Supporting Information

Recognition and complexation of hydrated fluoride anion: $F_2(H_2O)_6^{2-}$ templated formation of a dimeric capsule of a tripodal amide†

M. Arunachalam and Pradyut Ghosh*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700032, India.

E-mail: icpg@iacs.res.in

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Experimental Section

^{1}H NMR and ^{13}C NMR spectra for for **L**, **1**, **2, 3** and **4** were recorded on Bruker 300 MHz FT-NMR spectrometer (model: DPX-300) in DMSO-*d*6 at 25ºC. HRMS measurements were carried out on QTof-Micro YA 263 instruments. All the tetrabutylammonium salts used were purchased from Sigma-Aldrich, USA and were used as received. Synthesis of **L** was according to the literature procedure. 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene was prepared as per the modified literature procedure[1] where 1,3,5-tris(bromomethyl)-2,4,6-trimethyl benzene is used instead of 1,3,5-tris(bromomethyl)-2,4,6-triethyl benzene.

Compound L: 1,3,5-tris(aminomethyl) 2,4,6-trimethylbenzene (0.414 g, 2 mmol) and 0.8ml triethylamine was dissolved in 100ml chloroform and stirred at 0ºC using ice-bath for 15 minutes under nitrogen atmosphere. 2-nitrobenzoyl chloride (0.8ml, 6mmol, 3 equivalents) was added slowly drop-wise to the reaction mixture through syringe under nitrogen atmosphere with constant stirring. Formation of white precipitate was observed. The temperature of the reaction was gradually brought to room temperature and continued stirring for 24hrs. Filtered the precipitate and the residue was washed with plenty of water to remove triethylammonium chloride. Then the residue was washed with diethyl ether and it was air dried to give off-white powder of **L** in 0.940 g (72%) of **L**; ^{1}H NMR, 300MHz (DMSO-d_6) δ 2.41 (s, 9H, -CH_3), 4.50 (d, 6H, -CH_2, J=4.4 Hz), 7.53 (d, 3H, -CH_{Ar}, J=7.3 Hz), 7.64 (d, 3H, -CH_{Ar}, J=8.8 Hz), 7.73 (d, 3H, -CH_{Ar}, J=7.4 Hz), 8.01 (d, 3H, -CH_{Ar}, J=7.8 Hz), 8.73 (t, 3H, -NH, J=4.5 Hz) ; ^{13}C NMR, 75MHz (DMSO-d_6) δ 15.87, 38.7, 123.9, 129.3, 130.5, 132.1, 132.7, 133.5, 137.0, 146.8, 165.3; HRMS (ESI): m/z 655.5670 $[L+H]^+$, 677.5413 $[\mathbf{L}+Na]^+$, 693.5134 $[\mathbf{L}+K]^+$. Anal. Calcd for $C_{33}H_{30}N_6O_9$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.30; H, 4.68; N, 12.25.

Complex 1: Complex **1** was prepared by charging excess (10eq) of tetrabutylammonium fluoride to the suspension of **L** (52mg, 80 μmol) in 15ml dioxane. After addition of tetrabutylammonium fluoride the suspension turned clear and the solution was warmed to ~ 80ºC, then solution was filtered and allowed for slow evaporation at room temperature. After 5 days colorless crystals of **1** were obtained. Yield 23%. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.92 (t, J = 6.5 Hz, 12H, -$NCH_2CH_2CH_2\mathit{CH_3}$), 1.29 (q, J = 6.5 Hz, 8H, -$NCH_2CH_2\mathit{CH_2}CH_3$), 1.55 (m, 8H, -$NCH_2\mathit{CH_2}CH_2CH_3$), 2.41 (s, 9H, -$CH_3$), 3.15 (t, 8H, -$N\mathit{CH_2}CH_2CH_2CH_3$), 4.50 (s, 12H, -NH-$\mathit{CH_2}$), 7.53 (d, 3H, -$CH_{Ar}$, J=9 Hz), 7.64 (d, 3H, -CH_{Ar}, J=9 Hz), 7.73 (d, 3H, -CH_{Ar}, J=6 Hz), 8.01 (d, 3H, -CH_{Ar}, J=8 Hz), 8.84 (b, -*NH*). ^{13}C NMR, 75MHz (DMSO-d_6) δ 14.04, 16.43, 19.756, 23.61, 40.50, 58.08, 124.45, 129.92, 131.02, 132.70, 133.21, 134.05, 137.56, 147.42, 165.89. Anal. Calcd for $C_{49}H_{66}FN_7O_9.3H_2O$: C, 60.66; H, 7.48; N, 10.11. Found: C, 60.20; H, 7.30; N, 9.98.

Complex 2: Complex **2** was prepared by charging excess (10eq) of tetrabutylammonium chloride to the suspension of **L** (52mg, 80 μmol) in 15ml dioxane. After addition of tetrabutylammonium chloride the suspension turned clear and the solution was warmed to ~ 80ºC, then solution was filtered and allowed for slow evaporation at room temperature. After 3 - 4 days colorless crystals of **2** were obtained. Yield 36% ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.94 (t, J = 7.29 Hz, 12H, -$NCH_2CH_2CH_2\mathit{CH_3}$), 1.32 (q, J = 7.3 Hz, 8H, -$NCH_2CH_2\mathit{CH_2}CH_3$), 1.55 (m, 8H, -$NCH_2\mathit{CH_2}CH_2CH_3$), 2.51(s, 9H), 3.18 (t, 8H, -$N\mathit{CH_2}CH_2CH_2CH_3$), 4.52 (d, 6H, J = 4.5 Hz), 7.54 (d, 3H, -CH_{Ar}, J = 7.4 Hz), 7.66 (t, 3H, -CH_{Ar}, J = 7.8 Hz), 7.75 (t, 3H, -CH_{Ar}, J = 7.4 Hz), 8.03 (d, 3H, -CH_{Ar}, J = 8 Hz), 8.76 (t, -*NH*, J = 5.2 Hz). ^{13}C NMR, 75MHz (DMSO-d_6) δ 14.06, 16.47, 19.78, 23.64, 40.50, 58.11, 124.51, 129.92, 131.08, 132.74, 133.25, 134.12, 137.62, 147.38, 165.93. Anal. Calcd for $C_{49}H_{66}ClN_7O_9$: C, 63.11; H, 7.13; N, 10.51. Found: C, 62.96; H, 7.28; N, 10.29.

Complex 3: Complex **3** was prepared by charging excess (15eq) of tetrabutylammonium nitrate to the suspension of **L** (52mg, 80 μmol) in 15ml dioxane. After addition of tetrabutylammonium nitrate the suspension turned clear and the solution was warmed to ~ 80ºC, then solution was filtered and allowed for slow evaporation at room temperature. After 6 days colorless crystals of **2** were obtained. Yield 27% ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.94 (t, J = 7.29 Hz, 12H, -$NCH_2CH_2CH_2\mathit{CH_3}$), 1.32 (q, J = 7.3 Hz, 8H, -$NCH_2CH_2\mathit{CH_2}CH_3$), 1.55 (m, 8H, -$NCH_2\mathit{CH_2}CH_2CH_3$), 2.51(s, 9H), 3.18 (t, 8H, -$N\mathit{CH_2}CH_2CH_2CH_3$), 4.52 (d, 6H, J = 4.5 Hz), 7.54 (d, 3H, -CH_{Ar}, J = 7.4 Hz), 7.66 (t, 3H, -CH_{Ar}, J = 7.8 Hz), 7.75 (t, 3H, -CH_{Ar}, J = 7.4 Hz), 8.03 (d, 3H, -CH_{Ar}, J = 8 Hz), 8.76 (t, -*NH*, J = 5.2 Hz). ^{13}C NMR, 75MHz (DMSO-d_6) δ 13.86, 16.26, 19.59, 23.44, 40.50, 57.92, 124.31, 129.72, 130.88, 132.54, 133.06, 133.92, 137.42, 147.18, 165.72. Anal. Calcd for $C_{49}H_{66}N_8O_{12}$: C, 61.36; H, 6.94; N, 11.68. Found: C, 61.54; H, 7.12; N, 11.54.

Complex 4: Complex **3** was prepared by charging excess (10eq) of tetrabutylammonium acetate to the suspension of **L** (52mg, 80 μmol) in 15ml dioxane. After addition of tetrabutylammonium acetate the suspension turned clear and the solution was warmed to

~ 80ºC, then solution was filtered and allowed for slow evaporation at room temperature. After 5 days colorless crystals of **1** were obtained. Yield 29%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.93 (t, 12H, -$NCH_2CH_2CH_2\mathit{CH_3}$), 1.30 (q, J = 6.9 Hz, 8H, -$NCH_2CH_2\mathit{CH_2}CH_3$), 1.57 (b, 11H, -$NCH_2\mathit{CH_2}CH_2CH_3$ and $\mathit{CH_3}COO^-$), 2.43 (s, 9H, -CH_3), 3.16 (t, 8H, -$N\mathit{CH_2}CH_2CH_2CH_3$), 4.52 (s, 12H, -NH-$\mathit{CH_2}$), 7.56 (d, 3H, -$CH_{Ar}$, *J* = 7.4 Hz), 7.67 (t, 3H, -CH_{Ar}, *J* = 7.8 Hz), 7.74 (t, 3H, -CH_{Ar}, *J* = 7.4 Hz), 8.02 (d, 3H, -CH_{Ar}, *J* = 8 Hz), 8.80 (b, -*NH*). ^{13}C NMR, 75MHz (DMSO-d_6) δ 14.01, 16.42, 19.77, 23.64, 40.50, 58.11, 124.37, 130.01, 130.98, 132.63, 133.17, 133.92, 137.50, 147.54, 165.84, 173.67. Anal. Calcd for $C_{49}H_{66}N_8O_{12}$: C, 64.24; H, 7.57; N, 10.09. Found: C, 64.48; H, 7.36; N, 10.12.

X-Ray Crystallographic Refinement details

The crystallographic data and details of data collection for **1**, **2**, **3** and **4** are given in Table S1. In each case, a crystal of suitable size was selected from the mother liquor and immersed in partone oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for all four crystals were collected using Mo Kα (l = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100K. The data integration and reduction were processed with SAINT[2a] software. An empirical absorption correction was applied to the collected reflections with SADABS[2b]. The structures were solved by direct methods using SHELXTL[3] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[4] program package. Graphics are generated using PLATON[5] and MERCURY 1.3.[6] In all cases, non-hydrogen atoms are treated anisotropically except disordered water molecule in complex **4** (treated isotropically).

The amide hydrogen atoms of complex **1** have been geometrically fixed and the hydrogen atoms associated with water molecules were located in the fourier map and refined isotropically. One of the tetrabutylammonium cation in Complex **1**, is terribly disordered. The occupancy factors of these atoms were refined using the FVAR command of the SHELXTL program and is anisotropically refined. Least square restraints have been applied to fix the $C(sp^3)\_C(sp^3)$ bond distances in the disordered tetrabutyl

ammonium cation. The hydrogen atoms associated with amide and water molecule in complex **2**, complex **3** and complex **4** were located in the fourier map and refined isotropically. The water molecule in complex **4,** disordered at two sites and the occupancy factor were refined using the FVAR command of the SHELXTL program and is isotropically refined. Though good crystals have been selected and the data have been collected at 100 K, complex **1**, **2** and **3**, did not show diffraction beyond the respective *theta max* obtained even after several data collections and we have not omitted any reflection during refinement.

References:

(1) Nativi, C.; Cacciarini, M.; Francesconi, O.; Vacca, A.; Moneti, G.; Lenco, A.; Roelens, S. *J. Am. Chem. Soc*. 2007, **129**, 4377.

(2) (a) SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.Sheldrick, G. M. (b) *SADABS, empirical absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(3) Sheldrick, G. M. *SHELXTL Reference Manual:* V*ersion 5.1*; Bruker AXS: Madison, WI, 1997.

(4) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(5) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

(6) Mercury 1.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004.

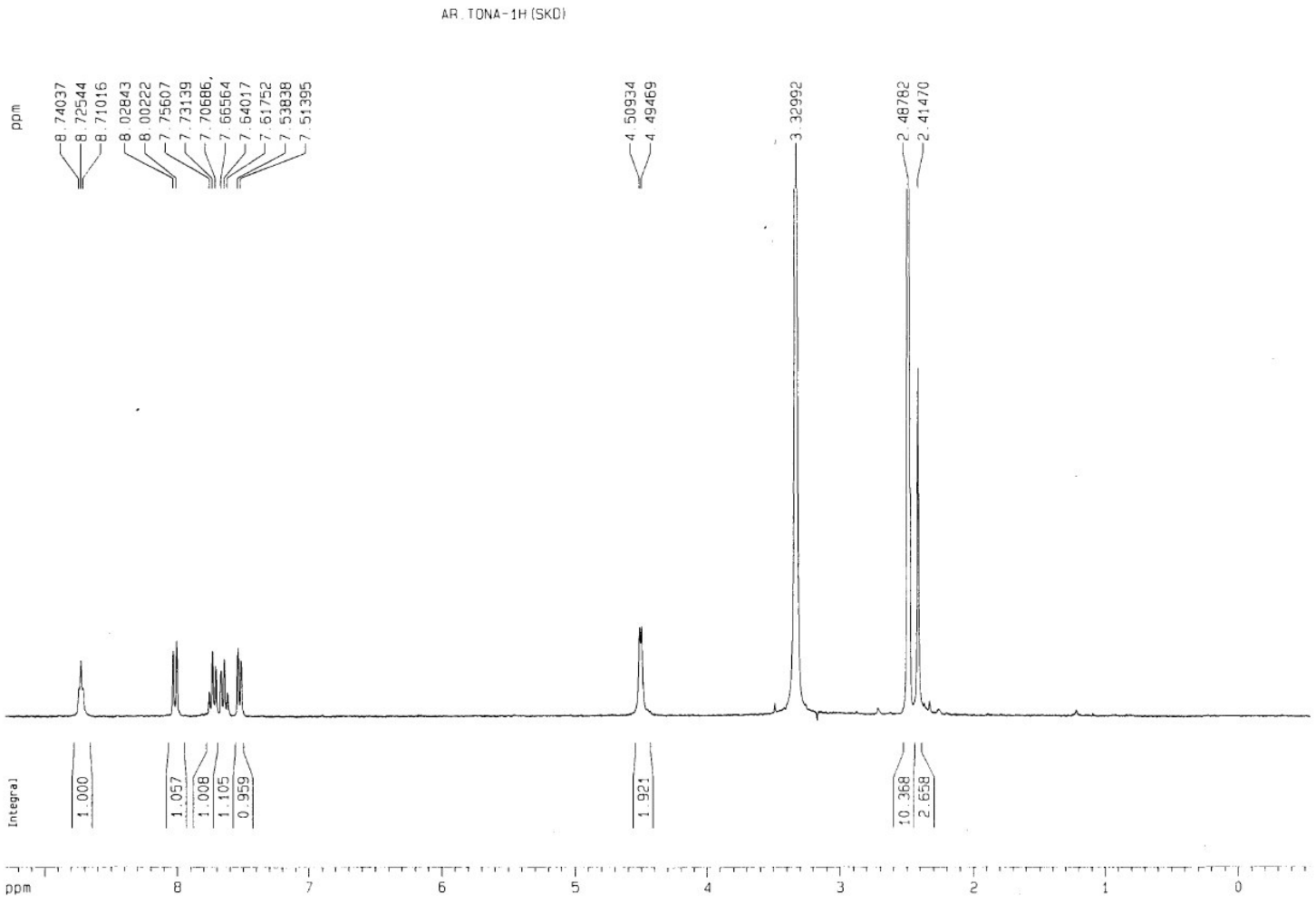

Figure S1. **^{1}H-NMR spectra of Complex L in DMSO-d_6 at 25°C**

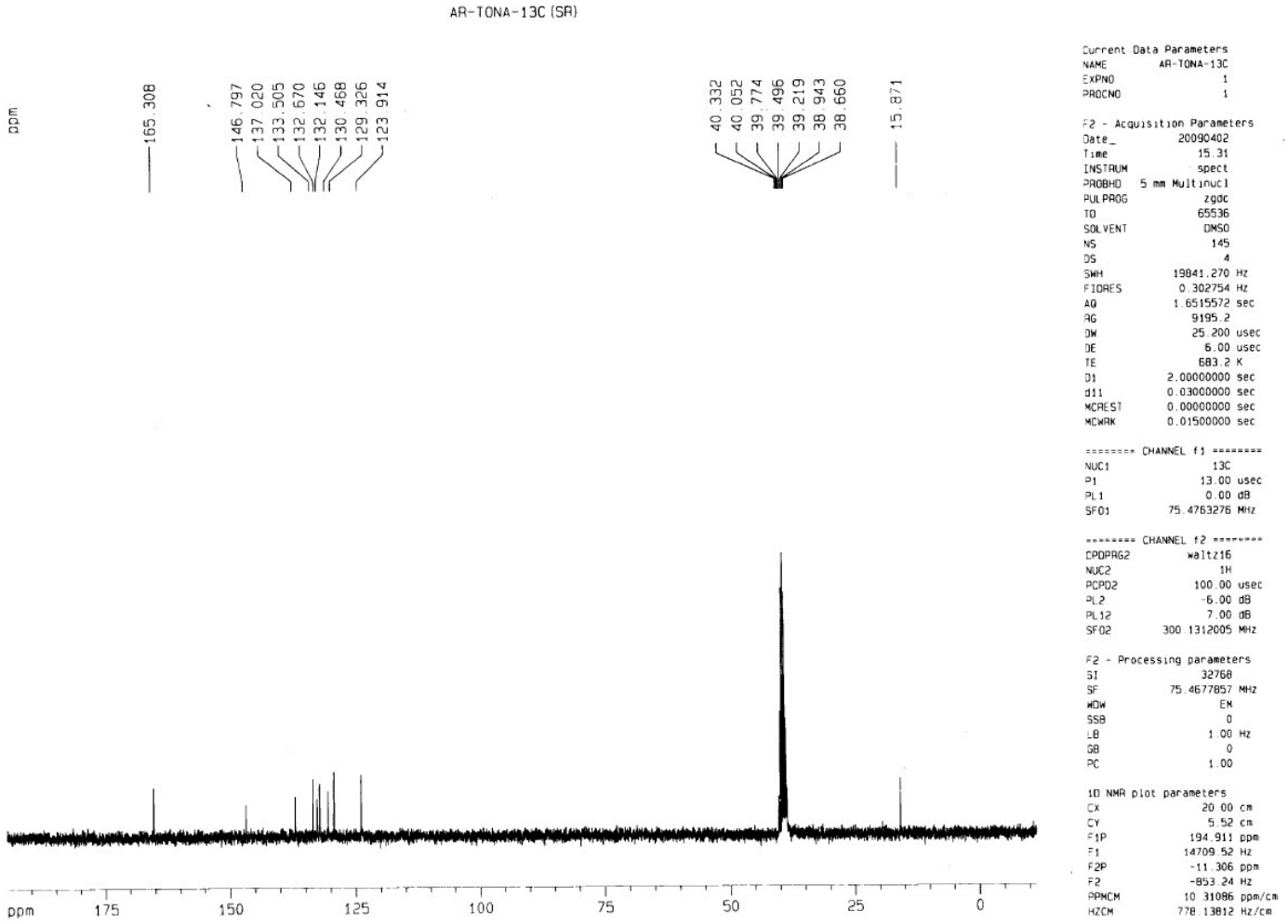

Figure S2. ^{13}C-NMR spectra of L in DMSO-d_6 at 25°C

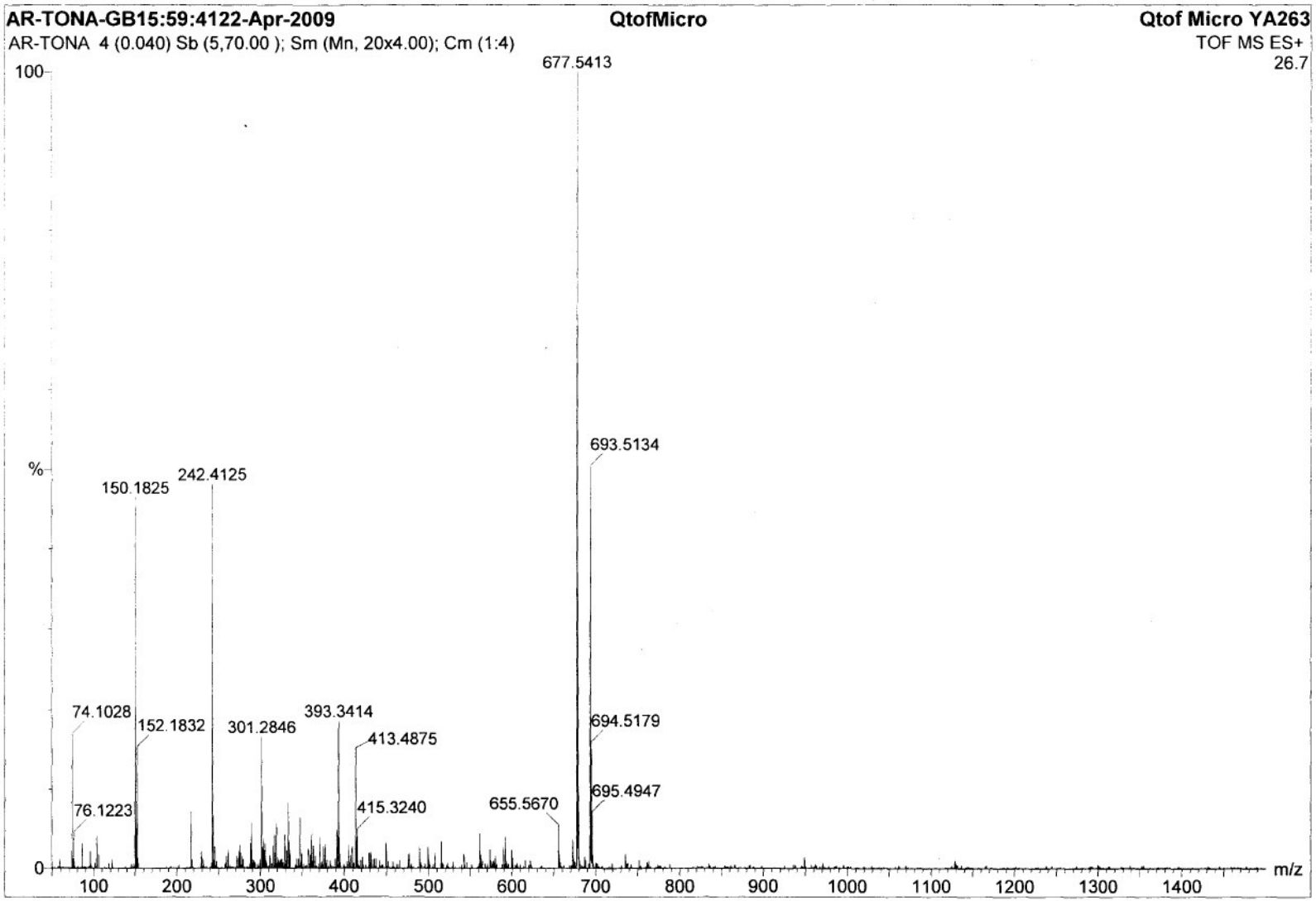

Figure S3. HRMS(ESI) spectrum of L.

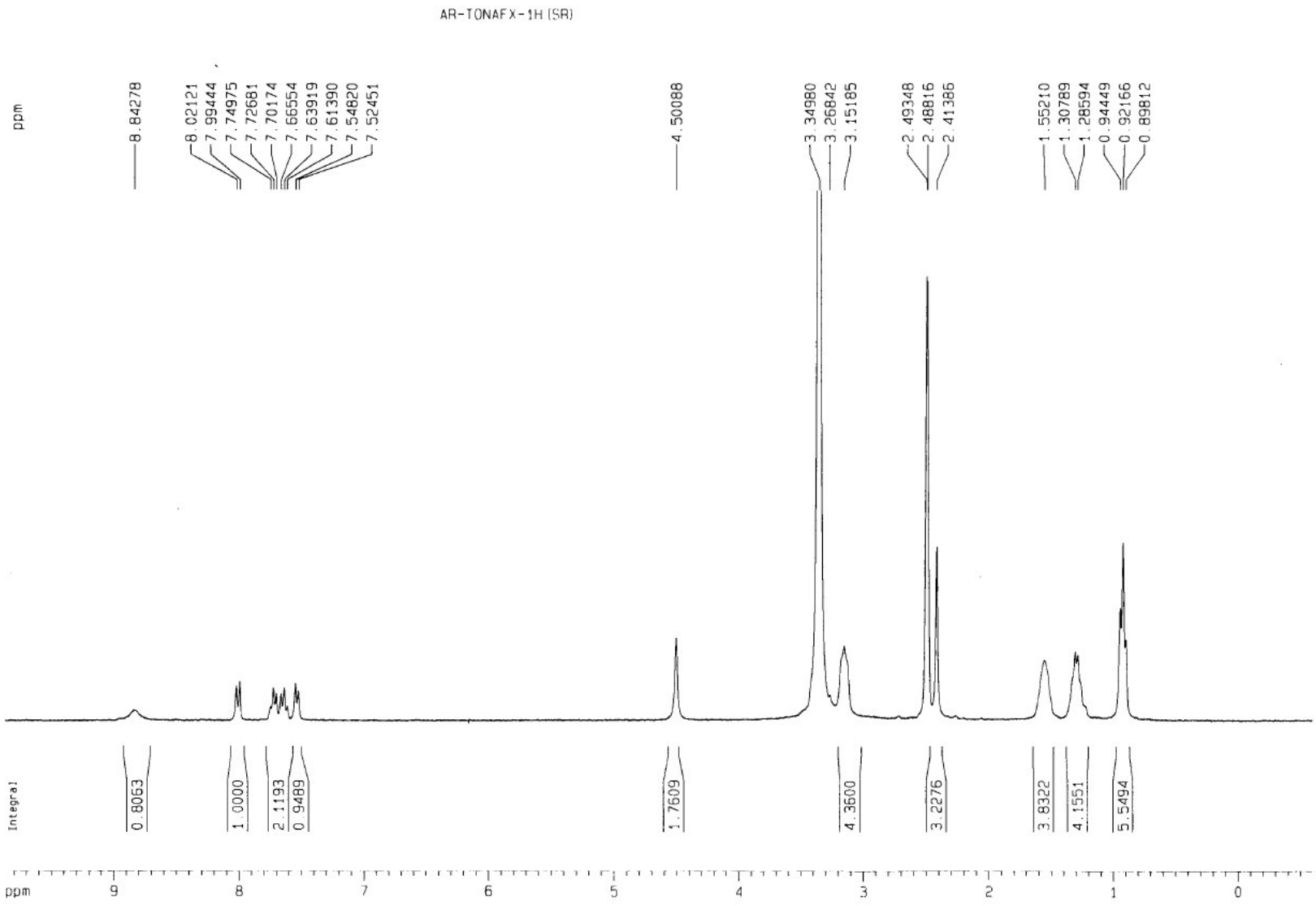

Figure S4. ^{1}H-NMR spectra of Complex 1 in DMSO-d_6 at 25^{o}C

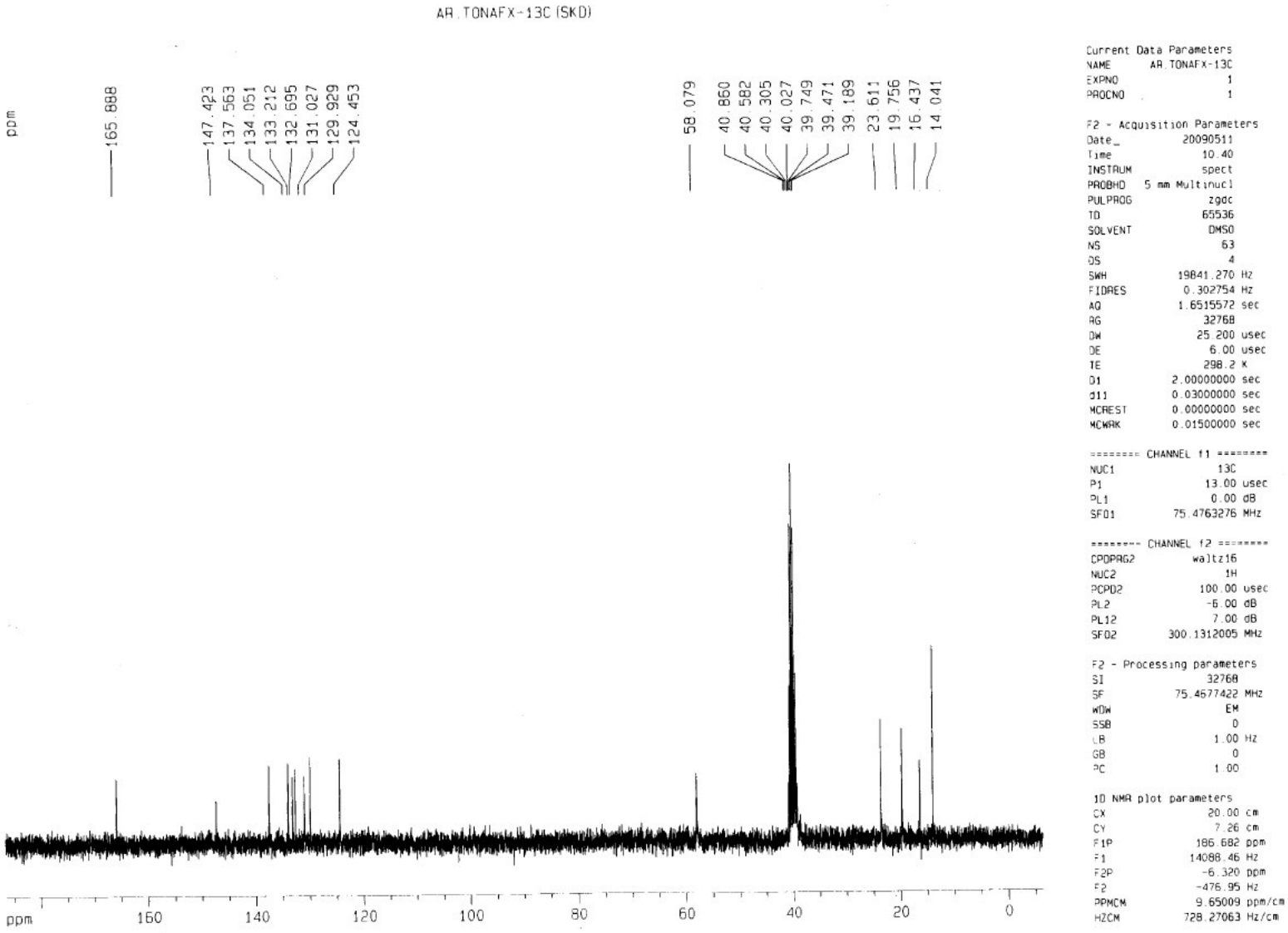

Figure S5. ^{13}C-NMR spectrum of Complex 1 DMSO-d_6 at 25°C.

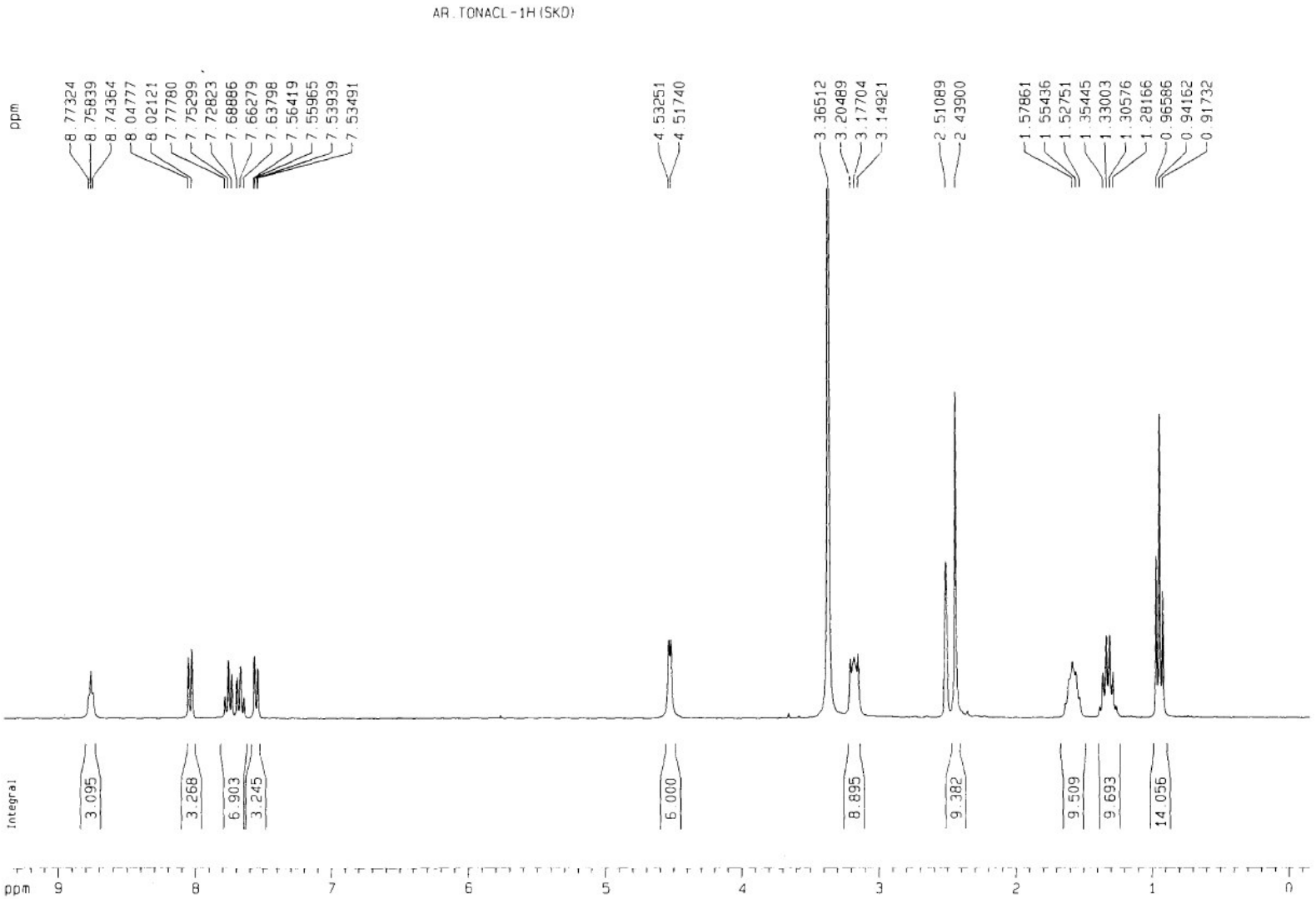

Figure S6. ^{1}H-NMR spectrum of Complex 2 DMSO-d_6 at 25°C.

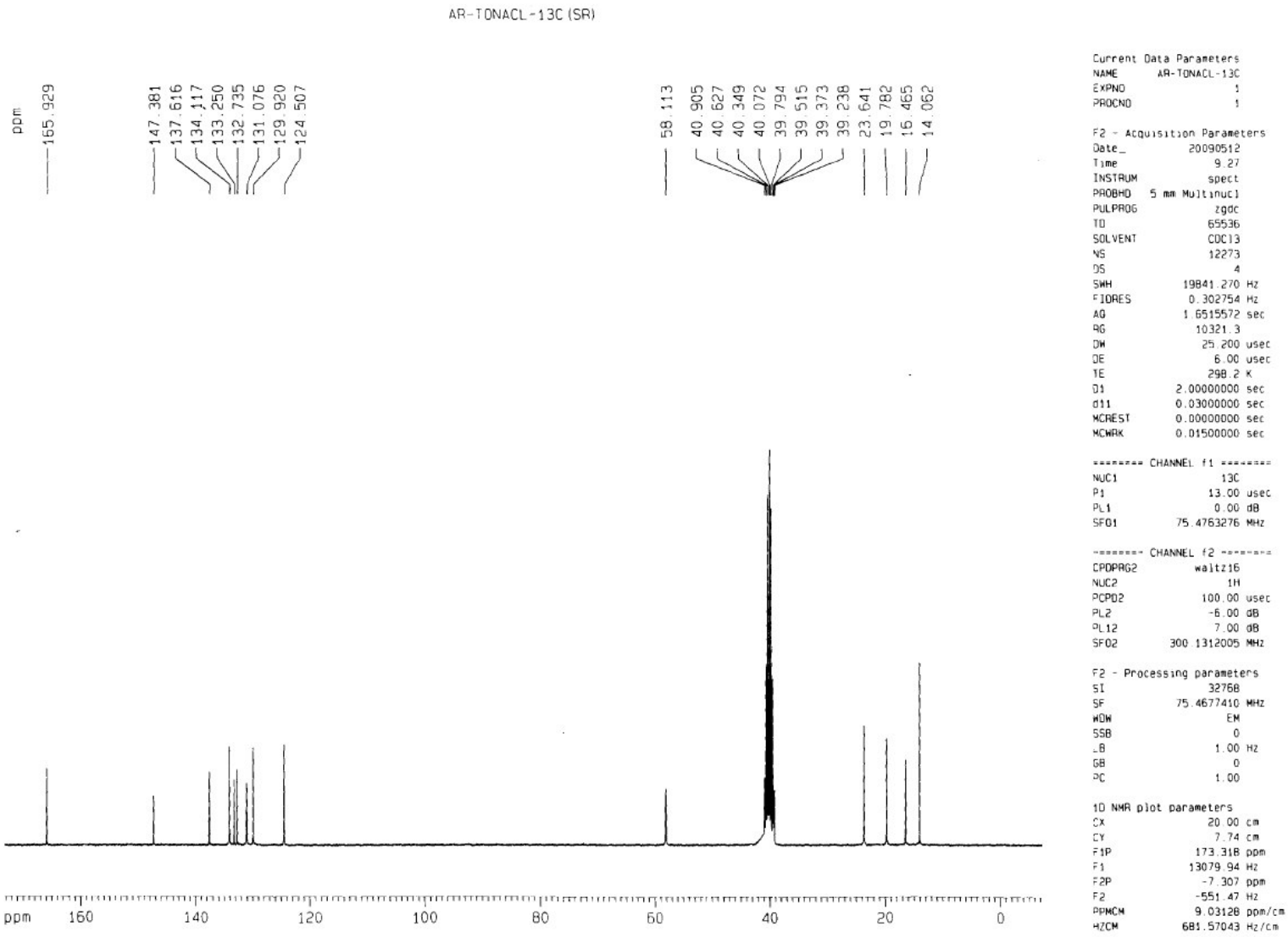

Figure S7. ^{13}C-NMR spectrum of Complex 2 DMSO-d_6 at 25^{o}C

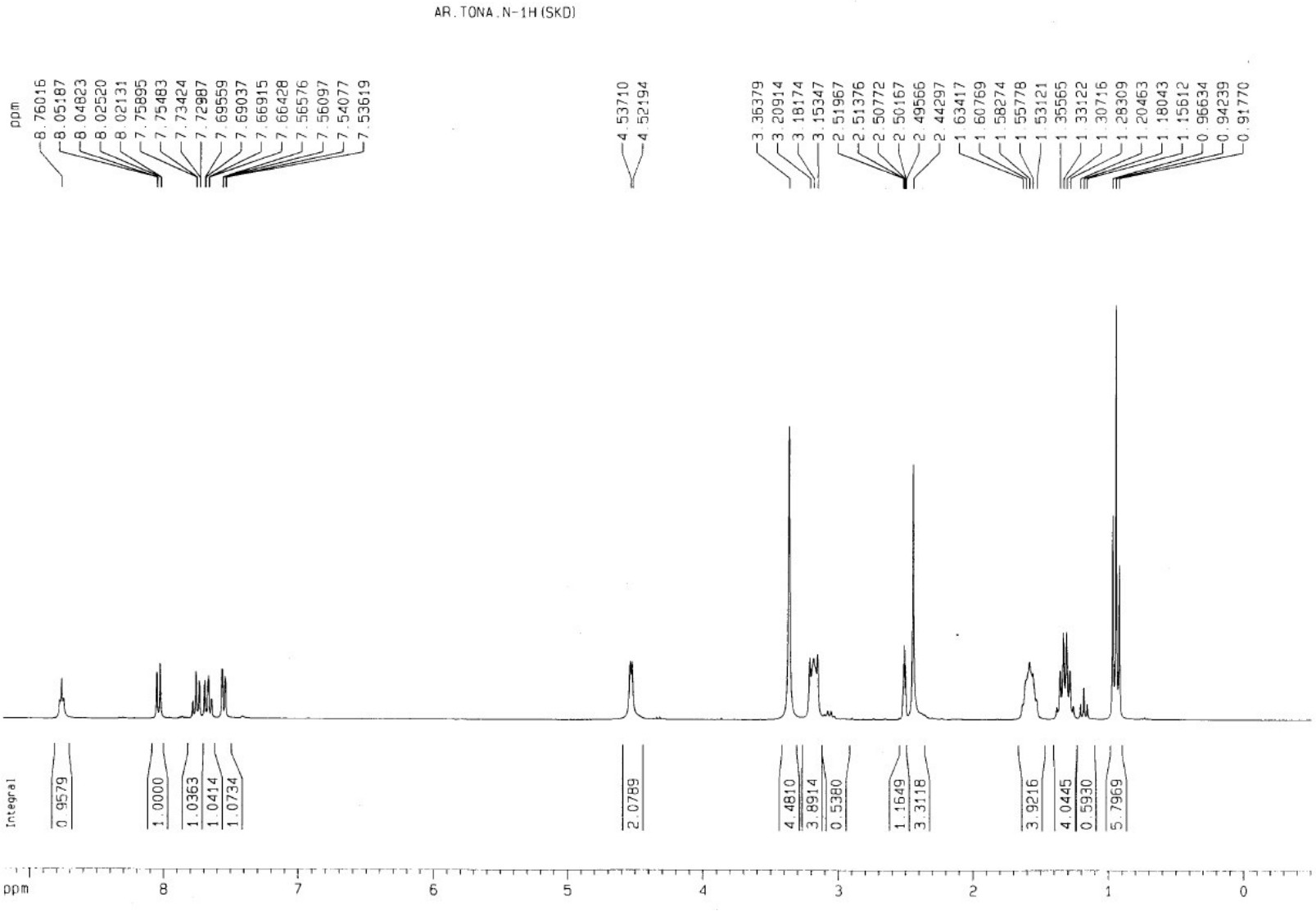

Figure S8. ^{1}H-NMR spectrum of Complex 3 DMSO-d_6 at 25ºC

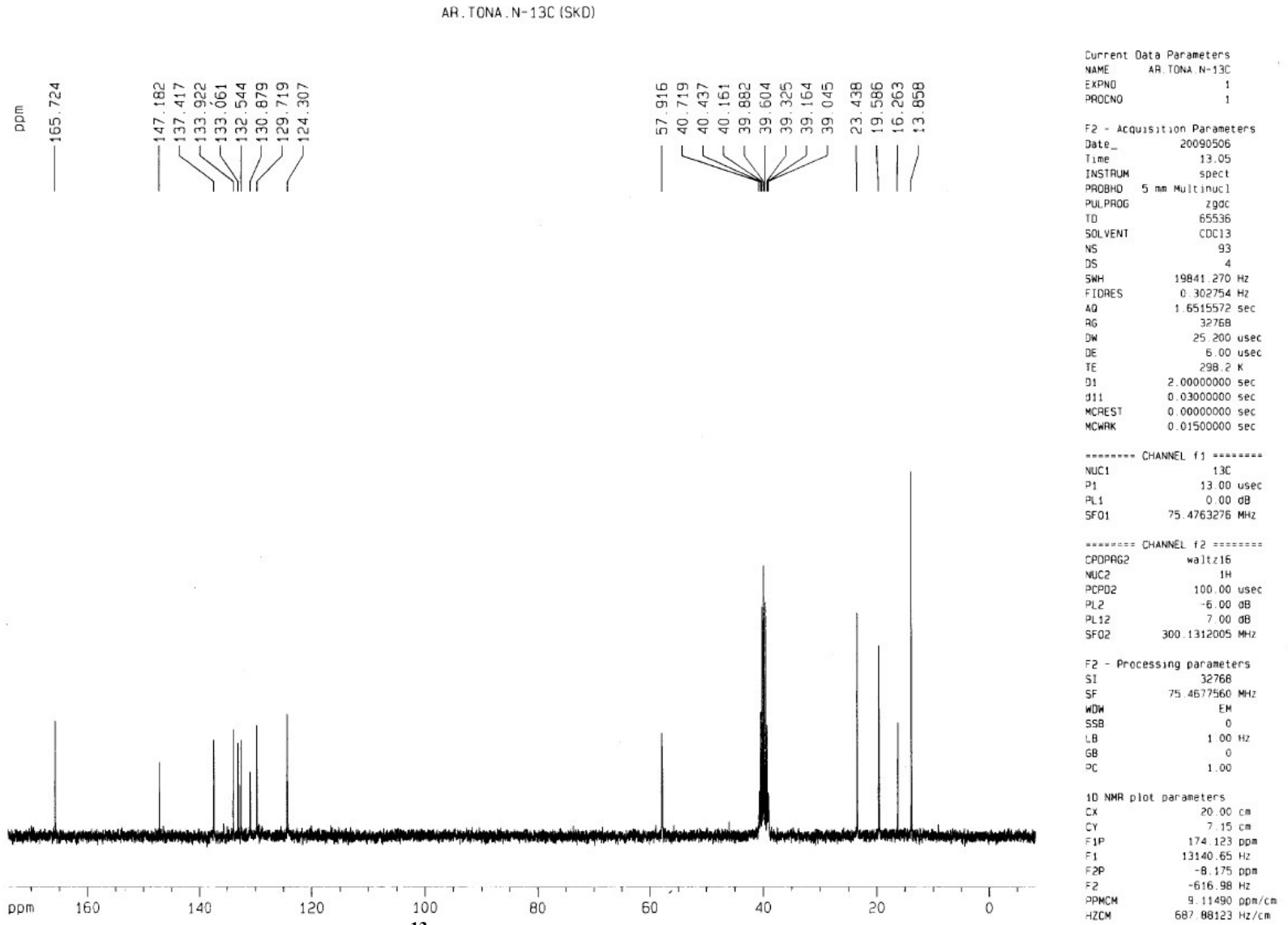

Figure S9. ^{13}C-NMR spectrum of Complex 3 DMSO-d$_6$ at 25ºC

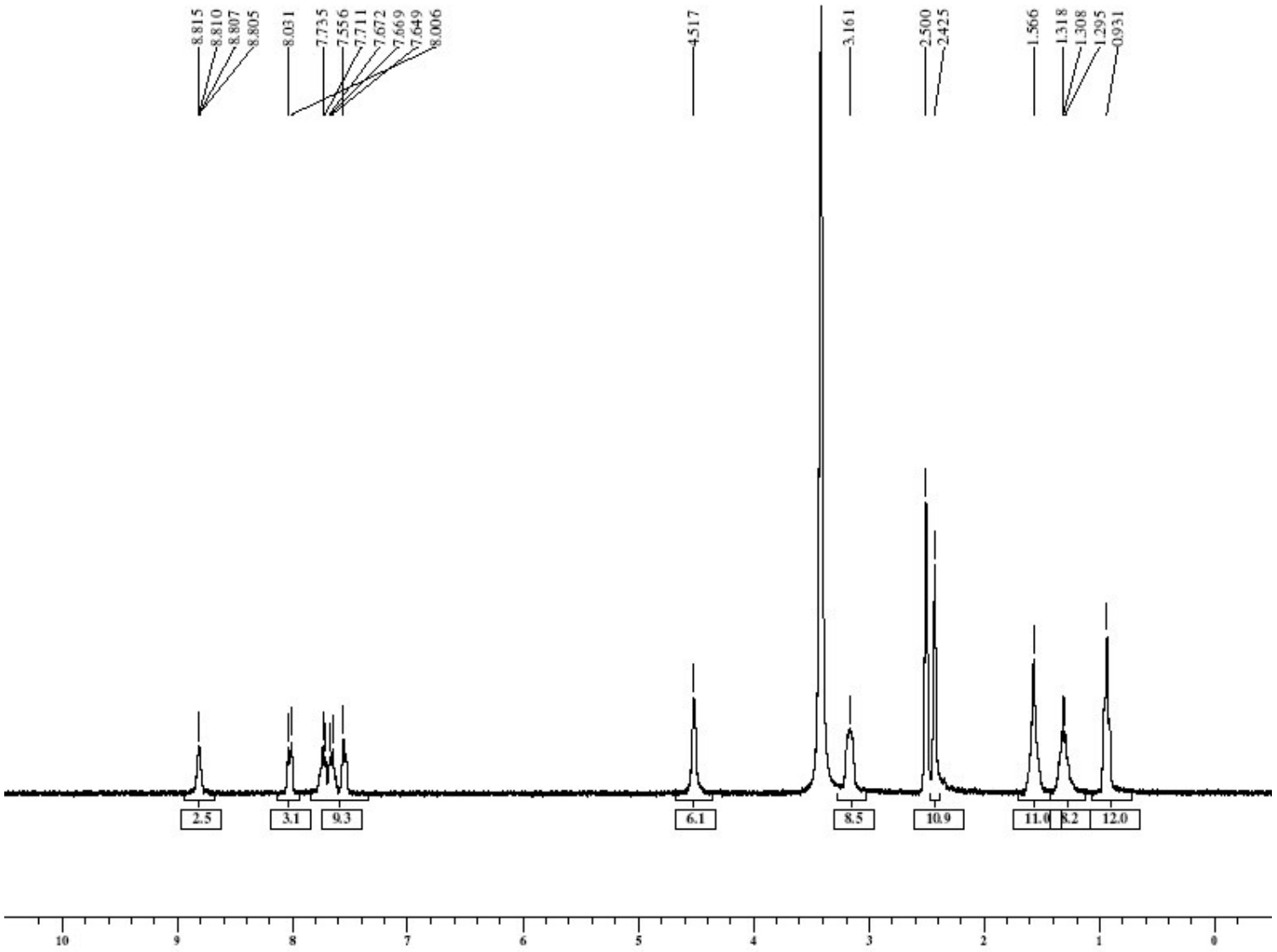

Figure S10. ^{1}H-NMR spectrum of Complex 4 DMSO-d_6 at 25^{o}C

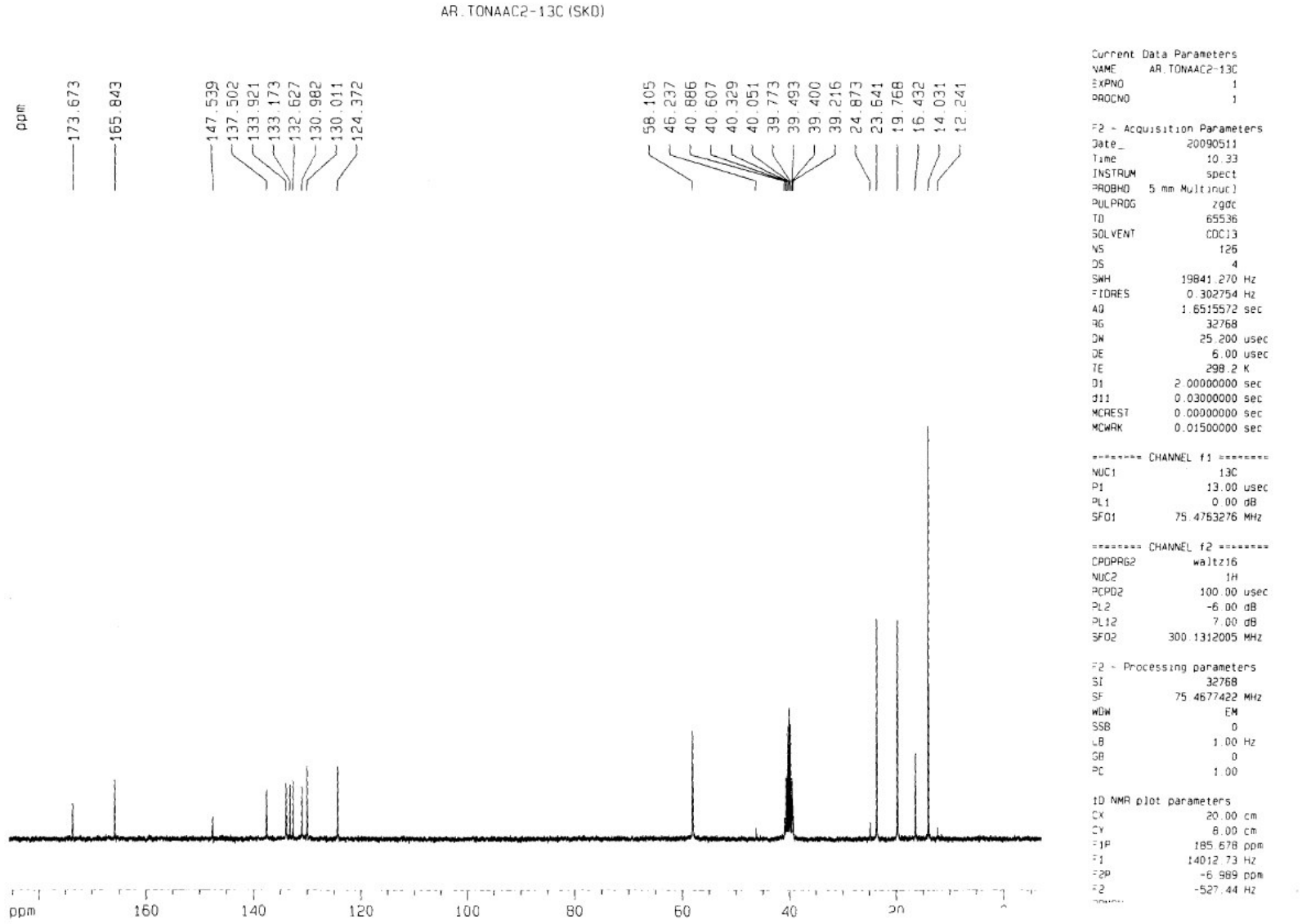

Figure S11. ^{13}C-NMR spectrum of Complex 3 DMSO-d_6 at 25ºC

Table S1. Table of Crystallographic parameters

Parameters	Complex 1	Complex 2	Complex 3	Complex 4
Empirical formula	$C_{106}H_{160}F_2N_{14}O_{28}$	$C_{49}H_{68}ClN_7O_{10}$	$C_{49}H_{66}N_8O_{12}$	$C_{51}H_{71}N_7O_{12}$
Formula weight	2113.48	950.55	959.10	974.15
crystal system	TRICLINIC	TRICLINIC	TRICLINIC	TRICLINIC
Space group	P-1	P-1	P-1	P-1
***a* (Å)**	12.9823(7)	12.945(2	12.922(6)	12.9277(19)
***b* (Å)**	20.3519(12)	14.4605(10)	14.152(7)	14.647(2)
***c* (Å)**	23.1725(13)	15.5879(12	15.351(7)	15.513(2)
***α* (deg)**	105.659(2	117.393(2)	116.614(6)	62.355(2)
***β* (deg)**	92.575(2)	95.911(2)	92.811(7)	73.693(2)
γ (deg)	105.648(2)	101.767(2)	101.864(7)	77.867(2)
***V* (Å^3)**	5630.8(5)	2470.5(5)	2424(2)	2486.4(6)
Z	2	2	2	2
d_{calc} (g/cm^3)	1.248	1.278	1.314	1.301
Crystal size (mm^3)	0.28 x 0.19 x 0.16	0.40 x 0.22 x 0.18	0.36 x 0.27 x 0.16	0.24 x 0.16 x 0.14
Diffractometer	Smart CCD	Smart CCD	Smart CCD	Smart CCD
***F*(000)**	2272	1016	1024	1044
μMoKα (mm^{-1})	0.71073	0.71073	0.71073	0.71073
***T* (K)**	100 (2)	100 (2)	100 (2)	100 (2)
2θ max	22.67	22.95	23.89	24.96
Observed Reflections	14944	6810	7484	8696
Parameters refined	1388	631	641	650
R_1; WR_2	0.0759; 0.2118	0.0415; 0.0873	0.0732;0.1747	0.0529;0.1383
GOF (F2)	1.034	1.001	0.965	1.027

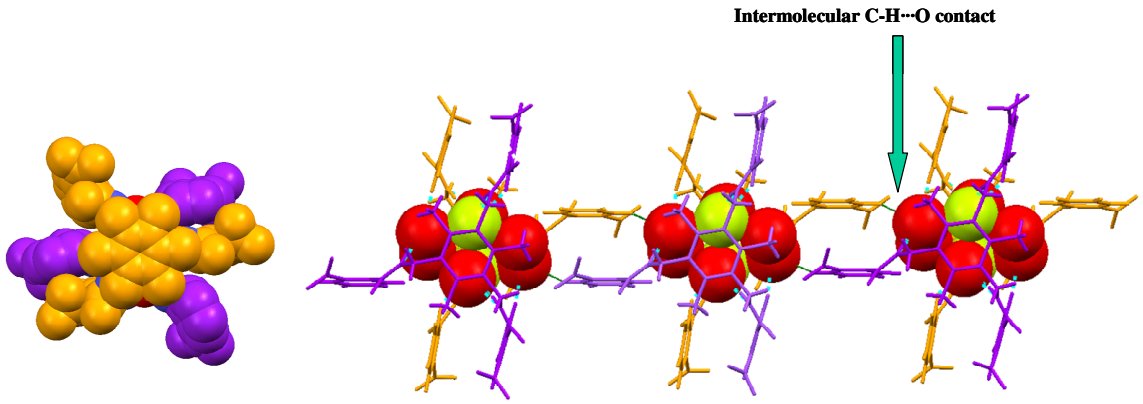

Figure S12. (a) Space fill view of the dimeric capsule of complex **1** showing the complete encapsulation of the $[F_2(H_2O)_6]^{2-}$ guest. (b) View showing the intermolecular C-H···O hydrogen bonding interactions in **1**.

Table S2. Hydrogen Bonding Parameters for **2**

D-H…A	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (º)**
O2-H2A···Cl1[1]	0.88(5)	2.30(5)	3.167(3)	168(4)
N7-H7···Cl1[2]	0.90(3)	2.27(3)	3.172(3)	178(2)
N23-H23···Cl1[2]	0.92(3)	2.35(3)	3.260(3)	169(2)
N39-H39···O2[3]	0.79(2)	2.14(2)	2.914(3)	172(3)
C27-H27···Cl1[2]	0.9288	2.7408	3.537(3)	144.34
C45-H45···Cl1[4]	0.9300	2.8224	3.404(3)	121.70
1 = 1+x,y,z; 2 = x,y,z; 3 = -1+x,y,z 4= -x,2-y,1-z				

Table S3. Hydrogen Bonding Parameters for Complex **3**

D-H…A	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (º)**
N9-H9···O4[1]	0.96(5)	2.12(6)	3.035(5)	160(5)
N25-H25···O2[1]	0.82(4)	2.15(4)	2.942(5)	162(4)
N41-H41···O3[1]	0.85(6)	2.15(6)	2.982(5)	169(6)
C29-H29···O2[1]	0.931(5)	2.509(4)	3.248(6)	136.5(3)
C48-H48···O2[2]	0.930	2.685	3.522	150.12
C13-H13···O3[1]	0.929(4)	2.554(3)	3.437(6)	158.8(3)
C30-H30···O3[2]	0.931	2.618	3.287	129.32
C13-H13···O4[1]	0.929	2.602	3.443	150.68
C16-H16···O4[3]	0.929	2.692	3.199(7)	115.16
1 = X, Y, Z; 2 = -x,1-y,1-z; 3= -x,-y,1-z				

Table S4. Hydrogen Bonding Parameters for Complex **4**

D-H…A	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (º)**
N10-H10···O5A[1]	0.92(3)	1.98(3)	2.877(3)	165(3)
N26-H26···O3[2]	0.87(3)	2.08(3)	2.886(3)	154(3)
N42-H42···O1[2]	0.80(3)	2.08(3)	2.853(3)	163(3)
C46-H46···O1[2]	0.9300	2.2546	3.161(3)	164.80
C17-H17···O3[1]	0.9299	2.3936	3.312(3)	169.57
1 = x, y, z; 2 = 2-x,1-y,1-z				

Crystal structure description of Complex 2, [L.TBA-Cl.H_2O]

The bowl shaped cavity of **L** consists one chloride (Cl1) and a water molecule (O2)**.** The encapsulated chloride(Cl1) is in two strong N-H···Cl interactions with the amide nitrogens N23 and N7, one aryl-C-H···Cl interactions with C27 and one O-H···Cl interaction with the encapsulated water O2. This encapsulated water O2 is in N-H···O interaction with amide nitrogen N39 of **L** (Table S2). The dimeric aggreation is favored via intermolecular aryl-C-H···Cl and aryl-C-H···O interactions of Cl1 and O2 with C45 and C14 of another unit of **L** respectively (Figure S13). It is important to note that in this case intermolecular interactions of chloride and water encapsulated receptor does not result the capsule formation as it is observed in case of **1**. This indicates that the size and shape of the resulting template of the anionic guest can tune the assembly of a receptor.

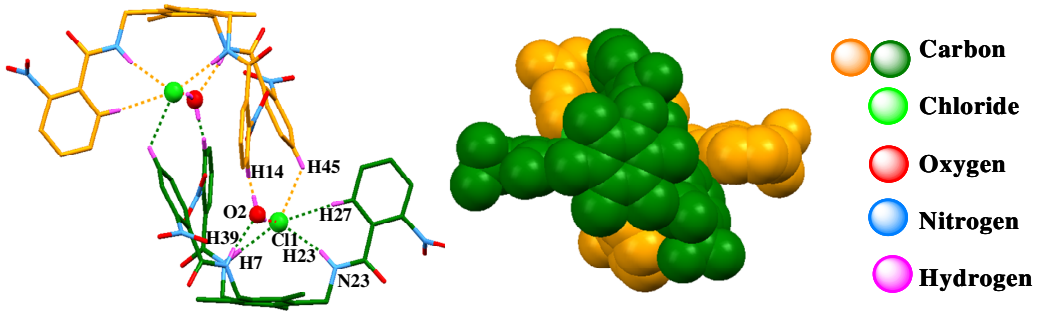

Figure S13. (a) View of the distorted dimeric capsular assembly of **2,** (b) View along the apical benzene cap of the non-capsular dimer**.** Tetrabutylammonium counter anion and the non-bonded hydrogen atoms were omitted for clarity.

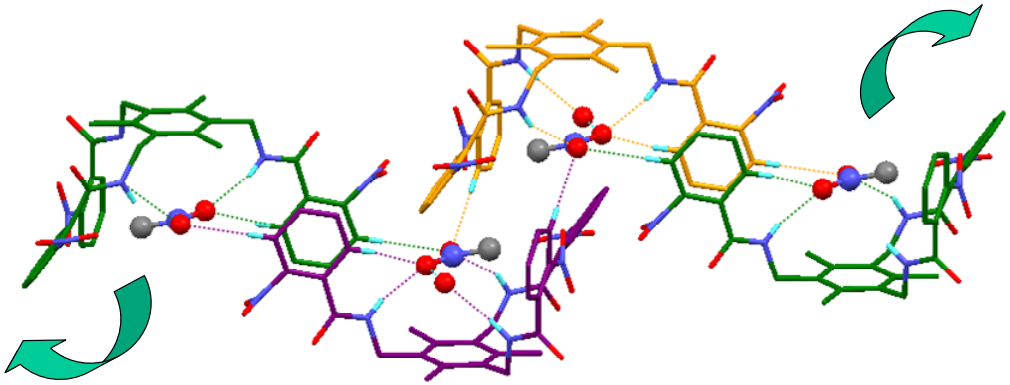

Figure S14. Partial view of the non-capsular assembly of **4** upon acetate encapsulation**.** Tetrabutylammonium counter anion, disordered oxygen atom and the non-bonded hydrogen atoms were omitted for clarity.

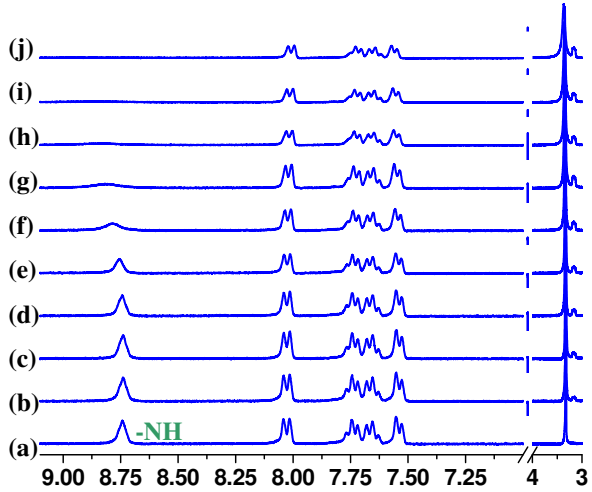

Figure S15. (a) ^{1}H-NMR (300 MHz) spectral changes of **L** with added n-Bu_4N^+ F^- in DMSO-d_6 (25ºC) ($[H]_0$ = 19.9 mM). Ratio of concentration [G]/[H]: (a) 0, (b) 0.09, (c) 0.15, (d) 0.2, (e) 0.24, (f) 0.29, (g) 0.34, (h) 0.39 (i) 0.44 and (j) 0.53.

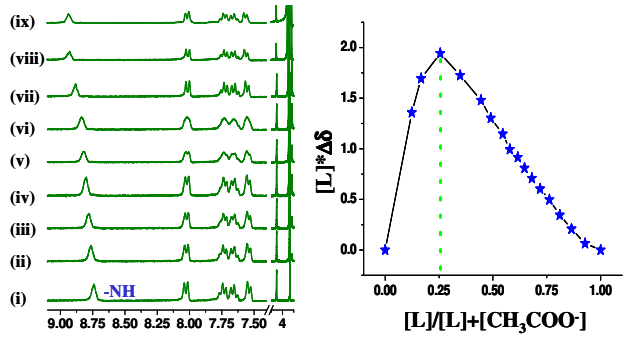

Figure S16. (a) ^{1}H-NMR (300 MHz) spectral changes of **L** with added n-Bu_4N^+ CH_3COO^- in DMSO-d_6 (25ºC) ($[H]_0$ = 16.5 mM). Ratio of concentration [G]/[H]: (i) 0, (ii) 0.3, (iii) 0.6, (iv) 0.8, (v) 1.0, (vi) 1.9, (vii) 3.0, (viii) 5.0 and (ix) 7.0 ; (b) Job's plot for the binding of acetate anion to the host **L**.