Supplementary Information

Table of Contents

1.	¹ H-NMR and ¹³ C-NMR Spectra of new compounds	S1
2.	X-ray Crystallography Information	S24

3. ¹H-NMR Experiments of 2*H*-Azirine 15a S24

1. NMR Spectra of New Compounds



Figure S2. ¹³C-NMR spectrum of compound 4.



Figure S4. ¹³C-NMR spectrum of compound 5.



Figure S6. ¹³C-NMR spectrum of compound 6a.







Figure S10. ¹³C-NMR spectrum of compound 6c.



Figure S12. ¹³C-NMR spectrum of compound 6d.



Figure S13. ¹H-NMR spectrum of compound 6e.



Figure S14. ¹³C-NMR spectrum of compound 6e.



Figure S16. ¹³C-NMR spectrum of compound 7a.



Figure S18. ¹³C-NMR spectrum of compounds 7b and b.



Figure S20. ¹³C-NMR spectrum of compound 7b.



Figure S22. ¹³C-NMR spectrum of compound 7c.



Figure S24. ¹³C-NMR spectrum of compound 7d.



Figure S26. ¹³C-NMR spectrum of compound 7e.



Figure S28. ¹³C-NMR spectrum of compound 7f.



Figure S30. ¹³C-NMR spectrum of compound 7g.



Figure S32. ¹³C-NMR spectrum of compound 7h.



Figure S34. ¹³C-NMR spectrum of compound 15a.



Figure S36. ¹³C-NMR spectrum of compound 15c.



Figure S38. ¹³C-NMR spectrum of compound 15d.



Figure S40. ¹³C-NMR spectrum of compound 15e.



Figure S42. ¹³C-NMR spectrum of compound 15f.



Figure S44. ¹³C-NMR spectrum of compound 15g.



Figure S46. ¹³C-NMR spectrum of compound 15h.

2. X-Ray Crystallography Information

	7c	7h	7e
Empirical formula	$C_{16}H_{12}ClN_7$	C14H10BrN7O	C14H10ClN7S
$M/g \text{ moL}^{-1}$	337.78	372.20	343.80
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$
a/Å	15.7997(3)	9.5864(4)	7.8375(2)
b/Å	7.1683(2)	12.3622(5)	23.7676(5)
c/Å	14.8956(3)	14.8024(7)	8.6855(2)
α/	90	90	90
β/	98.9320(10)	118.544(3)	105.1090(10)
γ/	90	90	90
<i>V</i> / Å ³	1666.57(7)	1540.99(12)	1561.99(6)
Ζ	4	4	4
$D_{ m calc}/{ m Mg}~{ m m}^{-3}$	1.346	1.604	1.462
µ/mm⁻¹	0.242	2.683	0.388
F(000)	696	744	704
Reflections collected	66567	37320	24263
Independent reflections	3836	3533	2745
Restraints/parameters	0/217	0/208	0/227
Goodness of fit on F^2	1.086	1.058	0.971
$R_1 (I > 2\sigma_I)$	0.0489	0.0457	0.0403
wR_2 (all reflections)	0.1192	0.1322	0.1130
Residual densities	0.172/-0.274	0.986/-0.721	0.176/-0.166

Table 1. XRD data collection and refinement details of compounds 7c, 7h and 7e.

3. 1H-NMR Experiments of 2H-Azirine 15a

The ¹H-NMR measurements of compound **15a** were run in DMSO with the original compound which was stored in the refrigerator for 3 months. In this experience the spectra were collected at 25 °C, 35 °C, 45 °C, 55 °C, 75 °C and 95 °C (Figures S48–S53). The ¹H-NMR spectrum of compound **15a** freshly prepared is presented in Figure S47.



Figure S47. ¹H-NMR spectrum of compound 15a in CDCl₃ at 25 °C.



Figure S49. ¹H-NMR spectrum of compound 15a in DMSO at 35 °C.



Figure S51. ¹H-NMR spectrum of compound 15a in DMSO at 55 °C.



Figure S53. ¹H-NMR spectrum of compound 15a in DMSO at 95 °C.