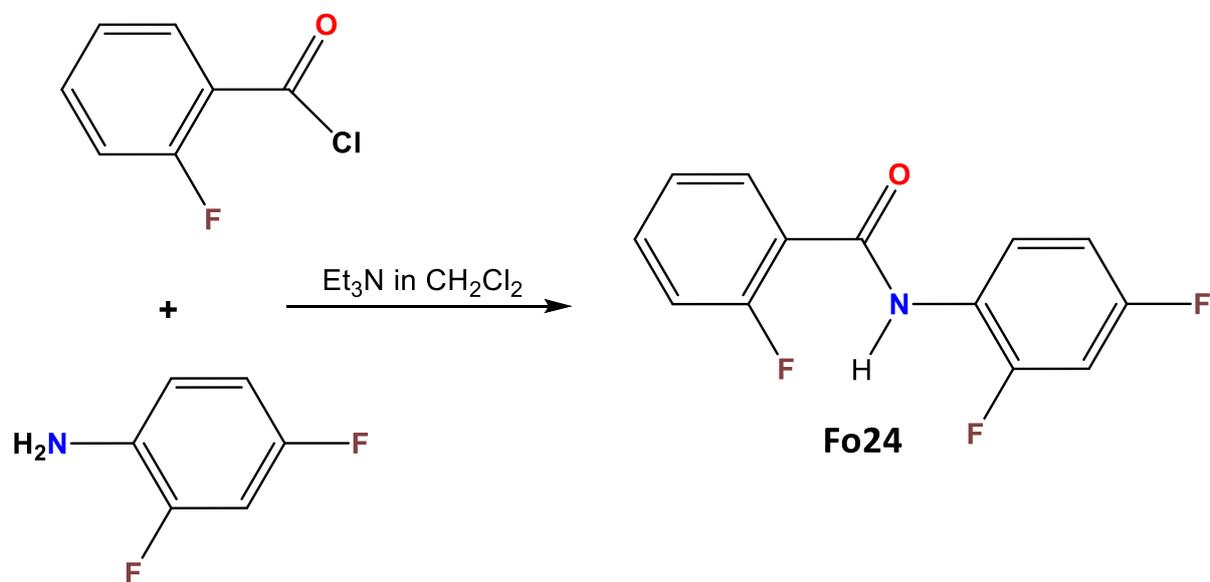
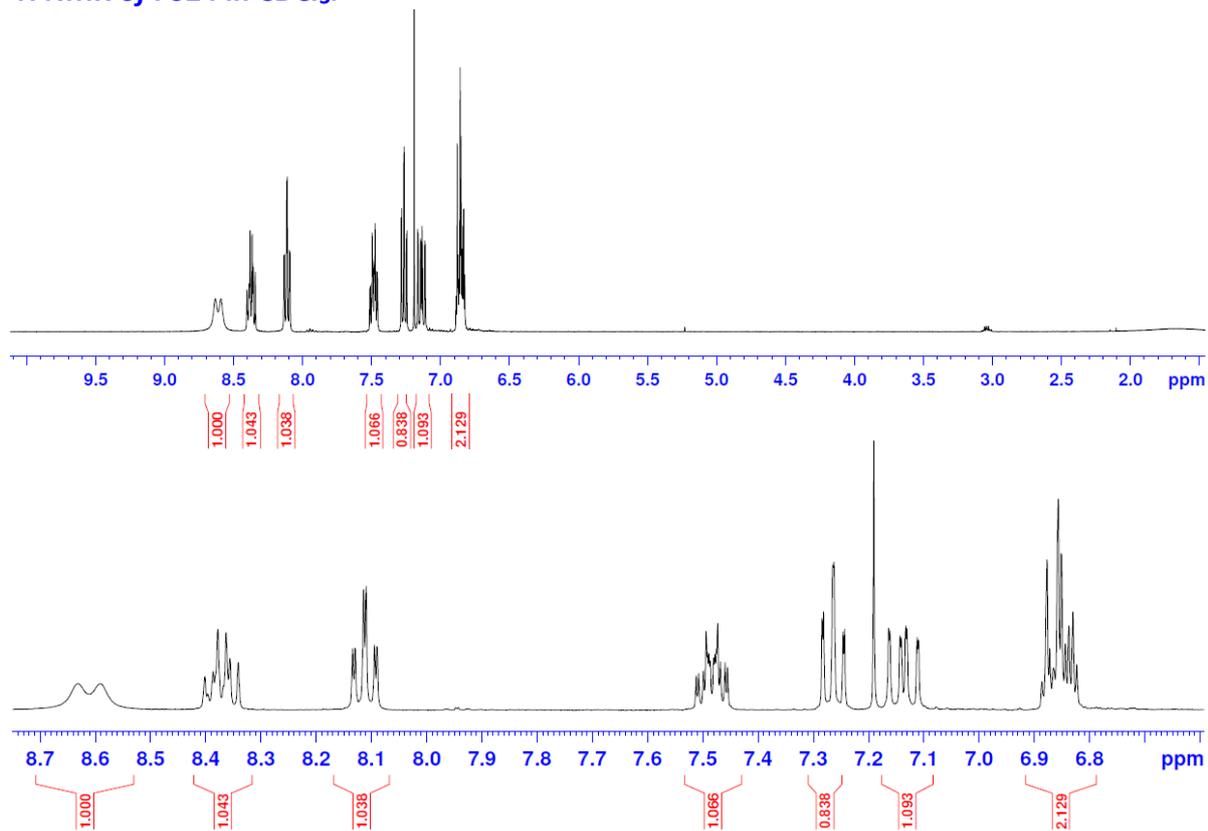


SUPPLEMENTARY DATA (NMR SPECTRA AND CRYSTAL STRUCTURE DATA).

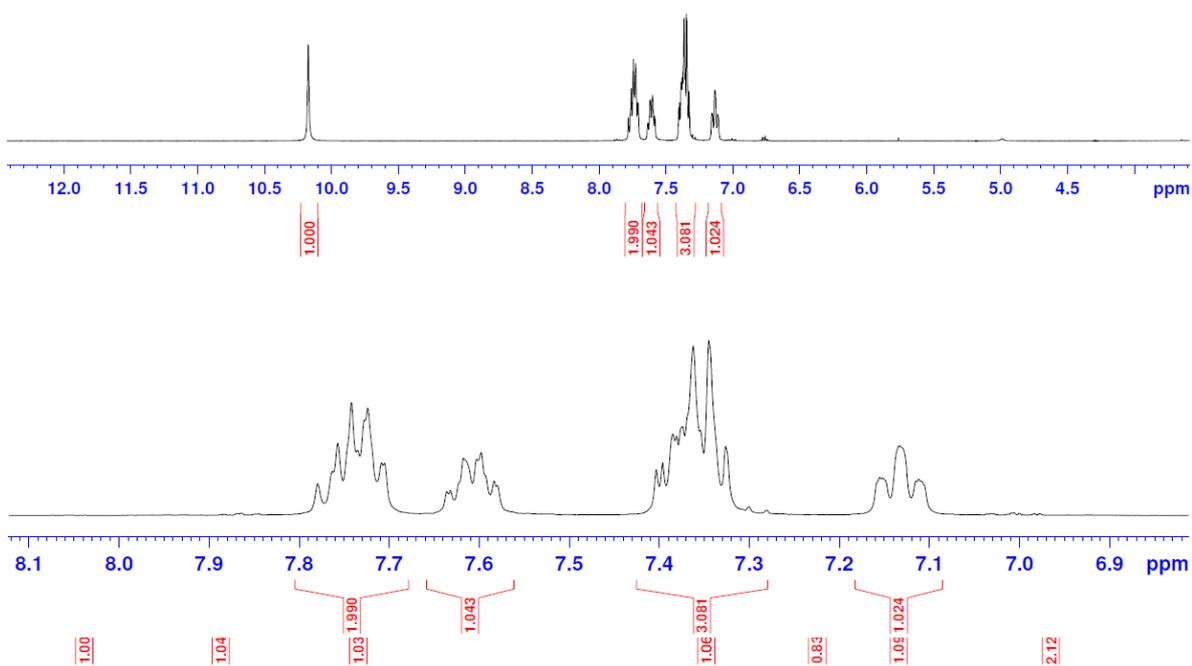
Reaction scheme for Fo24



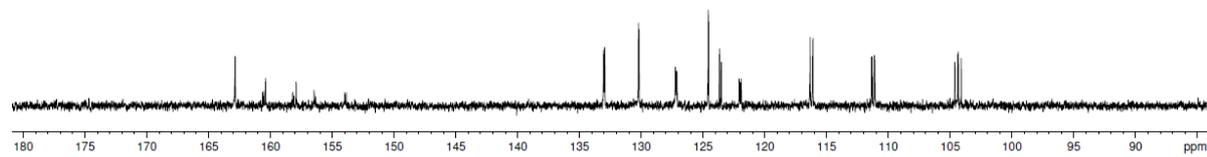
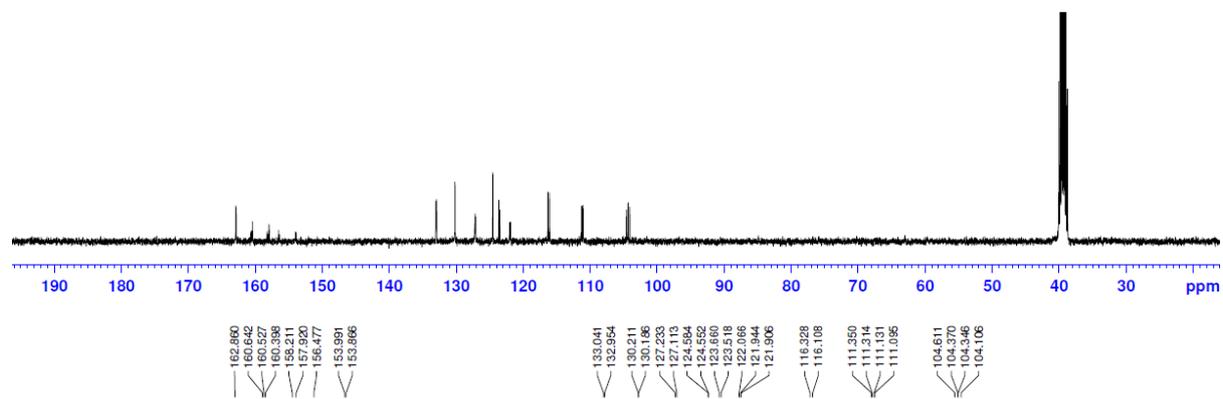
**<sup>1</sup>H NMR of Fo24 in CDCl<sub>3</sub>:**



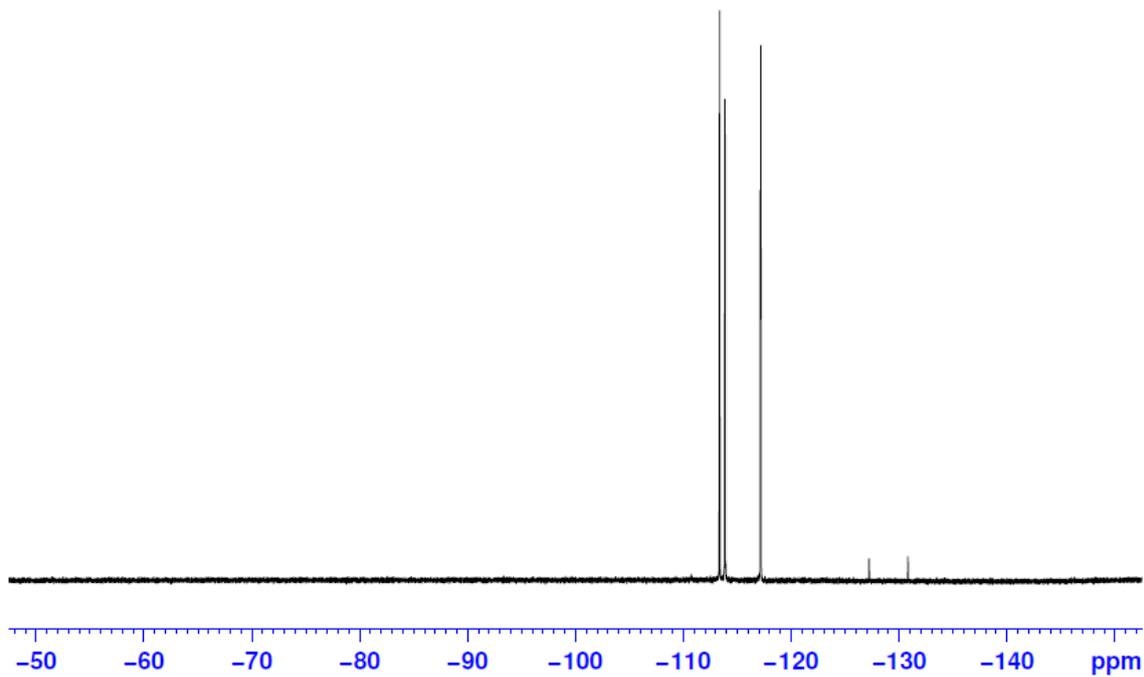
**<sup>1</sup>H NMR of Fo24 in DMSO:**



***<sup>13</sup>C NMR of Fo24 in DMSO:***



***<sup>19</sup>F NMR of Fo24 in DMSO:***



Supplementary Figure S1

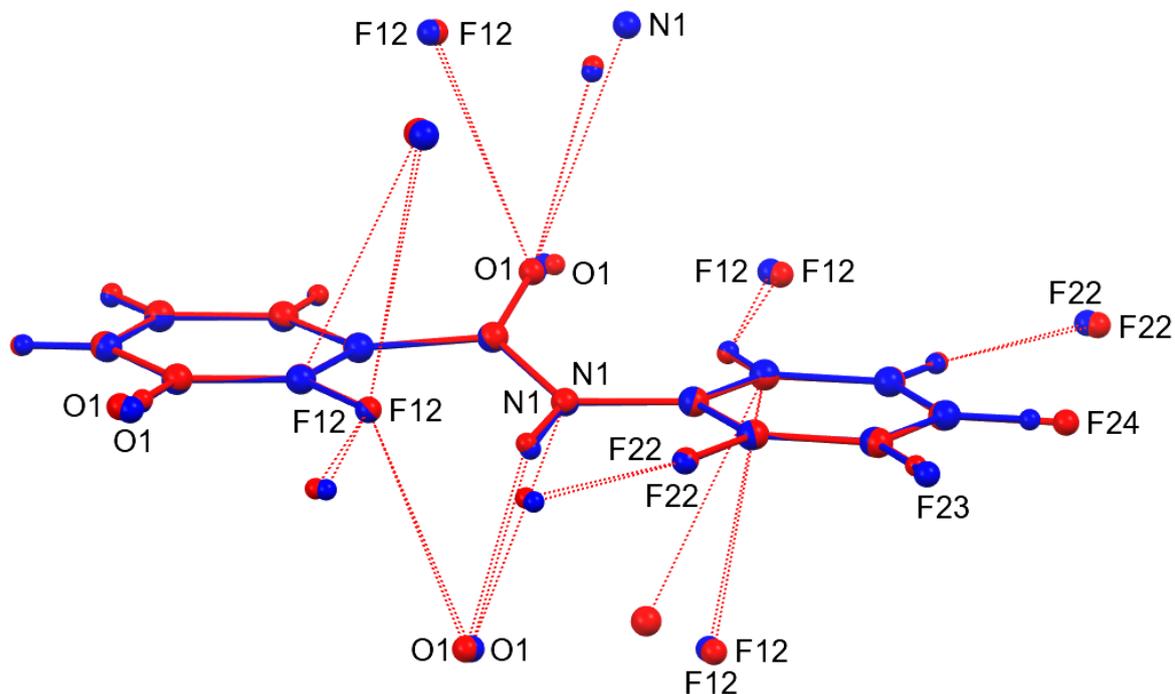


Figure S1: Overlay of the **Fo23** [10] and **Fo24** structures with intermolecular interactions.

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

$D-H\cdots A$	$D-H$ (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)  $x-1, y-1, z$ .

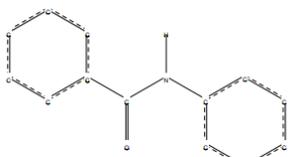
# CSD search for related trihalobenzamides on 19-12-2023.

## Search Overview

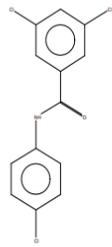
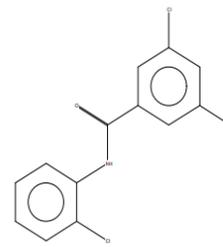
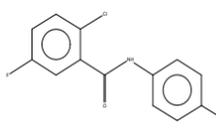
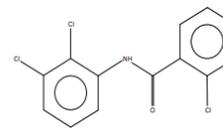
**Search:** search7  
**Date/Time done:** Tue Dec 19 17:24:13 2023  
**Database(s):** CSD version 5.45 (November 2023)  
**Restriction Info:** No refcode restrictions applied  
**Filters:** None  
**Percentage Completed:** 100%  
**Number of Hits:** 10

Summary of queries used. Search found structures that:

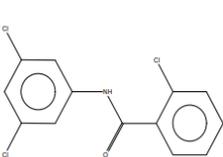
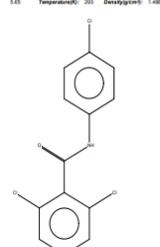
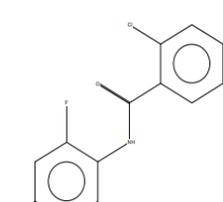
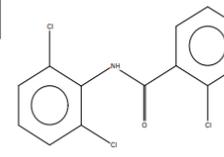
match  
**Query 7** **Query 8**

<b>Query 7</b>	Formula <b>C<sub>13</sub>H<sub>9</sub>N<sub>1</sub>O<sub>1</sub>[TA]3-3</b> Search on: <b>each molecule in turn</b> Allow other elements: <b>Yes</b>
<b>Query 8</b>	

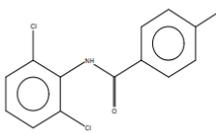
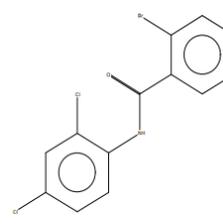
## Search: search7 (Tue Dec 19 17:24:13 2023): Hits 1-4

<p><b>CANYAV</b>                  Reference: Jin Zhang, Tian Li, Bai Hong, Ai-Qun Jia, Qian-Hong Zhang (2011) J Chem Cryst, 41, 108                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 3,5-dichloro-N-(4-chlorophenyl)benzamide                  Space Group: P-1, Cell: a: 5.241(16), b: 10.389(40), c: 13.300(20), α: 90°, β: 107.50(2), γ: 92.34(2)                  Space Group No.: 2                  #Refine: 6.61, Temperature(K): 296, Density(g/cm<sup>3</sup>): 1.627</p> 	<p><b>CANYEZ</b>                  Reference: Jin Zhang, Tian Li, Bai Hong, Ai-Qun Jia, Qian-Hong Zhang (2011) J Chem Cryst, 41, 108                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 3,5-dichloro-N-(2-chlorophenyl)benzamide                  Space Group: Pn, Cell: a: 5.201(15), b: 12.217(4), c: 11.672(15), α: 90°, β: 92.36(2), γ: 92.05                  Space Group No.: 7                  #Refine: 3.47, Temperature(K): 296, Density(g/cm<sup>3</sup>): 1.642</p> 
<p><b>ENJKAA</b>                  Reference: Qin Huang, Changyong Zhang, Kangping Ren, Lirong Qiao (2011) J Crystallogr Appl, 5, 124, 146                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-Chloro-N-(4-chlorophenyl)benzamide                  Space Group: P-1, Cell: a: 5.262(15), b: 8.700(2), c: 13.534(1), α: 90°, β: 107.52(2), γ: 92.26(2)                  Space Group No.: 2                  #Refine: 5.09, Temperature(K): 293, Density(g/cm<sup>3</sup>): 1.626</p> 	<p><b>JOFHAD</b>                  Reference: S T Gowda, S Fariq, B P Soman, H Fares (2008) Acta Crystallogr Sect B Struct Cryst, 64, 1342                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide                  Space Group: Pn, Cell: a: 12.210(1), b: 7.810(3), c: 14.407(3), α: 90°, β: 90°, γ: 111.50(1)                  Space Group No.: 7                  #Refine: 3.20, Temperature(K): 293, Density(g/cm<sup>3</sup>): 1.646</p> 

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

<p><b>KOOTUT</b>                  Reference: S T Gowda, S Fariq, B P Soman, H Fares (2008) Acta Crystallogr Sect B Struct Cryst, 64, 1342                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide                  Space Group: Pn, Cell: a: 12.210(1), b: 7.810(3), c: 14.407(3), α: 90°, β: 90°, γ: 111.50(1)                  Space Group No.: 7                  #Refine: 3.20, Temperature(K): 293, Density(g/cm<sup>3</sup>): 1.646</p> 	<p><b>LAGDOY</b>                  Reference: Jing Zhu, Ming Li, Hong-Jie Ren, Jun-Jiang Wang, Cheng-Lin (2012) Acta Crystallogr Sect B Struct Cryst, 68, 404                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2,6-Dichloro-N-(4-chlorophenyl)benzamide                  Space Group: P2<sub>1</sub>, Cell: a: 11.241(2), b: 13.360(2), c: 8.646(1), α: 90°, β: 90°, γ: 103.80(2)                  Space Group No.: 14                  #Refine: 5.65, Temperature(K): 200, Density(g/cm<sup>3</sup>): 1.488</p> 
<p><b>XEHZOD</b>                  Reference: A Ghosh, S Kumar, Nishu Jan (2022) Asian J Dig Chem, 15, 4033-4041                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>F<sub>1</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-chloro-N-(4-chloro-2-fluorophenyl)benzamide                  Space Group: Pn2<sub>1</sub>, Cell: a: 8.694(5), b: 21.305(1), c: 4.810(2), α: 90°, β: 90°, γ: 90.00                  Space Group No.: 23                  #Refine: 2.22, Temperature(K): 100, Density(g/cm<sup>3</sup>): 1.565</p> 	<p><b>YODDUR</b>                  Reference: S T Gowda, M Nataraj, S Ghosh, B P Soman, H Fares (2008) Acta Crystallogr Sect B Struct Cryst, 64, 1342                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-Chloro-N-(2,4-dichlorophenyl)benzamide                  Space Group: Pn2<sub>1</sub>, Cell: a: 21.305(1), b: 4.810(2), c: 12.504(5), α: 90°, β: 90°, γ: 90.00                  Space Group No.: 23                  #Refine: 2.74, Temperature(K): 200, Density(g/cm<sup>3</sup>): 1.500</p> 

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

<p><b>YOMMIG</b>                  Reference: M Tarek, S T Gowda, J Ghosh, B P Soman, H Fares (2008) Acta Crystallogr Sect B Struct Cryst, 64, 1342                  Formula: C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 4-Chloro-N-(2,4-dichlorophenyl)benzamide                  Space Group: P2<sub>1</sub>, Cell: a: 16.941(5), b: 18.320(2), c: 10.100(1), α: 90°, β: 90°, γ: 90.00                  Space Group No.: 14                  #Refine: 4.10, Temperature(K): 293, Density(g/cm<sup>3</sup>): 1.483</p> 	<p><b>ZAWUFL</b>                  Reference: U Faria, A Saad (2010) CSD Communications (Private Communication)                  Formula: C<sub>13</sub>H<sub>9</sub>Br<sub>1</sub>Cl<sub>2</sub>N<sub>1</sub>O<sub>1</sub>                  Compound Name: 2-bromo-N-(2,4-dichlorophenyl)benzamide                  Space Group: Pn, Cell: a: 5.686(1), b: 8.105(2), c: 14.343(10), α: 90°, β: 90°, γ: 90.00                  Space Group No.: 7                  #Refine: 4.08, Temperature(K): 100, Density(g/cm<sup>3</sup>): 1.808</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 (CH<sub>2</sub>Cl<sub>2</sub>) 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<sub>3</sub> 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)
<b>2-fluorobenzoyl chloride</b>	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
<b>2,4-difluoroaniline</b>	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> <sup>6</sup> (ppm)	N-H Peak CDCl <sub>3</sub> (ppm)	Significant IR peaks (cm <sup>-1</sup> )
<b>Fo23</b> <sup>10</sup>	100-102	1.14, (88%)	10.39	8.73	3370, 1661, 1546, 1469
<b>Fo24</b>	<b>110-112</b>	<b>1.09, (87%)</b>	<b>10.16</b>	<b>8.61</b>	<b>3375, 1656, 1610, 1481</b>
<b>Fo25</b>	63-65	1.10, (88%)	10.32	8.88	3398, 1669, 1611, 1475
<b>Fo26</b>	112-113	0.37, (30%)	10.13	8.05	3376, 1666, 1519, 1464
<b>Fo34</b>	126-128	1.10, (89%)	10.67	8.39	3337, 1661, 1538, 1482
<b>Fo35</b>	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>