Supporting Information

Expedient Synthesis of Pseudo-Pro-Containing Peptides: Towards Constrained Peptidomimetics and Foldamers

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*^{1}H-NMR analyses of **2a**, **2b**, **5**, **10**, **12a**, **12b**, **14**, in different solvents.*

*Ts-Ala-Oxd-Phe-NH_2 (**2a**).*

^{1}H-NMR (8:2 DMSO/H_2O) δ 1.11 (d, J=7.4 Hz, 3H, AlaMe), 2.39 (s, 3H, TsMe), 2.79 (dd, J=8.4, 13.6 Hz, 1H, PheHβ), 2.97 (dd, J=4.8, 13.6 Hz, 1H, PheHβ), 4.20 (dd, J=2.6, 9.2 Hz, 1H, OxdH5), 4.38 (q, J=8.0 Hz, 1H, PheHα), 4.52 (t, J=8.8 Hz, 1H, OxdH5), 4.69 (dd, J=2.6, 8.8 Hz, 1H, OxdH4), 5.06 (dq, J=6.8, 8.8 Hz, 1H, AlaHα), 7.09 (br.s, 1H, $CONH_2$), 7.15-7.30 (m, 5H, ArH), 7.36 (d, J=8.4 Hz, 2H, ArH), 7.51 (br.s, 1H, $CONH_2$), 7.65 (d, J=8.4 Hz, 2H, ArH), 8.25 (d, J=9.2 Hz, 1H, AlaNH), 8.42 (d, J=8.0 Hz, 1H, PheNH).

^{1}H-NMR (CH_3OH) δ 1.22 (d, J=7.1 Hz, 3H, AlaMe), 2.41 (s, 3H, TsMe), 2.80 (dd, J=8.0, 13.8 Hz, 1H, PheHβ), 3.03 (dd, J=4.6, 13.8 Hz, 1H, PheHβ), 4.22 (dd, J=3.0, 9.0 Hz, 1H, OxdH5), 4.43 (q, J=7.8 Hz, 1H, PheHα), 4.49-4.70 (m, 2H, OxdH5+OxdH4), 5.19 (quint, J=8.2 Hz, 1H, AlaHα), 7.15-7.30 (m, 6H, ArH+$CONH_2$), 7.36 (m, 3H, ArH+$CONH_2$), 7.67 (d, J=8.2 Hz, 2H, ArH), 8.36 (d, J=9.0 Hz, 1H, AlaNH), 8.67 (d, J=8.2 Hz, 1H, PheNH).

*Ts-Ala-D-Oxd-Phe-NH_2 (**2b**).*

^{1}H-NMR (8:2 DMSO/H_2O) δ ^{1}H-NMR (8:2 DMSO/H_2O) δ 1.06 (d, J=7.2 Hz, 3H, AlaMe), 2.36 (s, 3H, TsMe), 2.73 (dd, J=10.2, 13.0 Hz, 1H, PheHβ), 3.08 (dd, J=4.6, 13.0 Hz, 1H, PheHβ), 3.42 (d, J=8.6 Hz, 1H, D-OxdH5), 4.34 (t, J=8.8 Hz, 1H, D-OxdH5), 4.64 (m, 1H, PheHα), 4.72 (d, J=8.6 Hz, 1H, D-OxdH4), 5.12 (quint, J=7.6 Hz, 1H, AlaHα), 7.15 (br.s, 1H, $CONH_2$), 7.16-7.25 (m, 5H, ArH), 7.32 (d, J=7.8 Hz, 2H, ArH), 7.54 (br.s, 1H, $CONH_2$), 7.60 (d, J=7.8 Hz, 2H, ArH), 8.07 (d, J=9.2 Hz, 1H, AlaNH), 8.49 (d, J=8.8 Hz, 1H, PheNH).

^{1}H-NMR (CH_3OH) δ ^{1}H-NMR (8:2 DMSO/H_2O) δ ^{1}H-NMR (8:2 DMSO/H_2O) δ 1.30 (d, J=6.8 Hz, 3H, AlaMe), 2.19 (s, 3H, TsMe), 2.84 (dd, J=10.4, 14.0 Hz, 1H, PheHβ), 3.05 (dd, J=4.6, 14.0 Hz, 1H, PheHβ), 3.63 (dd, J=3.5, 8.8 Hz, 1H, D-OxdH5), 4.36 (t, J=9.2 Hz, 1H, D-OxdH5), 4.60 (m, 1H, PheHα), 4.64 (dd, J=4.4, 8.6 Hz, 1H, D-OxdH4), 5.26 (quint, J=6.8 Hz, 1H, AlaHα), 7.15-7.30 (m, 8H, ArH+$CONH_2$), 7.44 (br.s, 1H, $CONH_2$), 7.67 (d, J=7.8 Hz, 2H, ArH), 8.11 (d, J=9.0 Hz, 1H, AlaNH), 8.54 (d, J=8.2 Hz, 1H, PheNH).

*Ns-Ala-D-Oxd-Phe-Gly-NH_2 (**5**).*

^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 1.35 (d, J=7.3 Hz, 3H, Me), 2.70 (dd, J=6.4, 13.9 Hz, 1H, PheHβ), 3.12 (dd, J=6.8, 13.9 Hz, 1H, PheHβ), 3.40 (dd, J=4.0, 8.4 Hz, 1H, D-OxdH5), 3.69-3.76 (m, 2H, GlyHα), 4.34 (t, J=9.2 Hz, 1H, D-OxdH5), 4.65-4.74 (m, 2H, D-OxdH4+PheHα), 5.22 (quint, 7.1 Hz, 1H, AlaHα), 7.06 (br.s, 1H, $CONH_2$), 7.11-7.25 (m, 6H, ArH+$CONH_2$), 7.94 (d, J=8.5 Hz, 2H, ArH), 8.23 (t, J=7.9 Hz, 1H, GlyNH), 8.33 (d, J=8.5 Hz, 2H, ArH), 8.55 (d, J=8.0 Hz, 1H, PheNH), 8.66 (d, J=9.3 Hz, 1H, AlaNH).

^{1}H-NMR (CH_3OH) δ ^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 1.25 (d, J=7.1 Hz, 3H, Me), 2.86 (dd, J=9.0, 13.9 Hz, 1H, PheHβ), 3.20(dd, J=6.4, 13.9 Hz, 1H, PheHβ), 3.55 (dd, J=3.9, 8.5 Hz, 1H, D-OxdH5), 3.80-3.90 (m, 2H, GlyHα), 4.33 (dd, J=5.0, 9.0 Hz, 1H, D-OxdH5), 4.64 (ddd, J=6.4, 8.0, 9.0 Hz, 1H, PheHα) 4.72 ((dd, J=2.6, 8.8 Hz, 1H, D-OxdH4), 5.19 (quint, 7.0 Hz, 1H, AlaHα), 7.11 (br.s, 1H, $CONH_2$), 7.15-7.25 (m, 6H, ArH+$CONH_2$), 7.98 (d, J=8.5 Hz, 2H, ArH), 8.28 (t, J=8.0 Hz, 1H, GlyNH), 8.39 (d, J=8.5 Hz, 2H, ArH), 8.64 (d, J=8.0 Hz, 1H, PheNH), 8.69 (d, J=8.2 Hz, 1H, AlaNH).

*Ts-Oxd-Dha-OMe (**10**).*

^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 2.41 (s, 3H, Me), 3.89 (s, 3H, COOMe), 4.34 (dd, J=4.0, 9.2 Hz, 1H, OxdH5), 4.62 (t, J=8.8 Hz, 1H, OxdH5), 5.25 (dd, J=3.8, 9.0 Hz, 1H, OxdH4), 6.03 (s, 1H, =CH), 6.47 (s, 1H, =CH), 7.44 (d, J=8.4 Hz, 2H, ArH), 7.94 (d, J=8.4 Hz, 2H, ArH), 10.01 (s, 1H, DhaNH).

^{1}H-NMR (CH_3OH) δ 2.49 (s, 3H, Me), 3.79 (s, 3H, COOMe), 4.28 (dd, J=4.4, 8.6 Hz, 1H, OxdH5), 4.64 (t, J=9.0 Hz, 1H, OxdH5), 5.34 (dd, J=3.4, 9.0 Hz, 1H, OxdH4), 5.86 (s, 1H, =CH), 6.32 (s, 1H, =CH), 7.45 (d, J=8.4 Hz, 2H, ArH), 7.84 (d, J=8.4 Hz, 2H, ArH), 10.12 (s, 1H, DhaNH).

*Ts-Oxd^1-(5-Me-Oxd^2)-OMe (**12a**).*

^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 1.53 (d, J=5.6 Hz, 3H, 5-Me), 2.42 (s, 3H, Ts*Me*), 3.73 (s, 3H, COOMe), 4.32 (dd, J=2.6, 9.0 Hz, 1H, Oxd^{1}H5), 4.82-4.93 (m, 2H, Oxd^{2}H4+Oxd^{1}H5), 4.94 (quint, J=5.8 Hz, 1H, Oxd^{2}H5), 6.05 (dd, J=2.4, 9.6 Hz, 1H, Oxd^{1}H4), 7.47 (d, J=8.4 Hz, 2H, ArH), 7.93 (d, J=8.4 Hz, 2H, ArH).

^{1}H-NMR (CH_3OH) δ 1.61 (d, J=6.4 Hz, 3H, 5-Me), 2.49 (s, 3H, Ts*Me*), 3.82 (s, 3H, COOMe), 4.42 (dd, J=3.6, 9.2 Hz, 1H, Oxd^{1}H5), 4.79-4.83 (m, 2H, Oxd^{1}H5+Oxd^{2}H4), 4.90 (dq, J=4.0, 6.4 Hz, 1H, Oxd^{2}H5), 6.13 (dd, J=3.4, 9.8Hz, 1H, Oxd^{1}H4), 7.43 (d, J=8.2 Hz, 2H, ArH), 8.00 (d, J=8.2 Hz, 2H, ArH).

*Ts-D-Oxd^1-(5-Me-Oxd^2)-OMe (**12b**).*

^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 1.52 (d, J=6.4 Hz, 3H, 5-Me), 2.43 (s, 3H, Ts*Me*), 3.81 (s, 3H, COOMe), 4.57 (d, J=6.0 Hz, 1H, Oxd^{2}H4), 4.71 (dd, J=2.8, 8.8 Hz, 1H, D-Oxd^{1}H5), 4.74 (t, J=9.2 Hz, 1H, D-Oxd^{1}H5), 4.94 (quint, J=6.0 Hz, 1H, Oxd^{2}H5), 5.97 (dd, J=3.2, 8.8 Hz, 1H, D-Oxd^{1}H4), 7.46 (d, J=8.0 Hz, 2H, ArH), 7.86 (d, J=8.0 Hz, 2H, ArH).

^{1}H-NMR (CH_3OH) δ 1.61 (d, J=6.4 Hz, 3H, 5-Me), 2.49 (s, 3H, Ts*Me*), 3.91 (s, 3H, COOMe), 4.58 (dd, J=3.2, 9.2 Hz, 1H, Oxd^{1}H5), 4.63 (d, J=5.6 Hz, 1H, Oxd^{2}H4), 4.75 (t, J=9.6 Hz, 1H, Oxd^{1}H5), 4.86 (quint, J=6.4 Hz, 1H, Oxd^{2}H5), 6.06 (dd, J=3.2, 9.2 Hz, 1H, Oxd^{1}H4), 7.43 (d, J=8.0 Hz, 2H, ArH), 7.95 (d, J=8.0 Hz, 2H, ArH).

*Ts-Oxd^1-Phe^2-Oxd^3-Phe^4-OH (**14**).*

^{1}H-NMR (8:2 DMSO-d6/H_2O) δ 2.38 (s, 3H, Me), 2.68 (dd, J=3.3, 13.8 Hz, 1H, Phe^{2}Hβ),2.95-3.05 (m, 1H, Phe^{4}Hβ), 3.22 (m, 2H, Phe^{2}Hβ+Phe^{4}Hβ), 4.06 (dd, J=3.8, 8.4 Hz, 1H, Oxd^{1}H5), 4.20 (dd, J=4.0, 8.4 Hz, 1H, Oxd^{3}H5), 4.53 (q, J= 6.6 Hz, 1H, Phe^{4}Hα), 4.67 (t, J=9.0 Hz, 2H, Oxd^{1}H5+Oxd^{3}H5), 4.98 (dd, J=3.6, 8.8 Hz, 1H, Oxd^{3}H4), 5.02 (dd, J=3.8, 9.2 Hz, 1H, Oxd^{1}H4), 5.57 (q, J= 6.8 Hz, 1H, Phe^{2}Hα), 7.12-7.28 (m, 12H, Phe^{2}ArH+Phe^{4}ArH+TsArH), 7.64 (d, J=8.4 Hz, 2H, ArH), 8.85 (d, J=6.8 Hz, 1H, Phe^{4}NH), 8.93 (d, J=7.6 Hz, 1H, Phe^{2}NH).

^{1}H-NMR (CH_3OH) δ 2.45 (s, 3H, Me), 2.70 (dd, J=3.8, 13.6 Hz, 1H, Phe^{2}Hβ),3.00-3.12 (m, 2H, Phe^{4}Hβ), 3.18 (dd, J=5.6, 13.6 Hz, 1H, Phe^{2}Hβ), 4.14 (dd, J=3.6, 8.6 Hz, 1H, Oxd^{1}H5), 4.22 (q, J= 6.6 Hz, 1H, Phe^{4}Hα), 4.35 (dd, J=4.1, 8.5 Hz, 1H, Oxd^{3}H5), 4.59 (t, J=8.9 Hz, 2H, Oxd^{1}H5), 4.64 (t, J=8.8 Hz, 2H, Oxd^{1}H5), 4.76 (dd, J=3.8, 8.6 Hz, 1H, Oxd^{3}H4), 4.99 (dd, J=3.6, 9.0 Hz, 1H, Oxd^{1}H4), 5.68 (q, J= 6.8 Hz, 1H, Phe^{2}Hα), 7.18-7.30 (m, 10H, Phe^{2}ArH+Phe^{4}ArH), 7.38(d, J=8.4 Hz, 2H, ArH), 7.59 (d, J=8.4 Hz, 2H, ArH), 8.90 (d, J=6.8 Hz, 1H, Phe^{4}NH), 9.00 (d, J=7.4 Hz, 1H, Phe^{2}NH).

Table S1. VT-^{1}H-NMR Δδ/Δt values (p.p.b./K) of Ts-Ala-L/D-Oxd-Phe-NH_2 (**2a**, **2b)**, and Ts-Ala-D-Oxd-Phe-GlyNH_2 (**5**) in different solvents.

compd	solvent	AlaNH	PheNH	GlyNH	$CONH_2$
	$CDCl_3$	-12.9	-9.6	-	-11.2/-9.2
2a	8:2 DMSO-d6/H_2O	-6.8	-4.3	-	-5.9/-5.4
	CH_3OH	-7.0	-4.6	-	-6.1/-5.8
	$CDCl_3$	-6.7	-5.7	-	-5.9/-5.4
2b	8:2 DMSO-d6/H_2O	-4.2	-2.6	-	-5.6/-6.8
	CH_3OH	-4.4	-3.0	-	-6.0/-6.9
	9:1 $CDCl_3$/DMSO-d6	-5.9	-4.2	-6.5	-6.1/-6.4
5	8:2 DMSO-d6/H_2O	-4.8	-2.7	-7.4	-6.0/-6.4
	CH_3OH	-5.1	-3.1	-6.2	-6.0/-6.4

Table S2. VT-^{1}H-NMR Δδ/Δt values (p.p.b./K) of Ts-Oxd-DHA-OMe (**10**), in different solvents.

compd	solvent	DHANH
	$CDCl_3$	-1.8
10	8:2 DMSO-d6/H_2O	-4.6
	CH_3OH	-4.9

Table S3. VT-^{1}H-NMR Δδ/Δt values (p.p.b./K) of Ts-Oxd^1-Phe^2-Oxd^3-Phe^4-OH (**14**), in different solvents.

compd	solvent	Phe^{2}NH	Phe^{4}NH
	9:1 $CDCl_3$/DMSO-d6	-2.9	-4.2
14	8:2 DMSO-d6/H_2O	-5.2	-3.8
	CH_3OH	-5.6	-4.2

Table S4. Non-obvious ROESY cross-peaks observed for Ts-Ala-L-Oxd-Phe-NH_2 (**2a**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
PheNH-PheHβ$_{2.8}$	vs	PheNH-PheHβ$_{3.0}$	s
PheNH-OxdH5$_{4.2}$	s	PheNH-PheHα	m
PheNH-OxdH4	vs	PheNH-OxdH5$_{4.5}$	m
PheNH-PheArH	m	PheNH-CONH$_{7.3}$	m
AlaNH-AlaMe	vs	AlaNH-AlaHα	m
AlaNH-TsArH$_{7.8}$	m	TsArH$_{7.8}$-AlaHα	s
TsArH$_{7.8}$-AlaMe	m	CONH$_{7.3}$-PheHα	vs
CONH$_{7.3}$-PheHβ$_{3.0}$	s	CONH$_{7.3}$-PheHβ$_{2.8}$	s
PheArH-PheHβ$_{3.0}$	s	PheArH-PheHβ$_{2.8}$	s
PheArH-PheHα	s	CONH$_{7.0}$-PheHα	m
PheHα-PheHβ$_{3.0}$	s	PheHα-PheHβ$_{2.8}$	s

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S5. Non-obvious ROESY cross-peaks observed for Ts-Ala-D-Oxd-Phe-NH_2 (**2b**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
PheNH-PheHβ$_{2.7}$	s	PheNH-PheHβ$_{3.1}$	w
PheNH-OxdH5$_{3.4}$	m	PheNH-PheHα	m
PheNH-OxdH4	vs	PheNH-PheArH	m
PheNH-CONH$_{7.6}$	m	AlaNH-AlaMe	s
AlaNH-AlaHα	m	TsArH$_{7.6}$-AlaMe	m
TsArH$_{7.6}$-AlaHα	m	TsArH$_{7.6}$-AlaNH	w
CONH$_{7.6}$-PheHβ$_{3.1}$	m	CONH$_{7.6}$-PheHβ$_{2.7}$	w
CONH$_{7.6}$-PheHα	s	CONH$_{7.3}$-PheHβ$_{2.7}$	w
CONH$_{7.3}$-PheHβ$_{3.1}$	w	CONH$_{7.3}$-OxdH5$_{3.4}$	w
CONH$_{7.3}$-PheHα	w	PheArH-PheHβ$_{2.7}$	s
PheArH-PheHβ$_{3.1}$	s	PheArH-OxdH5$_{3.4}$	m
PheArH-PheHα	s	OxdH4-AlaMe	w
PheHα-PheHβ$_{2.7}$	s	PheHα-PheHβ$_{3.1}$	vs
TsMe-AlaMe	w		

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S6. Non-obvious ROESY cross-peaks observed for Ns-Ala-D-Oxd-Phe-GlyNH_2 (**5**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
AlaMe-AlaNH	s	AlaMe-$NsArH_{7.9}$	m
AlaMe-OxdH4	w	AlaNH-PheHα	w
AlaNH-AlaHα	m	PheNH-$OxdH5_{4.3}$	w
PheNH-GlyNH	w	PheNH-PheArH	w
PheNH-OxdH4	vs	PheNH-PheHα	m
PheNH-$OxdH5_{3.4}$	m	PheNH-$PheHβ_{2.7}$	vs
PheNH-$PheHβ_{3.2}$	w	PheNH-GlyHα	w
GlyNH-$CONH_{7.1}$	w	GlyNH-$CONH_{7.3}$	m
GlyNH-PheHα	vs	GlyNH-GlyHα	vs
GlyNH-$PheHβ_{3.2}$	m	GlyNH-$PheHβ_{2.7}$	w
GlyNH-AlaHα	w	$NsArH_{7.9}$-AlaHα	w
$NsArH_{8.2}$-AlaMe	w	$NsArH_{8.2}$-AlaHα	w
$NsArH_{8.2}$-GlyHα	w	PheArH-$PheHβ_{2.7}$	s
PheArH-$PheHβ_{3.2}$	s	PheArH-$OxdH5_{3.4}$	m
PheArH-PheHα	s	GlyHα-$CONH_{7.1}$	m
GlyHα-$CONH_{7.3}$	s	PheHα-$PheHβ_{2.7}$	m
PheHα-$PheHβ_{3.2}$	s	$NsArH_{7.9}$-$PheHβ_{2.7}$	w
$NsArH_{7.9}$-$PheHβ_{3.2}$	m	$NsArH_{7.9}$-GlyHα	w

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S7. Non-obvious ROESY cross-peaks observed for Ts-Oxd-Dha-OMe (**10**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
DhaNH-$OxdH5_{4.3}$	s	DhaNH-$OxdH5_{4.7}$	w
DhaNH-OxdH4	vs	DhaNH-C=$CH_{5.9}$	w
DhaNH-C=$CH_{6.3}$	m	DhaNH-COOMe	w
$TsArH_{7.8}$-C=$CH_{5.9}$	w	$TsArH_{7.8}$-C=$CH_{6.3}$	w
$TsArH_{7.8}$-OxdH4	s	$TsArH_{7.8}$-COOMe	w
$TsArH_{7.4}$-C=$CH_{5.9}$	w	$TsArH_{7.4}$-C=$CH_{6.3}$	w
$TsArH_{7.4}$-COOMe	w	COOMe-TsMe	w
C=$CH_{5.9}$-COOMe	m	$OxdH5_{4.3}$-TsMe	w
$OxdH5_{4.7}$-TsMe	w		

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S8. Non-obvious ROESY cross-peaks observed for Ts-Oxd^1-(5-Me-Oxd^2)-OMe (**12a**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
$TsArH_{7.9}$-Oxd^2H4	w	$TsArH_{7.9}$-Oxd^1H4	m
Oxd^1H4–Oxd^2H4	w	Oxd^2H5-COOMe	m
Oxd^2H4-COOMe	w	COOMe-$Oxd^1H5_{4.3}$	w
COOMe-5'Me	w		

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S9. Non-obvious ROESY cross-peaks observed for Ts-D-Oxd^1-(5-Me-Oxd^2)-OMe (**12b**) in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
$TsArH_{7.9}$-Oxd^1H4	w	$TsArH_{7.9}$-COOMe	w
$TsArH_{7.5}$-COOMe	w	Oxd^1H4-Oxd^2H4	w
$Oxd^1H5_{4.3}$-5'Me	w	Oxd^2H5-COOMe	m
Oxd^2H4-COOMe	w		

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

Table S10. Non-obvious ROESY cross-peaks observed for Ts-Oxd^1-Phe^2-Oxd^3-Phe^4-OH (**14**), in 8:2 DMSO-d6/H_2O.

Cross peak[a]	Intensity[b]	Cross peak[a]	Intensity[b]
Phe^2NH-$Phe^2H\beta_{2.6}$	vs	Phe^2NH-$Phe^2H\beta_{3.2}$	w
Phe^2NH-Oxd^1H4	vs	Phe^2NH-$Phe^2H\alpha$	m
Phe^2NH-$TsArH_{7.5}$	w	Phe^2NH-Phe^2ArH	m
Phe^4NH-$Phe^4H\beta_{3.0}$	s	Phe^4NH-$Phe^4H\alpha$	m
Phe^4NH-Oxd^3H4	vs	$TsArH_{7.3}$-$Oxd^1H5_{4.7}$	w
Phe^4ArH-$Phe^4H\beta_{3.0}$	vs	Phe^4ArH-$Phe^4H\alpha$	m
Phe^2ArH-$Phe^2H\beta_{2.6}$	s	Phe^2ArH-$Phe^2H\beta_{3.2}$	m
Phe^2ArH-$Phe^2H\alpha$	m	$Phe^4H\alpha$-$Phe^4H\beta_{3.0}$	vs
$Phe^4H\alpha$-$Phe^4H\beta_{3.2}$	w	$Phe^2H\alpha$-$Phe^2H\beta_{3.2}$	s
$Phe^2H\alpha$-$Phe^2H\beta_{2.6}$	w		

[a] Stereochemistry has been omitted. [b] vs = very strong, s = strong, m = medium, w = weak.

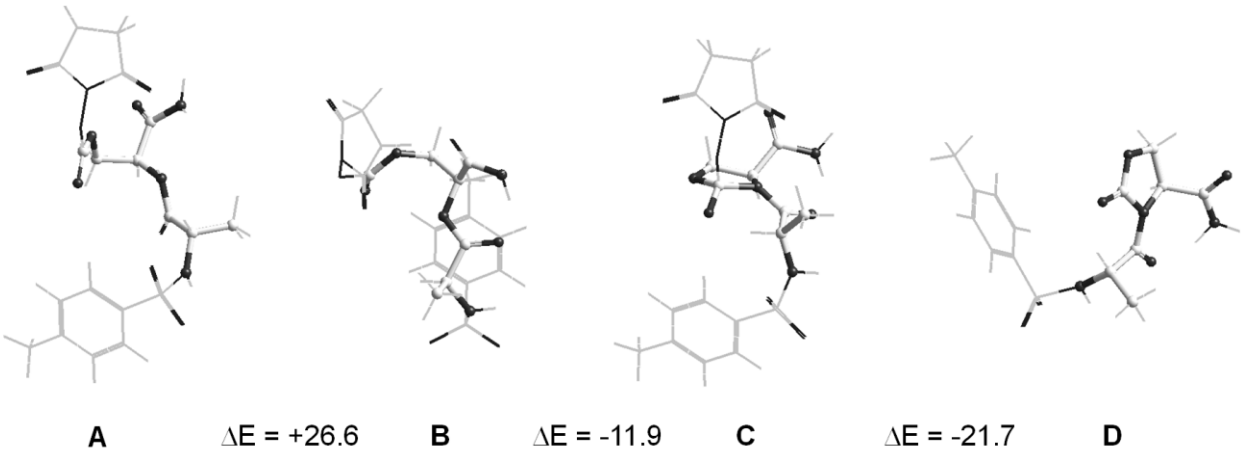

Figure S1. Structures and ΔE of the intermediates calculated for the cyclization of the model peptide Ts-Ala-Ser-NH_2 with DSC and DIPEA, employing ab initio molecular orbital (MO) theory. A systematic conformational analysis for the structures was done at the HF/6-31G* level. The conformers were re-optimized at the HF/6-31G** level. Backbones are rendered in balls-and-cylinders, the rest in sticks. Optimization was performed by conjugate gradient algorithm, convergence at 0.001; energies are expressed in Kcal mol^{-1}. The following structures were included in the computations of **A**-**D**, but are not visualized for clarity: **A**, DIPEA; **B**, $DIPEAH^+$; **C**, $DIPEAH^+$; **D**, 1-hydroxypyrrolidine-2,5-dione and DIPEA.

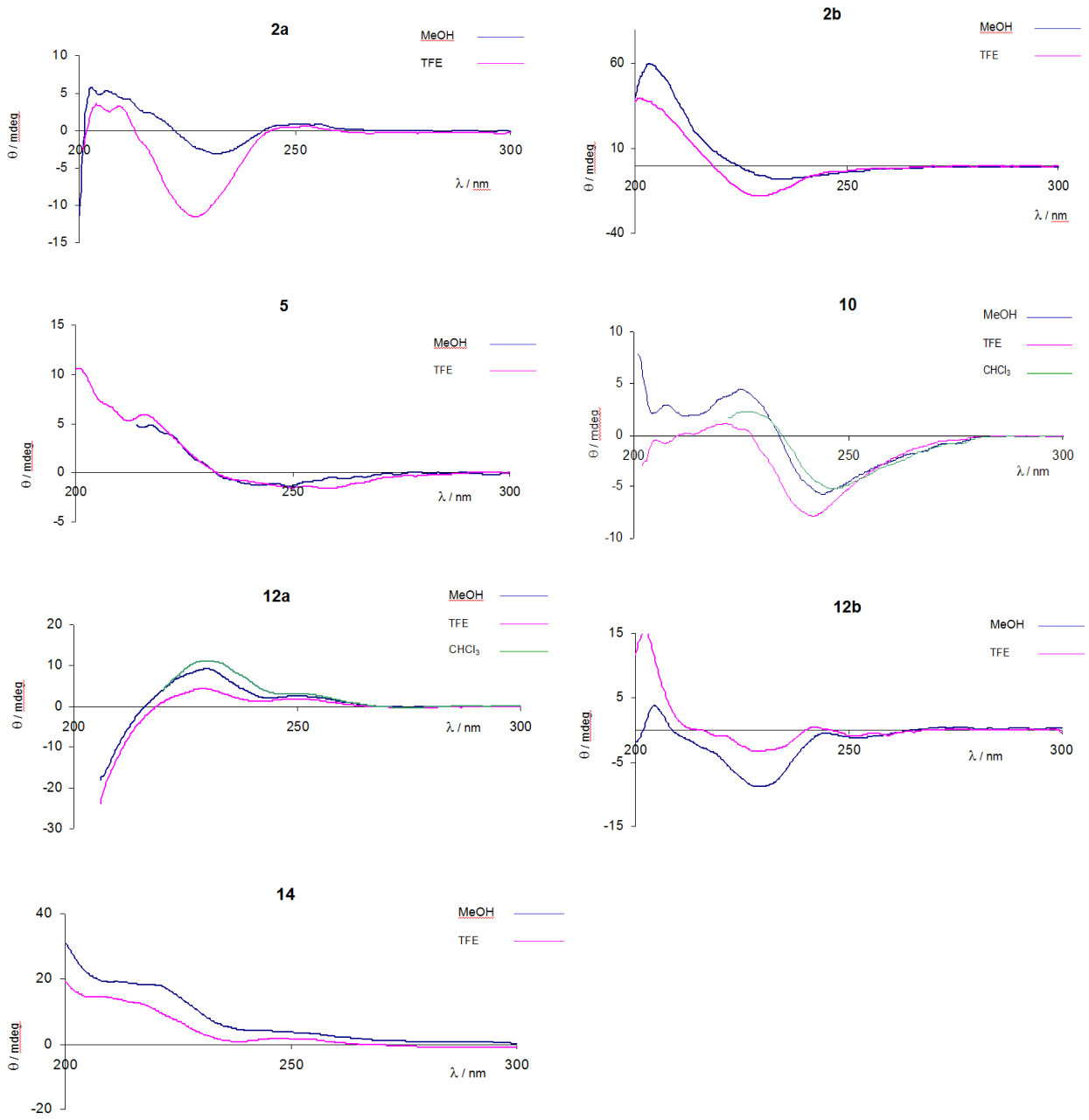

Figure S2. ECD spectra were recorded from 200 to 300 nm at 25 °C. Solutions were made up in spectral grade solvents and run in a 0.01 cm quartz cell. For each sample the absorbance value was set to 1.0 at λ_{max} (225÷260 nm); concentrations used were in the range 5÷11 mM. Data are reported in ellipticity (millidegree).