Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Branched and Bulky Substituted Ruthenium Sensitizers for Dye-Sensitized Solar Cells

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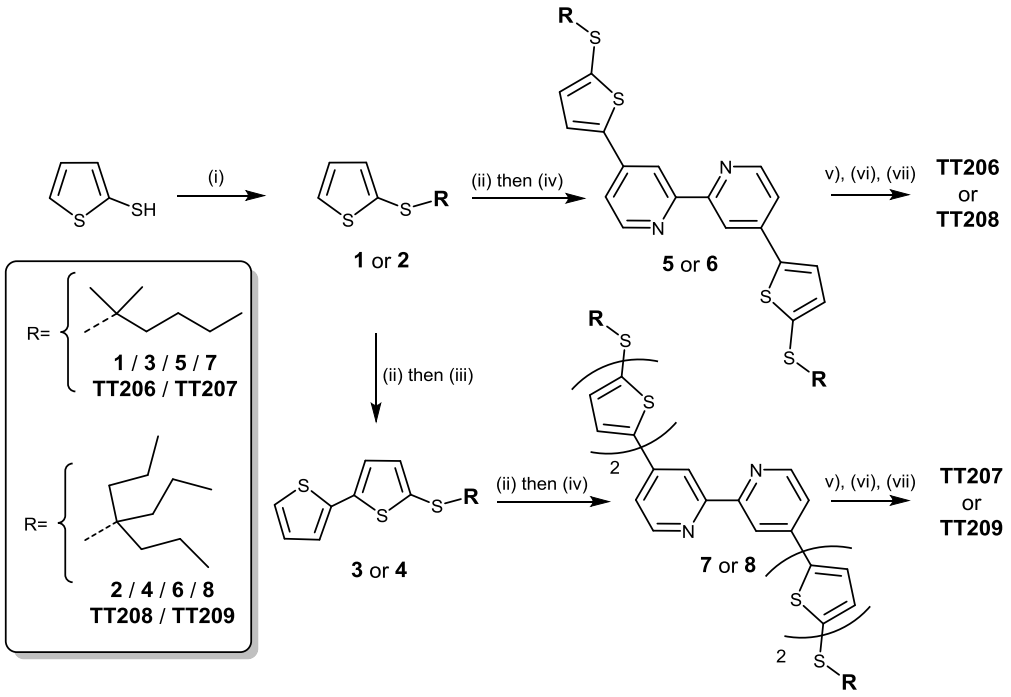
I. MATERIAL AND INSTRUMENTATION

Synthetic procedures were carried out under an inert argon atmosphere, in dry solvents unless otherwise noted. All dry solvents (anhydrous grade) were purchased at SDS, used without purification, dried over molecular sieves (3Å), and flushed under argon atmosphere, prior to use. THF was freshly distilled from sodium benzophenoneketyl prior to use. All reagents were reagent grade and used as received without further purification unless otherwise specified. (2,2'-bipyridine)-4,4'-dicarboxylic acid (dcapy), dichloro(*p*-cymene)-ruthenium(II) dimer ([Ru(*p*-cymene)Cl_2]$_2$) were purchased at TCI, and ammonium thiocyanate(NH_4NCS) at Aldrich. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm) or GE Healthcare Sephadex® LH-20. Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. MS experiments were performed by the *Servicio Interdepartamental de Investigación* (SIdI) at the Autonoma University of Madrid. FAB (matrix: *m*-NBA) and EI-TOF MS/HRMS spectra were recorded on a VG AutoSpec instrument. MALDI-TOF MS/HRMS spectra (matrix: dithranol) were recorded on a Bruker Reflex III spectrometer with a laser beam operating at 337 nm. Poly(ethyleneglycol)-1000 (PEGH) was used as an internal calibration reference for HRMS MALDI-TOF spectra. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC-300 equipment; chemical shifts(δ) are given in ppm relative to the residual solvent peak of the deuterated solvent, and coupling constants (*J*) are given in Hz. UV-Vis spectra were recorded on a JASCO V-660 instrument.

II. Synthetic procedures and tabulated data



Scheme S1. Synthesis of bipyridine ligands **5-8** and Ru(II) complexes **TT206**–**TT209**. Reagent and conditions:(i) $BF_3{\cdot}OEt_2$, CH_2Cl_2,2-methyl-2-hexanol (for **1**) or 4-propyl-4-heptanol (for **2**),-10 ºC, 2h (**1**: 62%,**2**: 55%);(ii) *n*-butyllithium, THF, -78 ºC (30 min) to RT (1.5h) then $SnBu_3Cl$, THF, -78 ºC (30 min) to RT overnight (quantitative); (iii) 2-bromothiophene, DMF reflux, 24h (**3**: 52%, **4**: 65%);(iv) 4,4'-dibromo-2,2'-bipyridine, $Pd(PPh_3)_4$, DMF reflux, 48h (**5**: 54%; **6**: 53%, **7**: 47%, **8**: 48%) (v) [Ru(*p*-cymene)Cl_2]$_2$, MW, 70 ºC, 20–25 min, followed by (vi) 4,4'-dicarboxylic acid-2,2'-bipyridine, DMF, MW 135–150 ºC, 20 min, and (vii) NH_4NCS, DMF, MW 135–150 ºC, 30–40 min (**TT206**: 83%, **TT207**: 56%, **TT208**: 82%, **TT209**: 48%).

2-[(2-Methylhex-2-yl)thio]thiophene (1). To a solution of 2-thiophenethiol (5.14 g, 44.3 mmol) and 2-methyl-2-hexanol (4.27 mL, 30.1 mmol) in anhydrous dichloromethane (40 mL) at -10 ºC and under argon, was added drop by drop a 7.93 M commercial solution of $BF_3{\bullet}OEt_2$ in Et_2O (4.20 mL, 33.15 mmol). At the end of the addition, the mixture was stirred for additional 2h at this temperature. Afterwards, the reaction mixture was washed with brine (100 mL) and extracted with CH_2Cl_2. After phase separation, the aqueous layer was extracted twice more with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$ and solvents evaporated to dryness under reduced pressure. Flash column chromatography on SiO_2 (Hexanes/$CHCl_3$ 10:1) yielded **1** (3.98 g, 62%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.40 (dd, *J* = 1,5.5 Hz, 1H), 7.12 (dd, *J* = 1,3.5 Hz, 1H), 7.03 (dd, J = 3.5, 5.5 Hz, 1H), 1.46 (m, 6H), 1.26 (s, 6H), 0.93 ppm (m, 3H); MS (EI^+-TOF): m/z: 214 $[M]^+$; HRMS (EI^+-TOF): *m/z* calcd for $C_{11}H_{18}S_2$: 214.0850 $[M]^+$; found: 214.0854.

2-(1,1-Dipropylbutylthio)thiophene (2): As described for **1**, with 2-thiophenethiol (3.36 g, 38.9 mmol), 4-propyl-4-heptanol (3.05 g, 19.3 mmol), a 7.93 M solution of $BF_3{\bullet}OEt_2$ in Et_2O (2.69 mL, 21.2 mmol), in solution in CH_2Cl_2 (25 mL). Flash column chromatography on SiO_2 (Hexanes/$CHCl_3$ 50:1) yielded **2** (2.70 g, 55%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.39 (dd, *J*= 1, 5 Hz, 1H), 7.06 (dd, *J* = 1, 3.5 Hz, 1H), 7.01 (dd, *J* = 3.5, 5 Hz, 1H), 1.43 (m, 6H), 1.36 (m, 6H), 0.90 ppm (m, 9H); MS (EI^+-TOF): *m/z* 256 $[M]^+$; HRMS (EI^+-TOF): *m/z* calcd for $C_{14}H_{24}S_2$: 256.1319 $[M]^+$; found: 256.1321.

General procedure for Stille coupling

i) Preparation of the stannyl derivatives: *n*BuLi (2.5 M in hexanes) was added dropwise to a solution containing the thiophene derivative dissolved in dry THF at -78°C under Ar. After addition, the solution was stirred for 30 min at this temperature, and then warmed slowly to RT over 1.5 h. The solution was cooled again at -78°C, then a solution of tributyltin chloride in dry THF was added dropwise. After addition, the mixture was stirred at the same temperature for 30 min, then let to warm to RT and stirred overnight. Afterwards, brine was added to the reaction mixture under vigorous stirring. The resulting mixture was taken up with a copious amount of CH_2Cl_2, and extracted three more time with CH_2Cl_2 (3×50 mL). The organic layers were combined, and successively washed with brine, then water, dried over $MgSO_4$, and the solvent evaporated to dryness. The stannyl product was used without further purification in the next reaction-step (yield taken quantitative for this step).

ii) Stille Coupling reaction: The crude stannyl derivative, brominated derivative, and catalyst $Pd(PPh_3)_4$, were refluxed in dry DMF (50 mL) for 24–48h under argon. After cooling to RT, DMF was removed from the flask under high-vacuum rotary evaporation. The remaining residue was re-dissolved in diisopropyl ether (50 mL), and the organic phase washed with a saturated aqueous solution of NH_4Cl (50 mL). The aqueous layers were extracted twice more with diisopropyl ether (2×50 mL). The organic layers were combined, successively washed with a saturated aqueous solution of $NaHCO_3$ (2×50 mL) then with brine (2×50 mL), dried over $MgSO_4$ and the solvents evaporated to dryness. The crude products were purified by the appropriated method: *Method A* (for compounds **4** and **5**): purification by flash chromatography column on SiO_2 (hexanes/CH_2Cl_2 100:1). *Method B* (for compounds **5–8**): the crude was dissolved in a minimum amount of CH_2Cl_2, and then hexane was added until complete precipitation of the bipyridine compound. The resulting suspension was filtered-off, washed with hexanes, and air-dried. If needed, these operations were repeated until obtaining a pure product.

5-[(2-Methylhex-2-yl)thio]-2,2'-dithiophene (3): According to the general procedure, the stannyl derivative of **1** was prepared from a solution of **1** (0.50 g, 2.31 mmol) in THF (20 mL), a 2.5 M solution of nBuLi in hexanes (1.20 mL, 3.00 mmol), and a solution of $SnBu_3Cl$ (0.84 mL, 3.09 mmol) in THF (10 mL). Next, a Stille coupling was performed between the crude stannyl derivative, 2-bromothiophene (0.35 g, 2.16 mmol), and $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) in DMF (50 mL). Purification by *method A* yielded **3** (0.33 g, 52%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.22 (dd, *J* = 1, 5 Hz, 1H), 7.17 (dd, *J* = 1, 3.6 Hz, 1H), 7.09 (d, *J* = 3.7 Hz, 1H), 7.03 (d, *J* = 3.7 Hz, 1H), 7.01 (dd, *J* = 3.6, 5 Hz, 1H). 1.55-1.43 (m, 6H), 1.28 (s, 6H), 0.93 ppm (t, J = 7.2 Hz, 3H); MS (FAB^+): *m/z* 296 $[M]^+$; HRMS (FAB^+): *m/z* calcd for $C_{15}H_{20}S_3$: 296.0727 $[M]^+$; found: 296.0734.

5-(1,1-Dipropylbutylthio)-2,2'-dithiophene (4): According to the general procedure, the stannyl derivative of **2** was prepared from a solution of **2** (1.55 g, 6.05 mmol) in THF (30 mL), a 2.5 M solution of *n*BuLi in hexanes (2.91 mL, 7.26 mmol), and a solution of $SnBu_3Cl$ (1.80 mL, 6.65 mmol) in THF (20 mL). Next, a Stille coupling was performed between the crude stannyl derivative, 2-bromothiophene (0.40 g, 2.47 mmol), and $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) in DMF (60 mL). Purification by *method A* yielded **4** (0.54 g, 65%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ 7.22 (d, *J* = 5 Hz, 1H), 7.17 (d, *J* = 3.7 Hz, 1H), 7.08 (d, *J*= 3.6 Hz, 1H), 7.01 (dd, *J* = 3.7, 5 Hz, 1H), 6.97 (d, *J* = 3.6 Hz, 1H), 1.48-1.35 (m, 12H), 0.88 ppm (t, *J* = 7 Hz, 9H); MS (FAB^+): *m/z* 338 $[M]^+$; HRMS (FAB^+): *m/z* calcd for $C_{18}H_{26}S_3$: 338.1197 $[M]^+$; found: 338.1184.

4,4'-Bis{2-[(2-methylhex-2-yl)thio]thien-5-yl}-2,2'-bipyridine (5). According to the general procedure, a solution of stannyl derivative of **1** (1.22 g, 2.42 mmol), 4,4'-dibromo-2,2'-bipyridine (0.25 g, 0.80 mmol) and $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), in refluxing DMF (50 mL) for 48 h. Purification by *method B* yielded **5** (0.25 g, 54%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.69 (d, *J* = 5 Hz, 2H),

8.64 (d, *J*= 1 Hz, 2H), 7.58 (d, *J*= 4 Hz, 2H), 7.49 (dd, *J* = 1, 5 Hz, 2H), 7.16 (d, *J* = 4 Hz, 2H), 1.53 (m, 12H), 1.31 (s, 12H), 0.93 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ = 156.8, 150.1, 146.1, 142.2, 138.4, 134.7, 126.0, 120.1, 117.5, 51.3, 42.0, 28.6, 27.2, 23.3, 14.3 ppm; MS (FAB^+): *m/z* 581 $[M+H]^+$; HRMS (FAB^+): *m/z* calcd for $C_{32}H_{41}N_2S_4$: 581.2153$[M+H]^+$; found: 581.2164.

4,4′-Bis[2-(1,1-dipropylbutylthio)thien-5-yl]-2,2′-bipyridine (6). According to the general procedure, a solution of stannyl derivative of **2** (1.00 g, 1.84 mol), 4,4'-dibromo-2,2'-bipyridine (0.19 g, 0.61 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol), in refluxing DMF (40 mL) for 48 h. Purification by *method B* yielded **6** (0.22 g, 53%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.67 (d, *J* = 5 Hz, 2H), 8.60 (d, *J* = 1.5 Hz, 2H), 7.55 (d, *J* = 4 Hz, 2H), 7.48 (dd, *J* = 5, 1.5 Hz, 2H), 7.10 (d, *J* = 4 Hz, 2H), 1.42 (m, 24H), 0.93 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ = 156.7, 150.0, 145.8, 142.2, 138.2, 134.4, 125.9, 120.1, 117.3, 59.2, 38.9, 17.2, 14.6 ppm; MS (FAB^+): *m/z* 665 $[M+H]^+$; HRMS (FAB^+): *m/z* calcd for $C_{38}H_{53}N_2S_4$: 665.3092 $[M+H]^+$; found: 665.3092.

4,4′-Bis{2-[2-(methylhex-2-yl)thio]dithien-5'-yl}-2,2′-bipyridine (7). According to the general procedure, a solution of stannyl derivative of **3** (1.26 g, 2.14 mmol), 4,4'-dibromo-2,2'-bipyridine (0.22 g, 0.72 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), in refluxing DMF (60 mL) for 48 h. Purification by *method B* yielded **7** (0.24 g, 47%) as a yellowish solid.^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.69 (d, *J* = 5 Hz, 2H), 8.64 (d, *J* = 1.5 Hz, 2H), 7.58 (d, *J* = 4 Hz, 2H), 7.50 (dd, *J* = 5, 1.5 Hz, 2H), 7.19 (d, *J* = 4 Hz, 2H), 7.17 (d, *J* = 4 Hz, 2H) 7.07 (d, *J* = 4 Hz, 2H), 1.52 (m, 12H), 1.30 (s, 12H), 0.94 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ = 156.8, 150.1, 142.2, 141.7, 140.4, 139.0, 138.1, 132.2, 126.7, 125.2, 124.6, 119.8, 117.2, 53.2, 42.0, 28.6, 27.2, 23.3, 14.3 ppm; MS (FAB^+): *m/z* 745 [M+H]+; HRMS (FAB^+): *m/z* calcd for $C_{40}H_{45}N_2S_6$: 745.1907 $[M+H]^+$; found: 745.1912 $[M+H]^+$.

4,4′-Bis[2-(1,1-dipropylbutylthio)dithien-5'-yl]-2,2′-bipyridine (8). According to the general procedure, a solution of stannyl derivative of **4** (2.00 g, 3.19 mmol), 4,4'-dibromo-2,2'-bipyridine (0.33 g, 1.06 mmol) and $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), in refluxing DMF (60 mL) for 48 h. Purification by *method B* yielded **8** (0.42 g, 48%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.69 (d, *J* = 5 Hz, 2H), 8.65 (d, *J* = 1.5 Hz, 2H), 7.58 (d, *J* = 4 Hz, 2H), 7.50 (dd, *J* = 1.5, 5 Hz, 2H), 7.21 (d, *J* = 4 Hz, 2H), 7.16 (d, *J* = 3.6 Hz, 2H), 7.01 (d, *J* = 3.6 Hz, 2H), 1.42 (m, 24H), 0.89 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS): δ = 156.7, 150.0, 142.2, 141.5, 140.4, 139.0, 138.1, 132.2, 126.6, 125.1, 124.5, 119.8, 117.2, 59.1, 38.8, 17.2, 14.6 ppm; MS (FAB^+): *m/z* 829 $[M+H]^+$; HRMS (FAB+): *m/z* calcd for $C_{46}H_{57}N_2S_6$: 829.2841 $[M+H]^+$; found: 829.2851.

General procedure for the synthesis of heteroleptic complexes TT206–209

In a sealed tube-flask (closed vessel), a stirred solution of $[Ru(p\text{-cymene})Cl_2]_2$ dimer (0.6 eq) and bipyridine ligand **5**, **6**, **7** or **8** (1 eq) in dry DMF (9 mL) was heated under MW irradiation at 70 ºC for 20–25 min. Then, a solution of 4,4'-dicarboxylic acid-2,2'-bipyridine (1.2 eq) in DMF (3 mL) was added, and the solution irradiated under MW at 135–150 ºC for additional 20 min. After cooling, a solution of NH_4SCN (25 eq) in DMF (3 mL), was added to the mixture, and irradiated again under MW at 135–150 ºC for 30–40 min. After cooling, DMF was removed from the flask by high-vacuum distillation. The remaining pasty solid was triturated in Et_2O (10mL), and the resulting suspension was filtered-off and then washed with Et_2O (2✕10mL). The remaining solid was air-dried, dissolved in basic MeOH (NaOH) and purified by chromatography column on Sephadex™ (MeOH). The main band was collected, and the solvent evaporated to dryness, to afford the desired complex under the disodium salt form. This salt was redissolved in MeOH, and the resulting solution acidified by addition of a 10^{-2} M solution of HNO_3 in MeOH (0.5 eq of HNO_3 per eq of complex), affording the complex under the mono sodium salt form.

Ru(II) complex TT206. According the general procedure, from [Ru(*p*-cymene)Cl_2]$_2$ (25.0 mg, 0.04 mmol), compound **6** (40.0 mg, 0.07 mmol), dcapy (20.0 mg, 0.08 mmol), and NH_4NCS, (131.0 mg, 1.73 mmol) to yield **TT206** (61 mg, 83%) as a dark-black reddish powder. ^{1}H NMR (300 MHz, [D6]DMSO, 25 ºC, TMS): δ = 9.45 (m, 2H), 9.18 (m, 1H), 9.09 (m, 1H), 8.94 (m, 1H), 8.32 (m, 1H), 8.19 (m, 2H), 8.02 (m, 2H), 7.92 (m, 1H), 7.63 (m, 2H), 7.42 (m, 1H), 7.33 (m, 2H), 1.52 (m, 4H), 1.43 (s, 12H), 1.30 (m, 4H), 1.21 (m, 4H), 0.88 ppm (m, 6H); UV-Vis (DMF): λ_{max}/nm (ε/M^{-1}·cm^{-1}) = 311 (35 600), 345 (sh., 24 200), 419 (sh., 12 100); MS (MALDI-TOF): *m/z* 984 [M-(NCS)]$^+$; HR-MS (MALDI-TOF): *m/z* calcd for $C_{45}H_{48}N_5O_4RuS_5$: 984.1353; found: 984.1361 [M-(NCS)]$^+$.

Ru(II) complex TT207. According the general procedure, from [Ru(*p*-cymene)Cl_2]$_2$ (20.0 mg, 0.03 mmol), compound **6** (40.0 mg, 0.05 mmol), dcapy (16.0 mg, 0.06 mmol), and NH_4NCS, (102.0 mg, 1.34 mmol) to yield **TT207** (37 mg, 56%) as a dark-black reddish powder. ^{1}H NMR (300 MHz, [D6]DMSO, 25 ºC, TMS): δ = 9.35 (m, 2H), 9.22 (m, 1H), 9.11 (m, 1H), 8.98 (m, 2H), 8.84 (m, 2H), 8.28 (m, 1H), 8.04 (m, 1H), 7.95 (m, 1H), 7.81 (m, 1H), 7.67 (m, 2H), 7.53 (m, 2H), 7.44 (m, 2H), 7.21 (m, 2H), 2.89 (m, 4H), 2.73 (s, 12H), 1.30 (m, 4H), 1.28 (m, 4H), 0.91 ppm (m, 6H); UV-Vis (DMF): λ_{max}/nm (ε/M^{-1}·cm^{-1})= 302 (39 900), 384 (33 800), 553 (15 300); MS (MALDI-TOF): *m/z* 1148 [M-(NCS)-Na+H)]$^+$, 1229 [M+H]$^+$; HRMS (MALDI-TOF): *m/z* calcd for $C_{54}H_{52}N_6O_4RuS_8$: 1206.0863[M-Na+H]$^+$; found: 1206.0820.

Ru(II) complex TT208. According the general procedure, from [Ru(*p*-cymene)Cl_2]$_2$ (22.0 mg, 0.04 mmol), compound **6** (40.0 mg, 0.06 mmol), dcapy (18.0 mg, 0.07 mmol), and NH_4NCS, (115.0 mg, 1.50 mmol) to yield **TT208** (56 mg, 82%) as a dark-black reddish powder. ^{1}H NMR (300 MHz, [D6]DMSO, 25 ºC, TMS): δ = 9.24 (m, 2H), 9.08 (m, 1H), 8.92 (m, 1H), 8.80 (m, 2H), 8.74 (m, 2H), 8.21 (m, 1H), 7.99 (m, 1H), 7.53 (m, 1H), 7.47 (m, 2H), 7.35 (m, 1H), 7.22 (m, 2H), 2.09 (m, 12H), 1.45 (m, 12H), 0.91 ppm (m, 18H); UV-Vis (DMF): λ_{max}/nm (ε/M^{-1}·cm^{-1})= 301 (43 800), 341 (30 200), 421 (12 200), 551 (13 100); MS (MALDI-TOF): *m/z* 1068 [M-(NCS)-Na+H]$^+$, 1149 [M+H]$^+$; HRMS (MALDI-TOF): *m/z* calcd for $C_{52}H_{60}N_6NaO_4RuS_6$: 1149.1946 [M+H]$^+$; found: 1149.1912 [M+H]$^+$

III. NMR, MS, HRMS and UV-Vis spectra

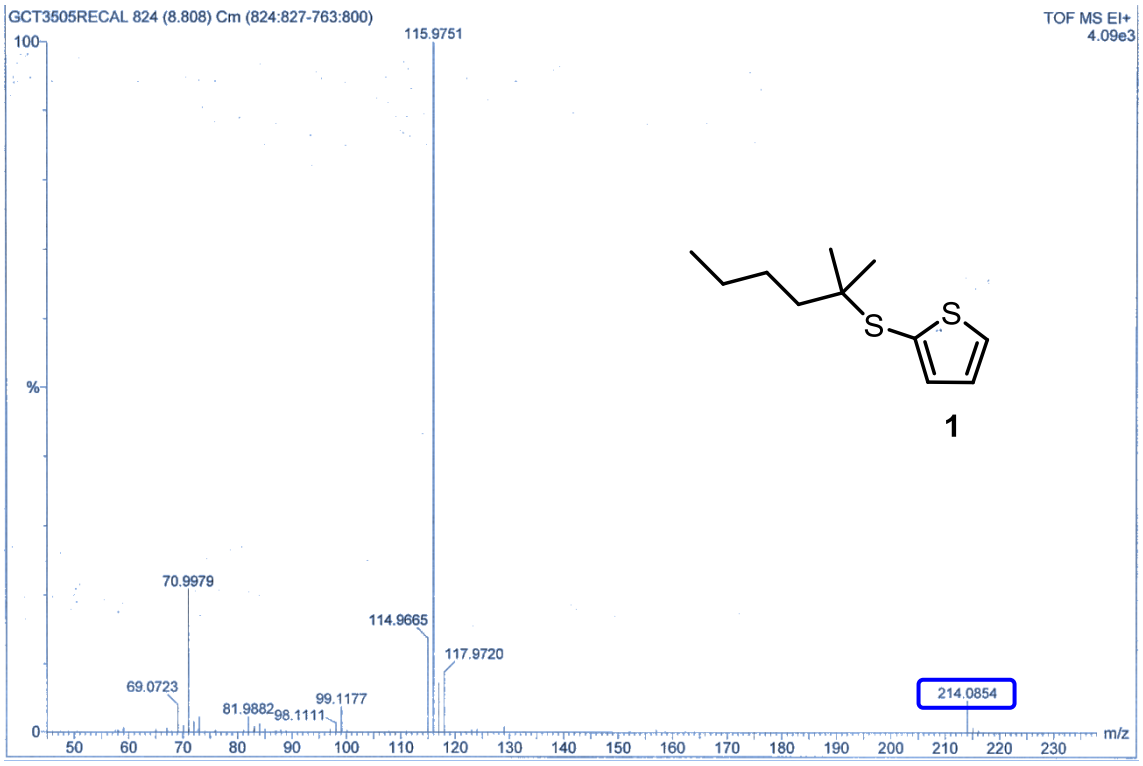


Figure S1. HRMS spectrum of compound **1** (EI^+-TOF).

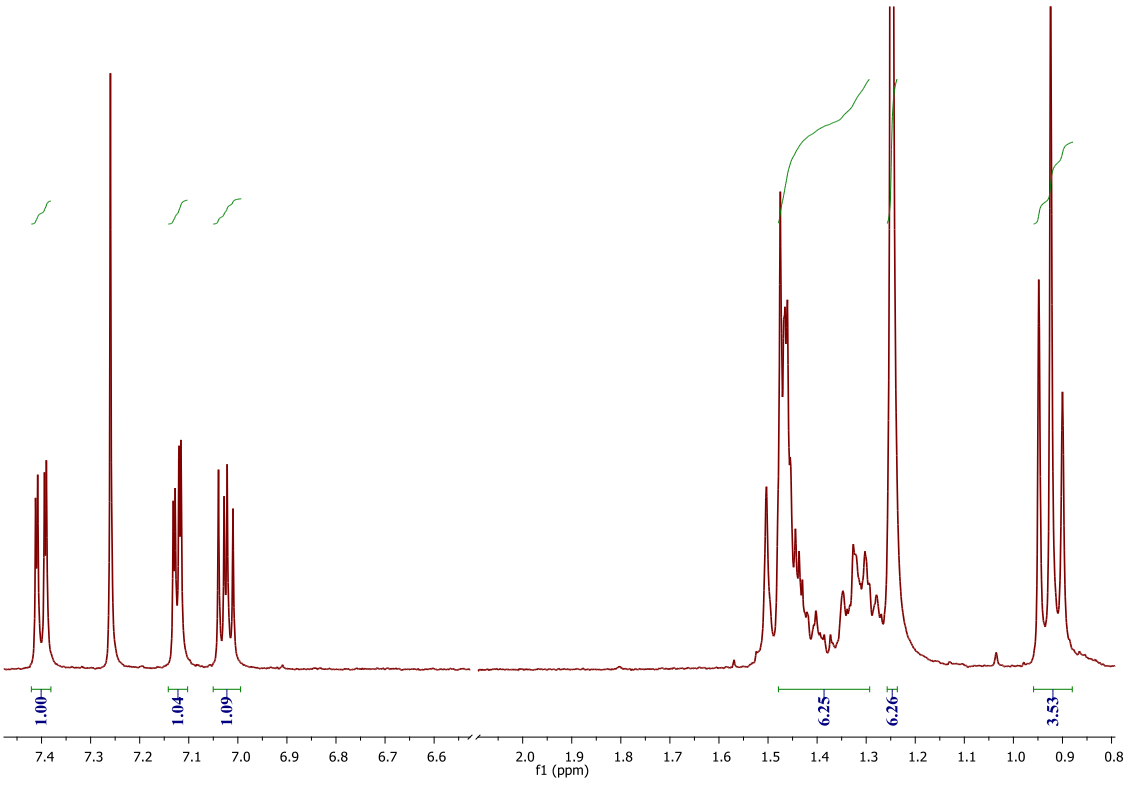


Figure S2. ^{1}H NMR spectrum of compound **1** ($CDCl_3$; 300 MHz).

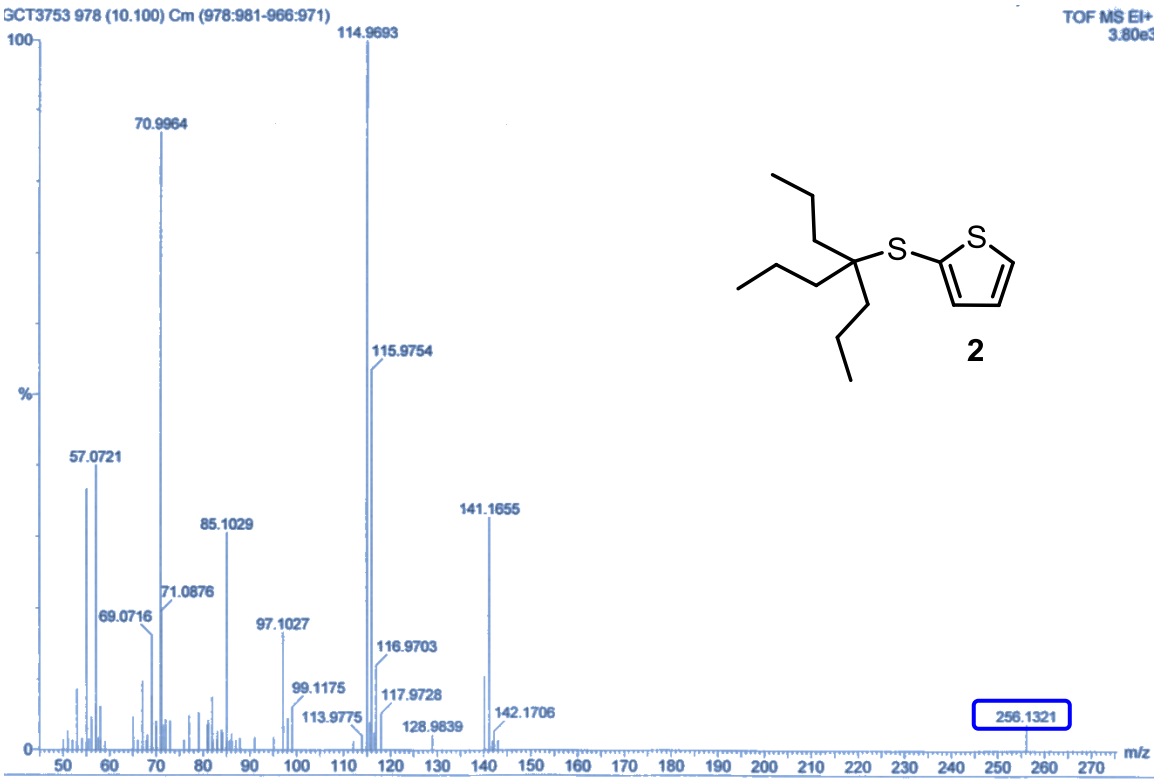


Figure S3. HRMS spectrum of compound **2** (EI^+-TOF).

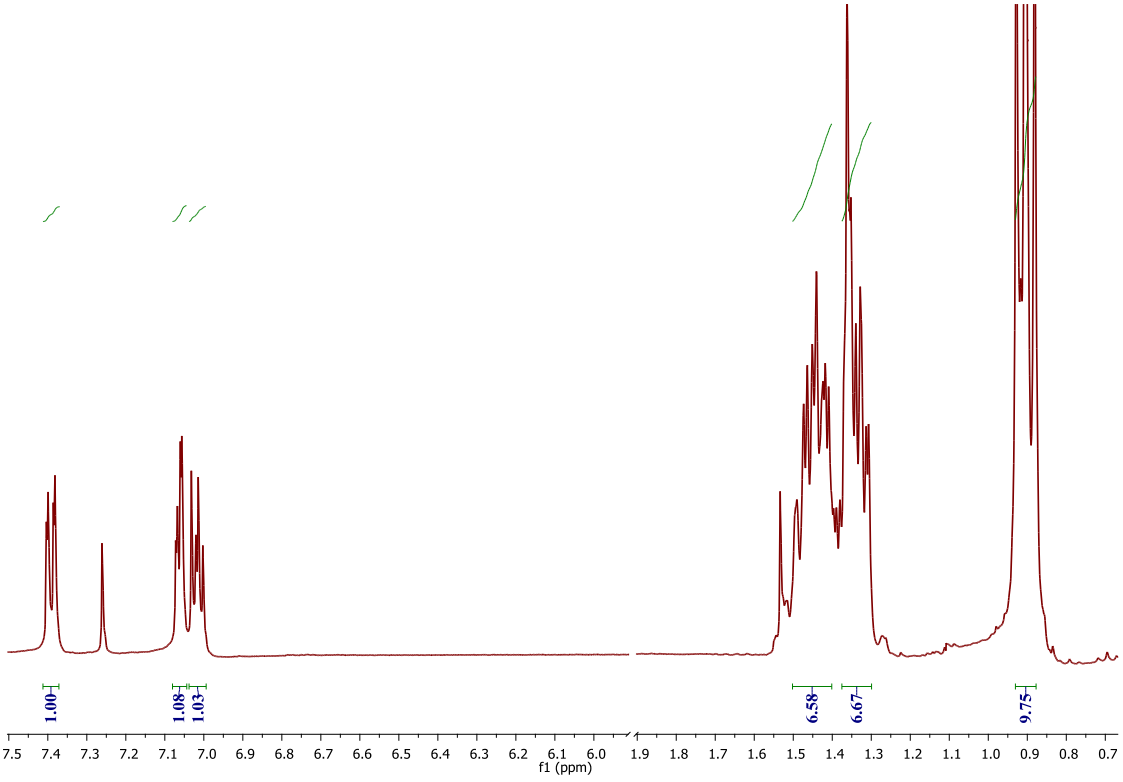


Figure S4. ^{1}H-NMR spectrum of compound **2** ($CDCl_3$, 300 MHz).

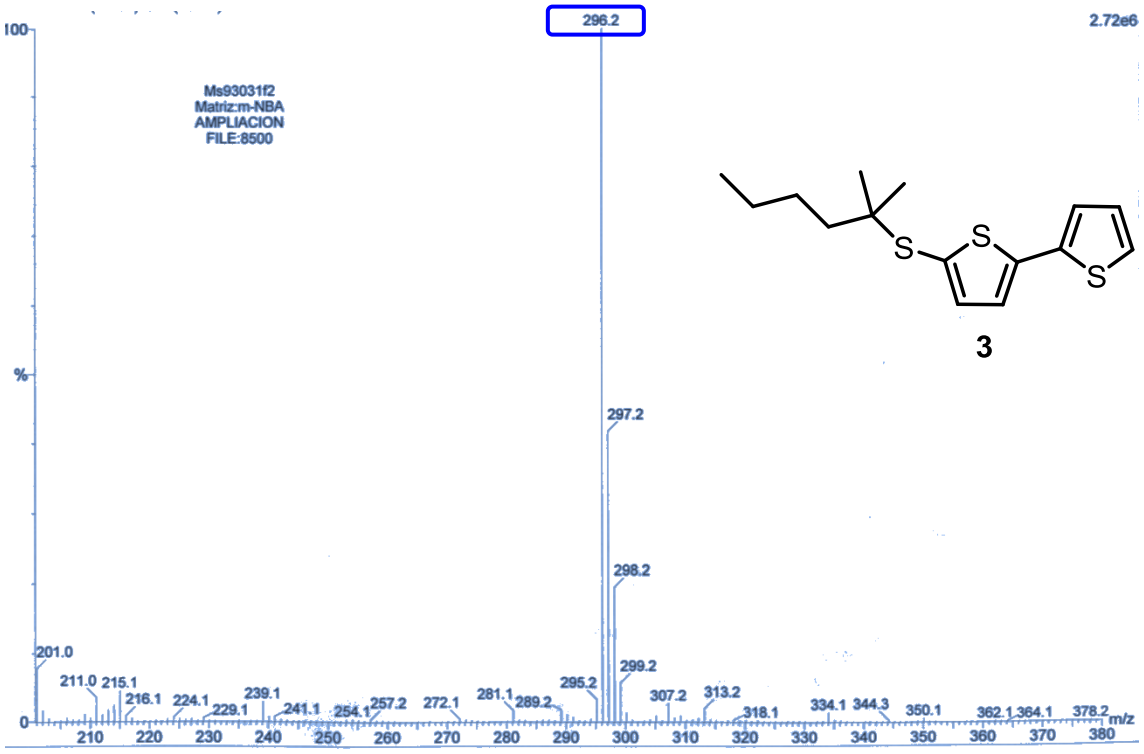


Figure S5. MS spectrum of compound **3** (FAB^+).

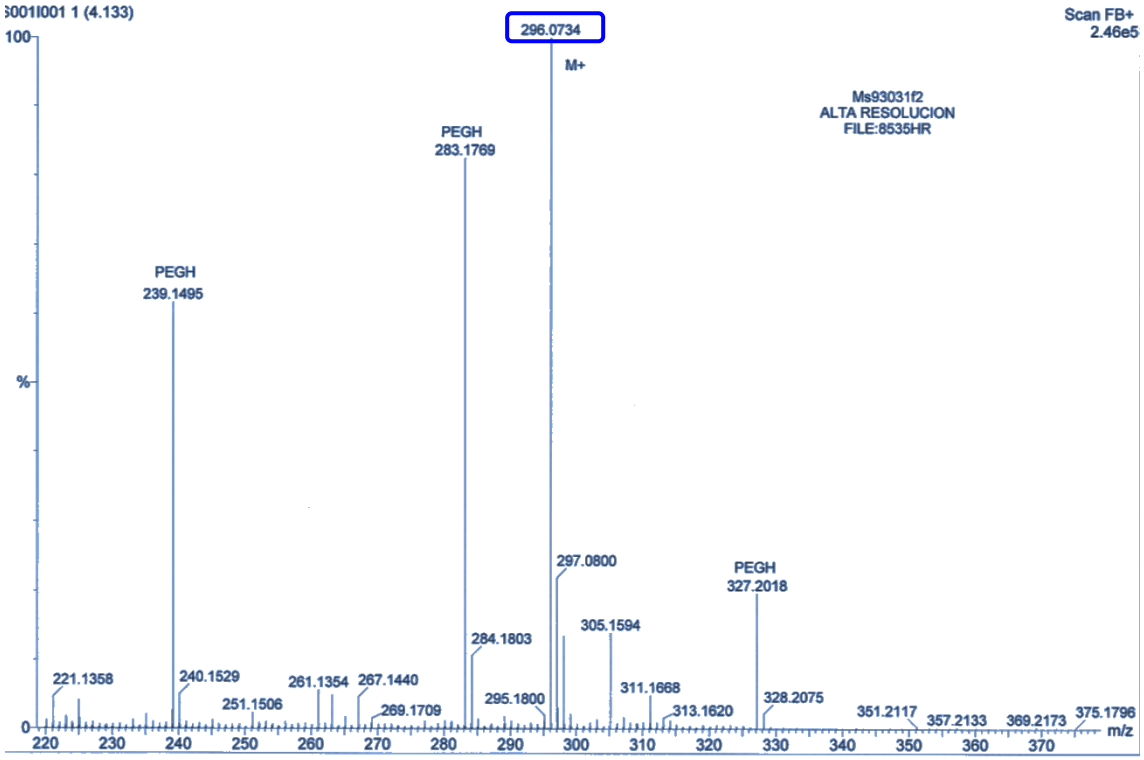


Figure S6. HRMS spectrum of compound **3** (FAB^+; internal calibration reference: PEGH).

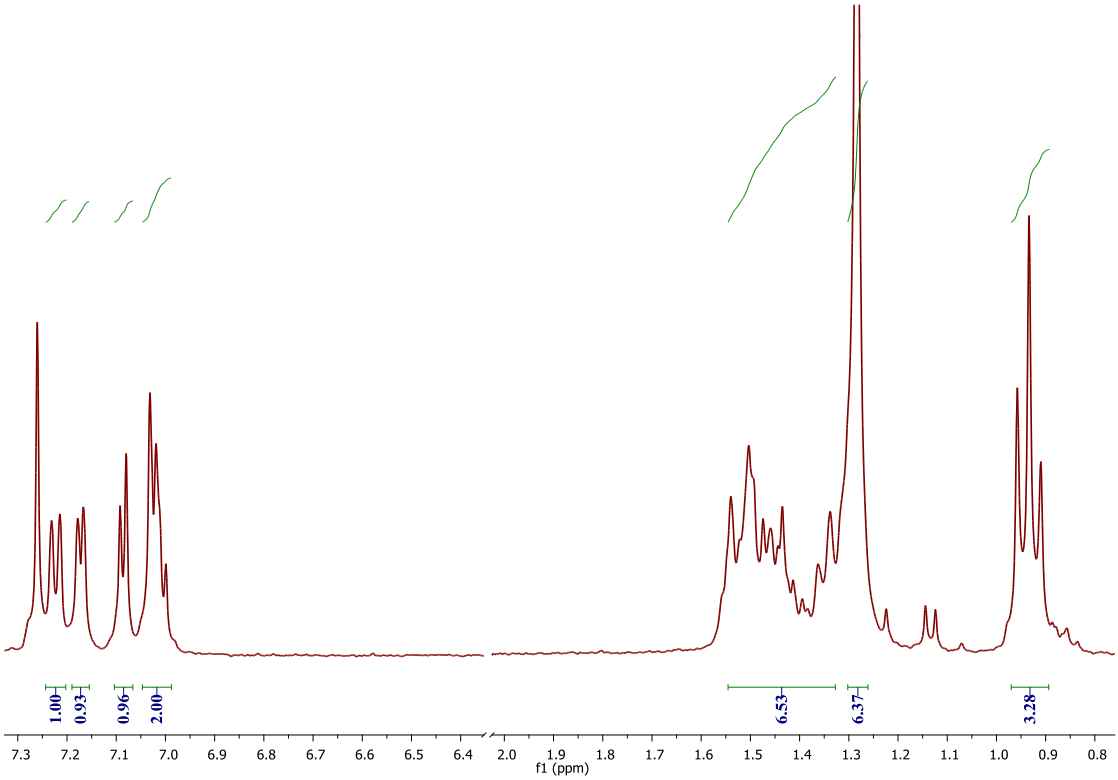


Figure S7. ^{1}H-NMR spectrum of compound **3** ($CDCl_3$, 300 MHz).

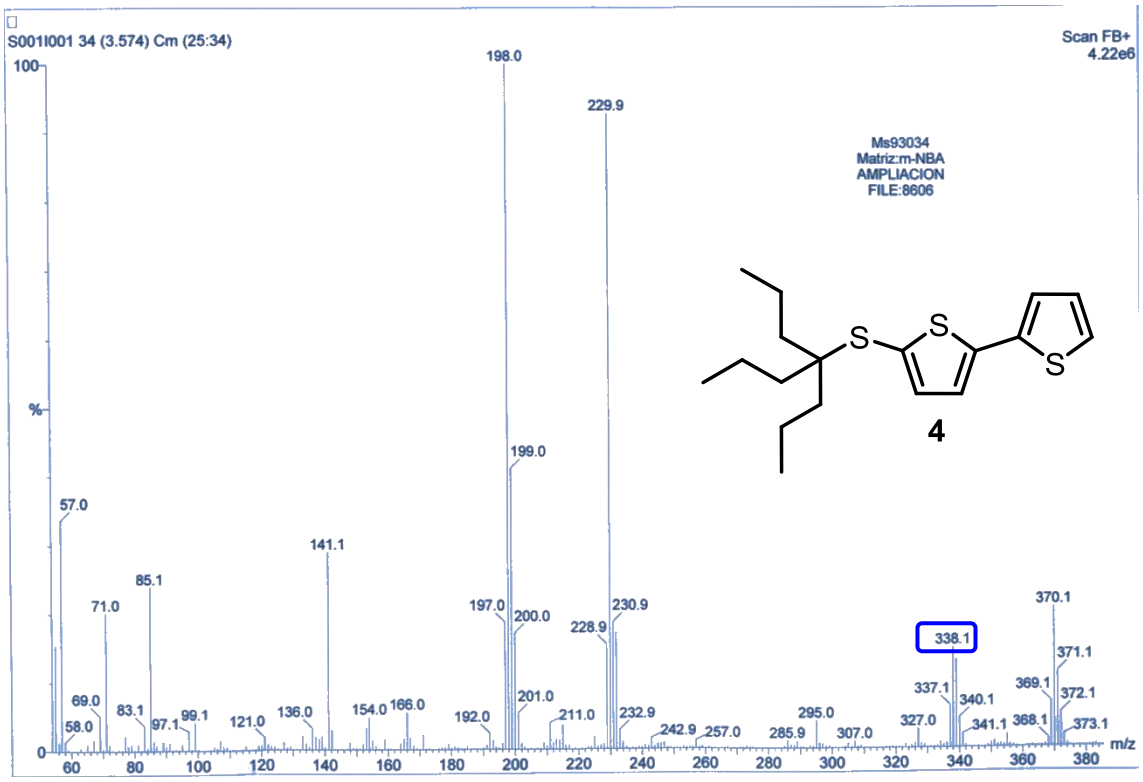


Figure S8. MS spectrum of compound **4** (FAB^+).

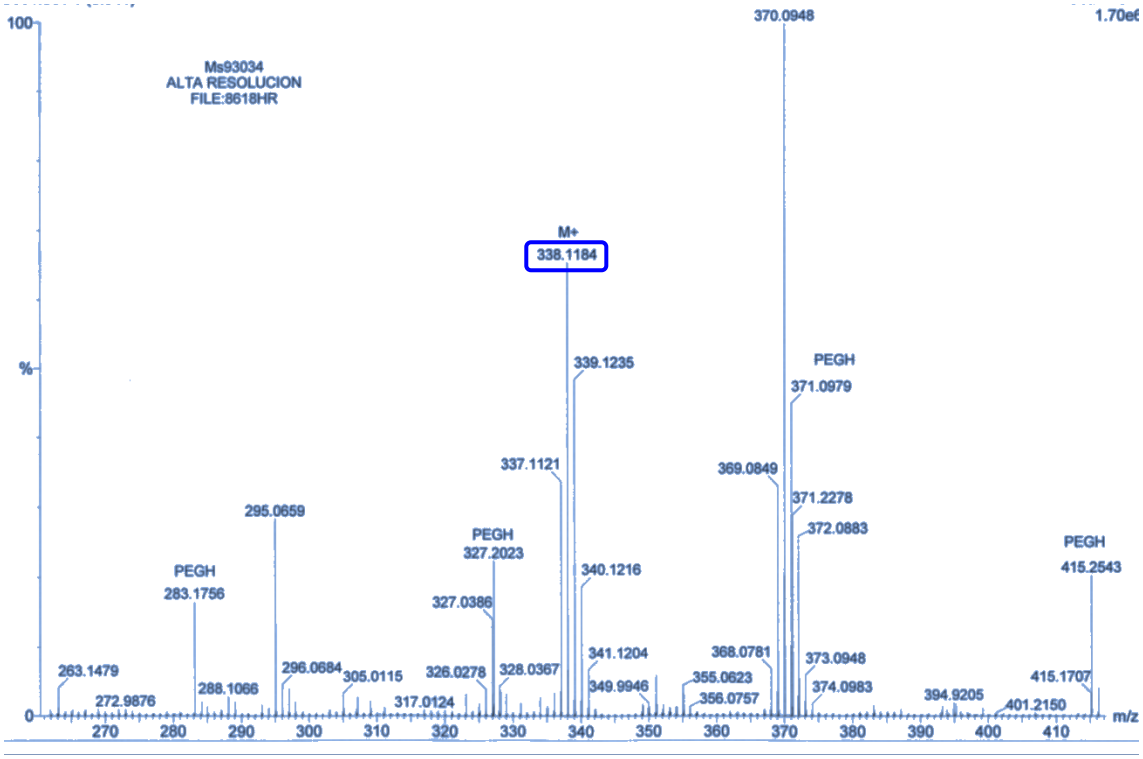


Figure S9. HRMS spectrum of compound **4** (FAB^+; internal calibration reference: PEGH).

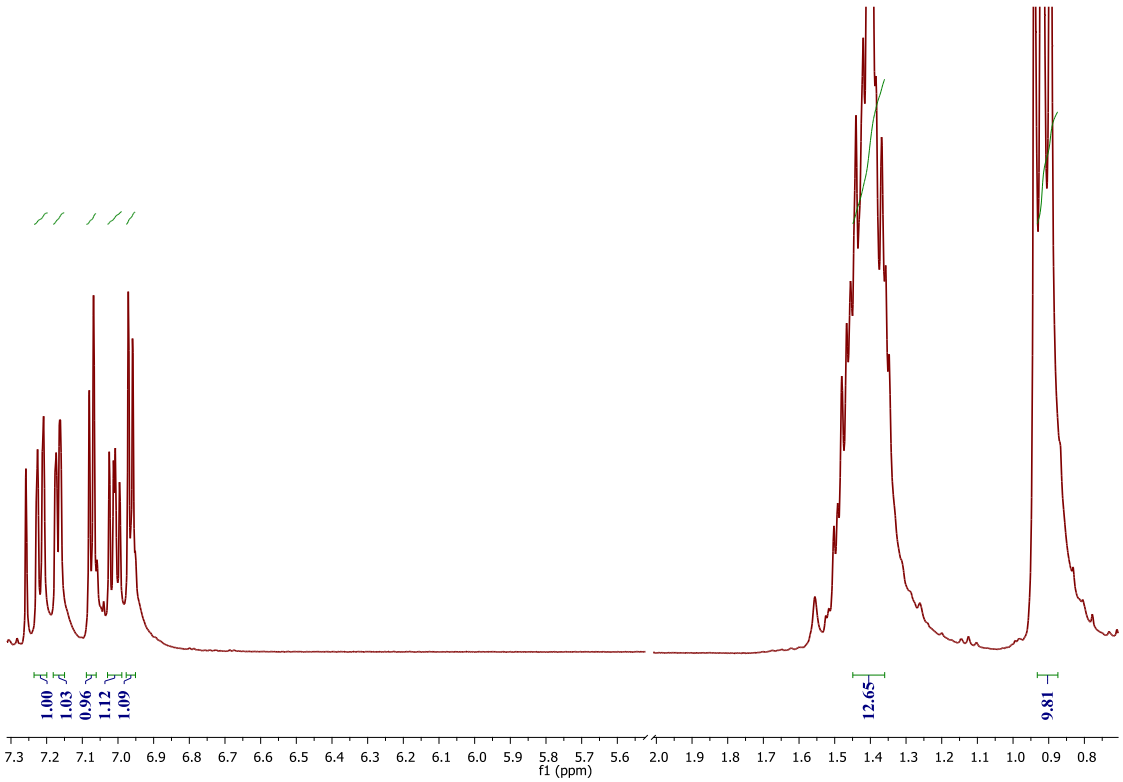


Figure S10. ^{1}H-NMR spectrum of compound **4** ($CDCl_3$, 300 MHz).

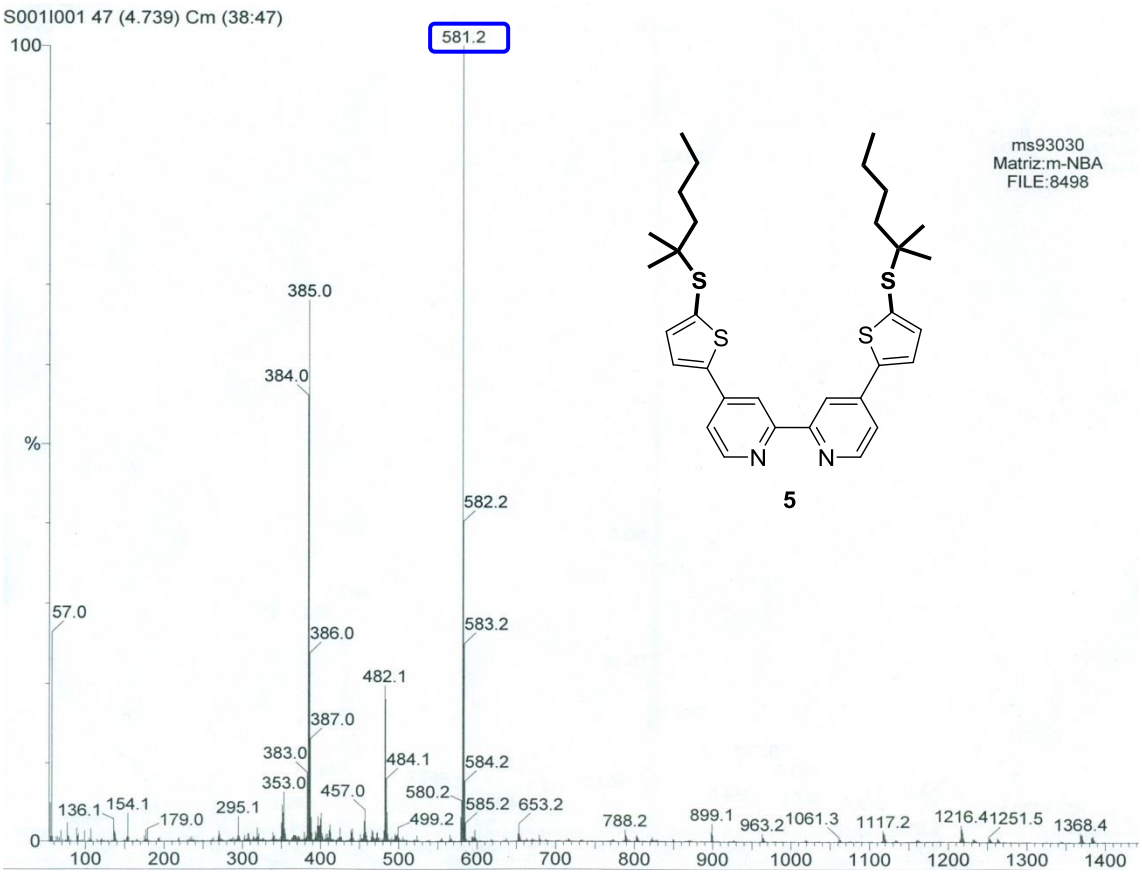


Figure S11. MS spectrum of compound **5** (FAB^+).

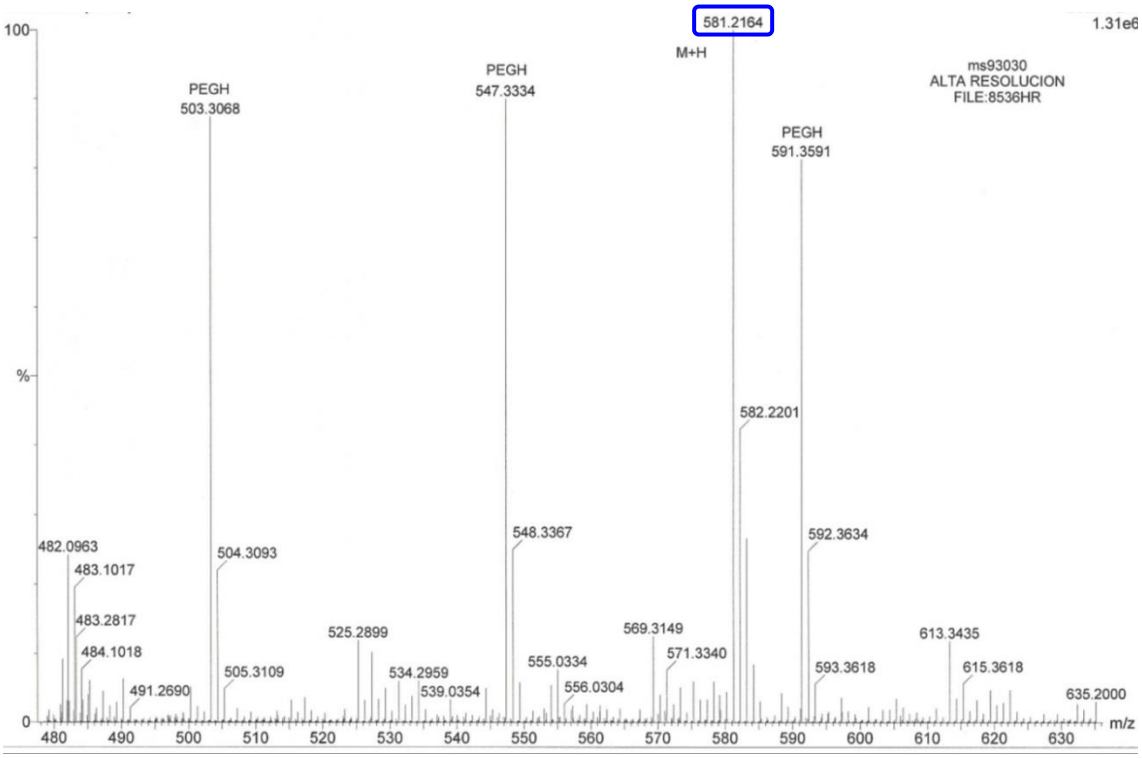


Figure S12. HRMS spectrum of compound **5** (FAB^+; internal calibration reference: PEGH).

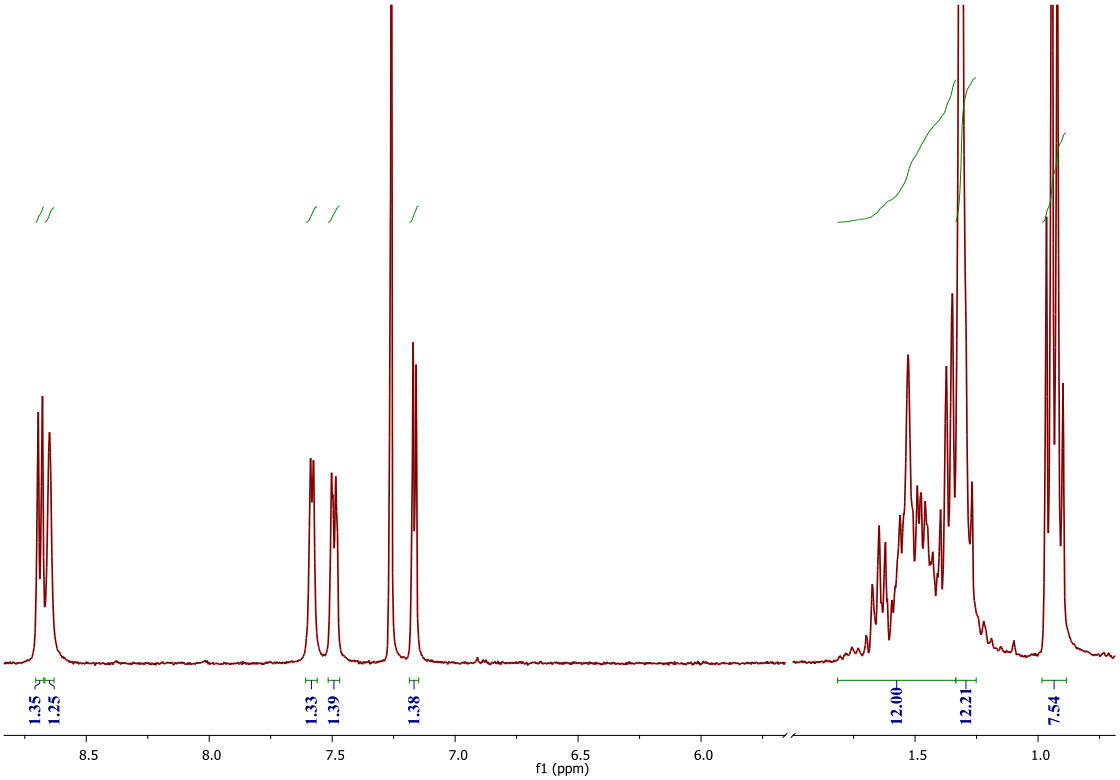


Figure S13. ^{1}H-NMR spectrum of compound **5** ($CDCl_3$, 300 MHz).

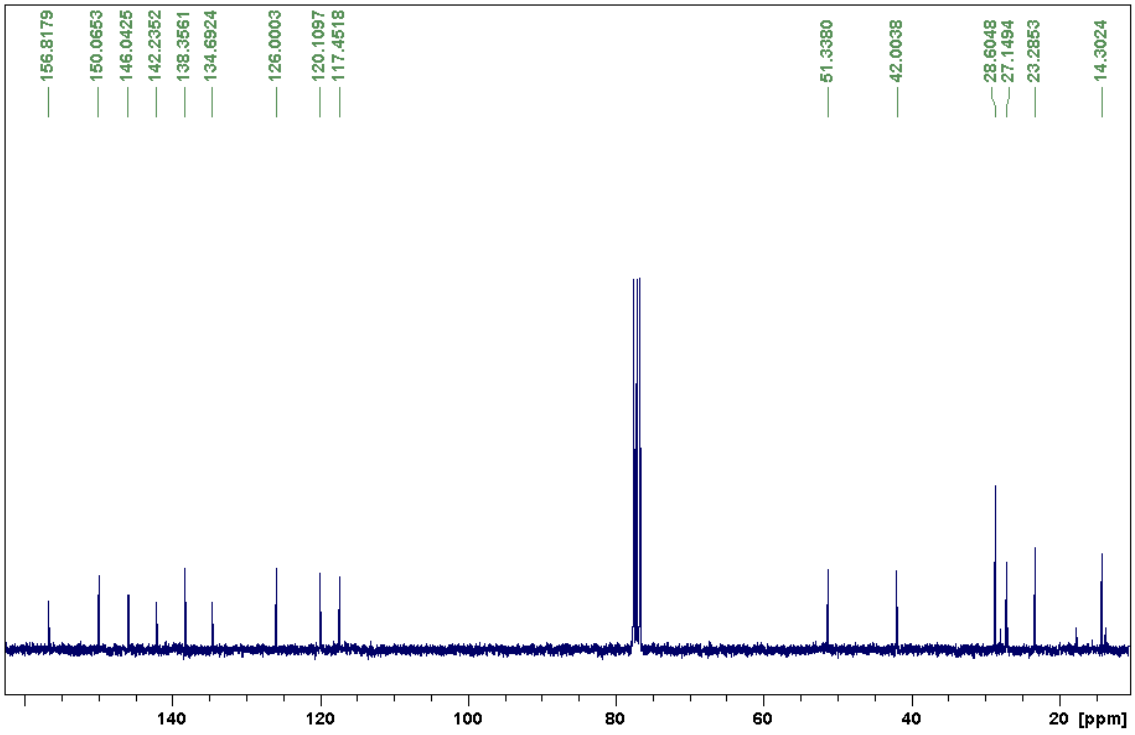


Figure S14. ^{13}C-NMR spectrum of compound **5** ($CDCl_3$, 75 MHz).

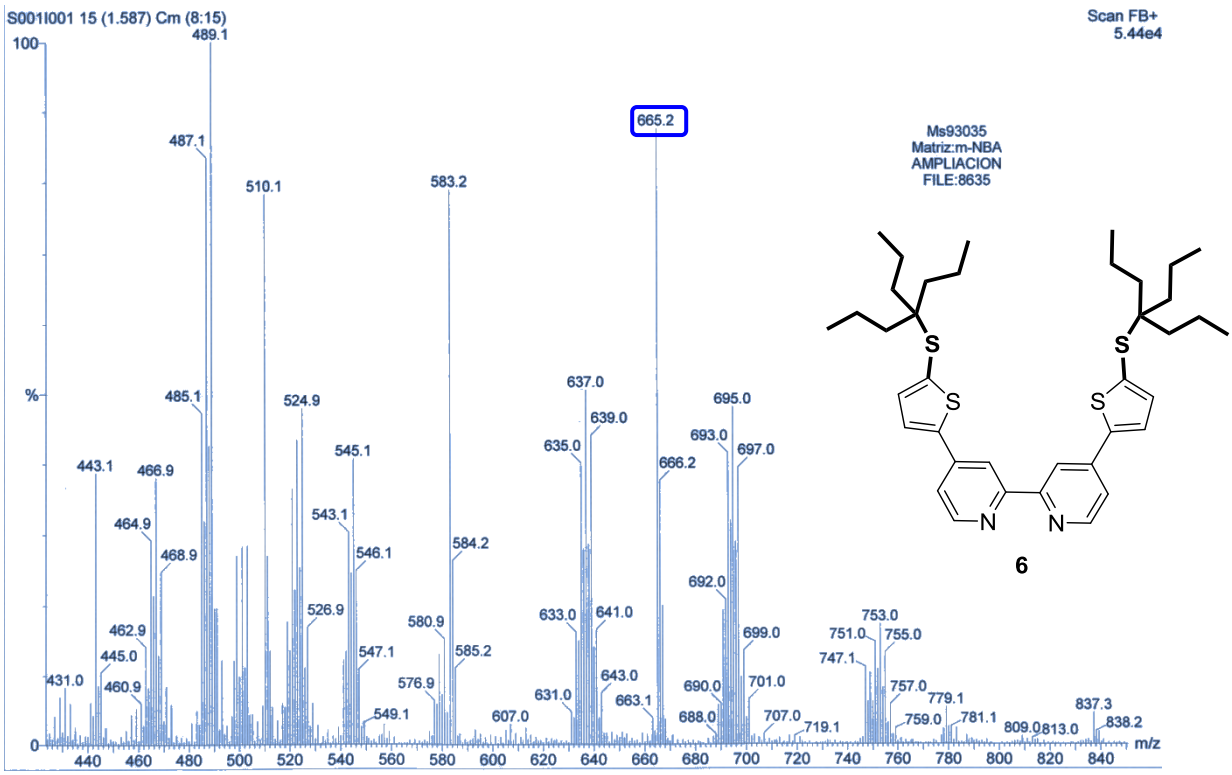


Figure S15. MS spectrum of compound **6** (FAB^+).

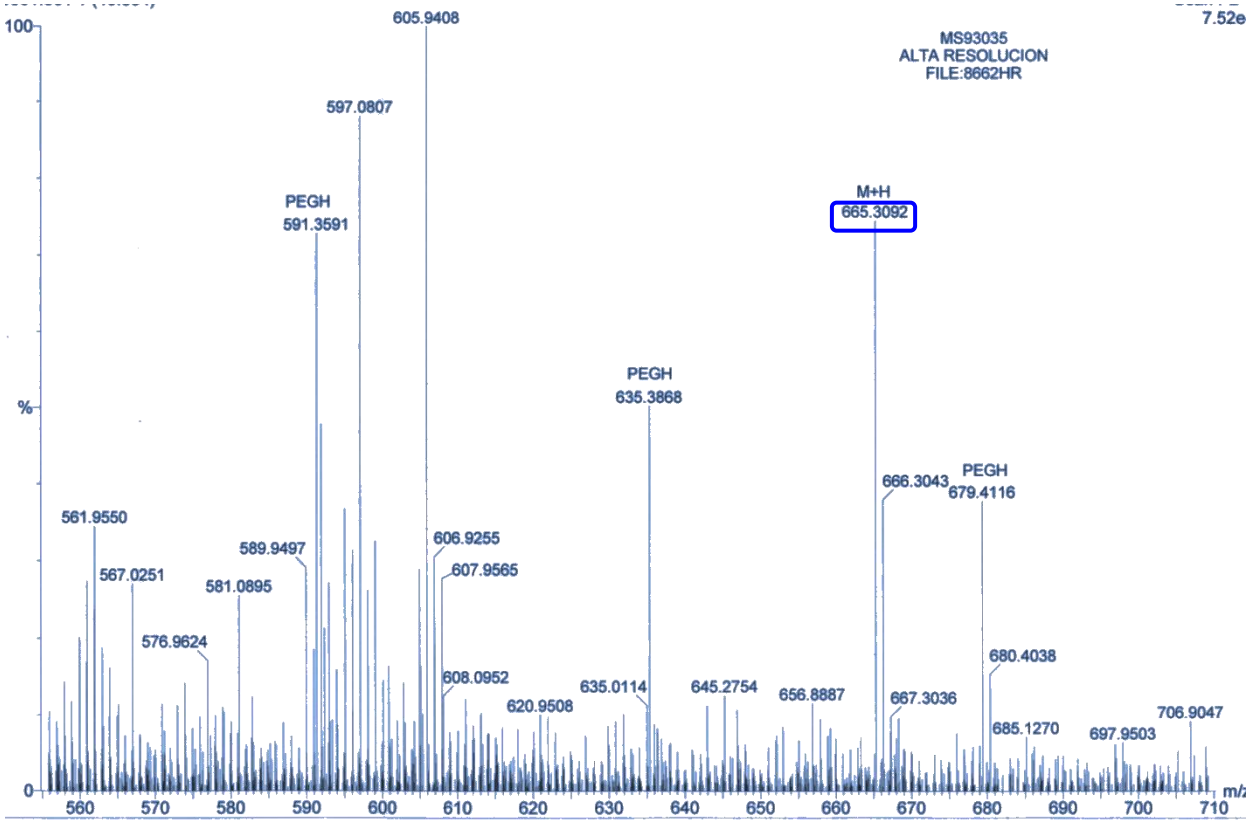


Figure S16. HRMS spectrum of compound **6** (FAB^+; internal calibration reference: PEGH).

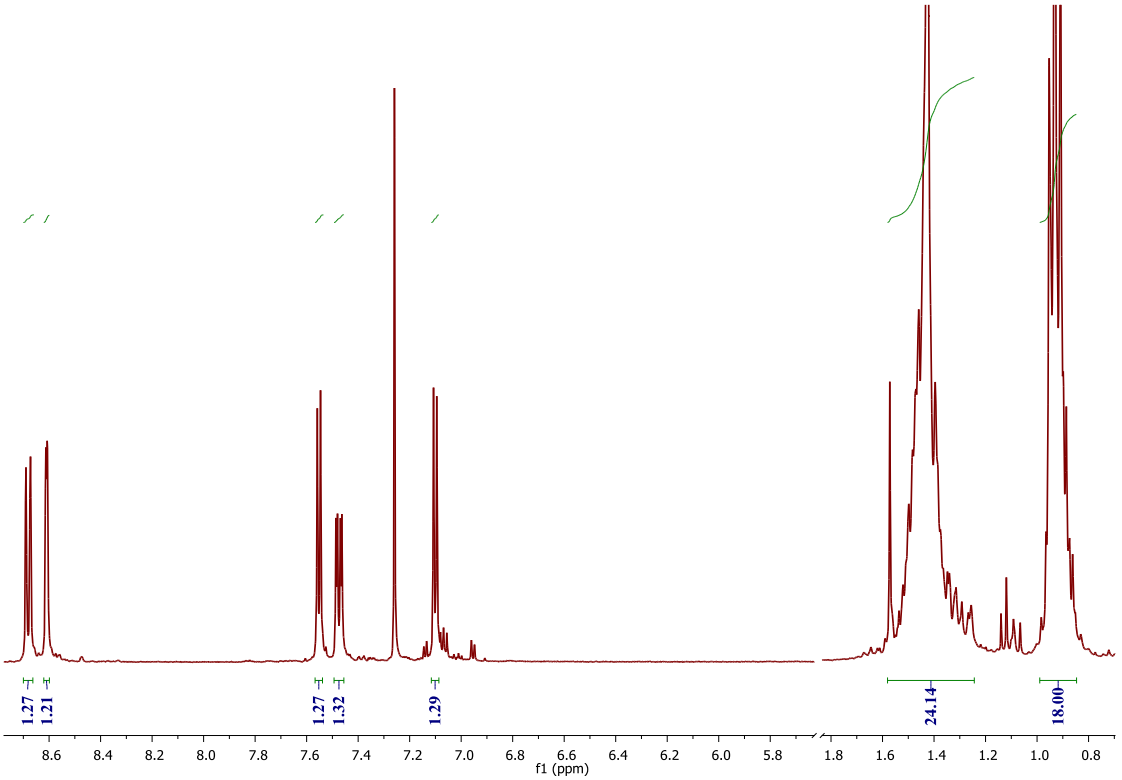


Figure S17. ^{1}H-NMR spectrum of compound **6** ($CDCl_3$, 300 MHz).

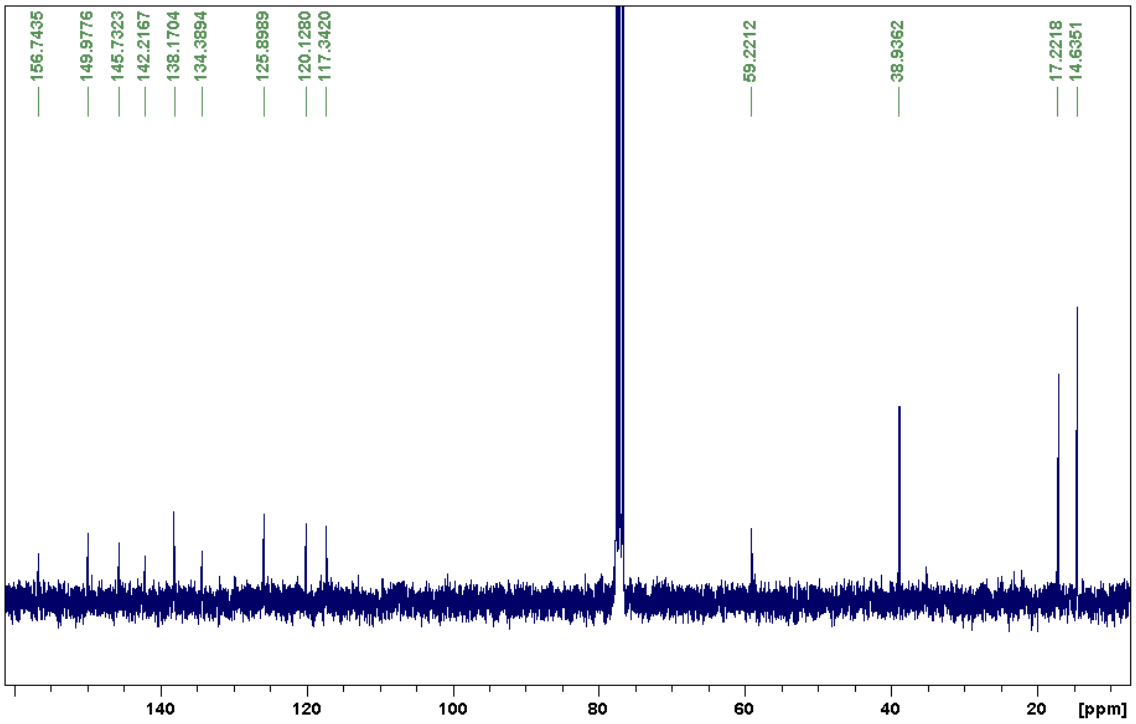


Figure S18. ^{13}C-NMR spectrum of compound **6** ($CDCl_3$, 75 MHz).

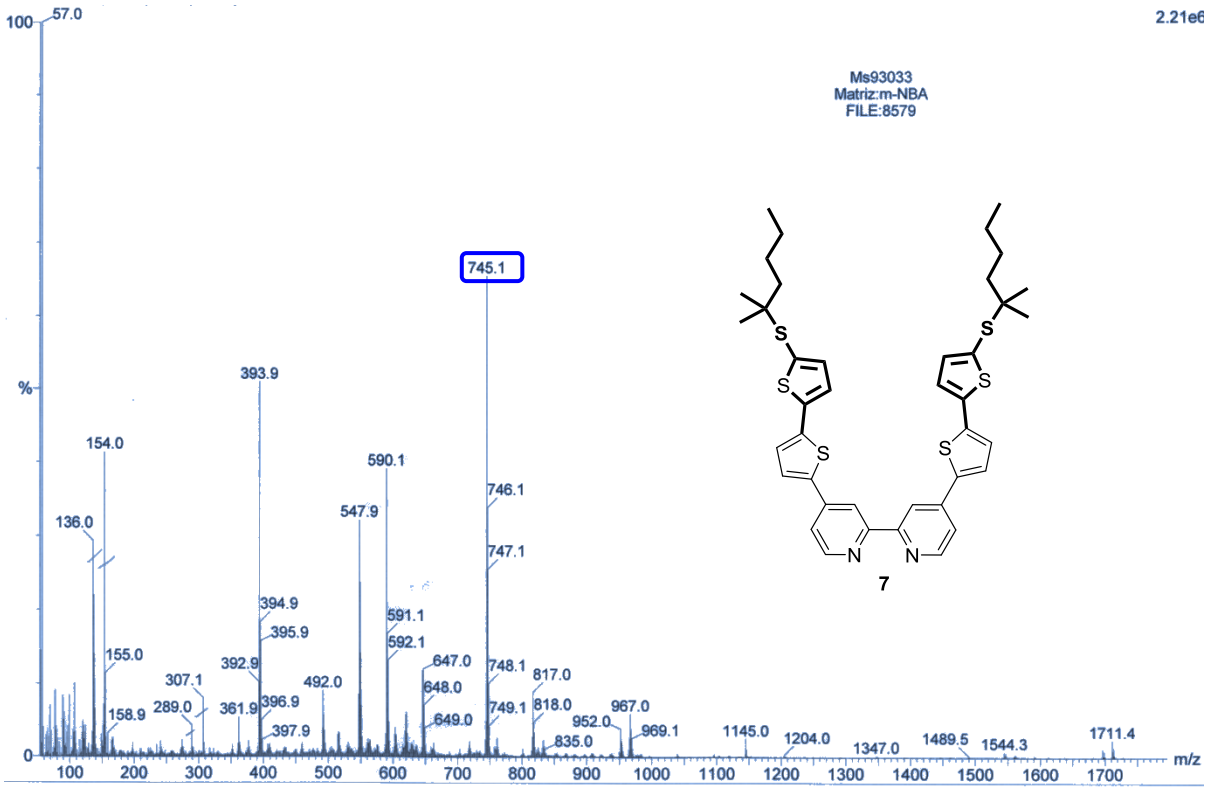


Figure S19. MS spectrum of compound **7** (FAB^+).

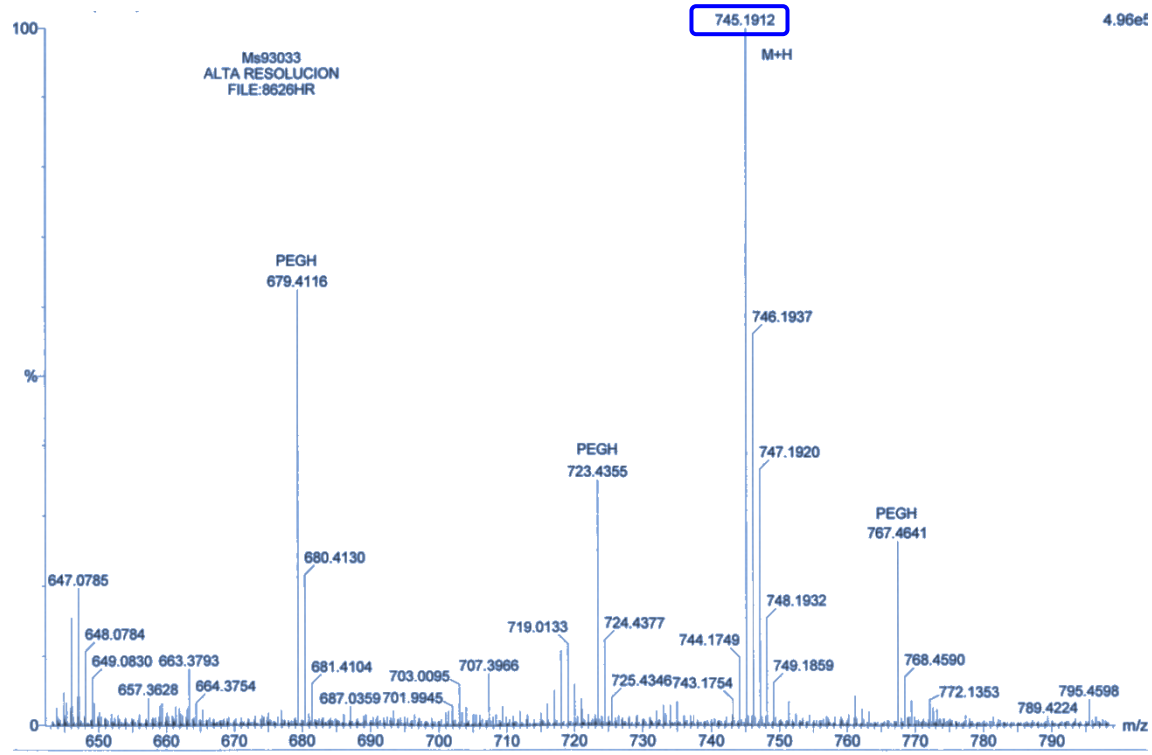


Figure S20. HRMS spectrum of compound **7** (FAB^+; internal calibration reference: PEGH).

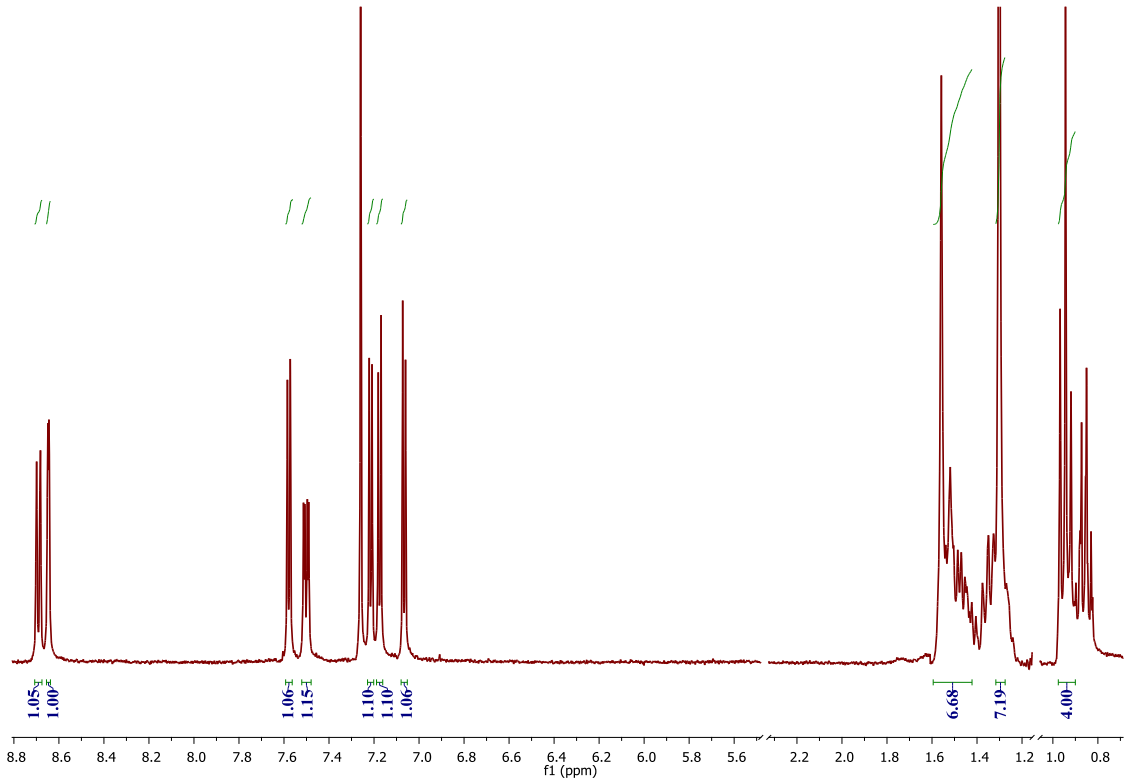


Figure S21. ^{1}H-NMR spectrum of compound **7** ($CDCl_3$, 300 MHz).

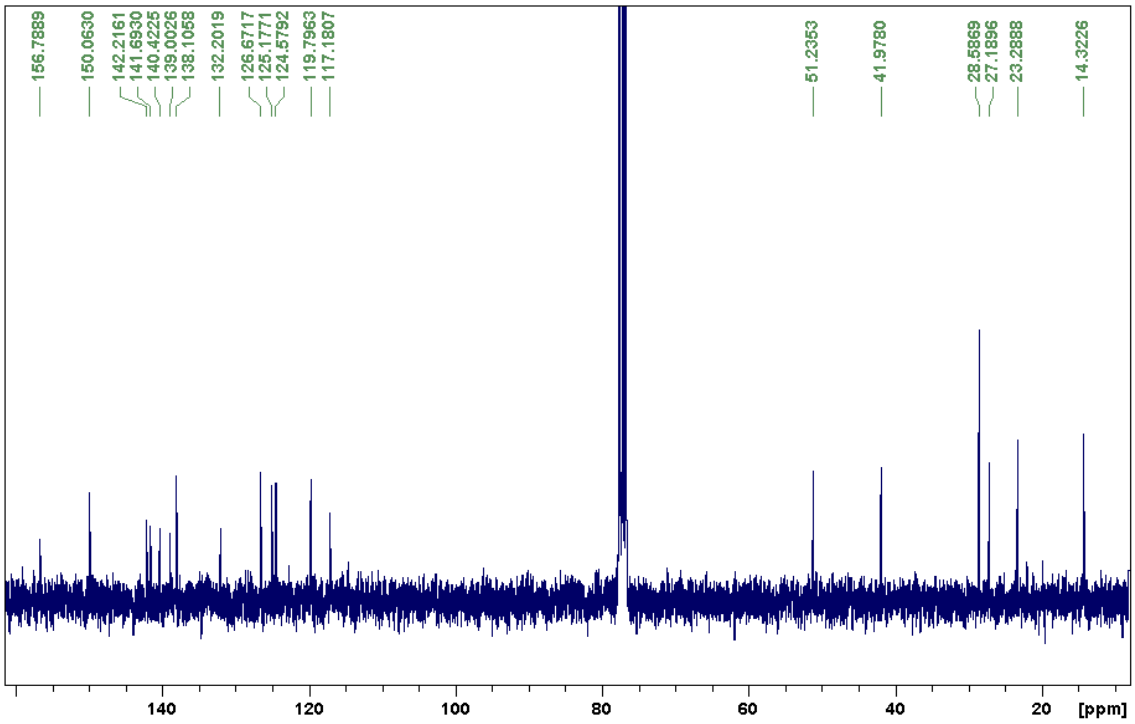


Figure S22. ^{13}C-NMR spectrum of compound **7** ($CDCl_3$, 75 MHz).

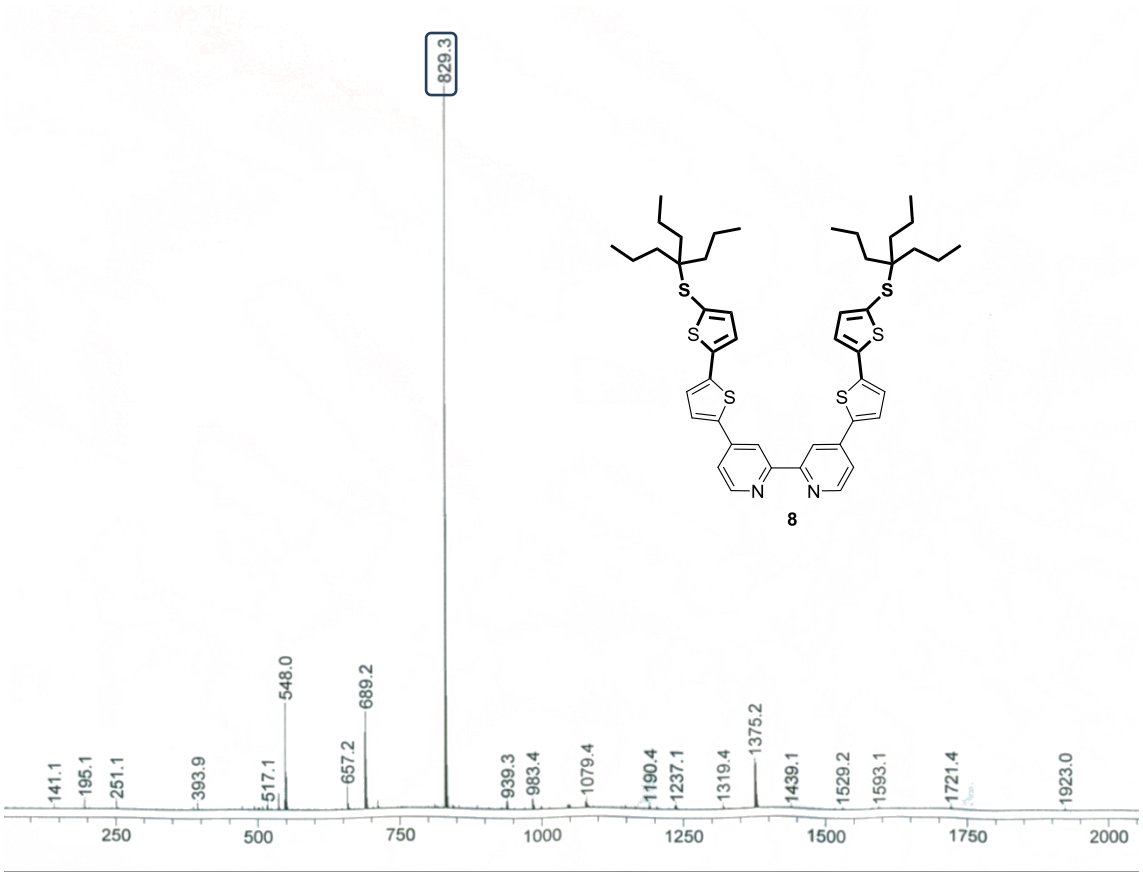


Figure S23. MS spectrum of compound **8** (MALDI-TOF).

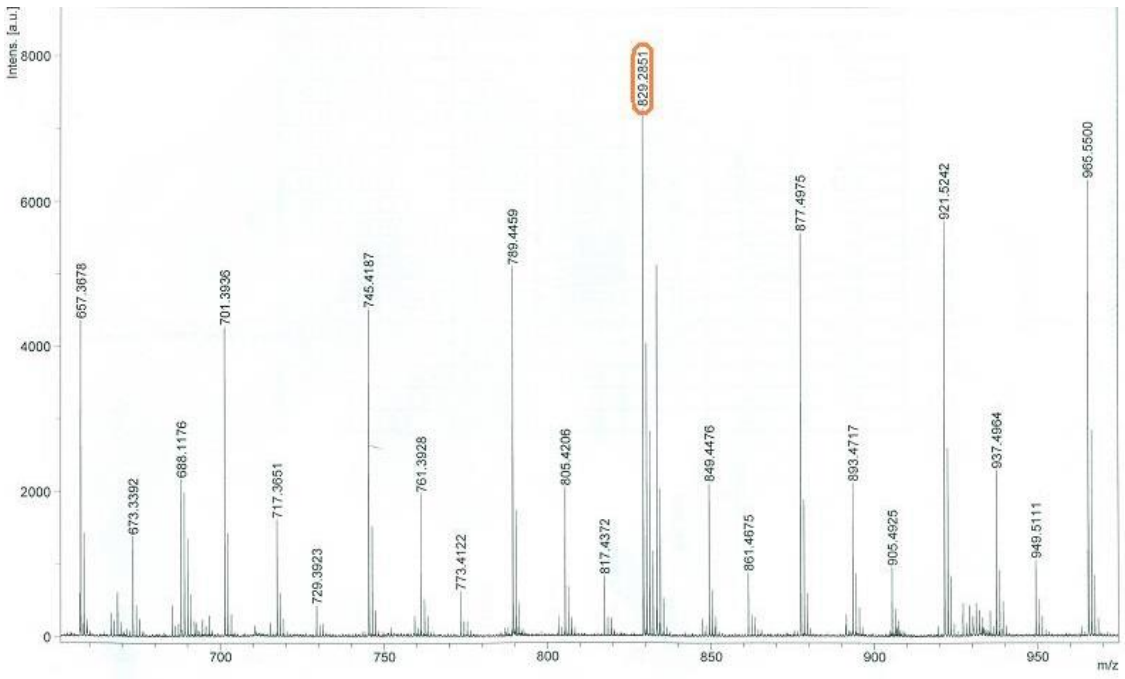


Figure S24. HRMS spectrum of compound **8** (MALDI-TOF; internal calibration reference: PEGH).

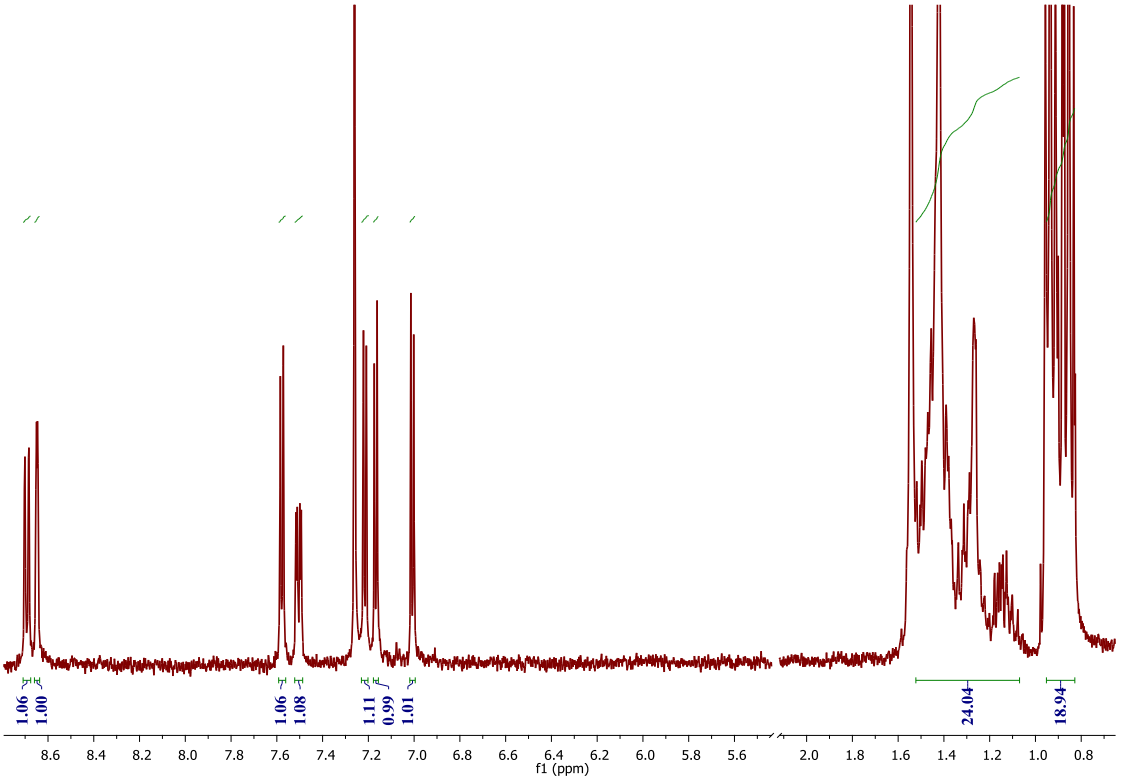


Figure S25. ^{1}H-NMR spectrum of compound **8** ($CDCl_3$, 300 MHz).

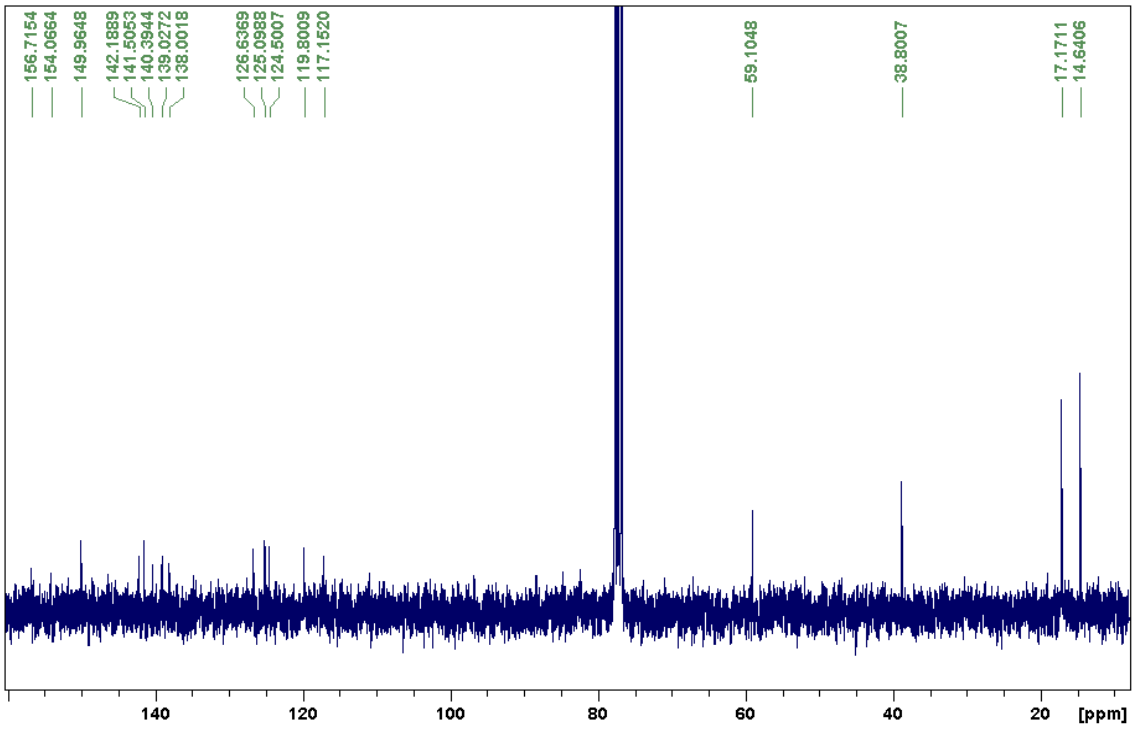


Figure S26. ^{13}C-NMR spectrum of compound **8** ($CDCl_3$, 75 MHz).

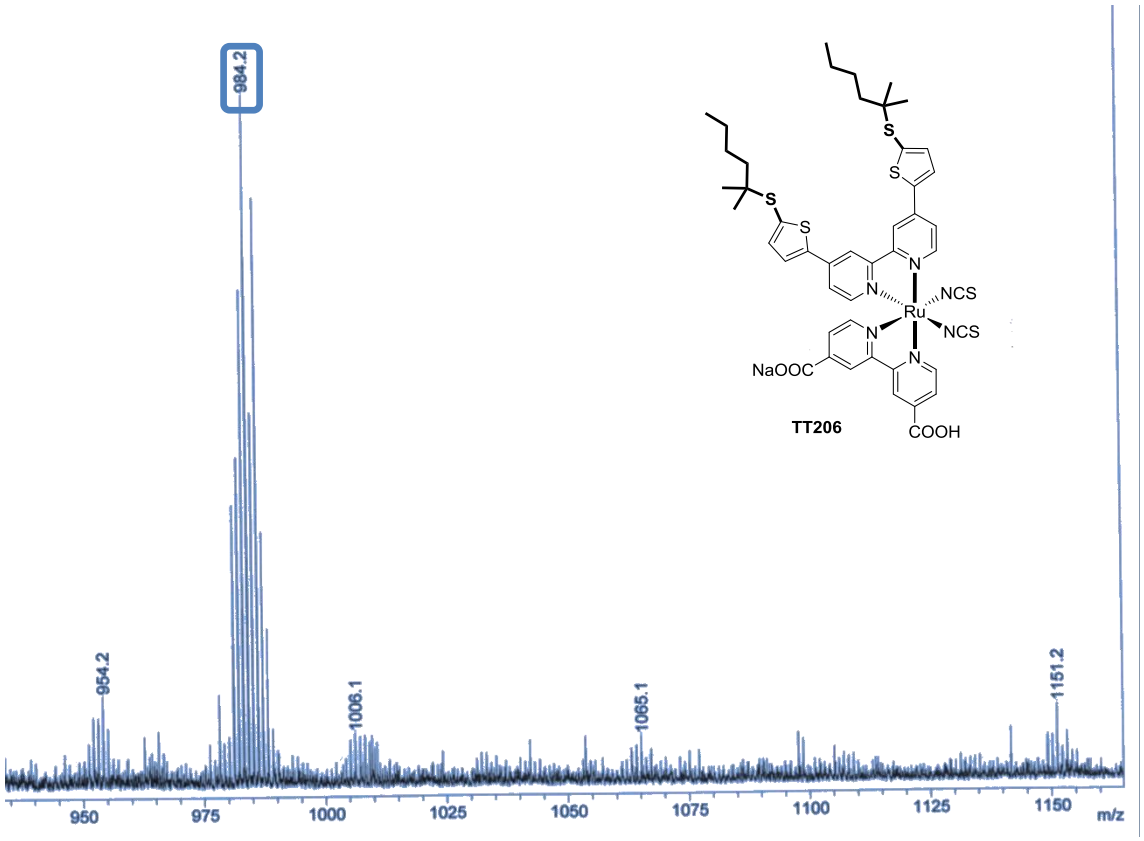


Figure S27. MS spectrum of **TT206** (MALDI-TOF).

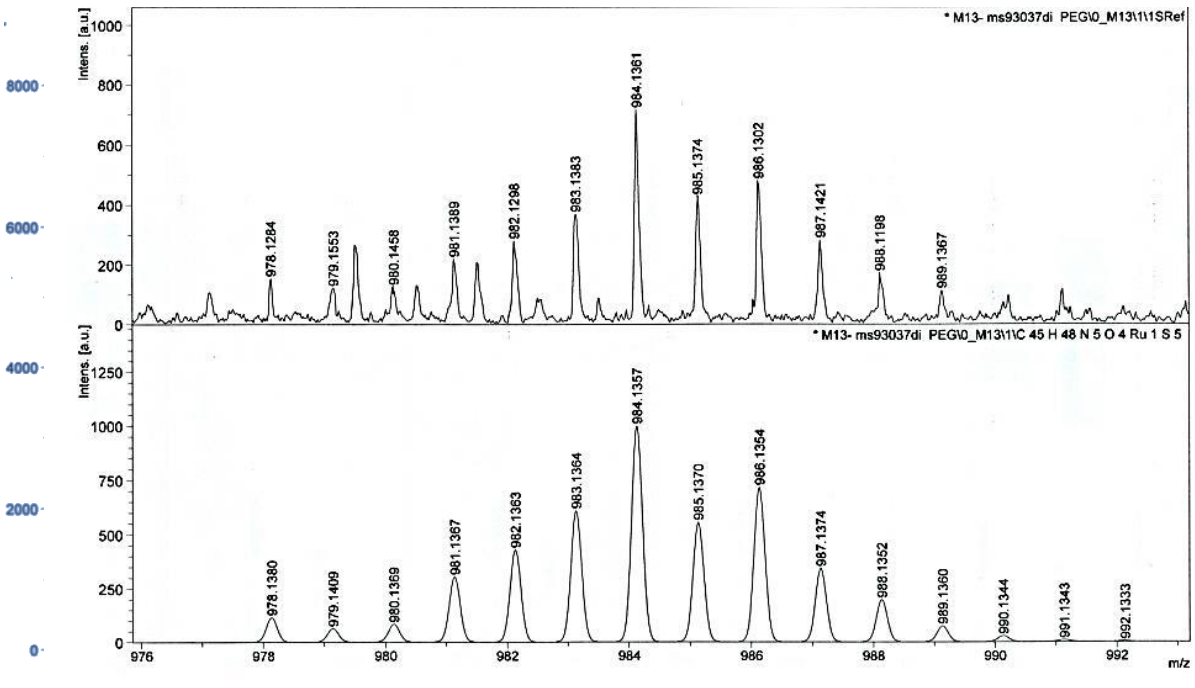


Figure S28. HRMS spectrum of **TT206** (MALDI-TOF; internal calibration reference: PEGH).

(Top inset: experimental; bottom inset: simulated isotopic distribution)

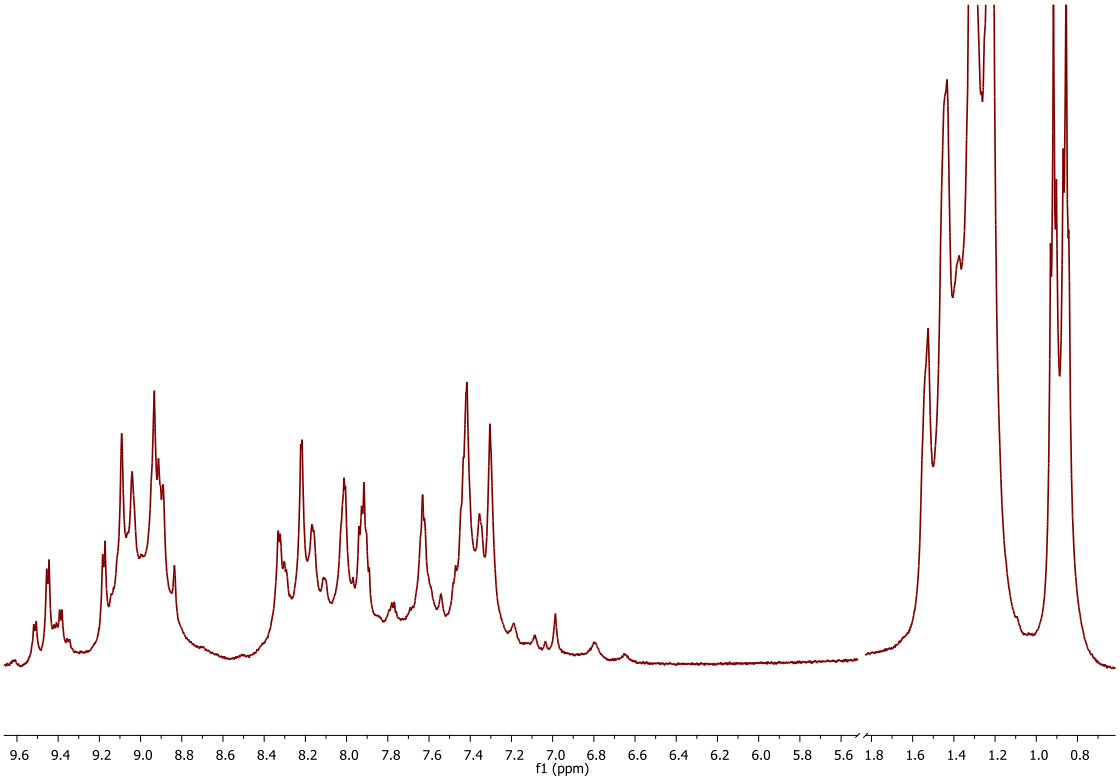


Figure S29. ^{1}H-NMR spectrum of **TT206** ([D6]DMSO, 300 MHz).

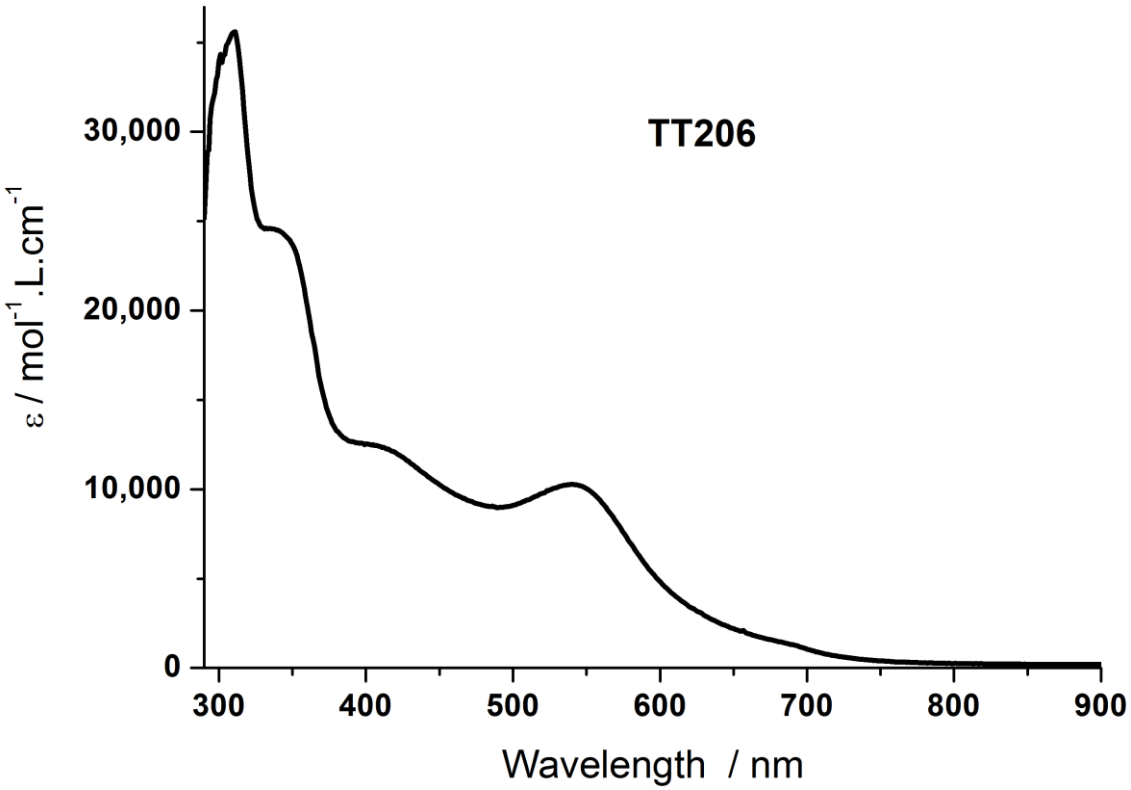


Figure S30. UV-Vis spectrum of **TT206** in DMF.

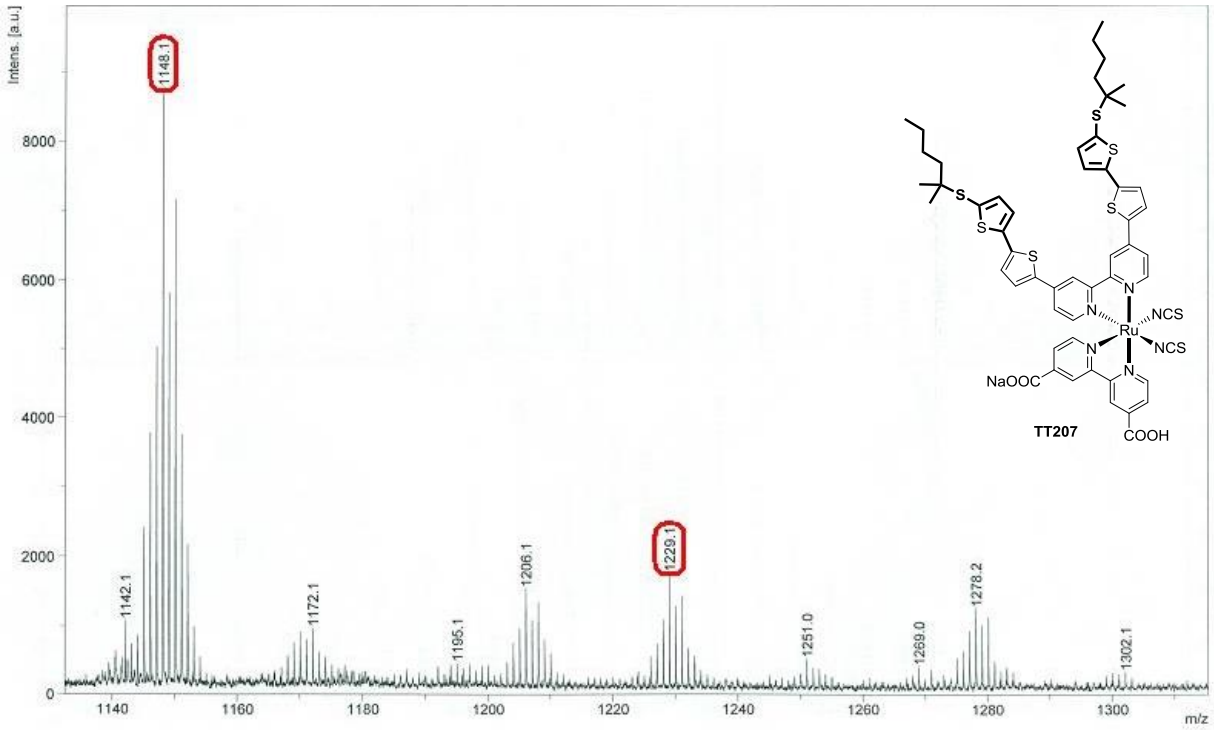


Figure S31. MS spectrum of **TT207** (MALDI-TOF).

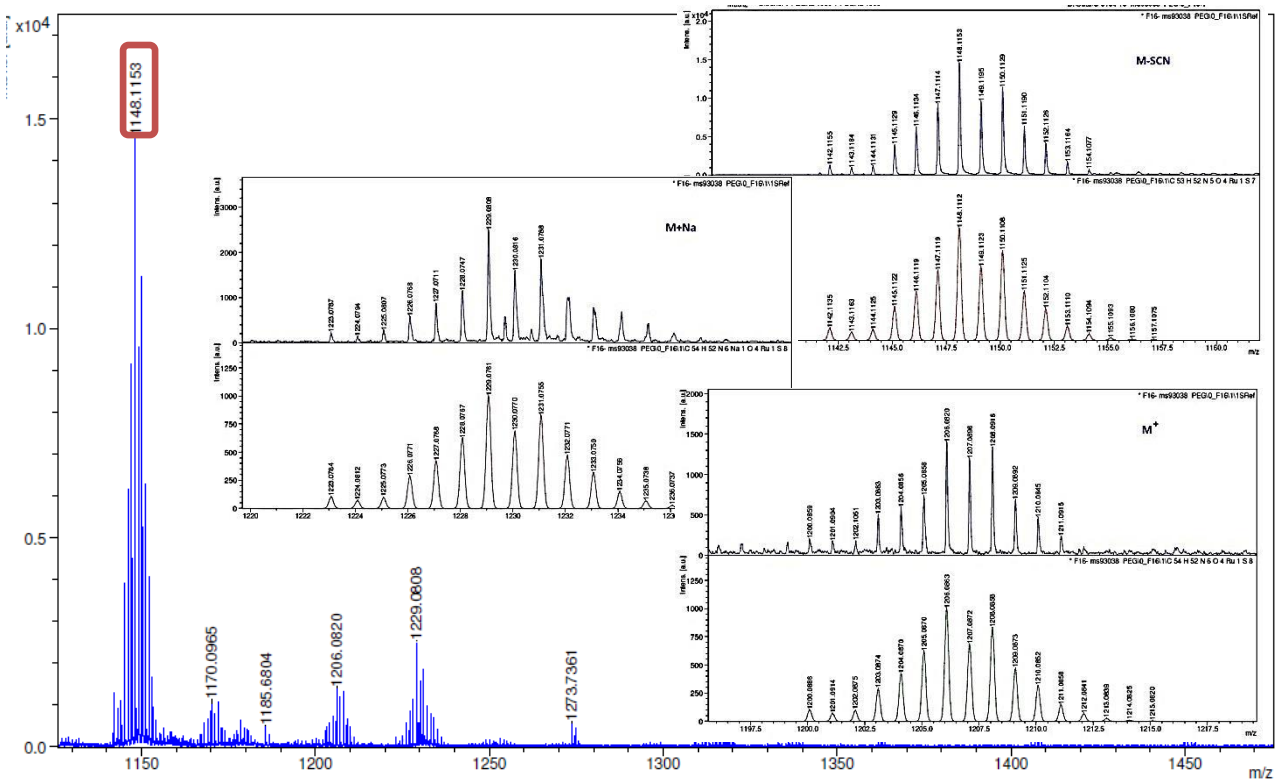


Figure S32. HRMS spectrum of **TT207** (MALDI-TOF; internal calibration reference: PEGH). Enlargement Insets: experimental (upper traces) and simulated isotopic distribution (bottom traces).

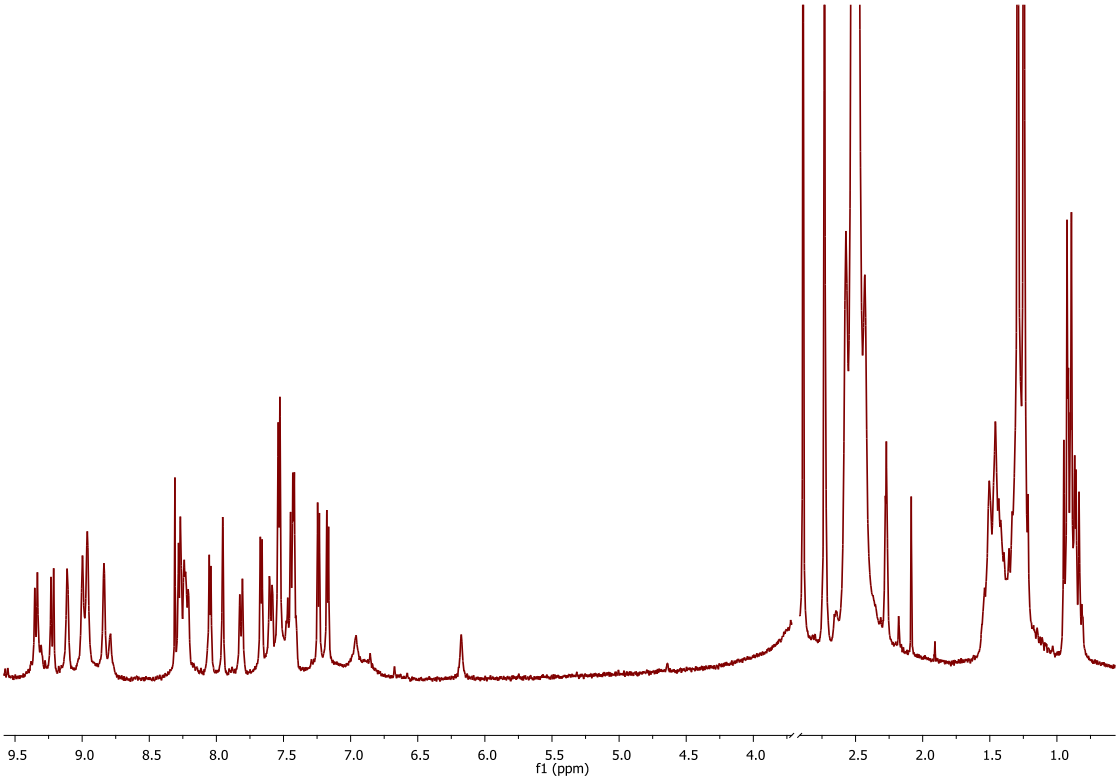


Figure S33. ^{1}H-NMR spectrum of **TT207** ([D6]DMSO, 300 MHz).

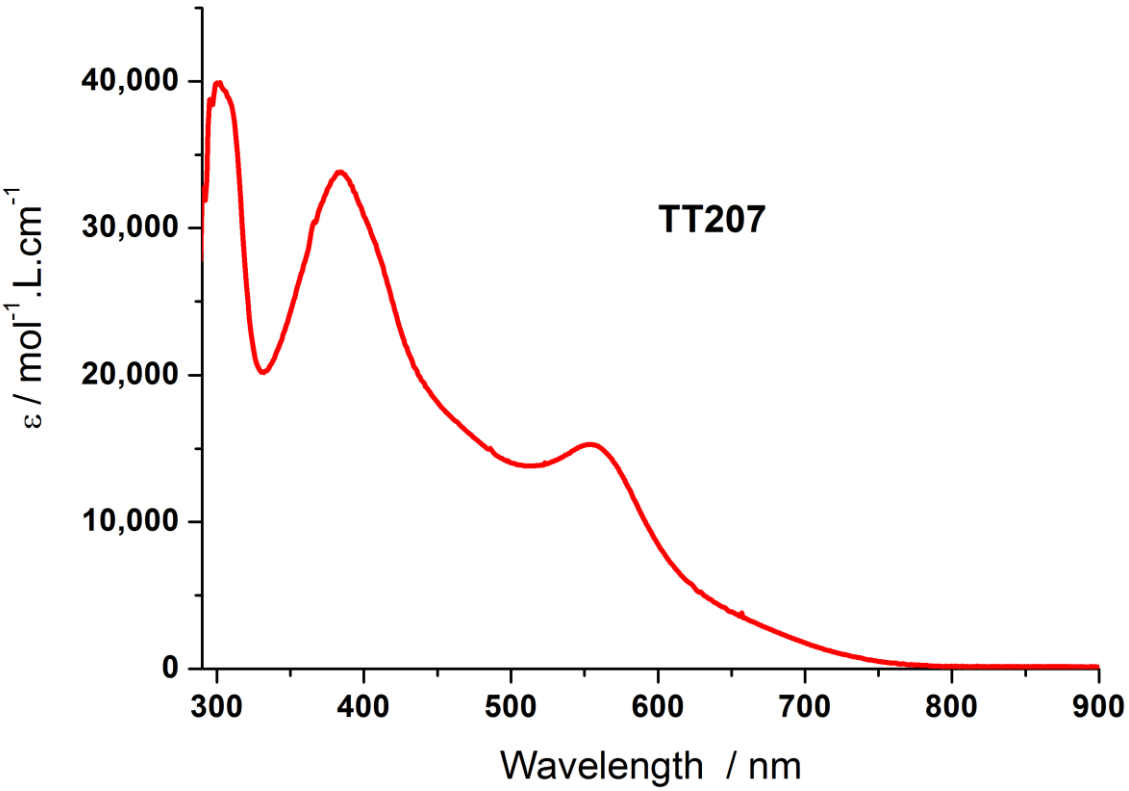


Figure S34. UV-Vis spectrum of **TT207** in DMF.

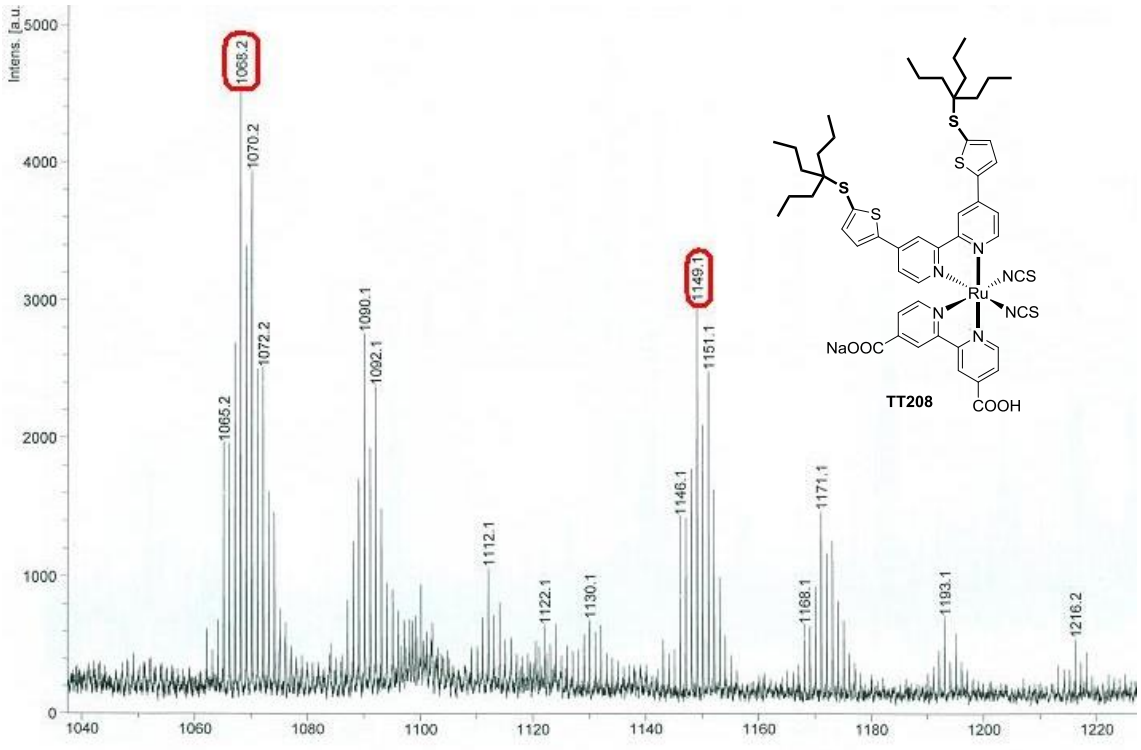


Figure S35. MS spectrum of **TT208** (MALDI-TOF).

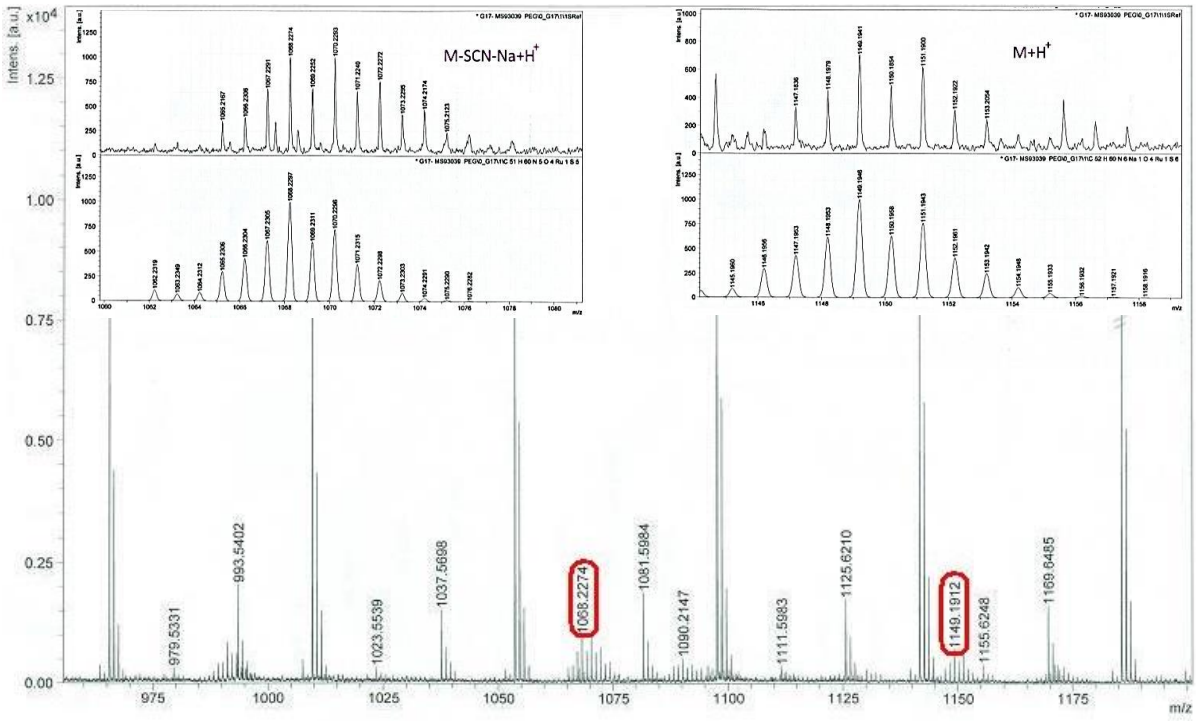


Figure S36. HRMS spectrum of **TT208** (MALDI-TOF; internal calibration reference: PEGH). Enlargement Insets: experimental (upper traces) and simulated isotopic distribution (bottom traces).

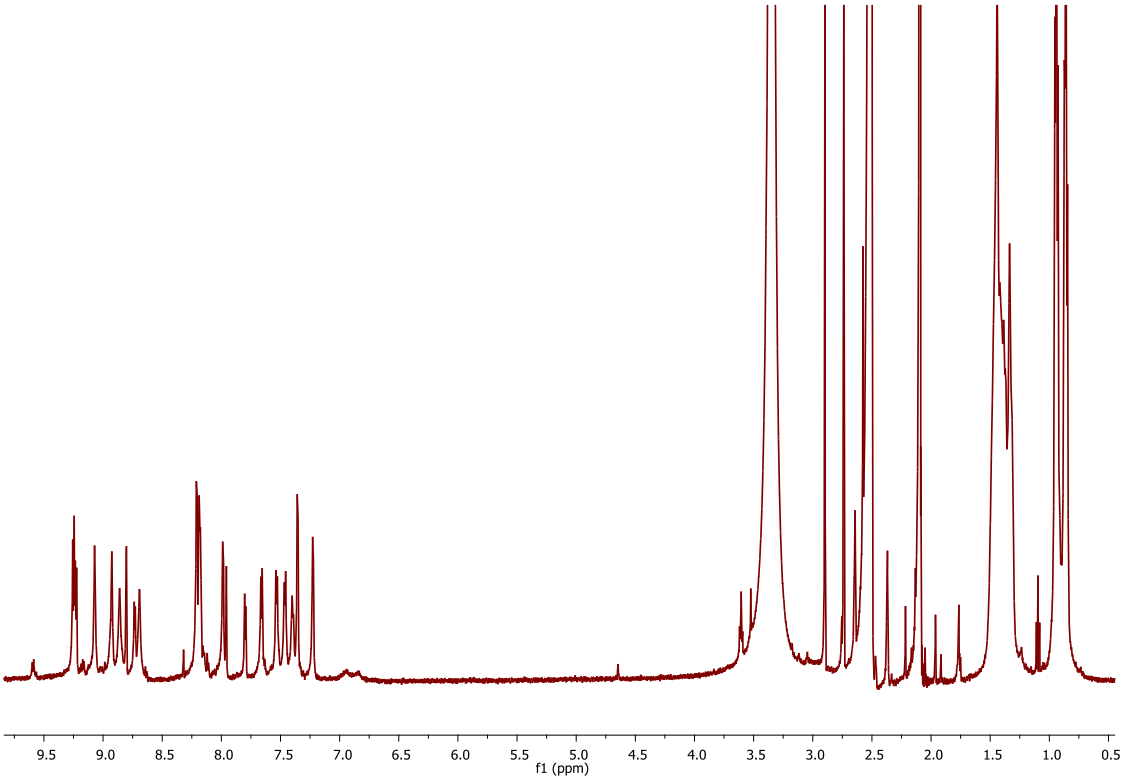


Figure S37. ^{1}H-NMR spectrum of **TT208** ([D6]DMSO, 300 MHz).

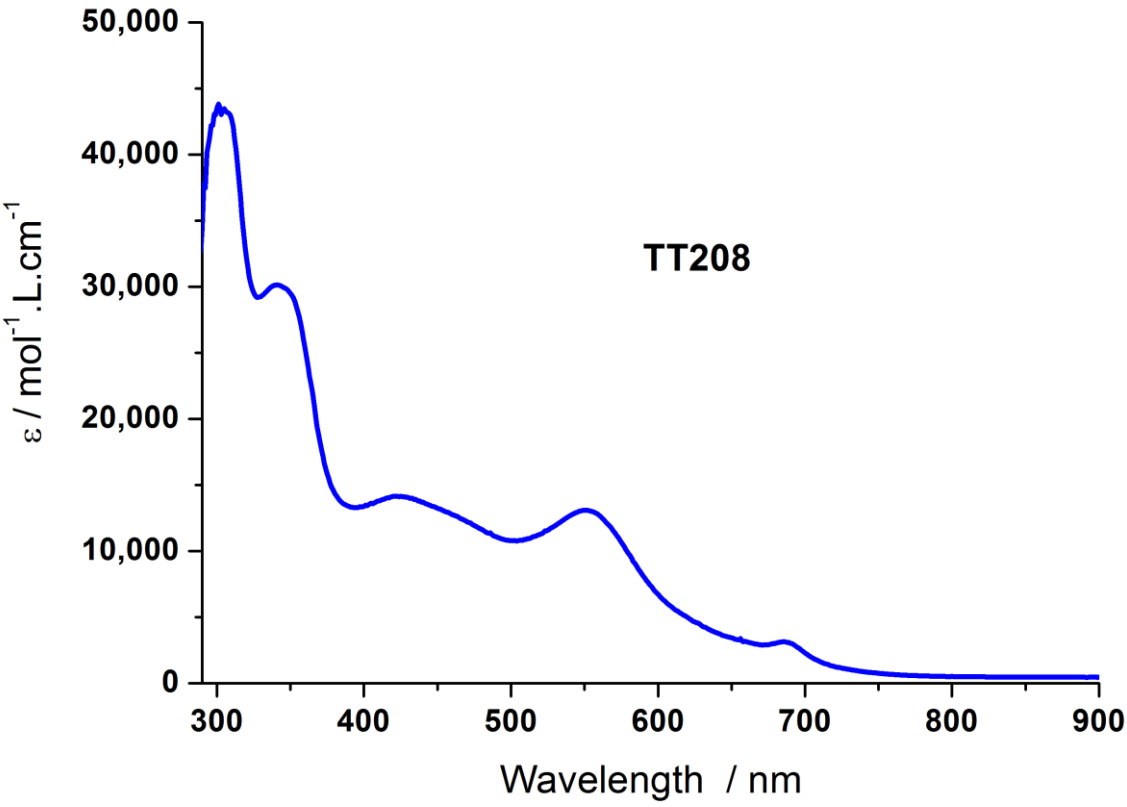


Figure S38. UV-Vis spectrum of **TT208** in DMF.

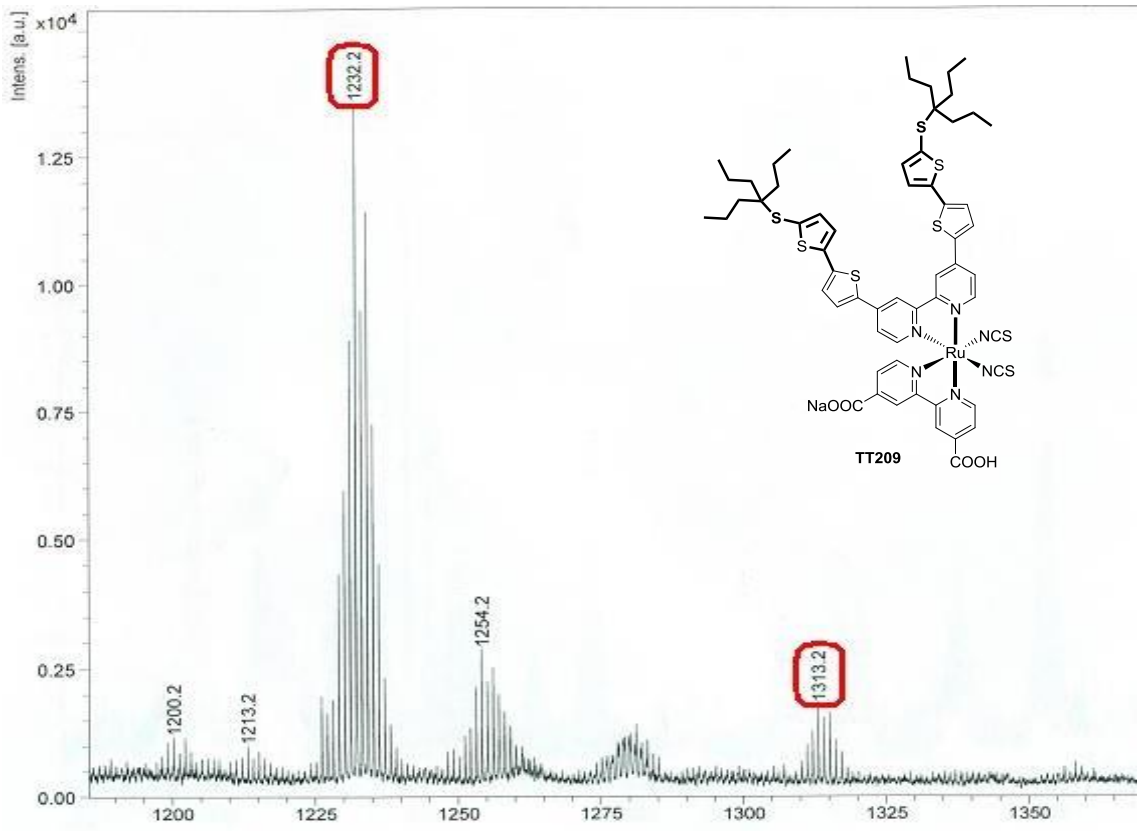


Figure S39. MS spectrum of **TT209** (MALDI-TOF).

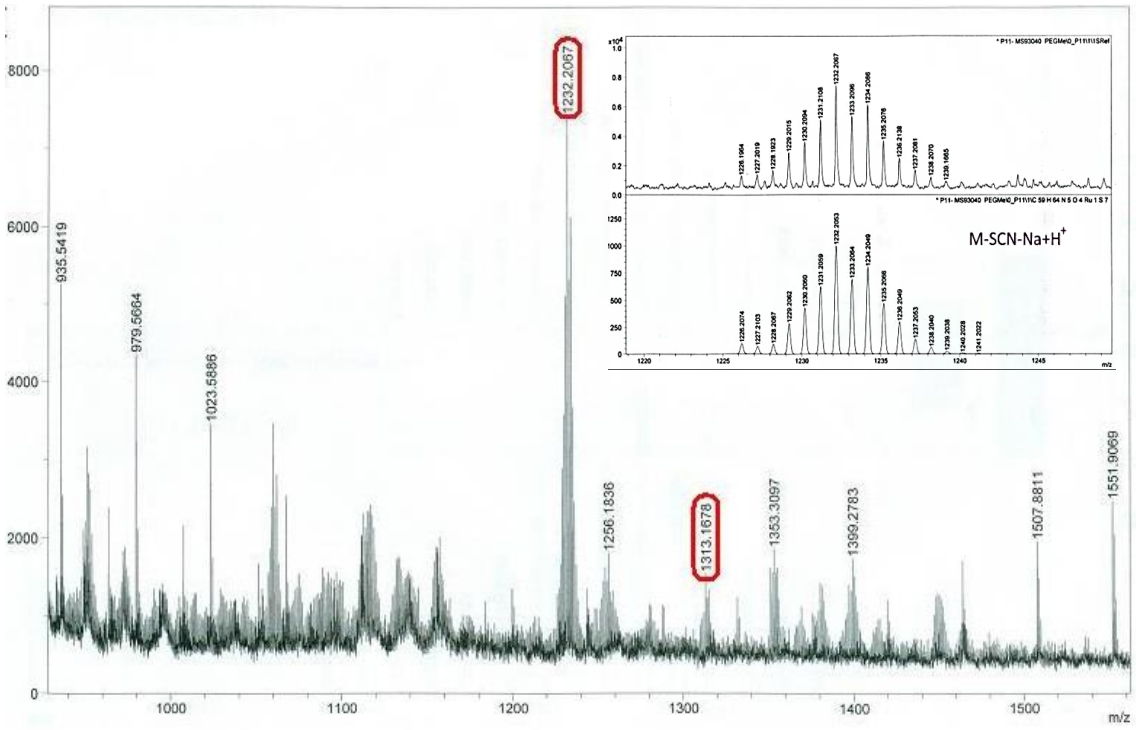


Figure S40. HRMS spectrum of **TT209** (MALDI-TOF; internal calibration reference: PEGH). Enlargement Inset: experimental (upper traces) and simulated isotopic distribution (bottom trace).

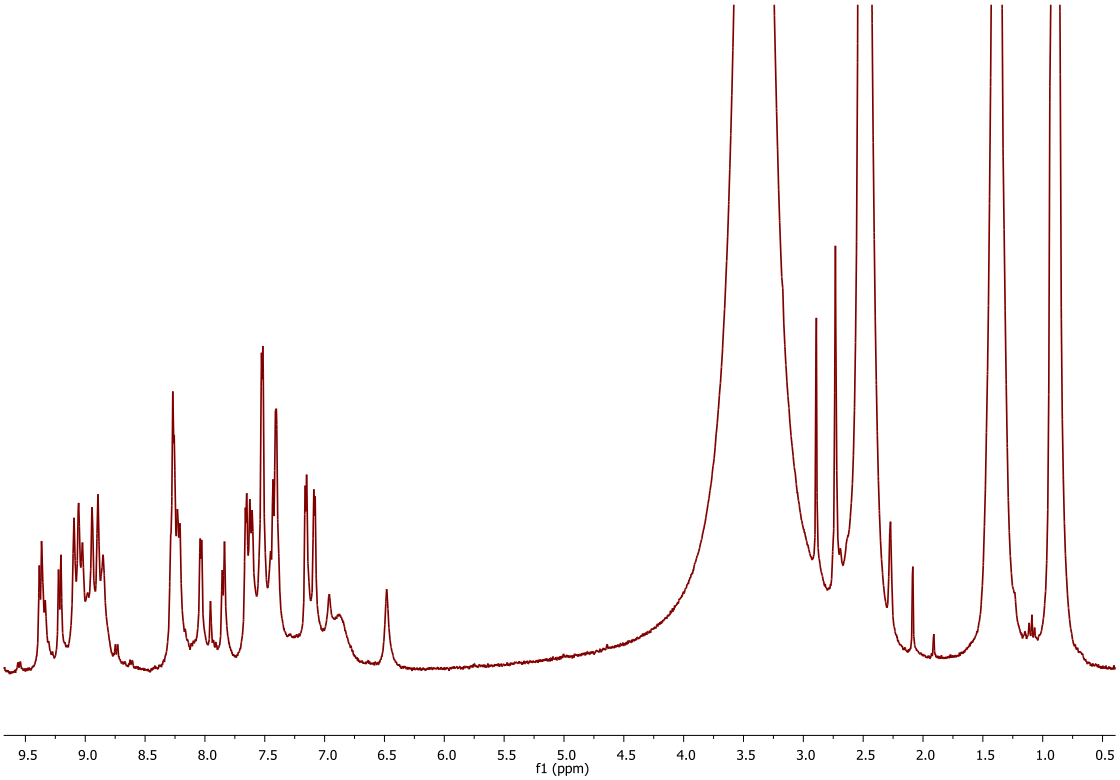


Figure S41. ^{1}H-NMR spectrum of **TT209** ([D6]DMSO, 300 MHz).

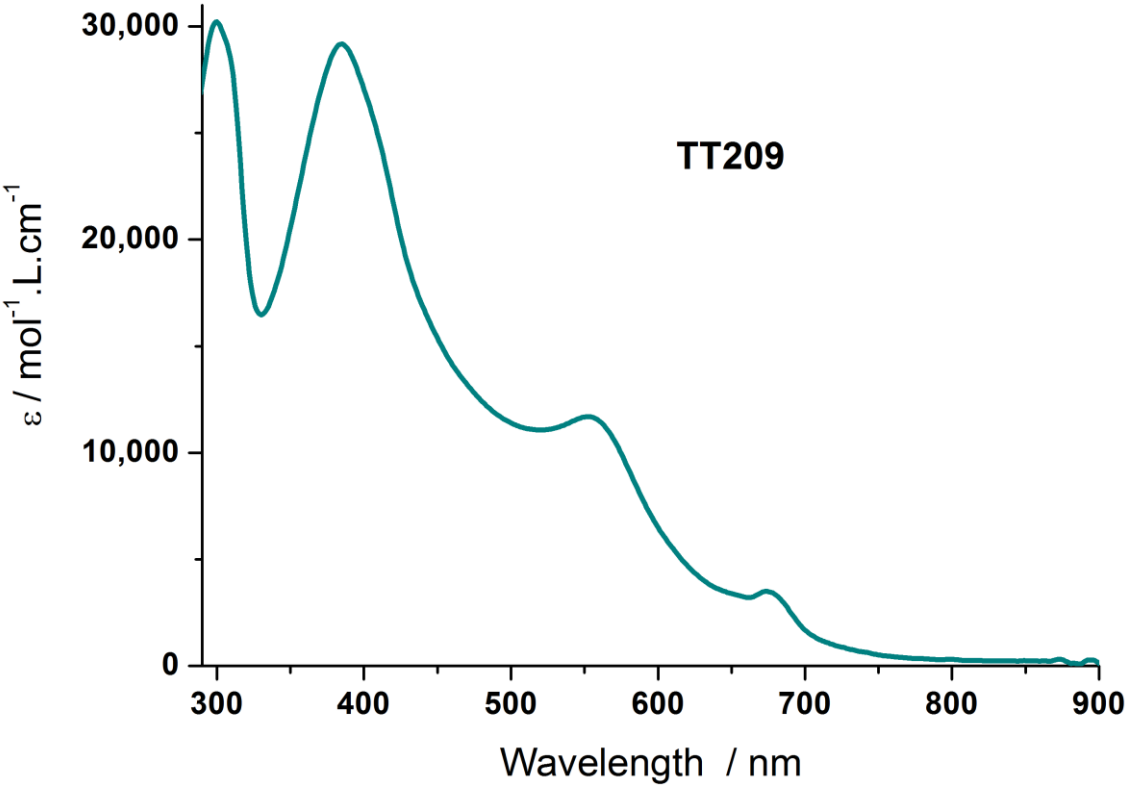


Figure S42. UV-Vis spectrum of **TT209** in DMF.