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Supplementary Experimental Results:

Wittig/Horner-Wadsworth-Emmons precursor PEG syntheses:

Fmoc-Gly-OPEG-OCH3 (2):
Polyethylene glycol 5000 monomethyl ether (35.5g, 7.10 mmol), Fmoc-Gly (4.65g, 15.6 mmol, 2.2 eq) and PPh_3 (4.09g, 15.6 mmol, 2.2 eq) were dissolved in CH_2Cl_2 (400mL) and cooled to 0°C, Diethylazodicarboxylate (2.46mL, 15.6 mmol, 2.2 eq) was added dropwise over 30 min, and the reaction warmed to rt overnight. The reaction washed (2x H_2O, 1x satd NaCl), evaporated to dryness, taken up in acetone and reevaporated, dissolved in a minimum volume of DMF, and added to Et_2O (600 mL). The precipitated product was filtered, rinsed with cold EtOH and Et_2O, dried, then recrystallized from EtOH (400 mL).

^1H NMR ($CDCl_3$): δ 7.76 (d, J=7.3, 2H), 7.61 (d, J=7.6, 2H), 7.40 (t, J=7.4, 2H), 7.314 (t, J=7.6, 1H), 7.312 (t, J=7.6, 1H), 5.56 (t, J=10.0, 1H), 4.41 (d, J=6.9, 2H), 4.32 (m, 2H), 4.24 (t, J=7.1, 1H), 4.03 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

H_2N-Gly-OPEG-OCH3:
Fmoc-Gly-OPEG-OCH3 **2** (20.2g, 3.82 mmol) was dissolved in CH_2Cl_2 (50 mL) and piperidine (10 ml) was added. After 30 min the volume was reduced and the solution added to Et_2O (400 mL). The precipitated product was filtered, rinsed with cold EtOH and Et_2O, dried, then recrystallized from EtOH.

^1H NMR ($CDCl_3$): δ 4.29 (m, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

Fmoc-Ala-Gly-OPEG-OCH3:
H_2N-Gly-OPEG-OCH3 (20.1 g, 3.97 mmol), Fmoc-Ala (2.47g, 7.94 mmol, 2.0 eq), PyBOP (4.13g, 7.94 mmol, 2.0 eq), and HOBt.H_2O (1.22g, 7.94 mmol, 2.0 eq) were dissolved in DMF (50 mL) and DIPEA (1.94 mL, 11.1 mmol, 2.8 eq)was added. After 2h the reaction was poured into Et_2O (700ml), filtered, and worked up as usual.

^1H NMR ($CDCl_3$): δ 7.75 (d, J=7.3, 2H), 7.59 (d, J=6.9, 2H), 7.39 (t, J=7.2, 2H), 7.30 (t, J=7.4, 2H), 6.74 (br s, 1H), 5.54 (br d, J=7.3, 1H), 4.42 (d, J=6.5, 2H), 4.35-4.25 (m, 2H), 4.20 (t, J=6.7, 1H), 4.1-4.0 (m 1H), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.40 (d, J=6.9, 3H).

H_2N-Ala-Gly-OPEG-OCH3 (3):
Fmoc-Ala-Gly-OPEG-OCH3 was deprotected as described earlier.

^1H NMR ($CDCl_3$): δ 7.84 (br s, 1H), 4.31-4.27 (m, 3H), 4.09 (dd, J=18.3,5.7, 1H, PEG), 4.04 (dd, J=18.3,5.3, 1H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 1.37 (d, J=6.9, 3H).

2-bromoethan-1-amide-Ala-Gly-OPEG-OCH3 (5):
H_2N-Ala-Gly-OPEG-OCH3 **3** (4.79g, 0.934 mmol) was dissolved in DMF (25 mL) and a solution of bromoacetic acid (0.290mL, 2.09 mmol, 2.2 eq) and diisopropylcarbodiimide (0.213mL, 2.09 mmol, 2.2 eq) in CH_2Cl_2 (5mL), preactivated for 10 min and filtered, was added. After 2.5 h the reaction was poured into Et_2O and worked up as usual.

^1H NMR ($CDCl_3$): δ 7.19 (d, J=7.2, 1H), 6.85 (t, J=5.2, 1H), 4.49 (quint, J=7.1, 1H), 4.34-4.24 (m, 2H), 4.08 (dd, J=17.9,5.7, 1H), 4.02 (dd, J=17.9,5.7, 1H), 3.90 (d, J=13.4, 1H), 3.87 (d, J=13.4, 1H), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.42 (d, J=7.2, 3H).

4-bromobut-2*E*-enoic acid:
Ethyl 4-bromocrotonate (4.77 g, 24.7 mmol) was stirred with LiOH.H_2O (1.55g, 37.0 mmol, 1.5 eq) in H_2O (20 mL) and EtOH (10 mL) for 1 h. The solution was washed with EtOAc (2x) and acidified with 2N HCl in the presence of CH_2Cl_2. The organic phase was removed, dried ($MgSO_4$), and

evaporated to dryness. Purification by flash column chromatography (80g silica, 2:1 EtOAc:Hex) gave 2.14 g of product (52%) which was recrystallized from Et_2O/hexane.

TLC (2:1 EtOAc:hex): R_f= 0.63; ^1H NMR ($CDCl_3$): δ 11.5 (br s, 1H), 7.12 (dt, J=15.1,7.3, 1H), 6.05 (dd, J=15.4,1.3, 1H), 4.03 (dd, J=7.3,1.3, 2H); ^{13}C NMR ($CDCl_3$): δ 170.37, 144.04, 123.59, 28.63.

4-bromobut-2*E*-en-1-amide-Ala-Gly-OPEG-OCH_3 (8):
H_2N-Ala-Gly-OPEG-OCH_3 **3** (0.956g, 0.186 mmol) was dissolved in DMF (5 mL) and a solution of bromocrotonic acid (0.062g, 0.372 mmol, 2.0 eq) and diisopropylcarbodiimide (0.058mL, 0.372 mmol, 2.0 eq) in CH_2Cl_2 (2mL), preactivated for 10 min and filtered, was added. After reaction overnight the solution was poured into Et_2O and worked up as usual.

^1H NMR ($CDCl_3$): δ 7.16 (t, J=6.1, 1H), 6.92 (dt, J=15.3,7.4, 1H), 6.84 (d, J=7.2, 1H), 6.12 (d, J=15.3, 1H), 4.59 (quint, J=7.2, 1H), 4.35-4.2 (m, 2H), 4.10 (dd, J=18.1,5.9, 1H, PEG), 4.02 (d, J=7.2, 2H), 3.98 (dd, J=17.9,5.3, 1H, PEG), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.41 (d, J=6.9, 3H).

***E*-diethylphosphonocrotonic acid:**
Methyl diethylphosphonocrotonate (0.540 g, 2.28 mmol) was stirred with LiOH.H_2O (0.162g, 3.87 mmol, 1.5 eq) in H_2O (10 mL) and EtOH (1 mL) for 1.5 h. The solution was washed with CH_2Cl_2 (2x) and acidified with 1N HCl in the presence of CH_2Cl_2. The organic phase was removed, dried ($MgSO_4$), and evaporated to give 0.365g (72%) of an oil which solidfied upon standing.

^1H NMR ($CDCl_3$): δ 9.2 (vbr s, 1H), 6.94 (dq, J=15.6,8.0, 1H), 5.96 (ddd, J=15.6,5.0,1.1, 1H), 4.2-4.1 (m, 4H), 2.79 (dd, J=23.3,8.0, 2H), 1.33 (t, J=7.0, 6H).

Wittig/Horner-Wadsworth-Emmons Reaction Products - see General Procedure and Table 1 for reaction conditions:

2-buten-1-amide-Ala-Gly-OPEG-OCH_3 (7, R = CH_3):

E: ^1H NMR ($CDCl_3$): δ 7.56 (br s, 1H), 6.92 (d, J=7.2, 1H), 6.84 (dq, J=14.4,6.9, 1H), 5.96 (dq, J=15.0,1.2, 1H), 4.60 (quint, J=7.2, 1H), 4.30-4.24 (m, 2H), 4.04 (dd, J=17.4,5.9, 1H, PEG), 3.97 (dd, J=17.9,5.5, 1H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 1.84 (dd, J=6.9,1.5, 3H), 1.42 (d, J=7.2, 3H).

Z: ^1H NMR ($CDCl_3$): δ 6.11 (dq, J=11.4,7.2, 1H), 5.89 (br d, J=11.8, 1H), 2.10 (dd, J=7.2,1.5, 3H), 1.405 (d, J=8.4, 3H).

5-phenyl-penta-2,4-dien-1-amide-Ala-Gly-OPEG-OCH_3 (7, R = CH=CH-Ph):

2*E*,4*E*: ^1H NMR ($CDCl_3$): δ 7.5-7.15 (m, 4H), 7.45 (d, J=7.6, 2H), 7.34 (t, J=7.4, 2H), 6.86 (m, 1H), 6.70 (d, J=6.5, 1H), 6.07 (d, J=14.9, 1H), 4.64 (quint, J=7.2, 1H), 4.30 (t, J=4.8, 1H), 4.25 (t, J=4.6, 1H), 4.10 (dd, J=17.9,5.7, 1H, PEG), 3.99 (dd, J=18.1,5.5, 1H, PEG), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.44 (d, J=6.9, 3H).

2*Z*:4*E*: ^1H NMR ($CDCl_3$): δ 8.29 (dd, J=15.6,11.4, 1H), 7.5-7.15 (m, 1H), 7.51 (d, J=7.6, 2H), 7.32 (t, J=7.6, 2H), 6.86 (m, 1H), 6.74 (d, J=15.6, 1H), 6.64 (d, J=6.9, 1H), 6.60 (t, J=11.2, 1H), 5.72 (d, J=11.1, 1H), 4.62 (quint, J=7.2, 1H), 4.32 (t, J=4.6, 1H), 4.23 (dd, J=5.5,3.6, 1H), 4.11 (dd, J=17.9,5.3, 1H, PEG), 4.01 (dd, J=17.9,5.9, 1H, PEG), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.44 (d, J=6.9, 3H).

hexa-2,4-dien-1-amide-Ala-Gly-OPEG-OCH_3 (7, R = CH=CH-CH_3):
Also prepared by coupling sorbic acid with H_2N-Ala-Gly-OPEG-OCH_3 using PyBOP/HOBt/NMM as decribed earlier.

2*E*,4*E*: ^{1}H NMR ($CDCl_3$): δ 7.18 (dd, J=15.1,10.5, 1H), 7.12 (br s, 1H), 6.51 (d, J=6.9, 1H), 6.16 (dd, J=15.8,10.5, 1H), 6.08 (dq, J=15.1,6.5, 1H), 5.82 (d, J=15.3, 1H), 4.61 (quint, J=7.1, 1H), 4.35-4.2 (m, 2H), 4.15-3.95 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.40 (d, J=6.9, 3H).

2*Z*:4*E*: ^{1}H NMR ($CDCl_3$): δ 7.47 (dd, J=16.4,10.7, 1H), 7.07 (br s, 1H), 6.46 (d, J=7.6, 1H), 6.39 (t, J=11.2, 1H), 5.99 (dq, J=15.3,6.9, 1H), 5.53 (d, J=11.4, 1H), 4.57 (quint, J=7.2, 1H), 4.35-4.2 (m, 2H), 4.15-3.95 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.37 (s, 3H, PEG), 1.40 (d, J=6.9, 3H).

4-methyl-penta-2,4-dien-1-amide-Ala-Gly-OPEG-OCH$_3$ (7, R = C(CH$_3$)=CH$_2$):

2*E*,4*E*: ^{1}H NMR ($CDCl_3$): δ 7.28 (d, J=14.9, 1H), 7.07 (t, J=4.6, 1H), 6.57 (d, J=7.2, 1H), 5.92 (d, J=15.3, 1H), 5.31 (s, 1H), 5.28 (s, 1H), 4.62 (quint, J=6.9, 1H), 4.35-4.2 (m, 2H), 4.15-3.95 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 1.87 (s, 3H), 1.41 (d, J=6.9, 3H).

2*Z*:4*E*: ^{1}H NMR ($CDCl_3$): δ 6.84 (br s, 1H), 6.46 (d, J=8.0, 1H), 6.28 (d, J=12.2, 1H), 5.78 (d, J=12.6, 1H), 5.11 (s, 2H), 4.56 (quint, J=6.9, 1H), 4.35-4.2 (m, 2H), 4.15-3.95 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 1.92 (s, 3H), 1.41 (d, J=6.9, 3H).

STILLE REACTIONS:

Organostannanes 16 - Synthesized by General Procedure A, B, or C:

1-(tri-n-butylstannane)-2-phenylethene:
Method A crude product: *E*:*Z*:gem 91:5:5
after purification by distillation: *E*:*Z*:gem 90:10:0

E: TLC (hex): R_f=0.75; ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J=7.3, 2H), 7.33 (t, J=7.6, 2H), 7.22 (t, J=7.2, 1H), 6.87 (m, 2H), 1.55 (m, 6H), 1.35 (sex, J=7.3, 6H), 0.97 (dd, J=8.4, 8.4, 6H), 0.91 (t, J=7.4, 9H). ^{13}C NMR: 146.08, 138.78, 129.28, 128.39, 127.44, 125.94, 29.17, 27.36, 13.75, 9.60.

Z: TLC (hex): R_f=0.75; ^{1}H NMR ($CDCl_3$): δ 7.63 (d, J=13.7, 1H), 7.42 (d, J=7.3, 2H), 7.33 (t, J=7.6, 2H), 7.22 (t, J=7.2, 1H), 6.20 (d, J=13.7, 1H), 1.55 (m, 6H), 1.35 (sex, J=7.3, 6H), 0.97 (dd, J=8.4, 8.4, 6H), 0.91 (t, J=7.4, 9H).
1-(tri-n-butylstannane)-1-phenylethene:

TLC (hex): R_f=0.75; ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J=7.3, 2H), 7.33 (t, J=7.6, 2H), 7.22 (t, J=7.2, 1H), 6.20 (s, 1H), 6.13 (s, 1H), 1.55 (m, 6H), 1.35 (sex, J=7.3, 6H), 0.97 (dd, J=8.4, 8.4, 6H), 0.91 (t, J=7.4, 9H).

1-(tri-n-butylstannane)-3,3-dimethyl-2-butene:
Method A crude product: *E*:*Z*:gem 100:0:0
after purification by distillation: *E*:*Z*:gem 100:0:0

E: TLC (hex): R_f=0.85; ^{1}H NMR ($CDCl_3$): δ 5.95 (d, J=19.5, 1H), 5.76 (d, J=19.5, 1H), 1.49 (quint, J=7.7, 6H), 1.30 (sex, J=7.3, 6H), 1.00 (s, 9H), 0.89 (t, J=7.4, 9H), 0.86 (dd, J=8.0, 8.0, 6H). ^{13}C NMR: 159.94, 119.67, 35.95, 29.24, 29.17, 27.30, 13.77, 9.43.

1-bromo-1-decyne:

^{1}H NMR ($CDCl_3$): δ 2.20 (t, J=7.2, 2H), 1.50 (quint, J=7.3, 2H), 1.4-1.35 (m, 2H), 1.35-1.20 (m, 8H), 0.88 (t, J=6.9, 3H). ^{13}C NMR ($CDCl_3$): δ 80.30, 37.41, 31.84, 29.19, 29.08, 28.82, 28.32, 22.67, 19.66, 14.07.

1-(tri-n-butylstannane)-1-decene:
Method A crude product: *E*:*Z*:gem 75:24:12
Method B crude product: *E*:*Z*:gem 85:11:4

Method C crude product: *E*:*Z*:gem 0:100:0
after purification by distillation (of *E* only): *E*:*Z*:gem 86:9:5

E: TLC (hex): R_f=0.82; ^{1}H NMR ($CDCl_3$): δ 5.94 (dt, J=19.1,6.0, 1H), 5.85 (d, J=19.1, 1H), 2.12 (q, J=6.7, 2H), 1.55-1.2 (m, 24H), 0.95-0.8 (m, 9H), 0.89 (t, J=7.4, 9H). ^{13}C NMR: 149.83, 126.86, 38.01, 31.78, 29.53, 29.41, 29.29, 29.20, 29.01, 27.36, 22.78, 14.15, 13.75, 9.42.

Z: TLC (hex): R_f=0.82; ^{1}H NMR ($CDCl_3$): δ 6.51 (dt, J=12.2,7.0, 1H), 5.77 (d, J=12.6, 1H), 2.01 (q, J=6.8, 2H), 1.55-1.2 (m, 24H), 0.95-0.8 (m, 9H), 0.89 (t, J=7.4, 9H).

1-bromo-3-methoxy-1-propyne:

^{1}H NMR ($CDCl_3$): δ 4.13 (s, 2H), 3.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 75.94, 60.49, 57.55, 45.97.

1-(tri-n-butylstannane)-3-methoxy-1-propene:
Method A crude product: *E*:*Z*:gem 60:22:18
Method B crude product: *E*:*Z*:gem 73:22:5
after purification by flash column chromatography (25:1 pent:Et_2O): *E*:*Z*:gem 92:5:3

E: TLC (20:1 pent:Et_2O): R_f=0.20 ; ^{1}H NMR ($CDCl_3$): δ 6.21 (dt, J=19.1, 1.2, 1H), 6.04 (dt, J=19.1,5.2, 1H), 3.95 (dd, J=5.2,1.3, 2H), 3.34 (s, 3H), 1.49 (quint, J=7.7, 6H), 1.30 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.4, 9H). ^{13}C NMR ($CDCl_3$): δ 144.35, 131.02, 76.24, 57.73, 29.05, 27.24, 13.63, 9.34.

Z: TLC (20:1 pent:Et_2O): R_f=0.31 ; ^{1}H NMR ($CDCl_3$): δ 6.61 (dt, J=13.0,5.3, 1H), 6.08 (dt, J=12.2,1.1, 1H), 3.90 (dd, J=5.3,1.5, 2H), 3.33 (s, 3H), 1.49 (quint, J=7.7, 6H), 1.30 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.4, 9H). ^{13}C NMR ($CDCl_3$): δ 143.75, 131.48, 75.02, 57.90, 29.13, 27.35, 13.67, 10.69.
2-(tri-n-butylstannane)-3-methoxy-1-propene:

TLC (20:1 pent:Et_2O): R_f=0.31; ^{1}H NMR ($CDCl_3$): δ 5.85 (q, J=1.9, 1H), 5.26 (dt, J=2.7, 1.4, 1H), 4.02 (t, J=1.5, 2H), 3.30 (s, 3H), 1.55-1.45 (m, 6H), 1.35-1.25 (m, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.4, 9H). ^{13}C NMR ($CDCl_3$): δ 152.94, 124.53, 79.67, 57.65, 29.06, 27.31, 13.67, 9.50.

1-(tri-n-butylstannane)-3-hydroxy-1-propene:
Method A crude product: *E*:*Z*:gem 51:29:20
after purification by flash column chromatography (20:1 hex:EtOAc): *E*:*Z*:gem 99:1:0, 0:69:31

E: TLC (5:1 hex:EtOAc): R_f=0.50; ^{1}H NMR ($CDCl_3$): δ 6.22 (d, J=19.1, 1H), 6.16 (dt, J=19.5,3.8, 1H), 4.18 (dt, J=6.1,3.8, 2H), 1.49 (quint, J=7.7, 6H), 1.31 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 147.01, 127.95, 66.07, 29.00, 27.21, 13.59, 9.30.

Z: TLC (5:1 hex:EtOAc): R_f=0.63; ^{1}H NMR ($CDCl_3$): δ 6.68 (dt, J=13.0,6.1, 1H), 6.07 (d, J=13.0, 1H), 4.11 (t, J=5.3, 2H), 1.49 (quint, J=7.7, 6H), 1.31 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 146.39, 130.96, 65.78, 29.10, 27.23, 13.59, 10.51.
2-(tri-n-butylstannane)-3-hydroxy-1-propene:

TLC (5:1 hex:EtOAc): R_f=0.63; ^{1}H NMR ($CDCl_3$): δ 5.88 (d, J=1.9, 1H), 5.24 (d, J=1.9, 1H), 4.28 (d, J=5.7, 2H), 1.49 (q, J=7.7, 6H), 1.31 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 154.45, 122.50, 69.12, 29.10, 27.30, 13.59, 9.34.

1-(tri-n-butylstannane)-3-(N,N'-dimethylamino)-1-propene:
Method A crude product: *E*:*Z*:gem 47:40:13
after purification by flash column chromatography (2:1 hex:EtOAc): *E*:*Z*:gem 93:7:0

E: TLC (1:1 hex:EtOAc): R_f=0.12 ; ^{1}H NMR ($CDCl_3$): δ 6.09 (d, J=19.1, 1H), 5.99 (dt, J=19.1, 5.8, 1H), 2.97 (br d, J=5.7, 2H), 2.23 (s, 6H), 1.49 (quint, J=7.7, 6H), 1.29 (sex, J=7.3, 6H),

0.88 (t, J=7.2, 15H). ^{13}C NMR ($CDCl_3$): δ 145.94, 131.24, 66.41, 45.05, 29.04, 27.18, 13.62, 9.32.

Z: TLC (1:1 hex:EtOAc): R_f=0.30 ; ^1H NMR ($CDCl_3$): δ 6.55 (dt, J=12.6,6.3, 1H), 6.01 (dd, J=12.6,0.7 1H), 2.90 (br d, J=6.1, 2H), 2.23 (s, 6H), 1.55-1.45 (m, 6H), 1.31 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.4, 9H). ^{13}C NMR ($CDCl_3$): δ 146.16, 131.05, 64.96, 45.33, 29.17, 27.32, 13.68, 10.39.

2-(tri-n-butylstannane)-3-(N,N'-dimethylamino)-1-propene:

TLC (1:1 hex:EtOAc): R_f=0.30 ; ^1H NMR ($CDCl_3$): δ 5.77 (m, 1H), 5.18 (m, 1H), 2.95 (br s, 2H), 2.12 (s, 6H), 1.55-1.45 (m, 6H), 1.31 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.4, 9H).). ^{13}C NMR ($CDCl_3$): δ 155.92, 124.74, 69.96, 45.33, 29.17, 27.46, 13.68, 9.55.

1-(tri-n-butylstannane)-3-amino-1-propene:

Method A crude product: *E*:*Z*:gem 69:19:12

after purification by flash column chromatography (1:2 hex:EtOAc): *E*:*Z*:gem 99:1:0

E: TLC (1:2 hex:EtOAc): R_f=0.15 ; ^1H NMR ($CDCl_3$): δ 6.12 (dt, J=19.1,4.2, 1H), 6.05 (d, J=19.1, 1H), 3.34 (d, J=4.2, 2H), 1.48 (quint, J=7.7, 6H), 1.30 (sex, J=7.3, 6H), 1.24 (br s, 2H), 0.95-0.85 (m, 6H), 0.88 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 149.28, 125.23, 47.18, 28.61, 26.80, 13.18, 8.86.

Z: TLC (1:2 hex:EtOAc): R_f=0.28 ; ^1H NMR ($CDCl_3$): δ 6.58 (dt, J=12.6,6.3, 1H), 5.89 (d, J=12.6, 1H), 3.24 (dd, J=6.3,1.0, 2H), 1.55-1.45 (m, 6H), 1.30 (sex, J=7.3, 6H), 1.10 (br s, 2H), 0.95-0.85 (m, 6H), 0.88 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 148.93, 128.77, 47.34, 28.97, 27.08, 13.46, 10.35.

2-(tri-n-butylstannane)-3-amino-1-propene:

TLC (1:2 hex:EtOAc): R_f=0.28 ; ^1H NMR ($CDCl_3$): δ 5.80 (d, J=1.7, 1H), 5.17 (d, J=1.8, 1H), 3.45 (t, J=1.7, 2H), 1.55-1.45 (m, 6H), 1.31 (sex, J=7.4, 6H), 1.10 (br s, 2H), 0.95-0.85 (m, 6H), 0.90 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 156.68, 121.91, 50.76, 28.97, 27.16, 13.36, 9.30.

N-(t-butyloxycarbonyl)-3-amino-1-propyne:

^1H NMR ($CDCl_3$): δ 4.74 (br s, 1H), 3.91 (br s, 2H), 2.21 (dd, J=2.9,2.1, 1H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 155.15, 80.02, 79.51, 70.89, 29.99, 28.08.

N-(t-butyloxycarbonyl-1-(tri-n-butylstannane)-3-amino-1-propene:

Method A crude product: *E*:*Z*:gem 65:24:11

after purification by flash column chromatography (25:1 hex:EtOAc): *E*:*Z*:gem 98:0:2

E: TLC (10:1 hex:EtOAc): R_f=0.51; ^1H NMR ($CDCl_3$): δ 6.08 (dt, J=19.1,1.4, 1H), 5.95 (dt, J=19.1,4.7, 1H), 4.60 (br s, 1H), 3.79 (br s, 2H), 1.48 (quint, J=7.6, 6H), 1.45 (s, 9H), 1.30 (sex, J=7.3, 6H), 0.89 (t, J=7.2, 9H), 0.87 (dd, J=8.8,7.3, 6H). ^{13}C NMR ($CDCl_3$): δ 155.57, 144.21, 128.63, 78.91, 45.84, 28.92, 28.26, 27.15, 13.56, 9.26.

Z: TLC (10:1 hex:EtOAc): R_f=0.57; ^1H NMR ($CDCl_3$): δ 6.49 (dt, J=12.6,6.5, 1H), 6.02 (d, J=12.6, 1H), 4.45 (br s, 1H), 3.70 (br t, J=5.3, 2H), 1.55-1.45 (m, 6H), 1.45 (s, 9H), 1.30 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 155.41, 144.11, 132.18, 79.14, 45.81, 29.06, 28.31, 27.18, 13.59, 10.22.

N-(t-butyloxycarbonyl-2-(tri-n-butylstannane)-3-amino-1-propene:

TLC (10:1 hex:EtOAc): R_f=0.57; ^1H NMR ($CDCl_3$): δ 5.79 (q, J=1.9, 1H), 5.22 (q, J=1.9, 1H), 4.52 (br s, 1H), 3.89 (br d, J=5.7, 2H), 1.55-1.45 (m, 6H), 1.45 (s, 9H), 1.30 (sex, J=7.3, 6H), 0.95-0.85 (m, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 155.41, 151.54, 124.75, 79.14, 29.01, 28.31, 27.18, 13.59, 9.32.

methyl 3-(tri-n-butylstannane)-prop-2-en-1-oate:
Method A crude product: *E*:*Z*:gem 38:60:2
after purification by flash column chromatography (50:1 hex:EtOAc): *E*:*Z*:gem 92:6:2 and 1:99:0

E: TLC (10:1 hex:EtOAc): R_f=0.62; ^{1}H NMR ($CDCl_3$): δ 7.75 (d, J=19.5, 1H), 6.30 (d, J=19.5, 1H), 3.75 (s, 3H), 1.50 (quint, J=7.7, 2H), 1.30 (sex, J=7.5, 6H), 0.97 (dd, J=9.0,7.1, 6H), 0.89 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 164.97, 152.41, 135.82, 51.28, 28.85, 27.12, 13.50, 9.49.

Z: TLC (10:1 hex:EtOAc): R_f=0.80; ^{1}H NMR ($CDCl_3$): δ 7.16 (d, J=13.0, 1H), 6.73 (d, J=13.0, 1H), 3.75 (s, 3H), 1.49 (quint, J=7.7, 2H), 1.29 (sex, J=7.4, 6H), 0.97 (dd, J=8.0,8.0, 6H), 0.88 (t, J=7.2, 9H). ^{13}C NMR ($CDCl_3$): δ 167.92, 157.32, 134.85, 51.44, 29.13, 27.32, 13.68, 10.96.

3-(tri-n-butylstannane)-prop-2-en-1-oic acid:
Methyl 3-(tri-n-butylstannane)-prop-2-en-1-oate (1.21 g of a 57:36:7 *E*:*Z*:gem mixture) was dissolved in MeOH (10 ml) and THF (10mL) and treated with $LiOH.H_2O$ (0.271g, 6.46 mmol, 2.0 eq) in H_2O (15mL). After stirring for 48h the mixture was washed with hexane, then acidified with 1N HCl and extracted with EtOAc. The organic fraction was dried ($MgSO_4$) and evaporated to dryness to give 0.98g (84%) of a 66:34:0 *E*:*Z*:gem mixture. Purification by flash column chromatography (10:1 hex:EtOAc): *E*:*Z*:gem 99:1:0 and 4:96:0

E: TLC (5:1 hex:EtOAc): R_f=0.21; ^{1}H NMR ($CDCl_3$): δ 11.8 (v br s, 1H), 7.91 (d, J=19.5, 1H), 6.32 (d, J=19.5, 1H), 1.51 (quint, J=7.7, 2H), 1.31 (sex, J=7.3, 6H), 0.99 (t, J=8.1, 6H), 0.89 (t, J=7.3, 9H). ^{13}C NMR ($CDCl_3$): δ 169.97, 156.44, 135.75, 28.95, 27.24, 13.64, 9.67.

Z: TLC (5:1 hex:EtOAc): R_f=0.42; ^{1}H NMR ($CDCl_3$): δ 12.3 (v br s, 1H), 7.39 (d, J=12.8, 1H), 6.77 (d, J=12.8, 1H), 1.49 (quint, J=7.7, 2H), 1.29 (sex, J=7.2, 6H), 0.97 (dd, J=8.5,7.6, 6H), 0.88 (t, J=7.3, 9H). ^{13}C NMR ($CDCl_3$): δ 173.12, 161.90, 134.65, 29.14, 27.34, 13.74, 11.16.

Stille Solid Phase Reactions: Preparation of Precursors
The Wang resin components were prepared under identical conditions as the PEG compounds, except for the initial coupling of Fmoc-Aca. All coupling reactions gave a negative Kaiser test.

3-bromoprop-2-en-1-oic acid:
Propiolic acid (2.09g, 29.8 mmol) and 48% HBr (4mL, 37 mmol HBr, 1.4 eq) were heated at 140°C for 3 hr. The product, which solidified on cooling, was dissolved in $CHCl_3$, washed with saturated NaCl, dried ($MgSO_4$), and evaporated to dryness to give 4.13 g (92%) of pure product, (*E*:*Z* 73:27). Recrystallization ($CHCl_3$) gave 1.67 g (37%) of very pure *E* product (*E*:*Z* >99.5:<0.5).

E: ^{1}H NMR ($CDCl_3$): δ 11.0 (vbr s, 1H), 7.76 (d, J=14.1, 1H), 6.54 (d, J=14.1, 1H).

Z: ^{1}H NMR ($CDCl_3$): δ 11.0 (vbr s, 1H), 7.17 (d, J=8.5, 1H), 6.67 (d, J=8.5, 1H).

3-bromo-2-methylprop-2-en-1-oic acid:
E: ^{1}H NMR ($CDCl_3$): δ 11.8 (vbr s, 1H), 7.71 (q, J=1.3, 1H), 2.02 (d, J=1.6, 1H); ^{13}C NMR ($CDCl_3$): δ 170.76, 133.37, 125.85, 15.21.

***E*-bromoacrylamide-Gly-OPEG-OCH_3 (14, R_1 = H, Xaa_2-Xaa_1 = Gly):**
H_2N-Gly-OPEG-OCH_3 **13** (3.2g, 0.63 mmol) was dissolved in DMF (15 mL) and a solution of bromoacrylic acid (0.189g, 1.25 mmol, 2.0 eq) and diisopropylcarbodiimide (0.247mL, 1.58 mmol, 2.5 eq) in CH_2Cl_2 (5mL), preactivated for 10 min and filtered, was added. After reaction overnight the solution was poured into Et_2O and worked up as usual.

^{1}H NMR ($CDCl_3$): δ 7.48 (d, J=13.4, 1H), 6.76 (br s, 1H), 6.62 (d, J=13.4, 1H), 4.29 (t, J=4.8, 2H, PEG), 4.10 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG)

Fmoc-Aca-OH:

6-Aminocaproic acid (4.08g, 31.1 mmol) and Na_2CO_3 (3.63g, 34.2 mmol, 1.1 eq) were dissolved in H_2O (190mL) and added dropwise over 1h to a solution of Fmoc-OSucc (10.5g, 31.1 mmol, 1.0 eq) in 1,4-dioxane (150 mL) at 0°C. The solution was allowed to warm to rt, and after 4 h was washed with Et_2O (2x), then acidified with 2N HCl in the presence of EtOAc. The organic fraction was removed and the aqueous fraction extracted with EtOAc (2x). The organic fractions were combined, washed with saturated NaCl, dried ($MgSO_4$) and evaporated to give 10.7g (97%) of white solid. The product was recrystallized from EtOAc/hex.

^1H NMR ($CDCl_3$, 2 conformers, 75:25) major: δ 10.0 (vbr s, 1H), 7.76 (d, J=7.6, 2H), 7.59 (d, J=7.2, 2H), 7.40 (t, J=7.6, 2H), 7.31 (t, J=7.2, 2H), 4.78 (t, J=4.6, 1H), 4.40 (d, J=6.9, 2H), 4.21 (t, J=6.9, 1H), 3.20 (q, J=6.6, 2H), 2.36 (t, J=7.4, 2H), 1.66 (quint, J=7.6, 2H), 1.53 (quint, J=7.2, 2H), 1.37 (quint, J=7.6, 2H); minor: δ 10.0, (vbr s, 1H), 7.76 (d, J=7.6, 2H), 7.59 (d, J=7.2, 2H), 7.40 (t, J=7.6, 2H), 7.31 (t, J=7.2, 2H), 5.32 (br s, 1H), 4.46 (br m, 2H), 4.25 (br m, 1H), 3.06 (br m, 2H), 2.36 (t, J=7.4, 2H), 1.60 (br m, 2H), 1.35 (br m, 2H), 1.30 (br m, 2H).

^1H NMR (CD_3OD, 2 conformers, 85:15) major: δ 7.79 (d, J=7.2, 2H), 7.64 (d, J=7.2, 2H), 7.38 (t, J=7.4, 2H), 7.30 (t, J=7.4, 2H), 7.08 (br t, 1H), 4.34 (d, J=6.9, 2H), 4.19 (t, J=6.9, 1H), 3.10 (q, J=6.6, 2H), 2.29 (t, J=7.4, 2H), 1.61 (quint, J=7.5, 2H), 1.50 (quint, J=7.2, 2H), 1.35 (quint, J=7.6, 2H); minor: δ 7.79 (d, J=7.2, 2H), 7.64 (d, J=7.2, 2H), 7.38 (t, J=7.4, 2H), 7.30 (t, J=7.4, 2H), 6.46 (br s, 1H), 4.52 (br m, 2H), 4.22 (br m, 1H), 2.79 (br m, 2H), 2.24 (br m, 2H), 1.50 (br m, 2H),1. 25-1.05 (br m, 4H).

Fmoc-Aca-OPEG-OCH3 (12, Xaa1 = Aca):
Polyethylene glycol 5000 monomethyl ether (15.3g, 3.05 mmol) and DMAP (0.019g, 0.153 mmol, 0.05 eq) were dissolved in CH_2Cl_2 (50 mL) and a solution of Fmoc-Aca (2.16g, 6.10 mmol, 2.0 eq) and diisopropylcarbodiimide (0.955mL, 6.10 mmol, 2.0 eq) in CH_2Cl_2 (50mL), preactivated for 10 min and filtered, was added. After reaction overnight the solution was poured into Et_2O and worked up as usual.

^1H NMR ($CDCl_3$, 2 conformers, 80:20) major: δ 7.74 (d, J=7.6, 2H), 7.57 (d, J=7.3, 2H), 7.38 (t, J=7.4, 2H), 7.29 (t, J=7.4, 2H), 4.93 (t, J=5.5, 1H), 4.39 (d, J=6.9, 2H), 4.20 (m, 3H, PEG + CH), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.17 (q, J=6.7, 2H), 2.33 (t, J=7.4, 2H), 1.63 (quint, J=7.4, 2H), 1.50 (quint, J=7.2, 2H), 1.33 (quint, J=7.7, 2H); minor: δ_7.74 (d, J=7.6, 2H), 7.57 (d, J=7.3, 2H), 7.38 (t, J=7.4, 2H), 7.29 (t, J=7.4, 2H),4.59 (br s, 1H), 4.40 (br m, 2H), 4.20 (m, 3H, PEG + CH), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.05 (br m, 2H), 2.33 (br m, 2H), 1.58 (br m, 2H), 1.3-1.2 (br m, 4H).

Fmoc-Aca-OWang (12, Xaa1 = Aca):
Wang resin (Advanced Chemtech, 100-200 mesh, 0.85 mmol/g, 1.12g, 0.98 mmol), Fmoc-Aca (0.83g, 2.4 mmol, 2.4 eq) and PPh_3 (0.62, 2.4 mmol, 2.4 eq) in DMF (20mL) at 0°C were treated with diisopropylazodicarboxylate (0.465mL, 2.4 mmol, 2.4 eq). After reaction overnight the solvent was removed and the resin rinsed with DMF (3x) and CH_2Cl_2 (3x), then dried.

H_2N-Aca-OPEG-OCH3:
Fmoc-Aca-OPEG-OCH_3 **12** was deprotected as described earlier.

^1H NMR ($CDCl_3$): δ 4.21 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 2.77 (t, J=6.9, 2H), 2.33 (t, J=7.2, 2H), 1.64 (quint, J=7.4, 2H), 1.55 (quint, J=7.2, 2H), 1.36 (quint, J=7.4, 2H).

Fmoc-Ala-Aca-OPEG-OCH3 (Xaa2-Xaa1 = Ala-Aca):
H_2N-Gly-OPEG-OCH_3 (20.1 g, 3.97 mmol) was coupled with Fmoc-Ala using PyBOP/HOBt/DIPEA as described earlier.

^1H NMR ($CDCl_3$): δ 7.74 (d, J=7.6, 2H), 7.57 (d, J=7.6, 2H), 7.38 (t, J=7.4, 2H), 7.29 (t, J=7.4, 2H), 6.15 (br s, 1H), 5.46 (br d, J=7.3, 1H), 4.39 (d, J=6.9, 2H), 4.19 (m, 3H, PEG + CH), 4.15

(m, 1H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.23 (br q, J=6.0, 2H), 2.31 (t, J=7.4, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.2, 2H), 1.36 (d, J=6.5, 3H), 1.32 (br quint, J=7.7, 2H).

Fmoc-Arg(Pbf)-Aca-OPEG-OCH3 (Xaa2-Xaa1 = Arg(Pbf)-Aca):
H_2N-Gly-OPEG-OCH_3 (20.1 g, 3.97 mmol) was coupled with Fmoc-Arg(Pbf) using PyBOP/HOBt/DIPEA as described earlier.

^1H NMR ($CDCl_3$): δ 7.74 (d, J=7.6, 2H), 7.58 (d, J=7.2, 2H), 7.37 (t, J=7.4, 2H), 7.28 (t, J=7.2, 2H), 7.30 (br s, 1H), 6.78 (br s, 2H), 5.85 (br s, 1H), 5.80 (d, J=8.4, 1H), 4.35 (d, J=6.9, 2H), 4.40-4.30 (m, 1H), 4.25-5.15 (m, 1H), 4.19 (t, J=5.1, 3H, PEG) 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.35-3.30 (br m, 1H), 3.19 (m, 2H), 3.15-3.05 (br m, 1H), 2.92 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.33 (t, J=7.2, 2H), 2.07 (s, 3H), 1.80 (br m, 1H), 1.65-1.40 (m, 3H), 1.63 (br quint, J=7.4, 2H), 1.55 (br quint, J=7.1, 2H), 1.42 (s, 6H), 1.35 (br quint, J=7.8, 2H).

H_2N-Ala-Aca-OPEG-OCH_3 (13, Xaa2-Xaa1 = Ala-Aca):
Fmoc-Ala-Aca-OPEG-OCH_3 was deprotected as described earlier.

^1H NMR ($CDCl_3$): δ 7.40 (br s, 1H), 4.20 (m, 3H, PEG + CH), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (br q, J=6.7, 2H), 2.32 (t, J=7.2, 2H), 1.63 (br quint, J=7.3, 2H), 1.52 (br quint, J=7.3, 2H), 1.35 (d, J=6.9, 3H), 1.35 (br quint, J=7.6, 2H).

H_2N-Arg(Pbf)-Aca-OPEG-OCH_3 (13, Xaa2-Xaa1 = Arg(Pbf)-Aca):
Fmoc-Arg(Pbf)-Aca-OPEG-OCH_3 was deprotected as described earlier.

^1H NMR ($CDCl_3$): δ 7.50 (br s, 1H), 6.26 (br s, 2H), 6.20 (br s, 1H), 4.20 (m, 3H, PEG + CH), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.30 (m, 1H), 3.22 (q, J=6.9, 2H), 3.15 (m, 1H), 2.94 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.32 (t, J=7.2, 2H), 2.07 (s, 3H), 1.80 (br m, 1H), 1.65-1.50 (m, 3H), 1.63 (br quint, J=7.4, 2H), 1.52 (br quint, J=7.3, 2H), 1.44 (s, 6H), 1.34 (br quint, J=7.6, 2H).

3-bromo-prop-2*E*-en-1-amide-Arg(Pbf)-Aca-OPEG-OCH_3 (14, R^1 = H, Xaa2-Xaa1 = Ala-Aca):
H_2N-Arg(Pbf)-Aca-OPEG-OCH_3 **13** was coupled with 3-bromoprop-2-en-1-oic acid using DIC as described earlier.

^1H NMR ($CDCl_3$): δ 7.42 (d, J=13.4, 1H), 7.34 (br s, 1H), 6.93 (d, J=6.9, 1H), 6.60 (d, J=13.4, 1H), 6.30 (br s, 2H), 5.95 (br s, 1H), 4.62 (br s, 1H), 4.19 (t, J=4.6, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.1 (m, 4H), 2.94 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.32 (t, J=7.2, 2H), 2.08 (s, 3H), 1.9-1.8 (br m, 1H), 1.65-1.45 (m, 3H), 1.62 (br quint, J=7.2, 2H), 1.53 (br quint, J=7.4, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.3, 2H).

Stille Coupling Products on PEG resin (see Table 3 for reaction conditions and product purity)

penta-2*E*,4-diene-1-amide-Gly-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = R^4 = H, Xaa2-Xaa1 = Gly):

^1H NMR ($CDCl_3$): δ 7.21 (dd, J=15.3,11.1 1H), 6.42 (dt, J=17.2, 10.5), 6.38 (br s, 1H), 5.96 (d, J=14.9, 1H), 5.55 (d, J=16.8, 1H), 5.42 (d, J=10.3, 1H), 4.29 (t, J=4.8, 2H, PEG), 4.14 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

penta-2*E*,4-diene-1-amide-Ala-Aca-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = R^4 = H, Xaa2-Xaa1 = Ala-Aca):

^1H NMR ($CDCl_3$): δ 7.18 (dd, J=15.3, 11.1, 1H), 6.45-6.35 (m, 3H), 5.91 (d, J=14.9, 1H), 5.55 (d, J=17.2, 1H), 5.41 (d, J=10.3, 1H), 4.50 (quint, J=7.1, 1H), 4.20 (t, J=4.8, 2H, PEG), 3.8-3.45

(m, PEG), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.4, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.37 (d, J=6.9, 3H), 1.33 (br quint, J=7.5, 2H).

penta-2*E*,4-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.14 (dd, J=15.1,11.2, 1H), 6.79 (d, J=8.0, 1H), 6.37 (dt, J=16.8, 10.4, 1H), 6.30 (br s, 2H), 5.99 (br s, 1H), 5.95 (d, J=15.3, 1H), 5.52 (d, J=17.2, 1H), 5.40 (d, J=9.9, 1H), 4.63 (br m, 1H), 4.19 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.26 (m, 2H), 3.19 (m, 2H), 2.94 (s, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 2.31 (t, J=7.2, 2H), 2.07 (s, 3H), 1.85 (br m, 1H), 1.7-1.4 (m, 3H), 1.61 (br quint, J=7.4, 2H), 1.53 (br quint, J=7.2, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.4, 2H).

2-methylpenta-2*E*,4-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = Me, R^2 = R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 6.87 (d, J=11.1, 1H), 6.60 (dt, J=16.4,10.7, 1H), 6.47 (d, J=6.9, 1H), 6.34 (t, J=4.8, 1H), 5.50 (d, J=16.8, 1H), 5.39 (d, J=10.3, 1H) 4.48 (quint, J=6.9, 1H), 4.20 (t, J=4.4, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.23 (q, J=6.5, 2H), 2.31 (t, J=7.2, 2H), 1.95 (s, 3H), 1.61 (br quint, J=7.3, 2H), 1.50 (br quint, J=7.3, 2H), 1.38 (d, J=6.9, 3H), 1.32 (br quint, J=7.6, 2H).

5-phenyl-penta-2*E*,4*E*-diene-1-amide-Gly-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Gly):

^{1}H NMR ($CDCl_3$): δ 7.44 (d, J=7.3, 2H), 7.33 (t, J=7.4, 2H), 7.45-7.25 (m, 2H), 6.85 (m, 2H), 6.47 (t, J=5.1, 1H), 6.06 (d, J=14.9, 1H), 4.30 (dd, J=5.5,4.0, 2H, PEG), 4.16 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

5-phenyl-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$):_ δ 7.43 (d, J=7.6, 2H), 7.37 (ddd, J=14.9, 7.4, 3.0, 1H), 7.33 (t, J=7.6, 2H), 7.28 (d, J=7.2, 1H), 6.85 (s, 1H), 6.84 (d, J=3.5, 1H), 6.44 (t, J=5.5, 1H), 6.39 (d, J=7.6), 6.00 (d, J=14.9, 1H), 4.52 (quint, J=7.1, 1H), 4.19 (t, J=4.8, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.4, 2H), 1.62 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.2, 2H), 1.39 (d, J=7.2, 3H), 1.33 (br quint, J=7.2, 2H).

5-phenyl-penta-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.42 (d, J=7.6), 7.35-7.25 (m, 1H), 7.32 (t, J=7.6, 2H), 7.27 (d, J=7.0, 1H), 6.84 (d, J=8.0), 6.81 (m, 2H), 6.31 (br s, 3H), 6.03 (d, J=14.9, 1H), 6.00 (br s, 1H), 4.64 (m, 1H), 4.18 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.15 (m, 4H), 2.93 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.31 (t, J=7.2, 2H), 2.08 (s, 3H), 1.9-1.8 (br m, 1H), 1.7-1.4 (m, 3H), 1.61 (br quint, J=7.5, 2H), 1.53 (br quint, J=7.4, 2H), 1.432 (s, 3H), 1.426 (s, 3H), 1.33 (br quint, J=7.5, 2H).

6,6-dimethyl-hepta-2*E*,4*E*-diene-1-amide-Gly-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = tBu, Xaa$_2$-Xaa$_1$ = Gly):

^{1}H NMR ($CDCl_3$):

EE δ 7.19 (dd, J=15.4,8.4, 1H), 6.24 (t, J=5.2, 1H), 6.06 (m, 2H), 5.85 (d, J=14.9, 1H), 4.29 (t, J=4.6, 2H, PEG), 4.13 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

EZ δ 8.29 (dd, J=15.6,11.4, 1H), 6.59 (t, J=5.0, 1H), 6.48 (t, J=11.2, 1H), 6.13 (d, J=15.6, 1H), 5.97 (d, J=11.1, 1H), 4.29 (t, J=4.6, 2H, PEG), 4.13 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

ZE δ 7.42 (dd, J=15.4,11.4, 1H), 6.71 (t, J=5.3, 1H), 6.41 (t, J=5.0, 1H), 5.55 (d, J=11.1, 1H), 4.29 (t, J=4.6, 2H, PEG), 4.13 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG).

6,6-dimethyl-hepta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = tBu, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.17 (dd, J=14.9,9.5, 1H), 6.42 (br t, J=5.1, 1H), 6.22 (d, J=7.6, 1H), 6.07 (m, 2H), 5.79 (d, J=14.9, 1H), 4.49 (quint, J=7.2, 1H), 4.20 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.21 (br quint, J=6.6, 2H), 2.31 (br t, J=7.4, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.2, 2H), 1.36 (d, J=6.9, 3H), 1.32 (br quint, J=7.2, 2H), 1.04 (s, 9H).

6,6-dimethyl-hepta-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = tBu, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.13 (dd, J=14.9,9.5), 6.63 (br d, J=8.0, 1H), 6.36 (br s, 1H), 6.28 (br s, 2H), 6.04 (m, 2H), 5.84 (d, J=15.3, 1H), 4.61 (br m, 1H), 4.19 (br m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.1 (m, 4H), 2.94 (s, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 2.31 (br t, J=7.4, 2H), 2.07 (s, 3H), 1.84 (br m, 1H), 1.65-1.4 (m, 3H), 1.61 (br quint, J=7.3, 2H), 1.52 (br quint, J=7.1, 2H), 1.44 (s, 6H), 1.32 (br quint, J=7.0, 2H), 1.03 (s, 9H).

trideca-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = (CH$_2$)$_7$CH$_3$, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.17 (dd, J=15.1,10.2, 1H), 6.40 (t, J=5.7, 1H), 6.22 (d, J=7.2, 1H), 6.12 (dd, J=15.1,9.7, 1H), 6.06 (dt, J=15.3,6.9, 1H), 4.49 (quint, J=7.2, 1H), 4.20 (dd, J=5.3,4.2, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.21 (q, J=6.6, 2H), 2.31 (t, J=7.4, 2H), 2.13 (q, J=7.4, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.45-1.2 (m, 14H), 1.36 (d, J=6.9, 3H), 0.86 (t, J=7.1, 3H).

trideca-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = (CH$_2$)$_7$CH$_3$, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.3o (br s, 1H), 7.12 (dd, J=15.1,9.7, 1H), 6.66 (d, J=8.0, 1H), 6.29 (br s, 2H), 6.1-5.9 (m, 3H), 5.80 (d, J=14.9, 1H), 4.61 (br m, 1H), 4.19 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.15 (m, 4H), 2.94 (s, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 2.31 (t, J=7.4, 2H), 2.12 (q, J=7.4, 2H), 2.08 (s, 3H), 1.84 (br m, 1H), 1.65-1.2 (m, 17H), 1.61 (br quint, J=7.4, 2H), 1.53 (br quint, J=7.2, 2H), 1.44 (s, 6H), 0.86 (t, J=6.9, 3H).

3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.42 (s, 1H), 7.36 (d, J=15.6, 1H), 6.54(d, J=3.1, 1H), 6.50-6.40 (m, 3H), 4.53 (quint, J=7.0, 1H), 4.19 (t, J=4.6, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.30 (t, J=7.4, 2H), 1.61 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.2, 2H), 1.39 (d, J=6.9, 3H), 1.32 (br quint, J=7.5, 2H).

3-(2'-furan)-prop-2*E*ene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.42 (s, 1H), 7.33 (d, J=15.6, 1H), 7.30 (br s, 1H), 6.83 (d, J=8.0, 1H), 6.51 (d, J=3.0, 1H), 6.42 (t, J=2.5, 1H), 6.39 (d, J=15.3, 1H), 6.28 (br s, 2H), 6.00 (br s, 1H), 4.66 (br m, 1H), 4.19 (br s, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.30-3.15 (m, 4H), 2.93 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.31 (t, J=7.2, 2H), 2.07 (s, 3H), 1.86 (br m, 1H), 1.7-1.4 (m, 3H), 1.61 (br quint, J=7.4, 2H), 1.53 (br quint, J=6.9, 2H), 1.43 (s, 6H), 1.33 (br quint, J=7.4, 2H).

3-(2'-thiophene)-prop-2*E*ene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = H, R^2 = R^4 = -SCH=CH-, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.71 (d, J=15.6, 1H), 7.30 (d, J=5.0, 1H), 7.20 (d, J=3.0, 1H), 7.02 (t, J=4.4, 1H), 6.55-6.45 (m, 2H), 6.27 (d, J=15.3, 1H), 4.54 (quint, J=7.1, 1H), 4.19 (br t, J=4.6, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.23 (m, 2H), 2.31 (t, J=7.4, 2H), 1.62 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.2, 2H), 1.39 (d, J=6.9, 3H), 1.33 (br quint, J=7.6, 2H).

3-(2'-thiophene)-prop-2*E*ene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = H, R^3 = R^4 = -SCH=CH-, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.67 (d, J=15.3, 1H), 7.30 (d, J=5.0, 1H), 7.30 (br s, 1H), 7.17 (d, J=3.4, 1H), 7.01 (t, J=4.2, 1H), 6.83 (d, J=8.0, 1H), 6.34 (d, J=15.3, 1H), 6.28 (br s, 2H), 5.99 (br s, 1H), 4.67 (br m, 1H), 4.19 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.30-3.15 (m, 4H), 2.93 (s, 2H), 2.62 (s, 3H), 2.54 (s, 3H), 2.32 (t, J=7.4, 2H), 2.08 (s, 3H), 1.87 (br m, 1H), 1.7-1.4 (m, 3H), 1.62 (br quint, J=7.5, 2H), 1.54 (br quint, J=7.2, 2H), 1.44 (s, 6H), 1.34 (br quint, J=7.5, 2H).

6-hydroxy-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CH$_2$OH, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.21 (dd, J=15.3,11.1, 1H), 6.49 (t, J=5.3, 1H), 6.43 (d, J=7.6, 1H), 6.38 (dd, J=15.3,11.1, 1H), 6.18 (dt, J=14.9,4.8, 1H), 5.90 (d, J=14.9, 1H), 4.50 (quint, J=7.1, 1H), 4.20 (t, J=4.6, 2H, PEG), 4.25 (t, J=4.8, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.24 (dt, J=13.4,6.6, 1H), 3.19 (dt, J=13.0,6.4, 1H), 2.30 (t, J=7.2, 2H), 2.23 (t, J=5.7, 1H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.37 (d, J=6.9, 3H), 1.31 (br quint, J=7.6, 2H).

6-hydroxy-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CH$_2$OH, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.17 (dd, J=14.9,11.1, 1H), 6.87 (br m, 3H), 6.86 (d, J=7.6, 1H), 6.15 (dt, J=15.3,4.8, 1H),6.00 (br s, 1H), 5.91 (d, J=15.3, 1H), 4.62 (br m, 1H), 4.19 (m, 2H, PEG), 4.24 (br m, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.15 (m, 4H), 2.94 (s, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 2.31 (t, J=7.4, 2H), 2.08 (s, 3H), 1.85 (br m, 1H), 1.7-1.45 (m, 3H), 1.61 (br quint, J=7.5, 2H), 1.53 (br quint, J=7.0, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.2vn, 2H).

6-hydroxy-hexa-2*E*,4*Z*diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^4 = H, R^3 = CH$_2$OH, Xaa$_2$-Xaa$_1$ = Ala-Aca):
mixture 80:20 Z:gem:

^{1}H NMR ($CDCl_3$): δ 7.50 (dd, J=14.7,12.0, 1H), 6.48 (m, 2H), 6.15 (t, J=11.4, 1H), 5.93 (dt, J=10.7,6.6, 1H), 5.92 (d, J=14.9, 1H), 4.50 (quint, J=7.2, 1H), 4.41 (m, 2H), 4.20 (t, J=4.8, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.15 (m, 2H), 2.31 (t, J=7.4, 2H), 2.23 (t, J=5.3, 1H), 1.61 (br quint, J=7.4, 2H), 1.49 (br quint, J=7.2, 2H), 1.37 (d, J=6.9, 3H), 1.31 (br quint, J=7.6, 2H).

4-hydroxymethyl-penta-2*E*,4-diene-1-amide-Ala-Aca-OPEG-OCH$_3$:

^{1}H NMR ($CDCl_3$): δ 6.08 (d, J=15.6, 1H), 5.56 (s, 1H), 5.45 (s, 1H), 4.30 (d, J=5.3, 1H).

6-methoxy-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CH$_2$OCH$_3$, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.20 (dd, J=15.3,11.1, 1H), 6.45-6.30 (m, 3H), 6.09 (dt, J=15.3,5.3, 1H), 5.88 (d, J=14.9, 1H), 4.49 (quint, J=7.1, 1H), 4.20 (t, J=4.8, 2H, PEG), 4.01 (d, J=5.0, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (q, J=7.1, 2H), 2.31 (t, J=7.4, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.37 (d, J=6.9, 3H), 1.32 (br quint, J=7.6, 2H).

6-methoxy-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = H, R^4 = CH_2OCH_3, Xaa_2-Xaa_1 = Arg(Pbf)-Aca):

^1H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.16 (dd, J=14.9,11.1, 1H), 6.71 (d, J=7.6, 1H), 6.35-6.25 (br m, 3H), 6.06 (dt, J=15.6,5.4, 1H), 5.98 (br s, 1H), 5.92 (d, J=14.9, 1H), 4.63 (br m, 1H), 4.19 (m, 2H, PEG), 4.01 (d, J=5.3, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.35-3.15 (m, 4H), 2.94 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.32 (t, J=7.2, 2H), 2.08 (s, 3H), 1.84 (br m, 1H), 1.65-1.45 (m, 3H), 1.62 (br quint, J=7.3, 2H), 1.54 (br quint, J=7.5, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.6, 2H).

6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = H, R^4 = CH_2NH_2, Xaa_2-Xaa_1 = Ala-Aca):

^1H NMR ($CDCl_3$): δ 7.21 (dd, J=15.1,10.9, 1H), 6.39 (t, J=4.8, 1H), 6.30 (d, J=6.9, 1H), 6.27 (dd, J=15.3,11.1, 1H), 6.16 (dt, J=15.3,5.5, 1H), 5.85 (d, J=14.9, 1H), 4.50 (quint, J=7.1, 1H), 4.20 (t, J=4.6, 2H, PEG), 3.8-3.45 (m, PEG + 2H), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.2, 2H), 1.61 (br quint, J=7.3, 2H), 1.50 (br quint, J=7.2, 2H), 1.37 (d, J=6.9, 3H), 1.32 (br quint, J=7.3, 2H).

6-amino-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = H, R^4 = CH_2NH_2, Xaa_2-Xaa_1 = Arg(Pbf)-Aca):

^1H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.17 (dd, J=14.7,10.9, 1H), 6.76 (d, J=6.5, 1H), 6.30 (br s, 2H), 6.23 (dd, J=14.1,11.8, 1H), 6.13 (dt, J=15.3,4.9, 1H), 6.06 (br s, 1H), 5.89 (d, J=15.1, 1H), 4.62 (br m, 1H), 4.19 (br m, 2H, PEG), 3.8-3.45 (m, PEG + 2H), 3.36 (s, 3H, PEG), 3.35-3.1 (br m, 4H), 2.94 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.32 (t, J=7.4, 2H), 2.08 (s, 3H), 1.84 (br m, 1H), 1.7-1.4 (m, 3H), 1.62 (br quint, J=7.2, 2H), 1.53 (br quint, J=6.8, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.0, 2H).

N-(t-butyloxycarbonyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH_3 (17, R^1 = R^2 = R^3 = H, R^4 = CH_2NHBoc, Xaa_2-Xaa_1 = Ala-Aca):

^1H NMR ($CDCl_3$): δ 7.18 (dd, J=14.9,11.1, 1H), 6.39 (br t, J=5.5, 1H), 6.32 (d, J=7.2, 1H), 6.24 (dd, J=15.3,11.1, 1H), 6.02 (dt, J=15.3,5.7, 1H), 5.86 (d, J=15.3, 1H), 4.49 (quint, J=7.2, 1H), 4.75 (br s, 1H), 4.20 (t, J=4.8, 2H, PEG), 3.84 (br m, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.4, 2H), 1.61 (br quint, J=7.4, 2H), 1.49 (br quint, J=7.3, 2H), 1.43 (s, 9H), 1.37 (d, J=6.9, 3H), 1.32 (br quint, J=7.6, 2H).

N-(t-butyloxycarbonyl)-6-aminohexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH_3, (17, R^1 = R^2 = R^3 = H, R^4 = CH_2NHBoc, Xaa_2-Xaa_1 = Arg(Pbf)-Aca):

^1H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.13 (dd, J=14.9,11.1, 1H), 6.74 (d, J=8.0, 1H), 6.28 (br s, 2H), 6.19 (dd, J=15.1,11.2, 1H), 6.00 (br s, 1H), 5.99 (dt, J=14.9,5.7, 1H), 5.89 (d, J=14.9, 1H), 4.78 (br s, 1H), 4.62 (br m, 1H), 4.19 (m, 2H, PEG), 3.83 (br m, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.1 (m, 4H), 2.93 (s, 2H), 2.60 (s, 3H), 2.52 (s, 3H), 2.31 (t, J=7.4, 2H), 2.08 (s, 3H), 1.84 (br m, 1H), 1.7-1.45 (m, 3H), 1.61 (br quint, J=7.4, 2H), 1.53 (br quint, J=7.3, 2H), 1.44 (s, 6H), 1.43 (s, 9H), 1.33 (br quint, J=7.5, 2H).

N-(t-butyloxycarbonyl)-6-amino-2-methylhexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH_3 (17, R^1 = Me, R^2 = R^3 = H, R^4 = CH_2NHBoc, Xaa_2-Xaa_1 = Ala-Aca):

^1H NMR ($CDCl_3$): δ 6.89 (d, J=10.7, 1H), 6.43 (br s, 1H), 6.40 (dd, J=13.9,11.2, 1H), 6.32 (br s, 1H), 5.96 (dt, J=15.3,5.9, 1H), 4.48 (quint, J=7.0, 1H), 4.73 (br s, 1H), 4.20 (t, J=4.6, 2H, PEG), 3.84 (br s, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.23 (q, J=6.5, 2H), 2.31 (t, J=7.2, 2H), 1.94 (s, 3H), 1.61 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.3, 2H), 1.44 (s, 9H), 1.38 (d, J=6.9, 3H), 1.32 (br quint, J=7.6, 2H).

(N,N'dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.20 (dd, J=15.3,11.1, 1H), 6.39 (br t, J=5.3, 1H), 6.31 (d, J=7.6, 1H), 6.25 (dd, J=15.1,10.9, 1H), 6.07 (dt, J=15.3,6.5, 1H), 5.84 (d, J=14.9, 1H), 4.49 (quint, J=7.2, 1H), 4.20 (t, J=4.8, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.21 (q, J=6.6, 2H), 2.99 (d, J=6.5, 2H), 2.21 (s, 6H), 2.31 (t, J=7.2, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.36 (d, J=6.9, 3H), 1.31 (br quint, J=7.6, 2H).

(N,N'dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 7.16 (dd, J=15.2,10.9, 1H), 6.70 (d, J=8.0, 1H), 6.29 (br s, 2H), 6.23 (dd, J=15.3,10.7, 1H), 6.05 (dt, J=15.3,7.0, 1H), 6.00 (br s, 1H), 5.89 (d, J=15.3, 1H), 4.63 (br m, 1H), 4.19 (m, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.1 (m, 4H), 2.99 (d, J=6.5, 2H), 2.94 (s, 2H), 2.60 (s, 3H), 2.53 (s, 3H), 2.31 (t, J=7.4, 2H), 2.21 (s, 6H), 2.07 (s, 3H), 1.84 (br m, 1H), 1.65-1.45 (m, 3H), 1.61 (br quint, J=7.4, 2H), 1.53 (br quint, J=7.3, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.6, 2H).

5-carboxy-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CO$_2$H, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.35-7.20 (m, 2H), 6.92 (br s, 1H), 6.52 (br s, 1H), 6.27 (br d, J=14.1, 1H), 6.17 (br d, J=14.1, 1H), 4.51 (quint, J=7.2, 1H), 4.20 (t, J=4.6, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.3-3.15 (m, 2H), 2.31 (t, J=7.2, 2H), 1.61 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.2, 2H), 1.38 (d, J=6.9, 3H), 1.33 (br quint, J=7.6, 2H).

5-carboxy-penta-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CO$_2$H, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.45 (br s, 1H), 7.4-7.15 (m, 2H), 6.35 (br d, J=14.1, 1H), 6.34 (br s, 3H), 6.15 (br d, J=13.7, 1H), 6.02 (vbr s, 1H), 4.70 (br s, 1H), 4.19 (br s, 2H, PEG), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.35-3.1 (m, 4H), 2.94 (s, 2H), 2.62 (s, 3H), 2.53 (s, 3H), 2.32 (t, J=7.2, 2H), 2.08 (s, 3H), 1.85 (br s, 1H), 1.7-1.45 (m, 3H), 1.61 (br quint, J=7.5, 2H), 1.53 (br s, 2H), 1.44 (s, 6H), 1.33 (br m, 2H).

5-carboxymethyl-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CO$_2$CH$_3$, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 7.35-7.20 (m, 2H), 6.66 (d, J=7.2, 1H), 6.36 (t, J=5.5, 1H), 6.23 (d, J=14.1, 1H), 6.16 (d, J=14.5, 1H), 4.49 (quint, J=7.1, 1H), 4.20 (t, J=4.8, 2H, PEG), 3.8-3.45 (m, PEG + 3H), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.2, 2H), 1.61 (br quint, J=7.4, 2H), 1.50 (br quint, J=7.3, 2H), 1.38 (d, J=7.2, 3H), 1.32 (br quint, J=7.6, 2H).

5-carboxymethyl-penta-2*E*,4*Z*diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^4 = H, R^3 = CO$_2$CH$_3$, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 8.24 (dd, J=15.1,11.6, 1H), 6.61 (t, J=11.4, 1H), 6.55 (d, J=7.2, 1H), 6.39 (t, J=4.2, 1H), 6.14 (d, J=15.3, 1H), 5.91 (d, J=11.1, 1H), 4.51 (quint, J=7.2, 1H), 4.20 (m, 2H, PEG), 3.8-3.45 (m, PEG + 3H), 3.36 (s, 3H, PEG), 3.3-3.2 (m, 2H), 2.31 (t, J=7.2, 2H), 1.62 (br quint, J=7.2, 2H), 1.50 (br quint, J=6.9, 2H), 1.38 (d, J=6.9, 3H), 1.32 (m, 2H).

5-carboxymethyl-penta-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^2 = R^3 = H, R^4 = CO$_2$CH$_3$, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.37 (br s, 1H), 7.35-7.15 (m, 2H), 6.93 (d, J=7.6, 1H), 6.28 (br s, 2H), 6.28 (d, J=15.3, 1H), 6.13 (d, J=14.1, 1H), 5.94 (br s, 1H), 4.68 (br s, 1H), 4.19 (br s, 2H, PEG), 3.8-3.45 (m, PEG + 3H), 3.36 (s, 3H, PEG), 3.35-3.1 (m, 4H), 2.94 (s, 2H), 2.61 (s, 3H), 2.53

(s, 3H), 2.32 (t, J=7.1, 2H), 2.08 (s, 3H), 1.86 (br m, 1H), 1.7-1.4 (m, 3H), 1.62 (br quint, J=7.5, 2H), 1.54 (br quint, J=6.8, 2H), 1.44 (s, 6H), 1.33 (br quint, J=7.4, 2H).

4-ethoxy-penta-2*E*,4*E*-diene-1-amide-Gly-OPEG-OCH$_3$ (17, R^1 = R^3 = R^4 = H, R^2 = OEt, Xaa$_2$-Xaa$_1$ = Gly):

^{1}H NMR ($CDCl_3$): δ 7.00 (d, J=15.3, 1H), 6.33 (t, J=5.0, 1H), 6.28 (d, J=15.3, 1H), 4.40 (m, 2H), 4.29 (t, J=4.8, 2H, PEG), 4.14 (d, J=5.3, 2H), 3.81 (q, J=7.0, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 1.34 (t, J=6.9, 3H).

4-ethoxypenta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = R^4 = H, R^2 = OEt, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 6.97 (d, J=15.3, 1H), 6.40 (t, J=5.0, 1H), 6.35 (d, J=7.6, 1H), 6.25 (d, J=14.9, 1H), 4.50 (quint, J=7.2, 1H), 4.40 (s, 2H), 4.20 (t, J=4.6, 2H, PEG), 3.81 (q, J=7.0, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.22 (m, 2H), 2.31 (t, J=7.2, 2H), 1.61 (br quint, J=7.5, 2H), 1.49 (br quint, J=7.3, 2H), 1.37 (d, J=6.9, 3H), 1.35-1.28 (m, 2H), 1.34 (t, J=6.9, 3H).

4-ethoxypenta-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OPEG-OCH$_3$ (17, R^1 = R^3 = R^4 = H, R^2 = OEt, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca):

^{1}H NMR ($CDCl_3$): δ 7.30 (br s, 1H), 6.93 (d, J=15.2, 1H), 6.68 (br d, J=7.6, 1H), 6.31 (d, J=14.8, 1H), 6.26 (br s, 2H), 4.98 (br s, 1H), 4.65 (br m, 1H), 4.38 (s, 2H), 4.19 (m, 2H, PEG), 3.80 (q, J=7.0, 2H), 3.8-3.45 (m, PEG), 3.36 (s, 3H, PEG), 3.26 (m, 2H), 3.19 (m, 2H), 2.94 (s, 2H), 2.61 (s, 3H), 2.53 (s, 3H), 2.32 (t, J=7.4, 2H), 2.07 (s, 3H), 1.84 (br m, 1H), 1.7-1.4 (m, 3H), 1.61 (br quint, J=7.3, 2H), 1.53 (br quint, J=7.0, 2H), 1.44 (s, 6H), 1.4-1.3 (m, 2H), 1.33 (t, J=6.9, 3H).

4-ethoxy-2-methyl-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH$_3$ (17, R^1 = Me, R^2 = OEt, R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Ala-Aca):

^{1}H NMR ($CDCl_3$): δ 6.63 (s, 1H), 6.45 (d, J=7.2, 1H), 6.31 (t, J=5.0, 1H), 4.46 (quint, J=7.1, 1H), 4.34 (s, 1H), 4.30 (d, J=1.5, 1H), 4.20 (t, J=4.8, 2H, PEG), 3.8-3.45 (m, PEG + 2H), 3.36 (s, 3H, PEG), 3.23 (q, J=6.7, 2H), 2.31 (t, J=7.2, 2H), 2.15 (s, 3H), 1.62 (br quint, J=7.5, 2H), 1.50 (br quint, J=7.2, 2H), 1.38 (d, J=6.9, 3H), 1.35-1.25 (m, 2H), 1.34 (t, J=6.9, 3H).

CLEAVED DIENES- from PEG

penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):

O.203 g (0.0385 mmol) of resin **17** was treated 2 eq of DBU in $MeOH/CH_2Cl_2$ according to the standard conditions, giving 0.0072g (63%) of product after column purification (2:1 EtOAc:hex).

TLC (2:1 EtOAc:hex): R_f=0.19; ^{1}H NMR ($CDCl_3$): δ 7.19 (dd, J=14.9, 11.1, 1H), 6.51 (br s, 1H), 6.42 (dt, J=16.8,10.5, 1H), 6.40 (d, J=6.5, 1H), 5.92 (d, J=15.3, 1H), 5.57 (d, J=17.2, 1H), 5.45 (d, J=10.3, 1H), 4.56 (quint, J=7.1, 1H), 3.66 (s, 3H), 3.24 (m, 2H), 2.30 (t, J=7.4, 2H), 1.62 (br quint, J=7.5, 2H), 1.52 (br quint, J=7.4, 2H), 1.40 (d, J=6.9, 3H), 1.33 (br quint, J=7.7, 2H); MS (ES^+): 297 (MH^+, 100), 146 (MH^+-151, 4).

3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):

O.199 g (0.0373 mmol) of resin **17** was treated 2 eq of DBU in $MeOH/CH_2Cl_2$ according to the standard conditions, giving 0.0100g (79%) of product after column purification (2:1 EtOAc:hex).

TLC (2:1 EtOAc:hex): R_f=0.27; ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J=1.9, 1H), 7.39 (d, J=15.3, 1H), 6.55 (d, J=3.4, 1H), 6.52 (t, J=5.5, 1H), 6.46 (d, J=7.6, 1H), 6.44 (dd, J=3.4,1.9, 1H), 6.34 (d,

J=15.3, 1H), 4.60 (quint, J=7.2, 1H), 3.65 (s, 3H), 3.25 (q, J=6.6, 2H), 2.30 (t, J=7.4, 2H), 1.62 (br quint, J=7.5, 2H), 1.52 (br quint, J=7.3, 2H), 1.43 (d, J=7.2, 3H), 1.34 (br quint, J=7.7, 2H); MS (ES+): 359 (MNa+, 12), 337 (MH+, 100), 146 (MH+-191, 22).

3-(2'-thiophene)-prop-2*E*ene-1-amide-Arg(Pbf)-OCH$_3$ (18, R^1 = R^3 = H, R^2 = R^4 = -SCH=CH-, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = Me):
O.190 g (0.0335 mmol) of resin **17** was treated 2 eq of DBU in MeOH/CH_2Cl_2 according to the standard conditions, giving 0.0177g (77%) of product after column purification (20:1 EtOAc:MeOH).

TLC (9:1 EtOAc:MeOH): R_f=0.63; ^{1}H NMR ($CDCl_3$): δ 7.67 (d, J=15.3, 1H), 7.30 (br s, 1H), 7.29 (d, J=5.0, 1H), 7.15 (d, J=3.0, 1H), 7.00 (dd, J=5.0,3.8, 1H), 6.41 (d, J=15.3, 1H), 6.33 (br s, 3H), 6.25 (vbr s, 1H), 4.62 (br s, 1H), 3.63 (s, 3H), 3.4-3.2 (m, 2H), 3.22 (m, 2H), 2.93 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.27 (t, J=7.4, 2H), 2.08 (s, 3H), 1.89 (br m, 1H), 1.77 (m, 1H), 1.65-1.45 (m, 2H), 1.59 (br quint, J=7.6, 2H), 1.52 (br quint, J=7.3, 2H), 1.44 (s, 6H), 1.31 (br quint, J=7.7, 2H); MS (ES+): 690 (MH+, 100), 337 (MH+-353, 22), 273 (MH+-417, 12), 229 (MH+-461, 15), 146 (MH+-544, 12). Anal. Calcd for CHNOS: C, 57.45; H, 6.87; N, 10.15; S, 9.29. Found: C, 57.52; H, 6.87; N, 9.90; S, 8.80.

(N,N'dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = Me):
O.172 g (0.0303 mmol) of resin **17** was treated 2 eq of DBU in MeOH/CH_2Cl_2 according to the standard conditions, giving 0.0167g (80%) of product after column purification (5:1:0.1 EtOAc:MeOH:Et_3N).

TLC (12:7:1 EtOAc:MeOH:Et_3N): R_f=0.54; ^{1}H NMR ($CDCl_3$): δ 7.77 (br s, 1H), 7.41 (br s, 1H), 7.14 (dd, J=15.3,11.1, 1H), 6.80 (br s, 1H), 6.53 (br s, 2H), 6.51 (dd, J=15.6,11.1, 1H), 6.23 (d, J=14.9, 1H), 6.14 (dt, J=15.3,7.3, 1H), 4.44 (br s, 1H), 3.64 (s, 6H), 3.63 (s, 3H), 3.61 (br m, 2H), 3.3-3.1 (m, 4H), 2.94 (s, 2H), 2.57 (s, 3H), 2.50 (s, 3H), 2.26 (t, J=7.4, 2H), 2.08 (s, 3H), 1.87 (br m, 1H), 1.76 (br m, 1H), 1.6-1.45 (m, 2H), 1.58 (br quint, J=7.6, 2H), 1.48 (br quint, J=7.5, 2H), 1.45 (s, 6H), 1.29 (br quint, J=7.7, 2H); MS (ES+): 691 (MH+, 15), 346 (MH+-345, 100.

5-carboxy-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = H, R^4 = CO$_2$H, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):
O.205 g (0.0370 mmol) of resin **17** was treated 2 eq of DBU in MeOH/CH_2Cl_2 according to the standard conditions, giving 0.0111g (88%) of product after column purification (10:1:0.1 EtOAc:MeOH:AcOH).

^{1}H NMR (CD_3CN): δ 9.4 (vbr s, 1H), 7.36 (dd, J=15.1,11.6, 1H), 7.25 (dd, J=14.9,11.4, 1H), 7.01 (d, J=6.9, 1H), 6.67 (br s, 1H), 6.40 (d, J=14.9, 1H), 6.21 (d, J=15.3, 1H), 4.35 (quint, J=7.1, 1H), 3.62 (s, 3H), 3.14 (q, J=6.5, 2H), 2.28 (t, J=7.4, 2H), 1.58 (br quint, J=7.5, 2H), 1.45 (br quint, J=7.3, 2H), 1.32 (d, J=7.2, 3H), 1.35-1.25 (m, 2H); MS (ES+): 363 (MNa+, 69), 341 (MH+, 100), 235 (MH+-106, 44), 153 (MH+-188, 15), 146 (MH+-195, 73), 102 (MH+-239, 78).

5-carboxymethyl-penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = H, R^4 = CO$_2$CH$_3$, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):
O.087 g (0.0164 mmol) of resin **17** was treated 2 eq of DBU in MeOH/CH_2Cl_2 according to the standard conditions, giving 0.0039g (70%) of product after column purification (10:1 EtOAc:MeOH).

^{1}H NMR (CD_3CN): δ 7.35-7.25 (m, 2H), 6.53 (d, J=7.6, 1H), 6.24 (t, 1H), 6.21 (d, J=14.5, 1H), 6.18 (d, J=14.5, 1H), 4.53 (quint, J=7.1, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.26 (q, J=6.6, 2H), 2.31 (t, J=7.4, 2H), 1.63 (br quint, J=7.5, 2H), 1.52 (br quint, J=7.3, 2H), 1.41 (d, J=6.9, 3H), 1.35-1.25 (m, 2H); MS (ES+): 363 (MNa+, 69), 341 (MH+, 100), 235 (MH+-106, 44), 153 (MH+-188, 15), 146 (MH+-195, 73), 102 (MH+-239, 78).

6-methoxy-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OCH_3 (18, $R^1 = R^2 = R^3 = H$, $R^4 = CH_2OCH_3$, Xaa_2-Xaa_1 = Arg(Pbf)-Aca, R = Me):
O.072 g (0.0127 mmol) of resin **17** was treated 2 eq of DBU in MeOH/CH_2Cl_2 according to the standard conditions, giving 0.0069g (79%) of product after column purification (20:1 EtOAc:MeOH).

^1H NMR ($CDCl_3$): δ 7.25 (vbr s, 1H), 7.17 (dd, J=15.3,11.1, 1H), 7.05 (br s, 1H), 6.31 (dd, J=15.3,11.1, 1H), 6.28 (br s, 2H), 6.15 (vbr s, 1H), 6.08 (dt, J=15.3,5.3, 1H), 6.00 (d, J=14.9, 1H), 4.55 (br s, 1H), 4.02 (d, J=5.3, 2H), 3.64 (s, 3H), 3.36 (s, 3H), 3.3-3.15 (m, 4H), 2.95 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.28 (t, J=7.4, 2H), 2.09 (s, 3H), 1.86 (br m, 1H), 1.75-1.45 (m, 3H), 1.60 (br quint, J=7.6, 2H), 1.52 (br quint, J=7.3, 2H), 1.46 (s, 6H), 1.31 (br quint, J=7.7, 2H); MS (ES^+): 678 (MH^+, 100),

CLEAVED DIENES- from WANG resin (Xaa_2-Xaa_1=Phe)

penta-2*E*,4*E*-diene-1-amide-Phe-OH (18, $R^1 = R^2 = R^3 = R^4 = H$, Xaa_2-Xaa_1 = Phe, R = H):
O.0223 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0051g (93%) of product.

^1H NMR (CD_3OD-partially soluble): δ 7.30-7.15 (m, 5H), 7.09 (dd, J=15.1, 10.9, 1H), 6.48 (dt, J=17.2, 10.3, 1H), 6.06 (d, J=15.3, 1H), 5.56 (d, J=17.2, 1H), 5.43 (d, J=10.3, 1H), 4.74 (dd, J=9.0,5.2, 1H), 3.23 (dd, J=13.9, 5.2, 1H), 2.99 (dd, J=13.9,9.0, 1H).

^1H NMR (DMSO-d_6): δ 8.41 (d, J=8.0, 1H), 7.30-7.15 (m, 5H), 6.97 (dd, J=15.1, 10.9, 1H), 6.47 (dt, J=16.8, 10.7, 1H), 6.09 (d, J=15.3, 1H), 5.58 (d, J=17.0, 1H), 5.41 (d, J=11.1, 1H), 4.50 (m, 1H), 3.08 (dd, J=13.7, 4.6, 1H), 2.88 (dd, J=13.7,9.9, 1H).

penta-2*E*,4*E*-diene-1-amide-Phe-OCH_3 (18, $R^1 = R^2 = R^3 = R^4 = H$, Xaa_2-Xaa_1 = Phe, R = Me):
O.021 mmol of resin **17** was treated with DBU according to the standard conditions, withh the produt filtered through a silica gel pad and eluted with EtOAc, giving 0.0041g (80%) of product.

^1H NMR ($CDCl_3$): δ 7.32-7.24 (m, 3H), 7.21 (dd, J=15.1, 11.1, 1H), 7.08 (d, J=6.5, 2H), 6.42 (dt, J=17.2, 10.5, 1H), 5.96 (d, J=7.6, 1H), 5.73 (d, J=15.3, 1H), 5.58 (d, J=16.8, 1H), 5.45 (d, J=9.9, 1H), 4.99 (dt, J=7.6,5.6, 1H), 3.74 (s, 3H), 3.20 (dd, J=13.9, 5.9, 1H), 3.15 (dd, J=13.7,5.3, 1H).

2-methylpenta-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = Me, $R^2 = R^3 = R^4 = H$, Xaa_2-Xaa_1 = Phe, R = H):
O.0229 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0037g (63%) of material, with a 65:35 product:sm ratio.

^1H NMR (CD_3OD-partially soluble): δ 7.30-7.20 (m, 5H), 6.72-6.64 (m, 2H), 5.47 (d, J=14.5, 1H), 5.38 (d, J=9.2, 1H), 4.71 (dd, J=9.4, 4.8, 1H), 3.28 (dd, J=14.1, 5.0, 1H), 3.06 (dd, J=14.1,9.5, 1H), 1.88 (s, 3H).

^1H NMR (DMSO-d_6): δ 8.37 (d, J=8.4, 1H), 7.30-7.10 (m, 5H), 6.72-6.62 (m, 2H), 5.47 (d, J=16.0, 1H), 5.37 (d, J=10.3, 1H), 4.44 (m, 1H), 3.11 (dd, J=13.9, 4.4, 1H), 2.93 (dd, J=13.7,10.7, 1H), 1.82 (s, 3H); MS (ES^+): 260 (MH^+, 100); (ES^-): 258 $(M-H)^-$, 100.

6-hydroxyhexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, $R^1 = R^2 = R^3 = H$, $R^4 = CH_2OH$, Xaa_2-Xaa_1 = Phe, R = H):
O.0136 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0091g (>100%) of product.

^1H NMR (acetone-d_6): δ 7.50 (d, J=8.0, 1H), 7.26 (m, 4H), 7.20 (m, 1H), 7.17 (dd, J=15.0,10.7, 1H), 6.55 (dd, J=15.3, 10.7, 1H), 6.18 (d, J=15.0, 1H), 6.14 (dt, J=15.3,6.5, 1H), 5.03 (d, J=6.5, 2H), 4.83 (td, J=8.2,5.2, 1H), 3.24 (dd, J=13.9, 5.2 1H), 3.05 (dd, J=13.9,8.2, 1H).

2-methyl-6-hydroxyhexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = CH_2OH, Xaa_2-Xaa_1 = Phe, R = H):

O.0145 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0054g (>100%) of product.

^{1}H NMR (acetone-d_6): δ 7.40-7.20 (m, 6H), 6.86-6.78 (m, 2H), 6.10 (dt, J=14.5,7.0, 1H), 5.04 (d, J=6.9, 2H), 4.77 (td, J=8.5,4.8, 1H), 3.27 (dd, J=14.1, 5.0, 1H), 3.09 (dd, J=13.7,8.8, 1H), 1.92 (s, 3H).

6-aminohexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = R^2 = R^3 = H, R^4 = CH_2NH_2, Xaa_2-Xaa_1 = Phe, R = H):

O.0134 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0091g (>100%) of product.

^{1}H NMR (acetone-d_6): δ 7.26 (m, 4H), 7.25-7.15 (m, 1H), 7.11 (dd, J=14.9,11.1, 1H), 6.54 (dd, J=15.3, 11.1 1H), 6.21 (d, J=14.9 1H), 6.18 (dt, J=15.3,6.3, 1H), 4.80 (dd, J=8.4,5.0, 1H), 4.60 (d, J=6.1, 2H), 3.23 (dd, J=14.1, 5.0 1H), 3.03 (dd, J=14.1,8.4, 1H); MS (ES+): 275 (MH^+, 100), 258 (MH^+-17, 35); (ES$^-$): 387 ((MTFA-H)-, 1), 258 ($(M-H)^-$, 1), 227 ((M-H)-- 46, 100).

2-methyl-6-aminohexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = CH_2NH_2, Xaa_2-Xaa_1 = Phe, R = H):

O.0135mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.01231g (>100%) of product.

^{1}H NMR (acetone-d_6): δ 7.29 (m, 4H), 7.25-7.20 (m, 1H), 6.85-6.75 (m, 2H), 6.07 (dt, J=14.5,5.9, 1H), 4.76 (dd, J=8.8,5.0, 1H), 4.60 (d, J=6.5, 2H), 3.26 (dd, J=13.9, 5.2, 1H), 3.08 (dd, J=13.9,9.0, 1H), 1.89 (s, 3H); MS (ES+): 289 (MH^+, 43), 272 (MH^+-17, 100).

***N,N*dimethyl-6-aminohexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = R^2 = R^3 = H, R^4 = CH_2NMe_2, Xaa_2-Xaa_1 = Phe, R = H):**

O.0208mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0123g (>100%) of product.

^{1}H NMR (acetone-d_6): δ 7.58 (d, J=8.0, 1H), 7.26 (m, 4H), 7.25-7.20 (m, 1H), 7.16 (dd, J=15.3,11.1, 1H), 6.69 (dd, J=14.9, 11.1 1H), 6.30 (d, J=15.3 1H), 6.26 (dt, J=15.3,7.5, 1H), 4.84 (td, J=8.2,5.2, 1H), 4.07 (d, J=6.9, 2H), 3.24 (dd, J=13.9, 5.2 1H), 3.07 (s, 6H), 3.04 (dd, J=14.1,8.4, 1H).

***N,N*,2-trimethyl-6-aminohexa-2*E*,4*E*-diene-1-amide-Phe-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = CH_2NMe_2, Xaa_2-Xaa_1 = Phe, R = H):**

O.0184 mmol of resin **17** was treated with TFA according to the standard conditions, giving 0.0068g (>100%) of impure product.

^{1}H NMR (acetone-d_6): δ 7.46 (d, J=7.2, 1H), 7.30 (m, 4H), 7.25-7.20 (m, 1H), 6.91 (m, 1H), 6.84 (m, 1H), 6.10 (dt, J=14.5,7.2, 1H), 4.76 (m, 1H), 4.30 (t, J=7.4, 1H), 3.95 (br d, J=6.1, 1H), 3.29 (s, 3H), 3.27 (dd, J=14.1, 5.0, 1H), 3.06 (dd, J=13.9,9.3, 1H), 1.91 (s, 3H).

CLEAVED DIENES- from WANG resin (Xaa_2-Xaa_1 = Ala-Aca)

penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^3 = R^4 = H, Xaa_2-Xaa_1 = Ala-Aca, R=H):

^{1}H NMR (acetone-d_6/CD_3OD): δ 7.13 (dd, J=15.1,10.9, 1H), 6.48 (dt, J=17.2, 10.6, 1H), 6.13 (d, J=15.3, 1H), 5.56 (d, J=16.0, 1H), 5.40 (d, J=9.9, 1H), 4.47 (quint, J=7.4, 1H), 3.2-3.1 (m, 2H), 2.3-2.2 (m, 2H), 1.7-1.2 (m, 6H), 1.37 (d, J=7.2, 3H).

penta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Ala-Aca, R=Me):
identical to product obtained from PEG resin

5-phenylpenta-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$= Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 87:13

^{1}H NMR (acetone-d$_6$): δ 7.55 (d, J=7.3, 2H), 7.52 (br m, 1H), 7.37 (t, J=7.4, 2H), 7.35 (dd, J=15.2, 10.5, 1H), 7.30 (d, J=7.3, 1H), 7.04 (dd, J=15.6, 10.5, 1H), 6.97 (d, J=15.8, 1H), 6.28 (d, J=15.0, 1H), 4.47 (quint, J=7.3, 1H), 3.19 (m, 2H), 2.28 (t, J=7.3, 2H), 1.7-1.2 (m, 6H), 1.31 (d, J=6.8, 3H); MS (ES$^+$): 472 (MH$^+$+113, 17), 359 (MH$^+$, 41), 246 (MH$^+$-113, 100); (ES$^-$): 357 ((M-H)$^-$, 30), 244 ((M-H)$^-$- 113, 100).

5-phenylpenta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 100:0

^{1}H NMR (CDCl$_3$): δ 7.5-7.3 (m, 6H), 6.9-6.8 (m, 2H), 6.21 (br s, 1H), 6.14 (d, J=7.3, 1H), 5.98 (d, J=14.9, 1H), 4.54 (quint, J=7.1, 1H), 3.66 (s, 3H), 3.26 (q, J=6.6, 2H), 2.31 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.42 (d, J=7.2, 3H); MS (ES$^+$): 395 (MNa$^+$, 11), 373 (MH$^+$, 51), 282 (MNa$^+$-113, 39), 260 (MH$^+$-113, 100).

5-phenylpenta-2*E*,4*Z*diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^4 = H, R^3 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 25:75

^{1}H NMR (acetone-d$_6$): δ 7.70 (dd, J=15.0,12.0, 1H), 7.55 (br m, 1H), 7.42 (t, J=7.3, 2H), 7.37 (d, J=6.0, 2H), 7.43 (d, J=7.3, 1H), 6.79 (d, J=11.5, 1H), 6.42 (t, J=11.8, 1H), 6.32 (d, J=15.0, 1H), 4.46 (quint, J=7.3, 1H), 3.18 (m, 2H), 2.27 (m, 2H), 1.7-1.2 (m, 6H), 1.30 (d, J=7.3, 3H); MS (ES$^+$): 472 (MH$^+$+113, 13), 359 (MH$^+$, 32), 246 (MH$^+$-113, 100); (ES$^-$): 357 ((M-H)$^-$, 21), 244 ((M-H)$^-$- 113, 100).

5-phenylpenta-2*E*,4*Z*diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^4 = H, R^3 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 22:78

^{1}H NMR (CDCl$_3$): δ 7.76 (dd, J=14.9,11.8, 1H), 7.4-7.25 (m, 6H), 6.78 (d, J=11.4, 1H), 6.34 (t, J=11.4, 1H), 6.18 (br s, 1H), 6.14 (d, J=7.3, 1H), 6.02 (d, J=14.9, 1H), 4.52 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.25 (q, J=6.7, 2H), 2.30 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.40 (d, J=6.9, 3H); MS (ES$^+$): 373 (MH$^+$, 29), 282 (MNa$^+$-113, 12), 260 (MH$^+$-113, 100).

2-methyl-5-phenylpenta-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 89:11

^{1}H NMR (acetone-d$_6$): δ 7.58 (d, J=7.3, 2H), 7.4-7.25 (br m, 2H), 7.36 (t, J=7.5, 2H), 7.29 (d, J=7.3, 1H), 7.26 (dd, J=15.4,11.1, 1H), 7.11 (d, J=11.1, 1H), 6.87 (d, J=15.4, 1H), 4.54 (quint, J=7.3, 1H), 3.21 (m, 2H), 2.28 (m, 2H), 2.09 (s, 3H), 1.7-1.2 (m, 6H), 1.34 (d, J=6.8, 3H); MS (ES$^+$): 508 (MNa$^+$+113, 5), 486 (MH$^+$+113, 24), 395, (MNa$^+$, 15), 373 (MH$^+$,72), 260 (MH$^+$-113, 100).

2-methyl-5-phenylpenta-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = Me, R^2 = R^3 = H, R^4 = Ph, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 90:10

^{1}H NMR ($CDCl_3$): δ 7.47 (d, J=7.2, 2H), 7.35 (t, J=7.4, 2H), 7.29 (d, J=8.4, 1H), 7.12 (dm, J=11.1, 1H), 7.04 (dd, J=15.1, 11.3, 1H), 6.84 (d, J=15.3, 1H), 6.42 (d, J=6.9, 1H), 6.22 (br s, 1H), 4.53 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.27 (q, J=6.6, 2H), 2.31 (t, J=7.4, 2H), 2.07 (d, J=1.1, 3H), 1.7-1.2 (m, 6H), 1.43 (d, J=7.2, 3H); MS (ES+): 409 (MNa^+, 4), 387 (MH^+, 35), 274 (MH^+-113, 98), 171 (MH^+-216, 100).

2-methyl-5-phenylpenta-2*E*,4*Z*diene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^2 = R^4 = H, R^3 = Ph, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 16:84

^{1}H NMR (acetone-d_6): δ 7.45 (d, J=12.0, 1H), 7.45-7.2 (m, 7H), 6.76 (d, J=11.5, 1H), 6.59 (t, J=11.8, 1H), 4.52 (quint, J=7.3, 1H), 3.19 (m, 2H), 2.35-2.25 (m, 2H), 2.06 (s, 3H), 1.7-1.2 (m, 6H), 1.41 (d, J=7.3, 3H); MS (ES+): 486 (MH^++113, 22), 395, (MNa^+, 12), 373 (MH^+,59), 260 (MH^+-113, 100).

2-methyl-5-phenylpenta-2*E*,4*Z*diene-1-amide-Ala-Aca-OCH_3 (18, R^1 = Me, R^2 = R^4 = H, R^3 = Ph, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 22:78

^{1}H NMR ($CDCl_3$): δ 7.5-7.25 (m, 5H), 7.36 (d, J=11.1, 1H), 6.76 (d, J=11.8, 1H), 6.49 (t, J=11.6, 1H), 6.32 (d, J=7.6, 1H), 6.21 (br s, 1H), 4.50 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.25 (q, J=6.6, 2H), 2.30 (t, J=7.4, 2H), 2.06 (d, J=1.1, 3H), 1.7-1.2 (m, 6H), 1.39 (d, J=6.9, 3H); MS (ES+): 409 (MNa^+, 6), 387 (MH^+, 57), 274 (MH^+-113, 100), 171 (MH^+-216, 100).

trideca-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^3 = H, R^4 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 88:12

^{1}H NMR (acetone-d_6): δ 11.1 (vbr s, 1H), 7.42 (d, J=6.9, 1H), 7.14 (dd, J=14.9,10.7, 1H), 6.21 (dd, J=15.3,10.7, 1H), 6.10 (dt, J=15.3,7.3, 1H), 6.04 (d, J=15.3, 1H), 4.44 (quint, J=7.1, 1H), 3.18 (m, 2H), 2.27 (t, J=7.6, 2H), 2.16 (q, J=7.1, 2H), 1.7-1.2 (m, 18H), 1.39 (d, J=7.2, 3H), 0.88 (t, J=6.9, 3H); MS (ES+): 395 (MH^+, 14), 282 (MH^+-113, 100); (ES-): 393 ($(M-H)^-$, 33), 280 ($(M-H)^-$- 113, 100).

trideca-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH_3 (18, R^1 = R^2 = R^3 = H, R^4 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 90:10

^{1}H NMR ($CDCl_3$): δ 7.20 (dd, J=15.1,10.1, 1H), 6.21 (br s, 1H), 6.15-6.05 (m, 2H), 6.01 (d, J=7.6, 1H), 5.75 (d, J=14.9, 1H), 4.51 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.25 (q, J=6.7, 2H), 2.31 (t, J=7.4, 2H), 2.15 (q, J=6.9 2H), 1.7-1.2 (m, 18H), 1.39 (d, J=6.9, 3H), 0.88 (t, J=7.1, 3H); MS (ES+): 431 (MNa^+, 5), 409 (MH^+, 93), 296 (MH^+-113, 100).

trideca-2*E*,4*Z*diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^4 = H, R^3 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 24:76

^{1}H NMR (acetone-d_6): δ 7.50 (dd, J=15.0, 10.7, 1H), 7.48 (d, J=6.0, 1H), 6.14 (t, J=11.5, 1H), 6.12 (d, J=15.0, 1H), 5.79 (dt, J=10.7,7.7, 1H), 4.45 (quint, J=7.3, 1H), 3.18 (m, 2H), 2.30 (q, J=7.5, 2H), 2.28 (m, 2H), 1.7-1.2 (m, 18H), 1.40 (d, J=7.3, 3H), 0.87 (t, J=7.1, 3H); MS (ES+): 395 (MH^+, 17), 282 (MH^+-113, 100); (ES-): 393 ($(M-H)^-$, 13), 280 ($(M-H)^-$- 113, 100).

trideca-2*E*,4*Z*diene-1-amide-Ala-Aca-OCH_3 (18, R^1 = R^2 = R^4 = H, R^3 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 23:77

^{1}H NMR ($CDCl_3$): δ 7.57 (dd, J=14.9, 11.8, 1H), 6.20 (br s, 1H), 6.15-6.00 (m, 2H), 6.09 (t, J=11.3, 1H), 5.86 (d, J=14.9, 1H), 4.53 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.25 (q, J=6.7, 2H), 2.35-2.25 (m, 4H), 1.7-1.2 (m, 18H), 1.40 (d, J=6.9, 3H), 0.88 (t, J=6.7, 3H); MS (ES^+): 409 (MH^+, 22), 330 (MH^+-79, 100), 296 (MH^+-113, 83).

2-methyltrideca-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 94:6

^{1}H NMR (acetone-d_6): δ 7.3-7.2 (br m, 2H), 6.90 (d, J=11.1, 1H), 6.41 (dd, J=15.0,11.1, 1H), 6.01 (dt, J=15.0,7.3), 4.50 (quint, J=7.3, 1H), 3.17 (m, 2H), 2.30 (t, J=7.4, 2H), 2.19 (q, J=7.4, 2H), 1.93 (s, 3H), 1.7-1.2 (m, 18H), 1.42 (d, J=7.3, 3H), 0.88 (m, 3H); MS (ES^+): 522 (MH^++113, 5), 409 (MH^+, 13), 296 (MH^+-113, 100).

2-methyltrideca-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH_3 (18, R^1 = Me, R^2 = R^3 = H, R^4 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 85:15

^{1}H NMR ($CDCl_3$): δ 6.90 (d, J=10.9, 1H), 6.35-6.20 (br m, 2H), 6.30 (dd, J=15.1,10.9, 1H), 6.03 (dt, J=14.9,7.2), 4.50 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.25 (q, J=6.7, 2H), 2.31 (t, J=7.4, 2H), 2.17 (q, J=7.1, 2H), 1.94 (s, 3H), 1.7-1.2 (m, 18H), 1.40 (d, J=6.9, 3H), 0.88 (t, J=6.9, 3H); MS (ES^+): 445 (MNa^+, 3), 423 (MH^+, 37), 310 (MH^+-113, 100).

2-methyltrideca-2*E*,4*Z*diene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^2 = R^4 = H, R^3 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 18:82

^{1}H NMR (acetone-d_6): δ 7.4-7.2 (br m, 2H), 7.27 (d, J=11.5, 1H), 6.32 (t, J=11.3, 1H), 5.76 (dt, J=10.7,7.9, 1H), 4.51 (quint, J=7.3, 1H), 3.19 (m, 2H), 2.35-2.25 (m, 4H), 1.95 (s, 3H), 1.7-1.2 (m, 18H), 1.42 (d, J=7.3, 3H), 0.87 (m, 3H); MS (ES^+): 522 (MH^++113, 21), 431 (MNa^+, 8), 409 (MH^+, 61), 296 (MH^+-113, 100).

2-methyltrideca-2*E*,4*Z*diene-1-amide-Ala-Aca-OCH_3 (18, R^1 = Me, R^2 = R^4 = H, R^3 = $(CH_2)_7CH_3$, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 15:85

^{1}H NMR ($CDCl_3$): δ 7.29 (d, J=10.7, 1H), 6.37 (d, J=7.2, 1H), 6.24 (t, J=11.3, 1H), 5.80 (dt, J=11.4,7.4, 1H), 4.52 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.26 (m, 2H), 2.30 (q, J=7.2, 2H), 2.28 (t, J=7.5, 2H), 1.95 (s, 3H), 1.7-1.2 (m, 18H), 1.42 (d, J=6.9, 3H), 0.88 (t, J=6.7, 3H); MS (ES^+): 445 (MNa^+, 12), 423 (MH^+, 75), 310 (MH^+-113, 100).

3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OH (18, R^1 = R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa_2-Xaa_1 = Ala-Aca, R = H):

^{1}H NMR (acetone-d_6): δ 7.63 (s, 1H), 7.33 (d, J=15.8, 1H), 6.71 (t, J=3.2, 1H), 6.56 (d, J=15.4, 1H), 6.54 (d, J=3.4, 1H), 4.48 (quint, J=7.3, 1H), 3.19 (m, 2H), 2.27 (m, 2H), 1.7-1.2 (m, 6H), 1.32 (d, J=7.3, 3H); MS (ES^+): 436 (MH^++113, 8), 323 (MH^+, 27), 208 (MH^+-113, 15), 187 (MH^+-136, 100); (ES^-): 332 ($(M-H)^-$, 74), 208 ($(M-H)^-$- 113, 100).

3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OCH_3, (18, R^1 = R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa_2-Xaa_1 = Ala-Aca, R = Me):

^{1}H NMR ($CDCl_3$): δ 7.44 (d, J=1.1, 1H), 7.40 (d, J=15.3, 1H), 6.56 (d, J=3.4, 1H), 6.45 (dd, J=3.4,1.5, 1H), 6.31 (d, J=15.3, 1H), 6.23 (br s, 1H), 6.19 (d, J=7.2, 1H), 4.56 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.26 (m, 2H), 2.31 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.42 (d, J=7.2, 3H).

2-methyl-3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa_2-Xaa_1 = Ala-Aca, R = H):

^{1}H NMR (acetone-d_6): δ 7.68 (d, J=1.7, 1H), 7.45 (br m, 2H), 7.18 (d, J=0.9, 1H), 6.67 (d, J=3.4, 1H), 6.57 (dd, J=3.4,1.7, 1H), 4.54 (quint, J=7.3, 1H), 3.17 (m, 2H), 2.30 (m, 2H), 2.22 (d, J=1.3, 3H), 1.7-1.2 (m, 6H), 1.45 (d, J=7.3, 3H).

2-methyl-3-(2'-furan)-prop-2*E*ene-1-amide-Ala-Aca-OCH_3 (18, R^1 = Me, R^3 = H, R^2 = R^4 = -OCH=CH-, Xaa_2-Xaa_1 = Ala-Aca, R = Me):

^{1}H NMR ($CDCl_3$): δ 7.50 (d, J=1.1, 1H), 7.20 (d, J=0.8, 1H), 6.55 (d, J=3.4, 1H), 6.47 (dd, J=3.4,1.9, 1H), 6.5-6.4 (br m, 1H), 6.20 (br s, 1H), 4.53 (quint, J=7.2, 1H), 3.66 (s, 3H), 3.27 (q, J=6.7, 2H), 2.31 (t, J=7.4, 2H), 2.26 (d, J=0.8, 3H), 1.7-1.2 (m, 6H), 1.43 (d, J=6.9, 3H).

6-hydroxy-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^3 = H, R^4 = CH_2OH, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 99:1

^{1}H NMR (acetone-d_6): δ 7.42 (d, J=7.3, 1H), 7.28 (br s, 1H), 7.20 (dd, J=15.0,11.1, 1H), 6.59 (dd, J=15.4, 11.1, 1H), 6.27 (d, J=15.4), 6.24 (dt, J=15.4,6.3, 1H), 5.04 (d, J=6.4, 2H), 4.45 (quint, J=7.3, 1H), 3.18 (m, 2H), 2.27 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.30 (d, J=7.3, 3H); MS (ES+): 313 (MH^+, 13), 200 (MH^+-113, 41), 187 (MH^+-126, 100).

6-hydroxy-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OPEG-OCH_3 (18, R^1 = R^2 = R^3 = H, R^4 = CH_2OH, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 100:0

^{1}H NMR ($CDCl_3$): δ 7.25 (dd, J=15.3,10.7, 1H), 6.39 (dd, J=15.3, 11.1, 1H), 6.29 (br s, 1H), 6.25 (d, J=8.0), 6.20 (dt, J=15.3,4.9, 1H), 5.88 (d, J=14.9, 1H), 4.53 (quint, J=7.2, 1H), 4.29 (dd, J=5.0,1.1, 2H), 3.66 (s, 3H), 3.25 (m, 2H), 2.30 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.40 (d, J=6.9, 3H); MS (ES+): 349 (MNa^+, 20), 327 (MH^+, 32), 214 (MH^+-113, 100).

6-hydroxy-hexa-2*E*,4*Z*diene-1-amide-Ala-Aca-OPEG-OH (18, R^1 = R^2 = R^4 = H, R^3 = CH_2OH, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 8:92; *EE*+*EZ*:gem 67:33

^{1}H NMR (acetone-d_6): δ 7.50 (dd, J=15.0,12.0, 1H), 6.47 (t, J=11.8, 1H), 6.30 (d, J=15.0), 5.93 (dt, J=10.7,7.3, 1H), 5.23 (d, J=7.3, 2H), 4.46 (q, J=6.8, 1H), 3.19 (m, 2H), 2.27 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.30 (d, J=7.3, 3H); MS (ES+): 426 (MH^++113, 17), 338 (MH^++25, 100), 313 (MH^+, 38), 200 (MH^+-113, 68), 187 (MH^+-126, 74),.

6-hydroxy-hexa-2*E*,4*Z*diene-1-amide-Ala-Aca-OPEG-OCH_3 (18, R^1 = R^2 = R^4 = H, R^3 = CH_2OH, Xaa_2-Xaa_1 = Ala-Aca, R = Me):
2*E*,4*E*:2*E*,4*Z* 10:90; *EE*+*EZ*:gem 65:35

^{1}H NMR ($CDCl_3$): δ 7.53 (dd, J=15.3,10.7, 1H), 6.18 (t, J=11.1, 1H), 6.00-5.90 (m, 2H), 4.53 (m, 1H), 4.45 (d, J=6.8, 2H), 3.66 (s, 3H), 3.25 (m, 2H), 2.30 (m, 2H), 1.7-1.2 (m, 6H), 1.40 (d, J=6.9, 3H); MS (ES+): 349 (MNa^+, 40), 327 (MH^+, 43), 214 (MH^+-113, 77), 199 (MH^+-128, 100).

(N,N-dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = R^2 = R^3 = H, R^4 = CH_2NMe_2, Xaa_2-Xaa_1 = Ala-Aca, R = H):
2*E*,4*E*:2*E*,4*Z* 94:6

^{1}H NMR (acetone-d_6): δ 7.51 (d, J=7.3, 1H), 7.30 (br s, 1H), 7.20 (dd, J=15.2,10.9, 1H), 6.67 (dd, J=15.4,11.1, 1H), 6.27 (d, J=15.0, 1H), 6.25 (dt, J=15.0,7.5, 1H), 4.45 (quint, J=7.3, 1H), 3.92 (d, J=7.3, 2H), 3.19 (m, 2H), 2.90 (s, 6H), 2.27 (t, J=7.4, 2H), 1.7-1.2 (m, 6H), 1.30 (d, J=6.8, 3H); MS (ES+): 453 (MH^++113, 4), 340 (MH^+, 38), 227 (MH^+-113, 100).

(N,N-dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me): crude product, DBU present

2*E*,4*E*:2*E*,4*Z* >90:<10

^{1}H NMR (CDCl$_3$): δ 7.15 (dd, J=15.1,10.9, 1H), 6.24 (dd, J=15.1,11.3, 1H), 6.00 (dt, J=15.3,7.2, 1H), 5.88 (d, J=15.3, 1H), 4.29 (quint, J=6.8, 1H), 2.98 (d, J=6.5, 2H), 2.31 (m, 2H), 2.21 (s, 6H), 1.7-1.2 (m, 6H), 1.37 (d, J=6.9, 3H); MS (ES+): only see DBU 171 (MNa+, 60), 153 (MH+, 100).

(N,N'dimethyl)-2-methyl-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OH (18, R^1 = Me, R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = H):

2*E*,4*E*:2*E*,4*Z* >90:<10

^{1}H NMR (acetone-d$_6$): δ 7.35 (d, J=6.4, 1H), 7.00-6.90 (m, 2H), 6.12 (dt, J=14.5,7.3, 1H), 4.44 (quint, J=7.3, 1H), 3.96 (d, J=7.3, 2H), 3.19 (m, 2H), 2.88 (s, 6H), 2.27 (m, 2H), 1.98 (s, 3H), 1.7-1.2 (m, 6H), 1.32 (d, J=7.3, 3H); MS (ES+): 467 (MH+ +113, 11), 354 (MH+, 37), 241 (MH+-113, 100).

(N,N'dimethyl)-2-methyl-6-amino-hexa-2*E*,4*E*-diene-1-amide-Ala-Aca-OCH$_3$ (18, R^1 = Me, R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Ala-Aca, R = Me): crude product, DBU present

2*E*,4*E*:2*E*,4*Z* >90:<10

^{1}H NMR (CDCl$_3$): δ 6.93 (d, J=11.1, 1H), 6.41 (dd, J=15.3,11.1, 1H), 5.95 (dt, J=14.9,7.3, 1H), 4.27 (quint, J=6.5, 1H), 3.00 (d, J=6.9, 2H), 2.23 (t, J=7.4, 2H), 2.21 (s, 6H), 1.97 (s, 3H), 1.7-1.2 (m, 6H), 1.44 (d, J=6.9, 3H); MS (ES+): mainly DBU 171 (MNa+, 65), 153 (MH+, 100); trace 368 (MH+, 1),

CLEAVED DIENES- from WANG resin (Xaa$_2$-Xaa$_1$ = Arg-Aca)

pent-2*E*ene-1-amide-Arg(Pbf)-OCH$_3$ (18, R^1 = R^2 = R^3 = R^4 = H, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = Me):

^{1}H NMR (CDCl$_3$): δ 7.25-7.15 (m, 1H), 7.0 (br s, 1H), 6.60 (br s, 2H), 6.50-6.35 (m, 1H), 6.00 (d, J=14.9, 1H), 5.57 (d, J=17.2, 1H), 5.46 (d, J=10.3, 1H), 5.4 (br s, 1H), 4.51 (br m, 1H), 3.65 (s, 3H), 3.5-3.1 (m, 4H), 2.96 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.30 (t, J=7.4, 2H), 2.10 (s, 3H), 2.0-1.2 (m, 10H), 1.47 (s, 6H); MS (ES+): 634 (MH+, 50), 521 (MH+-113, 100).

3-(2'-thiophene)-prop-2*E*ene-1-amide-Arg(Pbf)-OH (18, R^1 = R^3 = H, R^2 = R^4 = -SCH=CH-, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = H):

^{1}H NMR (CD$_3$OD): δ 7.69 (d, J=15.6, 1H), 7.49 (d, J=5.3, 1H), 7.31 (d, J=3.0, 1H), 7.08 (dd, J=5.0,3.8, 1H), 6.50 (d, J=15.3, 1H), 4.44 (dd, J=8.4,5.7, 1H), 3.3-3.1 (m, 4H), 2.30 (t, J=7.4, 2H), 2.2-1.3 (m, 10H); MS (ES+): 537 (MH+ +113, 12), 424 (MH+, 50), 311 (MH+-113, 100).

3-(2'-thiophene)-prop-2*E*ene-1-amide-Arg(Pbf)-OCH$_3$ (18, R^1 = R^3 = H, R^2 = R^4 = -SCH=CH, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = Me):

^{1}H NMR identical to product obtained from PEG resin

(N,N'dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OH (18, R^1 = R^2 = R^3 = H, R^4 = CH$_2$NMe$_2$, Xaa$_2$-Xaa$_1$ = Arg(Pbf)-Aca, R = H):

^{1}H NMR (CD$_3$OD): δ 7.22 (dd, J=15.6,10.2, 1H), 6.70 (dd, J=14.8,10.2, 1H), 6.35 (d, J=14.8, 1H), 6.15 (dt, J=14.8,7.0, 1H), 4.38 (m, 1H), 3.86 (d, J=7.6, 2H), 3.30-3.15 (m, 4H), 2.88 (s,

6H), 2.29 (t, J=7.2, 2H), 2.20-1.30 (m, 10H); MS (ES+): 538 (MH^++113, 4), 425 (MH^+, 8), 312 (MH^+-113, 28), 213 (MH^+-212, 72), 157 (MH^+-268, 100).

(N,N'dimethyl)-6-amino-hexa-2*E*,4*E*-diene-1-amide-Arg(Pbf)-Aca-OCH_3, (18, R^1 = R^2 = R^3 = H, R^4 = CH_2NMe_2, Xaa_2-Xaa_1 = Arg(Pbf)-Aca, R = Me):
^1H NMR identical to product obtained from PEG resin

1H), 1.7-1.2 (m, 9H), 1.44 (s, 6H).
DBU cleavage gave very little product, MS (ES+): 841 (MH^++30, 16), 841 (MH^+, 4).

Table 3. Summary of Stille Reaction Conditions to Prepare 17 (see Scheme 4)

Entry	R^1	R^2	R^3	R^4	Xaa_2	Xaa_1	P	eq Pd_2dba_3 / eq $AsPh_3$	eq $RSnR_3$	T (°C)	time (h)	prod: sm[a]	isomer ratio[b]	diene cleaved yield[c] (%)
1	H	H	H	H	-	Gly	PEG	0.025/0.1	1.2	rt	o/n	95:5	100:0	-
2	H	H	H	H	Ala	Aca	PEG	0.1/0.4	1.2	rt	1	100:0	>95:<5	R=Me (63)
3	H	H	H	H	Arg(Pbf)	Aca	PEG	0.1/0.4	1.2	rt	3.5	100:0	>95:<5	-
4	H	H	H	H	-	Phe	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	R=H (93)
												100:0	>95:<5	R=Me (80)
5	H	H	H	H	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	R=H
												100:0	>95:<5	R=Me
6	H	H	H	H	Arg(Pbf)	Aca	Wang	0.2/0.8	2	rt	o/n	100:0	>95:<5	R=Me
7	Me	H	H	H	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	15:85	>95:<5	-
8	Me	H	H	H	Ala	Aca	PEG	0.2/0.8	5	40	o/n	52:48	>95:<5	-
9	Me	H	H	H	Ala	Aca	PEG	0.2/0.8	10	60	o/n	87:13	>95:<5	-
10	Me	H	H	H	-	Phe	Wang	0.2/0.8	10	60	o/n	65:35	>95:<5	R=H (63)
11	Me	H	H	H	Ala	Aca	Wang	0.2/0.8	10	60	o/n	-	-	-
12	H	H	H	Ph	-	Gly	PEG	0.025/0.1	1.5	rt	o/n	95:5	100:0	-
13	H	H	H	Ph	Ala	Aca	PEG	0.1/0.4	1.2	rt	o/n	100:0	>85:<15	-
14	H	H	H	Ph	Arg(Pbf)	Aca	PEG	0.1/0.4	1.2	rt	o/n	100:0	>85:<15	-
15	H	H	H	Ph	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	87:13	R=H
												100:0	100:0	R=Me
16	H	H	Ph	H	Ala	Aca	Wang	0.2/0.8	5	60	o/n	100:0	25:75	R=H
												100:0	22:78	R=Me
17	Me	H	H	Ph	Ala	Aca	Wang	0.2/0.8	10	60	o/n	100:0	89:11	R=H
												100:0	90:10	R=Me
18	Me	H	Ph	H	Ala	Aca	Wang	0.2/0.8	10	60	o/n	100:0	16:84	R=H
												100:0	22:78	R=Me
19	H	H	H	tBu	-	Gly	PEG	0.025/0.1	1.5	rt	1	2:98	-	-
20	H	H	H	tBu	-	Gly	PEG	0.025/0.1	1.5	rt	o/n	40:60	39:51:10	-
21	H	H	H	tBu	-	Gly	PEG	0.1/0.4	1.2	rt	o/n	100:0	41:48:11	-
22	H	H	H	tBu	-	Gly	PEG	0.1/0.4	1.2	rt	o/n	100:0	87:11:2	-
23	H	H	H	tBu	Ala	Aca	PEG	0.2/0.8	10	rt	o/n	100:0	79:21	-
24	H	H	H	tBu	Arg(Pbf)	Aca	PEG	0.2/0.8	10	rt	o/n	100:0	89:11	-
25	H	H	H	$(CH_2)_7CH_3$	Ala	Aca	PEG	0.1/0.4	2.5	rt	o/n	100:0	83:17	-
26	H	H	H	$(CH_2)_7CH_3$	Arg(Pbf)	Aca	PEG	0.1/0.4	2.5	rt	0/n	100:0	71:29	-
27	H	H	H	$(CH_2)_7CH_3$	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	88:12	R=H
												100:0	90:10	R=Me

28	H	H	$(CH_2)_7CH_3$	H	Ala	Aca	Wang	0.2/0.8	5	60	o/n	100:0	24:76	R=H
												100:0	23:77	R=Me
29	Me	H	H	$(CH_2)_7CH_3$	Ala	Aca	Wang	0.2/0.8	10	60	o/n	100:0	94:6	R=H
												100:0	85:15	R=Me
30	Me	H	$(CH_2)_7CH_3$	H	Ala	Aca	Wang	0.2/0.8	10	60	o/n	100:0	18:82	R=H
												100:0	15:85	R=Me
31	H	$=R^4$	H	-CH=CH-O-	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	R=Me (79)
32	H	$=R^4$	H	-CH=CH-O-	Arg(Pbf)	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	-
33	H	$=R^4$	H	-CH=CH-O-	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	R=H
												100:0	>95:<5	R=Me
34	Me	$=R^4$	H	-CH=CH-O-	Ala	Aca	Wang	0.2/0.8	5	60	o/n	100:0	>95:<5	R=H
												100:0	>95:<5	R=Me
35	H	$=R^4$	H	-CH=CH-S-	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	-
36	H	$=R^4$	H	-CH=CH-S-	Arg(Pbf)	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	R=Me (77)
37	H	$=R^4$	H	-CH=CH-S-	Arg(Pbf)	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	R=H
												100:0	>95:<5	R=Me
38	H	H	H	CH_2OH	Ala	Aca	PEG	0.1/0.4	2	rt	o/n	100:0	>95:<5	-
39	H	H	H	CH_2OH	Arg(Pbf)	Aca	PEG	0.1/0.4	2	rt	o/n	100:0	>95:<5	-
40	H	H	H	CH_2OH	-	Phe	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	-
41	H	H	H	CH_2OH	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	99:1	R=H
												100:0	100:0	R=Me
42	H	H	CH_2OH	H	Ala	Aca	PEG	0.2/0.8	3	60	o/n	100:0	0:80:20	-
43	H	H	CH_2OH	H	Ala	Aca	Wang	0.2/0.8	5	60	o/n	100:0	8:92	R=H
												100:0	10:90	R=Me
44	Me	H	H	CH_2OH	-	Phe	Wang	0.2/0.8	10	60	o/n	100:0	>95:<5	R=H (>90)
48	H	H	H	CH_2NH_2	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	58:42	>95:<5	-
49	H	H	H	CH_2NH_2	Ala	Aca	PEG	0.2/0.8	3	rt	o/n	100:0	>95:<5	-
50	H	H	H	CH_2NH_2	Arg(Pbf)	Aca	PEG	0.1/0.4	1.5	rt	o/n	50:50	>95:<5	-
51	H	H	H	CH_2NH_2	Arg(Pbf)	Aca	PEG	0.2/0.8	3	rt	o/n	100:0	>90:<10	-
52	H	H	H	CH_2NHBoc	Ala	Aca	PEG	0.1/0.4	2.5	rt	o/n	100:0	>95:<5	-
53	H	H	H	CH_2NHBoc	Arg(Pbf)	Aca	PEG	0.1/0.4	2.5	rt	o/n	100:0	>95:<5	-
54	H	H	H	CH_2NHBoc	-	Phe	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	$R=H^d$ (>90)
55	Me	H	H	CH_2NHBoc	Ala	Aca	PEG	0.2/0.8	5	40	o/n	90:10	>95:<5	-
56	Me	H	H	CH_2NHBoc	Ala	Aca	PEG	0.2/0.8	10	60	o/n	100:0	>95:<5	-
57	Me	H	H	CH_2NHBoc	-	Phe	Wang	0.2/0.8	10	60	o/n	100:0	>95:<5	$R=H^d$ (>90)
58	H	H	H	CH_2NMe_2	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	-
59	H	H	H	CH_2NMe_2	Arg(Pbf)	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	R=Me (80)

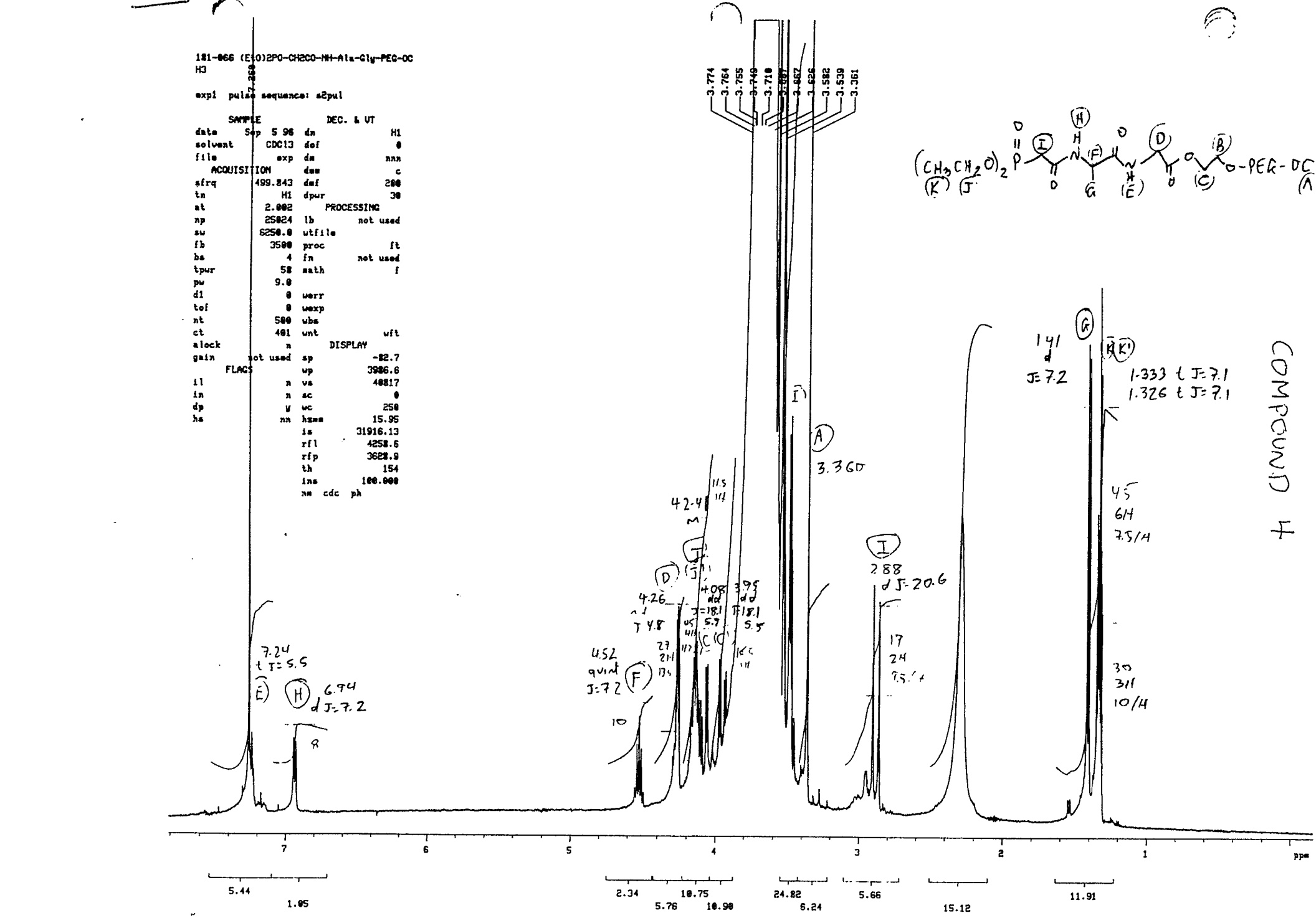
60	H	H	H	CH_2NMe_2	-	Phe	Wang	0.1/0.4	2	rt	o/n	100:0	>95:<5	R=H (>90)
61	H	H	H	CH_2NMe_2	Ala	Aca	Wang	0.1/0.4	2	rt	o/n	100:0	94:6	R=H
												100:0	>90:<10	R=Me
62	H	H	H	CH_2NMe_2	Arg(Pbf)	Aca	Wang	0.2/0.8	5	60	o/n	100:0	>95:<5	R=H
												100:0	>95:<5	R=Me
63	Me	H	H	CH_2NMe_2	-	Phe	Wang	0.2/0.8	10	60	o/n	100:0	>95:<5	R=H (>90)
64	Me	H	H	CH_2NMe_2	Ala	Aca	Wang	0.2/0.8	10	60	o/n	100:0	>90:<10	R=H
												100:0	>90:<10	R=Me
65	H	H	H	CO_2H	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	R=Me (88)
66	H	H	H	CO_2H	Arg(Pbf)	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>90:<10	-
67	H	H	H	CO_2Me	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>95:<5	R=Me (70)
68	H	H	CO_2Me	H	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	58:42	8:73:19	-
69	H	H	CO_2Me	H	Ala	Aca	PEG	0.2/0.8	3	60	o/n	100:0	22:44:33	-
70	H	H	CO_2Me	H	Ala	Aca	PEG	0.2/0.8	10	40	o/n	100:0	66:21:13	-
71	H	H	H	CO_2Me	Arg(Pbf)	Aca	PEG	0.1/0.4	1.2	rt	o/n	100:0	>95:<5	-
72	H	OEt	H	H	-	Gly	PEG	0.1/0.4	1.2	rt	o/n	100:0	>90:<10	-
73	H	OEt	H	H	Ala	Aca	PEG	0.1/0.4	1.2	rt	3.5	74:26	90:10	-
74	H	OEt	H	H	Ala	Aca	PEG	0.1/0.4	1.5	rt	o/n	100:0	>90:<10	-
75	H	OEt	H	H	Arg(Pbf)	Aca	PEG	0.1/0.4	1.2	rt	o/n	100:0	>90:<10	-
76	Me	OEt	H	H	Ala	Aca	PEG	0.2/0.8	10	rt	o/n	55:45	>90:<10	-
77	Me	OEt	H	H	Ala	Aca	PEG	0.2/0.8	10	60	o/n	>92:<8	>90:<10	-

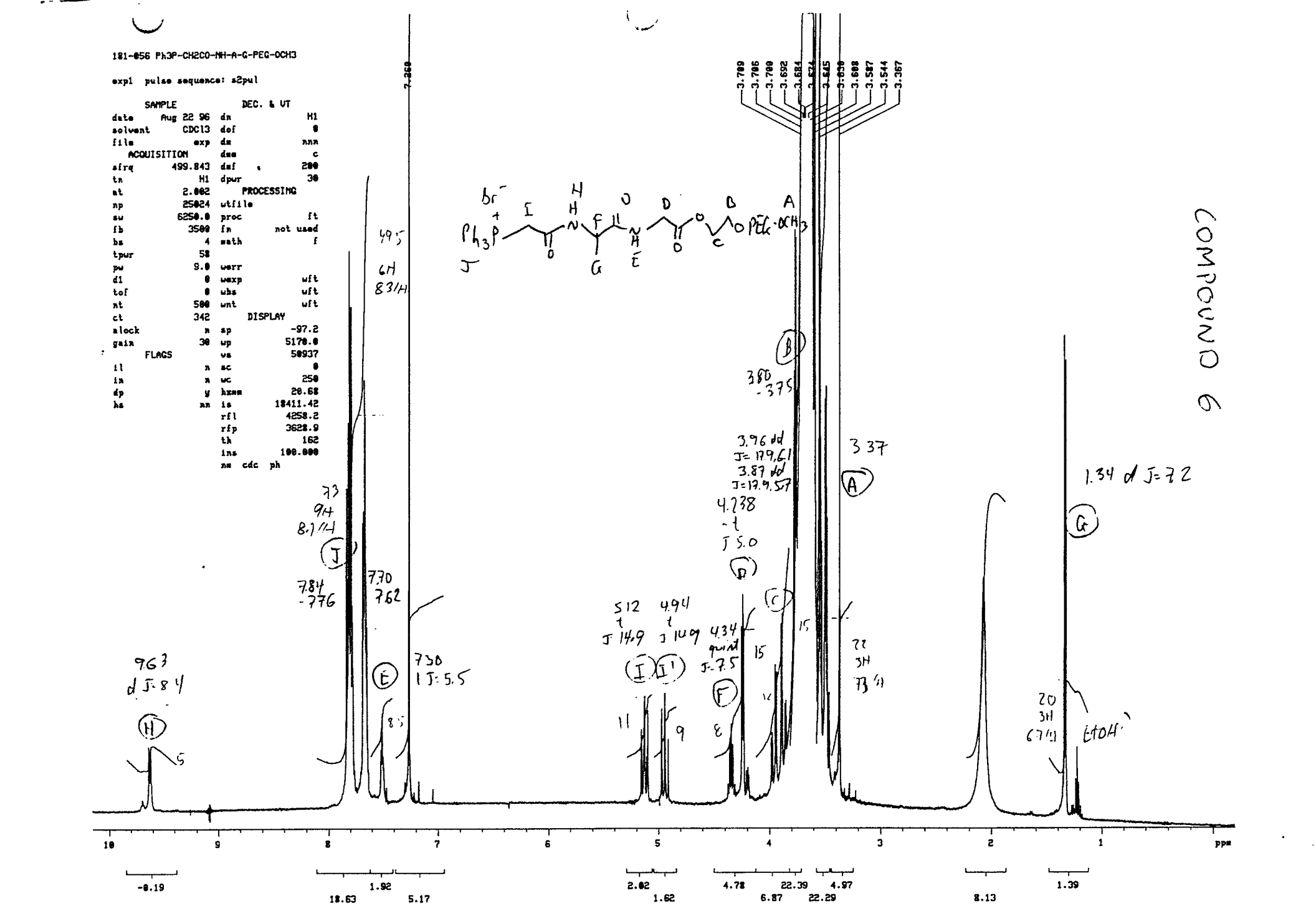
a) product:starting material ratio of PEG linked dienes, or Wang cleaved dienes determined by integration of ^{1}H NMR alkene region

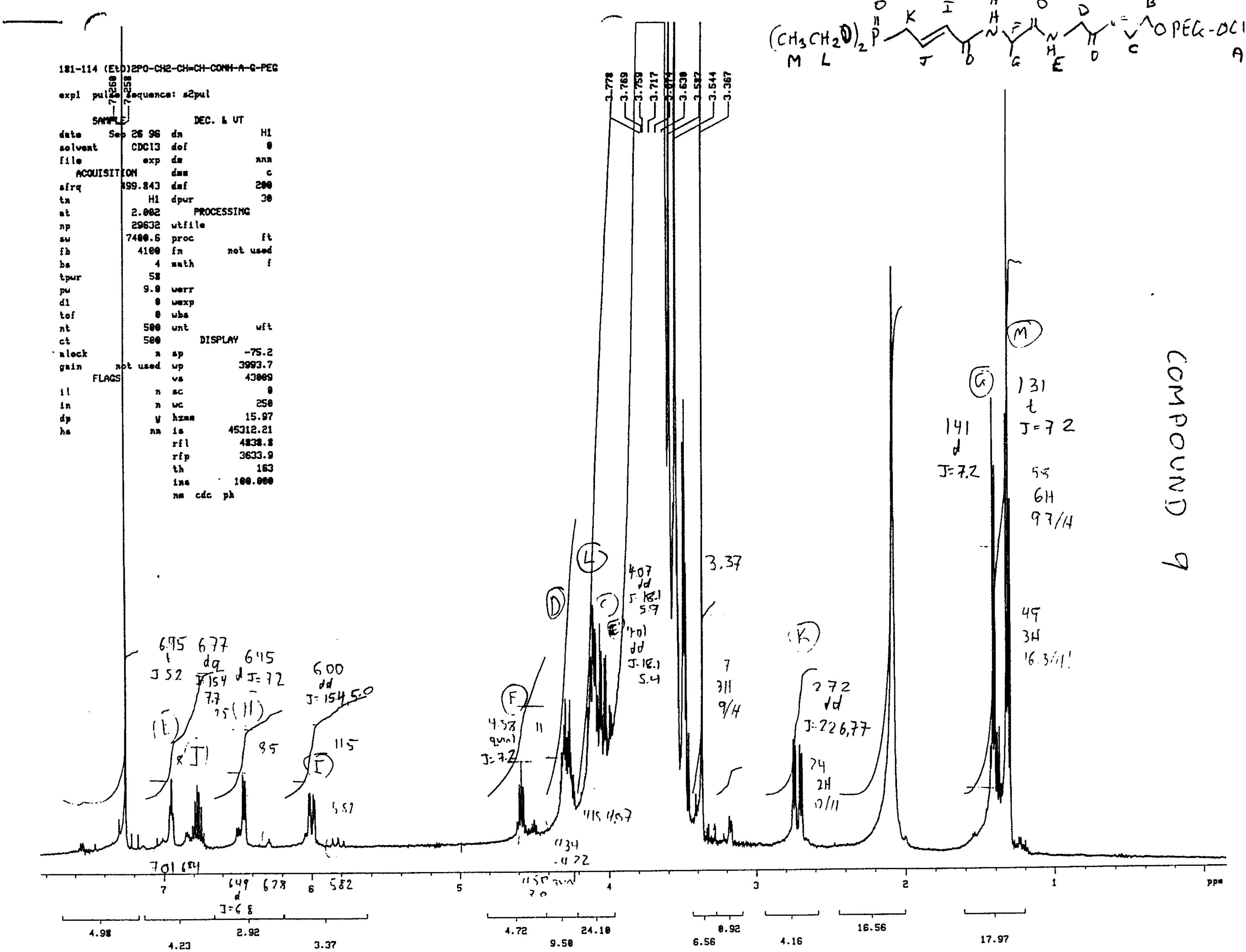
b) isomer ratio of PEG linked dienes, or Wang cleaved dienes determined by integration of ^{1}H NMR alkene region; if 2 numbers given = 2E,4E:all other isomers; if 3 numbers given =2E,4E:2E,4Z:all other isomers

c) for PEG and Phe-Wang cleaved dienes, isolated yields are given; for Aca-Wang linked dienes isolated quantities are too small for useful yield

d) $R^4 = CH_2NH_2$


181-066 (Et0)2PO-CH2CO-NH-Ala-Gly-PEG-OC
H3
expl pulse sequence: s2pul
SAMPLE
date Sep 5 96
solvent CDCl3
file exp
ACQUISITION
sfrq 499.843
tn H1
at 2.002
np 25824
sw 6250.0
fb 3500
bs 4
tpur 5s
pw 9.0
d1 0
tof 0
nt 500
ct 401
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
def 0
dm nnn
dmm c
dmf 200
dpwr 30
PROCESSING
lb not used
utfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
DISPLAY
sp -82.7
wp 3986.6
vs 40817
sc 0
wc 250
hzmm 15.95
is 31916.13
rfl 4258.6
rfp 3628.9
th 154
ins 100.000
nm cdc ph
3.774
3.764
3.755
3.749
3.718
3.667
3.626
3.582
3.539
3.361
7.24
t J=5.5
6.94
d J=7.2
4.52
quint
J=7.2
4.26
t J=4.8
4.08
dd
J=18.1
5.7
3.95
dd
J=18.1
5.5
3.360
2.88
d J=20.6
1.41
d
J=7.2
1.333 t J=7.1
1.326 t J=7.1
COMPOUND 4
ppm
5.44
1.95
2.34
10.75
5.76
10.98
24.82
6.24
5.66
15.12
11.91

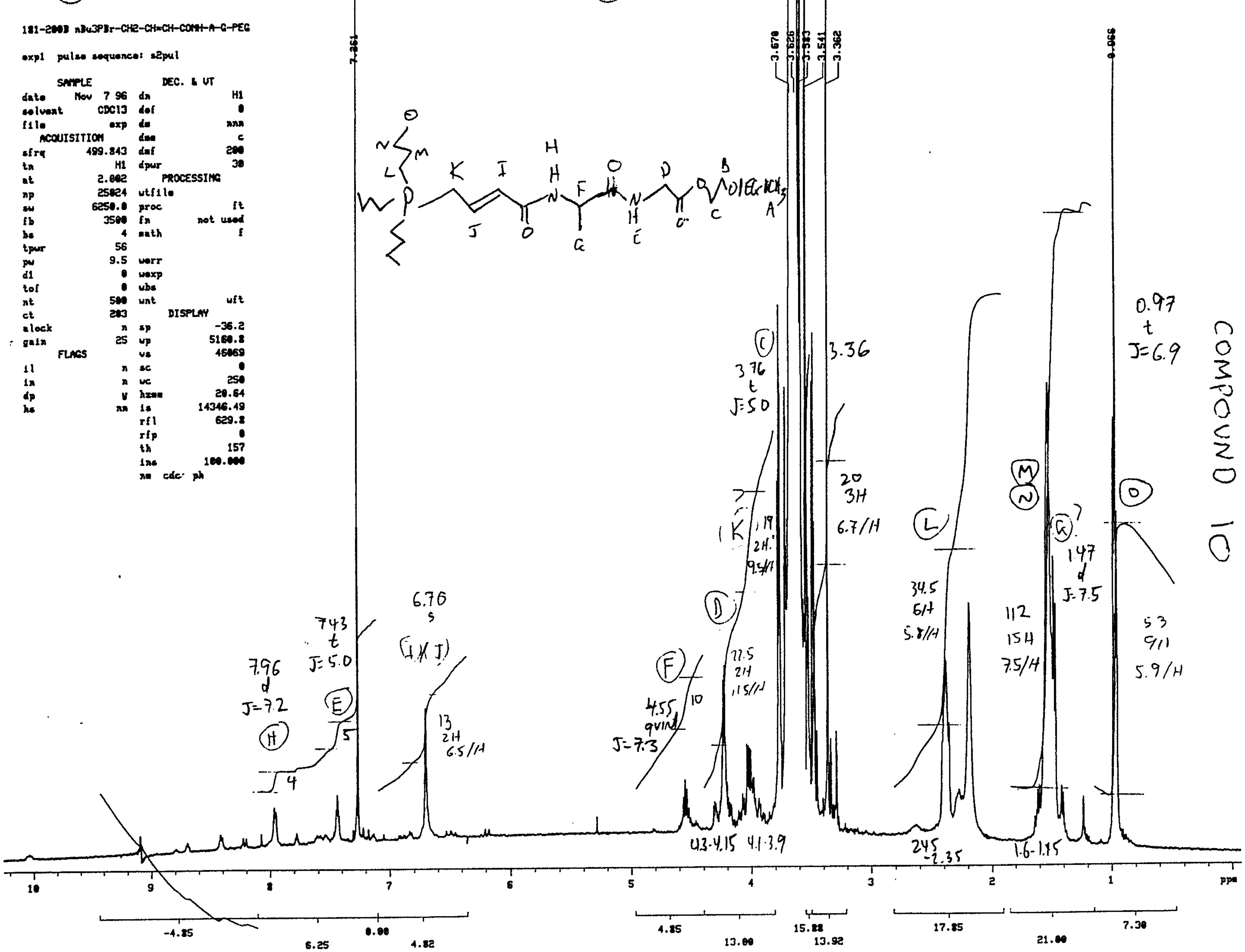

181-056 Ph3P-CH2CO-NH-A-G-PEG-OCH3
expl pulse sequence: s2pul
SAMPLE
date Aug 22 96
solvent CDCl3
file exp
ACQUISITION
sfrq 499.843
tn H1
at 2.002
np 25024
sw 6250.0
fb 3500
bs 4
tpur 58
pw 9.0
d1 0
tof 0
nt 500
ct 342
alock n
gain 30
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 30
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt wft
DISPLAY
sp -97.2
wp 5170.0
vs 50937
sc 0
wc 250
hzmm 28.68
is 18411.42
rfl 4258.2
rfp 3628.9
th 162
ins 100.000
nm cdc ph
COMPOUND 6
3.789
3.786
3.780
3.692
3.684
3.574
3.545
3.539
3.508
3.587
3.544
3.367
7.268
4.95
6H
8.31H
7.73
9H
8.71H
7.84
-7.76
7.70
7.62
7.30
1 J=5.5
9.63
d J=8.4
1H
5.12
t
J 14.9
4.94
t
J 14.9
4.34
quint
J=7.5
3.96 dd
J=17.9,6.1
3.87 dd
J=17.9,5.7
4.738
-t
J 5.0
3.80
-3.75
3.37
3H
7.73H
1.34 d J=7.2
2.0
3H
6.71H
EtOH
10
9
8
7
6
5
4
3
2
1
ppm
-8.19
18.63
1.92
5.17
2.02
1.62
4.78
6.87
22.39
22.29
4.97
8.13
1.39

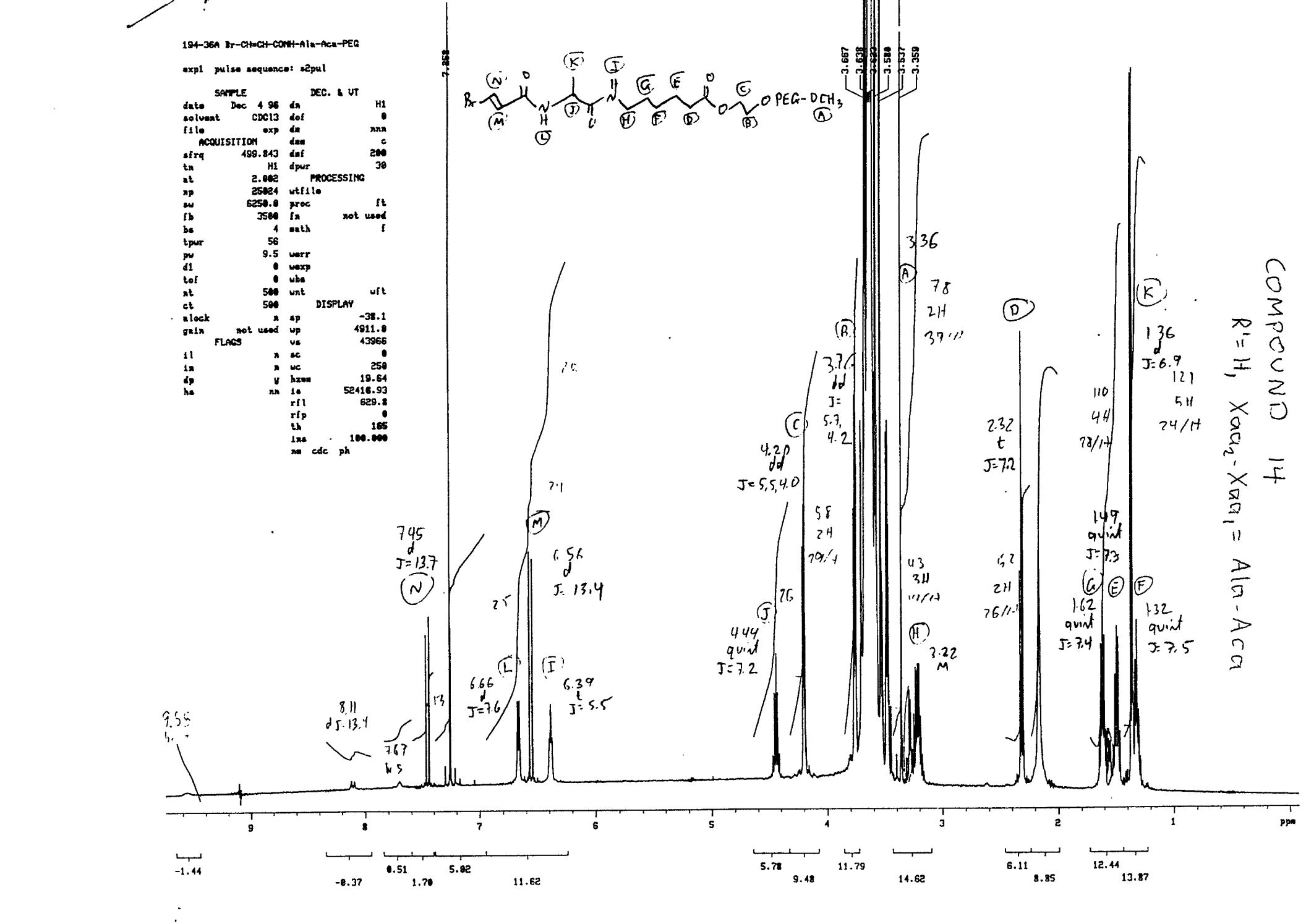

181-114 (EtO)2PO-CH2-CH=CH-CONH-A-G-PEG
exp1 pulse sequence: s2pul
SAMPLE
date Sep 26 96
solvent CDCl3
file exp
ACQUISITION
sfrq 499.843
tn H1
at 2.002
np 29632
sw 7400.6
fb 4100
bs 4
tpwr 58
pw 9.0
d1 0
tof 0
nt 500
ct 500
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 30
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
DISPLAY
sp -75.2
wp 3993.7
vs 43009
sc 0
wc 250
hzmm 15.97
is 45312.21
rfl 4838.8
rfp 3633.9
th 163
ins 100.000
nm cdc ph
7.260
7.258
3.778
3.769
3.759
3.717
3.674
3.630
3.587
3.544
3.367
ppm
7
6
5
4
3
2
1
4.98
4.23
2.92
3.37
4.72
9.50
24.10
6.56
0.92
4.16
16.56
17.97
COMPOUND 9

181-200B nBu3PBr-CH2-CH=CH-CONH-A-G-PEG

exp1 pulse sequence: s2pul

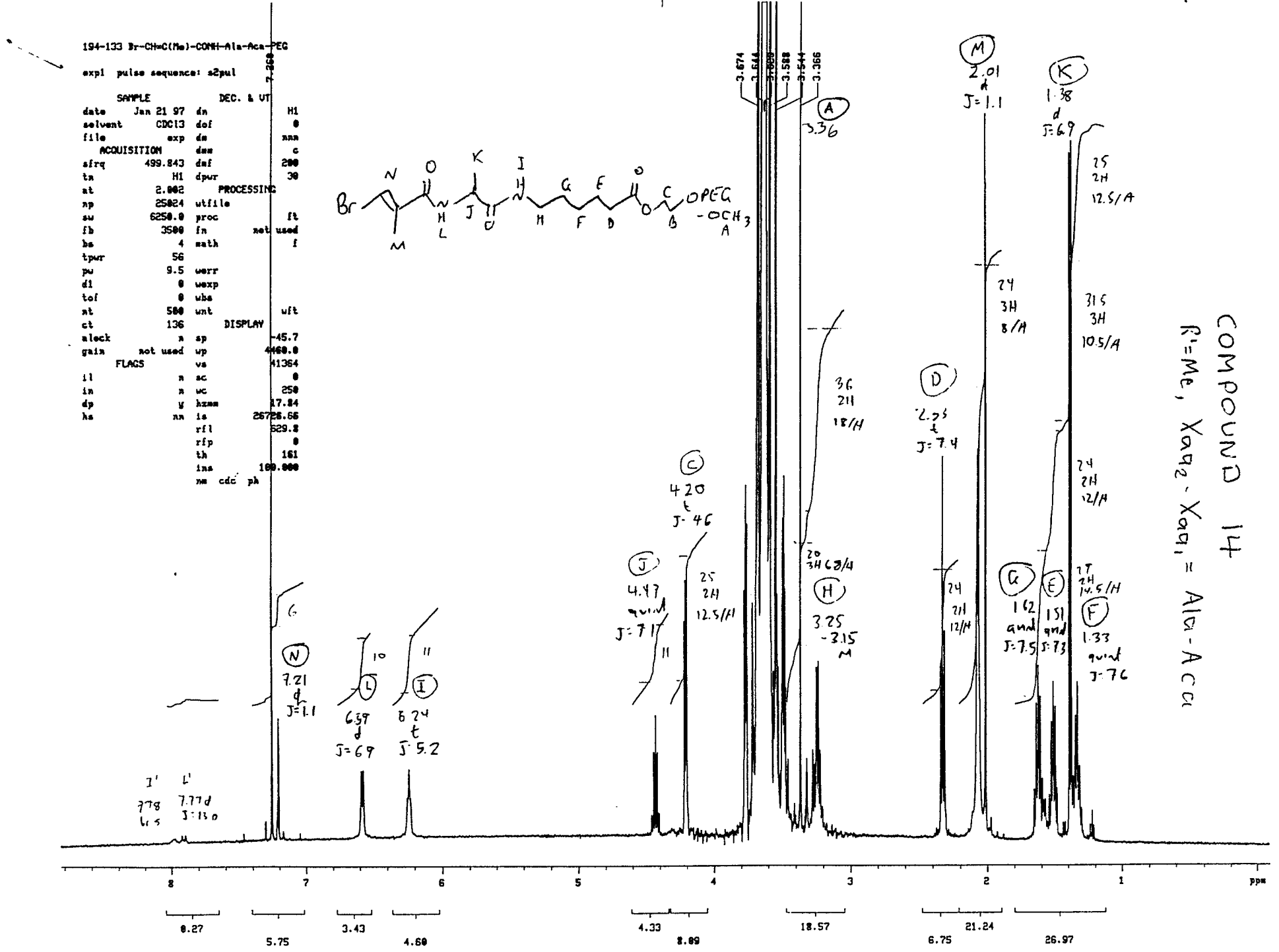
SAMPLE		DEC. & VT	
date	Nov 7 96	dn	H1
solvent	CDCl3	dof	0
file	exp	dm	nnn
ACQUISITION		dmm	c
sfrq	499.843	dmf	200
tn	H1	dpwr	30
at	2.002	PROCESSING	
np	25024	wtfile	
sw	6250.0	proc	ft
fb	3500	fn	not used
bs	4	math	f
tpwr	56		
pw	9.5	werr	
d1	0	wexp	
tof	0	wbs	
nt	500	wnt	wft
ct	203	DISPLAY	
alock	n	sp	-36.2
gain	25	wp	5160.8
FLAGS		vs	46069
il	n	sc	0
in	n	wc	250
dp	y	hzmm	20.64
hs	nn	is	14346.49
		rfl	629.2
		rfp	0
		th	157
		ins	100.000
		nm cdc ph	





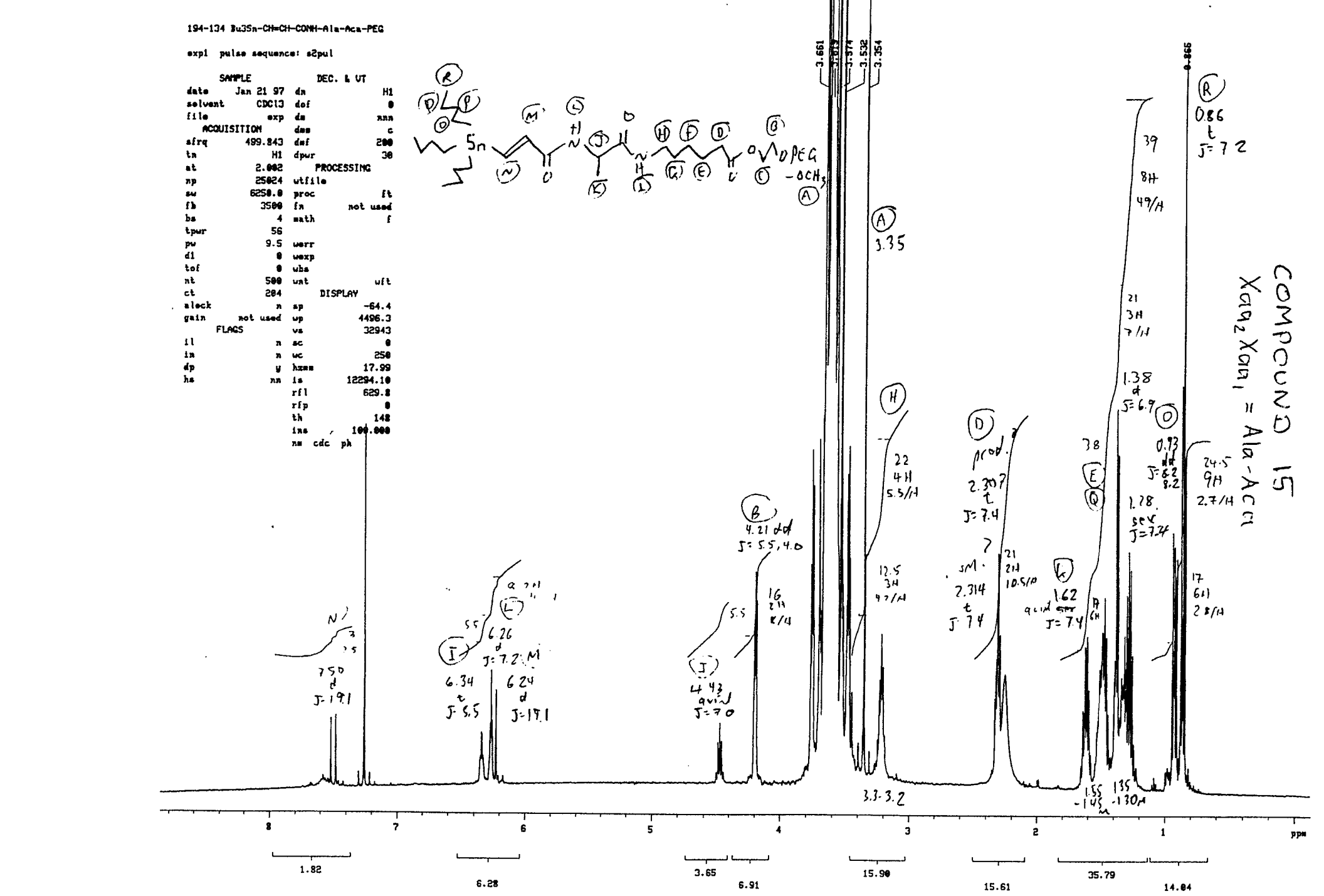
COMPOUND 14

R = H, Xaa_2-Xaa_1 = Ala-Aca



COMPOUND 14

R=Me, X_{aa_2}-X_{aa_1} = Ala-Aca


194-134 Bu3Sn-CH=CH-CONH-Ala-Aca-PEG
expl pulse sequence: s2pul
SAMPLE
date Jan 21 97
solvent CDCl3
file exp
ACQUISITION
sfrq 499.843
tn H1
at 2.002
np 25024
sw 6250.0
fb 3500
bs 4
tpur 56
pw 9.5
dl 0
tof 0
nt 500
ct 284
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & UT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 30
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
DISPLAY
sp -64.4
wp 4496.3
vs 32943
sc 0
wc 250
hzmm 17.99
is 12294.10
rfl 629.8
rfp 0
th 142
ins 100.000
nm cdc ph
COMPOUND 15
Xaa2 Xaa1 = Ala-Aca
A 3.35
B 4.21 dd J=5.5, 4.0
D 2.307 t J=7.4
E 1.38 d J=6.9
H 3.3-3.2
I 6.34 t J=5.5
J 4.43 quint J=7.0
L 6.26 d J=7.2
M 6.24 d J=19.1
N 7.50 d J=19.1
Q 1.62 quint J=7.4
R 0.86 t J=7.2
1.82
6.28
3.65
6.91
15.90
15.61
35.79
14.04
ppm