

Entry point into new trimeric and tetrameric imide-based macrocyclic esters derived from isophthaloyl dichloride and methyl 6-aminonicotinate

(EsIO)₃ and (EsIO)₄ spectroscopic and crystallographic data

by

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Electronic Supplementary Information

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 Additional comment on the crystal structure data:	
The crystallographic details (from the CIF file) are included as (EsIO) ₄ [‡] first (CSD – 894030) and then (EsIO) ₃ [§] (CSD – 894031) as the refinement for (EsIO) ₄ proceeded without any problems (no molecular disorder or any partial occupancy solvent molecules in the crystal lattice), whereas the (EsIO) ₃ crystals diffracted very weakly and required considerable attention. Therefore, the program SQUEEZE in PLATON (Spek, 2009) was used as ≈ 21% of the (EsIO) ₃ unit cell contained diffuse electron density from partially occupancy solvent molecules of indeterminate composition.	
5. <u>Mass Spectrometry (ESI-MS)</u>	37

1. Detailed description of synthetic and separation procedures for (EsIO)₃ and (EsIO)₄

The reaction mixture was prepared by dissolving DMAP (6.7 mg, 0.053 mmol) and triethylamine (Et₃N) (2.682 ml, 20 mmol) in 60 ml of anhydrous CH₂Cl₂

Isophthaloyl dichloride (1.3289 g, 6.57 mmol) was dissolved with stirring in the reaction flask in a 250 ml round bottom flask, under an inert atmosphere of N₂ and subsequently cooled on an ice bath (ice/NaCl/NH₄Cl/EtOH) to -15°C. Methyl-6-aminopyridine-3-carboxylate (1 g, 6.57 mmol) was suspended in 20 ml of anhydrous CH₂Cl₂ and was quickly and quantitatively added to the cooled flask (containing the dissolved isophthaloyl dichloride). The reaction mixture was stirred overnight with the solution temperature rising slowly to ambient temperature overnight.

The reaction mixture was diluted with technical grade CH₂Cl₂ to 200 ml, filtered over a funnel with a sintered glass frit to remove a polymeric by-product and washed three times with an aqueous solution of NH₄Cl (pH ≈ 5) (3 × 200 ml), dried over MgSO₄ and filtered. The clear, filtered product mixture was left to stand overnight. The solvent volume was reduced on a rotary-evaporator to afford a pale yellow 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 CHCl₃/ethyl acetate (1:1) to obtain two cleanly separated products as (EsIO)₃ and (EsIO)₄ in modest yields as white crystalline solids. Melting points ranges are 215–218°C (EsIO)₃ and 201–205°C (EsIO)₄.

Yield (EsIO)₃ = 300 mg (16%), calculated M_r (EsIO)₃ = 846.75 g.mol⁻¹

Yield (EsIO)₄ = 157 mg (9%), calculated M_r (EsIO)₄ = 1129 g.mol⁻¹

(EsIO)₃ and (EsIO)₄ on TLC [CHCl₃/ethyl acetate (1:1)]:

TLC analysis (arrow direction denotes the solvent movement and with diagram rotated by 90°)

$$R_f(\text{EsIO})_4 = 0.33 \text{ and } R_f(\text{EsIO})_3 = 0.60$$



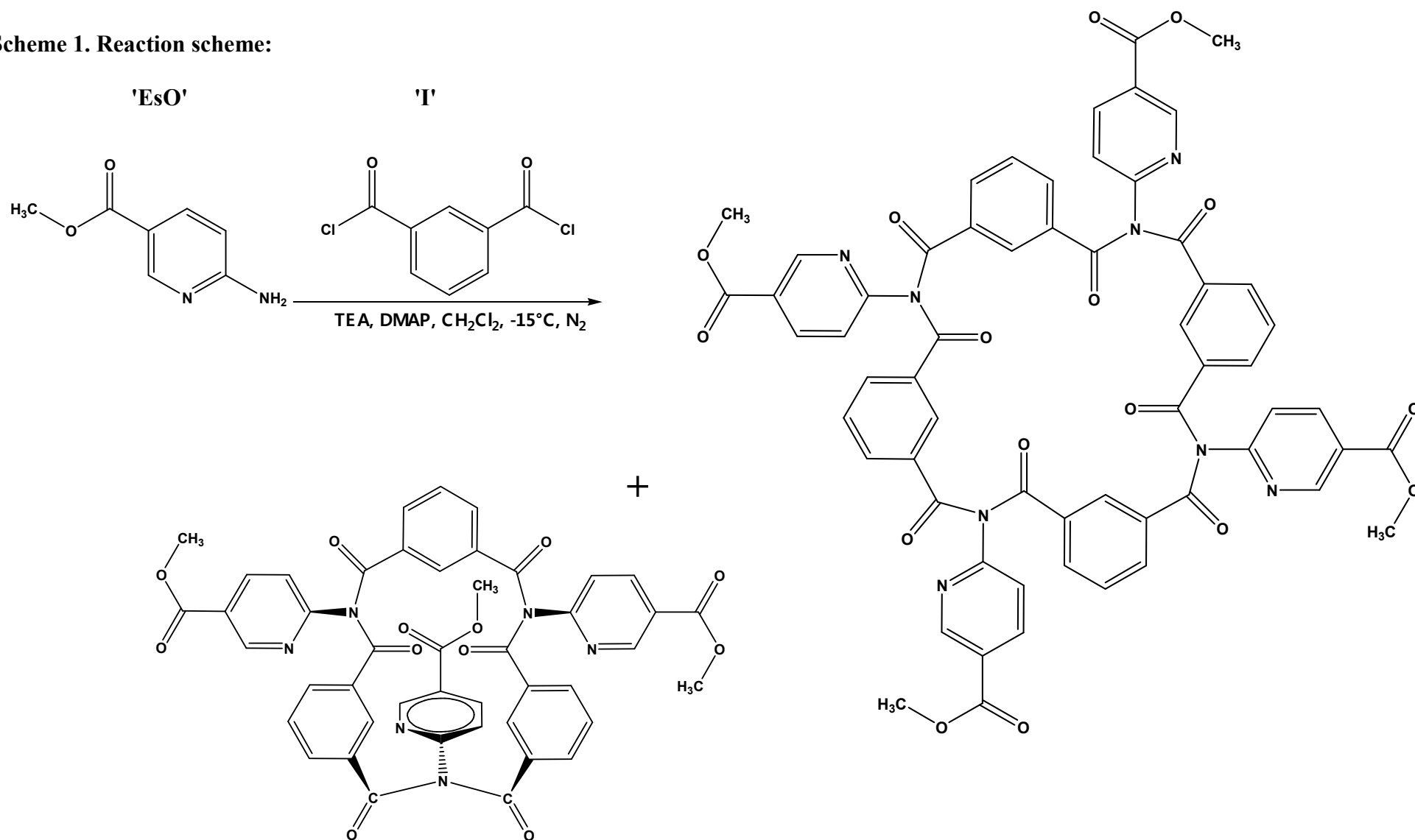
Note: Nomenclature of these macrocycles:

We have assigned general names to the two classes of compounds namely as **trezimides** for the trimers [*i.e.* (EsIO)₃] and **tennimides** for the tetramers [*i.e.* (EsIO)₄] so as to be distinct from triimides (see references) and tetraimides which have been used previously in different classes of 'locked' imide-based macrocycle derived from *e.g.* pyromellitic acid. The name derives from a combination of the **xO** and **I** starting materials (**x** = **Es**, ester functionality). In the spectral data section the compounds are often abbreviated to **EsIO3** and **EsIO4** for simplicity (in diagrams).

Mass spectrometry:

The mass spectral data (ESI) for both (EsIO)₃ (846.75) and (EsIO)₄ (1129) show the peaks due to their respective molecular ions and also fragmentation patterns yielding and consistent with their common molecular fragments based on the ester CO₂Me, isophthaloyl and 2-pyridinyl fragments.

Scheme 1. Reaction scheme:



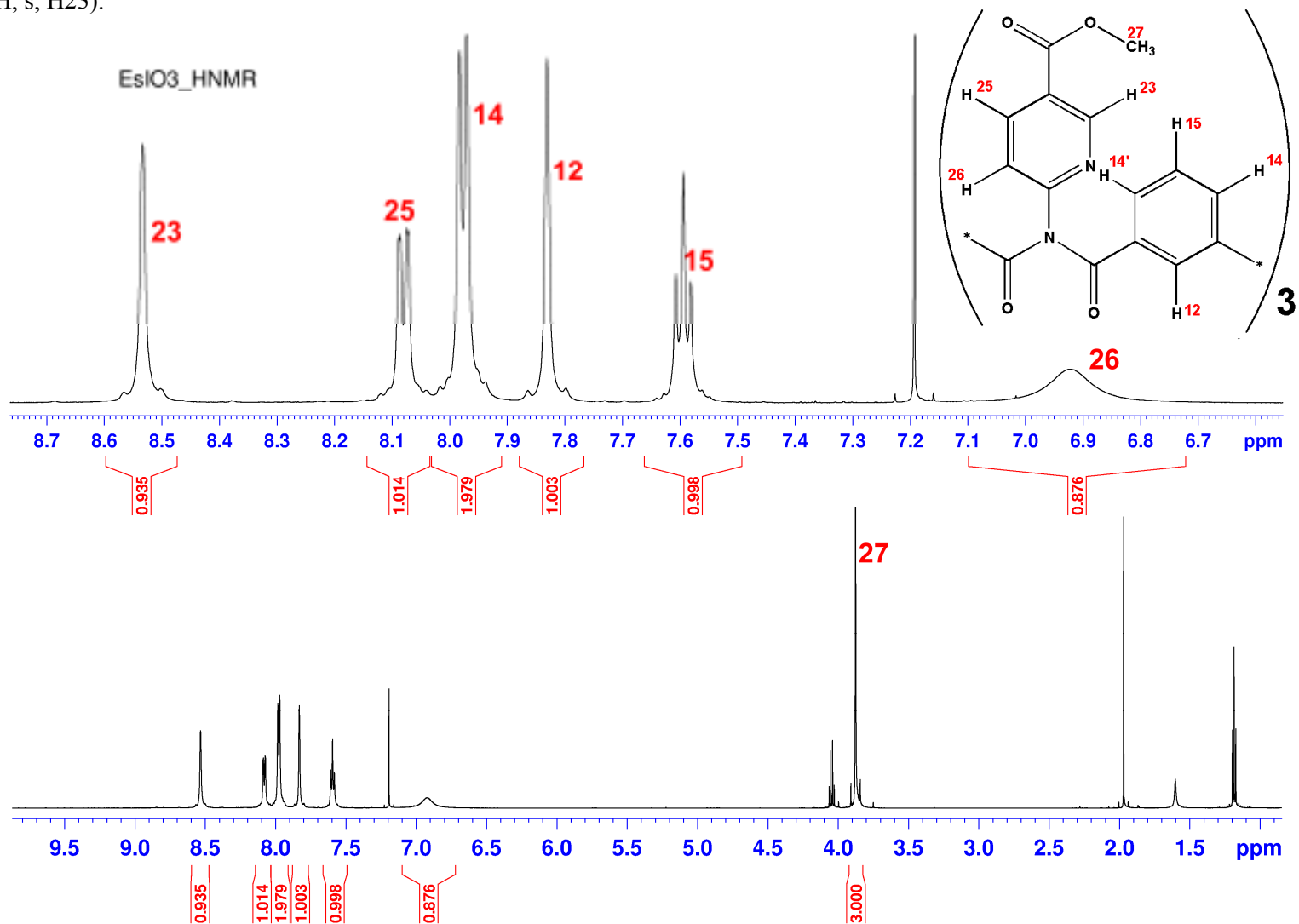
The (EsIO)₃ and (EsIO)₄ diagrams are depicted for clarity to show how the moieties are linked. Crystal structure diagrams are in Section 4

2. NMR data and spectra (600 MHz)

2.1. (EsIO)₃ (Room temperature, CDCl₃)

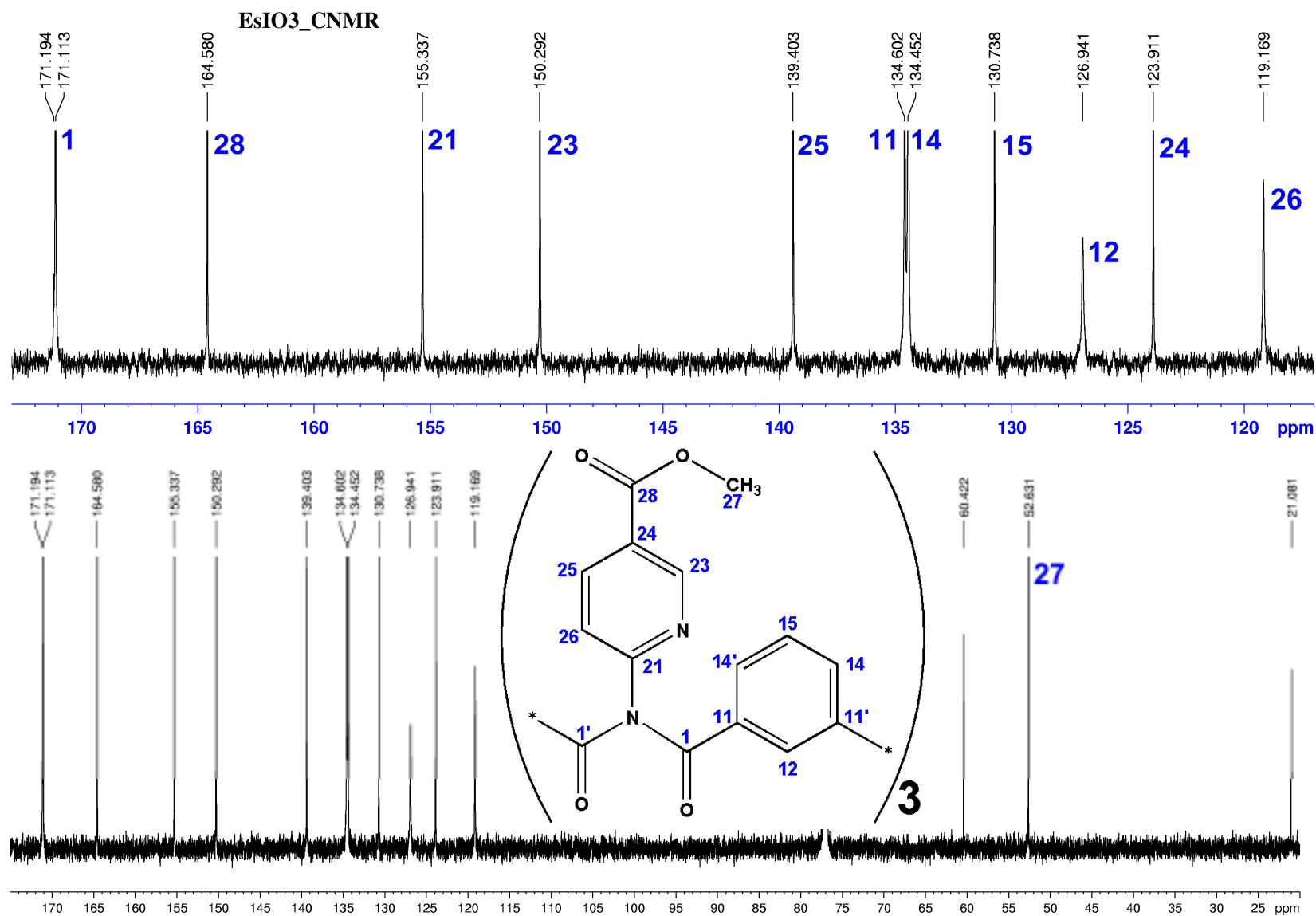
2.1.1. ¹H-NMR

δ 3.87 (3H, s, H27), 6.92 (1H, s, H26), 7.59 (1H, t, ³J = 7.8, H15), 7.83 (1H, s, H12), 7.98 (2H, d, ³J = 4, H14), 8.08 (1H, dd, ³J = 4.2, ⁴J = 1.6, H25), 8.53 (1H, s, H23).

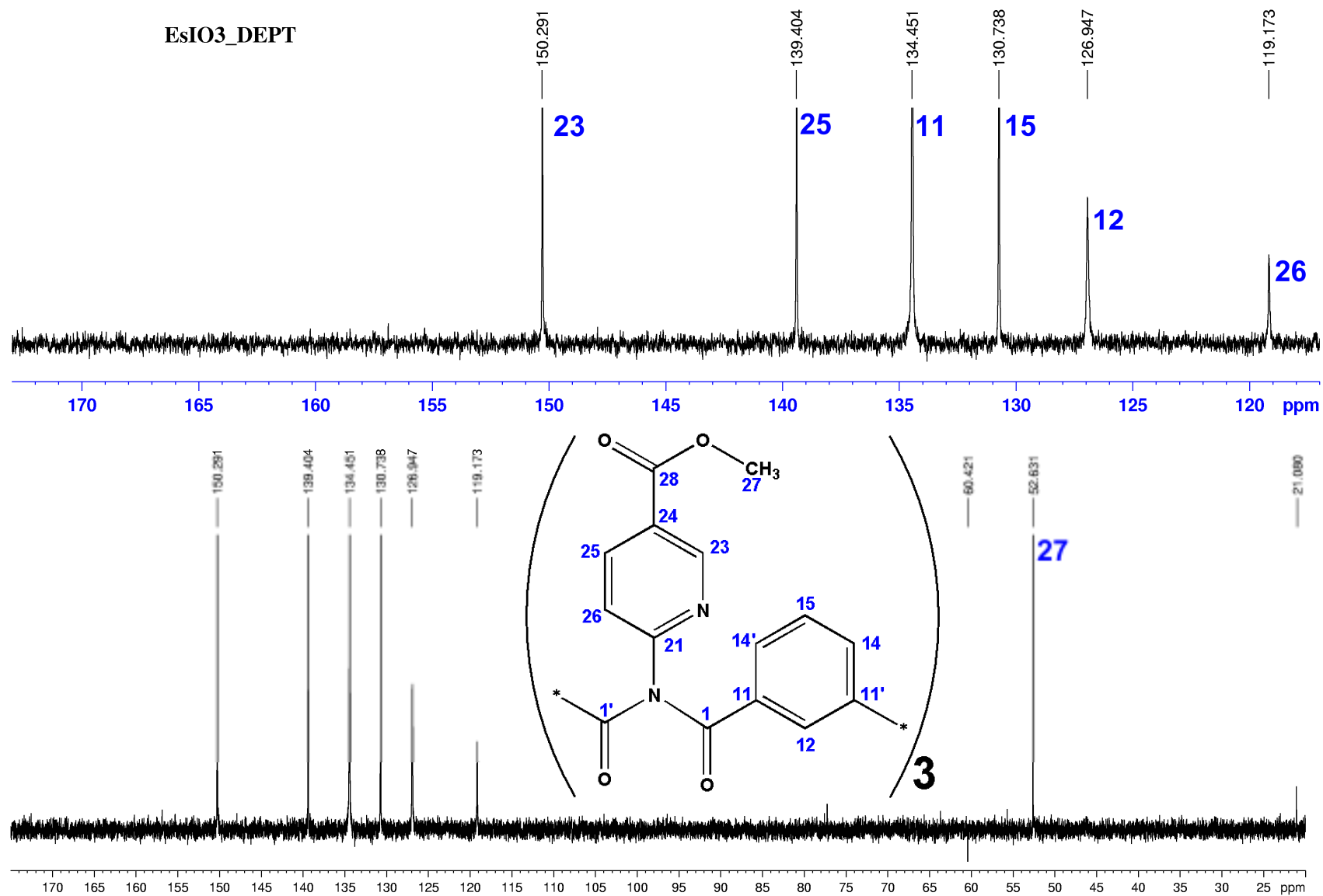


2.1.2. ^{13}C -NMR

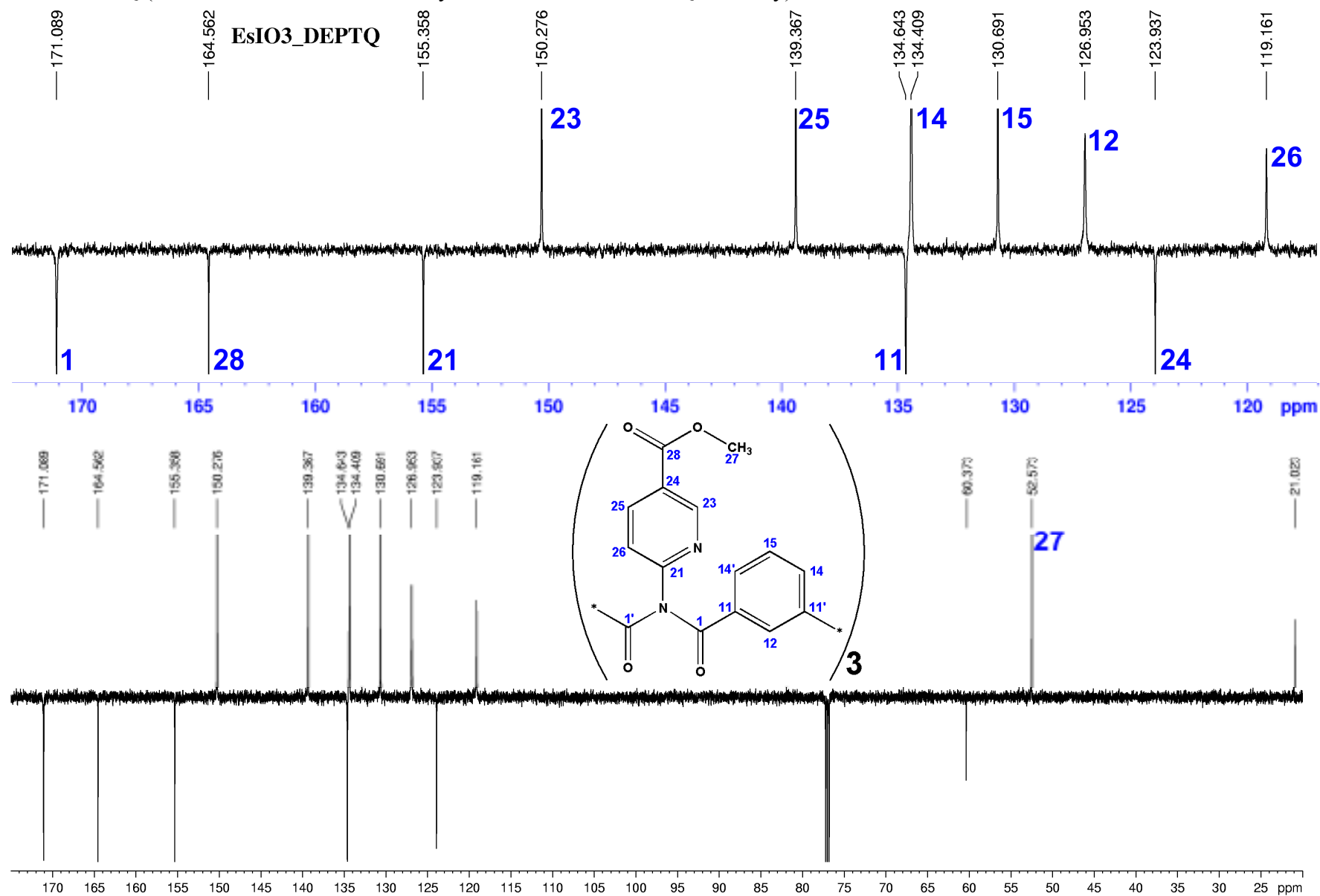
δ 52.63, 119.17, 123.91, 126.94, 130.74, 134.45, 134.60, 139.40, 150.30, 155.34, 164.58, 171.15



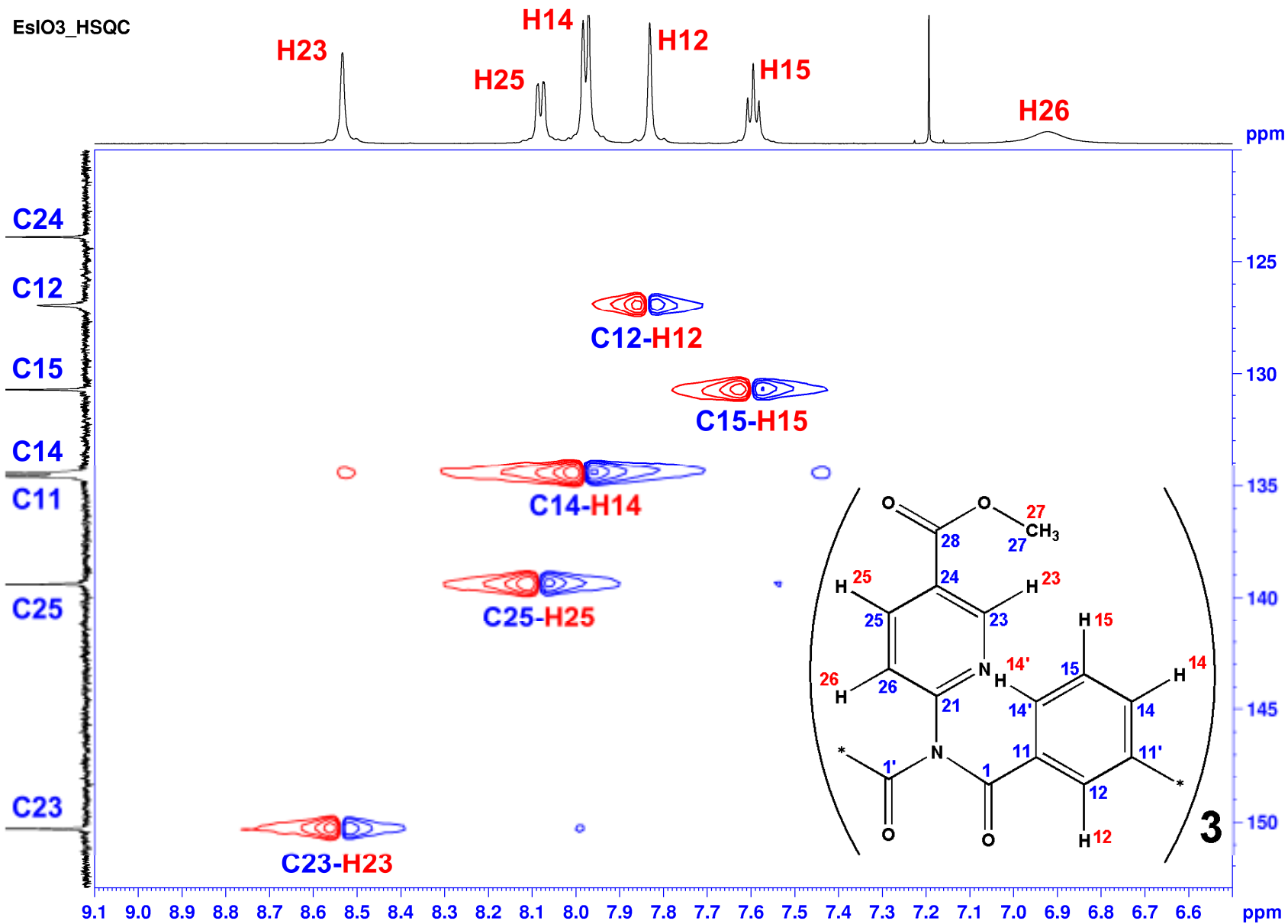
2.1.3. DEPT (Distortionless Enhancement by Polarization Transfer)

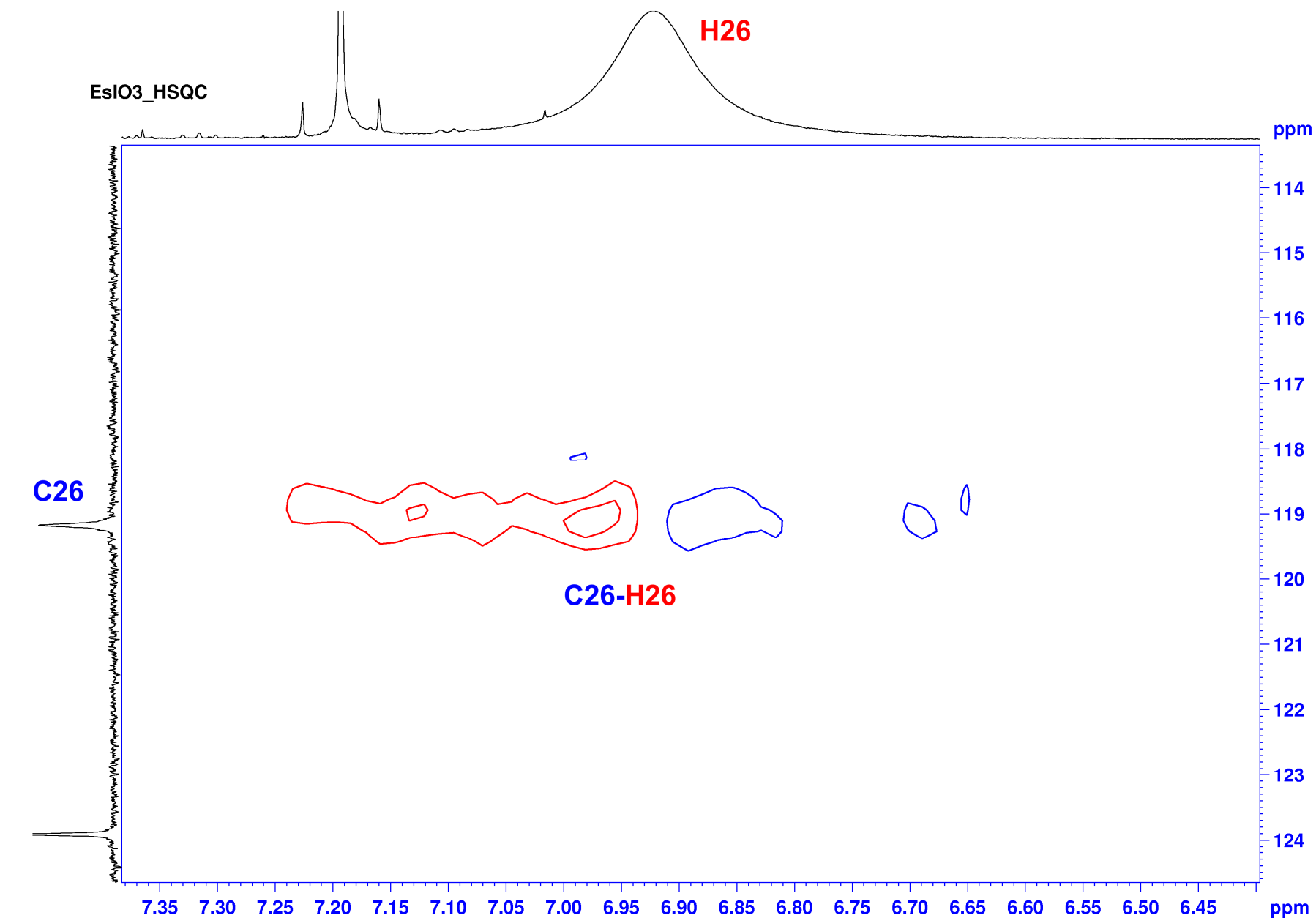


2.1.4. DEPT-Q (Distortionless Enhancement by Polarization Transfer - Quaternary)

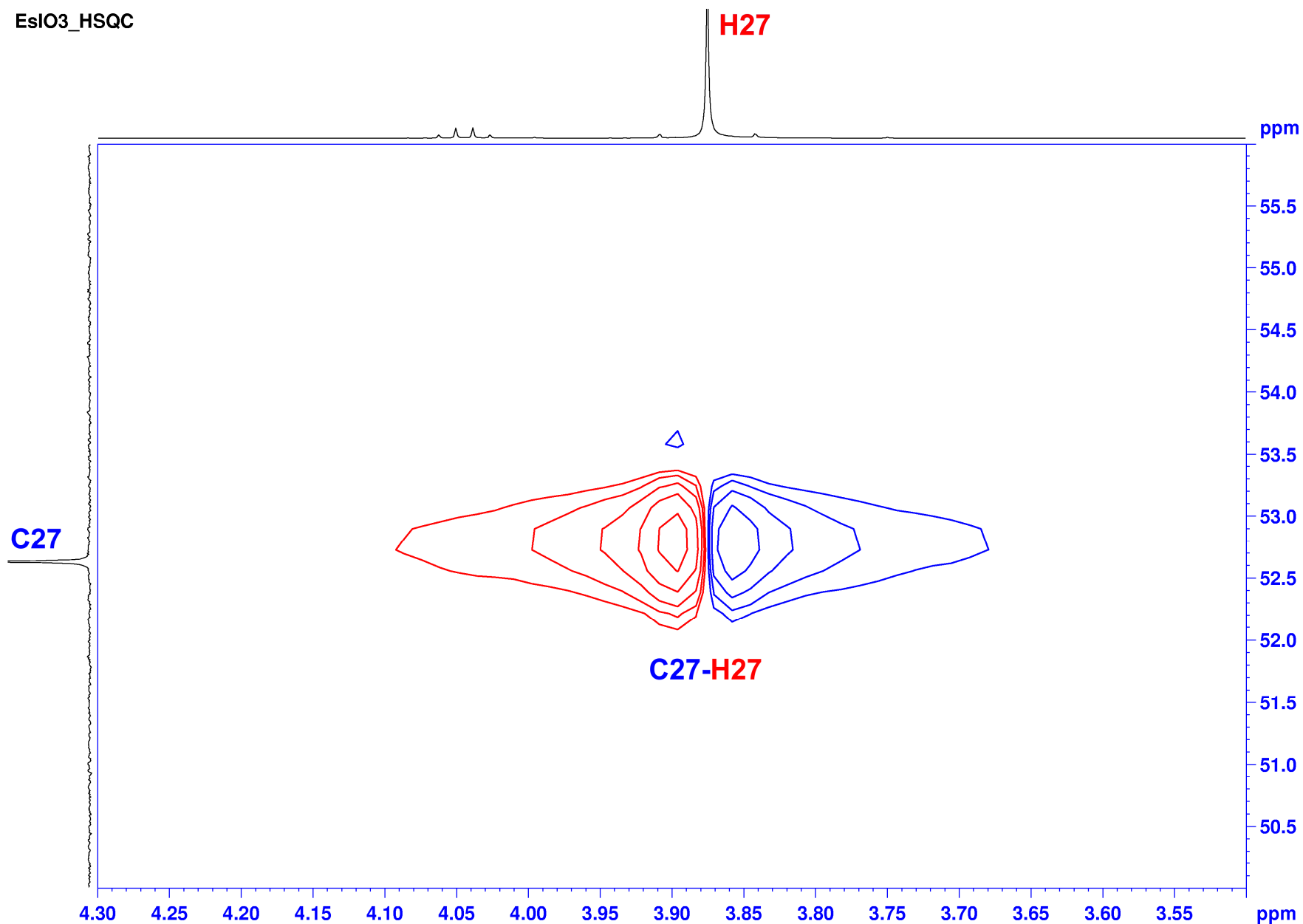


2.1.5. HSQC (Heteronuclear Single-Quantum Correlation)



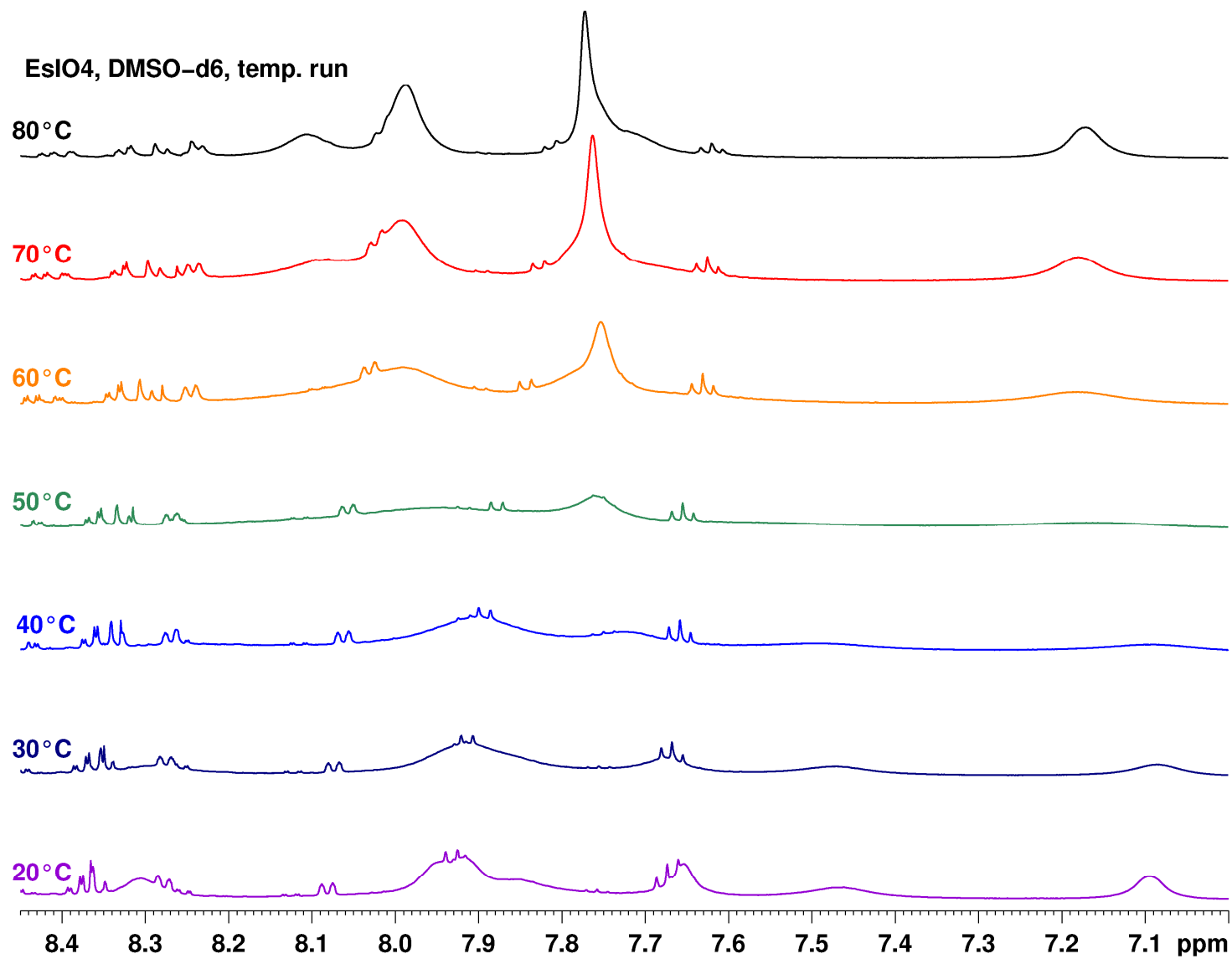


EslO3_HSQC



2.2 (EsIO)₄ (DMSO-*d*₆)

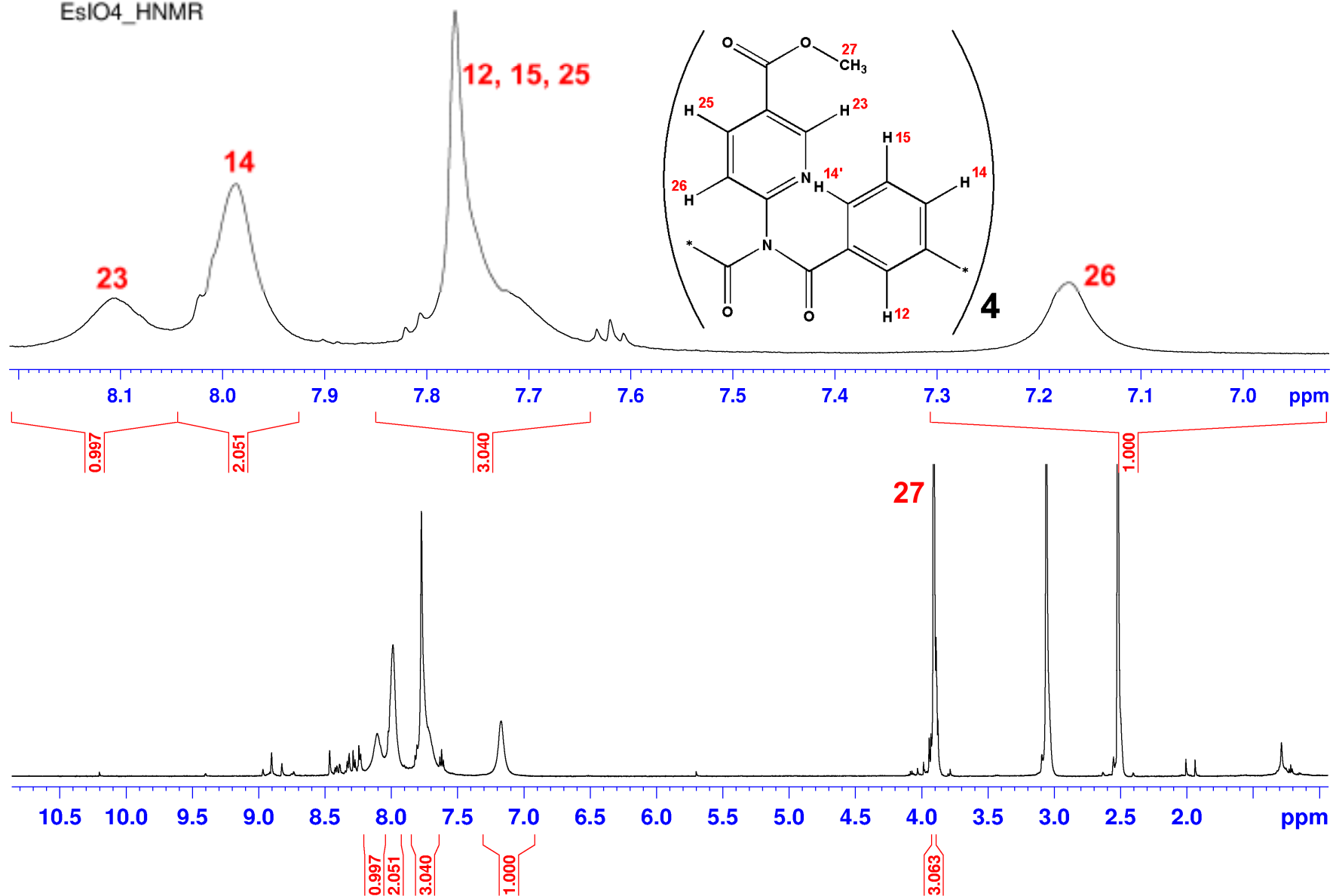
2.2.1. ¹H-NMR, variable temperature study



2.2.2 ^1H -NMR, 80°C, DMSO- d_6

δ 3.91 (3H, H27), 7.17 (1H, H26) 7.77 (3H, H12, H15, H25), 7.99 (2H, H14), 8.11 (1H, H23)

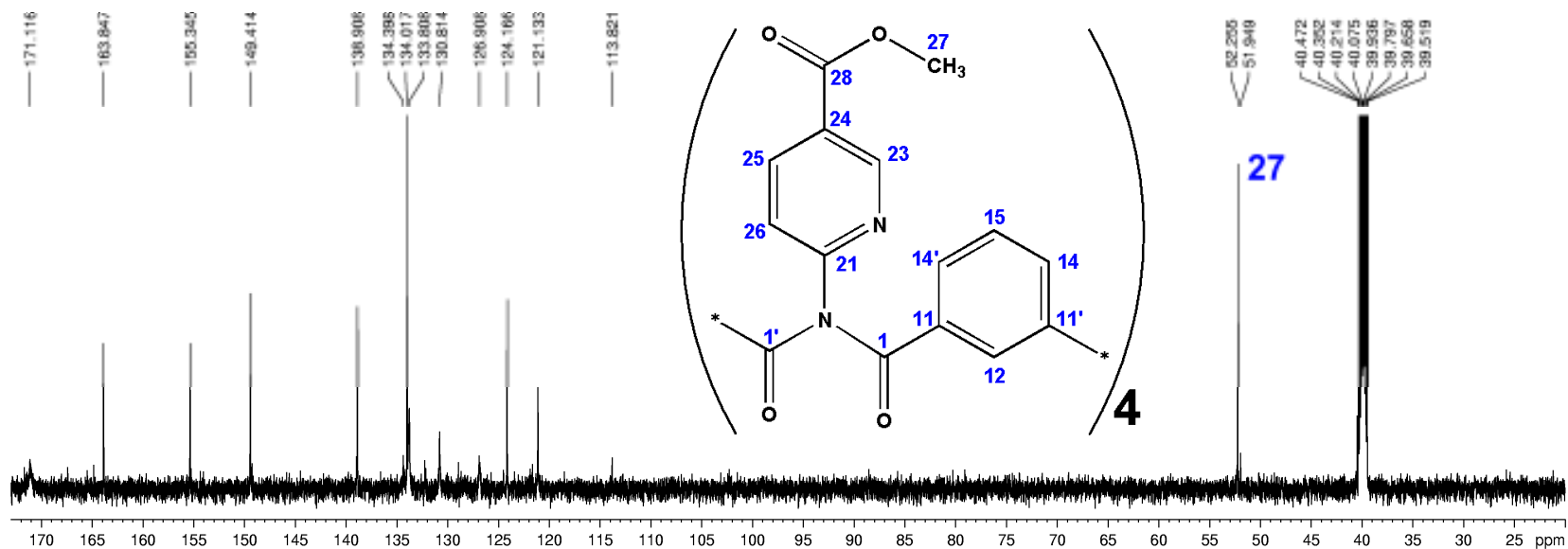
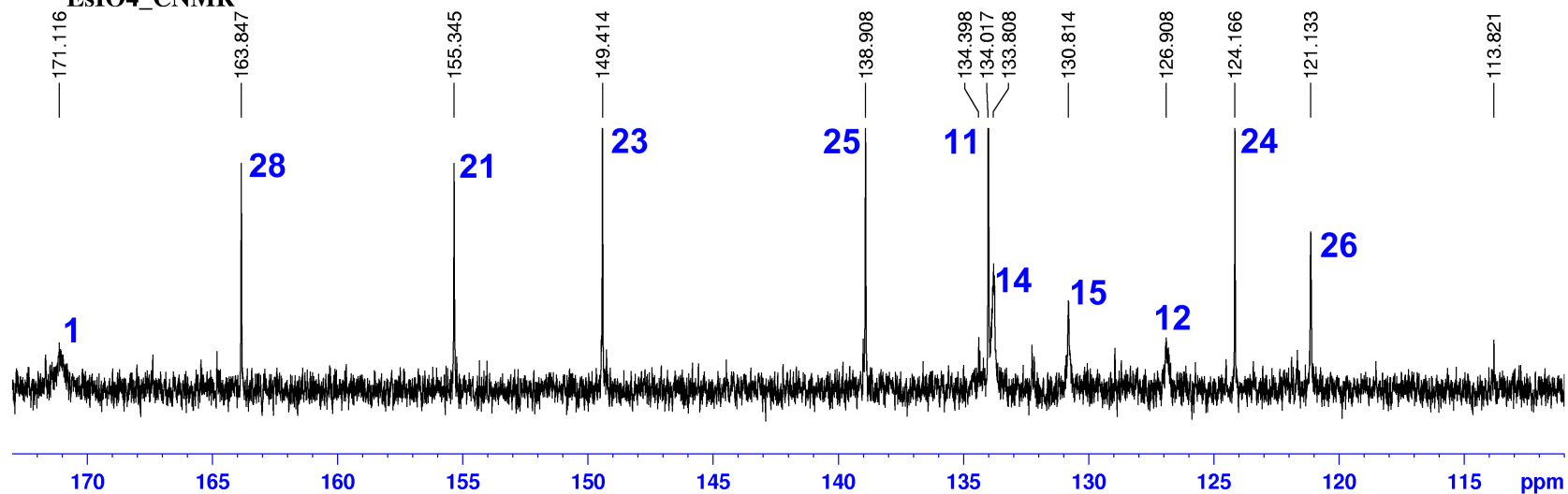
EsIO4_HNMR



2.2.3. ^{13}C -NMR, 80°C, DMSO- d_6

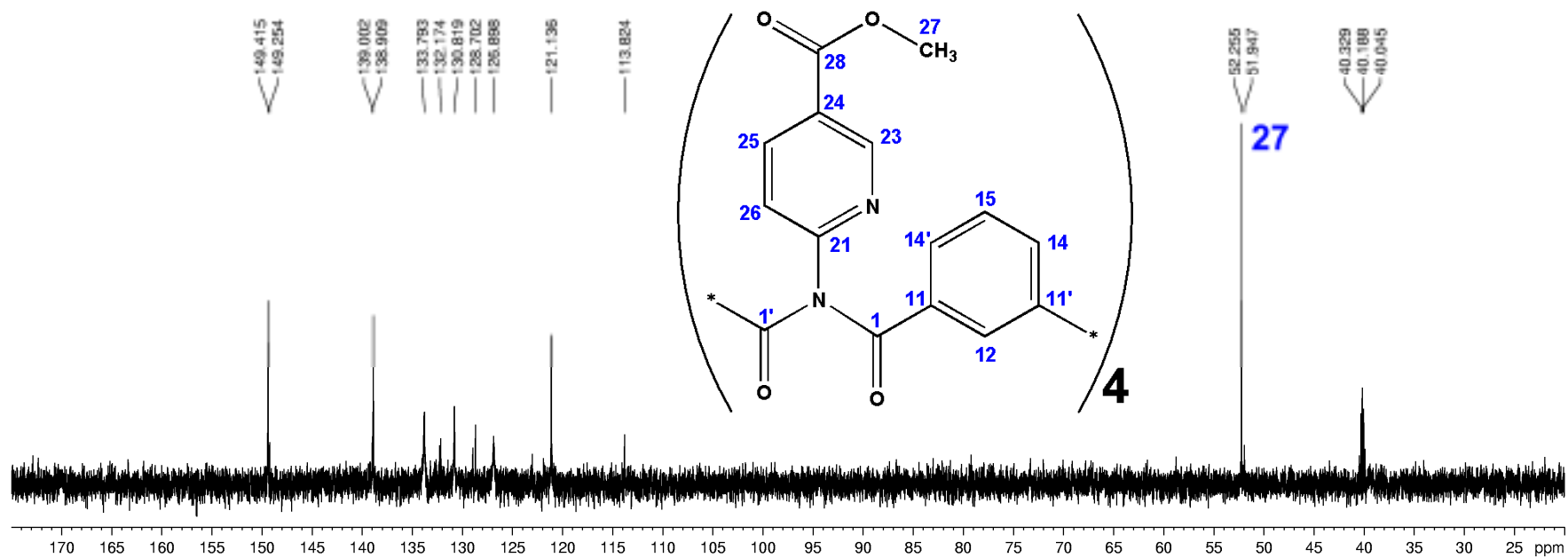
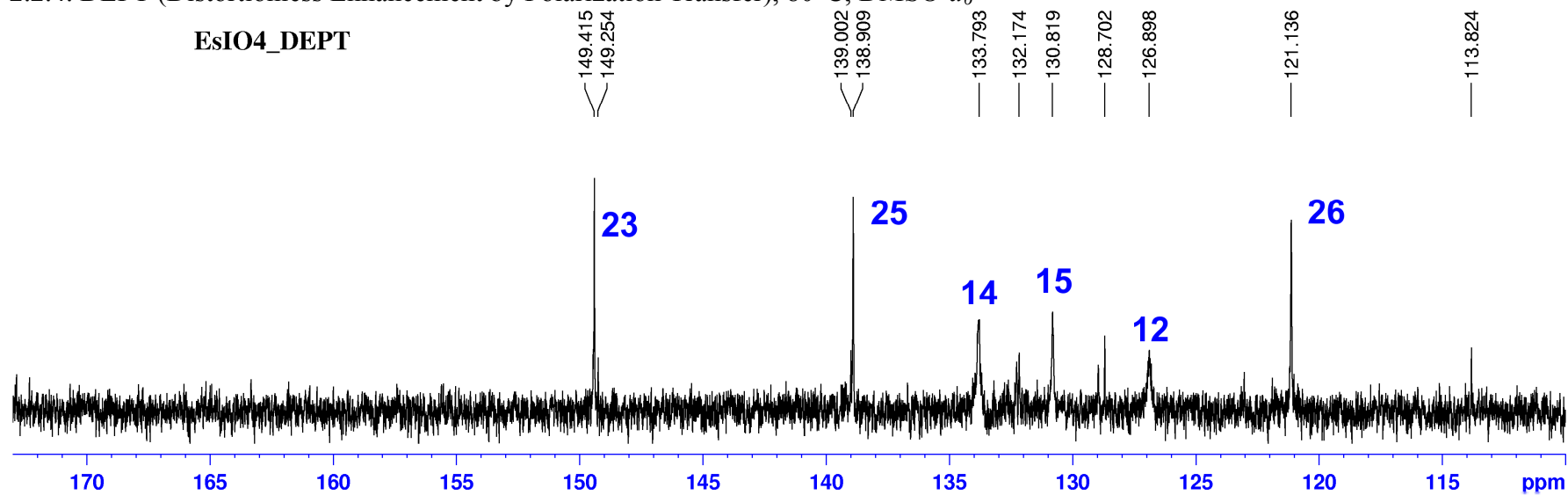
δ 52.55, 121.13, 124.16, 126.91, 130.81, 133.81, 134.02, 138.91, 149.41, 155.34, 163.85, 171.12.

EsIO4_CNMR



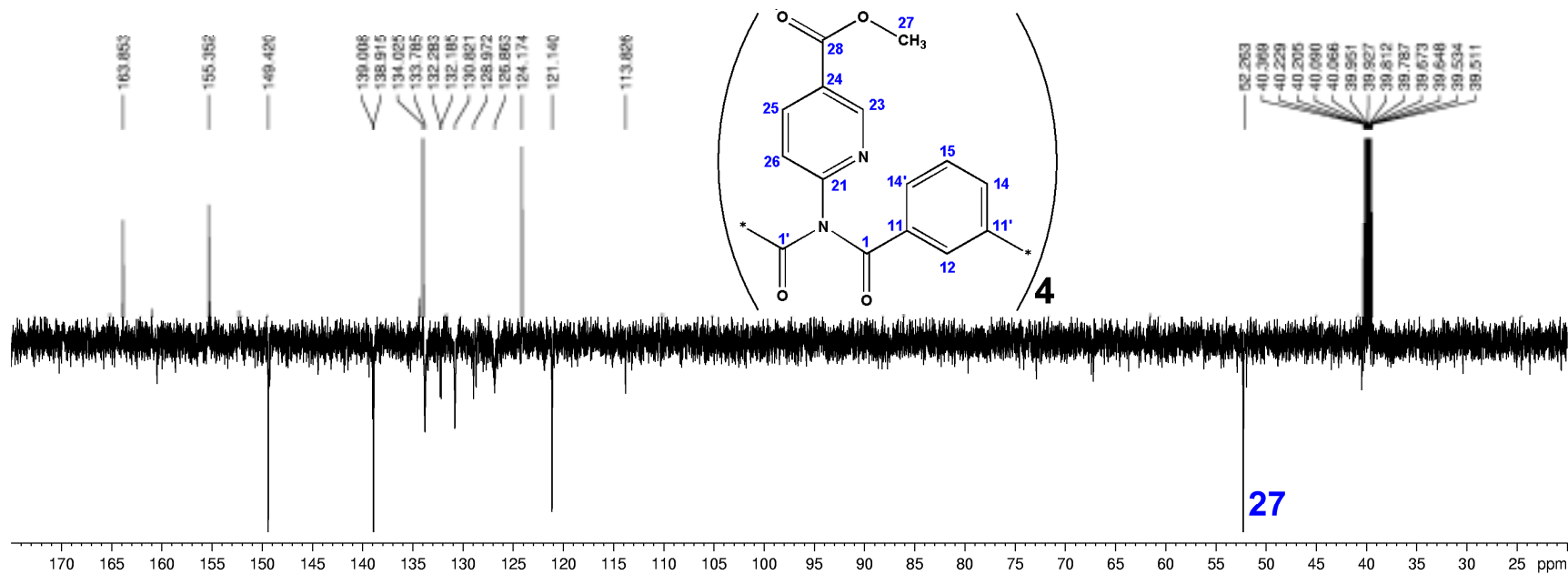
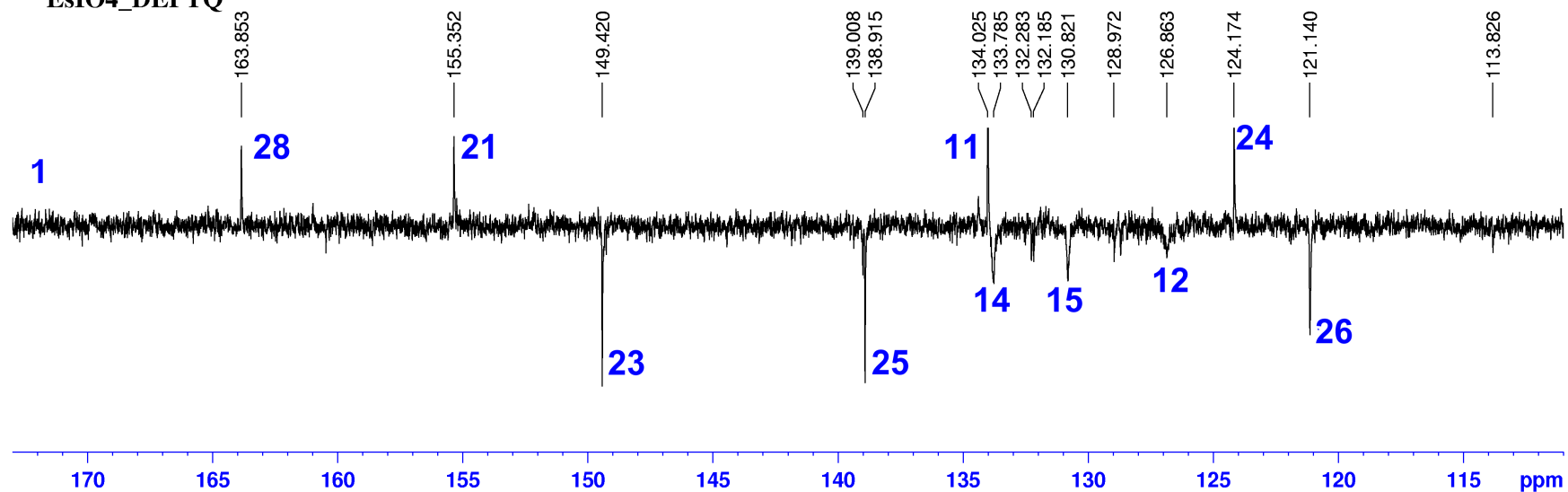
2.2.4. DEPT (Distortionless Enhancement by Polarization Transfer), 80°C, DMSO-*d*₆

EsIO4_DEPT



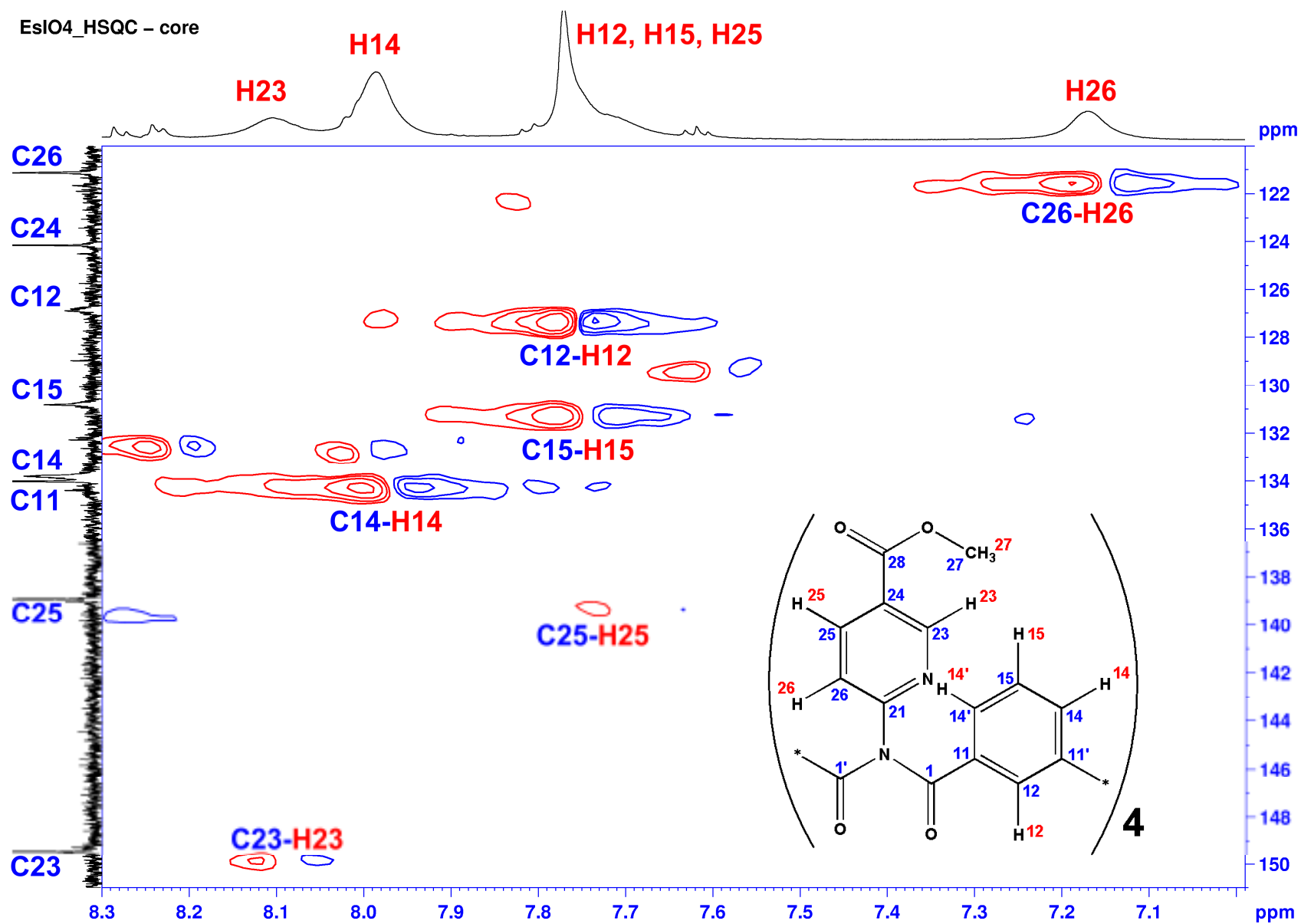
2.2.5. DEPT-Q (Distortionless Enhancement by Polarization Transfer - Quaternary), 80°C, DMSO-*d*₆

EsIO4_DEPTQ

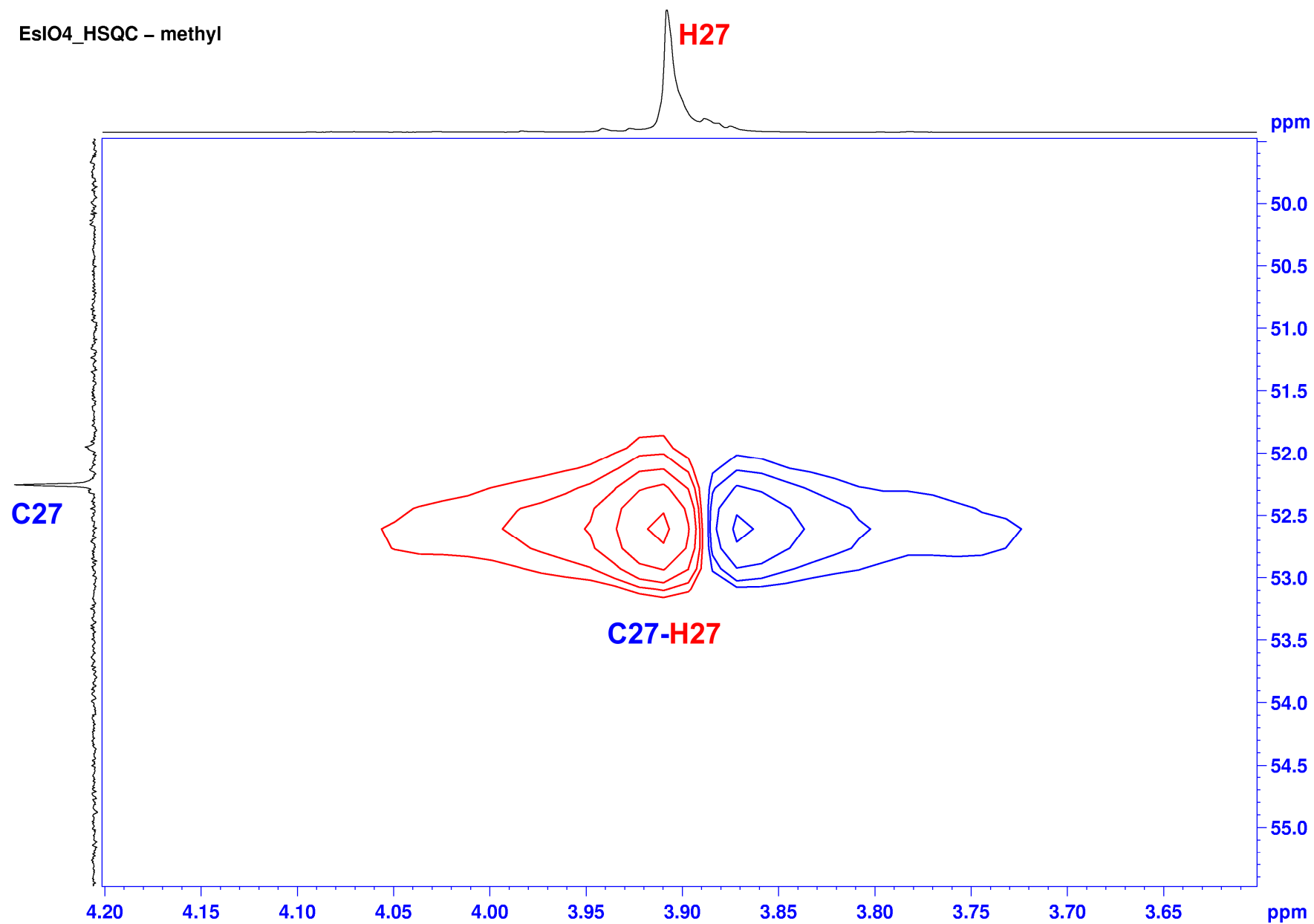


2.2.6. HSQC (Heteronuclear Single-Quantum Correlation), 80°C, DMSO-*d*₆

EsIO4_HSQC – core



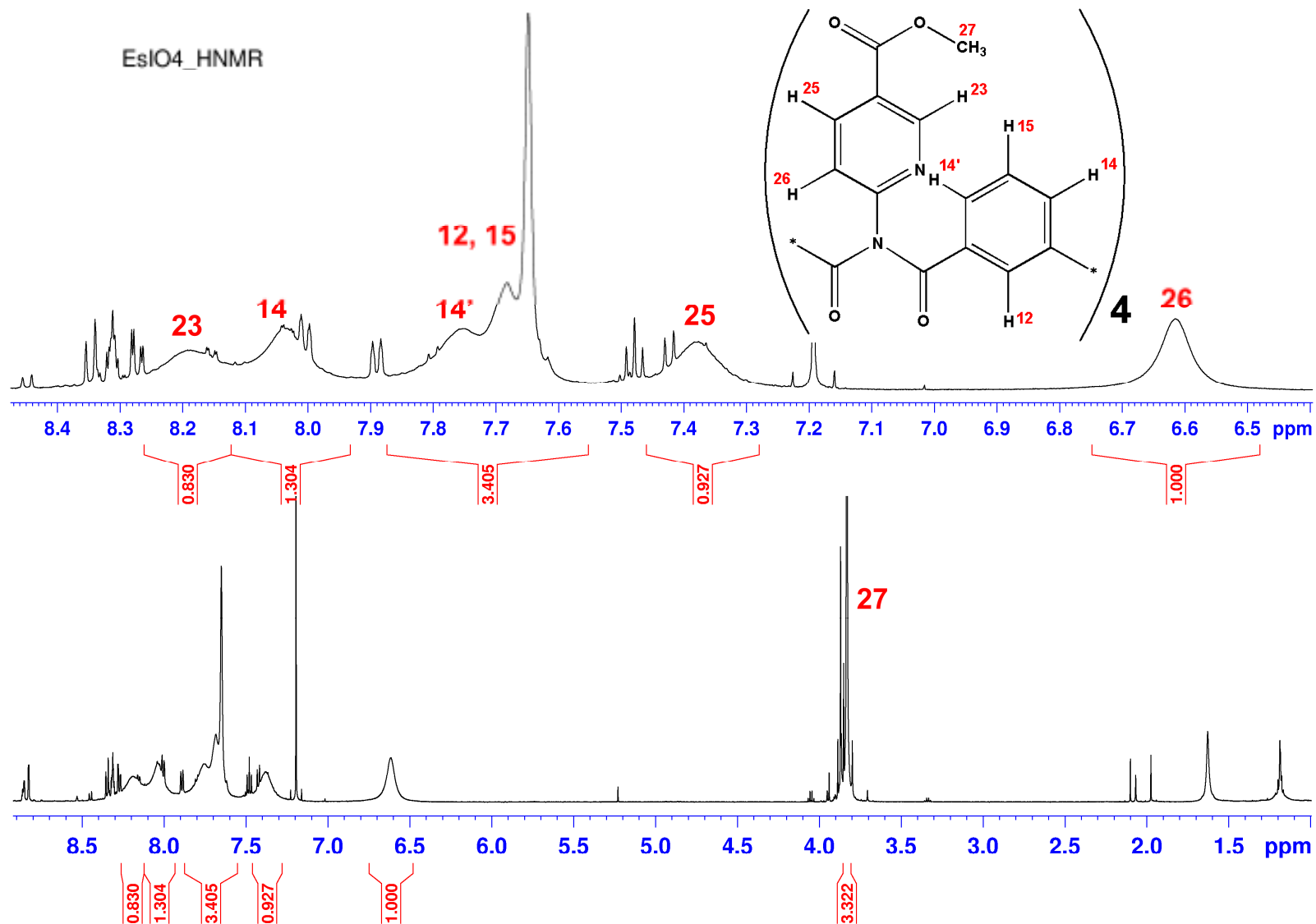
EsIO4_HSQC – methyl



2.3 (EsIO)₄ (Room temperature, CDCl₃)

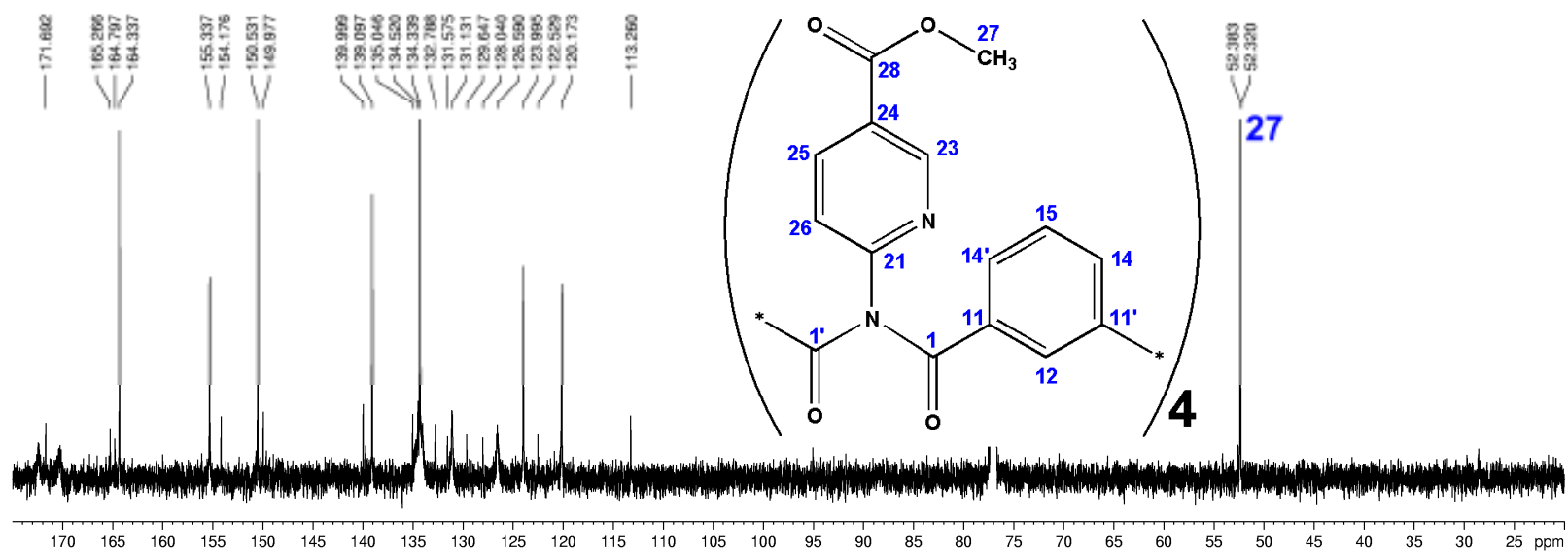
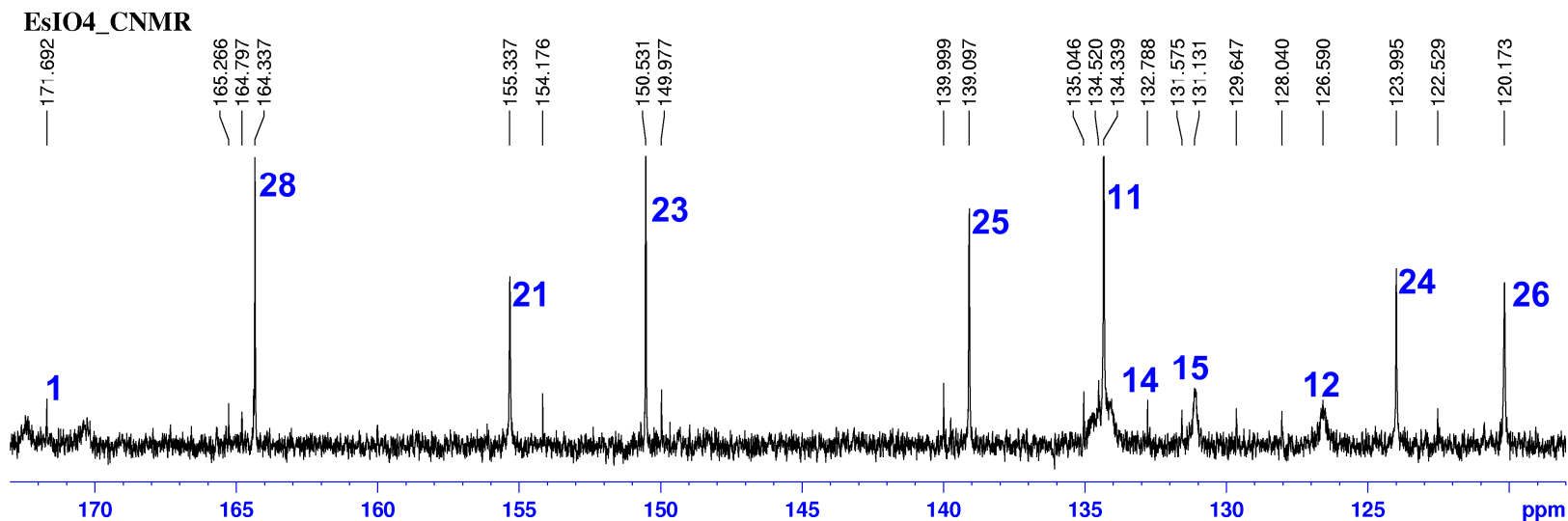
2.3.1. ¹H-NMR

δ 3.83 (3H, H27), 6.62 (1H, H26), 7.38 (1H, H25), 7.65 (1H, H12), 7.68 (1H, H15), 7.75 (1H, H14'), 8.03 (1H, H14), 8.19 (1H, H23)



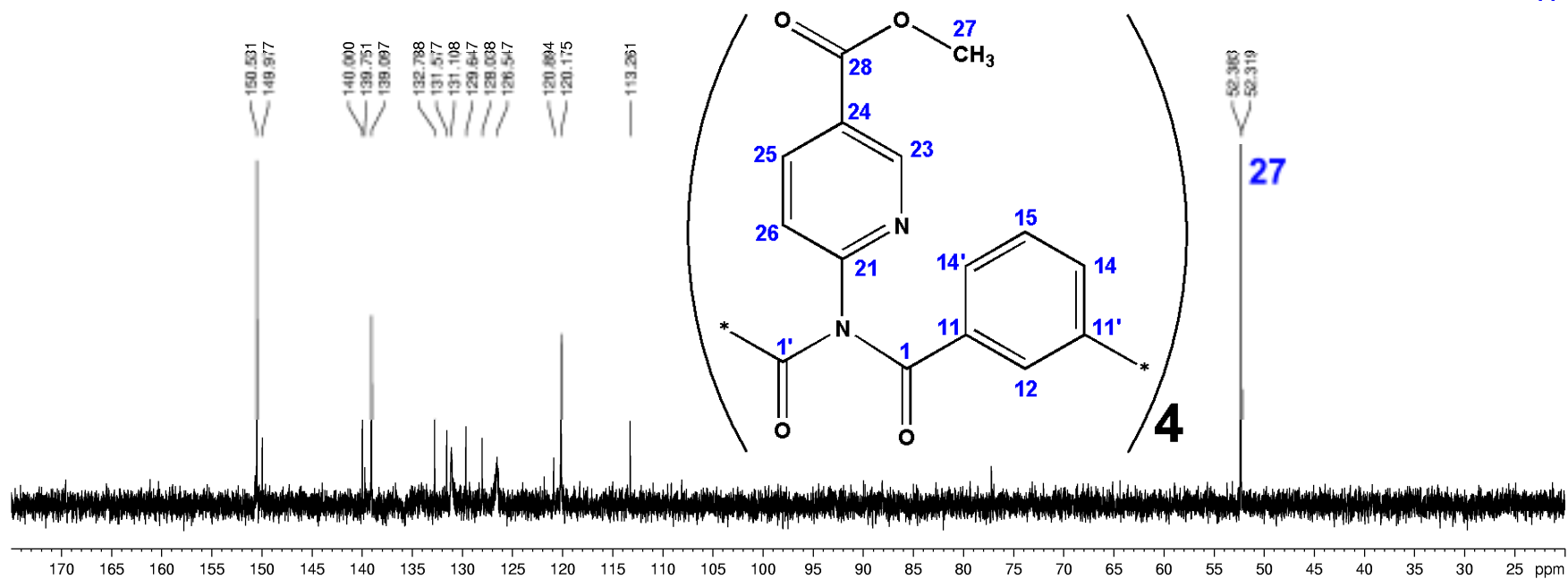
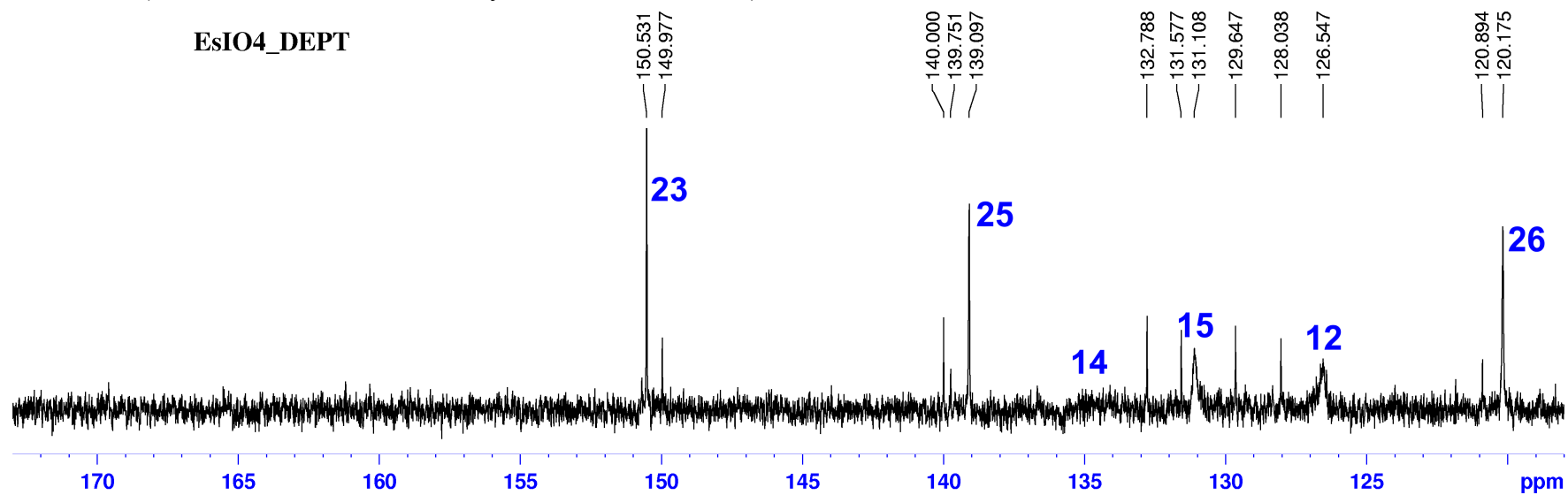
2.3.2. ^{13}C -NMR

δ 52.32, 120.17, 123.99, 126.59, 131.13, 133.13, 134.34, 139.10, 150.53, 155.34, 164.34, 170.28.

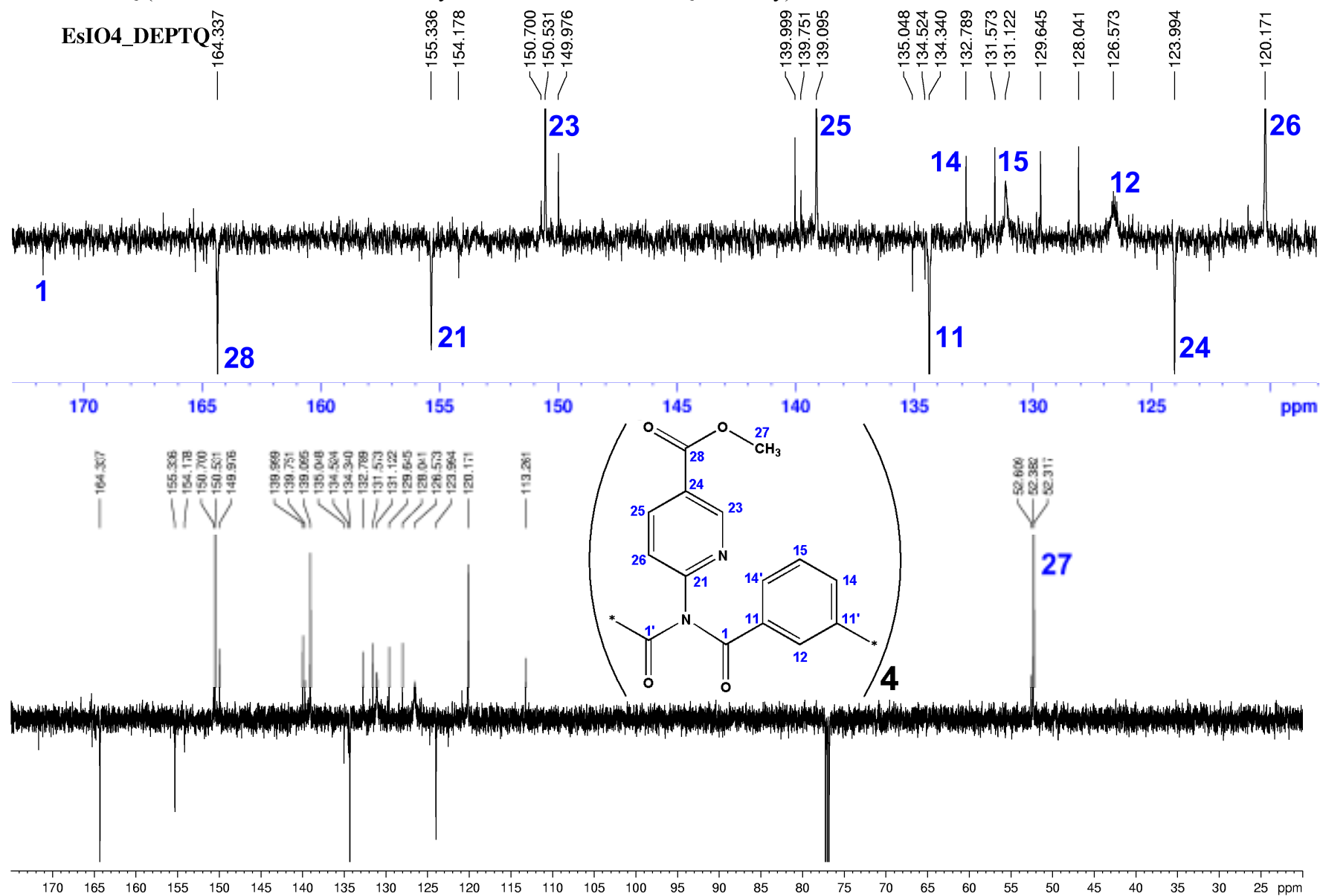


2.3.3. DEPT (Distortionless Enhancement by Polarization Transfer)

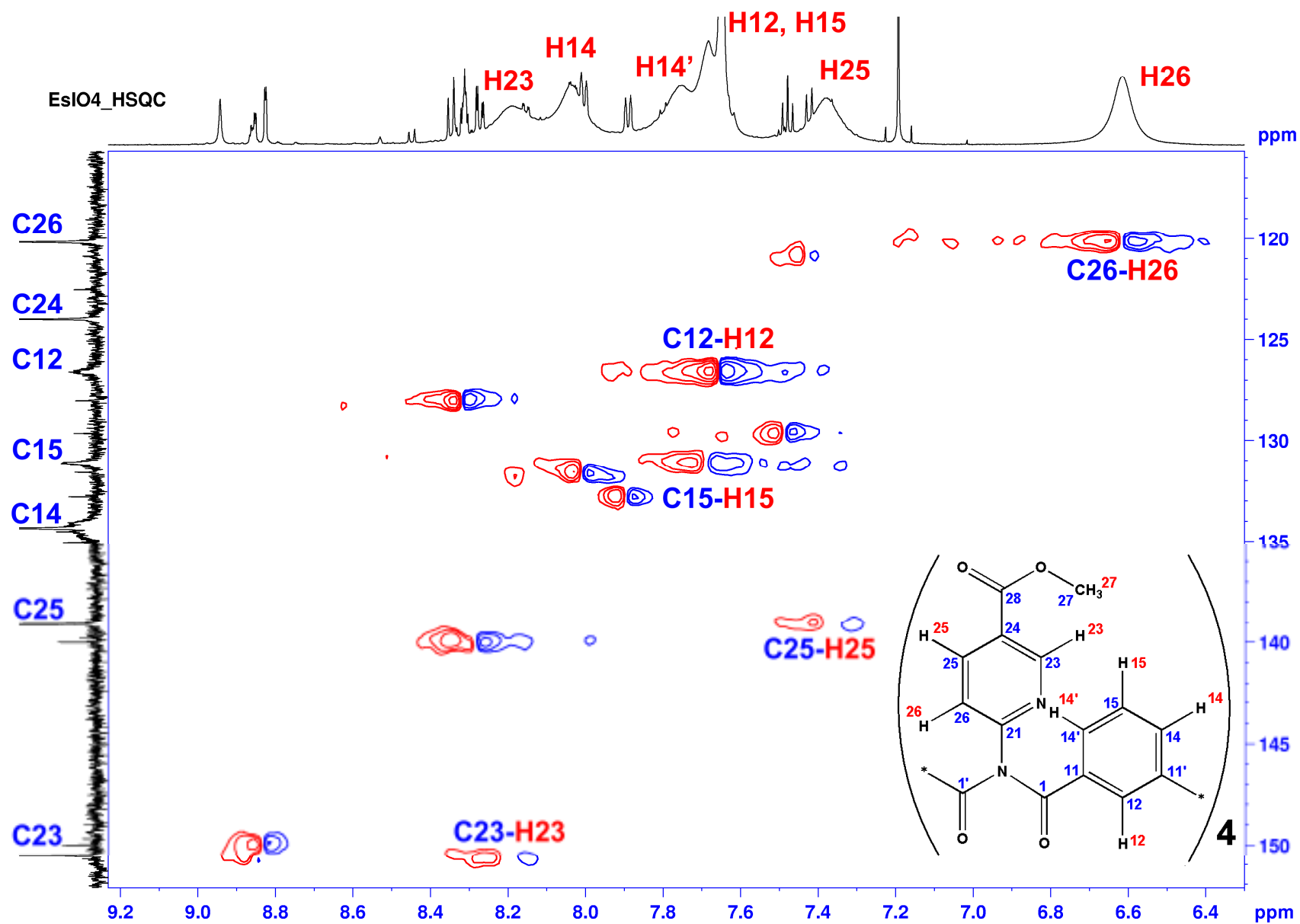
EsIO4_DEPT

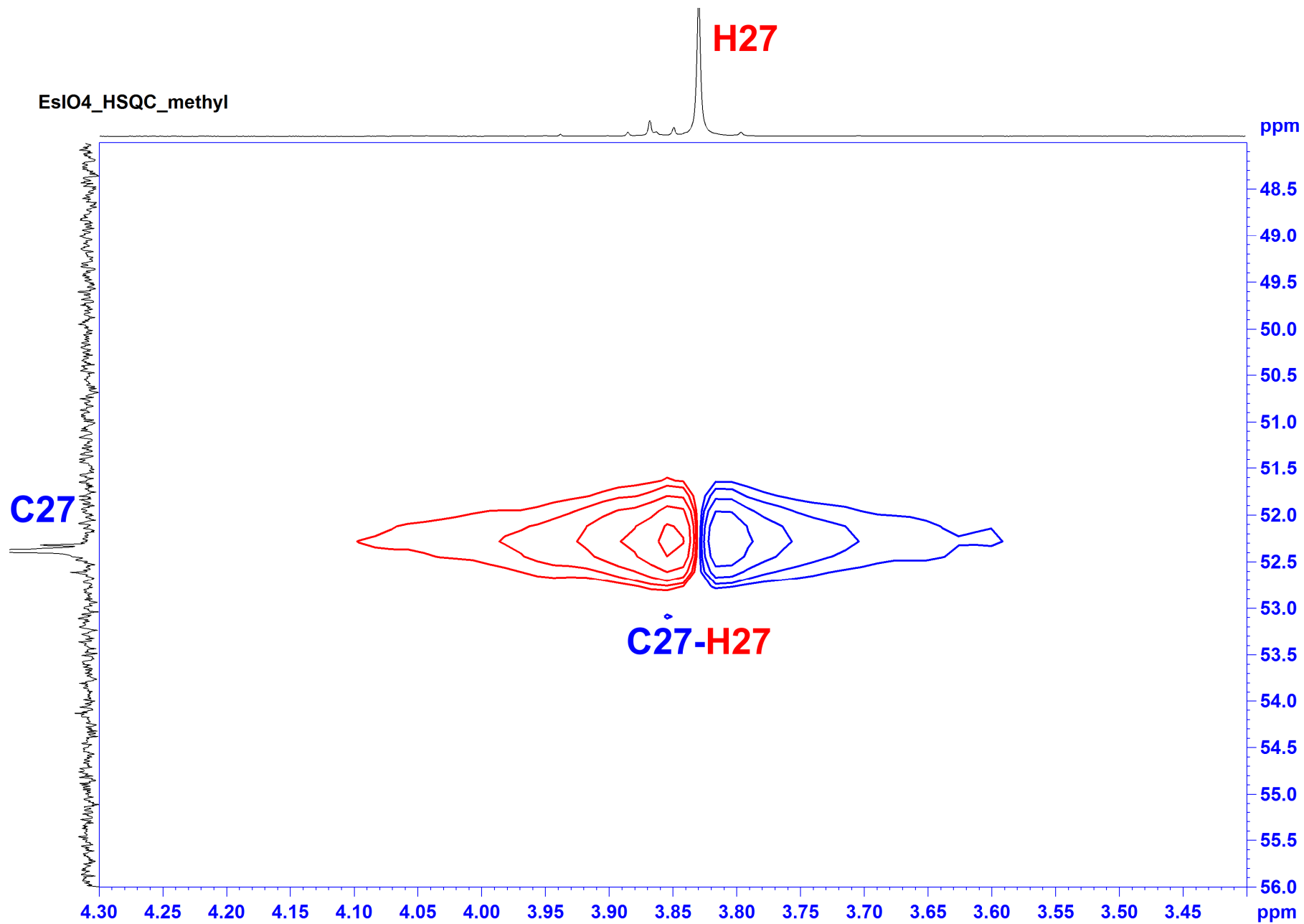


2.3.4. DEPT-Q (Distortionless Enhancement by Polarization Transfer - Quaternary)



2.3.5. HSQC (Heteronuclear Single-Quantum Correlation)

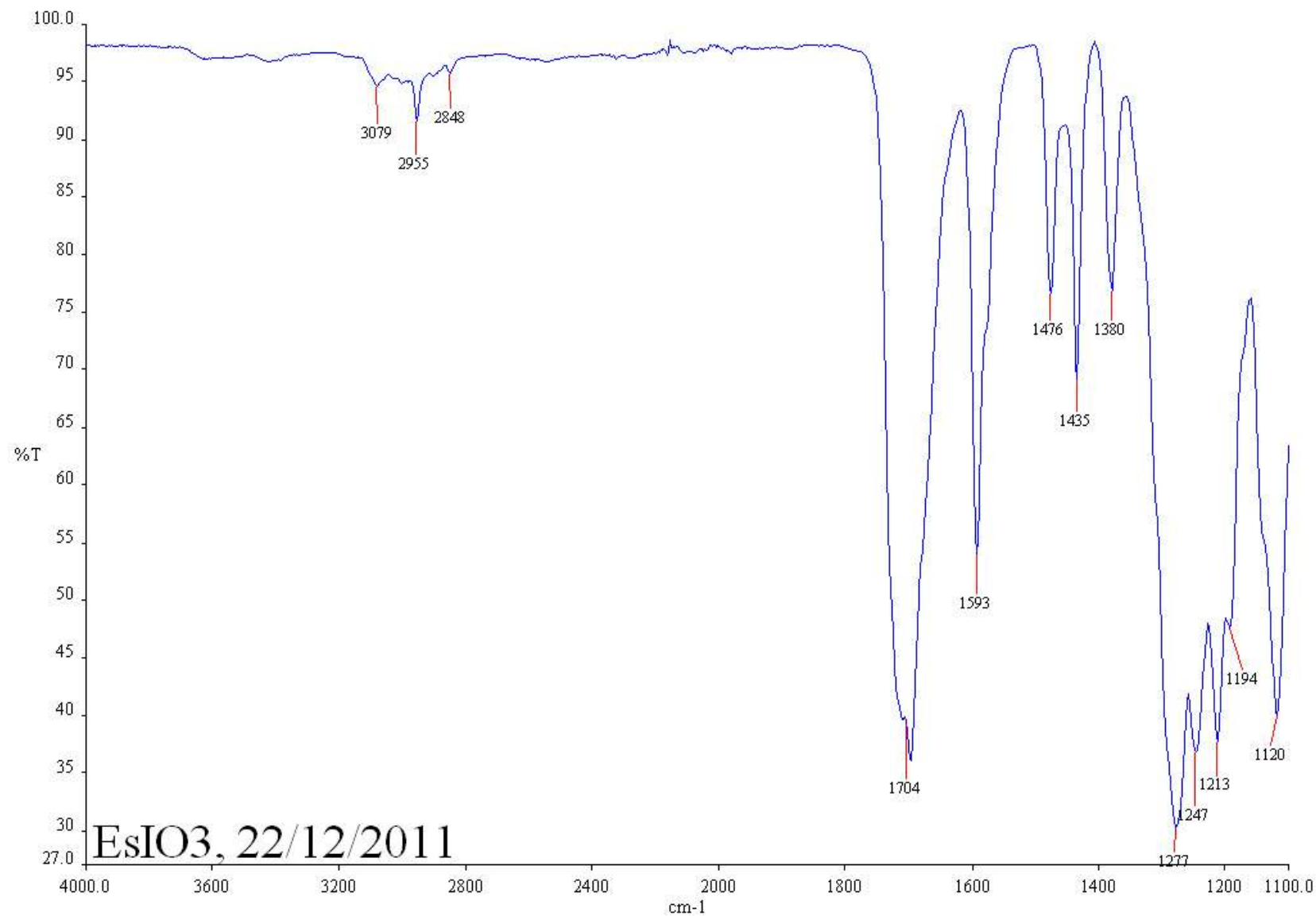




3. IR data and spectra (ATR)

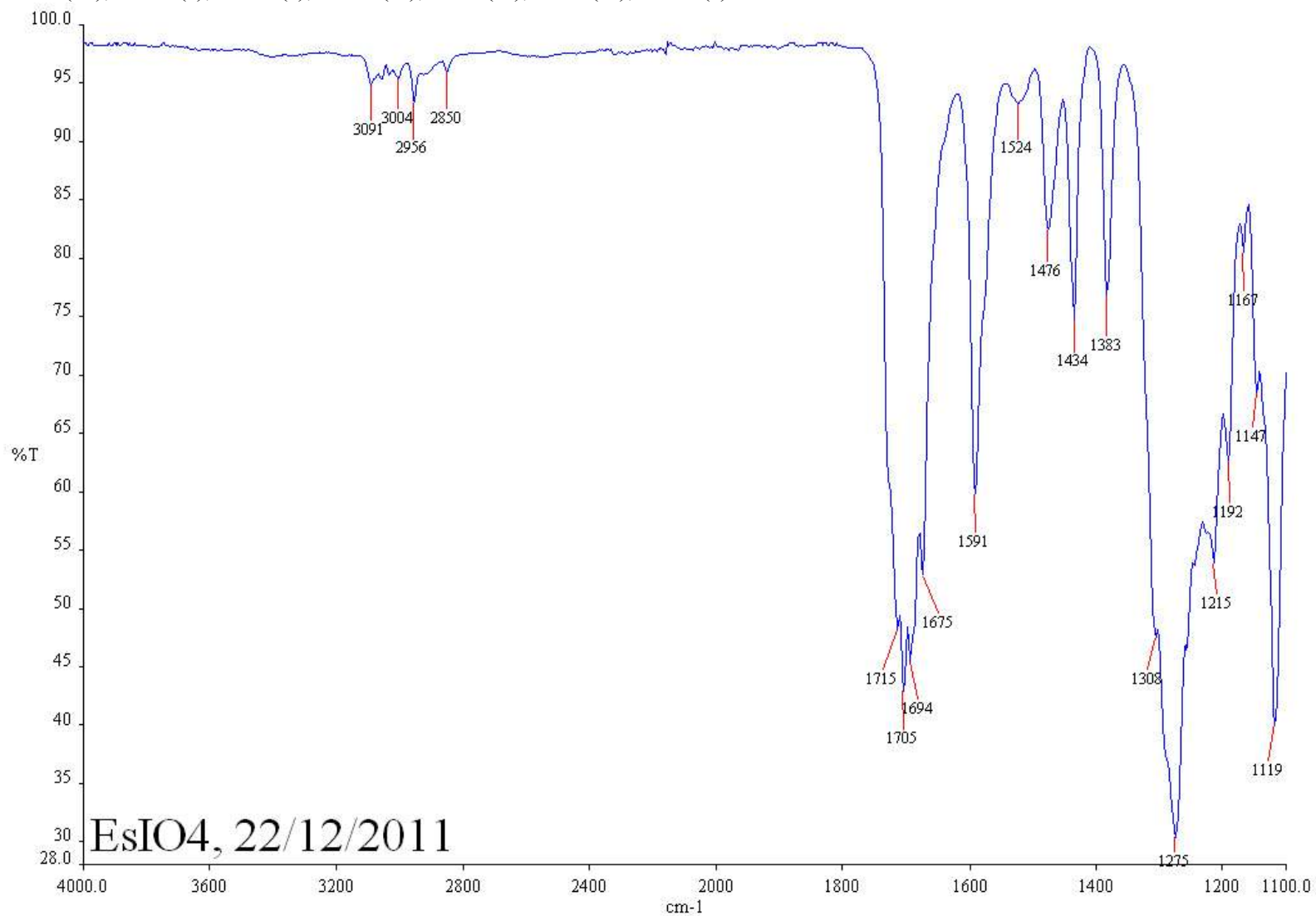
3.1. (EsIO)₃

ATR-FTIR: 3079 (w), 2955 (w), 2848 (w), 1704 (vs), 1593(s), 1476 (m), 1435 (m), 1380 (m), 1277 (s), 1247 (s), 1213 (s), 1194 (s), 1120 (s).



3.2. (EsIO)₄

ATR-FTIR: 3091 (w), 3004 (w), 2956 (w), 2850 (w), 1715 (s), 1705 (s), 1694 (s), 1675 (s), 1591 (s), 1524 (w), 1476(m), 1434(m), 1383(m), 1308 (sh), 1275 (s), 1215 (s), 1192 (m), 1167(m), 1147(m), 1119 (s).



4. Crystallographic details for (EsIO)₄[‡] (tennimide) and (EsIO)₃[§] (trezimide)

4.1 Table 1. Selected Experimental details

For both (EsIO)₄[‡] and (EsIO)₃[§] structures: $Z = 4$. Experiments were carried out at 294 K with Cu $K\alpha$ radiation using a (Sapphire3) Gemini Ultra S diffractometer. Analytical absorption correction using ABSFAC (Clark and Reid, 1998). FMLS refinement were performed with 0 restraints and H-atom parameters were constrained as riding atoms.

	(EsIO) ₄ [‡] - 894030 (CSD)	(EsIO) ₃ [§] - 894031 (CSD)
Chemical formula	C ₆₀ H ₄₀ N ₈ O ₁₆	C ₄₅ H ₃₀ N ₆ O ₁₂
M_r	1129.00	846.75
Crystal system, space group	Monoclinic, $P2_1/n$ (No. 14)	Triclinic, $P\bar{1}$ (No. 2)
a, b, c (Å)	10.6870(1), 22.4852(2), 22.6756(2)	16.3411(13), 16.5747(4), 17.4806(16)
α, β, γ (°)	90, 101.721(1), 90	87.273(5), 83.350(7), 89.825(4)
V (Å ³); Z, Z'	5335.31(8); 4, 1	4697.4(6), 4, 2
μ (mm ⁻¹)	0.88	0.75
Crystal size (mm)	0.58 × 0.06 × 0.05	0.60 × 0.08 × 0.02
Data collection and refinement		
T_{\min}, T_{\max}	0.631, 0.958	0.663, 0.989
No. of measured, independent and observed reflections	31765, 8619, 6947 with $\{I > 2\sigma(I)\}$	16648, 10048, 4137 with $\{I > 2\sigma(I)\}$
R_{int}	0.034	0.083
θ_{\max} (°)	63.3	51.4
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.120, 1.02	0.121, 0.352, 0.91
No. of reflections	8619	10048
No. of parameters	762	1141
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.27, -0.17	0.47, -0.35

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)

Footnote of data collection experimental and structure solution for (EsIO)₃:

Crystals of (EsIO)₃ grow as very fragile thin laths that diffracted very weakly. The 1st attempt (Mo radiation) gave a unit cell and diffraction data only to 2.5 Å resolution, whereas a second data collection gave reflection data to a 1.5 Å resolution limit [data were collected to 0.94 Å with Cu radiation, 1° ω -scans, the detector at 60mm and with three shells collected for 16s/48s/48s per frame]. This dataset was not sufficient to produce a structural solution (data redundancy were 1.7, $F^2 = 2.1$ and $R_{\text{int}} = 0.16$). Finally, on a 3rd attempt, using Cu radiation at 40kV/40mA over 72 hrs, reflection data were collected to a diffraction limit of 1.35 Å, with frames to 1.00 Å with 0.5° scans, shells collected for 24s/48s per frame and the detector at 60mm (data redundancy = 1.8, $F^2 = 4.3$ and $R_{\text{int}} = 0.083$). This enabled a structural solution from a moderate direct methods attempt. It was obvious at an intermediate stage of the refinement that there were considerable voids in the lattice amounting to 21% of the unit cell and containing solvent molecules of unknown composition and occupancy. The program SQUEEZE was used and the R -factor dropped from 18% to 12% after using this program. The FMLS refinement proceeded without any problems or use of restraints to give a satisfactory (EsIO)₃ structure (with $Z'=2$). There are small but significant differences between molecules A and B in the asymmetric unit and an indication of disorder in one pyridyl ring (N52) but this was not treated due to the low data:parameter ratio and negligible effect.

4.2. Table 2. Selected hydrogen-bond and contact parameters

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
(EsIO)₄[‡]				
C4A—H4A2 \cdots O5 ⁱ	0.96	2.56	3.491 (4)	165
C6A—H6A3 \cdots O3 ⁱⁱ	0.96	2.58	3.461 (4)	153
C26A—H26A \cdots O5A ⁱⁱ	0.93	2.42	3.333 (3)	167
C15A—H15A \cdots O4 ⁱⁱⁱ	0.93	2.38	3.133 (3)	138
C35A—H35A \cdots O7 ^{iv}	0.93	2.57	3.107 (3)	117
C36—H36 \cdots O6 ^v	0.93	2.48	3.400 (2)	171
C12—H12 \cdots N4	0.93	2.58	2.897 (2)	100
C13A—H13A \cdots O2A	0.93	2.40	2.722 (3)	100
C23A—H23A \cdots O3A	0.93	2.50	2.818 (3)	100
C33A—H33A \cdots O6A	0.93	2.45	2.768 (3)	100
(EsIO)₃[§]				
C35A—H35A \cdots O31A ^{vi}	0.93	2.36	3.204 (13)	150
C65A—H65A \cdots O61A ^{vii}	0.93	2.41	3.227 (14)	146
C12—H12 \cdots N3	0.93	2.58	2.907 (12)	101
C22—H22 \cdots N1	0.93	2.57	2.886 (14)	100
C23A—H23A \cdots O22A	0.93	2.42	2.736 (17)	100
C28A—H28A \cdots O21A	0.96	2.24	2.68 (2)	107
C33A—H33A \cdots O32A	0.93	2.40	2.731 (14)	101
C36A—H36A \cdots O5A	0.93	2.45	2.843 (13)	105
C38A—H38A \cdots O31A	0.96	2.19	2.630 (17)	107
C48A—H48A \cdots O41A	0.96	2.28	2.642 (16)	101
C55—H55 \cdots O3A	0.93	2.59	3.377 (14)	143
C55A—H55A \cdots O52A	0.93	2.41	2.735 (14)	100
C63A—H63A \cdots O62A	0.93	2.40	2.726 (13)	100
C66A—H66A \cdots O5B	0.93	2.52	2.858 (13)	101

Symmetry code(s):

(*i*) $x-1/2, -y+1/2, z+1/2$ (*ii*) $-x, -y+1, -z+1$; (*iii*) $x+1, y, z$ (*iv*) $-x+1/2, y+1/2, -z+1/2$ (*v*) $x-1, y, z$ (*vi*) $-x+1, -y+1, -z+2$ (*vii*) $-x+2, -y, -z$

The hydrogen bond data (for both imide-based macrocycles) display a myriad of weaker C-H \cdots O interactions.

Selected geometric parameters for (EsIO)₄[‡] (tennimide)

Cavity (channel core) entrance analysed for C...N_{pyr} and H...N_{pyr} distances (in Å).

4.097(3) Å for C16A...N32A (C...N) and 3.19 Å for H16A...N32A (H...N).

4.150(3) Å for C46A...N22A (C...N) and 3.31 Å for H46A...N22A (H...N)

Macrocyclic intra-annular cavity H...H_{isophthaloyl} distances (depicted overleaf on page 30).

3.07 Å for H12...H22, 4.13 Å for H12...H32, 3.07 Å for H12...H42.

3.03 Å for H22...H32, 4.18 Å for H22...H42, 3.07 Å for H32...H42.

Dihedral angles for the imide '**CO...CO**' twist and isophthaloyl '**OC...CO**' for each residue*.

+113.0(3)° O1=C1...C2=O2 9.6(3)° O2=C2...C3=O3

-112.5(3)° O3=C3...C4=O4 2.5(3)° O4=C4...C5=O5

+94.3(3)° O5=C5...C6=O6 6.2(3)° O6=C6...C7=O7

-88.9(2)° O7=C7...C8=O8 -25.4(3)° O8=C8...C1=O1

* These angles would be expected to be 0°/180° if the isophthaloyl group is *ideally* planar. The 8 carbonyl oxygen atoms are positioned by 0.584(2)→1.045(4) Å from the isophthaloyl group plane to which they are bonded and highlighting distortion from co-planarity with their C₆ ring; [0.904(4) Å for O1, 0.584(4) Å for O8], [0.993(4) Å for O2, 1.045(4) Å for O3], [-0.950(4) Å for O4, -0.719(4) Å for O5], [0.767(4) Å for O6, 0.952(4) Å for O7] with an average distance of 0.86 Å.

Selected geometric parameters for (EsIO)₃[§] (trezimide)

Macrocyclic intra-annular cavity H...H_{isophthaloyl} distances (in Å).

H12...H22 2.64 H12...H32 2.77 H22...H32 2.80

H42...H52 2.68 H42...H62 2.73 H52...H62 2.87

Dihedral angles for the imide '**CO...CO**' twist and '**OC...CO**' for each isophthaloyl residue[#].

+95.5(13)° O1A=C1A...C2A=O2A -17.8(18)° O1A=C1A...C6A=O6A

-111.3(14)° O3A=C3A...C4A=O4A +40.4(17)° O2A=C2A...C3A=O3A

-91.9(15)° O5A=C5A...C6A=O6A **128.7(14)° O4A=C4A...C5A=O5A**

+91.6(14)° O1B=C1B...C2B=O2B -18.7(17)° O1B=C1B...C6B=O6B

-108.8(15)° O3B=C3B...C4B=O4B +50.7(16)° O2B=C2B...C3B=O3B

-94.5(14)° O5B=C5B...C6B=O6B **121.9(17)° O4B=C4B...C5B=O5B**

-0.942(0.015) O1A 0.946(0.016) O1B [Paired as O1/O6]

0.651(0.018) O2A 0.709(0.016) O2B [Paired as O2/O3]

0.881(0.020) O3A 0.905(0.017) O3B

0.765(0.020) O4A 0.922(0.020) O4B [Paired as O4/O5]

-0.594(0.018) O5A -0.741(0.019) O5B

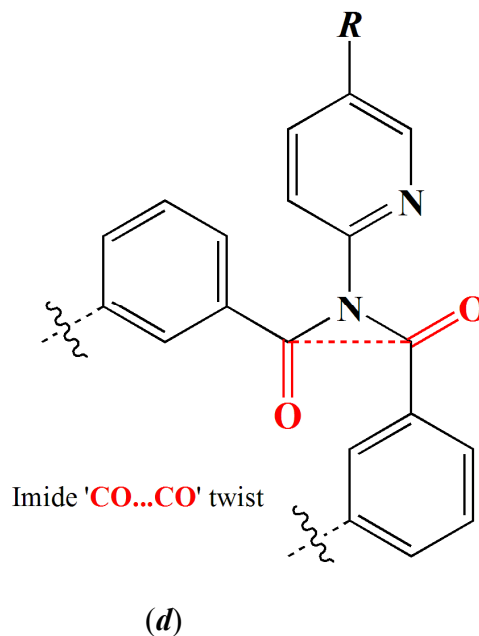
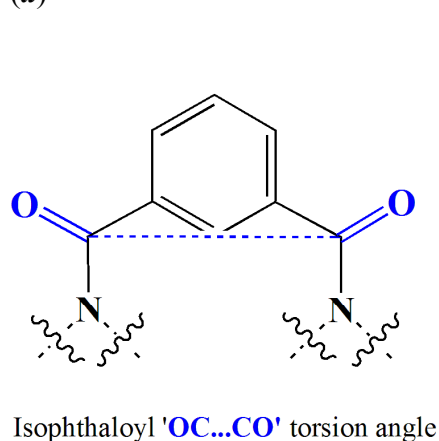
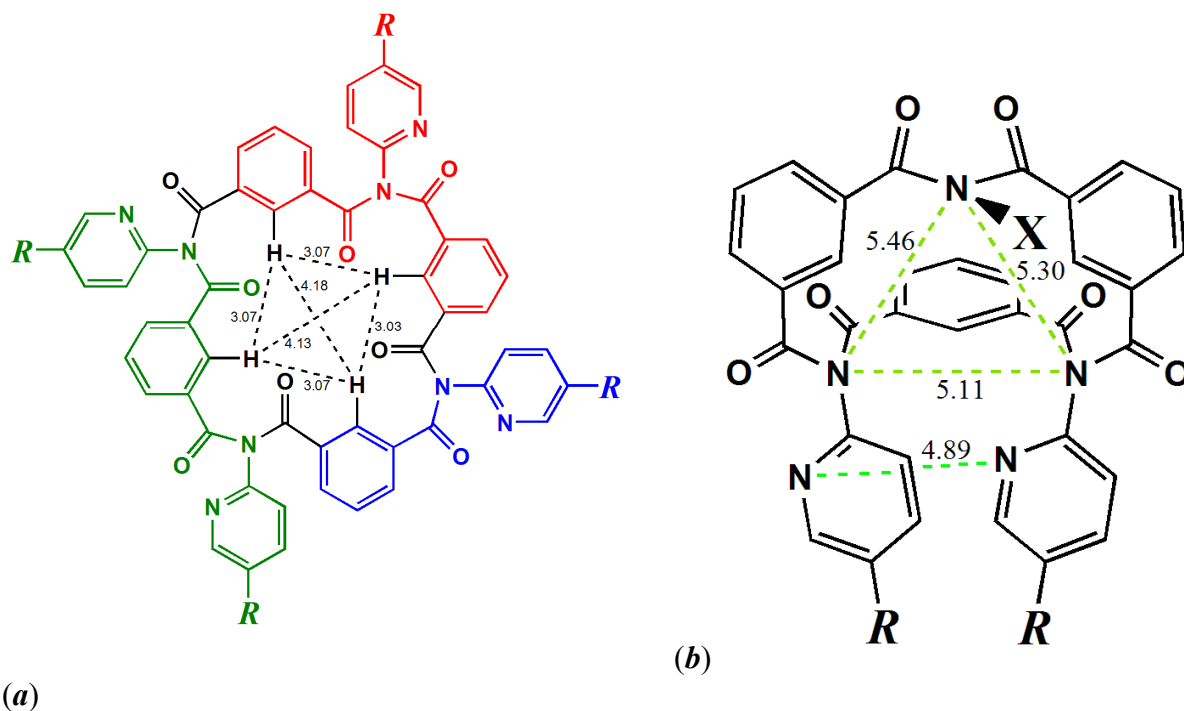
-0.496(0.016) O6A 0.500(0.016) O6B

The pairs of carbonyl O atoms in each macrocycle A, B (**O4_{A/B}**, **O5_{A/B}**) are on **opposite** sides of the isophthaloyl C₆ ring and can be described as *transoid* to one another BUT are *syn*-related.

These **OC...CO** torsion angles[#] are spread over a greater range than for the (EsIO)₄ tennimide. The average deviation of the C=O oxygen atoms from their C₆ planes to which they are attached is 0.72 Å (**for A**) and 0.79 Å (**for B**).

Molecular and Crystal structure diagrams for (EsIO)₄ and (EsIO)₃

Schematic diagrams for (EsIO)₄ and (EsIO)₃: (a) highlighting H...H intra-annular contacts (Å) in (EsIO)₄ (below left) and (b) N...N_{tertiary} distances (Å) in (EsIO)₃ (molecule A, below right). Of further note in (a) are the molecular fragments including the (1:1) benzamide (in blue = ¼), (2:1) imide (in red = ⅓) and (1:2) N,N'-di-2-pyridylbenzene-1,3-dicarboxamide (in green = ⅔). These common fragments have been reported on extensively in the literature.

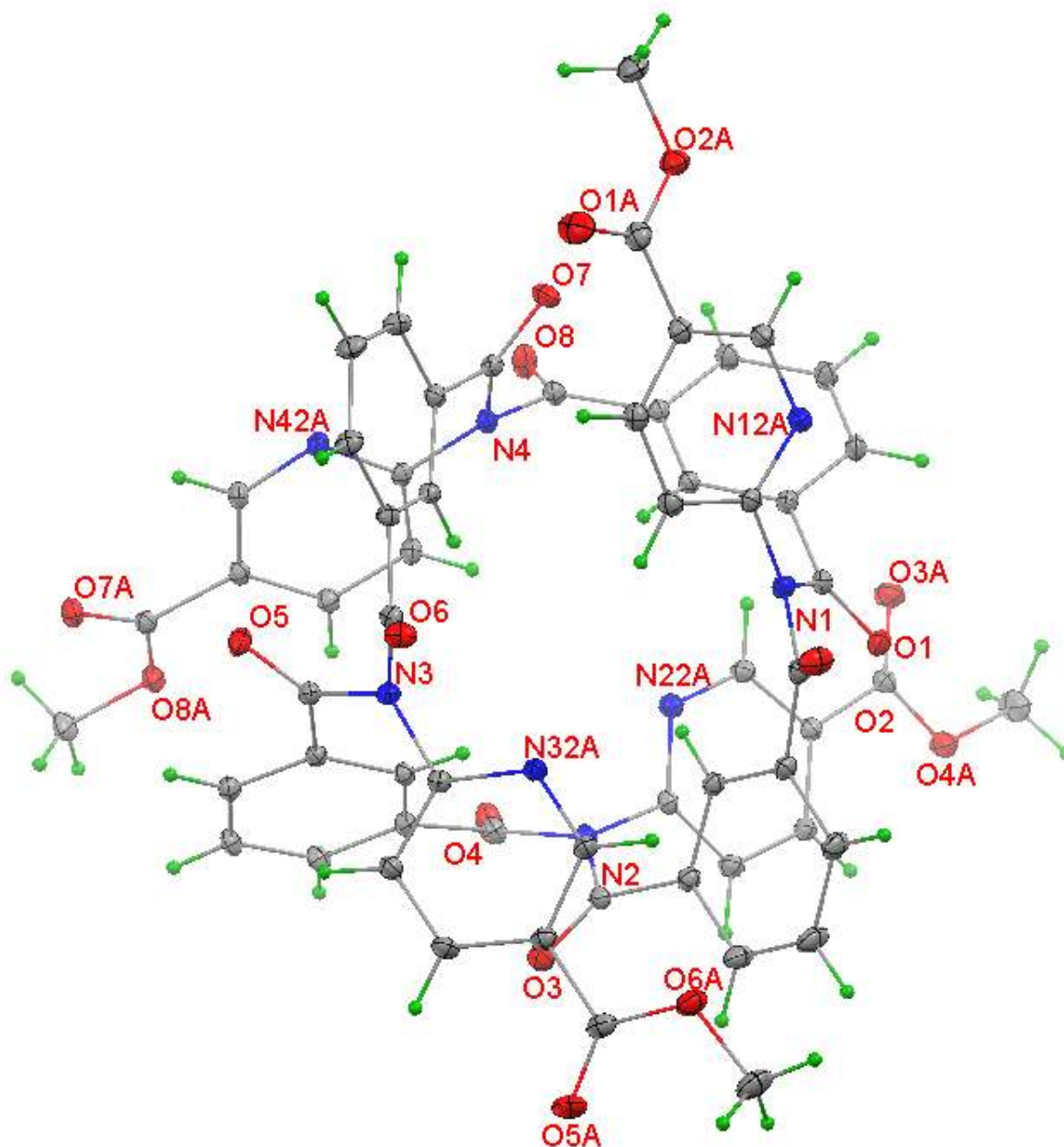


Schematic diagrams (c) and (d): the isophthaloyl OC...CO and imide CO...CO torsion angles.

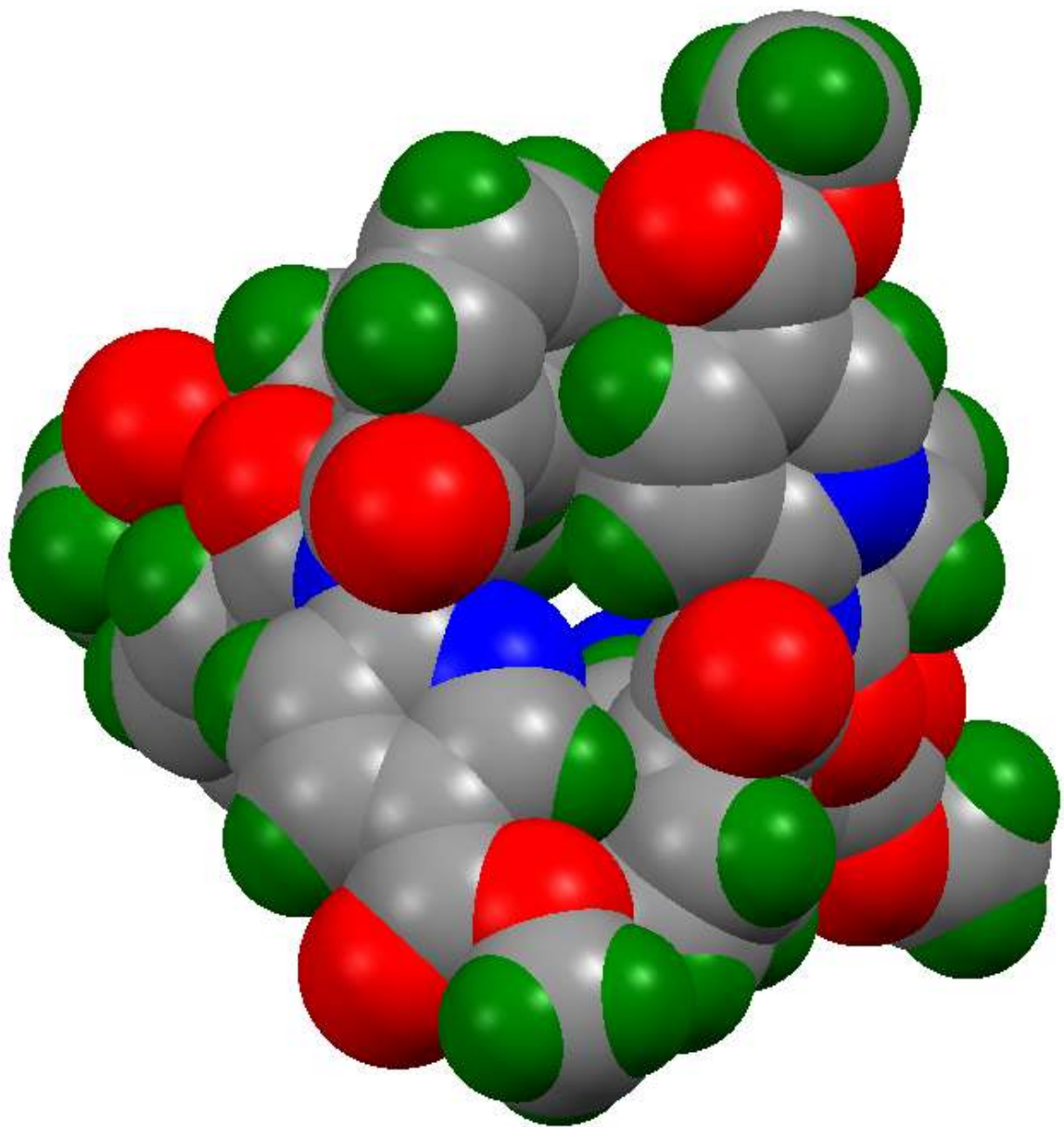
The isophthaloyl torsion angles are measured as O=C...C=O and written as 'OC...CO' in the text. The imide torsion angles are measured as O=C...C=O and BUT written as 'CO...CO' in the text.

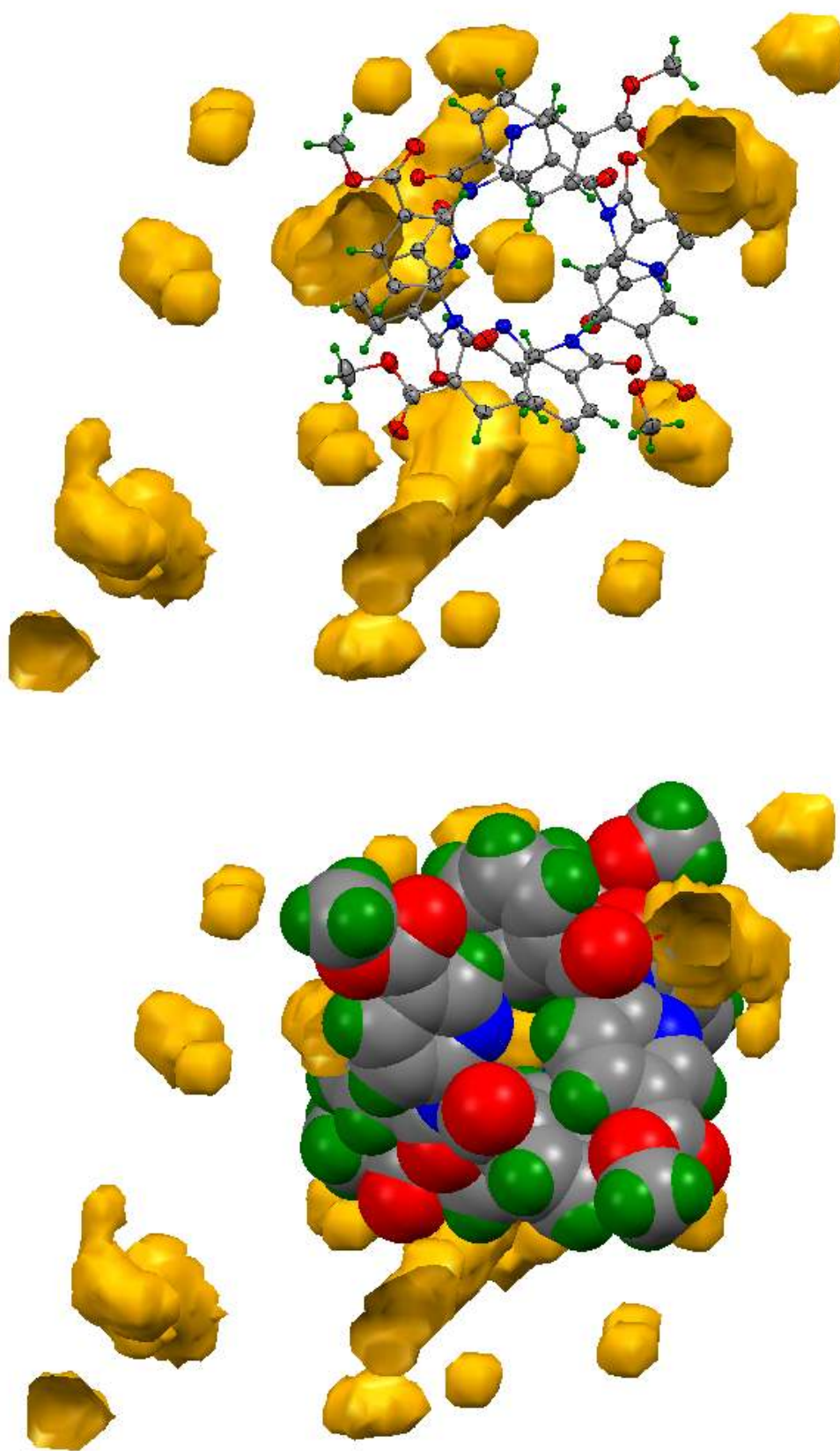
(EsIO)₄ tennimide molecular and crystal structure diagrams.

A view of (EsIO)₄ (through the internal molecular cavity) with all non-hydrogen atoms having ellipsoids at the 10% level. There is no disorder present in the molecule and the crystal structure contains voids that total <1% of the unit cell (and in which there is no associated electron density). Depth cueing has been liberally applied.



A view of $(\text{EsIO})_4$ (through the internal molecular cavity) with all atoms depicted as their van der Waals spheres (oxygen in **red**; nitrogen in **blue**; hydrogen in **green**). The diagram highlights the orientation of the stronger electron accepting groups as O=C and pyridinyl N.

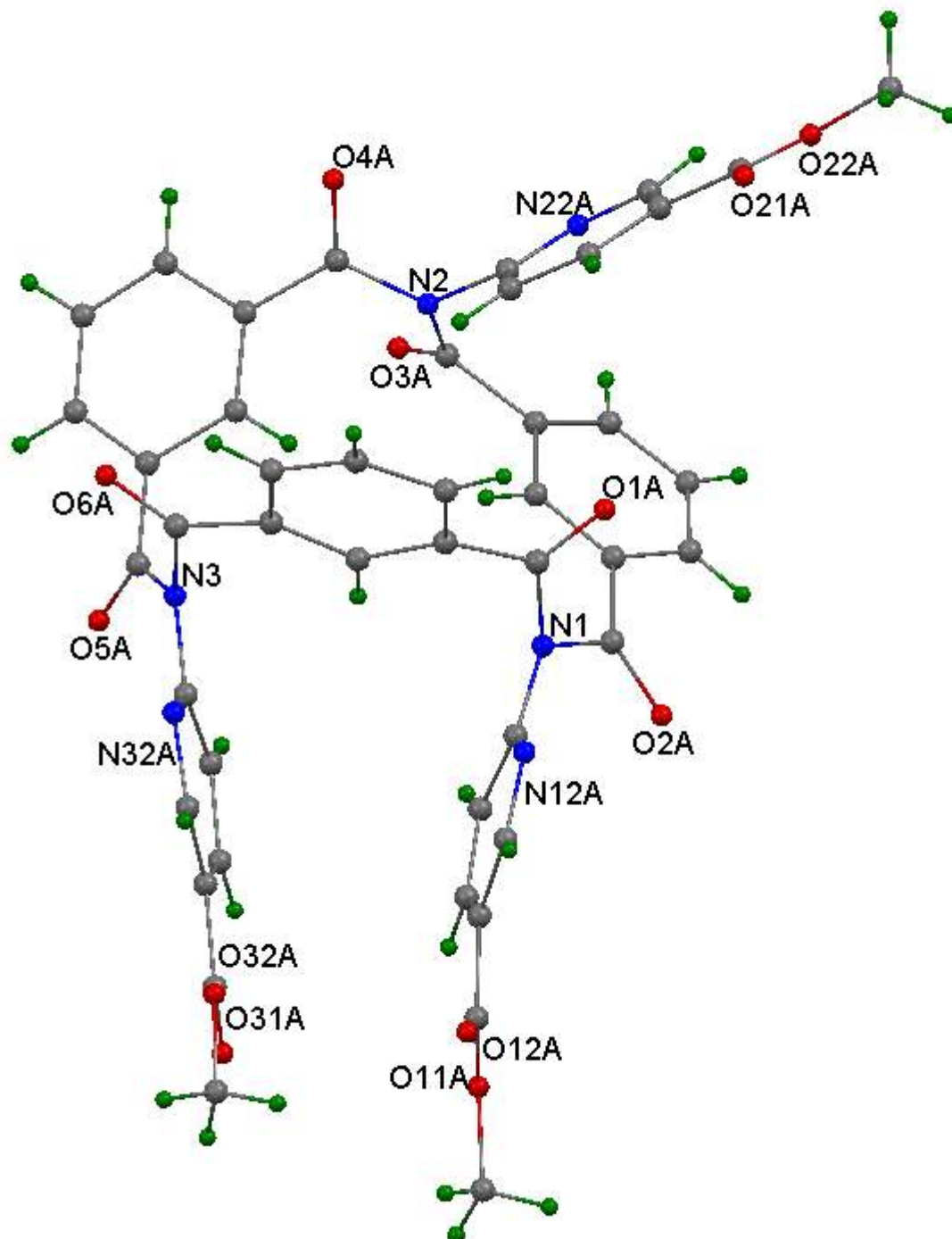




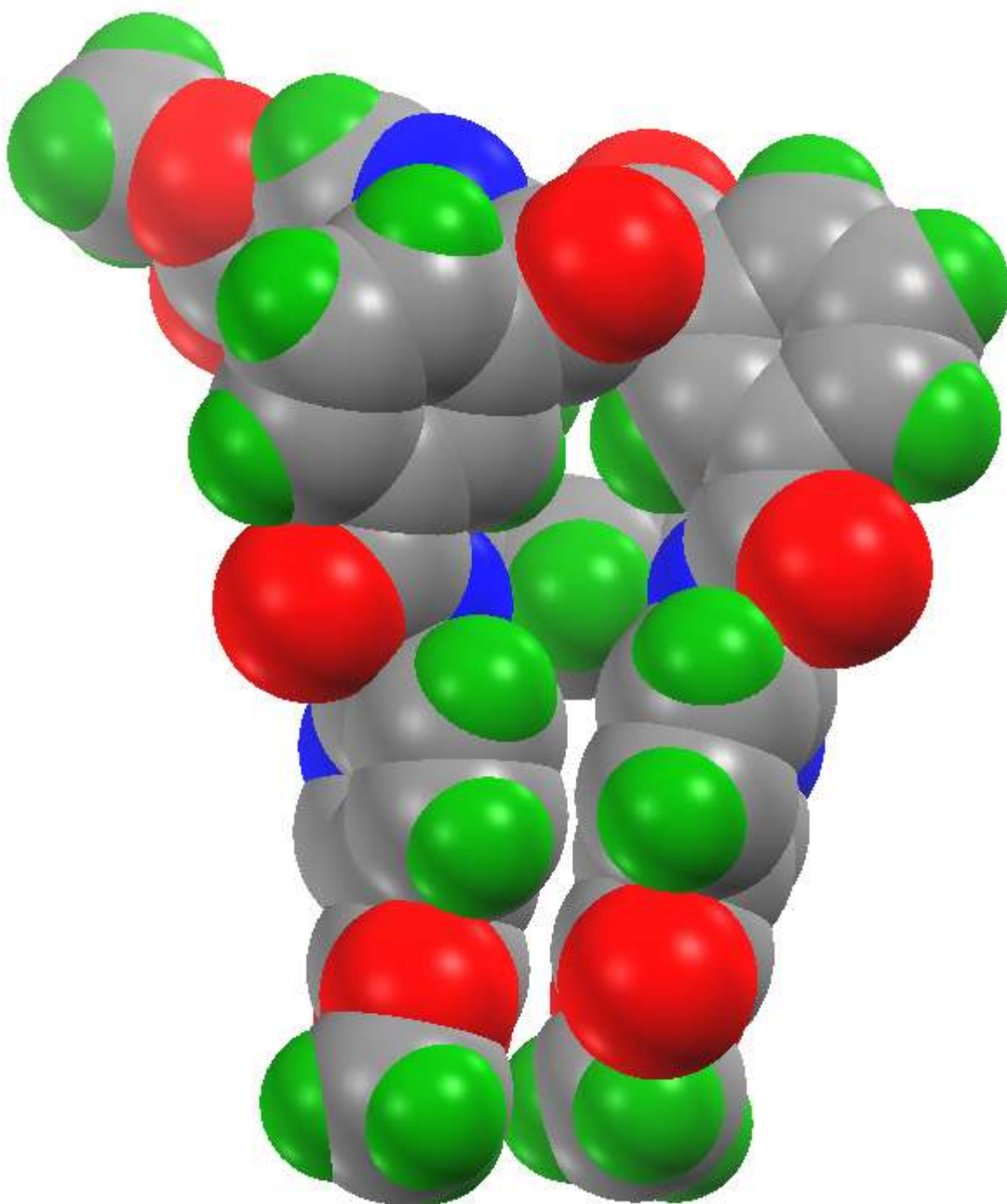
Two views of the unit cell of **(EsIO)₄** (generated using Mercury) and highlighting the contact surface (0.85, 0.45) for potential voids and showing that the available cavity volume is small.

(EsIO)₃ **trezimide** molecular and crystal structure diagrams.

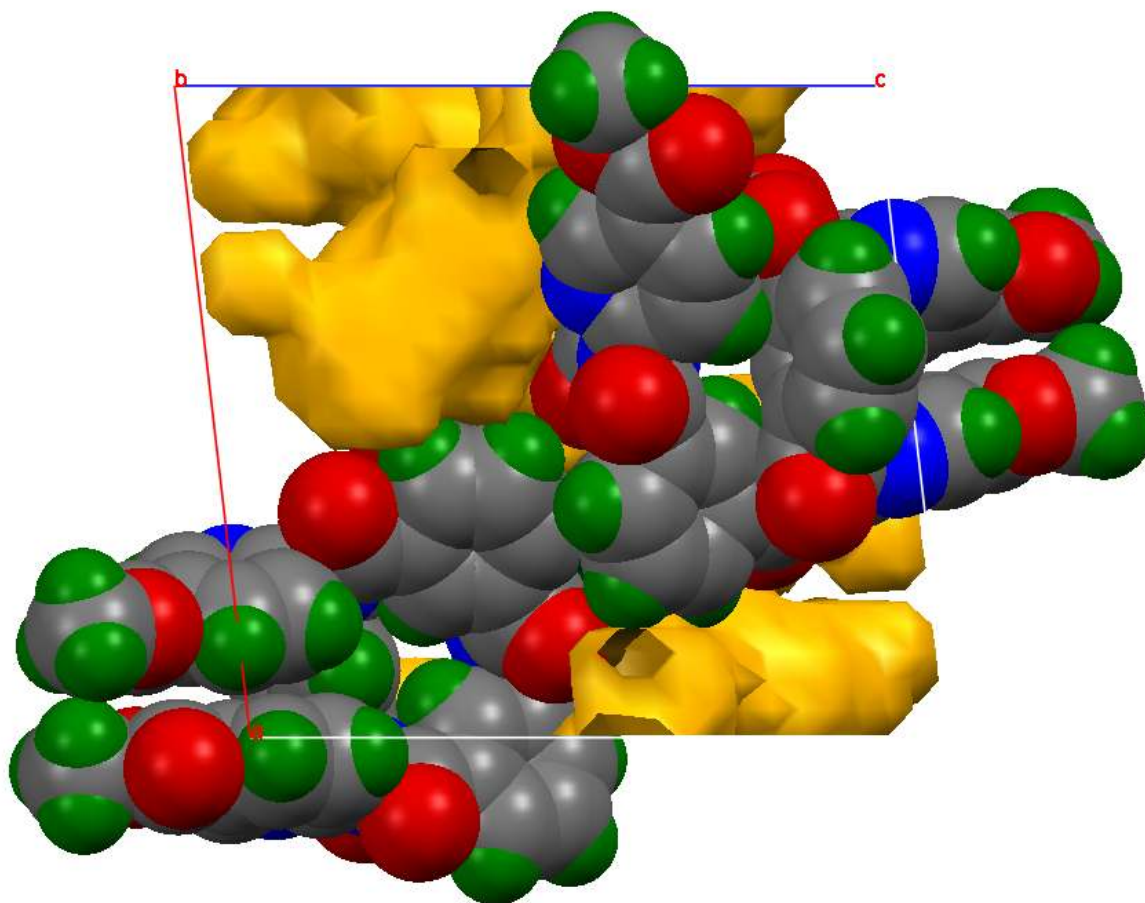
(EsIO)₃ as a ball and stick diagram showing the asymmetric nature of the molecule.



A view of $(\text{EsIO})_3$ (from the reverse direction to the previous page) through the internal molecular *niche* with all atoms depicted as their van der Waals spheres (oxygen in **red** and nitrogen in **blue**).



A view of the unit cell of (**EsIO**)₃ highlighting the solvent accessible voids (yellow).



The (**EsIO**)₃ crystal structure has 21% of each unit cell which is solvent accessible.

Additional Note on (EsIO**)₃:**

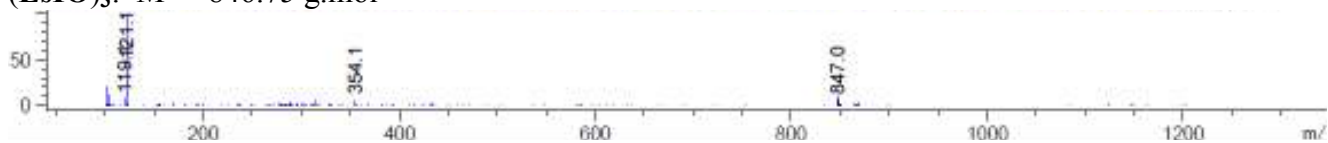
Crystals of (**EsIO**)₃ can be grown from acetonitrile (CH₃CN) solutions to produce colourless plates; however these decompose rapidly when handled (using several inert handling conditions) and we were able to observe diffraction and obtain a unit cell of one of these crystals: $a = 11.89(2)$ Å, $b = 12.24(2)$ Å, $c = 18.77(2)$ Å, $\alpha = 86.38(13)^\circ$, $\beta = 78.71(14)^\circ$, $\gamma = 65.49(16)^\circ$, Volume = $2439(7)$ Å³ which is consistent with triclinic ($Z = 2$) and an indeterminate solvent composition in the lattice voids. A second attempt yielded : $a = 11.91(2)$ Å, $b = 12.24(2)$ Å, $c = 18.67(3)$ Å, $\alpha = 86.75(14)^\circ$, $\beta = 78.71(15)^\circ$, $\gamma = 65.43(17)^\circ$, Volume = $2427(8)$ Å³. Crystals of (**EsIO**)₃ typically form poor quality plates.

CSD analysis as analysed on 21st August 2012:

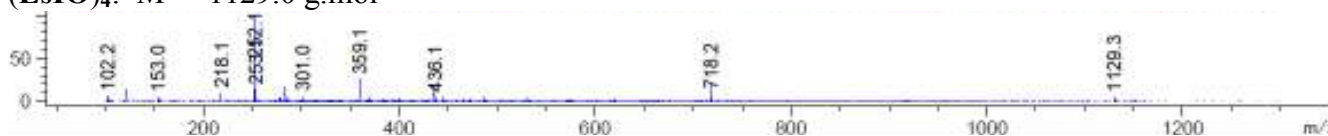
To date only two crystal structures namely IYUQUO and IYURAV (Gale & Evans, 2004) have been reported in the scientific literature and deposited on the CSD which are derived from open-chain imides though a range of systems derived from *e.g.* pyromellitic acid are well known.

5. Mass spectrometry details [ESI-MS]

(EsIO)₃: $M^+ = 846.75 \text{ g.mol}^{-1}$



(EsIO)₄: $M^+ = 1129.0 \text{ g.mol}^{-1}$



MS apparatus: Agilent 6100 Series Quadrupole LC/MS System

Ionisation method: Electrospray Ionisation

Solvent: Acetonitrile