Electronic Supporting Information

Probing the Folding Induction Ability of Orthanilic Acid in Peptides: Some Observations

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General Methods

Unless otherwise stated, all the chemicals and reagents were obtained commercially. Thin Layer Chromatography was done on precoated silica gel plates (kieselgel $60F_{254}$, Merck). Column Chromatographic purifications were done with 100-200 Mesh Silica gel. NMR spectra were recorded in $CDCl_3$ on AV 200 MHz, AV 400 MHz or AV-500 MHz Bruker NMR spectrometers. All chemical shifts are reported in δ ppm downfield to TMS and peak multiplicities as singlet (s), doublet (d), quartet (q), broad (b) broad singlet (bs) and multiplet (m). Elemental analyses were performed on an Elmentar-Vario-EL (Heraeus Company Ltd., Germany). IR spectra were recorded in $CHCl_3$ using Shimadzu FTIR-8400 spectrophotometer. Melting points were determined on a Buchi Melting Point B-540 instrument.

Experimental Section

Crystal data for **9:** $C_{37}H_{61}N_7O_9S$, M = 802.41, single crystals of the complex were grown by slow evaporation of the solution of pet-ether and ethyl acetate with few drops of DCM. Data were collected on SMART APEX-II CCD using Mo-Kα radiation (λ = 0.7107 Å) to a maximum θ range of 25.00°. Colourless needle like crystal of approximate size 0.49 x 0.25 x 0.10 mm^3 was used for data collection. Crystal to detector distance 5.00 cm, 512 x 512 pixels / frame, Oscillation / frame -0.5º, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24, Multirun data acquisition. Total scans = 2, total frames = 1384, exposure / frame = 10.0 sec / frame, θ range = 2.00 to 25.00 º, completeness to θ of 25.00 º, is 99.5 %. C37 H61 N7 O9 S, M = 779.99. Crystals belong to Orthorhombic, space group $P2_12_12_1$, a = 10.4234(2) , b = 10.5165(2), c = 39.4004(6) Å, V = 4318.98(13) $Å^3$, Z = 4, D_c = 1.200 g /cc, μ (Mo–Kα) = 0.132 mm^{-1}, 26845 reflections measured, 7584 unique [I>2σ(I)], R value 0.0399, wR2 = 0.0921. Largest diff. peak and hole 0.286 and -0.271 e. $Å^{-3}$. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model.

The conformation of the molecule was established by single crystal X-ray analysis shows C2 to have S configuration.

Experimental Procedures

(S)-methyl 1-(2-nitrophenylsulphonyl)pyrrolidine-2-carboxylate 1:

L-Proline methyl ester hydrochloride (0.82 g, 4.96 mmol) was added to a solution of 2-nitrobenzenesulfonylchloride (1.0 g, 4.51 mmol) in anhy. DCM (10 mL) at 0 °C followed

by the addition of Et_3N (1.45 mL, 10.38 mmol). The resulting mixture was then allowed to attain room temperature and was stirred for 12 h. It was then sequentially washed with sat. $NaHCO_3$, water, dil. HCl and brine. The organic layer was then dried over anhy. Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography furnished **1** as an off-white solid. Yield: 0.81 g (57%); mp: 85-86 °C; $[\alpha]^{26}_D$: -100.0° (*c*=1.6, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3621, 3418, 3020, 1746, 1640, 1546, 1371, 1216, 1163, 770; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 7.71-7.69 (m, 2H), 7.63-7.62 (s, 1H), 4.58-4.57 (d, *J* = 8 Hz, 1H), 3.66 (s, 3H), 3.62-3.60 (m, 1H), 3.55-3.52 (m, 1H), 2.29-2.22 (m, 1H), 2.10-1.94 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.2, 148.0, 133.6, 133.5, 132.7, 132.6, 131.6, 130.9, 124.0, 60.8, 52.3, 48.4, 30.8, 24.4; ESI MS: 337.04 $(M+Na)^+$; Anal. Calcd for $C_{12}H_{14}N_2O_6S$: C, 45.85; H, 4.49; N, 8.91; Found: C, 45.32; H, 4.73; N, 9.28.

***(S)*-methyl 1-(2-aminophenylsulphonyl)pyrrolidine-2-carboxylate 2:**

10% Pd/C (0.015 g) was added to a solution of **1** (0.15 g, 0.47 mmol) in methanol (6 mL). The reaction mixture was then stirred at 60 psi under hydrogen atmosphere for 8 h, followed by filtration of the catalyst through celite and the filtrate was evaporated to get product **2** which was carried forward without further purification.

***(S)*-methyl-1-(2-(2-bromo-2-methylpropanamido)phenylsulphonyl) pyrrolidine-2-carboxylate 3:**

To a solution of **2** (4.0 g, 14.1 mmol) in dry DCM (25 mL), anhy. Et_3N (2.55 mL, 18.3 mmol) was added at 0 °C followed by slow addition of 2-bromo-2-methylpropanoyl bromide (1.92 mL, 15.5 mmol). The resulting mixture was then allowed to come to room temperature and was stirred for 12 h, following which it was sequentially washed with sat. $NaHCO_3$, water and brine. Organic layer was then dried over anhydrous Na_2SO_4 and

evaporated under reduced pressure to get the crude product which on purification by column chromatography furnished **3** as a viscous liquid. Yield: 5.5 g (90%); $[\alpha]^{26}_{D}$: -63.08° (*c*=1.3, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3349, 3020, 1740, 1688, 1588, 1338, 1215, 1154, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.41 (s, 1H), 8.55-8.53 (d, *J* = 8 Hz, 1H), 7.91-7.89 (dd, *J* = 8.0, 1.6 Hz, 1H) 7.61-7.57 (t, *J* = 7 Hz, 1H), 7.26-7.22 (t, *J* = 7 Hz, 1H), 4.39-4.36 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.64-3.59 (m, 4H), 3.49-3.43 (m, 1H), 2.13-2.09 (m, 1H), 2.06 (s, 6H), 2.04-1.98 (m, 2H), 1.93-1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 170.4, 136.5, 134.2, 129.6, 125.8, 124.0, 122.1, 60.4, 59.9, 52.5, 48.4, 31.7, 31.0, 24.5; ESI MS: 455.01 $(M+Na)^+$; Anal. Calcd. for $C_{16}H_{21}BrN_2O_5S$: C, 44.35; H, 4.88; N, 6.46; Found: C, 44.62; H, 5.26; N, 6.08.

Methyl ((2-(2-azido-2-methylpropanamido)phenyl)sulphonyl)-*L*-prolinate 4:

Sodium azide (0.68 g, 10.5 mmol) was added to a solution of **3** (1.2 g, 3.5 mmol) in anhy. DMF (10 mL) and the reaction mixture was maintained at 70 °C for 12 h. It was then cooled to room temperature, following which EtOAc (40 mL) was added and the organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography gave **4** as a viscous liquid. Yield: 0.88 g (81%); $[\alpha]^{26}_{D}$: -50.53° (*c*=0.95, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3436, 3020, 2120, 1739, 1685, 1585, 1340, 1217, 1140, 770; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.39 (s, 1H), 8.52-8.50 (d, *J* = 8 Hz, 1H), 7.89-7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58-7.54 (t, *J* = 7 Hz, 1H), 7.24-7.20 (t, *J* = 7 Hz, 1H), 4.39-4.36 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.60-3.54 (m, 4H), 3.46-3.40 (m, 1H), 2.15-2.07 (m, 1H), 2.05-1.95 (m, 1H), 1.93-1.84 (m, 1H), 1.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.1, 136.1, 134.1, 129.7, 126.2, 124.0, 122.2, 64.6, 60.2, 52.4, 48.3, 31.0, 24.5;

ESI-MS: 418.07 (M+Na; Anal. Calcd for $C_{16}H_{21}N_5O_5S$: C, 48.60; H, 5.35; N, 17.71; Found: C, 48.29.; H, 5.11.; N, 17.09.

Methyl ((2-(2-amino-2-methylpropanamido)phenyl)sulphonyl)-*L*-prolinate 5:

The product **5** was obtained from **4**, following the procedure mentioned for **2**.

Methyl-((2-(2-(2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)-2-methylpropanamido)phenyl)sulphonyl)-*L*-prolinate 6a:

Representative procedure: EDC.HCl (0.142 g, 0.69 mmol) was added to a solution of **5** (0.17 g, 0.46 mmol) and Boc-Leu-OH (0.12 g, 0.50 mmol) in anhy. DCM at 0 °C followed by HOBt (0.062 g, 0.46 mmol). The resulting mixture was then stirred at 0 °C for 10 min and at room temperature for 12 h. To the reaction mixture, 30 mL DCM was added and the organic layer was washed sequentially with sat. $NaHCO_3$, water, sat. $KHSO_4$ and brine. It was concentrated under reduced pressure and finally purified by column chromatography to furnish a white solid. Yield: 0.24 g (85%); mp: 90-92 °C; $[\alpha]^{25}_D$: -82° (*c*=1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3337, 3020, 2400, 1700, 1503, 1337, 1215, 1155, 1022, 759, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ:10.12 (s, 1H), 8.63-8.61 (d, 1H, *J*= 8.53 Hz), 7.82-7.80 (d, 1H, *J*= 8.03 Hz), 7.58-7.54 (m, 1H), 7.20-7.16 (m, 1H), 6.93 (bs, 1H), 5.01 (bs, 1H), 4.34-4.31 (m, 1H), 4.19 (bs, 1H), 3.68 (s, 3H), 3.52-3.50 (m, 1H), 3.32-3.26 (m, 1H), 2.08-1.98 (m, 3H), 1.82-1.66 (m, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.54-1.48 (m, 1H), 1.45 (s, 9H), 0.94-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:174.6, 172.9, 171.5, 137.3, 134.8, 129.8, 123.4, 123.1, 122.7, 79.4, 61.8, 57.4, 56.1, 53.4, 52.4, 49.7, 40.0, 30.9, 28.2, 26.0, 25.0, 24.9, 24.7, 24.6, 24.3, 24.1, 22.9, 22.7, 22.0; LC-MS: 605.25 $(M+Na)^+$; Anal. Calcd. for $C_{27}H_{42}N_4O_8S$: C, 55.65; H, 7.27; N, 9.62; Found: C, 55.81; H, 7.05.; N, 9.75.

Methyl((2-(2-(2-((tert-butoxycarbonyl)amino)-2-methylpropanamido)-2-methylpropanamido)phenyl)sulphonyl)-*L*-prolinate 10a:

Tetramer **10a** was obtained as a white fluffy solid. Yield: 90%; mp: 67-69 ^{o}C; $[\alpha]^{25}_{D}$: -12° (*c*=1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3337, 3019, 2400, 1735, 1699, 1523, 1338, 1215, 1045, 928, 758, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.04 (s, 1H), 8.58-8.56 (d, 1H, *J*= 8.54 Hz), 7.82-7.79 (d, 1H, *J*= 8.03 Hz), 7.56-7.52 (m, 1H), 7.27 (bs, 1H), 7.19-7.15 (m, 1H), 5.03 (s, 1H), 4.33-4.30 (m, 1H), 3.64 (s, 3H), 3.53-3.48 (m, 1H), 3.35-3.29 (m, 1H), 2.11-1.92 (m, 3H), 1.86-1.77 (m, 1H), 1.61 (s, 6H), 1.49 (s, 6H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 173.2, 172.0, 155.0, 137.1, 134.2, 129.2, 124.8, 123.4, 122.3, 60.3, 57.4, 56.9, 52.4, 48.3, 30.8, 28.2, 25.3, 25.2, 24.9, 24.4; LC MS: 477.15 $(M+Na)^{+}$, 493.14 $(M+K)^{+}$; Anal. Calcd. for $C_{25}H_{38}N_4O_8S$: C, 54.14; H, 6.91; N, 10.10; Found: C, 54. 43; H, 6.68; N, 10.28.

Methyl((2-(2-methyl-2-((R)-1-pivaloylpyrrolidine-2-carboxamido)propan amido) phenyl)sulphonyl)-L-prolinate 13a:

Compound **13a** was obtained as a white fliffy solid. Yield: 88%; mp: 60-62 ^{o}C; $[\alpha]^{25}_{D}$: -88° (*c*=1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3336, 3019, 2400, 1739, 1699, 1585, 1522, 1338, 1215, 1152, 762, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ: $10.08_{rotamer}$ (0.2H), $10.04_{rotamer}$ (0.8H), $8.57_{rotamer}$ (0.2H), $8.56\text{-}8.54_{rotamer}$ (0.8H), 7.78-7.77 (m, 1H), $7.55_{rotamer}$ (0.2H), $7.52_{rotamer}$ (0.8H), 7.50-7.49 (m, 1H), 7.15-7.12 (m, 1H), $4.66_{rotamer}$ (0.2H), $4.64\text{-}4.62_{rotamer}$ (0.8H), $4.30\text{-}4.28_{rotamer}$ (0.8H), $4.26\text{-}4.25_{rotamer}$ (0.2H), 3.67-3.65 (m, 2H), $3.61_{rotamer}$ (2H), $3.61_{rotamer}$ (1H), 3.50-3.46 (m, 1H), 3.32-3.27 (m, 1H), 2.25-2.22 (m, 1H), 2.04-2.00 (m, 2H), 1.98-1.91 (m, 2H), 1.87-1.77 (m, 3H), 1.55-1.54 (m, 6H), $1.23_{rotamer}$ (7H), $1.23_{rotamer}$ (2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 173.1, 173.0, 171.9, 171.7, 171.6, 137.2, 134.1, 129.2, 129.1, 124, 9, 124.8, 123.3, 123.2, 122.2, 122.0, 61.8, 61.6, 60.3, 60.1, 57.4,

52.3, 48.2, 39.1, 30.7, 27.4, 25.8, 25.6, 24.5. 24.4, 23.9; LC MS: 573.23 $(M+Na)^+$, 589.20 $(M+K)^+$; Anal. Calcd. for $C_{25}H_{36}N_4O_7S$: C, 55.95; H, 6.76; N, 10.44; Found: C, 55.52; H, 6.99; N, 10.50.

((2-(2-(2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)-2-methylpropanamido)phenyl)sulphonyl)-*L*-proline 6b:

Representative procedure: LiOH ·H_2O (0.06 g, 1.3 mmol) was added to a solution of **8** (0.2 g, 0.34 mmol) in methanol (5 mL), followed by water (1 mL) at 0 °C. After complete consumption of the starting material (4 h), solvent was evaporated under reduced pressure, and the free acid was generated by treating with sat. $NaHSO_4$ solution followed by extraction with DCM (2 × 10 mL). Compound **6b** obtained after evaporation of the solvent under vacuum was carried forward without further purification.

Methyl-2-(2-((2S)-1-((2-(2-(2-((tert-butoxycarbonyl)amino)-4-methylpentan-amido)-2-methylpropanamido)phenyl)sulphonyl)pyrrolidine-2-carboxamido)-4-methylpentanamido)-2-methylpropanoate 8:

Representative procedure: A solution of free acid **6b** (0.2 g 0.35 mmol) and dimer amine **12** (0.09 g, 0.38 mmol) in anhy. DCM was cooled to 0 °C. To this mixture, EDC.HCl (0.11 g, 0.52 mmol) was added followed by HOBt (0.05 g, 0.35 mmol), and was stirred at 0 °C for 10 min followed by 12 h at room temperature. DCM (30 mL) was then added to the reaction mixture and the organic layer washed sequentially with sat. $NaHCO_3$, water, sat. $KHSO_4$ and brine, and concentrated under reduced pressure and was finally purified by column chromatography to furnish a white solid. Yield: 0.2 g (75%); mp: 115-117 °C; $[\alpha]^{25}_D$: -101.69° (*c*=1.18, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3394, 3019, 2400, 1674, 1523, 1338, 1215, 1046, 928, 755, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.17 (s, 1H), 8.52-8.51 (d, 1H, *J*= 7.93 Hz), 7.83-7.82 (d, 1H, *J*= 7.93 Hz), 7.61-7.58 (m, 1H), 7.43 (bs, 1H), 7.32 (bs, 1H), 7.23-7.20 (m, 1H), 5.64 (s, 1H), 4.17-4.14 (m, 2H), 3.70 (s, 3H), 3.67

(bs, 1H), 3.26-3.15 (m, 2H), 2.08-2.06 (m, 1H), 1.90 (bs, 1H), 1.84-1.82 (m, 2H), 1.75-1.72 (m, 1H), 1.64 (s, 3H), 1.61 (bs, 1H), 1.59-1.57 (m, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 1.43 (s, 9H), 0.96-0.95 (d, 3H, *J*= 6.71 Hz), 0.91-0.89 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 173.0, 171.5, 156.3, 137.3, 134.9, 129.8, 123.9, 123.2, 123.0, 79.9, 61.9, 57.5, 56.2, 53.4, 52.4, 49.8, 40.0, 31.0, 28.2, 26.1, 25.1, 24.9, 24.8, 24.7, 24.4, 24.1, 23.0, 22.8, 22.06; LC MS: 803.40 $(M+Na)^+$; Anal. Calcd. for $C_{37}H_{60}N_6O_{10}S$: C, 56.90; H, 7.74; N, 10.76; Found: C, 56.63.; H, 7.92.; N, 10.68.

Methyl-2-(2-((S)-1-((2-(2-(2-((tert-butoxycarbonyl)amino)-2-methylpropan amido)-2-methylpropanamido)phenyl)sulphonyl)pyrrolidine-2-carboxamido)-4-methylpentanamido)-2-methylpropanoate 11:

Hexapeptide **11** was obatined as a white fluffy soild. Yield: 82%; mp: 93-95 °C; $[\alpha]^{25}_D$: -101° (*c*=1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3393, 3019, 2981, 2401, 1725, 1675, 1523, 1294, 1216, 1155, 1073, 926, 759, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.97 (s, 1H), 8.51-8.49 (d, 1H, *J*= 8.24 Hz), 7.81-7.79 (d, 1H, *J*= 7.33 Hz), 7.61-7.58 (m, 1H), 7.36 (bs, 1H), 7.24-7.21 (m, 1H), 7.08-7.06 (d, 1H, *J*= 8.55 Hz), 5.20 (s, 1H), 4.46-4.41 (m, 1H), 4.19-4.17 (m, 1H), 3.69 (s, 3H), 3.60 (bs, 1H), 3.18-3.13 (m, 1H), 2.22 (bs, 1H), 2.07-2.04 (m, 1H), 1.91-1.86 (m, 1H), 1.82-1.79 (m, 2H), 1.72-1.71 (m, 1H), 1.60 (s, 3H), 1.58 (s, 3H), 1.54-1.52 (m, 1H), 1.50-1.49 (m, 6H), 1.47 (bs, 6H), 1.42 (s, 9H), 0.94-0.93 (d, 3H, *J*= 6.41 Hz), 0.91-0.89 (d, 3H, *J*= 6.41 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 174.6, 173.1, 171.1, 170.9, 155.1, 137.3, 134.9, 129.7, 123.9, 123.5, 123.0, 80.2, 77.2, 62.1, 57.3, 56.7, 56.1, 52.3, 51.8, 49.6, 40.3, 30.7, 28.2, 25.2, 25.1, 25.0, 24.6, 24.5, 22.9, 21.6; LC MS: 775.39 $(M+Na)^+$, 791.30 $(M+K)^+$; Anal. Calcd. for $C_{35}H_{56}N_6O_{10}S$: C, 55.83; H, 7.50; N, 11.16; Found: C, 56.03.; H, 7.29; N, 11.30.

methyl2-methyl-2-(4-methyl-2-(1-((2-(2-methyl-2-((S)-1-pivaloylpyrrolidine-2-carboxamido)propanamido)phenyl)sulphonyl)pyrrolidine-2-carboxamido) pentanamido)propanoate 14:

Hexapeptide **14** was obatined as a white fluffy soild. Yield: 73%; mp: 98-100 ^{o}C; $[\alpha]^{26}_{D}$: -129.52° (*c*=1.05, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3333, 3019, 2973, 2400, 1738, 1681, 1584, 1524, 1337, 1215, 1153, 926, 758, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ: $10.03_{rotamer}$ (0.8H), $9.96_{rotamer}$ (0.2H), $8.52\text{-}8.50_{rotamer}$ (0.8 H), $8.43\text{-}8.41_{rotamer}$ (0.2H), 7.79-7.77 (d, 1H, *J*= 7.94 Hz), 7.60-7.56 (m, 2H), 7.22-7.19 (m, 1H), 7.06 (bs, 1H), $6.98\text{-}6.96_{rotamer}$ (0.8H), $6.94_{rotamer}$ (0.2H), 4.66-4.65 (m, 1H), 4.49-4.46 (m, 1H), $4.18\text{-}4.17_{rotamer}$ (0.2H), $4.15\text{-}4.12_{rotamer}$ (0.8H), 3.68 (s, 3H), 3.65-3.61 (m, 2H), 3.15-3.10 (m, 1H), 2.20-2.18 (m, 1H), 2.07-2.01 (m, 2H), 1.91-1.76 (m, 5H), 1.70-1.68 (m, 1H), 1.55 (s, 3H), 1.54 (s, 3H), 1.53-1.50 (m, 1H), 1.48 (s, 3H), 1.45 (s, 3H), $1.22_{rotamer}$ (7H), $1.19_{rotamer}$ (2H), 0.93-0.92 (m, 3H), 0.89-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.1, 174.5, 173.3, 173.2, 172.0, 171.9, 171.1, 171.0, 170.8, 137.5, 134.8, 134.7, 129.6, 124.0, 123.9, 123.8, 123.2, 122.8, 62.3, 62.2, 61.7, 61.6, 57.4, 56.1, 52.3, 52.2, 51.6, 49.4, 48.4, 48.3, 40.3, 40.2, 39.0, 30.8, 30.7, 27.4, 27.3, 25.9, 25.8, 25.6, 25.1, 25.0, 24.9, 24.6, 24.5, 24.0, 21.6, 21.5; LC MS: 771.41 $(M+Na)^{+}$, 783.38 $(M+K)^{+}$; Anal. Calcd. for $C_{36}H_{56}N_6O_9S$: C, 57.73; H, 7.54; N, 11.22; Found: C, 57.51; H, 7.38; N, 11.60.

***tert*-butyl-(4-methyl-1-((2-methyl-1-((2-(((*2S*)-2-((4-methyl-1-((2-methyl-1-(methylamino)-1-oxopropan-2-yl)amino)-1-oxopentan-2-yl)carbamoyl) pyrrolidin-1-yl)sulphonyl)phenyl)amino)-1-oxopropan-2-yl)amino)-1-oxopentan-2-yl)carbamate 9:**

Representative procedure: To the ester **8** (0.15 g, 0.02 mmol), a saturated solution of methylamine in methanol was added at 0 °C and stirred for 12 h. Solvent was then stripped off to get the methyl amide **9** as a white solid. Yield: 0.13 g (90%); mp: 203-205 ^{o}C; $[\alpha]^{25}_{D}$: -55.55° (*c* 1.56, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3615, 3393, 3019, 2400, 1674,

1523, 1421, 1338, 1215, 1046, 759, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.15 (s, 1H), 8.63-8.62 (d, 1H, *J*= 7.93 Hz), 7.79-7.77 (d, 1H, *J*= 7.93 Hz), 7.72 (s, 1H), 7.61-7.58 (m, 1H), 7.32 (bs, 1H), 7.23-7.20 (m, 1H), 7.04 (s, 1H), 6.77 (s, 1h), 5.24 (bs, 1H), 4.25 (bs, 1H), 4.11 (bs, 1H), 4.05-4.04 (m, 1H), 3.64 (bs, 1H), 3.22-3.20 (m, 1H), 2.72 (s, 3H), 2.09 (bs, 2H), 1.78-1.72 (m, 3H), 1.71-1.64 (m, 3H), 1.61 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H), 1.46 (bs, 2H), 1.41 (s, 3H), 1.39 (s, 9H), 1.02-1.01 (m, 3H), 0.94-0.90 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 173.4, 173.1, 172.1, 171.9, 155.7, 137.6, 135.0, 129.6, 123.7, 122.9, 122.5, 79.5, 61.4, 57.6, 54.0, 52.6, 50.2, 41.5, 39.5, 30.6, 28.2, 26.5, 25.2, 24.9, 24.5, 24.3, 23.6, 23.0, 22.7, 22.0, 21.7; LC MS: 802.41 $(M+Na)^+$, 818.37 $(M+K)^+$; Anal. Calcd. for $C_{37}H_{61}N_7O_9S$: C, 56.98; H, 7.88; N, 12.57; Found: C, 56.50; H, 8.02; N, 12.89.

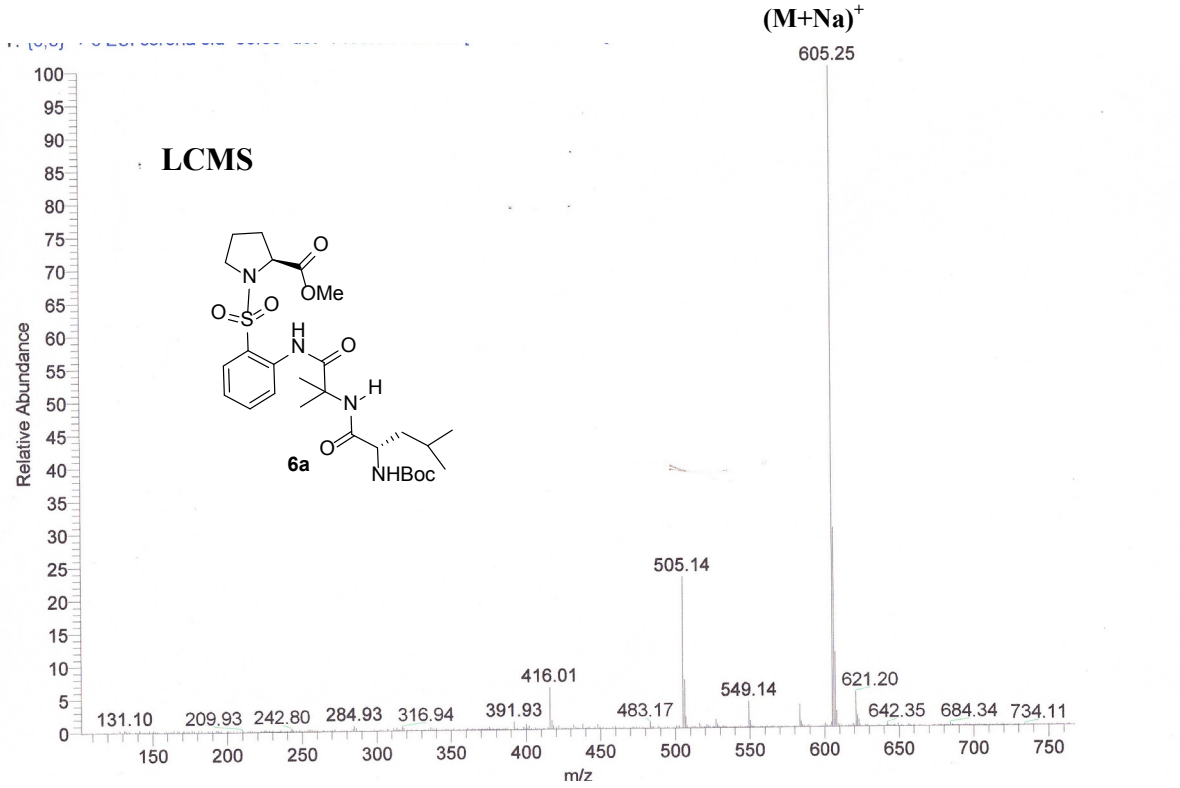
***tert*-butyl(2-methyl-1-((2-methyl-1-((2-(((*2S*)-2-((4-methyl-1-((2-methyl-1-(methylamino)-1-oxopropan-2-yl)amino)-1-oxopentan-2-yl)carbamoyl) pyrrolidin-1-yl)sulphonyl)phenyl)amino)-1-oxopropan-2-yl)amino)-1-oxopropan-2-yl)carbamate 12:**

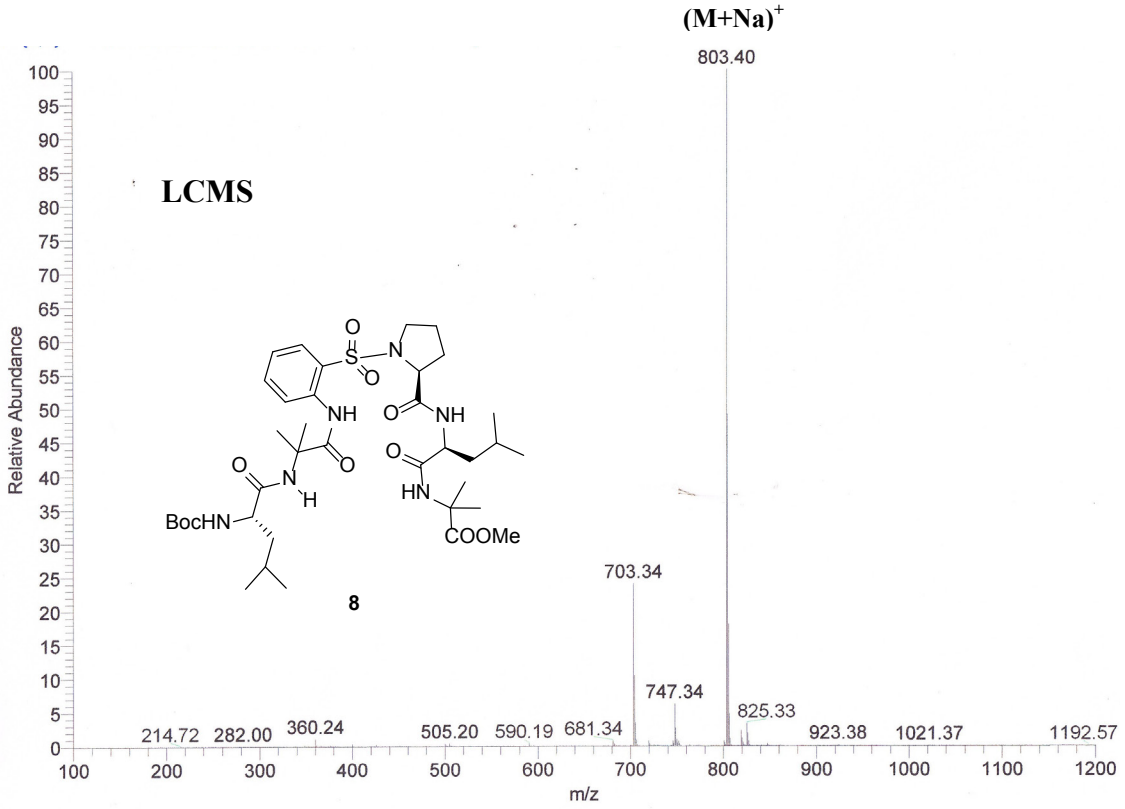
Compound **12** was obtained as a white solid. Yield: 82%, mp: 136-138 ^{o}C; $[\alpha]^{25}_{D}$: -63.52° (*c*= 0.85, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3627, 3393, 3019, 2400, 1674, 1522, 1422, 1338, 1215, 1046, 928, 757, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 8.50-8.49 (d, 1H, *J*= 8.24 Hz), 7.78-7.77 (m, 1H), 7.63-7.60 (m, 1H), 7.35 (bs, 1H), 7.25-7.20 (m, 2H), 6.82-6.81 (m, 1H), 5.17 (s, 1H), 4.28-4.26 (m, 1H), 4.15-4.13 (m, 1H), 3.66-3.62 (m, 1H), 3.18-3.13 (m, 1H), 2.79-2.76 (m, 3H), 2.06-2.02 (m, 2H), 1.94-1.88 (m, 1H), 1.82-1.79 (m, 2H), 1.75-1.69 (m, 1H), 1.63-1.62 (m, 1H), 1.62 (s, 3H), 1.60 (s, 3H), 1.51 (s, 6H), 1.50 (s, 3H), 1.49 (s, 3H), 0.98-0.97 (d, 3H, *J*= 6.41 Hz), 0.93-0.92 (d, 3H, *J*= 6.41 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 174.7, 173.2, 172.1, 171.3, 155.0, 137.3, 134.9, 129.6, 124.0, 123.7, 122.9, 80.2, 77.2, 62.1, 57.5, 57.4, 56.7, 53.1, 49.6,

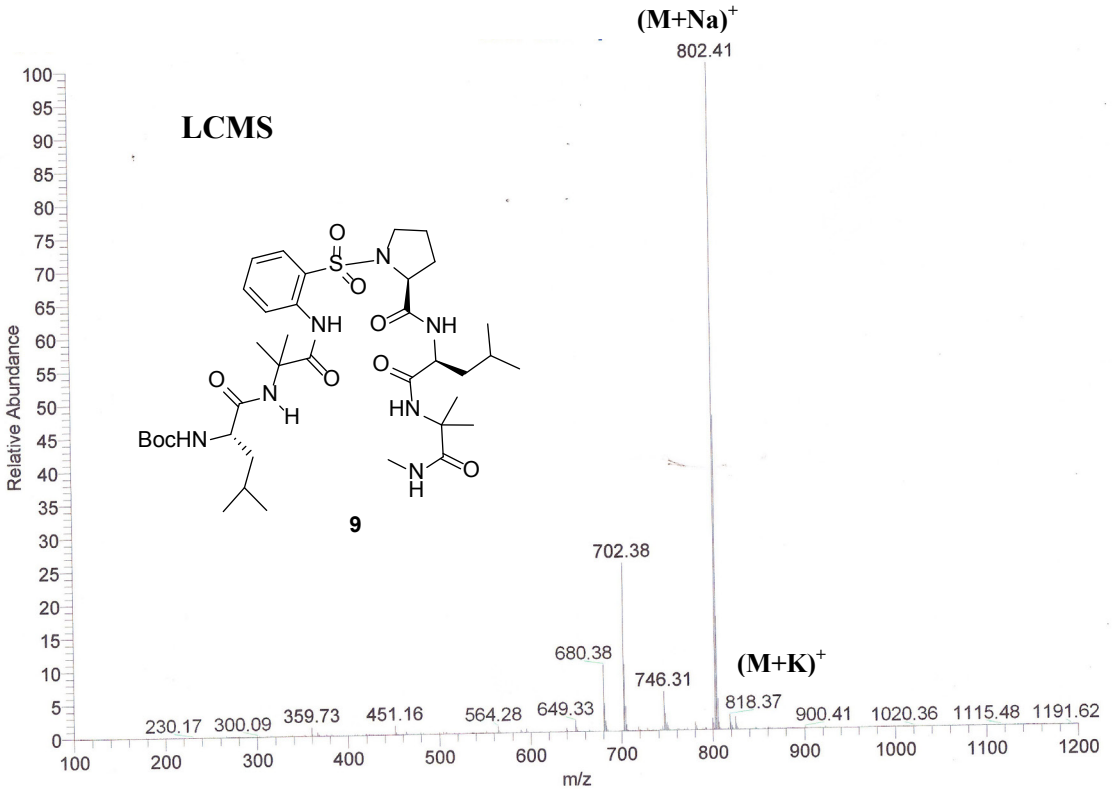
39.3, 30.7, 28.2, 26.5, 25.7, 25.5, 25.4, 25.3, 25.1, 24.6, 24.5, 22.9, 21.6; LC MS: 774.45 $(M+Na)^+$, 790.43 $(M+K)^+$; Anal. Calcd. for $C_{35}H_{57}N_7O_9S$: C, C, 55.91; H, 7.64; N, 13.04; Found: C, 56.13; H, 7.45; N, 13.28.

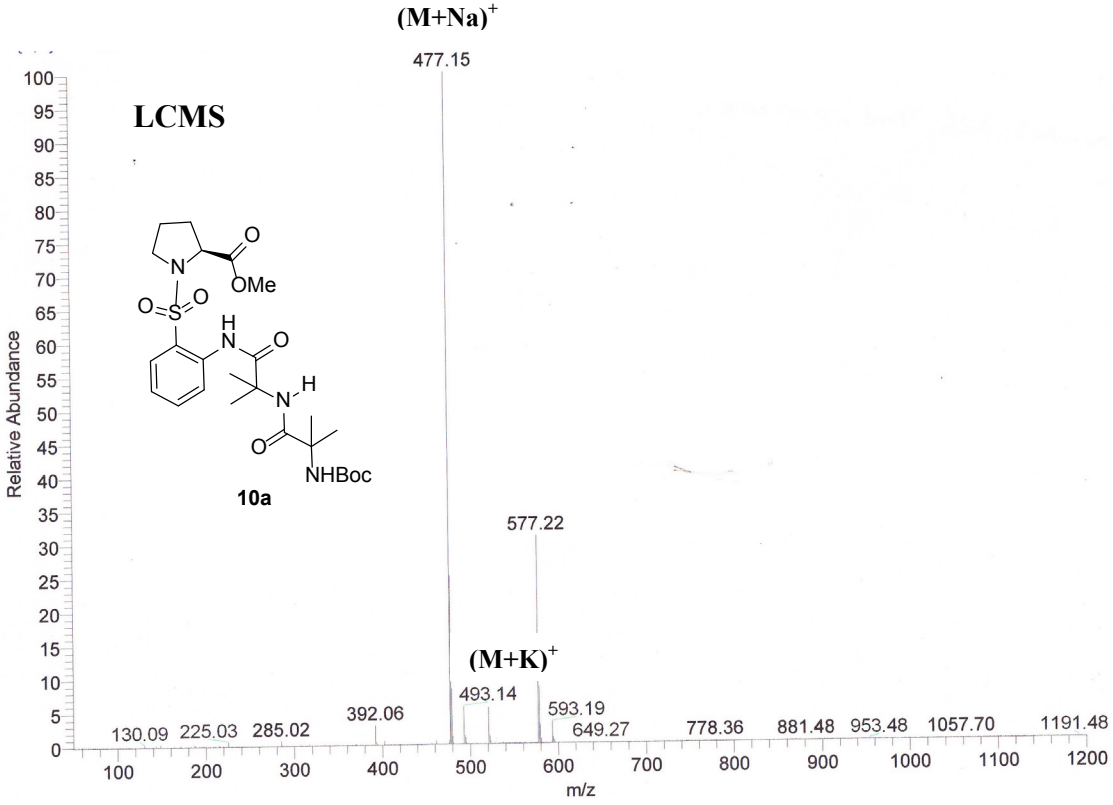
(*2S*)-N-(2-methyl-1-((2-(((*2S*)-2-((4-methyl-1-((2-methyl-1-(methylamino)-1-oxopropan-2-yl)amino)-1-oxopentan-2-yl)carbamoyl)pyrrolidin-1-yl)sulphonyl) phenyl)amino)-1-oxopropan-2-yl)-1-pivaloylpyrrolidine-2-carboxamide 15:

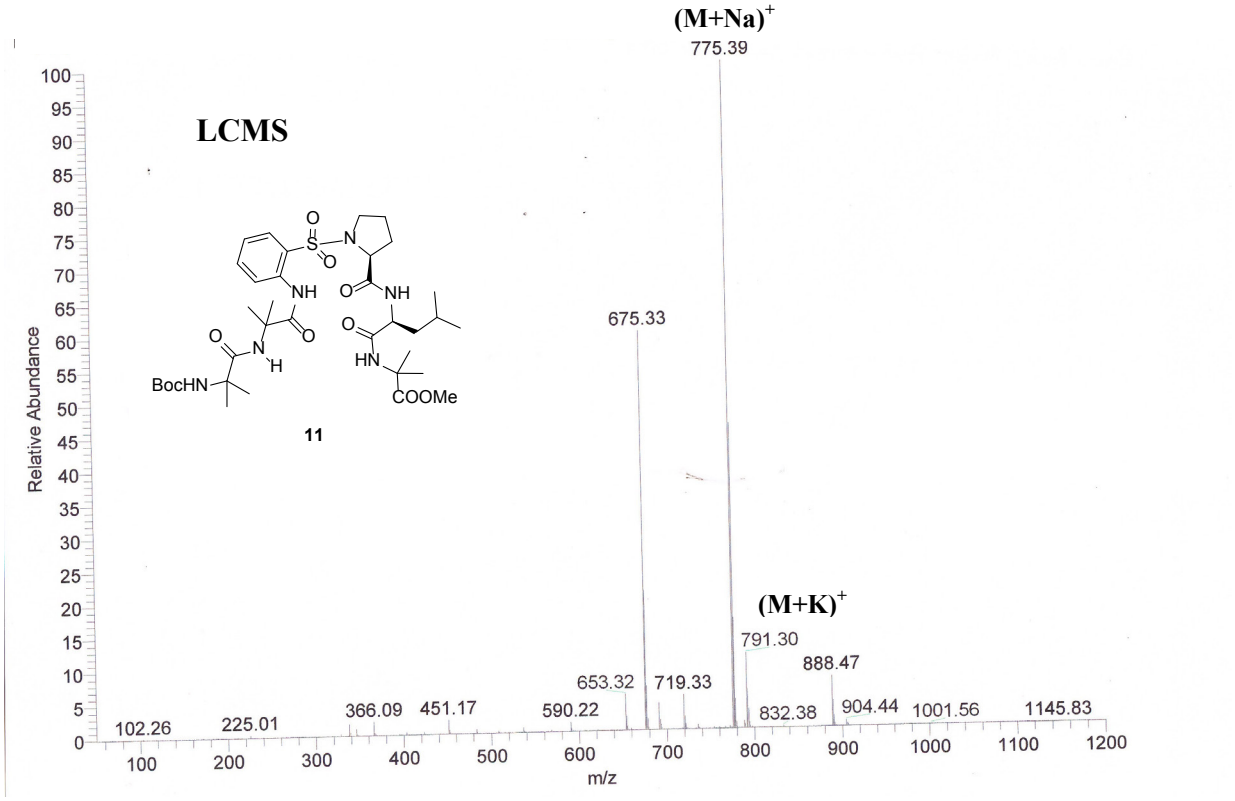
Compound **22** was obtained as a white solid. Yield: 86%; mp: 162-164 ^oC; $[\alpha]^{25}_D$: -104° (*c*=1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3615, 3393, 3019, 2400, 1674, 1523, 1421, 1338, 1215, 1046, 928, 767, 669; ^1H NMR (400 MHz, $CDCl_3$) δ: $9.94_{rotamer}$ (0.2 H), $9.91_{rotamer}$ (0.8 H), 8.43-8.42 (d, 1H, *J*= 8.31 Hz), 7.79-$7.77_{rotamer}$ (0.9H), $7.76_{rotamer}$ (0.7 H), $7.67_{rotamer}$ (0.7 H), $7.64_{rotamer}$ (0.3H), 7.61-7.58 (m, 1H), 7.25-7.22 (m, 1H), 7.07-7.04 (m, 2H), 6.92 (bs, 1H), 4.65-4.62 (m, 1H), 4.35-$4.30_{rotamer}$ (0.8 H), 4.28-$4.26_{rotamer}$ (0.2 H), 4.14-$4.13_{rotamer}$ (0.1 H), 4.12-$4.10_{rotamer}$ (0.9 H), 3.72-3.59(m, 3H), 3.16-3.11 (m, 1H), 2.78-$2.77_{rotamer}$ (2.5H), $2.76_{rotamer}$ (0.5 H), 2.19-2.14 (m, 1H), 2.12-2.08 (m,1 H), 2.04-1.96 (m, 3H), 1.93-1.87 (m, 2H), 1.82-1.77 (m, 2H), 1.73-1.69 (m, 1H), 1.63-1.58 (m, 1H), 1.55 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H), $1.20_{rotamer}$ (2H), $1.16_{rotamer}$ (7H), 0.99-0.97 (m, 3H), 0.93-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.1, 177.8, 174.9, 174.7, 172.3, 172.2, 172.2, 172.0, 171.7, 137.7, 137.6, 134.9, 129.7, 129.5, 124.3, 124.2, 124.1, 123.4, 61.9, 61.7, 57.6, 57.5, 57.3, 53.1, 52.9, 49.6, 48.3, 40.0, 39.1, 39.0, 30.9, 27.3, 26.5, 25.8, 25.7, 25.6, 25.5, 24.3, 25.1, 25.0, 24.6, 24.5, 23.0, 22.9, 21.6, 21.5; LC MS: 770.47 $(M+Na)^+$, 786.41 $(M+K)^+$; Anal. Calcd. for $C_{36}H_{57}N_7O_8S$: C, 57.81; H, 7.68; N, 13.11; Found: C, 57.55; H, 7.89; N, 13.35.

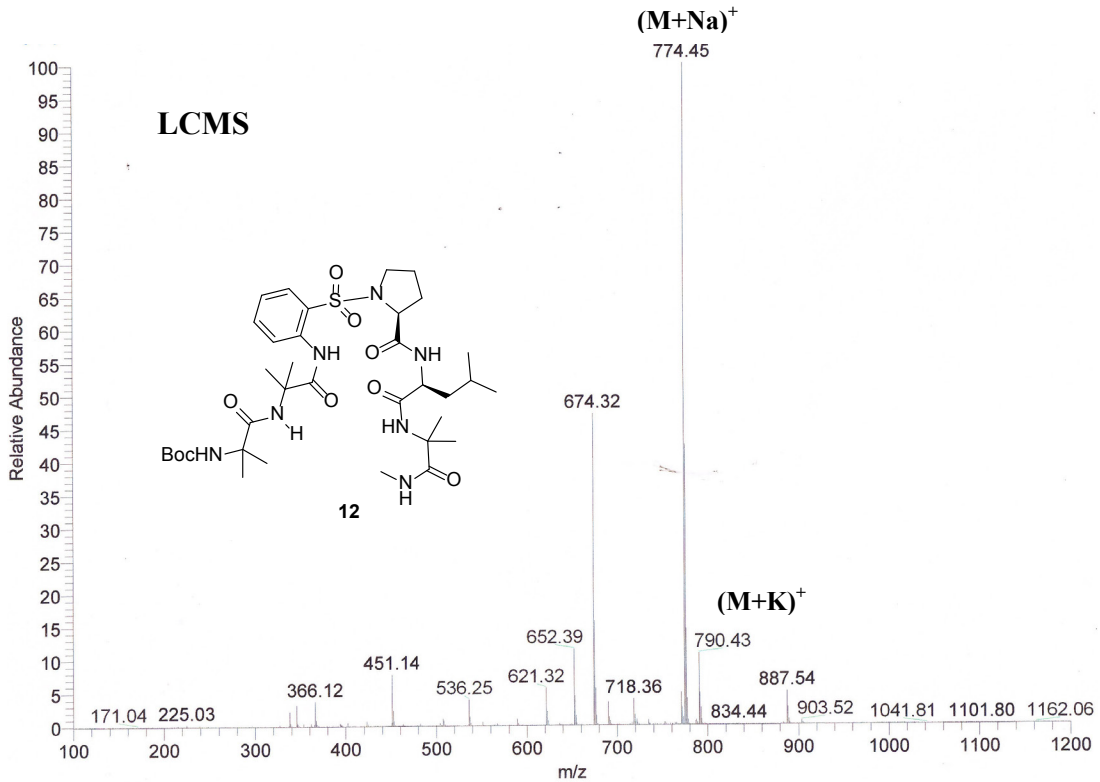

(M+Na)+
605.25
LCMS
Relative Abundance
m/z
505.14
416.01
549.14
621.20
131.10
209.93
242.80
284.93
316.94
391.93
483.17
642.35
684.34
734.11
6a
OMe
NHBoc

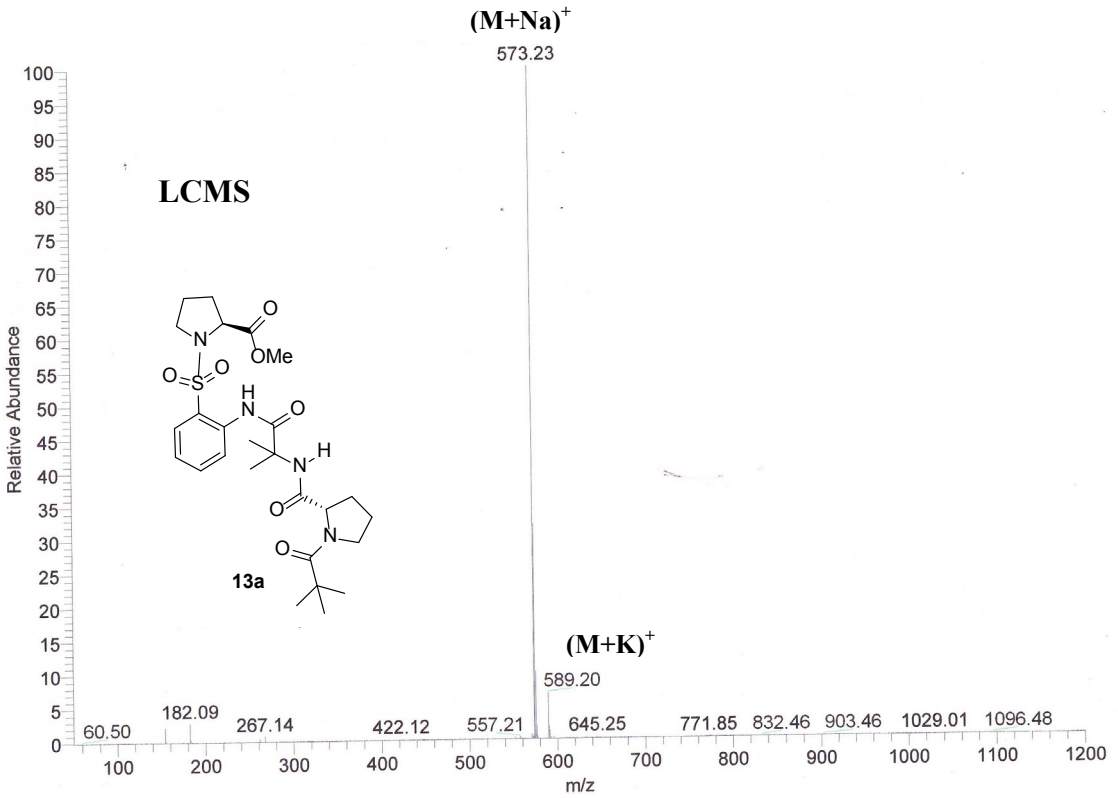

(M+Na)+
803.40
LCMS
Relative Abundance
m/z
703.34
747.34
825.33
214.72
282.00
360.24
505.20
590.19
681.34
923.38
1021.37
1192.57
8
BocHN
COOMe

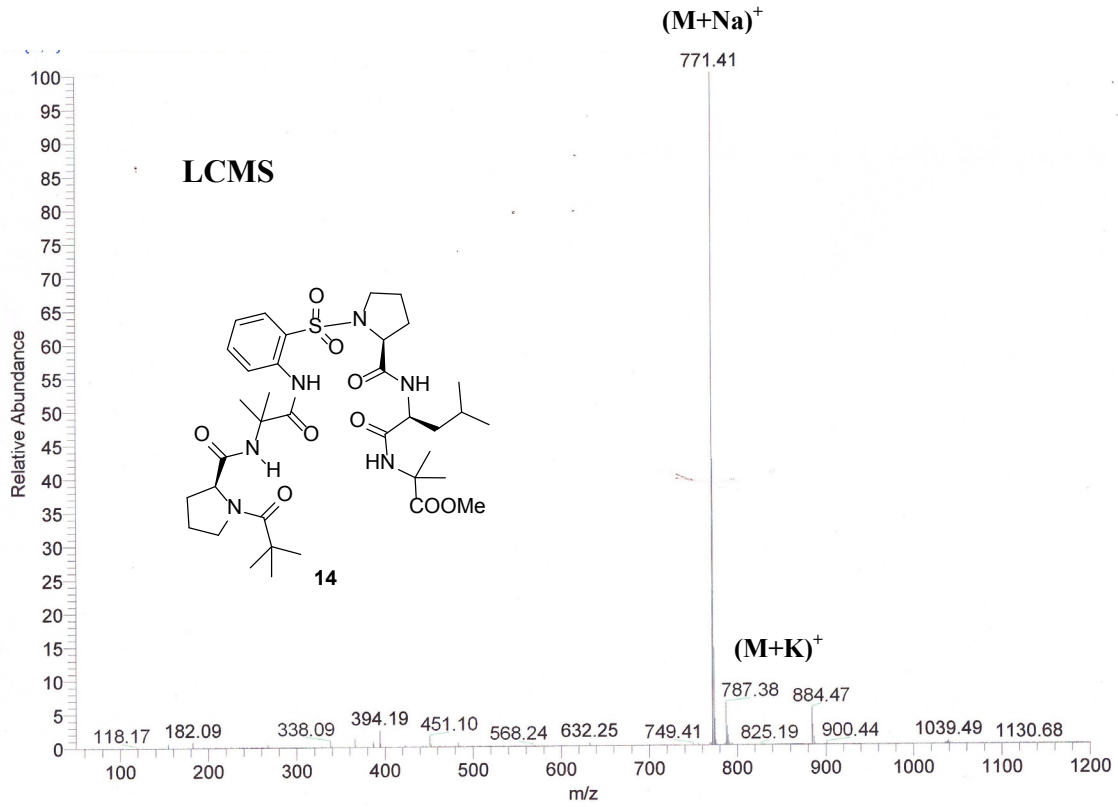

(M+Na)+
802.41
LCMS
Relative Abundance
m/z
9
702.38
680.38
746.31
(M+K)+
818.37
230.17
300.09
359.73
451.16
564.28
649.33
900.41
1020.36
1115.48
1191.62

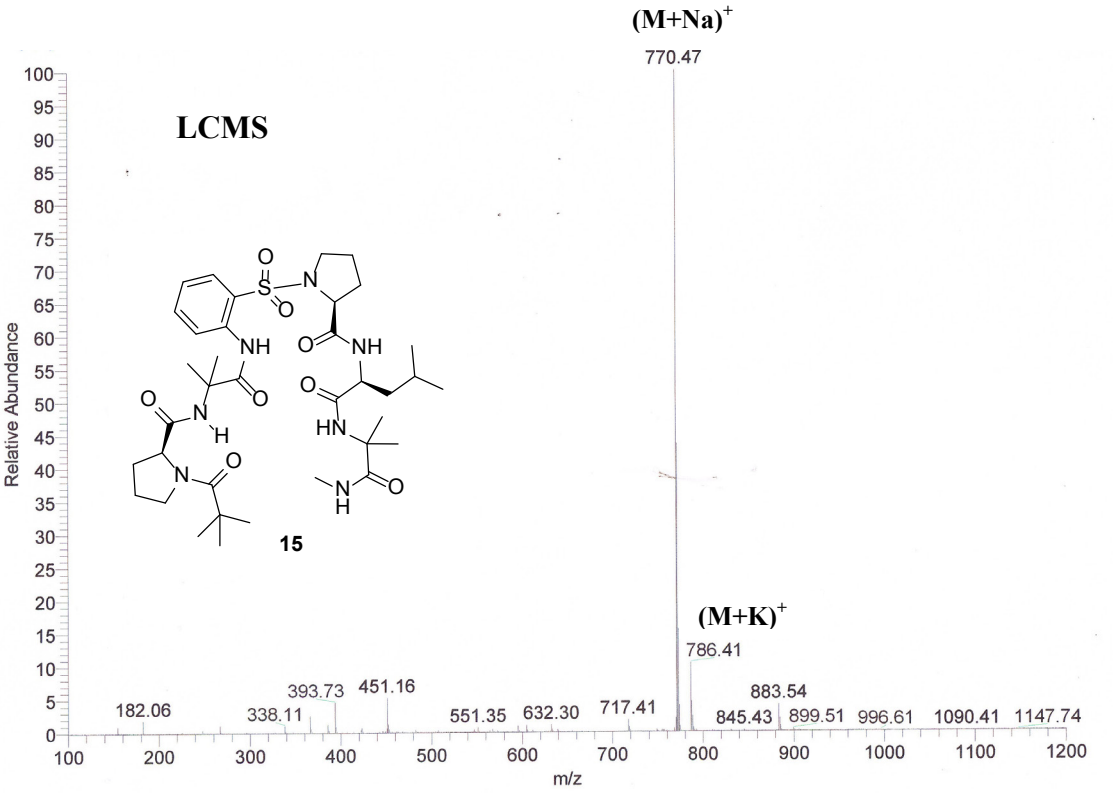

(M+Na)+
477.15
LCMS
Relative Abundance
m/z
10a
NHBoc
OMe
577.22
(M+K)+
493.14
392.06
593.19
649.27
778.36
881.48
953.48
1057.70
1191.48
130.09
225.03
285.02

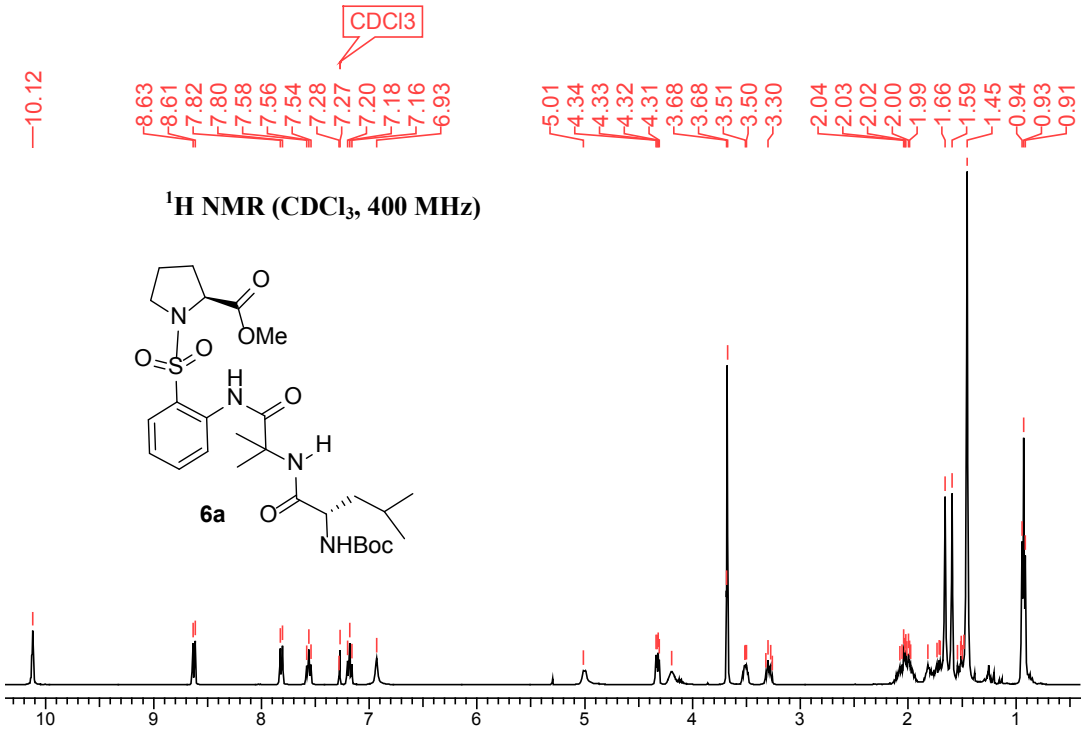

LCMS
(M+Na)+
775.39
675.33
(M+K)+
791.30
888.47
653.32
719.33
590.22
832.38
904.44
1001.56
1145.83
366.09
451.17
102.26
225.01
Relative Abundance
m/z
BocHN
COOMe
11

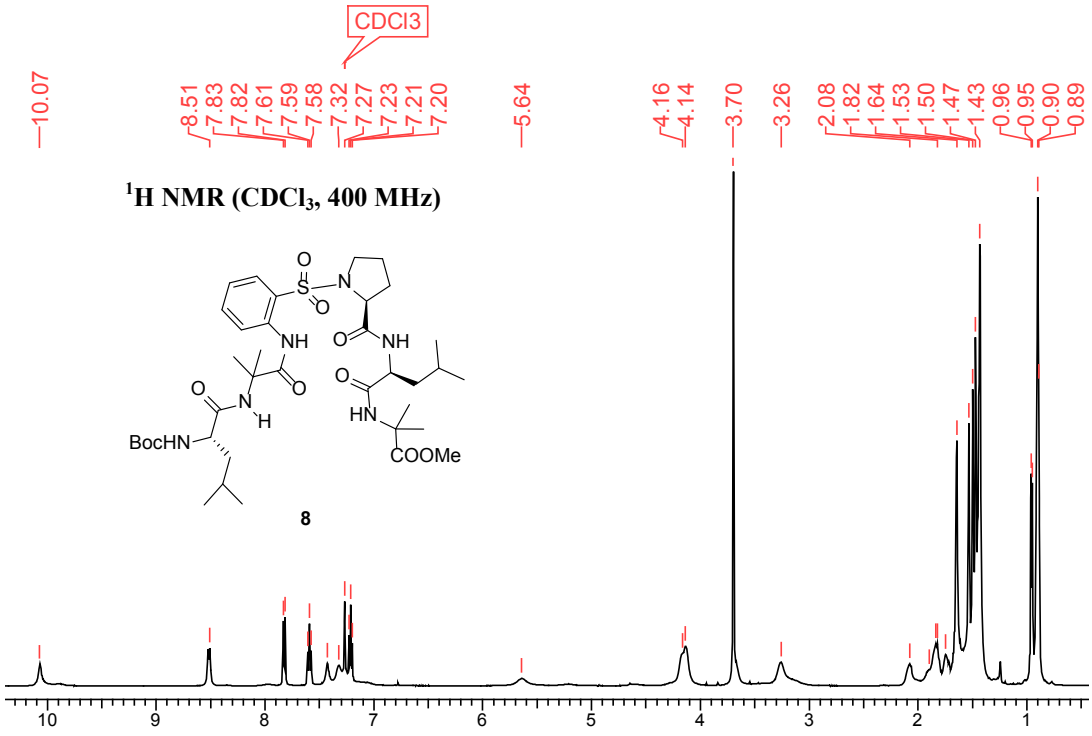

LCMS
(M+Na)+
774.45
674.32
(M+K)+
790.43
652.39
451.14
621.32
536.25
366.12
718.36
887.54
834.44
903.52
1041.81
1101.80
1162.06
171.04
225.03
Relative Abundance
m/z
BocHN
12

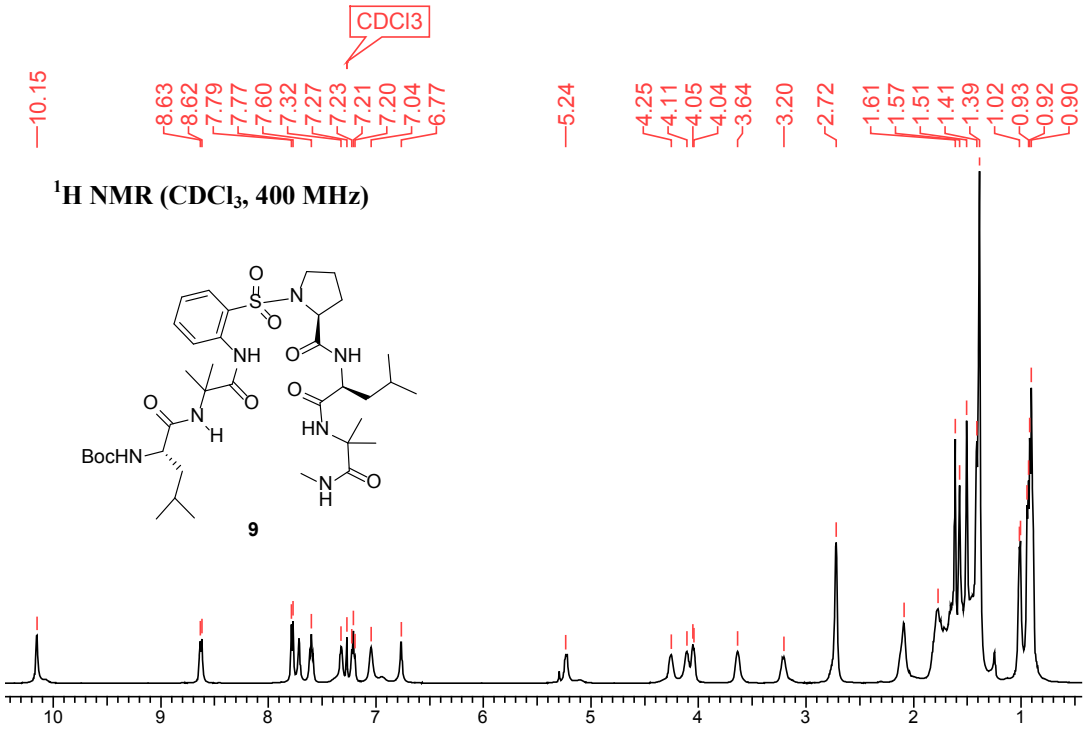


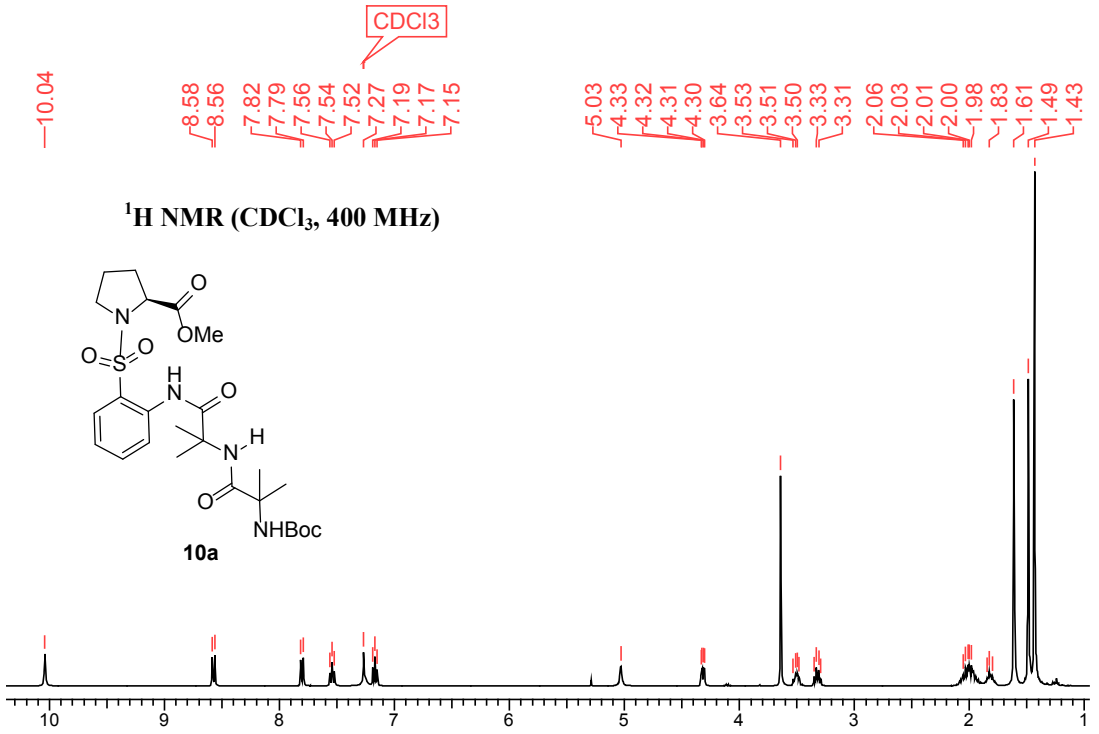


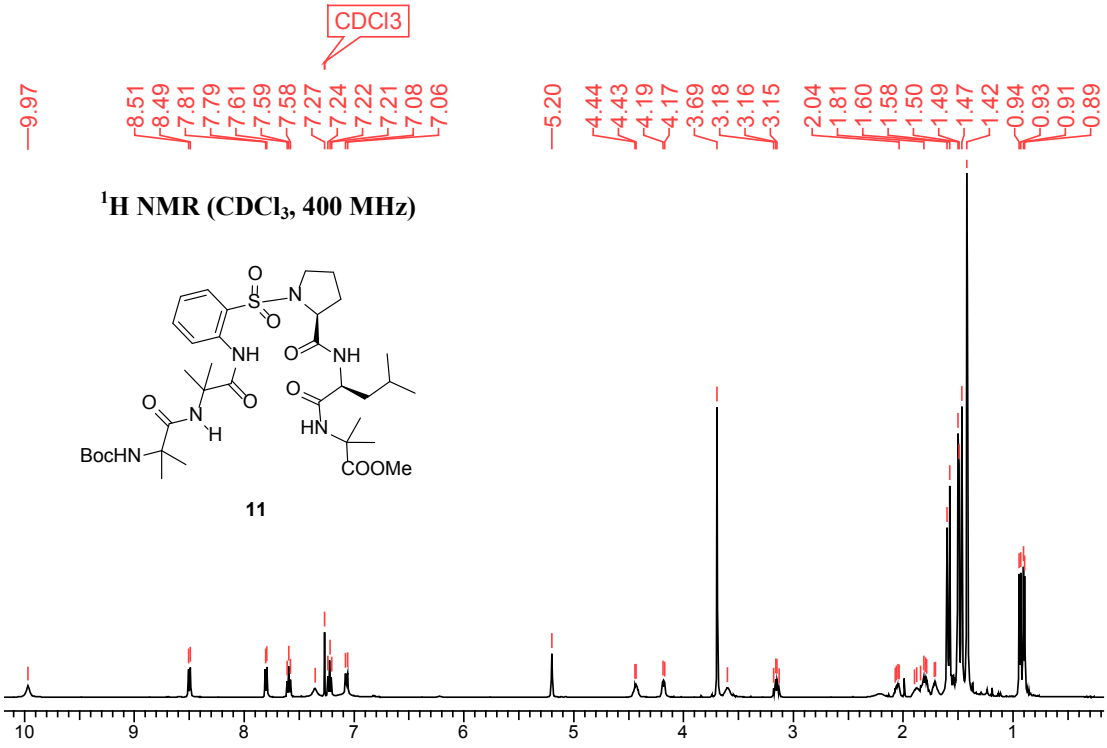

LCMS
(M+Na)+
770.47
(M+K)+
786.41
Relative Abundance
m/z
182.06
338.11
393.73
451.16
551.35
632.30
717.41
845.43
883.54
899.51
996.61
1090.41
1147.74
15

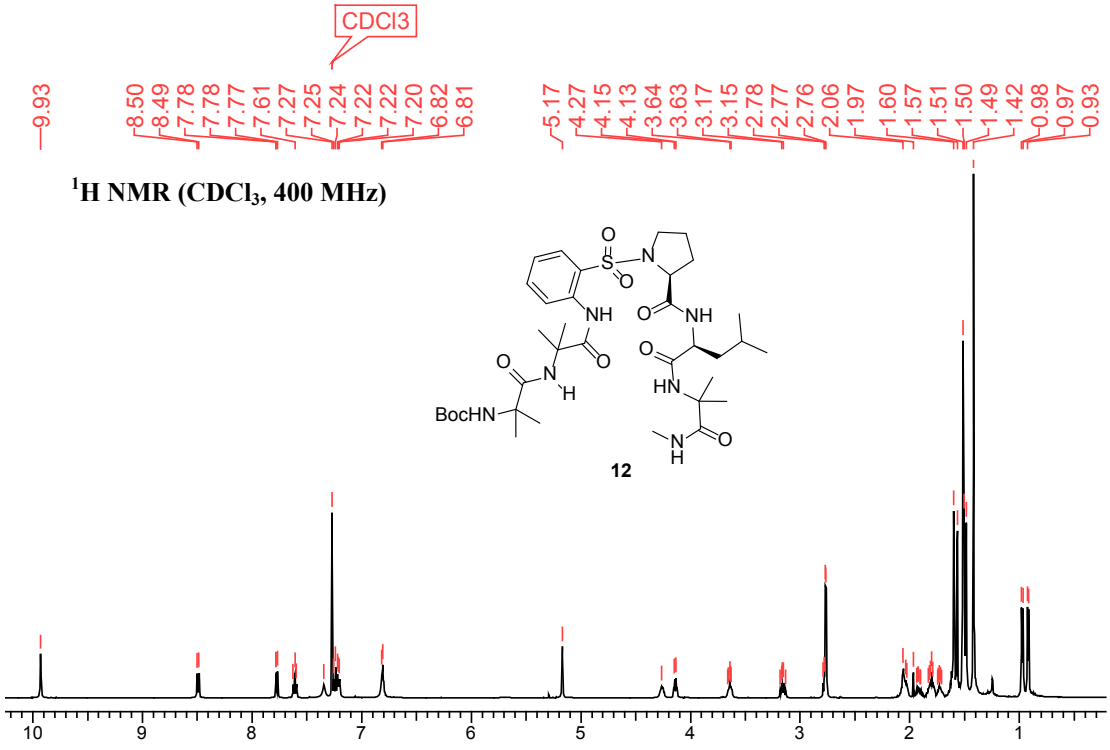

CDCl3
10.12
8.63
8.61
7.82
7.80
7.58
7.56
7.54
7.28
7.27
7.20
7.18
7.16
6.93
5.01
4.34
4.33
4.32
4.31
3.68
3.68
3.51
3.50
3.30
2.04
2.03
2.02
2.00
1.99
1.66
1.59
1.45
0.94
0.93
0.91
1H NMR (CDCl3, 400 MHz)
6a
OMe
NHBoc

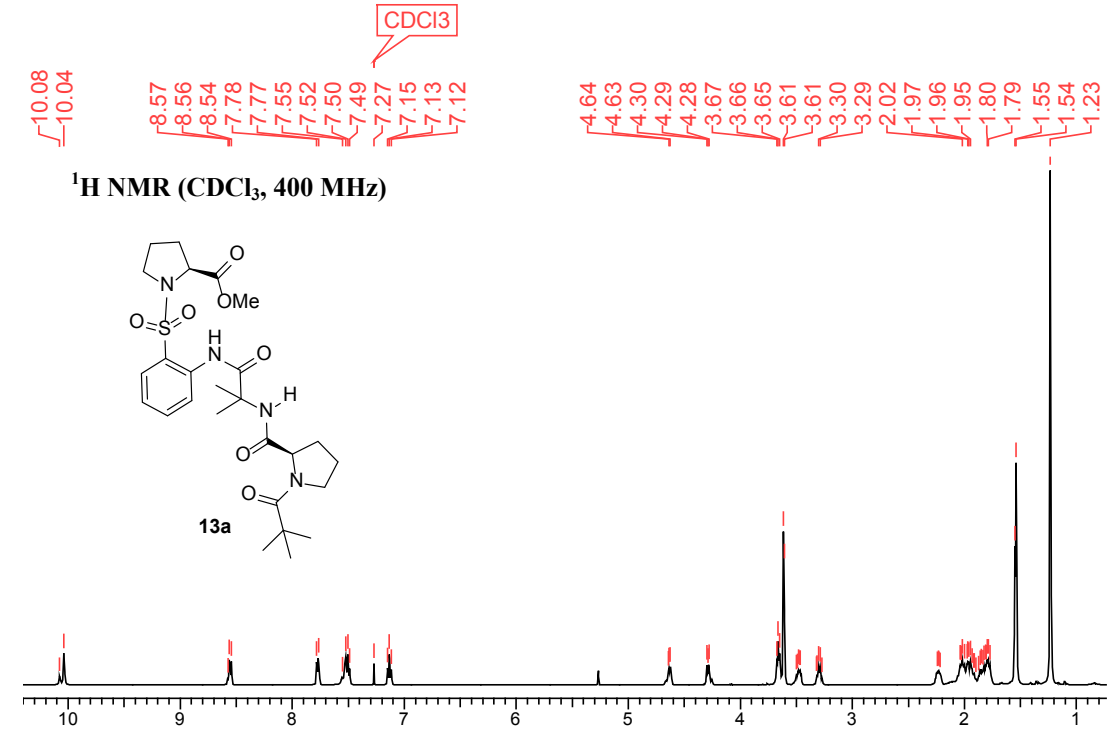


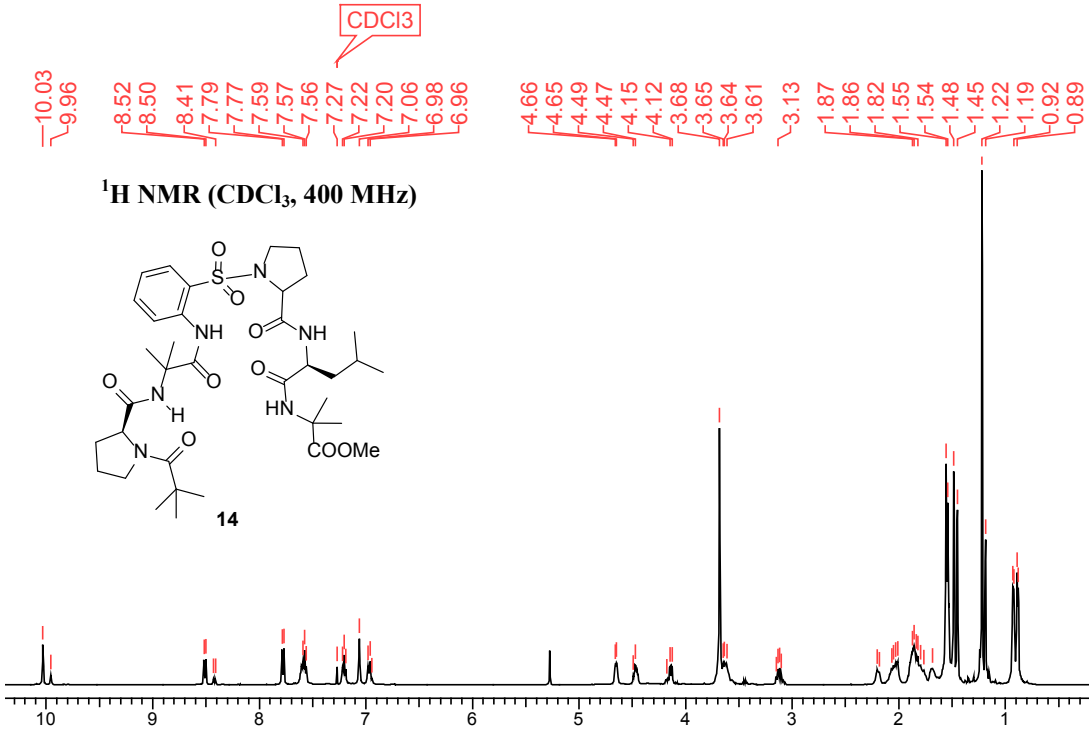






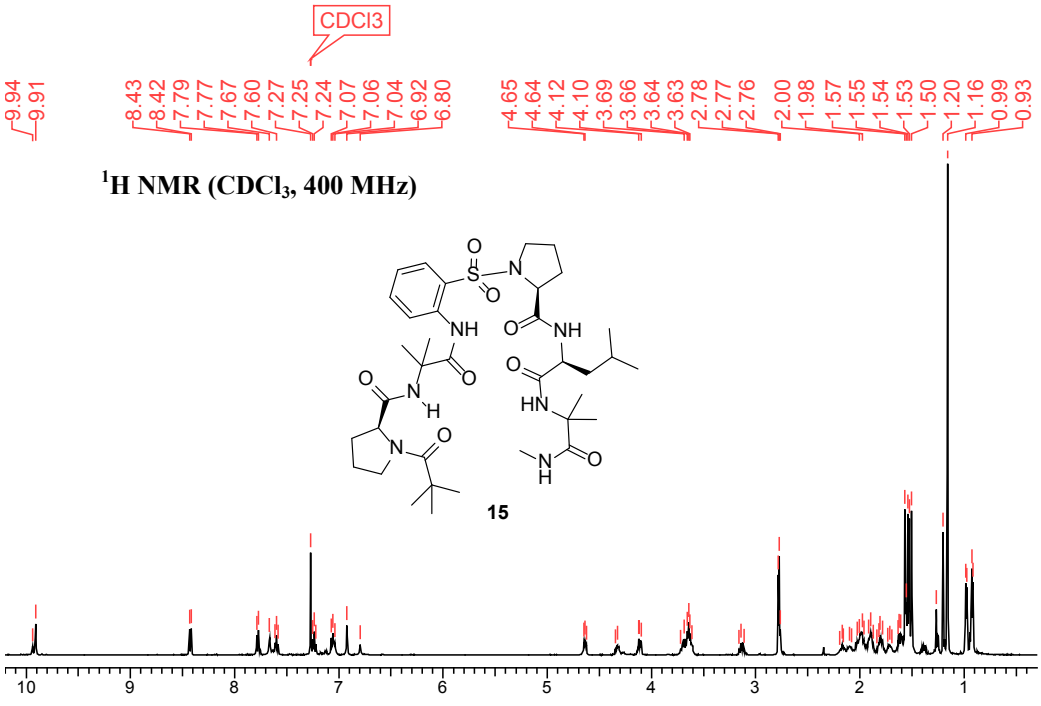






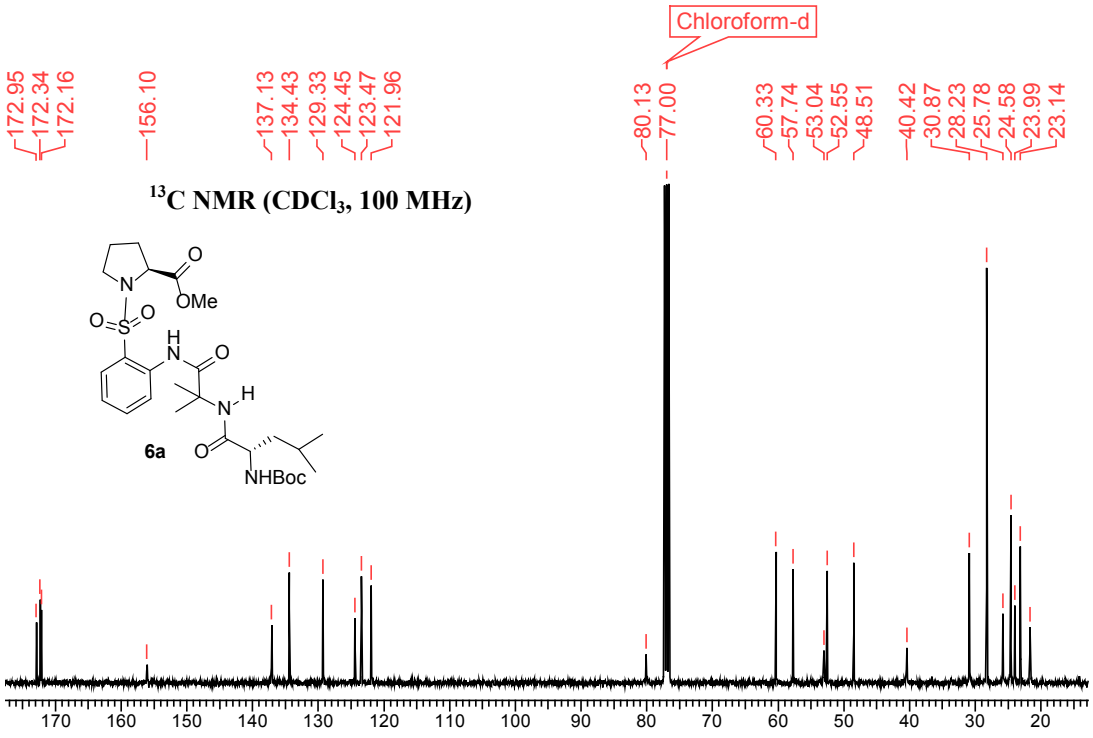
^{1}H NMR ($CDCl_3$, 400 MHz)

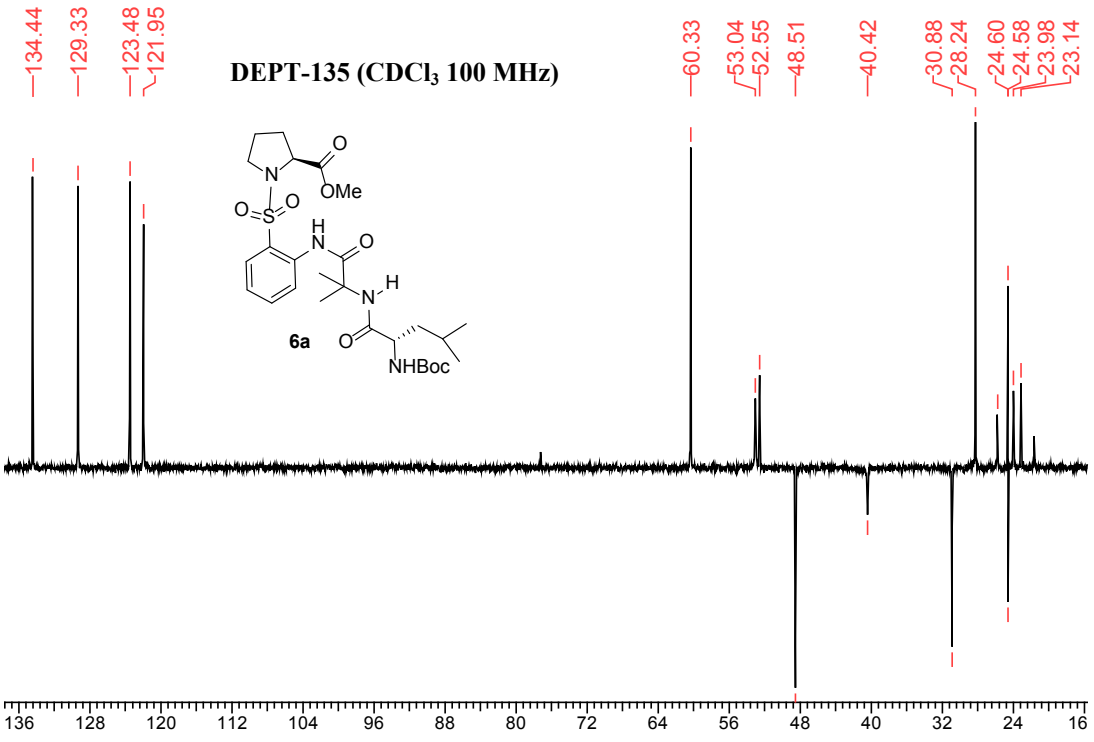
14

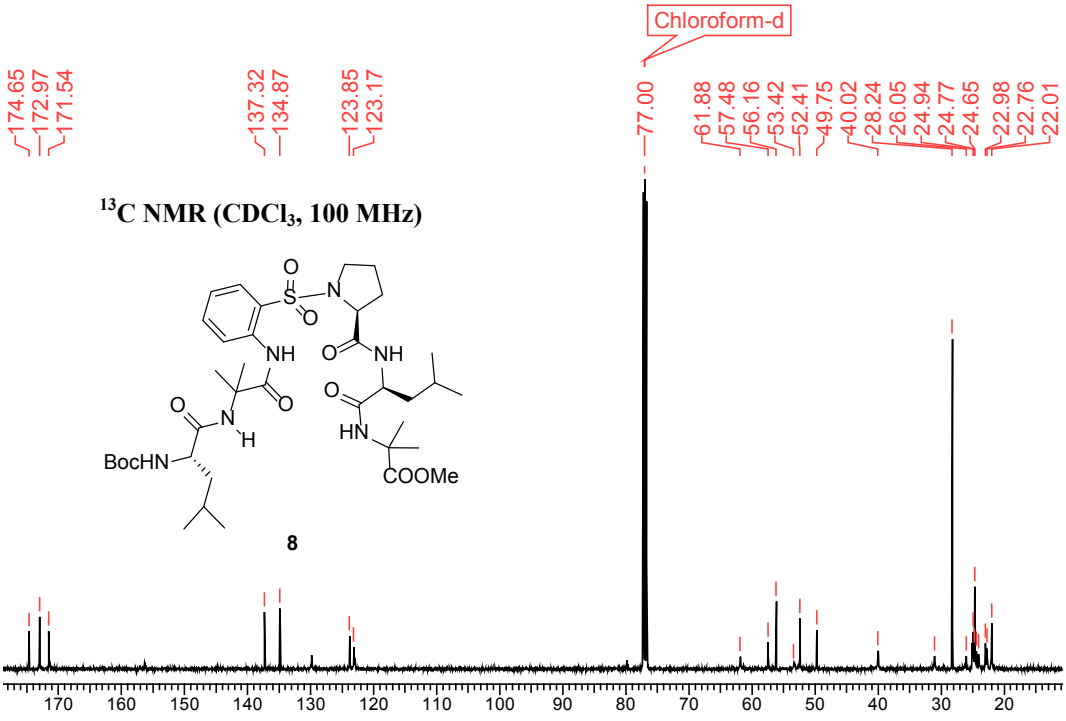


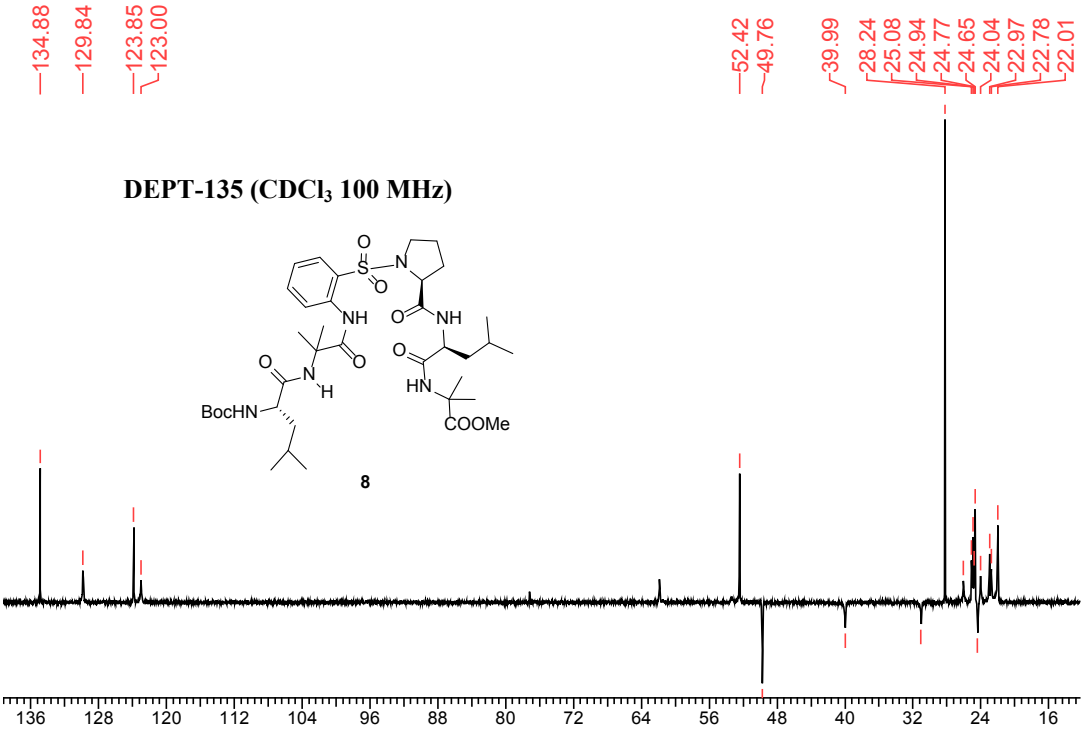
^{1}H NMR ($CDCl_3$, 400 MHz)

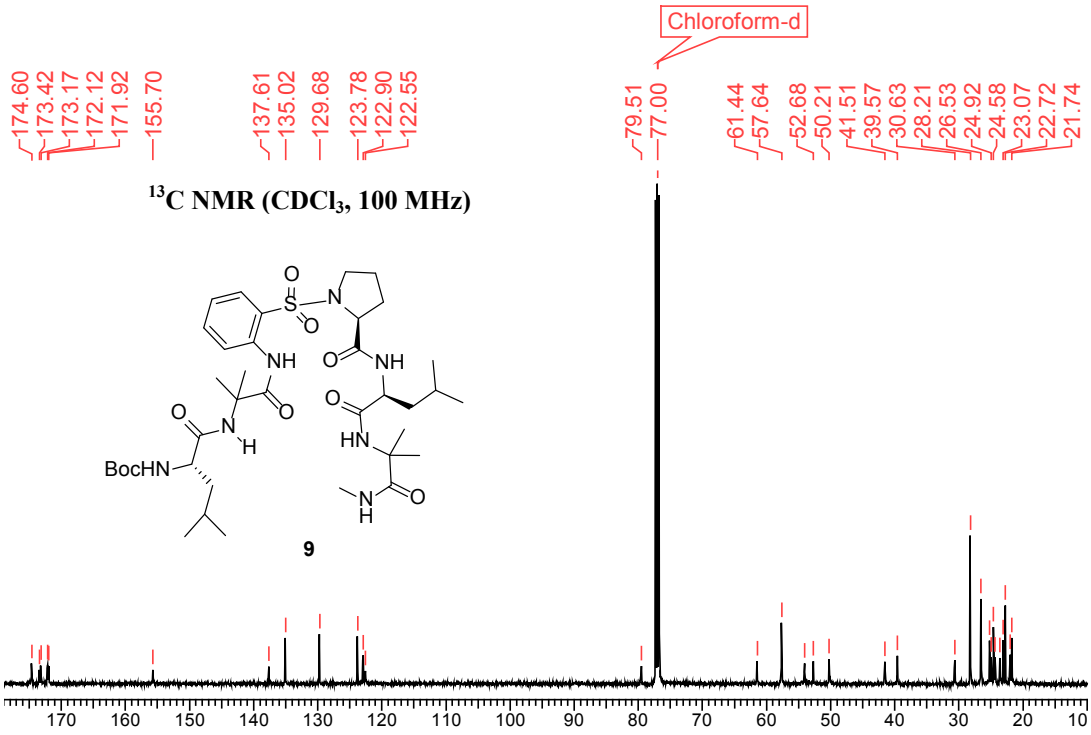
15





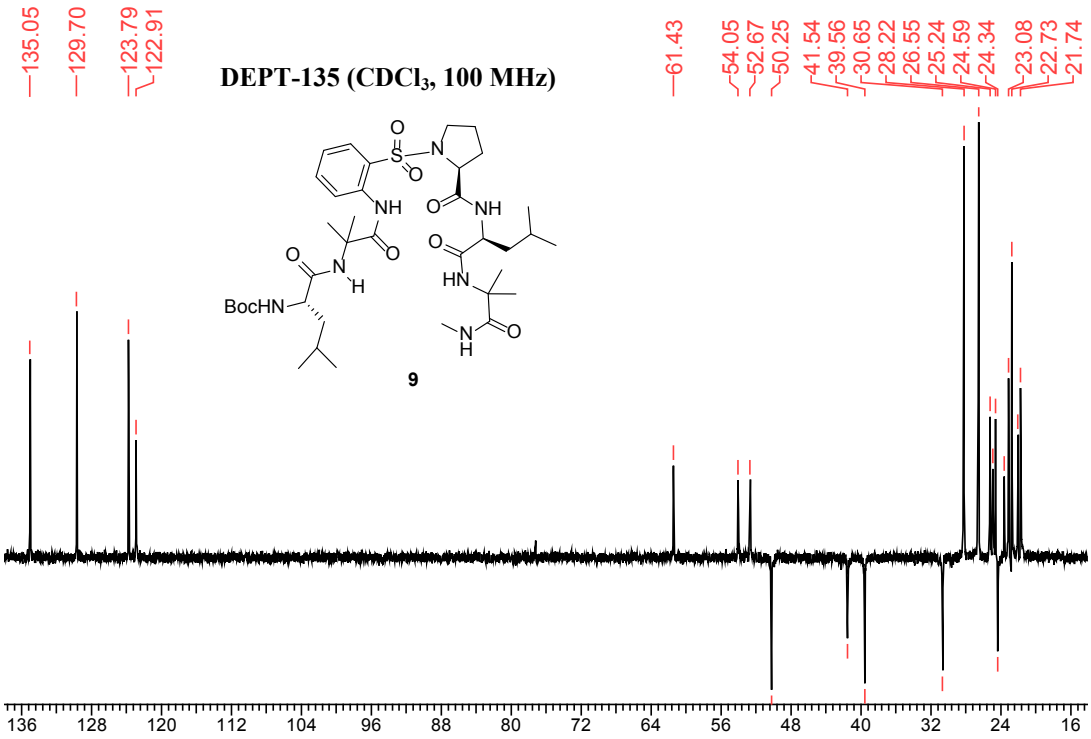






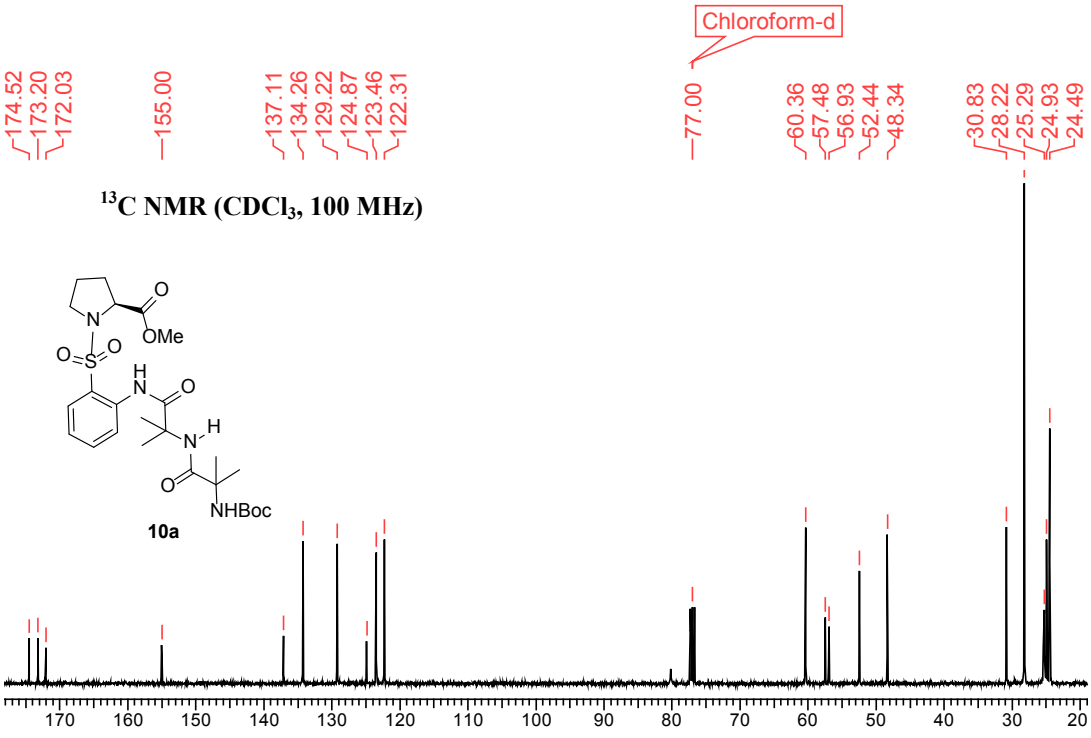
^{13}C NMR ($CDCl_3$, 100 MHz)

9



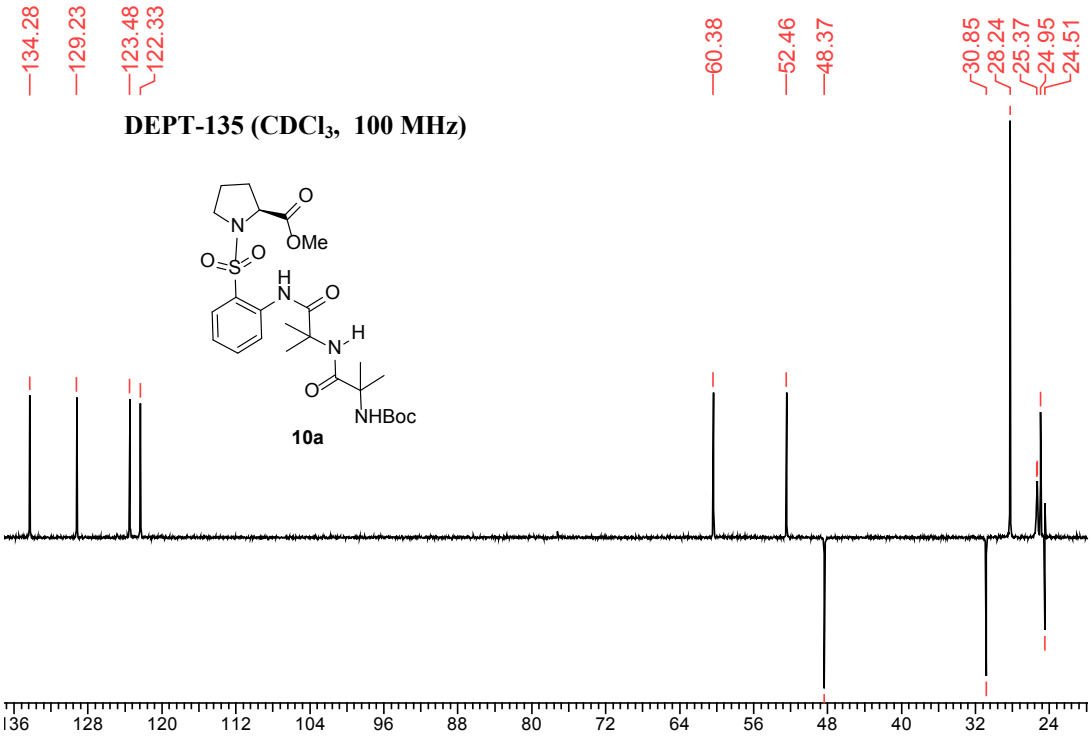
DEPT-135 ($CDCl_3$, 100 MHz)

9



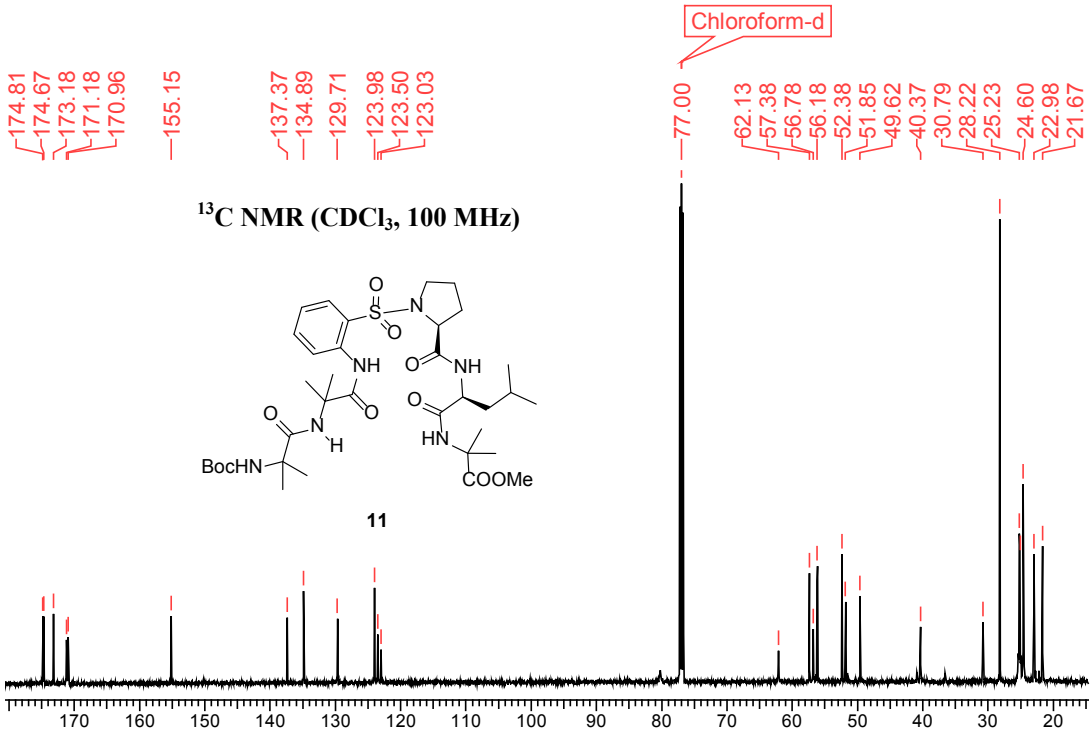
^{13}C NMR ($CDCl_3$, 100 MHz)

10a



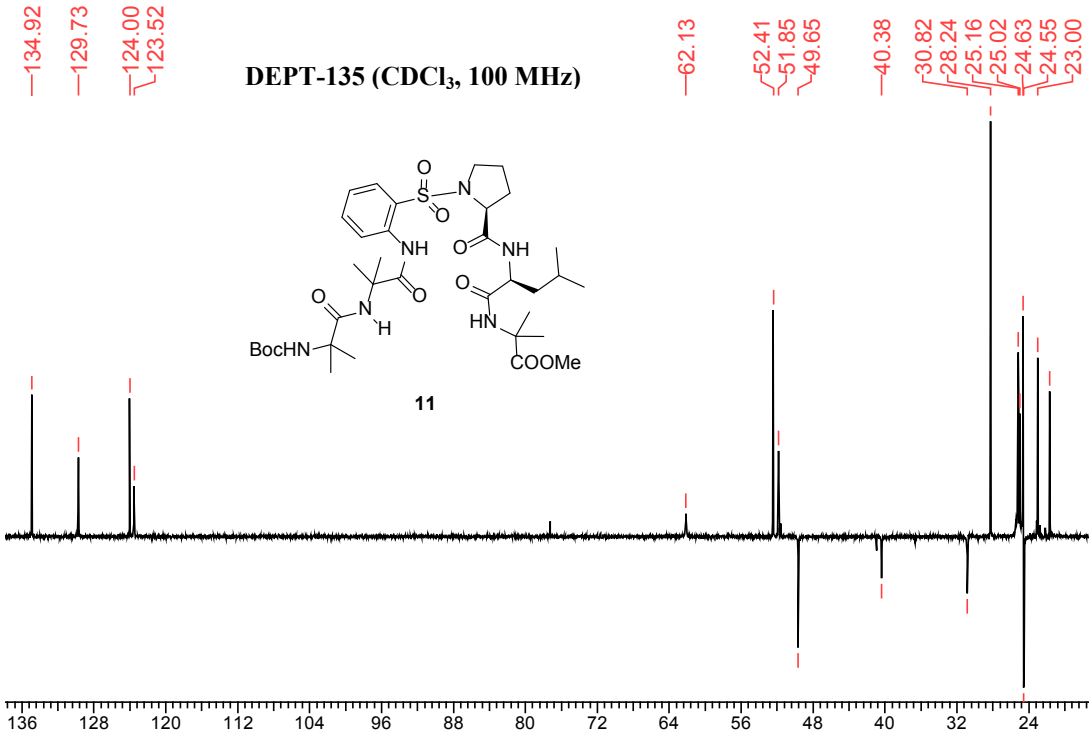
DEPT-135 ($CDCl_3$, 100 MHz)

10a



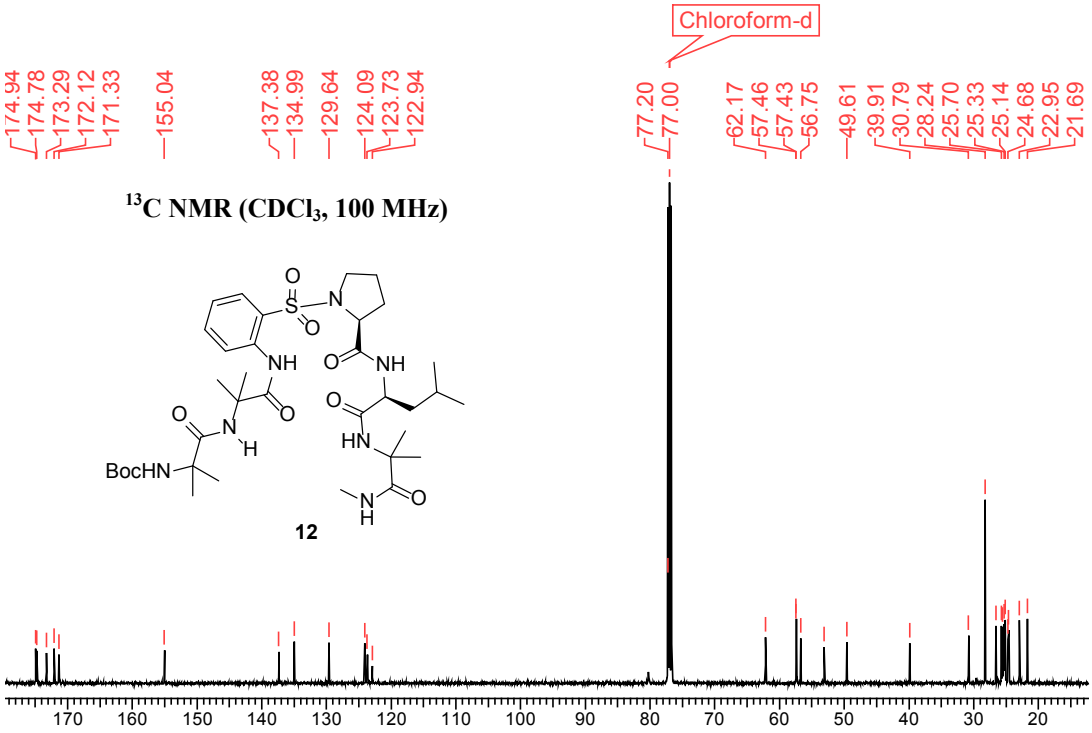
^{13}C NMR ($CDCl_3$, 100 MHz)

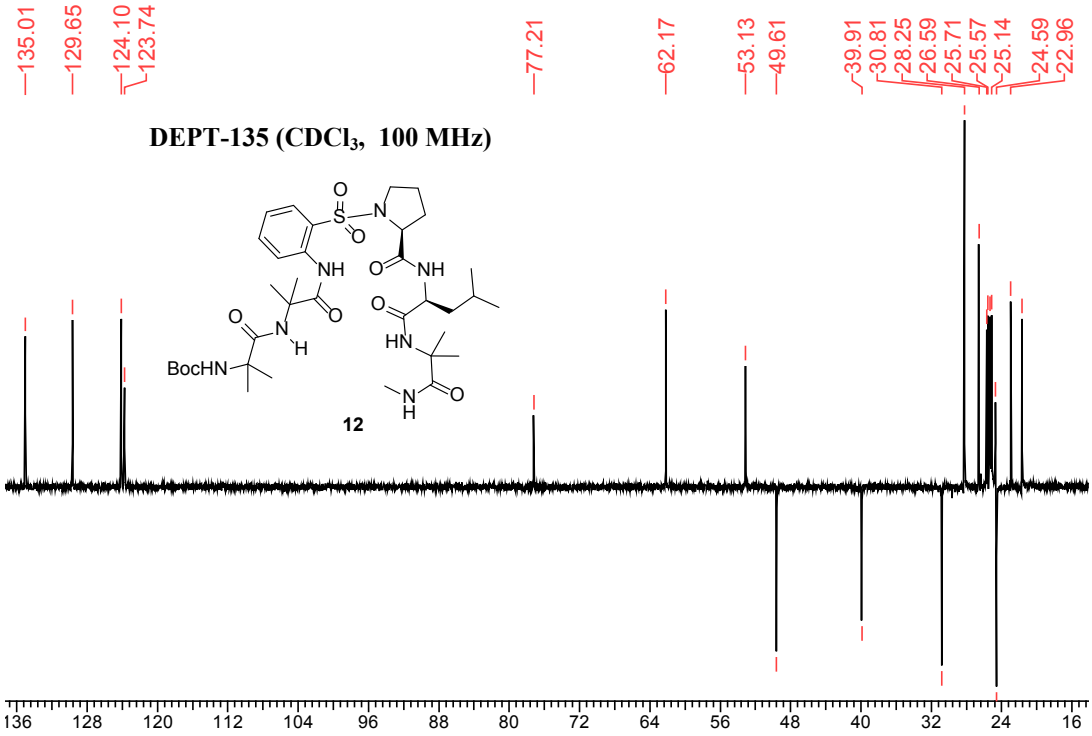
11

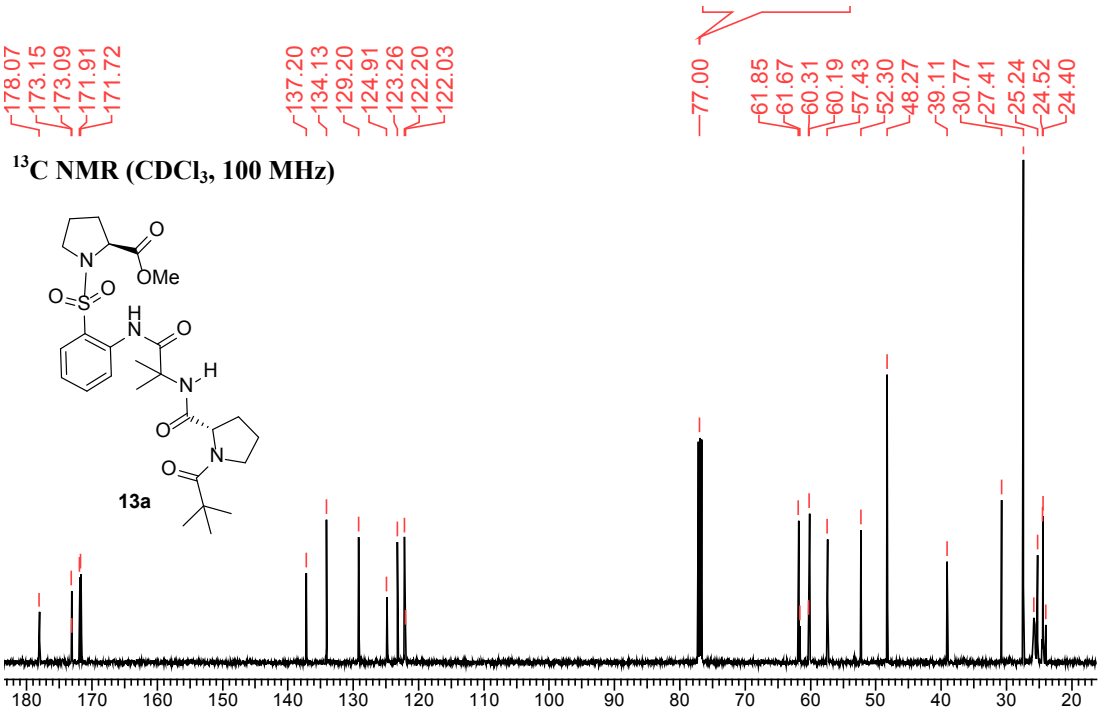


DEPT-135 ($CDCl_3$, 100 MHz)

11

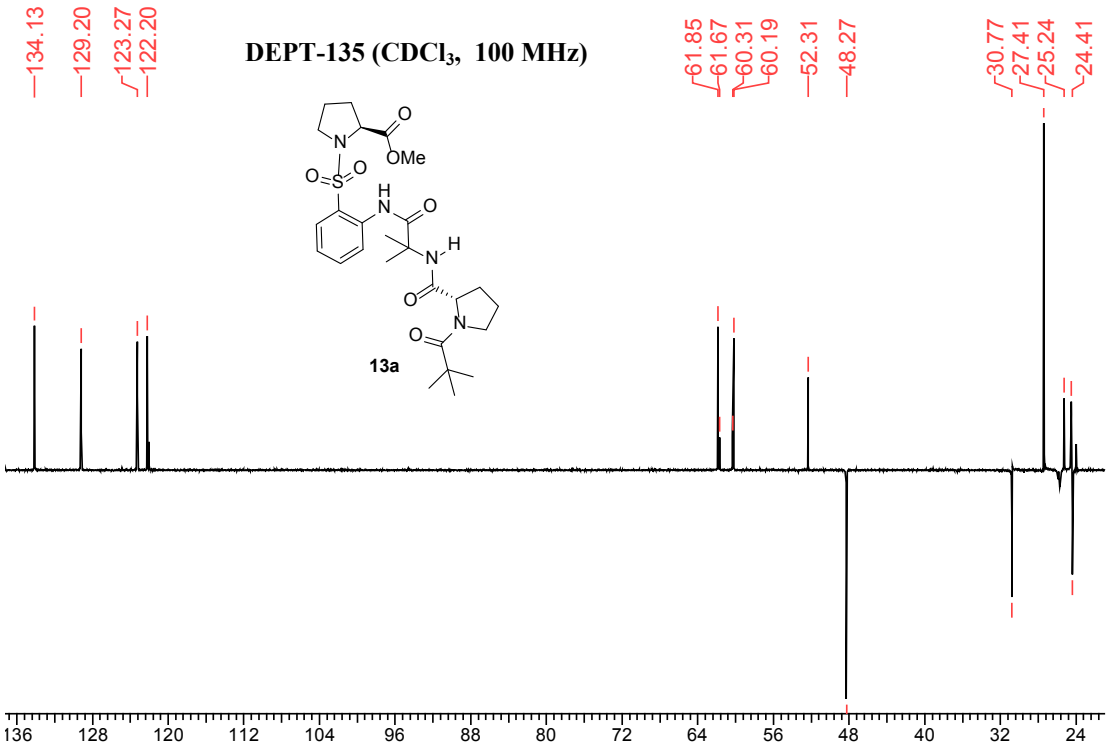






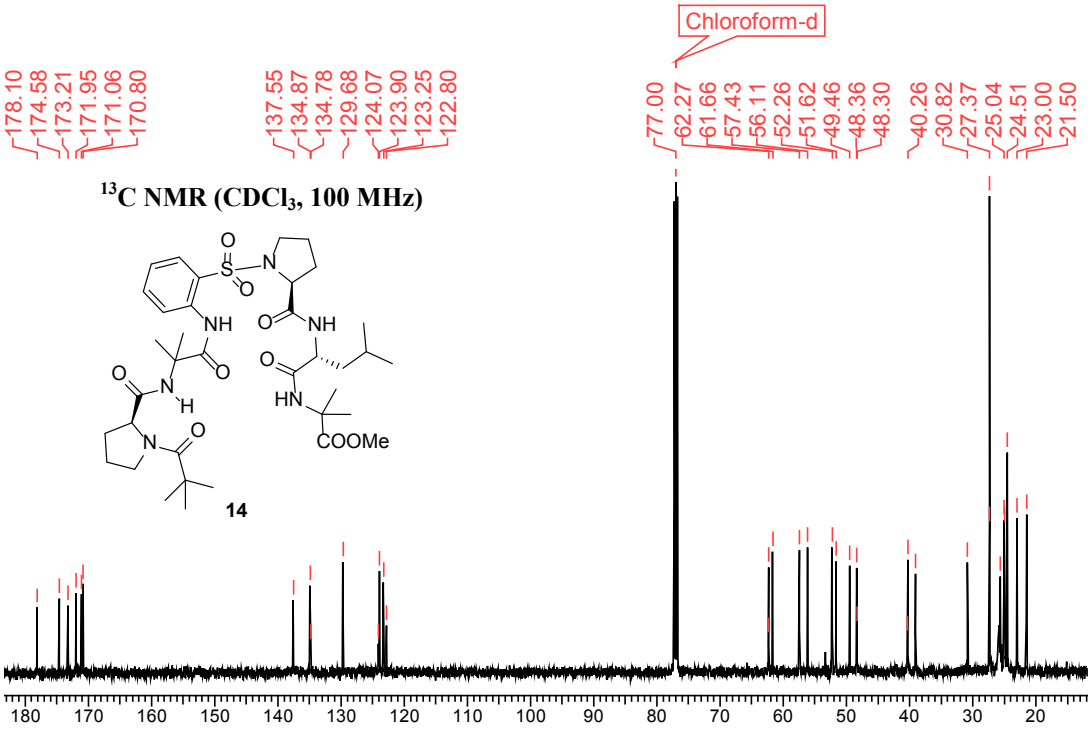
^{13}C NMR ($CDCl_3$, 100 MHz)

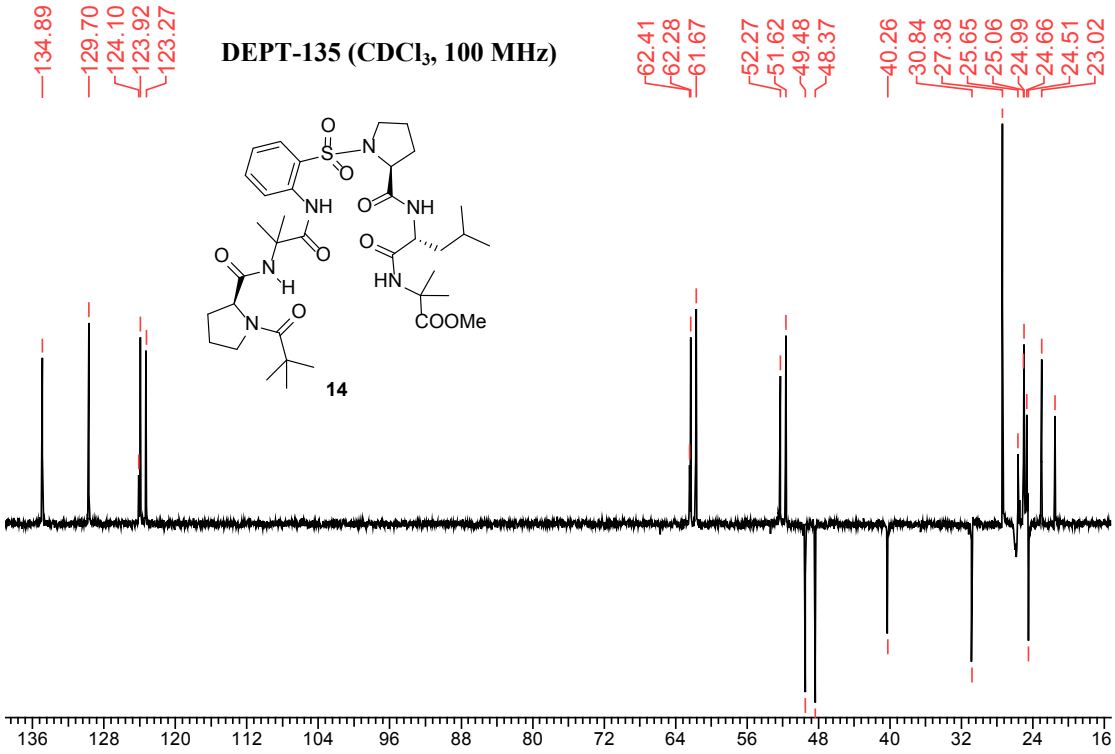
13a

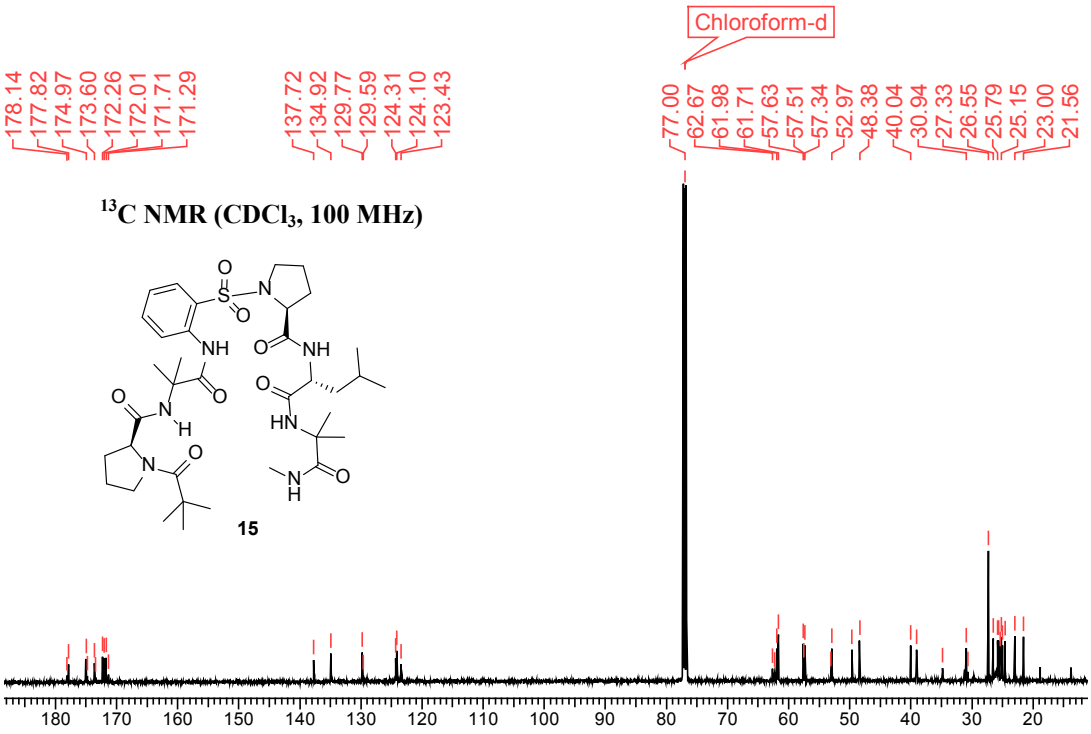


DEPT-135 ($CDCl_3$, 100 MHz)

13a

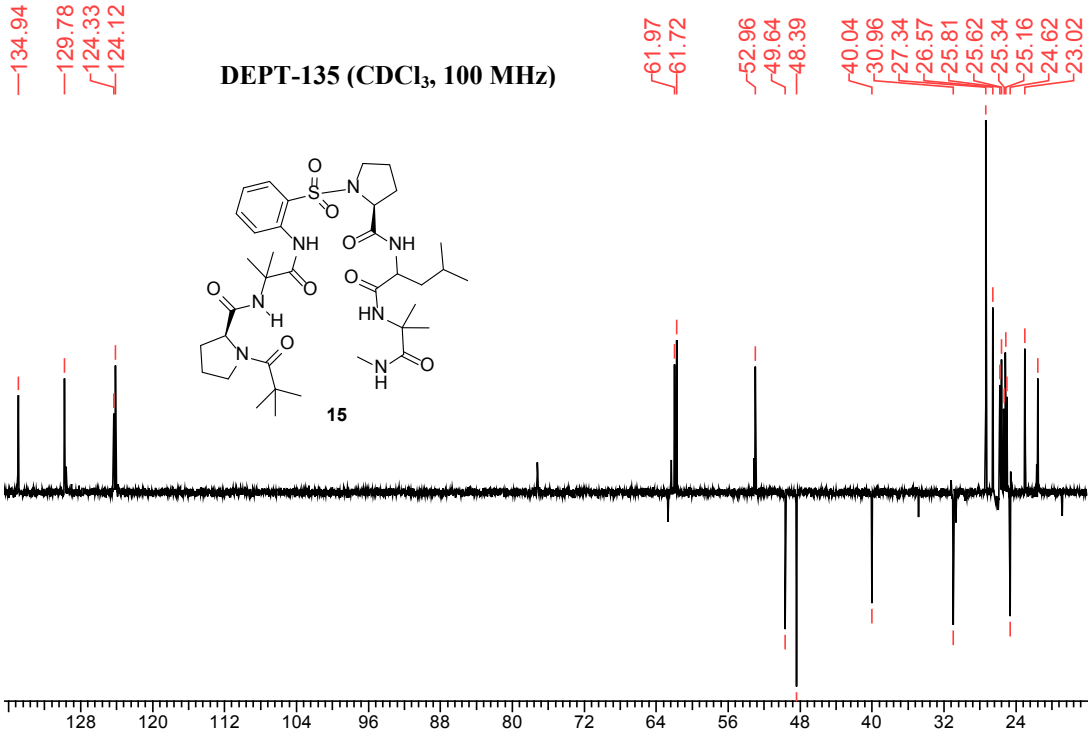






^{13}C NMR ($CDCl_3$, 100 MHz)

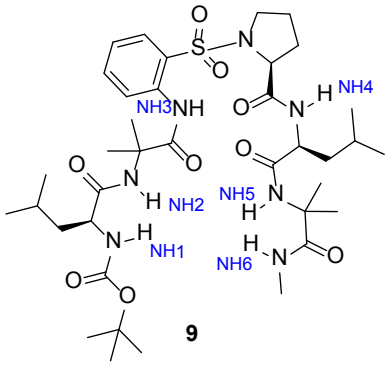
15



DEPT-135 ($CDCl_3$, 100 MHz)

15

Table 1 Titration Study of oligomer 9 (a) in $CDCl_3$ (10 mM) with DMSO-d_6 (volume of DMSO-d6 added at each addition = 5 μl) and temperature variation study (b) (10 mM, 400 MHz, $CDCl_3$)



9

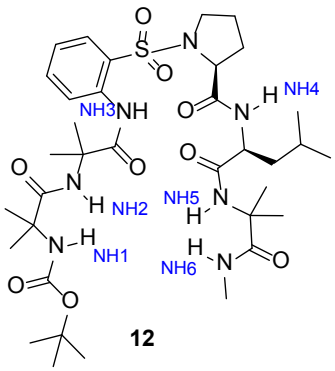
(a)

No	V $_{DMSO-d6}$ (in μ lit)	Chemical Shift (in ppm)					
		NH6	NH5	NH4	NH3	NH2	NH1
1	0	7.03	6.68	7.31	10.13	7.66	5.21
2	5	7.04	6.90	7.35	10.16	7.75	5.23
3	10	7.05	7.01	7.37	10.17	7.82	5.24
4	15	7.05	7.13	7.40	10.17	7.88	5.25
5	20	7.05	7.21	7.41	10.16	7.90	5.26
6	25	7.04	7.28	7.43	10.14	7.92	5.26
7	30	7.06	7.32	7.44	10.11	7.93	5.27
8	35	7.06	7.34	7.44	10.09	7.93	5.27
9	40	7.05	7.35	7.44	10.08	7.93	5.28
10	45	7.03	7.37	7.44	10.07	7.93	5.29
11	50	7.00	7.38	7.44	10.02	7.91	5.30

(b)

Temperature (in K)	Chemical Shift (in ppm)					
	NH6	NH5	NH4	NH3	NH2	NH1
268	7.12	6.69	7.40	10.19	7.81	5.22
273	7.11	6.68	7.38	10.17	7.78	5.22
278	7.10	6.68	7.35	10.16	7.76	5.22
283	7.08	6.68	7.33	10.15	7.73	5.22
288	7.07	6.67	7.31	10.14	7.70	5.22
293	7.04	6.67	7.30	10.13	7.66	5.21
298	7.01	6.67	7.28	10.12	7.63	5.21
303	6.99	6.67	7.26	10.11	7.61	5.20
308	6.98	6.68	7.25	10.10	7.57	5.19
313	6.95	6.68	7.24	10.09	7.53	5.18
318	6.93	6.68	7.22	10.08	7.49	5.17
323	6.91	6.68	7.20	10.07	7.45	5.16

Table 2 Titration Study of oligomer 12 (a) in $CDCl_3$ (10 mM) with DMSO-d_6 (volume of DMSO-d6 added at each addition = 5 μl) and temperature variation study (b) (10 mM, 400 MHz, $CDCl_3$).



12

(a)

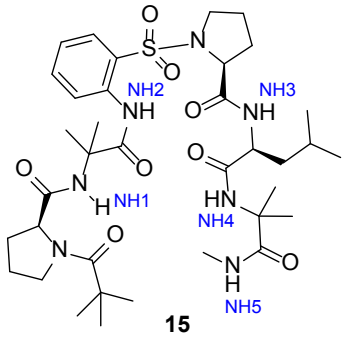
No	V $_{DMSO-d6}$ (in μ lit)	Chemical Shift (in ppm)					
		NH6	NH5	NH4	NH3	NH2	NH1
1	0	6.80	6.76	7.15	9.92	7.34	5.11
2	5	6.84	6.82	7.21	9.92	7.33	5.19
3	10	6.86	6.94	7.27	9.91	7.32	5.29
4	15	6.87	6.99	7.32	9.90	7.30	5.35
5	20	6.87	7.04	7.37	9.88	7.29	5.41
6	25	6.87	7.06	7.39	9.87	7.28	5.44
7	30	6.87	7.08	7.42	9.84	7.27	5.49
8	35	6.87	7.10	7.44	9.82	7.26	5.52
9	40	6.86	7.12	7.45	9.79	7.24	5.56
10	45	6.85	7.13	7.47	9.78	7.23	5.58
11	50	6.83	7.14	7.48	9.74	7.21	5.63

(b)

Temperature (in K)	Chemical Shift (in ppm)					
	NH6	NH5	NH4	NH3	NH2	NH1
268	6.83	6.86	7.36	9.94	7.39	5.21
273	6.83	6.84	7.31	9.93	7.39	5.19
278	6.82	6.83	7.26	9.93	7.38	5.17
283	6.82	6.81	7.22	9.93	7.36	5.15
288	6.81	6.80	7.18	9.93	7.35	5.13
293	6.81	6.77	7.15	9.92	7.34	5.11
298	6.79	6.75	7.13	9.92	7.33	5.10
303	6.78	6.73	7.11	9.92	7.33	5.09
308	6.77	6.72	7.10	9.92	7.32	5.08
313	6.76	6.71	7.08	9.92	7.32	5.07
318	6.75	6.70	7.07	9.92	7.31	5.06
323	6.74	6.69	7.05	9.92	7.30	5.05

Table 3 Titration Study of oligomer 15 (a) in $CDCl_3$ (10 mM) with DMSO-d_6 (volume of DMSO-d6 added at each addition = 5 μl) and temperature variation study (b) (10 mM, 400 MHz, $CDCl_3$).

(a)



15

No	V DMSO-d6 (in μ lit)	Chemical Shift (in ppm)				
		NH5	NH4	NH3	NH2	NH1
1	0	7.07	6.91	7.03	9.91	7.67
2	5	7.05	6.96	7.12	9.89	7.66
3	10	7.03	7.01	7.19	9.88	7.65
4	15	7.00	7.05	7.28	9.85	7.64
5	20	6.98	7.08	7.35	9.83	7.63
6	25	6.96	7.10	7.40	9.80	7.62
7	30	6.95	7.12	7.44	9.78	7.61
8	35	6.93	7.13	7.46	9.74	7.60
9	40	6.91	7.14	7.49	9.71	7.59
10	45	6.89	7.15	7.50	9.68	7.58
11	50	6.88	7.16	7.52	9.66	7.56

(b)

Temperature (in K)	Chemical Shift (in ppm)				
	NH5	NH4	NH3	NH2	NH1
268	7.14	7.01	7.18	9.92	7.76
273	7.13	6.99	7.14	9.91	7.74
278	7.12	6.97	7.11	9.91	7.73
283	7.11	6.95	7.08	9.91	7.71
288	7.09	6.94	7.06	9.91	7.69
293	7.07	6.91	7.04	9.91	7.67
298	7.05	6.89	7.02	9.91	7.66
303	7.03	6.87	7.01	9.91	7.64
308	7.01	6.86	7.00	9.91	7.63
313	6.99	6.84	6.99	9.91	7.61
318	6.97	6.82	6.98	9.91	7.60
323	6.94	6.80	6.97	9.91	7.59

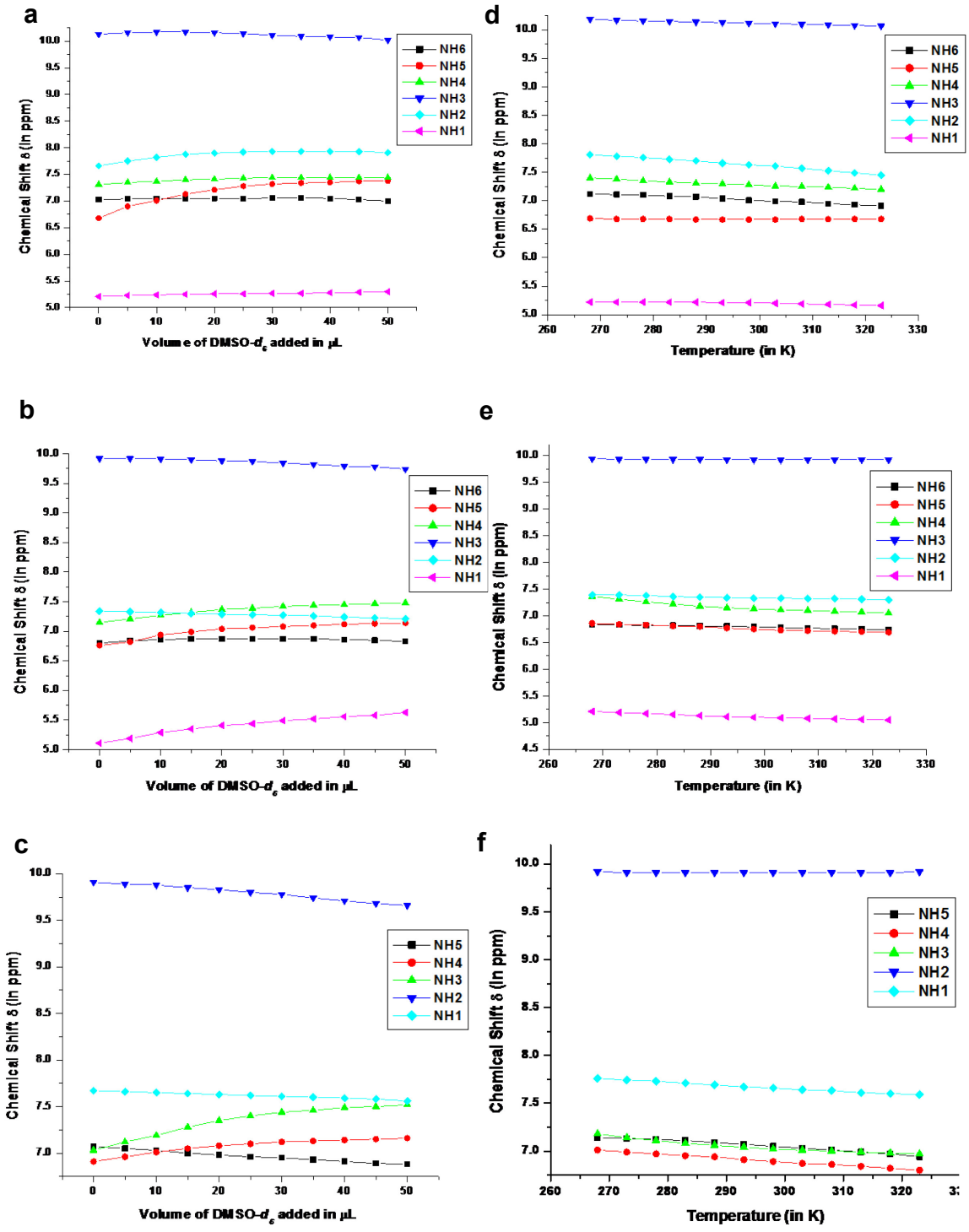


Fig. 1 DMSO-d_6 NMR titration plots of **9** (a), **12** (b) and **15** (c) in $CDCl_3$ (10 mM) and variable temparture plots of **9** (d), **12** (e) and **15** (f) in $CDCl_3$ (10 mM).

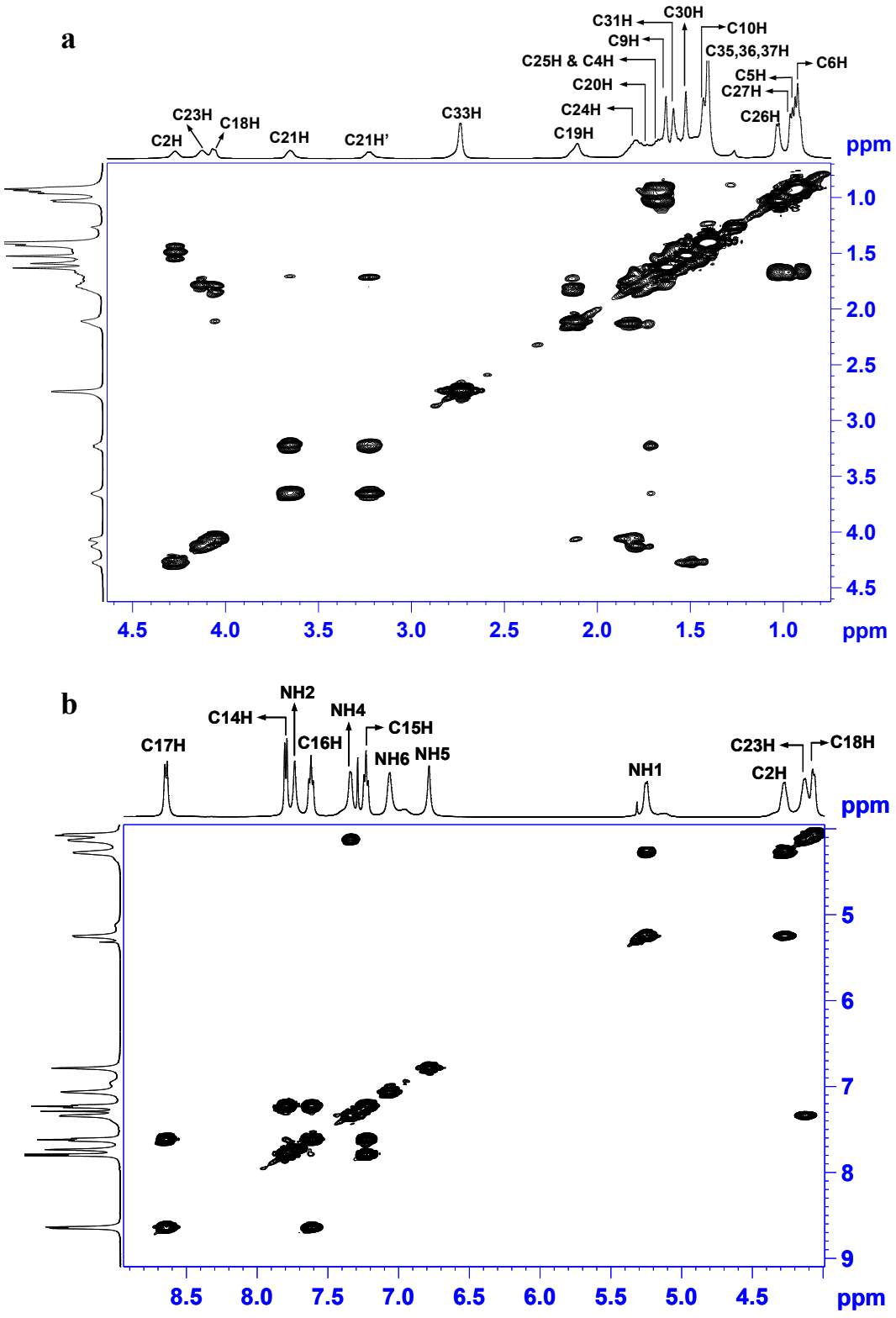


Fig. 2 Partial COSY spectrum (**a** and **b**) of oligomer **9** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

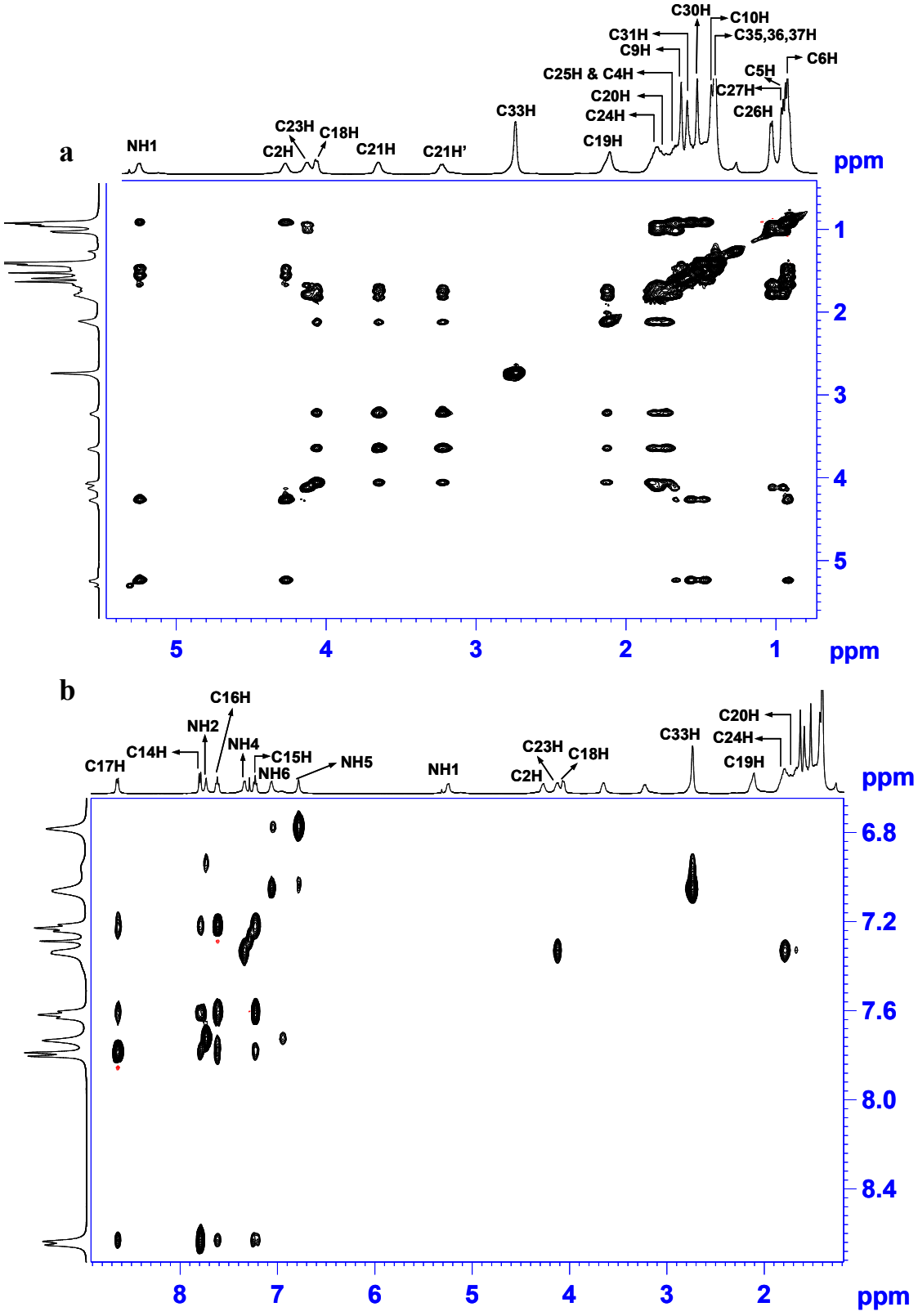


Fig. 3 Partial TOCSY spectrum (**a** and **b**) of oligomer **9** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

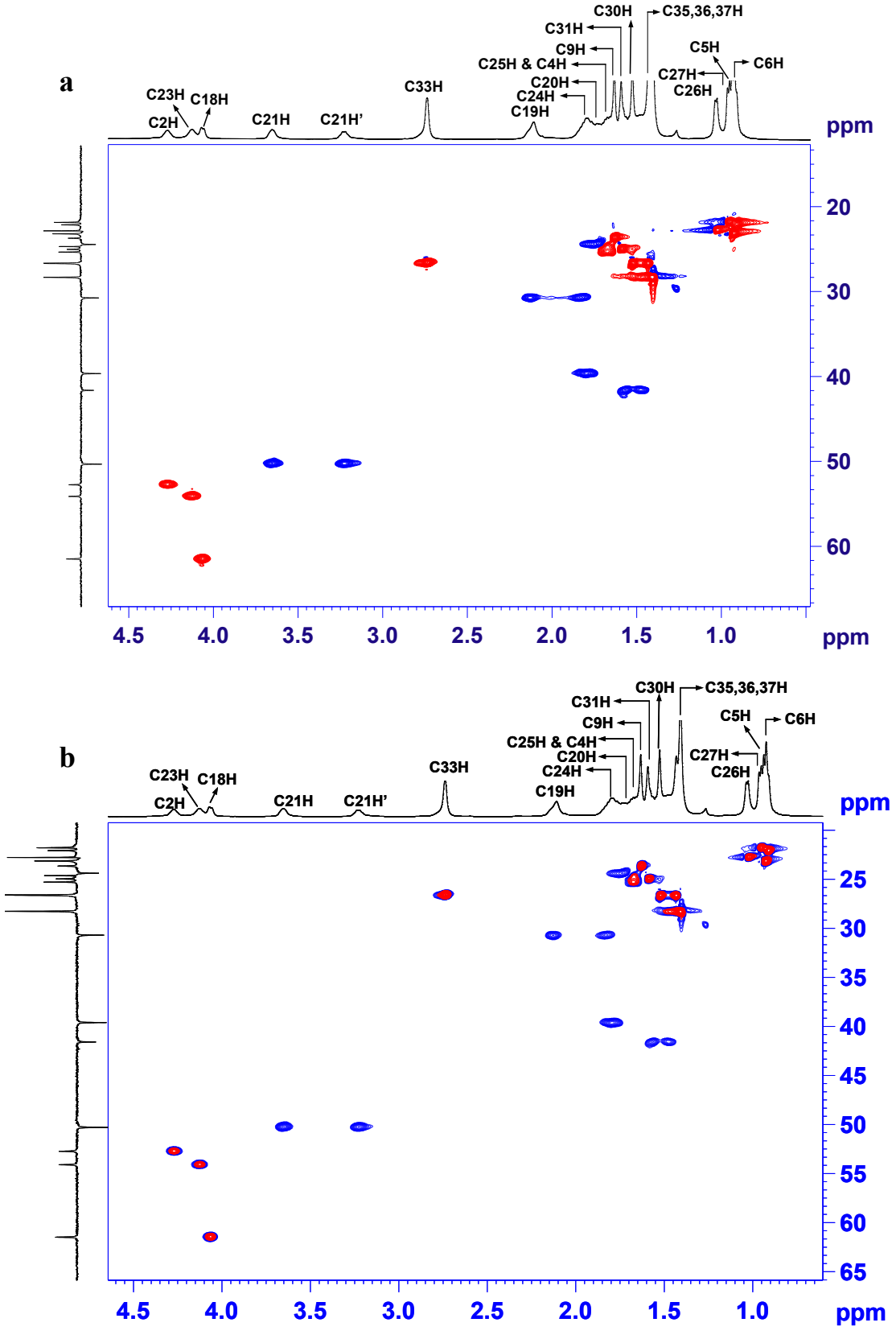


Fig. 4 Partial HSQC spectrum (**a** and **b**) of oligomer **9** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

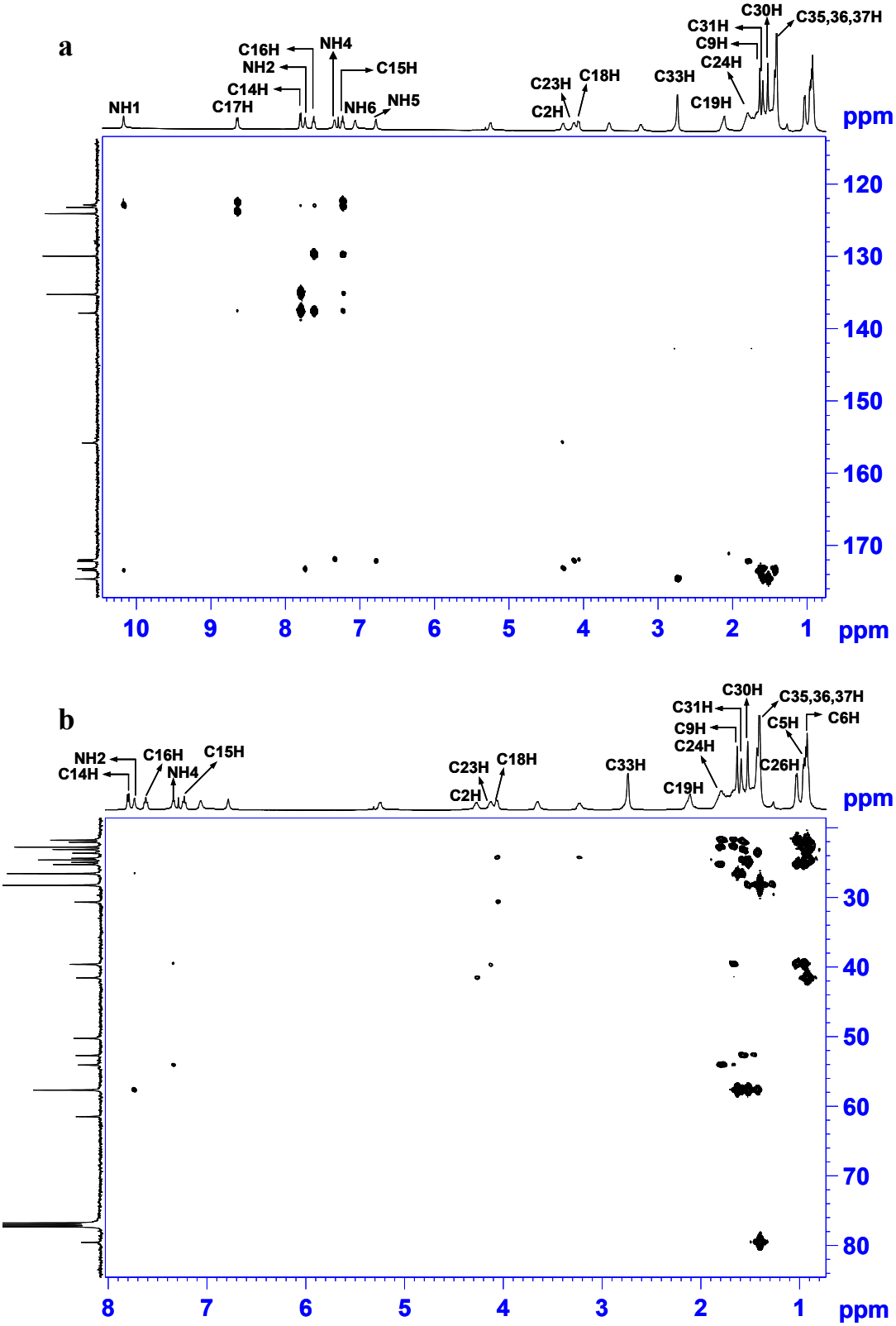


Fig. 5 Partial HMBC spectrum (**a** and **b**) of oligomer **9** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

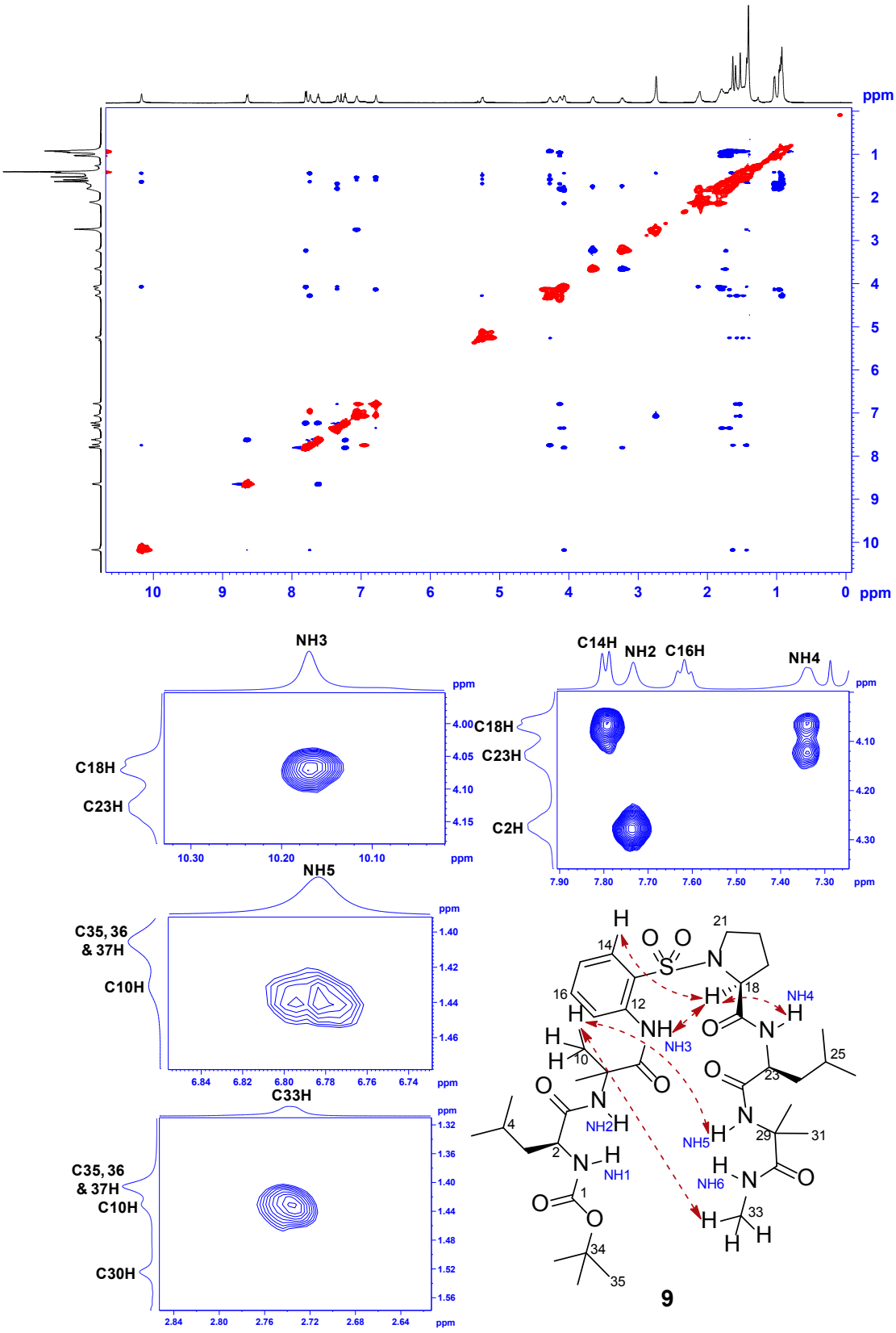


Fig. 6 NOESY spectrum and selected nOe excerpts of oligomer **9** (20 mM, 500 MHz, $CDCl_3$).

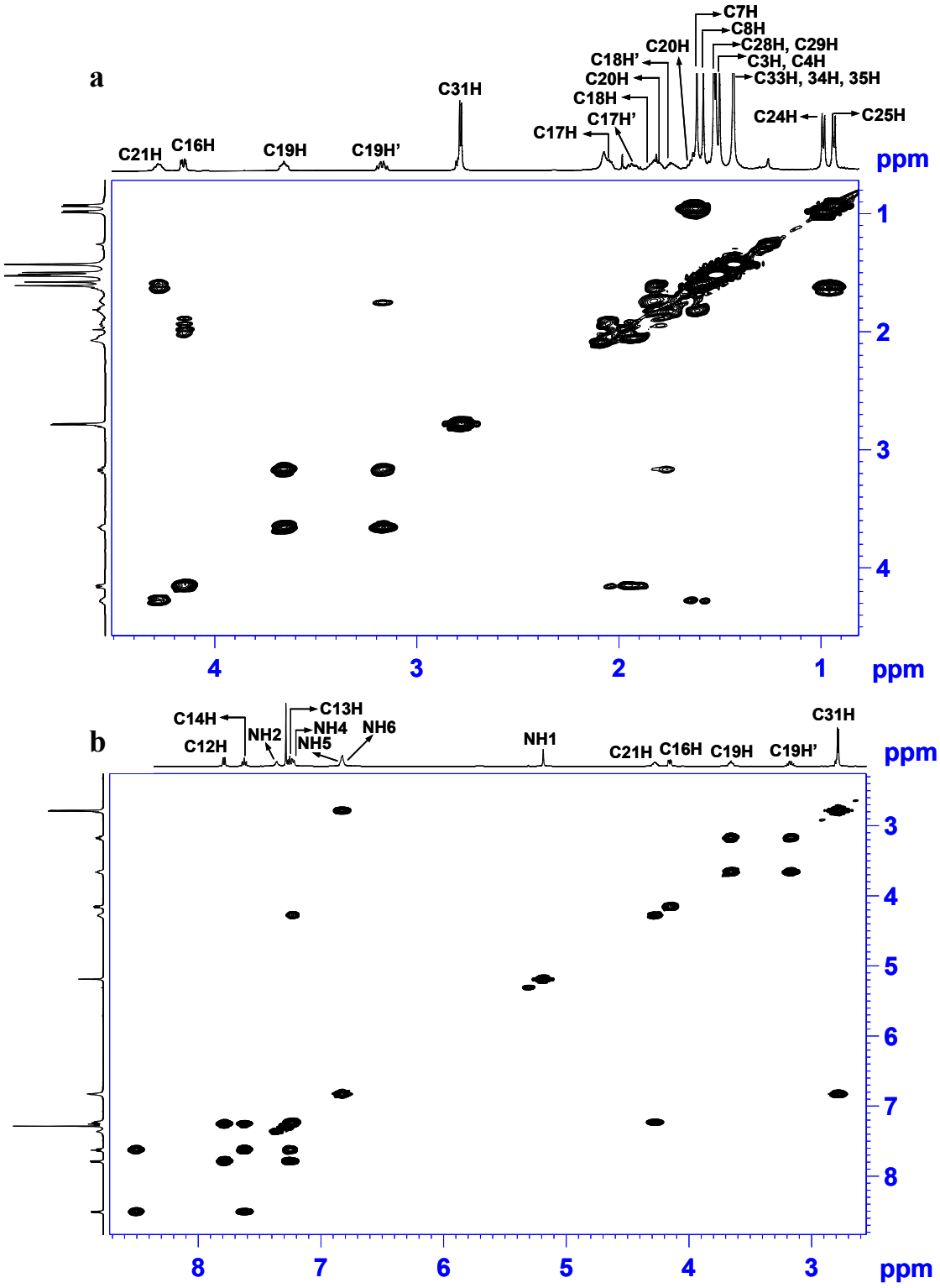


Fig. 7 Partial COSY spectrum (**a** and **b**) of oligomer **12** (20 mM, 500 MHz, $CDCl_3$).

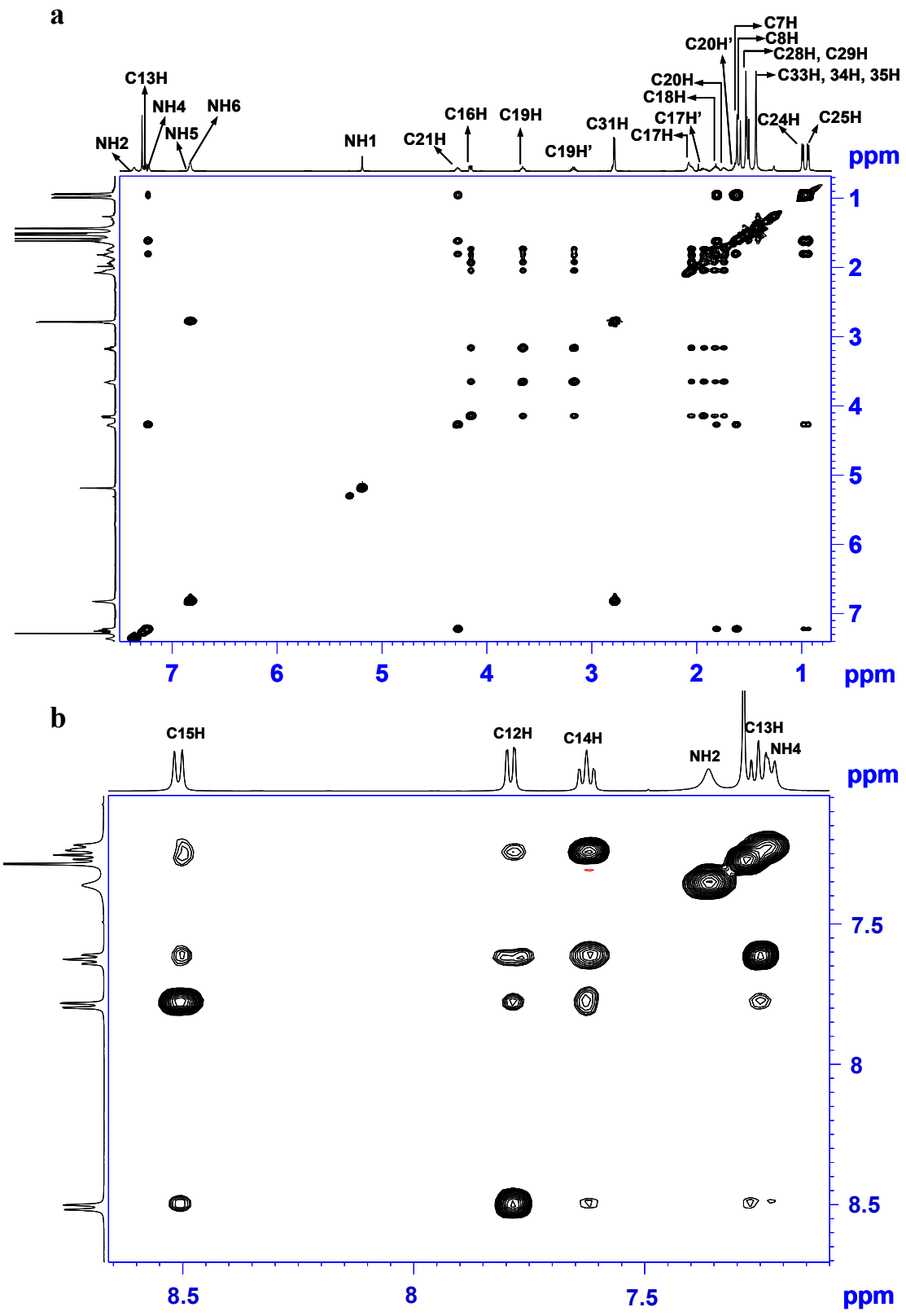


Fig. 8 Partial TOCSY spectrum (**a** and **b**) of oligomer **12** (20 mM, 500 MHz, $CDCl_3$).

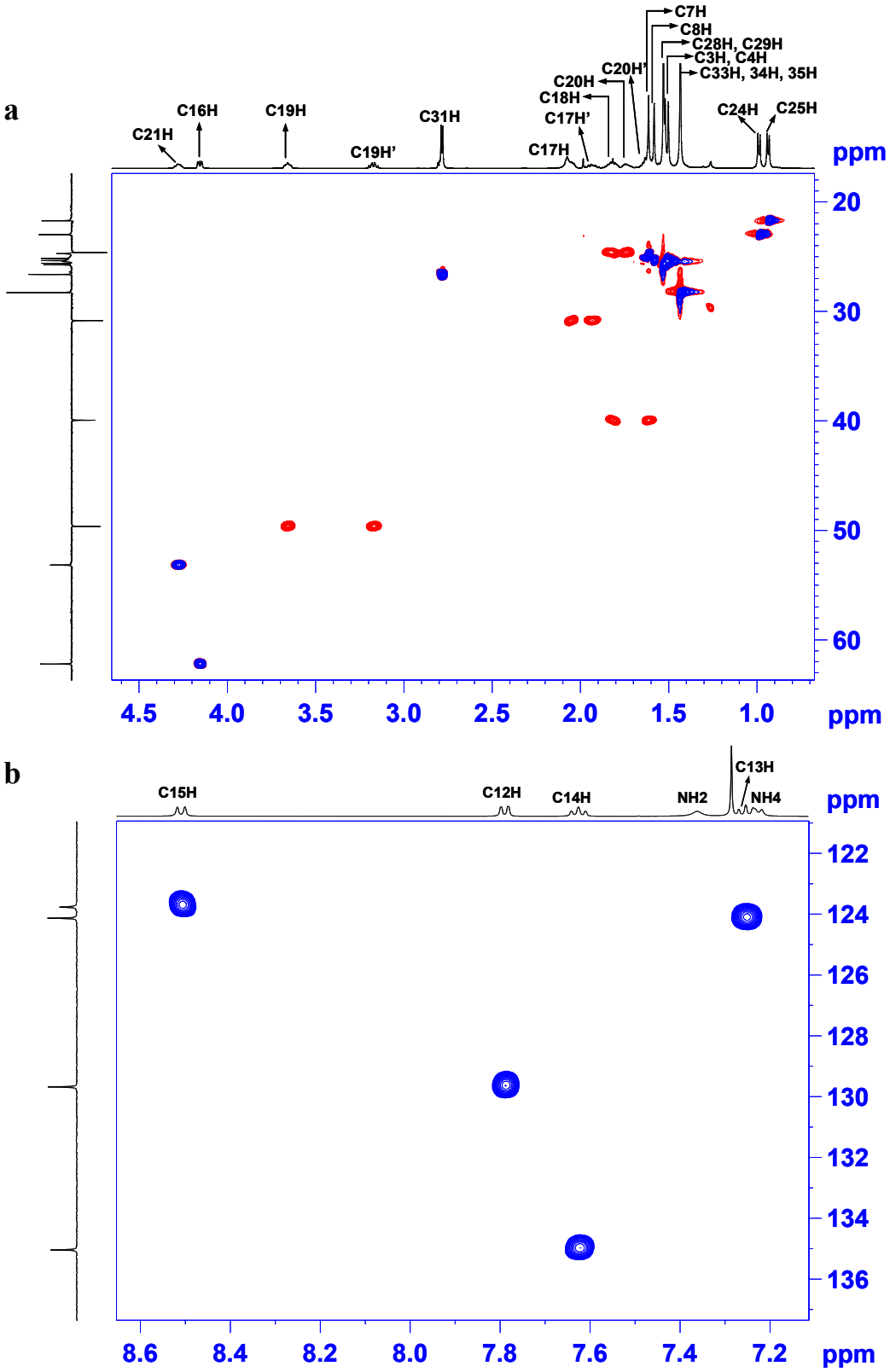


Fig. 9 Partial HSQC spectrum (**a** and **b**) of oligomer **12** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

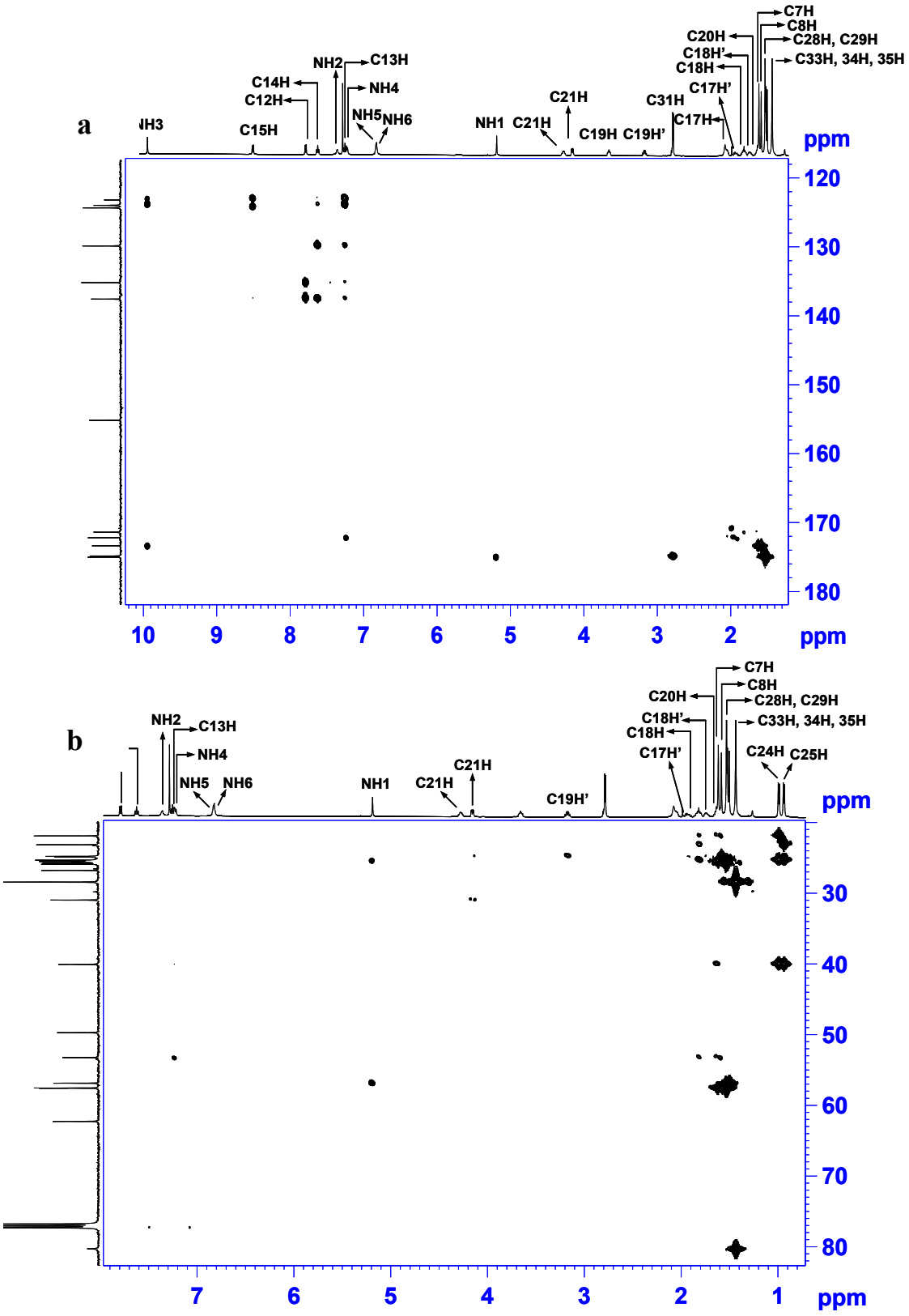


Fig. 10 Partial HMBC spectrum (**a** and **b**) of oligomer **12** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

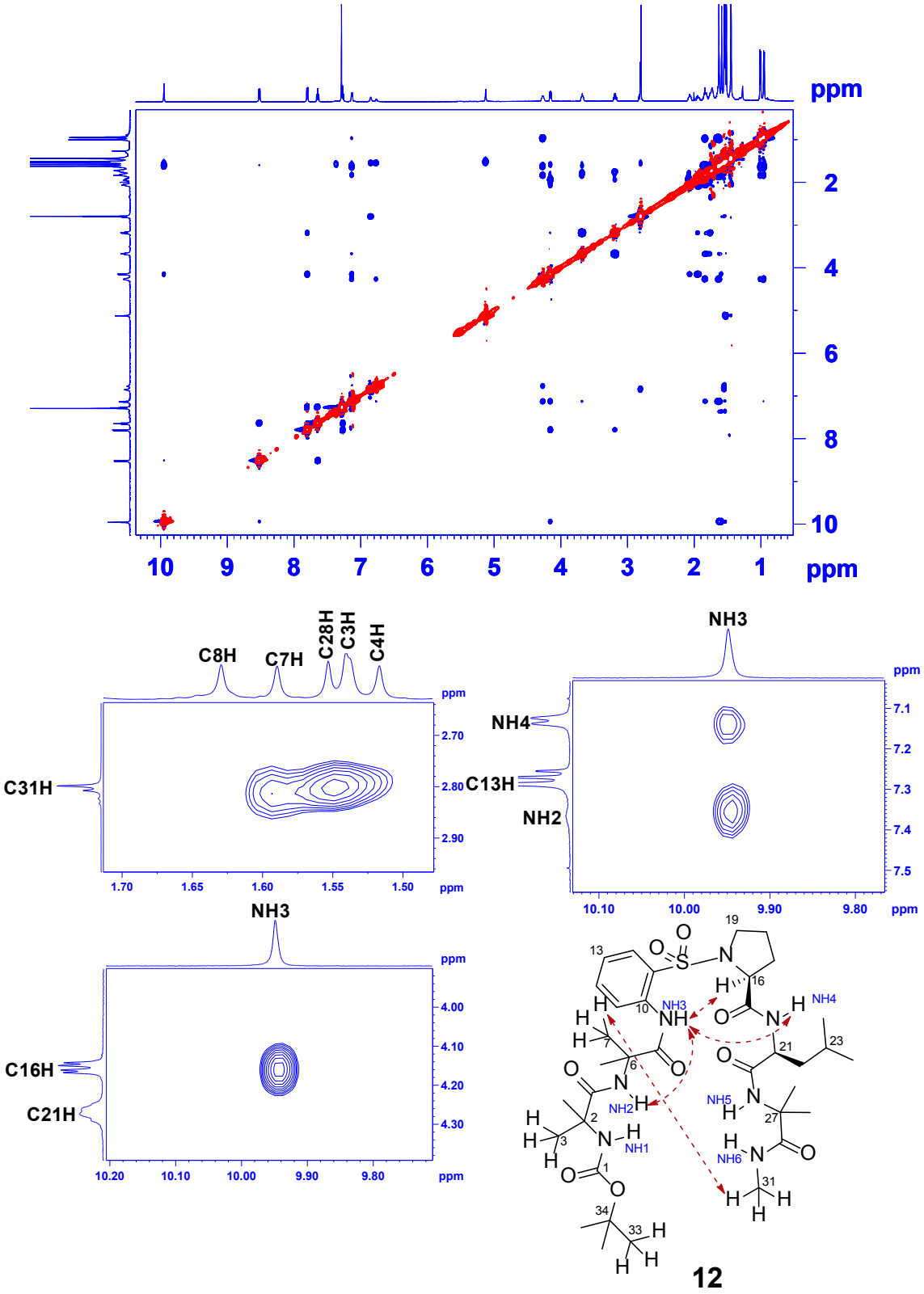


Fig. 11 NOESY spectrum and selected nOe excerpts of oligomer **12** (20 mM, 500 MHz, $CDCl_3$).

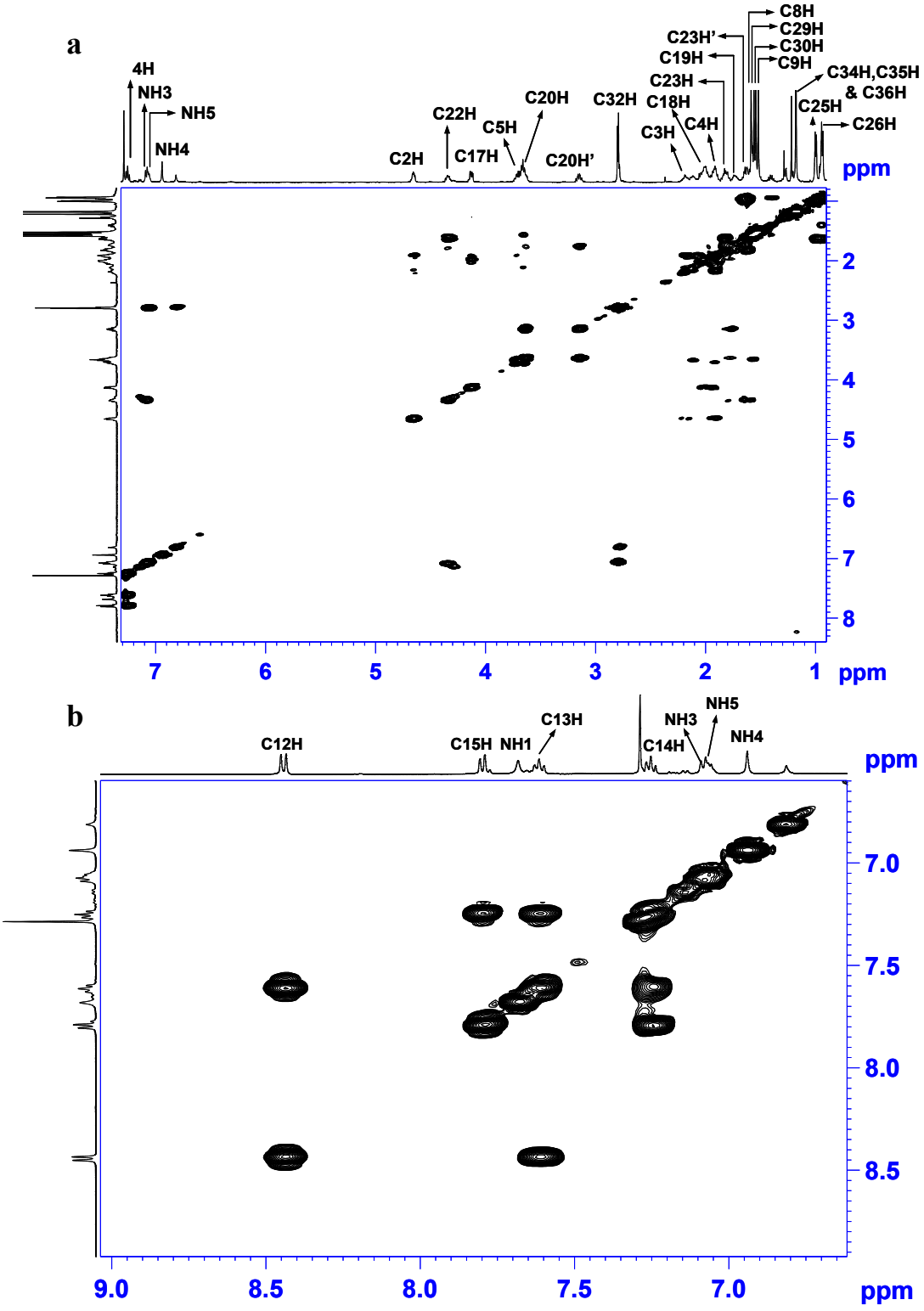


Fig. 12 Partial COSY spectrum (**a** and **b**) of oligomer **15** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

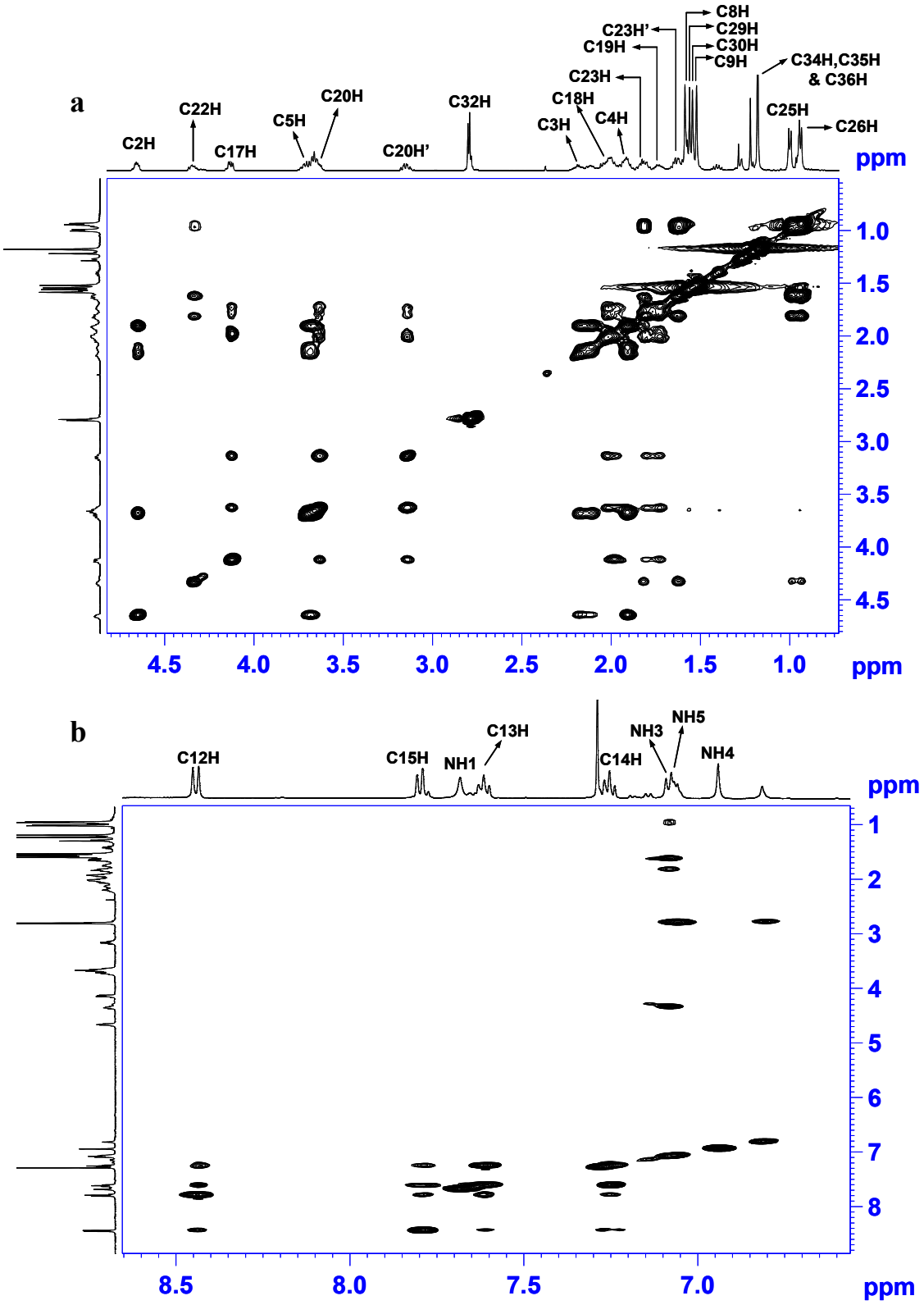


Fig. 13 Partial TOCSY spectrum (**a** and **b**) of oligomer **15** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

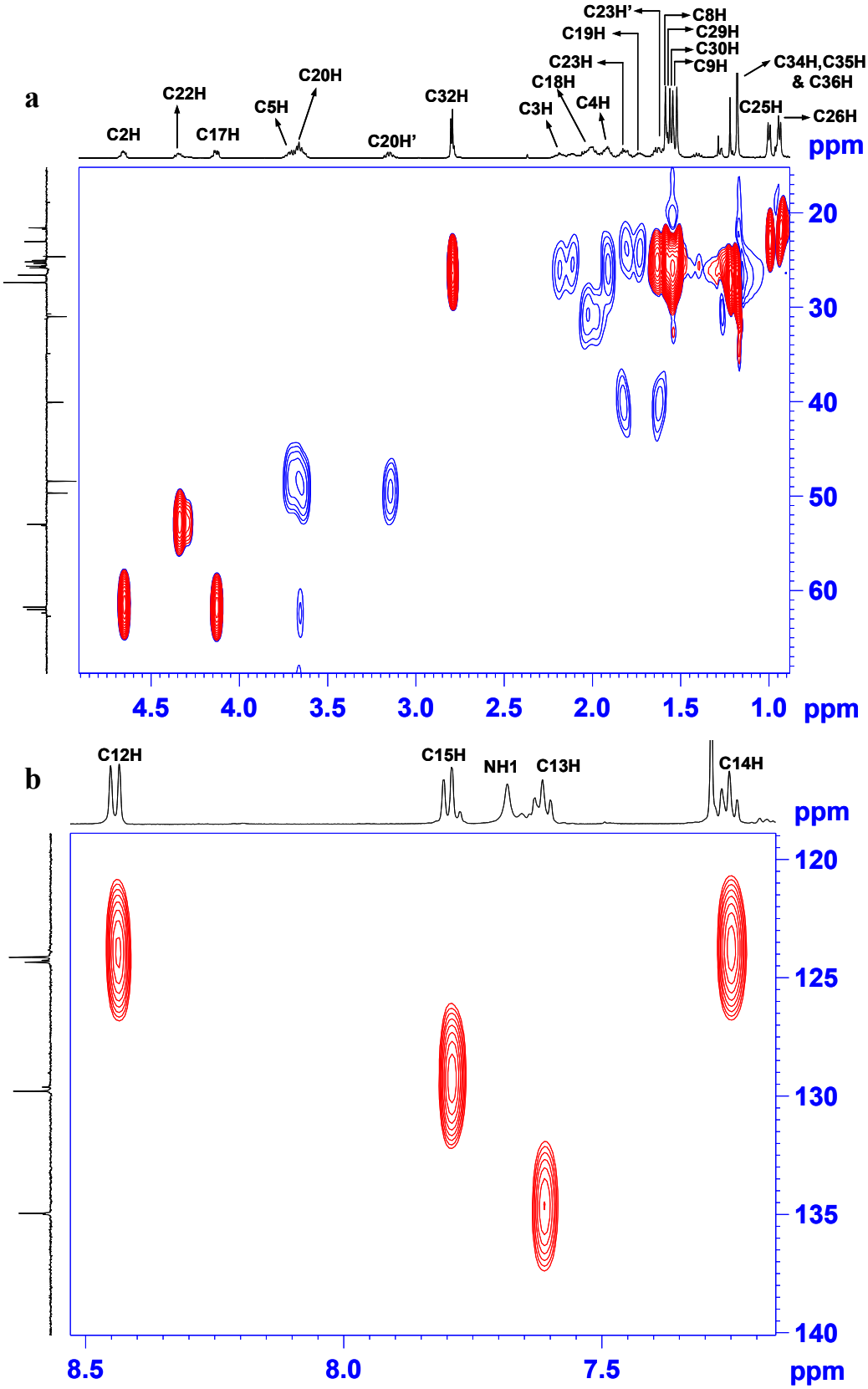


Fig. 14 Partial HSQC spectrum (**a** and **b**) of oligomer **15** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

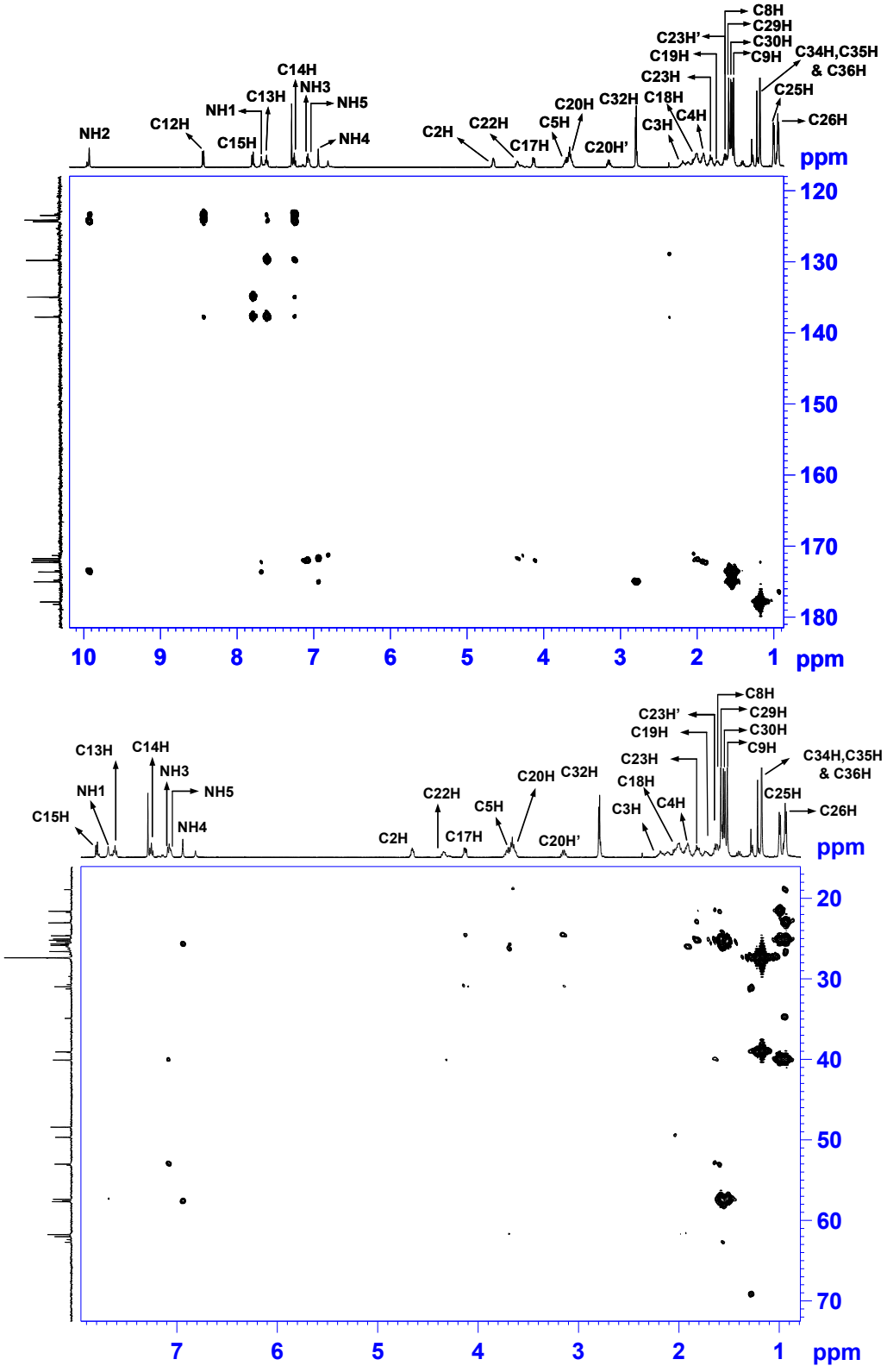


Fig. 15 Partial HMBC spectrum (**a** and **b**) of oligomer **15** (20 mM, 500 MHz, $CDCl_3$). For better view, aromatic and aliphatic regions are given separately.

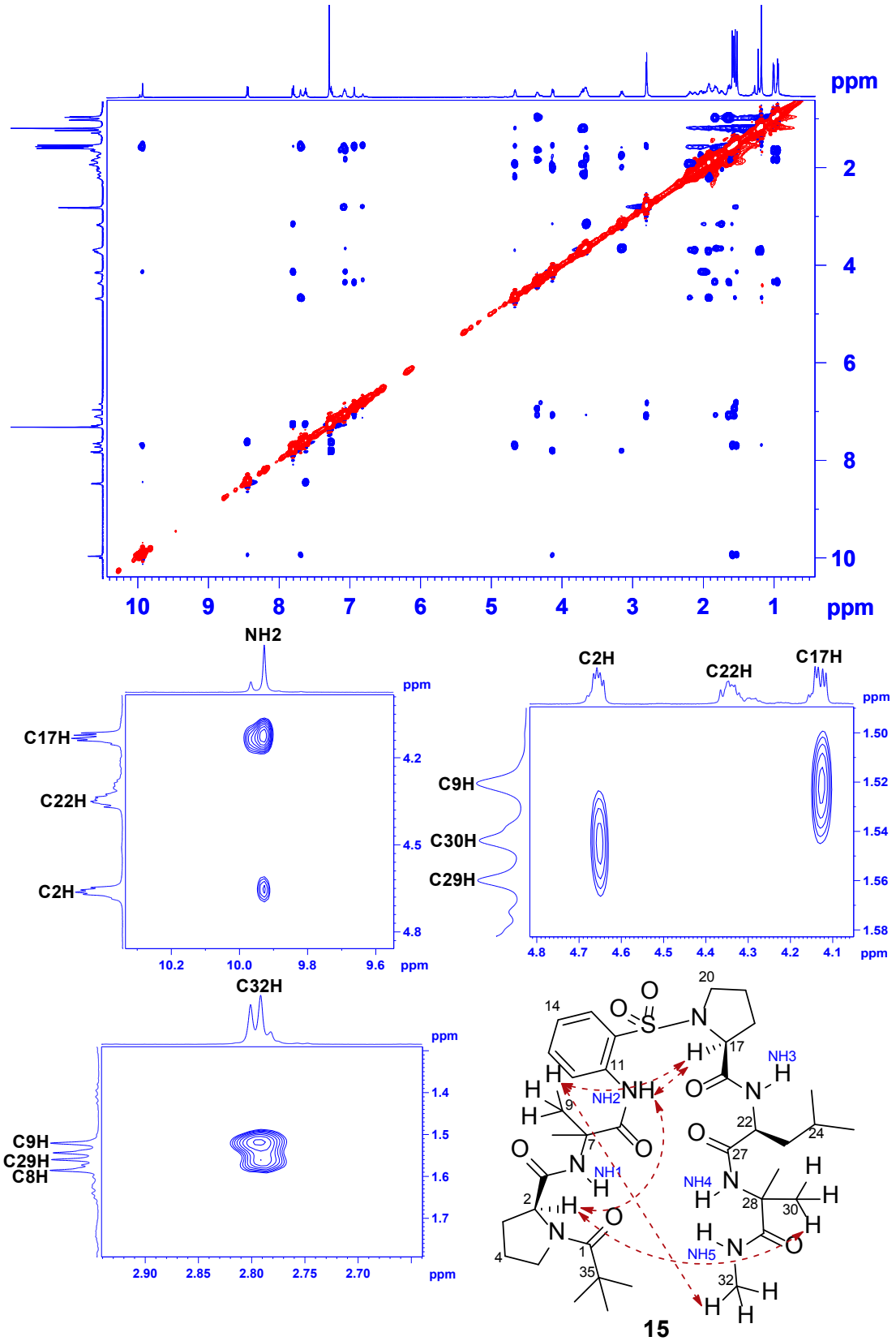


Fig. 16 NOESY spectrum and selected nOe excerpts of oligomer **15** (20 mM, 500 MHz, $CDCl_3$).

Table 4 Selected nOe distance restraints used to determine the solution state structure of oligomer **9**.

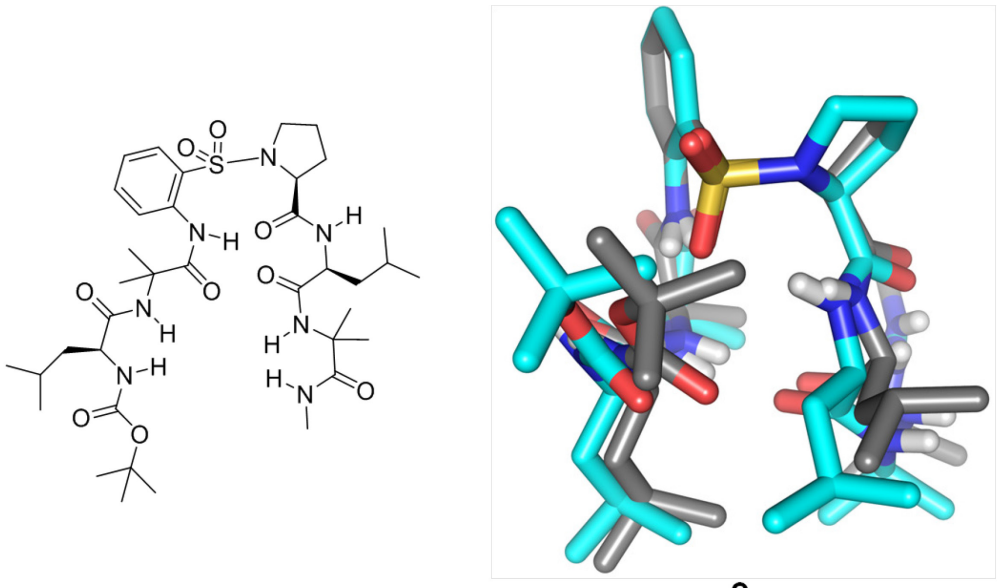
Atom I	atom II	Chemical Shift I	Chemical Shift II	Upper Bound	Lower Bound	Distance from the Crystal
17	NH3	8.6426	10.1753	4.6600	3.8127	3.5
NH2	NH3	7.7484	10.1753	3.9600	3.2400	2.5
18	NH3	4.0767	10.1753	3.4667	2.8364	2.5
10	NH3	1.6359	10.1753	3.3916	2.7750	2.9
9	NH3	1.4413	10.1753	3.6283	2.9686	3.8
9	17	1.4413	8.6426	5.7867	4.7345	4.9
9	NH2	1.4413	7.7484	3.3658	2.7538	2.5
10	NH2	1.6359	7.7484	3.5904	2.9376	3.1
14	21A	7.795	3.2298	3.3091	2.7074	2.5
14	18	7.795	4.0767	3.2652	2.6715	4.1
2	NH2	4.2819	7.7484	3.1164	2.5498	2.2
NH1	NH2	5.255	7.7371	4.4330	3.6270	4.1
26	NH4	0.9574	7.3479	5.2692	4.3111	3.6
20	NH4	1.6728	7.3479	3.3833	2.7681	3.6
24	NH4	2.1251	7.3479	4.8980	4.0074	2.5
21B	NH4	3.6559	7.3479	4.8772	3.9905	3.7
18	NH4	4.0767	7.3479	3.6335	2.9729	3.1
23	NH4	4.1241	7.3479	3.3704	2.7576	2.6
NH5	NH4	6.791	7.3479	3.9683	3.2468	4.4
30	NH6	1.5255	7.0612	3.4542	2.8261	2.8
31	NH6	1.5939	7.0612	3.5290	2.8873	4.0
33	NH6	2.7406	7.0612	3.0122	2.4645	2.2
27	NH5	1.0363	6.7877	5.5280	4.5229	4.0
30	NH5	1.515	6.7877	3.3896	2.7733	2.4
31	NH5	1.5991	6.7877	3.3384	2.7314	3.1
25	NH5	1.8095	6.7877	4.7222	3.8636	4.9
23	NH5	1.8095	6.7877	3.2189	2.6336	2.2
6	NH1	0.9311	5.2464	5.3238	4.3558	4.8
BOC	NH1	1.415	5.2464	4.1666	3.4091	4.3
3	NH1	1.415	5.2464	3.6025	2.9475	2.8
2	NH1	4.2661	5.2464	3.8061	3.1141	2.8
2	6	4.2661	0.9153	2.9529	2.4160	2.3
23	26	4.1312	0.9574	3.0893	2.5276	2.4
9	18	1.4466	4.076	3.8016	3.1104	3.4
23	20	4.1338	1.6675	3.5087	2.8707	4.0
10	33	1.4308	2.7478	3.7432	3.0626	2.5
31	33	1.5307	2.7478	4.6416	3.7977	4.5

Table 5 nOe distance restraints used to determine the solution state structure of oligomer **12**.

Atom I	Atom II	Chemical shift I	Chemical shift II	Upper Bound	Lower Bound
15	NH3	8.5188	9.9472	4.1897	3.4279
16	NH3	4.1559	9.9472	3.5851	2.9333
7	NH3	1.6111	9.9472	2.7159	2.2221
8	NH3	1.46	9.9472	3.6211	2.9627
7	15	1.6111	8.5188	4.0429	3.3078
12	19’	7.8018	3.1893	3.3499	2.7409
12	19	7.8018	3.6719	5.4713	4.4765
7	NH2	1.6111	7.3691	3.2756	2.6800
23	NH4	1.6056	7.1375	2.7899	2.2827
17	NH4	2.0591	7.1375	4.3316	3.5440
24	NH4	0.9732	7.1375	4.1401	3.3874
28	NH6	1.5501	6.8519	3.0606	2.5041
25	NH5	1.5584	6.7576	3.1717	2.5950
31	NH6	2.8024	6.8519	2.9171	2.3867
21	NH6	4.2599	6.8519	4.4338	3.6277
21	NH5	4.2599	6.7576	3.5880	2.9356
19	NH4	3.6802	7.1375	4.0895	3.3459
16	NH4	4.1337	7.1375	3.2511	2.6600
21	NH4	4.2988	7.1375	3.3505	2.7413
3	NH1	1.5044	5.1239	2.6991	2.2084
16	17	4.1573	1.9897	2.6182	2.1422
16	7	4.1573	1.6111	3.4722	2.8409
29	31	1.5443	2.8024	3.5909	2.9380
8	31	1.46	2.8024	3.8454	3.0053

Table 6 nOe distance restraints used to determine the solution state structure of oligomer **15**.

Atom I	Atom II	Chemical Shift I	Chemical Shift II	Upper Bound	Lower Bound
16	NH2	8.4313	9.9262	4.6873	3.8350
17	NH2	4.1307	9.9262	3.8322	3.1355
8	NH2	1.585	9.9262	3.0018	2.4560
9	NH2	1.52123	9.9262	3.3628	2.7514
34	16	1.1733	8.4423	5.3222	4.3545
34’	16	1.585	8.4423	5.2548	4.2994
Piv	NH1	1.1733	7.673	5.0630	4.1424
9	NH1	1.52123	7.673	3.4275	2.8043
8	NH1	1.585	7.673	2.9332	2.3999
13	20	7.7978	3.1449	3.3920	2.7753
13	17	7.7978	4.1307	2.9032	2.3753
2	NH1	4.6507	7.6841	2.7462	2.2469
29	NH5	1.5416	7.0612	3.2115	2.6276
18	NH3	2.0183	7.0829	4.7169	3.8592
32	NH5	2.7983	7.0612	2.9141	2.3842
17	NH3	4.1199	7.0829	3.4999	2.8635
22	NH3	4.3365	7.0829	3.4895	2.8550
22	NH4	4.3365	6.9421	3.2346	2.6465
2	35	4.6566	1.1733	4.0426	3.3076
2	4	4.6566	1.5525	4.1170	3.3685
2	30	4.6507	1.5413	4.6066	3. 8100
22	26	4.337	0.211	2.9643	2.4254
9	17	1.5178	4.1258	3.9916	3.2658
29	32	1.5512	2.7935	3.8613	3.1592
8	32	1.5202	2.7935	3.6221	2.9635
5	35	3.725	1.2167	2.6951	2.2051
5’	35	3.66	1.2167	2.6854	2.1971
NH1	NH2	7.673	9.9262	3.5527	2.9068
2	NH2	4.6615	9.9262	4.9115	4.0185



9

Fig. 17 Overlapped crystal and solution state derived structure of oligomer **9.**

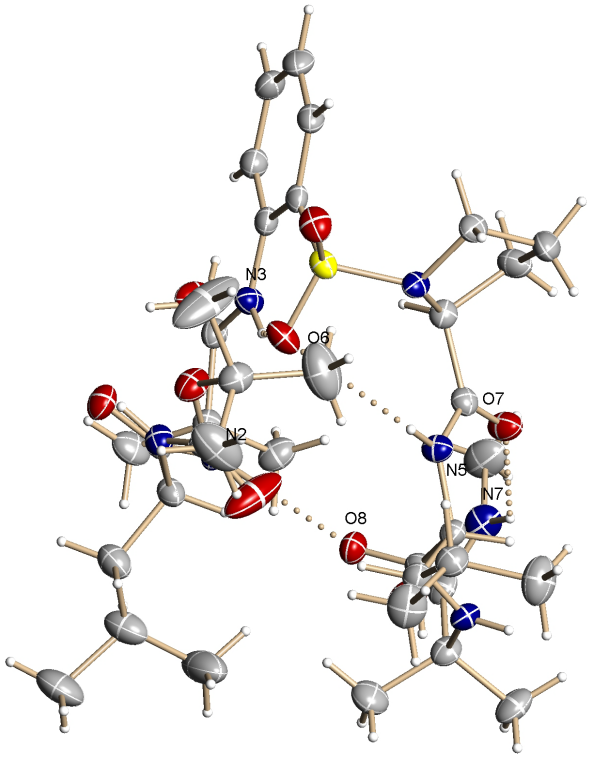


Fig. 17 Ortep diagram of oligomer **9.** Ellipsoids were drawn at 50% probability.