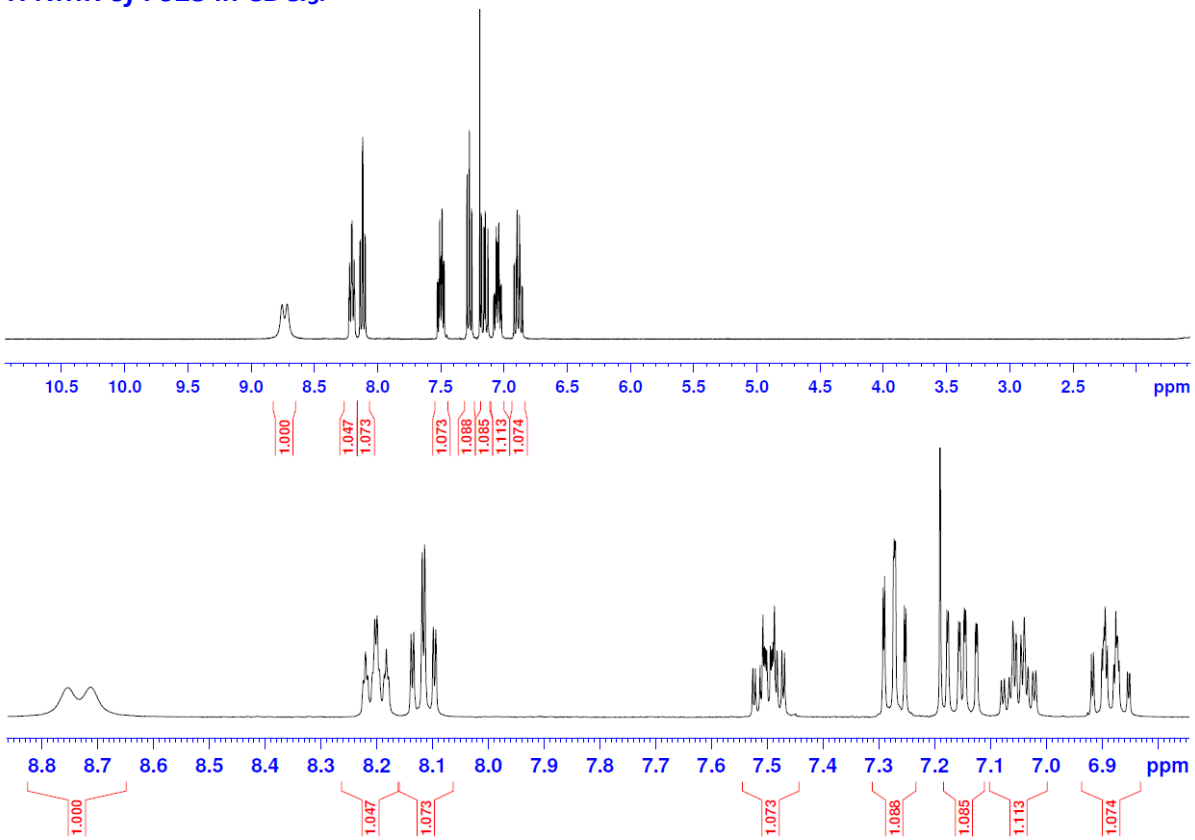
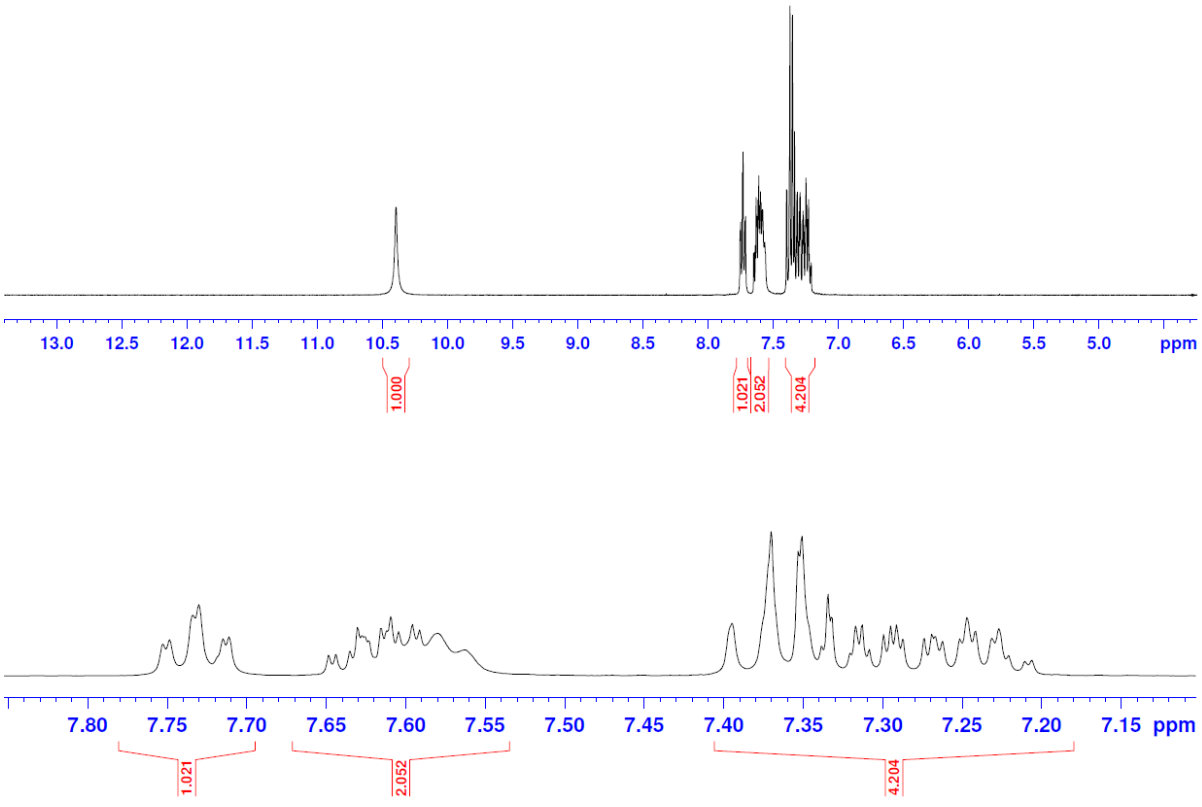
SUPPLEMENTARY DATA (SPECTRA AND CRYSTAL STRUCTURE DATA).

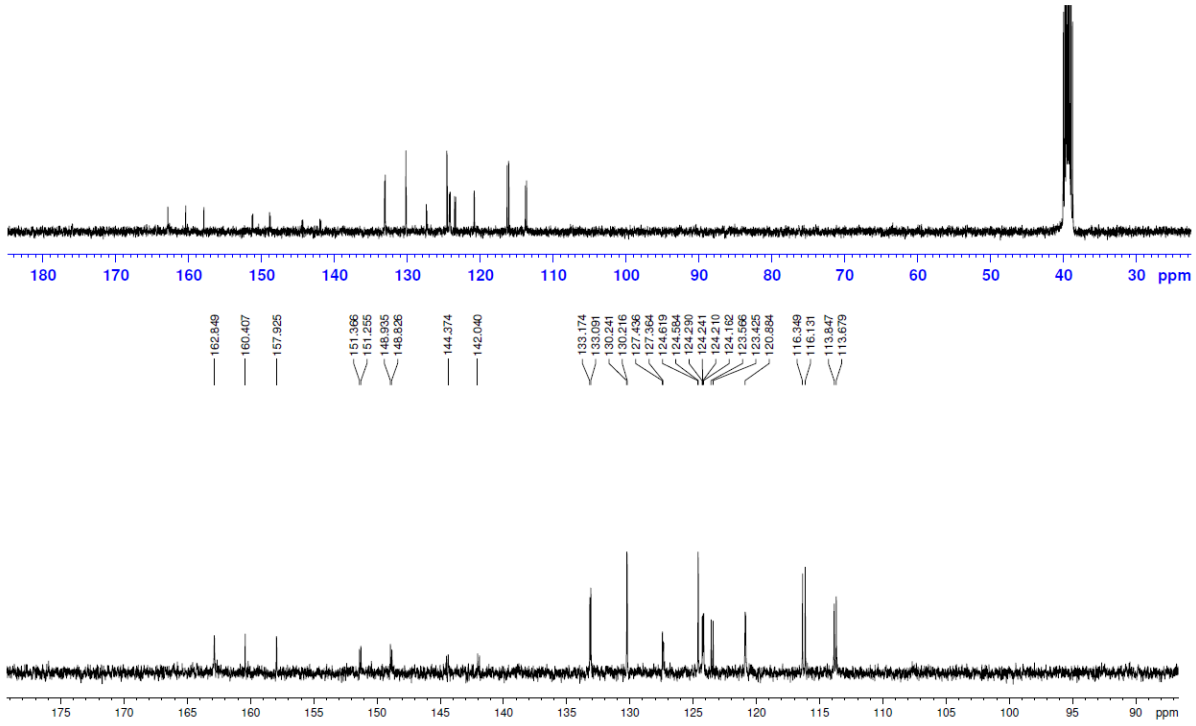
^{1}H NMR of Fo23 in $CDCl_3$:



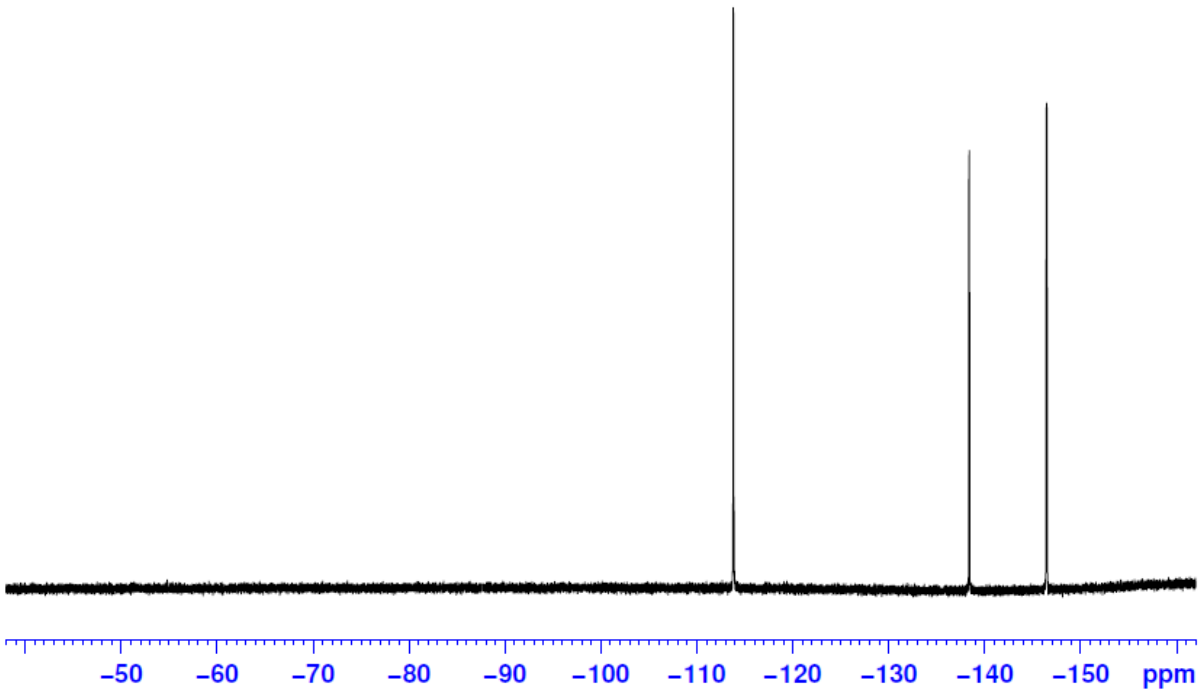
^{1}H NMR of Fo23 in DMSO:

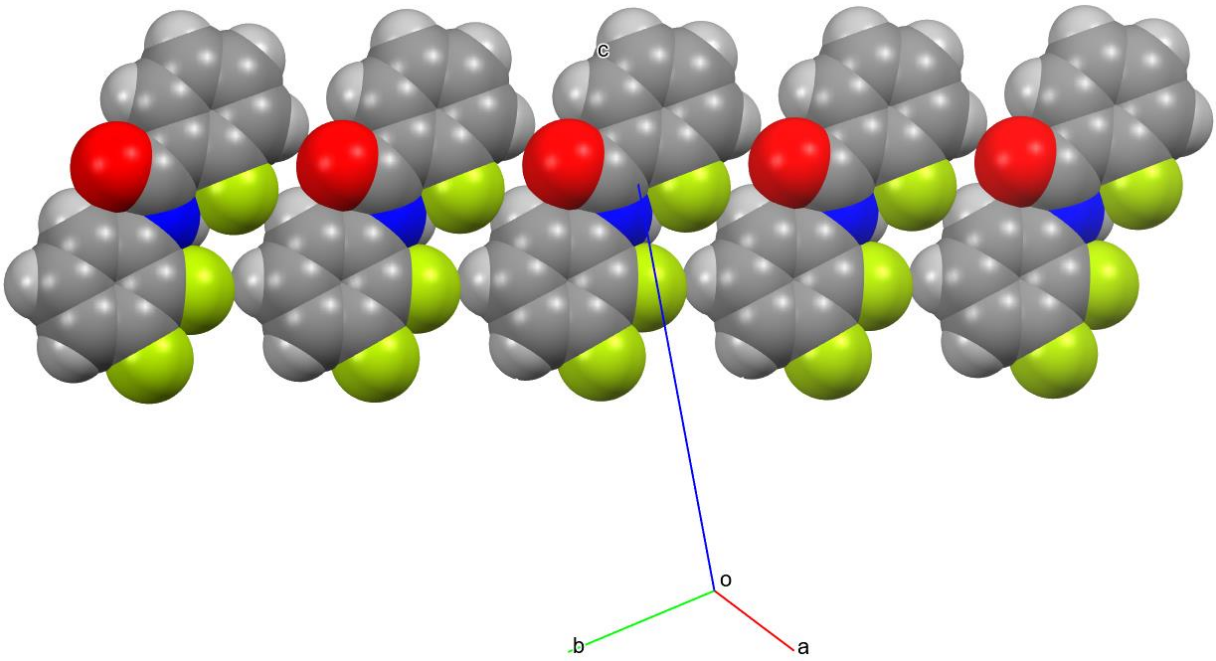


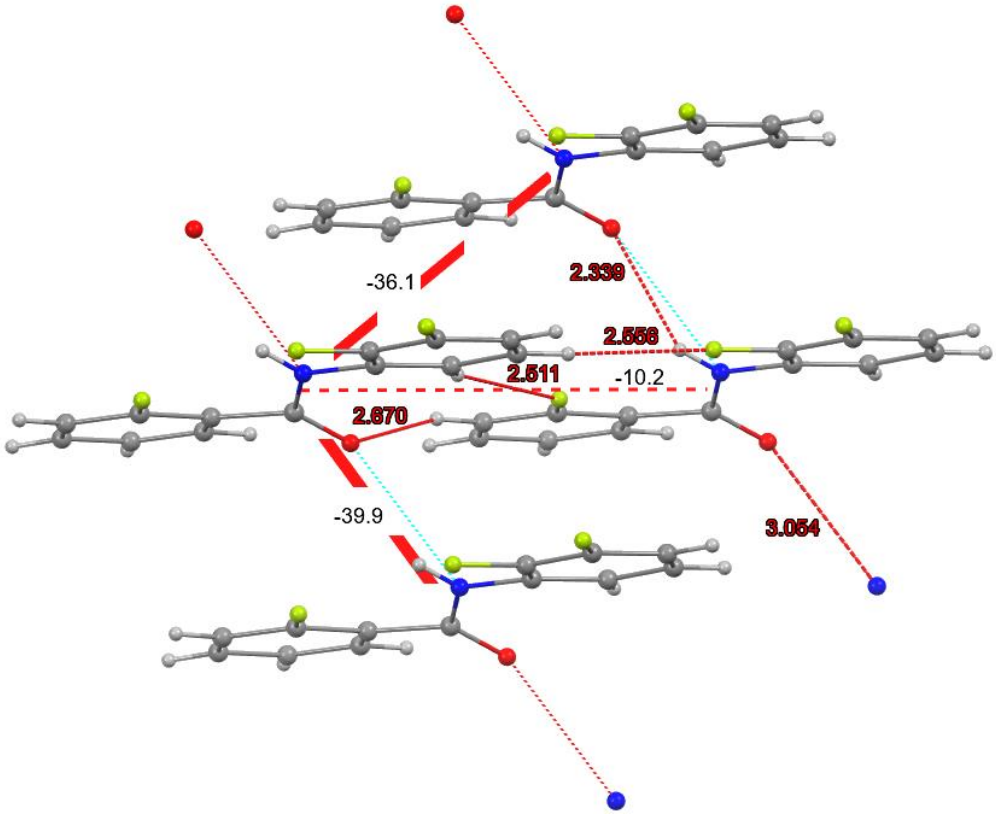
^{13}C NMR of Fo23 in DMSO:



^{19}F NMR of Fo23 in DMSO:



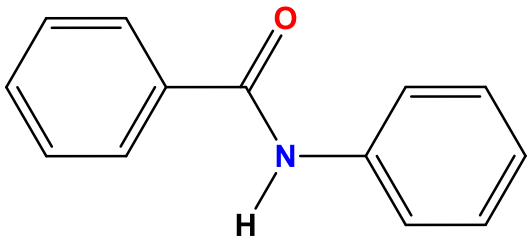




Supplementary Figures S1 and S2: (*S1*) A view of the weaker interactions and unit cell in **Fo23** with atoms as their van der Waals spheres and (*S2*) A view exploring the UNI intermolecular potentials using the ball and stick model in Mercury (with several distances included).

Analysis of the Cambridge Structural Database [21st July 2023].

CSD search analysis (of version 5.42+4 updates) using the *N*-(phenyl)benzamide schematic as depicted below plus a chemical formula such as $C_{13}H_8\mathbf{F}_3O_1N_1$ and including halides **X**.



Formula	Fluorine **F** ['hits'/structures]	Formula	Halide **X** ['hits'/structures]
$C_{13}H_{10}\mathbf{F}_1O_1N_1$	8/6	$C_{13}H_{10}\mathbf{X}_1O_1N_1$	24/16
$C_{13}H_9\mathbf{F}_2O_1N_1$	30/19	$C_{13}H_9\mathbf{X}_2O_1N_1$	89/74
$C_{13}H_8\mathbf{F}_3O_1N_1$	**0/0 [Fo23]**	$C_{13}H_8\mathbf{X}_3O_1N_1$	**10/10**
$C_{13}H_7\mathbf{F}_4O_1N_1$	29/27	$C_{13}H_7\mathbf{X}_4O_1N_1$	29/27

CSD analysis of close analogues of Fo23:
To place the **Fo23** crystal structure in context by analysing the CSD for tri-substituted simple benzamides of type C_6CONHC_6, it is noted that there are no tri-fluorinated structures available that are similar to **Fo23**. This is regardless of whether it is tri-fluorinated on one C_6 aromatic ring as C_6F_3 or in any combination of *o*-/*m*-/*p*-monosubstituted F and disubstituted as [2,3-; 2,4-; 2,5-; 2,6-; 3,4- and 3,5-F_2] on the second ring. In expanding the CSD search [3] and when analysing all combinations of trihalides, the majority are chloro-derived or a combination of halides. There are 10 such structural 'hits' and 10 crystal structures available on the CSD using $C_{13}H_8\mathbf{X}_3ON$.

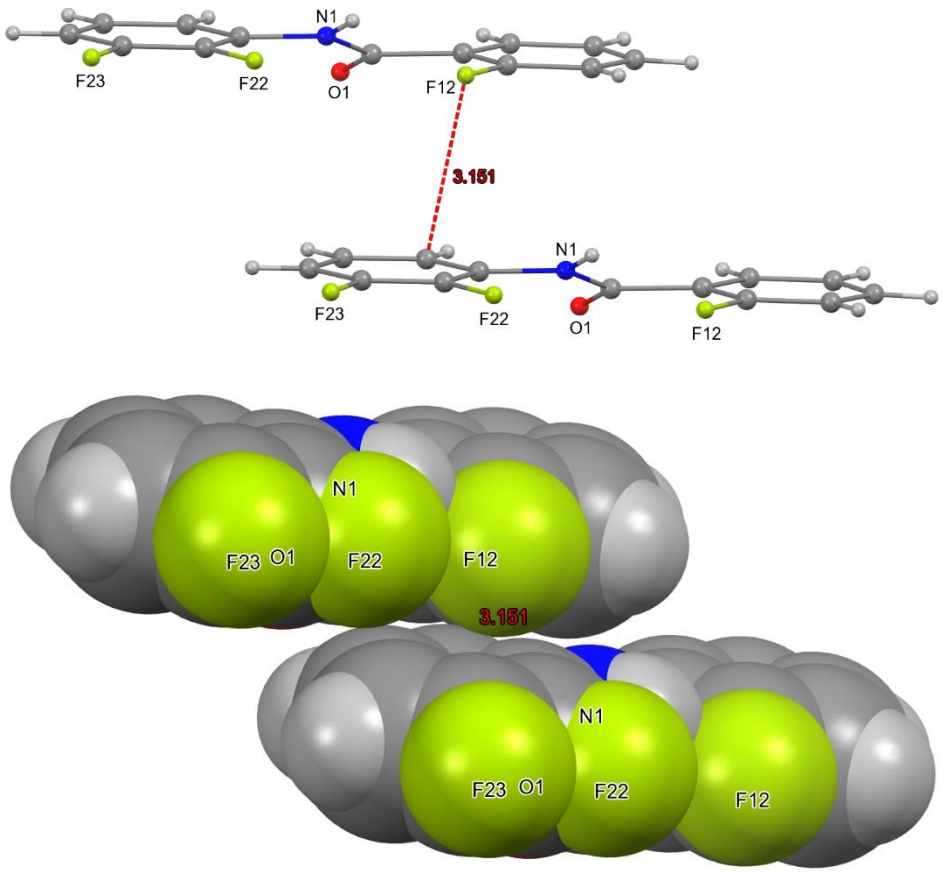
The data analysis contrasts with the difluorinated analogues (formula = $C_{13}H_9F_2O_1N_1$) where 30 difluorinated structural 'hits' are reported, with 19 individual molecules; with some datasets collected at different temperatures) [3,8-10]. There are a 89 structural 'hits' and 74 structures on widening the CSD search to include all halides **X** (**X** = F, Cl, Br, I). In addition there are 29 structure 'hits' and 27 individual crystal structures for the tetra-fluorinated benzamide series (formula = $C_{13}H_7F_4ON$) [3,8-10] and with no other Cl, Br, I combinations present.

Of further note are the mono-fluorinated *N*-phenylbenzamides [$C_{13}H_{10}FON$] which reveal a total of 8 'hits' and 6 crystal structures, although the crystal structure of **UXEZIH** is a mixed system [21]. Expanding this search to include all halides **X** (**X** = F, Cl, Br, I) reveals 24 'hits' and 16 structures. All analyses were conducted using the latest version of the CSD (21st July 2023). Therefore, the CSD analysis demonstrates that the crystal structure of **Fo23** is unique (thus far) in terms of it being the first structural report of a regular tri-fluorinated benzamide with chemical formula = $C_{13}H_8F_3ON$. Needless to say the group of 'missing' crystal structures will soon be reported and available for larger analyses using the CSD and AI approaches.

Table S1: Selected hydrogen-bond and contact parameters for Fo23.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N1—H1···F12	0.83 (4)	2.17 (3)	2.745 (3)	126 (3)
N1—H1···O1^{i}	0.83 (4)	2.34 (3)	3.054 (4)	145 (3)
C26—H26···F12^{ii}	0.93	2.51	3.307 (4)	144
C26—H26···O1	0.93	2.34	2.853 (5)	114
Data for additional Cg/C contacts involving the F12 atom				
X = F and Y = C	X···Cg (Å)	Y—X···Cg (°)		
C12—F12···Cg1^{iii}	3.399(2)	113.75(17)		
C12—F12···C26^{iii}	3.151(4)	89.99(18)		

Symmetry code(s): (*i*) *x*+1, *y*, *z*; (*ii*) *x*-1, *y*+1, *z*; (*iii*) x, y-1, z.
Cg1 is the ring centroid for the C_6 ring [C21,…,C26].
Geometric data as calculated using the SHELXL program and PLATON [15,17].



Supplementary Figures S3 and S4: (*S3*) A view of the C12—F12···C26^{iii} interaction (with contact distance in red) and atoms drawn using a ball and stick model, (*S4*) an offset (relative to Figure S3) CPK view with atoms as their van der Waals spheres.