



# Synthesis and spectroscopic and structural characterization of three new 2-methyl-4-styrylquinolines formed using Friedländer reactions between (2-aminophenyl)chalcones and acetone

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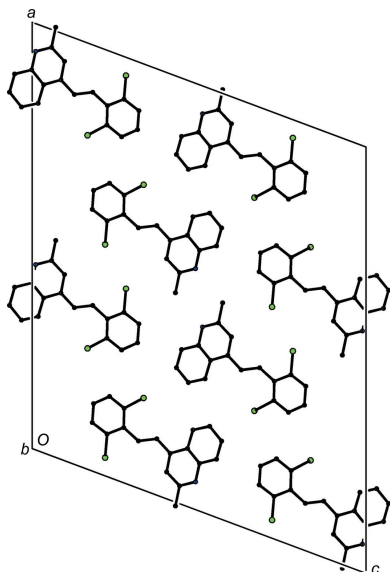
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Three new 2-methyl-4-styrylquinoline derivatives have been synthesized in high yields using Friedländer reactions between chalcones [1-(2-aminophenyl)-3-arylprop-2-en-1-ones] and acetone, and characterized using IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and mass spectrometry, and by crystal structure analysis. In (*E*)-4-(4-fluorostyryl)-2-methylquinoline, C<sub>18</sub>H<sub>14</sub>FN, (I), the molecules are joined into cyclic centrosymmetric dimers by C—H···N hydrogen bonds and these dimers are linked into sheets by  $\pi$ – $\pi$  stacking interactions. The molecules of (*E*)-2-methyl-4-[4-(trifluoromethyl)styryl]quinoline, C<sub>19</sub>H<sub>14</sub>F<sub>3</sub>N, (II), are linked into cyclic centrosymmetric dimers by C—H··· $\pi$  hydrogen bonds and these dimers are linked into chains by a single  $\pi$ – $\pi$  stacking interaction. There are no significant hydrogen bonds in the structure of (*E*)-4-(2,6-dichlorostyryl)-2-methylquinoline, C<sub>18</sub>H<sub>13</sub>Cl<sub>2</sub>N, (III), but molecules related by translation along [010] form stacks with an intermolecular spacing of only 3.8628 (2) Å. Comparisons are made with the structures of some related compounds.

## 1. Introduction

The quinoline nucleus constitutes a privileged scaffold because of the wide spectrum of promising biological activity exhibited by its derivatives (Kumar *et al.*, 2009). Among quinoline derivatives, 2-styrylquinolines have been studied extensively, mainly because of their potential as inhibitors of HIV-1 integrase (Leonard & Roy, 2008; Mahajan *et al.*, 2018; Mousnier *et al.*, 2004) and as antimicrobial (Kamal *et al.*, 2015), antifungal (Cieslik *et al.*, 2012) and anticancer agents (Mrozek-Wilczkiewicz *et al.*, 2015, 2019).

Accordingly, considerable efforts have been made in the development of effective methods for accessing new compounds containing the styrylquinoline scaffold (Musiol, 2020). Unlike 2-styrylquinolines, the 4-styrylquinoline regioisomers have been studied much less, with few published reports related to their synthesis and biological evaluation, which is probably due, at least in part, to a lack of generally applicable methodologies for their synthesis. In general, the published syntheses of 4-styrylquinolines have involved Heck coupling between 4-haloquinolines and different aryl–vinyl compounds (Omar & Hormi, 2009), and Knoevenagel-type condensation reactions between 4-methylquinolines and aromatic aldehydes using expensive and toxic heavy-metal catalysts (Jamal *et al.*, 2016) or microwave irradiation (Lee *et al.*, 2009). The use of palladium catalysts in the cross-coupling reaction between



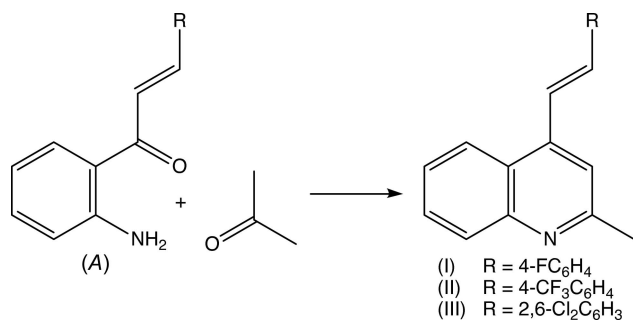
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4-chloroquinolines and alkenyltrifluoroborates under harsh reaction conditions has also been reported (Alacid & Nájera, 2009). Nonetheless, there still remains a need for alternative approaches for the construction of 4-styrylquinolines starting from readily accessible materials and characterized by high atom efficiency and low cost.

In this context, and as part of an ongoing program exploring the rational use of synthetically available 1-(2-aminophenyl)-3-arylprop-2-en-1-ones (Meléndez *et al.*, 2020) as appropriate precursors for the synthesis of novel quinoline derivatives, we have recently described a simple and efficient one-pot synthetic approach based on the Friedländer reaction to obtain polysubstituted 2-methyl-4-styrylquinolines starting from these simple precursors and different 1,3-dicarbonyl compounds (Meléndez *et al.*, 2020).

To expand further both the synthetic utility of 1-(2-aminophenyl)-3-arylprop-2-en-1-ones and the flexibility of our approach, we report here the synthesis, characterization and molecular and supramolecular structures of a matched set of three closely-related quinoline derivatives, namely, (*E*)-4-(4-fluorostyryl)-2-methylquinoline, (I), (*E*)-2-methyl-4-[4-(trifluoromethyl)styryl]quinoline, (II), and (*E*)-4-(2,6-dichlorostyryl)-2-methylquinoline, (III) (Scheme 1 and Figs. 1–3), which differ only in the nature of the substituents at the C4 and C2/C6 positions on the benzene ring of the styryl fragment. Using our synthetic approach (Meléndez *et al.*, 2020), (*E*)-1-(2-aminophenyl)-3-arylprop-2-en-1-ones of type (A) (Scheme 1) were subjected to Friedländer annulation with an excess of acetone in glacial acetic acid at 373 K, to provide the products (I)–(III) with yields in the range 77–94% (Scheme 1). These new 2-methylquinoline derivatives are intended for use as key precursors in the further development of more complex molecules of possible biological value, such as the bis-styrylquinolines (IV) (Scheme 2), (4-styrylquinolin-2-yl)chalcones of the type (V) and the molecular hybrids of types (VI) and (VII).

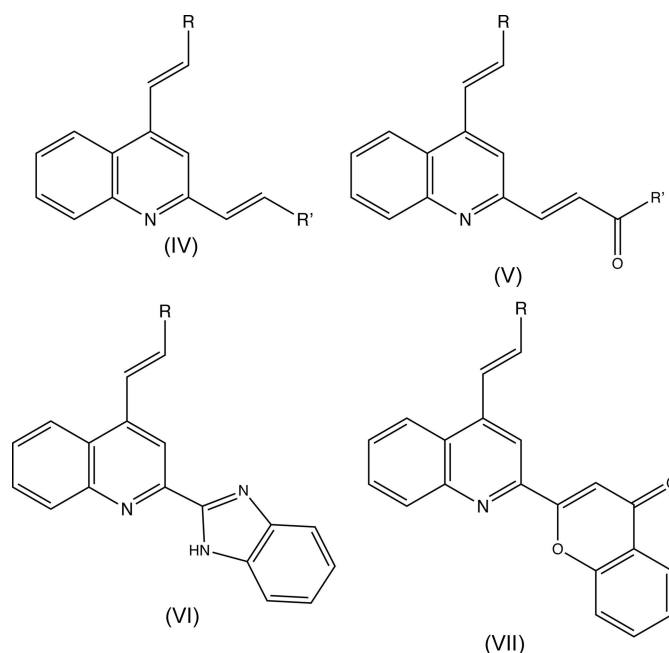


## 2. Experimental

### 2.1. Synthesis and crystallization

For the synthesis of compounds (I)–(III), a mixture of the appropriate 1-(2-aminophenyl)-3-arylprop-2-en-1-ones (A) (Meléndez *et al.*, 2020; see Scheme 1) (1.0 mmol) and acetone (12.0 mmol) in glacial acetic acid (3 ml) was stirred magnetically and heated at 353 K until the reactions were complete, as judged by the complete consumption of (A) (as monitored by

thin-layer chromatography, TLC); the reaction times for completion were 15 h for (I), 19 h for (II) and 14 h for (III). Each reaction mixture was then neutralized with a saturated aqueous sodium carbonate solution and extracted with ethyl acetate (3 × 50 ml). The combined organic layers were washed with water and dried over anhydrous sodium sulfate, and the solvent was then removed under reduced pressure. In each case, the resulting crude product was purified by flash chromatography on silica-gel using hexane–ethyl acetate mixtures as eluent (compositions ranged from 7:1 to 2:1 *v/v*) to give the required solid compounds (I)–(III). Crystallization from hexane–ethyl acetate (10:1 *v/v*) at ambient temperature and in the presence of air gave crystals suitable for single-crystal X-ray diffraction; these were yellow for (I) and (III), and colourless for (II).



Compound (I): yield 0.21 g (84%), m.p. 395–397 K,  $R_f = 0.28$  (16.6% ethyl acetate–hexane). FT-IR (ATR,  $\text{cm}^{-1}$ ): 1632 (C=N), 1598 (C=C<sub>vinyl</sub>), 1587 (C=C<sub>arom</sub>), 1506 (C=C<sub>arom</sub>), 965 (C–H<sub>trans</sub>). NMR ( $\text{CDCl}_3$ ):  $\delta(^1\text{H})$  8.13 (*dd*,  $J = 8.4, 1.4$  Hz, 1H, H5), 8.05 (*dd*,  $J = 8.4, 1.6$  Hz, 1H, H8), 7.69 (*ddd*,  $J = 8.4, 6.9, 1.4$  Hz, 1H, H7), 7.68 (*d*,  $J = 16.1$  Hz, 1H, H<sub>A</sub>–C=), 7.56–7.61 (*m*, 2H, H2', H6'), 7.52 (*ddd*,  $J = 8.3, 6.9, 1.4$  Hz, 1H, H6), 7.47 (*s*, 1H, H3), 7.27 (*d*,  $J = 16.1$  Hz, 1H, =CH<sub>B</sub>), 7.09–7.14 (*m*, 2H, H3', H5'), 2.77 (*s*, 3H, 2-CH<sub>3</sub>);  $\delta(^{13}\text{C})$  163.0 (*d*,  $J = 248.9$  Hz, C4'), 158.7 (C2), 148.4 (C8a), 142.8 (C4), 133.6 (=CH<sub>B</sub>), 132.9 (*d*,  $J = 3.6$  Hz, C1'), 129.4 (C8), 129.3 (C7), 128.7 (*d*,  $J = 8.1$  Hz, C2', C6'), 125.7 (C6), 124.7 (C4a), 123.2 (C5), 122.9 (*d*,  $J = 2.3$  Hz, H<sub>A</sub>C=), 117.9 (C3), 115.9 (*d*,  $J = 21.9$  Hz, C3', C5'), 25.4 (2-CH<sub>3</sub>). HRMS (ESI<sup>+</sup>)  $m/z$  found for  $[M + H]^+$  264.1181, C<sub>18</sub>H<sub>14</sub>FN requires 263.11

Compound (II): yield (77%); m.p. 391–392 K,  $R_f = 0.34$  (50% ethyl acetate–hexane). FT-IR (ATR,  $\text{cm}^{-1}$ ): 1620 (C=N), 1587 (C=C<sub>vinyl</sub>), 1505 (C=C<sub>arom</sub>), 1408 (C=C<sub>arom</sub>), 964 (C–H<sub>trans</sub>). NMR ( $\text{CDCl}_3$ ):  $\delta(^1\text{H})$  8.13 (*dd*,  $J = 8.3, 1.4$  Hz, 1H, H5), 8.06 (*dd*,  $J = 8.4, 1.5$  Hz, 1H, H8), 7.86 (*d*,  $J =$

**Table 1**  
Experimental details.

Experiments were carried out at 100 K with Mo  $K\alpha$  radiation using a Bruker D8 Venture diffractometer. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2016). H-atom parameters were constrained.

	(I)	(II)	(III)
<b>Crystal data</b>			
Chemical formula	C <sub>18</sub> H <sub>14</sub> FN	C <sub>19</sub> H <sub>14</sub> F <sub>3</sub> N	C <sub>18</sub> H <sub>13</sub> Cl <sub>2</sub> N
$M_r$	263.30	313.31	314.19
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
$a$ , $b$ , $c$ (Å)	13.5921 (7), 12.7103 (6), 7.6215 (3)	17.2696 (10), 10.8096 (7), 16.1495 (8)	30.5651 (15), 3.8629 (2), 25.5357 (13)
$\beta$ (°)	103.133 (2)	91.440 (2)	110.497 (2)
$V$ (Å <sup>3</sup> )	1282.25 (10)	3013.8 (3)	2824.1 (2)
$Z$	4	8	8
$\mu$ (mm <sup>-1</sup> )	0.09	0.11	0.45
Crystal size (mm)	0.20 × 0.08 × 0.07	0.16 × 0.14 × 0.12	0.20 × 0.10 × 0.06
<b>Data collection</b>			
$T_{\min}$ , $T_{\max}$	0.934, 0.994	0.888, 0.987	0.897, 0.973
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	38068, 2949, 2342	46287, 3750, 2921	28110, 3208, 2930
$R_{\text{int}}$	0.079	0.085	0.042
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.650	0.667	0.650
<b>Refinement</b>			
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.042, 0.100, 1.05	0.047, 0.121, 1.03	0.031, 0.079, 1.07
No. of reflections	2949	3750	3208
No. of parameters	182	209	191
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.26, -0.22	0.33, -0.30	0.33, -0.26

Computer programs: APEX3 (Bruker, 2018), SAINT (Bruker, 2017), SHELXT2014 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b) and PLATON (Spek, 2020).

16.1 Hz, 1H, H<sub>A</sub>—C=), 7.72 (*ddd*,  $J = 8.3, 6.9, 1.4$  Hz, 1H, H7), 7.72 (*d*,  $J = 8.5$  Hz, 2H, H2', H6'), 7.68 (*d*,  $J = 8.5$  Hz, 2H, H3', H5'), 7.54 (*ddd*,  $J = 8.3, 6.8, 1.3$  Hz, 1H, H6), 7.50 (*d*,  $J = 0.7$  Hz, 1H, H3), 7.32 (*d*,  $J = 16.1$  Hz, 1H, =CH<sub>B</sub>), 2.79 (*s*, 3H, 2-CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C) 158.8 (C2), 148.5 (C8a), 142.3 (C4), 140.0 (C1'), 133.2 (=CH<sub>B</sub>), 130.3 (*d*,  $J = 32.4$  Hz, C4'), 129.5 (C7), 129.4 (C8), 127.2 (C2', C6', C3', C5'), 125.9 (*q*,  $J = 3.7$  Hz, 4-CF<sub>3</sub>), 125.4 (C6), 124.7 (C4a), 123.1 (C5), 122.7 (H<sub>A</sub>—C=), 118.2 (C3), 25.4 (2-CH<sub>3</sub>). HRMS (ESI<sup>+</sup>)  $m/z$  found for  $[M + H]^+$  314.115, C<sub>19</sub>H<sub>14</sub>F<sub>3</sub>N requires 313.1078.

Compound (III): yield 0.25 g (94%), m.p. 410–412 K,  $R_f = 0.31$  (12.5% ethyl acetate–hexane). FT–IR (ATR, cm<sup>-1</sup>): 1629 (C=N), 1593 (C=C<sub>vinyl</sub>), 1554 (C=C<sub>arom</sub>), 1505 (C=C<sub>arom</sub>), 959 (=C—H<sub>trans</sub>). NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H) 8.10 (*dd*,  $J = 8.5, 1.4$  Hz, 1H, H5), 8.06 (*dd*,  $J = 8.5, 1.4$  Hz, 1H, H8), 7.85 (*dd*,  $J = 16.5, 0.87$  Hz, 1H, H<sub>A</sub>—C=), 7.70 (*ddd*,  $J = 8.4, 6.9, 1.4$  Hz, 1H, H7), 7.53 (*ddd*,  $J = 8.4, 6.9, 1.3$  Hz, 1H, H6), 7.53 (*s*, 1H, H3), 7.41 (*d*,  $J = 8.0$  Hz, 2H, H3', H5'), 7.18 (*dd*,  $J = 8.4, 7.7$  Hz, 1H, H4'), 7.28 (*d*,  $J = 16.5$  Hz, 1H, =CH<sub>B</sub>), 2.80 (*s*, 3H, 2-CH<sub>3</sub>).  $\delta$  (<sup>13</sup>C) 158.8 (C2), 148.4 (C8a), 142.2 (C4), 137.2 (C1'), 134.7 (C2', C6'), 133.8 (C3'), 132.4 (H<sub>A</sub>C=), 130.9 (=CH<sub>B</sub>), 130.1 (C4'), 129.3 (C7), 129.4 (C8), 127.4 (C5'), 125.9 (C6), 124.8 (C4a), 123.6 (C5), 118.5 (C3), 25.5 (2-CH<sub>3</sub>). HRMS (ESI<sup>+</sup>)  $m/z$  found for  $[M + H]^+$  314.0500, C<sub>18</sub>H<sub>13</sub>Cl<sub>2</sub>N requires 313.0425.

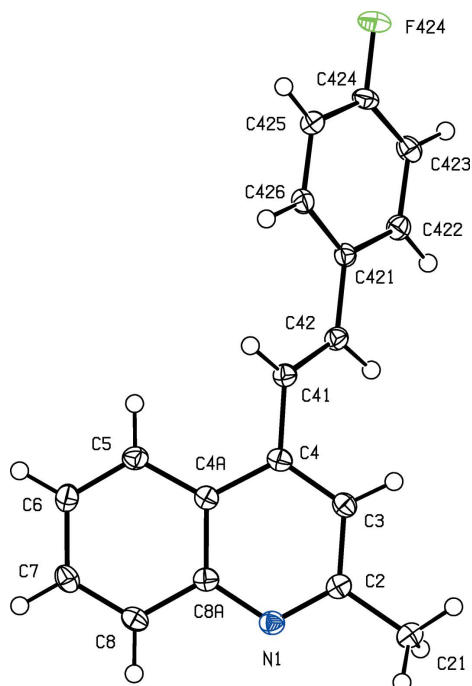
## 2.2. Refinement

Crystal data, data collection and refinement details are summarized in Table 1. A small number of bad outlier reflections [636 for (I), 204 and 336 for (II), and 16,0,0 and 339

for (III)] were omitted from the data sets. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.95 (alkenic and aromatic) and 0.98 Å (CH<sub>3</sub>), and with  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$ , where  $k = 1.5$  for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

## 3. Results and discussion

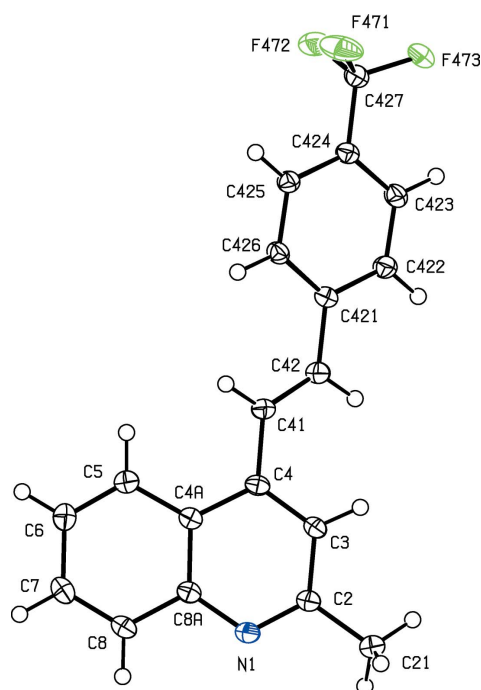
All compounds were fully characterized by standard spectroscopic and analytical methods. In the IR spectra of (I)–(III), the absence of any N—H stretching bands around 3275–3285 cm<sup>-1</sup>, which are characteristic in the spectra of (2-aminophenyl)chalcone precursors, was used for monitoring the formation of the quinoline ring. The formation of the 4-styrylquinoline scaffold was confirmed by a detailed analysis of the <sup>1</sup>H, <sup>13</sup>C and 2D NMR spectra, which showed no signals arising from the H atoms of the amino group; neither were there any signals from the carbonyl groups which had been present in the precursor chalcones. Instead, the <sup>13</sup>C spectra of the products contained signals from a new C<sub>aryl</sub>—H unit (C-3) in the range  $\delta$  117.9–118.5, and two new quaternary aromatic C atoms at  $\delta$  158.7–158.8 (C-2) and 142.2–142.8 (C-4). As in the spectra of the precursor chalcones, the <sup>1</sup>H spectra of products (I)–(III) contained signals from the *trans* vinylic protons —CH<sub>A</sub>=CH<sub>B</sub>—, appearing as two doublets (see Section 2.1). Finally, definitive confirmation of the molecular constitutions and the regio- and stereochemistry for compounds (I)–(III) was established by means of single-crystal X-ray diffraction,



**Figure 1**  
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

and thus we report here also the molecular and supramolecular structures for all three examples (Figs. 1–3).

These new 2-methylquinoline derivatives (I)–(III) are intended for use as key precursors in the further development of more complex molecules of possible biological value, such as the bis-styrylquinolines (IV) (Scheme 2), (4-styrylquinolin-2-yl)chalcones of the type (V), and the molecular hybrids of



**Figure 2**  
The molecular structure of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

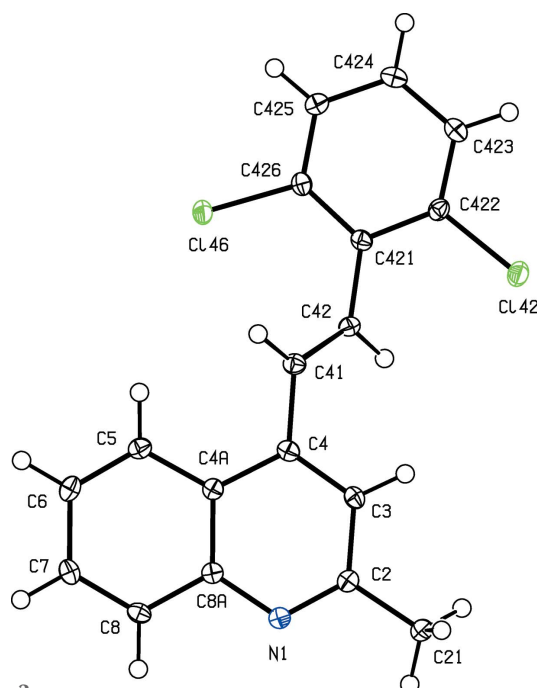
**Table 2**  
Selected torsion angles ( $^{\circ}$ ) for compounds (I)–(III).

Parameter	(I)	(II)	(III)
C3–C4–C41–C42	38.8 (2)	28.1 (2)	39.5 (2)
C41–C42–C421–C422	–174.47 (15)	–175.59 (15)	139.58 (15)

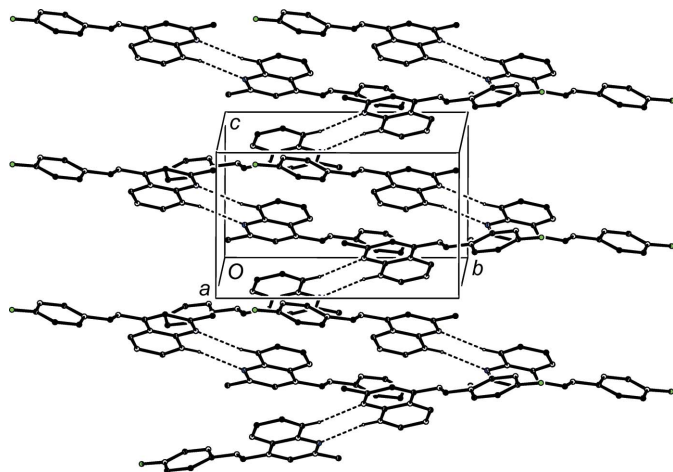
types (VI) and (VII), and the work reported here can be regarded as a continuation of an earlier crystallographic study which reported the structures of 2-methyl-4-styrylquinolines having either acetyl or carboethoxy functionalities at position C3 (Rodríguez *et al.*, 2020).

The molecules of compounds (I)–(III) exhibit no internal symmetry, as indicated by the key torsion angles (Table 2). They are thus not superimposable upon their mirror images and hence they are all conformationally chiral (Moss, 1996; Flack & Bernardinelli, 1999). The space groups (Table 1) confirm that the crystals of each compound contain equal numbers of the two conformational enantiomers; for each compound, the reference molecule was selected as one having a positive sign for the torsion angle C3–C4–C41–C42 (Table 2). Only in compound (II) is the styryl fragment involved in direction-specific intermolecular interactions, as discussed below, and hence there appears to be no simple interpretation of the conformational differences in compounds (I)–(III), other than to note that the barriers to rotation about the C–C single bonds are generally quite low, typically a few  $\text{kJ mol}^{-1}$  (Alkorta & Elguero, 1998).

The supramolecular assembly in compounds (I)–(III) is very simple (Table 3). There is a single hydrogen bond in the structure of (I). In the structure of (II), there is a C–H  $\cdots \pi$ (arene) hydrogen bond, but for the intermolecular C–

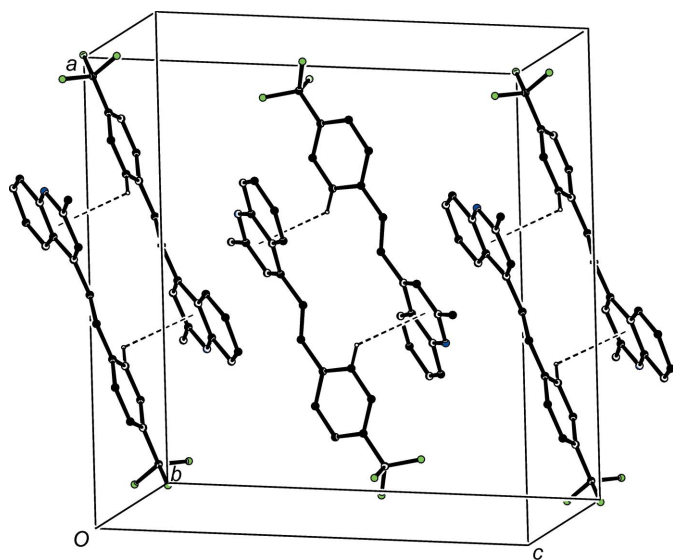


**Figure 3**  
The molecular structure of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 4**  
Part of the crystal structure of compound (I), showing the formation of a  $\pi$ -stacked sheet of hydrogen-bonded dimers lying parallel to (100). Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

H $\cdots$ N contact, the H $\cdots$ N distance exceeds the sum, 2.70 Å, of the van der Waals radii for these atoms (Rowland & Taylor, 1996); hence, this is just a normal intermolecular contact with no associated attractive interaction which could be regarded as structurally significant. The C—H $\cdots$ N contact in compound (III) involves a methyl group (Table 3), where the C—H bonds are of low acidity. More significantly, methyl groups are, in general, likely to be undergoing very fast rotation about the adjacent C—C bond in the solid state (Riddell & Rogerson, 1996, 1997). For methyl groups bonded to planar fragments such as aryl rings, the sixfold barrier to rotation is usually very small, only a few J mol<sup>-1</sup> rather than the typical order of magnitude in kJ mol<sup>-1</sup> (Naylor & Wilson, 1957; Tannenbaum *et al.*, 1956). Hence, this contact cannot be regarded as struc-



**Figure 5**  
Part of the crystal structure of compound (II), showing the formation of a  $\pi$ -stacked chain of hydrogen-bonded dimers running parallel to [001]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

**Table 3**

Parameters (Å, °) for hydrogen bonds and short intermolecular contacts in compounds (I)–(III).

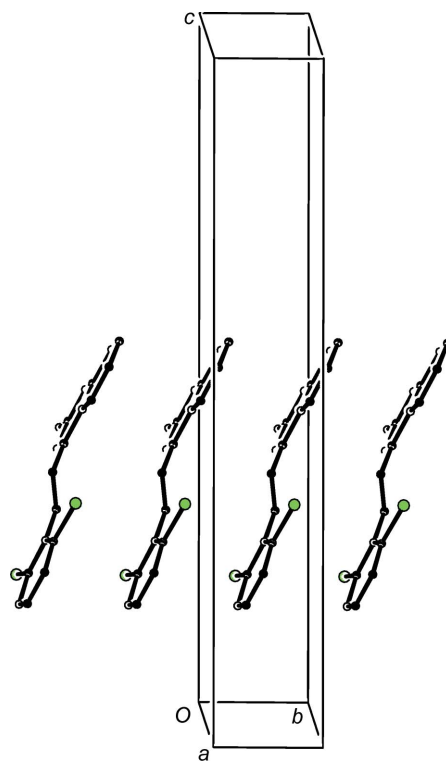
Cg1 represents the centroid of the N1/C2//C4/C4A/C8A ring.

	D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
(I)	C8—H8 $\cdots$ N1 <sup>i</sup>	0.95	2.62	3.561 (2)	170
(II)	C7—H7 $\cdots$ N1 <sup>ii</sup>	0.95	2.75	3.678 (3)	168
	C426—H426 $\cdots$ Cg1 <sup>iii</sup>	0.95	2.86	3.3627 (17)	114
(III)	C21—H21A $\cdots$ N1 <sup>iv</sup>	0.98	2.63	3.594 (3)	170

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y + 2, -z + 1$ .

turally significant. There are  $\pi$ – $\pi$  stacking interactions in each structure.

In the structure of (I), inversion-related pairs of molecules are linked by almost linear C—H $\cdots$ N hydrogen bonds (Table 3) to form centrosymmetric dimers characterized by an  $R_2^2(8)$  motif (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Fig. 4). Dimers of this type are linked into sheets by  $\pi$ – $\pi$  stacking interactions; the quinoline units of the molecule at  $(x, y, z)$ , makes dihedral angles of 9.21 (7)° with the corresponding rings of the molecules at  $(x, -y + \frac{1}{2}, z + \frac{1}{2})$  and  $(x, -y + \frac{1}{2}, z - \frac{1}{2})$ , with ring-centroid separations of 3.7682 (9) Å in each case, with the shortest distance between the centroid of one ring and the plane of the other of 3.5610 (6) Å. The combination of inversion and glide-plane



**Figure 6**  
Part of the crystal structure of compound (III), showing the formation of a  $\pi$ -stacked chain of hydrogen-bonded dimers running parallel to [010]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.



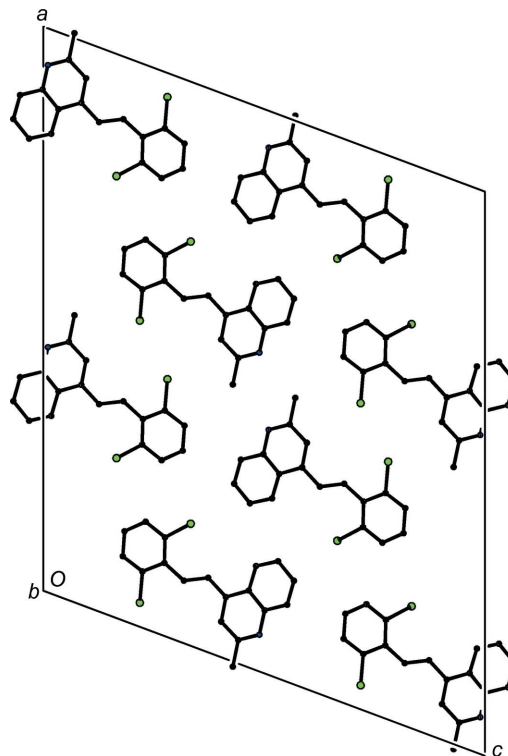
operations leads to the formation of a sheet of  $\pi$ -stacked dimers lying parallel to (100) (Fig. 4).

In the structure of compound (II), inversion-related pairs of molecules are linked by a C—H $\cdots\pi$ (arene) hydrogen bond to form centrosymmetric dimers (Fig. 5), and these dimers are linked into chains by a single  $\pi$ – $\pi$  stacking interaction; the heterocyclic rings in the molecules at  $(x, y, z)$  and  $(-x + 1, y, -z + \frac{1}{2})$  are strictly parallel, with an interplanar spacing of 3.5058 (6) Å and a ring-centroid separation of 3.6845 (9) Å, corresponding to a ring-centroid offset of 1.1335 (12) Å. By this means, the hydrogen-bonded dimers are linked into a chain running parallel to [001] (Fig. 5).

Although there are no hydrogen bonds in the structure of compound (III), the molecules which are related by translation along the [010] direction are stacked precisely in register with a spacing equal to the unit-cell vector  $b = 3.8629$  (2) Å (Fig. 6). Eight stacks of this kind pass through each unit cell (Fig. 7), but there are no direction-specific interactions between adjacent stacks.

We have previously reported (Rodríguez *et al.*, 2020) the synthesis and structures of a number of 4-styrylquinoline derivatives carrying either acetyl or carboethoxy substituents at position C-3. Of these, three closely related acetyl derivatives were found to be isomorphous, with their molecules linked into simple C(6) chains by a single C—H $\cdots$ O hydrogen bond. By contrast, the matching set of carboethoxy derivatives all exhibited different crystallization characteristics and different modes of supramolecular assembly, with one forming C(13) chains and the other two forming cyclic centrosymmetric dimers involving C—H $\cdots$ O hydrogen bonds in one case and C—H $\cdots\pi$  hydrogen bonds in the other. In addition, two other examples carrying acyl substituents have been reported (Meléndez *et al.*, 2020) on a proof-of-structure basis without detailed structure analysis or description, but subsequent re-examination (Rodríguez *et al.*, 2020) found a complex sheet structure in one of them, but no significant intermolecular interactions in the other.

The structures of a number of other styrylquinolines are recorded in the Cambridge Structural Database (CSD; Groom *et al.*, 2016), but it is striking that the majority of these structures are of 2-styrylquinoline derivatives, along with those of a small number of 8-styrylquinolines. This may reflect, at least in part, a lack of efficient, straightforward and versatile routes to other isomeric styrylquinolines. The structure of 2-styrylquinoline itself has been reported three times (Valle *et al.*, 1986; Gulakova *et al.*, 2011; Kuz'mina *et al.*, 2011), as have those of 2-[2-(4-methylphenyl)vinyl]quinoline (Gulakova *et al.*, 2011; Kuz'mina *et al.*, 2011; Das *et al.*, 2019) and 2-[2-(3,4-methoxyphenyl)vinyl]quinoline (Gulakova *et al.*, 2011; Kuz'mina *et al.*, 2011; Sharma *et al.*, 2021). There are two reports on the structure of 2-[2-(3-nitrophenyl)vinyl]quinoline (Gulakova *et al.*, 2011; Kuz'mina *et al.*, 2011) and one on the structure of 4-phenyl-2-styrylquinoline (Makela *et al.*, 2021). In all of these 2-styrylquinolines, the molecular skeleton is planar, in marked contrast to the nonplanar conformations of the 4-styrylquinoline derivatives (I)–(III) reported here, and of those reported previously (Rodríguez *et al.*, 2020). In both



**Figure 7**  
A projection along [010] of part of the crystal structure of compound (III), showing the arrangement of the molecular stacks within the unit cell. For the sake of clarity, all H atoms have been omitted.

8-styrylquinoline and 8-[2-(biphenyl-4-yl)vinyl]-2-methylquinoline, the styrylquinoline fragment is planar (Sharma *et al.*, 2015), as found in 2-styrylquinolines but again in marked contrast to 4-styrylquinolines. It is not easy to see why 4-styrylquinolines should adopt nonplanar conformations, while molecules of the 2-styryl and 8-styryl isomers appear consistently to adopt planar forms.

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## supporting information

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## Synthesis and spectroscopic and structural characterization of three new 2-methyl-4-styrylquinolines formed using Friedländer reactions between (2-aminophenyl)chalcones and acetone

**Diana Rocío Vera, Juan P. Mantilla, Alirio Palma, Justo Cobo and Christopher Glidewell**

### Computing details

For all structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINTE* (Bruker, 2017); data reduction: *SAINTE* (Bruker, 2017); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

### (*E*)-4-[2-(4-Fluorophenyl)ethenyl]-2-methylquinoline (I)

#### Crystal data

C<sub>18</sub>H<sub>14</sub>FN

*M<sub>r</sub>* = 263.30

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 13.5921 (7) Å

*b* = 12.7103 (6) Å

*c* = 7.6215 (3) Å

$\beta$  = 103.133 (2)°

*V* = 1282.25 (10) Å<sup>3</sup>

*Z* = 4

*F*(000) = 552

*D<sub>x</sub>* = 1.364 Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 2950 reflections

$\theta$  = 2.2–27.5°

$\mu$  = 0.09 mm<sup>-1</sup>

*T* = 100 K

Needle, yellow

0.20 × 0.08 × 0.07 mm

#### Data collection

Bruker D8 Venture  
diffractometer

Radiation source: INCOATEC high brilliance  
microfocus sealed tube

Multilayer mirror monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2016)

*T<sub>min</sub>* = 0.934, *T<sub>max</sub>* = 0.994

38068 measured reflections

2949 independent reflections

2342 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.079

$\theta_{\max}$  = 27.5°,  $\theta_{\min}$  = 2.2°

*h* = -17→17

*k* = -16→16

*l* = -9→9

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042

*wR*(*F*<sup>2</sup>) = 0.100

*S* = 1.05

2949 reflections

182 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0315*P*)<sup>2</sup> + 0.8512*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3



$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.38298 (9)	0.09596 (10)	0.33198 (16)	0.0184 (3)
C2	0.29100 (11)	0.11467 (12)	0.23444 (19)	0.0176 (3)
C3	0.25558 (11)	0.21776 (12)	0.18306 (19)	0.0176 (3)
H3	0.1892	0.2272	0.1115	0.021*
C4	0.31611 (11)	0.30404 (11)	0.23560 (19)	0.0167 (3)
C4A	0.41653 (10)	0.28596 (11)	0.33921 (19)	0.0163 (3)
C5	0.48647 (11)	0.36772 (12)	0.4033 (2)	0.0191 (3)
H5	0.4685	0.4386	0.3719	0.023*
C6	0.57984 (11)	0.34538 (12)	0.5101 (2)	0.0204 (3)
H6	0.6260	0.4008	0.5523	0.024*
C7	0.60735 (11)	0.24060 (12)	0.5574 (2)	0.0204 (3)
H7	0.6716	0.2261	0.6336	0.024*
C8	0.54267 (11)	0.15932 (12)	0.4950 (2)	0.0196 (3)
H8	0.5628	0.0889	0.5257	0.024*
C8A	0.44577 (11)	0.18016 (11)	0.38490 (19)	0.0170 (3)
C21	0.22304 (12)	0.02127 (12)	0.1834 (2)	0.0225 (3)
H21A	0.1914	0.0036	0.2830	0.034*
H21B	0.2628	-0.0388	0.1578	0.034*
H21C	0.1705	0.0381	0.0759	0.034*
C41	0.27793 (11)	0.41183 (11)	0.19305 (19)	0.0174 (3)
H41	0.3216	0.4626	0.1597	0.021*
C42	0.18432 (11)	0.44098 (11)	0.19947 (19)	0.0173 (3)
H42	0.1420	0.3877	0.2295	0.021*
C421	0.13959 (10)	0.54644 (11)	0.16520 (18)	0.0163 (3)
C422	0.04269 (11)	0.56378 (12)	0.1940 (2)	0.0191 (3)
H422	0.0077	0.5074	0.2345	0.023*
C423	-0.00317 (11)	0.66179 (12)	0.1644 (2)	0.0199 (3)
H423	-0.0691	0.6729	0.1835	0.024*
C424	0.04914 (11)	0.74221 (11)	0.10693 (19)	0.0187 (3)
F424	0.00528 (7)	0.83934 (7)	0.08198 (12)	0.0255 (2)
C425	0.14458 (11)	0.72940 (12)	0.0748 (2)	0.0192 (3)
H425	0.1785	0.7863	0.0333	0.023*
C426	0.18939 (11)	0.63090 (12)	0.10502 (19)	0.0181 (3)
H426	0.2551	0.6206	0.0845	0.022*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0183 (6)	0.0176 (6)	0.0200 (6)	0.0012 (5)	0.0059 (5)	0.0007 (5)
C2	0.0186 (7)	0.0177 (7)	0.0181 (7)	-0.0004 (6)	0.0075 (6)	-0.0006 (5)
C3	0.0159 (7)	0.0197 (7)	0.0177 (7)	0.0016 (6)	0.0050 (5)	0.0006 (5)
C4	0.0171 (7)	0.0175 (7)	0.0167 (7)	0.0023 (6)	0.0066 (5)	0.0014 (5)
C4A	0.0164 (7)	0.0177 (7)	0.0157 (7)	0.0010 (5)	0.0058 (5)	-0.0003 (5)
C5	0.0200 (7)	0.0164 (7)	0.0215 (7)	0.0020 (6)	0.0058 (6)	-0.0019 (6)
C6	0.0171 (7)	0.0220 (8)	0.0221 (7)	-0.0019 (6)	0.0046 (6)	-0.0052 (6)
C7	0.0158 (7)	0.0255 (8)	0.0198 (7)	0.0038 (6)	0.0038 (6)	-0.0014 (6)
C8	0.0184 (7)	0.0207 (8)	0.0205 (7)	0.0047 (6)	0.0057 (6)	0.0015 (6)
C8A	0.0180 (7)	0.0172 (7)	0.0172 (7)	0.0014 (5)	0.0071 (5)	-0.0002 (5)
C21	0.0231 (8)	0.0182 (8)	0.0259 (8)	-0.0017 (6)	0.0048 (6)	-0.0010 (6)
C41	0.0179 (7)	0.0164 (7)	0.0175 (7)	-0.0003 (6)	0.0035 (5)	0.0007 (5)
C42	0.0178 (7)	0.0161 (7)	0.0179 (7)	-0.0013 (5)	0.0041 (5)	0.0008 (5)
C421	0.0152 (7)	0.0169 (7)	0.0159 (7)	0.0003 (5)	0.0016 (5)	-0.0012 (5)
C422	0.0178 (7)	0.0195 (8)	0.0204 (7)	-0.0013 (6)	0.0051 (6)	0.0011 (5)
C423	0.0168 (7)	0.0239 (8)	0.0192 (7)	0.0040 (6)	0.0049 (6)	-0.0008 (6)
C424	0.0221 (8)	0.0153 (7)	0.0173 (7)	0.0060 (6)	0.0016 (6)	-0.0006 (5)
F424	0.0298 (5)	0.0174 (5)	0.0296 (5)	0.0095 (4)	0.0076 (4)	0.0024 (4)
C425	0.0201 (7)	0.0162 (7)	0.0207 (7)	-0.0014 (6)	0.0030 (6)	0.0002 (5)
C426	0.0152 (7)	0.0195 (7)	0.0193 (7)	0.0002 (5)	0.0030 (5)	-0.0001 (6)

*Geometric parameters (Å, °)*

N1—C2	1.3227 (19)	C21—H21A	0.9800
N1—C8A	1.3712 (19)	C21—H21B	0.9800
C2—C3	1.420 (2)	C21—H21C	0.9800
C2—C21	1.500 (2)	C41—C42	1.337 (2)
C3—C4	1.375 (2)	C41—H41	0.9500
C3—H3	0.9500	C42—C421	1.471 (2)
C4—C4A	1.432 (2)	C42—H42	0.9500
C4—C41	1.475 (2)	C421—C426	1.401 (2)
C4A—C5	1.418 (2)	C421—C422	1.401 (2)
C4A—C8A	1.423 (2)	C422—C423	1.388 (2)
C5—C6	1.373 (2)	C422—H422	0.9500
C5—H5	0.9500	C423—C424	1.373 (2)
C6—C7	1.408 (2)	C423—H423	0.9500
C6—H6	0.9500	C424—F424	1.3653 (16)
C7—C8	1.370 (2)	C424—C425	1.383 (2)
C7—H7	0.9500	C425—C426	1.388 (2)
C8—C8A	1.417 (2)	C425—H425	0.9500
C8—H8	0.9500	C426—H426	0.9500
C2—N1—C8A	118.08 (13)	C2—C21—H21B	109.5
N1—C2—C3	122.60 (13)	H21A—C21—H21B	109.5
N1—C2—C21	116.82 (13)	C2—C21—H21C	109.5

C3—C2—C21	120.56 (13)	H21A—C21—H21C	109.5
C4—C3—C2	120.85 (13)	H21B—C21—H21C	109.5
C4—C3—H3	119.6	C42—C41—C4	122.66 (14)
C2—C3—H3	119.6	C42—C41—H41	118.7
C3—C4—C4A	117.71 (13)	C4—C41—H41	118.7
C3—C4—C41	121.31 (13)	C41—C42—C421	127.21 (14)
C4A—C4—C41	120.94 (13)	C41—C42—H42	116.4
C5—C4A—C8A	118.70 (13)	C421—C42—H42	116.4
C5—C4A—C4	123.56 (13)	C426—C421—C422	118.18 (13)
C8A—C4A—C4	117.71 (13)	C426—C421—C42	123.07 (13)
C6—C5—C4A	120.64 (14)	C422—C421—C42	118.76 (13)
C6—C5—H5	119.7	C423—C422—C421	121.28 (14)
C4A—C5—H5	119.7	C423—C422—H422	119.4
C5—C6—C7	120.23 (14)	C421—C422—H422	119.4
C5—C6—H6	119.9	C424—C423—C422	118.29 (13)
C7—C6—H6	119.9	C424—C423—H423	120.9
C8—C7—C6	120.82 (14)	C422—C423—H423	120.9
C8—C7—H7	119.6	F424—C424—C423	118.45 (13)
C6—C7—H7	119.6	F424—C424—C425	118.63 (13)
C7—C8—C8A	120.11 (14)	C423—C424—C425	122.92 (14)
C7—C8—H8	119.9	C424—C425—C426	118.07 (14)
C8A—C8—H8	119.9	C424—C425—H425	121.0
N1—C8A—C8	117.46 (13)	C426—C425—H425	121.0
N1—C8A—C4A	123.03 (13)	C425—C426—C421	121.26 (13)
C8—C8A—C4A	119.48 (13)	C425—C426—H426	119.4
C2—C21—H21A	109.5	C421—C426—H426	119.4
C8A—N1—C2—C3	0.1 (2)	C5—C4A—C8A—N1	178.89 (13)
C8A—N1—C2—C21	-178.20 (13)	C4—C4A—C8A—N1	1.0 (2)
N1—C2—C3—C4	-0.9 (2)	C5—C4A—C8A—C8	1.1 (2)
C21—C2—C3—C4	177.35 (13)	C4—C4A—C8A—C8	-176.78 (13)
C2—C3—C4—C4A	1.7 (2)	C3—C4—C41—C42	38.8 (2)
C2—C3—C4—C41	-175.99 (13)	C4A—C4—C41—C42	-138.76 (15)
C3—C4—C4A—C5	-179.48 (13)	C4—C41—C42—C421	178.04 (14)
C41—C4—C4A—C5	-1.8 (2)	C41—C42—C421—C426	5.5 (2)
C3—C4—C4A—C8A	-1.72 (19)	C41—C42—C421—C422	-174.47 (15)
C41—C4—C4A—C8A	175.96 (13)	C426—C421—C422—C423	-0.2 (2)
C8A—C4A—C5—C6	-1.2 (2)	C42—C421—C422—C423	179.79 (14)
C4—C4A—C5—C6	176.49 (14)	C421—C422—C423—C424	-0.4 (2)
C4A—C5—C6—C7	0.0 (2)	C422—C423—C424—F424	-178.42 (13)
C5—C6—C7—C8	1.4 (2)	C422—C423—C424—C425	1.0 (2)
C6—C7—C8—C8A	-1.5 (2)	F424—C424—C425—C426	178.42 (13)
C2—N1—C8A—C8	177.65 (13)	C423—C424—C425—C426	-1.0 (2)
C2—N1—C8A—C4A	-0.2 (2)	C424—C425—C426—C421	0.4 (2)
C7—C8—C8A—N1	-177.65 (13)	C422—C421—C426—C425	0.2 (2)
C7—C8—C8A—C4A	0.3 (2)	C42—C421—C426—C425	-179.79 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C8—H8···N1 <sup>i</sup>	0.95	2.62	3.561 (2)	170

Symmetry code: (i)  $-x+1, -y, -z+1$ .

(*E*)-2-Methyl-4-{2-[4-(trifluoromethyl)phenyl]ethenyl}quinoline (II)

Crystal data

C <sub>19</sub> H <sub>14</sub> F <sub>3</sub> N	<i>F</i> (000) = 1296
<i>M<sub>r</sub></i> = 313.31	<i>D<sub>x</sub></i> = 1.381 Mg m <sup>-3</sup>
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation, λ = 0.71073 Å
<i>a</i> = 17.2696 (10) Å	Cell parameters from 3752 reflections
<i>b</i> = 10.8096 (7) Å	θ = 2.2–28.3°
<i>c</i> = 16.1495 (8) Å	μ = 0.11 mm <sup>-1</sup>
β = 91.440 (2)°	<i>T</i> = 100 K
<i>V</i> = 3013.8 (3) Å <sup>3</sup>	Block, colourless
<i>Z</i> = 8	0.16 × 0.14 × 0.12 mm

Data collection

Bruker D8 Venture diffractometer	46287 measured reflections
Radiation source: INCOATEC high brilliance microfocus sealed tube	3750 independent reflections
Multilayer mirror monochromator	2921 reflections with <i>I</i> > 2σ( <i>I</i> )
φ and ω scans	<i>R</i> <sub>int</sub> = 0.085
Absorption correction: multi-scan (SADABS; Bruker, 2016)	θ <sub>max</sub> = 28.3°, θ <sub>min</sub> = 2.2°
<i>T</i> <sub>min</sub> = 0.888, <i>T</i> <sub>max</sub> = 0.987	<i>h</i> = -22→22
	<i>k</i> = -14→14
	<i>l</i> = -21→20

Refinement

Refinement on <i>F</i> <sup>2</sup>	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.047	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0491 <i>P</i> ) <sup>2</sup> + 3.926 <i>P</i> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.121	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 1.03	(Δ/σ) <sub>max</sub> < 0.001
3750 reflections	Δρ <sub>max</sub> = 0.33 e Å <sup>-3</sup>
209 parameters	Δρ <sub>min</sub> = -0.29 e Å <sup>-3</sup>
0 restraints	
Primary atom site location: dual	

Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
N1	0.35530 (8)	0.65666 (13)	0.70993 (8)	0.0214 (3)
C2	0.40811 (9)	0.73252 (15)	0.68089 (10)	0.0220 (3)
C3	0.47497 (9)	0.69044 (15)	0.64043 (10)	0.0208 (3)

H3	0.5106	0.7490	0.6197	0.025*
C4	0.48905 (9)	0.56618 (15)	0.63077 (9)	0.0184 (3)
C4A	0.43320 (9)	0.48166 (15)	0.66242 (9)	0.0176 (3)
C5	0.44046 (9)	0.35106 (15)	0.65886 (10)	0.0216 (3)
H5	0.4847	0.3153	0.6345	0.026*
C6	0.38443 (10)	0.27589 (16)	0.69007 (10)	0.0242 (3)
H6	0.3905	0.1886	0.6874	0.029*
C7	0.31786 (10)	0.32625 (16)	0.72612 (10)	0.0245 (4)
H7	0.2789	0.2732	0.7465	0.029*
C8	0.30976 (9)	0.45181 (16)	0.73152 (10)	0.0221 (3)
H8	0.2651	0.4855	0.7562	0.026*
C8A	0.36711 (9)	0.53235 (15)	0.70072 (9)	0.0187 (3)
C21	0.39360 (11)	0.86894 (16)	0.69174 (13)	0.0324 (4)
H21A	0.3714	0.8837	0.7461	0.049*
H21B	0.3574	0.8978	0.6482	0.049*
H21C	0.4426	0.9141	0.6879	0.049*
C41	0.55777 (9)	0.52090 (15)	0.58805 (9)	0.0189 (3)
H41	0.5541	0.4430	0.5610	0.023*
C42	0.62479 (9)	0.58178 (15)	0.58464 (10)	0.0205 (3)
H42	0.6276	0.6595	0.6120	0.025*
C421	0.69464 (9)	0.54044 (15)	0.54269 (9)	0.0181 (3)
C422	0.76181 (9)	0.61241 (16)	0.55017 (10)	0.0224 (3)
H422	0.7611	0.6860	0.5824	0.027*
C423	0.82949 (9)	0.57845 (15)	0.51149 (10)	0.0229 (3)
H423	0.8747	0.6282	0.5172	0.027*
C424	0.83043 (9)	0.47101 (15)	0.46437 (9)	0.0188 (3)
C425	0.76429 (9)	0.39804 (15)	0.45619 (9)	0.0196 (3)
H425	0.7652	0.3246	0.4239	0.024*
C426	0.69721 (9)	0.43241 (15)	0.49513 (10)	0.0198 (3)
H426	0.6523	0.3820	0.4895	0.024*
C427	0.90242 (9)	0.43013 (16)	0.42322 (10)	0.0232 (3)
F471	0.93775 (6)	0.33641 (11)	0.46404 (8)	0.0390 (3)
F472	0.88912 (7)	0.38927 (13)	0.34613 (7)	0.0460 (3)
F473	0.95562 (6)	0.51919 (11)	0.41781 (8)	0.0390 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0182 (7)	0.0233 (7)	0.0229 (7)	0.0019 (5)	0.0041 (5)	-0.0005 (5)
C2	0.0196 (8)	0.0223 (8)	0.0245 (8)	0.0015 (6)	0.0053 (6)	0.0003 (6)
C3	0.0168 (7)	0.0223 (8)	0.0236 (8)	-0.0009 (6)	0.0048 (6)	0.0016 (6)
C4	0.0154 (7)	0.0235 (8)	0.0162 (7)	0.0020 (6)	0.0002 (5)	-0.0001 (6)
C4A	0.0160 (7)	0.0218 (8)	0.0150 (7)	0.0001 (6)	-0.0010 (5)	0.0004 (6)
C5	0.0208 (8)	0.0224 (8)	0.0216 (7)	0.0016 (6)	0.0010 (6)	-0.0013 (6)
C6	0.0270 (9)	0.0213 (8)	0.0241 (8)	-0.0028 (7)	-0.0003 (6)	0.0003 (6)
C7	0.0226 (8)	0.0278 (9)	0.0233 (8)	-0.0066 (7)	0.0022 (6)	0.0012 (6)
C8	0.0174 (7)	0.0280 (9)	0.0210 (7)	-0.0021 (6)	0.0033 (6)	-0.0005 (6)
C8A	0.0171 (7)	0.0228 (8)	0.0163 (7)	0.0005 (6)	0.0004 (6)	0.0004 (6)



C21	0.0306 (10)	0.0227 (9)	0.0448 (11)	0.0030 (7)	0.0160 (8)	-0.0003 (8)
C41	0.0173 (7)	0.0210 (7)	0.0186 (7)	0.0030 (6)	0.0013 (6)	0.0000 (6)
C42	0.0187 (7)	0.0225 (8)	0.0205 (7)	0.0012 (6)	0.0015 (6)	-0.0019 (6)
C421	0.0159 (7)	0.0217 (8)	0.0169 (7)	0.0007 (6)	0.0013 (5)	0.0011 (6)
C422	0.0196 (8)	0.0223 (8)	0.0254 (8)	-0.0014 (6)	0.0020 (6)	-0.0057 (6)
C423	0.0175 (8)	0.0236 (8)	0.0277 (8)	-0.0042 (6)	0.0021 (6)	-0.0033 (6)
C424	0.0160 (7)	0.0217 (8)	0.0189 (7)	0.0014 (6)	0.0013 (6)	0.0017 (6)
C425	0.0193 (7)	0.0199 (7)	0.0197 (7)	-0.0003 (6)	0.0018 (6)	-0.0021 (6)
C426	0.0158 (7)	0.0218 (8)	0.0220 (7)	-0.0025 (6)	0.0010 (6)	-0.0010 (6)
C427	0.0201 (8)	0.0248 (8)	0.0251 (8)	-0.0019 (6)	0.0041 (6)	-0.0024 (6)
F471	0.0287 (6)	0.0367 (6)	0.0522 (7)	0.0131 (5)	0.0118 (5)	0.0077 (5)
F472	0.0307 (6)	0.0758 (9)	0.0318 (6)	-0.0015 (6)	0.0096 (5)	-0.0237 (6)
F473	0.0274 (6)	0.0328 (6)	0.0578 (7)	-0.0076 (5)	0.0212 (5)	-0.0055 (5)

*Geometric parameters (Å, °)*

N1—C2	1.321 (2)	C21—H21C	0.9800
N1—C8A	1.368 (2)	C41—C42	1.334 (2)
C2—C3	1.416 (2)	C41—H41	0.9500
C2—C21	1.507 (2)	C42—C421	1.468 (2)
C3—C4	1.375 (2)	C42—H42	0.9500
C3—H3	0.9500	C421—C426	1.399 (2)
C4—C4A	1.432 (2)	C421—C422	1.400 (2)
C4—C41	1.471 (2)	C422—C423	1.388 (2)
C4A—C5	1.419 (2)	C422—H422	0.9500
C4A—C8A	1.422 (2)	C423—C424	1.389 (2)
C5—C6	1.369 (2)	C423—H423	0.9500
C5—H5	0.9500	C424—C425	1.392 (2)
C6—C7	1.411 (2)	C424—C427	1.491 (2)
C6—H6	0.9500	C425—C426	1.383 (2)
C7—C8	1.368 (2)	C425—H425	0.9500
C7—H7	0.9500	C426—H426	0.9500
C8—C8A	1.418 (2)	C427—F473	1.3350 (19)
C8—H8	0.9500	C427—F472	1.335 (2)
C21—H21A	0.9800	C427—F471	1.347 (2)
C21—H21B	0.9800		
C2—N1—C8A	117.72 (14)	H21A—C21—H21C	109.5
N1—C2—C3	122.85 (15)	H21B—C21—H21C	109.5
N1—C2—C21	116.62 (14)	C42—C41—C4	124.49 (15)
C3—C2—C21	120.53 (15)	C42—C41—H41	117.8
C4—C3—C2	120.99 (15)	C4—C41—H41	117.8
C4—C3—H3	119.5	C41—C42—C421	126.36 (15)
C2—C3—H3	119.5	C41—C42—H42	116.8
C3—C4—C4A	117.40 (14)	C421—C42—H42	116.8
C3—C4—C41	121.69 (14)	C426—C421—C422	118.27 (14)
C4A—C4—C41	120.90 (14)	C426—C421—C42	123.05 (14)
C5—C4A—C8A	118.29 (14)	C422—C421—C42	118.68 (14)

C5—C4A—C4	124.02 (14)	C423—C422—C421	121.30 (15)
C8A—C4A—C4	117.69 (14)	C423—C422—H422	119.4
C6—C5—C4A	120.77 (15)	C421—C422—H422	119.4
C6—C5—H5	119.6	C422—C423—C424	119.29 (15)
C4A—C5—H5	119.6	C422—C423—H423	120.4
C5—C6—C7	120.90 (16)	C424—C423—H423	120.4
C5—C6—H6	119.5	C423—C424—C425	120.34 (14)
C7—C6—H6	119.5	C423—C424—C427	120.88 (14)
C8—C7—C6	119.67 (15)	C425—C424—C427	118.77 (14)
C8—C7—H7	120.2	C426—C425—C424	119.97 (15)
C6—C7—H7	120.2	C426—C425—H425	120.0
C7—C8—C8A	120.89 (15)	C424—C425—H425	120.0
C7—C8—H8	119.6	C425—C426—C421	120.83 (14)
C8A—C8—H8	119.6	C425—C426—H426	119.6
N1—C8A—C8	117.23 (14)	C421—C426—H426	119.6
N1—C8A—C4A	123.33 (14)	F473—C427—F472	106.26 (14)
C8—C8A—C4A	119.44 (15)	F473—C427—F471	105.69 (14)
C2—C21—H21A	109.5	F472—C427—F471	105.82 (14)
C2—C21—H21B	109.5	F473—C427—C424	113.47 (14)
H21A—C21—H21B	109.5	F472—C427—C424	112.81 (14)
C2—C21—H21C	109.5	F471—C427—C424	112.17 (13)
C8A—N1—C2—C3	0.7 (2)	C4—C4A—C8A—C8	178.87 (14)
C8A—N1—C2—C21	179.91 (15)	C3—C4—C41—C42	28.1 (2)
N1—C2—C3—C4	-1.3 (3)	C4A—C4—C41—C42	-153.27 (16)
C21—C2—C3—C4	179.50 (16)	C4—C41—C42—C421	-179.85 (15)
C2—C3—C4—C4A	0.6 (2)	C41—C42—C421—C426	4.6 (3)
C2—C3—C4—C41	179.28 (15)	C41—C42—C421—C422	-175.68 (16)
C3—C4—C4A—C5	-178.50 (15)	C426—C421—C422—C423	0.2 (2)
C41—C4—C4A—C5	2.8 (2)	C42—C421—C422—C423	-179.59 (15)
C3—C4—C4A—C8A	0.6 (2)	C421—C422—C423—C424	0.1 (3)
C41—C4—C4A—C8A	-178.12 (13)	C422—C423—C424—C425	-0.2 (2)
C8A—C4A—C5—C6	1.3 (2)	C422—C423—C424—C427	-178.80 (15)
C4—C4A—C5—C6	-179.65 (15)	C423—C424—C425—C426	0.0 (2)
C4A—C5—C6—C7	0.4 (2)	C427—C424—C425—C426	178.65 (15)
C5—C6—C7—C8	-1.3 (3)	C424—C425—C426—C421	0.3 (2)
C6—C7—C8—C8A	0.5 (2)	C422—C421—C426—C425	-0.3 (2)
C2—N1—C8A—C8	-179.51 (14)	C42—C421—C426—C425	179.40 (15)
C2—N1—C8A—C4A	0.6 (2)	C423—C424—C427—F473	-16.7 (2)
C7—C8—C8A—N1	-178.81 (15)	C425—C424—C427—F473	164.64 (15)
C7—C8—C8A—C4A	1.1 (2)	C423—C424—C427—F472	-137.61 (16)
C5—C4A—C8A—N1	177.91 (14)	C425—C424—C427—F472	43.7 (2)
C4—C4A—C8A—N1	-1.2 (2)	C423—C424—C427—F471	102.99 (18)
C5—C4A—C8A—C8	-2.0 (2)	C425—C424—C427—F471	-75.67 (19)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C426—H426 $\cdots$ Cg1 <sup>i</sup>	0.95	2.86	3.3627 (17)	114

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

(E)-4-[2-(2,6-dichlorophenyl)ethenyl]-2-methylquinoline (III)

Crystal data

$C_{18}H_{13}Cl_2N$	$F(000) = 1296$
$M_r = 314.19$	$D_x = 1.478 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 30.5651 (15) \text{ \AA}$	Cell parameters from 3210 reflections
$b = 3.8629 (2) \text{ \AA}$	$\theta = 2.6\text{--}27.5^\circ$
$c = 25.5357 (13) \text{ \AA}$	$\mu = 0.45 \text{ mm}^{-1}$
$\beta = 110.497 (2)^\circ$	$T = 100 \text{ K}$
$V = 2824.1 (2) \text{ \AA}^3$	Needle, yellow
$Z = 8$	$0.20 \times 0.10 \times 0.06 \text{ mm}$

Data collection

Bruker D8 Venture diffractometer	28110 measured reflections
Radiation source: INCOATEC high brilliance microfocus sealed tube	3208 independent reflections
Multilayer mirror monochromator	2930 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.042$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.897$ , $T_{\text{max}} = 0.973$	$h = -38 \rightarrow 38$
	$k = -5 \rightarrow 4$
	$l = -33 \rightarrow 33$

Refinement

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 4.0386P]$
$wR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3208 reflections	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
191 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.56531 (4)	0.8852 (3)	0.48948 (5)	0.0130 (2)
C2	0.54198 (5)	0.7306 (3)	0.44182 (6)	0.0128 (3)
C3	0.56318 (5)	0.6274 (4)	0.40297 (6)	0.0137 (3)

H3	0.5448	0.5189	0.3690	0.016*
C4	0.60991 (5)	0.6819 (4)	0.41372 (5)	0.0125 (3)
C4A	0.63640 (5)	0.8465 (4)	0.46545 (5)	0.0119 (3)
C5	0.68484 (5)	0.9218 (4)	0.48195 (6)	0.0138 (3)
H5	0.7014	0.8612	0.4580	0.017*
C6	0.70793 (5)	1.0802 (4)	0.53186 (6)	0.0150 (3)
H6	0.7405	1.1247	0.5426	0.018*
C7	0.68373 (5)	1.1781 (4)	0.56761 (6)	0.0151 (3)
H7	0.7000	1.2881	0.6023	0.018*
C8	0.63677 (5)	1.1148 (4)	0.55238 (6)	0.0136 (3)
H8	0.6206	1.1858	0.5763	0.016*
C8A	0.61204 (5)	0.9449 (3)	0.50145 (5)	0.0118 (3)
C21	0.49105 (5)	0.6559 (4)	0.42929 (6)	0.0161 (3)
H21A	0.4794	0.8008	0.4530	0.024*
H21B	0.4871	0.4113	0.4368	0.024*
H21C	0.4735	0.7070	0.3899	0.024*
C41	0.63227 (5)	0.5763 (4)	0.37352 (6)	0.0137 (3)
H41	0.6627	0.4787	0.3873	0.016*
C42	0.61108 (5)	0.6134 (4)	0.31843 (6)	0.0135 (3)
H42	0.5808	0.7145	0.3062	0.016*
C421	0.62973 (5)	0.5137 (4)	0.27438 (5)	0.0123 (3)
C422	0.59998 (5)	0.3598 (4)	0.22471 (6)	0.0135 (3)
Cl42	0.54280 (2)	0.25868 (9)	0.21885 (2)	0.01765 (10)
C423	0.61385 (5)	0.2738 (4)	0.18021 (6)	0.0154 (3)
H423	0.5925	0.1695	0.1475	0.018*
C424	0.65948 (5)	0.3429 (4)	0.18423 (6)	0.0163 (3)
H424	0.6696	0.2848	0.1542	0.020*
C425	0.69023 (5)	0.4961 (4)	0.23194 (6)	0.0148 (3)
H425	0.7214	0.5450	0.2346	0.018*
C426	0.67535 (5)	0.5782 (4)	0.27589 (6)	0.0130 (3)
Cl46	0.71648 (2)	0.77500 (9)	0.33402 (2)	0.01667 (10)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0133 (5)	0.0127 (6)	0.0132 (5)	0.0006 (4)	0.0048 (4)	0.0009 (4)
C2	0.0125 (6)	0.0112 (6)	0.0143 (6)	0.0010 (5)	0.0043 (5)	0.0018 (5)
C3	0.0145 (6)	0.0146 (7)	0.0108 (6)	0.0001 (5)	0.0028 (5)	-0.0003 (5)
C4	0.0152 (6)	0.0113 (6)	0.0107 (6)	0.0022 (5)	0.0043 (5)	0.0022 (5)
C4A	0.0126 (6)	0.0113 (6)	0.0113 (6)	0.0009 (5)	0.0035 (5)	0.0026 (5)
C5	0.0138 (6)	0.0144 (7)	0.0140 (6)	0.0016 (5)	0.0059 (5)	0.0027 (5)
C6	0.0116 (6)	0.0146 (7)	0.0176 (7)	-0.0002 (5)	0.0034 (5)	0.0033 (5)
C7	0.0169 (7)	0.0138 (7)	0.0120 (6)	-0.0008 (5)	0.0021 (5)	-0.0001 (5)
C8	0.0174 (7)	0.0128 (6)	0.0116 (6)	0.0011 (5)	0.0063 (5)	0.0007 (5)
C8A	0.0133 (6)	0.0101 (6)	0.0119 (6)	0.0010 (5)	0.0044 (5)	0.0025 (5)
C21	0.0135 (7)	0.0175 (7)	0.0178 (7)	-0.0010 (5)	0.0062 (5)	-0.0023 (6)
C41	0.0145 (6)	0.0132 (7)	0.0138 (6)	0.0018 (5)	0.0054 (5)	0.0006 (5)
C42	0.0120 (6)	0.0151 (7)	0.0140 (6)	0.0011 (5)	0.0055 (5)	-0.0006 (5)

C421	0.0140 (6)	0.0128 (6)	0.0095 (6)	0.0017 (5)	0.0035 (5)	0.0021 (5)
C422	0.0111 (6)	0.0150 (7)	0.0137 (6)	0.0013 (5)	0.0035 (5)	0.0021 (5)
C142	0.01233 (16)	0.0229 (2)	0.01625 (17)	-0.00152 (13)	0.00313 (13)	0.00075 (13)
C423	0.0188 (7)	0.0138 (7)	0.0125 (6)	0.0007 (5)	0.0041 (5)	-0.0011 (5)
C424	0.0209 (7)	0.0160 (7)	0.0142 (6)	0.0019 (6)	0.0089 (5)	0.0000 (5)
C425	0.0140 (6)	0.0151 (7)	0.0162 (6)	0.0012 (5)	0.0065 (5)	0.0013 (5)
C426	0.0135 (6)	0.0122 (6)	0.0116 (6)	0.0008 (5)	0.0022 (5)	0.0016 (5)
C146	0.01376 (17)	0.02144 (19)	0.01317 (16)	-0.00336 (13)	0.00267 (12)	-0.00164 (13)

*Geometric parameters (Å, °)*

N1—C2	1.3186 (18)	C21—H21A	0.9800
N1—C8A	1.3713 (17)	C21—H21B	0.9800
C2—C3	1.4188 (19)	C21—H21C	0.9800
C2—C21	1.5034 (18)	C41—C42	1.3345 (19)
C3—C4	1.3730 (19)	C41—H41	0.9500
C3—H3	0.9500	C42—C421	1.4791 (18)
C4—C4A	1.4336 (19)	C42—H42	0.9500
C4—C41	1.4762 (18)	C421—C426	1.4035 (18)
C4A—C5	1.4203 (18)	C421—C422	1.4075 (18)
C4A—C8A	1.4227 (18)	C422—C423	1.3850 (19)
C5—C6	1.366 (2)	C422—C142	1.7454 (14)
C5—H5	0.9500	C423—C424	1.388 (2)
C6—C7	1.4130 (19)	C423—H423	0.9500
C6—H6	0.9500	C424—C425	1.384 (2)
C7—C8	1.3711 (19)	C424—H424	0.9500
C7—H7	0.9500	C425—C426	1.3874 (19)
C8—C8A	1.4159 (19)	C425—H425	0.9500
C8—H8	0.9500	C426—C146	1.7479 (14)
C2—N1—C8A	117.80 (12)	C2—C21—H21B	109.5
N1—C2—C3	122.74 (13)	H21A—C21—H21B	109.5
N1—C2—C21	117.92 (12)	C2—C21—H21C	109.5
C3—C2—C21	119.32 (12)	H21A—C21—H21C	109.5
C4—C3—C2	120.99 (13)	H21B—C21—H21C	109.5
C4—C3—H3	119.5	C42—C41—C4	122.10 (13)
C2—C3—H3	119.5	C42—C41—H41	119.0
C3—C4—C4A	117.69 (12)	C4—C41—H41	119.0
C3—C4—C41	121.40 (13)	C41—C42—C421	126.85 (13)
C4A—C4—C41	120.91 (12)	C41—C42—H42	116.6
C5—C4A—C8A	118.73 (12)	C421—C42—H42	116.6
C5—C4A—C4	123.91 (12)	C426—C421—C422	114.95 (12)
C8A—C4A—C4	117.34 (12)	C426—C421—C42	125.20 (12)
C6—C5—C4A	120.84 (13)	C422—C421—C42	119.73 (12)
C6—C5—H5	119.6	C423—C422—C421	123.63 (13)
C4A—C5—H5	119.6	C423—C422—C142	117.44 (11)
C5—C6—C7	120.43 (13)	C421—C422—C142	118.90 (10)
C5—C6—H6	119.8	C422—C423—C424	118.79 (13)



C7—C6—H6	119.8	C422—C423—H423	120.6
C8—C7—C6	120.11 (13)	C424—C423—H423	120.6
C8—C7—H7	119.9	C425—C424—C423	120.14 (13)
C6—C7—H7	119.9	C425—C424—H424	119.9
C7—C8—C8A	120.84 (13)	C423—C424—H424	119.9
C7—C8—H8	119.6	C424—C425—C426	119.72 (13)
C8A—C8—H8	119.6	C424—C425—H425	120.1
N1—C8A—C8	117.54 (12)	C426—C425—H425	120.1
N1—C8A—C4A	123.43 (12)	C425—C426—C421	122.76 (13)
C8—C8A—C4A	119.04 (12)	C425—C426—Cl46	116.38 (10)
C2—C21—H21A	109.5	C421—C426—Cl46	120.85 (10)
C8A—N1—C2—C3	-0.4 (2)	C5—C4A—C8A—C8	0.12 (19)
C8A—N1—C2—C21	178.35 (12)	C4—C4A—C8A—C8	-178.67 (12)
N1—C2—C3—C4	0.6 (2)	C3—C4—C41—C42	39.5 (2)
C21—C2—C3—C4	-178.06 (13)	C4A—C4—C41—C42	-140.35 (15)
C2—C3—C4—C4A	0.0 (2)	C4—C41—C42—C421	-179.23 (13)
C2—C3—C4—C41	-179.85 (13)	C41—C42—C421—C426	-44.5 (2)
C3—C4—C4A—C5	-179.50 (13)	C41—C42—C421—C422	139.58 (15)
C41—C4—C4A—C5	0.3 (2)	C426—C421—C422—C423	0.4 (2)
C3—C4—C4A—C8A	-0.78 (19)	C42—C421—C422—C423	176.74 (13)
C41—C4—C4A—C8A	179.06 (12)	C426—C421—C422—Cl42	178.52 (10)
C8A—C4A—C5—C6	1.1 (2)	C42—C421—C422—Cl42	-5.14 (18)
C4—C4A—C5—C6	179.83 (13)	C421—C422—C423—C424	-0.2 (2)
C4A—C5—C6—C7	-1.2 (2)	Cl42—C422—C423—C424	-178.36 (11)
C5—C6—C7—C8	0.0 (2)	C422—C423—C424—C425	-0.2 (2)
C6—C7—C8—C8A	1.3 (2)	C423—C424—C425—C426	0.5 (2)
C2—N1—C8A—C8	179.24 (12)	C424—C425—C426—C421	-0.3 (2)
C2—N1—C8A—C4A	-0.5 (2)	C424—C425—C426—Cl46	-179.35 (11)
C7—C8—C8A—N1	178.89 (13)	C422—C421—C426—C425	-0.2 (2)
C7—C8—C8A—C4A	-1.3 (2)	C42—C421—C426—C425	-176.27 (13)
C5—C4A—C8A—N1	179.88 (12)	C422—C421—C426—Cl46	178.89 (10)
C4—C4A—C8A—N1	1.1 (2)	C42—C421—C426—Cl46	2.8 (2)