Supporting information. Experimental procedures and full characterisation for compounds **3-7**.

Typical procedure for the alkylation of β-lactams 1 and 2.
β-lactam (1 mmol) was added to a solution of LiHMDS (2.5 equiv.) in THF (or Et_2O) at –78 °C (10 mL). The solution was stirred for 2 h at –78°C and MeI (4 mmol) was added. The mixture was then allowed to warm to rt. After 1 h, the reaction mixture was poured into a saturated ammonium chloride solution (10 mL) and extracted with Et_2O (3x25 mL). The combined organic extracts were washed (brine), dried ($MgSO_4$), and evaporated to give a residue that was purified by chromatography on silica gel (petrol ether-AcOEt, 70:30).

Cis-3-(benzyloxy)-1-(4-methoxyphenyl)-3-methyl-4-(trifluoromethyl)-2-azetanone (3) : 340 mg. (93 %), m.p. = 110 °C.

^{19}F NMR δ -68.1 (d, $^3J_{HF}$ = 6.1 Hz).

^{1}H NMR δ 1.6 (s, 3 H, CH_3), 3.6 (s, 3H, O*C*H_3), 4.2 (q, $^3J_{HF}$ = 5.8 Hz, 1 H, C*H*-CF_3), 4.8 (dd, $^2J_{AB}$ = 11.3 Hz, 2 H, C$H_A H_B$-C_6H_5), 6.8 (m, 4H, C_6H_4), 7.2 (m, 5 H, C_6H_5).

^{13}C NMR δ 19.5, 55.5, 63.9 (q, $^2J_{CF}$ = 31 Hz, *C*H-CF_3), 68.8, 86.8, 114.5, 119.8, 124.3 (q, $^1J_{CF}$ = 300 Hz, CF_3), 127.2, 127.7, 128.4, 129.5, 137.6, 157.4, 165.6.

Anal. Calcd for $C_{19}H_{19}O_3NF_3$: C, 62.46; H, 4.96; N, 3.83. Found : C, 62.39; H, 5.01; N, 3.75.

(3*S*,4*R*)-3-(benzyloxy)-3-methyl-1-[(1*S*)-1-phenethyl]-4-(trifluoromethyl)-2-azetanone (4) : 330 mg. (90 %), m.p. = 88 °C; $[\alpha]_D$ = +20.

^{19}F NMR δ -69.1 (d, $^3J_{HF}$ = 5.8 Hz).

^{1}H NMR δ 1.4 (s, 3 H, CH_3), 1.6 (d, *J* = 7 Hz, 3H, *CH*$_3$), 3.3 (q, $^3J_{HF}$ = 6.4 Hz, 1 H, C*H*-CF_3), 4.8 (dd, $^2J_{AB}$ = 14 Hz, 2 H, C$H_A H_B$-C_6H_5), 5.2 (q, *J* = 7 Hz, 1H), 7.2-7.4 (m, 10 H, C_6H_5).

^{13}C NMR δ 17.5, 18.5, 27.9, 42.9, 51.1, 62.1 (q, $^2J_{CF}$ = 31 Hz, *C*H-CF_3), 62.7, 68.8, 127.1 (q, $^1J_{CF}$ = 300 Hz, CF_3), 127.3, 127.6, 128.3, 128.4, 128.9, 137.7, 168.

Anal. Calcd for $C_{19}H_{18}O_3NF_3$:C, 66.1;H, 5.56; N, 3.86. Found : C, 65.97; H, 5.58; N, 3.78.

Typical procedure for the Wittig rearrangements of β-lactams 1 and 2.
β-lactam (1 mmol) was added to a solution of LiHMDS (2.5 equiv.) in THF (or Et_2O) at –78 °C (10 mL). The solution was stirred for 2 h at –78°C and then allowed to warm to rt. After 1 h, the reaction mixture was poured into a saturated ammonium chloride solution (10 mL) and extracted with Et_2O (3x25 mL). The combined organic extracts were washed (brine), dried ($MgSO_4$), and evaporated to give a residue that was purified by chromatography on silica gel (petrol ether-AcOEt, 70:30).

Cis-3-(benzyl)-3-(hydroxy)-1-(4-methoxyphenyl)-4-(trifluoromethyl)-2-azetanone (5) : 230 mg (65 %), m.p. = 92 °C.

^{19}F NMR δ -68.6 (d, $^3J_{HF}$ = 5.8 Hz).

^{1}H NMR δ 1.7 (br s, 1 H, O*H*), 3.2 (dd, $^2J_{AB}$ = 14 Hz, 2 H, C$H_A H_B$-C_6H_5), 3.8 (s, 3 H, OCH_3), 4.3 (q, $^3J_{HF}$ = 6 Hz, 1 H, C*H*-CF_3), 6.8 and 7.1 (dd, J_{AB} = 9 Hz, 4 H, C_6H_4), 7.35 (m, 5 H, C_6H_5).

^{13}C NMR δ 41.4, 55.5, 61.6 (q, $^2J_{CF}$ = 31 Hz, *C*H-CF_3), 85.7, 114.4, 120.3, 124.8 (q, $^1J_{CF}$ = 300 Hz, CF_3), 127.8, 128.6, 128.9, 130.0, 133.3, 157.5, 167.0.

Anal. Calcd for $C_{18}H_{16}O_3NF_3$: C, 61.54; H, 4.59; N, 3.99. Found : C, 61.53; H, 4.49; N, 3.93.

β-Lactams 6 and 7 : (60/40), 227 mg (65%).

(3*R*,4*R*)-3-benzyl-3-hydroxy-1-[(1*S*)-1-phenethyl]-4-(trifluoromethyl)-2-azetanone (6) : m.p. = 140 °C; $[\alpha]_D$ = +22.1.

^{19}F NMR δ -69.3 (d, $^3J_{HF}$ = 6.3 Hz).

^{1}H NMR δ 1.5 (d, *J* = 7.2 Hz, 3 H, *CH*$_3$-CH-C_6H_5), 3.1 (dd, $^2J_{AB}$ = 14 Hz, 2 H, C$H_A H_B$-C_6H_5), 3.2 (s, 1 H, O*H*), 3.6 (q, $^3J_{HF}$ = 6.3 Hz, 1 H, C*H*-CF_3), 4.8 (q, ^3J = 7.2 Hz, 1 H, C*H*-CH_3), 6.9 (m, 2 H, C_6H_5), 7.2 to 7.4 (m, 8 H, C_6H_5).

^{13}C NMR δ 18.0, 41.0, 52.0, 59.5 (q, $^2J_{CF}$ = 30 Hz, *C*H-CF_3), 86.0, (CF_3 no observed), 127.0, 130.0, 130.5, 133.5, 137.5, 169.0.

Anal. Calcd for $C_{19}H_{18}O_2NF_3$: C, 65.32; H, 5.19; N, 4.00. Found : C, 65.31; H, 5.37; N, 3.93.

(3*R*,4*R*)-3-hydroxy-3-(2-methylbenzyl)-1-[(1*S*)-1-phenethyl]-4-(trifluoromethyl)-2-azetanone (7) : m.p. = 104 °C**;** $[\alpha]_D$ = +62.7.

^{19}F NMR δ -67.9 (d, $^3J_{HF}$ = 5.9 Hz).

^{1}H NMR δ 1.7 (d, *J* = 7.2 Hz, 3 H, *CH*$_3$-CH-C_6H_5), 2.4 (s, 3 H, CH_3-C_6H_4), 3.7 (br s, 1 H, O*H*), 3.85 (q, $^3J_{HF}$ = 6.0 Hz, 1 H, C*H*-CF_3), 5.0 (q, ^3J = 7.2 Hz, 1 H, C*H*-CH_3), 7.14 (t, *J* = 7.5 Hz, 1H, Ar), 7.2 to 7.3 (m, 7 H, Ar), 7.5 (d, *J* = 7.7 Hz, 1H, Ar).

^{13}C NMR δ 18.5, 19.8, 52.8, 63.7 (q, $^2J_{CF}$ = 30 Hz, *C*H-CF_3), 87.3, 123.9 (q, $^1J_{CF}$ = 276 Hz, CF_3), 126.0, 127.0, 127.2, 128.1, 128.7, 129.5, 132.4, 135.0, 137.5, 138.0, 169.0.

Anal. Calcd for $C_{19}H_{16}O_2NF_3$: C, 65.32; H, 5.19; N, 4.00. Found : C, 65.24; H, 5.35; N, 3.90.