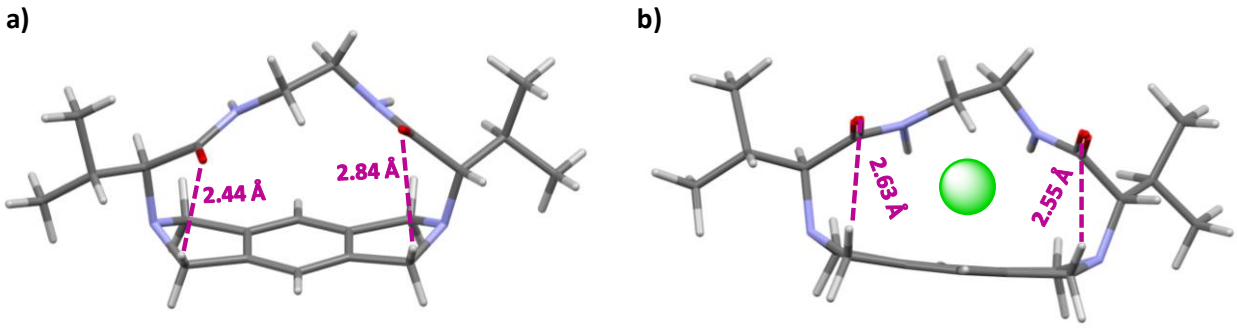


Figure S4. a) Structure of **3a** found in the crystal structure (*syn*-disposition of the amide groups). b) Lowest energy conformation for [**3a** + Cl^-] calculated using Spartan08 at the MMFF (Merck Molecular Force Field) level of theory. The lines display the distances between each C=O group and the closest hydrogen atom of the isoindolinic ring.

Table S5. Shifts observed for the NH_{amide} signals in the presence of 10 equivalent of Bu_4NX.[a]

Entry	Bu_4NX: 1	Cl	Br	I
1	$\Delta\delta$(NH) ppm	2.74	1.43	0.19

[a] Solvent: benzene-d_6 (0.5mM).

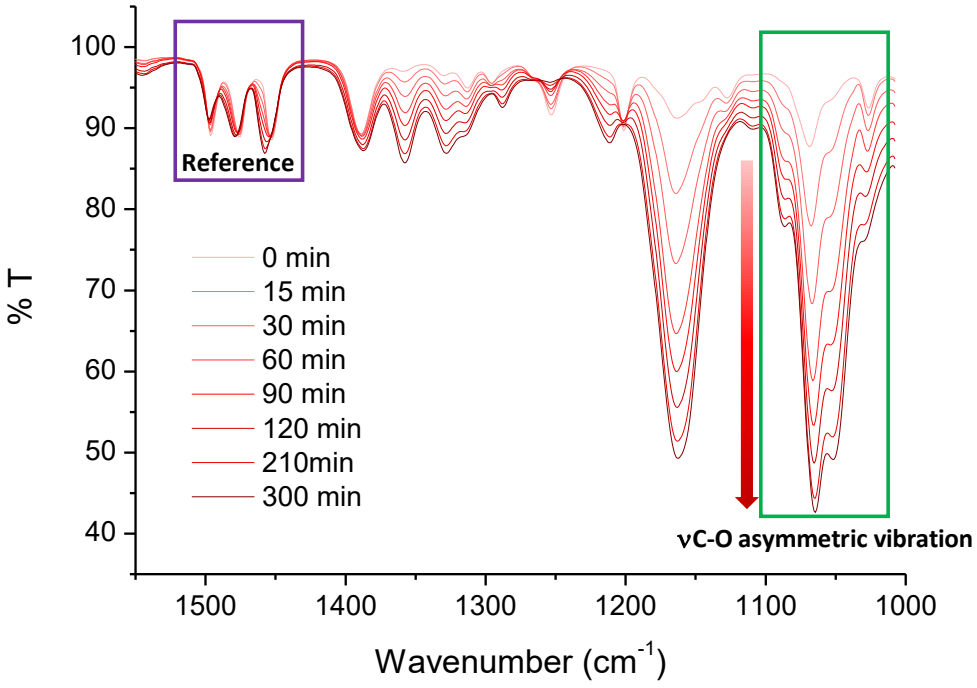


Figure S5. Partial FT-ATR-IR spectra used to obtain the kinetic profiles for the reaction between styrene oxide (**6**) and CO_2 to afford **7**. Reaction conditions: solventless, 100 ºC, 5 h, CO_2 balloon.

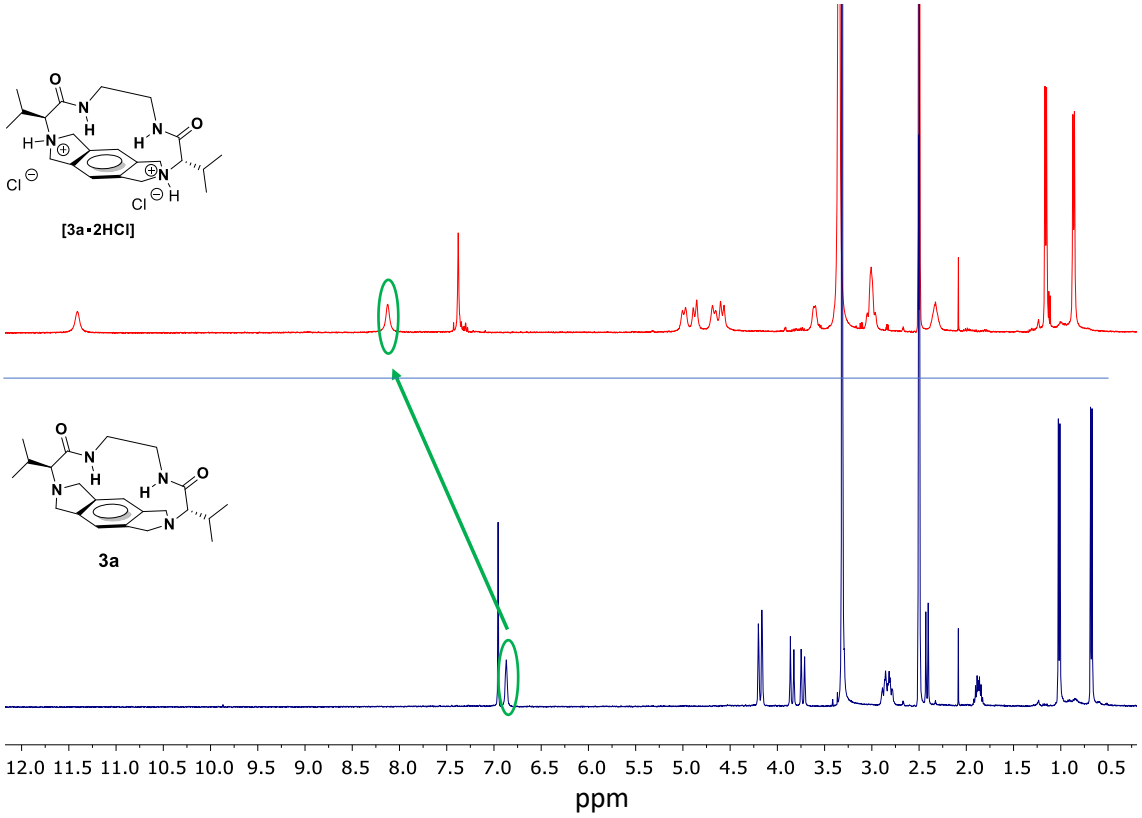


Figure S6. ^{1}H NMR (400 MHz, 30 ºC) spectra of **3a** and [**3a·2HCl**] using DMSO-d_6 as the solvent (9 mM). The downfield shift observed for the NH_{amide} has been highlighted in green.

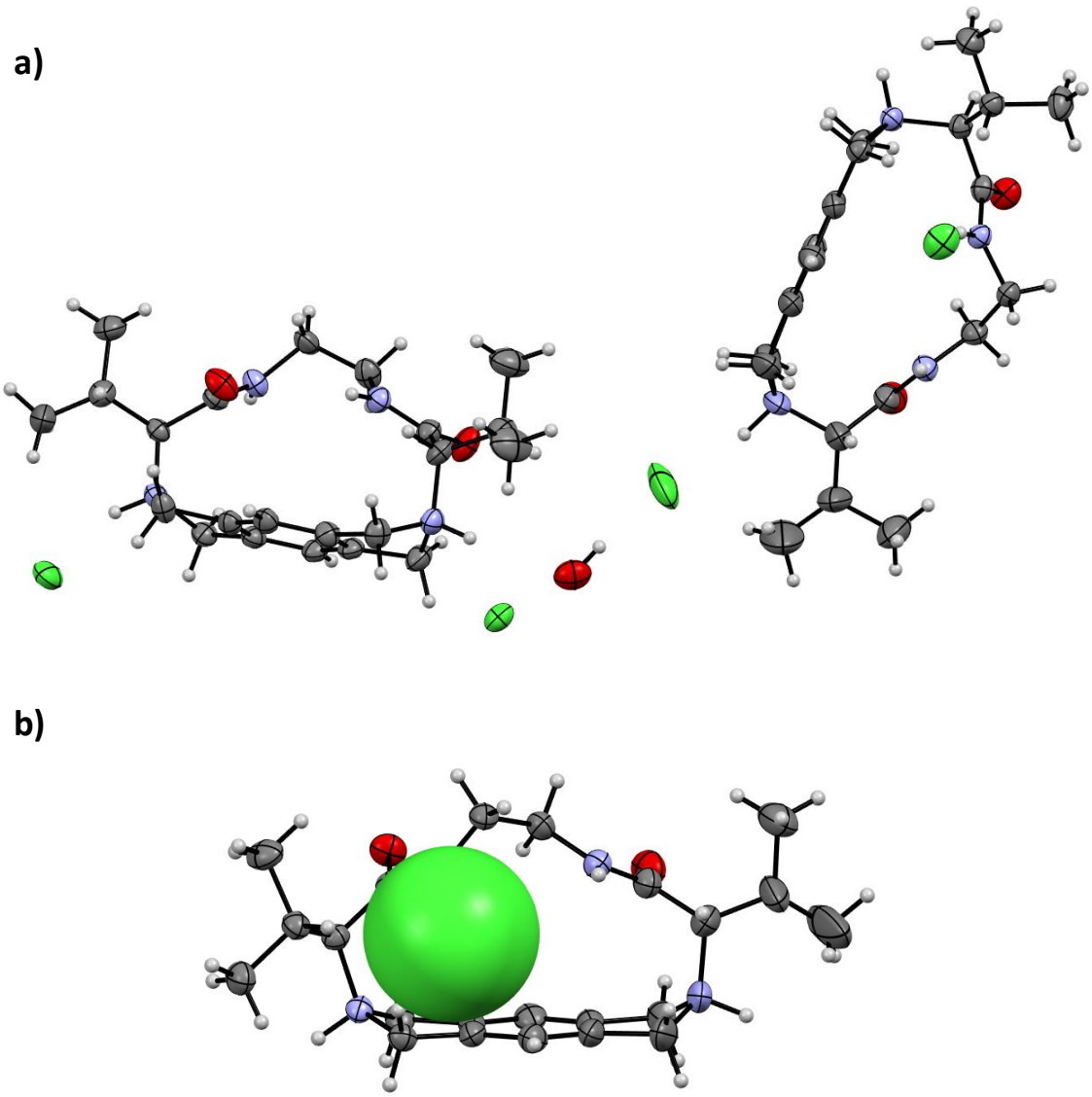


Figure S7. a) Unit cell for the crystal structure of the [**3a·2HCl**] salt displaying the two conformations present (*syn*- and *anti*-disposition of the amide groups). Ellipsoids at 50% of probability. Chloride anions are highlighted in green. One of the chloride anions can adopt two slightly different positions; only one is shown for clarity. b) Representation of the structure for the conformer with the *syn*-disposition of the amide groups highlighting the position of the chloride anion (CPK representation) interacting with the amide groups. The second chloride anion has been deleted for clarity.

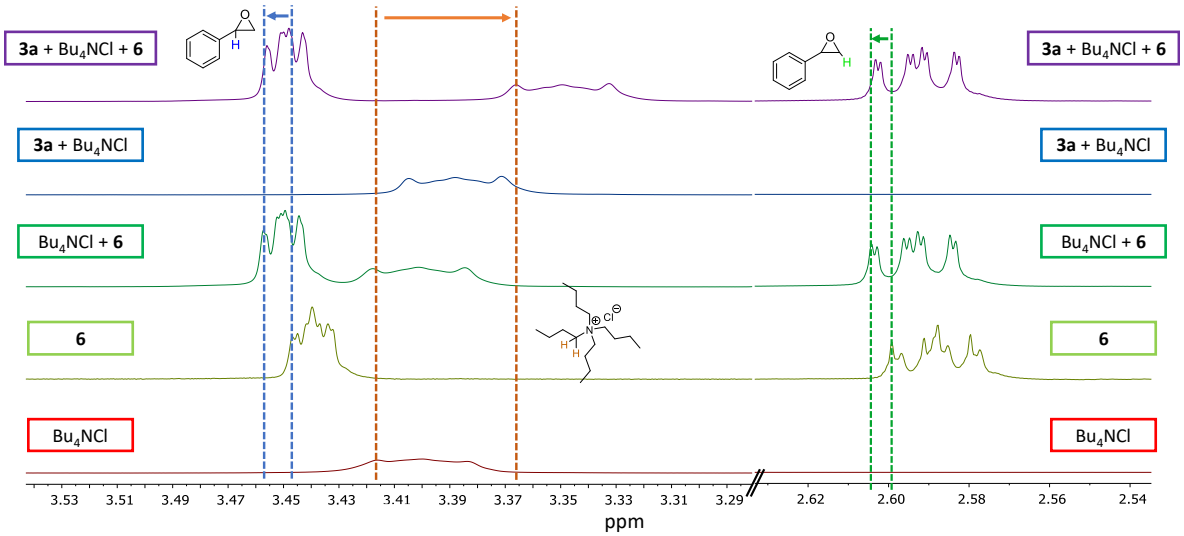


Figure S8. Partial ^{1}H NMR (500 MHz) spectra for Bu_4NCl, **6** and the mixtures [Bu_4NCl + **6**], [**3a** + Bu_4NCl] and [**3a** + Bu_4NCl + **6**] in C_6D_6. [**6**] = 240 mM; [Bu_4NCl] = 20 mM; [**3a**] = 2 mM (samples in 1 mL of C_6D_6).

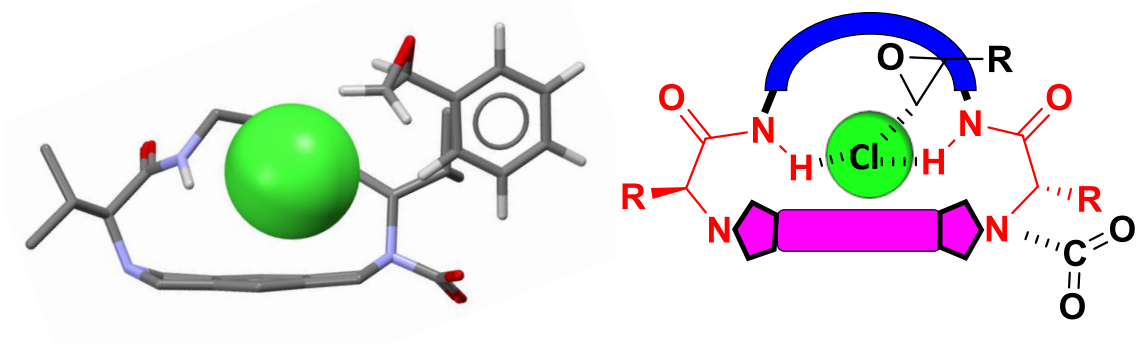


Figure S9. Lowest energy conformer calculated for the [**3a** + Cl^- + **6**] species in the presence of CO_2 activated by the tertiary amino group. MMFF level of theory. Non-essential hydrogen atoms are omitted for clarity.

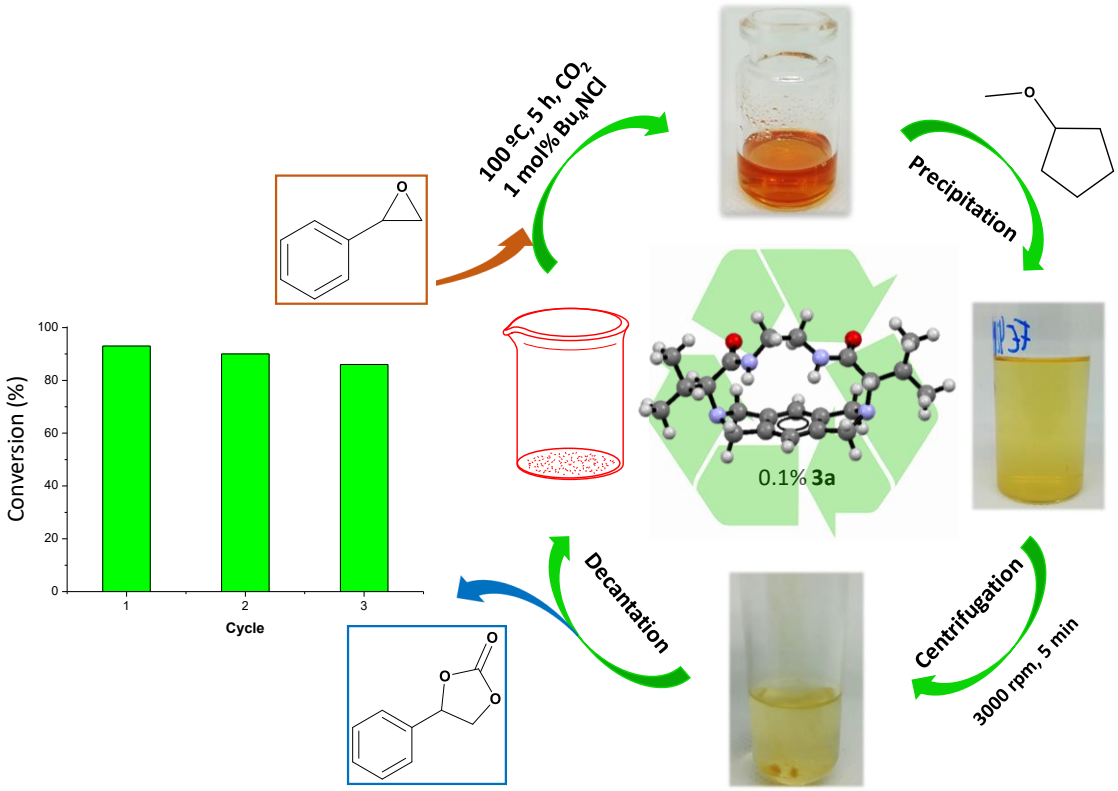
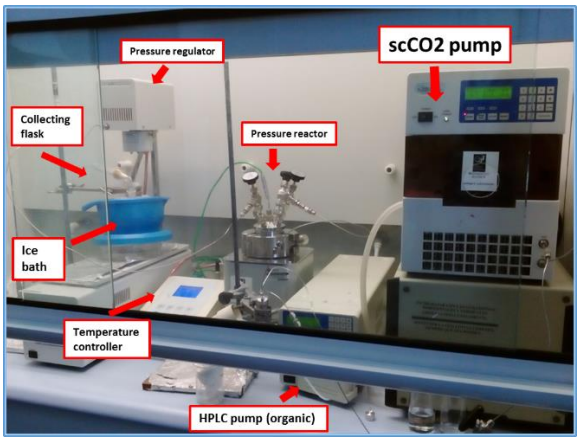


Figure S10. Schematic representation of the protocol for catalyst **3a** recycling.



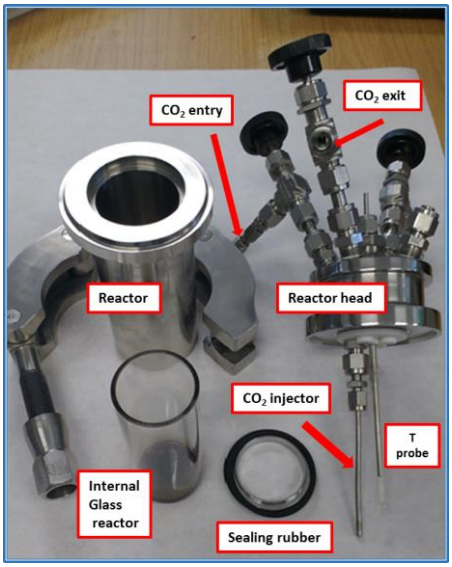


Figure S11. Reactor set-up used to perform the cycloaddition reaction under CO_2 pressure.

X-ray diffraction for [3a·2HCl]

Crystals of this salt suitable for X-Ray diffraction were obtained upon slow evaporation of a methanolic solution. The asymmetric unit contained two molecules displaying rather different conformations. In one of them, each chloride anion is strongly interacting with one of the R_3N^+H groups ($d_{Cl,H}$ = 2.051 and 2.316 Å), triggering an *anti*-disposition of the amide fragments with an intramolecular C=O···HN_{amide} hydrogen bond. The chloride displaying a larger $d_{Cl,H}$ value is also involved in an intermolecular Cl^-···HN_{amide} hydrogen bond. In the second conformer, one chloride anion keeps the same disposition (two possible locations of this chloride are possible, $d_{Cl,H}$ = 2.172 and 2.233 Å) while the other is strongly hydrogen bonded to one of the amide groups in a *syn*-disposition (Cl^-···HN_{amide} distances 2.393 and 4.151 Å) displaying an overall arrangement very similar to the one calculated for the [**3a** + Cl^- + **6**] species. Molecules in *syn*-disposition are connected through an array of hydrogen bonds involving the molecule of water present in the cell unit, which is connected to one chloride, one C=O_{amide} group and one $^+HNR_3$ fragment of three different molecules.

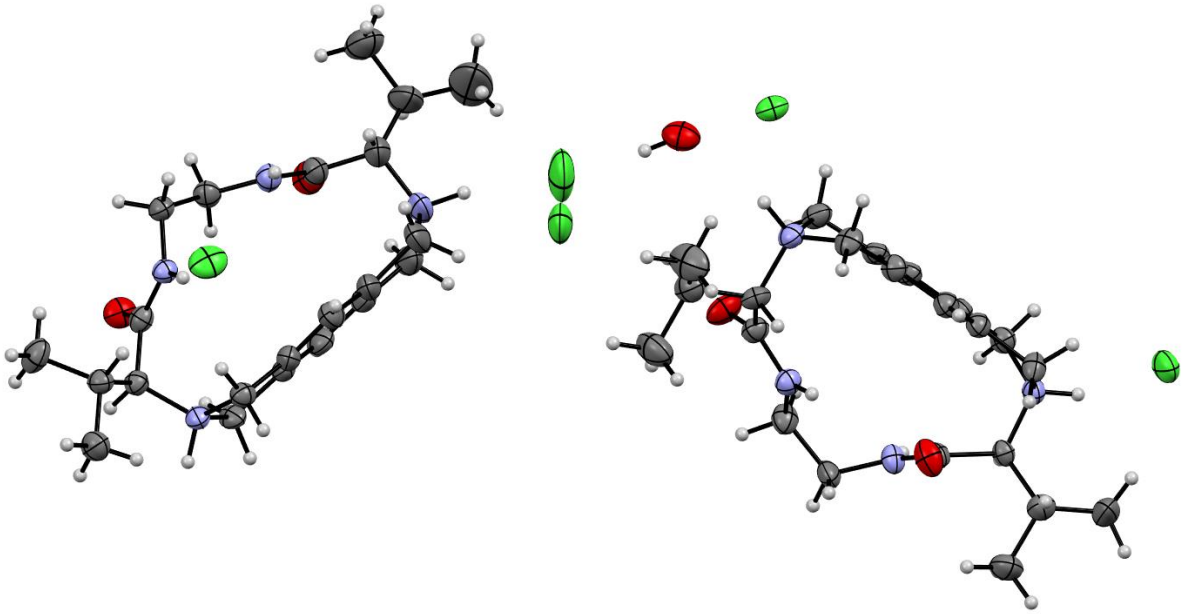


Figure S12. Thermal ellipsoid plot for the crystal structure of [**3a·2HCl**]. Ellipsoids at 50% of probability.

Table S6. Crystallographic and structural refinement data for compound [**3a·2HCl**].

Empirical formula	C22 H34 N4 O2, 2(Cl), 0.5(H2 O)
Formula weight	466.44
Temperature/K	200(2)
Crystal system	tetragonal
Space group	P 43 21 2
a/Å	11.20540(10)
b/Å	11.20540(10)
c/Å	83.0175(9)
α/°	90
β/°	90
γ/°	90
Volume/Å³	10423.8(2)
Z	16
ρcalcg/cm³	1.189
F(000)	3984
Crystal size/mm³	0.213 x 0.170 x 0.098
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.962 to 144.448
Index ranges	-13 ≤ h ≤ 10, -10 ≤ k ≤ 13, -100 ≤ l ≤ 102
Reflections collected	48906
Independent reflections	10188
Data/restraints/parameters	10188/2/571
Goodness-of-fit on F²	1.108
Final R indexes [I>=2σ (I)]	R1 = 0.0700, wR2 = 0.1758
Final R indexes [all data]	R1 = 0.0748, wR2 = 0.1783
Largest diff. peak/hole / e Å⁻³	1.33/-0.45
Flack parameter	0.030(6)

Characterization data: ^{1}H NMR, ^{13}C NMR and HRMS (ESI/Q-TOF)

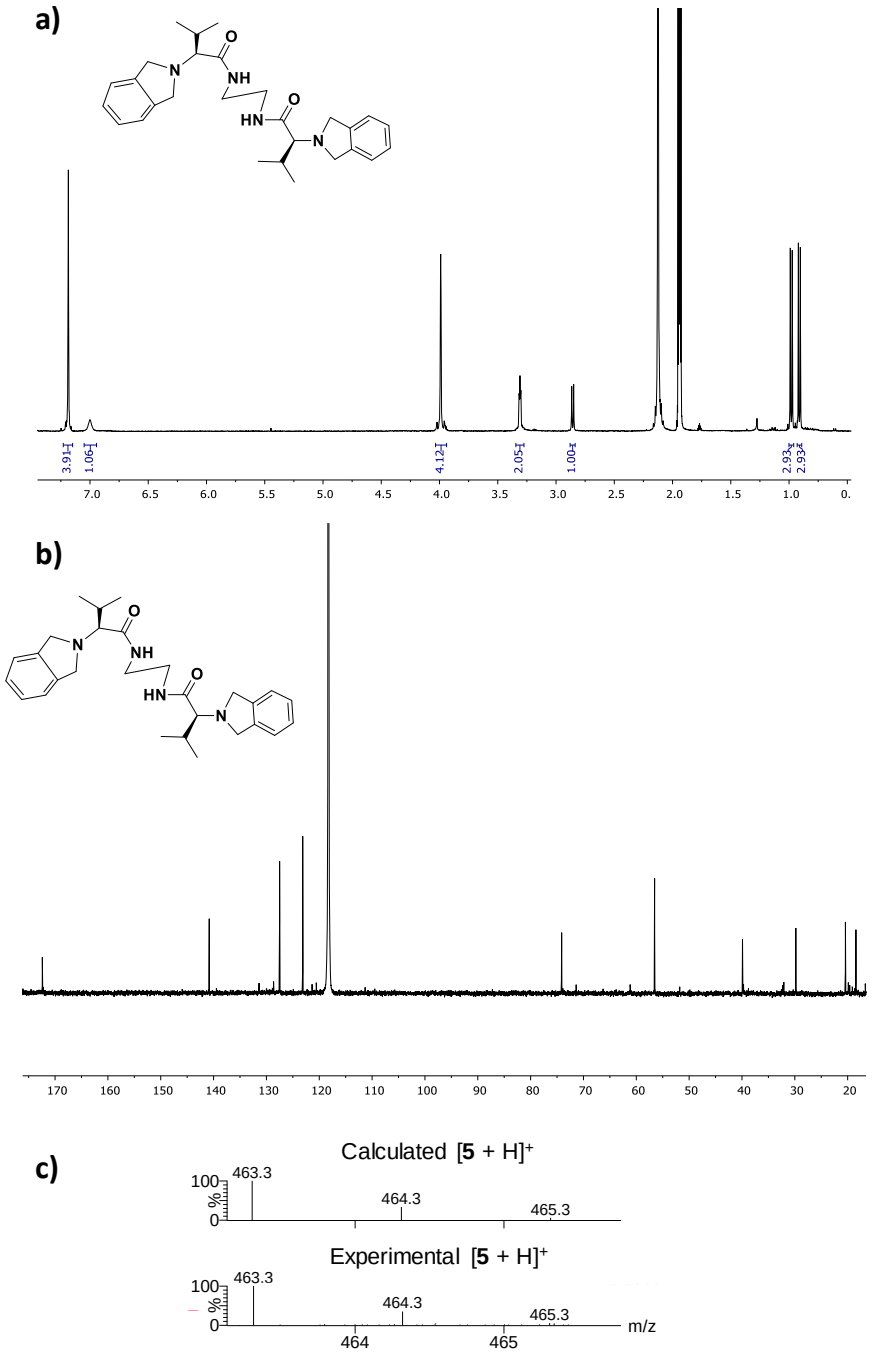
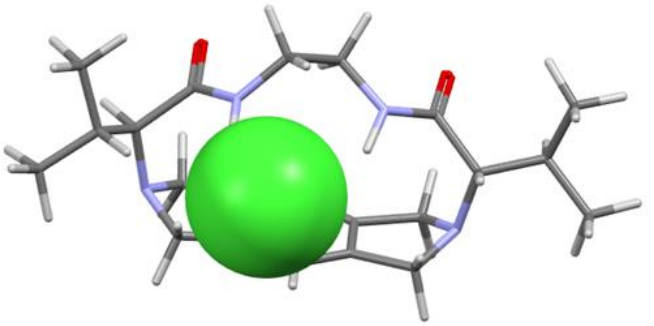


Figure S13. a) ^{1}H NMR (400 MHz, CD_3CN); b) $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) and c) HRMS (ESI/Q-TOF, CH_3OH) for pseudopeptide **5**.

Molecular modelling

- Lowest energy conformation for [**3a** + Cl^-].

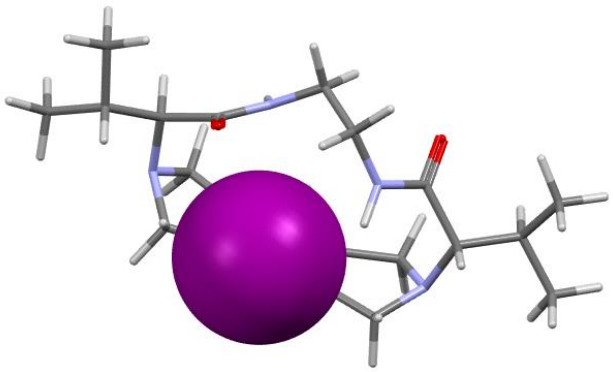


Cartesian coordinates (61 atoms), E (298 K) = 325.70 kJ/mol

1	H	-0.31635111	1.22634113	2.69699281
2	C	-0.66495149	1.38446012	1.68197073
3	C	-1.51063301	1.71300516	-1.04144796
4	C	-1.78602392	0.75552177	1.18244188
5	C	0.05877193	2.13087793	0.77412589
6	C	-0.34894053	2.29568000	-0.55787712
7	C	-2.20939468	0.91727425	-0.14724249
8	H	-1.81140076	1.81122221	-2.07675524
9	C	1.37015879	2.80763800	0.98338232
10	H	1.20021826	3.74569663	1.52490804
11	H	2.05050388	2.20074977	1.58003341
12	C	0.68265722	3.11439276	-1.26899486
13	H	0.30918637	4.14055083	-1.36783274
14	C	-2.66356676	-0.23579349	1.86467645
15	H	-2.09191775	-0.92782821	2.49167060
16	H	-3.37424698	0.29602183	2.50790554
17	C	-3.41565725	0.05584019	-0.36289143
18	H	-3.44349561	-0.41572071	-1.34862658
19	H	-4.31021869	0.68519208	-0.27985896
20	N	-3.41567556	-0.90941221	0.77390433
21	C	-2.83340639	-2.25100915	0.44415440
22	H	-2.36367401	-2.68581686	1.33699474
23	C	-1.75362088	-2.21718776	-0.67801115
24	N	-0.47007502	-1.89786516	-0.27921897
25	C	0.56512833	-1.74297039	-1.28959048
26	H	0.57348017	-2.66982105	-1.87575794
27	H	0.26057268	-0.93401566	-1.96222567
28	C	1.96600908	-1.51104789	-0.71572226
29	H	2.70809335	-1.79012615	-1.47321099
30	H	2.13795303	-2.13999920	0.16270642
31	N	2.23502399	-0.13184879	-0.34572118
32	C	2.48526644	0.82057011	-1.30368617
33	C	2.96535423	2.22820464	-0.85263300
34	H	3.31014110	2.70039774	-1.78621135
35	N	1.87562448	3.13311192	-0.37280959
36	H	0.89598895	2.74068039	-2.27506104
37	C	4.23213745	2.16778729	0.05250383
38	H	4.01255832	1.63282331	0.98228031
39	C	5.37235979	1.40393881	-0.63867690
40	H	6.26791529	1.39086073	-0.00778081
41	H	5.09932674	0.36213270	-0.83212464
42	H	5.64015267	1.86928801	-1.59340518

43	C	4.73704888	3.56920144	0.42068291
44	H	4.95852385	4.15870346	-0.47555073
45	H	4.00170622	4.11776135	1.01697263
46	H	5.65361181	3.50691191	1.01751339
47	C	-3.99934726	-3.21398503	0.05052572
48	H	-4.42676463	-2.89866497	-0.91054692
49	C	-3.49762830	-4.65849066	-0.10743452
50	H	-2.74412703	-4.74733185	-0.89486646
51	H	-3.05614095	-5.02673276	0.82508918
52	H	-4.32303647	-5.32728445	-0.37528555
53	C	-5.13172899	-3.21569422	1.08942421
54	H	-5.62954516	-2.24249851	1.14469976
55	H	-5.89941109	-3.95174916	0.82627290
56	H	-4.75317937	-3.46476207	2.08668917
57	O	-2.02436635	-2.47136248	-1.85449566
58	O	2.36442708	0.57002211	-2.50892833
59	H	-0.34488746	-1.37234906	0.58201681
60	H	2.31839841	0.06555778	0.65670236
61	Cl	2.30511464	-0.66705047	3.10324215

- Lowest energy conformation for [**3a** + I^-].

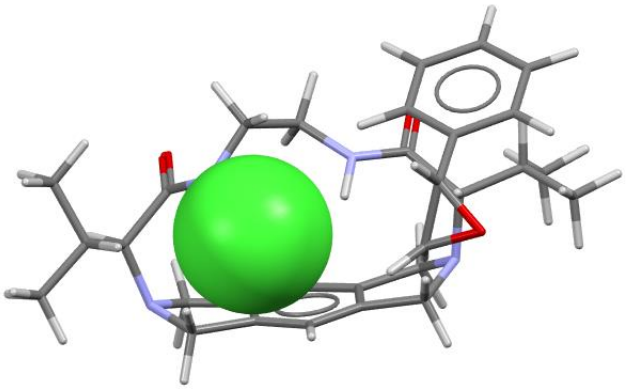


Cartesian coordinates (61 atoms), E (298 K) = 443,73 kJ/mol

1	H	-3.04356638	0.25652898	0.57555539
2	C	-2.27250284	-0.49265320	0.44792256
3	C	-0.17988070	-2.43813085	0.09713954
4	C	-1.49661574	-0.94108023	1.50167034
5	C	-1.93059994	-0.98470754	-0.79683880
6	C	-0.91718841	-1.94629020	-0.96530410
7	C	-0.46522273	-1.88268259	1.32971618
8	H	0.62461556	-3.15030625	-0.03749844
9	C	-2.44780177	-0.58241961	-2.14264096
10	H	-3.40478980	-1.08596349	-2.32201603
11	H	-2.61285742	0.49646524	-2.21996022
12	C	-0.75952637	-2.22220674	-2.42348302
13	H	-1.27744005	-3.15720857	-2.66736848
14	C	-1.50580104	-0.49708474	2.92630240
15	H	-1.68325383	0.57837835	3.02753290
16	H	-2.30746678	-1.02214453	3.45872548
17	C	0.24524878	-2.06827735	2.63413912
18	H	1.33119597	-2.12619022	2.51367272
19	H	-0.09483243	-3.00287929	3.09511775
20	N	-0.19962117	-0.92749694	3.47785755
21	C	0.80041186	0.17858025	3.56890648
22	H	0.28592132	1.08351700	3.92206974
23	C	1.48628627	0.54486477	2.20854354
24	N	0.72472865	1.30640249	1.34801374
25	C	1.28277506	2.04006783	0.22379694
26	H	0.48479715	2.68223131	-0.15789467
27	H	2.05243697	2.69986883	0.64235224
28	C	1.92406784	1.21936055	-0.90625562
29	H	2.69821082	0.55192251	-0.51732243
30	H	2.41634649	1.91608689	-1.59543013
31	N	1.04376777	0.39902973	-1.72255268
32	C	0.04244942	0.91513473	-2.51751508
33	C	-0.50599502	-0.05514638	-3.61942960
34	H	0.36394879	-0.55872148	-4.06440354
35	N	-1.44368127	-1.10077770	-3.10945395
36	H	0.28875400	-2.33287638	-2.71845734
37	C	-1.18268583	0.74657551	-4.77762269
38	H	-1.96497734	1.39827312	-4.36765016
39	C	-0.16226329	1.63925535	-5.50267238
40	H	0.28959720	2.37522160	-4.83217766
41	H	0.64492336	1.04102033	-5.93938147
42	H	-0.64390935	2.19603412	-6.31407234
43	C	-1.83627816	-0.17154082	-5.82182136

44	H	-1.11341529	-0.88799097	-6.22680973
45	H	-2.67422565	-0.73247923	-5.39615858
46	H	-2.23613600	0.41326147	-6.65757653
47	C	1.87082496	-0.16388421	4.65479896
48	H	2.52537118	-0.96500786	4.28791721
49	C	2.75301207	1.05608891	4.96671789
50	H	3.29857371	1.40492578	4.08578234
51	H	2.15222398	1.89113879	5.34341609
52	H	3.49893473	0.80832866	5.72998184
53	C	1.23828249	-0.64069026	5.97131322
54	H	0.71258615	-1.59220495	5.84376522
55	H	2.00644598	-0.80112434	6.73587562
56	H	0.52616027	0.09630059	6.35806631
57	O	2.64010184	0.21715281	1.93364789
58	O	-0.35642733	2.07183834	-2.38873800
59	H	-0.23790216	1.49641974	1.58317952
60	H	1.31116572	-0.56604402	-1.84467832
61	I	-2.60730223	3.37593632	0.07968760

- Lowest energy conformation for [**3a** + **6** + Cl^-].

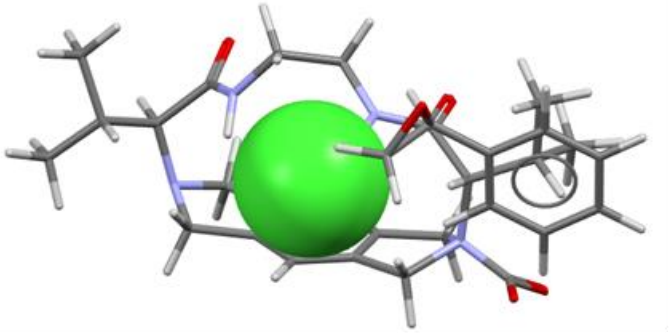


Cartesian coordinates (78 atoms), E (298 K) = 393.23 kJ/mol

1	H	-3.06299253	2.87899218	0.20235019
2	C	2.12446076	-2.67018507	-0.29518583
3	C	-0.35566245	-2.02832703	-1.59187004
4	C	2.07191920	-2.27290502	-1.62136007
5	C	0.91539758	-2.68566112	0.38179057
6	C	-0.29603939	-2.37604156	-0.25796119
7	C	0.85793319	-1.95165484	-2.24712182
8	H	-1.28299228	-1.73874550	-2.07443512
9	C	0.63539299	-2.92384787	1.83265240
10	H	0.60599498	-4.00573172	2.00973117
11	H	1.40562572	-2.50593599	2.48629464
12	C	-1.39979308	-2.39468928	0.74304711
13	H	-1.95599996	-3.33428824	0.64532569
14	C	3.18221711	-2.05267616	-2.60002991
15	H	4.06267524	-1.59085365	-2.14301233
16	H	3.49027205	-3.02392175	-3.00521100
17	C	1.12546582	-1.47417896	-3.63431001
18	H	0.52640538	-0.59982134	-3.88619127
19	H	0.86204050	-2.27207103	-4.33859676
20	N	2.59053251	-1.24773528	-3.70724711
21	C	2.99428620	0.19114730	-3.64160545
22	H	4.07394417	0.17289260	-3.85967046
23	C	2.91462331	0.82066796	-2.22218277
24	N	1.69256983	1.23244413	-1.74866529
25	C	1.59059674	2.00710766	-0.52382956
26	H	2.36744249	2.77980927	-0.56495222
27	H	0.62073669	2.51364224	-0.52361218
28	C	1.77562321	1.18863949	0.75821645
29	H	2.02175354	1.87219690	1.57933045
30	H	2.59753029	0.47043809	0.67147524
31	N	0.58669510	0.45214285	1.15374831
32	C	0.51147296	-0.12557466	2.40682373
33	C	-0.74500697	-1.00228257	2.67678835
34	H	-1.58194517	-0.42590705	2.25833243
35	N	-0.72920098	-2.37146625	2.06943958
36	H	-2.10341708	-1.57050510	0.59334987
37	C	-1.05091509	-1.10084258	4.20436011
38	H	-0.92120116	-0.10052855	4.63857635
39	C	-2.51168307	-1.50949517	4.44200381
40	H	-2.75149026	-1.48035049	5.51041392
41	H	-3.19791975	-0.82674625	3.93097118
42	H	-2.71154375	-2.52391145	4.08127105
43	C	-0.13572279	-2.05209692	4.98601402

44	H	0.92029140	-1.80140053	4.85759160
45	H	-0.35440502	-1.99135174	6.05815906
46	H	-0.27858153	-3.09490920	4.68449071
47	C	2.38428154	1.10889612	-4.74251227
48	H	1.31444847	1.25859680	-4.56583721
49	C	3.03429737	2.50113382	-4.72807807
50	H	2.85422744	3.01932616	-3.78130395
51	H	4.11699516	2.43519873	-4.88033271
52	H	2.62025193	3.13009910	-5.52380962
53	C	2.55217527	0.50659146	-6.14377460
54	H	2.00903895	-0.43806092	-6.24307403
55	H	2.15874884	1.18609849	-6.90775008
56	H	3.60727891	0.31962206	-6.37092060
57	O	3.94560383	0.96481514	-1.55420751
58	O	1.38061057	0.06786610	3.25917839
59	H	0.83398084	1.12713076	-2.29925052
60	H	0.01298754	0.07644147	0.40488930
61	Cl	-1.63777419	1.51549255	-2.73505371
62	C	-3.78552069	2.26335993	1.65567042
63	C	-2.02310955	2.76712903	3.80677667
64	C	-2.44266976	2.60831978	1.43301809
65	C	-4.21944837	2.18349781	2.98948767
66	C	-3.34992356	2.42916707	4.05591696
67	C	-1.56980897	2.85976289	2.49454403
68	H	-2.06961982	2.67465778	0.41011350
69	H	-5.25405375	1.91656887	3.19478141
70	H	-3.71000036	2.35076828	5.07748708
71	H	-0.53315043	3.11420336	2.28961214
72	H	-1.33902503	2.95045642	4.63052143
73	C	-4.71851615	2.01350922	0.50074861
74	H	-5.03971278	2.89263177	-0.05053423
75	C	-4.61078127	0.73732676	-0.29412520
76	H	-3.83750371	0.02729834	-0.03245077
77	H	-4.82514643	0.78818104	-1.35506212
78	O	-5.68253350	0.94841742	0.62983387

- Lowest energy conformation for [**3a**-CO_2 + **6** + Cl^-]

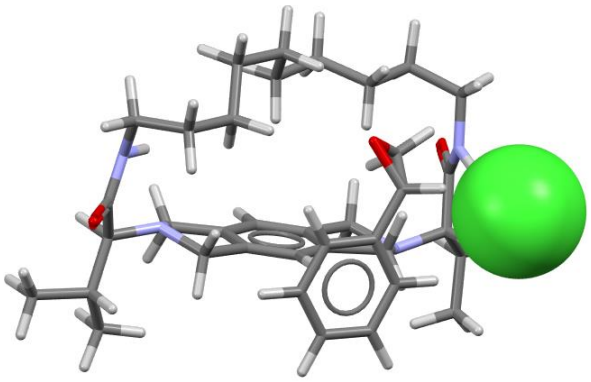


Cartesian coordinates (81 atoms), E (298 K) = -653.71 kJ/mol

1	H	2.32875536	-0.33181615	3.70059757
2	C	2.09976560	-0.90406229	2.80958913
3	C	1.49017423	-2.36117391	0.41005867
4	C	3.06788106	-1.20035537	1.86145460
5	C	0.80924573	-1.30976520	2.50848816
6	C	0.51521541	-2.00992717	1.32195003
7	C	2.76579264	-1.91909553	0.69485475
8	H	1.25181540	-2.87679779	-0.51449128
9	C	-0.47364591	-1.08227217	3.26156164
10	H	-0.54515058	-1.88580828	4.00591545
11	H	-0.54077921	-0.11063842	3.75346288
12	C	-0.95956517	-2.22756063	1.22018178
13	H	-1.17099954	-3.25409152	1.55139625
14	C	4.51838475	-0.83289401	1.83232574
15	H	4.68833888	0.20246815	2.14374826
16	H	5.06384352	-1.48695313	2.52246828
17	C	3.99039564	-2.05191843	-0.14304649
18	H	3.77223401	-1.87311343	-1.19795481
19	H	4.37373517	-3.07478740	-0.05029970
20	N	4.97853622	-1.12218968	0.44402284
21	C	5.23932755	0.11474563	-0.34462673
22	H	6.09298615	0.58908238	0.16420172
23	C	4.11127036	1.18135855	-0.27404214
24	N	2.97301185	0.96840381	-1.01560576
25	C	1.94881083	1.99234643	-1.13350476
26	H	2.46435300	2.94521482	-1.30420122
27	H	1.36351699	1.77889892	-2.03096000
28	C	1.05271133	2.14265164	0.09815752
29	H	0.50669804	3.09065784	0.01893596
30	H	1.65362044	2.19175509	1.01328304
31	N	0.04171280	1.10991949	0.26913932
32	C	-0.73796611	1.12146719	1.40641620
33	C	-1.93268268	0.11229321	1.48664922
34	H	-2.19172101	-0.16971876	0.45890520
35	N	-1.56978177	-1.22992742	2.21433089
36	H	-1.36587871	-2.06142721	0.22104025
37	C	-3.20118228	0.84481827	2.06077701
38	H	-4.04762905	0.14995072	2.01807041
39	C	-3.11600680	1.35702732	3.50319709
40	H	-2.49613140	2.25384343	3.59010833
41	H	-4.11621219	1.63519789	3.85584186
42	H	-2.72791929	0.61237701	4.19786758
43	C	-3.60324594	2.01747620	1.14809422
44	H	-3.67939425	1.69662909	0.10534988
45	H	-4.57937298	2.41673659	1.44486102

46	H	-2.88105242	2.83888813	1.19619672
47	C	5.71916769	-0.12765713	-1.80806409
48	H	4.89606245	-0.51746113	-2.41800445
49	C	6.17702803	1.18337233	-2.46651945
50	H	5.35658460	1.90342845	-2.54258875
51	H	6.98892361	1.65012243	-1.89840429
52	H	6.54016114	0.99980818	-3.48370443
53	C	6.87659907	-1.13320106	-1.87099175
54	H	6.56980410	-2.12306543	-1.52010782
55	H	7.23119720	-1.25268695	-2.90063943
56	H	7.72299514	-0.80138364	-1.25998039
57	O	4.27788957	2.21556191	0.37952431
58	O	-0.46633046	1.87765557	2.34445800
59	H	2.71158444	0.03729867	-1.31785081
60	H	-0.21298697	0.53306698	-0.54710880
61	Cl	-0.43522401	-0.74374727	-2.45612075
62	C	-4.94605248	0.43087639	-2.55164599
63	C	-6.70107583	-0.22332365	-0.43626294
64	C	-6.13248038	1.15229747	-2.33831140
65	C	-4.66659632	-0.62838658	-1.67273691
66	C	-5.53274911	-0.95482364	-0.62681905
67	C	-7.00357864	0.83081286	-1.29349370
68	H	-6.37548153	1.97935318	-3.00187597
69	H	-3.74928027	-1.20346391	-1.79809164
70	H	-5.28158419	-1.77361281	0.04558489
71	H	-7.91331090	1.40586078	-1.14958031
72	H	-7.36716637	-0.47621152	0.38361729
73	C	-3.98944694	0.79488571	-3.65503104
74	H	-3.13480983	1.39972783	-3.36376075
75	C	-3.76635179	-0.15223840	-4.80676610
76	H	-4.28864282	-1.10011369	-4.80971743
77	H	-2.77215182	-0.18454625	-5.23614540
78	O	-4.53780819	1.04243450	-4.96609204
79	C	-2.70822449	-1.84446236	2.71784783
80	O	-2.82843921	-1.86171253	3.96703486
81	O	-3.48404020	-2.32237920	1.85358214

- Lowest energy conformation for [**3e** + **6** + Cl^-].



Cartesian coordinates (102 atoms), E (298 K) = 313.34 kJ/mol

1	H	1.65760774	-3.20913941	1.37187359
2	C	1.57741642	-2.17749356	1.05425351
3	C	1.32963342	0.54671165	0.18948384
4	C	1.20740210	-1.16404144	1.92584534
5	C	1.81669507	-1.80119293	-0.25927541
6	C	1.68913150	-0.46657107	-0.68133296
7	C	1.09245994	0.17329171	1.49977017
8	H	1.22023449	1.56980505	-0.14480971
9	C	2.16728812	-2.65320219	-1.44506121
10	H	3.00312747	-3.32002692	-1.21314304
11	H	1.28160510	-3.24204660	-1.69915914
12	C	1.93428730	-0.38674165	-2.15752766
13	H	2.61512527	0.43439759	-2.40111899
14	C	0.86817800	-1.24217469	3.38332882
15	H	0.15216988	-2.04802453	3.57227935
16	H	1.78125207	-1.41973384	3.95612106
17	C	0.69394732	1.03466629	2.65598424
18	H	-0.11872668	1.71206185	2.37986269
19	H	1.56289511	1.61624483	2.97733655
20	N	0.25140559	0.05723647	3.66092300
21	C	0.10515393	0.50330316	5.04980514
22	H	-0.12606959	-0.37484861	5.66959074
23	C	-1.20447871	1.36511383	5.06401889
24	N	-2.26937837	0.70638504	4.46584567
25	C	-3.50518441	1.38588673	4.14348941
26	H	-4.29413075	0.62944234	4.10956022
27	C	-1.35104032	-2.28221155	-4.64208352
28	H	-1.90832619	-1.41432518	-5.00972956
29	N	0.00944465	-1.85832786	-4.40097778
30	C	1.03313586	-2.74800478	-4.16400655
31	C	2.42029526	-2.09985429	-3.89529719
32	H	2.52121487	-1.21676298	-4.53804478
33	N	2.55761362	-1.68235597	-2.48194438
34	H	0.97104472	-0.23354370	-2.64701014
35	C	3.57043226	-3.07590037	-4.28511485
36	H	3.45264751	-4.02287991	-3.74212776
37	C	3.53850204	-3.39203304	-5.78826969
38	H	3.64634238	-2.48036986	-6.38603030
39	H	4.35546364	-4.07006589	-6.05849239
40	H	2.60424856	-3.87948120	-6.08157091
41	C	4.95409486	-2.50491272	-3.94170803
42	H	5.08085778	-2.37874952	-2.86192998
43	H	5.74763090	-3.17973252	-4.28101007

44	H	5.11062663	-1.53224745	-4.42056643
45	C	1.29376082	1.26587584	5.70727184
46	H	1.36391001	2.27135045	5.27251748
47	C	1.06579354	1.43131340	7.22136996
48	H	1.89420828	1.98389934	7.67860852
49	H	0.15077449	1.98402073	7.44718391
50	H	0.99912206	0.45672992	7.71761765
51	C	2.65215522	0.57878316	5.52670966
52	H	3.43790713	1.13125131	6.05444852
53	H	2.63746140	-0.44007423	5.92794738
54	H	2.95283063	0.53598788	4.47684679
55	O	-1.29572629	2.49081556	5.54293196
56	O	0.85004051	-3.96645573	-4.10570151
57	H	-1.97532079	-0.05366357	3.85701658
58	H	0.25819266	-0.90224816	-4.69867958
59	H	-3.74716753	2.07818947	4.95759853
60	H	-1.33486480	-3.03639080	-5.43671428
61	C	-2.03118289	-2.86065402	-3.39786721
62	H	-1.46614002	-3.72316639	-3.02677375
63	C	-3.42315732	2.16368146	2.82723205
64	H	-2.62938791	2.91734582	2.90395377
65	H	-3.02259192	-3.23365729	-3.68266493
66	H	-4.36219048	2.71068918	2.68027150
67	C	-2.19036007	-1.83268251	-2.27306710
68	H	-1.22270431	-1.37500431	-2.04177082
69	H	-2.85821669	-1.03370552	-2.61209827
70	C	-3.14427485	1.30149554	1.58850236
71	H	-2.20569361	0.75776993	1.72255019
72	H	-2.99399599	1.97258866	0.73506464
73	C	-2.74428319	-2.48615784	-1.00485378
74	H	-2.06802260	-3.29570208	-0.70225259
75	H	-3.71631323	-2.94873003	-1.21383081
76	C	-4.27547065	0.32660032	1.25522012
77	H	-4.45410514	-0.35695312	2.09217848
78	H	-5.20132090	0.89577395	1.10688493
79	C	-2.87241959	-1.51253757	0.17061804
80	H	-3.06301205	-2.09896681	1.07797996
81	H	-1.91704761	-0.99797527	0.32060003
82	C	-4.00535738	-0.49722095	-0.01001076
83	H	-3.78608104	0.17584525	-0.84548049
84	H	-4.92658490	-1.03390062	-0.26827940
85	Cl	0.57053779	1.23836890	-5.58374653
86	O	-2.70160316	2.83210329	-1.89467020
87	C	-1.82953126	1.87732267	-2.50833221
88	H	-1.26761249	1.21172691	-1.86577888
89	H	-2.12820125	1.44082409	-3.45376884
90	C	-1.49622151	3.34716364	-2.49537680
91	H	-1.61289742	3.86977001	-3.44113675
92	C	-0.40018465	3.84734587	-1.59079814
93	C	1.68973916	4.77321628	0.07240681
94	C	-0.65549483	4.32487276	-0.29397936
95	C	0.93457797	3.85305506	-2.02978682
96	C	1.97003691	4.31095520	-1.21065680
97	C	0.37571017	4.77991926	0.53264570
98	H	-1.67851012	4.33290874	0.07680639
99	H	1.16858813	3.48157894	-3.02902370
100	H	2.99189342	4.29508052	-1.58016433
101	H	0.14817194	5.13722693	1.53305434
102	H	2.49456186	5.12485027	0.71119674