Supporting information for

A PEPTIDE TOPOLOGICAL TEMPLATE FOR THE DISPERSION OF [60]FULLERENE IN WATER

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CONTENTS

General Methods

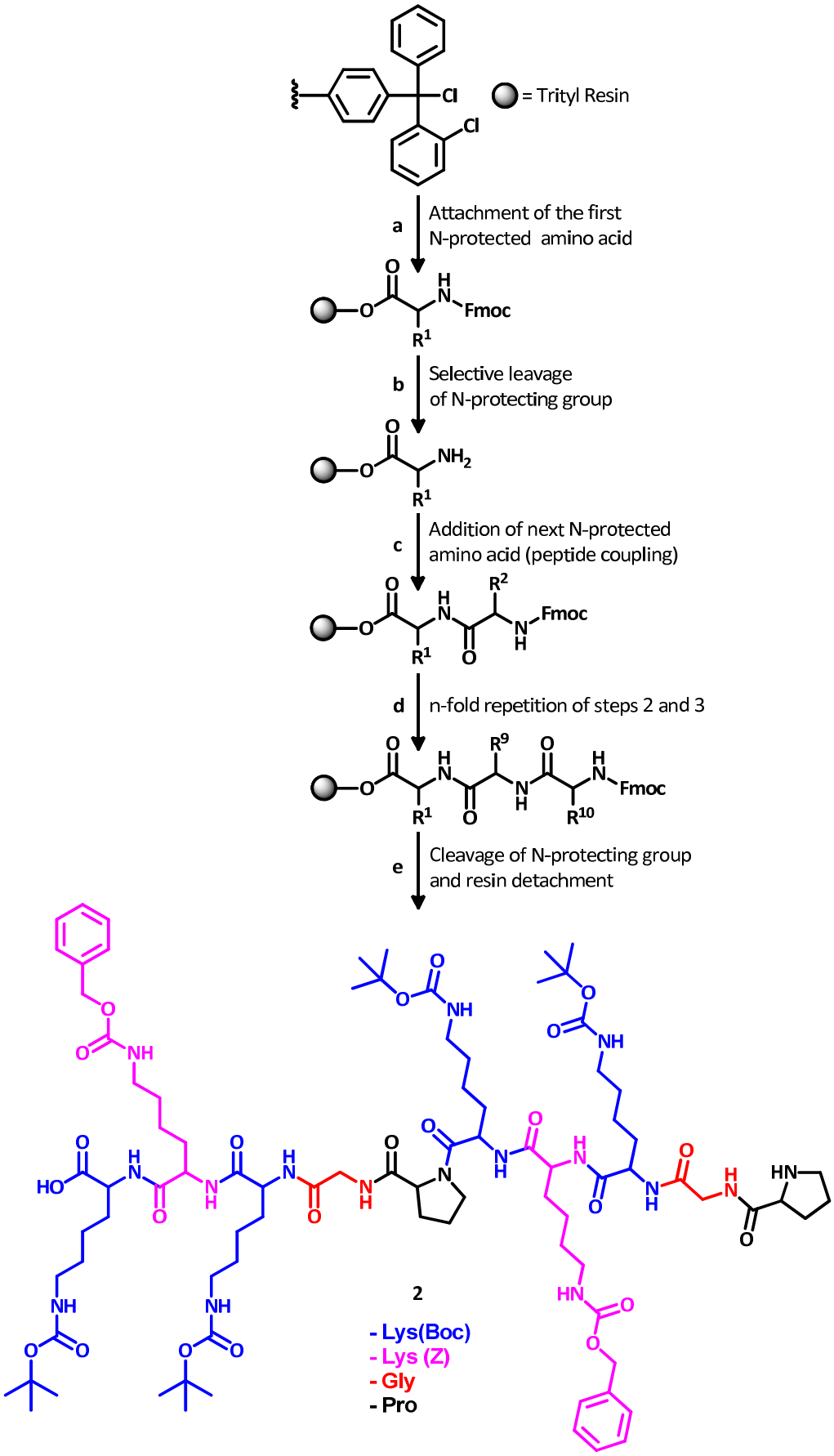
NMR. ^{1}H, ^{13}C and 2D NMR were recorded at 289 K on a Bruker Avance DPX 200, Bruker Avance III 500 and Bruker Avance DPX 600 instruments using the partially deuterated solvent as internal reference. The multiplicity of a signal is indicated as: s – singlet, d – doublet, t – triplet, m – multiplet , dd – doublet of doublets, etc. **FT-IR Absorption.** FT-IR absorption spectra were recorded with a Nicolet 5700 FT-IR spectrophotometer, at a nominal resolution of 2 cm^{-1}, averaging 100 scans. **Mass Spectrometry.** ESI-MS experiments were performed in a ESI-TOF Mariner™ Biospectrometry™ Workstation of Applied Biosystems by flow injection analysis using acetonitrile with formic acid (1%) as mobile phase. **HPLC.** The HPLC measurements were performed using an Agilent 1200 series apparatus (Palo Alto, CA), equipped with a UV detector at 226 nm. The working conditions used were: Kromasil C_{18} 100 A (stationary phase), 30-100% B, 20 min, 1 mL/min (eluents: A= 9:1 H_2O/CH_3CN, 0.05% TFA; B= 1:9 H_2O/CH_3CN, 0.05% TFA). **UV-Vis Absorption**. Uv-Vis spectra were recorded using a Varian Cary 100 spectrophotometer. A 1 cm path length quartz cell was used. **CD.** Circular Dichroism spectra were recorded using a Jasco J-715 spectrometer. A 0.02 cm path length quartz cell was used. **TGA.** Thermal gravimetric analysis were recorded with a TGA Q5000 IR (Q Series™) using Platimun-HT pan under Nitrogen and equilibrating at 100°C for 10 min and then increasing 10°C/min till 1000°C and equilibrating again for 10 min. **TEM**. Transmission electron microscopy (TEM) was registered on a Jeol 300PX instrument. Samples of the aqueous solutions were prepared before use, by 10-fold dilution with Milli-Q® water. A glow discharged carbon coated grid was floated on a small drop of solution and excess was removed by #50 hardened Whatman filter paper. Samples of the gels were prepared by dropping a small amount of gel into a glow discharged carbon coated grid and removing excess of gel with #50 hardened Whatman filter paper. **DLS and z-potential** measurements were conducted on a Malvern Instrument Zetasizer Nanoseries. **MALDI-TOF** experiments were performed in a AB Sciex instrument, reflector negative mode, no matrix was used. **High Speed Vibration Milling (HSVM).** High Speed Vibration Milling was performed by a MM400 Retsch using stainless-steel capsules and mixing balls. S**onication.** Sonication was performed by a Misonix Sonicator 3000. **Solvents and reagents.** Water was purified using Milli-Q® water purification system. Solvents were of analytical reagent grade, laboratory reagent grade or HPLC grade. All the other chemical reagents were used as received from Sigma-Aldrich.

Solid Phase Peptide Synthesis (SPPS) compound 2

Linear decapeptide **2** was synthesized using standard solid phase 9-fluorenylmethoxycarbonyl (Fmoc) chemistry. A glass reactor for solid phase peptide synthesis was employed and, when not in use, the resin was dried and stored in the freezer with the amino-terminus Fmoc-protected. Before each step, the resin was pre-swelled with 10 mL/g of DMF (1 x 20 min). The 2-chloro trytil chloride resin was purchased from Iris Biotech (commercial loading 1.63 mmol/g); *O*-(Benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HBTU), 1-Hydroxybenzotriazole hydrate (HOBt), *N*,*N*-Diisopropylethylamine, Piperidine (purified by redistillation), all the aminoacids and dry solvents were purchased from Sigma-Aldrich and used as provided.

The synthesis was carried out in 21 steps:

1. Attachment of the first Fmoc-protected amino acid to the resin;
2. Deprotection of the amino-terminus of the amino acid;
3. Coupling with the second amino acid;
4. N-fold repetition of steps 2 and 3;
5. Cleavage of N-protecting group and resin detachment.



Scheme 1. Solid phase synthesis of linear decapeptide **2**

1. **Attachment of the first amino acid: Fmoc-Lys(Boc)-OH**.

   A solution of Fmoc-Lys(Boc)-OH (1.2 eq relative to the resin) and *N*,*N*-Diisopropylethylamine (DIPEA) (4 eq relative to the resin) in 10 mL/g resin was prepared in dry dichloromethane (DCM). The resin was treated with this solution for 2h (1x). Then the resin was washed with a solution of DCM/MeOH/DIPEA 17:2:1 (4x), DCM/DMF (3x).

2. **Deprotection of the amino terminus of the aminoacid.**

   The resin was treated with a solution of piperidine/DMF 2:8 for 5 minutes (3x) and then washed with DMF/DCM/DMF (3x).

3. **Coupling with the second aminoacid: Fmoc-Lys(Z)-OH**

   A solution of Fmoc-Lys(Z)-OH (5 eq relative to the resin), HBTU (3.9 eq relative to the resin), HOBt (4.9 relative to the resin) and DIPEA (10 eq relative to the resin) in dry DMF (0.6 M relative to the aminoacid) was prepared and the resin was treated with it for 2h (1x). Then the resin was washed with DMF/DCM/DMF (3x).

4. **N-folding repetition of steps 2 and 3 using in order**: Fmoc-Lys(Boc)-OH, Fmoc-Gly-OH, Fmoc-Pro-OH, Fmoc-Lys(Boc)-OH, Fmoc-Lys(Z)-OH, Fmoc-Lys(Boc)-OH, Fmoc-Gly-OH, Fmoc-Pro-OH.

5. **Cleavage from the resin:** the resin was treated with a solution of TFA/DCM 1% (10mL/g resin) for 5 minutes (4x) checking by TLC the complete detachment and washing with DCM after every treatment. The combined filtrates were concentrated under reduced pressure and the compound was freeze-dried.

Compound 2

Compund **2** was obtained from 1.1 g of resin as a white solid (2.28 g, 72%)

^{1}H-NMR: δ_H (500 MHz; dmso-d_6) 12.63 (1H, s, OH), 9.39-6.81 (24H, m, amide and aromatic), 5.09 (4H, s, CH_2-Ph), 4.36-1,31 (107H, m, aliphatic)

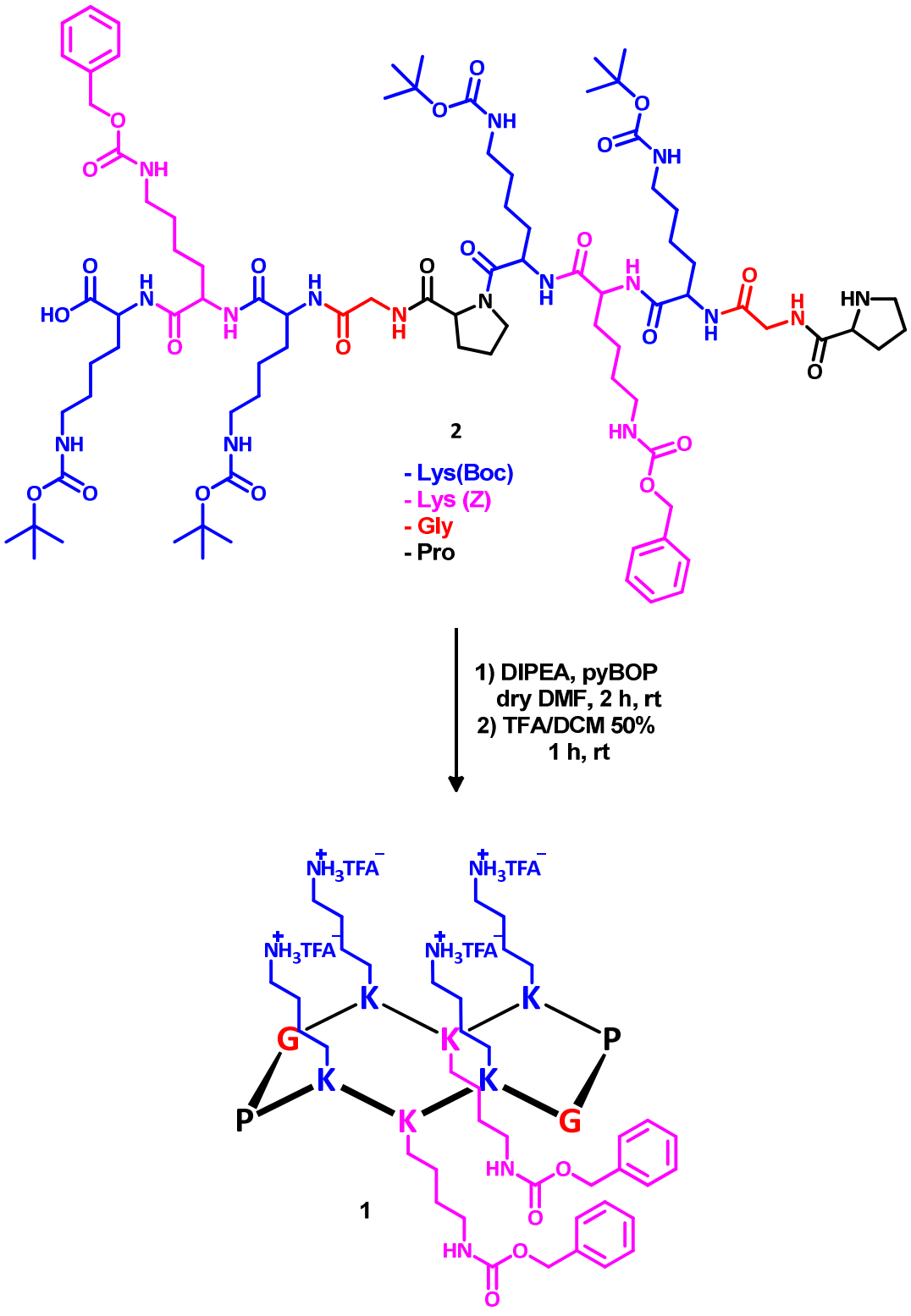
^{13}C-NMR: δ_c (50 MHz; dmso-d_6) 173.73, 172.60, 172.35, 170.40, 169.03, 168.20, 156.52, 156, 137.92, 129.02, 128.78, 128.17, 77.63, 65.58, 59.61, 52.25, 46.30, 34.61, 29.69, 28.70, 23.79, 23.11, 22.40

FT-IR (KBr): 3319, 3068, 2934, 2667, 1684, 1539, 1456, 1393, 1367, 1252, 1202, 1173, 1136, 1024, 800, 778, 721, 698, 667.

ESI-MS: m/z = 1765 $[M+H]^+$

m.p.: decomposition at 200-250°C

Synthesis of cyclic decapeptide 1



Scheme 2. Synthesis of cyclic decapeptide **1**

In a one-neck round bottom flask, 100 mL of dry DMF were introduced and degassed for 20 minutes. Two solutions were prepared: a) 100 mg (0.057 mmol, 1 eq) of compound **2** with 20 µl of DIPEA (0.114 mmol, 2 eq) in 20 mL of DMF; b) 35 mg (0.068 mmol, 1.2 eq) of (Benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate (pyBOP) in 80 mL of DMF.

Under vigorous stirring and always under nitrogen, solution a was added to solution b in 2 h by syringe pump. The solvent was removed under reduced pressure and the product was precipitated by the addition of diethyl ether, centrifuged and rinsed with cold diethyl ether obtaining a pale yellow oli that was treated with 10 mL of a solution trifluoroacetic acid (TFA)/DCM 50% for 1 h for deprotecting the amino terminus of Lys(Boc). The mixture was concentrated under reduced pressure obtaining a pale yellow solid that was taken with acetonitrile (5x5 mL) in order to remove any TFA traces. The product was precipitated by the addition of diethyl ether, centrifuged and rinsed with cold diethyl ether.

Compound 1

Compund **1** was obtained as a sand-colored powder (80 mg, 95%).

^{1}H-NMR: δ_H (500 MHz; dmso-d_6) 9.45-7.33 (32H, m, amide, amine and aromatic), 5.09 (4H, s, CH_2-Ph), 4.38-1.39 (72H, m, amine and aliphatic)

^{13}C-NMR: δ_c (125 MHz; dmso-d_6) 156.11, 137.15, 128.81, 128.56, 127.82, 124.72, 65.58, 54.94, 54.31, 53.92, 46.33, 44.52, 40.23, 26.39, 24.18, 18.46, 12.72

FT-IR (KBr): 3295.38, 3067.43, 2947.80, 1675.40, 1539.34, 1456.64, 1253.92, 1203.16, 1134.29, 1026.59, 835.89, 799.69, 741.20, 721.88, 698.89, 516.73

ESI-MS: m/z = 1346 $[M+H]^+$

m.p.: decomposition around 200-220°

Synthesis of 1/C_{60} nanocomposites

In a typical experiment 20 mg of **1** and 5 mg of C_{60} were used following the procedure here below.

HSVM. The solids were placed in a stainless-steel capsule with five stainless-steel mixing ball and mixed vigorously by shaking at 30 Hz for 10 minutes.

Manual grinding. An agate mortar was used and the solids were triturated for 20 minutes.

Sonication. The solids were suspended in a tube with 1.5 mL of mmQ water and sonicated for 1 h (3 sec on/3 sec off, power level: 3).

For solid state procedures, a dark brown powder was obtained and suspended in 1.5 mL of mmQ water, stirred at rt 1 hour and centrifuged first at 4000 rpm (1x 5min) and then at 14000 rpm (3x 5 min). The supernatants were filtered through a 45µm cellulose-membrane filter.

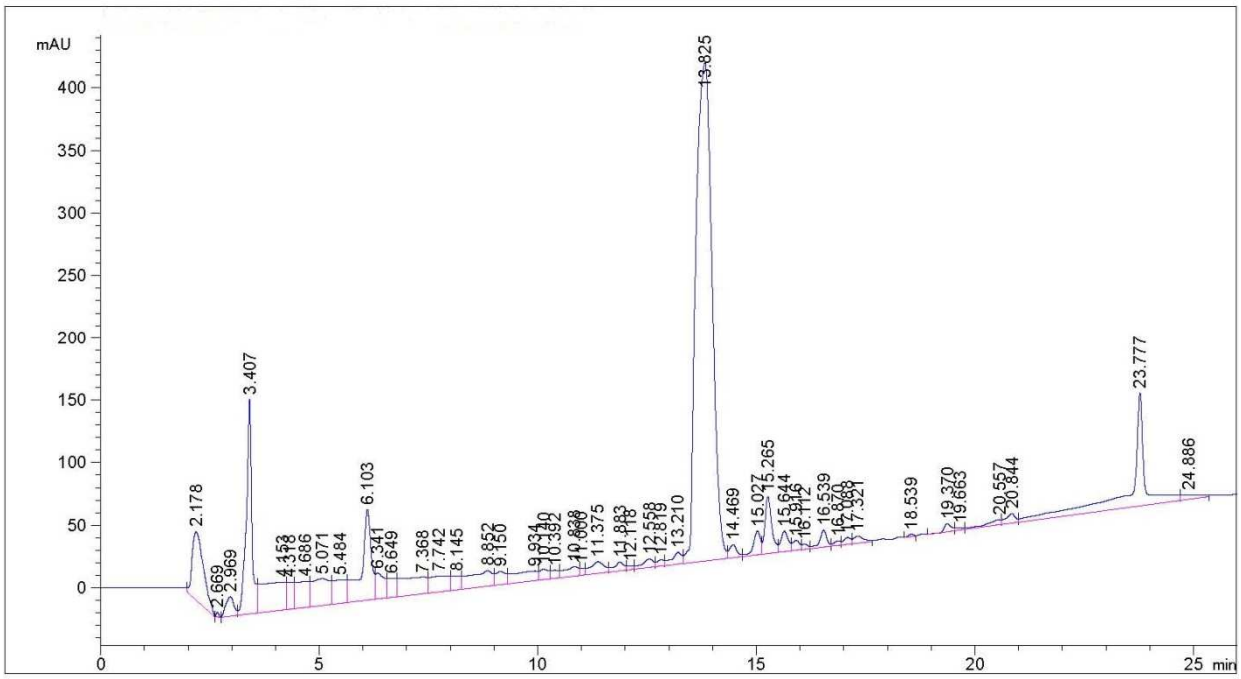


Figure S1. HPLC traces of compound **2**

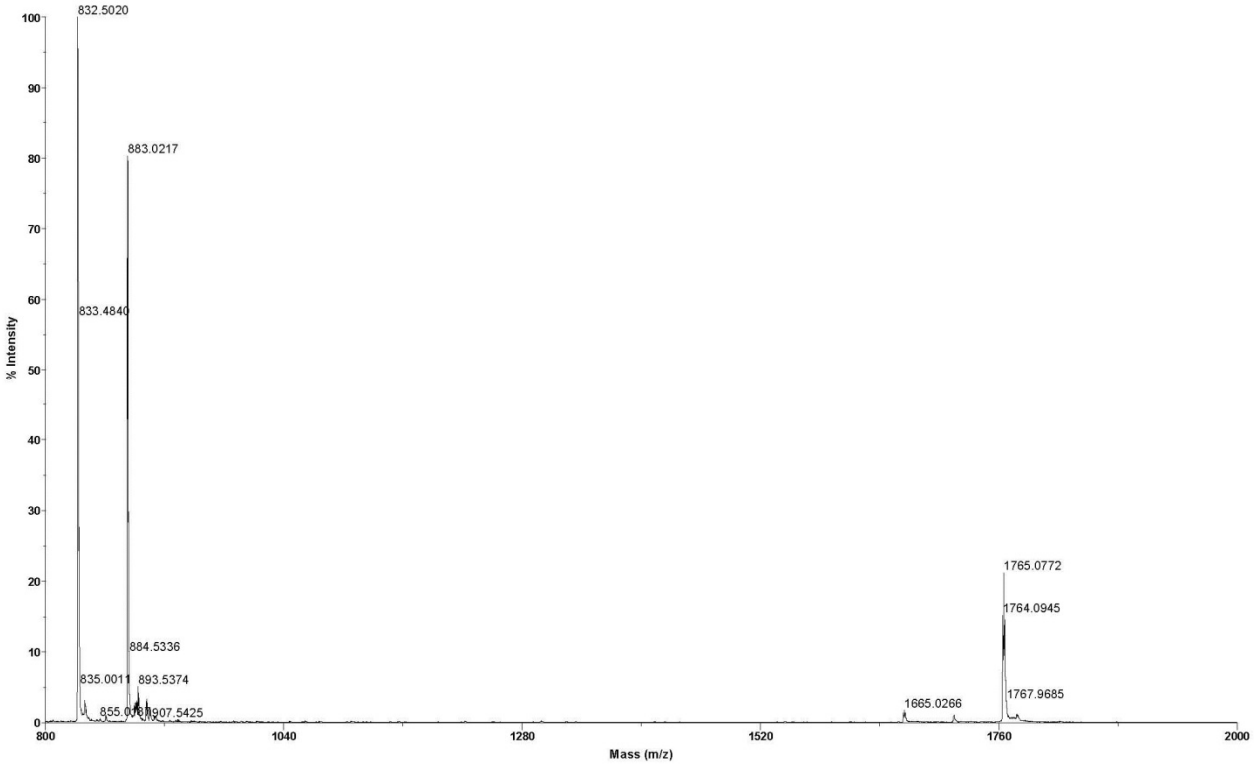


Figure S2. ESI-MS spectra of compound **2**

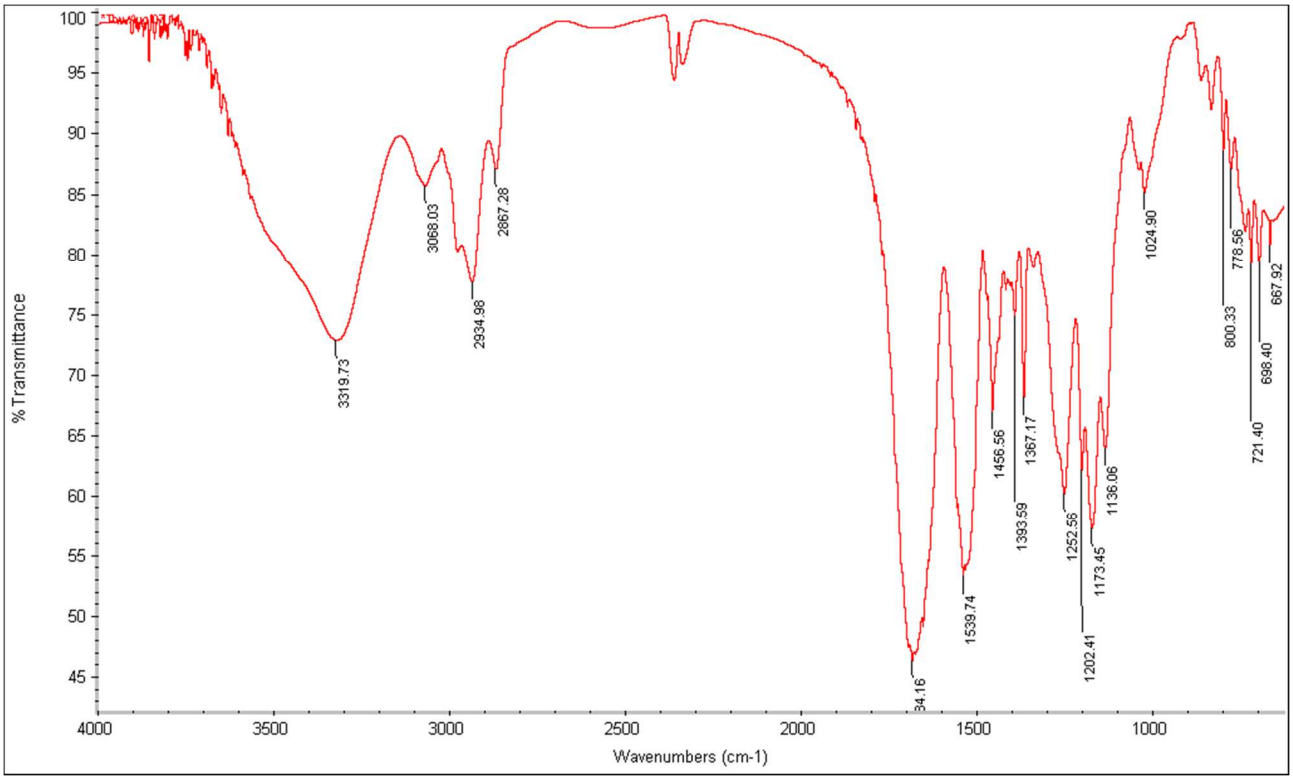


Figure S3. FT-IR (KBr disc) of compound **2**

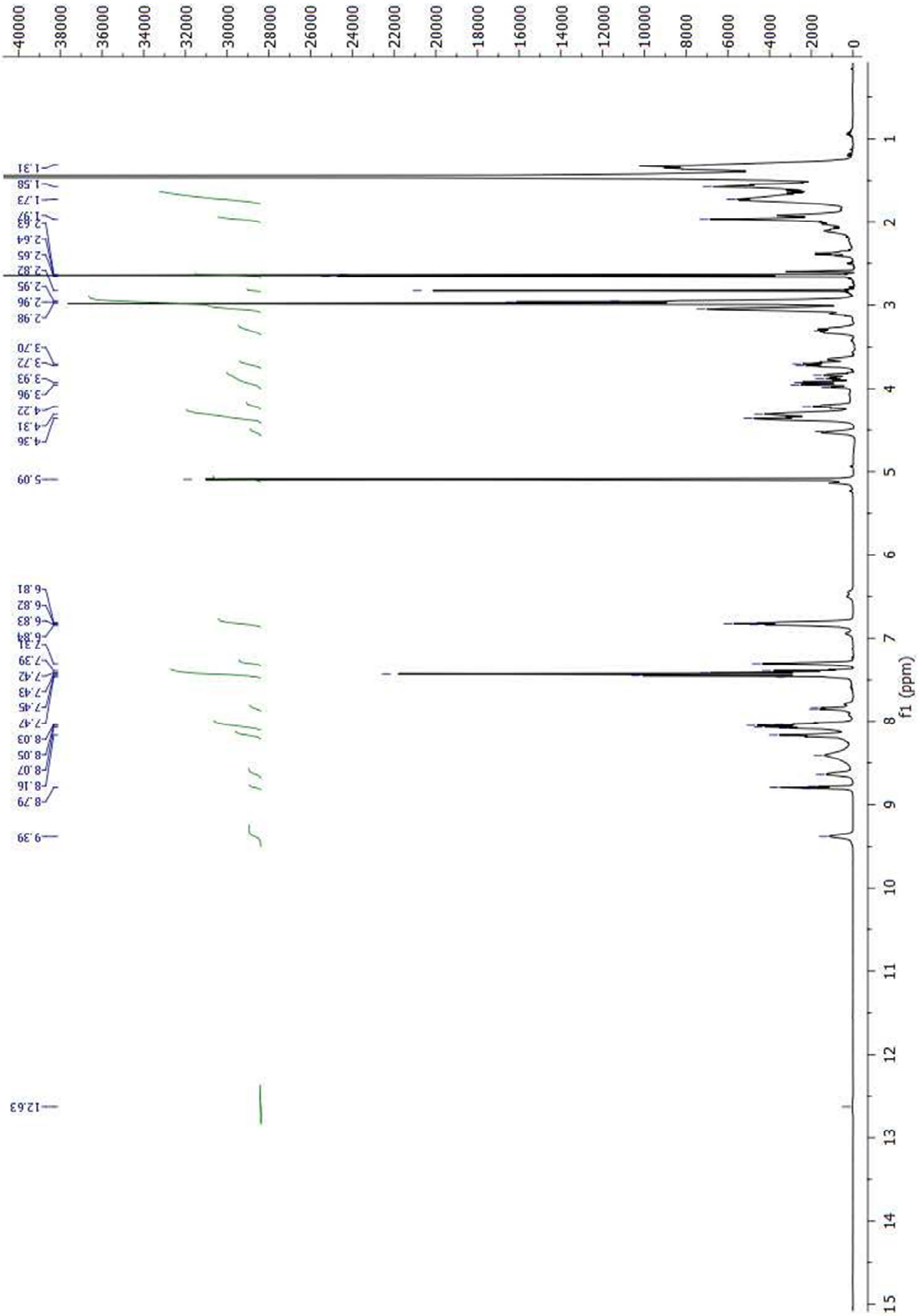


Figure S4. ^{1}H-NMR (500 MHz; dmso-d_6) of compound **2**

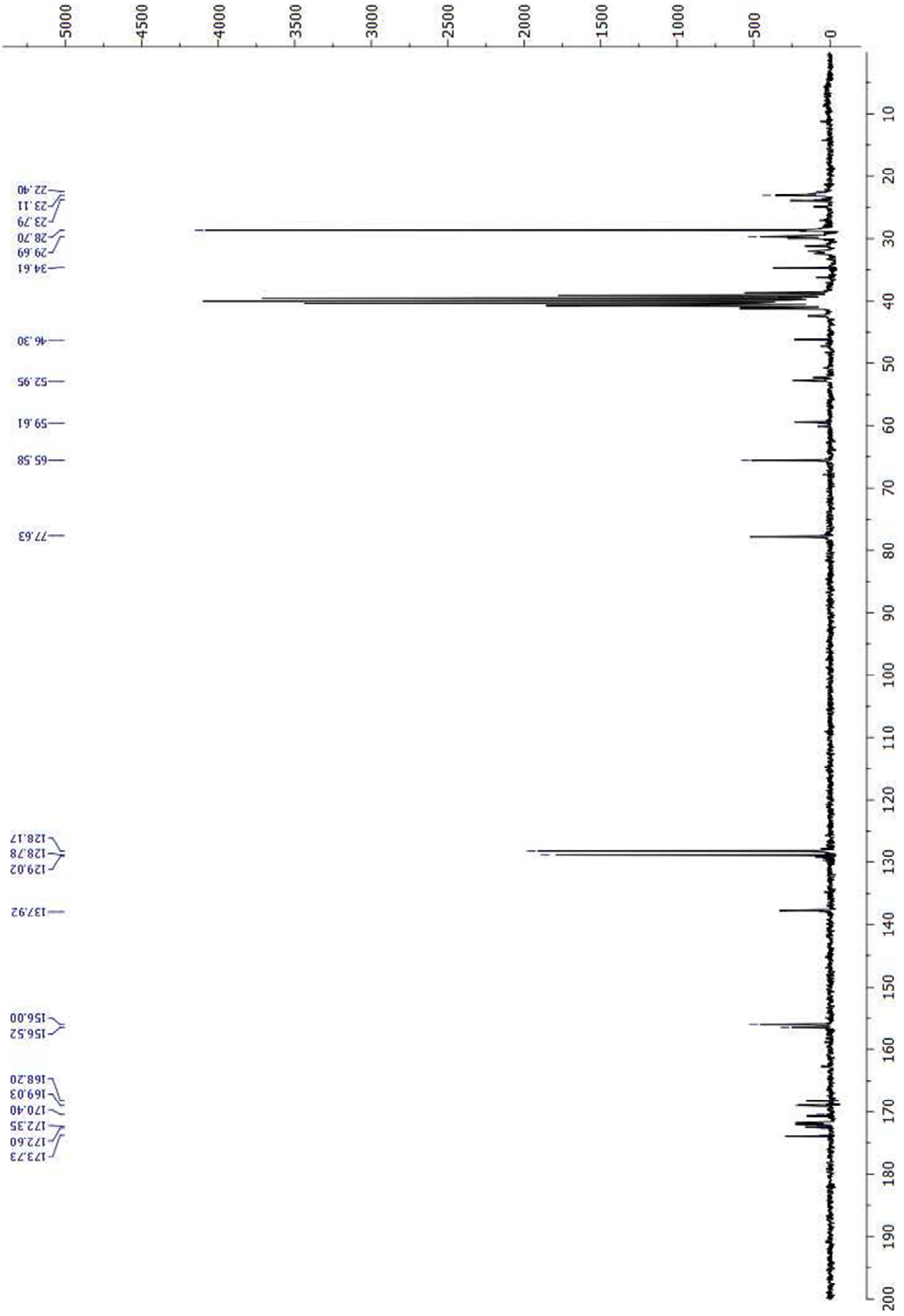


Figure S5. ^{13}C-NMR (50 MHz; dmso-d_6)of compound **2**

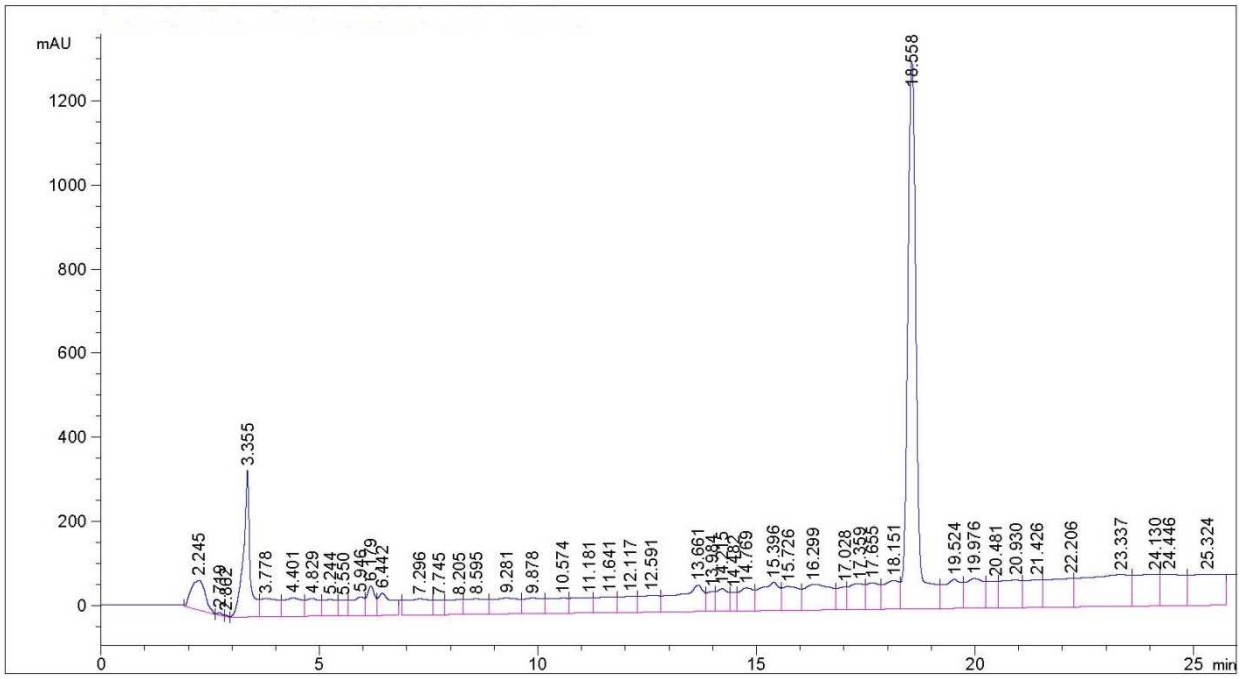


Figure S6. HPLC traces of compound **1**

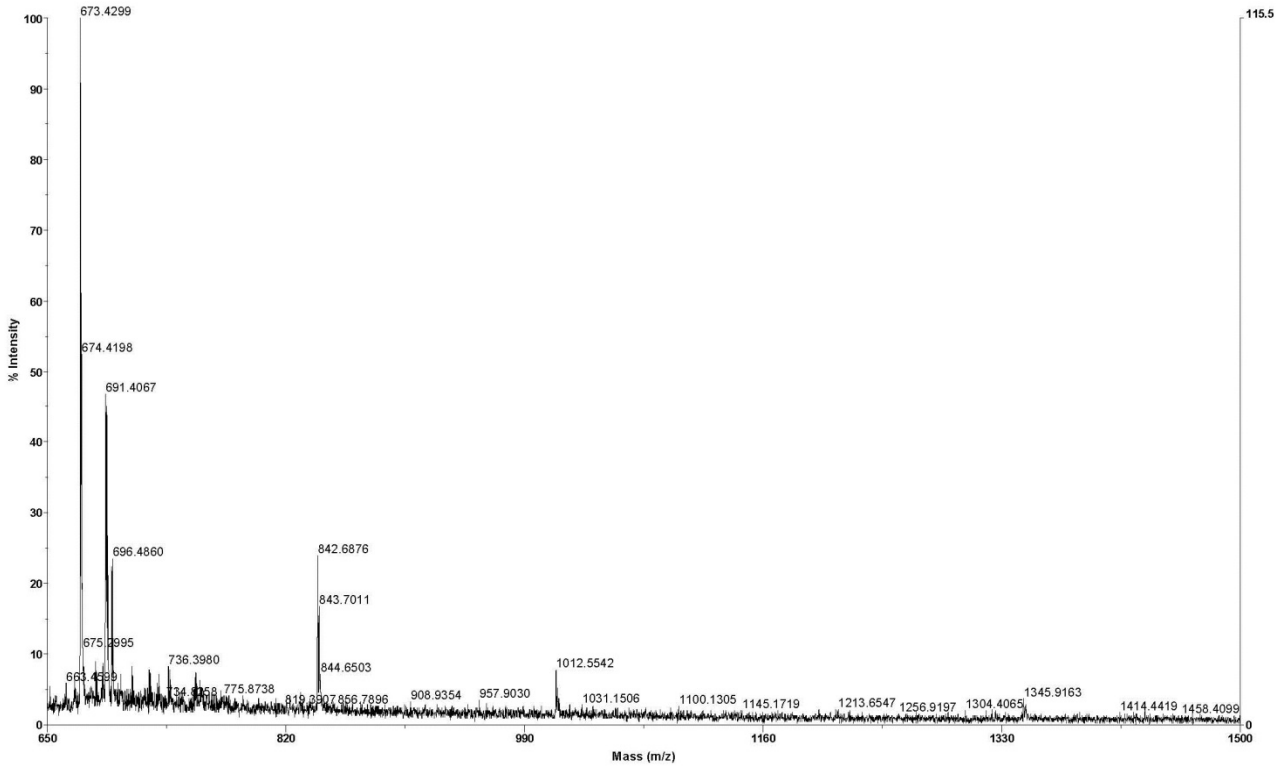


Figure S7. ESI-MS spectra of compound **1**

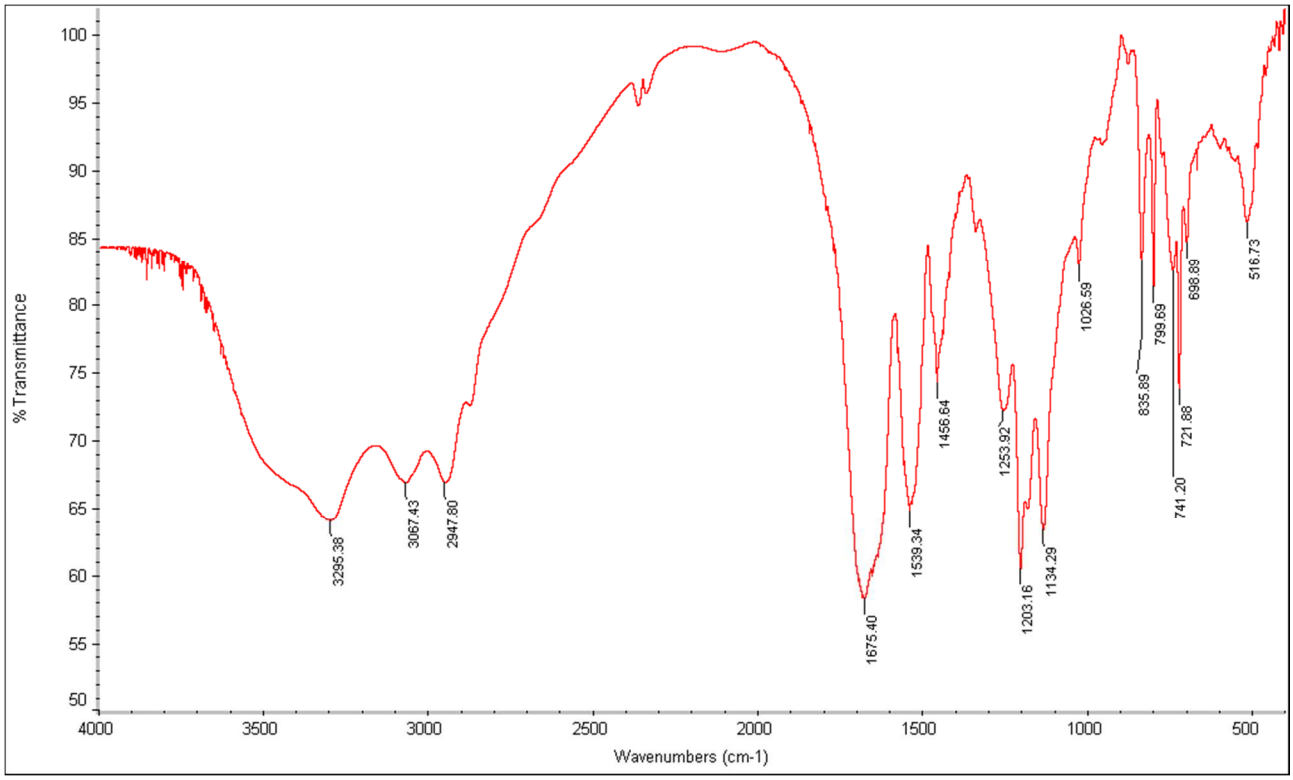


Figure S8. FT-IR (KBr disc) of compound **1**

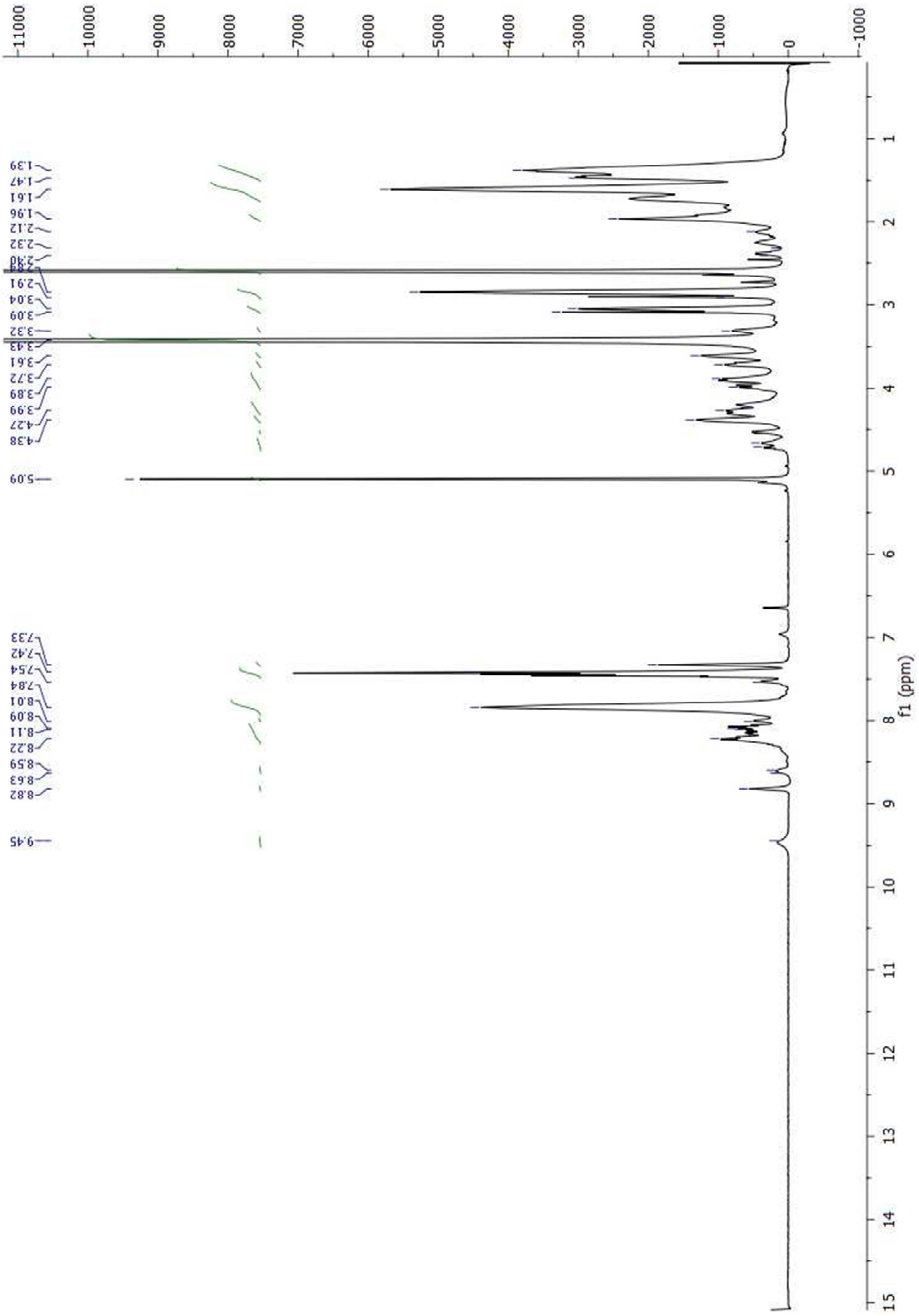


Figure S9. ^{1}H-NMR (500 MHz; dmso-d_6) compound **1**

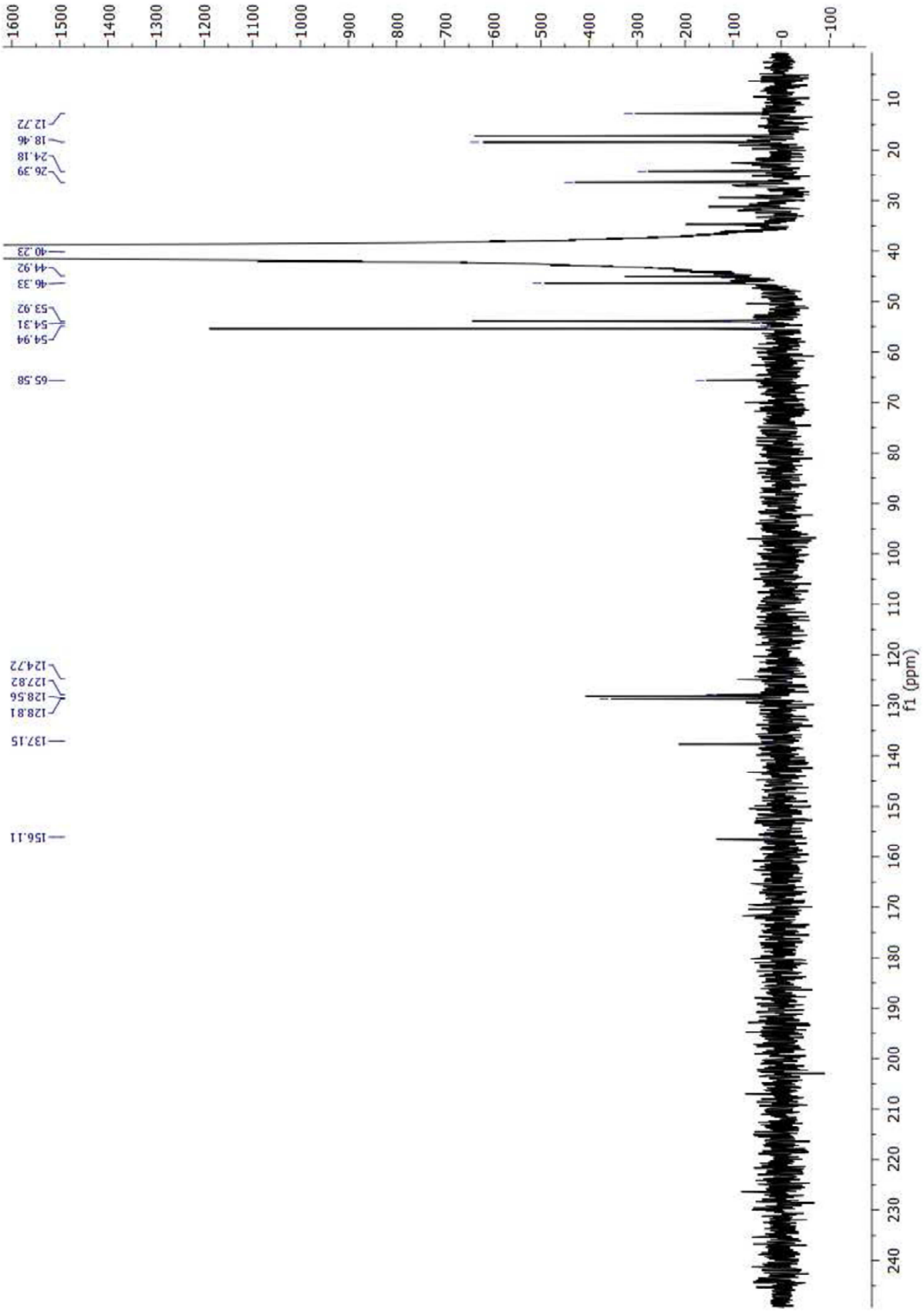


Figure S10. ^{13}C-NMR (125 MHz; dmso-d_6)compound **1**

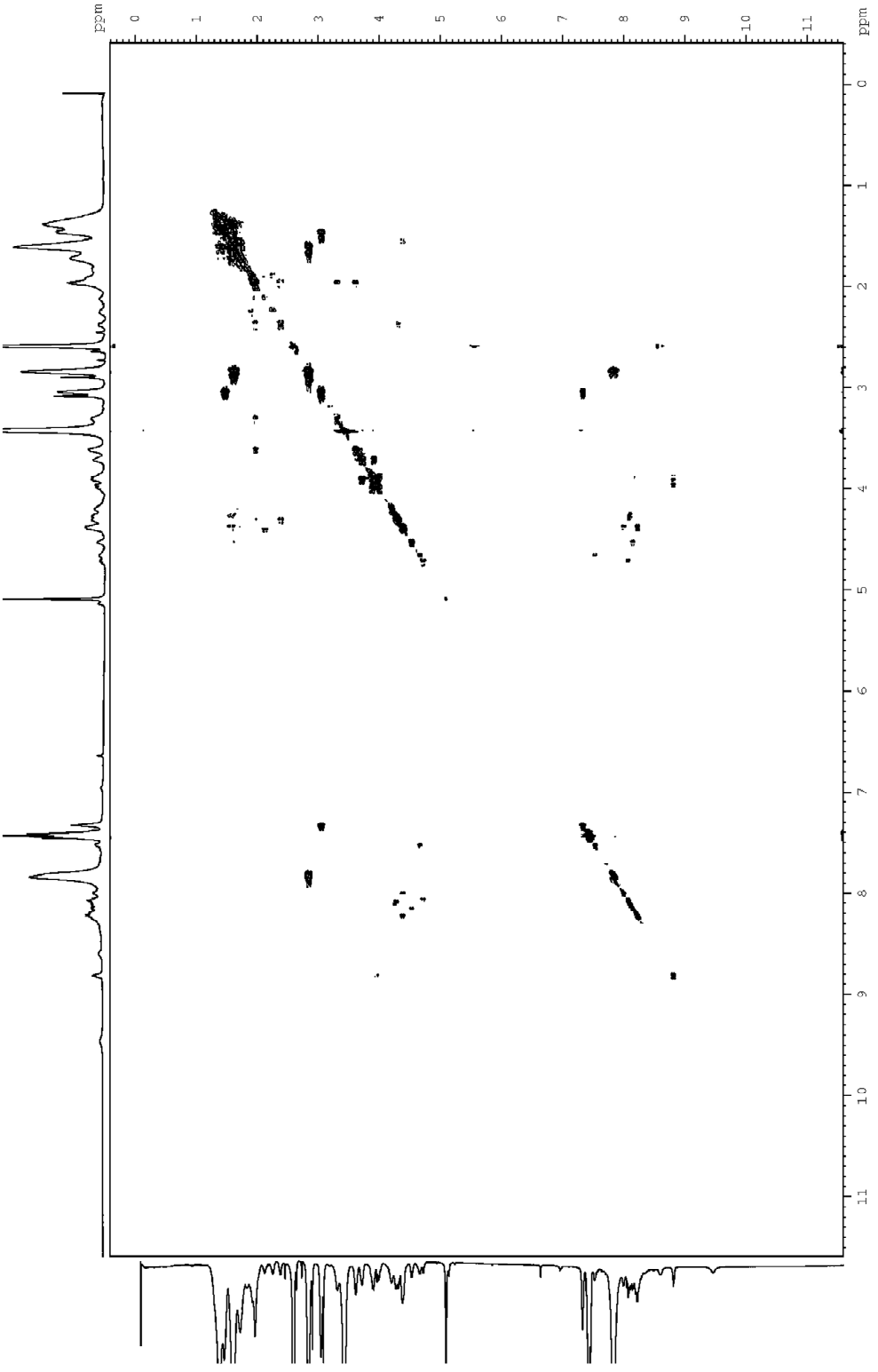


Figure S11. COSY (500 MHz; dmso-d_6) of compound **1**

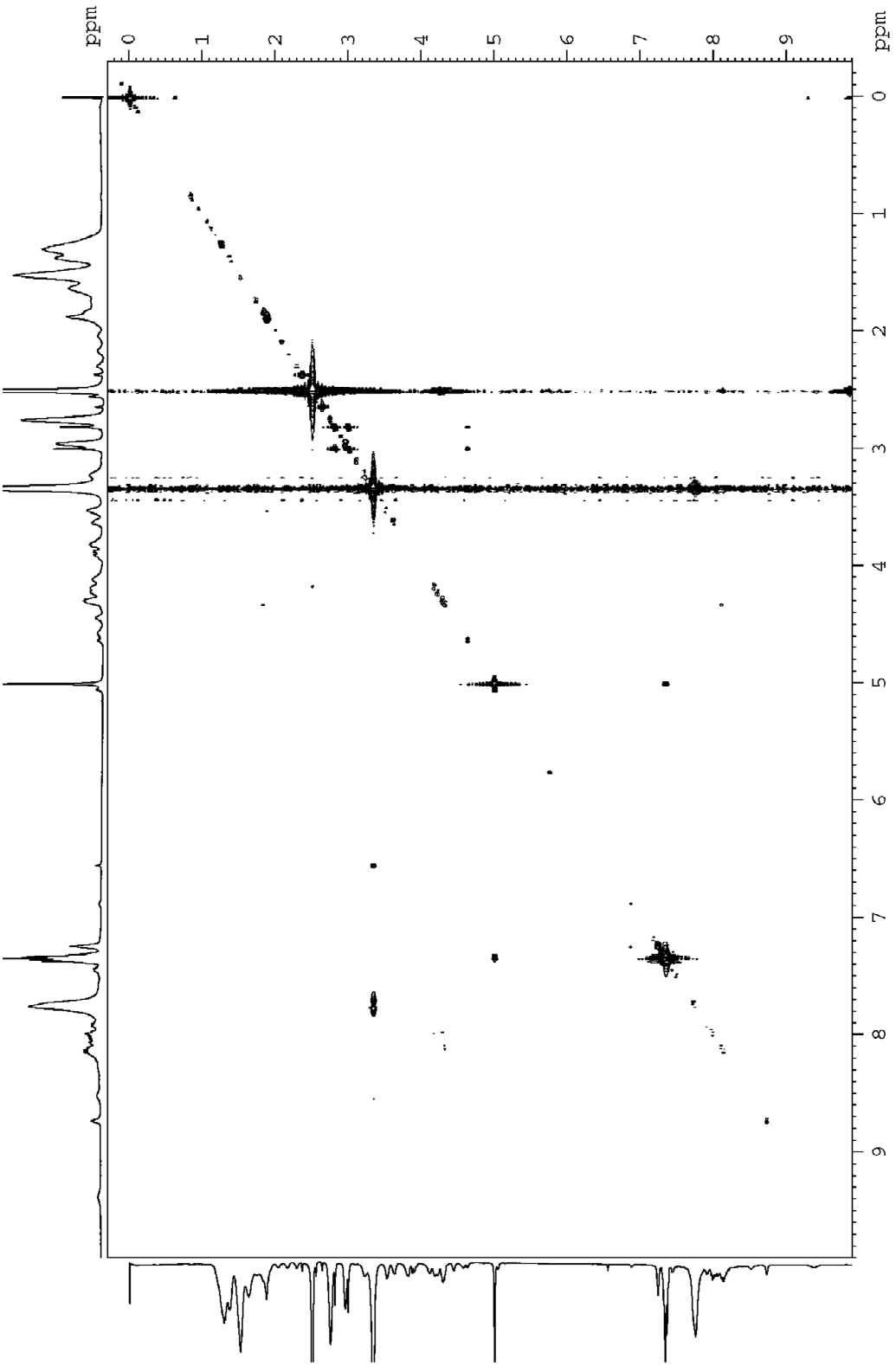


Figure S12. NOESY (500 MHz; dmso-d_6) of compound **1**

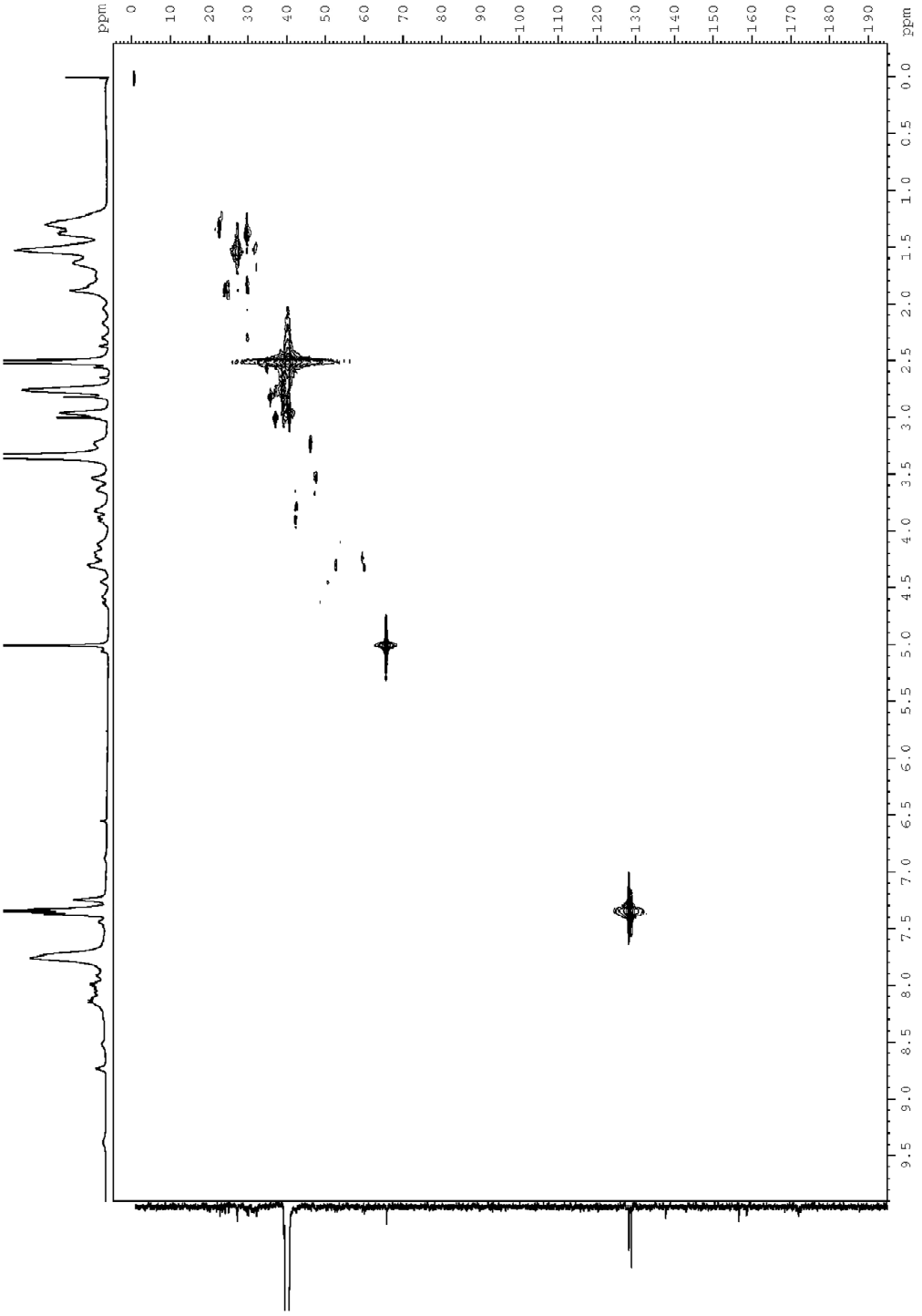


Figure S13. ^{1}H-^{13}C HMQC (600 MHz; dmso-d_6) of compound **1**

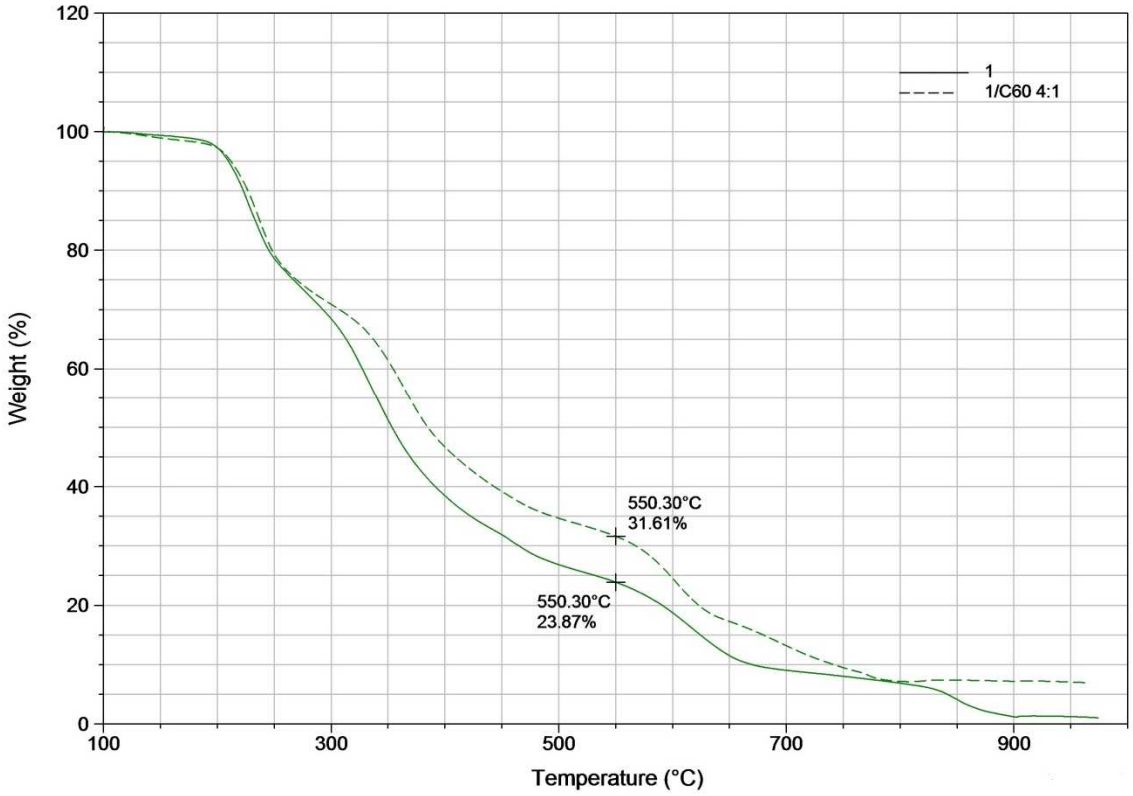


Figure S14. TGA analysis (under nitrogen atmosphere) of [60]fullerene, **1** and the **1**/C_{60} solution obtained by manual grinding.

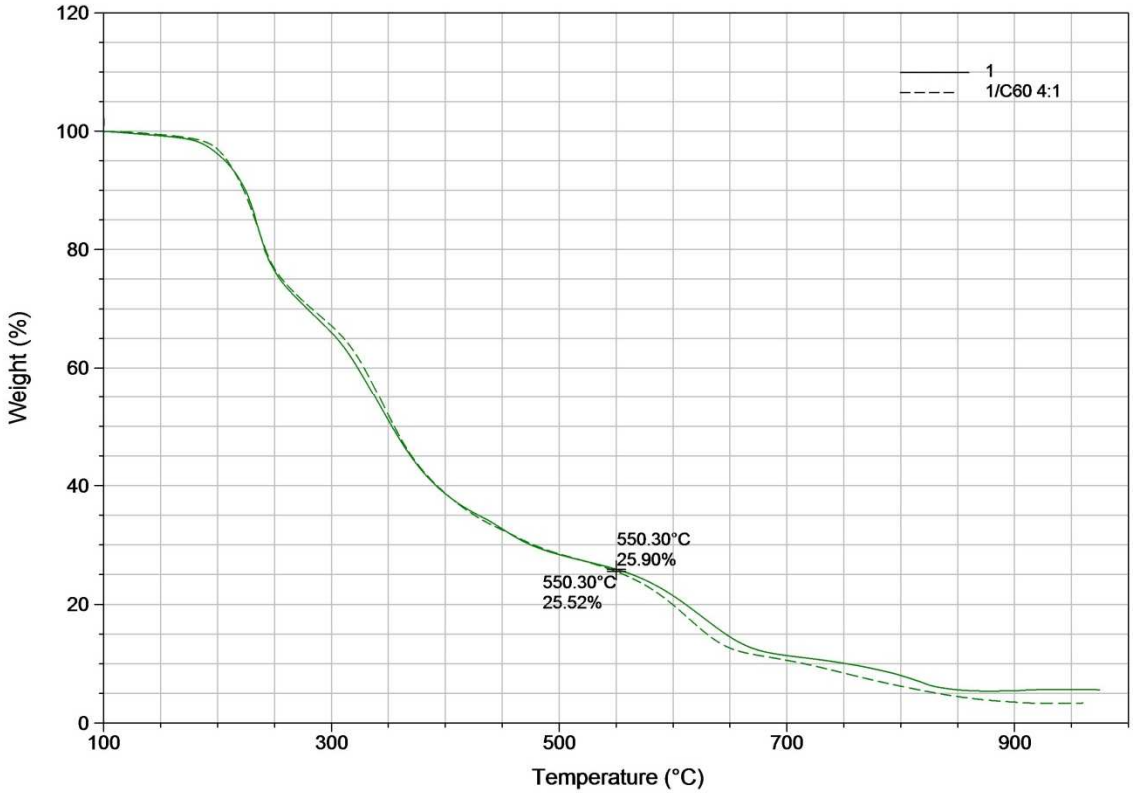


Figure S15. TGA analysis (under nitrogen atmosphere) of [60]fullerene, **1** and the **1**/C_{60} solution obtained by sonication.

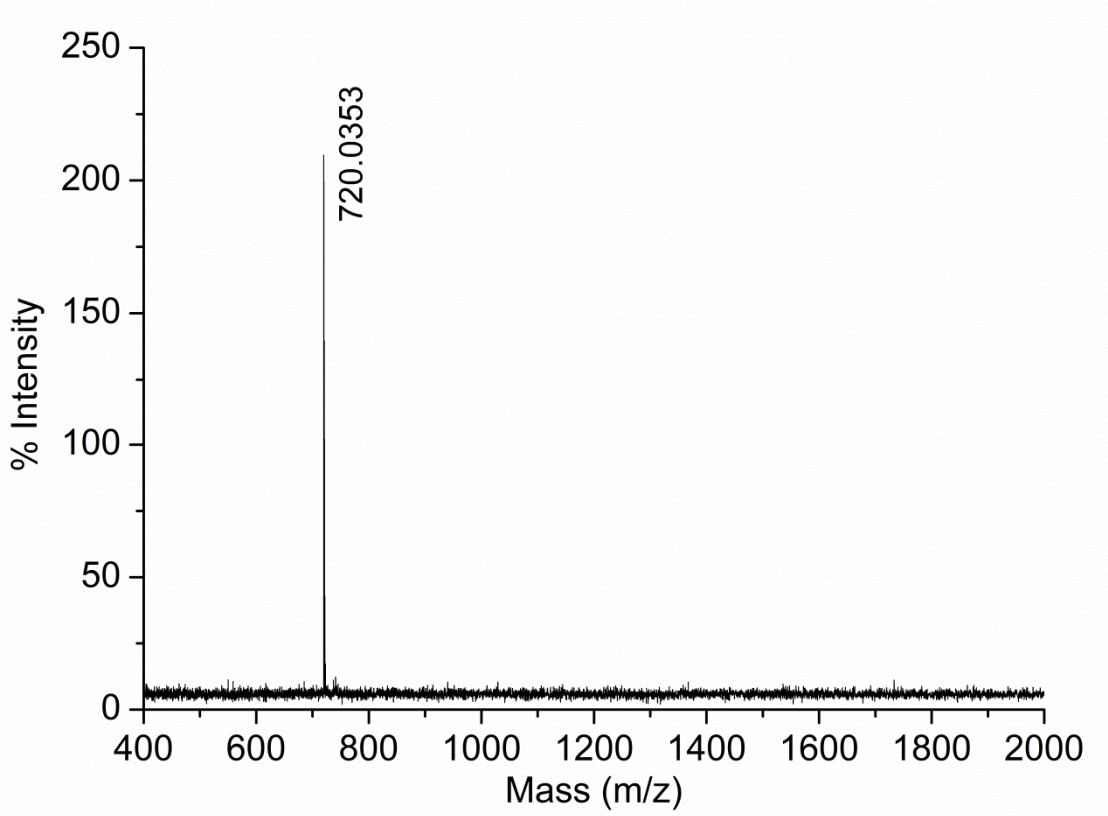


Figure S16. MALDI-TOF mass spectrum the **1**/C_{60} solution obtained by HSVM

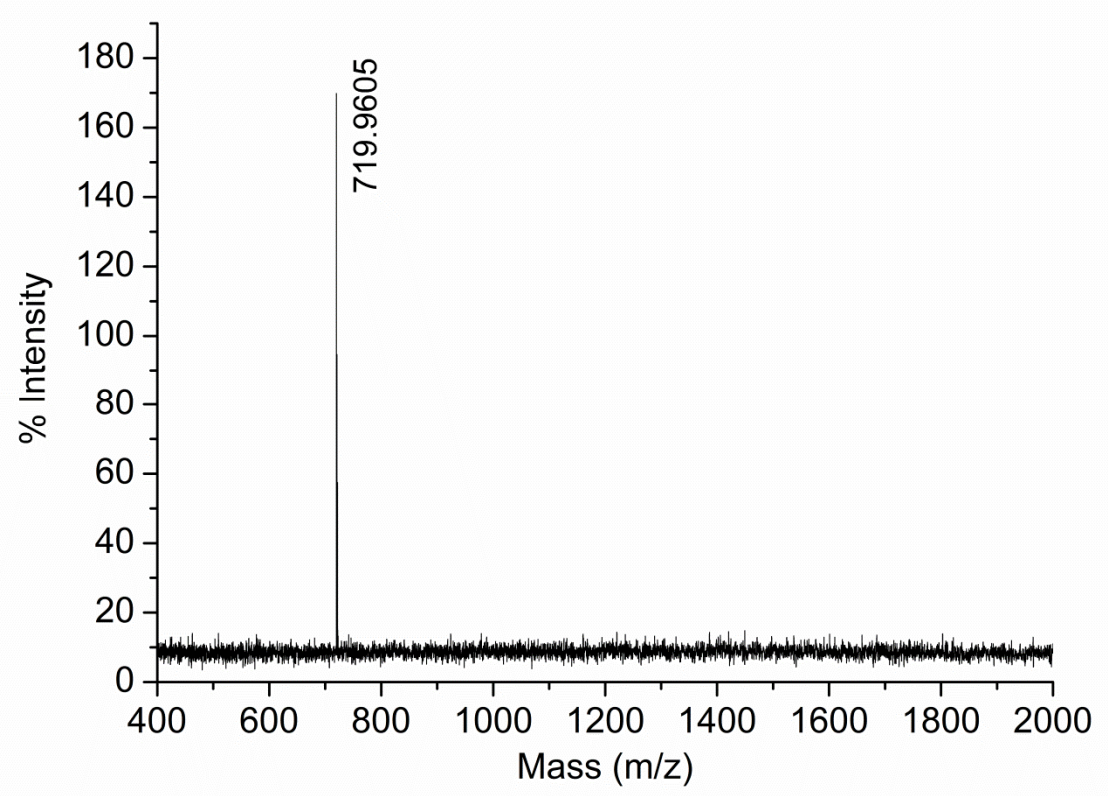


Figure S17. MALDI-TOF mass spectrum of the **1**/C_{60} solution obtained by manual grinding.

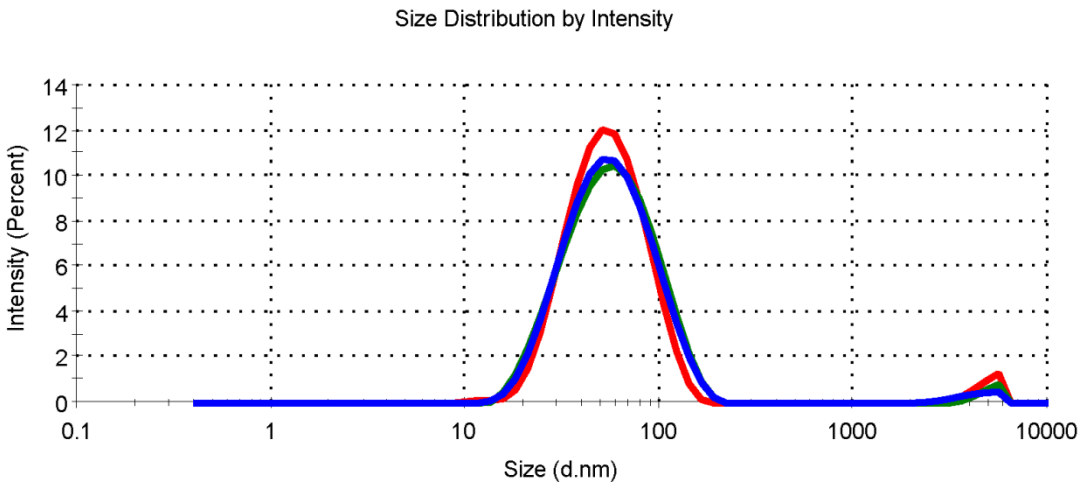


Figure S18. DLS measurements after re-dissolution of lyophilized **1**/C_{60} obtained by HSVM