

**Highly soluble germanium dioxide as a new source of germanium  
for derivatization with organic compounds**

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## 1. General

$^1\text{H NMR}$  (300 MHz) and  $^{13}\text{C NMR}$  (75 MHz) were recorded in  $\text{D}_2\text{O}$  and DMSO on Bruker AM300 at ambient temperature. **FTIR spectra** of the complexes were recorded on a BRUKER Vertex-70 FTIR spectrometer. **High-resolution mass spectra (MALDI)** were recorded on a Solarix XR FT/ICR mass spectrometer equipped with a 15 T superconducting magnet, a ParaCell analyzer cell and an ESI Apollo II and MALDI SmartBeam-II ion source. External calibration of the mass spectrometer was performed using a low-concentration sodium trifluoroacetate solution (0.1 mg/ml in acetonitrile/water, 1:1). The data set size was 2M with 16 scans. All MALDI-FT-ICR-MS measurements were recorded in positive/negative ion mode with MTP 384 ground steel target plate (matrix, with a scan range of  $m/z$  150 – 1500, laser frequency – 20%) All data visualization was processed using Data Analysis 5.1 software package from Bruker Daltonics and Machine Learning<sup>S1</sup>. Sample (20  $\mu\text{l}$ ) was mixed with matrix (20  $\mu\text{l}$ ) as saturated solutions in THF using a pipette and placed onto a MTP 384 ground steel target plate (Bruker Daltonics, Bremen, Germany) and allowed to dry at room temperature. **High-resolution mass spectra (ESI)** were measured on a Bruker micrOTOF II instrument. The measurements were done in a negative ion mode (interface capillary voltage 4.5 kV); mass range from  $m/z$  50 to  $m/z$  1600; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for the solutions in  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (flow rate 3  $\mu\text{l}/\text{min}$ ). Nitrogen was applied as a dry gas (flow rate 4  $\text{dm}^3 \text{min}^{-1}$ ); the interface temperature was set at 200 °C.

Oxidation and reduction were analyzed by **cyclic voltammetry** using a digital potentiostat IPC-Pro-MF (Econix). The studied compounds dissolved in a phosphate buffer solution ( $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ , pH = 6.86) were electrochemically tested in a standard three-electrode glass cell at the potential scan rates of 0.1  $\text{V s}^{-1}$ . The working electrode was a glassy carbon disc electrode with a diameter of 1.7 mm. Before using, it was polished with abrasive paper and then GOI paste until the surface attained a mirror shine. The counter electrode was a Pt wire pre-annealed in a gas burner flame to remove oxides and other possible contaminations. The potentials of the studied processes were measured versus the Ag/AgCl reference electrode separated from the bulk electrolyte solution by an electrolytic bridge filled with the phosphate buffer. **UV spectroscopy** was performed using an Agilent 8453 instrument. The spectra were registered in deionized water in a 10 mm quartz cell. Each CV curve and UV-vis spectrum were reproduced at least three times.

**Thermal analysis** was performed on DTG-60 Simultaneous Thermogravimetry/Differential Thermal Analyzers, Shimadzu (Japan). All experiments were carried out in alumina crucible under argon flow at a heating rate of 10  $\text{K min}^{-1}$ .

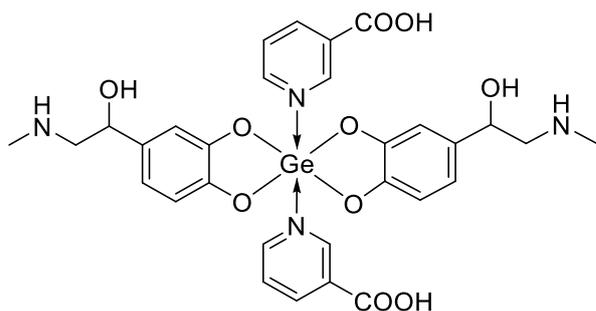
All reagents were purchased from Sigma Aldrich and used as received.

## 2. Preparation of complexes 1-10

Epinephrine (134.5 mg, 0.734 mmol) and nicotinic acid (90.4 mg, 0.734 mmol) were dissolved in deionized water (30 ml), and freshly prepared HSGO<sup>S2</sup> (38.4 mg, 0.367 mmol) was then added. The mixture was stirred at ambient temperature (23-26 °C) under argon for 5 h, and water was removed on a rotary evaporator. The product was dried with oil pump. Yield: 250.0 mg (0.367 mmol) of **1**.

Synthesis of **3** was carried out in the similar way, synthesis of **2** with using 1 molar equivalent of nicotinamide, synthesis of **4-10** without N-donor. The reaction time was increased to 48 hours in case of **5**, **7** and **8**. In case of **7** the mixture water/methanol (1:1) was used, while synthesis of **8** was carried out in a water suspension (initial phenol and product are insoluble in water).

### Complex 1.



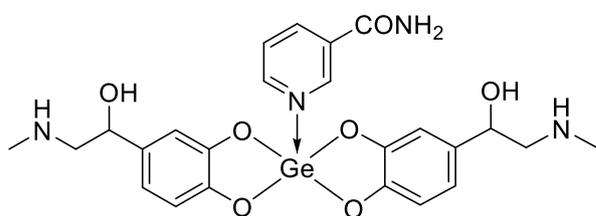
$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.68 (s, 6H, 2 $\text{CH}_3$ ), 3.18-3.28 (m, 4H, 2 $\text{CH}_2$ ), 4.76-4.80 (m, 2H, 2CH), 6.56-6.64 (M, 6H, 6 $\text{CH}_{\text{Ar}}$ ), 7.77-7.82 (m, 2H, Py), 8.57-8.61 (m, 2H, Py), 8.66-8.68 (m, 2H, Py), 8.96 (s, 2H, Py).

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 34.2 ( $\underline{\text{C}}\text{H}_3$ ); 55.7 ( $\underline{\text{C}}\text{H}_2$ ); 70.2; 110.8; 112.9; 117.2; 127.2; 129.9; 135.8; 144.5; 146.3; 150.2; 150.3; 171.0 ( $\underline{\text{C}}\text{OOH}$ ).

FTIR (KBr,  $\text{cm}^{-1}$ ): 421w; 442w; 499w; 643s; 694m; 747m; 770w; 812s; 866w; 919w; 973w; 1036m; 1073m; 1117m; 1166w; 1187w; 1249s; 1299m; 1323m; 1381m; 1434m; 1492s; 1558w; 1599s; 1713m; 1952w; 2362w; 2439w; 2810w; 3070w; 3415s.

HRMS (MALDI) for  $^{74}\text{Ge}$  [M+H] $^+$  683.14223 (calculated 683.14101).

### Complex 2.

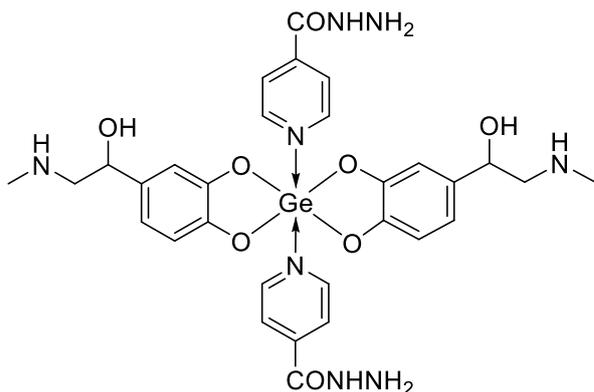


$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.58 (s, 6H, 2 $\text{CH}_3$ ); 3.0-3.17 (m, 4H, 2 $\text{CH}_2$ ); 4.72-4.75 (m, 2H, 2CH); 6.55-6.63 (m, 6H, 6 $\text{CH}_{\text{Ar}}$ ); 7.46-7.51 (m, 1H,  $\text{H}_{\text{Py}}$ ); 8.11-8.15 (m, 1H,  $\text{H}_{\text{Py}}$ ); 8.59-8.62 (m, 1H,  $\text{H}_{\text{Py}}$ ); 8.82 (m, 1H,  $\text{H}_{\text{Py}}$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 33.2; 54.9; 69.7; 109.5; 109.7; 111.7; 116.0; 124.2; 129.0; 129.2; 136.4; 147.6; 149.1; 151.8; 170.7.

FTIR (KBr,  $\text{cm}^{-1}$ ): 414w; 441w; 513w; 624s; 643s; 703m; 777m; 813s; 867w; 907w; 972w; 1028m; 1074m; 1120m; 1152w; 1201w; 1249s; 1324w; 1343w; 1394m; 1425m; 1491s; 1573w; 1596m; 1619s; 1678s; 3371s.

### Complex 3.

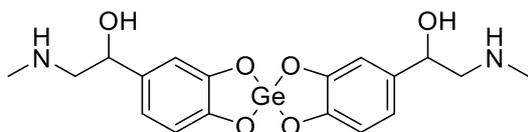


$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.67 (s, 6H,  $2\text{CH}_3$ ); 3.15-3.28 (m, 4H,  $2\text{CH}_2$ ), 4.76-4.80 (m, 2H,  $2\text{CH}$ ); 6.56-6.64 (m, 6H,  $6\text{CH}_{\text{Ar}}$ ); 7.61-7.63 (m, 3H, Py); 8.59-8.61 (m, 5H, Py).

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 33.0; 54.5; 69.1; 109.6; 111.8; 116.0; 121.7; 128.6; 140.8; 149.0; 149.1; 149.5; 167.4.

FTIR (KBr,  $\text{cm}^{-1}$ ): 438w; 484w; 577w; 657w; 679w; 778m; 846w; 1074m; 1123m; 1165w; 1252s; 1339w; 1374w; 1436w; 1493s; 1553w; 1636s; 1729w; 2930w; 2961w; 3454s.

### Complex 4.



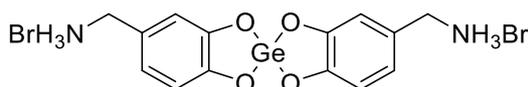
$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.57 (s, 6H,  $2\text{CH}_3$ ); 2.96-3.17 (m, 4H,  $2\text{CH}_2$ ); 4.67-4.73 (m, 2H,  $2\text{CH}$ ); 6.54-6.61 (m, 6H,  $6\text{CH}_{\text{Ar}}$ )

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 33.3; 54.9; 69.7; 109.6; 109.7; 111.7; 116.0; 129.1; 149.0.

FTIR (KBr,  $\text{cm}^{-1}$ ): 421w; 438w; 648m; 744w; 775m; 812m; 868w; 906w; 948w; 973w; 1073m; 1121m; 1164w; 1253s; 1323w; 1349w; 1433s; 1492s; 1632s; 1646s; 1662s; 1678w; 1693w; 1728m; 2060w; 2311w; 2353w; 2410w; 2857w; 2929w; 2959w; 3440bs; 3466bs.

HRMS (MALDI) for  $^{74}\text{Ge}$   $[\text{M}+\text{H}]^+$  437.01722 (calculated 437.07624).

### Complex 5.

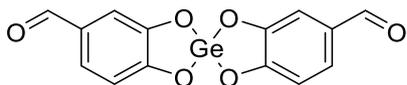


$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 3.82 (s, 4H,  $2\text{CH}_2$ ); 6.56-6.64 (m, 6H,  $\text{CH}_{\text{Ar}}$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 43.0; 111.4; 112.4; 115.9; 117.0; 118.9; 120.7; 122.7; 145.6; 149.4; 149.7.

FTIR (KBr,  $\text{cm}^{-1}$ ): 425s; 540w; 570m; 608m; 689s; 739m; 809s; 834s; 880m; 921m; 995w; 1054m; 1088m; 1130s; 1154m; 1214s; 1261s; 1287m; 1311w; 1329s; 1375w; 1441s; 1504s; 1582s; 3457s.

### Complex 6.



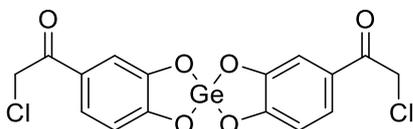
$^1\text{H}$  NMR (300 MHz, DMSO,  $\delta$ , ppm): 6.82 (d, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J=7,9$  Hz); 7.11 (d, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J=1,8$  Hz), 7.22 (dd, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J_1=7,9$  Hz,  $J_2 = 1,8$  Hz); 9.67 (s, 2H,  $2\text{C}(\text{O})\text{H}$ ).

$^{13}\text{C}$  NMR (75 MHz, DMSO,  $\delta$ , ppm): 109.7; 112.0; 125.2; 128.1; 149.6; 156.3; 191.5 ( $\underline{\text{C}}(\text{O})\text{H}$ ).

FTIR (KBr,  $\text{cm}^{-1}$ ): 441w; 575w; 592w; 629m; 699m; 771s; 817s; 833m; 887w; 933w; 973w; 1003w; 1121s; 1162m; 1232m; 1269s; 1343w; 1398w; 1446s; 1491s; 1574s; 1591s; 1653s; 2848w; 2930w.

HRMS (ESI) for  $^{74}\text{Ge}$  [ $\text{M}+\text{OH}$ ] $^-$  362.9579 (calculated 362.9568).

### Complex 7.



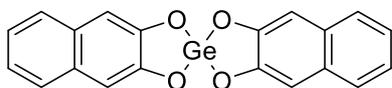
$^1\text{H}$  NMR (300 MHz, DMSO,  $\delta$ , ppm): 4.99 (s, 4H,  $2\text{CH}_2$ ), 6.75 (d, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J=8,4$  Hz), 7.26 (d, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J=2,1$  Hz), 7.36 (dd, 2H,  $2\text{CH}_{\text{Ar}}$ ,  $J_1 = 2,1$  Hz,  $J_2 = 8,1$ Hz).

$^{13}\text{C}$  NMR (75 MHz, DMSO,  $\delta$ , ppm): 47.5; 111.0; 111.7; 121.7; 125.0; 149.2; 155.6; 190.2.

FTIR (KBr,  $\text{cm}^{-1}$ ): 421m; 441w; 477w; 586w; 611m; 625m; 682s; 752s; 793s; 810s; 843s; 867s; 910m; 1126s; 1157s; 1207w; 1311m; 1330m; 1401m; 1439s; 1501s; 1604s; 1684s; 2389w; 2941m; 2986m.

HRMS (ESI) for  $^{74}\text{Ge}$  [ $\text{M}+\text{OH}$ ] $^-$  458.9118 (calculated 458.9094).

### Complex 8.



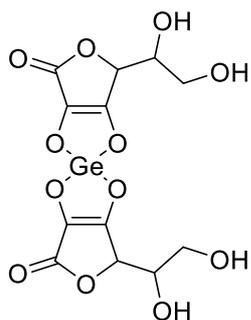
$^1\text{H}$  NMR (300 MHz, DMSO,  $\delta$ , ppm): 7.01 (s, 4H,  $4\text{CH}_{\text{Ar}}$ ); 7.13 (dd, 4H,  $4\text{CH}_{\text{Ar}}$ ,  $J_1=6,1$ Hz,  $J_2 = 3,3$  Hz); 7.55 (dd, 4H,  $4\text{CH}_{\text{Ar}}$ ,  $J_1=6,1$ Hz,  $J_2 = 3,3$  Hz).

$^{13}\text{C}$  NMR (75 MHz, DMSO,  $\delta$ , ppm): 105.8; 122.4; 126.0; 129.4; 150.3.

FTIR (KBr,  $\text{cm}^{-1}$ ): 409w; 430w; 482s; 550w; 567w; 589w; 617w; 657w; 686m; 741s; 764s; 837s; 862s; 877s; 917w; 953m; 1102s; 1142m; 1160s; 1190m; 1205w; 1249m; 1273s; 1326w; 1360w; 1373w; 1397s; 1425s; 1460s; 1485s; 1527s; 1585m; 1603w; 1633m; 3449s; 3498s.

HRMS (ESI) for  $^{74}\text{Ge}$  [ $\text{M}+\text{OH}$ ] $^-$  406.9997 (calculated 406.9984).

**Complex 9.**



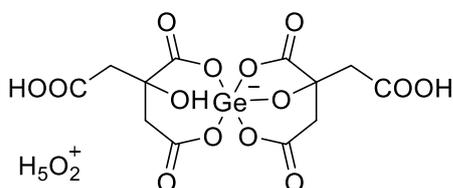
$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 3.68 (m, 4H, 2 $\text{CH}_2$ ); 3.98-4.03 (m, 2H, 2CH); 4.90(d, 2H, 2CH,  $J = 1.8\text{Hz}$ )

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 62.1; 68.9; 76.2; 117.8; 155.8; 173.3.

FTIR (KBr,  $\text{cm}^{-1}$ ): 448m; 472w; 518w; 565m; 629w; 685m; 720w; 756s; 821m; 872s; 886s; 962w; 989m; 1027s; 1044m; 1074m; 1118s; 1141s; 1199m; 1222m; 1249w; 1275s; 1321s; 1364w; 1389w; 1459w; 1498w; 1674s; 1755s; 2637w; 2714w; 2917m; 3030m; 3218m; 3315s; 3411s; 3526s.

HRMS (ESI) for  $^{74}\text{Ge}$  [ $\text{M}-\text{H}$ ] $^-$ : 420.9474 (calculated 420.9471).

**Complex 10.**



$^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.73-2.79 (m, 4H, 2 $\text{CH}_2$ ); 2.86-2.98 (m, 4H, 2 $\text{CH}_2$ )

$^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 43.2; 73.3; 75.0; 173.3.

FTIR (KBr,  $\text{cm}^{-1}$ ): 471w; 546m; 588m; 637w; 735s; 816w; 864s; 926s; 1018w; 1081s; 1156m; 1226s; 1341s; 1405s; 1727s; 2558m; 3444s.

HRMS (MALDI) for  $^{74}\text{Ge}$  [ $\text{M}$ ] $^-$ : 452.93682 (calculated 452.93661).

### 3. NMR spectroscopy

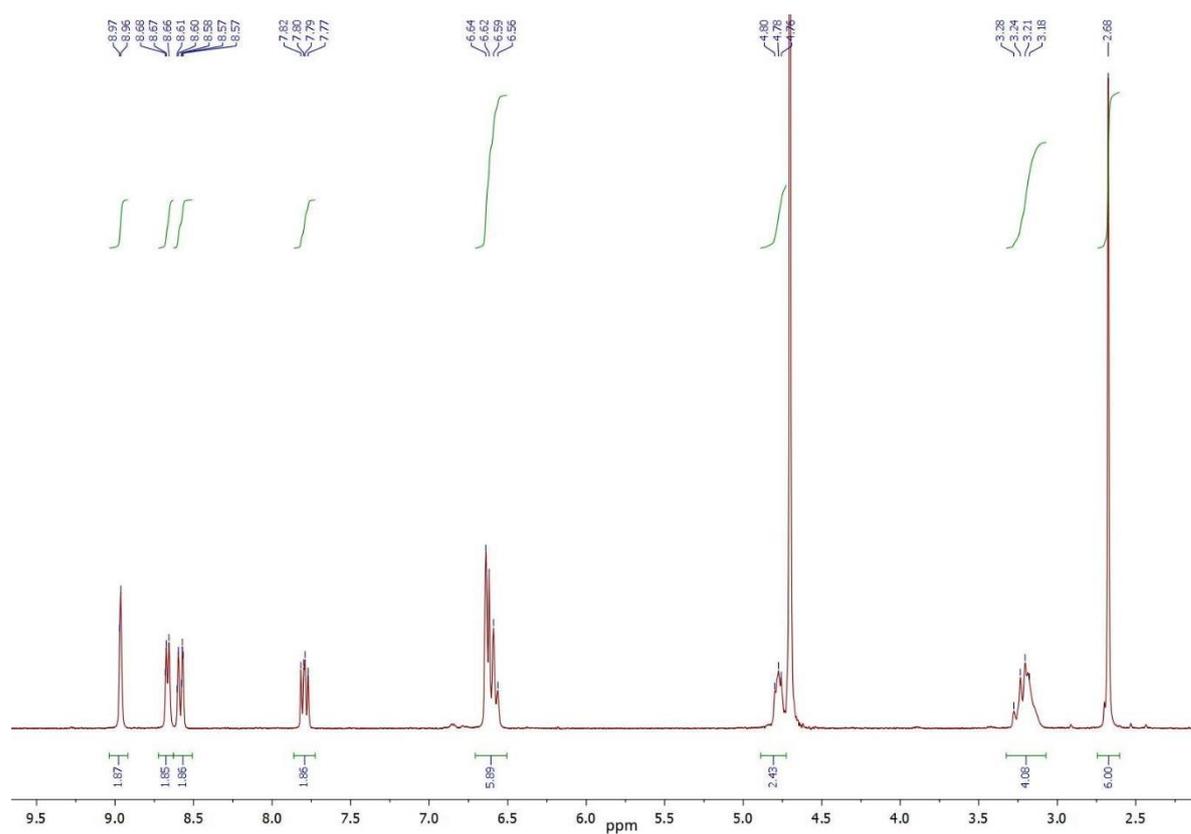


Figure S1. <sup>1</sup>H NMR spectrum of **1** in D<sub>2</sub>O.

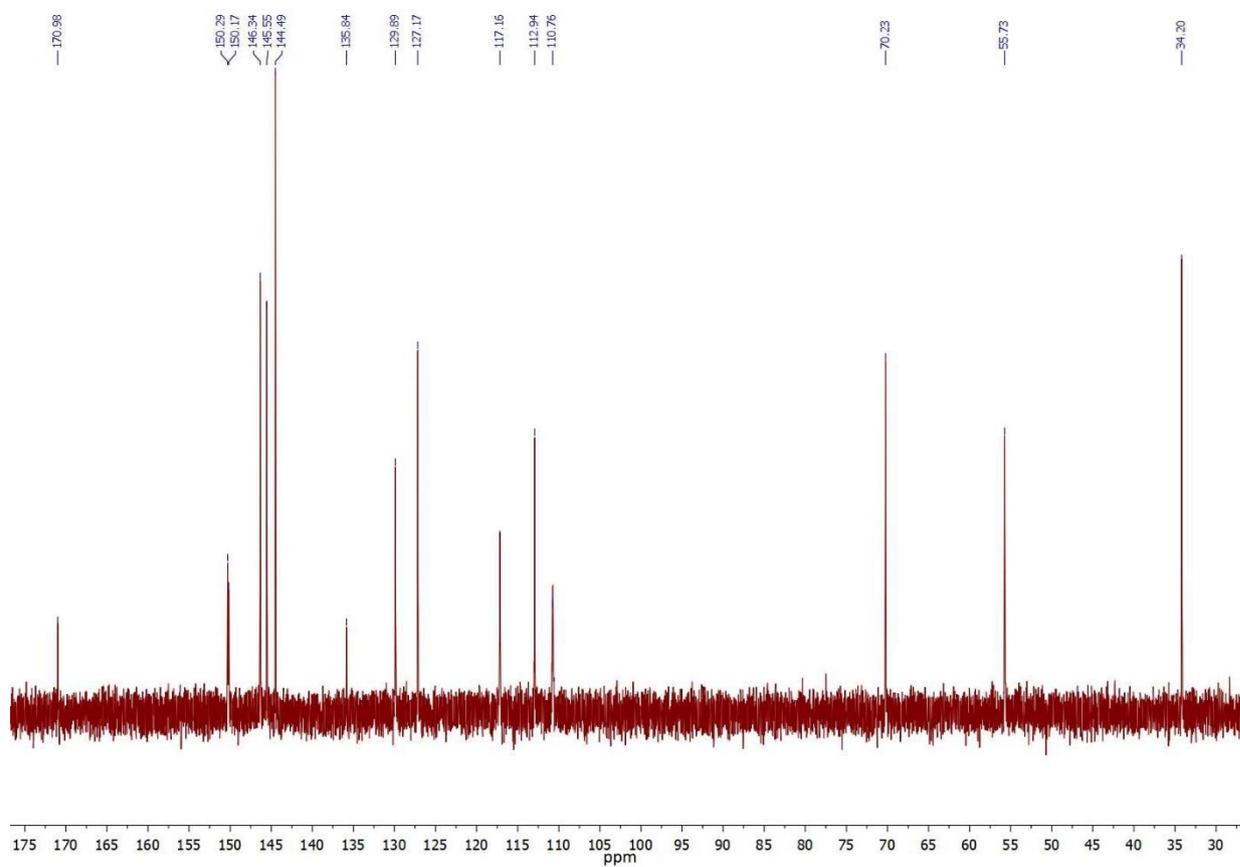


Figure S2. <sup>13</sup>C NMR spectrum of **1** in D<sub>2</sub>O.

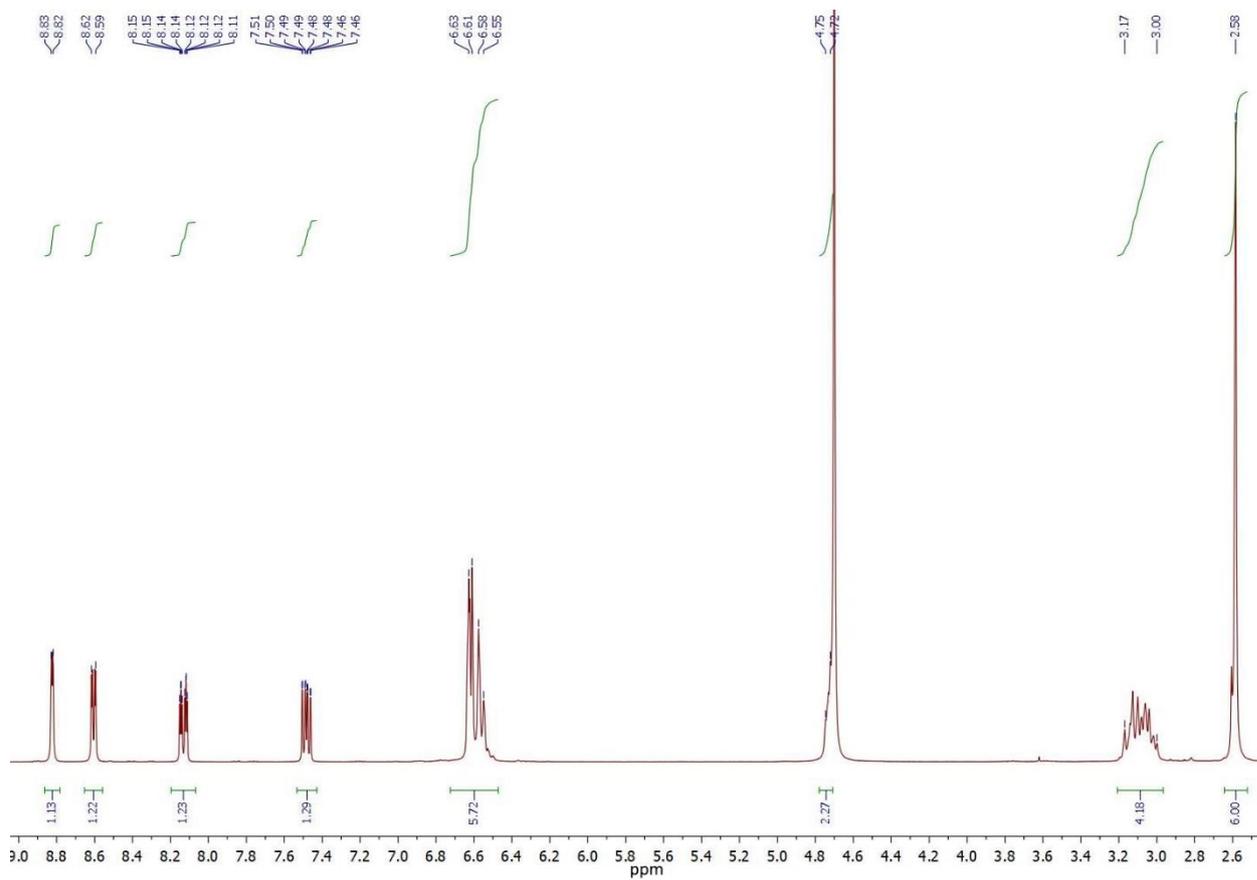


Figure S3.  $^1\text{H}$  NMR spectrum of **2** in  $\text{D}_2\text{O}$ .

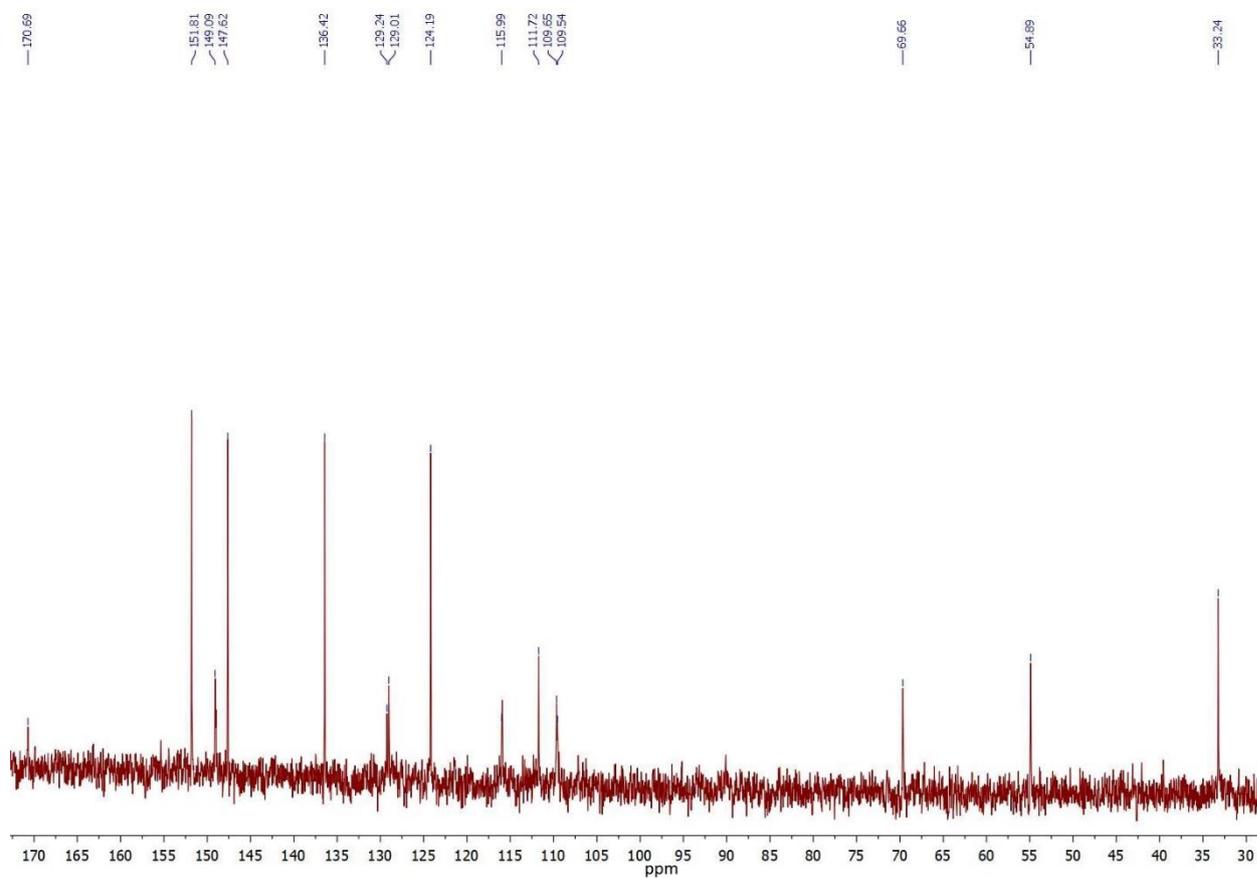


Figure S4.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{D}_2\text{O}$ .

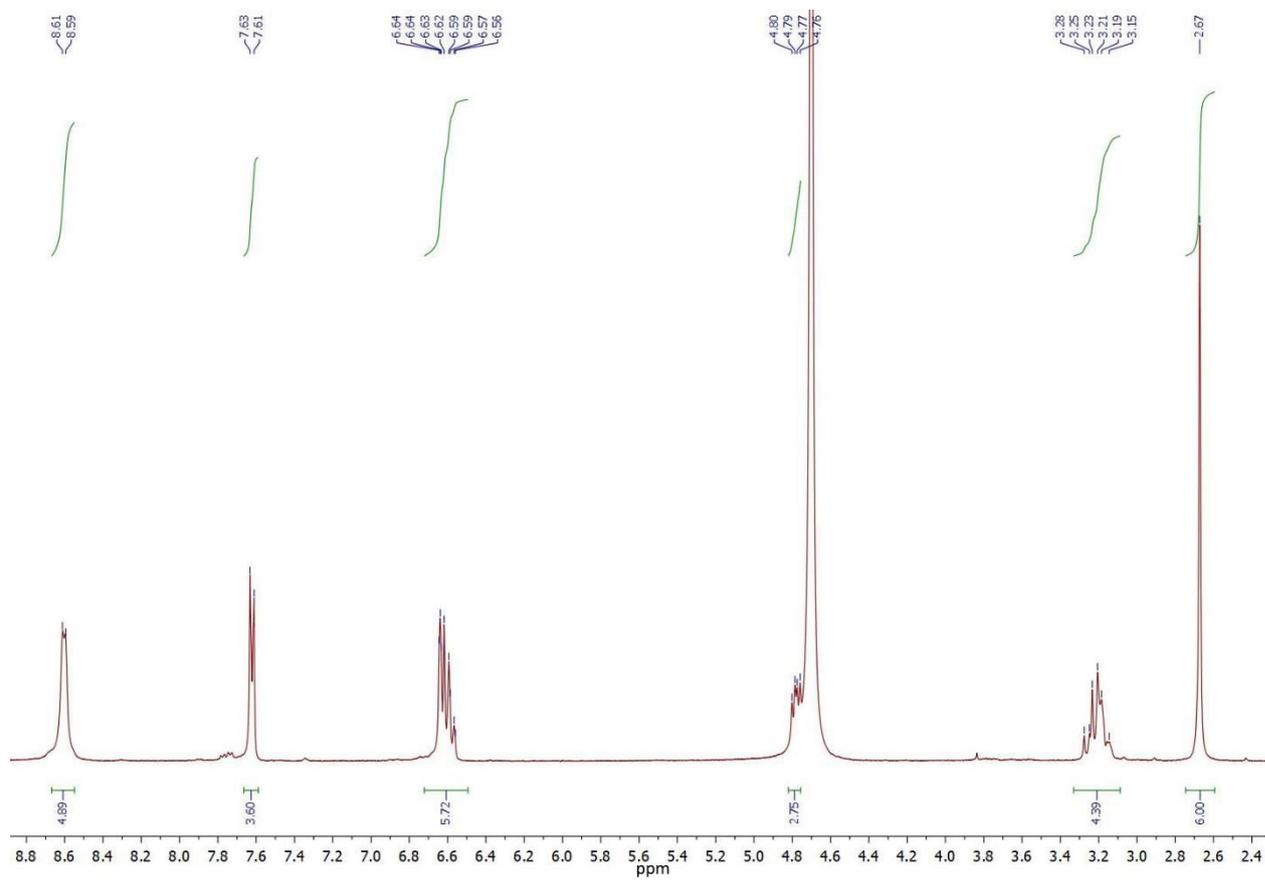


Figure S5.  $^1\text{H}$  NMR spectrum of **3** in  $\text{D}_2\text{O}$ .

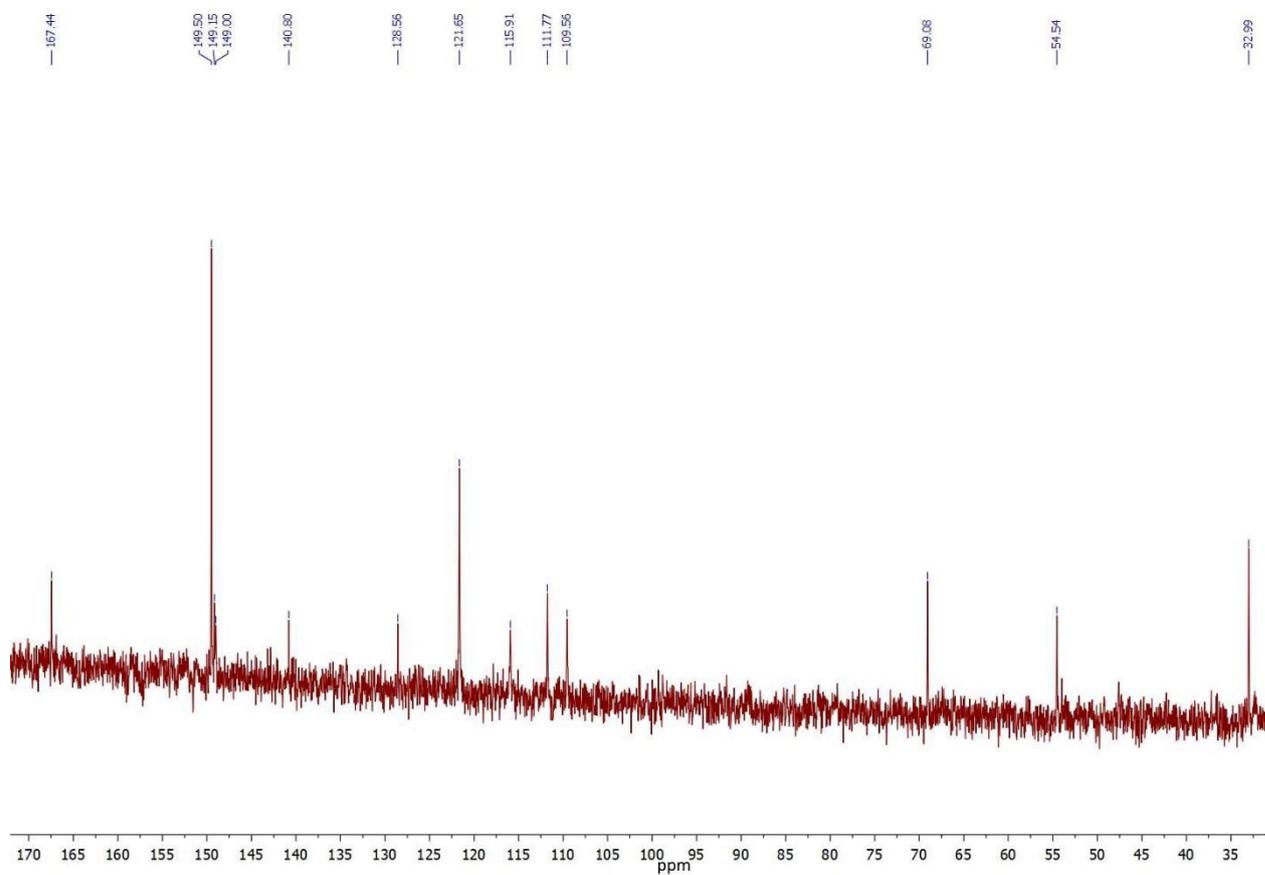


Figure S6.  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{D}_2\text{O}$ .

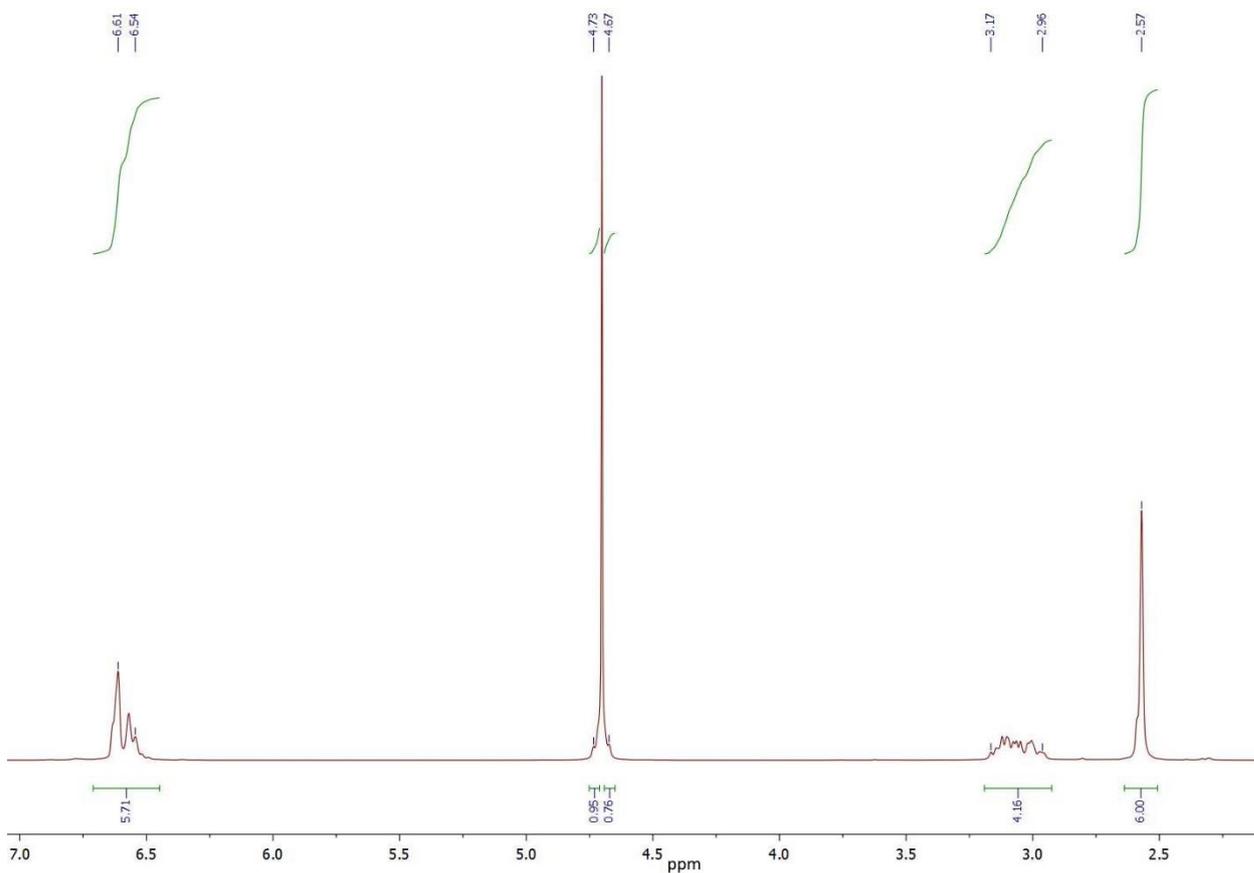


Figure S7.  $^1\text{H}$  NMR spectrum of **4** in  $\text{D}_2\text{O}$ .

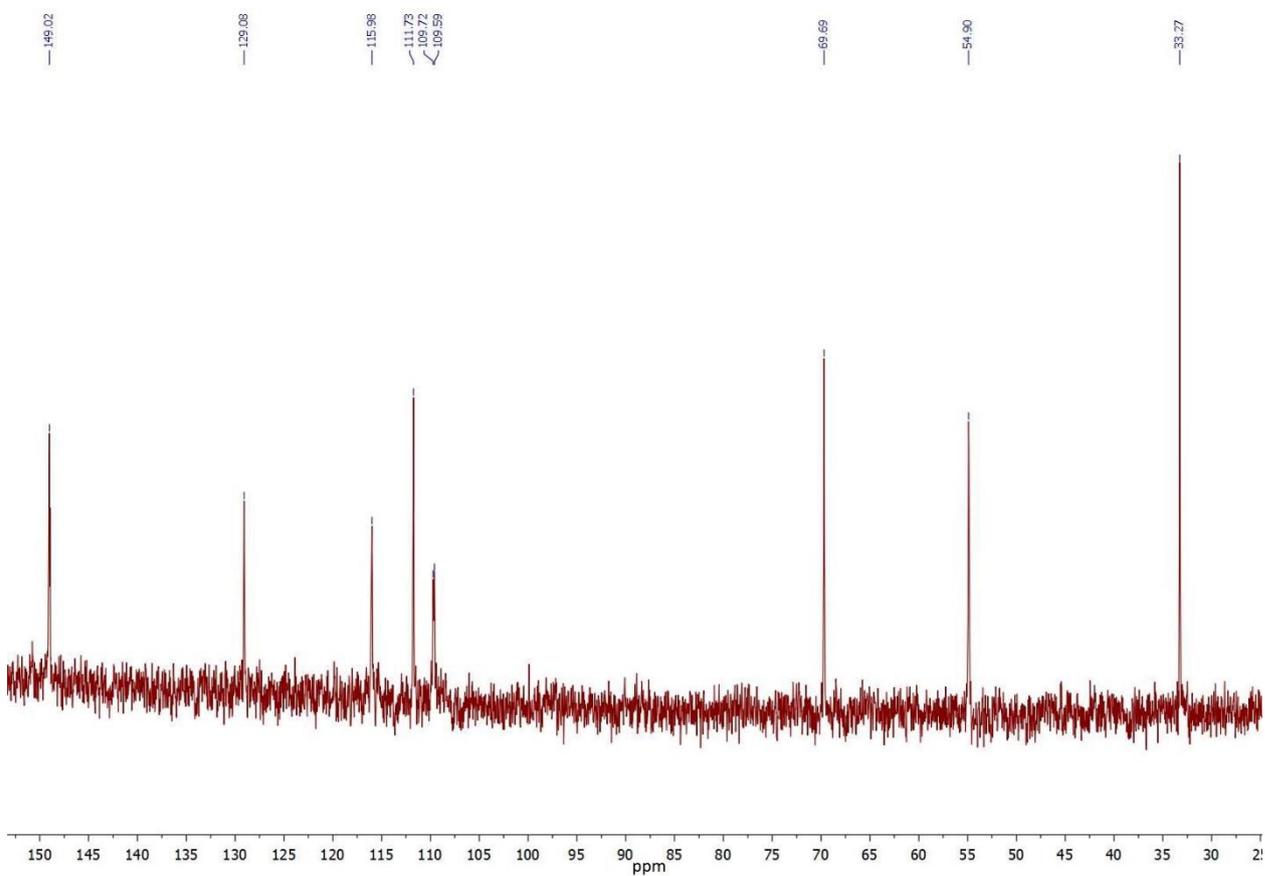
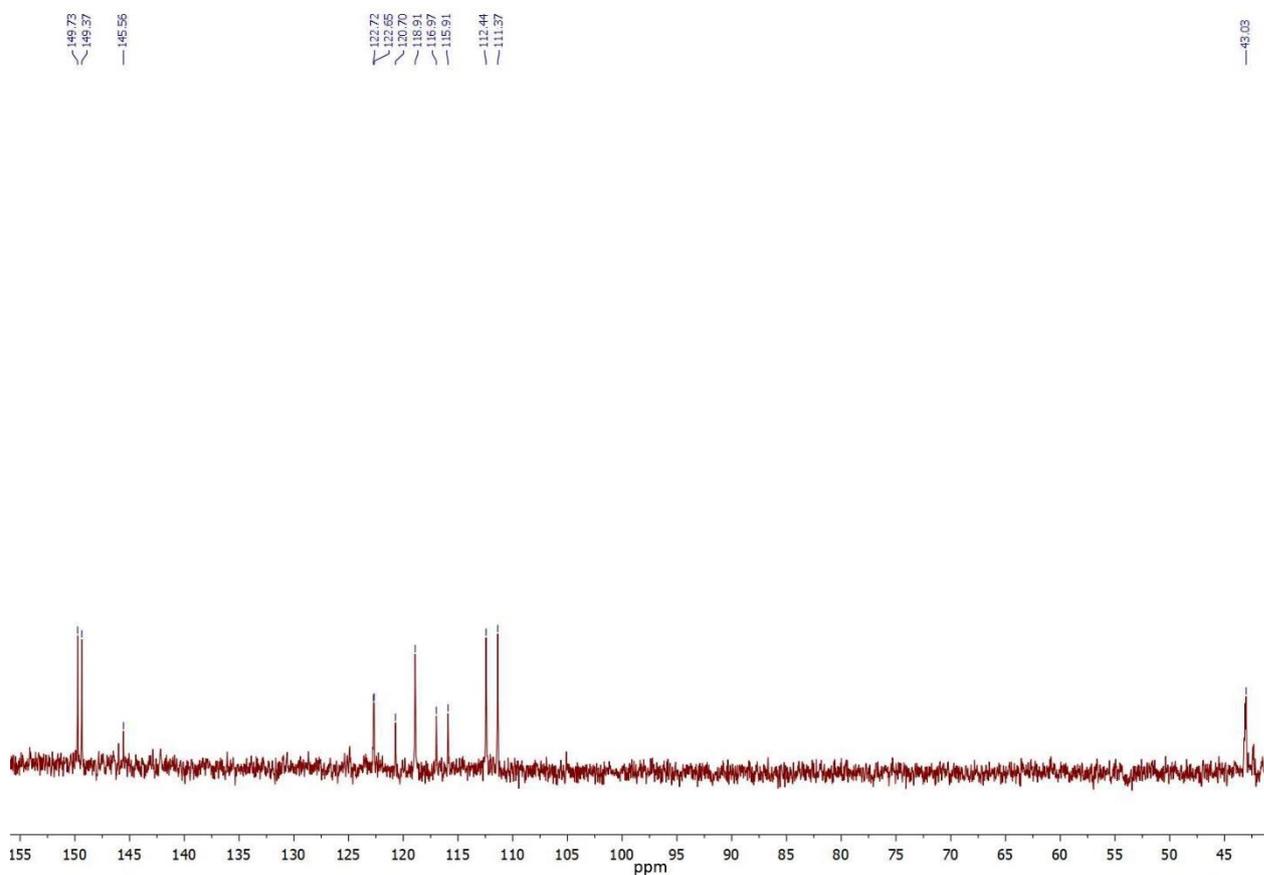
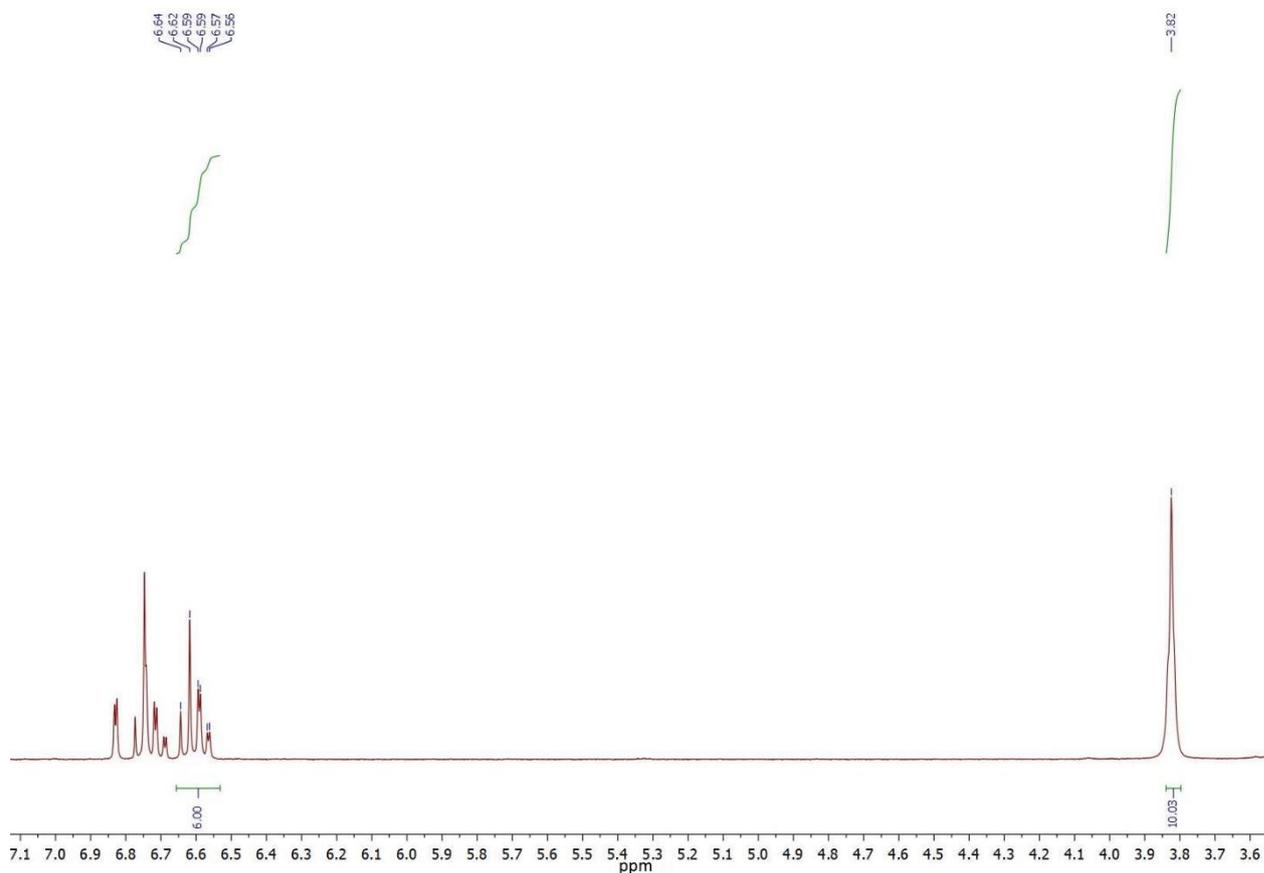


Figure S8.  $^{13}\text{C}$  NMR spectrum of **4** in  $\text{D}_2\text{O}$ .



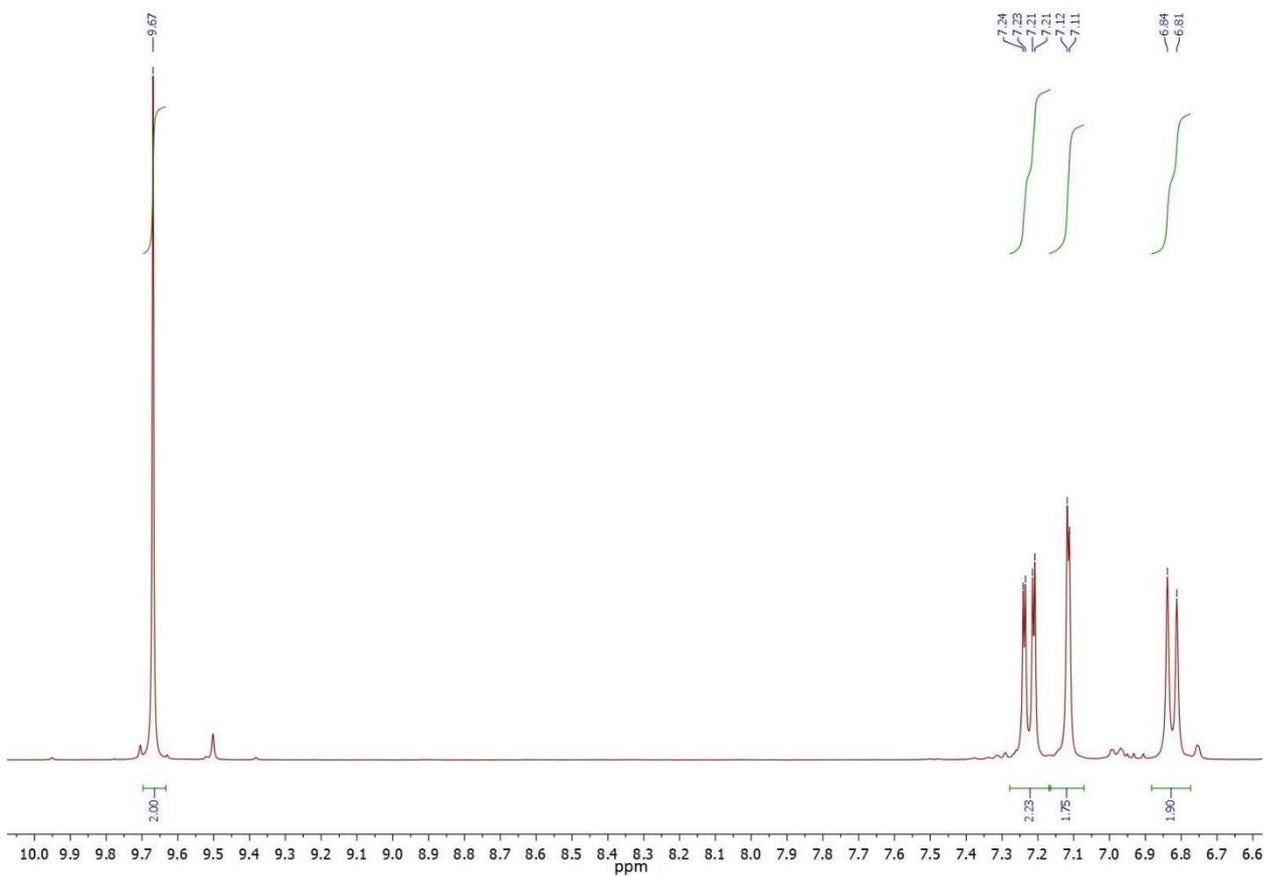


Figure S11.  $^1\text{H}$  NMR spectrum of **6** in  $\text{d}_6$ -DMSO.

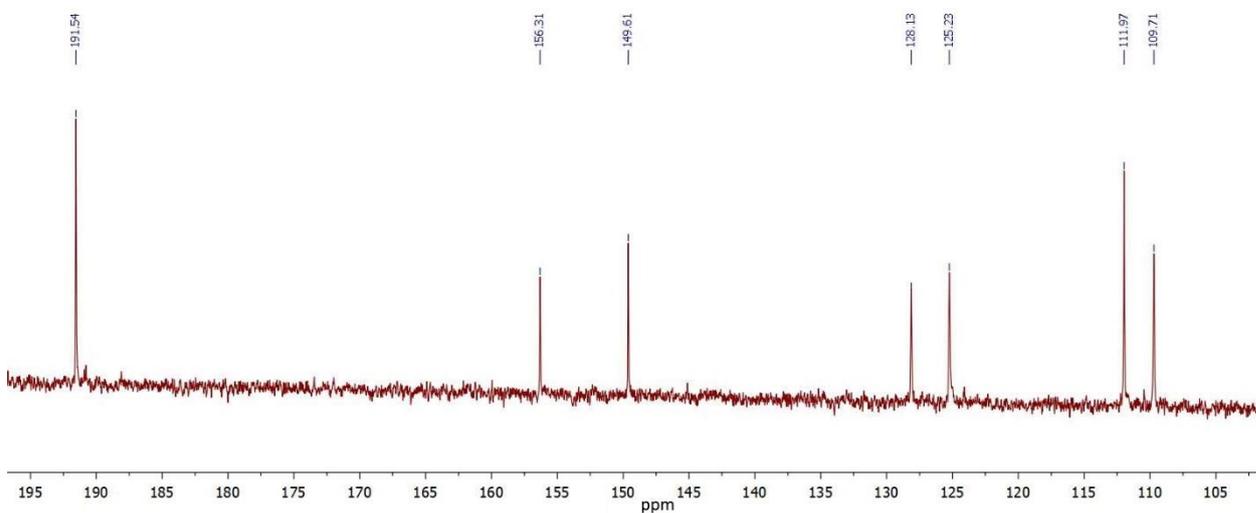


Figure S12.  $^{13}\text{C}$  NMR spectrum of **6** in  $\text{d}_6$ -DMSO.

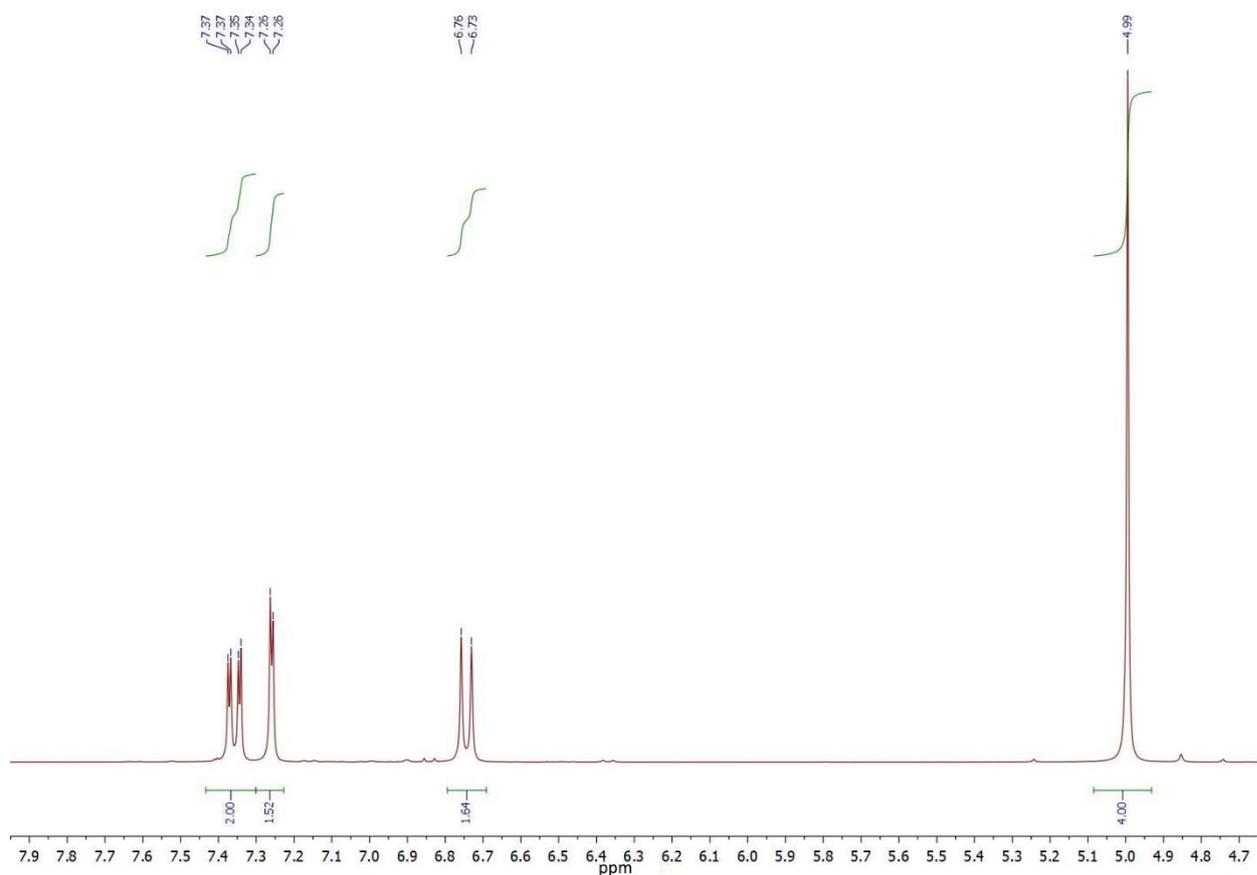


Figure S13.  $^1\text{H}$  NMR spectrum of **7** in  $\text{d}_6$ -DMSO.

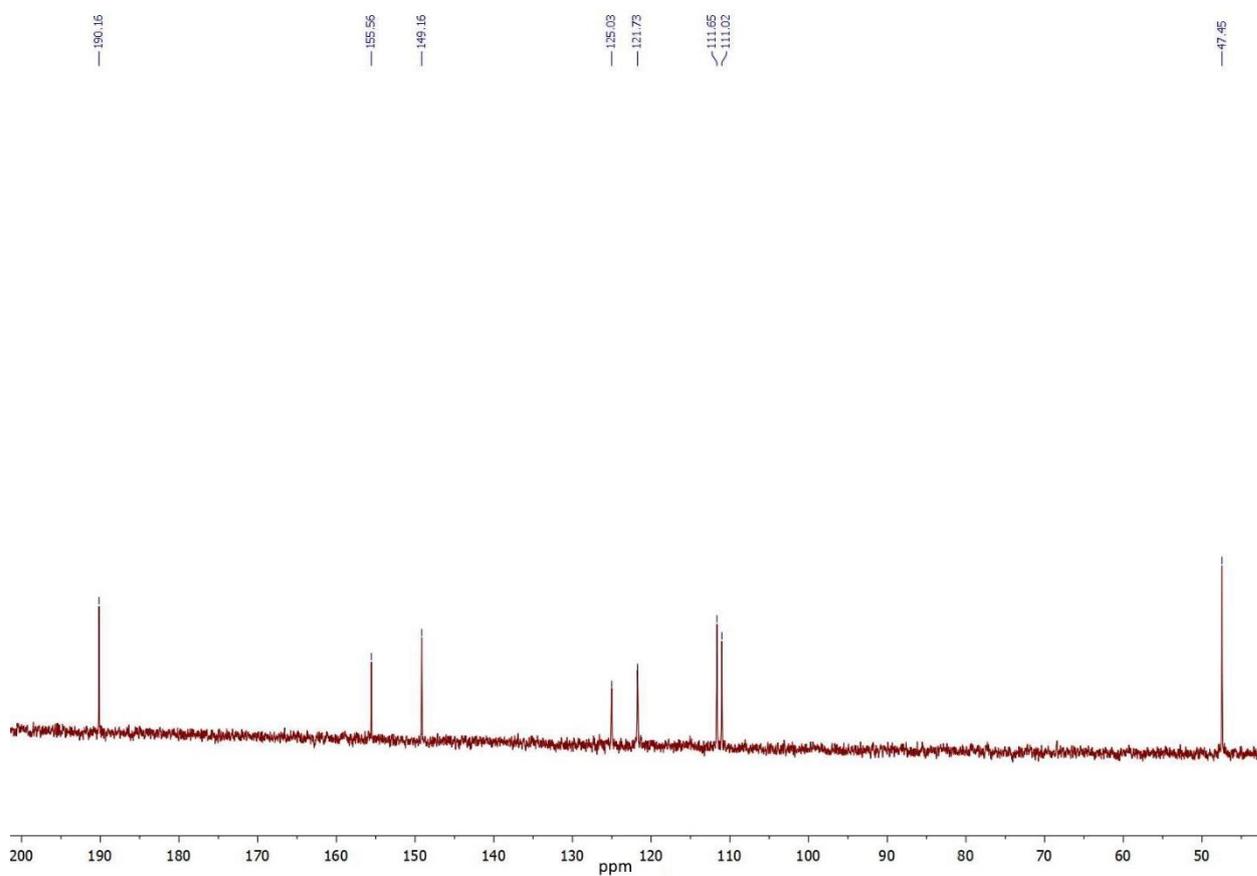


Figure S14.  $^{13}\text{C}$  NMR spectrum of **7** in  $\text{d}_6$ -DMSO.

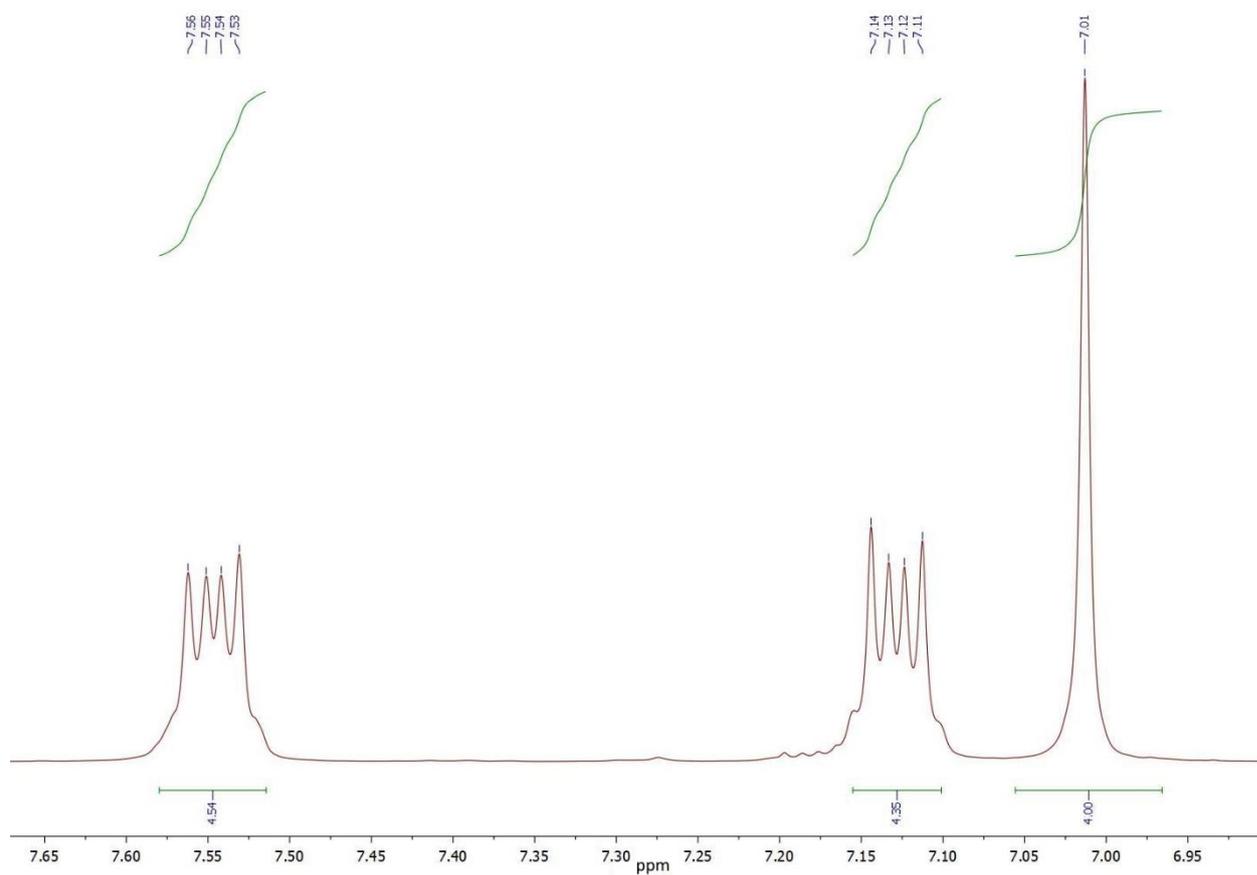


Figure S15.  $^1\text{H}$  NMR spectrum of **8** in  $\text{d}_6$ -DMSO.

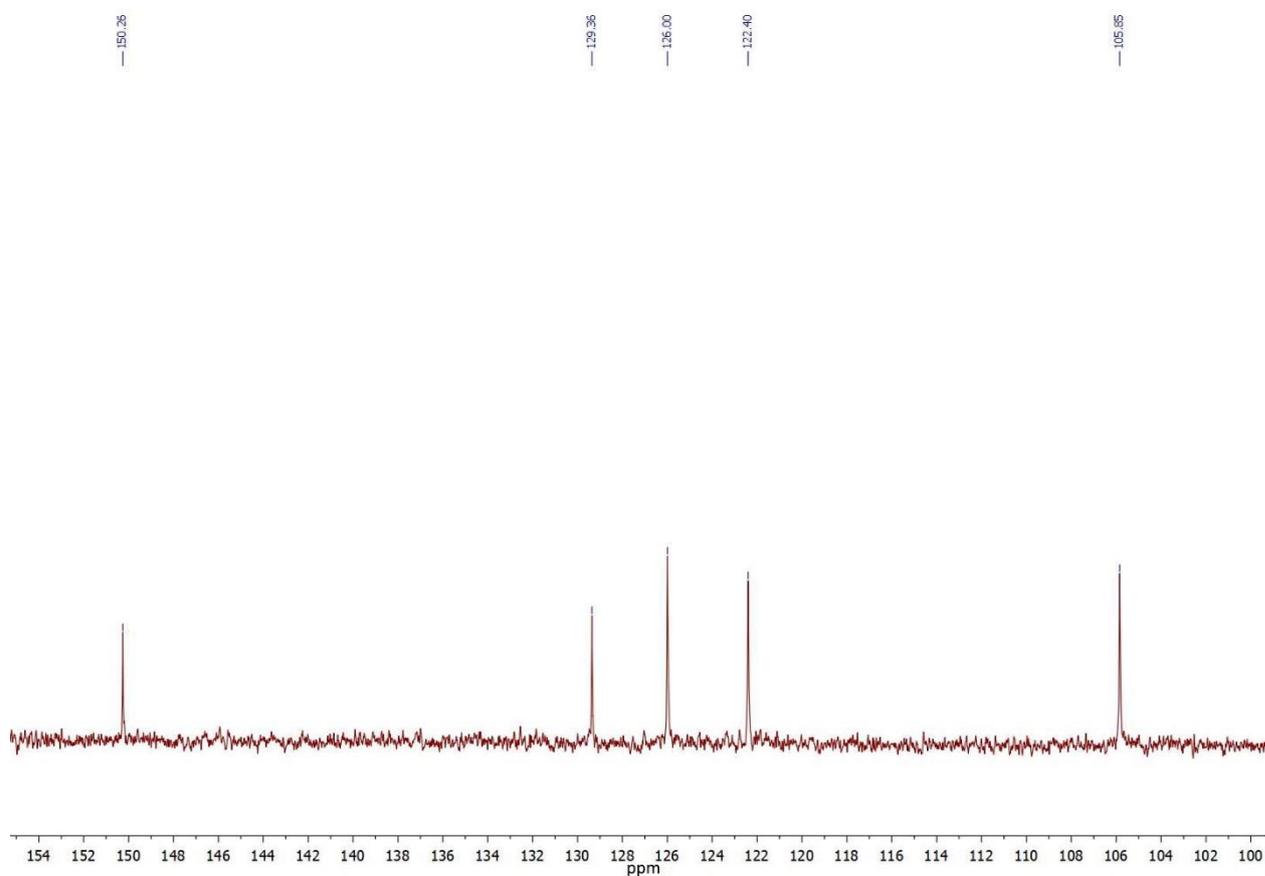


Figure S16.  $^{13}\text{C}$  NMR spectrum of **8** in  $\text{d}_6$ -DMSO.

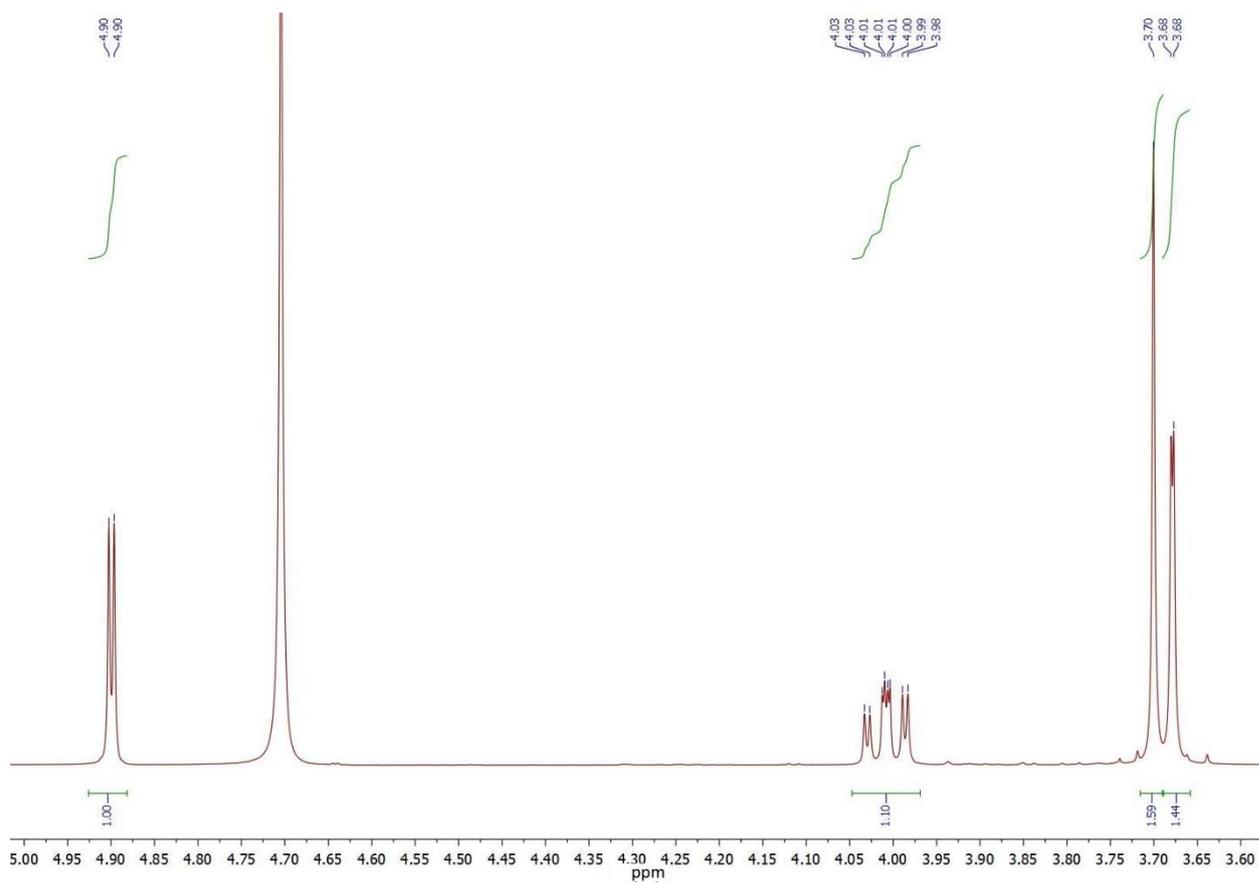


Figure S17.  $^1\text{H}$  NMR spectrum of **9** in  $\text{D}_2\text{O}$ .

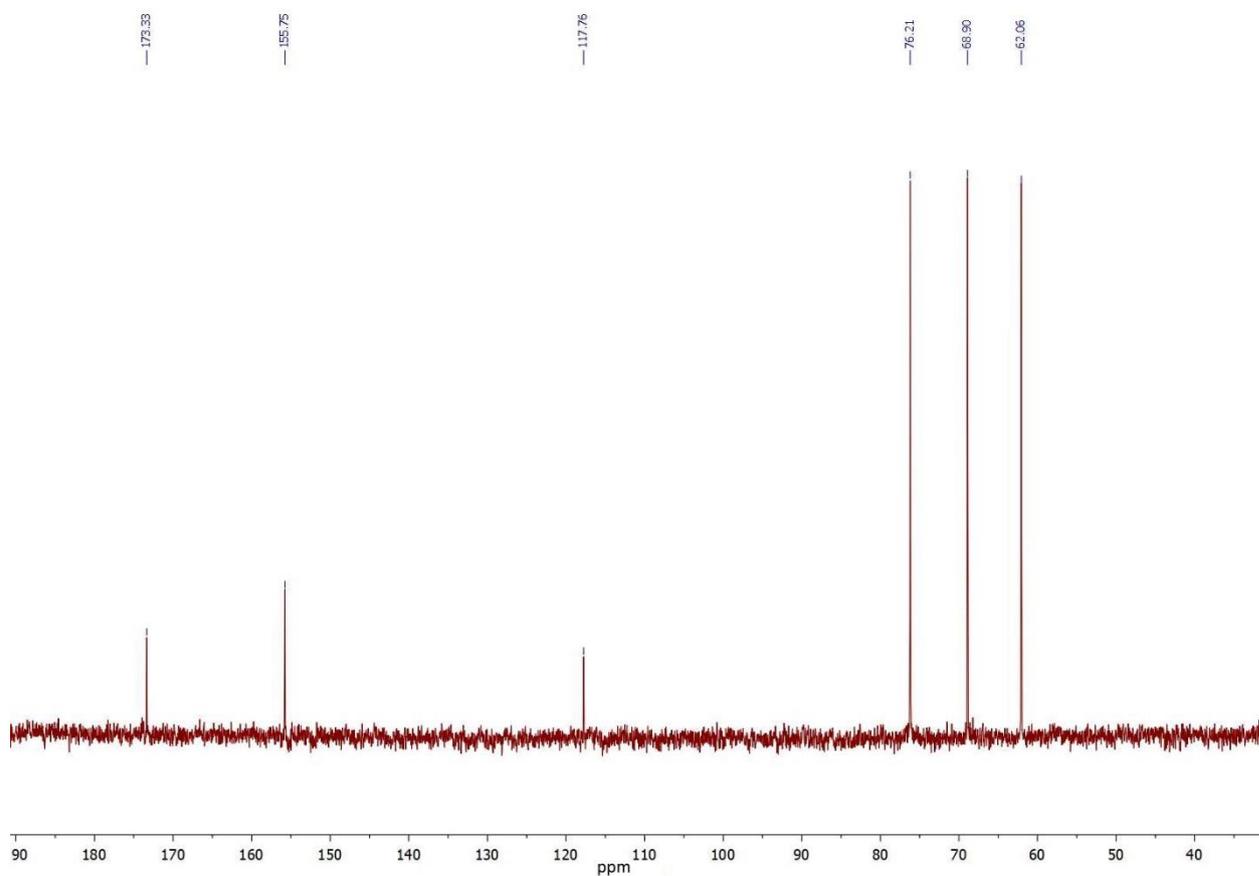


Figure S18.  $^{13}\text{C}$  NMR spectrum of **9** in  $\text{D}_2\text{O}$ .

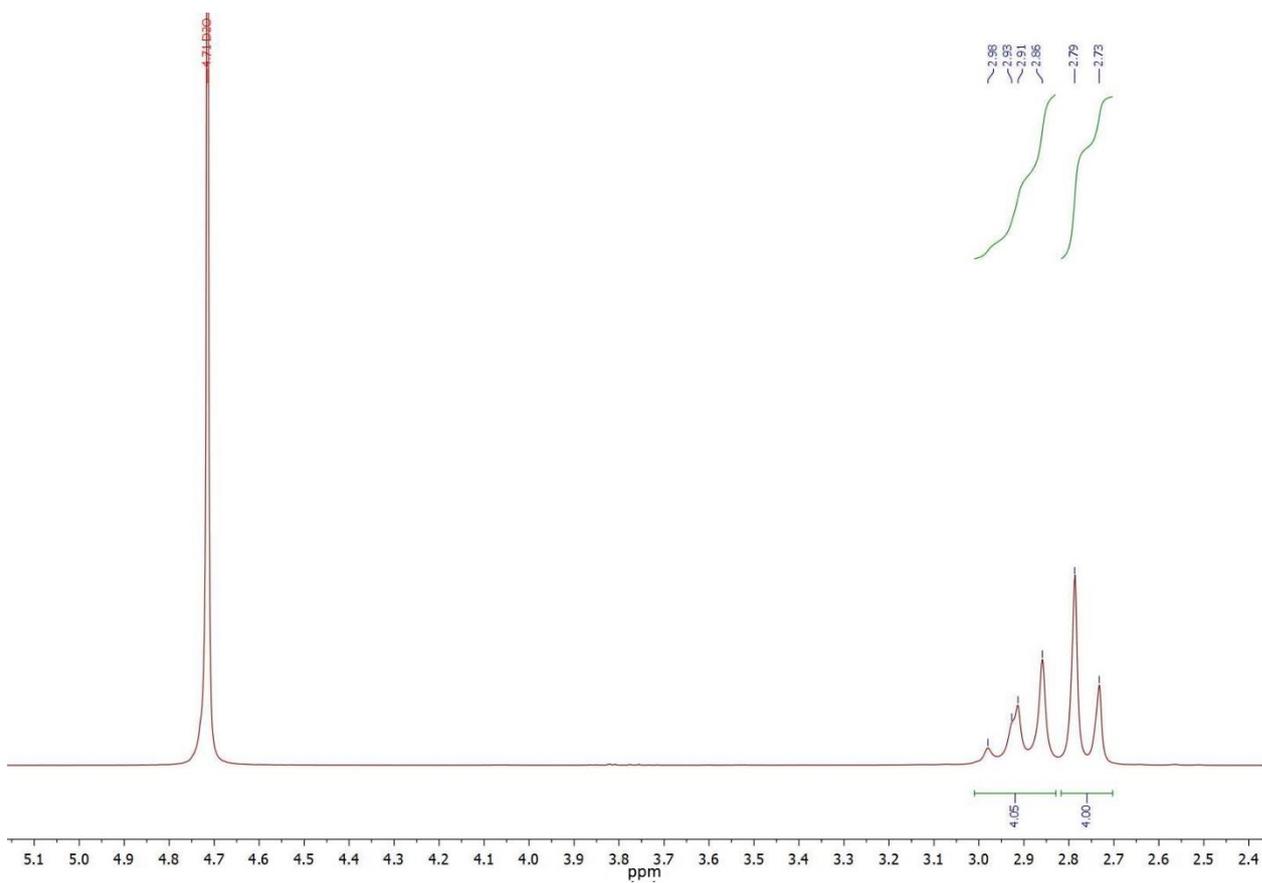


Figure S19.  $^1\text{H}$  NMR spectrum of **10** in  $\text{D}_2\text{O}$ .

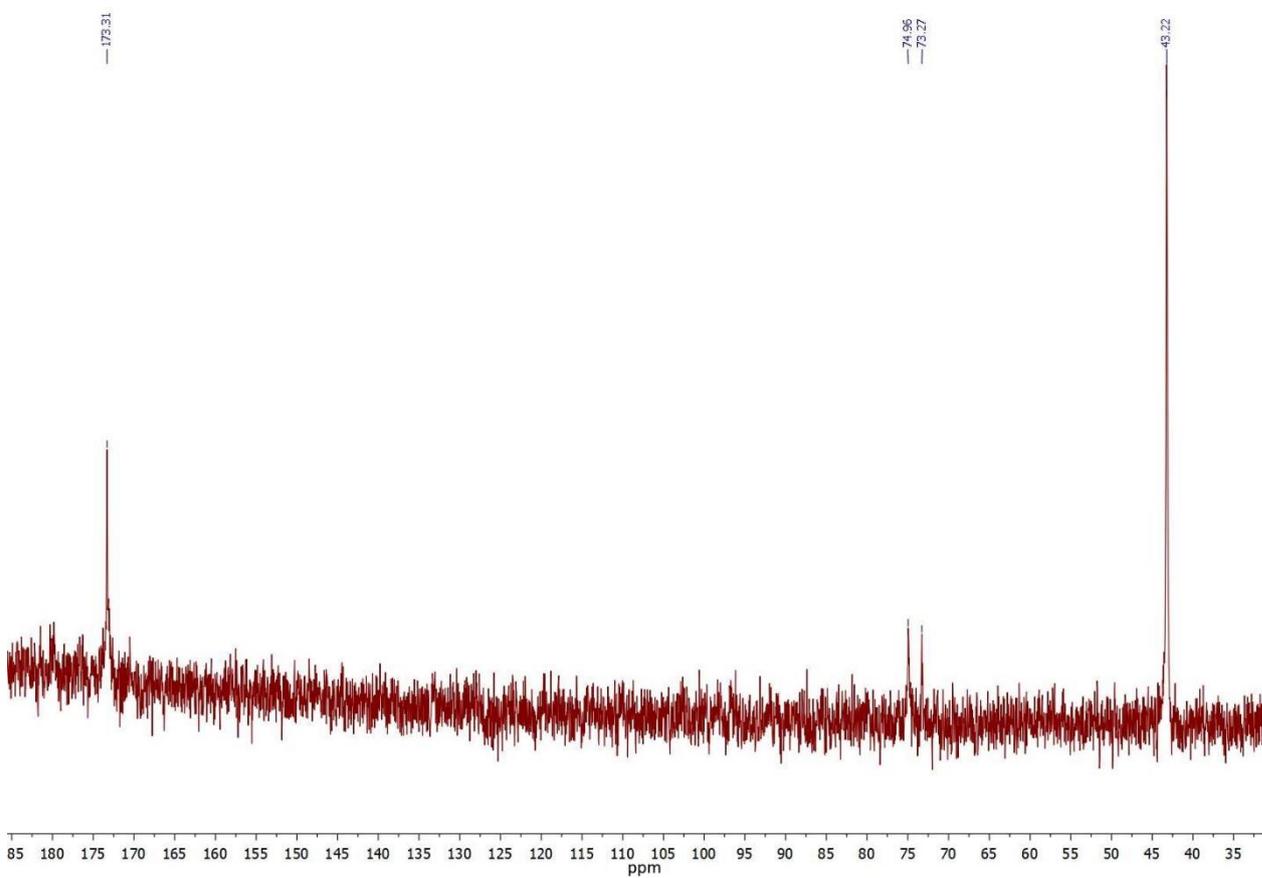


Figure S20.  $^{13}\text{C}$  NMR spectrum of **10** in  $\text{D}_2\text{O}$ .

#### 4. IR spectroscopy

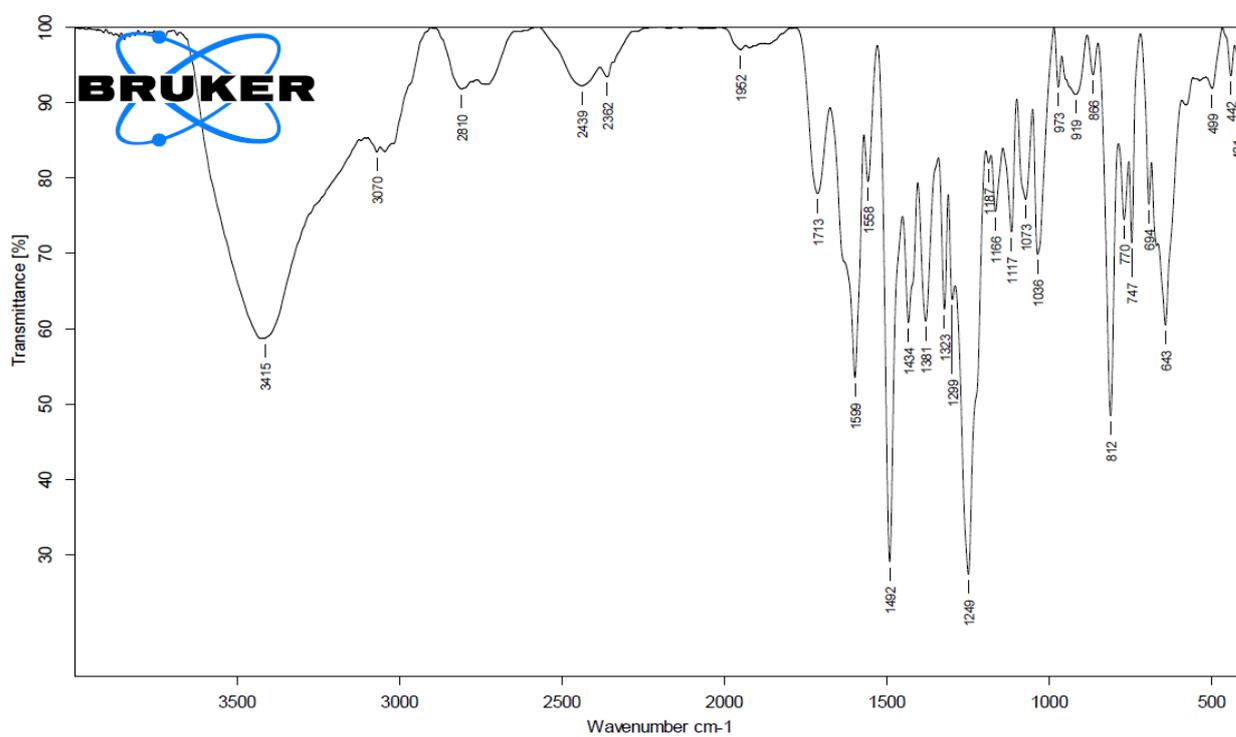


Figure S21. IR spectrum of **1**.

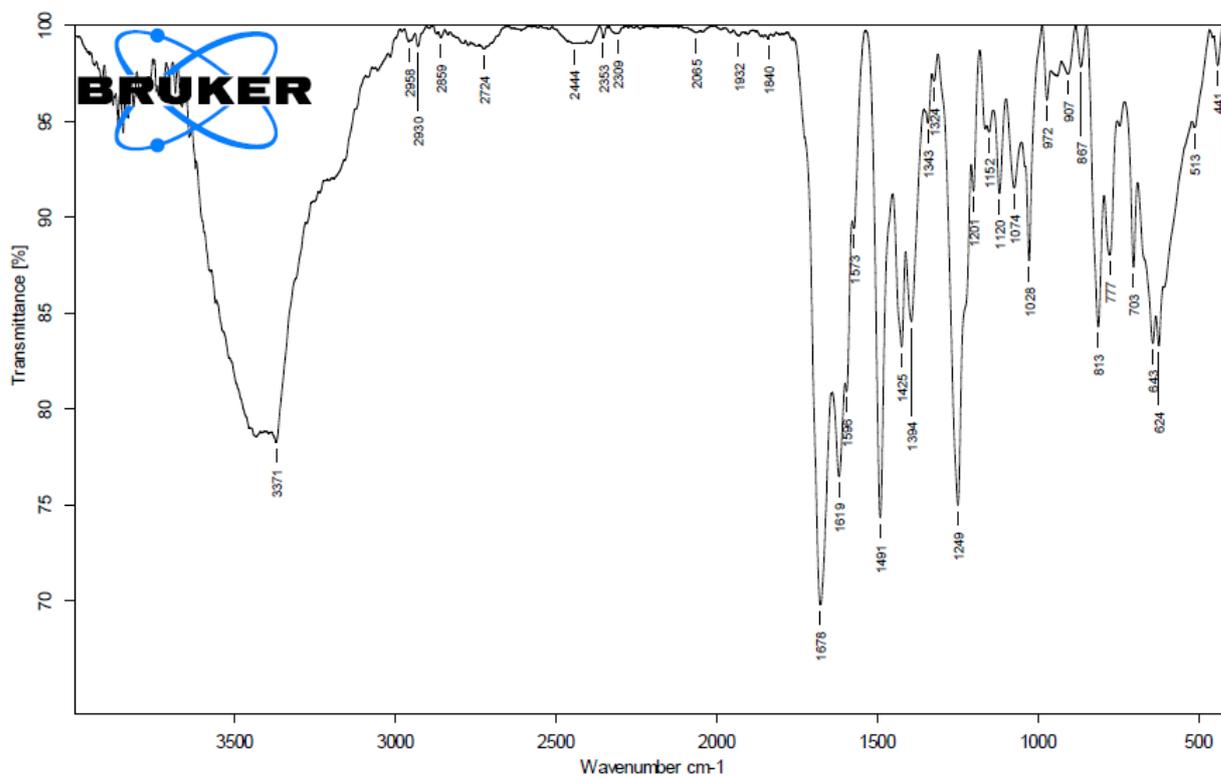


Figure S22. IR spectrum of **2**.

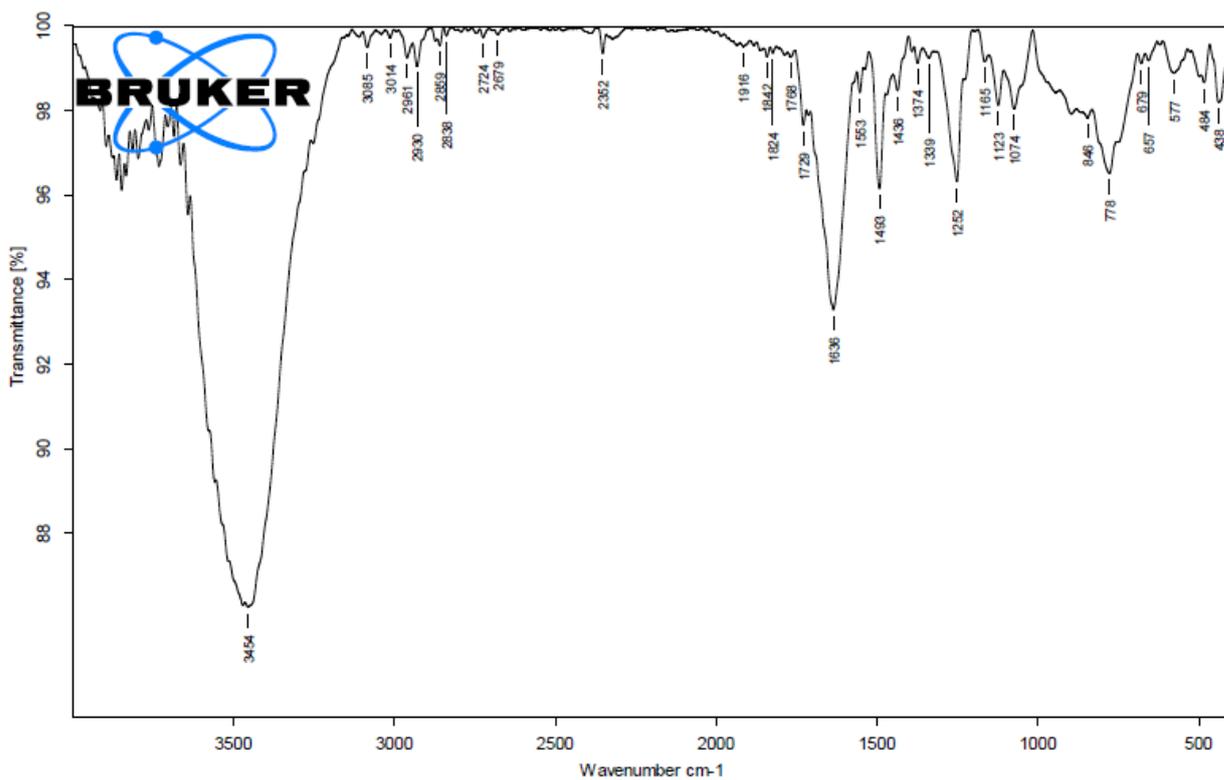


Figure S23. IR spectrum of 3.

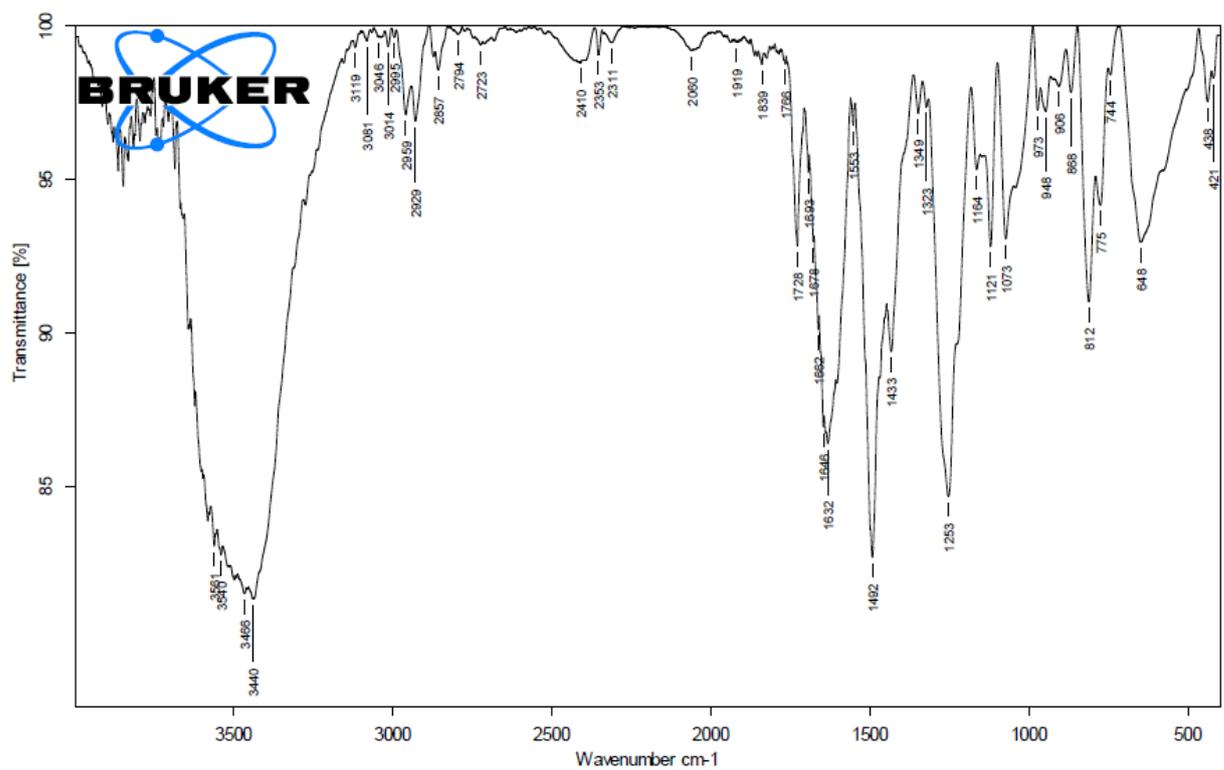


Figure S24. IR spectrum of 4.

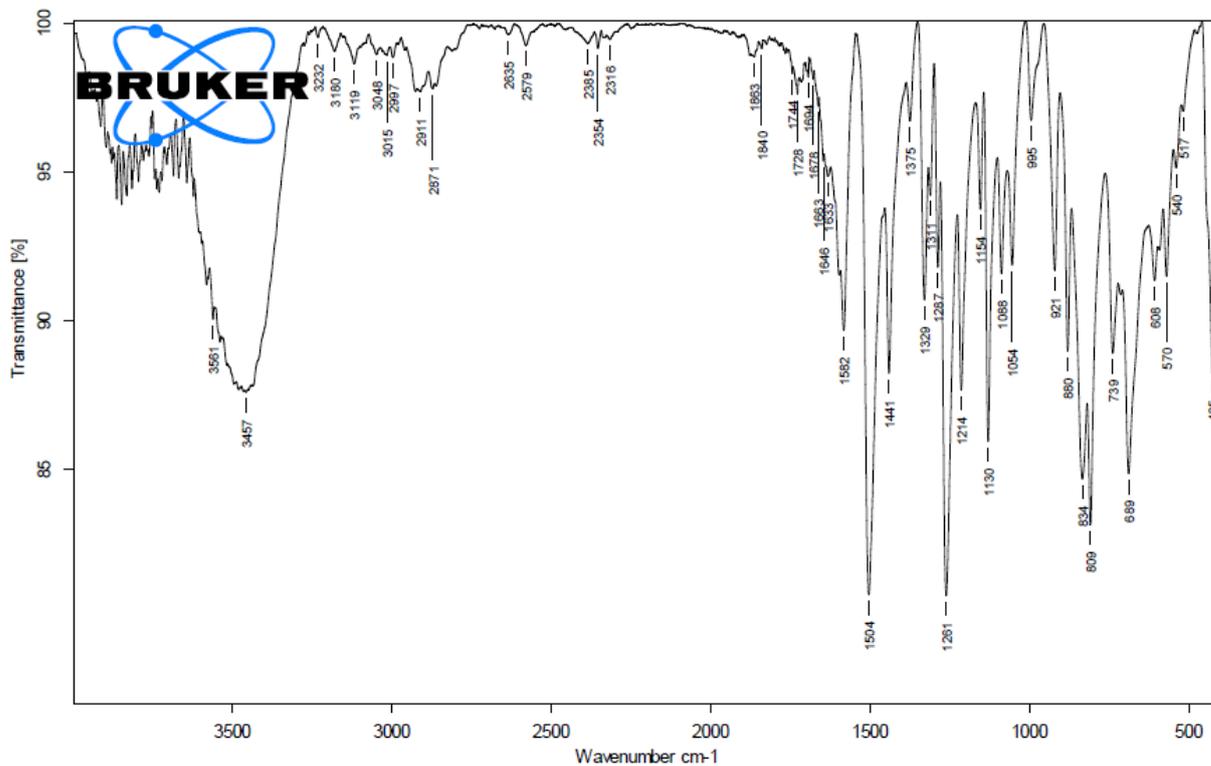


Figure S25. IR spectrum of **5**.

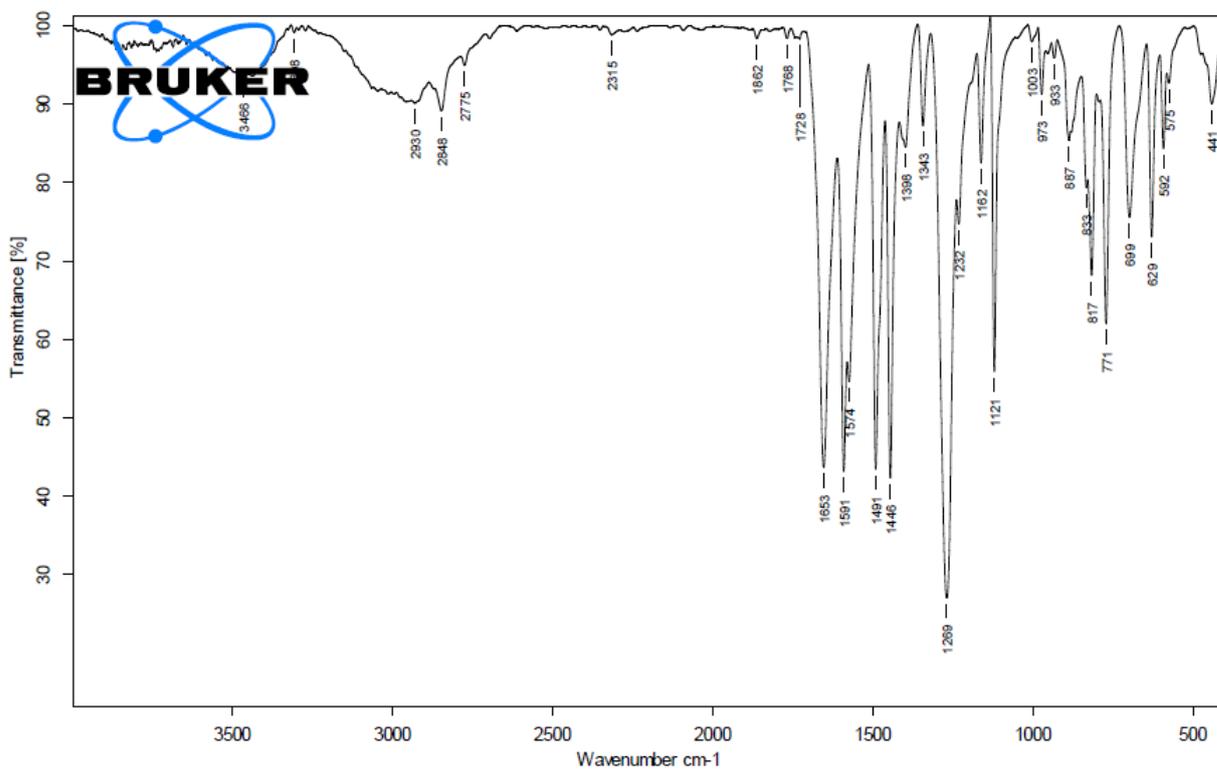


Figure S26. IR spectrum of **6**.

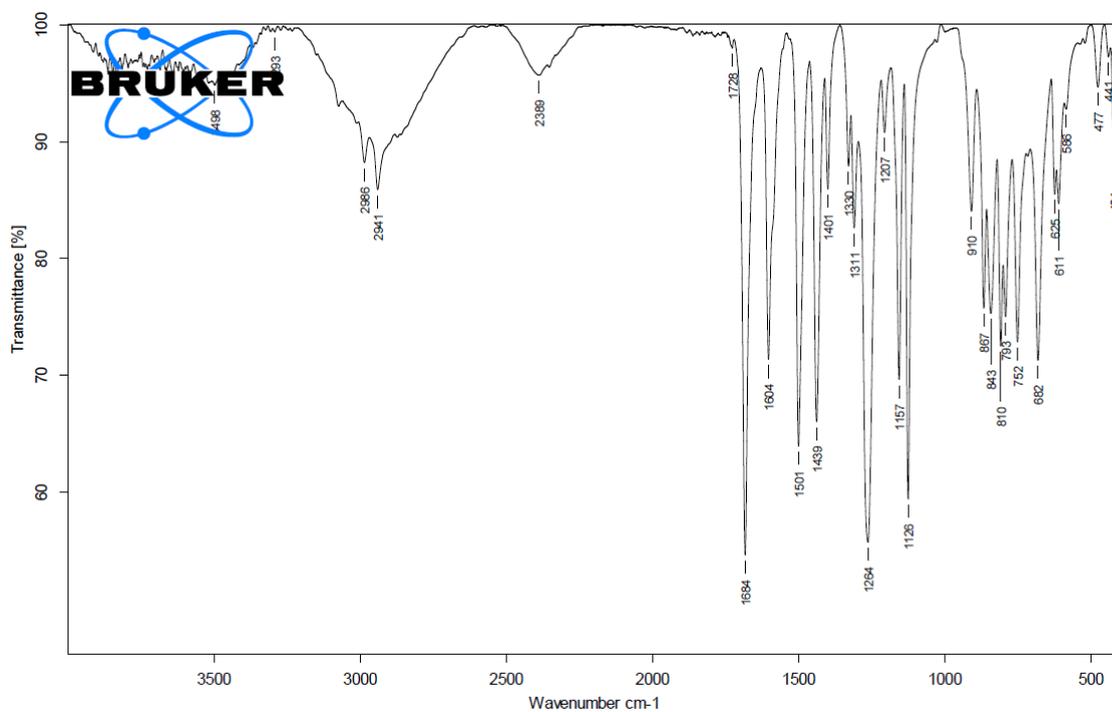


Figure S27. IR spectrum of **7**.

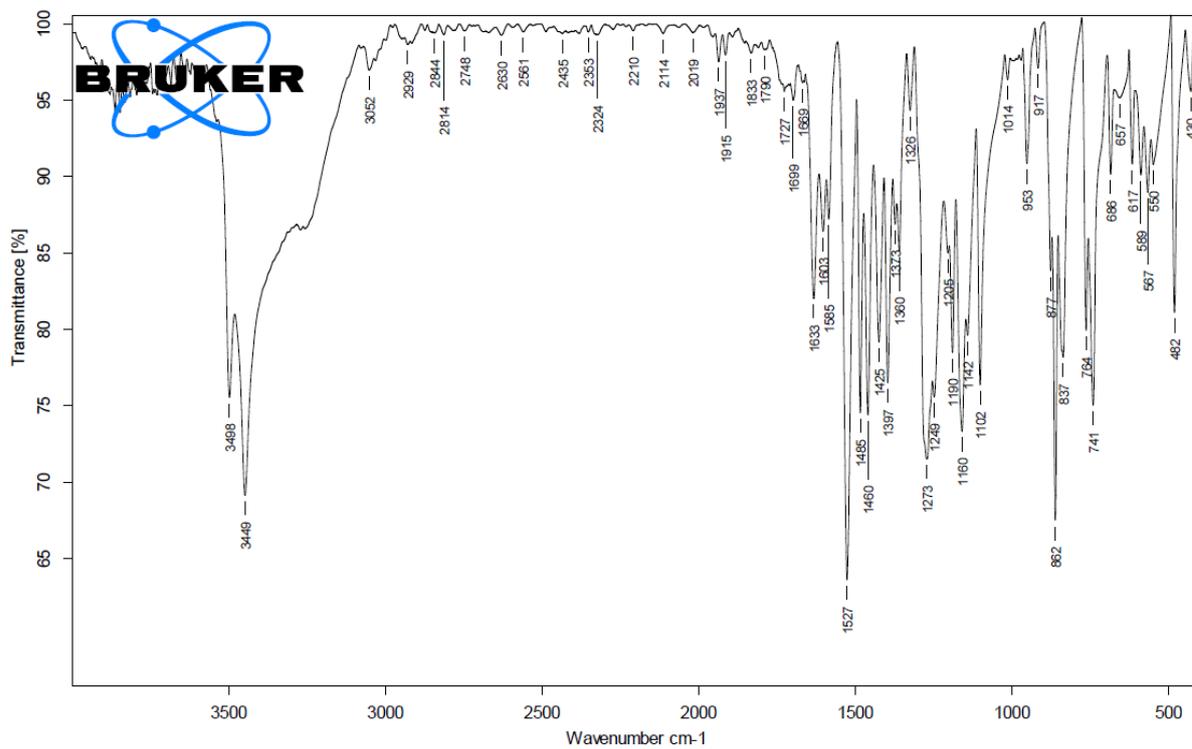


Figure S28. IR spectrum of **8**.

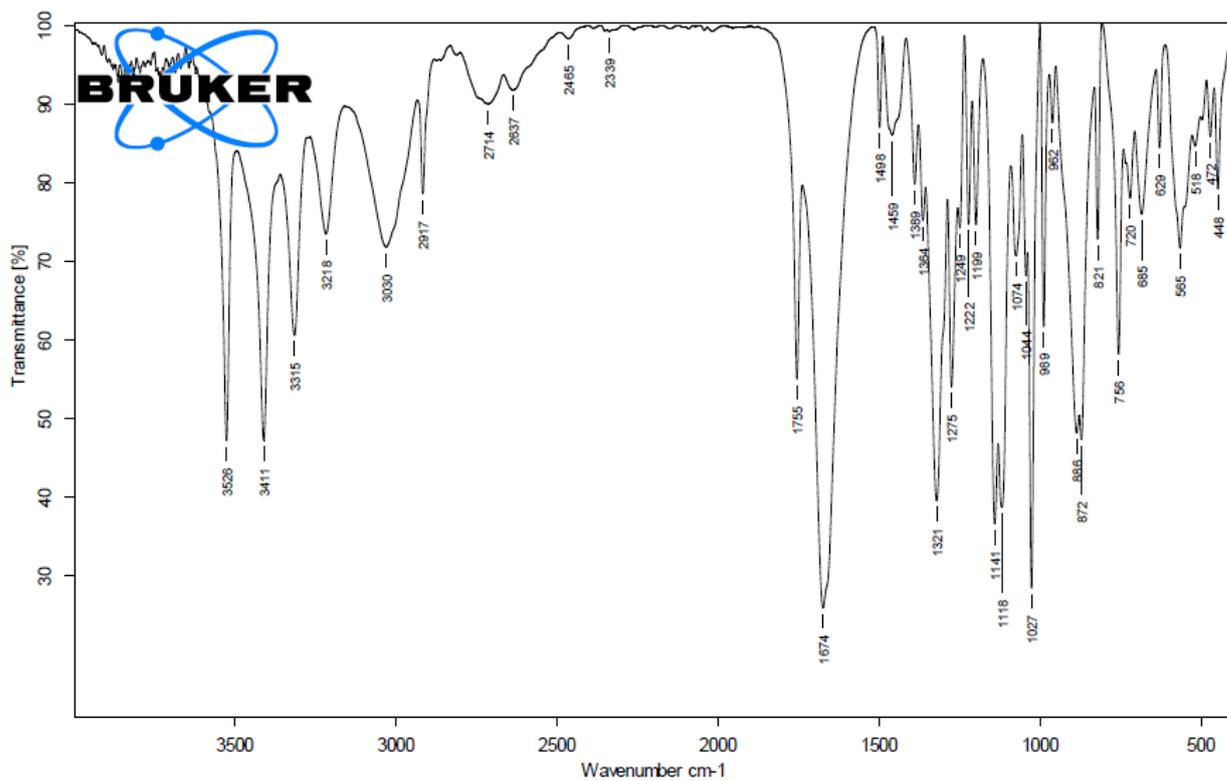


Figure S29. IR spectrum of **9**.

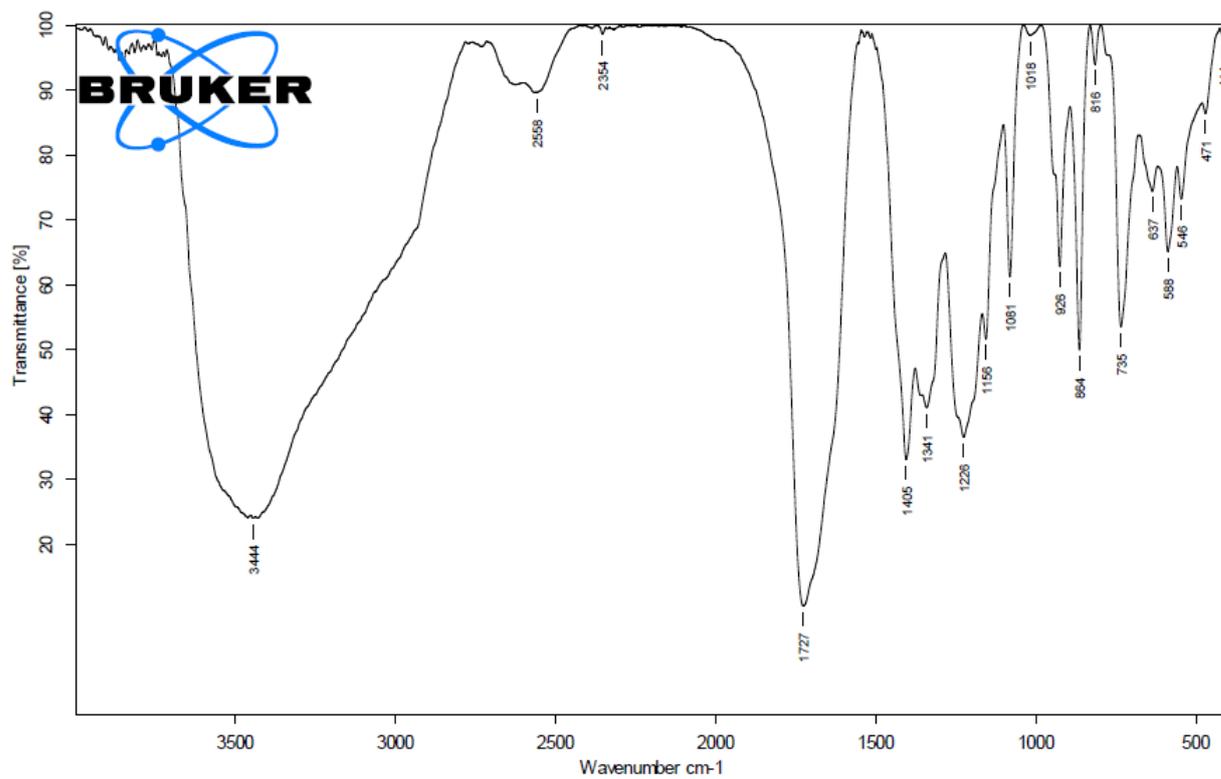


Figure S30. IR spectrum of **10**.

## 5. HRMS (MALDI)

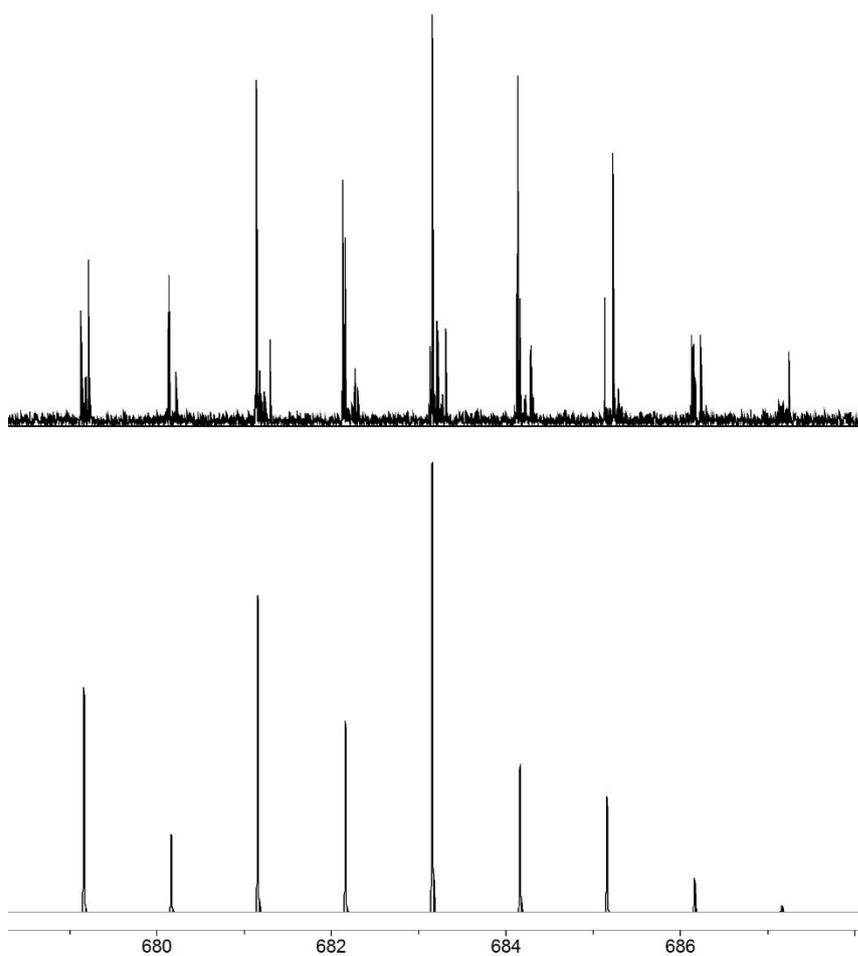


Figure S31. Experimental (*top*) and calculated (*bottom*) HRMS (MALDI) spectra of **1**.

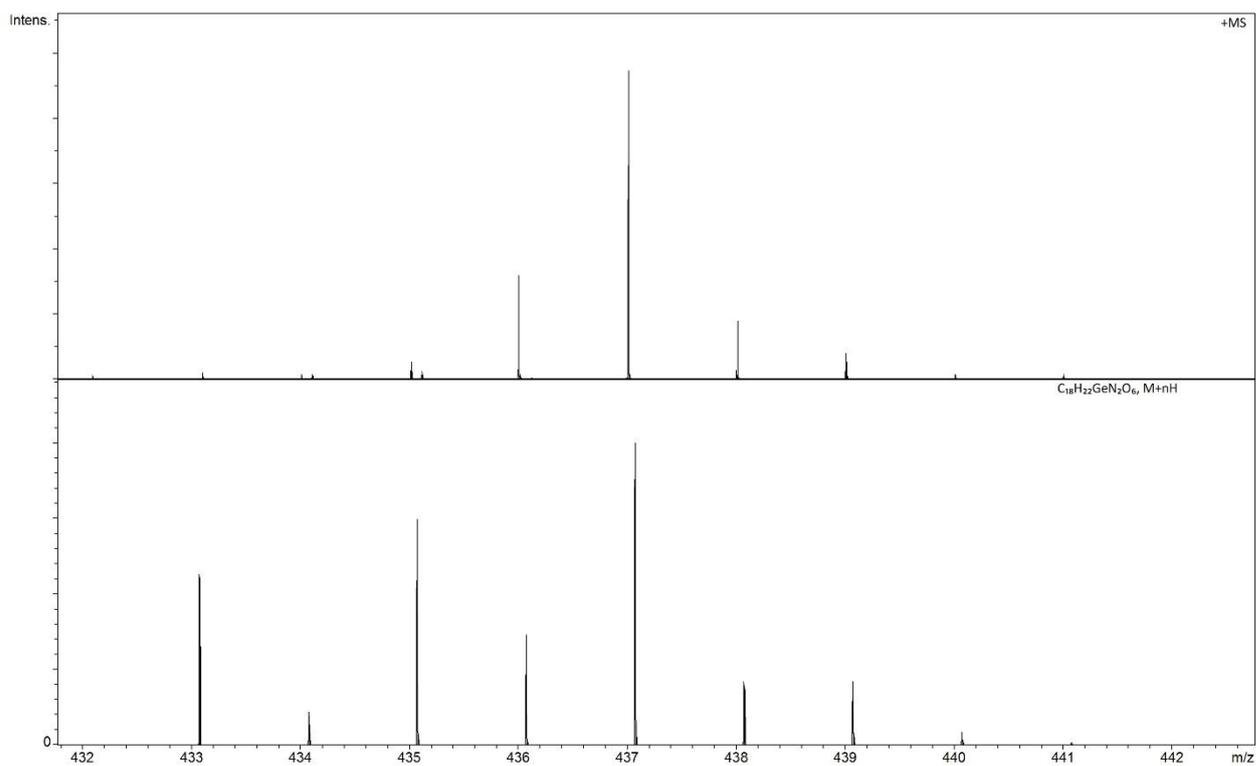


Figure S32. Experimental (*top*) and calculated (*bottom*) HRMS (MALDI) spectra of **4**.

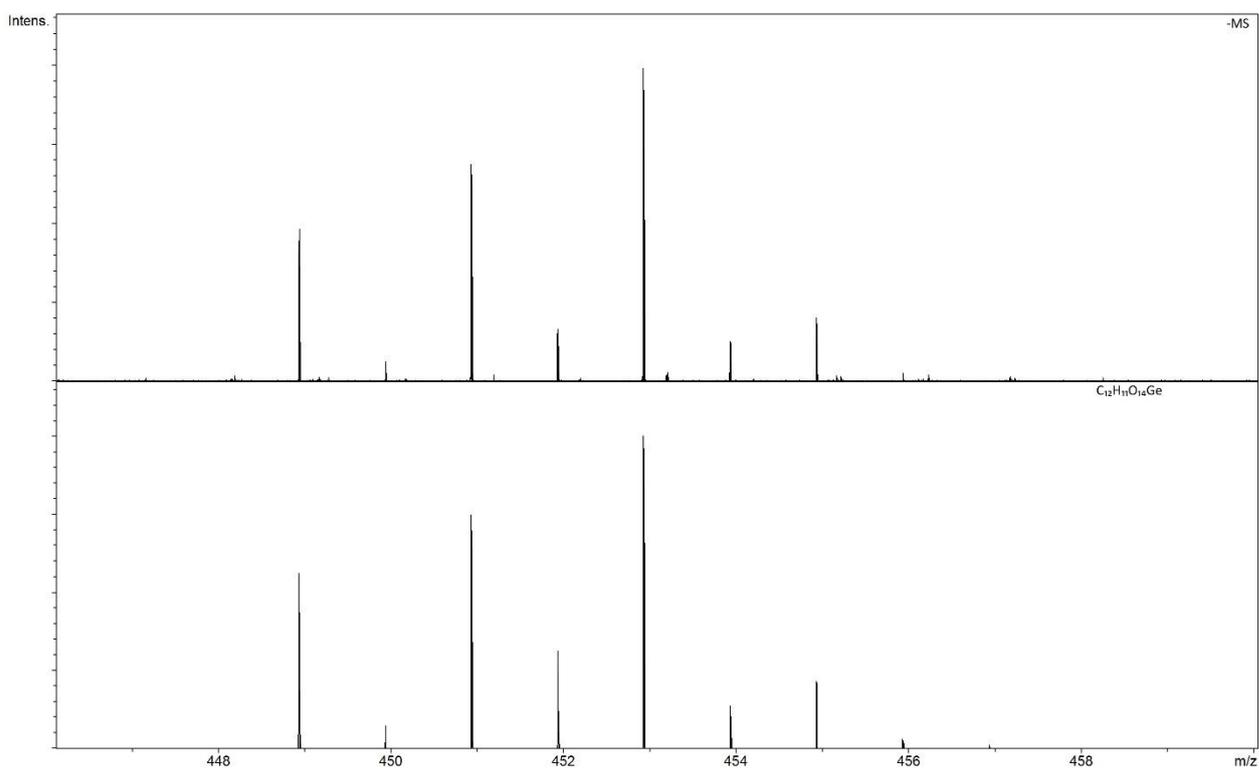


Figure S33. Experimental (*top*) and calculated (*bottom*) HRMS (MALDI) spectra of **10**.

## 6. HRMS (ESI)

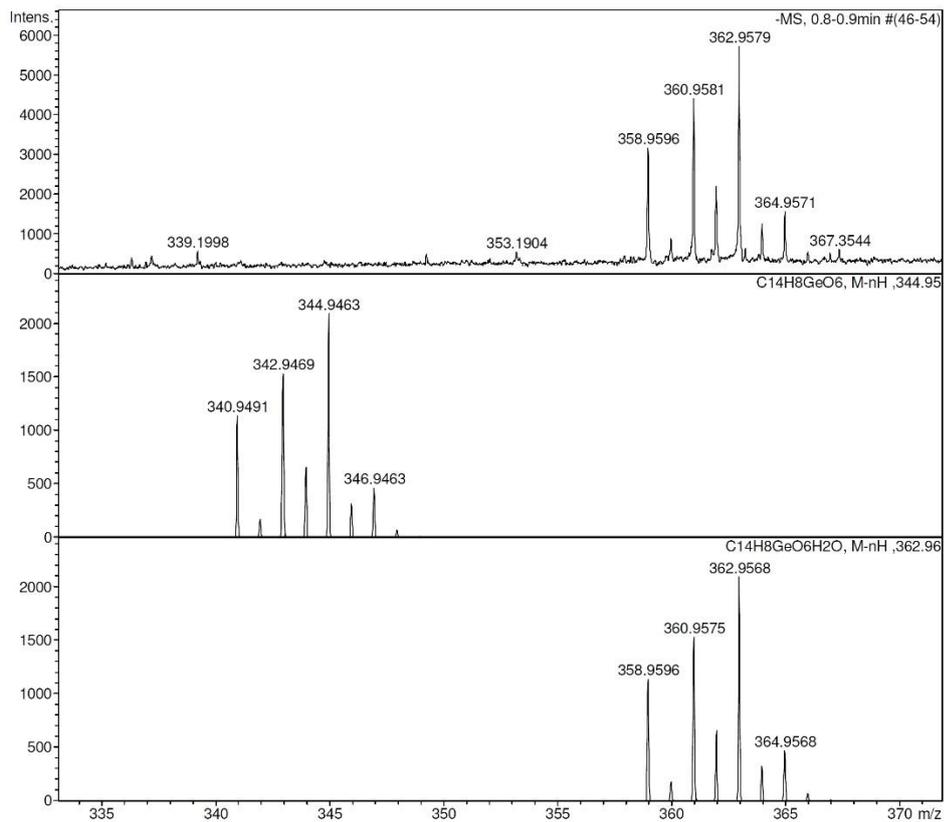


Figure S34. Experimental (*top*) and calculated (*bottom*) HRMS (ESI) spectra of **6**.

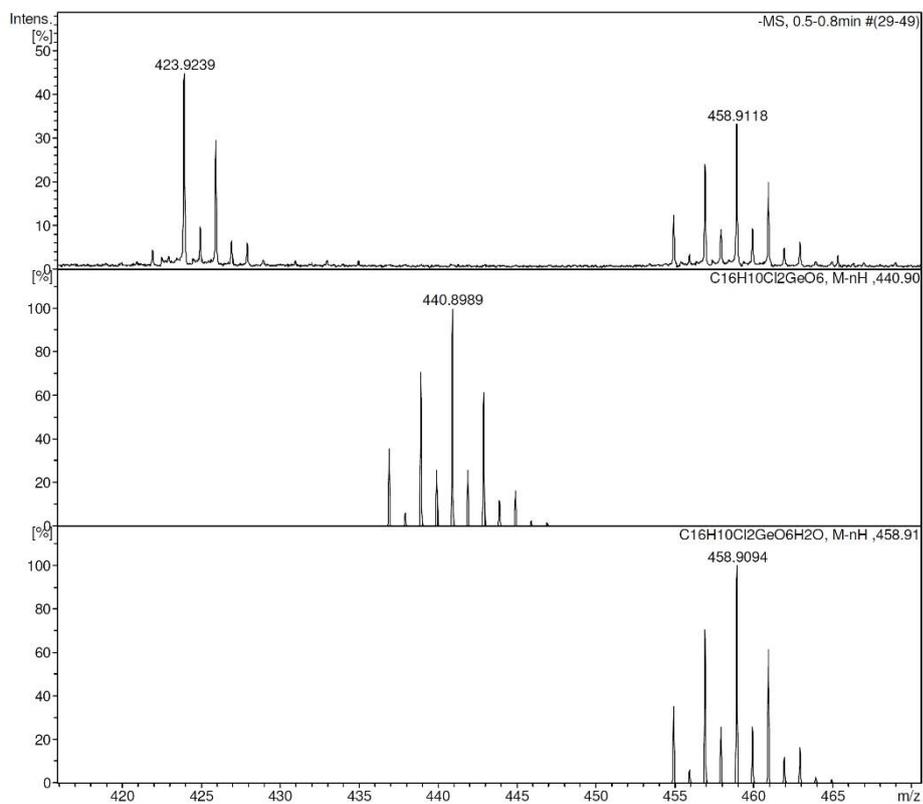


Figure S35. Experimental (*top*) and calculated (*bottom*) HRMS (ESI) spectra of **7**.

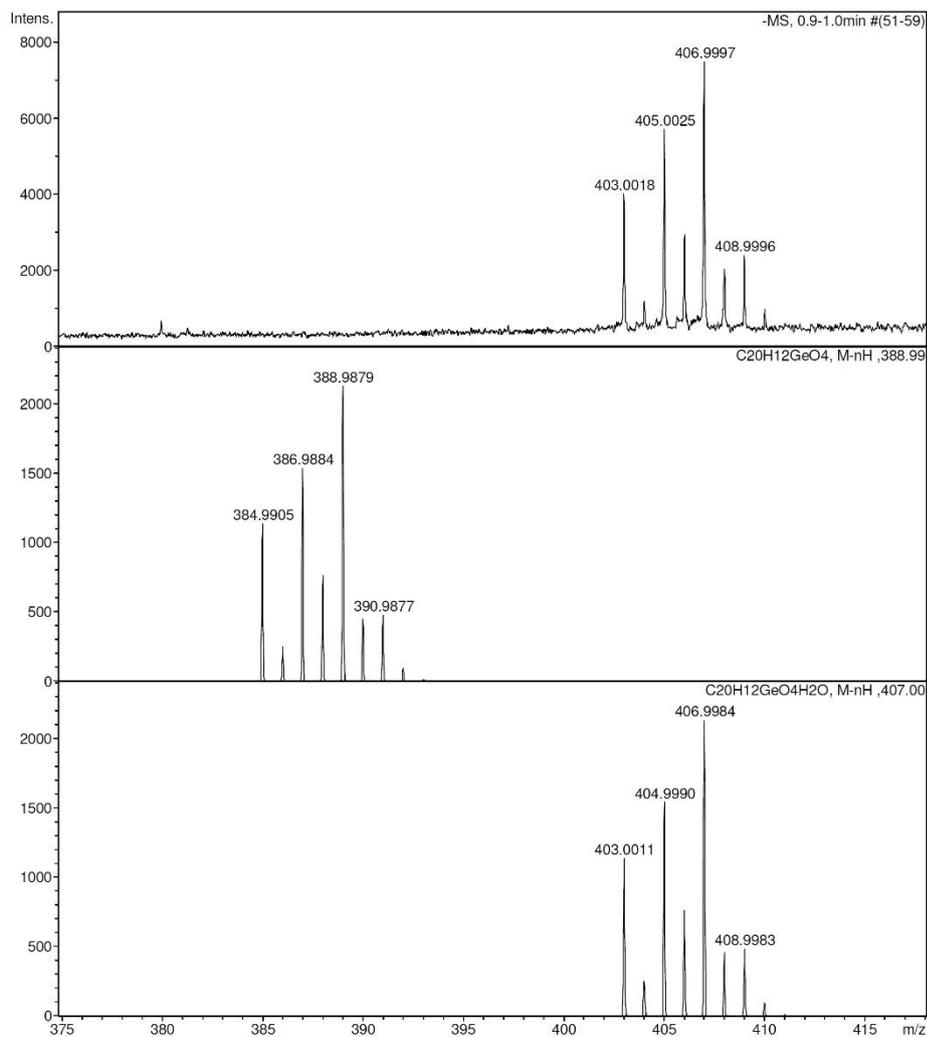


Figure S36. Experimental (*top*) and calculated (*bottom*) HRMS (ESI) spectra of **8**.

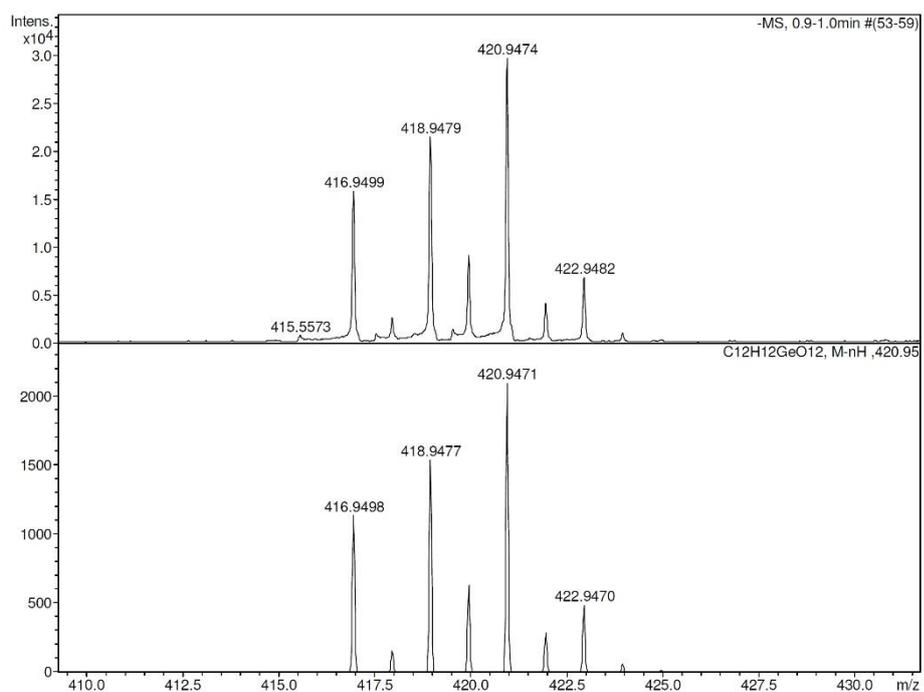


Figure S37. Experimental (*top*) and calculated (*bottom*) HRMS (ESI) spectra of **9**.

## 7. CV and UV of 2-3

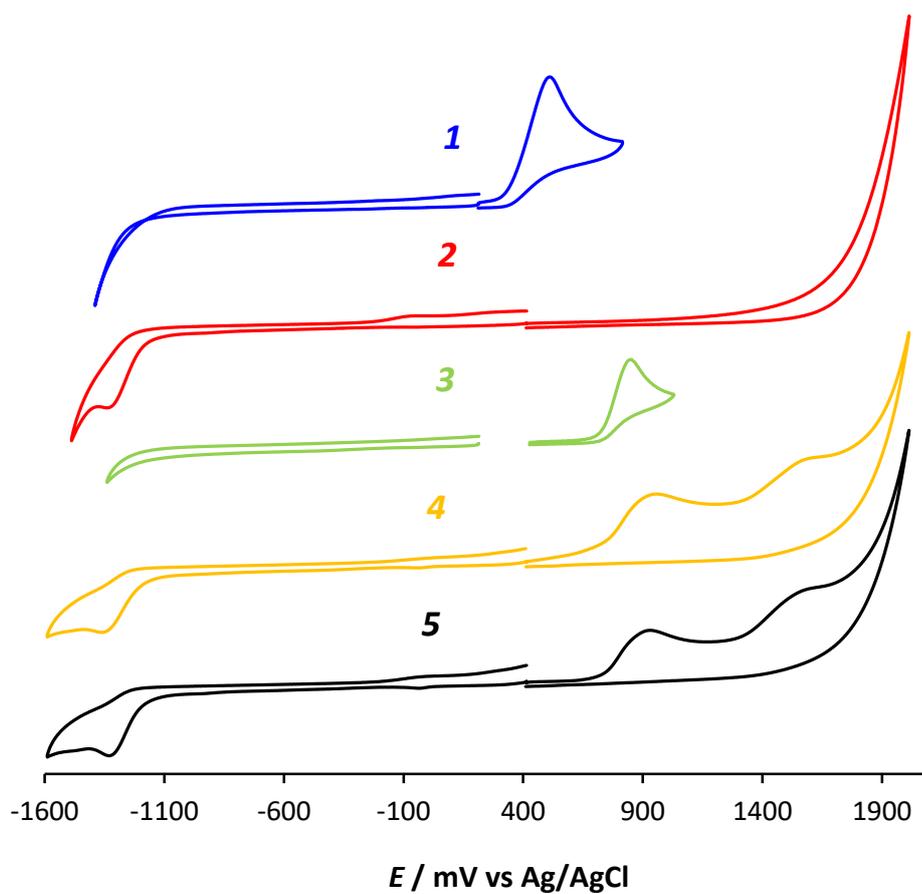


Figure S34. CV curves for 2 mM of epinephrine (1), 1 mM of nicotinamide (2), a mixture of 2 mM of epinephrine and 1 mM of HSGO before (3) and after adding 1 mM nicotinamide (4), 1 mM of 2 (5) recorded on a glassy carbon disc electrode in a phosphate buffer solution ( $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ , pH = 6.86). A scan rate  $0.1 \text{ V s}^{-1}$ .

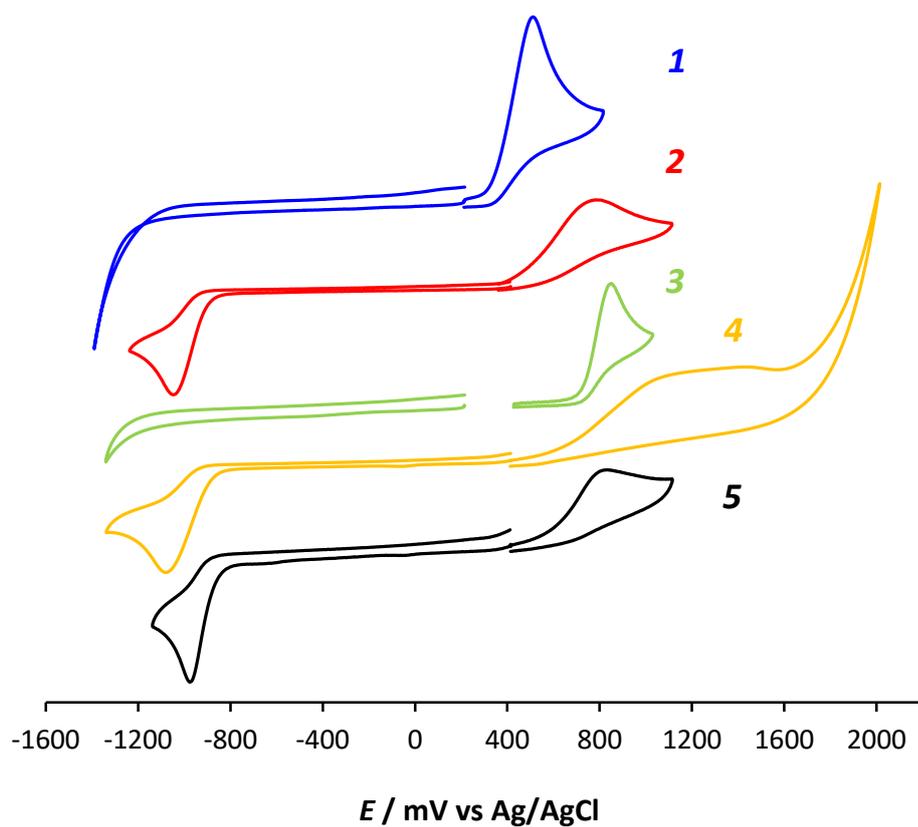


Figure S35. CV curves for 2 mM of epinephrine (1), 2 mM of isoniazide (2), a mixture of 2 mM of epinephrine and 1 mM of HSGO before (3) and after adding 2 mM isoniazide (4), 1 mM of **3** (5) recorded on a glassy carbon disc electrode in a phosphate buffer solution ( $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ , pH = 6.86). A scan rate  $0.1 \text{ V s}^{-1}$ .

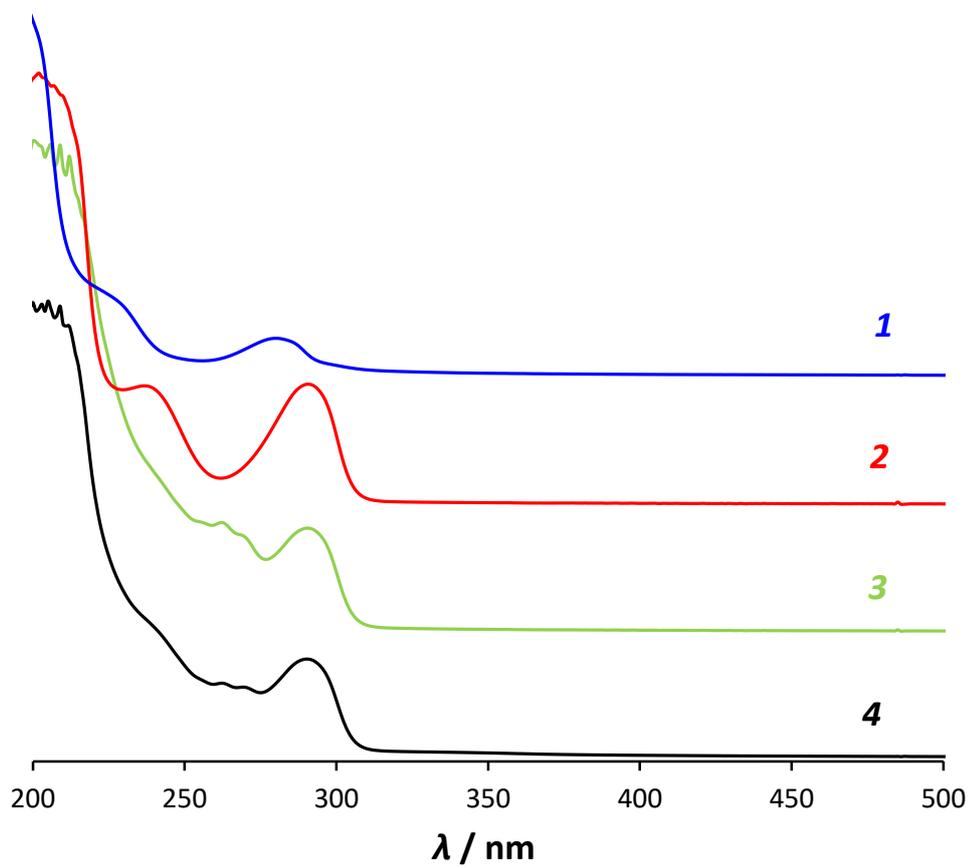


Figure S36. UV spectra for  $2 \cdot 10^{-4}$  M of epinephrine (1), a mixture of  $2 \cdot 10^{-4}$  M of epinephrine and  $1 \cdot 10^{-4}$  M of HSGO before (2) and after adding  $1 \cdot 10^{-4}$  M nicotinamide (3), and  $1 \cdot 10^{-4}$  M of **2** (4) in a deionized water.

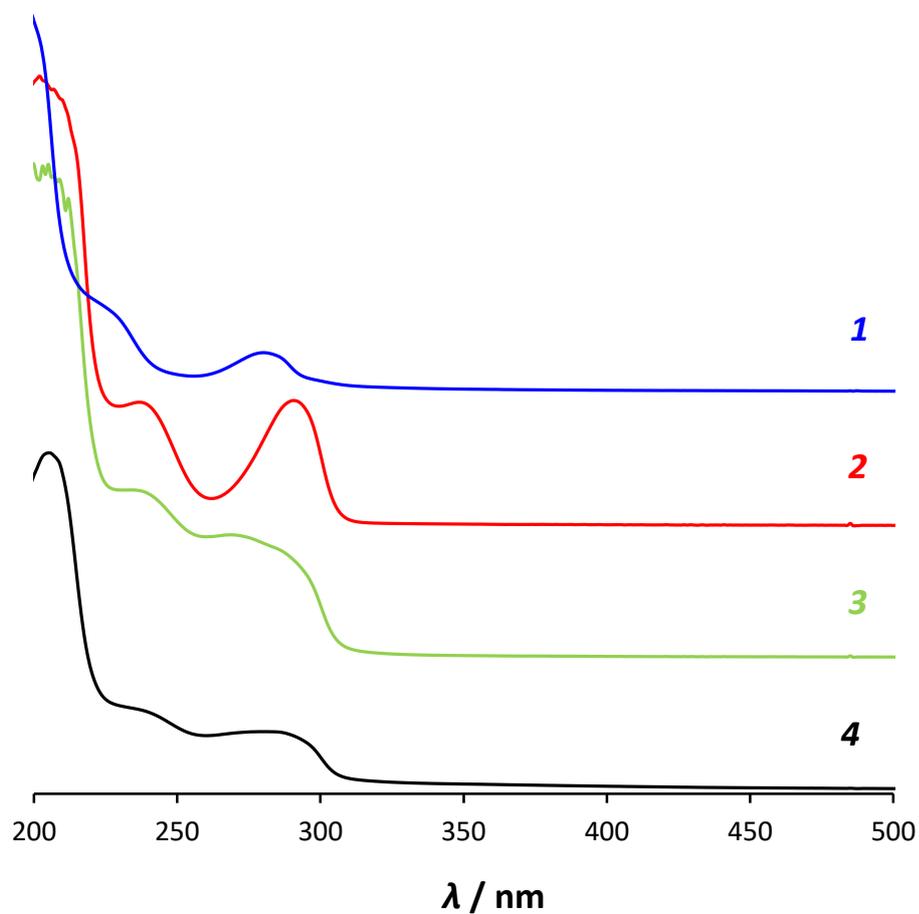


Figure S37. UV spectra for  $2 \cdot 10^{-4}$  M of epinephrine (1), a mixture of  $2 \cdot 10^{-4}$  M of epinephrine and  $1 \cdot 10^{-4}$  M of HSGO before (2) and after adding  $2 \cdot 10^{-4}$  M isoniazide (3), and  $1 \cdot 10^{-4}$  M of **3** (4) in a deionized water.

### References

- S1. J.V. Burykina, D.A. Boiko, V.V. Ilyushenkova, D.B. Eremin and V.P. Ananikov. *Doklady Physical Chemistry*, 2020, **492**, 51. Doi: 10.1134/S0012501620050024.
- S2. D.A. Grishanov, A.V. Churakov, A.G. Medvedev, A.A. Mikhaylov, O.Lev and P.V. Prihodchenko, *Inorg. Chem.*, 2019, **58**, 1905. Doi: 10.1021/acs.inorgchem.8b02747.