Supporting information attached to manuscript:

A concise and convergent route to 5,8-disubstituted indolizidine and 1,4-disubstituted quinolizidine ring cores by diastereoselective Aza-Diels-Alder reaction.

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Experimental

General Methods. All reactions were carried out under N_2 employing solvents dried following standard procedures. For isolation, organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. All purchased reagents were of reagent grade quality and were used without purification.

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200 or 300 MHz, and ^{13}C NMR spectra at 75 MHz in $CDCl_3$ at room temperature (RT); chemical shift values are given in parts per million (ppm) relative to the residual solvent peak (δ) and coupling constants in Hz. Analytical TLC was carried out using Merck aluminium-backed 0.2 mm silica gel 60 F-254 plates. Column chromatography was conducted using silica gel 60, 230-240 Mesh .

Dienes **1** and **1'** were prepared as previously reported.[1] Imines **2** were obtained following literature procedures.[2]

General procedure for the preparation of piperidones 5.

To a solution of $Yb(TfO)_3$ (130 mg, 0.2 mmol, 20 mol %) in THF (10 mL) the correspondent imine **2** (2 mmol) was added, and the mixture was cooled to 0ºC. Aminodiene **1'** (290 mg, 1 mmol) was added dropwise and the mixture was stirred at room temperature overnight. The reaction was quenched with $NaHCO_3$ sat. aqueous solution (10 mL) and the resultant mixture was extracted with AcOEt (2x 10 mL). The organics were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash chromatography afforded pure piperidones **5**.

[1] (a) Barluenga, J.; Aznar, F.; Valdés, C.; Cabal, M.P. *J. Org. Chem.* **1991**, *56*, 6166-6171. (b) Barluenga, J.; Aznar, F.; Ribas, C.; Valdés, C.; Fernández, M.; Cabal, M.P.; Trujillo, J. *Chem. Eur. J.* **1996**, *2*, 805-811.
[2] Look, G.C.; Murphy M. M.; Campbell. D. A.; Gallop; M. A. *Tetrahedron Lett.* **1995**, *36*, 2937-2940

(2*S, 3*S**, 6*R**)-*N*-allyl-2-(*tert*-butyldimethylsililoxymethyl)-3-methyl-6-phenylpiperidin-4-one (5a).** Prepared from imine **2a** (300 mg, 2 mmol) according to the general procedure described above to afford after flash chromatography (hexanes:*tert*-butyldimethylether 20:1) compound **5a** as a brown oil (223 mg, 60%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.21 (m; 5H), 5.79-5.62 (m; 1H), 5.16-5.03 (m; 2H), 4.47 (dd, $^3J_{aa}$=9.4, $^3J_{ae}$=5.4; 1H), 4.11 (d, ^2J=11.1; 1H), 3.62 (dd, ^2J=11.1, ^3J=3.1; 1H), 3.31-3.27 (m; 1H), 3.15 (ddd, ^2J=14.5, ^3J=2.2, ^4J=2.2; 1H), 2.90 (dd, ^2J=14.5, ^3J=8.6, 1H), 2.82-2.71 (m; 1H), 2.55-2.41 (m; 2H), 1.15 (d, ^3J=6.9; 3H), 0.92 (s, 9H), 0.12 (s; 3H), 0.09 (s; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 208.5 (C), 144.1 (C), 136.5 (CH), 128.7 (CH), 127.3 (CH), 127.2 (CH), 116.6 (CH_2), 63.7 (CH), 61.5 (CH), 57.7 (CH_2), 52.4 (CH_2), 49.0 (CH_2), 45.9 (CH), 25.7 (CH_3), 18.1 (C), 11.1 (CH_3), -5.9 (CH_3), -5.8 (CH_3). HRMS: calcd. for $C_{22}H_{35}NO_2Si$: 373.2437, found 373.2439.

(2*S, 3*S**, 6*R**)-*N*-(3-butenyl)-2-(*tert*-butyldimethylsililoxymethyl)-3-methyl-6-phenylpiperidin-4-one (5b).** Prepared from imine **2b** (318 mg, 2 mmol) according to the general procedure described above to afford after flash chromatography (hexanes:*tert*-butyldimethylether 40:1) compound **5b** as a brown oil (247 mg, 64%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.21 (m; 5H), 5.72-5.58 (m; 1H), 4.97-4.89 (m; 2H), 4.43 (dd, $^3J_{aa}$=8.7, $^3J_{ae}$=4.3; 1H), 4.09 (dd, ^2J=11.1;^3J=1.1; 1H), 3.70 (dd, ^2J=11.1, ^3J=3.2; 1H), 3.31-3.27 (m; 1H), 2.85-2.74 (m; 1H), 2.55-2.40 (m; 4H), 2.12-2.03 (m; 1H), 1.62-1.54 (m; 1H), 1.15 (d, ^3J=6.9; 3H), 0.91 (s, 9H), 0.10 (s; 3H), 0.07 (s; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 208.5 (C), 144.1 (C), 136.6 (CH), 128.6 (CH), 127.5 (CH), 127.4 (CH), 115.4 (CH_2), 64.1 (CH), 62.0 (CH), 58.3 (CH_2), 48.9 (CH_2), 48.4 (CH_2), 46.0 (CH), 32.6 (CH_2), 29.7 (CH_3), 25.8 (CH_3), 18.1 (C), 11.2 (CH_3), 1.0 (CH_3), -5.8 (CH_3). HRMS: calcd. for $C_{23}H_{37}NO_2Si$: 387.2594, found 387.2591.

General procedure for the preparation of hydroxypiperidines 6. To a solution of piperidone **4** (0.5 mmol) in absolute EtOH (10 ml) cooled to 0ºC, $NaBH_4$ (57 mg, 1.5 mmol) was added and the mixture was stirred at room temperature for 1h, when water (10 mL) was added. After extraction with AcOEt (2x10 mL), the organics were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography afforded compounds **6**.

(2*S, 3*S**, 4*R**, 6*R**)-*N*-allyl-4-hydroxy-2-(*tert*-butyldimethylsililoxymethyl)-3-methyl-6-phenylpiperidine (6a).** Prepared from piperidone **5a** (186 mg, 0.5 mmol) according to the general procedure described above. Flash chromatography (hexanes:*tert*-butyldimethylether 20:1) afforded compound **6a** as a brown oil (178 mg, 95%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.19 (m; 5H), 5.98-5.80 (m; 1H), 5.06 (d, ^{3}J=10.5; 1H), 4.90 (d, ^3J=17.3; 1H), 3.93(dd, ^3J=9.6, ^3J=5.4; 1H), 3.83-3.72 (m; 1H), 3.58-3.45 (m; 2H), 3.08 (dd, ^2J=15.9, ^3J=5.2; 1H), 2.89 (dd, ^2J=16.1, ^3J=7.3, 1H), 2.75-2.66

(m; 1H), 2.37-2.26 (m; 1H), 1.77-1.71 (m; 2H), 1.03 (d, ^3J=6.5; 3H), 0.90 (s, 9H), 0.07 (s; 3H), 0.05 (s; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 144.3 (C), 133.5 (CH), 128.4 (CH), 127.5 (CH), 127.0 (CH), 117.4 (CH_2), 71.5 (CH), 64.6 (CH), 63.0 (CH_2), 62.6 (CH), 51.6 (CH_2), 39.6 (CH_2), 35.7 (CH), 25.9 (CH_3), 18.2 (C), 5.6 (CH_3), -5.4 (CH_3), -5.5 (CH_3). HRMS: calcd. for $C_{22}H_{37}NO_2Si$: 375.2594, found 375.2600.

(2*S, 3*S**, 4*R**, 6*R**)-*N*-(3-butenyl)-4-hydroxy-2-(*tert*-butyldimethylsililoxymethyl)-3-methyl-6-phenylpiperidine (6b).** Prepared from piperidone **5b** (193 mg, 0.5 mmol) according to the general procedure described above. Flash chromatography (hexanes:*tert*-butyldimethylether 20:1) afforded compound **6b** as a brown oil (180 mg, 93%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.45-7.18 (m; 5H), 5.49-5.36 (m; 1H), 4.85-4.73 (m, 2H), 3.87 (dd, $^3J_{aa}$=9.6, $^3J_{ae}$=5.1; 1H), 3.58 (dd, ^3J=9.6, ^3J=7.9; 1H), 3.51-3.45 (m; 1H), 2.74-2.67 (m; 1H), 2.45-2.36 (m; 2H), 2.34-2.27 (m; 2H), 2.12-2.02 (m; 2H), 1.77-1.71 (m; 2H), 1.02 (d, ^3J=6.8; 3H), 0.92 (s, 9H), 0.09 (s; 3H), 0.08 (s; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 143.0 (C), 136.6 (CH), 128.4 (CH), 127.5 (CH), 127.0 (CH), 115.3 (CH_2), 71.5 (CH), 64.3 (CH), 63.2 (CH_2), 62.1 (CH), 48.2 (CH_2), 43.4 (CH_2), 39.4 (CH_2), 35.8 (CH), 25.9 (CH_3), 18.3 (C), 5.7 (CH_3), -5.4 (CH_3), -5.3 (CH_3). HRMS: calcd. for $C_{23}H_{39}NO_2Si$: 389.2750, found 389.2749.

(2*S, 3*S**, 4*R**, 6*R**)-*N*-allyl-4-hydroxy-2-hydroxymethyl-3-methyl-6-phenylpiperidine (7a).** A solution of **6a** (25 mg, 0.07 mmol) in THF (5 mL) was treated with tetrabutylammonium fluoride hydrate (11 mg, 0.35 mmol) and stirred for 1h. The mixture was quenched with water (10 mL), and extracted with AcOEt (2 x 10 mL). The combined organic layers were washed with water, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography (CH_2Cl_2:methanol 40:1) followed by recrystallization from toluene gave **7a** as a white solid (17.9 mg, 98%): mp 126-128 ºC; ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.35-7.25 (m; 5H), 6.02-5.82 (m; 1H), 5.12 (dd, ^3J=10.2, ^2J=1.7; 1H), 5.01 (dd, ^3J=17.1, ^2J=1.7; 1H), 3.91-3.81 (m; 1H), 3.75 (dd, , ^3J=11.1, ^2J=6.1; 1H), 3.61 (dd, $^3J_{aa}$=11.3, $^3J_{ae}$=3.9; 1H), 3.18 (dd, ^2J=15.9, ^3J=5.7; 1H), 2.97 (dd, ^2J=15.9, ^3J=7.4; 1H), 2.79-2.75 (m; 1H), 2.24-2.19 (m; 1H), 1.87-1.68 (m; 2H), 1.13 (d, ^3J=7.0; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz):143.9 (C), 133.0 (CH), 128.4 (CH), 127.3 (CH), 127.0 (CH), 117.9 (CH_2), 70.5 (CH), 63.6 (CH), 62.4 (CH_2), 61.8 (CH), 52.1 (CH_2), 39.5 (CH_2), 36.8 (CH), 7.1 (CH_3). HRMS: calcd. for $C_{16}H_{23}NO_2$-CH_2OH: 230.1544, found 230.1542.

(2*S, 3*S**, 4*R**, 6*R**)-*N*-(3-butenyl)-4-hydroxy-2-hydroximethyl-3-methyl-6-phenylpiperidine (7b)**. Prepared from **6b** following the same procedure as for **7a**. Flash chromatography (CH_2Cl_2:methanol 20:1) followed by recrystallization from toluene gave **7b** as a white solid (19 mg, 99%): mp 144-146 ºC; ^{1}H-NMR ($CDCl_3$, 300 MHz):7.34-7.31 (m; 5H), 5.54-

5.39 (m; 1H), 4.90-4.86 (m; 1H), 4.84-4.82 (m; 1H), 3.90-3.80 (m; 2H), 3.73 (dd, ^3J=10.8, ^2J=6.3; 1H), 3.58 (dd, $^3J_{aa}$=11.4, $^3J_{ae}$=3.4; 1H), 2.83-2.78 (m; 1H), 2.57-2.39 (m; 2H), 2.30-2.20 (m; 1H), 2.15-2.10 (m; 2H), 1.93-1.85 (m; 1H), 1.82-1.67 (m; 1H), 1.15 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz):143.8 (C), 136.3 (CH), 128.4 (CH), 127.3 (CH), 127.2 (CH), 115.7. (CH_2), 70.3 (CH), 63.0 (CH), 62.5 (CH_2), 61.5 (CH), 49.3 (CH_2), 39.8 (CH), 36.8 (CH), 27.3 (CH_2), 8.1 (CH_3). HRMS: calcd. for $C_{17}H_{25}NO_2$-CH_2OH: 244.1701, found 244.1696.

(2*S, 3*R**, 6*R**)-(*E*)-*N*-allyl-2-(1-ethenyl-2-methoxycarbonyl)-3-methyl-6-phenylpiperidin-4-one (11a)**. To a cooled (-65ºC) solution of $(COCl)_2$ (0.05 mL, 0.57 mmol) in dry CH_2Cl_2 (5 mL), dry DMSO (0.08 mL, 1.14 mmol) was added dropwise and stirring was continued at this temperature for 15 min. Then, a solution of diol **7a** (50 mg, 0.19 mmol) in dry THF (2 mL) was added dropwise, and the reaction mixture was stirred at -65ºC for 90 min. Thereafter, dry NEt_3 (0.2 mL, 1.71 mmol) was added and the temperature was permitted to reach -15ºC during 90 min. Afterwards, Ph_3P=$CHCO_2Me$ (450 mg, 1.4 mmol) was added in one portion, and the reaction mixture was warmed to room temperature and stirred overnight. To the reaction mixture CH_2Cl_2 (10 mL) was added, and the solution extracted with water (2x10 mL) and washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography (hexanes:AcOEt 2:1) afforded conjugated ester **11a** (44 mg, 74%) as a yellowish oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.40-7.31 (m; 5H), 6.83 (dd, J_{trans}=15.9, ^3J=9.7; 1H), 5.95 (d, J_{trans}=15.9; 1H), 5.80-5.65 (m; 1H), 5.12 (dd, ^3J=10.2, ^2J=2.3; 1H), 4.84 (dd, ^3J=17.1, ^2J=2.3; 1H), 3.82 (dd, $^3J_{aa}$=11.9, $^3J_{ae}$=3.4; 1H), 3.77 (s ;3H), 3.76-3.75 (m ;1H), 3.20 (dd, ^3J=14.8, ^2J=6.8; 1H), 3.08 (dd, ^3J=15.3, ^2J=6.8; 1H), 2.79-2.68 (m; 1H), 2.62-2.54 (m, 1H), 2.48 (dd, $^2J_{gem}$=13.7, J_{ae}=3.4; 1H), 0.96 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 207.6 (C), 166.2 (C), 148.2 (CH), 141.8 (C), 130.3 (CH), 128.7 (CH), 127.8 (CH), 127.2 (CH), 123.3 (CH), 119.8 (CH_2), 68.9 (CH), 64.9 (CH_3), 52.3 (CH_2), 51.7 (CH), 50.4 (CH_2), 47.5 (CH), 11.0 (CH_3). HRMS: calcd. for $C_{19}H_{23}NO_3$: 313.1678, found 313.1681.

(2*S, 3*S**, 6*R**)-(*E*)-*N*-(3-butenyl)-2-(1-ethenyl-2-methoxycarbonyl)-3-methyl-6-phenylpiperidin-4-one (11b').** An adaptation of the experimental procedure described for compound **11a** was applied to diol **7b** (50 mg, 0.18 mmol), carrying out the Wittig reaction with Ph_3P=$CHCO_2Me$ refluxing in CH_2Cl_2 overnight. Flash chromatography through a short SiO_2 column (5 cm height x 3 cm width) (hexanes:AcOEt 2:1) afforded **11b'** as a yellowish oil (48 mg, 77%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.28 (m; 5H), 6.96 (dd, J_{trans}=15.4, ^3J=6.8; 1H), 6.28 (dd, J_{trans}=15.4, ^4J=1.7; 1H), 5.60-5.48 (m; 1H), 4.92-4.84 (m ;2H), 4.08.(dd, $^3J_{aa}$=11.9, $^3J_{ae}$=3.4; 1H), 3.82-3.78 (m; 1H), 3.75 (s, 3H), 3.73-3.64 (m ;1H), 2.98-2.91 (m; 1H), 2.60-2.52 (m ; 2H), 2.45 (dd, $^2J_{gem}$=15.9, ^3J=2.3; 1H), 2.15-2.05 (m ; 2H), 1.23 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.8 (C), 166.5 (C), 147.8 (CH), 142.3 (C), 135.8 (CH), 128.8 (CH), 127.3 (CH), 126.5 (CH), 122.6 (CH), 116.1

(CH_2), 63.1 (CH), 62.3 (CH_3), 52.1 (CH), 51.6 (CH_2), 47.5 (CH_2), 46.2 (CH), 29.9 (CH_2), 11.2 (CH_3). HRMS: calcd. for $C_{20}H_{25}NO_3$-OCH_3: 296.1650, found 296.1655.

(2*S, 3*R**, 6*R**)-(*E*)-*N*-(3-butenyl)-2-(1-ethenyl-2-methoxycarbonyl)-3-methyl-6-phenylpiperidin-4-one (11b).** Compound **11b'** was chromatographed with a longer column (15 cm height) using as eluent a gradient of hexanes:diethylether from 50:10 to 10:1 to afford epimer **11b** (43 mg, 90%). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.40-7.31 (m; 5H), 6.90 (dd, J_{trans}=15.4, ^3J=9.1; 1H), 5.96 (d, J_{trans}=15.4; 1H), 5.42-5.27 (m; 1H), 4.82-4.72 (m ; 2H), 3.82 (dd, $^3J_{aa}$=11.9, $^3J_{ae}$=3.4; 1H), 3.77 (s; 3H), 3.76-3.70 (m; 1H), 3.18-3.10 (m; 1H), 2.80-2.73 (m; 1H), 2.65-2.45 (m; 3H), 2.00-2.93 (m; 2H), 0.97 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 207.7 (C), 166.2 (C), 148.1 (CH), 141.6 (C), 135.5 (CH), 128.8 (CH), 127.3 (CH), 123.0 (CH), 115.9 (CH_2), 69.2 (CH), 65.2 (CH_3), 51.8 (CH), 51.8 (CH), 50.2 (CH_2), 49.6 (CH_2), 47.7 (CH), 26.2 (CH_2), 11.0 (CH_3). HRMS: calcd. for $C_{20}H_{25}NO_3$-OCH_3: 296.1650 , found 296.1651.

(6*R, 8a*S**, 5*R**)-5-phenyl-8-methylindolizidin-7-one (14)**.

(a) *Metathesis step*: A stream of nitrogen was bubbled for 5 min to a solution of diene **11a** (31 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) at 0ºC. The solution was warmed to room temperature and Grubbs catalyst **G** was added in one portion (1.5 mg, 0.00175 mmol). After stirring overnight another portion of **G** was added and stirring was continued for another 12 h. Then, the reaction mixture was exposed to air for 10 min and concentrated under vacuum. The residue was filtered through a thin pad of SiO_2 and concentrated to afford the crude bicyclic unsaturated indolizidinone which was used in the next step without purification.

(b) *Hydrogenation step*: The brown oil obtained was mixed with Pd/C 10% (10 mg), the flask was capped with a rubber septum, evacuated with the aid of a needle and filled with hydrogen with a balloon. Afterwards, EtOH (5 mL) was added to the flask through the septum with a syringe and a needle. The mixture was stirred at room temperature for 15 h when the balloon and the septum were removed. Filtration through celite and concentration under vacuum gave a dark oil which was purified by flash chromatography (gradient hexanes:diethylether 200:1 to 20:1). Compound **14** was isolated as a yellowish solid (19 mg, 82%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.40-7.25 (m; 5H), 3.32 (dd, $^3J_{aa}$=11.4, $^3J_{ae}$=3.4; 1H), 2.84-2.78 (m; 1H), 2.72-2.64 (m; 1H), 2.56-2.44 (m; 2H), 2.16-1.65 (m; 6H), 1.06 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.1 (C), 142.3 (C), 128.6 (CH), 127.6 (CH), 127.1 (CH), 70.6 (CH), 67.4 (CH), 51.9 (CH_2), 50.4 (CH_2), 49.7 (CH_2), 30.3 (CH_2), 21.5 (CH_2), 10.5 (CH_3). HRMS: calcd. for $C_{15}H_{19}NO$: 229.1467, found 229.1467.

(1*S, 4*R**, 9a*R**)-1-methyl-4-phenyl-$\Delta^{8,9}$-quinolizidin-2-one (12').** Identical procedure as for **14** was applied for the metathesis step using diene **11b'**. The residue obtained in this reaction was chromatographed (Al_2O_3, hexanes:AcOEt 20:1) to afford **12'** as a colorless oil (18 mg, 75%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.50-7.31 (m; 5H), 5.95-5.82 (m ;1H), 5.35-5.30 (m; 1H), 3.38 (dd, $^3J_{aa}$=11.4, $^3J_{ae}$=3.9; 1H), 3.22-3.18 (m; 1H), 2.85-2.73 (m; 2H), 2.52-2.35 (m ;2H), 2.31-2.18 (m; 1H), 1.95 (dd, ^2J=10.8, ^3J=3.4; 1H), 1.92-1.80 (m; 1H), 1.29 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 211.9 (C), 142.7 (C), 128.8 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 68.9 (CH), 63.2 (CH), 49.7 (CH), 47.5 (CH_2), 47.2 (CH_2), 26.2 (CH_2), 12.2 (CH_3). HRMS: calcd. for $C_{16}H_{19}NO$: 241.1500, found 241.1504.

(1*R, 4*R**, 9a*R**)-1-methyl-4-phenyl-$\Delta^{8,9}$-quinolizidin-2-one (12).** Identical procedure as for **12'** was applied for the metathesis step using diene **11b**. The residue obtained in this reaction was chromatographed (Al_2O_3, hexanes:AcOEt 20:1) to afford **12** as a colourless oil (19 mg, 77%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.30 (m; 5H), 5.94-5.84 (m; 1H), 5.80-5.72 (m; 1H), 3.50 (dd, $^3J_{aa}$=11.9, $^3J_{ae}$=3.9; 1H), 2.82-2.70 (m; 4H), 2.55 (dd, ^2J=13.6, ^3J=3.4; 1H), 2.35-2.18 (m; 1H), 2.05 (dd, ^2J=10.8, ^3J=3.4; 1H), 1.95-1.82 (m; 1H), 1.15 (d, ^3J=6.8; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.1 (C), 142.4 (C), 128.8 (CH), 127.6 (CH), 127.2 (CH), 127.3 (CH), 126.9 (CH), 68.8 (CH), 66.8 (CH), 50.4 (CH), 48.8 (CH_2), 47.8 (CH_2), 26.4 (CH_2), 9.9 (CH_3). HRMS: calcd. for $C_{16}H_{19}NO$: 241.1500, found 241.1495.

(1*S, 4*R**, 9a*R**)-1-methyl-4-phenylquinolizidin-2-one (15').** A flask containing insaturated quinolizidinone **12'** (20 mg, 0.08 mmol) and Pd/C 10% (15 mg) was capped with a rubber septum, evacuated with the aid of a needle and filled with hydrogen with a balloon. Afterwards, EtOH (5 mL) was added to the flask through the septum with a syringe and a needle. The mixture was stirred at room temperature for 15 h when the balloon and the septum were removed. Filtration through celite and concentration under vacuum gave a dark oil which was purified by flash chromatography (Al_2O_3, gradient hexanes:diethylether 500:1 to 20:1). Compound **15'** was isolated as a colourless oil (15 mg, 76%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.38-7.28 (m; 5H), 3.30 (dd, $^3J_{aa}$=11.9, $^3J_{ae}$=2.8; 1H), 2.82-2.65 (m; 3H), 2.60-2.41 (m; 3H), 2.08-1.91 (m; 2H), 1.82-1.75 (m; 1H), 1.71-1.60 (m; 1H), 1.50-1.42 (m; 2H), 1.06 (d, ^3J=6.3; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.5 (C), 143.0 (C), 128.7 (CH), 127.4 (CH), 127.1 (CH), 70.5 (CH), 69.0 (CH), 53.1 (CH_2), 50.6 (CH_2), 49.8 (CH), 31.9 (CH_2), 25.5 (CH_2), 24.3 (CH_2), 10.1 (CH_3). HRMS: calcd. for $C_{16}H_{21}NO$: 243.1623, found 243.1654.

(1*S, 4*R**, 9a*R**)-1-methyl-4-phenylquinolizidin-2-one (15).** The procedure is identical to that described for **15'** using unsaturated quinolizidinone **12** as starting material. Column chromatography (Al_2O_3, gradient hexanes:diethylether 500:1 to 20:1) gave compound **15** as a

colourless oil (18 mg, 91%): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.48-7.35 (m; 5H), 3.33 (dd, $^{3}J_{aa}$=12.1, $^{3}J_{ae}$=3.3; 1H), 2.74-2.65 (m; 3H), 2.63-2,50 (m; 3H), 2.45-2.33 (m; 1H), 2.03-1.96 (m; 1H), 1.78-1.69 (m; 1H), 1.59-1.43 (m; 3H), 1.11 (d, ^{3}J=6.4; 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 212.1 (C), 142.4 (C), 128.9 (CH), 127.7 (CH), 126.9 (CH), 72.1 (CH), 68.0 (CH), 54.3 (CH_2), 49.8 (CH_2), 49.1 (CH), 33.4 (CH_2) 25.3 (CH_2), 24.1 (CH_2), 13.1 (CH_3). HRMS: calcd. for $C_{16}H_{21}NO$: 243.1623, found 243.1654.