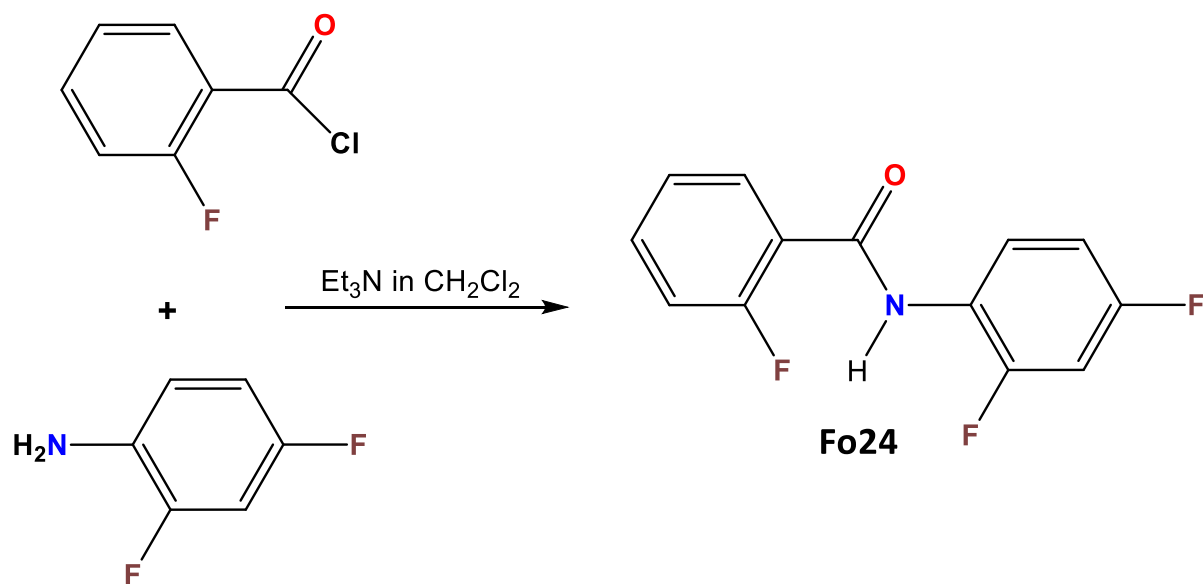
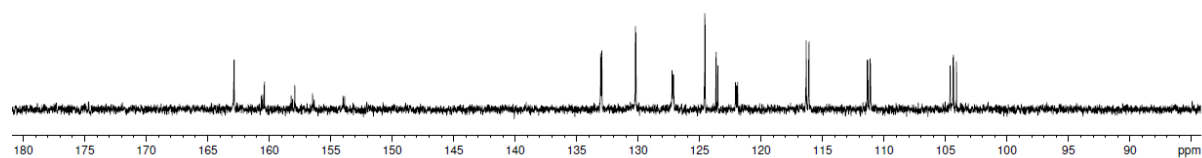
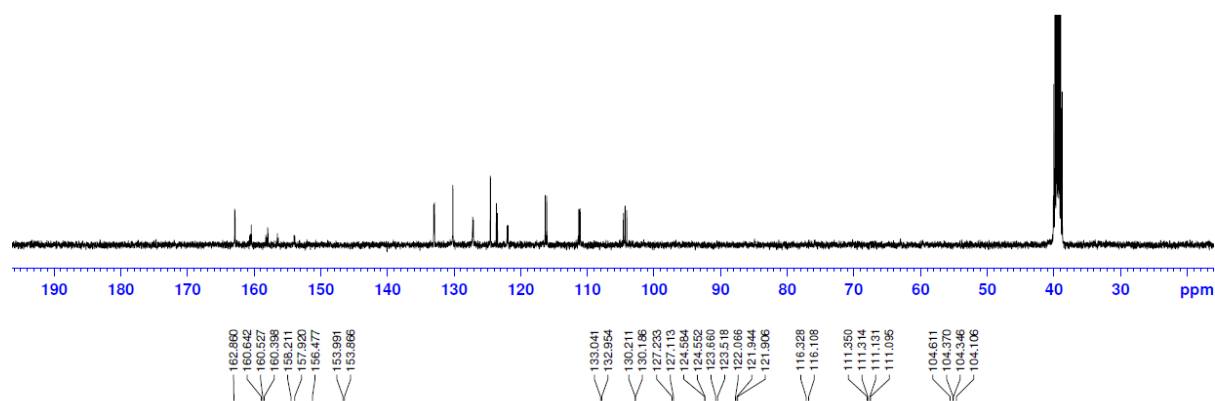


SUPPLEMENTARY DATA (NMR SPECTRA AND CRYSTAL STRUCTURE DATA).

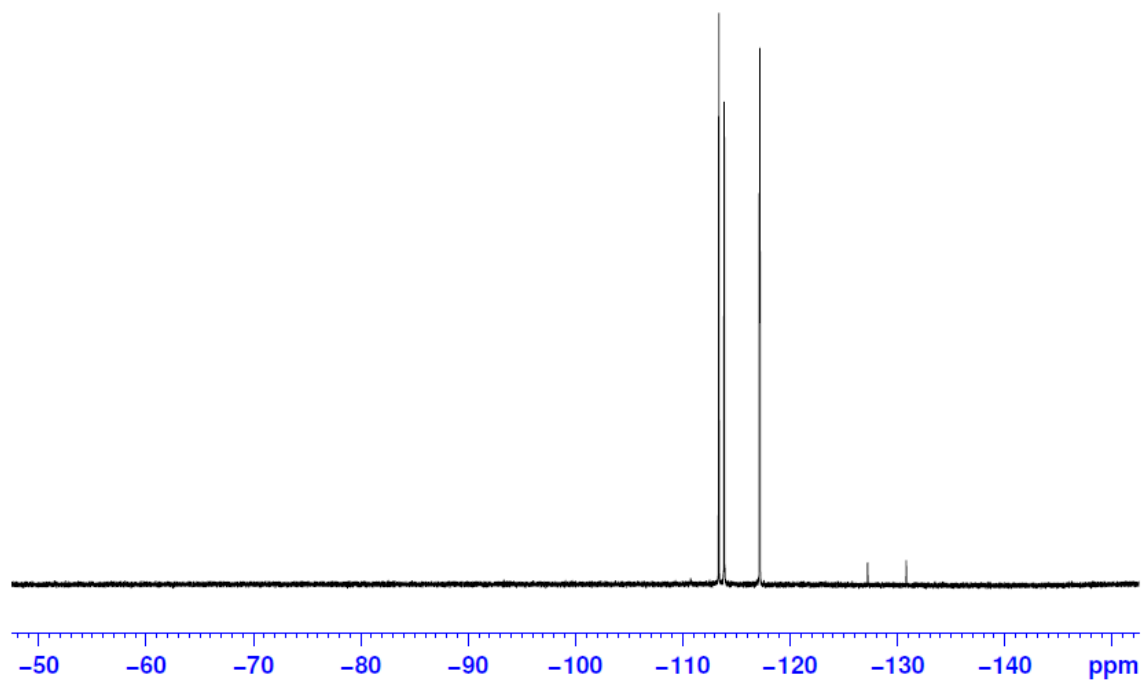
Reaction scheme for Fo24



¹³C NMR of Fo24 in DMSO:



¹⁹F NMR of Fo24 in DMSO:



Supplementary Figure S1

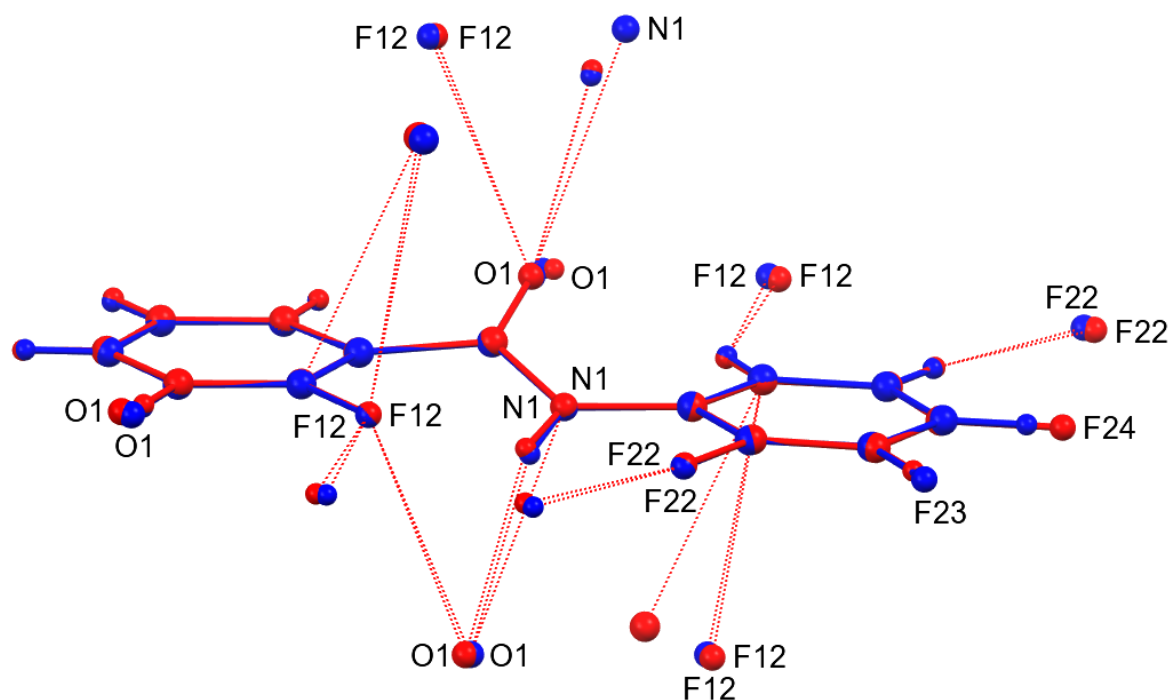


Figure S1: Overlay of the **Fo23** [10] and **Fo24** structures with intermolecular interactions.

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

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
$N1-H1\cdots F12$	0.82 (4)	2.12 (4)	2.737 (3)	132 (3)
$N1-H1\cdots O1^i$	0.82 (4)	2.41 (4)	3.092 (3)	141 (3)
$C26-H26\cdots O1$	0.93	2.35	2.858 (5)	114.4
$C26-H26\cdots F12^{ii}$	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:

Query 7 match Query 8

Query 7	Formula <chem>C13H9N1O1[7A]3-3</chem> Search on: each molecule in turn Allow other elements: Yes
Query 8	

Page 1

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

<p>CANYAV</p> <p>Reference: Jin Zhang, Yue Li, Bai Hong, Ai-Qun Jia, Qian-Hong Zhang (2021) J Chem Cryst, 51, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 3,5-dichloro-N-(4-chlorophenyl)benzamide</p> <p>Space Group: P-1 Space Group No.: 2 a [Å]: 5.047(16) b [Å]: 10.389(4) c [Å]: 12.360(20) V [Å³]: 617.5(4) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>	<p>CANYEZ</p> <p>Reference: Jin Zhang, Yue Li, Bai Hong, Ai-Qun Jia, Qian-Hong Zhang (2021) J Chem Cryst, 51, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 3,5-dichloro-N-(2-chlorophenyl)benzamide</p> <p>Space Group: Pn Space Group No.: 7 a [Å]: 8.581(3) b [Å]: 12.277(4) c [Å]: 11.072(3) V [Å³]: 96.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>
<p>ENUKAA</p> <p>Reference: Qin Huang, Chang Zhang, Kangping Rao, Lihong Zhao (2017) J Crystallogr, Adv Cryst Struct, 248, 16</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: P-1 Space Group No.: 2 a [Å]: 5.042(3) b [Å]: 10.700(3) c [Å]: 12.534(1) V [Å³]: 617.5(2) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>	<p>JOFHIO</p> <p>Reference: S.T. Gonsky, S. Fries, B.P. Sorenson, H. Fries (2008) Acta Crystallogr, Sect B Struct Cryst, 64, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: Pn Space Group No.: 7 a [Å]: 8.581(3) b [Å]: 12.277(4) c [Å]: 11.072(3) V [Å³]: 96.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>

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Search: search7 (Tue Dec 19 17:24:13 2023): Hits 5-8

<p>KOOTUT</p> <p>Reference: S.T. Gonsky, S. Fries, B.P. Sorenson, H. Fries (2008) Acta Crystallogr, Sect B Struct Cryst, 64, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: Pn Space Group No.: 7 a [Å]: 8.581(3) b [Å]: 12.277(4) c [Å]: 11.072(3) V [Å³]: 96.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>	<p>LAGDOY</p> <p>Reference: Jing Zhu, Ming Li, Hong-Wei Shi, Jun-Gang Wang, Chang-Lin (2012) Acta Crystallogr, Sect B Struct Cryst, 68, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2,6-Dichloro-N-(4-chlorophenyl)benzamide</p> <p>Space Group: P21/c Space Group No.: 14 a [Å]: 11.241(2) b [Å]: 12.580(2) c [Å]: 9.502(1) V [Å³]: 1068.0(2) Z: 4 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>
<p>XEHZOD</p> <p>Reference: A. Gents, S. Fries, N. H. Jan (2022) Acta Cryst Chem, 19, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2-chloro-N-(4-chloro-2-fluorophenyl)benzamide</p> <p>Space Group: Pna21 Space Group No.: 29 a [Å]: 8.894(5) b [Å]: 21.350(1) c [Å]: 4.970(2) V [Å³]: 95.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 100 DataCollection: 1.027</p>	<p>YODDUR</p> <p>Reference: S.T. Gonsky, S. Fries, B.P. Sorenson, H. Fries (2008) Acta Crystallogr, Sect B Struct Cryst, 64, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: Pna21 Space Group No.: 29 a [Å]: 8.894(5) b [Å]: 21.350(1) c [Å]: 4.970(2) V [Å³]: 95.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>

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Search: search7 (Tue Dec 19 17:24:13 2023): Hits 9-10

<p>YOMMIG</p> <p>Reference: M. Tolmachev, S.T. Gonsky, J. Kozlov, B.P. Sorenson, H. Fries (2008) Acta Crystallogr, Sect B Struct Cryst, 64, 102</p> <p>Formula: <chem>C13H9Cl3N1O1</chem></p> <p>Compound Name: 4-Chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: P21/c Space Group No.: 14 a [Å]: 16.541(5) b [Å]: 10.370(2) c [Å]: 10.550(2) V [Å³]: 1715.0(3) Z: 4 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 295 DataCollection: 1.027</p>	<p>ZAWUFI</p> <p>Reference: J. Fries, A. Gents (2016) CSD Communication (Private Communication)</p> <p>Formula: <chem>C13H9Br1Cl3N1O1</chem></p> <p>Compound Name: 2-chloro-N-(2,4-dichlorophenyl)benzamide</p> <p>Space Group: Pn Space Group No.: 7 a [Å]: 8.581(3) b [Å]: 12.277(4) c [Å]: 11.072(3) V [Å³]: 96.0(3) Z: 2 Dens(g/cm³): 1.6134(5)</p> <p>R-Factor (R): 0.01 Temperature(K): 100 DataCollection: 1.027</p>
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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 (CH₂Cl₂) 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 × 30 mL of 2% NaHCO₃ 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 <i>d</i> 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>