Regioselection in *C*-Bromo-*N*-phenylnitrilimine Cycloaddition to (*Z*)-4-(Arylmethylidene)azol-5-ones

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The results of a study of the cycloaddition reaction of bromonitrilimine with (*Z*)-4-(arylmethylidene)isoxazol-5-ones and pyrazol-5-ones are reported. Spectroscopic and X-ray crystallographic data are presented to support structural assignments of the reaction products.

The chemistry of pyrazoles has inspired intense research activity for some time, since this class of heterocycles is associated with a large number of mainly synthetic derivatives that exhibit a variety of valuable applications [1].

In line with a research program focusing on the synthesis and reactivity of N-heterocyclic compounds of potential biopharmacological interest, we recently refined the synthesis of *C*-bromo-*N*-phenylnitrilimine (**1**), a novel dipole, which enabled us to easily obtain excellent yields of 3-bromopyrazoles by cycloaddition with dipolarophiles containing C=C and C≡C bonds [2].

As an extension of this, we undertook a study of the reactivity of this dipole towards some selected arylmethylidene derivatives. This topic does not appear to have been satisfactorily studied, and only a few, in some ways conflicting, cases are reported in the literature [3]. With this in mind, we examined the reactions of **1** with (*Z*)-4-(arylmethylidene)-4,5-dihydroisoxazol-5-ones **2** and 4,5-dihydro-1*H*-pyrazol-5-ones **3**, and now report the results obtained.

The treatment of **2** or **3** with *C*-bromo-*N*-phenylnitrilimine (**1**), generated *in situ*, leads to the formation of spirocycloadducts **4** and **5**, or **6** and **7**, respectively (*Scheme*). The results are summarized in *Table 1*.

The structures of products **4**–**7** are consistent with analytical and spectroscopic data. The mass spectra show the formation of monobrominated adducts, while IR and ^{1}H-NMR data support regioselective cycloaddition to the arylmethylenic substrate. In particular, the shift to higher frequencies of the isoxazolone carbonyl stretching in the IR spectra and one new ^{1}H-NMR resonance in the region between 5.01 and 6.06 ppm demonstrate both the presence of the 4,4-disubstituted isoxazol-5-one ring and the formation of the two possible 4′,4-type (**4** and **6**) and 5′,4-type (**5** and **7**) regioisomers. These are easily differentiated on the basis of the relative δ values of the benzylic H-

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Scheme

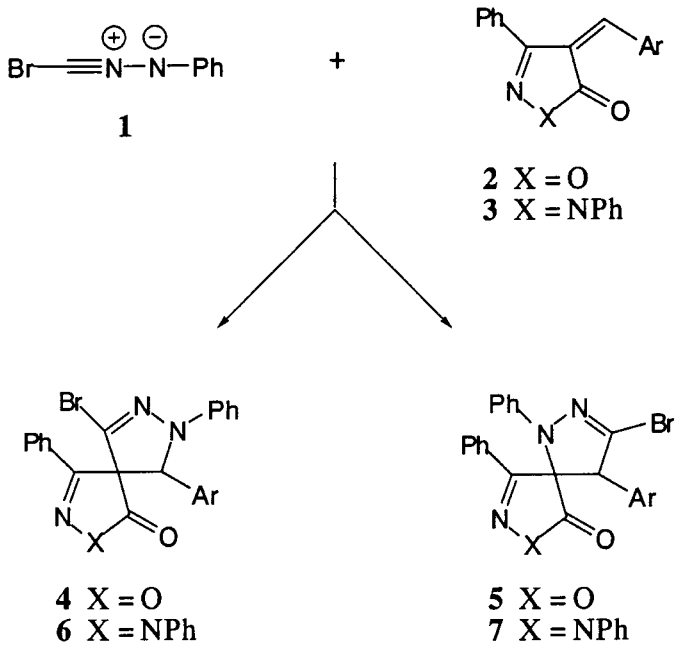

Table 1. *Synthesis of Spiro Derivatives* **4**–**7**

		Spiroisoxazolones **2**		Spiropyrazolones **3**	
	Ar	4′,4 [%][a])	5′,4 [%][a])	4′,4 [%][a])	5′,4 [%][a])
a	Ph	**4a** 54	–	–	**7a** 47
b	4-Me–C_6H_4	–	**5b** 51	–	**7b** 57
c	4-MeO–C_6H_4	–	**5c** 57	–	**7c** 62
d	4-Cl–C_6H_4	**4d** 7	**5d** 43	–	**7d** 55
e	2-NO_2–C_6H_4	**4e** 50	–	**6e** 44	**7e** 6
f	2-Cl–C_6H_4	–	–	**6f** 44	–

[a]) Yields determined by ^{1}H-NMR of the crude mixture.

atom, which are shifted to higher frequencies in 4′,4 spirans due to the close proximity of the N-atoms.

The configurational features of spirans **4**–**7** were assigned on the basis of 2D-NOESY-NMR experiments and X-ray crystallographic data.

Considering that the starting arylmethylidene substrates **2** [4] and **3** [5] are pure (*Z*)-derivatives, it can be argued that the reactions with **1** proceed with complete stereochemical control [6]. Indeed, in the corresponding spiro structures **4**–**7**, the concerted 1,3-dipole attack locates *H*–C(9) *syn* with respect to *Ph*–C(4) and *anti* with respect to the CO group of isoxazolone.

In agreement with the proposed structures, dipolar interactions between *H*–C(9) and H_o of Ph–C(4) were evidenced by 2D-NOESY-NMR spectra. In particular, for

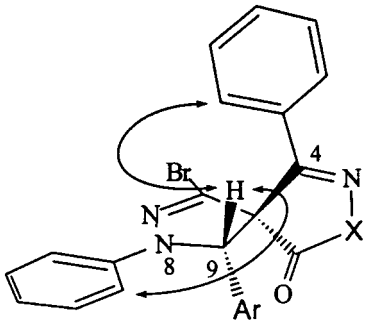

Fig. 1. *Dipolar interactions of 4′,4-type structures* **4** *and* **6** *observed by 2D-NOESY measurements*

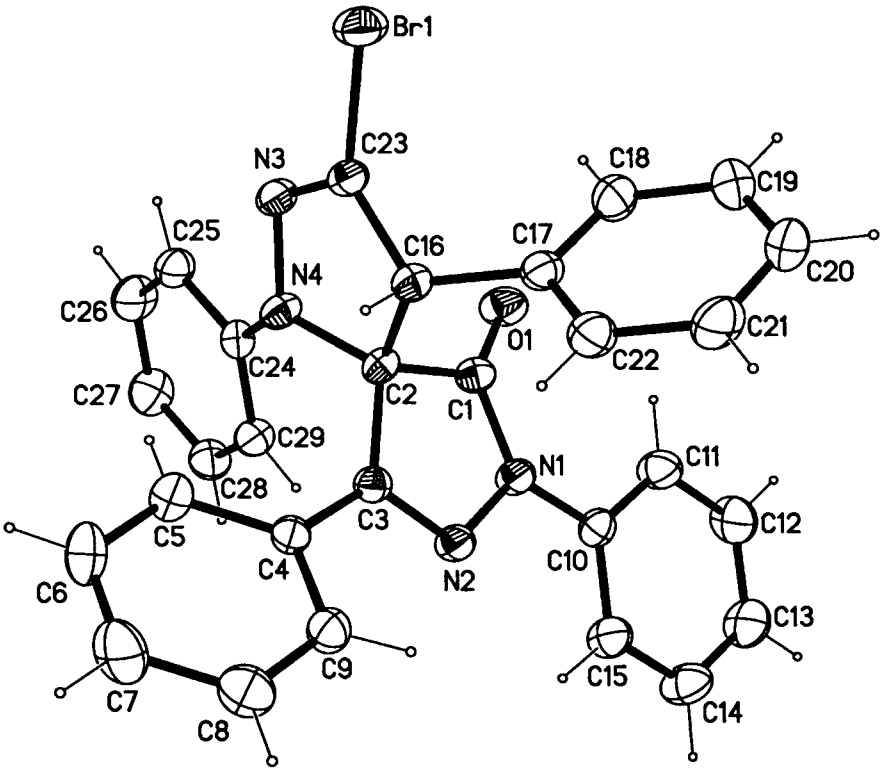

Fig. 2. *ORTEP View of molecule* **7a** *with atom-numbering scheme and thermal ellipsoids at 30% of probability, while the H size is arbitrary.* Selected bond lengths [Å] and angles [°]: Br(1)–C(23) 1.869(3), N(4)–N(3) 1.395(3), N(4)–C(24) 1.409(3), N(4)–C(2) 1.474(3), N(3)–C(23) 1.267(3), O(1)–C(1) 1.209(3), N(1)–C(1) 1.369(3), N(1)–N(2) 1.405(3), N(1)–C(10) 1.426(3), N(2)–C(3) 1.290(3), C(3)–C(4) 1.465(4); N(3)–N(4)–C(2) 110.7(2), C(23)–N(3)–N(4) 107.8(2), C(23)–C(16)–C(2) 98.5(2), N(1)–C(1)–C(2) 105.2(2), C(1)–N(1)–N(2) 112.4(2), C(3)–N(2)–N(1) 109.1(2), N(2)–C(3)–C(2) 111.6(2), N(2)–C(3)–C(4)–C(9) 26.9(4), N(2)–N(1)–C(10)–C(15) 5.4(4), N(3)–N(4)–C(24)–C(25) –14.3(4).

compounds **4** and **6**, dipolar cross-peaks were also observed between $H-C(9)$ and H_{io} of $Ph-N(8)$, further supporting the assigned 4′,4-type structures for these spirocycloadducts (*Fig. 1*).

The assignments of 5′,4-type regioisomers were again verified by an X-ray analysis carried out on **7a** (*Fig. 2*).

The observed regiochemistry was in agreement with that expected (FMO method) [7], and the levels of selectivity depended upon the stereoelectronic nature of both isoxazolone and pyrazolone systems, **2** and **3**, respectively. Thus, on the basis of the results listed in *Table 1*, the formation of the 5′,4 regioisomers prevailed in cases **b**–**d** with electron-donating and/or *para*-substituents; in cases **e** and **f**, with electron-withdrawing and *ortho*-substituents, 4′,4-type regioisomers were predominant. Both benzylidene derivatives, which showed opposite behaviors, constituted exceptions: while **2a** only afforded **4a**, the analogous **3a** gave the derivative **7a**. This rather ambiguous behavior is probably due to variations in frontier-orbital energy with consequent inversion of $HOMO_{dipole}$-$LUMO_{dipolarophile}$ interaction.

Experimental Part

General. All solvents and reagents were obtained from commercial sources and purified before use if necessary. (Arylmethylidene)isoxazolones **2** and pyrazolones **3** were prepared according to literature procedures [8][9]. Flash column chromatography (FC): 200–300 mesh silica gel at increased pressure. M.p.: *Reichert-Kofler* hot stage apparatus; uncorrected. IR Spectra: *Nicolet FT-IR Impact 400D* spectrometer. ^{1}H-NMR Spectra: *Bruker ARX-300* spectrometer, in the solvent indicated; chemical shifts (δ) refer to TMS as an internal reference. MS: *Finnigan-Mat 90* spectrometer. Elemental analyses for C, H, and N on a *Carlo-Erba 1102*.

General Procedure for the Synthesis of Spiro Derivatives (**2**–**7**). To a stirred soln. of glyoxylic acid phenylhydrazone [10] (3.3 g, 20 mmol) in DMF (40 ml) at $-5°$ was added dropwise a soln. of *N*-bromosuccinimide (NBS; 7.1 g, 40 mmol) in DMF (20 ml) under an atmosphere of N_2. After additional stirring (15 min) at r.t., a DMF soln. (100 ml) of the appropriate arylmethylidene derivative (40 mmol) and TEA (2.2 g, 10 mmol) were added dropwise. The mixture was left at r.t. for 5 h, then poured into cold H_2O (200 ml), and extracted with Et_2O (3×). The combined Et_2O extracts were dried (Na_2SO_4), the solvent was removed at reduced pressure, and the resultant oil was purified by FC (silica gel; Et_2O/petroleum ether 1:4).

*4-Benzylidene-3-phenyl-4*H-*isoxazol-5-one* (**2a**; 9.96 g, 40 mmol) and **1** gave 4.8 g (54%) of *6-bromo-4,8,9-triphenyl-2-oxa-3,7,8-triazaspiro[4.4]nona-3,6-dien-1-one* (**4a**). Colorless needles. M.p. 163–164° (MeCN). IR (nujol): 1798, 1597, 889, 693. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.55 (*s*, 1 H); 6.82–7.81 (*m*, 15 H). EI-MS: 445/447 (M^+). Anal. calc. for $C_{23}H_{16}BrN_3O_2$: C 61.90, H 3.61, N 9.42; found: C 62.06, H 3.72, N 9.53.

*4-(4-Methylbenzylidene)-3-phenyl-4*H-*isoxazol-5-one* (**2b**; 10.52 g, 40 mmol) and **1** gave 4.6 g (50%) of *3-bromo-4-(4-methylphenyl)-1,9-diphenyl-7-oxa-1,2,8-triazaspiro[4.4]nona-2,8-dien-6-one* (**5b**). Colorless needles. M.p. 145–146° (MeCN). IR (nujol): 1800, 1597, 752, 694. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 2.34 (*s*, 3 H); 5.02 (*s*, 1 H); 7.00–8.05 (*m*, 14 H). EI-MS: 459/461 (M^+). Anal. calc. for $C_{24}H_{18}BrN_3O_2$: C 62.62, H 3.94, N 9.13; found: C 62.79, H 3.99, N 9.19.

*4-(4-Methoxybenzylidene)-3-phenyl-4*H-*isoxazol-5-one* (**2c**; 11.16 g, 40 mmol) and **1** gave 5.4 g (57%) of *3-bromo-4-(4-methoxyphenyl)-1,9-diphenyl-7-oxa-1,2,8-triazaspiro[4.4]nona-2,8-dien-6-one* (**5c**). Colorless needles. M.p. 142–143° (MeCN). IR (nujol): 1798, 1597, 889, 693. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 3.81 (*s*, 3 H); 5.01 (*s*, 1 H); 6.87–8.04 (*m*, 14 H). EI-MS: 475/477 (M^+). Anal. calc. for $C_{24}H_{18}BrN_3O_3$: C 60.52, H 3.81, N 8.82; found: C 60.70, H 3.88, N 8.96.

*4-(4-Chlorobenzylidene)-3-phenyl-4*H-*isoxazol-5-one* (**2d**; 11.32 g, 40 mmol) and **1** gave 0.66 g (7%) of *6-bromo-9-(4-chlorophenyl)-4,8-diphenyl-2-oxa-3,7,8-triazaspiro[4.4]nona-3,6-dien-1-one* (**4d**). Colorless oil. IR (nujol): 1798, 1601, 835, 691. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.50 (*s*, 1 H); 6.83–8.03 (*m*, 14 H). EI-MS: 479/481 (M^+). Anal. calc. for $C_{23}H_{15}BrClN_3O_2$: C 57.46, H 3.14, N 8.74; found: C 57.31, H 3.05, N 8.82) and *3-bromo-4-(4-chlorophenyl)-1,9-diphenyl-7-oxa-1,2,8-triazaspiro[4.4]nona-2,8-dien-6-one* (**5d**). Colorless needles. M.p. 165–166° (MeOH). IR (nujol): 1798, 1596, 863, 765, 696. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.02 (*s*, 1 H); 7.06–8.03 (*m*, 14 H). EI-MS: 479/481 (M^+). Anal. calc. for $C_{23}H_{15}BrClN_3O_2$: C 57.46, H 3.14, N 8.74; found: C 57.60, H 3.23, N 8.88).

*4-(2-Nitrobenzylidene)-3-phenyl-4*H*-isoxazol-5-one* (**2e**; 11.76 g, 40 mmol) and **1** gave 4.9 g (50%) of *6-bromo-9-(2-nitrophenyl)-4,8-diphenyl-2-oxa-3,7,8-triazaspiro[4.4]nona-3,6-dien-1-one* (**4e**). Yellow plates. M.p. 183–184° (MeOH). IR (nujol): 1792, 1594, 749, 691. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 6.01 (*s*, 1 H); 6.70–8.15 (*m*, 15 H). EI-MS: 445/447 (M^+). Anal. calc. for $C_{23}H_{15}BrN_4O_4$: C 56.23, H 3.08, N 11.40; found: C 56.40, H 3.16, N 11.52.

*4-Benzylidene-4,5-dihydro-1,3-diphenyl-1*H*-pyrazol-5-one* (**3a**; 12.96 g, 40 mmol) and **1** gave *3-Bromo-1,4,7,9-tetraphenyl-1,2,7,8-tetraazaspiro[4.4]nona-2,8-dien-6-one* (**7a**). Colorless needles. M.p. 186–187° (MeCN). IR (nujol): 1716, 1597, 748, 697. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.11 (*s*, 1 H); 6.89–8.15 (*m*, 20 H). EI-MS *m*/*z* 520/522 (M^+). Anal. calc. for $C_{29}H_{21}BrN_4O$: C 66.80, H 4.06, N 10.75; found: C 66.97, H 4.11, N 10.87.

*4,5-Dihydro-4-(4-methylbenzylidene)-1,3-diphenyl-1*H*-pyrazol-5-one* (**3b**; 13.5 g, 40 mmol) and **1** gave 6.1 g (57%) of *3-bromo-4-(4-methylphenyl)-1,7,9-triphenyl-1,2,7,8-tetraazaspiro[4.4]nona-2,8-dien-6-one* (**7b**). Colorless needles. M.p. 201–202° (MeCN). IR (nujol): 1723, 1598, 753, 690. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 2.24 (*s*, 3 H); 5.08 (*s*, 1 H); 6.89–8.15 (*m*, 19 H). EI-MS: 534/536 (M^+). Anal. calc. for $C_{30}H_{23}BrN_4O$: C 67.30, H 4.33, N 10.46; found: C 67.47, H 4.39, N 10.57.

*4,5-Dihydro-4-(4-methoxybenzylidene)-1,3-diphenyl-1*H*-pyrazol-5-one* (**3c**; 14.16 g, 40 mmol) and 6.8 g (62%) of **1** gave *3-bromo-4-(4-methoxyphenyl)-1,7,9-triphenyl-1,2,7,8-tetraazaspiro[4.4]nona-2,8-dien-6-one* (**7c**). Colorless needles. M.p. 192–193° (MeCN). IR (nujol): 1717, 1597, 753, 691. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 3.71 (*s*, 1 H); 5.07 (*s*, 1 H); 6.78–8.14 (*m*, 19 H). EI-MS: 550/552 (M^+). Anal. calc. for $C_{30}H_{23}BrN_4O_2$: C 65.34, H 4.20, N 10.16; found: C 65.46, H 4.28, N 10.26.

*4-(4-Chlorobenzylidene)-4,5-dihydro-1,3-diphenyl-1*H*-pyrazol-5-one* (**3d**; 14.32 g, 40 mmol) and **1** gave 6.1 g (55%) of *3-bromo-4-(4-chlorophenyl)-1,7,9-triphenyl-1,2,7,8-tetraazaspiro[4.4]nona-2,8-dien-6-one* (**7d**). Colorless needles. M.p. 207–208° (MeOH). IR (nujol): 1716, 1598, 747, 689. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.08 (*s*, 1 H); 6.91–8.14 (*m*, 19 H). EI-MS: 554/556 (M^+). Anal. calc. for $C_{29}H_{20}BrClN_4O$: C 62.66, H 3.63, N 10.08; found: C 62.78, H 3.69, N 10.21.

*4,5-Dihydro-4-(2-nitrobenzylidene)-1,3-diphenyl-1*H*-pyrazol-5-one* (**3e**; 14.76 g, 40 mmol) and **1** gave 5 g (44%) of *6-bromo-9-(2-nitrophenyl)-2,4,8-triphenyl-2,3,7,8-tetraazaspiro[4.4]nona-3,6-dien-1-one* (**6e**). (Yellow-orange needles. M.p. 184–185° (MeOH). IR (nujol): 1716, 1598, 747, 688. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 6.01 (*s*, 1 H); 6.72–8.05 (*m*, 19 H). EI-MS: 565/567 (M^+). Anal. calc. for $C_{29}H_{20}BrN_5O_3$: C 61.49, H 3.56, N 12.36; found: C 61.63, H 3.62, N 12.47) and 0.68 g (6%) of *3-bromo-4-(2-nitrophenyl)-1,7,9-triphenyl-1,2,7,8-tetraazaspiro[4.4]nona-2,8-dien-6-one* (**7e**). Yellow-orange needles. M.p. 204–205° (MeOH). IR (nujol): 1730, 1588, 758, 690. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 5.69 (*s*, 1 H); 6.86–7.96 (*m*, 15 H). EI-MS: 565/567 (M^+). Anal. calc. for $C_{29}H_{20}BrN_5O_3$: C 61.49, H 3.56, N 12.36; found: C 61.58, H 3.63, N 12.49).

*4-(2-Chlorobenzylidene)-4,5-dihydro-1,3-diphenyl-1*H*-pyrazol-5-one* (**3f**; 9.96 g, 40 mmol) and **1** gave 4.9 g (44%) of *6-bromo-9-(2-chlorophenyl)-2,4,8-triphenyl-2,3,7,8-tetraazaspiro[4.4]nona-3,6-dien-1-one* (**6f**). Colorless oil. IR (nujol): 1720, 1595, 754, 689. ^{1}H-NMR (300 MHz, r.t.; $CDCl_3$): 6.06 (*s*, 1 H); 6.74–8.02 (*m*, 15 H). EI-MS: 554/556 (M^+). Anal. calc. for $C_{29}H_{20}BrClN_4O$: C 62.66, H 3.63, N 10.08; found: C 68.81, H 3.74, N 10.29.

X-Ray Crystal-Structure Determination of **7a**[2]) (see *Table 2* and *Fig. 2*). Crystals suitable for X-ray analysis were obtained by recrystallization from MeCN solns. Diffraction data were collected at r.t. from a colorless $0.18 \times 0.35 \times 0.37$ mm^3 prismatic crystal sample with a *Siemens P4* automated four-circle single-crystal diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). No crystal decay was evidenced by the check reflections monitored after every 197 measurements. Intensities were evaluated by profile fitting of a 96-steps peak scan among 2q shells procedure [11] and then corrected for *Lorentz* polarization effects. Absorption effects were not taken into account. Data collection and reduction was performed by XSCANS [12] and SHELXTL packages [13]. Structure was solved by a combination of standard direct methods [14] and *Fourier* synthesis, and refined by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$ with the full-matrix least-squares technique based on all independent F^2 values with SHELXL97 [15]. H-Atoms were located on the difference *Fourier* maps and included in the model as isotropic atoms, while all the non-H-atoms were anisotropic. An empirical extinction parameter was included in the last refinement cycles. Final geometric calculations and drawings were carried out with the PARST program [16] and the XPW utility of the *Siemens* package, respectively.

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[2]) Further details of crystal structure of compound **7a** can be obtained, free of charge, on application to *Cambridge Crystallographic Data Centre* (*CCDC*), 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk), quoting the deposition No. CCDC-163175.

Table 2. *Crystal Data and Structure Refinement for Compound* **7a**

Empirical formula	$C_{29}H_{21}BrN_4O$
Formula weight	521.41
Crystal system	Monoclinic
Space group	$P2_1/n$ (ITC No. 14)
Lattice parameters	
a, b, c [Å]	10.095(2), 13.676(4), 17.859(3)
β [°]	103.76(1).
V	2394.8(9)
Z	4
Density (calculated)	1.446 mg/m^3
Absorption coefficient	1.747 mm^{-1}
$F(000)$	1064
Reflections collected	5339 [θ range = 1.90–25.02°]
Independent reflections	4167 [R(int) = 0.0185]
Data/restraints/parameters	4167/0/401
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0366$, $wR2 = 0.0796$
R Indices (all data)	$R1 = 0.0572$, $wR2 = 0.0900$
Extinction coefficient	0.0035(4)
Largest diff. peak and hole	0.459 and -0.506 e·Å^{-3}

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