Supporting Information

Lysine-based 2:1-[α/aza]- pseudopeptide series used as additives in polymeric membranes for CO_2 capture: synthesis, structural studies, and application

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Characterization data

N-tert-butyloxycarbonylaminophtalimide **(2)** was obtained as a white crystal (yield 86%) after recrystallization from ethyl acetate; m.p. 214 - 216 °C; **^{1}H NMR** (300 MHz**, CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 1.49 (2 s, 9H, C(CH$_3$)$_3$), 6.61 (br s, 1H, NH), 7.76-7.79 (m, 2H, H arom Phth), 7.89-7.92 (m, 2H, H arom Phth). **^{13}C NMR** (75 MHz, **CDCl$_3$**, 8.0 mmol L^{-1}) δ_c 28.4 (C(CH$_3$)$_3$), 83.81 (C(CH$_3$)$_3$), 124.65 (CH arom Phth), 130.68 (C arom Phth), 135.37 (CH arom Pht), 154.07 (N-COO*t*-Bu), 166.13 (O=C-Pht). **IR (KBr)** $\tilde{\upsilon}_{max}$ = 3395 cm^{-1} (NH); 1706 cm^{-1}, 1740 cm^{-1}, 1783 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{13}H_{14}N_2O_4$]: calculated [M+H]$^+$ (m/z) 263.0954; found, 263.1034.

N-benzyl-*N*-tert-butyloxycarbonylaminophtalimide **(3)** was obtained as white solid (yield 90%) after flash chromatography (0.04 − 0.063 µm) using (15% ethyl acetate : 85% petroleum ether) as eluent; m.p. 107 - 109 °C; **^{1}H NMR** (300 MHz**, CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 1.37 and 1.52 (2 s, 9H, C(CH$_3$)$_3$), 4.85 and 4.89 (2 s, 2H, NCH$_2$), 7.27 - 7.44 (2 m, 5H, H arom Ph), 7.73-7.84 (m, 4H, H arom Phth). **^{13}C NMR** (75 MHz, **CDCl$_3$**, 8.0 mmol L^{-1}**)** δ_c 28.59 and 28.86 (C(CH$_3$)$_3$), 53.35 and 55.32 (NCH$_2$), 83.17 and 83.95 (C(CH$_3$)$_3$), 124.41 (CH arom Phth), 128.58 (CH arom Ph), 129.02 (CH arom Ph), 129.20 (CH arom Ph), 129.73 (CH arom Ph), 130.44 (C arom), 130.64 (C arom), 135.20 (CH arom Phth), 154.18 (N-COO*t*-Bu), 165.71 (O=C-Pht). **IR (NaCl)** $\tilde{\upsilon}_{max}$ = 1737 cm^{-1}, 1796 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{20}H_{20}N_2O_4$]: calculated [M+Na]$^+$ (m/z) 375.1321; found, 375.1314.

N-alkylaminophtalimide **(4)** was obtained as a pure yellow solid (quantitative 100%) without purification; m.p. 109 - 110 °C; **^{1}H NMR** (300 MHz, **CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 4.22 (s, 2H, NCH$_2$), 4.56 (br, 1H, NH), 7.27-7.47 (m, 5H, H arom Ph), 7.71-7.83 (m, 4H, H arom Phth). **^{13}C NMR** (75 MHz, **CDCl$_3$**, 10.0 mmol L^{-1}) δ_c 55.97 (NCH2), 124.07 (CH arom Phth), 128.73 (CH arom Ph), 129.22 (CH arom Ph), 129.89 (CH arom Ph), 130.92 (C arom Phth), 134.87 (CH arom Phth), 136.69 (C arom Ph), 167.06 (O=C-Phth). **IR (NaCl)** $\tilde{\upsilon}_{max}$ = 3290 cm^{-1} (NH); 1774 cm^{-1}, 1719 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{15}H_{12}N_2O_2$]: calculated [M+H]$^+$ (m/z) 253.0977; found, 253.0963.

Pht-azaPhe-Ala-OMe **(5a)** was obtained as a pure white solid (yield 92%) after trituration with cold diethyl ether; m.p. 158 - 161 °C; **^{1}H NMR (**300 MHz**, CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 1.38 and 1.40 (d, 3H, CH$_3$), 3.72 (s, 3H, COOCH$_3$), 4.53 (m, 1H, C$^{\alpha}$H), 4.86–4.97 (m, 2H, CH$_2$), 5.31 and 5.37 (d, 1H, NH), 7.23-7.42 (m, 5H, H arom Ph), 7.75-7.85 (m, 4H, H arom Phth). **^{13}C NMR** (75 MHz, **CDCl$_3$**, 10.0 mmol L^{-1}) δ_c 19.60 (CH$_3$), 50.19 (C$^{\alpha}$H), 53.14 (COOCH$_3$), 53.62 (NCH2), 124.62 (CH arom Phth), 128.89 (CH arom Ph), 129.20 (CH arom Ph), 129.80 (C arom Phth), 135.33 (C arom Ph), 135.51 (CH arom Phth), 156.15 (O=C-NH), 165.84 (O=C-Phth), 174.32 (COOCH$_3$). **IR (ATR)** $\tilde{\upsilon}_{max}$ = 3353 cm^{-1} (NH); 1647 cm^{-1}, 1677 cm^{-1}, 1736 cm^{-1}, 1751 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{20}H_{19}N_3O_5$]: calculated [M+Na+MeOH]$^+$ (m/z) 436.1479; found, 436.1457.

Boc-azaPhe-Ala-OMe **(6a)** was obtained as a pure white solid (yield 89%) after flash chromatography (0.04 − 0.063 µm) using (30% ethyl acetate : 70% petroleum ether) as eluent; m.p. 90 - 91 °C; **^{1}H NMR (**300 MHz**, CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 1.42-1.47 (m, 12H, CH$_3$ and C(CH$_3$)$_3$), 3.76 (s, 3H, COOCH$_3$), 4.50-4.60 (m, 1H, C$^{\alpha}$H), 4.85 (br s, 2H, NCH$_2$), 5.91 and 5.94 (d, 1H, NH), 5.97 (br s, 1H, NHBoc), 7.26-7.37 (m, 5H, H arom Ph). **^{13}C NMR** (75 MHz, CDCl$_3$, 10.0 mmol L^{-1}) δ_c 19.70 (CH$_3$), 28.75 (C(CH$_3$)$_3$), 49.84 (C$^{\alpha}$H), 51.25 (NCH$_2$), 52.99 (COOCH$_3$), 83.04 (C(CH$_3$)$_3$), 128.53 (CH

arom Ph), 129.45 (CH arom Ph), 129.59 (CH arom Ph), 136.73 (C arom Ph), 154.90 (COO*t*-Bu), 157.61 (O=C-NH), 174.75 ($\underline{C}OOCH_3$). **IR (ATR)** $\tilde{\upsilon}_{max}$ = 3207 cm^{-1}, 3415 cm^{-1} (NH); 1647 cm^{-1}, 1723 cm^{-1}, 1732 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{17}H_{25}N_3O_5]$: calculated $[M+H]^+$ (m/z) 352.1872; found, 352.1878.

Boc-azaPhe-Lys(z)-OMe **(6b)** was obtained as an oily sticky product (yield 85%) after flash chromatography (0.04 − 0.063 µm) using (45% ethyl acetate : 55% petroleum ether) as eluent; **^{1}H NMR** (300 MHz**, $CDCl_3$,** 8.0 mmol L^{-1}) δ_H 1.40-1.90 (m, 15H, ($C^{\beta}H_2$, $C^{g}H_2$, $C^{\delta}H_2$) and $C(CH_3)_3$), 3.15-3.21 (m, 2H, $C^{\varepsilon}H_2$), 3.73 (s, 3H, $COOCH_3$), 4.51-4.58 (m, 1H, $C^{\alpha}H$), 4.99 (br s, 2H, NCH_2), 5.07 (s, 2H, CH_2(Z)), 5.89 and 5.92 (d, 1H, NH), 6.02 (br s, 1H, NHBoc), 7.22-7.33 (m, 10H, H arom Ph). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ_c .70 (CH_3), δ_c 22.89 ($C^{\gamma}H_2$), 28.73 ($C(\underline{C}H_3)_3$), 29.82($C^{\delta}H_2$), 33.33 ($C^{\beta}H_2$), 41.39 ($C^{\varepsilon}H_2$), 51.39 (NCH_2), 53.00 (OCH_3), 53.61 ($C^{\alpha}H$), 67.23 ($O\underline{C}H_2$), 83.10 ($\underline{C}(CH_3)_3$), 128.56 (CH arom Ph), 128.70 (CH arom Ph), 128.76 (CH arom Ph), 129.15 (CH arom Ph), 129.46 (CH arom Ph), 129.59 (CH arom Ph), 136.72 (C arom Ph), 137.38 (C arom Ph), 154.87 (COO*t*-Bu), 156.17 (O=$\underline{C}$-NH), 157.86 ($\underline{C}OOCH_2Ph$), 174.13 ($\underline{C}OOCH_3$). **IR (ATR)** $\tilde{\upsilon}_{max}$ = 3331 cm^{-1}, 3439 cm^{-1} (NH); 1656 cm^{-1}, 1701 cm^{-1}, 1718 cm^{-1}, 1735 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{28}H_{38}N_4O_7]$: calculated $[M+Na]^+$ (m/z) 565.2638; found, 565.2643; calculated $[M+K]^+$ (m/z) 581.3723; found, 581.2377.

Boc-Phe-azaPhe-Ala-OMe **(7a)** was obtained as a white solid (yield 74%) after flash chromatography (0.04 − 0.063 µm) using (50% ethyl acetate : 50% petroleum ether) as eluent; m.p. 149 - 150 °C; **^{1}H NMR** (300 MHz**, $CDCl_3$,** 10.0 mmol L^{-1}) δ_H 1.37-1.43 (m, 12H, CH_3 and $C(CH_3)_3$), 2.88-2.95 and 3.01-3.08 (m, 2H, CH_2), 3.71 (s, 3H, $COOCH_3$), 4.03 (m, 1H, CH), 4.28 (br s, 1H, NHBoc), 4.43-4.51 (m, 1H, CH), 4.90-4.95 (br m, 2H, NCH_2), 6.2 (br s, 1H, NH), 7.06-7.30 (m, 10H, H arom Ph), 7.73 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_c 18.71 (CH_3), 28.88 ($C(\underline{C}H_3)_3$), 37.83 (CH_2), 50.11 ($C^{\alpha}H$), 52.01 (NCH_2), 52.86 ($COO\underline{C}H_3$), 56.0 ($C^{\alpha}H$), 81.55 ($\underline{C}(CH_3)_3$), 128.05 (CH arom Ph), 128.25 (CH arom Ph), 129.15 (CH arom Ph), 129.42 (CH arom Ph), 129.63 (CH arom Ph), 129.85 (CH arom Ph), 136.45 (C arom Ph), 137.10 (C arom Ph), 156.43 (COO*t*-Bu), 157.57 (O=C-NH), 171.08 (O=C-NH), 174.88 ($\underline{C}OOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3370 cm^{-1}, 3440 cm^{-1} (NH); 1656 cm^{-1}, 1673 cm^{-1}, 1705 cm^{-1}, 1723 cm^{-1}, 1743 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{26}H_{34}N_4O_6]$: calculated $[M+Na]^+$ (m/z) 521.2376; found, 521.2344.

Boc-D-Phe-azaPhe-Ala-OMe **(7b)** was obtained as a white solid (yield 70%) after flash chromatography (0.04 − 0.063 µm) using (50% ethyl acetate : 50% petroleum ether) as eluent; m.p. 72 - 73 °C; **^{1}H NMR** (300 MHz, **$CDCl_3$,** 8.0 mmol L^{-1}) δ_H 1.39-1.41 (m, 12H, CH_3 and $C(CH_3)_3$), 2.82-2.89 and 3.09-3.16 (m, 2H, CH_2), 3.71 (s, 3H, $COOCH_3$), 4.09-4.16 (m, 1H, $C^{\alpha}H$), 4.42-4.49 (br m, 1H, $C^{\alpha}H$), 4.67 (br s, 2H, NCH_2), 4.79 (br d, 1H, NHBoc), 6.04 (br s, 1H, NH), 7.12-7.35 (m, 10H, H arom Ph), 7.52 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ_c 18.57 (CH_3), 28.88 ($C(\underline{C}H_3)_3$), 37.90 (CH_2), 50.03 ($C^{\alpha}H$), 51.86 (NCH_2), 52.85 ($COO\underline{C}H_3$), 56.27 ($C^{\alpha}H$), 81.96 ($\underline{C}(CH_3)_3$), 128.16 (CH arom Ph), 128.35 (CH arom Ph), 129.23 (CH arom Ph), 129.56 (CH arom Ph), 129.75 (CH arom Ph), 129.82 (CH arom Ph), 136.30 (C arom Ph), 137.18 (C arom Ph), 156.69 (COO*t*-Bu), 157.54 (O=C-NH), 170.90 (O=C-NH), 174.67 ($\underline{C}OOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3372 cm^{-1}, 3439 cm^{-1} (NH), 1657 cm^{-1}, 1674 cm^{-1}, 1705 cm^{-1}, 1721 cm^{-1}, 1741 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{26}H_{34}N_4O_6]$: calculated $[M+Na]^+$ (m/z) 521.2376; found, 521.2389.

Boc-Lys(z)-azaPhe-Lys(z)-OMe **(7c)** was obtained as a white foam (yield 72%) after flash chromatography (0.04 − 0.063 μm) using (60% dichloromethane : 38.5% ethyl acetate : 1.5% methanol) as eluent; **^{1}H NMR** (300 MHz**, $CDCl_3$**, 8.0 mmol L^{-1}) δ_H 1.31 (s, 9H, $C(CH_3)$), 1.32-1.78 (m, 12H, 2*($C^{\beta}H_2$, $C^{g}H_2$, $C^{\delta}H_2$)), 2.98-3.04 (m, 2H, $C^{\varepsilon}H_2$), 3.07-3.14 (m, 2H, $C^{\varepsilon}H_2$), 3.62 (s, 3H, $COOCH_3$), 3.73 (br m, 1H, $C^{\alpha}H$), 4.45-4.47 (m, 1H, $C^{\alpha}H$), 4.78 (br s, 1H, NHZ), 4.36 and 4.86 (m, 2H, NCH_2), 4.99 (s, 2H, CH_2(Z)), 5.00 (s, 2H, CH_2(Z)), 5.06 (br, 1H, NHBoc), 5.24 (br s, 1H, NHZ), 5.91 (br s, 1H, NH), 7.17-7.26 (m, 15H, H arom Ph), 7.75 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ 22.79 ($C^{\gamma}H_2$), 22.93 ($C^{\gamma}H_2$), 29.01 ($C(\underline{C}H_3)$), 29.51($C^{\delta}H_2$), 29.98 ($C^{\delta}H_2$), 31.23 ($C^{\beta}H_2$), 32.41 ($C^{\beta}H_2$), 40.70 ($C^{\varepsilon}H_2$), 41.32 ($C^{\varepsilon}H_2$), 51.91 (NCH_2), 52.92 (OCH_3), 53.76 ($C^{\alpha}H$), 54.02 ($C^{\alpha}H$), 67.33 (OCH_2), 67.43 (OCH_2), 81.27 ($\underline{C}(CH_3)_3$), 128.40 (CH arom Ph), 128.75 (CH arom Ph), 128.85 (CH arom Ph), 129.19 (CH arom Ph), 129.30 (CH arom Ph), 129.35 (CH arom Ph), 137.20 (C arom Ph), 156.69 ($\underline{C}$OO*t*-Bu), 157.29 (O=$\underline{C}$-CH_2Ph), 157.68 (O=$\underline{C}$-NH), 172.20 (O=C-NH), 174.06 ($\underline{C}OOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3378 cm^{-1}, 3449 cm^{-1} (NH), 1652 cm^{-1}, 1677 cm^{-1}, 1701 cm^{-1}, 1717 cm^{-1}, 1735 cm^{-1}, 1748 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{42}H_{56}N_6O_{10}]$: calculated $[M+Na]^+$ (m/z) 827;3956 found, 827.3978; calculated $[M+K]^+$ (m/z) 843.3695 found, 843.3715.

Boc-D-Lys(z)-azaPhe-Lys(z)-OMe **(7d)** was obtained as a white foam (yield 69%) after flash chromatography (0.04 − 0.063 μm) using (60% dichloromethane : 38.5% ethyl acetate : 1.5% methanol) as eluent; **^{1}H NMR** (300 MHz**, $CDCl_3$**, 8.0 mmol L^{-1}) δ_H 1.41 (s, 9H, $C(CH_3)$), 1.42-1.87 (m, 12H, 2*($C^{\beta}H_2$, $C^{g}H_2$, $C^{\delta}H_2$)), 3.06-3.11 (m, 2H, $C^{\varepsilon}H_2$), 3.16-3.20 (m, 2H, $C^{\varepsilon}H_2$), 3.68 (s, 3H, $COOCH_3$), 3.80 (m, 1H, $C^{\alpha}H$), 4.41-4.44 (m, 1H, $C^{\alpha}H$), 4.48 and 5.00 (m, 2H, NCH_2), 4.82 br s, 1H, NHZ), 5.05 (s, 2H, CH_2(Z)), 5.08 (s, 2H, CH_2(Z)), 5.24 (br, 1H, NHBoc), 5.43 (br s, 1H, NHZ), 6.15 and 6.16 (br d, 1H, NH), 7.26-7.34 (m, 15H, H arom Ph), 7.83 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ 22.51 ($C^{\gamma}H_2$), 23.13 ($C^{\gamma}H_2$), 28.99 ($C(\underline{C}H_3)$), 29.43 ($C^{\delta}H_2$), 30.21 ($C^{\delta}H_2$), 30.92 ($C^{\beta}H_2$), 31.71 ($C^{\beta}H_2$), 40.27 ($C^{\varepsilon}H_2$), 40.91 ($C^{\varepsilon}H_2$), 51.96 (NCH_2), 52.82 (OCH_3), 54.18 ($C^{\alpha}H$), 55.36 ($C^{\alpha}H$), 67.09 (OCH_2), 67.48 (OCH_2), 81.81($\underline{C}(CH_3)_3$), 128.35 (CH arom Ph), 128.65 (CH arom Ph), 128.83 (CH arom Ph), 128.91 (CH arom Ph), 129.15 (CH arom Ph), 129.23 (CH arom Ph), 129.59 (CH arom Ph), 137.10 (C arom Ph), 137.39 (C arom Ph), 137.55 (C arom Ph), 157.25 ($\underline{C}$OO*t*-Bu), 157.41 (O=$\underline{C}$-CH_2Ph), 157.63 (O=$\underline{C}$-CH_2Ph), 157.97 (O=C-NH), 171.82 (O=C-NH), 174.28 ($\underline{C}OOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3302 cm^{-1}, 3375 cm^{-1}, 3449 cm^{-1} (NH), 1652 cm^{-1}, 1675 cm^{-1}, 1702 cm^{-1}, 1718 cm^{-1}, 1734 cm^{-1}, 1749 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{42}H_{56}N_6O_{10}]$: calculated $[M+Na]^+$ (m/z) 827.3956 found, 827.3986; calculated $[M+K]^+$ (m/z) 843.3695 found, 843.3714.

Boc-Phe-azaPhe-Lys(z)-OMe **(7e)** was obtained as a white foam (yield 65%) after flash chromatography (0.04 − 0.063 μm) using (70% dichloromethane : 29% ethyl acetate : 1.0% methanol) as eluent; **^{1}H NMR** (300 MHz**, $CDCl_3$**, 10.0 mmol L^{-1}) δ_H 1.38 (s, 9H, $C(CH_3)$), 1.48-1.85 (m, 6H, ($C^{\beta}H_2$, $C^{g}H_2$, $C^{\delta}H_2$)), 2.74-2.80 and 2.94-3.01 (m, 2H, CH_2), 3.18-3.26 (m, 2H, $C^{\varepsilon}H_2$), 3.69 (s, 3H, $COOCH_3$), 3.97 (m, 1H, $C^{\alpha}H$), 4.02 (br s, 1H, NHBoc), 4.48-4.54 (m, 1H, $C^{\alpha}H$), 5.02 and 5.03 (br d, 2H, NCH_2), 5.08 (s, 2H, CH_2(Z)), 5.40 (br s, 1H, NHZ), 5.97 and 5.99 (br d, 1H, NH), 6.97-7.34 (m, 15H, H arom Ph), 7.58 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ 22.89 ($C^{\gamma}H_2$), 28.96 ($C(\underline{C}H_3)$), 29.49 ($C^{\delta}H_2$), 32.33 ($C^{\beta}H_2$), 37.61 (CH_2Ph), 41.23 ($C^{\varepsilon}H_2$), 52.12 (NCH_2), 52.80 (OCH_3), 53.75 ($C^{\alpha}H$), 55.91 ($C^{\alpha}H$), 67.28 (OCH_2), 81.61($\underline{C}(CH_3)_3$), 128.01 (CH arom Ph), 128.28 (CH arom Ph), 128.74 (CH arom Ph), 128.90 (CH arom Ph), 129.18 (CH arom Ph), 129.36 (CH arom Ph),

129.57 (CH arom Ph), 129.93 (CH arom Ph), 136.55 (C arom Ph), 137.07 (C arom Ph), 137.35 (C arom Ph), 156.46 (COO*t*-Bu), 157.19 (O=C-CH_2Ph), 157.45 (O=C-NH), 171.20 (O=C-NH), 173.87 ($COOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3374 cm^{-1}, 3444 cm^{-1} (NH), 1653 cm^{-1}, 1674 cm^{-1}, 1706 cm^{-1}, 1721 cm^{-1}, 1744 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{37}H_{47}N_5O_8$]: calculated $[M+Na]^+$ (m/z) 712.3322 found, 712.3339; calculated $[M+K]^+$ (m/z) 728.3062 found, 728.3042.

Boc-D-Phe-azaPhe-Lys(z)-OMe **(7f)** was obtained as a white foam (yield 62%) after flash chromatography (0.04−0.063 µm) using (70% dichloromethane : 29% ethyl acetate : 1.0% methanol) as eluent; **^{1}H NMR** (300 MHz**, $CDCl_3$**, 10.0 mmol L^{-1}) δ_H 1.37 (s, 9H, $C(CH_3)$), 1.23-1.87 (m, 6H, ($C^{\beta}H_2$, $C^{g}H_2$, $C^{\delta}H_2$)), 2.71-2.79 and 2.93-3.00 (m, 2H, CH_2), 3.18-3.23 (m, 2H, $C^{\varepsilon}H_2$), 3.68 (s, 3H, $COOCH_3$), 4.11-4.14 (m, 1H, $C^{\alpha}H$), 4.37-4.44 (m, 1H, $C^{\alpha}H$), 4.55 and 4.68 (br, 2H, NCH_2), 4.75 (br s, 1H, NHBoc), 5.02 (s, 2H, CH_2(Z)), 5.24-5.31 (br m, 1H, NHZ), 6.08 and 6.10 (br d, 1H, NH), 7.10-7.33 (m, 15H, H arom Ph), 7.78 (br s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$, 10.0 mmol L^{-1}) δ 23.37 ($C^{\gamma}H_2$), 28.90 ($C(CH_3)$), 29.51 ($C^{\delta}H_2$), 31.70 ($C^{\beta}H_2$), 37.81 (CH_2Ph), 41.01 ($C^{\varepsilon}H_2$), 52.07 (NCH_2), 52.78 (OCH_3), 54.18 ($C^{\alpha}H$), 56.18 ($C^{\alpha}H$), 67.13 (OCH_2), 81.09 ($C(CH_3)_3$), 128.15 (CH arom Ph), 128.30 (CH arom Ph), 128.69 (CH arom Ph), 129.17 (CH arom Ph), 129.52 (CH arom Ph), 129.73 (CH arom Ph), 136.11 (C arom Ph), 137.36 (C arom Ph), 156.95 (COO*t*-Bu), 157.22 (O=C-CH_2Ph), 157.85 (O=C-NH), 171.10 (O=C-NH), 174.04 ($COOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3376 cm^{-1}, 3444 cm^{-1} (NH), 1652 cm^{-1}, 1673 cm^{-1}, 1707 cm^{-1}, 1720 cm^{-1}, 1744 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{37}H_{47}N_5O_8$]: calculated $[M+Na]^+$ (m/z) 712.3322 found, 712.3327; calculated $[M+K]^+$ (m/z) 728.3062 found, 728.3028.

Boc-(Phe-azaPhe-Ala)$_2$-OMe **(8a)** was obtained as a white solid (yield 87%) after flash chromatography (0.04 − 0.063 µm) using (60% ethyl acetate : 40% petroleum ether) as eluent; m.p. 132 - 133 °C; **^{1}H NMR** (300 MHz, **CD_3CN**, 8.0 mmol L^{-1}) δ_H 1.18 and 1.21 (d, 3H, CH_3), 1.34-1.38 (m, 12H, CH_3 and $C(CH_3)_3$), 2.77-2.84 (m, 1H, CH_2), 2.96-3.04 (m, 2H, CH_2), 3.18-3.24 (m, 1H, CH_2), 3.62 (s, 3H, $COOCH_3$), 3.89-3.98 (m, 1H, $C^{\alpha}H$), 4.02-4.09 (m, 1H, $C^{\alpha}H$), 4.20-4.29 (m, 2H, 2*$C^{\alpha}H$), 4.48-4.84 (br m, 4H, 2*NCH_2), 5.62 (br s, 1H, NH), 6.37 (br s, 1H, NH), 6.53 (br s, 1H, NH), 7.17-7.32 (m, 21H: 20H, arom Ph, and 1H, NH), 9.01 (br s, 2H, 2*NH). **^{13}C NMR** (75 MHz, **CD_3CN**, 10.0 mmol L^{-1}**)** δ_c 17.33 (CH_3), 18.02 (CH_3), 28.62 ($C(CH_3)_3$), 37.46 (CH_2), 37.59 (CH_2), 50.52 ($C^{\alpha}H$), 50.66 ($C^{\alpha}H$), 52.75 ($C^{\alpha}H$ and $COOCH_3$), 52.94 (NCH_2), 53.32 (NCH_2), 54.63 ($C^{\alpha}H$), 81.3 ($C(CH_3)_3$), 127.81 (CH arom Ph), 128.30 (CH arom Ph), 128.78 (CH arom Ph), 129.19 (CH arom Ph), 129.34 (CH arom Ph), 129.53 (CH arom Ph), 129.70 (CH arom Ph), 129.83 (CH arom Ph), 130.20 (CH arom Ph), 130.28 (CH arom Ph), 130.37 (CH arom Ph), 130.68 (CH arom Ph), 137.61 (C arom Ph), 138.01 (C arom Ph), 138.52 (C arom Ph), 139.91 (C arom Ph), 158.03 (O=C-NH), 159.41 (O=C-NH), 171.4 (O=C-NH), 175.33 ($COOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3259 cm^{-1}, 3351 cm^{-1}, 3401 cm^{-1}, 3438 cm^{-1} (NH), 1665 cm^{-1}, 1700 cm^{-1}, 1741 cm^{-1} (C=O). **HRMS (ESI)** for [$C_{46}H_{56}N_8O_9$]: calculated $[M+Na]^+$ (m/z) 887.4062 found, 887.4068.

Boc-(D-Phe-azaPhe-Ala)$_2$-OMe **(8b)** was obtained as a white solid (yield 85%) after flash chromatography (0.04 − 0.063 µm) using (60% ethyl acetate : 40% petroleum ether) as eluent; m.p. 172 - 173 °C; **^{1}H NMR** (300 MHz, **CD_3CN**, 8.0 mmol L^{-1}) δ_H 1.28 and 1.30 (d, 3H, CH_3), 1.34 (s, 9H, $C(CH_3)_3$),1.35 and 1.37 (d, 3H, CH_3), 2.73-2.81 (m, 1H, CH_2), 2.91-2.98 (m, 1H, CH_2), 3.06-3.10 (m, 1H, CH_2), 3.17-3.23 (m, 1H, CH_2), 3.62 (s, 3H, $COOCH_3$), 3.89-4.08 (m, 2H, 2*$C^{\alpha}H$), 4.10-4.24

(m, 2H, 2*C$^{\alpha}$H), 4.33-4.67 (br m, 4H, 2*NCH$_2$), 5.62 (br s, 1H, NH), 6.45-6.57 (br, 2H, 2NH), 7.12-7.31 (m, 21H: 20H, arom Ph, and 1H, NH), 8.73 (s, 1H, NH), 9.13 (br s, 1H, NH). **^{13}C NMR** (75 MHz, **CD$_3$CN**, 10.0 mmol L^{-1}) δ_c 17.11 (CH$_3$), 18.11 (CH$_3$), 28.70 (C(<u>C</u>H$_3$)$_3$), 36.81 (CH$_2$), 37.36 (CH$_2$), 50.52 (C$^{\alpha}$H), 52.27 (NCH$_2$), 52.64 (C$^{\alpha}$H and COO<u>C</u>H$_3$), 52.86 (NCH$_2$), 55.63 (C$^{\alpha}$H), 56.43 (C$^{\alpha}$H), 81.18 (<u>C</u>(CH$_3$)$_3$), 127.83 (CH arom Ph), 127.96 (CH arom Ph), 128.13 (CH arom Ph), 128.43 (CH arom Ph), 129.20 (CH arom Ph), 129.28 (CH arom Ph), 129.61 (CH arom Ph), 129.77 (CH arom Ph), 130.35 (CH arom Ph), 137.95 (C arom Ph), 138.41 (C arom Ph), 138.96 (C arom Ph), 158.32 (O=C-NH), 159.12 (O=C-NH), 171.26 (O=C-NH), 176.38 (<u>C</u>OOCH$_3$). **IR (CDCl$_3$)** $\tilde{\upsilon}_{max}$ = 3240 cm^{-1}, 3351 cm^{-1}, 3423 cm^{-1} (NH), 1635 cm^{-1}, 1665 cm^{-1}, 1704 cm^{-1}, 1741 cm^{-1} (C=O). **HRMS (ESI)** for [C$_{46}$H$_{56}$N$_8$O$_9$]: calculated [M+Na]$^+$ (m/z) 887.4062 found, 887.4066.

Boc-(Lys(z)-azaPhe-Lys(z))$_2$-OMe **(8c)** was obtained as a white foam (yield 64%) after flash chromatography (0.04 − 0.063 µm) using (50% dichloromethane : 48% ethyl acetate : 2% methanol) as eluent; **^{1}H NMR** (300 MHz, **CD$_3$CN**, 8.0 mmol L^{-1}) δ_H 1.37 (s, 9H, C(CH$_3$),), 1.38-1.78 (m, 24H, 4*(C$^{\beta}$H$_2$, C^{g}H$_2$, and C$^{\delta}$H$_2$)), 3.02-3.09 (m, 8H, 4* (C$^{\varepsilon}$H$_2$)), 3.64 (s, 3H, COOCH$_3$), 3.66-3.69 (br m, 1H, C$^{\alpha}$H), 3.93-3.99 (m, 2H, 2*C$^{\alpha}$H), 4.13-4.20 (m, 1H, C$^{\alpha}$H), 4.32-4.95 (br m, 4H, 2*NCH$_2$), 5.02 (s, 2H, CH$_2$(Z)), 5.04 (s, 2H, CH$_2$(Z)), 5.68 (br s, 2H, 2*NHZ), 5.76 (br s, 1H, NHZ), 5.83 (br s, 1H, NHZ), 5.93 (br, 1H, NHBoc), 6.29 and 6.31 (d, 1H, NH), 6.53 (br s, 1H, NH), 7.03 (d, 1H, NH), 7.16-7.34 (m, 30H, H arom Ph), 8.91 (br s, 1H, NH), 9.02 (br s, 1H, NH). **^{13}C NMR** (75 MHz, **CD$_3$CN**, 10.0 mmol L^{-1}) δ_C 23.21 (C$^{\gamma}$H$_2$), 24.06 (C$^{\gamma}$H$_2$), 28.77 (C(<u>C</u>H$_3$)), 30.29 (C$^{\delta}$H$_2$), 31.11 (C$^{\delta}$H$_2$), 31.49 (C$^{\beta}$H$_2$), 32.19 (C$^{\beta}$H$_2$), 40.88 (C$^{\varepsilon}$H$_2$), 41.43 (C$^{\varepsilon}$H$_2$), 41.49 (C$^{\varepsilon}$H$_2$), 41.62 (C$^{\varepsilon}$H$_2$), 52.09 (N<u>C</u>H$_2$), 52.56 (OCH$_3$), 53.02 (N<u>C</u>H$_2$), 54.91 (C$^{\alpha}$H), 66.74 (OCH$_2$), 66.79 (OCH$_2$), 66.88 (OCH$_2$), 66.94 (OCH$_2$), 81.15(<u>C</u>(CH$_3$)$_3$), 128.22 (CH arom Ph), 128.60 (CH arom Ph), 128.73 (CH arom Ph), 128.83 (CH arom Ph), 128.89 (CH arom Ph), 128.95 (CH arom Ph), 129.33 (CH arom Ph), 129.52 (CH arom Ph), 130.22 (CH arom Ph), 138.50 (C arom Ph), 138.59 (C arom Ph), 138.67 (C arom Ph), 138.81 (C arom Ph), 157.50 (<u>C</u>OO*t*-Bu), 157.81 (O=<u>C</u>-CH$_2$Ph), 158.56 (O=<u>C</u>-CH$_2$Ph), 159.80 (O=C-NH), 159.98 (O=C-NH), 172.07 (O=C-NH), 174.69 (<u>C</u>OOCH$_3$). **IR (CDCl$_3$)** $\tilde{\upsilon}_{max}$ = 3256 cm^{-1}, 3349 cm^{-1}, 3450 cm^{-1} (NH), 1651 cm^{-1}, 1667 cm^{-1}, 1699 cm^{-1}, 1712 cm^{-1}, 1724 cm^{-1}, 1740 cm^{-1} (C=O). **HRMS (ESI)** for [C$_{78}$H$_{100}$N$_{12}$O$_{17}$]: calculated [M+Na]$^+$ (m/z) 1499.7227, found, 1499.7181; calculated [M^{2+}+Na] (m/z) 761.3615, found 761.3664.

Boc-(D-Lys(z)-azaPhe-Lys(z))$_2$-OMe **(8d)** was obtained as a white foam (yield 62%) after flash chromatography (0.04 − 0.063 µm) using (50% dichloromethane : 48% ethyl acetate : 2% methanol) as eluent; **^{1}H NMR** (300 MHz, **CDCl$_3$**, 8.0 mmol L^{-1}) δ_H 1.36 (s, 9H, C(CH$_3$), 1.37-1.77 (m, 24H, 4*(C$^{\beta}$H$_2$, C^{g}H$_2$, and C$^{\delta}$H$_2$)), 3.03-3.14 (m, 8H, 4*(C$^{\varepsilon}$H$_2$)), 3.46 (s, 3H, COOCH$_3$), 3.70-3.75 (br m, 1H, C$^{\alpha}$H), 3.87-3.93 (m, H, C$^{\alpha}$H), 4.04-4.08 (m, 1H, C$^{\alpha}$H), 4.56-4.60 (m, 1H, C$^{\alpha}$H), 4.21 (d) and 5.23 (br s) (2H, NCH$_2$), 4.40 (d) and 4.64 (br s) (2H, NCH$_2$), 4.82-4.87 (br s, 2H, 2*NHZ), 5.05 (s, 2H, CH$_2$(Z)), 5.07 (s, 2H, CH$_2$(Z)), 5.10 (s, 2H, CH$_2$(Z)), 5.11 (s, 2H, CH$_2$(Z)), 5.3 (br s, 1H, NHZ), 5.46 (br, 1H, NHBoc), 5.88 (br s, 1H, NHZ), 6.21 and 6.23 (d, 1H, NH), 6.54 (br s, 1H, NH), 7.16-7.34 (m, 31H; 30H arom Ph and 1H, NH), 8.85 (br s, 1H, NH), 9.46 (br s, 1H, NH). **^{13}C NMR** (75 MHz, **CDCl$_3$**, 10.0 mmol L^{-1}) δ_C 21.66 (C$^{\gamma}$H$_2$), 22.42 (C$^{\gamma}$H$_2$), 23.24 (C$^{\gamma}$H$_2$), 23.56 (C$^{\gamma}$H$_2$), 29.27 (C(<u>C</u>H$_3$)), 29.58 (C$^{\delta}$H$_2$), 30.23 (C$^{\delta}$H$_2$), 30.39 (C$^{\delta}$H$_2$), 31.77 (C$^{\beta}$H$_2$), 32.18 (C$^{\beta}$H$_2$), 40.75 (C$^{\varepsilon}$H$_2$), 40.83 (C$^{\varepsilon}$H$_2$), 40.85 (C$^{\varepsilon}$H$_2$), 40.99 (C$^{\varepsilon}$H$_2$), 51.67 (NCH$_2$), 52.29 (NCH$_2$), 52.59 (OCH$_3$), 53.45 (C$^{\alpha}$H), 55.32 (C$^{\alpha}$H), 56.59 (C$^{\alpha}$H),

56.93 ($C^{\alpha}H$), 66.93 (OCH_2), 67.12 (OCH_2), 67.44 (OCH_2), 67.74 (OCH_2), 81.65($\underline{C}(CH_3)_3$), 127.81 (CH arom Ph), 128.20 (CH arom Ph), 128.66 (CH arom Ph), 128.82 (CH arom Ph), 129.00 (CH arom Ph), 129.09 (CH arom Ph), 129.15 (CH arom Ph), 129.30 (CH arom Ph), 130.16 (CH arom Ph), 136.36 (C arom Ph), 136.91 (C arom Ph), 137.15 (C arom Ph), 137.52 (C arom Ph), 137.81 (C arom Ph), 157.17 ($\underline{C}$OO*t*-Bu), 157.44 (O=$\underline{C}$-CH_2Ph), 157.79 (O=$\underline{C}$-CH_2Ph), 157.96 (O=$\underline{C}$-CH_2Ph), 158.21(O=C-NH), 159.41 (O=C-NH), 171.13 (O=C-NH), 171.62 (O=C-NH), 175.8 ($\underline{C}OOCH_3$). **IR ($CDCl_3$)** $\tilde{\upsilon}_{max}$ = 3212 cm^{-1}, 3342 cm^{-1}, 3450 cm^{-1} (NH), 1637 cm^{-1}, 1652 cm^{-1}, 1667 cm^{-1}, 1690 cm^{-1}, 1705 cm^{-1}, 1718 cm^{-1}, 1738 cm^{-1} (C=O). **HRMS (ESI)** for $[C_{78}H_{100}N_{12}O_{17}]$: calculated $[M+Na]^+$ (m/z) 1499.7227, found, 1499.7153; calculated $[M^{2+}+Na]$ (m/z) 761.3615, found 761.3592.

Table S1. Assignment of the CO groups in **7c** and **7d**, (3.0 mmol L^{-1}, $CDCl_3$)

CO Molecule 7c	**Free methyl ester**	**Free Lys1**	**Free CO(Z) (Lys1+Lys2)**	**Free Boc**	**Free azaPhe**	**Bound Boc**
Wavenumber (cm^{-1})	1748	1735	1717	1701	1677	1652
CO Molecule 7d	Free methyl ester	Free Lys1	Free CO(Z) *D*-Lys1	Free CO(z) Lys2 + Boc	Free azaPhe	Bound Boc
Wavenumber (cm^{-1})	1749	1734	1718	1702	1675	1652

Table S2. Mean values of the dihedral angles of molecules **(7c)** and **(7d)** calculated from 25.000 structures issued of the molecular dynamic simulations *versus* the classical values of β-turns in natural peptides

	Φ1	**Ψ1**	**Φ2**	**Ψ2**	**Φ3**	**Ψ3**
Molecule 7c	-29.70°	26.37°	-89.07°	47.89°	-138.60°	125.56°
Molecule 7d	128.40°	-64.94°	91.81°	38.83°	-146.91°	125.82°
βIV-turn	-61°	10°	-53°	17°	--	--
βI'-turn	60°	30°	90°	0°	--	--

Table S3. The possible intramolecular hydrogen bonds predicted from 25.000 structures in **(7c)** and **(7d)** issued of the molecular dynamic simulations

Molecule	**Bond Ref.**	**Residue**	**Residue**	**Distance (Å) N-----O**	**Angle (°)**	**H-bond (%)**
7c	i	CO (i)	HN (i + 2)	2.86	139.5	36
	ii	CO (i + 2)	HN^{ε} (i + 3)	2.96	159.04	35
7d	i	CO(Z) (i + 3)	HN (i + 2)	2.89	162.01	40
	ii	CO(Z) (i + 3)	HN (i + 1)	2.91	158.44	26
	iii	CO (i)	HN^{ε} (i + 1)	2.98	159.42	22

Table S4. Mean dihedral angles of molecules **(8c)** and **(8d)** calculated from 25.000 structures obtained by the molecular dynamic simulations versus the classical torsion angles in peptides and proteins

Torsion angles in (8c) and (8d)

Compound	Φ1	Ψ1	Φ2	Ψ2	Φ3	Ψ3	Φ4	Ψ4	Φ5	Ψ5
8c	-85.81°	23.79°	86.23°	-68.93°	-66.15°	26.77°	-129.05°	13.11°	-88.26°	21.62°
8d	83.43°	-27.38°	79.51°	-112.39°	-68.92°	5.67°	131.28°	30.66°	97.04°	-9.78°

Classical torsion angles in peptides and proteins

Turn	φ_i	ψ_i	φ_{i+1}	ψ_{i+1}
βI'	60°	30°	90°	0°
βII'	60°	-120°	-80°	0°
βIV	-61°	10°	-53	17°
βV	-80°	80°	80°	-80°
βV'	80°	-80°	-80°	80°

Table S5. Mean values of the bond distances and bond angles for the predicted intramolecular hydrogen bonds calculated from 25.000 structures in **(8c)** and **(8d)** obtained by the molecular dynamic simulations

Intramolecular H-bonds in compounds (8c) and (8d)

Molecule	Bond Ref.	Residue	Residue	Distance (Å) N-----O	Angle (°)	H-bond (%)
8c	i	CO (i+2)	NH (i + 4)	2.78	146.35	90.8
	ii	CO (i + 1)	$N^{\varepsilon}H$ (i + 4)	2.91	157.18	64.9
	iii	CO (i)	NH (i + 2)	2.89	140.85	48.9
	iv	CO (i+2)	NH (i + 5)	3.02	147.36	32.9
8d	i	CO (i + 1)	NH (i + 5)	2.97	149.60	59.1
	ii	CO(z) (i + 6)	NH (i + 1)	2.90	156.03	58.7
	iii	CO (i + 2)	NH (i + 4)	2.94	137.64	38.8
	iv	CO (i)	NH (i + 2)	2.84	143.62	29.5
	v	CO(z) (i + 4)	$N^{\varepsilon}H$ (i + 1)	2.95	159.04	26.9
	vi	CO (i + 5)	$N^{\varepsilon}H$ (i + 3)	2.94	155.21	23.0

Table S6. Average percentages of the expected intramolecular hydrogen bonds in **(8c)** obtained by the molecular dynamic simulations

Molecule	Bond Ref.	No. of frames	Frames (%)	Bond Ref.	No. of frames	Frames (%)
8c	(i + ii)	15115	60.5	(i + ii + iii)	7368	29.5
	(i + iii)	11154	44.6	(i + iii + iv)	3607	14.4
	(i + iv)	6952	27.8	(i + ii + iv)	4282	17.3
	(ii + iii)	7892	31.8	(ii + iii + iv)	2560	10.2
	(ii + iv)	4921	19.7	(i + ii + iii + iv)	2259	9.0
	(iii + iv)	4215	16.9			

Table S7. Average percentages of the expected intramolecular hydrogen bonds in **(8d)** obtained by the molecular dynamic simulations

Molecule	Bond Ref.	No. of frames	Frames (%)	Bond Ref.	No. of frames	Frames (%)
8d	(i + ii)	8941	35.8	(iv + v)	2614	10.5
	(i + iii)	3069	12.3	(iv + vi)	1775	7.1
	(i + iv)	5439	21.8	(v + vi)	1997	8.0
	(i + v)	4378	17.5	(i + ii + iii)	1862	7.5
	(i + vi)	2306	9.2	(i + iii + iv)	1142	4.5
	(ii + iii)	4257	17.0	(i + ii + iv)	2972	11.9
	(ii + iv)	4753	19.0	(ii + iii + iv)	1405	5.6
	(ii + v)	4363	17.4	(iv + v +vi)	766	3.0
	(ii + vi)	4219	16.9	(i + ii + iii + iv)	650	2.6
	(iii + iv)	2871	11.5	(ii + iii + iv + v)	582	2.3
	(iii + v)	2314	9.2	(i + iv + v + vi)	473	1.9
	(iii + vi)	2277	9.1	(i + ii + iii + vi + v)	402	1.6

Table S8. Membrane permeation properties for CO_2 and N_2 pure gases at 35 °C and 2 bar

	Pseudopeptide oligomer	P (CO_2) (Barrer)	P (N_2) (Barrer)	D (CO_2) x 10^6 (cm^2/s)	D (N_2) x 10^7 (cm^2/s)	S (CO_2) x 10^2 (cm^3(STP).cm^{-3}.$cmHg^{-1}$)	S (N_2) x 10^4 (cm^3(STP).cm^{-3}.$cmHg^{-1}$)
Pebax 1074		132.67 ± 0.52	3.10 ± 0.17	1.19 ± 0.02	3.76 ± 0.40	1.12 ± 0.02	8.31 ± 1.10
Trimer without Lys	**7a**	116.00 ± 0.17	2.58 ± 0.05	1.10 ± 0.04	4.11 ± 0.52	1.09 ± 0.05	6.39 ± 0.91
Protected hexamer	**8c**	115.28 ± 0.24	3.00 ± 0.00	1.03 ± 0.02	3.96 ± 0.34	1.16 ± 0.06	7.58 ± 0.55
Protected trimer	**7c**	119.23 ± 0.15	2.66 ± 0.29	1.13 ± 0.01	2.41 ± 0.18	1.05 ± 0.01	10.39 ± 0.68
Protected dimer	**6b**	122.48 ± 1.39	2.60 ± 0.00	1.05 ± 0.05	3.09 ± 0.50	1.16 ± 0.05	8.57 ± 1.31
Deprotected hexamer	**8c'***	123.85 ± 0.31	3.35 ± 0.35	0.85 ± 0.02	6.16 ± 0.93	1.47 ± 0.04	5.59 ± 1.41
Deprotected trimer	**7c'***	133.20 ± 0.14	3.06 ± 0.06	0.92 ± 0.01	5.40 ± 0.38	1.46 ± 0.02	5.71 ± 0.33
Deprotected dimer	**6b'***	147.65 ± 0.13	3.10 ± 0.00	1.35 ± 0.03	3.68 ± 0.13	1.10 ± 0.02	8.42 ± 0.24

*Deprotected azapeptides **6b'**, **7b'** and **8b'** have obtained from the corresponding protected analogues by catalytic hydrogenolysis (**See Experimental Section**).

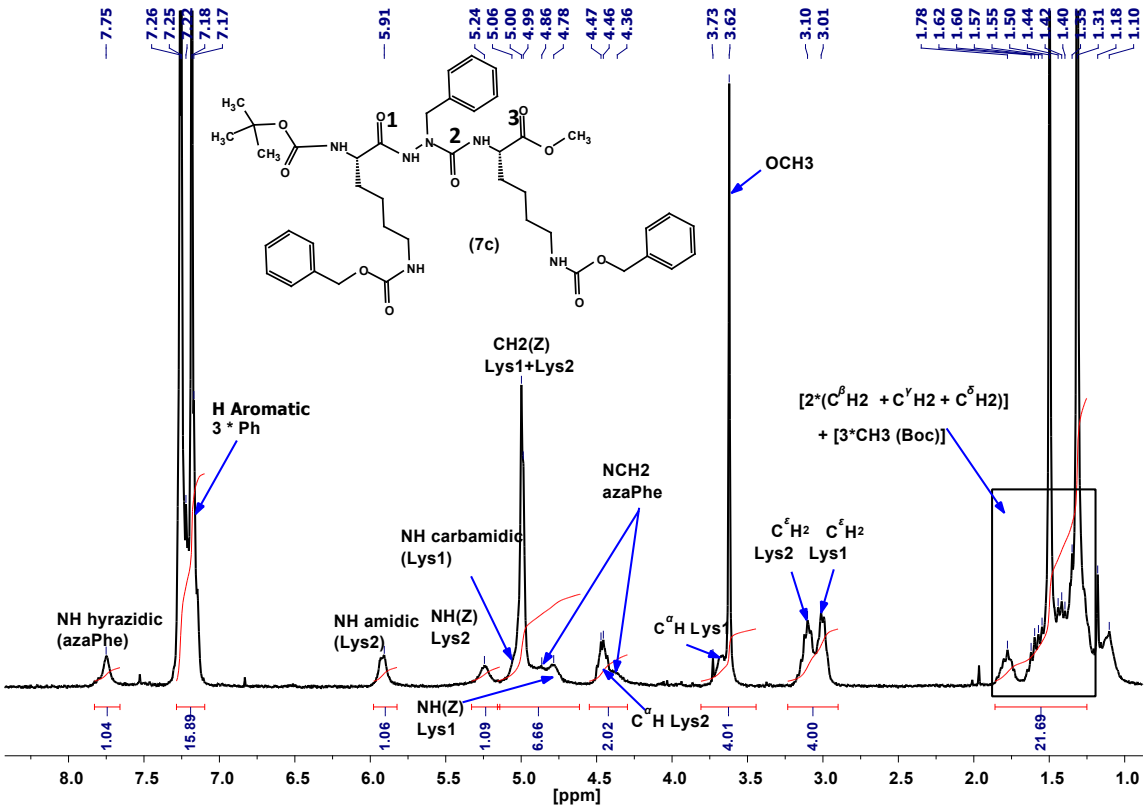


Figure S1a. The ^{1}H spectrum of **7c**; (3.0 mmol L^{-1}, $CDCl_3$, 300 K).

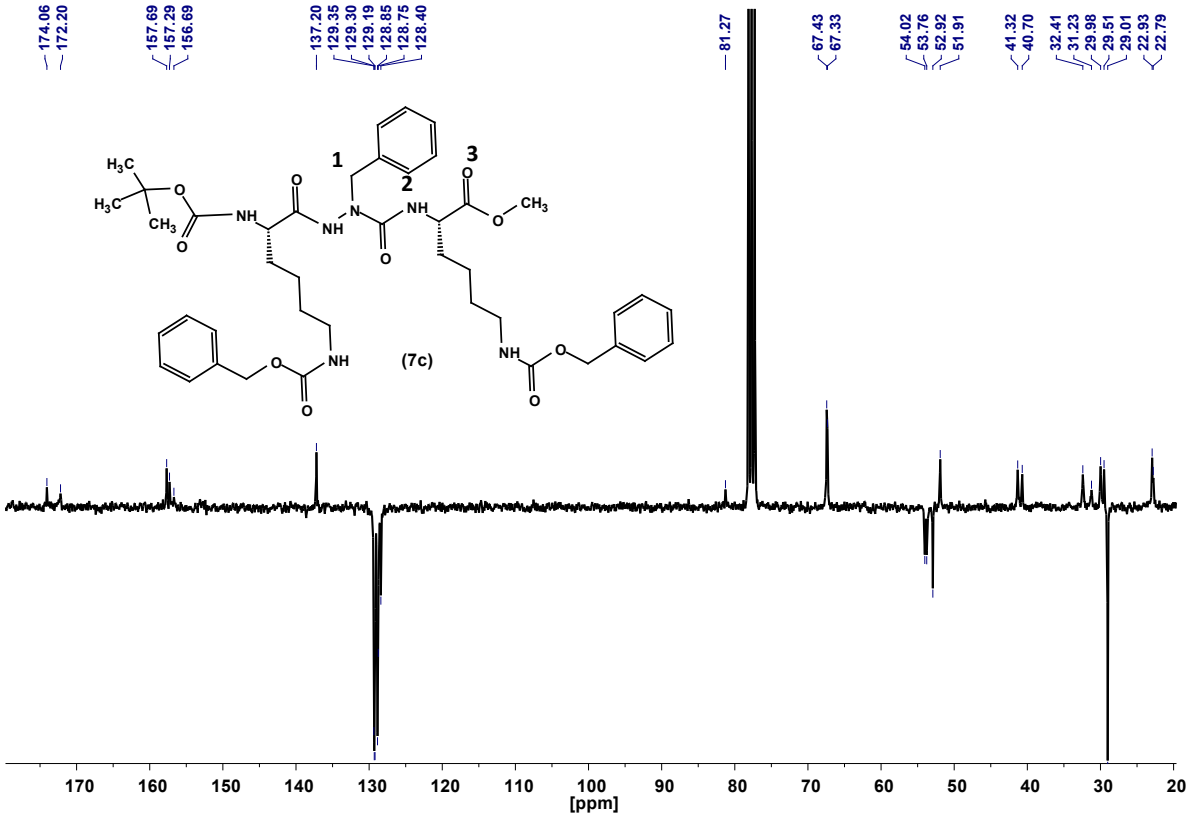


Figure S1b. The ^{13}C spectrum of **7c**; (5.0 mmol L^{-1}, $CDCl_3$, 300 K).

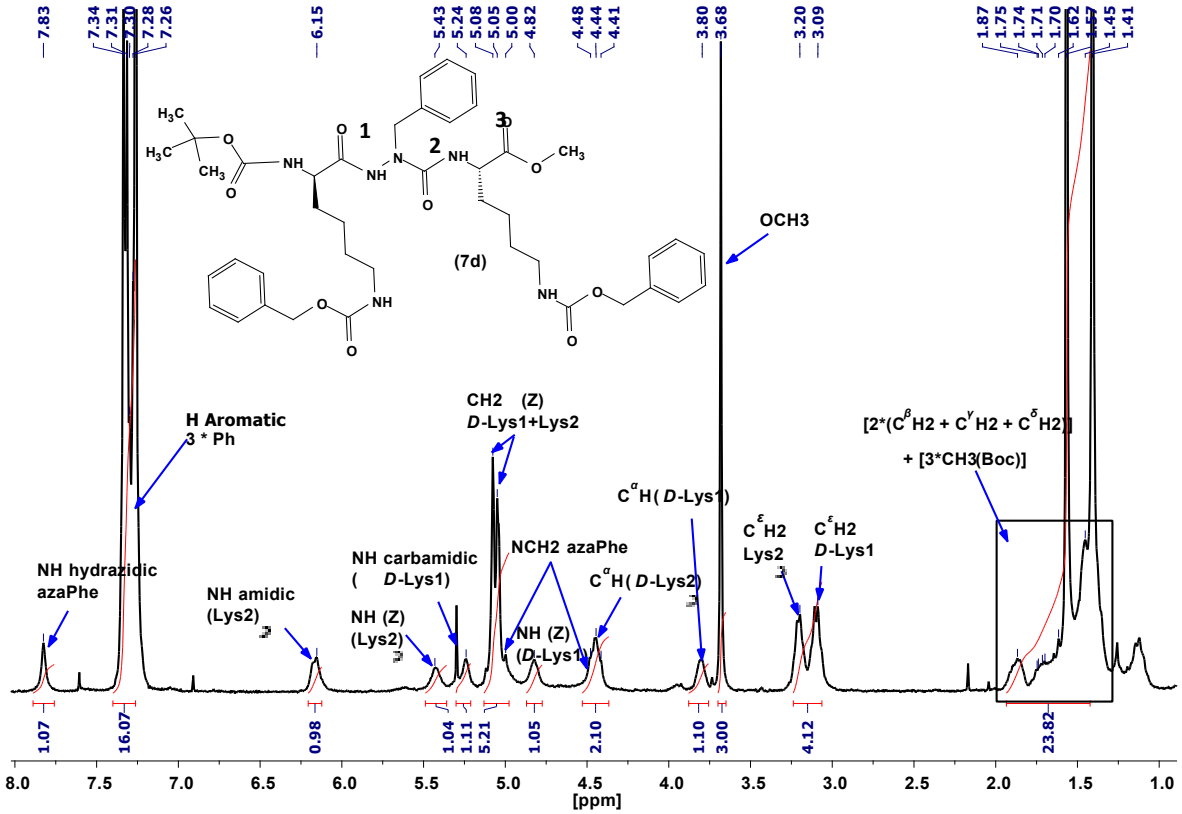


Figure S2a. The ^{1}H spectrum of **7d**; (3.0 mmol L^{-1}, $CDCl_3$, 300 K).

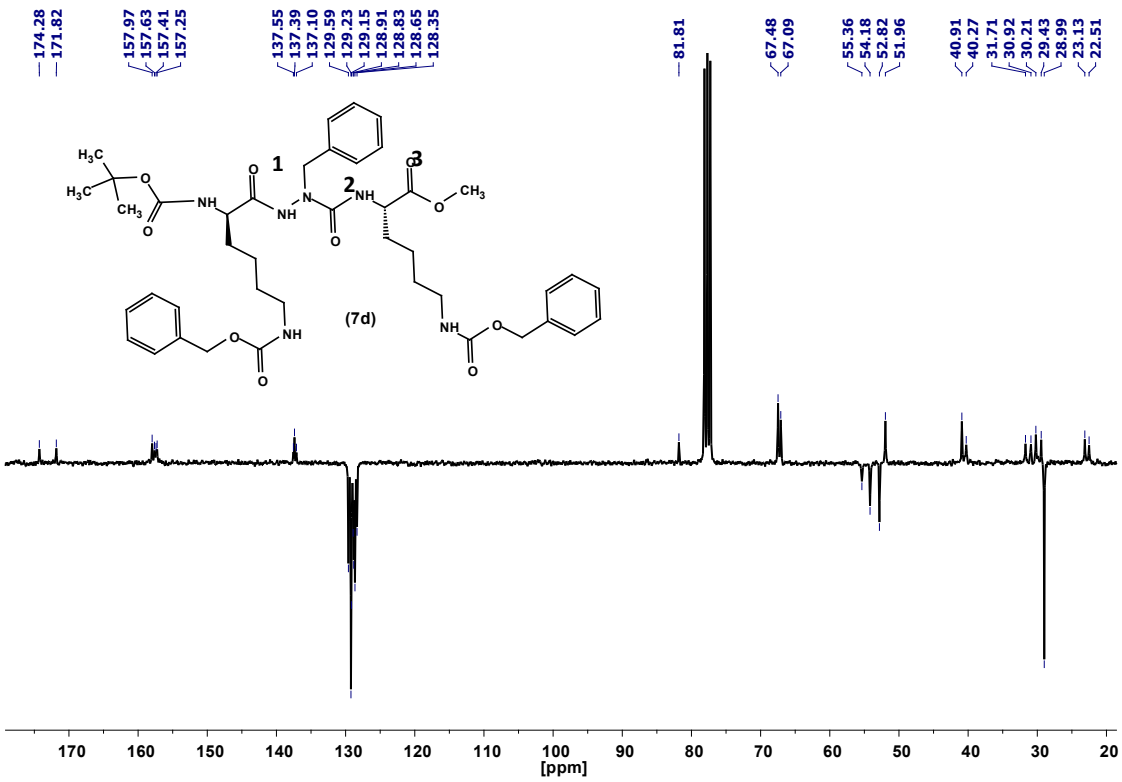


Figure S2b. The ^{13}C spectrum of **7d**; (5.0 mmol L^{-1}, $CDCl_3$, 300 K).

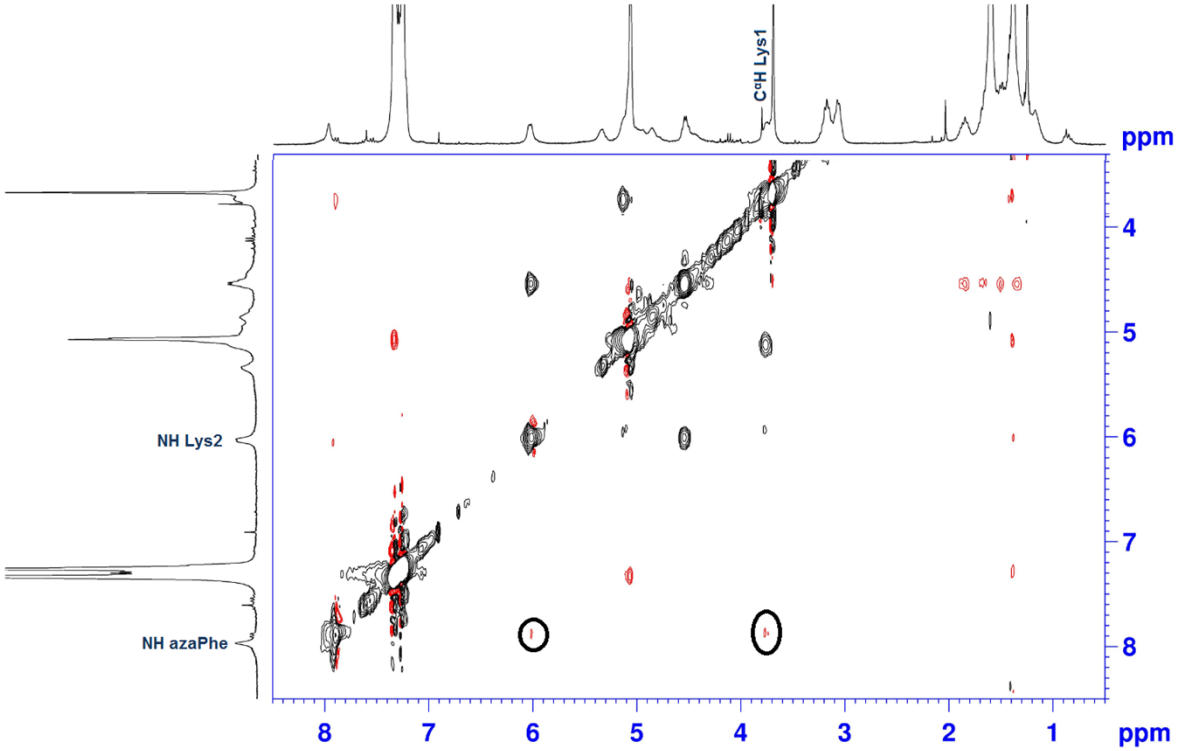


Figure S3. The 2D ROESY spectrum illustrating the correlations of βII-turn conformation in **7c** (300 MHz, 3.0 mmol L^{-1}, $CDCl_3$, 300 K).

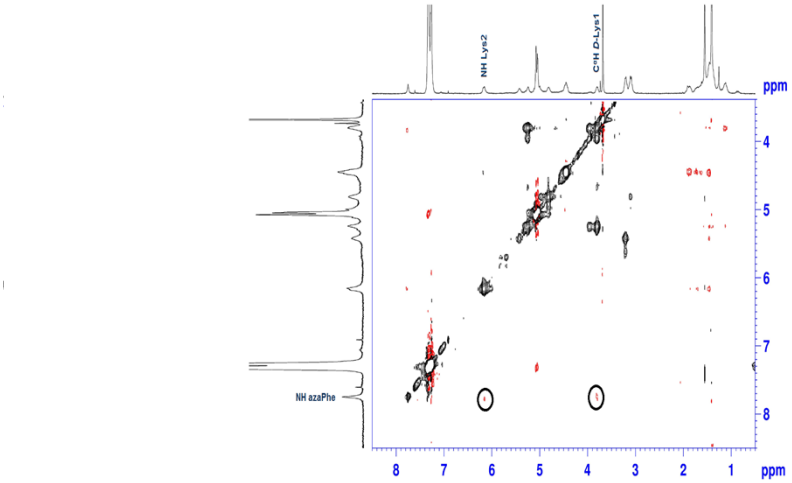


Figure S4. The 2D ROESY spectrum illustrating the correlations of βII'-turn conformation in **7d** (300 MHz, 3.0 mmol L^{-1}, $CDCl_3$, 300 K).

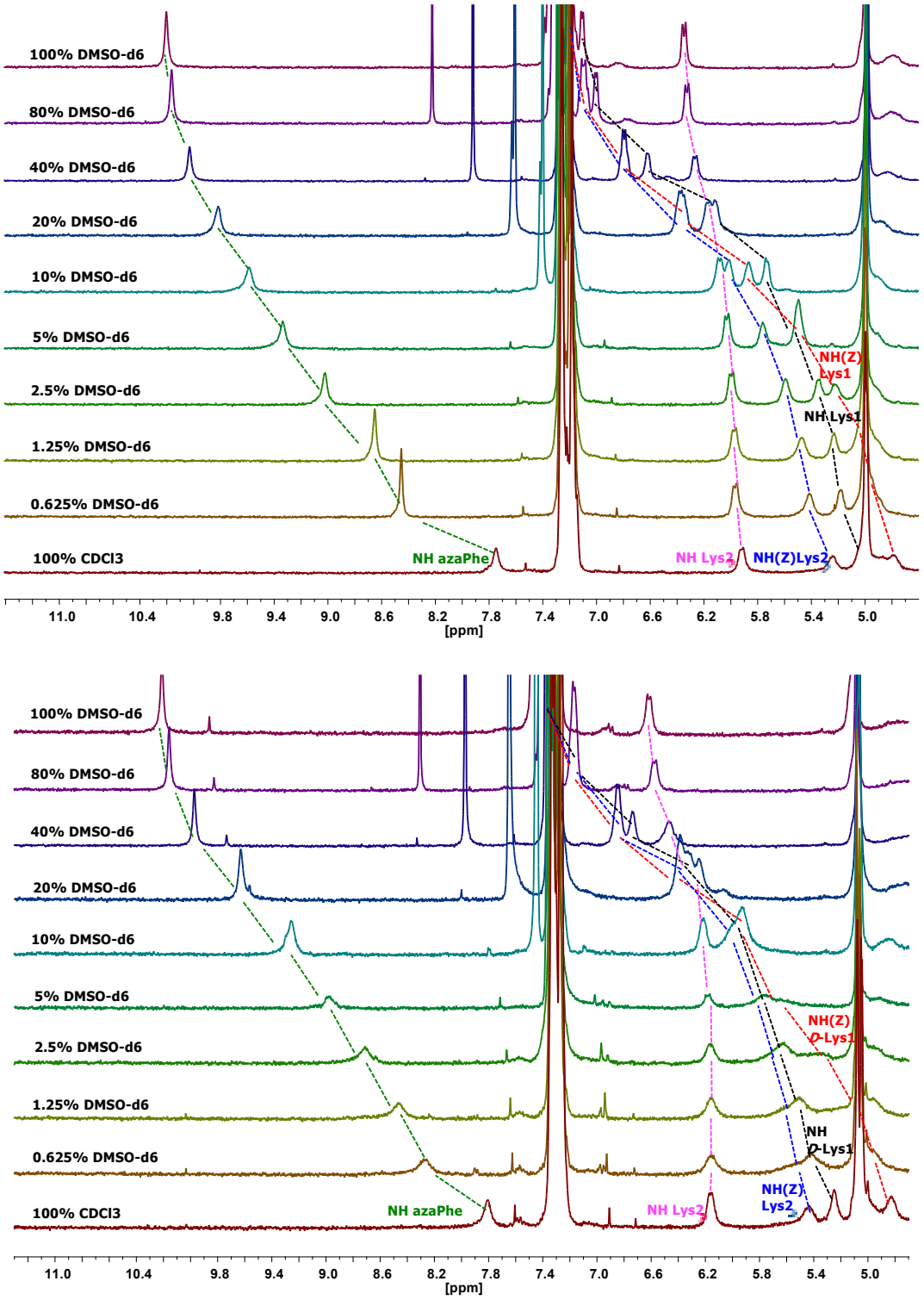


Figure S5. Chemical shift-variations (δ) ppm of NH protons for: **7c** (up); and **7d** (bottom) as a function of % [$CDCl_3$/DMSO-d_6] mixtures; (300 MHz, 3.0 mmol L^{-1}).

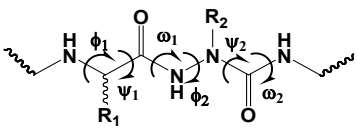


Figure S6. Nomenclature used for the backbone dihedral angles of four oligomers **(7c, 7d, 8c** and **8d)**.

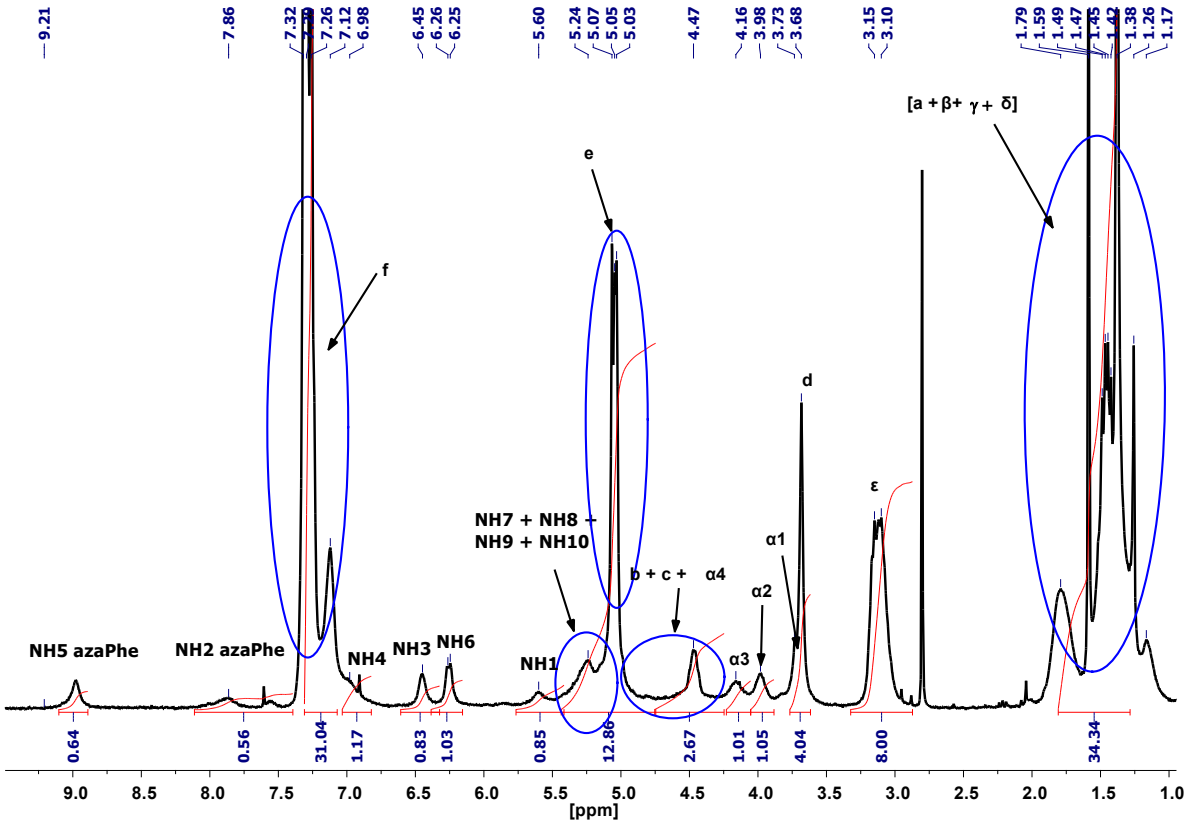
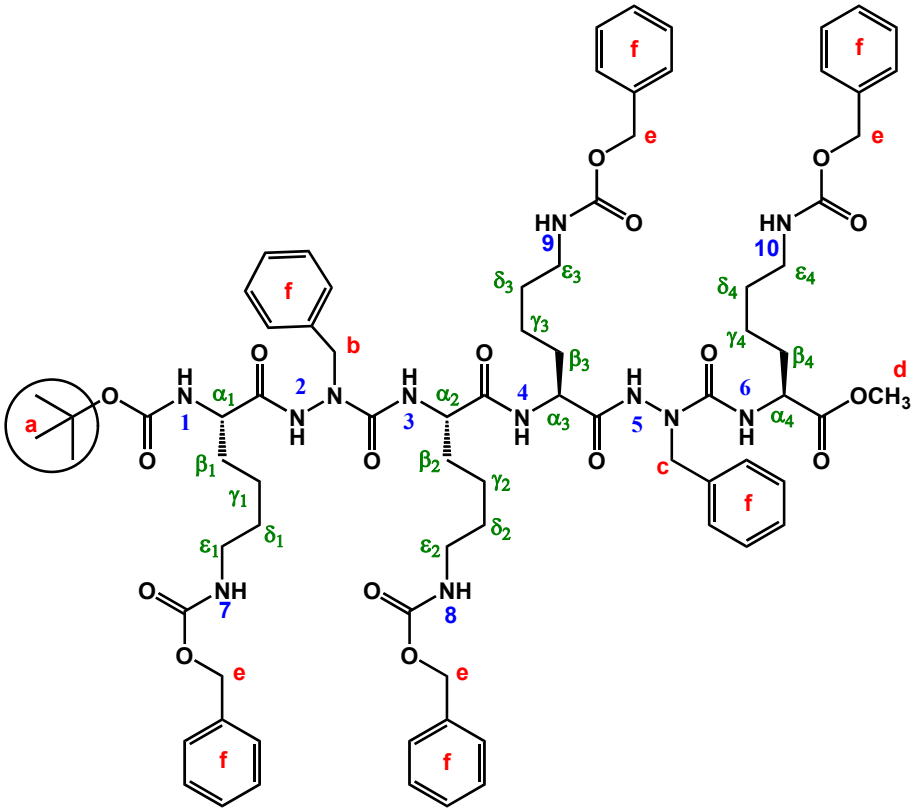


Figure S7. The ^{1}H spectrum of **8c** (4.0 mmol L^{-1}, $CDCl_3$, 300 K).



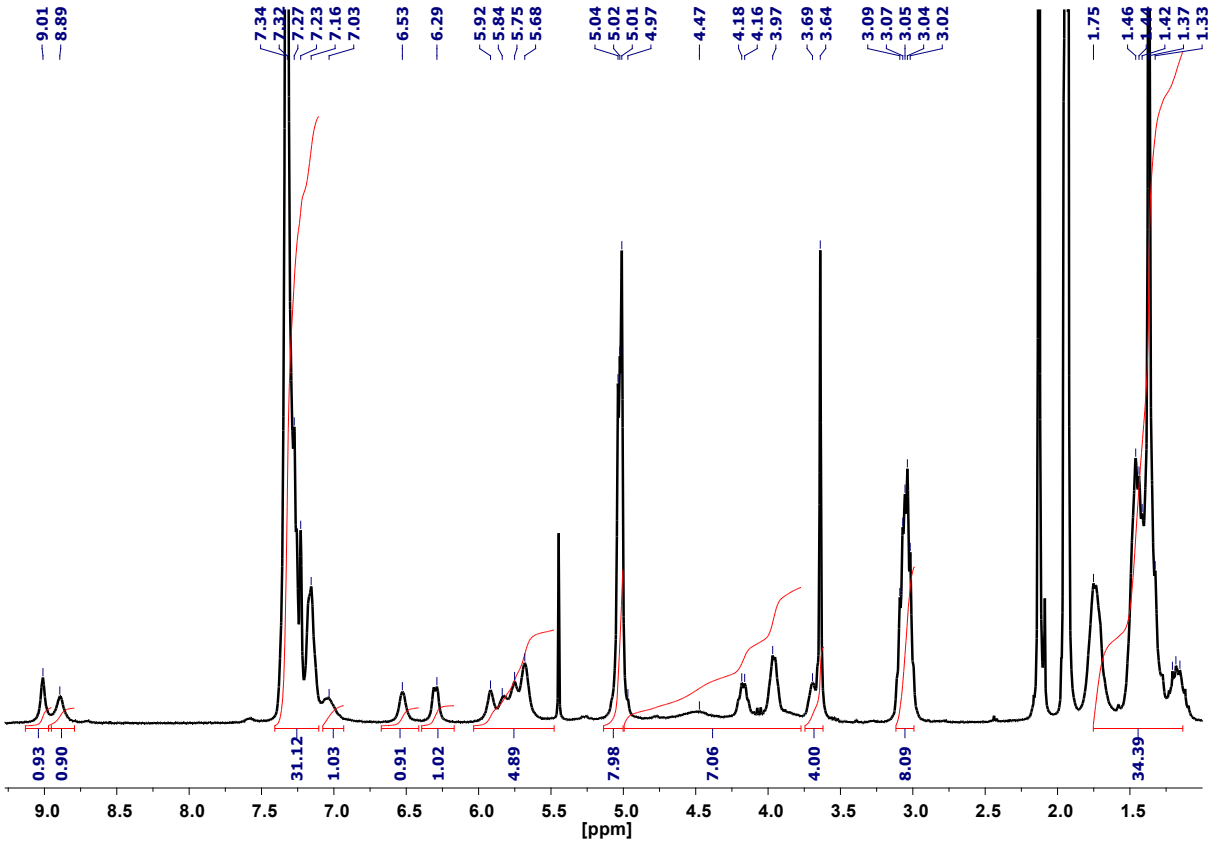


Figure S8a. The ^{1}H spectrum of **8c** (4.0 mmol L^{-1}, CD_3CN, 300 K).

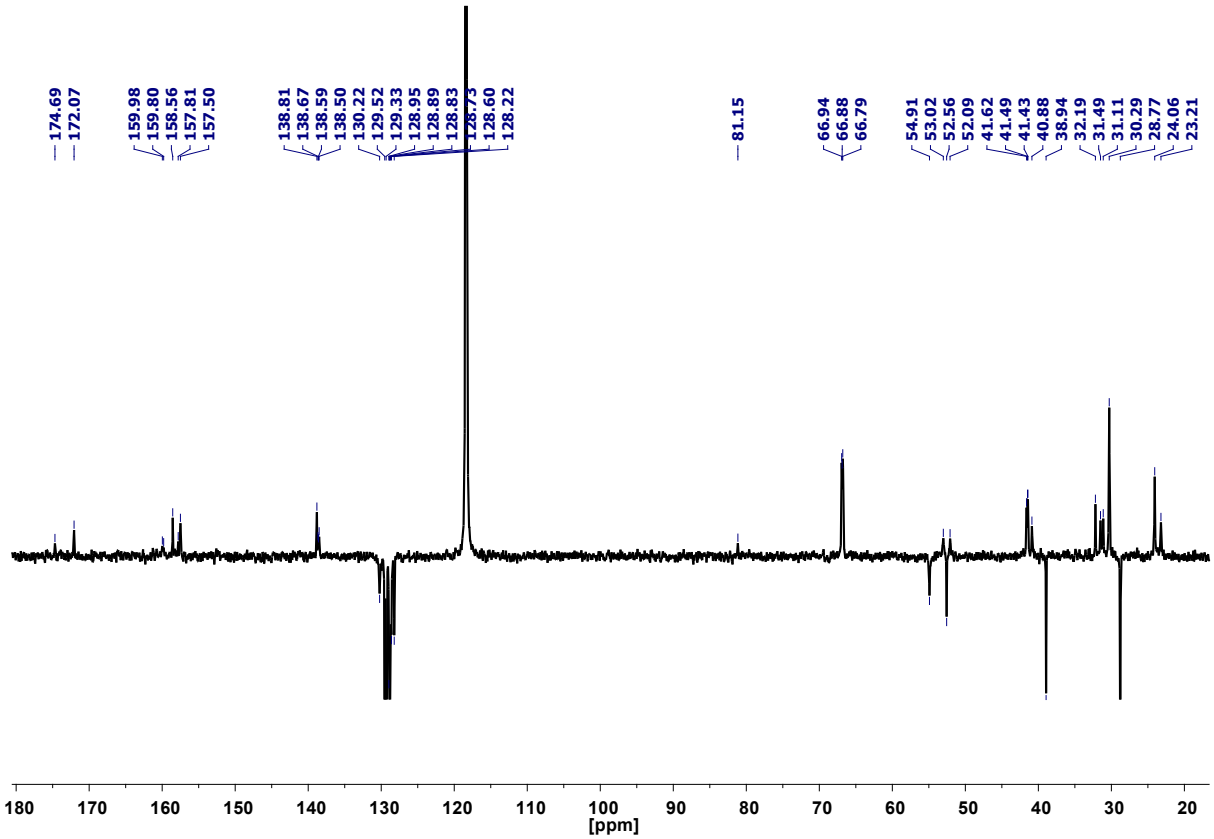


Figure S8b. The ^{13}C spectrum of **8c** (4.0 mmol L^{-1}, CD_3CN, 300 K).

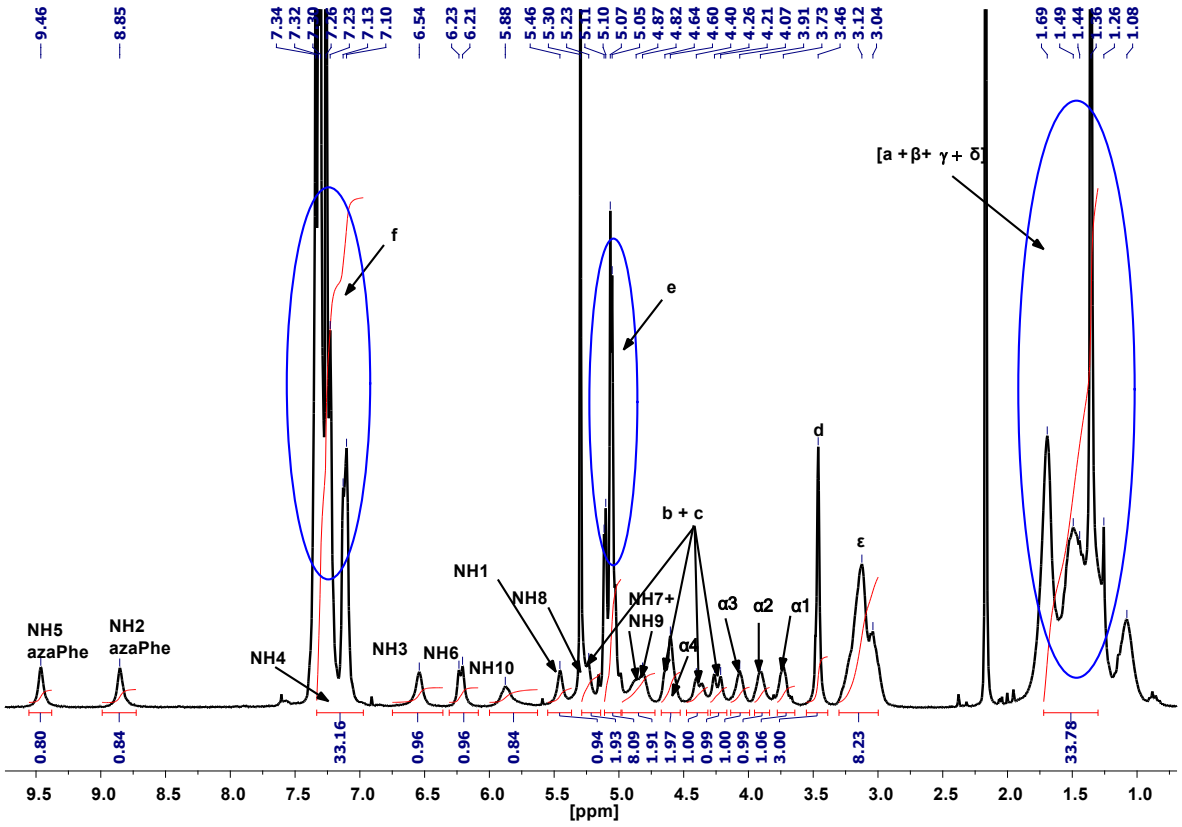
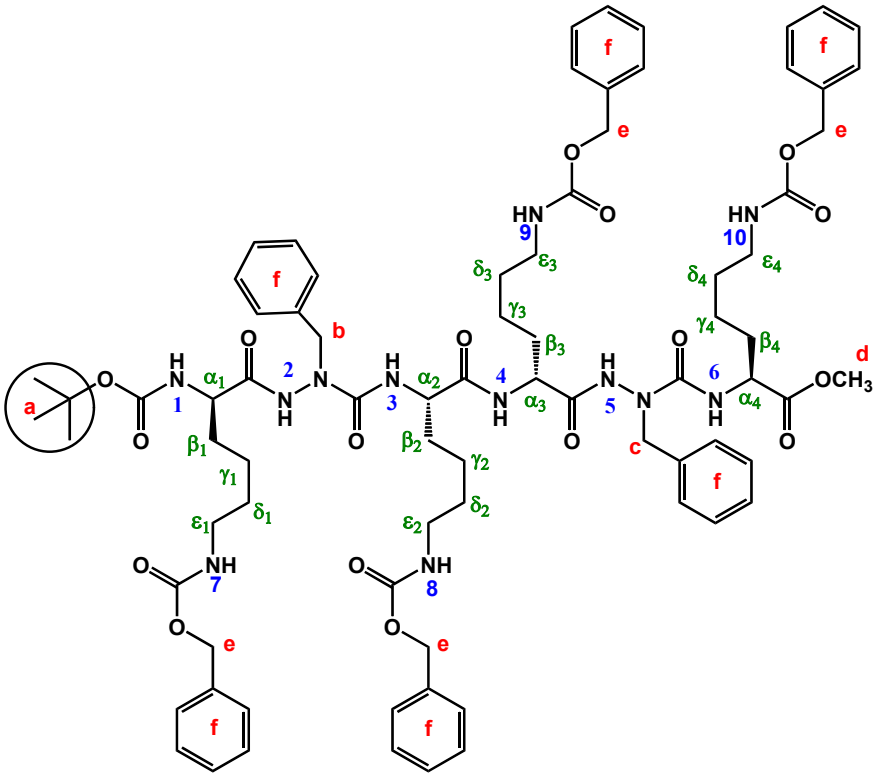


Figure S9a. The ^{1}H spectrum of **8d** (4.0 mmol L^{-1}, $CDCl_3$, 300 K).



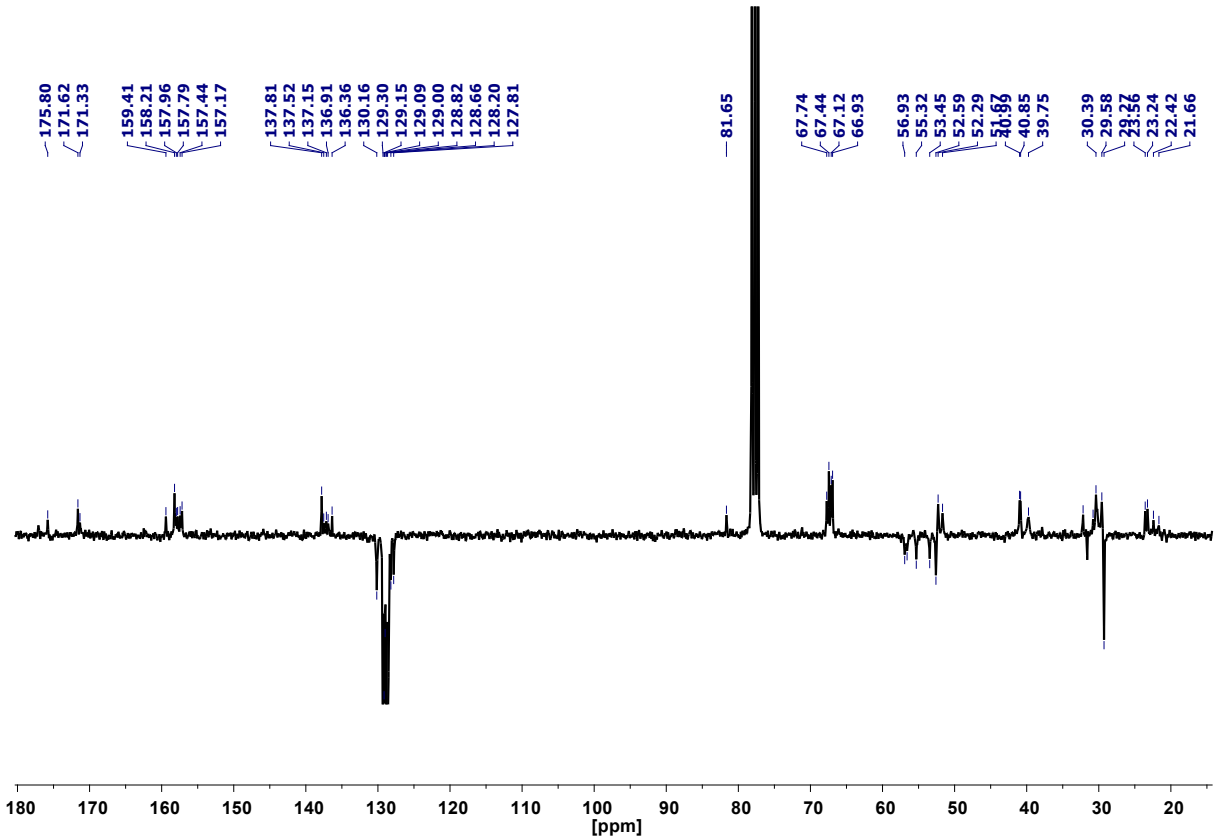


Figure S9b. The ^{13}C spectrum of **8d** (5.0 mmol L^{-1}, $CDCl_3$, 300 K).

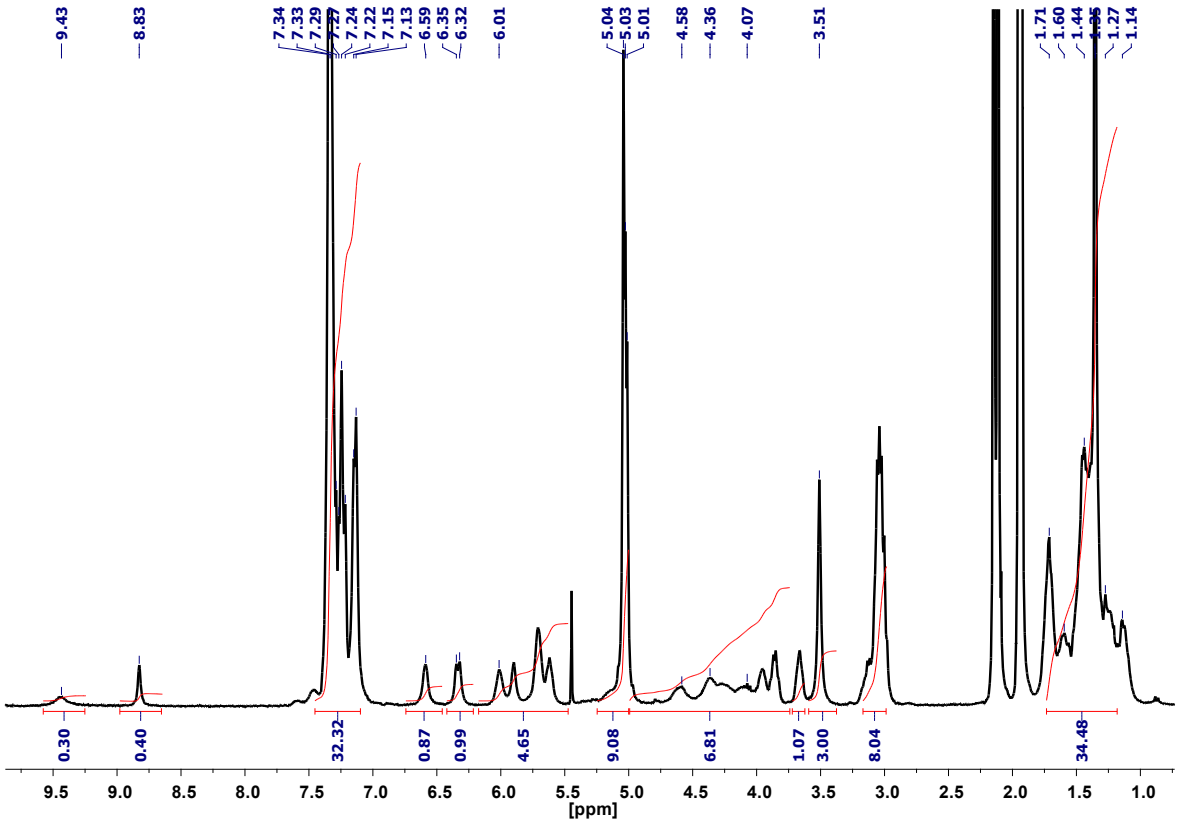


Figure S10. The ^{1}H spectrum of **8d** (4.0 mmol L^{-1}, CD_3CN, 300 K).

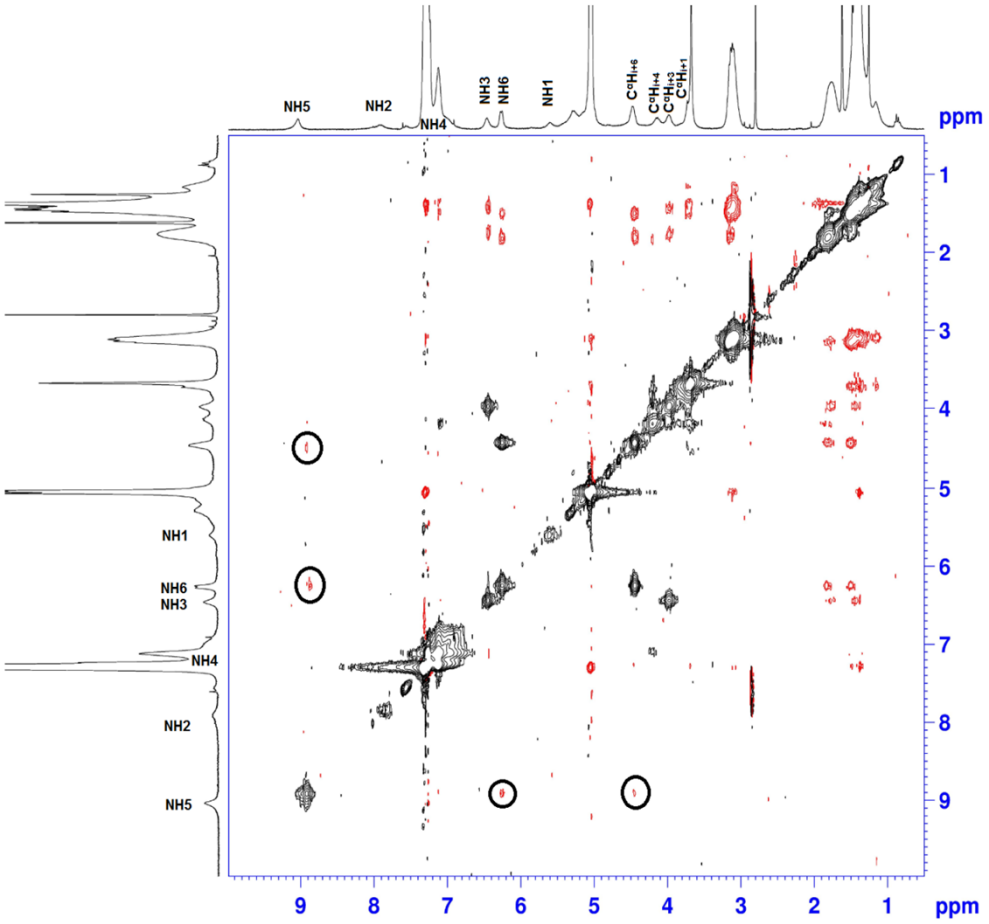


Figure S11. The 2D ROESY spectrum illustrating the β-turn conformation in **8c**; (300 MHz, 4.0 mmol L^{-1}, $CDCl_3$, 300 K).

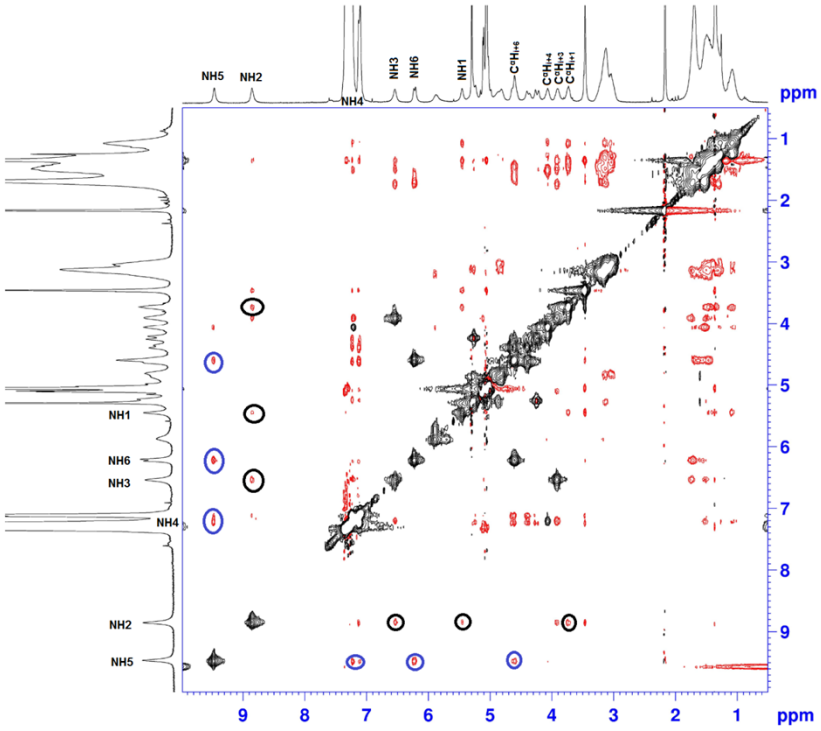


Figure S12. The 2D ROESY spectrum illustrating the correlations of β-turn conformation in **8d**, (300 MHz, 4.0 mmol L^{-1}, $CDCl_3$, 300 K).

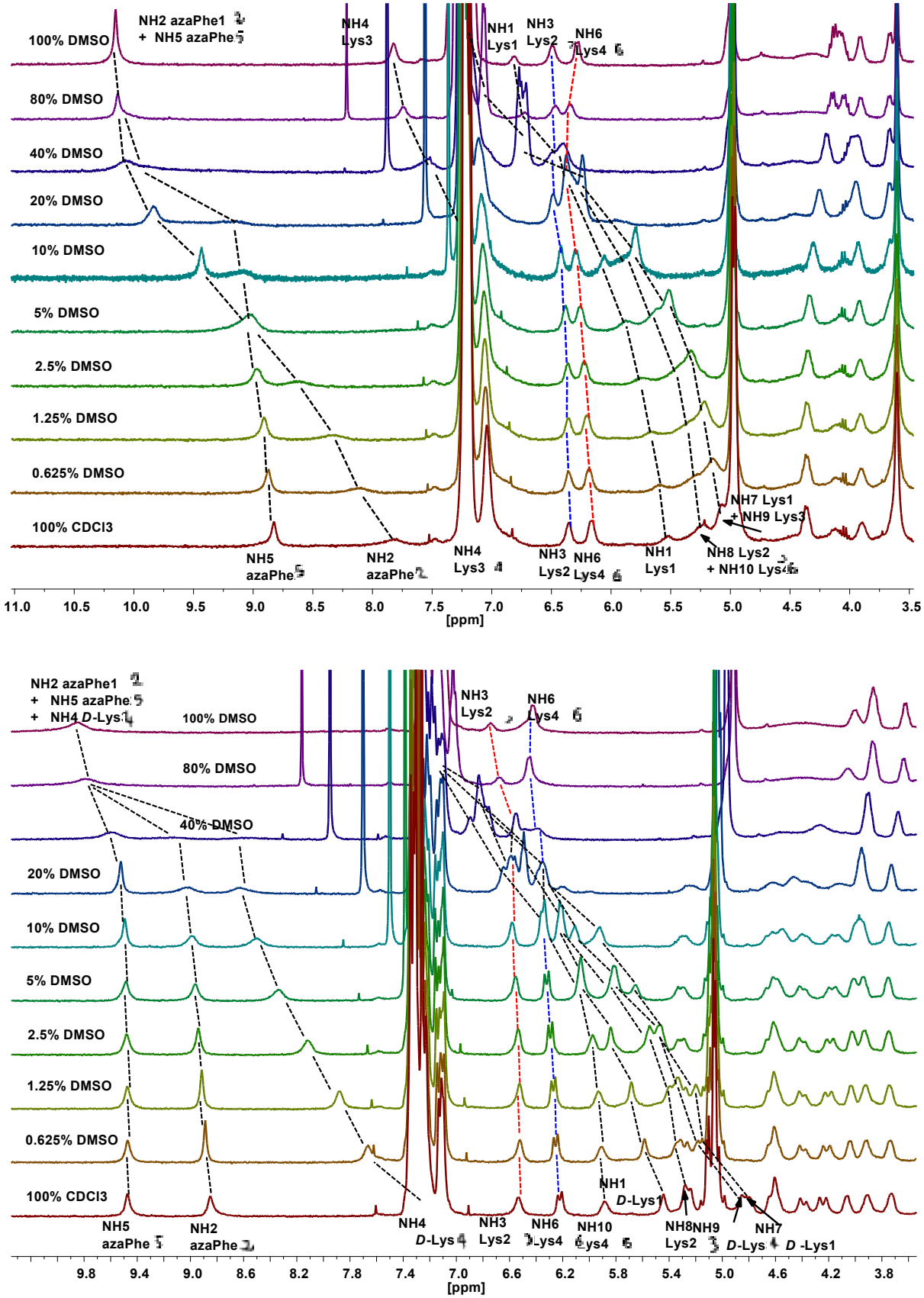
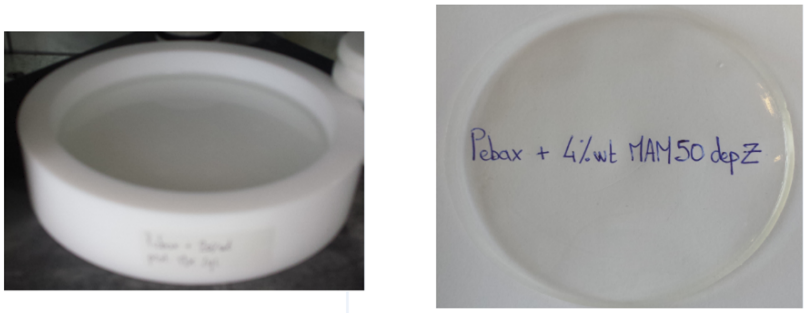


Figure S13. Chemical shift-variations (δ) of NH protons for: **8c** (up); and **8d** (bottom) as a function of % [$CDCl_3$/DMSO-d_6] mixtures.



(a) (b)

Figure S14. (a) Evaporation of butanol during membrane casting on a PTFE mold, and(b) example of a prepared membrane containing 4.0 wt% of the deprotected trimer **(7c')** pseudopeptide as additive in Pebax®1074 polymer before gases separation test.