Supplementary Information for

New asymetric synthesis of protein farnesyltransferase inhibitors via palladium-catalysed cross-coupling reactions of 2-iodo-imidazoles.

Jennifer Kerhervé,[a] Candice Botuha[b] and Joëlle Dubois*[a]

[a] *Institut de Chimie des Substances Naturelles, UPR2301 CNRS, Centre de Recherche de Gif-sur-Yvette, Avenue de la Terrasse, 91198 Gif-sur-Yvette cedex, France;*
E-mail: joelle.dubois@icsn.cnrs-gif.fr

[b] *Université Pierre et Marie Curie-Paris VI. IPCM, Laboratoire de Chimie Organique. UMR 7201-Tour 44-45-Case 183, 4,Place Jussieu-75252 Paris Cedex 05*

1-Experimental data

Table. Different assays of Heck cross-coupling on imidazole 7[a]

Entry	Cat/phosphine	Base	Solvent	Time, temp.	Yield[b]
1	$Pd(OAc)_2/PPh_3$	NEt_3	DMF	140°C, 72h	50% (**9**)
2	$Pd(OAc)_2/PPh_3$	NEt_3	NEt_3	90°C, 24h	100% (**7**)
3	$Pd(OAc)_2/P(o\text{-tol})_3$	KOAc	DMF	140°C, 5h	100% (**7**)
4	$Pd(OAc)_2$	KOAc	DMF	140°C, 5h	100% (**7**)
5	$Pd(OAc)_2/PPh_3$	KOAc, NBu_4Br	H_2O/CH_3CN	80°C, 5h	100% (**7**)
6	Hermann cat.[c]	KOAc	DMA	140°C, 24h	100% (**7**)
7	Pd/C	KOAc	DMA	140°C, 2h	decomp.
8	$Pd(PPh_3)_4$[d]	NEt_3	NEt_3	20°C, 24h	100% (**7**)
9	$Pd(PPh_3)_4$[d]	NEt_3	NEt_3	90°C, 18h	50% (**7**)
10	$Pd(PPh_3)_4$[d]	KOAc	DMF	140°C, 18h	15% (**5**)
11	$Pd(PPh_3)_4$[d]	KOAc	DMF	140°C, 15min[e]	5% (**5**)
12	PCPpincer Pd[f]	Na_2CO_3	DMF	180°C, 72h	100% (**7**)

[a] Conditions: 5 mol% catalyst loading, 10 mol% phosphine, 3 equiv. of base, reflux. [b] Measured by 1H-NMR. [c] 1% mol. catalyst[1]. [d] 5% mol. $Pd(PPh_3)_4$. [e] Microwave heating, P = 150W. [f] 5% mol. palladium (II) phosphinito PCP pincer complex.[2, 3]

3-(methyl-1H-imidazol-2-yl)prop-2yn-1-ol (10a). Prepared according to general procedure A on compound **7** (48 mg, 0.23 mmol) in NEt_3 (2 mL) with $Pd(PPh_3)_4$ (13 mg, 0.0115 mmol),

CuI (4.3 mg, 0.023 mmol) and propargyl alcohol (0.13 mL, 2.3 mmol) . The reaction mixture was stirred at RT for 3 days. After work-up and column chromatography (CH_2Cl_2/MeOH : 9 : 1) **10a** (14 mg, 44%) was obtained as a yellow oil. ^{1}H NMR (300 MHZ, $CDCl_3$) δ 3.73 (s, 3H), 4.00 (bs, 1H), 4.55 (s, 2H), 6.89 (bs, 1H), 7.01 (bs, 1H). IR (neat) : 3245, 2955, 1472, 1067. MS (EI) *m/z* 137 (10), 136 (M^+, 60), 107 (75), 76 (15), 52 (35), 42 (100). HRMS (ESI^+) calcd for $C_7H_9N_2O$ $[M+H]^+$ 137.0715, found 137.0717.

4-(methyl-1H-imidazol-2-yl)but-3yn-1-ol (10b). Prepared according to general procedure A on compound **7** (108 mg, 0.5 mmol) in NEt_3 (2 mL) with $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), CuI (9 mg, 0.05 mmol) and 3-butynol (0.19 mL, 2.5 mmol). The reaction mixture was stirred at 40°C for 18h. After work-up and column chromatography (EtOAc/EtOH : 9 : 1) **10b** (20 mg, 26%) was obtained as a yellow oil. ^{1}H NMR (300 MHZ, $CDCl_3$) δ 2.74 (t, J = 6.5 Hz, 2H), 3.43 (bs, 1H), 3.70 (s, 3H), 3.88 (t, J = 6.5 Hz, 2H), 6.87 (bs, 1H), 6.99 (bs, 1H). ^{13}C NMR (75 MHZ, $CDCl_3$) δ 23.9, 33.6, 60.4, 70.8, 92.8, 120.8, 125.7, 128.2. IR (neat) : 3368, 2956, 2888, 1473, 1286, 1050. MS (EI) *m/z* 151 (10), 151 (M^+, 75), 120 (100), 119 (85), 78 (70), 51 (95). HRMS (ESI^+) calcd for $C_8H_{11}N_2O$ $[M+H]^+$ 151.0871, found 151.0883.

3-(5-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1*H*-imidazol-2-yl)prop-2-yn-1-ol (12). Prepared according to general procedure A on compound **11** (176 mg, 0.5 mmol) in NEt_3 (2 mL) with $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), CuI (9 mg, 0.05 mmol) and 3-butynol (0.19 mL, 2.5 mmol). The reaction mixture was stirred at 40°C for 18h. After work-up and column chromatography (EtOAc/EtOH: 9 : 1) **12** (132 mg, 89%) was obtained as a white amorphous solid. ^{1}H NMR (300 MHZ, $CDCl_3$) δ 0.04 (s, 6H), 0.87 (s, 9H), 2.75 (t, J = 7.0 Hz, 2H), 3.67 (s, 3H), 3.89 (t, J = 7.0 Hz, 2H), 4.60 (s, 2H), 6.83 (s, 1H), 6.99 (bs, 1H). ^{13}C NMR (75 MHZ, $CDCl_3$) δ -5.3, 18.1, 23.8, 25.7, 31.4, 55.3, 60.4, 71.4, 92.2, 127.1, 131.5,133.3. IR (neat) : 3326, 2981, 2883, 1219, 1069. MS (EI) *m/z* 295 (5), 294 (M^+, 10), 277 (13), 238 (25), 237 (100), 164 (65), 163 (70), 145 (95), 133 (65), 131 (80), 75 (50). HRMS (ESI^+) calcd for $C_{15}H_{27}N_2O_2Si$ $[M+H]^+$ 295.1851, found 295.1842.

1-methyl-2-vinylimidazole (14).

Suzuki coupling. To a solution of iodoimidazole derivative **7** (100 mg, 0.48 mmol) in anhydrous DMF (1.2 mL) under argon was added $Pd(PPh_3)_4$ (28 mg, 0.024 mmol, 5 mol %), powdered Na_2CO_3 (93 mg, 0.88 mmol, 1.8 equiv.) and pinacol vinylboronate **13** (98 µL, 0.58 mmol, 1.1 equiv.). The mixture was heated under an argon atmosphere at 130°C for 3h. After the mixture had been cooled down to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH : 95:5) to afford **14** (49 mg, 94%) as a colorless liquid. Spectroscopic data were identical to those previously reported.[4]

Stille coupling. To a solution of iodoimidazole derivative **7** (100 mg, 0.48 mmol) in anhydrous DMF (1.2 mL) under argon was added $Pd(PPh_3)_4$ (28 mg, 0.024 mmol, 5 mol %), and vinyltributylstannane (170 µL, 0.58 mmol, 1.1 equiv.). The mixture was heated under an argon atmosphere at 130°C for 2h. After the mixture had been cooled down to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH : 95:5) to afford **14** (40 mg, 77%) as a colorless liquid (non optimized yield). Spectroscopic data were identical to those previously reported.[4]

4-(*S*)-Benzyloxazolidin-2-one (17a). a) To a solution of $NaBH_4$ (182 mg, 2.4 mmol, 1.2 equiv.) in THF (5 mL) was added L-phenylalanine (330 mg, 2 mmol) in one portion and the solution wad cooled to 0°C under argon atmosphere. Iodine (508 mg, 2 mmol, 1 equiv.) in solution in THF (1 mL) was added dropwise over a 30 min. period resulting in vigorous evolution of hydrogen. After addition was complete and gas evolution ceased, the flask was heated to reflux for 18 h and then cooled to room temperature. Methanol was added cautiously until mixture became clear. After stirring for 30 min., solvent was removed leaving a white paste which was dissolved by addition of 20% aqueous KOH (5 mL). The solution was stirred for 4 h and extracted with dichloromethane (3 x 10 mL). Organic layers were dried over sodium sulfate, filtered and concentrated affording a white solid. The crude material was recrystallized from toluene to yield L-phenylalaninol (223 mg, 74%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (dd, J = 6.0, 9.0 Hz, 1H), 2.82 (dd, J = 3.0, 9.0 Hz, 1H), 3.14 (m, 1H), 3.41 (dd, J = 5.0, 6.0 Hz, 1H), 3.65 (dd, J = 3.0, 6.0 Hz, 1H), 7.21-7.35 (m, 5H). **b)** To a suspension of L-phenylalaninol (220 mg, 1.46 mmol) in water (1.5 mL) was added Boc_2O (350 mg, 1.60 mmol, 1.1 equiv.) and the mixture was stirred for 1 h at 30-35°C.

Boc-phenylalaninol (365 mg, quant.) was obtained after being extracted with ethyl acetate (3 x 5 mL), dried over sodium sulfate, filtered and concentrated. **c)** Potassium *t*-butoxide (200 mg, 1.77 mmol, 1.2 equiv.) was added in one portion to a stirred solution of Boc-phenylalaninol (365 mg, 1.46 mmol) in freshly distilled THF (25 mL) at 0°C under argon atmosphere. After 2 h, saturated NH_4Cl solution (30 mL) and ethyl acetate (20 mL) were added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (2 X 20 mL), the combined organic layer was washed with brine and dried over sodium sulfate, and concentrated. Purification by flash chromatography on silica gel (EtOAc/ heptane : 1:1) afforded pure **17a** (155 mg, 60%) as a white solid. Spectroscopic data were identical to those previously reported.[5] $[\alpha]_D^{23} = -62$ (*c* 0.6 in $CHCl_3$).

4-(*R*)-Benzyloxazolidin-2-one (17b).

Prepared according to the protocol used for the synthesis of **17a** on D-Phe (7g, 42.4 mmol). After final purification **17b** (3.81 g, 52%) was isolated as a white amorphous solid. Spectroscopic data were identical to those previously reported. $[\alpha]_D^{23} = +63$ (*c* 0.56 in $CHCl_3$).

4-(*R*)-Benzyl-3-pent-4-enoyloxazolidin-2-one (18b).

Prepared according to the protocol used for the synthesis of **18a** on **17b** (1.9 g, 10.7 mmol). After work-up and column chromatography (EtOAc /Heptane 1:1) **18b** (2.78 g, 94%) was isolated as a colorless oil. Spectroscopic data were identical to those reported for **18a**. $[\alpha]_D^{23} = -55$ (*c* 0.8 in $CHCl_3$).

Ethyl 3-(*S*)-(4-(*R*)-benzyl-2-oxazolidine-3-carbonyl) hex-5-enoate (19b).

Prepared according to the same protocol as used for the synthesis of **19a** on **18b** (2.5 g, 9.7 mmol). After work-up and column chromatography (EtOAc /Heptane 1:9 to 2:8) **(3*S*,4*R*)-19b** (2.34 g, 70%) was isolated together with **(3*R*,4*R*)-19'b** (0,5 g, 15%) as white amorphous solids. Spectroscopic data of **19b** were identical to those reported for **19a**. $[\alpha]_D^{23} = -47$ (*c* 1.05 in $CHCl_3$).

(3*R*,4*R*)-19'b : ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7 Hz, 3H), 2.22-2.29 (m, 1H), 2.45-2.51 (m, 1H), 2.49 (dd, *J* = 4.0, 17.0 Hz, 1H), 2.68 (dd, *J* = 10.0, 13.0 Hz, 1H), 2.86 (dd, *J* = 10.0, 17.0 Hz, 1H), 3.26 (dd, *J* = 3.0, 13.0 Hz, 1H), 4.03-4.26 (m, 4H), 4.67-4.72 (m, 1H), 5.08-5.12 (m, 2H), 5.72-5.83 (m, 1H), 7.12-7.32 (m, 5H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 14.4, 35.4, 36.6, 38.5, 38.8, 55.6, 60.9, 66.4, 118.4, 127.5, 128.8, 129.1, 129.6, 134.3, 135.6, 153.4, 172.4, 175.1. MS (ESI+) m/z 368 $[M+Na]^+$. $[\alpha]_D^{23}$ = -24 (*c* 0.95 in $CHCl_3$).

Diethyl 2-(*S*)-allylsuccinate (16b).

Prepared according to the protocol used for the synthesis of **16a** on **19b** (345 mg, 1 mmol). After work-up and column chromatography (EtOAc /Heptane 4:6) **16b** (137 mg, 64%) was isolated as a colorless liquid. Spectroscopic data were identical to those reported for **16a**. $[\alpha]_D^{23}$ = -4.1 (*c* 2.3 in $CHCl_3$).

Diethyl 2-(*S*)-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)succinate (15b).

Prepared according to the protocol used for the synthesis of **15a** on **16b** (305 mg, 1.42 mmol). After work-up and column chromatography (EtOAc /Heptane 10:90 to 15:85) **(*E*)-15b** (414 mg, 86%) and **(*Z*)-15b** (93 mg, 19%) were isolated as amorphous solids. Spectroscopic data were identical to those reported for **(*E*)-15a** and **(*Z*)-15a**.

(*E*)-diethyl 2-(*S*)-(3-(4-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1*H*-imidazol-2-yl)allyl) succinate 24b.

Prepared according to general procedure B with **23** (352 mg, 1 mmol) in DMF (4 mL) with **(*E*)-15b** (530 mg), Na_2CO_3 (115 mg) and Pd $(PPh_3)_4$ (115 mg). After work-up, purification by flash chromatography on silicagel (heptane/ EtOAc : 1/1) afforded pure **24b** (409 mg, 93%) as a white amorphous solid. Spectroscopic data were identical to those reported for **24a**.

(*E*)-diethyl 2-(*R*)-(3-(5-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1*H*-imidazol-2-yl)allyl) succinate 25a.

Prepared according to general procedure B with **11** (630 mg, 1.8 mmol) in DMF (7 mL) with **(*E*)-15a** (970 mg), Na_2CO_3 (202 mg) and Pd $(PPh_3)_4$ (202 mg). After work-up, purification by flash chromatography on silicagel (heptane/ EtOAc : 1/1) afforded pure **25a** (450 mg, 57%) as a white amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 6H), 0.83 (s, 9H), 1.18 (t, *J* = 6.0 Hz, 3H), 1.20 (t, *J* = 6.0 Hz, 3H), 2.37-2.52 (m, 2H), 2.56-2.65 (m, 1H), 2.69 (dd, *J* = 9.0 15.0 Hz, 1H), 2.91-3.01 (m, 1H), 3.58 (s, 3H), 4.08 (q, *J* = 6.0 Hz, 2H), 4.12 (q, *J* = 6.0 Hz, 2H), 4.58 (s, 2H), 6.27 (d, *J* = 15.0 Hz, 1H), 6.49-6.59 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1, 14.3, 14.4, 18.4, 26.0, 30.4, 35.3, 35.5, 41.2, 55.6, 60.8, 61.0, 119.1,

127.6, 131.3, 131.6, 146.2, 171.9, 174.3. HRMS (ESI^+) calcd for $C_{22}H_{39}N_2O_5Si$ $[M+H]^+$: 439.2628 found: 439.2611. IR 1462, 1730, 2855, 2928 cm^{-1}. $[\alpha]_D^{23}$= +8.0 (*c* 1.0 in $CHCl_3$).

(*E*)-diethyl 2-(*S*)-(3-(5-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1*H*-imidazol-2-yl)allyl) succinate 25b.

Prepared according to general procedure B with **11** (274 mg, 0.8 mmol) in DMF (3.5 mL) with **(*E*)-15b** (414 mg), Na_2CO_3 (90 mg) and Pd $(PPh_3)_4$ (90 mg). After work-up, purification by flash chromatography on silicagel (heptane/ EtOAc : 1/1) afforded pure **25b** (313 mg, 92%) as a white amorphous solid. Spectroscopic data were identical to those reported for **25a**. $[\alpha]_D^{23}$ = -6.5 (*c* 1.4 in $CHCl_3$).

Compound 26b. Prepared according to general procedure C.

a- From **24b** (409 mg, 0.9 mmol) in THF (5 mL) with TBAF (1M in THF, 1.4 ml). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 95/5) afforded the expected alcohol (209 mg, 64%) as a white amorphous solid. Spectroscopic data were identical to those reported for corresponding compound. $[\alpha]_D^{23}$ = -5.0 (*c* 1.0 in $CHCl_3$).

b- From the alcohol (190 mg) in CH_2Cl_2 (6 mL) with MnO_2 (334 mg). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2) afforded the expected aldehyde (156 mg, 82%) as a white amorphous solid. Spectroscopic data were identical to those reported for corresponding compound. $[\alpha]_D^{23}$ = -1.5 (*c* 1.0 in $CHCl_3$).

c- From NH_2-VFM-OMe (200 mg, 0.48 mmol) in MeOH/CH_2Cl_2 (3/1, 6 mL), and the aldehyde (156 mg, 0.48 mmol) in MeOH/CH_2Cl_2 (1/1, 1 mL) then sodium cyanoborohydride (47 mg) in MeOH/AcOH (1:0.1, 1 mL). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2 to 95/5) afforded the compound **26b** (274 mg, 80%) as a white amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ. ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.57 (d, *J* = 6.0 Hz, 3H), 0.90 (d, *J* = 6.0 Hz, 3H), 1.23-1.30 (m, 6H), 1.94-2.00 (m, 2H), 2.06 (s, 3H), 2.08-2.22 (m, 1H), 2.44 (t, *J* = 8.0 Hz, 1H), 2.47-2.58 (m, 2H), 2.60-2.78 (m, 2H), 2.86 (d, *J* = 5.0 Hz, 1H), 2.98-3.17 (m, 4H), 3.23 (d, *J* = 4.0 Hz, 1H), 3.53 (s, 3H), 3.74 (s, 3H), 4.10-4.22 (m, 4H), 4.59-4.69 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.54-6.58 (m, 1H), 6.80 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.21-7.32 (m, 5H), 7.85 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 15.6, 15.8, 19.7, 30.0, 30.8, 31.7, 35.3, 35.5, 37.6, 43.0, 51.8, 52.7, 54.4, 60.1, 68.1, 119.0, 127.1, 128.8, 129.0, 129.4, 136.5, 137.0, 171.2, 172.1, 173.9, 174.2, 175.1. HRMS (ESI^+) calcd for $C_{36}H_{54}N_5O_8S$

$[M+H]^+$: 716.3693 found: 716.3709. IR 1435, 1543, 1639, 1731, 2956, 3286 cm^{-1}. $[\alpha]_D^{23}$ = -32 (*c* 1.0 in $CHCl_3$).

Compound 27a. Prepared according to general procedure C.

a- From **25a** (440 mg, 1.02 mmol) in THF (4 mL) with TBAF (1M in THF, 2 ml). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 95/5) afforded the expected alcohol (298 mg, 91%) as a white amorphous solid. ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, *J* = 6.0 Hz, 3H), 1.23 (t, *J* = 6.0 Hz, 3H), 2.41-2.53 (m, 2H), 2.59-2.68 (m, 2H), 2.71 (dd, *J* = 9.0, 15.0 Hz, 1H), 2.94-3.03 (m, 1H), 3.61 (s, 3H), 4.09 (q, *J* = 6.0 Hz, 2H), 4.14 (q, *J* = 6.0 Hz, 2H,), 4.57 (s, 2H), 6.29 (d, *J* = 15.0 Hz, 1H), 6.52-6.62 (m, 1H), 6.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, , 30.4, 35.2, 35.5, 41.2, 54.9, 60.9, 61.1, 118.9, 128.2, 131.6, 132.0, 146.6, 171.9, 174.1. HRMS (ESI^+) calcd for $C_{16}H_{25}N_2O_5$ $[M+H]^+$: 325.1763 found: 325.1760. IR 1467, 1725, 2977, 3175 cm^{-1}. $[\alpha]_D^{23}$ = +6.0 (*c* 1.0 in $CHCl_3$).

b- From the alcohol (285 mg) in CH_2Cl_2 (9 mL) with MnO_2 (390 mg). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2) afforded the expected aldehyde (224 mg, 79%) as a white amorphous solid. ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, *J* = 6.0 Hz, 3H), 1.22 (t, *J* = 6.0 Hz, 3H), 2.48 (dd, *J* = 9.0, 18.0 Hz, 1H), 2.50-2.55 (m, 1H), 2.61-2.68 (m, 1H), 2.71 (dd, *J* = 9.0, 18.0 Hz, 1H), 2.96-3.07 (m, 1H), 3.89 (s, 3H), 4.08 (q, *J* = 6.0 Hz, 2H), 4.14 (q, *J* = 6.0 Hz, 2H), 6.34 (d, *J* = 15.0 Hz, 1H), 6.83-6.93 (m, 1H), 7.69 (s, 1H), 9.64 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 32.2, 35.3, 35.6, 40.9, 60.9, 61.2, 117.3, 132.0, 138.0, 144.1, 151.6, 171.7, 173.8, 179.1. HRMS (ESI^+) calcd for $C_{16}H_{22}N_2O_5Na$ $[M+Na]^+$: 345.1426 found: 345.1414. IR 1466, 1524, 1659, 1725, 2980 cm^{-1}. $[\alpha]_D^{23}$ = +12 (*c* 1.0 in $CHCl_3$).

c- From NH_2-VFM-OMe (138 mg, 0.38 mmol) in MeOH/CH_2Cl_2 (3/1, 5.2 mL), and the aldehyde (112 mg, 0.38 mmol) in MeOH/CH_2Cl_2 (1/1, 1 mL) then sodium cyanoborohydride (45 mg) in MeOH/AcOH (1:0.1, 1 mL). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2 to 95/5) afforded the compound **27a** (207 mg, 76%) as a white amorphous solid. ^1H NMR (300 MHz, $CDCl_3$) δ 0.68 (d, *J* = 6.0 Hz, 3H), 0.75 (d, *J* = 6.0 Hz, 3H), 1.17 (t, *J* = 6.0 Hz, 3H), 1.18 (t, *J* = 6.0 Hz, 3H), 1.82-1.93 (m, 2H), 1.97 (s, 3H), 1.98-2.09 (m, 1H), 2.35 (t, *J* = 6.0 Hz, 3H), 2.40-2.49 (m, 2H),

2.53-2.61 (m, 1H), 2.65 (dd, *J* = 6.0, 15.0 Hz, 1H), 2.77 (d, *J* = 3.0 Hz, 1H), 2.89-3.03 (m, 3H), 3.41 (d, *J* = 12.0 Hz, 1H), 3.45 (s, 3H), 3.52 (d, *J* = 12.0 Hz, 1H), 4.06 (q, *J* = 6.0 Hz, 2H), 4.10 (q, *J* = 6.0 Hz, 2H), 4.51-4.57 (m, 1H), 4.63-4.71 (m, 1H), 6.29 (m, 1H), 6.46-6.56 (m, 1H), 6.71 (s, 1H), 6.74 (d, *J* = 9.0 Hz, 1H), 7.14-7.27 (m, 5H), 7.30 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 15.5, 18.1, 19.6, 29.9, 30.4, 31.5, 31.6, 35.3, 35.5, 38.2, 41.2, 43.00, 51.8, 52.7, 54.1, 60.8, 61.0, 68.1, 118.6, 119.0, 127.8, 128.8, 128.9, 129.4, 131.6, 136.5, 146.1, 171.0, 171.9, 172.0, 173.9, 174.1. HRMS (ESI^+) calcd for $C_{36}H_{53}N_5O_8SNa$ $[M+Na]^+$: 738.3513 found: 738.3503. IR 1469, 1542, 1640, 1730, 2956, 3298 cm^{-1}. $[\alpha]_D^{23}$ = -22 (*c* 1.05 in $CHCl_3$).

Compound 27b. Prepared according to general procedure C.

a- From **25b** (393 mg, 0.9 mmol) in THF (5 mL) with TBAF (1M in THF, 1.35 ml). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 95/5) afforded the expected alcohol (246 mg, 84%) as a white amorphous solid. Spectroscopic data were identical to those reported for corresponding compound. $[\alpha]_D^{23}$ = -4.0 (*c* 1.0 in $CHCl_3$).

b- From the alcohol (246 mg) in CH_2Cl_2 (7.5 mL) with MnO_2 (433 mg). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2) afforded the expected aldehyde (197 mg, 80%) as a white amorphous solid. Spectroscopic data were identical to those reported for corresponding compound. $[\alpha]_D^{23}$ = -7.0 (*c* 1.0 in $CHCl_3$).

c- From NH_2-VFM-OMe (118 mg, 0.32 mmol) in MeOH/CH_2Cl_2 (3/1, 4 mL), and the aldehyde (93 mg, 0.32 mmol) in MeOH/CH_2Cl_2 (1/1, 1 mL) then sodium cyanoborohydride (45 mg) in MeOH/AcOH (1:0.1, 1 mL). Purification by flash chromatography on silicagel (CH_2Cl_2/MeOH: 98/2 to 95/5) afforded the compound **27b** (176 mg, 85%) as a white amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (d, *J* = 6.0 Hz, 3H), 0.76 (d, *J* = 6.0 Hz, 3H), 1.21-1.25 (m, 6H), 1.86-1.99 (m, 2H), 2.03 (s, 3H), 2.08-2.21 (m, 1H), 2.38-2.55 (m, 4H), 2.62-2.76 (m, 2H), 2.93 (d, *J* = 3.0 Hz, 1H), 2.98-3.09 (m, 2H), 3.18 (dd, *J* = 6.0, 15.0 Hz, 1H), 3.45-3.58 (m, 2H), 3.70 (s, 3H), 4.08-4.18 (m, 4H), 4.60-4.72 (m, 2H), 6.37 (d, *J* = 15.0 Hz, 1H), 6.48-6.57 (m, 1H), 6.67 (s, 1H), 7.11 (d, *J* = 6.0 Hz, 1H), 7.15-7.28 (m, 5H), 8.03 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 15.5, 17.8, 19.4, 30.0, 31.4, 31.7, 32.9, 35.2, 35.5, 37.6, 41.1, 46.1, 51.7, 52.6, 54.5, 60.8, 61.0, 67.8, 118.7, 119.1, 127.0, 128.8, 129.4, 131.6, 137.4, 139.3,

145.1, 171.5, 171.9, 172.0, 174.0, 174.6. HRMS (ESI^+) calcd for $C_{36}H_{53}N_5O_8SNa$ $[M+Na]^+$: 738.3513 found: 738.3517. IR 1439, 1513, 1644, 1730, 2955, 3296 cm^{-1}. $[\alpha]_D^{23}$ = -40 (*c* 0.7 in $CHCl_3$).

Compound 30b.

Prepared according to the protocol used for the synthesis of **30a** on **26a** (120 mg, 0.17 mmol) Purification on by preparative TLC silica gel (CH_2Cl_2/MeOH: 95/5, v/v) afforded pure **30b** (90 mg, 75%) as a white amorphous solid. ^1H NMR (300 MHz, $CDCl_3$) δ 0.63 (d, *J* = 6.0 Hz, 3H), 0.73 (d, *J* = 6.0 Hz, 3H), 1.21-1.27 (m, 6H), 1.59-1.67 (m, 1H), 1.68-1.78 (m, 3H), 1.87-2.00 (m, 2H), 2.05 (s, 3H), 2.06-2.12 (m, 1H), 2.39-2.47 (m, 3H), 2.64-2.74 (m, 3H), 2.80-2.91 (m, 2H), 3.07 (dd, *J* = 6.0, 15.0 Hz, 1H), 3.18 (dd, *J* = 6.0, 15.0 Hz, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 3.52 (s, 3H), 3.57 (d, *J* = 12.0 Hz, 1H), 3.71 (s, 3H), 4.11 (q, *J* = 6.0 Hz, 2H), 4.14 (q, *J* = 6.0 Hz, 2H), 4.59-4.70 (m, 2H), 6.63 (s, 1H), 7.06 (d, *J* = 6.0 Hz, 1H), 7.19-7.29 (m, 5H), 8.05 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 15.5, 17.8, 19.5, 25.6, 26.6, 30.0, 31.3, 31.7, 31.8, 32.8, 36.3, 37.4, 41.2, 45.9, 51.7, 52.6, 54.6, 60.8, 60.9, 67.4, 118.5, 127.0, 128.8, 129.4, 137.1, 148.1, 171.4, 172.0, 174.7. HRMS (ESI^+) calcd for $C_{36}H_{55}N_5O_8NaS$ $[M+Na]^+$: 740.3669 found: 740.3646. IR 1439, 1454, 1504, 1537, 1643, 1730, 2956, 3294 cm^{-1}. $[\alpha]_D^{23}$= -32 (*c* 0.9 in $CHCl_3$).

Compound 31a.

Prepared according to the protocol used for the synthesis of **30a** on **27a** (97 mg, 0.13 mmol) Purification on by preparative TLC silica gel (CH_2Cl_2/MeOH: 95/5, v/v) afforded pure **31a** (55 mg, 57%) as a white amorphous solid. ^1H NMR (300 MHz, $CDCl_3$) δ 0.68 (d, *J* = 6.0 Hz, 3H), 0.77 (d, *J* = 6.0 Hz, 3H), 1.14-1.21 (m, 6H), 1.54-1.75 (m, 4H), 1.80-1.94 (m, 2H), 1.97 (s, 3H), 2.00-2.10 (m, 1H), 2.34-2.42 (m, 3H), 2.56-2.67 (m, 3H), 2.74-2.82 (m, 2H), 2.93-3.08 (m, 2H), 3.36-3.42 (m, 4H), 3.50 (d, *J* = 12.0 Hz, 1H), 3.65 (s, 3H), 1.01-4.11 (m, 4H), 4.51-4.58 (m, 1H), 4.73 (q, *J* = 6.0 Hz, 1H), 6.62 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.12-7.25 (m, 5H), 7.42 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 15.5, 18.1, 19.6, 25.1, 27.1, 30.0, 30.3, 31.5, 31.6, 31.7, 32.8, 36.2, 38.2, 41.2, 43.1, 51.7, 52.6, 53.9, 60.5, 60.7, 68.0, 126.4, 127.1, 128.8, 129.4, 136.6, 148.8, 171.1, 172.0, 174.0, 174.8. HRMS (ESI^+) calcd for $C_{36}H_{55}N_5O_8NaS$ $[M+Na]^+$: 740.3669 found: 740.3651. IR 1440, 1537, 1639, 1730, 2956, 3298 cm^{-1}. $[\alpha]_D^{23}$= -21 (*c* 0.7 in

$CHCl_3$).

Compound 31b.

Prepared according to the protocol used for the synthesis of **30a** on **27b** (170 mg, 0.23 mmol) Purification on by preparative TLC silica gel (CH_2Cl_2/MeOH: 95/5, v/v) afforded pure **31b** (100 mg, 59%) as a white amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, *J* = 6.0 Hz, 3H), 0.80 (d, *J* = 6.0 Hz, 3H), 1.20 (t, *J* = 6.0 Hz, 3H), 1.58-1.98 (m, 8H), 2.01 (s, 3H), 2.02-2.12 (m, 1H), 2.36-2.45 (m, 3H), 2.61-2.71 (m, 4H), 2.76-2.80 (m, 1H), 2.81 (d, *J* = 6.0 Hz, 1H), 3.03-3.07 (m, 1H), 3.42 (d, *J* = 12.0 Hz, 1H), 3.43 (s, 3H), 3.53 (d, *J* = 12.0 Hz, 1H), 3.69 (s, 3H), 4.08 (q, *J* = 6.0 Hz, 2H), 4.11 (q, *J* = 6.0 Hz, 2H), 4.54-4.60 (m, 1H), 4.70 (q, *J* = 6.0 Hz, 1H), 6.66 (s, 1H), 6.72 (d, *J* = 6.0 Hz, 1H), 7.17-7.25 (m, 5H), 7.36 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 15.6, 18.1, 19.6, 25.2, 27.0, 30.0, 30.4, 31.6, 31.7, 36.3, 38.2, 41.3, 43.2, 51.8, 52.7, 54.2, 60.8, 60.9, 68.2, 126.1, 127.3, 129.0, 129.4, 129.5, 136.6, 148.8, 171.1, 172.0, 172.1, 174.0, 174.8. HRMS (ESI^+) calcd for $C_{36}H_{56}N_5O_8S$ $[M+H]^+$: 718.3850 found: 718.3845. IR 1440, 1497, 1545, 1640, 1730, 2955, 3297 cm^{-1}. $[\alpha]_D^{23}$= -37 (*c* 0.8 in $CHCl_3$).

Compound 28b.

Prepared according to general procedure D on **25b** (50 mg, 0.070 mmol) in 1.7 mL solvent with LiOH,1H_2O (12 mg, 4.1 equiv.). Compound **27b** (45 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.76 (d, *J* = 6.0 Hz, 3H), 0.79 (d, *J* = 6.0 Hz, 3H), 1.79-1.89 (m, 1H), 1.92-2.03 (m, 1H), 2.06 (s, 3H), 2.09-2.21 (m, 1H), 2.43-2.53 (m, 4H), 2.56-2.69 (m, 2H), 2.84-2.90 (m, 1H), 2.90 (d, *J* = 6.0 Hz, 1H), 2.98 (dd, *J* = 9.0, 15.0 Hz, 1H), 3.25 (dd, *J* = 6.0, 15.0 Hz, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 3.65 (s, 3H), 4.31 (dd, *J* = 3.0, 6.0 Hz, 1H), 4.79 (dd, *J* = 6.0, 9.0 Hz, 1H), 6.45 (d, *J* = 15.0 Hz, 1H), 6.55-6.66 (m, 1H), 6.80 (s, 1H), 7.15-7.31 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.4, 18.8, 19.8, 31.3, 32.6, 33.6, 34.1, 36.9, 38.7, 39.7, 45.0, 45.6, 55.7, 55.8, 68.5, 118.2, 121.3, 128.0, 129.7, 130.5, 136.4, 138.0, 138.7, 146.6, 172.8, 175.6, 177.7, 179.2, 181.4. HRMS (ESI^+) calcd for $C_{31}H_{44}N_5O_8S$ $[M+H]^+$: 646.2911 found: 66.2982. $[\alpha]_D^{23}$= -20 (*c* 0.37 in MeOH).

Compound 29a.

Prepared according to general procedure D on **27a** (54 mg, 0.075 mmol) in 1.2 mL solvent

with LiOH,1H_2O (11 mg, 3.6 equiv.). Compound **29a** (49 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.67 (d, *J* = 6.0 Hz, 3H), 0.71 (d, *J* = 6.0 Hz, 3H), 1.53-1.66 (m, 1H), 1.79-1.89 (m, 1H), 1.92 (s, 3H), 1.95-2.04 (m, 1H), 2.28 (dd, *J* = 6.0, 15.0 Hz, 1H), 2.43-2.50 (m, 5H), 2.60 (d, *J* = 8.0 Hz, 1H), 2.61-2.74 (m, 1H), 2.79 (dd, *J* = 10.0, 15.0 Hz, 1H), 3.08 (m, 2H), 3.43 (s, 3H), 4.18 (dd, *J* = 3.0, 5.0 Hz, 1H), 4.71 (dd, *J* = 6.0, 12.0 Hz, 1H), 6.30 (d, *J* = 15.0 Hz, 1H), 6.40 (m, 2H), 7.00-7.25 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.5, 19.4, 20.2, 31.1, 31.3, 32.9, 34.2, 37.0, 38.8, 40.2, 42.3, 45.6, 55.8, 55.9, 68.7, 118.4, 126.5, 128.0, 129.7, 130.5, 132.0, 136.5, 139.0, 147.3, 172.8, 176.7, 177.9, 179.8, 181.9. HRMS (ESI^-) calcd for $C_{31}H_{42}N_5O_8S$ $[M-H]^+$: 644.2754 found: 644.2731. IR 1402, 1556, 1632, 2960, 3279 cm^{-1}. $[\alpha]_D^{23}$= -14 (*c* 0.44 in MeOH).

Compound 29b.

Prepared according to general procedure D on **27b** (45 mg, 0.063 mmol) in 1.2 mL solvent with LiOH,1H_2O (10 mg, 3.8 equiv.). Compound **29b** (41 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.61 (d, *J* = 6.0 Hz, 3H), 0.63 (d, *J* = 6.0 Hz, 3H), 1.65-1.71 (m, 1H), 1.77-1.91 (m, 1H), 1.93 (s, 3H), 1.95-2.06 (m, 1H), 2.24-2.53 (m, 6H), 2.66-2.76 (m, 2H), 2.85 (dd, *J* = 9.0, 15.0 Hz, 1H), 3.10 (dd, *J* = 6.0, 15.0 Hz, 1H), 3.16-3.22 (m, 1H), 3.33 (d, *J* = 15.0 Hz, 1H), 3.50 (s, 3H), 4.18 (dd, *J* = 3.0, 6.0 Hz, 1H), 4.65 (dd, *J* = 3.0, 10.0 Hz, 1H), 6.30 (d, *J* = 15.0 Hz, 1H), 6.40-6.50 (m, 1H), 6.64 (s, 1H), 7.01-7.18 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.4, 18.8, 19.9, 31.2, 32.7, 33.4, 34.2, 37.1, 38.7, 40.6, 45.8, 45.9, 55.7, 55.9, 68.6, 118.4, 127.9, 129.7, 130.5, 136.2, 138.7, 138.9, 16.8, 172.8, 176.2, 177.8, 180.1, 181.3. HRMS (ESI^+) calcd for $C_{31}H_{44}N_5O_8S$ $[M+H]^+$: 646.2911 found: 646.2928. IR 1407, 1567, 2958, 3282 cm^{-1}. $[\alpha]_D^{23}$= -23 (*c* 0.19 in MeOH).

Compound 1a.

Prepared according to general procedure D on **31a** (40 mg, 0.056 mmol) in 1.4 mL solvent with LiOH,1H_2O (9 mg, 3.8 equiv.). Compound **1a** (36 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.81(d, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 6.0 Hz, 3H), 1.53-1.66 (m, 1H), 1.79-1.89 (m, 1H), 1.92 (s, 3H), 1.95-2.04 (m, 1H), 2.36-2.62 (m, 5H), 2.67-2.87 (m, 5H), 2.92 (dd, *J* = 11.0, 15.0 Hz, 1H), 3.26 (m, 2H), 3.35 (s, 3H), 4.31 (dd, *J* = 4.0, 6.0 Hz, 1H), 4.85 (dd, *J* = 4.0, 12.0 Hz, 1H), 6.67 (s, 1H), 7.17-

7.34 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.4, 19.3, 20.2, 31.3, 31.5, 32.6, 32.9, 34.2, 38.8, 40.4, 42.3, 45.0, 55.7, 55.8, 68.8, 122.7, 128.0, 129.7, 130.6, 132.4, 138.9, 150.1 172.8, 176.6, 177.8, 179.5, 182.3. HRMS (ESI^+) calcd for $C_{31}H_{46}N_5O_8S$ $[M+H]^+$: 648.3072 found: 648.3067. $[\alpha]_D^{23}$= -14 (*c* 0.38 in MeOH).

Compound 1b.

Prepared according to general procedure D on **31b** (84 mg, 0.117 mmol) in 2.3 mL solvent with LiOH,1H_2O (18 mg, 3.6 equiv.). Compound **1b** (76 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.65 (d, *J* = 6.0 Hz, 3H), 0.69 (d, *J* = 6.0 Hz, 3H), 1.41-1.64 (m, 5H), 1.75-1.88 (m, 1H), 1.90 (s, 3H), 1.93-2.02 (m, 1H), 2.23 (dd, *J* = 6.0, 15.0 Hz, 1H), 2.27-2.35 (m, 2H), 2.41 (dd, *J* = 6.0, 15.0 Hz, 1H), 2.49-2.55 (m, 1H), 2.56 (d, *J* = 6.0 Hz, 1H), 2.64-2.69 (m, 2H), 2.77 (dd, *J* = 10.0, 15.0 Hz, 1H), 3.08 (dd, *J* = 13.0, 15.0 Hz, 1H), 3.14 (m, 1H), 3.19 (s, 3H), 3.21 (d, *J* = 15.0 Hz, 1H), 4.16 (dd, *J* = 3.0, 6.0 Hz, 1H), 4.69 (dd, *J* = 3.0, 9.0 Hz, 1H), 6.52 (s, 3H), 6.99-7.18 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.4, 19.3, 20.2, 26.2, 26.9, 31.2, 31.5, 32.7, 32.9, 34.1, 38.8, 40.5, 42.3, 45.1, 55.7, 55.8, 68.8, 122.6, 128.0, 129.6, 130.5, 132.3, 138.9, 150.1, 172.8, 176.6, 177.8, 179.6, 182.4. HRMS (ESI^+) calcd for $C_{31}H_{46}N_5O_8S$ $[M+H]^+$: 648.3067 found: 648.3071. IR 1403, 1572, 2922, 3280 cm^{-1}. $[\alpha]_D^{23}$= -23 (*c* 0.51 in MeOH).

Compound 2b.

Prepared according to general procedure D on **30b** (70 mg, 0.098 mmol) in 1.2 mL solvent with LiOH,1H_2O (15 mg, 3.6 equiv.). Compound **2b** (63 mg, quant.) was obtained as a white amorphous solid. ^{1}H NMR (300 MHz, CD_3OD) δ 0.77 (d, *J* = 6.0 Hz, 3H), 0.78 (d, *J* = 6.0 Hz, 3H), 1.54-1.87 (m, 5H), 1.92-2.02 (m, 1H), 2.05 (s, 3H), 2.09-2.20 (m, 1H), 2.36-2.63 (m, 5H), 2.66-2.90 (m, 4H), 2.97 (dd, *J* = 10.0, 15.0 Hz, 1H), 3.25 (dd, *J* = 4.0, 15.0 Hz, 1H), 3.49 (q, *J* = 15.0 Hz, 2H), 3.62 (m, 1H), 3.65 (s, 3H), 4.32 (dd, *J* = 4.0, 7.0 Hz, 1H), 4.80 (dd, *J* = 4.0, 10.0 Hz, 1H), 6.84 (s, 1H), 7.14-7.32 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD) δ 15.4, 18.9, 19.8, 20.2, 26.3, 26.5, 31.3, 32.5, 33.8, 34.1, 38.8, 39.8, 44.4, 44.6, 55.8, 68.3, 121.5, 127.9, 129.7, 130.5, 138.8, 149.7, 172.8, 175.1, 177.7, 179.0, 181.8. HRMS (ESI^+) calcd for $C_{31}H_{45}N_5O_8NaS$ $[M+Na]^+$: 670.2887 found: 670.2863. $[\alpha]_D^{25}$= -15 (*c* 0.59 in MeOH).

2- Crystallographic data.

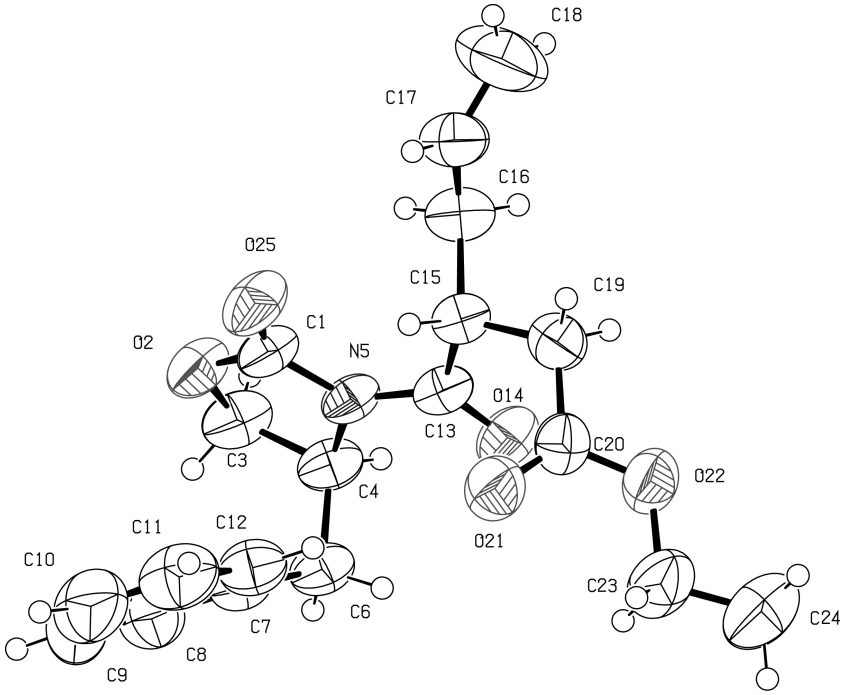

Fig. 1 X-ray structure ethyl 3-(*R*)-(4-(*S*)-benzyl-2-oxazolidine-3-carbonyl) hex-5-enoate (**19a**) (50% probability thermal ellipsoids).

Data from the X-ray crystallographic analysis was deposited at Cambridge crystallographic data base centre (CCDC).‡ ORTEP drawing (50% probability thermal ellipsoids) is of ethyl 3-(R)-(4- (S)-benzyl-2-oxazolidine-3-carbonyl)hex-5-enoate **19a**. A colourless plate-like single crystal (0.60 x 0.58 x 0.10 mm) grown from heptane/ethyl acetate was used for the unit-cell determination.[6,7]

Representative data is as follows: $C_{19}H_{23}NO_5$; M = 345.38; monoclinic, space group $P\,2_1$ (#4), Z = 2 with a = 7.361(3) Å, b = 10.817(4) Å, c = 12.310(4) Å , β = 106.652 (8)°, V = 939.1(6) Å^3 and Dcalc. = 1.221g cm^{-3}. The structure was solved by direct methods.[8] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were attached at the idealized position and not refined.[9] The final *R1* ($I > 2\sigma(I)$), *R* all reflections, and *wR2* all reflections factors after full-matrix least-squares refinements were 0.041, 0.056, and 0.108 respectively, for 1647 observed reflections.

‡ CCDC reference number xxxxxx. For crystallographic data in CIF or other electronic format see DOI: xxxx

References

1. W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller and H. Fischer, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1844-1848.

2. D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R. E. Cramer and C. M. Jensen, *Inorg. Chim. Acta*, 2000, **300-302**, 958-963.
3. M. R. Eberhard, *Org. Lett.*, 2004, **6**, 2125-2128.
4. J. Waser, B. Gaspar, H. Nambu and E. M. Carreira, *J. Am. Chem. Soc.*, 2006, **128**, 11693-11712.
5. J.-F. Li, R. Yang, L. Nie, R. Huang and J. Lin, *J. Pept. Res.*, 2005, **66**, 319-323.
6. Nonius, B. V. (1999). COLLECT, data collection software.
7. Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Volume 276,Macromolecular Crystallography, part A, edited by C.W. Carter, Jr. & R.M.Sweet, 307-326, 1997, New York: Academic Press.
8. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.
9. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.