

Supporting Information

Organic and Organometallic Derivatives of Dihydrogen-encapsuled [60]Fullerene

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1. Procedures for Synthesis of 1-4

General. All experiments in this paper were performed with the use of an abundant H₂-containing H₂@C₆₀ (H₂@C₆₀/C₆₀ = 4/1). ¹H (400 MHz, 500 MHz) and ¹³C (100 MHz, 125 MHz) NMR spectra were recorded on a JEOL ECA500 spectrometer. ¹H and ¹³C NMR spectra were referenced to internal tetramethylsilane (δ 0.00) and residual solvent carbons (CDCl₃: δ 77.0; THF: δ 67.4), respectively. Except the signal due to encapsulated hydrogen, NMR signals matched with those of empty authentic samples. Mass spectra were measured on a JEOL JMS-T100LC APCI/ESI-TOF mass spectrometer.

Synthesis of 6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro(C₆₀-I_h)[5,6]fullerene-incar-dihydrogen (1). To a white powder of CuBr·SMe₂ (22 mg, 0.10 mmol) was added a THF (0.5 mL) solution of PhMgBr (0.10 mmol) and then was added H₂@C₆₀ (5.0 mg, 0.0069 mmol) in 1,2-dichlorobenzene (0.5 mL) at room temperature. After stirring for 12 hour at 30 °C, proceeding of the reaction was checked with HPLC (Buckyprep column; eluent: toluene/2-propanol = 7/3; flow rate: 1.0 mL/min; retention time: ca. 5.7 min) and quenched with saturated aqueous solution of NH₄Cl (0.5 mL). The mixture was diluted with toluene and filtered by passing through a pad of silica gel. The filtrate was evaporated under reduced pressure to a small volume, and diluted quickly with MeOH to precipitate orange powder. Solid was collected by filtration and washed with MeOH and hexane to obtain the title compound (92% yield). ¹H NMR (500 MHz, CDCl₃/CS₂ 1/1): δ -10.39 (s, 2H (80%), *incar*-H₂), 5.29 (s, 1H, FullereneCp-H), 7.0-7.7 (m, 25H, Ph). ¹³C NMR (125 MHz, CDCl₃/CS₂ 1/1): δ 58.58 (C₆₀-Ph-sp³), 58.73 (C₆₀-Ph-sp³), 60.81 (C₆₀-Ph-sp³), 62.97 (FullereneCp-sp³), 127.05, 127.35, 127.52, 127.62, 127.83, 127.97, 128.47, 128.67, and 128.76 (*o*-, *m*-, and *p*-Ph), 139.33, 139.37, 143.05, 143.64, 143.97, 144.00, 144.21, 144.32, 145.27, 145.55, 145.61, 146.09, 147.07, 147.10, 147.42, 147.73, 148.07, 148.16, 148.38, 148.65, 148.71, 151.48, 152.03, 152.30, and 155.93 (C₆₀-sp² and *ipso*-Ph). MS (APCI) calcd for [M-H⁺] 1108, found 1108.

Synthesis of [6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro(C₆₀-I_h)[5,6]fulleren-incar-dihydrogen-1(6H)-yl]potassium (2). A Schlenk tube was charged with C₆₀Ph₅H (4.0 mg, 0.0036 mmol) and excess amount of potassium hydride (4.0 mg, 0.10 mol) which was washed with dried hexane. Addition of THF (1.0 mL) to the Schlenk tube gave dark

red solution with evolving H₂ gas. After stirring for 10 min at 25 °C, the reaction mixture was transferred to a centrifugation tube via cannula. The dark red solution was separated from potassium hydride by centrifugation and transferred to a Schlenk tube. Solvent was removed under reduced pressure to obtain dark red microcrystalline solid which was washed with dried hexane to obtain the title compound (95% yield). ¹H NMR (500 MHz, THF-*d*₈): δ -9.79 (br s, 2H (80%), *incar*-H₂), 7.03 (br s, 15H, *m*- and *p*-Ph), 7.91 (br s, 10H, *o*-Ph). ¹³C NMR (125 MHz, THF-*d*₈): δ 62.40 (C₆₀-sp³), 126.10 (*p*-Ph), 128.08 (*m*-Ph), 128.99 (FullereneCp), 129.41 (*o*-Ph), 143.26 (C₆₀-sp²), 146.38 (C₆₀-sp²), 146.68 (C₆₀-sp²), 147.33 (*ipso*-Ph), 147.45 (C₆₀-sp²), 149.46 (C₆₀-sp²), 160.08 (C₆₀-sp²).

Synthesis

of

(η⁵-cyclopentadienyl)[6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro(C₆₀-I_h)[5,6]fulleren-*incar*-dihydrogen-1(6*H*)-yl]iron(II) (3). Compound **1** (5.0 mg, 0.0045 mmol) and [FeCp(CO)₂]₂ (2.4 mg, 0.0068 mmol) in PhCN (1.00 mL) was degassed under reduced pressure (~0.3 mmHg) over 30 min at 0 °C, and the resulting mixture was stirred at 180 °C for 20 h. Solvent was removed under reduced pressure at 50 °C, and the resulting black solid was extracted with toluene (10 mL). The red toluene solution was filtered with a pad of silica gel, and toluene was evaporated to obtain orange microcrystals of the title compound (71% yield). ¹H NMR (500 MHz, CDCl₃/CS₂ 1/1): δ -10.44 (s, 2H (80%), *incar*-H₂), 3.20 (s, 15H, Cp), 7.35 (t, 10H, *m*-Ph), 7.40 (t, 5H, *p*-Ph), 7.94 (d, 10H, *o*-Ph). ¹³C NMR (125 MHz, CDCl₃/CS₂ 1/1): δ 58.53 (C₆₀-sp³), 73.37 (C₅H₅), 92.98 (FullereneCp), 127.73 (*p*-Ph), 127.84 (*m*-Ph), 129.29 (*o*-Ph), 143.20 (C₆₀-sp²), 143.36 (*ipso*-Ph), 144.17 (C₆₀-sp²), 147.54 (C₆₀-sp²), 148.34 (C₆₀-sp²), 148.59 (C₆₀-sp²), 152.73 (C₆₀-sp²). MS (APCI) calcd for [M] 1229, found 1229.

6,12,15,18-Tetra(piperidin-1-yl)-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-*incar*-dihydrogen (4a). A mixture of H₂@C₆₀ (1.00 mg, 1.4 μmol) and piperidine (0.71 mg, 8.3 μmol) in O₂-saturated solution of 20% DMSO in chlorobenzene (0.1 mL/0.4 mL) was stirred at ambient temperature for 12 h. The yield of the title compound **4a** was estimated to be 80% by HPLC analysis (ODS column) using 9,10-dibromoanthracene as an internal standard. The title compound **4a** was isolated and purified by the same procedure reported for C₆₀. ¹H NMR (500 MHz, CDCl₃) δ -10.77 (s, 2H (80%), *incar*-H₂), 1.53-1.79 (br m, 24H), 3.10-3.37 (br m, 16H); MS (ESI) calcd for [M⁺] 1074, found 1074.

6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)ox

ireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-incar-dihydrogen (4b). A mixture of H₂@C₆₀ (1.00 mg, 1.4 μmol) and 4-(hydroxyethyl)piperidine (1.08 mg, 8.3 μmol) in O₂-saturated solution of 20% DMSO in chlorobenzene (0.1 mL/0.4 mL) was stirred at ambient temperature for 24 h. The yield of the title compound **4b** was estimated to be 78% by HPLC analysis (ODS column) using 1-acetyl-3-hydroxyindole as an internal standard. The title compound **4b** was isolated and purified by the same procedure reported for C₆₀. The compound has an amphiphilic character and dissolves in various solvents. The ¹H NMR spectra of the compound were therefore obtained in various deuterated solvents. ¹H NMR (500 MHz, D₂O/DMSO-*d*₆ 1/9) δ -10.85 (s, 2H (80%), *incar-H*₂), 1.11-1.28 (m, 12H), 1.29-1.35 (m, 2H), 1.36-1.51 (m, 2H), 1.52-1.64 (m, 2H), 1.70-1.82 (m, 2H), 1.97-2.16 (m, 22H), 2.72-2.81 (m, 2H), 3.13-3.22 (m, 2H), 3.33-3.47 (m, 6H); ¹H NMR (500 MHz, DMSO-*d*₆) δ -10.80 (s, 2H (80%), *incar-H*₂), 1.20-1.31 (br m, 8H), 1.38-1.46 (br m, 12H), 1.74-1.87 (br m, 8H), 2.72-2.79 (br m, 2H), 2.85-3.13 (br m, 6H), 3.43-3.60 (m, 12H), 3.67 (d, *J* = 12 Hz, 2H), 3.81 (d, *J* = 12 Hz, 2H), 4.37 (t, *J* = 6 Hz, 2H), 4.38 (t, *J* = 6 Hz, 2H); ¹H NMR (400 MHz, DMSO-*d*₆/toluene-*d*₈ 1/1) δ -10.76 (s, 2H (80%), *incar-H*₂), 1.38-2.20 (br m, 28H), 2.78-2.90 (m, 10H), 2.90-3.17 (m, 6H), 3.80-4.14 (m, 8H), 4.69-4.83 (m, 4H); ¹H NMR (400 MHz, THF-*d*₈) δ -10.74 (s, 2H (80%), *incar-H*₂), 1.47-1.66 (m, 20 H), 1.82-1.96 (m, 8H), 2.63-2.72 (m, 2H), 2.72-2.91 (m, 6H), 3.19-3.30 (m, 4H), 3.30-3.42 (m, 8H), 3.78 (d, *J* = 13 Hz, 2H), 3.94 (d, *J* = 13 Hz, 2H); MS (APCI) calcd for [M⁺] 1250, found 1250.

2. X-ray Crystallographic Data for 2 and 3

Single crystals of **2** and **3** suitable for X-ray diffraction studies were grown and subjected to data collection. The data sets were collected on a MacScience DIP2030 Imaging Plate diffractometer using MoK α (graphite monochromated, $\lambda = 0.71069$ Å) radiation. Crystal data and data statistics are summarized in Table S1. The structure of **2** and **3** was solved by the direct method (SIR97).¹ The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.² Encapsulated H₂ molecules are placed at differential Fourier peak and refined isotropically. Another hydrogen atoms were placed at calculated positions and refined riding on their corresponding carbon atoms. In the subsequent refinement, the function $\sum \omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum (||F_o| - |F_c||) / \sum |F_o|$ and $wR2 = [\sum \omega (F_o^2 - F_c^2)^2 / \sum (\omega F_o^4)]^{1/2}$. Figure S1 shows ORTEP diagram of the crystal structure of **3**. Figure S2 shows electron density maps (PLATON contour maps) for **2** and **3**.

Table S1. Crystal Data and Structure Analysis Results for **2** and **3**.

	2 ·(THF) ₃	3 ·CS ₂
formula	C ₁₁₄ H _{74.6} KO ₆	C ₉₆ H _{31.6} FeS ₂
crystal system	monoclinic	orthorhombic
space group	<i>C2/c</i> (No. 15)	<i>P2₁2₁2₁</i> (No. 19)
<i>R</i> , <i>R_w</i> (<i>I</i> > 2σ(<i>I</i>))	0.1348, 0.3420	0.0652, 0.1661
<i>R</i> 1, <i>wR</i> 2 (all data)	0.2623, 0.4264	0.0743, 0.1765
GOF on <i>F</i> ²	1.163	1.021
<i>a</i> , Å	23.698(3)	15.167(1)
<i>b</i> , Å	14.500(2)	17.366(2)
<i>c</i> , Å	43.921(5)	20.553(8)
α, deg	90	90
β, deg	98.740(5)	90
γ, deg	90	90
<i>V</i> , Å ³	14916.8(9)	5413.5(7)
<i>Z</i>	8	4
<i>T</i> , K	153(2)	153(2)
crystal size, mm	0.80, 0.50, 0.12	0.40, 0.15, 0.10
<i>D</i> _{calcd} , g/cm ³	1.407	1.601
2θ _{min} , 2θ _{max} , deg	4.12, 51.38	4.60, 51.44
no. refl. measured (unique)	57742	37937
no. refl. measured (<i>I</i> > 2σ(<i>I</i>))	13738	5162
no. parameters	992	901

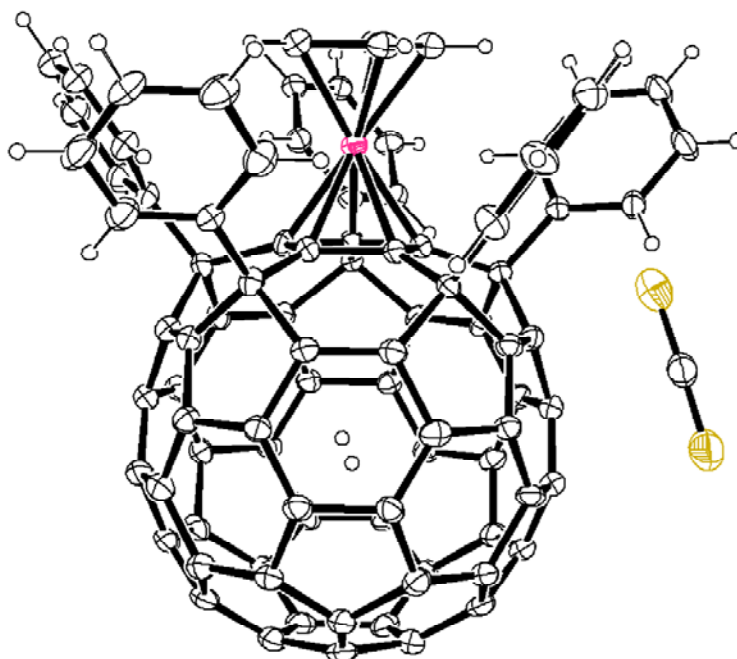
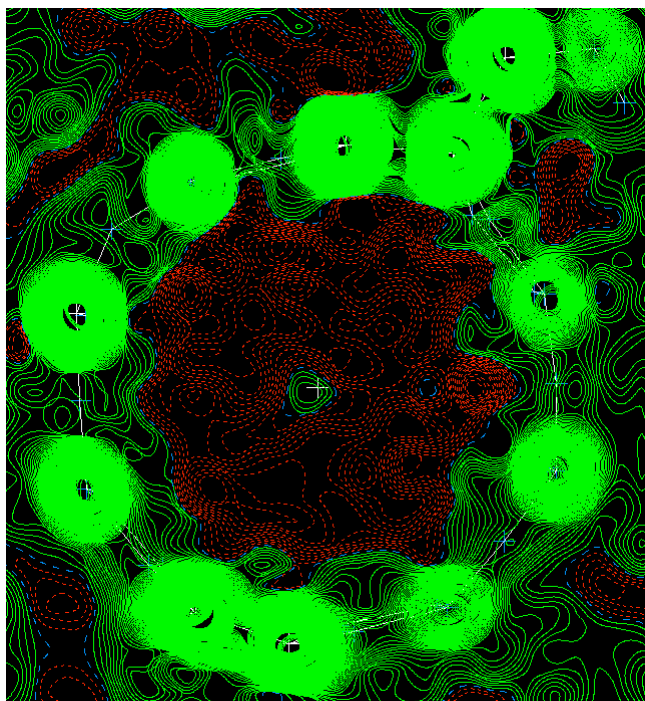


Figure S1. ORTEP drawing of the crystal structure of **3**. Thermal ellipsoids are drawn in 30% probability level.

(a)



(b)

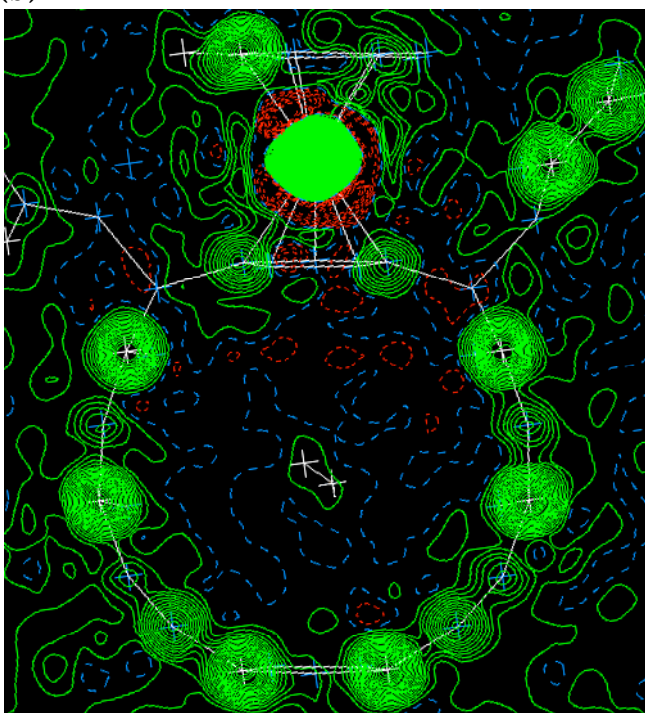


Figure S2. Electron density maps (PLATON contour maps) for **2** and **3**. (a) The map for **2**. (b) The map for **3**. The figures show the cross section around the center area of C₆₀ cages. Green full lines indicate positive electron density. Red dashed lines indicate negative electron density.

3. Theoretical Calculation of $C_{60}H_5$ Anion

In order to obtain insight about relation between 1H NMR chemical shift and location of H_2 , we performed theoretical investigation of magnetic anisotropic effect in the fullerene cage. With structural information of X-ray data for **2**, geometry optimization calculation of model compound, $C_{60}H_5$ anion was carried out by the use of hybrid density functional method (B3LYP/6-31G*). Then we estimated nucleus independent chemical shift (NICS)³ values by means of gauge-invariant atomic orbital (GIAO)⁴ calculation with Hartree-Fock method (HF/6-31G*). The NICS values at the position along molecular C_{5v} axis is shown in Figure S3. Data showed that the centroid C_{60} is strongly shielded (NICS = -6.76) and the shielding effect increase with lower (bottom) part of the cage. This result give us a valuable information to understand deshielding NMR shift of the encapsulated molecular hydrogen in **2**. Comparing H_2 -position determined by X-ray analysis of **2** and **3**, H_2 of **2** is located more upper ward than that of **3**. In other word, molecular hydrogen of **2** is in more deshielding region than that of **3**, and this is consistent with NMR data.

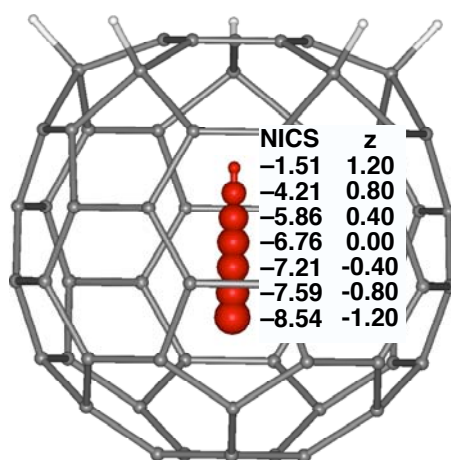


Figure S3. NICS values of inside of the cage. Observation points (red balls) aligned along molecular C_{5v} axis at interval of 0.40 Å. Size of red balls represent magnitude of NICS values.

4. NMR and MS Spectra of 1-4

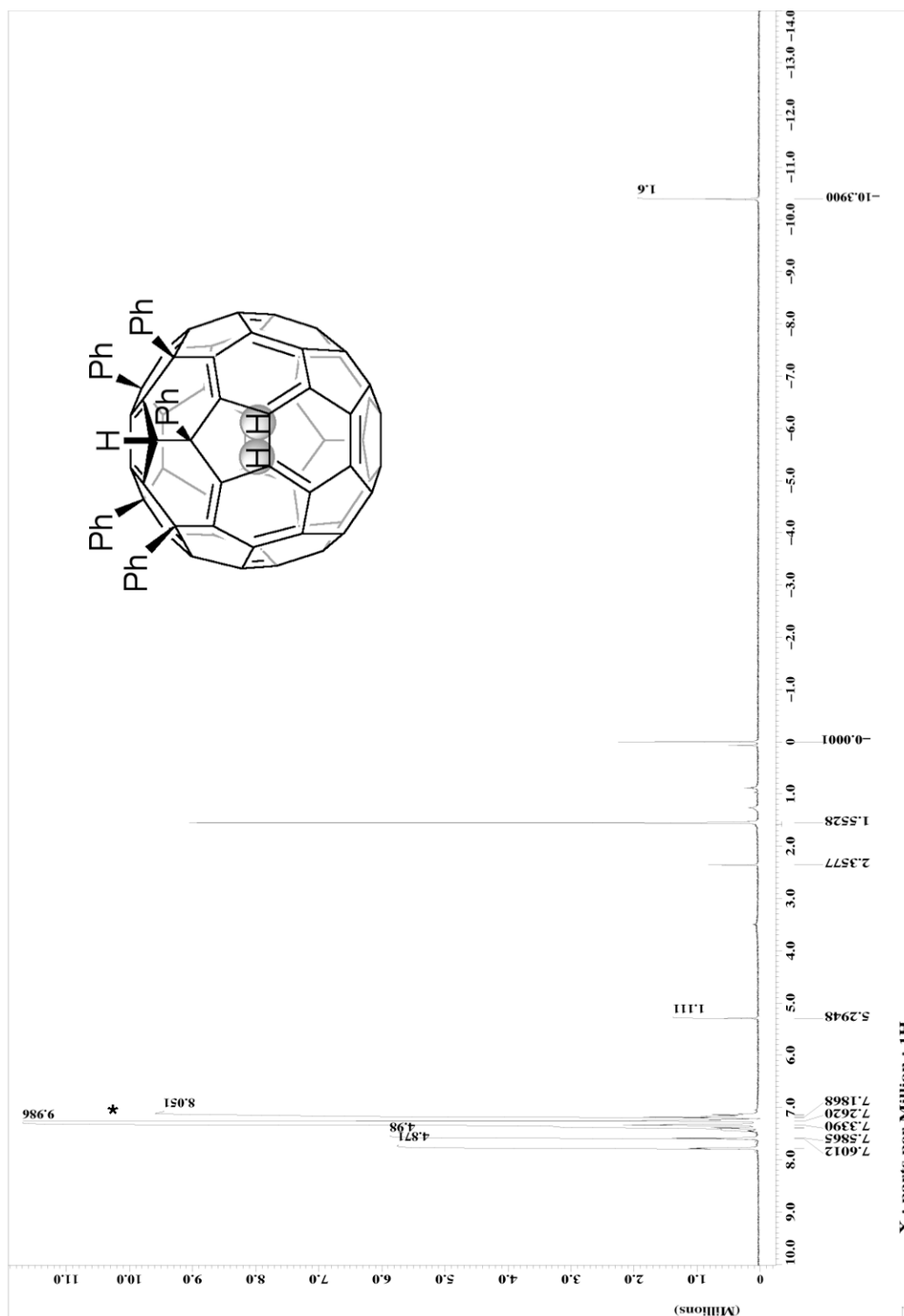


Figure S4. ^1H NMR spectrum of 6,9,12,15,18-pentaphenyl-1,6,9,12,15,18-hexahydro($\text{C}_{60}\text{-I}_h$)[5,6]fullerene-incar-dihydrogen in 1:1 $\text{CDCl}_3/\text{CS}_2$. Asterisk indicate the solvent signal.

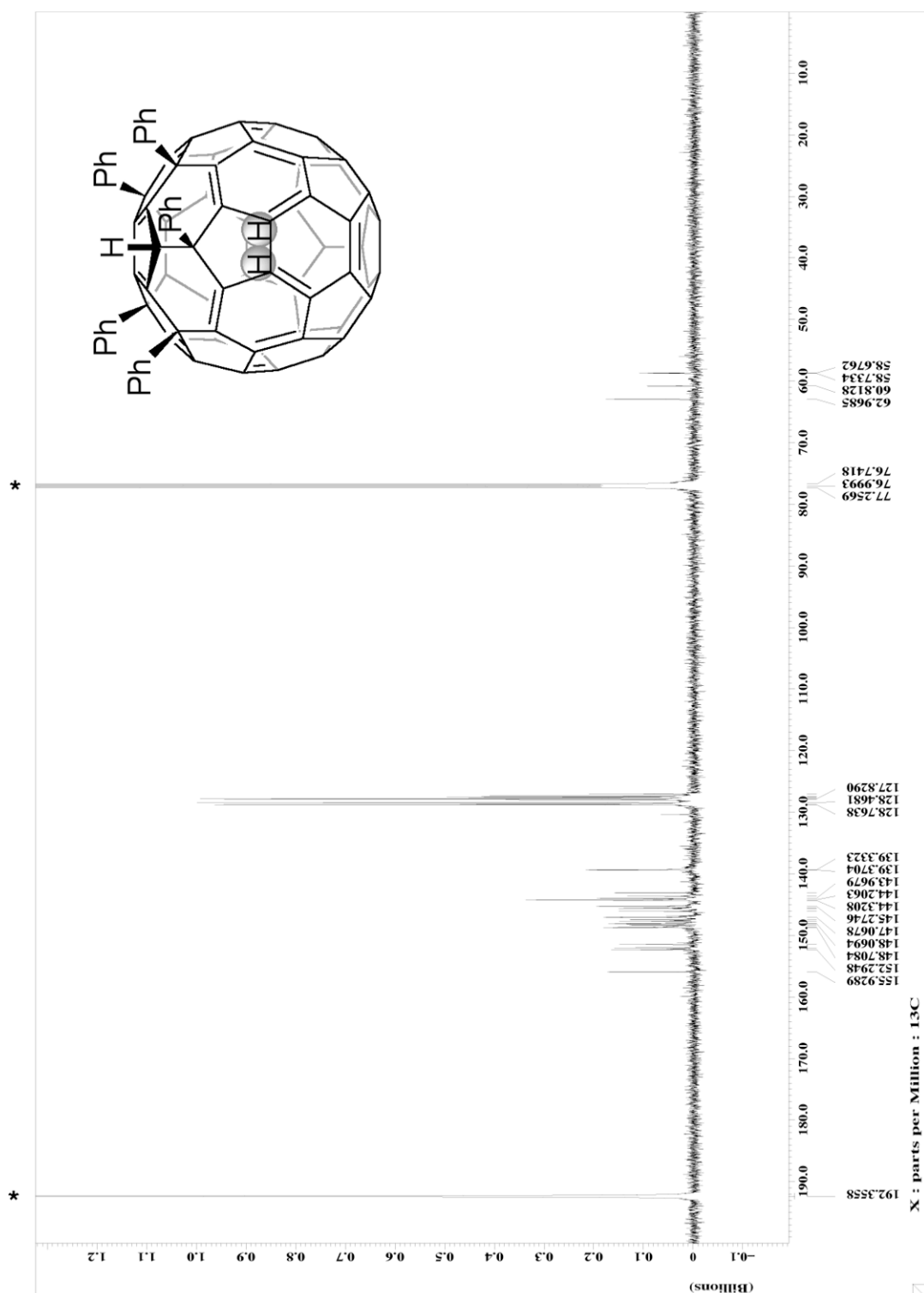


Figure S5. ¹³C NMR spectrum of 6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro(C₆₀-I_h)[5,6]fullerene-incar-dihydrogen in 1:1 CDCl₃/CS₂. Asterisk indicate the solvent signal.

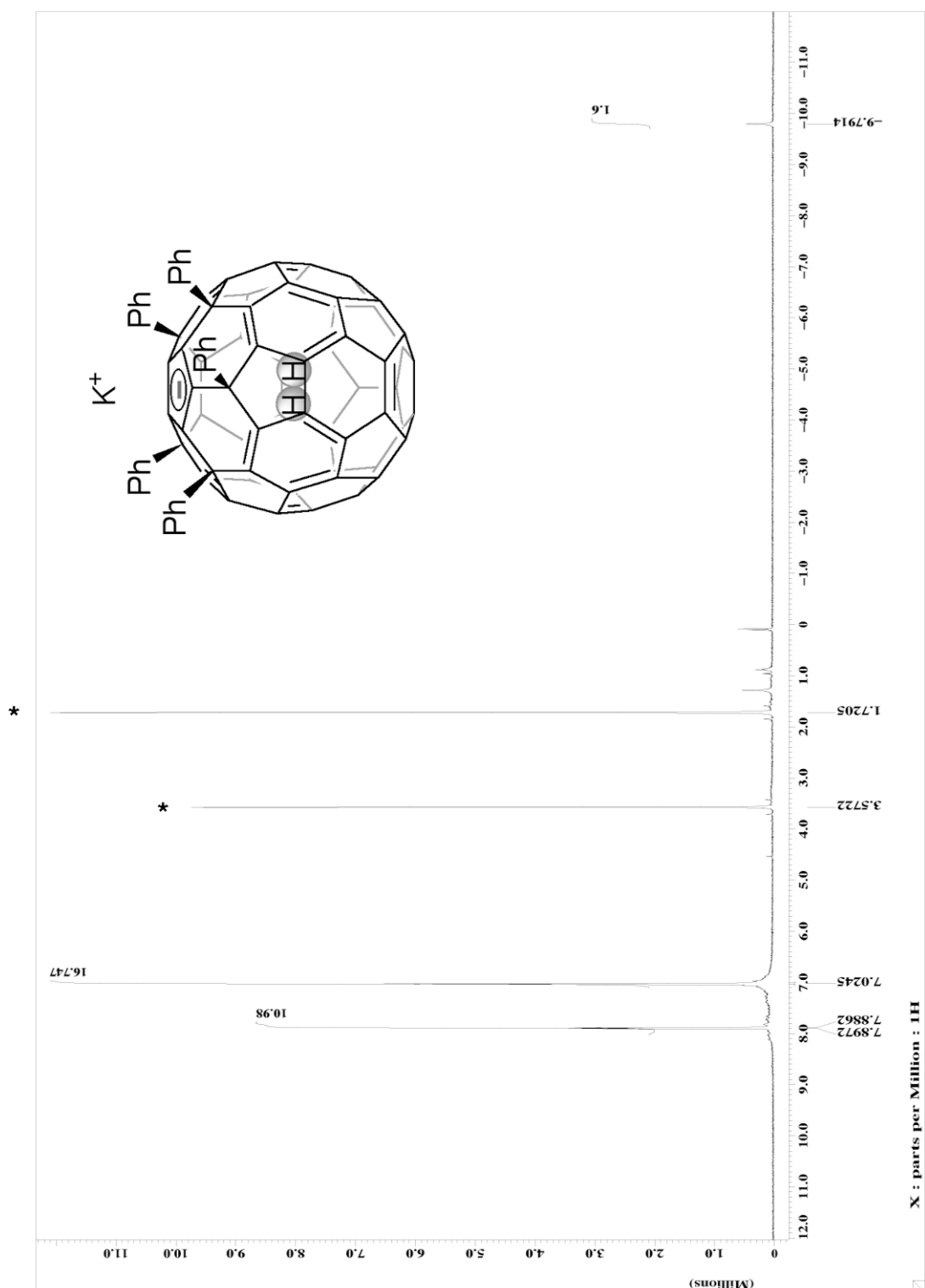


Figure S6. ^1H NMR spectrum of [6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro($\text{C}_{60}\text{-I}_h$)[5,6]fullerene-*incar*-dihydro gen-1(6H)-yl]potassium in $\text{THF-}d_8$. Asterisk indicate the solvent signal.

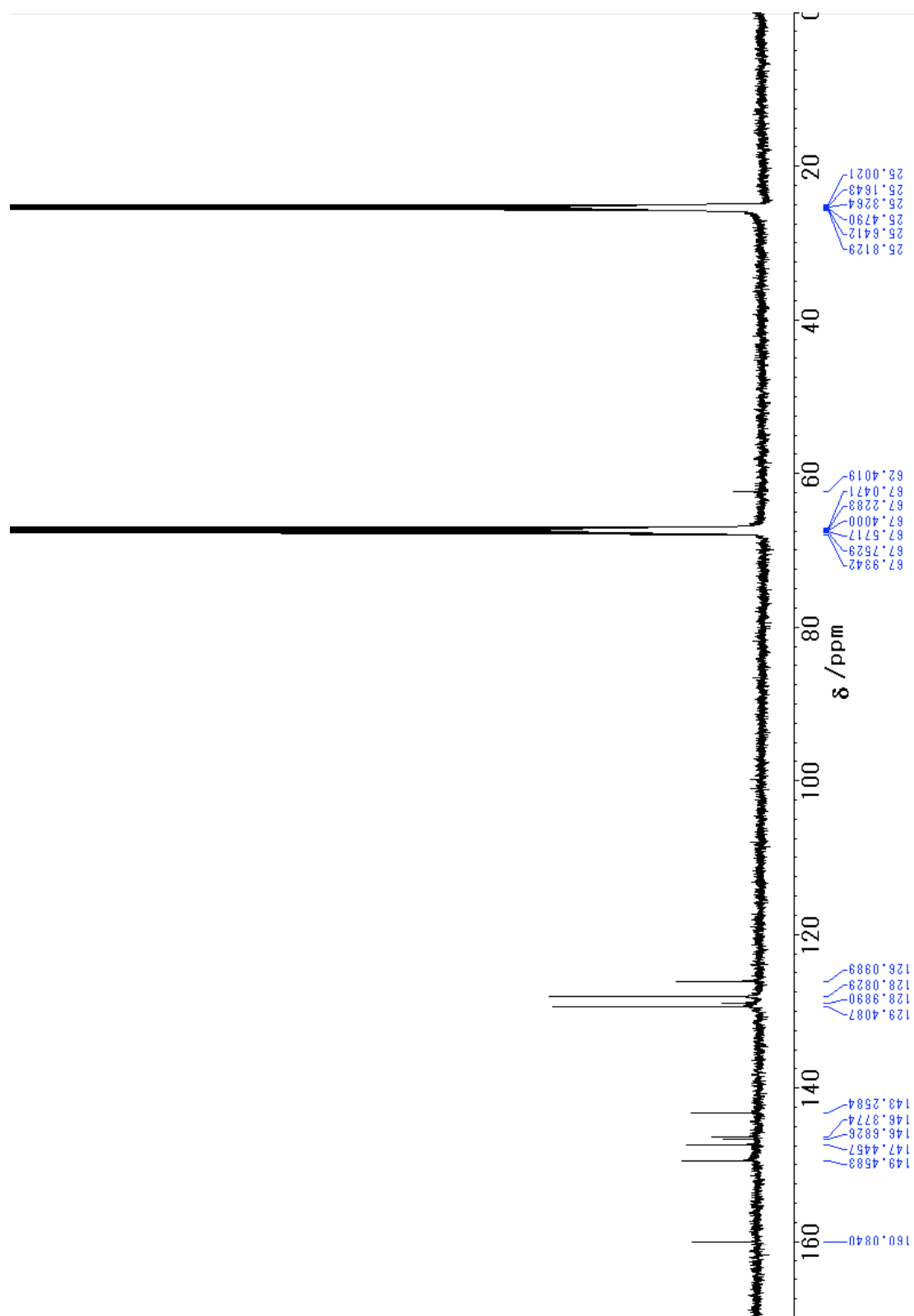


Figure S7. ^{13}C NMR spectrum of [6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro($\text{C}_{60}\text{-I}_h$)[5,6]fullerene-*incar*-dihydro gen-1(6*H*)-yl]potassium in $\text{THF-}d_8$.

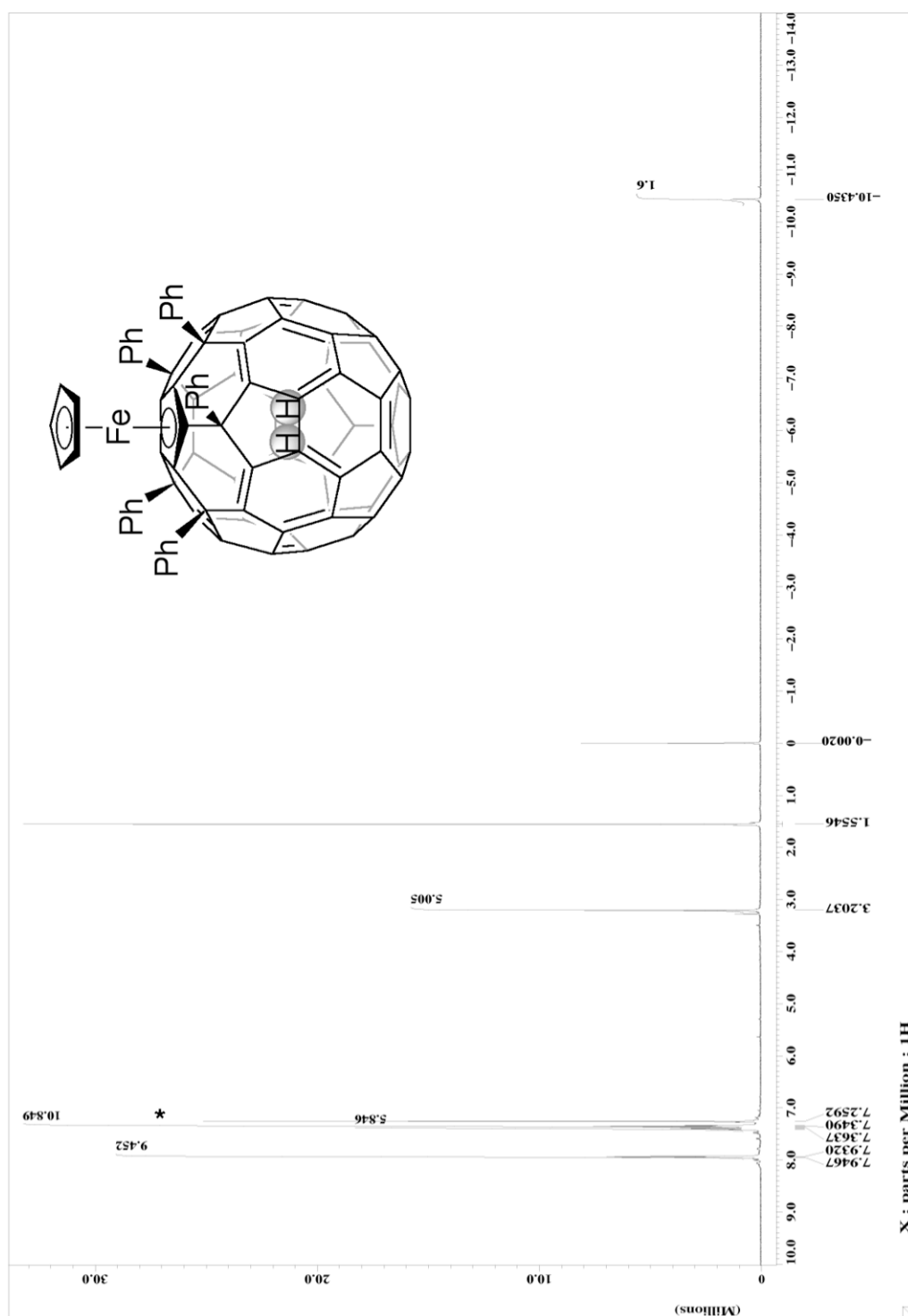


Figure S8. ^1H NMR spectrum of $(\eta^5\text{-cyclopentadienyl})[6,9,12,15,18\text{-Pentaphenyl-1,6,9,12,15,18-hexahydro}(\text{C}_{60}\text{-I}_h)[5,6]\text{fullerene-incar-dihydrogen-1(6H)-yl}] \text{iron(II)}$ in 1:1 $\text{CDCl}_3/\text{CS}_2$. Asterisk indicate the solvent signal.

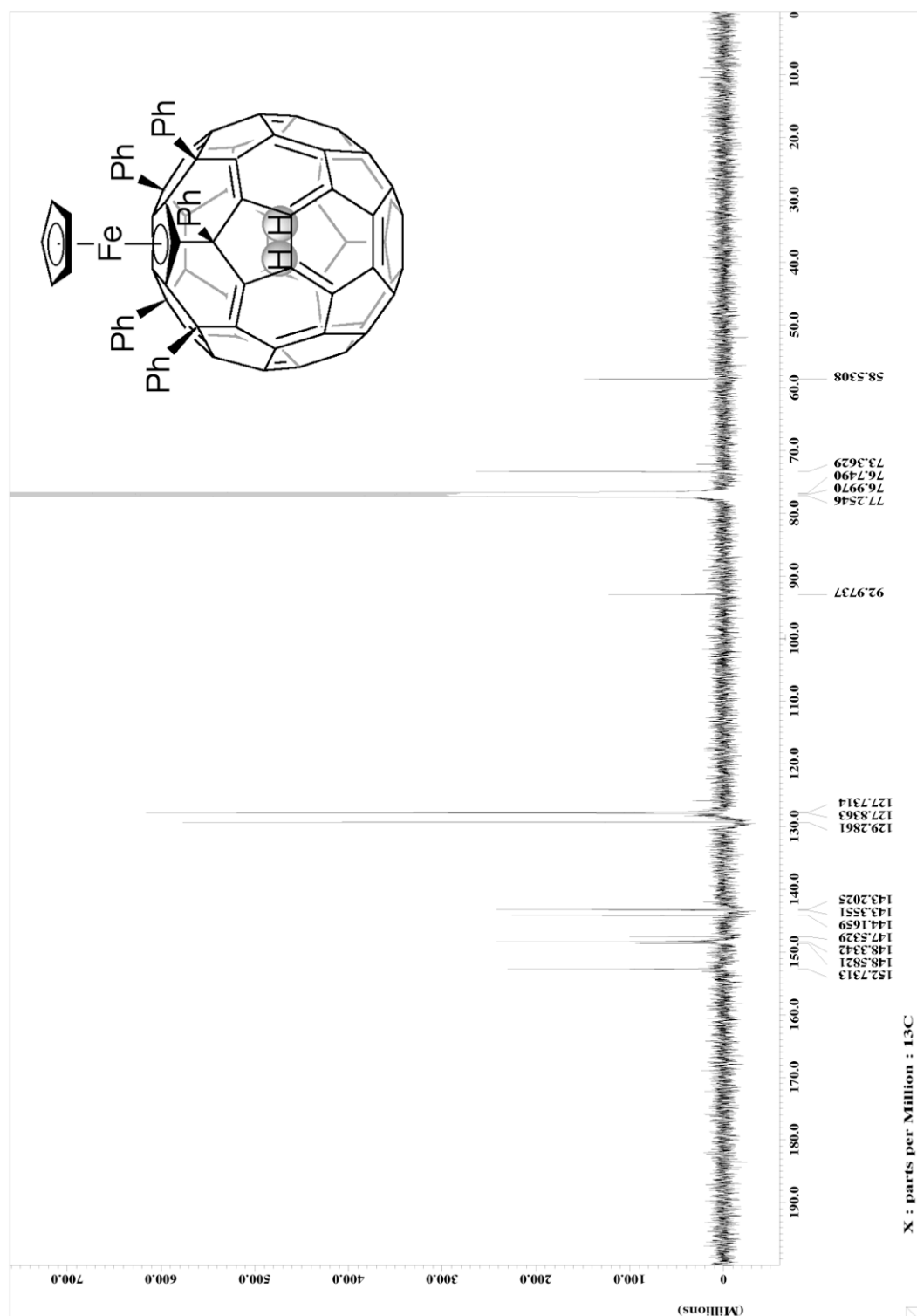


Figure S9. ¹³C NMR spectrum of (η⁵-cyclopentadienyl)[6,9,12,15,18-Pentaphenyl-1,6,9,12,15,18-hexahydro(C₆₀-I_h)[5,6]f ullerene-incar-dihydrogen-1(6*H*)-yl]iron(II) in 1:1 CDCl₃/CS₂. Asterisk indicate the solvent signal.

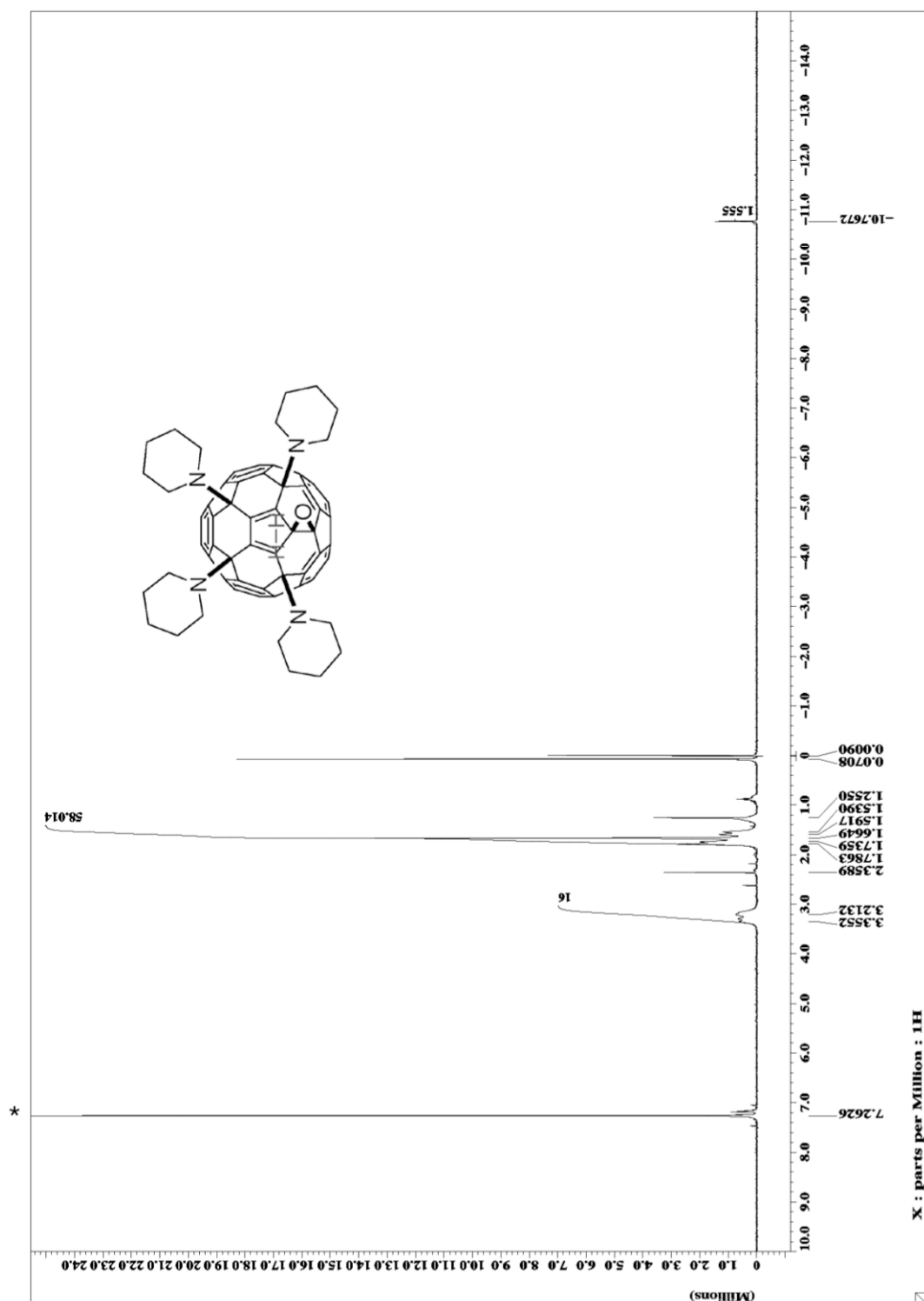


Figure S10. ^1H NMR spectrum of 6,12,15,18-Tetra(piperidin-1-yl)-6,12,15,18-(tetrahydro)oxireno[2',3':1,9]($\text{C}_{60}\text{-I}_h$)[5,6]fullerene-*incar*-hydrogen in CDCl_3 . Asterisk indicate the solvent signal.

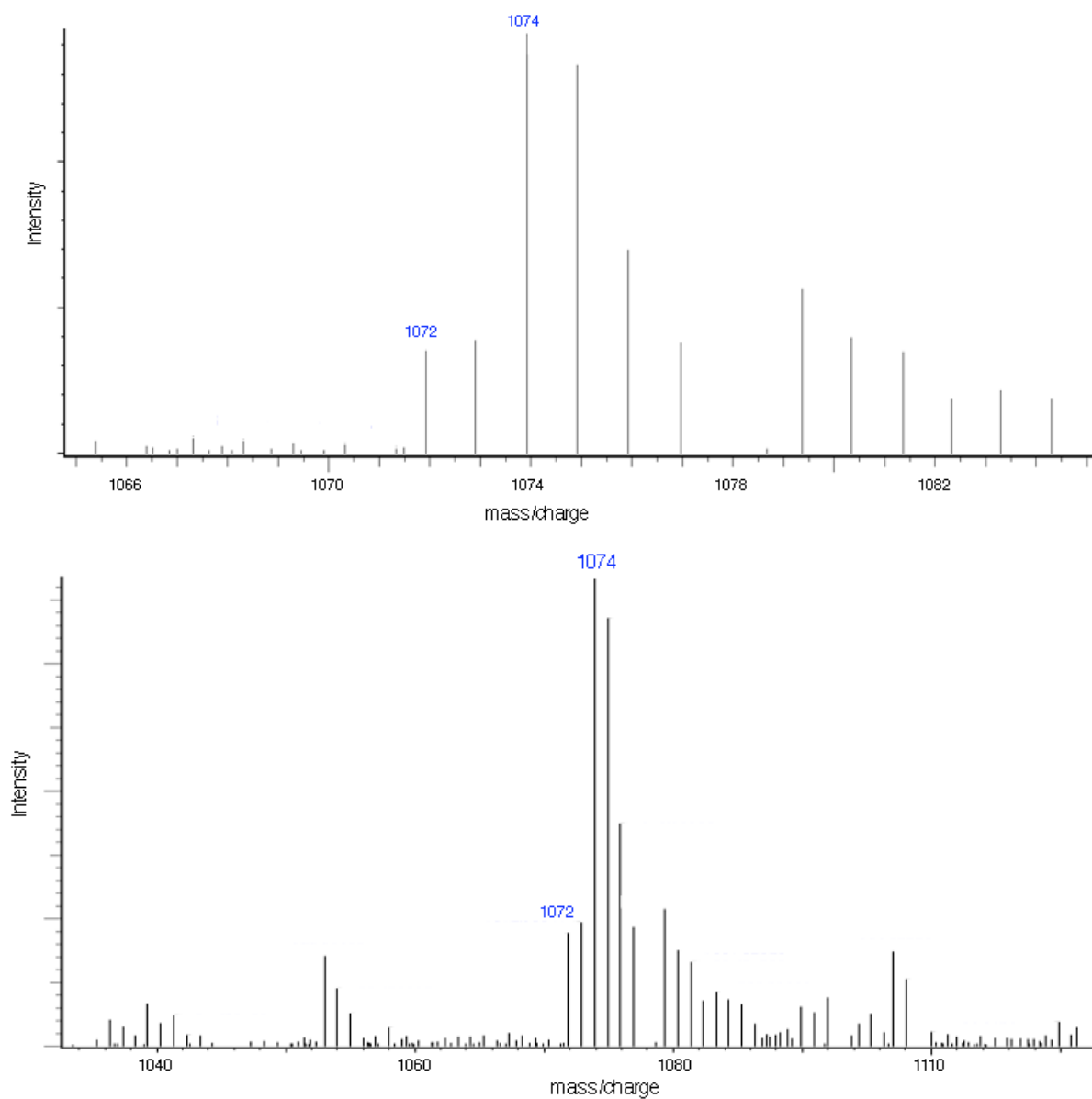


Figure S11. MS spectrum of 6,12,15,18-Tetra(piperidin-1-yl)-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-*incar*-hydrogen.

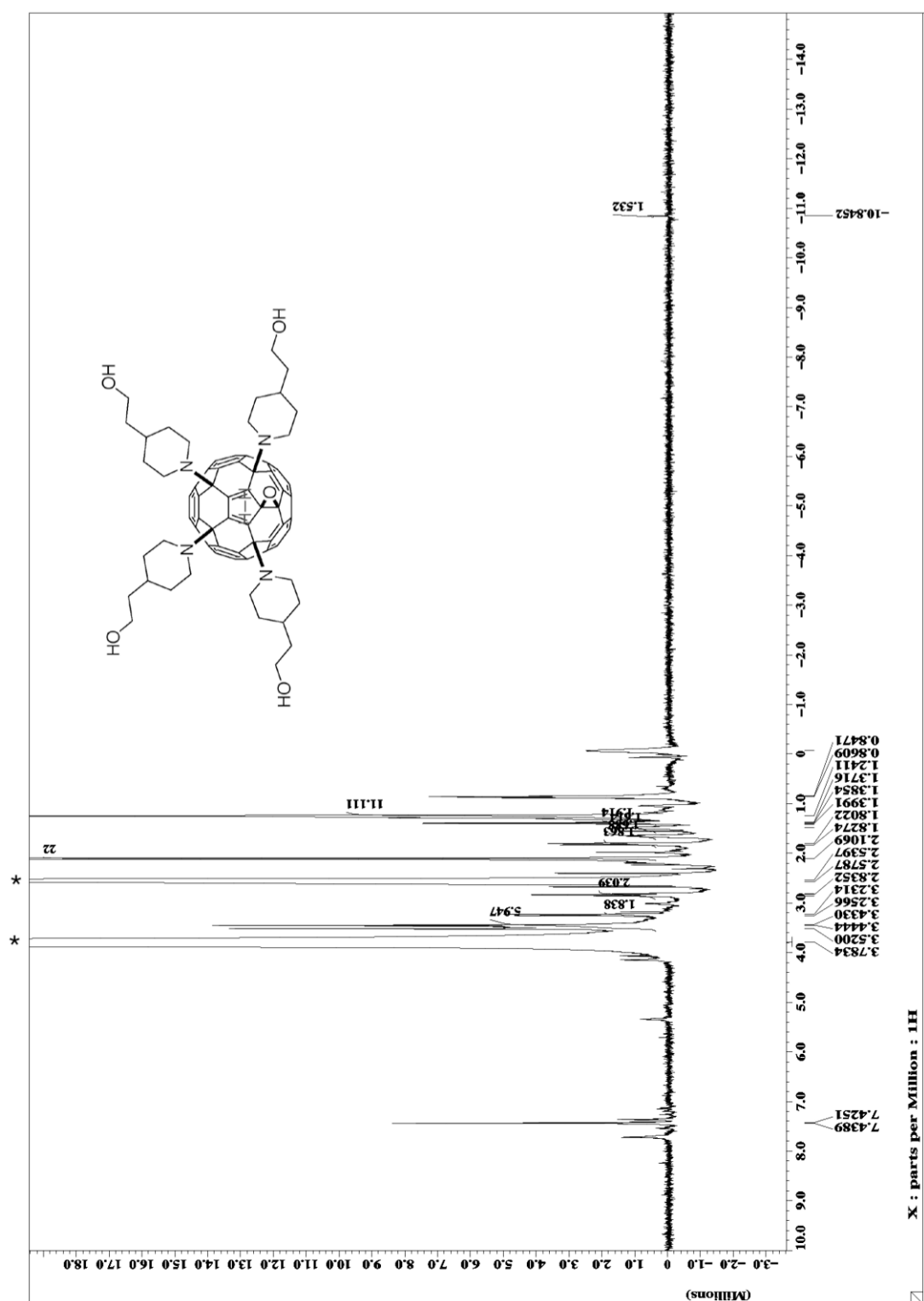


Figure S12. ^1H NMR spectrum of 6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-*incar*-hydrogen in 1:9 D₂O/DMSO-d₈. Asterisks indicate the solvent signals.

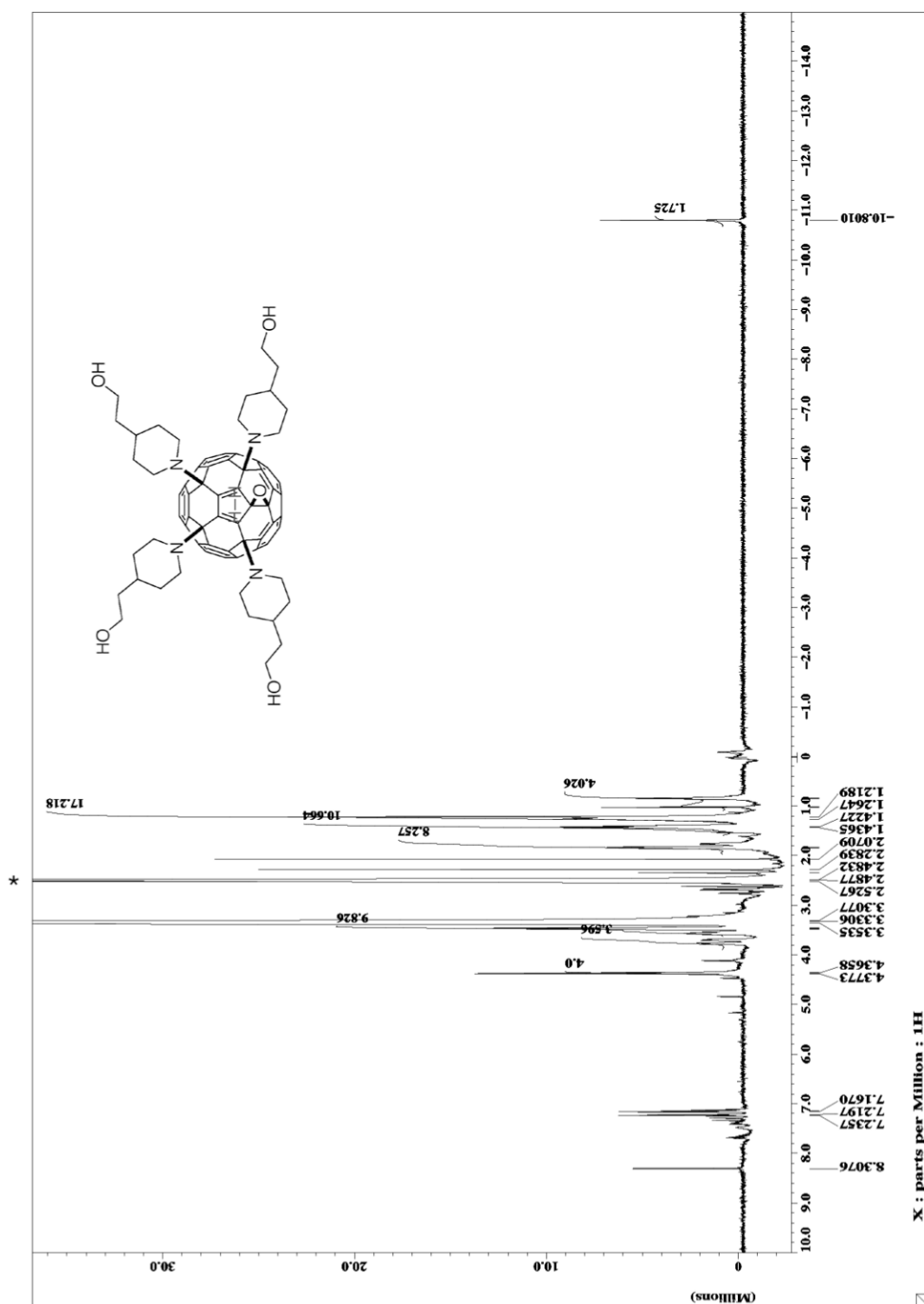


Figure S13. ¹H NMR spectrum of 6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-incar-hydrogen in DMSO-d₆. Asterisk indicate the solvent signal.

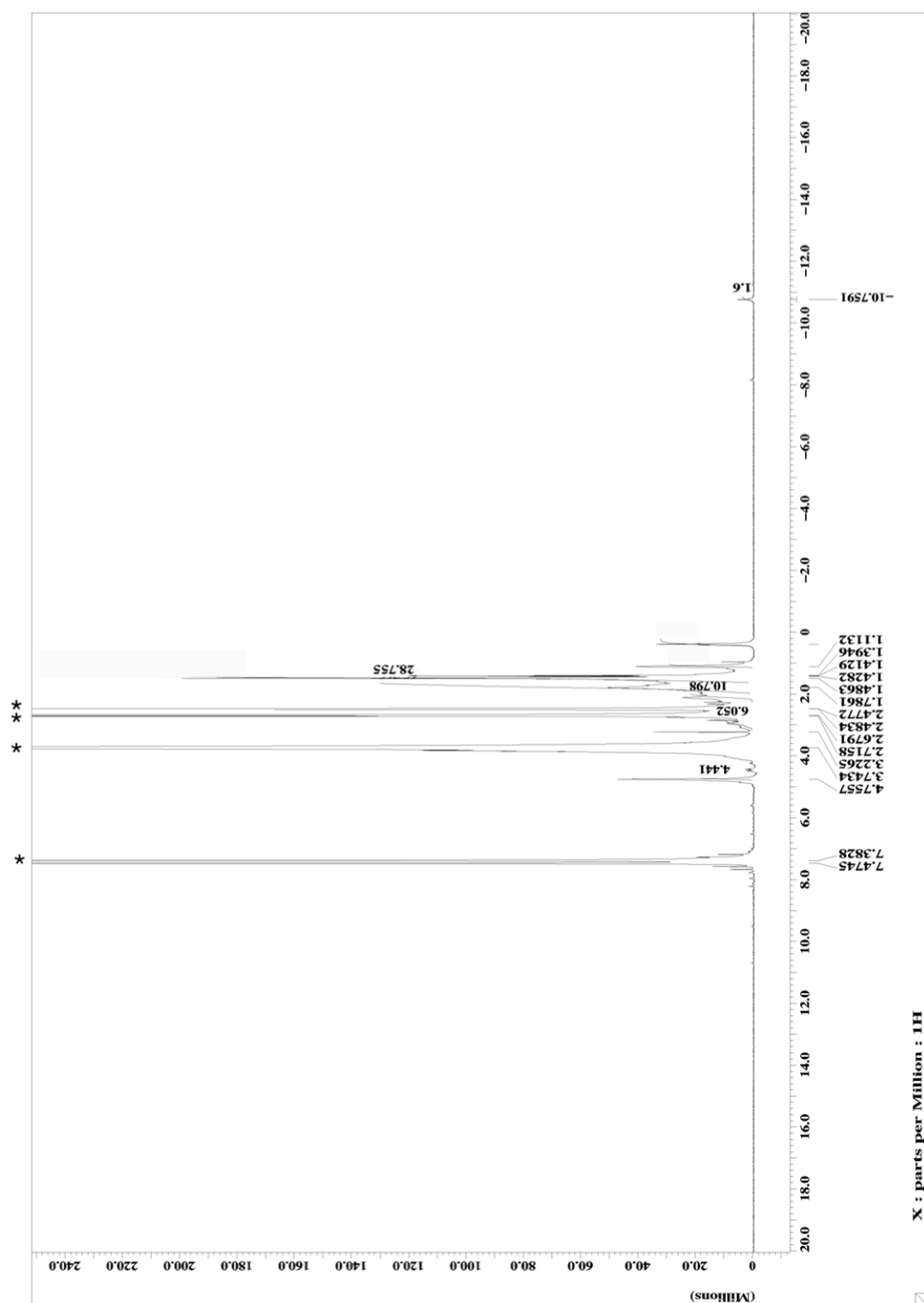


Figure S14. ^1H NMR spectrum of 6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-incar-hydrogen in 1:1 DMSO- d_6 /toluene- d_8 . Asterisks indicate the solvent signals.

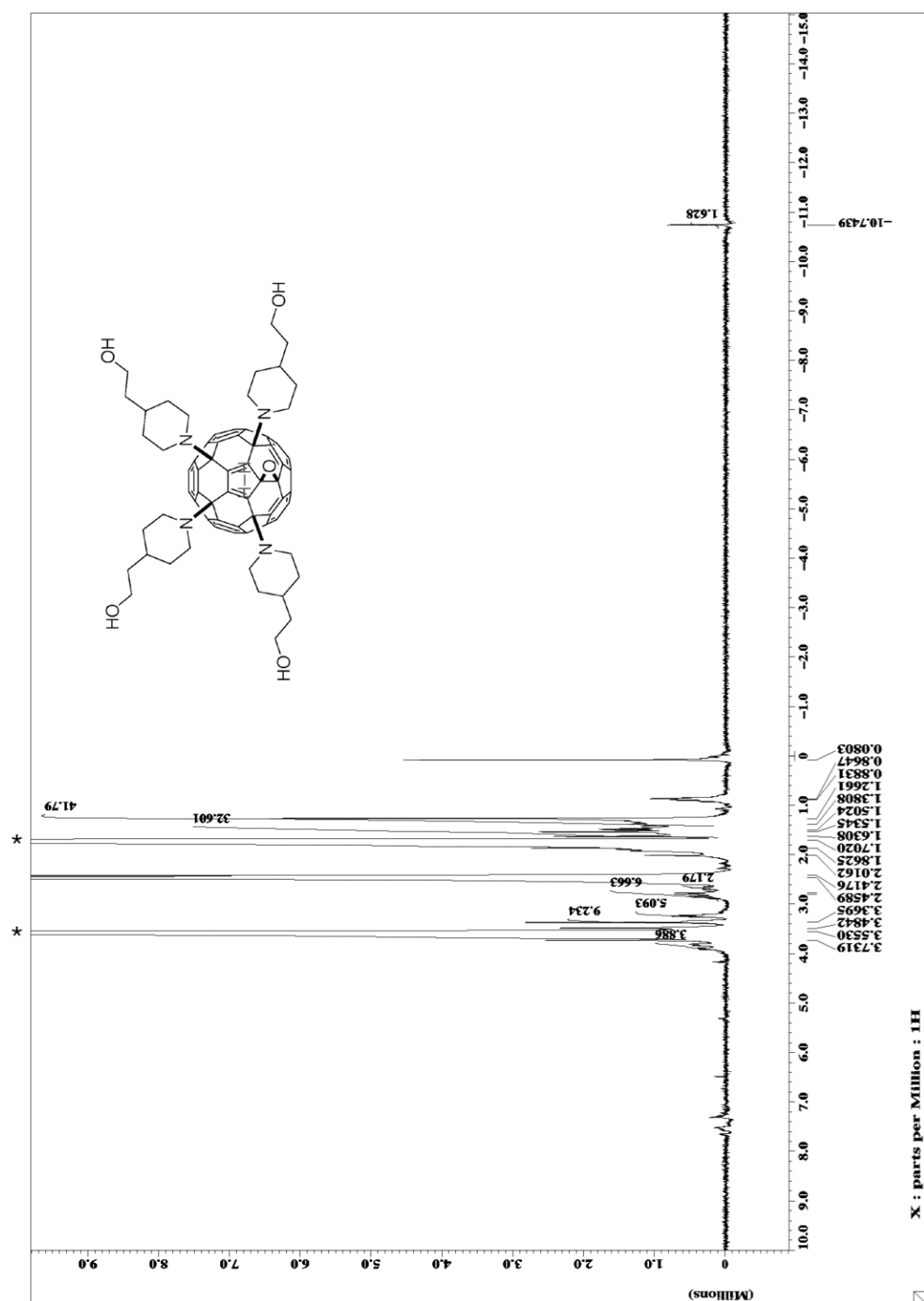


Figure S15. ¹H NMR spectrum of 6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-incar-hydrogen in THF-d₈. Asterisks indicate the solvent signals.

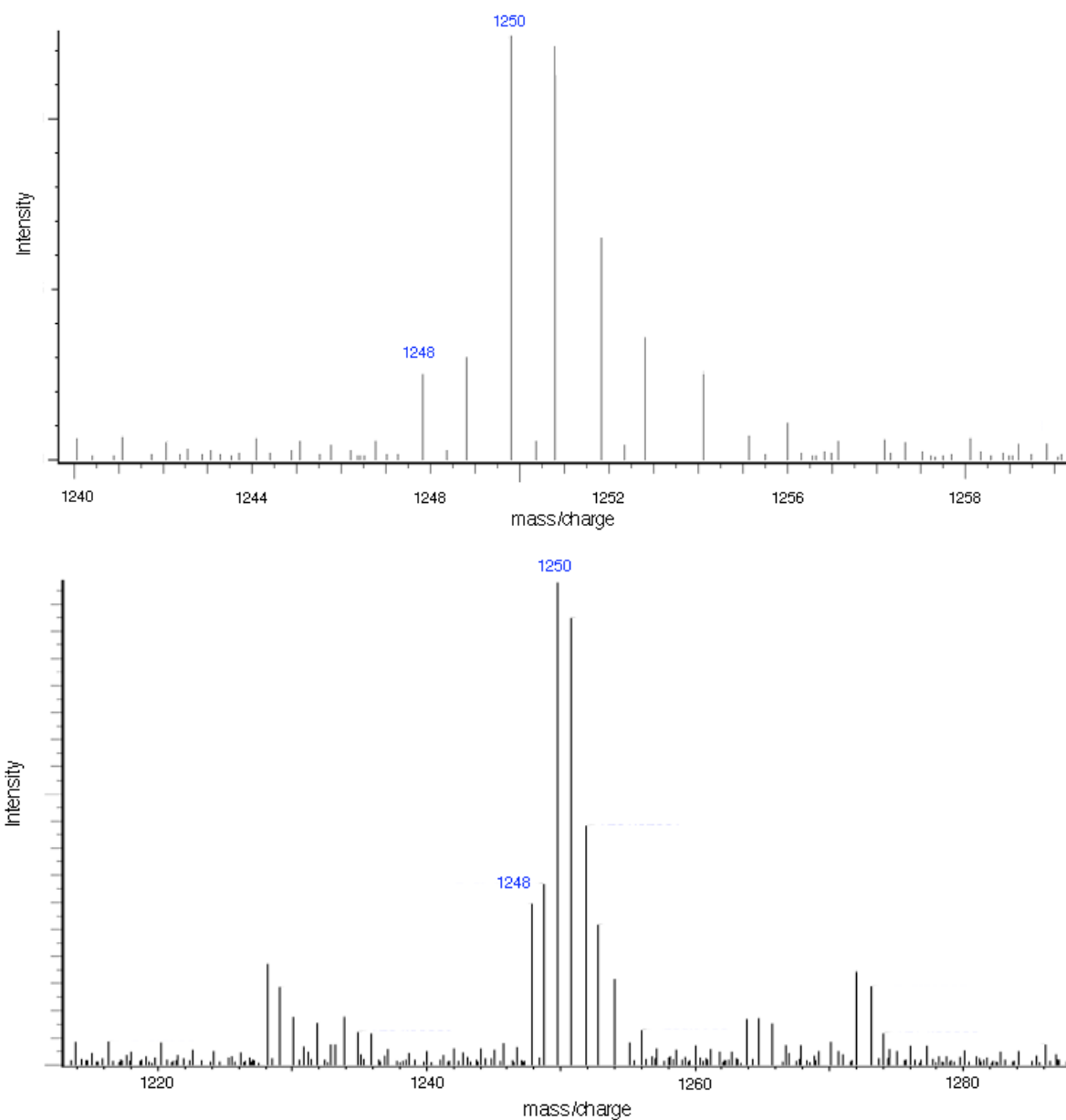


Figure S16. MS spectrum of 6,12,15,18-Tetra[4-(2-hydroxyethyl)piperidin-1-yl]-6,12,15,18-(tetrahydro)oxireno[2',3':1,9](C₆₀-I_h)[5,6]fullerene-*incar*-hydrogen.

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