

Supporting Information

Photochromic heteroarylethenes with fast thermal isomerization kinetics

Jaume Garcia-Amorós,^{a,b} M. Cidália R. Castro,^c M. Manuela M. Raposo^{c,*} and Dolores Velasco^{a,b,*}

^a *Departament de Química Inorgànica i Orgànica (Secció de Química Orgànica), Universitat de Barcelona, Martí i Franqués 1, E-08028 Barcelona, Spain*

^b *Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona*

^c *Centro de Química, Universidade do Minho, Campus de Gualtar, R. da Universidade, 4710-057 Braga, Portugal*

1.- Synthesis of the heteroarylethenes	S2
2.- ¹ H and ¹³ C NMR spectra of compounds 1-6	S3
3.- Monitorization of the <i>E</i> -to- <i>Z</i> photoisomerization of 1 by NMR spectroscopy	S9
4.- Detection of the possible by-products of the isomerization of 1 and 6 by MS	S10
5.- References	S11

1.- Synthesis of the heteroarylethenes

Heteroarylethenes **2-6** functionalized with the benzothiazolium EWG were previously synthesized by us.^[1] On the other hand, 1,4-dimethylquinolin-1-ium iodide (**8**)^[2] and ethene **1**,^[3] in the form of triflate salt, were reported earlier by others.

1,4-Dimethylquinolin-1-ium iodide (8).^[2] Methyl iodide (0.852 g, 6.0 mmol) was added to a solution of 4-methylquinoline (0.143 g, 1.0 mmol) in acetonitrile (10 mL). The solution was stirred at reflux for 6 hours. The precipitate was filtered and washed with acetonitrile (10 mL). Compound **8** was obtained as a white solid in a quantitative yield. ¹H NMR (DMSO-*d*₆) δ 2.99 (s, 3H, NCH₃); 4.56 (s, 3H, N⁺CH₃), 8.03-8.08 (m, 2H, 3 and 6-H), 8.26 (dt, 1H, *J* = 8.4 and 0.8 Hz, 7-H), 8.47 (broad d, 1H, *J* = 8.8 Hz, 5-H), 8.52 (dd, 1H, *J* = 8.4 and 0.8 Hz, 8-H), 9.32 (d, 1H, *J* = 6.0 Hz, 2-H) ppm.

(E)-1-Methyl-4-(2-(1-methyl-1H-pyrrol-2-yl)vinyl)quinolin-1-ium iodide (1).^[3] A solution of **7** (0.109 g, 1 mmol), **8** (0.285 g, 1 mmol) and piperidine (1 drop) in ethanol (10 mL) was heated at reflux for 10 hours. After this time, the solid that precipitated from the reaction mixture was filtered and washed with cold ethanol to give the pure heterocyclic ethene **1** as a dark orange solid in a yield of 71%. M.p. 253-254 °C. ¹H NMR (DMSO-*d*₆) δ 3.88 (s, 3H, NCH₃); 4.45 (s, 3H, N⁺CH₃); 6.29-6.31 (m, 1H, 4'-H), 7.19-7.20 (m, 1H, 3'-H), 7.36 (dd, 1H, *J* = 4.4 and 1.6 Hz, 5'-H) 7.91 (d, 1H, *J* = 15.6 Hz, C=CH_β), 7.97 (dt, 1H, *J* = 8.4 and 0.8 Hz, 6-H), 8.15 (d, 1H, *J* = 15.6 Hz, C=CH_α), 8.21 (dt, 1H, *J* = 8.4 and 0.8 Hz, 7-H), 8.34 (d, 1H, *J* = 8.4 Hz, 5-H), 8.47 (d, 1H, *J* = 6.8 Hz, 3-H), 8.95 (d, 1H, *J* = 8.4 Hz, 8-H), 9.11 (d, 1H, *J* = 6.8 Hz, 2-H) ppm. ¹³C NMR (DMSO-*d*₆) δ 34.0, 44.0, 110.5, 113.4, 114.0, 114.5, 119.1, 125.6, 126.2, 128.6, 130.0, 131.4, 131.7, 134.6, 138.8, 146.7, 152.9 ppm. HMRS: *m/z* (ESI) for C₁₇H₇N₂; calcd: 249.13917; found: 249.13930.

2.- ^1H and ^{13}C NMR spectra of compounds 1-6

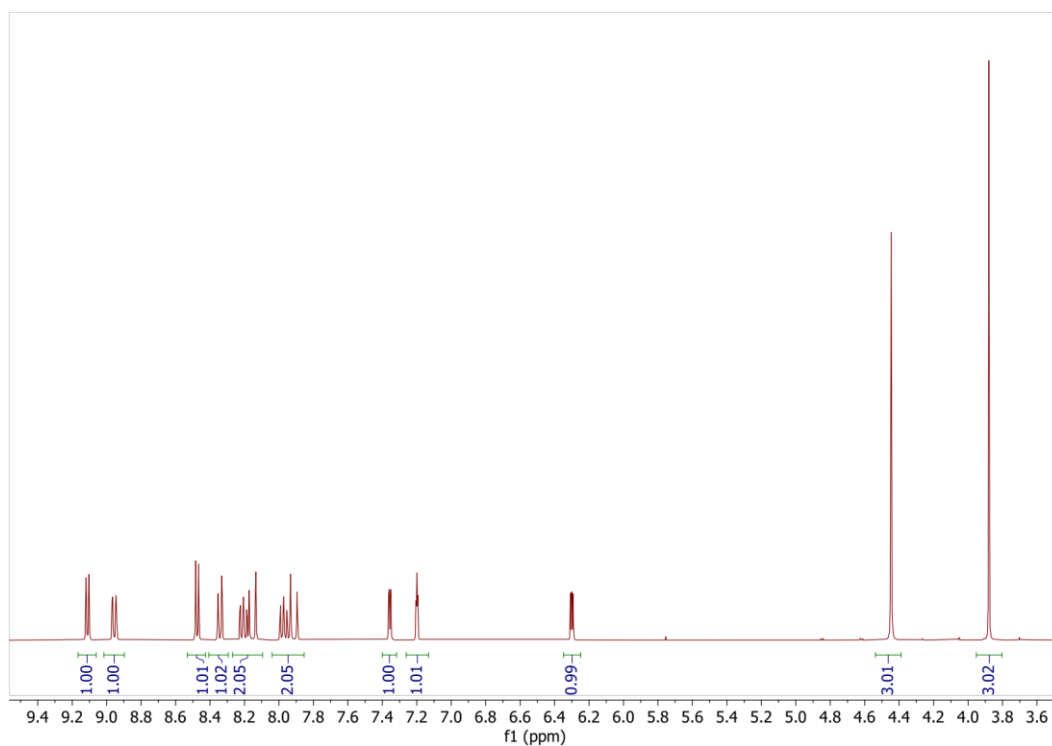


Fig. S1. ^1H NMR spectrum of 1 in $\text{DMSO-}d_6$.

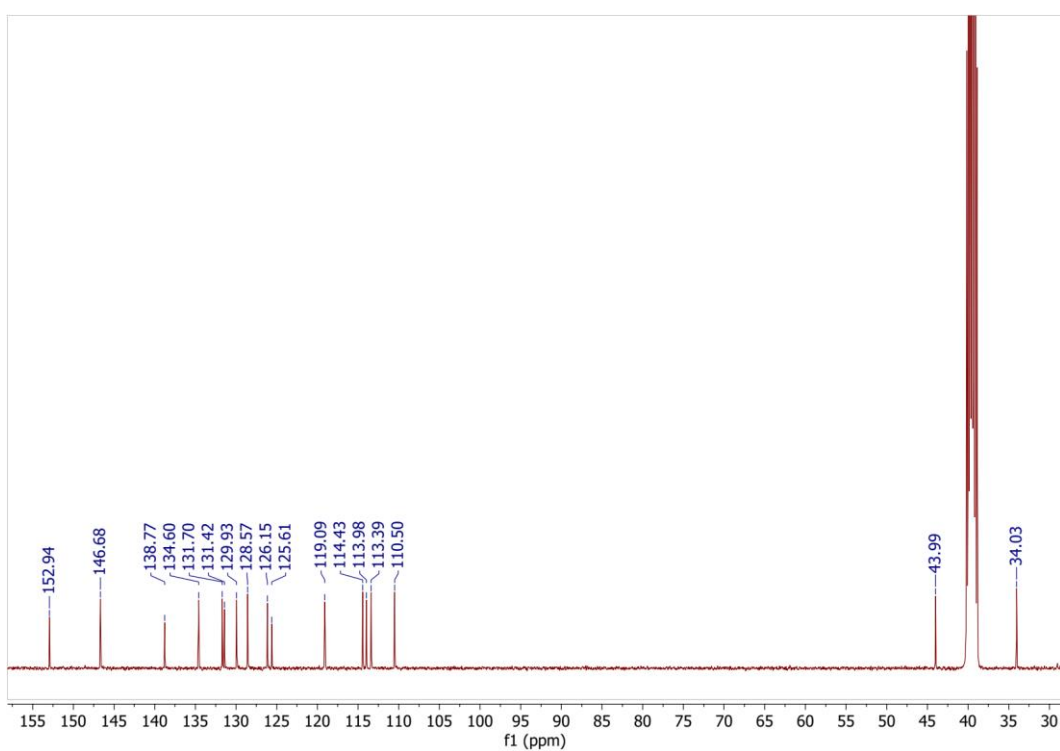


Fig. S2. ^{13}C NMR spectrum of 1 in $\text{DMSO-}d_6$.

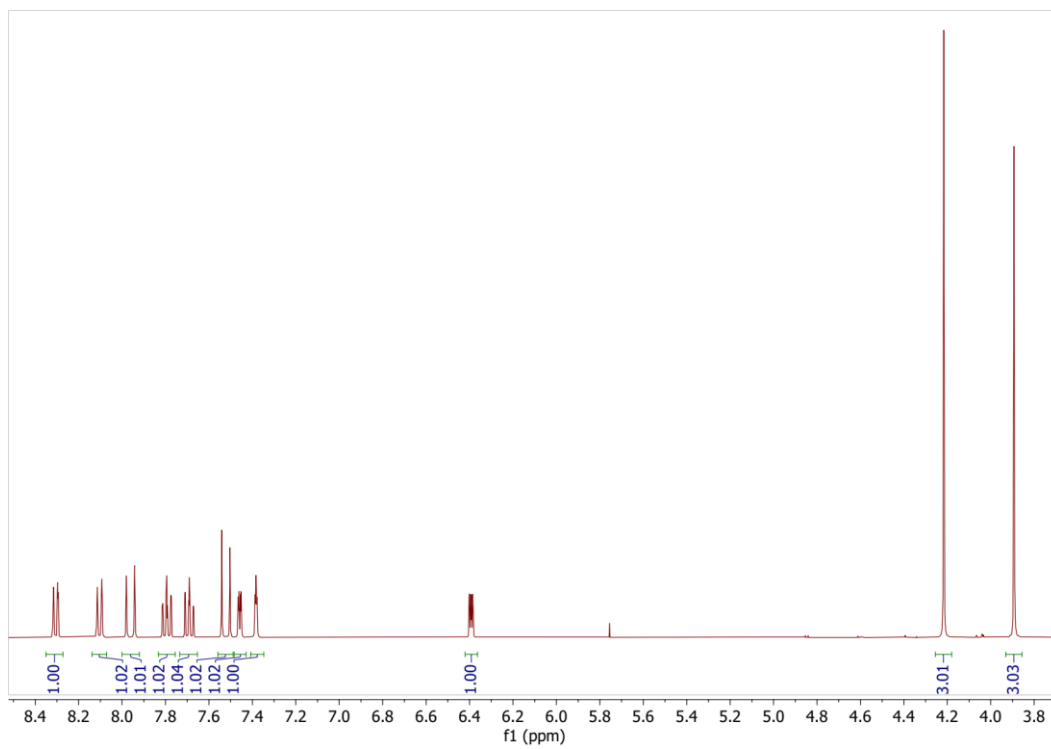


Fig. S3. ^1H NMR spectrum of **2** in $\text{DMSO-}d_6$.

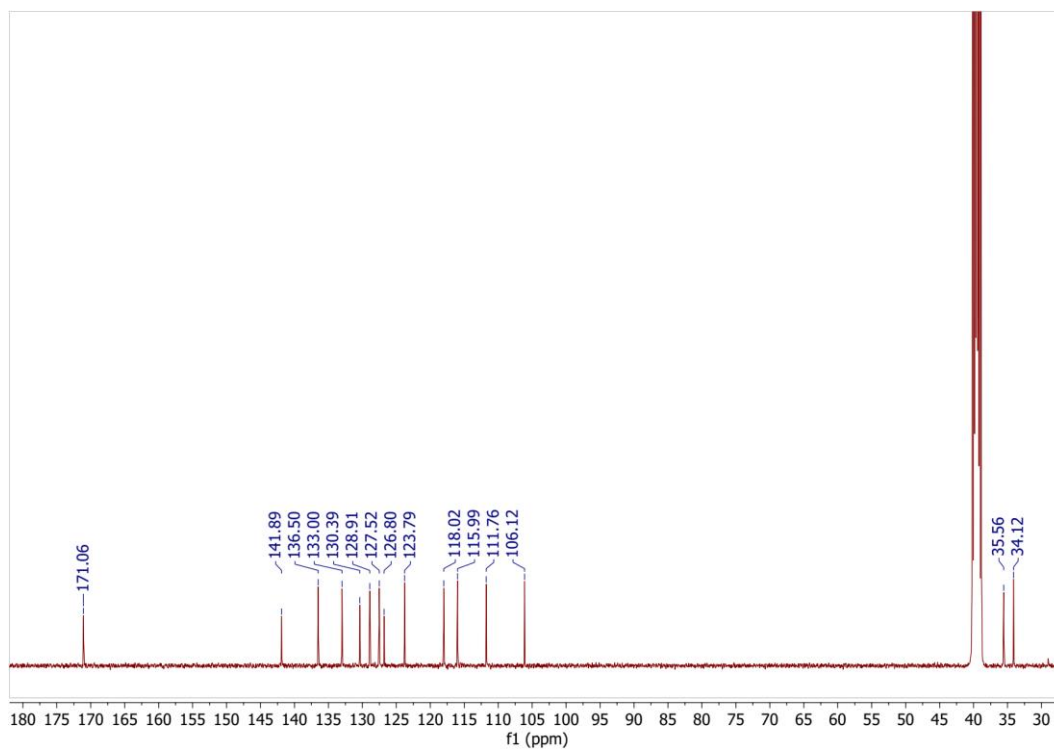


Fig. S4. ^{13}C NMR spectrum of **2** in $\text{DMSO-}d_6$.

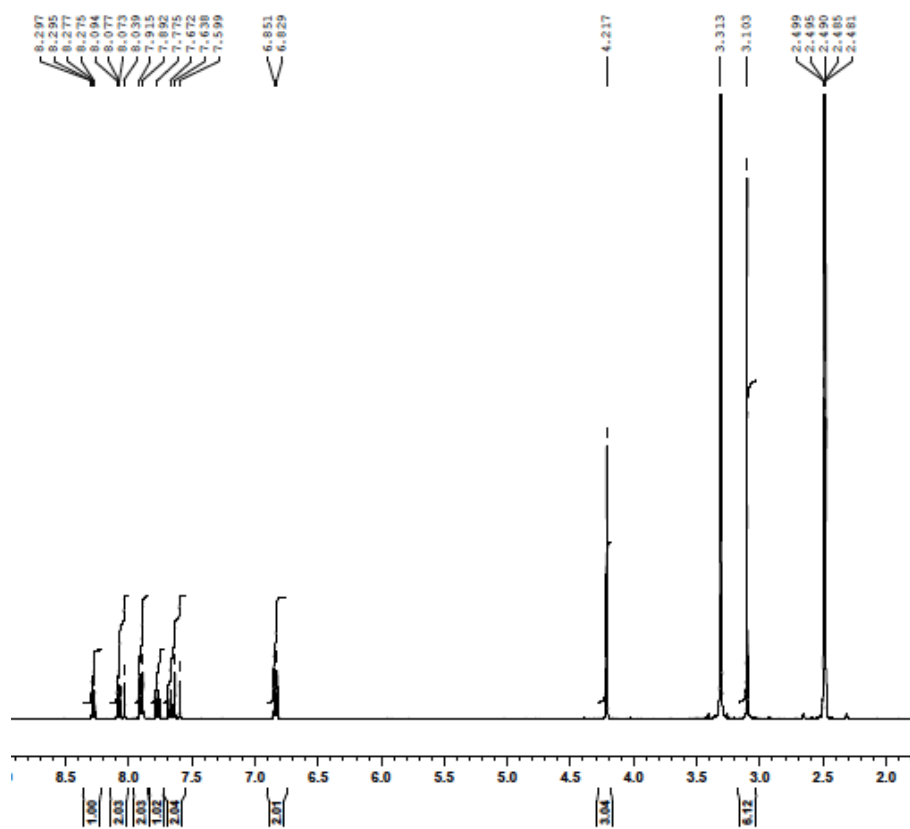


Fig. S5. ^1H NMR spectrum of **3** in $\text{DMSO-}d_6$.

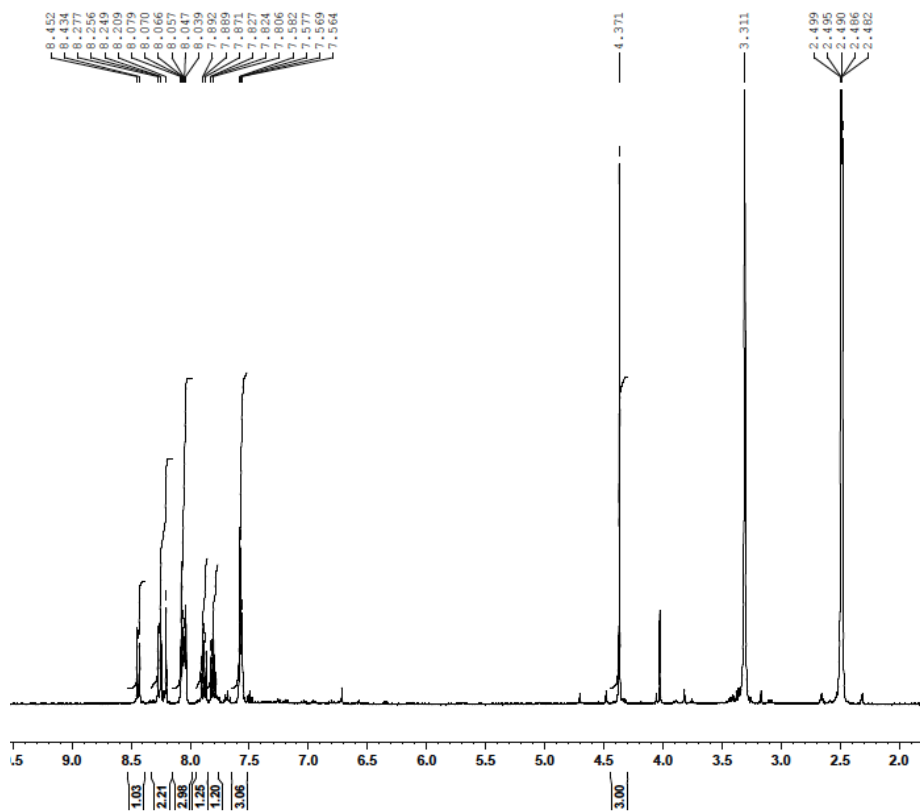


Fig. S6. ^1H NMR spectrum of **4** in $\text{DMSO-}d_6$.

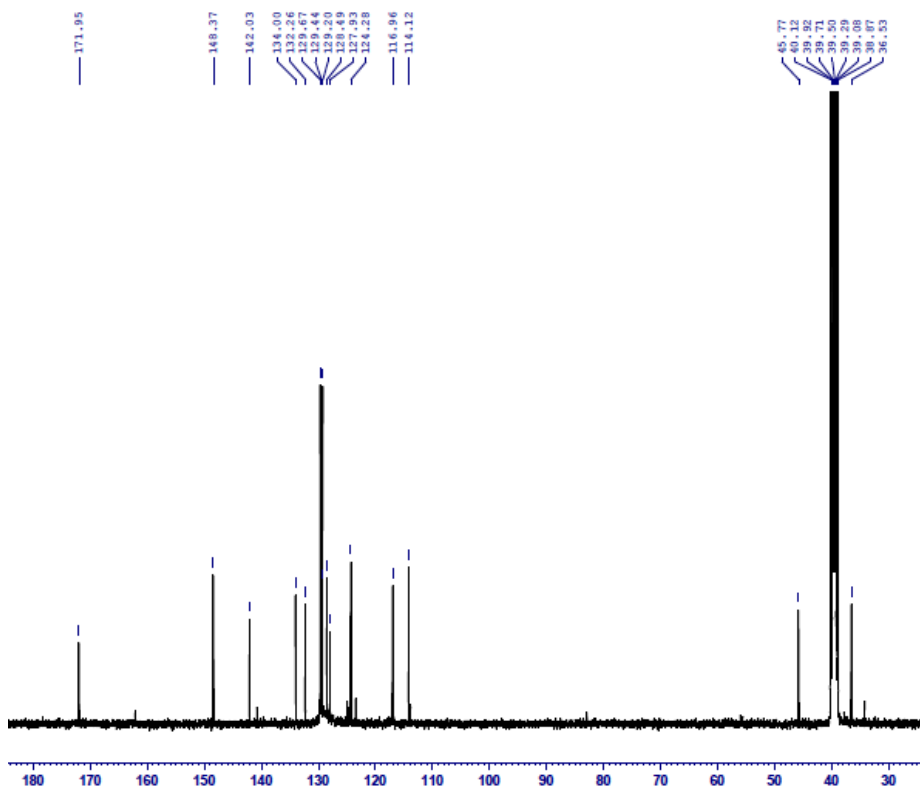


Fig. S7. ^{13}C NMR spectrum of **4** in $\text{DMSO-}d_6$.

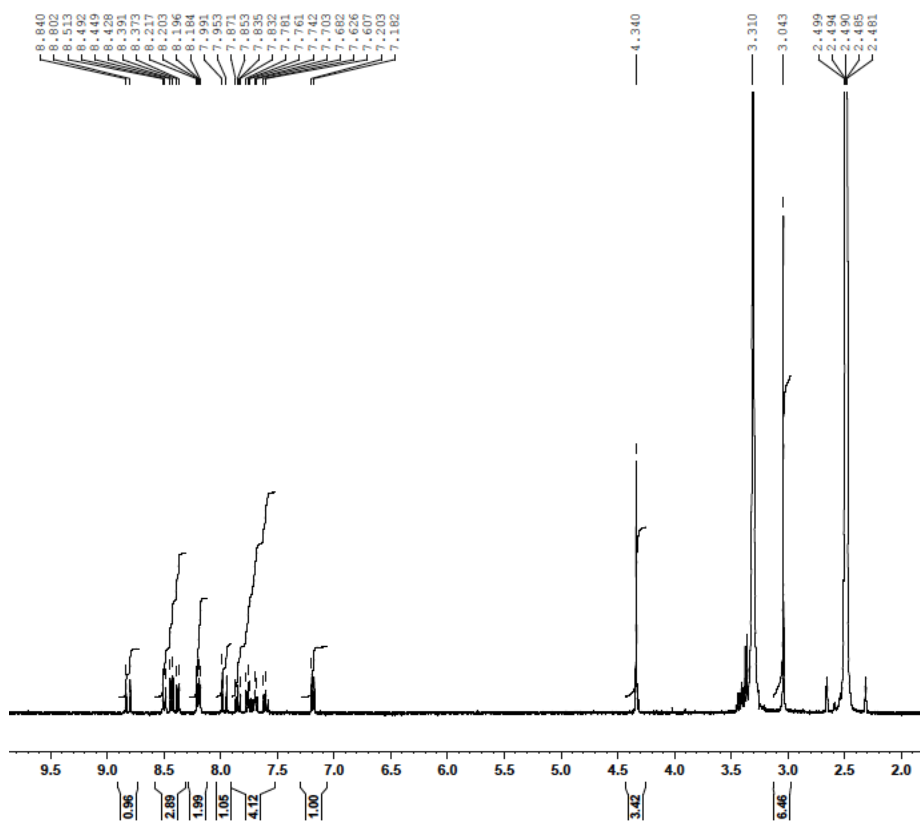


Fig. S8. ^1H NMR spectrum of **5** in $\text{DMSO-}d_6$.

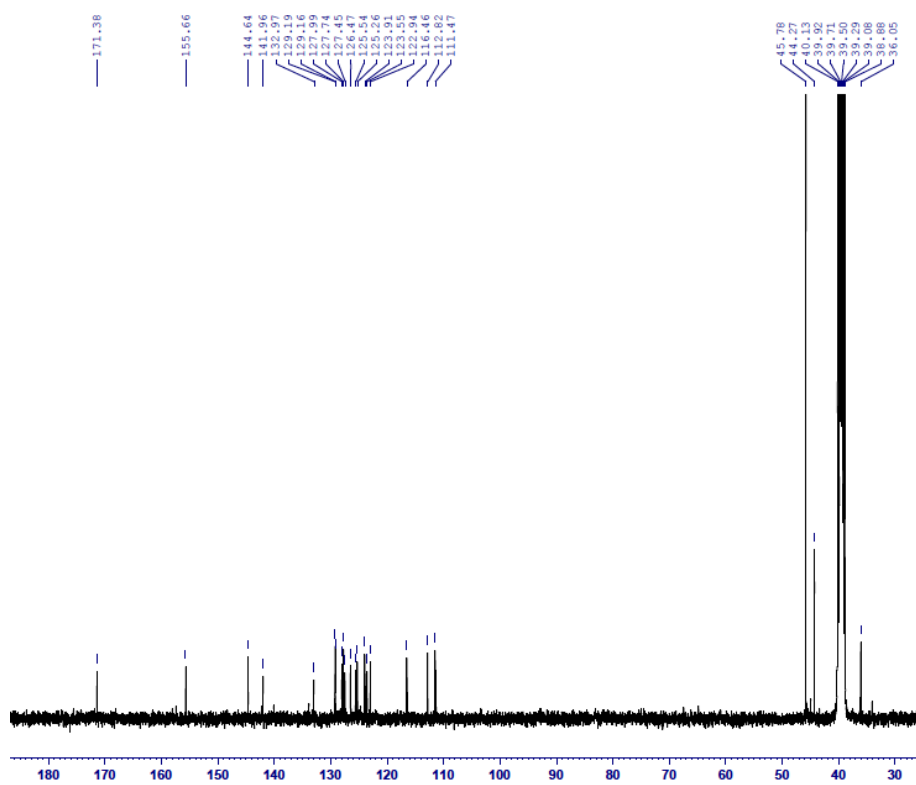


Fig. S9. ^{13}C NMR spectrum of **5** in $\text{DMSO-}d_6$.

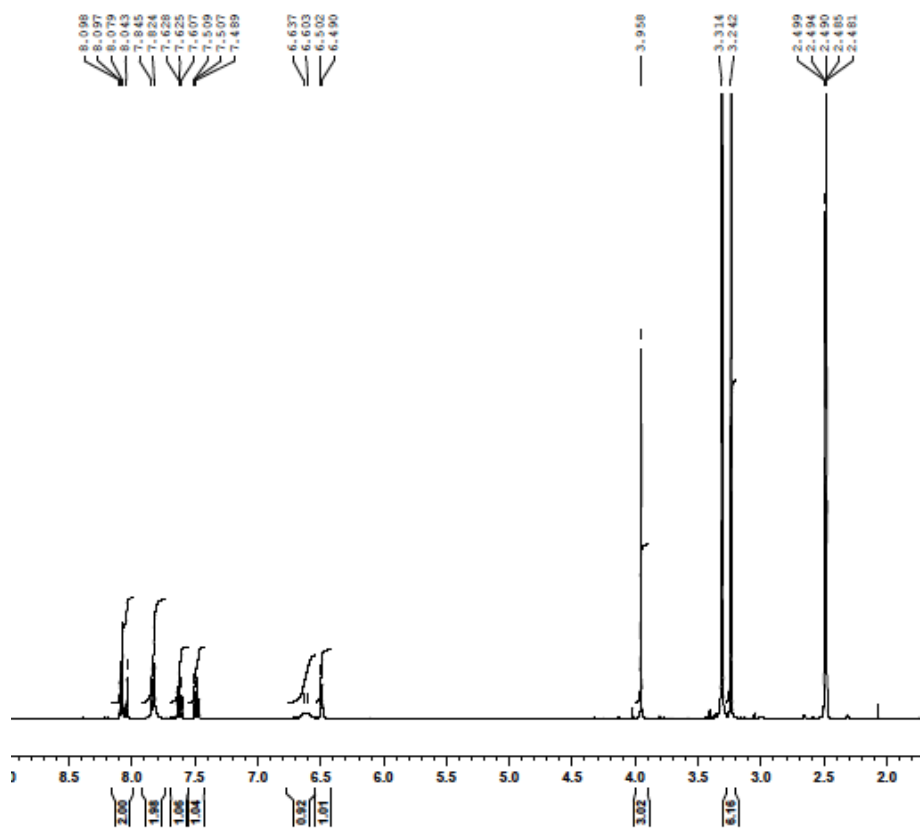


Fig. S10. ^1H NMR spectrum of **6** in $\text{DMSO-}d_6$.

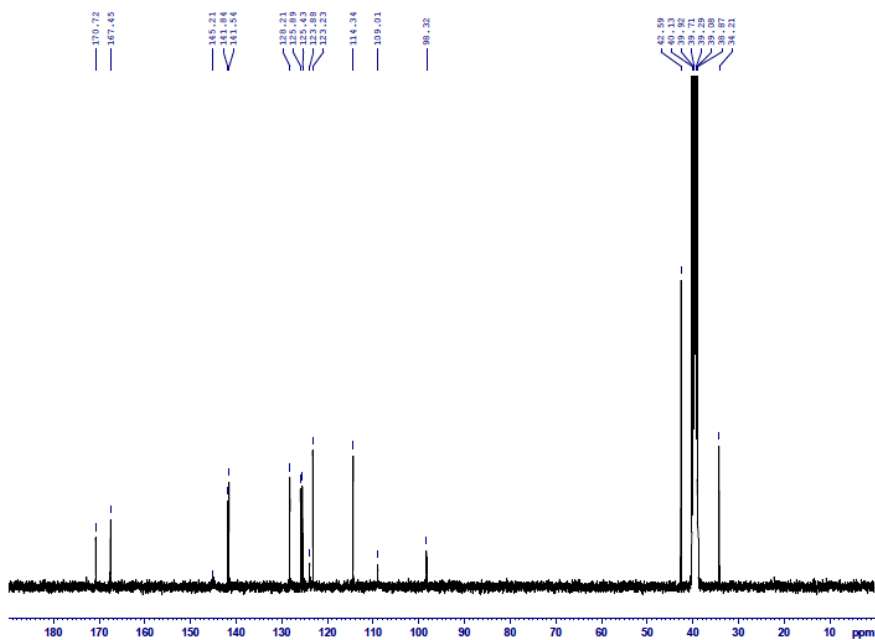


Fig. S11. ^{13}C NMR spectrum of **6** in $\text{DMSO-}d_6$.

3.- Monitorization of the *E*-to-*Z* photoisomerization of **1** by NMR spectroscopy.

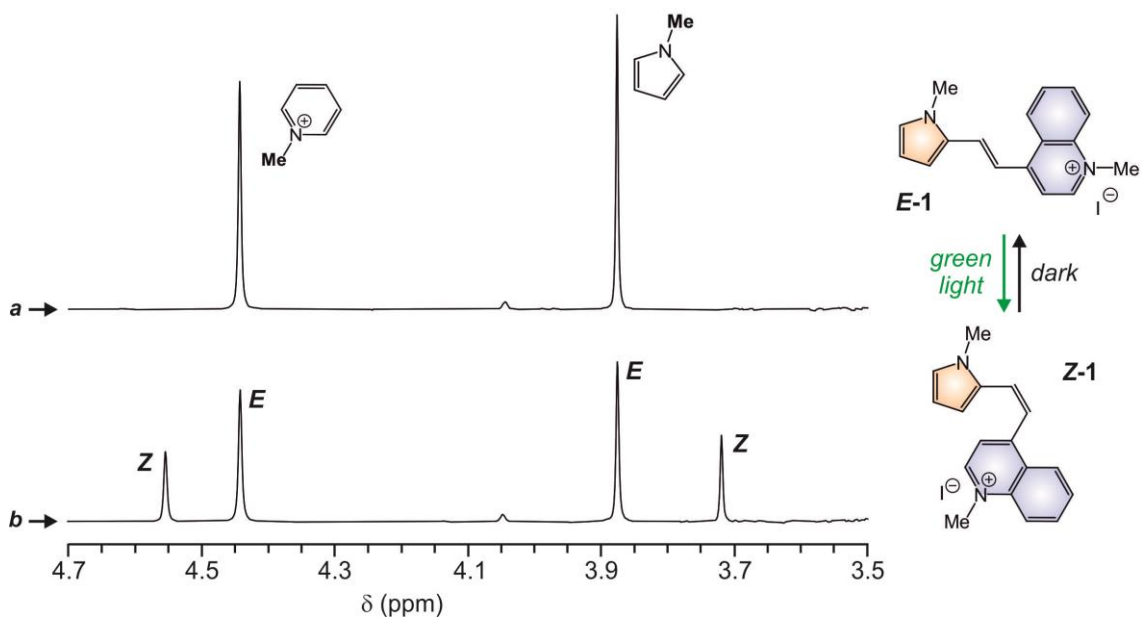


Fig. S12. Aliphatic region of the ¹H NMR spectrum of **1**, recorded in DMSO-*d*₆, before (a) and after (b) irradiation with continuous green light ($\lambda_{\text{Ex}} = 520$ nm, Thorlabs collimated laser diode module, 4.5 mW) for 1 hour.

4.- Detection of the possible by-products of the isomerization of **1** and **6** by MS.

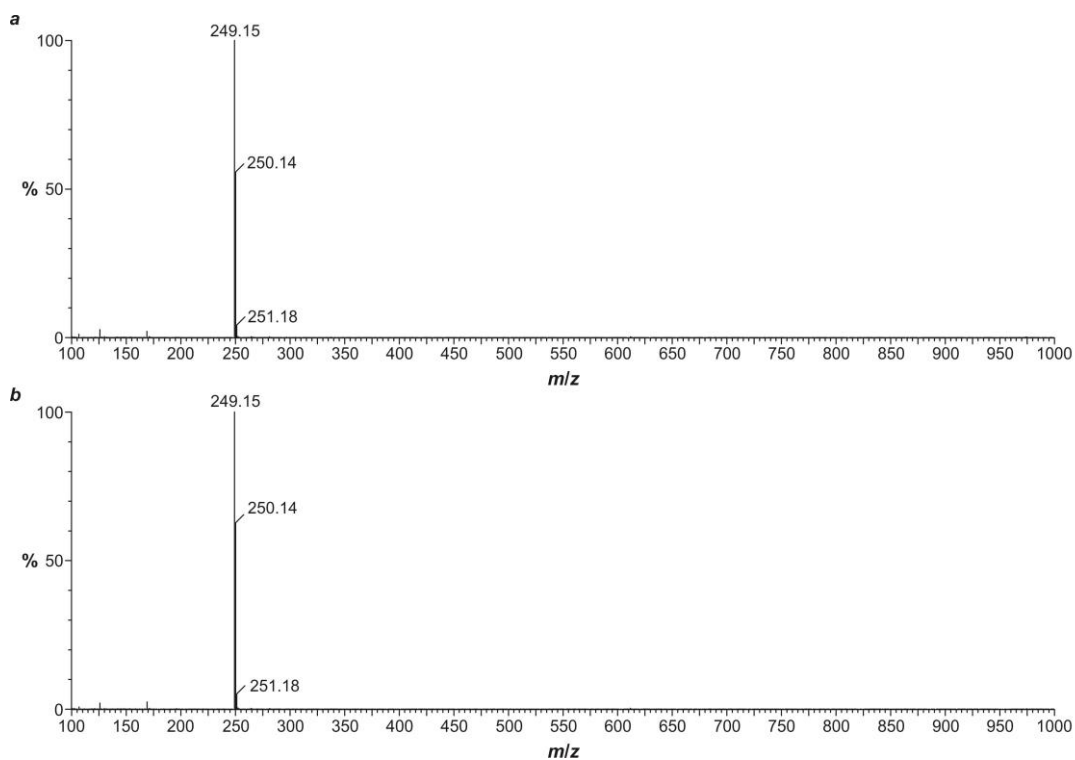


Fig. S13. Mass spectrum corresponding to the HPLC peaks detected at a retention time of 6.00 (*a*) and 6.40 min (*b*) for a photostationary solution of **1** in DMSO.

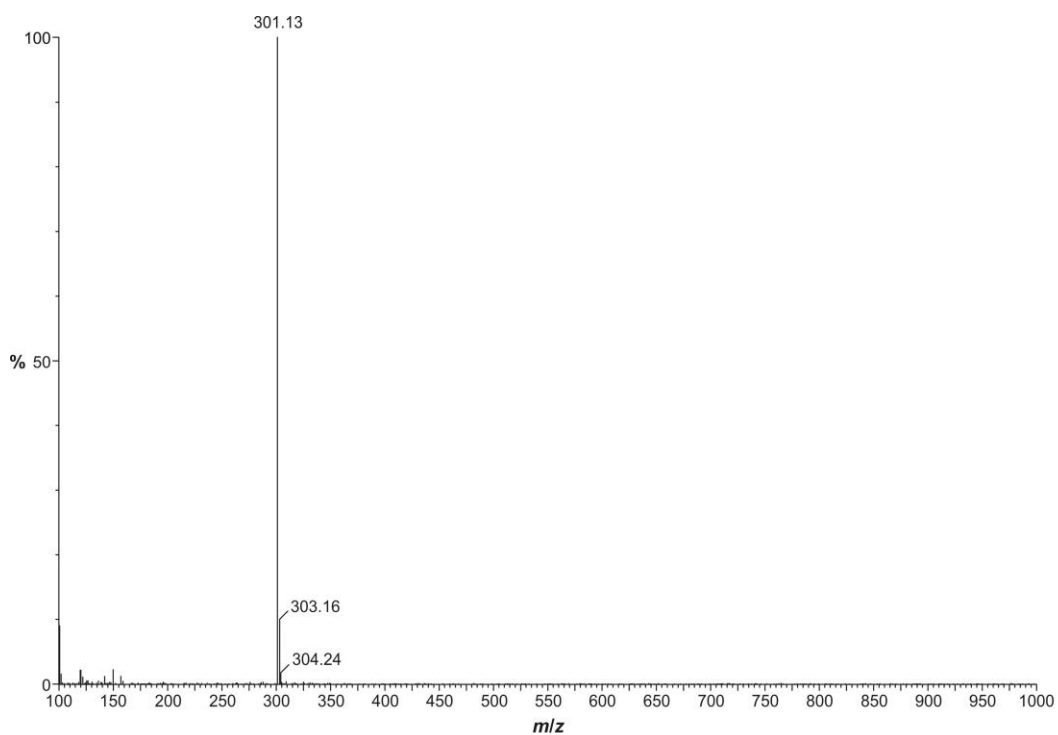


Fig. S14. Mass spectrum corresponding to the HPLC peak detected at a retention time of 7.49 min for a solution of **6** in DMSO.

5.- References

- [1] P. J. Coelho, M. C. R. Castro, M. M. M. Raposo, *Dyes Pigm.* **2015**, *117*, 163–169.
- [2] https://pubchem.ncbi.nlm.nih.gov/compound/1_4-Dimethylquinolinium-iodide.
- [3] A. Abboto, L. Beverina, R. Bozio, R. Facchetti, C. Ferrante, G. A. Pagani, D. Pedron, R. Signorini, *Org. Lett.* **2002**, *4*, 1495–1498.