Supporting Information for:

Reactivity of 1,3-dichloro-1,3-*bis*(dimethylamino)propenium salts with primary amines

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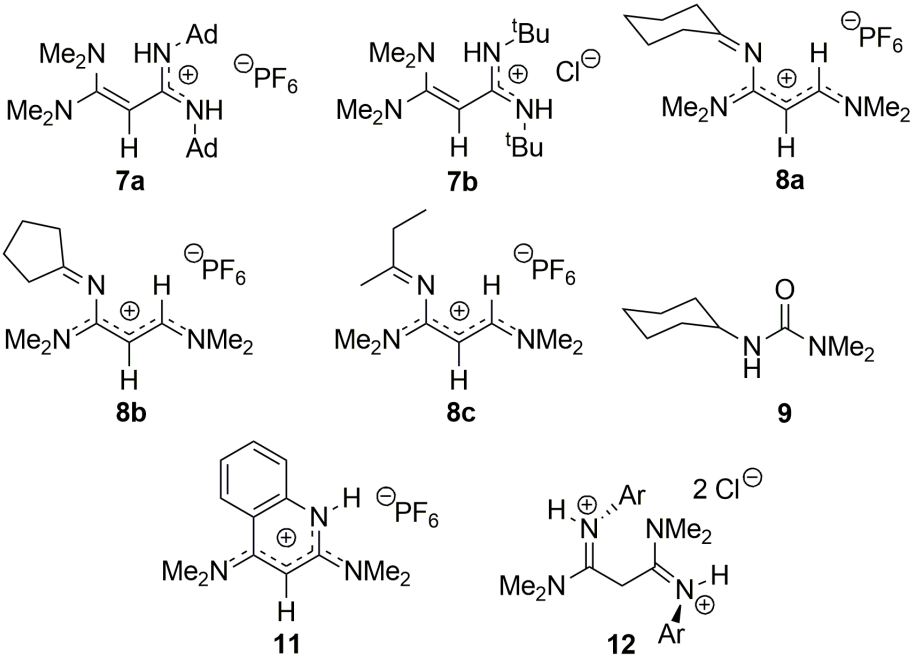
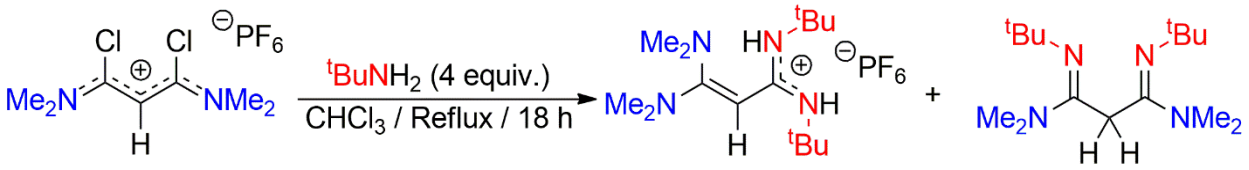
Summary of Compounds



Additional Experimental Details

Analysis of the crude mixture from the synthesis of 1,1-*bis*(dimethylamino)-3,3-*bis*(*tert*-butylamino)propenium chloride, 7b



tert-Butylamine (0.62 mL, 5.90 mmol) was added to a solution of **1'** (0.50 g, 1.46 mmol) in 30 mL of chloroform and the mixture was heated at reflux for 18 hours, under nitrogen. After cooling to room temperature, the volatiles were removed *in vacuo* resulting in a beige/yellow oily mixture. The crude residue was analysed immediately after removal of the volatiles *in vacuo*, and an aqueous workup was not performed. An excess of *tert*-butylamine was used instead of *N*,*N*-diisopropylethylamine as an auxiliary base to simplify the ^{1}H NMR spectrum of the crude mixture. ^{1}H NMR analysis of the mixture revealed primarily **7b** (Figure S7). It should be noted that the N*H* signal has a different chemical shift than that in an authentic sample of **7b** and this has been attributed to the different counter ion (PF_6^- instead of Cl^-); a similar phenomenon was also observed with the adamantyl analogue **7a**. Additionally, signals that have been tentatively assigned to be the malonamidine (**4a**, R = ^{t}Bu) were also observed, in *ca.* 28% yield with respect to **7b**.

NMR and IR Spectroscopy of Compounds

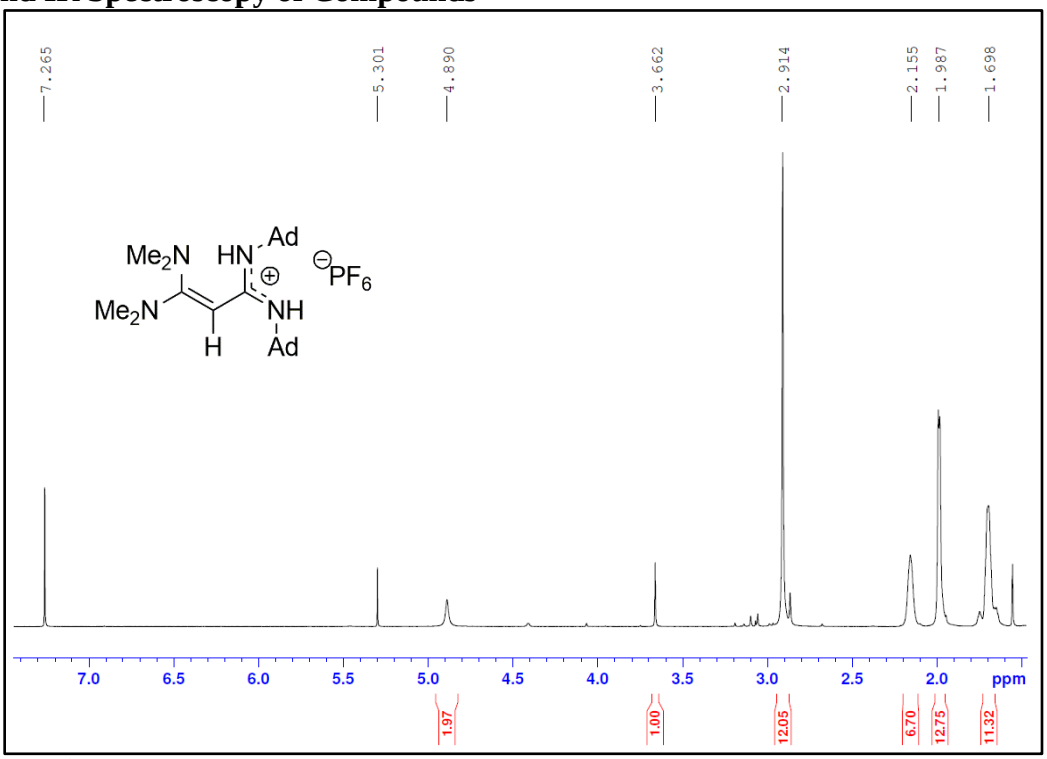


Figure S1: ^{1}H NMR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(adamantylamino)propenium hexafluorophosphate **7a** in $CDCl_3$. Some CH_2Cl_2 is present at 5.301 ppm.

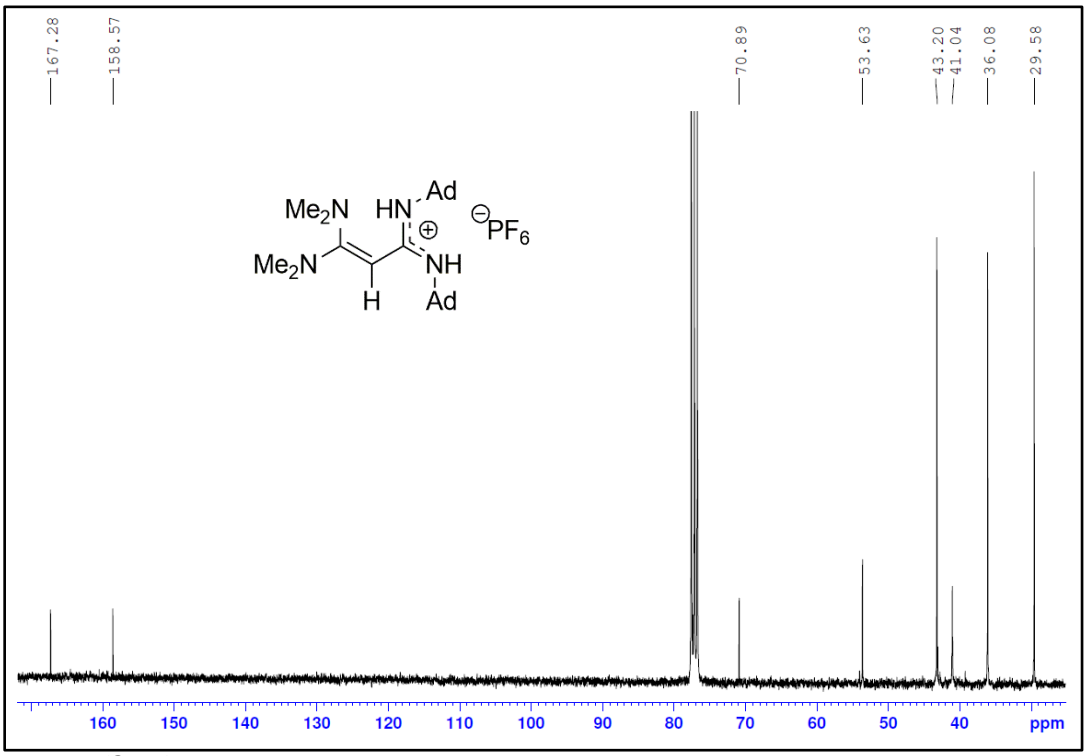


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(adamantylamino)-propenium hexafluorophosphate **7a** in $CDCl_3$.

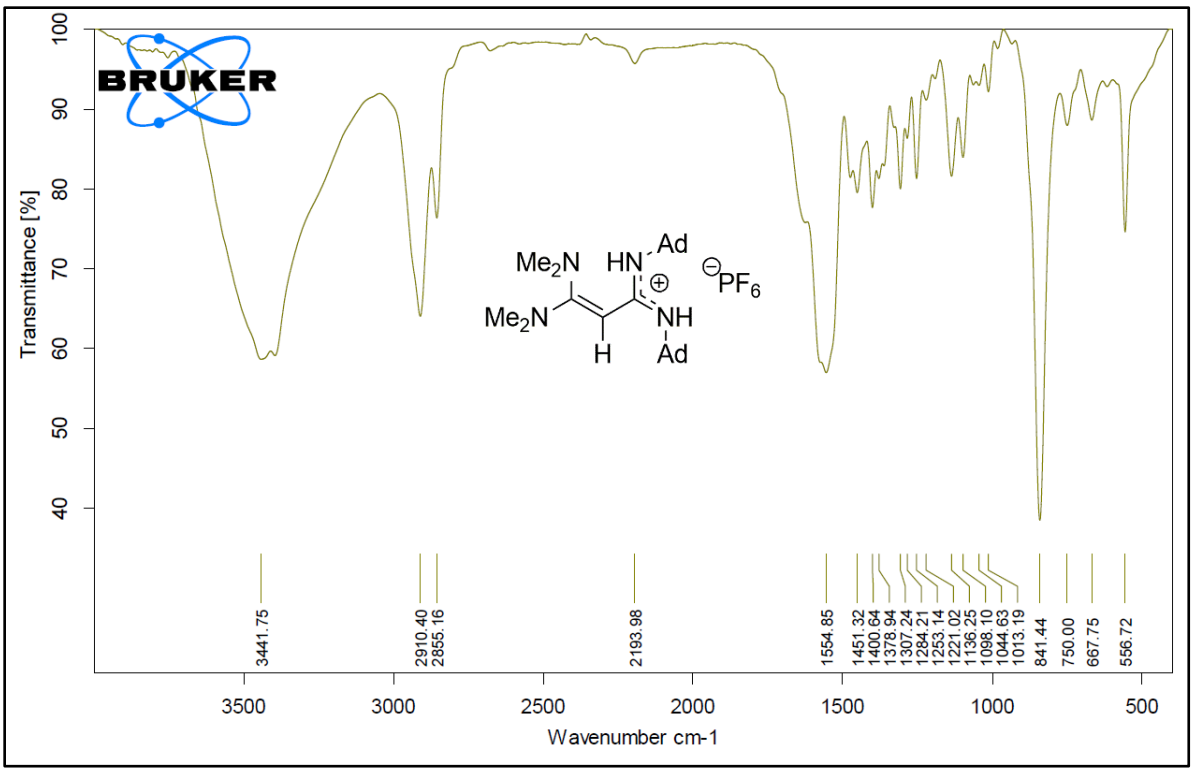


Figure S3: IR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(adamantylamino)-propenium hexafluorophosphate **7a**, obtained as a KBr pellet.

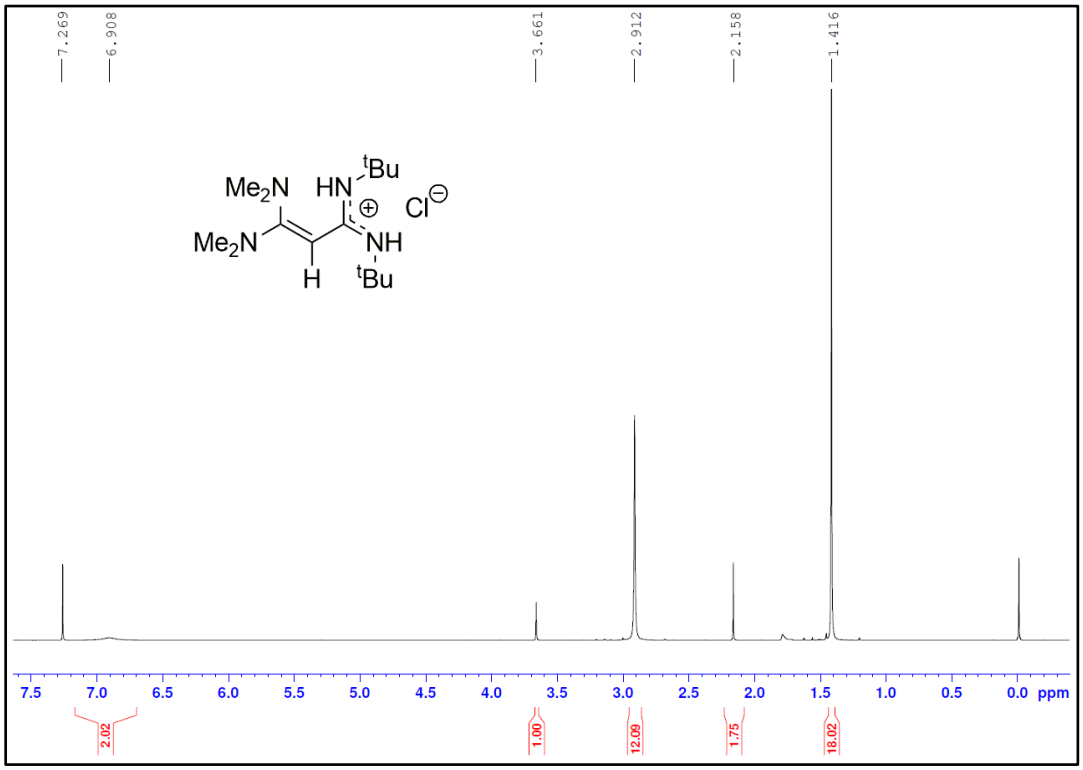


Figure S4: ^{1}H NMR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(*tert*-butylamino)propenium chloride **7b** in $CDCl_3$. Some acetone is present at 2.158 ppm.

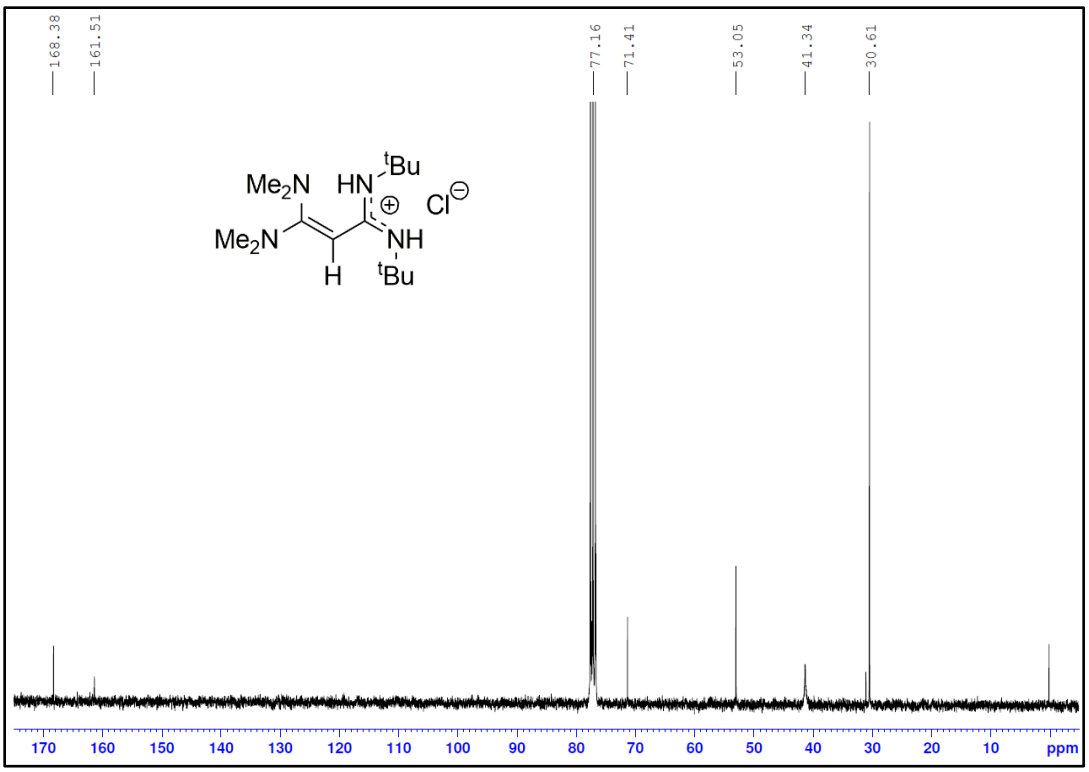


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(*tert*-butylamino)-propenium chloride **7b** in $CDCl_3$.

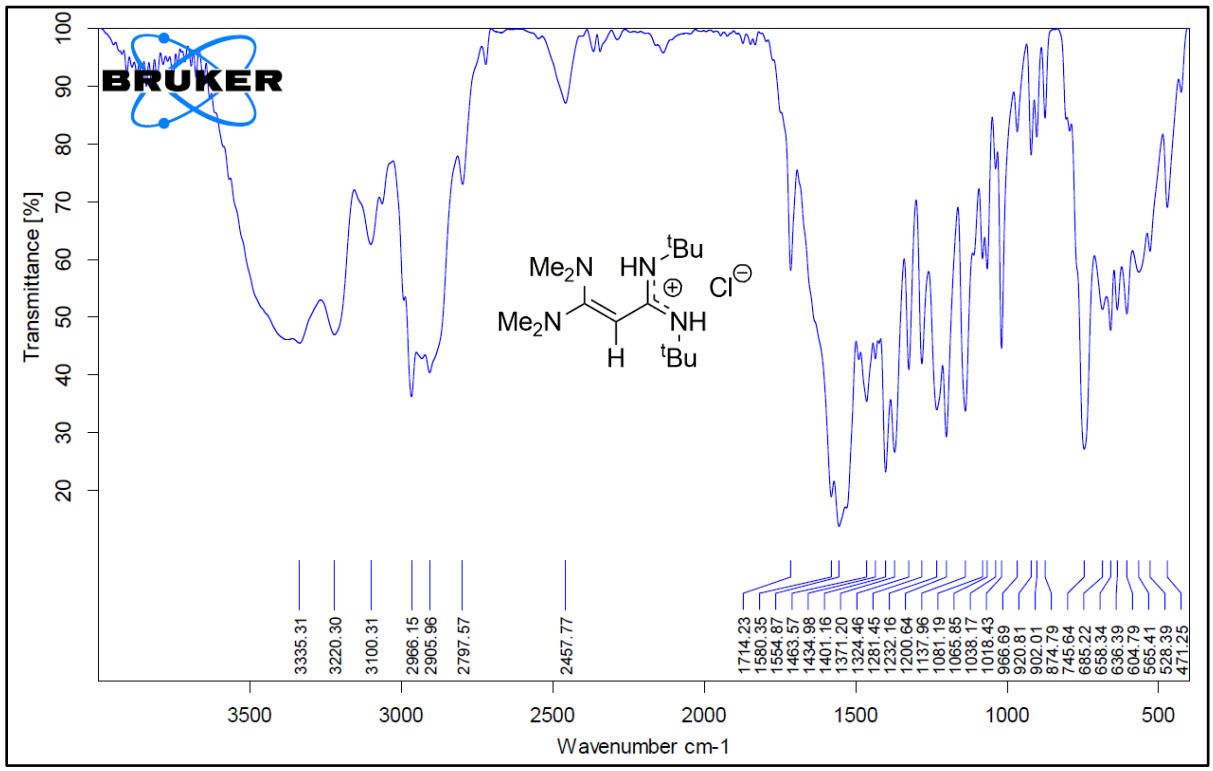


Figure S6: IR spectrum of 1,1-*bis*(dimethylamino)-3,3-*bis*(*tert*-butylamino)-propenium chloride **7b**, obtained as a KBr pellet.

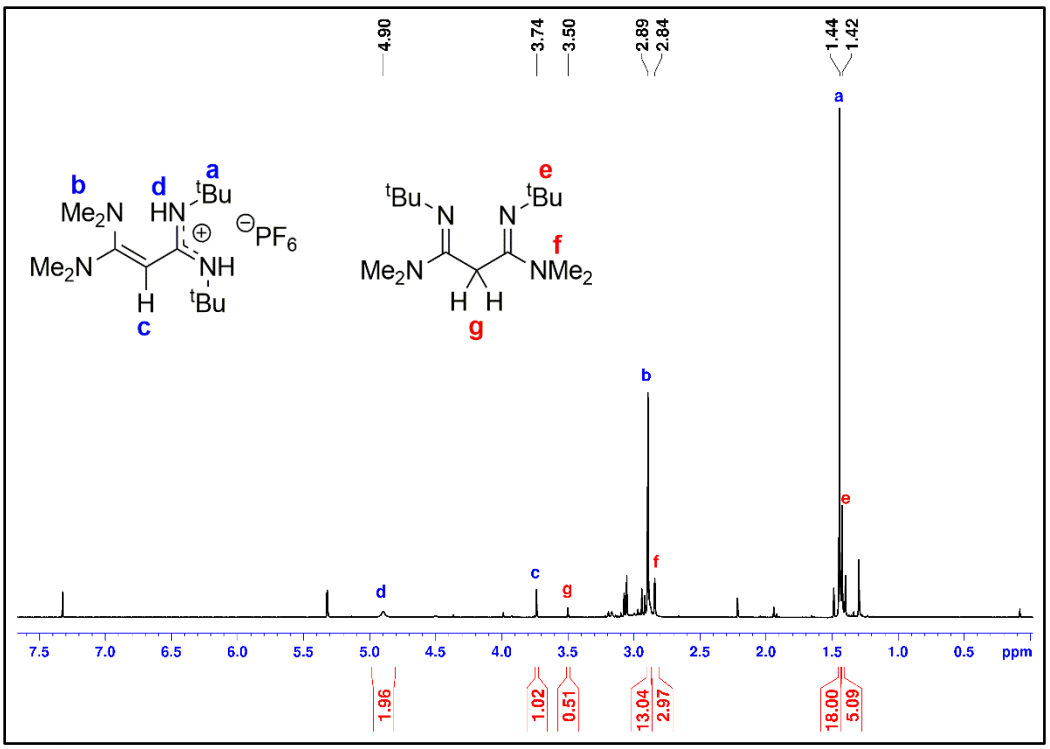


Figure S7: ^{1}H NMR spectrum of the crude mixture obtained from the synthesis of **7b**, in $CDCl_3$, prior to aqueous workup. All assignments are tentative. Assignment 'd' has a different chemical shift compared to that in Figure S4 due to a different counter ion being present.

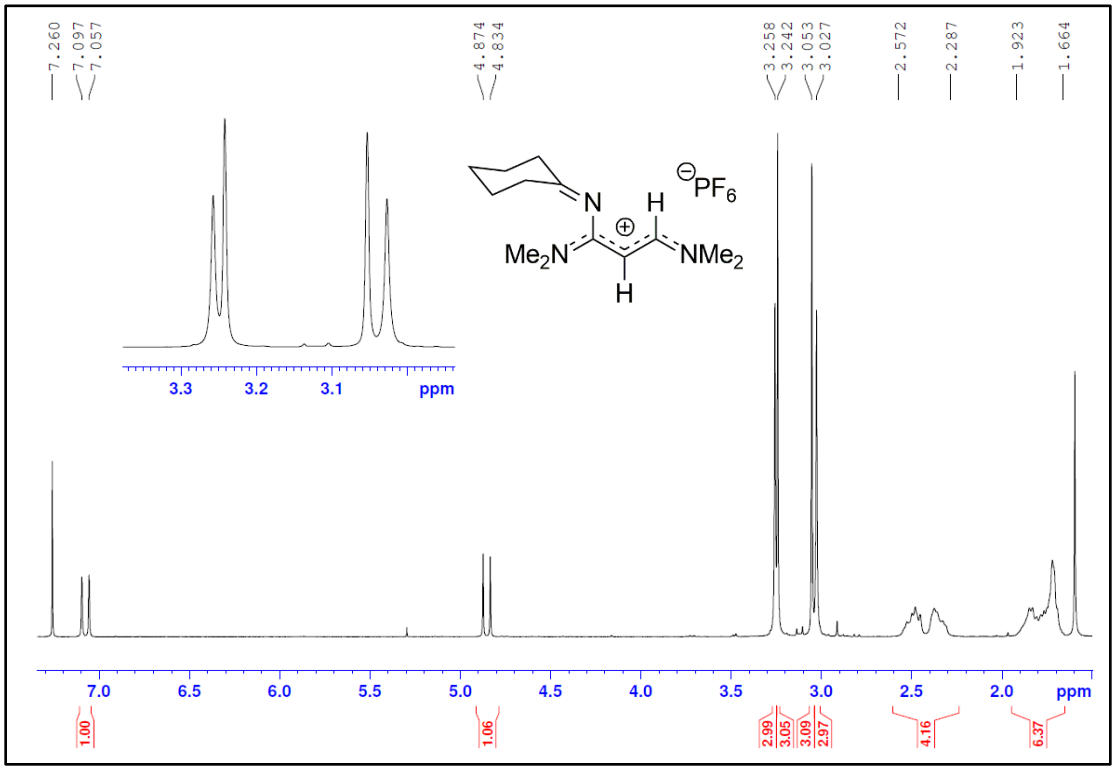


Figure S8: ^{1}H NMR spectrum of 1-(cyclohexylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8a**, in $CDCl_3$.

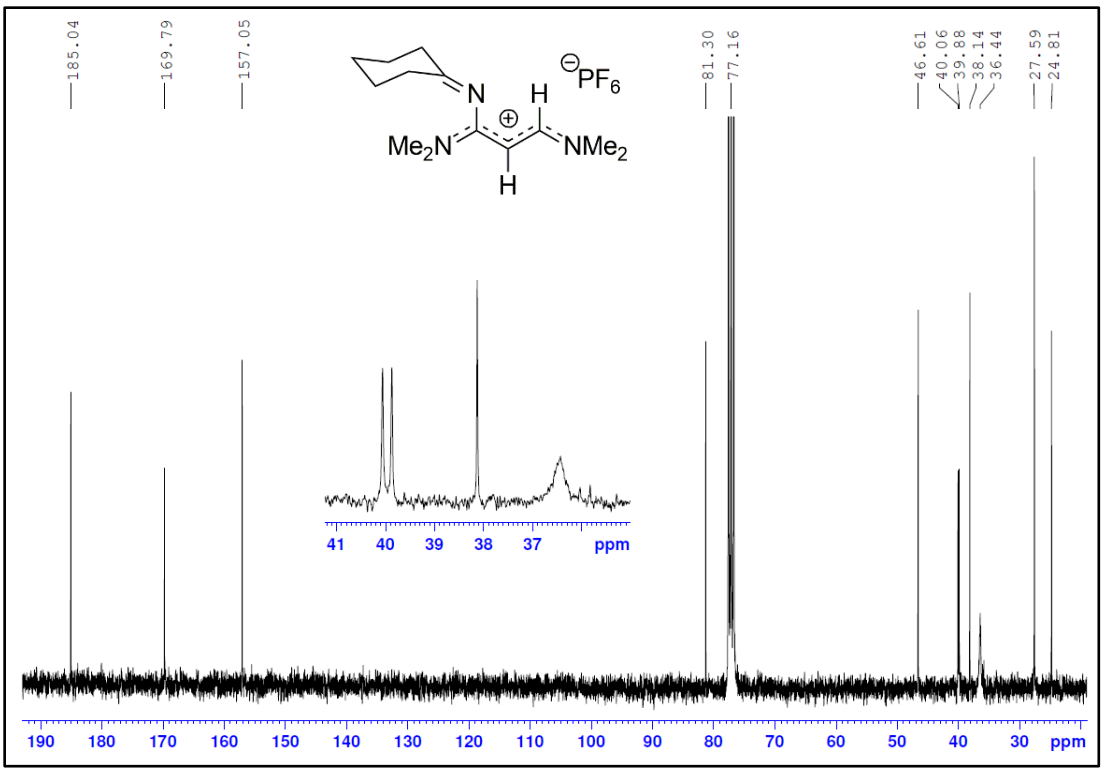


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of 1-(cyclohexylidene)amino-1,3-*bis*(dimethylamino)-propenium hexafluorophosphate **8a**, in $CDCl_3$.

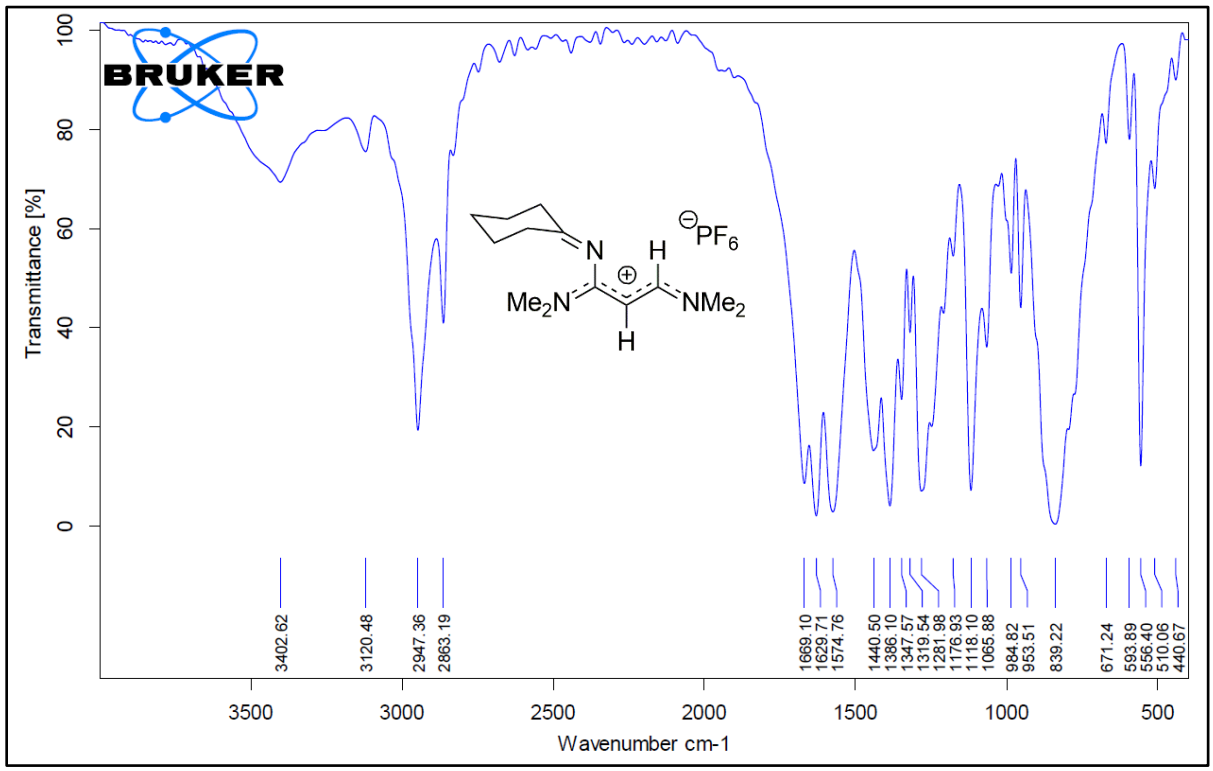


Figure S10: IR spectrum of 1-(cyclohexylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8a**, obtained as a KBr pellet.

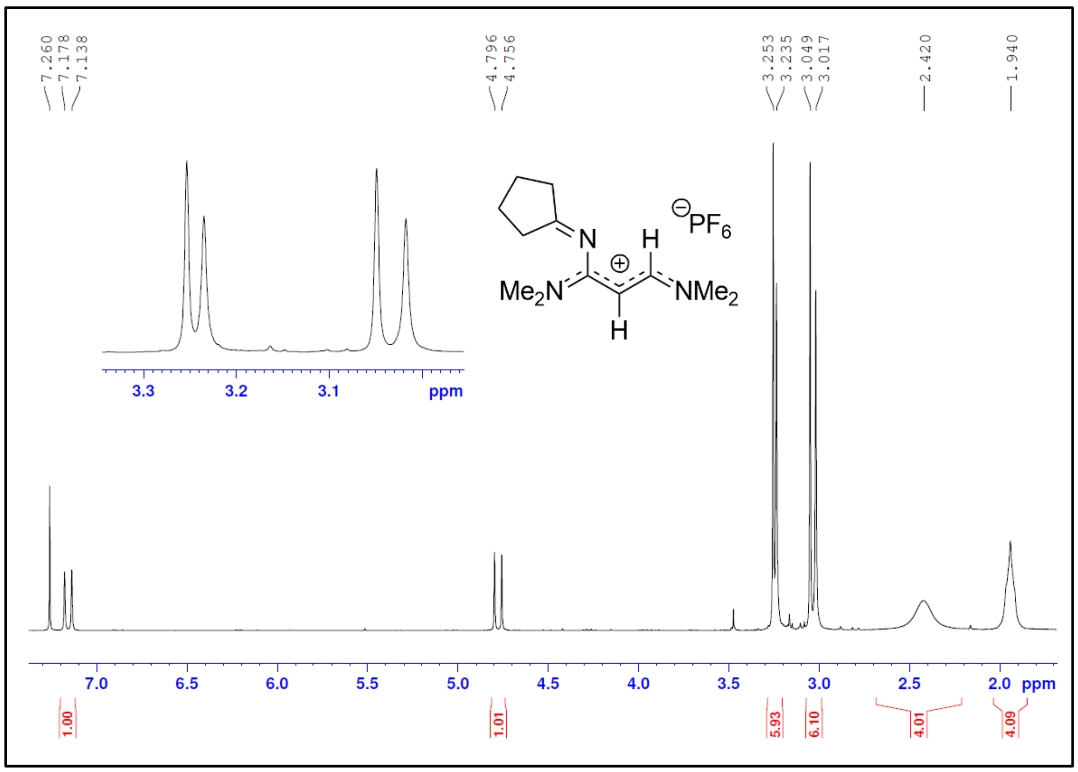


Figure S11: ^{1}H NMR spectrum of 1-(cyclopentylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8b**, in $CDCl_3$.

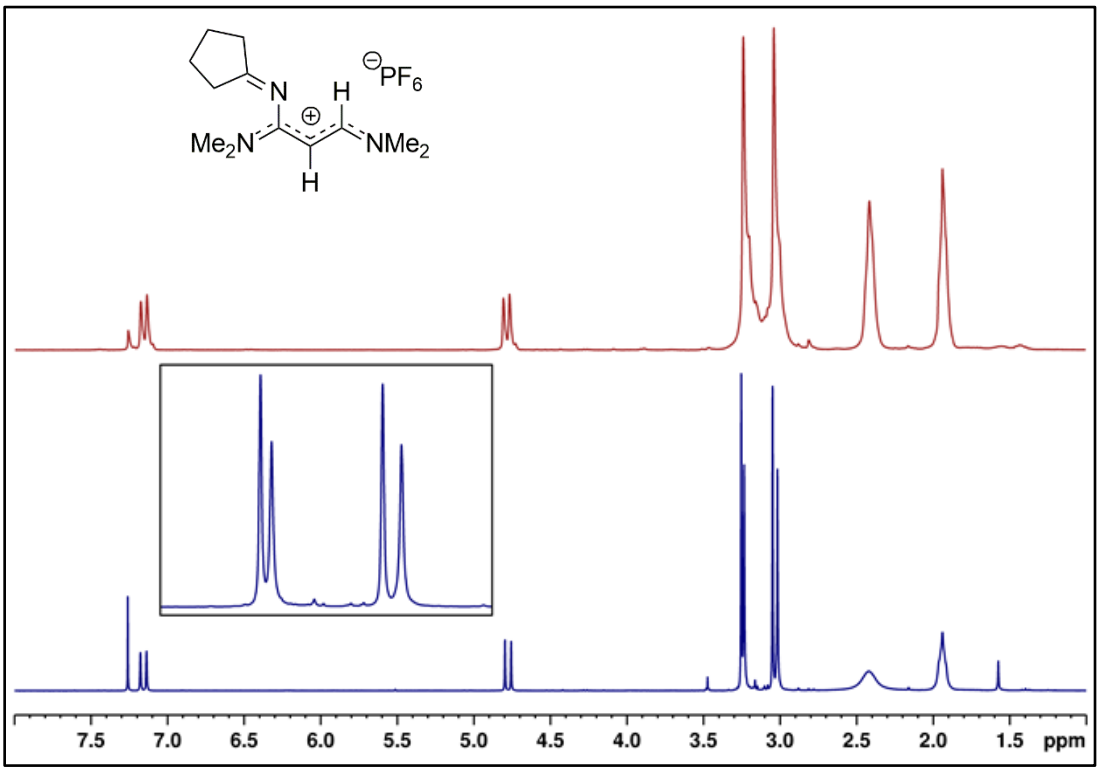


Figure S12: ^{1}H NMR spectra of **8b** in $CDCl_3$ at room temperature (blue, bottom) and at 60 ºC red, top). The region between 2.87 and 3.42 ppm of the room temperature spectrum is explicitly shown.

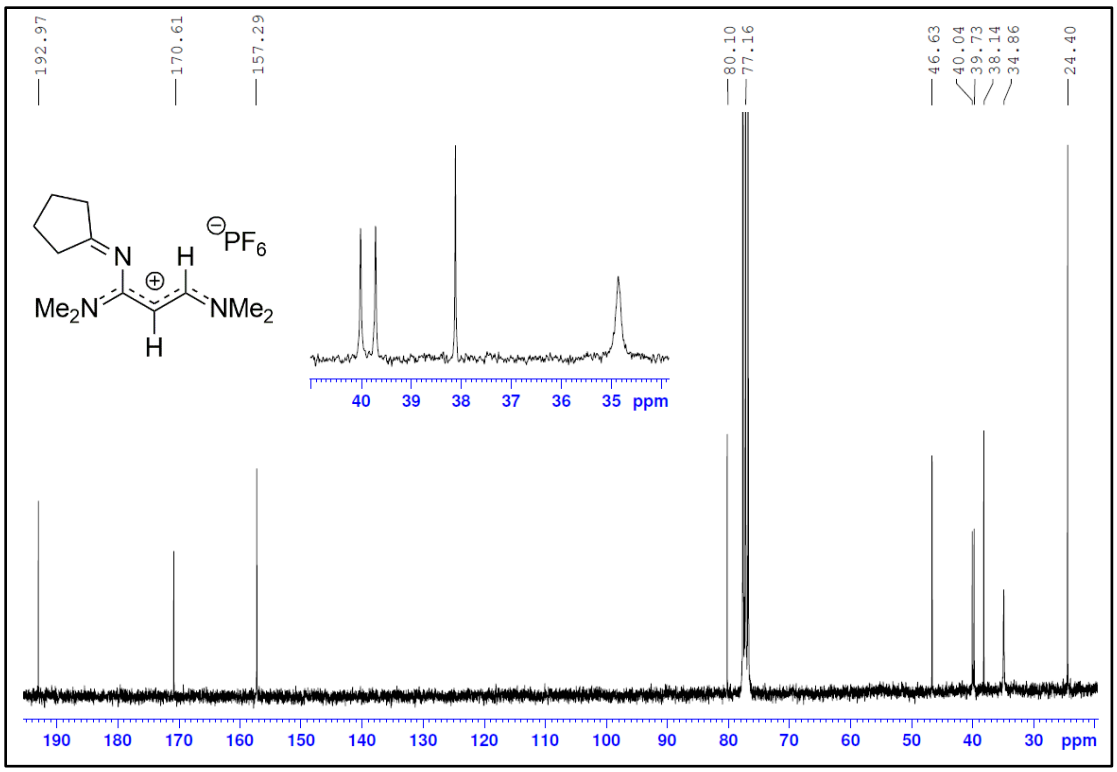


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of 1-(cyclopentylidene)amino-1,3-*bis*(dimethylamino)-propenium hexafluorophosphate **8b**, in $CDCl_3$.

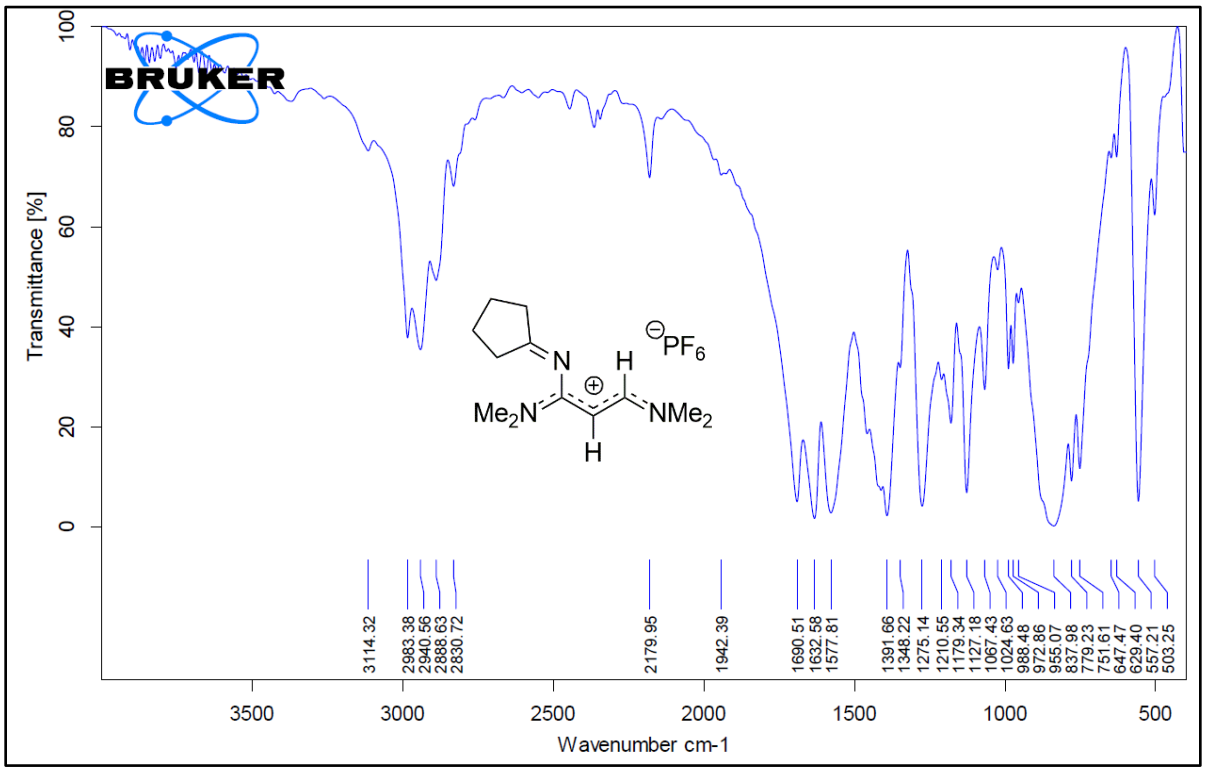


Figure S14: IR spectrum of 1-(cyclopentylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8b**, obtained as a KBr pellet.

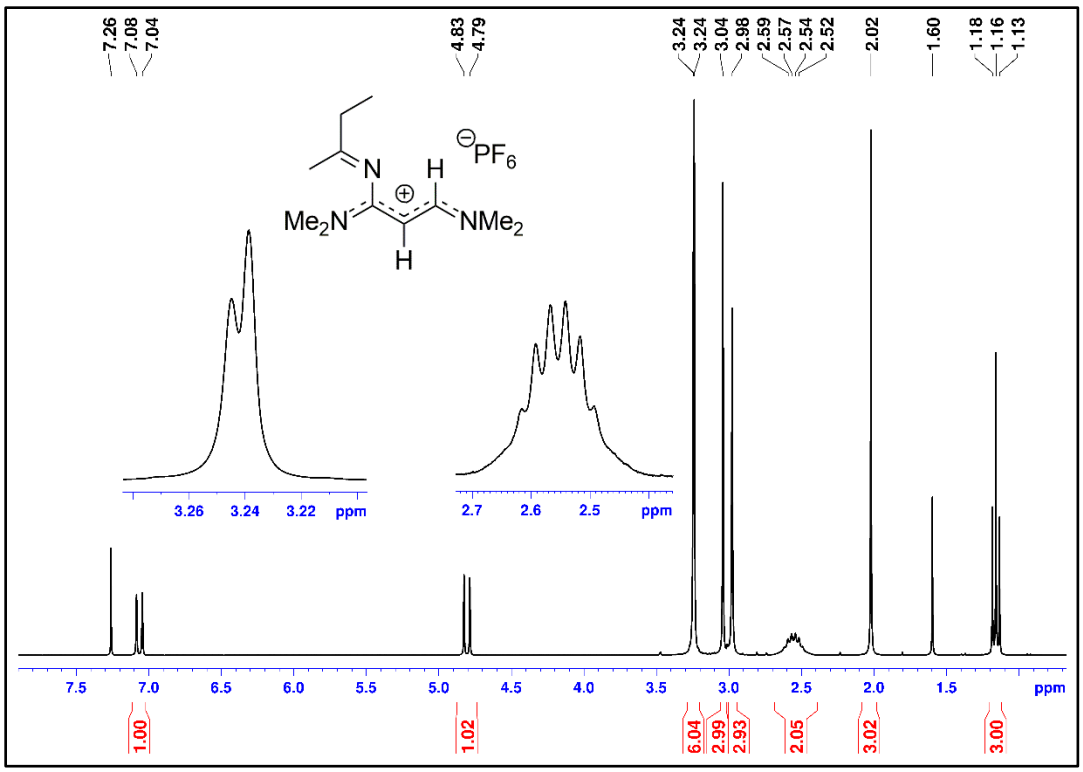


Figure S15: ^{1}H NMR spectrum of 1-(butan-2-ylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8b**, in $CDCl_3$. Some water is present at 1.60 ppm.

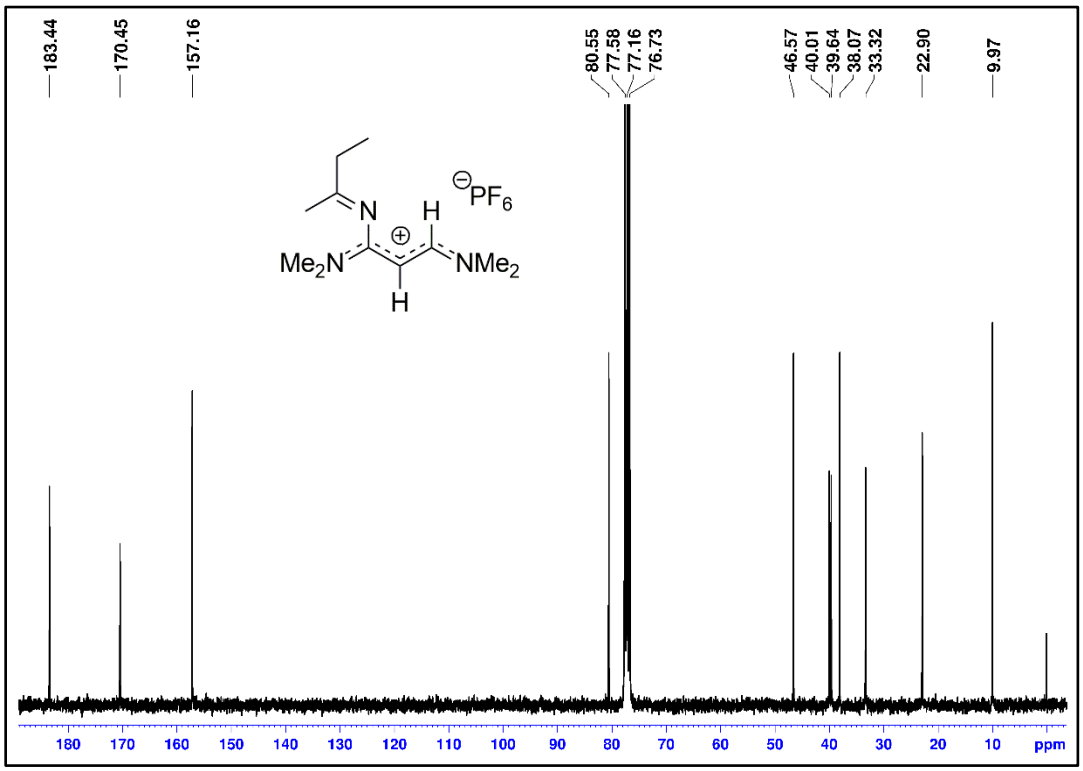


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of 1-(butan-2-ylidene)amino-1,3-*bis*(dimethylamino)-propenium hexafluorophosphate **8b**, in $CDCl_3$.

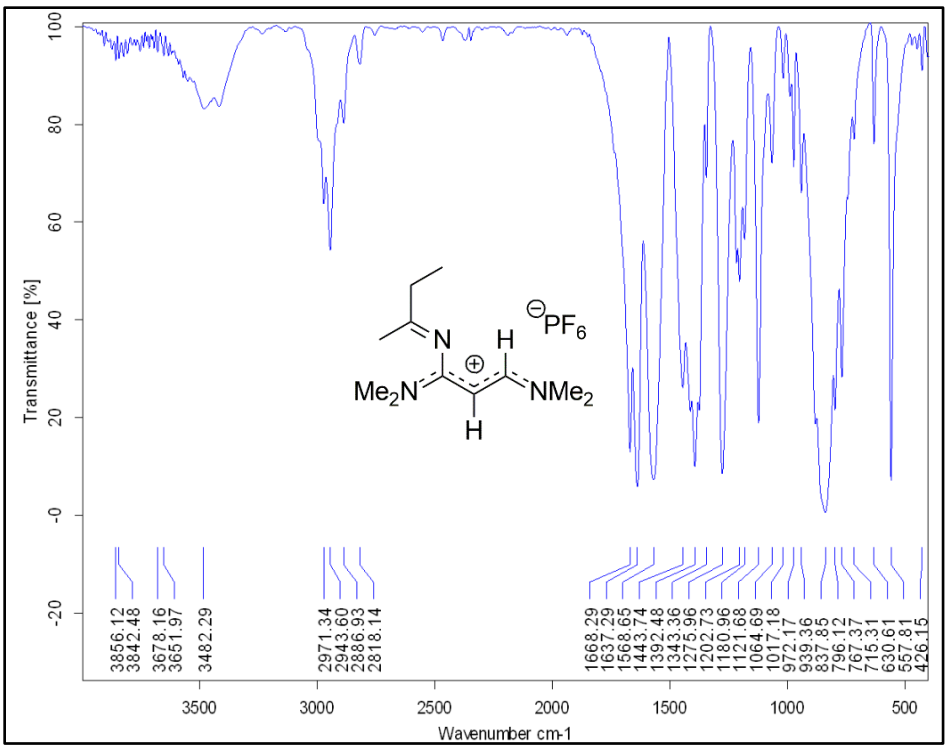


Figure S17: IR spectrum of 1-(butan-2-ylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8c**, obtained as a KBr pellet.

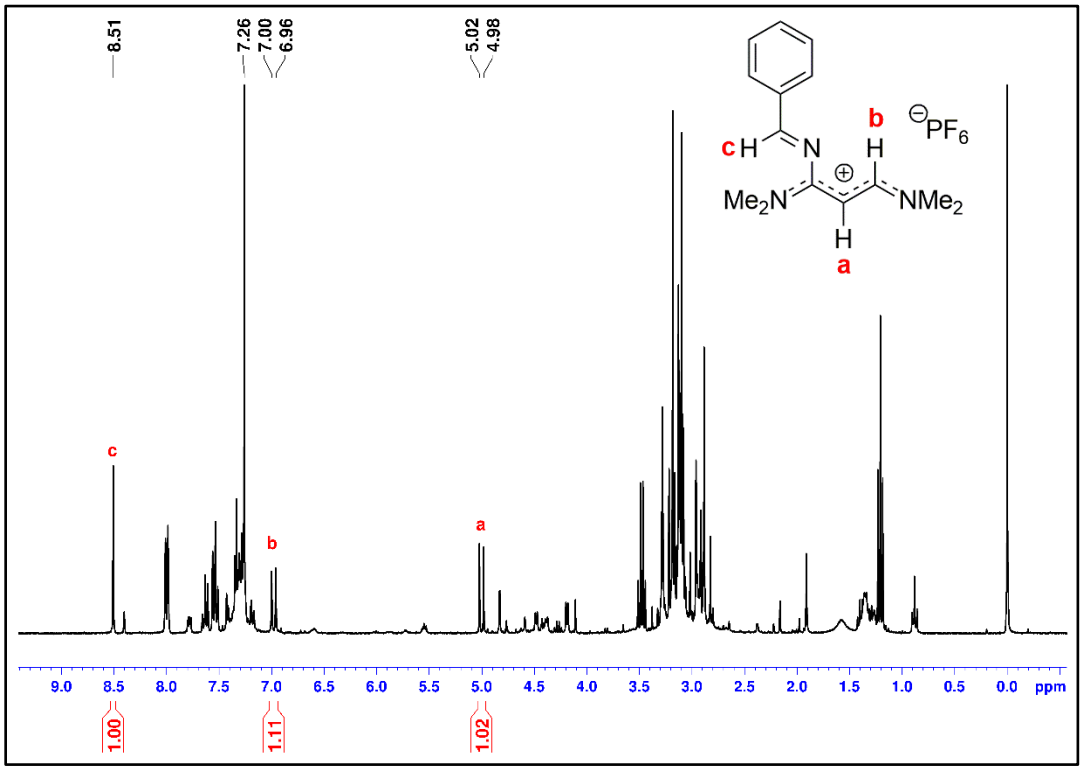


Figure S18: ^{1}H NMR spectrum of the crude mixture obtained from the attempted synthesis of (benzylidene)amino-1,3-*bis*(dimethylamino)propenium hexafluorophosphate **8d**, in $CDCl_3$. Only diagnostic signals are labeled.

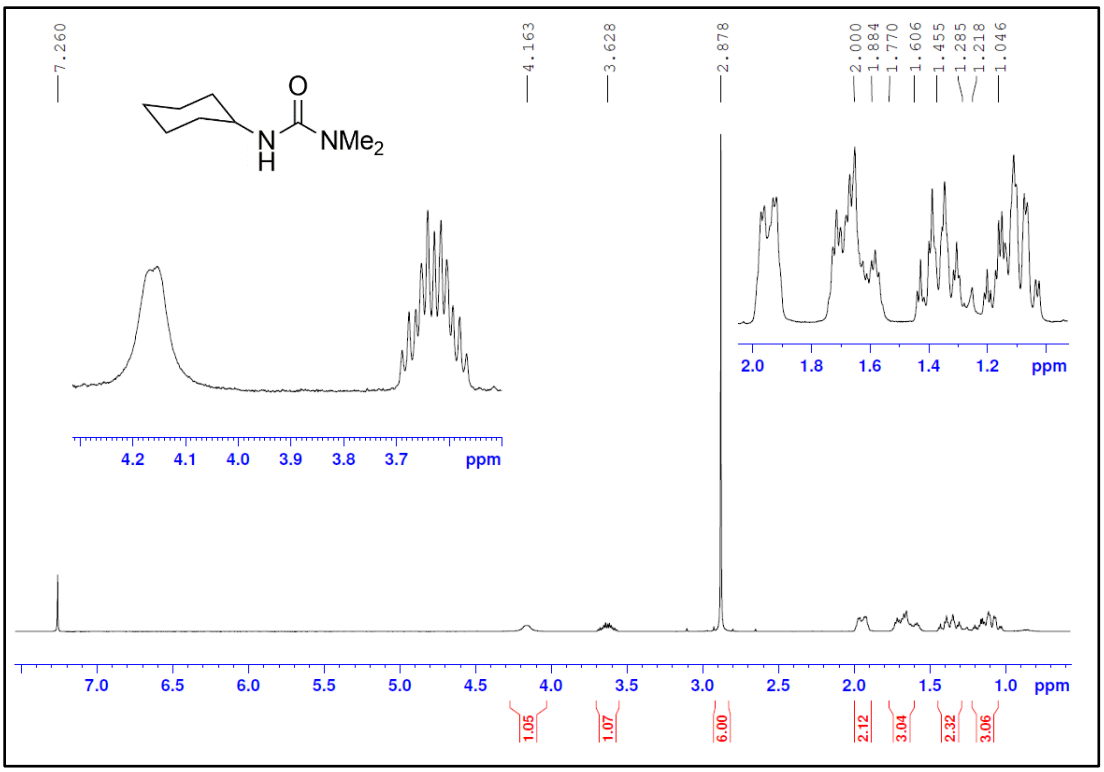


Figure S19: ^{1}H NMR spectrum of 3-cyclohexyl-1,1-dimethylurea **9**, in $CDCl_3$.

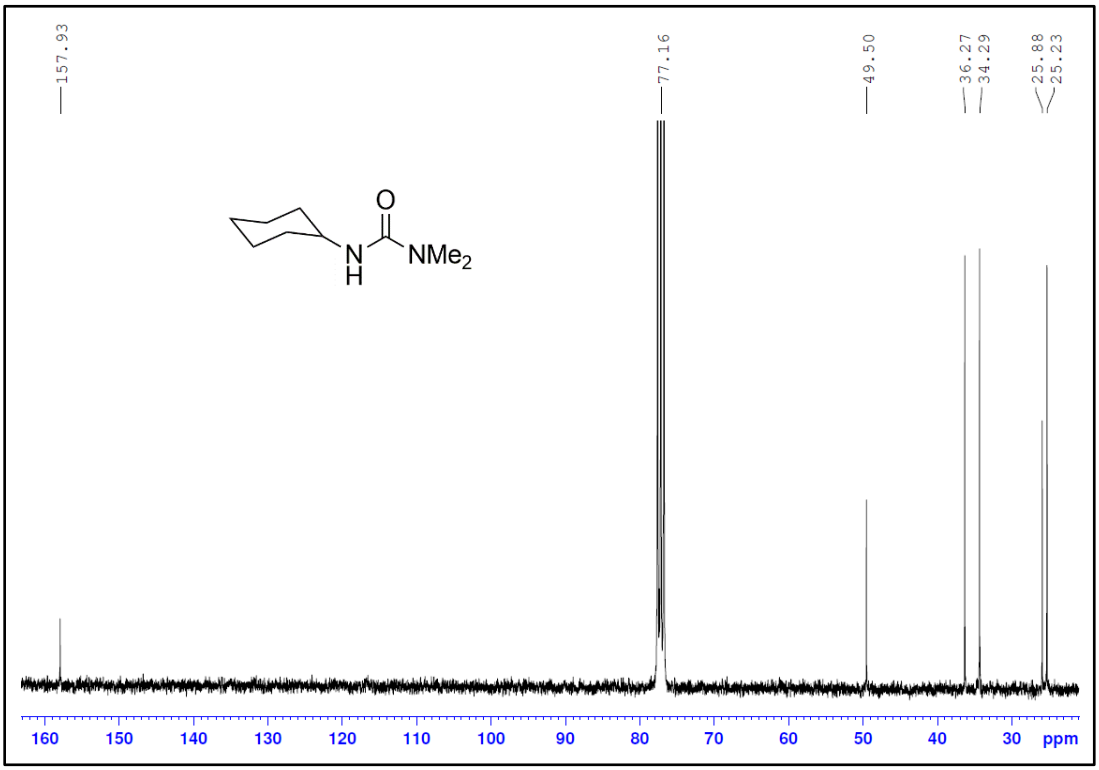


Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum of 3-cyclohexyl-1,1-dimethylurea **9**, in $CDCl_3$.

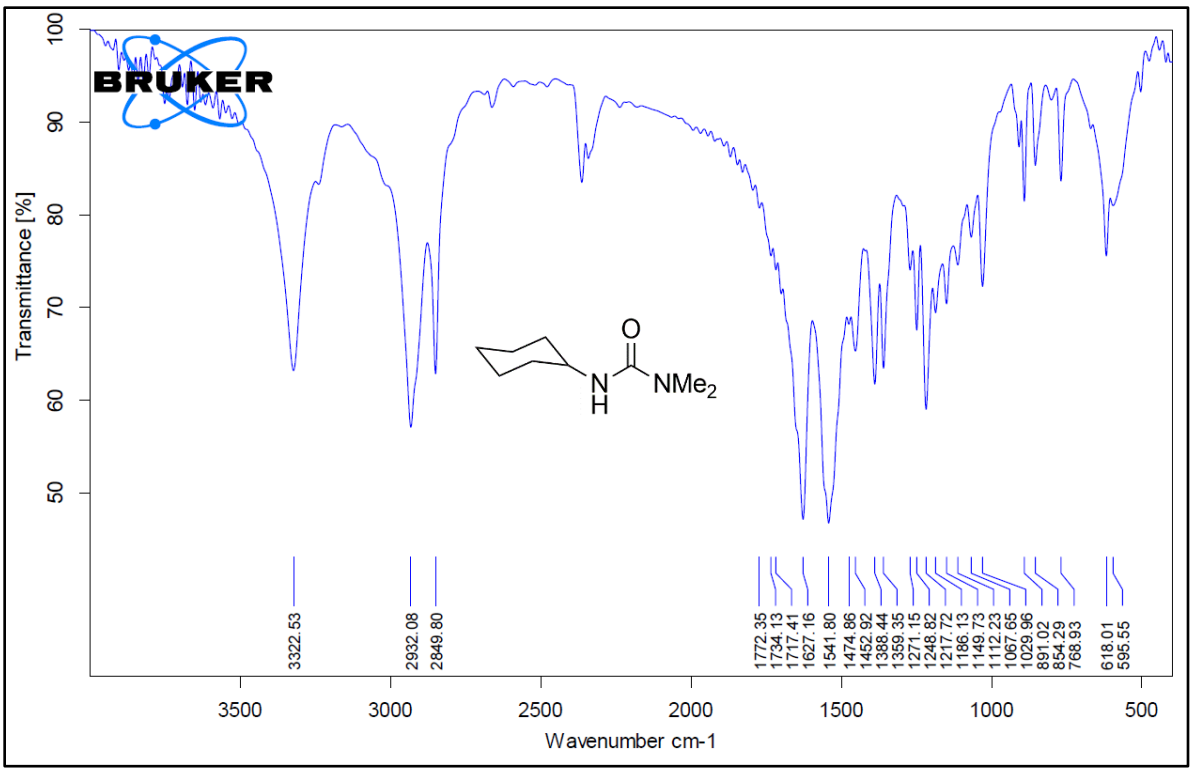


Figure S21: IR spectrum of 3-cyclohexyl-1,1-dimethylurea **9**, obtained as a KBr pellet.

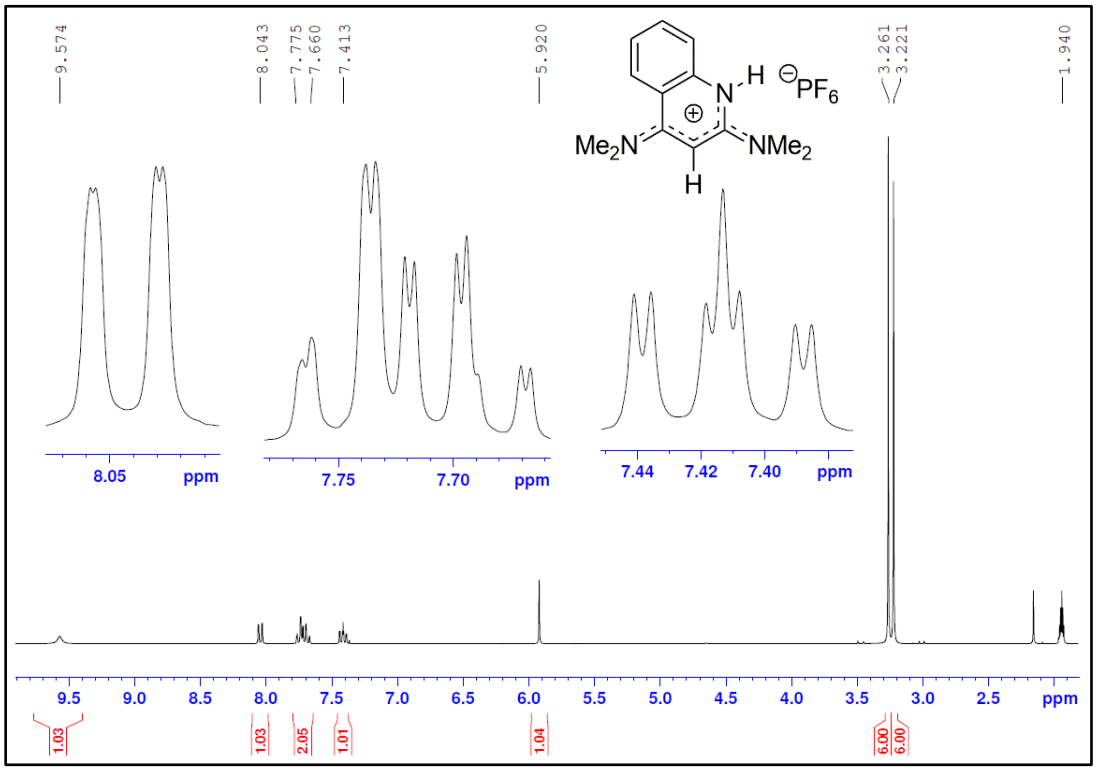


Figure S22: ^{1}H NMR spectrum of 2,4-*bis*(dimethylamino)quinolinium hexafluorophosphate **11**, in CD_3CN.

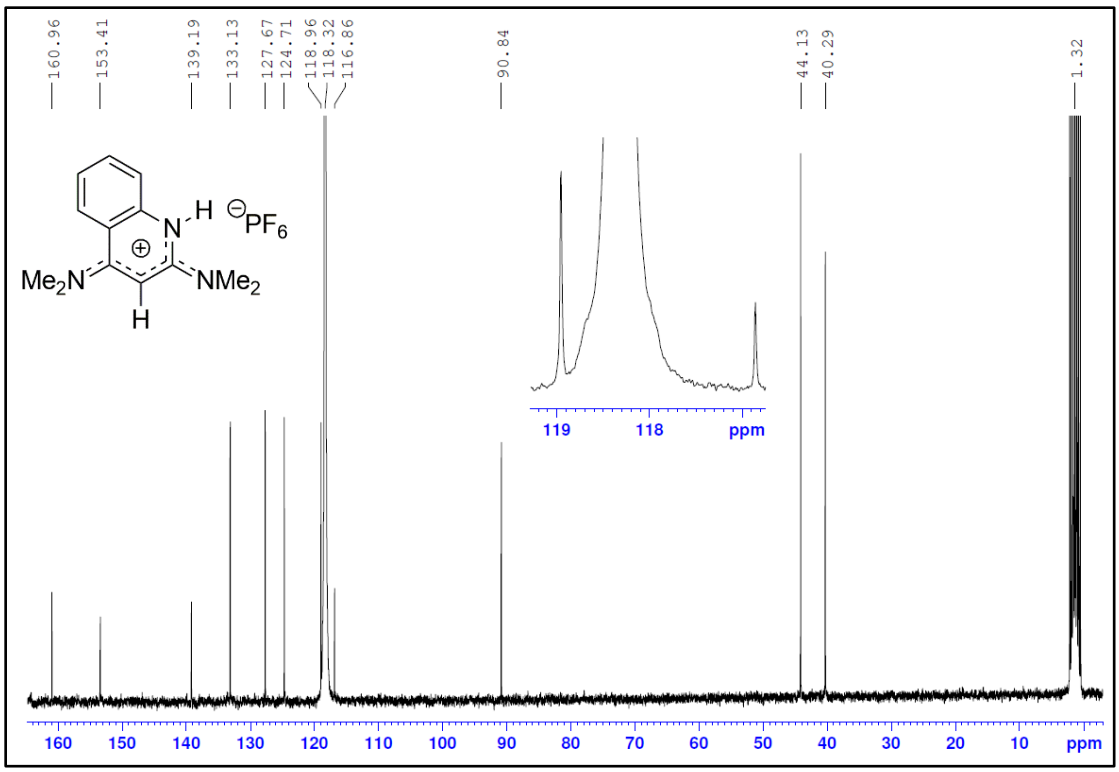


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of 2,4-*bis*(dimethylamino)quinolinium hexafluorophosphate **11**, in CD_3CN.

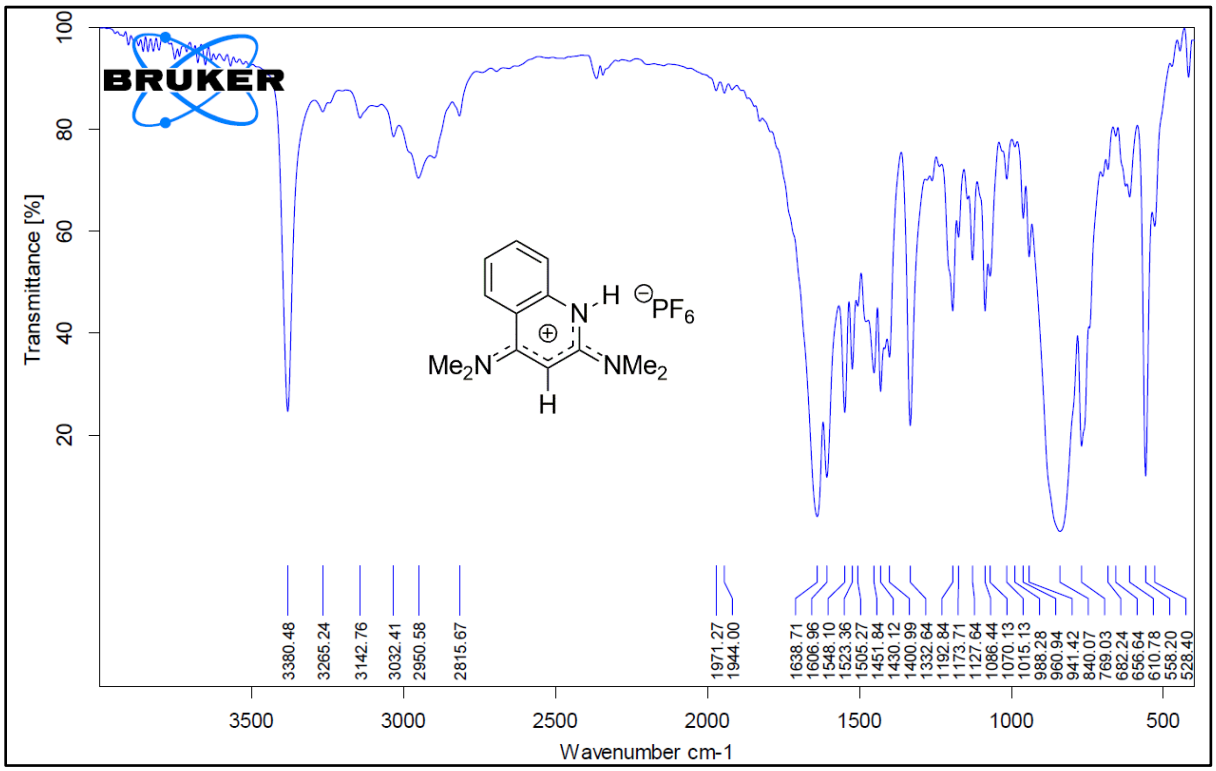


Figure S24: IR spectrum of 2,4-*bis*(dimethylamino)quinolinium hexafluorophosphate **11**, obtained as a KBr pellet.

Additional Crystallographics Details, Images, and Discussions

X-ray General

The crystal chosen was attached to the tip of a 400 μm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K unless otherwise specified [1]. The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 1-10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 10-120 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT [2] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS or TWINABS [3]). The structures were solved using SHELXT-2014 [4] and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018 [4]. The refinements were generally unremarkable. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens. Hydrogen atoms bound to oxygen, nitrogen or part of HCl_2 anions was located in the next to final difference Fourier maps. They were included in the final cycle of refinement and their positions allowed to refine isotropically. If necessary, U_{iso} H was fixed at 1.5 U_{eq} of the atom to which it was bonded and/or the H-X distance was restrained to a reasonable value.

The structures reported in this manuscript have been deposited. CCDC 2062043 (**7a**), 2062050 (**7b**), 2062048 (**8a**), 2062046 (**8b**), 2062047 (**8c**), 2062044 (**9**), 2062049 (**11**) and 2062045 (**12**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data and structural refinement details.

Identification code	**7a**	**7b**	**8a**	**8b**
CCDC deposit number	2062043	2062050	2062048	2062046
Empirical formula	$C_{28}H_{47}Cl_2F_6N_4P$	$C_{16}H_{35}Cl_3N_4$	$C_{13}H_{24}F_6N_3P$	$C_{12}H_{22}F_6N_3P$
Formula weight	655.56	389.83	367.32	353.29
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions	a = 11.1649(14)	a = 9.5341(8)	a = 10.4385(9)	a = 8.0339(11)
(Å and °)	b = 11.6494(14)	b = 20.2391(17)	b = 11.3473(9)	b = 13.7156(19)
	c = 13.3995(16)	c = 11.4827(10)	c = 14.6522(12)	c = 15.213(2)
	α = 95.442(2)	α = 90	α = 90	α = 90
	β = 100.844(2)	β = 100.2170(10)	β = 90	β = 102.7100(10)
	γ = 111.648(1)	γ = 90	γ = 90	γ = 90
Volume (Å^3)	1565.0(3)	2180.6(3)	1735.5(2)	1635.3(4)
Z	2	4	4	4
Density (calc., Mg/m^3)	1.391	1.187	1.406	1.435
Absorption coeff. (mm^{-1})	0.320	0.425	0.217	0.227
F(000)	692	840	768	736
Crystal size (mm^3)	0.350x0.225x0.150	0.500x0.400x0.350	0.300x0.275x0.150	0.500x0.200x0.200
Theta range (°)	1.912 to 26.020	2.012 to 28.842	2.270 to 29.014	2.022 to 28.955
Index ranges (*h*,*k*,*l*)	-13/13, -14/14, -16/16	-12/12, -27/27, -15/15	-14/14, -14/15, -19/18	-10/10, -18/18, -19/20
Reflections collected	16587	26196	21271	19599
Independent refl. [R(int)]	6139 [0.0337]	5434 [0.0178]	4325 [0.0238]	4095 [0.0247]
Completeness to θ = 25.242°	99.7%	100.0%	100.0%	100.0%
Max./min. transmission	0.7456 / 0.6415	0.7458 / 0.7059	0.7458 / 0.7033	0.7458 / 0.7024
Data / restraints / parameters	6139 / 166 / 530	5434 / 116 / 309	4325 / 0 / 212	4095 / 857 / 415
Goodness-of-fit on F^2	1.021	1.028	1.034	1.040
Final R indices [I>2σ(I)]	R1 = 0.0472	R1 = 0.0288	R1 = 0.0276	R1 = 0.0410
	wR2 = 0.1113	wR2 = 0.0749	wR2 = 0.0665	wR2 = 0.1102
R indices (all data)	R1 = 0.0699	R1 = 0.0342	R1 = 0.0320	R1 = 0.0543
	wR2 = 0.1221	wR2 = 0.0789	wR2 = 0.0688	wR2 = 0.1195
Absolute structure par.	n.a.	n.a.	0.07(3)	n.a.
Extinction coefficient	n.a.	n.a.	n.a.	n.a.
Largest diff. peak/hole (e.Å^{-3})	0.277 / -0.340	0.328 / -0.162	0.201 / -0.251	0.371 / -0.372

Table S1. Crystal data and structural refinement details.

Identification code	**8c**	**9**	**11**	**12**
CCDC deposit number	2062047	2062044	2062049	2062045
Empirical formula	$C_{11}H_{22}F_6N_3P$	$C_9H_{18}N_2O$	$C_{13}H_{18}F_6N_3P$	$C_{22}H_{36}Cl_4N_4O_2$
Formula weight	341.28	170.25	361.27	530.35
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_12_12_1$
Unit cell dimensions	a = 11.7611(9)	a = 11.014(3)	a = 19.8863(12)	a = 7.6928(14)
(Å and °)	b = 10.3655(8)	b = 10.060(2)	b = 10.6006(6)	b = 17.170(3)
	c = 14.2459(11)	c = 10.165(2)	c = 14.2336(8)	c = 20.590(4)
	α = 90	α = 90	α = 90	α = 90
	β = 113.5370(10)	β = 117.450(3)	β = 92.0370(10)	β = 90
	γ = 90	γ = 90	γ = 90	γ = 90
Volume (Å^3)	1592.2(2)	999.4(4)	2998.6(3)	2719.7(8)
Z	4	4	8	4
Density (calc., Mg/m^3)	1.424	1.132	1.600	1.295
Absorption coefficient (mm^{-1})	0.231	0.075	0.250	0.460
F(000)	712	376	1488	1120
Crystal size (mm^3)	0.550x0.300x0.275	0.240x0.225x0.075	0.350x0.325x0.225	0.400x0.125x0.090
Theta range (°)	1.910 to 28.891	2.024 to 27.643	2.049 to 28.868	1.544 to 28.858
Index ranges (h,k,l)	-15/15, -13/13, -19/19	-14/14, -13/13, -13/13	-26/26, -13/14, -19/19	-10/10, -23/22, -26/27
Reflections collected	18685	11666	17775	32866
Independent refl. [R(int)]	3940 [0.0209]	2318 [0.0697]	3748 [0.0287]	6791 [0.0659]
Completeness to θ = 25.242°	99.9%	100.0%	100.0%	100.0%
Max. / min. transmission	0.7458 / 0.6966	0.7455 / 0.6248	0.7458 / 0.6915	0.7458 / 0.6522
Data / restraints / parameters	3940 / 0 / 196	2318 / 0 / 115	3748 / 99 / 279	6791 / 6 / 312
Goodness-of-fit on F^2	1.047	1.030	1.033	1.007
Final R indices [I>2σ(I)]	R1 = 0.0351	R1 = 0.0563	R1 = 0.0361	R1 = 0.0441
	wR2 = 0.1009	wR2 = 0.1249	wR2 = 0.0933	wR2 = 0.0811
R indices (all data)	R1 = 0.0427	R1 = 0.0946	R1 = 0.0457	R1 = 0.0728
	wR2 = 0.1069	wR2 = 0.1436	wR2 = 0.1008	wR2 = 0.0912
Absolute structure parameter	n.a.	n.a.	n.a.	-0.02(3)
Extinction coefficient	n.a.	n.a.	n.a.	n.a.
Largest diff. peak / hole (e.Å^{-3})	0.391 / -0.265	0.287 / -0.238	0.445 / -0.206	0.387 / -0.366

Table S2. Selected Bond Lengths and Angles [Å, °].

Group 1	**7a**	**7b**	Group 2	**12**	Group 3	**8a**	**8b**	**8c**	**11**
N(1)-C(1)	1.369(3)	1.3584(12)	N(1)-C(1)	1.312(4)	N(1)-C(1)	1.329(2)	1.3288(18)	1.3291(17)	1.3401(17)
N(2)-C(1)	1.358(3)	1.3569(12)	N(2)-C(3)	1.317(4)	N(1)-C(4)	1.467(2)	1.4630(19)	1.4707(18)	1.4647(17)
N(3)-C(3)	1.341(3)	1.3461(12)	N(3)-C(1)	1.324(4)	N(1)-C(5)	1.464(2)	1.4650(19)	1.4671(17)	1.4599(17)
N(3)-C(8)	1.485(3)	1.4813(11)	N(3)-C(8)	1.441(4)	N(2)-C(3)	1.322(2)	1.3178(18)	1.3144(16)	1.3554(17)
N(3)-H(3N)	0.888(16)	0.865(11)	N(3)-H(3N)	0.87(2)	N(2)-C(6)	1.459(2)	1.4604(18)	1.4597(16)	1.4616(19)
N(4)-C(3)	1.344(3)	1.3534(12)	N(4)-C(3)	1.321(4)	N(2)-C(7)	1.459(2)	1.4607(19)	1.4599(17)	1.4732(18)
N(4)-C(18) or C(12)	1.485(3)	1.4829(12)	N(4)-C(15)	1.434(4)	N(3)-C(8) (A)/(B)	1.275(2)	1.276(6) / 1.297(16)	1.2803(17)	1.3863(18)
N(4)-H(4N)	0.862(16)	0.877(11)	N(4)-H(4N)	0.87(2)	N(3)-C(1)	1.398(2)	1.3930(17)	1.3938(16)	1.3549(17)
C(1)-C(2)	1.393(3)	1.4017(13)	C(1)-C(2)	1.514(4)	C(1)-C(2)	1.411(2)	1.4108(19)	1.4096(18)	1.4066(19)
C(2)-C(3)	1.419(3)	1.4165(12)	C(2)-C(3)	1.517(4)	C(2)-C(3)	1.382(3)	1.3788(19)	1.3847(18)	1.3937(19)
					N(3)-H(3N)				0.824(19)
N(1)-C(1)-N(2)	116.2(2)	115.98(8)	N(1)-C(1)-N(3)	120.4(3)	N(1)-C(1)-N(3)	117.10(15)	116.00(12)	116.83(11)	117.57(12)
N(2)-C(1)-C(2)	124.4(2)	120.47(9)	N(1)-C(1)-C(2)	121.0(3)	N(1)-C(1)-C(2)	121.77(16)	122.02(12)	122.45(12)	124.03(12)
N(1)-C(1)-C(2)	119.4(2)	123.47(8)	N(3)-C(1)-C(2)	118.6(3)	N(3)-C(1)-C(2)	120.82(16)	121.81(12)	120.53(12)	118.37(12)
C(1)-C(2)-C(3)	127.4(2)	124.39(9)	C(1)-C(2)-C(3)	113.0(2)	C(1)-C(2)-C(3)	120.79(16)	121.11(12)	120.14(11)	122.19(13)
N(3)-C(3)-N(4)	118.9(2)	119.06(8)	N(2)-C(3)-N(4)	120.9(3)	C(2)-C(3)-N(2)	125.46(16)	126.47(13)	126.22(12)	120.18(13)
N(3)-C(3)-C(2)	120.4(2)	118.02(8)	N(2)-C(3)-C(2)	120.0(3)	C(1)-N(1)-C(4)	123.19(15)	121.30(12)	122.25(12)	121.29(12)
N(4)-C(3)-C(2)	120.6(2)	122.86(8)	N(4)-C(3)-C(2)	119.1(3)	C(1)-N(1)-C(5)	121.61(15)	121.69(12)	121.32(12)	122.68(12)
					C(4)-N(1)-C(5)	115.17(15)	117.02(12)	116.42(12)	116.00(11)
					N(2)-C(3)-C(13)				121.83(12)
					C(2)-C(3)-C(13)				117.97(12)

Compound 7a – Adamantyl PF_6 Salt Solvated with CH_2Cl_2

Four reflections (0 0 2; -1 0 1; 1 0 0; 0 0 1) were removed from the refinement as they were partially obscured by the beam stop. The quality of the collected data also deteriorated quite rapidly at higher angles. A SHEL instruction was added to limit the data used in the refinement to a maximum theta value (θ_{max}) of 26.02°.

One adamantyl group of the cation was disordered. It was split over two positions with the occupancy of each part set to 50 %. The geometries of each part were restrained to be similar using a SAME instruction in the refinement. The thermal parameters of the carbon atoms in this group were restrained to be similar.

The PF_6 anion was disordered (spinning about the F1-P1-F2 axis). The remaining fluorine atoms (F3 to F6) of the anion were split over two sets of positions. These were restrained with a SAME instruction to have similar geometries. Occupancies of the two parts were refined with one free variable to a total occupancy of one. The values of the occupancies refined to 67(5) and 33 % for Parts 1 and 2, respectively.

In this structure the asymmetric unit was found to contain one cation, one anion and one disordered molecule of dichloromethane. It was split over three positions and the occupancies of each part were refined to a total of 100 % with the use of a SUMP restraint. The geometries of each part of the disordered molecule were restrained to be similar using a different SAME command for each part. In addition, the thermal parameters of each type of heavy atom in the solvent molecule were restrained to be similar. The occupancies for the three parts of the solvent molecule refined to 46.2(3), 39.5(3), and 14.4(3) %, respectively.

There are two N-H groups in the cation, both of which form N-H…F hydrogen bonds with different anions. H4N contacts 3 different fluorine atoms in the same anion, one (or possibly two) contact split into three by the disorder of the anion. The N3-H3N…F1 hydrogen bond, involving a second anion, is much less linear than the bonds of H4N. As a result, H3N also forms a pair of close intramolecular contacts (N-H…H-C) with the same hydrogen atom in both parts of the disordered adamantyl group closing 6-membered rings in the cation.

The solvent molecules occur in pairs in the structure, joined by one close Cl…Cl contact that is fragmented by the disorder (Table S5 and Figure S30). The C-H bonds of the solvent are some of the most polarized in the structure and thus form strong C-H type hydrogen bonds with the fluorine atoms of one anion. Chlorine atoms of the solvent are also good hydrogen bond acceptors and participate as such with a number of C-H groups of the cation (Table S4 and Figures S29 and S30). The C-H hydrogen bonding pattern is complicated by the large amount of disorder in the structure. However, as can be seen in Figure S29, each cation does interact with 5 anions and 3 different solvent molecules at reasonable distances.

Table S3. Hydrogen bonds for **7a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...F(1)#1	0.888(16)	2.68(2)	3.291(2)	127.3(19)
N(3)-H(3N)...H(27A)	0.888(16)	1.83(2)	2.650(9)	153(2)
N(3)-H(3N)...H(27D)	0.888(16)	2.17(2)	2.913(9)	140(2)
N(4)-H(4N)...F(4A)#2	0.862(16)	2.50(3)	3.33(2)	162(2)
N(4)-H(4N)...F(6A)#2	0.862(16)	2.76(3)	3.484(15)	143(2)
N(4)-H(4N)...F(6B)#2	0.862(16)	2.46(3)	3.23(3)	149(2)

Symmetry transformations used to generate equivalent atoms:
#1 +x-1,+y-1,+z #2 -x+1,-y+1,-z

Table S4. Selected C-H contacts for **7a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4A)...F(6A)#2	0.98	2.79	3.446(12)	125.1
C(4)-H(4B)...F(2)	0.98	2.68	3.186(3)	112.5
C(4)-H(4C)...F(2)	0.98	2.83	3.186(3)	102.3
C(5)-H(5A)...F(3A)	0.98	2.64	3.407(16)	134.9
C(5)-H(5A)...F(3B)	0.98	2.81	3.51(3)	129.4
C(5)-H(5C)...N(2)	0.98	2.45	2.847(3)	103.8
C(6)-H(6A)...N(1)	0.98	2.51	2.846(3)	99.9
C(6)-H(6B)...F(4A)#2	0.98	2.72	3.216(8)	112.0
C(6)-H(6B)...F(4B)#3	0.98	2.61	3.584(18)	174.1
C(6)-H(6B)...F(4B)#2	0.98	2.85	3.41(2)	117.5
C(6)-H(6B)...F(5A)#3	0.98	2.81	3.556(14)	133.0
C(7)-H(7A)...Cl(2B)#4	0.98	3.05	3.619(7)	118.5
C(7)-H(7C)...N(4)	0.98	2.68	3.063(3)	104.0
C(7)-H(7A)...C(2)	0.98	2.65	2.988(3)	100.4
C(7)-H(7A)...C(3)	0.98	2.71	3.123(3)	105.6
C(7)-H(7C)...F(5A)#3	0.98	2.81	3.354(13)	115.8

C(7)-H(7C)...F(5B)#3	0.98	2.76	3.31(2)	116.3
C(7)-H(7C)...N(4)	0.98	2.68	3.063(3)	104.0
C(9)-H(9B)...Cl(1A)#4	0.99	2.91	3.878(4)	166.6
C(9)-H(9B)...Cl(1B)#4	0.99	2.97	3.939(9)	165.0
C(9)-H(9B)...Cl(2A)#4	0.99	2.99	3.709(6)	130.8
C(9)-H(9B)...Cl(2C)#4	0.99	2.82	3.49(2)	125.5
C(10)-H(10)...Cl(2C)#4	1.00	3.06	3.65(2)	118.8
C(11)-H(11A)...F(3A)#4	0.99	2.72	3.537(11)	140.1
C(11)-H(11A)...F(3B)#4	0.99	2.86	3.64(2)	136.4
C(12)-H(12)...Cl(1A)#1	1.00	3.05	3.882(4)	141.0
C(12)-H(12)...Cl(1B)#1	1.00	2.97	3.789(9)	140.0
C(13)-H(13A)...F(1)#1	0.99	2.73	3.575(3)	144.0
C(13)-H(13A)...F(3A)#1	0.99	2.69	3.613(15)	156.0
C(13)-H(13A)...F(3B)#1	0.99	2.59	3.51(3)	155.4
C(14)-H(14B)...Cl(2A)	0.99	2.90	3.804(6)	152.3
C(14)-H(14B)...Cl(2B)	0.99	2.92	3.808(7)	149.1
C(17)-H(17A)...F(1)#1	0.99	2.80	3.632(3)	141.9
C(19)-H(19A)...N(3)	0.99	2.56	3.138(3)	117.4
C(19)-H(19B)...Cl(1A)#4	0.99	2.96	3.588(4)	122.4
C(19)-H(19B)...Cl(1B)#4	0.99	2.95	3.568(8)	121.4
C(21)-H(21B)...F(2)#3	0.99	2.84	3.660(3)	141.1
C(22B)-H(22B)...F(2)#3	1.00	2.71	3.303(7)	118.1
C(23A)-H(23B)...F(1)#2	0.99	2.46	3.397(9)	157.7
C(23A)-H(23B)...F(4A)#2	0.99	2.61	3.216(15)	119.5
C(23B)-H(23C)...F(1)#2	0.99	2.77	3.625(9)	145.5
C(23B)-H(23D)...F(4B)#3	0.99	2.69	3.26(2)	117.0
C(24A)-H(24A)...F(3A)#1	0.99	2.83	3.670(17)	143.2
C(24B)-H(24D)...F(3B)#1	0.99	2.74	3.71(3)	166.6
C(25A)-H(25)...F(6A)#1	1.00	2.44	3.221(17)	134.9
C(27A)-H(27A)...F(1)#1	0.99	2.33	3.228(8)	149.8
C(27A)-H(27A)...N(3)	0.99	2.65	3.231(9)	117.7
C(27B)-H(27C)...F(1)#2	0.99	2.57	3.497(8)	155.6
C(27B)-H(27D)...F(1)#1	0.99	2.64	3.620(8)	172.9
C(28A)-H(28A)...Cl(1A)#5	0.99	2.90	3.66(2)	134.8
C(28A)-H(28B)...F(2)	0.99	2.37	3.300(17)	155.6
C(28A)-H(28B)...F(3A)	0.99	2.72	3.60(3)	149.1

C(28A)-H(28B)...F(5A)	0.99	2.55	3.39(2)	142.7
C(28B)-H(28C)...F(5B)	0.99	2.42	2.81(3)	103.0
C(28B)-H(28D)...F(2)	0.99	2.58	3.128(16)	114.9
C(28B)-H(28D)...F(3B)	0.99	2.74	3.59(4)	144.8
C(28C)-H(28E)...F(2)	0.99	2.19	3.0805(4)	148.9
C(28C)-H(28E)...F(5A)	0.99	2.50	3.2106(3)	128.9
C(28C)-H(28F)...F(3A)	0.99	2.54	3.0434(3)	111.1

Symmetry transformations used to generate equivalent atoms:

#1 +x-1,+y-1,+z #2 -x+1,-y+1,-z #3 +x,+y-1,+z #4 -x+1,-y+1,-z+1 #5 -x+1,-y+2,-z+1

Table S5. Cl…Cl contacts of the disordered solvent less than the sum of the van der Waals radii + 0.2 Å in **7a**.

2.8135 (0.0203)	Cl1C…Cl1A_$1	138.92 (1.83)	C28C - Cl1C…Cl1A_$1
2.8241 (0.0226)	Cl1C…Cl1B_$1	137.69 (1.85)	C28C - Cl1C…Cl1B_$1
2.0588 (0.0387)	Cl1C…Cl1C_$1	153.97 (2.21)	C28C - Cl1C…Cl1C_$1

Symmetry transformations used to generate equivalent atoms:

#1 +x-1,+y-1,+z

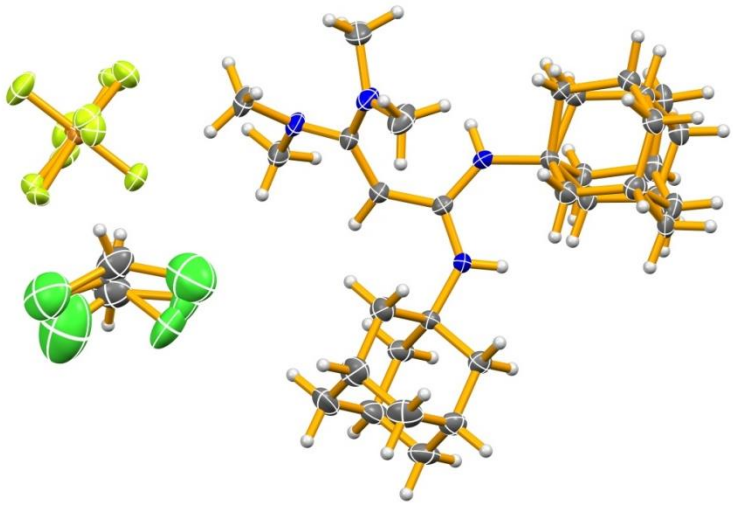


Figure S25: Structure of **7a** including the disordered positions of the cation, the anion and the solvent. Thermal ellipsoids have been drawn at the 50% probability level. None of the atoms have been labelled.

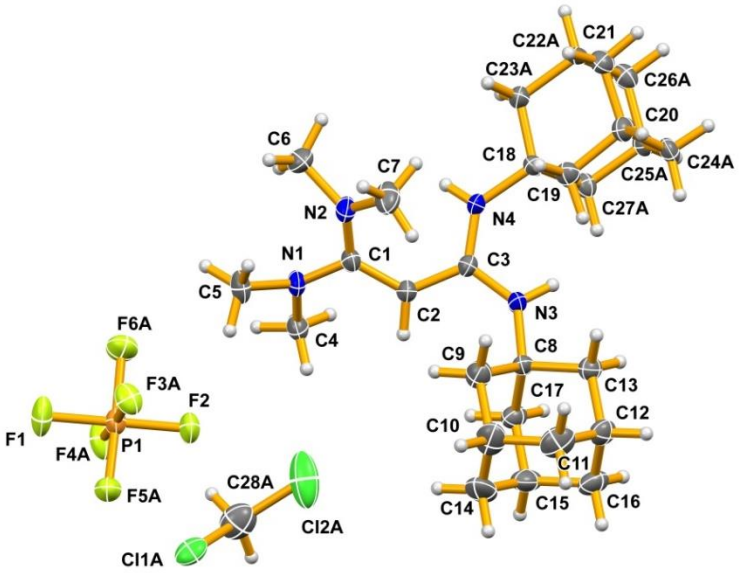


Figure S26: Structure of **7a** with the disorder of the cation, the anion and the solvent removed (major contributor shown). Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

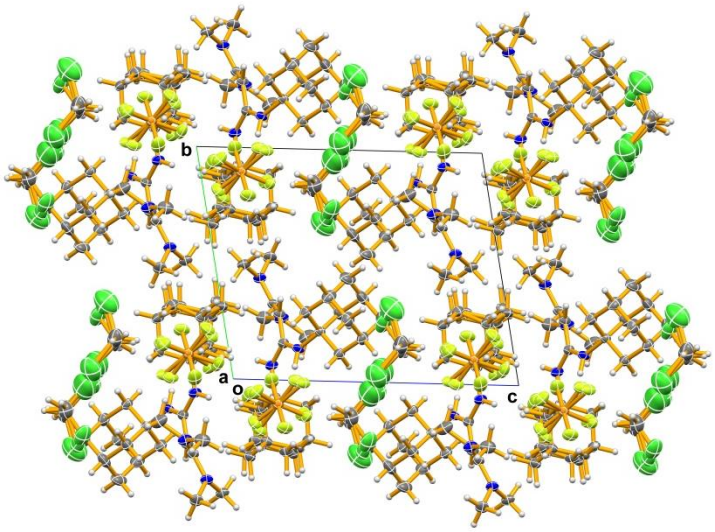


Figure S27: Packing diagram of **7a** viewed down the *X*-axis. Thermal ellipsoids have been drawn at the 50% probability level.

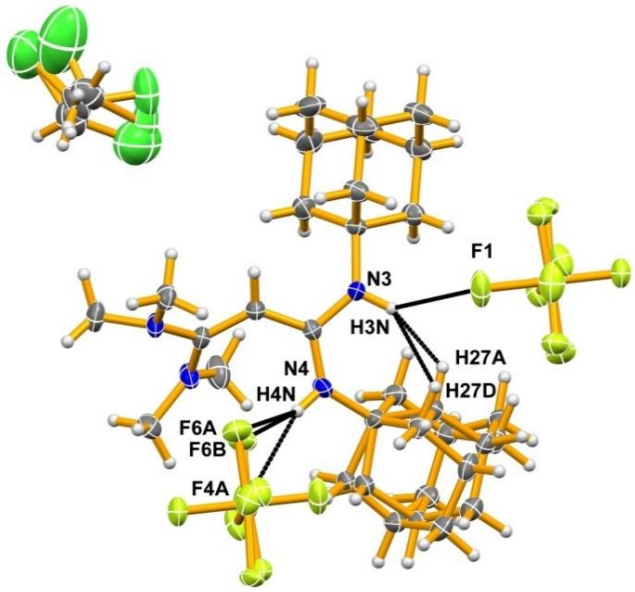


Figure S28: N-H hydrogen bonding (dotted lines) in **7a** (see Table S3). Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the hydrogen bonding have been labelled. The disorder has not been removed.

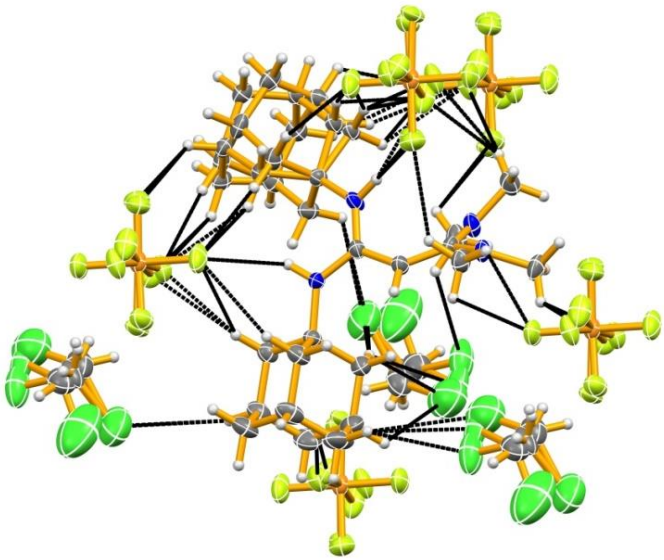


Figure S29: C-H hydrogen bonding (dotted lines) in **7a** (see Table S4) drawn from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. The atoms have not been labelled. The disorder has not been removed to illustrate the complexity of the interactions.

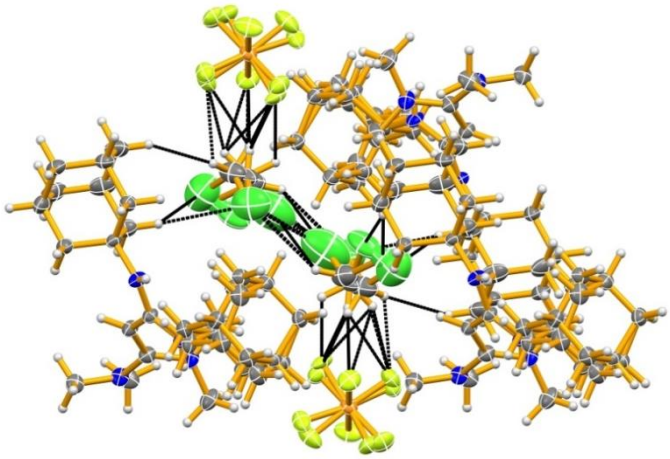


Figure S30: Cl…Cl contacts between two disordered molecules of the solvent (dotted lines) in **7a** (Table S5). The C-H hydrogen bonds (donor and acceptor) of the solvent are also shown. Thermal ellipsoids have been drawn at the 50% probability level. Atoms have not been labelled.

Compound 7b – *t*-Butyl Cl Salt Solvated with CH_2Cl_2

In this structure the asymmetric unit was found to contain one cation, one anion and one disordered molecule of dichloromethane. It was split over four positions and the occupancies of each part were refined. They refined to a total of 100 % without the use of a SUMP restraint. The geometries of each part of the disordered molecule were restrained to be similar using a different SAME command for each part. In addition, the thermal parameters of each type of heavy atom in the solvent molecule were restrained to be similar. The occupancies for the four parts of the molecule refined to 47(1), 41(2), 8(1) and 4 (1) %, respectively.

The cation has two H(N) atoms that hydrogen bond, both to Cl anions, but having different symmetries (Table S6). In addition most of the C-H groups of the cation form intra- or intermolecular hydrogen bonds (Table S7), the latter of which are shown in Figure S34. The disordered solvent molecule also donates and accepts hydrogen bonds (Table S7 and Figure S35).

The anion does make one contact (C1…Cl1, Table S8) that suggests that it interacts with electron density in the backbone of the cation, although the distances to neighbouring atoms of the cation are much longer. The angles of the interaction between the anion and the bonds of the cation backbone are close to 90°, as previously observed in other such interactions in these complexes. There are intramolecular C-H groups that form contacts with this electron density as well. Finally, there is also one contact between Cl atoms in neighbouring solvent molecules (Cl…Cl, Table S8), though it may arise only because of the disorder of the solvent bringing them closer together than would normally be expected.

Table S6. Hydrogen bonds for **7b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...Cl(1)	0.865(11)	2.369(11)	3.2054(8)	162.8(11)
N(4)-H(4N)...Cl(1)#1	0.877(11)	2.697(12)	3.4922(8)	151.4(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S7. Selected C-H contacts for **7b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4A)...Cl(2D)#2	0.98	3.02	3.55(2)	114.6
C(4)-H(4A)...N(3)	0.98	2.81	3.1565(13)	101.3
C(4)-H(4B)...Cl(1)#2	0.98	3.11	3.8960(11)	138.6
C(4)-H(4C)...C(2)	0.98	2.61	2.9714(14)	101.7
C(4)-H(4C)...C(3)	0.98	2.75	3.1414(13)	104.2
C(5)-H(5B)...Cl(1)#2	0.98	2.80	3.6768(11)	149.0
C(5)-H(5B)...Cl(3B)#2	0.98	3.13	3.703(4)	118.6
C(5)-H(5C)...Cl(2D)#2	0.98	3.07	3.76(2)	128.5
C(6)-H(6A)...Cl(1)#2	0.98	2.96	3.8902(11)	158.5
C(6)-H(6A)...N(1)	0.98	2.46	2.8159(13)	100.8
C(6)-H(6C)...Cl(3A)#3	0.98	2.88	3.792(5)	155.4
C(6)-H(6C)...Cl(3B)#3	0.98	2.90	3.818(4)	156.8
C(6)-H(6C)...Cl(3C)#3	0.98	2.68	3.553(12)	147.9
C(7)-H(7A)...Cl(3A)#3	0.98	3.11	3.849(5)	133.8
C(7)-H(7A)...Cl(3B)#3	0.98	3.04	3.773(4)	132.1
C(7)-H(7A)...Cl(3D)#4	0.98	3.03	3.358(12)	100.8
C(7)-H(7C)...Cl(1)	0.98	3.11	3.7636(11)	125.6
C(7)-H(7C)...Cl(3D)#4	0.98	3.10	3.358(12)	97.0
C(9)-H(9C)...Cl(1)	0.98	3.07	3.8546(11)	138.2
C(9)-H(9C)...Cl(3D)	0.98	3.15	3.842(13)	128.8

C(10)-H(10A)...C(3)	0.98	2.99	3.0778(14)	85.7
C(10)-H(10A)...N(4)	0.98	2.53	3.0420(14)	112.3
C(10)-H(10B)...Cl(3A)#5	0.98	3.14	4.069(5)	158.9
C(10)-H(10B)...Cl(3B)#5	0.98	3.14	4.075(4)	160.0
C(10)-H(10B)...Cl(3C)#5	0.98	2.94	3.801(10)	146.9
C(11)-H(11A)...C(3)#1	0.98	2.87	3.5362(14)	126.2
C(11)-H(11A)...N(4)#1	0.98	2.93	3.8308(14)	152.9
C(11)-H(11B)...Cl(3C)#5	0.98	3.15	4.00(2)	146.4
C(11)-H(11B)...Cl(3D)#5	0.98	2.56	3.511(9)	163.6
C(11)-H(11C)...Cl(1)#1	0.98	2.73	3.7006(12)	172.3
C(13)-H(13C)...Cl(1)#1	0.98	2.81	3.6903(11)	150.5
C(14)-H(14C)...Cl(2D)#3	0.98	3.13	3.90(2)	136.6
C(15)-H(15A)...C(2)	0.98	2.52	3.1156(14)	118.7
C(15)-H(15A)...C(3)	0.98	2.89	3.0452(13)	89.5
C(15)-H(15B)...Cl(3B)#6	0.98	3.10	3.817(6)	131.3
C(16A)-H(16A)...Cl(1)	0.99	2.49	3.388(11)	151.1
C(16B)-H(16D)...Cl(1)	0.99	2.55	3.487(15)	157.3
C(16C)-H(16F)...Cl(1)	0.99	2.48	3.42(4)	158.6
C(16D)-H(16G)...Cl(1)	0.99	2.53	3.47(4)	157.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 +x,-y+3/2,+z+1/2 #3 +x+1,-y+3/2,+z+1/2

#4 +x+1,+y,+z #5 -x,-y+1,-z+1 #6 +x+1,+y,+z+1

Table S8. Solvent/solvent and cation/anion contacts involving Cl less than the sum of the van der Waals radii + 0.2 Å in **7b**.

3.60 (2) Cl3B…Cl2C_$1	142.8(6) C16B - Cl3B…Cl2C_$1
3.612(1) C1…Cl1	94.60(6) N1 - C1…Cl1

Symmetry transformations used to generate equivalent atoms:

#1 +x, -y+3/2, +z-1/2

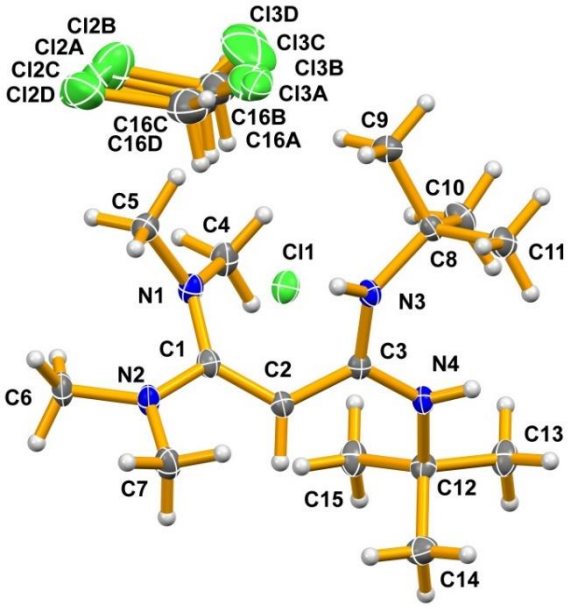


Figure S31: Structure of **7b** including the disordered positions of the solvent. Thermal ellipsoids have been drawn at the 50% probability level. The hydrogen atoms have not been labelled.

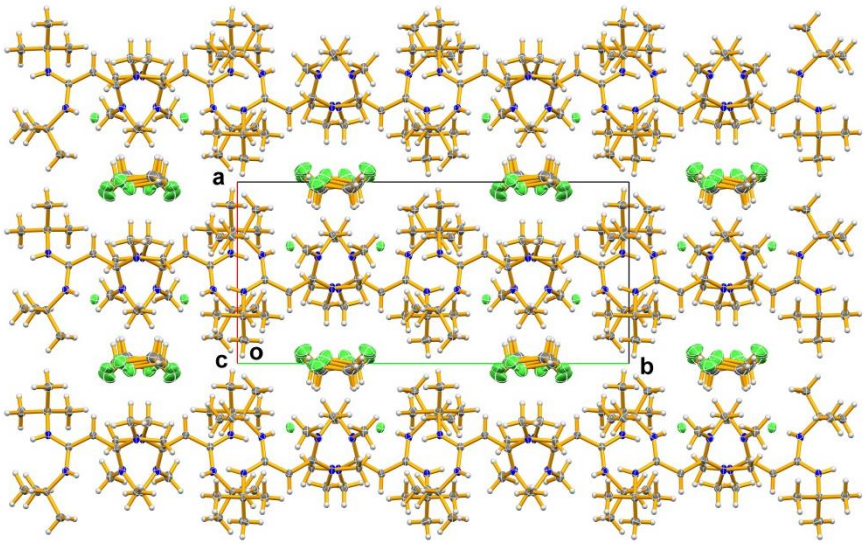


Figure S32: Packing diagram of **7b** viewed down the *Z*-axis. Thermal ellipsoids have been drawn at the 50% probability level.

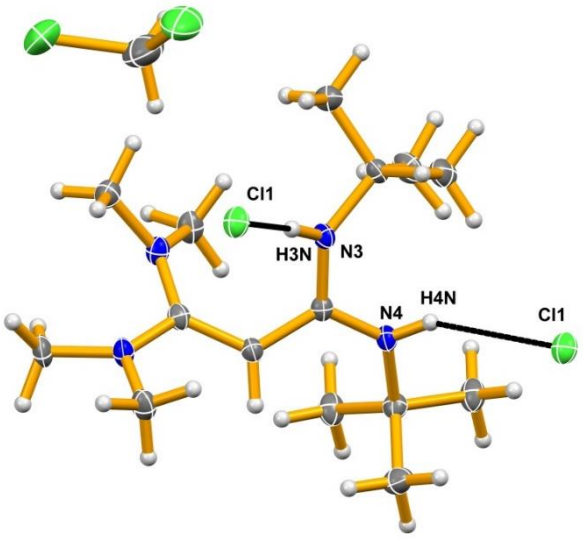


Figure S33: N-H hydrogen bonding (dotted lines) in **7b** (see Table S6). Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the hydrogen bonding have been labelled. The disorder of the solvent has been removed.

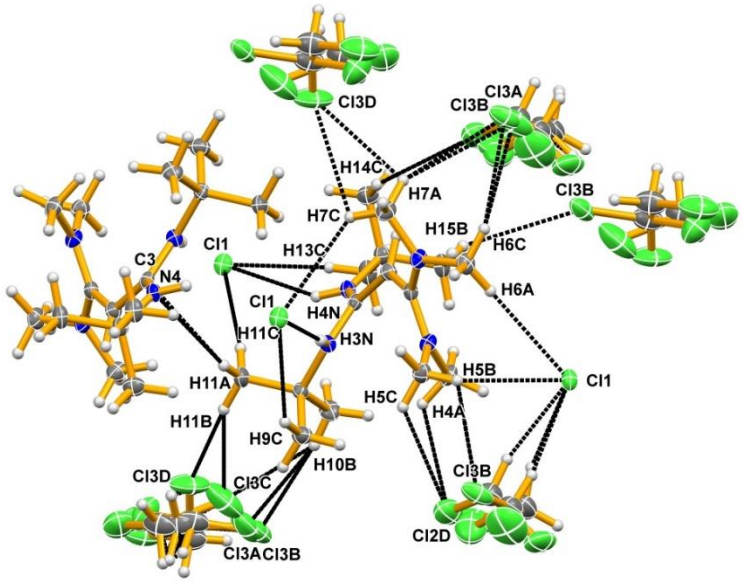


Figure S34: Intermolecular C-H and N-H hydrogen bonding (dotted lines) in **7b** (see Tables S6 and S7) drawn from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the interactions have been labelled. The disorder of the solvent has not been removed.

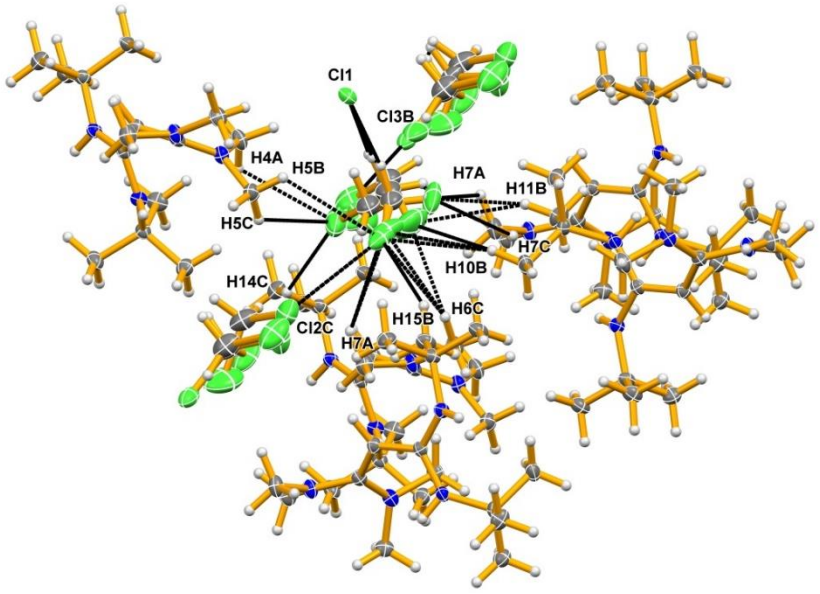


Figure S35: C-H hydrogen bonds (donor and acceptor) and Cl…Cl contacts between disordered solvent molecules (dotted lines) in **7b** (Tables S7 and S8). Thermal ellipsoids have been drawn at the 50% probability level. Only the non-solvent atoms involved in the interactions have been labelled.

Compound 8a – Cyclohexyl PF_6 Salt

The Shelxl calculated Flack and Parson's parameters were 0.03(9) and 0.08(3), respectively. These results are supported by values calculated for the Hooft, Flack and Parson's parameters using the program Platon [5]. These values came out to 0.07(2), 0.07(3) and 0.08(3), respectively. All of this suggests that the correct absolute configuration has been chosen.

There is no solvent, no disorder, no halogen contacts and no H(N) protons in this structure. Thus a large proportion of intermolecular C-H…F hydrogen bonds are formed (Table S9), with each cation interacting with 7 different anions (Figure S38). Because there are no competing types of contacts in this structure, many of the C-H…F contacts are quite short and linear.

Table S9. Selected C-H contacts for **8a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...F(3)#1	0.95	2.71	3.613(2)	159.1
C(2)-H(2)...F(6)#1	0.95	2.72	3.585(2)	151.5
C(3)-H(3)...F(4)#2	0.95	2.57	3.471(2)	159.0
C(3)-H(3)...N(3)	0.95	2.49	2.844(2)	102.2
C(3)-H(3)...C(8)	0.95	2.79	3.371(2)	120.5

C(4)-H(4A)...N(3)	0.98	2.31	2.768(3)	107.8
C(4)-H(4B)...F(4)#3	0.98	2.46	3.389(2)	157.7
C(4)-H(4C)...F(5)	0.98	2.46	3.275(2)	140.0
C(5)-H(5A)...F(2)	0.98	2.75	3.315(3)	117.1
C(5)-H(5A)...F(3)#1	0.98	2.63	3.422(2)	138.0
C(5)-H(5B)...F(3)	0.98	2.86	3.606(3)	133.2
C(5)-H(5C)...F(1)#1	0.98	2.87	3.301(2)	107.5
C(5)-H(5C)...F(6)#1	0.98	2.81	3.457(3)	124.1
C(6)-H(6A)...F(6)#1	0.98	2.68	3.518(2)	143.2
C(6)-H(6B)...F(3)#4	0.98	2.76	3.569(2)	140.0
C(6)-H(6B)...F(5)#4	0.98	2.83	3.681(2)	146.0
C(6)-H(6C)...F(3)#1	0.98	2.81	3.423(2)	121.5
C(7)-H(7A)...F(1)#2	0.98	2.62	3.489(2)	147.6
C(7)-H(7A)...F(4)#2	0.98	2.66	3.594(2)	159.9
C(7)-H(7A)...F(6)#2	0.98	2.79	3.494(2)	129.5
C(7)-H(7B)...F(5)#4	0.98	2.70	3.332(2)	122.9
C(9)-H(9A)...F(2)#2	0.99	2.67	3.521(2)	143.6
C(9)-H(9A)...F(4)#2	0.99	2.50	3.238(2)	131.0
C(10)-H(10B)...F(6)#5	0.99	2.74	3.476(2)	131.2
C(11)-H(11B)...F(1)#6	0.99	2.86	3.821(3)	162.9
C(12)-H(12B)...F(5)	0.99	2.55	3.206(3)	123.5
C(13)-H(13B)...F(2)#2	0.99	2.69	3.521(2)	142.1

Symmetry transformations used to generate equivalent atoms:

#1 +x+1/2,-y+1/2,-z+1 #2 -x+1,+y+1/2,-z+1/2 #3 -x+1/2,-y+1,+z+1/2 #4 +x+1,+y,+z

#5 +x,+y+1,+z #6 -x,+y+1/2,-z+1/2

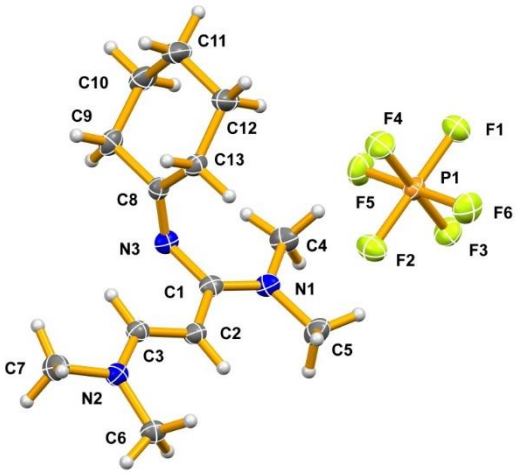


Figure S36: Structure of **8a**. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

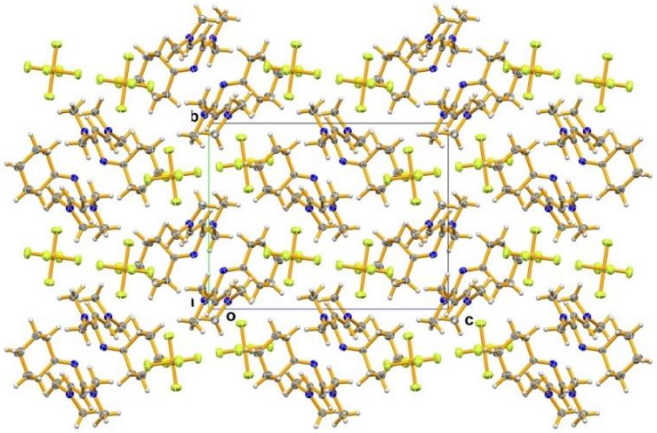


Figure S37: Packing diagram of **8a** viewed down the *X*-axis. Thermal ellipsoids have been drawn at the 50% probability level.

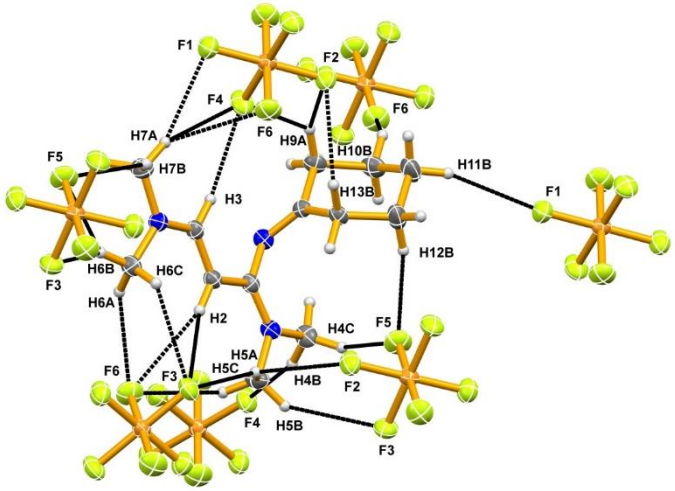


Figure S38: Intermolecular C-H hydrogen bonding (dotted lines) in **8a** (see Table S9) drawn from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the interactions have been labelled.

Compound 8b – Cyclopentyl PF_6 Salt

The cyclopentyl ring of the cation was disordered. It was split over two positions with the occupancies of each part refined. The geometries of each part were restrained to be similar using a SAME instruction in the refinement. The thermal parameters of the ring carbon atoms were allowed to refine freely but enhanced rigid bond restraints (RIGU) were placed over the entire structure. The occupancies of Parts 1 and 2 refined to 73.2(6) and 26.8 %, respectively.

The PF_6 anion was very disordered (spinning). Ultimately it was split over four sets of positions, even though this still left most of the top Fourier peaks in the anion. All 4 parts of the PF_6 anion were restrained with SAME instructions to have similar geometries. All F atoms were restrained to have similar thermal parameters. Occupancies of the four parts were refined but restrained with a SUMP instruction to a total occupancy of one. The refined values actually totaled to 1.002, with individual occupancies of 42.2(9), 23.9(6), 24.9(8) and 9.2(2) % for Parts1, 2, 3 and 4, respectively. This left only minor level C alerts in the checkcif file.

The structure of the cyclopentyl compound is similar to that of its cyclohexyl analogue, with an extra measure of disorder thrown in. As in the cyclohexyl compound there are no H(N) atoms with which to form traditional hydrogen bonds and there are no halogen contacts. The C-H…F interactions are more diverse because of the heavy disorder of the anion in the cyclopentyl structure. Every cation interacts with 8 different anions and also with two other cations, through interactions with electron density in the bonds of the cation backbone (Figure S42).

Table S10. Selected C-H contacts for **8b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...F(1A)#1	0.95	2.66	3.605	176.8
C(2)-H(2)...F(1B)#1	0.95	2.51	3.437	166.1
C(2)-H(2)...F(1C)#1	0.95	2.87	3.819	179.6
C(2)-H(2)...F(1D)#1	0.95	2.59	3.474	155.4
C(3)-H(3)...F(5A)#2	0.95	2.37	3.2735(3)	158.8
C(3)-H(3)...F(5B)#2	0.95	2.67	3.5683(3)	158.1
C(3)-H(3)...F(5C)#2	0.95	2.54	3.3725(3)	147.1
C(3)-H(3)...F(5D)#2	0.95	2.77	3.6696(4)	158.0
C(3)-H(3)...N(3)	0.95	2.49	2.8584(3)	102.9
C(3)-H(3)...C(8A)	0.95	2.65	3.1998(3)	117.5
C(3)-H(3)...C(8B)	0.95	2.65	3.1591(3)	113.8
C(4)-H(4C)...F(1B)#1	0.98	2.54	3.0970(3)	116.3
C(4)-H(4A)...N(1)#3	0.98	2.80	3.7158(5)	155.0
C(4)-H(4A)...C(1)#3	0.98	3.05	3.8507(5)	140.1

C(4)-H(4B)...F(3A)#3	0.98	2.57	3.5037(4)	159.2
C(4)-H(4B)...F(3B)#3	0.98	2.31	3.2358(4)	157.8
C(4)-H(4B)...F(3C)#3	0.98	2.51	3.4056(4)	152.6
C(4)-H(4B)...F(5D)#3	0.98	2.63	3.4830(4)	146.0
C(4)-H(4C)...F(1B)#1	0.98	2.54	3.0970(3)	116.3
C(4)-H(4C)...F(6A)#1	0.98	2.74	3.5897(4)	145.9
C(4)-H(4C)...F(6C)#1	0.98	2.74	3.6422(3)	153.6
C(4)-H(4C)...F(6D)#1	0.98	2.70	3.4099(4)	129.3
C(5)-H(5A)...N(3)	0.98	2.32	2.7169(3)	103.3
C(5)-H(5B)...F(2B)#3	0.98	2.66	3.5906(4)	158.6
C(5)-H(5B)...F(5D)#3	0.98	2.75	3.6723(4)	157.6
C(5)-H(5C)...F(1A)#4	0.98	2.55	3.5117(3)	167.3
C(5)-H(5C)...F(1C)#4	0.98	2.50	3.4446(3)	162.1
C(6)-H(6A)...F(1A)#1	0.98	2.69	3.4652(3)	136.5
C(6)-H(6A)...F(1B)#1	0.98	2.74	3.5916(4)	145.2
C(6)-H(6A)...F(1D)#1	0.98	2.20	3.1199(3)	156.4
C(6)-H(6A)...F(3A)#1	0.98	2.72	3.6426(4)	156.2
C(6)-H(6A)...F(3C)#1	0.98	2.51	3.3897(4)	149.6
C(6)-H(6B)...F(4B)#5	0.98	2.67	3.4356(3)	135.2
C(6)-H(6B)...F(4C)#5	0.98	2.40	3.2376(3)	143.5
C(6)-H(6B)...F(6D)#5	0.98	2.44	3.3407(3)	153.3
C(6)-H(6C)...F(2A)	0.98	2.47	3.2501(3)	136.7
C(6)-H(6C)...F(2C)	0.98	2.36	3.0852(3)	129.9
C(6)-H(6C)...F(4D)	0.98	2.78	3.4090(4)	122.6
C(7)-H(7A)...F(6B)	0.98	2.53	3.2875(4)	134.1
C(7)-H(7B)...F(4A)#5	0.98	2.53	3.4436(4)	155.7
C(7)-H(7B)...F(4B)#5	0.98	2.42	3.3056(4)	150.0
C(7)-H(7B)...F(4C)#5	0.98	2.77	3.5516(4)	137.3
C(7)-H(7B)...F(2D)#5	0.98	2.20	3.0606(3)	146.2
C(7)-H(7C)...F(3D)#2	0.98	2.67	3.6478(4)	172.3
C(7)-H(7C)...F(4A)#2	0.98	2.71	3.5893(4)	149.8
C(7)-H(7C)...F(5A)#2	0.98	2.66	3.5593(3)	152.3
C(7)-H(7C)...F(5B)#2	0.98	2.59	3.5435(3)	164.1
C(7)-H(7C)...F(5C)#2	0.98	2.41	3.3227(3)	155.7
C(9A)-H(9A)...F(3B)#2	0.99	2.52	3.4743(3)	162.5
C(9A)-H(9A)...F(3C)#2	0.99	2.52	3.5009(4)	169.0

C(9A)-H(9A)...F(5A)#2	0.99	2.51	3.2617(3)	133.0
C(9A)-H(9A)...F(5B)#2	0.99	2.53	3.2535(4)	130.1
C(9A)-H(9A)...F(5D)#2	0.99	2.27	3.1232(3)	143.2
C(9A)-H(9B)...F(6A)#6	0.99	2.76	3.6532(3)	150.3
C(10A)-H(10A)...F(2B)#7	0.99	2.77	3.4358(5)	125.5
C(10A)-H(10B)...F(4A)#4	0.99	2.85	3.6045(4)	133.6
C(11A)-H(11A)...F(5B)#2	0.99	2.77	3.5154(3)	132.5
C(11A)-H(11B)...N(2)#8	0.99	2.85	3.7427(4)	150.7
C(11A)-H(11B)...C(3)#8	0.99	3.02	3.8898(4)	147.1
C(12A)-H(12A)...F(3D)#4	0.99	2.61	3.4786(4)	146.5
C(12A)-H(12A)...F(4A)#4	0.99	2.37	3.2674(3)	151.0
C(12A)-H(12A)...F(4B)#4	0.99	2.46	3.3809(3)	153.8
C(12A)-H(12A)...F(4C)#4	0.99	2.46	3.4206(3)	163.0
C(12A)-H(12A)...F(6D)#4	0.99	2.82	3.7841(3)	164.3
C(12A)-H(12B)...F(3A)	0.99	2.54	3.1544(3)	120.2
C(12A)-H(12B)...F(3B)	0.99	2.85	3.4900(4)	122.8
C(12A)-H(12B)...F(3C)	0.99	2.74	3.2904(4)	115.6
C(12A)-H(12B)...F(4D)	0.99	2.56	3.4072(3)	143.5
C(9B)-H(9C)...F(3B)#2	0.99	2.54	3.4861(3)	160.6
C(9B)-H(9C)...F(3C)#2	0.99	2.59	3.5322(4)	159.0
C(9B)-H(9C)...F(5A)#2	0.99	2.63	3.2702(3)	122.7
C(9B)-H(9C)...F(5B)#2	0.99	2.79	3.3063(4)	113.0
C(9B)-H(9C)...F(5D)#2	0.99	2.30	3.1150(3)	139.1
C(9B)-H(9D)...F(6A)#6	0.99	2.87	3.6118(3)	132.3
C(10B)-H(10C)...F(2A)#7	0.99	2.82	3.7824(5)	164.5
C(10B)-H(10C)...F(2B)#7	0.99	2.71	3.5948(5)	148.8
C(10B)-H(10C)...F(2D)#7	0.99	2.84	3.7675(5)	155.6
C(10B)-H(10D)...F(1C)#2	0.99	2.86	3.6789(4)	141.1
C(10B)-H(10D)...F(5B)#2	0.99	2.46	3.2320(3)	134.5
C(11B)-H(11C)...N(2)#8	0.99	2.67	3.4096(3)	132.0
C(11B)-H(11C)...C(3)#8	0.99	2.93	3.8122(3)	149.3
C(11B)-H(11D)...F(3D)#4	0.99	2.66	3.4786(4)	140.2
C(11B)-H(11D)...F(4A)#4	0.99	2.01	2.8938(3)	147.5
C(11B)-H(11D)...F(4B)#4	0.99	2.14	2.9976(3)	143.6
C(11B)-H(11D)...F(4C)#4	0.99	2.52	3.2443(3)	129.7
C(12B)-H(12C)...F(4C)#4	0.99	2.86	3.4742(3)	121.0

C(12B)-H(12D)...F(3A)	0.99	2.56	3.0378(3)	109.4
C(12B)-H(12C)...F(3C)	0.99	2.80	3.1815(4)	103.6
C(12B)-H(12D)...F(4D)	0.99	2.52	3.2891(3)	134.3
C(12B)-H(12D)...F(6C)	0.99	2.77	3.5785(4)	139.6

Symmetry transformations used to generate equivalent atoms:

#1 +x+1/2,-y+1/2,+z+1/2 #2 +x+1,+y,+z #3 -x+1,-y+1,-z+1 #4 -x+1/2,+y+1/2,-z+1/2

#5 -x+1,-y,-z+1 #6 -x+3/2,y+1/2,-z+1/2 #7 +x+1/2,-y+1/2,+z-1/2 #8 +x-1/2,-y+1/2,+z-1/2

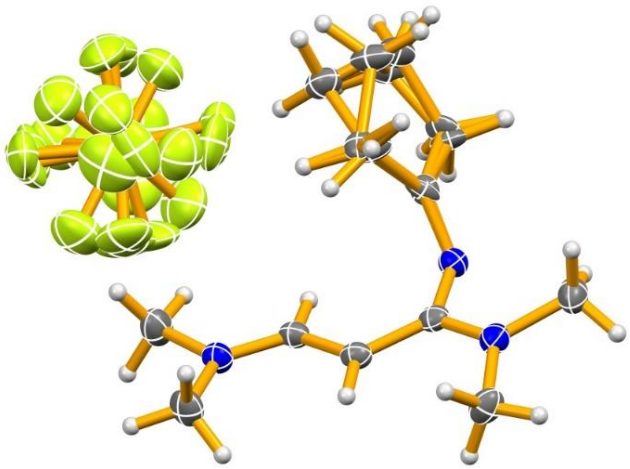


Figure S39: Structure of **8b** including the disordered positions of the cation and the anion. Thermal ellipsoids have been drawn at the 50% probability level. None of the atoms have been labelled.

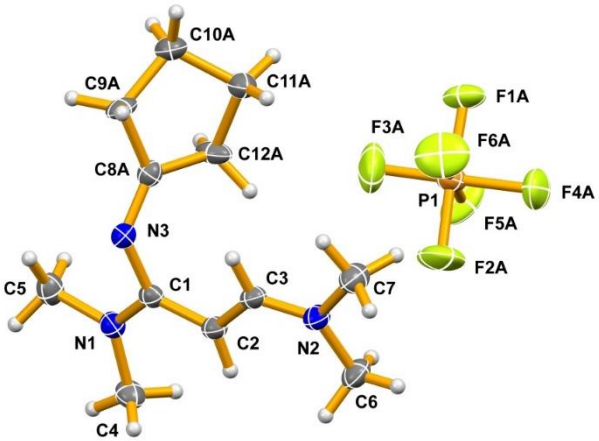


Figure S40: Structure of **8b** with the disorder of the cation and the anion removed (major contributors shown). Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

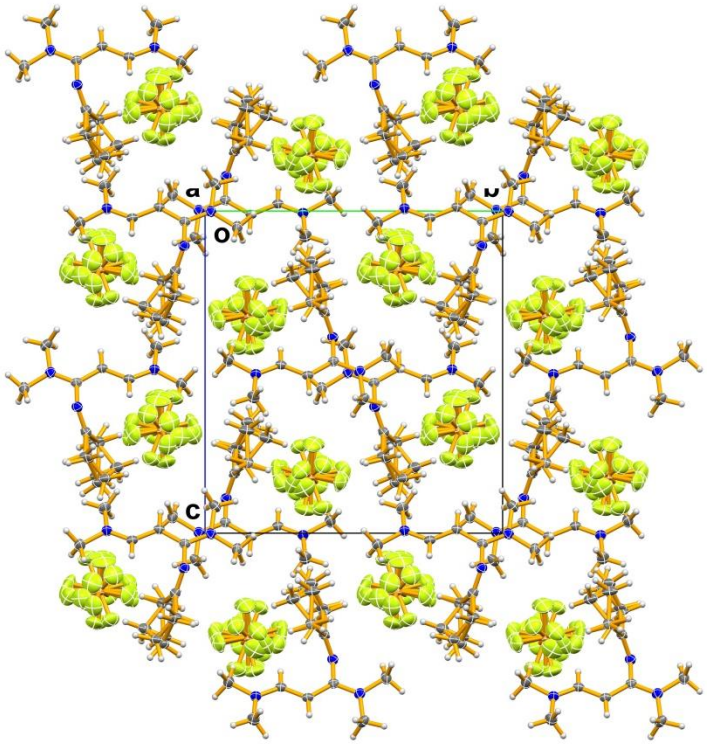


Figure S41: Packing diagram of **8b** viewed down the *X*-axis. Thermal ellipsoids have been drawn at the 50% probability level.

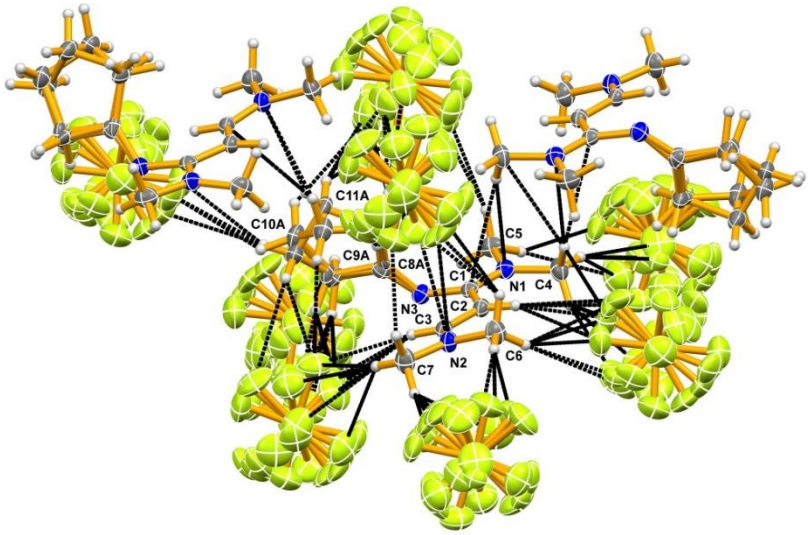


Figure S42: C-H hydrogen bonding (dotted lines) in **8b** (see Table S10) drawn from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. The heavy atoms of the central cation have been labelled to aid in its identification. The disorder has not been removed to illustrate the complexity of the interactions.

Compound 8c – *sec*-Butyl PF_6 Salt

This structure has no disorder and no H(N) atoms for hydrogen bonding. Intermolecular C-H…F hydrogen bonds dominate the interactions, with each cation participating in close contacts with 7 different anions (Table S11 and Figure S45). There are also intramolecular C-H…C/N contacts formed to electron density in the backbone of the same cation. The anion does make one contact between a fluorine atom and electron density in the bonds of the backbone of a neighbouring cation (Table S12 and Figure S46).

Table S11. Selected C-H contacts for **8c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...F(6)#1	0.95	2.80	3.7389(16)	170.6
C(3)-H(3)...F(2)#2	0.95	2.44	3.0112(15)	118.1
C(3)-H(3)...N(3)	0.95	2.43	2.8147(17)	103.8
C(3)-H(3)...C(8)	0.95	2.88	3.4156(17)	117.2
C(4)-H(4A)...F(5)#3	0.98	2.60	3.565(2)	166.5
C(4)-H(4B)...F(4)#4	0.98	2.80	3.6819(19)	149.6
C(4)-H(4C)...F(1)#5	0.98	2.79	3.7037(19)	155.5
C(5)-H(5B)...F(2)#4	0.98	2.76	3.6459(18)	150.5
C(5)-H(5B)...F(4)#4	0.98	2.41	3.3133(18)	152.3
C(6)-H(6A)...F(2)#1	0.98	2.84	3.5883(18)	133.8
C(6)-H(6A)...C(3)#6	0.98	2.96	3.889(2)	159.2
C(6)-H(6C)...F(3)#1	0.98	2.71	3.1701(18)	109.2
C(6)-H(6C)...F(4)	0.98	2.62	3.1227(18)	111.8
C(7)-H(7A)...F(2)#2	0.98	2.61	3.2326(17)	121.2
C(7)-H(7B)...F(1)	0.98	2.52	3.4108(17)	150.9
C(9)-H(9A)...N(1)	0.98	2.89	3.4230(19)	115.1
C(9)-H(9A)...C(1)	0.98	2.44	2.8619(19)	105.6
C(9)-H(9A)...C(2)	0.98	3.01	3.5721(19)	117.8
C(9)-H(9B)...F(1)#3	0.98	2.59	3.5285(17)	160.4
C(9)-H(9B)...F(3)#3	0.98	2.54	3.4004(17)	146.6
C(9)-H(9C)...F(2)#2	0.98	2.58	3.2490(17)	125.6
C(9)-H(9C)...F(3)#2	0.98	2.63	3.5792(18)	163.9
C(10)-H(10B)...F(3)#3	0.99	2.60	3.4584(17)	145.3
C(11)-H(11B)...F(1)#7	0.98	2.67	3.6330(18)	166.1
C(11)-H(11B)...F(5)#7	0.98	2.73	3.4643(19)	131.7

C(11)-H(11C)...F(1)#5	0.98	2.78	3.741(2)	165.8

Symmetry transformations used to generate equivalent atoms:

#1 +x+1/2,-y+1/2,+z+1/2 #2 -x+1/2,+y-1/2,-z+1/2 #3 +x+1,+y,+z #4 -x+1,-y+1,-z+1

#5 -x+1/2,+y+1/2,-z+1/2 #6 -x+1,-y,-z+1 #7 +x+1/2,-y+1/2,+z-1/2

Table S12. Cation/anion contacts less than the sum of the van der Waals radii + 0.1 Å in **8c**.

3.0132 (0.0015) F4…N2	123.11 (0.05) P1 - F4…N2
3.2378 (0.0016) F4…C3	132.36 (0.06) P1 - F4…C3

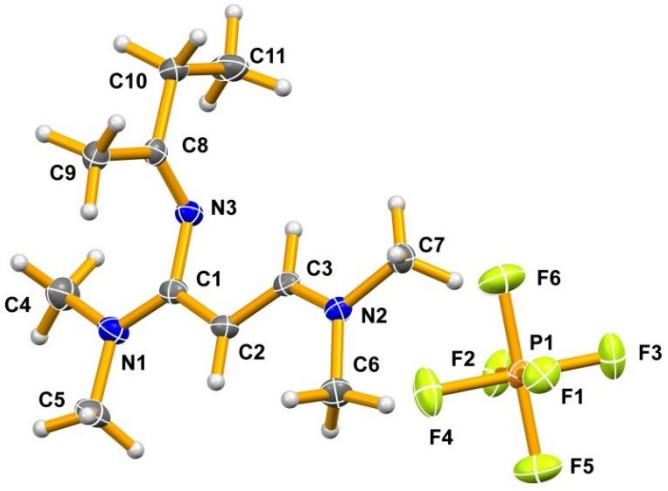


Figure S43: Structure of **8c**. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

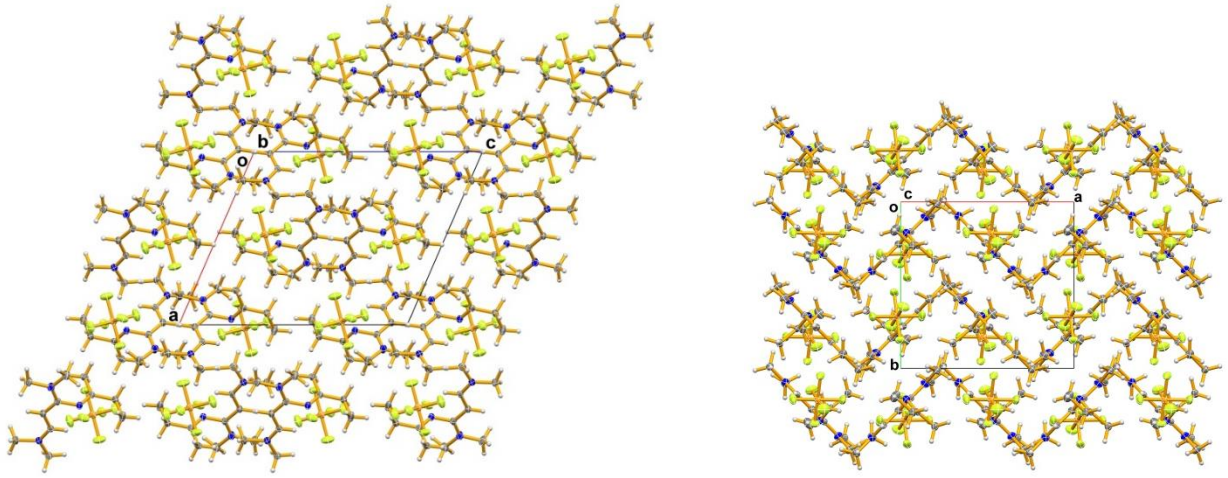


Figure S44: Packing diagram of **8c** viewed down the *Y*-axis (left) and *Z*-axis (right). Thermal ellipsoids have been drawn at the 50% probability level.

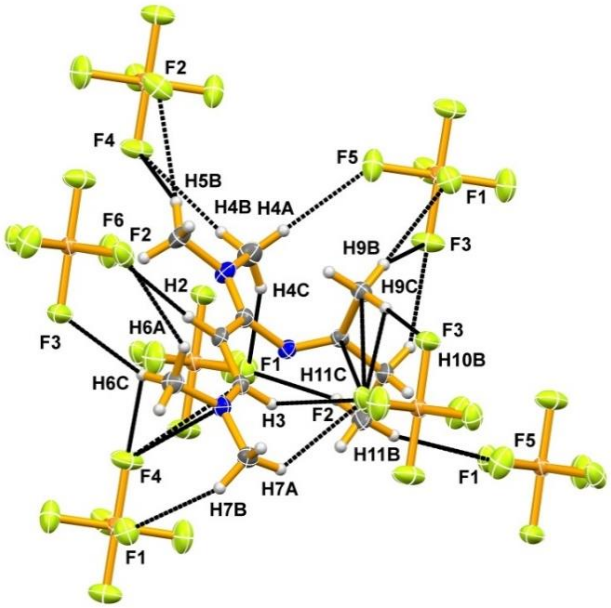


Figure S45: Intermolecular C-H hydrogen bonding (dotted lines) in **8c** (see Table S11) drawn from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the interactions have been labelled.

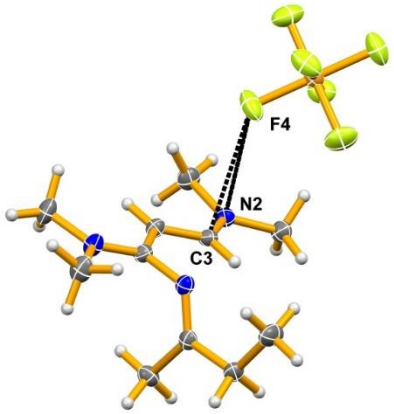


Figure S46: Cation/anion contacts between a fluorine atom of the anion and electron density in the backbone of the cation (dotted lines) in **8c** (Table S12). Thermal ellipsoids have been drawn at the 50% probability level. Only the atoms involved in the interaction have been labelled.

Compound 9 – Cyclohexyl Urea Hydrolysis Product

The Twin Rot Max routine in Platon [5] showed that the crystal chosen for data collection was twinned. The twin law (1 0 1 0 -1 0 0 0 -1) was added to the refinement and the BASF value refined to a final value of 0.359(2) using the HKLF4 data. Once the original twinning had been resolved, another run of Twin Rot Max suggested that there were three additional twin components present in the chosen crystal. However, attempts to include this (minor) twinning into the refinement model did not result in any noticeable improvement in the results. The original two component twin results were used and are reported here.

In this structure, the cyclohexyl group adopts a chair conformation. It is a neutral product, so there are no cation/anion charged interactions stabilizing the crystal. The intermolecular interactions are thus important, particularly the N-H…O hydrogen bond that joins the molecules together in linear chains running parallel to the *Z*-axis (Table S13, Figures S49 and S50). The oxygen atom also acts as the acceptor to all of the close intermolecular (3) and intramolecular (2) C-H…O bonds formed (Table S14, Figures S49 and S50).

Table S13. Hydrogen bonds for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.89(3)	2.04(3)	2.899(3)	163(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2

Table S14. Selected C-H contacts for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3B)...O(1)	0.99	2.76	3.246(3)	110.4
C(7)-H(7A)...O(1)#2	0.99	2.78	3.687(3)	152.9
C(7)-H(7B)...O(1)#1	0.99	2.64	3.316(3)	126.0
C(8)-H(8C)...O(1)#1	0.98	2.45	3.296(3)	144.2
C(9)-H(9A)...O(1)	0.98	2.27	2.719(3)	106.6

Symmetry transformations used to generate equivalent atoms:

#1 +x,-y+1/2,+z-1/2 #2 -x,-y+1,-z

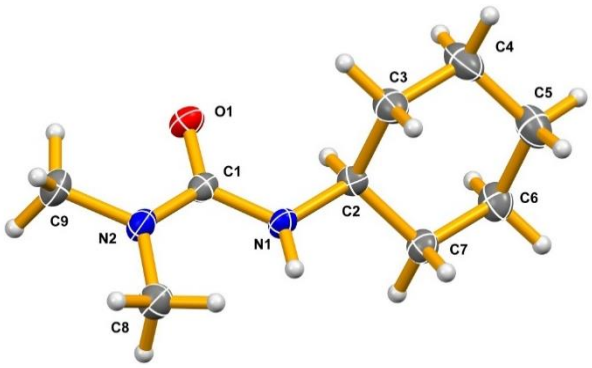


Figure S47: Structure of **9**. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

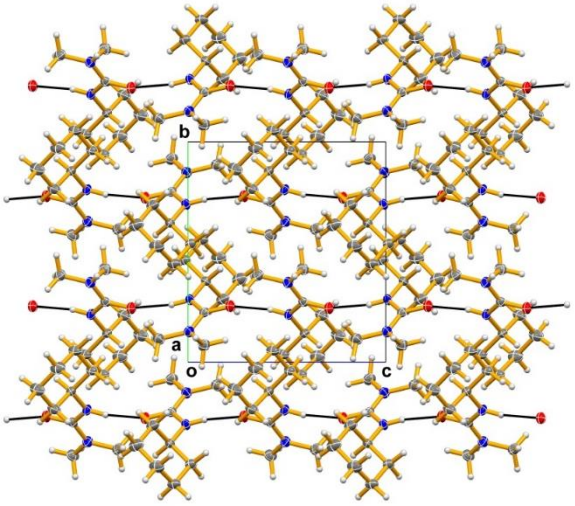


Figure S48: Packing diagram of **9** viewed down the *X*-axis. N-H…O hydrogen bonds are shown by the dotted lines which join chains of molecules running parallel to the *Z*-axis in this view. Thermal ellipsoids have been drawn at the 50% probability level.

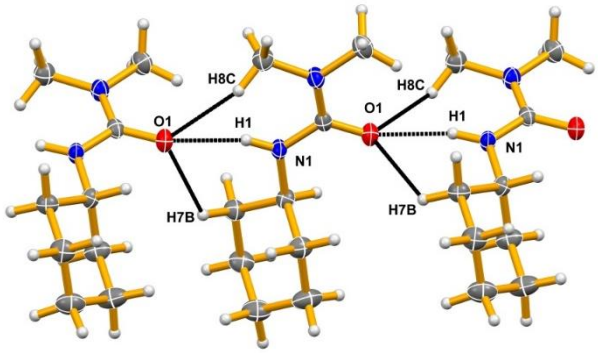


Figure S49: N-H…O hydrogen bonding (dotted lines) in ML134 (see Table S13). C-H…O hydrogen bonds involving the same molecules have also been included. Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the hydrogen bonding have been labelled.

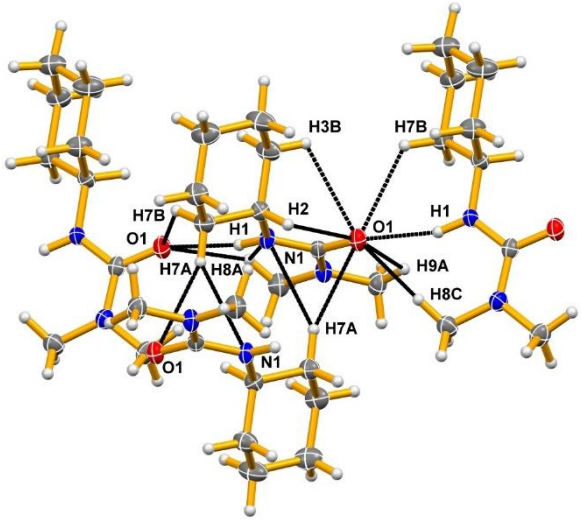


Figure S50: Hydrogen bonding (dotted lines) in **9** (see Tables S13 and S14). Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the interactions have been labelled.

Compound 11 – Quinolinium PF_6 Salt

The PF_6 anion was disordered. It was split over two sets of positions, which were restrained with a SAME instruction to have similar geometries. All F atoms were restrained to have similar thermal parameters as were the two P atoms. The occupancies of the two parts were refined to a total occupancy of one using a free variable. Refined values of 76.6(9) and 23.4 % were obtained for Parts1 and 2, respectively.

The N-H…F hydrogen bond is bifurcated because of the disorder of the anion. There are many close C-H…F hydrogen bonds, more than normally would be expected, again because of the disorder in the anion. Fluorine acts as the acceptor in all of the C-H contacts, with one cation interacting with 8 different anions.

The entire cation is quite planar, with only the methyl groups lying slightly out of the plane defined by the ring atoms. It does thus exhibit some weak/long ring stacking interactions. The center of gravity of the six-membered consisting of the N3, C1, C2, C3, C8 and C13 atoms lies 3.697(1) Å from its 1-x, +y, -z+1/2 symmetry generated partner and 3.798(1) Å from the same ring generated with the symmetry operator -x+1, -y+1, -z. These are a bit long, lying +0.30 Å and +0.40Å beyond the sum of the van der Waals' radii, respectively. However, they are unusual in this series of compounds and so were included here.

Table S15. N-H…F hydrogen bonds for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...F(3A)	0.824(19)	2.230(19)	2.994(4)	154.5(17)
N(3)-H(3N)...F(3B)	0.824(19)	2.18(2)	2.945(12)	154.6(17)

Table S16. Selected C-H…F contacts for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4A)...F(1A)	0.98	2.60	3.188(3)	119.0
C(4)-H(4A)...F(1B)	0.98	2.65	3.271(15)	121.9
C(4)-H(4B)...F(4A)#1	0.98	2.63	3.224(3)	119.2
C(4)-H(4C)...F(3A)	0.98	2.60	3.247(4)	123.9
C(4)-H(4C)...F(3B)	0.98	2.86	3.416(15)	116.7
C(4)-H(4C)...F(5B)	0.98	2.64	3.405(11)	135.3
C(4)-H(4C)...F(5A)#2	0.98	2.48	3.156(3)	125.7
C(4)-H(4C)...F(5B)#2	0.98	2.50	3.255(10)	133.5
C(5)-H(5A)...F(2A)#3	0.98	2.74	3.608(4)	148.2
C(5)-H(5A)...F(4A)#3	0.98	2.74	3.066(3)	100.1
C(5)-H(5A)...F(4B)#3	0.98	2.81	3.150(9)	101.0

C(5)-H(5B)...F(2B)#2	0.98	2.73	3.675(14)	161.8
C(5)-H(5C)...F(1A)#1	0.98	2.60	3.372(3)	136.1
C(5)-H(5C)...F(1B)#1	0.98	2.67	3.417(12)	133.4
C(5)-H(5C)...F(4A)#3	0.98	2.56	3.066(3)	112.3
C(5)-H(5C)...F(4B)#3	0.98	2.73	3.150(9)	106.4
C(6)-H(6A)...F(6A)#3	0.98	2.58	3.354(3)	136.0
C(6)-H(6A)...F(6B)#3	0.98	2.58	3.291(11)	129.4
C(6)-H(6B)...F(2A)#4	0.98	2.69	3.622(4)	158.9
C(6)-H(6B)...F(2B)#4	0.98	2.68	3.619(15)	160.7
C(6)-H(6B)...F(3A)#4	0.98	2.87	3.393(4)	114.0
C(6)-H(6C)...F(2A)#3	0.98	2.75	3.405(4)	124.5
C(7)-H(7A)...F(3A)#4	0.98	2.79	3.481(3)	128.1
C(7)-H(7A)...F(5B)#5	0.98	2.87	3.654(13)	138.0
C(7)-H(7B)...F(4A)#6	0.98	2.68	3.482(3)	139.7
C(7)-H(7B)...F(6A)#6	0.98	2.73	3.693(3)	168.4
C(7)-H(7B)...F(6B)#6	0.98	2.43	3.387(11)	165.2
C(9)-H(9)...F(3A)	0.95	2.66	3.357(4)	130.9
C(9)-H(9)...F(3B)	0.95	2.33	3.089(12)	137.0
C(9)-H(9)...F(6A)	0.95	2.78	3.722(3)	173.0
C(10)-H(10)...F(1A)#7	0.95	2.83	3.314(4)	112.6
C(10)-H(10)...F(1B)#7	0.95	2.69	3.188(13)	113.6
C(11)-H(11)...F(4A)#5	0.95	2.67	3.417(3)	136.3
C(11)-H(11)...F(4B)#5	0.95	2.24	2.970(10)	132.9
C(12)-H(12)...F(5A)#5	0.95	2.55	3.344(3)	141.2
C(12)-H(12)...F(5B)#5	0.95	2.87	3.731(16)	151.0
C(12)-H(12)...F(4B)#5	0.95	2.86	3.268(12)	107.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,+y-1/2,-z+1/2 #2 -x+1/2,-y+3/2,-z #3 +x,+y-1,+z #4 -x+1,-y+1,-z

#5 +x+1/2,+y-1/2,+z #6 -x+1,+y-1,-z+1/2 #7 -x+1,+y,-z+1/2

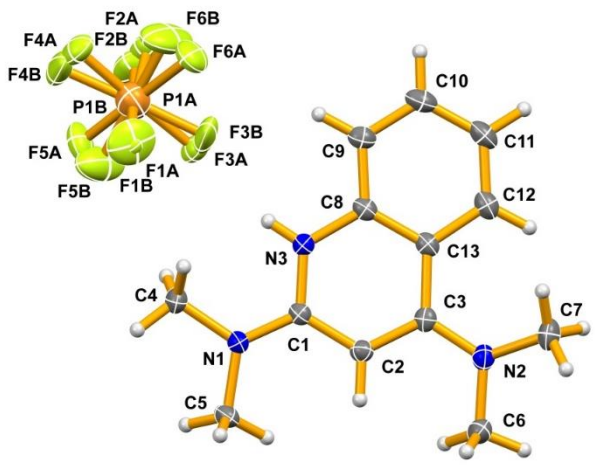


Figure S51: Structure of **11** including the disordered positions of the anion. Thermal ellipsoids have been drawn at the 50% probability level. The hydrogen atoms have not been labelled.

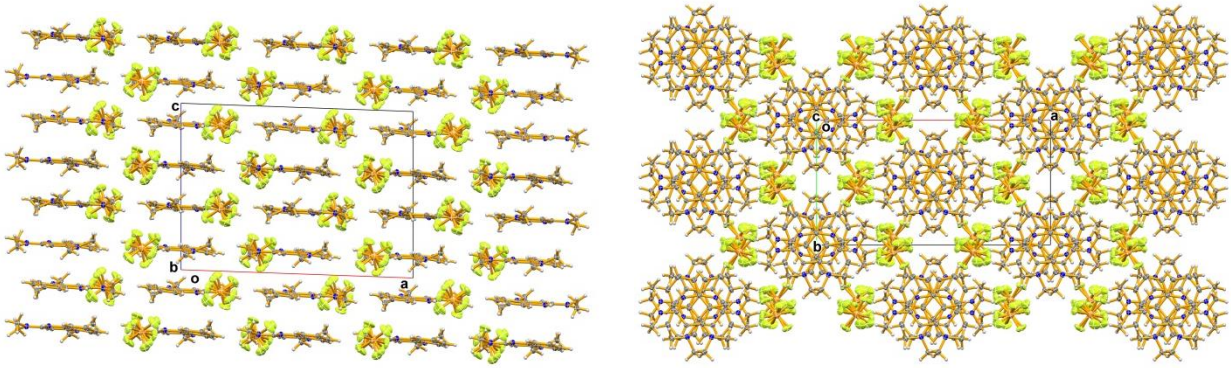


Figure S52: Packing diagram of **11** viewed down the *Y*-axis (left) and *Z*-axis (right). Thermal ellipsoids have been drawn at the 50% probability level.

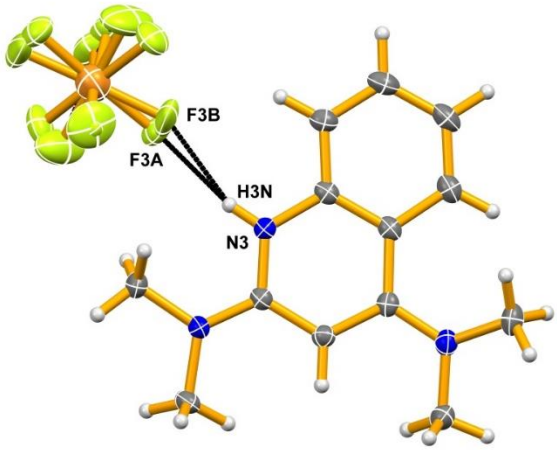


Figure S53: N-H…F hydrogen bonding (dotted lines) in **11** (see Table S15). Thermal ellipsoids have been drawn with 50% probability. Only the atoms involved in the hydrogen bonding have been labelled. The disorder of the anion has not been removed.

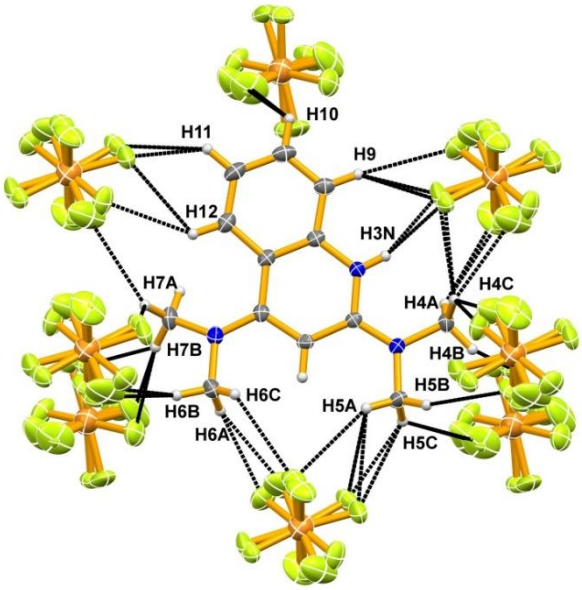


Figure S54: C-H…F hydrogen bonds (dotted lines) in **11** (Table S16) drawn from the perspective of one central cation. The N-H…F hydrogen bond has also been included. Thermal ellipsoids have been drawn at the 50% probability level. Only the atoms of the cations involved in the interactions have been labelled.

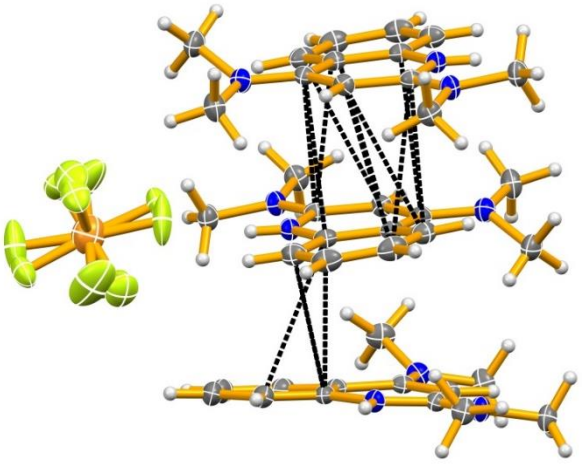


Figure S55: Ring stacking interactions in **11**. Dotted lines join ring atoms that are within the sum of the van der Waals' radii + 0.2 Å. Thermal ellipsoids have been drawn at the 50% probability level. None of the atoms have been labelled.

Compound 12 – *p*-Tolyl(2+) Cl Salt CH_2Cl_2 and $2H_2O$ Solvate

The Shelxl calculated Flack and Parson's parameters were -0.03(7) and -0.02(3), respectively. This result is supported by values calculated for the Hooft, Flack and Parson's parameters using the program Platon [5]. These values came out to -0.03(3), -0.02(3) and -0.02(3), respectively, which suggests that the correct absolute configuration has been chosen.

The structure was found to contain one complete cation(2+), two chloride anions, two complete molecules of water and one molecule of dichloromethane in the asymmetric unit. This results in the formation of an extended network of "traditional" hydrogen bonds (N-H…Cl and O-H…Cl) involving the cations (N-H), the water molecules (O-H) and the chlorides anions (acceptors) that runs throughout the crystal (Table S17 and Figure S58). The water and dichloromethane molecules do not act as acceptors in this network. However, they do accept multiple C-H type hydrogen bonds (Table S18 and Figure S59) and also participate in O…Cl and Cl…Cl contacts, respectively (Table S19 and Figure S60). In addition, the oxygen atoms of the water molecules form contacts with electron density in the bonds of the cation backbone (Table S20 and Figure S59). Finally, C-H groups of the cation do make intramolecular contacts with electron density in bonds of close phenyl rings (Table S18, not shown). The overall result of this complex mixture of both hydrogen bond donors and acceptors results in a complicated arrangement of contacts in the structure.

Table S17. Hydrogen bonds for **12** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...Cl(1)#1	0.84(2)	2.42(2)	3.265(3)	179(5)
O(1)-H(2O)...Cl(2)#2	0.86(2)	2.50(3)	3.347(3)	170(4)
O(2)-H(3O)...Cl(2)	0.87(2)	2.38(3)	3.220(3)	164(4)
O(2)-H(4O)...Cl(2)#3	0.88(2)	2.40(3)	3.267(3)	174(4)
N(3)-H(3N)...Cl(1)	0.87(2)	2.34(3)	3.134(3)	150(3)
N(4)-H(4N)...Cl(1)#1	0.87(2)	2.26(2)	3.088(3)	158(3)

Symmetry transformations used to generate equivalent atoms:

#1 +x-1,+y,+z #2 -x+1/2,-y+1,+z-1/2 #3 +x+1/2,-y+1/2,-z+1

Table S18. C-H contacts for **12** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2A)...Cl(2)	0.99	2.96	3.928(3)	165.6
C(2)-H(2B)...Cl(2)#4	0.99	2.64	3.483(3)	143.3
C(4)-H(4C)...Cl(1)	0.98	3.10	3.641(4)	116.6
C(4)-H(4C)...N(4)#5	0.98	2.96	3.937(5)	176.2
C(4)-H(4C)...C(15)#5	0.98	2.85	3.730(5)	149.3
C(4)-H(4C)...C(20)#5	0.98	2.88	3.590(5)	130.3
C(5)-H(5A)...O(1)#6	0.98	2.69	3.598(5)	154.9
C(5)-H(5A)...O(2)	0.98	2.78	3.238(5)	109.0
C(5)-H(5B)...C(19)	0.98	2.85	3.489(5)	123.4
C(5)-H(5B)...C(20)	0.98	3.12	3.393(5)	97.5
C(6)-H(6A)...Cl(1)#1	0.98	2.94	3.471(4)	115.0
C(6)-H(6B)...Cl(4)#7	0.98	3.14	4.001(4)	147.4
C(6)-H(6A)...Cl(1)#1	0.98	3.11	3.471(4)	103.4
C(6)-H(6C)...O(2)#1	0.98	2.55	3.228(5)	126.1
C(7)-H(7B)...Cl(3)#7	0.99	2.89	3.529(4)	123.3
C(7)-H(7B)...C(12)	0.99	2.92	3.558(5)	123.2
C(7)-H(7B)...C(13)	0.99	3.08	3.383(5)	99.2
C(7)-H(7C1)...Cl(2)	0.99	3.11	3.775(4)	123.3
C(7)-H(7C1)...O(2)#4	1.02	2.55	3.474(5)	149.4
C(7)-H(7C2)...Cl(2)	0.99	2.79	3.775(4)	171.0
C(9)-H(9)...O(1)	0.95	2.89	3.689(5)	142.9
C(13)-H(13)...Cl(2)	0.95	2.83	3.721(4)	157.4
C(14)-H(14A)...Cl(4)#8	0.98	3.14	3.633(4)	112.9
C(16)-H(16)...Cl(3)	0.95	3.04	3.643(4)	122.7
C(16)-H(16)...O(1)	0.95	2.82	3.723(4)	158.0
C(19)-H(19)...Cl(1)#6	0.95	2.71	3.631(3)	165.1
C(20)-H(20)...Cl(2)#4	0.95	3.09	3.960(3)	153.2
C(21)-H(21C)...Cl(4)#9	0.98	3.08	3.654(4)	118.4
C(22)-H(22A)...Cl(2)#10	0.99	2.75	3.714(4)	166.0
C(22)-H(22B)...Cl(1)	0.99	2.52	3.374(4)	144.8

Symmetry transformations used to generate equivalent atoms:

#1 +x-1,+y,+z #2 -x+1/2,-y+1,+z-1/2 #3 +x+1/2,-y+1/2,-z+1 #4 +x-1/2,-y+1/2,-z+1
#5 +x+1,+y,+z #6 -x+1,+y-1/2,-z+1/2 #7 -x+1/2,-y+1,+z+1/2 #8 -x+1,+y+1/2,-z+1/2
#9 +x-1/2,-y+1/2,-z #10 -x+3/2,-y+1,+z-1/2

Table S19. Contacts involving chlorine (solvent) with the chloride anion Cl…Cl and the water molecule Cl…O less than the sum of the van der Waals radii + 0.3 Å in **12**.

3.719 (1) Cl3…Cl1	64.9(1) C22 - Cl3…Cl1
3.274(3) Cl3…O1	168.1 (1) C22 - Cl3…O1

Table S20. Cation/water C…O and N…O contacts made to electron density in the bonds of the cation backbone that are less than the sum of the van der Waals radii + 0.2 Å in **12**.

3.177(4) C1…O2	96.9(2) C2 - C1 - O2
3.050(4) N1…O2	83.3(2) C1 - N1 - O2
3.3801(4) C3…O2_$1	114.7(2) C2 - C3…O2_$1
3.210(4) N2…O2_$1	85.9(2) C3 - N2…O2_$1

Symmetry transformations used to generate equivalent atoms:
#1 +x-1, +y, +z

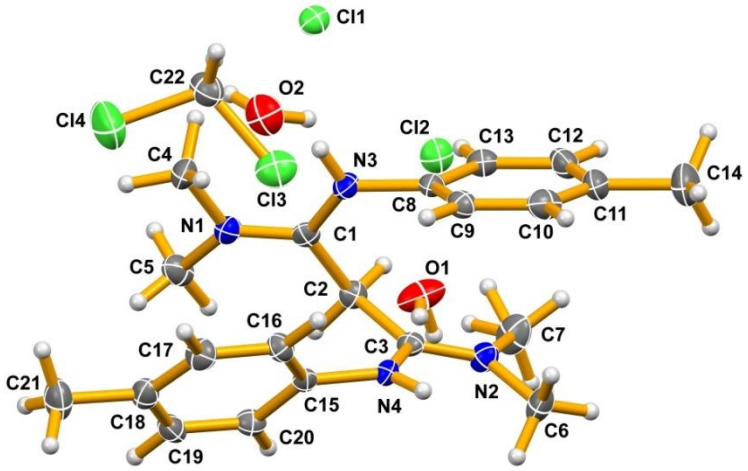


Figure S56: Structure of **12**. There are one cation, two chloride anions, one molecule of dichloromethane and two molecules of water in the asymmetric unit. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have not been labelled.

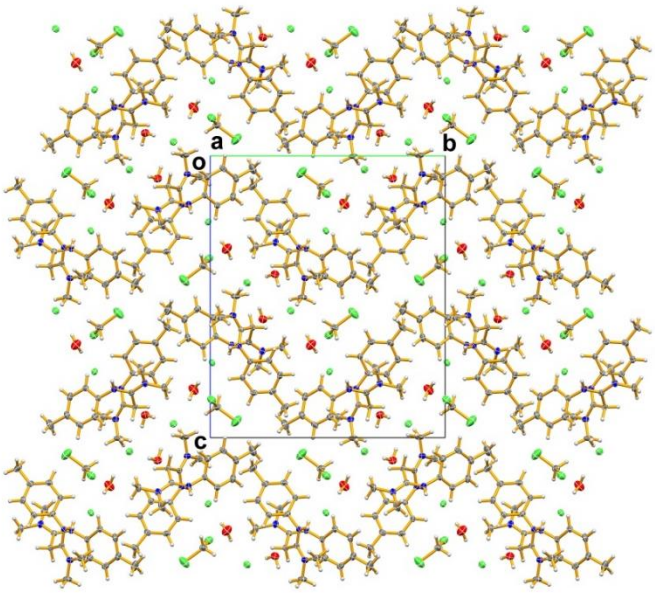


Figure S57: Packing diagram of **12** viewed down the *X*-axis. Thermal ellipsoids have been drawn at the 50% probability level.

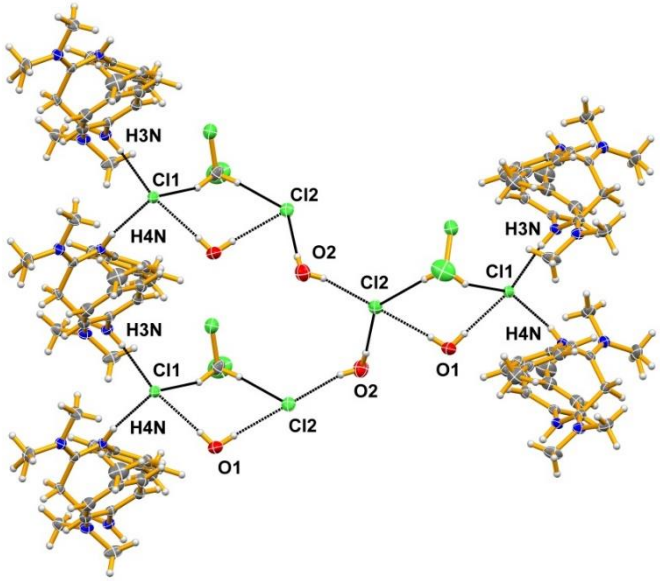


Figure S58: N-H…Cl and O-H…Cl hydrogen bonds (Table S17) in the structure of **12**. These form a 3D network that extends through the entire crystal. Thermal ellipsoids have been drawn at the 50% probability level. Only the atoms involved in the hydrogen bonds have been labelled.

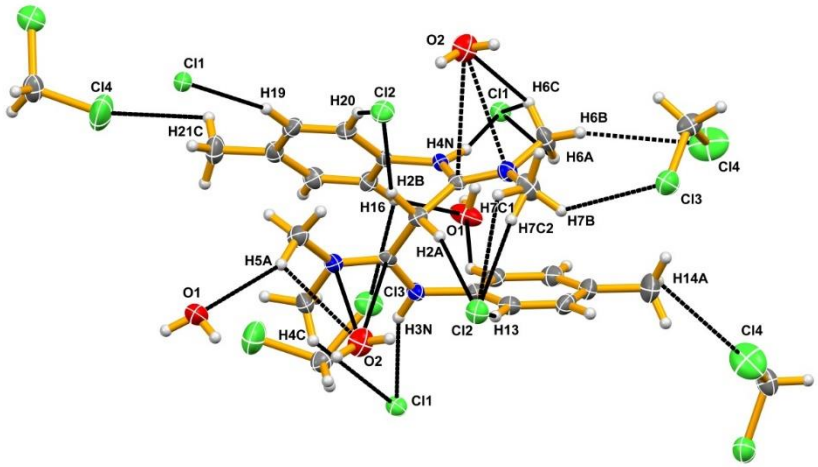


Figure S59: Interactions involving the cation (dotted lines) in **12**. C-H…Cl and C-H…O hydrogen bonding (Table S18) and contacts from water molecules to electron density in the backbone of the cation (Table S20) are shown from the perspective of one central cation. Thermal ellipsoids have been drawn with 50% probability. Only the atoms participating in the contacts have been labelled.

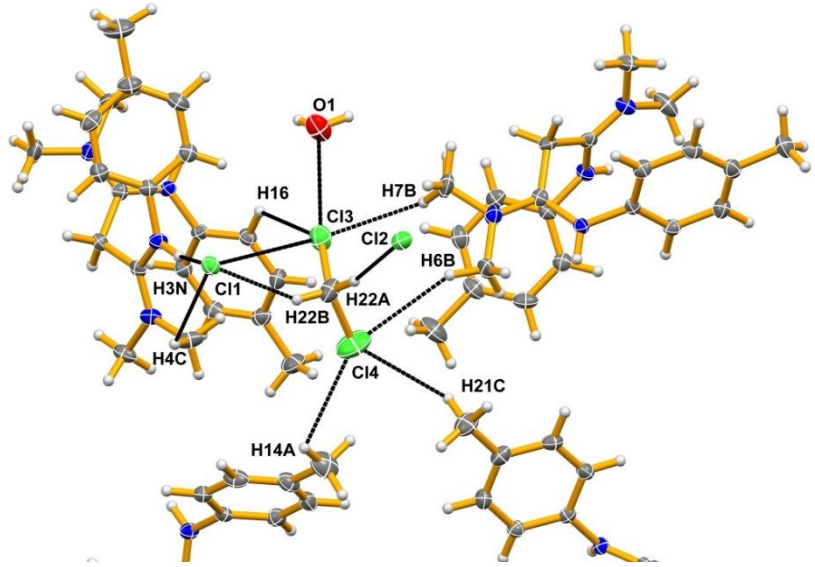


Figure S60: Selected solvent Cl…Cl and Cl…O contacts (Table S19), and C-H…Cl contacts (Table S18) in the structure of **12** shown from the perspective of one central dichloromethane molecule. Thermal ellipsoids have been drawn at the 50% probability level. Only atoms involved in the contacts have been labelled. The lower two cations have been cut off beyond the phenyl groups shown.

Additional Computational Details, Images, and Coordinates

Table S21: Electronic Energies and Thermodynamic Parameters at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

	E_{elec} (hartree)	**ZPE (hartree)**	**H° (hartree)**	**S° (cal/mol•K)**	**G° (hartree)**
INT 1	-1056.813428	0.325008	-1056.468552	140.452	-1056.535285
TS 1-2	-1056.782283	0.323177	-1056.438696	144.144	-1056.507183
TS 1-2a	-1056.761927	0.323511	-1056.419290	134.235	-1056.483070
INT 2	-1056.817367	0.325897	-1056.471083	145.054	-1056.540003
TS 2-3	-1056.805038	0.323373	-1056.460863	150.769	-1056.532498
INT 3	-1056.839882	0.325970	-1056.493371	146.593	-1056.563022
TS 3-4	-1270.639083	0.478551	-1270.133321	176.269	-1270.217072
INT 4	-1270.667807	0.479466	-1270.161131	174.026	-1270.243817
INT 5a	-809.815111	0.464231	-809.325640	162.819	-809.403001
INT 5	-1270.711562	0.479843	-1270.204290	173.629	-1270.286787
$H_2N(tBu)$	-213.805568	0.149079	-213.648852	76.900	-213.685390
DIPEA	-371.032234	0.263135	-370.756582	101.616	-370.804863
DIPEA HCl	-831.902664	0.279909	-831.608167	113.288	-831.661994
INT 6a	-1094.915544	0.334119	-1094.561708	144.591	-1094.630407
TS 6-7a	-1094.882605	0.330977	-1094.531820	143.733	-1094.600112
INT 7a	-1094.971460	0.334843	-1094.616178	147.539	-1094.686279
INT 6b	-1017.503814	0.296919	-1017.188154	136.834	-1017.253168
TS 6-7b	-1017.469200	0.293371	-1017.156665	139.546	-1017.222968
INT 7b	-1017.557168	0.296837	-1017.240223	145.965	-1017.309576

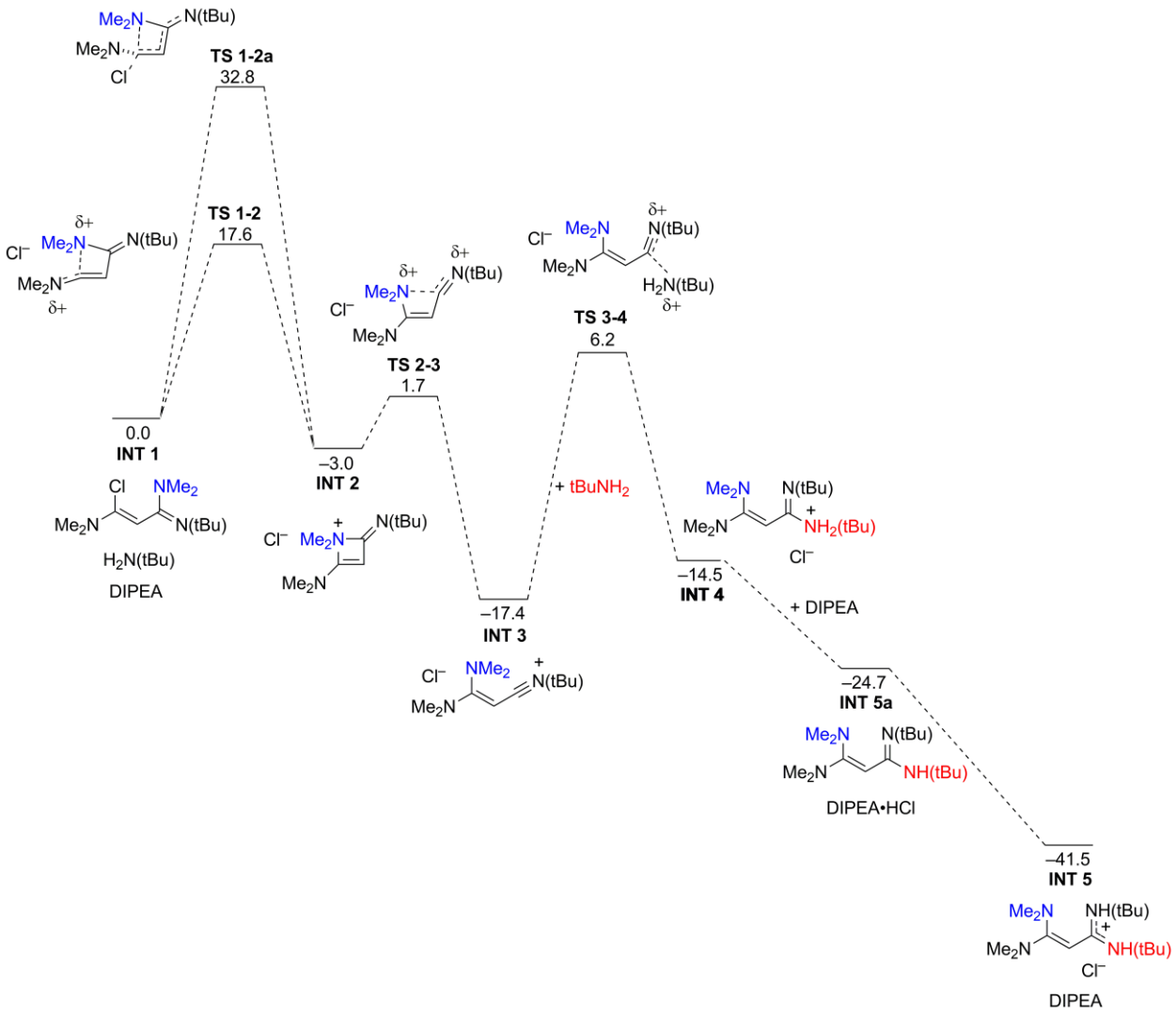


Figure S61: Calculated relative free energy diagram for the transformation of **INT1** to **INT5**. Optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform. Gibbs energies are in kcal/mol.

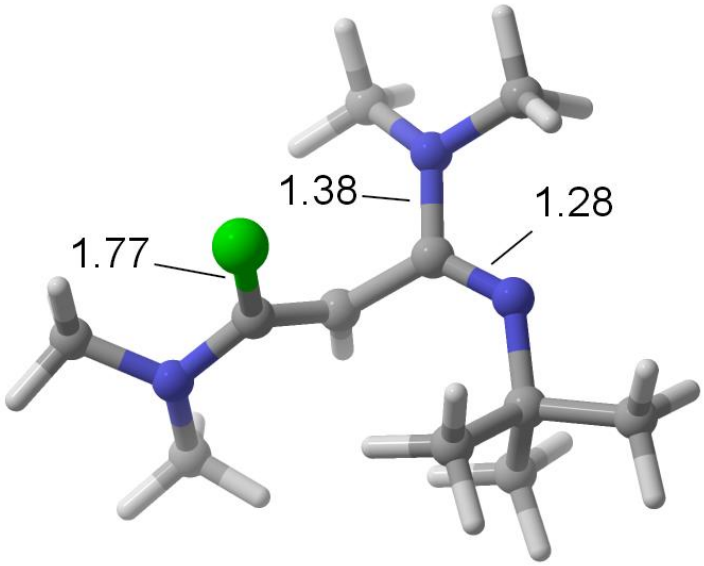


Figure S62: Optimized structure of **INT 1**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform. All DFT images were prepared using CYLview20 [6].

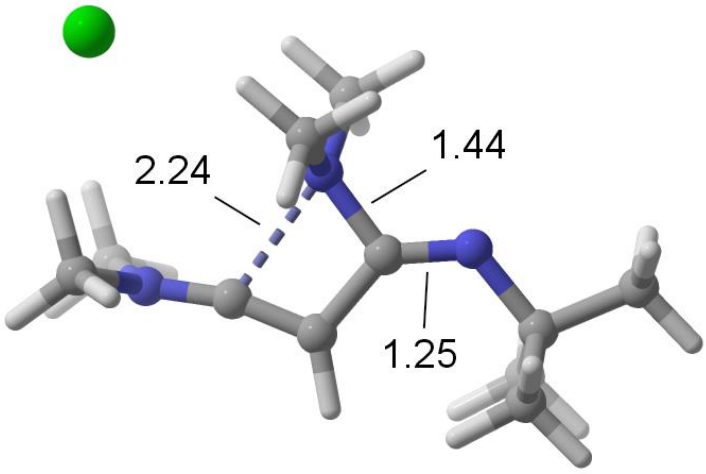


Figure S63: Optimized structure of **TS 1-2**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

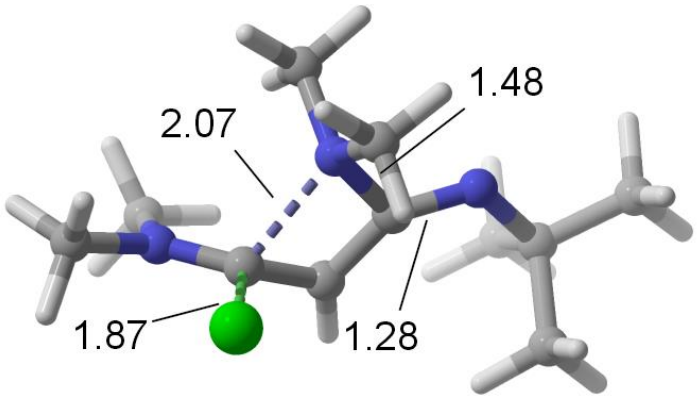


Figure S64: Optimized structure of **TS 1-2a**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

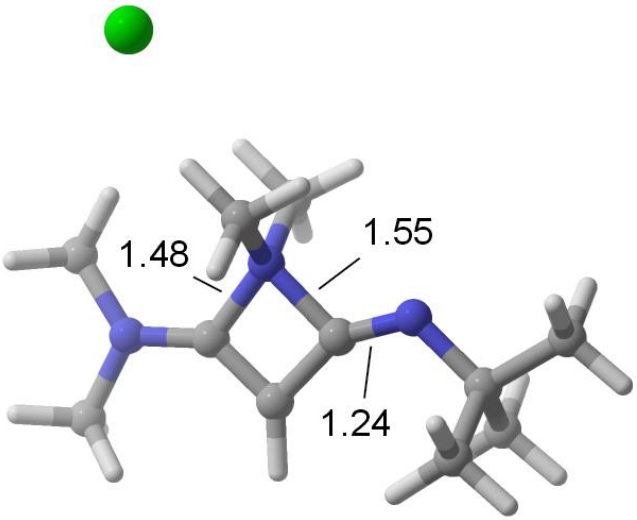


Figure S65: Optimized structure of **INT 2**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

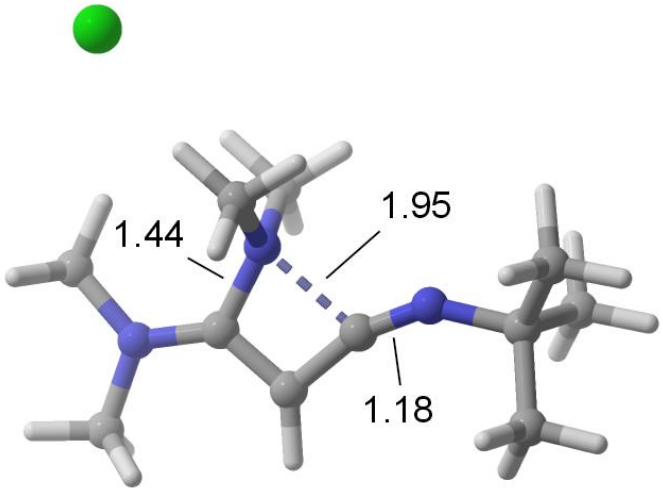


Figure S66: Optimized structure of **TS 2-3**. Geometry optimizations were performed at the *ω*B97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

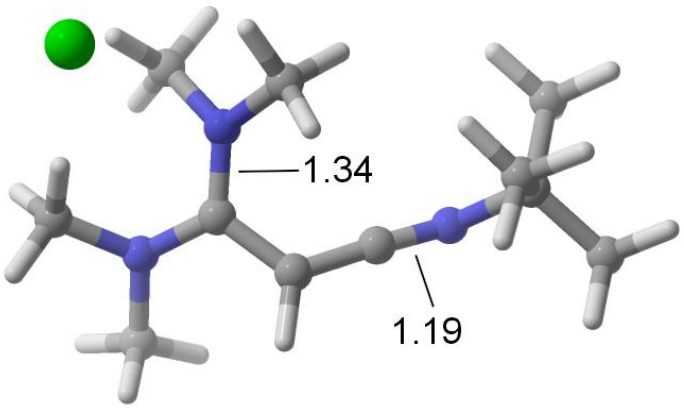


Figure S67: Optimized structure of **INT 3**. Geometry optimizations were performed at the *ω*B97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

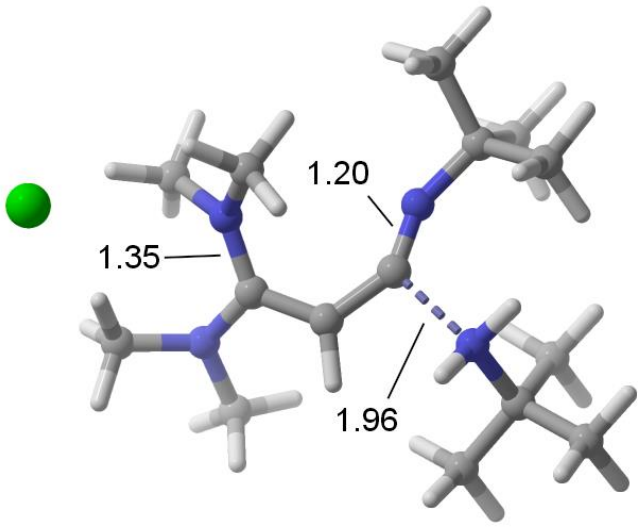


Figure S68: Optimized structure of **TS 3-4**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

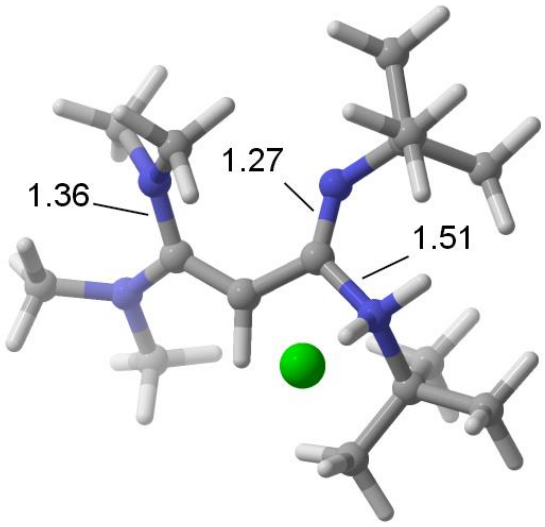


Figure S69: Optimized structure of **INT 4**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

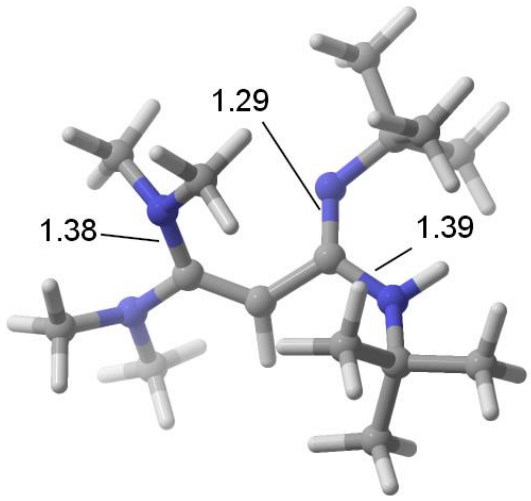


Figure S70: Optimized structure of **INT 5a**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

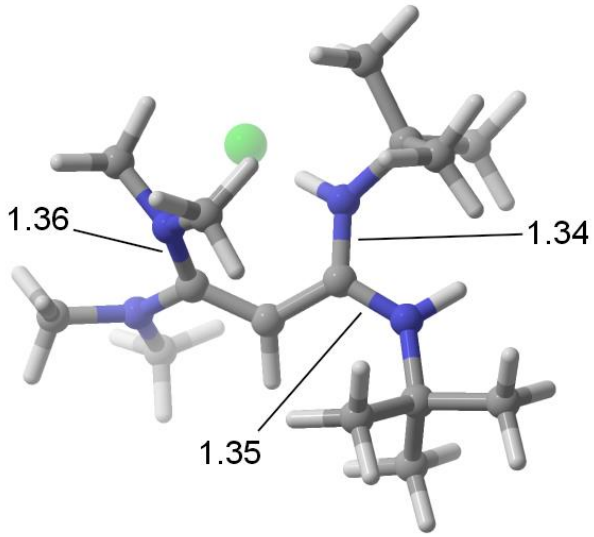


Figure S71: Optimized structure of **INT 5**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

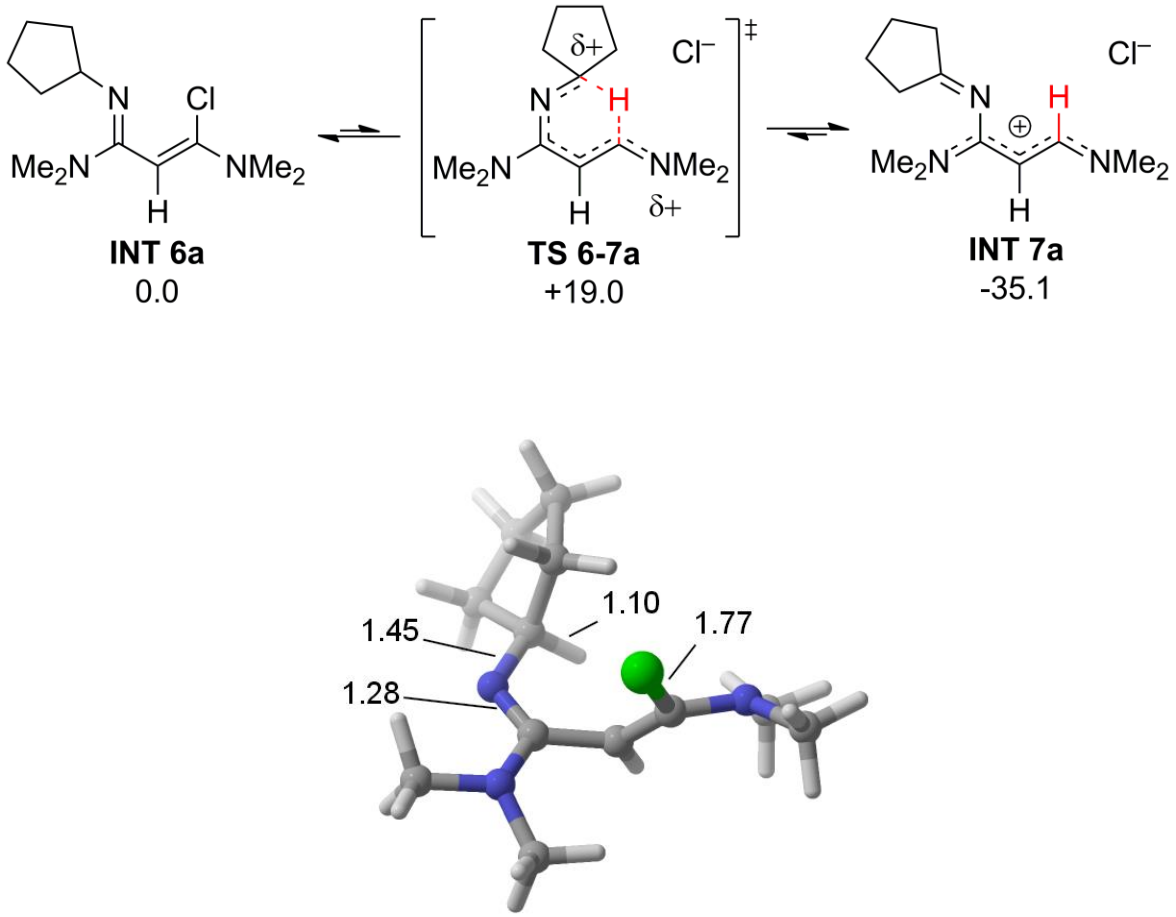


Figure S72: Optimized structure of **INT 6a**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

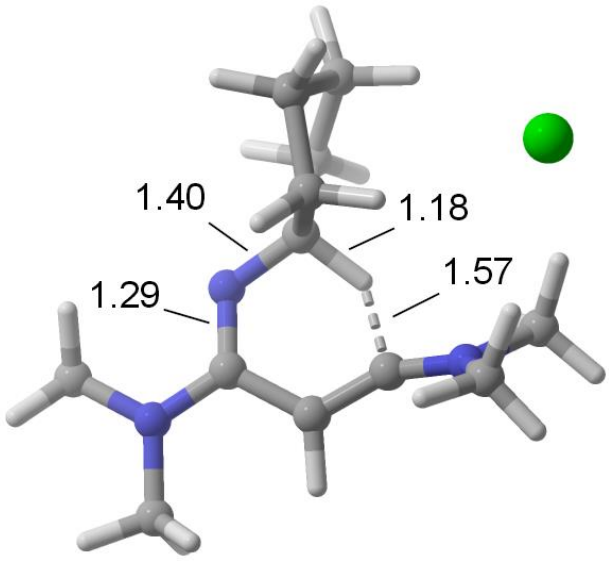


Figure S73: Optimized structure of **TS 6-7a**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

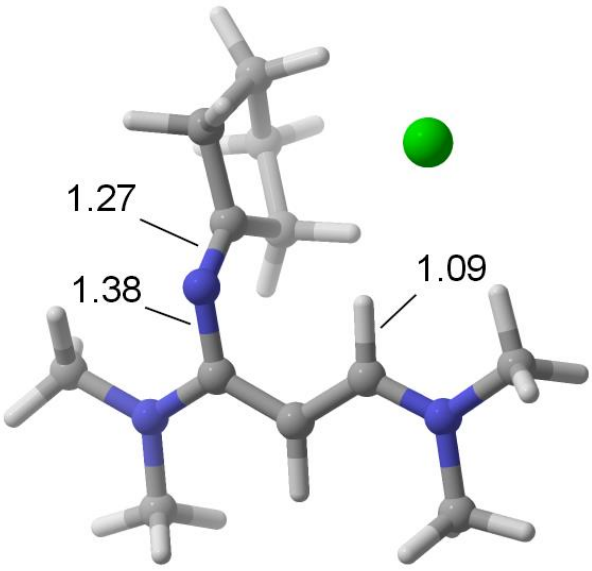


Figure S74: Optimized structure of **INT 7a**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

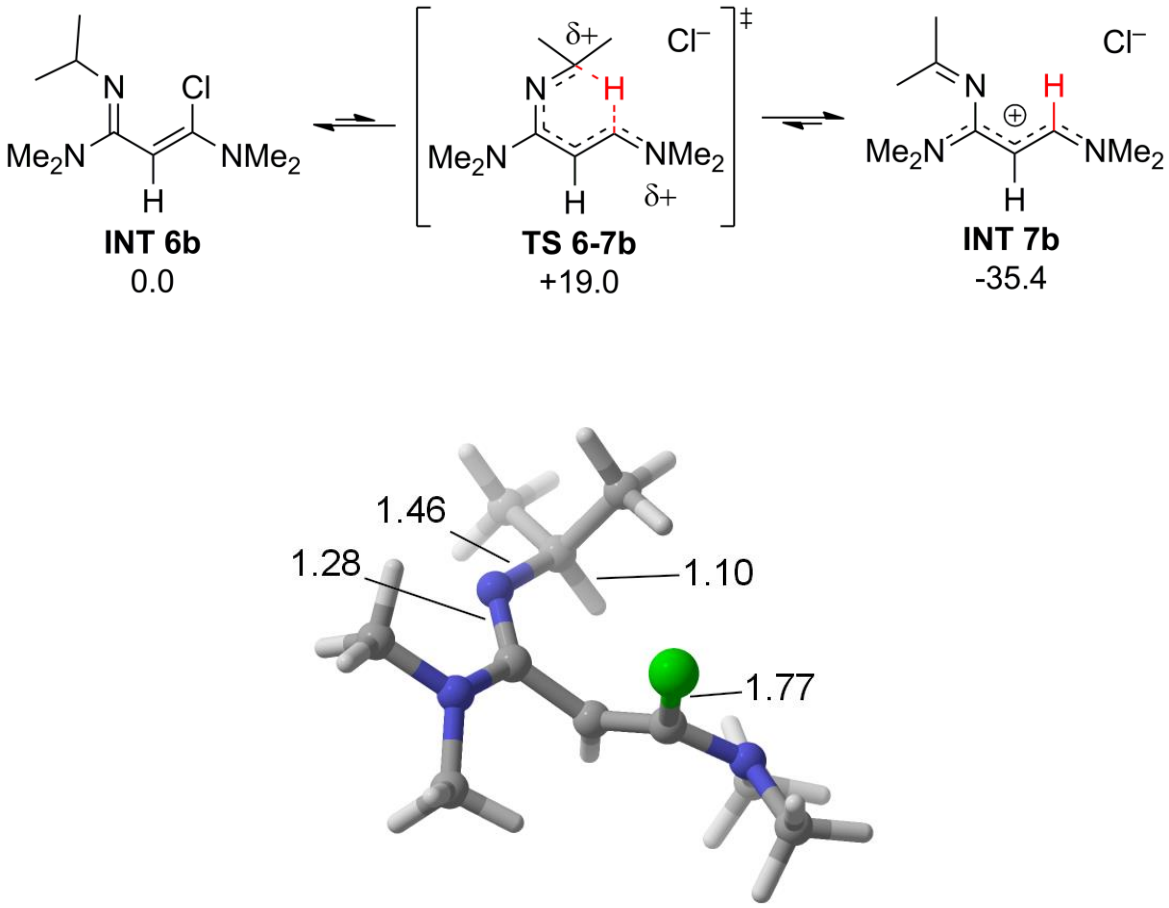


Figure S75: Optimized structure of **INT 6b**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

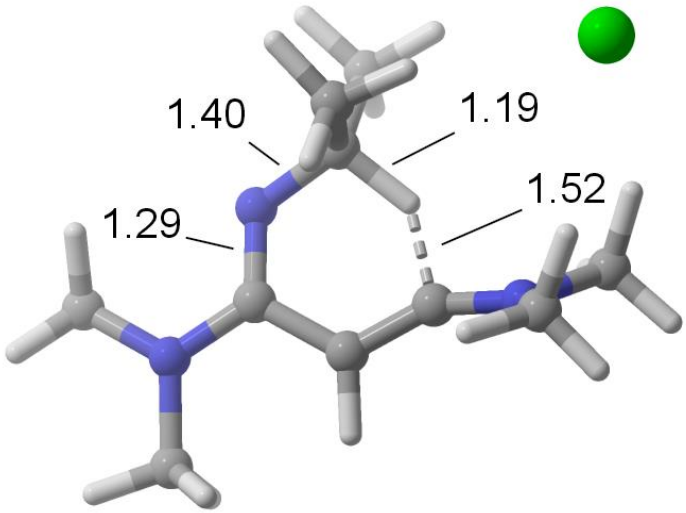


Figure S76: Optimized structure of **TS 6-7b**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

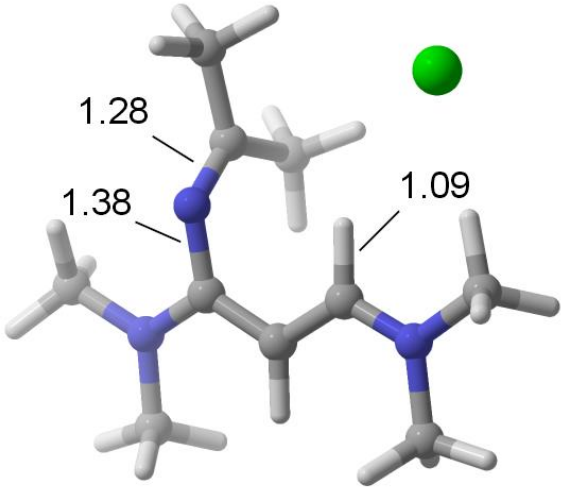


Figure S77: Optimized structure of **INT 7b**. Geometry optimizations were performed at the ωB97X-D/6-311G(d,p) level of theory with a C-PCM solvent model for chloroform.

Atomic Coordinates:

INT1

atom	x	y	z	atom	x	y	z
C	-1.504000	-0.091000	0.073000	C	2.038000	2.815000	0.007000
Cl	-1.495000	0.663000	1.673000	H	1.804000	3.862000	0.212000
N	-2.593000	-0.908000	-0.149000	H	2.776000	2.768000	-0.806000
C	-3.929000	-0.355000	0.047000	H	2.489000	2.362000	0.889000
H	-4.223000	0.299000	-0.786000	H	-0.498000	-0.336000	-1.726000
H	-3.973000	0.214000	0.973000	C	2.105000	-1.298000	0.101000
H	-4.643000	-1.177000	0.116000	C	3.580000	-1.477000	0.493000
C	-2.500000	-1.800000	-1.292000	H	4.229000	-1.057000	-0.281000
H	-1.560000	-2.353000	-1.255000	H	3.829000	-2.535000	0.622000
H	-2.564000	-1.270000	-2.253000	H	3.786000	-0.952000	1.429000
H	-3.323000	-2.514000	-1.239000	C	1.869000	-2.048000	-1.219000
C	-0.450000	0.082000	-0.728000	H	2.430000	-1.574000	-2.029000
C	0.835000	0.743000	-0.347000	H	0.814000	-2.068000	-1.496000
N	1.928000	0.152000	-0.041000	H	2.207000	-3.085000	-1.129000
N	0.812000	2.123000	-0.330000	C	1.236000	-1.894000	1.220000
C	-0.132000	2.891000	-1.119000	H	1.535000	-2.928000	1.415000
H	-0.371000	3.821000	-0.598000	H	0.177000	-1.893000	0.961000
H	-1.054000	2.332000	-1.260000	H	1.366000	-1.320000	2.142000
H	0.276000	3.147000	-2.107000				

TS1-2

atom	x	y	z	atom	x	y	z
C	0.764000	1.304000	0.071000	C	0.590000	-1.446000	1.441000
Cl	4.120000	-1.343000	-0.200000	H	1.633000	-1.765000	1.425000
N	1.971000	1.648000	-0.004000	H	-0.056000	-2.301000	1.679000
C	2.646000	1.782000	-1.307000	H	0.463000	-0.685000	2.214000
H	1.901000	1.762000	-2.099000	H	-1.135000	2.162000	0.251000
H	3.337000	0.941000	-1.401000	C	-3.385000	-0.010000	-0.076000
H	3.184000	2.730000	-1.314000	C	-4.444000	-1.109000	-0.215000
C	2.829000	1.673000	1.196000	H	-4.262000	-1.699000	-1.116000
H	2.204000	1.612000	2.083000	H	-5.446000	-0.675000	-0.279000
H	3.386000	2.609000	1.190000	H	-4.409000	-1.780000	0.646000
H	3.504000	0.816000	1.132000	C	-3.436000	0.894000	-1.315000
C	-0.538000	1.264000	0.167000	H	-3.195000	0.320000	-2.213000
C	-0.978000	-0.149000	0.114000	H	-2.743000	1.735000	-1.250000
N	-2.091000	-0.711000	0.003000	H	-4.443000	1.303000	-1.429000
N	0.265000	-0.884000	0.129000	C	-3.651000	0.782000	1.210000
C	0.409000	-1.861000	-0.947000	H	-4.665000	1.188000	1.189000
H	1.450000	-2.187000	-0.962000	H	-2.962000	1.619000	1.339000
H	0.171000	-1.387000	-1.901000	H	-3.562000	0.129000	2.082000
H	-0.252000	-2.724000	-0.803000				

TS1-2a

atom	x	y	z	atom	x	y	z
C	-1.446000	0.215000	-0.465000	C	-0.241000	-2.285000	1.034000
Cl	-2.088000	-1.265000	-1.404000	H	-1.161000	-2.719000	1.432000
N	-2.459000	0.978000	-0.070000	H	0.603000	-2.566000	1.673000
C	-3.859000	0.554000	-0.039000	H	-0.068000	-2.675000	0.032000
H	-3.953000	-0.423000	0.436000	H	0.176000	1.418000	-1.355000
H	-4.277000	0.507000	-1.045000	C	2.984000	0.251000	-0.220000
H	-4.418000	1.283000	0.544000	C	4.281000	-0.303000	0.380000
C	-2.211000	2.330000	0.432000	H	4.333000	-0.068000	1.446000
H	-1.142000	2.520000	0.443000	H	5.161000	0.119000	-0.115000
H	-2.618000	2.428000	1.441000	H	4.309000	-1.391000	0.272000
H	-2.702000	3.055000	-0.222000	C	2.973000	1.778000	-0.038000
C	-0.106000	0.641000	-0.661000	H	2.997000	2.026000	1.027000
C	0.671000	-0.140000	0.211000	H	2.079000	2.231000	-0.471000
N	1.889000	-0.378000	0.523000	H	3.848000	2.230000	-0.516000
N	-0.386000	-0.835000	0.973000	C	2.940000	-0.109000	-1.714000
C	-0.615000	-0.251000	2.289000	H	3.807000	0.309000	-2.235000
H	-1.543000	-0.649000	2.706000	H	2.037000	0.271000	-2.196000
H	-0.699000	0.832000	2.198000	H	2.957000	-1.196000	-1.836000
H	0.215000	-0.479000	2.967000				

INT2

atom	x	y	z	atom	x	y	z
C	-0.65400	1.22300	-0.00300	C	-0.86900	-0.96700	-1.24600
Cl	-4.06800	-2.19200	-0.02700	H	-1.93400	-1.19600	-1.20800
N	-1.79800	1.87300	-0.06300	H	-0.29400	-1.89100	-1.27400
C	-1.73100	3.33000	-0.06400	H	-0.61800	-0.34200	-2.10100
H	-0.83800	3.66100	-0.59600	H	1.24400	2.43300	0.03500
H	-1.71300	3.71900	0.95800	C	3.34800	-0.43600	0.00300
H	-2.60800	3.71700	-0.58100	C	4.09200	-1.77200	-0.01700
C	-3.11400	1.27600	0.14200	H	3.82700	-2.36700	0.86000
H	-3.80100	1.69000	-0.59700	H	5.17300	-1.61000	-0.01500
H	-3.48000	1.51500	1.14400	H	3.82600	-2.34200	-0.91100
H	-3.10300	0.19400	0.02000	C	3.70600	0.34000	1.27600
C	0.68100	1.51800	0.01400	H	3.40800	-0.22500	2.16300
C	1.03900	0.12700	0.00300	H	3.21200	1.31500	1.30600
N	1.90700	-0.75900	0.00200	H	4.78500	0.50600	1.32100
N	-0.46700	-0.24900	-0.00400	C	3.70400	0.37600	-1.24800
C	-0.86700	-0.98400	1.23000	H	4.78400	0.54200	-1.29000
H	-1.92600	-1.23900	1.17800	H	3.21300	1.35300	-1.24800
H	-0.64000	-0.35900	2.09200	H	3.40400	-0.16200	-2.15000
H	-0.26800	-1.89300	1.25900				

TS2-3

atom	x	y	z	atom	x	y	z
C	-0.804000	1.244000	0.021000	C	-0.901000	-0.897000	-1.242000
Cl	-4.089000	-2.373000	-0.004000	H	-1.923000	-1.286000	-1.243000
N	-1.974000	1.850000	-0.046000	H	-0.201000	-1.734000	-1.309000
C	-1.989000	3.307000	-0.041000	H	-0.740000	-0.231000	-2.089000
H	-1.201000	3.692000	-0.691000	H	0.880000	2.730000	0.153000
H	-1.846000	3.695000	0.971000	C	3.561000	-0.441000	-0.012000
H	-2.951000	3.648000	-0.421000	C	3.835000	-1.620000	-0.947000
C	-3.263000	1.171000	0.029000	H	3.334000	-2.520000	-0.587000
H	-3.872000	1.465000	-0.828000	H	4.910000	-1.811000	-0.992000
H	-3.776000	1.464000	0.948000	H	3.479000	-1.401000	-1.956000
H	-3.158000	0.088000	0.020000	C	4.020000	-0.762000	1.413000
C	0.479000	1.732000	0.082000	H	3.517000	-1.656000	1.787000
C	1.215000	0.528000	0.046000	H	3.803000	0.071000	2.086000
N	2.116000	-0.240000	0.033000	H	5.097000	-0.941000	1.416000
N	-0.599000	-0.179000	0.001000	C	4.228000	0.836000	-0.529000
C	-0.887000	-0.933000	1.227000	H	5.310000	0.690000	-0.582000
H	-1.909000	-1.323000	1.226000	H	4.025000	1.676000	0.138000
H	-0.719000	-0.291000	2.092000	H	3.864000	1.083000	-1.529000
H	-0.186000	-1.771000	1.264000				

INT3

atom	x	y	z	atom	x	y	z
C	-0.973000	0.908000	0.028000	C	-0.297000	-1.439000	0.309000
Cl	-3.635000	-2.360000	-0.758000	H	-0.984000	-2.286000	0.320000
N	-2.019000	1.743000	0.005000	H	0.525000	-1.618000	1.010000
C	-1.854000	3.165000	-0.273000	H	0.090000	-1.332000	-0.702000
H	-1.990000	3.379000	-1.338000	H	0.184000	1.994000	-1.479000
H	-0.872000	3.505000	0.046000	C	3.608000	-0.297000	-0.062000
H	-2.611000	3.711000	0.290000	C	3.806000	-1.041000	1.259000
C	-3.404000	1.270000	-0.002000	H	4.059000	-0.346000	2.061000
H	-3.921000	1.775000	-0.821000	H	4.623000	-1.758000	1.147000
H	-3.913000	1.513000	0.934000	H	2.904000	-1.589000	1.539000
H	-3.443000	0.196000	-0.184000	C	4.860000	0.503000	-0.427000
C	0.234000	1.301000	-0.650000	H	5.114000	1.208000	0.367000
C	1.450000	0.922000	-0.242000	H	4.709000	1.058000	-1.356000
N	2.539000	0.694000	0.168000	H	5.698000	-0.184000	-0.567000
N	-1.056000	-0.253000	0.686000	C	3.221000	-1.254000	-1.188000
C	-1.925000	-0.442000	1.844000	H	4.048000	-1.940000	-1.382000
H	-2.796000	-1.046000	1.581000	H	3.007000	-0.706000	-2.110000
H	-2.234000	0.523000	2.242000	H	2.345000	-1.847000	-0.918000
H	-1.345000	-0.962000	2.609000				

TS3-4

atom	x	y	z	atom	x	y	z
C	1.442000	-0.661000	0.375000	H	-1.581000	4.583000	0.267000
Cl	5.365000	0.450000	-1.517000	H	-0.524000	3.678000	-0.832000
N	2.088000	-1.724000	0.917000	C	-2.553000	2.475000	1.707000
C	1.353000	-2.882000	1.394000	H	-1.790000	2.480000	2.488000
H	1.197000	-3.626000	0.602000	H	-3.196000	1.606000	1.855000
H	0.387000	-2.575000	1.791000	H	-3.161000	3.377000	1.807000
H	1.928000	-3.352000	2.194000	C	-2.964000	2.455000	-0.779000
C	3.521000	-1.935000	0.734000	H	-3.487000	3.413000	-0.762000
H	3.673000	-2.914000	0.272000	H	-3.715000	1.678000	-0.624000
H	4.050000	-1.916000	1.692000	H	-2.509000	2.339000	-1.766000
H	3.944000	-1.178000	0.073000	N	-2.263000	-0.703000	-1.155000
C	0.151000	-0.843000	-0.160000	H	-1.804000	-1.156000	-1.943000
C	-0.827000	0.154000	-0.141000	H	-2.773000	0.085000	-1.544000
N	-1.054000	1.269000	0.253000	C	-3.229000	-1.650000	-0.516000
N	2.078000	0.527000	0.371000	C	-2.507000	-2.953000	-0.174000
C	3.045000	0.905000	1.392000	H	-1.754000	-2.800000	0.600000
H	4.063000	0.900000	0.989000	H	-2.025000	-3.386000	-1.056000
H	2.976000	0.228000	2.241000	H	-3.232000	-3.679000	0.199000
H	2.803000	1.916000	1.731000	C	-3.772000	-1.006000	0.758000
C	1.897000	1.509000	-0.684000	H	-2.962000	-0.769000	1.451000
H	2.886000	1.777000	-1.066000	H	-4.457000	-1.697000	1.254000
H	1.389000	2.399000	-0.307000	H	-4.327000	-0.090000	0.539000
H	1.313000	1.080000	-1.495000	C	-4.366000	-1.925000	-1.506000
H	-0.121000	-1.829000	-0.493000	H	-4.889000	-1.001000	-1.770000
C	-1.895000	2.443000	0.322000	H	-5.094000	-2.610000	-1.063000
C	-0.990000	3.671000	0.156000	H	-3.984000	-2.382000	-2.423000
H	-0.205000	3.671000	0.915000				

INT4

atom	x	y	z	atom	x	y	z
C	-2.164000	-0.312000	-0.035000	H	1.321000	4.596000	-0.759000
Cl	1.669000	-1.363000	2.999000	H	-0.188000	3.988000	-0.050000
N	-3.127000	-1.162000	-0.507000	C	2.408000	2.207000	-1.445000
C	-2.790000	-2.236000	-1.420000	H	1.969000	2.021000	-2.428000
H	-2.493000	-3.151000	-0.892000	H	3.073000	1.373000	-1.205000
H	-1.974000	-1.926000	-2.073000	H	3.040000	3.095000	-1.513000
H	-3.665000	-2.464000	-2.033000	C	1.890000	2.582000	1.011000
C	-4.409000	-1.310000	0.165000	H	2.582000	3.429000	1.043000
H	-5.240000	-1.057000	-0.501000	H	2.444000	1.700000	1.346000
H	-4.449000	-0.664000	1.040000	H	1.092000	2.760000	1.735000
H	-4.531000	-2.347000	0.496000	N	1.597000	-0.510000	0.085000
C	-0.829000	-0.690000	-0.067000	H	1.576000	-0.879000	1.082000
C	0.285000	0.195000	-0.178000	H	2.312000	0.211000	0.100000
N	0.234000	1.436000	-0.438000	C	2.119000	-1.611000	-0.849000
N	-2.616000	0.864000	0.480000	C	1.806000	-1.248000	-2.295000
C	-3.694000	1.610000	-0.143000	H	2.295000	-0.321000	-2.599000
H	-4.550000	1.724000	0.531000	H	0.730000	-1.148000	-2.453000
H	-4.024000	1.104000	-1.049000	H	2.172000	-2.050000	-2.940000
H	-3.332000	2.607000	-0.414000	C	3.628000	-1.646000	-0.594000
C	-1.931000	1.549000	1.553000	H	4.102000	-0.693000	-0.849000
H	-2.676000	1.921000	2.263000	H	4.083000	-2.419000	-1.214000
H	-1.336000	2.387000	1.178000	H	3.838000	-1.875000	0.454000
H	-1.266000	0.857000	2.069000	C	1.514000	-2.967000	-0.480000
H	-0.628000	-1.747000	-0.056000	H	1.517000	-3.125000	0.601000
C	1.299000	2.443000	-0.404000	H	2.124000	-3.747000	-0.940000
C	0.608000	3.767000	-0.766000	H	0.500000	-3.086000	-0.860000
H	0.161000	3.696000	-1.760000				

INT5

atom	x	y	z	atom	x	y	z
C	-1.53000	-0.97800	0.30200	H	-0.23100	3.19400	1.50000
N	-2.56400	-1.63900	-0.26900	C	1.90500	2.82200	-1.19500
C	-2.52400	-2.02200	-1.66900	H	1.15200	2.96700	-1.97300
H	-2.13700	-3.04000	-1.80200	H	2.63600	2.09800	-1.56600
H	-1.90600	-1.31700	-2.22200	H	2.43300	3.76600	-1.03900
H	-3.53900	-1.98200	-2.07000	C	2.25800	2.17400	1.23200
C	-3.67200	-2.17900	0.50100	H	2.68700	3.14500	1.48900
H	-4.60500	-1.64400	0.29900	H	3.08200	1.51600	0.95900
H	-3.45100	-2.12000	1.56500	H	1.77900	1.76500	2.12500
H	-3.80900	-3.23000	0.23300	N	2.06100	-0.42300	-0.39300
C	-0.24000	-1.12000	-0.22600	H	2.64600	0.33600	-0.69600
C	0.75800	-0.12200	-0.22700	C	2.78500	-1.69300	-0.17400
N	0.40300	1.17000	-0.11100	C	2.61100	-2.64700	-1.36300
N	-1.80900	-0.26000	1.42300	H	2.89200	-2.14800	-2.29300
C	-3.02800	0.52700	1.54300	H	1.58400	-3.00100	-1.45900
H	-3.67900	0.14800	2.33700	H	3.25400	-3.52100	-1.23200
H	-3.55800	0.53500	0.59300	C	4.26200	-1.29600	-0.06700
H	-2.75400	1.56100	1.77600	H	4.60100	-0.79700	-0.98000
C	-0.82000	-0.01000	2.45000	H	4.87800	-2.18500	0.07700
H	-1.29900	-0.10100	3.42900	H	4.42500	-0.62500	0.78100
H	-0.39500	0.99500	2.36000	C	2.35400	-2.35400	1.13900
H	-0.01500	-0.73900	2.38100	H	2.46900	-1.65500	1.97100
H	-0.03200	-2.02800	-0.76900	H	2.98900	-3.22300	1.32700
C	1.22900	2.37400	0.11000	H	1.31700	-2.68800	1.10800
C	0.24000	3.46200	0.55000	H	-0.54600	1.36800	-0.43800
H	-0.54400	3.59600	-0.19800	Cl	-2.30900	1.82800	-1.77900
H	0.76600	4.41000	0.68100				

INT5a

atom	x	y	z	atom	x	y	z
C	1.954000	0.026000	-0.091000	H	-2.466000	-4.086000	-0.316000
N	3.180000	0.429000	-0.612000	H	-0.954000	-3.645000	0.506000
C	3.214000	1.214000	-1.825000	C	-2.847000	-1.756000	-1.665000
H	2.998000	2.280000	-1.650000	H	-2.269000	-1.977000	-2.566000
H	2.488000	0.827000	-2.541000	H	-3.237000	-0.740000	-1.765000
H	4.213000	1.143000	-2.263000	H	-3.707000	-2.433000	-1.635000
C	4.283000	0.710000	0.293000	C	-2.746000	-1.645000	0.871000
H	5.231000	0.409000	-0.163000	H	-3.595000	-2.328000	0.969000
H	4.151000	0.160000	1.222000	H	-3.140000	-0.628000	0.908000
H	4.338000	1.783000	0.526000	H	-2.097000	-1.780000	1.741000
C	0.792000	0.617000	-0.493000	N	-1.599000	0.959000	-0.467000
C	-0.552000	0.039000	-0.453000	H	-2.496000	0.517000	-0.559000
N	-0.689000	-1.241000	-0.524000	C	-1.704000	2.227000	0.291000
N	2.072000	-0.970000	0.861000	C	-1.041000	3.394000	-0.453000
C	2.862000	-2.152000	0.575000	H	-1.390000	3.430000	-1.488000
H	3.458000	-2.437000	1.449000	H	0.046000	3.311000	-0.455000
H	3.535000	-1.958000	-0.258000	H	-1.298000	4.340000	0.033000
H	2.210000	-2.996000	0.311000	C	-3.207000	2.514000	0.392000
C	1.084000	-1.159000	1.895000	H	-3.656000	2.583000	-0.603000
H	1.587000	-1.517000	2.799000	H	-3.379000	3.459000	0.910000
H	0.314000	-1.880000	1.599000	H	-3.721000	1.725000	0.952000
H	0.593000	-0.212000	2.119000	C	-1.122000	2.100000	1.703000
H	0.876000	1.566000	-1.002000	H	-1.581000	1.260000	2.233000
C	-1.963000	-1.959000	-0.420000	H	-1.313000	3.014000	2.272000
C	-1.579000	-3.447000	-0.369000	H	-0.043000	1.940000	1.666000
H	-1.005000	-3.714000	-1.260000				

$tBuNH_2$

atom	x	y	z	atom	x	y	z
N	0.000000	0.255000	1.468000	H	-0.886000	1.892000	-0.571000
C	0.000000	-0.006000	0.018000	H	0.000000	1.088000	-1.878000
C	1.253000	-0.822000	-0.304000	C	-1.253000	-0.822000	-0.304000
H	1.292000	-1.073000	-1.368000	H	-1.263000	-1.749000	0.275000
H	1.263000	-1.749000	0.275000	H	-1.292000	-1.073000	-1.368000
H	2.158000	-0.256000	-0.059000	H	-2.158000	-0.256000	-0.059000
C	0.000000	1.293000	-0.803000	H	-0.809000	0.823000	1.703000
H	0.886000	1.892000	-0.571000	H	0.809000	0.823000	1.703000

DIPEA

atom	x	y	z	atom	x	y	z
N	0.044000	0.132000	-0.124000	H	-0.817000	-1.550000	-0.947000
C	1.310000	-0.520000	0.241000	H	-1.949000	0.416000	-1.877000
C	2.485000	0.422000	-0.037000	H	-3.081000	-0.749000	-1.161000
C	1.542000	-1.826000	-0.520000	H	-2.707000	0.750000	-0.311000
H	1.321000	-0.759000	1.322000	H	-0.742000	-1.977000	1.514000
H	2.409000	1.360000	0.516000	H	-1.934000	-0.696000	1.772000
H	3.425000	-0.056000	0.252000	H	-2.374000	-2.139000	0.854000
H	2.526000	0.658000	-1.104000	C	-0.224000	1.329000	0.683000
H	0.852000	-2.619000	-0.226000	C	-0.161000	2.620000	-0.129000
H	1.447000	-1.662000	-1.598000	H	0.483000	1.384000	1.520000
H	2.555000	-2.183000	-0.319000	H	-1.210000	1.259000	1.152000
C	-1.118000	-0.758000	-0.259000	H	-0.352000	3.490000	0.506000
C	-2.281000	-0.037000	-0.940000	H	0.821000	2.741000	-0.594000
C	-1.565000	-1.429000	1.048000	H	-0.908000	2.605000	-0.927000

DIPEA·HCl

atom	x	y	z	atom	x	y	z
N	-0.211000	-0.034000	-0.200000	H	0.843000	-2.133000	1.079000
C	-0.231000	0.746000	-1.483000	H	-0.859000	-2.243000	1.596000
C	0.508000	2.071000	-1.415000	H	-0.210000	-3.400000	0.442000
H	-1.267000	0.882000	-1.788000	C	-0.945000	0.594000	0.977000
H	0.254000	0.101000	-2.216000	C	-2.176000	1.395000	0.573000
H	0.581000	2.468000	-2.429000	C	0.025000	1.396000	1.837000
H	-0.008000	2.814000	-0.807000	H	-1.283000	-0.253000	1.571000
H	1.520000	1.932000	-1.029000	H	-2.863000	0.824000	-0.052000
C	-0.570000	-1.493000	-0.441000	H	-2.709000	1.665000	1.487000
C	-2.026000	-1.690000	-0.834000	H	-1.921000	2.322000	0.057000
C	-0.174000	-2.354000	0.753000	H	0.880000	0.789000	2.137000
H	0.072000	-1.773000	-1.279000	H	0.398000	2.281000	1.320000
H	-2.314000	-1.095000	-1.703000	H	-0.499000	1.724000	2.737000
H	-2.167000	-2.741000	-1.094000	H	0.809000	-0.082000	0.050000
H	-2.701000	-1.464000	-0.006000	Cl	2.851000	-0.374000	0.090000

INT6a

atom	x	y	z	atom	x	y	z
C	-1.509000	-0.659000	-0.007000	C	0.121000	3.643000	0.221000
Cl	-1.767000	-0.151000	1.670000	H	-0.553000	4.396000	0.634000
N	-2.012000	-1.910000	-0.292000	H	0.659000	4.079000	-0.632000
C	-3.421000	-2.173000	-0.021000	H	0.859000	3.361000	0.970000
H	-4.071000	-1.720000	-0.783000	H	-0.684000	-0.175000	-1.850000
H	-3.699000	-1.781000	0.956000	C	1.972000	-0.015000	-0.325000
H	-3.584000	-3.251000	-0.017000	C	1.988000	-0.836000	0.978000
C	-1.529000	-2.530000	-1.514000	C	3.461000	0.159000	-0.627000
H	-0.440000	-2.475000	-1.550000	H	1.539000	-0.644000	-1.119000
H	-1.940000	-2.062000	-2.421000	C	4.049000	-1.223000	-0.327000
H	-1.825000	-3.580000	-1.507000	H	3.865000	0.912000	0.059000
C	-0.792000	0.126000	-0.815000	H	3.649000	0.500000	-1.648000
C	0.017000	1.304000	-0.383000	C	3.228000	-1.752000	0.877000
N	1.287000	1.254000	-0.208000	H	5.121000	-1.191000	-0.123000
N	-0.654000	2.482000	-0.163000	H	3.907000	-1.877000	-1.193000
C	-1.943000	2.760000	-0.763000	H	3.813000	-1.713000	1.799000
H	-2.533000	3.386000	-0.088000	H	2.945000	-2.797000	0.728000
H	-2.488000	1.834000	-0.934000	H	1.057000	-1.388000	1.124000
H	-1.842000	3.288000	-1.721000	H	2.087000	-0.135000	1.813000

TS6-7a

atom	x	y	z	atom	x	y	z
N	3.470000	-0.223000	-0.352000	H	-2.389000	2.265000	0.857000
C	4.229000	1.015000	-0.395000	H	-1.629000	3.862000	0.882000
H	3.623000	1.799000	-0.848000	H	-0.378000	3.326000	-1.186000
H	5.126000	0.859000	-0.995000	H	-2.014000	2.732000	-1.520000
H	4.521000	1.349000	0.607000	H	0.021000	0.957000	-1.772000
C	4.213000	-1.472000	-0.316000	H	-1.444000	0.491000	-0.881000
H	3.708000	-2.251000	-0.891000	C	1.413000	-1.402000	0.190000
H	4.387000	-1.831000	0.705000	H	1.930000	-2.351000	0.256000
H	5.181000	-1.307000	-0.787000	C	0.128000	-1.438000	0.470000
C	2.164000	-0.144000	0.018000	N	-1.008000	-2.010000	0.424000
N	1.615000	0.996000	0.279000	C	-1.949000	-1.927000	1.549000
C	0.219000	1.063000	0.411000	H	-2.811000	-1.340000	1.219000
C	-0.269000	2.200000	1.332000	H	-1.456000	-1.459000	2.397000
C	-1.475000	2.816000	0.612000	H	-2.259000	-2.939000	1.812000
C	-1.146000	2.612000	-0.869000	C	-1.501000	-2.659000	-0.804000
C	-0.596000	1.184000	-0.901000	H	-0.743000	-2.576000	-1.578000
H	-0.106000	0.052000	0.915000	H	-2.420000	-2.149000	-1.102000
H	0.549000	2.920000	1.408000	H	-1.701000	-3.707000	-0.579000
H	-0.495000	1.848000	2.340000	Cl	-4.136000	-0.175000	-0.676000

INT7a

atom	x	y	z	atom	x	y	z
C	1.809000	-0.075000	-0.169000	C	-1.815000	3.161000	-0.619000
Cl	0.173000	-3.264000	-0.442000	H	-2.488000	3.095000	0.241000
N	3.043000	-0.448000	0.116000	H	-2.171000	2.494000	-1.401000
C	4.029000	0.512000	0.591000	H	-1.819000	4.183000	-0.996000
H	3.696000	0.976000	1.524000	C	-1.572000	-0.146000	-0.260000
H	4.198000	1.293000	-0.155000	C	-2.604000	-1.051000	-0.879000
H	4.967000	-0.008000	0.774000	C	-1.595000	-0.301000	1.239000
C	3.482000	-1.828000	-0.060000	H	1.995000	2.006000	0.285000
H	2.634000	-2.444000	-0.359000	H	1.154000	-0.878000	-0.507000
H	3.884000	-2.207000	0.882000	C	-3.169000	-1.862000	0.293000
H	4.264000	-1.873000	-0.823000	H	-2.162000	-1.660000	-1.668000
C	1.335000	1.221000	-0.049000	H	-3.370000	-0.411000	-1.333000
C	0.008000	1.555000	-0.379000	C	-2.952000	-0.957000	1.516000
N	-0.857000	0.649000	-0.952000	H	-1.416000	0.640000	1.764000
N	-0.450000	2.803000	-0.244000	H	-0.783000	-0.993000	1.490000
C	0.385000	3.850000	0.331000	H	-2.585000	-2.778000	0.405000
H	1.233000	4.080000	-0.320000	H	-4.216000	-2.134000	0.151000
H	0.756000	3.557000	1.315000	H	-3.732000	-0.189000	1.564000
H	-0.217000	4.748000	0.446000	H	-2.966000	-1.506000	2.459000

INT6b

atom	x	y	z	atom	x	y	z
C	-1.387000	-0.052000	0.019000	H	-0.634000	2.382000	-1.163000
Cl	-1.340000	0.704000	1.620000	H	0.784000	3.066000	-1.982000
N	-2.547000	-0.752000	-0.229000	C	2.500000	2.401000	0.096000
C	-3.823000	-0.061000	-0.078000	H	2.401000	3.448000	0.388000
H	-4.025000	0.608000	-0.926000	H	3.214000	2.331000	-0.737000
H	-3.832000	0.524000	0.840000	H	2.903000	1.826000	0.929000
H	-4.621000	-0.803000	-0.019000	H	-0.374000	-0.404000	-1.757000
C	-2.514000	-1.667000	-1.357000	C	1.845000	-1.682000	-0.059000
H	-1.629000	-2.302000	-1.293000	C	1.483000	-2.131000	1.358000
H	-2.509000	-1.146000	-2.327000	H	2.256000	-1.807000	2.062000
H	-3.402000	-2.299000	-1.314000	H	1.399000	-3.221000	1.413000
C	-0.308000	0.025000	-0.764000	H	0.532000	-1.695000	1.671000
C	1.038000	0.529000	-0.357000	C	3.135000	-2.344000	-0.536000
N	2.030000	-0.238000	-0.092000	H	3.965000	-2.071000	0.121000
N	1.193000	1.893000	-0.265000	H	3.382000	-2.017000	-1.549000
C	0.352000	2.814000	-1.004000	H	3.038000	-3.434000	-0.539000
H	0.235000	3.739000	-0.433000	H	1.032000	-2.003000	-0.727000

TS6-7b

atom	x	y	z	atom	x	y	z
N	-3.289000	0.197000	-0.284000	H	0.256000	-2.538000	-1.526000
C	-4.159000	-0.967000	-0.300000	H	0.165000	-0.795000	-1.827000
H	-3.655000	-1.791000	-0.802000	C	-1.101000	1.176000	0.133000
H	-5.072000	-0.718000	-0.839000	H	-1.526000	2.170000	0.191000
H	-4.417000	-1.295000	0.714000	C	0.190000	1.097000	0.367000
C	-3.915000	1.506000	-0.170000	N	1.354000	1.624000	0.344000
H	-3.392000	2.250000	-0.773000	C	2.261000	1.491000	1.492000
H	-3.974000	1.856000	0.867000	H	3.056000	0.793000	1.216000
H	-4.928000	1.433000	-0.562000	H	1.703000	1.126000	2.351000
C	-1.976000	-0.008000	-0.001000	H	2.678000	2.474000	1.713000
N	-1.517000	-1.196000	0.208000	C	1.929000	2.180000	-0.891000
C	-0.128000	-1.390000	0.244000	H	1.166000	2.193000	-1.666000
C	0.298000	-2.454000	1.242000	H	2.769000	1.547000	-1.186000
C	0.521000	-1.555000	-1.128000	H	2.272000	3.194000	-0.683000
H	0.328000	-0.384000	0.686000	Cl	4.141000	-0.746000	-0.534000
H	-0.064000	-3.428000	0.900000	H	1.609000	-1.485000	-1.046000
H	-0.125000	-2.254000	2.228000	H	1.386000	-2.495000	1.315000

INT7b

atom	x	y	z	atom	x	y	z
C	0.945000	1.051000	-0.254000	H	-2.571000	2.267000	1.331000
Cl	2.865000	-2.051000	0.178000	H	-4.164000	1.988000	0.620000
N	1.936000	1.913000	-0.128000	C	-3.748000	-0.291000	-0.291000
C	1.682000	3.309000	0.192000	H	-4.013000	-0.795000	0.643000
H	1.168000	3.396000	1.153000	H	-3.417000	-1.032000	-1.014000
H	1.069000	3.778000	-0.583000	H	-4.628000	0.218000	-0.683000
H	2.632000	3.835000	0.254000	C	-0.776000	-1.846000	-0.021000
C	3.323000	1.514000	-0.341000	C	-0.506000	-3.160000	-0.678000
H	3.375000	0.434000	-0.477000	H	-1.140000	-3.934000	-0.237000
H	3.920000	1.786000	0.533000	H	0.537000	-3.431000	-0.489000
H	3.726000	2.026000	-1.219000	H	-0.683000	-3.101000	-1.751000
C	-0.395000	1.364000	-0.096000	C	-0.590000	-1.785000	1.465000
C	-1.407000	0.397000	-0.265000	H	-1.123000	-2.612000	1.938000
N	-1.130000	-0.860000	-0.752000	H	-0.923000	-0.840000	1.894000
N	-2.693000	0.694000	-0.070000	H	0.478000	-1.919000	1.668000
C	-3.097000	2.010000	0.409000	H	-0.684000	2.376000	0.142000
H	-2.904000	2.780000	-0.343000	H	1.252000	0.033000	-0.485000

References

[1] APEX II (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.

[2] SAINT (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.

[3] SADABS (Bruker, 2009) Bruker AXS Inc., Madison, Wisconsin, USA.
TWINABS (Bruker, 2009) Bruker AXS Inc., Madison, Wisconsin, USA.

[4] Sheldrick, G.M. (2008) *Acta Cryst*., A64, 112-122; Sheldrick, G.M. (2015) *Acta Cryst*., A71, 3-8; Sheldrick, G.M. (2015) *Acta Cryst*., C71, 3-8.

[5] Spek, A. L. (2003). J. Appl. Cryst. 36, 7-13.

[6] CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).