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Ethynyl π-extended 2,5-diphenyl-1,3,4-oxadiazoles and 2-phenyl 5-(2-thienyl)-1,3,4-oxadiazoles: synthesis, X-ray crystal structures and optical properties†

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2-(4-*tert*-Butylphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole **1** reacts with a series of heteroaryl iodides under standard Sonogashira cross-coupling conditions ($Pd[PPh_3]_2Cl_2$, CuI, triethylamine, THF) to yield products **2a–g** in 40–79% yields (heteroaryl = 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrazyl, 5-bromo-2-pyrimidyl, 2-thienyl and 3-thienyl, respectively). Compound **2f** was lithiated followed by electrophilic iodination (BuLi, perfluorohexyl iodide) to give **3**, which by a two-step sequence gave the terminal ethynylthienyl derivative **5**. Conversion of **5** into the terminal ethynylaldehyde derivative **7**, *via* acetal derivative **6**, proceeded in high yield. Starting from 2-iodo-5-methoxycarbonylthiophene, a five-step sequence afforded 2-(4-*tert*-butylphenyl)-5-(4-ethynylthienyl)-1,3,4-oxadiazole **13** (13% overall yield). Reactions of **13** gave terminal pyridyl, pyrazyl, pyrimidyl and thienyl derivatives, analogous to those obtained from **1**. Two-fold reaction of **13** with 2,5-diiodothiophene gave the bis(ethynylthienyl)thiophene derivative **15** (30% yield). Solution UV-Vis absorption and photoluminescence spectra establish that replacement of the phenyl ring in the 2,5-diphenyl-1,3,4-oxadiazole series **2a–g** by a thienyl ring [*i.e.* the 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole series **14a–g**] leads to a red shift in the lowest energy band in both the absorption spectra and emission spectra. The X-ray crystal structures of compounds **2d**, **2g**, **5** and **14d**·$CHCl_3$ reveal that the molecular structures are approximately planar although there are substantial differences in the conformations.

Introduction

2,5-Diphenyl-1,3,4-oxadiazole derivatives have been widely studied in diverse areas of chemistry. In particular, due to the electron-deficient properties of the oxadiazole ring, their luminescence properties and their good thermal and chemical stabilities,[1] a range of derivatives (*e.g.* low molecular weight monomers,[2] star-shaped oligomers[3] and polymers[4]) have been used as emissive materials and/or electron-transporting/hole-blocking compounds in organic light emitting devices (OLEDs).[5] Furthermore, many 1,3,4-oxadiazole derivatives are biologically active and continue to find applications in medicinal chemistry.[6] This combination of properties ensures that new functionalised derivatives are of considerable interest.

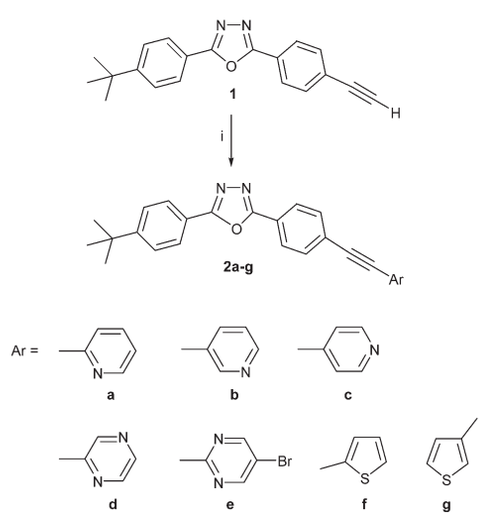
Very recently, the first 2,5-diphenyl-1,3,4-oxadiazole derivative possessing an alkyne substituent, compound **1**, was reported independently by Cha *et al.*[3] and by ourselves.[7] From a synthetic viewpoint, the ethynyl substituent offers unprecedented scope for functionalisation reactions which will extend the π-conjugation at the periphery of the framework. Compound **1** is, therefore, a very attractive building block in the light of the current interest in conjugation of aryl/heteroaryl rings through sp hybridised carbon linkages,[8] and the study of ethynyl derivatives of arenes and heteroarenes as "molecular wires".[9] In this article we report the synthesis of the novel thienyl analogue **13** and describe organometallic cross-coupling reactions at the terminal alkyne positions of **1** and **13** to obtain heteroaryl-functionalised derivatives possessing extended π-electron conjugation. The optical absorption and photoluminescence properties of the products are reported, along with four X-ray crystal structures.

Results and discussion

Synthesis

Compound **1** reacted with a series of heteroaryl iodides under standard Sonogashira conditions[10] [$Pd(PPh_3)_2Cl_2$, triethylamine, CuI, THF] to afford products **2a–g** in 40–79% yields (Scheme 1). Electron-deficient heterocycles (pyridyl, pyrazyl and pyrimidyl: **a**–**e**) and electron-rich thienyl derivatives (**f**, **g**) reacted similarly. Compound **2f** (obtained in 79% from **1**) was lithiated followed by electrophilic iodination (BuLi, perfluorohexyl iodide)[11] to give **3** in 83% yield (Scheme 2). This two-step sequence from **1** was more efficient than the direct reaction of **1** with 2,5-diiodothiophene, which gave **3** in 33% yield.

The terminal iodo substituent in compound **3** enabled further functionalisation reactions (Scheme 2). Sonogashira reaction with 2-methyl-3-butyn-2-ol gave product **4** (70% yield), which was deprotected under standard basic conditions[12] with loss



Scheme 1 Reagents and conditions: i, iodoheterocycle, CuI, $Pd[PPh_3]_2Cl_2$, THF, NEt_3, reflux.

† Electronic supplementary information (ESI) available: crystal structure data; full synthetic details and characterisation data for compounds **2a–g**, **3–7**, **14a–g** and **15**; UV-Vis absorption and photoluminescence spectra for compounds **2g** and **14g**; packing diagrams for compounds **2d**, **2g**, **5** and **14d**·$CHCl_3$. See http://www.rsc.org/suppdata/ob/b4/b407698m/

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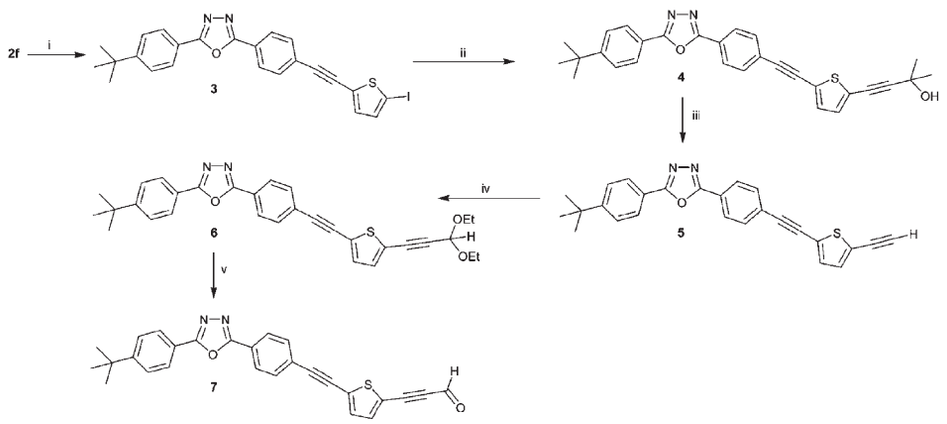
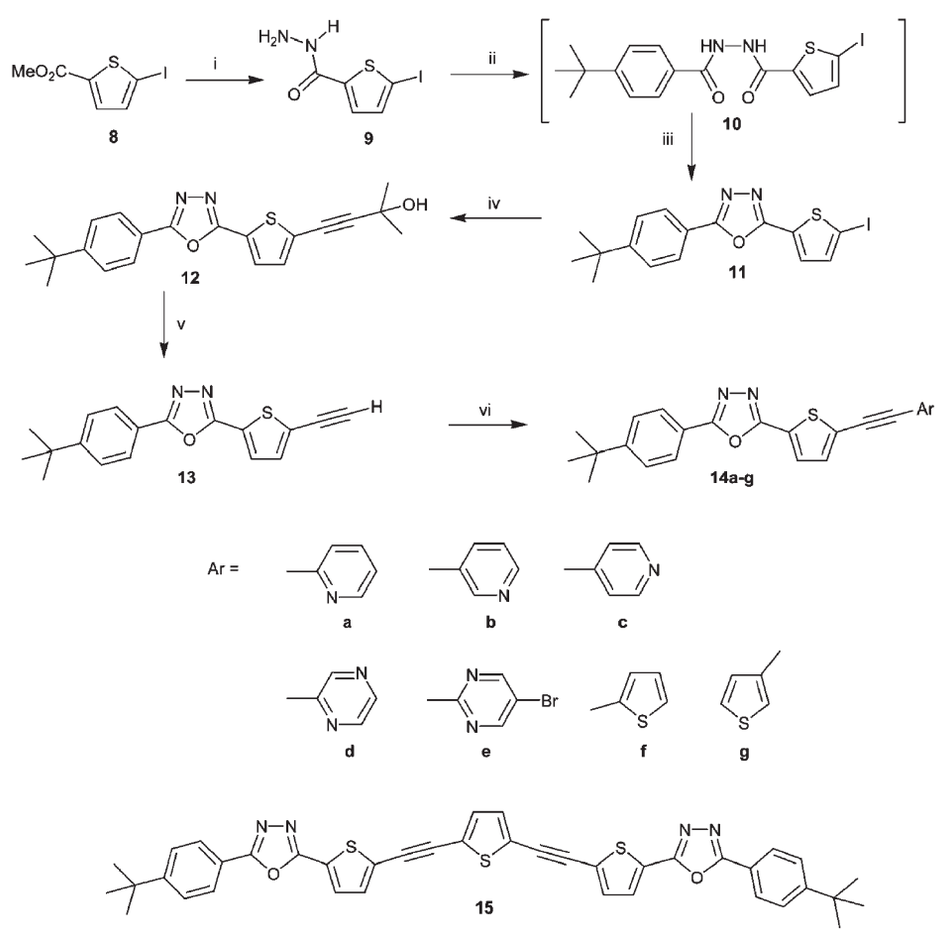


Scheme 2 Reagents and conditions: i, n-BuLi, THF, $C_6F_{13}I$, −78 °C to 20 °C; ii, 2-methyl-3-butyn-2-ol, CuI, $Pd[PPh_3]_2Cl_2$, THF, NEt_3, reflux; iii, NaOH, toluene, reflux; iv, triethyl orthoformate, ZnI_2, 140 °C; v, Amberlyst-15, acetone–water, 20 °C.

of acetone to give the new terminal alkyne derivative **5** (79% yield). One reason for synthesising **5** was that we thought that the low nucleophilicity of the acetylide anion of **1** towards carbonyl groups was due to the strongly electron-withdrawing effect of the oxadiazole ring.[7a] The insertion of an additional electron-rich thiophene ring should offset this effect and the nucleophilicity of the acetylide anion of **5** would thereby be increased compared to that of **1**. However, attempted functionalisation of the alkyne group of **5** by deprotonation (with NaH, DBU, LDA or *tert*-BuLi) and subsequent reaction with 4-ethoxybenzaldehyde or DMF gave only recovered starting material in high yield in each case, with no substitution product being detected. Similar to compound **1**,[7a] functionalisation of **5** using triethyl orthoformate proceeded smoothly in the presence of zinc iodide[13] to yield **6** (89% yield) which was hydrolysed with the ion exchange resin Amberlyst-15 in acetone–water[14] to give aldehyde **7** (88% yield).

To explore the effect of replacing the alkynylphenyl moiety of compound **1** with an alkynylthienyl moiety, a series of novel 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole derivatives was synthesised as shown in Scheme 3.[15] The readily available thiophene derivative **8**[16] was converted into the hydrazide derivative **9**. Reaction of **9** with *tert*-butylbenzoyl chloride gave the intermediate diacylhydrazine compound **10**, which was not purified. The crude product **10** was cyclodehydrated under the standard conditions for the formation of 1,3,4-oxadiazoles[17] using phosphorus oxychloride, to give the 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole system **11**. By analogy with the reactions of **3** (Scheme 2), Sonogashira reaction of **11** with 2-methyl-3-butyn-2-ol gave **12**, from which the target alkyne



Scheme 3 Reagents and conditions: i, hydrazine hydrate, MeOH, reflux; ii, 4-*tert*-butylbenzoyl chloride, pyridine, reflux; iii, $POCl_3$, reflux; iv, 2-methyl-3-butyn-2-ol, CuI, $Pd[PPh_3]_2Cl_2$, THF, NEt_3, reflux; v, NaOH, toluene, reflux; vi, iodoheterocycle (2,5-diiodothiophene for **15**), CuI, $Pd[PPh_3]_2Cl_2$, THF, NEt_3, reflux.

13 was obtained (13% overall yield from compound **8**). Cross-coupling reactions analogous to those shown in Scheme 1, using the corresponding iodoheterocycle, gave the terminal heteroaryl derivatives **14a–g** in 33–65% yield. Two-fold reaction of **13** with 2,5-diiodothiophene gave the π-extended bis(ethynylthienyl)-thiophene derivative **15** (30% yield).

X-Ray crystal structures of compounds 2d, 2g, 5 and 14d

The molecular structures of **2d**, **2g**, **5** and **14d**, shown in Fig. 1, can be described as approximately planar. The deviations of all non-hydrogen atoms (except the methyl carbons) from their mean plane are small [average 0.22 (**2d**), 0.21 (**2g**), 0.11 (**5**) and 0.15 Å (**14d**)] compared to the total lengths of the molecules [*ca.* 22.5 (**2d**, **2g**), 25.4 (**5**) and 23.2 Å (**14d**)]. Largely, this planarity is due to the molecules having few degrees of conformational freedom, as they comprise a number of planar rings on a rigid 'rod'. However, the rings can rotate, and there are substantial differences in the conformations. The asymmetric unit of structure **2d** comprises two molecules. In each of them, both benzene rings are nearly coplanar (within 1.5 to 4.8°) with the oxadiazole ring, while the angle between benzene ring B and the pyrazine ring is 42.5 or 39.3°. In molecule **2g** the oxadiazole ring is inclined by 24.7 and 18.1° (in the opposite sense) to the benzene rings A and B, while the latter is inclined to the thiophene ring by 3.5°. The corresponding interplanar angles in molecule **5** are 6.8, 14.3 and 11.0°, respectively. The acetylenic H atom does not participate in any hydrogen bond. Compound **14d** crystallises as a monosolvate, with the asymmetric unit comprising one molecule of **14d** and one of $CHCl_3$, linked by a weak hydrogen bond $Cl_3C–H\cdots N(2)$ (H···N 2.48 Å for the idealised C–H distance of 1.08 Å). The dihedral angles between benzene and oxadiazole rings are 13.6°; oxadiazole and thiophene 6.1°; thiophene and pyrazine 18.5°.

The crystal packing diagrams are included in the Supplementary Information.† The motifs of **2g** and **5** (and their lattices) are similar, with stacks of molecules running in the *y* direction. The structure of **2d** has a herringbone motif, while **14d**·$CHCl_3$ comprises double layers of molecules **14d** separated by single layers of chloroform molecules.

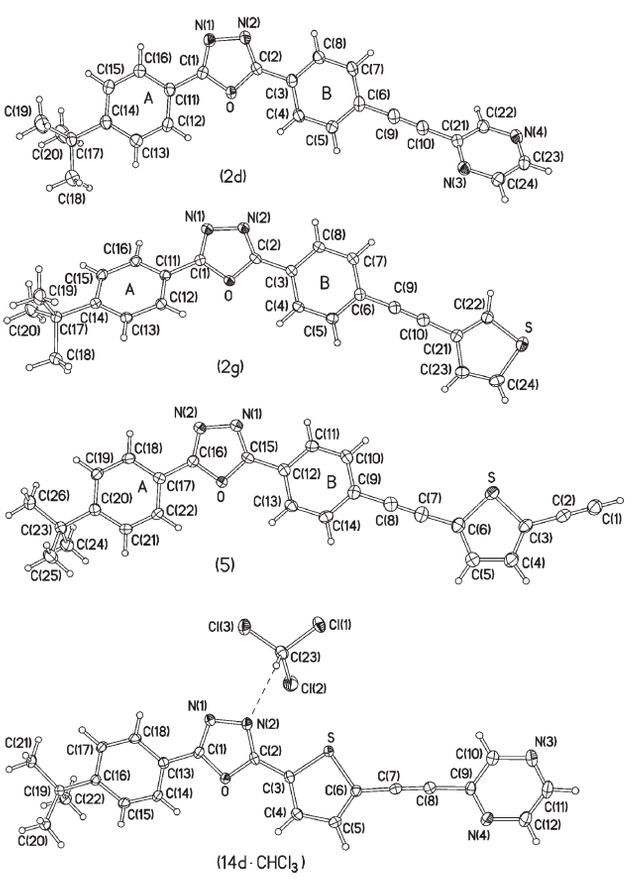


Fig. 1 X-Ray molecular structures of **2d**, **2g**, **5** and **14d**·$CHCl_3$.

Table 1 Absorption and steady state emission spectra at 20 °C in DCM

Compound	λ_{max}(abs)	λ_{max}(PL) (PLQY)[a]
2a	322	354, 374
2b	319	354, 373
2c	320	375
2d	323	380 (24%)
2e	325	384
2f	335	389 (10%)
2g	325	361, 376 (28%)
14a	352	386, 408
14b	348	385, 408
14c	351	388, 409
14d	353	396, 415 (22%)
14e	361	420
14f	355	407, 425
14g	347	395, 413
15	400	452, 480

[a]Standards were quinine sulfate (Φ = 0.577 in 0.1 M H_2SO_4) and β-carbolene (Φ = 0.60 in 0.5 M H_2SO_4); excited at 350 nm.

Optical absorption and emission properties

The UV-Vis absorption and photoluminescence properties in dichloromethane solution for the two series of compounds **2a–g** and **14a–g**, **15** are collated in Table 1. Fig. 2 shows the absorption and emission spectra for selected compounds. The Stokes shift in λ_{max} values for all the compounds is in the range 50–80 nm, which agrees with known diphenyl-1,3,4-oxadiazole derivatives[18] and diaryl(heteroaryl)ethynes where there is a relatively small conformational change upon photoexcitation.[8a] An interesting trend is that replacement of a phenyl ring (compounds **2a–g**) by the thienyl ring (compounds **14a–g**) leads to a red shift in the lowest energy band in both the absorption and emission spectra. This can be explained by a "push-pull effect" of the conjugated electron-donating thiophene ring and the electron-accepting oxadiazole ring lowering the HOMO–LUMO gap.[19] In the absorption spectra, this shift is within the range 21–36 nm. In the PL spectra the red shift which occurs on replacing phenyl with thienyl is remarkably similar for all the analogues [$\Delta\lambda_{max}$(em) 34–37 nm]. An additional feature of the data in Table 1 is a further red shift in the absorption and emission peaks of **15** compared to **14f** [$\Delta\lambda_{max}$(abs) 45 nm; $\Delta\lambda_{max}$(em) 55 nm], which is consistent with extended π-conjugation through the central bis(ethynylthiophene) unit of **15**.[20] Photoluminescence quantum yield (PLQY) values were obtained for compounds **2d**, **2f**, **2g** and **14d** and fall within the range 10–28% (Table 1). These values are considerably lower than those reported for model compounds which lack the ethynyl bond, *viz.* 2,5-diphenyl-1,3,4-oxadiazole

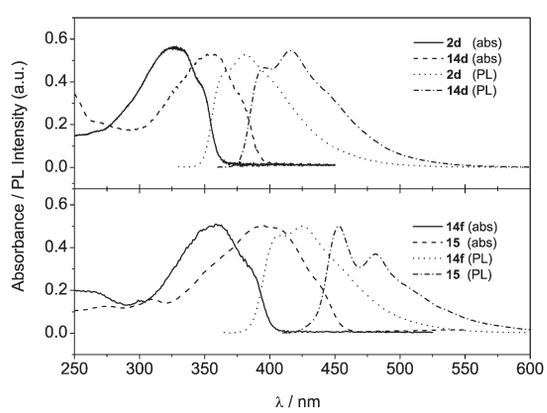


Fig. 2 UV-Vis absorption and photoluminescence spectra (excitation at 355 nm) in dichloromethane, 20 °C: compounds **2d** and **14d** (top) and compounds **14f** and **15** (bottom).

(89%) and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (83%) in non-polar solvents,[21] and are consistent with the data obtained for a series of simpler di(aryl/heteroaryl)ethynyl derivatives.[22]

Cyclic voltammetry

Cyclic voltammograms of **2d** and **14d**, representing each of the two series of analogues, were recorded (Fig. 3). These two compounds had similar redox behaviour featuring a reversible one-electron reduction and another irreversible two-electron reduction wave. We assume that the wave at lower reduction potential was due to the reduction of the most electron-deficient oxadiazole ring of the molecule, and the irrversible wave at higher reduction potential was attributed to the reduction of the triple bond. Due to the reduced HOMO–LUMO gap from the introduction of the thiophene unit, the reduction of **14d** is *ca.* 100 mV less negative than its phenylene analogue **2d**.

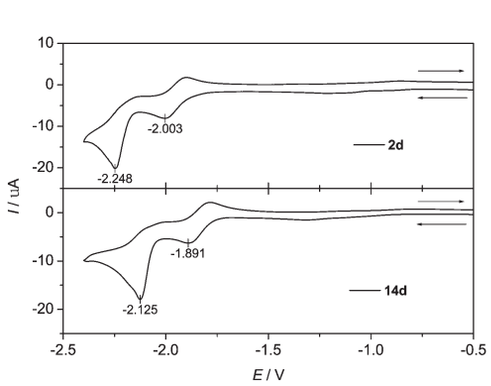


Fig. 3 Cyclic voltammograms of compounds **2d** (upper) and **14d** (lower) in DMF solution containing 0.1 M NBu_4PF_6. The potentials were relative to Ag/Ag^+, using a Pt disk (Φ = 1.6 mm) as the working electrode and a Pt wire as the counter electrode, and scanned at 100 mV s^{-1}.

Conclusions

We have achieved efficient functionalisation of the terminal ethynyl carbon of compound **1** by cross-coupling reactions with a series of heteroaryl iodides using Sonogashira methodology. The first ethynyl derivative of 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole and its cross-coupled derivatives are reported: a five-step sequence from the readily available 2-iodo-5-methoxycarbonylthiophene gives 2-(4-*tert*-butylphenyl)-5-(4-ethynylthienyl)-1,3,4-oxadiazole **13** in 16% overall yield. Subsequent functionalisation of **13** proceeds smoothly by analogy with **1**. Spectroscopic studies in solution establish that replacement of the phenyl ring (*i.e.* the 2,5-diphenyl-1,3,4-oxadiazole series **2a–g**) by a thienyl ring (*i.e.* the 2-phenyl-5-thienyl-1,3,4-oxadiazole series **14a–g**) leads to a significant red shift in the lowest energy band in both the absorption spectra and emission spectra. Conjugation is extended further in the bis(ethynylthienyl)thiophene derivative **15**. X-Ray crystal structure analyses reveal that the π-systems of compounds **2d**, **2g**, **5** and **14d** adopt predominantly planar conformations. This work clearly establishes that the alkynes **1** and **13** are synthetically viable and versatile building blocks for the construction of extended functional π-electron systems with interesting optoelectronic and structural properties.

Experimental

General details are the same as those reported previously.[2b]

Cross-coupling reactions: general procedure

A mixture of the alkyne (1.0 mmol), the halo compound (1.0 mmol), CuI powder (20 mg) and $Pd[PPh_3]_2Cl_2$ (70 mg) in THF (15 cm^3) was stirred at 20 °C for 5 min to afford a yellow solution (CuI remained undissolved). Triethylamine (5 cm^3) was added in one portion and the solution turned orange, then red and brown within 15 min of the addition. The mixture was stirred at 20 °C for 12 h to yield a yellow suspension. Additional THF (5 cm^3) was added and the suspension was heated at reflux for 5 h. The mixture was evaporated *in vacuo* and the residue was chromatographed on a silica column to yield the product.

Compound 9

Compound **8**[16] (10.0 g, 37.3 mmol) was dissolved in methanol (70 cm^3). Hydrazine hydrate (7.2 cm^3, 149 mmol) was added and the mixture was heated under reflux overnight. The solvent was partially evaporated *in vacuo* and the resulting yellow solid was isolated by filtration and recrystallised from methanol to yield **9** as yellow crystals (4.60 g, 46%), mp 146–147 °C. δ_H (DMSO-d_6): 4.44 (s, 2H), 7.34 (d, 1H, J = 4.0 Hz), 7.37 (d, 1H, J = 4.0 Hz), 9.77 (s, 1H). δ_C (DMSO-d_6): 82.43, 129.09, 137.72, 144.08, 160.02. MS (EI) *m*/*z* (%): 268 (M^+, 100). Anal. for $C_5H_5IN_2OS$: calcd. C, 22.40; H, 1.88; N, 10.45. Found C, 22.35; H, 1.87; N, 10.49%.

Compound 11

Compound **9** (7.50 g, 27.9 mmol) was dissolved in pyridine (20 cm^3) and 4-*tert*-butylbenzoyl chloride (5.50 g, 27.9 mmol) was added. The mixture was stirred at 20 °C under Ar for 1 h then refluxed for 1 h. The pyridine was removed *in vacuo* and methanol (100 cm^3) was added to the insoluble white residue. This mixture was boiled for 2 min (to extract impurities), cooled, and the solid (compound **10**) was isolated by suction filtration and thoroughly dried under vacuum overnight. The anhydrous **10** was mixed with phosphorus oxychloride (75 cm^3) and the mixture was refluxed for 3 h. The excess $POCl_3$ was removed by vacuum distillation. The viscous residue was crystallised from chloroform–ethanol, yielding **11** as pale yellow plates (6.04 g, 53%), mp 170–172 °C. δ_H ($CDCl_3$): 1.37 (s, 9H), 7.33 (d, 1H, J = 4.0 Hz), 7.46 (d, 1H, J = 4.0 Hz), 7.52 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.4 Hz). δ_C ($CDCl_3$): 31.08, 35.09, 79.61, 120.60, 126.08, 126.79, 130.67, 1311.10, 137.99, 155.55, 159.44, 164.16. MS (EI) *m*/*z* (%): 410 (M^+, 100). Anal. for $C_{16}H_{15}IN_2OS$: calcd. C, 46.84; H, 3.69; N, 6.83. Found C, 46.58; H, 3.62; N, 6.73%.

Compound 12

Compound **11** (5.0 g, 12.2 mmol), 2-methyl-3-butyn-2-ol (2.6 cm^3, 26.7 mmol), $Pd[PPh_3]_2Cl_2$ (0.86 g) and CuI (0.23 mg) were added to a mixture of THF–Et_3N (100 cm^3, 1:1 v/v), stirred at 20 °C overnight and refluxed for 3 h, followed by chromatography on a silica column (eluent DCM–diethyl ether, 95:5 v/v). The product was recystallised from ethanol–H_2O, yielding **12** as golden needles (3.2 g, 72%), mp 161–163 °C. δ_H ($CDCl_3$): 1.41 (s, 9H), 1.69 (s, 6H), 2.30 (s, 1H), 7.20 (d, 1H, J = 3.5 Hz), 7.53 (d, 2H, J = 8.0 Hz), 7.66 (d, 1H, J = 4.0 Hz), 8.01 (d, 2H, J = 8.0 Hz). δ_C ($CDCl_3$): 31.08, 31.16, 65.74, 74.59, 100.59, 120.62, 125.70, 126.08, 126.80, 127.32, 129.20, 132.64, 155.55, 159.87, 164.26. MS (EI) *m*/*z* (%): 366 (M^+, 100). Anal. for $C_{21}H_{22}N_2O_2S$: calcd. C, 68.82; H, 6.05; N, 7.64. Found: C, 68.61; H, 6.00, N, 7.54%.

Compound 13

Compound **12** (2.62 g, 7.15 mmol) was dissolved in dry toluene (40 cm^3). Sodium hydroxide powder (0.34 g, freshly ground from pellets) was added and the mixture was refluxed under Ar until the reaction had gone to completion (*ca.* 40 min – tlc monitoring). The solvent was removed *in vacuo* and the residue was dissolved in DCM (15 cm^3), and chromatographed on a silica column (eluent DCM–diethyl ether, 98:2 v/v). The product was recystallised from ethanol–H_2O, yielding **13** as golden needles (1.54 g, 72%), mp 165–166 °C. δ_H ($CDCl_3$): 1.36 (s, 9H), 3.51 (s, 1H), 7.31 (d, 1H, J = 3.5 Hz), 7.53 (d, 2H, J = 8.0 Hz), 7.67 (d, 1H, J = 3.5 Hz), 8.01 (d, 2H, J = 9.0 Hz).

Table 2 Crystal data

Compound	**2d**	**2g**	**5**	**14d**
Formula	$C_{24}H_{20}N_4O$	$C_{24}H_{20}N_2OS$	$C_{26}H_{20}N_2OS$	$C_{22}H_{18}N_4OS{\cdot}CHCl_3$
Formula weight	380.44	384.48	408.50	505.83
T/K	120	120	120	120
Symmetry	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/a$ (# 14)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)
a/Å	22.881(3)	6.1665(5)	6.345(2)	6.1798(4)
b/Å	6.314(1)	6.9748(5)	6.985(2)	26.851(8)
c/Å	28.860(4)	22.943(3)	23.672(8)	13.650(1)
α/°	90	83.55(1)	94.24(1)	90
β/°	109.86(1)	84.09(1)	91.96(1)	92.26(1)
γ/°	90	83.67(1)	91.93(1)	90
V/Å^3	3921.4(10)	970.45(16)	1045.0(6)	2263.2(7)
Z	8	2	2	4
μ/mm^{-1}	0.08	0.18	0.18	0.52
Reflns. collected	44484	18140	13306	26697
Unique reflns.	9004	5663	4788	5191
R_{int}	0.073	0.021	0.040	0.076
Reflns. $F^2 > 2\sigma(F^2)$	5530	5010	3407	3576
$R[F^2 > 2\sigma(F^2)]$	0.050	0.037	0.045	0.035
$wR(F^2)$, all data	0.154	0.108	0.137	0.081

δ_C ($CDCl_3$): 31.08, 35.10, 75.85, 84.30, 120.59, 126.09, 126.28, 126.41, 126.83, 129.05, 133.71, 155.60, 159.76, 164.35. MS (EI) m/z (%): 308 (M^+, 100). Anal. for $C_{18}H_{16}N_2OS$: calcd. C, 70.10; H, 5.23; N, 9.08. Found C, 69.93; H, 5.22; N, 8.93%.

X-Ray crystallography

Single-crystal diffraction experiments (Table 2) were carried out on a Bruker 3-circle diffractometer with a SMART 6000 CCD area detector, using graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[23] Non-H atoms were refined with anisotropic displacement parameters; H atoms in **2g** and **14d** were refined in anisotropic approximation; in **2d** and **5** methyl groups were treated as rigid bodies; other H atoms in 'riding' model. Structure **5** shows an insignificant (5%) contribution of another conformer, differing by a 180° rotation of the thiophene ring around the C(6)–C(7) bond. Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 239476–239479 for **2d**, **2g**, **5** and **14d**, respectively.

Acknowledgements

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