Halogen bonding directed Supramolecular Assembly in Bromo-substituted Trezimides and Tennimides.

by

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Nomenclature note:

In the Supporting Information diagrams the following labels have often been shortened for the sake of brevity/clarity (and frequently during the $^{1}H/^{13}C$ spectral acquisition stages):

$(BrIO)_3$	often shortened to **BrIO3**
$(BrIO)_4$	often shortened to **BrIO4**
$(26BrIO)_3$	often shortened to **26BrIO3**
$(26BrIO)_4$	often shortened to **26BrIO4**

Detailed description of synthetic and separation procedures

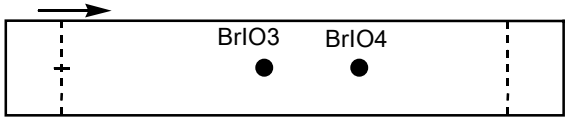
The synthetic procedures for both **(BrIO)$_{3/4}$** and **(26BrIO)$_{3/4}$** are practically identical.

The reaction medium was prepared by dissolving DMAP (10 mg, 0.08 mmol) and triethylamine (4 ml, 29.8 mmol) in 80 (60) ml of anhydrous CH_2Cl_2. The 2-amino-5-bromopyridine (1.6964 g, 9.8 mmol) was suspended in 20 ml of anhydrous CH_2Cl_2. For the **(26BrIO)$_{3/4}$** reaction, 2-amino-5-bromopyrimidine was used (1.7053 g, 9.8 mmol) and suspended in 40 ml of anhydrous CH_2Cl_2. Isophthaloyl dichloride (1.98 g, 9.8 mmol) was dissolved with stirring in 80 ml of reaction media in a 250 ml round bottom flask, under an inert atmosphere of N_2 and cooled on an ice bath (ice/NaCl/NH_4Cl/EtOH) to –15°C. The 2-amino-5-bromopyridine/pyrimidine suspension was quickly and quantitatively added to the cooled flask containing the dissolved isophthaloyl dichloride. The reaction mixture was stirred overnight. The reaction mixture was diluted with technical grade CH_2Cl_2 to 200 ml, filtered over a funnel with a sintered glass frit to remove a polymeric by-product and washed three times with aqueous solutions of NH_4Cl (pH ≈ 5) (3 × 200 ml), dried over $MgSO_4$ and filtered. The clear, filtered product mixture was left to stand overnight.
Subsequently the solvent was removed on a rotary-evaporator to afford a dark red resin. This resin was immediately purified by column chromatography on silica gel (Davisil, 70 μm, 82 g, column dimension: l = 25 cm, d = 3 cm) eluting with a mobile phase of $CHCl_3$/ethyl acetate (4:1) to obtain the separated and clean, pure macrocyclic products.

Yield **(BrIO)$_3$** = 212 mg (7%), calculated M_r **(BrIO)$_3$** = 909.33 g.mol^{-1}
Yield **(BrIO)$_4$** = 177 mg (6%), calculated M_r **(BrIO)$_4$** = 1212.44 g.mol^{-1}

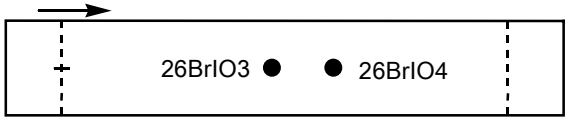
Yield **(26BrIO)$_3$** = 164 mg (6%), calculated M_r **(26BrIO)$_3$** = 912.33 g.mol^{-1}
Yield **(26BrIO)$_4$** = 110 mg (4%), calculated M_r **(26BrIO)$_4$** = 1216.40 g.mol^{-1}

(BrIO)$_3$ and **(BrIO)$_4$** [$CHCl_3$/ethyl acetate (4:1)]:
TLC analysis (→ denotes solvent movement)



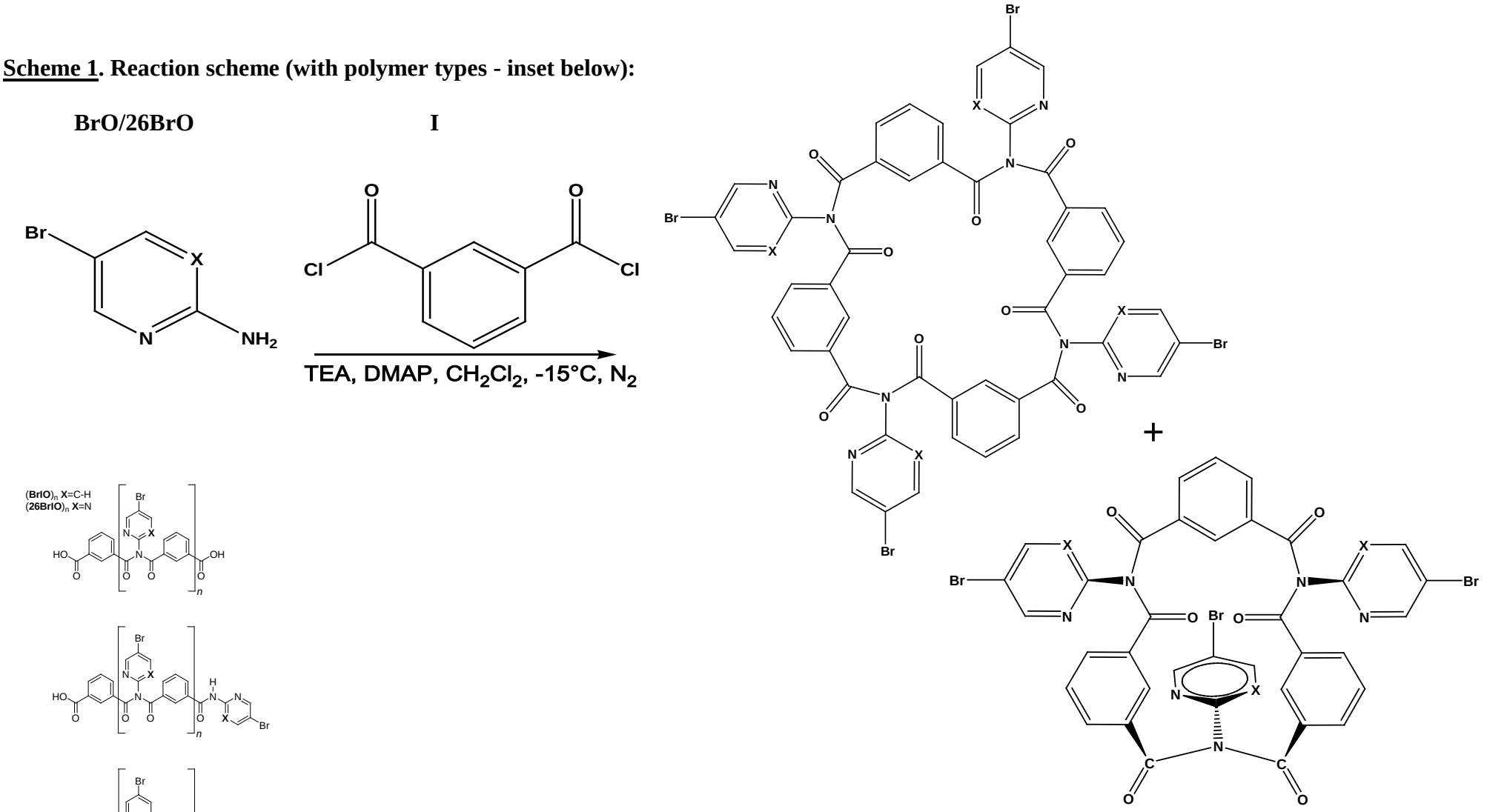
R_f **(BrIO)$_3$** = 0.45 and R_f **(BrIO)$_4$** = 0.67

26BrIO3 and **26BrIO4** [$CHCl_3$/ethyl acetate (4:1)]:
TLC analysis (→ denotes solvent movement)



R_f **(26BrIO)$_3$** = 0.47 and R_f **(26BrIO)$_4$** = 0.61

Scheme 1. Reaction scheme (with polymer types - inset below):



Imide/amide Oligomer/Polymer types

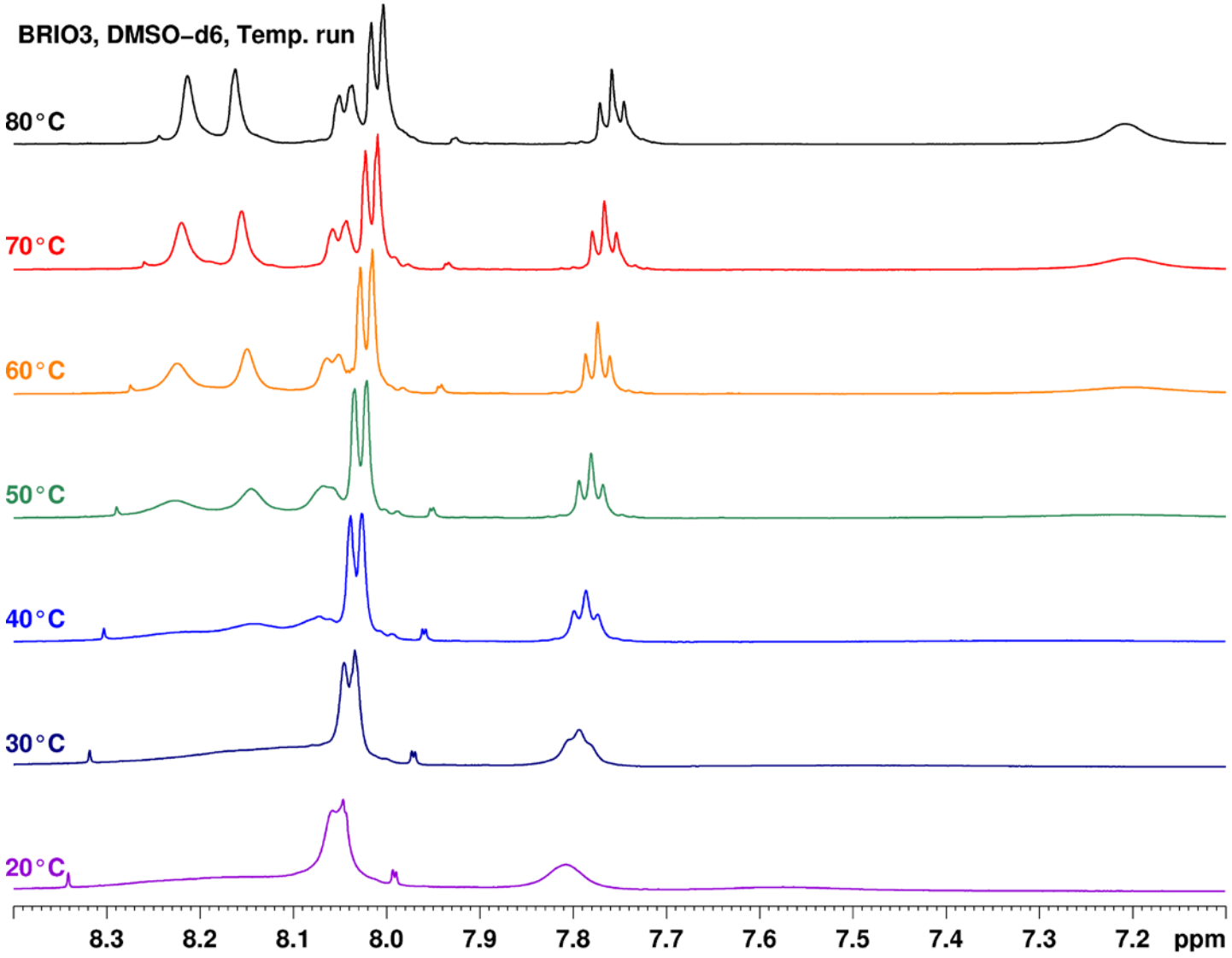
X = C-H [for $(BrIO)_{3/4}$] or N [for $(26BrIO)_{3/4}$]

General scheme for the synthesis of the trezimides and tennimides

2. NMR data and spectra

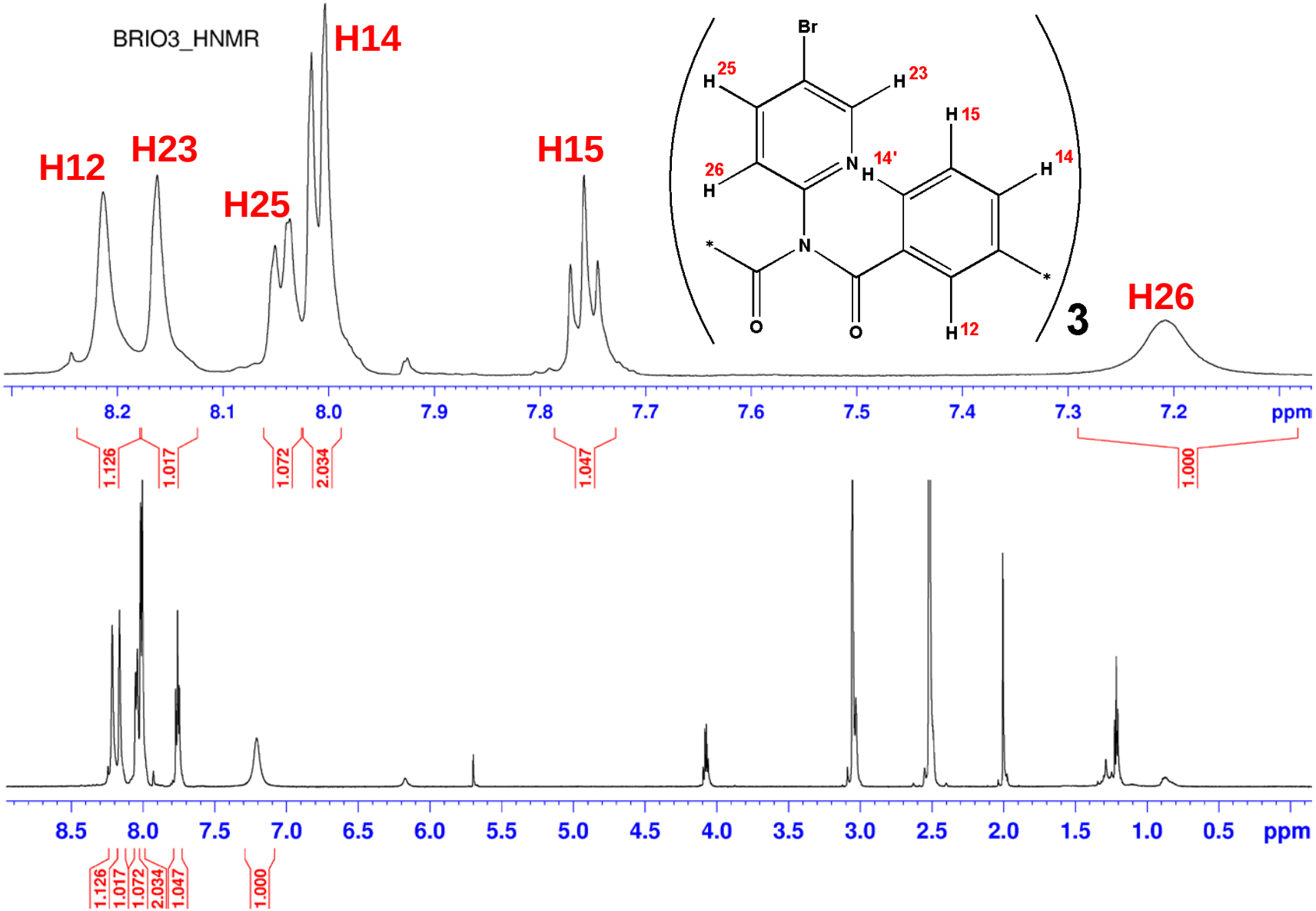
2.1. (**BrIO**)$_3$ (for the NMR shifts of common trace impurities see: H. E. Gottlieb *et al*., *J. Org. Chem*. **1997**, *62*, 7512–7515).

2.1.1. ^{1}H-NMR variable temperature run, DMSO-d_6

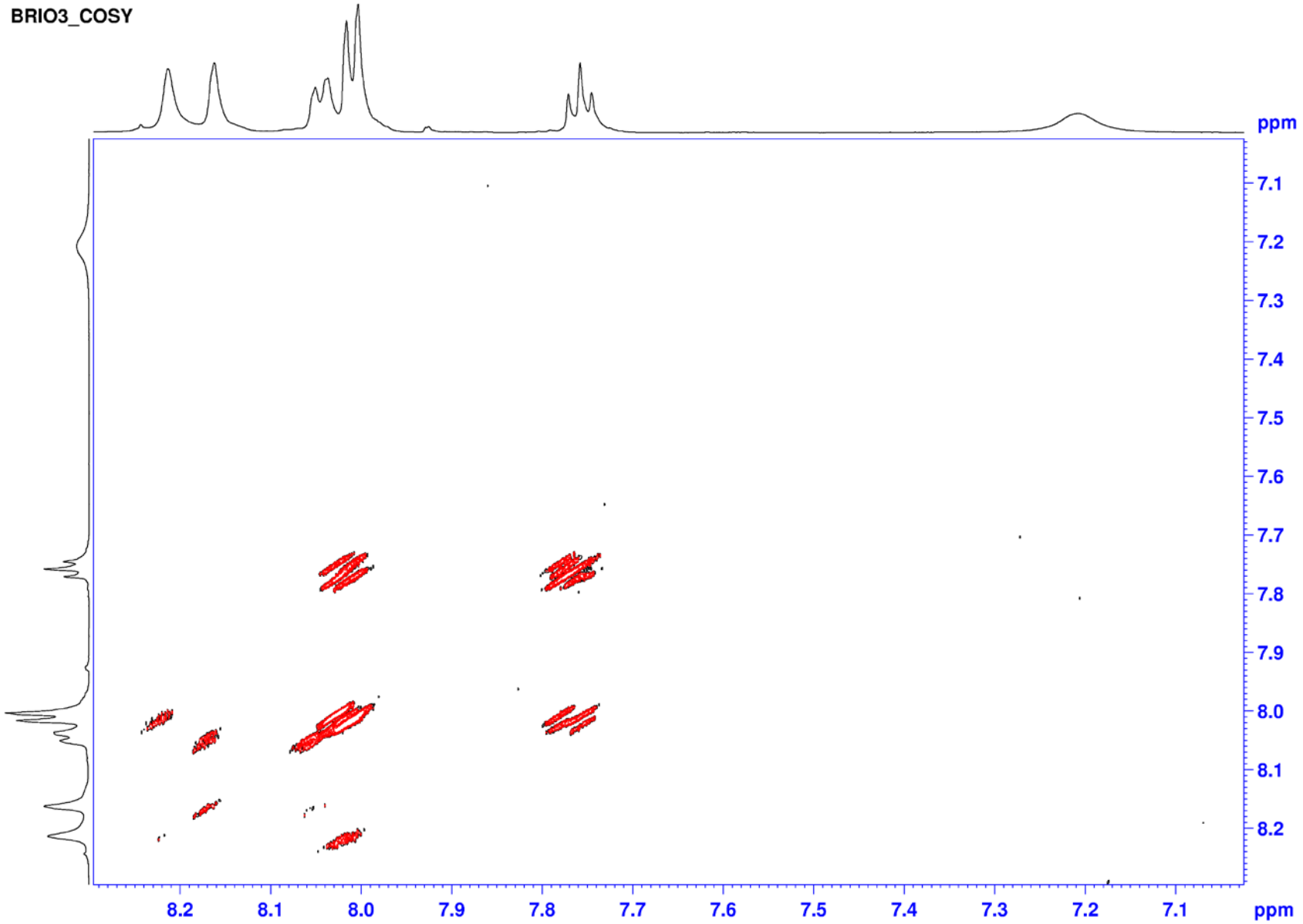


2.1.2. ^{1}H-NMR, 80°C, DMSO-d_6

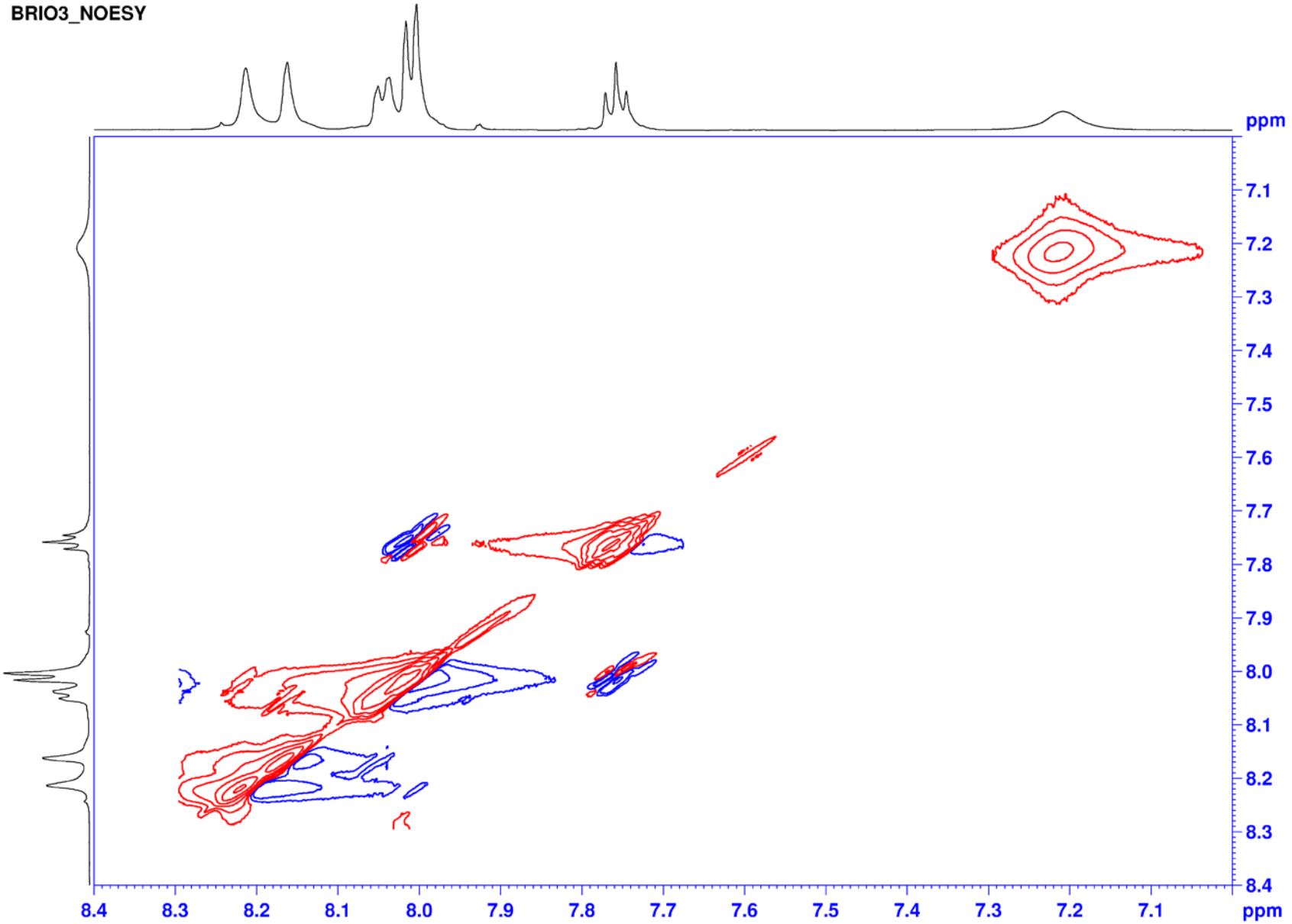
δ 7.21 (1H, s, H26), 7.76 (1H, t, ^{3}J = 8, H15), 8.01 (2H, d, ^{3}J = 8, H14), 8.04 (1H, d, ^{3}J = 8, H25), 8.16 (1H, s, H23), 8.21 (1H, s, H12);



2.1.3. COSY, 80°C, DMSO-d_6

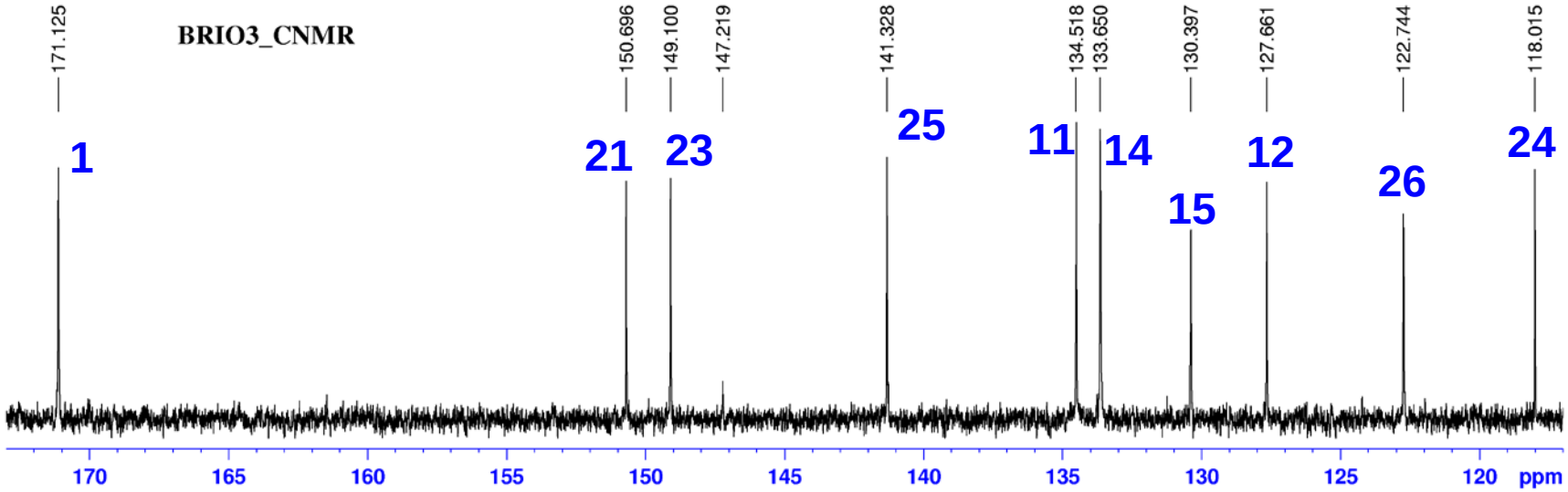


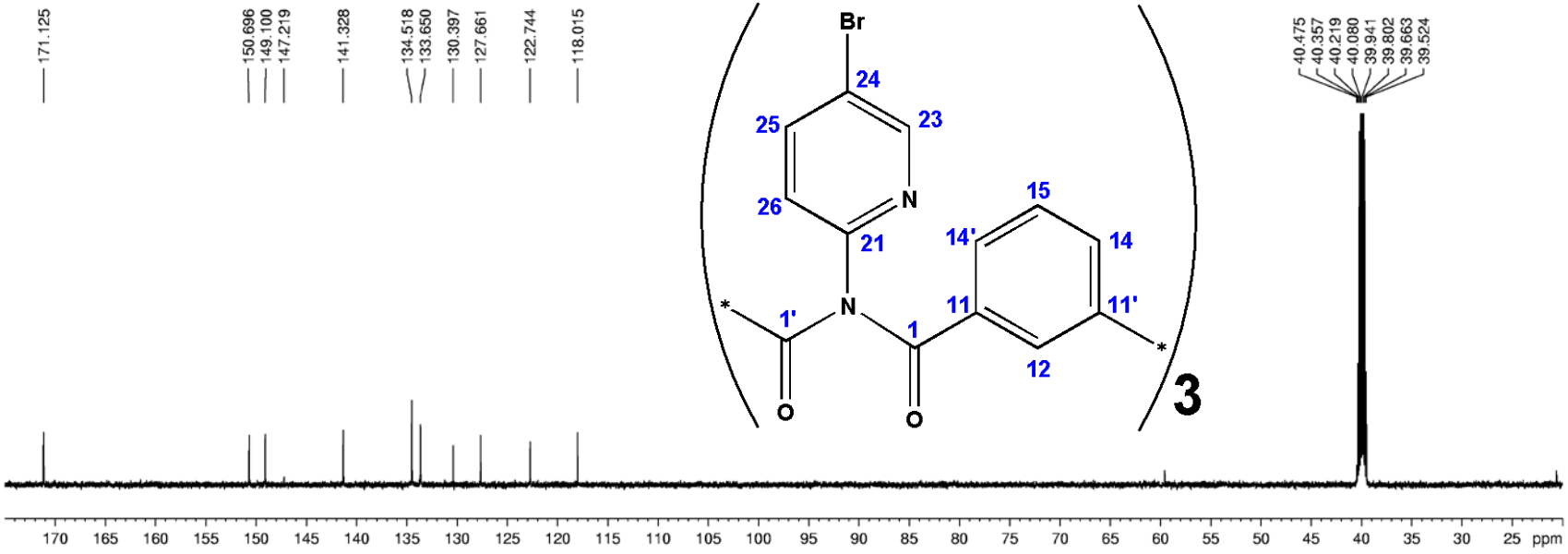
2.1.4. NOESY, 80°C, DMSO-d_6



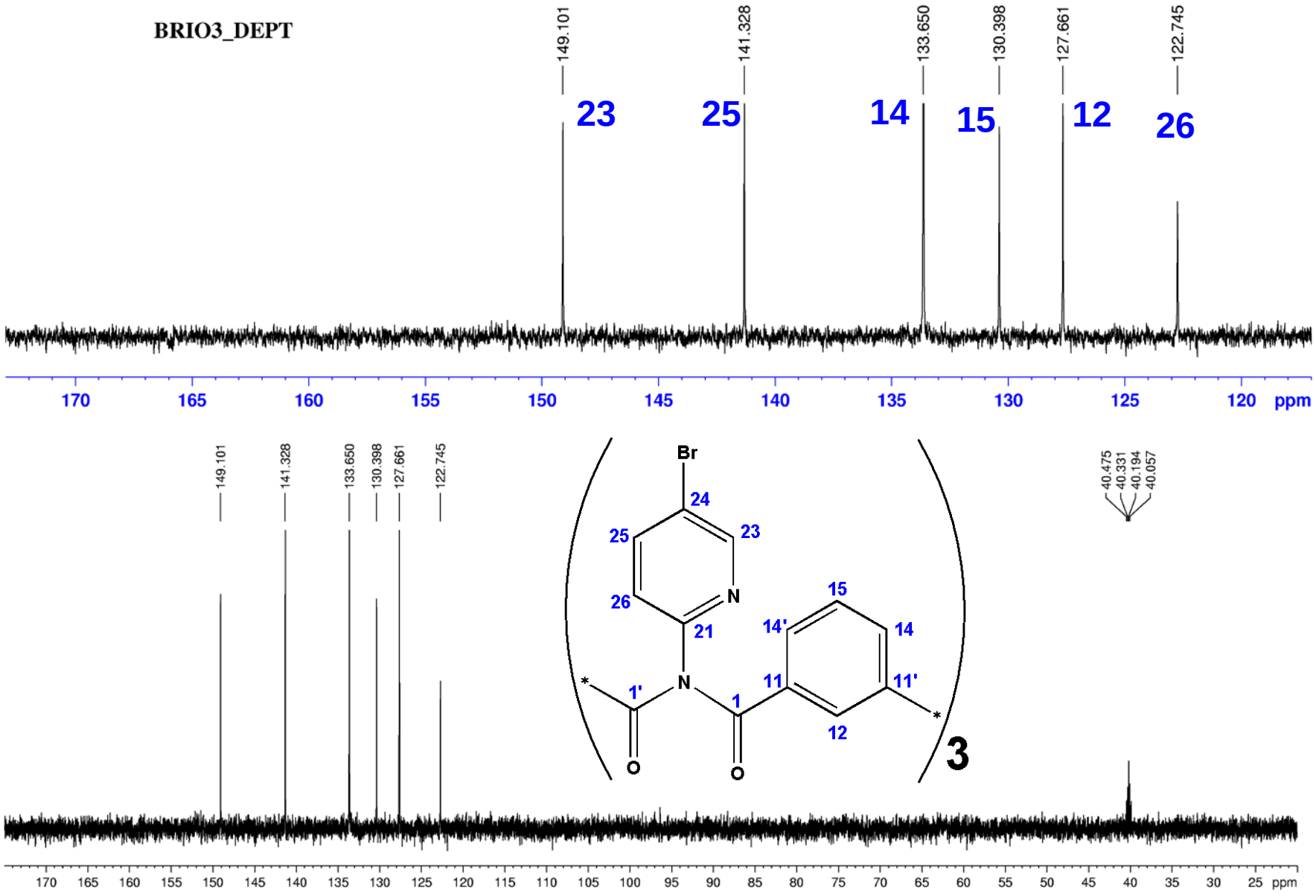
2.1.5. ^{13}C-NMR, 80°C, DMSO-d_6

δ 118.01, 122.74, 127.66, 130.40, 133.65, 134.52, 141.33, 149.10, 150.70, 171.12;

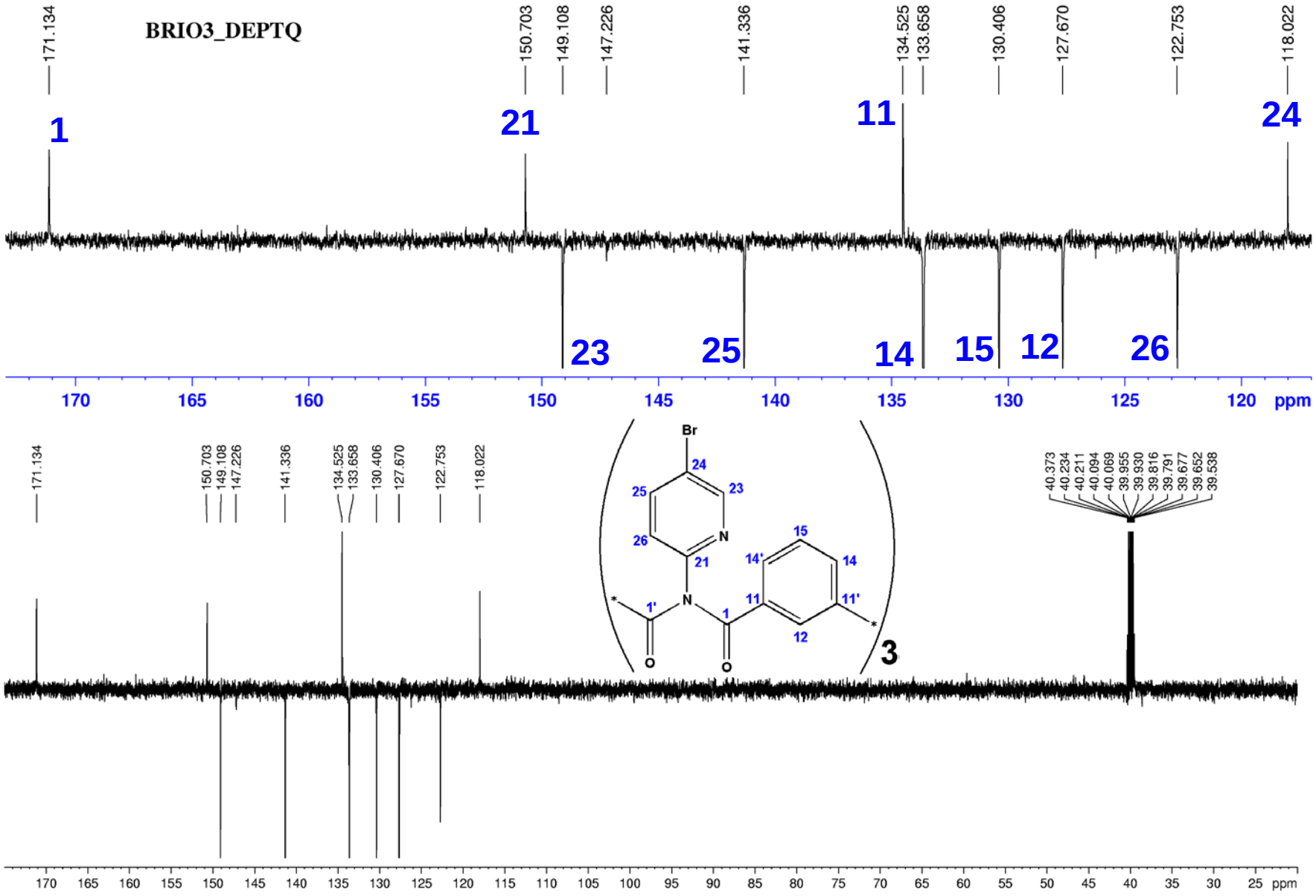




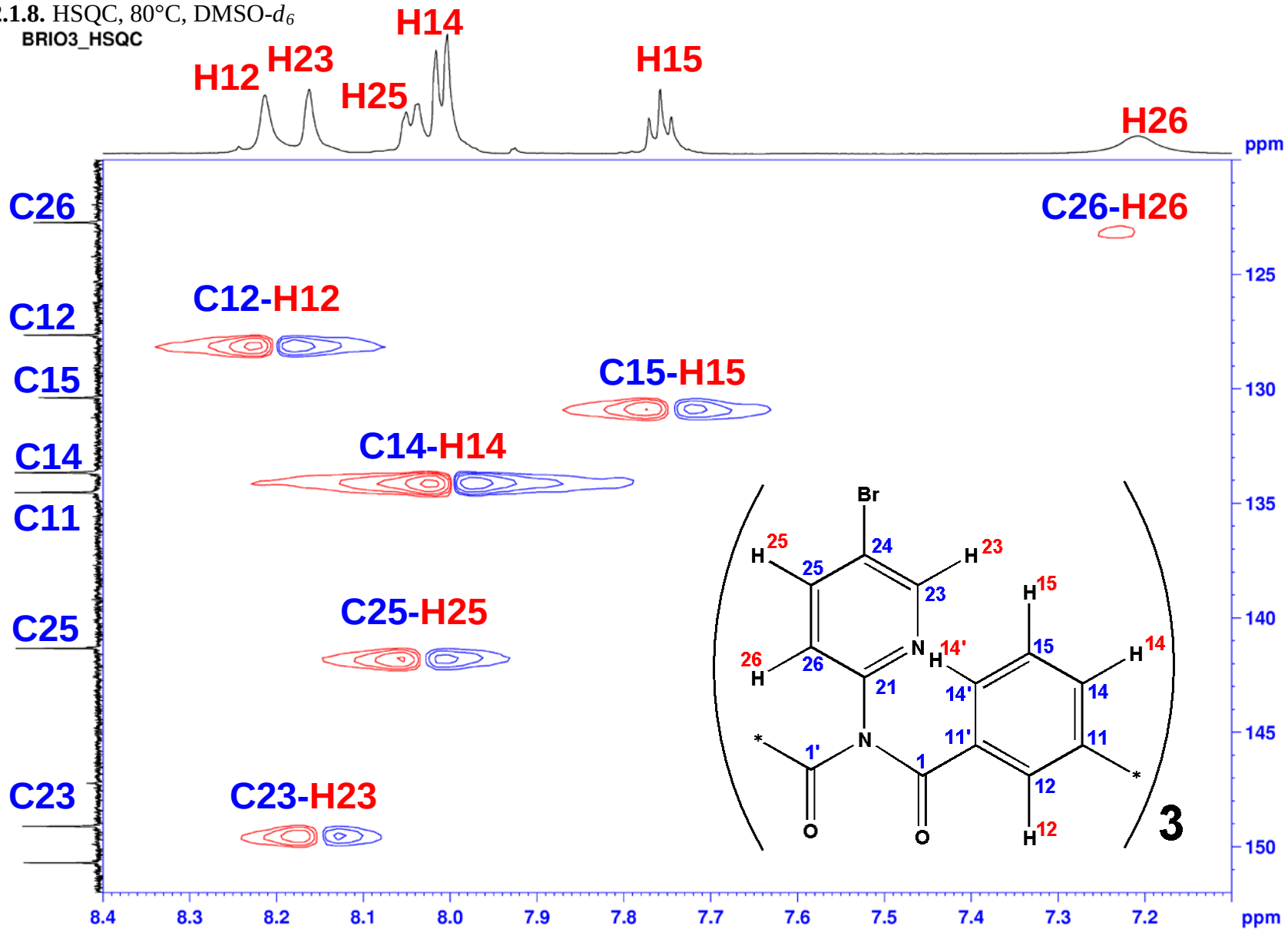
2.1.6. DEPT, 80°C, DMSO-d_6



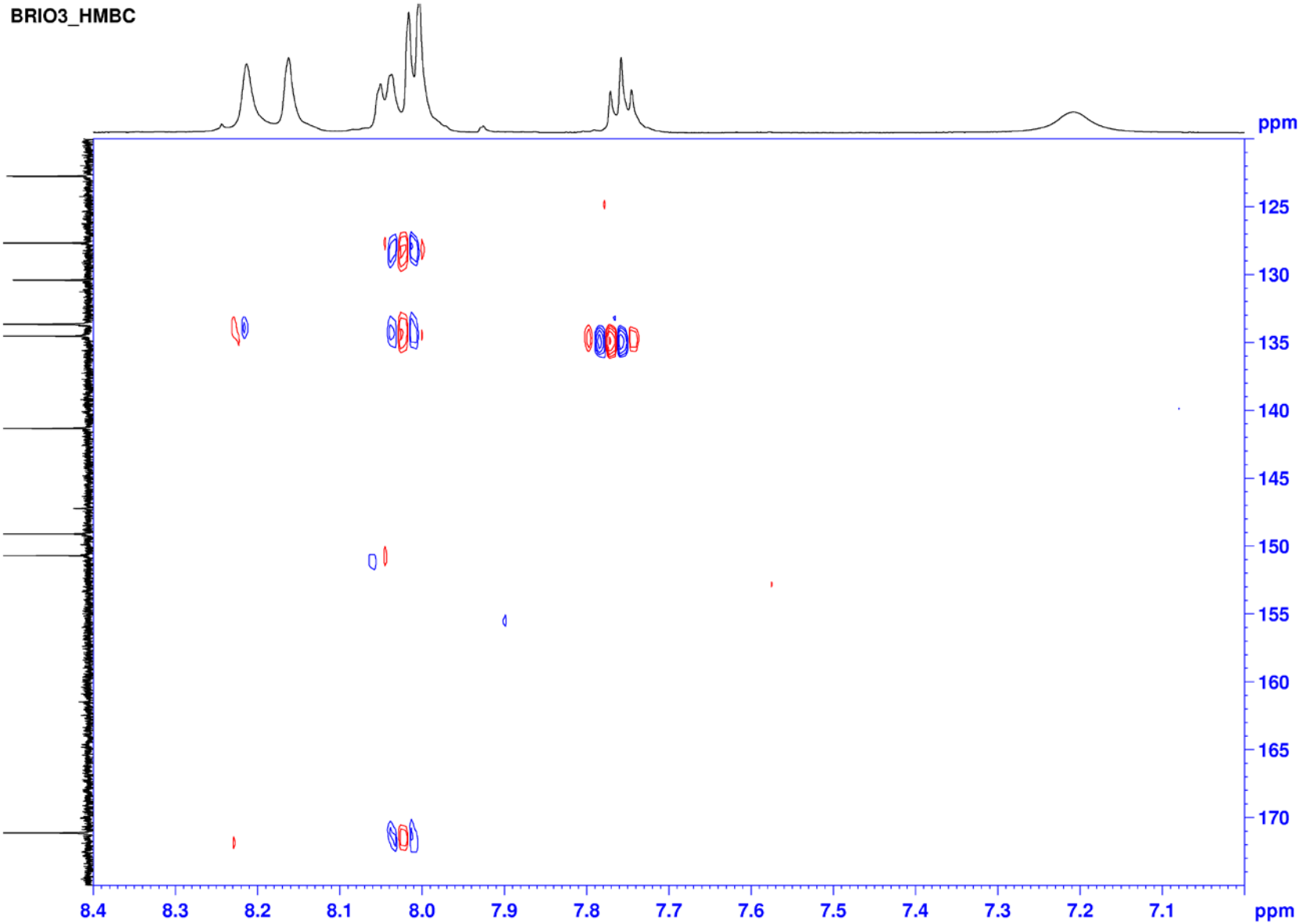
2.1.7. DEPT-Q, 80°C, DMSO-d_6



2.1.8. HSQC, 80°C, DMSO-d_6

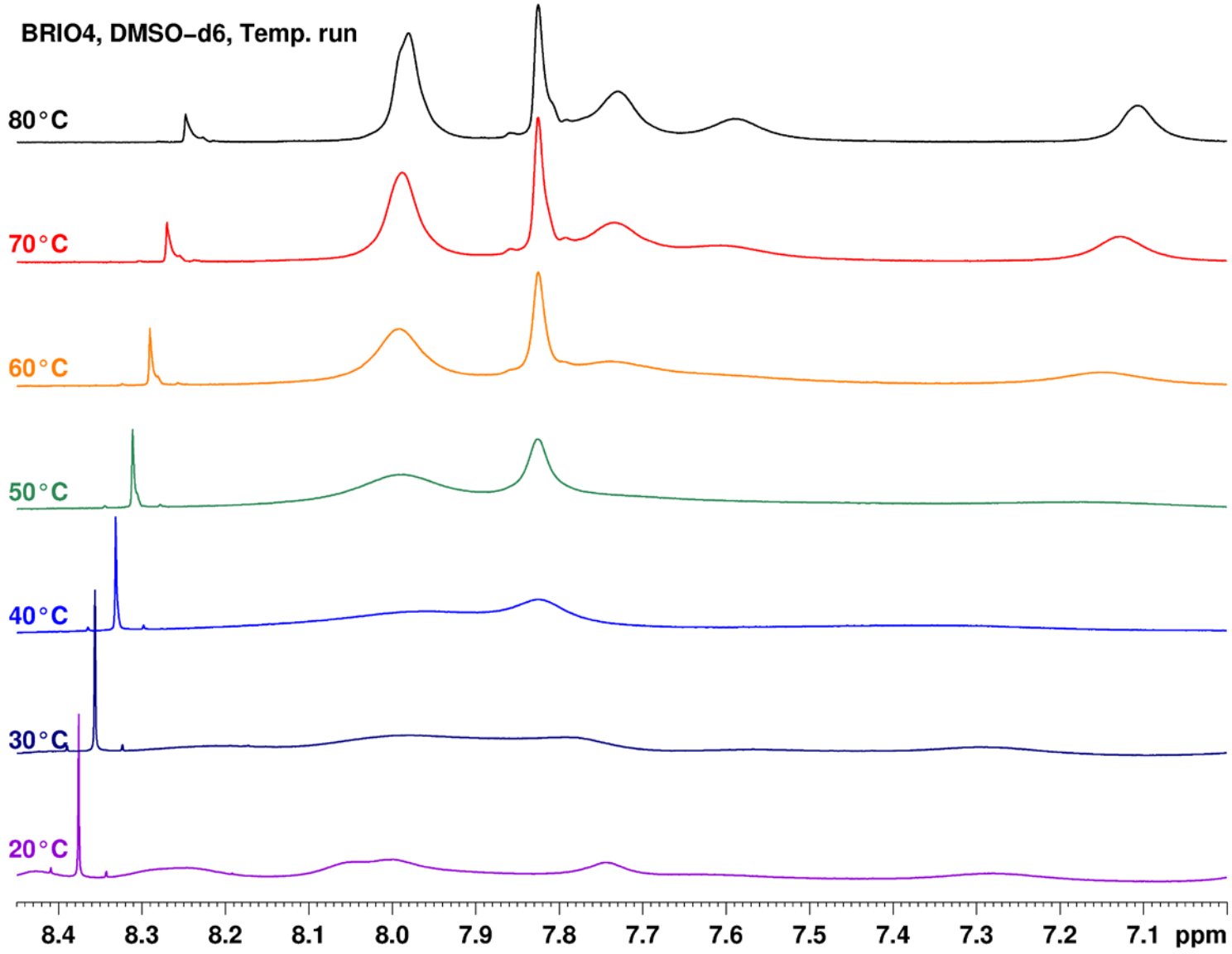


2.1.9. HMBC, 80°C, DMSO-d_6



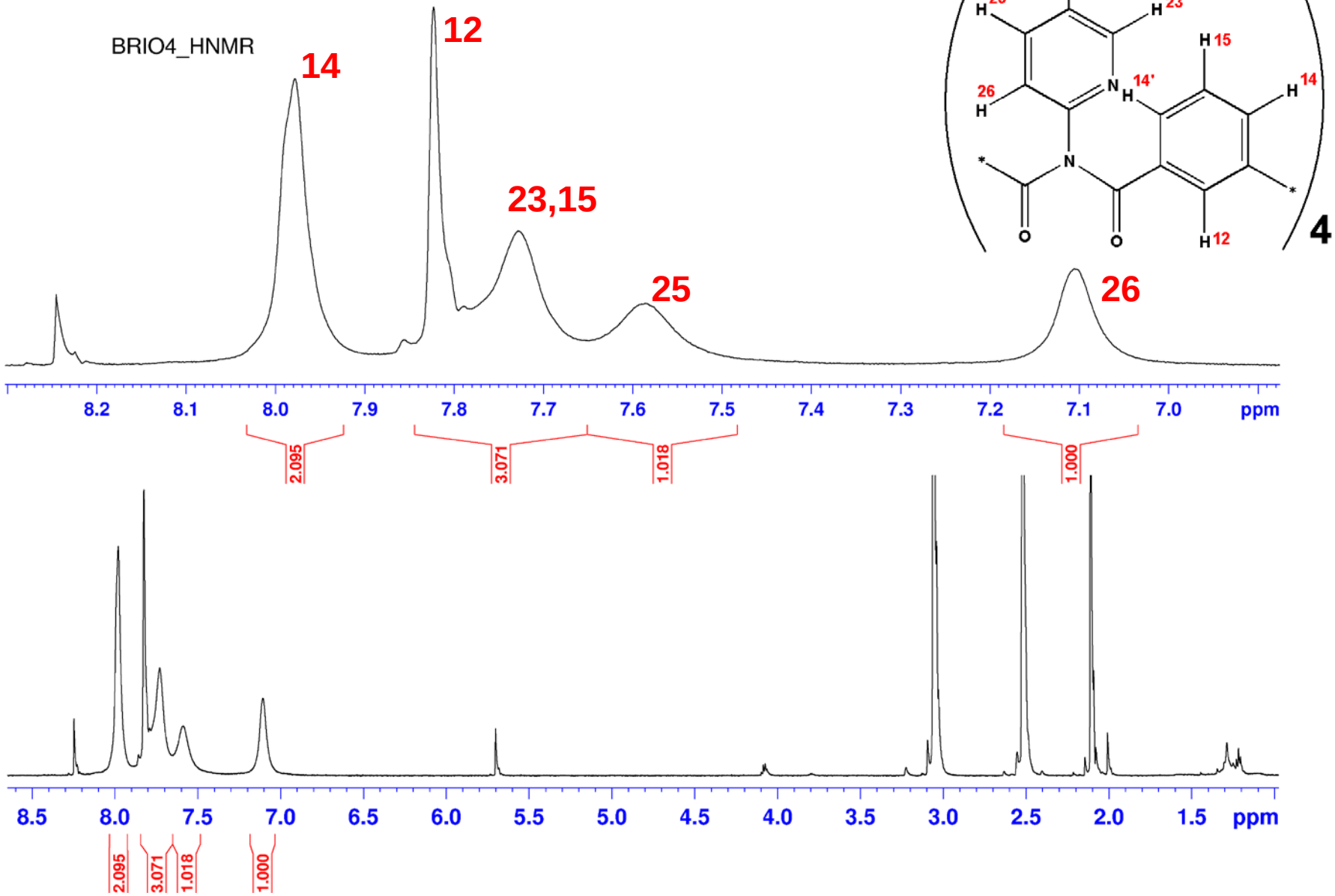
2.2. (BrIO)$_4$

2.2.1. Variable temperature ^{1}H-NMR run - DMSO-d_6

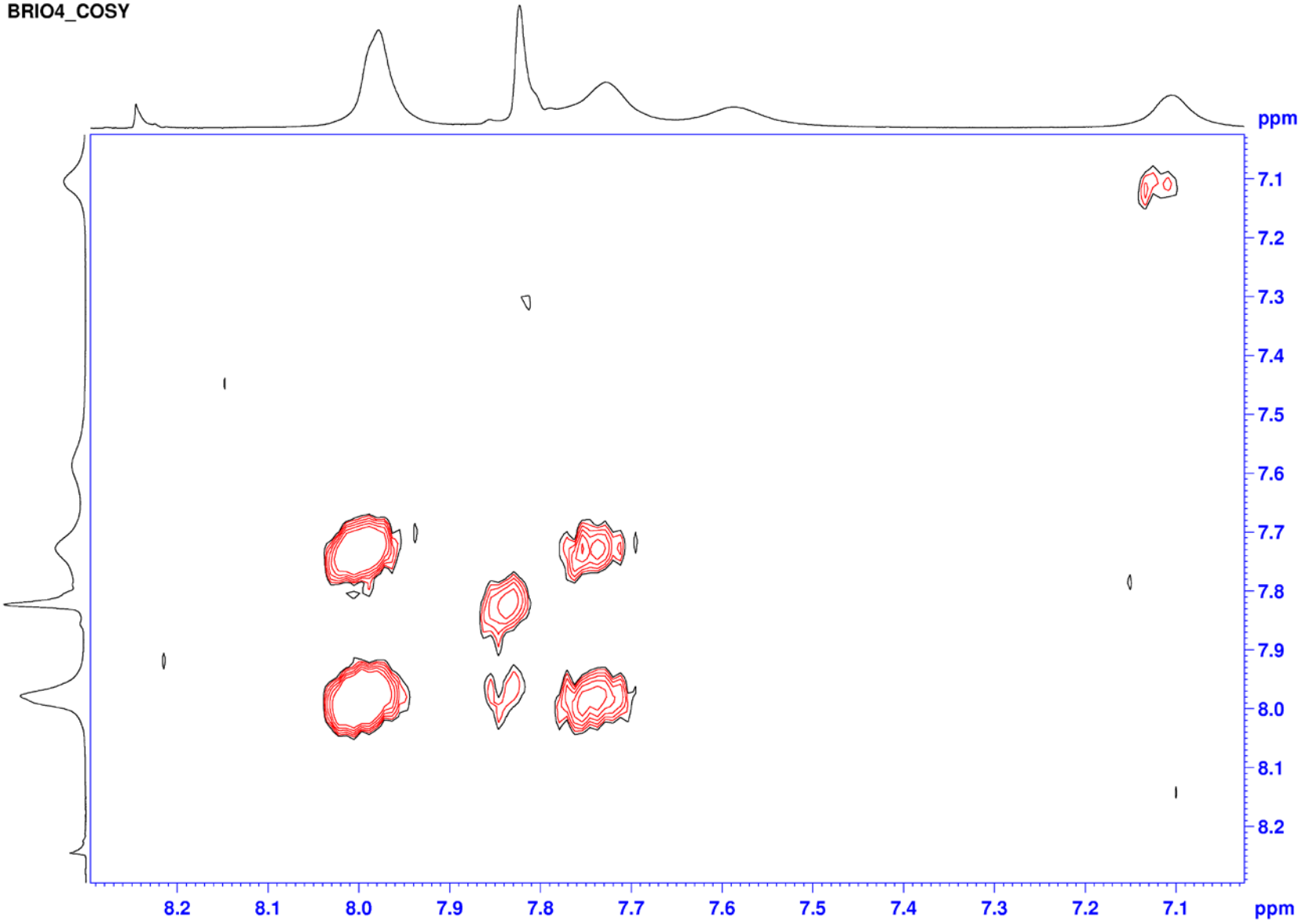


2.2.2. ^{1}H-NMR, 80°C, DMSO-d_6

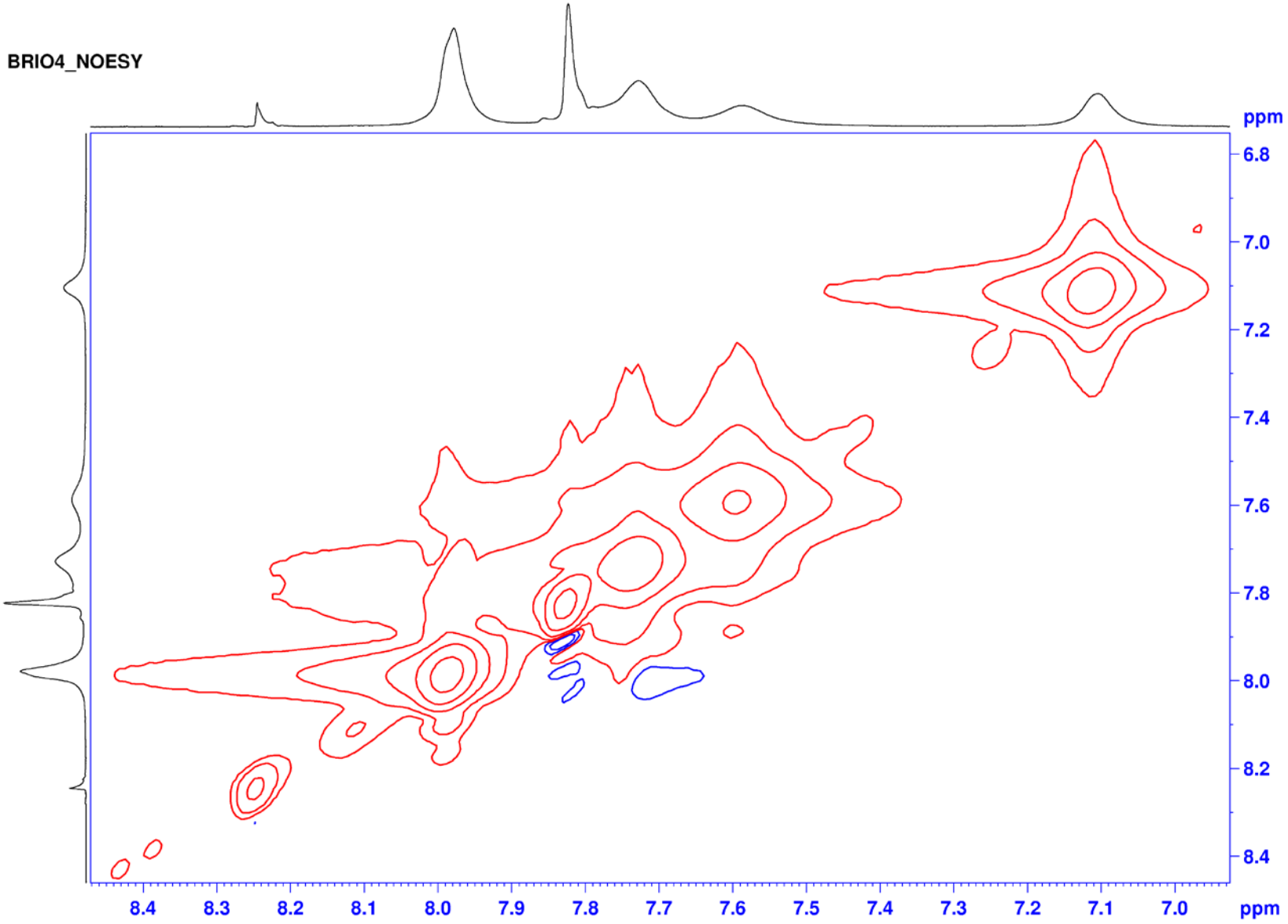
δ 7.10 (1H, s, H26), 7.59 (1H, s, H25), 7.73 (2H, s, H23/H15), 7.82 (1H, s, H12), 7.98 (2H s, H14);



2.2.3. COSY, 80°C, DMSO-d_6

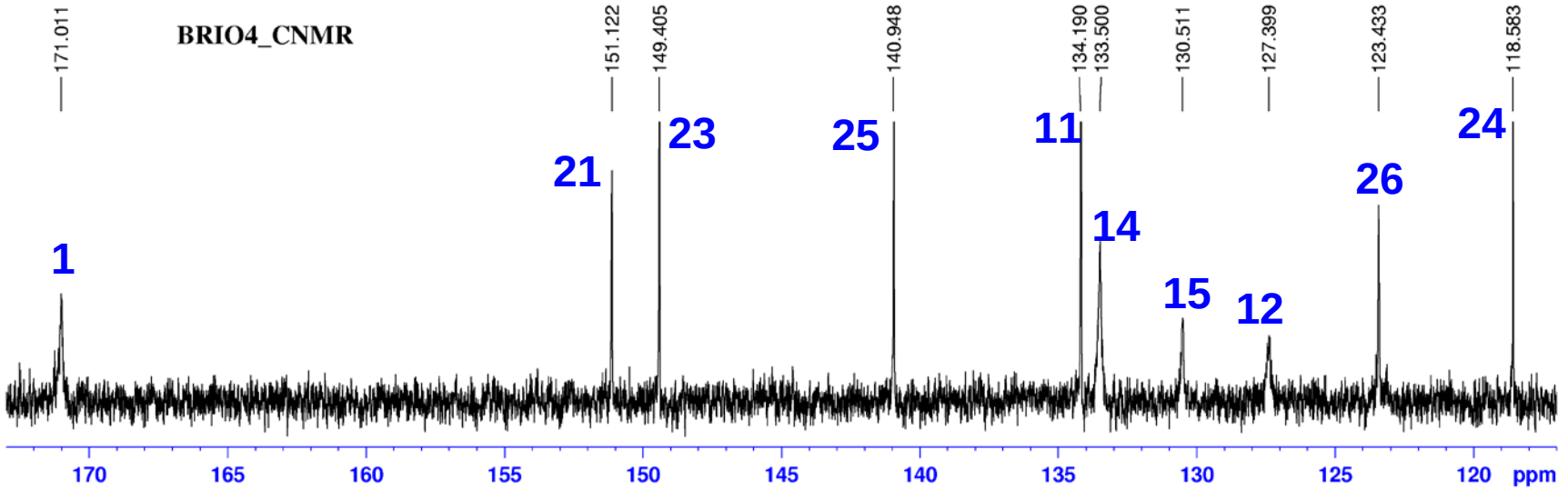


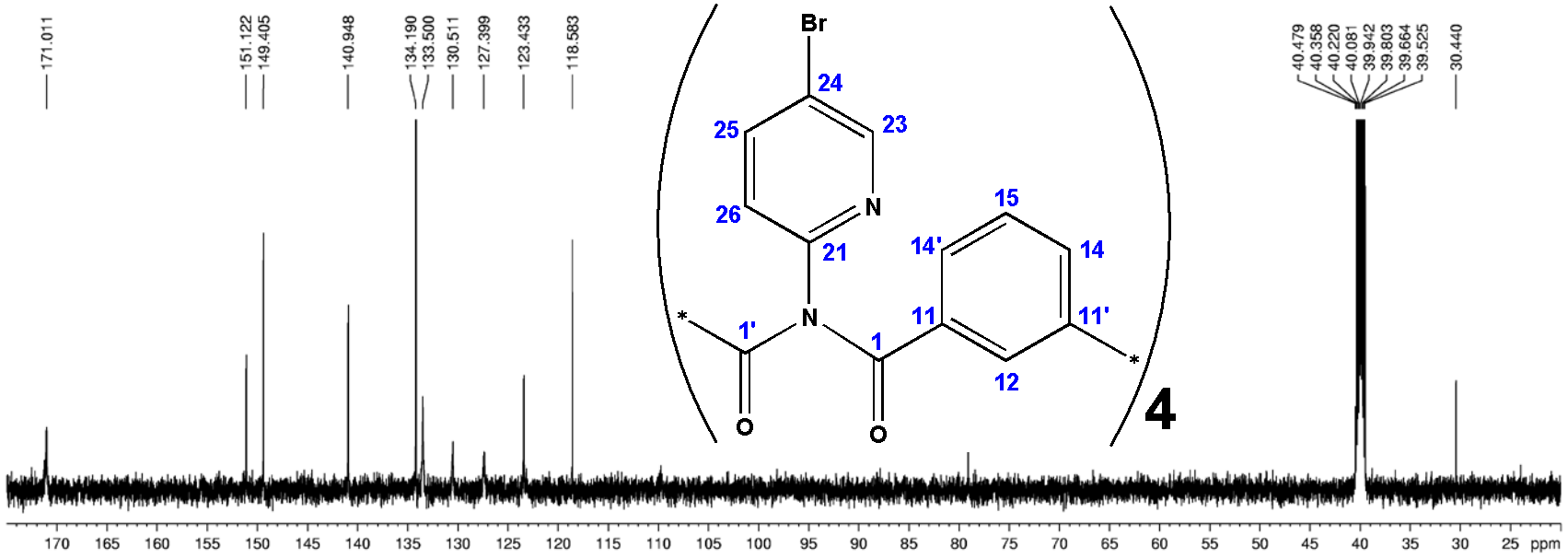
2.2.4. NOESY, 80°C, DMSO-d_6



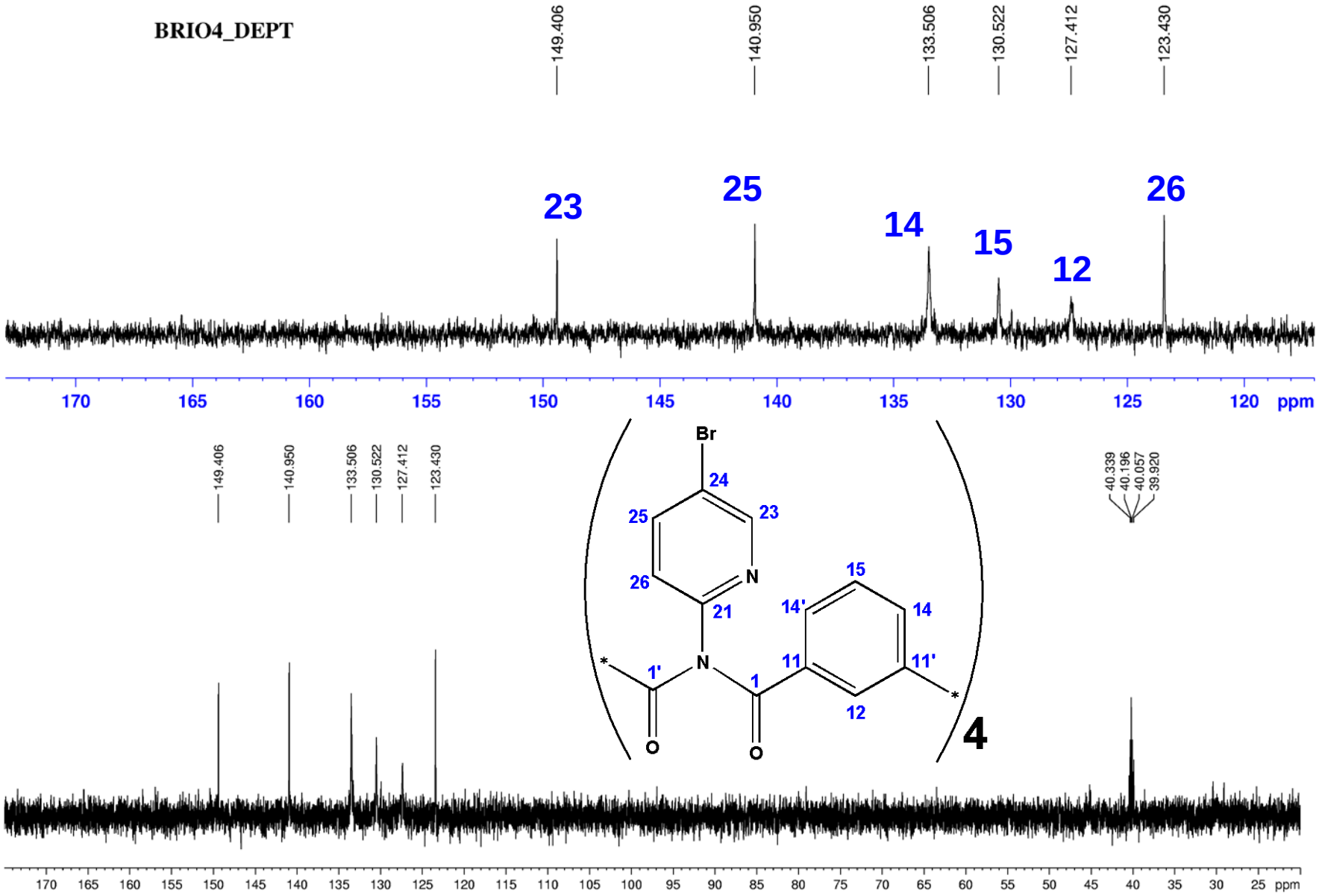
2.2.5. ^{13}C-NMR, 80°C, DMSO-d_6

δ 118.58, 123.43, 127.40, 130.51, 133.50, 134.19, 140.95, 149.40, 151.12, 171.01;

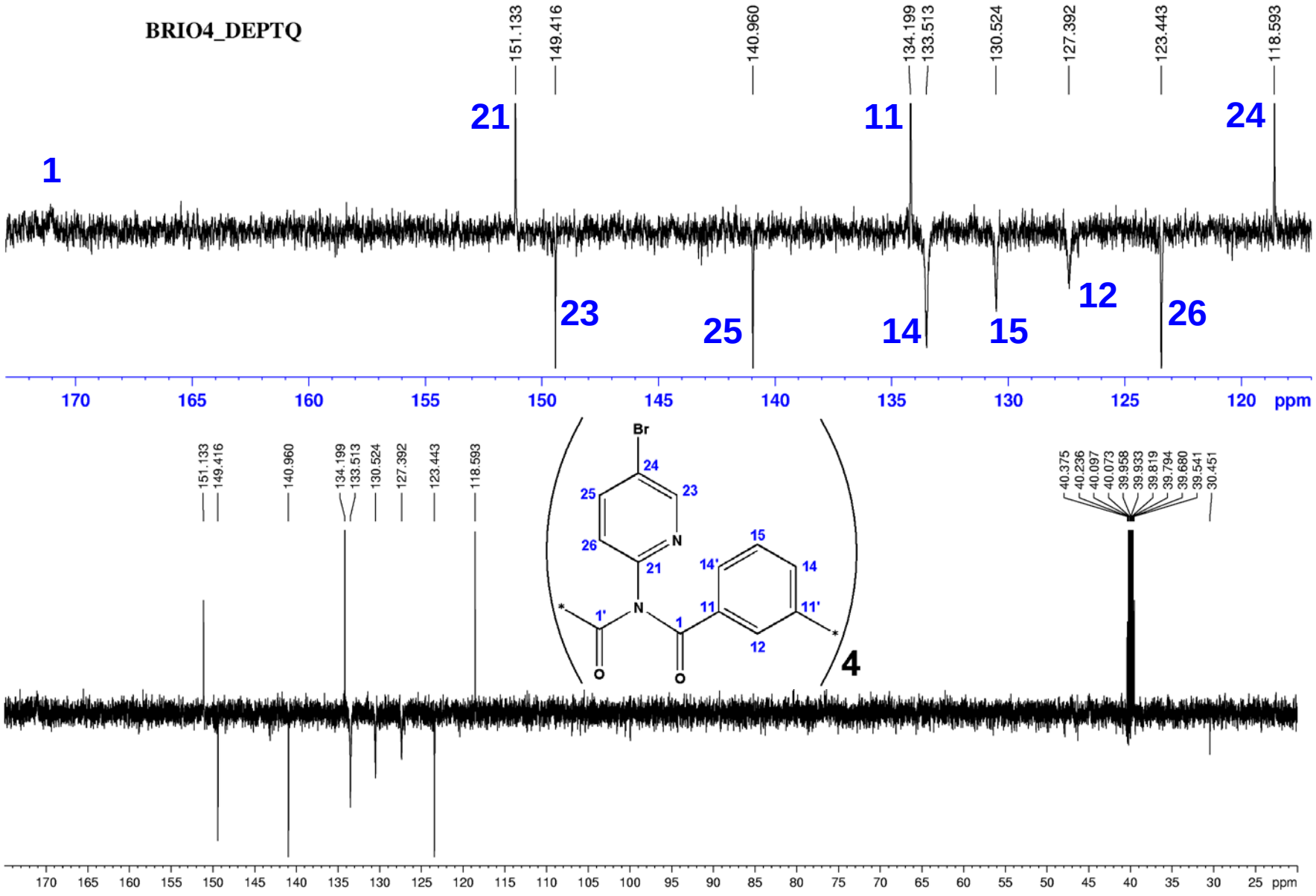




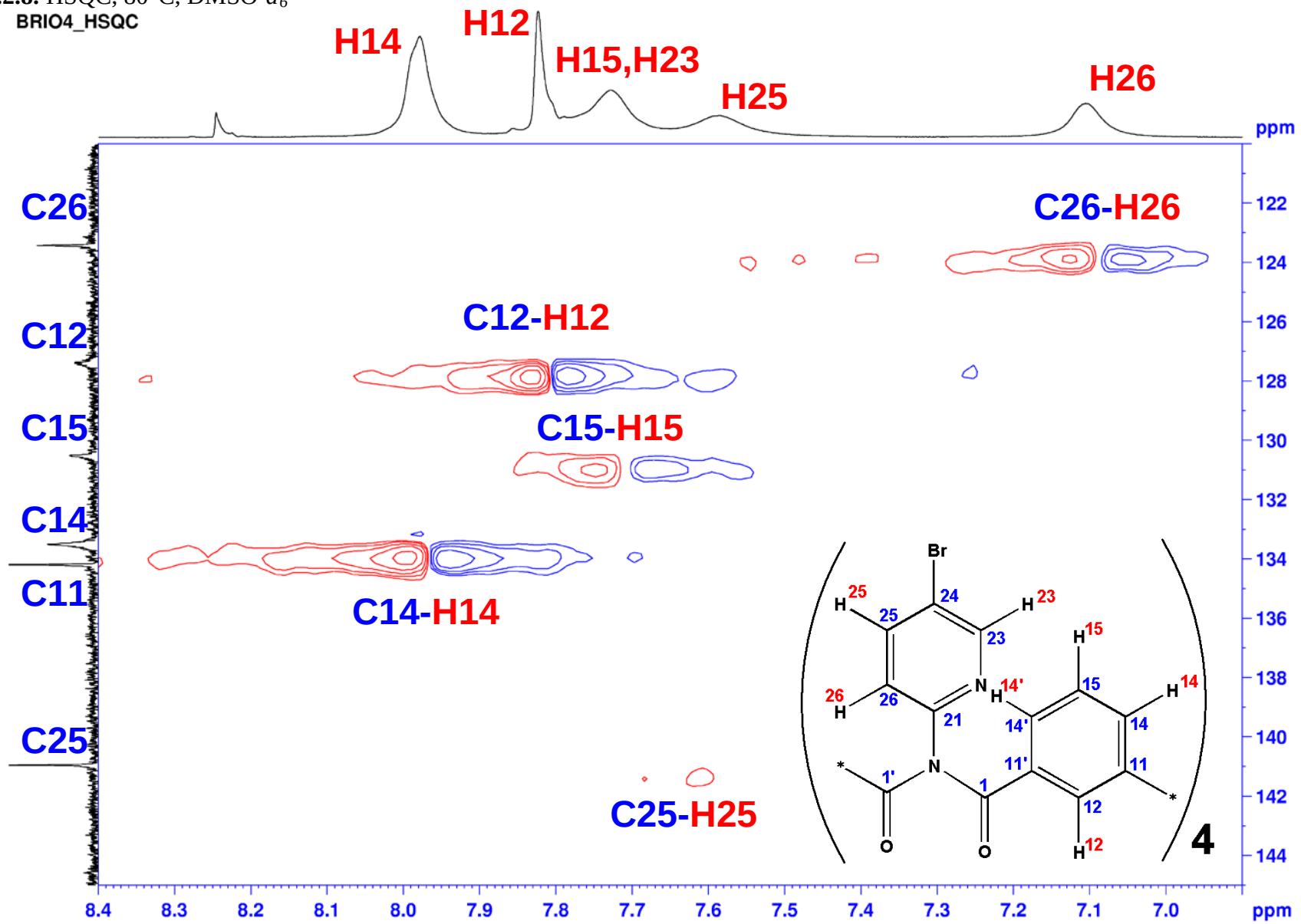
2.2.6. DEPT, 80°C, DMSO-d_6



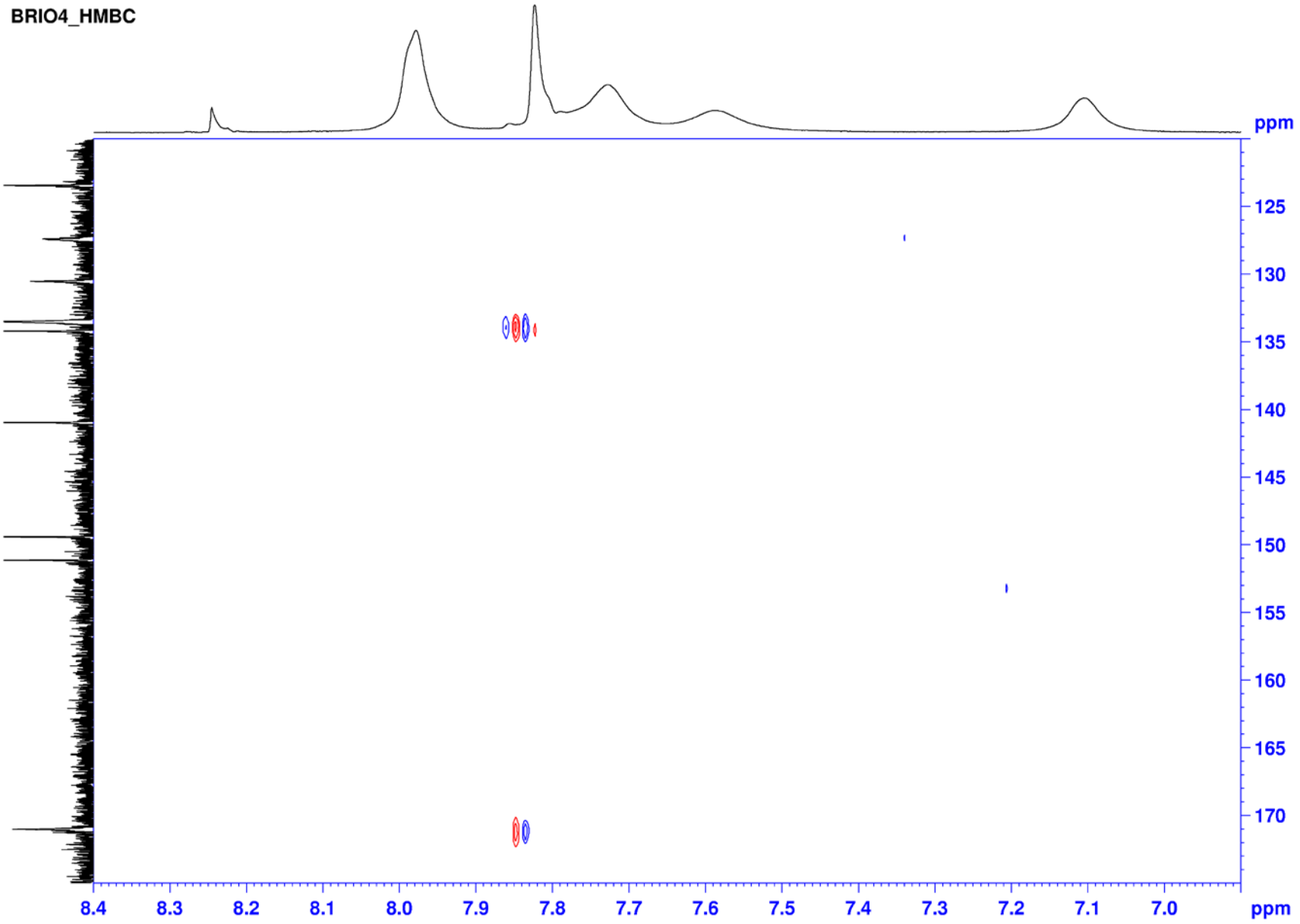
2.2.7. DEPT-Q, 80°C, DMSO-d_6



2.2.8. HSQC, 80°C, DMSO-d_6

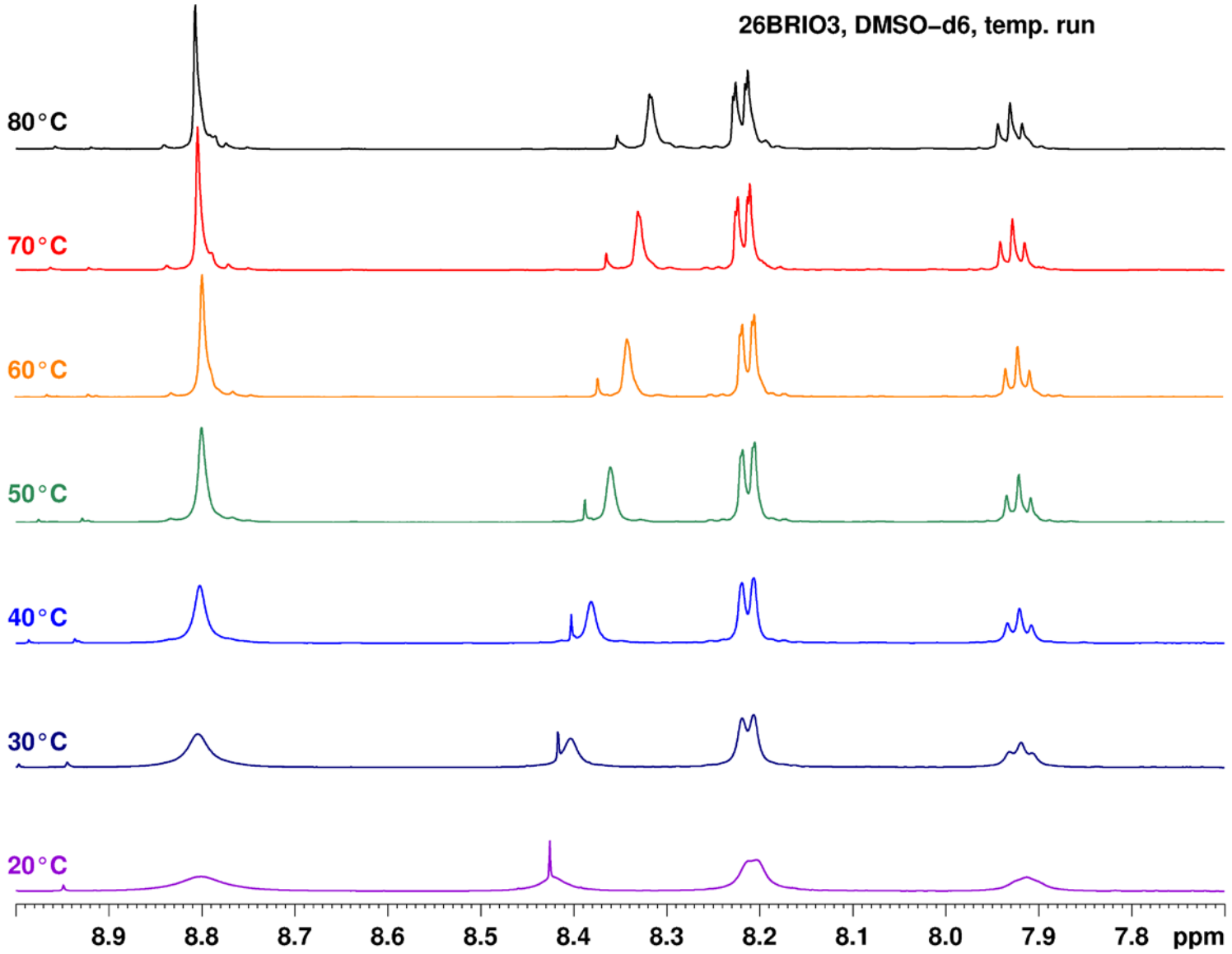


2.2.9. HMBC, 80°C, DMSO-d_6



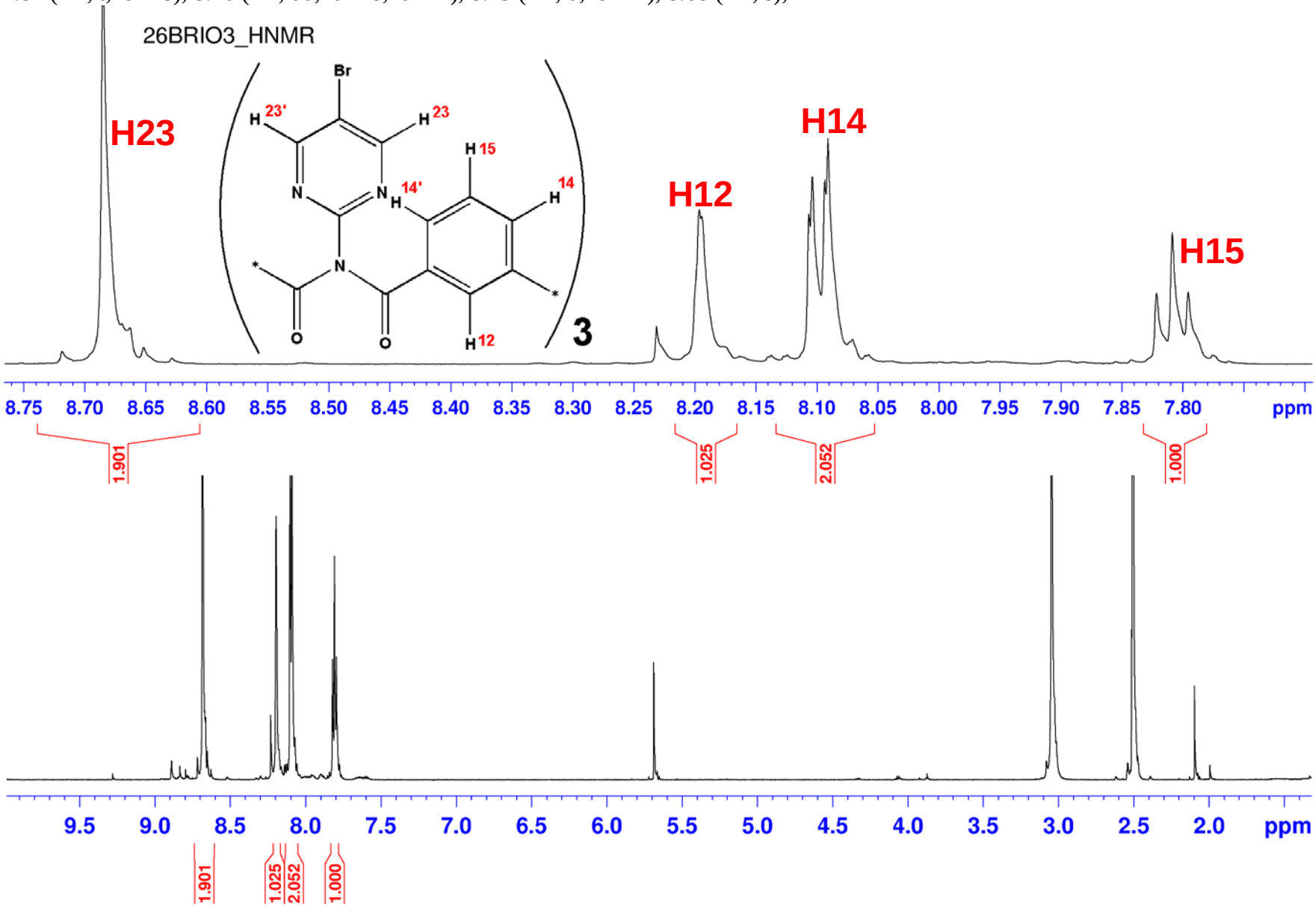
2.3. (26BrIO)$_3$

2.3.1. ^{1}H-NMP variable temperature run, DMSO-d_6

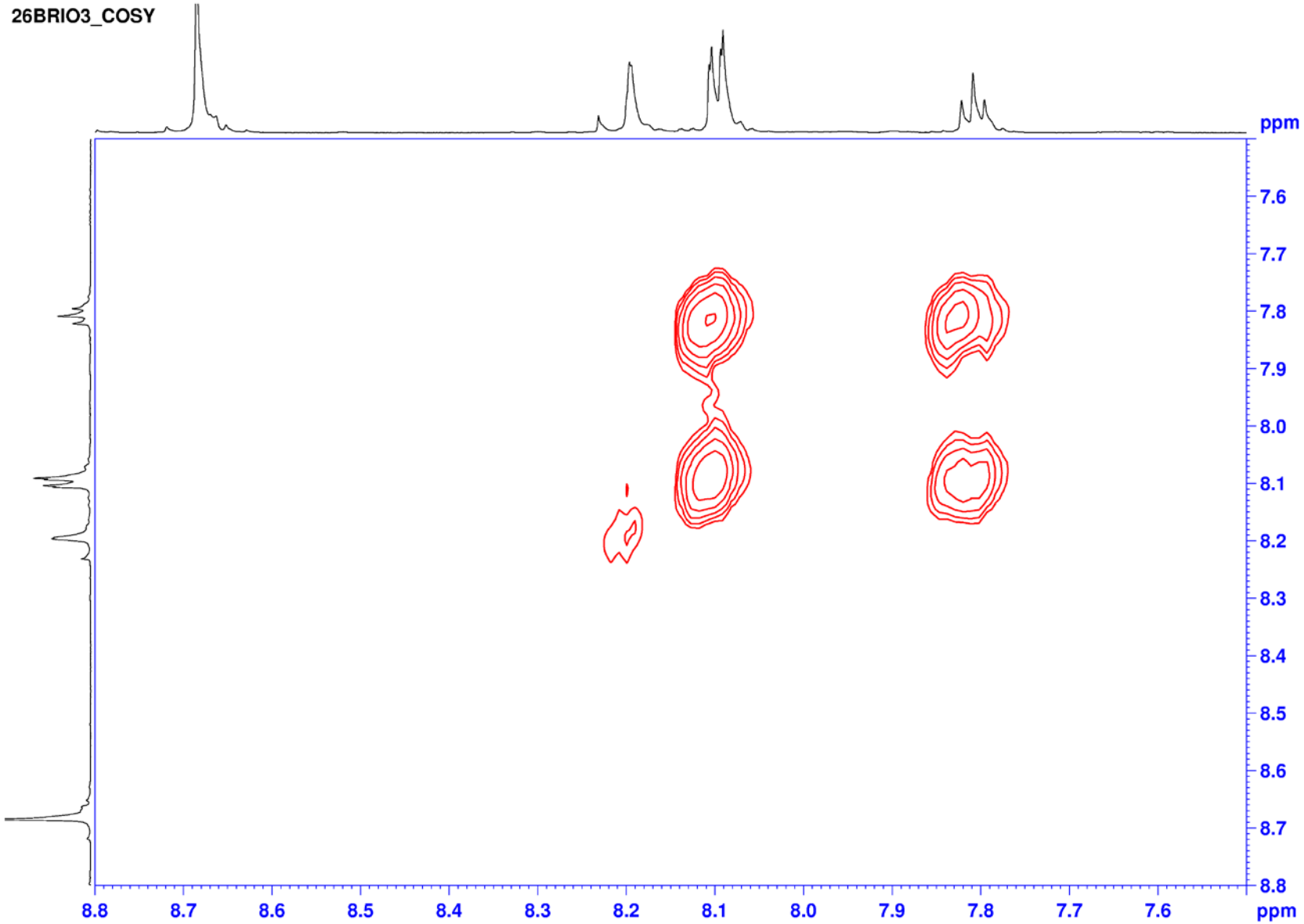


2.3.2. ^{1}H-NMR, 80°C, DMSO-d_6

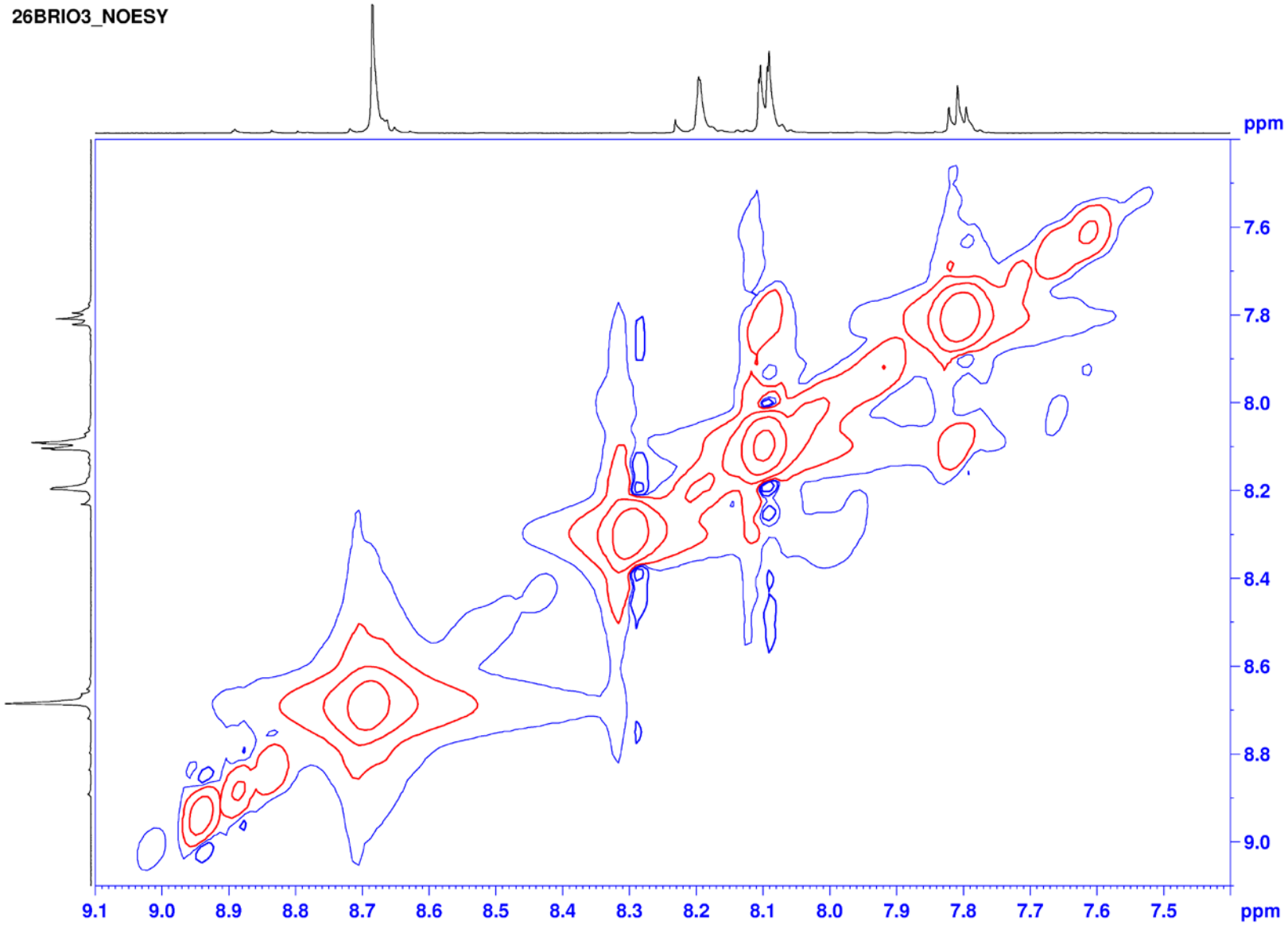
δ 7.81 (1H, t, ^{3}J = 8), 8.10 (2H, dd, ^{3}J = 8, ^{4}J = 2), 8.19 (1H, d, ^{3}J = 1), 8.68 (2H, s);



2.3.3. COSY, 80°C, DMSO-d_6

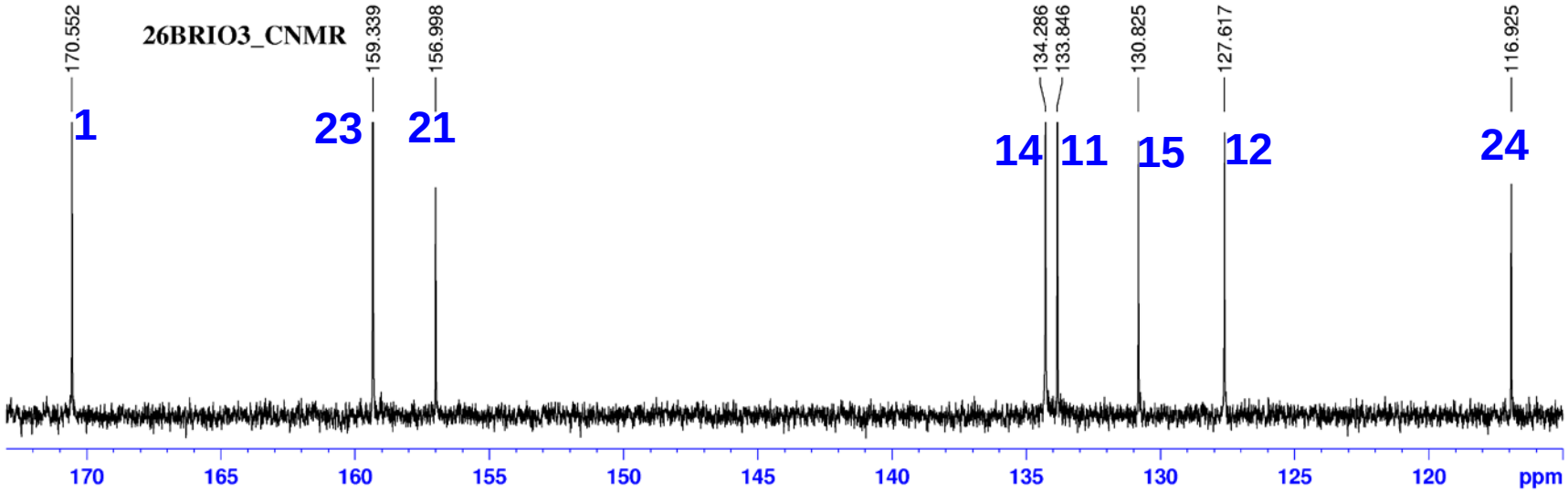


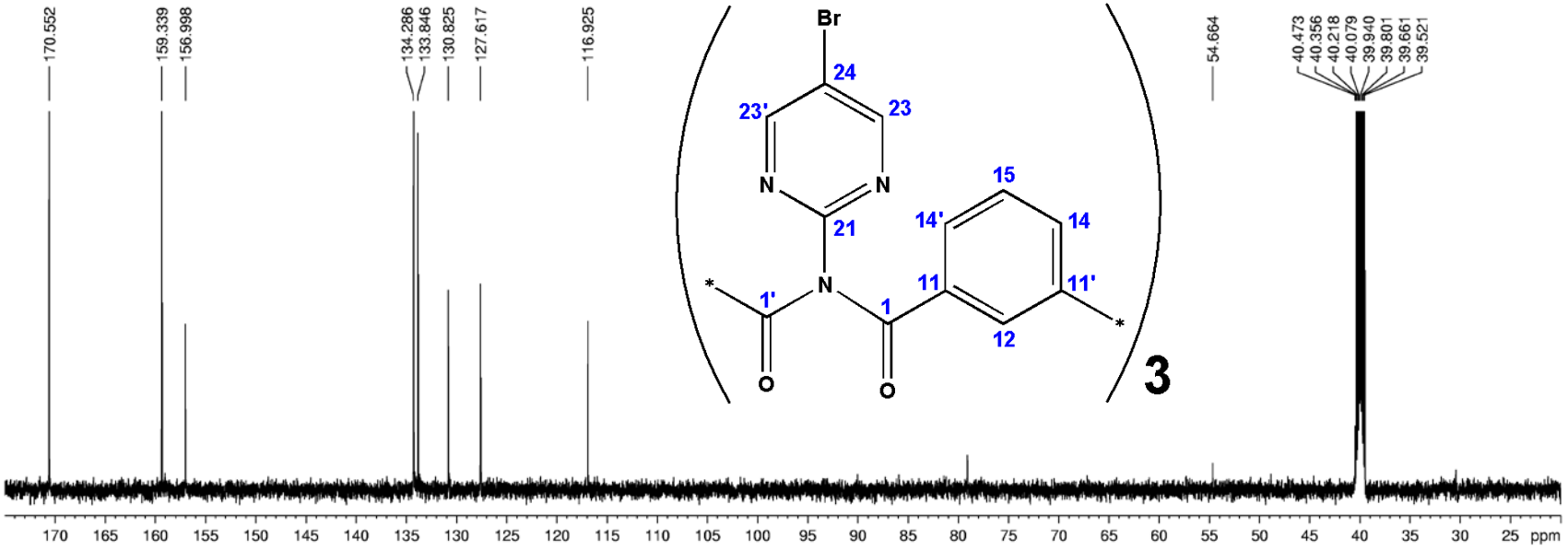
2.3.4. NOESY, 80°C, DMSO-d_6



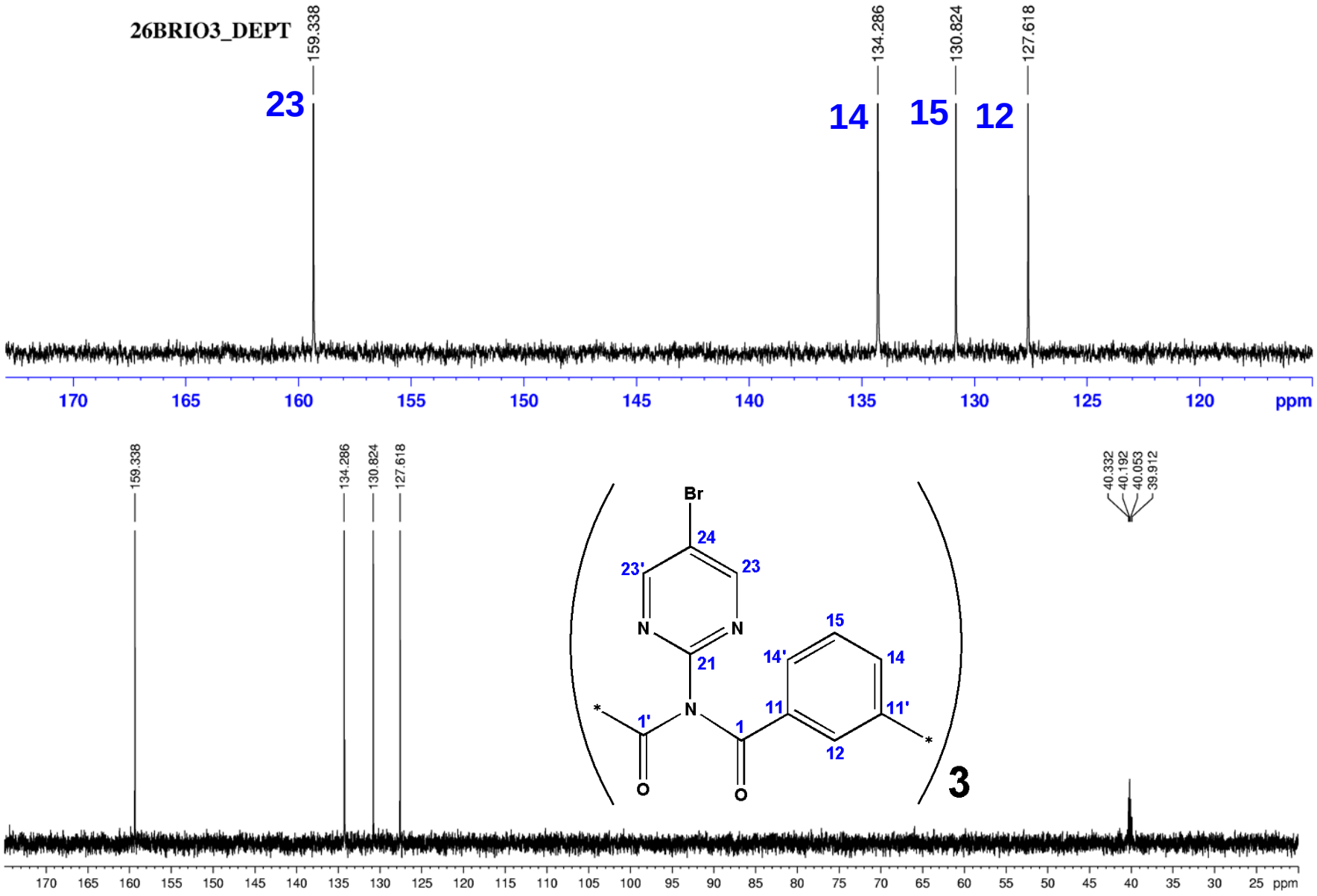
2.3.5. ^{13}C-NMR, 80°C, DMSO-d_6

δ 116.92, 127.62, 130.82, 133.85, 134.29, 157.00, 159.34, 170.55;

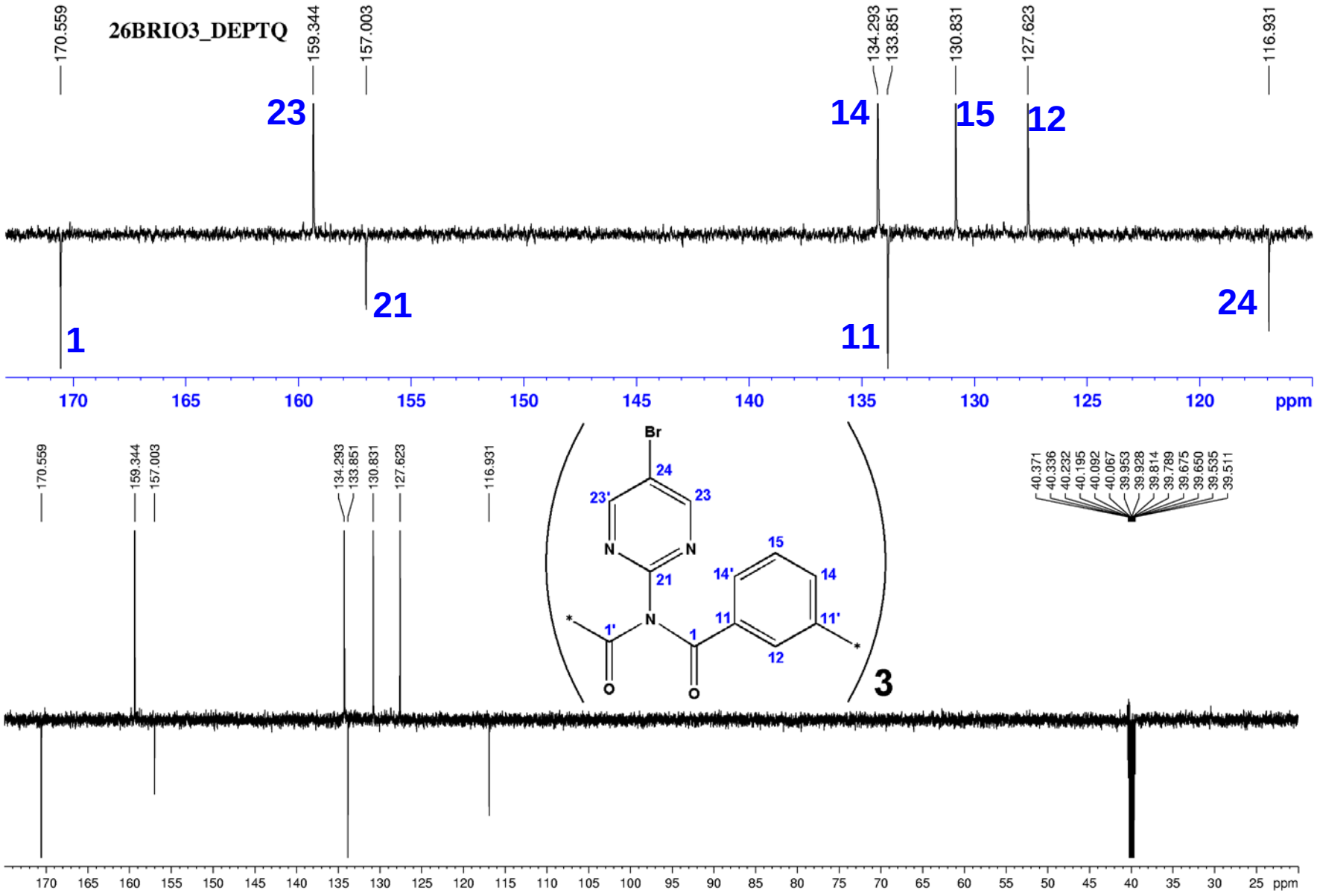




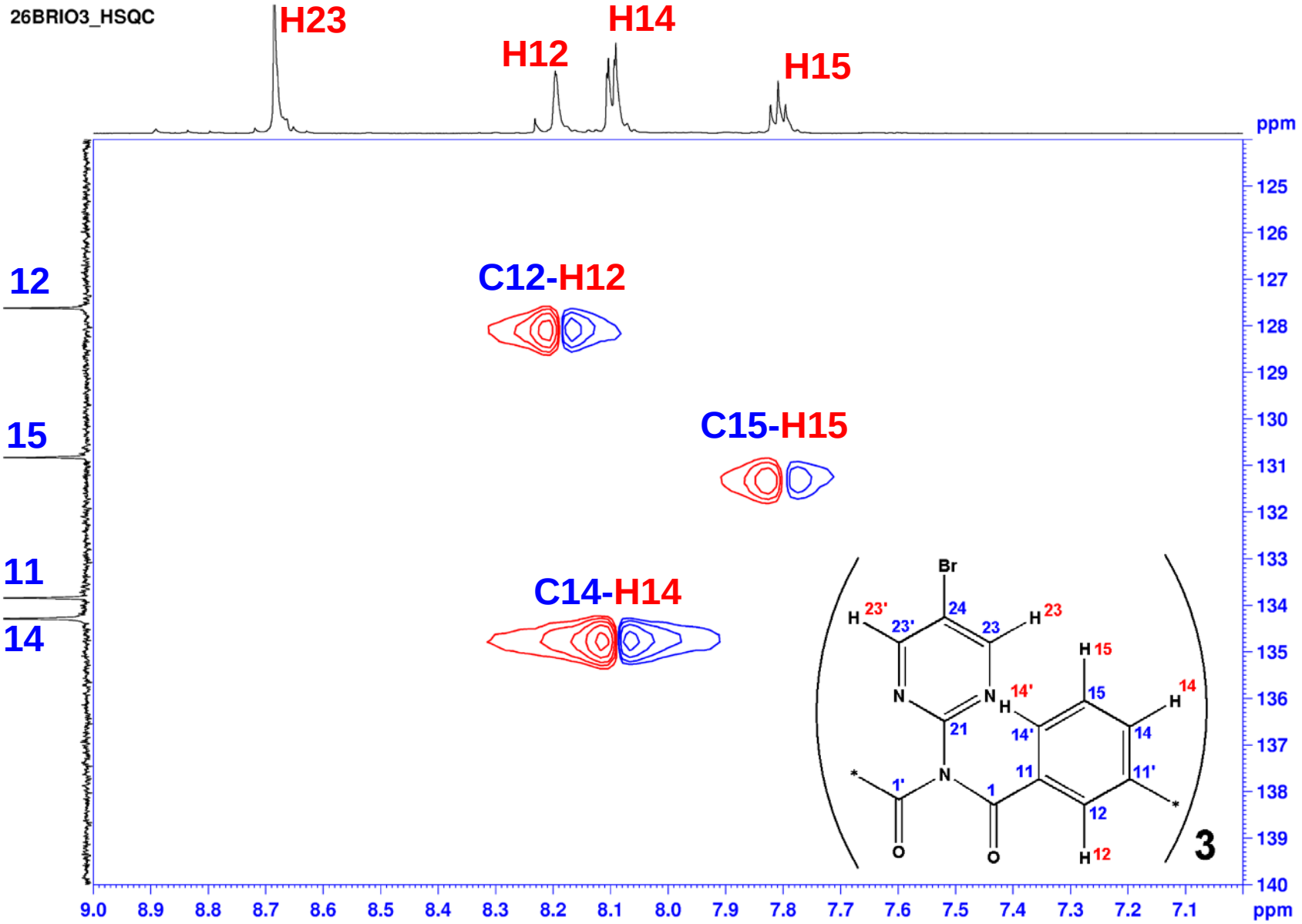
2.3.6. DEPT, 80°C, DMSO-d_6



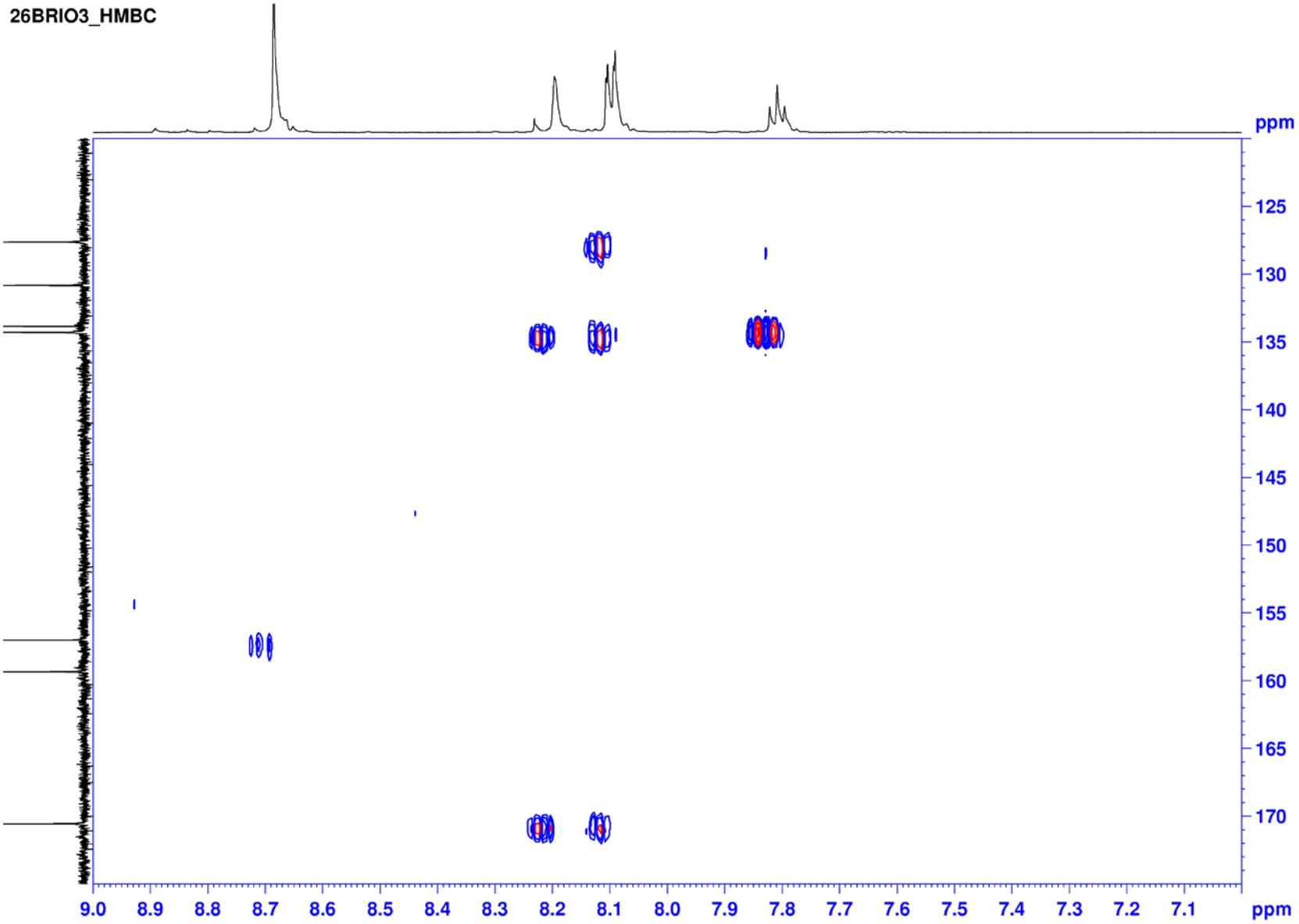
2.3.7. DEPT-Q, 80°C, DMSO-d_6



2.3.8. HSQC, 80°C, DMSO-d_6

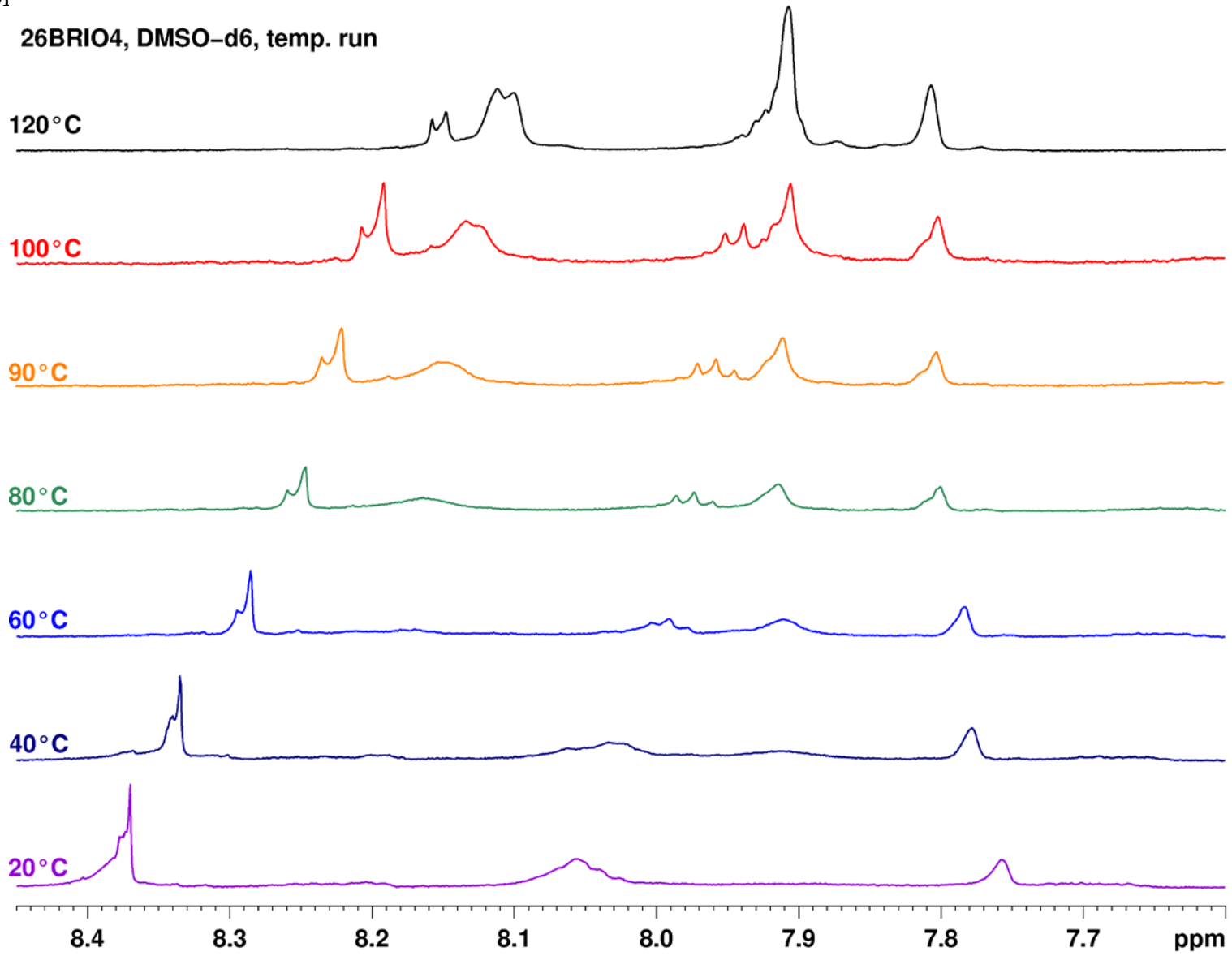


2.3.9. HMBC, 80°C, DMSO-d_6



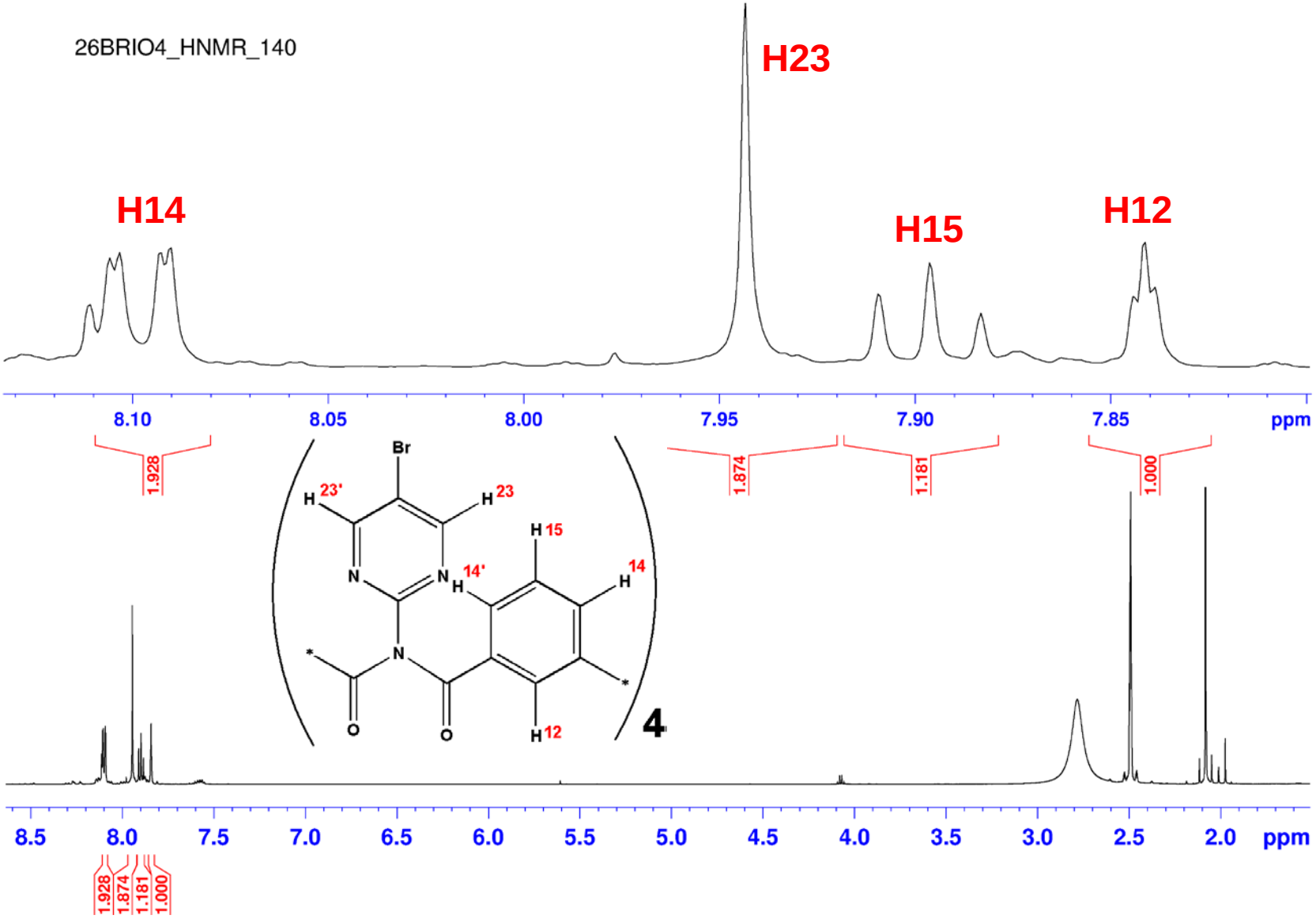
2.4. (26BrIO)$_4$

2.4.1. ^{1}H-NMR variable temperature run, DMSO-d_6

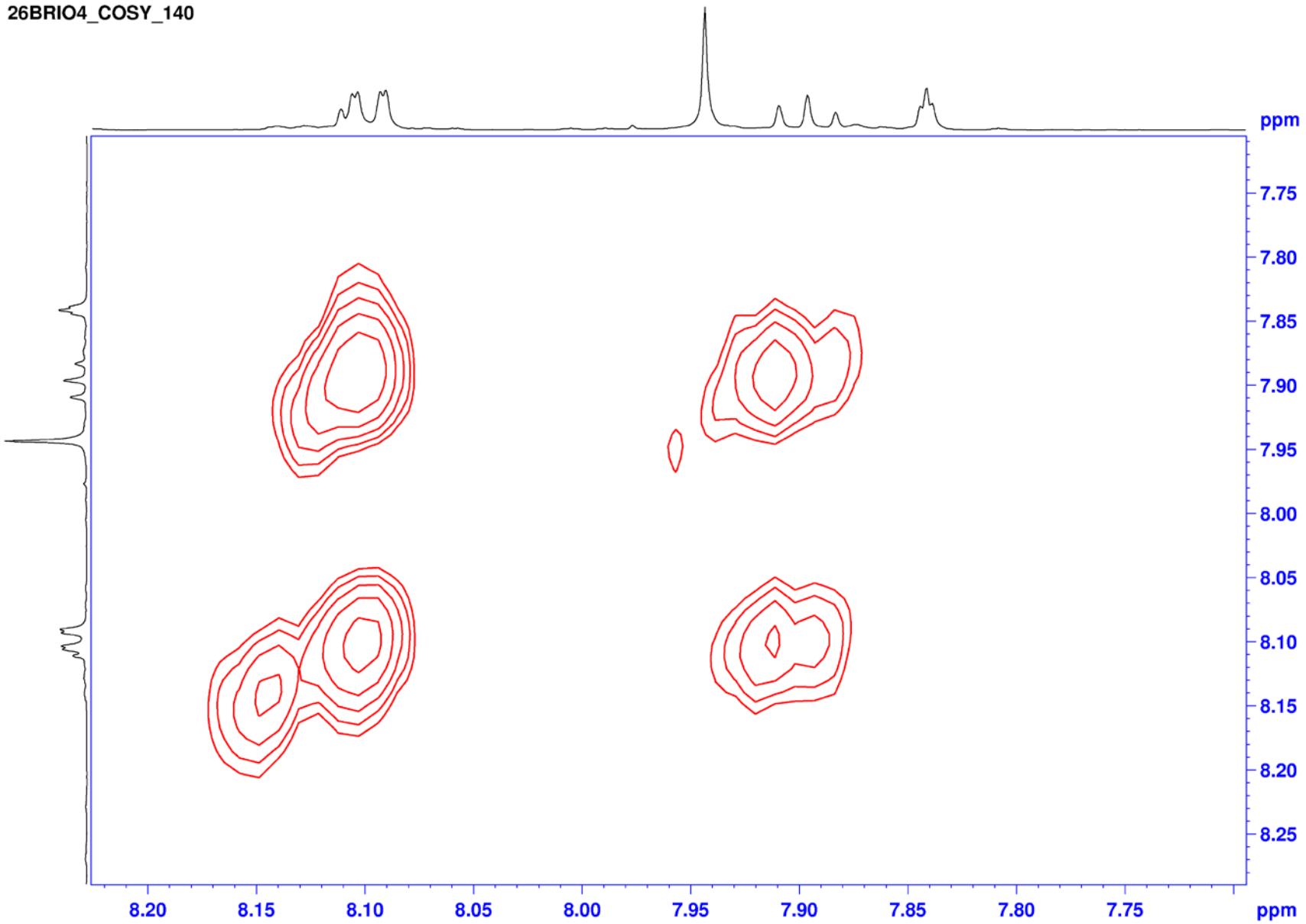


2.4.2. ^{1}H-NMR, 140°C, DMSO-d_6

δ 7.84 (1H, t, ^{3}J = 2), 7.90 (1H, t, ^{3}J = 8), 7.94 (2H, s), 8.10 (2H, dd, ^{3}J = 8, ^{4}J = 2);

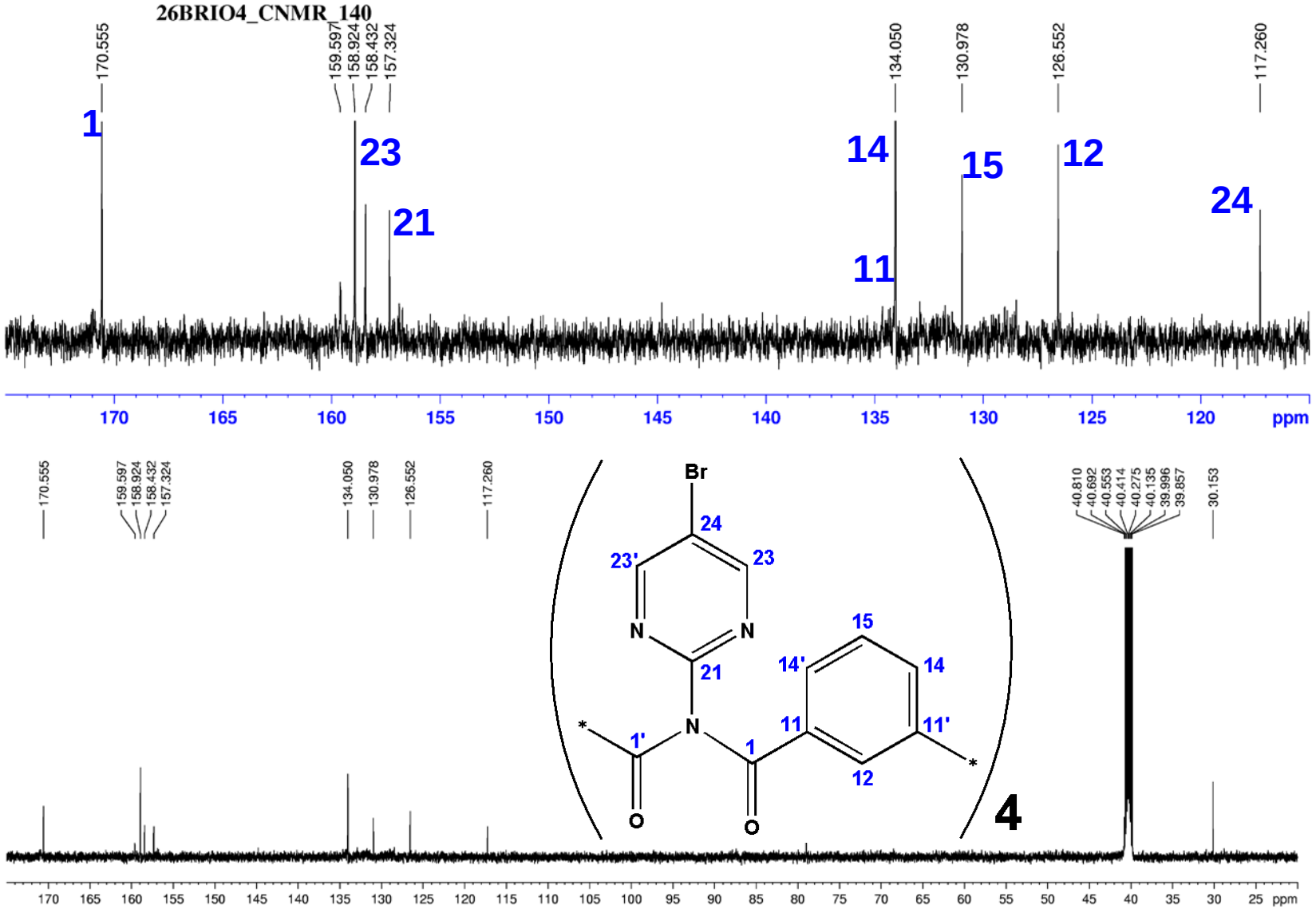


2.4.3. COSY, 140°C, DMSO-d_6

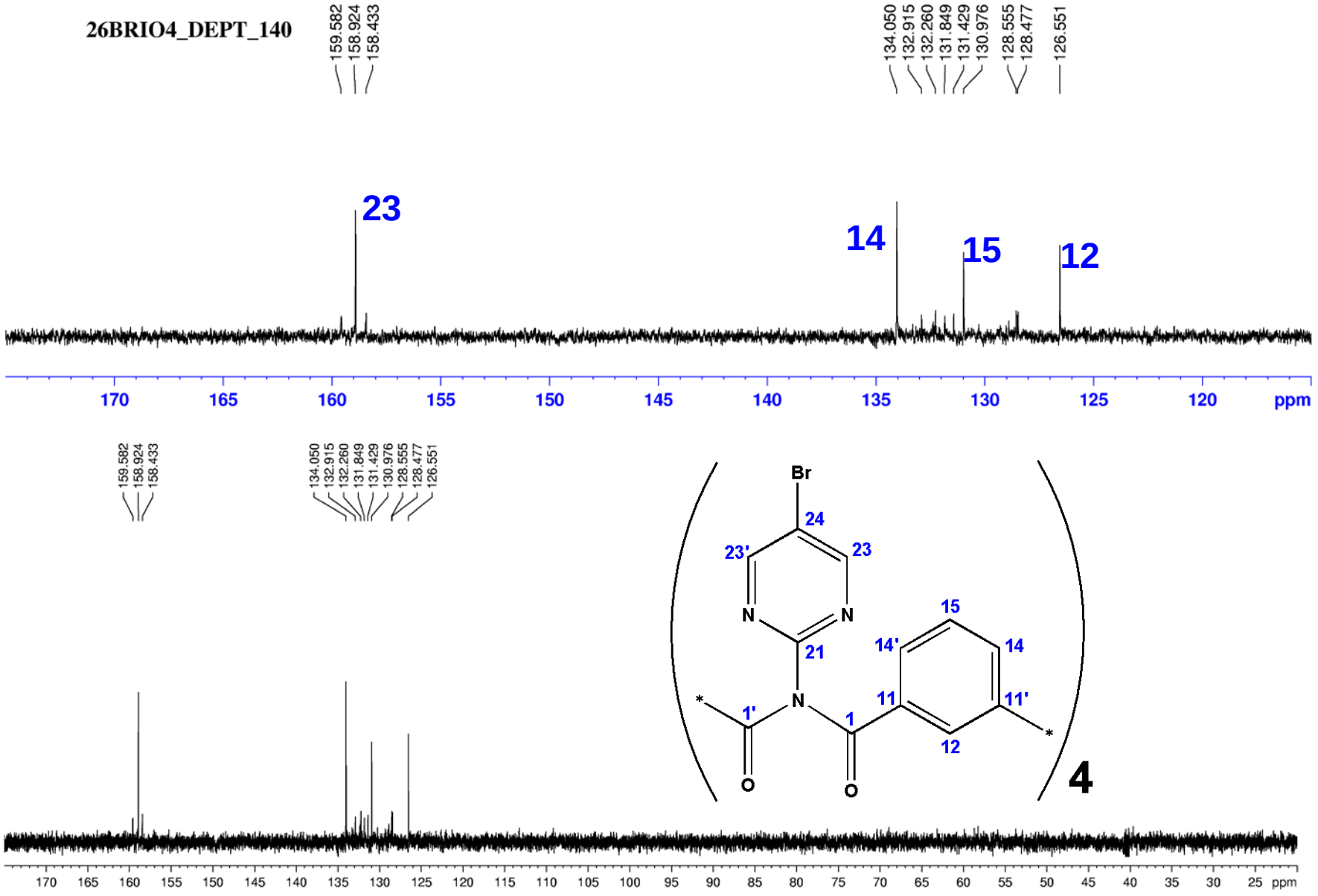


2.4.4. ^{13}C-NMR, 140°C, DMSO-d_6

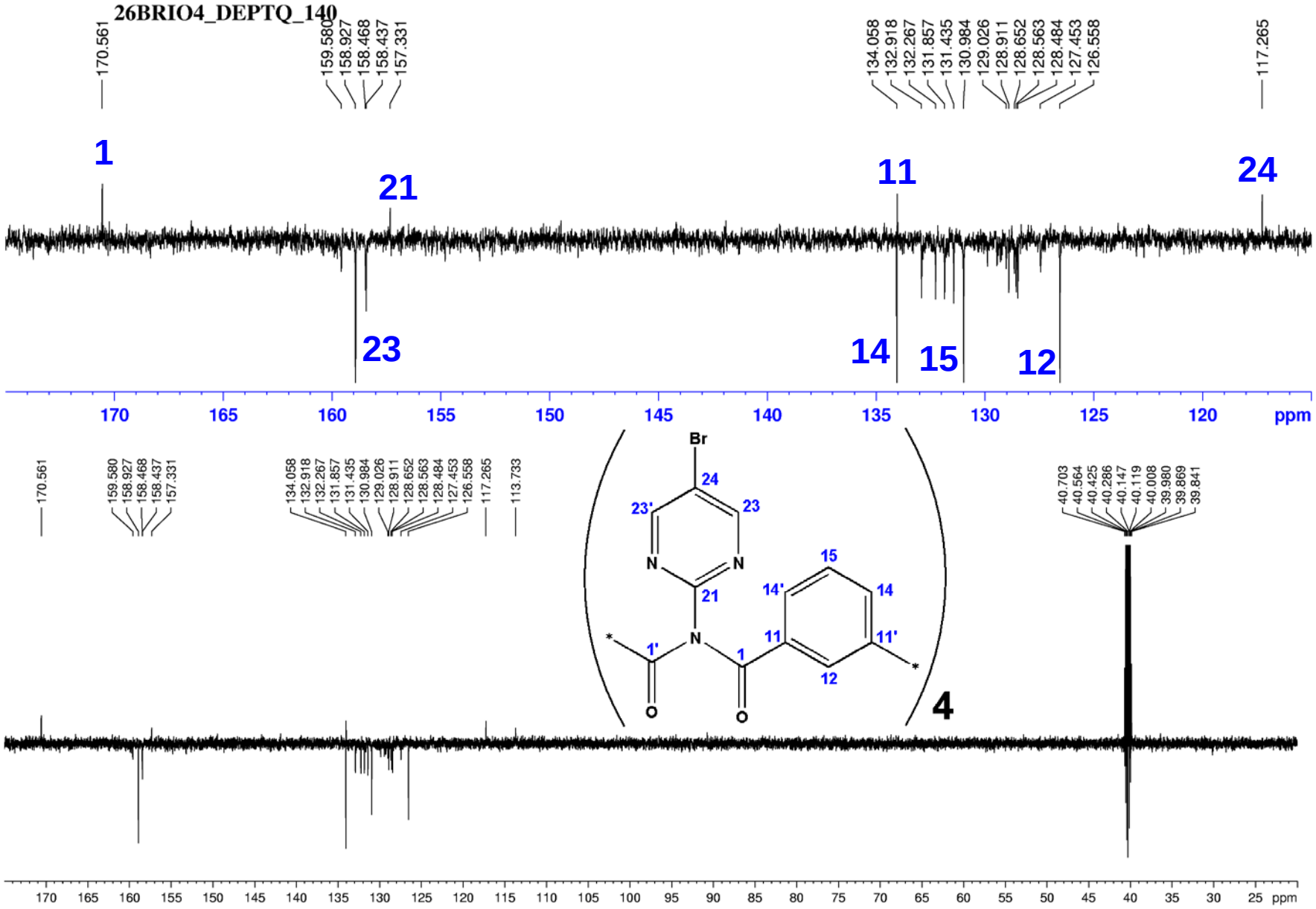
δ 117.26, 126.55, 130.98, 134.00, 134.05, 157.32, 158.92, 170.55



2.4.5. DEPT, 140°C, DMSO-d_6

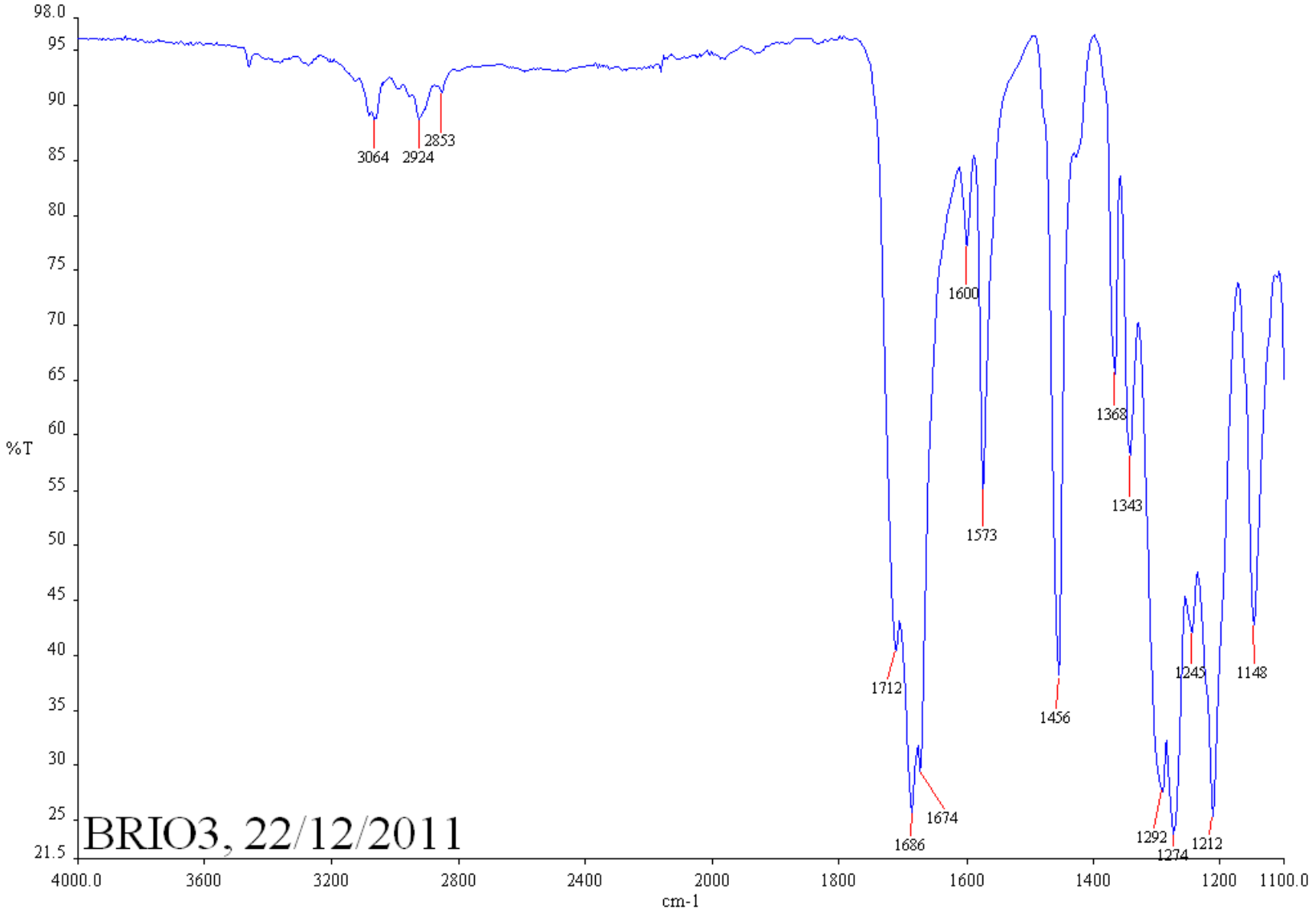


2.4.6. DEPT-Q, 140°C, DMSO-d_6

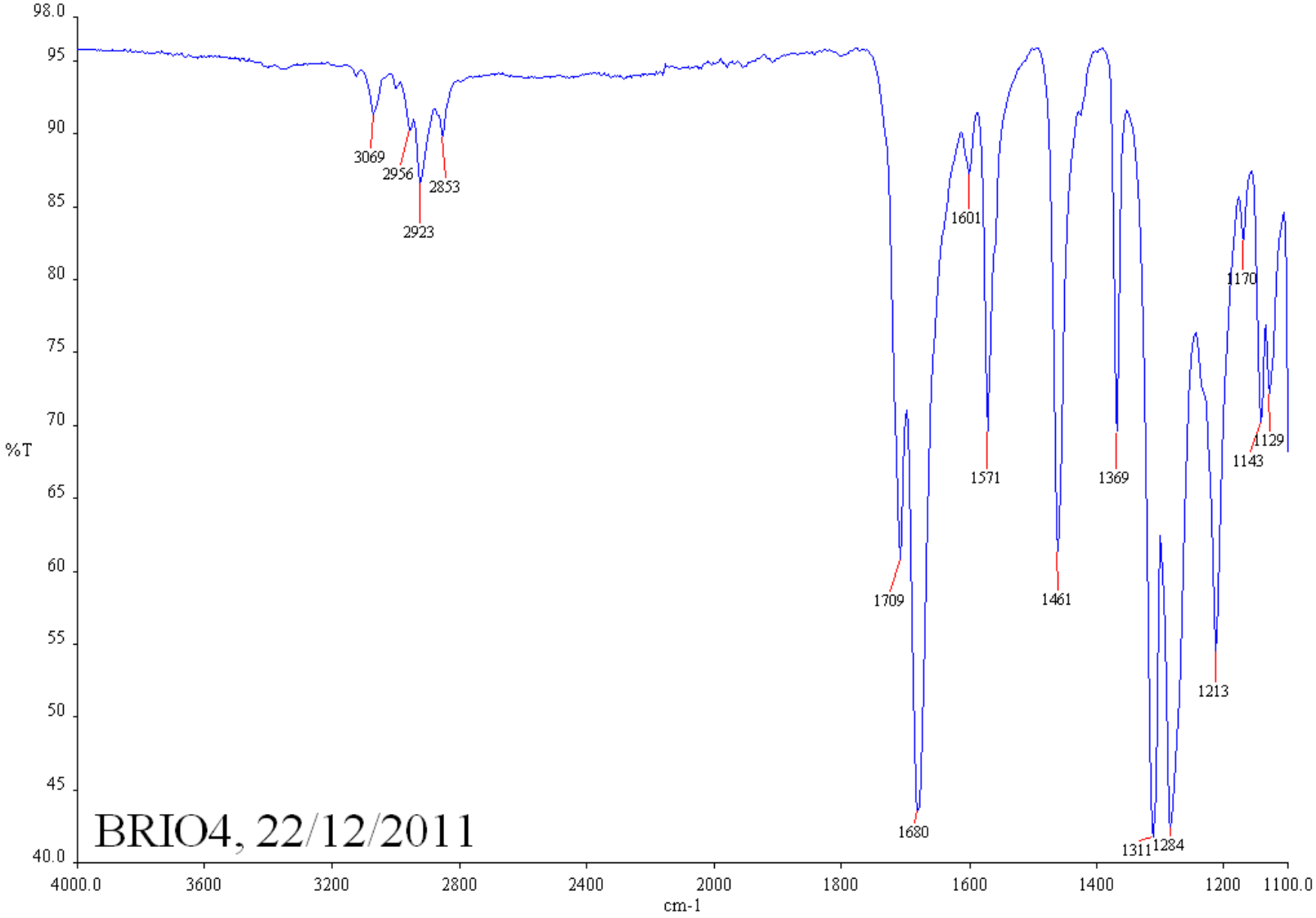


3. <u>IR data and spectra (ATR)</u>

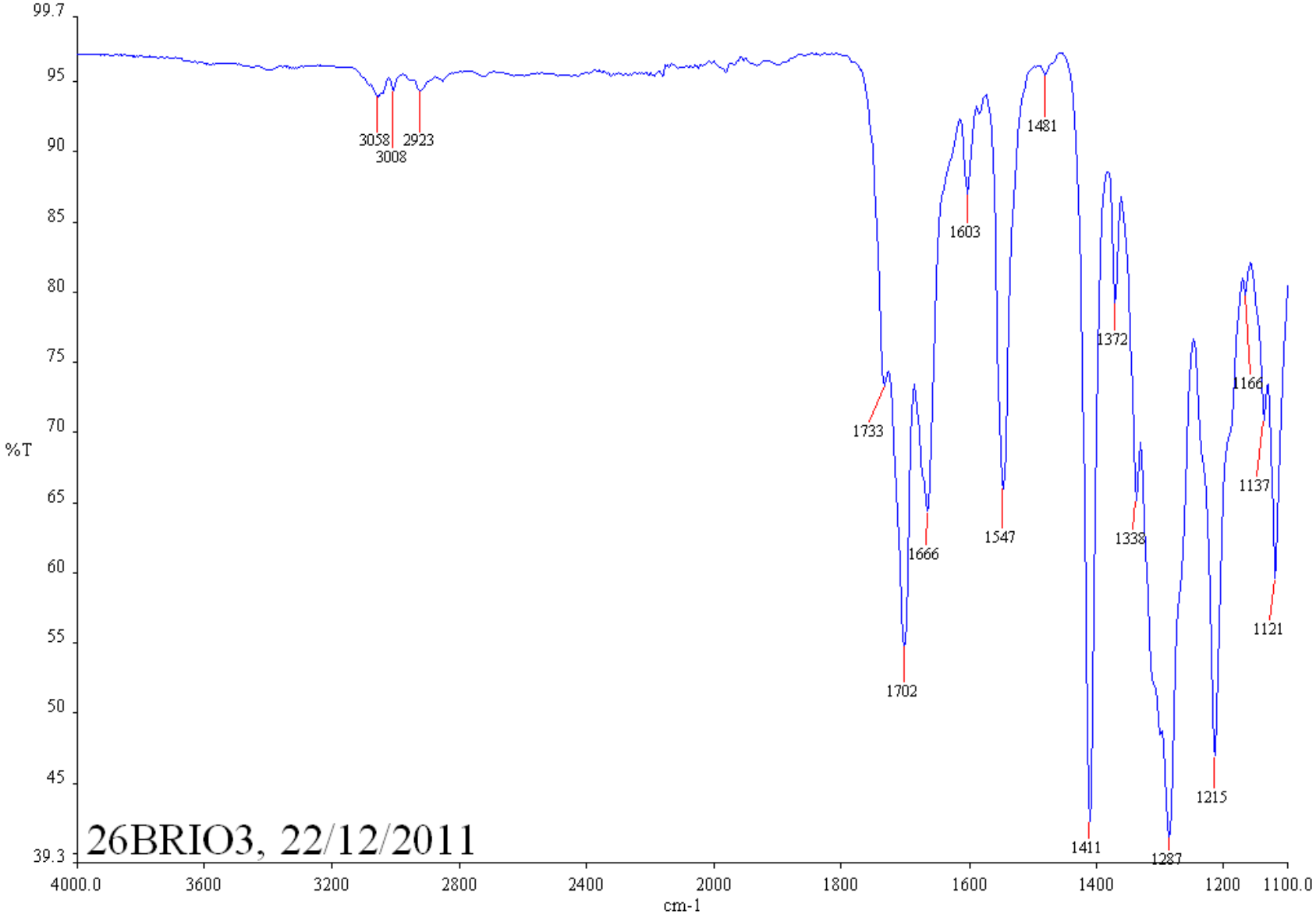
3.1. (**BrIO**)$_3$: 3064 (w), 2924 (w), 2853 (w), 1712 (s), 1686 (s), 1674 (s), 1600 (m), 1573 (m), 1456 (s), 1368 (m), 1343 (m), 1292 (s), 1274 (s), 1245 (s), 1212 (s);



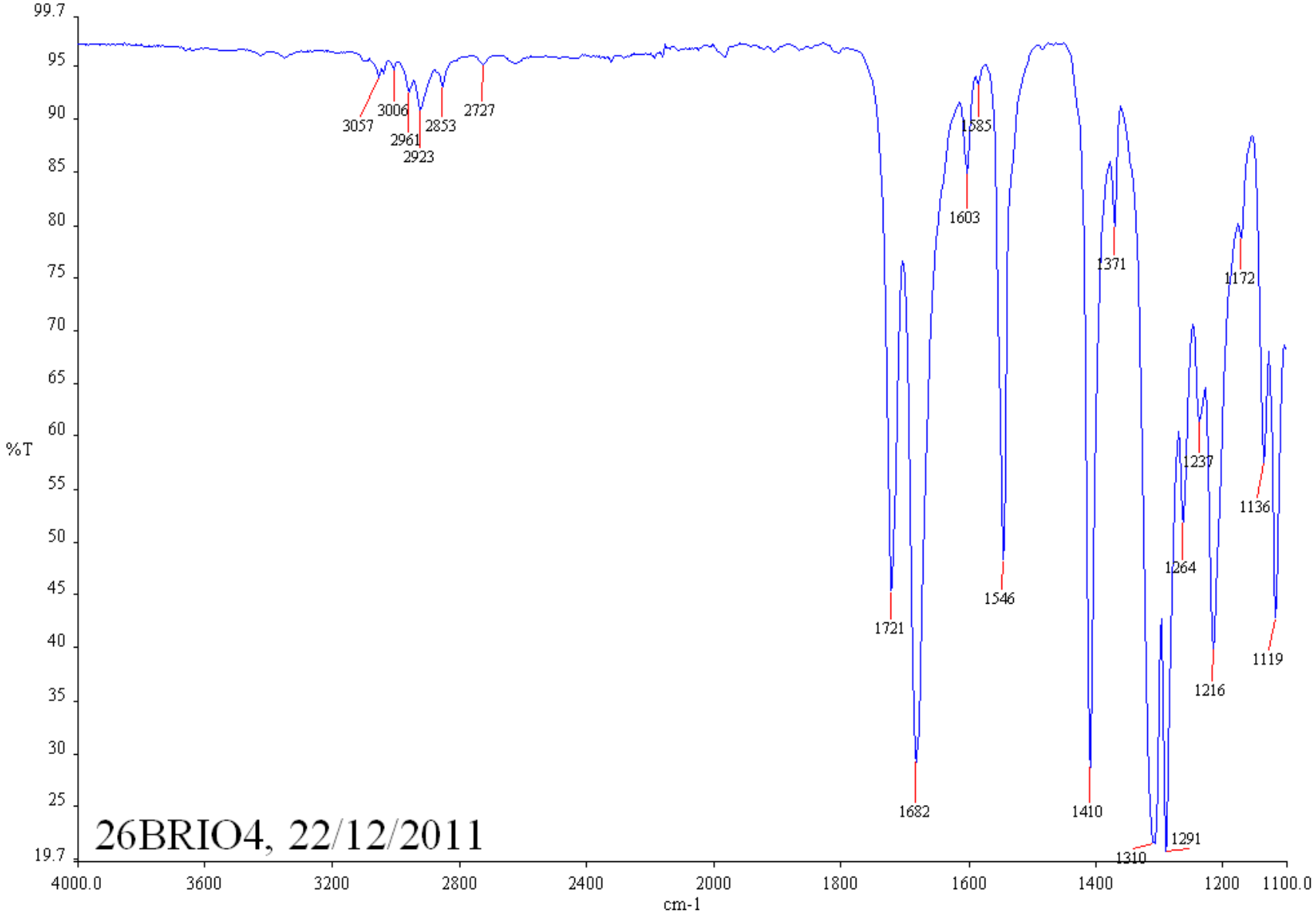
3.2. (**BrIO**)$_4$: 3069 (w), 2956 (w), 2923 (w), 2853 (w), 1709 (s), 1680 (s), 1601 (w), 1571 (m), 1461 (m), 1369 (m), 1311 (s), 1284 (s), 1213 (s);



3.3. (**26BrIO**)$_3$: IR (ATR): 3058 (w), 3008 (w), 2923 (w), 1733 (s), 1702 (s), 1666 (s), 1603 (w), 1547 (w), 1481 (w), 1411 (s), 1372 (m), 1338 (s), 1287 (s), 1215 (s);



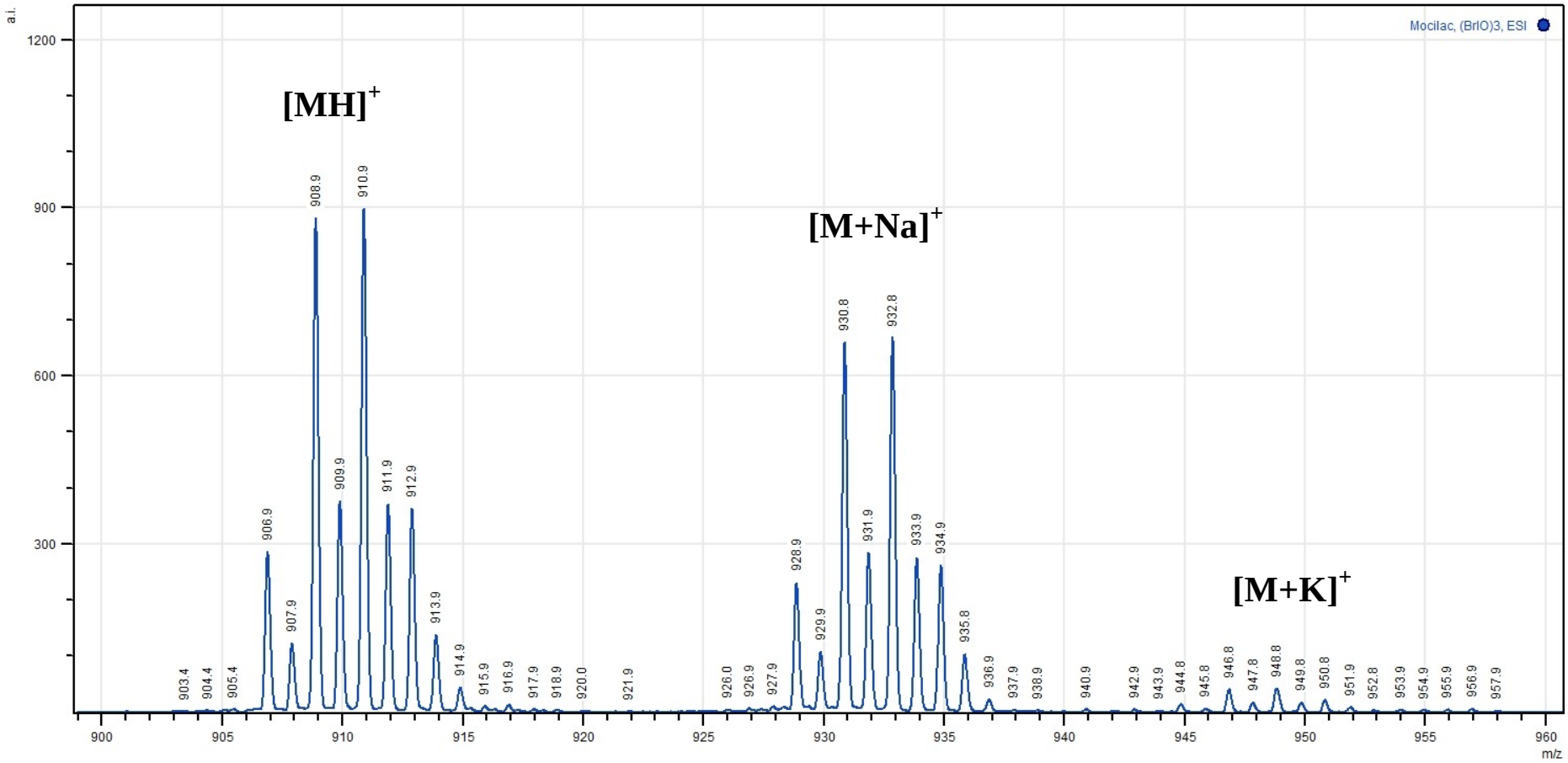
3.4. **(26BrIO)$_4$** IR (ATR): 3057 (w), 3006 (w), 2961 (w), 2923 (w), 2853 (w), 2727 (w), 1721 (s), 1682 (s), 1603 (w), 1585 (w), 1546 (s), 1410 (s), 1371 (w), 1310 (s), 1291 (s), 1264 (m), 1237 (m), 1216 (s);



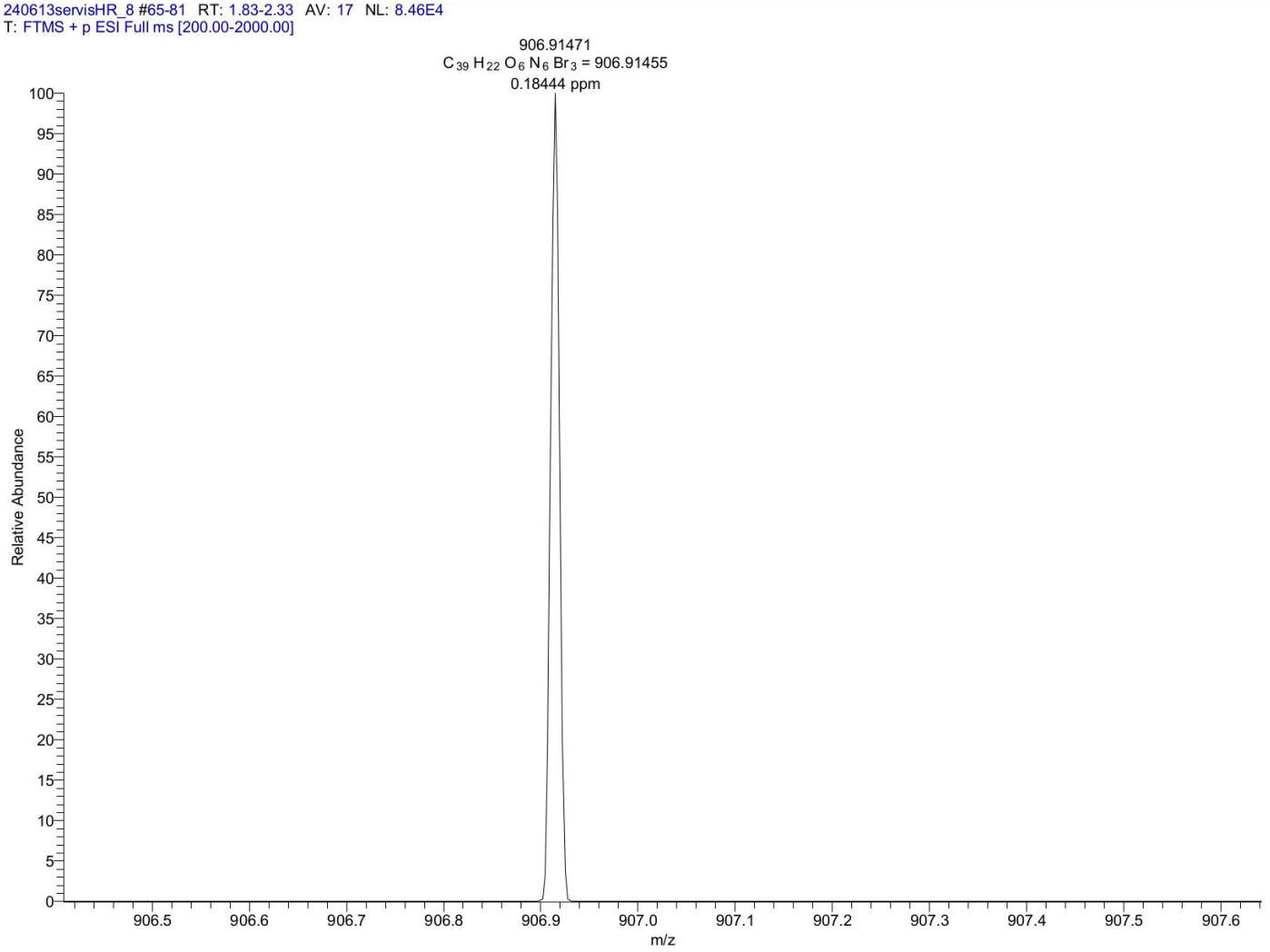
4. MS and HRMS data and spectra (June/July 2013)

The tri- and tetrabrominated (Br_3/Br_4) macrocycles correspond both to their molecular weights and from cluster analysis of isotope patterns. The lecture by R Gross has further information on MS at *academic.pgcc.edu/~rgross/Presentation%20PGCC%20Nov%2016.ppt*

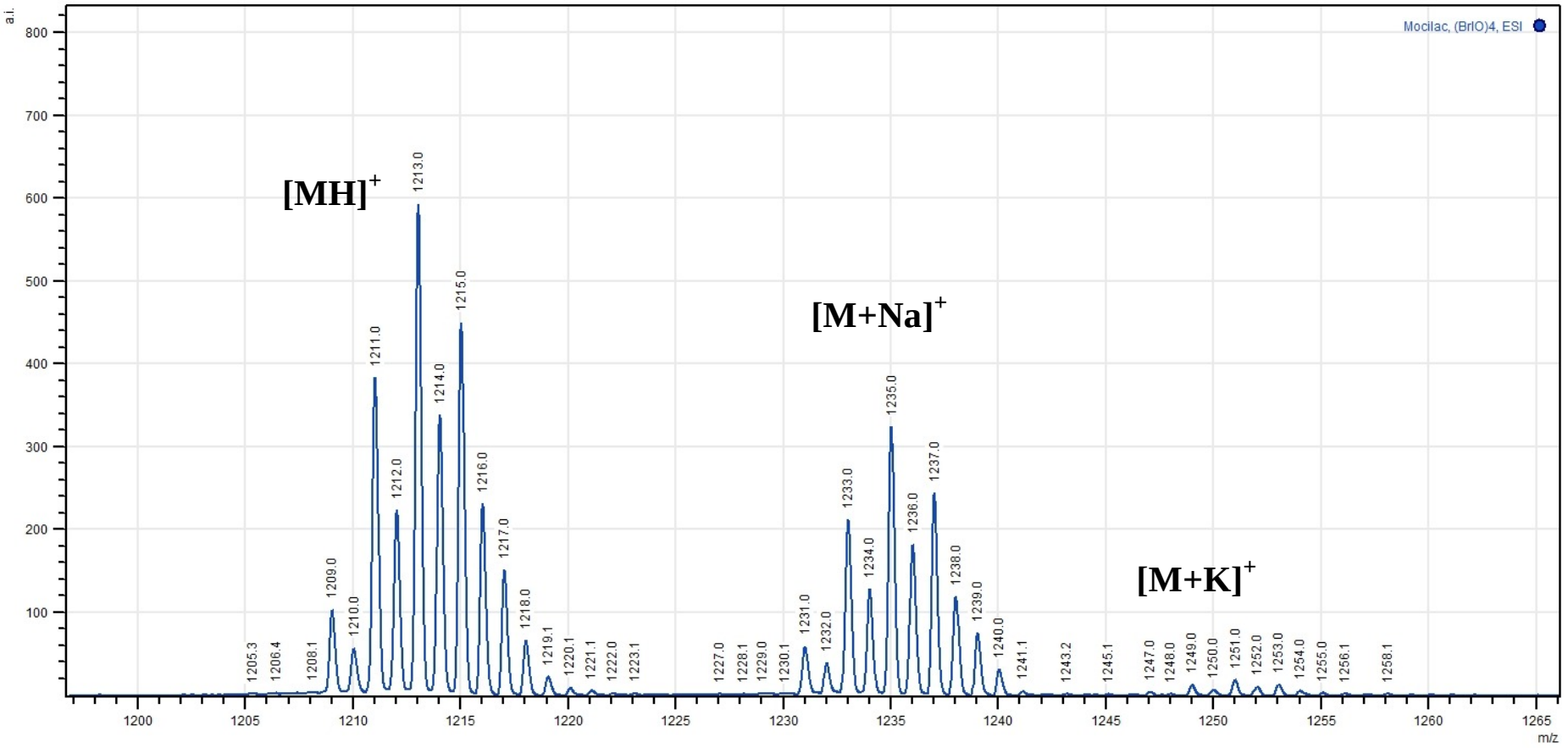
(BrIO)$_3$: $[MH]^+$ = 908.9; $[M + Na]^+$ = 930.8; $[M + K]^+$ = 948.8



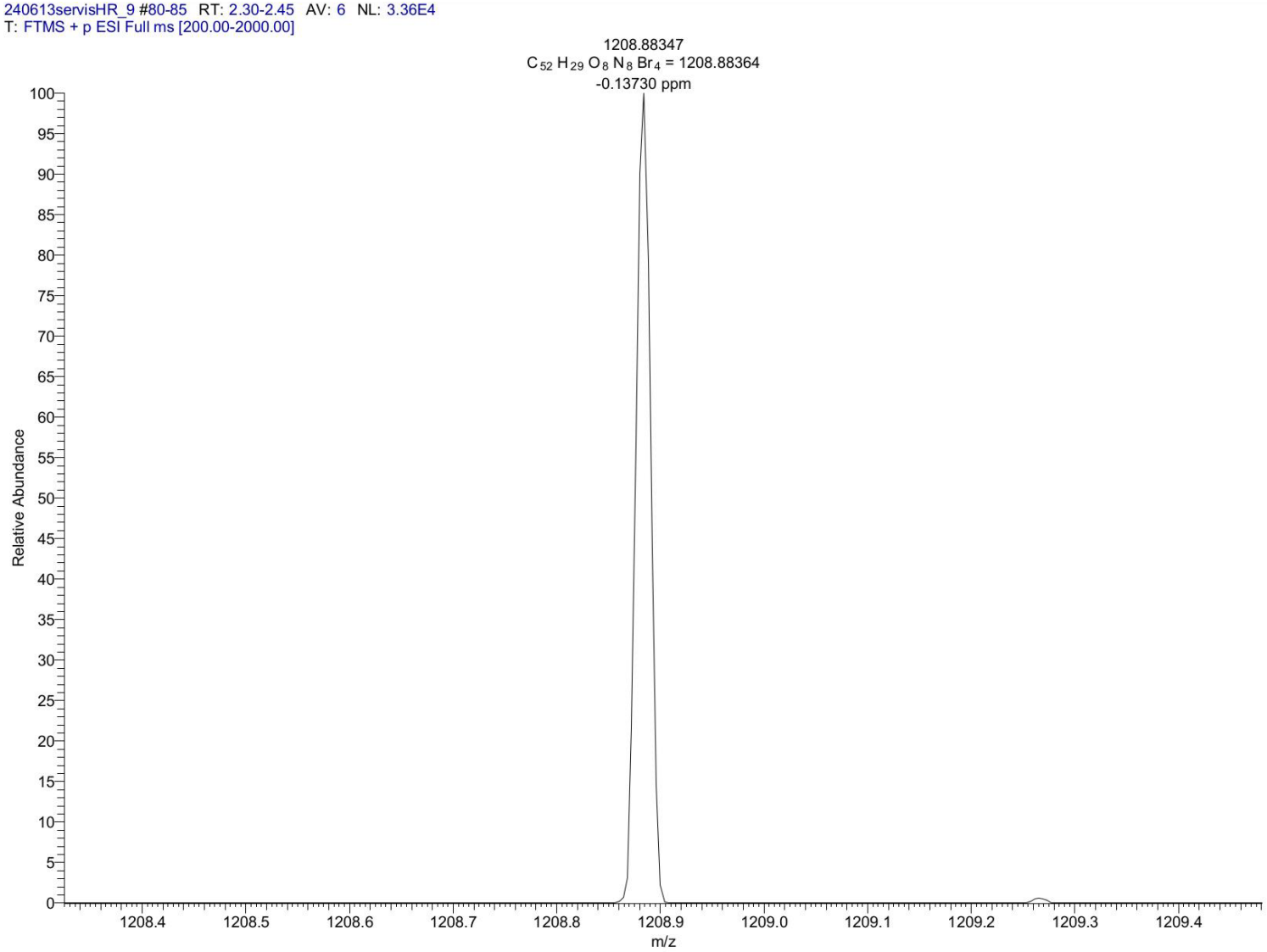
High Resolution Mass Spectrum: Exact mass (MH^+) = 906.91471



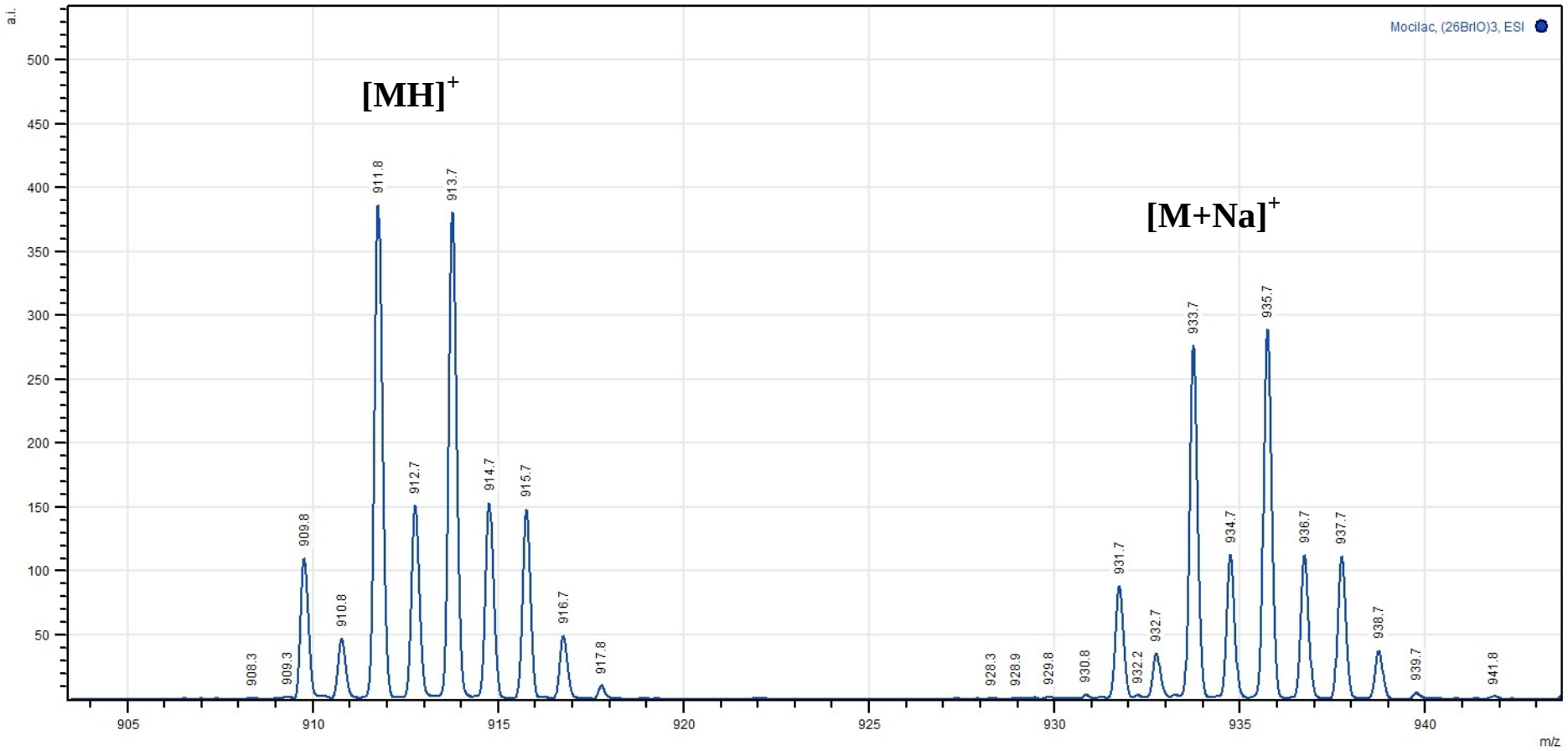
$(BrIO)_4$: $[MH]^+ = 1213$; $[M + Na]^+ = 1235$; $[M + K]^+ = 1251$



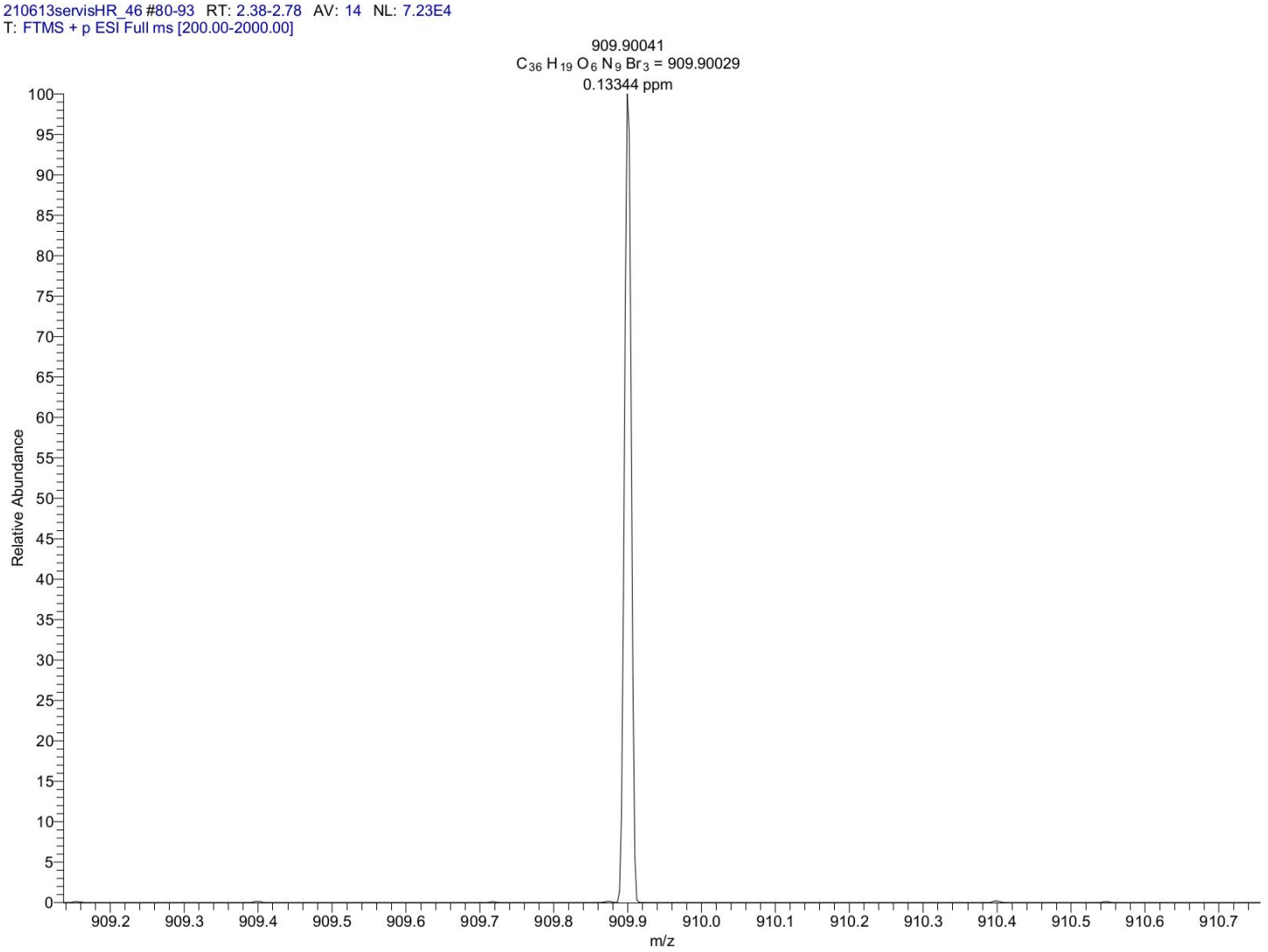
High Resolution Mass Spectrum: Exact mass (MH^+) = 1208.88347



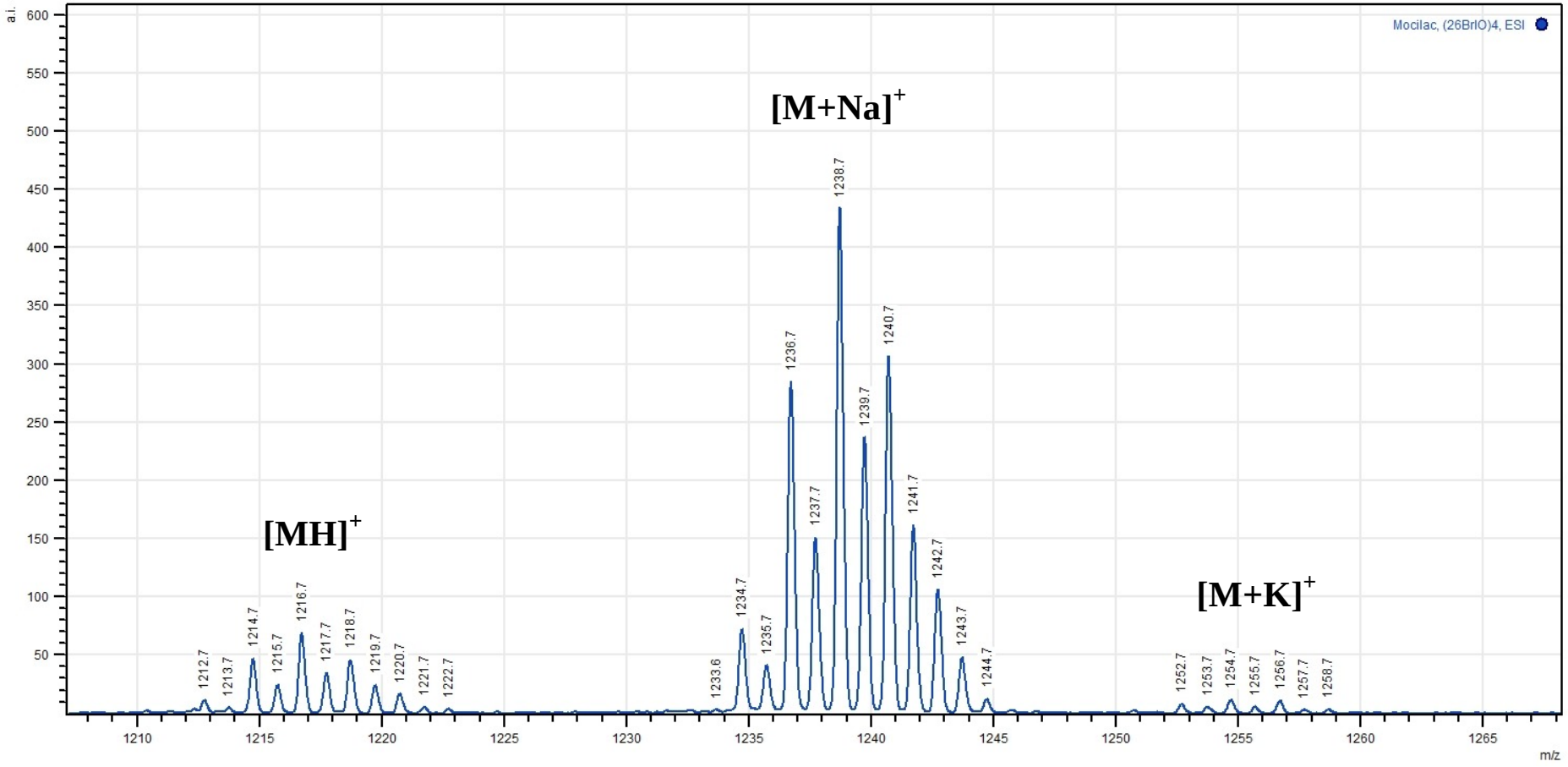
(26BrIO)$_3$: $[MH]^+$ = 911.9; $[M + Na]^+$ = 933.7



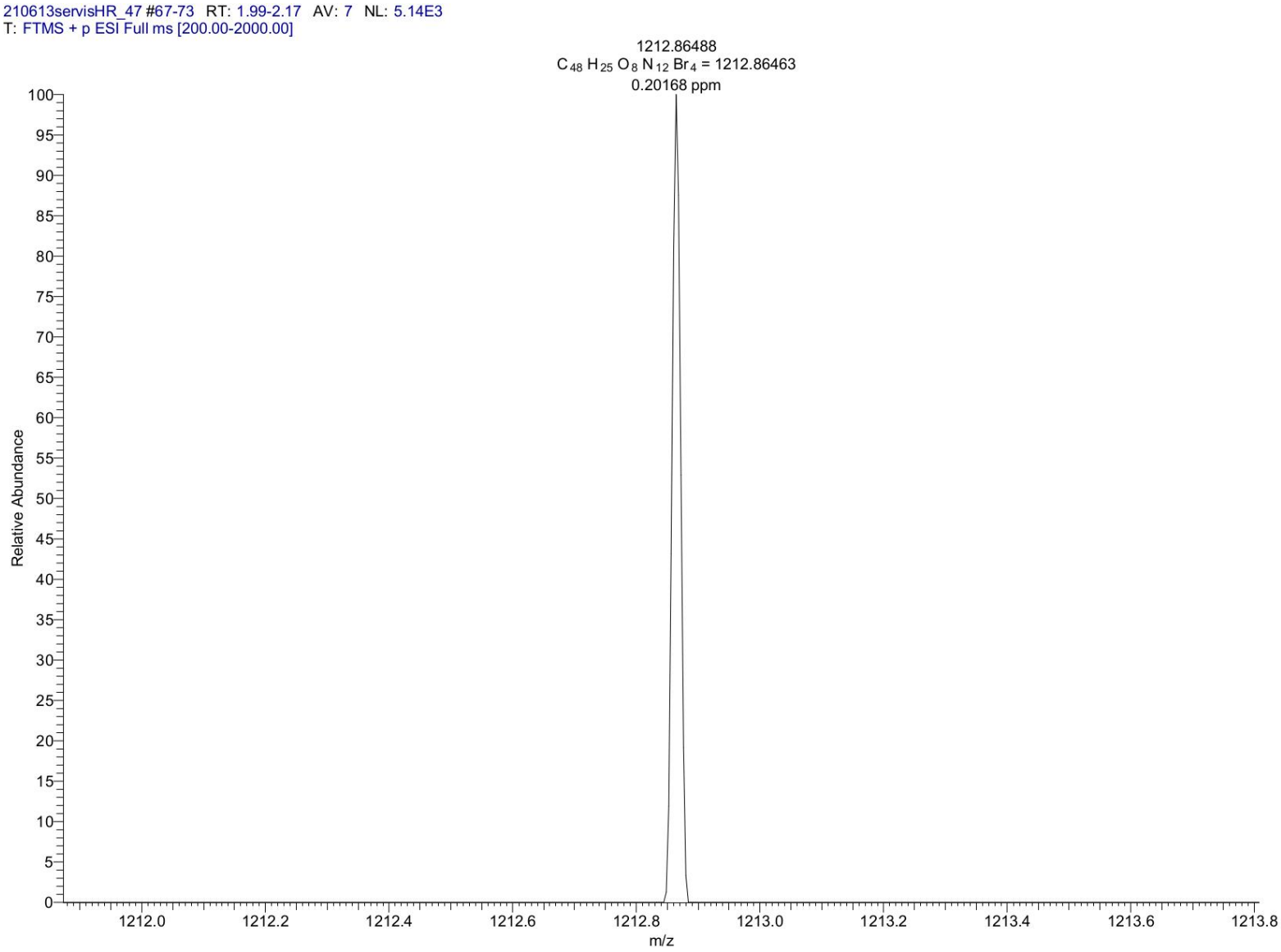
High Resolution Mass Spectrum: Exact mass (MH^+) = 909.90041



(26BrIO)$_4$: $[MH]^+$ = 1216.7; $[M + Na]^+$ = 1238.7; $[M + K]^+$ = 1254.7



High Resolution Mass Spectrum: Exact mass (MH^+) = 1212.86488



5. Crystallographic details

Table 1. Experimental details

Crystal details for the five (**BrIO**)$_3$; (**BrIO**)$_4$; (**26BrIO**)$_3$[†], (**26BrIO**)$_3$[‡]; and (**26BrIO**)$_4$ crystal structures. Experiments were carried out at 294 K using a Xcalibur, Sapphire3, Gemini Ultra diffractometer and an Analytical absorption correction was used, (ABSFAC, Clark and Reid, 1998). H atom parameters were constrained.

Compound	(**BrIO**)$_3$	(**BrIO**)$_4$	(**26BrIO**)$_3$ [†]	(**26BrIO**)$_3$ [‡]	(**26BrIO**)$_4$
CCDC codes	**930689**	**930690**	**930691**	**930692**	**930693**
Crystal data					
Chemical formula	$2(C_{39}H_{21}Br_3N_6O_6)\cdot C_4H_8O_2$	$C_{52}H_{28}Br_4N_8O_8\cdot 0.8(CHCl_3)$	$C_{36}H_{18}Br_3N_9O_6\cdot 2(CHCl_3)$	$C_{36}H_{18}Br_3N_9O_6\cdot 2(CH_2Cl_2)$	$2(C_{48}H_{24}Br_4N_{12}O_8)\cdot 3.8(CHCl_3)\cdot H_2O$
Crystals grown from	Ethyl acetate	Chloroform	Chloroform	Dichloromethane	Chloroform
M_r	1906.74	1307.96	1151.06	1082.18	2904.40
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, *Pccn*	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	10.9440(3) 65.6499(13) 11.2294(3)	14.0441(4) 19.1432(3) 19.1482(4)	12.8150(6) 13.6159(5) 25.7452(11)	12.2390(5) 13.6149(5) 13.6447(5)	10.5779(3) 13.2805(3) 40.7855(13)
α, β, γ (°)	90, 110.447(3), 90	90, 90, 90	84.442(3), 87.666(4), 80.070(4)	100.749(3), 99.990(3), 95.463(3)	90, 95.936(2), 90
V (Å^3), Z	7559.7(3), *4*	5148.0(2), *4*	4402.8(3), *4*	2180.69(14), *2*	5698.8(3), *2*
Radiation type	Mo *K*α	Cu *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ(mm^{-1})	3.26	5.50	3.17	3.08	3.16
Crystal size (mm)	0.52×0.29×0.08	0.35×0.13×0.09	0.34×0.17×0.04	0.49×0.38×0.15	0.39×0.35×0.22
Data collection and Refinement					
T_{min}, T_{max}	0.282, 0.780	0.249, 0.638	0.412, 0.884	0.314, 0.656	0.372, 0.544
Measured, Independent, Observed [$I>2\sigma(I)$], R_{int}	32690, 15826, 10079, 0.051	30530, 4178, 3574, 0.039	38013, 18957, 8469, 0.058	16290, 9391, 5817, 0.024	41540, 12192, 7949, 0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.639	0.579	0.656	0.657	0.642
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, *S (GoF)*	0.075, 0.159, 1.10	0.044, 0.122, 1.04	0.079, 0.193, 1.01	0.067, 0.187, 1.01	0.076, 0.205, 1.03
No. of reflections, parameters, restraints	15826, 1047, 0	4178, 457, 170	18957, 1153, 30	9391, 568, 47	12192, 754, 39
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.69, –0.83	0.97, –0.66	1.26, –1.19	1.45, –1.29	1.16, –1.22

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET) (compiled Jan 20 2011,15:58:25), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and SORTX (McArdle, 1995), *PLATON* (Spek, 2009), *SHELXL97*.

[†] $CHCl_3$ solvate and [‡] CH_2Cl_2 solvates of (**26BrIO**)$_3$

A shortened version of this table is used as **Table 1** in the manuscript.

Full details have been deposited on the Cambridge Structural Database.

Table 2. Selected torsion angles [imide *hinge* and isophthaloyl groups (°)]

Compound (**Imide *hinge* torsion**)	**CO…CO** [1]	**Isophthaloyl group**	**OC…CO** [2]
(BrIO)$_3$			
O1A=C1A…C2A=O2A	109.6(9)	O1A=C1A…C6A=O6A	7.44 (8)
O3A=C3A…C4A=O4A	86.9 (6)	O2A=C2A…C3A=O3A	-105.8 (9)
O5A=C5A…C6A=O6A	-99.9 (7)	O4A=C4A…C5A=O5A	-26.0 (7)
O1B=C1B…C2B=O2B	-97.9 (8)	O1B=C1B…C6B=O6B	-14.3 (9)
O3B=C3B…C4B=O4B	-99.4 (6)	O2B=C2B…C3B=O3B	107.4 (9)
O5B=C5B…C6B=O6B	100.2 (7)	O4B=C4B…C5B=O5B	23.9 (8)
(BrIO)$_4$ *			
O1=C1…C2=O2	94.3 (5)	O1=C1…C4=O4	15.5 (7)
O3=C3…C4=O4	-103.9 (5)	O2=C2…C3*=O3*	-13.2 (7)
(26BrIO)$_3$ †			
O1A=C1A…C2A=O2A	-95.4 (10)	O1A=C1A…C6A=O6A	-23.1 (11)
O3A=C3A…C4A=O4A	-88.5 (8)	O2A=C2A…C3A=O3A	94.6 (13)
O5A=C5A…C6A=O6A	94.3 (8)	O4A=C4A…C5A=O5A	34.7 (10)
O1B=C1B…C2B=O2B	-90.4 (10)	O1B=C1B…C6B=O6B	-19.1 (10)
O3B=C3B…C4B=O4B	-85.8 (6)	O2B=C2B…C3B=O3B	89.4 (13)
O5B=C5B…C6B=O6B	96.9 (9)	O4B=C4B…C5B=O5B	26.8 (11)
(26BrIO)$_3$ ‡			
O1=C1…C2=O2	-94.7 (8)	O1=C1…C6=O6	-17.8 (8)
O3=C3…C4=O4	-86.6 (5)	O2=C2…C3=O3	92.9 (10)
O5=C5…C6=O6	95.7 (8)	O4=C4…C5=O5	26.6 (8)
(26BrIO)$_4$			
O1=C1…C2=O2	86.7 (7)	O1=C1…C8=O8	23.6 (11)
O3=C3…C4=O4	-101.3 (7)	O2=C2…C3=O3	-4.4 (10)
O5=C5…C6=O6	112.0 (8)	O4=C4…C5=O5	1.7 (9)
O7=C7…C8=O8	-97.2 (7)	O6=C6…C7=O7	-19.4 (10)

Footnotes:

1 The **CO…CO** twist is the imide *hinge* torsion angle as measured by **O=C…C=O**.[Reference 13]

2 The **OC…CO** torsion is the isophthaloyl torsion angle as measured by **O=C…C=O**.[Reference 13]

* Symmetry operation: * = ½-x, ½-y, z in space group *Pccn*.

Solvates † $CHCl_3$ solvate and ‡ CH_2Cl_2 solvates of **(26BrIO)$_3$**

Table 3: Summary of C–Br…O=C/N$_{(pyrimidine)}$/C$_\pi$ halogen bonding and contacts.[11,12]

Macrocycle **Br…O/N/C$_\pi$** (Å) [N_c][11,12]	**Br…O=C/H–C/C$_\pi$/N** (°)	**C–Br…O/H/C$_\pi$/N** (°)
(BrIO)$_3$ #		
Br3B…O6B[1] 3.167(4) [**0.94**]	Br3B…O6B[1]=C6B[1] 135.8(4)	C34B–Br3B…O6B[1] 160.5(2)
Br3A…C15[2] 3.424(6) [**0.97**]	–	C34A–Br3A…C15[2] 169.5(2)
(26BrIO)$_3$ †		
Br1A…O4A[3] 3.036(4) [**0.90**] Br1A…C4A[3] 3.407(6) [**0.96**]	Br1A…O4A[3]=C4A[3] 97.0(4) Br1A…C4A[3]=O4A[3] 62.2(4)	C14A–Br1A…O4A[3] 150.9(2) C14A–Br1A…C4A[3] 154.4(3)
Br1B…O4B[4] 2.955(4) [**0.88**]	Br1B…O4B[4]=C4B[4] 113.2(4)	C14B–Br1B…O4B[4] 171.9(3)
Br2A…C34[5] 3.366(6) [**0.95**] (Br…π) Br2B…C64[6] 3.404(7) [**0.96**] (Br…π)		C24A–Br2A…C34[5] 147.0(3) C24B–Br2A…C64[6] 147.2(2)
(26BrIO)$_3$ ‡		
Br14…O4[7] 2.982(3) [**0.89**]	Br14…O4[7]=C4[7] 111.7(3)	C14–Br14…O4[7] 149.39(7)
Br24…C35[8] 3.362(6) [**0.95**] (Br…π)		C24A–Br24...C35[8] 162.8(2)
(26BrIO)$_4$ (as Br...N$_{pyrimidine}$)		
Br24…N16A[4] 3.028(5) [**0.89**]	C24A–Br24…N16A[4] 165.5(2)	Br24…N16A[4]…C13A[4] 139.0(2)

Footnotes:
† as the $CHCl_3$ and ‡ as the CH_2Cl_2 solvates of **(26BrIO)$_3$**.
[N_c][11,12] - this has been discussed at length in several papers in references 11, 12 of the main paper.
refers to the Br1A...H4S3 hydrogen bonding contact of 2.69 Å and with Br...H–C/C–Br...H angles of 172/169°.
Symmetry operations: [1] = –1/2+x, 1/2–y, –1/2+z; [2] = 2–x, –y, –z in **(BrIO)$_3$**.
Symmetry operations: [3] = x, y–1, z; [4] = x, 1+y, z; [5] –x, 1–y, –z ; [6] 1–x, 1–y, 1–z and mainly in **(26BrIO)$_3$**.
Symmetry operations: [7] = x, y, 1–z; [8] = –x, 1–y, 2–z.

Note on the effect of perfluorinated systems on halogen bonding interactions:
Several compounds and molecular structures that also contain one or more C–F groups (usually aromatic) have a profound influence on the halogen bonding interactions and are typically up to 0.1–0.2 Å shorter (see Table 4, in **reference 11b** by Metrangolo, Resnati and co-workers) and from analysis of relevant crystal structure data on the CSD.[15]

Short Interactions of note:
The crystal structures **IBIYOJ** and **CEGVUF** (as NBS with DABCO) have short halogen bonding interactions with short halogen bonding **Br**...**N** distances of 2.35/2.36 Å as described in the halogen bonding review article, **reference 11m** by R.W. Troff, T. Makela, F. Topic, A. Valkonen, K. Raatikainen, K. Rissanen, *Eur. J. Org. Chem*. 2013, **9,** 1617-1637.

Table 4. Selected hydrogen-bond and contact parameters (Å, °).

D—H···*A*	*D*—H (in Å)	H···*A* (in Å)	*D*···*A* (in Å)	*D*—H···*A* (in °)
(BrIO)$_3$				
C15A—H15A···O5A^{i}	0.93	2.53	3.422 (7)	161
C16A—H16A···O1S	0.93	2.44	3.333 (9)	162
C35A—H35A···O5A^{i}	0.93	2.44	3.219 (8)	142
C35B—H35B···O3B^{ii}	0.93	2.53	3.190 (7)	128
C54—H54···O1A^{iii}	0.93	2.40	3.142 (7)	136
C1S—H1S3···O4A	0.96	2.53	3.301 (9)	138
(BrIO)$_4$				
C22—H22···N2	0.93	2.58	2.896 (4)	101
C23A—H23A···O2^{v}	0.93	2.44	3.275 (19)	150
C23A—H23A···O2^{v}	0.93	2.44	3.275 (19)	150
(26BrIO)$_3$ (ex–$CHCl_3$)†				
C3S—H3S···O1A	0.98	2.22	3.004 (11)	136
C4S—H4S···N16A	0.98	2.49	3.208 (19)	130
C12—H12···N1A	0.93	2.54	2.875 (9)	101
C22—H22···N2A	0.93	2.56	2.883 (8)	101
C52—H52···N2B	0.93	2.60	2.919 (8)	101
C62—H62···N3B	0.93	2.60	2.912 (7)	100
C44—H44···O3B^{vi}	0.93	2.56	3.291 (8)	135
C2S—H2S···N12B^{vi}	0.98	2.58	3.533 (11)	165
(26BrIO)$_3$ (ex–CH_2Cl_2)‡				
C1S—H1S2···O5	0.97	2.54	3.436 (10)	153
C1S—H1S1···N16A^{vii}	0.97	2.62	3.263 (9)	124
C12—H12···N1	0.93	2.61	2.918 (7)	100
C22—H22···N2	0.93	2.58	2.886 (6)	100
C25—H25···O4^{viii}	0.93	2.56	3.272 (6)	134
(26BrIO)$_4$				
C12—H12···N1	0.93	2.59	2.910 (7)	101
C42—H42···N4	0.93	2.61	2.918 (7)	100
C43A—H43A···O5^{ix}	0.93	2.46	3.197 (8)	136
C14—H14···O8^{x}	0.93	2.48	3.114 (6)	126
C15—H15···O8^{x}	0.93	2.60	3.174 (7)	120
C15A—H15A···O4^{v}	0.93	2.49	3.356 (7)	155
C34—H34···O3^{xi}	0.93	2.38	3.288 (7)	165

Symmetry code(s): (i) -*x*+1, -*y*, -*z*; (ii) *x*, *y*, *z*-1; (iii) *x*, *y*, *z*+1; (iv) -*x*+1, -*y*, -*z*-1; (v) -*x*, -*y*+1, -*z*; (vi) -*x*+2, -*y*+1, -*z*+1; (vii) -*x*, -*y*, -*z*+1; (viii) -*x*+1, -*y*, -*z*+2; (ix) *x*-1, *y*, *z*; (x) -*x*+1/2, *y*-1/2, -*z*+1/2; (xi) *x*+1, *y*, *z*.

Table 5. Selected Trezimide and Tennimide intramolecular distances (Å)

	$(BrIO)_3$ (for A/B)[1]	**$(BrIO)_4$**	**$(26BrIO)_3$**[†]	**$(26BrIO)_3$**[‡]	**$(26BrIO)_4$**
H...H$_{(intraannular)}$	2.57, 2.53 2.80, 2.96 2.93, 2.97	3.02 3.19 4.13 4.35	2.53, 2.57 2.93, 2.93 2.99, 3.08	2.48 2.93 3.02	2.97, 4.06 3.05, 4.20 3.06 3.10
N...N$_{(tertiary)}$	5.168(6), 5.186(6) 5.342(5), 5.193(6) 5.434(6), 5.425(6)	5.198(4) 5.358(4) 5.685(7) 5.935(6)	5.098(7), 5.159(7) 5.172(7), 5.262(8) 5.462(7), 5.323(7)	5.117(6) 5.179(6) 5.432(5)	5.190(6) 5.211(6) 5.220(6) 5.297(6) 5.816(7) 5.832(6)
N...N$_{(pyr/pyrim)}$	5.824(7), 5.287(7) 6.664(6), 8.102(7) 6.779(7), 9.094(7)	Disordered group	3.832(8), 4.088(11)[2] 5.384(8), 5.343(9)[2]	3.899(7)[2] 5.364(8)[2]	4.467(7) 4.563(7)
O...O$_{(isophthaloyl)}$	6.648(6), 6.723(5) 6.743(6), 6.816(6) 6.995(5), 6.963(6)	6.869(4) 7.050(4)	6.807(6), 6.787(7) 6.819(7), 6.871(6) 7.039(7), 7.046(7)	6.773(6) 6.818(5) 7.038(6)	6.727(6) 6.856(6) 6.876(6) 6.927(7)
O...O$_{(imide)}$	3.459(6), 3.653(6) 3.784(6), 3.708(6) 3.934(7), 3.847(5)	3.524(5) 3.652(5)	3.416(7), 3.405(6) 3.771(7), 3.658(8) 3.785(7), 3.790(7)	3.399(5) 3.731(7) 3.804(6)	3.396(8) 3.586(7) 3.687(6) 3.829(7)
Br...Br	4.4321(13), 4.0315(11) 10.664(5), 12.765(3) 11.555(5), 14.165(3)	11.0808(9) 11.1123(8) 11.3021(8) 11.8026(15)	3.9751(14), 4.1161(16) 11.1582(14), 11.1087(13) 12.2451(14), 12.3450(14)	4.0198(13) 10.9816(12) 12.0190(12)	10.7484(12) 11.0821(11) 11.3855(14) 11.5428(14) 11.8029(13) 12.2607(12)

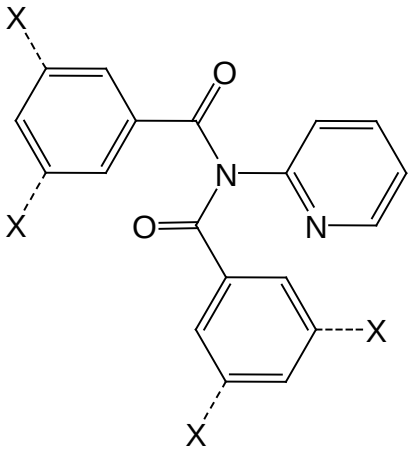
The **O...O** (isophthaloyl) and **O...O** (imide) distances refer to the isophthaloyl **O=C...C=O** and imide **O=C...C=O** torsion angles (refered to as the '**CO...CO**' twist) are listed above.

1 The major component of the Br2A/C and Br2B/D atom disorder is used in the analysis.
2 *cis*–related pyrimidyl N atoms only.

Full details have been deposited on the Cambridge Structural Database.

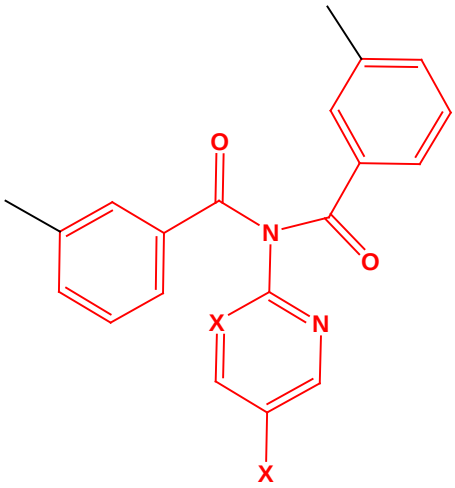
Section 5.6: Schematic diagram of related **Fxod** and **Mxod** (2:1) imides

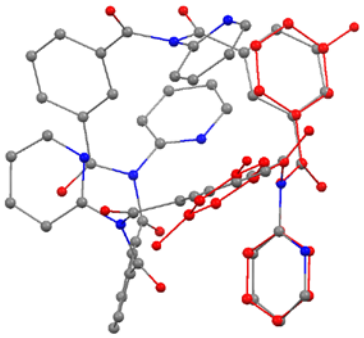
Fmod and **Mmod** structures (X = **F** or **M**)



X can adopt either position (due to rotation about the O=CCC torsion angle) in the 2:1 imides but this will be 'locked' in the **trezimide** and **tennimide** macrocycles.

Fmod - Reference **2h**) J. F. Gallagher, K. Donnelly, A. J. Lough, *Acta Crystallogr., Sect. E:* Struct. Rep. Online, 2009, **65**, o102-o103.
Food - Reference **2i**) J. F. Gallagher, K. Donnelly, A. J. Lough, *Acta Crystallogr., Sect. E:* Struct. Rep. Online, 2009, **65**, o486-o487.





Bottom left: (2:1) imide component constituting 3/8 of a tennimide core and
Bottom right: **Fmod** superimposed on a tennimide core (as Scheme 4, main paper)

Overlap of non-hydrogen atoms between 2:1 imide and tennimides.
The 2:1 imides[2h,i] constitute 3/8 of a tennimide core and conformationally (in crystal structures) display a reasonably close overlap with the tennimide core (in terms of the non-hydrogen atoms). The formation of tennimides can be rationalised in terms of a favourable conformations adopted by the reactive fragments in macrocycle ring closure.