

Supporting Information

Competitive Formation of Homocircuit [3]Rotaxanes in Synthetically Useful Yields in the Bipyridine-Mediated Active Template CuAAC Reaction

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General Experimental Information

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. All reactions were carried out under an atmosphere of N₂ using anhydrous solvents unless otherwise stated. Anhydrous THF, toluene, DMF, diethyl ether and methylene chloride were either obtained by passing the solvent through an activated alumina column on an MBRAUN MB SPS-800 solvent purification system or purchased from Acros, otherwise solvents were used without further purification. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Microwave-assisted reactions were undertaken on a CEM Discover SP reactor. Flash column chromatography was performed using a Biotage Isolera 4 automated chromatography system, employing Biotage ZIP or SNAP KP-SIL cartridges. Analytical NMR spectra were recorded on Bruker AV400, AMX400 or AV600 instruments, at a constant temperature of 300 K, by the NMR service at Queen Mary, University of London. ¹³C-NMR were typically recorded as DEPT-Q135 experiments (phased spectrum including quaternary Cs). Chemical shifts are reported in parts per million from low to high field and referenced to residual solvent. Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. Low resolution mass spectrometry was carried out by the mass spectrometry service at Queen Mary, University of London using an Agilent SL Ion Trap MSD (**5-8**, **S9-S16**) or the EPSRC National Mass Spectrometry Service Centre in Swansea (**10**). High resolution mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre in Swansea.

Macrocycles **1a-d**,^{1,2} alkyne **2**,³ azide **3**,³ thread **S1**,^{1,3} 1-(4-(tri(4-*tert*-butylphenyl)methyl)phenoxy)hexyl bromide (**S2**),⁴ 4-(tri(4-*tert*-butylphenyl)methyl)phenol (**S3**),⁵ 6-tosyloxyhex-1-yne (**S4**),⁶ 11-tosyloxyundec-1-yne (**S5**),⁷ 6,6'-di(3-(4-hydroxyphenyl)propyl)-2,2'-bipyridine (**S18**)⁸ and macrocycle **9d**⁸ were synthesised according to literature procedures.

Experimental Procedures

General Procedure for Scheme 1 and Screening of Reaction Conditions

The desired macrocycle (1 eq.), azide (1 eq.), alkyne (1 eq.) and Cu(MeCN)₄.PF₆ (0.90 eq.) were weighed dry into an 8 mL CEM microwave vial. solvent was added to make a 0.01M solution (wrt. macrocycle), the vial sealed under N₂ and the mixture stirred at the desired temperature to react for the specified time. The solution was allowed to return to room temperature before dilution with CH₂Cl₂ (50 mL) and washing with 16% aqueous EDTA tetrasodium-saturated ammonia solution (50 mL). The organic layer was retained and the aqueous layer extracted twice further with CH₂Cl₂ (50 mL portions). The organic extracts were combined, dried over MgSO₄ and dried *in vacuo*.

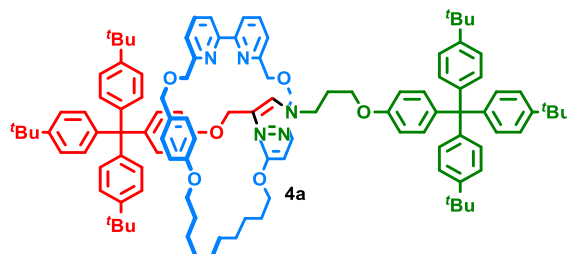
Conditions A

A 0.05 M solution of the desired macrocycle (1 eq.), azide (1.20 eq.), alkyne (1.20 eq.), NⁱPr₂Et (1.10 eq.) and Cu(MeCN)₄.PF₆ (0.10 eq.) in anhydrous THF was stirred at 30 °C for 6 hours (unless specified otherwise). The solution was allowed to return to room temperature before dilution with CH₂Cl₂ (50 mL) and washing with 16% aqueous EDTA tetrasodium-saturated ammonia solution (50 mL). The organic layer was retained and the aqueous layer extracted twice further with CH₂Cl₂ (50 mL portions). The organic extracts were combined, dried over MgSO₄ and dried *in vacuo*.

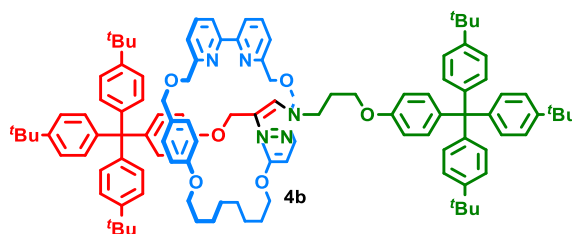
Conditions B

A 0.01M solution of the desired macrocycle (1 eq.), azide (1.20 eq.), alkyne (1.20 eq.) and Cu(MeCN)₄.PF₆ (0.96 eq.) in anhydrous CH₂Cl₂ was stirred at in an 8 mL CEM microwave vial at 100 °C with microwave heating (150W) for 20 minutes (unless specified otherwise). The solution was allowed to return to room temperature before dilution with further CH₂Cl₂ (50 mL) and washing with 16% aqueous EDTA tetrasodium-saturated ammonia solution (50 mL). The organic layer was retained and the aqueous layer extracted twice further with CH₂Cl₂ (50 mL portions). The organic extracts were combined, dried over MgSO₄ and dried *in vacuo*.

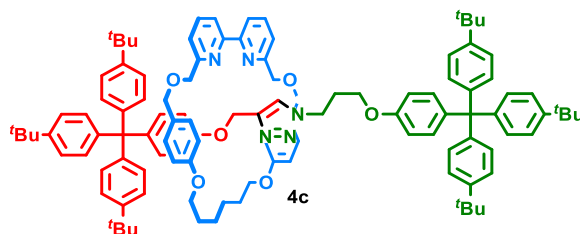
Selective Synthesis of [2]Rotaxanes **4**



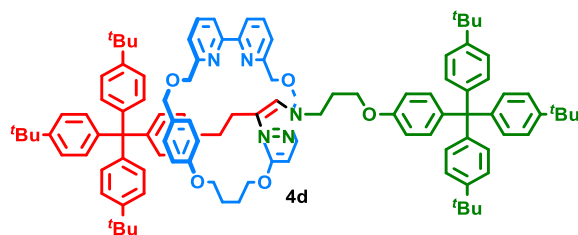
[2]Rotaxane **4a** was made according to conditions A, using macrocycle **1a** (14.1 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol), N^iPr_2Et (4.8 μ L, 0.028 mmol), and $Cu(MeCN)_4PF_6$ (0.93 mg, 0.0025 mmol) in THF (0.5 mL) stirred at rt for 6 h. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 40.3 mg (95% yield) of [2]rotaxane **4a** as a white foam. All analytical data was in accord with previously reported literature data.¹



[2]Rotaxane **4b** was made according to conditions A, using macrocycle **1b** (13.4 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol), N^iPr_2Et (4.8 μ L, 0.028 mmol), and $Cu(MeCN)_4PF_6$ (0.93 mg, 0.0025 mmol) in THF (0.5 mL) stirred at rt for 6 h. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 39.3 mg (94% yield) of [2]rotaxane **4b** as a white foam. All analytical data was in accord with previously reported literature data.²

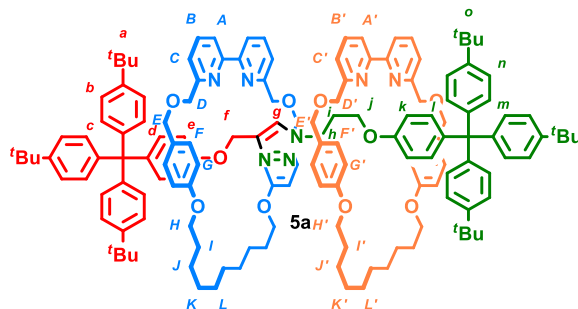


[2]Rotaxane **4c** was made according to conditions A, using macrocycle **1b** (12.7 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol), N^iPr_2Et (4.8 μ L, 0.028 mmol), and $Cu(MeCN)_4PF_6$ (0.93 mg, 0.0025 mmol) in THF (0.5 mL) stirred at rt for 6 h. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 40.6 mg (99% yield) of [2]rotaxane **4c** as a white foam. All analytical data was in accord with previously reported literature data.²

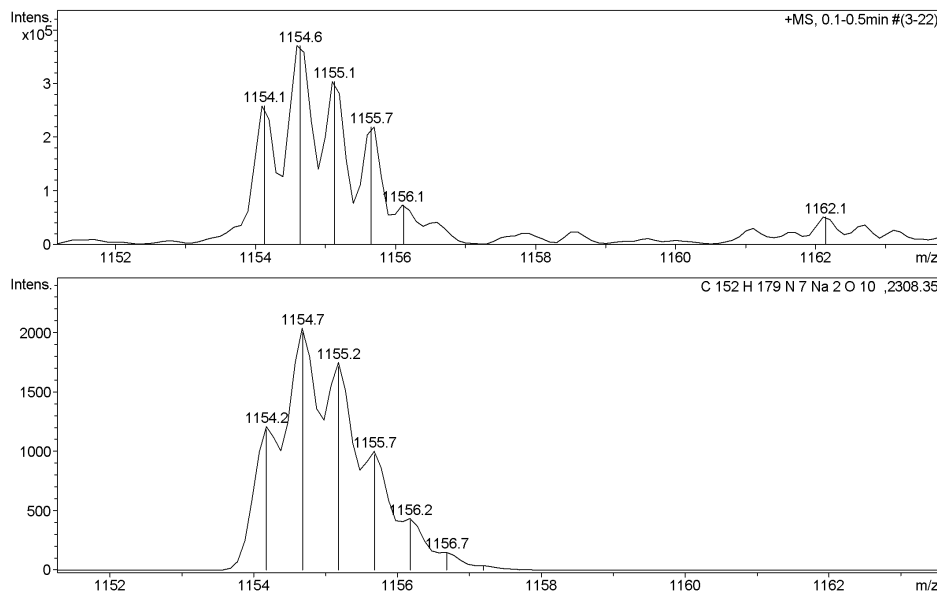


[2]Rotaxane **4d** was made according to conditions A, using macrocycle **1d** (1.4 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol), $N^t\text{Pr}_2\text{Et}$ (4.8 μL , 0.028 mmol), and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (0.93 mg, 0.0025 mmol) in THF (0.5 mL) stirred at rt for 6 h. Flash column chromatography (0-30% MeCN/1:1 hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 39.9 mg (99% yield) of [2]rotaxane **4d** as a white foam. All analytical data was in accord with previously reported literature data.²

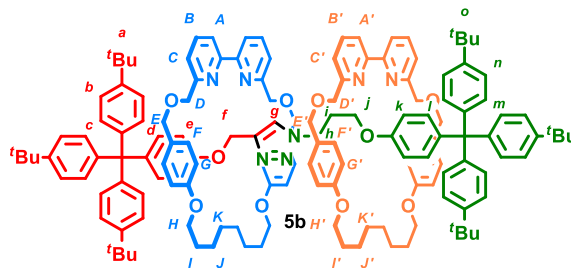
Synthesis of [3]Rotaxane **5a**



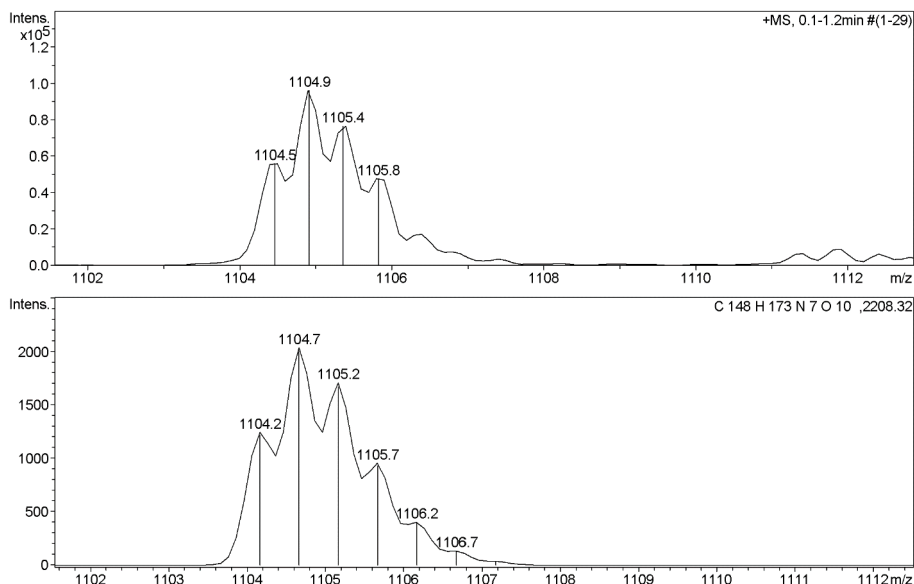
[3]Rotaxane **5a** was made according to conditions B, using macrocycle **1a** (14.1 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.9 mg, 0.024 mmol) in CH_2Cl_2 (2.5 mL) stirred at 100°C in a 150W microwave reactor for 20 minutes. Flash column chromatography (0-30% $\text{MeCN}/1:1$ hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 14.1 mg (49% yield) of [3]rotaxane **5a** as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.97 (d, $J=7.6$, 2H, H_A), 7.96 (d, $J=7.6$, 2H, H_A'), 7.43 (t, $J=7.6$, 2H, H_B), 7.40 (t, $J=7.6$, 2H, H_B'), 7.21 - 7.30 (m, 16H, H_C , H_C' , H_B and H_B'), 7.09 (d, $J=8.7$, 6H, H_C or H_m), 7.05 (d, $J=8.7$, 6H, H_C or H_m), 6.96 (d, $J=8.7$, 4H, H_F), 6.94 (s, 1H, H_g), 6.93 (d, $J=8.7$, 4H, H_F'), 6.80 (d, $J=9.1$, 2H, H_d or H_l), 6.74 (d, $J=9.1$, 2H, H_d or H_l), 6.51 (d, $J=8.7$, 4H, H_G), 6.49 (d, $J=8.7$, 4H, H_G'), 6.04 (d, $J=9.1$, 2H, H_e or H_j), 5.97 (d, $J=9.1$, 2H, H_e or H_j), 4.56 - 4.58 (m, 8H, H_D and H_D'), 4.52 - 4.56 (m, 8H, H_E and H_E'), 3.58 - 3.76 (m, 10H, H_H , H_H' and H_j), 2.99 (t, $J=5.7$, 2H, H_h), 1.52 - 1.60 (m, 8H, H_I and H_I'), 1.39 - 1.46 (m, 2H, H_i), 1.28 - 1.37 (m, 54H, H_a and H_o), 1.17 - 1.28 (m, 8H, H_J and H_J'), 1.00 - 1.15 (m, 16H, H_K , H_K' , H_L and H_L'); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 158.7 (C), 158.7 (C), 158.4 (C), 158.3 (C), 156.2 (C), 156.1 (C), 155.6 (C), 155.4 (C), 148.5 (C), 148.4 (C), 148.3 (C), 144.5 (2 x C), 139.4 (C), 139.3 (C), 137.3 (CH), 137.2 (CH), 131.9 (CH), 130.9 (2 x CH), 129.8 (CH), 129.8 (CH), 129.7 (C), 124.2 (CH), 124.2 (CH), 122.9 (CH), 121.6 (CH), 121.5 (CH), 120.0 (CH), 119.9 (CH), 114.5 (CH), 114.5 (CH), 112.8 (CH), 112.8 (CH), 72.6 (CH_2), 72.5 (2 x CH_2), 72.4 (CH_2), 67.8 (CH_2), 67.7 (CH_2), 64.0 (CH_2), 63.2 (C), 63.1 (C), 61.4 (CH_2), 47.0 (CH_2), 34.5 (2 x C), 31.6 (CH_3), 31.6 (CH_3), 29.8 (CH_2), 29.5 (2 x CH_2), 29.0 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 25.9 (CH_2), 25.9 (CH_2); LRMS (ESI+) m/z 1154.7 $[\text{M}+2\text{Na}]^{2+}$.



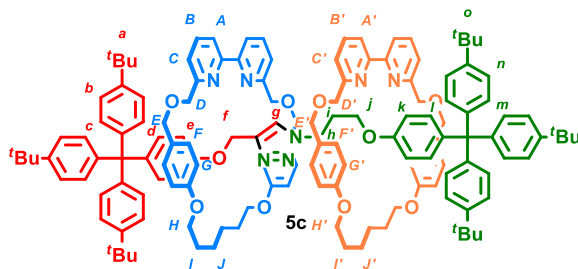
Synthesis of [3]Rotaxane **5b**



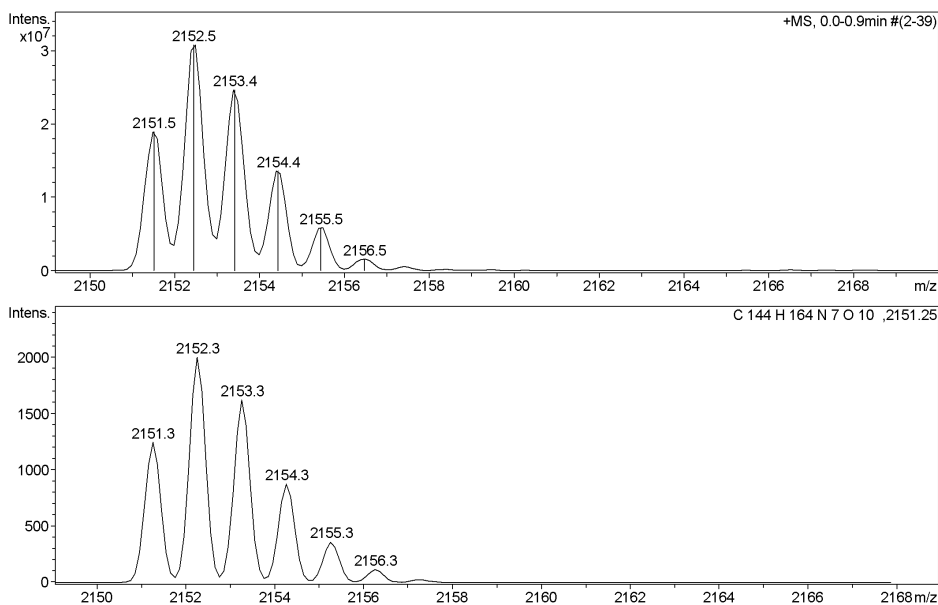
[3]Rotaxane **5b** was made according to conditions B, using macrocycle **1b** (13.4 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol) and Cu(MeCN)₄.PF₆ (8.9 mg, 0.024 mmol) in CH₂Cl₂ (2.5 mL) stirred at 100°C in a 150W microwave reactor for 20 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 13.9 mg (50%) of the target material as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.83 (d, *J*=7.8, 4H, H_A and H_{A'}), 7.48 (t, *J*=7.8, 2H, H_B or H_{B'}), 7.46 (t, *J*=7.8, 2H, H_B or H_{B'}), 7.36 (d, *J*=7.8, 2H, H_C or H_{C'}), 7.35 (d, *J*=7.8, 2H, H_C or H_{C'}), 7.21 - 7.33 (m, 20H, H_b and H_m), 7.14 (s, 1H, H_g), 7.10 (d, *J*=8.7, 6H, H_c or H_m), 7.06 (d, *J*=8.7, 6H, H_c or H_m), 6.99 (d, *J*=8.7, 4H, H_F or H_{F'}), 6.96 (d, *J*=8.7, 4H, H_F or H_{F'}), 6.69 (d, *J*=8.7, 2H, H_d or H_l), 6.58 (d, *J*=8.7, 2H, H_d or H_l), 6.55 (d, *J*=8.7, 4H, H_G or H_{G'}), 6.51 (d, *J*=8.7, 4H, H_G or H_{G'}), 5.79 (d, *J*=8.7, 2H, H_e or H_k), 5.78 (d, *J*=8.7, 2H, H_e or H_k), 4.49 - 4.62 (m, 16H, H_D, H_{D'}, H_E and H_{E'}), 4.24 (s, 2H, H_j), 3.61 - 3.82 (m, 8H, H_H and H_{H'}), 3.55 - 3.60 (m, 2H, H_j), 2.90 (t, *J*=5.7, 2H, H_h), 1.45 - 1.64 (m, 8H, H_I and H_{I'}), 1.34 - 1.39 (m, 2H, H_i), 1.36 (s, 27H, H_a and H_o), 1.35 (s, 27H, H_a and H_o), 0.87 - 0.96 (m, 10H, H_J, H_{J'}, H_K and H_{K'}); ¹³C NMR (100 MHz, CDCl₃) δ ppm 158.8 (C), 158.8 (C), 158.6 (C), 158.6 (C), 156.0 (C), 156.0 (C), 155.7 (C), 155.5 (C), 148.4 (C), 148.3 (C), 148.2 (C), 144.6 (2 x C), 139.0 (C), 137.2 (CH), 137.1 (CH), 131.7 (CH), 131.6 (CH), 131.0 (CH), 131.0 (CH), 129.9 (2 x CH), 129.7 (C), 129.5 (C), 124.2 (CH), 124.2 (CH), 123.2 (CH), 120.9 (CH), 120.7 (CH), 120.1 (CH), 119.9 (CH), 114.7 (CH), 114.6 (CH), 112.8 (CH), 112.7 (CH), 72.6 (CH₂), 72.5 (CH₂), 71.8 (CH₂), 71.5 (CH₂), 67.8 (CH₂), 67.7 (CH₂), 63.9 (CH₂), 63.2 (C), 63.1 (C), 61.2 (CH₂), 47.0 (CH₂), 34.5 (2 x C), 31.6 (CH₃), 31.6 (CH₃), 29.7 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 25.9 (CH₂), 25.9 (CH₂); LRMS (ESI⁺) *m/z* 1104.5 [M+2H]²⁺



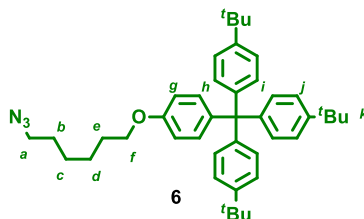
Synthesis of [3]Rotaxane **5c**



[3]Rotaxane **5c** was made according to conditions B, using macrocycle **1a** (12.7 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol) and Cu(MeCN)₄.PF₆ (8.9 mg, 0.024 mmol) in CH₂Cl₂ (2.5 mL) stirred at 100°C in a 150W microwave reactor for 20 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 5.2 mg (23%) of the target material as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.61 (d, *J*=7.6, 2H, H_A), 7.62 (d, *J*=7.6, 2H, H_{A'}), 7.48 - 7.54 (m, 4H, H_B and H_{B'}), 7.39 (d, *J*=7.6, 2H, H_C), 7.38 (d, *J*=7.6, 2H, H_{C'}), 7.25 - 7.29 (m, 6H, H_b or H_n), 7.29 (d, *J*=8.7, 6H, H_b or H_n), 7.17 (s, 1H, H_g), 7.10 (d, *J*=8.7, 6H, H_c or H_m), 7.05 (d, *J*=8.7, 6H, H_c or H_m), 6.97 (d, *J*=8.7, 2H, H_F or H_{F'}), 6.93 (d, *J*=8.7, 2H, H_F or H_{F'}), 6.60 (d, *J*=9.1, 2H, H_d or H_l), 6.54 (d, *J*=8.6, 2H, H_G or H_{G'}), 6.51 (d, *J*=8.6, 2H, H_G or H_{G'}), 5.58 - 5.66 (m, 4H, H_e and H_k), 4.36 - 4.61 (m, 16H, H_D, H_{D'}, H_E and H_{E'}), 4.22 (s, 2H, H_f), 3.74 - 3.87 (m, 4H, H_H or H_{H'}), 3.70 (dt, *J*=9.7, 6.6, 2H, H_H or H_{H'}), 3.69 (dt, *J*=9.7, 6.6, 2H, H_H or H_{H'}), 3.50 (m, *J*=7.9, 2H, H_h), 2.83 (t, *J*=6.0, 2H, H_i), 1.48 - 1.58 (m, 8H, H_I and H_{I'}), 1.35 (s, 27H, H_a), 1.35 (s, 27H, H_o), 1.25 - 1.29 (m, 2H, H_i), 0.87 - 0.96 (m, 8H, H_J and H_{J'}); ¹³C NMR (100 MHz, CDCl₃) δ ppm 158.9 (C), 158.9 (C), 158.9 (C), 158.7 (C), 156.0 (C), 155.8 (C), 155.7 (C), 155.6 (C), 148.2 (C), 148.2 (C), 148.1 (C), 144.4 (2 x C), 138.5 (C), 137.0 (CH), 136.9 (CH), 131.4 (CH), 130.9 (CH), 130.8 (CH), 129.9 (2 x CH), 129.3 (C), 129.1 (C), 124.1 (CH), 124.0 (CH), 124.0 (CH), 124.0 (CH), 120.2 (CH), 120.0 (CH), 119.9 (CH), 115.0 (CH), 114.9 (CH), 112.7 (CH), 112.7 (CH), 72.4 (CH₂), 72.4 (CH₂), 70.8 (CH₂), 70.5 (CH₂), 67.8 (CH₂), 63.8 (CH₂), 63.0 (C), 62.9 (C), 60.7 (CH₂), 46.7 (CH₂), 34.3 (2 x C), 31.5 (CH₃), 31.4 (CH₃), 29.7 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 29.0 (CH₂), 25.3 (CH₂), 25.2 (CH₂); LRMS (ESI+) *m/z* 2152.5 [M+H]⁺.

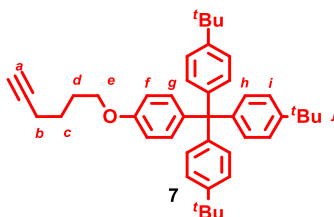


Synthesis of 6-(4-(Tri(4-*tert*-butylphenyl)methyl)phenoxy)hexyl azide (6)



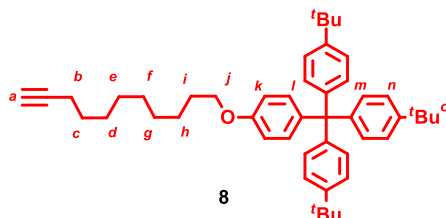
A solution of 6-(4-(tri(4-*tert*-butylphenyl)methyl)phenoxy)hexyl bromide (**S2**) (725 mg, 1.086 mmol) and NaN₃ (141.2 mg, 2.172 mmol) in dry NMP (16 mL) was stirred at 80 °C for 18 hours. Water was added (50 mL) and the reaction mixture extracted twice with CH₂Cl₂ (50 mL). The organic layers were then combined, dried over MgSO₄ and reduced *in vacuo* to afford a cream solid (CAUTION: Care should be taken with azides under reduced pressure). Recrystallisation from hot MeCN/CHCl₃ afforded 253.2 mg (38%) of the target material as a white solid: m.p. 200-202 °C (dec.); ¹H NMR (600 MHz, CDCl₃) δ ppm 7.26 (d, *J*=8.7, 6H, H_j), 7.06 - 7.14 (m, 8H, H_i and H_g or H_h), 6.78 (d, *J*=8.9, 2H, H_g or H_h), 3.96 (t, *J*=6.3, 2H, H_a), 3.31 (t, *J*=6.9, 2H, H_f), 1.77 - 1.85 (m, 2H, H_b), 1.66 (m, 2H, H_e), 1.44 - 1.55 (m, 4H, H_c and H_d), 1.33 (s, 27H, H_k); ¹³C NMR (150 MHz, CDCl₃) δ ppm 157.0 (C), 148.5 (C), 144.3 (C), 139.6 (C), 132.4 (CH), 130.9 (CH), 124.2 (CH), 113.1 (CH), 67.7 (CH₂), 63.2 (C), 52.0 (CH₂), 34.4 (C), 31.5 (CH₃), 29.4 (CH₂), 29.0 (CH₂), 26.7 (CH₂), 25.9 (CH₂); HRMS (APCI+) *m/z* 647.4691 [M+NH₄]⁺ (calc. for C₄₃H₅₉N₄O 647.4683).

Synthesis of 6-(4-(Tri(4-*tert*-butylphenyl)methyl)phenoxy)hex-1-yne (7)



A solution of 4-(tri(4-*tert*-butylphenyl)methyl)phenol (**S3**) (510 mg, 1.01 mmol), 6-tosyloxyhex-1-yne (**S4**) (255 mg, 1.01 mmol) and K₂CO₃ (698 mg, 5.05 mmol) in acetone (10 mL) was refluxed with stirring for 18 hours. The reaction mixture was filtered, dried (MgSO₄) then reduced *in vacuo* to afford a beige solid. Recrystallisation from hot MeCN/CHCl₃ afforded 94.3 mg (16%) of the target material as a white solid: m.p. 231-233 °C; ¹H NMR (600 MHz, CDCl₃) δ ppm 7.24 (d, *J*=8.7, 6H, H_h or H_i), 6.99 - 7.16 (m, 8H, H_f or H_g and H_h or H_i), 6.76 (d, *J*=8.9, 2H, H_f or H_g), 3.97 (t, *J*=6.2, 2H, H_e), 2.28 (td, *J*=7.1, 2.6, 2H, H_b), 1.97 (t, *J*=2.6 Hz, 1H, H_a), 1.86 - 1.95 (m, 2H, H_d), 1.73 (m, 2H, H_c), 1.31 (s, 27H, H_j); ¹³C NMR (150 MHz, CDCl₃) δ ppm 157.0 (C), 148.5 (C), 144.3 (C), 139.7 (C), 132.4 (CH), 130.9 (CH), 124.2 (CH), 113.1 (CH), 68.7 (C), 67.3 (CH₂), 63.2 (C), 34.4 (C), 31.5 (CH₃), 28.5 (CH₂), 25.3 (CH₂), 18.3 (CH₂); HRMS (APCI+) *m/z* 585.4092 [M+H]⁺ (calc. for C₄₃H₅₃O 585.4091).

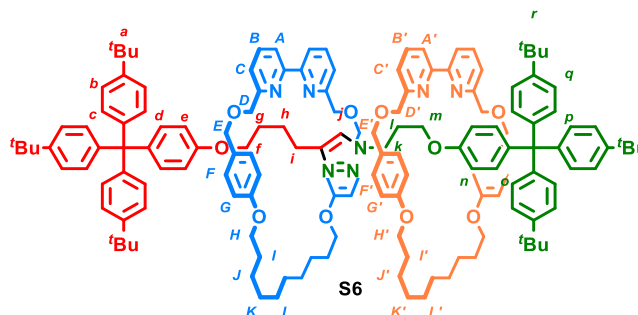
Synthesis of 11-(4-(Tri(4-*tert*-butylphenyl)methyl)phenoxy)undec-1-yne (8)



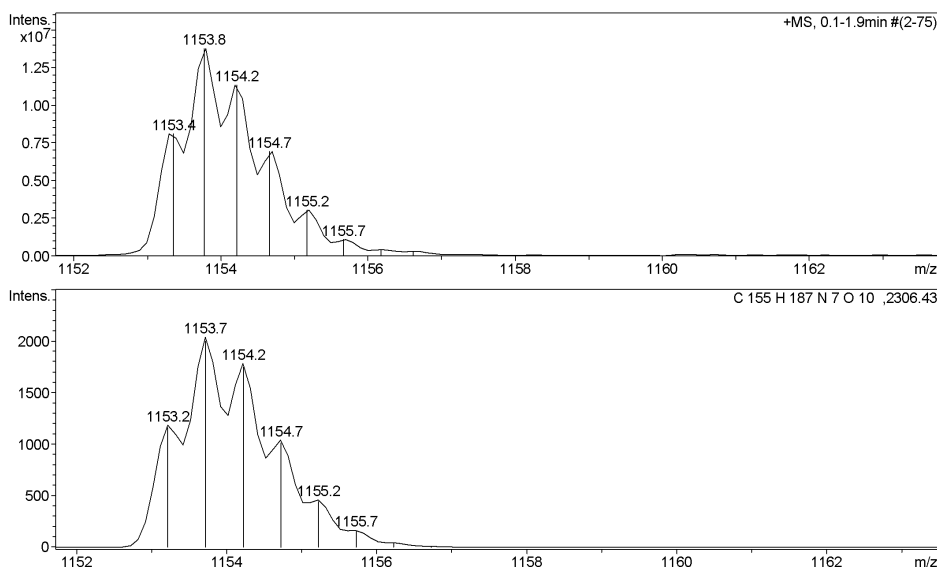
A solution of 4-(tri(4-*tert*-butylphenyl)methyl)phenol (**S3**) (252 mg, 0.05 mmol), 11-tosyloxyundec-1-yne (**S5**) (161 mg, 0.05 mmol) and K₂CO₃ (276 mg, 2 mmol) in acetone (5 mL) was refluxed with stirring for 18 hours. The reaction mixture was filtered, dried (MgSO₄) then reduced *in vacuo* to afford a beige solid. Column chromatography

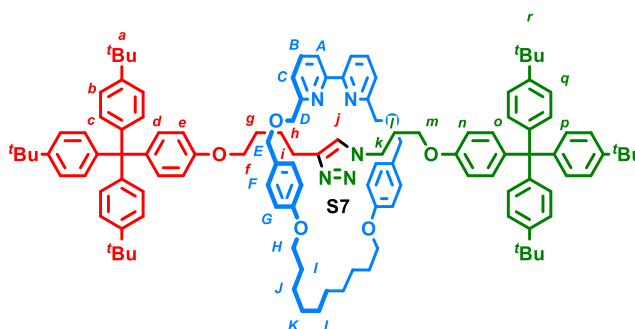
(0-10% CH₂Cl₂/petrol) afforded 111.7 mg (34%) of the target material as a white solid: m.p. 155-159 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.24 (d, *J*=8.6, 6H, H_m or H_n), 7.10 (d, *J*=8.6, 6H, H_m or H_n), 7.09 (d, *J*=8.8, 2H, H_k or H_l), 6.77 (d, *J*=8.8, 2H, H_k or H_l), 3.94 (t, *J*=6.5, 2H, H_j), 2.19 (td, *J*=7.0, 2.5, 2H, H_b), 1.94 (t, *J*=2.5, 1H, H_a), 1.77 (m, 2H, H_i), 1.12 - 1.60 (m, 12H, H_c, H_d, H_e, H_f, H_g and H_h), 1.31 (s, 27H, H_o); ¹³C NMR (150 MHz, CDCl₃) δ ppm 157.1 (C), 148.4 (C), 144.4 (C), 139.5 (C), 132.4 (CH), 130.9 (CH), 124.2 (CH), 113.1 (CH), 68.2 (C), 68.0 (CH₂), 63.2 (C), 34.4 (3 x C), 31.5 (9 x CH₃), 29.6 (CH₂), 29.5 (2 x CH₂), 29.2 (CH₂), 28.9 (CH₂), 28.6 (CH₂), 26.2 (CH₂), 18.5 (CH₂); HRMS (APCI+) *m/z* 672.5136 [M+NH₄]⁺ (calc. for C₄₃H₅₃O 672.5139).

Synthesis of [3]Rotaxane **S6**

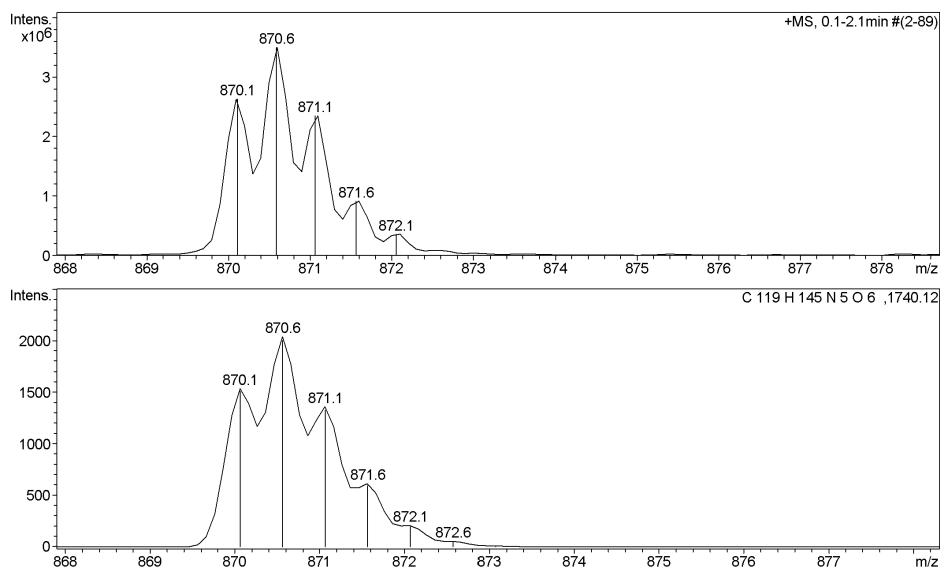


[3]Rotaxane **S6** was made according to conditions B, using macrocycle **1a** (14.2 mg, 0.025 mmol), alkyne **7** (17.5 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol) and Cu(MeCN)₄.PF₆ (8.9 mg, 0.024 mmol) in CH₂Cl₂ (2.5 mL) stirred at 100°C in a 150W microwave reactor for 1 hour. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 9.4 mg (32%) of the target material as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.98 (d, *J*=8.1, 2H, H_A or H_{A'}), 8.00 (d, *J*=8.1, 2H, H_A or H_{A'}), 7.44 (t, *J*=8.1, 2H, H_B or H_{B'}), 7.47 (t, *J*=8.1, 2H, H_B or H_{B'}), 7.27 (d, *J*=8.6, 6H, H_b or H_q), 7.25 (d, *J*=8.6, 6H, H_b or H_q), 7.21-7.31 (m, 4H, H_C and H_{C'}), 7.10 (d, *J*=8.2, 6H, H_c or H_p), 7.08 (d, *J*=8.5, 6H, H_c or H_p), 6.99 (d, *J*=8.6, 4H, H_F or H_{F'}), 6.97 (d, *J*=8.6, 4H, H_F or H_{F'}), 6.84 (d, *J*=8.8, 2H, H_d), 6.79 (d, *J*=8.8, 2H, H_o), 6.67 (s, 1H, H_j), 6.55 (d, *J*=8.6, 4H, H_G or H_{G'}), 6.54 (d, *J*=8.6, 4H, H_G or H_{G'}), 6.06 (d, *J*=8.8, 2H, H_e), 6.05 (d, *J*=8.8, 2H, H_n), 4.57 (s, 8H, H_D and H_{D'} or H_E and H_{E'}), 4.56 (s, 8H, H_D and H_{D'} or H_E and H_{E'}), 3.64 - 3.79 (m, 10H, H_H), 3.10 (t, *J*=6.1, 2H, H_j), 3.06 (t, *J*=5.7, 2H, H_m), 2.26 (t, *J*=7.2, 2H, H_i), 1.47 - 1.66 (m, 10H, H_I, H_{I'} and H_I), 1.19 - 1.39 (m, 12H, H_J, H_{J'}, H_G and H_h), 1.33 (s, 27H, H_a or H_r), 1.33 (s, 27H, H_a or H_r), 1.03 - 1.18 (m, 16H, H_K, H_{K'}, H_L and H_{L'}); ¹³C NMR (150 MHz, CDCl₃) δ ppm 158.7 (C), 158.7 (C), 158.4 (2 x C), 156.7 (C), 156.2 (C), 155.6 (C), 155.4 (C), 148.4 (C), 148.3 (C), 147.4 (C), 144.5 (C), 144.4 (C), 139.4 (C), 138.8 (C), 137.3 (CH), 137.2 (CH), 131.9 (CH), 131.8 (CH), 130.9 (CH), 130.9 (CH), 129.8 (2 x C), 129.8 (CH), 129.8 (CH), 124.2 (CH), 124.2 (CH), 121.6 (CH), 121.5 (CH), 120.8 (CH), 120.0 (CH), 119.8 (CH), 114.5 (CH), 114.5 (CH), 112.9 (CH), 72.6 (CH₂), 72.5 (CH₂), 72.5 (CH₂), 72.4 (CH₂), 67.8 (CH₂), 67.8 (CH₂), 66.9 (CH₂), 63.9 (CH₂), 63.2 (C), 63.2 (C), 46.8 (CH₂), 34.5 (C), 34.5 (C), 31.6 (2 x CH₃), 29.9 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.1 (2 x CH₂), 29.0 (CH₂), 29.0 (CH₂), 26.0 (CH₂), 26.0 (CH₂), 25.7 (CH₂), 25.4 (CH₂); LRMS (ESI+) 1153.2 m/z [M+2H]²⁺.

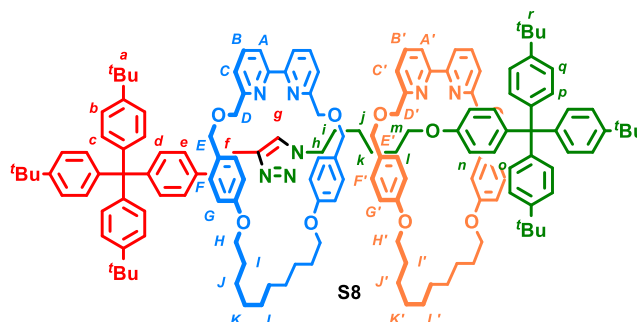




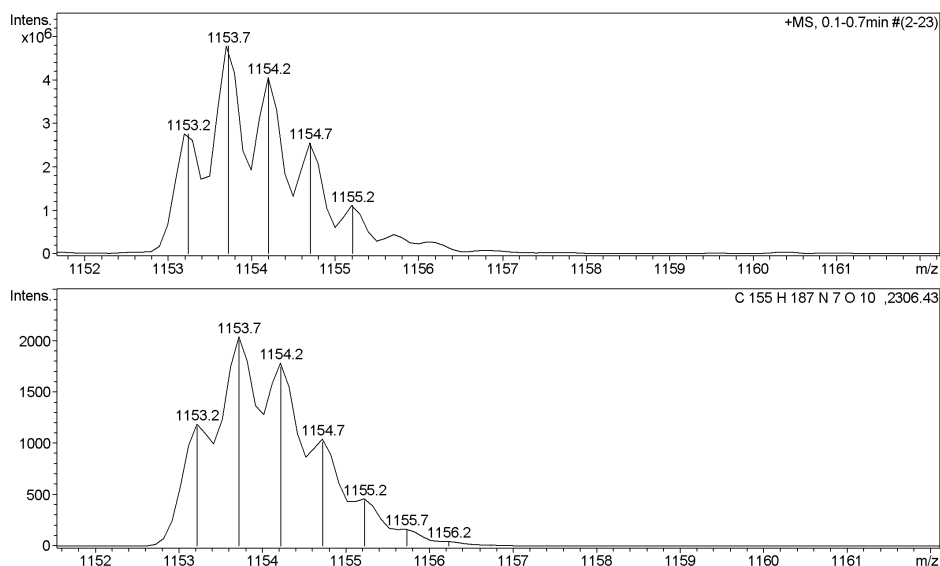
[2]Rotaxane **S7** was also isolated (17.9 mg, 41%) as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.97 (d, $J=7.8$, 2H, H_d), 7.49 (t, $J=7.8$, 2H, H_B), 7.29 (d, $J=7.8$, 2H, H_C), 7.25 (d, $J=8.7$, 6H, H_b or H_q), 7.24 (d, $J=8.6$, 6H, H_b or H_q), 7.10 (d, $J=8.6$, 6H, H_c or H_p), 7.11 (d, $J=8.7$, 6H, H_c or H_p), 6.97 - 7.05 (m, 8H, H_F , H_d and H_o), 6.78 (s, 1H, H_j), 6.58 (d, $J=9.0$, 2H, H_e), 6.59 (d, $J=8.7$, 4H, H_G), 6.42 (d, $J=9.0$, 2H, H_n), 4.57 (s, 4H, H_D or H_E), 4.55 (s, 4H, H_D or H_E), 3.90 (t, $J=7.3$, 2H, H_k), 3.76 (t, $J=6.5$, 4H, H_H), 3.66 (t, $J=5.8$, 2H, H_j), 3.40 (t, $J=5.7$, 2H, H_m), 2.45 (t, $J=7.1$, 2H, H_i), 1.73 - 1.82 (tt, $J=7.3$, 5.7, 2H, H_l), 1.45 - 1.65 (m, 8H, H_I , H_e and H_h), 1.22 - 1.37 (m, 4H, H_J), 1.32 (s, 27H, H_a or H_r), 1.31 (s, 27H, H_a or H_r), 1.09 - 1.21 (m, 8H, H_K and H_L); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 158.6 (C), 158.2 (C), 156.8 (C), 156.2 (C), 155.5 (C), 148.3 (C), 148.3 (C), 147.4 (C), 144.3 (C), 144.2 (C), 139.7 (C), 139.3 (C), 137.1 (CH), 132.1 (CH), 130.8 (CH), 130.7 (CH), 129.7 (C), 129.7 (CH), 124.1 (CH), 124.0 (CH), 121.5 (CH), 121.0 (CH), 119.9 (CH), 114.4 (CH), 112.9 (CH), 112.9 (CH), 72.5 (CH_2), 72.3 (CH_2), 67.7 (CH_2), 67.2 (CH_2), 63.9 (CH_2), 63.1 (2 x C), 46.6 (CH_2), 34.3 (2 x C), 31.4 (2 x CH_3), 29.8 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.8 (CH_2), 25.8 (CH_2), 25.8 (CH_2), 25.2 (CH_2); LRMS (ESI+) m/z 870.1 $[\text{M}+2\text{H}]^+$.

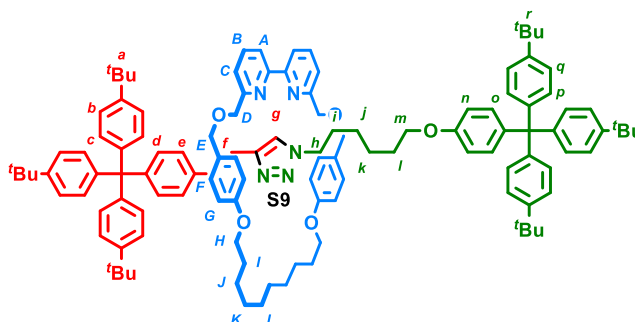


Synthesis of [3]Rotaxane **S8**

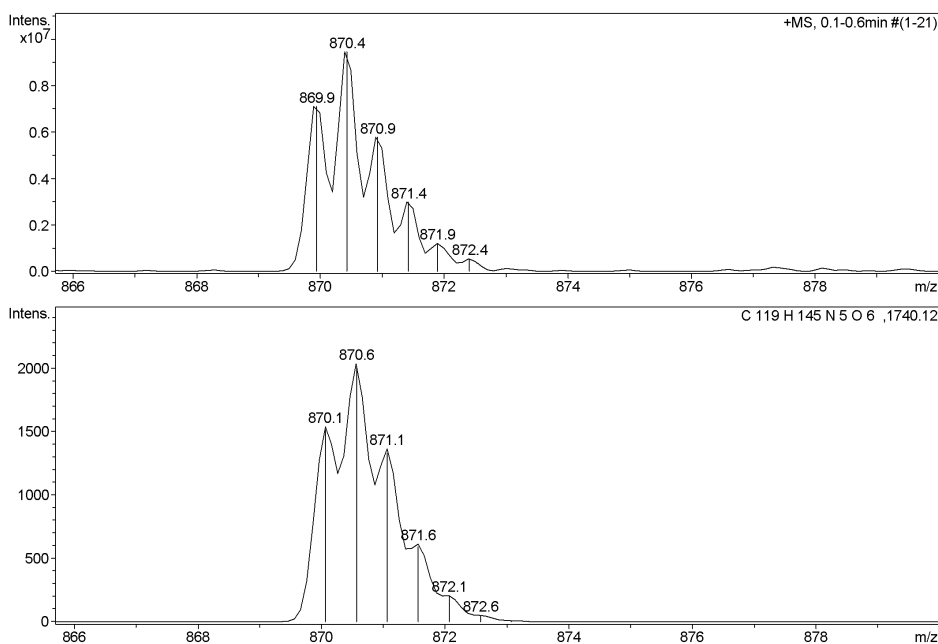


[3]Rotaxane **S8** was made according to conditions B, using macrocycle **1a** (14.2 mg, 0.025 mmol), alkyne **2** (16.3 mg, 0.030 mmol), azide **6** (18.9 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.9 mg, 0.024 mmol) in CH_2Cl_2 (2.5 mL) stirred at 100°C in a 150W microwave reactor for 1 hour. Flash column chromatography (0-30% MeCN/1:1 hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 13.7 mg (48%) of the target material as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 8.01 (d, $J=7.7$, 2H, H_A or $\text{H}_{A'}$), 7.96 (d, $J=7.7$, 2H, H_A or $\text{H}_{A'}$), 7.47 (t, $J=7.7$, 2H, H_B or $\text{H}_{B'}$), 7.46 (t, $J=7.7$, 2H, H_B or $\text{H}_{B'}$), 7.31 – 7.22 (m, 4H, H_C and $\text{H}_{C'}$), 7.25 (d, $J=8.7$, 6H, H_b or H_q), 7.25 (d, $J=8.7$, 6H, H_b or H_q), 7.09 (d, $J=8.7$, 6H, H_c or H_p), 7.07 (d, $J=8.7$, 6H, H_c or H_p), 7.06 (s, 1H, H_g), 7.00 (d, $J=8.7$, 4H, H_F or $\text{H}_{F'}$), 6.97 (d, $J=8.8$, 4H, H_F or $\text{H}_{F'}$), 6.84 (d, $J=8.8$, 2H, H_d), 6.85 (d, $J=8.8$, 2H, H_o), 6.54 (d, $J=8.7$, 4H, H_G or $\text{H}_{G'}$), 6.56 (d, $J=8.8$, 4H, H_G or $\text{H}_{G'}$), 6.26 (d, $J=8.8$, 2H, H_e), 6.14 (d, $J=8.8$, 2H, H_n), 4.45 – 4.62 (m, 16H, H_D , $\text{H}_{D'}$, H_E and $\text{H}_{E'}$), 4.49 (s, 2H, H_f), 3.66 – 3.78 (m, 8H, H_H and $\text{H}_{H'}$), 3.52 (t, $J=7.7$, 2H, H_h), 3.06 (t, $J=6.5$, 2H, H_m), 1.51 – 1.66 (m, 8H, H_I and $\text{H}_{I'}$), 1.32 (s, 54H, H_a and H_r), 1.19 – 1.37 (m, 8H, H_J and $\text{H}_{J'}$), 1.12 (d, $J=7.7$, 18H, H_K , $\text{H}_{K'}$, H_L , $\text{H}_{L'}$ and H_j), 0.55 – 0.76 (m, 4H, H_k and H_l); ^{13}C NMR (150 MHz, CDCl_3) δ ppm 158.7 (C), 158.7 (C), 158.4 (C), 158.4 (C), 156.8 (C), 156.2 (C), 155.5 (2 x C), 148.3 (2 x C), 147.4 (C), 144.5 (C), 144.4 (C), 139.6 (C), 139.0 (C), 137.2 (CH), 137.2 (CH), 132.0 (CH), 131.9 (CH), 130.9 (2 x CH), 129.8 (2 x C), 129.8 (CH), 129.8 (CH), 124.2 (CH), 124.2 (CH), 122.9 (CH), 121.5 (CH), 121.5 (CH), 120.0 (CH), 119.9 (CH), 114.5 (CH), 114.5 (CH), 113.0 (CH), 112.9 (2 x CH), 72.6 (CH_2), 72.5 (CH_2), 72.4 (CH_2), 72.4 (CH_2), 67.8 (CH_2), 67.7 (CH_2), 67.0 (CH_2), 63.2 (2 x C), 61.6 (CH_2), 49.7 (CH_2), 34.5 (2 x C), 31.6 (2 x CH_3), 29.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 29.0 (2 x CH_2), 28.9 (CH_2), 28.9 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.2 (CH_2); LRMS (ESI+) 1153.2 m/z $[\text{M}+2\text{H}]^{2+}$.

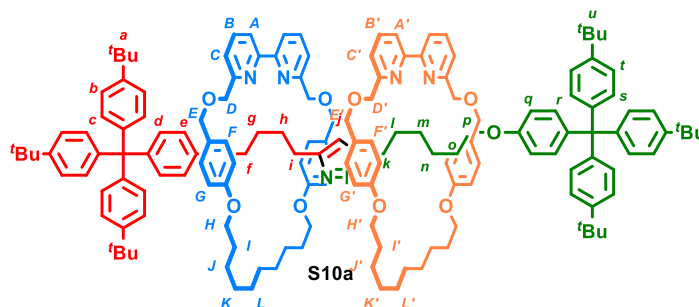




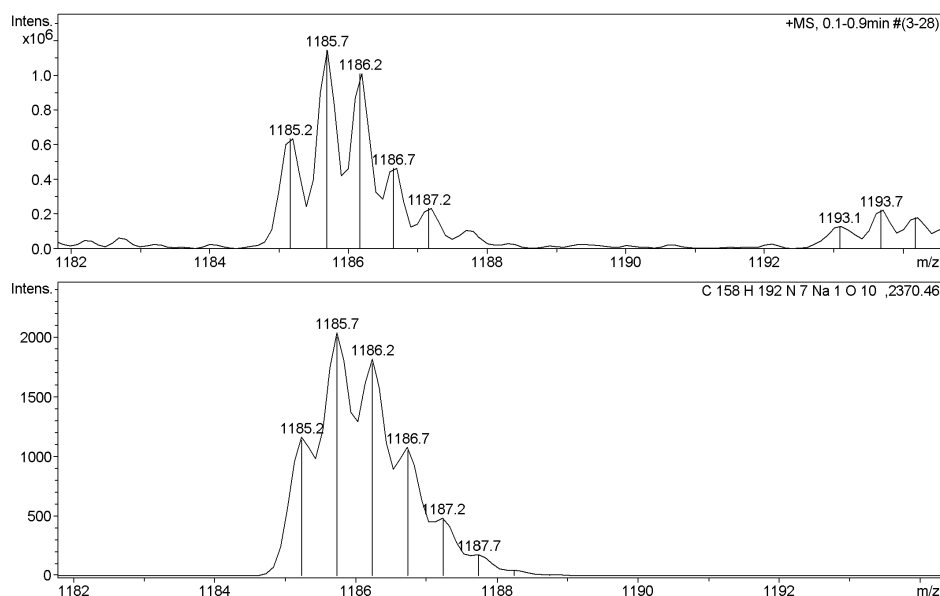
[2]Rotaxane **S9** was also isolated (19.6 mg, 45%) as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.97 (d, $J=7.8$, 2H, H_A), 7.52 (t, $J=7.8$, 2H, H_B), 7.31 (d, $J=7.8$, 2H, H_C), 7.25 (d, $J=8.6$, 6H, H_b or H_g), 7.24 (d, $J=8.6$, 6H, H_b or H_g), 7.12 (d, $J=8.6$, 6H, H_c or H_p), 7.09 (d, $J=8.6$, 6H, H_c or H_p), 7.04 (d, $J=8.6$, 4H, H_F), 7.00 - 7.16 (m, 4H H_g , H_d and H_o), 6.74 (d, $J=9.0$, 2H, H_e), 6.61 (d, $J=8.6$, 4H, H_G), 6.59 (d, $J=9.1$, 2H, H_n), 4.94 (s, 2H, H_j), 4.57 (s, 4H, H_D or H_E), 4.56 (s, 4H, H_D or H_E), 3.79 (t, $J=6.4$, 4H, H_H), 3.61 (t, $J=7.6$, 2H, H_h), 3.51 (t, $J=6.4$, 2H, H_m), 1.62 (tt, $J=7.2$, 6.4, 4H, H_I), 1.06 - 1.37 (m, 16H, H_J , H_K , H_L , H_i and H_l), 1.32 (s, 27H, H_a), 1.31 (s, 27H, H_r), 0.90 (m, 2H, H_j), 0.74 (m, 2H, H_k); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 158.8 (C), 158.4 (C), 157.0 (C), 156.4 (C), 155.7 (C), 148.5 (C), 148.4 (C), 144.4 (C), 144.3 (C), 143.8 (C), 140.1 (C), 139.4 (C), 137.2 (CH), 132.4 (CH), 132.3 (CH), 130.9 (2 x CH), 129.8 (CH), 124.2 (2 x CH), 122.9 (CH), 121.6 (CH), 120.0 (CH), 114.5 (CH), 113.3 (CH), 113.1 (CH), 72.6 (CH_2), 72.3 (CH_2), 67.8 (CH_2), 67.3 (CH_2), 63.2 (2 x C), 62.0 (CH_2), 49.8 (CH_2), 34.4 (2 x C), 31.5 (2 x CH_3), 29.7 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 26.0 (CH_2), 26.0 (CH_2), 25.2 (CH_2); LRMS (ESI+) 869.9 m/z [$\text{M}+2\text{H}$] $^{2+}$.

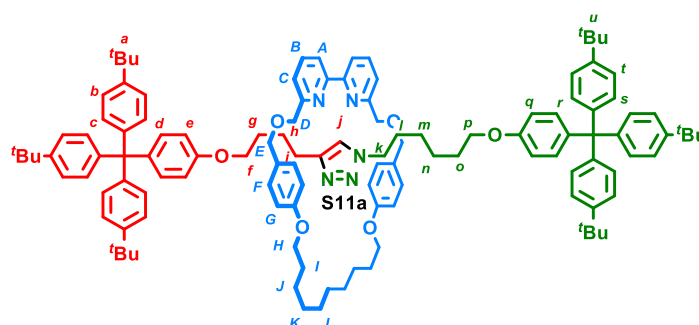


Synthesis of [3]Rotaxane **S10a**

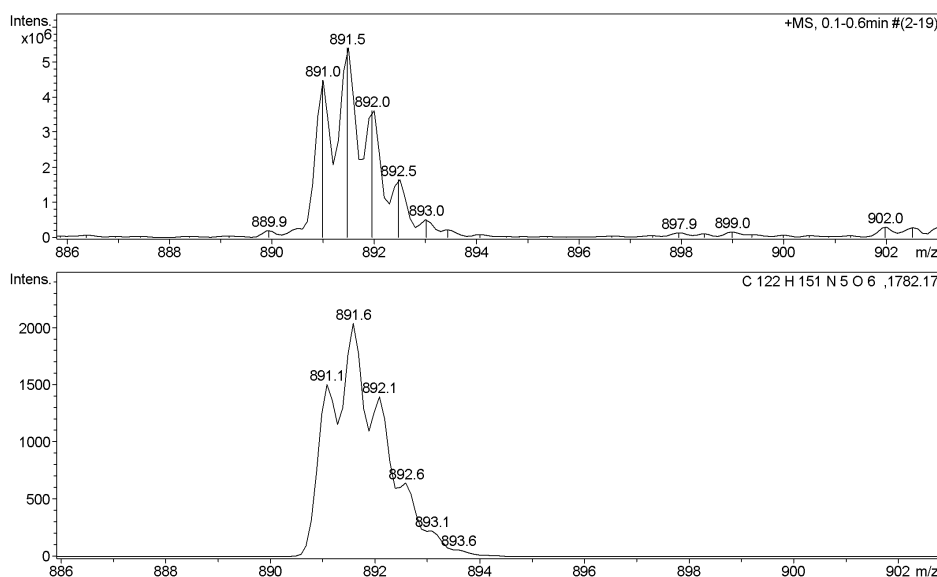


[3]Rotaxane **S10a** was made according to conditions B, using macrocycle **1a** (14.2 mg, 0.025 mmol), alkyne **7** (17.5 mg, 0.030 mmol), azide **6** (18.9 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.9 mg, 0.024 mmol), in CH_2Cl_2 (2.5 mL) stirred at 100°C in a 150W microwave reactor for 45 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 11.3 mg (35%) of the target material as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 8.01 (d, $J=7.8$, 2H, H_A or $\text{H}_{A'}$), 8.00 (d, $J=7.8$, 2H, H_A or $\text{H}_{A'}$), 7.51 (t, $J=7.8$, 2H, H_B or $\text{H}_{B'}$), 7.48 (t, $J=7.8$, 2H, H_B or $\text{H}_{B'}$), 7.31 (d, $J=7.8$, 2H, H_C or $\text{H}_{C'}$), 7.29 (d, $J=7.8$, 2H, H_C or $\text{H}_{C'}$), 7.25 (d, $J=8.5$, 12H, H_b and H_i), 7.10 (d, $J=8.5$, 6H, H_c or H_s), 7.09 (d, $J=8.5$, 6H, H_c or H_s), 7.02 (d, $J=8.7$, 4H, H_F or $\text{H}_{F'}$), 6.99 (d, $J=8.7$, 4H, H_F or $\text{H}_{F'}$), 6.90 (d, $J=8.8$, 2H, H_d), 6.85 (d, $J=8.8$, 2H, H_r), 6.80 (s, 1H, H_j), 6.59 (d, $J=8.7$, 4H, H_G or $\text{H}_{G'}$), 6.57 (d, $J=8.7$, 4H, H_G or $\text{H}_{G'}$), 6.25 (d, $J=8.8$, 2H, H_e), 6.17 (d, $J=8.8$, 2H, H_q), 4.54 - 4.61 (m, 16H, H_D , $\text{H}_{D'}$, H_E and $\text{H}_{E'}$), 3.70 - 3.81 (m, 8H, H_H), 3.65 (m, $J=7.7$, 2H, H_p), 3.21 (t, $J=5.8$, 2H, H_j), 3.16 (t, $J=6.5$, 2H, H_k), 2.32 (t, $J=7.1$, 2H, H_l), 1.51 - 1.68 (m, 6H, H_b , H_i), 1.08 - 1.37 (m, 14H, H_g , H_l , H_o , H_J and H_K), 1.32 (s, 54H, H_a and H_u), 0.80 - 0.96 (m, 4H, H_L), 0.62 - 0.80 (m, 4H, H_m and H_n); ^{13}C NMR (150 MHz, CDCl_3) δ ppm 158.7 (2 x C), 158.4 (2 x C), 156.8 (C), 156.8 (C), 155.6 (C), 155.5 (C), 148.4 (C), 148.3 (C), 147.4 (C), 144.5 (C), 144.5 (C), 139.1 (C), 139.0 (C), 137.2 (CH), 137.2 (CH), 132.0 (CH), 131.9 (CH), 130.9 (2 x CH), 129.9 (2 x C), 129.8 (CH), 129.8 (CH), 124.2 (CH), 124.2 (CH), 121.5 (2 x CH), 120.6 (CH), 119.9 (CH), 119.9 (CH), 114.5 (CH), 114.5 (CH), 113.0 (CH), 112.9 (CH), 72.5 (2 x CH_2), 72.4 (CH_2), 72.3 (CH_2), 67.8 (CH_2), 67.8 (CH_2), 67.1 (CH_2), 67.0 (CH_2), 63.2 (2 x C), 49.7 (CH_2), 34.5 (2 x C), 31.6 (2 x CH_3), 30.0 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 25.5 (CH_2), 25.2 (CH_2); LRMS (ESI+) m/z 1185.7 $[\text{M}+\text{Na}+\text{H}]^{2+}$.

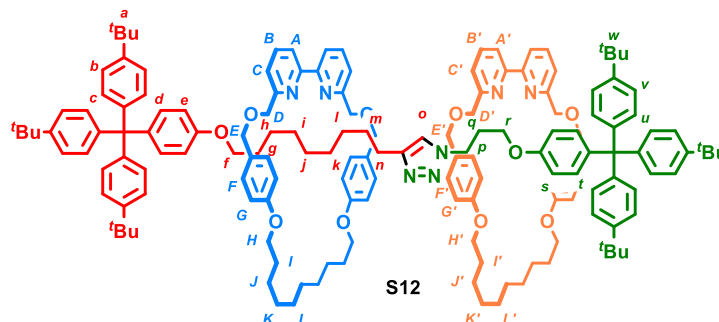




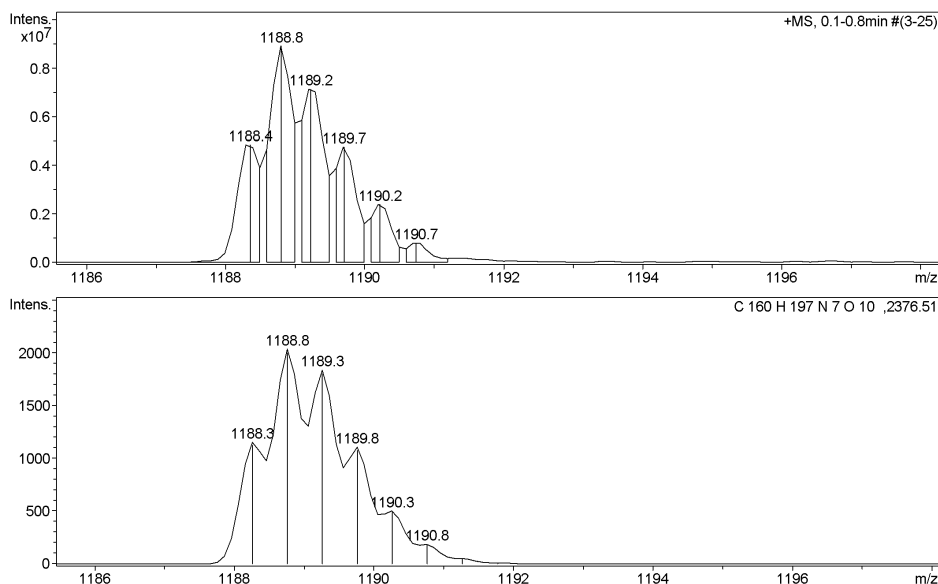
[2]Rotaxane **S11a** was also isolated (27.5 mg, 55%) as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.99 (d, $J=7.7$, 2H, H_A), 7.55 (t, $J=7.7$, 2H, H_B), 7.33 (d, $J=7.7$, 2H, H_C), 7.21 - 7.26 (m, 12H, H_b and H_l), 7.10 (t, $J=8.2$, 12H, H_c and H_s), 7.00 - 7.06 (m, 8H, H_F , H_d and H_r), 6.93 (s, 1H, H_j), 6.62 (d, $J=8.5$, 4H, H_G), 6.59 (d, $J=9.1$, 2H, H_e), 6.57 (d, $J=8.9$, 2H, H_q), 4.57 (s, 4H, H_D or H_E), 4.56 (s, 4H, H_D or H_E), 3.74 - 3.81 (m, 6H, H_H and H_k), 3.71 (t, $J=5.8$, 2H, H_j), 3.53 (t, $J=6.4$, 2H, H_p), 2.54 (t, $J=7.1$, 2H, H_i), 1.59 - 1.66 (m, 8H, H_F , H_g and H_h), 1.23 - 1.43 (m, 8H, H_J , H_l and H_o), 1.31 (s, 27H, H_a or H_u), 1.31 (s, 27H, H_a or H_u), 1.11 - 1.22 (m, 8H, H_K and H_L), 1.00 (m, 2H, H_n), 0.80 - 0.96 (m, 2H, H_m); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 158.8 (C), 158.5 (C), 156.9 (2 x C), 155.7 (C), 148.4 (C), 148.4 (C), 147.6 (C), 144.4 (C), 144.2 (C), 139.4 (C), 139.4 (C), 137.2 (CH), 132.2 (CH), 130.9 (2 x CH), 129.8 (C), 129.8 (CH), 124.2 (2 x CH), 121.5 (CH), 120.7 (CH), 120.0 (CH), 114.5 (CH), 113.0 (CH), 72.6 (CH₂), 72.3 (CH₂), 67.8 (CH₂), 67.3 (CH₂), 63.2 (2 x C), 49.8 (CH₂), 34.4 (2 x C), 31.5 (2 x CH₃), 30.0 (CH₂), 29.6 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 29.0 (2 x CH₂), 26.2 (CH₂), 26.0 (CH₂), 26.0 (2 x CH₂), 25.5 (CH₂), 25.4 (CH₂); LRMS (ESI+) 891.0 m/z $[\text{M}+2\text{H}]^{2+}$

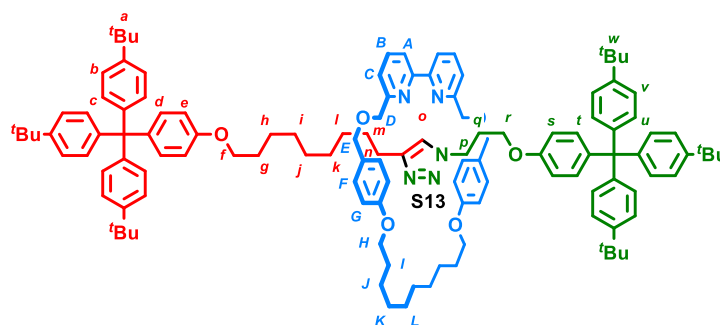


Synthesis of [3]Rotaxane S12

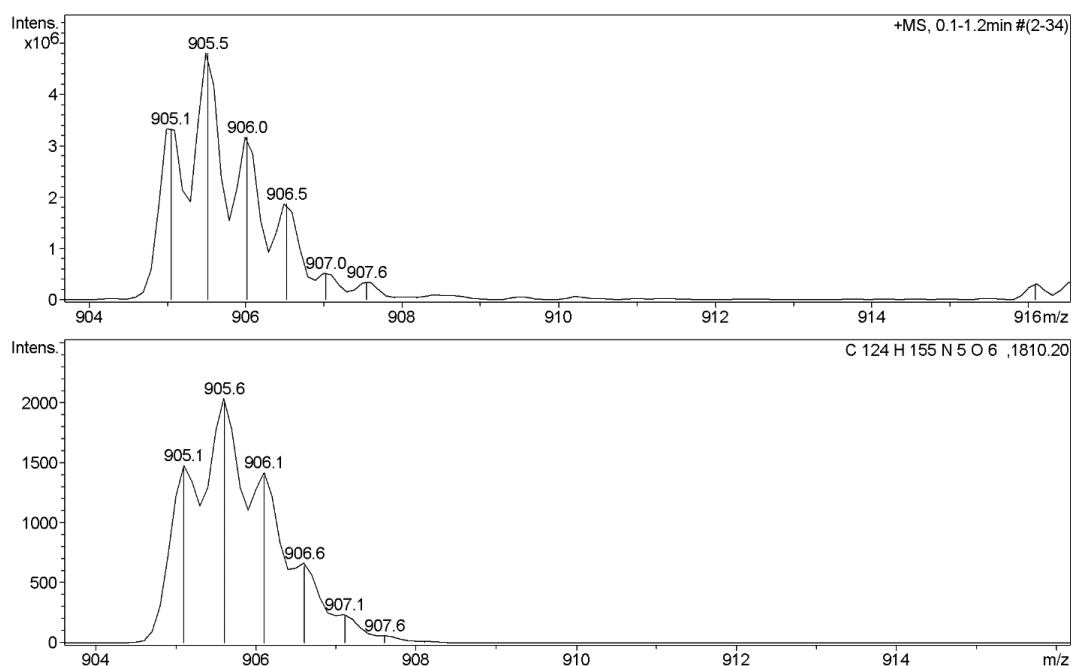


[3]Rotaxane **S12** was made according to conditions B, using macrocycle **1a** (14.2 mg, 0.025 mmol), alkyne **8** (19.7 mg, 0.030 mmol), azide **3** (17.6 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.9 mg, 0.024 mmol) in CH_2Cl_2 (2.5 mL) stirred at 100°C in a 150W microwave reactor for 2 hours. Flash column chromatography (0-30% MeCN/1:1 hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 10.3 mg (34%) of the target material as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 8.05 (d, $J=7.8$, 2H, H_A or $\text{H}_{A'}$), 7.99 (d, $J=7.8$, 2H, H_A or $\text{H}_{A'}$), 7.52 (t, $J=7.8$, 3H, H_B or $\text{H}_{B'}$), 7.51 (t, $J=7.8$, 2H, H_B or $\text{H}_{B'}$), 7.31 (d, $J=7.8$, 4H, H_C and $\text{H}_{C'}$), 7.21 - 7.29 (m, 12H, H_b and H_v), 7.11 (d, $J=8.4$, 6H, H_c or H_u), 7.10 (d, $J=8.4$, 6H, H_c or H_u), 7.04 (d, $J=8.7$, 4H, H_F or $\text{H}_{F'}$), 7.02 (d, $J=8.7$, 4H, H_F or $\text{H}_{F'}$), 6.91 (d, $J=8.8$, 2H, H_d or H_l), 6.89 (d, $J=8.8$, 2H, H_d or H_l), 6.75 (s, 1H, H_o), 6.61 (d, $J=8.7$, 4H, H_G or $\text{H}_{G'}$), 6.58 (d, $J=8.7$, 4H, H_G or $\text{H}_{G'}$), 6.26 (d, $J=8.8$, 2H, H_e or H_s), 6.20 (d, $J=8.8$, 2H, H_e or H_s), 4.53 - 4.63 (m, 16H, H_D , H_D' , H_E and $\text{H}_{E'}$), 3.68 - 3.83 (m, 10H, H_I , H_I' and H_p), 3.20 (t, $J=6.7$, 2H, H_j), 3.16 (t, $J=5.6$, 2H, H_r), 2.38 - 2.46 (m, 2H, H_n), 1.52 - 1.69 (m, 10H, H_I , H_I' and H_q), 0.75 - 1.41 (m, 28H, H_J , H_J' , H_K , H_K' , H_L , H_L' , H_b , H_b , H_v , H_j , H_k , H_l and H_m), 1.33 (s, 54H, H_a and H_w); ^{13}C NMR (150 MHz, CDCl_3) δ ppm 158.8 (C), 158.8 (C), 158.4 (2 x C), 156.9 (C), 156.3 (C), 155.6 (C), 155.5 (C), 148.4 (C), 148.3 (C), 148.0 (C), 144.5 (C), 144.4 (C), 139.6 (C), 138.9 (C), 137.3 (CH), 137.1 (CH), 132.0 (CH), 132.0 (CH), 130.9 (CH), 130.9 (CH), 129.9 (C), 129.8 (C), 129.8 (CH), 129.8 (CH), 124.2 (CH), 124.2 (CH), 121.6 (CH), 121.3 (CH), 120.8 (CH), 120.0 (CH), 119.7 (CH), 114.5 (2 x CH), 113.0 (CH), 112.9 (CH), 72.6 (CH₂), 72.4 (2 x CH₂), 72.2 (CH₂), 67.8 (2 x CH₂), 67.4 (CH₂), 64.0 (C), 63.2 (C), 46.7 (CH₂), 34.5 (2 x C), 31.6 (2 x CH₃), 29.9 (CH₂), 29.8 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.2 (CH₂), 29.1 (2 x CH₂), 29.0 (CH₂), 29.0 (CH₂), 26.0 (CH₂), 26.0 (CH₂), 25.9 (2 x CH₂), 25.9 (CH₂); LRMS (ESI+) m/z 1188.3 $[\text{M}+2\text{H}]^{2+}$.

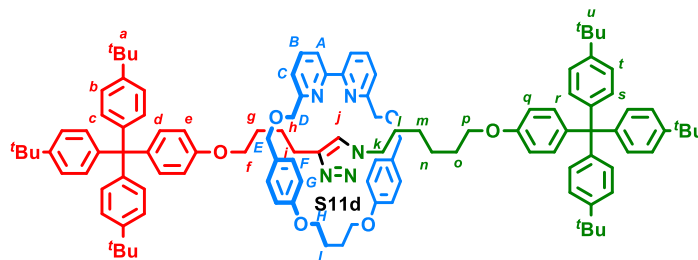




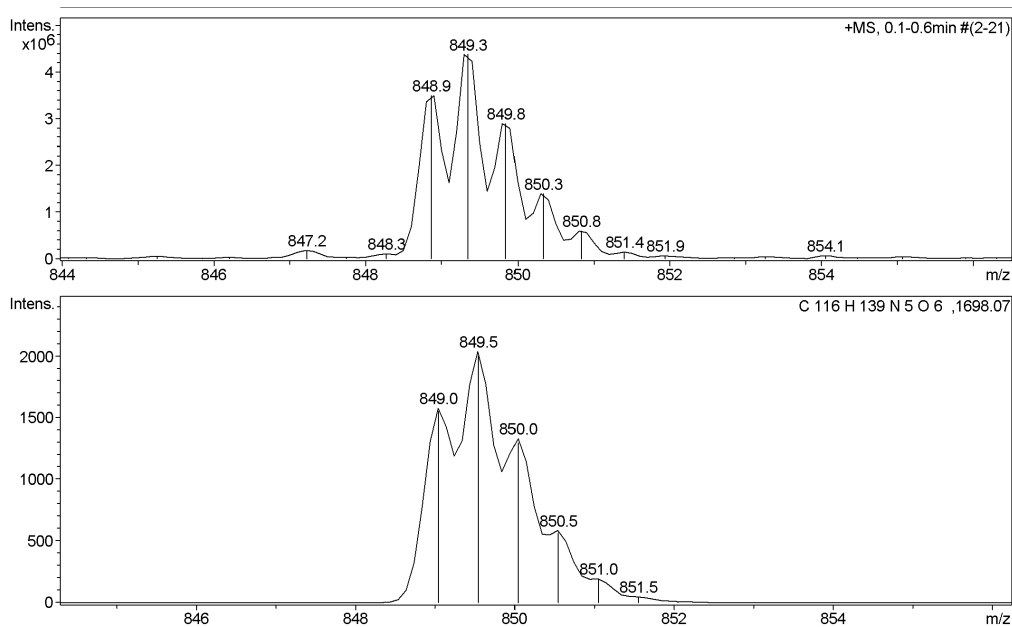
[2]Rotaxane **S13** was also isolated (21.4 mg, 47%) as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 8.01 (d, $J=7.8$, 2H, H_A), 7.53 (t, $J=7.8$, 2H, H_B), 7.32 (d, $J=7.7$, 2H, H_C), 7.25 (d, $J=8.5$, 6H, H_b or H_v), 7.24 (d, $J=8.4$, 6H, H_b or H_v), 7.10 (d, $J=8.4$, 6H, H_c or H_u), 7.10 (d, $J=8.5$, 6H, H_c or H_u), 6.98 - 7.07 (m, 8H, H_F , H_d and H_l), 6.92 (s, 1H, H_o), 6.61 (d, $J=8.4$, 4H, H_G), 6.60 (d, $J=8.8$, 2H, H_e), 6.46 (d, $J=8.8$, 2H, H_s), 4.58 (s, 4H, H_D or H_E), 4.58 (s, 4H, H_D or H_E), 4.03 (t, $J=7.3$, 2H, H_p), 3.78 (t, $J=6.5$, 4H, H_{II}), 3.67 (t, $J=6.5$, 2H, H_j), 3.49 (t, $J=5.7$, 2H, H_r), 2.50 (t, $J=7.8$, 2H, H_n), 1.84 - 1.93 (m, 2H, H_q), 1.39 - 1.66 (m, 8H, H_g , H_l , H_m), 1.04 - 1.39 (m, 20H, H_h , H_i , H_j , H_k , H_l , H_m , H_n , H_o , H_p , H_q , H_r , H_s , H_t , H_u , H_v , H_w , H_x , H_y , H_z), 1.32 (s, 54H, H_w); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 158.8 (C), 158.4 (C), 157.1 (C), 156.4 (C), 155.6 (C), 148.5 (C), 148.4 (C), 148.2 (C), 144.4 (C), 144.3 (C), 139.9 (C), 139.3 (C), 137.2 (CH), 132.3 (CH), 132.2 (CH), 130.9 (CH), 130.9 (CH), 129.9 (C), 129.8 (CH), 124.3 (CH), 124.2 (CH), 121.5 (CH), 121.0 (CH), 119.9 (CH), 114.5 (CH), 113.1 (CH), 113.0 (CH), 72.5 (CH_2), 72.3 (CH_2), 67.8 (CH_2), 64.1 (CH_2), 63.2 (C), 63.2 (C), 46.8 (CH_2), 34.4 (2 x C), 31.6 (2 x CH_3), 30.0 (CH_2), 29.6 (2 x CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (2 x CH_2), 29.1 (CH_2), 29.0 (CH_2), 26.1 (CH_2), 26.0 (2 x CH_2), 25.8 (CH_2); LRMS (ESI+) 905.1 m/z [$\text{M}+2\text{H}$] $^{2+}$.



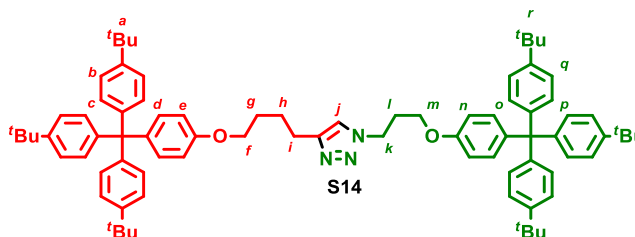
Synthesis of [2]Rotaxane S11d



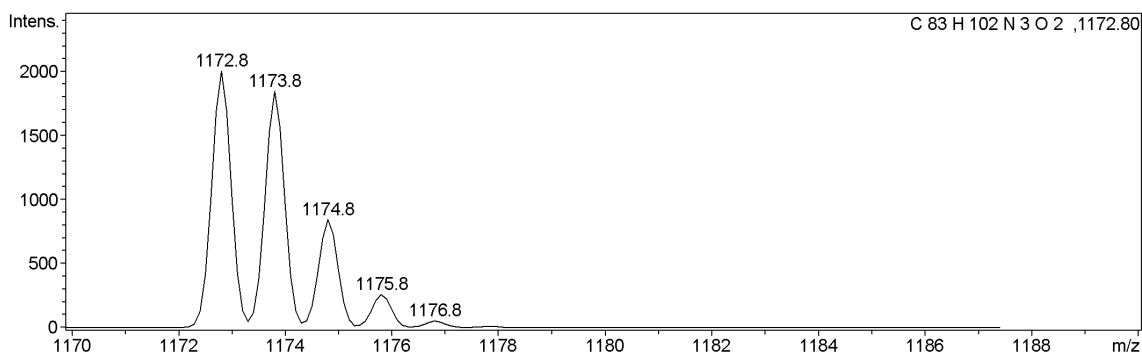
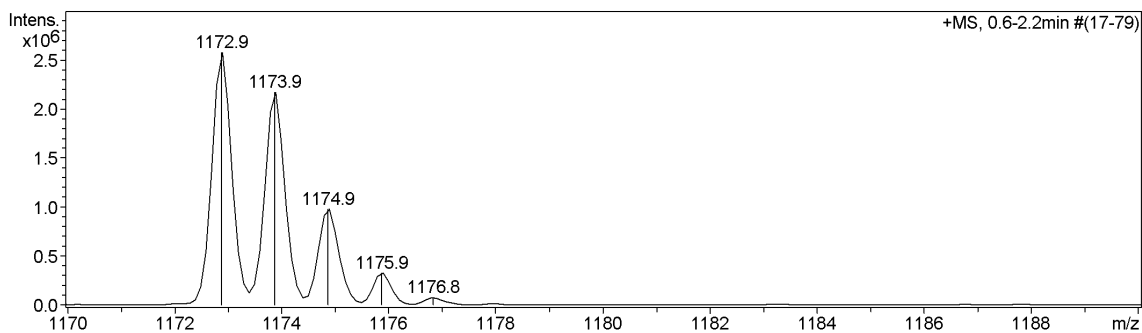
[2]Rotaxane **S11d** was made according to conditions B, using macrocycle **1d** (12.1 mg, 0.025 mmol), alkyne **7** (17.5 mg, 0.030 mmol), azide **6** (18.9 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.9 mg, 0.024 mmol), in CH_2Cl_2 (2.5 mL) stirred at 100°C in a 150W microwave reactor for 1 hour. Flash column chromatography (0-30% $\text{MeCN}/1:1$ hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 42.9 mg (93%) of the target material as a white foam: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.62 (t, $J=7.7$, 2H, H_B), 7.63 (s, 1H, H_j), 7.44 (app. t, $J=7.8$, 4H, H_d and H_C), 7.22 - 7.26 (m, 12H, H_b and H_l), 7.03 - 7.14 (m, 16H, H_c , H_s , H_d and H_r), 6.97 (d, $J=8.7$, 4H, H_D), 6.63 - 6.72 (m, 8H, H_E , H_e and H_q), 4.42 - 4.60 (m, 4H, four of H_D/H_E), 4.27 - 4.35 (m, 2H, two of H_H), 4.19 - 4.27 (m, 4H, four of H_D/H_E), 4.02 - 4.09 (m, 2H, two of H_H), 3.79 (t, $J=6.3$, 2H, H_j), 3.62 (t, $J=6.5$, 2H, H_k), 3.16 - 3.23 (m, 2H, H_p), 2.56 (t, $J=7.6$, 2H, H_i), 1.97 - 2.11 (m, 2H, two of H_j), 1.82 - 1.97 (m, 2H, two of H_j), 1.63 - 1.71 (m, 2H, H_g), 1.52 - 1.64 (m, 2H, H_k), 1.31 (s, 27H, H_a or H_u), 1.31 (s, 27H, H_a or H_u), 0.78 - 0.86 (m, 2H, H_m), 0.65 - 0.74 (m, 2H, H_o), 0.52 - 0.59 (m, 2H, H_n); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.3 (C), 159.0 (C), 157.1 (C), 157.0 (C), 156.5 (C), 148.4 (2 x C), 146.6 (C), 144.4 (C), 144.4 (C), 139.5 (C), 139.4 (C), 137.3 (CH), 132.3 (CH), 130.9 (2 x CH), 130.3 (CH), 129.1 (C), 124.2 (2 x CH), 122.1 (CH), 121.1 (CH), 121.0 (CH), 115.1 (CH), 113.1 (CH), 113.1 (CH), 113.1 (CH), 72.9 (CH_2), 70.9 (CH_2), 67.5 (CH_2), 67.5 (CH_2), 66.6 (CH_2), 63.2 (C), 63.2 (C), 49.2 (CH_2), 34.4 (2 x C), 31.5 (2 x CH_3), 29.0 (CH_2), 28.8 (CH_2), 28.8 (CH_2), 25.9 (CH_2), 25.9 (CH_2), 25.5 (CH_2), 25.2 (CH_2), 24.8 (CH_2); LRMS (ESI+) m/z 848.9 $[\text{M}+2\text{H}]^{2+}$.



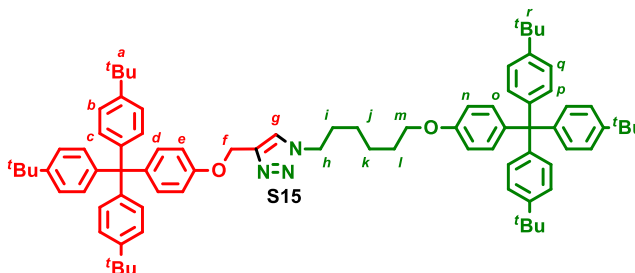
Synthesis of Thread Triazole **S14**



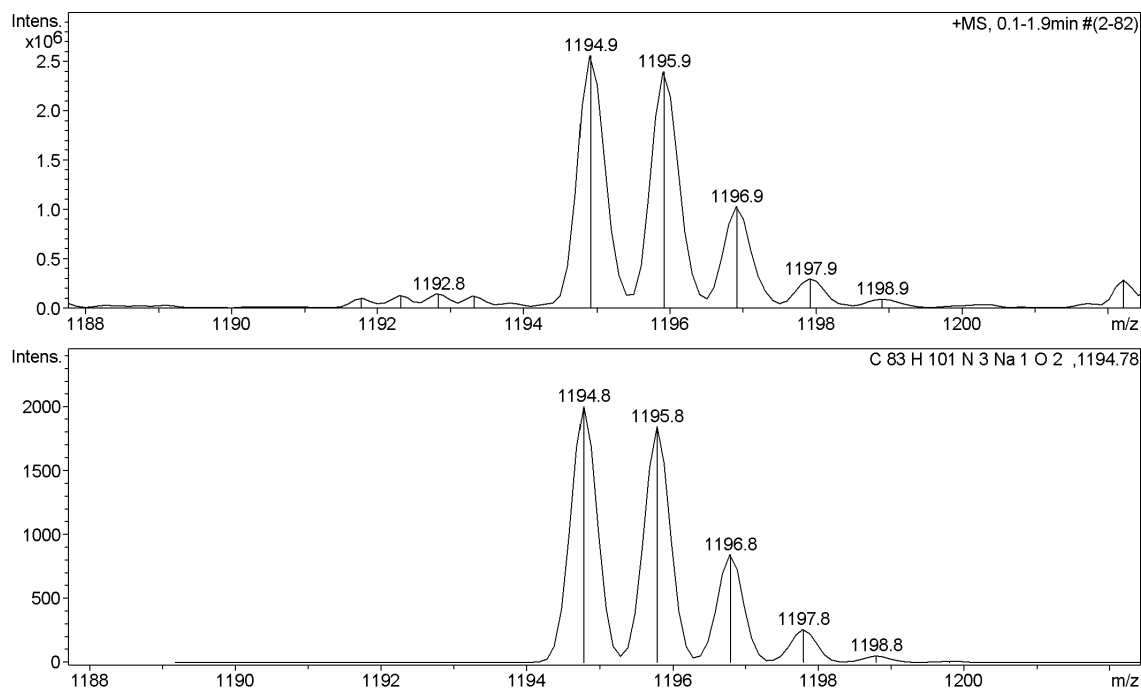
An analytical sample of triazole **S14** was isolated as a by-product of [3]rotaxane **S10** (*vide supra*). Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded triazole **S14** as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.30 (s, 1H, H_j), 7.23 (d, *J*=8.8, 6H, H_b or H_q), 7.23 (d, *J*=8.8, 6H, H_b or H_q), 7.10 (d, *J*=8.8, 2H, H_d or H_o), 7.08 (d, *J*=8.6, 6H, H_c or H_p), 7.08 (d, *J*=8.6, 6H, H_c or H_p), 7.06 (d, *J*=8.8, 2H, H_d or H_o), 6.74 (d, *J*=8.8, 2H, H_e or H_r), 6.72 (d, *J*=8.8, 2H, H_e or H_r), 4.54 (t, *J*=6.9, 2H, H_k), 3.94 (t, *J*=5.6, 2H, H_m), 3.94 (t, *J*=5.8, 2H, H_j), 2.79 (t, *J*=7.0, 2H, H_i), 2.36 (tt, *J*=6.9, 5.6, 2H, H_l), 1.78 - 1.90 (m, 4H, H_g and H_h), 1.30 (s, 27H, H_a or H_r); ¹³C NMR (150 MHz, CDCl₃) δ ppm 156.9 (C), 156.4 (C), 148.5 (C), 148.4 (C), 148.0 (C), 144.3 (C), 144.2 (C), 140.3 (C), 139.6 (C), 132.5 (CH), 132.4 (CH), 130.9 (CH), 130.9 (CH), 124.2 (CH), 124.2 (CH), 121.4 (CH), 113.1 (CH), 113.1 (CH), 67.5 (CH₂), 64.1 (CH₂), 63.2 (2 x C), 47.1 (CH₂), 34.4 (2 x C), 31.5 (2 x CH₃), 30.2 (CH₂), 29.0 (CH₂), 26.2 (CH₂), 25.5 (CH₂); LRMS (ESI+) *m/z* 1172.8 [M+H]⁺.



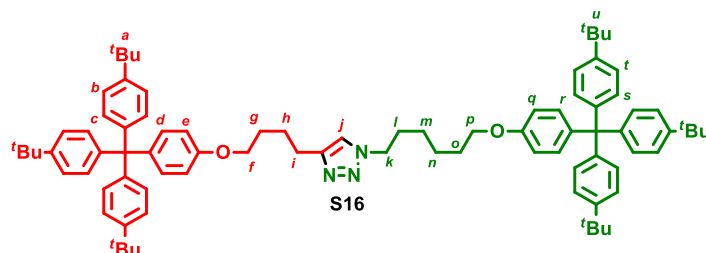
Synthesis of Thread Triazole **S15**



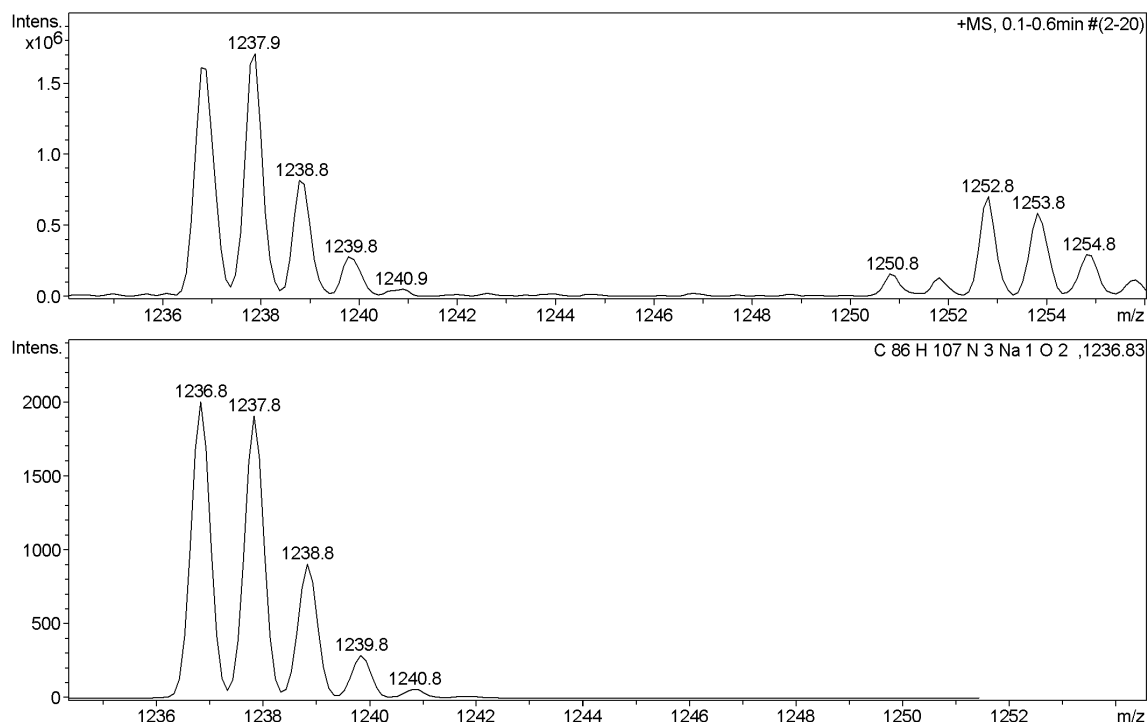
An analytical sample of triazole **S15** was isolated as a by-product of [3]rotaxane **S11** (*vide supra*). Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded triazole **S15** as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.59 (s, 1H, H_g), 7.24 (d, *J*=8.7, 6H, H_b or H_q), 7.23 (d, *J*=8.7, 6H, H_b or H_q), 7.08 (d, *J*=8.7, 6H, H_c or H_p), 7.08 (d, *J*=8.8, 6H, H_c or H_p), 7.03 - 7.14 (m, 4H, H_d and H_o), 6.85 (d, *J*=9.0, 2H, H_e or H_n), 6.74 (d, *J*=9.0, 2H, H_e or H_n), 5.18 (s, 2H, H_j), 4.38 (t, *J*=7.2, 2H, H_h), 3.92 (t, *J*=6.3, 2H, H_m), 1.96 (tt, *J*=7.2, 7.6, 2H, H_i), 1.72 - 1.81 (m, 2H, H_i), 1.48 - 1.59 (m, 2H, H_j), 1.37 - 1.47 (m, 2H, H_k), 1.31 (s, 27H, H_a or H_r), 1.28 (s, 27H, H_a or H_r); ¹³C NMR (150 MHz, CDCl₃) δ ppm 157.0 (C), 156.3 (C), 148.5 (C), 148.5 (C), 144.6 (C), 144.3 (C), 144.2 (C), 140.3 (C), 139.7 (C), 132.5 (CH), 132.4 (CH), 130.9 (2 x CH), 124.2 (CH), 124.2 (CH), 122.5 (CH), 113.4 (CH), 113.1 (CH), 67.5 (CH₂), 63.2 (2 x C), 62.3 (CH₂), 50.5 (CH₂), 34.4 (2 x C), 31.5 (2 x CH₃), 30.4 (CH₂), 29.2 (CH₂), 26.4 (CH₂), 25.8 (CH₂); LRMS (ESI+) *m/z* 1194.8 [M+Na]⁺.



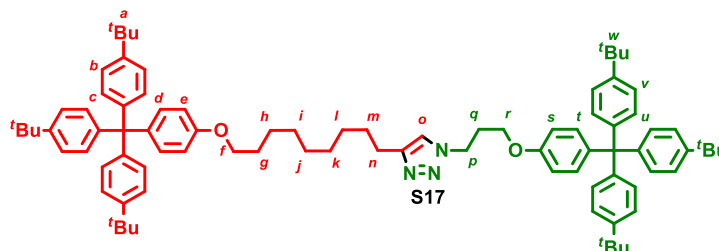
Synthesis of Thread Triazole S16



A solution of alkyne **7** (14.6 mg, 0.025 mmol), azide **6** (15.7 mg, 0.025 mmol) and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.4 mg, 0.0225 mmol), in CH_2Cl_2 (2.5 mL) was stirred at 25 °C for 72 hours in the absence of macrocycle. The solution was diluted with further CH_2Cl_2 (50 mL) and washed with 16% aqueous EDTA tetrasodium-saturated ammonia solution (50 mL). The organic layer was retained and the aqueous layer extracted twice further with CH_2Cl_2 (50 mL portions). The organic extracts were combined, dried over MgSO_4 and dried *in vacuo*. Flash column chromatography (0-50% CH_2Cl_2 /petrol) afforded 23.0 mg (76%) of triazole **S16** as a white foam: ^1H NMR (600 MHz, CDCl_3) δ ppm 7.28 (s, 1H, H_j), 7.21 - 7.25 (d, $J=8.7$, 12H, H_b and H_l), 7.06 - 7.11 (m, 16H, H_c , H_s , H_d and H_r), 6.75 (d, $J=9.1$, 2H, H_e or H_q), 6.74 (d, $J=9.1$, 2H, H_e or H_q), 4.32 (t, $J=7.2$, 2H, H_k), 3.96 (t, $J=5.9$, 2H, H_j), 3.92 (t, $J=6.3$, 2H, H_p), 2.80 (t, $J=7.1$, 2H, H_i), 1.93 (tt, $J=7.8$, 7.2, 2H, H_l), 1.81 - 1.89 (m, 4H, H_g and H_h), 1.73 - 1.81 (m, 2H, H_o), 1.48 - 1.56 (m, 2H, H_n), 1.34 - 1.43 (m, 2H, H_m), 1.31 (s, 54H, H_a and H_u); ^{13}C NMR (150 MHz, CDCl_3) δ ppm 157.0 (C), 148.4 (C), 148.4 (C), 148.1 (C), 144.3 (2 x C), 139.7 (C), 139.6 (C), 132.4 (2 x CH), 130.9 (2 x CH), 124.2 (2 x CH), 120.6 (CH), 113.1 (2 x CH), 67.6 (CH_2), 67.5 (CH_2), 63.2 (2 x C), 50.2 (CH_2), 34.4 (2 x C), 31.5 (2 x CH_3), 30.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 25.8 (CH_2), 25.6 (CH_2); LRMS (ESI+) m/z 1236.8 $[\text{M}+\text{Na}]^+$.



Synthesis of Thread Triazole **S17**

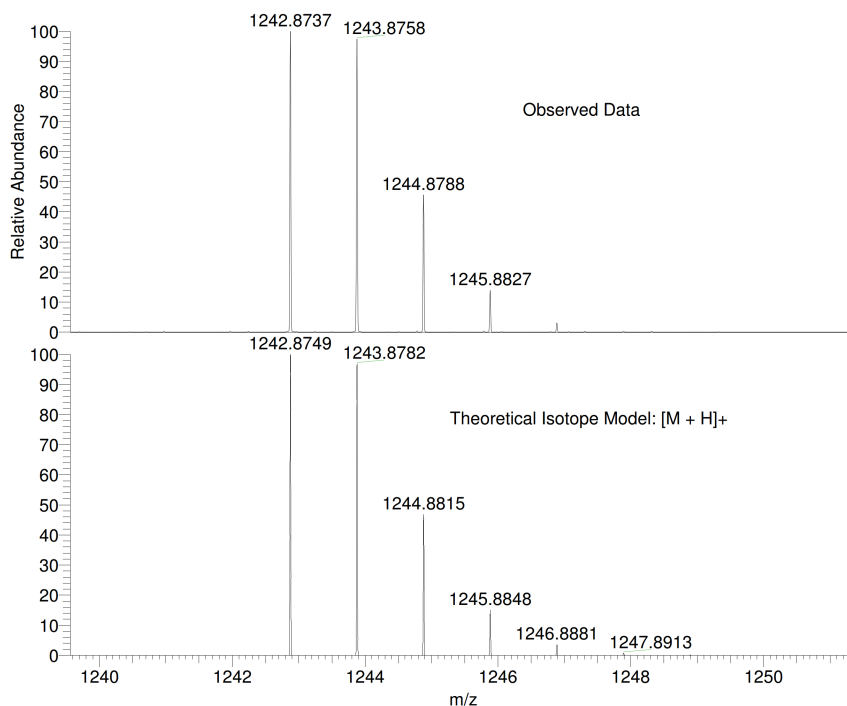


An analytical sample of triazole **S17** was isolated as a by-product of [3]rotaxane **S13** (*vide supra*). Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded triazole **S17** as a white foam: ¹H NMR (400 MHz, CDCl₃) δ ppm 7.27 (s, 1H, H_o), 7.24 (d, *J*=8.5, 6H, H_b or H_v), 7.24 (d, *J*=8.7, 6H, H_b or H_v), 7.09 (m, 16H, H_c, H_v, H_d and H_l), 6.75 (d, *J*=8.8, 4H, H_e and H_s), 4.54 (t, *J*=6.8, 2H, H_p), 3.95 (t, *J*=5.4, 2H, H_r), 3.92 (t, *J*=6.4, 2H, H_j), 2.71 (t, *J*=7.7, 2H, H_n), 2.37 (tt, *J*=6.8, 5.4, 2H, H_q), 1.76 (tt, *J*=7.7, 6.7, 2H, H_m), 1.66 (m, 2H, H_g), 1.13 - 1.49 (m, 10H, H_h, H_i, H_j, H_k and H_l), 1.31 (s, 54H, H_a and H_w); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.1 (C), 156.5 (C), 148.6 (C), 148.5 (C), 148.4 (C), 144.4 (C), 144.2 (C), 140.3 (C), 139.5 (C), 132.5 (CH), 132.4 (2 x CH), 130.9 (CH), 130.9 (CH), 124.2 (CH), 124.2 (CH), 121.2 (CH), 113.1 (2 x CH), 68.0 (CH₂), 64.1 (CH₂), 63.2 (C), 63.2 (C), 47.1 (CH₂), 34.4 (6 x C), 31.5 (18 x CH₃), 30.2 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 26.2 (CH₂), 25.8 (CH₂); LRMS (ESI+) *m/z* 1242.8 [M+H]⁺.

EAN 484 MW=1241?
C88H111O2N3
(DCM)/MeOH + NH4OAc

EPSRC National Facility Swansea
LTQ Orbitrap XL

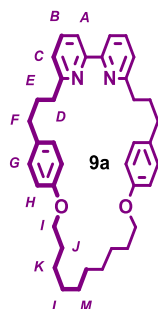
Ed Neal
06/05/2014 08:38:50



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FTMS + p NSI Full ms
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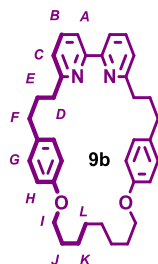
NL:
8.85E3
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C₈₈ H₁₁₂ O₂ N₃
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R: 100000 Res .Pwr .@FWHM

Synthesis of Macrocycle 9a



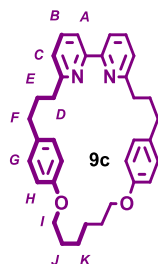
To a solution of bisphenol **S18** (1 g, 2.36 mmol) in DMF (1 L) were added 1,10-dibromodecane (0.707 g, 2.36 mmol) and K_2CO_3 (1.628 g, 11.8 mmol, 5 eq). The solution was stirred at 60 °C for 72 hours and dried *in vacuo*. The residue was twice extracted with Et_2O in 250 mL portions, with the extracts dried over $MgSO_4$ and dried *in vacuo*. Flash column chromatography (0-10% MeCN/1:1 petrol: CH_2Cl_2 ; 0-20% Et_2O /petrol) afforded 164 mg (12%) of macrocycle **9a** as a white solid: m.p. 78-80 °C; 1H NMR (400 MHz, $CDCl_3$) δ ppm 8.02 (d, J = 7.7, 2H, H_A), 7.64 (t, J = 7.7, 2H, H_B), 7.08 (d, J = 7.7, 2H, H_C), 6.99 (d, J = 7.9, 4H, H_G), 6.71 (d, J = 7.9, 4H, H_H), 3.91 (t, J = 5.9, 4H, H_I), 2.91 (t, J = 6.8, 4H, H_D), 2.62 (t, J = 7.5, 4H, H_F), 2.09 (tt, J = 7.5, 6.8, 4H, H_E), 1.68 (tt, J = 7.1, 5.9, 4H, H_J), 1.37 (br. s., 4H, H_K), 1.24 (br. s., 8H, H_L and H_M); ^{13}C NMR δ ppm (100 MHz, $CDCl_3$) δ 161.7 (C), 157.1 (C), 156.7 (C), 136.8 (CH), 134.6 (C), 129.4 (CH), 122.6 (CH), 118.8 (CH), 114.8 (CH), 68.0 (CH_2), 38.1 (CH_2), 34.6 (CH_2), 32.1 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 25.9 (CH_2); HRMS (ESI+) m/z 563.3624 $[M+H]^+$ (calc. for $C_{38}H_{47}N_2O_2$ 563.3632).

Synthesis of Macrocycle 9b



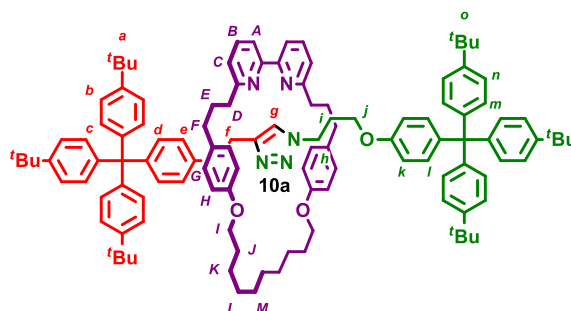
Macrocycle **9b** was made using the same method as macrocycle **9a** except using 1,8-dibromooctane (0.641 g, 0.45 mL, 2.36 mmol) to afford 187 mg (15%) of macrocycle **9b** as a white solid: m.p. 120-123 °C; 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.91 (d, J = 7.7, 2H, H_A), 7.62 (t, J = 7.7, 2H, H_B), 7.07 (d, J = 7.7, 2H, H_C), 6.98 (d, J = 8.6, 4H, H_G), 6.69 (d, J = 8.6, 4H, H_H), 3.91 (t, J = 6.3, 4H, H_I), 2.91 (t, J = 7.2, 4H, H_D), 2.62 (dd, J = 8.2, 7.4, 4H, H_F), 2.08 (ddt, J = 8.2, 7.4, 7.2, 4H, H_E), 1.66 (tt, J = 7.3, 6.3, 4H, H_J), 1.37 (tt, J = 7.3, 6, 4H, H_K), 1.20 - 1.32 (m, 4H, H_L); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.8 (C), 157.0 (C), 157.0 (C), 136.8 (CH), 134.6 (C), 129.4 (CH), 122.5 (CH), 119.0 (CH), 114.8 (CH), 67.9 (CH_2), 38.1 (CH_2), 34.5 (CH_2), 32.1 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 25.7 (CH_2); HRMS (ESI+) m/z 535.3312 $[M+H]^+$ (calc. for $C_{36}H_{43}N_2O_2$ 535.3319).

Synthesis of Macrocycle **9c**

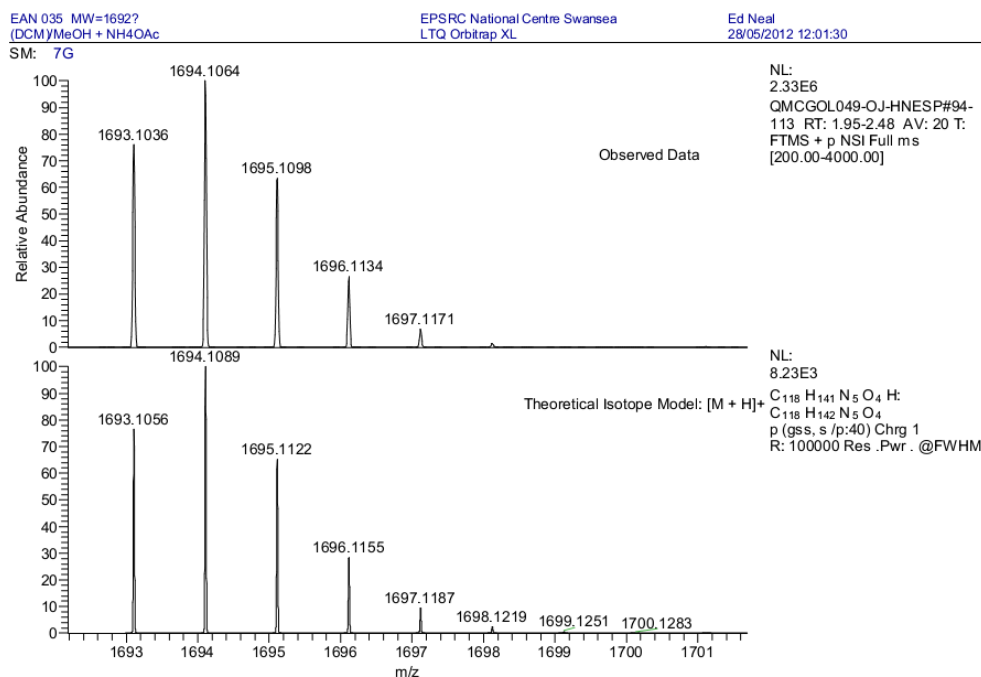


Macrocycle **9c** was made using the same method as macrocycle **9a** except using 1,6-dibromohexane (0.575 g, 0.36 mL, 2.36 mmol) to afford 120 mg (10%) of macrocycle **9c** as a white solid: m.p. 121-125 °C; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.75 (d, $J = 7.8$, 2H, H_A), 7.61 (t, $J = 7.8$, 2H, H_B), 7.07 (d, $J = 7.8$, 2H, H_C), 6.98 (d, $J = 8.4$, 4H, H_G), 6.68 (d, $J = 8.4$, 4H, H_H), 3.94 (t, $J = 6.1$, 4H, H_I), 2.91 (t, $J = 7.5$, 4H, H_D), 2.64 (t, $J = 7.5$, 4H, H_F), 2.12 (app. quin, $J = 7.5$, 4H, H_E), 1.72 (app. quin, $J = 6.1$, 4H, H_J), 1.48 (m, 4H, H_K); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 162.1 (C), 157.2 (C), 157.2 (C), 136.7 (CH), 134.5 (C), 129.5 (CH), 122.4 (CH), 119.2 (CH), 114.9 (CH), 67.9 (CH_2), 37.9 (CH_2), 34.6 (CH_2), 31.6 (CH_2), 28.5 (CH_2), 25.2 (CH_2); HRMS (ESI+) m/z 507.3000 $[\text{M}+\text{H}]^+$ (calc. for $\text{C}_{34}\text{H}_{39}\text{N}_2\text{O}_2$ 507.3006).

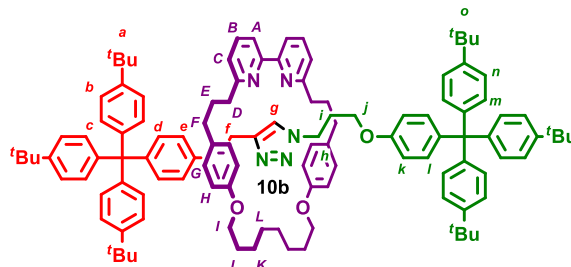
Synthesis of [2]Rotaxane 10a



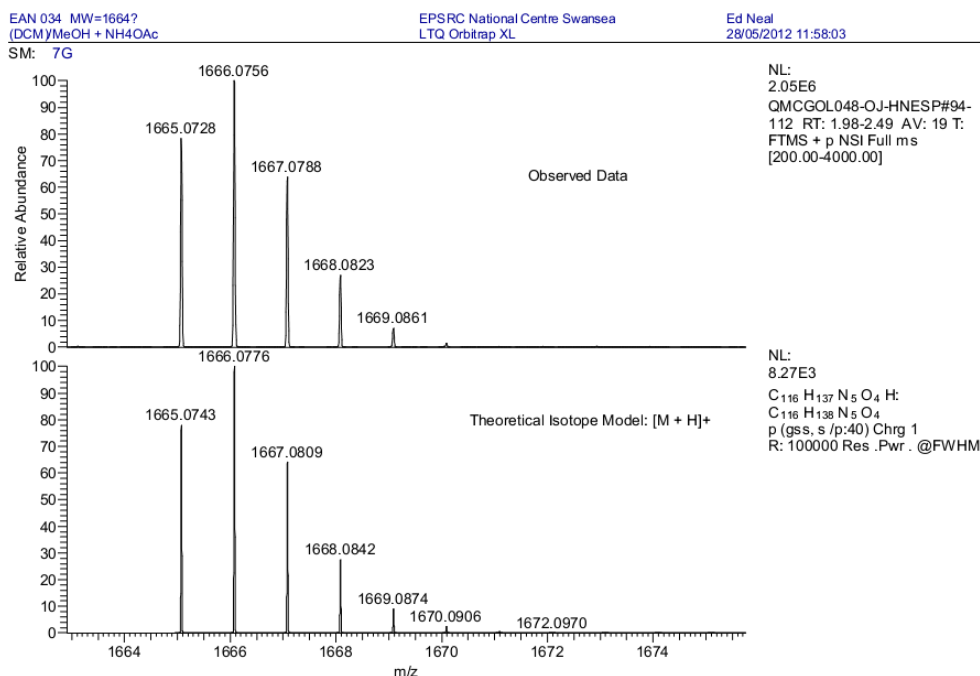
[2]Rotaxane **10a** was made according to condition B (except at 0.05 M), using macrocycle **9a** (14.1 mg, 0.025 mmol), azide **3** (17.6 mg, 0.030 mmol), alkyne **2** (16.3 mg, 0.030 mmol) and Cu(MeCN)₄PF₆ (8.9 mg, 0.024 mmol), in CH₂Cl₂ (0.5 mL) stirred at 100°C in a 150W microwave reactor for 15 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 40.5 mg (96%) of [2]rotaxane **10a** as a white solid: m.p. 114-116 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.94 (d, *J* = 7.8, 2H, H_A), 7.40 (t, *J* = 7.8, 2H, H_B), 7.26 (d, *J* = 8.7, 6H, H_b or H_n), 7.24 (d, *J* = 8.7, 6H, H_b or H_n), 7.10 (d, *J* = 8.7, 6H, H_c or H_m), 7.08 (d, *J* = 8.7, 6H, H_c or H_m), 7.04 (d, *J* = 8.9, 2H, H_d), 7.00 (s, 1H, H_g), 6.92 (d, *J* = 8.8, 2H, H_i), 6.92 (d, *J* = 7.8, 2H, H_C), 6.72 (d, *J* = 8.6, 4H, H_G), 6.70 (d, *J* = 8.9, 2H, H_e), 6.50 (d, *J* = 8.6, 4H, H_H), 6.26 (d, *J* = 8.8, 2H, H_k), 4.88 (s, 2H, H_J), 3.79 (t, *J* = 7.3, 2H, H_h), 3.76 (t, *J* = 6.7, 4H, H_I), 3.24 (t, *J* = 5.7, 2H, H_J), 2.80 (t, *J* = 7.6, 4H, H_D), 2.48 (t, *J* = 7.6, 4H, H_F), 1.87 (quin., *J* = 7.6, 4H, H_E), 1.65 (tt, *J* = 7.3, 5.7, 2H, H_I), 1.57 (tt, *J* = 7.1, 6.7, 4H, H_J), 1.33 (s, 27H, H_a or H_o), 1.31 (s, 27H, H_a or H_o), 1.22 - 1.28 (m, 4H, H_K), 1.08 - 1.19 (m, 8H, H_L and H_M); ¹³C NMR (100 MHz, CDCl₃) δ ppm 161.6 (C), 157.0 (C), 156.7 (C), 156.4 (C), 156.2 (C), 148.4 (2 x C), 144.4 (C), 144.3 (C), 143.8 (C), 140.0 (C), 139.7 (C), 137.0 (CH), 134.2 (C), 132.3 (CH), 132.1 (CH), 130.9 (2 x CH), 129.2 (CH), 124.2 (CH), 124.2 (CH), 123.1 (CH), 122.7 (CH), 118.9 (CH), 114.6 (CH), 113.3 (CH), 112.9 (CH), 67.8 (CH₂), 63.6 (CH₂), 63.2 (C), 63.2 (C), 61.8 (CH₂), 46.9 (CH₂), 38.0 (CH₂), 34.5 (C), 34.4 (C), 34.4 (CH₂), 32.3 (CH₂), 31.6 (CH₃), 31.5 (CH₃), 29.7 (CH₂), 29.6 (CH₂), 29.0 (CH₂), 28.8 (CH₂), 25.7 (CH₂); LRMS (ESI+) 1693 m/z [M+H]⁺.



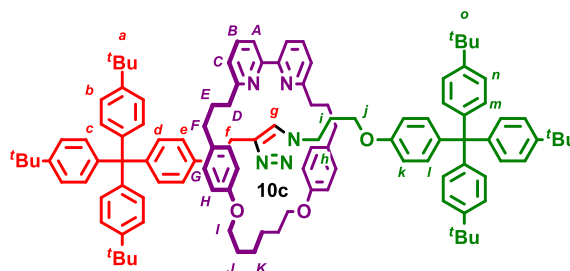
Synthesis of [2]Rotaxane 10b



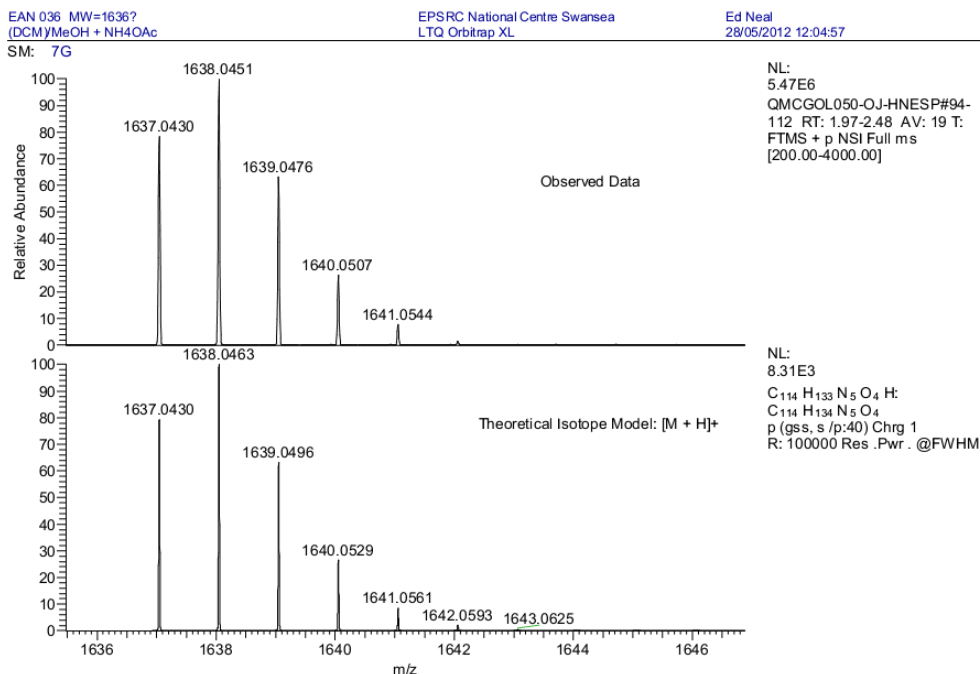
[2]Rotaxane **10b** was made according to condition B (except at 0.05 M), using macrocycle **9b** (13.4 mg, 0.025 mmol), azide **3** (17.6 mg, 0.030 mmol), alkyne **2** (16.3 mg, 0.030 mmol) and Cu(MeCN)₄.PF₆ (8.9 mg, 0.024 mmol), in CH₂Cl₂ (0.5 mL) stirred at 100°C in a 150W microwave reactor for 15 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 39.2 mg (95%) of the target material as a white solid: m.p. 128-130 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.80 (d, *J* = 7.8, 2H, H_A), 7.40 (t, *J* = 7.8, 2H, H_B), 7.27 (d, *J* = 8.3, 6H, H_b or H_n), 7.23 (d, *J* = 8.6, 6H, H_b or H_n), 7.11 (d, *J* = 8.8, 6H, H_m or H_c), 7.09 (d, *J* = 8.8, 6H, H_m or H_c), 7.08 (s, 1H, H_g), 7.03 (d, *J* = 8.8, 2H, H_d), 6.94 (d, *J* = 7.8, 2H, H_C), 6.89 (d, *J* = 8.8, 2H, H_I), 6.70 (d, *J* = 8.8, 2H, H_e), 6.69 (d, *J* = 8.6, 4H, H_G), 6.48 (d, *J* = 8.6, 4H, H_H), 6.18 (d, *J* = 8.8, 2H, H_k), 4.89 (s, 2H, H_J), 3.77 (t, *J* = 6.8, 4H, H_J), 3.64 (t, *J* = 7.2, 2H, H_h), 3.10 (t, *J* = 5.7, 2H, H_j), 2.78 (t, *J* = 7.5, 4H, H_D), 2.45 (t, *J* = 7.8, 4H, H_F), 1.79 (ttd, *J* = 7.8, 7.5, 3.7, 4H, H_E), 1.55 (m, 4H, H_J), 1.33 (s, 27H, H_a or H_o), 1.31 (s, 27H, H_a or H_o), 1.20 - 1.26 (m, 4H, H_K), 1.46 - 1.53 (m, 4H, H_i), 1.11 - 1.19 (m, 4H, H_L); ¹³C NMR (100 MHz, CDCl₃) δ ppm 161.8 (C), 157.2 (C), 156.9 (C), 156.4 (C), 156.1 (C), 148.4 (C), 148.4 (C), 144.4 (C), 144.3 (2 x C), 143.7 (CH), 140.0 (C), 139.5 (C), 136.9 (CH), 134.1 (C), 132.3 (CH), 132.0 (CH), 130.9 (2 x CH), 129.1 (CH), 124.0 (CH), 124.0 (CH), 123.2 (CH), 122.4 (CH), 119.3 (CH), 114.7 (CH), 113.3 (CH), 112.9 (CH), 67.7 (CH₂), 63.5 (CH₂), 63.2 (C), 63.2 (C), 61.8 (CH₂), 46.8 (CH₂), 38.0 (CH₂), 34.5 (C), 34.4 (C), 34.4 (CH₂), 32.6 (CH₂), 31.6 (CH₃), 31.5 (CH₃), 29.4 (CH₂), 29.3 (CH₂), 28.9 (CH₂), 26.0 (CH₂); LRMS (ESI⁺) 1665 m/z [M+H]⁺.



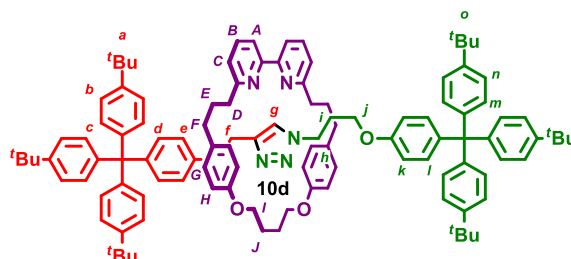
Synthesis of [2]Rotaxane **10c**



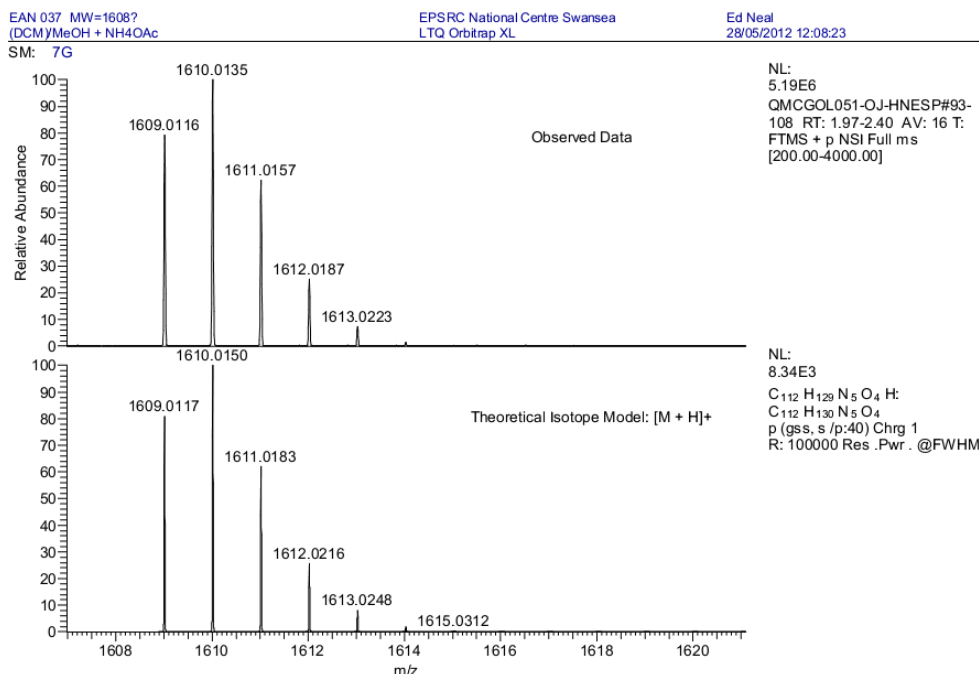
[2]Rotaxane **10c** was made according to conditions B (except at 0.05 M), using macrocycle **9c** (12.7 mg, 0.025 mmol), azide **3** (17.6 mg, 0.030 mmol), alkyne **2** (16.3 mg, 0.030 mmol) and $\text{Cu}(\text{MeCN})_4\cdot\text{PF}_6$ (8.9 mg, 0.024 mmol), in CH_2Cl_2 (0.5 mL) stirred at 100°C in a 150W microwave reactor for 15 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane: CH_2Cl_2 (+0.25% EtOH)) afforded 40.2 mg (95%) of the target material as a white solid: m.p. 135-139 °C; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.52 (s, 1H, H_g), 7.52 (d, $J = 7.8$, 2H, H_A), 7.43 (t, $J = 7.8$, 2H, H_B), 7.28 (d, $J = 8.6$, 6H, H_b or H_n), 7.23 (d, $J = 8.6$, 6H, H_b or H_n), 7.13 (d, $J = 8.6$, 6H, H_c or H_m), 7.09 (d, $J = 8.6$, 6H, H_c or H_m), 7.04 (d, $J = 8.9$, 2H, H_d), 6.97 (d, $J = 7.8$, 2H, H_C), 6.90 (d, $J = 8.9$, 2H, H_l), 6.72 (d, $J = 8.9$, 2H, H_e), 6.66 (d, $J = 8.5$, 4H, H_G), 6.49 (d, $J = 8.5$, 4H, H_H), 6.21 (d, $J = 8.9$, 2H, H_k), 4.89 (s, 2H, H_f), 3.86 (dt, $J = 11.3$, 10.2, 6.4, 4H, H_I), 3.44 (t, $J = 7.5$, 2H, H_h), 3.03 (t, $J = 5.8$, 2H, H_j), 2.69 (t, $J = 7.8$, 4H, H_D), 2.46 (t, $J = 7.5$, 4H, H_F), 1.68 (tt, $J = 7.8$, 7.5, 4H, H_E), 1.63 (m, 4H, H_I), 1.33 (s, 27H, H_a or H_o), 1.31 (s, 27H, H_a or H_o), 1.25 - 1.29 (m, 6H, H_K and H_j); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 162.2 (C), 158.0 (C), 157.1 (C), 156.4 (C), 156.2 (C), 148.4 (C), 148.4 (C), 144.4 (C), 144.3 (C), 143.5 (C), 139.9 (C), 139.3 (C), 136.9 (CH), 133.9 (C), 132.3 (CH), 131.9 (CH), 130.9 (2 x CH), 129.2 (CH), 124.2 (CH), 124.2 (CH), 123.7 (CH), 122.0 (CH), 119.9 (CH), 114.9 (CH), 113.3 (CH), 112.9 (CH), 67.8 (CH_2), 63.7 (CH_2), 63.2 (C), 63.2 (C), 61.8 (CH_2), 46.5 (CH_2), 37.8 (CH_2), 34.5 (C), 34.5 (CH_2), 34.4 (C), 32.7 (CH_2), 31.6 (CH_3), 31.5 (CH_3), 29.0 (CH_2), 29.0 (CH_2), 25.5 (CH_2); LRMS (ESI+) 1637 m/z $[\text{M}+\text{H}]^+$.



Synthesis of [2]Rotaxane **10d**



[2]Rotaxane **10d** was made according to conditions B (except at 0.05 M), using macrocycle **9d** (12.0 mg, 0.025 mmol), azide **3** (17.6 mg, 0.030 mmol), alkyne **2** (16.3 mg, 0.030 mmol) and Cu(MeCN)₄.PF₆ (8.9 mg, 0.024 mmol), in CH₂Cl₂ (0.5 mL) stirred at 100°C in a 150W microwave reactor for 15 minutes. Flash column chromatography (0-30% MeCN/1:1 hexane:CH₂Cl₂ (+0.25% EtOH)) afforded 42.4 mg (>99%) of the target material as a white solid; m.p. 151-154 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.42 (s, 1H, H_g), 7.53 (t, *J* = 7.7, 2H, H_B), 7.32 (d, *J* = 7.7, 2H, H_A), 7.28 (d, *J* = 8.7, 6H, H_b' and H_n'), 7.23 (d, *J* = 8.7, 6H, H_b and H_n), 7.13 (d, *J* = 8.7, 6H, H_c' and H_m'), 7.09 (d, *J* = 8.7, 6H, H_c and H_m), 7.03 (d, *J* = 9.1, 2H, H_d), 7.03 (d, *J* = 7.7, 2H, H_C), 6.97 (d, *J* = 8.9, 2H, H_I), 6.76 (d, *J* = 9.1, 2H, H_e), 6.70 (d, *J* = 8.7, 4H, H_G), 6.63 (d, *J* = 8.7, 4H, H_H), 6.45 (d, *J* = 8.9, 2H, H_k), 4.90 (s, 2H, H_j), 4.31 (dd, *J* = 16.3, 6.9, 2H, H_I'), 3.98 - 4.11 (m, 2H, H_j), 3.38 - 3.45 (m, 2H, H_h), 3.37 (t, *J* = 6.1, 2H, H_j), 2.51 (td, *J* = 12.5, 5.3, 2H, H_D'), 2.43 (td, *J* = 12.5, 5.3, 2H, H_D), 2.37 - 2.62 (m, 4H, H_F and H_F'), 2.09 - 2.21 (m, 2H, H_I'), 1.88 - 2.01 (m, 2H, H_j), 1.62 - 1.83 (m, 1H, H_E and H_E'), 1.28 - 1.39 (m, 54H, H_a and H_o), 1.16 - 1.24 (m, 2H, H_i); ¹³C NMR (100 MHz, CDCl₃) δ ppm 162.7 (C), 157.8 (C), 157.5 (C), 156.6 (C), 156.4 (C), 148.4 (2 x C), 144.4 (C), 144.3 (C), 142.6 (C), 139.8 (C), 139.1 (C), 136.8 (CH), 133.2 (C), 132.2 (CH), 132.0 (CH), 130.9 (CH), 130.8 (CH), 129.5 (CH), 125.1 (CH), 124.2 (CH), 124.1 (CH), 121.6 (CH), 120.3 (CH), 115.0 (CH), 113.3 (CH), 113.0 (CH), 66.6 (CH₂), 64.6 (CH₂), 63.2 (C), 63.2 (C), 61.7 (CH₂), 46.7 (CH₂), 37.2 (CH₂), 35.0 (CH₂), 34.4 (C), 34.4 (C), 32.1 (CH₂), 31.6 (CH₃), 31.5 (CH₃), 28.6 (CH₂), 24.9 (CH₂); LRMS (ESI⁺) 1609 m/z [M+H]⁺.



Lithiation Experiments (Scheme 4)

Step 1

A solution of macrocycle **1b** (26.9 mg, 0.05 mmol) and Cu(MeCN)₄.PF₆ (0.96 eq., 17.9 mg, 0.048 mmol) in THF (2.5 mL) was stirred at rt for 15 min, to form a solution of [**1b**.Cu].PF₆ (0.02 M). Separately, a solution of alkyne **1** (21.7 mg, 0.04 mmol) in THF (2.0 mL) was cooled to -78 °C and ⁿBuLi (2.5 M in hexanes, 0.16 µL, 0.04 mmol) was added. After 15 min the solution of the lithiated alkyne was transferred to an ice bath, a portion of the solution of [**1b**.Cu].PF₆ (2.0 mL) was added and the resulting mixture allowed to warm to rt to give a solution of macrocycle bound Cu-acetylide (0.01M).

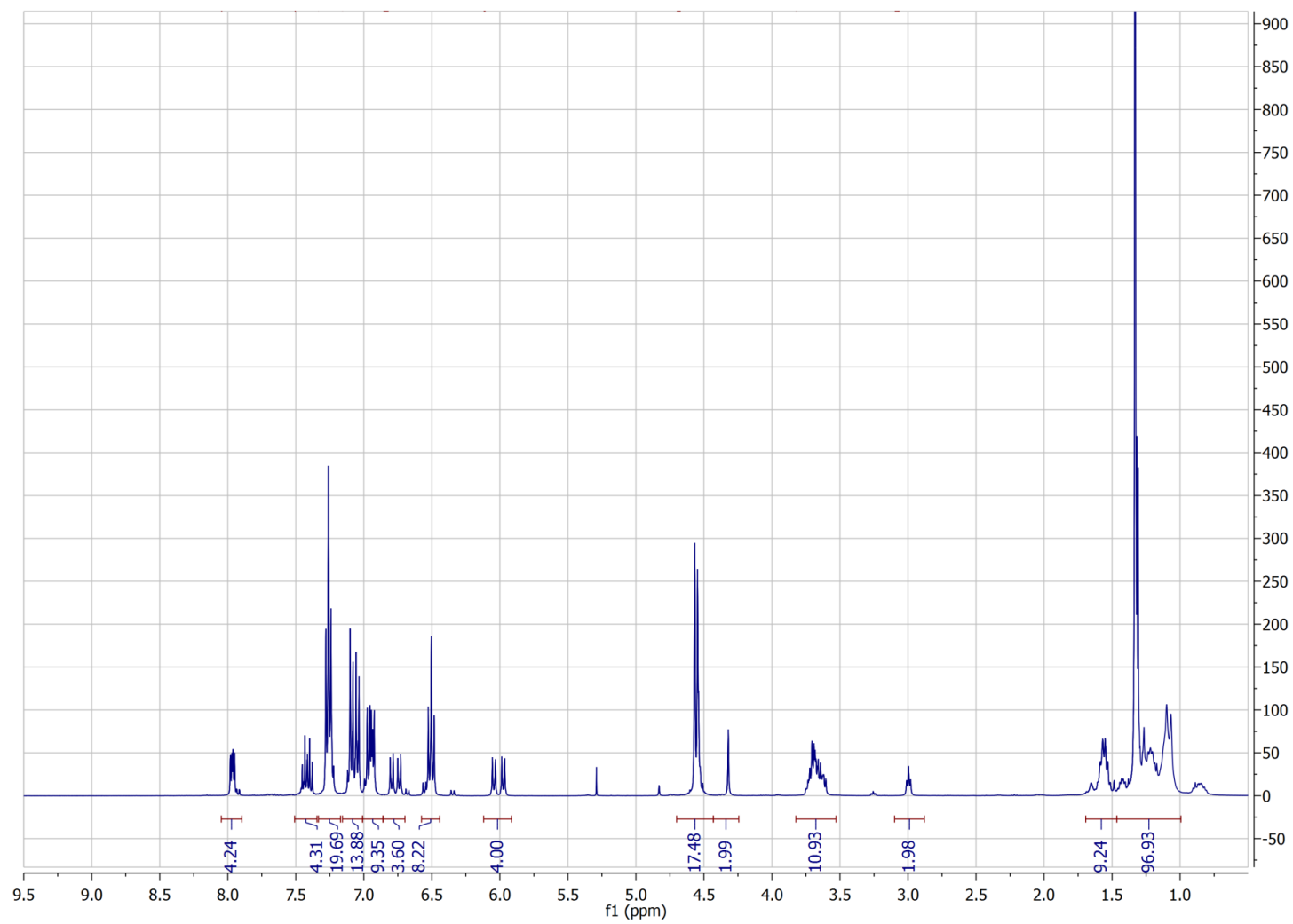
Step 2 (no extra [**1b**.Cu].PF₆)

A portion of the solution of macrocycle bound Cu-acetylide (0.50 mL, 0.005 mmol) was added to azide **3** (2.9 mg, 0.005 mmol) in THF (0.5 mL) and the mixture heated at 80 °C for 16 h. The solution was allowed to return to rt before dilution with further CH₂Cl₂ (20 mL) and washing with 16% aqueous EDTA tetrasodium-saturated ammonia solution (20 mL). The aqueous layer was extracted with CH₂Cl₂ (2×20 mL). The organic extracts were combined, dried over MgSO₄ and dried *in vacuo*. The residue was analysed by ¹H NMR. All macrocycle **1b** was consumed in the formation of rotaxane **4b**, the only interlocked product formed (ratio **4b** : **5b** = >99% : <1%)

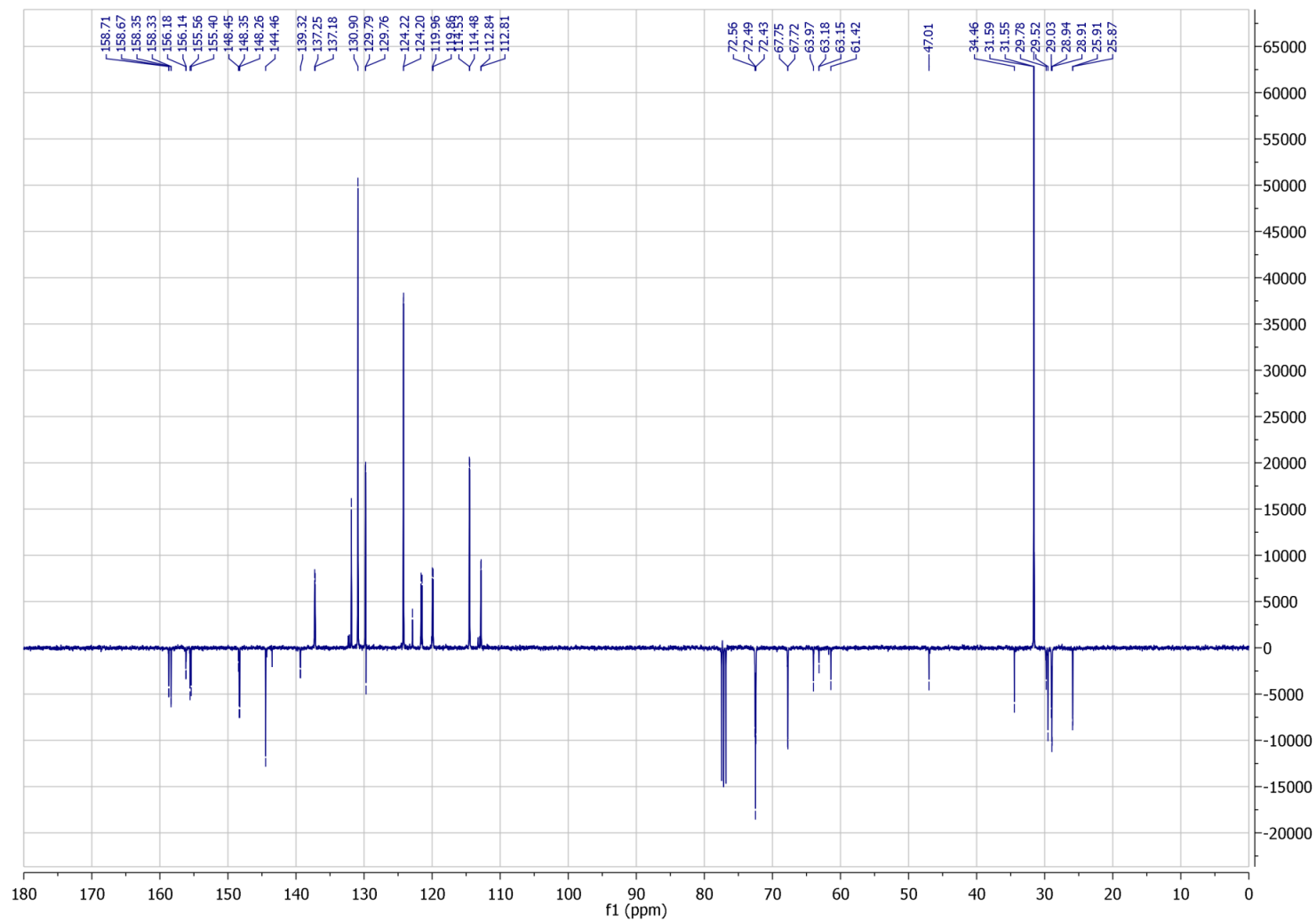
Step 2 (additional [**1b**.Cu].PF₆)

A portion of the solution of [**1b**.Cu].PF₆ (0.25 mL, 0.005 mmol) was added to azide **3** (2.9 mg, 0.005 mmol) in THF (0.25 mL) followed by a portion of the solution of macrocycle bound Cu-acetylide (0.50 mL, 0.005 mmol) and the resulting mixture heated at 80 °C for 16 h. The solution was allowed to return to rt before dilution with further CH₂Cl₂ (20 mL) and washing with 16% aqueous EDTA tetrasodium-saturated ammonia solution (20 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The organic extracts were combined, dried over MgSO₄ and dried *in vacuo*. The residue was analysed by ¹H NMR. Rotaxanes **4b** and **5b** formed in a 90 : 10 ratio.

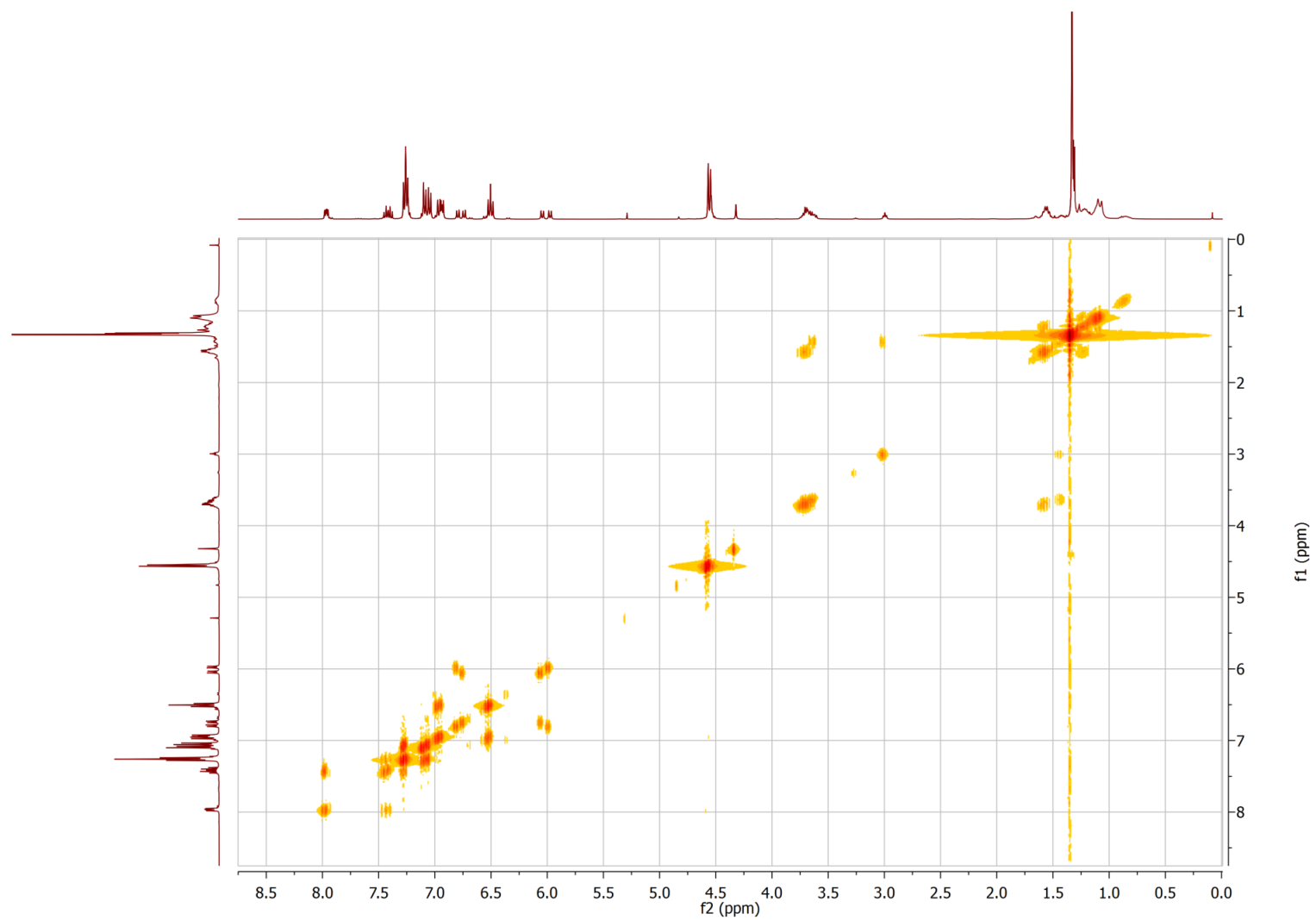
[3]Rotaxane 5a ^1H NMR (CDCl_3 , 400 MHz, 300 K)



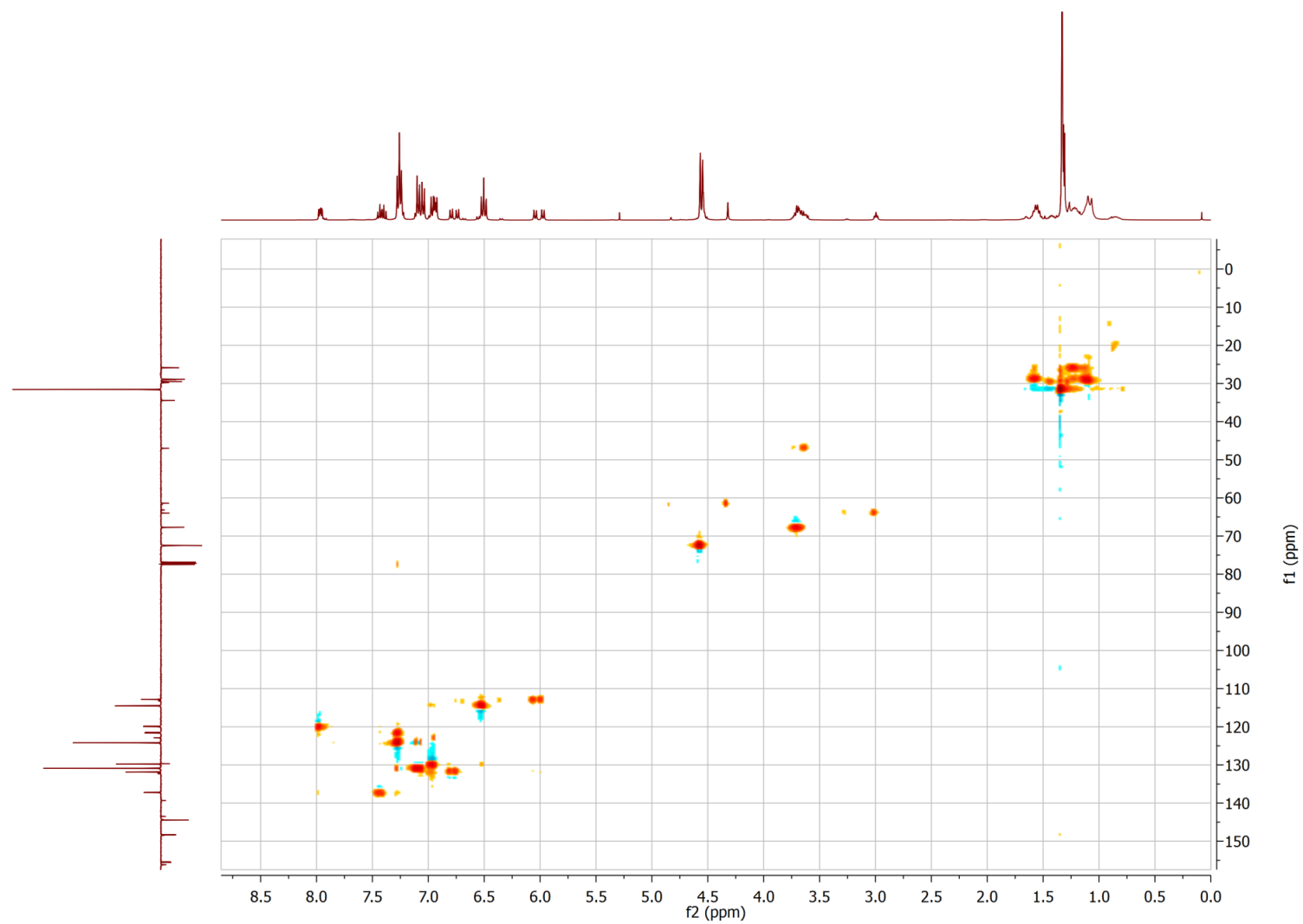
[3]Rotaxane 5a DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



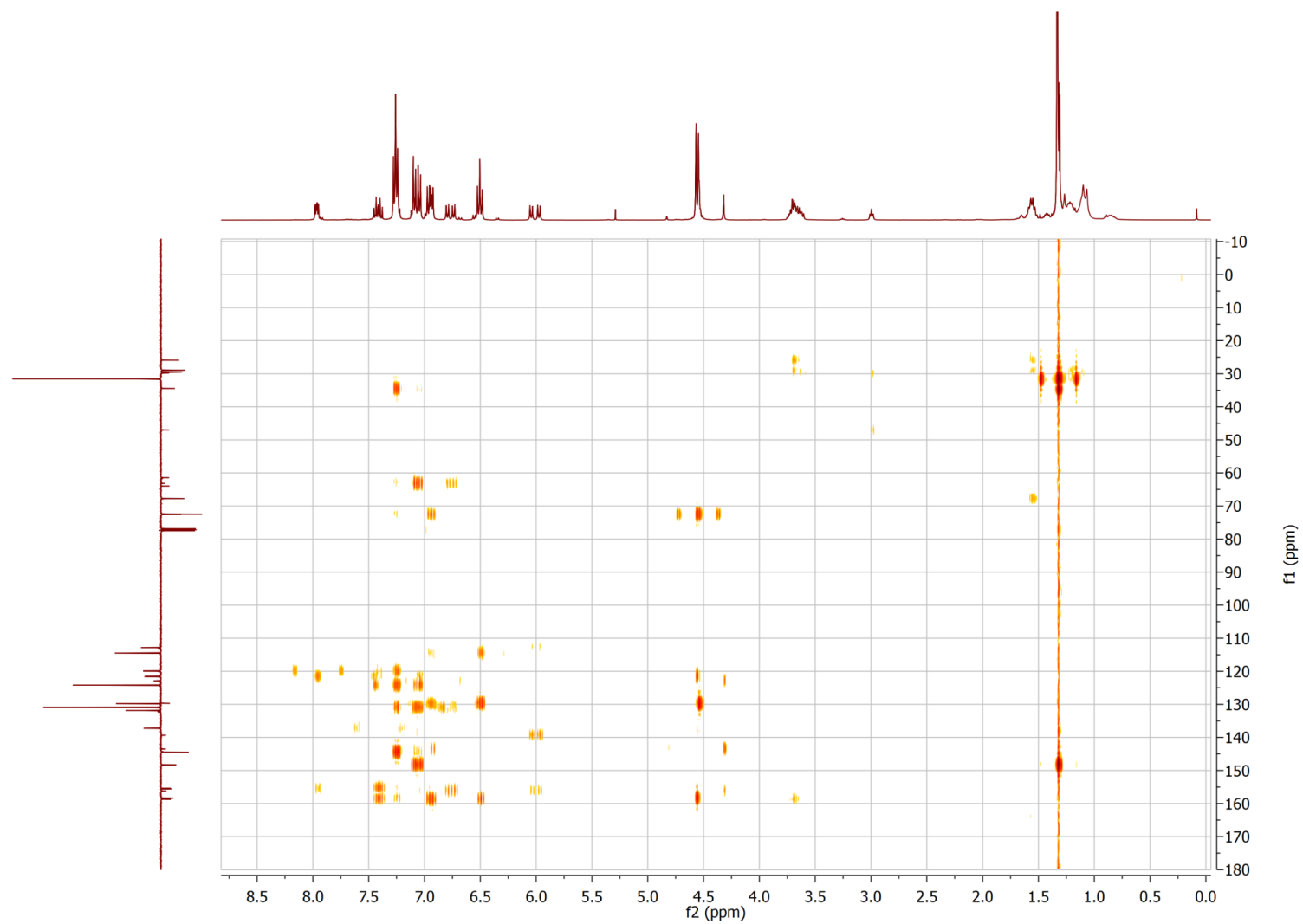
[3]Rotaxane 5a COSY (CDCl₃, 400 MHz, 300 K)



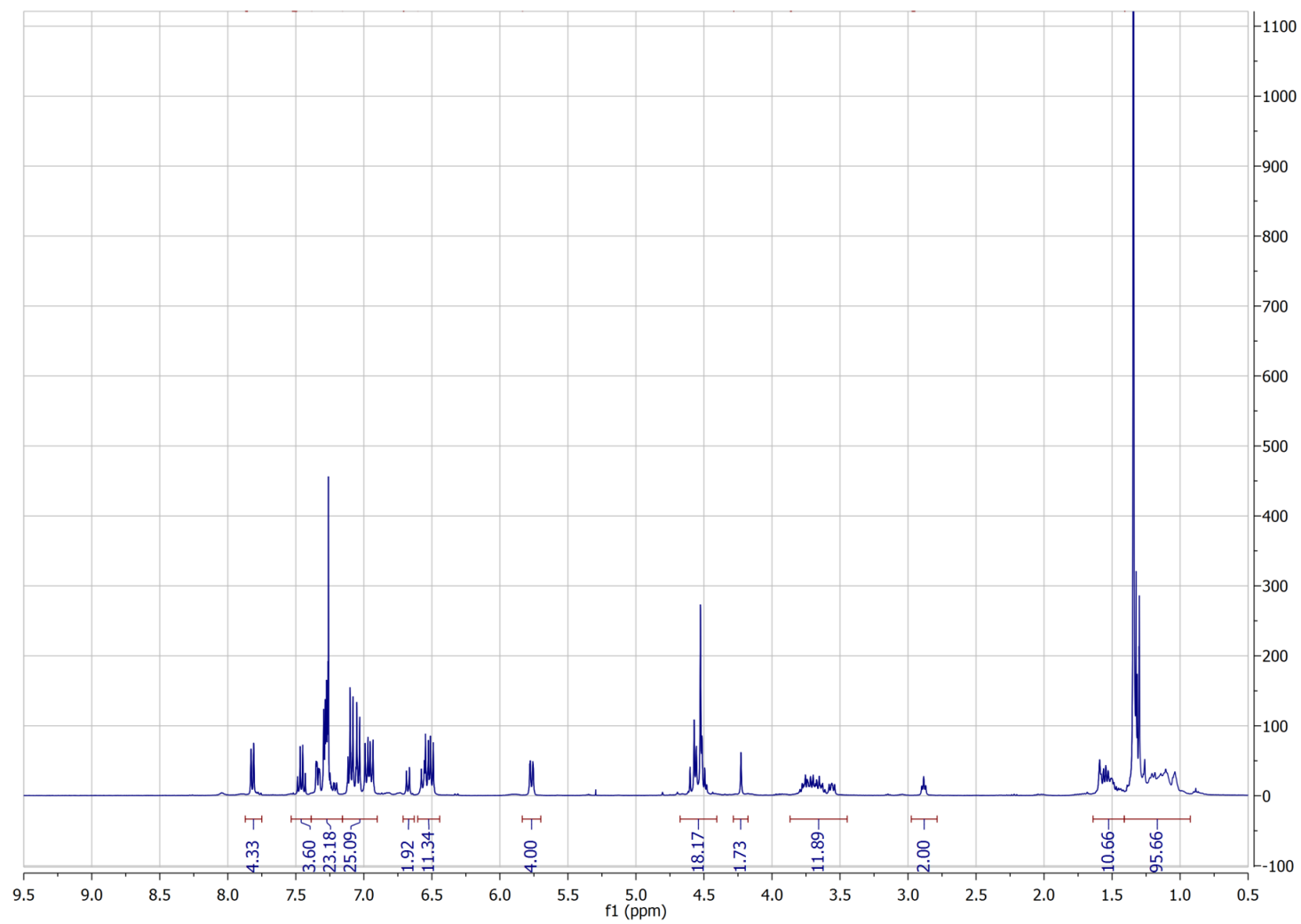
[3]Rotaxane 5a HSQC NMR (CDCl₃, 400 MHz, 300 K)



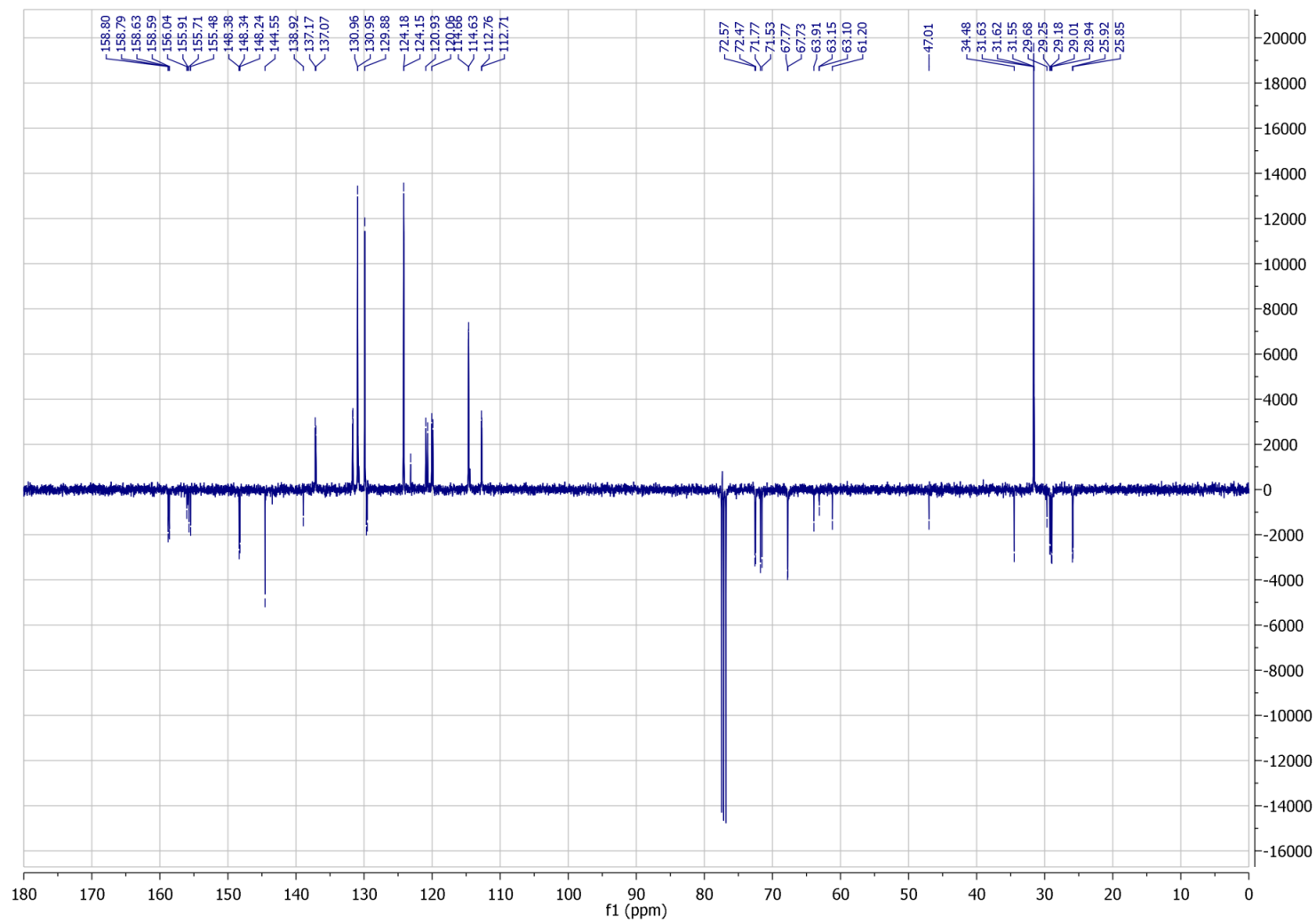
[3]Rotaxane 5a HMBC NMR (CDCl₃, 400 MHz, 300 K)



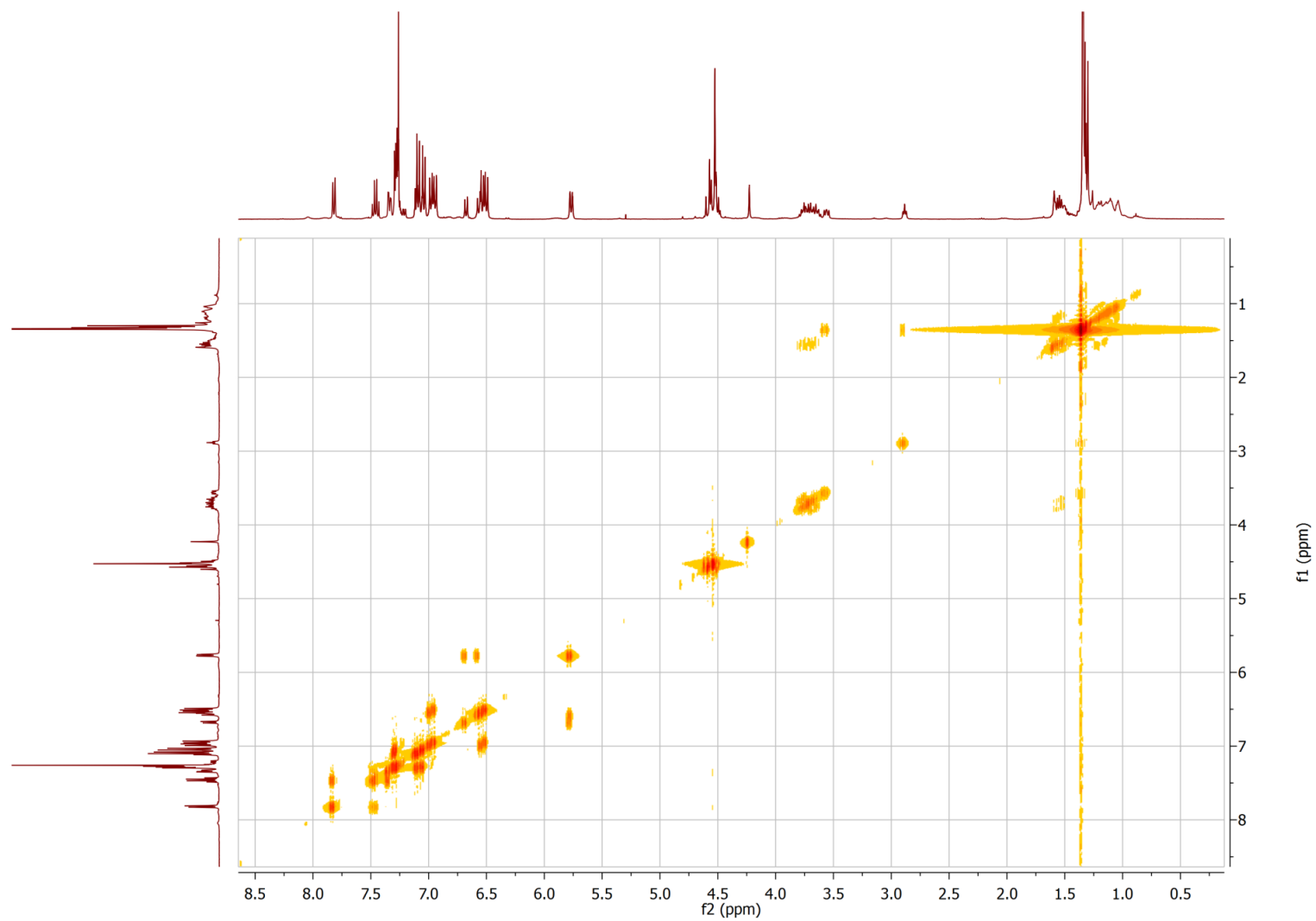
[3]Rotaxane 5b ^1H NMR (CDCl_3 , 400 MHz, 300 K)



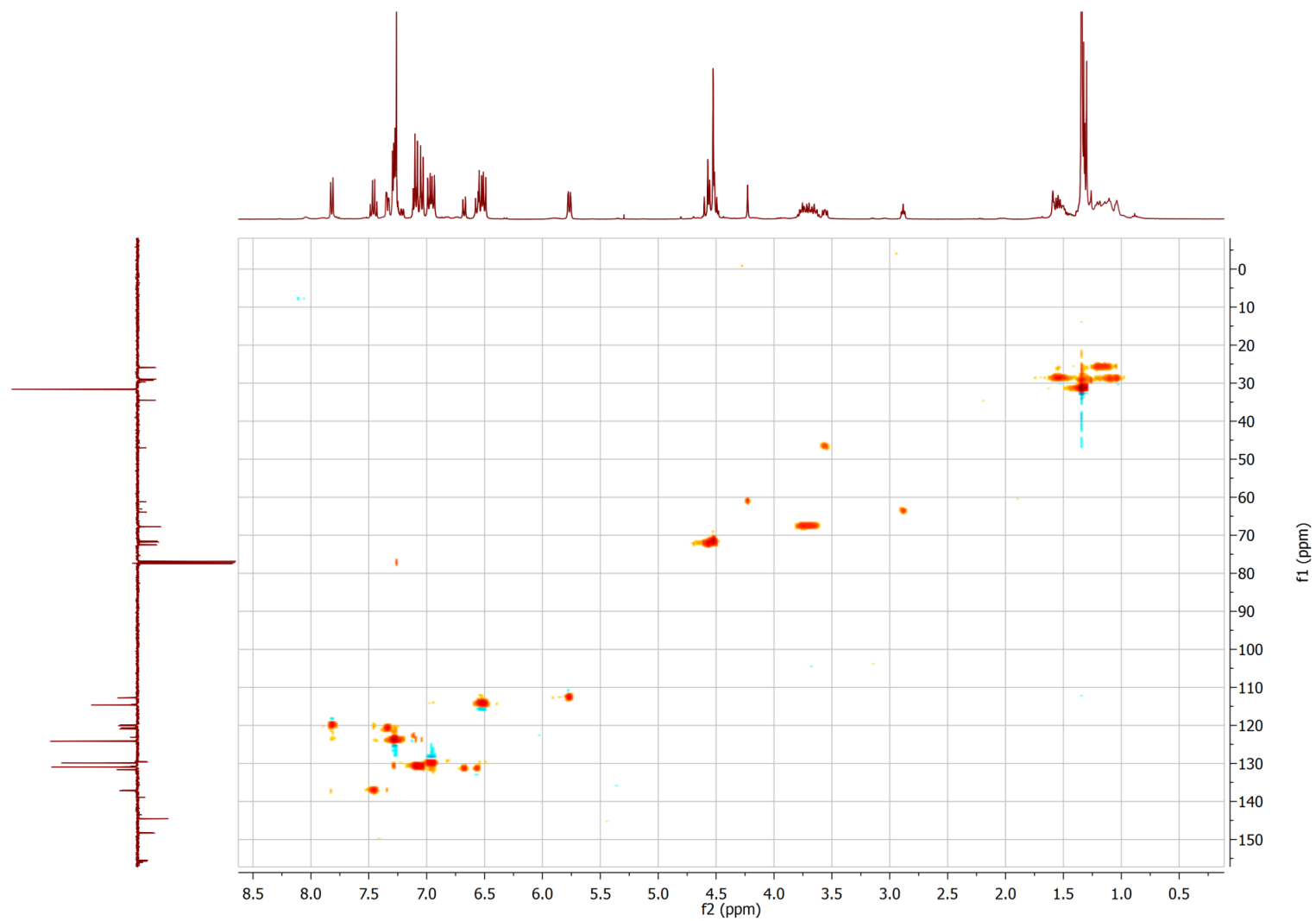
[3]Rotaxane 5b DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)

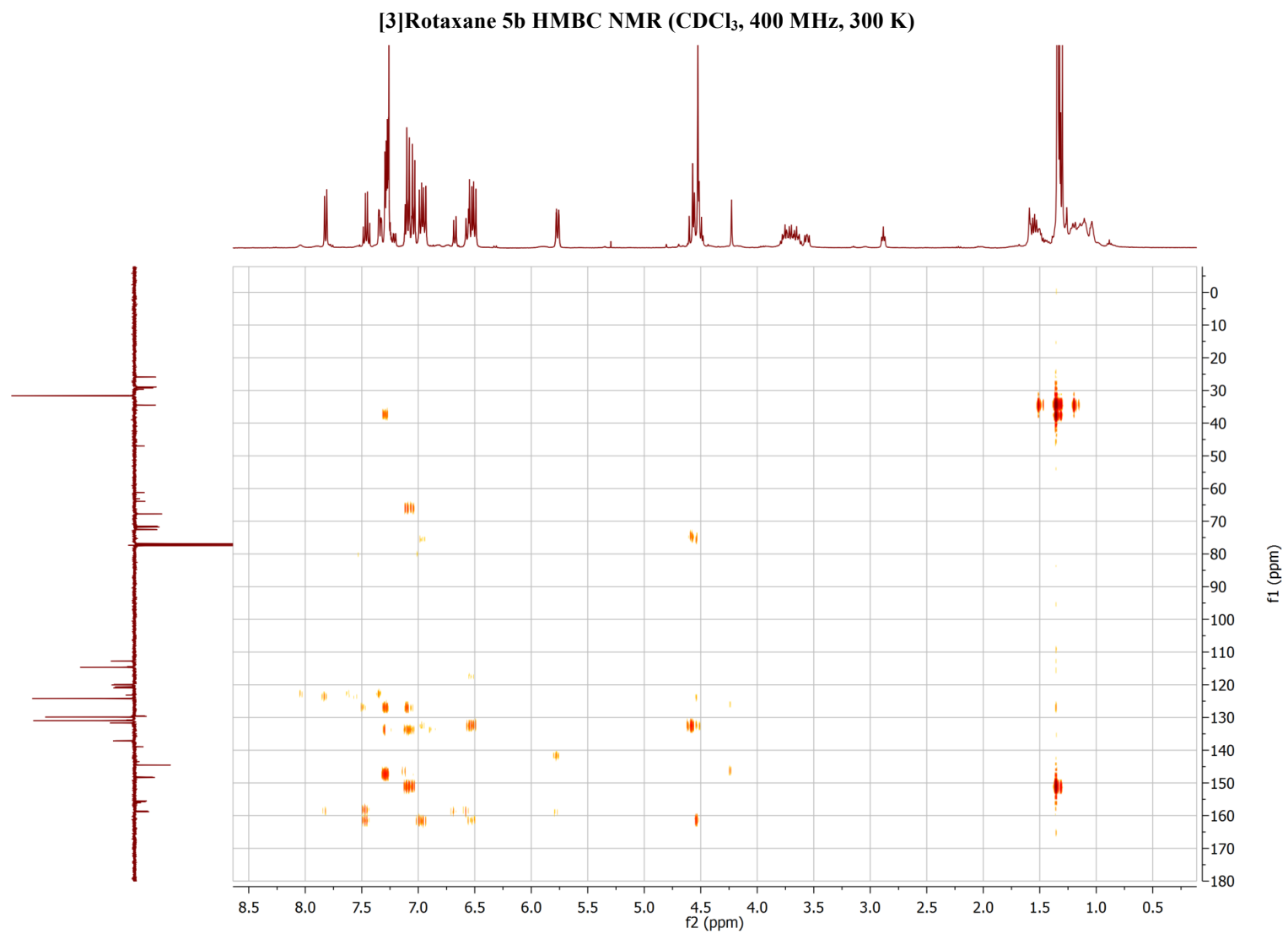


[3]Rotaxane 5b COSY (CDCl₃, 400 MHz, 300 K)

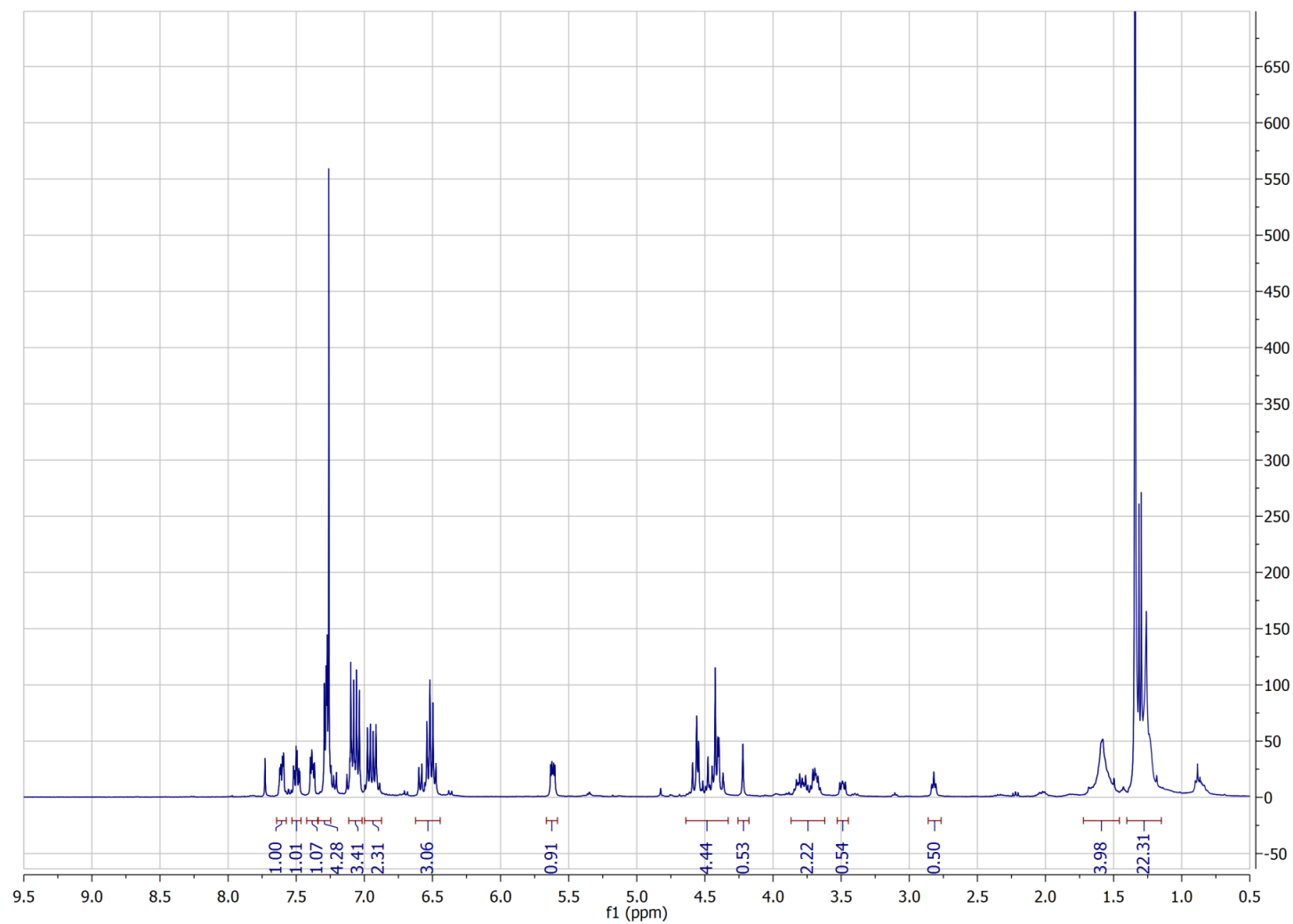


[3]Rotaxane 5b HSQC NMR (CDCl₃, 400 MHz, 300 K)

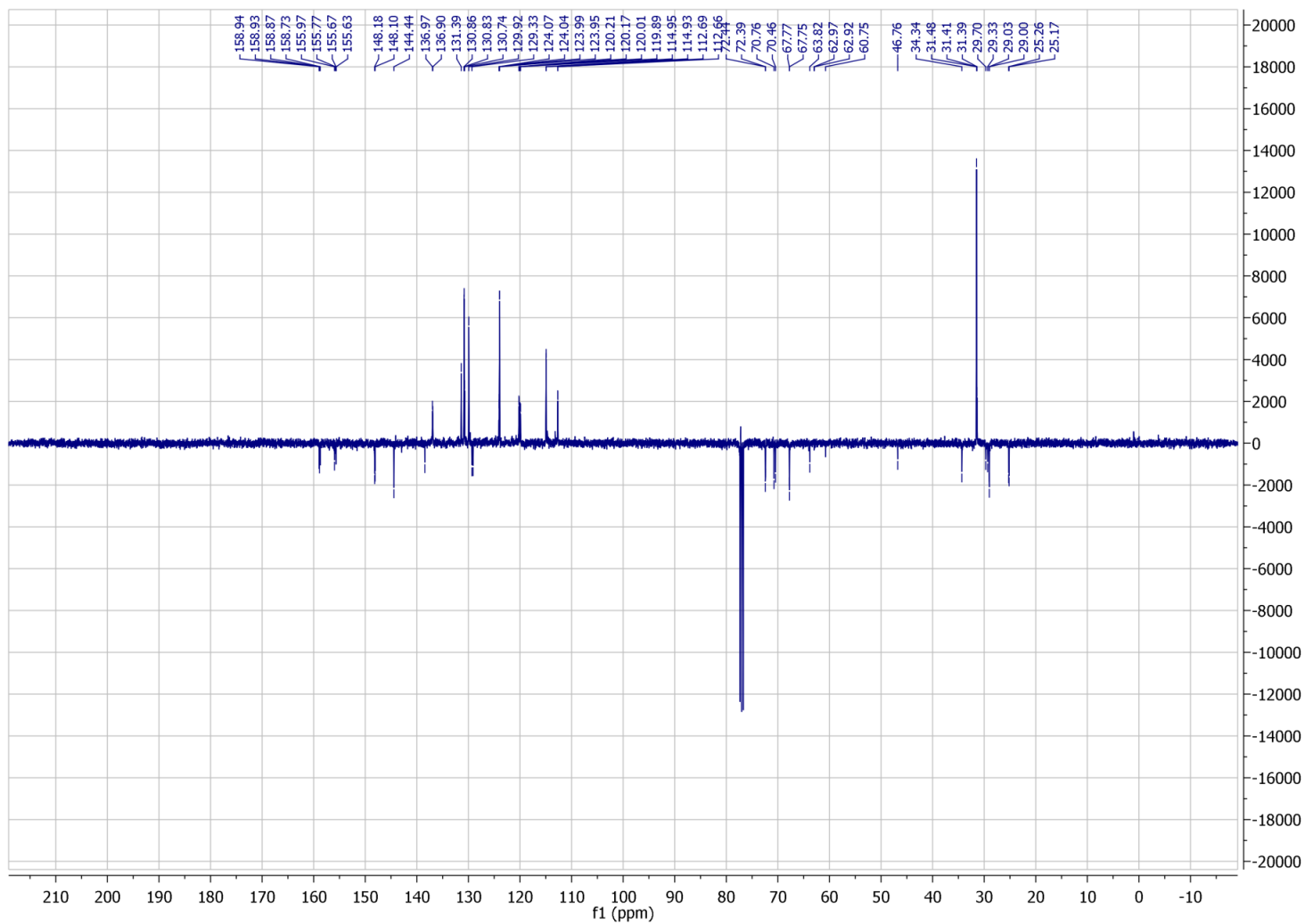




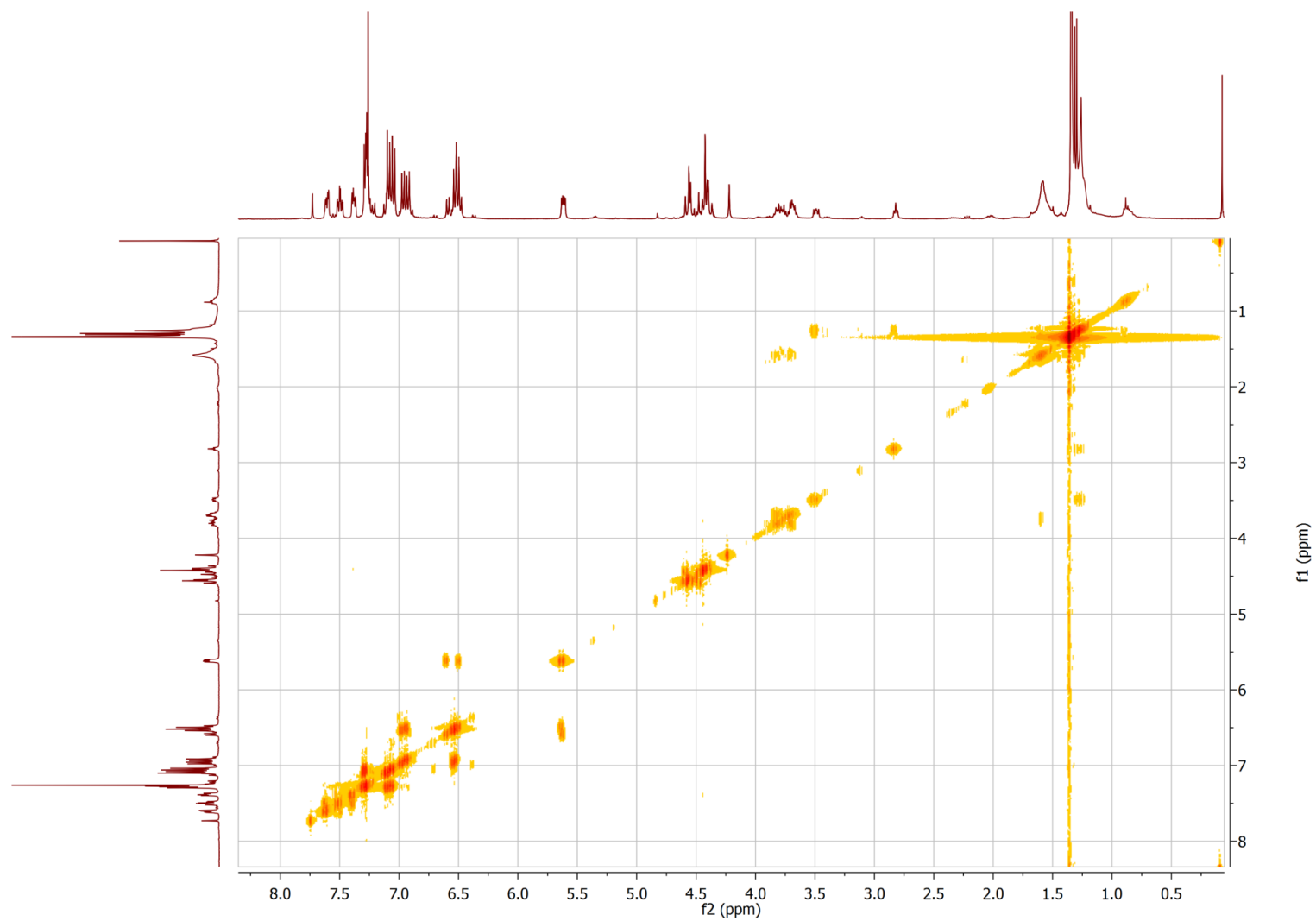
[3]Rotaxane 5c ^1H NMR (CDCl_3 , 400 MHz, 300 K)



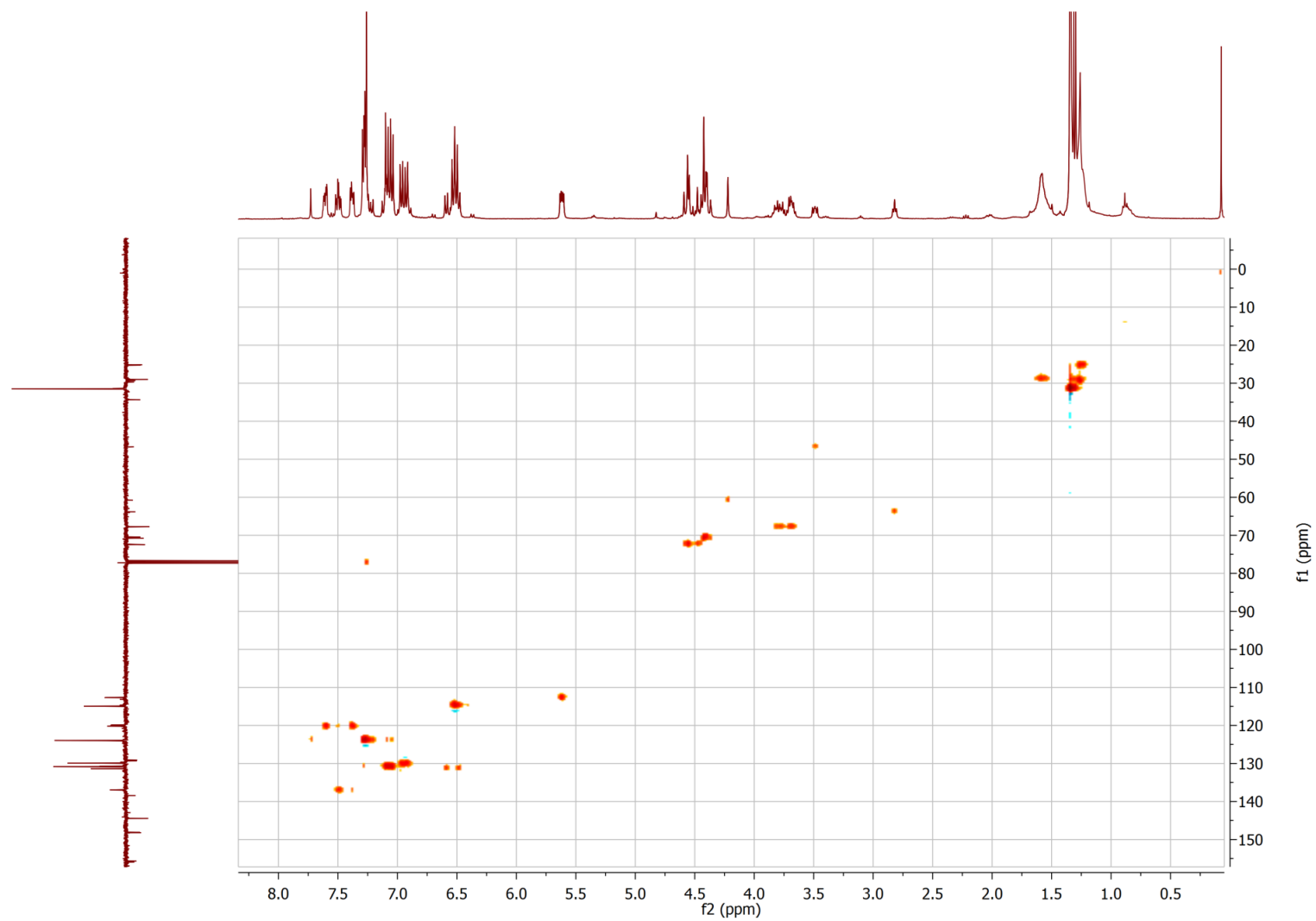
[3]Rotaxane 5c DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



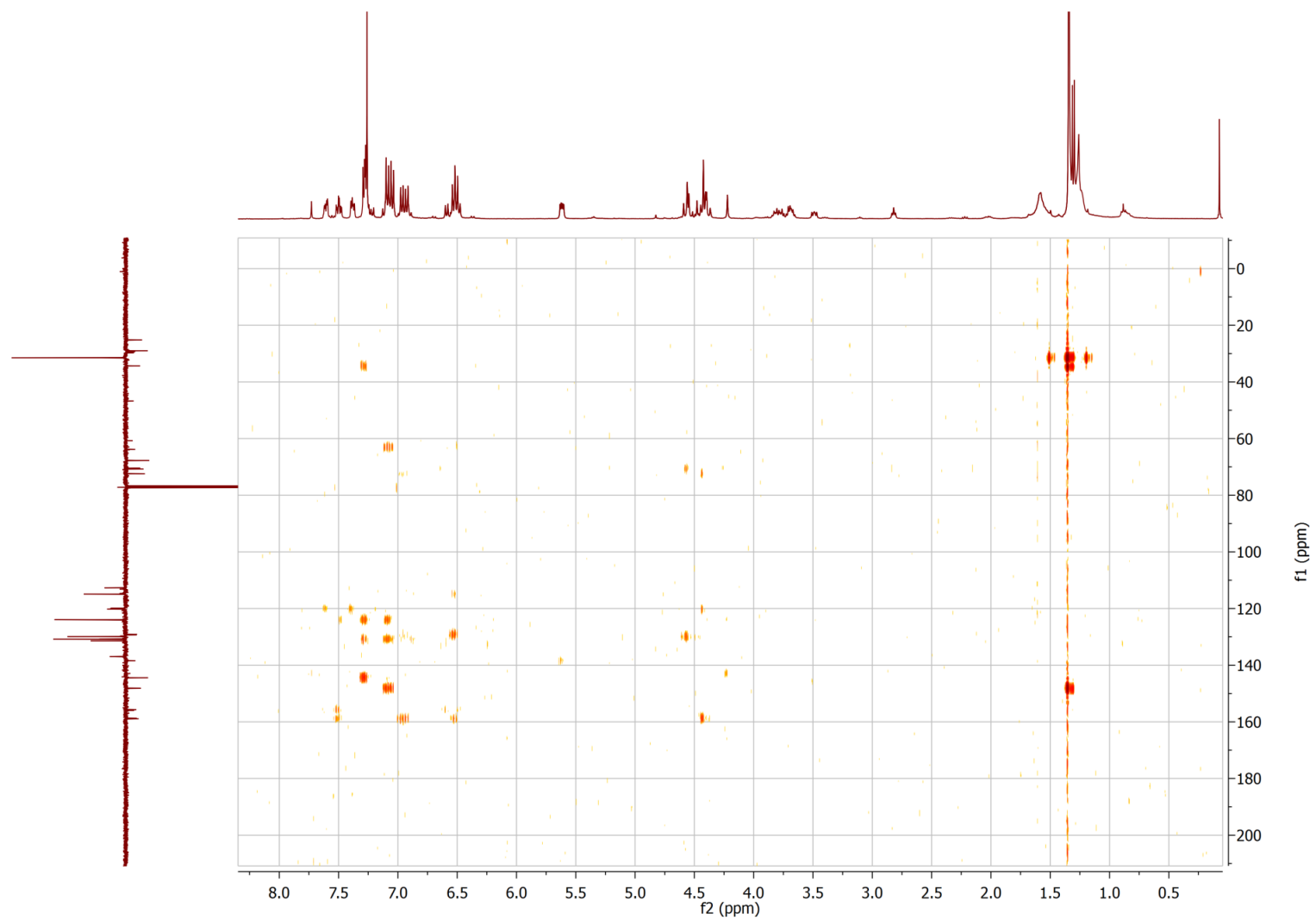
[3]Rotaxane 5c COSY (CDCl₃, 400 MHz, 300 K)



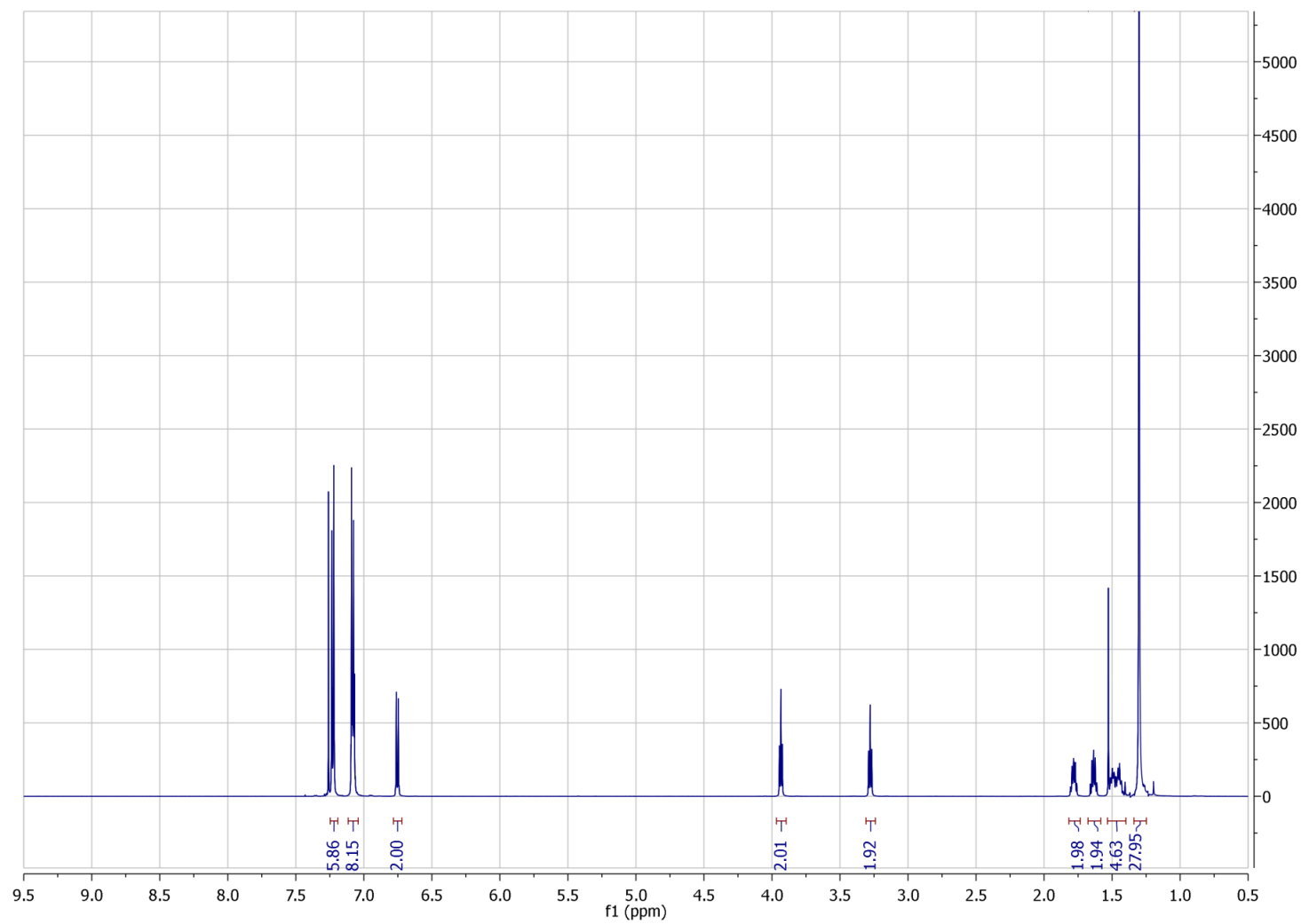
[3]Rotaxane 5c HSQC NMR (CDCl₃, 400 MHz, 300 K)



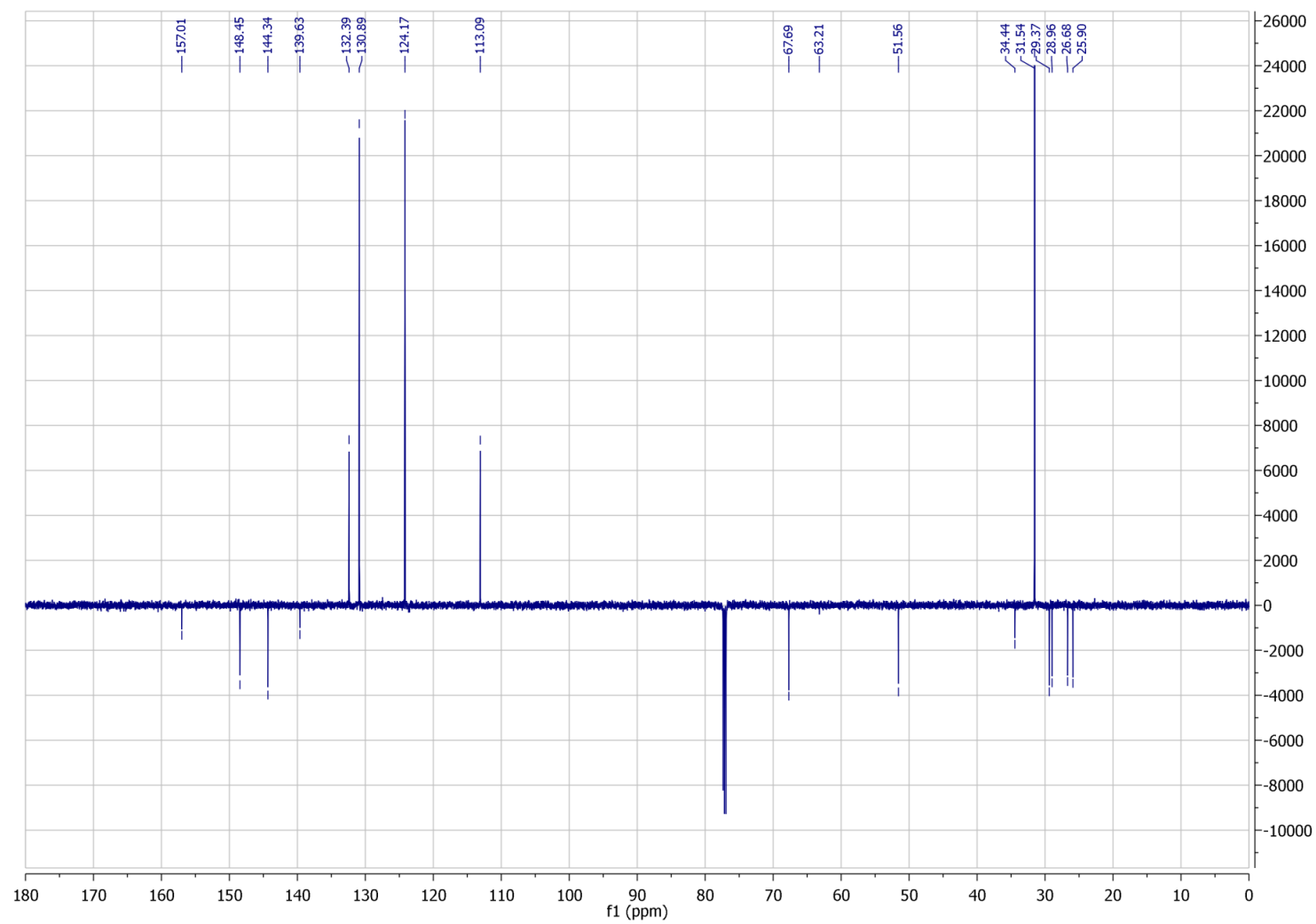
[3]Rotaxane 5c HMBC NMR (CDCl₃, 400 MHz, 300 K)



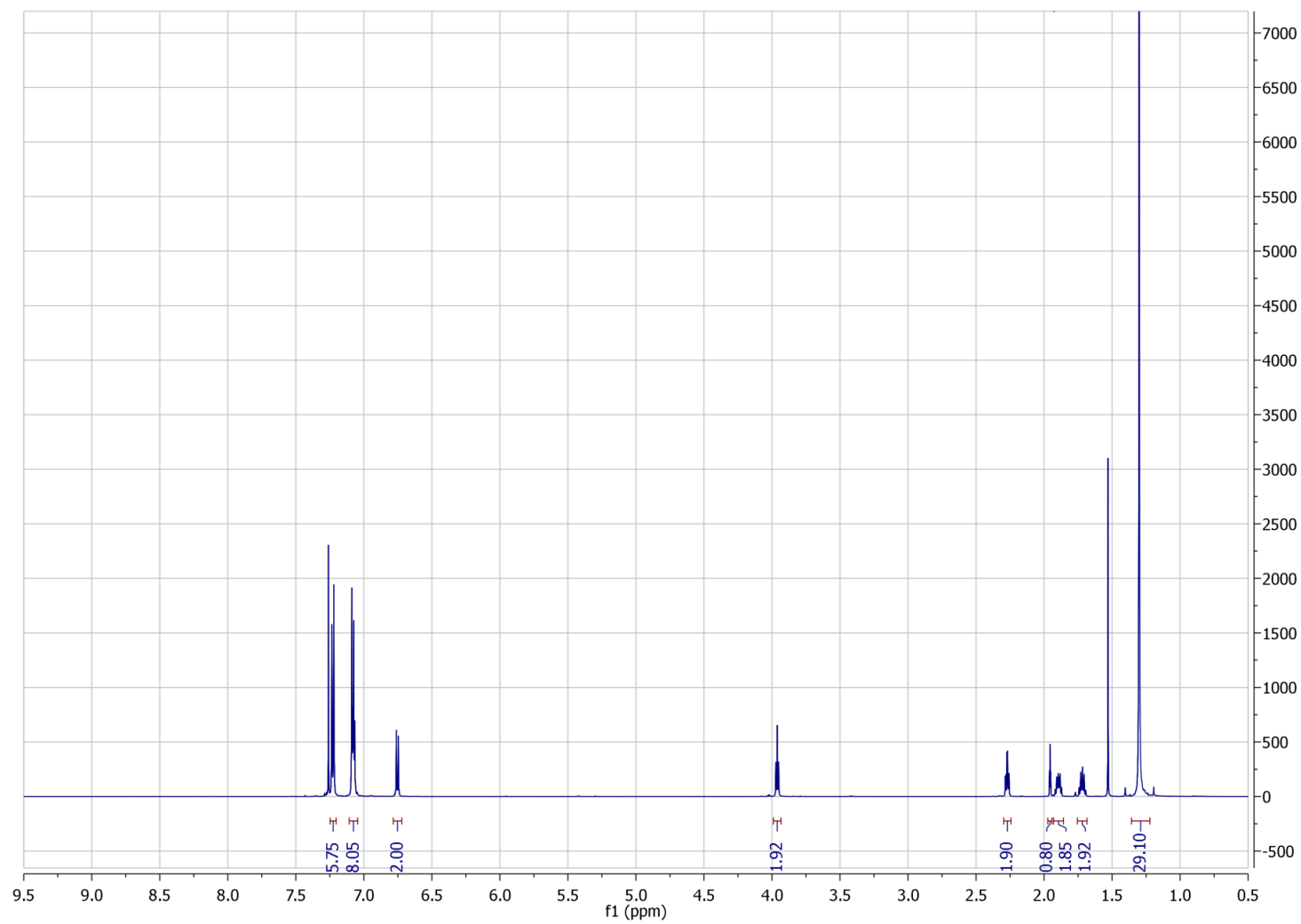
Azide 6 ^1H NMR (CDCl_3 , 600 MHz, 300 K)



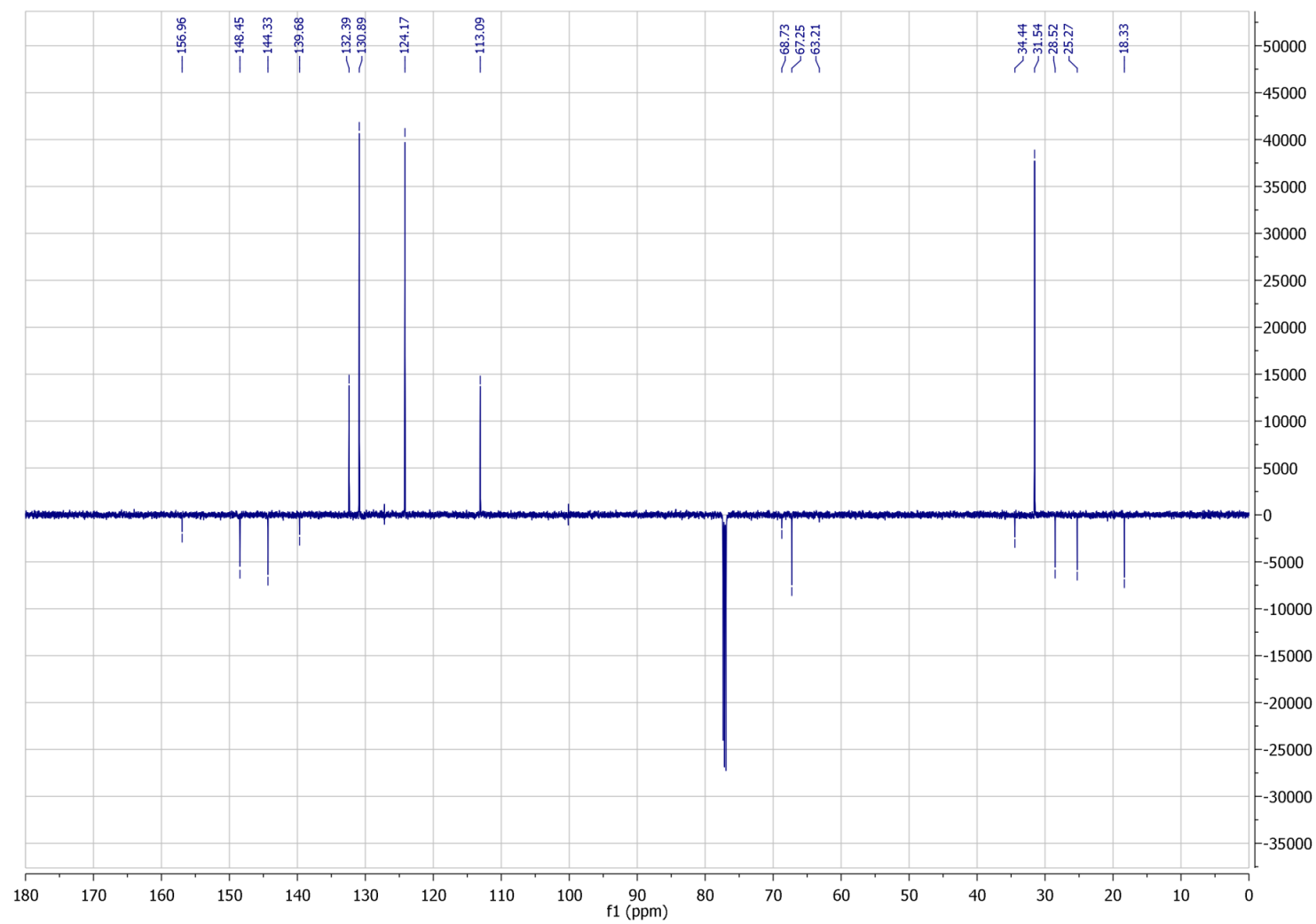
Azide 6 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



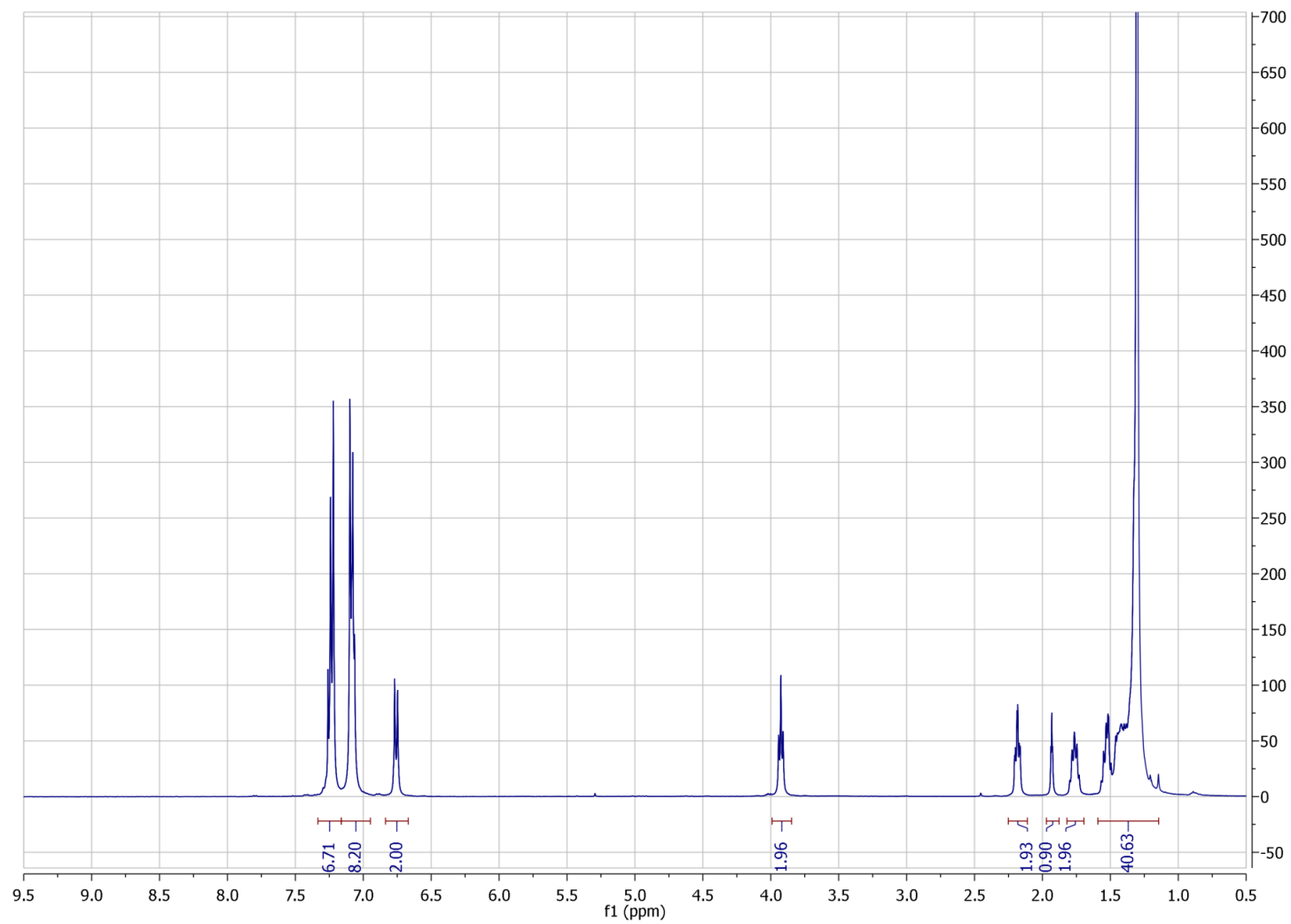
Alkyne 7 ^1H NMR (CDCl_3 , 600 MHz, 300 K)



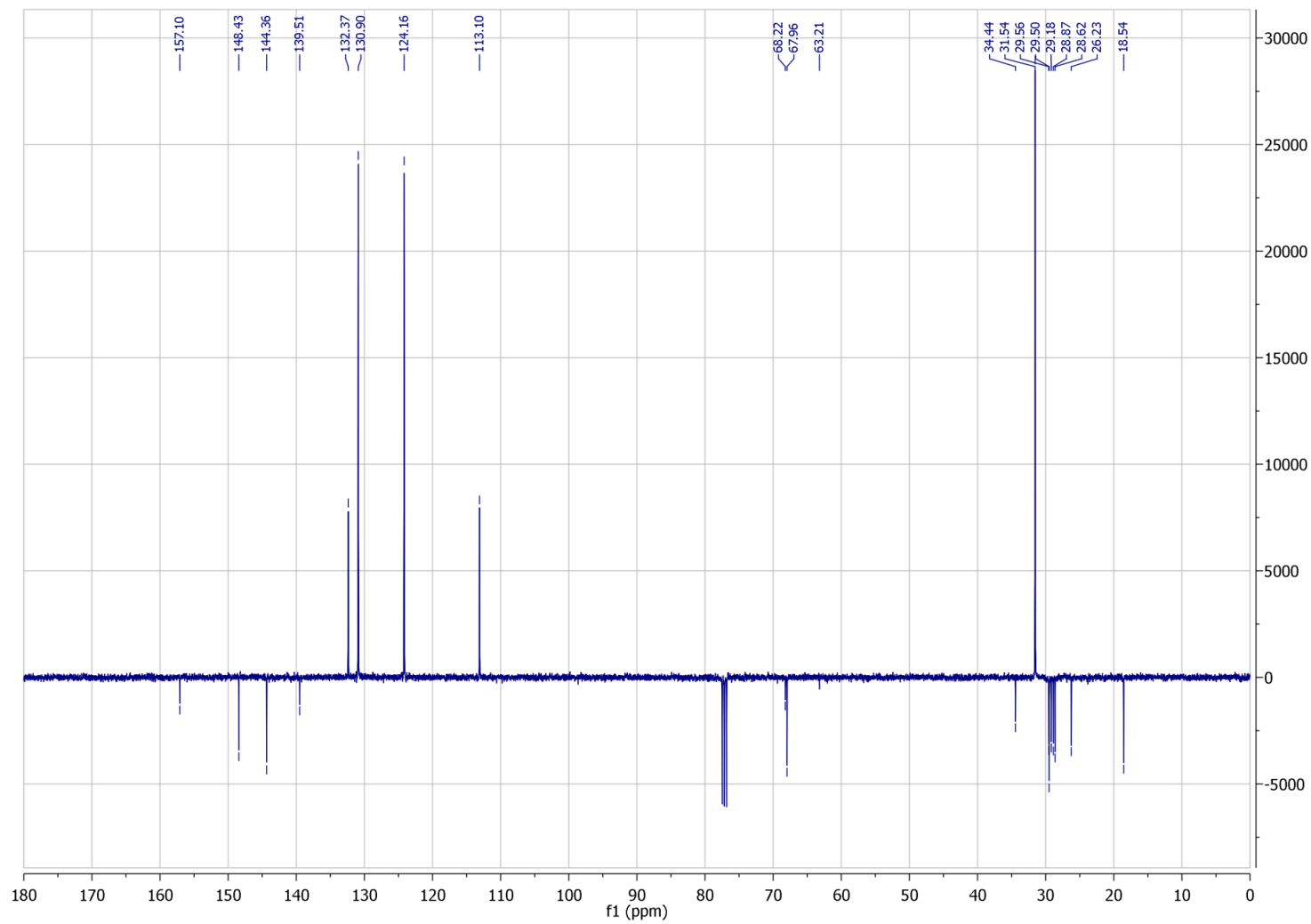
Alkyne 7 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



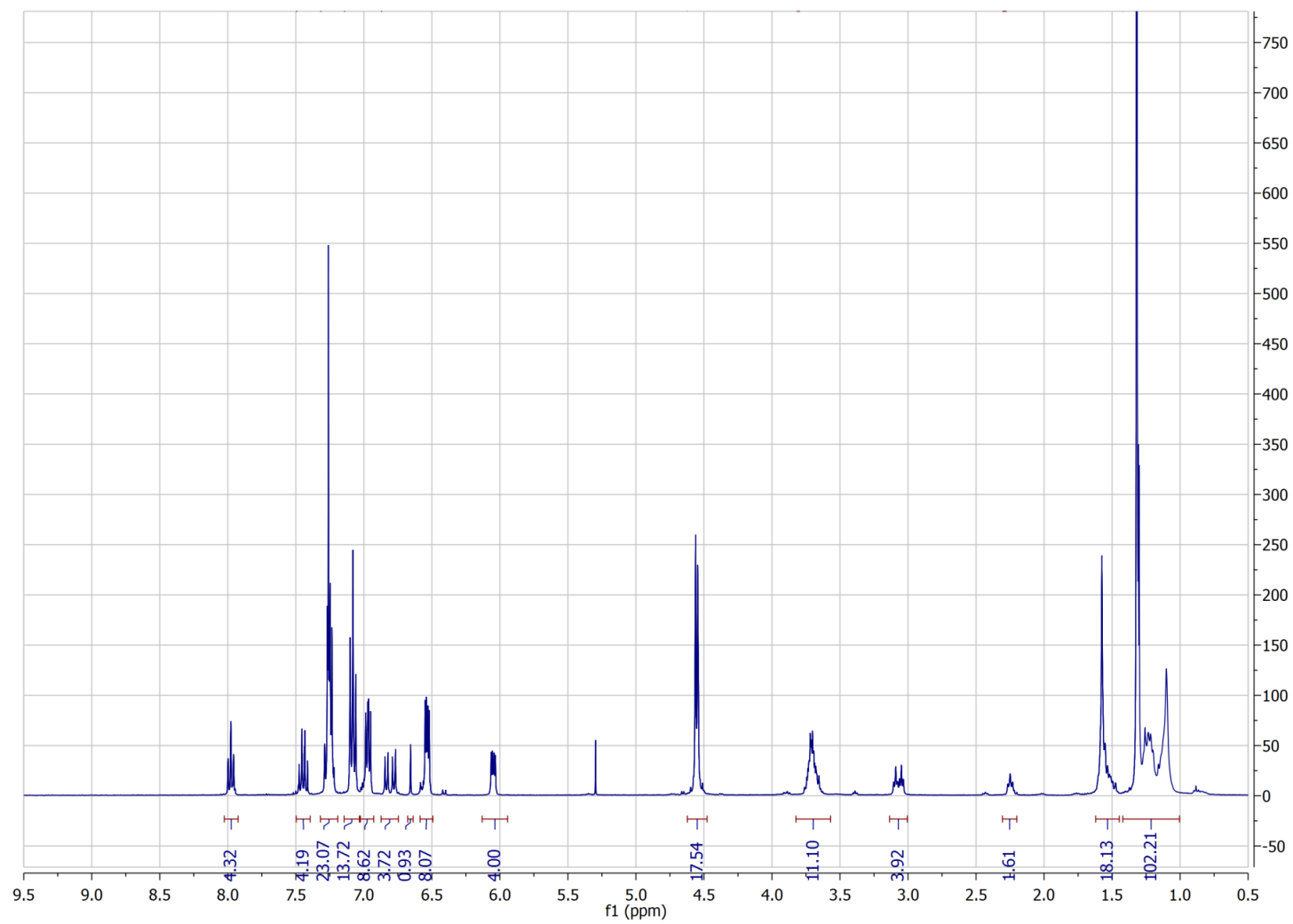
Alkyne 8 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



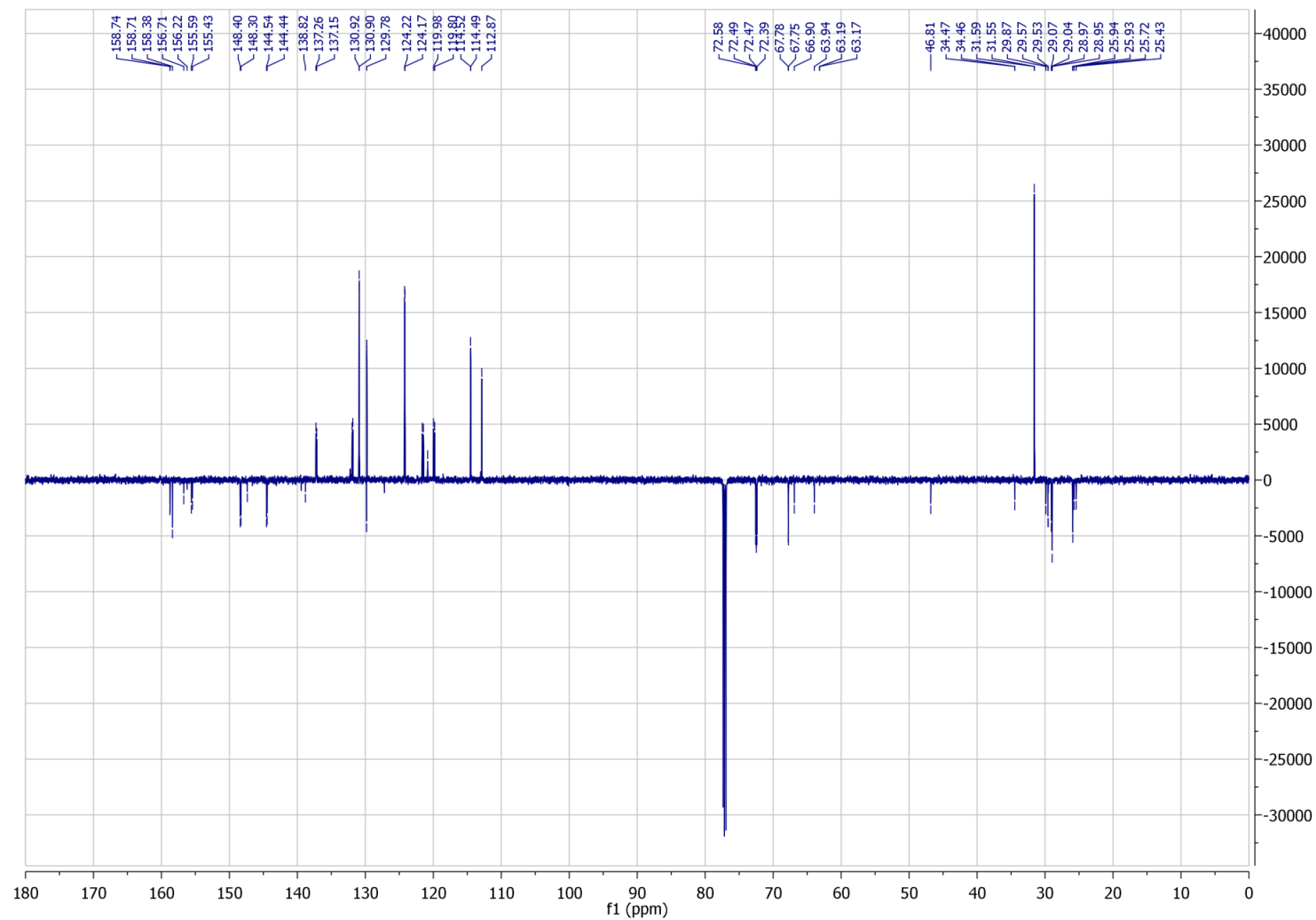
Alkyne 8 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



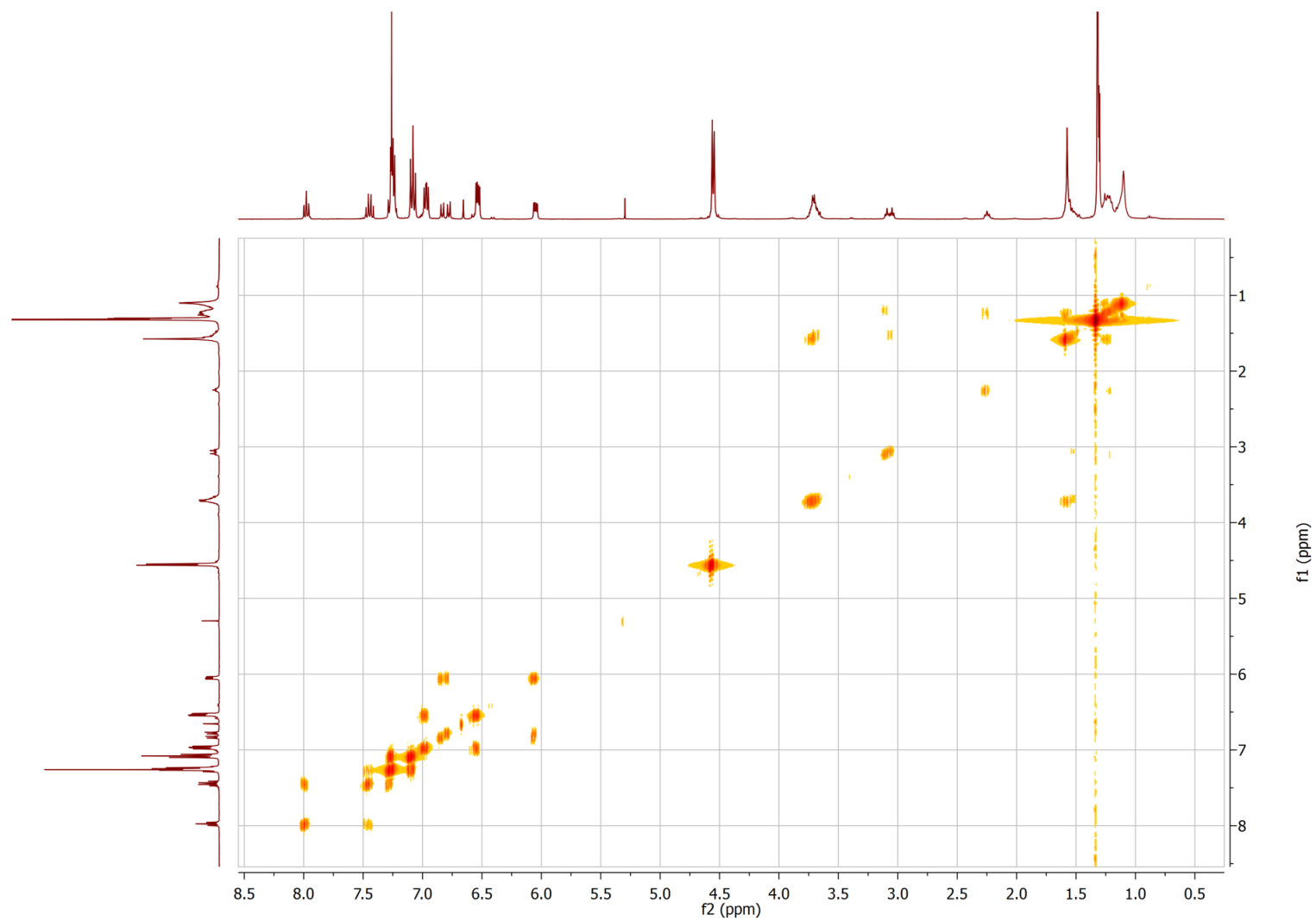
[3]Rotaxane S6 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



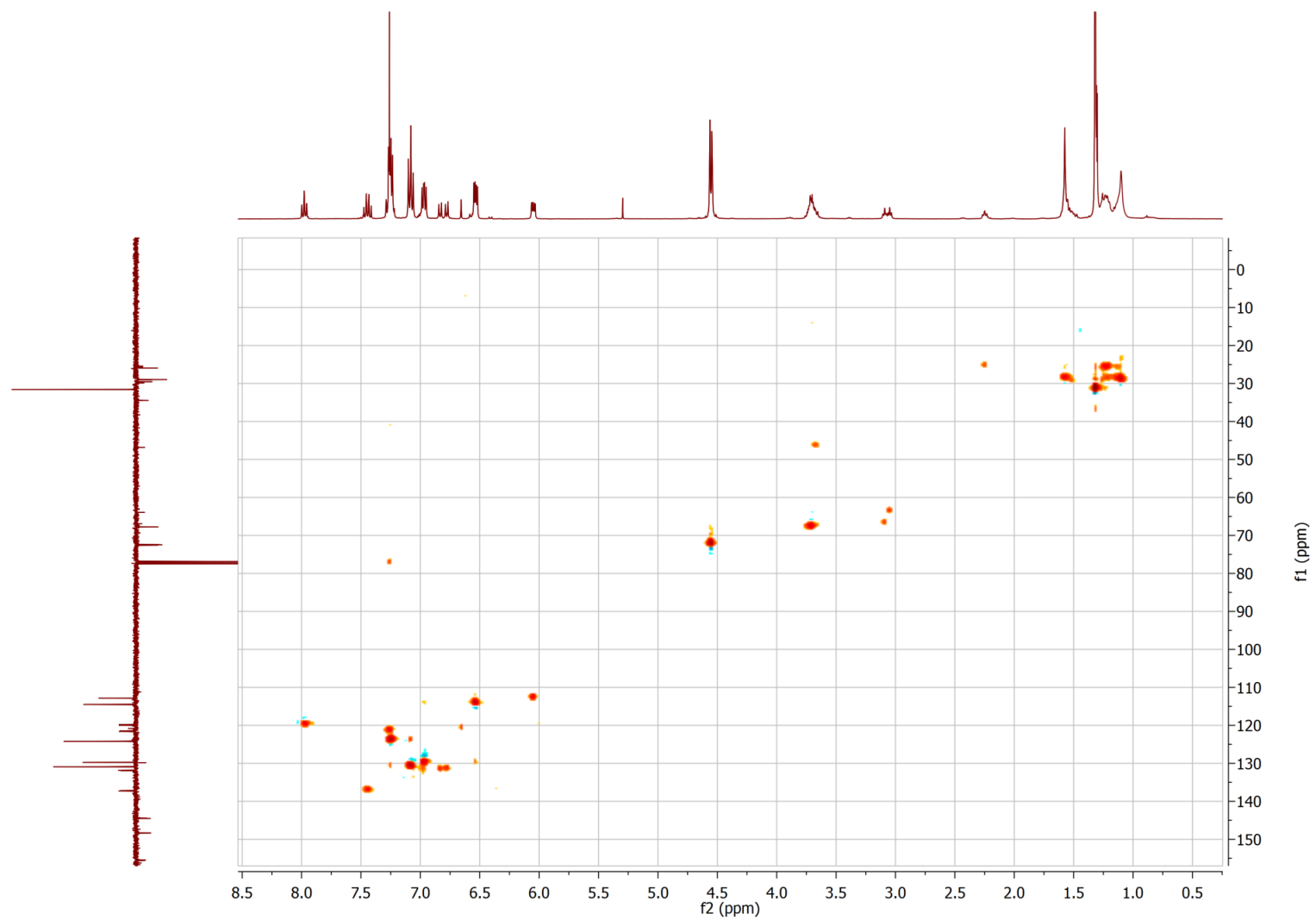
[3]Rotaxane S6 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



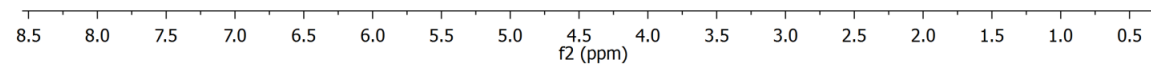
[3]Rotaxane S6 COSY (CDCl₃, 400 MHz, 300 K)



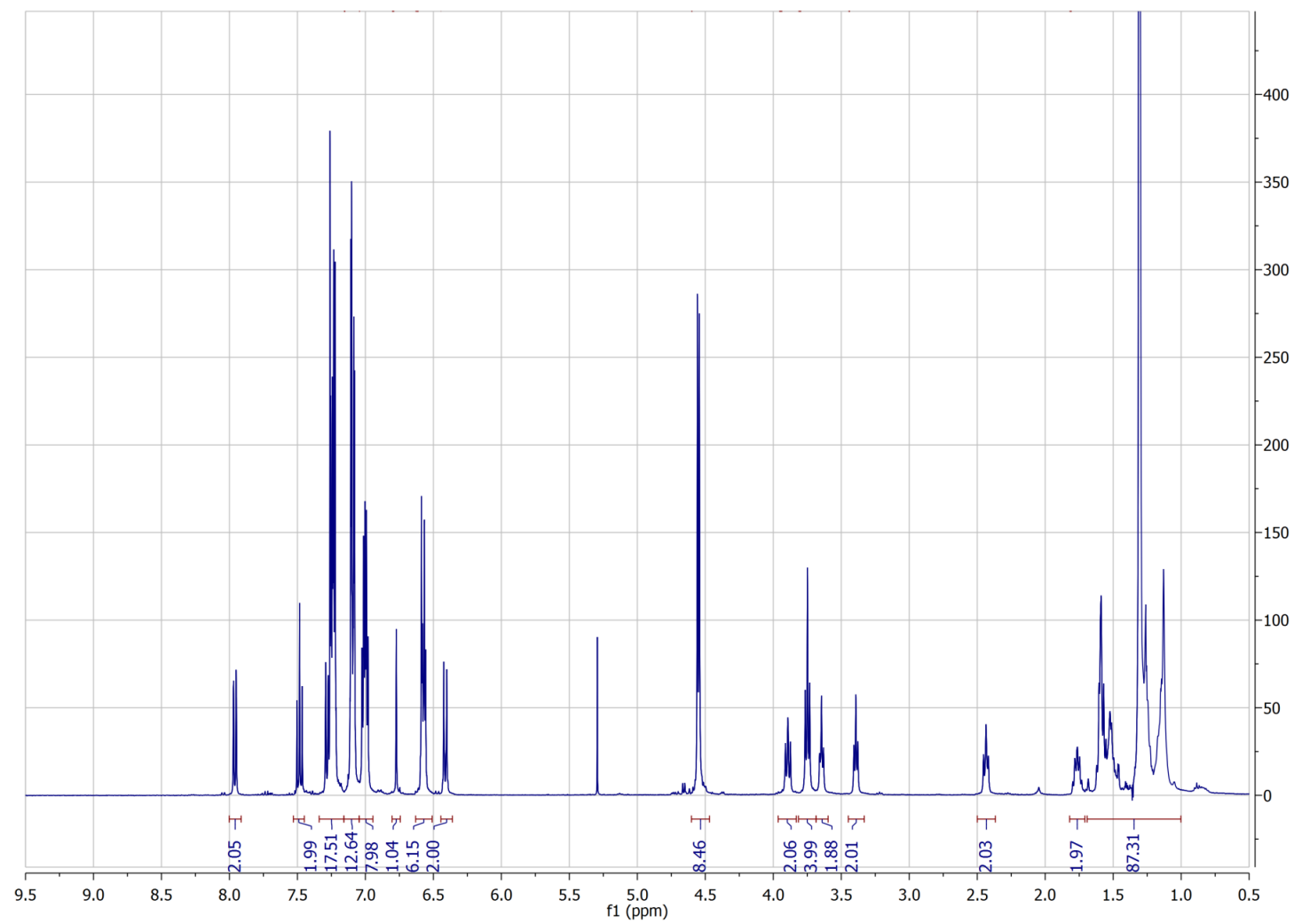
[3]Rotaxane S6 HSQC NMR (CDCl₃, 400 MHz, 300 K)



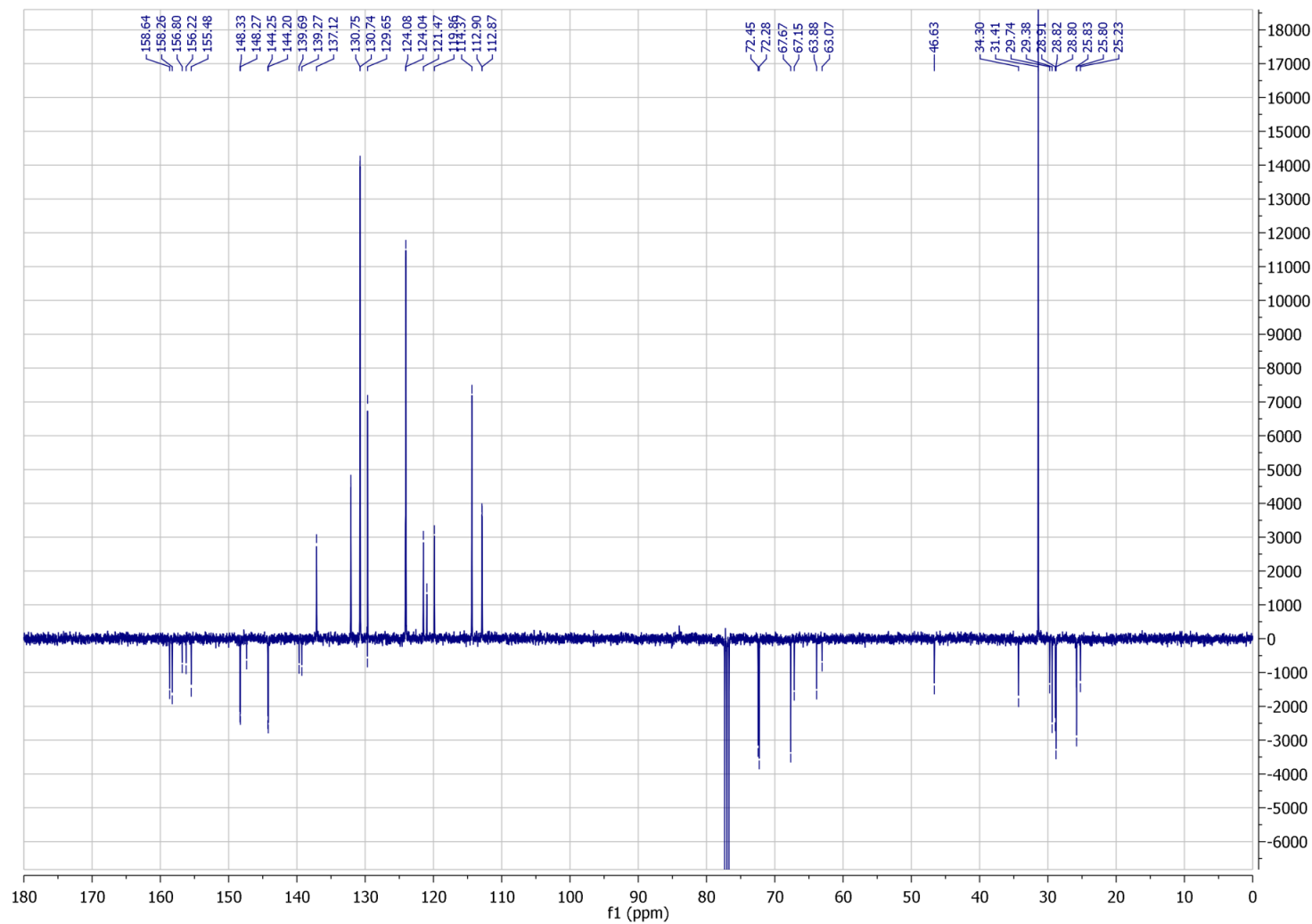
[3]Rotaxane S6 HMBC NMR (CDCl₃, 400 MHz, 300 K)



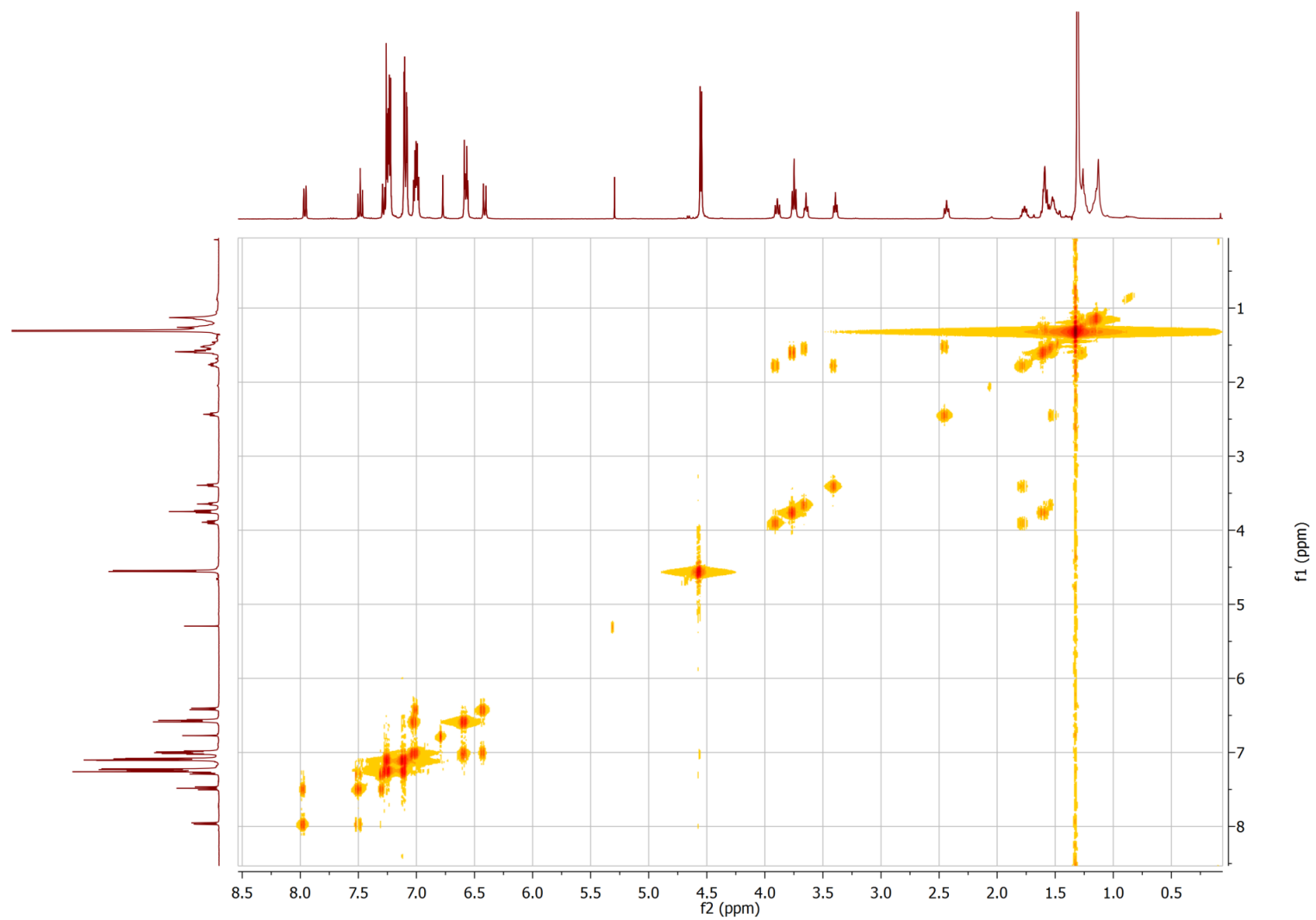
[2]Rotaxane S7 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



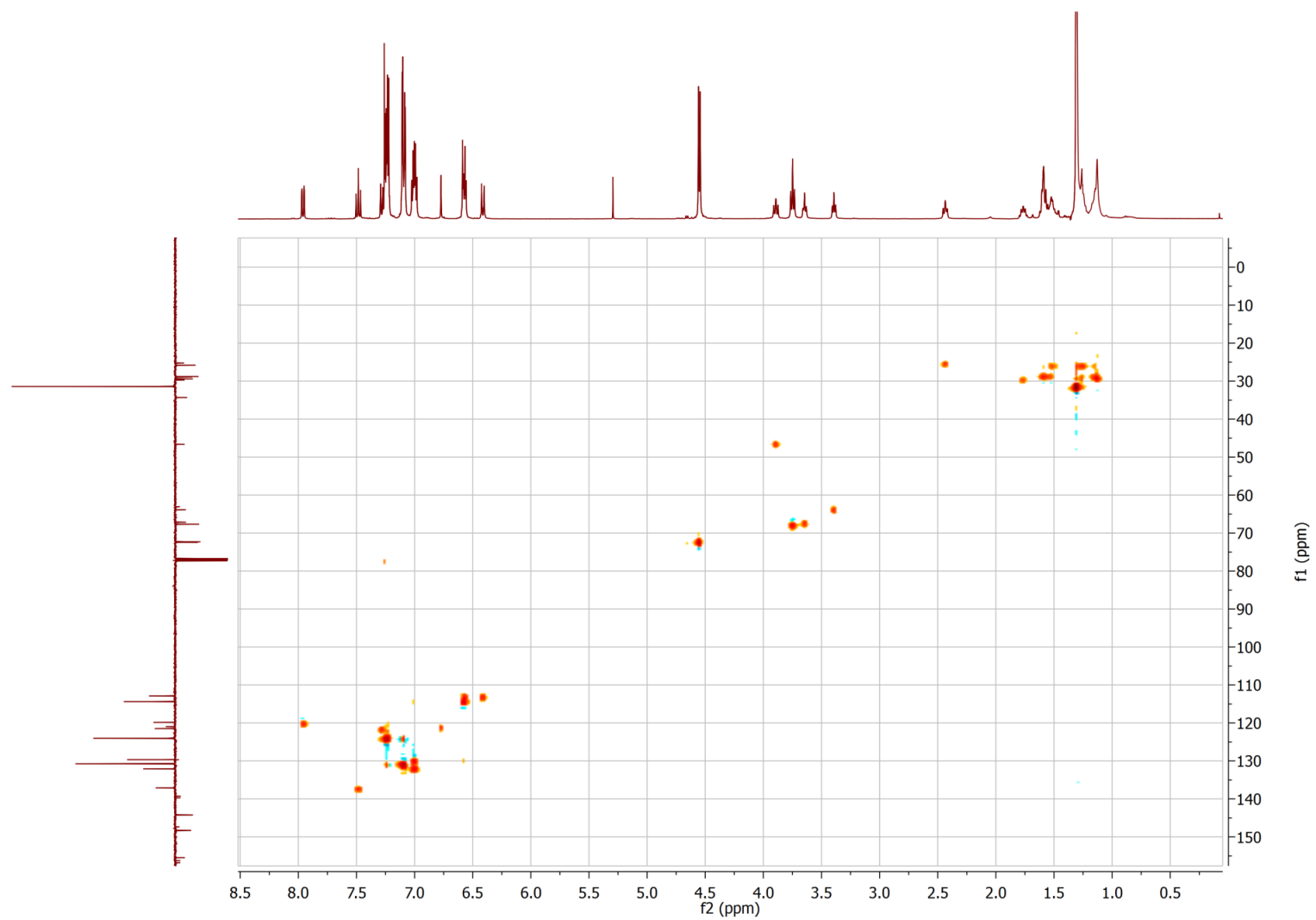
[2]Rotaxane S7 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



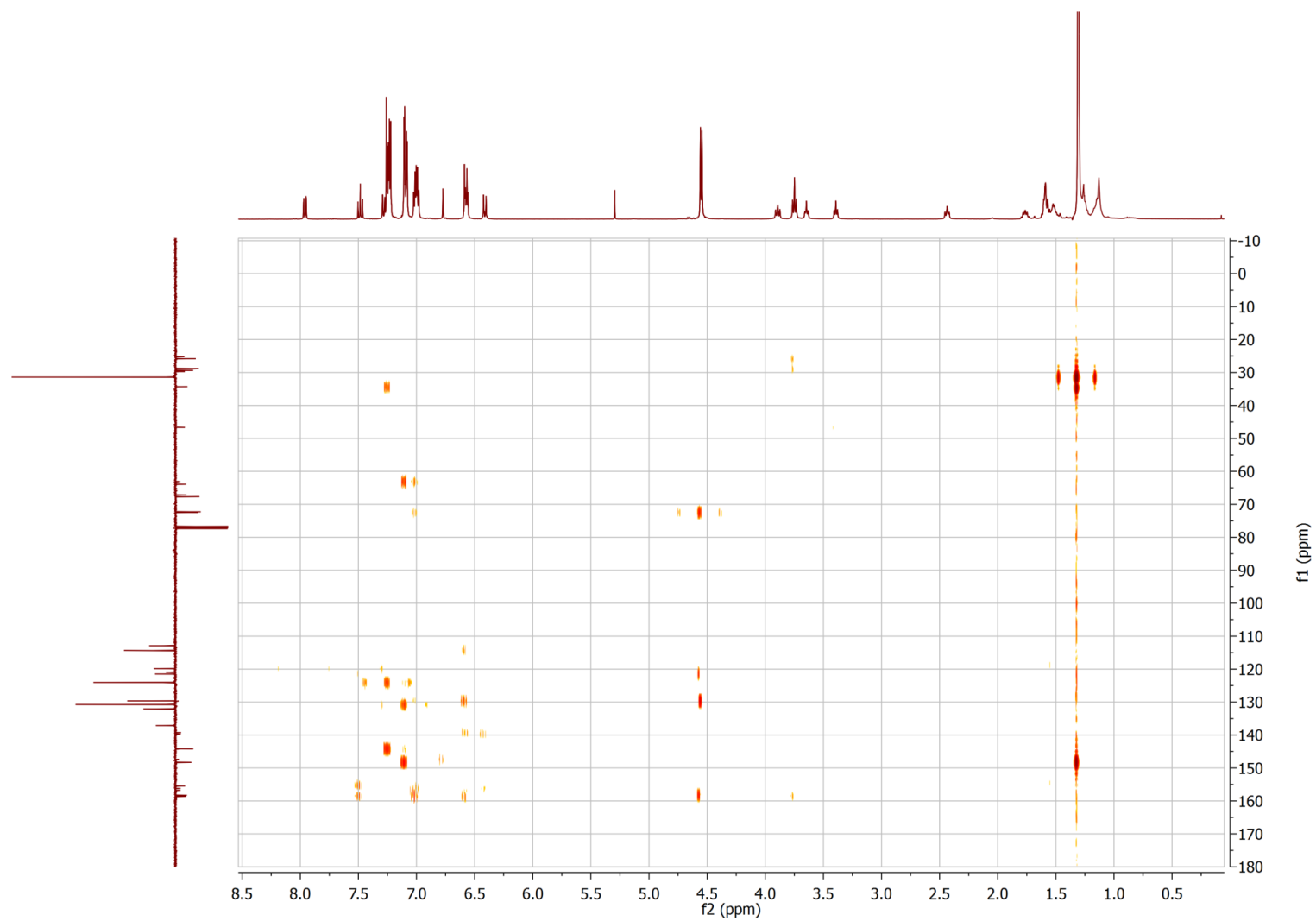
[2]Rotaxane S7 COSY (CDCl₃, 400 MHz, 300 K)



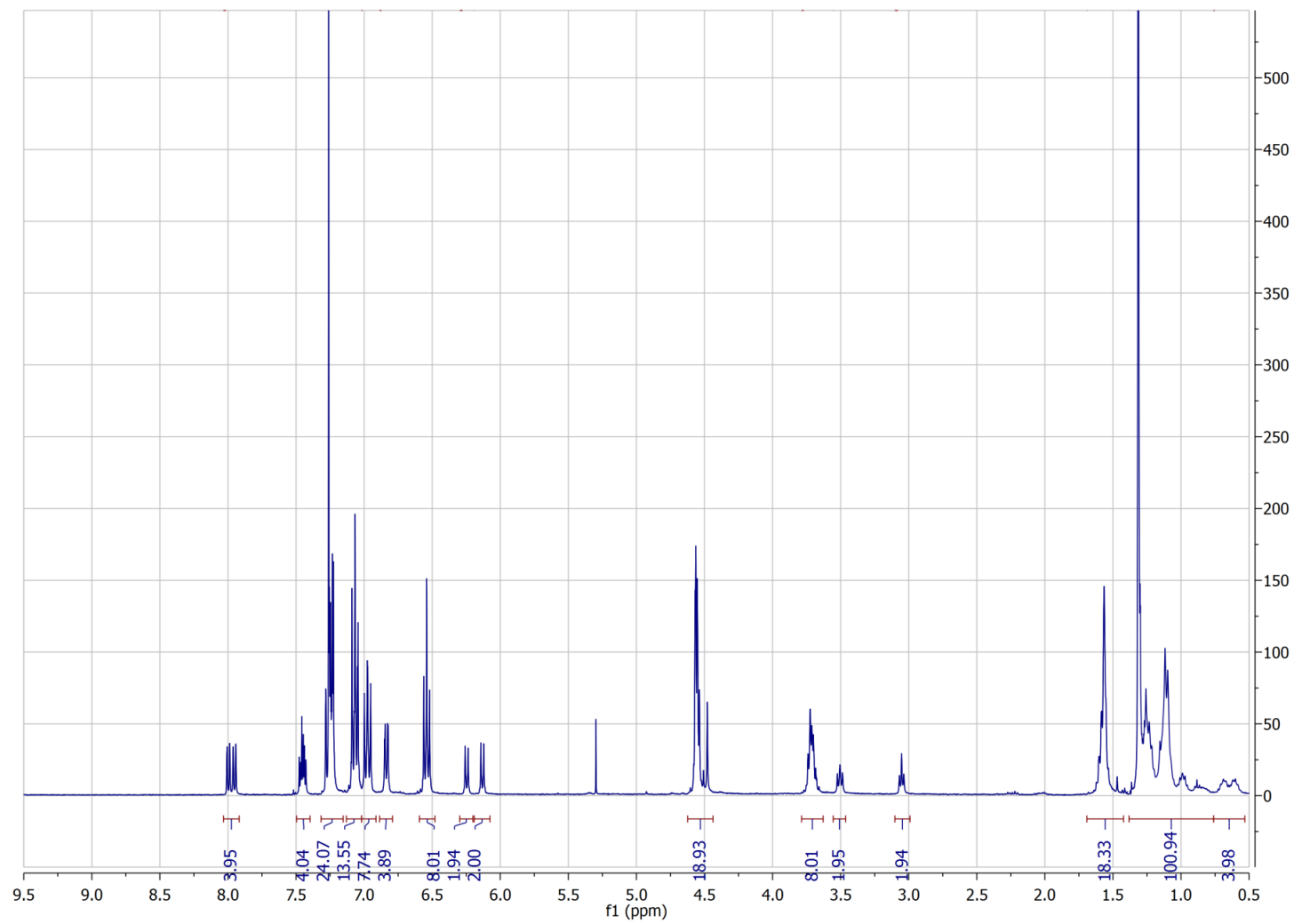
[2]Rotaxane S7 HSQC NMR (CDCl₃, 400 MHz, 300 K)



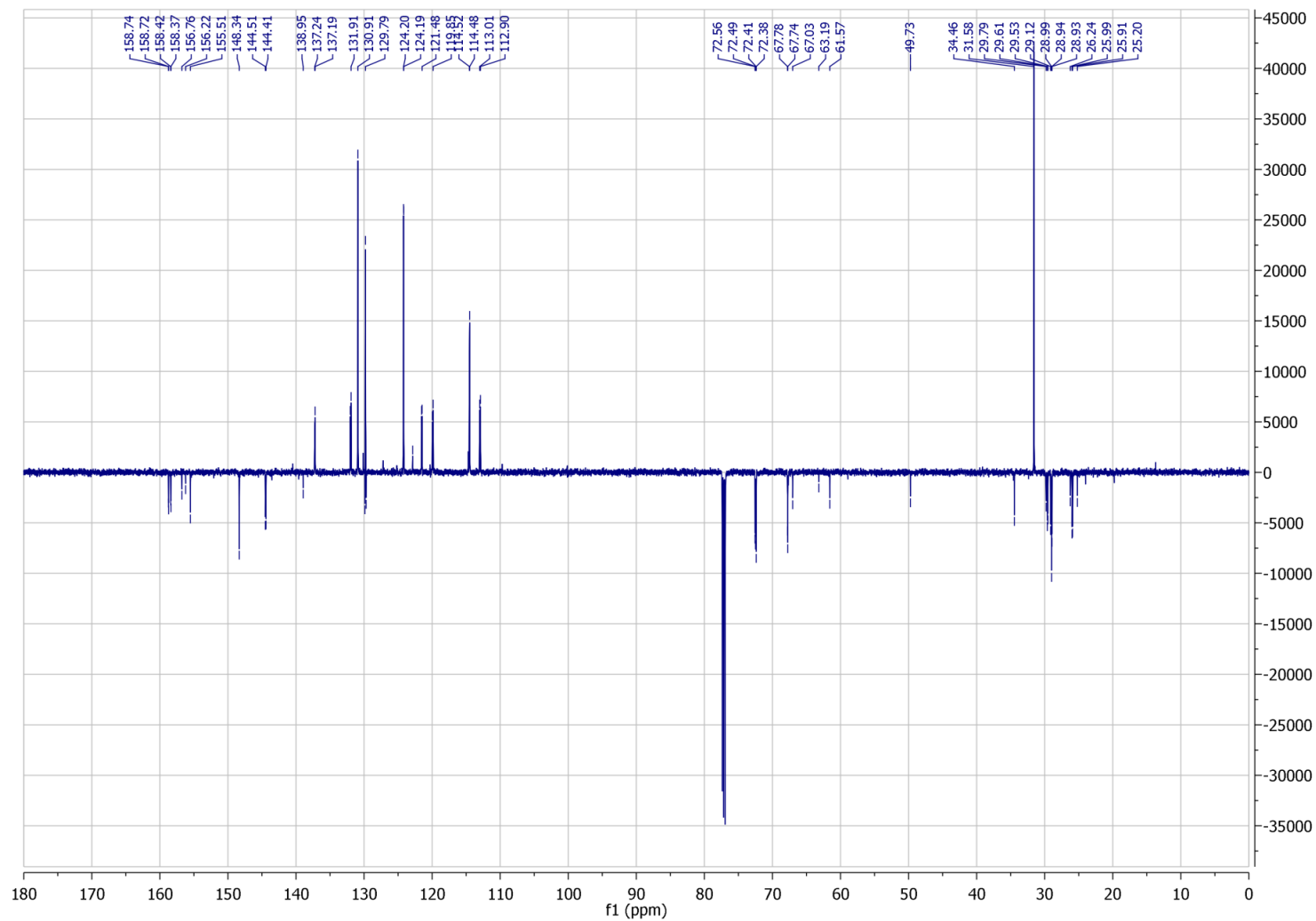
[2]Rotaxane S7 HMBC NMR (CDCl₃, 400 MHz, 300 K)



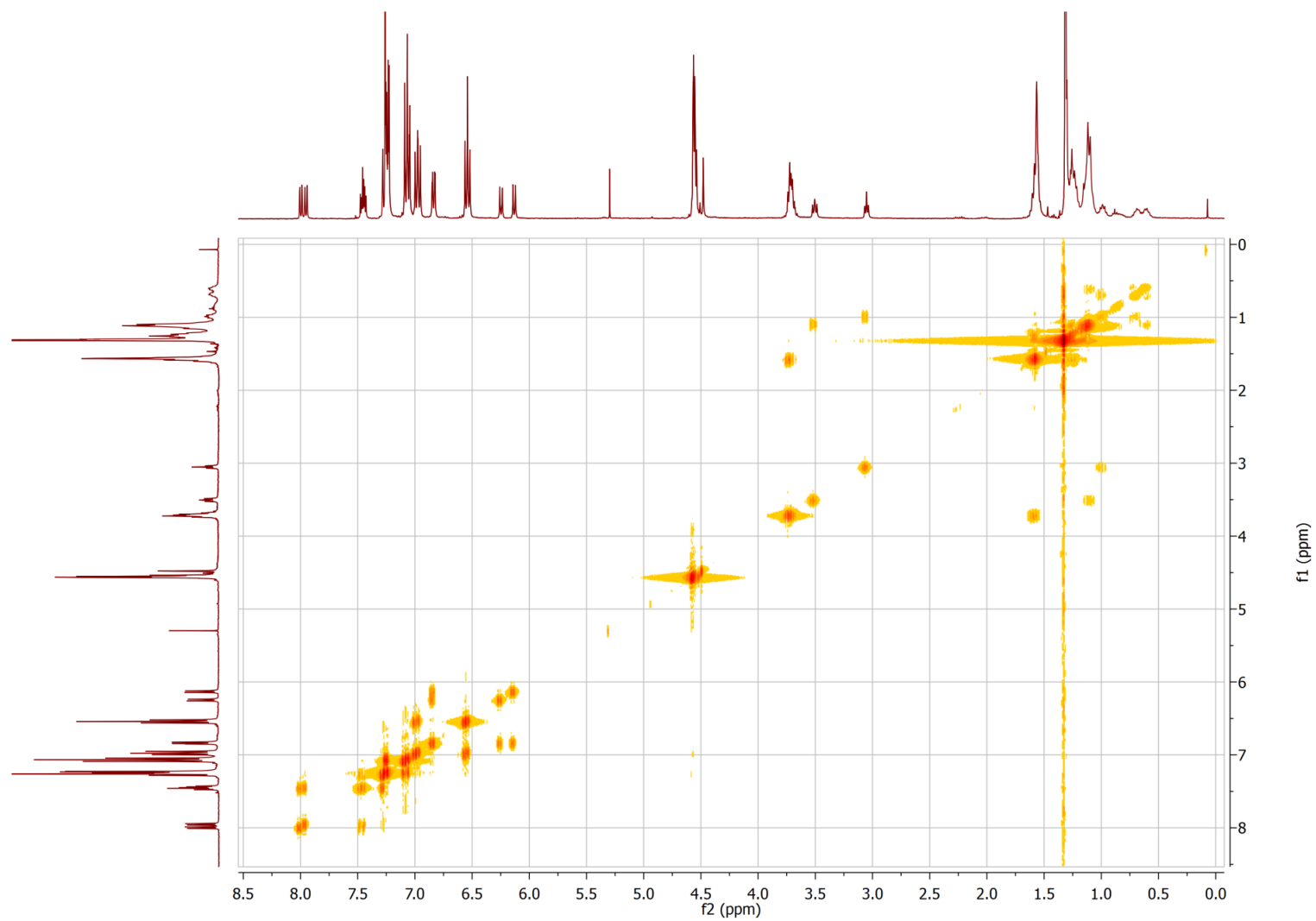
[3]Rotaxane S8 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



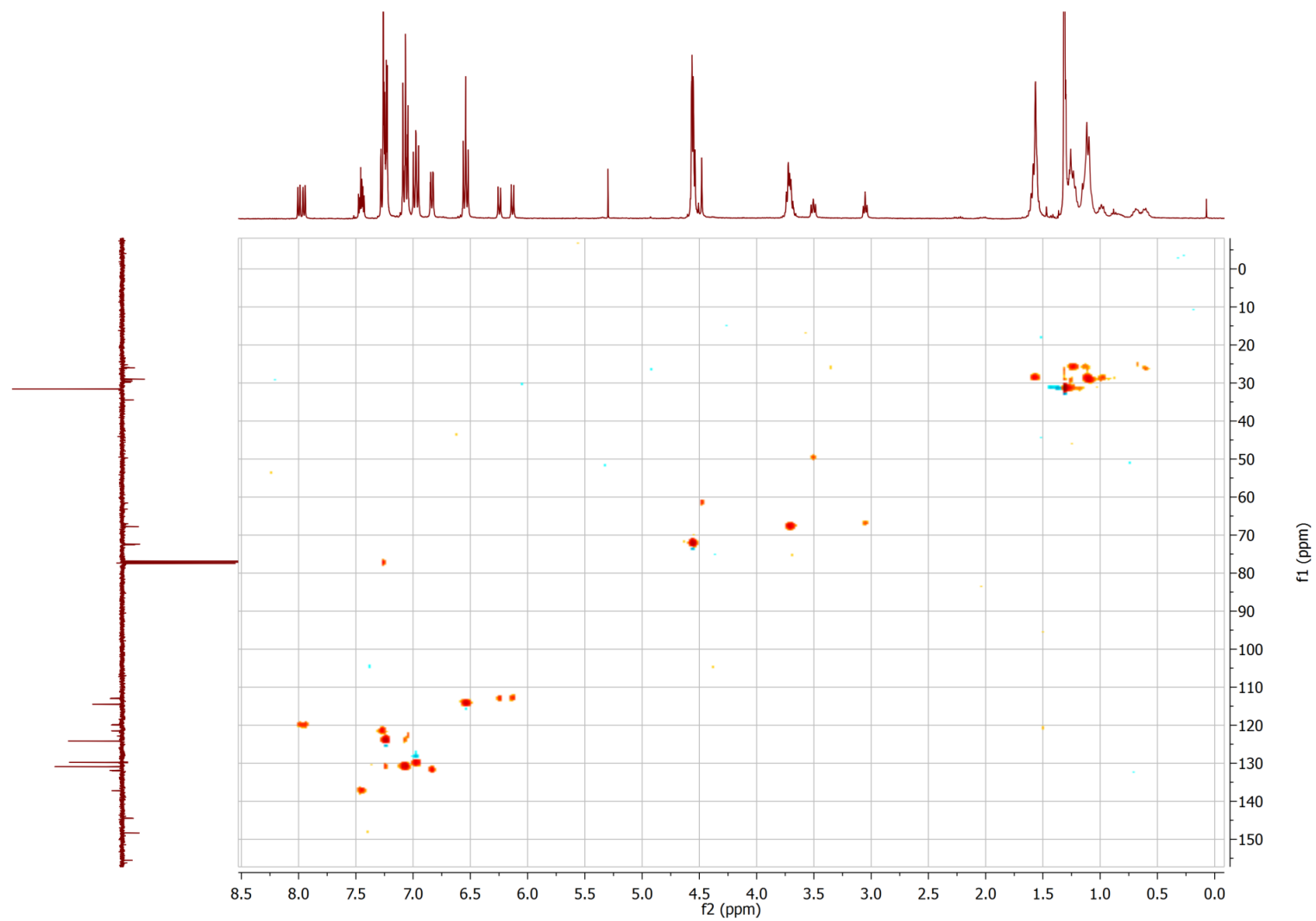
[3]Rotaxane S8 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



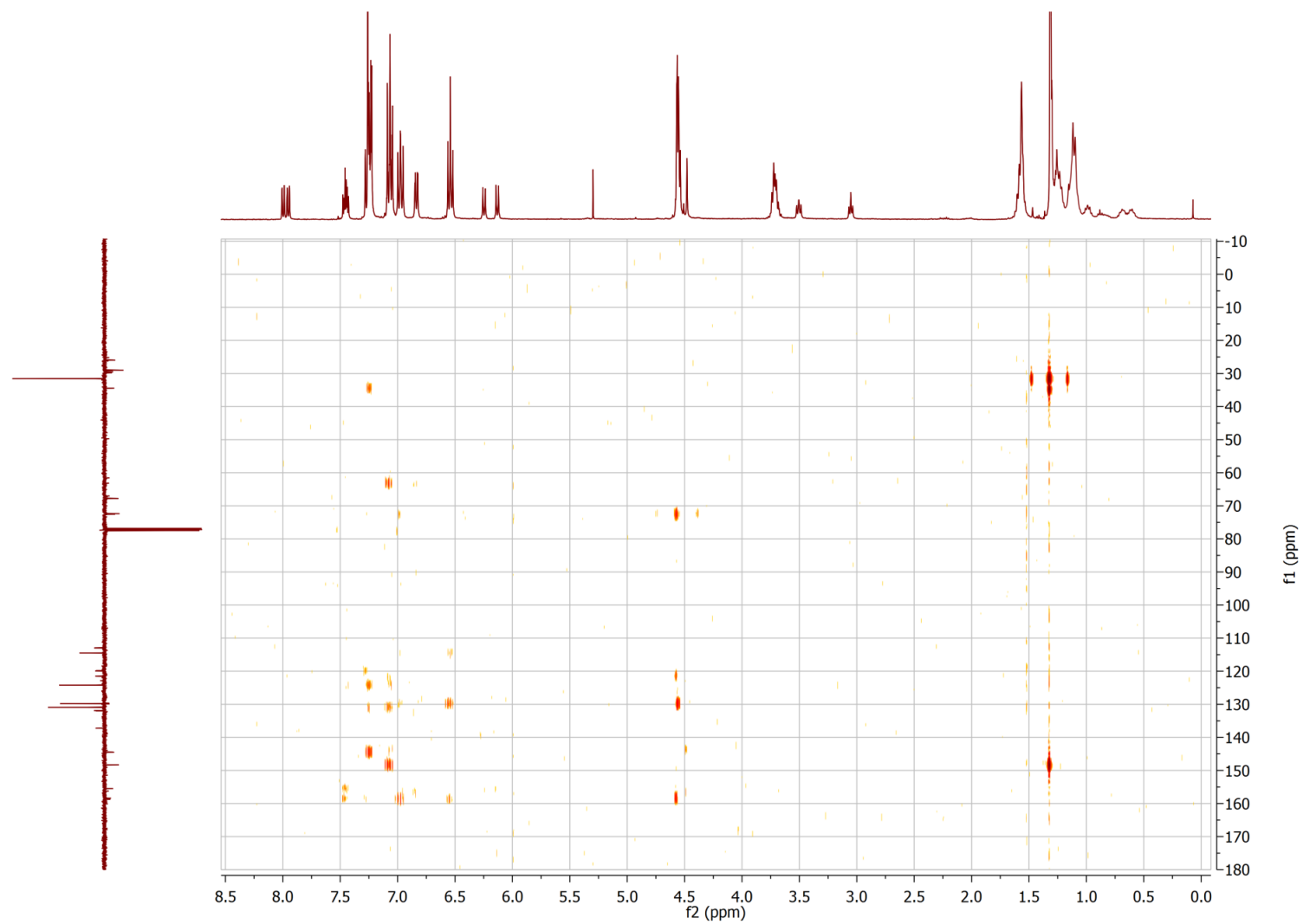
[3]Rotaxane S8 COSY (CDCl₃, 400 MHz, 300 K)



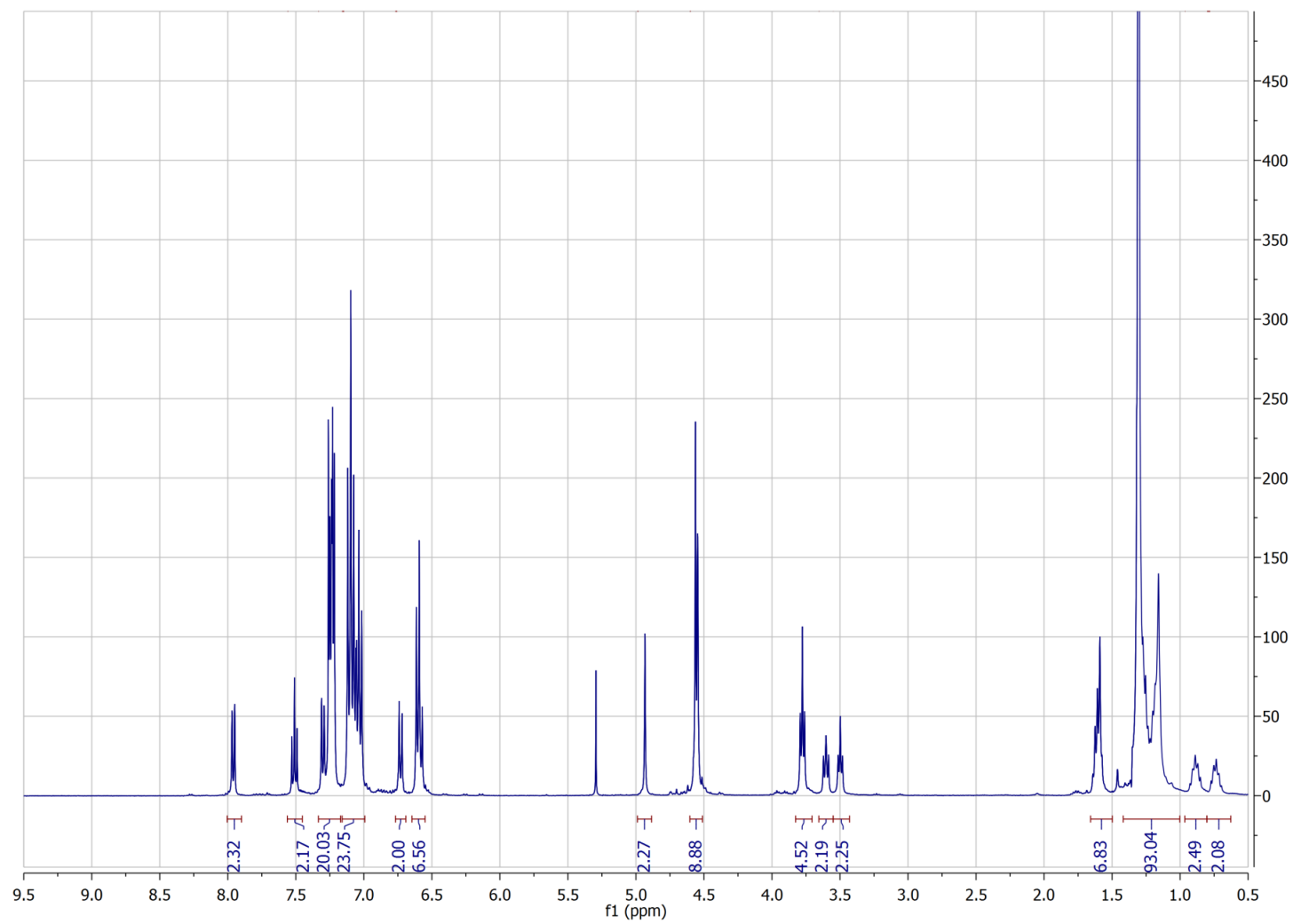
[3]Rotaxane S8 HSQC NMR (CDCl₃, 400 MHz, 300 K)



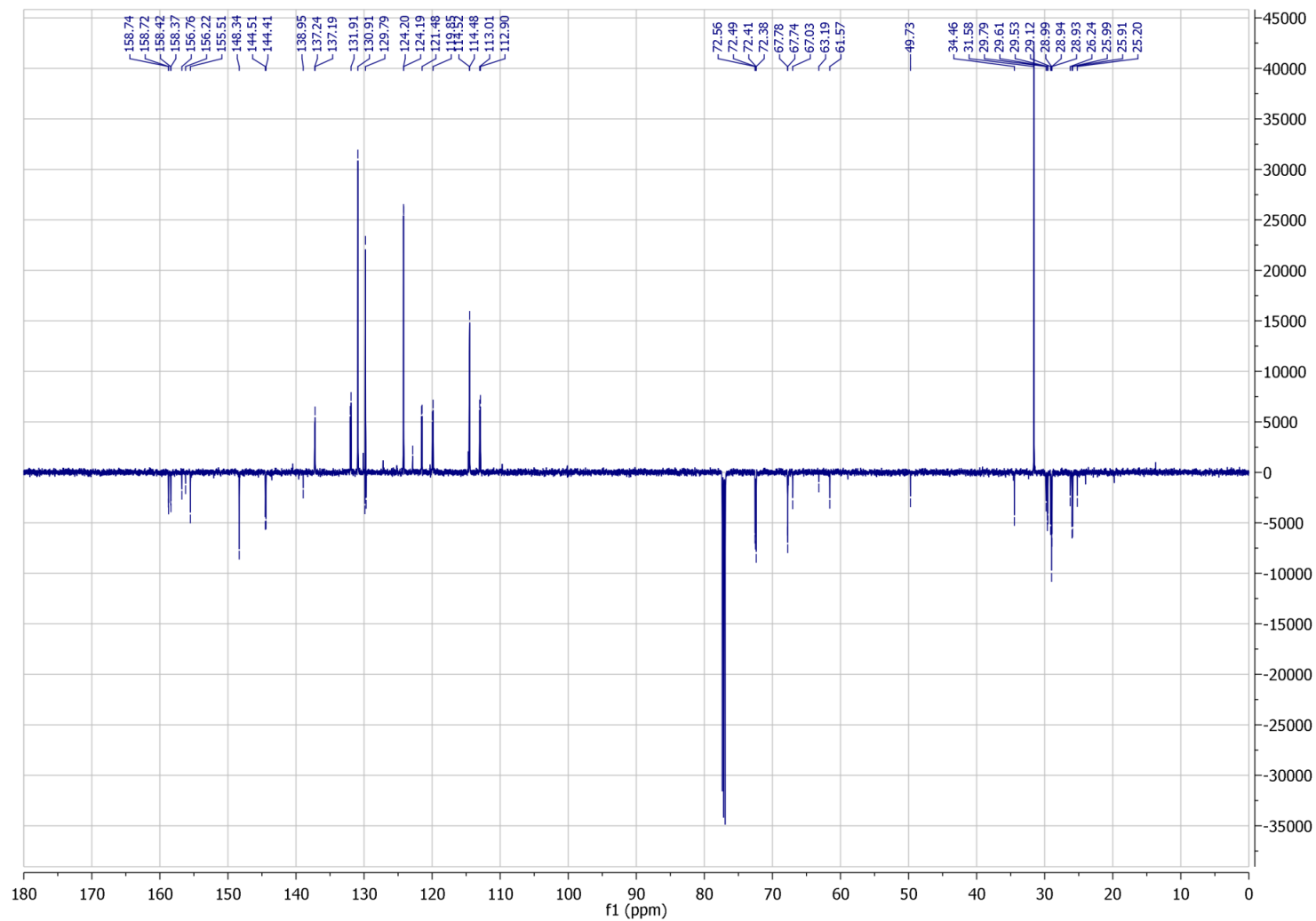
[3]Rotaxane S8 HMBC NMR (CDCl₃, 400 MHz, 300 K)



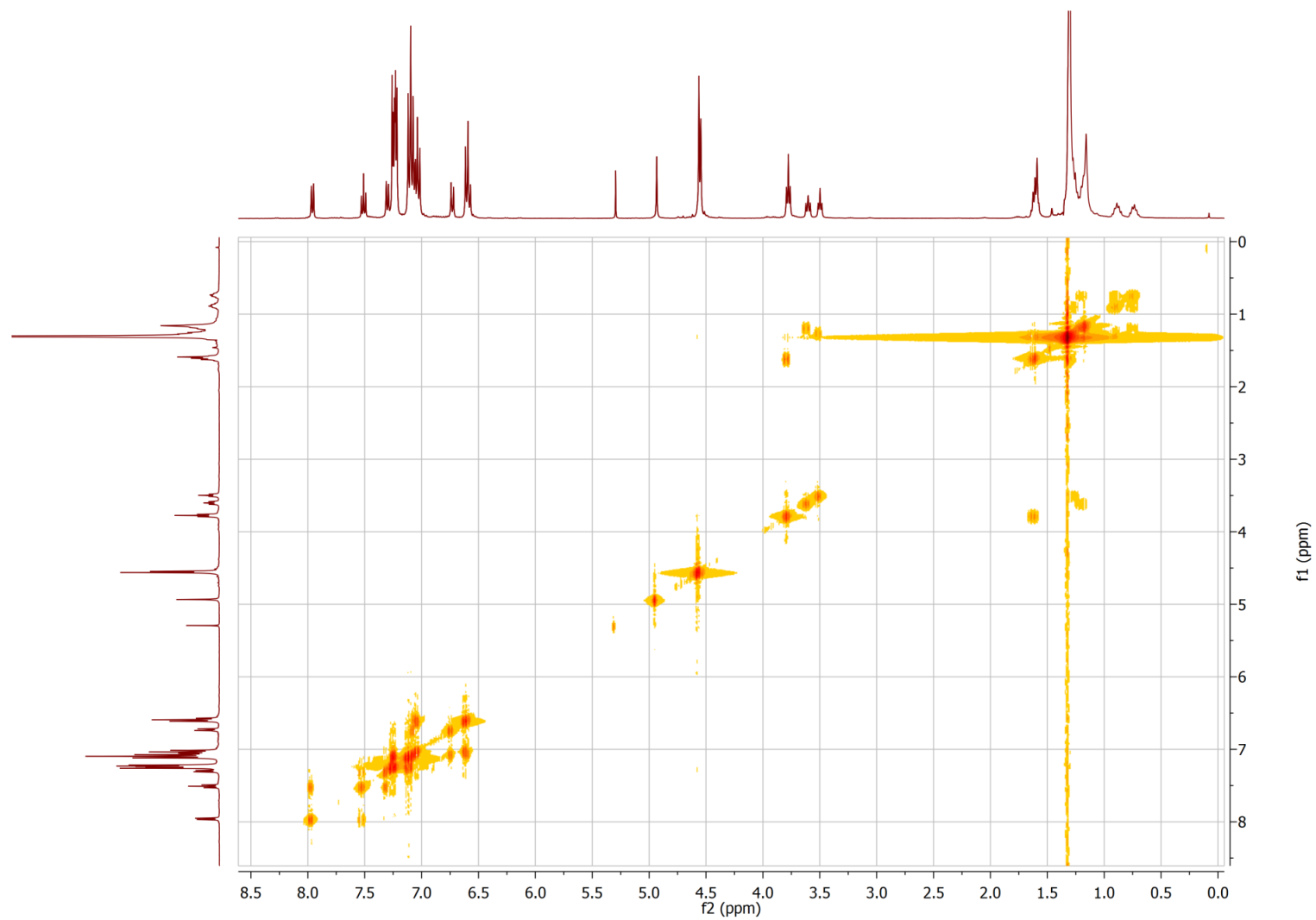
[2]Rotaxane S9 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



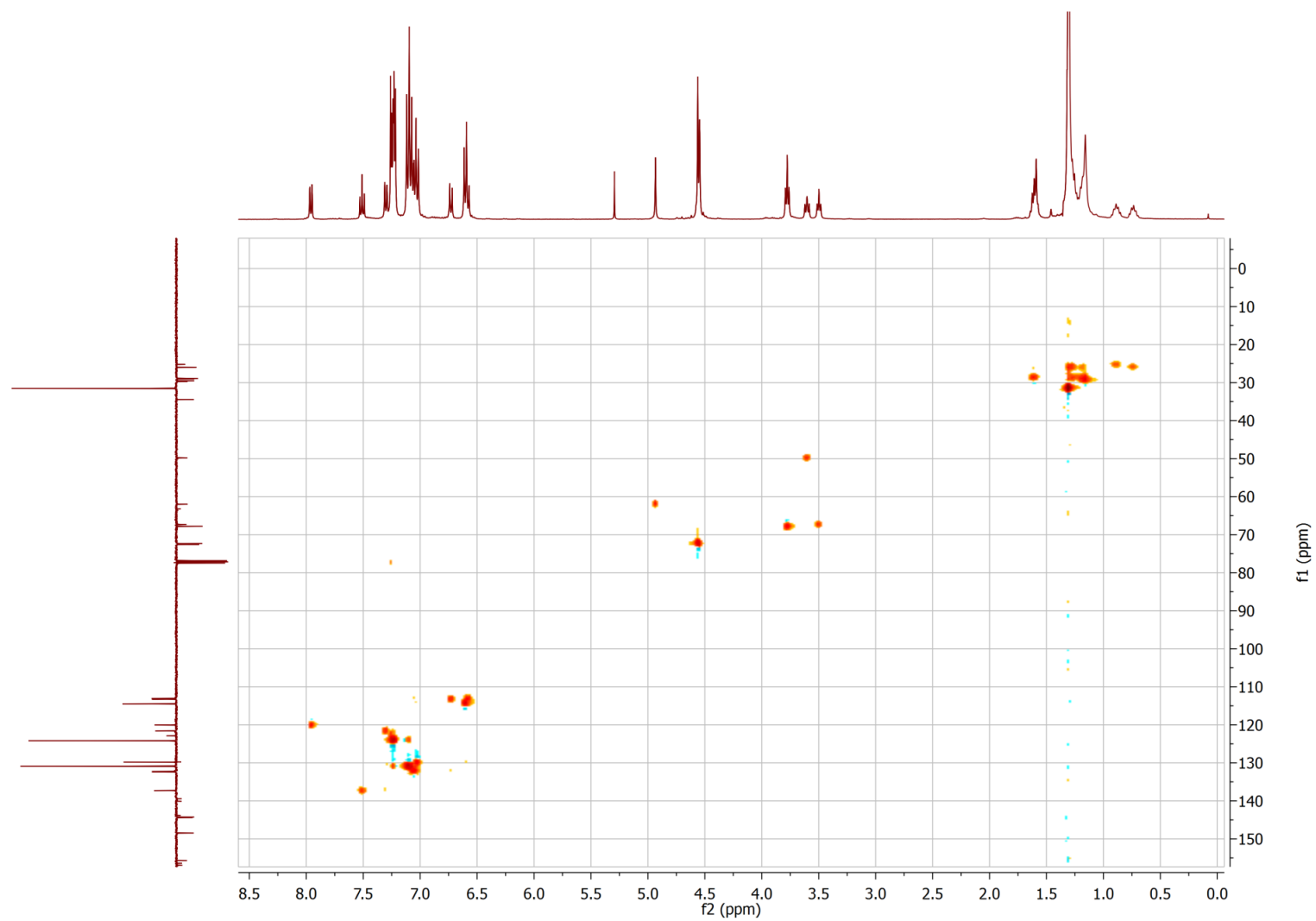
[2]Rotaxane S9 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



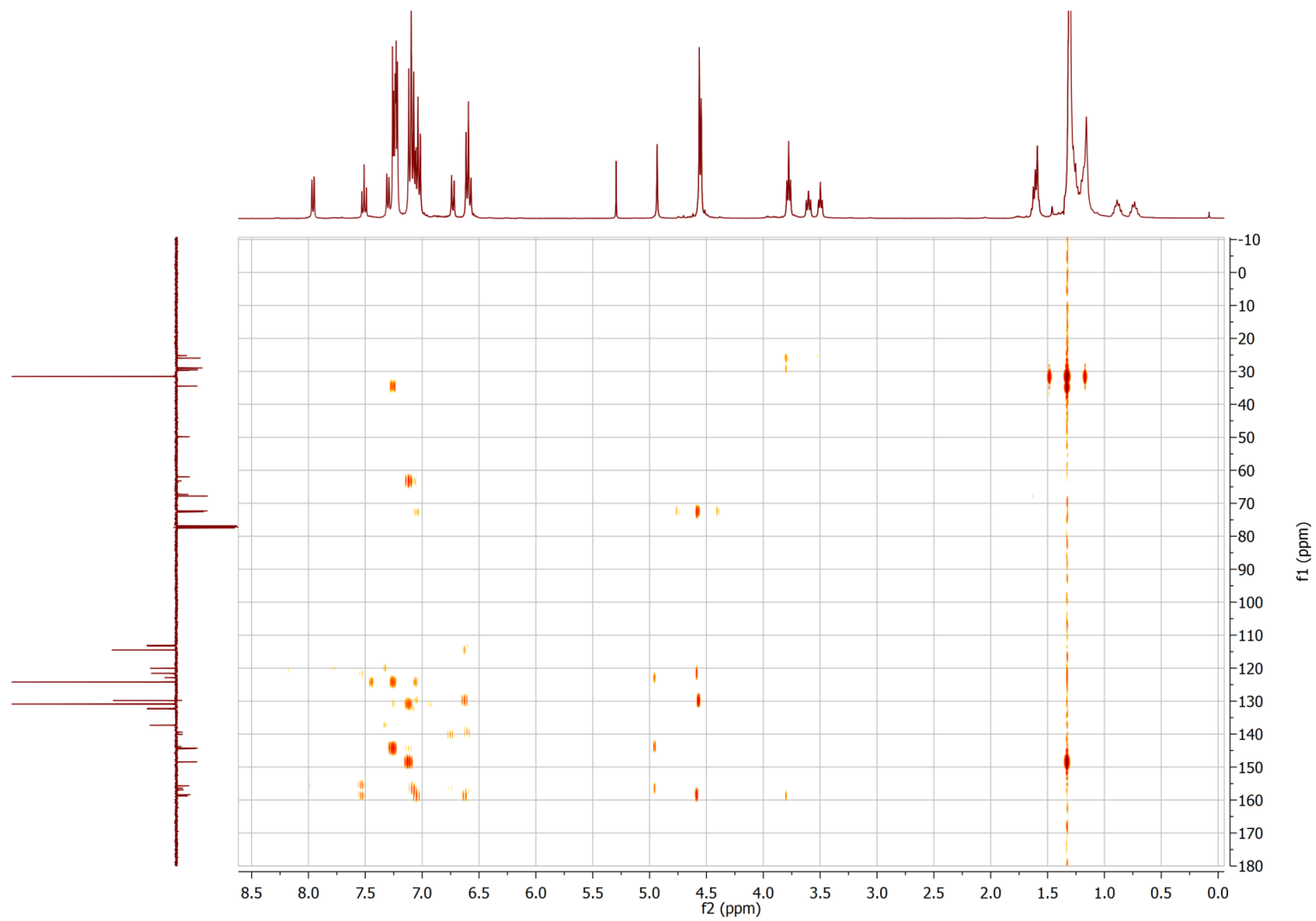
[2]Rotaxane S9 COSY (CDCl₃, 400 MHz, 300 K)



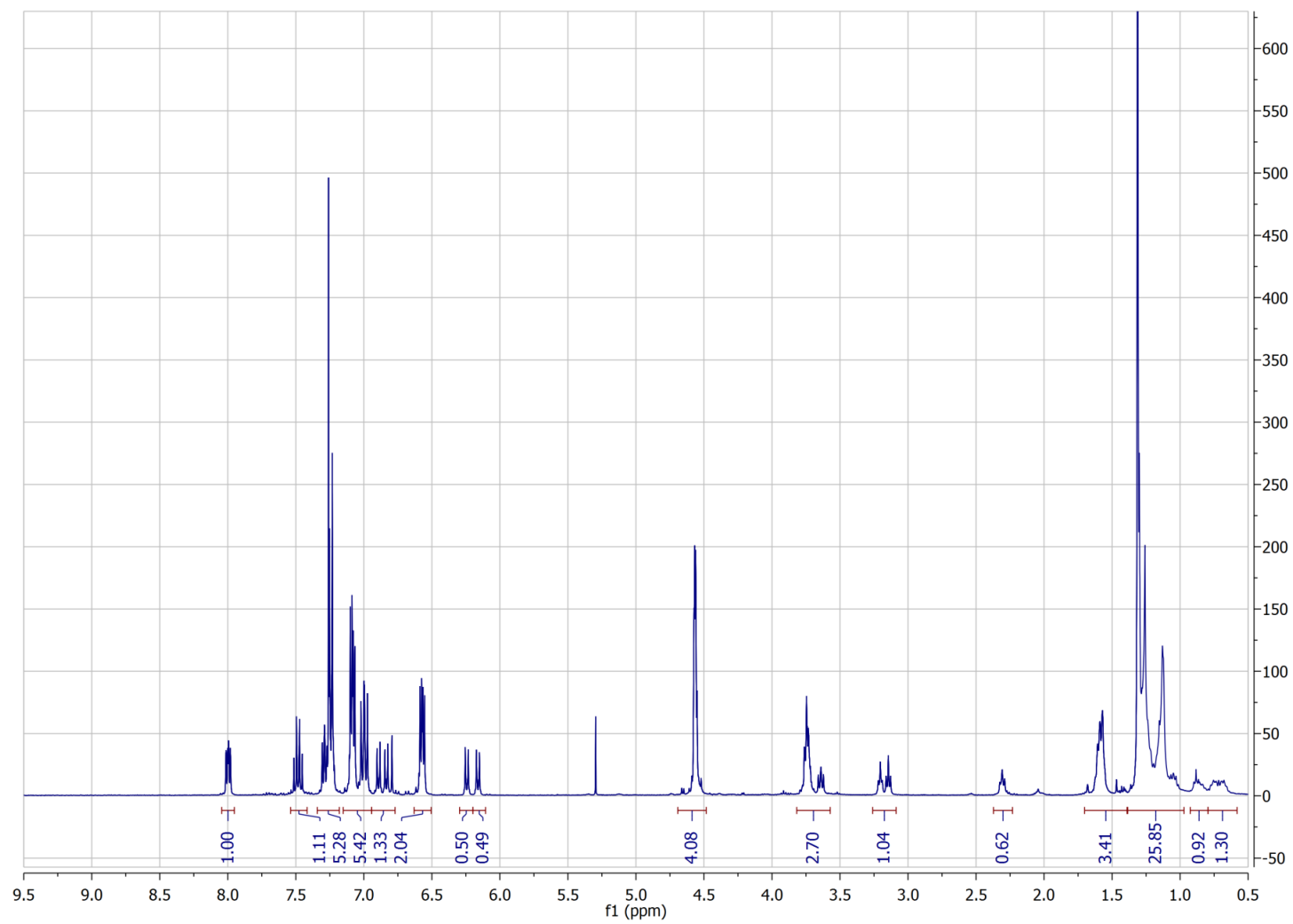
[2]Rotaxane S9 HSQC NMR (CDCl₃, 400 MHz, 300 K)



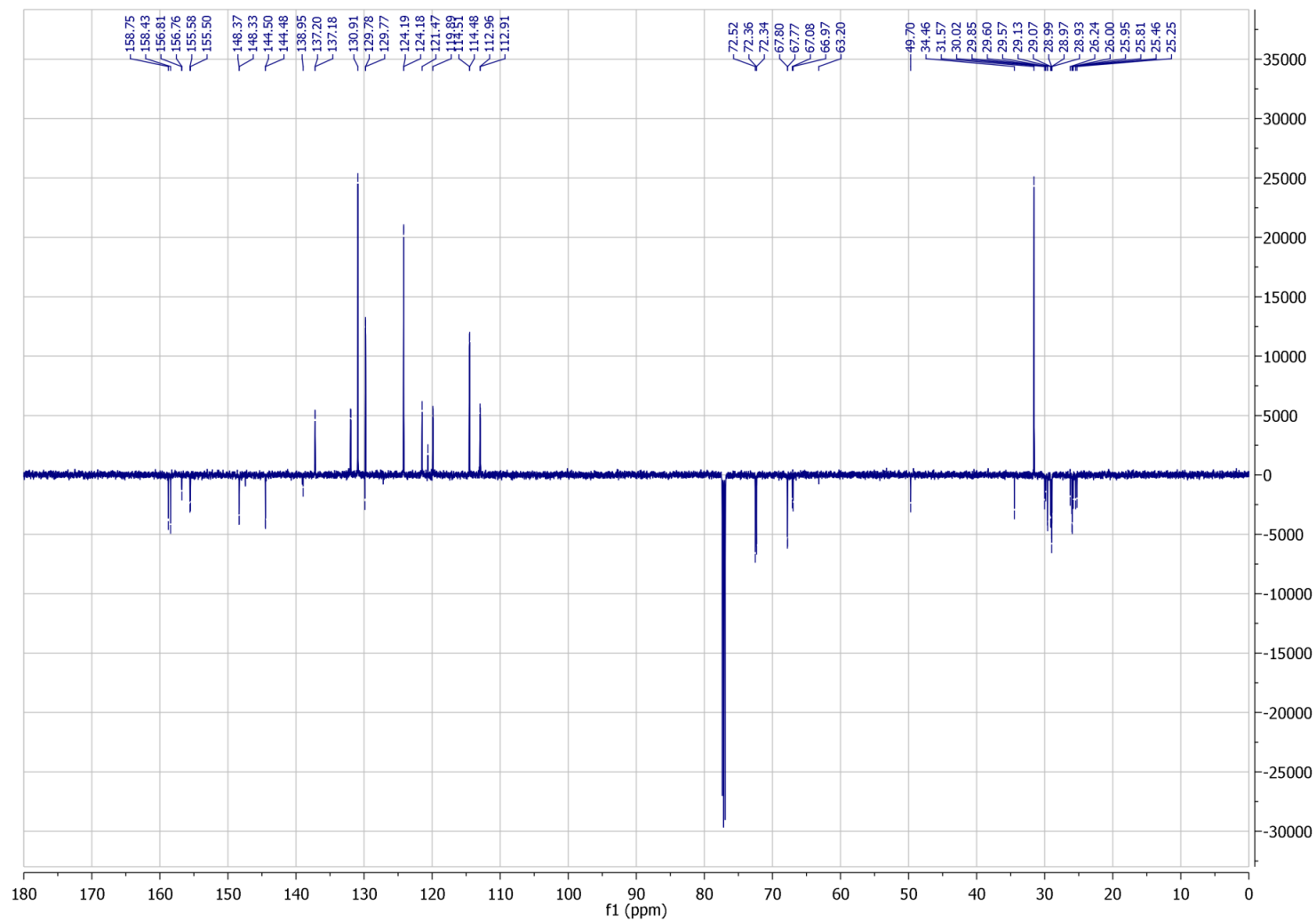
[2]Rotaxane S9 HMBC NMR (CDCl₃, 400 MHz, 300 K)



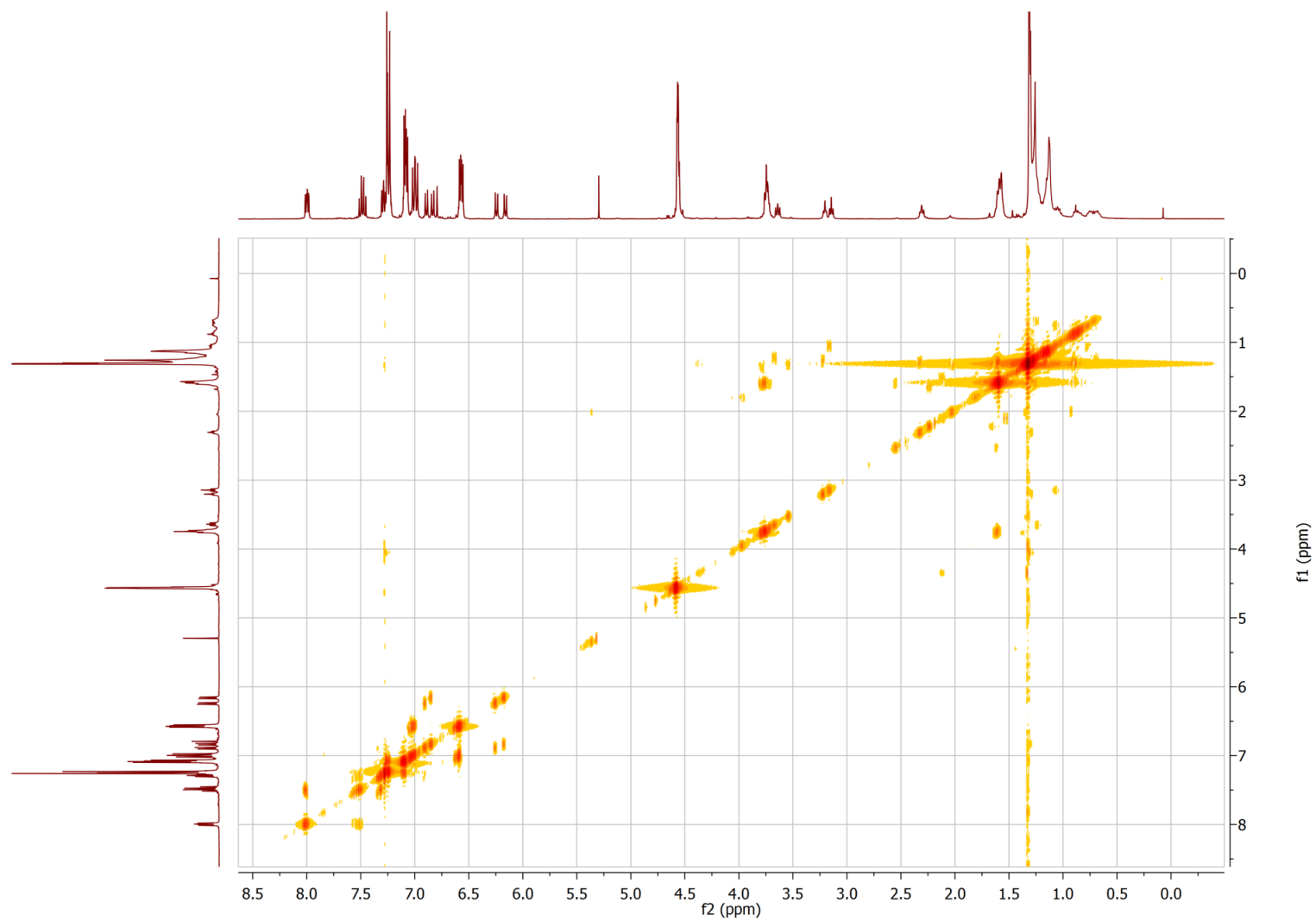
[3]Rotaxane S10a ^1H NMR (CDCl_3 , 400 MHz, 300 K)



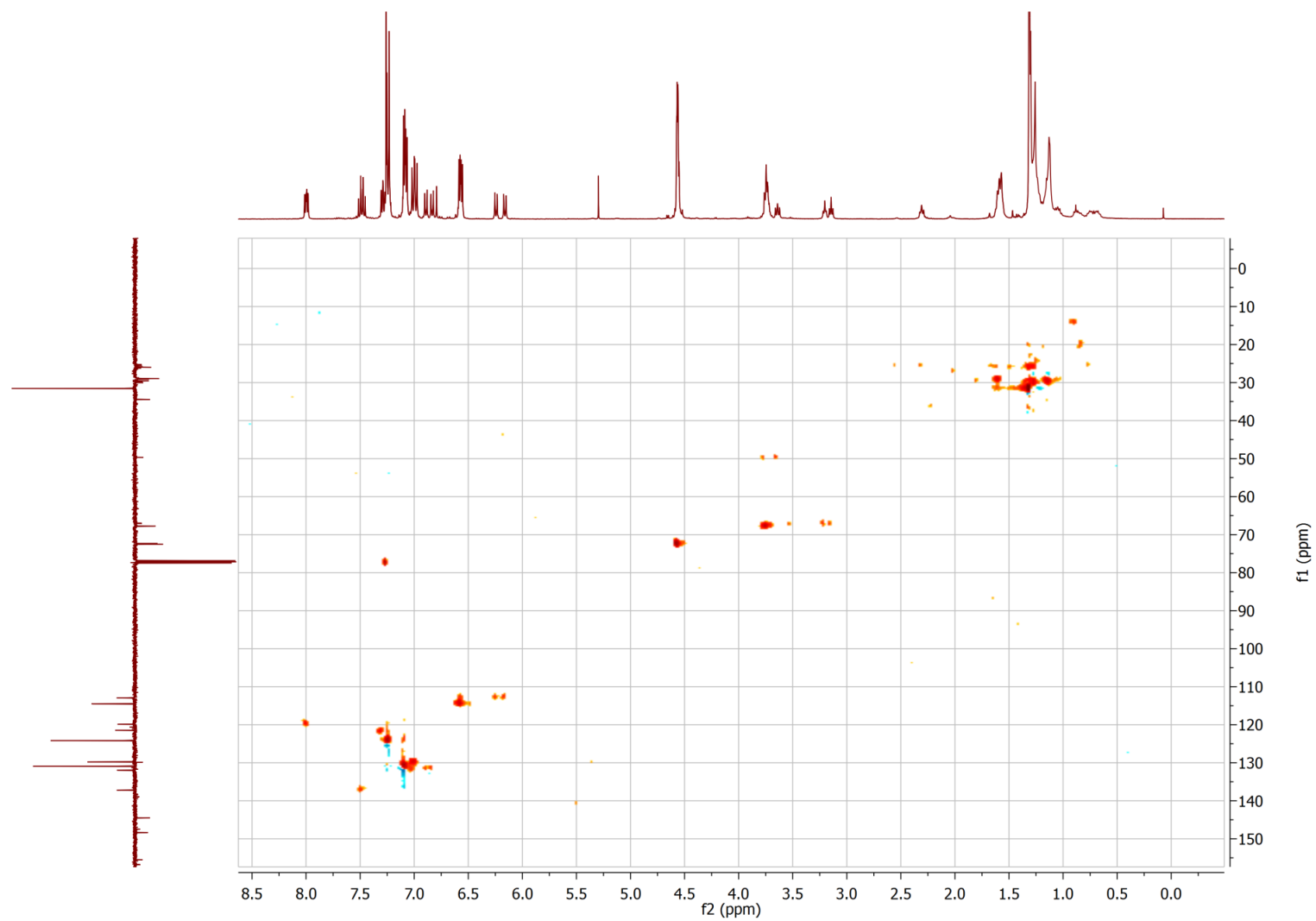
[3]Rotaxane S10a DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



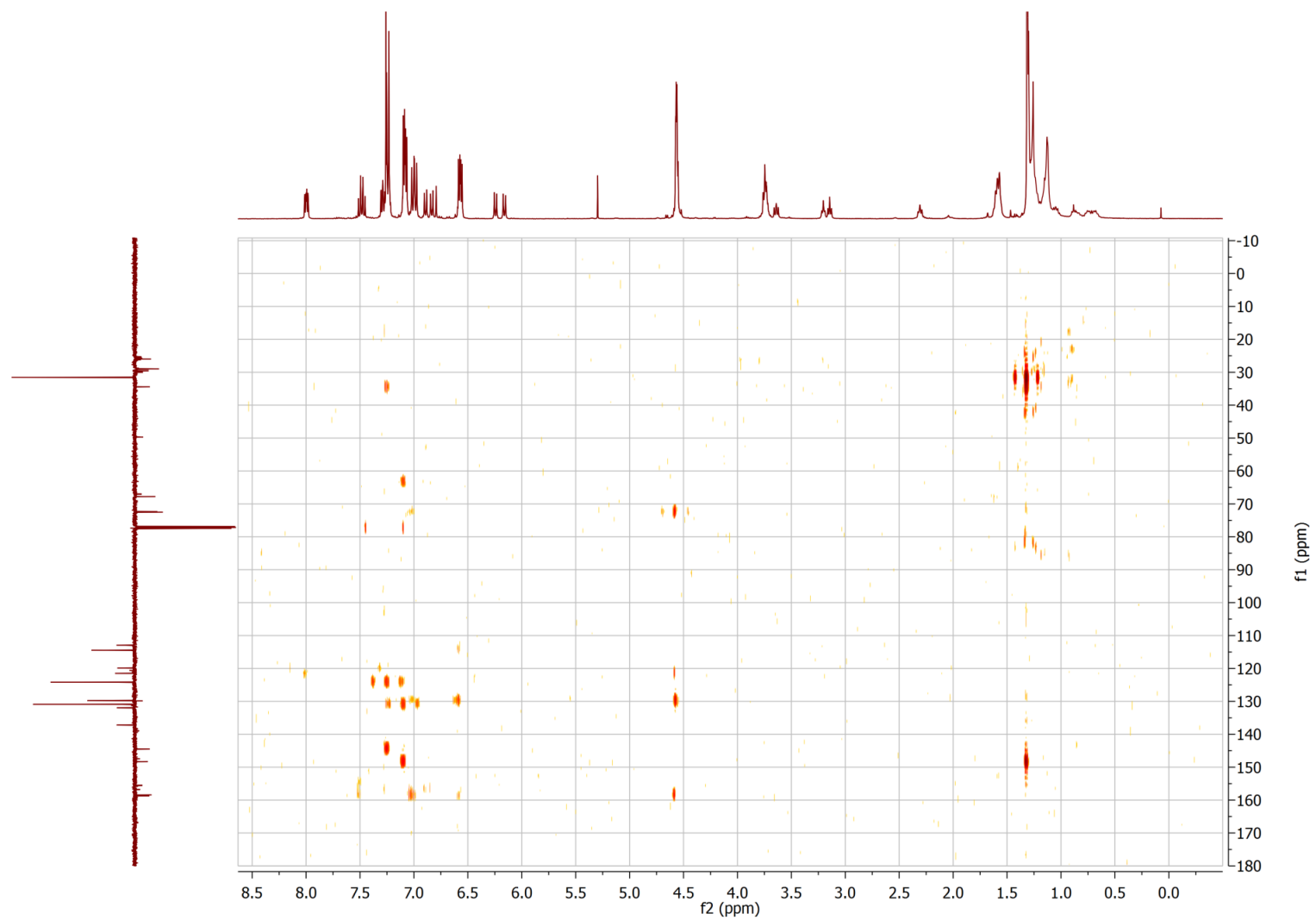
[3]Rotaxane S10a COSY (CDCl₃, 600 MHz, 300 K)



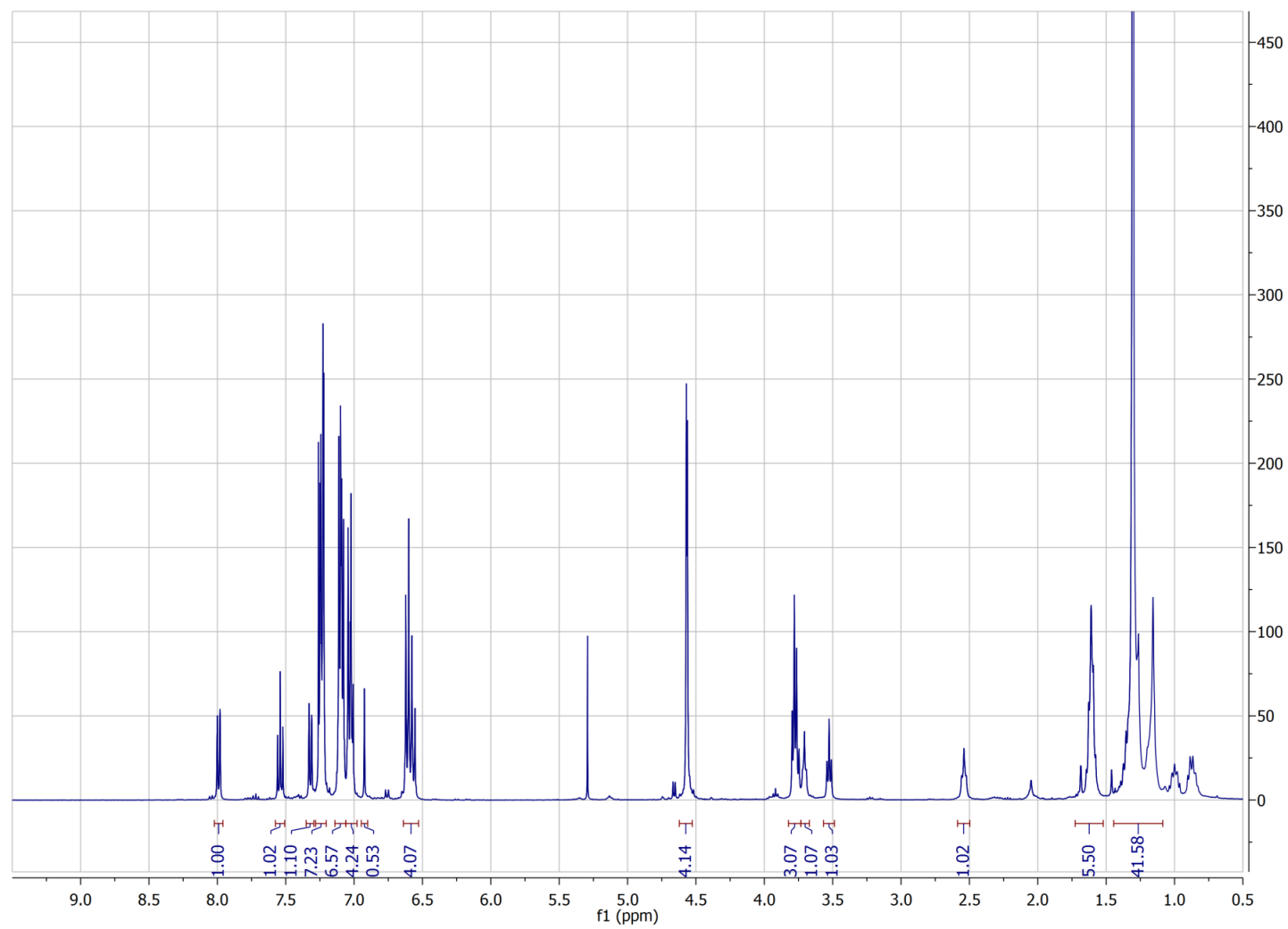
[3]Rotaxane S10a HSQC NMR (CDCl₃, 600 MHz, 300 K)



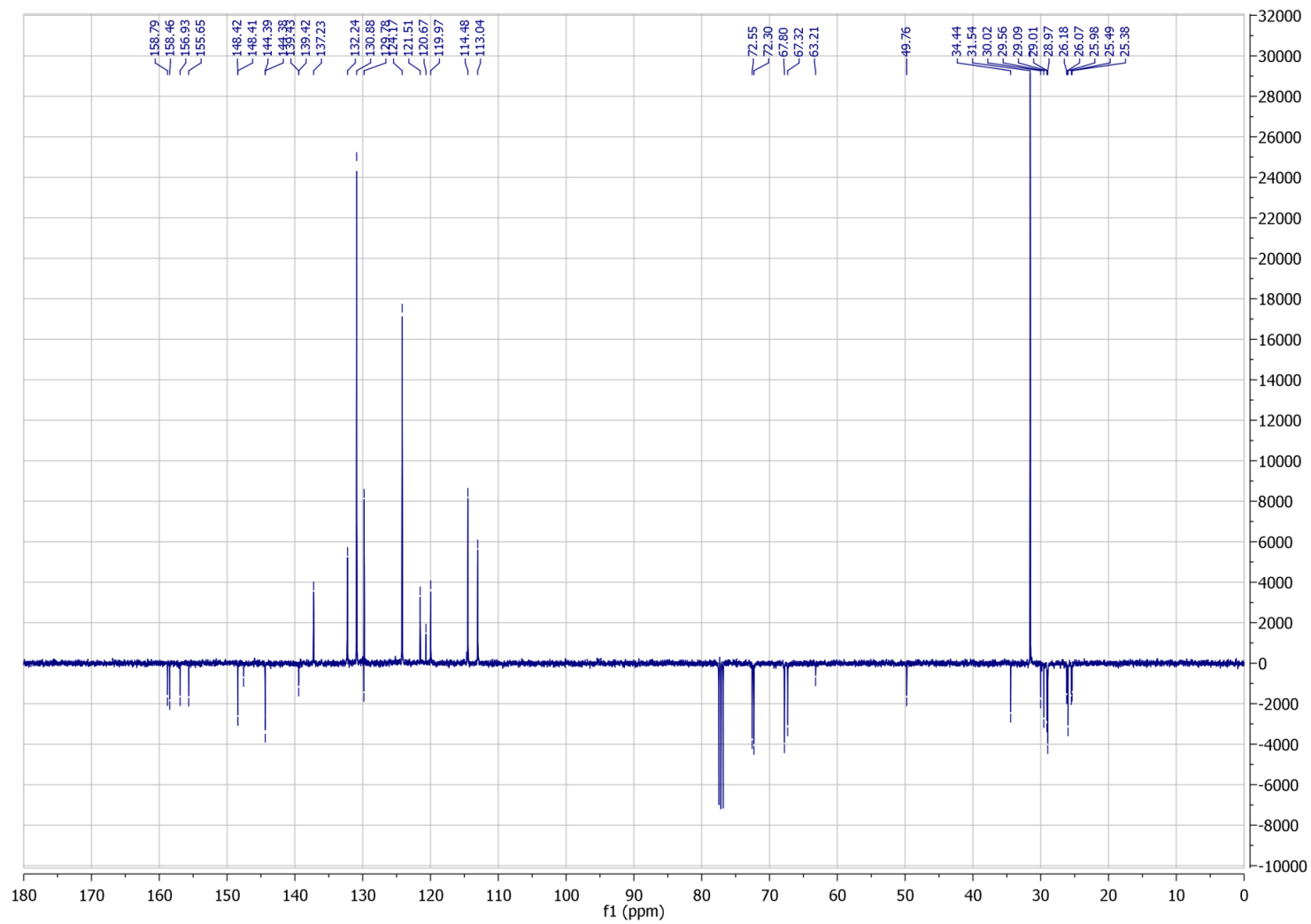
[3]Rotaxane S10a HMBC NMR (CDCl₃, 600 MHz, 300 K)



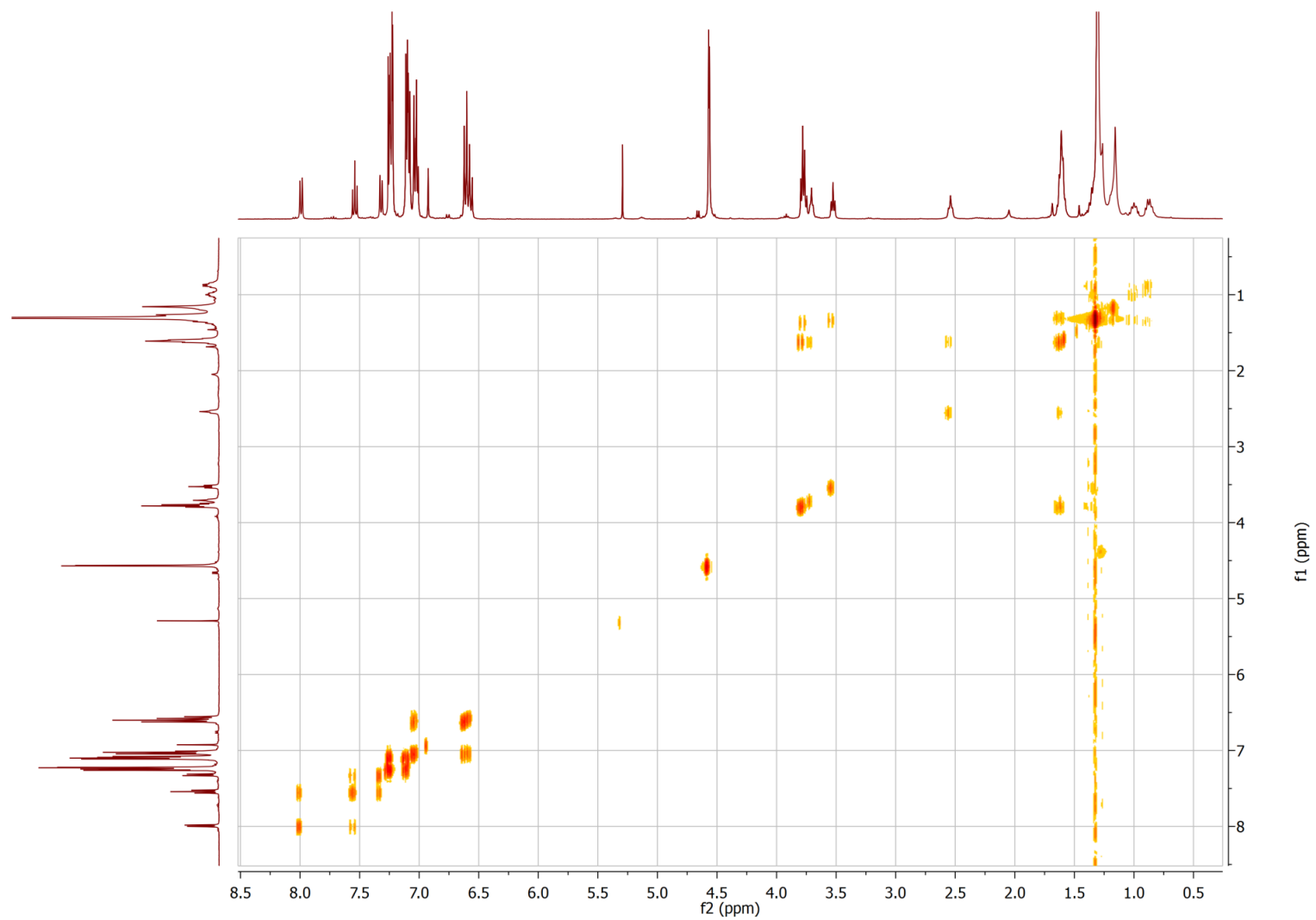
[2]Rotaxane S11a ^1H NMR (CDCl_3 , 400 MHz, 300 K)



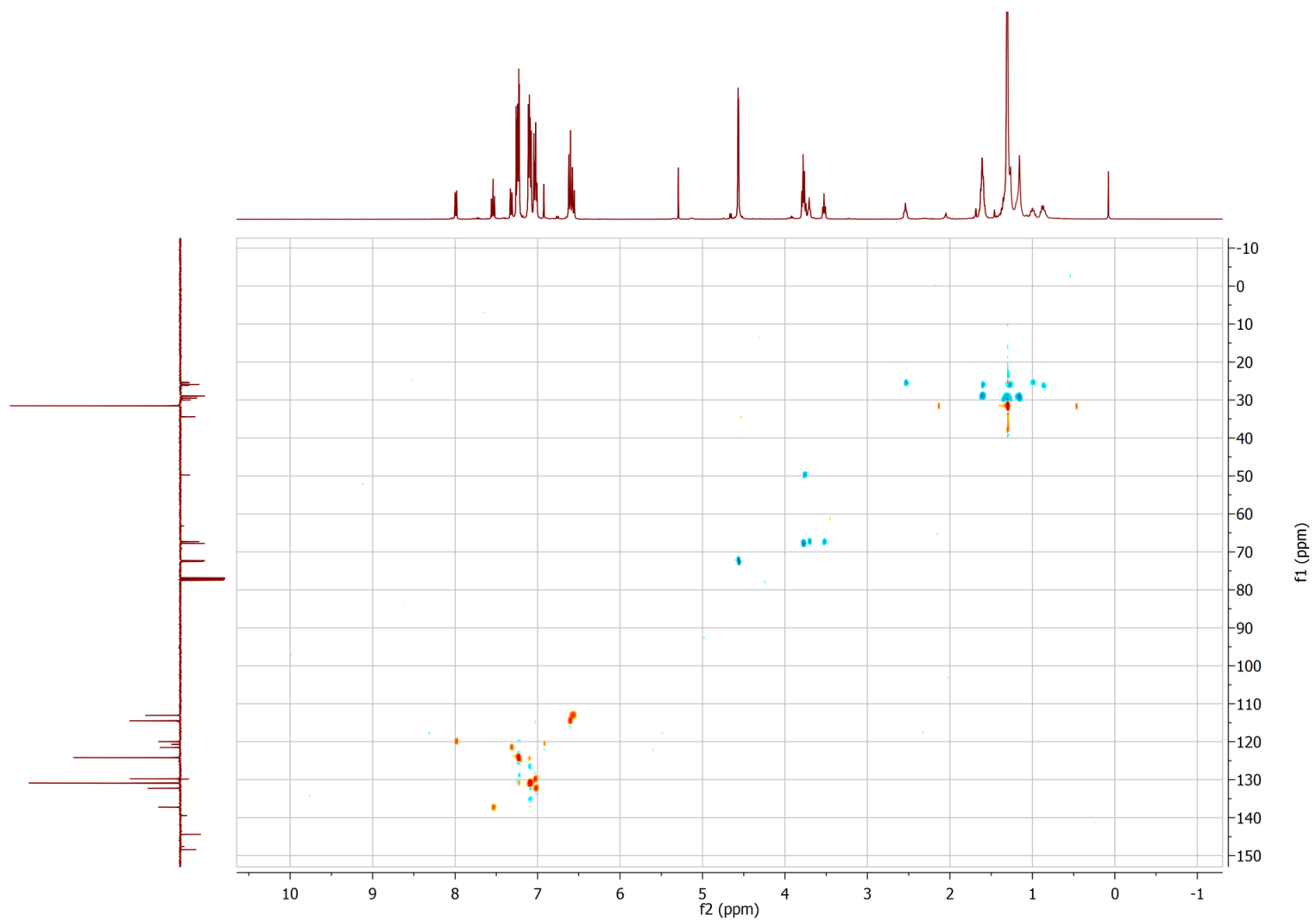
[2]Rotaxane S11a DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



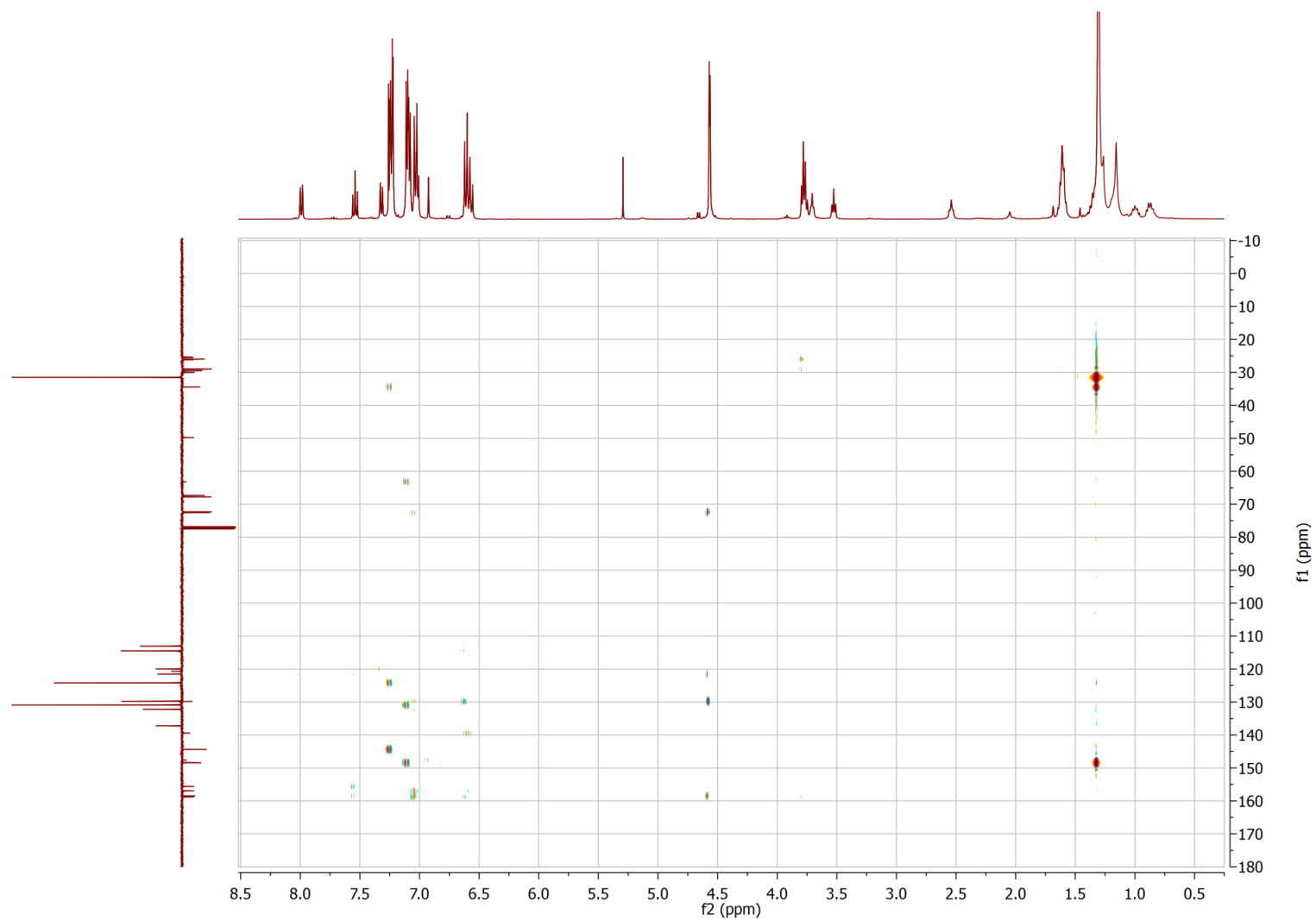
[2]Rotaxane S11a COSY (CDCl₃, 400 MHz, 300 K)



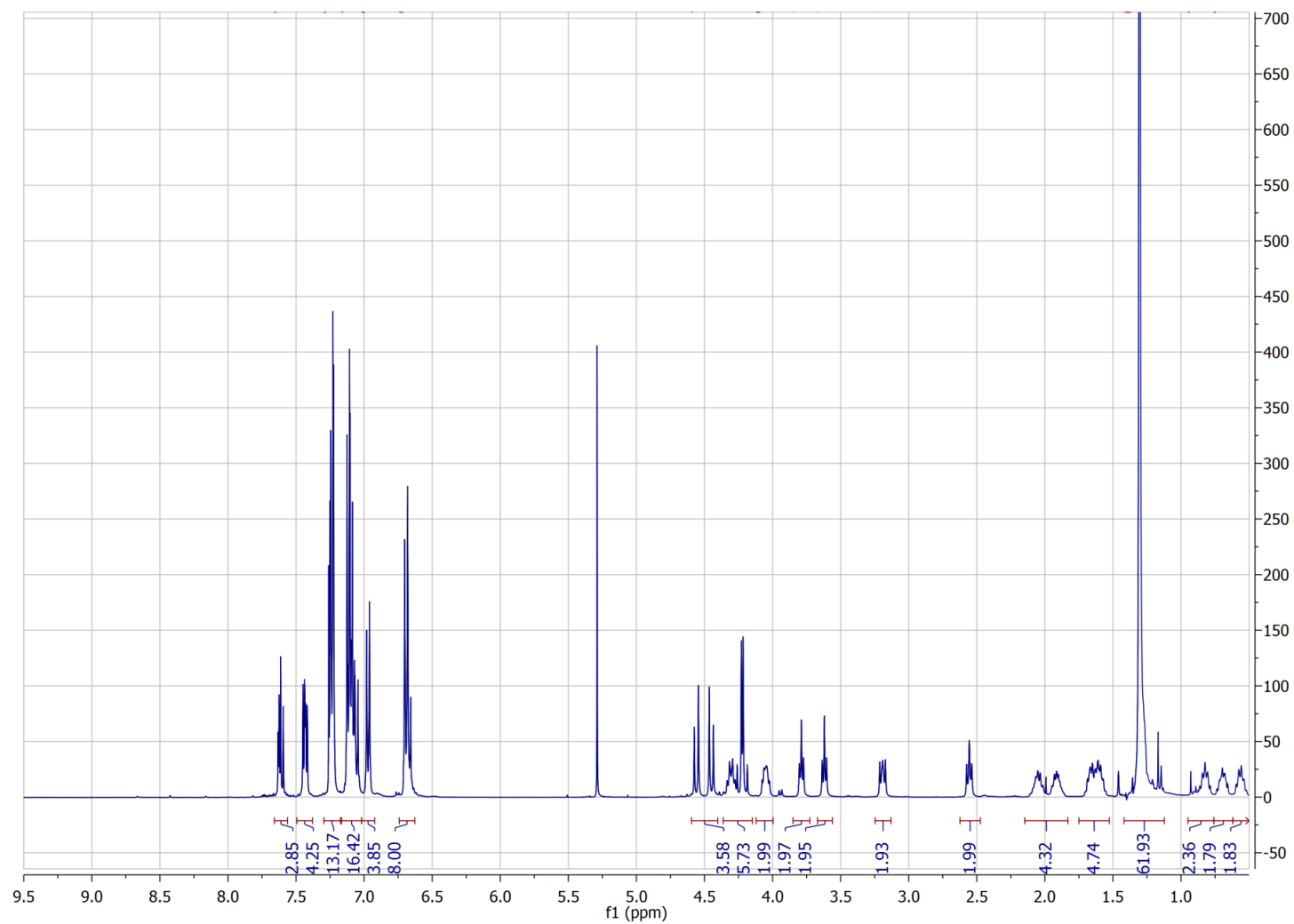
[2]Rotaxane S11a HSQC NMR (CDCl₃, 400 MHz, 300 K)



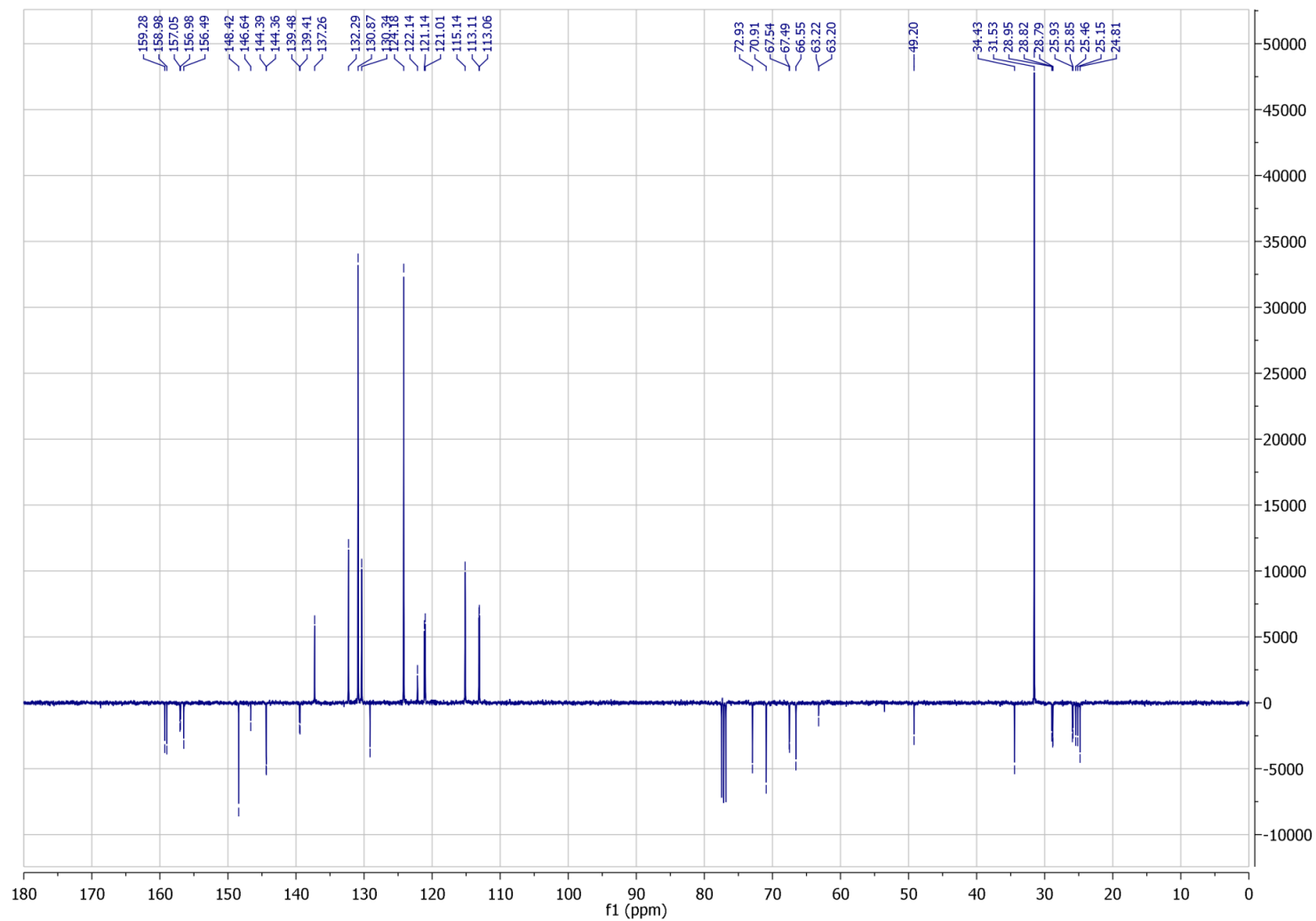
[2]Rotaxane S11a HMBC NMR (CDCl₃, 400 MHz, 300 K)



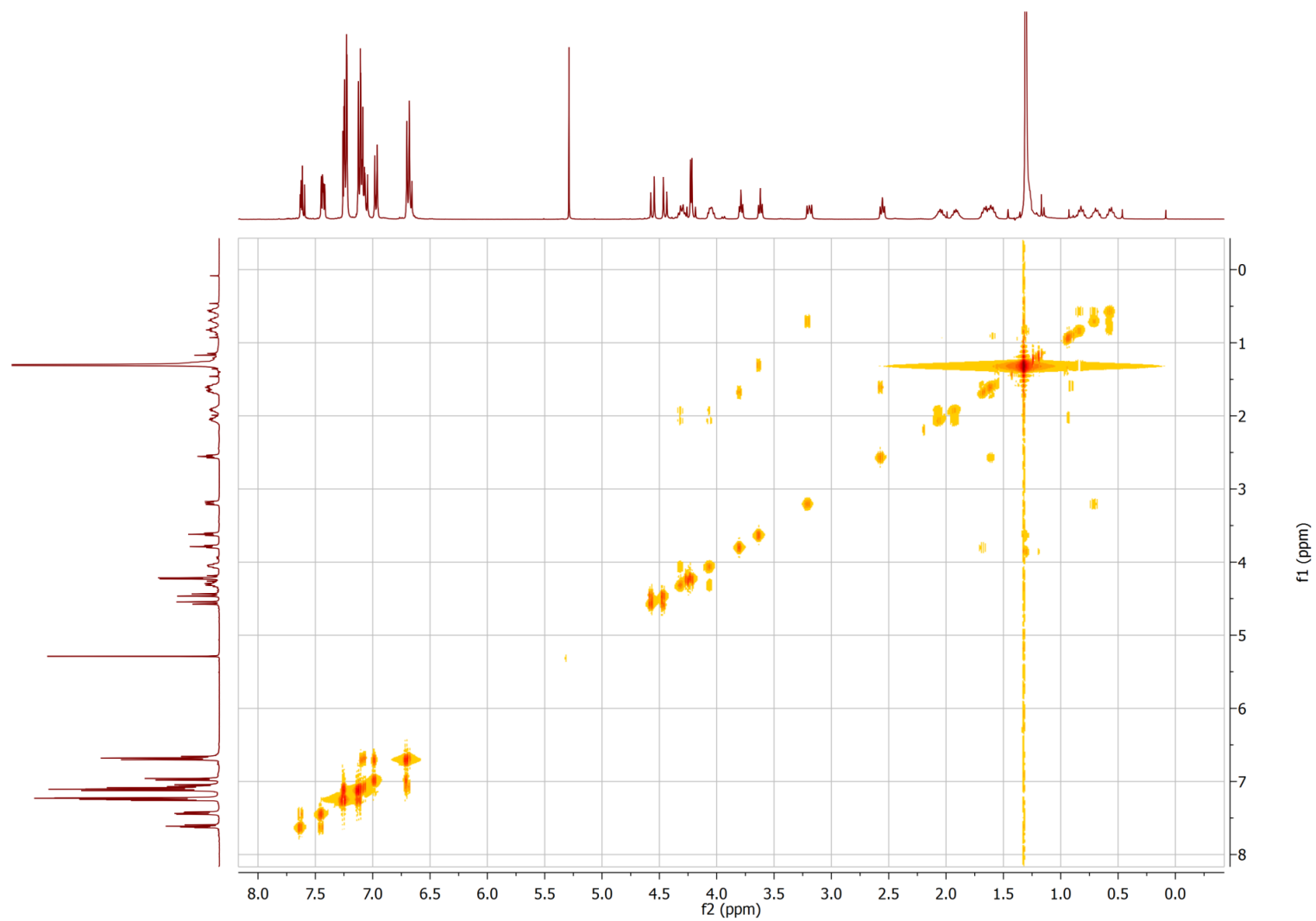
[2]Rotaxane S11d ^1H NMR (CDCl_3 , 400 MHz, 300 K)



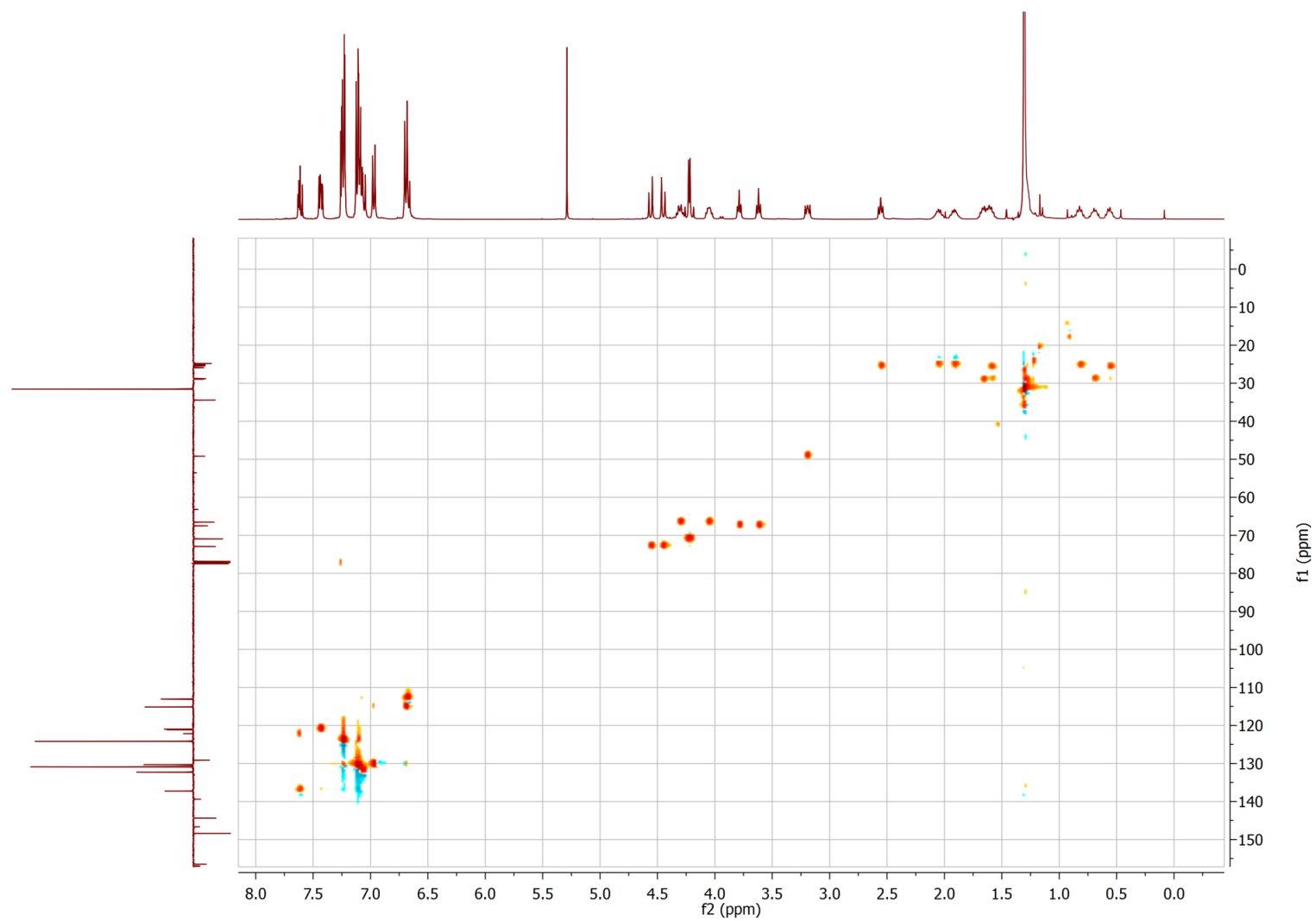
[2]Rotaxane S11d DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



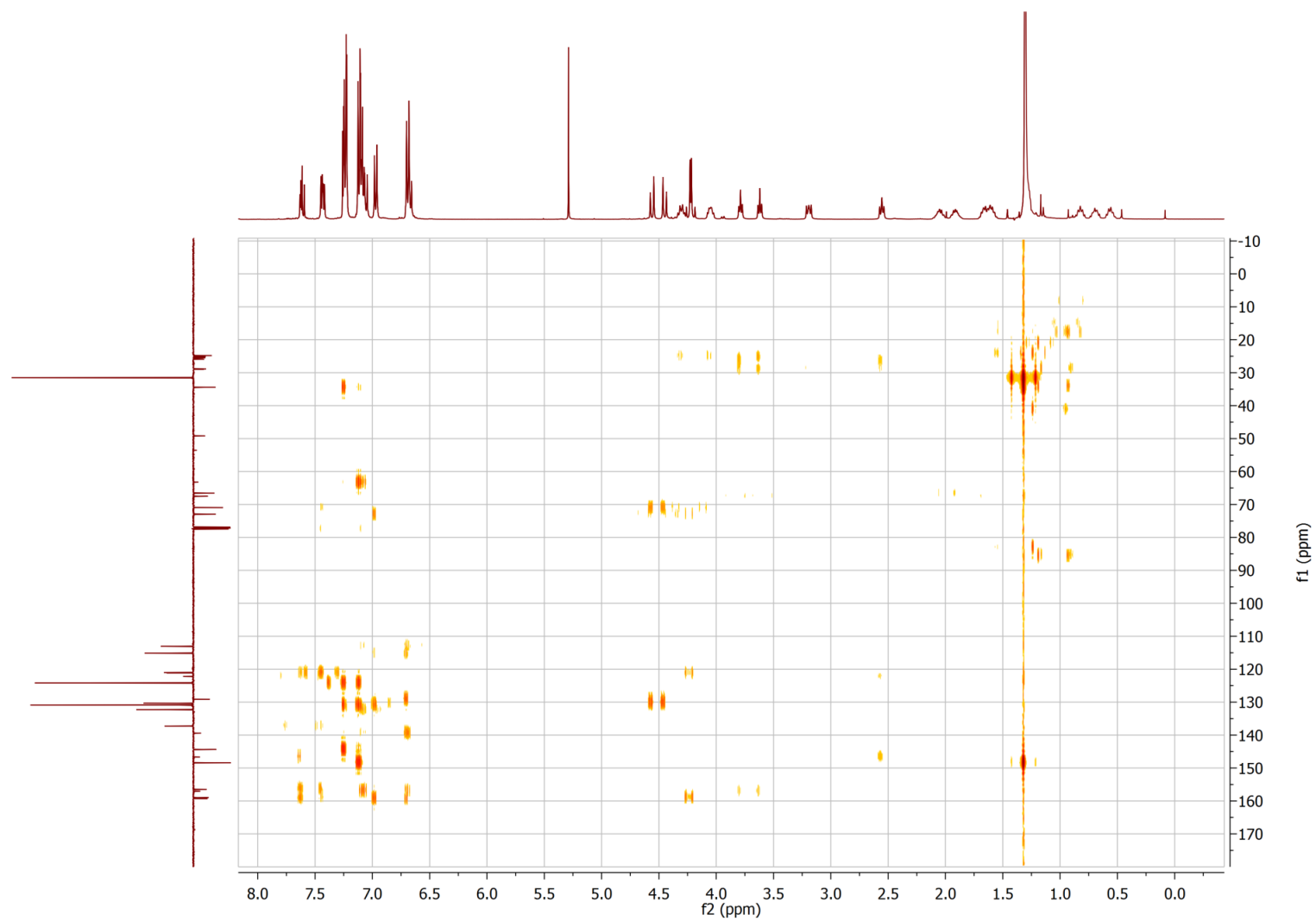
[2]Rotaxane S11d COSY (CDCl₃, 600 MHz, 300 K)



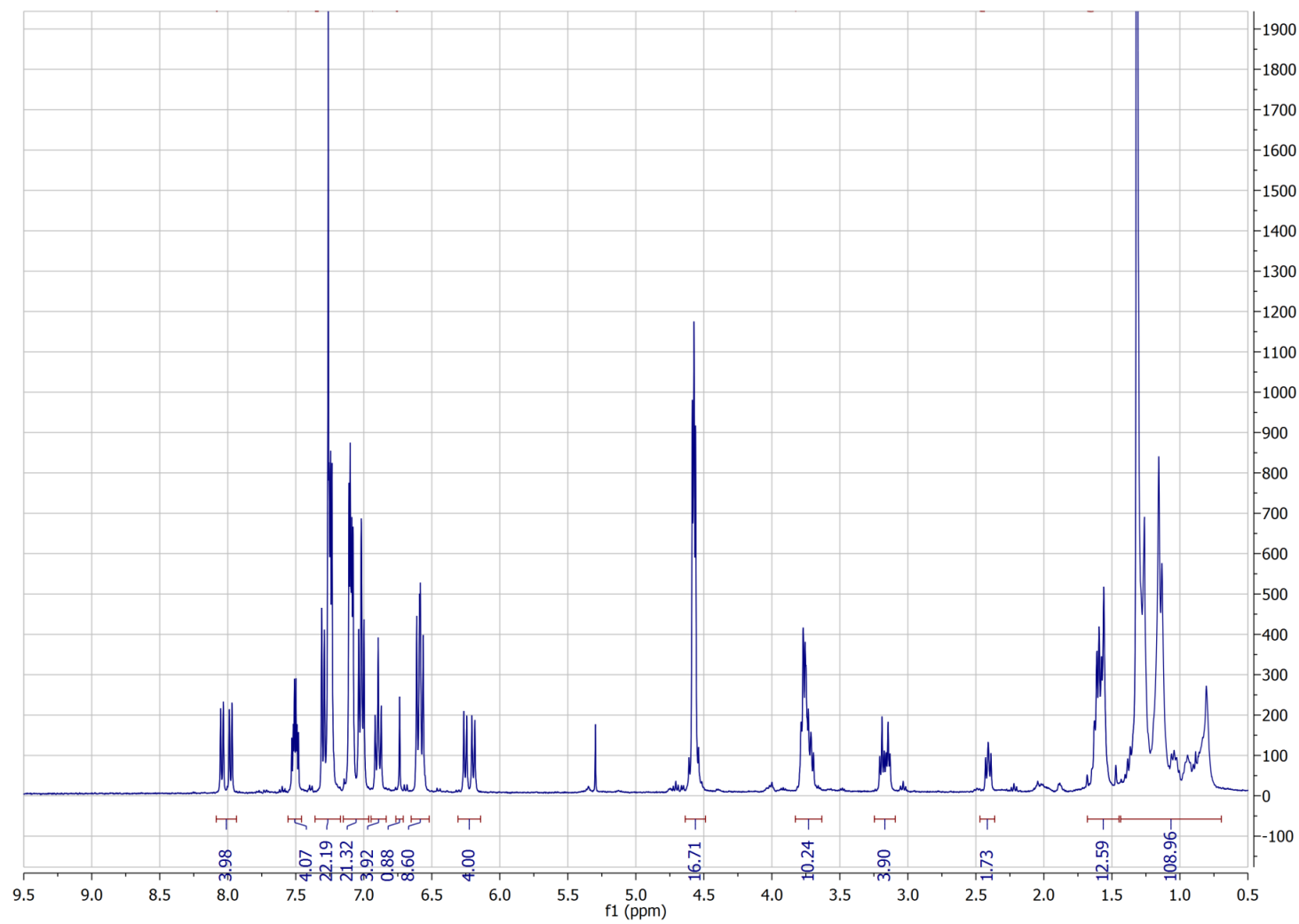
[2]Rotaxane S11d HSQC NMR (CDCl₃, 600 MHz, 300 K)



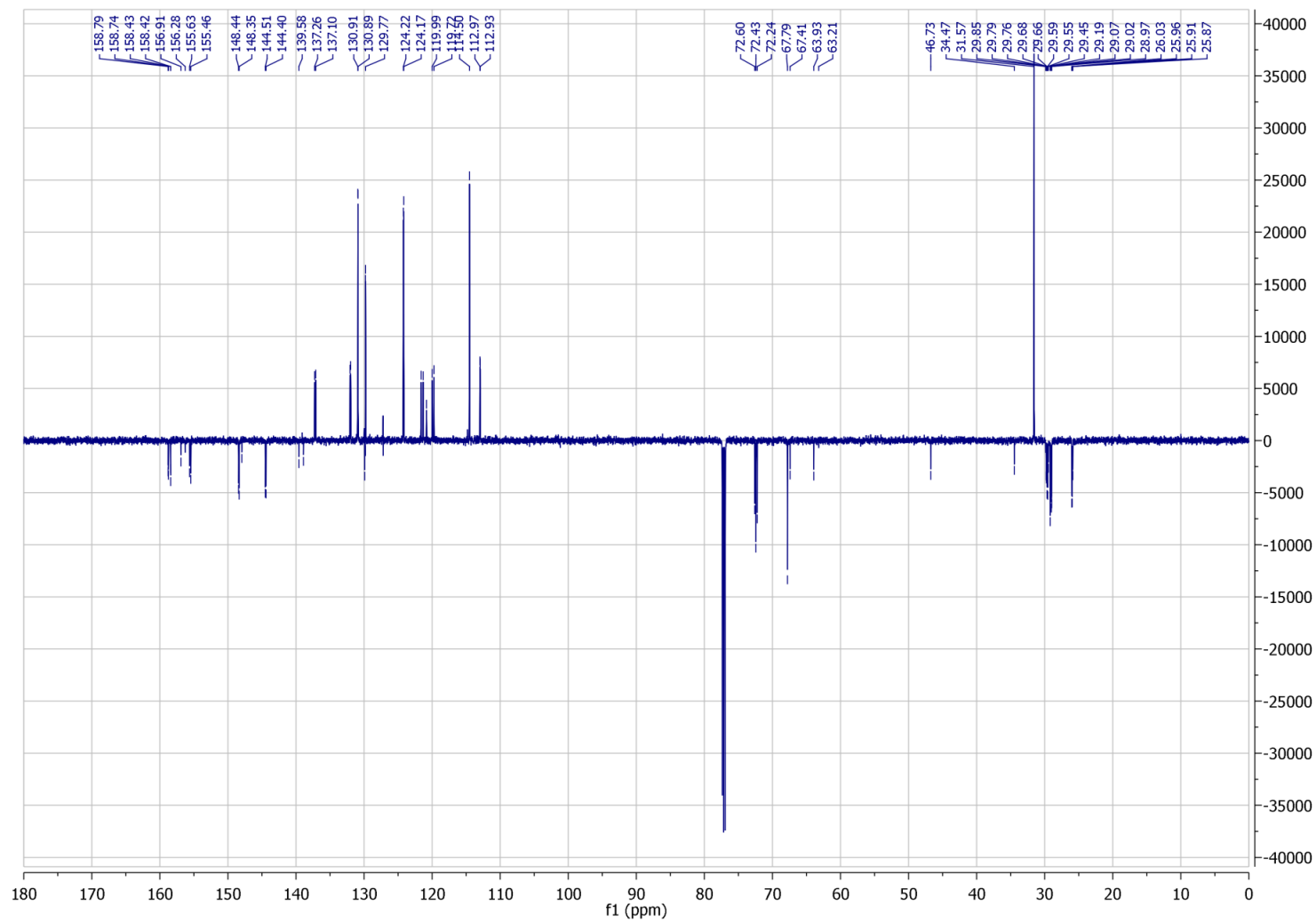
[2]Rotaxane S11d HMBC NMR (CDCl₃, 600 MHz, 300 K)



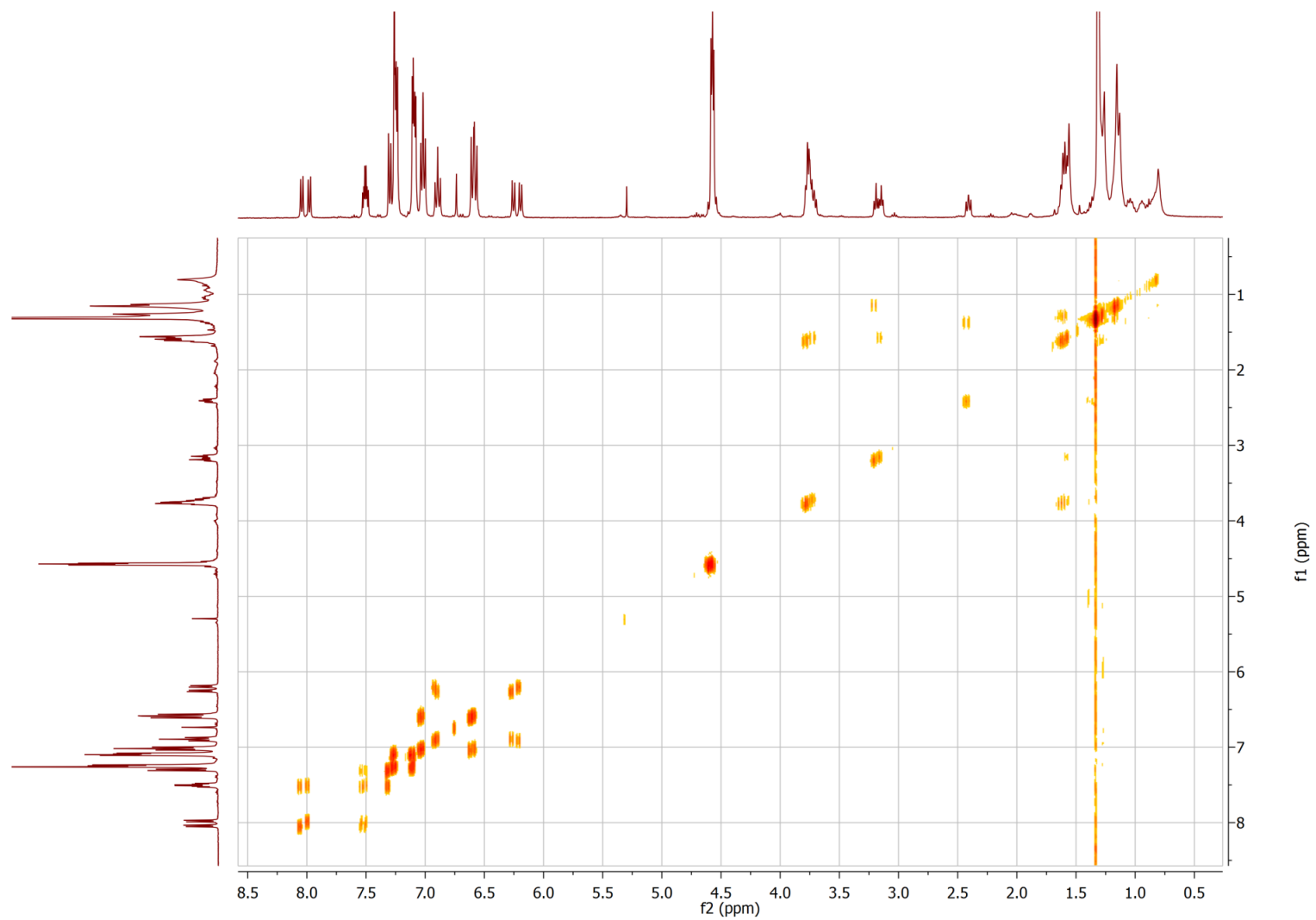
[3]Rotaxane S12 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



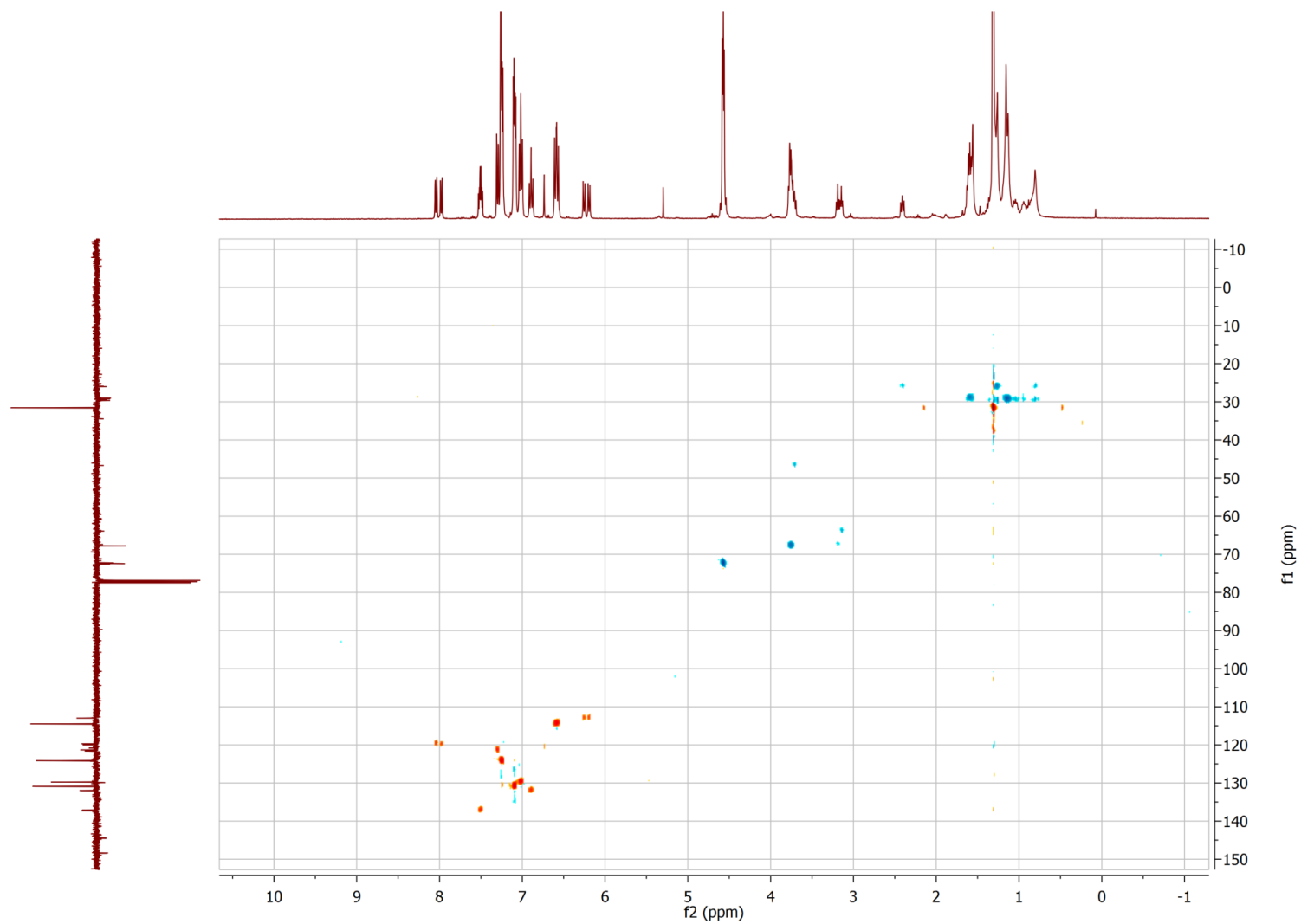
[3]Rotaxane S12 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



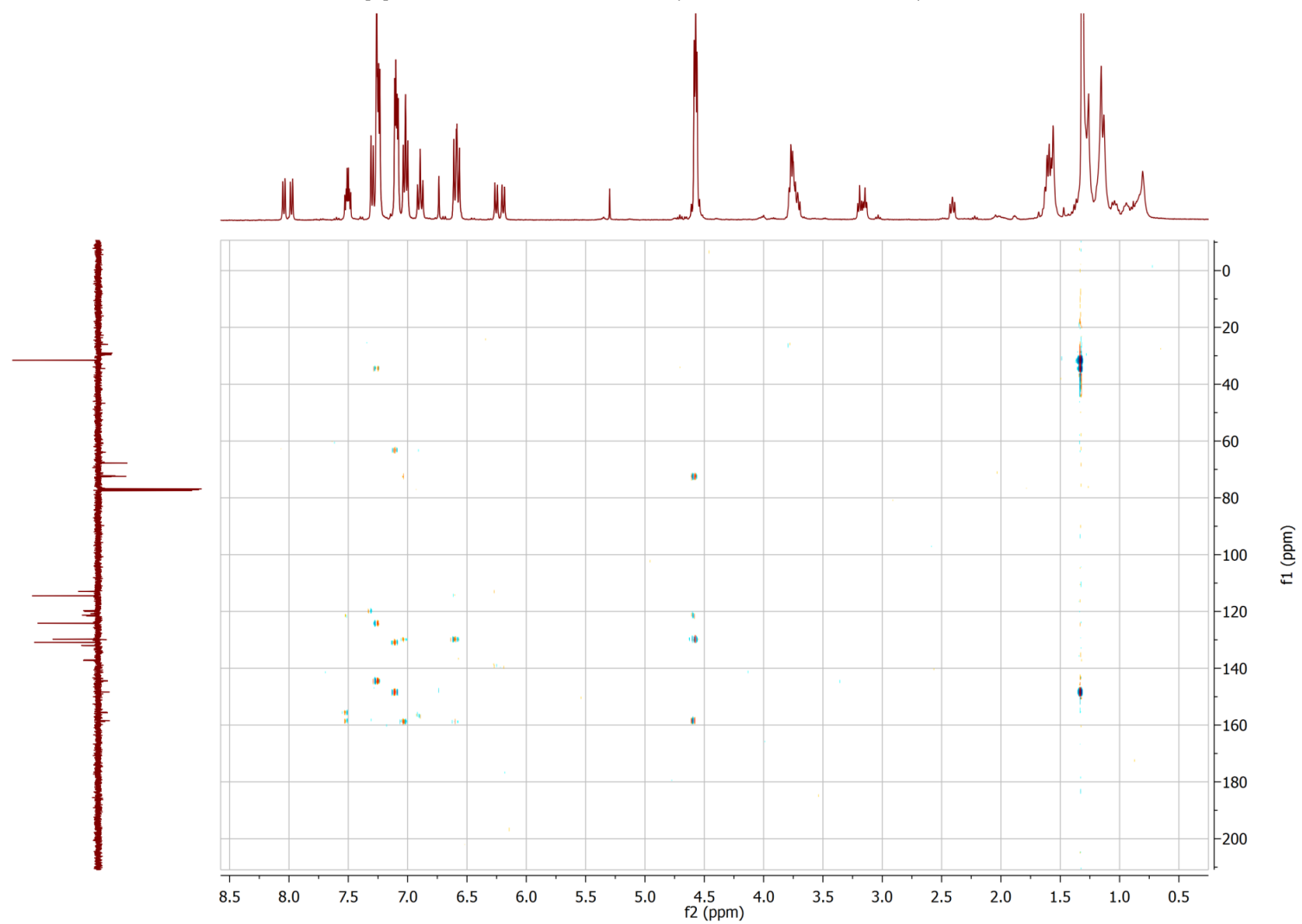
[3]Rotaxane S12 COSY (CDCl₃, 400 MHz, 300 K)



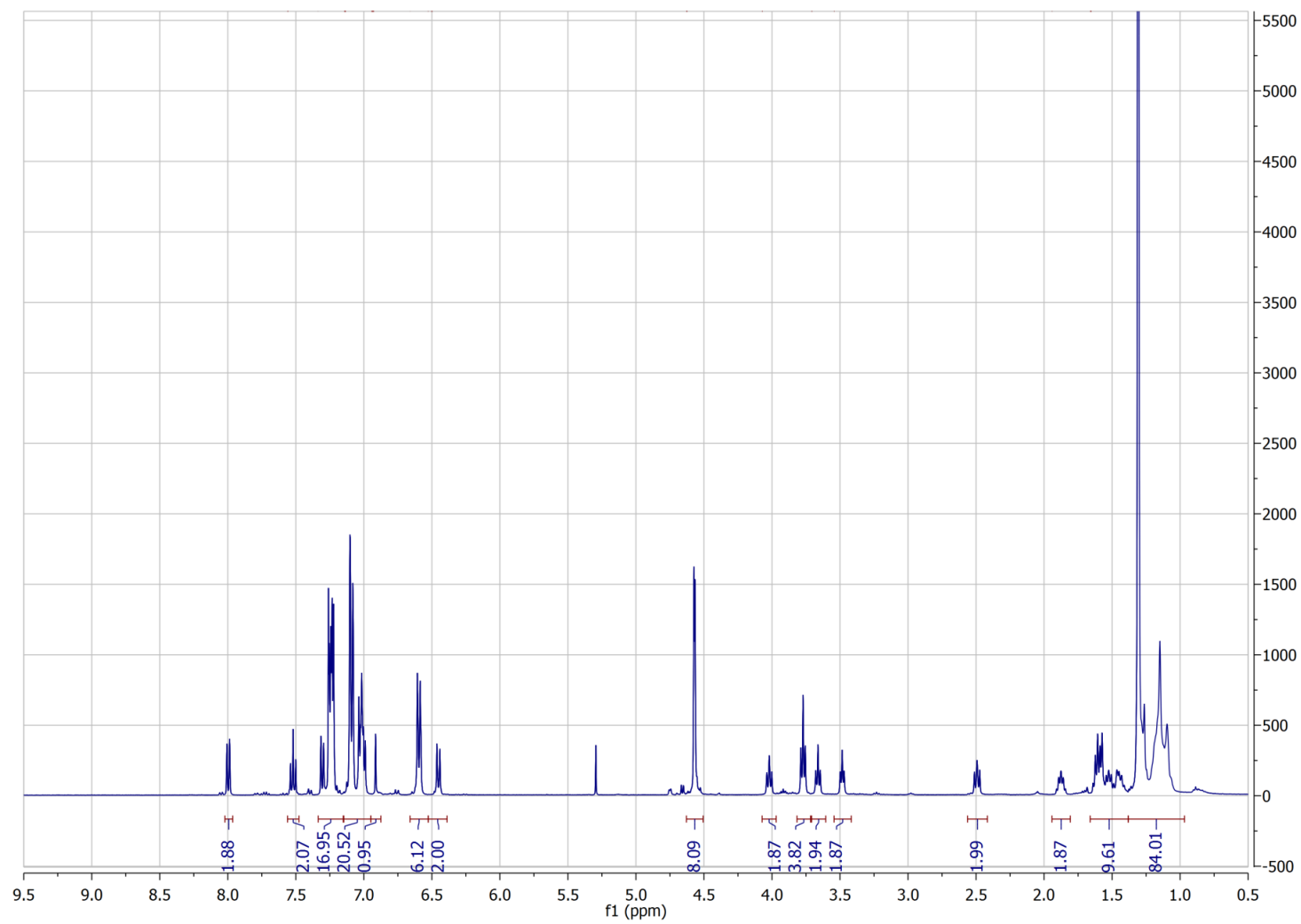
[3]Rotaxane S12 HSQC NMR (CDCl₃, 400 MHz, 300 K)



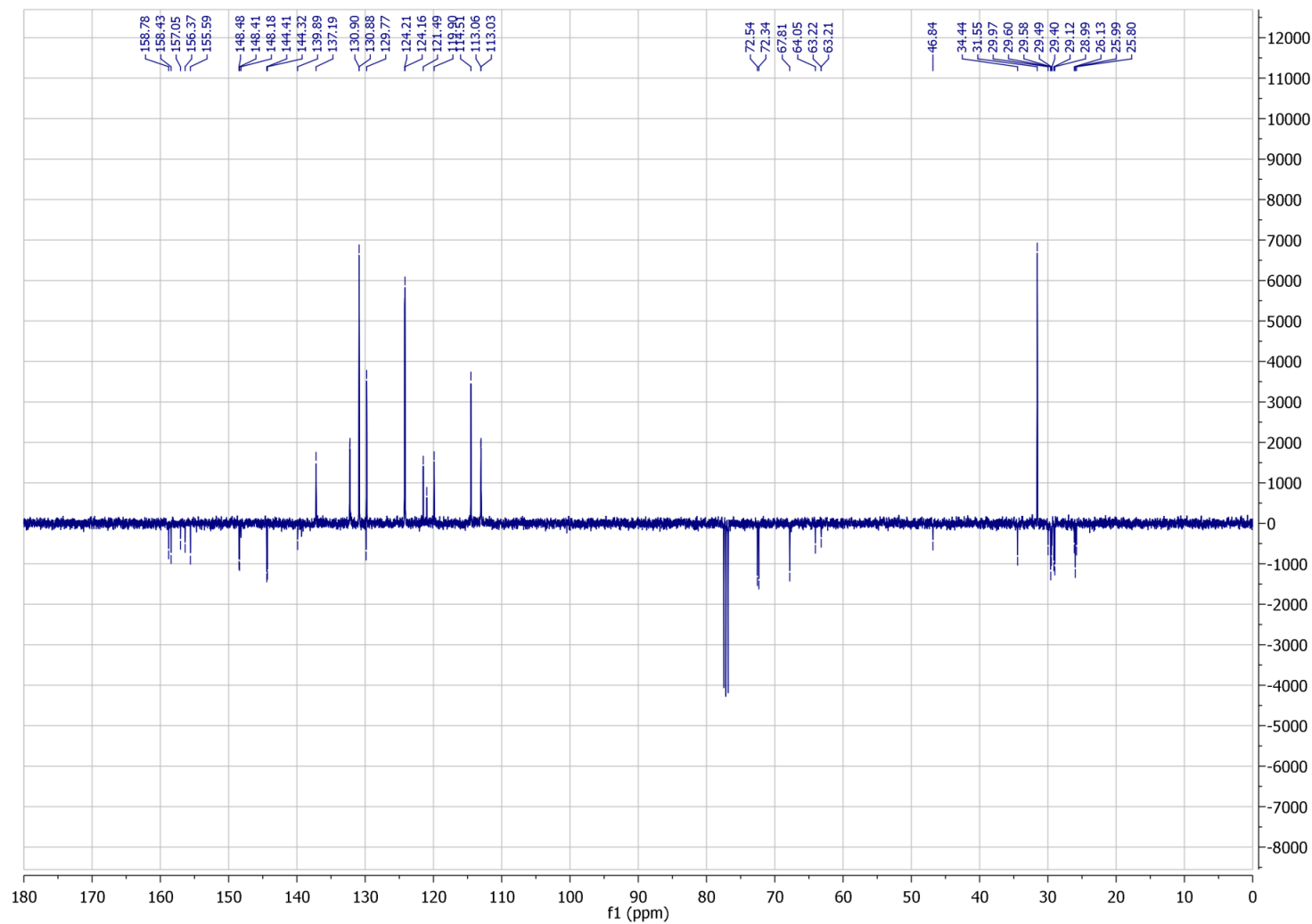
[3]Rotaxane S12 HMBC NMR (CDCl₃, 400 MHz, 300 K)



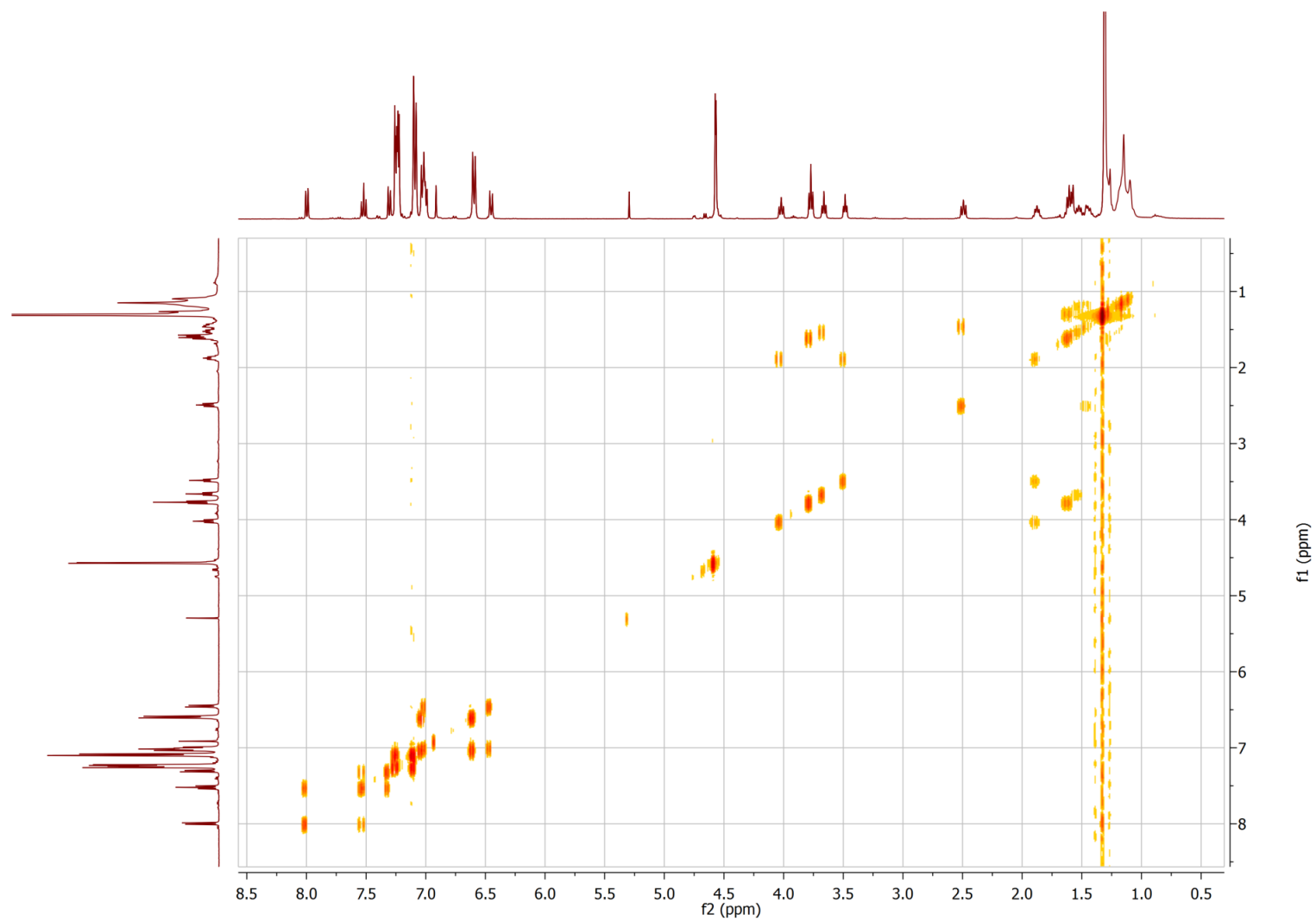
[2]Rotaxane S13 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



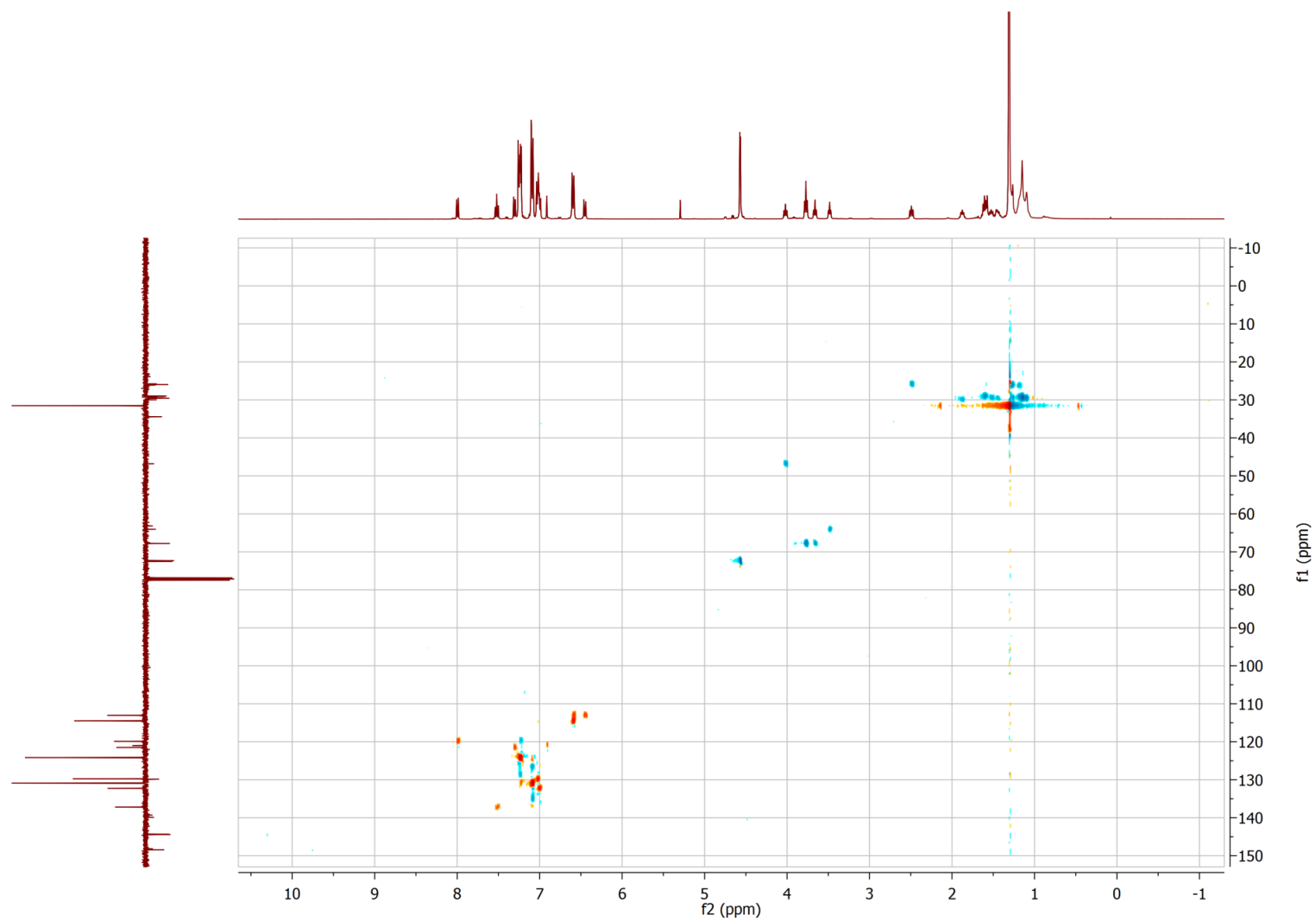
[2]Rotaxane S13 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



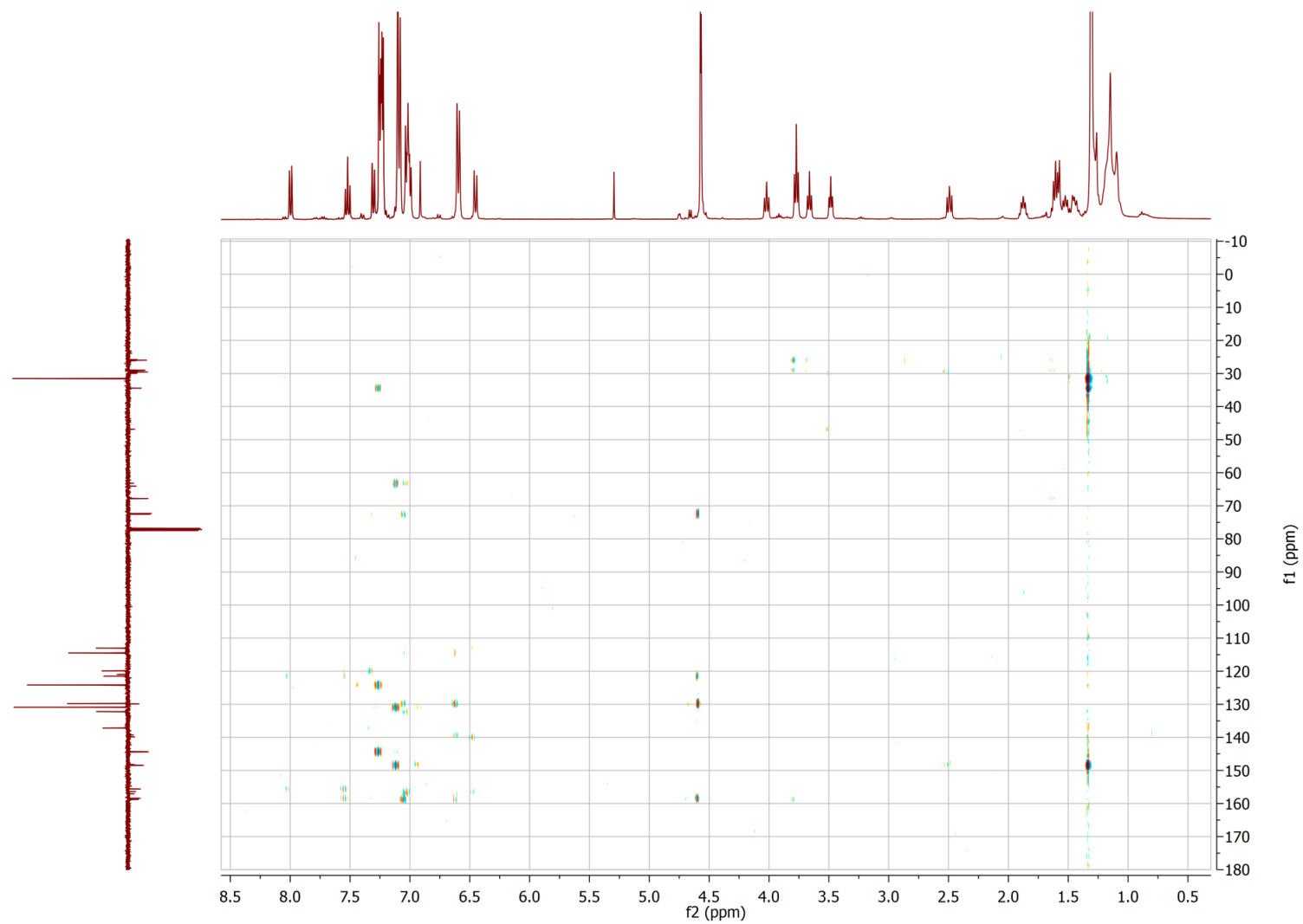
[2]Rotaxane S13 COSY (CDCl₃, 400 MHz, 300 K)



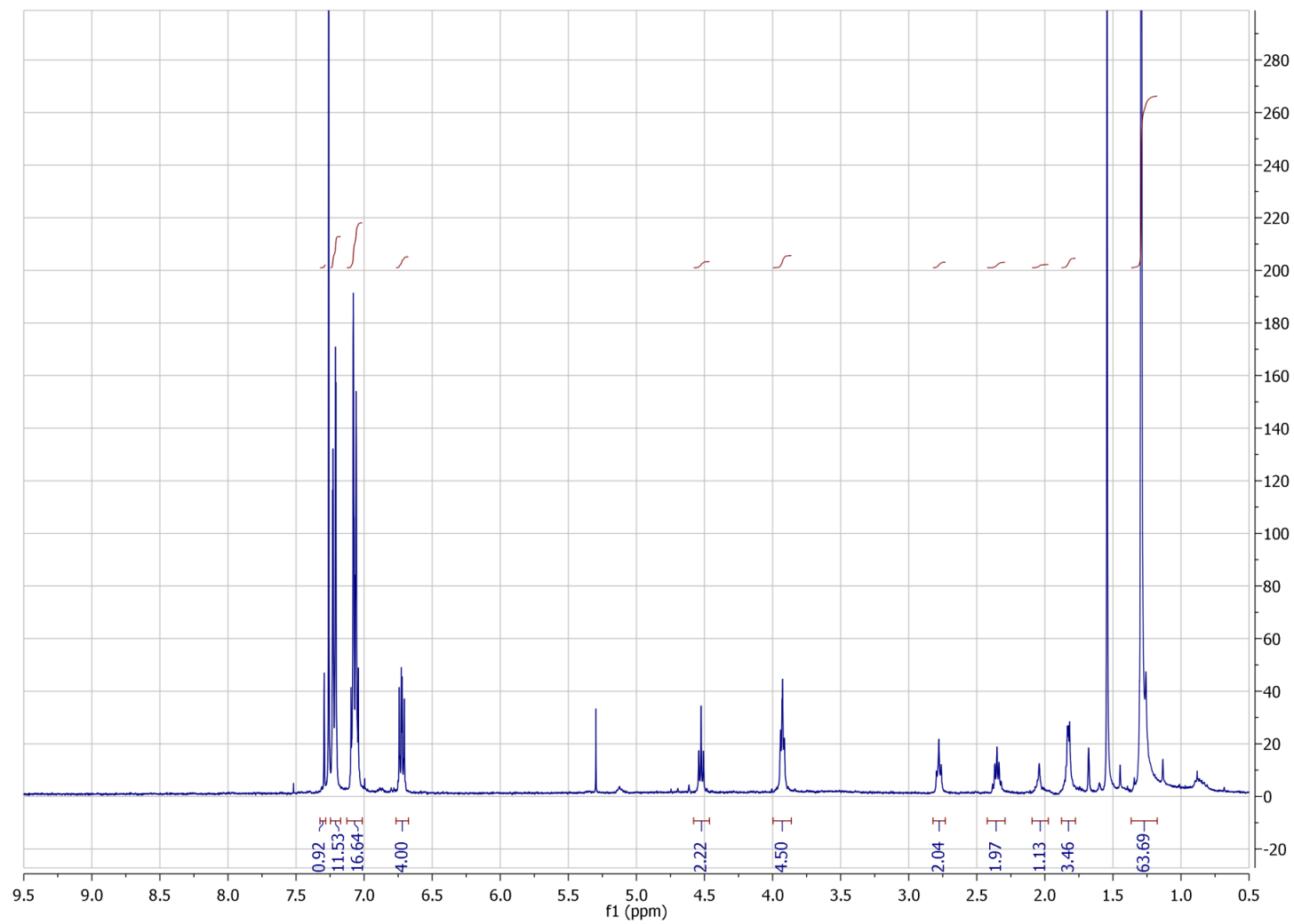
[2]Rotaxane S13 HSQC NMR (CDCl₃, 400 MHz, 300 K)



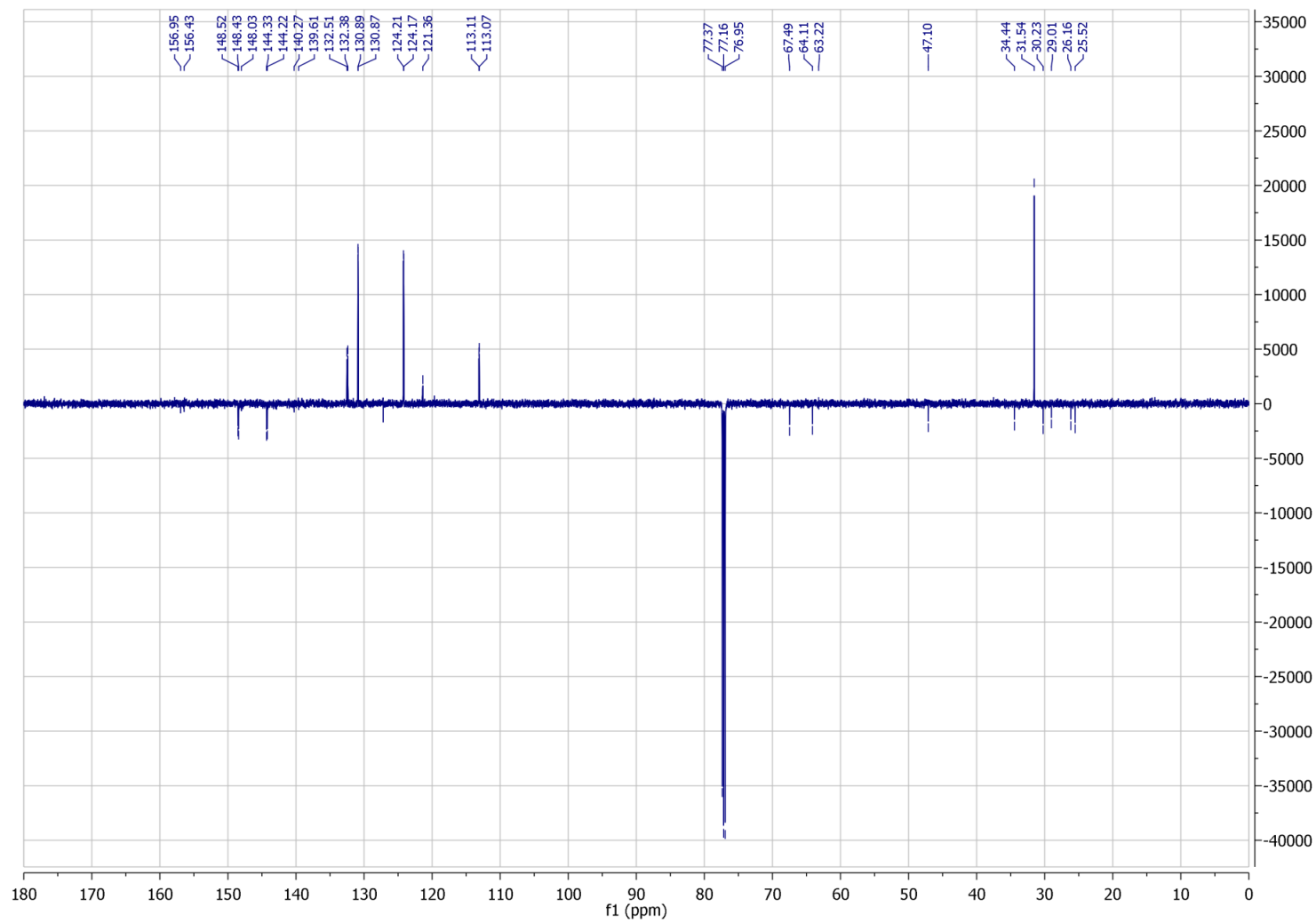
[2]Rotaxane S13 HMBC NMR (CDCl₃, 400 MHz, 300 K)



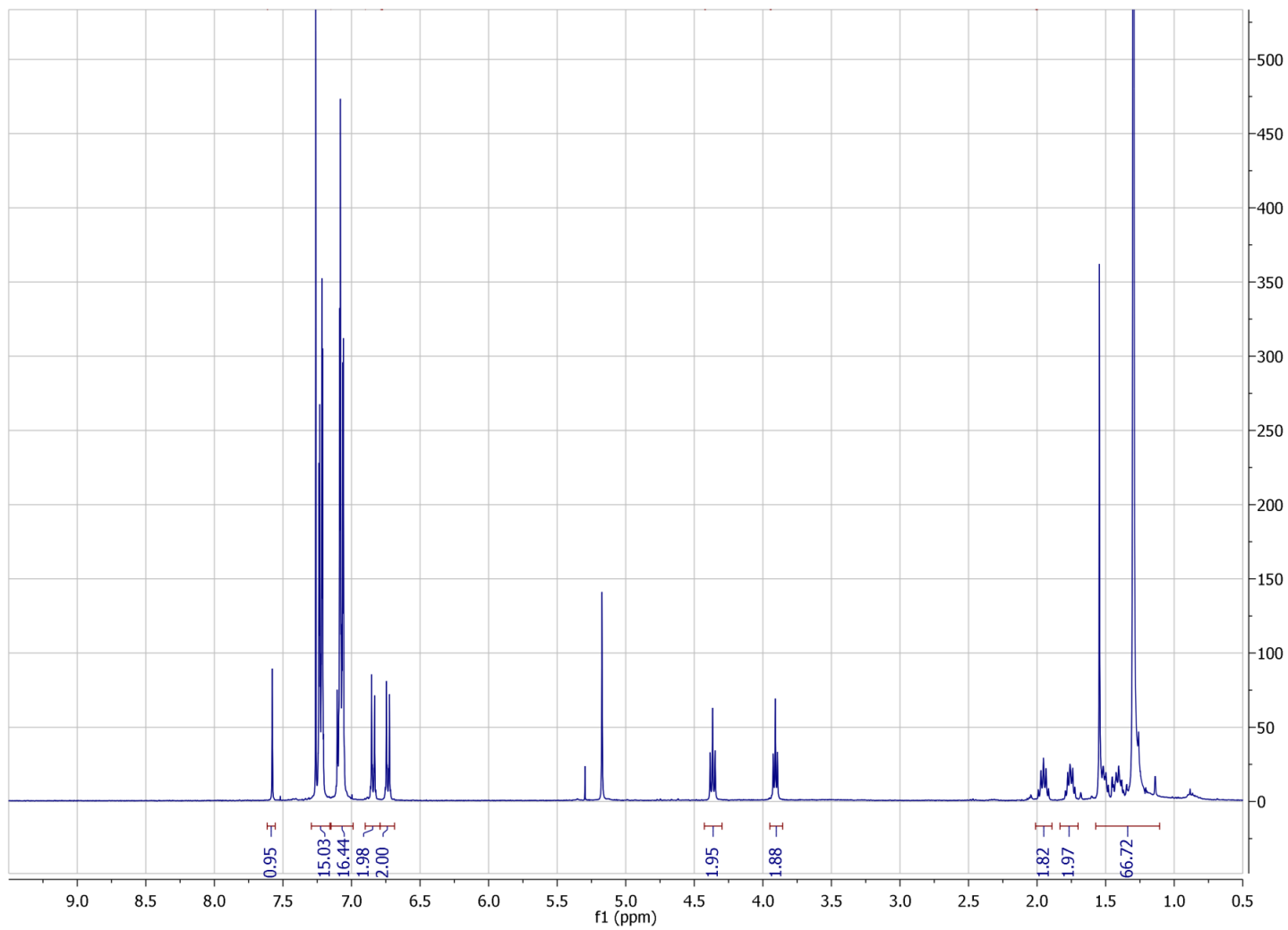
Thread S14 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



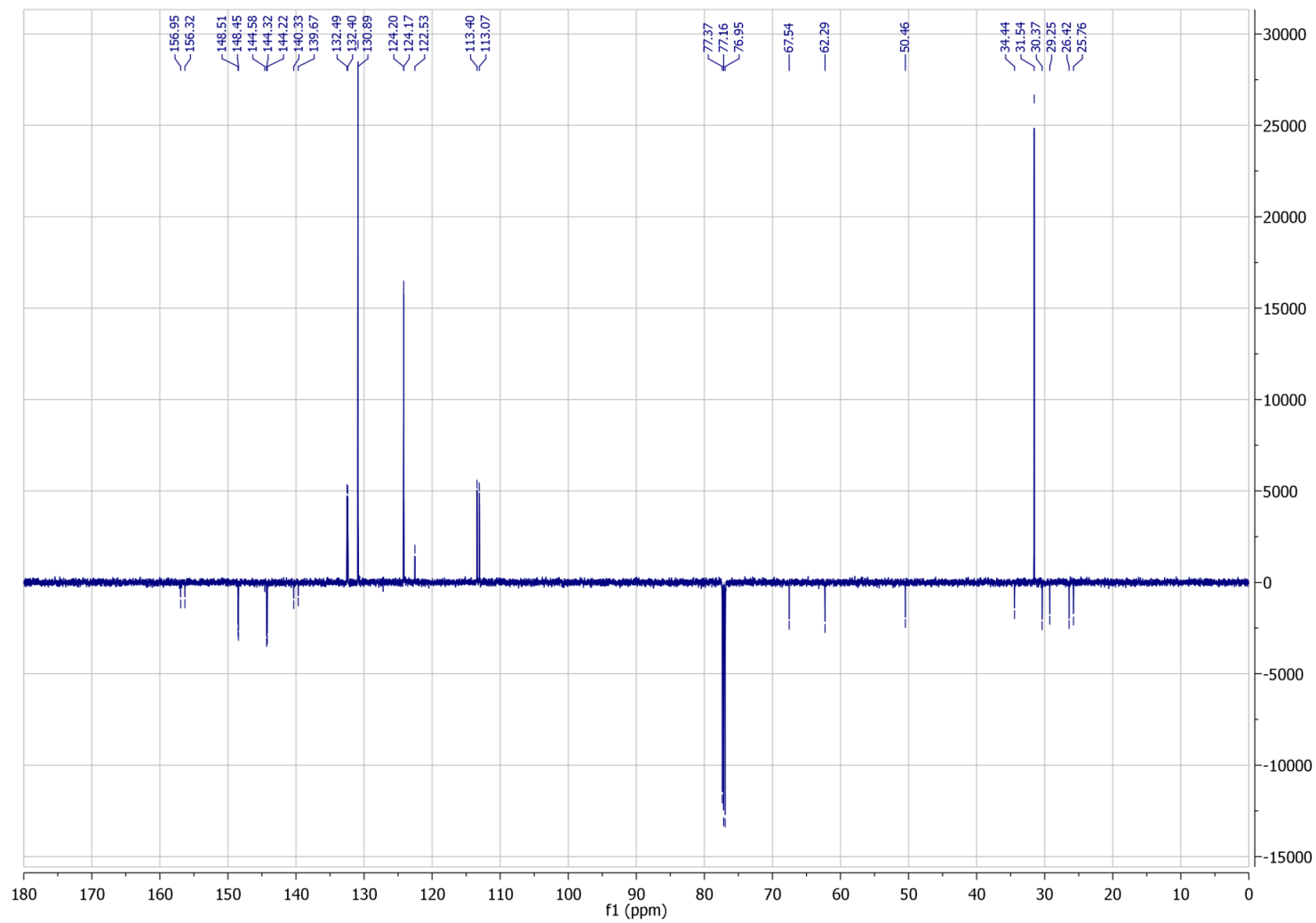
Thread S14 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



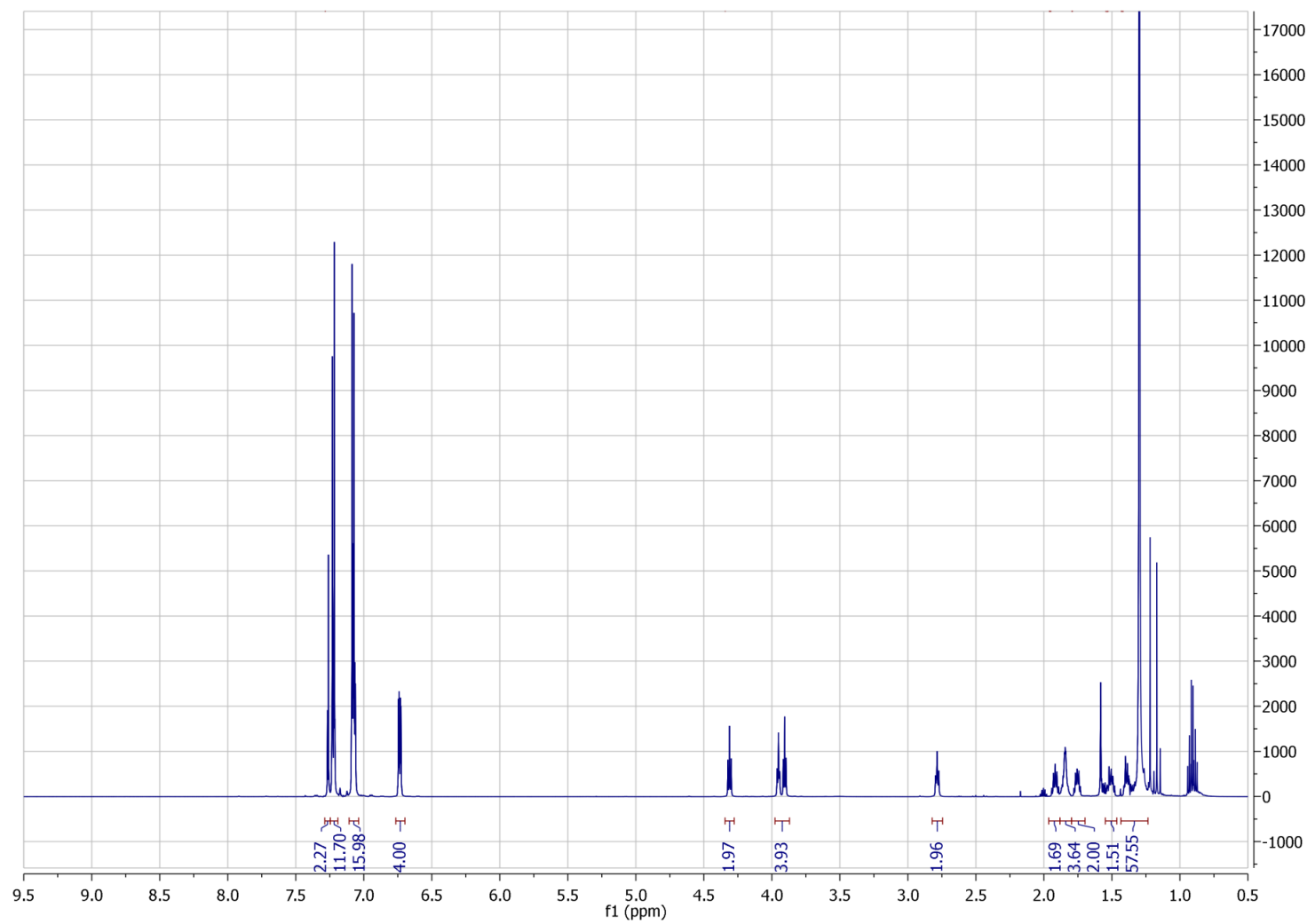
Thread S15 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



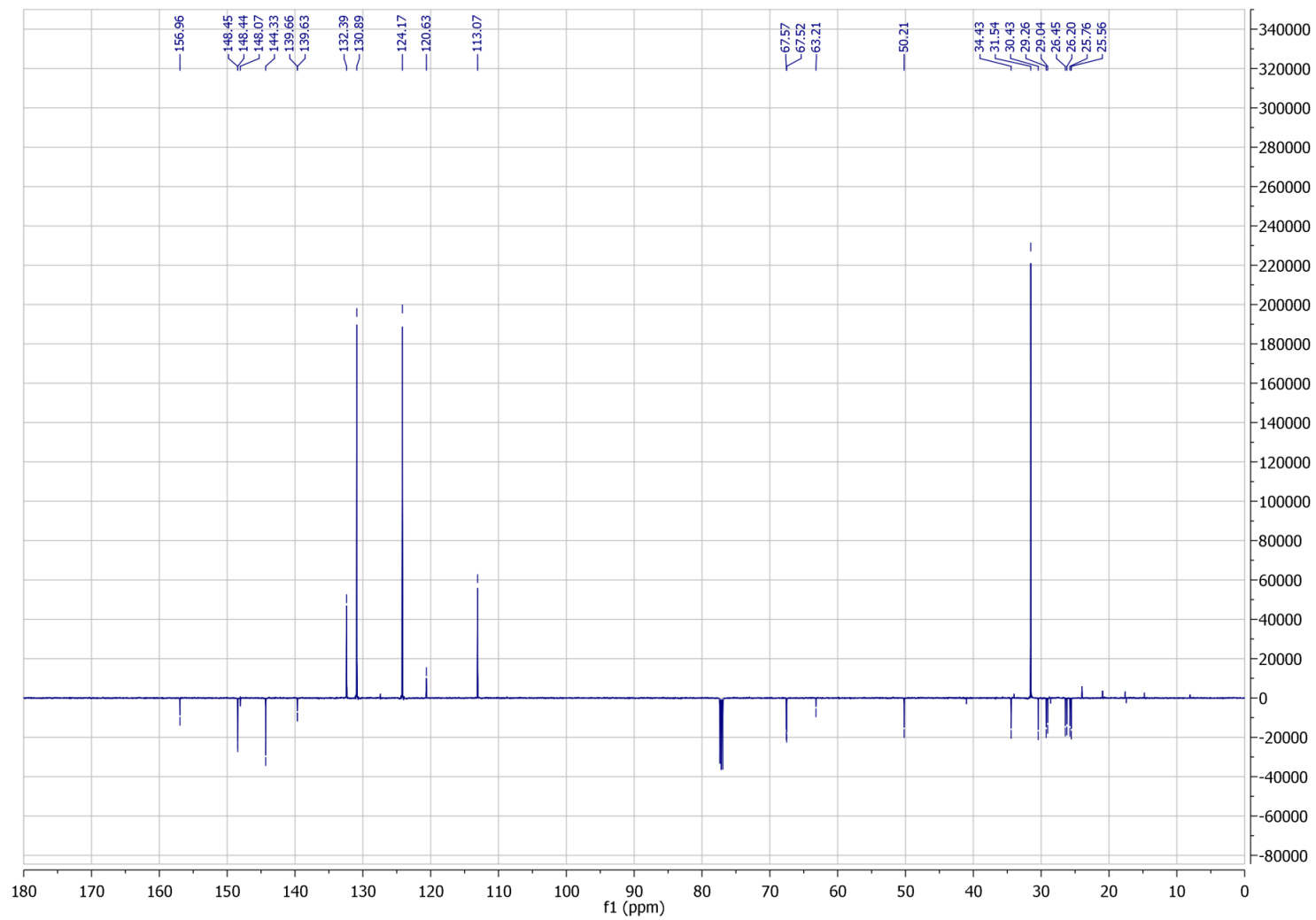
Thread S15 DEPTQ135 NMR (CDCl₃, 150 MHz, 300 K)



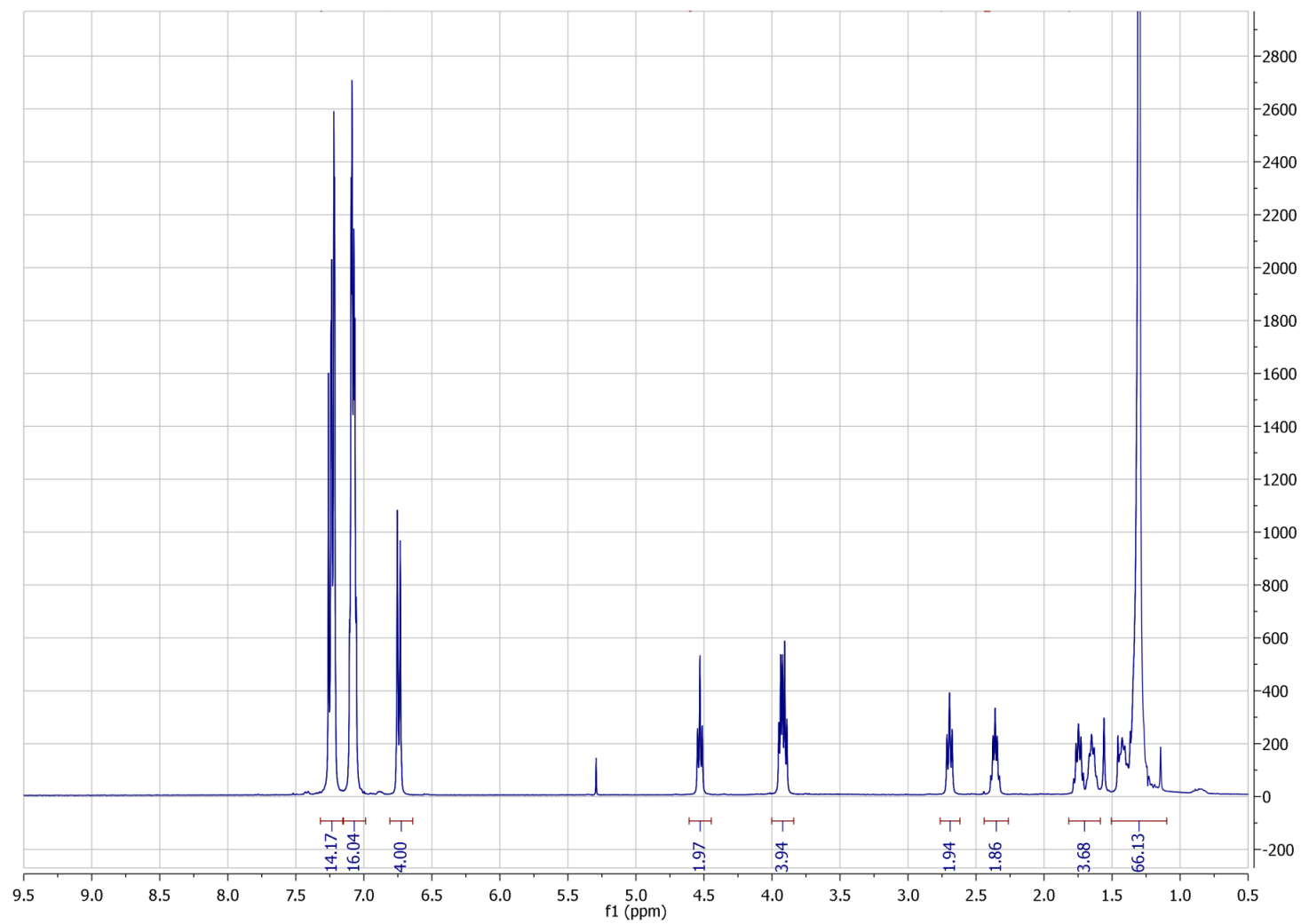
Thread S16 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



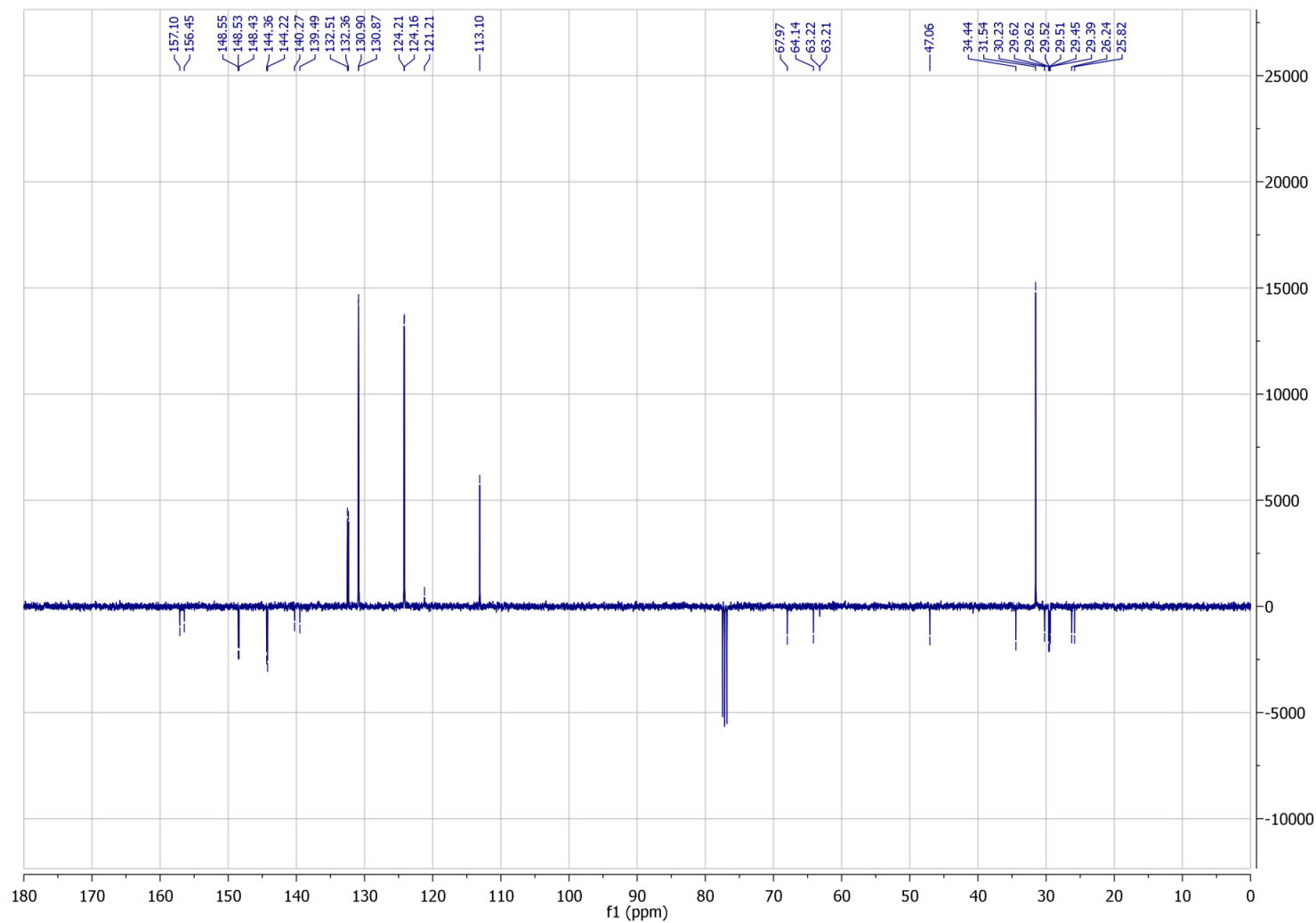
Thread S16 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



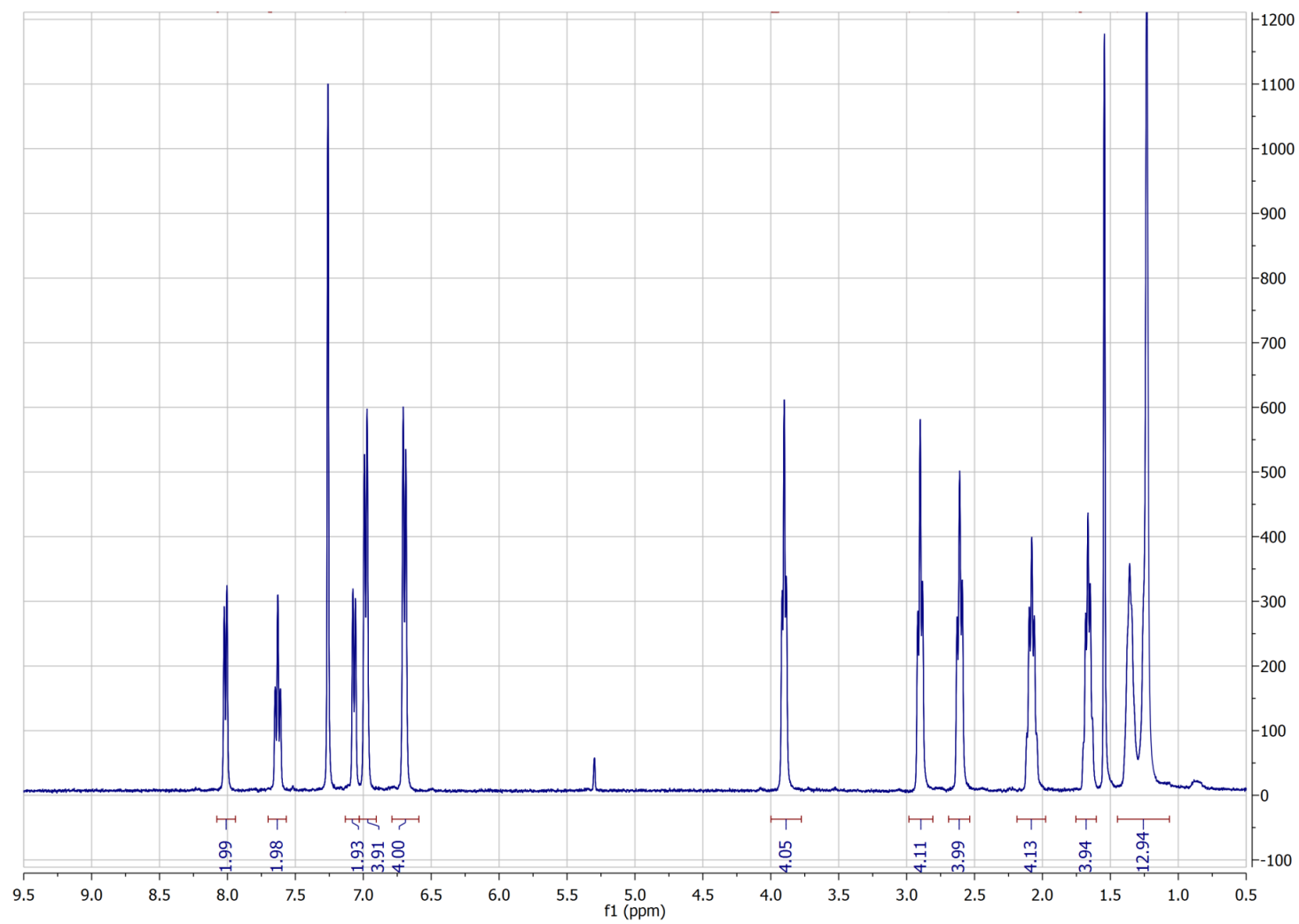
Thread S17 ^1H NMR (CDCl_3 , 400 MHz, 300 K)



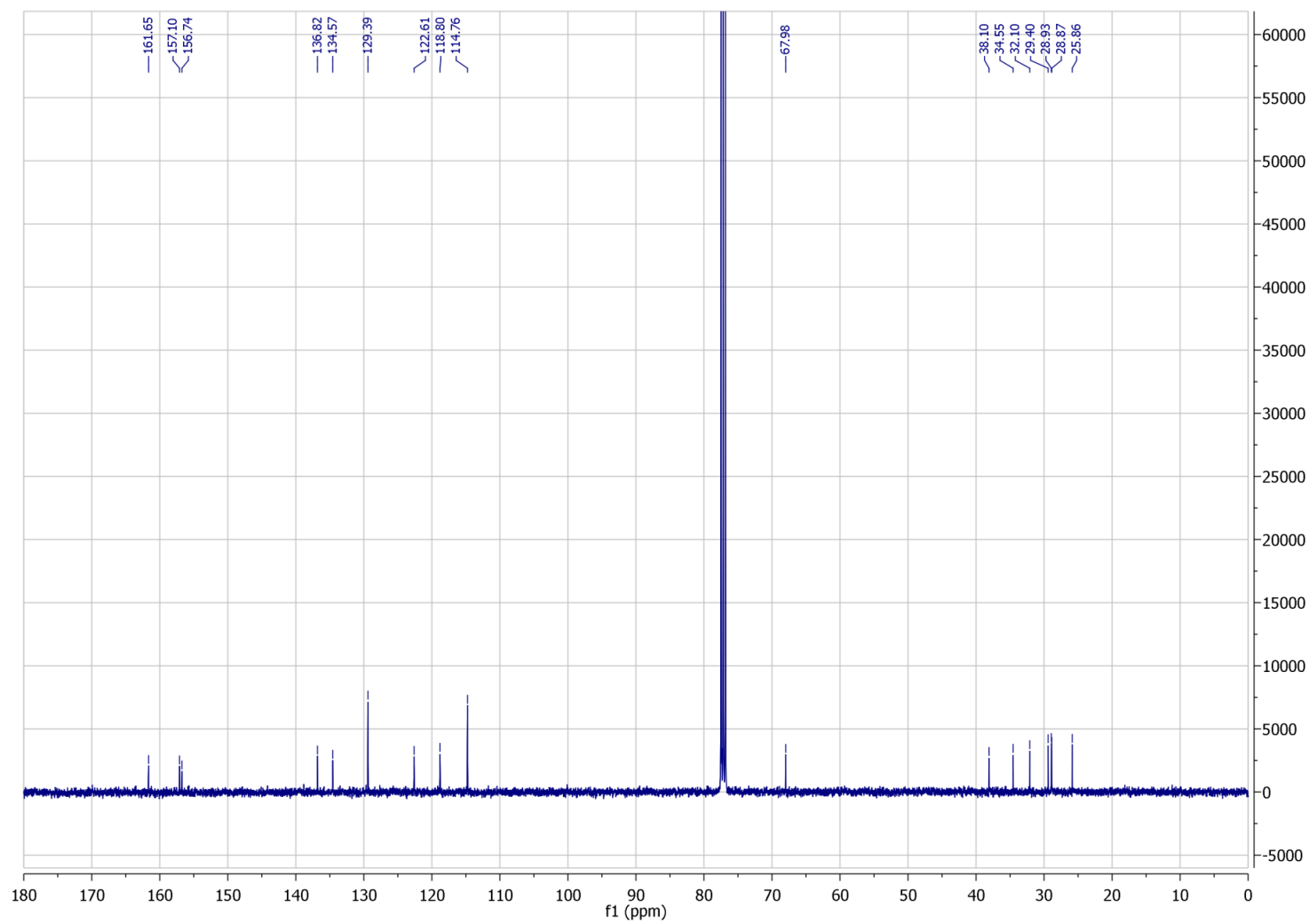
Thread S17 DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



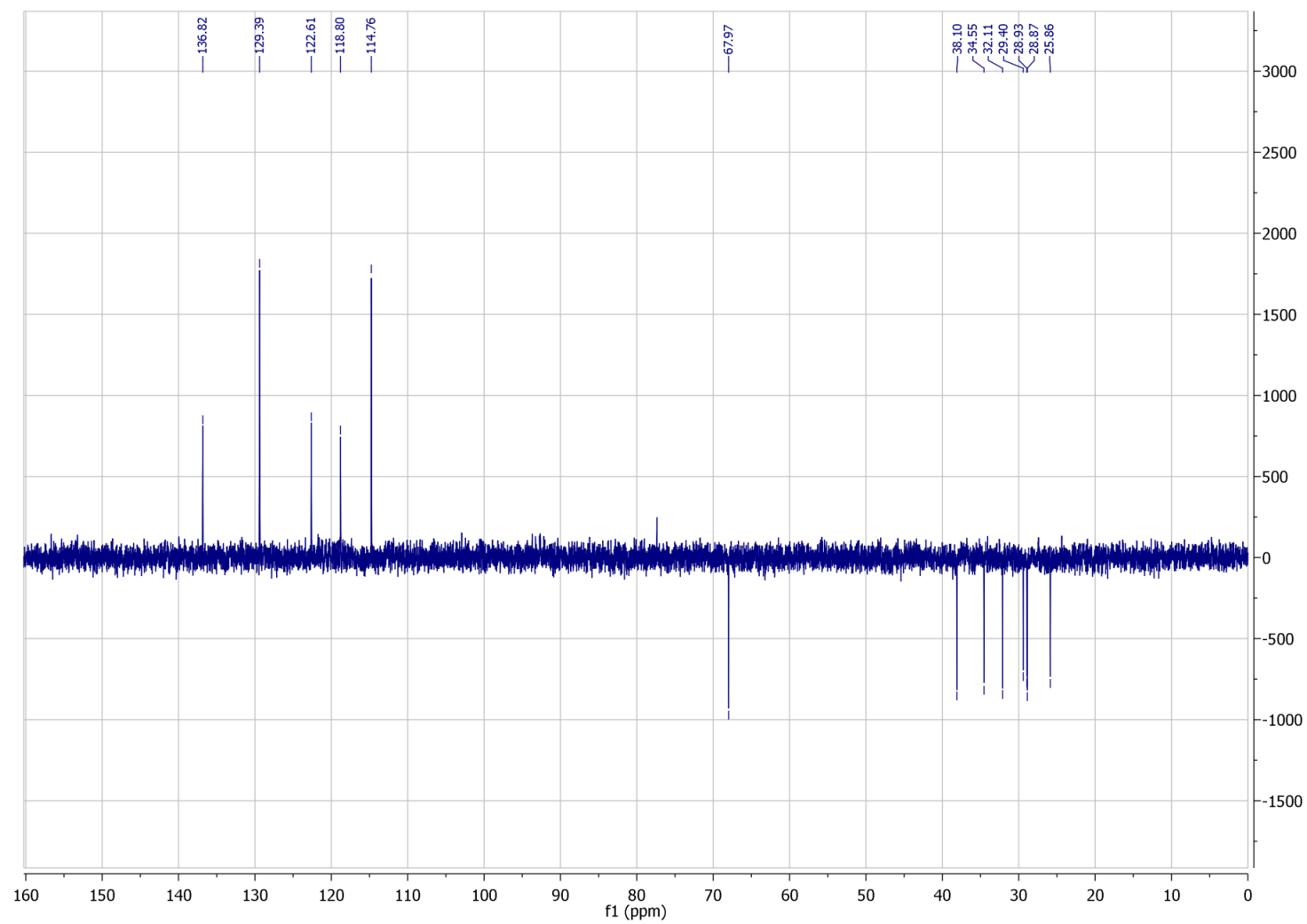
Macrocycle 9a ^1H NMR (CDCl_3 , 400 MHz, 300 K)



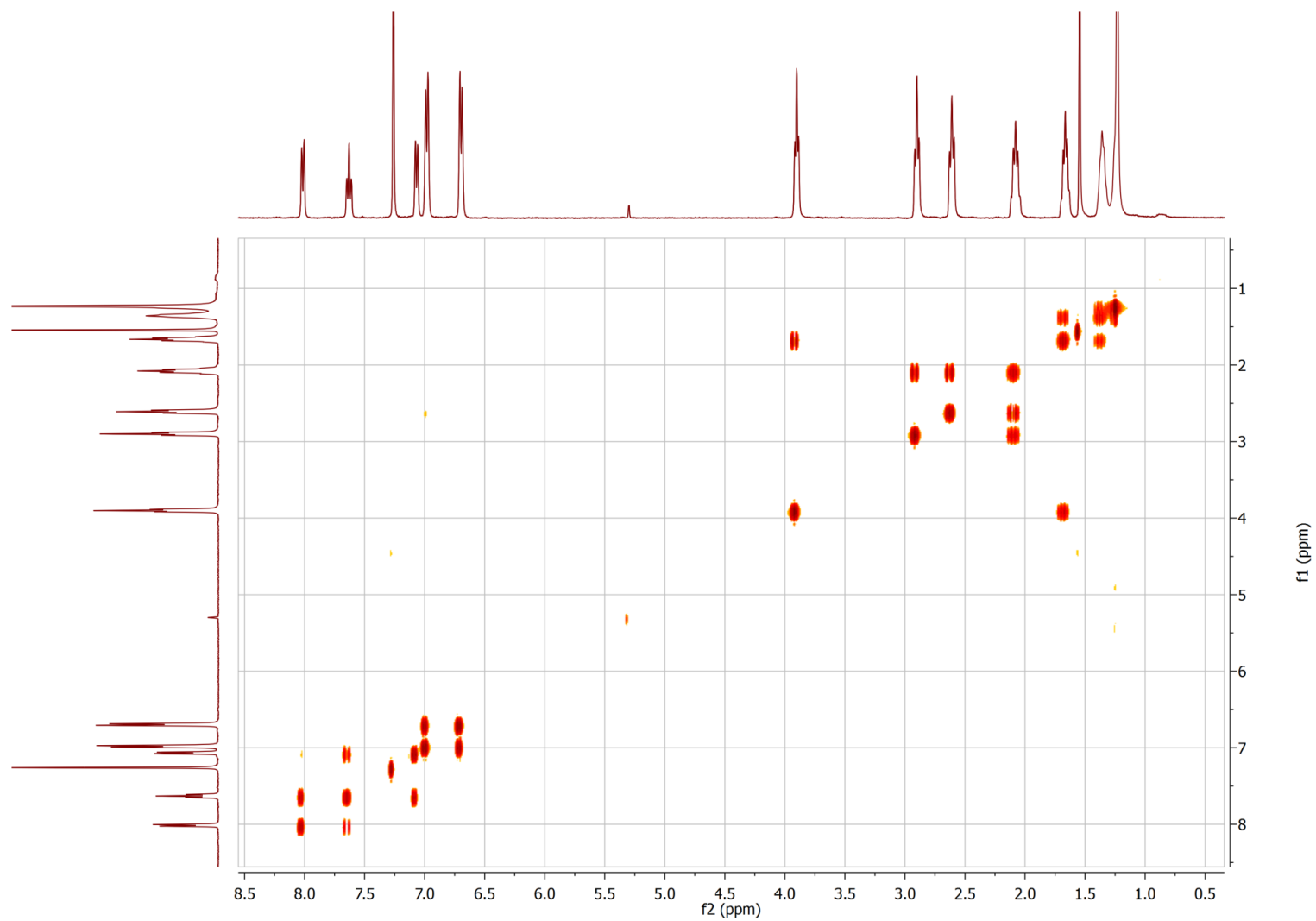
Macrocycle 9a ^{13}C NMR (CDCl_3 , 100 MHz, 300 K)



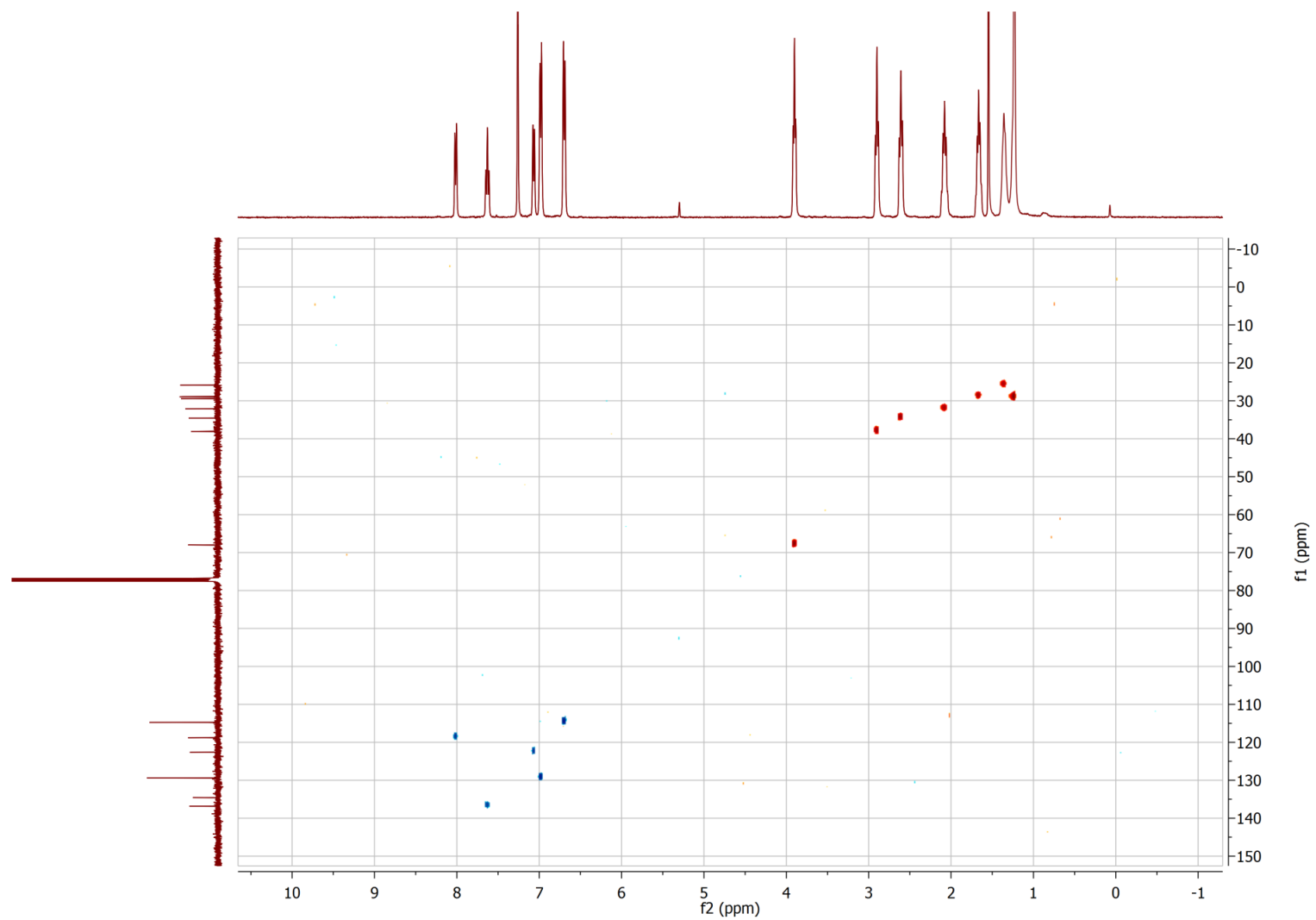
Macrocycle 9a DEPT135 NMR (CDCl₃, 100 MHz, 300 K)



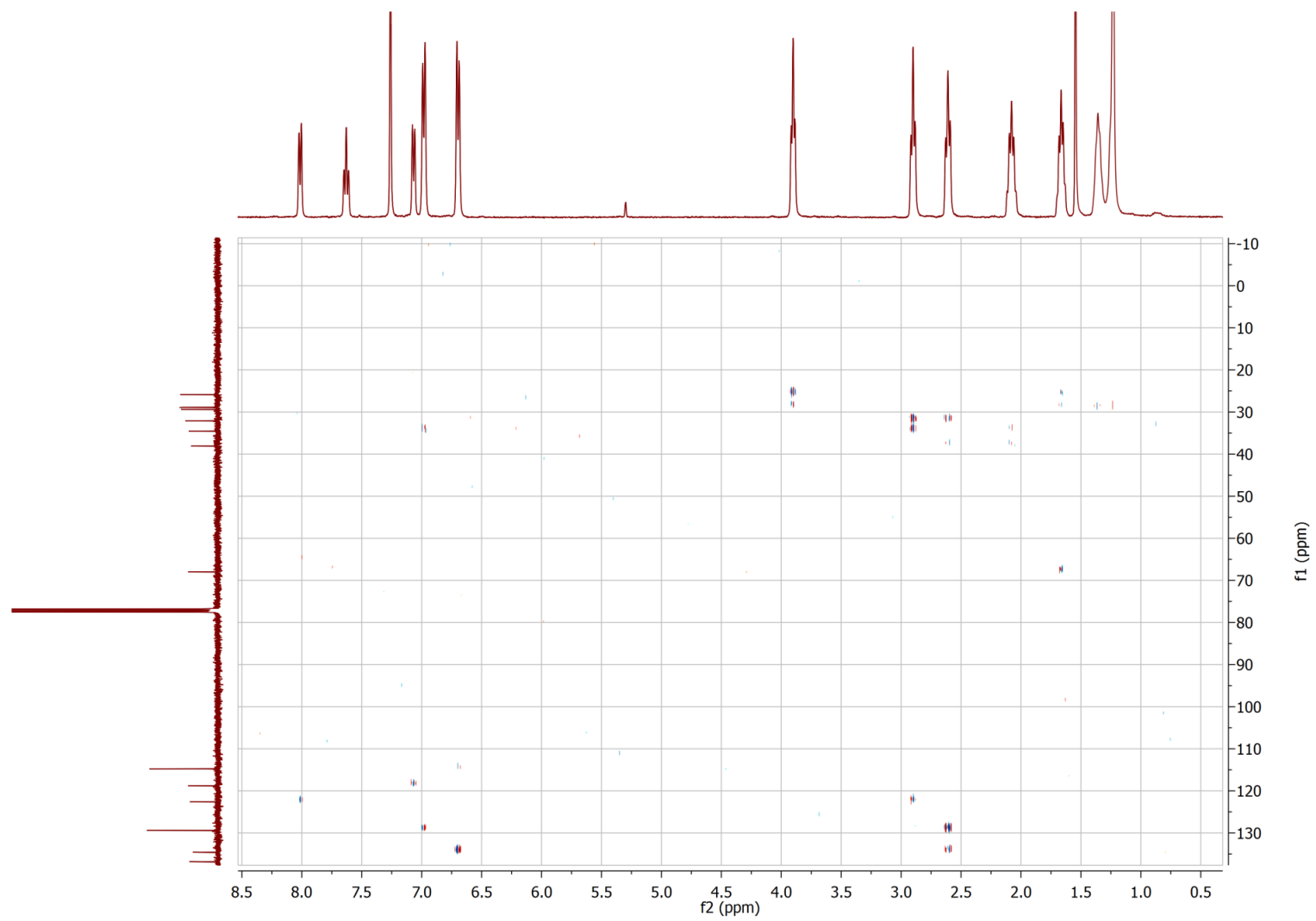
Macrocycle 9a COSY (CDCl₃, 400 MHz, 300 K)



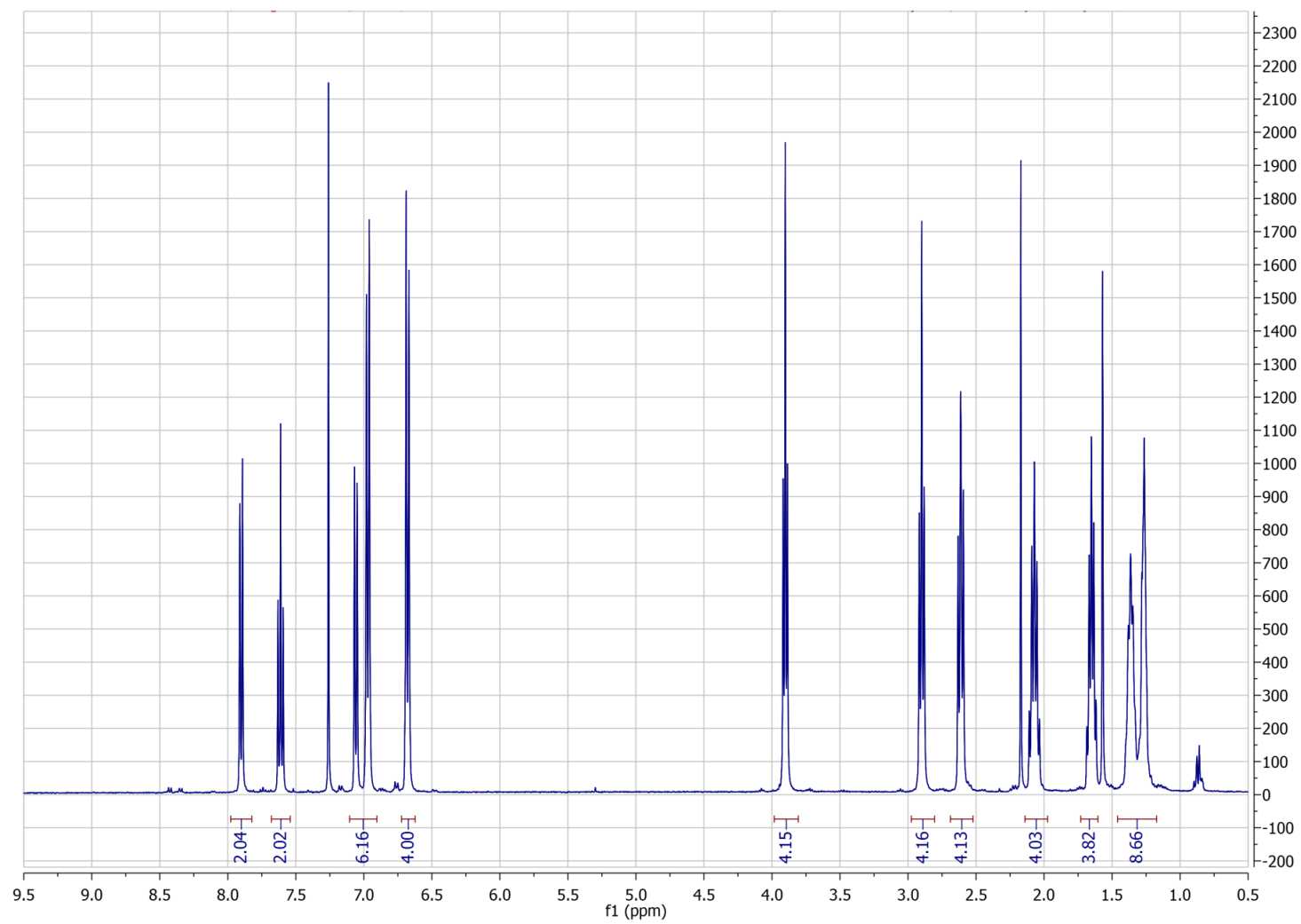
Macrocycle 9a HSQC NMR (CDCl₃, 400 MHz, 300 K)



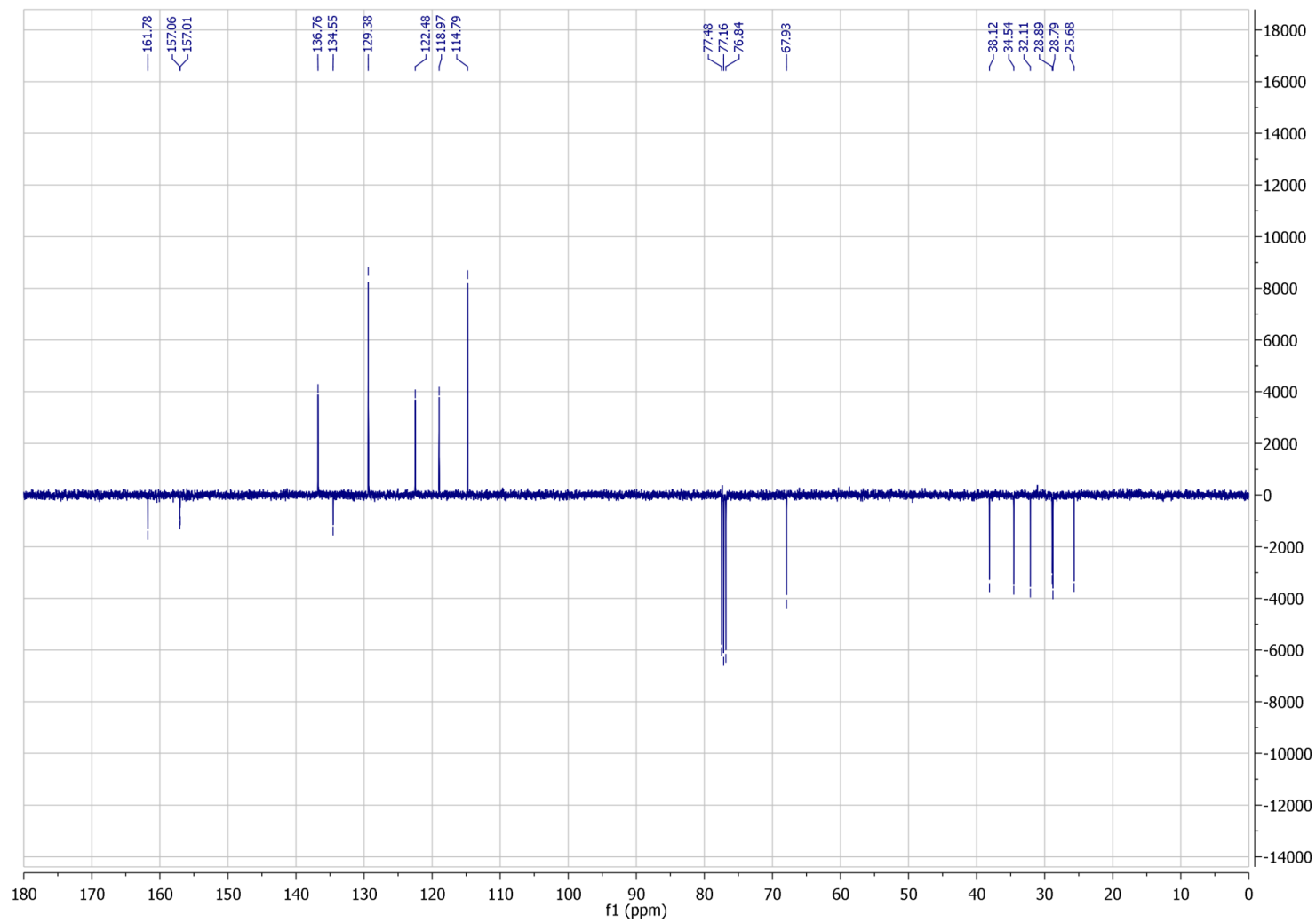
Macrocycle 9a HMBC NMR (CDCl₃, 400 MHz, 300 K)

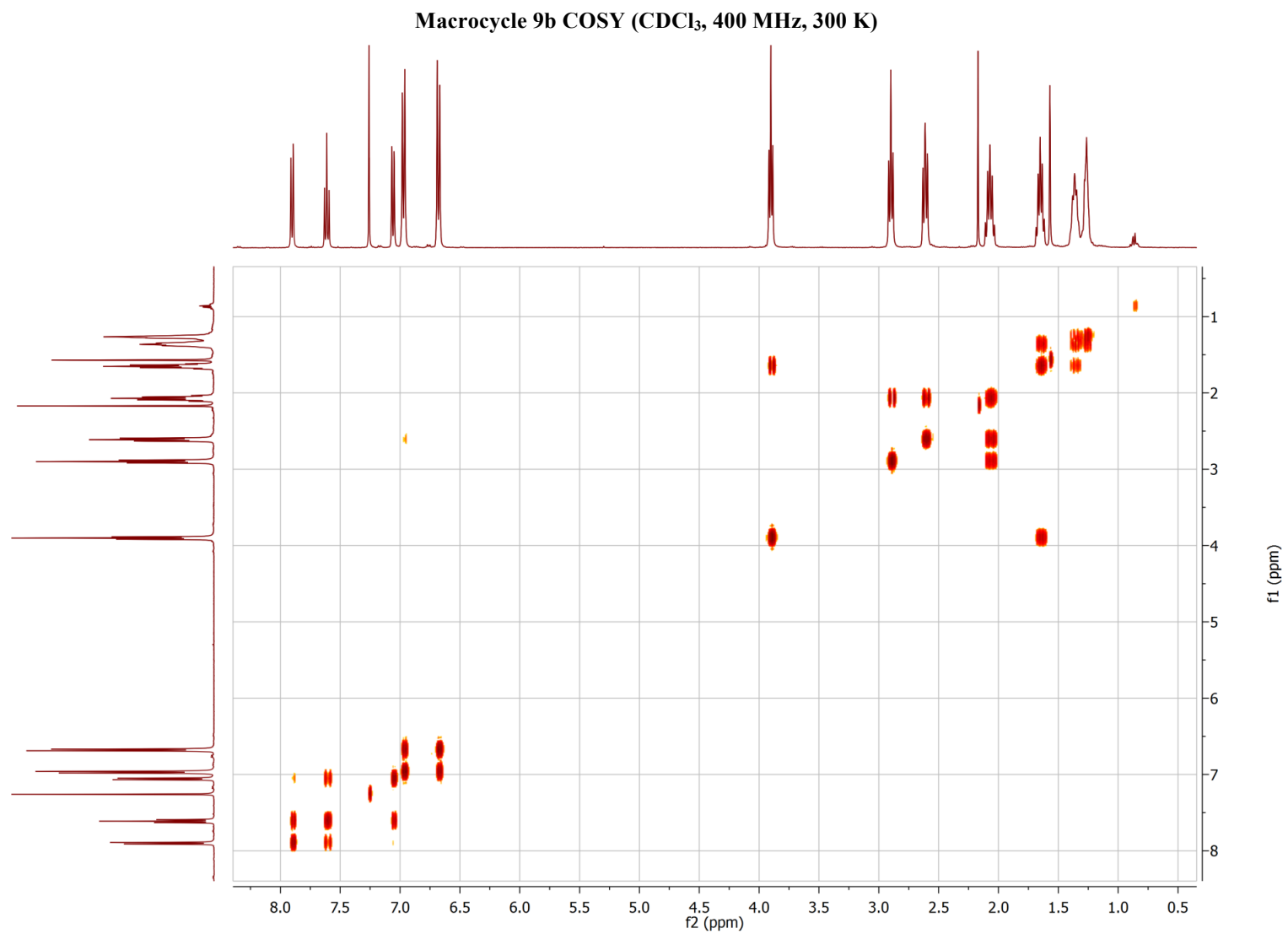


Macrocycle 9b ^1H NMR (CDCl_3 , 400 MHz, 300 K)

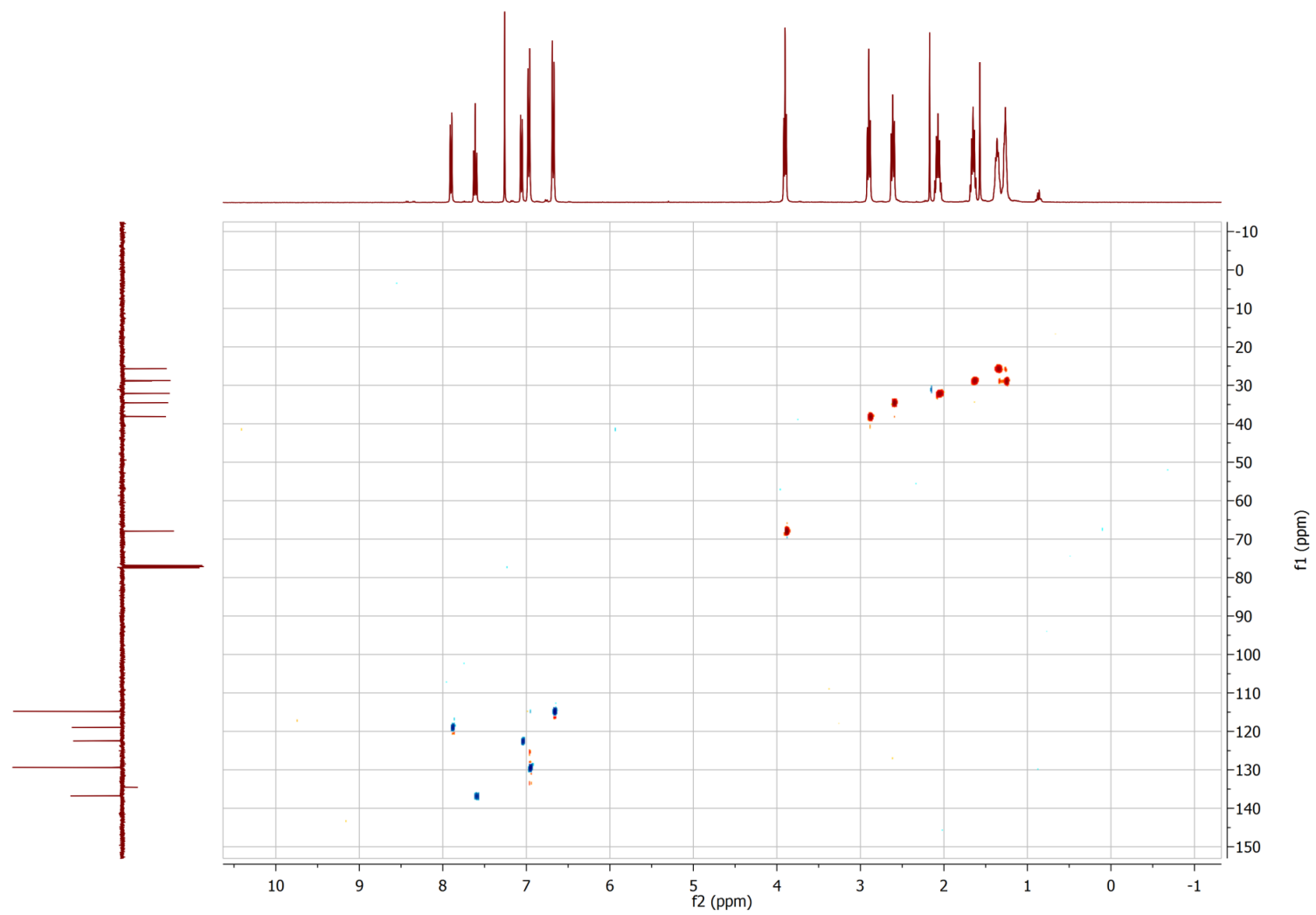


Macrocycle 9b DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)

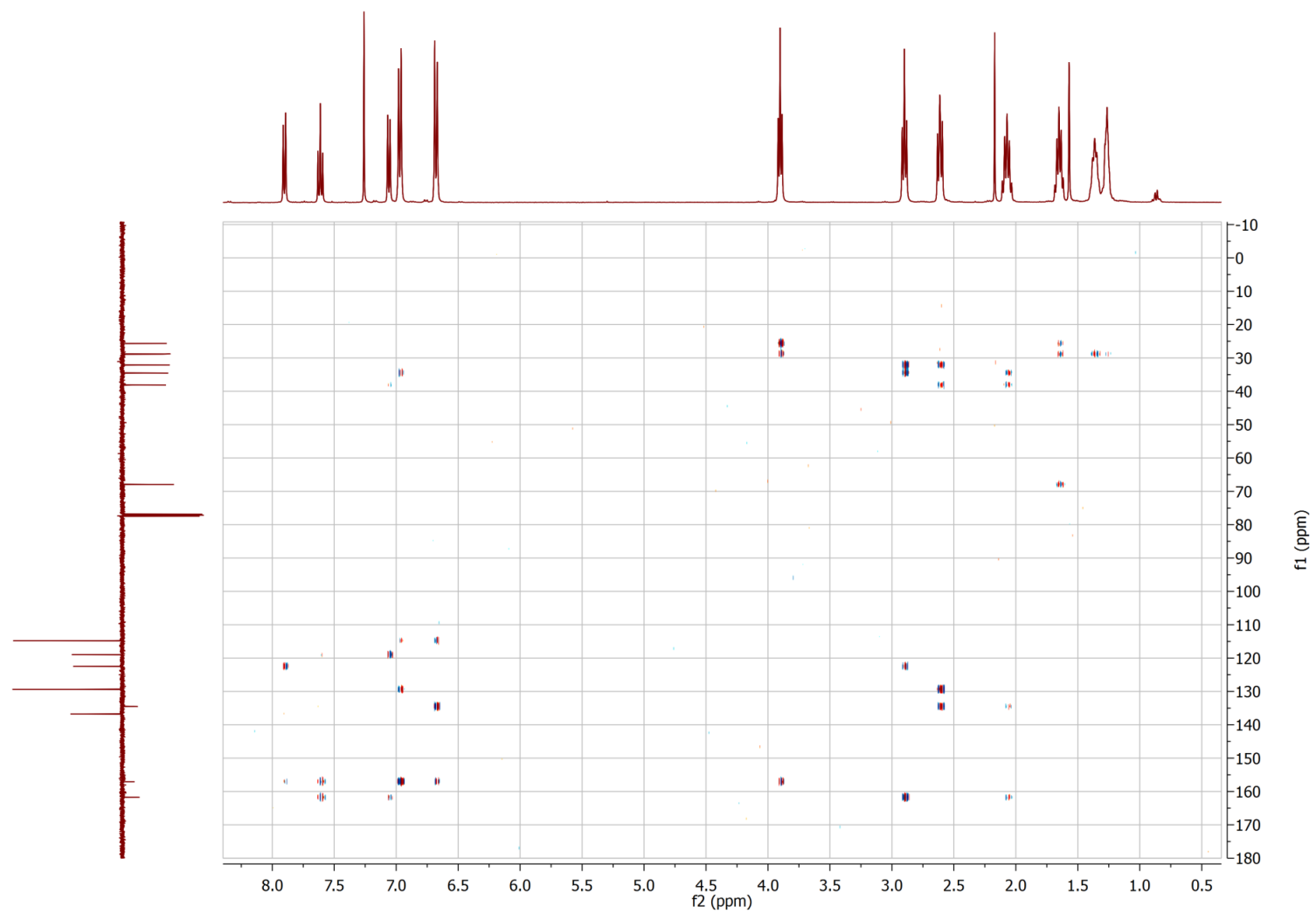




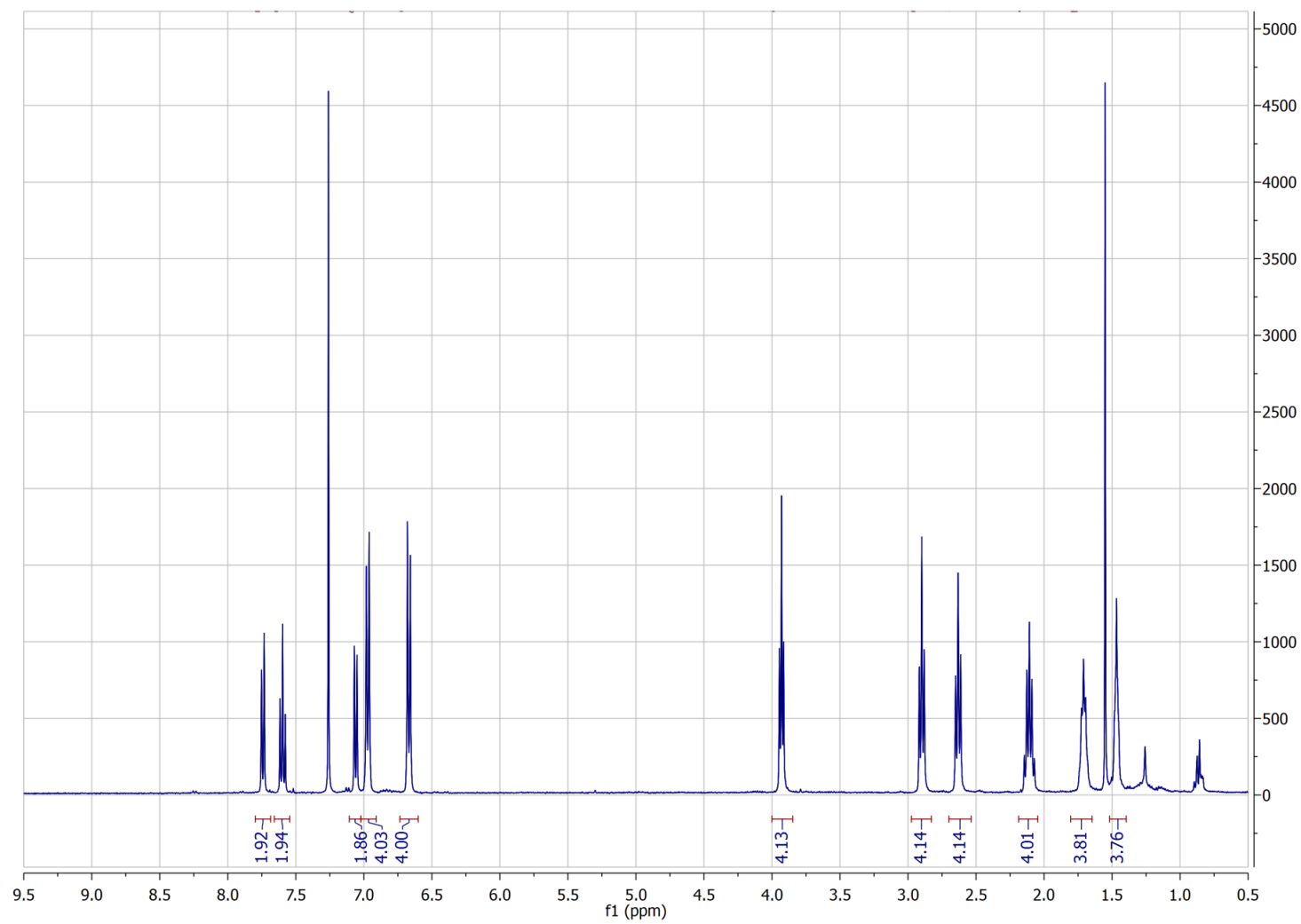
Macrocycle 9b HSQC NMR (CDCl₃, 400 MHz, 300 K)



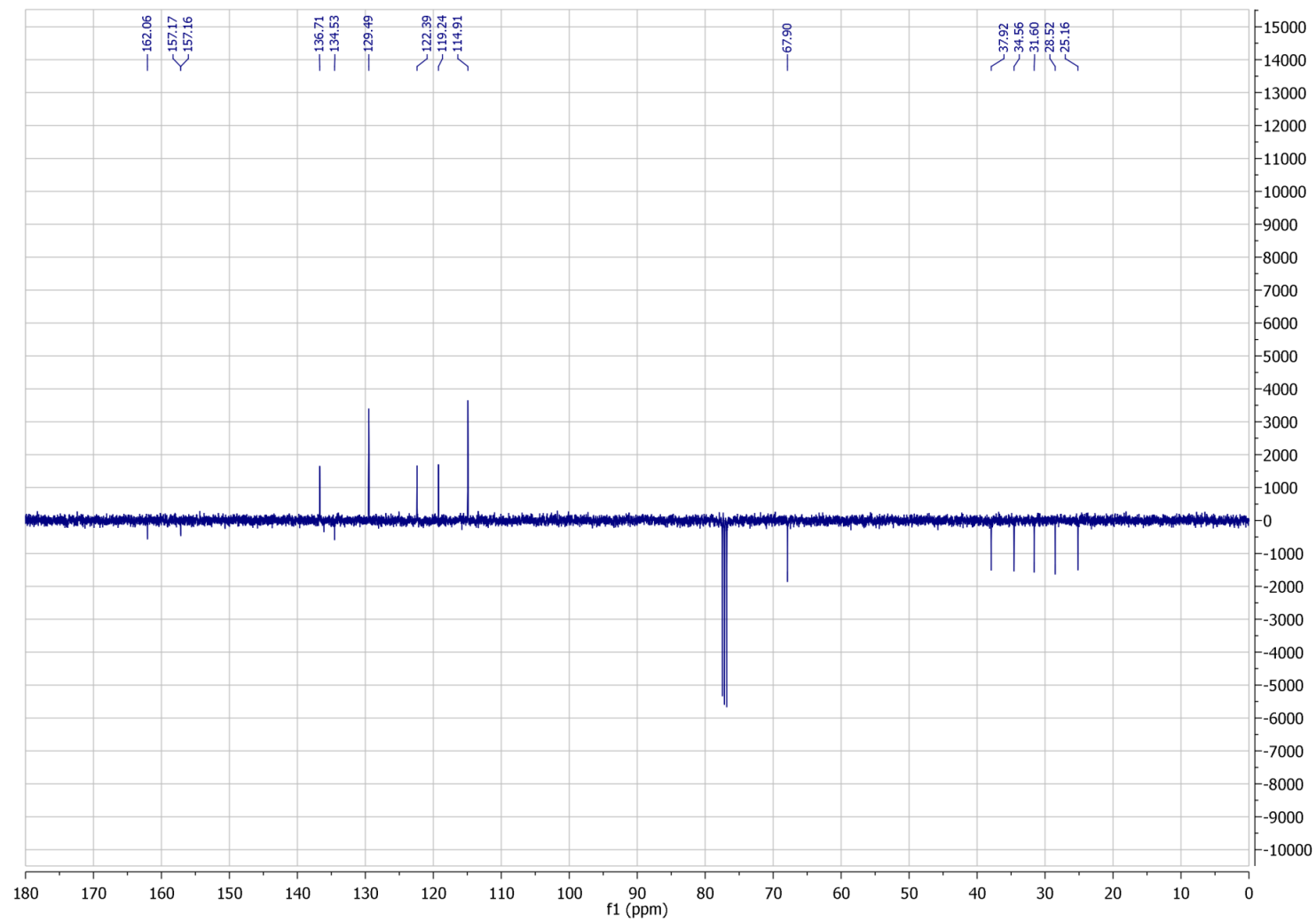
Macrocycle 9b HMBC NMR (CDCl₃, 400 MHz, 300 K)



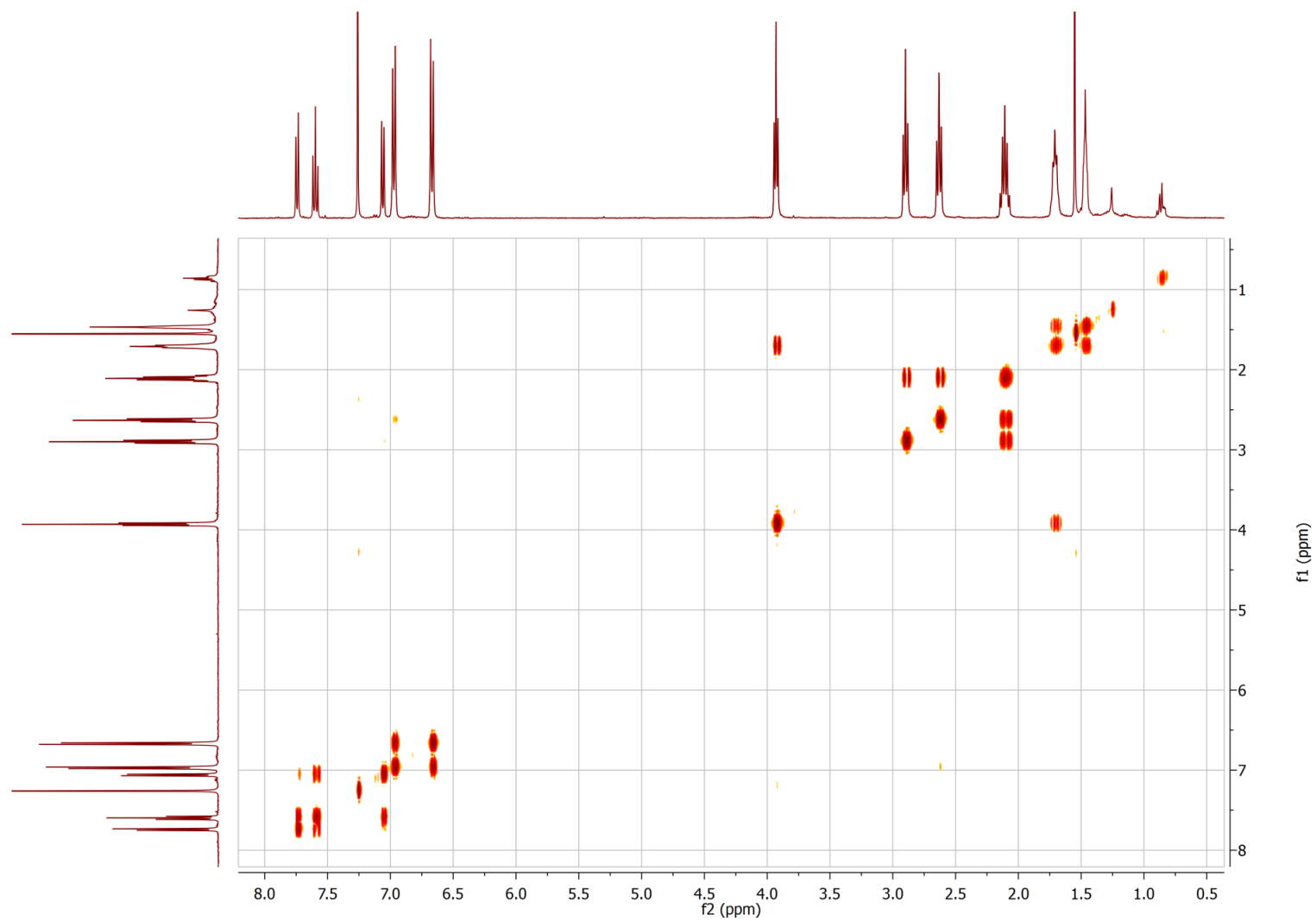
Macrocycle 9c ^1H NMR (CDCl_3 , 400 MHz, 300 K)



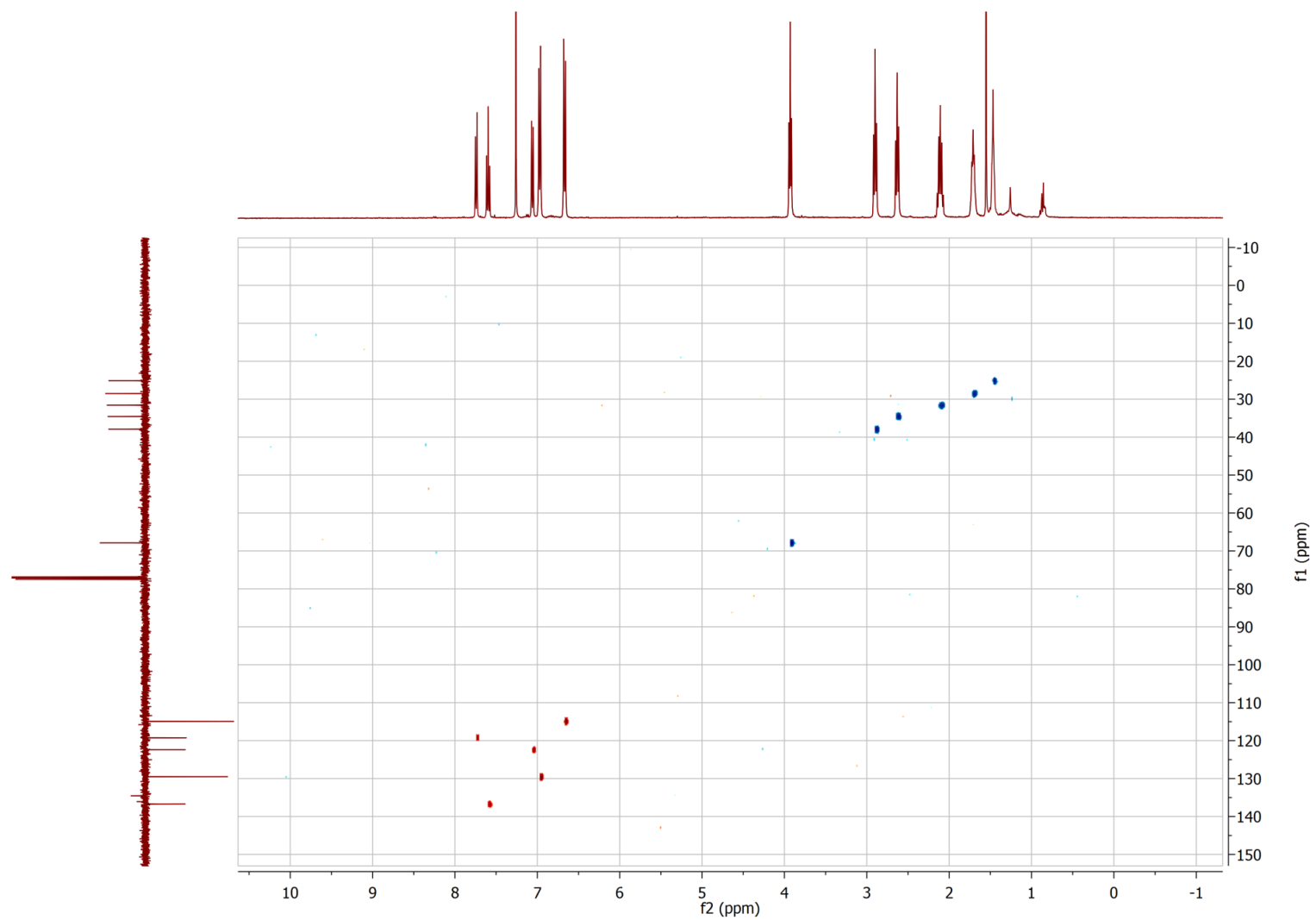
Macrocycle 9c DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



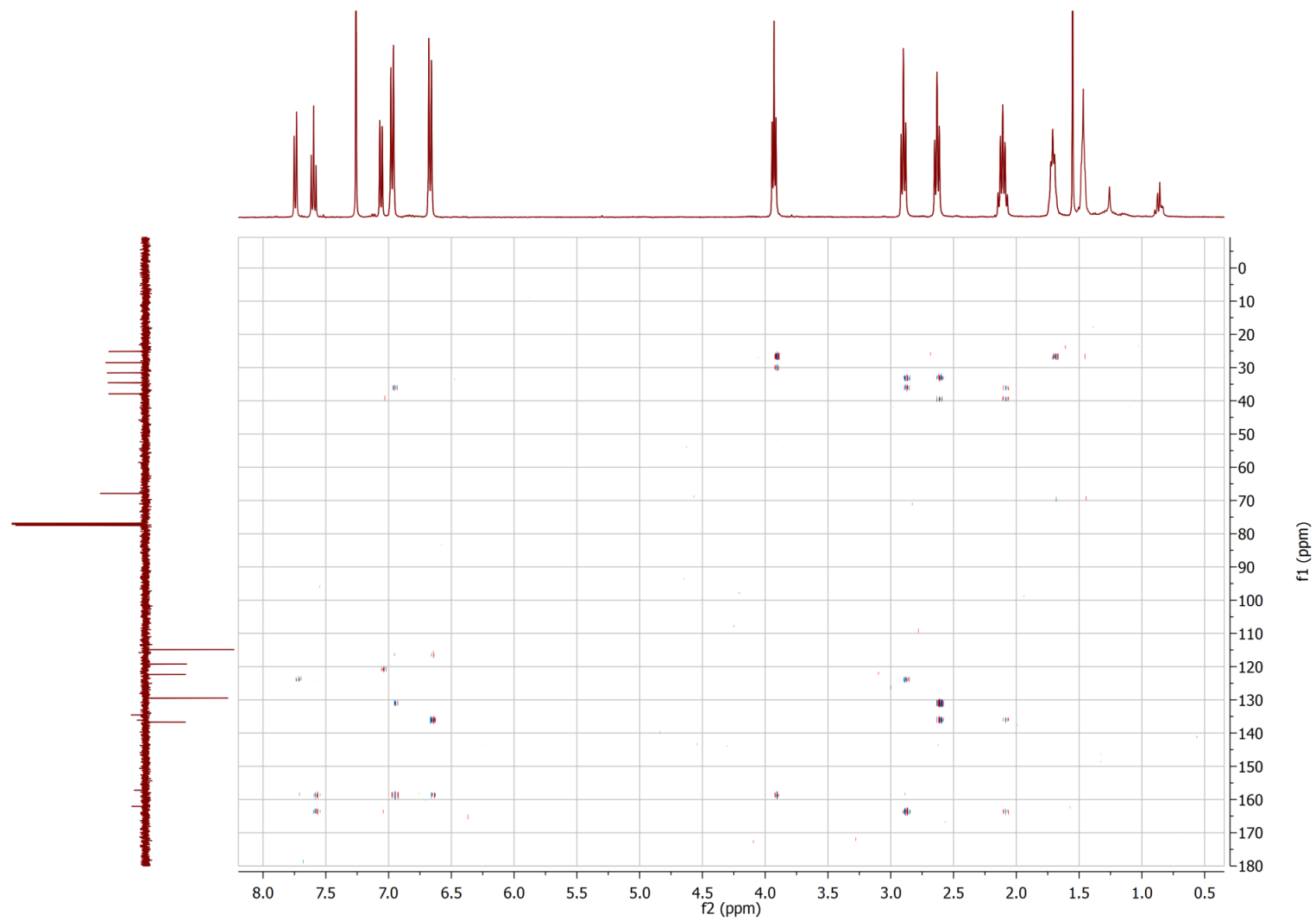
Macrocycle 9c COSY (CDCl₃, 400 MHz, 300 K)



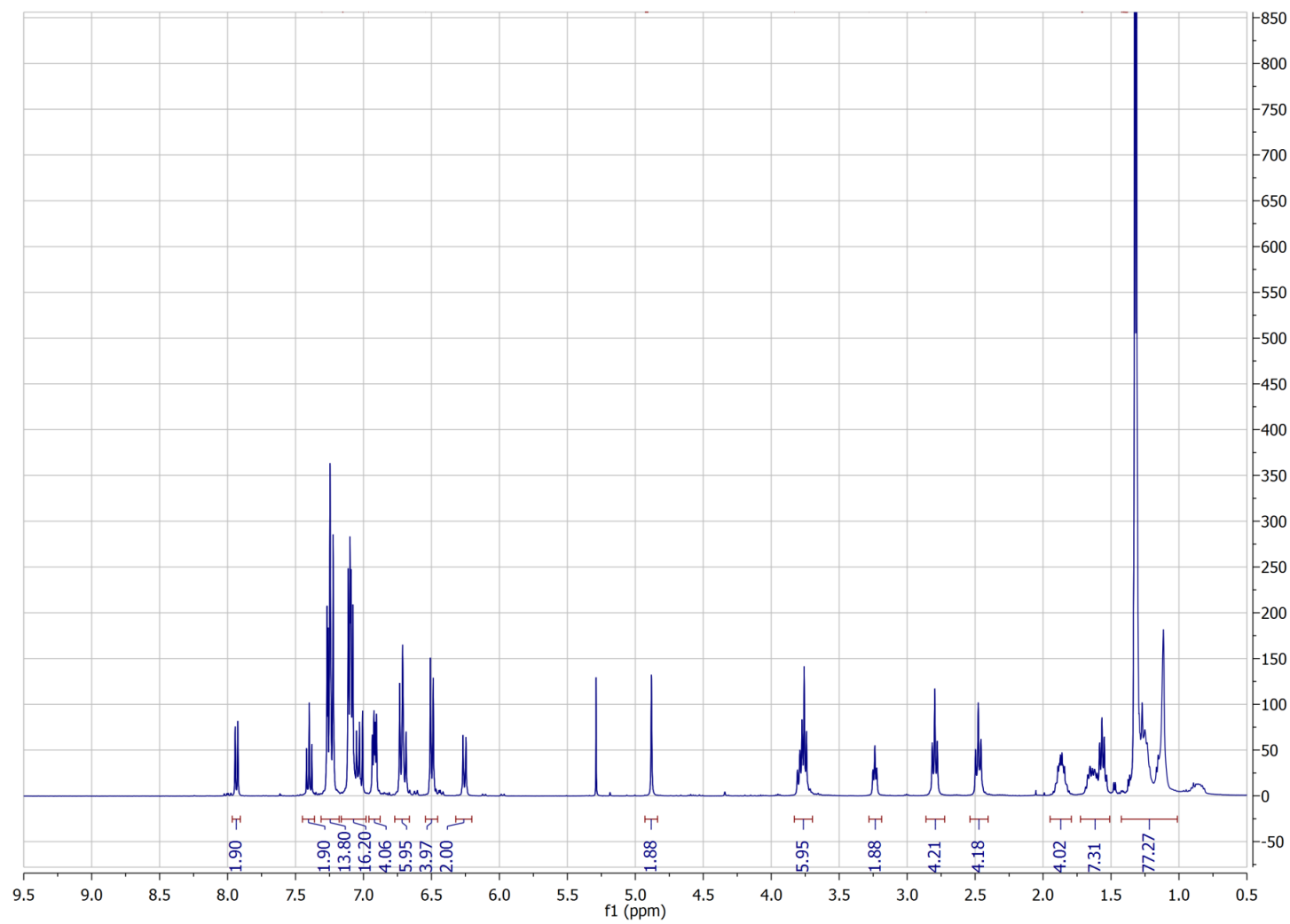
Macrocycle 9c HSQC NMR (CDCl₃, 400 MHz, 300 K)



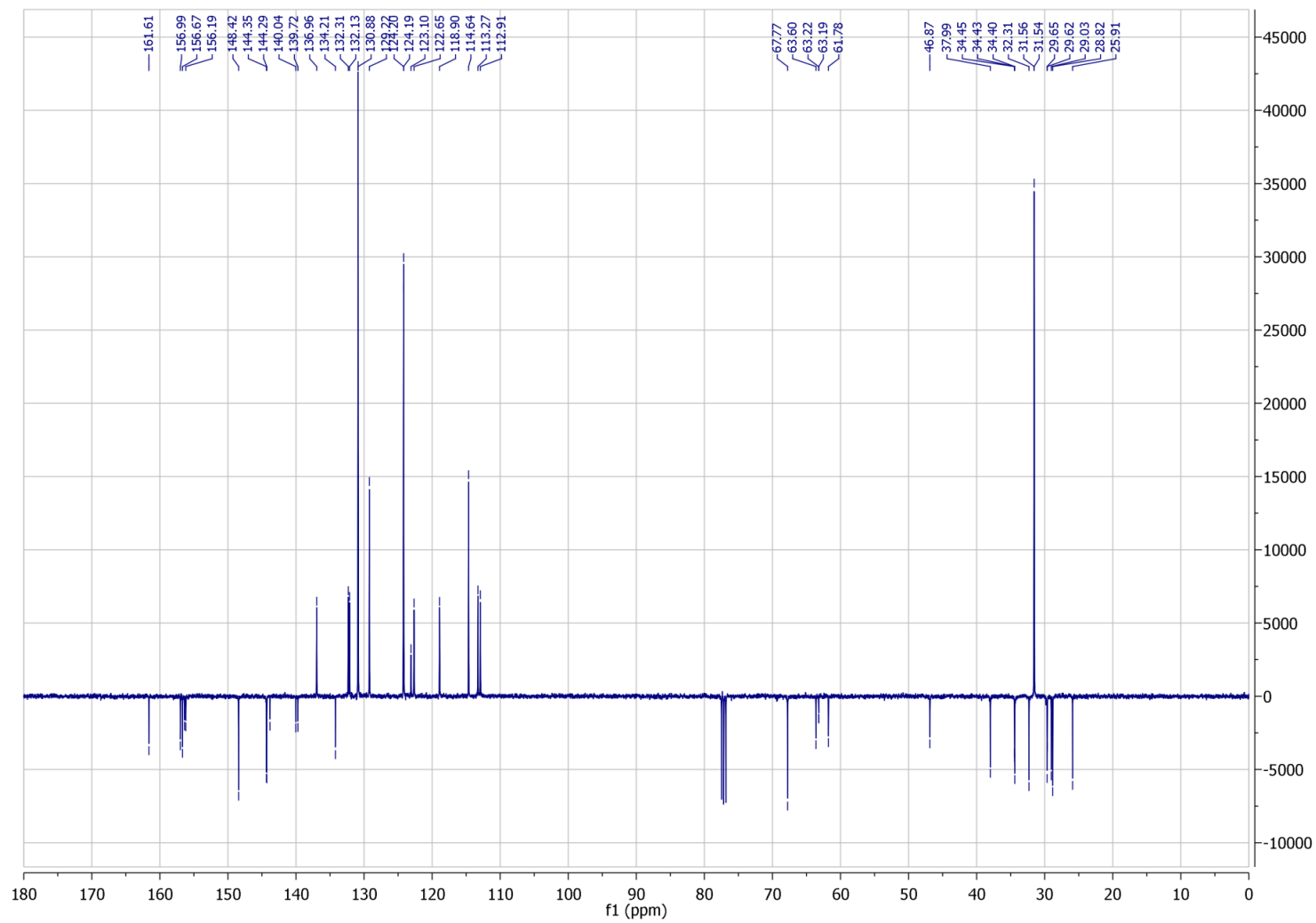
Macrocycle 9c HMBC NMR (CDCl₃, 400 MHz, 300 K)



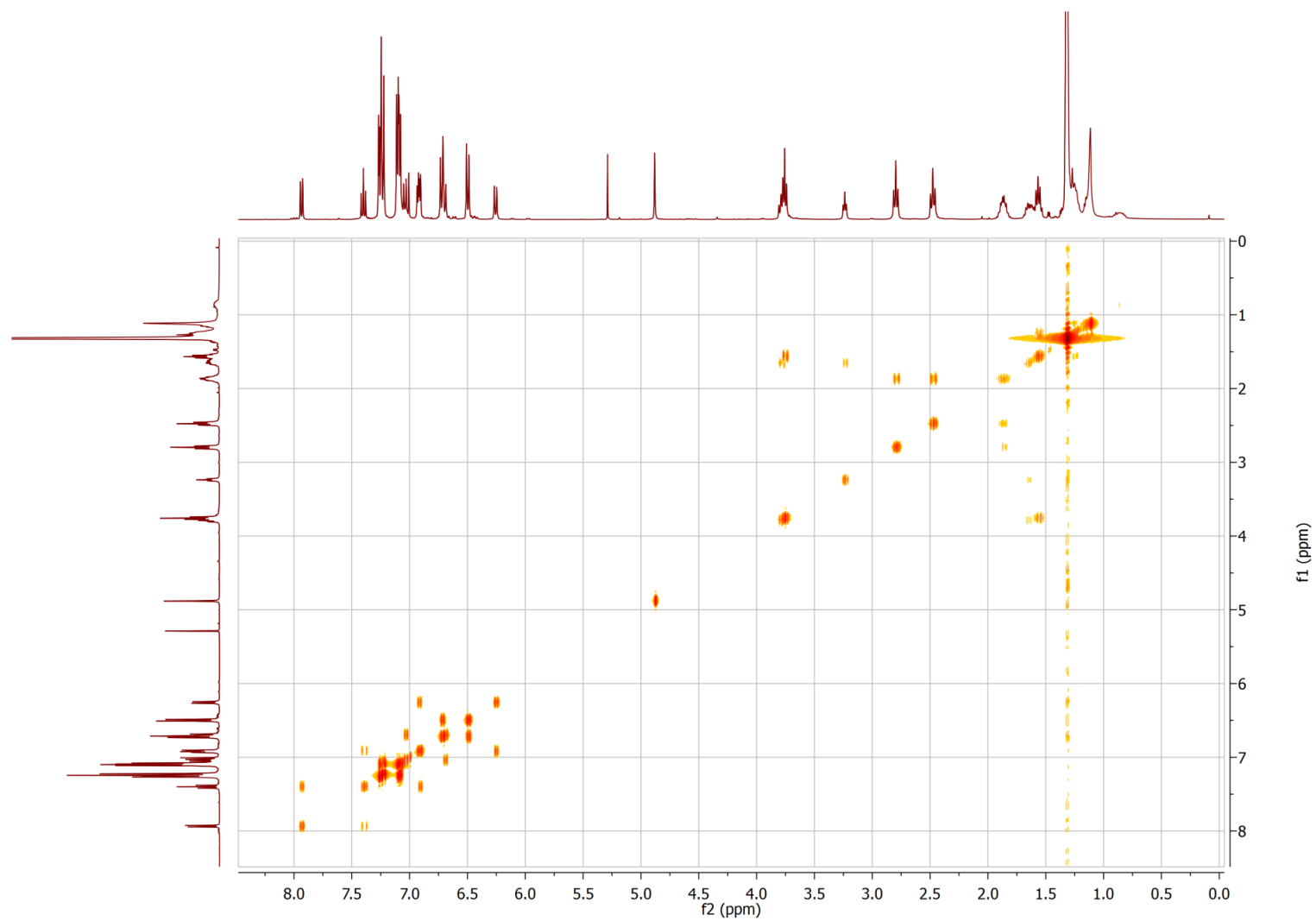
[2]Rotaxane 10a ^1H NMR (CDCl_3 , 400 MHz, 300 K)



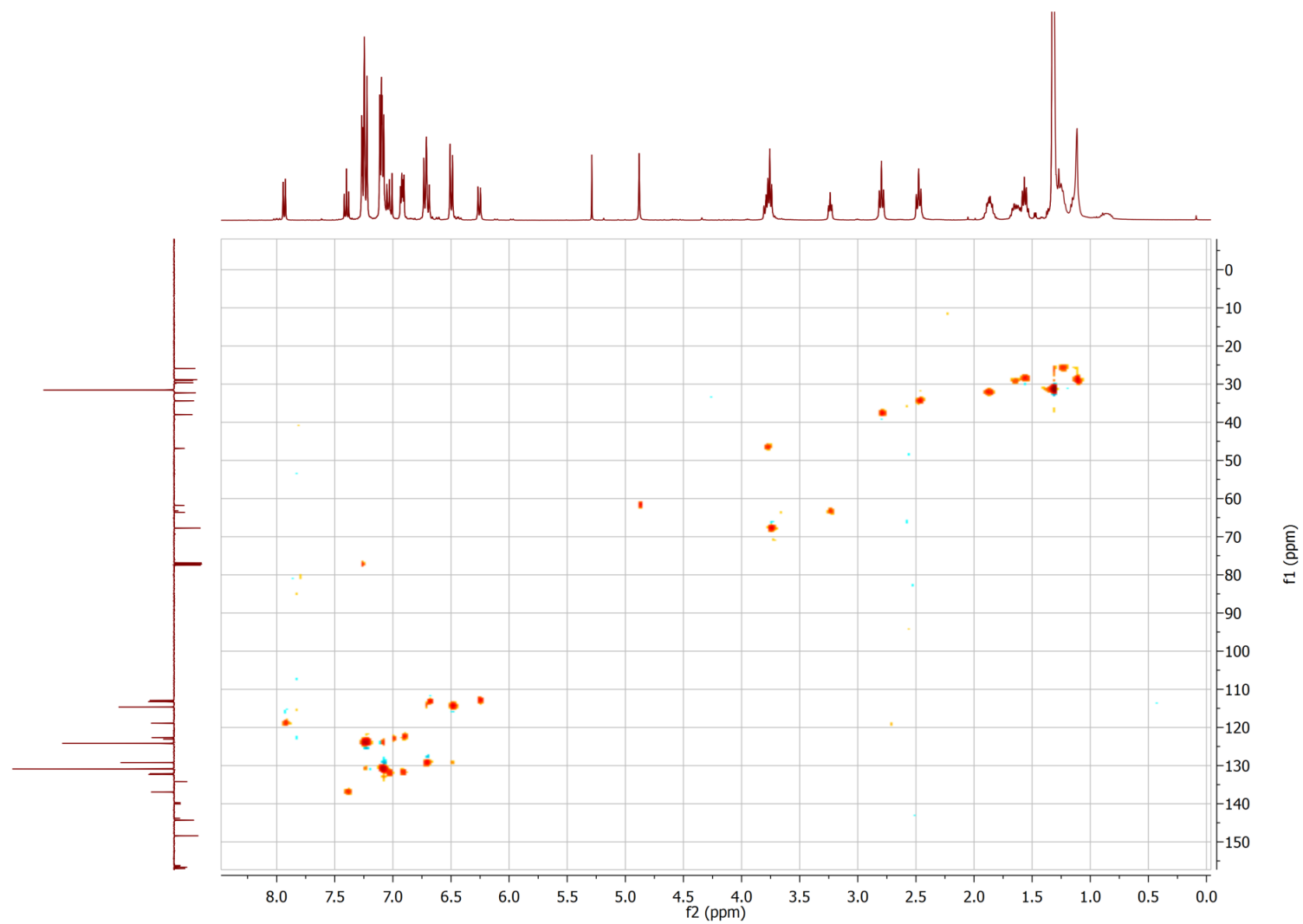
[2]Rotaxane 10a DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



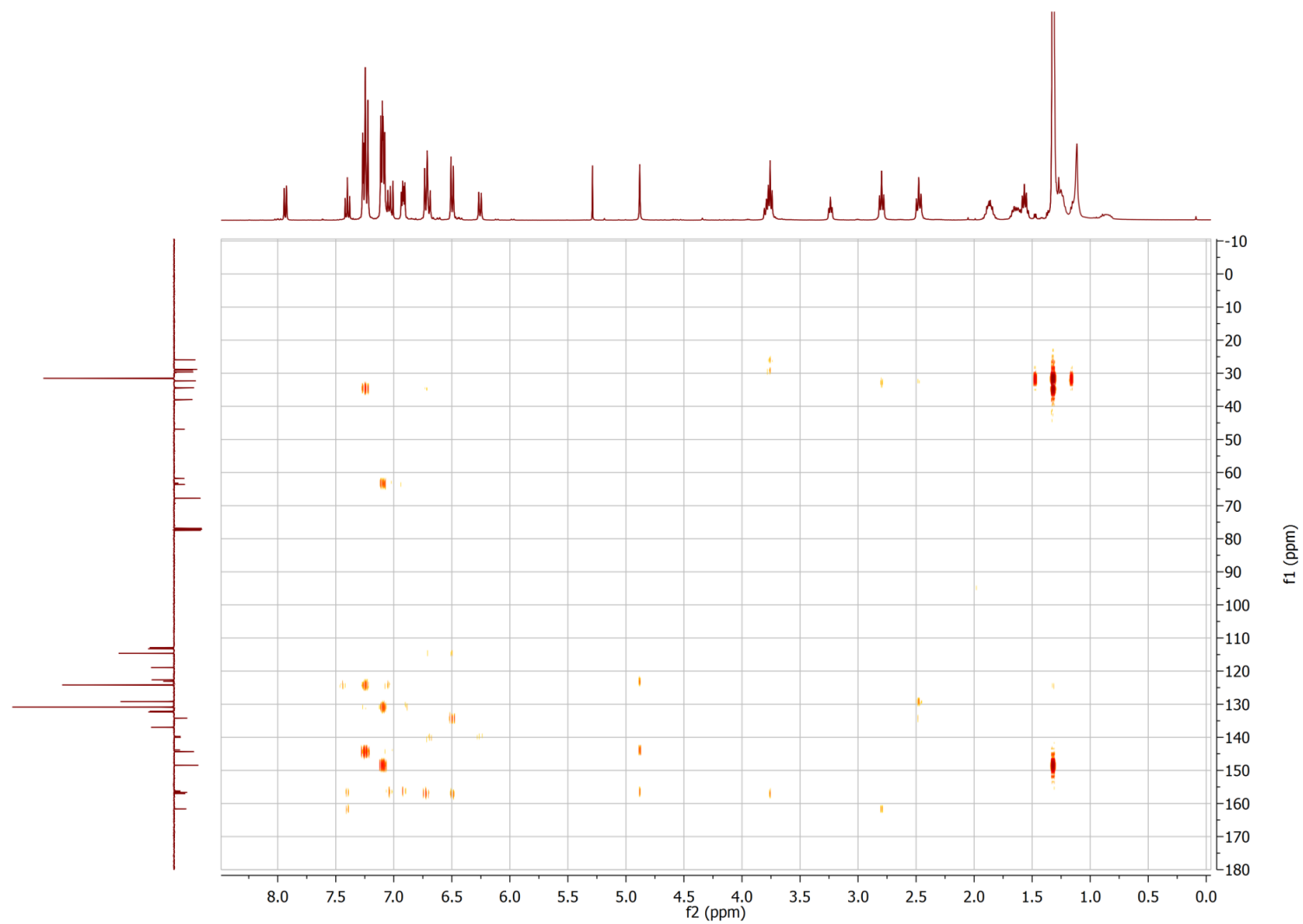
[2]Rotaxane 10a COSY (CDCl₃, 600 MHz, 300 K)



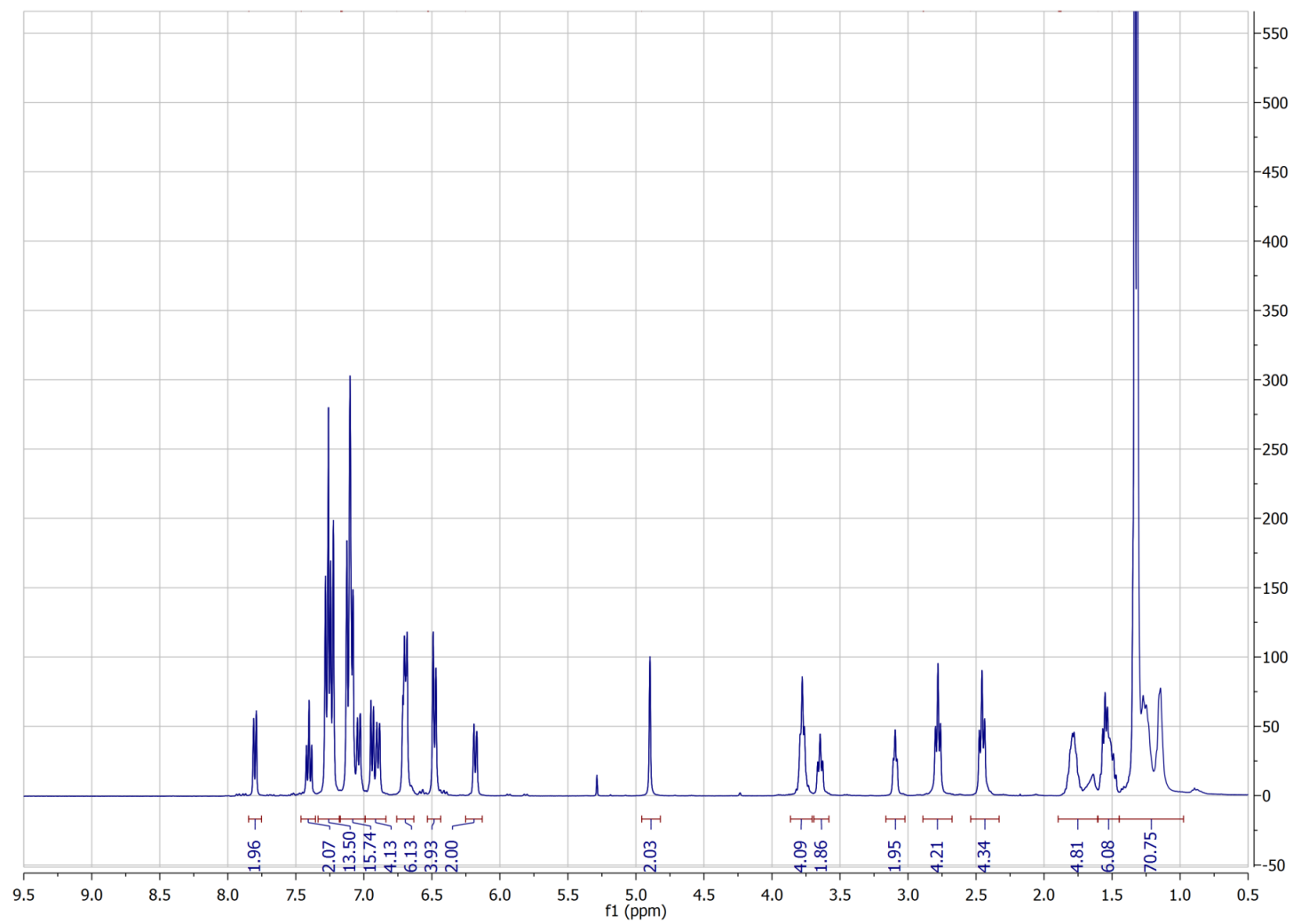
[2]Rotaxane 10a HSQC NMR (CDCl₃, 600 MHz, 300 K)



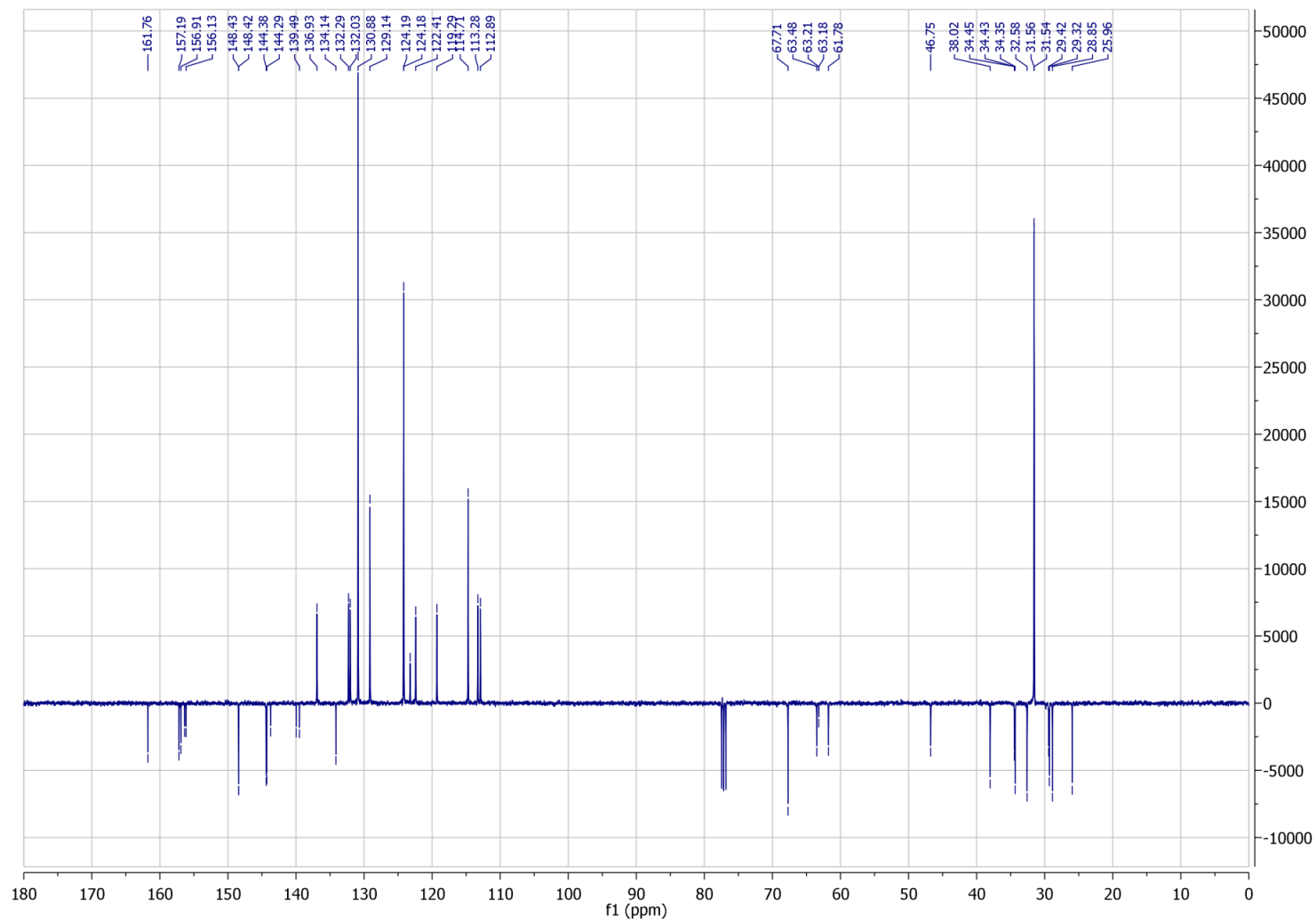
[2]Rotaxane 10a HMBC NMR (CDCl₃, 600 MHz, 300 K)



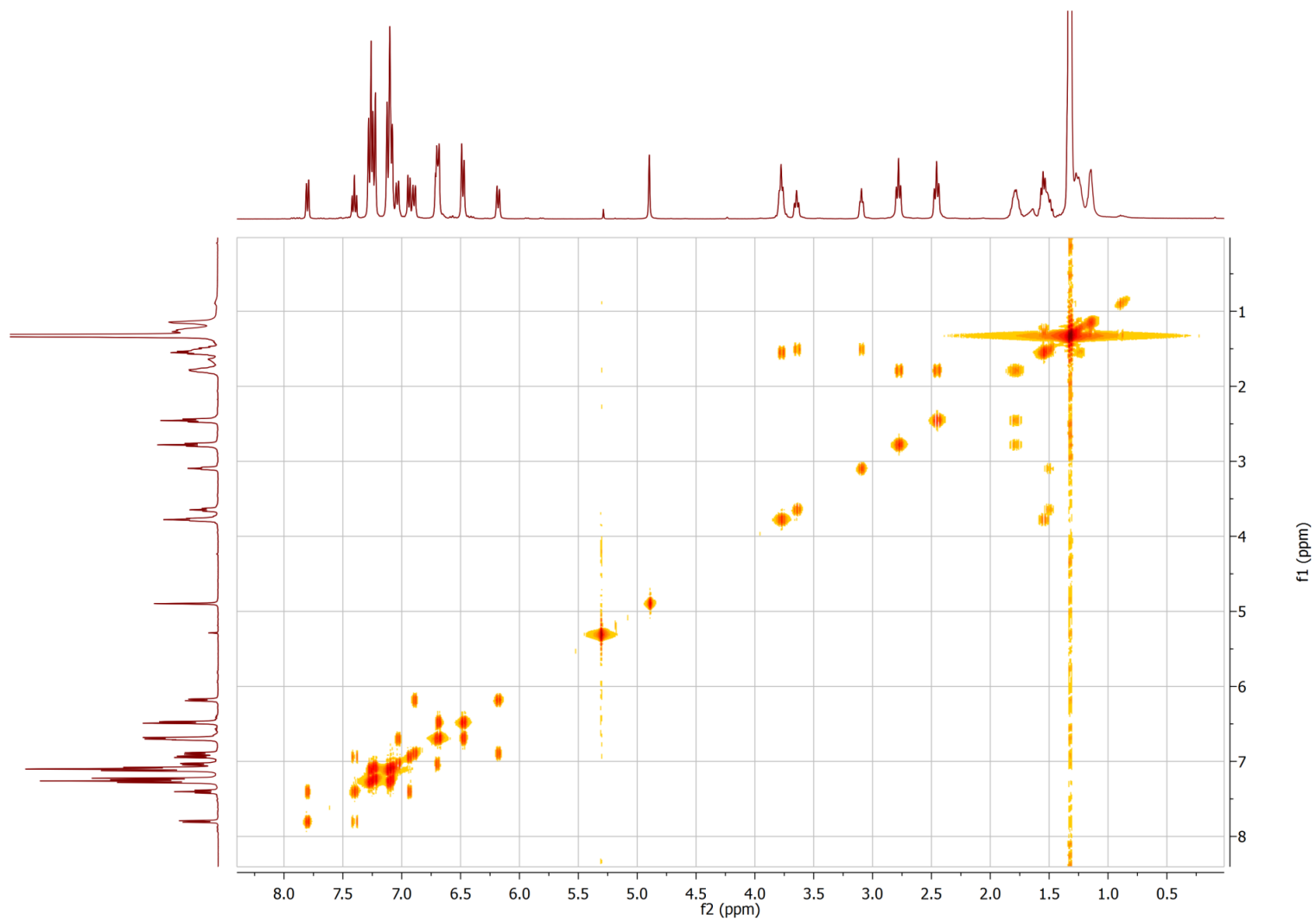
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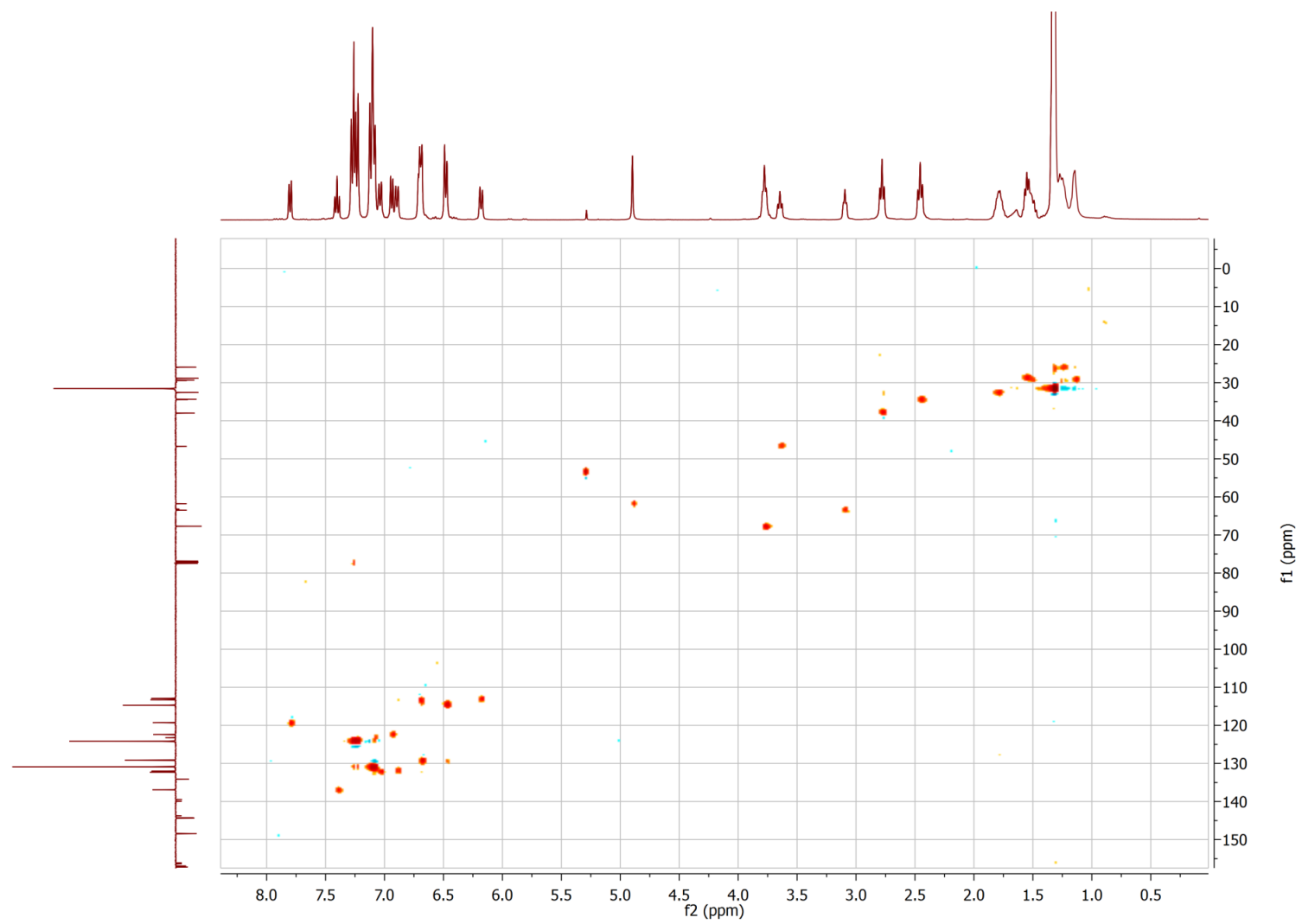
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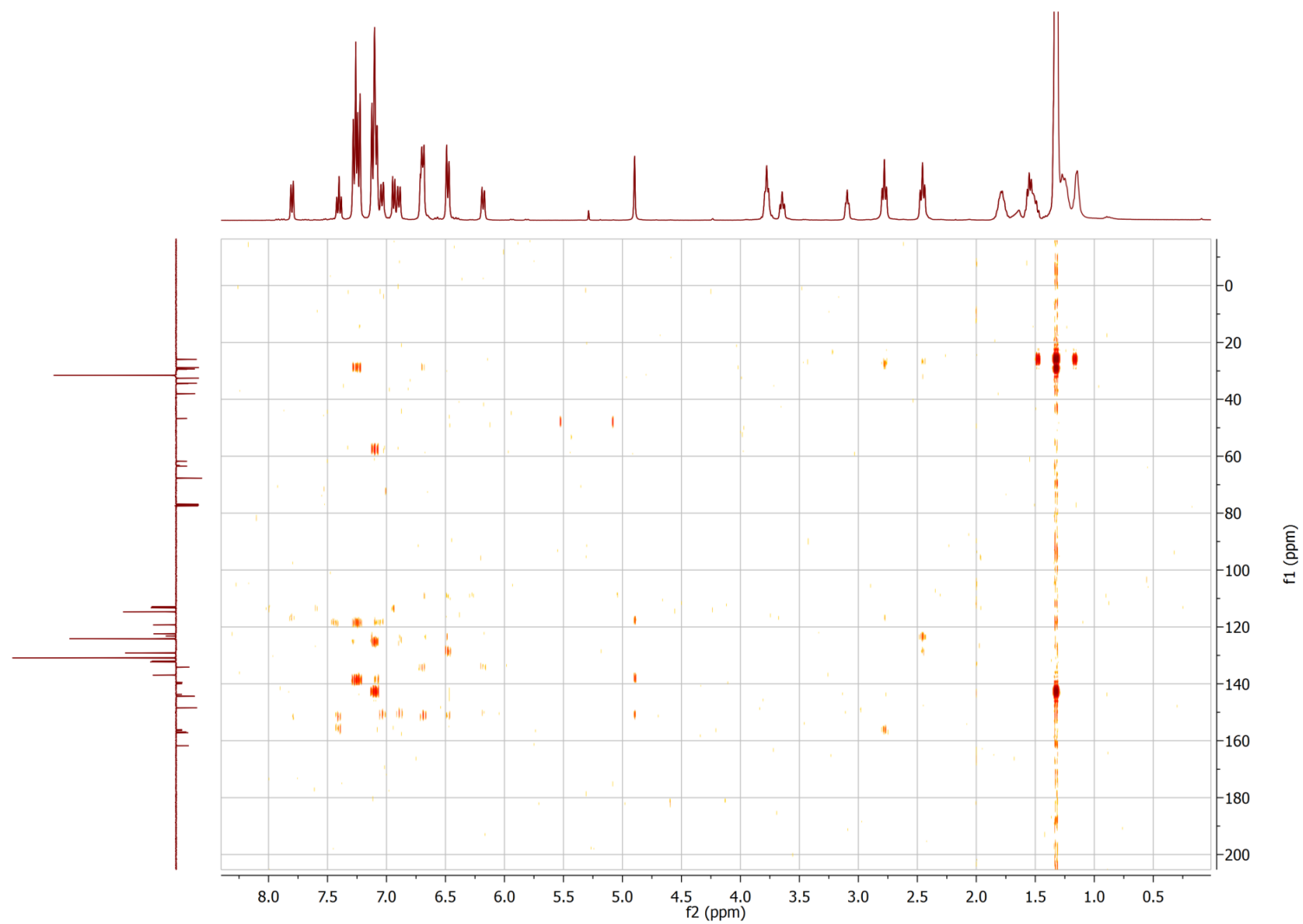
[2]Rotaxane 10b COSY (CDCl₃, 600 MHz, 300 K)



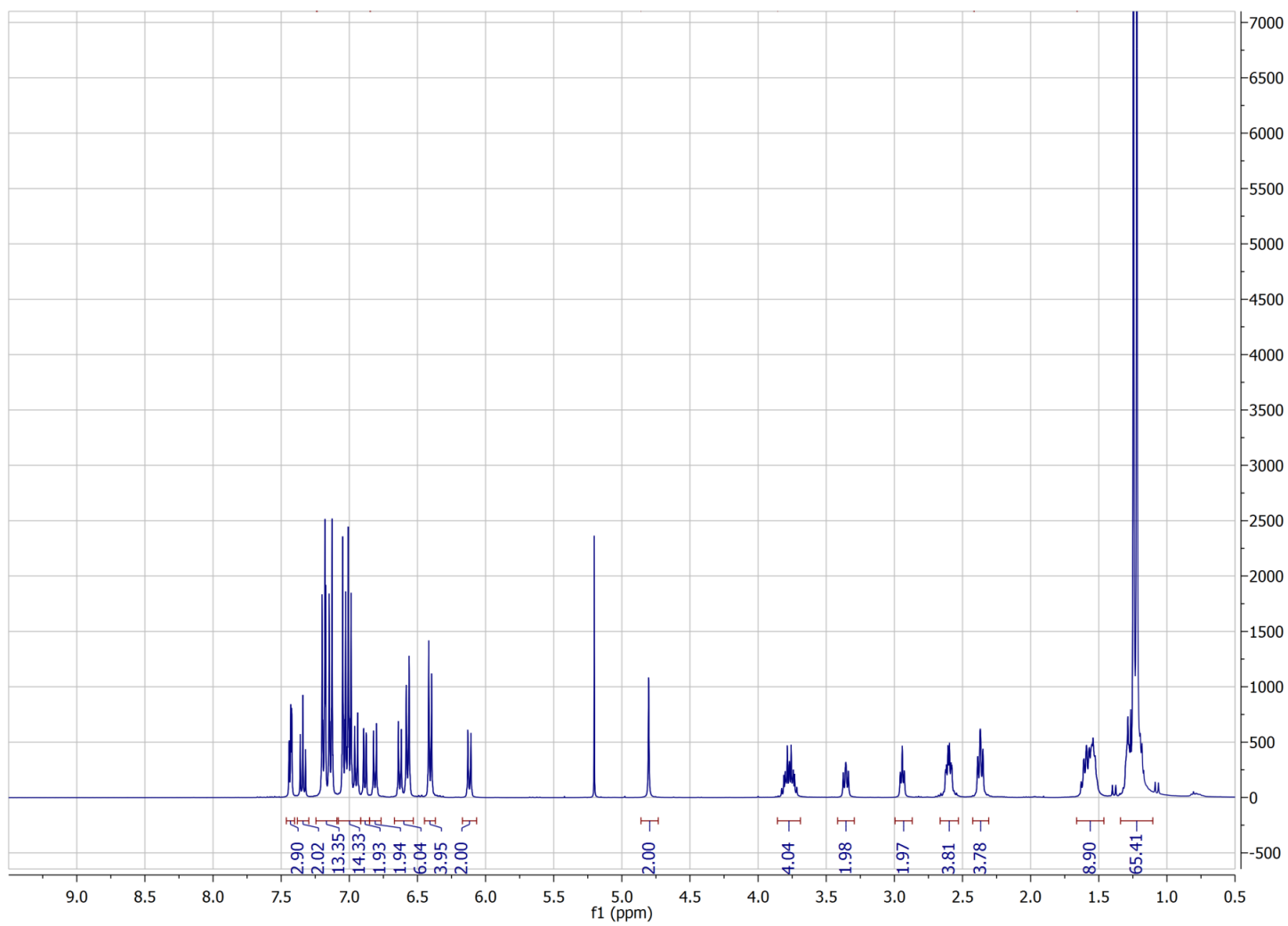
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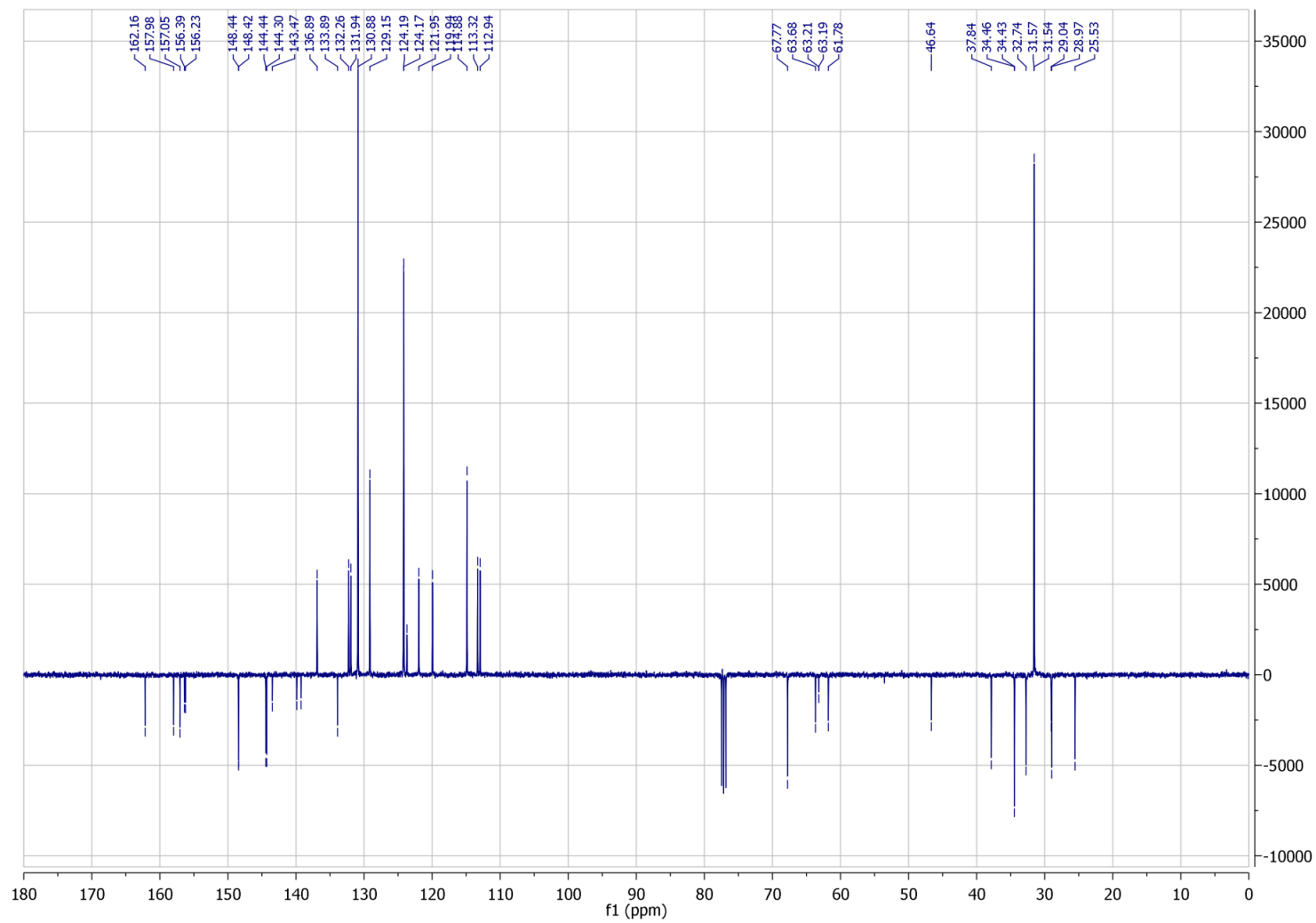
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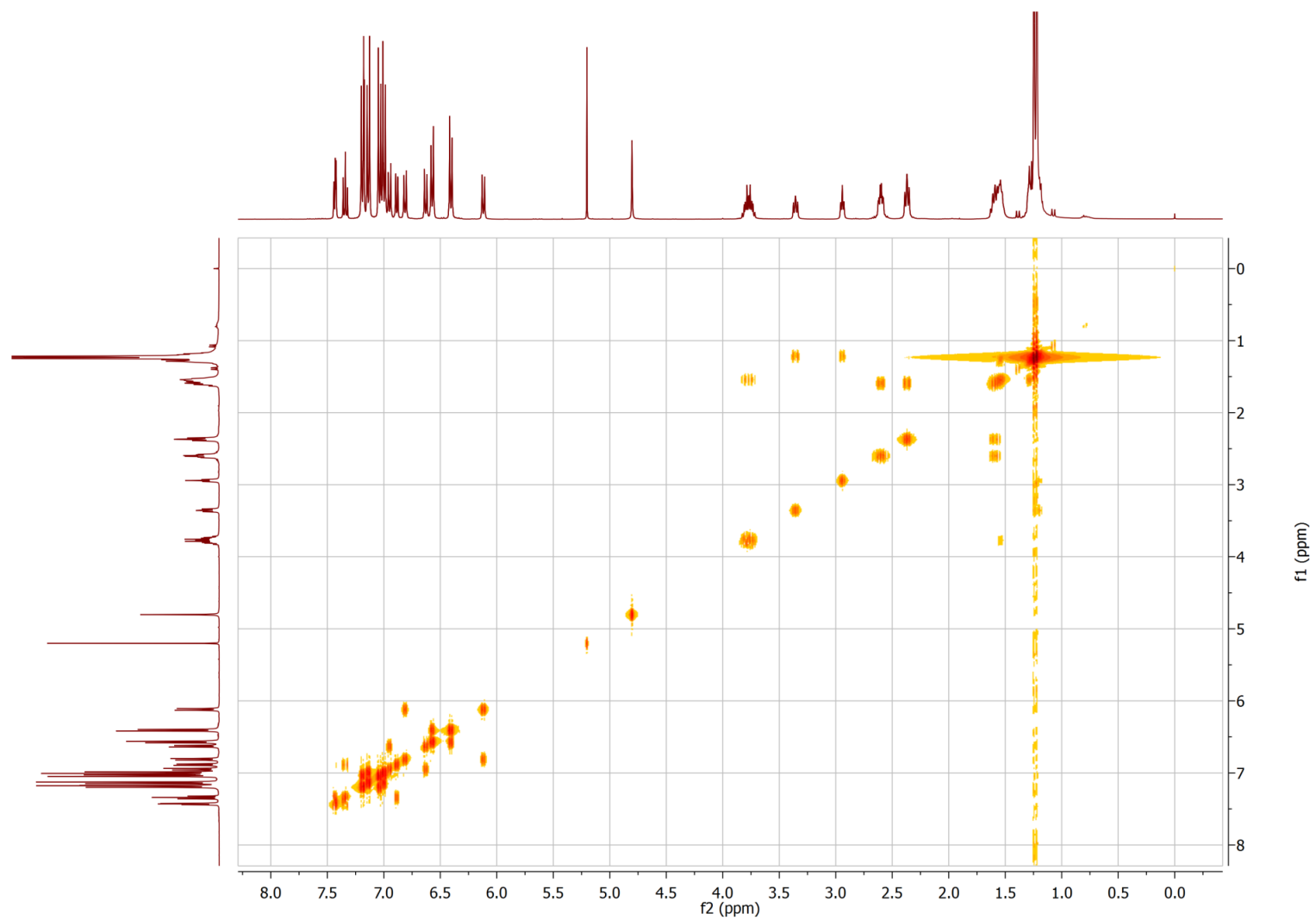
[2]Rotaxane 10c ^1H NMR (CDCl_3 , 400 MHz, 300 K)



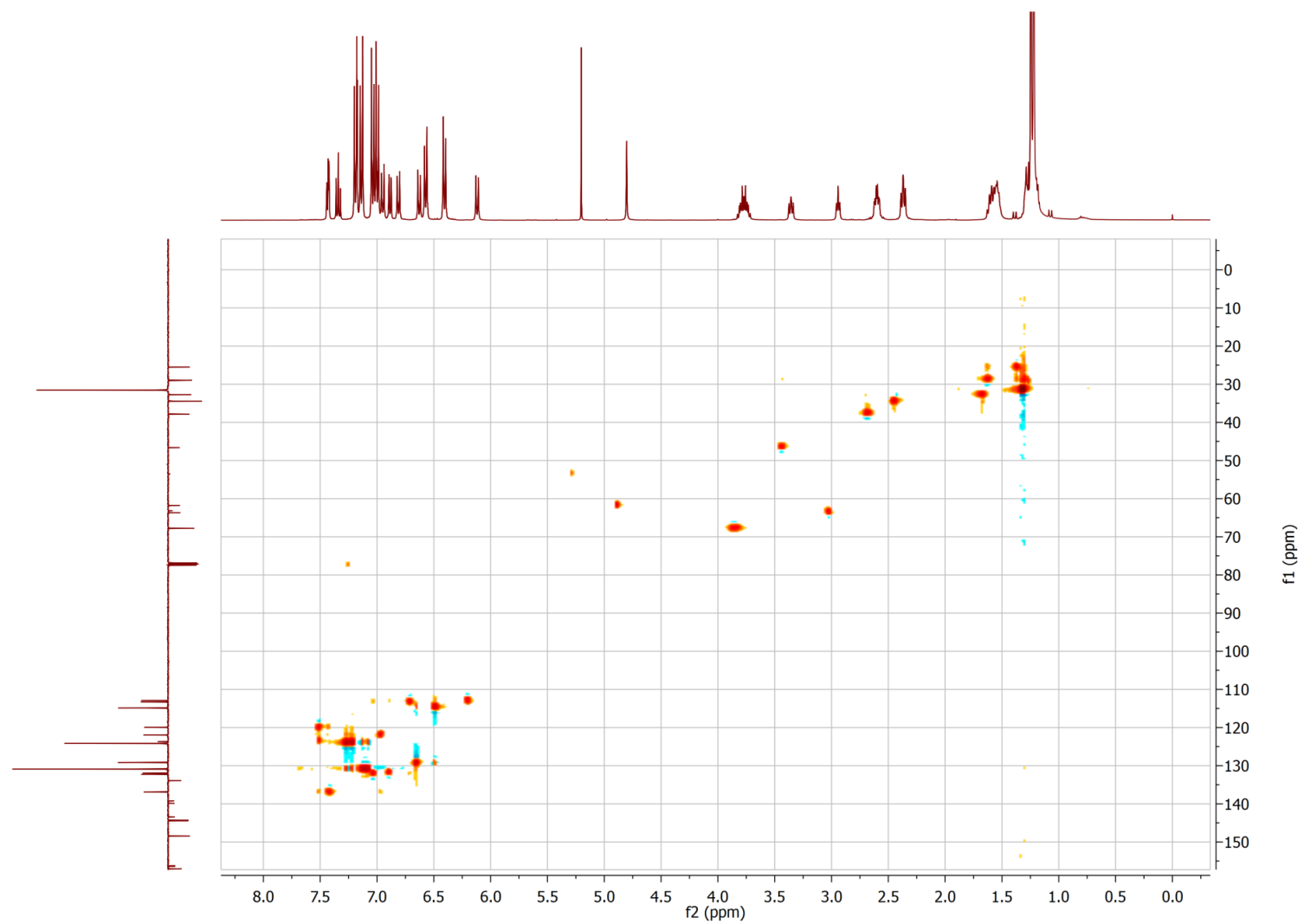
[2]Rotaxane 10c DEPTQ135 NMR (CDCl₃, 100 MHz, 300 K)



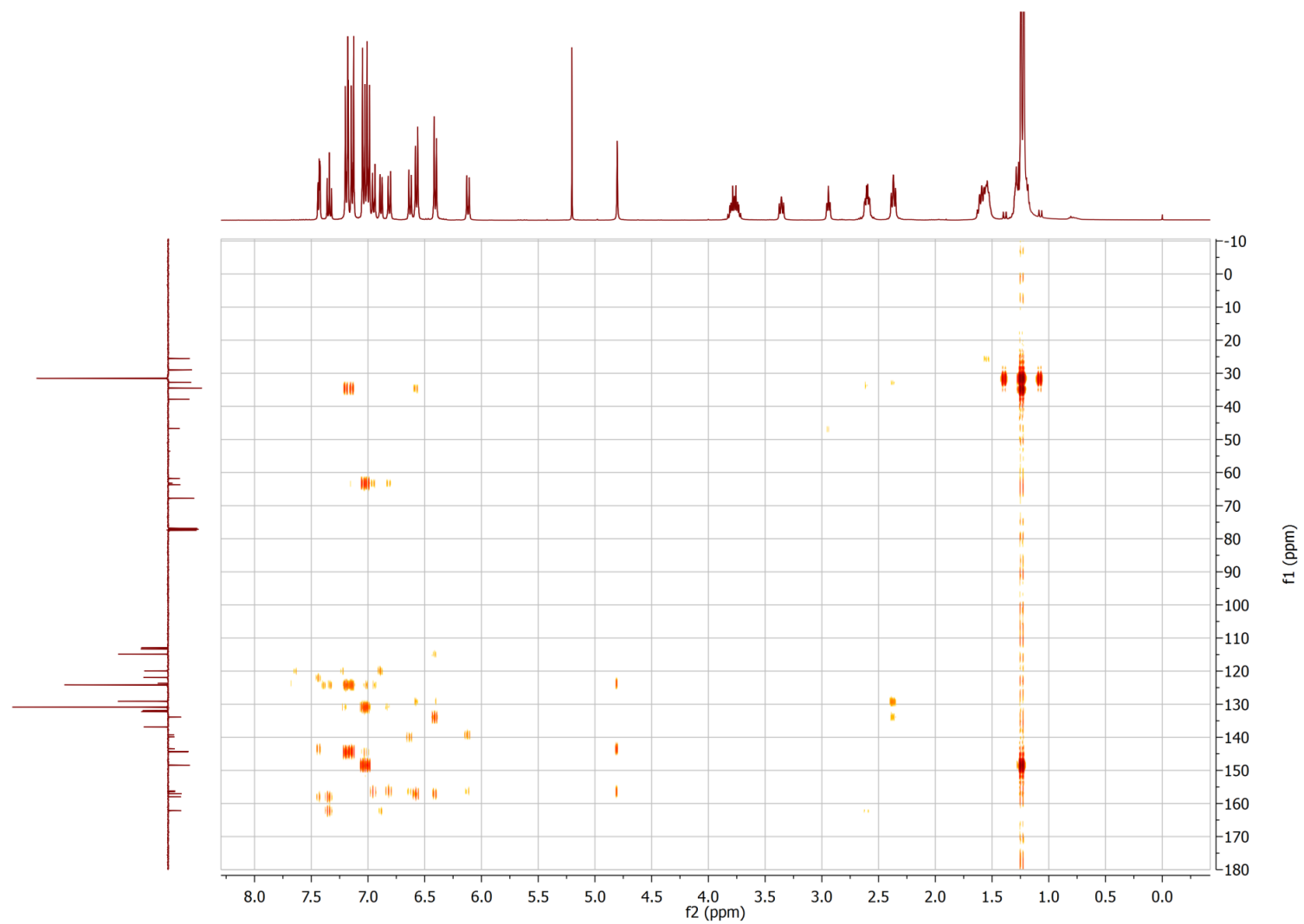
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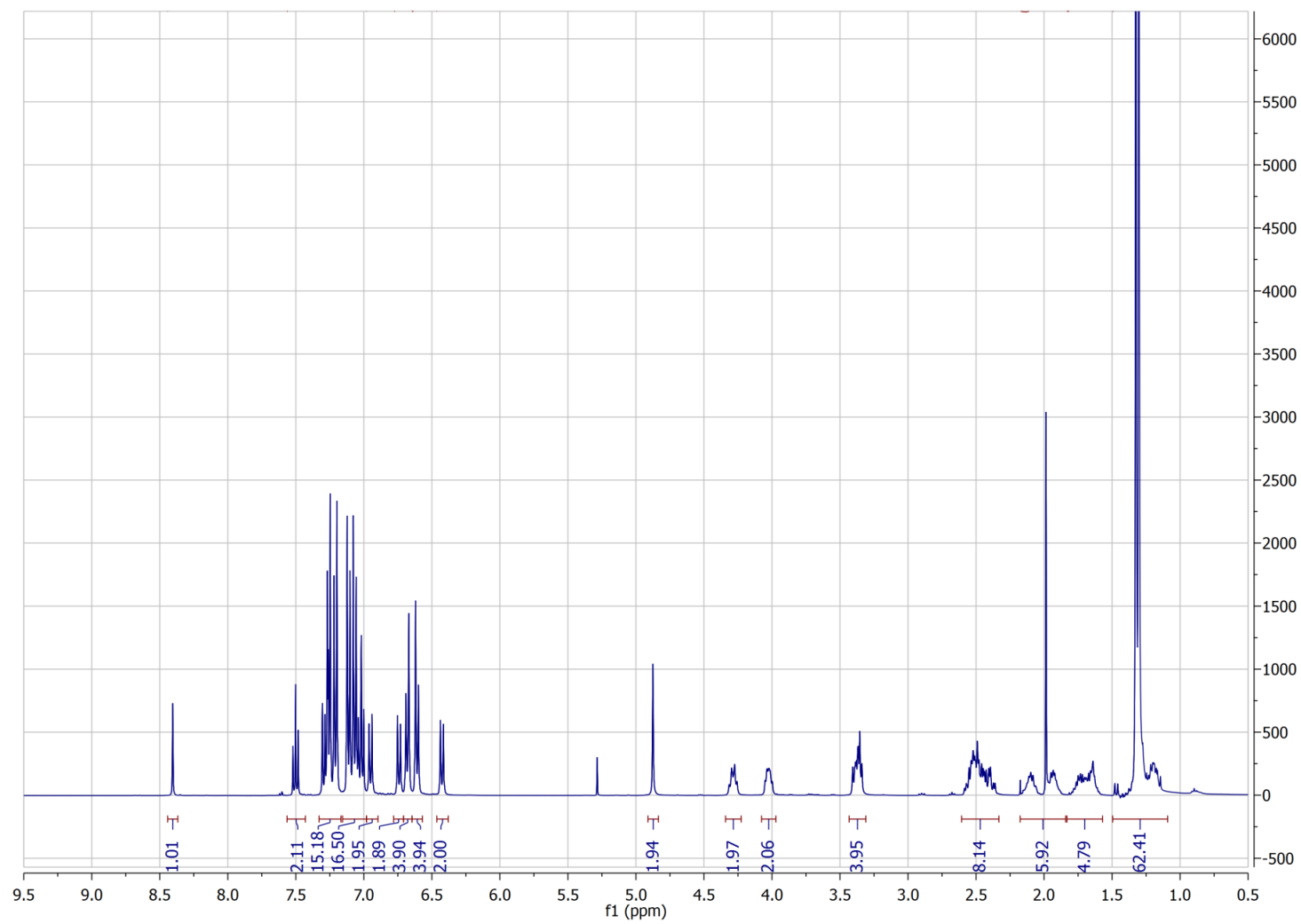
[2]Rotaxane 10c HSQC NMR (CDCl₃, 400 MHz, 300 K)



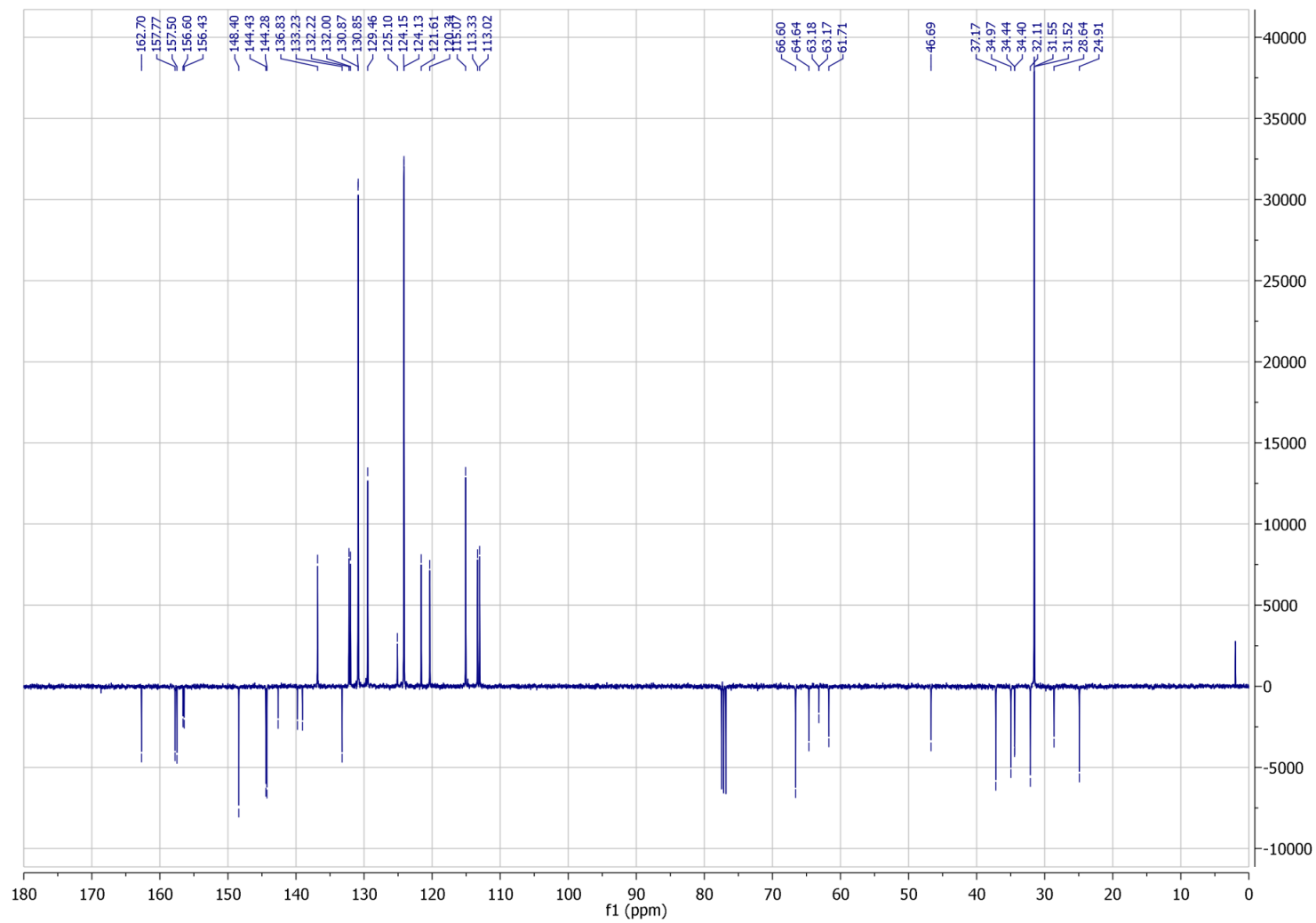
[2]Rotaxane 10c HMBC NMR (CDCl₃, 400 MHz, 300 K)



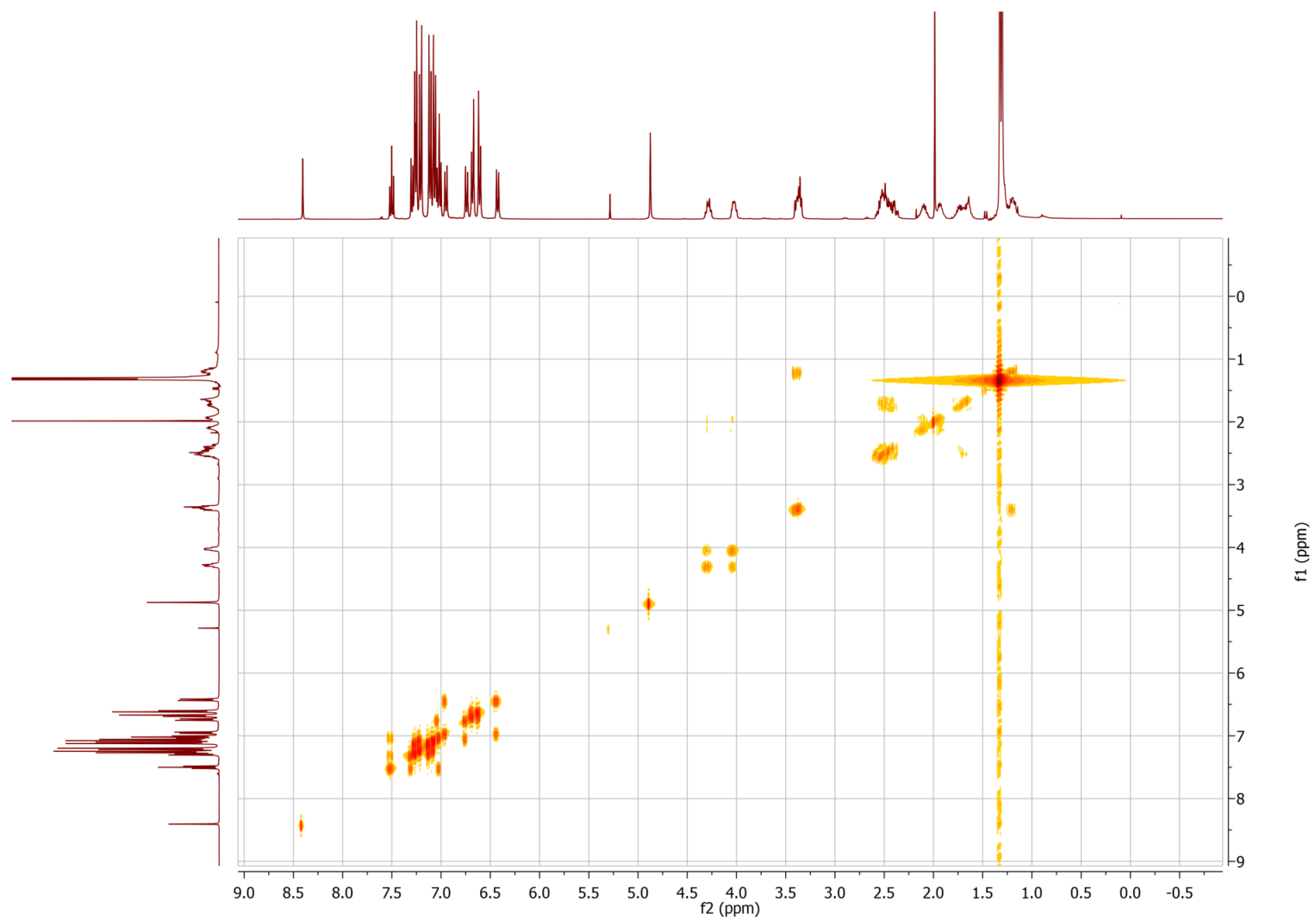
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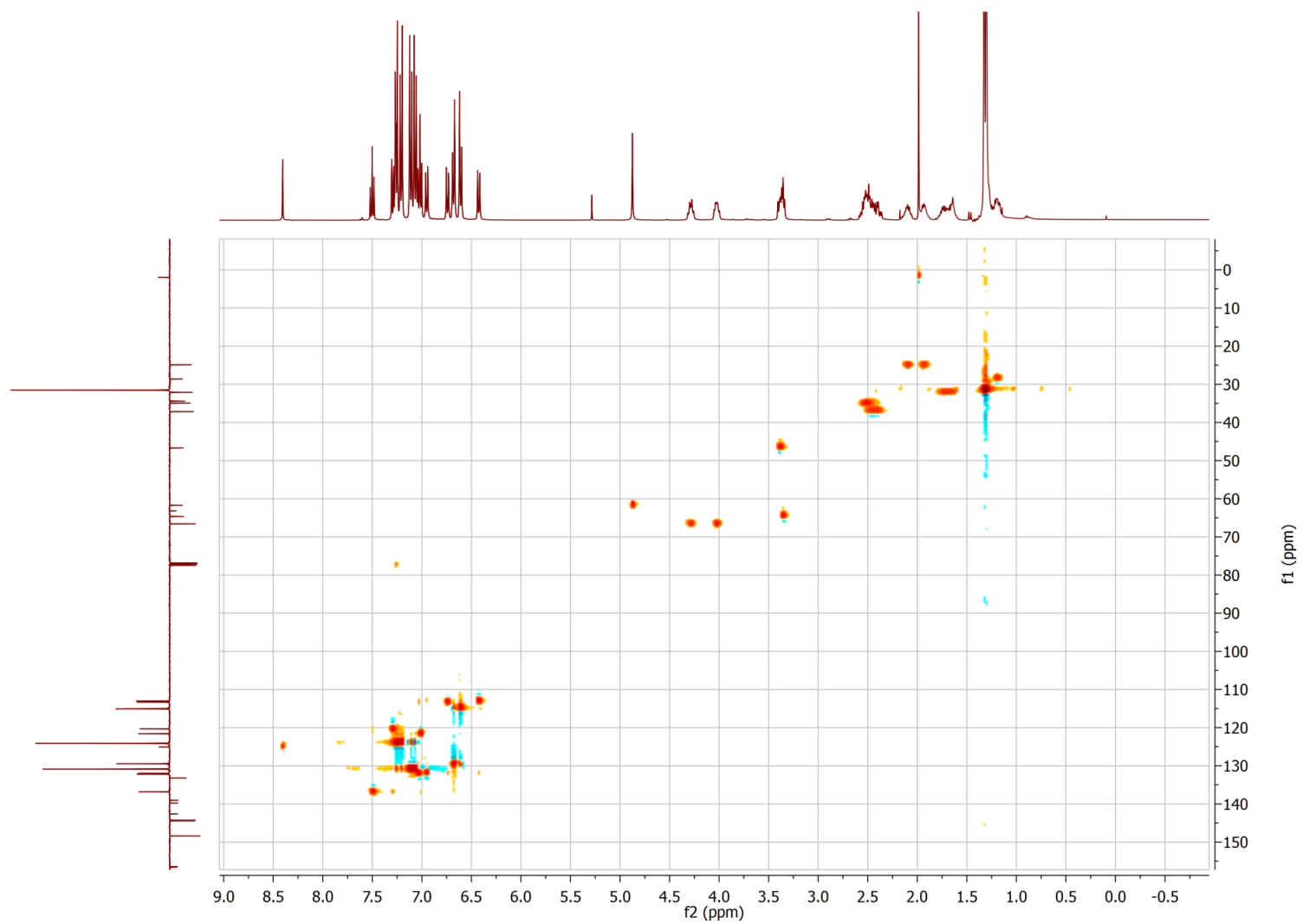
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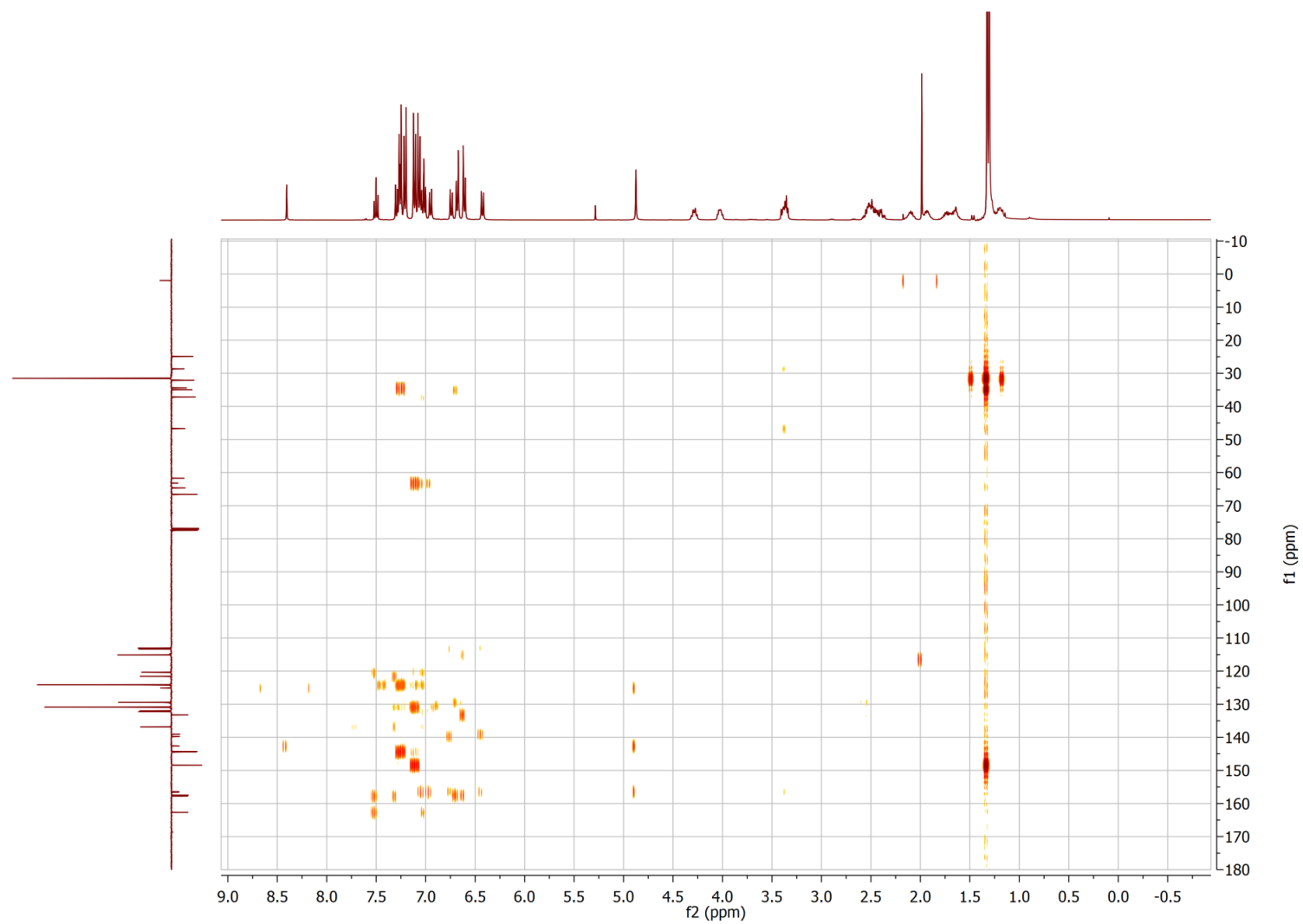
[2]Rotaxane 10d COSY (CDCl₃, 400 MHz, 300 K)



[2]Rotaxane 10d HSQC NMR (CDCl₃, 400 MHz, 300 K)



[2]Rotaxane 10d HMBC NMR (CDCl₃, 400 MHz, 300 K)



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