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Electronic Supplementary Information

Intermolecular (4+3) Cycloadditions of Aziridinyl Enolsilanes

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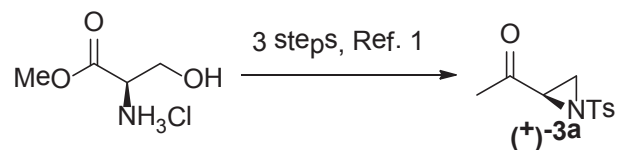
General Experimental

Preparative: All anhydrous reactions were performed in oven-dried round-bottomed flasks under a positive pressure of dry argon. Air and moisture-sensitive compounds were introduced via syringes or cannulae using standard inert atmosphere techniques. Reactions were monitored by thin layer chromatography (TLC) using E. Merck silica gel plates, Kieselgel 60 F₂₅₄ with 0.2 mm thickness. Components were visualized by illumination with short-wavelength ultra-violet light and/or staining. Flash column chromatography was performed with E. Merck silica gel 60 (230-400 mesh ASTM). Solvents and chemicals were purified according to standard procedures. All solvents used for reactions were distilled or dried by passing through drying columns. Tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), nitroethane (EtNO₂), furan, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were distilled from CaH₂ under argon. Cyclopentadiene was prepared from freshly cracking dicyclopentadiene. Other reagents were used as received.

Analytical: ¹H and ¹³C NMR nuclear magnetic resonance spectra were recorded in deuteriochloroform (CDCl₃), with tetramethylsilane (TMS) as an internal standard at ambient temperature on a Bruker DX 300 spectrometer, Bruker Avance 400 spectrometer, Bruker DX 500 spectrometer, or Bruker Avance 600 operating at 300 MHz, 400 MHz, 500 MHz or 600 MHz respectively for ¹H, and at 75 MHz, 100 MHz, 125 MHz or 150 MHz respectively for ¹³C. All spectra were calibrated at δ 7.26 or δ 0.00 ppm for ¹H spectra (residual CHCl₃ or TMS respectively), and 77.16 ppm for ¹³C spectra. Splitting patterns were designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR absorption spectra were recorded as solutions in CH₂Cl₂ on a Bio-Rad FTS 165 spectrometer from 4000 cm⁻¹ to 400 cm⁻¹. Electron impact mass spectrometry was recorded on a Finnigan MAT 95 mass spectrometer or API QSTAR PULSAR iLC/MS/TOF System for both low resolution and high resolution, with accurate mass reported for the molecular ion (M⁺) or next largest fragment thereof. Analytical HPLC was carried out on a Waters Analytical/Preparative HPLC system equipped with a 1525 Binary Pump, a 2707 Autosampler, and a variable wavelength Waters 2498 UV detector operating with Breeze 2 software. Preparative HPLC was carried out on a Waters HPLC with a 510 HPLC pump and 410 differential refractometer.

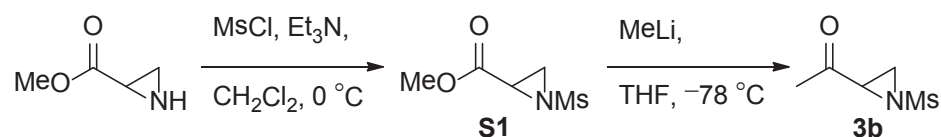
Preparation of Aziridinyl Ketones 3a-m

Preparation of 3a



Aziridinyl ketone **3a** was prepared according to literature procedure in 3 steps from D-serine methyl ester hydrochloride.¹ **(R)-1-(1-Tosylaziridin-2-yl)ethanone ((+)-3a)**: White solid; $R_f = 0.69$ (50% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 3.25 (dd, $J = 7.2, 4.1$ Hz, 1H), 2.77 (d, $J = 7.4$ Hz, 1H), 2.48 (d, $J = 4.1$ Hz, 1H), 2.744 (s, 3H), 2.06 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 201.6, 145.5, 133.9, 130.1, 128.3, 42.0, 32.0, 26.0, 21.8 ppm. The spectral characteristics corresponded to those of **3a** in the literature.¹ The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OF, 1.0 mL/min, $\lambda = 254$ nm, 40% IPA in hexane, t_R (major) = 20.38 min, t_R (minor) = 22.66 min] to be 99% ee.

Preparation of 3b



To a solution of methyl aziridine-2-carboxylate (0.4226 g, 4.180 mmol) in CH₂Cl₂ (50 mL) at 0 °C was added Et₃N (1.2 mL, 8.6 mmol) and MsCl (0.62 mL, 8.0 mmol). The resulting mixture was stirred for 1 h at 0 °C. The reaction was quenched with aqueous NaHCO₃ and extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 40% EtOAc in hexane to afford **S1** (0.7463 g, 99% yield). **Methyl 1-(methylsulfonyl)aziridine-2-carboxylate (S1)**: Colourless oil; $R_f = 0.48$ (50% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 3.25 (s, 3H), 3.13 (dd, $J = 7.1, 4.1$ Hz, 1H), 2.43 (s, 3H), 2.30 (d, $J = 7.1$ Hz, 1H), 2.14 (d, $J = 4.1$ Hz, 1H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 167.1, 52.2, 38.9, 35.2, 31.1 ppm; IR (CH₂Cl₂) 3058, 2956, 1755 (C=O), 1444, 1394 cm⁻¹; LRMS (EI, 20 eV) m/z 148 (M⁺-OCH₃, 18), 120 (59), 100 (100), 79 (62), 72 (19); HRMS (EI, 20 eV) Calculated for C₅H₉NO₄S (M⁺-OCH₃) 148.0063, Found 148.0075.

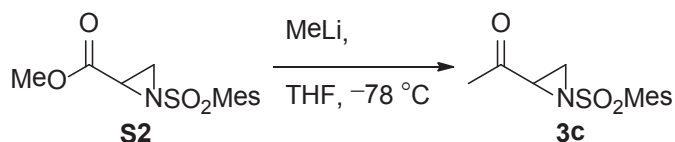
To a solution of **S1** (1.605 g, 8.968 mmol) in anhydrous THF (90 mL) at -78 °C was added 1.45 M

¹ A. B. Smith, III, D.-S. Kim, *Org. Lett.* 2005, **7**, 3247.

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MeLi (6.5 mL, 9.4 mmol). The resulting mixture was stirred for 20 min at $-78\text{ }^{\circ}\text{C}$. The reaction was quenched with aqueous NH_4Cl at $-78\text{ }^{\circ}\text{C}$ and extracted with Et_2O . The combined organic layers were dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 35% EtOAc in hexane to afford **3b** (0.4989 g, 34% yield). **1-(1-(Methylsulfonyl)aziridin-2-yl)ethanone (3b)**: Colourless oil; R_f 0.38 (50% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 3.05 (dd, $J = 7.4, 4.2$ Hz, 1H), 2.35 (s, 3H), 2.24 (d, $J = 7.4$ Hz, 1H), 1.81 (d, $J = 4.2$ Hz, 1H), 1.62 (s, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 200.2, 41.1, 38.8, 31.0, 25.6 ppm; IR (CH_2Cl_2) 3062, 2939, 1720 (C=O), 1411, 1326 cm^{-1} ; LRMS (EI, 20 eV): m/z 163 (M^+ , 17), 148 (29), 122 (100), 120 (58), 107 (25), 84 (26); HRMS (EI, 20 eV) Calculated for $\text{C}_5\text{H}_9\text{N}$ (M^+) 163.0298, Found 163.0303.

Preparation of 3c

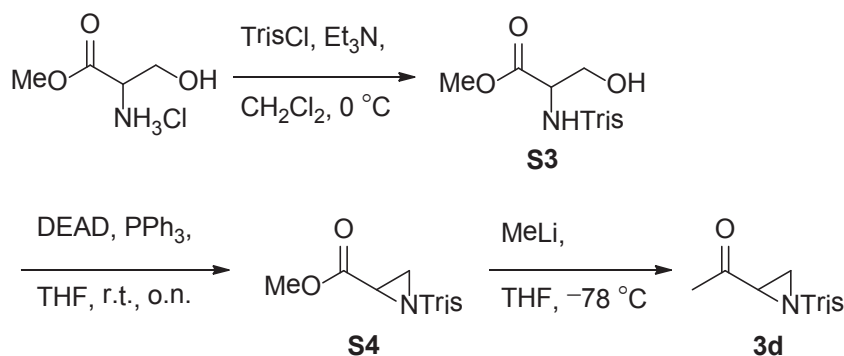


Aziridinyl methyl ester **S2** was prepared according to literature procedure.² To a solution of **S2** (1.040 g, 3.673 mmol) in anhydrous THF (40 mL) at $-78\text{ }^{\circ}\text{C}$ was added 1.45 M MeLi (2.6 mL, 3.7 mmol). The resulting mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$. The reaction was quenched with aqueous NH_4Cl at $-78\text{ }^{\circ}\text{C}$ and extracted with Et_2O . The combined organic layers were dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 15% EtOAc in hexane to afford **S3** (0.7244 g, 74% yield). **1-(1-(Mesitylsulfonyl)aziridin-2-yl)ethanone (3c)**: White solid; mp: 33-36 $^{\circ}\text{C}$; $R_f = 0.52$ (20% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 6.61 (s, 2H), 3.14 (dd, $J = 7.3, 4.1$ Hz, 1H), 2.70 (s, 6H), 2.34 (d, $J = 7.3$ Hz, 1H), 1.85 (s, 3H), 1.69 (d, $J = 4.1$ Hz, 1H), 1.48 (s, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 200.5, 143.6, 140.4, 132.6, 132.1, 41.1, 31.3, 25.4, 23.0, 20.7 ppm; IR (CH_2Cl_2) 3047, 2977, 2939, 1712 (C=O), 1604, 1450 cm^{-1} ; LRMS (EI, 20 eV) m/z 267 (M^+ , 17), 153 (35), 149 (34), 136 (48), 119 (78), 106 (35), 89 (54), 81 (69); HRMS (EI, 20 eV) Calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$ (M^+) 267.0924, Found 267.0917.

² H. Tamamura, T. Tanaka, H. Tsutsumi, K. Nemoto, S. Mizokami, N. Ohashi, S. Oishi, N. Fujii, *Tetrahedron*, 2007, **63**, 9243.

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Preparation of 3d



To a solution of DL-Serine methyl ester hydrochloride (1.556 g, 9.999 mmol) in CH₂Cl₂ (40 mL) at 0 °C was added Et₃N (3.0 mL, 21 mmol) and 2, 4, 6-triisopropylbenzenesulfonyl chloride (3.514 g, 11.60 mmol). The resulting mixture was stirred overnight at 0 °C. The reaction was quenched with aqueous NaHCO₃ and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 35% EtOAc in hexane to afford **S3** (3.5504 g, 92% yield).

3-Hydroxy-2-(2,4,6-triisopropylphenylsulfonamido) propanoate (S3): White solid; mp: 117-119 °C; $R_f = 0.20$ (35% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.16 (s, 2H), 5.56 (d, $J = 7.2$ Hz, 1H), 4.12-4.04 (m, 3H), 3.91 (d, $J = 3.7$ Hz, 2H), 3.63 (s, 3H), 2.89 (septet, $J = 6.9$ Hz, 1H), 2.24 (br, s, 1H), 1.28-1.23 (m, 18H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 153.3, 150.4, 132.2, 124.0, 63.7, 57.2, 53.0, 34.2, 30.0, 25.0, 24.8, 23.7, 23.6 ppm; IR (CH₂Cl₂) 3340, 2960, 2931, 2869, 1743 (C=O), 1332 cm⁻¹; LRMS (EI, 20 eV) m/z 385 (M⁺, 1), 267 (100), 251 (37), 236 (13), 221 (30), 218 (28); HRMS (EI, 20 eV) Calculated for C₁₉H₃₁NO₅S (M⁺) 385.1917, Found 385.1925.

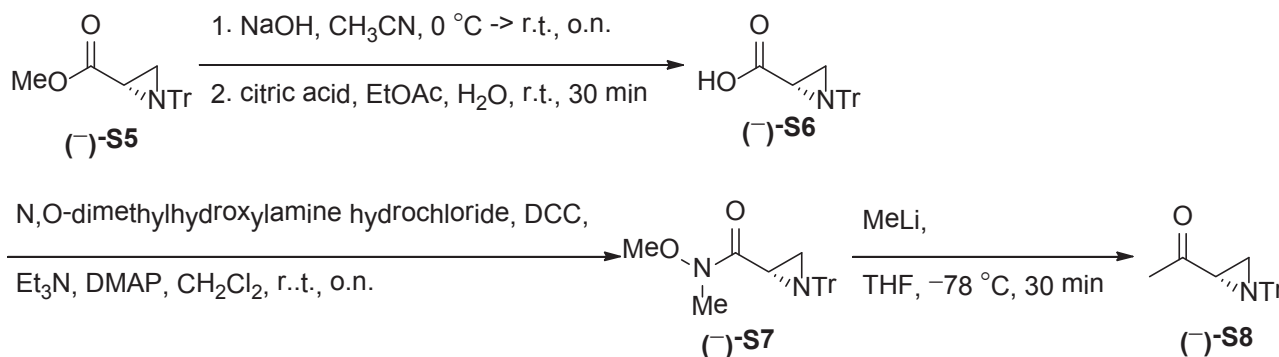
To a solution of **S3** (3.411 g, 8.859 mmol) in THF (80 mL) at 0 °C was added PPh₃ (2.947 g, 11.25 mmol) and diethylazodicarboxylate (1.8 mL, 11 mmol). The resulting mixture was stirred overnight from 0 °C to room temperature. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 8% EtOAc in hexane to afford **S4** (2.9513 g, 91% yield). **Methyl 1-((2,4,6-triisopropylphenyl)sulfonyl)aziridine-2-carboxylate (S4):** White solid; mp: 54-56 °C; $R_f = 0.33$ (10% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 7.19 (s, 2H), 4.65 (septet, $J = 6.7$ Hz, 2H), 3.28 (dd, $J = 7.0, 4.0$ Hz, 1H), 3.10 (s, 3H), 2.62 (septet, $J = 6.9$ Hz, 1H), 2.50 (d, $J = 7.0$ Hz, 1H), 2.14 (d, $J = 4.0$ Hz, 1H), 1.32 (d, $J = 6.7$ Hz, 6H), 1.29 (d, $J = 6.7$ Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 154.1, 151.9, 131.8, 124.2, 52.0, 35.8, 34.4, 31.6, 30.2, 25.1, 25.0, 23.5 ppm; IR (CH₂Cl₂) 3064, 2956, 2929, 2900, 2869, 1743 (C=O), 1598, 1564 cm⁻¹; LRMS (EI, 20eV) m/z 367 (M⁺, 1), 294 (3), 266 (43), 251 (79), 233 (3), 218 (62); HRMS (EI,

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20 eV) Calculated for C₁₉H₂₉NO₄S (M⁺) 367.1812, Found 367.1808.

To a solution of **S4** (1.512 g, 4.119 mmol) in anhydrous THF (80 mL) at -78 °C was added 1.45 M MeLi (2.9 mL, 4.2 mmol). The resulting mixture was stirred for 20 min at -78 °C. The reaction was quenched with aqueous NH₄Cl at -78 °C and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 8% EtOAc in hexane to afford **3d** (0.12284 g, 85% yield). **1-(1-((2,4,6-Triisopropylphenyl)sulfonyl)aziridin-2-yl)ethanone (3d)**: Colourless oil; R_f = 0.50 (20% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 7.20 (s, 2H), 4.59 (septet, *J* = 6.8 Hz, 2H), 3.24 (dd, *J* = 7.3, 4.1 Hz, 1H), 2.64 (septet, *J* = 6.9 Hz, 1H), 2.43 (d, *J* = 7.3 Hz, 1H), 1.83 (d, *J* = 4.1 Hz, 1H), 1.56 (s, 3H), 1.29 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.08 (d, *J* = 6.9 Hz, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 200.1, 154.2, 151.9, 131.7, 124.3, 41.6, 34.4, 31.6, 30.1, 25.3, 25.1, 25.0, 23.6 ppm; IR (CH₂Cl₂) 3060, 2964, 2929, 2871, 2893, 1712 (C=O), 1598, 1560 cm⁻¹; LRMS (EI, 20 eV) *m/z* 351 (M⁺, 1), 266 (66), 251 (74), 249 (4), 235 (2), 233 (3); HRMS (EI, 20 eV) Calculated for C₁₉H₂₉NO₃S (M⁺) 351.1863, Found 351.1859.

Preparation of 3e



Aziridinyl methyl ester **S5** was prepared according to literature procedure from L-serine.³

To a solution of (-)-**S5** (19.02 g, 55.37 mmol) in CH₃CN (60 mL) was added NaOH (3.452 g, 86.27 mmol) in H₂O (60 mL) at 0 °C. The reaction mixture was stirred overnight from 0 °C to room temperature. The bulk of the CH₃CN was removed *in vacuo*. H₂O (110 mL) and citric acid monohydrate (23.62 g, 112.4 mmol) in EtOAc (400 mL) was added and the resulting mixture was stirred at room temperature for 30 min. The two layers were separated and the aqueous layer was

³ F. Liu, J. Thomas, T. R. Bureke Jr., *Synthesis*, 2008, **15**, 2432; A. M. King, C. Salomé, J. Dinsmore, E. Salomé-Grosjean, M. De Ryck, R. Kaminski, A. Valade, H. Kohn, *J. Med. Chem.*, 2011, **54**, 4815.

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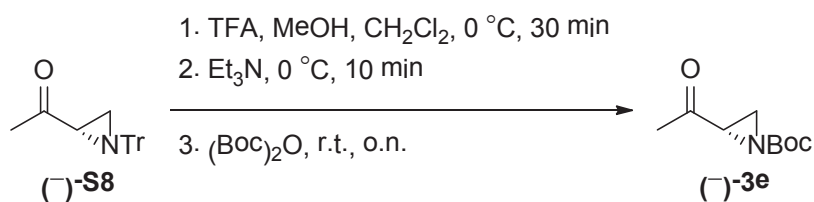
extracted with EtOAc (100 mL x 5). The combined organic layers were dried over anhydrous MgSO₄ and the volatiles were removed *in vacuo*. The crude product of (–)-**S6** was subjected to the subsequent reaction without further purification.

To a solution of (–)-**S6** in CH₂Cl₂ (300 mL) was added DMAP (0.6810 g, 5.574 mmol), Et₃N (11.6 mL, 83.5 mmol), N,O-dimethylhydroxylamine hydrochloride (5.593 g, 57.34 mmol) and DCC (11.65 g, 56.44 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and quenched with brine. The mixture was extracted with CH₂Cl₂ (200 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 25% EtOAc in hexane to afford (–)-**S7** (18.4927 g, 41% yield).

(S)-N-Methoxy-N-methyl-1-tritylaziridine-2-carboxamide ((–)-S7): White solid; mp: 58-60 °C; R_f = 0.30 (20% EtOAc in hexane); [α]_D²⁰ = –53.3° (c = 1.08, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.52 (m, 6H), 7.29-7.19 (m, 9H), 3.37 (s, 3H), 3.20 (s, 3H), 2.37-2.33 (m, 2H), 1.41 (dd, J = 5.9, 1.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 144.0, 129.5, 127.7, 127.0, 74.6, 61.5, 32.7, 29.2, 28.1 ppm; IR (CH₂Cl₂) 3042, 2980, 1665 (C=O), 1489, 1341, 1244, 1017 cm⁻¹; LRMS (EI, 20 eV) m/z 341 (M⁺-CH₃O, 1), 243 (100), 165 (47); HRMS (EI, 20 eV) Calculated for C₂₃H₂₁N₂O (M⁺-CH₃O) 341.1654, Found 341.1648.

To a solution of (–)-**S7** (8.241 g, 22.13 mmol) in THF (90 mL) was added MeLi (2.39 M in diethoxymethane, 9.8 mL, 23 mmol) slowly at –78 °C. The reaction mixture was stirred for 30 min at –78 °C before quenching with aqueous NH₄Cl at –78 °C. The mixture was extracted with Et₂O (100 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using CH₂Cl₂ to afford (–)-**S8** (7.0657 g, 98% yield). **(S)-1-(1-Tritylaziridin-2-yl)ethanone ((–)-S8):** Colourless oil; R_f = 0.68 (20% EtOAc in hexane); [α]_D²⁰ = –69.3° (c = 0.73, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.40 (m, 6H), 7.30-7.20 (m, 9H), 2.28 (s, 3H), 2.20 (dd, J = 2.7, 1.1 Hz, 1H), 1.98 (dd, J = 6.4, 2.7 Hz, 1H), 1.44 (dd, J = 6.4, 1.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 207.8, 143.5, 129.3, 127.8, 127.1, 74.6, 39.4, 29.1, 25.2 ppm; IR (CH₂Cl₂) 3086, 3067, 2984, 1701 (C=O), 1489, 1447, 1356, 1217, 1003 cm⁻¹; LRMS (EI, 20 eV) m/z 327 (M⁺, 1), 243 (100), 165 (46); HRMS (EI, 20 eV) Calculated for C₂₃H₂₁NO (M⁺) 327.1623, Found 327.1619.

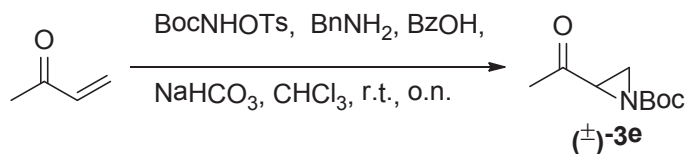
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To a solution of (-)-**S8** (2.361 g, 7.212 mmol) in CH₂Cl₂ (35 mL) was added MeOH (0.300 mL, 7.41 mmol) and TFA (1.1 mL, 14 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Et₃N (3.0 mL, 22 mmol) was added and the resulting mixture was stirred at 0 °C for 10 min. (Boc)₂O (1.8 mL, 7.8 mmol) was then added and the mixture was stirred at room temperature overnight before washing with 10% citric acid solution, H₂O and brine. The organic layer was dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford (-)-**3e** (1.1299 g, 85%).

(S)-tert-Butyl 2-acetylaziridine-1-carboxylate((-)-3e): Colourless oil; $R_f = 0.39$ (20% EtOAc in hexane); $[\alpha]_D^{20} = -104.2^\circ$ ($c = 0.54$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.10 (dd, $J = 6.0, 3.2$ Hz, 1H), 2.45 (dd, $J = 6.0, 1.2$ Hz, 1H), 2.40 (dd, $J = 3.2, 1.2$ Hz, 1H), 2.20 (s, 3H), 1.45 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 203.7, 160.0, 82.3, 41.1, 31.8, 27.9, 27.0 ppm; IR (CH₂Cl₂) 2992, 2982, 1724 (C=O), 1711 (C=O), 1370, 1283 cm⁻¹; LRMS (EI, 20 eV) m/z 170 (M⁺-CH₃, 2), 150 (5), 126 (28), 112 (100), 105 (29), 85 (77), 77 (10); HRMS (EI, 20 eV) Calculated for C₈H₁₂NO₃ (M⁺-CH₃) 170.0817, Found 170.0810. The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 6% IPA in hexane, t_R (major) = 15.03 min, t_R (minor) = 12.27 min] to be 99% ee.

The racemic aziridinyl ketone **3e** could be obtained in one step from methyl vinyl ketone as described below:



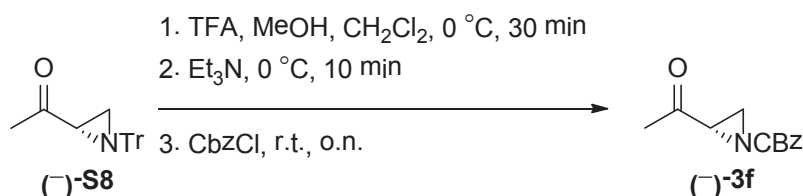
The solution of BnNH₂ (8.0 mL, 73 mmol) and BzOH (3.775 g, 30.92 mmol) in CHCl₃ (250 mL) was stirred at room temperature for 10 min. Methyl vinyl ketone (10.9 mL, 134 mmol) was added and the resulting mixture was stirred for 10 min. BocNHOTs⁴ (21.36 g, 76.33 mmol) was added and the mixture was stirred for 5 min. NaHCO₃ (10.47 g, 124.6 mmol) was added and the reaction

⁴ J. P. Lajiness, W. M. Robertson, I. Dunwiddie, M. A. Broward, G. A. Vielhauer, S. J. Weir, D. L. Boger, *J. Med. Chem.*, 2010, **53**, 7731.

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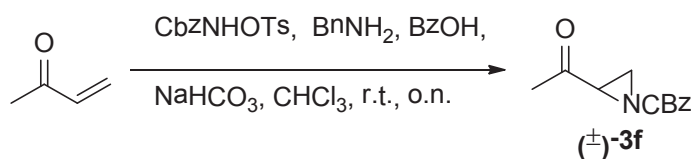
mixture was stirred at room temperature overnight. The mixture was filter through a short pad of silica gel and washed with CH_2Cl_2 . The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford (\pm)-**3e** (12.9158 g, 94% yield).

Preparation of **3f**



To a solution of ($-$)-**S8** (0.1014 g, 0.3097 mmol) in CH_2Cl_2 (1.6 mL) was added MeOH (0.015 mL, 0.37 mmol) and TFA (0.050 mL, 0.65 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Et_3N (0.130 mL, 0.935 mmol) was added and the resulting mixture was stirred at 0 °C for 10 min. CBzCl (0.050 mL, 0.35 mmol) was then added and the mixture was stirred at room temperature overnight before washing with 10% citric acid solution, H_2O and brine. The organic layer was dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 25% EtOAc in hexane to afford ($-$)-**3f** (0.0372 g, 55%). (**S**)-Benzyl 2-acetylaziridine-1-carboxylate (($-$)-**3f**): Colourless oil; $R_f = 0.42$ (35% EtOAc in hexane); $[\alpha]_D^{20} = -71.1^\circ$ ($c = 0.59$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 5H), 5.17 (d, $J = 12.1$ Hz, 1H), 5.11 (d, $J = 12.1$ Hz, 1H), 3.19 (dd, $J = 6.0, 3.3$ Hz, 1H), 2.52 (dd, $J = 6.0, 1.2$ Hz, 1H), 2.46 (dd, $J = 3.3, 1.2$ Hz, 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 203.2, 161.1, 135.4, 128.7, 128.6, 128.5, 68.8, 41.0, 32.0, 27.1 ppm. The spectral characteristics corresponded to those of (\pm)-**3f** in the literature.⁵ The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, $\lambda = 210$ nm, 20% IPA in hexane, t_R (major) = 23.76 min, t_R (minor) = 20.13 min] to be 99% ee.

The racemic aziridinyl ketone **3f** could be obtained in one step from methyl vinyl ketone as described below.



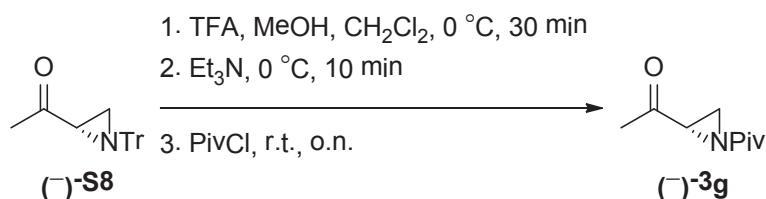
The solution of BnNH_2 (2.750 mL, 25.18 mmol) and BzOH (1.288 g, 10.55 mmol) in CHCl_3 (84 mL)

⁵ S. Minakata, Y. Murakami, R. Tsuruoka, S. Kitanaka, *Chem. Commun.*, 2008, 6363.

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was stirred at room temperature for 10 min. Methyl vinyl ketone (1.7 mL, 21 mmol) was added and the resulting mixture was stirred for 10 min. CBzNHOTs⁶ (8.099 g, 25.20 mmol) was added and the mixture was stirred for 5 min. NaHCO₃ (3.527 g, 41.98 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was filter through a short pad of silica gel and washed with CH₂Cl₂. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford (±)-**3f** (1.7522 g, 38% yield).

Preparation of **3g**



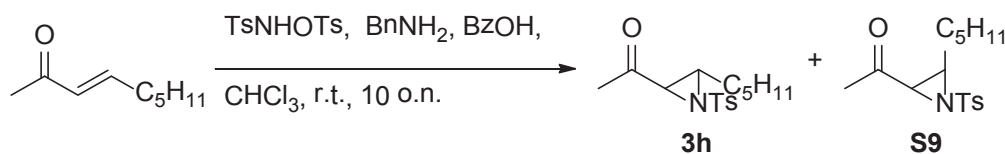
To a solution of (-)-**S8** (2.344 g, 7.158 mmol) in CH₂Cl₂ (35.8 mL) was added MeOH (0.290 mL, 7.16 mmol) and TFA (1.1 mL, 14 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Et₃N (3.0 mL, 22 mmol) was added and the resulting mixture was stirred at 0 °C for 10 min. PivCl (1.0 mL, 8.1 mmol) was then added and the mixture was stirred at room temperature overnight before washing with 10% citric acid solution, H₂O and brine. The organic layer was dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 25% EtOAc in hexane to afford (-)-**3g** (1.0018 g, 83%).

(S)-1-(2-Acetylaziridin-1-yl)-2,2-dimethylpropan-1-one ((-)-3g): Colourless oil; $R_f = 0.36$ (20% EtOAc in hexane); $[\alpha]_D^{20} = -169.9^\circ$ ($c = 0.44$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.09 (dd, $J = 6.3, 3.1$ Hz, 1H), 2.58 (dd, $J = 6.3, 1.2$ Hz, 1H), 2.43 (dd, $J = 3.1, 1.2$ Hz, 1H), 2.15 (s, 3H), 1.22 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 204.0, 189.7, 41.3, 41.2, 30.6, 27.7, 25.6 ppm; IR (CH₂Cl₂) 2972, 2938, 1711 (C=O), 1694 (C=O), 1479, 1396, 1277, 1198 cm⁻¹; LRMS (EI, 20 eV) m/z 169 (M⁺, 2), 154 (4), 126 (43), 112 (10), 85 (100); HRMS (EI, 20 eV) Calculated for C₉H₁₅NO₂ (M⁺) 169.1103, Found 169.1095. The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AY-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, t_R (major) = 22.42 min, t_R (minor) = 16.21 min] to be 99% ee.

⁶ L. Qin, Z. Zhou, J. Wei, T. Yan, H. Wen, *Synth. Commun.*, 2010, **40**, 642.

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Preparation of 3h



The solution of BnNH₂ (0.105 mL, 0.961 mmol) and BzOH (0.0503 g, 0.412 mmol) in CHCl₃ (3.2 mL) was stirred at room temperature for 10 min. Trans-3-nonen-2-one (0.135 mL, 0.816 mmol) was added and the resulting mixture was stirred for 10 min. TsNHOTs⁷ (0.3301 g, 0.9669 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was filter through a short pad of silica gel and washed with CH₂Cl₂. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford **3i** and **S9** (0.1443 g, 57% yield, 17.9:1). Analytically pure **3h** and **S9** were obtained by further careful column chromatography using 80% CH₂Cl₂ in hexane.

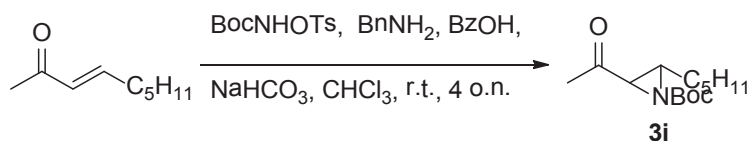
1-((2S*,3R*)-3-Pentyl-1-tosylaziridin-2-yl)ethanone (3h): Colourless oil; R_f = 0.64 (80% CH₂Cl₂ in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.28 (d, *J* = 4.0 Hz, 1H), 2.91 (qd, *J* = 5.3, 4.1 Hz, 1H), 2.43 (s, 3H), 2.22-2.14 (m, 1H), 1.98-1.93 (m, 1H), 1.92 (s, 3H), 1.59-1.41 (m, 2H), 1.38-1.27 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 202.5, 144.7, 136.9, 129.9, 127.6, 50.3, 49.8, 31.3, 28.1, 27.6, 26.0, 22.5, 21.7, 14.0 ppm; IR (CH₂Cl₂) 3053, 2961, 2930, 2861, 1713 (C=O), 1599, 1458, 1444, 1406, 1331, 1163 cm⁻¹; LRMS (EI, 20 eV) *m/z* 366 (M⁺-C₂H₃O, 2), 210 (3), 154 (100), 91 (43), 84 (36); HRMS (EI, 20 eV) Calculated for C₁₄H₂₀NO₂S (M⁺-C₂H₃O) 266.1215, Found 266.1210.

1-((2S*,3S*)-3-Pentyl-1-tosylaziridin-2-yl)ethanone (S9): Colourless oil; R_f = 0.48 (80% CH₂Cl₂ in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.39 (d, *J* = 7.7 Hz, 1H), 2.92 (dq, *J* = 7.9, 5.1 Hz, 1H), 2.43 (s, 3H), 1.91 (s, 3H), 1.49-1.42 (m, 1H), 1.34-1.25 (m, 1H), 1.22-1.12 (m, 6H), 0.78 (t, *J* = 6.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 201.3, 145.2, 134.3, 129.9, 128.3, 47.3, 45.9, 31.1, 29.4, 27.3, 26.7, 22.4, 21.7, 13.8 ppm; IR (CH₂Cl₂) 3048, 2959, 2930, 2861, 1726 (C=O), 1599, 1410, 1331, 1163 cm⁻¹; LRMS (EI, 20 eV) *m/z* 309 (M⁺, 1), 266 (11), 210 (11), 154 (100), 91 (44), 84 (51); HRMS (EI, 20 eV) Calculated for C₁₆H₂₃NO₃S (M⁺) 309.1399, Found 309.1393.

⁷ Ł. Albrecht, H. Jiang, G. Dickmeiss, B. Gschwend, S. G. Hansen, K. A. Jørgensen, *J. Am. Chem. Soc.*, 2010, **132**, 9188.

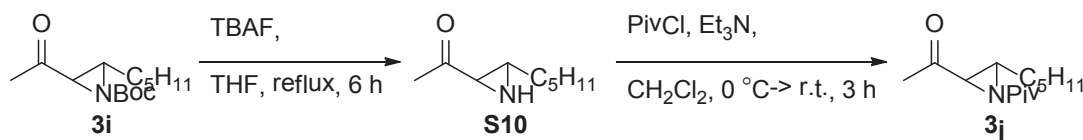
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Preparation of **3i**



The solution of BnNH₂ (2.380 mL, 21.79 mmol) and BzOH (1.116 g, 9.139 mmol) in CHCl₃ (73 mL) was stirred at room temperature for 10 min. Trans-3-nonen-2-one (3.0 mL, 18 mmol) was added and the resulting mixture was stirred for 10 min. BocNHOTs⁴ (6.272 g, 21.81 mmol) was added and the mixture was stirred for 5 min. NaHCO₃ (10.47 g, 124.6 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was filter through a short pad of silica gel and washed with CH₂Cl₂. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 10% EtOAc in hexane to afford **3i** (3.8041 g, 82% yield). **(2S*,3R*)-tert-Butyl 2-acetyl-3-pentylaziridine-1-carboxylate (3i)**: Colourless oil; R_f = 0.56 (20% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 2.96 (d, *J* = 2.7 Hz, 1H), 2.65-2.62 (m, 1H), 2.25 (s, 3H), 1.59-1.55 (m, 1H), 1.44 (m, 12H), 1.39-1.24 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 202.8, 159.2, 81.7, 46.7, 45.6, 31.4, 31.3, 29.1, 28.0, 26.6, 22.6, 14.0 ppm. The spectral characteristics corresponded to those of **3i** in the literature.⁸

Preparation of **3j**



To a solution of **3i** (1.153 g, 4.515 mmol) in THF (22.6 mL) was added TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol). The reaction mixture was heated under reflux for 6 h and then cooled to room temperature. The reaction was quenched with aqueous NaHCO₃, extracted with EtOAc (50 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 30% EtOAc in hexane to afford **S10** (0.4324 g, 63% yield). **1-((2S*,3R*)-3-Pentylaziridin-2-yl)ethanone (S10)**: Colourless oil; R_f = 0.38 (35% EtOAc in hexane); ¹H NMR (500 MHz, 333 K, CDCl₃) δ 2.51 (d, *J* = 2.3 Hz, 1H), 2.28 (s, 3H), 2.01 (td, *J* = 5.5, 2.3 Hz, 1H), 1.65 (br s, 1H), 1.50-1.39 (m, 4H), 1.34-1.31 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 205.6, 42.9, 42.3, 33.2, 31.5, 28.8, 26.8, 22.5, 13.8 ppm; IR (CH₂Cl₂) 3323 (NH), 3065, 3036, 2959, 2932, 2859, 1701 (C=O), 1458, 1425, 1377, 1231,

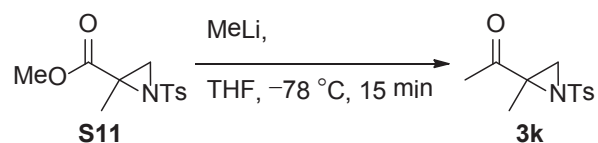
⁸ F. Pesciaioli, F. De Vincentiis, P. Galzerano, G. Bencivenni, G. Bartoli, A. Mazzanti, P. Melchiorre, *Angew. Chem. Int. Ed.*, 2008, **47**, 8703.

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1173 cm^{-1} ; LRMS (EI, 20 eV) m/z 155 (M^+ , 1), 112 (7), 84 (100); HRMS (EI, 20 eV) Calculated for $C_9H_{17}NO$ (M^+) 155.1310, Found 155.1296.

To a solution of **S10** (0.0558 g, 0.364 mmol) in CH_2Cl_2 (1.8 mL) was added Et_3N (0.100 mL, 0.719 mmol) and PivCl (0.065 mL, 0.53 mmol) at 0 °C. The reaction mixture was stirred at 0 °C and warmed to room temperature gradually. After 3 h, the reaction was quenched with brine, extracted with EtOAc (10 mL x 3), separated and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 10% EtOAc in hexane to afford **3j** (0.0644 g, 74% yield). **1-((2*S**,3*R**)-2-Acetyl-3-pentylaziridin-1-yl)-2,2-dimethylpropan-1-one (3j)**: Colourless oil; $R_f = 0.50$ (20% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 3.12 (d, $J = 2.4$ Hz, 1H), 2.82 (dddd, $J = 7.3, 4.8, 2.4$ Hz, 1H), 2.28 (s, 3H), 1.92-1.84 (m, 1H), 1.46-1.37 (m, 3H), 1.33-1.28 (m, 4H), 1.21 (s, 9H), 0.88 (t, $J = 6.7$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 203.0, 187.5, 46.9, 45.9, 41.1, 31.5, 31.4, 29.0, 27.6, 26.3, 22.6, 14.1 ppm; IR (CH_2Cl_2) 2990, 2963, 2934, 1717 (C=O), 1674 (C=O), 1425, 1311, 1117, 1080 cm^{-1} ; LRMS (EI, 20 eV) m/z 239 (M^+ , 1), 224 (1), 210 (1), 196 (12), 168 (6), 154 (26), 140 (10), 102 (15), 84 (100); HRMS (EI, 20 eV) Calculated for $C_{14}H_{25}NO_2$ (M^+) 239.1885, Found 239.1878.

Preparation of 3k



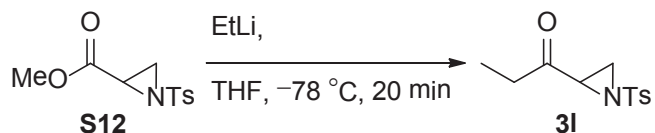
Aziridinyl methyl ester **S11** was prepared according to the literature procedure.⁹ To a solution of **S11** (1.550 g, 5.754 mmol) in anhydrous THF (30 mL) was added MeLi (1.96 M in diethoxymethane, 3.0 mL, 5.9 mmol) slowly at -78 °C and the mixture was stirred at -78 °C for 15 min. The reaction was quenched with aqueous NH_4Cl at -78 °C, extracted with Et_2O (100 mL x 3), separated and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford **3k** (0.8376 g, 57% yield). **1-(2-Methyl-1-tosylaziridin-2-yl)ethanone (3k)**: White solid; mp: 107-110 °C; $R_f = 0.57$ (30% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 2.81 (s, 1H), 2.53 (s, 1H), 2.44 (s, 3H), 2.07 (s, 3H), 1.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 203.9, 144.8, 136.9, 129.8, 127.7, 52.3, 38.4, 24.2, 21.7, 13.5 ppm; IR (CH_2Cl_2) 3071, 2986, 2947, 1715 (C=O), 1599, 1495, 1456, 1329, 1256, 1165 cm^{-1} ; LRMS (EI, 20 eV) m/z 253 (M^+ , 1), 210 (20),

⁹ B. G. M. Burgaud, D. C. Horwell, A. Padova, M. C. Pritchard, *Tetrahedron*, 1996, **52**, 13035.

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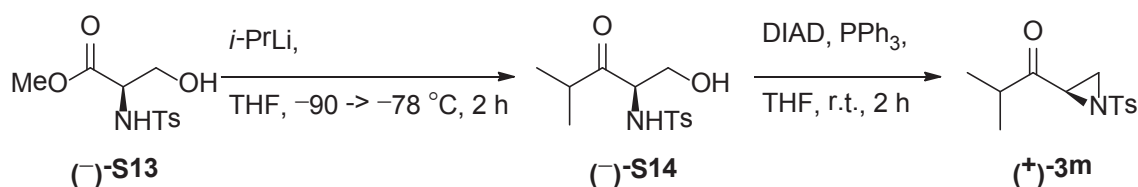
155 (75), 98 (90), 91 (100); HRMS (EI, 20 eV) Calculated for C₁₂H₁₅NO₃S (M⁺) 253.0773, Found 253.0765.

Preparation of **3l**



Aziridiny methyl ester **S12** was prepared according to the literature procedure.¹ To a solution of **S12** (1.102 g, 4.316 mmol) in anhydrous THF (17 mL) was added EtLi (0.84 M in dibutylether, 5.4 mL, 4.5 mmol) slowly at -78 °C and the reaction mixture was stirred at -78 °C for 20 min. The reaction was quenched with aqueous NH₄Cl at -78 °C, extracted with Et₂O (30 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using CH₂Cl₂ to afford **3l** (0.4252 g, 39% yield). **1-(1-Tosylaziridin-2-yl)propan-1-one (**3l**):** White solid; R_f = 0.45 (30% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.31 (dd, *J* = 7.3, 4.2 Hz, 1H), 2.74 (d, *J* = 7.3 Hz, 1H), 2.47 (d, *J* = 4.2 Hz, 1H), 2.45 (s, 3H), 2.43-2.35 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 204.0, 145.4, 134.1, 130.0, 128.3, 41.2, 32.7, 32.2, 21.8, 7.2 ppm. The spectral characteristics corresponded to those of **3l** in the literature.¹⁰

Preparation of **3m**



S13 was prepared according to the literature procedure.¹ To a solution of **S13** (8.830 g, 32.34 mmol) in anhydrous THF (300 mL) at -90 °C was added 0.55 M *i*-PrLi (181 mL, 100 mmol). The resulting mixture was stirred for 2 h from -90 °C to -78 °C. The reaction was quenched with aqueous NH₄Cl at -78 °C, neutralized to pH 7 by addition of 3 M HCl and extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 30% EtOAc in hexane to afford **(-)-14** (4.3291 g, 47% yield). **(R)-N-(1-Hydroxy-4-methyl-3-oxopentan-2-yl)-4-methylbenzene sulfonamide ((-)-14):** White solid; mp: 132-135 °C; R_f = 0.48 (50% EtOAc in

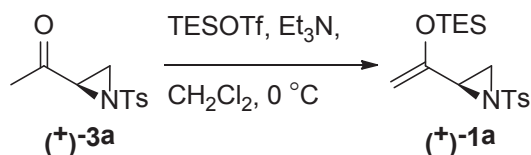
¹⁰ D. Chen, C. Timmons, L. Guo, X. Xu, G. Li, *Synthesis*, 2004, 2479.

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hexane); $[\alpha]_D^{20} = -89.6^\circ$ ($c = 1.35$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 5.92 (d, $J = 7.0$, 1H), 3.99-3.95 (m, 1H), 3.80-3.71 (m, 2H), 2.68 (septet, $J = 6.9$ Hz, 1H), 2.61 (t, $J = 6.7$ Hz, 1H), 2.29 (s, 3H), 0.89 (d, $J = 6.7$, 3H), 0.68 (d, $J = 7.0$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 209.9, 144.0, 136.3, 129.8, 127.3, 63.2, 61.8, 37.3, 21.5, 18.7, 17.3 ppm; IR (CH_2Cl_2) 3581, 3296, 3062, 2976, 2931, 1718 (C=O), 1598 cm^{-1} ; LRMS (EI, 20 eV) m/z 214 ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}$, 24), 184 (13), 155 (54), 91 (100), 71 (24); HRMS (EI) Calculated for $\text{C}_9\text{H}_{12}\text{NO}_3\text{S}$ ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}$) 214.0532, Found 214.0530.

To a solution of (–)-**14** (4.329 g, 15.19 mmol) in THF (1.9 L) at 0 °C was added PPh_3 (7.863 g, 30.01 mmol) and diisopropylazodicarboxylate (5.9 mL, 30 mmol). The resulting mixture was stirred for 2 h at room temperature. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 12% EtOAc in hexane to afford (+)-**3m** (2.1516 g, 53% yield). **(R)-2-Methyl-1-(1-tosylaziridin-2-yl)propan-1-one ((+)-3m)**: Colourless oil; $R_f = 0.24$ (10% EtOAc in hexane); $[\alpha]_D^{20} = +66.9^\circ$ ($c = 1.86$, CHCl_3); $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.78 (d, $J = 8.3$ Hz, 2H), 6.73 (d, $J = 8.1$ Hz, 2H), 3.32 (dd, $J = 7.1$, 4.2 Hz, 1H), 2.40 (d, $J = 7.1$ Hz, 1H), 2.26 (septet, $J = 6.9$ Hz, 1H), 2.07 (d, $J = 4.2$ Hz, 1H), 1.84 (s, 3H), 0.84 (d, $J = 6.9$, 3H), 0.80 (d, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 205.2, 144.7, 135.4, 129.8, 128.4, 39.3, 38.7, 32.0, 21.1, 17.7, 17.4 ppm; IR (CH_2Cl_2) 3056, 2978, 2936, 2877, 1717 (C=O), 1598, 1494 cm^{-1} ; LRMS (EI, 20 eV) m/z 267 (M^+ , 3), 224 (4), 212 (6), 155 (72), 136 (8), 112 (52), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$ (M^+) 267.0924, Found 267.0916. The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OF, 1.0 mL/min, $\lambda = 254$ nm, 30% IPA in hexane, $t_R(\text{major}) = 21.16$ min, $t_R(\text{minor}) = 28.58$ min] to be 92% ee.

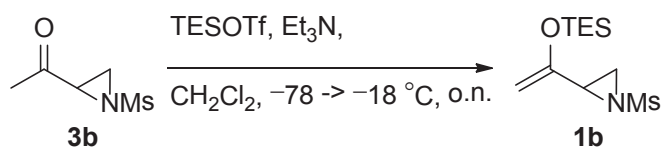
Preparation of Azridinyl Enolsilanes 1a-m



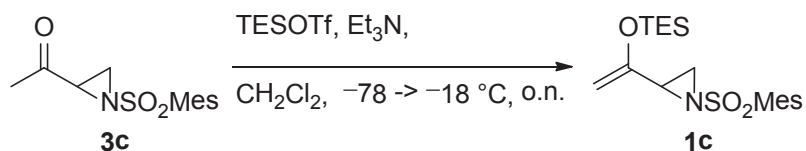
To a solution of (+)-**3a** (0.9596 g, 4.010 mmol) in CH_2Cl_2 (40 mL) at -78 °C was added Et_3N (1.7 mL, 12 mmol) and TESOTf (1.85 mL, 8.12 mmol). The resulting mixture was stirred at 0 °C for 3 h. The reaction was quenched with aqueous NaHCO_3 , extracted with Et_2O (100 mL x 3), separated

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and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 5% EtOAc and 1% Et_3N in hexane to afford **(+)-1a** (1.2760 g, 90% yield). **(R)-1-Tosyl-2-(1-(triethylsilyloxy)vinyl)aziridine ((+)-1a)**: Colourless oil; $R_f = 0.45$ (10% EtOAc in hexane); $[\alpha]_D^{20} = +42.8^\circ$ ($c = 1.12$, CHCl_3); $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.84 (d, $J = 8.2$ Hz, 2H), 6.77 (d, $J = 8.1$ Hz, 2H), 4.27 (d, $J = 1.4$ Hz, 1H), 4.17 (d, $J = 1.4$ Hz, 1H), 3.26 (dd, $J = 7.0, 4.4$ Hz, 1H), 2.50 (d, $J = 7.0$ Hz, 1H), 2.17 (d, $J = 4.4$ Hz, 1H), 1.86 (s, 3H), 0.85 (t, $J = 7.9$ Hz, 9H), 0.51 (q, $J = 7.9$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 152.4, 144.1, 136.5, 129.7, 128.2, 94.6, 41.2, 31.3, 21.1, 6.7, 5.0 ppm; IR (CH_2Cl_2) 3067, 2960, 2914, 2878, 1636 (C=C), 1598 cm^{-1} ; LRMS (EI, 20eV) m/z 353 (M^+ , 1), 324 (100), 296 (25), 198 (5), 177 (6), 155 (12), 115 (15); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{27}\text{NO}_3\text{SSi}$ (M^+) 353.1480, Found 353.1480.



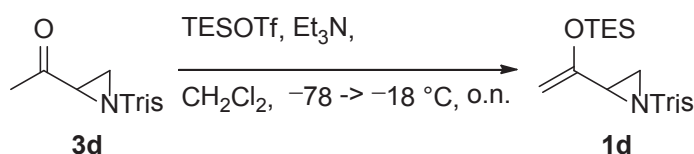
To a solution of **3b** (0.4873 g, 2.990 mmol) in CH_2Cl_2 (20 mL) at -78°C was added Et_3N (1.3 mL, 9.2 mmol) and TESOTf (1.4 mL, 6.2 mmol). The resulting mixture was stirred overnight from -78°C to -18°C . The reaction was quenched with aqueous NaHCO_3 and extracted with Et_2O . The combined organic layers were dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 8% EtOAc and 0.1% Et_3N in hexane to afford **1b** (0.6523 g, 79% yield). **1-(Methylsulfonyl)-2-(1-(triethylsilyloxy)vinyl)aziridine (1b)**: Colourless oil; $R_f = 0.34$ (10% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 4.26 (d, $J = 1.6$ Hz, 1H), 4.21 (d, $J = 1.6$ Hz, 1H), 3.08 (dd, $J = 7.1, 4.4$ Hz, 1H), 2.38 (s, 3H), 2.34 (d, $J = 7.1$ Hz, 1H), 2.09 (d, $J = 4.4$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 152.4, 94.3, 40.4, 39.1, 30.7, 6.7, 5.0 ppm; IR (CH_2Cl_2) 3062, 2958, 2877, 1635 (C=C), 1458, 1411 cm^{-1} ; LRMS (EI, 20 eV) m/z 277 (M^+ , 1), 248 (100), 220 (89), 206 (35), 190 (3), 181 (1); HRMS (EI, 20 eV) Calculated for $\text{C}_{11}\text{H}_{23}\text{NO}_3\text{SSi}$ (M^+) 277.1162, Found 277.1164.



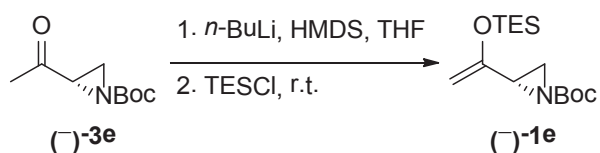
To a solution of **3c** (0.6404 g, 2.400 mmol) in CH_2Cl_2 (20 mL) at -78°C was added Et_3N (1.3 mL, 9.2 mmol) and TESOTf (1.4 mL, 6.2 mmol). The resulting mixture was stirred overnight from -78°C to -18°C . The reaction was quenched with aqueous NaHCO_3 and extracted with Et_2O . The

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combined organic layers were dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 3% EtOAc and 0.1% Et_3N in hexane to afford **1c** (0.8569 g, 94% yield). **1-(Mesitylsulfonyl)-2-(1-(triethylsiloxy)vinyl)aziridine (1c)**: Colourless oil; $R_f = 0.36$ (5% EtOAc in hexane); ^1H NMR (400 MHz, C_6D_6) δ 6.60 (s, 2H), 4.23 (d, $J = 1.5$ Hz, 1H), 4.13 (d, $J = 1.5$ Hz, 1H), 3.23 (dd, $J = 7.0, 4.3$ Hz, 1H), 2.74 (s, 6H), 2.48 (d, $J = 7.0$ Hz, 1H), 2.10 (d, $J = 4.3$ Hz, 1H), 1.91 (s, 3H), 0.83 (t, $J = 7.9$ Hz, 9H), 0.49 (q, $J = 7.9$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 152.8, 142.8, 140.2, 133.8, 132.0, 93.7, 40.7, 30.6, 23.3, 20.7, 6.7, 5.0 ppm; IR (CH_2Cl_2) 2962, 2916, 2877, 1635 (C=C), 1604, 1566 cm^{-1} ; LRMS (EI, 20 eV) m/z 381 (M^+ , 4), 352 (58), 317 (8), 269 (5), 205 (8), 198 (14), 119 (100), 115 (50), 87 (44), 77 (23); HRMS (EI, 20 eV): Calculatd for $\text{C}_{19}\text{H}_{31}\text{NO}_3\text{SSi}$ (M^+) 381.1788, Found 381.1793.

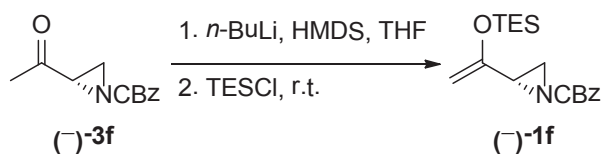


To a solution of **3d** (0.6509 g, 1.854 mmol) in CH_2Cl_2 (20 mL) at -78 °C was added Et_3N (0.8 mL, 5.7 mmol) and TESOTf (0.9 mL, 4.0 mmol). The resulting mixture was stirred overnight from -78 °C to -18 °C. The reaction was quenched with aqueous NaHCO_3 and extracted with Et_2O . The combined organic layers were dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 2% EtOAc and 0.1% Et_3N in hexane to afford **1d** (0.7655 g, 89% yield). **2-(1-(Triethylsiloxy)vinyl)-1-((2,4,6-triisopropylphenyl)sulfonyl) aziridine (1d)**: Colourless oil; $R_f = 0.47$ (5% EtOAc in hexane); ^1H NMR (400 MHz, C_6D_6) δ 7.19 (s, 2H), 4.70 (septet, $J = 6.8$ Hz, 2H), 4.26 (d, $J = 1.6$ Hz, 1H), 4.14 (d, $J = 1.6$ Hz, 1H), 3.35 (dd, $J = 7.0, 4.4$ Hz, 1H), 2.63 (septet, $J = 6.9$ Hz, 1H), 2.51 (d, $J = 7.0$ Hz, 1H), 2.11 (d, $J = 4.4$ Hz, 1H), 1.35 (d, $J = 7.1$ Hz, 6H), 1.33 (d, $J = 7.1$ Hz, 6H), 1.08 (d, $J = 6.9$ Hz, 6H), 0.85 (t, $J = 7.8$ Hz, 9H), 0.53 (q, $J = 7.8$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 153.5, 152.8, 151.7, 132.9, 124.0, 93.4, 40.9, 34.4, 31.6, 30.1, 25.3, 25.2, 23.6, 6.7, 5.0 ppm; IR (CH_2Cl_2) 2960, 2933, 2875, 1635 (C=C), 1598, 1560 cm^{-1} ; LRMS (EI, 20 eV) m/z 465 (M^+ , 1), 450 (3), 436 (59), 396 (88), 386 (10), 381 (14), 366 (23), 267 (33); HRMS (EI, 20 eV) Calculated for $\text{C}_{25}\text{H}_{43}\text{NO}_3\text{SSi}$ (M^+) 465.2727, Found 465.2731.



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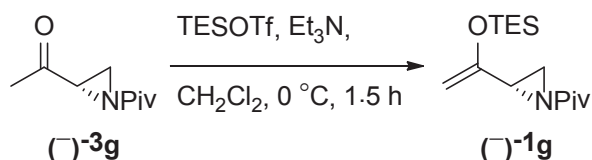
To a solution of HMDS (2.8 mL, 13 mmol) in anhydrous THF (10 mL) at 0 °C was added *n*-BuLi (1.28 M in hexane, 6.6 mL, 9.5 mmol). The mixture was stirred for 30 min at 0 °C and then cooled to -78 °C. To this was added (-)-**3e** (1.1938 g, 4.6752 mmol) in THF (4.0 mL) via cannula. The resulting solution was stirred for 1 h at -78 °C. TESCl (0.700 mL, 4.17 mmol) was added and the reaction was allowed to warm to room temperature. After stirring for 1 h, aqueous NaHCO₃ was added and the mixture was extracted with Et₂O (30 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 2% EtOAc and 1% Et₃N in hexane to afford (-)-**1e** (0.6596 g, 53% yield).
(S)-tert-Butyl 2-(1-(triethylsiloxy)vinyl)aziridine-1-carboxylate ((-)-1e): Colourless oil; *R_f* = 0.41 (5% EtOAc in hexane); $[\alpha]_{\text{D}}^{20} = -70.9^{\circ}$ (*c* = 1.13, CH₂Cl₂); ¹H NMR (400 MHz, C₆D₆) δ 4.44 (d, *J* = 1.2 Hz, 1H), 4.29 (d, *J* = 1.2 Hz, 1H), 2.74 (dd, *J* = 5.8, 3.5 Hz, 1H), 2.24 (dd, *J* = 3.5, 1.2 Hz, 1H), 2.07 (dd, *J* = 5.8, 1.2 Hz, 1H), 1.36 (s, 9H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.64 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 1641.6, 154.4, 93.0, 80.3, 39.5, 30.3, 28.0, 6.9, 5.2 ppm; IR (CH₂Cl₂) 3067, 3044, 2992, 2980, 1715 (C=O), 1634, 1458, 1416, 1369, 1288, 1007 cm⁻¹; LRMS (EI, 20 eV) *m/z* 242 (M⁺-C₄H₉, 4), 240 (6), 214 (55), 199 (23), 170 (71), 142 (45), 128 (50), 115 (70), 103 (74), 87 (100), 75 (60); HRMS (EI, 20 eV) Calculated for C₁₁H₂₀NO₃Si (M⁺-C₄H₉) 242.1212, Found 242.1208.



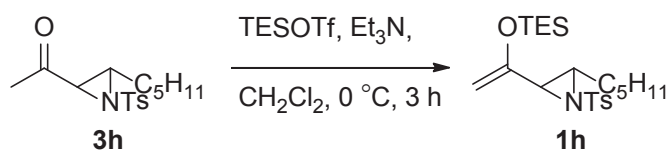
To a solution of HMDS (0.250 mL, 1.18 mmol) in anhydrous THF (0.8 mL) at 0 °C was added *n*-BuLi (1.09 M in hexane, 0.6 mL, 0.7 mmol). The mixture was stirred for 30 min at 0 °C and then cooled to -78 °C. To this was added (-)-**3f** (0.0723 g, 0.330 mmol) in THF (1.0 mL) via cannula. The resulting solution was stirred for 1 h at -78 °C. TESCl (0.050 mL, 0.30 mmol) was added and the reaction was allowed to warm to room temperature. After stirring for 1 h, aqueous NaHCO₃ was added and the mixture was extracted with Et₂O (10 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 2% EtOAc and 1% Et₃N in hexane to afford (-)-**1f** (0.0430 g, 43% yield).
(S)-Benzyl 2-(1-(triethylsiloxy)vinyl)aziridine-1-carboxylate((-)-1f): Colourless oil; *R_f* = 0.46 (5% EtOAc in hexane); $[\alpha]_{\text{D}}^{20} = -37.8^{\circ}$ (*c* = 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.30 (m, 5H), 5.15 (d, *J* = 12.4 Hz, 1H), 5.1 (d, *J* = 12.4 Hz, 1H), 4.50 (s, 1H), 4.34 (s, 1H), 2.96 (dd, *J* = 5.5, 3.7 Hz, 1H), 2.44 (d, *J* = 3.6 Hz, 1H), 2.33 (d, *J* = 5.5 Hz, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.69 (q, *J* = 8.0 Hz,

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6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 152.6, 136.0, 128.6, 128.3, 128.1, 93.8, 68.1, 39.8, 29.8, 6.7, 4.9 ppm; IR (CH_2Cl_2) 3065, 3046, 2959, 2940, 1721 (C=O), 1634, 1385, 1300, 1194 cm^{-1} ; LRMS (EI, 20 eV) m/z 304 ($\text{M}^+ - \text{C}_2\text{H}_5$, 1), 260 (7), 198 (4), 115 (10), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{Si}$ ($\text{M}^+ - \text{C}_2\text{H}_5$) 304.1369, Found 304.1362.



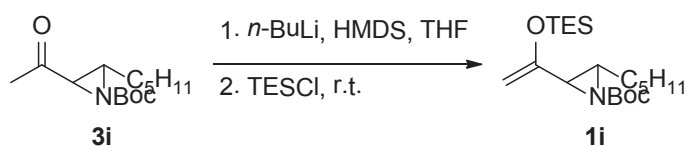
To a solution of **(-)-3g** (0.9000 g, 5.319 mmol) in CH_2Cl_2 (26.6 mL) at $-78\text{ }^\circ\text{C}$ was added Et_3N (1.5 mL, 11 mmol) and TESOTf (1.8 mL, 7.9 mmol). The resulting mixture was stirred at $0\text{ }^\circ\text{C}$ for 1.5 h. The reaction was quenched with aqueous NaHCO_3 , extracted with Et_2O (30 mL x 3), separated and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 1% EtOAc and 1% Et_3N in hexane to afford **(-)-1g** (1.3941 g, 92% yield). **(S)-2,2-Dimethyl-1-(2-(1-(triethylsilyloxy)vinyl)aziridin-1-yl)propan-1-one ((-)-1g)**: Colourless oil; $R_f = 0.56$ (5% EtOAc in hexane); $[\alpha]_D^{20} = -77.8^\circ$ ($c = 0.38$, CH_2Cl_2); ^1H NMR (400 MHz, C_6D_6) δ 4.34 (d, $J = 1.3$ Hz, 1H), 4.25 (d, $J = 1.3$ Hz, 1H), 2.63 (dd, $J = 6.0, 3.4$ Hz, 1H), 2.23 (dd, $J = 6.0, 1.0$ Hz, 1H), 2.17 (dd, $J = 3.4, 1.2$ Hz, 1H), 1.22 (s, 9H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.62 (q, $J = 8.0$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 190.2, 154.6, 92.5, 41.3, 39.8, 29.1, 28.0, 6.8, 5.2 ppm; IR (CH_2Cl_2) 3044, 2980, 2961, 1682 (C=O), 1633, 1479, 1458, 1416, 1366, 1296, 1287, 1244, 1119 cm^{-1} ; LRMS (EI, 20 eV) m/z 283 (M^+ , 13), 254 (28), 227 (15), 198 (35), 171 (45), 143 (70), 129 (27), 115 (78), 87 (100), 75 (28); HRMS (EI, 20 eV) Calculated for $\text{C}_{15}\text{H}_{29}\text{NO}_2\text{Si}$ (M^+) 283.1968, Found 283.1960.



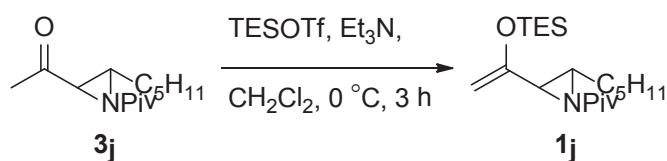
To a solution of **3h** (0.5884 g, 1.902 mmol) in CH_2Cl_2 (20 mL) at $-78\text{ }^\circ\text{C}$ was added Et_3N (0.8 mL, 5.8 mmol) and TESOTf (0.85 mL, 3.7 mmol). The resulting mixture was stirred at $0\text{ }^\circ\text{C}$ for 3 h. The reaction was quenched with aqueous NaHCO_3 , extracted with Et_2O (50 mL x 3), separated and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 7% EtOAc and 1% Et_3N in hexane to afford **1h** (0.8041 g, 100% yield). **(2R*,3S*)-2-Pentyl-1-tosyl-3-(1-(triethylsilyloxy)vinyl)aziridine (1h)**: Colourless oil; $R_f = 0.68$ (10% EtOAc in hexane); ^1H NMR (400 MHz, C_6D_6) δ 7.96 (d, $J = 8.2$ Hz, 2H), 6.76 (d, J

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= 8.1 Hz, 2H), 4.30 (d, $J = 1.1$ Hz, 1H), 4.17 (d, $J = 1.1$ Hz, 1H), 3.42 (d, $J = 4.3$ Hz, 1H), 2.93 (qd, $J = 4.9, 4.3$ Hz, 1H), 2.40-2.32 (m, 1H), 2.09-2.00 (m, 1H), 1.87 (s, 3H), 1.51-1.40 (m, 1H), 1.38-1.27 (m, 1H), 1.21-1.12 (m, 4H), 0.87-0.79 (m, 12H), 0.46 (q, $J = 7.7$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 153.5, 143.4, 139.5, 129.5, 127.8, 93.3, 49.5, 49.1, 31.6, 28.6, 28.0, 22.8, 21.1, 14.1, 6.8, 5.0 ppm; IR (CH_2Cl_2) 3068, 2996, 2960, 2934, 2876, 1636, 1599, 1458, 1416, 1321, 1261, 1159 cm^{-1} ; LRMS (EI, 20 eV) m/z 394 ($\text{M}^+ - \text{C}_2\text{H}_5$, 6), 352 (7), 268 (100), 183 (12), 155 (15), 115 (74), 87 (77), 77 (29); HRMS (EI, 20 eV) Calculated for $\text{C}_{20}\text{H}_{32}\text{NO}_3\text{SSi}$ ($\text{M}^+ - \text{C}_2\text{H}_5$) 394.1872, Found 394.1867.



To a solution of HMDS (3.0 mL, 14 mmol) in anhydrous THF (10 mL) at 0 °C was added *n*-BuLi (1.28 M in hexane, 7.4 mL, 9.5 mmol). The mixture was stirred for 30 min at 0 °C and then cooled to -78 °C. To this was added **3i** (1.1938 g, 4.6752 mmol) in THF (4.0 mL) via cannula. The resulting solution was stirred for 1 h at -78 °C. TESCl (0.750 mL, 4.47 mmol) was added and the reaction was allowed to warm to room temperature. After stirring for 1 h, aqueous NaHCO_3 was added and the mixture was extracted with Et_2O (30 mL x 3), separated and dried over anhydrous MgSO_4 . The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 1% EtOAc and 1% Et_3N in hexane to afford **1i** (1.1823 g, 72% yield). **(2*R**,3*S**)-tert-Butyl 2-pentyl-3-(1-(triethylsiloxy)vinyl)aziridine-1-carboxylate (1i)**: Colourless oil; $R_f = 0.43$ (5% EtOAc in hexane); ^1H NMR (400 MHz, C_6D_6) δ 4.47 (d, $J = 1.4$ Hz, 1H), 4.33 (d, $J = 1.4$ Hz, 1H), 2.75 (td, $J = 6.3, 3.0$ Hz, 1H), 2.70 (d, $J = 3.0$ Hz, 1H), 1.69-1.59 (m, 1H), 1.44 (s, 9H), 1.41-1.36 (m, 1H), 1.30-1.24 (m, 1H), 1.23-1.17 (m, 5H), 1.00 (t, $J = 8.0$ Hz, 9H), 0.84 (t, $J = 6.9$ Hz, 3H), 0.67 (q, $J = 8.0$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 160.1, 154.2, 93.2, 79.9, 46.0, 41.9, 31.8, 31.5, 28.2, 27.1, 23.0, 14.2, 7.0, 5.3 ppm; IR (ν) 3051, 2959, 2934, 2878, 1713 (C=O), 1632, 1458, 1422, 1319, 1157 cm^{-1} ; LRMS (EI, 20 eV) m/z 312 ($\text{M}^+ - \text{C}_4\text{H}_9$, 1), 268 (86), 140 (30), 198 (53), 182 (12), 157 (11), 115 (100), 87 (99); HRMS (EI, 20 eV) Calculated for $\text{C}_{16}\text{H}_{30}\text{NO}_3\text{Si}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) 312.1995, Found 312.2006.

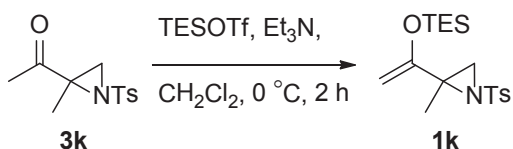


To a solution of **3j** (0.3837 g, 1.603 mmol) in CH_2Cl_2 (8.6 mL) at -78 °C was added Et_3N (0.5 mL,

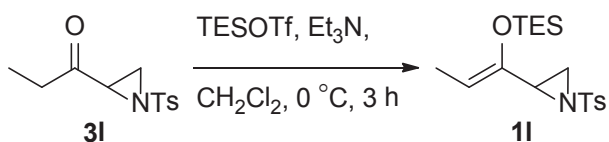
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3.6 mmol) and TESOTf (0.6 mL, 3 mmol). The resulting mixture was stirred at 0 °C for 3 h. The reaction was quenched with aqueous NaHCO₃, extracted with Et₂O (30 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 3% EtOAc and 1% Et₃N in hexane to afford **1j** (0.4677 g, 83% yield).

2,2-Dimethyl-1-((2*R,3*S**)-2-pentyl-3-(1-(triethylsiloxy)vinyl)aziridin-1-yl)propan-1-one (1j):** Colourless oil; *R_f* = 0.46 (5% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 4.32 (d, *J* = 1.6 Hz, 1H), 4.21 (d, *J* = 1.6 Hz, 1H), 2.88 (ddd, *J* = 7.0, 5.6, 2.9 Hz, 1H), 2.78 (d, *J* = 2.9 Hz, 1H), 1.72-1.63 (m, 1H), 1.41-1.36 (m, 2H), 1.35 (s, 9H), 1.30-1.18 (m, 5H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.85 (t, *J* = 6.8 Hz, 3H), 0.64 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 187.5, 155.0, 92.7, 48.1, 41.0, 39.7, 31.9, 31.7, 28.0, 27.2, 22.9, 14.2, 6.9, 5.2 ppm; IR (CH₂Cl₂) 3061, 3050, 2959, 2936, 1667 (C=O), 1423, 1283 cm⁻¹; LRMS (EI, 20 eV) *m/z* 353 (M⁺, 9), 324 (21), 282 (25), 268 (100), 115 (66), 87 (55); HRMS (EI, 20 eV) Calculated for C₂₀H₃₉NO₂Si (M⁺) 353.2750, Found 353.2752.

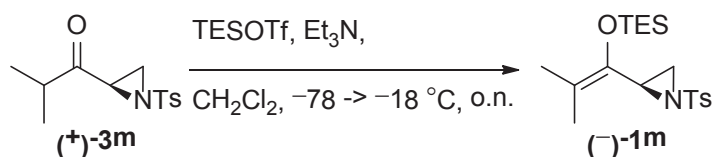


To a solution of **3k** (0.8323 g, 3.286 mmol) in CH₂Cl₂ (35 mL) at -78 °C was added Et₃N (1.4 mL, 10 mmol) and TESOTf (1.5 mL, 6.6 mmol). The resulting mixture was stirred at 0 °C for 2 h. The reaction was quenched with aqueous NaHCO₃, extracted with Et₂O (100 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 5% EtOAc and 1% Et₃N in hexane to afford **1k** (1.1232 g, 93% yield). **2-Methyl-1-tosyl-2-(1-(triethylsiloxy)vinyl)aziridine (1k):** Colourless oil; *R_f* = 0.34 (5% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 7.91 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 4.46 (d, *J* = 1.1 Hz, 1H), 4.25 (d, *J* = 1.1 Hz, 1H), 2.52 (s, 1H), 2.28 (s, 1H), 1.94 (s, 3H), 1.86 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 157.1, 143.4, 139.3, 129.5, 127.8, 91.8, 49.9, 39.8, 21.1, 16.7, 6.9, 5.1 ppm; IR (CH₂Cl₂) 3050, 2959, 2878, 1634, 1599, 1458, 1321, 1285, 1186, 1159 cm⁻¹; LRMS (EI, 20 eV) *m/z* 338 (M⁺-C₂H₅, 84), 212 (78), 155 (48), 155 (88), 91 (100); HRMS (EI, 20 eV) Calculated for C₁₆H₂₄NO₃SSi (M⁺-C₂H₅) 338.1246, Found 338.1241.



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To a solution of **31** (0.6970 g, 2.751 mmol) in CH₂Cl₂ (27.5 mL) at -78 °C was added Et₃N (1.150 mL, 8.274 mmol) and TESOTf (1.250 mL, 5.485 mmol). The resulting mixture was stirred at 0 °C for 3 h. The reaction was quenched with aqueous NaHCO₃, extracted with Et₂O (100 mL x 3), separated and dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 4% EtOAc and 1% Et₃N in hexane to afford **11** (0.8280 g, 82% yield). **(Z)-1-Tosyl-2-(1-(triethylsiloxy)prop-1-en-1-yl)aziridine (11)**: White solid; mp: 52-58 °C; R_f = 0.29 (5% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.85 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 4.66 (q, *J* = 6.8 Hz, 1H), 3.30 (dd, *J* = 7.1, 4.5 Hz, 1H), 2.44 (d, *J* = 7.1 Hz, 1H), 2.07 (d, *J* = 4.5 Hz, 1H), 1.84 (s, 3H), 1.44 (d, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.60 (qd, *J* = 7.7, 2.7 Hz, 6H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 145.6, 144.4, 137.0, 130.0, 128.7, 108.0, 42.2, 31.8, 21.5, 11.4, 7.3, 6.1 ppm; IR (CH₂Cl₂) 3071, 2959, 2878, 1674, 1599, 1387 cm⁻¹; LRMS (EI, 20 eV) *m/z* 367 (M⁺, 2), 338 (85), 310 (11), 256 (21), 224 (55), 212 (40), 155 (66), 115 (61), 91 (100); HRMS (EI, 20 eV) Calculated for C₁₈H₂₉NO₃SSi (M⁺) 367.1637, Found 367.1648.



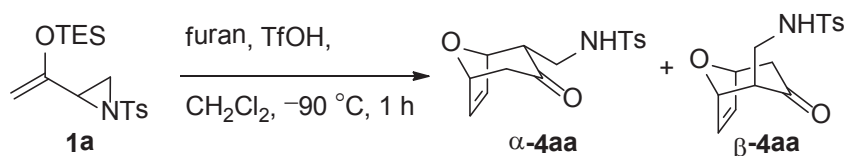
To a solution of (+)-**3m** (2.137 g, 8.002 mmol) in CH₂Cl₂ (40 mL) at -78 °C was added Et₃N (4.5 mL, 32 mmol) and TESOTf (5.4 mL, 24 mmol). The resulting mixture was stirred overnight from -78 °C to -18 °C. The reaction was quenched with aqueous NaHCO₃ and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography using 5% EtOAc and 0.1% Et₃N in hexane to afford (-)-**1m** (1.6641 g, 55% yield). **(R)-2-(2-Methyl-1-(triethylsiloxy)prop-1-en-1-yl)-1-tosyl aziridine ((-)-1m)**: White solid; mp: 56-59 °C; R_f = 0.43 (10% EtOAc in hexane); ¹H NMR (400 MHz, C₆D₆) δ 7.85 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 3.78 (dd, *J* = 7.1, 4.5 Hz, 1H), 2.49 (d, *J* = 7.1 Hz, 1H), 2.24 (d, *J* = 4.5 Hz, 1H), 1.87 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.70-0.57 (m, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ 144.1, 138.2, 136.6, 129.6, 128.3, 117.0, 38.1, 31.0, 21.1, 18.9, 18.0, 7.1, 5.7 ppm; IR (CH₂Cl₂) 3068, 2958, 2915, 2877, 1673 (C=C), 1598 cm⁻¹; LRMS (EI, 20 eV) *m/z* 381 (M⁺, 5), 352 (35), 256 (45), 226 (64), 224 (48), 210 (13), 196 (13), 177 (10); HRMS (EI, 20 eV) Calculated for C₁₉H₃₁NO₃SSi (M⁺) 381.1788, Found 381.1789.

General Experimental Procedure for (4+3) Cycloadditions

To a solution of the aziridinyl enolsilane in EtNO₂ (or other reaction solvent) pre-cooled to -90 °C (or alternative target temperature) was added the diene and TFA (or TfOH). The progress of the reaction was monitored by TLC. When the reaction was complete as judged by TLC, aqueous NaHCO₃ was added to the reaction mixture. The organic layer was separated. The aqueous layer was back extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography on silica gel.

(4 + 3) Cycloadditions of aziridinyl enolsilanes **1a** with furan (Table 1, Selected entries)

Table 1, entry 1:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3521 g, 0.9975 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.100 mL, 1.13 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts α -**4aa** and β -**4aa** (0.1715 g, 56% yield, 60:40).

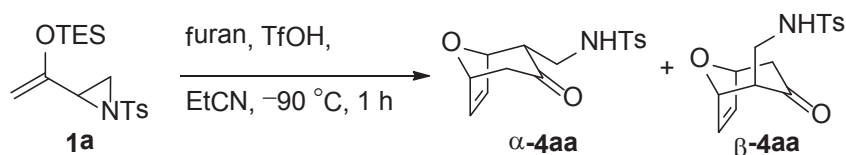
4-Methyl-N-(((1R*,2S*,5R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (α -4aa**):** White solid; mp: 117-119 °C; R_f = 0.21 (35% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.85 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 6.00 (dd, J = 6.0, 1.6 Hz, 1H), 5.65 (dd, J = 6.0, 1.6 Hz, 1H), 5.14 (dd, J = 7.6, 5.9 Hz, 1H), 4.80 (dd, J = 4.5, 1.6 Hz, 1H), 4.48 (d, J = 5.0 Hz, 1H), 3.01-2.93 (m, 2H), 2.70-2.67 (m, 1H), 2.29 (dd, J = 15.5, 5.0 Hz, 1H), 2.00 (s, 3H), 1.91 (d, J = 15.5 Hz, 1H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 206.4, 143.3, 138.4, 134.8, 132.4, 130.1, 127.7, 79.8, 78.2, 57.2, 45.8, 40.8, 21.4 ppm; IR (CH₂Cl₂) 3380 (NH), 3059, 2965, 2926, 1709 (C=O), 1653 (C=C), 1410 cm⁻¹; LRMS (EI, 20 eV) m/z 307 (M⁺, 1), 239 (13), 184 (15), 171 (21), 155 (51); HRMS (EI, 20 eV) Calculated for C₁₅H₁₇NO₄S (M⁺) 307.0873, Found 307.0871.

4-Methyl-N-(((1S*,2S*,5S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (β -4aa**):** White solid; mp: 137-139 °C; R_f = 0.17 (35% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.90 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 5.64 (dd, J = 6.1, 1.5 Hz, 1H), 5.62 (dd, J = 6.1, 1.4 Hz, 1H), 5.21 (t, J = 6.0 Hz, 1H), 4.45 (s, 1H), 4.42 (d, J = 5.2 Hz, 1H), 3.33-3.22 (m, 2H),

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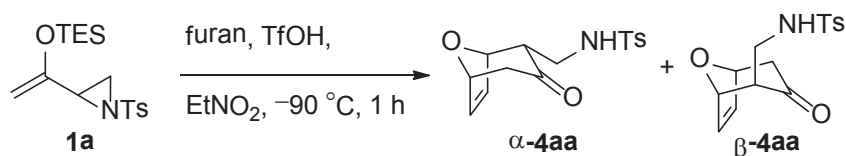
2.35 (dd, $J = 16.8, 5.2$ Hz, 1H), 2.21 (t, $J = 7.1$ Hz, 1H), 2.00 (s, 3H), 1.91 (d, $J = 16.8$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 205.7, 143.3, 138.3, 134.5, 133.1, 130.1, 127.9, 79.3, 77.7, 55.5, 45.4, 44.1, 21.4 ppm; IR (CH_2Cl_2) 3683 (NH), 3063, 2957, 2927, 2855, 1717 (C=O), 1605 (C=C), 1465 cm^{-1} ; LRMS (EI, 20 eV) m/z 307 (M^+ , 2), 261 (6), 239 (4), 226 (2), 184 (33), 171 (19), 155 (68); HRMS (EI, 20 eV) Calculatd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$ (M^+) 307.0873, Found 307.0873.

Table 1, entry 2:



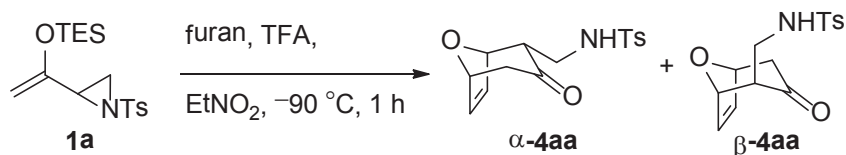
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3543 g, 1.003 mmol) in EtCN (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TfOH (0.100 mL, 1.13 mmol) at -90 °C. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts **α -4aa** and **β -4aa** (0.2104 g, 68% yield, 38:62).

Table 1, entry 3:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3531 g, 0.9999 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TfOH (0.100 mL, 1.13 mmol) at -90 °C. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts **α -4aa** and **β -4aa** (0.2628 g, 86% yield, 50:50).

Table 1, entry 6:

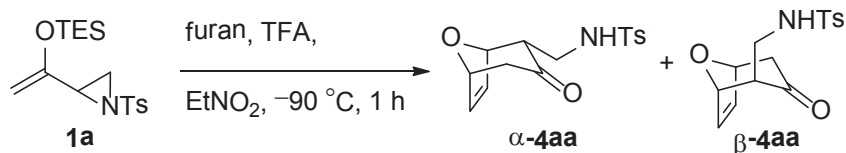


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3539 g, 1.002 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO_3 was added and the reaction was

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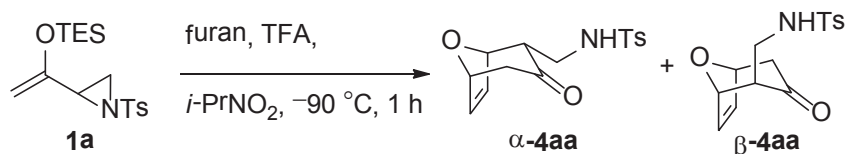
worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts α -4aa and β -4aa (0.3048 g, 99% yield, 55:45).

Table 1, entry 8:



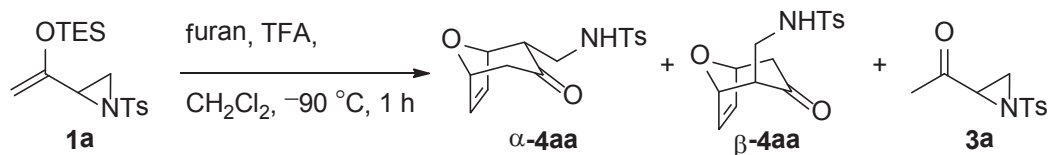
According to the general procedure for the cycloaddition reaction, aziridinylnonsilane **1a** (0.3554 g, 1.006 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.11 mL, 1.5 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts α -4aa and β -4aa (0.2583 g, 84% yield, 60:40).

Table 1, entry 10:



According to the general procedure for the cycloaddition reaction, aziridinylnonsilane **1a** (0.3533 g, 1.000 mmol) in *i*-PrNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts α -4aa and β -4aa (0.3039 g, 99% yield, 50:50).

Table 1, entry 12:

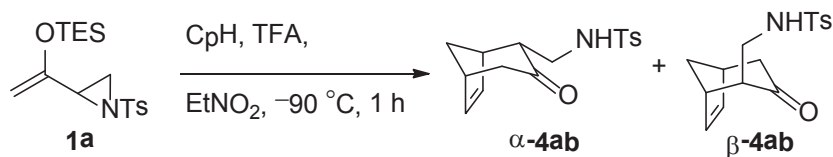


According to the general procedure for the cycloaddition reaction, aziridinylnonsilane **1a** (0.3538 g, 1.001 mmol) in CH₂Cl₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts α -4aa and β -4aa (0.0834 g, 27% yield, 52:48) and aziridinylnonsilane ketone **3a** (0.1730 g, 72% yield).

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(4 + 3) Cycloaddition of aziridinyl enolsilanes **1a-g** with dienes (Table 2)

Table 2, entry 1:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3538 g, 1.002 mmol) in EtNO₂ (10 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.41 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 1% acetone in CH₂Cl₂ to afford cycloadducts α -**4ab** and β -**4ab** (0.2846g, 93% yield, 54:46).

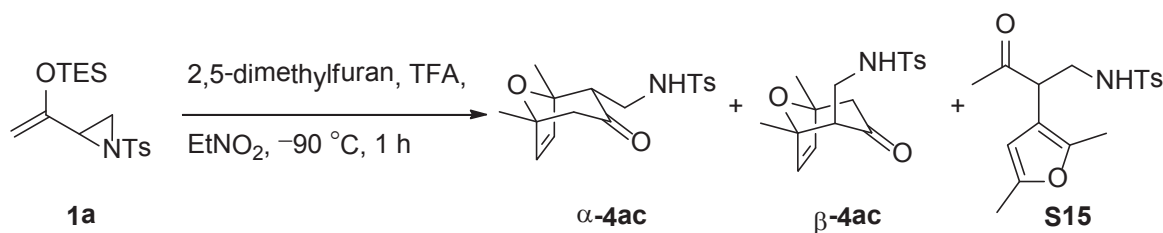
4-Methyl-N-(((1*R**,2*R**,5*R**)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide

(α -4ab): Colourless oil; R_f = 0.50 (CH₂Cl₂); ¹H NMR (500 MHz, C₆D₆) δ 7.84 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.74 (dd, J = 8.7, 4.4 Hz, 1H), 5.69 (dd, J = 5.7, 2.6 Hz, 1H), 5.62 (dd, J = 5.7, 2.6 Hz, 1H), 3.14 (ddd, J = 12.9, 7.2, 4.5 Hz, 1H), 2.93 (ddd, J = 12.9, 8.7, 6.5 Hz, 1H), 2.60-2.57 (m, 1H), 2.43-2.39 (m, 1H), 2.31-2.27 (m, 1H), 2.03 (dt, J = 16.0, 2.7 Hz, 1H), 1.94 (dd, J = 16.0, 3.4 Hz, 1H), 1.93 (s, 3H), 1.74-1.69 (m, 1H), 1.33 (d, J = 10.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 210.4, 143.3, 138.6, 137.5, 133.9, 130.2, 127.7, 56.7, 46.0, 43.8, 43.5, 42.7, 39.7, 21.5 ppm; IR (CH₂Cl₂) 3339 (NH), 2956, 2877, 1702 (C=O), 1599, 1455 cm⁻¹; LRMS (EI, 20 eV) m/z 305 (M⁺, 2), 262 (1), 239 (4), 184 (6), 171 (6), 155 (67), 150 (100), 122 (78); HRMS (EI, 20 eV) Calculated for C₁₆H₁₉NO₃S (M⁺) 305.1080, Found 305.1081.

4-Methyl-N-(((1*S,2*R**,5*S**)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (β -4ab)**: White solid; mp: 118-119 °C; R_f = 0.31 (CH₂Cl₂); ¹H NMR (500 MHz, C₆D₆) δ 7.98 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 5.75-5.73 (m, 2H), 5.54 (dd, J = 7.2, 4.9 Hz, 1H), 3.24-3.10 (m, 2H), 2.57-2.56 (m, 1H), 2.34-2.31 (m, 2H), 2.13-2.09 (m, 1H), 2.05-2.01 (m, 4H), 1.66-1.61 (m, 1H), 1.50 (d, J = 11.5 Hz, 1H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 210.9, 143.3, 138.6, 137.2, 136.2, 130.2, 127.8, 54.3, 45.2, 44.9, 40.8, 38.3, 36.9, 21.4 ppm; IR (CH₂Cl₂) 3350 (NH), 3045, 2997, 2952, 2879, 1699 (C=O), 1598 cm⁻¹; LRMS (EI, 20 eV) m/z 305 (M⁺, 4), 239 (7), 224 (7), 184 (77), 171 (118), 155 (424); HRMS (EI, 20 eV) Calculated for C₁₆H₁₉NO₃S (M⁺) 305.1080, Found 305.1075.

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Table 2, entry 2:

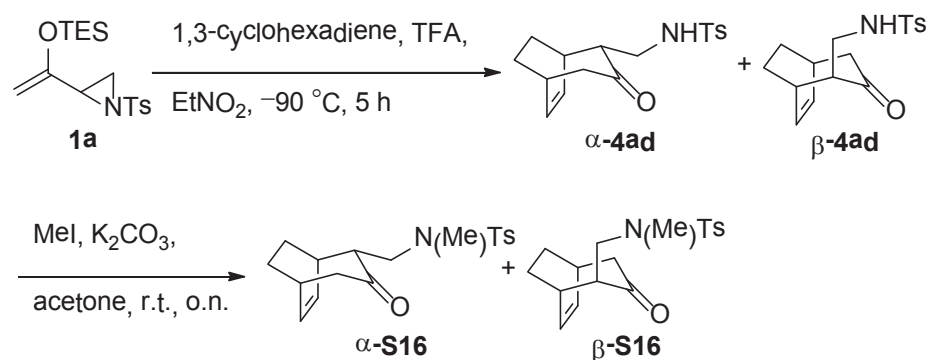


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3541 g, 1.003 mmol) in EtNO₂ (10 mL) was subjected to reaction with 2,5-dimethylfuran (0.53 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -**4ac** and β -**4ac** (0.0847g, 25% yield, 79:21) and alkylation product **S15** (0.0367 g, 11% yield). **N-(((1R*,2S*,5R*)-1,5-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (α -4ac)**: White solid; mp: 128-131 °C; *R_f* = 0.45 (35% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.85 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.88 (d, *J* = 5.8 Hz, 1H), 5.52 (d, *J* = 5.8 Hz, 1H), 5.32 (t, *J* = 6.5 Hz, 1H), 3.26-3.21 (m, 1H), 3.07-3.02 (m, 1H), 2.44 (dd, *J* = 6.7, 3.2 Hz, 1H), 2.21 (d, *J* = 15.2 Hz, 1H), 2.16 (d, *J* = 15.2 Hz, 1H), 2.05 (s, 3H), 1.50 (s, 3H), 1.21 (s, 3H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 207.6, 142.9, 138.7, 136.5, 135.7, 129.8, 127.3, 86.4, 84.0, 61.1, 51.0, 40.0, 23.1, 21.5, 21.0 ppm; IR (CH₂Cl₂) 3668 (NH), 3070, 2979, 2934, 1707 (C=O), 1600 cm⁻¹; LRMS (EI, 20 eV) *m/z* 335 (M⁺, 4), 239 (11), 180 (100), 162 (13), 155 (14), 153 (12), 138 (46); HRMS (EI, 20 eV) Calculated for C₁₇H₂₁NO₄S (M⁺) 335.1186, Found 335.1184. **N-(((1S*,2S*,5S*)-1,5-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (β -4ac)**: White solid; mp: 121-124 °C; *R_f* = 0.33 (35% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.94 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.81 (dd, *J* = 7.2, 4.0 Hz, 1H), 5.50 (d, *J* = 5.7 Hz, 1H), 5.46 (d, *J* = 5.7 Hz, 1H), 3.55-3.50 (m, 1H), 3.67-3.31 (m, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 2.19 (d, *J* = 16.2 Hz, 1H), 2.16 (dd, *J* = 7.6, 4.6 Hz, 1H), 1.98 (s, 3H), 1.14 (s, 3H), 1.03 (s, 3H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 207.5, 143.3, 138.3, 137.7, 136.9, 130.1, 127.9, 85.2, 84.8, 55.9, 50.9, 42.0, 23.0, 21.4, 19.9 ppm; IR (CH₂Cl₂) 3328 (NH), 3060, 2981, 1712 (C=O), 1598, 1444 cm⁻¹; LRMS (EI, 20 eV): *m/z* 335 (M⁺, 1), 279 (2), 224 (5), 184 (9), 180 (77), 171 (7), 167 (9), 155 (52); HRMS (EI, 20 eV) Calculated for C₁₇H₂₁NO₄S (M⁺) 35.1186, Found 335.1191. **N-(2-(2,5-Dimethylfuran-3-yl)-3-oxobutyl)-4-methylbenzenesulfonamide (S15)**: Colourless oil; *R_f* = 0.62 (35% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 4.84 (t, *J* = 6.7 Hz, 1H), 3.69 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.32-3.25 (m, 1H), 3.03-2.96 (m, 1H), 2.41 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 2.00 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 208.0,

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150.9, 147.9, 143.5, 137.1, 129.8, 127.1, 114.2, 105.2, 50.2, 43.6, 28.7, 21.6, 13.5, 11.6 ppm; IR (CH₂Cl₂): 3060, 2923, 1710 (C=O), 1598, 1583 cm⁻¹; LRMS (EI, 20 eV) m/z 335 (M⁺, 3), 183 (1), 164 (8), 155 (19), 152 (100), 137 (21), 136 (18), 122 (11), 121 (15); HRMS (EI, 20 eV) Calculated for C₁₇H₂₁NO₄S (M⁺) 335.1186, Found 335.1190.

Table 2, entry 3:

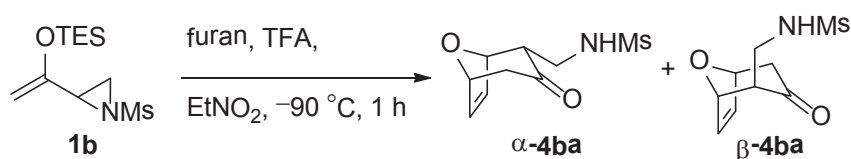


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1a** (0.3543 g, 1.004 mmol) in EtNO₂ (10 mL) was subjected to reaction with 1,3-cyclohexadiene (0.48 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 5 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts **α-4ad** and **β-4ad** with some polymer from 1,3-cyclohexadiene. To a solution of this mixture in acetone (10 mL) was added K₂CO₃ (0.9661 g, 7.001 mmol) and MeI (0.19 mL, 3.0 mmol) at room temperature. The resulting mixture was stirred overnight at room temperature. The reaction mixture was filtered through a short pad of silica gel and washed with Et₂O. The volatiles were removed *in vacuo*. The residue was purified by flash column chromatography using 10% EtOAc in hexane to afford **α-S16** and **β-S16** (0.2089 g, 63% yield, 41:59). **N,4-Dimethyl-N-(((1R*,2R*,5R*)-3-oxobicyclo[3.2.2]non-6-en-2-yl)methyl)benzenesulfonamide (α-S16)**: Colourless oil; R_f = 0.38 (20% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.38-6.32 (m, 2H), 3.25 (dd, *J* = 13.4, 9.9 Hz, 1H), 2.91-2.87 (m, 2H), 2.70-2.67 (m, 5H), 2.58-2.50 (m, 2H), 2.41 (s, 3H), 1.91-1.76 (m, 4H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 211.9, 143.4, 135.7, 134.0, 132.6, 129.7, 127.4, 58.1, 51.3, 49.1, 35.3, 30.7, 29.1, 26.4, 26.1, 21.4 ppm; IR (CH₂Cl₂) 3055, 2939, 2869, 1689 (C=O), 1458, 1342 cm⁻¹; LRMS (EI, 20 eV) m/z 333 (M⁺, 1), 253 (1), 198(73), 185 (13), 178 (41); HRMS (EI, 20 eV) Calculated for C₁₈H₂₃NO₃S (M⁺) 333.1393, Found 333.1388. **N,4-Dimethyl-N-(((1S*,2R*,5S*)-3-oxobicyclo[3.2.2]non-6-en-2-yl)methyl)benzenesulfonamide (β-S16)**: Colourless oil; R_f (20% EtOAc in hexane) 0.47; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* =

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8.2 Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.45-6.41 (m, 2H), 3.41 (dd, $J = 14.0, 10.6$ Hz, 1H), 3.00 (dd, $J = 14.0, 4.0$ Hz, 1H), 2.87 (br s, 1H), 2.67 (s, 3H), 2.63-2.55 (m, 3H), 2.42-2.39 (m, 4H), 1.78-1.59 (m, 4H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 211.6, 143.4, 136.0, 135.4, 134.0, 129.7, 127.4, 55.1, 50.0, 49.2, 35.7, 29.9, 29.0, 24.7, 21.4, 20.4 ppm; IR (CH_2Cl_2) 3055, 2931, 2869, 1689 (C=O), 1596, 1458 cm^{-1} ; LRMS (EI, 20 eV) m/z 333 (M^+ , 1), 295 (1), 253 (1), 241 (1), 198 (24), 185 (12), 178 (12), 155 (39), 120 (9); HRMS (EI, 20 eV) Calculated for $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{S}$ (M^+) 333.1393, Found 333.1382.

Table 2, entry 4:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1b** (0.2781 g, 1.004 mmol) in EtNO_2 (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90°C . After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 75% EtOAc in hexane to afford cycloadducts α -**4ba** and β -**4ba** (0.2183 g, 94% yield, 52:48).

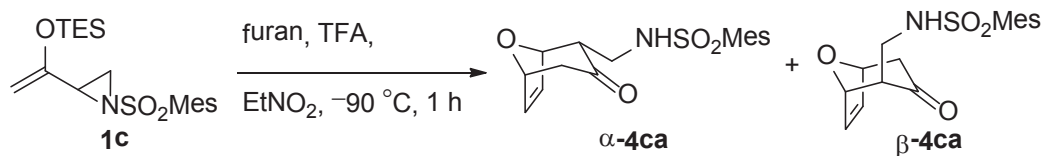
N-(((1R*,2S*,5R*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)methanesulfonamide (α -4ba): White solid; mp: 108-111 $^\circ\text{C}$; $R_f = 0.39$ (70% EtOAc in hexane); ^1H NMR (500 MHz, CD_3OD) δ 6.38 (dd, $J = 6.1, 1.6$ Hz, 1H), 6.36 (dd, $J = 6.1, 1.6$ Hz, 1H), 5.08 (dd, $J = 4.5, 1.5$ Hz, 1H), 5.01 (dt, $J = 5.0, 1.2$ Hz, 1H), 3.44 (dd, $J = 13.6, 5.0$ Hz, 1H), 3.00-2.97 (m, 1H), 2.91 (dd, $J = 13.6, 8.7$ Hz, 1H), 2.75 (dd, $J = 15.7, 5.0$ Hz, 1H), 2.25 (dd, $J = 15.7, 0.7$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 207.7, 136.1, 132.8, 80.4, 79.5, 58.4, 46.4, 40.6, 39.7 ppm; IR (CH_2Cl_2): 3352 (NH), 3058, 2968, 1708 (C=O), 1423, 1406 cm^{-1} ; LRMS (EI, 20 eV) m/z 231 (M^+ , 2), 163 (11), 150 (35), 136 (60), 108 (24), 95 (23), 81 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_9\text{H}_{13}\text{NO}_4\text{S}$ (M^+) 231.0560, Found 231.0554.

N-(((1S*,2S*,5S*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)methanesulfonamide (β -4ba): White solid; mp: 136-138 $^\circ\text{C}$; $R_f = 0.26$ (70% EtOAc in hexane); ^1H NMR (500 MHz, CD_3OD) δ 6.35 (dd, $J = 6.0, 1.6$ Hz, 1H), 6.31 (dd, $J = 6.0, 1.7$ Hz, 1H), 4.98 (d, $J = 5.1$ Hz, 1H), 4.93 (s, 1H), 4.48 (dd, $J = 13.3, 8.4$ Hz, 1H), 3.37 (dd, $J = 13.3, 7.0$ Hz, 1H), 2.94 (s, 3H), 2.80 (dd, $J = 16.6, 5.1$ Hz, 1H), 2.43 (t, $J = 8.0$ Hz, 1H), 2.26 (d, $J = 16.6$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 208.4, 135.6, 133.9, 79.8, 78.9, 57.9, 46.2, 43.9, 40.2 ppm; IR (CH_2Cl_2) 3375 (NH), 3066, 3051, 2966, 1714 (C=O), 1425, 1407 cm^{-1} ; LRMS (EI, 20 eV) m/z 231 (M^+ , 1), 163 (6), 150 (31), 148 (11),

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136 (45), 124 (17), 108 (20); HRMS (EI, 20 eV) Calculated for C₉H₁₃NO₄S (M⁺) 231.0560, Found 231.0564.

Table 2, entry 5:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1c** (0.3816 g, 1.002 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -**4ca** and β -**4ca** (0.3781 g, 85% yield, 57:43).

2,4,6-Trimethyl-N-(((1*R,2*S**,5*R**)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-**

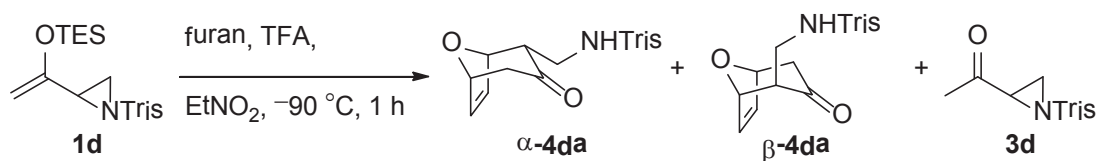
benzenesulfonamide (α -4ca**):** White solid; mp: 125-127 °C; R_f = 0.34 (35% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.95 (s, 2H), 6.25 (dd, J = 6.1, 1.6 Hz, 1H), 6.21 (dd, J = 6.1, 1.6 Hz, 1H), 5.35 (dd, J = 7.7, 5.7 Hz, 1H), 5.00 (d, J = 5.0 Hz, 1H), 4.94 (dd, J = 4.4, 1.6 Hz, 1H), 2.96-2.93 (m, 1H), 2.91-2.84 (m, 2H), 2.72 (dd, J = 15.6, 5.0 Hz, 1H), 2.63 (s, 6H), 2.61-2.25 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.3, 142.2, 138.8, 134.5, 133.3, 132.0, 131.8, 79.5, 77.8, 56.6, 45.5, 39.4, 22.7, 20.8 ppm; IR (CH₂Cl₂) 3633 (NH), 3062, 2970, 1705 (C=O), 1566, 1404 cm⁻¹; LRMS (EI, 20 eV) m/z 335 (M⁺, 1), 267 (6), 199 (16), 183 (18), 165 (10), 152 (18), 149 (13); HRMS (EI, 20 eV) Calculated for C₁₇H₂₁NO₄S (M⁺) 335.1186, Found 335.1194.

2,4,6-Trimethyl-N-(((1*S,2*S**,5*S**)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzene-**

sulfonamide (β -4ca**):** White solid; mp: 188-191 °C; R_f = 0.26 (35% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.95 (s, 2H), 6.29 (dd, J = 6.0, 1.5 Hz, 1H), 6.21 (dd, J = 6.0, 1.7 Hz, 1H), 5.27 (dd, J = 8.1, 3.6 Hz, 1H), 4.99 (d, J = 5.4 Hz, 1H), 4.82 (d, J = 1.5 Hz, 1H), 3.35-3.29 (m, 1H), 3.16-3.11 (m, 1H), 2.67-2.63 (m, 1H), 2.62 (s, 6H), 2.37 (t, J = 6.7 Hz, 1H), 2.30-2.26 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.4, 142.4, 139.2, 134.5, 132.9, 132.7, 132.0, 79.4, 77.2, 54.3, 45.1, 43.2, 22.9, 20.9 ppm; IR (CH₂Cl₂) 3381 (NH), 3057, 2989, 2941, 1716 (C=O), 1458 cm⁻¹; LRMS (EI, 20 eV) m/z 335 (M⁺, 3), 267 (2), 212 (19), 183 (37), 153 (19), 136 (39); HRMS (EI, 20 eV) Calculated for C₁₇H₂₁NO₄S (M⁺) 335.1186, Found 335.1185.

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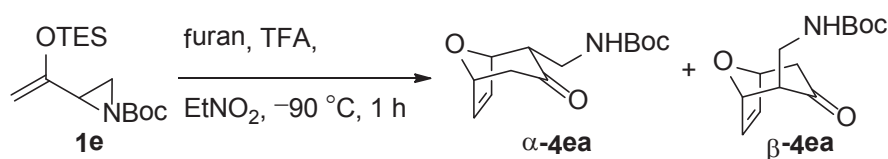
Table 2, entry 6:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1d** (0.4498 g, 0.9673 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts α -**4da** and β -**4da** (0.3405 g, 84% yield, 57:43) and aziridinyl ketone **3d** (0.0493 g, 15% yield). **2,4,6-Triisopropyl-N-(((1R*,2S*,5R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (α -4da)**: White solid; mp: 129-132 °C; R_f = 0.51 (35% EtOAc in hexane); ¹H NMR (500 MHz, C₆D₆) δ 7.21 (s, 2H), 5.67 (dd, J = 6.0, 1.6 Hz, 1H), 5.45 (dd, J = 6.0, 1.6 Hz, 1H), 5.32 (dd, J = 8.3, 5.1 Hz, 1H), 4.51 (septet, J = 6.7 Hz, 2H), 4.46 (dd, J = 4.5, 1.5 Hz, 1H), 4.31 (d, J = 5.0 Hz, 1H), 2.96-2.84 (m, 2H), 2.66-2.58 (m, 2H), 2.10 (dd, J = 15.5, 5.0 Hz, 1H), 1.73 (d, J = 15.5 Hz, 1H), 1.37 (d, J = 6.7 Hz, 6H), 1.36 (d, J = 6.7 Hz, 6H), 1.09 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 207.0, 153.1, 151.0, 134.7, 134.4, 132.2, 124.4, 80.0, 78.1, 57.3, 45.8, 40.6, 34.7, 30.5, 25.5, 24.0 ppm; IR (CH₂Cl₂) 3685 (NH), 2964, 2929, 2869, 1708 (C=O), 1600, 1564 cm⁻¹; LRMS (EI, 20 eV) m/z 419 (M⁺, 1), 282 (3), 267 (37), 266 (18), 251 (35), 232 (2); HRMS (EI, 20 eV) Calculated for C₂₃H₃₃NO₄S (M⁺) 419.2125, Found 419.2123. **2,4,6-Triisopropyl-N-(((1S*,2S*,5S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (β -4da)**: White solid; mp: 175-178 °C; R_f = 0.50 (35% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.15 (s, 2H), 6.31 (dd, J = 6.0, 1.5 Hz, 1H), 6.23 (dd, J = 6.0, 1.7 Hz, 1H), 5.17 (dd, J = 8.5, 3.4 Hz, 1H), 5.01 (d, J = 5.5 Hz, 1H), 4.88 (d, J = 1.5 Hz, 1H), 4.11 (septet, J = 6.7 Hz, 2H), 3.42-3.36 (m, 1H), 3.26-3.22 (m, 1H), 2.89 (septet, J = 6.9 Hz, 1H), 2.72 (dd, J = 17.0, 4.9 Hz, 1H), 2.44 (t, J = 6.5 Hz, 1H), 2.32 (d, J = 17.0 Hz, 1H), 1.26-1.24 (m, 18H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.3, 152.9, 150.4, 134.6, 132.7, 131.6, 123.8, 79.5, 77.3, 54.3, 45.3, 43.4, 34.1, 29.6, 24.9, 24.8, 23.5 ppm; IR (CH₂Cl₂) 3685 (NH), 2964, 2929, 2869, 1714 (C=O), 1600 cm⁻¹; LRMS (EI, 20 eV) m/z 419 (M⁺, 1), 267 (83), 251 (36), 216 (26), 187 (100), 161 (15), 159 (51), 117 (31), 91 (35), 85 (40); HRMS (EI, 20 eV) Calculated for C₈H₁₀NO₄S (M⁺) 419.2125; Found 419.2124.

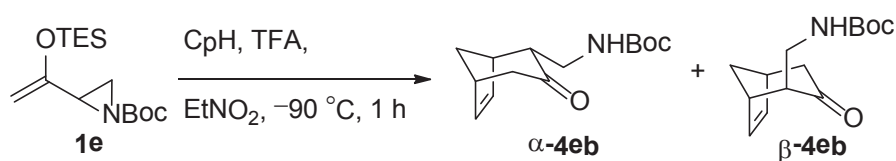
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Table 2, entry 7:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1e** (0.1499 g, 0.5005 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with furan (0.180 mL, 2.47 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts **α-4ea** and **β-4ea** (0.0674 g, 53% yield, 53:47). **tert-Butyl (((1*R**,2*S**,5*R**)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (α-4ea)**: White solid; mp: 92-95 °C; *R_f* = 0.59 (50% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.28 (d, *J* = 6.2, 1.2 Hz, 1H), 6.25 (dd, *J* = 6.1, 1.1 Hz, 1H), 5.03-5.02 (m, 1H), 4.99-4.97 (m, 2H), 3.35-3.29 (m, 1H), 3.21-3.16 (m, 1H), 2.90 (ddd, *J* = 6.1, 4.9, 4.9 Hz, 1H), 2.74 (dd, *J* = 15.6, 4.9 Hz, 1H), 2.29 (d, *J* = 15.6 Hz, 1H), 1.43 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.2, 156.0, 134.4, 132.2, 79.9, 79.5, 77.6, 58.2, 45.6, 37.0, 28.4 ppm; IR (CH₂Cl₂) 3451 (NH), 3067, 3044, 2992, 2980, 1711 (C=O), 1506, 1368, 1269, 1171 cm⁻¹; LRMS (EI, 20 eV) *m/z* 253 (M⁺, 1), 197 (5), 185 (18), 153 (30), 137 (39), 129 (59), 124 (100), 107 (23), 95 (28), 85 (44), 81 (46), 70 (39); HRMS (EI, 20 eV) Calculated for C₁₃H₁₉NO₄ (M⁺) 253.1314, Found 253.1299. **tert-Butyl (((1*S**,2*S**,5*S**)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (β-4ea)**: White solid; mp: 91-94 °C; *R_f* = 0.46 (50% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.30 (dd, *J* = 6.0, 1.5 Hz, 1H), 6.26 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.02-5.01 (m, 1H), 4.83-4.81 (m, 2H), 3.58-3.48 (m, 2H), 2.85 (dd, *J* = 16.7, 4.7 Hz, 1H), 2.41 (dd, *J* = 7.4, 7.4 Hz, 1H), 2.29 (d, *J* = 16.7 Hz, 1H), 1.43 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.8, 155.8, 134.3, 132.9, 79.7, 79.4, 78.1, 56.0, 45.1, 41.2, 28.4 ppm; IR (CH₂Cl₂) 3347 (NH), 3069, 3044, 2992, 2980, 1713 (C=O), 1506, 1368, 1337, 1244, 1167 cm⁻¹; LRMS (EI, 20 eV) *m/z* 253 (M⁺, 1), 197 (8), 180 (7), 153 (20), 137 (37), 124 (87), 95 (100), 81 (50), 70 (21); HRMS (EI, 20 eV) Calculated for C₁₃H₁₉NO₄ (M⁺) 253.1314, Found 253.1311.

Table 2, entry 8:

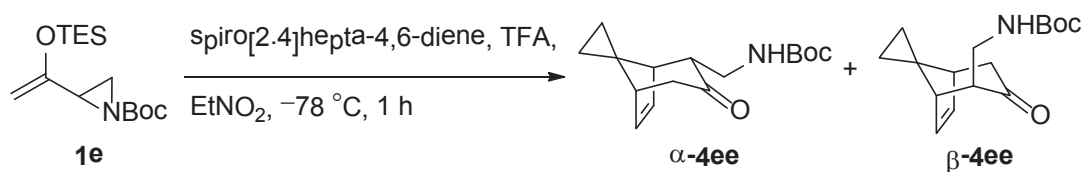


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1e** (0.1497 g, 0.4987 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene

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(0.210 mL, 2.54 mmol) and TFA (0.045 mL, 0.59 mmol) at $-90\text{ }^{\circ}\text{C}$. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts α -**4eb** and β -**4eb** (0.0938 g, 75% yield, 59:41). Analytically pure samples of α -**4eb** and β -**4eb** were obtained by further careful column chromatography using 1% acetone in CH_2Cl_2 . **tert-Butyl (((1*R**,2*R**,5*R**)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (α -**4eb**):** Colourless oil; $R_f = 0.63$ (30% EtOAc in hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.04 (dd, $J = 5.7, 2.7$ Hz, 1H), 5.96 (dd, $J = 5.8, 2.7$ Hz, 1H), 5.15 (br s, 1H), 3.29 (ddd, $J = 13.8, 8.1, 4.3$ Hz, 1H), 3.12 (ddd, $J = 13.6, 7.9, 4.6$ Hz, 1H), 2.91-2.84 (m, 2H), 2.62-2.59 (m, 1H), 2.43 (dd, $J = 15.9, 3.3$ Hz, 1H), 2.29 (ddd, $J = 15.9, 2.8, 2.8$ Hz, 1H), 2.16-2.10 (m, 1H), 1.86 (d, $J = 11.0$ Hz, 1H), 1.42 (s, 9H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 211.8, 156.0, 136.9, 133.7, 79.1, 57.3, 45.9, 43.6, 43.2, 40.5, 39.4, 28.4 ppm; IR (CH_2Cl_2) 3451 (NH), 3067, 3044, 2992, 2980, 1705 (C=O), 1504, 1456, 1368, 1269, 1242, 1171 cm^{-1} ; LRMS (EI, 20 eV) m/z 251 (M^+ , 2), 195 (21), 178 (6), 134 (27), 129 (34), 122 (100), 107 (28), 91 (23), 79 (36), 77 (31); HRMS (EI, 20 eV) Calculated for $\text{C}_{14}\text{H}_{21}\text{NO}_3$ (M^+) 251.1521, Found 251.1518. **tert-Butyl (((1*S**,2*R**,5*S**)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (β -**4eb**):** White solid; mp: 80-83 $^{\circ}\text{C}$; $R_f = 0.54$ (50% EtOAc in hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.07 (dd, $J = 5.7, 2.7$ Hz, 1H), 6.03 (dd, $J = 5.7, 2.9$ Hz, 1H), 4.83 (br s, 1H), 3.42-3.30 (m, 2H), 2.86-2.83 (m, 1H), 2.77-2.76 (m, 1H), 2.49 (dd, $J = 17.7, 3.0$ Hz, 1H), 2.34-2.28 (m, 2H), 1.96-1.91 (m, 2H), 1.42 (s, 9H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 212.2, 155.9, 136.9, 135.8, 79.5, 54.8, 45.0, 42.0, 41.2, 38.0, 36.9, 28.4 ppm; IR (CH_2Cl_2) 3447 (NH), 3069, 3044, 2992, 2980, 1707 (C=O), 1504, 1368, 1242, 1169 cm^{-1} ; LRMS (EI, 20 eV) m/z 251 (M^+ , 6), 195 (42), 178 (8), 151 (17), 134 (41), 129 (100), 122 (69), 107 (18), 91 (32), 79 (34), 70 (28); HRMS (EI, 20 eV) Calculated for $\text{C}_{14}\text{H}_{21}\text{NO}_3$ (M^+) 251.1521, Found 251.1519.

Table 2, entry 9:

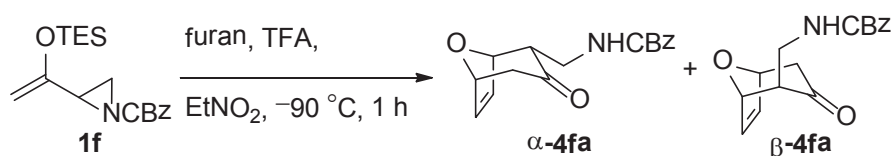


According to the general procedure for the cycloaddition reaction, aziridiny enolsilane **1e** (0.1090 g, 0.3640 mmol) in EtNO_2 (3.6 mL) was subjected to reaction with spiro[2,4]hepta-4,6-diene (0.185 mL, 1.85 mmol) and TFA (0.035 mL, 0.46 mmol) at $-90\text{ }^{\circ}\text{C}$. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts α -**4ee** and β -**4ee** (0.0701 g, 69% yield, 83:17). **tert-Butyl (((1*R**,2*R**,5*R**)-3-oxospiro[bicyclo[3.2.1]oct[6]ene-8,1'-cyclopropan]-**

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2-yl)methyl)carbamate (α -4ee): White solid; mp: 138-141 °C; R_f = 0.49 (20% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 6.16 (dd, J = 5.9, 2.7 Hz, 1H), 6.08 (dd, J = 5.9, 2.7 Hz, 1H), 5.16 (br s, 1H), 3.29 (ddd, J = 12.9, 8.0, 4.2 Hz, 1H), 3.13 (ddd, J = 12.8, 7.5, 4.6 Hz, 1H), 2.66 (ddd, J = 7.6, 3.5, 3.5 Hz, 1H), 2.50 (dd, J = 15.7, 3.4 Hz, 1H), 2.33 (dd, J = 15.7, 2.7 Hz, 1H), 2.16-2.14 (m, 2H), 1.42 (s, 9H), 0.74-0.64 (m, 4H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 212.0, 156.0, 137.3, 134.7, 79.1, 57.0, 49.9, 46.1, 45.4, 40.1, 36.8, 28.4, 13.7, 7.7 ppm; IR (CH_2Cl_2) 3449 (NH), 3068, 2980, 2934, 1705 (C=O), 1506, 1368, 1244, 1167 cm^{-1} ; LRMS (EI, 20 eV) m/z 277 (M^+ , 3), 221 (24), 177 (16), 160 (58), 129 (43), 120 (58), 104 (54), 91 (100), 85 (75), 70 (77); HRMS (EI, 20 eV) Calculated for $\text{C}_{16}\text{H}_{23}\text{NO}_3$ (M^+) 277.1678, Found 277.1670. ***tert*-Butyl (((1*S**,2*R**,5*S**)-3-oxospiro[bicyclo[3.2.1]oct[6]ene-8,1'-cyclopropan]-2-yl)methyl)carbamate (β -4ee):** Colourless oil; R_f = 0.43 (20% EtOAc in hexane); ^1H NMR (600 MHz, CDCl_3) δ 6.19-6.17 (m, 2H), 4.85 (br s, 1H), 3.45 (ddd, J = 13.5, 9.5, 4.2 Hz, 1H), 3.39 (ddd, J = 13.2, 11.0, 4.8 Hz, 1H), 2.65 (dd, J = 17.2, 3.2 Hz, 1H), 2.40-2.36 (m, 2H), 2.19 (s, 1H), 2.09 (s, 1H), 1.42 (s, 9H), 1.02-0.98 (m, 1H), 0.80-0.76 (m, 1H), 0.51-0.48 (m, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 212.5, 155.8, 137.0, 136.8, 79.7, 56.1, 47.8, 45.6, 44.3, 41.1, 32.1, 28.4, 10.9, 8.1 ppm; IR (CH_2Cl_2) 3445 (NH), 3067, 2992, 2980, 1705 (C=O), 1506, 1244, 1169 cm^{-1} ; LRMS (EI, 20 eV) m/z 221 (52), 220 ($\text{M}^+ - \text{C}_4\text{H}_9$, 5), 206 (7), 178 (30), 160 (38), 148 (30), 134 (52), 117 (69), 105 (50), 92 (100), 91 (51), 77 (27); HRMS (EI, 20 eV) Calculated for $\text{C}_{12}\text{H}_{14}\text{NO}_3$ ($\text{M}^+ - \text{C}_4\text{H}_9$) 220.0974, Found 220.0966.

Table 2, entry 10:

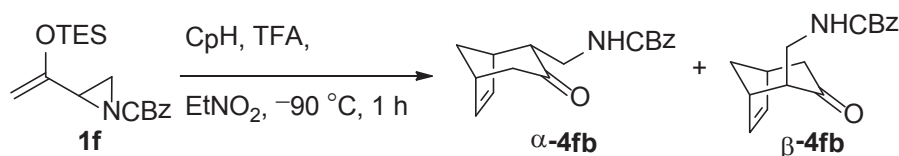


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1f** (0.0723 g, 0.217 mmol) in EtNO_2 (2.2 mL) was subjected to reaction with furan (0.080 mL, 1.10 mmol) and TFA (0.020 mL, 0.26 mmol) at $-90\text{ }^\circ\text{C}$. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts α -4fa and β -4fa (0.0393 g, 54% yield, 51:49). **Benzyl (((1*R**,2*S**,5*R**)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (α -4fa):** Colourless oil; R_f = 0.56 (50% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.30 (m, 5H), 6.27 (dd, J = 6.0, 1.7 Hz, 1H), 6.02 (dd, J = 6.0, 1.1 Hz, 1H), 5.26 (br s, 1H), 5.11 (d, J = 12.3 Hz, 1H), 5.08 (d, J = 12.3 Hz, 1H), 5.02 (ddd, J = 5.0, 1.1, 1.1 Hz, 1H), 4.98 (dd, J = 4.1, 1.1 Hz, 1H), 3.40 (ddd, J = 13.8, 7.7, 5.3 Hz, 1H), 3.24 (ddd, J = 13.8, 6.3, 5.5 Hz, 1H), 2.94-2.91 (m, 1H), 2.74 (dd, J = 15.6, 5.0 Hz, 1H), 2.29

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(dd, $J = 15.6, 0.5$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 207.2, 156.4, 136.5, 134.6, 132.0, 128.6, 128.2, 128.1, 79.8, 78.0, 66.8, 57.9, 45.6, 37.6 ppm; IR (CH_2Cl_2) 3445 (NH), 3069, 3044, 2992, 2967, 1719 (C=O), 1512, 1244, 1225 cm^{-1} ; LRMS (EI, 20 eV) m/z 287 (M^+ , 1), 219 (9), 176 (4), 136 (9), 107 (16), 91 (100), 81 (22), 79 (13), 70 (11); HRMS (EI, 20 eV) Calculated for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ (M^+) 287.1158, Found 287.1158. **Benzyl (((1S*,2S*,5S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (β -4fa)**: White solid; mp: 101-102 °C; $R_f = 0.42$ (50% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.29 (m, 5H), 6.30 (dd, $J = 6.0, 1.5$ Hz, 1H), 6.25 (dd, $J = 6.0, 1.1$ Hz, 1H), 5.15 (br s, 1H), 5.09 (s, 2H), 5.01 (d, $J = 4.7$ Hz, 1H), 4.84 (s, 1H), 3.65-3.55 (m, 2H), 2.83 (dd, $J = 16.7, 5.0$ Hz, 1H), 2.43 (dd, $J = 7.2, 7.2$ Hz, 1H), 2.30 (d, $J = 16.7$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 206.7, 156.3, 136.4, 134.3, 132.8, 128.5, 128.5, 128.2, 79.4, 77.4, 66.9, 55.7, 45.1, 41.6 ppm; IR (CH_2Cl_2) 3445 (NH), 3044, 2959, 1721 (C=O), 1607, 1514, 1337, 1242, 1219 cm^{-1} ; LRMS (EI, 20 eV) m/z 287 (M^+ , 2), 219 (3), 185 (10), 176 (3), 136 (14), 108 (22), 91 (100), 81 (23), 79 (17), 70 (11); HRMS (EI, 20 eV) Calculated for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ (M^+) 287.1158, Found 287.1152.

Table 2, entry 11:

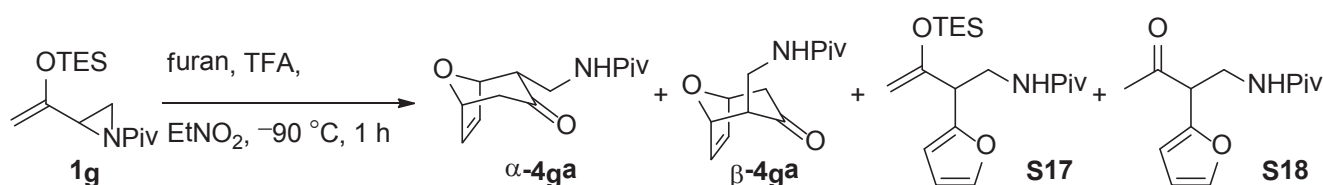


According to the general procedure for the cycloaddition reaction, aziridinylolefin **1f** (0.0728 g, 0.218 mmol) in EtNO₂ (2.2 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.090 mL, 1.1 mmol) and TFA (0.020 mL, 0.26 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts α -**4fb** and β -**4fb** (0.0494 g, 79% yield, 58:42). Analytically pure samples of α -**4fb** and β -**4fb** were obtained by further careful column chromatography using 1% acetone in CH₂Cl₂. **Benzyl (((1R*,2R*,5R*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (α -4fb)**: Colourless oil; $R_f = 0.60$ (30% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.28 (m, 5H), 6.05 (dd, $J = 5.8, 2.8$ Hz, 1H), 5.95 (dd, $J = 5.6, 2.6$ Hz, 1H), 5.42 (br s, 1H), 5.10 (d, $J = 12.4$ Hz, 1H), 5.07 (d, $J = 12.4$ Hz, 1H), 3.38 (ddd, $J = 13.9, 8.4, 4.5$ Hz, 1H), 3.19 (ddd, $J = 13.9, 8.2, 4.4$ Hz, 1H), 2.92-2.88 (m, 2H), 2.63 (ddd, $J = 7.5, 3.8, 3.2$ Hz, 1H), 2.43 (dd, $J = 16.0, 3.3$ Hz, 1H), 2.30 (ddd, $J = 16.0, 2.7, 2.7$ Hz, 1H), 2.16-2.11 (m, 1H), 1.86 (d, $J = 11.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 211.7, 156.5, 137.1, 136.6, 133.5, 128.5, 128.1, 128.0, 66.6, 57.1, 45.9, 43.6, 43.2, 41.1, 39.4 ppm; IR (CH_2Cl_2) 3445 (NH), 3069, 3044, 2953, 1719 (C=O), 1510, 1225 cm^{-1} ; LRMS (EI, 20 eV) m/z 285 (M^+ , 5), 219 (8), 194 (19), 150 (5), 134 (6),

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122 (7), 114 (15), 108 (23), 91 (100), 79 (36), 77 (11); HRMS (EI, 20 eV) Calculated for C₁₇H₁₉NO₃ (M⁺) 285.1365, Found 285.1366. **Benzyl (((1S*,2R*,5S*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate (β -4fb):** Colourless oil; R_f = 0.51 (30% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.30 (m, 5H), 6.09 (dd, *J* = 5.5, 2.6 Hz, 1H), 6.03 (dd, *J* = 5.3, 2.6 Hz, 1H), 5.09 (s, 3H), 3.48 (ddd, *J* = 13.6, 7.0, 7.0 Hz, 1H), 3.40 (ddd, *J* = 13.6, 8.7, 4.9 Hz, 1H), 2.86 (s, 1H), 2.77 (s, 1H), 2.49 (dd, *J* = 17.7, 3.6 Hz, 1H), 2.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.32 (d, *J* = 17.6 Hz, 1H), 1.94 (s, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.1, 156.4, 137.0, 136.5, 135.7, 128.5, 128.1, 128.1, 66.8, 54.6, 45.0, 42.4, 41.1, 38.0, 36.9 ppm; IR (CH₂Cl₂) 3443 (NH), 3069, 3044, 2992, 2980, 1719 (C=O), 1699, 1508, 1223 cm⁻¹; LRMS (EI, 20 eV) *m/z* 285 (M⁺, 4), 219 (3), 194 (12), 150 (5), 134 (8), 122 (27), 108 (25), 91 (100), 79 (39), 77 (18); HRMS (EI, 20 eV) Calculated for C₁₇H₁₉NO₃ (M⁺) 285.1365, Found 285.1359.

Table 2, entry 12:

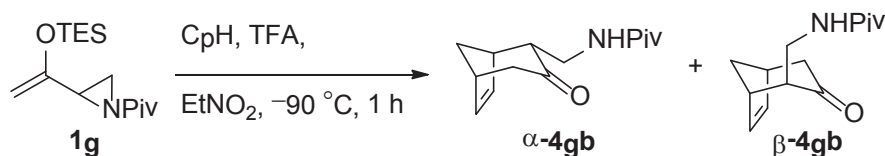


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1g** (0.1419 g, 0.5006 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with furan (0.180 mL, 2.47 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 40% EtOAc in hexane to afford cycloadducts α -**4ga** (0.0225 g, 14% yield) and β -**4ga** (0.0238 g, 20% yield) and alkylation product **S17** (0.0475 g, 27% yield) and **S18** (0.0169 g, 14% yield). **N-(((1R*,2S*,5R*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide (α -4ga):** White solid; mp: 128-130 °C; R_f = 0.35 (50% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.31 (br s, 1H), 6.29 (dd, *J* = 6.1, 1.6 Hz, 1H), 6.24 (dd, *J* = 6.1, 1.6 Hz, 1H), 5.03 (ddd, *J* = 5.0, 1.2, 1.2 Hz, 1H), 4.95 (dd, *J* = 4.5, 1.5 Hz, 1H), 3.57 (ddd, *J* = 13.8, 7.6, 4.8 Hz, 1H), 3.13 (ddd, *J* = 13.8, 7.3, 4.8 Hz, 1H), 2.88 (ddd, *J* = 7.4, 4.6, 4.6 Hz, 1H), 2.75 (dd, *J* = 15.8, 5.0 Hz, 1H), 2.30 (d, *J* = 15.8 Hz, 1H), 1.17 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.9, 178.4, 134.5, 132.3, 79.9, 78.0, 57.8, 45.7, 38.7, 36.0, 27.5 ppm; IR (CH₂Cl₂) 3464 (NH), 3069, 3044, 2992, 2967, 1709 (C=O), 1657 (C=O), 1514, 1481, 1366, 1200 cm⁻¹; LRMS (EI, 20 eV) *m/z* 237 (M⁺, 5), 208 (54), 169 (98), 156 (31), 136 (100), 126 (25), 114 (29), 102 (30), 94 (24), 85 (63), 70 (22); HRMS (EI, 20 eV) Calculated for C₁₃H₁₉NO₃ (M⁺) 237.1365, Found 237.1361. **N-(((1S*,2S*,5S*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-**

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yl)methyl)pivalamide (β -4ga): White solid; mp: 173-176 °C; R_f = 0.18 (50% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 6.30 (dd, J = 6.0, 1.6 Hz, 1H), 6.26 (dd, J = 6.0, 1.6 Hz, 1H), 6.09 (br s, 1H), 5.02 (d, J = 5.3 Hz, 1H), 4.82 (s, 1H), 3.67 (ddd, J = 13.8, 6.3, 5.8 Hz, 1H), 3.58 (ddd, J = 13.8, 9.3, 4.9 Hz, 1H), 2.85 (dd, J = 16.7, 5.1 Hz, 1H), 2.40 (dd, J = 9.3, 5.3 Hz, 1H), 2.29 (d, J = 16.7 Hz, 1H), 1.17 (s, 9H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 207.0, 178.6, 134.3, 132.9, 79.8, 77.4, 55.1, 45.1, 40.1, 38.7, 27.5 ppm; IR (CH_2Cl_2) 3466 (NH), 3067, 3046, 2992, 2967, 1711 (C=O), 1663 (C=O), 1516, 1366, 1337, 1180 cm^{-1} ; LRMS (EI, 20 eV) m/z 237 (M^+ , 4), 208 (32), 169 (44), 136 (100), 124 (53), 107 (43), 94 (46), 85 (53), 77 (64), 70 (24); HRMS (EI, 20 eV) Calculated for $\text{C}_{13}\text{H}_{19}\text{NO}_3$ (M^+) 237.1365, Found 237.1374. **N-(2-(Furan-2-yl)-3-(triethylsilyloxy)but-3-en-1-yl)pivalamide (S17):** Colourless oil; R_f = 0.58 (20% EtOAc in hexane); ^1H NMR (300 MHz, CDCl_3) δ 3.33-3.32 (m, 1H), 6.30 (dd, J = 3.1, 2.0 Hz, 1H), 6.13 (d, J = 3.2 Hz, 1H), 5.86 (br s, 1H), 4.18 (d, J = 1.1 Hz, 1H), 4.14 (d, J = 1.1 Hz, 1H), 3.70-3.59 (m, 3H), 1.15 (s, 9H), 0.92 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 7.7 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 156.6, 153.6, 141.4, 110.4, 106.6, 91.3, 45.7, 40.1, 38.8, 27.6, 6.7, 4.8 ppm; IR (CH_2Cl_2) 3468 (NH), 3061, 2961, 2913, 2787, 1659 (C=O), 1481, 1460, 1364, 1225, 1200, 1011 cm^{-1} ; LRMS (EI, 20 eV) m/z 351 (M^+ , 59), 308 (8), 250 (44), 221 (42), 136 (81), 124 (100), 94 (36); HRMS (EI, 20 eV) Calculated for $\text{C}_{19}\text{H}_{33}\text{NO}_3\text{Si}$ (M^+) 351.2230, Found 351.2226. **N-(2-(Furan-2-yl)-3-oxobutyl)pivalamide (S18):** White solid; mp: 71-74 °C; R_f = 0.59 (50% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.61 (dd, J = 1.8, 0.7 Hz, 1H), 6.59 (dd, J = 3.2, 1.8 Hz, 1H), 6.47 (d, J = 3.2 Hz, 1H), 6.31 (br s, 1H), 4.36 (dd, J = 7.8, 6.0 Hz, 1H), 3.98-3.83 (m, 2H), 2.35 (s, 3H), 1.88 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 206.0, 178.8, 149.9, 142.8, 110.9, 108.6, 52.0, 39.2, 38.8, 29.1, 27.6 ppm; IR (CH_2Cl_2) 3468 (NH), 3067, 3044, 2965, 2936, 1717 (C=O), 1659 (C=O), 1514, 1364, 1200, 1165, 1011 cm^{-1} ; LRMS (EI, 20 eV) m/z 237 (M^+ , 13), 195 (18), 136 (61), 124 (100), 94 (47); HRMS (EI, 20 eV) Calculated for $\text{C}_{13}\text{H}_{19}\text{NO}_3$ (M^+) 237.1365, Found 237.1364.

Table 2, entry 13:



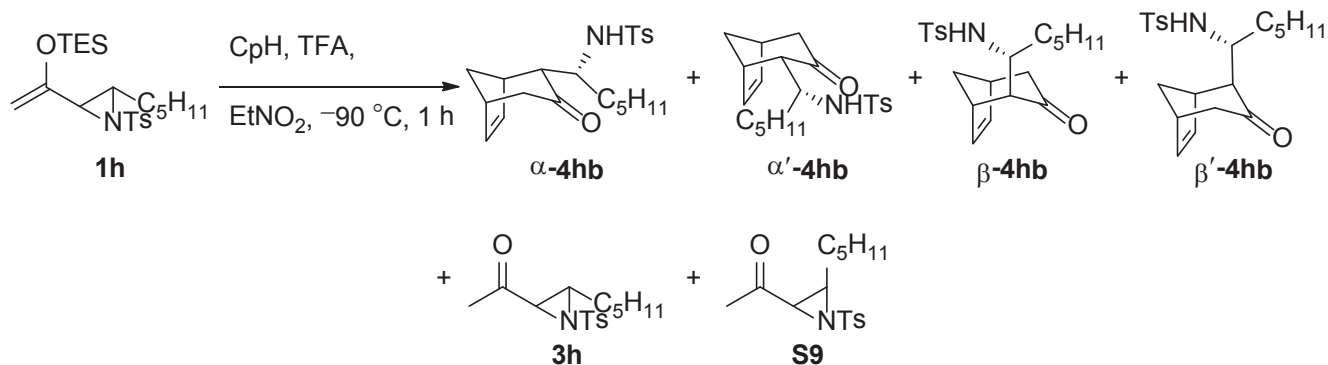
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1g** (0.1418 g, 0.5002 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -4gb and β -4gb (0.0843 g,

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72% yield, 58:42). **N-(((1*R**,2*R**,5*R**)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide (α -4gb):** White solid; mp: 106-109 °C; $R_f = 0.47$ (50% EtOAc in hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.51 (br s, 1H), 6.05 (dd, $J = 5.7, 2.7$ Hz, 1H), 5.96 (dd, $J = 5.7, 2.7$ Hz, 1H), 3.61 (ddd, $J = 13.4, 8.3, 4.0$ Hz, 1H), 3.01 (ddd, $J = 13.6, 8.9, 3.9$ Hz, 1H), 2.91-2.89 (m, 1H), 2.87-2.85 (m, 1H), 2.58 (ddd, $J = 8.8, 3.6, 3.6$ Hz, 1H), 2.44 (dd, $J = 16.1, 3.4$ Hz, 1H), 2.31 (ddd, $J = 16.1, 1.7$ Hz, 1H), 2.15-2.10 (m, 1H), 1.85 (d, $J = 11.0$ Hz, 1H), 1.15 (s, 9H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 212.5, 178.3, 137.0, 133.7, 56.9, 46.0, 43.5, 43.4, 39.7, 39.3, 38.6, 27.5 ppm; IR (CH_2Cl_2) 3464 (NH), 3067, 3044, 2992, 2959, 1701 (C=O), 1655 (C=O), 1514, 1481, 1418, 1356, 1269, 1198 cm^{-1} ; LRMS (EI, 20 eV) m/z 235 (M^+ , 11), 206 (5), 192 (5), 169 (27), 134 (100), 102 (26), 91 (22), 85 (20); HRMS (EI, 20 eV) Calculated for $\text{C}_{14}\text{H}_{21}\text{NO}_2$ (M^+) 235.1572, Found 235.1567. **N-(((1*S**,2*R**,5*S**)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide (β -4gb):** White solid; mp: 175-177 °C; $R_f = 0.41$ (50% EtOAc in hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.13 (br s, 1H), 6.09 (dd, $J = 5.6, 2.8$ Hz, 1H), 6.04 (dd, $J = 5.7, 2.8$ Hz, 1H), 3.58 (ddd, $J = 13.6, 6.4, 5.9$ Hz, 1H), 3.34 (ddd, $J = 13.6, 10.5, 4.1$ Hz, 1H), 2.88-2.86 (m, 1H), 2.75-2.73 (m, 1H), 2.52 (dd, $J = 18.0, 3.9$ Hz, 1H), 2.35-2.30 (m, 2H), 1.97-1.94 (m, 2H), 1.18 (s, 9H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 212.8, 178.6, 136.9, 135.8, 54.1, 45.1, 41.6, 40.9, 38.7, 38.1, 37.1, 27.5 ppm; IR (CH_2Cl_2) 3464 (NH), 3067, 3044, 2992, 2980, 1701 (C=O), 1659 (C=O), 1516, 1200 cm^{-1} ; LRMS (EI, 20 eV) m/z 235 (M^+ , 8), 206 (6), 192 (5), 169 (16), 134 (100), 122 (51), 102 (33), 91 (41), 85 (36); HRMS (EI, 20 eV) Calculated for $\text{C}_{14}\text{H}_{21}\text{NO}_2$ (M^+) 235.1572, Found 235.1566.

(4 + 3) Cycloaddition of aziridinyl enolsilanes 1h-m with dienes (Table 3)

Table 3, entry 1:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1h** (0.2107 g, 0.4973 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.190 mL, 2.48 mmol) at -90 °C. After 1 h, aqueous NaHCO₃

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was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts **α -4hb**, **α' -4hb**, **β -4hb** and **β' -4hb** (0.1139 g, 61% yield, 54:4:38:4) and desilylation product **3i** and **S9** (0.0363 g, 24% yield, 14.4:1).

4-Methyl-N-((R*)-1-((1R*,2R*,5R*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)benzenesulfonamide (α -4hb): Colourless oil; $R_f = 0.53$ (90% CH₂Cl₂ in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 6.09 (dd, $J = 5.7, 2.9$ Hz, 1H), 5.96 (dd, $J = 5.7, 2.8$ Hz, 1H), 4.88 (d, $J = 8.6$ Hz, 1H), 3.47 (dddd, $J = 14.0, 8.4, 5.9, 2.9$ Hz, 1H), 2.99-2.97 (m, 1H), 2.88-2.85 (m, 2H), 2.42-2.38 (m, 4H), 2.20 (ddd, $J = 15.5, 2.6, 2.6$ Hz, 1H), 2.11 (dddd, $J = 10.4, 5.1, 5.1, 2.8$ Hz, 1H), 1.81 (d, $J = 10.7$ Hz, 1H), 1.44-1.36 (m, 1H), 1.12-0.83 (m, 7H), 0.71 (t, $J = 7.1$ Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.1, 143.2, 138.3, 135.3, 135.3, 129.6, 127.0, 60.8, 55.2, 45.6, 45.2, 43.1, 39.6, 34.0, 31.2, 26.2, 22.4, 21.4, 13.8 ppm; IR (CH₂Cl₂) 3379 (NH), 3073, 2990, 2957, 2932, 2872, 1703 (C=O), 1599, 1420, 1348, 1329, 1281, 1159, 1093 cm⁻¹; LRMS (EI, 20 eV) m/z 375 (M⁺, 1), 304 (11), 254 (13), 204 (13), 155 (52), 91 (100); HRMS (EI, 20 eV) Calculated for C₂₁H₂₉NO₃S (M⁺) 375.1868, Found 375.1860.

4-Methyl-N-((R*)-1-((1S*,2S*,5S*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)benzenesulfonamide (α' -4hb): White solid; mp: 79-80 °C; $R_f = 0.31$ (70% CH₂Cl₂ in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 6.02-5.99 (m, 2H), 5.15 (d, $J = 9.7$ Hz, 1H), 3.28 (dddd, $J = 14.0, 9.7, 4.3, 4.3$ Hz, 1H), 2.86-2.83 (m, 2H), 2.73 (dd, $J = 4.6, 2.5$ Hz, 1H), 2.41 (s, 3H), 2.30 (dd, $J = 16.0, 3.5$ Hz, 1H), 2.17 (ddd, $J = 16.0, 2.6, 2.6$ Hz, 1H), 2.10 (dddd, $J = 10.6, 5.1, 5.1, 2.6$ Hz, 1H), 1.70 (d, $J = 10.6$ Hz, 1H), 1.47-1.39 (m, 1H), 1.30-1.22 (m, 1H), 1.15-1.01 (m, 5H), 0.93-0.83 (m, 1H), 0.75 (t, $J = 6.8$ Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.6, 143.1, 138.5, 136.5, 134.4, 129.5, 127.1, 61.4, 55.5, 45.5, 45.2, 42.7, 39.3, 32.3, 31.4, 26.0, 22.5, 21.5, 13.9 ppm; IR (CH₂Cl₂) 3376 (NH), 3069, 2957, 2932, 2872, 1701 (C=O), 1599, 1418, 1159, 1092 cm⁻¹; LRMS (EI, 20 eV) m/z 375 (M⁺, 1), 304 (2), 254 (27), 155 (43), 91 (100); HRMS (EI, 20 eV) Calculated for C₂₁H₂₉NO₃S (M⁺) 375.1868, Found 375.1862.

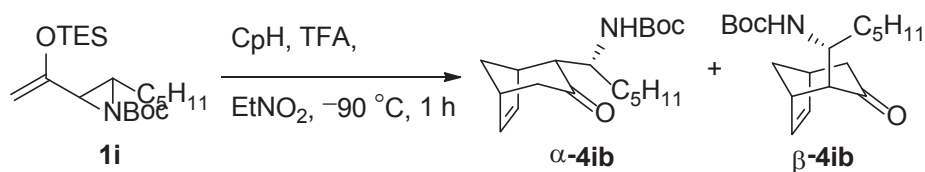
4-Methyl-N-((R*)-1-((1S*,2R*,5S*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)benzenesulfonamide (β -4hb): White solid; mp: 131-133 °C; $R_f = 0.28$ (90% CH₂Cl₂ in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 6.02 (dd, $J = 5.7, 2.7$ Hz, 1H), 5.92 (dd, $J = 5.7, 2.9$ Hz, 1H), 4.89 (d, $J = 6.5$ Hz, 1H), 3.47 (dddd, $J = 13.1, 10.1, 6.1, 4.2$ Hz, 1H), 2.75-2.72 (m, 2H), 2.41 (s, 3H), 2.18 (d, $J = 9.2$ Hz, 1H), 2.08 (d, $J = 17.2$ Hz, 1H), 1.89-1.82 (m, 3H), 1.67-1.61 (m, 1H), 1.43-1.36 (m, 1H), 1.22-1.05 (m, 6H), 0.80 (t, $J = 6.9$ Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.8, 143.3, 137.5, 137.5, 135.2, 129.5, 127.4, 57.1, 54.1, 45.3, 40.3, 38.2,

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36.7, 33.2, 31.6, 23.2, 22.5, 21.5, 13.9 ppm; IR (CH₂Cl₂) 3370 (NH), 3073, 2957, 2932, 2861, 1697 (C=O), 1599, 1418, 1348, 1163, 1094 cm⁻¹; LRMS (EI, 20 eV) m/z 375 (M⁺, 1), 304 (3), 254 (57), 155 (66), 91 (100); HRMS (EI, 20 eV) Calculated for C₂₁H₂₉NO₃S (M⁺) 375.1868, Found 375.1867.

4-Methyl-N-((R*)-1-((1R*,2S*,5R*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)benzenesulfonamide (β'-4hb): Colourless oil; R_f = 0.17 (70% CH₂Cl₂ in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.03 (dd, J = 5.6, 2.7 Hz, 1H), 5.89 (dd, J = 5.6, 2.8 Hz, 1H), 4.87 (d, J = 9.4 Hz, 1H), 3.57 (dddd, J = 13.7, 9.3, 6.4, 4.5 Hz, 1H), 2.81-2.77 (m, 2H), 2.41 (s, 3H), 2.34 (dd, J = 17.4, 3.8 Hz, 1H), 2.24 (ddd, J = 17.4, 2.3, 2.3 Hz, 1H), 2.10 (d, J = 6.4 Hz, 1H), 2.02 (d, J = 11.5 Hz, 1H), 1.85-1.80 (m, 1H), 1.43-1.36 (m, 1H), 1.29-1.15 (m, 2H), 1.12-1.01 (m, 4H), 0.99-0.91 (m, 1H), 0.76 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.3, 143.4, 138.2, 137.2, 136.2, 129.6, 127.1, 58.1, 55.4, 46.0, 40.2, 37.9, 37.4, 33.8, 31.4, 25.0, 22.4, 21.5, 13.9 ppm; IR (CH₂Cl₂) 3376 (NH), 3071, 2957, 2932, 2861, 1701 (C=O), 1599, 1425, 1418, 1336, 1279, 1161, 1092 cm⁻¹; LRMS (EI, 20 eV) m/z 375 (M⁺, 1), 304 (1), 254 (60), 155 (63), 91 (100); HRMS (EI, 20 eV) Calculated for C₂₁H₂₉NO₃S (M⁺) 375.1868, Found 375.1862.

Table 3, entry 2:



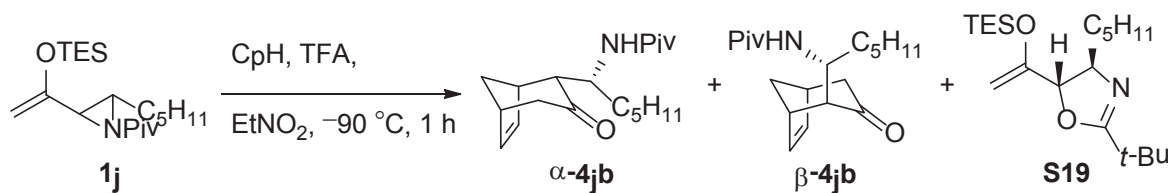
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1i** (0.1847 g, 0.4997 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 10% EtOAc in hexane to afford cycloadducts **α-4ib** and **β-4ib** (0.1603 g, 100% yield, 60:40).

tert-Butyl ((R*)-1-((1R*,2R*,5R*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)carbamate (α-4ib): Colourless oil; R_f = 0.62 (20% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 5.96-5.93 (m, 2H), 4.89 (d, J = 10.0 Hz, 1H), 3.69 (dddd, J = 10.2, 10.0, 4.9, 1.7 Hz, 1H), 2.91-2.89 (m, 1H), 2.86-2.84 (m, 1H), 2.68 (s, 1H), 2.39 (dd, J = 15.4, 3.2 Hz, 1H), 2.21 (ddd, J = 15.4, 2.7, 2.7 Hz, 1H), 2.11-2.06 (m, 1H), 1.83 (d, J = 10.7 Hz, 1H), 1.68-1.61 (m, 1H), 1.47-1.43 (m, 1H), 1.41 (s, 9H), 1.32-1.20 (m, 6H), 0.84 (t, J = 6.7 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.8, 155.7, 135.1, 134.8, 78.7, 61.2, 52.8, 46.0, 45.6, 45.1, 39.7, 35.8, 31.5, 28.5, 26.4, 22.6, 14.0 ppm; IR (CH₂Cl₂) 3443 (NH), 3067, 3048, 2988, 2957, 2934, 1705 (C=O), 1605, 1499, 1422, 1281, 1171 cm⁻¹; LRMS (EI, 20 eV) m/z 321 (M⁺, 2), 265 (7), 250 (8), 204 (23), 194 (47), 144 (33), 100

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(100), 79 (25), 70 (79); HRMS (EI, 20 eV) Calculated for C₁₉H₃₁NO₃ (M⁺) 321.2304, Found 321.2302. **tert-Butyl ((R*)-1-((1S*,2R*,5S*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)carbamate (β-4ib)**: White solid; mp: 138-142 °C; R_f = 0.57 (20% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 6.05 (dd, *J* = 5.6, 2.7 Hz, 1H), 5.96 (dd, *J* = 5.6, 2.7 Hz, 1H), 4.44 (d, *J* = 9.8 Hz, 1H), 3.94 (dddd, *J* = 9.3, 9.3, 9.3, 3.2 Hz, 1H), 2.86-2.83 (m, 1H), 2.80-2.078 (m, 1H), 2.68 (dd, *J* = 16.3, 3.3 Hz, 1H), 2.22 (dd, *J* = 16.3, 1.1 Hz, 1H), 2.18 (d, *J* = 11.3 Hz, 1H), 2.11 (d, *J* = 9.3 Hz, 1H), 1.90-1.85 (m, 1H), 1.71-1.68 (m, 1H), 1.38 (s, 9H), 1.33-1.23 (m, 7H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.3, 155.7, 137.2, 135.0, 79.4, 30.1, 51.5, 45.6, 41.6, 38.8, 36.6, 33.9, 31.6, 28.3, 24.9, 22.5, 14.0 ppm; IR (CH₂Cl₂) 3435 (NH), 3069, 2959, 2934, 1707 (C=O), 1606, 1505, 1422, 1368, 1173 cm⁻¹; LRMS (EI, 20 eV) *m/z* 321 (M⁺, 1), 265 (1), 205 (16), 144 (57), 122 (33), 100 (100), 79 (34), 70 (17); HRMS (EI, 20 eV) Calculated for C₁₉H₃₁NO₃ (M⁺) 321.2304, Found 321.2295.

Table 3, entry 3:

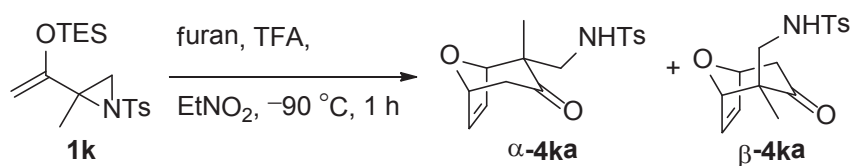


According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1j** (0.0770 g, 0.219 mmol) in EtNO₂ (2.2 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.090 mL, 1.1 mmol) and TFA (0.020 mL, 0.26 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts **α-4jb** and **β-4jb** (0.0574 g, 86% yield, 65:35) and rearrangement product **S19** (0.049 g, 6.4% yield). **N-((R*)-1-((1R*,2R*,5R*)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)pivalamide (α-4jb)**: White solid; mp: 92-93 °C; R_f = 0.61 (2% acetone in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 6.24 (d, *J* = 9.8 Hz, 1H), 5.94 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.88 (s, *J* = 5.8, 2.9 Hz, 1H), 4.07 (dddd, *J* = 15.2, 9.8, 5.3, 1.4 Hz, 1H), 2.94-2.92 (m, 1H), 2.88-2.85 (m, 1H), 2.72 (dd, *J* = 1.7, 1.7 Hz, 1H), 2.44 (dd, *J* = 15.4, 3.2 Hz, 1H), 2.24 (ddd, *J* = 15.4, 2.8, 2.8 Hz, 1H), 2.09 (dddd, *J* = 13.4, 10.6, 5.2, 3.0 Hz, 1H), 1.84 (d, *J* = 10.8 Hz, 1H), 1.72-1.65 (m, 1H), 1.52-1.46 (m, 1H), 1.29-1.20 (m, 6H), 1.15 (s, 9H), 0.85 (t, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.8, 177.3, 135.1, 134.8, 61.0, 51.0, 46.2, 46.2, 45.1, 39.7, 38.7, 36.2, 31.5, 27.5, 26.3, 22.6, 14.0 ppm; IR (CH₂Cl₂) 3457 (NH), 3065, 3046, 2959, 2934, 2862, 1701 (C=O), 1651 (C=O), 1510, 1283, 1275 cm⁻¹; LRMS (EI, 20 eV) *m/z*

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305 (M^+ , 9), 234 (59), 220 (25), 204 (29), 184 (81), 154 (100), 102 (55), 85 (60), 70 (63); HRMS (EI, 20 eV) Calculated for $C_{19}H_{31}NO_2$ (M^+) 305.2355, Found 305.2347. **N-((R^*)-1-((($1S^*$, $2R^*$, $5S^*$)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)hexyl)pivalamide (β -4jb):** White solid; mp: 113-115 °C; R_f = 0.45 (2% acetone in CH_2Cl_2); 1H NMR (500 MHz, $CDCl_3$) δ 6.07 (dd, J = 5.7, 2.7 Hz, 1H), 5.97 (dd, J = 5.7, 2.9 Hz, 1H), 5.52 (d, J = 9.0 Hz, 1H), 4.31-4.25 (m, 1H), 2.86-2.83 (m, 1H), 2.83-2.81 (m, 1H), 2.59 (dd, J = 16.3, 3.4 Hz, 1H), 2.24-2.18 (m, 2H), 2.15 (dd, J = 10.1, 0.7 Hz, 1H), 1.93-1.88 (m, 1H), 1.80-1.74 (m, 1H), 1.38-1.23 (m, 7H), 1.14 (s, 9H), 0.88 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.3, 178.0, 137.4, 134.9, 59.8, 49.2, 45.6, 41.6, 38.8, 38.6, 36.7, 33.8, 31.6, 27.4, 24.9, 22.5, 14.0 ppm; IR (CH_2Cl_2) 3449 (NH), 3063, 3053, 2959, 2934, 1701 (C=O), 1655 (C=O), 1512, 1348, 1120 cm^{-1} ; LRMS (EI, 20 eV) m/z 305 (M^+ , 1), 234 (3), 204 (4), 184 (100), 154 (9), 100 (20), 85 (49), 70 (11); HRMS (EI, 20 eV) Calculated for $C_{19}H_{31}NO_2$ (M^+) 305.2355, Found 305.2346. **($4R^*$, $5S^*$)-2-(*tert*-Butyl)-4-pentyl-5-(1-(triethylsiloxy)vinyl)-4,5-dihydrooxazole (S19):** Colourless oil; R_f = 0.74 (10% EtOAc in hexane); 1H NMR (600 MHz, C_6D_6) δ 4.41 (d, J = 1.1 Hz, 1H), 4.33 (d, J = 6.6 Hz, 1H), 4.23 (dt, J = 6.6, 6.5 Hz, 1H), 4.19 (d, J = 1.1 Hz, 1H), 1.73-1.66 (m, 1H), 1.58-1.51 (m, 2H), 1.50-1.45 (m, 1H), 1.34 (s, 9H), 1.26-1.24 (m, 4H), 0.97 (t, J = 7.9 Hz, 9H), 0.86 (t, J = 6.7 Hz, 3H), 0.65 (q, J = 7.9 Hz, 6H) ppm; ^{13}C NMR (150 MHz, C_6D_6) δ 172.2, 157.9, 89.2, 85.2, 71.9, 37.4, 33.7, 32.5, 28.5, 26.2, 23.3, 14.6, 7.2, 5.5 ppm; IR (CH_2Cl_2) 3065, 2980, 2961, 2934, 1661, 1636, 1481, 1458, 1317, 1142 cm^{-1} ; LRMS (EI, 20 eV) m/z 353 (M^+ , 12), 324 (25), 296 (16), 282 (63), 252 (26), 241 (100), 223 (29), 166 (57), 157 (42), 125 (50), 110 (89), 84 (42); HRMS (EI, 20 eV) Calculated for $C_{20}H_{39}NO_2Si$ (M^+) 353.2750, Found 353.2742.

Table 3, entry 4:



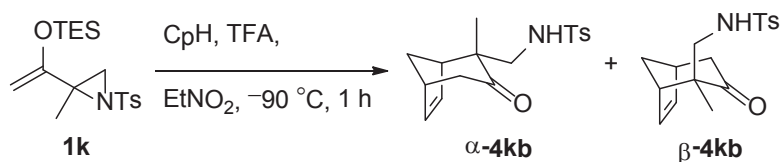
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1k** (0.1829 g, 0.4976 mmol) in $EtNO_2$ (5.0 mL) was subjected to reaction with furan (0.180 mL, 2.47 mmol) and TFA (0.190 mL, 2.48 mmol) at -90 °C. After 1 h, aqueous $NaHCO_3$ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 40% EtOAc in hexane to afford cycloadducts α -**4ka** and β -**4ka** (0.1503 g, 94% yield, 87:13). **4-Methyl-N-((($1R^*$, $2S^*$, $5R^*$)-2-methyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzene-sulfonamide (α -4ka):** White solid; mp: 120-123 °C; R_f = 0.31 (35% EtOAc in hexane); 1H NMR

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(600 MHz, CDCl₃) δ 7.70 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.40 (dd, J = 6.0, 1.7 Hz, 1H), 6.23 (dd, J = 6.0, 1.5 Hz, 1H), 5.13 (dd, J = 6.7, 6.7 Hz, 1H), 4.96 (d, J = 5.0 Hz, 1H), 4.54 (d, J = 1.6 Hz, 1H), 2.86-2.82 (m, 3H), 2.41 (s, 3H), 2.15 (d, J = 16.0 Hz, 1H), 1.34 (s, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 211.0, 143.5, 136.6, 134.0, 132.9, 129.8, 126.9, 83.9, 77.8, 56.5, 46.2, 43.1, 21.5, 20.0 ppm; IR (CH₂Cl₂) 3362 (NH), 3071, 2970, 2934, 1705 (C=O), 1599, 1420, 1410, 1335, 1269, 1163, 1092 cm⁻¹; LRMS (EI, 20 eV) m/z 321 (M⁺, 2), 240 (7), 184 (12), 155 (48), 150 (52), 91 (100); HRMS (EI, 20 eV) Calculated for C₁₆H₁₉NO₄S (M⁺) 321.1035, Found 321.1033.

4-Methyl-N-(((1S*,2S*,5S*)-2-methyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (β -4ka): White solid; mp: 142-146 °C; R_f = 0.25 (35% EtOAc in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.35 (dd, J = 6.1, 1.2 Hz, 1H), 6.26 (dd, J = 6.1, 1.2 Hz, 1H), 5.13 (dd, J = 6.2, 6.2 Hz, 1H), 4.98 (d, J = 4.9 Hz, 1H), 4.56 (s, 1H), 3.18 (d, J = 6.7 Hz, 2H), 2.70 (dd, J = 16.7, 5.1 Hz, 1H), 2.43 (s, 3H), 2.25 (d, J = 16.8 Hz, 1H), 0.92 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 208.1, 143.6, 136.6, 135.8, 131.9, 129.8, 127.1, 83.5, 78.2, 55.5, 49.6, 44.5, 21.5, 16.3 ppm; IR (CH₂Cl₂) 3360 (NH), 3071, 2978, 2940, 1715 (C=O), 1599, 1414, 1337, 1163 cm⁻¹; LRMS (EI, 20 eV) m/z 321 (M⁺, 4), 240 (5), 184 (29), 155 (79), 138 (42), 109 (72), 91 (100); HRMS (EI, 20 eV) Calculated for C₁₆H₁₉NO₄S (M⁺) 321.1035, Found 321.1031.

Table 3, entry 5:



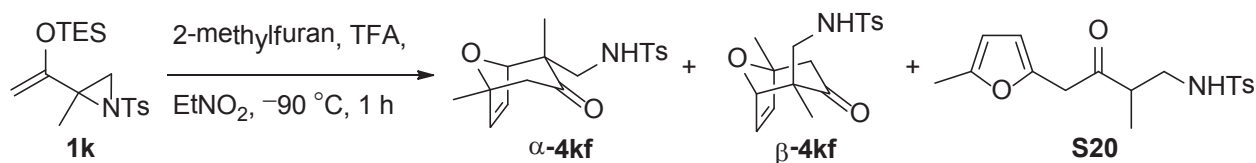
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1k** (0.1818 g, 0.4946 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.190 mL, 2.48 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -**4kb** and β -**4kb** (0.1074 g, 68% yield, 47:53). Analytically pure samples of α -**4kb** and β -**4kb** were obtained by further careful column chromatography using 1% acetone in CH₂Cl₂. **4-Methyl-N-(((1R*,2R*,5R*)-2-methyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (α -4kb):** White solid; mp: 138-141 °C; R_f = 0.44 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.05-6.02 (m, 2H), 5.30 (d, J = 8.6 Hz, 1H), 2.90 (dd, J = 12.5, 4.0 Hz, 1H), 2.83-2.78 (m, 2H), 2.53 (dd, J = 16.6, 3.4 Hz, 1H), 2.50 (dd, J = 5.2, 1.6 Hz, 1H), 2.42 (s, 3H), 2.18 (ddd, J = 16.6, 2.8, 2.8

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Hz, 1H), 2.12 (d, $J = 11.5$ Hz, 1H), 1.92 (dddd, $J = 11.2, 5.1, 5.1, 2.8$ Hz, 1H), 1.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 215.5, 143.2, 137.2, 137.1, 134.8, 129.7, 127.0, 54.0, 49.3, 48.2, 43.5, 38.7, 38.7, 21.5, 20.8 ppm; IR (CH_2Cl_2) 3368 (NH), 3071, 2955, 2930, 1697 (C=O), 1599, 1420, 1406, 1335, 1269, 1252, 1163, 1087 cm^{-1} ; LRMS (EI, 20 eV) m/z 319 (M^+ , 4), 184 (5), 164 (20), 155 (52), 136 (98), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ (M^+) 319.1242, Found 319.1236.

4-Methyl-N-(((1*S,2*R**,5*S**)-2-methyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzene-sulfonamide (β -4kf):** White solid; mp: 117-119 °C; $R_f = 0.21$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.11 (dd, $J = 5.8, 2.8$ Hz, 1H), 6.05 (dd, $J = 5.8, 3.0$ Hz, 1H), 4.71 (br s, 1H), 3.07 (dd, $J = 12.6, 7.7$ Hz, 1H), 3.02 (dd, $J = 12.6, 4.9$ Hz, 1H), 2.80-2.77 (m, 1H), 2.58 (dd, $J = 4.3, 3.3$ Hz, 1H), 2.43 (s, 3H), 2.28 (dd, $J = 17.8, 3.8$ Hz, 1H), 2.22 (ddd, $J = 17.8, 2.4, 2.4$ Hz, 1H), 1.93 (d, $J = 11.4$ Hz, 1H), 1.92-1.88 (m, 1H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 213.8, 143.6, 138.0, 136.7, 134.7, 129.8, 127.1, 53.6, 49.2, 46.1, 44.0, 38.3, 37.8, 21.5, 20.0 ppm; IR (CH_2Cl_2) 3364 (NH), 3069, 2953, 1701 (C=O), 1599, 1418, 1339, 1271, 1163, 1094, 1067 cm^{-1} ; LRMS (EI, 20 eV) m/z 319 (M^+ , 1), 184 (5), 155 (51), 136 (93), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ (M^+) 319.1242, Found 319.1235.

Table 3, entry 6:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1k** (0.1808 g, 0.4919 mmol) in EtNO_2 (5.0 mL) was subjected to reaction with 2-methylfuran (0.225 mL, 2.49 mmol) and TFA (0.190 mL, 2.48 mmol) at -90°C . After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -4kf and β -4kf (0.1503 g, 94% yield, 87:13) and alkylation product **S20** (0.0246 g, 15% yield). **N-(((1*R**,2*S**,5*R**)-2,5-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (α -4kf):** White solid; mp: 120-123 °C; $R_f = 0.69$ (35% EtOAc in hexane); ^1H NMR (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 6.31 (dd, $J = 6.0, 1.6$ Hz, 1H), 6.00 (d, $J = 6.0$ Hz, 1H), 5.14-5.11 (m, 1H), 4.54 (d, $J = 1.7$ Hz, 1H), 2.88-2.82 (m, 2H), 2.61 (d, $J = 15.9$ Hz, 1H), 2.42 (s, 3H), 2.22 (d, $J = 15.9$ Hz, 1H), 1.46 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 211.5, 143.5, 137.1, 136.6, 132.8, 129.8, 126.9, 84.5, 84.3, 54.7, 49.0, 46.3, 22.8, 21.5, 19.9 ppm; IR (CH_2Cl_2) 3362

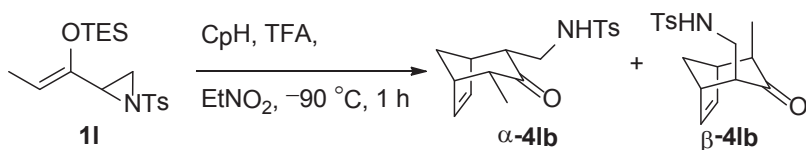
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(NH), 3071, 2980, 2934, 1703 (C=O), 1599, 1452, 1410, 1335, 1163, 1092 cm^{-1} ; LRMS (EI, 20 eV) m/z 335 (M^+ , 3), 254 (5), 238 (4), 184 (10), 180 (78), 155 (71), 109 (50), 91 (100); HRMS (EI, 20 eV) Calculated for $C_{17}H_{21}NO_4S$ (M^+) 335.1191, Found 335.1184.

N-(((1*S,2*S**,5*S**)-2,5-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methyl-benzenesulfonamide (β -4kf):** White solid; mp: 142-146 °C; R_f = 0.44 (35% EtOAc in hexane); ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.18 (dd, J = 6.1, 1.9 Hz, 1H), 6.11 (d, J = 6.0 Hz, 1H), 5.00 (dd, J = 7.4, 5.2 Hz, 1H), 4.56 (d, J = 1.8 Hz, 1H), 3.21-3.13 (m, 2H), 2.45 (d, J = 16.5 Hz, 1H), 2.43 (s, 3H), 2.32 (d, J = 16.5 Hz, 1H), 1.46 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 208.6, 143.6, 138.7, 136.6, 131.8, 129.8, 127.2, 84.7, 84.1, 53.4, 50.3, 49.5, 22.9, 21.6, 16.4 ppm; IR (CH_2Cl_2) 3360 (NH), 3071, 2980, 2932, 1713 (C=O), 1599, 1414, 1383, 1337, 1163, 1084 cm^{-1} ; LRMS (EI, 20 eV) m/z 335 (M^+ , 2), 184 (18), 180 (41), 155 (56), 123 (100), 109 (33), 91 (58); HRMS (EI, 20 eV) Calculated for $C_{17}H_{21}NO_4S$ (M^+) 335.1191, Found 335.1188.

4-Methyl-N-(2-methyl-4-(5-methylfuran-2-yl)-3-oxobutyl)benzenesulfonamide (S20): Colourless oil; R_f = 0.54 (20% EtOAc in hexane); ^1H NMR (600 MHz, CDCl_3) δ 7.70 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.04 (d, J = 2.9 Hz, 1H), 5.91 (d, J = 2.9 Hz, 1H), 4.80 (t, J = 6.7 Hz, 1H), 3.67 (s, 2H), 3.04-2.96 (m, 2H), 2.93-2.87 (m, 1H), 2.42 (s, 3H), 2.26 (s, 3H), 1.12 (d, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 209.3, 152.1, 145.4, 143.5, 136.9, 129.8, 127.0, 109.4, 106.6, 45.2, 44.8, 41.1, 21.5, 14.5, 13.5 ppm; IR (CH_2Cl_2) 3377 (NH), 3069, 2926, 2857, 1712 (C=O), 1599, 1421, 1381, 1335, 1275, 1163, 1094 cm^{-1} ; LRMS (EI, 20 eV) m/z 335 (M^+ , 10), 240 (8), 184 (38), 155 (68), 95 (100), 91 (92); HRMS (EI, 20 eV) Calculated for $C_{17}H_{21}NO_4S$ (M^+) 335.1191, Found 335.1186.

Table 3, entry 7:



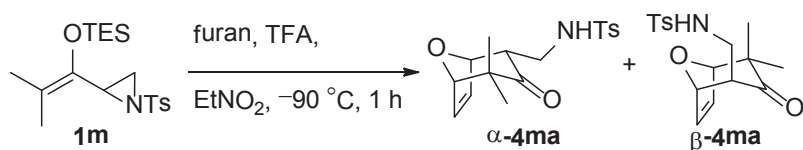
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **11** (0.1826 g, 0.4968 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.190 mL, 2.48 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts α -**4lb** and β -**4lb** (0.1174 g, 74% yield, 51:49). Analytically pure samples of α -**4lb** and β -**4lb** were obtained by further careful column chromatography using 1% acetone in CH₂Cl₂. **4-Methyl-N-(((1*R**,2*R**,4*R**,5*S**)-4-**

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methyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide (α -4lb**):** Colourless oil; $R_f = 0.54$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 6.04 (dd, $J = 5.8, 2.9$ Hz, 1H), 5.96 (dd, $J = 5.8, 2.7$ Hz, 1H), 5.26 (dd, $J = 9.2, 4.0$ Hz, 1H), 2.96 (ddd, $J = 12.6, 9.2, 4.4$ Hz, 1H), 2.86 (ddd, $J = 12.7, 8.6, 4.3$ Hz, 1H), 2.81 (ddd, $J = 5.4, 2.7, 2.7$ Hz, 1H), 2.74 (ddd, $J = 5.3, 2.8, 2.8$ Hz, 1H), 2.68 (dddd, $J = 7.7, 7.7, 4.1, 3.1$ Hz, 1H), 2.49 (qd, $J = 6.9, 3.0$ Hz, 1H), 2.42 (s, 3H), 2.13 (ddd, $J = 10.8, 5.4, 5.4$ Hz, 1H), 1.94 (d, $J = 10.8$ Hz, 1H), 0.97 (t, 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 212.9, 143.3, 137.1, 135.6, 134.9, 129.8, 127.0, 55.7, 50.1, 46.4, 44.6, 44.0, 43.5, 21.5, 13.7 ppm; IR (CH_2Cl_2) 3339 (NH), 3069, 2943, 2872, 1701 (C=O), 1599, 1454, 1354, 1159, 1094 cm^{-1} ; LRMS (EI, 20 eV) m/z 321 (M^+ , 3), 184 (5), 171 (21), 155 (39), 136 (35), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ (M^+) 319.1242, Found 319.1234.

4-Methyl-N-(((1*S,2*R**,4*R**,5*R**)-4-methyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)benzene-sulfonamide (β -4**lb**):** White solid; mp: 107-109 °C; $R_f = 0.34$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 6.09 (dd, $J = 5.6, 2.8$ Hz, 1H), 6.00 (dd, $J = 5.8, 2.9$ Hz, 1H), 5.08 (dd, $J = 8.1, 3.1$ Hz, 1H), 3.10 (ddd, $J = 12.5, 8.3, 6.7$ Hz, 1H), 2.98 (ddd, $J = 12.4, 8.4, 3.5$ Hz, 1H), 2.69-2.67 (m, 1H), 2.51-2.50 (m, 1H), 2.42 (s, 3H), 2.29-2.21 (m, 2H), 1.83-1.78 (m, 2H), 1.02 (d, $J = 7.5$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 216.4, 143.5, 137.7, 136.6, 136.1, 129.8, 127.1, 52.4, 48.3, 45.4, 43.8, 40.5, 32.5, 21.5, 18.2 ppm; IR (CH_2Cl_2) 3349 (NH), 3069, 2988, 2942, 2876, 1697 (C=O), 1599, 1454, 1305, 1290, 1155 cm^{-1} ; LRMS (EI, 20 eV) m/z 319 (M^+ , 1), 184 (4), 171 (21), 155 (38), 136 (28), 91 (100); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ (M^+) 319.1242, Found 319.1231.

Table 3, entry 8:



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1m** (0.3805 g, 0.9987 mmol) in EtNO_2 (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO_3 was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts α -4**ma** and β -4**ma** (0.2358 g, 71% yield, 93:7).

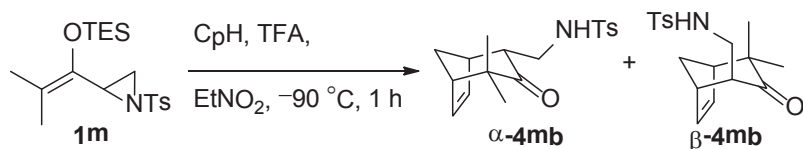
N-(((1*R,2*S**,5*S**)-4,4-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methyl-benzenesulfonamide (α -4**ma**):** White solid; mp: 133-136 °C; $R_f = 0.43$ (35% EtOAc in hexane); ^1H NMR (500 MHz, C_6D_6) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.19 (dd, $J = 6.1, 1.5$ Hz,

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1H), 5.98 (dd, $J = 6.1, 1.5$ Hz, 1H), 5.76 (dd, $J = 8.1, 5.4$ Hz, 1H), 4.97 (dd, $J = 4.2, 1.5$ Hz, 1H), 4.23 (d, $J = 1.5$ Hz, 1H), 3.19 (dt, $J = 12.3, 5.5$ Hz, 1H), 3.08-2.99 (m, 2H), 2.07 (s, 3H), 1.21 (s, 3H), 0.84 (s, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 211.8, 143.6, 138.2, 134.7, 133.5, 130.3, 127.7, 86.9, 80.4, 53.2, 51.6, 41.0, 24.8, 21.5, 20.0 ppm; IR (CH_2Cl_2) 3344 (NH), 3064, 2968, 2944, 1703 (C=O), 1597 cm^{-1} ; LRMS (EI, 20 eV) m/z 335 (M^+ , 2), 317 (1), 254 (5), 226 (8), 184 (10), 171 (24), 155 (46); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ (M^+) 335.1186.

N-(((1S*,2S*,5R*)-4,4-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (β -4ma): White solid; mp: 122-124 °C; $R_f = 0.33$ (35% EtOAc in hexane); ^1H NMR (500 MHz, C_6D_6) δ 7.91 (d, $J = 8.2$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 5.86 (dd, $J = 6.1, 1.7$ Hz, 1H), 5.75 (dd, $J = 6.1, 1.8$ Hz, 1H), 5.15 (dd, $J = 6.9, 5.0$ Hz, 1H), 4.64 (d, $J = 1.7$ Hz, 1H), 4.13 (d, $J = 1.7$ Hz, 1H), 3.40-3.29 (m, 2H), 2.28 (t, $J = 7.8$ Hz, 1H), 1.99 (s, 3H), 1.09 (s, 3H), 0.81 (s, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 212.2, 143.3, 138.2, 134.4, 133.6, 130.1, 127.9, 86.1, 79.4, 54.5, 52.2, 45.1, 26.0, 21.4, 20.7 ppm; IR (CH_2Cl_2) 3348 (NH), 3061, 2939, 1705 (C=O), 1598 cm^{-1} ; LRMS (EI, 20 eV) m/z 335 (M^+ , 2), 254 (7), 226 (11), 184 (14), 171 (19), 164 (9) 155 (60); HRMS (EI, 20 eV) Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ (M^+) 335.1186, Found 335.1183.

Table 3, entry 9:



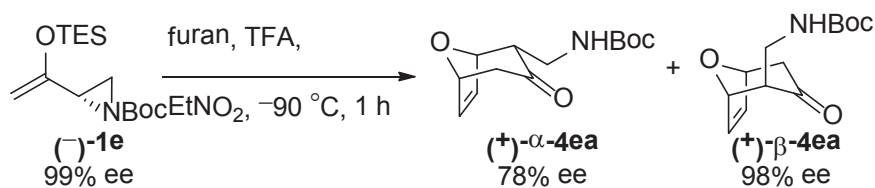
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **1m** (0.3814 g, 1.001 mmol) in EtNO₂ (10 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.41 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 0.5% acetone in CH₂Cl₂ to afford cycloadducts α -4mb and β -4mb (0.2416 g, 72% yield, 50:50).

N-(((1R*,2R*,5S*)-4,4-Dimethyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (α -4mb): Colourless oil; $R_f = 0.50$ (CH_2Cl_2); ^1H NMR (500 MHz, C_6D_6) δ 7.82 (d, $J = 8.2$ Hz, 2H), 6.82 (d, $J = 8.0$ Hz, 2H), 5.78 (dd, $J = 5.8, 2.7$ Hz, 1H), 5.73 (dd, $J = 5.8, 2.7$ Hz, 1H), 5.58 (dd, $J = 8.7, 4.4$ Hz, 1H), 3.09-3.04 (m, 1H), 2.98-2.92 (m, 1H), 2.52-2.49 (m, 1H), 2.45-2.43 (m, 1H), 1.98 (dd, $J = 4.8, 2.7$ Hz, 1H), 1.90 (s, 3H), 1.71 (d, $J = 11.3$ Hz, 1H), 1.59-1.55 (m, 1H), 0.89 (s, 3H), 0.84 (s, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 215.3, 143.2, 138.7, 137.8, 134.9, 130.1, 127.7, 52.9, 51.4, 50.1, 44.2, 43.3, 39.7, 26.1, 24.3, 21.4 ppm; IR (CH_2Cl_2) 3348 (NH), 3055, 2931,

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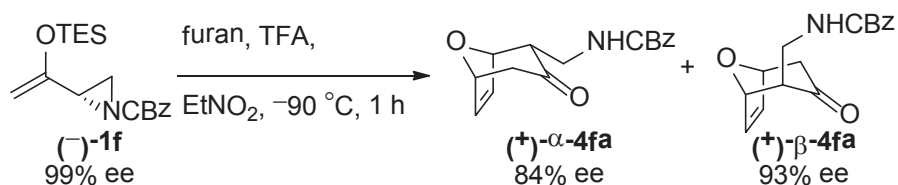
2877, 1697 (C=O), 1596, 1458 cm^{-1} ; LRMS (EI, 20 eV) m/z 333 (M^+ , 9), 184 (10), 178 (29), 171 (11), 162 (14), 155 (52), 150 (49); HRMS (EI, 20 eV) Calculated for $C_{18}H_{23}NO_3S$ (M^+) 333.1393, Found 333.1391. **N-(((1*S**,2*R**,5*R**)-4,4-Dimethyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (β -4mb):** Colourless oil; R_f = 0.35 (CH_2Cl_2); ^1H NMR (500 MHz, C_6D_6) δ 7.85 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 5.81 (dd, J = 5.7, 2.8 Hz, 1H), 5.72 (dd, J = 5.7, 2.9 Hz, 1H), 5.52 (dd, J = 7.5, 4.5 Hz 1H), 3.20-3.06 (m, 2H), 2.50 (br s, 1H), 2.22-2.18 (m, 1H), 1.95 (dd, J = 5.1, 2.8 Hz, 1H), 1.90 (s, 3H), 1.79 (d, J = 11.9 Hz, 1H), 1.58-1.53 (m, 1H), 0.88 (s, 3H), 0.82 (s, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 216.8, 143.3, 138.4, 137.4, 136.8, 130.1, 127.8, 53.3, 50.8, 49.5, 46.1, 40.8, 34.4, 27.6, 25.0, 21.4 ppm; IR (CH_2Cl_2) 3332 (NH), 3055, 2931, 1697 (C=O), 1596, 1465 cm^{-1} ; LRMS (EI, 20 eV) m/z 333 (M^+ , 1), 226 (1), 184 (11), 178 (43), 155 (59), 150 (60); HRMS (EI, 20 eV) Calculated for $C_{18}H_{23}NO_3S$ (M^+) 333.1393, Found 333.1394.

Asymmetric (4+3) Cycloadditions of Aziridinyl Enolsilanes



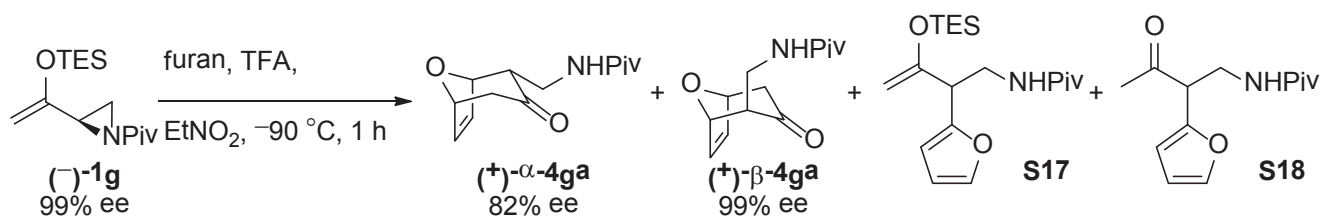
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **(-)-1e** (0.1499 g, 0.5005 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with furan (0.180 mL, 2.47 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts **(+)- α -4ea** and **(+)- β -4ea** (0.0674 g, 53% yield, 53:47). **tert-Butyl (((1*R*,2*S*,5*R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)- α -4ea):** $[\alpha]_D^{20} = +37.7^\circ$ ($c = 0.54$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, t_R (major) = 21.09 min, t_R (minor) = 24.41 min] to be 78% ee. **tert-Butyl (((1*S*,2*S*,5*S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)- β -4ea):** $[\alpha]_D^{20} = +77.1^\circ$ ($c = 0.35$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, t_R (major) = 33.96 min, t_R (minor) = 25.63 min] to be 98% ee.

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According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **(-)-1f** (0.0723 g, 0.217 mmol) in EtNO₂ (2.2 mL) was subjected to reaction with furan (0.080 mL, 1.10 mmol) and TFA (0.020 mL, 0.26 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts **(+)-α-4fa** and **(+)-β-4fa** (0.0393 g, 54% yield, 51:49).

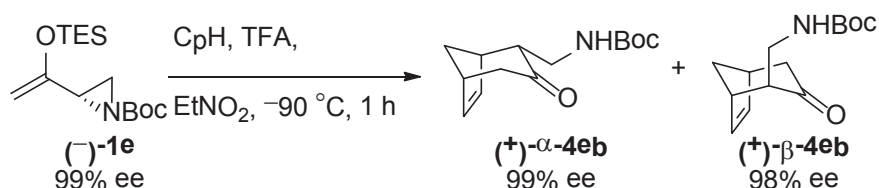
Benzyl (((1*R*,2*S*,5*R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)-α-4fa): $[\alpha]_D^{20} = +26.9^\circ$ ($c = 0.61$, CH₂Cl₂). The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, $\lambda = 210$ nm, 20% IPA in hexane, t_R (major) = 39.92 min, t_R (minor) = 36.11 min] to be 84% ee. **Benzyl (((1*S*,2*S*,5*S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)-β-4fa):** $[\alpha]_D^{20} = +58.0^\circ$ ($c = 0.25$, CH₂Cl₂). The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, $\lambda = 210$ nm, 20% IPA in hexane, t_R (major) = 40.81 min, t_R (minor) = 36.29 min] to be 93% ee.



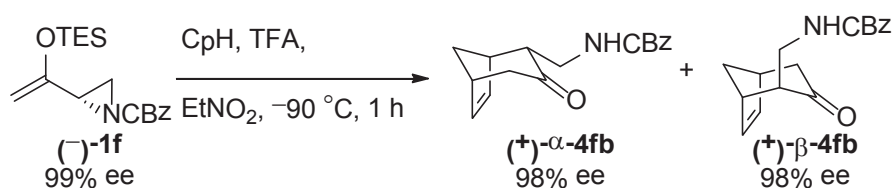
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **(-)-1g** (0.1419 g, 0.5006 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with furan (0.180 mL, 2.47 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 40% EtOAc in hexane to afford cycloadducts **(+)-α-4ga** and **(+)-β-4ga** (0.0463 g, 39% yield, 49:51) and alkylation product **S16** (0.0475 g, 27% yield) and **S17** (0.0169 g, 14% yield). **N-(((1*R*,2*S*,5*R*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide ((+)-α-4ga):** $[\alpha]_D^{20} = +8.5^\circ$ ($c = 0.41$, CH₂Cl₂). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, t_R (major) = 26.29 min, t_R (minor) = 24.70 min] to be 82% ee. **N-(((1*S*,2*S*,5*S*)-3-Oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide ((+)-β-4ga):** $[\alpha]_D^{20} = +49.2^\circ$ ($c = 0.50$, CH₂Cl₂). The enantiomeric excess

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was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, $t_R(\text{major}) = 28.74$ min, $t_R(\text{minor}) = 22.37$ min] to be 99% ee.



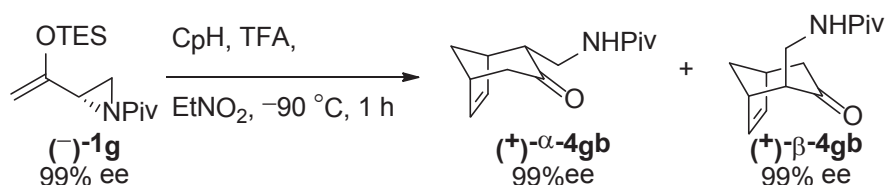
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **(-)-1e** (0.1497 g, 0.4987 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts **(+)-α-4eb** and **(+)-β-4eb** (0.0938 g, 75% yield, 59:41). Analytically pure samples of **(+)-α-4eb** and **(+)-β-4eb** were obtained by further careful column chromatography using 1% acetone in CH₂Cl₂. **tert-Butyl (((1R,2R,5R)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)-α-4eb)**: $[\alpha]_D^{20} = +23.8^\circ$ ($c = 1.76$, CH₂Cl₂). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AY-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, $t_R(\text{major}) = 18.14$ min, $t_R(\text{minor}) = 16.28$ min] to be 99% ee. **tert-Butyl (((1S,2R,5S)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)-β-4eb)**: $[\alpha]_D^{20} = +44.8^\circ$ ($c = 0.98$, CH₂Cl₂). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AY-3, 0.5 mL/min, $\lambda = 210$ nm, 10% IPA in hexane, $t_R(\text{major}) = 16.53$ min, $t_R(\text{minor}) = 19.83$ min] to be 98% ee.



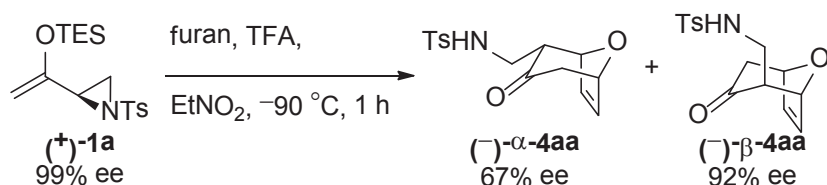
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane **(-)-1f** (0.0728 g, 0.218 mmol) in EtNO₂ (2.2 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.090 mL, 1.1 mmol) and TFA (0.020 mL, 0.26 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 20% EtOAc in hexane to afford cycloadducts **(+)-α-4fb** and **(+)-β-4fb** (0.0494 g, 79% yield, 58:42). Analytically pure samples of **(+)-α-4fb** and **(+)-β-4fb** were obtained by further careful column chromatography using 1% acetone in CH₂Cl₂. **Benzyl**

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(((1*R*,2*R*,5*R*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)- α -4fb): $[\alpha]_D^{20} = +24.1^\circ$ ($c = 0.89$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, $\lambda = 210$ nm, 16% IPA in hexane, $t_R(\text{major}) = 31.48$ min, $t_R(\text{minor}) = 24.78$ min] to be 98% ee. **Benzyl (((1*S*,2*R*,5*S*)-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)carbamate ((+)- β -4fb):** $[\alpha]_D^{20} = +29.3^\circ$ ($c = 0.63$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, $\lambda = 210$ nm, 16% IPA in hexane, $t_R(\text{major}) = 27.70$ min, $t_R(\text{minor}) = 26.18$ min] to be 98% ee.



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane (-)-1g (0.1418 g, 0.5002 mmol) in EtNO₂ (5.0 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.210 mL, 2.54 mmol) and TFA (0.045 mL, 0.59 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 30% EtOAc in hexane to afford cycloadducts (+)- α -4gb (0.0225 g, 14% yield) and (+)- β -4gb (0.0238 g, 20% yield). **N-(((1*R*,2*R*,5*R*)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide ((+)- α -4gb):** $[\alpha]_D^{20} = +12.5^\circ$ ($c = 0.27$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 4% IPA in hexane, $t_R(\text{major}) = 28.57$ min, $t_R(\text{minor}) = 27.11$ min] to be 99% ee. **N-(((1*S*,2*R*,5*S*)-3-Oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)pivalamide ((+)- β -4gb):** $[\alpha]_D^{20} = +25.0^\circ$ ($c = 0.16$, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, $\lambda = 210$ nm, 6% IPA in hexane, $t_R(\text{major}) = 17.10$ min, $t_R(\text{minor}) = 19.46$ min] to be 99% ee.



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane (+)-1a (0.3539 g, 1.002 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction

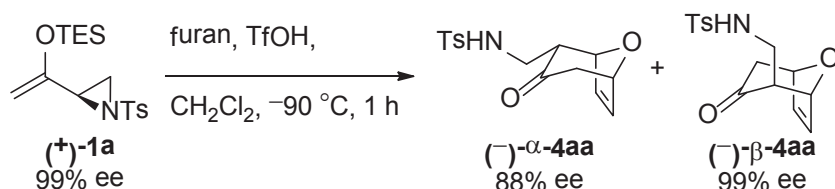
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was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts (–)-**α-4aa** and (–)-**β-4aa** (0.3048 g, 99% yield, 55:45).

4-Methyl-N-(((1*S*,2*R*,5*S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide

((–)-α-4aa**)**. The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AS-3, 0.25 mL/min, $\lambda = 254$ nm, 80% IPA in hexane, $t_R(\text{major}) = 53.80$ min, $t_R(\text{minor}) = 44.77$ min] to be 67% ee.

4-Methyl-N-(((1*R*,2*R*,5*R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide **((–)-**β-4aa**)**: The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AS-3, 0.25 mL/min, $\lambda = 254$ nm, 80% IPA in hexane, $t_R(\text{major}) = 77.38$ min, $t_R(\text{minor}) = 66.52$ min] to be 88% ee.



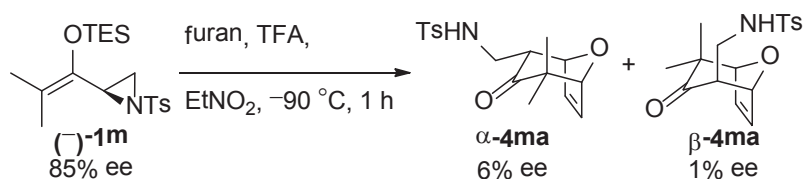
According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane (+)-**1a** (0.3521 g, 0.9975 mmol) in CH₂Cl₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TfOH (0.100 mL, 1.13 mmol) at –90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 35% EtOAc in hexane to afford cycloadducts (–)-**α-4aa** and (–)-**β-4aa** (0.1715 g, 56% yield, 60:40).

4-Methyl-N-(((1*S*,2*R*,5*S*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide

((–)-α-4aa**)**: $[\alpha]_D^{20} = -23.4^\circ$ ($c = 1.19$, CHCl₃). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AS-3, 0.25 mL/min, $\lambda = 254$ nm, 80% IPA in hexane, $t_R(\text{major}) = 53.88$ min, $t_R(\text{minor}) = 44.48$ min] to be 92% ee.

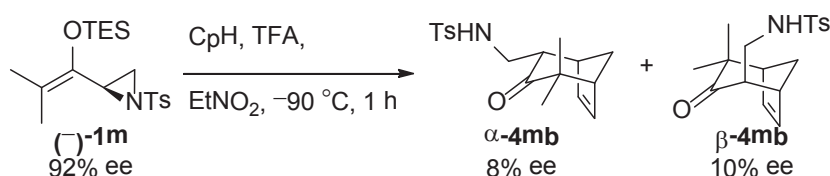
4-Methyl-N-(((1*R*,2*R*,5*R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)benzenesulfonamide

((–)-β-4aa**)**: $[\alpha]_D^{20} = -96.7^\circ$ ($c = 0.43$, CHCl₃). The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AS-3, 0.25 mL/min, $\lambda = 254$ nm, 80% IPA in hexane, $t_R(\text{major}) = 77.47$ min, $t_R(\text{minor}) = 65.45$ min] to be 99% ee.



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According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane (**(-)-1m**) (0.3805 g, 0.9987 mmol) in EtNO₂ (10 mL) was subjected to reaction with furan (0.36 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 25% EtOAc in hexane to afford cycloadducts **α-4ma** and **β-4ma** (0.2358 g, 71% yield, 93:7). **N-(((1S,2R,5R)-4,4-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (α-4ma)**: The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-H, 1.0 mL/min, λ = 254 nm, 15% IPA in hexane, t_R(major) = 27.69 min, t_R(minor) = 33.12 min] to be 6% ee. **N-(((1R,2R,5S)-4,4-Dimethyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (β-4ma)**: The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 0.5 mL/min, λ = 254 nm, 40% IPA in hexane, t_R(major) = 11.21 min, t_R(minor) = 12.93 min] to be 1% ee.



According to the general procedure for the cycloaddition reaction, aziridinyl enolsilane (**(-)-1m**) (0.3814 g, 1.001 mmol) in EtNO₂ (10 mL) was subjected to reaction with freshly cracked cyclopentadiene (0.41 mL, 5.0 mmol) and TFA (0.37 mL, 5.0 mmol) at -90 °C. After 1 h, aqueous NaHCO₃ was added and the reaction was worked up. The crude product was purified by flash column chromatography using 0.5% acetone in CH₂Cl₂ to afford cycloadducts **α-4mb** and **β-4mb** (0.2416 g, 72% yield, 50:50). **N-(((1S,2S,5R)-4,4-Dimethyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (α-4mb)**: The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AD-3, 0.5 mL/min, λ = 254 nm, 30% IPA in hexane, t_R(major) = 28.68 min, t_R(minor) = 21.80 min] to be 8% ee. **N-(((1R,2S,5S)-4,4-Dimethyl-3-oxobicyclo[3.2.1]oct-6-en-2-yl)methyl)-4-methylbenzenesulfonamide (β-4mb)**: The enantiomeric excess was determined by HPLC analysis [Daicel chiralpak AY-3, 0.5 mL/min, λ = 254 nm, 40% IPA in hexane, t_R(major) = 60.89 min, t_R(minor) = 30.97 min] to be 10% ee.