

Selective Binding of Spherical and Linear Anions by Tetraphenyl(thio)urea Based Dihomooxacalix[4]arene Receptors

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Supporting information

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Table S1. Dihedral angles for the crystallographic independent molecules **I** and **II** found in the structure of compound **4c**

	A	B	C	D
I	99.2(1)	118.2(2)	74.1(2)	134.8(2)
II	100.9(1)	119.1(1)	71.8(1)	144.7(2)

Table S2. Hydrogen bonding interactions detected in the structure of compound **4c**

D-H...A ^a	d(D...A) (Å)
N(4n)-H(4n)...O(3p)	3.021(9)
N(4q)-H(4q)...O(3p)	2.859(7)
N(1n)-H(1n)...O(4p)	2.973(9)
N(1q)-H(1q)...O(4p)	2.898(8)
N(2n)-H(2n)...O(5p)	2.911(7)
N(2q)-H(2q)...O(5p)	3.058(7)
N(8n)-H(8n)...O(7p)	2.902(7)
N(8q)-H(8q)...O(7p)	2.891(8)
N(7n)-H(7n)...O(6p)	2.875(9)
N(7q)-H(7q)...O(6p)	2.861(7)
O(2et)-H(2et)...O(1wa)	2.65(1)
O(1wa)...O(2p)	2.617(9)

^aThe atom labels used in the structure are completed in parenthesis.

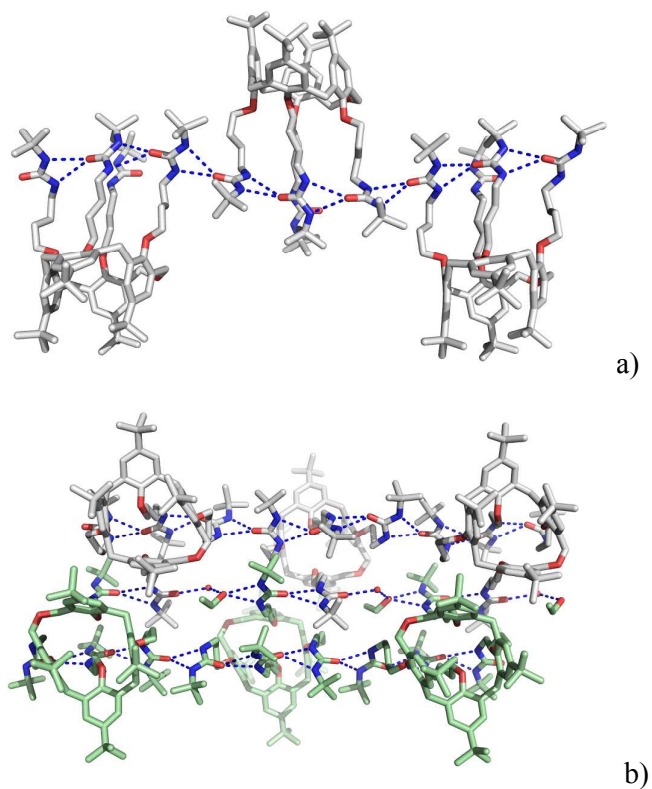


Figure S1. a) The crystal packing shows that a network of two intramolecular and one intermolecular N–H···O double hydrogen bonds, formed by three of the four ureido groups, create chains of dihomooxalixarene molecules, with the cavity oriented in an up-down fashion; b) Two antiparallel crystallographically independent chains are interconnected by one N–H···O double hydrogen bond formed by the remaining ureido group not involved in intramolecular H-bonds. This H-bond network is completed by water and ethanol solvent molecules sandwiched between two dihomooxalixarene chains.

Crystal structure attempts in presence of TBA salts

Attempts to co-crystallise **4c** in presence of TBA salts resulted in crystals in which did not incorporate a guest, but the structure was that of **4c** only. Furthermore, attempts to obtain suitable crystals for structural determination of **4a** and **4b** were unsuccessful. In the case of **4a**, small crystals were obtained in various crystallisation trials, including co-crystallisation in the presence of TBA HSO₄, TBA Br and TBA AcO. In all cases however, the crystals proved to be unsuitable even for data collection with synchrotron radiation. Low-resolution data-sets (ca 1.8 Å) with markedly anisotropic diffraction patterns were always obtained, which generally allowed the cell dimensions to be determined ($a = 12.18 \text{ \AA}$, $b = 16.07 \text{ \AA}$, $c = 26.28 \text{ \AA}$, $\alpha = 94.43$, $\beta = 90.11$, $\gamma = 109.48$), but which did not allow a solution to be found in any case. We believe that the overall behaviour observed is indicative of extensive disorder in the structures. In the case of compound **4b**, the crystallisation trials, both in the presence and absence of TBA salts, resulted mainly in the formation of amorphous glass-like deposits.

Table S3. Crystal data and structure refinement for compound **4c**

	4c
Empirical formula	2(C ₈₁ H ₁₃₀ N ₈ O ₉), 0.5(C ₂ H ₆ O), H ₂ O
Formula weight	2741.39
Temperature (K)	100(2)
Wavelength (Å)	0.85
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ /n
Unit cell dimensions (Å, °)	<i>a</i> = 20.693(3), <i>α</i> = 90 <i>b</i> = 36.935(1), <i>β</i> = 107.018(3) <i>c</i> = 23.506(2), <i>γ</i> = 90
Volume (Å ³)	17179(3)
<i>Z</i>	4
ρ_{calcd} (g/cm ³)	1.060
μ (mm ⁻¹)	0.102
F(000)	5967
Reflections collected	59168
Independent reflections	21388 [R(int) = 0.0679]
Data / restraints / parameters	21388 / 129 / 1931
Goof	1.062
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.1389, <i>wR</i> ₂ = 0.3624
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1481, <i>wR</i> ₂ = 0.3705
CCDC code	1551953

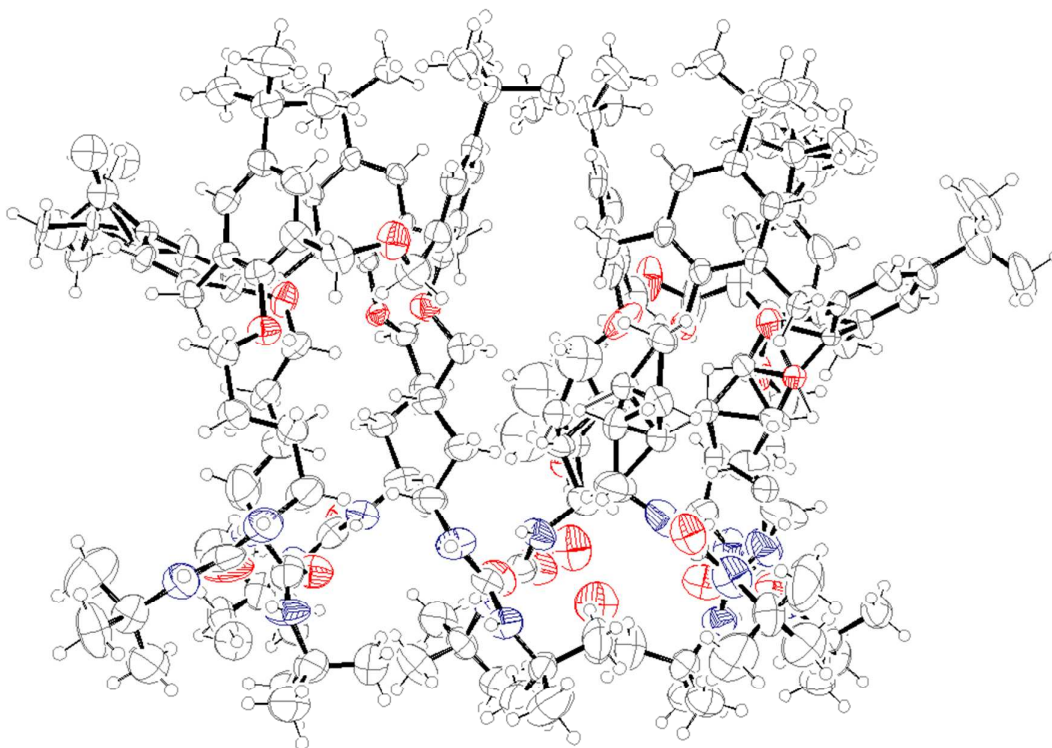


Figure S2. ORTEP view of compound **4c**. Carbon atoms are drawn as grey ellipsoids, oxygen atoms as red ellipsoids and nitrogen atoms as blue ellipsoids. Hydrogen atoms are shown as small circles. Probability is set at 50%.

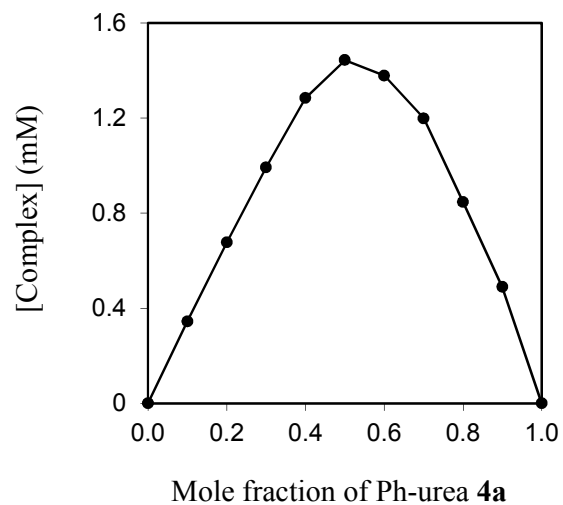


Figure S3. Job plot based on ^1H NMR data for Ph-urea **4a** + Cl^- ; total concentration 5×10^{-3} M in CDCl_3 .

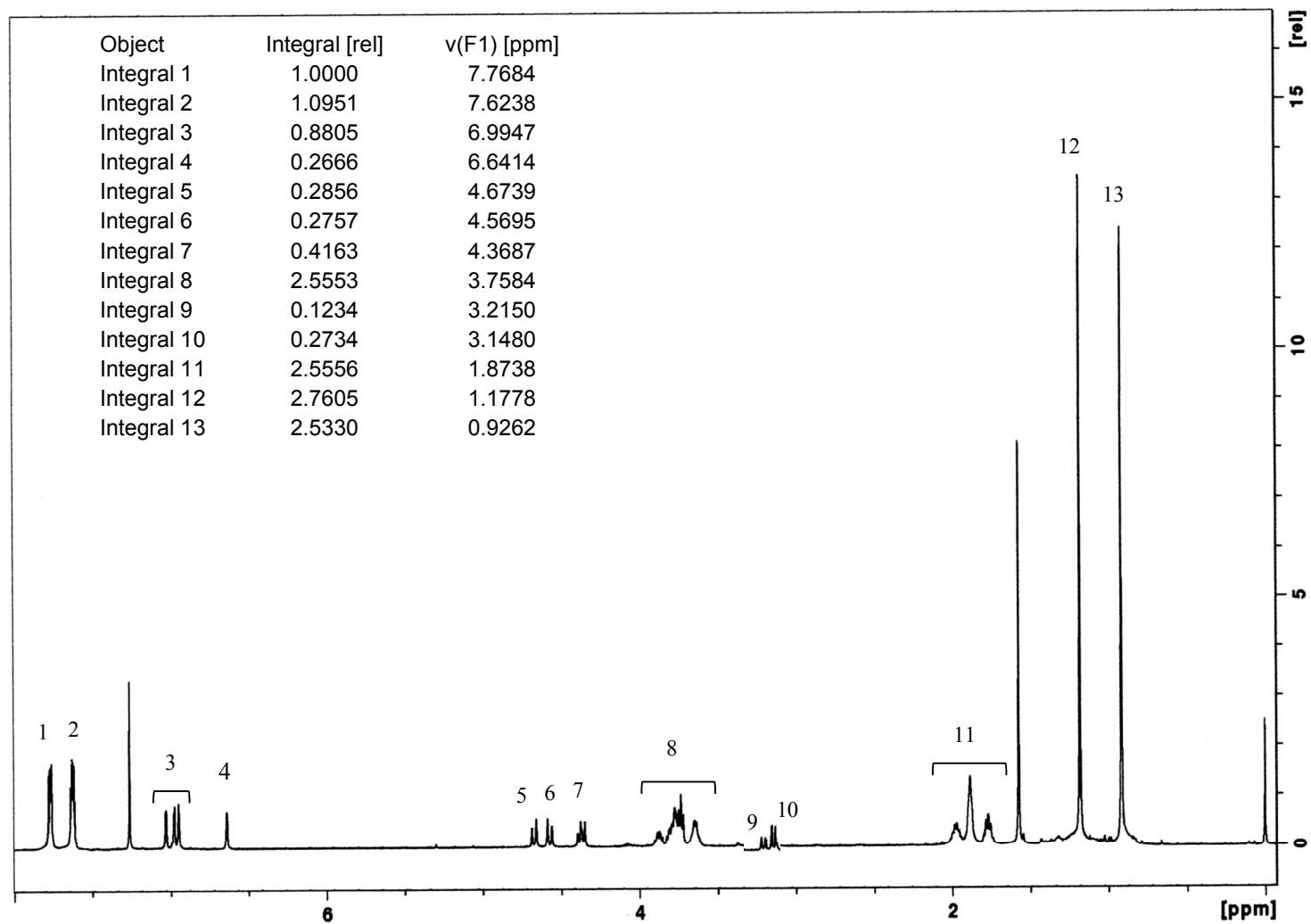


Figure S4. ¹H NMR spectrum of tetraphthalimide **2**. Insert: Integration values and corresponding peak chemical shifts.

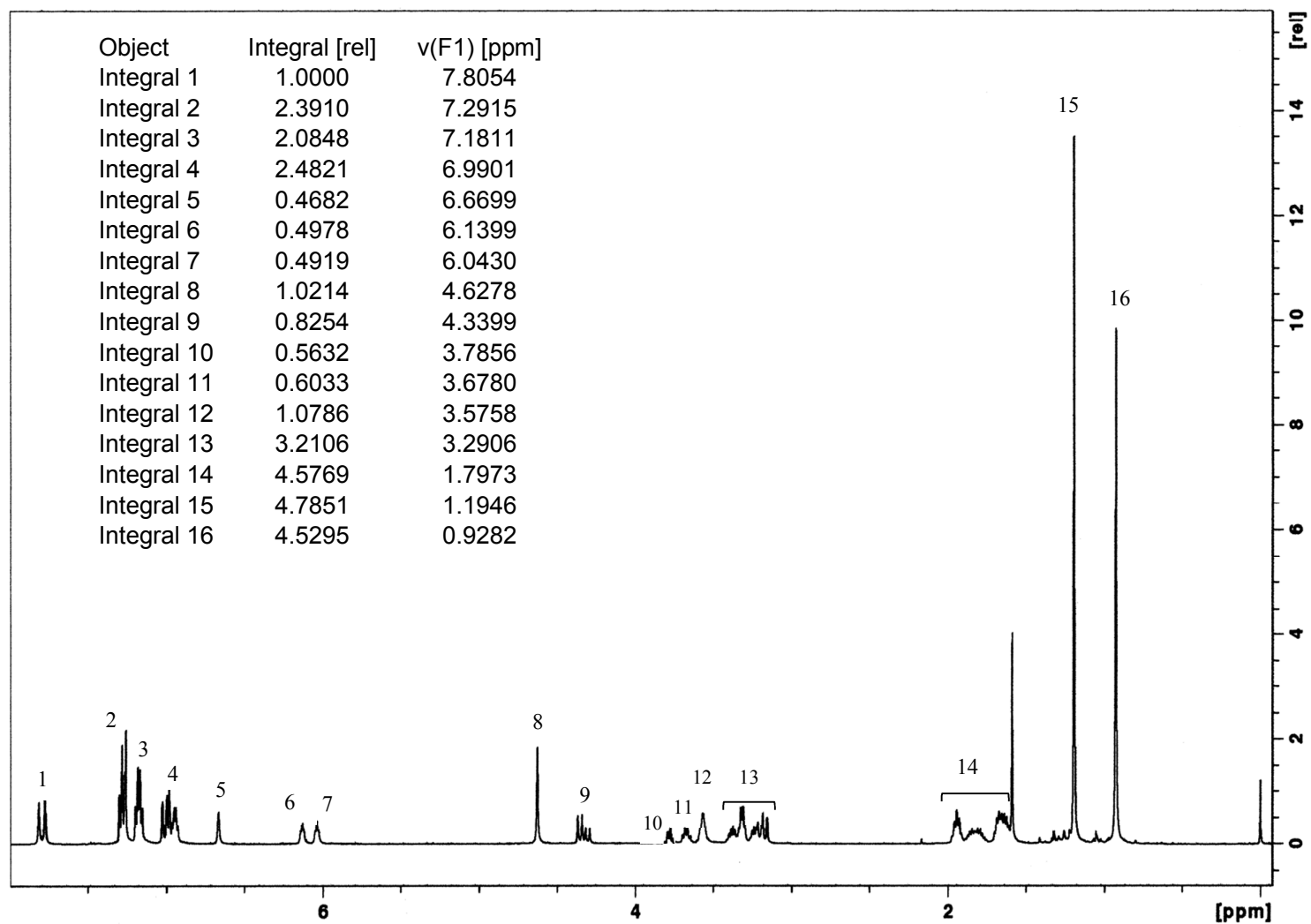


Figure S5. ^1H NMR spectrum of tetraphenyl urea **4a**. Insert: Integration values and corresponding peak chemical shifts.

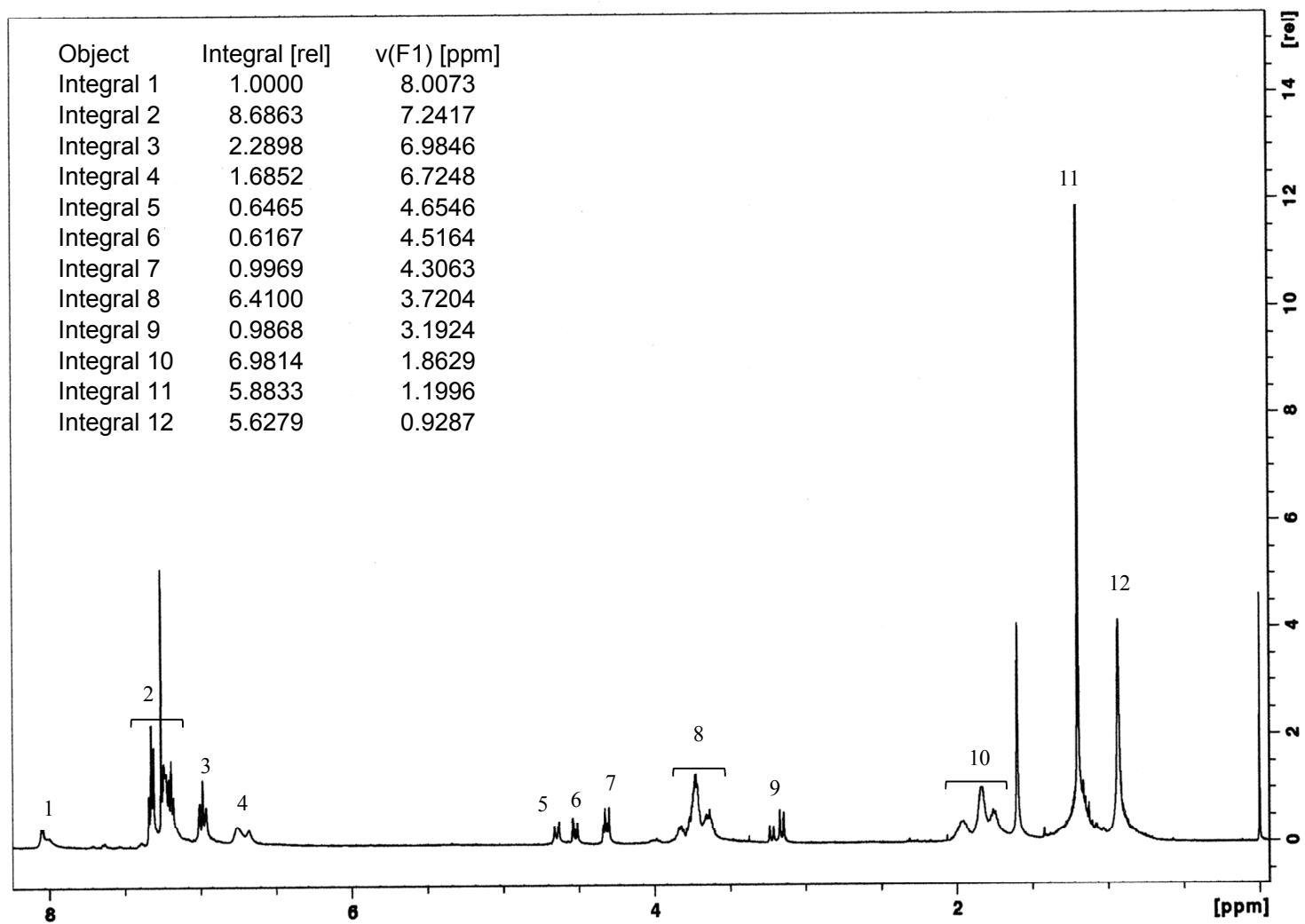


Figure S6. ^1H NMR spectrum of tetraphenyl thiourea **4b**. Insert: Integration values and corresponding peak chemical shifts.

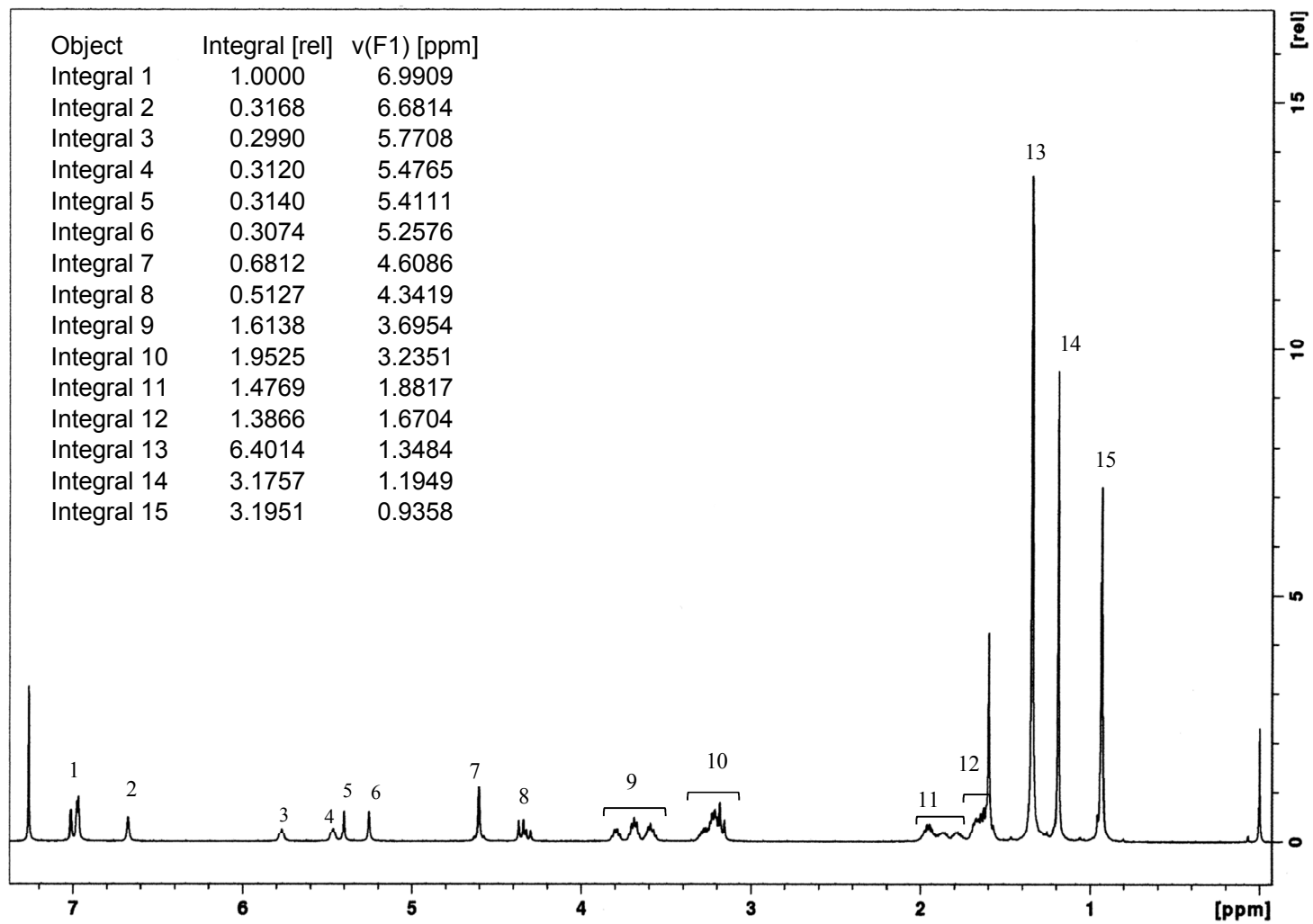


Figure S7. ¹H NMR spectrum of tetra-*tert*-butyl urea **4c**. Insert: Integration values and corresponding peak chemical shifts.

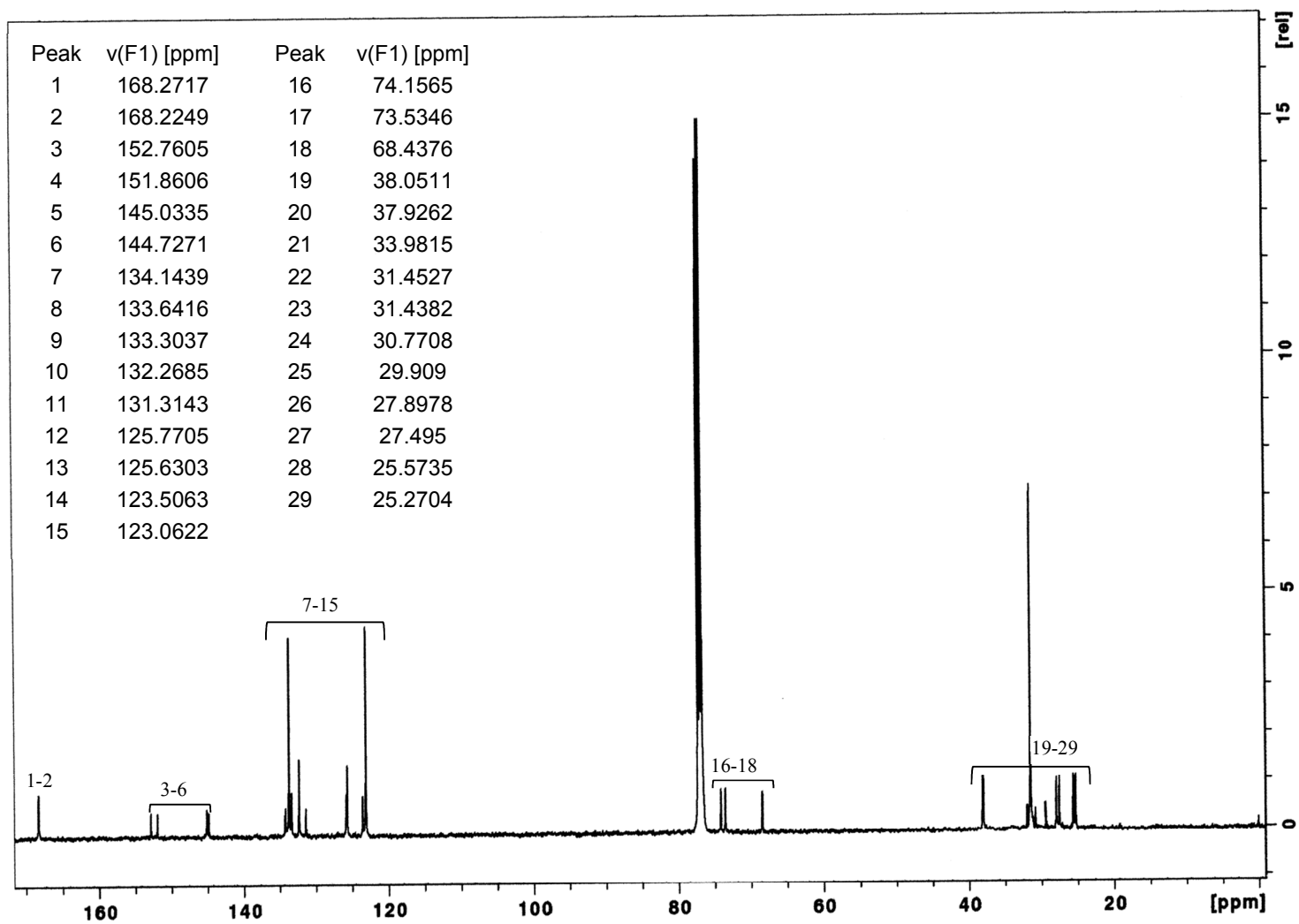


Figure S8. ^{13}C NMR spectrum of tetraphthalimide **2**. Insert: Peak numbers and corresponding chemical shifts.

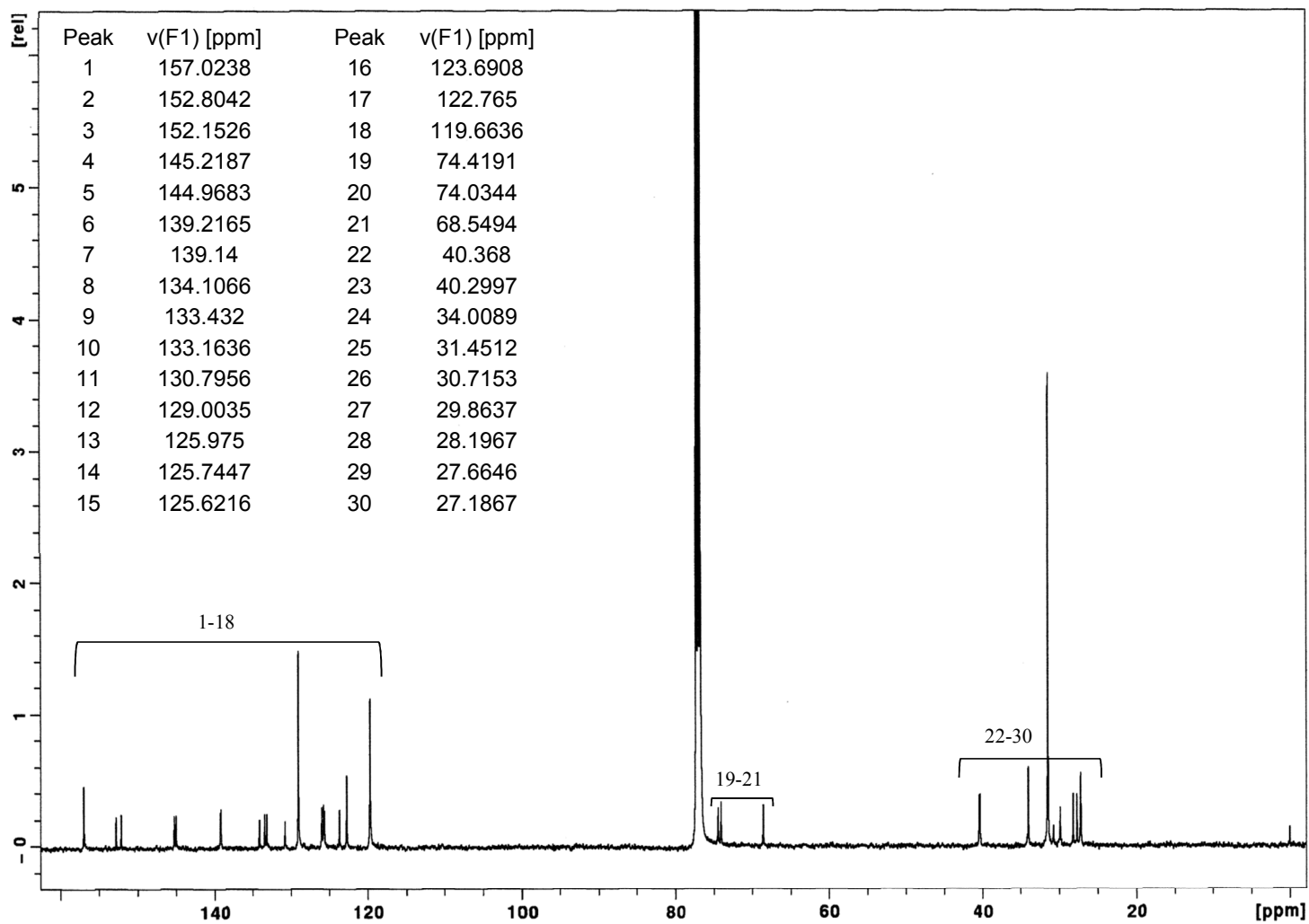


Figure S9. ^{13}C NMR spectrum of tetraphenyl urea **4a**. Insert: Peak numbers and corresponding chemical shifts.

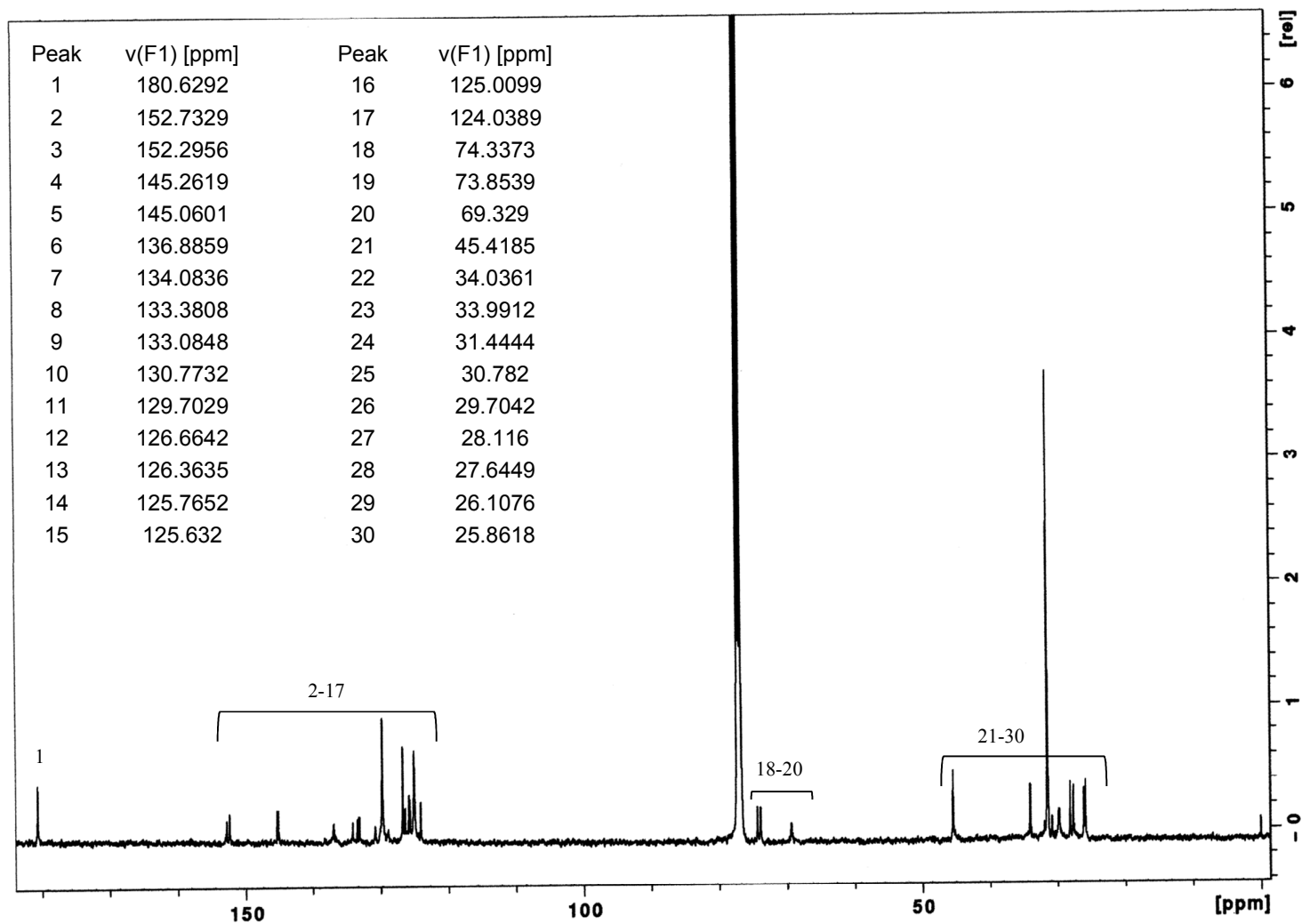


Figure S10. ^{13}C NMR spectrum of tetraphenyl thiourea **4b**. Insert: Peak numbers and corresponding chemical shifts.

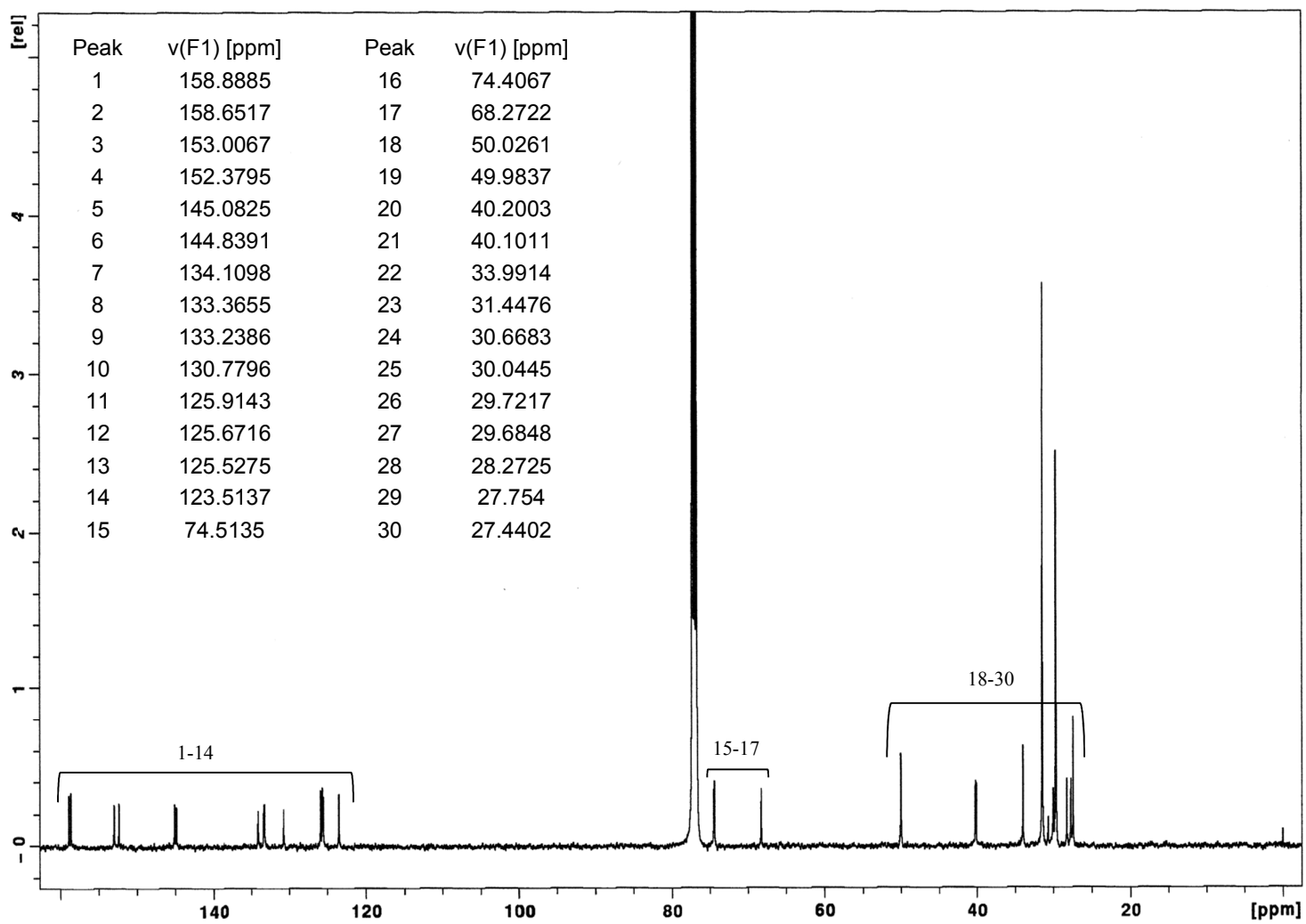


Figure S11. ^{13}C NMR spectrum of tetra-*tert*-butyl urea **4c**. Insert: Peak numbers and corresponding chemical shifts.