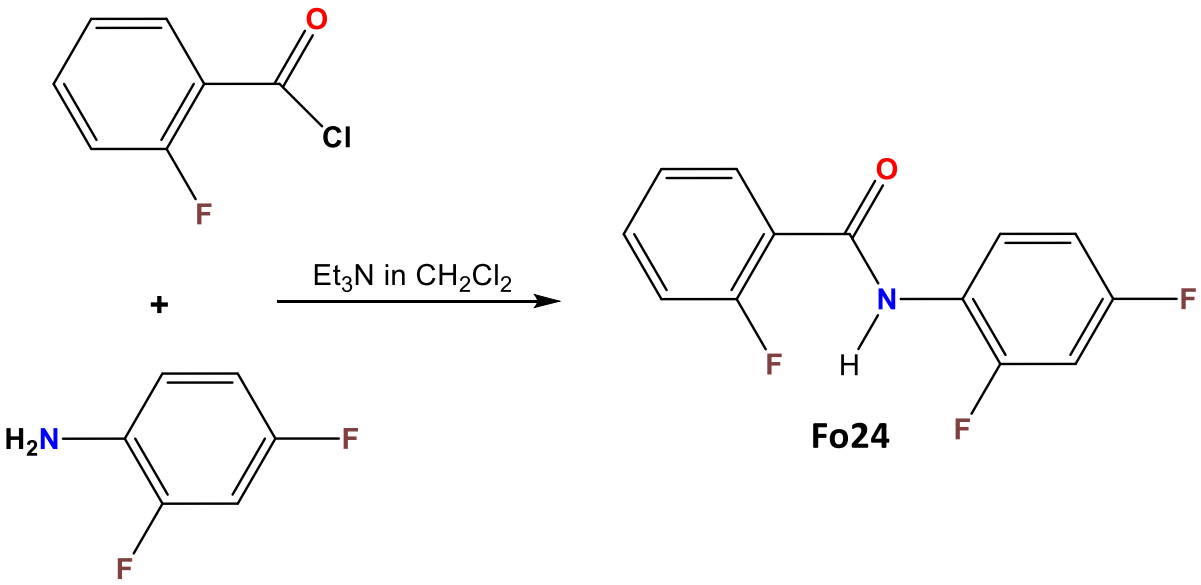
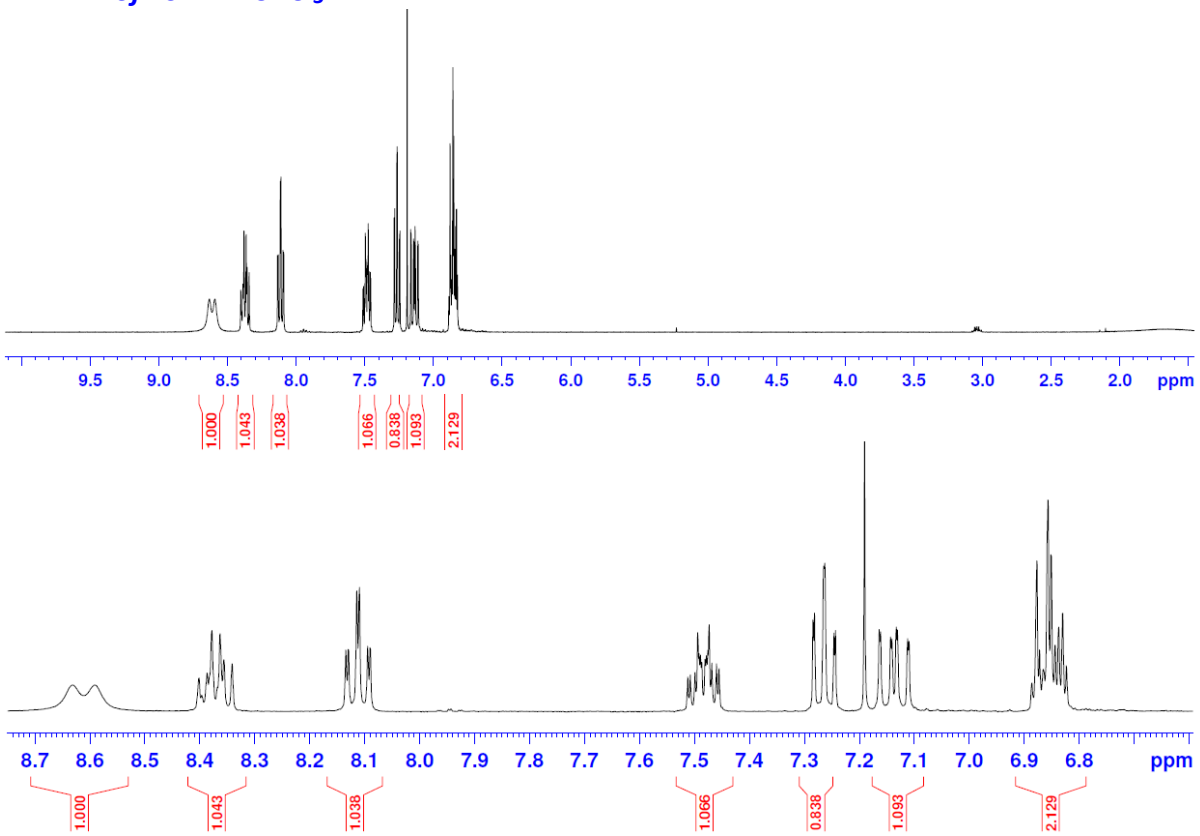
SUPPLEMENTARY DATA (NMR SPECTRA AND CRYSTAL STRUCTURE DATA).

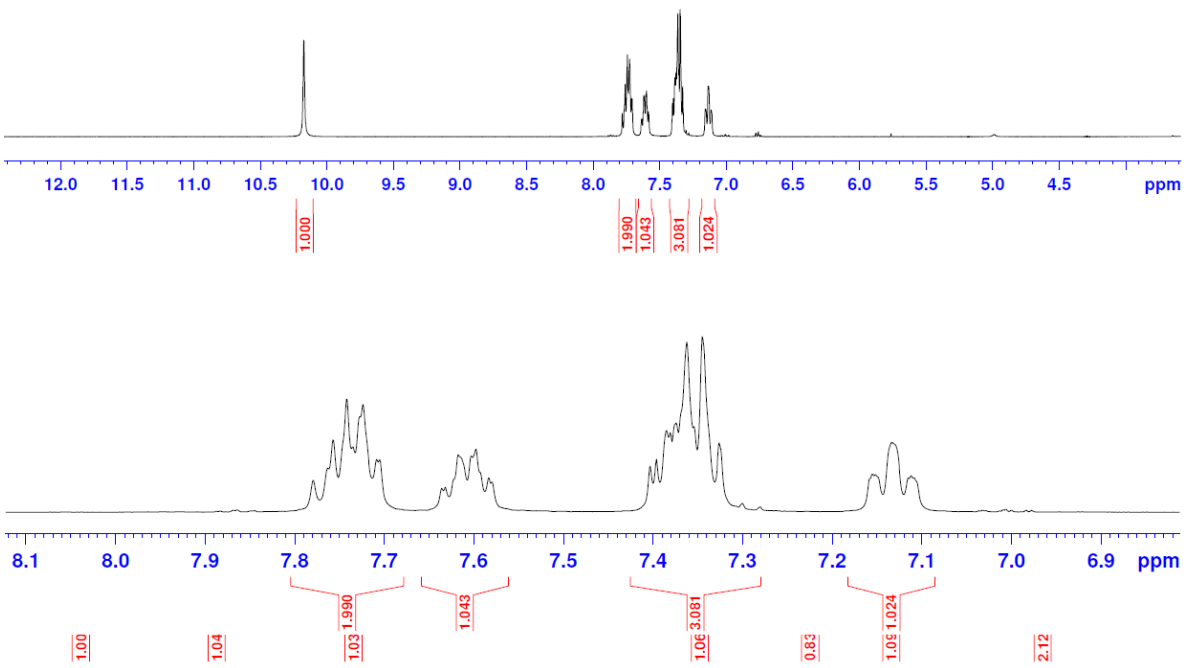
Reaction scheme for Fo24



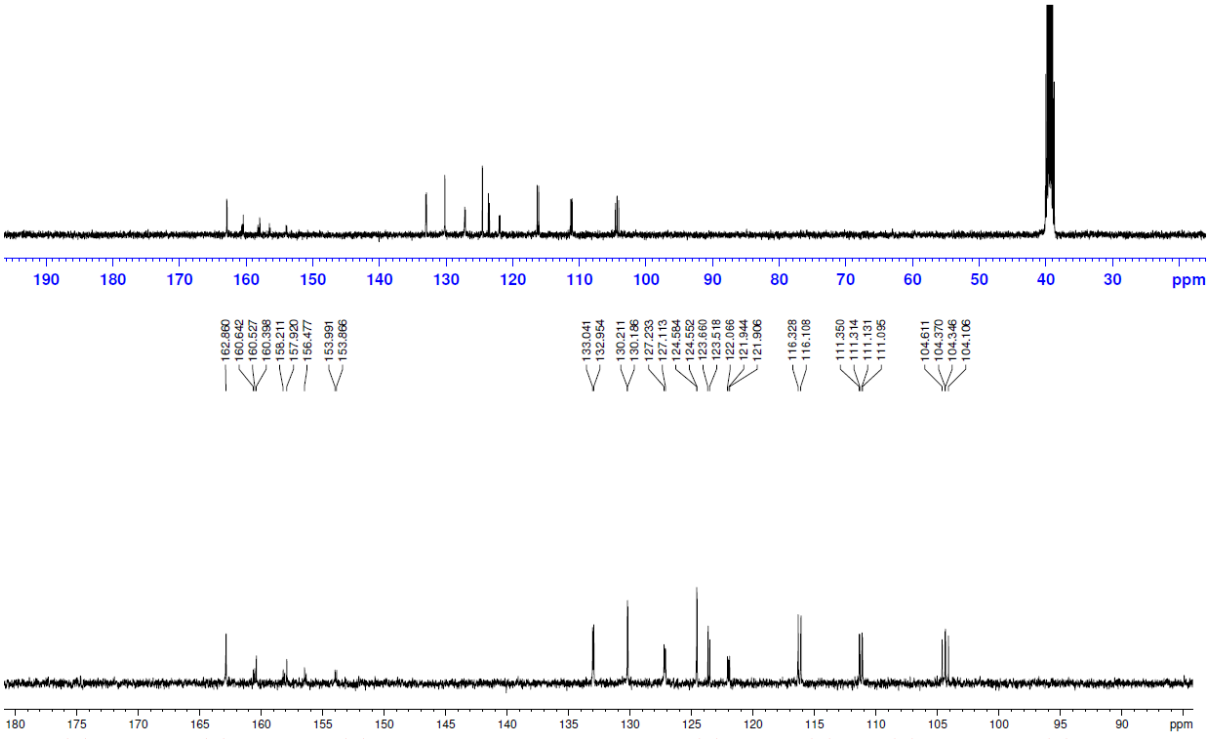
^{1}H NMR of Fo24 in $CDCl_3$:



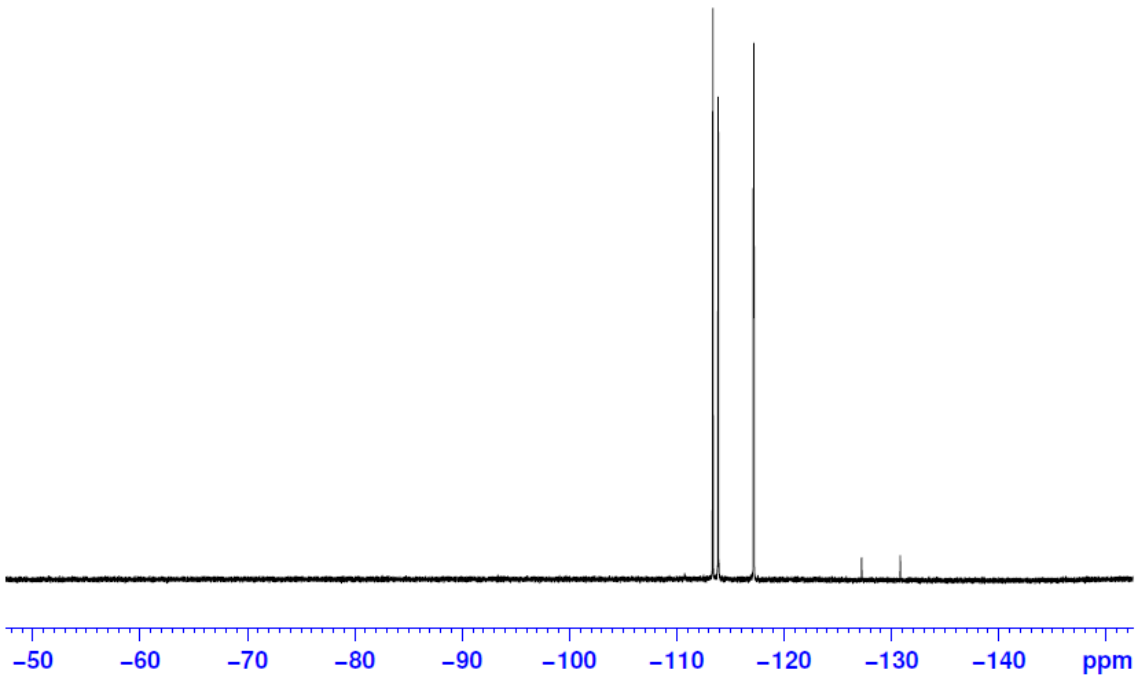
^{1}H NMR of Fo24 in DMSO:



^{13}C NMR of Fo24 in DMSO:



^{19}F NMR of Fo24 in DMSO:



Supplementary Figure S1

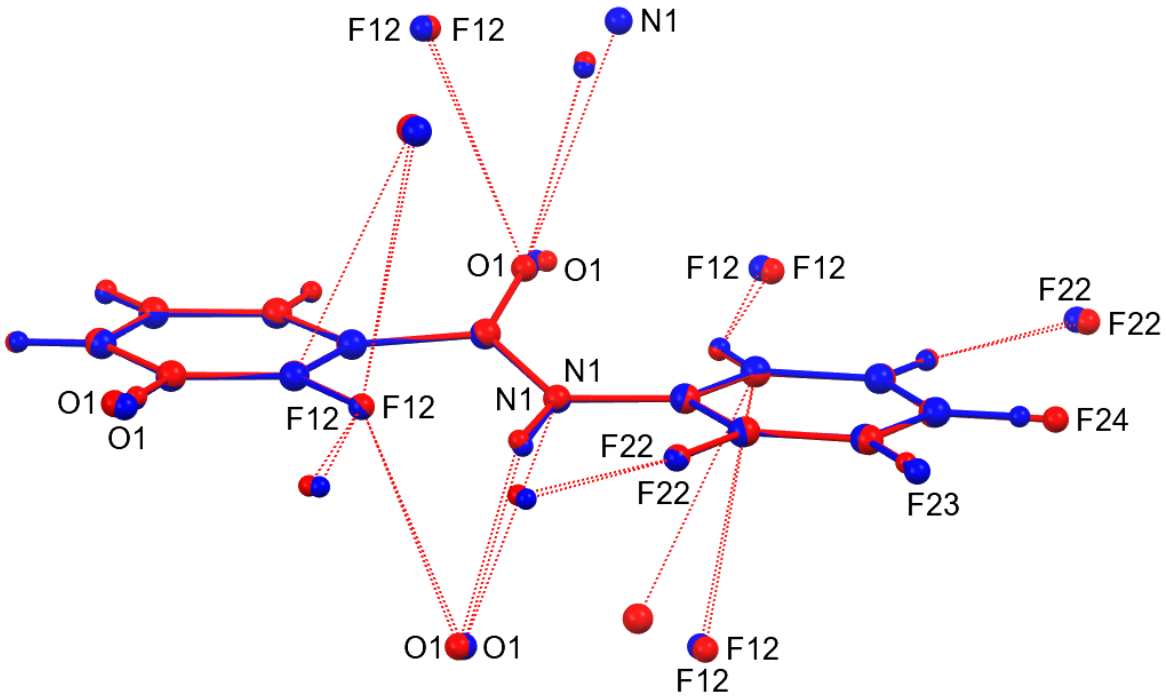


Figure S1: Overlay of the **Fo23** [10] and **Fo24** structures with intermolecular interactions.

Table S1: Selected hydrogen-bond and contact parameters for Fo24.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N1—H1···F12	0.82 (4)	2.12 (4)	2.737 (3)	132 (3)
N1—H1···O1^{i}	0.82 (4)	2.41 (4)	3.092 (3)	141 (3)
C26—H26···O1	0.93	2.35	2.858 (5)	114.4
C26—H26···F12^{ii}	0.93	2.49	3.259 (3)	140.4

Symmetry code(s): (*i*) *x*, *y*+1, *z*; (*ii*) *x*-1, *y*-1, *z*.

CSD search for related trihalobenzamides on 19-12-2023.

Search Overview

Search:	search7
Date/Time done:	Tue Dec 19 17:24:13 2023
Database(s):	CSD version 5.45 (November 2023)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	10

Summary of queries used. Search found structures that:

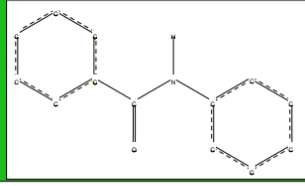
match

Query 7 **Query 8**

Query 7

Formula $C_{13}H_8N_1O_1[7A]_{3-3}$
Search on: **each molecule in turn**
Allow other elements: **Yes**

Query 8



Search: search7 (Tue Dec 19 17:24:13 2023): Hits 1-4

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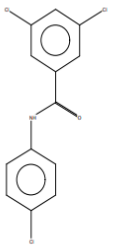

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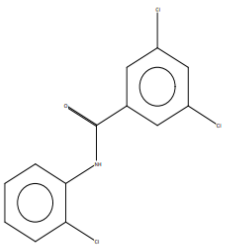

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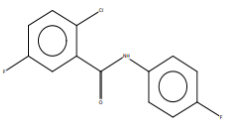
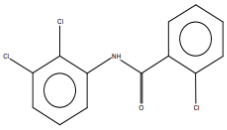


JOFHAO



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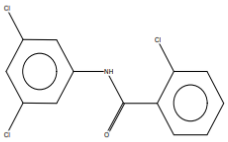
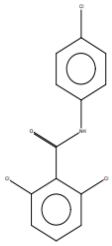
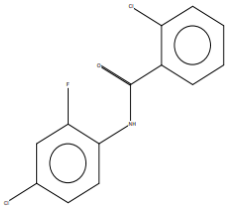
KODTUT



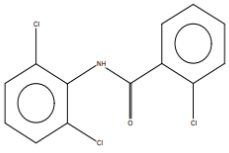
LAQDOY



XEHZOD



YODDUR



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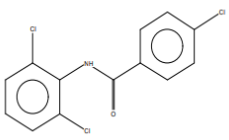
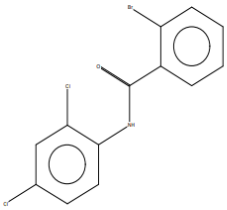


ZAJWUF



General synthesis of Fo24 and some comparisons with related Foxx compounds:

Into a 100 mL clean, dry round-bottom flask containing 30 mL of dichloromethane (CH_2Cl_2) and a magnetic stirrer, a 0.005 mol (0.504 mL) solution of 2,4-difluoroaniline was introduced. Subsequently, 0.005 mol (0.597 mL) of the *ortho*-fluorobenzoyl chloride and 0.005 mol of triethylamine were added to the solution in the round-bottom flask. The solution mixture was allowed to stir continuously overnight. The resulting solution was then washed carefully with 5 × 30mL of 2% $NaHCO_3$ in a separating funnel. The organic phase was then removed under reduced pressure to remove all traces of solvent, and the final product was carefully weighed out and subsequently analyzed.

*Reagents used for fluoro-substituted series: the **Fo24** reagents are highlighted in blue.*

	Molar mass (g/mol)	**Density (g/mL)**	**Volume(mL)**
2-fluorobenzoyl chloride	158.56	1.328	0.597
3-fluorobenzoyl chloride	158.56	1.304	0.607
4-fluorobenzoyl chloride	158.56	1.342	0.591
2,3-difluoroaniline	129.11	1.274	0.507
2,4-difluoroaniline	129.11	1.282	0.504
2,5-difluoroaniline	129.11	1.283	0.503
2,6-difluoroaniline	129.11	1.277	0.506
3,4-difluoroaniline	129.11	1.302	0.496
3,5-difluoroaniline	129.11	1.295	0.6455

*Results of **Foxx** reactions: Comparison of **Fo24** with the other five isomers*

	Melting point (°C)	**Yield (g), (%)**	**N-H Peak DMSO d^6 (ppm)**	**N-H Peak $CDCl_3$ (ppm)**	**Significant IR peaks (cm^{-1})**
Fo23 [10]	100-102	1.14, (88%)	10.39	8.73	3370, 1661, 1546, 1469
Fo24	**110-112**	**1.09, (87%)**	**10.16**	**8.61**	**3375, 1656, 1610, 1481**
Fo25	63-65	1.10, (88%)	10.32	8.88	3398, 1669, 1611, 1475
Fo26	112-113	0.37, (30%)	10.13	8.05	3376, 1666, 1519, 1464
Fo34	126-128	1.10, (89%)	10.67	8.39	3337, 1661, 1538, 1482
Fo35	130-132	1.15, (91%)	10.81	8.45	3348, 1660, 1606, 1458

Reference 10 of the manuscript:
Hehir, N.; Gallagher, J.F. *N*-(2,3-difluorophenyl)-2-fluorobenzamide. *Molbank* **2023**, *2023*(3), M1717; https://doi.org/10.3390/M1717