Supporting Information
for
Isotopic labelling studies for a gold-catalysed skeletal rearrangement of alkynyl aziridines

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General Experimental

Asynt DrySin heating blocks on stirrer hotplates were employed for reactions with temperature control via an external probe. Infrared spectra were recorded neat on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Only selected absorbencies ($\nu_{\text{max}}$) are reported, in cm$^{-1}$. High resolution mass spectra (HRMS) were recorded on a VG ProSpec or a VG-ZabSpec at 70 eV when utilising electron impact ionisation (EI). A Micromass LCT using a methanol mobile phase was used for HRMS utilising electrospray ionisation. In both cases (EI or ES), HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as $m/z$. NMR: Spectra were recorded on Bruker AC300 ($^1$H = 300 MHz, $^{13}$C = 75.5 MHz), Bruker AV300 ($^1$H = 300 MHz, $^{13}$C = 75.5 MHz) or Bruker AV400 ($^1$H = 400 MHz, $^{13}$C = 101 MHz), in the solvents indicated; Chemical shifts ($\delta$) are given in ppm relative to TMS. Solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl$_3$: $\delta$C = 77.0 ppm; CHCl$_3$ in CDCl$_3$: $\delta$H = 7.26 ppm). Coupling constants ($J$) are reported in Hz. Multiplicity is denoted in $^1$H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet) and m (multiplet). $^{13}$C NMR spectra were recorded using the PENDANT pulse sequence from the Bruker standard pulse program library. Melting points were recorded in open glass capillaries on a Stuart Scientific apparatus and are uncorrected. Reactions were followed by thin layer chromatography (TLC) using Macherey Nagel silica gel 60F254 analytical plates (plastic support) which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), and potassium permanganate/Δ. Purification by flash chromatography was performed on Fluorochem silica gel 60 (0.043–0.063 mm). All reactions in non-aqueous solvents were conducted in flame-dried glassware under an argon atmosphere and with magnetic stirring. Volumes of less than 0.2 mL were measured and dispensed with gas tight syringes. Evaporation and concentration under reduced pressure was performed at 10–700 mbar at 40 °C. All pure products of reactions were dried under high vacuum (<1 mbar).

All reagents were obtained from commercial sources and used without further purification. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: Diethyl ether (sodium benzophenone ketyl), toluene (sodium), dichloromethane (CaH$_2$) and dichloroethane (CaH$_2$). Dess-Martin periodinane was prepared from 2-iodoxybenzoic acid (IBX) [1] following a known procedure [2].
Procedures and Characterisation

Preparation of alkynyl aziridines

Formation of aziridines from imine and sulfonium salt: General Procedure 1 (GP1):
The corresponding sulfonium salt (1.2 mmol) and Cs₂CO₃ (1.2 mmol) were added sequentially to a solution of the imine (1.0 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature until completion and filtered through a pad of silica to remove the inorganic salts. The filtrate was then concentrated under reduced pressure and the residue purified by flash chromatography to afford the alkynyl aziridine.

Sulfonium salt preparation: General procedure 2 (GP2)
Dimethyl sulfide (15.0 mmol, 932 mg, 1.1 mL) was added to a solution of the bromide (5 mmol) in acetone (5 mL) and the reaction mixture stirred at room temperature for 3 days. A white solid was formed which was removed by filtration, washed with diethyl ether (4 × 10 mL) and dried to afford the corresponding pure sulfonium salt.

Sonogashira coupling of aryl iodides with propargyl alcohol: General procedure 3 (GP3)
Pd(PPh₃)₂Cl₂ (0.75 mmol, 530 mg), CuI (1.5 mmol, 285 mg) and piperidine (47.8 mmol, 4.72 mL) were added to a solution of aryl iodide (25 mmol) in toluene (30 mL) at room temperature. After stirring for 5 min at room temperature, propargyl alcohol (25.5 mmol, 1.48 mL) was added dropwise. The reaction mixture was then heated at 40 °C for 12 h. After cooling to room temperature, the reaction was filtered through a plug of silica and eluted with EtOAc. The filtrate was concentrated under reduced pressure and purification of the residue by flash chromatography gave the pure propargylic alcohol.

Preparation of propargylic bromides from propargylic alcohols: General procedure 4 (GP4)
Bromine (1.9 equiv) was added dropwise to a solution of PPh₃ (1.1 equiv) in CH₂Cl₂ at 0 °C. The reaction mixture was stirred for 20 min at 0 °C before a solution of the alcohol (1 equiv) in CH₂Cl₂ was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h. Water (25 mL) was added to quench the reaction and the two phases were separated. The aqueous phase was washed with CH₂Cl₂ (3 × 20 mL) and the combined organic extracts were washed with brine (20 mL), dried (Na₂SO₄) and concentrated under
reduced pressure. Purification of the residue by flash chromatography gave the corresponding propargylic bromide.

4-Methylbenzaldehyde-α-d

Ethyl 4-methylbenzoate 5 (2.5 mmol, 0.39 mL) was added to a suspension of LiAlD₄ (3.5 mmol, 147 mg) in Et₂O (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. After cooling to 0 °C, water (2.5 mL) was cautiously added to quench the reaction. A solution of HCl (10%, 2.5 mL) was added to solubilise the suspension and the two phases were separated. The aqueous phase was washed with Et₂O (3 × 10 mL). The combined organic abstracts were washed with brine (10 mL), dried (Na₂SO₄), and concentrated under reduced pressure to give 4-methylbenzyl alcohol-α,α-d.

A solution of the crude deuterated alcohol in CH₂Cl₂ (2 mL) was added to a solution of DMP (3 mmol, 1.26 g) in CH₂Cl₂ (5 mL). The reaction mixture was stirred at room temperature for 2 h and a solution of Na₂S₂O₃ (5 mL) added to quench the reaction. The two phases were separated and the aqueous phase was washed with CH₂Cl₂ (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The residue was purified by distillation under reduced pressure (78 °C at 10 mmHg) to give the product as a colourless liquid (455 mg, 85%); δH (300 MHz; CDCl₃) 2.43 (3H, s, CH₃), 7.30 (2H, d, J 7.9, 2 × CH), 7.75 (2H, d, J 7.9, 2 × CH); δC (75 MHz; CDCl₃) 21.9 (CH₃), 129.7 (2C, 2 × CH), 129.9 (2C, 2 × CH), 134.2 (C quat), 145.5 (C quat).

N-(Deuteriophenylmethylene)-4-methylbenzenesulfonamide (6)

A mixture of 4-methylbenzaldehyde-α-d (2 mmol, 428 mg), p-toluenesulfonamide (1.9 mmol, 325 mg), amberlyst (150 mg) and 4 Å molecular sieve (150 mg) in toluene was stirred under reflux in a Dean–Stark apparatus. After 12 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue recrystallized from ethyl acetate/n-pentane to give imine 6 as a white solid (383 mg, 70%); 99–100 °C; νmax (neat)/cm⁻¹ 3356, 3260, 1582, 1552, 1508, 1494, 1445, 1409, 1387, 1318, 1303, 1288, 1155, 1089, 1033, 1018, 905, 858, 821, 809, 785, 753, 705; δH (300 MHz; CDCl₃) 2.43 (6H, s, 2 × CH₃), 7.28 (2H, d, J 7.9, 2 × CH), 7.34 (2H, d, J 7.9, 2 × CH), 7.81 (2H, d, J 8.2, 2 × CH), 7.88 (2H, d, J 8.2, 2 × CH); δC (75 MHz; CDCl₃) 21.6 (CH₃), 22.0 (CH₃), 128.0 (2C, 2 × CH), 129.8 (2C, 2 × CH), 129.9 (2C, 2 × CH), 131.4 (2C, 2 × CH),
135.5 (C_{quat}), 144.4 (2C, 2 × C_{quat}), 146.4 (2C, 2 × C_{quat}); HRMS m/z (TOF ES+) 297.0791. C_{13}H_{14}DNO_2NaS requires 297.0784.

2-Deuterio-3-hex-1-ynyl-1-(toluene-4-sulfonyl)-2-p-tolylaziridine (4)

Following GP1 from imine 6 and sulfonium salt 7, reaction time 3 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave aziridine 4 as a beige solid (143 mg, 77%, 14:1 cis:trans); υ_{max} (neat)/cm\(^{-1}\) 2961, 2926, 2874, 2248, 1921, 1598, 1518, 1458, 1410, 1363, 1323, 1301, 1181, 1161, 1133, 1090, 1019, 914, 894, 838, 805, 757, 704; δ\(_H\) (300 MHz; CDCl\(_3\)) 0.76 (3H, t, J 7.2, CH\(_3\)), 1.05–1.18 (2H, m, CH\(_2\)), 1.22–1.31 (2H, m, CH\(_2\)), 2.02 (2H, td, J 6.9 and 1.8, CH\(_2\)), 2.32 (3H, s, CH\(_3\)), 2.43 (3H, s, CH\(_3\)), 3.60 (1H, t, J 1.8, CH), 7.09 (2H, d, J 8.1, 2 × CH), 7.21 (2H, d, J 8.1, 2 × CH), 7.33 (2H, d, J 8.4, 2 × CH), 7.87 (2H, d, J 8.4, 2 × CH); δ\(_C\) (75 MHz; CDCl\(_3\)) 13.4 (CH\(_3\)), 18.3 (CH\(_2\)), 21.2 (CH\(_3\)), 21.5 (CH\(_2\)), 21.6 (CH\(_3\)), 30.0 (CH\(_2\)), 36.1 (CH), 72.3 (C_{quat}), 86.6 (C_{quat}), 127.6 (2C, 2 × CH), 127.9 (2C, 2 × CH), 128.6 (2C, 2 × CH), 129.1 (C_{quat}), 129.7 (2C, 2 × CH), 134.8 (C_{quat}), 138.0 (C_{quat}), 144.7 (C_{quat}); HRMS m/z (TOF ES+) 391.1563. C_{22}H_{24}DNO_2NaS requires 391.1566.

13C-enriched benzaldehyde

A solution of 13C-enriched benzoic acid (5 mmol, 610 mg, 13C:12C 1:5) in Et\(_2\)O (5 mL), was added dropwise to a suspension of LiAlH\(_4\) (12 mmol, 504 mg) in Et\(_2\)O (25 mL) at 0 °C. After 20 min stirring the reaction mixture was heated at 50 °C for 2 h. After cooling to 0 °C, water (15 mL) was cautiously added to quench the reaction. A solution of HCl (10%, 5 mL) was added to solubilise the suspension and the two phases were separated. The aqueous phase was washed with Et\(_2\)O (3 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried (Na\(_2\)SO\(_4\)), and concentrated under reduced pressure to give 13C-enriched benzyl alcohol.

A solution of the crude 13C-enriched benzyl alcohol in CH\(_2\)Cl\(_2\) (5 mL) was added to a solution of DMP (7.5 mmol, 3.16 g) in CH\(_2\)Cl\(_2\) (30 mL). The reaction mixture was stirred at room temperature for 4 h and a solution of Na\(_2\)S\(_2\)O\(_3\) (15 mL) added to quench the reaction. The two phases were separated and the aqueous phase was washed with CH\(_2\)Cl\(_2\) (3 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried (Na\(_2\)SO\(_4\)) and concentrated under reduced pressure. The residue was purified by distillation under reduced
pressure (75 °C at 10 mmHg) to give $^{13}$C-enriched benzaldehyde as a colourless liquid (425 mg, 80%); $\delta_H$ (300 MHz; CDCl$_3$) 7.50–7.73 (3H, m, 3 × CH), 7.75–7.92 (2H, m, 2 × CH), 10.07 (1H, s, CH); $\delta_C$ (75 MHz; CDCl$_3$) 129.2 (2C, 2 × CH), 130.0 (2C, 2 × CH), 134.7 (CH), 136.7 (C$_{quat}$), 192.6 ($^{13}$C-enriched signal, C$_{quat}$).

$^{13}$C-enriched N-benzylidene-4-methylbenzenesulfonamide (10)

A 1:5 mixture of benzaldehyde-$\alpha$-$^{13}$C and benzaldehyde (5.5 mmol, 589 mg), p-toluenesulfonamide (5.0 mmol, 856 mg), amberlyst 15 (380 mg) and 4Å molecular sieve (380 mg) in toluene (30 mL) was stirred at 130 °C in a Dean-Stark apparatus. After 12 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from ethyl acetate/n-pentane to give $^{13}$C-enriched imine 10 as a white solid (907 mg, 70%); mp 102–103 °C; $\nu_{max}$ (neat)/cm$^{-1}$ 2922, 2853, 2179, 1598, 1449, 1413, 1364, 1326, 1291, 1245, 1158, 1135, 1090, 1061, 994, 959, 859, 838, 824, 815, 749, 701; $\delta_H$ (300 MHz; CDCl$_3$) 2.41 (3H, s, CH$_3$), 7.35 (2H, d, $J$ 8.0, 2 × CH), 7.49 (2H, d, $J$ 8.0, 2 × CH), 7.59–7.64 (1H, m, CH), 7.88–7.94 (4H, m, 4 × CH), 9.03 (1H, s, CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 128.0 (2C, 2 × CH), 129.1 (2C, 2 × CH), 129.8 (2C, 2 × CH), 131.3 (2C, 2 × CH), 132.4 (C$_{quat}$), 134.9 (CH), 135.1 (C$_{quat}$), 144.6 (C$_{quat}$), 170.1 ($^{13}$C-enriched signal, CH); HRMS $m/z$ (TOF ES+) 283.0592. C$_{13}^{13}$CH$_{13}$NO$_2$NaS requires 283.0598.

$^{13}$C-enriched 2-(hex-1-ylnyl)-3-phenyl-1-(toluene-4-sulfonyl)aziridine (11)

Following GPI from $^{13}$C-enriched imine 10 and sulfonium salt 7 [3], reaction time 3 h. Purification by flash chromatography [hexane:ethyl acetate (12:1)] gave $^{13}$C-enriched aziridine 11 as a white solid (212 mg, 60%, 8:1 cis:trans); $\nu_{max}$ (neat)/cm$^{-1}$ 2960, 2934, 2252, 1601, 1497, 1455, 1381, 1319, 1305, 1292, 1230, 1187, 1158, 1088, 1038, 1025, 871, 811, 784, 754, 738, 717, 695, 672; $\delta_H$ (300 MHz; CDCl$_3$) 0.75 (3H, t, $J$ 7.2, CH$_3$), 1.01–1.32 (4H, m, 2 × CH$_2$), 1.98 (2H, td, $J$ 6.8 and 1.7, CH$_2$), 2.42 (3H, s, CH$_3$), 3.63 (1H, dt, $J$ 6.9 and 1.7, CH), 3.94 (1H, d, $J$ 6.9, CH), 7.21–7.39 (7H, m, 7 × CH), 7.88 (2H, d, $J$ 8.3, 2 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 13.4 (CH$_3$), 18.2 (CH$_2$), 21.4 (CH$_2$), 21.6 (CH$_3$), 30.0 (CH$_2$), 36.2 (CH), 46.1 ($^{13}$CH, enriched signal, CH), 72.1 (C$_{quat}$), 86.7 (C$_{quat}$), 127.7 (2C, 2 × CH) 127.9 (4C, 4 × CH), 128.2
(CH), 129.8 (2C, 2 × CH), 132.2 (C_{quat}), 134.7 (C_{quat}), 144.6 (C_{quat}); HRMS m/z (TOF ES+) 377.1376. C_{20}^{13}CH_{23}NO_2NaS requires 377.1381.

**13C-enriched 2-phenyl-3-(phenylethynyl)-1-(toluene-4-sulfonyl)aziridine (14)**

Following GP1 from $^{13}$C-enriched imine 10 and sulfonium salt 12 [3], reaction time 1.5 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave $^{13}$C-enriched aziridine 14 (298 mg, 80%, 12:1 cis:trans); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3032, 2950, 2926, 2240, 1597, 1490, 1457, 1441, 1319, 1157, 1087, 1071, 873, 854, 784, 757, 708; $\delta_H$ (300 MHz; CDCl$_3$) 2.44 (3H, s, CH$_3$), 3.87 (1H, d, J 6.9, CH), 4.09 (1H, d, J 6.9, CH), 7.12–7.28 (4H, m, 4 × CH), 7.29–7.45 (8H, m, 8 × CH), 7.92 (2H, d, J 8.3, 2 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.7 (CH$_3$), 36.3 (CH), 46.5 ($^{13}$C-enriched signal, CH), 81.6 (C_{quat}), 85.1 (C_{quat}), 121.8 (C_{quat}), 127.8 (2C, 2 × CH), 128.0 (4C, 4 × CH), 128.1 (2C, 2 × CH), 128.5 (CH), 128.8 (CH), 129.9 (2C, 2 × CH), 131.8 (2C, 2 × CH), 132.1 (C_{quat}), 134.6 (C_{quat}), 144.9 (C_{quat}); HRMS m/z (TOF ES+) 397.1074. C$_{22}^{13}$CH$_{18}$NO$_2$NaS requires 397.1068.

**13C-enriched 2-phenyl-3-(4-phenylbut-1-yn-1-yl)-1-(toluene-4-sulfonyl)aziridine (15)**

Following GP1 from $^{13}$C-enriched imine 10 and sulfonium salt 13 [3], reaction time 4 h. Purification by flash chromatography [hexane:ethyl acetate (20:1)] gave $^{13}$C-enriched aziridine 15 (269 mg, 67%, 14:1 cis:trans). $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3029, 2925, 2248, 1597, 1495, 1454, 1384, 1327, 1291, 1235, 1158, 1090, 1021, 875, 814, 783, 742, 695; $\delta_H$ (300 MHz; CDCl$_3$) 2.27–2.33 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 2.50–2.65 (2H, m, CH$_2$), 3.62 (1H, dt, J 6.9 and 1.8, CH), 3.94 (1H, d, J 6.9, CH), 6.95–7.01 (2H, m, 2 × CH), 7.14–7.24 (3H, m, 3 × CH), 7.29 (5H, s, 5 × CH), 7.34 (2H, d, J 8.3, 2 × CH), 7.88 (2H, d, J 8.3, 2 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 20.8 (CH$_2$), 21.7 (CH$_3$), 34.1 (CH$_2$), 36.1 (CH), 46.1 ($^{13}$C-enriched signal, CH), 73.0 (C_{quat}), 85.8 (C_{quat}), 126.2 (2C, 2 × CH), 127.8 (2C, 2 × CH), 127.9 (2C, 2 × CH), 128.0 (2C, 2 × CH), 128.3 (5C, 5 × CH), 129.8 (2C, 2 × CH), 132.2 (C_{quat}), 134.7 (C_{quat}), 140.2 (C_{quat}), 144.8 (C_{quat}); HRMS m/z (TOF ES+) 425.1373. C$_{24}^{13}$CH$_{23}$NO$_2$NaS requires 425.1381.
3-(4-Trifluoromethylphenyl)prop-2-yn-1-ol (24) [4]

Following GP3 from 1-iodo-4-(trifluoromethyl)benzene (6.80 g, 3.67 mL). Purification by flash chromatography [hexane:ethyl acetate (4:1)] gave alcohol 24 as a brown solid (2.75 g, 90%); ν_max (neat)/cm⁻¹ 3350, 3080, 2890, 2275, 1622, 1532, 1405, 1328, 1186, 1129, 953, 786, 732, 689; δ_H (300 MHz; CDCl₃) 1.91 (1H, t, J 5.5, OH), 4.54 (2H, d, J 5.5, CH₂), 7.50 (2H, d, J 8.5, 2 × CH), 7.54 (2H, d, J 8.5, 2 × CH); δ_C (75 MHz; CDCl₃) 51.5 (CH₂), 84.3 (C_quat), 89.6 (C_quat), 122.5 (q, J 272.2, C_quat), 125.2 (2C, q, J 3.5, 2 × CH), 126.4 (C_quat), 130.2 (q, J 32.9, C_quat), 131.9 (2C, 2 × CH).

3-(4-Methoxyphenyl)prop-2-yn-1-ol (25) [5]

Following GP3 using 4-iodoanisol (5.85 g). Purification by flash chromatography [hexane:ethylacetate (2:1)] gave alcohol 25 as a brown solid (2.64 g, 65%); δ_H (300 MHz; CDCl₃) 1.83 (1H, s, OH), 3.81 (3H, s, CH₃), 4.49 (2H, s, CH₂), 6.85 (2H, d, J 6.5, 2 × CH), 7.40 (2H, d, J 6.5, 2 × CH); δ_C (75 MHz; CDCl₃) 51.7 (CH₂), 55.3 (CH₃), 85.7 (C_quat), 85.9 (C_quat), 114.0 (2C, 2 × CH), 114.6 (C_quat), 133.2 (2C, 2 × CH), 159.8 (C_quat); HRMS m/z (TOF EI+) 162.0683. C₁₀H₁₀O₂ requires 162.0681.

1-(3-Bromo-1-ynyl)-4-(trifluoromethyl)benzene (26) [6]

Following GP4 using PPh₃ (11 mmol, 2.88 g), Br₂ (10.9 mmol, 0.55 mL) and alcohol 24 (2.00 g) in CH₂Cl₂ (30 mL). Purification by flash chromatography (n-pentane) gave bromine 26 as a yellow oil (2.36 g, 90%); ν_max (neat)/cm⁻¹ 3012, 2232, 2199, 1930, 1725, 1669, 1516, 1407, 1423, 1329, 1129, 1073, 1052, 1022, 850, 769; δ_H (300 MHz; CDCl₃) 4.16 (2H, s, CH₂), 7.54 (2H, d, J 8.4, 2 × CH), 7.57 (2H, d, J 8.4, 2 × CH); δ_C (75 MHz; CDCl₃) 14.4 (CH₂), 86.6 (C_quat), 123.9 (q, J 272.2, C_quat), 125.3 (2C, q, J 3.8, 2 × CH), 125.9 (C_quat), 130.6 (q, J 32.8, C_quat), 132.1 (2C, 2 × CH); HRMS m/z (TOF EI+) 261.9590. C₁₀H₇BrF₃ requires 261.9605.

1-(3-Bromo-1-ynyl)-4-methoxybenzene (27) [7]

Following GP4 from PPh₃ (11 mmol, 2.88 g), Br₂ (10.9 mmol, 0.55 mL) and alcohol 25 (1.62 g) in CH₂Cl₂ (30 mL). Purification by flash chromatography (hexane) gave bromine 27 as a colourless oil (2.02 g, 90%); ν_max (neat)/cm⁻¹ 2228, 1609, 1602, 1518, 1471, 1102, 1001, 960, 820; δ_H (300 MHz; CDCl₃) 3.79
(3H, s, CH₃), 4.17 (2H, d, J 9.0, 2 × CH), 7.39 (2H, d, J 9.0, 2 × CH); δC (75 MHz; CDCl₃) 16.0 (CH₂), 55.3 (CH₃), 83.0 (C_quat), 86.9 (C_quat), 114.0 (2C, 2 × CH), 114.1 (C_quat), 133.5 (2C, 2 × CH), 160.0 (C_quat).

Dimethyl(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)sulfonium bromide (28)

Following GP2 from bromide 26 (1.315 g) gave sulfonium salt 28 (1.625 g, 50%); mp 139–140 °C; ν_max (neat)/cm⁻¹ 3006, 2924, 2891, 2245, 1618, 1407, 1319, 1231, 1162, 1126, 1107, 1067, 1045, 1017, 1001, 982, 840, 712; δ_H (300 MHz; CDCl₃) 3.36 (6H, s, 2 × CH₃), 5.43 (2H, s, CH₂), 7.60–7.70 (4H, m, 4 × CH); δ_C (75 MHz; CDCl₃) 24.9 (2C, 2 × CH₃), 33.7 (CH₂), 76.9 (C_quat), 89.5 (C_quat), 123.5 (q, J 272.7, C_quat), 124.3 (C_quat), 125.7 (2C, q, J 3.3, 2 × CH), 131.6 (q, J 33.6, C_quat), 132.5 (2C, 2 × CH); HRMS m/z (TOF ES+) 245.0607. C₁₂H₁₂F₃S requires 245.0612.

3-(4-Methoxyphenyl)prop-2-yn-1-yl)dimethylsulfonium bromide (29)

Following GP2 from bromide 27 (1.125 g) gave sulfonium salt 29 (1.335 g, 93%); mp 124–125 °C; ν_max (neat)/cm⁻¹ 2969, 2907, 2864, 2216, 1605, 1565, 1509, 1459, 1421, 1325, 1296, 1276, 1246, 1180, 1169, 1105, 1046, 1021, 1009, 828, 800, 703; δ_H (300 MHz; CDCl₃) 3.31 (6H, s, 2 × CH₃), 3.81 (3H, s, CH₃), 5.31 (2H, s, CH₂), 6.85 (2H, d, J 8.8, 2 × CH), 7.40 (2H, d, J 8.8, 2 × CH); δ_C (75 MHz; CDCl₃) 24.6 (2C, 2 × CH₃), 34.2 (CH₂), 55.3 (CH₃), 73.0 (C_quat), 91.2 (C_quat), 112.5 (C_quat), 114.2 (2C, 2 × CH), 133.7 (2C, 2 × CH), 160.6 (C_quat); HRMS m/z (TOF ES+) 207.0844. C₁₂H₁₅OS requires 207.0840.

13C-enriched 2-phenyl-1-(toluene-4-sulfonyl)-3-((4-trifluoromethyl)phenyl)ethynyl)-aziridine (30)

Following GP1 from 13C-enriched imine 10 and sulfonium salt 28, reaction time 30 min. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave 13C-enriched aziridine 30 (287 mg, 65%, 15:1 cis:trans); ν_max (neat)/cm⁻¹ 3065, 3012, 1617, 1596, 1496, 1456, 1405, 1378, 1320, 1157, 1127, 1106, 1088, 1059, 1016, 973, 870, 838, 812, 785, 737, 696; δ_H (300 MHz; CDCl₃) 2.44 (3H, s, CH₃), 3.90 (1H, d, J 6.8, CH), 4.13 (1H, d, J 6.8, CH), 7.27 (2H, d,
Following GPI from $^{13}$C-enriched imine 10 and sulfonium salt 29, reaction time 45 min. Purification by flash chromatography [hexane:ethyl acetate (20:1)] gave $^{13}$C-enriched aziridine 31 (242 mg, 60 %, 16:1 cis:trans); ν$_{max}$ (neat)/cm$^{-1}$ 3036, 2933, 2838, 2228, 1603, 1509, 1455, 1327, 1291, 1247, 1156, 1089, 1027, 976, 872, 831, 812, 786, 733, 697; δ$_H$ (300 MHz; CDCl$_3$) 2.43 (3H, s, CH$_3$), 3.76 (3H, s, CH$_3$), 3.86 (1H, d, J 6.9, CH), 4.07 (1H, d, J 6.9, CH), 6.73 (2H, d, J 8.9, 2 × CH), 7.11 (2H, d, J 8.9, 2 × CH), 7.30–7.41 (7H, m, 7 × CH), 7.91 (2H, d, J 8.3, 2 × CH); δ$_C$ (75 MHz; CDCl$_3$) 21.7 (CH$_3$), 36.5 (CH), 46.5 ($^{13}$C-enriched signal, CH), 55.2 (CH$_3$), 80.2 (C$_{\text{quat}}$), 85.3 (C$_{\text{quat}}$), 113.8 (2C, 2 × CH), 127.8 (2C, 2 × CH), 128.0 (5C, 5 × CH, C$_{\text{quat}}$), 128.4 (CH), 129.8 (2C, 2 × CH), 132.2 (C$_{\text{quat}}$), 133.4 (2C, 2 × CH), 134.7 (C$_{\text{quat}}$), 144.9 (C$_{\text{quat}}$), 159.9 (C$_{\text{quat}}$); HRMS m/z (TOF ES+) 426.1089. C$_{23}^{13}$CH$_2$NO$_3$F$_3$NaS requires 426.1095.

$^{13}$C-enriched 2-((4-methoxyphenyl)ethynyl)-3-phenyl-1-(toluene-4-sulfonyl)aziridine (31)
Cycloisomerisation experiments using D-labelled alkynyl aziridine 4

Gold-catalysed cycloisomerisations of alkynyl aziridines using Ph3PAuCl/AgOTf:
general procedure 5 (GP5):
The catalyst system was prepared by the addition of anhydrous CH2Cl2 (0.5 mL) to Ph3PAuCl (0.01 mmol, 5.0 mg) and AgOTf (0.01 mmol, 2.5 mg) in a flame-dried Schlenk flask under an argon atmosphere. After stirring for 10 min at room temperature, a white precipitate of AgCl was observed and a solution of the corresponding alkynyl aziridine (0.2 mmol) in anhydrous CH2Cl2 (0.5 mL) was added. The reaction mixture was stirred at room temperature until complete consumption of aziridine before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure. The residue was purified by flash chromatography as indicated.

2-Butyl-3-deuterio-1-(toluene-4-sulfonyl)-4-p-tolyl-1H-pyrrole (8b)

Following GP5 from aziridine 4 (74 mg), reaction time 1 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave a mixture of 2,4-disubstituted pyrrole 8b, 2,4-disubstituted pyrrole 8c and 2,5-disubstituted pyrrole 9 (13 mg, 18%, 10.5:3:1:8b:8a:9); δH (300 MHz; CDCl3) 0.90 (3H, t, J 7.3, CH3), 1.30–1.43 (2H, m, CH2), 1.53–1.64 (2H, m, CH2), 2.35 (3H, s, CH3), 2.40 (3H, s, CH3), 2.68 (2H, t, J 7.4, CH2), 7.16 (2H, d, J 8.2, 2 × CH), 7.28 (2H, d, J 8.4, 2 × CH), 7.40 (1H, s, CH), 7.68 (2H, d, J 8.4, 2 × CH); δC (75 MHz; CDCl3) 13.9 (CH3), 21.1 (CH3), 21.6 (CH3), 22.4 (CH2), 26.9 (CH2), 30.7 (CH2), 117.3 (CH), 125.3 (2C, 2 × CH), 126.7 (2C, 2 × CH,129.4 (2C, 2 × CH), 129.9 (2C, 2 × CH), 130.8 (C quat), 136.4 (C quat), 136.5 (C quat), 136.6 (C quat), 136.9 (C quat), 144.7 (C quat); HRMS m/z (TOF ES+) 391.1559. C22H24DNO2NaS requires 391.1566.
Cycloisomerisation experiments using $^{13}$C-labelled alkynyl aziridine 11

Gold-catalysed cycloisomerisations of alkynyl aziridines using Ph$_3$PAuCl/AgOTs:

general procedure 6 (GP6):

The catalyst system was prepared by the addition of anhydrous ClCH$_2$CH$_2$Cl (0.5 mL) to Ph$_3$PAuCl (0.01 mmol, 5.0 mg) and AgOTs (0.01 mmol, 2.8 mg) in a flame-dried Schlenk flask under an argon atmosphere. After stirring for 10 min at room temperature, a white precipitate of AgCl was observed and a solution of the corresponding alkynyl aziridine (0.2 mmol) in anhydrous ClCH$_2$CH$_2$Cl (0.5 mL) was added. The reaction mixture was stirred at the indicated temperature until aziridine was completely consumed, before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure. When required the residue was purified by flash chromatography as indicated.

$^{13}$C-enriched 2-butyl-5-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (16)

Following GP6 from $^{13}$C enriched aziridine 11 (71 mg) at 70 °C for 4 h gave pyrrole 16 (69 mg, 98%); ν$_{\text{max}}$ (neat)/cm$^{-1}$ 3060, 2956, 2928, 2861, 1737, 1596, 1527, 1482, 1444, 1366, 1169, 1116, 1092, 911, 809, 759; δ$_H$ (300 MHz; CDCl$_3$) 0.97 (3H, t, $J$ 7.3, CH$_3$), 1.38–1.50 (2H, m, CH$_2$), 1.66–1.76 (2H, m, CH$_2$), 2.36 (3H, s, CH$_3$), 2.92 (2H, t, $J$ 7.7, CH$_2$), 6.04 (1H, d, $J$ 3.3, CH), 6.08 (1H, d, $J$ 3.3, CH), 7.14 (2H, d, $J$ 8.4, 2 × CH), 7.28 (2H, d, $J$ 8.4, 2 × CH), 7.32 (5H, s, 5 × CH); δ$_C$ (75 MHz; CDCl$_3$) 14.0 (CH$_3$), 21.6 (CH$_3$), 22.5 (CH$_2$), 29.3 (CH$_2$), 31.6 (CH$_2$), 112.6 (CH), 115.6 (CH), 126.4 (2C, 2 × CH), 127.2 (2C, 2 × CH), 127.7 (CH), 129.3 (2C, 2 × CH), 130.4 (2C, 2 × CH), 133.3 (C$_{\text{quat}}$), 136.4 (C$_{\text{quat}}$), 138.0 ($^{13}$C-enriched signal, C$_{\text{quat}}$), 139.9 (C$_{\text{quat}}$), 144.2 (C$_{\text{quat}}$); HRMS $m/z$ (TOF ES$^+$) 377.1373. C$_{20}$H$_{23}$NO$_2$NaS requires 377.1381.
Mixture of $^{13}$C-enriched 2-butyl-4-phenyl-1-(toluene-4-sulfonyl)-$1H$-pyrroles (17a and 17b) with 2-butyl-5-phenyl-1-(toluene-4-sulfonyl)-$1H$-pyrrole (16).

Following GP5 from $^{13}$C-enriched aziridine 11 (71 mg) at room temperature for 2 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave a mixture of 2,4-disubstituted pyrroles 17a, 17b and 2,5-disubstituted pyrrole 16 (50 mg, 71%, 16:(17a+17b) 1:5); HRMS $m/z$ (TOF ES+) 377.1378. $C_{20}^{13}$CH$_3$NO$_2$NaS requires 377.1381.

$^{13}$C-enriched 2-butyl-4-phenyl-1-(toluene-4-sulfonyl)-$1H$-pyrroles (17a/b):

$\delta_H$ (300 MHz; CDCl$_3$) 0.91 (3H, t, $J$ 7.3, CH$_3$), 1.31–1.43 (2H, m, CH$_2$), 1.54–1.61 (2H, m, CH$_2$), 2.41 (3H, s, CH$_3$), 2.69 (2H, t, $J$ 7.6, CH$_2$), 6.33 (1H, dt, $J$ 1.9 and 1.0, CH), 7.29 (2H, d, $J$ 8.4, 2 × CH), 7.32 (2H, d, $J$ 8.4, 2 × CH), 7.37 (1H, d, $J$ 8.2, CH), 7.51 (2H, dd, $J$ 8.4 and 8.2, 2 × CH), 7.58 (1H, d, $J$ 1.9, CH), 7.69 (2H, d, $J$ 8.4, 2 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 13.9 (CH$_3$), 21.6 (CH$_3$), 22.4 (CH$_2$), 26.9 (CH$_2$), 30.7 (CH$_2$), 110.4 (CH), 117.7 ($^{13}$C-enriched signal in 17a, CH), 125.4 (2C, 2 × CH), 126.7 (2C, 2 × CH), 126.8 (CH), 126.9 ($^{13}$C-enriched signal in 17b C$_{quat}$), 128.7 (2C, 2 × CH), 130.0 (2C, 2 × CH), 133.7 ($C_{quat}$), 136.3 ($C_{quat}$), 136.9 ($C_{quat}$), 144.8 ($C_{quat}$).
Cycloisomerisation experiment using $^{13}$C-labelled alkynyl aziridine 14

Mixture of $^{13}$C-enriched 2,4-diphenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (19) and 2,5-diphenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (18)

Following GP5 from $^{13}$C-enriched 2-phenyl-3-(phenylethynyl)-1-(toluene-4-sulfonyl)aziridine (75 mg) at room temperature for 2 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave a mixture of 2,4-disubstituted pyrrole 19 and 2,5-disubstituted pyrrole 18 (49 mg, 65%, 18:19 1:10); HRMS m/z (TOF ES+) 397.1075. $\text{C}_{22}^{^{13}}\text{CH}_{19}\text{NO}_{2}\text{NaS}$ requires 397.1068.

$^{13}$C-enriched 2,4-diphenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (19):

$\delta_H$ (300 MHz; CDCl$_3$) 2.34 (3H, s, CH$_3$), 6.49 (1H, d, J 2.0, CH), 7.24–7.37 (10H, m, 10 × CH), 7.53 (2H, d, J 7.1, 2 × CH), 7.73 (1H, d, J 2.0, CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 114.3 (CH), 119.5 ($^{13}$C-enriched signal, CH), 125.5 (2C, 2 × CH), 127.0 (CH), 127.1 (2C, 2 × CH), 127.4 (2C, 2 × CH), 128.4 (CH), 128.8 (2C, 2 × CH), 129.4 (2C, 2 × CH), 130.8 (2C, 2 × CH), 131.2 (C$_{\text{quat}}$), 133.3 (C$_{\text{quat}}$), 135.4 (C$_{\text{quat}}$), 136.9 (C$_{\text{quat}}$), 141.2 (C$_{\text{quat}}$), 144.7 (C$_{\text{quat}}$).

$^{13}$C-enriched 2,5-diphenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (18):

$\delta_H$ (300 MHz; CDCl$_3$) 2.34 (3H, s, CH$_3$), 6.24 (2H, m, 2 × CH), 7.06 (4H, m, 4 × CH), 7.35–7.46 (6H, m, 6 × CH), 7.49–7.53 (4H, m, 4 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 117.3 (2C, 2 × CH), 127.0 (4C, 4 × CH), 127.5 (2C, 2 × CH), 127.9 (2C, 2 × CH), 128.8 (4C, 4 × CH), 129.6 (2C, 2 × CH), 133.3 (2C, 2 × C$_{\text{quat}}$), 134.6 (C$_{\text{quat}}$), 141.3 (2C, $^{13}$C-enriched signal, 2 × C$_{\text{quat}}$), 144.3 (C$_{\text{quat}}$).
Cycloisomerisation experiment using $^{13}$C-labelled alkynyl aziridine 15

$^{13}$C-enriched 2-phenethyl-4-phenyl-1-(toluene-4-sulfonyl)-1$H$-pyrroles (21a and 21b) and 2-phenethyl-5-phenyl-1-(toluene-4-sulfonyl)-1$H$-pyrrole (20)

Following GP5 from $^{13}$C-enriched aziridine 15 (81 mg) was stirred at room temperature for 2 h. Purification by flash chromatography [hexane:ethyl acetate (20:1)] gave a mixture of 2,4-disubstituted pyroles 21a, 21b and 2,5-disubstituted pyrrole 20 (32 mg, 40%, 20:(21a+21b) 1:2); HRMS m/z (TOF ES+) 425.1376. C$_{24}$$^{13}$CH$_{23}$NO$_2$NaS requires 425.1381.

$^{13}$C-enriched 2-phenethyl-4-phenyl-1-(toluene-4-sulfonyl)-1$H$-pyrrole (21a/b):

$\delta_H$ (300 MHz; CDCl$_3$) 2.34 (3H, s, CH$_3$), 2.85–2.90 (2H, m, CH$_2$), 2.94–2.99 (2H, m, CH$_2$), 6.35 (1H, dt, $J$ 2.0 and 0.9, CH), 7.12–7.28 (8H, m, 8 × CH), 7.30–7.33 (2H, m, 2 × CH), 7.42–7.45 (2H, m, 2 × CH), 7.54 (1H, d, $J$ 2.0, CH), 7.63 (2H, d, $J$ 8.4, 2 × CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 29.3 (CH$_2$), 35.4 (CH$_2$), 111.2 (CH), 118.0 ($^{13}$C-enriched signal for 21a, CH), 125.5 (2C, 2 × CH), 126.1 (CH), 126.8 (2C, 2 × CH), 126.9 (CH), 127.0 ($^{13}$C-enriched signal for 21b, C$_{quat}$), 127.3 (4C, 4 × CH), 128.4 (2C, 2 × CH), 130.1 (2C, 2 × CH), 133.6 (C$_{quat}$), 136.0 (C$_{quat}$), 138.5 (C$_{quat}$), 141.2 (C$_{quat}$), 144.9 (C$_{quat}$).
$^{13}$C-enriched 2-phenethyl-5-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (20):

$\delta_H$ (300 MHz; CDCl$_3$) 2.36 (3H, s, CH$_3$), 3.05 (2H, m, CH$_2$), 3.24 (2H, m, CH$_2$), 6.02–6.09 (2H, m, 2 × CH), 7.13 (2H, d, $J$ 8.0, 2 × CH), 7.19–7.31 (7H, m, 7 × CH), 7.34 (5H, 5 × CH);

$\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 31.8 (CH$_2$), 36.3 (CH$_2$), 113.5 (CH), 115.7 (CH), 126.0 (CH), 126.4 (2C, 2 × CH), 127.3 (2C, 2 × CH), 127.8 (CH), 128.4 (2C, 2 × CH), 128.5 (2C, 2 × CH), 129.4 (2C, 2 × CH), 130.5 (2C, 2 × CH), 133.2 (C$_{quat}$), 136.3 (C$_{quat}$), 138.5 ($^{13}$C-enriched signal, C$_{quat}$), 138.8 (C$_{quat}$), 141.6 (C$_{quat}$), 144.4 (C$_{quat}$).
Cycloisomerisation experiments using $^{13}$C-labelled alkylnyl aziridine 30

$^{13}$C-enriched 4-phenyl-1-(toluene-4-sulfonyl)-2-(4-(trifluoromethyl)phenyl)-1H-pyrroles (32a) and (32b)

Following GP5 from $^{13}$C-enriched 2-phenyl-1-(toluene-4-sulfonyl)-3-((4-trifluoromethyl)phenyl)ethynyl)aziridine (88 mg) at room temperature for 2 h. Purification by flash chromatography [hexane:ethyl acetate (25:1)] gave a mixture of 2,4-disubstituted pyrroles 32a and 32b (39 mg, 45%); $\delta_H$ (300 MHz; CDCl$_3$) 2.36 (3H, s, CH$_3$), 6.55 (1H, d, $J$ 1.9, CH), 7.13 (2H, d, $J$ 8.1, 2 × CH), 7.26–7.31 (3H, m, 3 × CH), 7.37–7.46 (4H, m, 4 × CH), 7.51–7.55 (2H, m, 2 × CH), 7.61 (2H, d, $J$ 8.1, 2 × CH), 7.76 (1H, d, $J$ 1.9, CH); $\delta_C$ (75 MHz; CDCl$_3$) 21.6 (CH$_3$), 115.4 (CH), 120.4 ($^{13}$C-enriched signal in 32a, CH), 123.6 (q, $J$ 272.6, C$_{quat}$), 124.4 (2C, q, $J$ 3.1, 2 × CH), 125.5 (2C, 2 × CH), 127.0 (2C, 2 × CH), 127.3 (CH), 128.0 ($^{13}$C-enriched signal in 32b, C$_{quat}$), 128.9 (2C, 2 × CH), 129.6 (2C, 2 × CH), 130.2 (q, $J$ 32.8, C$_{quat}$), 130.9 (2C, 2 × CH), 132.9 (C$_{quat}$), 134.9 (C$_{quat}$), 135.2 (C$_{quat}$), 135.4 (C$_{quat}$) 145.1 (C$_{quat}$); HRMS $m/z$ (TOF ES+) 465.0939. C$_{23}^{13}$CH$_{18}$NO$_2$F$_3$NaS requires 465.0942.
Cycloisomerisation experiments using $^{13}$C-labelled alkynyl aziridine 31

Mixture of $^{13}$C-enriched 2-(4-methoxyphenyl)-5-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (33) and 2-(4-methoxyphenyl)-4-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (34)

Following GP5 from $^{13}$C enriched aziridine 31 (80 mg) at room temperature for 45 min. Purification by flash chromatography [hexane:ethyl acetate (20:1)] gave a mixture of 2,4-disubstituted pyrrole 34 and 2,5-disubstituted pyrrole 33 (8 mg, <10%, 33:34 2:3).

Only a complex and a “dirty” mixture of pyrroles was obtained. Characteristic resonances of the expected 2,4 and 2,5-disubstituted pyrroles are visible in $^1$H NMR:

2-(4-methoxyphenyl)-5-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (33): $\delta_H$ (300 MHz; CDCl$_3$) 2.35 (3H, s, CH$_3$), 3.87 (3H, s, CH$_3$), 6.16 (1H, d, $J$ 3.3, CH), 6.23 (1H, d, $J$ 3.3, CH), 6.85–7.50 (13H, m, 13 $\times$ CH), 7.70 (1H, d, $J$ 2.0, CH).

$^{13}$C NMR shows a $^{13}$C-enriched signal at 140.7 ppm characteristic of $^{13}$C enrichment at C-5 for a 2,5-pyrrole.

2-(4-methoxyphenyl)-4-phenyl-1-(toluene-4-sulfonyl)-1H-pyrrole (34): $\delta_H$ (300 MHz; CDCl$_3$) 2.35 (3H, s, CH$_3$), 3.88 (3H, s, CH$_3$), 6.43 (1H, d, $J$ 2.0, CH), 6.85–7.50 (13H, m, 13 $\times$ CH), 7.70 (1H, d, $J$ 2.0, CH).

$^{13}$C NMR shows a $^{13}$C-enriched signal at 119.2 ppm characteristic of $^{13}$C enrichment at C-5 for a 2,4-pyrrole.
References


