

Supporting Information for:

**C–F bond activation of perfluorinated arenes
by a bioxazoline-derived N-heterocyclic carbene**

Jack Emerson-King, Simone A. Hauser and Adrian B. Chaplin*

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK.

E-mail: a.b.chaplin@warwick.ac.uk

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1. Experimental

1.1 General experimental methods

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 150°C overnight and flamed under vacuum prior to use. Anhydrous cyclohexane was freeze-pump-thaw degassed three times before being placed under an atmosphere of argon. Fluoroarenes were dried over CaH₂, distilled, and stored over thoroughly dried 3 Å MS. CD₂Cl₂ was dried over thoroughly dried 3 Å molecular sieves and freeze-pump-thaw degassed three times before being placed under an atmosphere of argon. IBioxMe₄ was prepared following a literature procedure.¹ NMR spectra were recorded on Bruker Avance III HD 300 MHz or 500 MHz spectrometers at 298 K. ¹H NMR spectra recorded in fluorobenzene solvents were referenced with the aid of an internal sealed capillary of C₆D₆. Chemical shifts are quoted in ppm and coupling constants in Hz. Elemental analysis performed by Stephen Boyer at London Metropolitan University.

1.2 Preparation of new compounds

1.2.1 Imidazoliumolate 1a

To a solution of IBioxMe₄ (10.4 mg, 0.050 mmol) in 1,2-difluorobenzene (0.5 mL) was added octafluorotoluene (35.4 μL, 0.250 mmol). The colour of the solution immediately became deep red and was left to stand overnight at RT. Layering the solution with cyclohexane (*ca.* 5 mL) afforded the product as a red crystalline solid on diffusion, which was washed with cyclohexane (3 x 1 mL) and dried *in vacuo*. Yield = 7.1 mg (32% yield).

¹H NMR (CD₂Cl₂, 500 MHz): δ 4.92 (d, ²J_{FH} = 47.2, 2H, CH₂F), 4.48 (s, 2H, oxazoline CH₂), 1.47 (d, ⁴J_{FH} = 1.8, 6H, C(CH₃)₂CH₂F), 1.35 (s, 6H, oxazoline CH₃).

¹³C{¹H} NMR (CD₂Cl₂, 126 MHz): δ 147.0 (dd, ¹J_{FC} = 252, ²J_{FC} = 15, {C}Ar^F), 144.7 (dd, ¹J_{FC} = 265, ²J_{FC} = 16, {C}Ar^F), 140.7 (s, CO⁻), 131.2 (s, C=OCH₂), 121.0 (q, ¹J_{CF} = 276, CF₃), 114.7 (t, ³J_{FC} = 19, CCF), 91.6 (s, NCN), 86.1 (d, ¹J_{FC} = 176, CH₂F), 85.3 (s, oxazoline CH₂), 65.8 (s, oxazoline C(CH₃)₂), 63.3 (d, ²J_{FC} = 18, C(CH₃)₂CH₂F), 24.9 (s, oxazoline CH₃), 23.7 (d, ³J_{FC} = 5, C(CH₃)₂CH₂F). One CCF signal was not unambiguously located; it may be coincident with the other CCF signal.

¹⁹F NMR (CD₂Cl₂, 377 MHz): δ -56.81 (t, ⁴J_{FF} = 21.9, CF₃), -133.14 – -132.95 (m, Ar^F), -138.80 – -138.47 (m, Ar^F), -224.59 (t of m, ²J_{FH} = 47.2, CH₂F).

¹⁹F{¹H} NMR (CD₂Cl₂, 377 MHz): δ -56.81 (t, ⁴J_{FF} = 21.9, CF₃), -133.12 – -132.97 (m, Ar^F), -138.80 – -138.48 (m, Ar^F), -224.58 (t, J = 5.5, CH₂F).

Anal. Calc. for C₁₈H₁₆F₈N₂O₂ (444.33 g·mol⁻¹): C, 48.66; H, 3.63; N, 6.30. Found: C, 48.79; H, 3.55; N, 6.40.

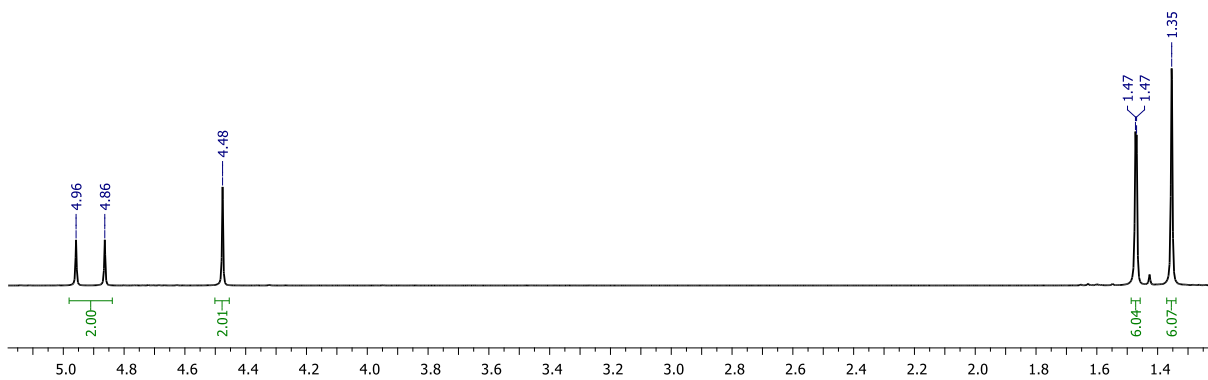


Figure S-1: ^1H NMR spectrum of **1a** (CD_2Cl_2 , 500 MHz).

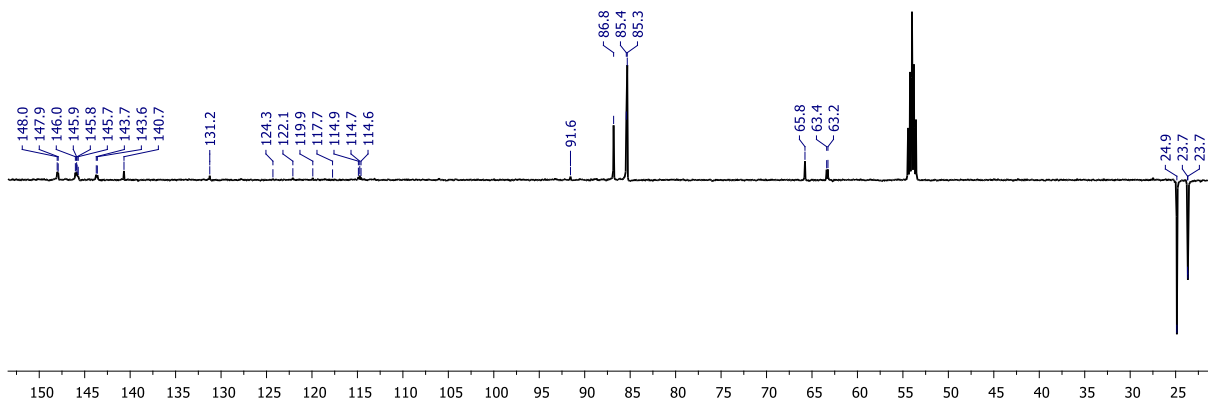


Figure S-2: $^{13}\text{C}\{^1\text{H}\}$ APT NMR spectrum of **1a** (CD_2Cl_2 , 126 MHz).

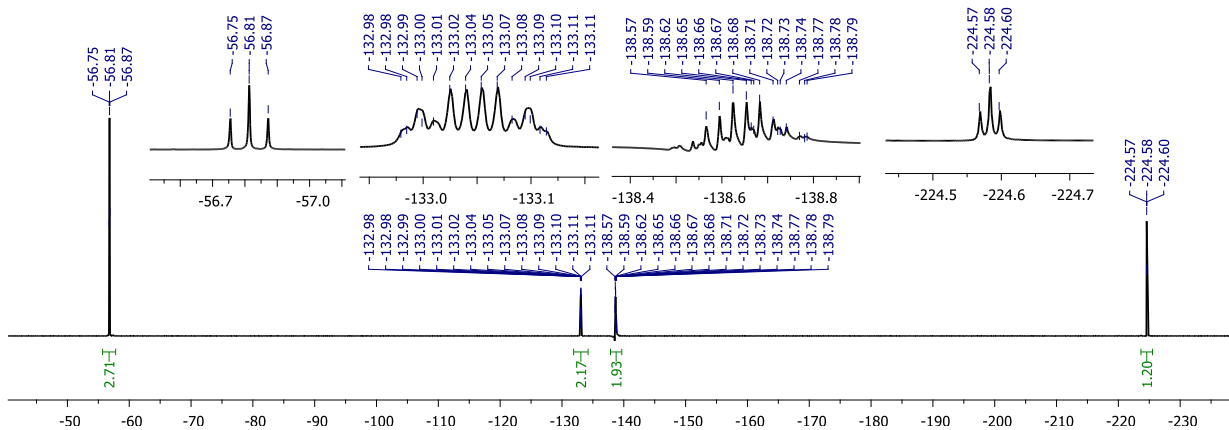


Figure S-3: ^{19}F NMR spectrum of **1a** (CD_2Cl_2 , 377 MHz).

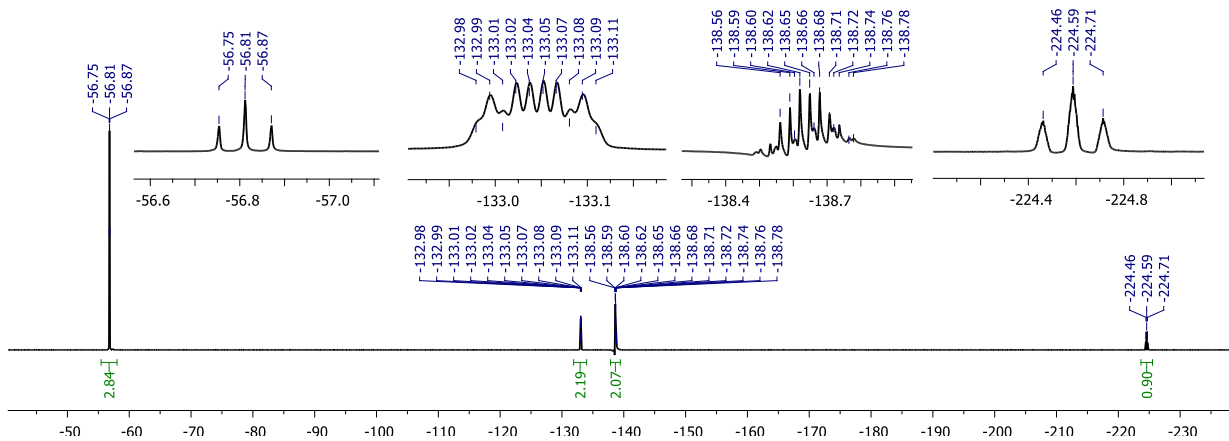


Figure S-4: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **1a** (CD_2Cl_2 , 377 MHz).

1.2.2 Imidazoliumolate 2

To a solution of IBioxMe₄ (10.4 mg, 0.050 mmol) in 1,2-difluorobenzene (0.5 mL) was added hexafluorobenzene (28.9 μ L, 0.250 mmol). The colour of the solution immediately became deep red. The product, as a mixture of rotamers, crystallised out of solution on standing at RT overnight and was isolated by cold filtration (0 $^{\circ}$ C), washing with cold 1,2-difluorobenzene (3 x 2 mL; 0 $^{\circ}$ C). Yield = 5.7 mg (19%) as a microcrystalline red solid. Despite repeated attempts, satisfactory microanalysis data could not be obtained, presumably due to the extremely air and moisture sensitive nature of this compound. Although the rotamers form in a \sim 1:1 ratio, variation of this ratio was found for isolated material. NMR data presented here is for material with the rotamers in a \sim 1:1.6 ratio.

¹H NMR (CD₂Cl₂, 500 MHz, major rotamer): δ 4.89 (d, ²J_{FH} = 47.3, 2H, CH₂F), 4.49 (s, 2H, oxazoline CH₂), 1.52 (d, ⁴J_{FH} = 1.4, 6H, C(CH₃)₂CH₂F), 1.37 (s, 6H, oxazoline CH₃).

¹H NMR (CD₂Cl₂, 500 MHz, minor rotamer): δ 4.91 (d, ²J_{FH} = 47.3, 2H, CH₂F), 4.50 (s, 2H, oxazoline CH₂), 1.50 (d, ⁴J_{FH} = 1.4, 6H, C(CH₃)₂CH₂F), 1.38 (s, 6H, oxazoline CH₃).

¹³C{¹H} NMR (CD₂Cl₂, 126 MHz, major rotamer): δ 147 (dd, ¹J_{FC} \sim 250, ²J_{FC} \sim 12, {C}Ar^F), 140.6 (s, CO⁻), 131 (s, COCH₂), 92 (s, NCN), 86.3 (d, ¹J_{FC} = 176, CH₂F), 85.3 (s, oxazoline CH₂), 65.7 (s, oxazoline, C(CH₃)₂), 63.3 (d, ²J_{FC} = 18, C(CH₃)₂CH₂F), 24.9 (s, oxazoline CH₃), 23.4 (d, ³J_{FC} = 5, C(CH₃)₂CH₂F).

The CCF signal was not unambiguously located.

¹³C{¹H} NMR (CD₂Cl₂, 126 MHz, minor rotamer): δ 147 (dd, ¹J_{FC} \sim 250, ²J_{FC} \sim 12, {C}Ar^F), 140.7 (s, CO⁻), 131 (s, COCH₂), 92 (s, NCN), 86.2 (d, ¹J_{FC} = 176, CH₂F), 85.2 (s, oxazoline CH₂), 65.5 (s, oxazoline, C(CH₃)₂), 63.5 (d, ²J_{FC} = 18, C(CH₃)₂CH₂F), 25.0 (s, oxazoline CH₃), 23.5 (d, ³J_{FC} = 5, C(CH₃)₂CH₂F). The CCF signal was not unambiguously located.

¹⁹F NMR (CD₂Cl₂, 377 MHz, major rotamer): δ -133.71 (br. t, *J* = 2, Ar^F), -223.44 (t, ²J_{FF} = 47.3, CH₂F).

¹⁹F NMR (CD₂Cl₂, 377 MHz, minor rotamer): δ -133.63 (br. t, *J* = 2, Ar^F), -223.89 (t, ²J_{FF} = 47.3, CH₂F).

¹⁹F{¹H} NMR (CD₂Cl₂, 377 MHz, major rotamer): δ -133.71 (br. t, *J* = 2, Ar^F), -223.44 (br, CH₂F).

¹⁹F{¹H} NMR (CD₂Cl₂, 377 MHz, minor rotamer): δ -133.63 (br. t, *J* = 2, Ar^F), -223.89 (br, CH₂F).

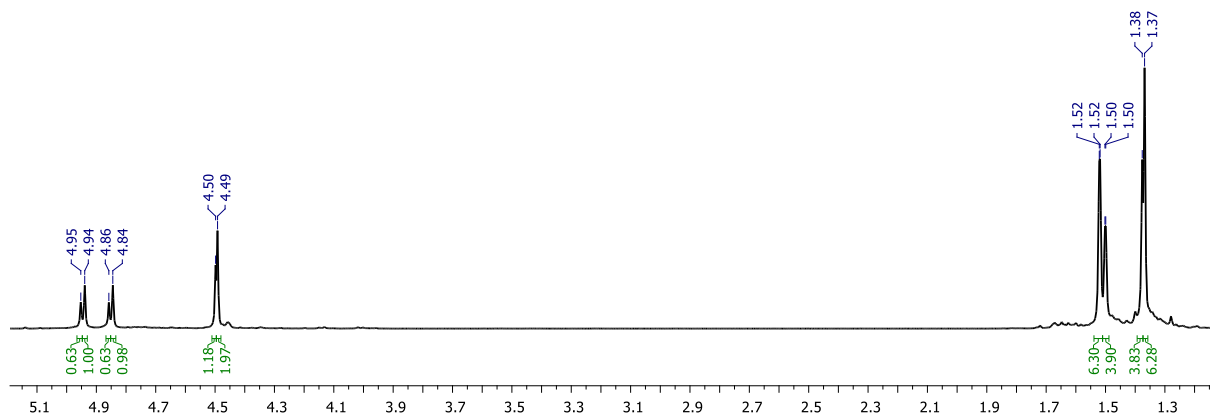


Figure S-5: ^1H NMR spectrum of **2** (CD_2Cl_2 , 500 MHz).

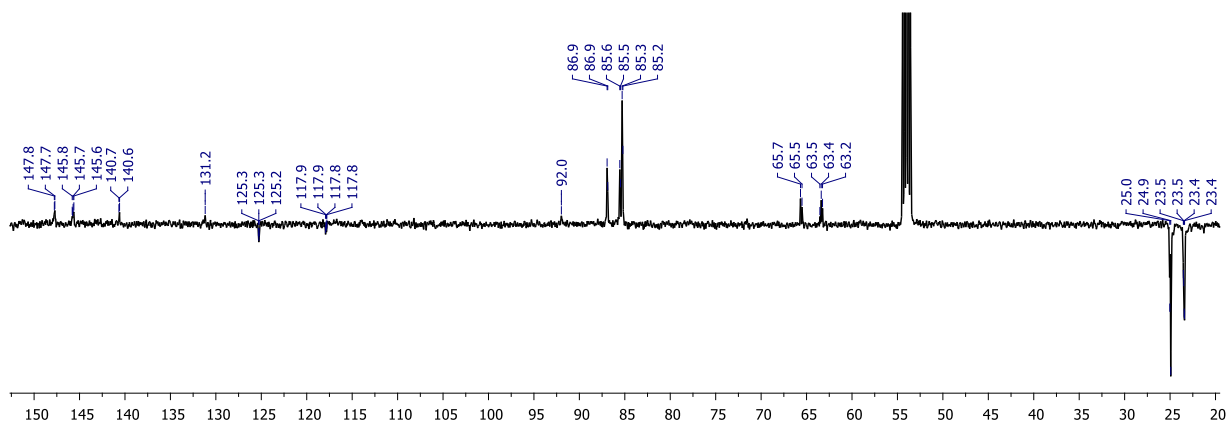


Figure S-6: $^{13}\text{C}\{^1\text{H}\}$ APT NMR spectrum of **2** (CD_2Cl_2 , 126 MHz).

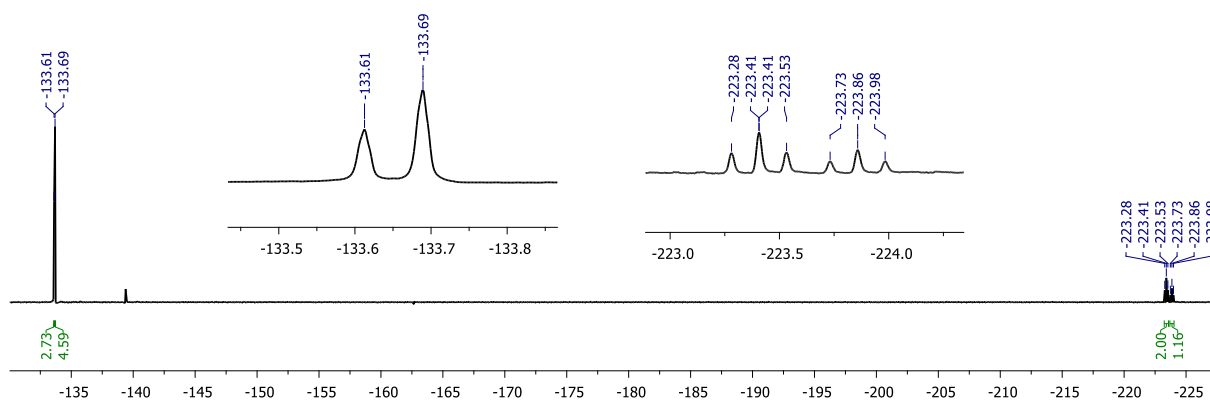


Figure S-7: ^{19}F NMR spectrum of **1** (CD_2Cl_2 , 377 MHz). Residual 1,2-difluorobenzene at -139.4 ppm.

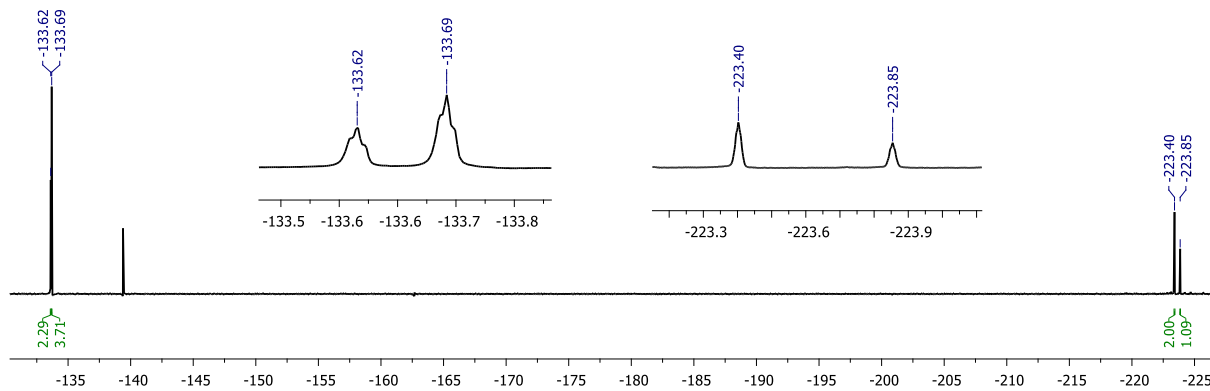


Figure S-8: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **2** (CD_2Cl_2 , 377 MHz). Residual 1,2-difluorobenzene at -139.4 ppm.

1.3 NMR scale reactions – general procedure.

To a J. Young's NMR tube containing a solution of IBioxMe₄ (2.1 mg, 10.0 μmol) in 1,2-difluorobenzene (0.5 mL) was added octafluorotoluene or hexafluorobenzene (50.0 μmol), resulting in red solutions. NMR spectroscopy indicated quantitative formation of compounds **1a** and **2** (rotamers ~ 1:1) within 1 and 4 hours respectively.

2. Computational details

2.1 Geometry optimisation and free energy calculations

Density functional theory (DFT) calculations were implemented in the Gaussian 03 suite of programs² at the BP86/6-31++G(d,p) level.³ Geometry optimisations were performed without symmetry constraints based on starting geometries prepared in the following ways:

- Multiple conformations of **1a** arising from free rotation of the alkyl fluoride moiety were initiated from the geometry of the obtained crystal structure.
- The lowest energy conformer of **1a** was appropriately modified for use as the starting geometry for **1b**.
- **2** was constructed in the same manner as **1b**, considering two possible conformers of each rotamer (see Figure S-9) to arrive at the local minima for each rotamer.
- Hexafluorobenzene and octafluorotoluene were optimised from handmade structures

Optimised geometries and energies are provided in xyz format. The absence of imaginary vibrational modes confirmed the structures as minima on the potential energy surface. Thermal corrections (298.15 K, 1 atm) were applied to deduce relevant thermodynamic parameters (see Table S-1).

Table S-1: Thermodynamic parameters of optimised compounds: $E_0 = E_{elec} + ZPE$, $E = E_0 + E_{vib} + E_{rot} + E_{trans}$, $H = E + RT$, $G = H - TS$. Energies quoted in atomic units.

Species	E_0	E	H	G
octafluorotoluene	-1065.418892	-1065.406091	-1065.405146	-1065.459307
hexafluorobenzene	-827.610464	-827.600474	-827.599529	-827.645933
1a	-1753.939516	-1753.910500	-1753.909556	-1753.999509
1b	-1516.130891	-1516.104693	-1516.103749	-1516.186453
2 – anti-rotamer, cis-C–F	-2204.651210	-2204.608781	-2204.607836	-2204.726109
2 – anti-rotamer, trans-C–F	-2204.649937	-2204.607448	-2204.606504	-2204.725083
2 – syn-rotamer, cis-C–F	-2204.648874	-2204.606457	-2204.605513	-2204.724091
2 – syn-rotamer, trans-C–F	-2204.650200	-2204.607819	-2204.606875	-2204.724972

2.2 Geometries of isomers of 2

syn-rotamer, *trans*-C-F

syn-rotamer, *cis*-C-F

anti-rotamer, *trans*-C-F

anti-rotamer, *cis*-C-F

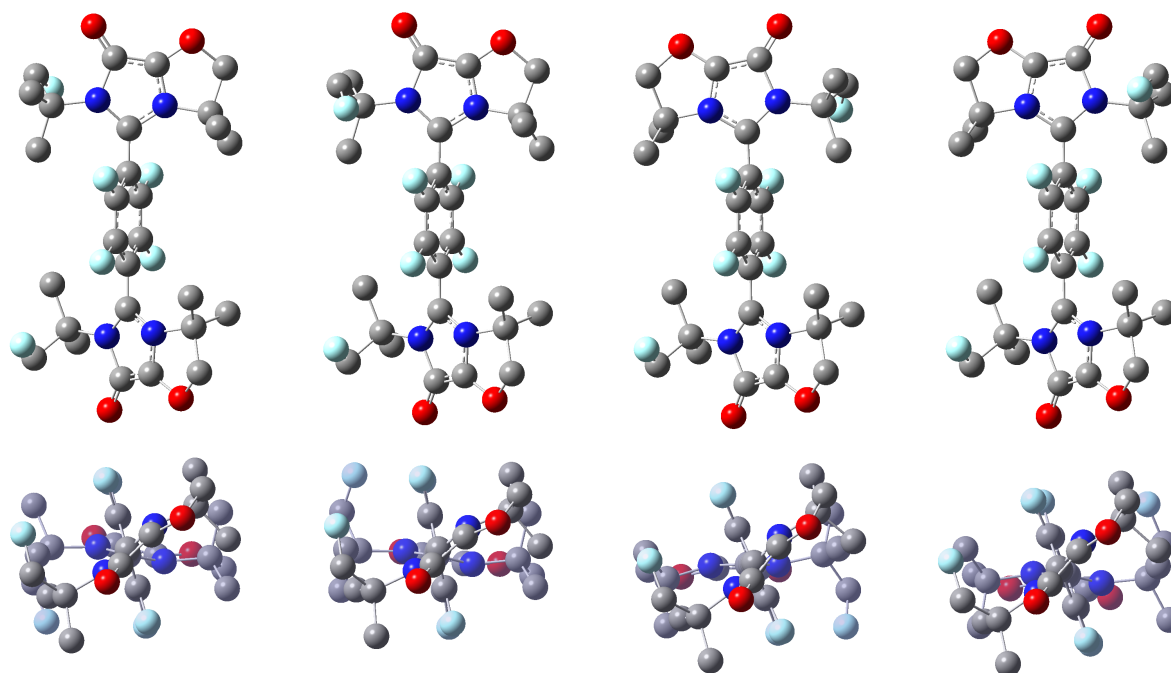


Figure S-9: Optimised structures of selected rotamers of **2**. Hydrogen atoms omitted for clarity, orthogonal 'bottom up' view shown.

2.3 Natural charges of **1a**, **1b**, octafluorotoluene and hexafluorobenzene

-1.000  1.000

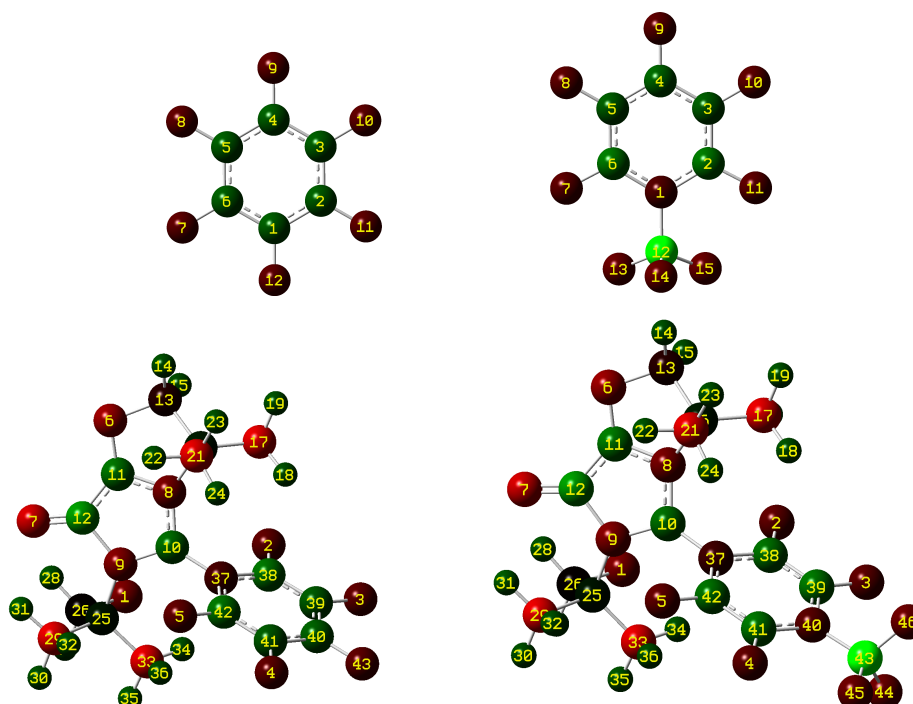


Figure S-10: Optimised structures of **1a**, **1b**, octafluorotoluene and hexafluorobenzene, coloured by calculated natural charges. See Table S-2 for values.

Table S-2: Natural charges for **1a**, **1b**, octafluorotoluene and hexafluorobenzene

1a			1b			octafluorotoluene			hexafluorobenzene		
F	1	-0.38734	F	1	-0.38834	C	1	-0.25746	C	1	0.29007
F	2	-0.29893	F	2	-0.29573	C	2	0.37533	C	2	0.29006
F	3	-0.29147	F	3	-0.29078	C	3	0.28697	C	3	0.29009
F	4	-0.28935	F	4	-0.29103	C	4	0.31606	C	4	0.29007
F	5	-0.30205	F	5	-0.29952	C	5	0.28696	C	5	0.29006
O	6	-0.47894	O	6	-0.48626	C	6	0.37523	C	6	0.29009
O	7	-0.63491	O	7	-0.64914	F	7	-0.28864	F	7	-0.29007
N	8	-0.36674	N	8	-0.36713	F	8	-0.28788	F	8	-0.29008
N	9	-0.40319	N	9	-0.40527	F	9	-0.28322	F	9	-0.29006
C	10	0.34240	C	10	0.33703	F	10	-0.28786	F	10	-0.29007
C	11	0.37578	C	11	0.35559	F	11	-0.28875	F	11	-0.29008
C	12	0.48004	C	12	0.47550	C	12	1.02960	F	12	-0.29006
C	13	-0.12109	C	13	-0.11878	F	13	-0.32399			
H	14	0.24996	H	14	0.24732	F	14	-0.32817			
H	15	0.23556	H	15	0.23215	F	15	-0.32419			
C	16	0.08677	C	16	0.08665						
C	17	-0.69288	C	17	-0.69248						
H	18	0.25054	H	18	0.24796						
H	19	0.25530	H	19	0.25435						
H	20	0.26453	H	20	0.26299						
C	21	-0.69435	C	21	-0.69269						
H	22	0.25998	H	22	0.26034						
H	23	0.25137	H	23	0.24921						
H	24	0.25130	H	24	0.24916						
C	25	0.07134	C	25	0.07088						
C	26	-0.01703	C	26	-0.01579						
H	27	0.21160	H	27	0.20949						
H	28	0.25153	H	28	0.25190						
C	29	-0.69662	C	29	-0.69580						
H	30	0.24269	H	30	0.24096						
H	31	0.28013	H	31	0.28137						
H	32	0.25150	H	32	0.24903						
C	33	-0.69649	C	33	-0.69498						
H	34	0.25894	H	34	0.25698						
H	35	0.25792	H	35	0.25658						
H	36	0.24196	H	36	0.24004						
C	37	-0.19801	C	37	-0.21665						
C	38	0.34635	C	38	0.35937						
C	39	0.36607	C	39	0.27820						
C	40	-0.27418	C	40	0.30140						
C	41	0.36081	C	41	0.27718						
C	42	0.34783	C	42	0.35528						
C	43	1.04975	F	43	-0.28655						
F	44	-0.33488									
F	45	-0.32616									
F	46	-0.33733									

3. References

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- 3 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824; (c) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.