Catalyst-free aziridination and unexpected homologation of aziridines from imines†

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Aziridination and unpredicted homologation reaction of *N*-sulfonylimines were achieved easily with a very simple, rapid and mild procedure through the use of diazomethane without the presence of any catalyst. The method represents an attractive alternative to metal-catalyzed processes.

Introduction

The use of aziridines in modern synthetic chemistry is unavoidable due to their value as useful substrates for the preparation of important biologically active substances, and also due to their versatility as chiral reagents and chiral auxiliaries, precious in stereoselective synthesis.[1] Great efforts and progress have been made in the development of various aziridination methods;[2,3] however, the simplest approach is either the addition of a nitrene moiety to an olefin or the addition of a carbene moiety to an imine. Transition metals have been found to act as effective catalysts in both cases, although the metal-mediated nitrene transfer to olefins[4] has been examined in much more detail than the reaction of a metal-carbene with an imine.[5] The reaction of a variety of imines with diazocompounds is limited to substituted diazomethanes in the presence of catalytic amounts of catalyst.[6] Metal-free catalyzed processes are interesting alternatives since they are often more economical and environmentally friendly. It is known that the addition of diazomethane to various Schiff bases forms 1,2,3-triazolines, and all the attempts to obtain aziridines by pyrolysis or photolysis of the above triazolines have failed.[7] To our surprise, reports on the reactions of diazomethane with imines to produce aziridines are scarce in literature and limited to fluorine-substituted imines,[8] 1-phosphono-2-aza-1,3-dienes[9] and iminium salts.[10] As part of our general interest in the area of small-ring synthesis, we have been investigating new methods to prepare aziridines.[11] We report herein our preliminary results of a mild procedure, very simple and rapid method for the preparation of *N*-sulfonyl-2-substituted aziridines, by aziridination and/or homologation–aziridination reaction of *N*-sulfonylimines using diazomethane as the carbene source. The method represents an attractive alternative to metal-catalyzed processes, notably because of its lower cost. Also has the advantage of being a new method for the synthesis of 2-benzylaziridines which complement the existing methods.

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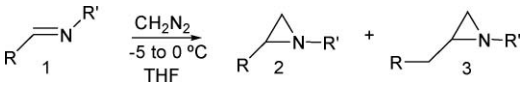
† Electronic supplementary information (ESI) available: General methods, NMR spectra, and mass spectra of all compounds. See DOI: 10.1039/c001894e

Table 1 Aziridination and homologation reaction of *N*-tosylimines



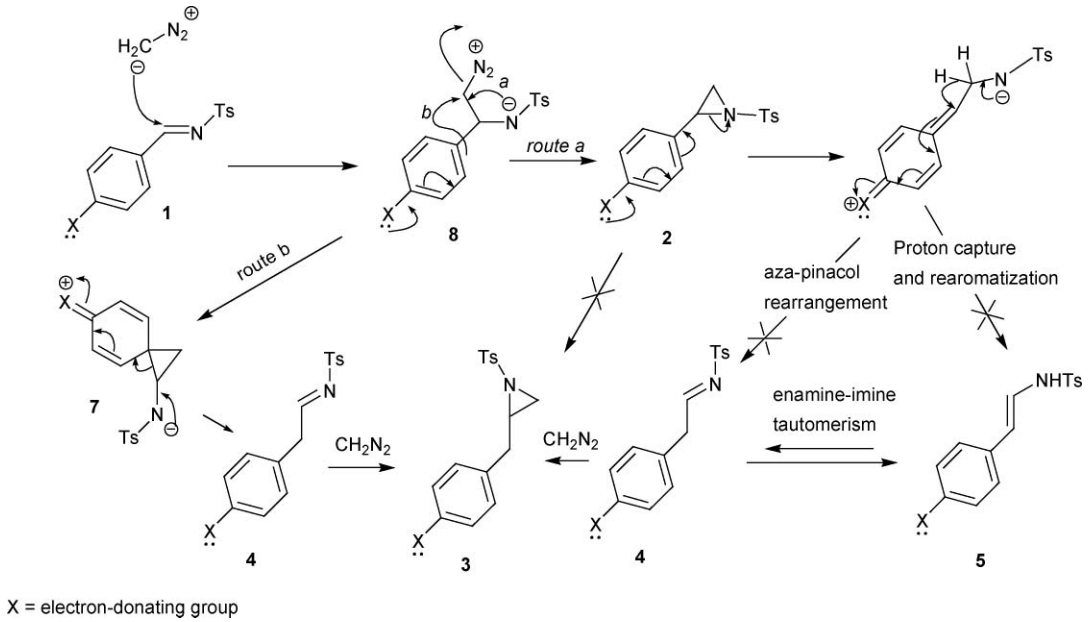
Entry	*R*	*R′*	Time/min	**2** *η* (%)	**3** *η* (%)
a	Ph	Ts	30	71	0
b	Ph	Bs	30	70	0
c	Ph	Ms	20	70[a]	0
d	4-BrC_6H_4	Ts	30	75	0
e	4-BrC_6H_4	Bs	30	71	0
f	3-ClC_6H_4	Bs	30	45	0
g	4-ClC_6H_4	Ts	30	78	0
h	2-$NO_2C_6H_4$	Ts	30	72	0
i	4-$NO_2C_6H_4$	Bs	30	67	0
j	4-$NO_2C_6H_4$	Ts	30	74	0
k	4-MeOC_6H_4	Ts	30	0	72
l	4-MeOC_6H_4	Bs	30	0	68
m	4-MeOC_6H_4	Nz	25	0	78
n	2,4-$(MeO)_2C_6H_3$	Ts	30	0	74
o	2-MeC_6H_4[b]	Ts	10	10	65
p	2-MeC_6H_4	Bs	30	0	73
q	Furanyl	Ts	30	0	77
r	Ph–CH=CH	Ts	40	0	68
s	3,4-Methylenedioxyphenyl	Ts	30	0	76
t	3,4-Methylenedioxyphenyl	Bs	30	0	72
u	Anthracene	Ts	20	0	65
v	2-Br-4,5-(methylenedioxy)-phenyl	Ts	20	30	50
x	Ph	Ph	120	0	0

[a] Yield of crude product; any attempts to purify the product failed. The ^{1}H NMR of crude shows aziridine peaks, compared with the reported ^{1}H NMR. [b] The reaction was quenched after 10 min.

Results and discussion

We began our investigation with a model aziridination reaction between *N*-benzylidene-4-methylbenzenesulfonamide (**1a**) and diazomethane. As illustrated in Table 1, treatment of 1 equiv. of **1a** with 5 (approximately) equivalents of diazomethane in THF at –5 to 0 °C gave the desired aziridine, **2a**, in 71% yield.

When electron-withdrawing aromatic substituents groups are present, the reaction gave good yields of aziridine **2** (Table 1, entry a–j). However, in the presence of electron-donating groups (Table 1, entry k–v), the reaction products show a slightly different ^{1}H NMR pattern, indicating two extra protons, one extra carbon in ^{13}C NMR and more 14 a.m.u. on the mass spectra. To this



Scheme 1 The proposed mechanism for the homologation–aziridination reaction of *N*-tosylimines.

compound was then attributed the structure **3**, which agrees with the incorporation of two methylene groups starting from the imine. The complete structural elucidation of **3** was accomplished using two-dimensional NMR spectroscopy. Moreover, our spectroscopic data are in consonance with those presented for two related compounds reported in literature,[12] *N*-tosyl-benzylaziridine and *N*-(4-methoxybenzenesulfonyl)benzylaziridine. The results, summarized in Table 1, show that the carbene insertion into the imine double bond[13] with concomitant formation of the aziridine ring is limited to *N*-sulfonylimines **1** (entry a–v). In fact, no reaction is observed with *N*-benzylidene aniline (entry x). *N*-Benzenesulfonyl imines or *N*-tosylimines participate with a similar degree of efficiency (entry a *vs.* b or k *vs.* l, among others). Spectroscopic data obtained for compound **2** agree with those already published in literature[14] and also those from the imine substrates **1** used.[15] To study the reaction mechanism, the reaction of 2-methylphenyl-*N*-tosylimine with diazomethane was quenched after 10 min (entry o). Both aziridines **2o** and **3o** were isolated from the reaction medium. Initially, this result lead us to propose a reaction mechanism involving a ring opening reaction of the aziridine primarily formed, which occurs due to the electron-donating property of the ring substituent (Scheme 1, route a).

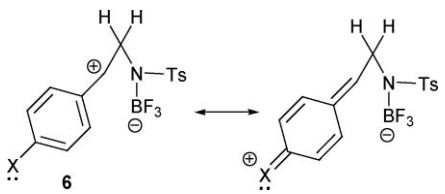
The ring opening product can subsequently undergo an aza-pinacol rearrangement to the *N*-tosylimine **4** or a proton capture and re-aromatization to **5** followed by enamine–imine tautomerism to **4**. Both the cases result in homologation of the initial *N*-tosylimine by a methylene group. The proposed reaction mechanism is outlined in Scheme 1, route a. Any attempt to trap this *N*-tosylimine intermediate **4** by a Diels–Alder reaction with 2,3-dimethylbutadiene or 2,3-diphenylbutadiene was unsuccessful.

If compound **5** was involved as an intermediate in the reaction (the tautomeric conversion to **4** was not expected to be so fast since **5** is more stable due to conjugation) other type of products would result from its reaction with diazomethane.

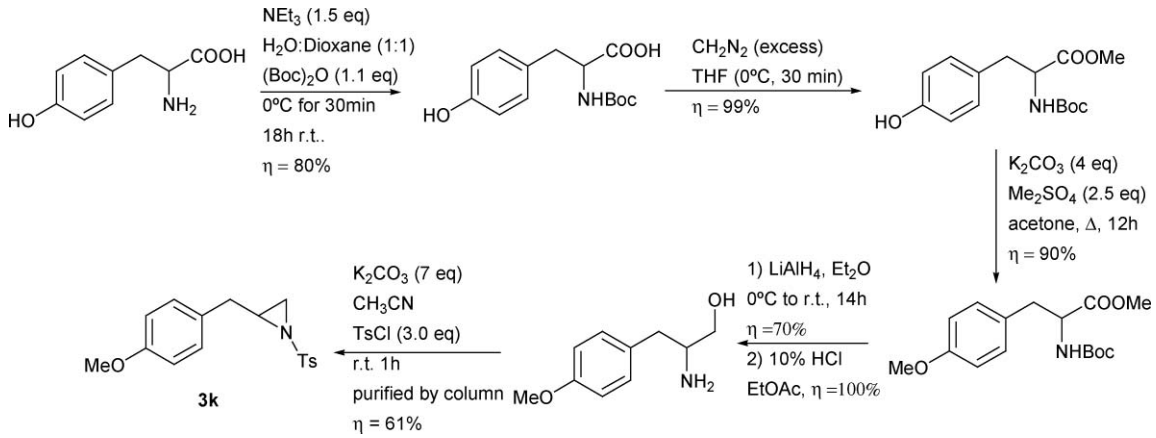
In an attempt to prepare 2-phenyl-*N*-tosylethanimine (**4**, X = H) using the routine procedure,[13] the tautomeric form **5** was formed since, in the *in situ* reaction with diazomethane, the methylated compound *N*-methyl-*N*-(2-phenylethenyl)-*p*-toluenesulfonamide[16] was the only product obtained. Hence, to prepare 2-phenyl-*N*-tosylethanimine (**4**, X = H) a different procedure[3,17] was then followed which involved the reaction of phenylacetaldehyde and *N*-sulfinylsulfonamides. Any attempt to isolate **4** was fruitless and, therefore, the aziridination of **4** with diazomethane was accomplished *in situ* and the aziridine **3a** was obtained in 50% yield.

It should be reported that the net rearrangement of aziridines to imines has been reported under thermal conditions[18] or under Lewis acid catalysis.[19] Indeed the aza-pinacol rearrangement of **2a** to **3a** using BF_3 was observed. After total consumption of **2a**, the reaction mixture was neutralized with solid sodium bicarbonate, and diazomethane was added to the reaction medium. Compound **3a** was obtained in low yield, 33% (Table 2-*via* a, entry e) which can be explained by the fact that, in these conditions, some hydrolysis of the imine intermediate **4** can occur. Roughly the same result was obtained *in situ* starting from imine **1a**. In these case, without isolation of the aziridine **2a** the aza-pinacol rearrangement was accomplished with BF_3 (Table 2-*via* b, entry a).

As expected, a substituent unable of stabilizing intermediate **6** would not favour the imine homologation *via* aza-pinacol rearrangement (Table 2 entry c and f).

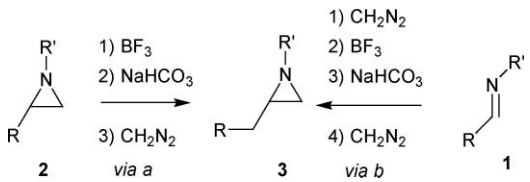


To further strengthen the reaction mechanism, we tried the homologation of **2o** to **3o** under the same reaction conditions. But unexpectedly, the conversion of **2o** to **3o** was not observed, creating



Scheme 2 Schematic representation of the synthesis of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3k**) from tyrosine.

Table 2 Aza pinacol rearrangement of aziridines



Entry	Substrate	*R*	*R′*	**3** *η* (%)
a	**1a**	Ph	Ts	38
b	**1e**	4-BrC_6H_4-	Bs	25
c	**1i**	4-$NO_2C_6H_4$-	Bs	—
d	**1f**	3-ClC_6H_4-	Bs	18.3[a]
e	**2a**	Ph	Ts	33
f	**2i**	4-$NO_2C_6H_4$-	Bs	—

[a] 50 µl of H_2SO_4 was used as catalyst instead of BF_3.

doubt in the mechanism involving the aza-pinacol rearrangement. To get further insight on the reaction mechanism, we have performed an experiment involving the quenching of a definite part of the reaction mixture in scheduled times of 1/4/8/15/20/30 min. The solvent and the rest of diazomethane were evaporated and the crude sample was analyzed by ^{1}H NMR. To our surprise, the imine **1o** was consumed immediately, the amount of aziridine **2o** was constant throughout the reaction, and the amount of **3o** increased. The ratio of **2o** to **3o** increased from 1 : 1 to 1 : 3. The quantification was done by ^{1}H NMR using two sets of signals from the aromatic and the aliphatic part. The signals used for quantification were the pair of doublets at 7.58 ($ArH_{2'+6'}$ from **3o**) and 7.82 ($ArH_{2'+6'}$ from **2o**) and the double doublet at 3.80–3.77 (H_2 from **2o**), the multiplet at 2.90–2.84 (H_3 from **3o** and H_2 from **2o**) and the double doublet at 2.75 ($H_{1'a}$ from **3o**). In light of the above observations, a mechanism involving aza-pinacol rearrangement is not plausible. To justify our results, a different mechanism involving intermediate **7** is proposed (Scheme 1, route b). This mechanism is supported by a report on the reaction of quinazolinium salts with diazomethane.[20] Therein, they propose the attack of diazomethane on the polarized double bond and a subsequent ring closure. The cycloaddition of diazomethane to the imine double bond forming a triazole is discarded because it cannot justify the lack of reaction with substrate **1x** (Table 1). In Scheme 1, in both cases (route a or b), the proposed homologated imine **4** is an intermediate. To support the mechanism, imine **1v** (Table 1), *N*-(3,4-methylenedioxy-benzylidene)-4-methylbenzenesulfonamide, having a bulky group on the *ortho* position, was prepared and subjected to the reaction. Aziridines **2v** and **3v** were obtained in 30 and 50% yield, respectively. As expected, the rate of the reaction to aziridine **3v**, became slower than that of **3s**, due to the presence of bromine. These results led us to conclude that the steric hindrance of the bromine could have an affect on the cyclization forming the intermediate **7** (Scheme 1).

In parallel, the synthesis of compound **3k** was accomplished by a different procedure starting from tyrosine and the structure was confirmed (Scheme 2). The synthesis started with the amino group protection with Boc followed by methylation of the carboxylic acid with diazomethane. Methylation of the hydroxylic aromatic group was subsequently achieved using $K_2CO_3/(MeO)_2SO_2$. After Boc removal,[21] the reduction with $LiAlH_4$ lead to the 1,2-amino alcohol. The final step of cyclization to the aziridine ring was carried out by tosyl chloride and potassium carbonate[22] and compound **3k** was obtained in 30% overall yield.

Conclusions

In summary, we have demonstrated that the aziridination or homologation–aziridination reaction of *N*-sulfonylimines are achieved easily with a very simple, rapid and mild procedure by using diazomethane without any catalyst. The method uses readily available reagents and occurs under experimentally straightforward conditions. The recently reported work[23] on the instantaneous deprotection of *N*-tosylaziridines will enlarge the scope of its application. The method represents an attractive alternative to metal-catalyzed processes, notably because of its lower cost. To the best for our knowledge, this is the first time that *in situ* homologation of imines is reported. Additional studies with other diazocompounds, such as phenyldiazomethane or trimethylsilyldiazomethane, are currently underway.

Experimental

General experimental

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer

chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 precoated were used, respectively. The spots were visualized using UV light and a DNP solution followed by heating. Medium performance liquid chromatography and flash column chromatography were performed using Merck, Kieselgel 60 with (0.063–0.200 mm) and (0.040–0.063 mm), respectively. Infrared spectra were recorded on a Perkin Elmer spectrum 1000. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer at 400 and 100.62 MHz, respectively. ^{1}H shifts are reported relative to internal TMS. Carbon shifts are given relative to the ^{13}C signal of $CDCl_3$ (δ 77.0 ppm) as reference. Mass spectra were recorded at the Mass Spectrometry Unit at the University of Santiago de Compostela, Spain. The electron impact mass spectra were recorded using a magnetic Micromass Autospec apparatus. For electrospray ionization the apparatus Bruker Microtof ESI-TOF was used.

General procedure for aziridination

To a solution of *N*-tosylimine (0.2 mmol) in dry THF (10 mL) cooled to −5 to 0 °C under nitrogen atmosphere was added 3 ml (nearly 5 equivalents) of a diazomethane solution in ethyl ether prepared according to Vogel's procedure.[24] The reaction was complete in 10–30 min, depending on substrate. The reaction mixture was concentrated and purified by flash column chromatography (5% ethyl acetate in hexane as eluent).

***N*-(Benzenesulfonyl)-2-(4-bromophenyl) aziridine (2e).** Oil, obtained in 71% yield. IR(film) ν_{max}: 1324 (S=O), 1163 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.98 (2H, d, J = 7.4 Hz, $ArH_{2'+6'}$), 7,65 (1H, t, J = 7.2 Hz, $ArH_{4'}$), 7,55 (2H, t, J = 7.2 Hz, $ArH_{3'+5'}$), 7.42 (2H, d, J = 8.0 Hz, ArH_{3+5}), 7.09 (2H, d, J = 8.0 Hz, ArH_{2+6}), 3.75 (1H, dd, J=7.1 and 4.3 Hz, H_2), 3.01 (1H, d, J = 7.1 Hz, H_{3b}), 2.36 (1H, d, J = 4.3 Hz, H_{3a}). MSEI(+) m/z: 338 [M^{81}Br+ H]$^+$ (21.92), 340 [M^{79}Br + H]$^+$ (21.77), 196 [M-Bs]$^+$ (71.2). HRMSEI(+) calcd for $C_{14}H_{12}BrNO_2S$ [M]$^+$ 338.9990 found 338.9985

***N*-(*p*-Toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxyphenyl) aziridine (2v).** Oil, obtained in 30% yield. IR(film) ν_{max}: 1321 (S=O), 1160 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.88 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,35 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.94 (1H, s, ArH_3), 6.64 (1H, s, ArH_6), 5.93 (2H, s, OCH_2O), 3.91 (1H, dd, J=7.0 and 4.4 Hz, H_2), 2.98 (1H, d, J = 7 Hz, H_{3a}), 2.45 (3H, s, $ArCH_3$), 2.20 (1H, d, J = 4 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 148.2, 147.5, 144.9, 134.6, 129.8, 129.5, 128.1, 113.9, 112.5, 107.6 (ArC), 101.9 (OCH_2O), 41.2 (C_2), 35.9 (C_3), 21.7 ($ArCH_3$). MSEI(+) m/z: 397 [M^{81}Br]$^+$ (4.34), 395 [M^{79}Br]$^+$ (4.0), 240 [M^{79}Br-Ts]$^+$ (55.6), 161 [M-Ts-Br]$^+$ (100). HRMSEI(+) calcd for $C_{16}H_{14}NO_4S^{79}Br$ [M]$^+$ 394.9827 found 394.9827.

***N*-(*p*-Toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (3k).** White solid (108–109°C, ethyl acetate–hexane), obtained in 72% yield. IR(film) ν_{max}: 1321 (S=O), 1160 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.67 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,21 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.95 (2H, d, J = 8.3 Hz, ArH_{2+6}), 6.68 (2H, d, J = 8.0 Hz, ArH_{3+5}), 3.77 (3H, s, OCH_3), 2.94-2.88 (1H, m, H_2), 2.77 (1H, dd, J=14.5 and 4.9 Hz, $H_{1'a}$), 2.70 (1H, d, J = 6.8 Hz, H_{3a}), 2.60 (1H, dd, J=14.5 and 7.2 Hz, $H_{1'b}$), 2.43 (3H, s, $ArCH_3$), 2.14 (1H, d, J = 4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.3 (ArC_4), 144.3 ($ArC_{4'}$), 134.8 ($ArC_{1'}$), 129.6 (ArC_{2+6}), 129.5 ($ArC_{3'+5'}$), 129.0 (ArC_1), 127.8 ($ArC_{2'+6'}$), 113.8 (ArC_{3+5}), 55.1 (OCH_3), 41.4 (C_2), 36.5 ($C_{1'}$), 32.7 (C_3), 21.5 ($ArCH_3$). MSEI(+) m/z: 317 [M]$^+$ (14.6), 162 [M-Ts)]$^+$ (98.5), 121 [$MeOC_6H_4CH_2$]$^+$ (100). HRMSEI(+) calcd for $C_{17}H_{19}NO_3S$ [M]$^+$ 317.10856 found 317.1081.

***N*-(Benzenesulfonyl)-2-(4-methoxybenzyl)aziridine (3l).** Oil, obtained in 68% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.81 (2H, d, J = 7.7 Hz, $ArH_{2'+6'}$), 7.58 (1H, t, J = 7.4 Hz, $ArH_{4'}$), 7,44 (2H, t, J = 7,7 Hz, $ArH_{3'+5'}$), 6.95 (2H, d, J = 8.4 Hz, ArH_{2+6}), 6.68 (2H, d, J = 8.4 Hz, ArH_{3+5}), 3.77 (3H, s, OCH_3), 2.99-2.93 (1H, m, H_2), 2.77 (1H, dd, J=14.7 and 5 Hz, $H_{1'a}$), 2.72 (1H, d, J = 6.9 Hz, H_{3a}), 2.62 (1H, dd, J=14.5 and 7.2 Hz, $H_{1'b}$), 2.16 (1H, d, J = 4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.3 (ArC_4), 138.0 ($ArC_{1'}$), 133.3 ($ArC_{4'}$), 129.6 (ArC_{2+6}), 128.9 ($ArC_{3'+5'}$+ ArC_1), 127.8 ($ArC_{2'+6'}$), 113.8 (ArC_{3+5}), 55.2 (OCH_3), 41.6 (C_2), 36.5 ($C_{1'}$), 32.8 (C_3). MSEI(+) m/z: 303 [M]$^+$ (11), 162 [M-Bs]$^+$ (96.5), 160 [M − Bs − H_2]$^+$ (100). HRMSEI(+) calcd for $C_{16}H_{17}NO_3S$ [M]$^+$ 303.0929 found 303.0924.

***N*-(*p*-Nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (3m).** Oil, obtained in 78% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.17 (2H, d, J = 8.8, $ArH_{3'+5'}$), 7.88 (2H, d, J = 8.8, $ArH_{2'+6'}$), 6.87 (2H, d, J = 8.6, ArH_{2+6}), 6.59 (2H, d, J = 8.6, ArH_{3+5}), 3.71 (3H, s, OCH_3), 3.01-2.90 (2H, m, H_2 + $H_{1'a}$), 2.88 (1H, d, J = 6.8, H_{3a}), 2.39 (1H, dd, J=14.2 and 8.2 Hz, $H_{1'b}$), 2.30 (1H, d, J = 4.5 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.5 (ArC_4), 150.2 ($ArC_{1'/4'}$), 143.4 ($ArC_{1'/4'}$), 129.6 (ArC_{2+6}), 129.0 ($ArC_{2'+6'}$), 128.7 (ArC_1), 123.9 ($ArC_{3'+5'}$), 113.6 (ArC_{3+5}), 55.0 (OCH_3), 43.1 (C_2), 36.5 ($C_{1'}$), 33.5 (C_3). MSEI(+) m/z: 348 [M]$^+$ (26.7), 162 [M-Nz]$^+$ (100), 121 [$MeOC_6H_4CH_2$]$^+$ (83.9). HRMSEI(+) calcd for $C_{16}H_{16}N_2O_5S$ [M]$^+$ 348.0780 found 348.0778.

***N*-(*p*-Toluenesulfonyl)-2-(2,4-dimethoxybenzyl)aziridine (3n).** Oil, obtained in 74% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.66 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,19 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.82 (1H, d, J = 8.2 Hz, ArH_6), 6.32 (1H, d, J = 2.0 Hz, ArH_3), 6.24 (1H, dd, J=8.2 and 2.0 Hz, ArH_5), 3.77 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.03-2.97 (1H, m, H_2), 2.78 (1H, dd, J=14.1 and 5.4 Hz, $H_{1'a}$), 2.68 (1H, d, J = 6.9 Hz, H_{3a}), 2.54 (1H, dd, J=14.1 and 6.9 Hz, $H_{1'b}$), 2.41 (3H, s, $ArCH_3$), 2.16 (1H, d, J = 4.5 Hz, H_{3b}); ^{13}C NMR ($CDCl_3$) δ: 159.9 (ArC_4), 158.1 (ArC_2), 144.0 ($ArC_{4'}$), 135.1 ($ArC_{1'}$), 130.7 (ArC_6), 129.4 ($ArC_{3'+5'}$), 127.8 ($ArC_{2'+6'}$), 117.8 (ArC_1), 103.9 (ArC_5), 98.3 (ArC_3), 55.2 (OCH_3), 40.5 (C_2), 33.3 (C_3), 31.8 ($C_{1'}$), 21.5 ($ArCH_3$); MSEI(+) m/z: 347 [M]$^+$ (29.1), 192 [M-Ts]$^+$ (100), 151 [$(MeO)_2C_6H_4CH_2$]$^+$ (64.2). HRMSEI calcd for $C_{18}H_{21}NO_4S$ [M]$^+$ 347,1191 found 347,1196.

***N*-(*p*-Toluenesulfonyl)-2-(2-methylbenzyl)aziridine (3o).** White solid (128–129°C ethyl acetate–hexane), obtained in 74% yield. IR(film) ν_{max}: 1320 (S=O), 1159 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.58 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,12 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.99-6.90 (4H, m, ArH), 2.90-2.84 (1H, m, H_2), 2.75 (1H, dd, J=14.7 and 5 Hz, $H_{1'a}$), 2.65-2.60 (2H, m, $H_{1'b}$ + H_{3a}), 2.34 (3H, s, $ArCH_3$), 2.12 (3H, s, $ArCH_3$), 2.06 (1H, d, J = 4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 144.2, 136.0, 135.2, 134.7, 130.1, 129.4, 129.3, 127.7, 126.6, 125.9 (ArC), 40.4 (C_2), 34.4, 32.7 ($C_{1'}$/C_3), 21.5 ($ArCH_3$), 19.4 ($ArCH_3$). MSEI(+) m/z: 301 [M]$^+$ (9.1), 146 [M − Ts]$^+$ (70.4), 130 [M-TsN-2H]$^+$ (100); HRMSEI calcd for $C_{17}H_{19}NO_2S$ [M]$^+$ 301,11365 obtained 301.1132.

***N*-(Benzenesulfonyl)-2-(2-methylbenzyl)aziridine (3p).** Oil, obtained in 73% yield. IR(film) ν_{max}: 1322 (S=O), 1163 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, J = 7.8 Hz, $ArH_{2'+6'}$), 7.57 (1H, m, $ArH_{4'}$), 7,43 (2H, t, J = 7.7 Hz, $ArH_{3'+5'}$), 7.11-7.00 (4H, m, $ArH_{3+4+5+6}$), 3.04-2.98 (1H, m, H_2), 2.85 (1H, dd, J=14.7 and 5.5 Hz, $H_{1'a}$), 2.73 (1H, d, J = 6.7 Hz, H_{3a}), 2.36 (1H, dd, J=14.5 and 4.7 Hz, $H_{1'b}$), 2.19 (3H, s, $ArCH_3$), 2.16 (1H, d, J = 4.5 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 137.8, 136.0, 135.1, 133.3, 130.2, 129.3, 128.8, 127.6, 126.8, 125.9 (ArC), 40.6 (C_2), 34.3, 32.8 ($C_{1'}/C_3$), 19.4 ($ArCH_3$). MS(EI): 387 $[M]^+$ (3.61), 146 [M^+-Bs] (43.9), 132 [M^+ – TsN] (79.6), 130 [M^+-TsN-2H] (100); HRMSEI calcd for $C_{16}H_{17}NO_2S$ $[M]^+$ 287,0980 obtained 287.10979.

***N*-(*p*-Toluenesulfonyl)-2-(2-furanyl)methylaziridine (3q).** oil, obtained in 77% yield. IR(film) ν_{max}: 1322 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.77 (2H, d, J = 8.1 Hz, $ArH_{2'+6'}$), 7,30 (2H, d, J = 8.1 Hz, $ArH_{3'+5'}$), 7.18 (1H, s, $FuranylH_4$), 6.21-6.20 (1H, m, $FuranylH_3$), 6.01 (1H, d, J = 3 Hz, $FuranylH_2$), 3.04-2.98 (1H, m, H_2), 2.80 (2H, d, J = 6 Hz, $H_{1'}$), 2.70 (1H, d, J = 7 Hz, H_{3a}), 2.44 (3H, s, $ArCH_3$), 2.17 (1H, d, J = 4.4 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 150.7 ($FuranylC_1$), 144.4 ($ArC_{4'}$), 141.6 ($FuranylC_4$), 134.9 ($ArC_{1'}$), 129.6 ($ArC_{3'+5'}$), 127.9 ($ArC_{2'+6'}$), 110.2 (FuranylC3), 106.7 ($FuranylC_2$), 38.4 (C_2), 32.9 (C_3), 30.2 ($C_{1'}$), 21.5 ($ArCH_3$). MSEI(+) m/z: 278 $[M+H]^+$ (1), 171 $[Ts]^+$ (25.4), 155 $[Ts]^+$ (31.2), 91 $[C_7H_7]^+$ (100). HRMSEI calcd for $C_{14}H_{15}NaNO_3S$ $[M + Na]^+$ 300.06703 found 300.0664.

***N*-(*p*-Toluenesulfonyl)-2-(2-phenylethenyl)aziridine (3r).** White solid (90–91°C ethyl acetate–hexane), obtained in 68% yield. IR(film) ν_{max}: 1322 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, J = 7.9 Hz, $ArH_{2'+6'}$), 7,28-7.14 (7H, m, PhH + $ArH_{3'+5'}$), 6.32 (1H, d, J = 15.9 Hz, $H_{3'}$), 5.81 (1H, dt, J=15.9 and 7.5 Hz, $H_{2'}$), 2.81-2.78 (1H, m, H_2), 2.73 (1H, d, J = 6.8 Hz, H_3), 2.51-2.43 (1H, m, $H_{1'a}$), 2.32 (3H, s, $ArCH_3$), 2.22-2.14 (1H, d, $H_{1'b}$), 2.17 (1H, d, J = 4.8 Hz, H_{3b}); ^{13}C ($CDCl_3$) δ: 144.5 ($ArC_{4'}$), 136.8 (ArC_1), 132.6 ($C_{3'}$), 129.6 ($ArC_{3'+5'}$), 128.4 (ArC_{3+5}), 128.0 ($ArC_{2'+6'}$), 127.3 (ArC_4), 126.1 (ArC_{2+6}), 124.5 ($C_{2'}$), 41.3 (C_2), 34.6 ($C_{1'}$), 32.9 (C_3), 21.5 ($ArCH_3$); MSEI(+) m/z: 313 $[M]^+$ (3.1), 222 $[M\text{-}C_7H_7]^+$ (100), 91 $[C_7H_7]^+$ (97.4). HRMSEI calcd for $C_{18}H_{19}NO_2S$ $[M]^+$ 313.1137 found 313.1133.

***N*-(*p*-Toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (3s).** Oil, obtained in 76% yield. IR(film) ν_{max}: 1320 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.67 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,22 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.57 (1H, d, J = 8.3 Hz, ArH_6), 6.48-6.46 (2H, m, ArH_{2+5}), 5.88 (2H, dd, J = 1.4 Hz, OCH_2O), 2.89-2.97 (1H, m, H_2), 2.76 (1H, dd, J=14.5 and 4.7 Hz, $H_{1'a}$), 2.71 (1H, d, J = 6.8 Hz, H_{3a}), 2.50 (1H, dd, J=14.1 and 7.5 Hz, $H_{1'b}$), 2.42 (3H, s, $ArCH_3$), 2.14 (1H, d, J = 4.4 Hz, H_{3b}); ^{13}C ($CDCl_3$) δ: 147.4 (ArC_4), 146.2 (ArC_3), 144.3 ($ArC_{4'}$), 134.7 ($ArC_{1'}$), 130.7 (ArC_1), 129.4 ($ArC_{3'+5'}$), 127.8 ($ArC_{2'+6'}$), 121.6 (ArC_2), 109.1 (ArC_5), 108.1 (ArC_6), 100.8 (OCH_2O), 41.2 (C_2), 37.2($C_{1'}$), 32.6 (C_3), 21.5 ($ArCH_3$). MSEI(+) m/z: 331 $[M]^+$ (24.3), 176 $[M\text{-}Ts]^+$ (100), 91 $[C_7H_7]^+$ (46.8). HRMSEI calcd for $C_{17}H_{17}NO_4S$ $[M]^+$ 331.0878 found 331.0875.

***N*-(Benzenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (3t).** Oil, obtained in 72% yield. IR(film) ν_{max}: 1321 (S=O), 1159 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, J = 7.6 Hz, $ArH_{2'+6'}$), 7,58 (1H, t, J = 7.2 Hz, $ArH_{4'}$), 7,44 (2H, t, J = 7.2 Hz, $ArH_{3'+5'}$), 6.58 (1H, d, J = 7.8 Hz, ArH_6), 6.49-6.46 (2H, m, ArH_{2+5}), 5.89 (2H, s, OCH_2O), 2.94-2.88 (1H, m, H_2), 2.79-2.73 (2H, m, $H_{1'a+3a}$), 2.51 (1H, dd, J=14.4 and 7.5 Hz, $H_{1'b}$), 2.17 (1H, d, J = 4.5 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 147.4 ($ArC_{3/4}$), 146.3 ($ArC_{3/4}$), 137.8 ($ArC_{1'}$), 133.3, 130.6, 128.8, 127.8, 121.6, 109.1, 108.2 (ArC), 100.8 (OCH_2O), 41.6 (C_2), 37.1, 32.8 ($C_{3/1'}$). MSEI(+) m/z: 317 $[M]^+$ (18.6), 176 $[M\text{-}Bs]^+$ (51.7), 77 $[C_6H_5]^+$ (100). HRMSEI(+) calcd for $C_{16}H_{15}NO_4S$ $[M]^+$ 317.0722. found 317.0725

***N*-(*p*-Toluenesulfonyl)-2-(Anthracen-9-ylmethylene)aziridine (3u).** Oil, obtained in 65% yield. IR(film) ν_{max}: 1321 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 8.24 (1H, s, ArH_{10}), 8.07-8.05 (2H, m, ArH_{8+1}), 7.93-7.91 (2H, m, ArH_{4+5}), 7.44-742 (4H, m, $ArH_{2+3+6+7}$), 7.04 (2H, d, J = 8 Hz, $ArH_{2'+6'}$), 6.50 (2H, d, J = 8 Hz, $ArH_{3'+5'}$), 3.92 (1H, dd, J=15.1 and 3.1 Hz, $H_{1'a}$), 3.47 (1H, dd, J=15.1 and 8.5 Hz, $H_{1'b}$), 3.10-3.08 (1H, m, H_2), 2.89 (1H, d, J = 6.8 Hz, $H_{3'a}$), 2.42 (1H, d, J = 4.4 Hz, $H_{3'b}$), 2.21 (3H, s, $ArCH_3$). ^{13}C ($CDCl_3$) δ: 143.5 ($ArC_{4'}$), 133.6 ($ArC_{1'}$), 131.3 (ArC_9), 129.9 (ArC_{12+13}), 128.8 (ArC_{4+5}), 128.5 ($ArC_{3'+5'}$), 126.9 ($ArC_{2'+6'}$), 126.3 (ArC_{11+14}), 125.8, 124.8 ($ArC_{2/3/6/7}$), 124.3 (ArC_{8+1}), 41.2 (C_2), 32.6, 28.8 ($C_{1'/3}$), 21.5 ($ArCH_3$). MSEI(+) m/z: 387 $[M]^+$ (38.4), 210 [M-Anthr.]$^+$ (75.6), 91 $[C_7H_7]^+$ (100). HRMSEI(+) calcd for $C_{24}H_{21}NO_2S$ $[M]^+$ 387.1293 found 387.1293.

***N*-(*p*-Toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxybenzyl)-aziridine (3v).** Oil, obtained in 50% yield. IR(film) ν_{max}: 1320 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.65 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7,20 (2H, d, J = 8.0 Hz, $ArH_{3'+5'}$), 6.85 (1H, s, ArH_3), 6.44 (1H, s, ArH_6), 5.93 (1H, s, OCH_2O), 5.88 (1H, s, OCH_2O), 3.04 (1H, dd, J=14.2 and 4.2 Hz, $H_{1'a}$), 2.97-2.92 (1H, m, H_2), 2.78 (1H, d, J = 6.8 Hz, H_{3a}), 2.46 (1H, dd, J=14.5 and 7.7 Hz, $H_{1'b}$), 2.42 (3H, s, $ArCH_3$), 2.20 (1H, d, J = 4.3 Hz, H_{3b}); ^{13}C ($CDCl_3$) δ: 147.2, 147.0, 144.2, 134.6, 129.6, 129.4, 127.9, 114.2, 112.4, 110.8 (ArC), 101.5 (OCH_2O), 39.9 (C_2), 37.4, 32.8 ($C_{3/1'}$), 21.5 ($ArCH_3$). MSEI(+) m/z: 411 $[M^{81}Br]^+$ (4.83), 409 $[M^{79}Br]^+$ (4.62), 330 $[M\text{-}Br]^+$ (23.6), 175 $[M\text{-}Ts\text{-}Br]^+$ (67.34), 175 $[M\text{-}Ts\text{-}Br + H]^+$ (100). HRMSEI(+) calcd for $C_{17}H_{16}NO_4S^{81}Br$ $[M]^+$ 410.9963 found 410.9967.

Procedure for the *in situ* homologation–aziridination of 1

To a solution of *N*-tosylimine (0.36 mmol) in dry THF (10 mL) cooled to −5 to 0 °C under nitrogen atmosphere was added 3 ml (nearly 5 equivalents) of a diazomethane solution in ethyl ether prepared according to Vogel's procedure.[24] The reaction was monitored by TLC (30% ethyl acetate in hexane as eluent). Once the reaction was complete, BF_3–etherate (10 mol%) was added and the reaction allowed to come to room temperature and stirred for a further 2 h. The reaction mixture was then neutralized with solid sodium bicarbonate, cooled to 0 °C and 3 ml more of diazomethane was added. The reaction mixture was allowed to stir for 30 min and then filtered through Celite cake, concentrated and purified by flash column chromatography (5% ethyl acetate in hexane).

***N*-(Benzenesulfonyl)-2-(4-bromobenzyl)aziridine (3e).** Oil, obtained in 25% yield. IR(film) ν_{max}: 1318 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.74 (2H, d, J = 8.0 Hz, $ArH_{2'+6'}$), 7.61 (1H, t, J = 7.5 Hz, $ArH_{4'}$), 7,41 (2H, t, J = 7.6 Hz, $ArH_{3'+5'}$), 7.20 (2H, d, J = 8.1 Hz, ArH_{3+5}), 6.87 (2H, d, J = 8.1 Hz, ArH_{2+6}), 2.94-2.84 (2H, m, $H_{1'+2a}$), 2.77 (1H, d, J = 6.7 Hz, H_{3b}), 2.48 (1H, dd, J=14 and 8 Hz, $H_{1'b}$), 2.19 (1H, d, J = 4.4 Hz, H_{3a}). ^{13}C NMR ($CDCl_3$)

δ: 137.66, 135.93, 133.35, 131.47, 130.33, 128.92, 127.76, 120.65 (ArC), 41.34 (C_{2a}), 36.83 ($C_{1'/3a}$), 32.72 ($C_{1'/3a}$). HRMSEI(+) calcd for $C_{15}H_{14}BrNO_2S$ $[M]^+$ 350.9929 found 350.9923.

***N*-(Benzenesulfonyl)-2-(4-chlorobenzyl)aziridine (3f).** In this case 50 µl of H_2SO_4 were used for the rearrangement instead of BF_3. Obtained in 18.3%. IR (film): ν_{max}: 1323 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.79 (2H, d, J = 7.8 Hz, $ArH_{2'+6'}$), 7.57 (1H, t, J = 7.4 Hz, $ArH_{4'}$), 7.44 (2H, t, J = 7.8 Hz, $ArH_{3'+5'}$), 7.09 (2H, m, ArH_{4+5}), 7.00 (1H, s, ArH_2), 6.93 (1H, d, J = 7.2 Hz, ArH_6), 2.95 (1H, m, H_{2a}), 2.86 (1H, dd, J=4.6 e 14.4 Hz, $H_{1'a}$), 2.77 (1H, d, J = 6.8, H_{3a}), 2.56 (1H, dd, J=7.6 e 14.4 Hz, $H_{1'b}$), 2.18 (1H, d, J = 4.36 Hz, H_{3b}), ^{13}C-RMN ($CDCl3$) δ: 138.94, 137.63, 134.16, 133.56, 129.70, 128.93, 127.72, 126.97, 126.85 (ArC), 41.01, 37.11, 32.74 ($C_{1'a+2a+3a}$). MSEI(+) m/z: 307 $[M]^+$ (8.1), 166 $[M\text{-}Bs]^+$ (100). HRMSEI(+) calcd for $C_{15}H_{14}ClNO_2S$ $[M]^+$ 307.0434 found 307.0431.

Procedure for the *in situ* homologation–aziridination of 2a

To a solution of *N*-(*p*-toluenesulfonyl)phenyl aziridine (**2a**, 0.1 g, 0.366 mmol) in dry THF (10 mL) at room temperature was added BF_3–etherate (10 mol%) and the reaction stirred for 2 h. The reaction mixture was then neutralized with solid sodium bicarbonate and cooled to 0 °C. To this solution it was added 3 ml (nearly 5 equivalents) of a diazomethane solution in ethyl ether. The reaction mixture was allowed to stir for 30 min and then filtered through Celite cake, concentrated and purified by flash column chromatography (5% ethyl acetate in hexane as eluent). *N*-Tosyl-benzylaziridine (**3a**) was obtained in 33% yield. Spectroscopic data agree with those from literature.[12]

Aziridination of 2-phenyl-*N*-tosylethanimine (4, X = H)

In a 250 ml round-bottomed flask fitted with a reflux condenser and a $CaCl_2$ drying tube, a mixture of 2.50 g of *p*-toluenesulfonamide (0.0146 mol) and 2.00 g of thionyl chloride (0.0168 mol) in 40 ml of dry toluene was heated for 5 d at reflux. After cooling to room temperature, the solvent and excess of $SOCl_2$ were evaporated to leave approximately 3.00 g of dark orange oil. Kugelrohr distillation gave a total of 1.2 g of *N*-sulfinyl-*p*-toluenesulfonamide (130–140 °C, 0.06 Torr) which crystallized upon standing to a bright yellow solid, mp 47–51 °C (lit.[25] mp 47–51 °C).

To a two-necked 25 mL flask fitted with a syringe cap and an argon inlet was added 3 mL of dry CH_2C1_2 followed by *N*-sulfinyl-*p*-toluenesulfonamide (0.45 mmol, 98 mg) in 2 mL of dry CH_2C1_2. The phenyl acetaldehyde (0.3 mmol) was added *via* syringe, and the reaction mixture was stirred for 1–2 h at room temperature. The reaction mixture was kept between 20 and 30 °C. After complete conversion of aldehyde (seen by TLC) the reaction mixture was cooled to 0 °C and diazomethane added. The reaction was monitored by TLC until complete conversion of the imine. *N*-Tosyl-benzylaziridine (**3a**) was obtained in 50% yield. Spectroscopic data agree with those from literature.[12]

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Notes and references

1 P. S. Branco, in *Recent Research developments in Heterocyclic Chemistry*, ed. T. M. V. D. P. e. Melo, Research Signpost, India, 2007, pp. 1–26; G. S. Singh, M. D'Hooghe and N. De Kimpe, *Chem. Rev.*, 2007, 107, 2080-2135; D. Tanner, *Angew. Chem., Int. Ed.*, 1994, **33**, 599–619.
2 N. De Kimpe, N. Schamp and R. Verhe, *Synth. Commun.*, 1975, **5**, 403–408; N. De Kimpe, R. Verhe, L. De Buyck and N. Schamp, *Synth. Commun.*, 1975, **5**, 269–274; J. M. Concellon, H. Rodriguez-Solla, P. L. Bernad and C. Simal, *J. Org. Chem.*, 2009, **74**, 2452–2459; E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353–1364; J. A. Halfen, *Curr. Org. Chem.*, 2005, **9**, 657–669; S. Minakata, Y. Murakami, R. Tsuruoka, S. Kitanaka and M. Komatsu, *Chem. Commun.*, 2008, 6363–6365; B. Musio, G. J. Clarkson, M. Shipman, S. Florio and R. Luisi, *Org. Lett.*, 2009, **11**, 325–328; F. Pesciaioli, F. De Vincentiis, P. Galzerano, G. Bencivenni, G. Bartoli, A. Mazzanti and P. Melchiorre, *Angew. Chem., Int. Ed.*, 2008, **47**, 8703–8706; Y. M. Shen, M. X. Zhao, J. X. Xu and Y. Shi, *Angew. Chem., Int. Ed.*, 2006, **45**, 8005–8008; J. Vesely, I. Ibrahem, G. L. Zhao, R. Rios and A. Cordova, *Angew. Chem., Int. Ed.*, 2007, **46**, 778–781; N. De Kimpe, P. Sulmon, R. Verhe, L. De Buyck and N. Schamp, *J. Org. Chem.*, 1983, **48**, 4320–4326; N. De Kimpe, R. Verhe, L. De Buyck and N. Schamp, *J. Org. Chem.*, 1980, **45**, 5319–5325.
3 J. M. Concellon, H. Rodriguez-Solla and C. Simal, *Org. Lett.*, 2008, **10**, 4457–4460.
4 S. Fantauzzi, E. Gallo, A. Caselli, C. Piangiolino, F. Ragaini and S. Cenini, *Eur. J. Org. Chem.*, 2007, 6053–6059; G. Y. Gao, J. E. Jones, R. Vyas, J. D. Harden and X. P. Zhang, *J. Org. Chem.*, 2006, **71**, 6655–6658; A. C. Mayer, A. F. Salit and C. Bolm, *Chem. Commun.*, 2008, 5975–5977.
5 J. C. Antilla and W. D. Wulff, *J. Am. Chem. Soc.*, 1999, **121**, 5099–5100; K. B. Hansen, N. S. Finney and E. N. Jacobsen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 676–678; P. Muller and C. Fruit, *Chem. Rev.*, 2003, **103**, 2905–2919; K. G. Rasmussen and K. A. Jorgensen, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1287–1291.
6 R. Bartnik and G. Mloston, *Synthesis*, 1983, 924–925; A. M. Harm, J. G. Knight and G. Stemp, *Tetrahedron Lett.*, 1996, **37**, 6189–6192; Z. Li, K. R. Conser and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1993, **115**, 5326–5327; D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson and D. M. Barnes, *J. Am. Chem. Soc.*, 1993, **115**, 5328–5329; K. G. Rasmussen and K. A. Jorgensen, *J. Chem. Soc., Chem. Commun.*, 1995, 1401–1402; J. M. Mohan, B. S. Uphade, V. R. Choudhary, T. Ravindranathan and A. Sudalai, *Chem. Commun.*, 1997, 1429–1430; K. Juhl, R. G. Hazell and K. A. Jorgensen, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2293–2297; Z. L. Zhu and J. H. Espenson, *J. Am. Chem. Soc.*, 1996, **118**, 9901–9907; T. B. Gunnoe, P. S. White, J. L. Templeton and L. Casarrubios, *J. Am. Chem. Soc.*, 1997, **119**, 3171–3172; W. H. Xie, J. W. Fang, J. Li and P. G. Wang, *Tetrahedron*, 1999, **55**, 12929–12938; D. Morales, J. Perez, L. Riera, V. Riera, R. Corzo-Suarez, S. Garcia-Granda and D. Miguel, *Organometallics*, 2002, **21**, 1540–1545; M. P. Doyle, W. H. Hu and D. J. Timmons, *Org. Lett.*, 2001, **3**, 933–935; V. K. Aggarwal and M. Ferrara, *Org. Lett.*, 2000, **2**, 4107–4110; H. J. Ha, J. M. Suh, K. H. Kang, Y. G. Ahn and O. Han, *Tetrahedron*, 1998, **54**, 851–858.
7 A. Mustafa, *J. Chem. Soc.*, 1949, 234–236; P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, 1961, **26**, 2331; H. Giera, R. Huisgen and K. Polborn, *Eur. J. Org. Chem.*, 2005, 3781–3790; J. M. Stewart, R. L. Clark and P. E. Pike, *J. Chem. Eng. Data*, 1971, **16**, 98.
8 A. L. Logothetis, *J. Org. Chem.*, 1964, **29**, 3049.
9 B. Vanderhoydonck and C. V. Stevens, *Synthesis*, 2004, 722–734; C. Stevens, M. Gallant and N. De Kimpe, *Tetrahedron Lett.*, 1999, **40**, 3457–3460.
10 N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, 1960, **82**, 6418–6419; N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, 1962, **84**, 4806–4813.
11 A. M. M. Antunes, V. D. B. Bonifacio, S. C. C. Nascimento, A. M. Lobo, P. S. Branco and S. Prabhakar, *Tetrahedron*, 2007, **63**, 7009–7017; A. M. M. Antunes, S. J. L. Marto, P. S. Branco, S. Prabhakar and A. M. Lobo, *Chem. Commun.*, 2001, 405–406.
12 D. A. Alonso and P. G. Andersson, *J. Org. Chem.*, 1998, **63**, 9455–9461.
13 L. C. Vishwakarma, O. D. Stringer and F. A. Davis, *Org. Synth*, 1988, **66**, 203–210.

14 D. A. Evans, M. M. Faul and M. T. Bilodeau, *J. Am. Chem. Soc.*, 1994, **116**, 2742–2753; J. L. Han, Y. F. Li, S. J. Zhi, Y. Pan, C. Timmons and G. G. Li, *Tetrahedron Lett.*, 2006, **47**, 7225–7228; J. W. W. Chang, T. M. U. Ton, Z. Y. Zhang, Y. J. Xu and P. W. H. Chan, *Tetrahedron Lett.*, 2009, **50**, 161–164; U. K. Nadir and A. Arora, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2605–2609.
15 A. Hasaninejad, A. Zare, H. Sharghi and M. Shekouhy, *Arkivoc*, 2008, 64–74; K. Y. Lee, C. G. Lee and J. N. Kim, *Tetrahedron Lett.*, 2003, **44**, 1231–1234; J. H. Wynne, S. E. Price, J. R. Rorer and W. M. Stalick, *Synth. Commun.*, 2003, **33**, 341–352.
16 F. W. Stacey, J. C. Sauer and B. C. McKusick, *J. Am. Chem. Soc.*, 1959, **81**, 987–992; A. Stojanovic and P. Renaud, *Helv. Chim. Acta*, 1998, **81**, 353–373.
17 J. Sisko and S. M. Weinreb, *J. Org. Chem.*, 1990, **55**, 393–395.
18 N. De Kimpe, R. Verhe, L. De Buyck and N. Schamp, *Recl. Trav. Chim. Pays-Bas-J. Roy. Neth. Chem. Soc.*, 1977, **96**, 242–246.
19 Y. Sugihara, S. Iimura and J. Nakayama, *Chem. Commun.*, 2002, 134–135.
20 Y. Yamada, T. Oine and I. Inoue, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 343–347.
21 M. K. Gurjar, S. Karmakar, D. K. Mohapatra and U. D. Phalgune, *Tetrahedron Lett.*, 2002, **43**, 1897–1900.
22 L. W. Bieber and M. C. F. de Araujo, *Molecules*, 2002, **7**, 902–906.
23 T. Ankner and G. Hilmersson, *Org. Lett.*, 2009, **11**, 503–506.
24 A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford and P. W. G. Smith, *Vogel's Textbook of Practical Organic Chemistry*, 5th edn, 1989, Prentice Hall, England.
25 T. Hori, S. P. Singer and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 1456–1459.

