

# Arylazopyrazoles: Azoheteroarene photoswitches offering quantitative isomerization and long thermal half-lives.

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Supporting Information Placeholder

**ABSTRACT:** Arylazopyrazoles, a novel class of 5-membered azo photoswitches, offer quantitative photoswitching and high thermal stability of the *Z*-isomer (half-lives of 10 and ~1000 days). The conformation of the *Z*-isomers of these compounds, and also the arylazopyrroles, is highly dependent on the substitution pattern on the heteroarene, allowing a twisted or planar geometry, which in turn has a significant impact on the electronic spectral properties of the compounds.

Photoswitchable compounds have diverse applications, from photopharmacology and optochemical genetics, to optical data storage.<sup>1–8</sup> Azobenzenes are easy to synthesize and highly versatile photoswitches. These molecules have high extinction coefficients and quantum yields, allowing low intensity light to be used to elicit photoisomerisation, and are stable to repeated switching cycles.<sup>9</sup> Photochemical *E-Z* isomerization induces a substantial change in the shape of these molecules, including a significant difference in the end-to-end distance.<sup>9</sup> This has been exploited, for example, in the direct conversion of light into mechanical energy.<sup>10–12</sup> Generally, the *E*-isomers are more thermodynamically stable than the *Z*-isomers; the notable exception being Temps and co-workers' tricyclic ethylene-bridged azobenzene, which has reversed stability due to the ring strain present in the *E*-isomer.<sup>13</sup>

A large array of azobenzenes have been reported, with an assortment of applications, however there are still a number of drawbacks that limits their practical use for certain purposes. Firstly, incomplete photoswitching is often observed due to overlapping absorbances in the irradiation regions of interest.<sup>3</sup> Secondly, the *Z*-isomer often rapidly thermally converts back to the *E*-isomer. High thermal stability is particularly required for the use of photochromic compounds in ultrahigh-density optical data storage; an area currently dominated by diarylethylenes.<sup>7,8</sup> Since the properties of azobenzenes can be varied substantially by altering the substituents on the aromatic rings, a number of specific azobenzenes have been recently reported that address such limitations.<sup>14–17</sup> For example, Hecht and co-workers recently reported that 2,2',6,6'-tetrafluoroazobenzene shows near-quantitative photoswitching and the longest thermal half-life reported for an azobenzene molecule (~700 days at 25 °C in DMSO).<sup>16</sup>

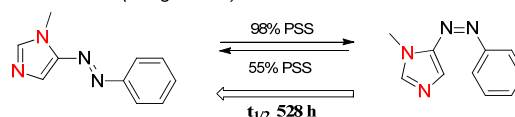
5-Membered azoheteroarenes, and in particular their photochromism, are far less studied. Much of the work on azoheteroarenes has concentrated on developing donor- $\pi$ -acceptor systems with strong nonlinear optic and solvatochromic properties.<sup>18–24</sup> Of the photochromic compounds studied, generally, these heteroaromatic compounds have incomplete *E-Z* conversion and fast thermal half-lives (usually under 1 min).<sup>19,20,22</sup> Velasco and co-workers recently exploited this property to develop extremely fast photoswitches ( $t_{1/2} \sim \mu\text{s}$  to ns) that tolerate thousands of switching cycles without decomposition.<sup>25,26</sup> Conversely, for applications

requiring long half-lives and high *E-Z* conversion, the arylazoimidazoles are the only 5-membered azoheteroarenes reported to date to show promise,<sup>27–29</sup> with Herges and co-workers demonstrating the ability to photoswitch 1-methyl-5-phenylazoimidazole to a photostationary state (PSS) containing 98% *Z*-isomer, which possesses a thermal half-life of 528 hours.<sup>27</sup> However, the best PSS for the backswitching only contained 55% of the *E*-isomer.

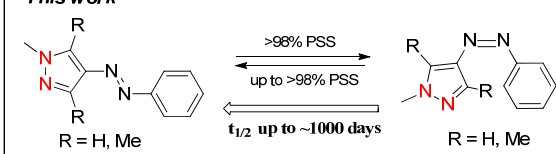
Herein we report a new class of highly promising photoswitchable azoheteroarenes, the arylazopyrazoles (Figure 1),<sup>30</sup> which we have directly compared to the related arylazopyrroles. Our arylazopyrazoles show high thermal stability in solution at room temperature ( $t_{1/2}$  up to 1000 days); comparable to the highest known value for an azobenzene. A large separation of the  $\lambda_{\text{max}}$  of the *E*- and *Z*-isomers allows good to quantitative two-way photoswitching. Furthermore, by virtue of their 5-membered rather than 6-membered aromatic ring, we find that such compounds can access a *Z*-isomer conformation not accessible to azobenzenes; a conformation that can be sterically tuned by substitution on the heterocyclic ring. Such conformational properties significantly affect the intensity of the  $n-\pi^*$  absorbance, and thus it is likely that azoheteroarenes will open new avenues in the area of azo photoswitches, through access to photophysical and photochemical properties not achievable with the ubiquitous azobenzenes.

**Figure 1.** Azoheteroarenes with extended thermal half-lives and good photoswitching.

Previous work (Herges et al)



This work



The properties of some 5-membered azoheteroarenes were studied computationally at the B3LYP/6-31G(d,p) and CAM-B3LYP/6-311G(2df,2p) levels for geometry optimisation and TDDFT spectral predictions respectively (see SI). Altering the electronics and sterics of the rings, by changing the heteroarene and its substituents, was predicted to change the position and intensities of their absorption maxima. Four compounds (Scheme 1), predicted to have interesting optical properties due to differing electronic and steric effects, were prepared for this study.

The *N*-heterocyclic compounds chosen were all *N*-methylated to prevent rapid *Z-E* thermal isomerisation through a tautomerisation-isomerisation mechanism.<sup>29,31</sup> Arylazopyrroles **2** and **5** and

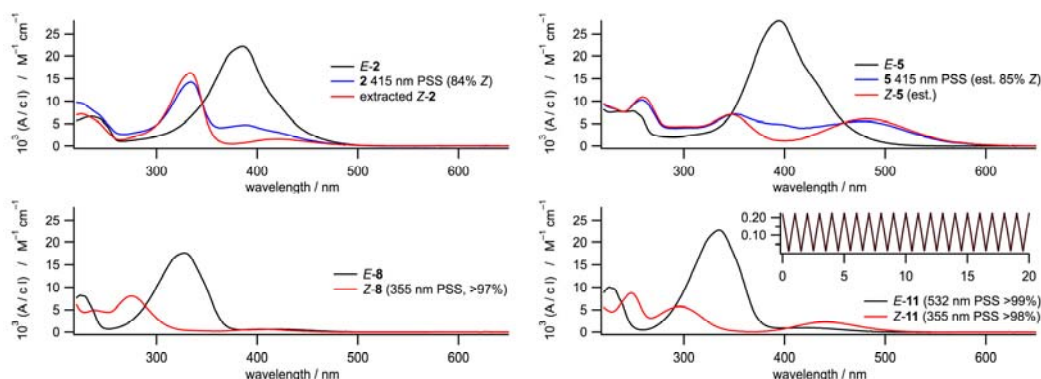
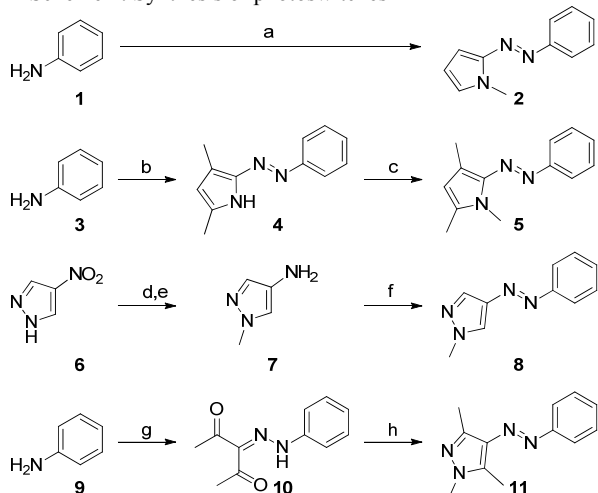


Figure 2: UV/vis spectra of azoheteroarenes in acetonitrile. Inset: repeated photoswitching cycles of azopyrazole **11**. The Z-2 and Z-5 spectra are determined as described in the SI.

the fully substituted arylazopyrazole **11** were prepared using standard diazo coupling methods. Arylazopyrrole **8** was prepared from 4-amino-1-methylpyrrole and nitrosobenzene, *via* a modified Mills reaction (Scheme 1) in a modest unoptimised yield, in line with the highly substrate-dependent literature yields for such a reaction.<sup>32</sup> The scope for this method has previously included various aminopyridines and aminoquinolines,<sup>32,33</sup> however, our study demonstrates it is also suitable for the preparation of azo compounds containing 5-membered heteroarenes, of which few syntheses exist.<sup>25,27,34</sup>

The UV/vis spectra of azoheteroarenes **2**, **5**, **8** and **11** are shown in Figure 2. The pyrroles in **2** and **5** are better  $\pi$ -donors to the electron withdrawing azo function ( $\sigma_p = +0.39$ ),<sup>35</sup> resulting in a red-shifted  $\pi$ - $\pi^*$   $\lambda_{\max}$ . This is consistent with  $\pi$ -deficient azopyridines, having a blue-shifted  $\pi$ - $\pi^*$   $\lambda_{\max}$  compared to azobenzene.<sup>36</sup> The other notable difference in the spectra of the *E*-isomers was that the *E*-pyrazoles (**8** and **11**) showed a weak  $n$ - $\pi^*$  absorbance, well separated from the  $\pi$ - $\pi^*$ , whereas *E*-**2** and *E*-**5** had a slight shoulder on their  $\pi$ - $\pi^*$ , due to a weak  $n$ - $\pi^*$ , poorly separated from the  $\pi$ - $\pi^*$  absorbance. The separation of the  $n$ - $\pi^*$  and  $\pi$ - $\pi^*$   $\lambda_{\max}$  is qualitatively consistent with the TDDFT calculations (see SI).

#### Scheme 1: Synthesis of photoswitches



Reagents and conditions. (a) conc. HCl, aq. NaNO<sub>2</sub>, acetone/H<sub>2</sub>O, 0 °C, then add to Na<sub>2</sub>CO<sub>3</sub>, *N*-methylpyrrole, acetone/H<sub>2</sub>O, 0 °C – rt, 52%; (b) conc. HCl, aq. NaNO<sub>2</sub>, H<sub>2</sub>O, 0 °C; then 2,4-dimethylpyrrole, MeOH/pyridine, 0 °C, 71%; (c) NaH, MeI, THF, 0 – 60 °C, 58%; (d) K<sub>2</sub>CO<sub>3</sub>, MeI, MeCN, rt; (e) Pd/C, H<sub>2</sub>, MeOH, rt, 58% from **6**; (f) nitrosobenzene, 40% aq. NaOH/pyridine, 80 °C, 33%; (g) conc. HCl, aq. NaNO<sub>2</sub>, AcOH, 0 °C; then add to NaOAc, acetylacetone, EtOH/H<sub>2</sub>O, 0 °C – rt, quant.; (h) NH<sub>2</sub>NHMe, EtOH, reflux, quant.

Exciting the  $\pi$ - $\pi^*$  transition of azopyrazoles *E*-**8** and *E*-**11** at 355 nm using monochromatic light achieved complete photoswitching (>98% *Z*-isomer in both cases). Near-quantitative switching was also achieved with broadband 330-400 nm light (see SI). To our knowledge, the only azo compound for which ~100% *E*-*Z* photoswitching has been achieved is the ethylene-bridged azobenzene reported by Temps and co-workers.<sup>15</sup> *Z*-**11** has a stronger  $n$ - $\pi^*$  absorbance than *E*-**11**, while the  $n$ - $\pi^*$  absorbance of *Z*-**8** was similar to that of *E*-**8** (Table 1). Irradiating the tail of the  $n$ - $\pi^*$  absorbance of azopyrazole *Z*-**11** at 532 nm switched it back to >98% *E*-isomer. Thus **11** can be quantitatively switched in both directions, a result which surpasses the state-of-the-art ethylene-bridged azobenzene,<sup>15</sup> and the 2,2',6,6'-tetrafluoroazobenzene reported by Hecht and co-workers.<sup>16</sup>

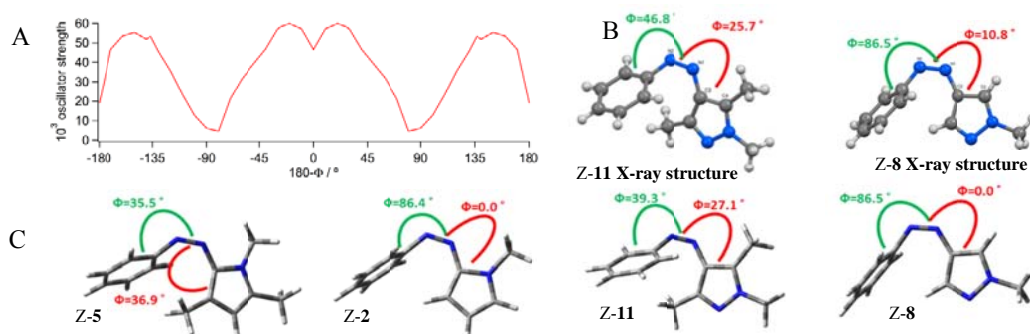
In contrast, varying the substitution pattern or heterocycle resulted in less complete photoswitching, demonstrating the value in surveying a range of heteroaromatic scaffolds. Azopyrazole *Z*-**8** only reached a PSS containing (70 ± 3)% *E*-isomer after excitation with 532 nm irradiation, due to overlap of the *Z*- and *E*-isomer  $n$ - $\pi^*$  absorbances. Irradiation of azopyrroles *E*-**2** and *E*-**5** with 415 nm light led to PSSs containing (84 ± 2)% and (85 ± 3)% *Z*-isomer respectively (Figure 2). Similar to the azopyrazoles, azopyrrole *Z*-**5** had a relatively intense  $n$ - $\pi^*$  absorbance compared to *Z*-**2** and *E*-**5** (Table 1). Excitation of the  $n$ - $\pi^*$  transition of azopyrrole *Z*-**5** using 532 nm irradiation led to quantitative (>98%) photoswitching to the *E*-isomer. Prolonged irradiation of the tail of the  $n$ - $\pi^*$  absorbance of *Z*-**2** at 532 nm led to a PSS containing (82 ± 3)% *E*-isomer. Quantum yields were determined where possible (Table 1 and SI). All compounds were photoswitched 20 times in each direction and no significant degradation was observed, demonstrating high fatigue resistance (see SI).

For the arylazoimidazoles, Herges and co-workers have reported that both isomers have a weak  $n$ - $\pi^*$  absorbance and are calculated to adopt a conformation in which the heteroarene and azo function are co-planar.<sup>27</sup> In our calculations, all *E*-isomers are predicted to be planar. For azopyrazole *Z*-**8** and azopyrrole *Z*-**2** (without two “*ortho*” methyl groups on the heterocycle) a conformation with the phenyl ring approximately orthogonal to the planar heteroarene-azo functionality is calculated, while the two methyl groups in azopyrazole *Z*-**11** and azopyrrole *Z*-**5** are predicted to force these species into a twisted conformation. TDDFT predicts low intensity  $n$ - $\pi^*$  absorbances for all *E*-isomers and for *Z*-**2** and *Z*-**8** (with the heteroarene and azo group coplanar – oscillator strengths of 0.0023 and 0.0026 respectively), as is seen in the experimental spectra. Conversely, the twisted azopyrazole *Z*-**11** and azopyrrole *Z*-**5** are calculated and observed to have large  $n$ - $\pi^*$  absorbances.

**Table 1: Spectral and kinetic data for compounds**

	<i>E</i> -isomer $\pi$ - $\pi^*$		<i>E</i> -isomer $n$ - $\pi^*$		<i>Z</i> -isomer $\pi$ - $\pi^*$		<i>Z</i> -isomer $n$ - $\pi^*$		half-life	$\Phi_{E-Z}^{\pi-\pi^*}$	$\Phi_{Z-E}^{n-\pi^*}$
	$\lambda_{\max}$ / nm	$10^{-2} \epsilon$ / $M^{-1} \text{cm}^{-1}$	$\lambda_{\max}$ / nm	$10^{-2} \epsilon$ / $M^{-1} \text{cm}^{-1}$	$\lambda_{\max}$ / nm	$10^{-2} \epsilon$ / $M^{-1} \text{cm}^{-1}$	$\lambda_{\max}$ / nm	$10^{-2} \epsilon$ / $M^{-1} \text{cm}^{-1}$			
<b>2</b>	385	221±18	~413 <sup>a</sup>	- <sup>a</sup>	333	157±13	423	17.9±1.4	2.95±0.05 h	0.50±0.07 <sup>d</sup>	0.41±0.05 <sup>e</sup>
<b>5</b>	394	282±23	~430 <sup>a</sup>	- <sup>a</sup>	346	70.4±5.7 <sup>b</sup>	479	60.8±4.9 <sup>b</sup>	21.2±0.5 s <sup>c</sup>	<sup>f</sup>	0.41±0.05 <sup>e</sup>
<b>8</b>	328	176±14	417	6.44±0.51	275	80.6±6.4	403	6.66±0.53	~1000 d	0.61±0.06 <sup>g</sup>	0.60±0.06 <sup>d</sup>
<b>11</b>	335	227±18	425	9.63±0.76	296	57.7±4.6	441	23.0±1.8	10±0.03 d	0.46±0.04 <sup>g</sup>	0.56±0.04 <sup>e</sup>

<sup>a</sup>  $n$ - $\pi^*$  absorbance appears as a shoulder on the  $\pi$ - $\pi^*$  absorbance, hence  $\epsilon$  cannot be obtained. <sup>b</sup> these values are for the estimated pure *Z*-isomer (see SI). <sup>c</sup> rate was very sensitive to water present in the sample (see SI). <sup>d</sup> excited at 415 nm; <sup>e</sup> excited at 532 nm; <sup>f</sup> not determined due to competing thermal reaction; <sup>g</sup> excited at 355 nm.



**Figure 3:** A) the effect of dihedral angle on  $n$ - $\pi^*$  intensity for *Z*-11; B) Crystal structures for *Z*-11 and *Z*-8; C) Calculated conformations for *Z*-isomers (B3LYP/6-31G(d,p)), with dihedral angles annotated. All values, except  $\Phi_{\text{NNhet}}$  for *Z*-5, are given as  $180-\Phi$ .

A similar trend is observed for the  $n$ - $\pi^*$  absorbance in planar *E*-azobenzene and non-planar *Z*-azobenzene, whereby the former has a very low intensity absorbance and the latter has a large absorbance.<sup>9</sup> If both arenes are coplanar with, or orthogonal to, the azo group (provided the arene is symmetrically substituted), a mirror plane exists through the plane of the azo function and the  $n$ - $\pi^*$  transition becomes symmetry-forbidden at the equilibrium geometry. Vibrational and rotational motion results in the molecule existing in conformations with a weakly-allowed  $n$ - $\pi^*$  transition, thus resulting in a small absorbance. Therefore the spectroscopic findings suggest azopyrazole *Z*-8 and azopyrrole *Z*-2 exist in planar (or near planar) conformations, and the more sterically congested bis(*o*-methylated) azopyrazole *Z*-11 and azopyrrole *Z*-5 adopt twisted conformations. It should be noted that the 6-membered arenes of *Z*-azobenzenes *always* adopt a twisted conformation.<sup>9</sup> Therefore, these 5-membered heteroarenes allow steric tuning of the spectral properties not available to standard azobenzenes. In support of this argument, TDDFT calculations were performed (on constrained-optimised structures of azopyrazole *Z*-11 for illustration) to predict the effect of the dihedral angle between the heteroarene and azo groups on the  $n$ - $\pi^*$  intensity. The results demonstrate that the intensity of the  $n$ - $\pi^*$  transition is minimal at planar ( $\Phi=0, \pm 180^\circ$ ) and orthogonal geometries ( $\Phi=\pm 90^\circ$ ) (Figure 3A).

To explore this further, crystal structures were obtained for pyrazoles *Z*-11 and *Z*-8. The  $\Phi_{\text{NNhet}}$  dihedral angle of  $25.7^\circ$  for *Z*-11 observed in the solid state structure matched well with the calculated value of  $27.1^\circ$  (Figure 3). Although the *Z*-8 crystal structure was found to have a  $\Phi_{\text{NNhet}}$  dihedral angle of  $10.8^\circ$  (cf. the calculated value of  $0.0^\circ$ ), this was still considerably smaller than the value of  $25.7^\circ$  for *Z*-11, as predicted. The difference between the calculated and X-ray structure dihedral angles is consistent with the work by Jacquemin and co-workers on *E*-azobenzene, which is believed to adopt a planar structure in solution and a twisted one in the solid state,<sup>37</sup> due to packing effects.

Thermal isomerisation kinetics were obtained for all compounds, using UV/vis (for **5**) or <sup>1</sup>H-NMR (for the slower azopyrazoles and azopyrrole **2**) spectroscopy (Table 1), and all showed first order isomerization. The presence of two “*ortho*” methyls on the heteroarene accelerates the isomerisation. This is presumably due to reduced steric interactions between the “*ortho*” methyl substituents and the azo nitrogens in the transition state of such compounds, compared to the ground state *Z*-isomer. There is some debate as to the mechanism by which thermal isomerisation of azoarenes occurs.<sup>38–40</sup> However both the inversion and the rotation transition states would relieve the steric strain in the bis(*o*-methylated) molecules, by increasing the distance between the methyl substituents and the azo nitrogens, lowering the barrier for thermal isomerisation compared to the molecules lacking the bis(*o*-methyls) (see SI for scheme). Comparatively, this has been studied for a range of methylated azobenzenes.<sup>41</sup>

Overall, the azopyrazoles had much slower thermal rates than the azopyrroles. An Eyring plot of the kinetics of thermal isomerisation of azopyrazole *Z*-8 in DMSO between 80 and 120 °C gave activation parameters for this process ( $\Delta H^\ddagger = (+115 \pm 1) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = (-13 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}$ ) that are very similar to those obtained by Hecht and co-workers for 2,2',6,6'-tetrafluoroazobenzene ( $\Delta H^\ddagger = (+109 \pm 3) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = (-29 \pm 9) \text{ J K}^{-1} \text{ mol}^{-1}$ ); the slowest isomerising azobenzene known to date.<sup>16</sup> Using these parameters, we estimate a half-life of ~1000 days at 298 K. This compares highly favourably to those observed for diarylethenes, and suggests that azoheteroarenes, may hold potential in applications focused on optical data storage.<sup>7</sup> The rate at 70 °C in acetonitrile was about 20% slower than that in DMSO, suggesting that the extrapolated value at 25 °C from the Eyring plot for DMSO is an underestimate of the half-life in acetonitrile. Substituted azopyrazole **11** was found to have a half-life of 10 days at 25 °C in acetonitrile. Conversely, azopyrrole **5** had a very fast thermal rate in acetonitrile, ~10<sup>3</sup> faster than that for 4-dimethylaminoazobenzene in a similar polar aprotic solvent.<sup>42</sup> By substituting the phenyl ring

of **5** with a *para*-electron withdrawing group, push-pull azopyrrole systems can be generated with rapid thermal isomerisation rates. Many such compounds have been reported, the fastest rate being for a pyrrolyl azobenzothiazole compound, with a thermal half-life of 70  $\mu$ s in ethanol.<sup>25</sup>

In conclusion, we have demonstrated that the underexploited 5-membered azoheteroarenes, hold significant potential in comparison to their more common azobenzene counterparts. Specifically, we have found that azopyrazoles are readily accessible synthetically, and provide highly exciting properties for further study. For example, azopyrazole **11** can be quantitatively photoswitched in both directions; to the best of our knowledge, this ability is superior to all the other azobenzenes reported to date.<sup>13,16</sup> Furthermore, azopyrazole **8** has a very long thermal half-life (~1000 days), which is comparable to some of the slowest azo photoswitches published to date, and positions this compound class excellently with respect to photochromic compounds used in optical storage devices.<sup>16,43</sup>

More generally, we report that the *Z*-isomers of such 5-membered azoheteroarenes can access a conformation with a coplanar heteroarene-azo function approximately orthogonal to the phenyl group. This conformation results in a dramatic reduction of the  $n\text{-}\pi^*$  absorbance intensity, on symmetry grounds. The *Z*-isomer of a corresponding azobenzene photoswitch cannot access such a conformation due to the increased ring size (6-membered rather than 5-membered). This conformation effect for 5-membered azoheteroarenes is readily tuned, using steric interactions alone, by a judicious choice of the substituents on the heteroaromatic ring. We believe, therefore, that the azoheteroarene photoswitches will provide unique opportunities in terms of the applications of these molecules, through access to photophysical and photochemical properties not achievable in the more commonly used parental azobenzenes.

## ASSOCIATED CONTENT

### Supporting Information

Synthetic methods, NMR and crystallographic data, photochemical methods including additional spectra and kinetics, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

We thank the Engineering and Physical Sciences Research Council for support. RR thanks the Leverhulme Trust (Grant No. RPG-2012-441) for funding. We would also like to thank Dr Marina Kuimova for equipment access.

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