Cyclization of Bifunctional 3,5-Diamino-1H-1,2,4-triazole-1-carboximidamide, 5-Amino-3-hydrazinotriazole and 3,6-Diguanidino-1,2,4,5-tetrazine: A One-Step Route to Fluorinated Heteropolycycles

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Abstract: A series of new fluorine-containing triazolopyrimidines and pyrimidinoaminotetrazines results from one-pot reactions of 3,5-diamino-1H-1,2,4-triazole-1-carboximidamide hydrochloride and 1,4-diguanidino-2,3,4,5-tetrazine with fluoro-1,3-diketones. Bicyclization of a variety of fluorinated 1,3-diketones gave three fluorinated heterocyclic pyrazolo[1,2,4]triazolo[1,5-a]pyrimidines in moderate yield in a single step.

Key words: cyclization, bifunctional heterocycles, fluorinated polyheterocycles, triazolopyrimidines, pyrazolo[1,2,4]triazolo[1,5-a]pyrimidines

It is well-known that introduction of a fluorine atom or a fluoroalkyl group into heterocyclic compounds has a profound influence on their chemical, physical and biological properties. Fluorinated heterocycles are widely recognized as important species in the development of new pharmaceuticals and agrochemicals. In the formation of these heterocyclic compounds, cyclic addition reactions have been mainly applied to the synthesis of fluorinated five-membered heterocyclic rings, such as furan, pyrazole, isoxazole, 1,2,3-triazole, and six-membered heterocyclic rings, such as pyrimidine, quinoline and pyridine. It is worthwhile developing new fluorinated heterocyclic rings which may have advantageous properties. Fluorinated heteropolycyclic systems are among some new fluorinated heterocyclic rings that are currently attracting attention. For example, the bicyclic heterocycle, 1,2,4-triazolo[1,5-a]pyrimidine, a subtype of a purine bio-isosteric analogue, is reported to be useful in controlling noxious fungi, and to be a potent and selective A2A adenosine receptor antagonist, in addition to possessing potential anti-tumor activities (Figure 1). The properties of 1,2,4-triazole–iridium complexes, such as flexibility, make them well-suited for organic light-emitting materials and devices. The tricyclic heterocyclic tetrazine compound shown in Figure 1 has also been shown to retard the ripening or senescence of fruit or other plants.

Previously, a bicyclic triazolopyrimidine was prepared by condensation of 3-amino-1,2,4-triazole or 3-amino-5-benzylthio-1,2,4-triazole and dicarbonyl compounds, or by a multiple-step process. However, the efficient syntheses of fluorinated bicyclic or polycyclic triazolopyrimidine, pyrazolo-triazolopyrimidine, or pyrimidinotetrazine compounds have not been reported. Our efforts have been directed toward the development of new synthetic methodologies for the successful preparation of fluorinated heterocyclic compounds as bioactive molecules as well as nitrogen-rich energetic materials. A large number of fluorinated pyrazole, triazole and tetrazolate quaternary salts are ionic liquids. While 3,5-diamino-1H-1,2,4-triazole-1-carboximidamide, 5-amino-3-hydrazino-1,2,4-triazole and 1,4-diguanidino-2,3,4,5-tetrazine are bifunctional heteronucleophiles (Scheme 1), there appears to be no reports of

**Figure 1** Triazole and tetrazine heterocycles

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cyclization reactions of such materials to yield fluorinated heteropolycyclic compounds. Therefore, we now report the facile and straightforward syntheses of fluorinated triazolylaminopyrimidine, pyrazolo-triazolopyrimidine, and pyrimidino(amino)tetrazine heteropolycycles by cyclizing 3,5-diamino-1\(^{1H}\)-1,2,4-triazole-1-carboximidamide, 5-amino-3-hydrazino-1,2,4-triazole, and 1,4-diguanidino-2,3,4,5-tetrazine with fluorine-containing 1,3-diketones.

The commercially available starting material, 3,5-diamino-1,2,4-triazole, was reacted with cyanamide in ethanol under reflux for six hours to form 3,5-diamino-1\(^{1H}\)-1,2,4-triazole-1-carboximidamide, not the previously reported product 5-amino-3-guanidino-1,2,4-triazole\(^{15}\), which, after workup, was isolated as the hydrochloride salt, \(\text{1}\), in 75% yield (Scheme 2). Previously, 2-(3,5-diamino-1\(^{1H}\)-1,2,4-triazol-1-yl)-4,6-dimethylpyrimidine was isolated from the reaction of 4,6-dimethyl-2-hydrazinopyrimidine hydrochloride and dicyandiamide in pyrimidine\(^{16}\), or from the 3,5-diamino-1\(^H\)-1,2,4-triazole-1-carboximidamide\(^{17}\). Cyclization of \(\text{1}\) with fluorine-containing 1,3-diketones \(\text{2a}\)–\(\text{c}\) (1:1), in acetic acid at 110 °C for 24 hours, generated the fluorinated triazolylaminopyrimidines \(\text{3a}\)–\(\text{c}\) in high yields (Scheme 2). An attempt to form the bicyclic product, 4,6-bis(trifluoromethyl)-2-(1,2,4-triazolo[1,5-\(a\)]pyrimidin-5-ylamino)pyrimidine, by treating \(\text{3a}\) with additional 1,1,1,5,5,5-hexafluoropentane-2,4-dione (\(\text{2a}\)) in acetic acid at 110 °C was unsuccessful. After refluxing \(\text{1}\) and \(\text{2a}\) (1:2 ratio) in ethanol with sulfuric acid as catalyst, the \(^{19}\)F NMR spectrum of the reaction mixture showed resonances at \(\delta\) = –68.8 ppm (\(\text{3a}\)), and at \(\delta\) = –69.0 and –70.0 ppm (\(\text{4}\)). Separation of the reaction mixture gave \(\text{3a}\) (70% yield) and \(\text{4}\) (30%).

While no bicyclization reactions occurred, it was found that \(\text{4}\) could also be obtained in 60% yield by reacting 3,5-diamino-1,2,4-triazole with \(\text{2a}\) under the same conditions.

The formation of compound \(\text{4}\) from the 3,5-diamino-1\(^H\)-1,2,4-triazole-1-carboximidamide.
1,2,4-triazole-1-carboximidamide hydrochloride, 1, may involve an initial solvolysis of the guanyl moiety to yield 3,5-diamo-1,2,4-triazole which would react with the diketone to produce 4.

The bicyclization of 5-amino-3-hydrazino-1,2,4-triazole dihydrochloride (5) to three fluorinated pyrazolo[1,2,4]triazolo[1,5-α]pyrimidine heterocycles in one step was also investigated; the starting material, 5, was produced in two steps from 3,5-diamo-1,2,4-triazole. 13 In an effort to prepare 5-amino-3-[3,5-bis(trifluoromethyl)pyrazolo]-1,2,4-triazole, 5 was reacted with 2a to give a mixture of 5,7-bis(trifluoromethyl)-2-[3,5-bis(trifluoromethyl)pyrazolo]-1,2,4-triazolo[1,5-α]pyrimidine (6) and the corresponding dihydro compound 7 (Scheme 3). The mixture was easily separated by chromatography to give 6 (10%) and 7 (60%). The structure of compound 6 was confirmed by 19F and 1H NMR, mass spectrometry and elemental analysis [four 19F NMR resonances (δ = −68.38, −68.26, −62.94 and −59.16 ppm), and aromatic proton signals in the 1H NMR spectrum (δ = 8.21 and 7.54 ppm)]. The structure of 7 was unambiguously assigned using 1H (1H−13C HSQC, HMBC) and 19F NMR spectroscopy, mass spectrometry, and elemental analysis. In the 1H HSQC spectrum of 7, a clear decoupled 1H singlet at δ = 6.21 ppm could be assigned to the hydroxyl group. When 5 and pentane-2,4-dione were heated at reflux for 24 hours under the same conditions, only 5,7-dimethyl-2-(3,5-dimethylpyrazolo)-1,2,4-triazolo[1,5-α]pyrimidine (8) was obtained in 70% yield. Based on the observed formation of a single compound, 8, it can be seen that the formation of 7 arises either as a direct result of the presence of a high concentration of the enol isomer of bis(trifluoromethyl)acetylacetone or because the dehydration step is more difficult under the reaction conditions when a fluorinated group is present. 18 Dehydration of 7 under the influence of acetic anhydride at 120 °C, gave 6 in 90% yield. This is thus a simple and convenient one-step route for the preparation of fluorinated heterocyclic derivatives of pyrazolo-[1,2,4]-triazolo[1,5-α]pyrimidine.

The result obtained with 2a encouraged us to extend this approach to the synthesis of asymmetry-fluorinated pentane-2,4-diones in order to synthesize the fluorinated heteropolycycles, pyrazolo-1,2,4-triazolo-pyrimidines, using 1,1,1-trifluoropentane-2,4-dione (2b; Scheme 4). Upon column chromatographic purification of the reaction mixture, 7-methyl-5-trifluoromethyl-2-(5-methyl-3-trifluoromethylpyrazolo)-1,2,4-triazolo[1,5-α]pyrimidine (9), and a three-component isomeric mixture were obtained. Compound 9 was identified using 1H (1H−13C HMBC) and 19F NMR spectroscopy, mass spectra, elemental analysis and single-crystal X-ray structure determination. The 19F NMR signals at δ = −69.76 and −63.46 ppm were assigned to the trifluoromethyl groups on the pyrimidine and pyrazole rings, respectively, based on 1H−13C HMBC and 19F NMR spectroscopy; the coupling constants (J_{CF}) between the fluorine atoms of the trifluoromethyl groups and the carbon atom were 275 and 266 Hz, respectively. The mixture containing the isomeric compounds 10, 11 and 12 could not be separated by normal column chromatography because of their very similar polarities. The GC-MS chromatogram, however, exhibited three peaks at 14.1 (m/z = 350), 14.6 (m/z = 350) and 15.7 (m/z = 350) minutes, corresponding to the three isomers. These isomeric structures were identified by comparison of the 19F NMR spectra with those of 6 and 9.

Furly pyrimidine derivatives have been reported to be important antitumor agents. 19 Condensation of furyl-substi-

**Scheme 3** Cyclization reactions of 5-amino-3-hydrazino-1,2,4-triazole

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tuted 4,4,4-trifluoro-1-(2-furyl)butane-1,3-dione with 5, gave a mixture of two isomers 13 and 14 (Scheme 5). The GC-MS chromatogram exhibited two peaks at 19.9 (m/z = 454) and 20.3 (m/z = 454) minutes. The ratio of 13 and 14 was 22:78, based on comparison of peak intensities in the $^{19}$F NMR spectra. Their structures were assigned by comparison with the $^{19}$F NMR spectra of 6 and 9.

The synthesis of 3,6-bis[4,6-bis(trifluoromethyl)pyrimidino-2-amino]tetrazine (16), a fluorinated heteropolycyclic, in 75% yield also succeeded by heating 3,6-diguanidino-1,2,4,5-tetrazine (15)$^{14}$ and 2a, at reflux in dioxane (Scheme 6). However, no reaction occurred when 15 was heated under the same conditions with 1,1,1-trifluoropentane-2,4-dione (2b).

Scheme 4  Synthesis of asymmetrically fluorinated pyrazolo-1,2,4-triazolo-pyrimidines

Scheme 5  Synthesis of asymmetrically fluorinated pyrazolo-1,2,4-triazolo-pyrimidines

Scheme 6  Synthesis of fluorinated pyrimidinotetrazine
The solid-state structure of 9 was confirmed by single-crystal X-ray diffraction as shown in Figure 2. Suitable colorless plate crystals were obtained by slow concentration of an ethyl acetate/hexane solution of 9. A notable feature of this molecule is the approximate co-planarity of the pyrazole and pyrimidine moieties (only a 2.2° angle between the pyrazole and pyrimidine mean planes). This, as well as the short C–N bond length joining the two systems (C7–N12, 1.394(2) Å), indicates a delocalization of the aromaticity across both ring-systems. This conformation enables the molecules to pack in alternating ABAB stacks parallel to the a-axis with a gap of ~3.45 Å between each ‘planar’ unit as shown in Figure 2b.

In conclusion, a new and highly effective one-step route has been developed for the preparation of fluorine-containing heteropolycycles. Cyclization of bifunctional nucleophiles, 3,5-diamino-1H-1,2,4-triazole-1-carboximidamide hydrochloride and 3,6-diguanidino-1,2,4,5-tetrazine, with fluorine-containing 1,3-diketones results in the formation of fluorinated triazolylaminopyrimidines and pyrimidinoaionitetrazines in high yield. Combination of 5-amino-3-hydradizo-1,2,4-triazole dihydrochloride with a variety of fluorinated 1,3-diketones yields three symmetric and asymmetric fluorinated heterocycles, pyrazolo[1,2,4]triazolo[1,5-a]pyrimidines, in one step in moderate yields.

All the reagents used were analytical reagents purchased from commercial sources and used as received. The following materials were prepared and purified according to reported procedures: 5-amino-3-hydrazino-1,2,4-triazole dihydrochloride and 3,6-diguanidino-1,2,4,5-tetrazine.  

1H, 19F and 13C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer operating at 300.13, 282 and 75.48 MHz, respectively. 1H–13C HSQC and HMBC spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. Chemical shifts are reported relative to DMS (1H and 13C NMR) or CF3CCl3 (19F NMR). The solvent used was CD3CN unless otherwise specified. Melting points were recorded on a differential scanning calorimeter (DSC) at a scan rate of 10 °C/min. Elemental analyses were performed on an EXETER CE-440 Elemental Analyzer. GC-MS spectra were recorded on a Shimadzu GCMS-QP5050A using a capillary column.

3,5-Diamino-1H-1,2,4-triazole-1-carboximidamide Hydrochloride (1)  
To a round-bottom flask fitted with a reflux condenser, was added 3,5-diamino-1H-1,2,4-triazole hydrochloride (3 mmol) and cyanamide (1 mmol) in AcOH (10 mL). The reaction was heated at reflux for 24 h, then the mixture was filtered and washed with EtOH (15 mL), and the white solid was recrystallized from methanol to give 1. Yield: 75% white solid; mp (DSC) 210 °C (dec.).

1H NMR (DMSO-d6): δ = 8.8 (s, 4 H), 7.4 (s, 2 H), 5.8 (s, 2 H).
13C NMR (DMSO-d6): δ = 164.3, 157.6, 152.7.

Preparation of Fluorinated Triazolopyrimidines 3a–c; General Procedure  
To a round-bottom flask fitted with a reflux condenser, was added 3,5-diamino-1H-1,2,4-triazole-1-carboximidamide hydrochloride (1; 1 mmol) and fluorinated 1,3-β-diketone (1 mmol) in AcOH (10 mL). The reaction was heated at reflux for 24 h then AcOH was removed under reduced pressure and the residue was recrystallized from 1,4-dioxane to give 3a–c in good yields.

2-(3,5-Diamino-1H-1,2,4-triazol-1-yl)-4,6-difluoromethylpyrimidine (3a)  
Yield: 80%; yellow solid; mp 319 °C.
1H NMR (DMSO-d6): δ = 8.1 (s, 1 H), 7.5 (s, 2 H), 5.8 (s, 2 H).
13C NMR (DMSO-d6): δ = 164.1, 159.5 (q, JCF = 37.0 Hz, CCF2), 157.9, 156.5, 126.9 (q, JCF = 276.0 Hz, CF3), 108.9.
19F NMR (DMSO-d6): δ = –68.8 (s, 6 F).
GC-MS (EI): m/z = 313 [M]+.

2-(3,5-Diamino-1H-1,2,4-triazol-1-yl)-4-methyl-6-trifluoromethylpyrimidine (3b)  
Yield: 70%; yellow solid; mp 322 °C.
1H NMR (DMSO-d6): δ = 7.6 (s, 1 H), 7.5 (s, 2 H), 5.6 (s, 2 H), 2.5 (s, 3 H).
13C NMR (DMSO-d6): δ = 172.6, 162.1 156.3, 155.32, 154.8 (q, JCF = 35.0 Hz, CCF2), 121.5 (q, JCF = 276.0 Hz, CF3), 111.1, 24.0.
19F NMR (DMSO-d6): δ = –69.0 (s, 3 F).
GC-MS (EI): m/z = 259 [M]+.

2-(3,5-Diamino-1H-1,2,4-triazol-1-yl)-4-phenyl-6-trifluoromethylpyrimidine (3c)  
Yield: 62%; yellow solid; mp 324 °C.
1H NMR (DMSO-d6): δ = 8.3 (d, J = 6.8 Hz, 2 H), 8.2 (s, 1 H), 7.8 (s, 2 H), 7.6 (m, 3 H).
13C NMR (DMSO-d6): δ = 169.3, 161.4, 157.4 (q, JCF = 35.0 Hz, CCF2), 156.7, 135.9, 134.0, 130.6, 129.3, 121.7 (q, JCF = 275.0 Hz, CF3), 109.5.
19F NMR (DMSO-d6): δ = –68.6 (s, 3 F).
GC-MS (EI): m/z = 321 [M]+.
Anal. Calcd for C14H13F3N6·H2O: C, 49.32; H, 3.86; N, 26.84. Found: C, 49.08; H, 3.20; N, 26.43.
Preparation of 3a and 5,7-Bis(trifluoromethyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine-2-amine (4): Method 1
To a round-bottom flask fitted with a reflux condenser, 1 (1 mmol), 1,1,5,5,5-hexafluoropentane-2,4-dione (2a; 2 mmol) and concd H2SO4 (6 drops) in EtOH (15 mL) was brought to reflux for 24 h. The mixture was cooled to r.t. and neutralized with sat NaHCO3, EtOH was removed under reduced pressure, MeCN (40 mL) was added to the residue and the solution was stirred for 1 h. The solution was filtered and the residue was recrystallized (1,4-dioxane) to yield a yellow solid (3a), which was identified by 1H NMR, 19F NMR, GC-MS.

Yield: 10%; colorless solid; mp 167 °C.

Preparation of 5,7-Dimethyl-2-[3,5-bis(trifluoromethyl)pyrazolo]-[1,2,4]-triazolo[1,5-a]pyrimidine (8)
The reaction was carried out as described above with 5-amino-3-hydrazone-1,2,4-triazole dihydrochloride (5; 1 mmol) and pentane-2,4-dione (2 mmol). The solvent was removed and the crude product was recrystallized (EtOH) to give 8.

Yield: 70%; colorless solid; mp 172 °C.

Preparation of Pyrazolo-1,2,4-triazolopyrimidines 9–12
The reaction was carried out as described above with 5 (1 mmol) and 2b (2 mmol). After addition of NaHCO3, H2O (15 mL) was added, the solution was extracted with EtOAc (3 × 15 mL) and the organic extracts were dried over anhydrous Na2SO4. After the solvent was removed, the crude product was purified by column chromatography (hexane–EtOAc, 5:1 then 2:1) to give 9 and a mixture of the three isomers 10, 11 and 12 (30:40:10 mixture by 19F NMR spectra).

Yield: 10%; colorless solid; mp 162 °C.

Preparation of 5,7-Bis(trifluoromethyl)-2-[3,5-bis(trifluoromethyl)pyrazolo]-[1,2,4]-triazolo[1,5-a]pyrimidine (6)
The reaction was carried as described above with 5 (1 mmol) and 2a (2 mmol). After the addition of NaHCO3, H2O (15 mL) was added, the solution was extracted with EtOAc (3 × 15 mL) and the organic extracts were dried over anhydrous Na2SO4. The solvent was removed and the crude product was recrystallized by column chromatography (hexane–EtOAc, 3:1) to give 6 and 7.

Yield: 10%; colorless solid; mp 167 °C.

Preparation of 7-Methyl-5-trifluoromethyl-2-(5-methyl-3-trifluoromethyl-pyrimidine)-[1,2,4]-triazolo[1,5-a]pyrimidine (9)
Yield: 10%; colorless solid; mp 162 °C.

Preparation of 4,4,4-trifluoro-1-(2-furyl)butane-1,3-dione (2a; 2 mmol). The solvent was removed and the crude product was recrystallized (EtOH) to give 2a.

Yield: 60%; colorless solid; GC peaks at 14.3 min, 14.5 min and 14.7 min.

Preparation of 5,7-Dimethyl-2-[3,5-bis(trifluoromethyl)pyrazolo]-[1,2,4]-triazolo[1,5-a]pyrimidine (8)
The reaction was carried out as described above with 5-amino-3-hydrazone-1,2,4-triazole dihydrochloride (5; 1 mmol) and pentane-2,4-dione (2 mmol). The solvent was removed and the crude product was recrystallized (EtOH) to give 8.

Yield: 70%; colorless solid; mp 172 °C.

Preparation of Pyrazolo-1,2,4-triazolopyrimidines 9–12
The reaction was carried out as described above with 5 (1 mmol) and 2b (2 mmol). After addition of NaHCO3, H2O (15 mL) was added, the solution was extracted with EtOAc (3 × 15 mL) and the organic extracts were dried over anhydrous Na2SO4. After the solvent was removed, the crude product was purified by column chromatography (hexane–EtOAc, 5:1 then 2:1) to give 9 and a mixture of the three isomers 10, 11 and 12 (30:40:10 mixture by 19F NMR spectra).

Yield: 10%; colorless solid; mp 162 °C.

Preparation of 5,7-Dimethyl-2-[3,5-bis(trifluoromethyl)pyrazolo]-[1,2,4]-triazolo[1,5-a]pyrimidine (8)
The reaction was carried out as described above with 5-amino-3-hydrazone-1,2,4-triazole dihydrochloride (5; 1 mmol) and pentane-2,4-dione (2 mmol). The solvent was removed and the crude product was recrystallized (EtOH) to give 8.

Yield: 70%; colorless solid; mp 172 °C.
dition of NaHCO₃, H₂O (15 mL) was added, the mixture was ex-
tacted with EtOAc (3 × 15 mL) and the organic extracts were dried 
on anhydrous Na₂SO₄. The solvent was removed and the crude 
product was purified by column chromatography (hexane–EtOAc, 
5:1) to give a mixture of the isomers 13 and 14.
Yield: 50% (isolated yield of 13 + 14 in 22:78 ratio based on 
¹⁹F NMR spectra); colorless solid; GC peaks at 19.9 min and 20.3 min. 
¹³C NMR (DMSO-d₆): δ = 8.05 (s, 1 H), 7.90 (m, 1 H), 7.62 (d, J = 3.5 
Hz, 1 H), 7.58 (m, 1 H), 7.13 (s, 1 H), 6.84 (m, 1 H), 6.77 (q, J = 1.7 
Hz, 1 H), 6.54 (q, J = 1.7 Hz, 1 H).
GC-MS (EI): m/z = 454 [M⁺] (19.9 min), 454 [M⁺] (20.3 min). 

Preparation of 3,6-Bis[4,6-bis(trifluoromethyl)pyrimidino-2-
amino]tetrazine (16)
The reaction was carried out as described above with 
15 (0.5 mmol) and 2a (1 mmol) in 1,4-dioxane (10 mL) under reflux. The 
mixture was reacted for 24 h then cooled to r.t. and filtered. The residue was 
washed with EtOH (3 × 15 mL) and dried in vacuo to give 16.
Yield: 75%; red solid; mp 225 °C.
¹³C NMR (DMSO-d₆): δ = 12.4 (s, 2 H), 8.0 (s, 2 H).
¹⁹F NMR (DMSO-d₆): δ = –68.6 (s, 6 F).
Anal. Calcd for C₂₂H₂₁F₆N₆O₂: C, 47.59; H, 1.77; N, 18.50. Found: 
C, 47.62; H, 1.64; N, 18.26.

X-ray Crystallographic Analysis of 9
Crystals of compound 9 were removed from the flask and a suitable 
crystal was selected, attached to a glass fiber and data were collect-
ed at 90(2) K using a Bruker/Siemens SMART APEX instrument 
(Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool 
Neverice low-temperature device. Data were measured using omeg-
ga scans of 0.3° (omega and phi scans of 0.5°) per frame for 20 s for 
9, and a full sphere of data was collected. A total of 2400 (2565) 
frames were collected with a final resolution of 0.83 Å. Cell para-
tures were solved by analysis of systematic absences. All non-hydro-
ogen atoms were refined anisotropically. No decomposition was 
observed during data collection.
X-ray crystal data for 9: Empirical formula: C₉₋₁²⁺H₁₂F₆N₆; Formula 
weight 350.24; Crystal system = triclinic; Space group PT #22; 
T = 90(2) K; a = 7.0943(4) Å, b = 7.3652(4) Å, c = 13.4329(7) Å, 
a = 102.400(10)°, b = 103.172(10)°, g = 97.1310(10)°; 
V = 656.33(6) Å³; Z = 2; F(000) = 352; μ = 0.174 mm⁻¹; reflections 
collected = 7561, independent reflections = 2574 [R(int) = 0.0158]; 
R1, wR2 [I > 2σ(I)] = 0.0421, 0.0444.

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