Supporting Information

Iron-catalysed aziridination reactions promoted by an ionic liquid

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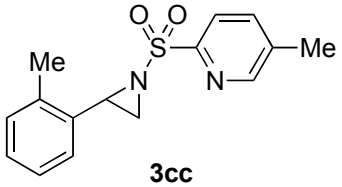
General methods.
All reactions were carried out in oven-dried glassware under an atmosphere of Argon. CH_3CN was distilled over CaH_2 under Argon prior to use. Molecular sieves were activated by heating to 120 °C under vacuum for 5 h. $Fe(OTf)_2$[1] and 5-methyl-2-pyridinesulfonyliminophenyliodinane (**2c**)[2] were prepared according to known procedures. All other commercial reagents were used as obtained.
Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates (Merck). TLC visualisation was carried out with UV light (254 nm) and treatment with 2.5% aqueous $KMnO_4$ or 5% ethanolic phosphomolybdic acid, followed by heating. Flash column chromatography was carried out on silica gel (0.035 – 0.070 mm, Acros). Nuclear magnetic resonance spectroscopy was recorded on a Varian Mercury 300 (300 MHz ^{1}H, 75 MHz ^{13}C) or a Varian Inova 400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376 MHz ^{19}F) instrument. Chemical shifts are reported in ppm with respect to TMS (0 ppm). Multiplicities are denoted as follows: br s (broad singlet), s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), q (quartet), m (multiplet). Coupling constants (*J*) are given in Hz. The abbreviation Ar is used to denote aromatic. Infrared spectra were recorded on a Perkin Elmer PE-1760 FT either as a capillary sample or as a KBr disc. Only characteristic peaks are quoted. Melting points were recorded on a Büchi Melting Point B-540 and are uncorrected. Mass spectrometric data (*m/z*) was acquired on a Varian MAT 212 (electron impact (EI) or chemical ionisation (CI, methane)) or on a Finnigan Mat 95 (high resolution mass spectrometry). Elemental analyses were carried out on a CHN-Rapid by Heraeus in the Microanalytic Laboratory at the Institute of Organic Chemistry at RWTH Aachen University.

General procedure for the aziridination of olefins:

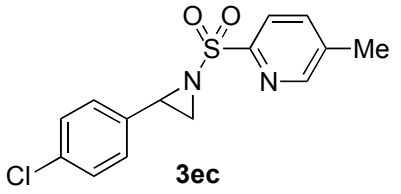
A dry Schlenk tube was charged with activated molecular sieves 4Å (20 mg), evacuated and then filled with Ar. Dry CH_3CN (1 mL), ionic liquid **7** (10 μL, 38 μmol, 8 mol%) and $Fe(OTf)_2$ (8.9 mg, 25 μmol, 5 mol%) were then added, resulting in a yellow suspension. Upon addition of ligand **5** (13.0 mg, 75 μmol, 15 mol%), a colour change to red was observed. The olefin (1 mmol, 1.0 equiv.) and, eventually, the iminoiodinane (1 mmol, 1.0 equiv.) were then added leading to a yellow suspension. The flask was sealed under Ar and put into a preheated oil bath at 85 °C. The reaction mixture was stirred for 1-3 hrs, then cooled to room temperature, diluted with dist. DCM (10 mL), filtered through a short plug of Celite (DCM) and concentrated under reduced pressure. The residue was purified by silica gel chromatography (pentane:ethyl acetate 95:5 to 65:35) to give the desired product.

Compounds **3aa**[3] and **3ab**[4] were described earlier. Compounds **3ac**, **3bc**, **3dc**, **3fc**, **3ic**, **3jc** and **9** were prepared according to the general procedure. Their analytical data has been described earlier.[5]



3cc

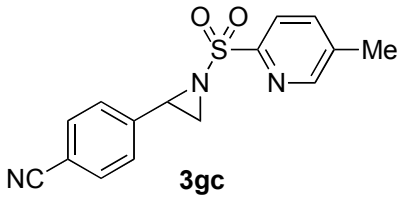
***N*-(5-Methyl-2-pyridinesulfonyl)-(2-methyl)phenylaziridine (3cc)**.
Pale yellow oil (60%), ν_{max}/cm^{-1} (cap.) 2982, 2924, 1782, 1723, 1427, 1367, 1209, 1169 and 1023; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.42-2.43 (4H, m, CH_3 and CH_A), 2.44 (3H, s, CH_3), 3.20 (1H, d, *J* 7.1, CH_B), 4.06 (1H, dd, *J* 7.1, 4.7, CH_C), 7.07-7.19 (4H, m, H_{Ar}), 7.73 (1H, m, H_{Ar}), 8.04 (1H, d, *J* 8.3, H_{Ar}) and 8.56 (1H, br s, H_{Ar}); δ_C(100 MHz; $CDCl_3$) 18.8, 19.2, 35.6, 39.7, 122.8, 125.9, 126.0, 128.1, 129.9, 133.1, 136.8, 138.2, 138.3, 150.8 and 153.2; *m/z* (CI, methane) 290 (19%), 289 (M+H, 100), 225 (50), 133 (52) and 132 (37); HRMS (EI) $C_{15}H_{16}N_2O_2S$ requires 288.3647, found 132.0813 (M-$C_6H_6NO_2S$).



3ec

***N*-(5-Methyl-2-pyridinesulfonyl)-(4-chloro)phenylaziridine (3ec).**

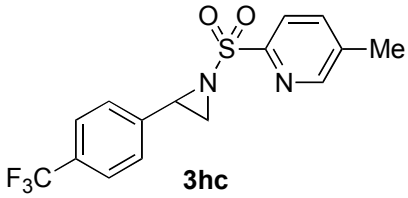
White solid (36%); mp 70 °C; ν_{max}/cm^{-1} (KBr) 3057, 2361, 2343, 1696, 1648, 1507, 1328, 1172, 1097, 910, 829, 667 and 560; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.44 (3H, s, CH_3), 2.46 (1H, br d, *J* 4.7, CH_A), 3.19 (1H, dd, *J* 7.1, 1.1, CH_B), 3.96 (1H, dd, *J* 7.1, 4.7, CH_C), 7.18-7.21 (2H, m, H_{Ar}), 7.25-7.27 (2H, m, H_{Ar}), 7.72-7.74 (1H, m, H_{Ar}), 8.01 (1H, dd, *J* 8.0, 0.6, H_{Ar}) and 8.55 (1H, br s, H_{Ar}); δ_C(100 MHz; $CDCl_3$) 18.8, 36.1, 40.8, 122.8, 128.0, 128.7, 133.5, 134.2, 138.2, 138.4, 150.8 and 153.0; *m/z* (CI, methane) 311 (M[^{37}Cl]+H, 41%), 309 (M[^{35}Cl]+H, 100), 245 (75), 153 (57) and 152 (38); HRMS (EI) $C_{14}H_{13}N_2SO_2Cl$ requires 308.0386, found 152.0267 (M-$C_6H_6NO_2S$).



3gc

***N*-(5-Methyl-2-pyridinesulfonyl)-(4-cyano)phenylaziridine (3gc)**.

White solid (60%), mp 117 °C; ν_{max}/cm^{-1} (KBr) 2227, 1608, 1571, 1453, 1382, 1322, 1171, 1138, 1099, 982, 915, 847, 788, 743, 697 and 655; Anal. Calcd for $C_{15}H_{13}N_3O_2S$ (299.3): C, 60.18, H, 4.38, N, 14.04; Found: C, 60.12; H, 4.45; N, 13.80; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.38 (3H, s, CH_3), 2.40 (1H, d, *J* 4.5, CH_A), 3.15 (1H, d, *J* 7.1, CH_B), 3.95 (1H, dd, *J* 7.1, 4.5, CH_C), 7.32 (2H, dt, *J* 8.2, 1.7, H_{Ar}), 7.52 (2H, dt, *J* 8.2, 1.7, H_{Ar}), 7.68 (1H, ddd, *J* 8.2, 2.2, 0.7, H_{Ar}), 7.95 (1H, d, *J* 8.2, H_{Ar}) and 8.47 (1H, dd, *J* 2.2, 0.7, H_{Ar}); δ_C(75 MHz; $CDCl_3$) 18.7, 36.3, 40.4, 112.2, 118.4, 122.8, 127.5, 132.4, 138.3, 138.7, 140.5, 150.9 and 152.9; *m/z* (EI) 300 (M+H, 5%), 234 (61), 208 (73), 207 (65), 144 (52), 143 (92), 142 (85), 117 (50) and 116 (95).



3hc

***N*-(5-Methyl-2-pyridinesulfonyl)-(4-trifluoromethyl)-phenylaziridine (3hc)**.

White solid (65%); mp 92 °C; ν_{max}/cm^{-1} (KBr) 1620, 1376, 1456, 1379, 1323, 1174, 1129, 913, 701 and 560; Anal. Calcd for $C_{15}H_{13}F_3N_2O_2S$ (342.0): C, 52.63; H, 3.83, N, 8.18; Found: C, 52.72; H, 3.77; N, 8.02; δ_H(100 MHz; $CDCl_3$; Me_4Si) 2.36 (3H, s, CH_3), 2.41 (1H, d, *J* 4.5, CH_A), 3.14 (1H, d, *J* 7.2, CH_B), 3.96 (1H, dd, *J* 7.2, 4.5, CH_C), 7.31 (2H, d, *J* 8.0, H_{Ar}), 7.47 (2H, d, *J* 8.1, H_{Ar}), 7.66 (1H, ddd, *J* 8.0, 1.6, 0.7, H_{Ar}), 7.94 (1H, d, *J* 8.0, H_{Ar}) and 8.47 (1H, br dd, *J* 1.6, 0.7, H_{Ar}); δ_C(100 MHz; $CDCl_3$) 18.7, 36.2, 40.7, 122.8, 123.9 (q, $^1J_{CF}$ 270), 125.5 (q, $^3J_{CF}$ 4), 127.1, 130.4 (q, $^2J_{CF}$ 33), 138.2, 138.5, 139.0, 150.8 and 152.9; δ_F(376 MHz; $CDCl_3$) -62.7; *m/z* (EI) 343 (M+H, 18%), 278 (41), 277 (85), 259 (20), 251 (74) and 250 (88).

References

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[2] M. Nakanishi, A.-F. Salit and C. Bolm, *Adv. Synth. Catal.*, 2008, **350**, 1835.
[3] D. A. Evans, M. M. Faul and M. T. Bilodeau, *J. Am. Chem. Soc.*, 1994, **116**, 2742.
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[5] H. Han, I. Bae, E. J. Yoo, J. Lee, Y. Do and S. Chang, *Org. Lett.*, 2004, **6**, 4109.