Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Table of contents

I. SYNTHESIS AND TABULATED DATA OF COMPOUNDS

I.1. MATERIAL

Synthetic procedures were carried out under an inert argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and used as received without further purification unless otherwise specified. (2,2'-bipyridine)-4,4'-dicarboxylic acid, dichloro(*p*-cymene)-ruthenium(II) dimer were purchased at TCI, (4,4'-dimethyl)-2,2'-bipyridine at Fluka, ammonium thiocyanate and lithium diisopropyl amide (1.8 or 2M solution in THF/hexane) at Aldrich. Pyridinium *p*-toluenesulfonate salt (PTPS) was prepared by dissolving *p*-toluenesulfonic acid in an excess of pyridine. After removal of the excess of pyridine under vacuum, the salt was dried under high vacuum and kept under argon. Hexyl-substituted nTV-CHO were prepared according to literature methods.[1] THF was freshly distilled from sodium benzophenoneketyl under argon prior to use. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm) and/or size-exclusion chromatography (Bio-rad Bio-beds, SX-1). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra were obtained on Bruker TopSpin AV-300 (300 MHz) or AV-400 (400 MHz) spectrometers. Chemical shifts are reported in parts per million (ppm) from the residual signal peak of the deuterated solvent: δ = 7.27 ppm ($CDCl_3$) and δ = 3.31 ppm (MeOD-d4) for ^{1}H NMR and δ = 77.0 ppm ($CDCl_3$) for ^{13}C NMR. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants, *J*, are given in Hz. UV/Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH_2Cl_2, with absorption between 0.5–1 of absorbance using a 1 cm UV cuvette (QS).

I.2. GENERAL PROCEDURES

I.2.1. GENERAL PROCEDURE FOR MCMURRY COUPLING

$TiCl_4$ was added slowly in THF at 0ºC under argon and vigorous stirring. At the end of the addition, the mixture was let to RT and stirred for 15 min. Subsequently, the mixture was cooled again at 0ºC and then zinc was added in small portion. The mixture was heated to reflux for 1h, then let to RT, and cooled again at 0ºC. Afterwards, a solution of the appropriate aldehyde and pyridine in THF was added. The mixture was heated again to reflux for the indicated time. After cooling to RT, the mixture was poured into crushed ice and stirred for 15 min. A 1M HCL aqueous solution was then added carefully drop by drop into the mixture to neutralize the media until no more effervescence was observed. The mixture was the extracted with CH_2Cl_2. After phase separation the aqueous layer was extracted twice more with CH_2Cl_2. The organic layers were combined, and then successively washed with a saturated aqueous solutions of $NaHCO_3$, brine, deionized water, dried over $MgSO_4$, filtrated and evaporated to dryness.

1 I. Jestin, P. Frère, N. Mercier, E. Levillain, D. Stievenard, J. Roncali, *J. Am. Chem. Soc.* **1998**, *120*, 8150-8158.

I.2.2. General procedure for Vilsmeier-Haack formylation

$POCl_3$ was added with a syringe under argon to a solution of the appropriate derivative and DMF in 1,2-dichloroethane (DCE). The solution was heated to reflux for 3–15h. After cooling down to room temperature, a saturated AcONa solution in H_2O was poured and the resulting mixture stirred vigorously for 30 min. Afterwards, the mixture was extracted with CH_2Cl_2 and the aqueous layer extracted twice more with CH_2Cl_2. The organic layers were combined then successively washed with deionized water, dried over $MgSO_4$, filtrated and evaporated to dryness.

I.2.3. General procedure for the synthesis of the bipyridine ligands

Step1: General procedure for the preparation of Donor-functionalized hydroxy-bipyridines:

4,4'-dimethyl,2,2'-bipyridine was introduced in an oven dried 50 mL Schlenk, then three cycles of Vacuum-Argon were realized. Afterwards, THF (5–10 mL) was introduced under argon with a syringe and the obtained solution stirred at room temperature until the complete dissolution of the material. Next, the mixture was cooled at -78°C for 10 min and a 1.8 or 2.0 M commercial solution of LDA in heptane/THF was added by syringe to the colourless solution, which turned brown immediately. The solution was stirred at this temperature for 25–45 min, and then warmed at -10°C for 25 min (the solution progressively turned deep dark black-reddish in the case of the bis-anion and dark brown for the mono-anion). The solution was cooled again at -78°C, and then a solution of the appropriate aldehyde (nTV-CHO) in THF (3–5 mL) was transferred under argon in the Schlenk flask with a cannula. The colour of the solution turned light yellow or dark orange-red according to the aldehyde in presence. The mixture was stirred at -78°C to -60°C for 2–3h then warmed at -10°C for 30 min. Finally, few drops of an aqueous saturated NH_4Cl solution (≈ 0.1 mL) were added to quench the reaction. After 10 min of stirring, the reaction mixture was diluted in CH_2Cl_2 (≈ 40 mL), successively dried over Na_2SO_4, filtered through a small plug of Celite, and solvents removed under vacuum. The crude was then purified as outlined in the text.

Step 2. General procedure for the one-pot dehydration/trans-isomerization of the hydroxy-bipyridines:

In a typical experiment, a solution of I_2 (1–3 mol%) in toluene was added to a solution of the above-mentioned diol and PTPS (≈ 0.4 equiv.) in dry toluene. The mixture was refluxed in a Dean-Stark apparatus for 24–48h (the colour of the solution progressively turned from light yellow or light orange to deep orange-reddish or dark purple). After cooling down to room temperature, Et_3N (≈ 0.5 mL) was added to the solution (the colour of the solution immediately turned to bright yellow or purple) and solvents removed under vacuum. The crude product was purified by the appropriate method(s) as outlined in the text. In most of the cases, small amounts of incomplete dehydrated[2] and/or *cis*[3] products were separated after purifications. If necessary, these fractions could be recycled by treating them again under the same previous conditions.

2 Typical multiplets (CHOH) are observed between 4.0 and 5.3 ppm.

3 Two types of typical multiplets are usually observed for *cis* double bonds: upshifted multiplets at around 7.7 ppm for *cis* double bonds close to the bipyridine moiety and downshifted multiplets between 6.5 and 7 ppm for *cis* nTV double bonds ($^3J_{cis} \approx 12$ Hz).

I.2.4. General procedure for the microwave-assisted synthesis and purification of the (cis)tris-heteroleptic ruthenium(II) complexes.

- *Step1 (Formation of the mononuclear, half-sandwich Ru(II) complex):*

In a 10 mL flask topped with a condenser, the appropriate bipyridine ligand (1.0 eq) and dichloro(*p*-cymene)-ruthenium(II) dimer (0.55–0.65 eq, *i.e.* 1.1–1.3 eq of formal Ru(II)) were dissolved under Ar in a 1:1 mixture of $CHCl_3$ and EtOH (4 mL). The obtained solution was stirred and heated to reflux (c.a. 60–70 °C) under microwave irradiation (15–30 W) for 45 min in the dark. After removing the solvents under reduced pressure, the **Ru[L]** complexes were obtained as bright deep-red oils. All these crude intermediates were characterized by ^1H NMR ($CDCl_3$), and then used as well in the next step.

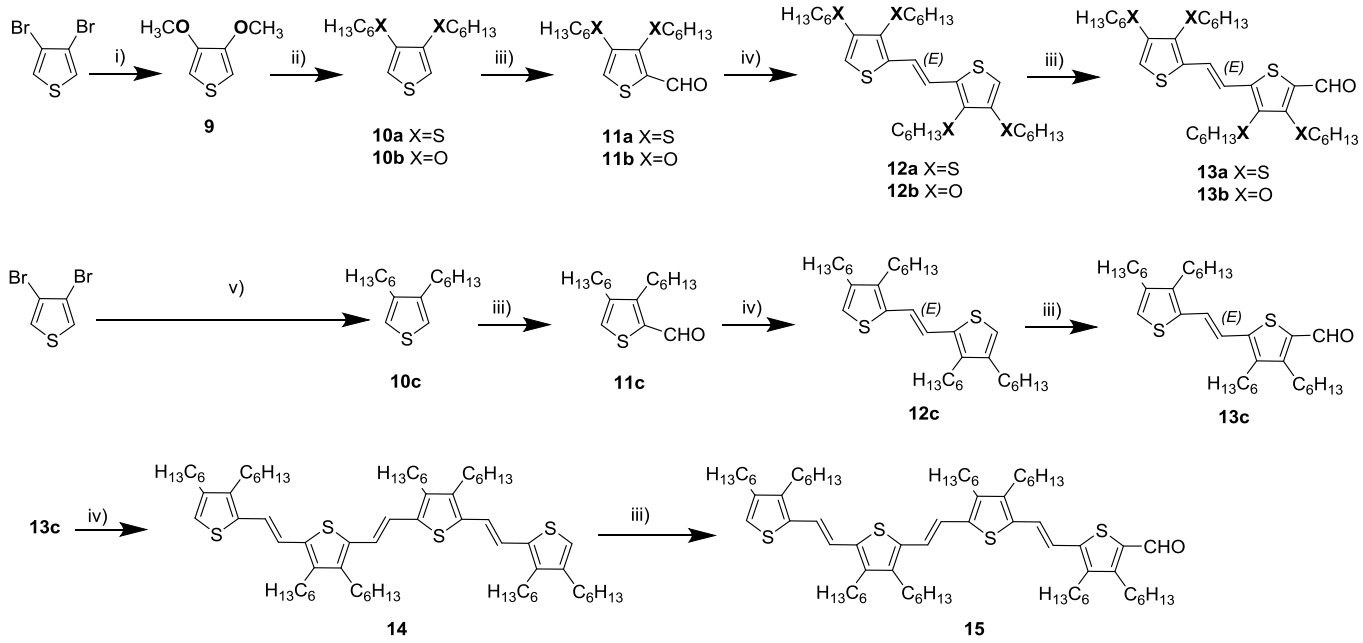
- *Step 2.1 and 2.2:*

Next, the above-mentioned crude intermediate was dissolved in PhCl (0.5 mL) under argon, and then a solution of 4,4'-dicarboxylic acid-2,2'-bipyridine "**dcbpy**" (appropriate excess 1.2–1.6 eq) in dry DMF (4.5 mL) was added. The solution was irradiated under MW (80–115 W) to reach gradually 130–140 °C (reflux) within c.a. 10–15 min. The MW irradiation was then regulated automatically to maintain this range of temperature for additional 45 min. After cooling back to room temperature, NH_4NCS (50–75 equivalents) was added to the resulting deep dark-green solution, and then irradiated again at 130–140 °C (reflux) for additional 40 min, affording a deep dark brown-red solution. Finally, DMF was removed from the reaction flask by high-vacuum rotary evaporation to afford a deep dark-red pasty solid. This paste was then triturated with a 0.05 M HCl aqueous solution (≈25 mL), and the resulting fine black suspension was successively filtrated, washed with a copious amount of a 0.05 M HCl aqueous solution, air-dried, and washed with the necessary amount of MeOH until the disappearance of a red-coloured filtrate (N3 dye). The filtrates were discarded and the remaining insoluble black solid recovered by dissolution in a mixture of THF/MeOH 7:3. After evaporation of solvents, crude was purified by gel permeation chromatography (Bio-rad Bio-beds® SX-1, eluent: THF/MeOH (7:3). The main fraction was evaporated to dryness and purification achieved by trituration in MeOH. The resulting fine dark black suspension was filtrated and washed with MeOH. The filtrates were discarded and the insoluble remaining product recovered with a mixture of CH_2Cl_2/MeOH 7:3.

I.3. SYNTHETIC PROCEDURES AND SCHEMES

I.3.1. SYNTHESIS OF THE nTV-CHO BUILDING BLOCKS

The synthesis of the four nTV-CHO building blocks depicted in Scheme S1. Hexyl- 2TV-CHO and 4TV-CHO were previously reported by others,[4] and hexylthioether- and hexyloxy- 2TV-CHO are reported for the first time.

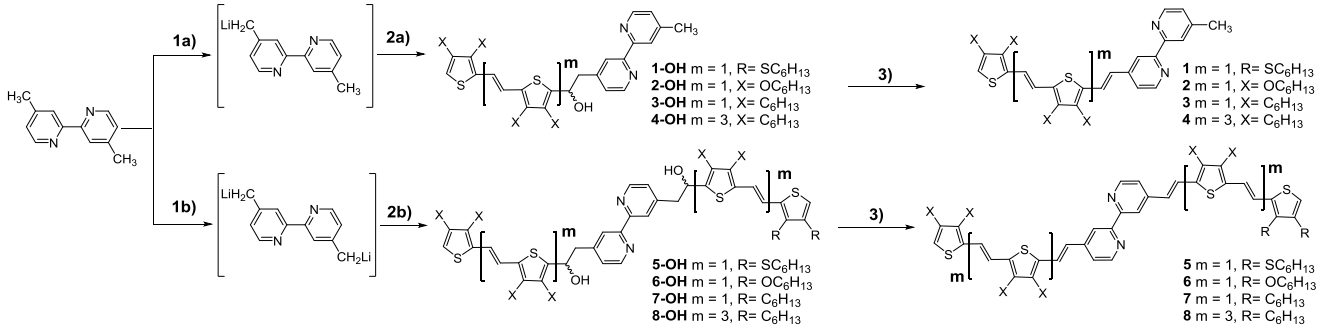


Scheme S1. Synthesis of compounds **9**–**15**. Reagent and conditions: i) MeONa, CuO, KI, MeOH (**9**: 64%); ii) *n*hexanol or *n*hexylthioether, *p*-toluene sulfonic acid, toluene (**10a**: 67%; **10b**: 90%); iii) *Vilsmeier-Haack formylation*: $POCl_3$, DMF, DCE, reflux 3–15h (**11a**: 98%, **11b**: 80%; **11c**: 95%; **13a**: 57%; **13b**: 80%; **13c**: 97%; **15**: 54%); iv) *McMurry coupling*: $TiCl_4$, Zn, pyridine, THF, 0ºC→ reflux overnight (**12a**: 79%, **12b**: 78%; **12c**: 70%; **14**: 61%). v) *Kumada coupling*: $NiCl_2$(dpppe), *n*HexMgBr, Et_2O, 0ºC→ reflux 24h (**10c**: 87%). DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, $NiCl_2$(dpppe) = [1,2-bis(diphenylphosphino)ethane]dichloronickel(II)].

4 I. Jestin, P. Frère, N. Mercier, E. Levillain, D. Stievenard and J. Roncali, *J. Am. Chem. Soc.*, 1998, **120**, 8150-8158.

I.3.2. SYNTHESIS OF THE nTV-FUNCTIONALIZED BIPYRIDINE LIGANDS

The bipyridine ligands **1**–**8** were then synthetized in a three-step reaction following modified procedures previously reported by us (Scheme S2).[5] First, deprotonation / lithiation of 4,4´-dimethyl-2,2´ -bipyridine with LDA in THF at low temperature occur selectively at the methyl groups positions. The formation of either the mono- or bis-anion could be controlled by treatment with 1eq or an excess (3 eq) of LDA respectively. The *in situ* generated anions were subsequently quenched by reaction with an excess of nTV-aldehyde, to afford the corresponding alcohols (**1**–**8**-OH) under racemic mixtures of enantiomers. In a third step, a dehydration / isomerization was done in a one-pot reaction at reflux of toluene (Dean-Stark apparatus) for 1–3 days, in the presence of PTPS. The presence of a catalytic amount of iodine was found necessary to ensure the all trans (*E*) configuration of the ethylene bounds.

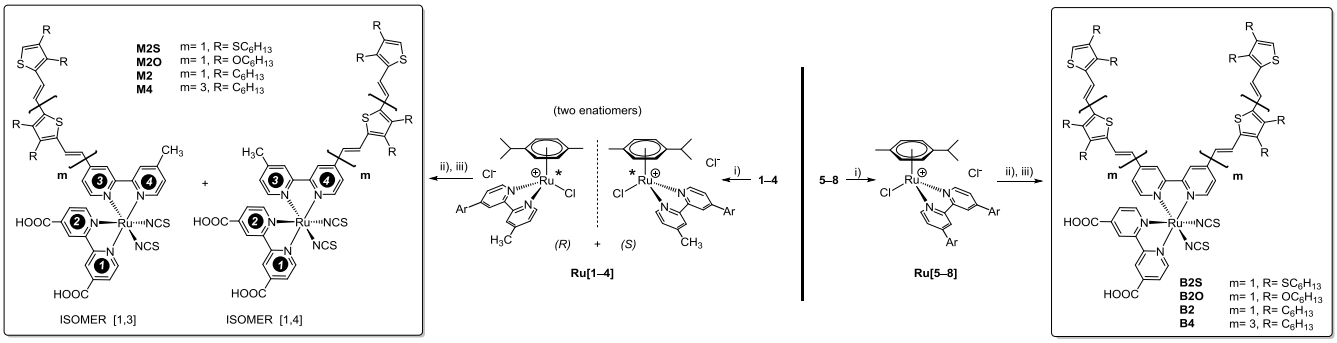


Scheme S2. Synthesis of the nTV-functionalized bipyridine ligands **1**–**8**. Reagents and conditions: 1) LDA (a) 1 eq or (b) 2.2 eq, THF, -78°C, 25min→ -10°C, 20min ; 2) hexyl-, hexyloxy- or hexylthio- nTV-CHO **13a**–**c** or **15** (a) 0.5–0.6 eq or (b) 3 eq in THF -78°C, 1h → rt, 30 min, then H_2O followed by 3) PTPS, I_2 (cat.), toluene reflux, Dean-Stark trap, 16–48h (**1**: 54%; **2**: 78%; **3**: 82%, **4**: 65%, **5:** 27%; **6**: 62% **7**: 74%, **8**: quantitative (3 steps)). LDA = lithium diisopropylamide, PTPS = pyridinium *p*-toluenesulfonate.

5 M. Urbani, M. Medel, S. A. Kumar, M. Ince, A. N. Bhaskarwar, D. González-Rodríguez, M. Grätzel, M. K. Nazeeruddin and T. Torres, *Chem. Eur. J.*, 2015, **21**, 16252-16265.

I.3.3. SYNTHESIS OF OF THE (CIS)*TRIS*-HETEROLEPTIC RU(II) COMPLEXES

All the (cis)*tris*-heteroleptic Ru(II) complexes were synthetized under MW-assisted procedures and optimized conditions previously developed by us for the synthesis of amphiphilic Ru(II)-complex with a highly-lipophilic character.[5] The first step involves the formation of a cationic, mononuclear, (p-cymene)Ru(II) half-sandwich chelate complex {[(η^6-*p*-cymene)(k^2-*N*,*N*-bipy)(k-Cl)]$^+$} with a chloride counter anion.[6,7] as the first intermediate from Ru_2Cl_4(*p*-cymene)$_2$ and the nTV-functionalized bipyridines **1**–**8**. Subsequently, the (cis)*tris*-heteroleptic Ru(II) complexes were obtained in a two-steps one-pot reaction from the half-sandwich complex Ru[**L**] (with L = **1**–**8**; Scheme 2, step i-ii). The coordination of the (2,2'-bipyridine)- 4,4'-dicarboxylic acid (L´) to the metal center of Ru[**L**] primarily lead to the formation of the octahedral Ru(II) complex RuLL´Cl_2, followed by the exchange of the chloride by isothiocyanate k^1-bonded ligands to give RuLL´$(NCS)_2$. All the target complexes could be obtained in good to excellent yields (60-95%) after purifications, except **B2O** (37%) and **M2S** (49%) that were obtained in relative low yields. As we previously observed for other amphiphilic Ru(II)-complex with high-lipophilic character,[5] the (bis)-heteroleptic complexes $RuL_2(NCS)_2$ were also formed as minor by-product during the synthesis in variable yield of ca. 5-20%. Hence, the yields strongly depend on the amount of (bis)-heteroleptic by-product formed during the reaction and on the easiness of the subsequent separation by size-exclusion chromatography column (the higher number and longer nTV moieties facilitate the separation). In addition, pre- and post-purification were achieved by trituration in MeOH. On this line, some hexyloxy- and hexylthioether-complexes display a non-negligible solubility in MeOH, which also participated to render the purification less easy and hence lower the yield in some of these cases (all hexyl-substituted ones are fully insoluble in MeOH).

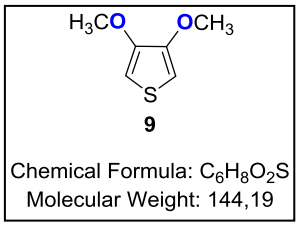


Scheme S3. Microwave-assisted synthesis of Ru(II) complex ruthenium complexes. Reagents and conditions: i) $CHCl_3$/EtOH (1:1), MW 70°C, 45 min (quantitative); ii) dcapy, DMF/PhCl (9:1), MW 140°C, 45 min followed by iii) NH4NCS, MW 140°C, 45 min (**M2S**: 49%; **M2O**: 71%; **M2**: 62% ; **M4**: 84% **B2S**: 60%; **B2**: 66%; **B2O**: 37%; **B4**: 95%). MW = microwave, dcapy = (2,2'-bipyridine)- 4,4'-dicarboxylic acid, PhCl = chlorobenzene, DMF = N,N-dimethylformamide, nTV = (oligo) thienylenevinylene (with n = 2 or 4). The numbering of the pyridyl groups and nomenclature used to distinguish the two regioisomers is arbitrary.

6 B. Therrien, *Coord. Chem. Rev.*, 2009, **253**, 493-519.

7 K. Severin, *Chem. Commun.*, 2006, 3859-3867.

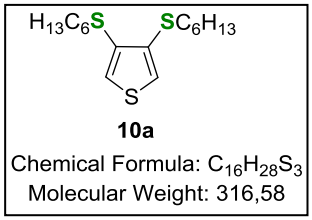
I.4. TABULATED DATA OF COMPOUNDS



9

Chemical Formula: $C_6H_8O_2S$
Molecular Weight: 144,19

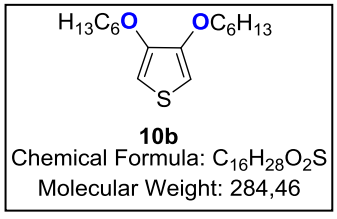
3,4-dimethoxythiophene (9): Sodium (2.0 g, 86.9 mmol) was added in small portion under argon in MeOH (25 mL) under stirring (**CAUTION! Exothermic reaction and H_2 release**). After consumption of all the sodium metal, a clear solution was obtained (MeONa 3.5 M in MeOH). Afterwards, 3,4-dibromothiophene (2.21 g, 9.13 mmol), CuO (0.48 g, 6.06 mmol), and KI (0.15 mg, 0.91 mmol) were successively added to the solution, and the resulting mixture heated to reflux for 72h. After cooling to RT, the reaction mixture was poured carefully in crushed ice (c.a. 100 g) and stirred for additional 30 min. The mixture was then extracted with AcOEt. After phase separation, the aqueous layer was extracted twice more with AcOEt. The organic layers were combined, and then successively washed with deionised water, dried over $MgSO_4$, filtrated and evaporated to dryness. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 3:1), compound **9** was obtained in 64% yield (0.84 g, 5.83 mmol) as a clear yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.19 (s, 2H; 2Ar*H*), 3.86 (s, 6H; 2OCH_3).



10a

Chemical Formula: $C_{16}H_{28}S_3$
Molecular Weight: 316,58

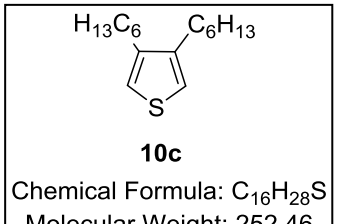
3,4-bis(hexylthio)thiophene (10a): A solution of **9** (1.00 g, 6.94 mmol), hexane-1-thiol (4.92 mL; 4.10 g, 34.7 mmol) and *p*-toluene sulfonic acid (0.11 g, 0.58 mmol) in toluene (10 mL) was heated to reflux for 48h. After cooling to RT, the mixture was taken up with CH_2Cl_2, and then a saturated aqueous solution of $NaHCO_3$ was added. After phase separation, the aqueous layer was extracted twice more with CH_2Cl_2. The organic layers were combined, and then successively washed with deionised water, dried over $MgSO_4$ filtrated and evaporated to dryness. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 4:1), compound **10a** was obtained in 67% yield (1.47 g, 4.64 mmol) as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 7.09 (s, 2H; 2Ar*H*), 2.86 (t, ^3J= 7.4 Hz, 4H; 2SCH_2), 2.53 (dt, ^3J = 15 Hz and 7.4 Hz, 4H; 2CH_2), 1.69–1.54 (m, 4H; 2CH_2), 1.47–1.22 (m, 8H; 2CH_2), 0.91–0.87 (m, 6H; 2CH_3).



10b

Chemical Formula: $C_{16}H_{28}O_2S$
Molecular Weight: 284,46

3,4-bis(hexyloxy)thiophene (10b): Following the same procedure as described for **10a**, with **9** (0.84 g, 5.83 mmol), 1-hexanol (2.94 mL; 2.39 g, 23.32 mmol) and *p*-toluene sulfonic acid (0.11 g, 0.58 mmol) in toluene (7 mL) at reflux for 48h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 4:1), compound **10b** was obtained in 90% yield (1.50 g, 5.26 mmol) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.16 (s, 2H; 2Ar*H*), 3.97 (t, ^3J= 6.8 Hz, 4H; 2OCH_2), 1.87–1.75 (m, 4H; 2CH_2), 1.49–1.39 (m, 4H; 2CH_2), 1.36–1.29 (m, 8H; 4CH_2), 0.93–0.86 (m, 6H; 2CH_3).

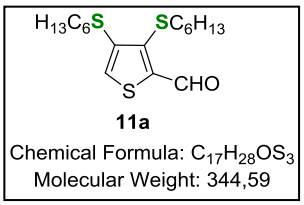


10c

Chemical Formula: $C_{16}H_{28}S$
Molecular Weight: 252,46

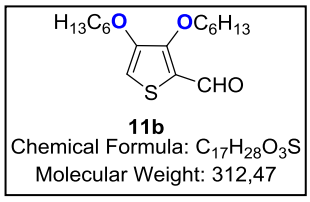
3,4-dihexylthiophene (10c): To a suspension of $NiCl_2$(dppp) (224 mg, 0.42 mmol) and 3,4-dibromothiophene (2.26 ml; 5.00 g, 20.7 mmol) in Et_2O (60 ml) at 0 ºC, was added drop by drop trough a cannula a 2.76 M solution of *n*HexMgBr in Et_2O

(30 ml, 82.8 mmol). At the end of the addition, the mixture was let to reach RT then heated to reflux for 24h. Afterwards, a 1M HCL aqueous solution (10 mL) was added **carefully** to the mixture under vigorous stirring. After 30 min, the resulting mixture was filtered over celite, and the filtrate evaporated to dryness. The residue was then extracted with CH_2Cl_2 and a saturated aqueous solution of NaCl. After phase separation, the aqueous layer was extracted twice more with CH_2Cl_2. The organic layers were combined, and then successively washed with deionised water, dried over $MgSO_4$ filtrated and evaporated to dryness. The crude was pre-purified by filtration over a small plug of silica gel (eluent: CH_2Cl_2 100%). Purification was achieved by distillation under reduced pressure (140ºC, $9•10^{-2}$ mbar) to afford compound **10c** (4.54 g, 18.0 mmol) in 87% yield as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.89 (s, 2H; 2Ar*H*), 2.56–2.47 (m, 4H; 2ArCH_2), 1.71–1.56 (m, 4H; 2CH_2), 1.43–1.26 (m, 12H; 6CH_2), 0.91 (t, *J*= 6.5 Hz, 6H; 2CH_3).



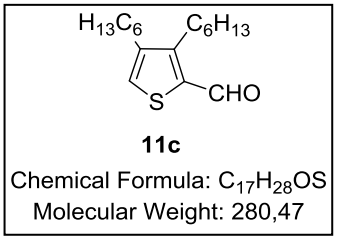
11a
Chemical Formula: $C_{17}H_{28}OS_3$
Molecular Weight: 344,59

3,4-bis(hexylthio)thiophene-2-carbaldehyde (11a): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with **9** (1.45 g, 4.58 mmol), DMF (0.71 ml; 0.67 g , 9.16 mmol), $POCl_3$ (0.68 ml; 1.12 g, 7.33 mmol) in DCE (15 ml) at reflux for 4h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 2:1), compound **11a** was obtained in 98% yield (1.55 g, 4.50 mmol) as a yellowish oil. ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 184.3(*C*HO), [145.2, 140.9, 140.5, 127.6] (4Ar*C*), 36.3 (SC*H*2), [33.7, 31.4, 31.3, 29.7, 28.7, 28.6, 28.2, 22.6, 22.5] (9*C*H_2), 14.0 (2s; 2*C*H_3). MS (FAB+, m-NBA): *m/z* found 345 [M+H]+. HRMS (FAB+): $[M]^+$ m/z calcd for $C_{17}H_{28}OS_3$: 344.1302; found: 344.1286.



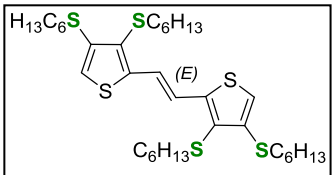
11b
Chemical Formula: $C_{17}H_{28}O_3S$
Molecular Weight: 312,47

3,4-bis(hexyloxy)thiophene-2-carbaldehyde (11b): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with **9** (1.40 g, 4.92 mmol), DMF (0.76 ml; 0.72 g, 9.84 mmol), $POCl_3$ (0.73 ml; 1.20 g, 7.87 mmol) in DCE (18 ml) at reflux for 4h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **11b** was obtained in 80% yield (1.24 g, 3.96 mmol) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz MHz) δ(ppm): 9.99 (s, 1H; C*H*O), 6.61 (s,1H; Ar*H*), 4.32 (t, ^3J = 6.6 Hz, 2H; OCH_2), 3.97 (t, ^3J = 6.4 Hz, 2H; OCH_2), 1.85–1.70 (m, 4H; 2CH_2), 1.50–1.40 (m, 4H; 2CH_2), 1.36–1.30 (m, 8H; 4CH_2), 0.93–0.87 (m, 6H; 2CH_3).



11c
Chemical Formula: $C_{17}H_{28}OS$
Molecular Weight: 280,47

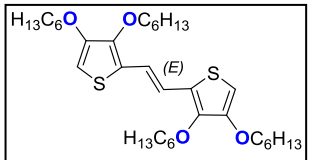
3,4-dihexylthiophene-2-carbaldehyde (11c): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with **10c** (2.15 g, 8.52 mmol), $POCl_3$ (1.27 ml, 13.6 mmol) and DMF (1.2 ml, 15.3 mmol) in DCE (20 mL) at reflux for 12h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **11c** was obtained in 95% yield (2.27 g, 8.09 mmol) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm):10.01 (s, 1H; C*H*O), 7.33 (s, 1H; Ar*H*), 2.87 (t, ^3J= 8 Hz, 2H; ArCH_2), 2.53 (t, ^3J = 8 Hz, 2H; ArCH_2), 1.79–1.45 (m, 4H; 2CH_2), 1.42–1.26 (m, 12H; 6CH_2), 0.89 (2×t, ^3J= 7 Hz, 6H; 2CH_3).



12a

Chemical Formula: $C_{34}H_{56}S_6$
Molecular Weight: 657,18

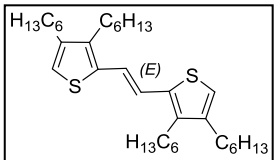
(*E*)-1,2-bis(3,4-bis(hexylthio)thiophen-2-yl)ethane (12a): Prepared according to the general procedure described for *McMurry coupling* with $TiCl_4$ (1.00 mL; 1.73g, 9.12 mmol) and Zn (1.19 g, 18.2 mmol) in THF (15 mL), followed by a solution of **11a** (1.57 g, 4.56 mmol) in pyridine (1 mL) and THF (15 mL). Reflux 4h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 2:1), compound **12a** was obtained in 79% yield (1.18 g, 1.79 mmol) as an orange-yellowish solid. UV-vis: $\lambda_{max}(CH_2Cl_2)$/nm = 229 (log [ε/dm^3 mol^{-1} cm^{-1}]: 4.3) 324 (4.0), 381 (4.0). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 7.52 (s, 2H; 2C=C*H*), 6.80 (s, 2H; 2Ar*H*), 2.92 (t, ^3J = 7 Hz, 4H; 2SCH_2), 2.76 (t, ^3J = 7 Hz, 4H; 2SCH_2), 1.76–1.64 (m, 8H; 4CH_2), 1.55–1.36 (m, 8H; 4CH_2), 1.34–1.21 (m, 16H; 8CH_2), 0.93–0.80 (m, 12H; 4CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): [146.1, 139.2, 130.0, 122.2, 116.7] (Ar*C*+C=*C*H), 53.6 (S*C*H$_2$), [36.6, 33.6, 31.6, 29.7, 28.9, 28.8, 28.4, 22.7 (2s)] (*C*H$_2$), 14.2 (2s; *C*H$_3$). MS (FAB+, m-NBA): *m/z* found 657 [M+H]+. HRMS (FAB+): [M]$^+$ m/z calcd for $C_{34}H_{56}S_6$: 656.2706; found: 656.2699.



12b

Chemical Formula: $C_{34}H_{56}O_4S_2$
Molecular Weight: 592,94

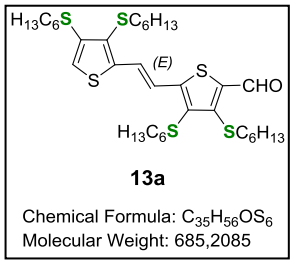
(*E*)-1,2-bis(3,4-bis(hexyloxy)thiophen-2-yl)ethene (12b): Prepared according to the general procedure described for *McMurry coupling* with $TiCl_4$ (0.84 mL; 1.46g, 7.68 mmol) and Zn (1.00g, 15.4 mmol) in THF (15 mL), followed by a solution of **11b** (1.20 g; 3.84 mmol) in pyridine (1 mL) and THF (15 mL), reflux for 18h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **12b** was obtained in 78% yield (0.89 g, 1.50 mmol) as an orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.96 (s, 2H; 2C=*C*H), 5.99 (s, 2H; 2Ar*H*), 4.05 (t, ^3J = 6.6 Hz, 4H; 2OCH_2), 3.94 (t, ^3J = 6.4 Hz, 4H; 2OCH_2), 1.85–1.67 (m, 8H; 4CH_2), 1.52–1.40 (m, 8H; 4CH_2), 1.38–1.28 (m, 16H; 8CH_2), 0.95–0.86 (m, 12H; 4CH_3).



12c

Chemical Formula: $C_{34}H_{56}S_2$
Molecular Weight: 528,94

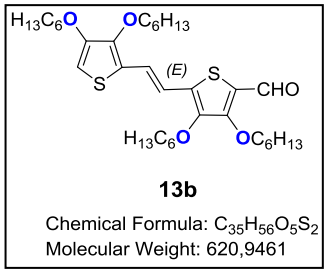
(*E*)-1,2-bis(3,4-dihexylthiophen-2-yl)ethane (12c): Prepared according to the general procedure described for *McMurry coupling* with $TiCl_4$ (0.91 mL; 1.57 g, 8.29 mmol) and Zn (1.09 g, 16.6 mmol) in THF (15 mL) followed by a solution of **11c** (1.55 g, 5.53 mmol) and pyridine (1 mL) in THF (15 mL), reflux for 18h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:9), compound **12c** was obtained in 70% yield (1.02 g, 1.93 mmol) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.99 (s, 2H; 2C=CH), 6.74 (s, 2H; 2Ar*H*), 2.59 (t, ^3J= 7.4 Hz, 4H; 2ArCH_2), 2.48 (t, ^3J= 7.4 Hz, 4H; 2ArCH_2), 1.74–1.54 (m, 8H; 4CH_2), 1.50–1.17 (m, 24H; 12CH_2), 0.92–0.90 (m, 12H; 4CH_3).



13a

Chemical Formula: $C_{35}H_{56}OS_6$
Molecular Weight: 685,2085

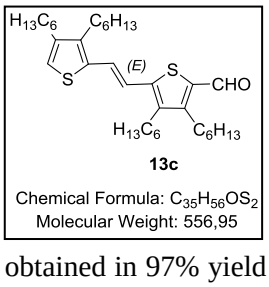
(*E*)-5-(2-(3,4-bis(hexylthio)thiophen-2-yl)vinyl)-3,4 bis(hexylthio) thiophene -2-carbaldehyde (13a): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with **12a** (0.80 g, 1.22 mmol), $POCl_3$ (0.14 mL; 0.23 g, 1.76 mmol) and DMF (0.15 ml; 0.14 g, 1.95 mmol) in DCE (30 mL), reflux for 2h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **13a** was obtained in 57% yield (0.48 g, 0.69 mmol) as a red solid. UV-vis: $\lambda_{max}(CH_2Cl_2)$/nm = 407 (log [ε/dm^3 mol^{-1} cm^{-1}]: 3.9), 266 (3.9), 226 (4.1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 10.27 (s, 1H; C*H*O), 7.82 (d, 1H, $^3J_{trans}$= 16 Hz; C=CH), 7.59 (d, 1H, $^3J_{trans}$= 16 Hz, C=CH), 6.90 (s, 1H; Ar*H*), 3.05 (t, ^3J= 7 Hz, 2H; SCH_2), 2.94 (t, ^3J= 7 Hz, 2H; SCH_2), 2.87 (t, ^3J= 7 Hz, 2H; SCH_2), 2.81 (t, ^3J= 7 Hz, 2H; SCH_2), 1.63–1.22 (m, 32H; 16CH_2), 0.94–0.83(m, 12H; 4CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 183.6 (C*H*O), [153.4, 146.7, 144.8, 141.5, 139.8, 135.8, 132.4, 125.9, 121.1, 118.0] (Ar*C*+C=*C*H), [37.0, 36.4, 34.7, 33.5] (S*C*H$_2$), [31.6, 31.5, 31.4, 31.4, 29.8, 29.7, 29.6 (2s), 29.1, 28.8, 28.7, 28.4, 28.3, 25.3, 22.7, 22.6 (3s)] (*C*H$_2$), [14.1, 14.0 (2s)] (*C*H$_3$). MS (FAB+, m-NBA): *m/z* found 685 [M+H]+. HRMS (FAB+): [M]$^+$ *m/z* calcd for $C_{35}H_{56}OS_6$: 684.2655; found: 684.2643.



13b

Chemical Formula: $C_{35}H_{56}O_5S_2$
Molecular Weight: 620,9461

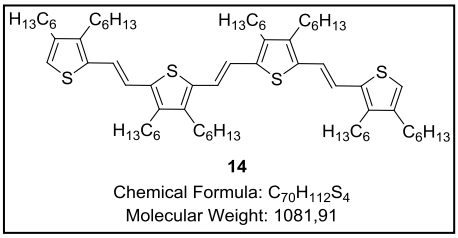
(*E*)-5-(2-(3,4-bis(hexyloxy) thiophen-2-yl) vinyl)-3,4-bis(hexyloxy) thiophene- 2-carbaldehyde (13b): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with $POCl_3$ (0.17 mL; 0.28 g, 1.80 mmol) **12b** (0.89 g, 1.50 mmol) and DMF (0.16 ml; 0.18 g, 2.40 mmol) in DCE (35 mL). Reflux for 3h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **13b** was obtained in 80% yield (0.74 g, 1.19 mmol) as a yellow solid. UV-vis: $\lambda_{max}(CH_2Cl_2)$/nm = 391 (log [ε/dm^3 mol^{-1} cm^{-1}]: 3.4), 286 (3.6), 236 (3.7). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.94 (s, 1H; C*H*O), 7.25 (d, 1H, $^3J_{trans}$= 16 Hz; C=CH), 6.93 (d, 1H, $^3J_{trans}$= 16 Hz; C=CH), 6.11 (s, 1H; Ar*H*), 4.28 (t, ^3J= 7 Hz, 2H; OCH_2), 4.10 (t, ^3J= 7 Hz, 2H; OCH_2), 4.00 (t, ^3J= 7 Hz, 2H; OCH_2), 3.95 (t, ^3J= 7 Hz, 2H; OCH_2), 1.82–1.71 (m, 8H; 4CH_2), 1.51–1.40 (m, 8H; 4CH_2), 1.39–1.29 (m, 8H; 4CH_2), 0.95–0.87 (m, 12H; 4CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 180.6 (*C*HO), [157.0, 150.6, 145.9, 145.8, 137.2, 123.8, 121.9, 121.3, 115.5, 96.4] (Ar*C*+C=*C*H), [74.7, 73.6, 70.2] (O*C*H$_2$), [31.7, 31.6, 30.2, 30.1, 30.0, 29.8, 29.2, 25.9, 25.8, 25.7, 25.6, 22.7 (3s)] (*C*H$_2$), 14.1 (2s; *C*H$_3$).



13c

Chemical Formula: $C_{35}H_{56}OS_2$
Molecular Weight: 556,95

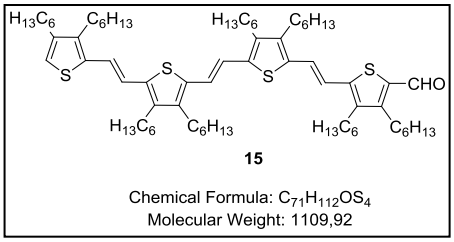
(*E*)-5-(2-(3,4-dihexylthiophen-2-yl)vinyl) -3,4-dihexylthiophene -2-carbaldehyde (13c): Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with $POCl_3$ (0.22 mL; 0.35 g, 2.27 mmol), **12c** (1.00 g, 1.89 mmol) and DMF (0.20 ml; 0.19 g, 2.65 mmol) in DCE (40 mL), reflux for 12h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 1:1), compound **13c** was obtained in 97% yield (1.02 g, 1.83 mmol) as an orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.97 (s, 1H; C*H*O), 7.27 (d, 1H, $^3J_{trans}$= 16 Hz; C=C*H*), 6.96 (d, 1H, $^3J_{trans}$= 16 Hz; C=C*H*), 6.84 (s, 1H; Ar*H*), 2.84 (t, ^3J= 7 Hz, 2H; ArCH_2), 2.64–2.56 (m, 4H; 2CH_2), 2.49 (t, ^3J= 7 Hz, 2H; CH_2), 1.71–1.17 (m, 32H; 16CH_2), 0.92–0.89 (m, 12H; 4CH_3).



14

Chemical Formula: $C_{70}H_{112}S_4$
Molecular Weight: 1081,91

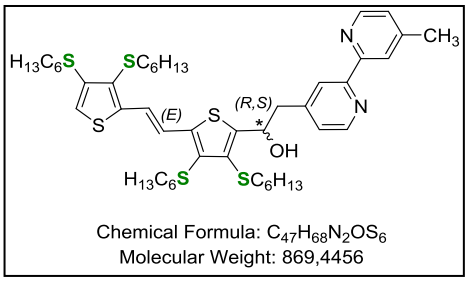
Compound 14. Prepared according to the general procedure described for *McMurry coupling* with $TiCl_4$ (0.17 mL; 0.30 g, 1.58 mmol) and Zn (0.20 g, 3.15 mmol) in THF (15 mL) followed by a solution of **13c** (0.80 g, 1.44 mmol) and pyridine (1 mL) in THF (15 mL), reflux for 18h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 9:1), compound **14** was obtained in 61% yield (0.48 g, 1.44 mmol) as a dark-purple red solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 6.98 (s, 4H; 4C=C*H*), 6.97 (s, 2H; 2C=C*H*), 6.75 (s, 2H; 2Ar*H*), 2.59–2.46 (m, 16H; 8ArCH_2), 1.66–1.57 (m, 4H; 2CH_2), 1.52–1.47 (m, 12H; 6CH_2), 1.40–1.31 (m, 48H; 24CH_2), 0.97–0.83 (m, 24H; 8CH_3).



15

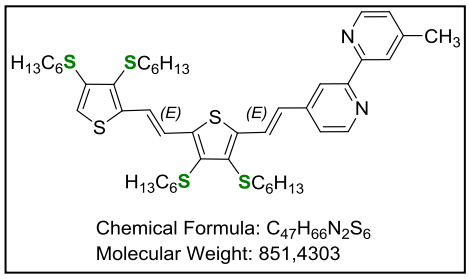
Chemical Formula: $C_{71}H_{112}OS_4$
Molecular Weight: 1109,92

Compound 15. Prepared according to the general procedure described for *Vilsmeier-Haack formylation* with $POCl_3$ (0.08 mL; 0.14 g, 0.88 mmol), **14** (0.95 g, 0.88 mmol) and DMF (0.08 ml; 0.07 g, 1.03 mmol) in DCE (80 mL), reflux for 12h. After purification by column chromatography on SiO_2 (eluent: hexanes/CH_2Cl_2 3:2), compound **15** was obtained in 54% yield (0.52g, 0.47 mmol) as a dark-purple red solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.97 (s, 1H; C*H*O), 7.03–6.90 (m, 6H; 6C=C*H*), 6.76 (s, 1H; Ar*H*), 2.85 (t, ^3J= 8 Hz, 2H; ArCH_2), 2.66–2.54 (m, 12H; 6ArCH_2), 2.49 (t, ^3J= 7 Hz, 2H; ArCH_2), 1.67–1.26 (m, 64H; 32CH_2), 0.97–0.84 (m, 24H; 8CH_3).

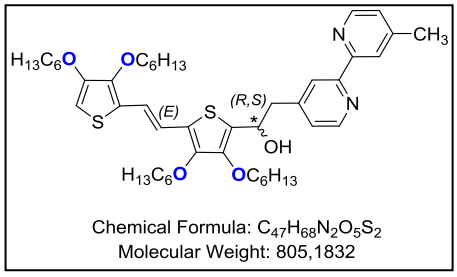


Chemical Formula: $C_{47}H_{68}N_2OS_6$
Molecular Weight: 869,4456

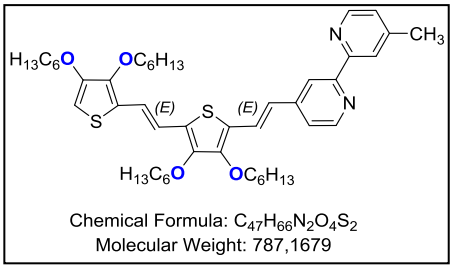
Compound 1-OH (racemic mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (60.75 mg, 0.33 mmol) in THF (5 mL), a 2M solution of LDA in Heptane/THF (0.16 mL, 0.32 mmol) and a solution of **13a** (150 mg, 0.17 mmol) in THF (5 mL). The crude was purified by flash chromatography over a small plug of SiO_2 gel, using first CH_2Cl_2 as eluent to remove nonpolar residual products such unreacted excess of aldehyde **13a**, then CH_2Cl_2/MeOH 9:1 with 1 % of Et_3N. After evaporation of the solvents, the resulting solid was triturated in a copious amount of hexanes and the solution filtrated through a small plug of celite (eluent: hexanes). The hexane-soluble filtrate was evaporated to dryness under reduced pressure and the resulting residue purified by size-exclusion chromatography column (eluent: toluene), affording **1-OH** as a yellow solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.48 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.45 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.30 (br s, 1H; Ar*H* bipy), 8.16 (br s, 1H; Ar*H* bipy), 7.52 (br s, 2H; 2C=C*H*), 7.14 (dd, ^3J = 5 Hz and ^4J = 1Hz, 1H; Ar*H* bipy), 7.07 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 6.77 (s, 1H; Ar*H*), 5.62 (pseudo t (dd), ^3J= 6.4 Hz and 6.7 Hz, 1H; *C*H*OH), 3.20 (br s, 1H; *CC*H*´), 3.18 (br s, 1H; *CC*H*´H), 2.90 (t, ^3J = 7 Hz, 2H; SCH_2), 2.82–2.67 (m, 6H; 4 SCH_2), 2.38 (s, 3H; ArCH_3 bipy), 1.70 (m, $^3J \approx$ 7–8 Hz, 2H; CH_2), 1.57–1.04 (m, 30*H*; 15CH_2), 0.94–0.77 (m (4×t), $^3J \approx$ 7 Hz, 12H; 4CH_3).



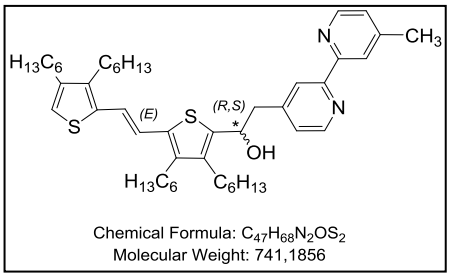
Compound 1: Prepared according to the general procedure with **1-OH** (172.5 µmol) and PTPS (22 mg, 87.5 µmol) in toluene (20 mL) and a 1.5 mM solution of I_2 in toluene (1.2 mL, 1.80 µmol; 0.75 mol%), reflux overnight (the solution turned progressively from light yellow to dark red). The crude was purified by chromatography column on SiO_2 gel (eluent CH_2Cl_2 containing 0.75% MeOH and 0.1% Et_3N). Purification was achieved by recrystallization in hexanes (1–2 mL) at low temperature (-20°C). Compound **1** (98 mg, 115 µmol) was obtained as an orange solid in an overall 67% yield (2 steps). UV-vis: $\lambda_{max}(CH_2Cl_2)$/nm = 247 (ε /dm^3 mol^{-1} cm^{-1}: 32 500), 281 (25 100), 325 (20 700), 435 (34 400), 459 (br sh, 27 100).^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.64 (d, ^3J = 5 Hz, 1H), 8.56 (d, ^3J = 5 Hz, 1H), 8.49 (br s, 1H), 8.24 (br s, 1H), 7.99 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.59 (s, 1H), 7.41 (dd, ^3J = 5 Hz and ^4J = 1.5 Hz, 1H), 7.41 (dd, ^3J = 5 Hz and ^4J ≈ 1 Hz, 1H), 7.03 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.82 (s, 1H), 2.92 (t, ^3J = 7 Hz, 2H), 2.88 (t, ^3J = 7 Hz, 2H), 2.86 (t, ^3J = 7 Hz, 2H), 2.81 (t, ^3J = 7 Hz, 2H), 2.44 (s, 3H), 1.70 (pseudo quintet, ^3J ≈ 7 Hz, 2H), 1.60–1.36 (m, 14H), 1.36–1.17 (m, 16H), 0.94–0.77 (m (4×t), ^3J ≈ 7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.8, 155.7, 149.4, 148.9, 148.0, 145.7, 145.1, 144.4, 142.4, 139.3, 137.2, 135.6, 130.4, 127.4, 125.4, 124.7, 122.9, 121.9, 121.7, 120.2, 118.7, 116.8, 37.0, 36.4, 33.3, 31.4, 31.3, 29.5, 29.4, 28.6 (2s), 28.3 (3s), 22.6, 22.5 (2s), 21.1, 14.0–13.9 (4s). MS (MALDI-TOF, Dithranol): *m/z* found 851.4 $[M+H]^+$. HRMS (MALDI-TOF, DCTB+PPGNa600+ PPGNa1000): $[M+H]^+$ *m/z* calcd for $C_{47}H_{67}N_2S_6$: 851.3623 found 851.3632.



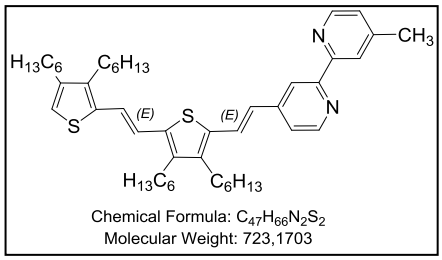
Compound 2-OH (racemic mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (70.0 mg, 0.38 mmol) in THF (5 mL), a 2M solution of LDA in Heptane/THF (0.19 mL, 0.38 mmol) and a solution of **13b** (150 mg, 0.24 mmol) in THF (5 mL). The crude was purified by flash chromatography on a small plug of SiO_2 gel using first CH_2Cl_2 as eluent to remove nonpolar residual products such unreacted excess of aldehyde **13b**, then CH_2Cl_2/MeOH 9:1 with 1 % of Et_3N to recover the main product. After evaporation of the solvents, the resulting solid was triturated in a copious amount of hexane and the solution filtrated through a small plug of celite (eluent: hexane). The hexane-soluble filtrate was evaporated to dryness under reduced pressure and the obtained crude purified by gel permeation chromatography column (eluent: toluene), affording **2-OH** as a yellow solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.51 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.48 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.29 (br s, 1H; Ar*H* bipy), 8.17 (br s, 1H; Ar*H* bipy), 7.13 (dd, ^3J = 5 Hz and ^4J = 1 Hz, 1H; Ar*H* bipy), 7.11–7.08 (m, 1H; Ar*H* bipy), 6.97 (d, $^3J_{trans}$ = 16 Hz, 1H; C=C*H*), 6.90 (d, $^3J_{trans}$ = 16 Hz, 1H; C=C*H*), 5.99 (s, 1H; Ar*H*), 5.28 (dd, ^3J= 6 Hz and 7.5 Hz, 1H; *C*H*OH), 4.06 (t, ^3J = 6.5 Hz, 2H; OCH_2), 3.93 (t, ^3J = 6.5 Hz, 2H; OCH_2), 3.91 (t, ^3J = 6.5 Hz, 2H; OCH_2), 3.83 (t, ^3J = 6.5 Hz, 2H; OCH_2), 3.21 (dd, ^2J= 13.4 Hz, ^3J= 7.5 Hz, 1H; *CC*H*H´), 3.13 (dd, ^2J= 13.4 Hz, ^3J= 6 Hz, 1H; *CC*H´*H), 2.40 (s, 3H; ArCH_3 bipy), 1.82–1.62 (m, 8H; 4CH_2), 1.61–1.11 (m, 24H; 12CH_2), 0.97–0.77 (m, 12H; ; 4CH_3).



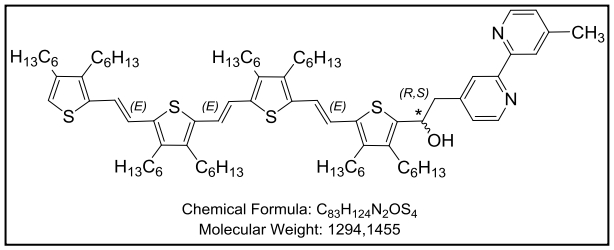
Compound 2: Prepared according to the general procedure with **2-OH** (240 μmol) and PTPS (24.0 mg, 95.5 μmol) in toluene (20 mL), and a 10.64 mM solution of I_2 in toluene (0.18 mL, 1.9 μmol; 0.8 mol%), reflux overnight (the solution turned progressively from light yellow to dark red). The crude was purified by chromatography column on SiO_2 gel (eluent CH_2Cl_2 containing 0.75% MeOH and 0.1% Et_3N). Purification was achieved by recrystallization in *n*-pentane (1–2 mL) at low temperature (-20°C). Compound **2** (148.5 mg, 189 μmol) was obtained as a yellow-brownish solid in an overall 79% yield (2 steps). UV-vis: $\lambda_{max}(CH_2Cl_2)$/nm = 291 (ε /dm^3 mol^{-1} cm^{-1} 21 600), 427 (32 700). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.60 (d, ^3J = 5 Hz, 1H), 8.56 (d, ^3J = 5 Hz, 1H), 8.44 (br s, 1H), 8.24 (br s, 1H), 7.56 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.31 (dd, ^3J = 5 Hz and ^4J = 1.5 Hz, 1H), 7.14 (dd, ^3J = 5 Hz and ^4J = 1 Hz, 1H), 7.05 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.96 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.81 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.03 (s, 1H), 4.11 (t, ^3J = 6.5 Hz, 2H), 4.10 (t, ^3J = 6.5 Hz, 2H), 4.05 (t, ^3J = 6.5 Hz, 2H), 3.94 (t, ^3J = 6.5 Hz, 2H), 2.44 (s, 3H), 1.84–1.71 (m, 8H), 1.58–1.43 (m, 8H), 1.43–1.26 (m, 16H), 0.98–0.83 (m, 12H). ^{13}C and DEPT-135 NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.6, 155.9, 150.4, 149.3, 149.1, 148.8, 147.9, 147.1, 145.6, 144.5, 126.0, 124.7, 124.6, 123.3, 122.7, 122.0, 121.8, 120.0, 118.1, 117.9, 116.0, 94.7, 74.1, 74.0, 73.4, 69.9, 31.6, 31.6, 31.4, 30.02, 29.94, 29.03, 25.68, 25.65, 22.64, 22.56, 22.49, 21.0, 14.01, 13.95, 13.92, 13.90. MS (MALDI-TOF, DCTB): *m/z* found 786.5 [M$^+$]. HRMS (MALDI-TOF, DCTB+PPGNa790+NaI): [M]$^+$ *m/z* calcd for $C_{47}H_{66}N_2O_4S_4$: 786.4452; found 786.4452.



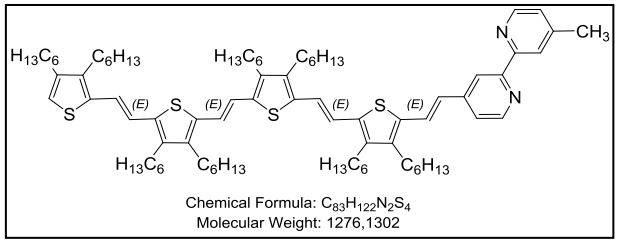
Compound 3-OH (racemic mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (74.8 mg, 0.41 mmol) in THF (5 mL), a 2M solution of LDA in Heptane/THF (0.22 mL, 0.44 mmol) and a solution of **13c** (150 mg, 0.27 mmol) in THF (5 mL). The crude was purified by flash chromatography on a small plug of SiO_2 gel using first CH_2Cl_2 as eluent to remove nonpolar residual products such unreacted excess of aldehyde **13c**, then CH_2Cl_2/MeOH 9:1 with 1 % of Et_3N to recover the product. After evaporation of the solvents, the resulting solid was triturated in a copious amount of hexane and the solution filtrated through a small plug of celite (hexanes). The filtrate was evaporated to dryness under reduced pressure, affording **3-OH** (180 mg, 0.24 mmol) as a yellow solid in 89 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.52 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.46 (d, ^3J = 5 Hz, 1H; Ar*H* bipy), 8.30 (s, 1H; Ar*H* bipy), 8.20 (s, 1H; Ar*H* bipy), 7.18–7.06 (m, 4H; 2Ar*H* bipy+2C=C*H*), 6.76 (s, 1H), 5.25 (dd, ^3J = 5.5 and 8 Hz, 1H; *C*H*OH), 3.30 (dd, ^2J = 13.4 Hz and ^3J = 8 Hz, 1H; *CC*H*H´), 3.14 (dd, ^2J = 13.4 Hz and ^3J = 5.5 Hz, 1H; *CC*H´*H), 2.63 (t, ^3J = 8 Hz, 2H; ArCH_2), 2.56–2.46 (m, 4H; 2ArCH_2), 2.42 (s, 3H; ArCH_3 bipy), 2.37–2.25 (m, 2H; CH_2), 1.64 (m, $^3J \approx 8$ Hz, 2H; CH_2), 1.57–1.06 (m, 30H; 15CH_2), 0.98–0.78 (m, 12H; 4CH_3).



Compound 3: Prepared according to the general procedure with **3-OH** (180 mg, 243 µmol) and PTPS (27 mg, 107 µmol) in toluene (20 mL), and a 6.93 mM solution of I_2 in toluene (0.2 mL, 1.4 µmol, 0.6 mol%), reflux overnight (during the reaction, the colour of the solution turned progressively from light yellow to deep orange-reddish; after addition of Et_3N (0.5 mL), the solution turned bright yellow. The crude was purified by chromatography column on SiO_2 gel (eluent CH_2Cl_2 containing 1% MeOH and 0.2% Et_3N). Compound **3** (159 mg, 220 µmol) was obtained as a fine deep-yellow powder in 91% yield (overall 82% yield, 2 steps). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 289 (ε /dm^3 mol^{-1} cm^{-1} 26 500), 423 (26 200). ^{1}H and 2D-COSY NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.62 (d, ^3J = 5 Hz, 1H), 8.58 (d, ^3J = 5 Hz, 1H), 8.45 (br s, 1H), 8.26 (br s, 1H), 7.55 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.34 (dd, ^3J = 5 Hz and ^4J = 1.5 Hz, 1H), 7.16 (dd, ^3J = 5 Hz and ^4J = 1 Hz, 1H,), 7.08 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.99 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.89 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.79 (s, 1H), 2.70–2.56 (m, 6H), 2.51 (t, ^3J = 8 Hz, 2H), 2.46 (s, 3H), 1.71–1.22 (m, 32H), 0.98–0.78 (m, 12H). ^{13}C and DEPT-90/-135 NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.5, 155.8, 149.2, 148.7, 147.8, 145.6, 143.7, 143.2, 141.0, 140.3, 137.0, 136.7, 133.4, 124.5(2s), 124.4, 121.8, 120.8, 120.0, 118.7, 118.2, 118.0, 31.62, 31.56, 31.47, 31.45, 31.3, 31.1, 30.9, 29.5, 29.2, 29.1, 28.9, 27.0, 26.8, 22.6, 22.5, 21.0, 14.1, 14.0. MS (MALDI-TOF, DCTB): *m/z* (%) found 722.5 (100) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa600): $[M]^+$ *m/z* calcd for $C_{47}H_{66}N_2S_2$: 722.4662; found: 722.4646.

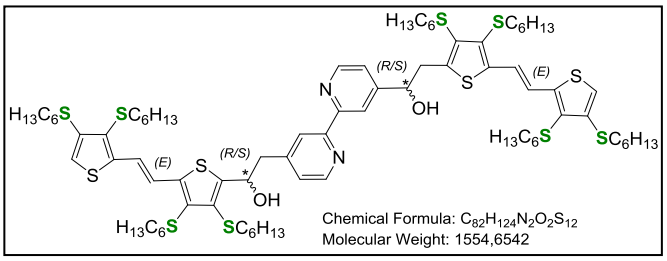


Compound **4-OH** (racemic mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (100 mg; 54.3 µmol, 6 eq) in THF (10mL), a 1.8 M solution of LDA in heptane/THF (0.3 mL; 0.54 mmol, 6eq) and a solution of **15** (100 mg, 90.1 µmol, 1 eq) in THF (5 mL). Crude **4-OH** was obtained as a light orange pasty solid and used without further purification in the next step (yield considered quantitative for this step).

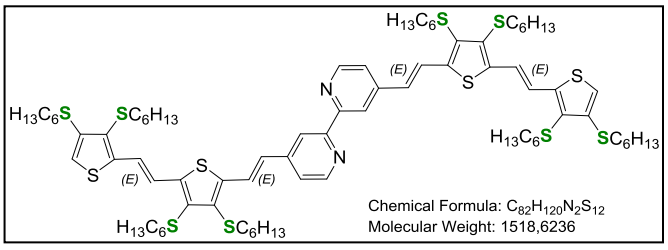


Compound 4: Prepared according to the general procedure with **4-OH** (90.1 µmol) and PTPS (40 mg, 159 µmol) in toluene (30 mL) and a 1g/l solution of I_2 in toluene (0.5 mL; 2 µmol, 2 mol%), reflux for 24h (during the reaction, the colour of the solution turned progressively from light orange to deep dark-red; after addition of Et_3N (0.5 mL), the solution turned bright orange-reddish). Crude was dissolved in a minimum amount of CH_2Cl_2 and the remaining excess of 4,4'-dimethyl-2,2' bipyridine was precipitated by addition of a large amount of hexane. The solution was filtrated, evaporated to dryness and the resulting solid purified twice by exclusion size chromatography (eluent: toluene), followed by chromatography on neutral SiO_2 (eluent Hexane/CH_2Cl_2 6/4 with 1% of Et_3N). Compound **4** (75 mg, 58.8 µmol) was obtained as a dark purple-red pasty solid in overall 65% yield (2 steps). UV-vis (CH_2Cl_2), $\lambda_{max}(\varepsilon)$: 299 nm (31 600), 544 nm (48 300). ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.63 (d, ^3J = 5 Hz, 1H), 8.59 (d, ^3J = 5 Hz, 1H), 8.46 (s, 1H), 8.27

(s, 1H), 7.57 (d, $^3J_{trans}$= 16 Hz, 1H), 7.35 (d, ^3J = 5 Hz, 1H), 7.17 (d, ^3J = 5 Hz, 1H), 7.08 (d, $^3J_{trans}$= 15.5 Hz, 1H), 7.01 (br s, 5H), 6.99 (d, $^3J_{trans}$= 15.5 Hz, 1H), 6.90 (d, $^3J_{trans}$= 16 Hz, 1H), 6.80 (s, 1H), 2.71–2.55 (m, 14H), 2.51 (t, ^3J = 8 Hz, 2H), 2.47 (s, 3H), 1.69–1.61 (m, 2H), 1.61–1.50 (m, 14H), 1.50–1.29 (m, 48H), 1.03–0.84 (m, 24H). APT ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm): 156.6, 155.9, 149.3, 148.9, 148.1, 145.8, 144.0, 143.4, 142.3, 141.7, 141.6, 141.4, 140.0, 137.3, 137.1, 135.7, 135.1, 134.9, 134.8, 133.7, 124.7 (2s), 124.5, 122.0, 120.5, 120.2, 119.9, 119.7, 119.2 (2s), 118.9, 118.2, 117.9, 31.7 (2s), 31.6, 31.5, 31.3, 31.2 (2s), 30.9, 29.7, 29.6, 29.4 (2s), 29.3, 29.0, 27.1 (2s), 27.0, 26.9, 22.7, 22.6, 14.2, 14.1 (2s). MS (MALDI-TOF, DCTB): *m/z* (%) found: 1274.8 (100), 1275.8 (98) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa1000): $[M]^+$, *m/z* (%) calcd for $C_{83}H_{122}N_2S_4$: 1274.8485 (100); found: 1274.8463 (100).

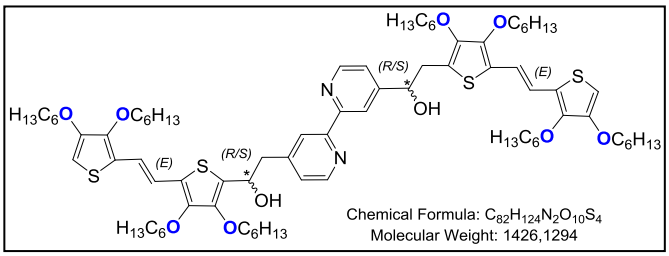


Compound 5-OH (racemic mixture). Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (30.5 mg, 0.17 mmol) in THF (5 mL), a 2 M solution of LDA in heptane/THF (0.2 mL, 0.40 mmol) and a solution of **13a** (339 mg, 0.49 mmol) in THF (5 mL). After flash chromatography column on SiO_2 gel (eluent CH_2Cl_2 1% Et_3N), the R/S alcohols mixture of bisadduct **5-OH** was obtained as a yellow-brownish solid and used as well in the next step (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.49 (d, ^3J = 5 Hz, 2H; 2Ar*H* bipy), 8.31 (s, 2H; 2Ar*H* bipy), 7.53 (br s, 4C=C*H*), 7.18 (d, ^3J = 5 Hz, 2H; 2Ar*H* bipy), 6.79 (s, 2H; 2Ar*H*), 5.64 (pseudo t, $^3J \approx 6$ Hz, 2H; 2*C*H*OH), 3.21 (br s, 2H; 2*CC*H*H´), 3.19 (br s, 2H; 2*CC*H´*H), 3.00–2.60 (m, 16H; 8SCH_2), 1.70 (pseudo quintet, $^3J \approx$ 7–8 Hz, 4H; 2CH_2), 1.60–0.98 (m, 60H; 30CH_2), 0.84 (m (4×t), $^3J \approx$ 6–7 Hz, 24H; 8CH_3).

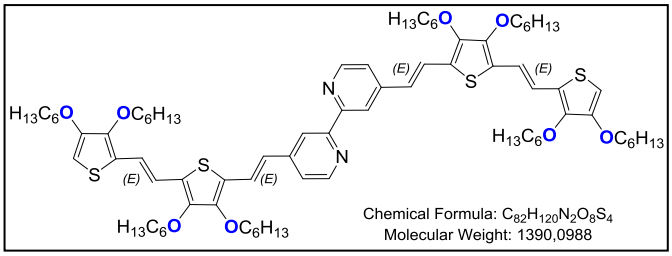


Compound 5: Prepared according to the general procedure with **5-OH** (166 µmol) and PTPS (33 mg, 131 µmol) in toluene (20 mL) and a 1.5 mM solution of I_2 in toluene (2.2 mL, 3 µmol; 2 mol%), reflux for 48h (the solution turned progressively from deep yellow to dark red). Crude was successively purified by flash chromatography column on SiO_2 gel (eluent CH_2Cl_2 with 5% MeOH and 1% Et_3N), followed by gel permeation chromatography (eluent: toluene) and chromatography column on SiO_2 gel (eluent: CH_2Cl_2 with 2.5% MeOH and 0.25% Et_3N). Compound **5** (69 mg, 45.4 µmol) was obtained as an orange solid in an overall 27 % yield (2 steps). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 253 (ε /dm^3 mol^{-1} cm^{-1}: 38 800), 332 (35 600), 438 (70 700), 462 (br sh, 61 000). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.70 (d, ^3J = 5 Hz, 2H), 8.52 (br s, 2H), 8.02 (d, $^3J_{trans}$= 16 Hz, 2H), 7.60 (s, 4H), 7.45 (dd, ^3J = 5 Hz and ^4J = 1.5 Hz, 2H), 7.06 (d, $^3J_{trans}$= 16 Hz, 2H), 6.83 (s, 2H), 2.94 (t, ^3J = 7 Hz, 4H), 2.90 (t, ^3J = 7 Hz, 4H), 2.87 (t, ^3J = 7 Hz, 4H), 2.82 (t, ^3J = 7 Hz, 4H), 1.72 (pseudo quintet, $^3J \approx$ 7–7.5 Hz, 4H), 1.63–1.37 (m, 28H), 1.37–1.18 (m, 32H), 0.94–0.80 (m (4×t), $^3J \approx$ 7 Hz, 24H). ^{13}C and DEPT-135 NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.7, 149.5, 145.7, 145.1, 144.5, 142.5, 139.3, 137.3, 135.7, 130.5, 127.4, 125.5, 122.9, 121.8, 120.4, 118.7, 116.9, 37.1, 36.5,

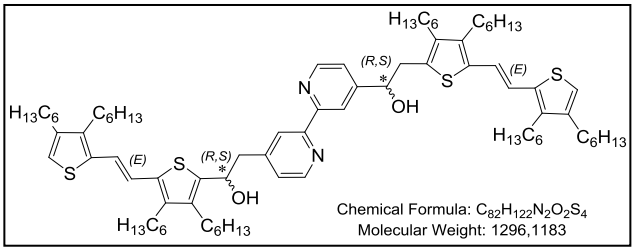
33.4, 31.4 (2s), 29.6, 29.5 (3s), 28.7, 28.6, 28.3 (3s), 22.6, 22.5 (2s), 14.0 (3s). MS (MALDI-TOF, Dithranol): *m/z* found 1519.6 $[M+H]^+$. HRMS (MALDI-TOF, DCTB+PPGNa1500): $[M+H]^+$ *m/z* (%) calcd for $C_{82}H_{121}N_2S_{12}$: 1517.6173 (96), 1518.6202 (96), 1519.6179 (100) found 1517.6145 (93), 1518.6210 (100), 1519.6128 (97).



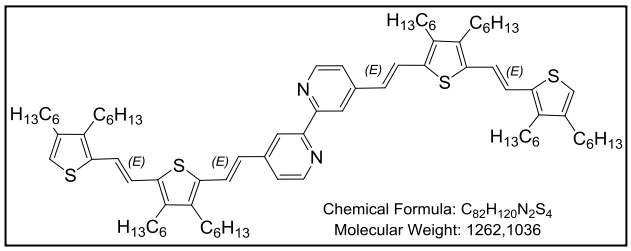
Compound 6-OH (racemic mixture). Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (37.7 mg; 0.205 mmol) in THF (5 mL), a 2 M solution of LDA in heptane/THF (0.25 mL; 0.500 mmol) and a solution of **13b** (350 mg, 0.564 mmol) in THF (5 mL). After flash chromatography column on SiO_2 gel (eluent CH_2Cl_2 1% Et_3N), the R/S alcohols mixture of bisadduct **6-OH** was obtained as a yellow-brownish solid and used as well in the next step (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.46 (d, ^3J = 5 Hz, 2H; 2Ar*H* bipy), 8.26 (s, 2H; 2Ar*H* bipy), 7.16–7.07 (m, 2H; 2Ar*H* bipy), 6.98 (d, $^3J_{trans}$= 16 Hz, 2H; 2C=C*H*), 6.91 (d, $^3J_{trans}$= 16 Hz, 2H; 2C=C*H*), 5.99 (s, 2H; 2Ar*H*), 5.28 (pseudo t, $^3J \approx$ 6–8 Hz, 2H; 2*C*H*OH), 4.06 (t, ^3J = 6.5 Hz, 4H; 2OCH_2), 3.97–3.84 (m, 12H; 6OCH_2), 3.76–3.64 (m, 2H; OCH_2), 3.19 (dd, ^2J= 14 Hz, ^3J=8Hz, 2H; 2*CC*H*H´), 3.12 (dd, ^2J= 14 Hz, ^3J = 6Hz, 2H; 2*CC*H´*H), 1.83–1.14 (m, 64H; 32CH_2), 0.95–0.80 (m, 24H; 8CH_3).



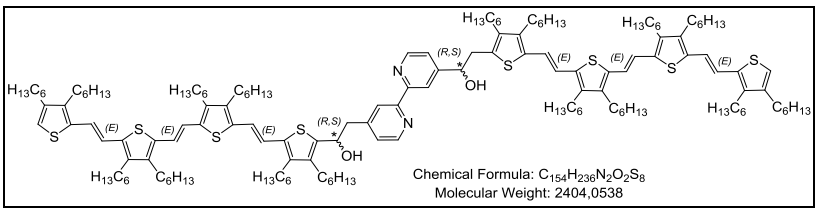
Compound 6: Prepared according to the general procedure with **6-OH** (205 µmol) and PTPS (41 mg, 163 µmol) in toluene (25 mL), and a 10.64 mM solution of I_2 in toluene (0,4 mL, 4 µmol; 2 mol%), reflux for 48h (the solution turned progressively from deep yellow to dark red). Crude was successively purified by flash chromatography column on SiO_2 gel (eluent CH_2Cl_2 with 5% MeOH and 0.5% Et_3N, followed by gel permeation chromatography (eluent: toluene) and chromatography column on SiO_2 gel (eluent: CH_2Cl_2 with 2.5% MeOH and 0.25% Et_3N). Purification was achieved by successive recrystallizations in mixtures of *n*-pentane and hexanes (1–2 mL) at low temperature (- 20°C). Compound **6** (176 mg, 127 µmol) was obtained as a yellow-brownish solid in an overall 62% yield (2 steps). UV-vis: $\lambda_{max}(CHCl_3)$/nm = 309 (ε /dm^3 mol^{-1} cm^{-1}: 35 500), 432 (69 000). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.63 (d, ^3J = 5 Hz, 2H), 8.46 (s, 2H), 7.58 (d, $^3J_{trans}$= 16 Hz, 2H), 7.34 (d, ^3J = 5 Hz, 2H), 7.06 (d, $^3J_{trans}$= 16 Hz, 2H), 6.97 (d, $^3J_{trans}$= 16 Hz, 2H), 6.03 (s, 2H), 4.12 (t, ^3J = 6.5 Hz, 4H), 4.11 (t, ^3J = 6.5 Hz, 4H), 4.05 (t, ^3J = 6.5 Hz, 4H), 3.94 (t, ^3J = 6.5 Hz, 4H), 1.87–1.70 (m, 16H), 1.61–1.25 (m, 48H), 1.01–0.85 (m, 24H). ^{13}C- and DEPT-135 -NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.5, 150.4, 149.3, 149.1, 147.1, 145.6, 144.4, 126.0, 124.7, 123.3, 122.7, 122.1, 120.1, 118.1, 117.9, 116.0, 94.6, 74.1, 74.0, 73.4, 69.9, 31.6 (2s), 31.4, 30.0 (2s), 29.0, 25.7 (2s), 22.7, 22.6, 22.5, 14.0–13.9 (4s). MS (MALDI-TOF, DCTB): *m/z* (%) found 1388.7 (97) $[M^+]$, 1389.7 (100) $[M^+]/[M+H]^+$. HRMS (MALDI-TOF, DCTB+PPGNa790+NaI): $[M]^+$ *m/z* (%) calcd for $C_{82}H_{120}N_2O_8S_4$: 1388.7922 found 1388.7915 (90).



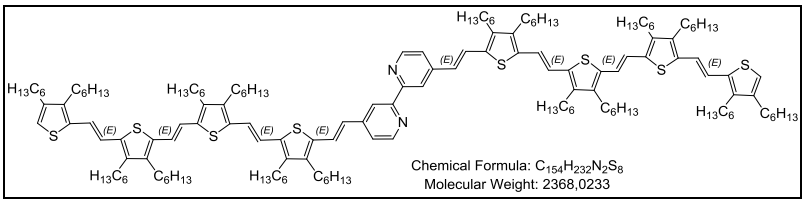
Compound 7-OH (streroisomeric mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (50 mg, 0.27 mmol) in THF (5 mL), a 1.8 M solution of LDA in heptane/THF (0.4 mL; 0.72 mmol) and a solution of **13c** (400 mg, 0.72 mmol) in THF (5 mL). The crude was purified by flash chromatography on a small plug of SiO_2 gel using first CH_2Cl_2 as eluent to remove nonpolar residual products such the excess of unreacted aldehyde **13c**, then CH_2Cl_2/MeOH 9:1 with 1 % of Et_3N to recover the product. Diol **7-OH** (350 mg; 0.27 mmol) was obtained as a light yellow-orange solid in 99 % yield, and used as well in the next step. ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.47 (d, ^3J = 4.5 Hz, 2H; 2Ar*H* bipy), 8.26 (s, 2H; 2Ar*H* bipy), 7.15 (br s, 2H; 2Ar*H* bipy), 7.03 (d, $^3J_{trans}$= 16 Hz, 2H; 2C=C*H*), 6.98 (d, $^3J_{trans}$= 16 Hz, 2H; 2C=C*H*), 6.74 (s, 2H; 2Ar*H*), 5.25 (m, 2H; 2*C*H*OH), 3.15 (m, 4H; 2*CC*H*H´+ 2*CC*H´*H), 2.67–2.57 (m, 4H; 2ArCH_2), 2.57–2.44 (m, 8H; 4ArCH_2), 2.44–2.25 (m, 4H; 2ArCH_2), 1.68–1.57 (m, 4H; 2CH_2), 1.56–1.11 (m, 60H; 30CH_2), 0.98–0.77 (m, 24H).



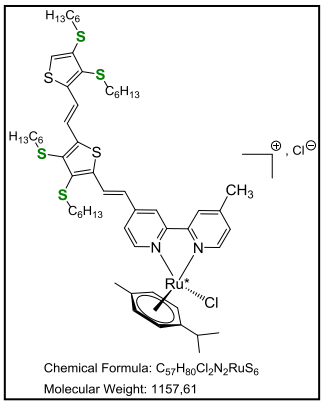
Compound 7: Prepared according to the general procedure with **7-OH** (350 mg, 270 µmol) and PTPS (27 mg, 107 µmol) in benzene (25 mL) and a 1g/l solution of I_2 in toluene (2 mL; 8 µmol, 3 mol%), reflux for 36h (during the reaction, the colour of the solution turned progressively from yellow to deep dark-red; after addition of Et_3N (0.5 mL), the solution turned bright deep-yellow). Crude was purified by flash chromatography column on SiO_2 gel (eluent CH_2Cl_2 1% Et_3N). Purification was achieved by three successive recrystallizations in hexane at low temperature (- 20°C), affording compound **3** (251 mg, 199 µmol) in 74% yield as an orange solid. UV-vis (CH_2Cl_2), $\lambda_{max}(\varepsilon)$: 246 nm (38 100), 312 nm (35 300), 439 nm (50 900). ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.66 (d, ^3J = 5 Hz, 2H), 8.48 (s, 2H), 7.58 (d, $^3J_{trans}$= 16 Hz, 2H), 7.37 (d, ^3J = 5 Hz, 2H), 7.09 (d, $^3J_{trans}$= 15.5 Hz, 2H), 7.00 (d, $^3J_{trans}$= 15.5 Hz, 2H), 6.90 (d, $^3J_{trans}$= 16 Hz, 2H), 6.80 (s, 2H), 2.72–2.57 (m, 12H), 2.51 (t, ^3J = 8 Hz, 4H), 1.66 (q, ^3J = 8 Hz, 4H), 1.60–1.49 (m, 12H), 1.48–1.29 (m, 48H), 0.98–0.89 (m, 24H). APT ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm): 156.5, 149.3, 145.8, 143.9, 143.4, 141.2, 140.5, 137.1, 136.7, 133.5, 124.6, 121.0, 120.3, 118.8, 118.3, 118.1, 31.7 (2s), 31.6 (2s), 31.4, 31.2, 31.0, 29.6, 29.4, 29.3, 29.2, 29.0, 27.1, 27.0, 22.7, 22.6, 14.2, 14.1. MS (MALDI-TOF, dithranol): *m/z* (%) found: 1261.9 (100), 1262.9 (90) $[M+H]^+$. HR-MS (MALDI-TOF, dithranol + PEGNa1000 + PEGNa1500): $[M+H]^+$ *m/z* (%) calcd for $C_{82}H_{121}N_2S_4$: 1261.8407 (100); found 1261.8390 (100).



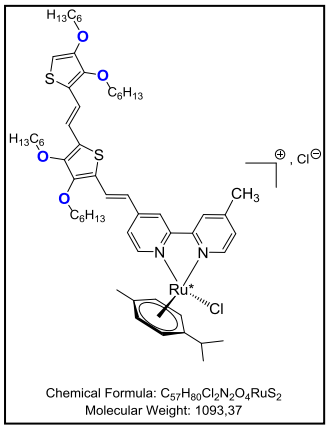
Compound 8-OH (streroisomeric mixture): Prepared according to the general procedure with 4,4'-dimethyl-2,2'-bipyridine (28 mg, 152 µmol) in THF (5 mL), a 2M solution of LDA in heptane/THF (0.18 mL; 360 µmol) and a solution of **15** (500 mg, 450 µmol) in THF (4 mL). The crude was purified by flash chromatography column on SiO_2 using first CH_2Cl_2 as eluent to remove nonpolar residual products such the excess of aldehyde **15**, then CH_2Cl_2/MeOH 9:1 with 1 % of Et_3N. Diol **8-OH** was obtained as a dark purple solid and used as well in the next step (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.54 (d, ^3J = 5 Hz, 2H; 2Ar*H* bipy), 8.37 (s, 2H; 2Ar*H* bipy), 7.18 (d, ^3J = 5 Hz, 2H; 2Ar*H* bipy), 7.03 (br s, 12H; 12C=*CH)*, 6.78 (s, 2H; 2Ar*H*), 5.28 (m, 2H; *C*H*OH), 3.42–3.03 (m, 4H; 2*CC*H*H´+2*CC*H´*H), 2.84–2.31 (m, 32H; 16ArCH_2), 1.73–1.11 (m, 128H; 64CH_2), 1.06–0.79 (m, 48H; 16CH_3).



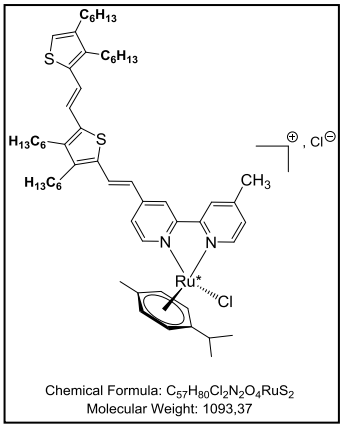
Compound 8: Prepared according to the general procedure with **8-OH** (152 µmol) and PTPS (30 mg, 119 µmol) in toluene (40 mL), and a 10.6 mM solution of I_2 in toluene (0.4 mL, 4.3 µmol; 3 mol%) reflux for 48h (during the reaction, the solution turned progressively from orange-reddish to deep dark purple-blue; after addition of Et_3N (0.5 mL), the solution turned bright deep-purple). After evaporation of toluene, the obtained crude was re-dissolved in a minimum amount of toluene, filtrated through a small plug of Celite (toluene) and purified by size-eclusion column chromatography (eluent toluene), followed by column chromatography on SiO_2 (eluent CH_2Cl_2 containing 0.5% MeOH and 0.2% Et_3N). After evaporation of solvents, purification was achieved by trituration of the resulting solid in a copious amount of MeOH. The fine black suspension was filtrated through a small plug of celite and washed with MeOH. The filtrates were discarded and the insoluble remaining solid recovered with CH_2Cl_2. The solution was evaporated to dryness, to afford compound **8** (360 mg, 152 µmol) as a dark purple solid in quantitative yield (2 steps). UV-vis (CH_2Cl_2), λ_{max}/nm (ε): 298 (77 700), 354 (37 600), 525 (162 000), 560 (br sh, 133 500). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.69 (d, ^3J = 5 Hz, 2H), 8.50 (s, 2H), 7.60 (d, $^3J_{trans}$= 16 Hz, 2H), 7.60 (d, $^3J_{trans}$= 16 Hz, 2H), 7.11 (d, $^3J_{trans}$= 15.5 Hz, 2H), 6.93 (d, $^3J_{trans}$= 15.5 Hz, 2H), 7.03 (br s, 10H), 7.01 (d, $^3J_{trans}$= 15 Hz, 2H), 2.66 (br s, 28H), 2.52 (t, ^3J = 8 Hz, 4H), 1.75–1.28 (m, 128H), 1.04–0.87 (m, 48H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 156.6, 149.4, 145.8, 144.0, 143.4, 142.2, 141.6 (2s), 141.4, 140.0, 137.4, 137.1, 135.7, 135.2, 134.9, 134.8, 133.8, 124.8, 124.5, 120.5, 120.3, 120.0, 119.7, 119.3, 119.2, 119.0, 118.2, 118.0, 31.7 (2s), 31.6 (2s), 31.5, 31.3, 31.2, 30.9, 29.7, 29.4 (3s), 29.3 (2s), 29.0, 27.1, 27.0, 26.9, 22.7, 22.6, 14.2, 14.1 (2s). MS (MALDI-TOF, DCTB): *m/z* (%) found: 2367.4 (100) $[M]^+$. HRMS (MALDI-TOF, DCTB + PMMANa 2100 + NaI): $[M]^+$ *m/z* (%) calcd for $C_{154}H_{232}N_2S_8$: 2365.5976 (52); found: 2365.6011 (53).



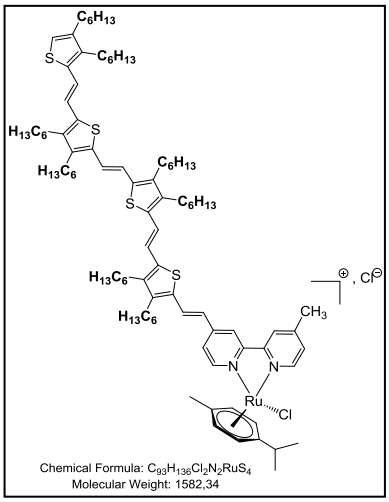
Compound Ru[1] (two enantiomers, racemic): prepared according to the general procedure with **1** (21.6 mg, 25.4 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (8.65 mg, 14.1 µmol) in a mixture of $CHCl_3$ (2 mL) and EtOH (2 mL). Crude product was obtained as a bright red pasty solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.72 (br s, 1H), 9.72 (br s, 1H), 8.07 (s, 1H), 8.02 (br s, 1H), 7.98 (s, 1H), 7.85–7.74 (m, 1H), 7.69–7.43 (m, 3H), 6.96 (d, 1H, $^3J_{trans}$ = 16 Hz), 6.84 (s, 1H), 6.29 (br s, 2H), 6.14 (br s, 2H), 3.00–2.64 (m, 9H), 2.58 (s, 3H), 2.28 (s, 3H), 1.70 (app quint, $^3J \approx 7$ Hz, 2H), 1.60–1.34 (m, 14H), 1.34–1.15 (m, 16H), 1.06 (d, $^3J = 6$ Hz, 6H), 0.92–0.75 (m, 12H).



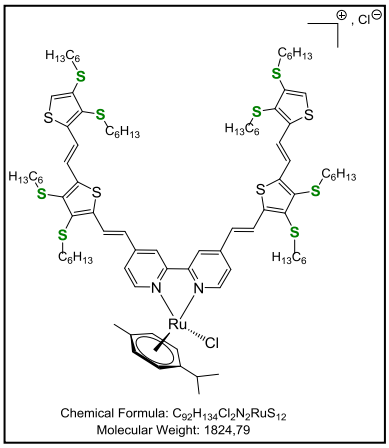
Compound Ru[2] (two enantiomers, racemic): prepared according to the general procedure with **2** (28.7 mg, 36.5 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (12.8 mg, 20.9 µmol) in a mixture of $CHCl_3$ (3 mL) and EtOH (3 mL). Crude product was obtained as a deep red pasty solid (yield supposed to be quantitative). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.58 (d, 1H, ^3J = 6 Hz), 9.55 (d, 1H, ^3J = 6 Hz), 7.89 (br s, 2H), 8.24 (br d, 1H, $^3J \approx 6$ Hz), 7.57 (d, 1H, $^3J_{trans}$ = 16 Hz), 7.53 (br s, 1H), 7.04 (d, 1H, $^3J_{trans}$ = 16 Hz), 6.94 (d, 1H, $^3J_{trans}$ = 16 Hz), 6.67 (d, 1H, $^3J_{trans}$ = 16 Hz), 6.62 (d, 2H, ^3J = 6 Hz), 6.06 (d, 2H, ^3J = 6 Hz), 6.05 (s, 1H), 4.13 (t, ^3J = 6.5 Hz, 2H), 4.09 (t, ^3J = 6.5 Hz, 2H), 4.01 (t, ^3J = 6.5 Hz, 2H), 3.93 (t, ^3J = 6.5 Hz, 2H), 2.66 (m, ^3J = 7 Hz, 1H), 2.51 (s, 3H), 2.24 (s, 3H), 1.76 (app quint, $^3J \approx 7$ Hz, 8H), 1.53–1.18 (m, 24H), 1.01 (d, ^3J = 7 Hz, 6H), 0.95–0.77 (m, 12H).



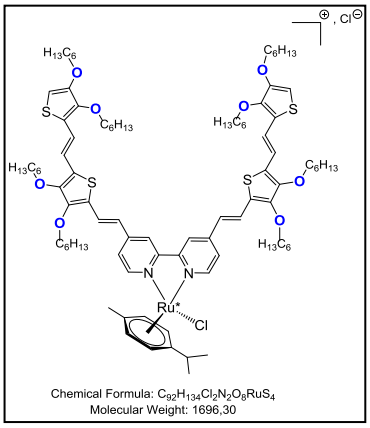
Compound Ru[3] (two enantiomers, racemic): prepared according to the general procedure with **3** (25.4 mg, 35.1 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (13.0 mg, 21.2 µmol) in $CHCl_3$ (3 mL) and EtOH (3 mL). Crude product was obtained as a deep red solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.59 (d, ^3J = 6 Hz, 1H), 9.49 (d, ^3J = 5.5 Hz, 1H), 7.99 (s, 1H), 7.94 (s, 1H), 7.70 (d, ^3J = 6 Hz, 1H), 6.65 (d, $^3J_{trans}$ = 16 Hz, 1H) 7.50 (d, ^3J = 5.5 Hz, 1H), 7.08 (d $^3J_{trans}$ = 15.5 Hz, 1H), 6.96 (d, $^3J_{trans}$ = 15.5 Hz,1H), 6.79 (s, 1H), 6.69 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.23 (d, ^3J = 6 Hz, 1H), 6.15 (d, ^3J = 6 Hz, 1H), 6.09 (d, ^3J = 6 Hz, 1H), 6.01 (d, ^3J = 6 Hz, 1H), 2.76–2.42 (m, 9H + 1s, 3H), 2.25 (s, 3H), 1.62 (app quint, $^3J \approx 7$ Hz, 2H), 1.57–1.20 (m, 30H), 1.02 (d, 6H, ^3J = 7 Hz), 0.94–0.84 (m, 12H)



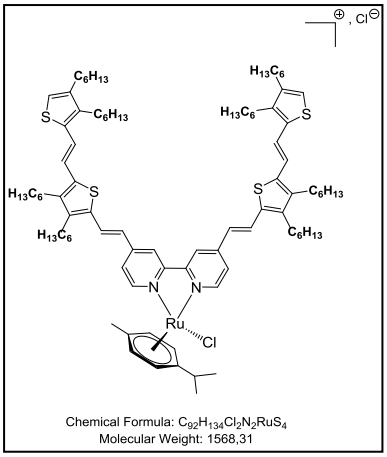
Compound Ru[4] (two enantiomers, racemic): prepared according to the general procedure with **4** (21.0 mg, 16.5 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (5.67 mg, 92.6 µmol) in $CHCl_3$ (2 mL) and EtOH (2 mL). The crude product was obtained as a dark-purple solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.58 (d, ^3J = 4.5 Hz, 1H), 9.50 (d, ^3J = 4.5 Hz, 1H), 8.01 (s, 1H), 7.96 (s, 1H), 7.76–7.71 (m, 1H), 7.69 (d, $^3J_{trans}$ = 15.5 Hz, 1H), 7.57–7.48 (m, 1H), 7.09 (d, $^3J_{trans}$ = 15.5 Hz, 1H), 6.99 (br s, 4H), 6.97 (d, $^3J_{trans}$ = 15.5 Hz, 1H), 6.74 (d, $^3J_{trans}$ = 15.5 Hz, 1H), 6.23 (d, ^3J = 5 Hz, 1H), 6.27 (d, ^3J = 5 Hz, 1H), 6.17 (d, ^3J = 5 Hz, 1H), 6.03 (d, ^3J = 5 Hz, 1H), 2.79–2.53 (m, 15H), 2.56 (s, 3H), 2.52 (t, ^3J = 8 Hz, 2H), 2.28 (s, 3H), 1.18–1.13 (m, 64H), 1.05 (d, ^3J = 6.5 Hz, 6H), 1.00–0.83 (m, 24H).



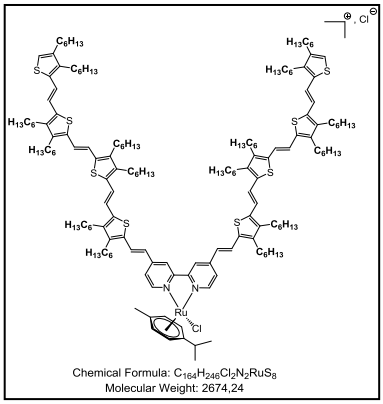
Compound Ru[5]. Prepared according to the general procedure with **5** (16.1 mg, 10.6 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (3.10 mg, 5.06 µmol) in a mixture of $CHCl_3$ (2 mL) and EtOH (2 mL). Crude product was obtained as a deep red pasty oil (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.74 (br s, 2H), 8.14–8.03 (m, 4H), 7.93–7.50 (m, 6H), 7.00 (d, $^3J_{trans}$= 16 Hz, 2H), 6.85 (s, 2H), 6.25 (br s, 4H), 3.21 (br s, 1H), 2.94 (t, ^3J = 7 Hz, 8H), 2.87 (t, ^3J = 7 Hz, 4H), 2.80 (t, ^3J = 7 Hz, 4H), 2.33 (s, 3H), 1.71 (app quint, $^3J \approx 7$ Hz, 4H), 1.62–1.36 (m, 28H), 1.36–1.17 (m, 32H), 1.12 (br s, 6H), 0.93–0.77 (m, 24H).



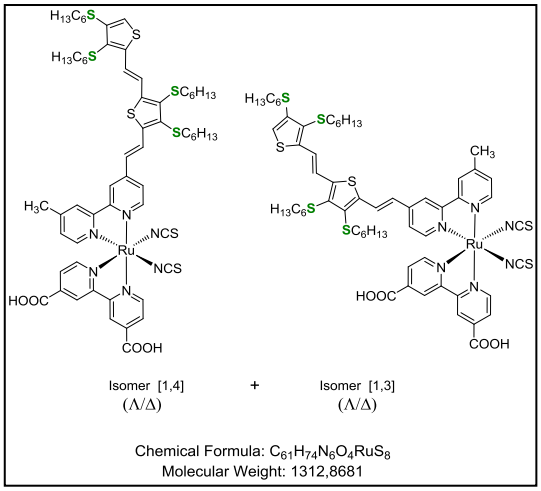
Compound Ru[6]. Prepared according to the general procedure with **6** (26.0 mg, 18.7 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (6.80 mg, 11.1 µmol) in a mixture of $CHCl_3$ (2 mL) and EtOH (2 mL). Crude product was obtained as a deep red pasty solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.54 (d, ^3J = 5.5 Hz, 2H), 7.70 (d, ^3J = 5.5 Hz, 2H), 7.61 (d, $^3J_{trans}$= 16 Hz, 2H), 7.08 (d, ^3J = 5 Hz, 2H), 6.97 (d, $^3J_{trans}$= 16 Hz, 2H),), 6.72 (d, $^3J_{trans}$= 16 Hz, 2H), 6.24 (d, ^3J = 5.5 Hz, 2H), 6.12 (d, ^3J = 5.5 Hz, 2H), 6.07 (s, 2H), 4.16 (t, ^3J = 6.5 Hz, 4H), 4.11 (t, ^3J = 6.5 Hz, 4H), 4.04 (t, ^3J = 6.5 Hz, 4H), 3.95 (t, ^3J = 6.5 Hz, 4H), 2.74 (m, ^3J = 7 Hz, 1H), 2.29 (s, 3H), 1.85–1.70 (m, 16H), 1.55–1.21 (m, 48H), 1.08 (d, ^3J = 7 Hz, 6H), 0.96–0.82 (m, 24H).



Compound Ru[7]. Prepared according to the general procedure with **7** (14.2 mg, 11.25 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (3.89 mg, 6.35 µmol) in $CHCl_3$ (2 mL) and EtOH (2 mL). The crude product was obtained as a bright deep-red solid (yield considered quantitative for this step). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.52 (br s, 2H), 7.91 (s, 2H), 7.82–7.53 (m, 4H), 7.08 (d, $^3J_{trans}$= 15.5 Hz, 2H), 6.97 (d, $^3J_{trans}$= 15.5 Hz, 2H), 6.80 (s, 2H), 6.73 (d, $^3J_{trans}$= 15.5 Hz, 2H), 6.18 (br s, 4H), 2.75–2.53 (m, 13H), 2.49 (t, 4H, ^3J = 8 Hz), 2.29 (s, 3H), 1.63 (app quint, 4H, ^3J = 8 Hz), 1.58–1.17 (m, 60H), 1.08 (br s, 6H), 0.97–0.81 (m, 24H).

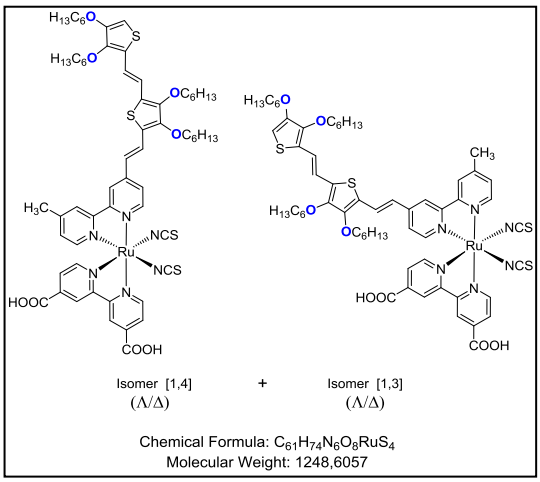


Compound Ru[8]. Prepared according to the general procedure with **8** (43.0 mg, 18.2 µmol), dichloro(*p*-cymene)-ruthenium(II) dimer (6.70 mg, 10.9 µmol) in $CHCl_3$ (2 mL) and EtOH (2 mL). The crude product was obtained as a dark-purple pasty solid (yield supposed to be quantitative). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.55 (d, 2H, ^{3}J = 6 Hz), 7.97 (s, 2H), 7.75 (d, 2H, ^3J = 6 Hz), 7.70 (d, 2H, $^3J_{trans}$ = 16 Hz), 7.10 (d, 2H, $^3J_{trans}$ = 15.5 Hz), 7.04 (d, 2H, $^3J_{trans}$ = 16 Hz), 7.01 (br s, 6H), 6.98(d, 2H, $^3J_{trans}$ = 15.5 Hz), 6.78 (d, 2H, $^3J_{trans}$ = 15.5 Hz), 6.77 (s, 2H), 6.25 (d, 2H, ^3J = 6 Hz), 6.12 (d, 2H, ^3J = 6 Hz), 2.79–2.69 (m, 4H), 2.63 (br s, 21H), 2.50 (t, ^3J =8 Hz, 4H), 2.30 (s, 3H), 1.68–1.24 (m, 128H), 1.10 (d, 6H, ^3J = 7 Hz), 1.00–0.84 (m, 48H).

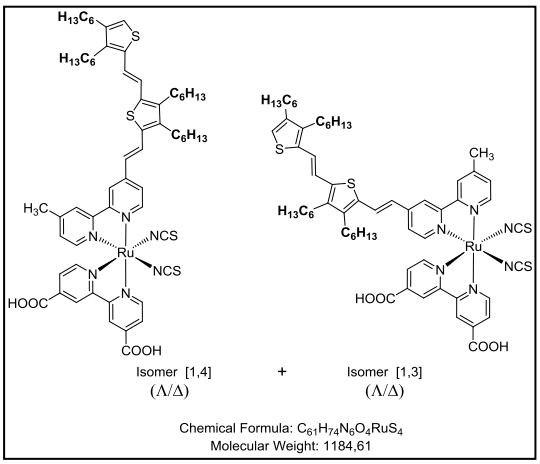


M2S (mixtures of isomers): Prepared and purified according to the general procedure described for the microwave assisted synthesis of ruthenium complexes, from **Ru[1]** (supposed to be 25.4 µmol), dcapy (7.61 mg, 3.12 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (0.5 mL) and DMF (4.5 mL). **M2S** (16.4 mg, 12.5 µmol) was obtained in a 49 % yield as a fine black powder. UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 313 (ε /dm^{3}mol^{-1} cm^{-1}: 39 940), 456 (32 300), 567 (broad sh., 19 200). ^{1}H NMR ($CDCl_3$/MeOD d^4 (7:4), 300 MHz) δ(ppm): 9.72-9.61 (m, 2H), 9.34 (d, 1H, ^{3}J = 5.5 Hz), 9.23 (d, 1H, ^{3}J = 5 Hz), 8.88 (br s, 2H), 8.73 (br s, 2H), 8.27 (s, 1H), 8.24-8.04 (m, 5H), 7.87 (d, 1H, $^3J_{trans}$ = 16.5 Hz), 7.82-7.64 (m, 3H), 7.64-7.42 (m, 7H), 7.27 (d, 1H, ^{3}J = 5.5 Hz), 7.20 (d, 1H, ^{3}J = 5.5 Hz), 7.16-7.03 (m, 3H), 6.89 (s, 1H), 6.86 (s, 1H), 6.85 (d, $^3J_{trans}$ = 16 Hz, 1H), 3.03-2.73 (m, 16H), 2.69 (s, 3H), 2.45 (s, 3H), 1.74-1.04 (m, 64H), 0.95-0.68 (m, 24H). MS (MALDI-TOF, DCTB): *m/z* (%) found 1254.3 (25) [M-(NCS)]$^+$, 1312.3 (100) [M]$^+$. HRMS (MALDI-TOF, DCTB+PMMANa1000+NaI): [M+Na]$^+$ *m/z* (%) calcd for

$^{96}RuC_{61}H_{74}N_6S_8$+Na: 1329.2505 (10), $^{102}RuC_{61}H_{74}N_6O_4S_8$+Na: 1335.2484 (100); found 1329.2437 (10), 1335.2452 (100).

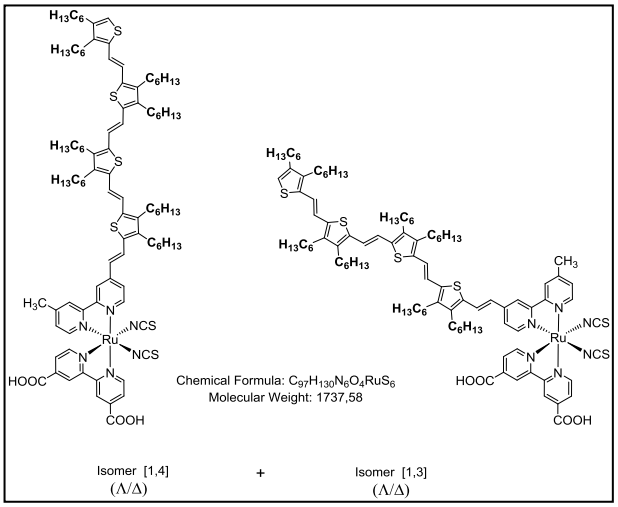


M2O (mixtures of isomers): Prepared and purified according to the general procedure described for the microwave assisted synthesis of ruthenium complexes, from **Ru[2]** (supposed to be 36.5 µmol), dcapy (12.9 mg, 52.8 µmol) and NH_4NCS (80 mg, 1.05 mmol) in PhCl (1 mL) and DMF (9mL). **M2O** (16.7 mg, 13.4 µmol) was obtained in a 37 % yield as a fine black powder. UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 310 (ε /dm^{3}mol^{-1} cm^{-1}: 38 500), 459.4 (34 700), 509 (broad sh., 28 800), 568.6 (broad sh., 21 000). ^{1}H NMR ($CDCl_3$/MeOD d^4 (7:4), 300 MHz) δ(ppm): 9.66 (pseudo d, 2H, $^3J_{apparent}$ = 6 Hz), 9.26 (d, 1H, ^3J = 6 Hz), 9.23 (d, 1H, ^3J = 5.5 Hz), 8.87 (s, 2H), 8.73 (s, 2H), 8.20 (br s, 4H), 8.13-8.01 (m, 2H), 7.74 (d, 1H, ^3J = 6 Hz), 7.70 (pseudo d, 2H, $^3J_{apparent}$ = 6 Hz), 7.68 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.62-7.51 (m, 3H), 7.43 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.18 (pseudo d, 2H, $^3J_{apparent}$ = 6 Hz), 7.07 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.99 (broad s, 1H), 7.00 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.97 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.91 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.87 (broad s, 1H), 6.86 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.61 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.12 (s, 1H), 6.10 (s, 1H), 4.18 (t, 2H), 4.14-4.90 (m, 14H), 2.68 (s, 3H), 2.43 (s, 3H), 1.61-1.90 (m, 16H), 1.60-1.07 (m, 48H), 0.98-0.70 (m, 24H). MS (MALDI-TOF, DCTB): *m/z* (%) found 1190.4 (34) [M-(NCS)]$^+$, 1248.4 (100) [M]$^+$. HRMS (MALDI-TOF, DCTB+PPGNa1000+ PPGNa2000): [M]$^+$ *m/z* (%) calcd for $^{96}RuC_{61}H_{74}N_6O_8S_4$: 1242.3521 (11), $^{102}RuC_{61}H_{74}N_6O_8S_4$: 1248.3503 (100); found 1242.3540 (11), 1248.3508 (100).

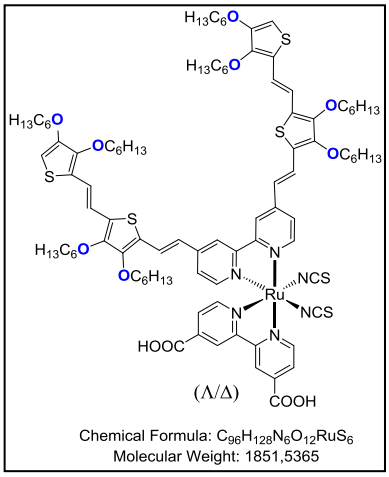


Compound M2 (mixture of isomers). Prepared and purified according to the general procedure with **Ru[3]** (35.1 µmol), dcapy (12.5 mg, 51.2 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (1 mL) and DMF (9 mL). **M2** was obtained as a fine black powder in 62 % yield (26.0 mg, 21.9 µmol). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 318 (ε /dm^{3}mol^{-1} cm^{-1}: 35 900), 463 (33 000), 506 (br sh, 29 100), 571 (br sh, 21 400). ^{1}H and 2D-COSY NMR ($CDCl_3$/MeOD d^4 (7:4), 300 MHz) δ(ppm): 9.61 (d, 1H, ^3J = 6 Hz), 9.59 (d, 1H, ^3J = 6 Hz), 9.19 (d, 1H, ^3J = 5.5 Hz), 9.17 (d, 1H, ^3J = 5.5 Hz), 8.82 (s, 2H), 8.67 (s, 2H), 8.23 (s, 1H), 8.14 (s, 1H), 8.10 (s, 1H), 8.05 (dd, 1H, ^3J = 6 Hz and ^4J = 1 Hz), 8.02 (dd, 1H, ^3J = 6 Hz and ^4J = 1.5 Hz), 7.96 (s, 1H), 7.70 (d, $^3J_{trans}$ = 15.5 Hz, 1H), 7.70 (d, ^3J = 6 Hz, 1H), 7.64 (d, 1H, ^3J = 6 Hz), 7.58–7.48 (m, 4H), 7.44 (d, ^3J =

5.5 Hz, 1H), 7.12 (d, 1H, ^3J = 6 Hz), 7.11 (d, 1H, ^3J = 6 Hz), 7.06 (d, 1H, $^3J_{trans}$ = 15.5 Hz), 7.02 (d, 1H, $^3J_{trans}$ = 15.5 Hz), 6.95 (d, 2H, $^3J_{trans}$ = 15.5 Hz), 6.82 (d, 2H, ^3J = 6 Hz), 6.80 (s, 1H), 6.79 (d, 1H, $^3J_{trans}$ = 15.5 Hz), 6.78 (s, 1H), 6.53 (d, 1H, $^3J_{trans}$ = 15.5 Hz), 2.95–2.53 (m, 15H), 2.49–2.44 (m, 4H), 2.39 (s, 3H), 1.69–1.15 (m, 64H), 0.98–0.76 (m, 24H). MS (MALDI-TOF, DCTB): *m/z* (%) found: 1126.4 (54) $[M-(NCS)]^+$, 1184.4 (100) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa1000): most abundant peak *m/z* (%) calcd for $C_{61}H_{74}N_6O_4RuS_4$: 1184.3706 (100) found 1184.3674 (100) $[M]^+$.

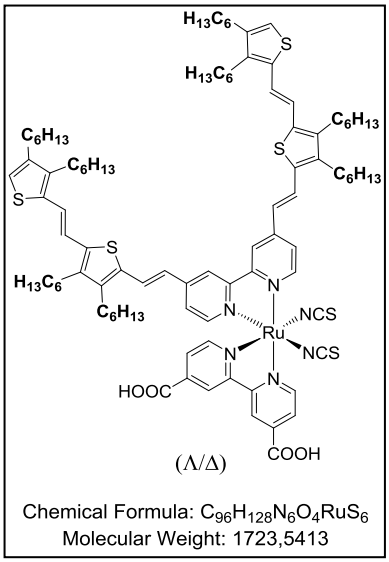


Compound M4 (mixtures of isomers): Prepared and purified according to the general procedure with **Ru[4]** (16.5 µmol), dcapy (5.08 mg, 20.8 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (0.5 mL) and DMF (4.5 mL). **M4** was obtained as a fine dark black-reddish powder in 84 % yield (24 mg, 13.8 µmol). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 305 (ε /dm^3mol^{-1} cm^{-1} : 40 100), 364 (br, 16 100), 555 (52 400). ^{1}H NMR ($CDCl_3$/MeOD-d^4 (7:4), 300 MHz) δ(ppm): 9.65 (two d, 2H, ^3J = 6 Hz), 9.24 (d, 1H, ^3J = 6 Hz), 9.21 (d, 1H, ^3J = 6 Hz), 8.84 (s, 2H), 8.69 (s, 2H), 8.18 (s, 1H), 8.17–8.10 (m, 4H), 8.09 (s, 1H), 7.99 (s, 1H), 7.74 (d, 1H, ^3J = 6 Hz), 7.68 (d, 1H, ^3J = 6 Hz), 7.63 (br s, 2H), 7.56 (d, 1H, ^3J = 6 Hz), 7.50 (d, 1H, ^3J = 6 Hz), 7.44(br s, 1H), 7.15 (two d, 2H, ^3J = 6 Hz), 7.10–6.86 (m, 16H), 6.84 (d, 1H, ^3J = 6 Hz), 6.74 (br s, 1H), 2.65 (s, 3H), 2.63–2.43 (m, 32H), 2.42 (s, 3H), 1.64–1.11 (m, 128H), 0.96–0.77 (m, 48H). MS (MALDI-TOF, DCTB): *m/z* found (%) 832.6 (100) $[3TV(C_2H_5)]^{*+}$, 1108.8 (28) $[4TV(C_2H_5)]^{*+}$, 1678.8 (22) $[M-(NCS)]^{*+}$, 1736.8 (34) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa1500 + PEGNa2000 + NaI): most abundant peak *m/z* (%) calcd for $C_{97}H_{130}N_6O_4RuS_6$: 1736.7538 (100); found 1736.7486 (100) $[M]^+$; monoisotopic mass *m/z* (%) calcd for $^{92}RuC_{97}H_{130}N_6O_4S_6$: 1730.7548 (8); found 1730.7555 (14) $[M]^+$.

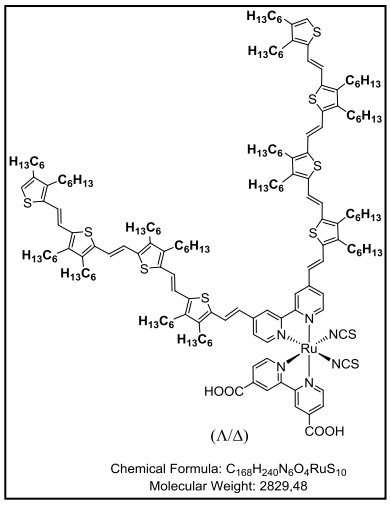


Compound B2O: Prepared and purified according to the general procedure described for the microwave assisted synthesis of ruthenium complexes, from **Ru[6]** (supposed to be 18.7 µmol), dcapy (6.31 mg, 25.8 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (0.5 mL) and DMF (4.5 mL). **TT-237** (24.7 mg, 13.3 µmol) was obtained in a 71 % yield as a fine black-reddish powder. UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 320 (ε /dm^3mol^{-1} cm^{-1}: 52 000), 464 (69 500), 580 (broad, 34 100). ^{1}H NMR ($CDCl_3$/MeOD d^4 (7:4), 300 MHz) δ(ppm): 9.65 (d, 1H, ^{3}J = 6 Hz), 9.25 (d, 1H, ^{3}J = 6 Hz), 8.87 (s, 1H), 8.73 (s, 1H), 8.20 (s, 1H), 8.15 (d, 1H, ^{3}J = 6 Hz), 8.06 (s, 1H), 7.72 (d, ^{3}J = 6 Hz, 1H), 7.69 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.67 (d, ^{3}J = 6 Hz, 1H), 7.58 (d, 1H, ^{3}J = 6 Hz), 7.44 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.18 (d, 2H, ^{3}J = 6 Hz), 7.08 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.01 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.96 (broad s, 1H), 6.98 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.91 (d, $^3J_{trans}$ = 16

Hz, 1H), 6.87 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.64 (d, $^3J_{trans}$ = 16 Hz, 1H), 6.11 (s, 1H), 6.09 (s, 1H), 4.19 (t, ^3J = 6.5 Hz, 2H), 4.15-3.87 (m: 7 x t, $^3J \approx$ 6-7 Hz, 14H), 1.90-1.64 (m, 18H), 1.61-1.16 (m, 48H), 0.99-0.74 (m, 24H). MS (MALDI-TOF, DCTB): *m/z* (%) found 1792.6 (23), 1793.6 (22), 1794.6 (23) $[M-(NCS)]^+$, 1850.6 (100), 1851.6 (86), 1852.6 (89) $[M]^+$. HRMS (MALDI-TOF, DCTB+PPGNa2000): $[M]^+$ *m/z* (%) calcd for $^{96}RuC_{96}H_{128}N_6O_{12}S_6$: 1844.6985 (8), $^{102}RuC_{96}H_{128}N_6O_{12}S_6$: 1850.6975 (100); found 1844.6934 (7), 1850.6962 (100).



Compound B2: Prepared and purified according to the general procedure with **Ru[7]** (11.25 µmol), dcapy (3.54 mg, 14.5 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (0.5 mL) and DMF (4.5 mL). **B2** was obtained as a fine dark black-reddish powder in 92 % yield (18 mg, 10.4 µmol). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 320 (ε /dm^{3}mol^{-1} cm^{-1}: 46 600), 465 (57 100), 578 (br sh, 28 800). ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm): 9.56 (d, 1H, ^3J = 5 Hz), 9.20 (d, 1H, ^3J = 5 Hz), 8.82 (s, 1H), 8.68 (s, 1H), 8.16 (s, 1H), 8.12–7.90 (br s, 1H), 8.07 (s, 1H), 7.73 (d, $^3J_{trans}$= 16 Hz, 1H), 7.72 (d, 1H, ^3J = 6 Hz), 7.59 (br s, 1H), 7.54 (d, 1H, ^3J = 6 Hz), 7.17–6.96 (m, 7H), 6.86 (d, $^3J_{trans}$= 16 Hz, 1H), 6.79 (s, 1H), 6.76 (s, 1H), 6.63 (d, $^3J_{trans}$= 16 Hz, 1H), 2.81 (br s, 2H), 2.61 (m, 10H), 2.49 (d, 2, ^3J = 8 Hz), 2.44 (d, 2H, ^3J = 8 Hz), 1.67–1.14 (m, 64H), 0.95–0.74 (m, 24H). MS (MALDI-TOF, DCTB): *m/z* (%) found: 1664.8 (98) $[M-(NCS)]^{*+}$, 1722.8 (100) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa2000): most abundant peak *m/z* (%) calcd for $C_{96}H_{128}N_6O_4Ru\ S_6$: 1722.7382 (100); found 1722.7357 (100) $[M]^+$; monoisotopic mass: *m/z* (%) calc. for $^{92}RuC_{96}H_{128}N_6O_4S_6$: 1716.7392 (8); found 1716.7366 (10) $[M]^+$.



Compound B4: Prepared and purified according to the general procedure with **Ru[8]** (18.2 µmol), dcapy (6.28 mg, 10.25 µmol) and NH_4NCS (50 mg, 657 µmol) in PhCl (0.5 mL) and DMF (4.5 mL). **B4** was obtained as a fine dark purple-black powder in 95 % yield (49 mg, 17.3 µmol). UV-Vis: $\lambda_{max}(CH_2Cl_2)$/nm = 303 (ε /dm^{3}mol^{-1} cm^{-1}: 70 800), 534 (111 300). ^{1}H NMR ($CDCl_3$/MeOD-d^4 (7:4), 300 MHz) δ(ppm): 9.56 (d, 1H, ^3J = 6 Hz), 9.29 (d, 1H, ^3J = 6 Hz), 8.89 (s, 1H), 8.76 (s, 1H), 8.14 (bs, 2H), 8.00 (s, 1H), 7.74 (bs, 2H), 7.68 (d, 1H, ^3J = 6 Hz), 7.56 (d, 1H, ^3J = 6 Hz), 7.45 (d, 1H, $^3J_{trans}$ = 16 Hz), 7.25–6.79 (m, 12H), 6.73 (bs, 6H), 2.84–2.20 (m, 32H), 1.68–1.01 (m, 128H), 1.00–0.62 (m, 48H). MS (MALDI-TOF, DCTB): *m/z* (%) found 832.6 (100) $[3TV(C_2H_5)]^{*+}$, 1108.7 (11) $[4TV(C_2H_5)]^{*+}$, 2771.4 (2) $[M-(NCS)]^{*+}$, 2829.4 (7) $[M]^+$. HRMS (MALDI-TOF, DCTB + PEGNa3400): *m/z* (%) most abundant peak calcd for $C_{168}H_{240}N_6O_4RuS_{10}$: 2829.5054 (100); found 2829.5075 (100) $[M]^+$.

II. NMR SPECTROSCOPY

^{1}H NMR spectra were obtained on Bruker TopSpin AV-300 (300 MHz) and AV-400 (400 MHz) spectrometers. Unless noted, chemical shifts are reported in parts per million (ppm) relative to the chloroform solvent residual peak ($CDCl_3$, 7.27 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.0 ppm). In the particular cases of the heteroleptic ruthenium complexes, ^{1}H NMR spectra were performed in mixtures of $CDCl_3$ and MeOD d^4 (7:4 or 8:3). Lock was performed on methanol signal and spectra were systematically calibrated on the multiplet residual solvent peak of MeOD d^4 at 3.31 ppm. Under these conditions, we observed that the residual solvent peak of chloroform appeared at around 7.40-7.50 ppm. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants, *J*, are given in Hz. ^{1}H-decoupled ^{13}C NMR spectra were obtained on a Bruker TopSpin *AV-300* (75 MHz) and *AV-400* (100 MHz) spectrometers.

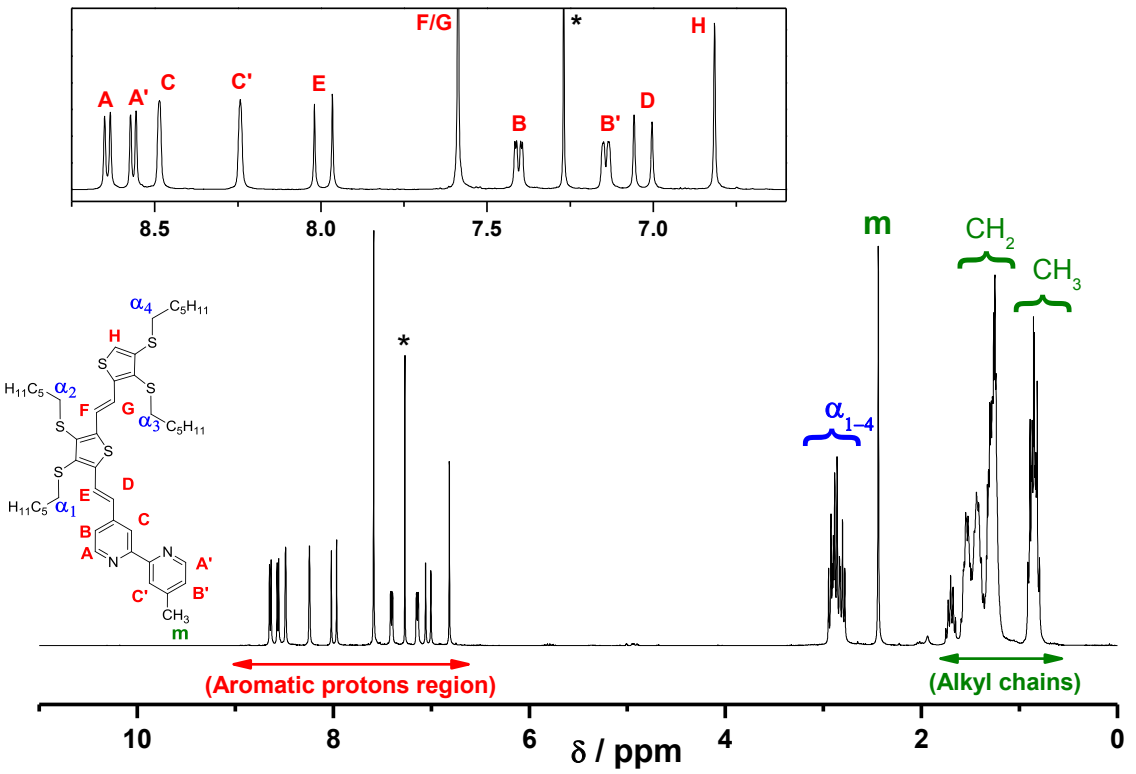


Figure S1. ^{1}H NMR spectrum of **1** ($CDCl_3$, 300MHz; *denotes the $CHCl_3$ residual peak of $CDCl_3$ solvent).

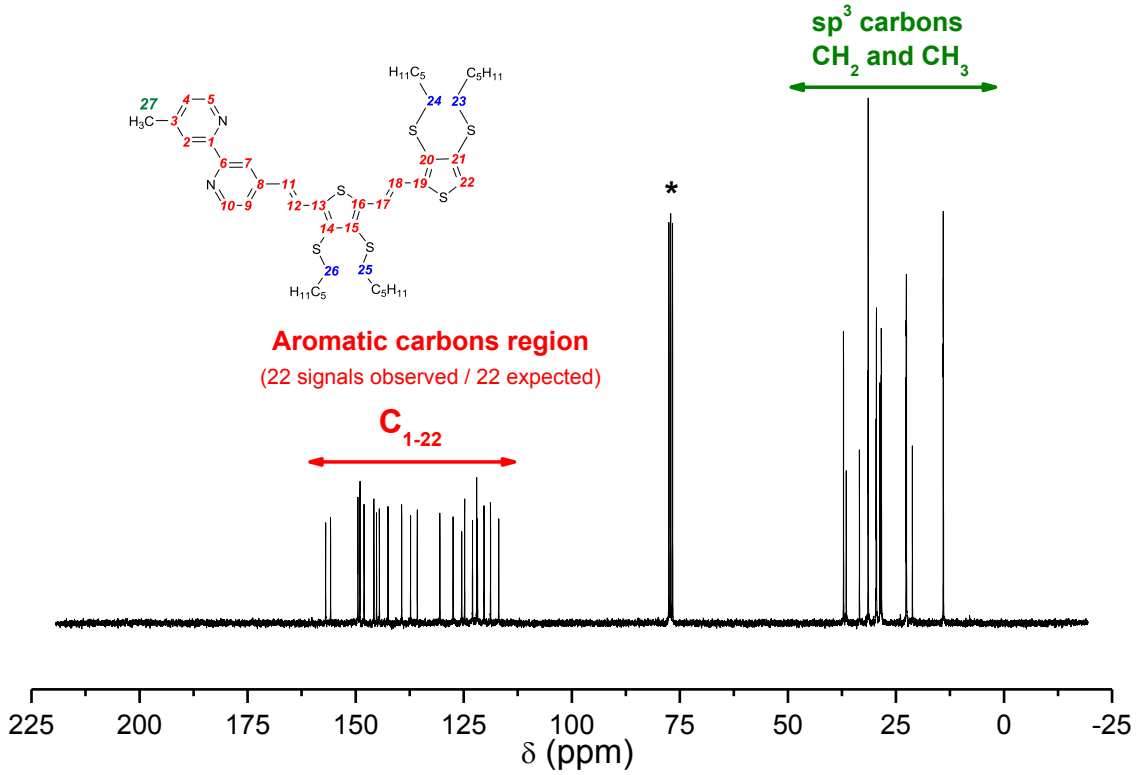


Figure S2. ^{13}C NMR spectrum of **1** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent).

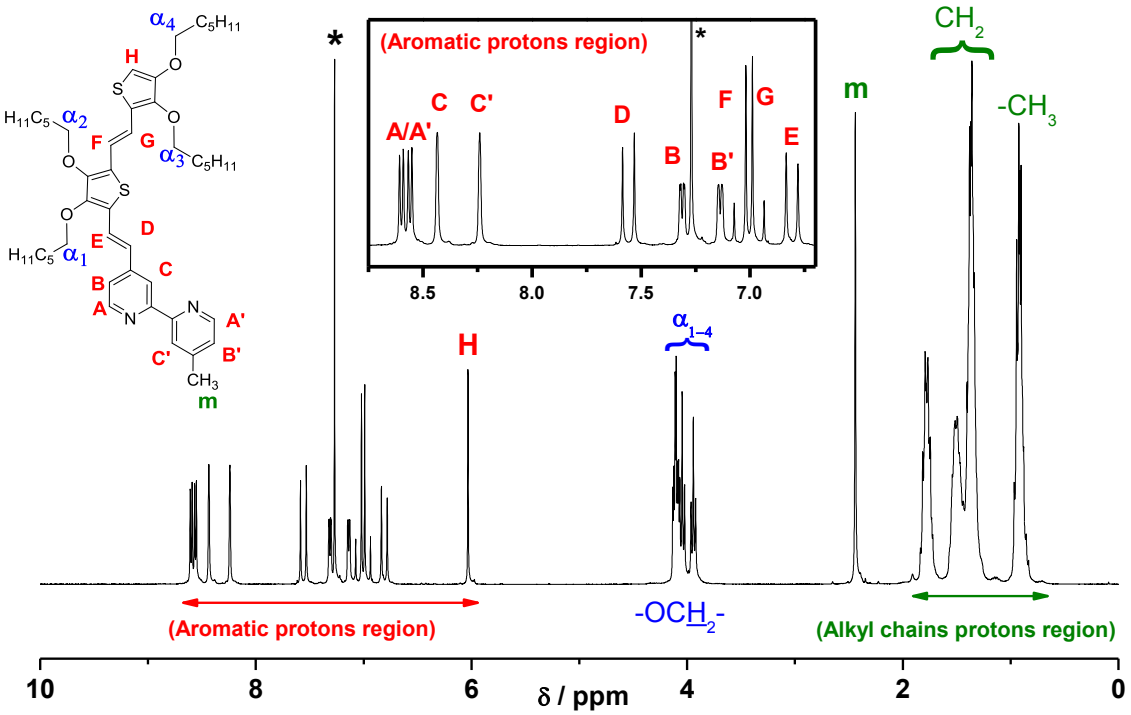


Figure S3. ^{1}H NMR spectrum of **2** ($CDCl_3$, 300MHz; *denotes the $CHCl_3$ residual peak of $CDCl_3$ solvent).

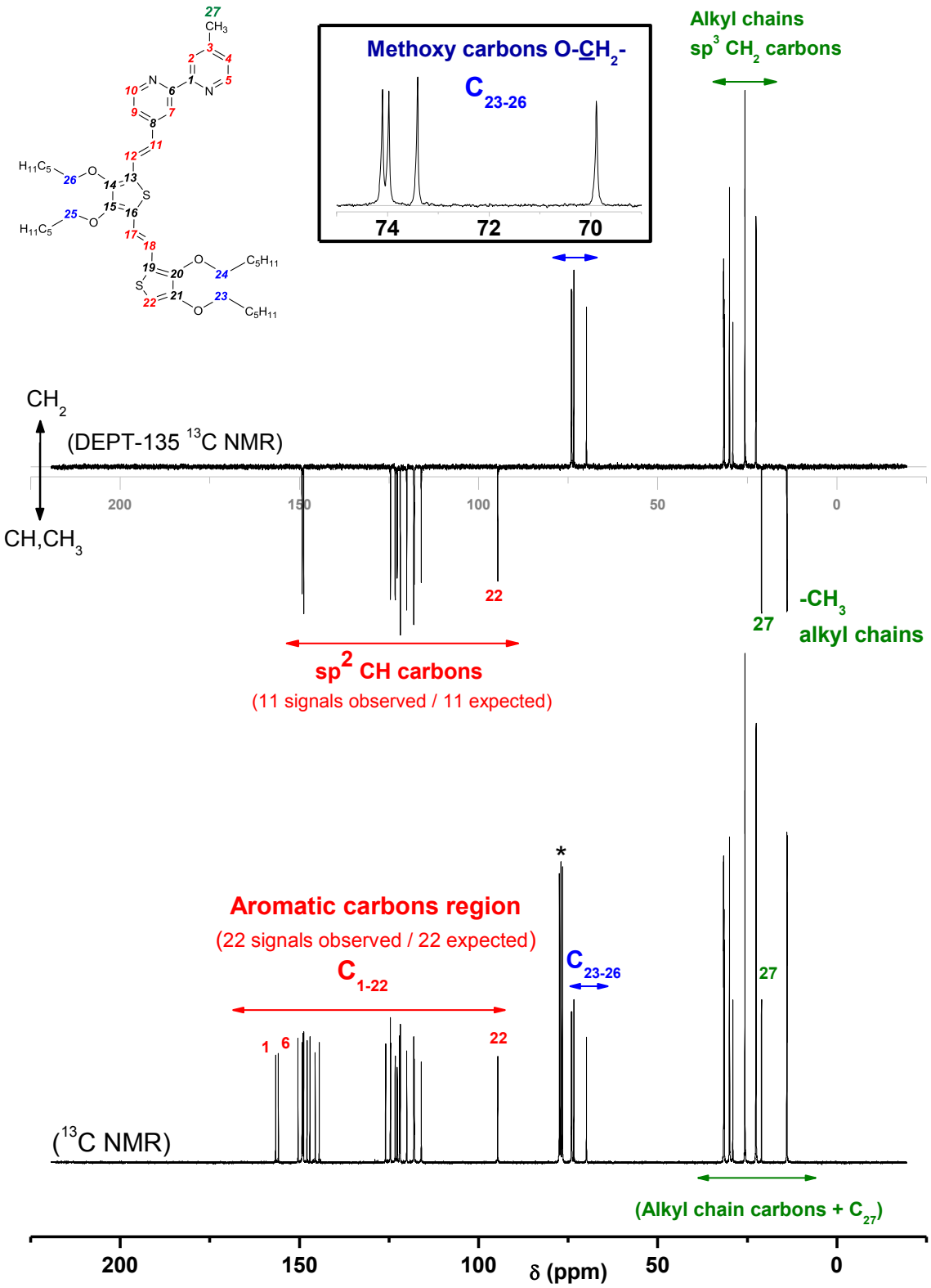


Figure S4. DEPT-135 (Top) and ^{13}C (bottom) NMR spectra of **2** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent).

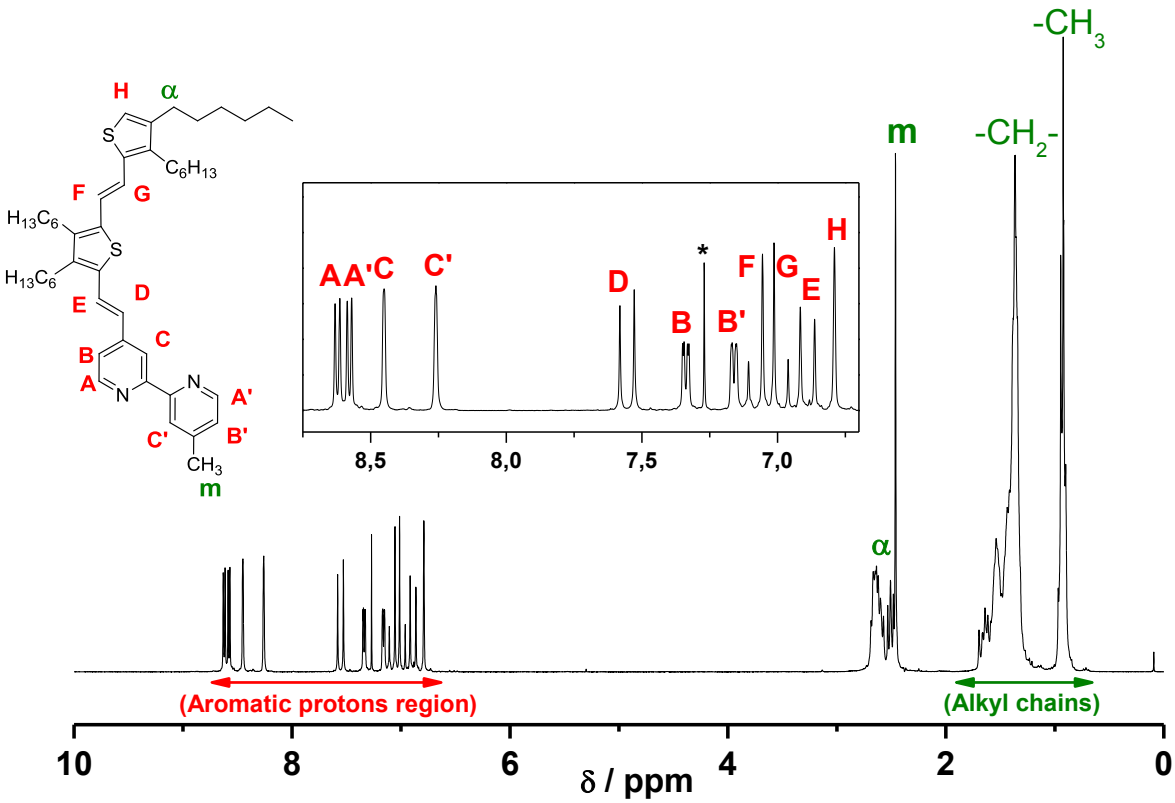


Figure S5. ^{1}H NMR spectrum of **3** ($CDCl_3$, 300MHz; *denotes the $CHCl_3$ residual peak of $CDCl_3$ solvent).

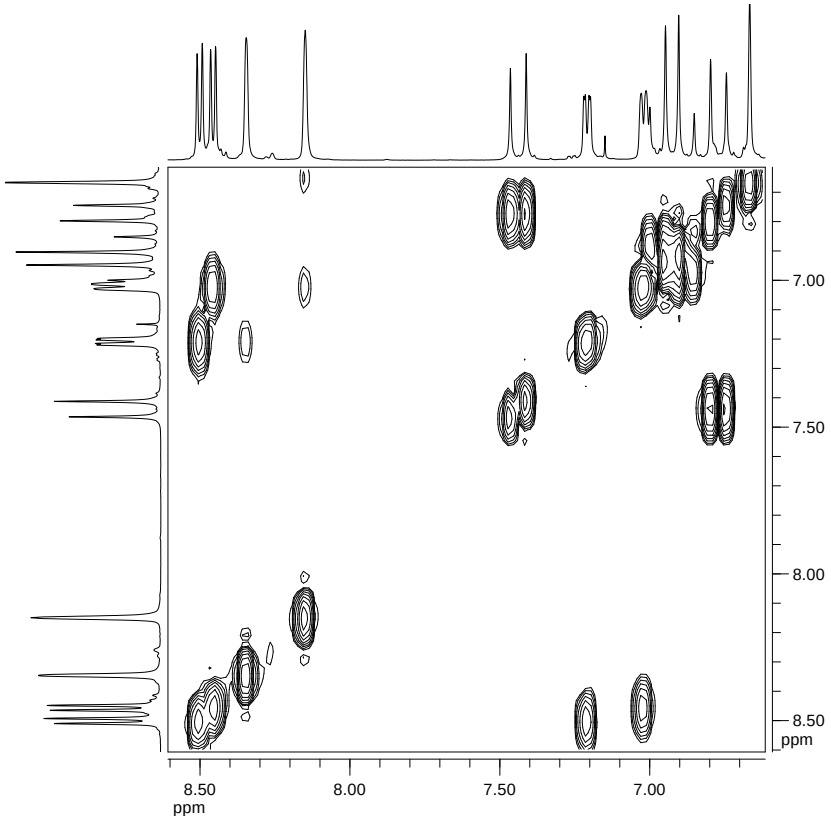


Figure S6. 2D-COSY 45 ^{1}H/^{1}H NMR spectrum of **3** ($CDCl_3$, 300 MHz; aromatic protons region).

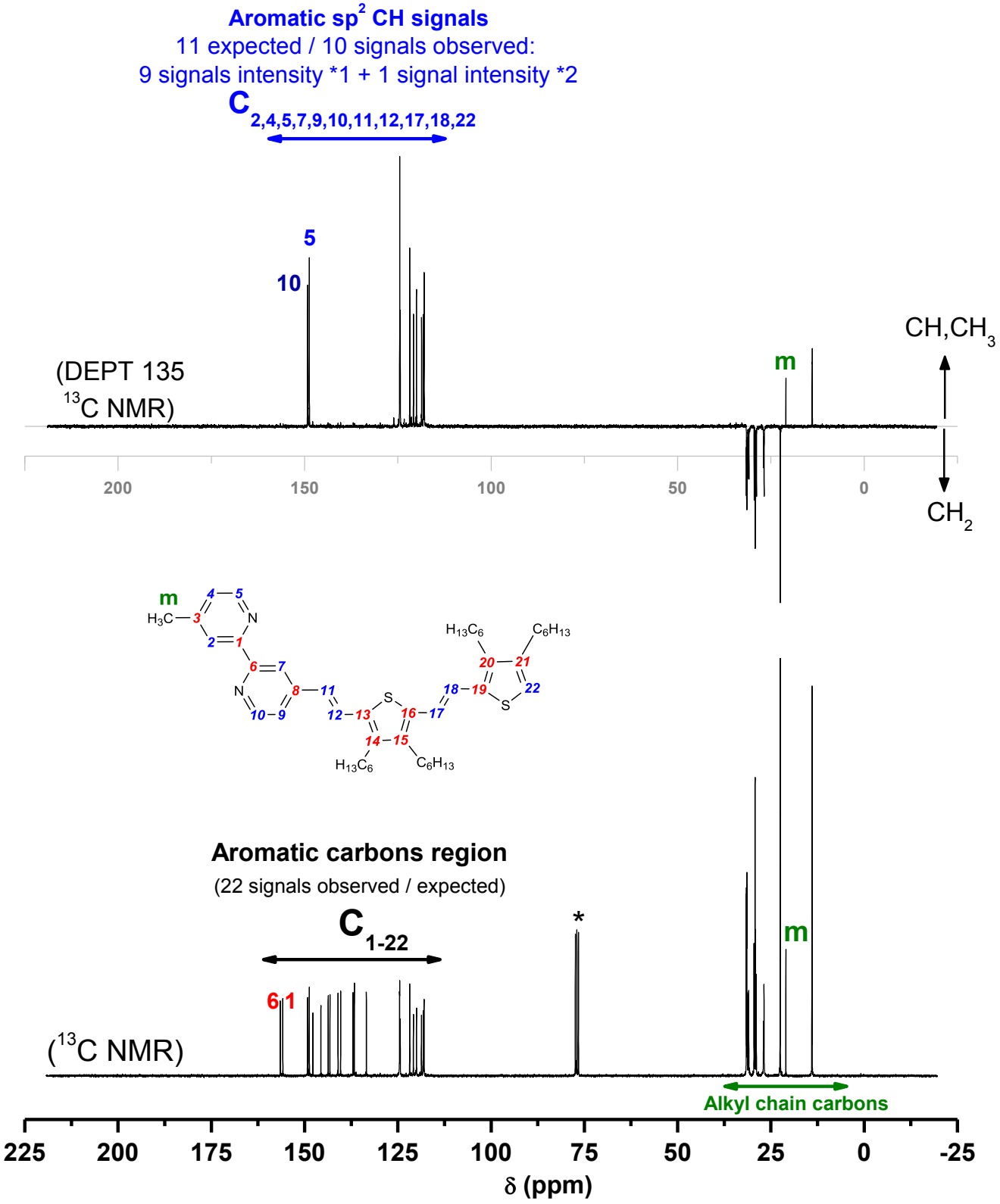


Figure S7. DEPT 135 (top) and ^{13}C (bottom) NMR spectra of **3** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent).

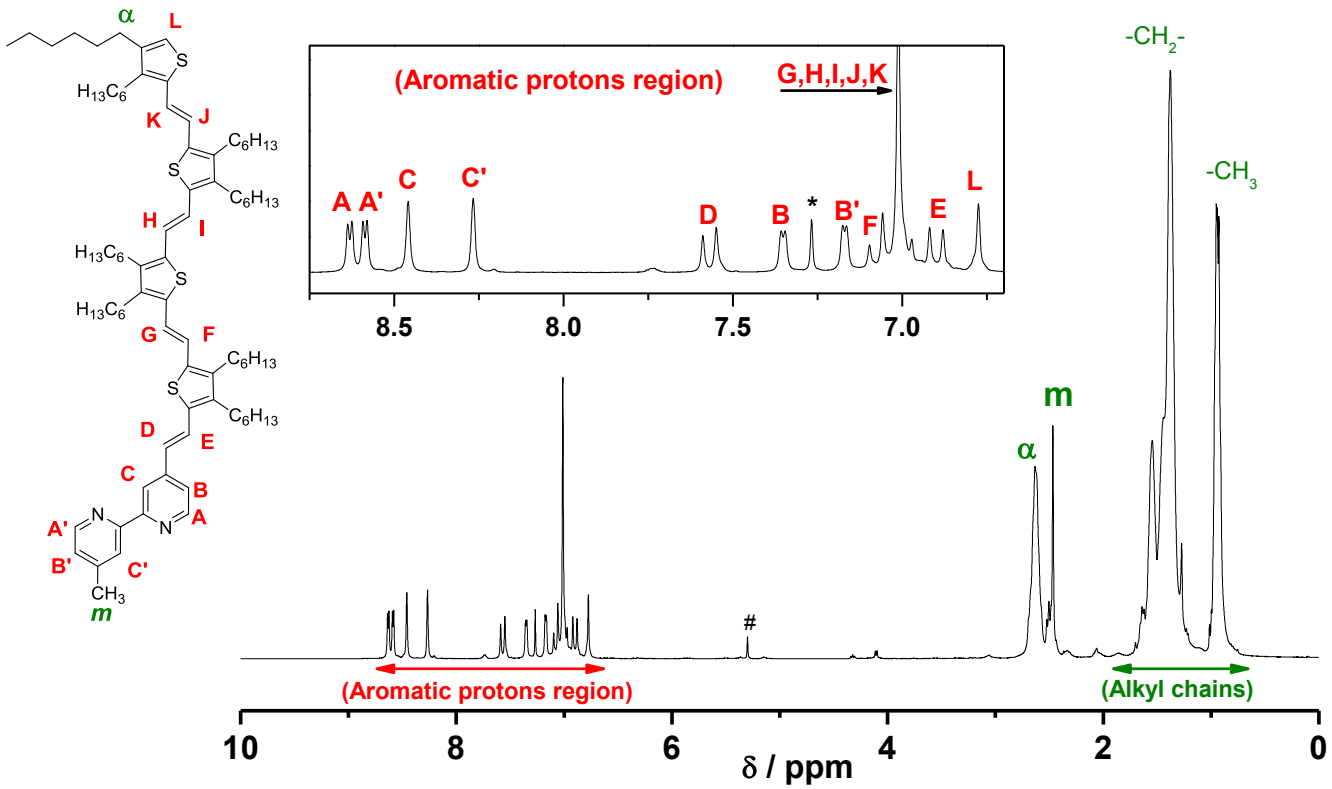


Figure S8. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz; * denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # a peak due to an impurity: CH_2Cl_2 solvent).

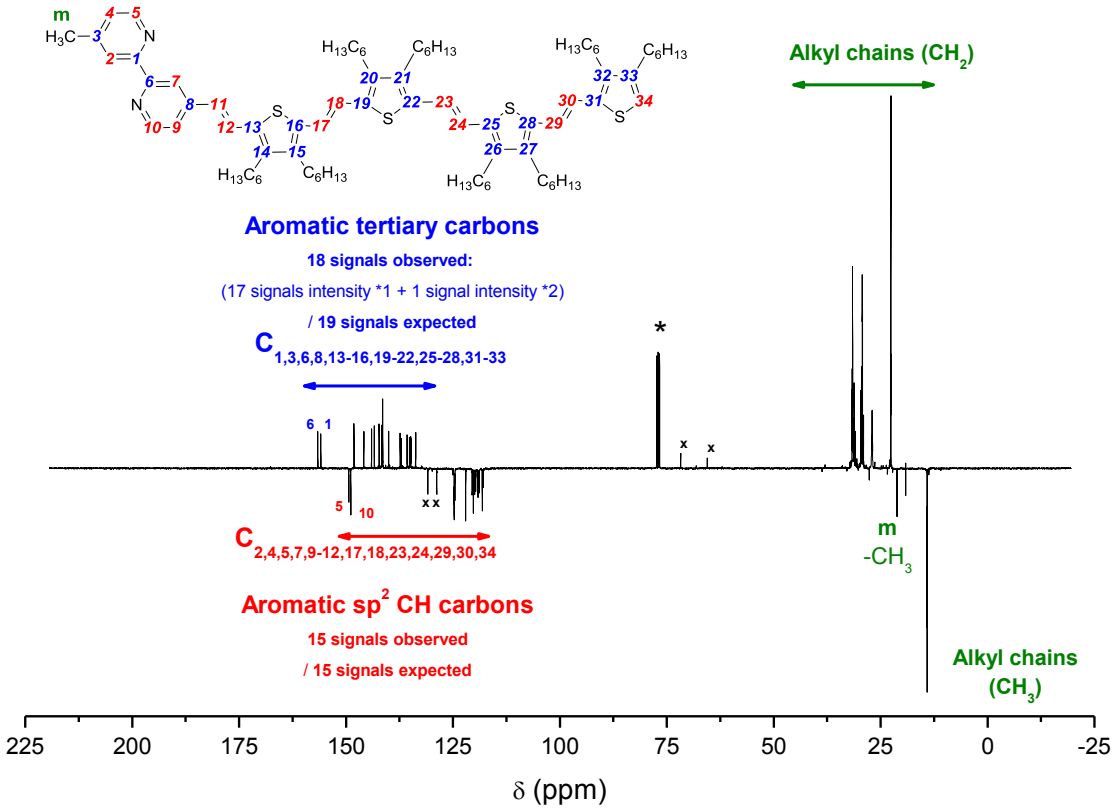


Figure S9. APT ^{13}C NMR spectrum of **4** ($CDCl_3$, 100 MHz; * denotes the signal of the $CDCl_3$ solvent, and **x** an impurity).

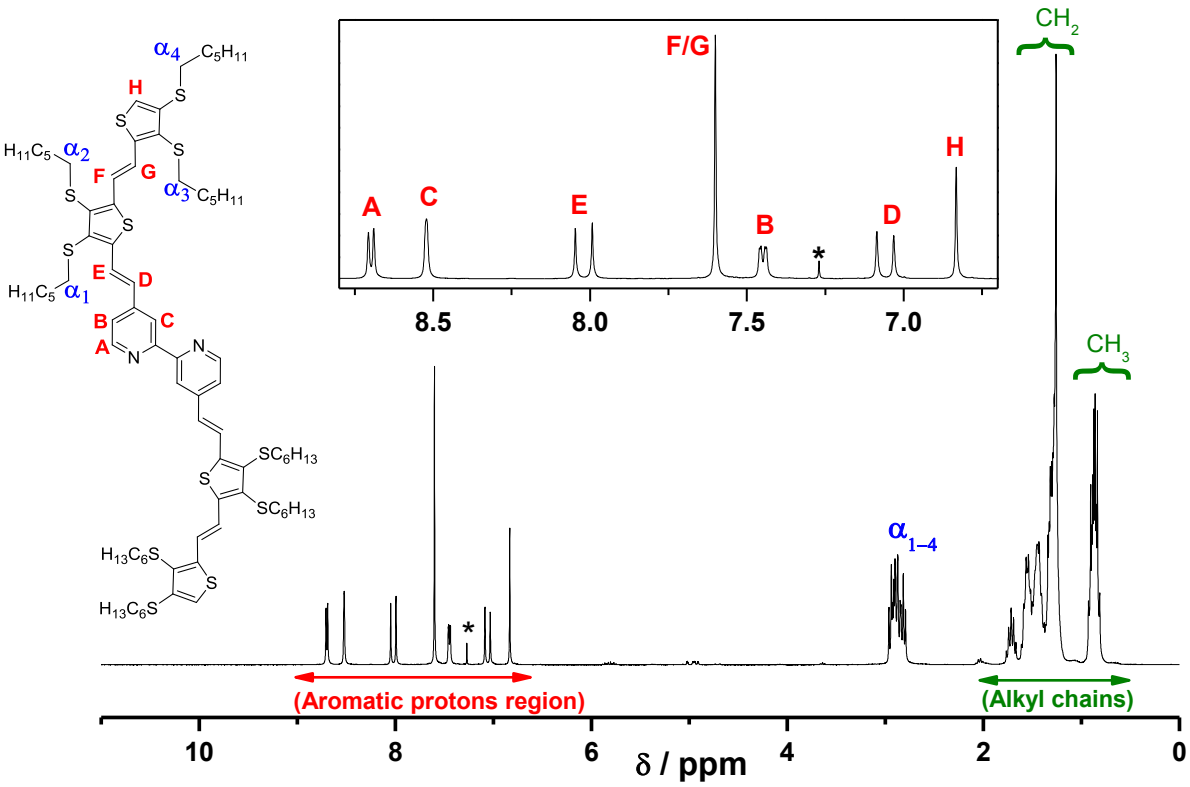


Figure S10. ^{1}H NMR spectrum of **5** ($CDCl_3$, 300MHz; * denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent).

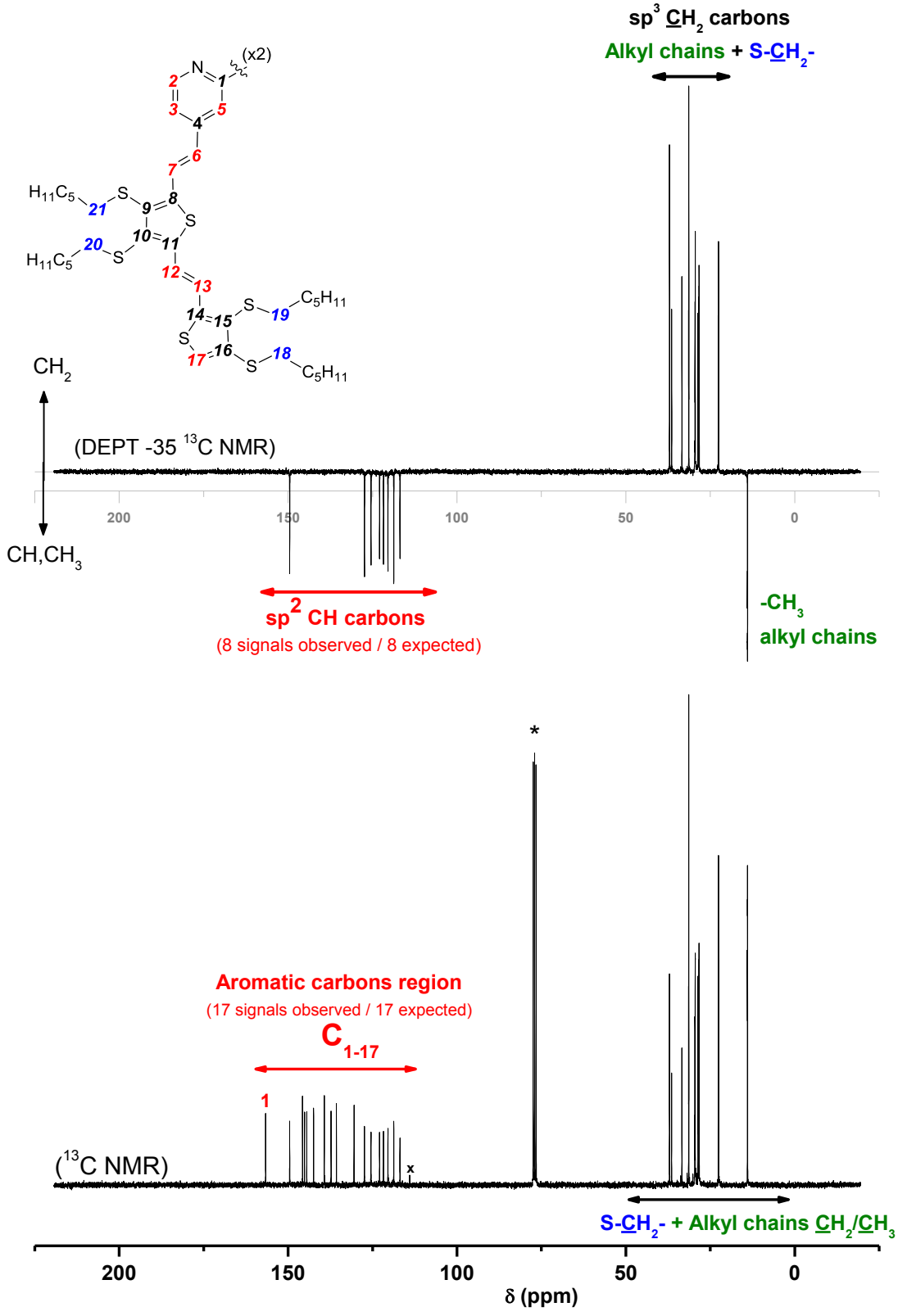


Figure S11. DEPT-135 (Top) and ^{13}C (bottom) NMR spectra of **5** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent, and **x** an impurity).

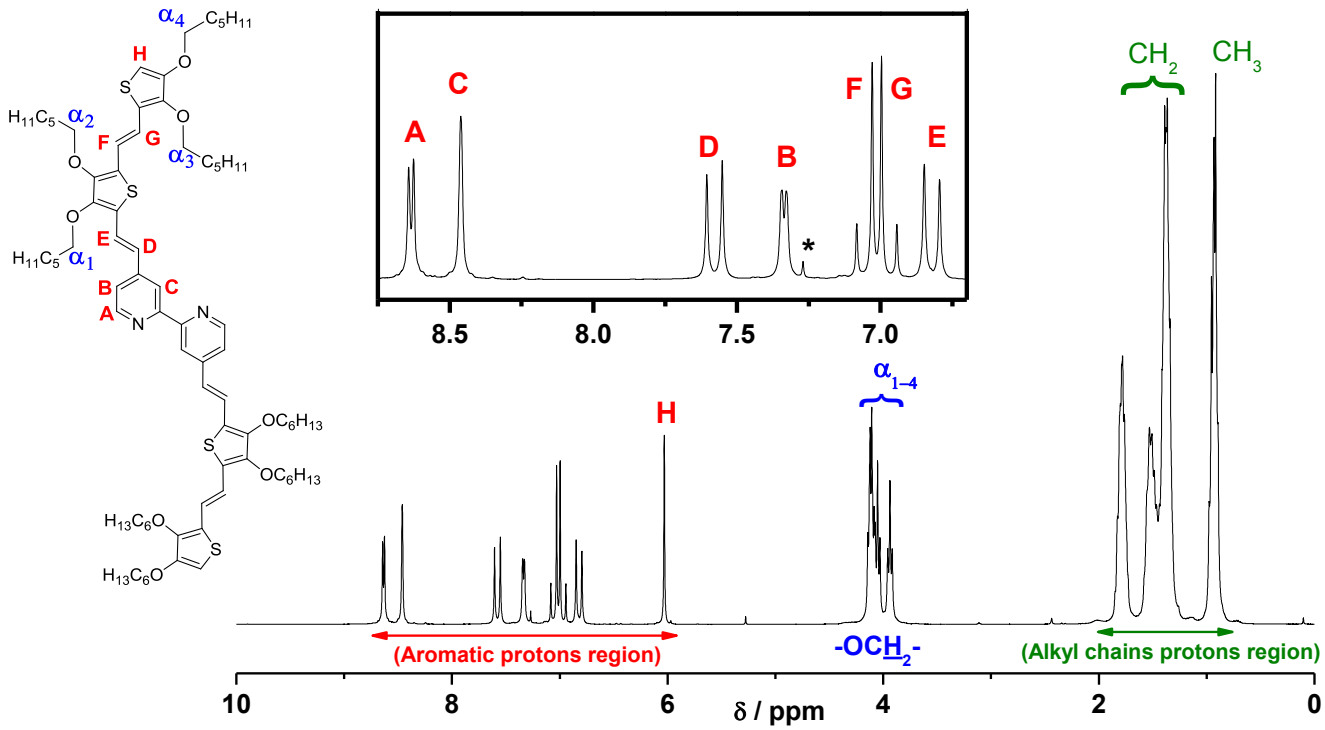


Figure S12. ^{1}H NMR spectrum of **6** ($CDCl_3$, 300MHz; * denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent).

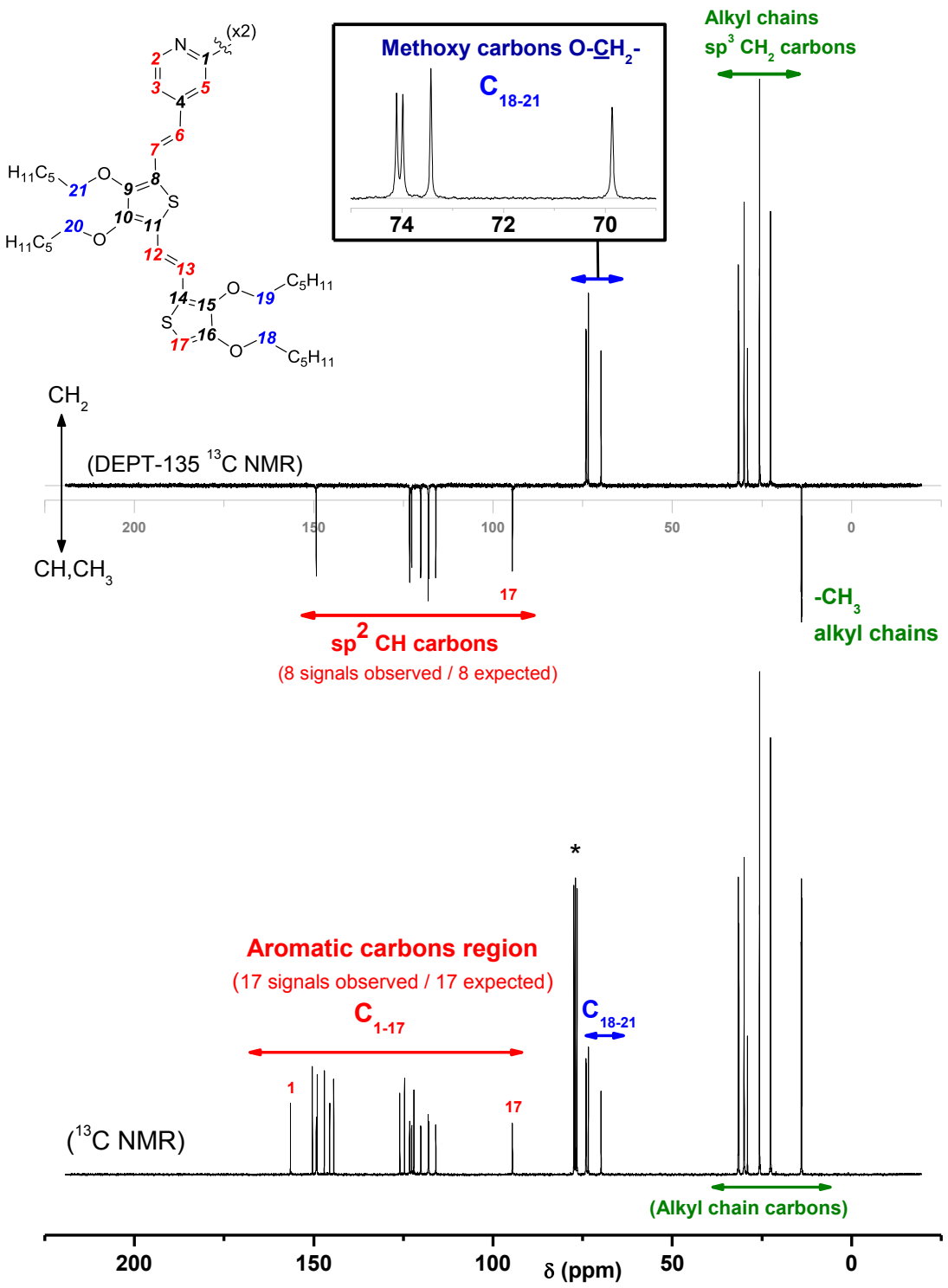


Figure S13. DEPT-135 (Top) and ^{13}C (bottom) NMR spectra of **6** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent).

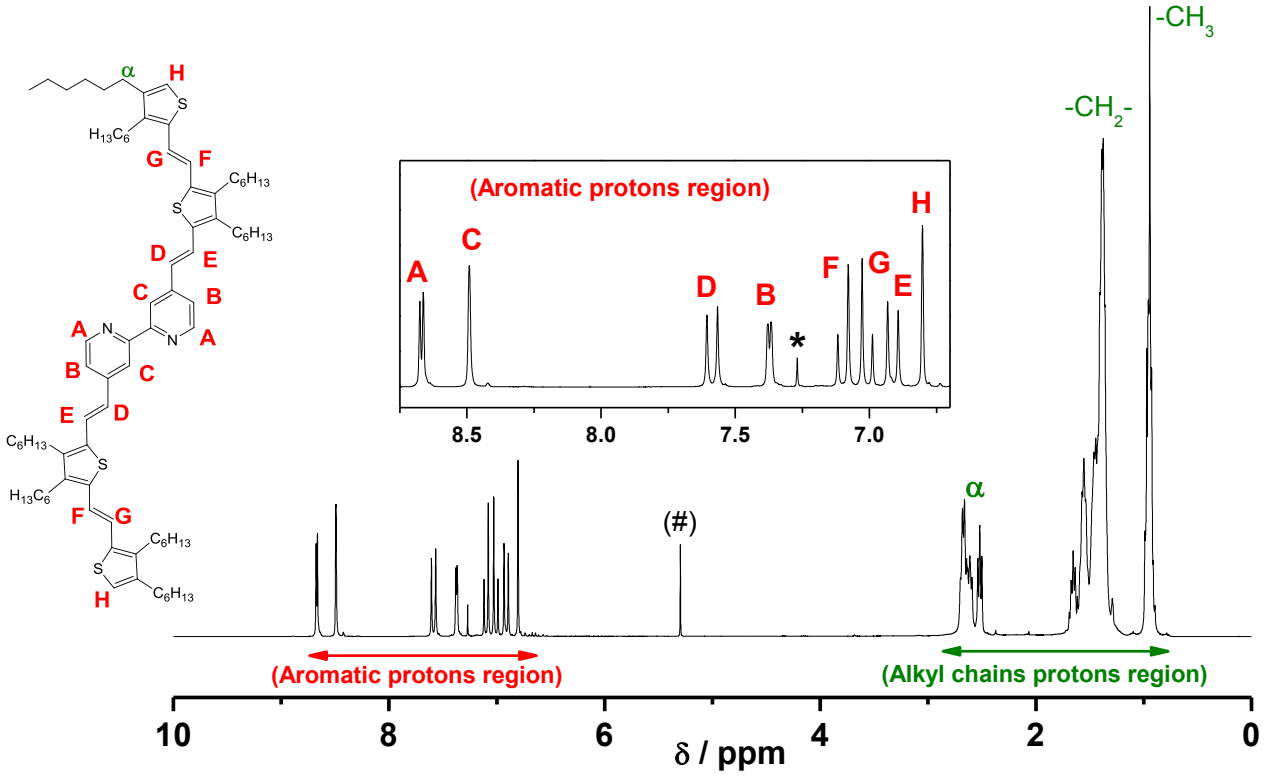


Figure S14. ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz; * denotes the residual $CHCl_3$ signal the of $CDCl_3$ solvent and # a peak due to an impurity: CH_2Cl_2 solvent).

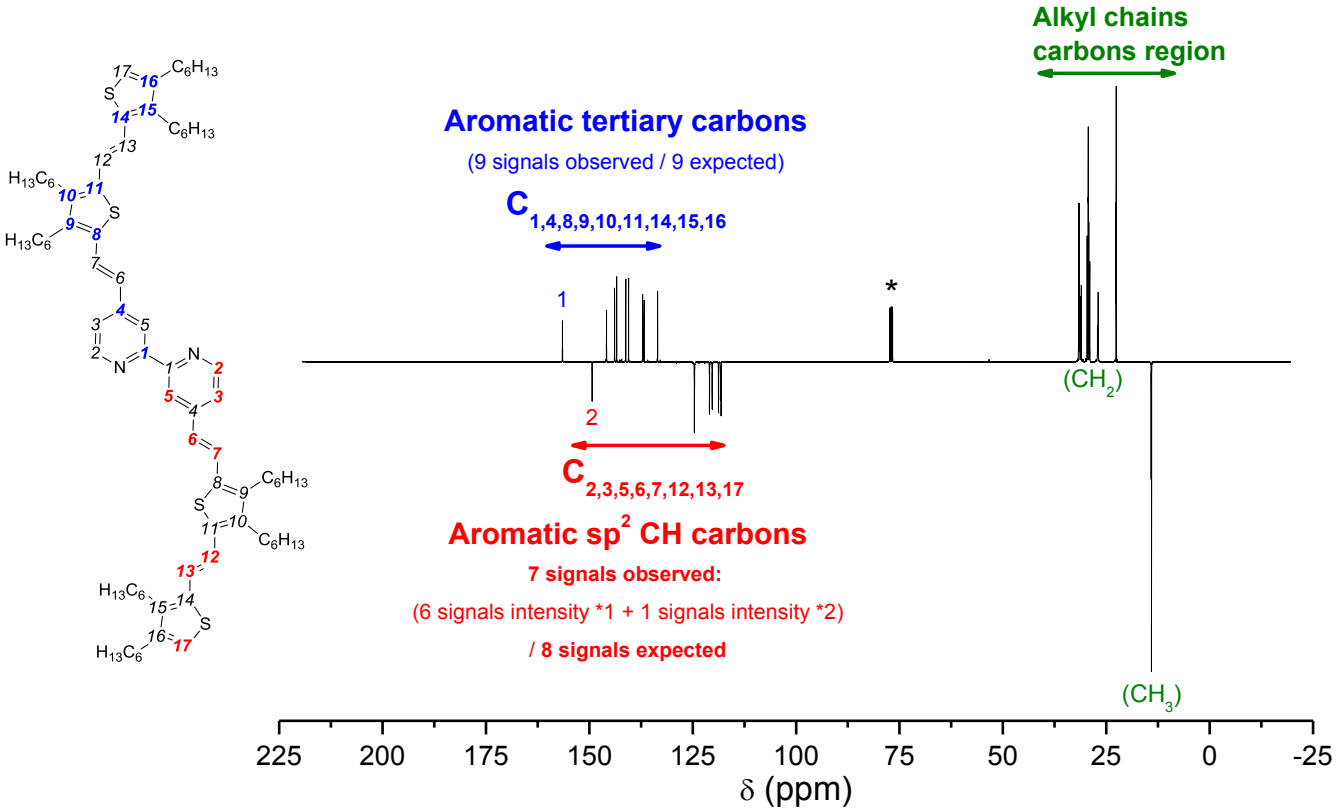


Figure S15. APT ^{13}C NMR spectrum of **7** ($CDCl_3$, 100 MHz; * denotes the signal of the $CDCl_3$ solvent).

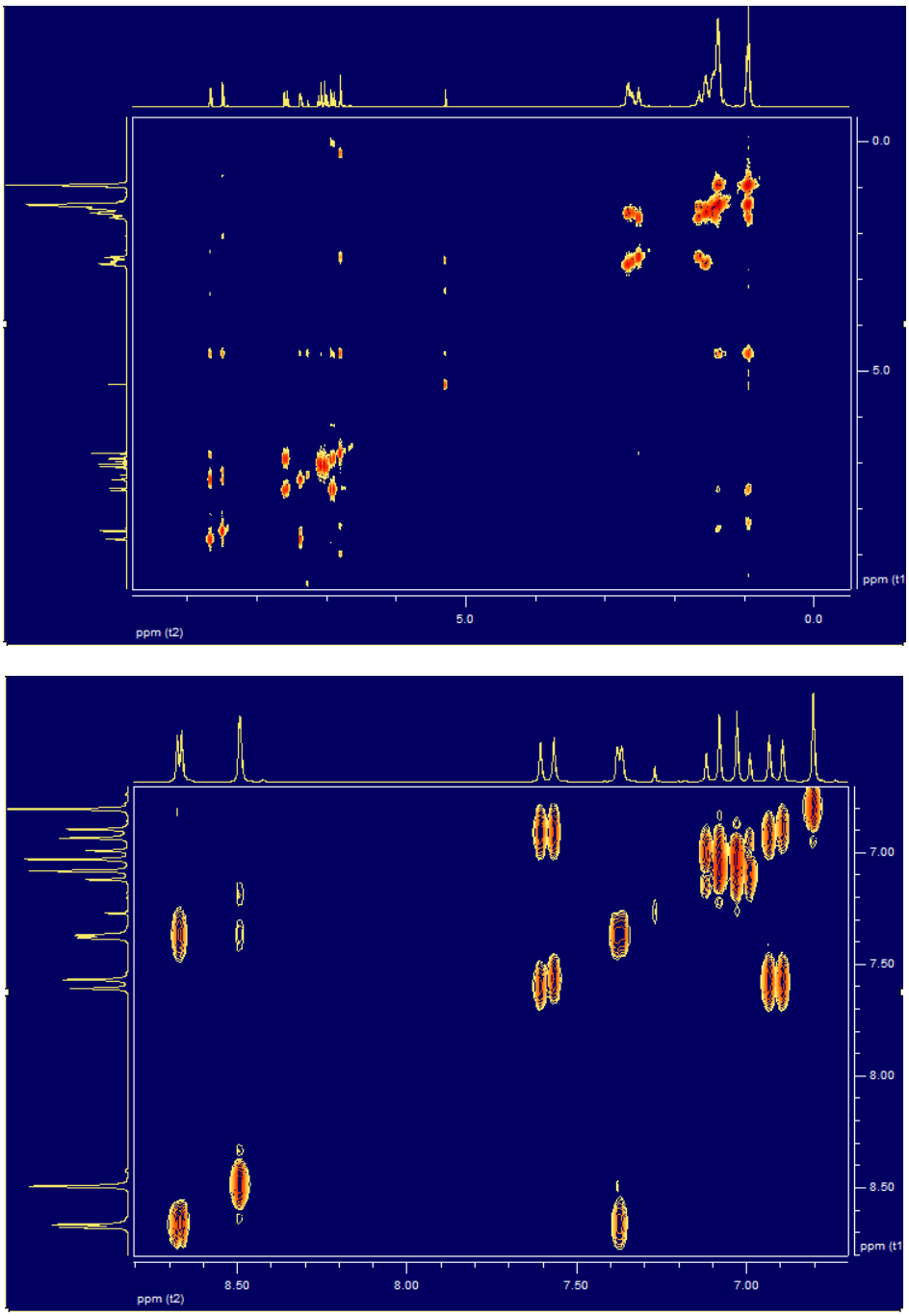


Figure S16. 2D-COSY 45 $^{1}H/^{1}H$ NMR spectrum of **7** ($CDCl_3$, 400 MHz; top: full range spectrum, bottom: expanded region of the aromatic protons).

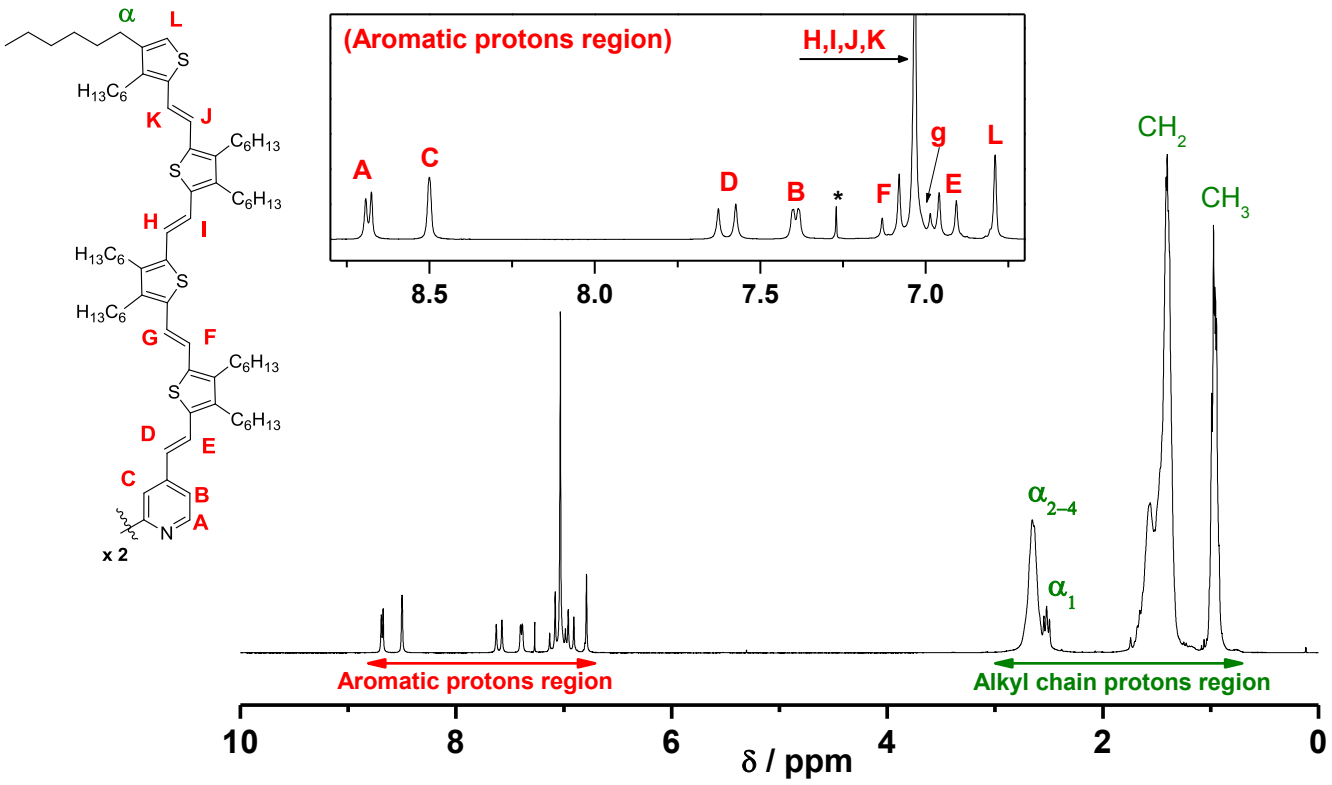


Figure S17. ^{1}H NMR spectrum of **8** ($CDCl_3$, 300 MHz; * denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent).

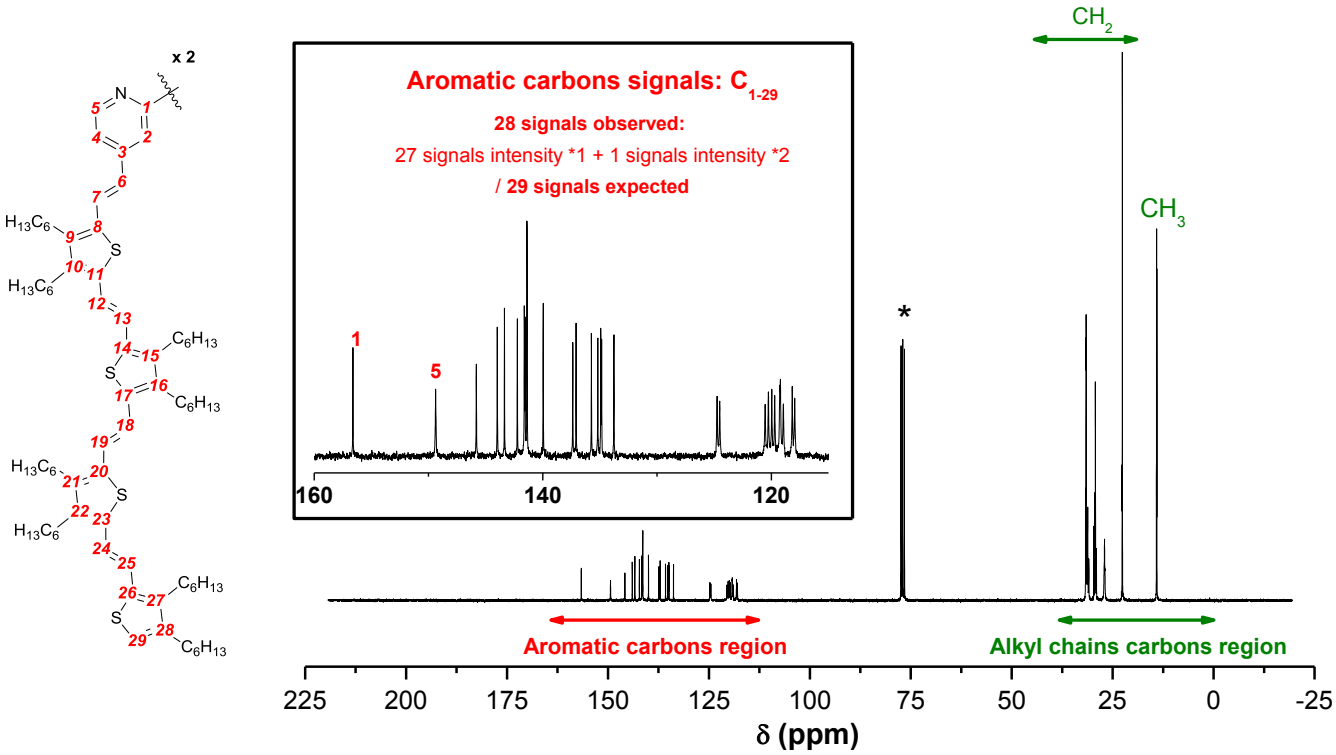


Figure S18. ^{13}C NMR spectrum of **8** ($CDCl_3$, 75 MHz; * denotes the signal of the $CDCl_3$ solvent).

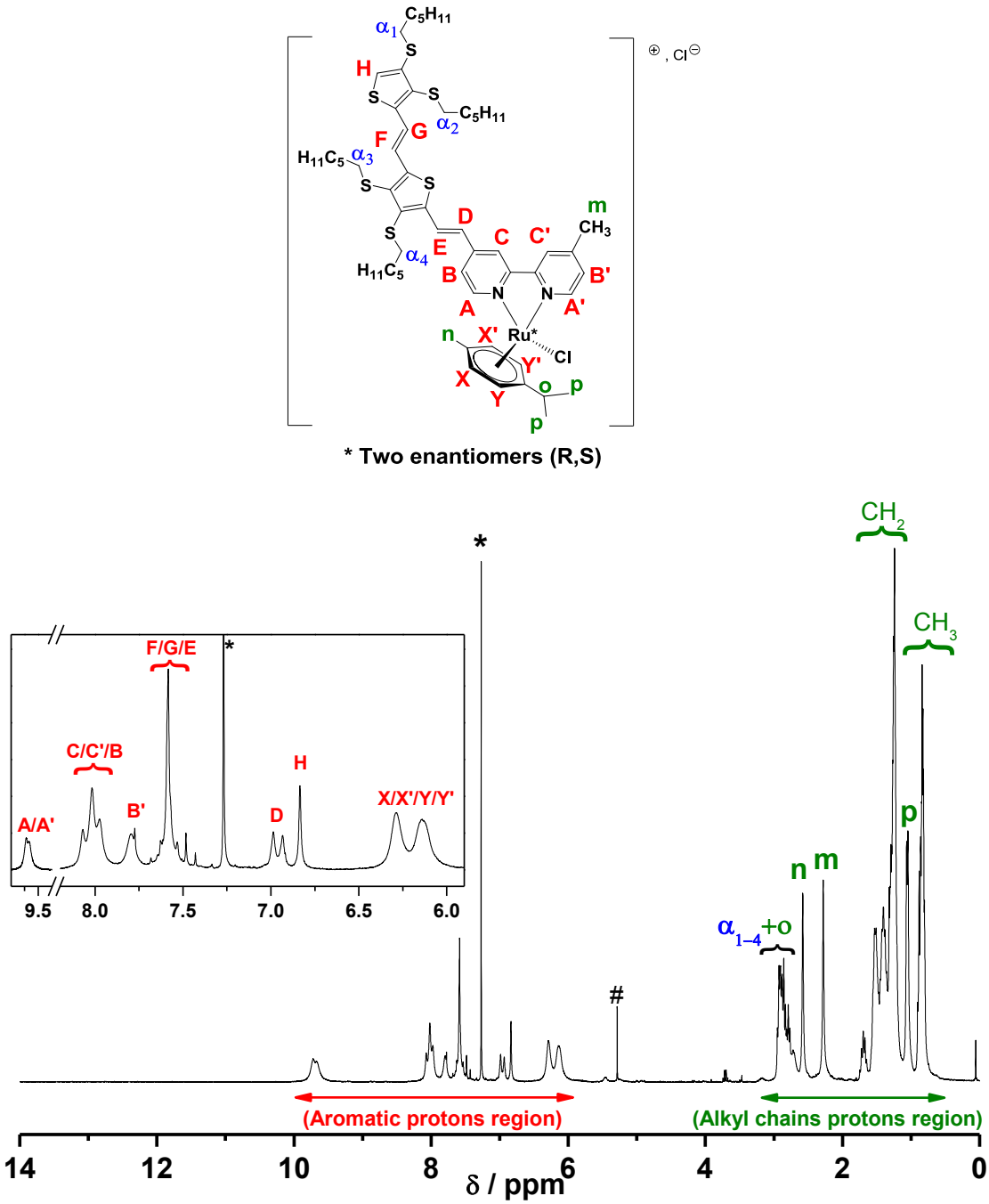


Figure S19. ^{1}H NMR spectrum of crude complex **Ru[1]** ($CDCl_3$, 300MHz; * denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # a peak due to an impurity: CH_2Cl_2 solvent).

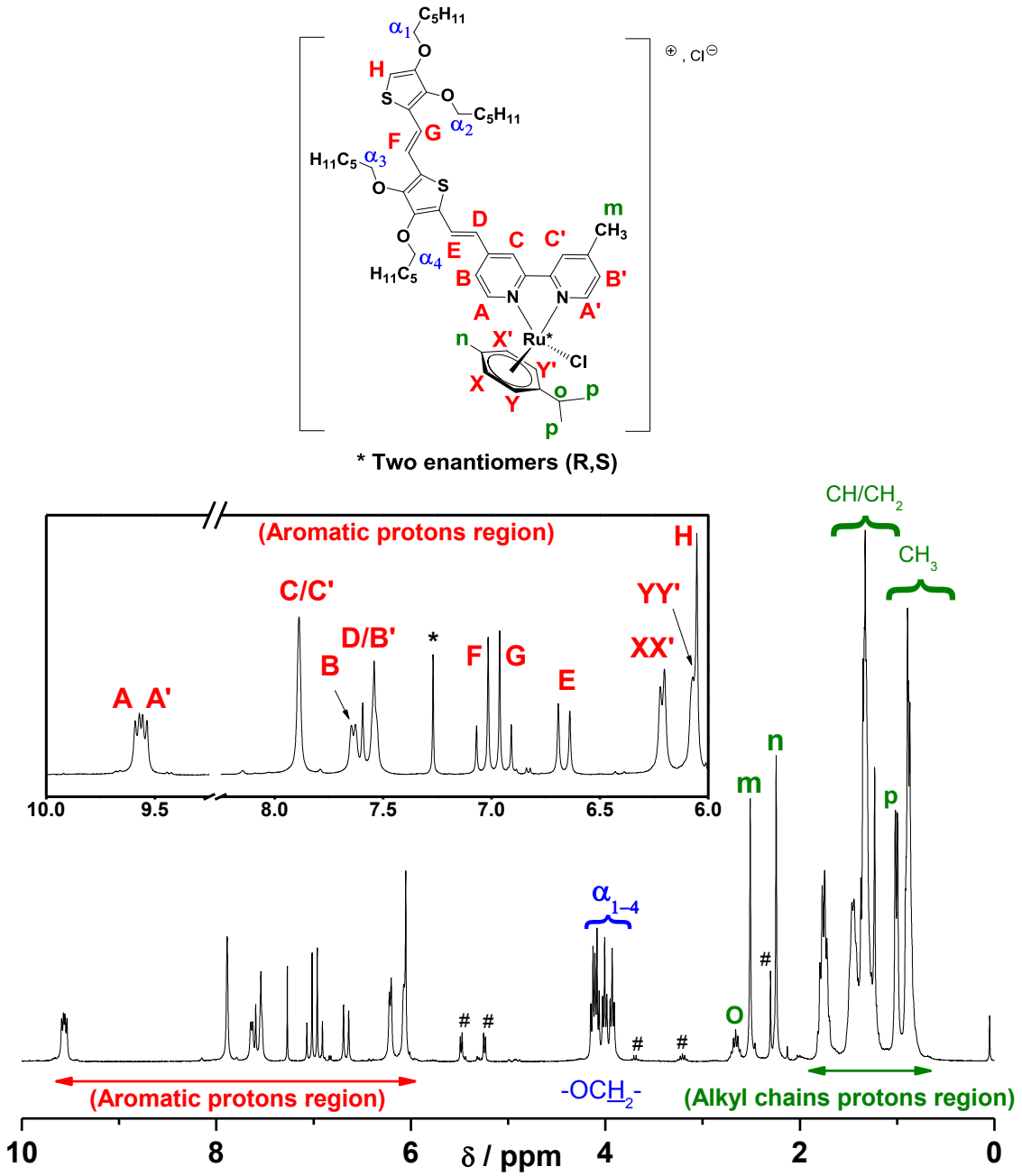


Figure S20. ^{1}H NMR spectrum of crude complex **Ru[2]** ($CDCl_3$, 300MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # the signals arising from the excess of dichloro(*p*-cymene)-Ru(II) dimer).

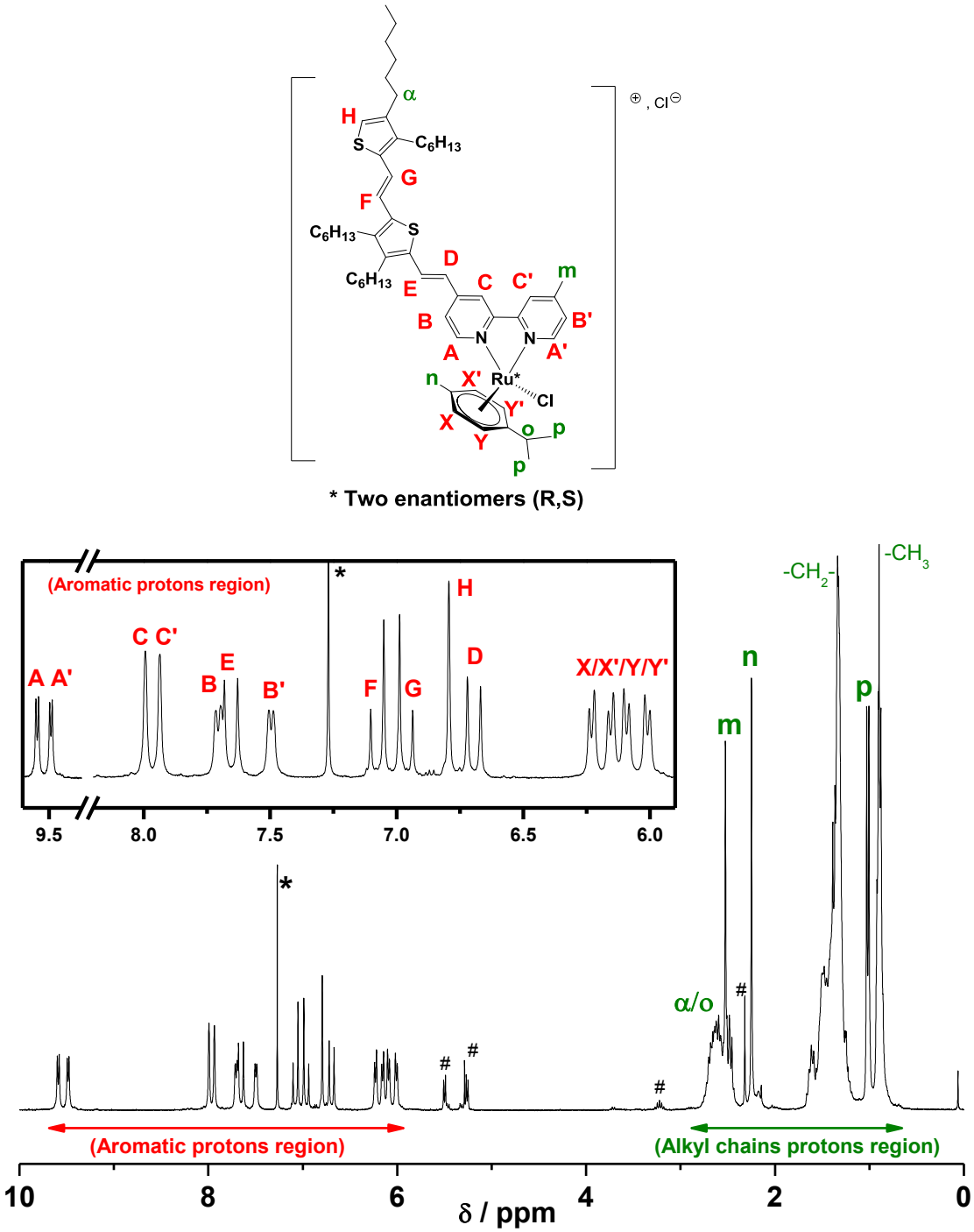


Figure S21. ^{1}H NMR spectrum of the crude complex **Ru[3]** ($CDCl_3$, 300 MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and $^{\#}$ the signals arising from the excess of dichloro(p-cymene)-Ru(II) dimer).

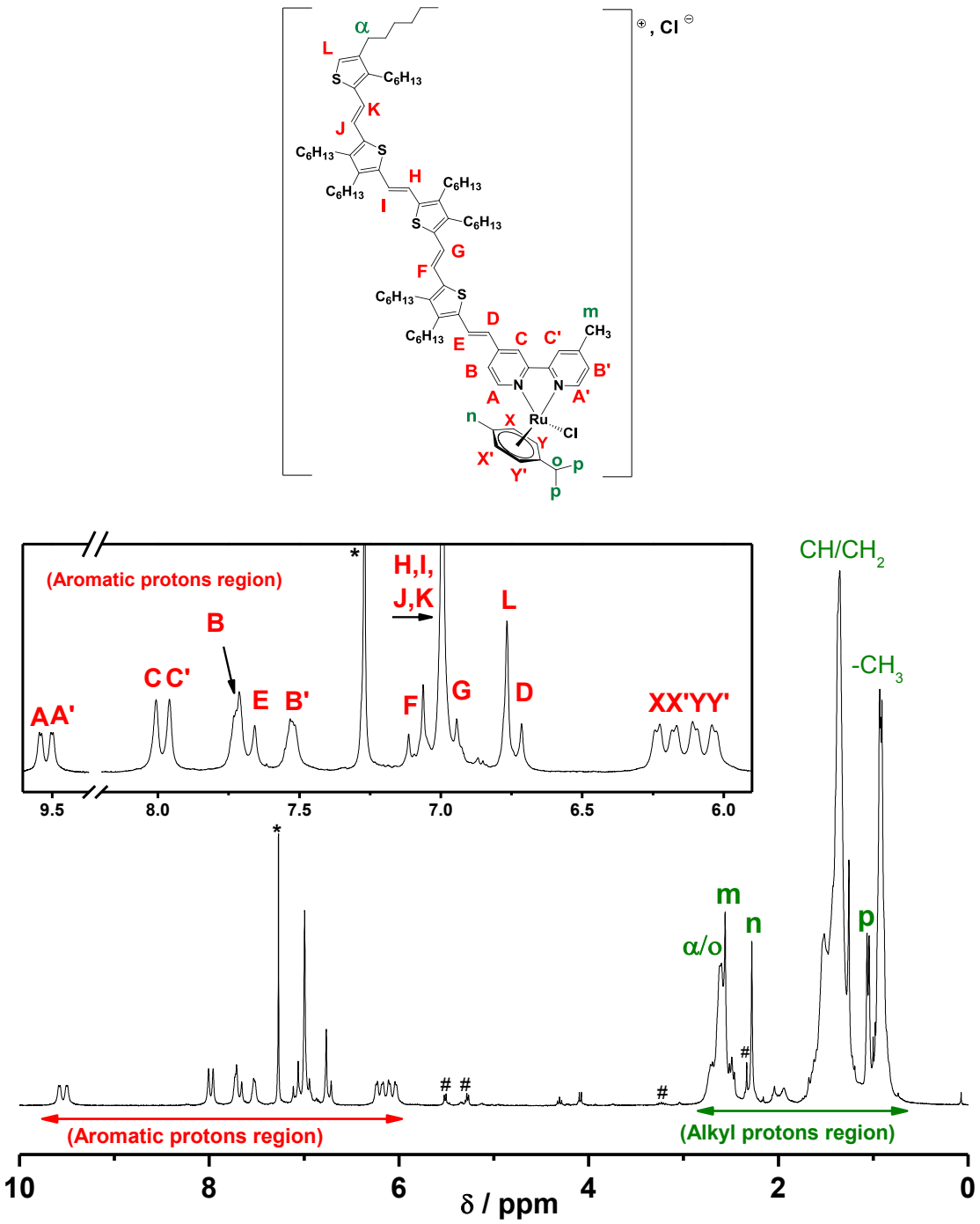


Figure S22. ^{1}H NMR spectrum of the crude complex **Ru[4]** ($CDCl_3$, 300 MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # the signals arising from the excess of dichloro(p-cymene)-Ru(II) dimer).

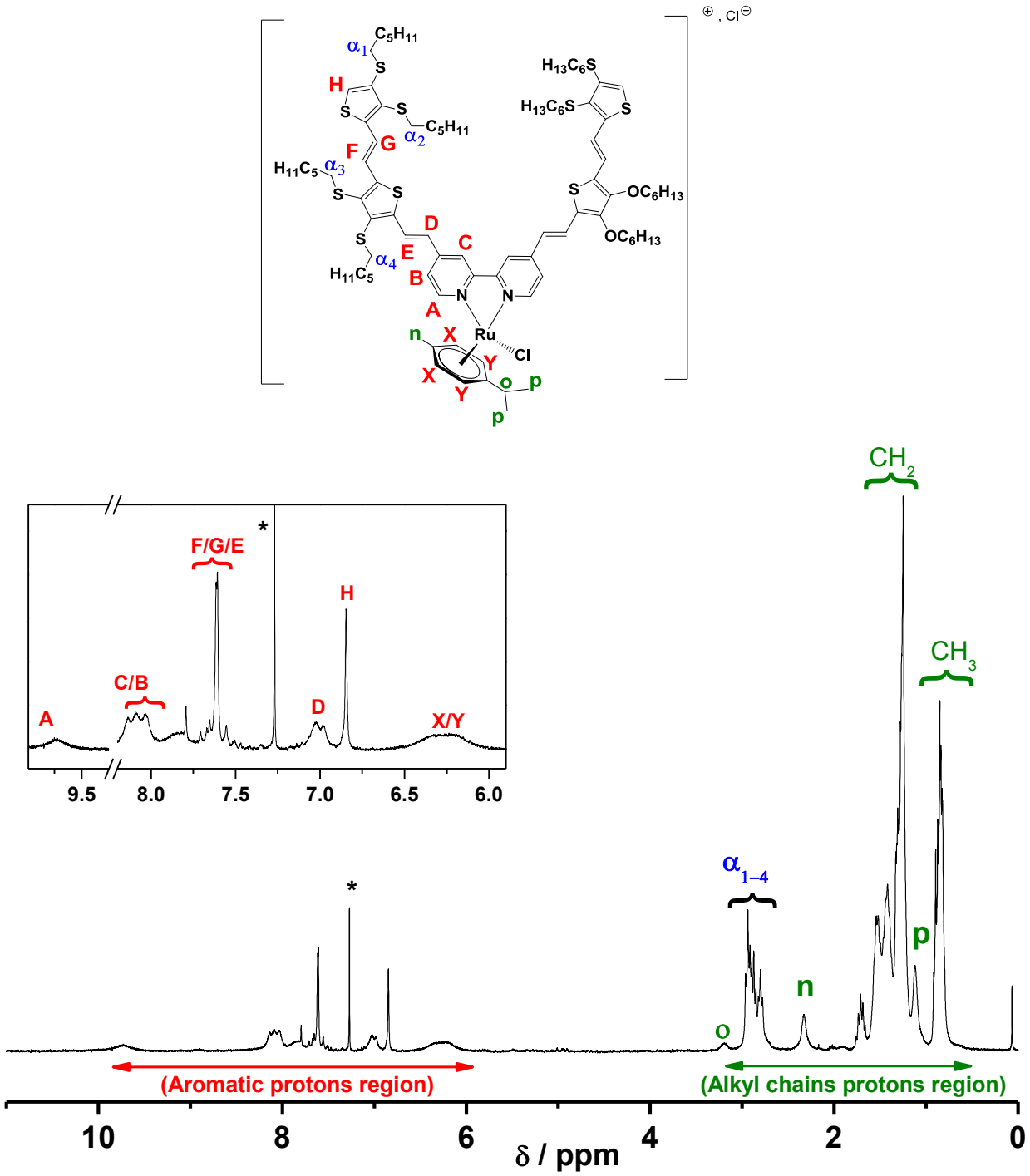


Figure S23. ^{1}H NMR spectrum of the crude complex **Ru[5]** ($CDCl_3$, 300MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent).

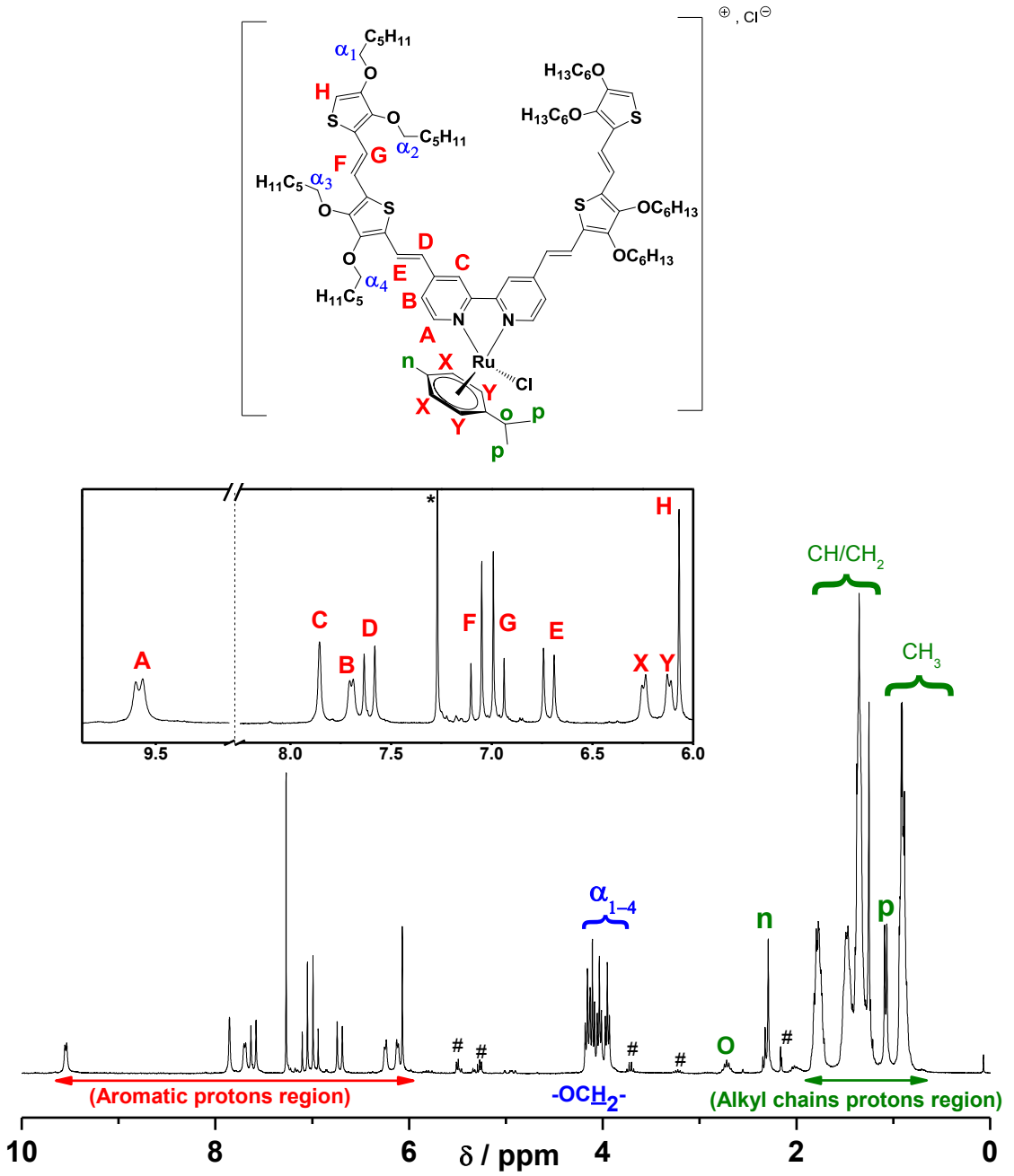


Figure S24. ^{1}H NMR spectrum of the crude complex **Ru[6]** ($CDCl_3$, 300MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # the signals arising from the excess of dichloro(*p*-cymene)-Ru(II) dimer).

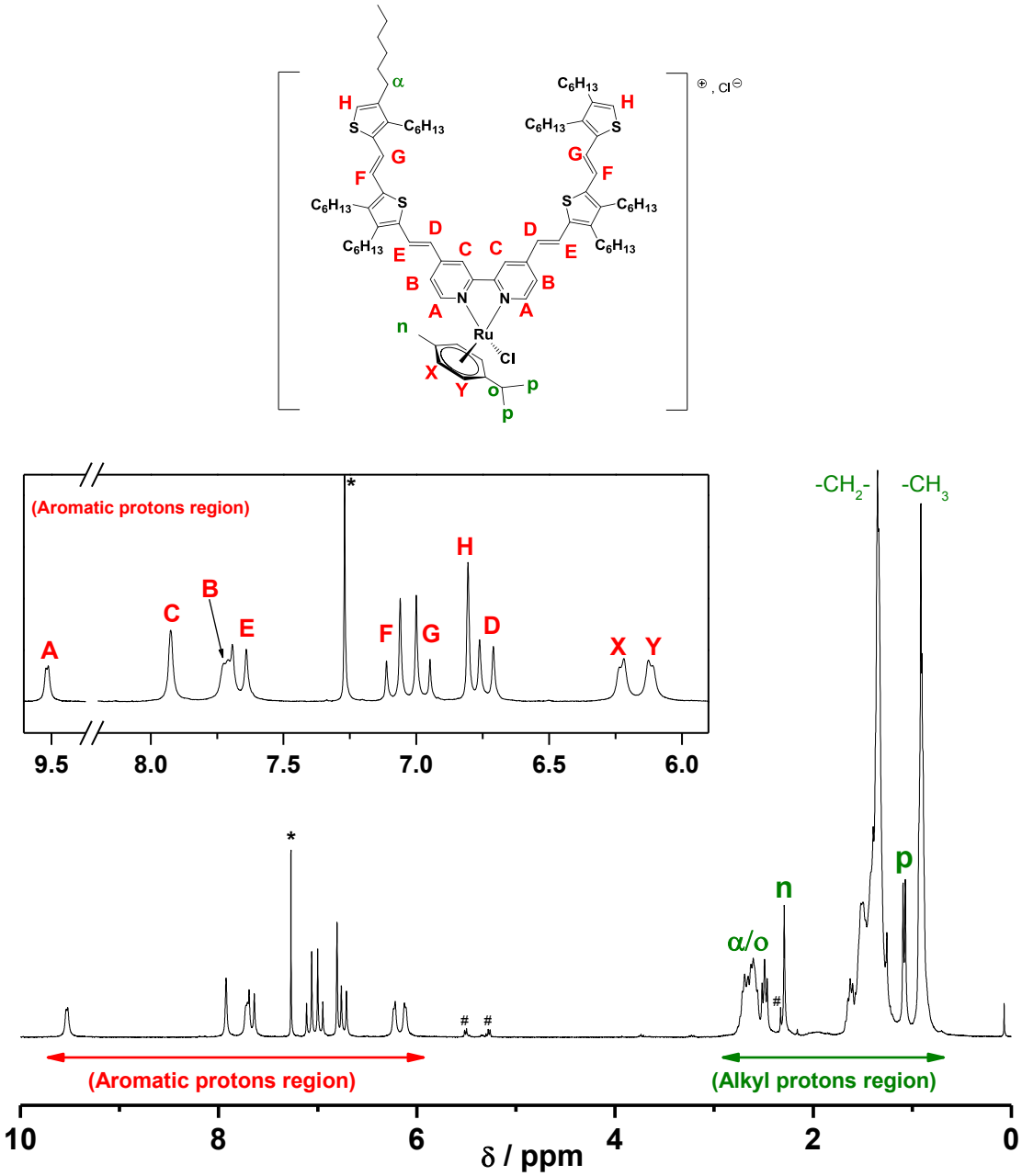


Figure S25. ^{1}H NMR spectrum of the crude complex **Ru[7]** ($CDCl_3$, 300 MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # the signals arising from the excess of dichloro(p-cymene)-Ru(II) dimer).

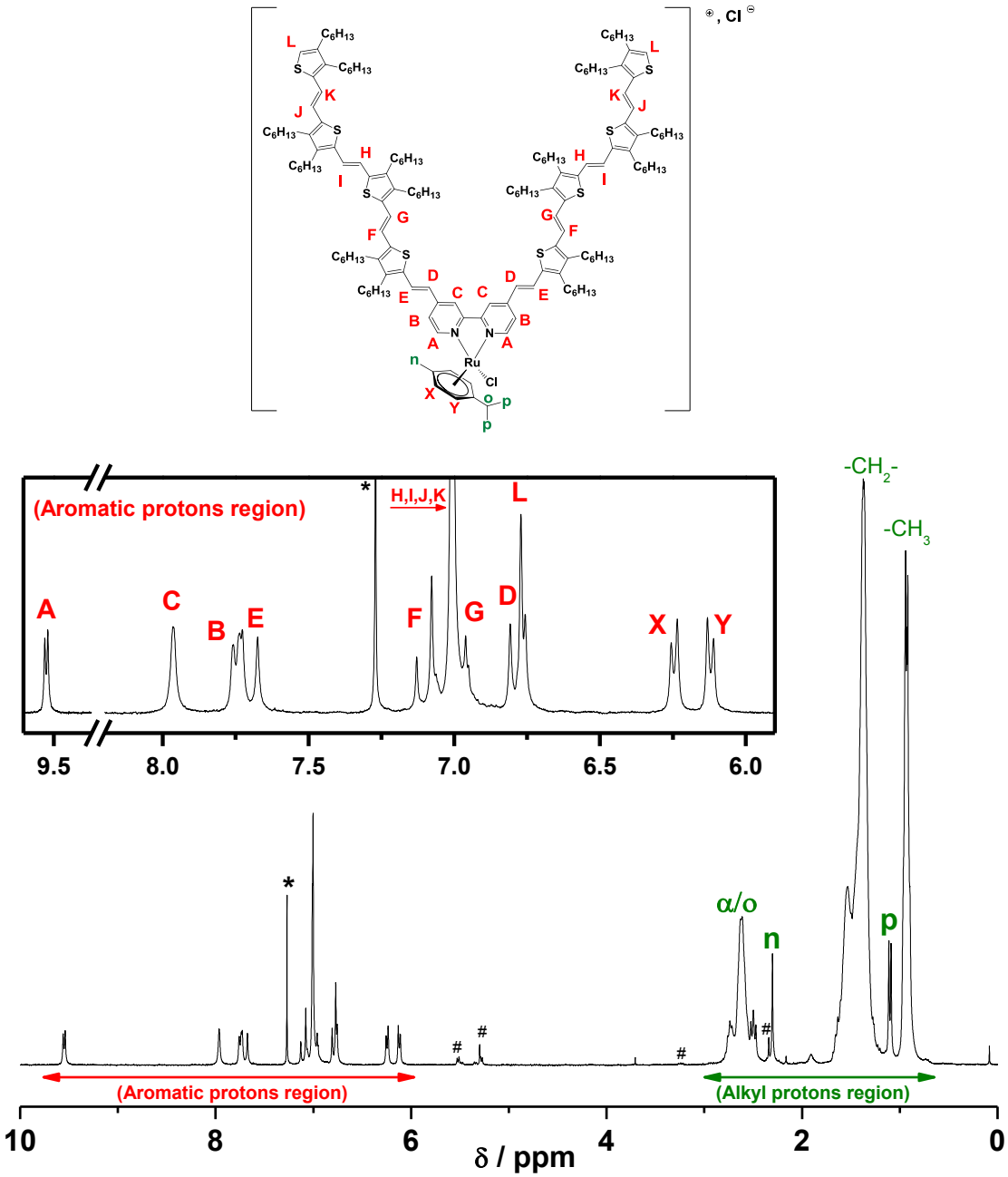


Figure S26. ^{1}H NMR spectrum of the crude complex **Ru[8]** ($CDCl_3$, 300 MHz; *denotes the residual $CHCl_3$ signal of the $CDCl_3$ solvent, and # the signals arising from the excess of dichloro(*p*-cymene)-Ru(II) dimer).

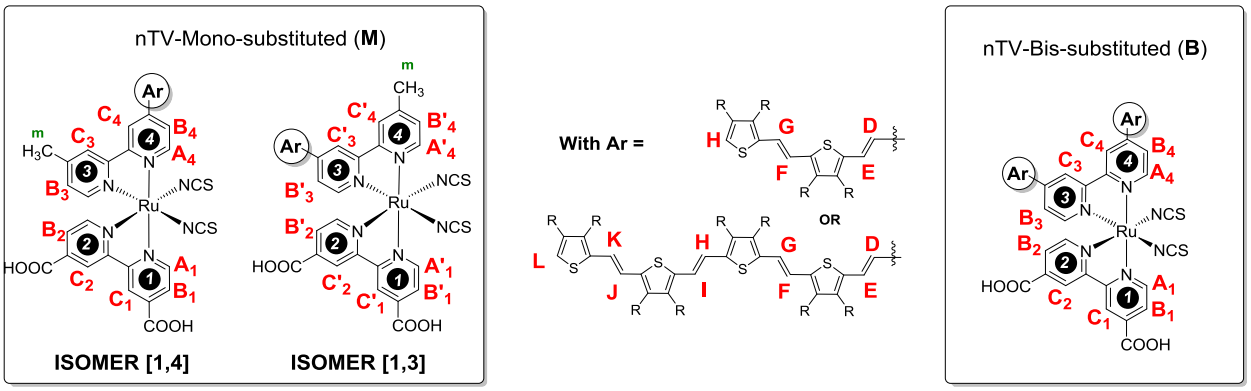


Figure S27. General ^{1}H NMR nomenclature of the (cis)bis-heteroleptic Ru(II)complexes

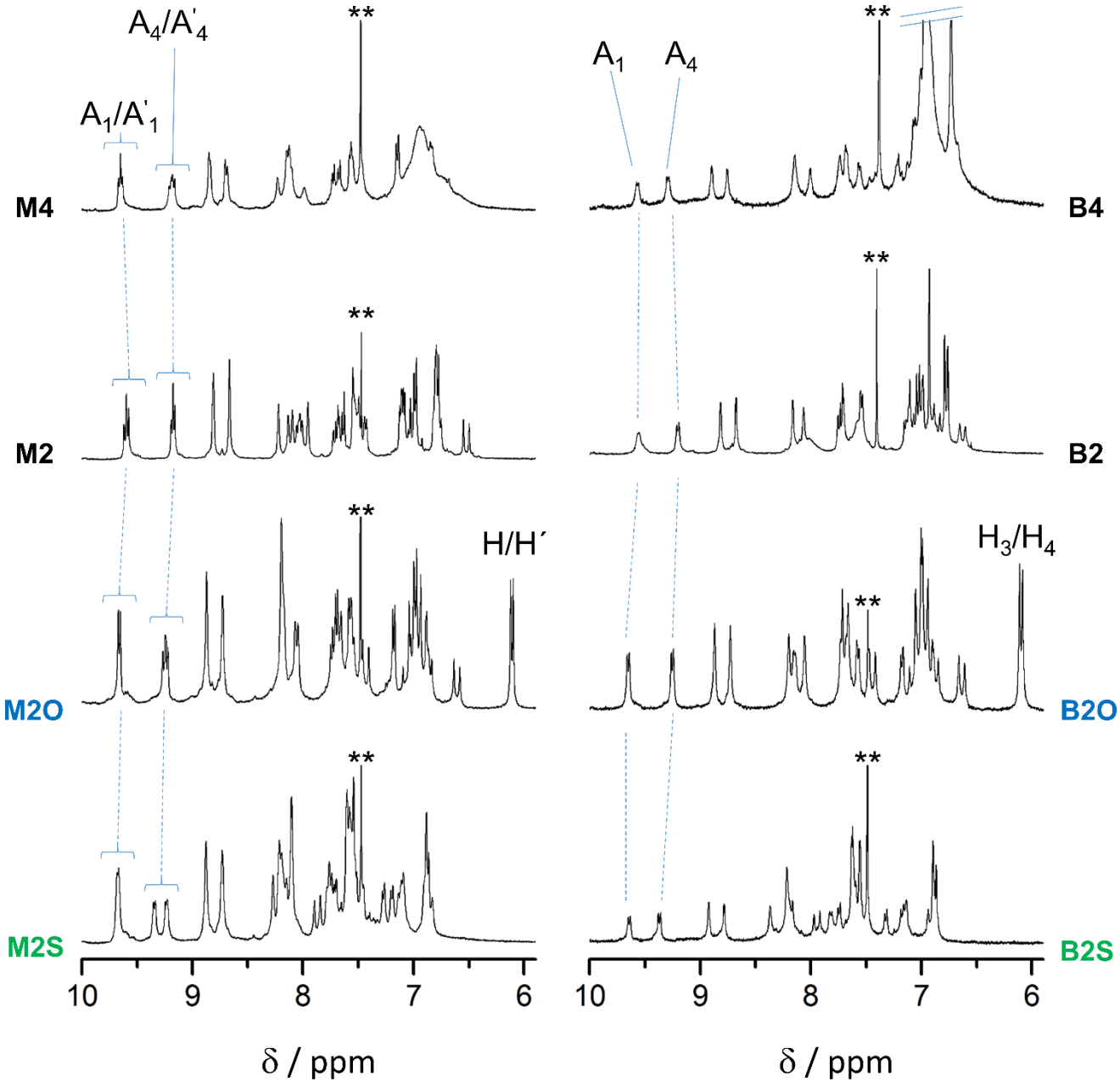


Figure S28. Comparative ^{1}H NMR spectra of the (*cis*)bis-heteroleptic Ru(II) complexes ($CDCl_3$/MeOD-d^4 7:4, 300MHz; aromatic protons region; *denote the residual solvent peaks of MeOD-d^4 (calibration peak: δ= 3.31 ppm, and ** the residual $CHCl_3$ siganl of $CDCl_3$).

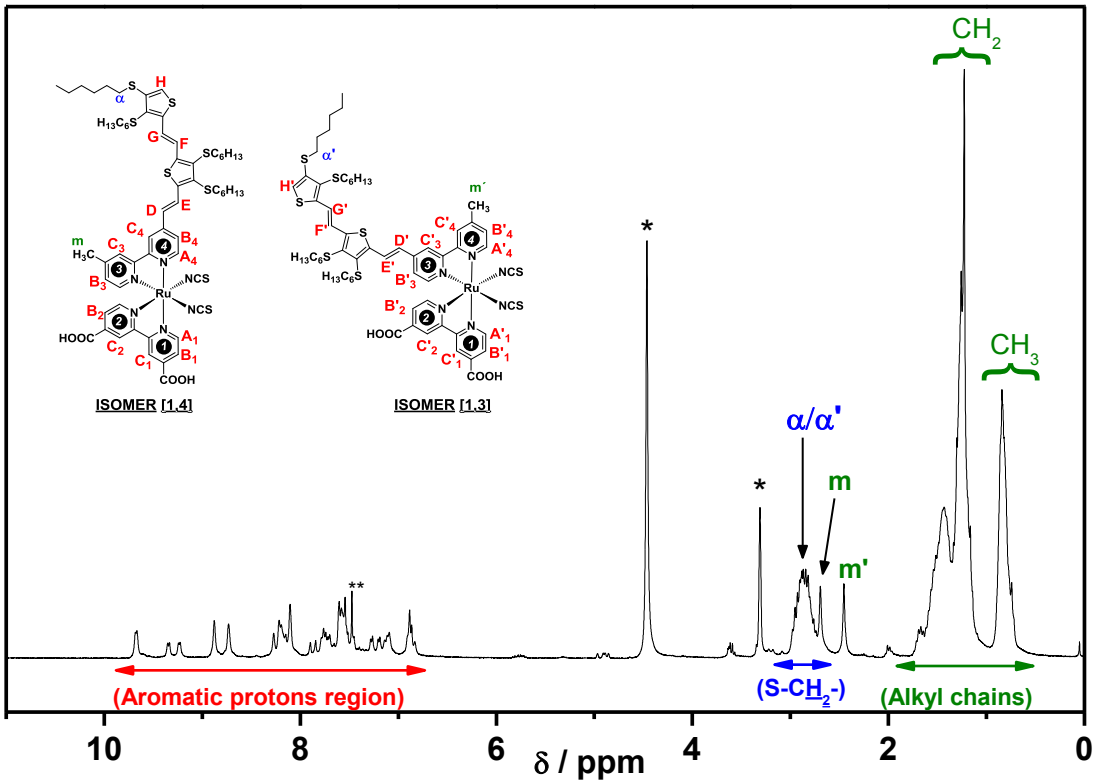


Figure S29. ^{1}H NMR spectrum of **M2S** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denote the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm, and ** the residual $CHCl_3$ signal of $CDCl_3$).

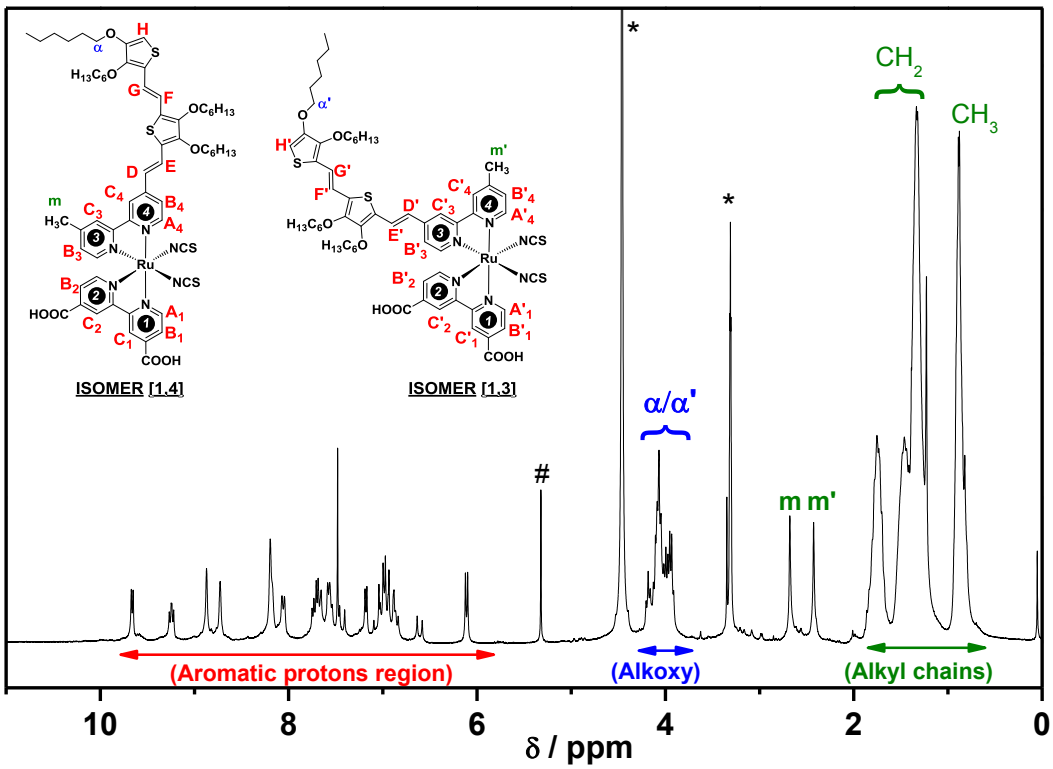


Figure S30. ^{1}H NMR spectrum of **M2O** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denote the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm), ** the residual $CHCl_3$ peak of $CDCl_3$, and # a peak due to an impurity (CH_2Cl_2 solvent)).

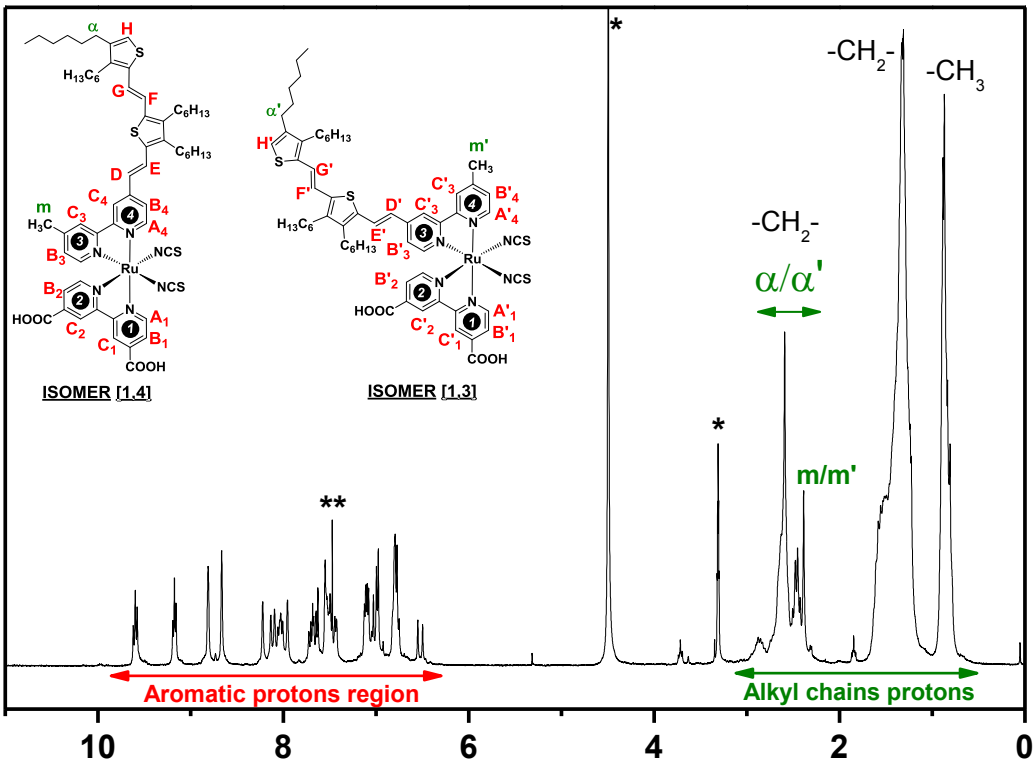


Figure S31. ^{1}H NMR spectrum of **M2** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denote the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm, and ** the residual $CHCl_3$ peak of $CDCl_3$).

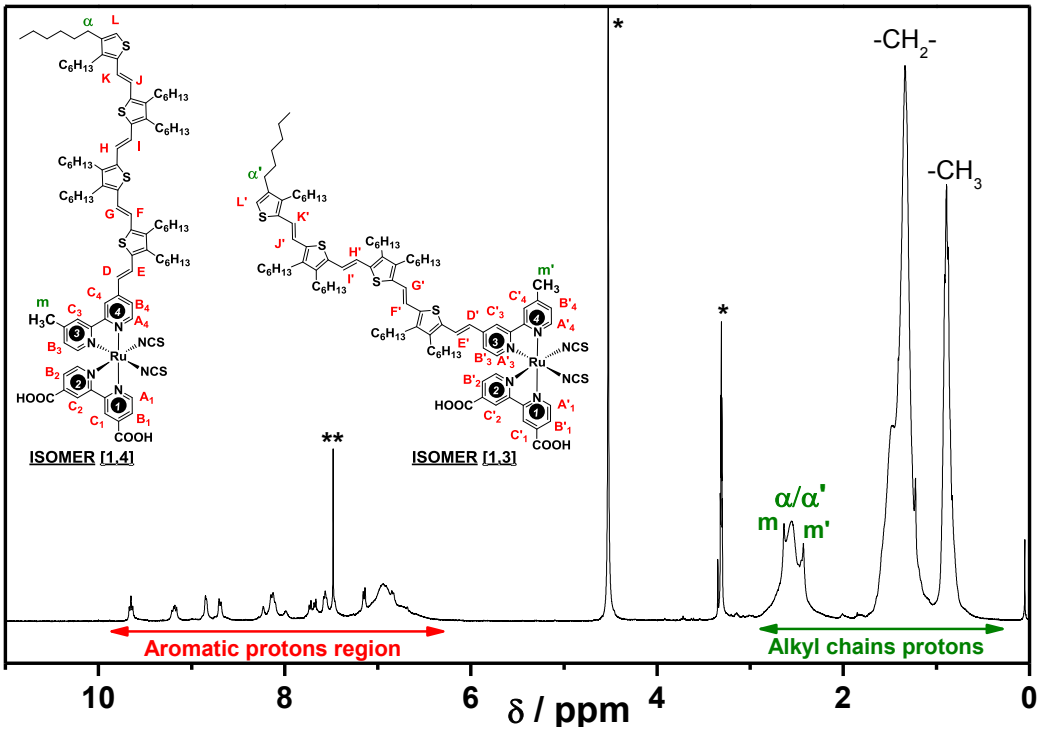


Figure S32. ^{1}H NMR spectrum of **M4** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denote the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm, and ** the residual $CHCl_3$ peak of $CDCl_3$).

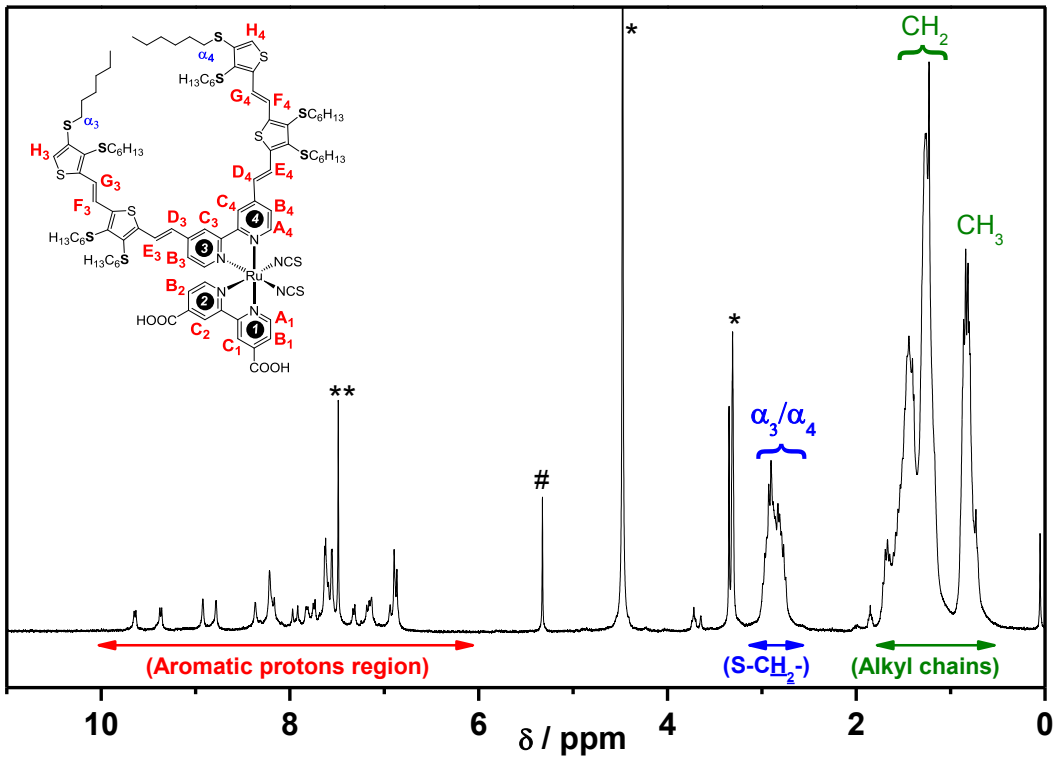


Figure S33. ^{1}H NMR spectrum of **B2S** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denotes the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm), ** the residual $CHCl_3$ peak of $CDCl_3$, and # a peak due to an impurity (CH_2Cl_2 solvent)).

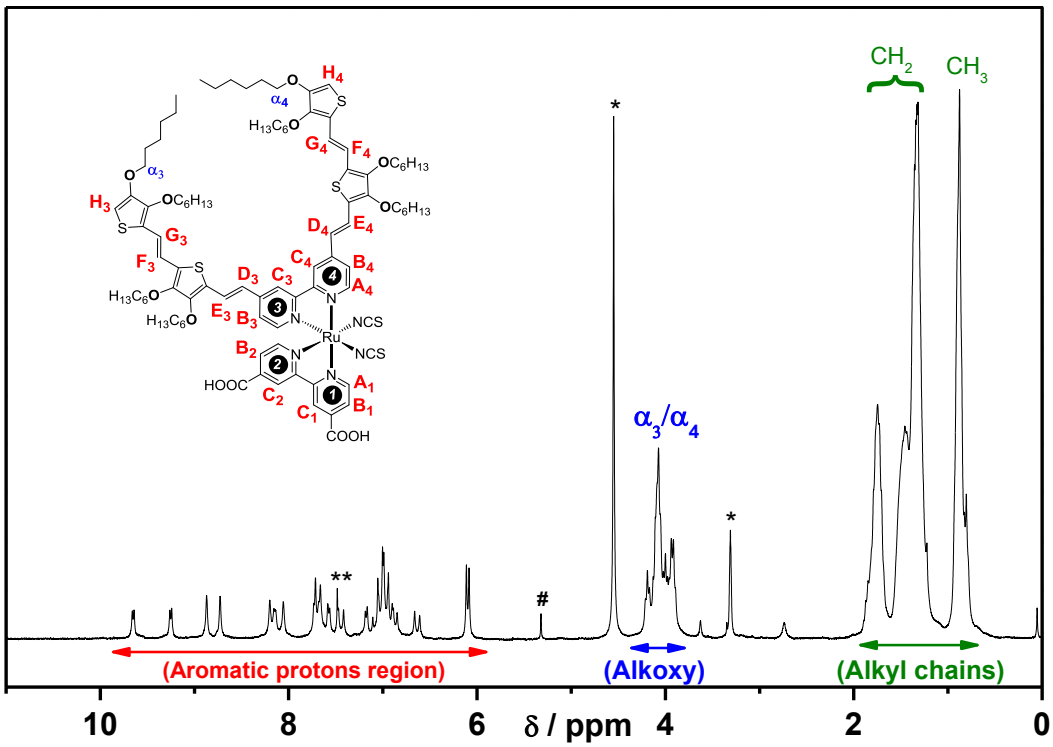


Figure S34. ^{1}H NMR spectrum of **B2O** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denotes the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm), ** the residual $CHCl_3$ peak of $CDCl_3$ in MeOD d^4, and # a peak due to an impurity (CH_2Cl_2 solvent)).

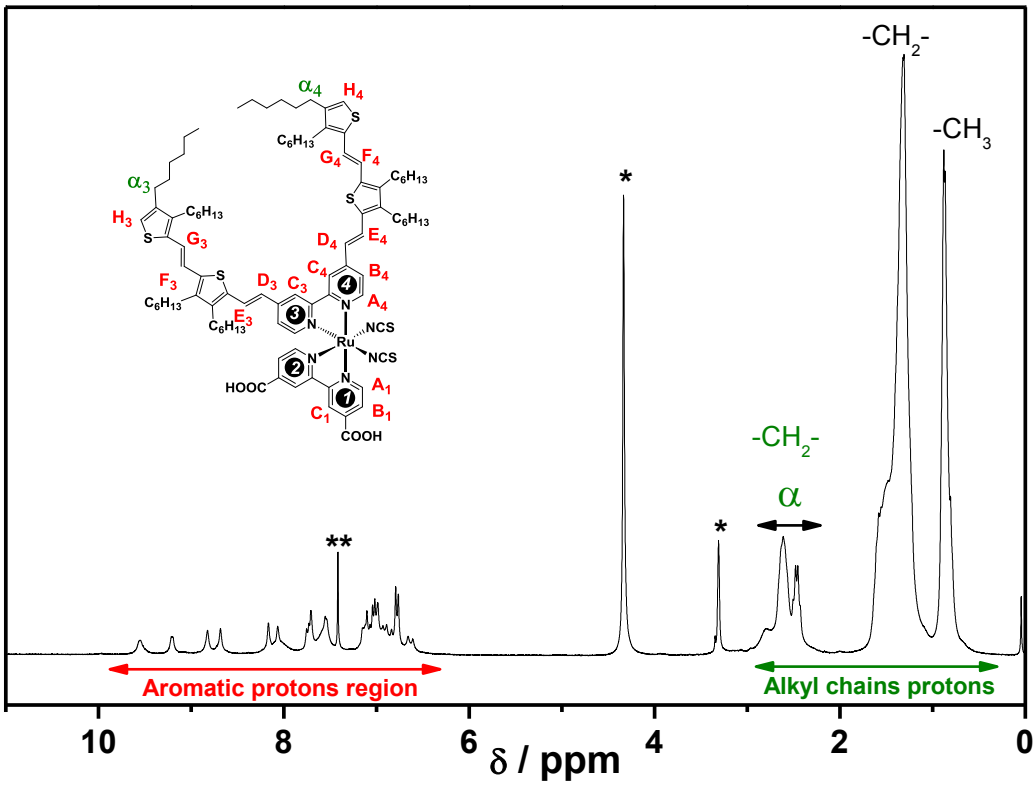


Figure S35. ^{1}H NMR spectrum of **B2** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denotes the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm), and ** the residual $CHCl_3$ peak of $CDCl_3$).

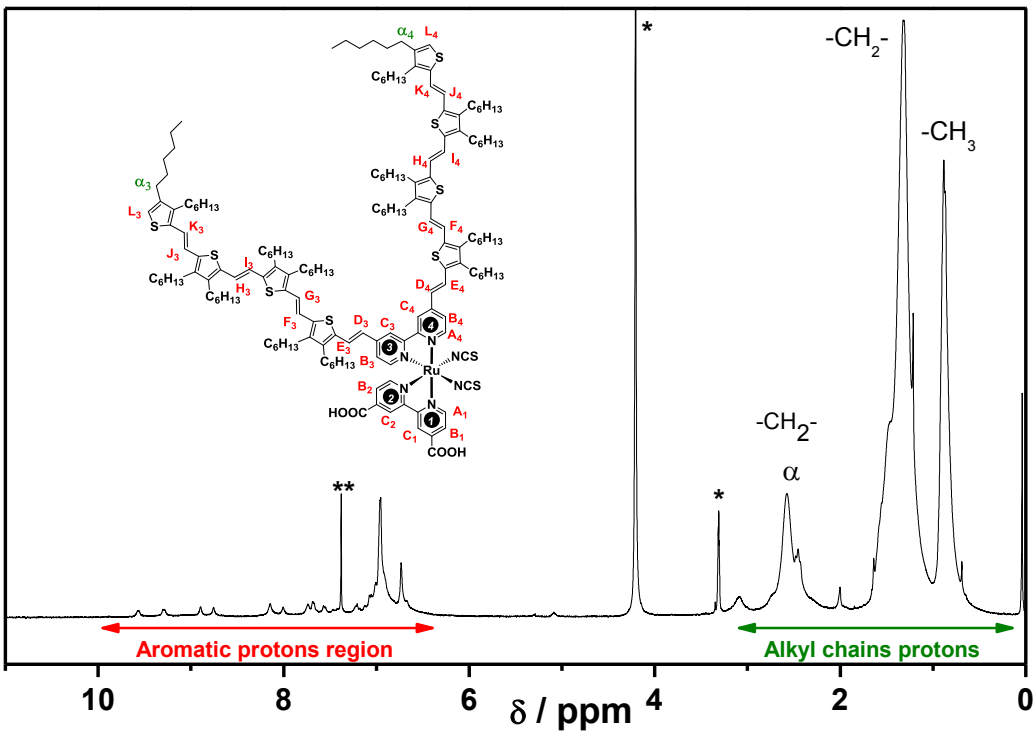


Figure S36. ^{1}H NMR spectrum of **B2** ($CDCl_3$/MeOD-d^4 7:4, 300MHz; *denotes the residual solvent peaks of MeOD-d^4 (calibration peak: δ = 3.31 ppm) and ** denotes the residual $CHCl_3$ peak of $CDCl_3$).

III. UV-VIS SPECTRA

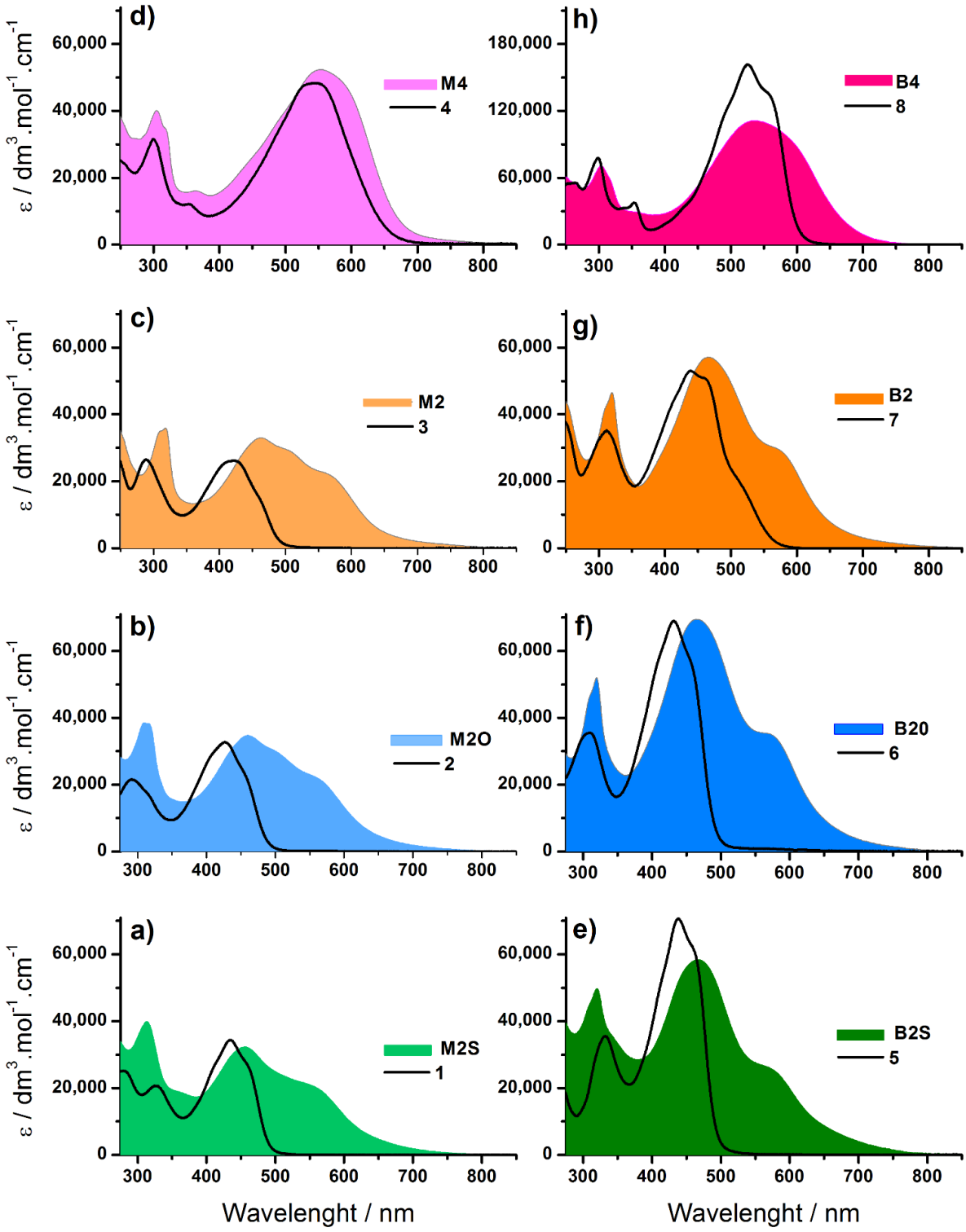


Figure S37. UV-Vis spectra in CH_2Cl_2 solutions of the bipyridine ligands **1–8** (solid black lines) and the corresponding (*cis*)bis-heteroleptic complexes (filled curves); note that the y-scale for spectra h (0–213,000) is 3 times higher than for spectra a–g (0–71,000); x-scale is the same for all spectra.

IV. MASS SPECTROMETRY (MALDI-TOF)

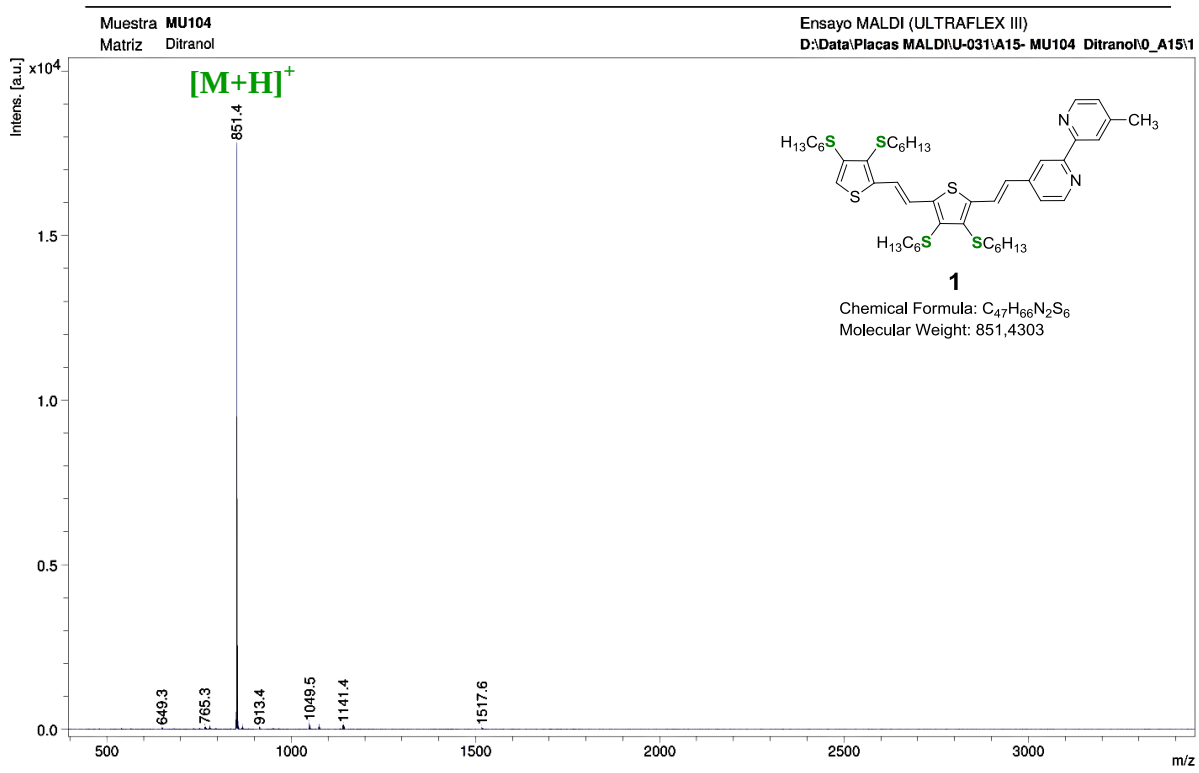


Figure S38. MS spectrum of **1** (MALDI-TOF, matrix: dithranol).

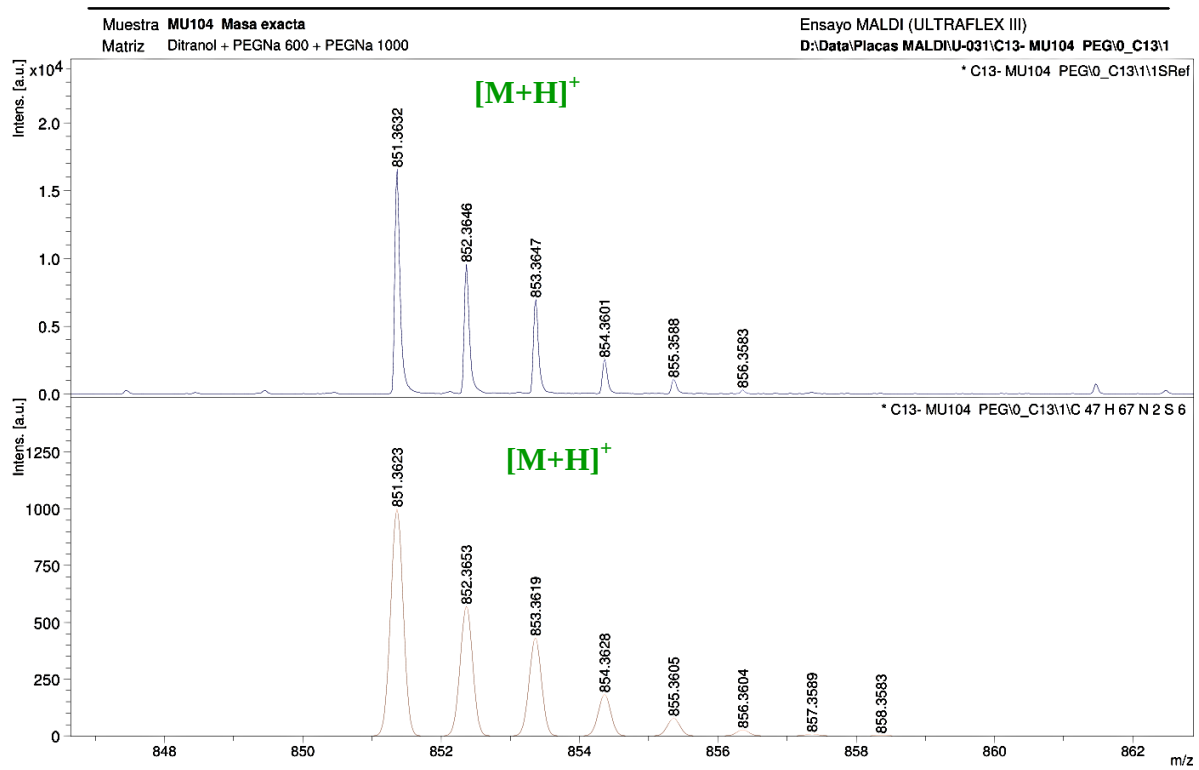


Figure S39. HRMS spectrum of **1** (MALDI-TOF, matrix: dithranol + PEGNa 600 + PEGNa 1000): experimental (top) and theoretical isotopic distribution calculated for $[M+H]^+$ (bottom).

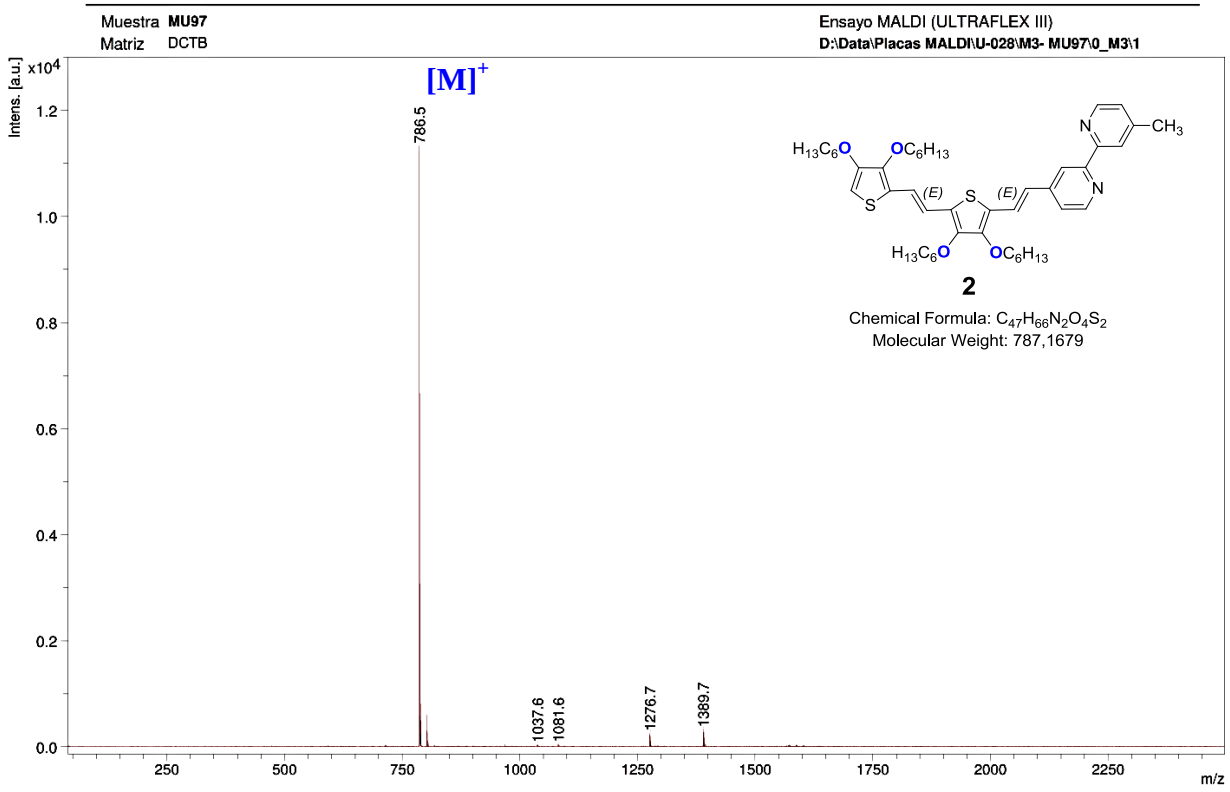


Figure S40. MS spectrum of **2** (MALDI-TOF, matrix: DCTB).

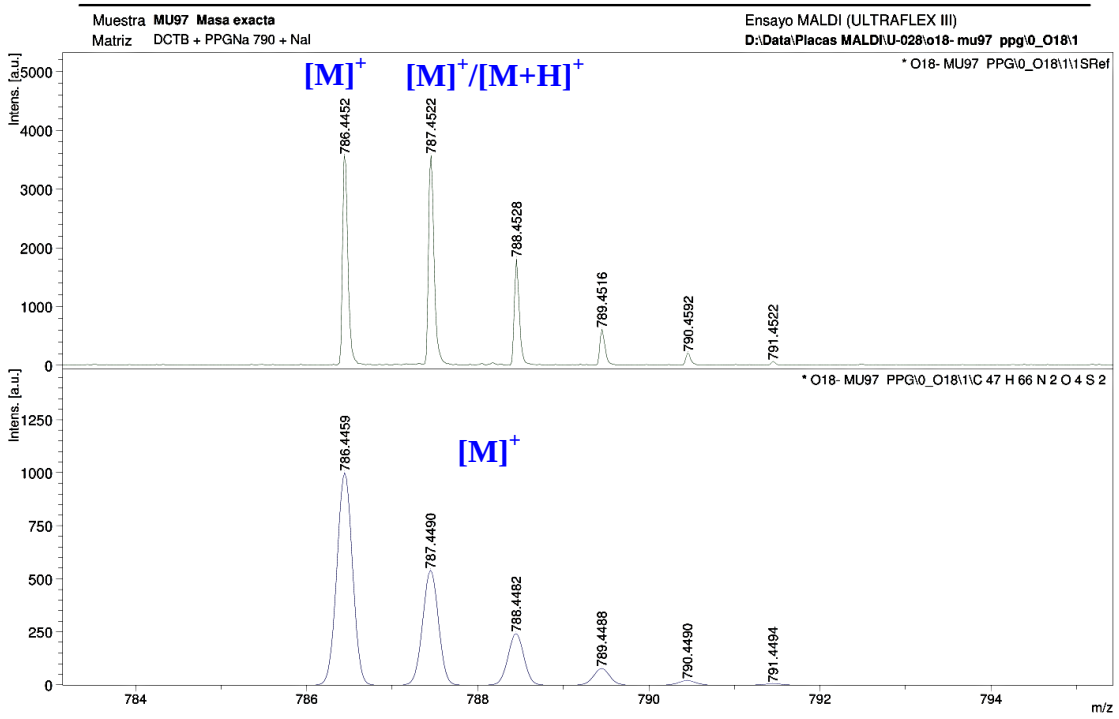


Figure S41. HRMS spectrum of **2** (MALDI-TOF, matrix: DCTB + PPGNa 790 + NaI): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

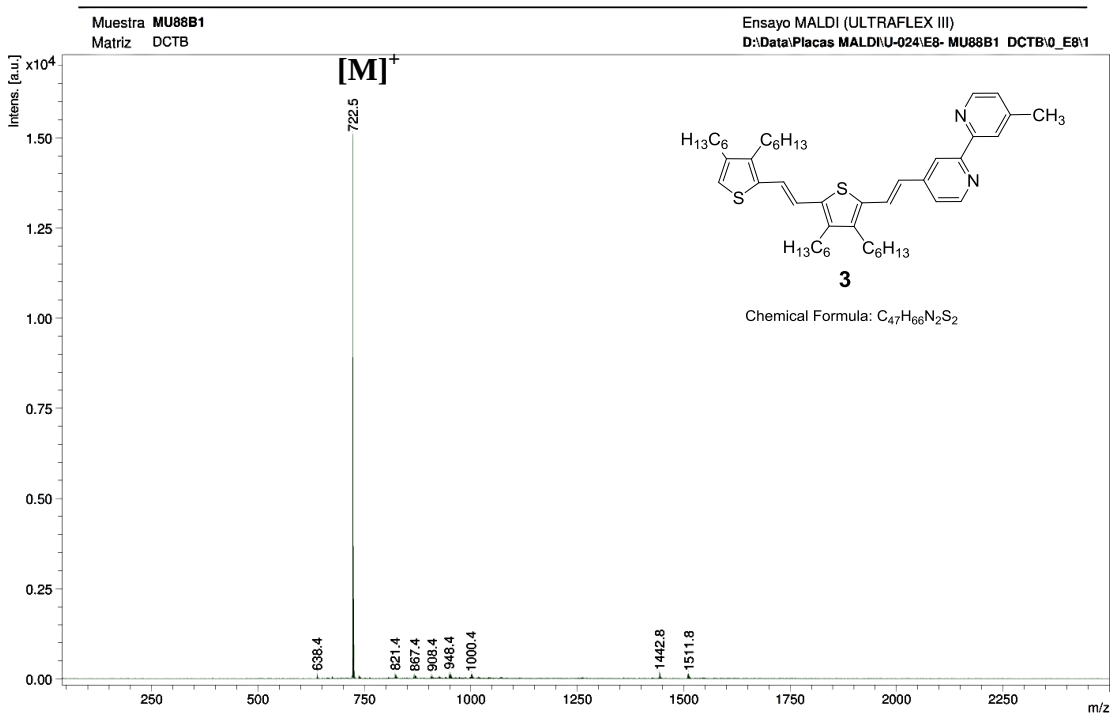


Figure S42. MS spectrum of **3** (MALDI-TOF, matrix: DCTB).

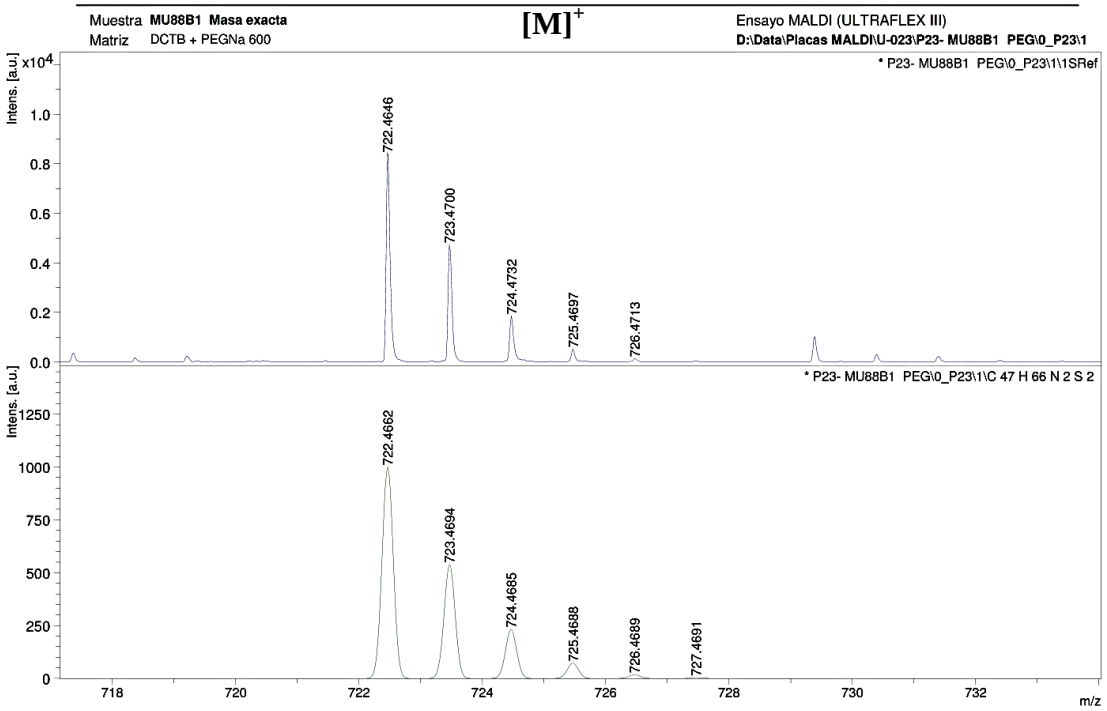


Figure S43. HRMS spectrum of **3** (MALDI-TOF, matrix: DCTB + PEGNa 600): experimental (top) and theoretical isotopic distribution calculated for [M]+ (bottom).

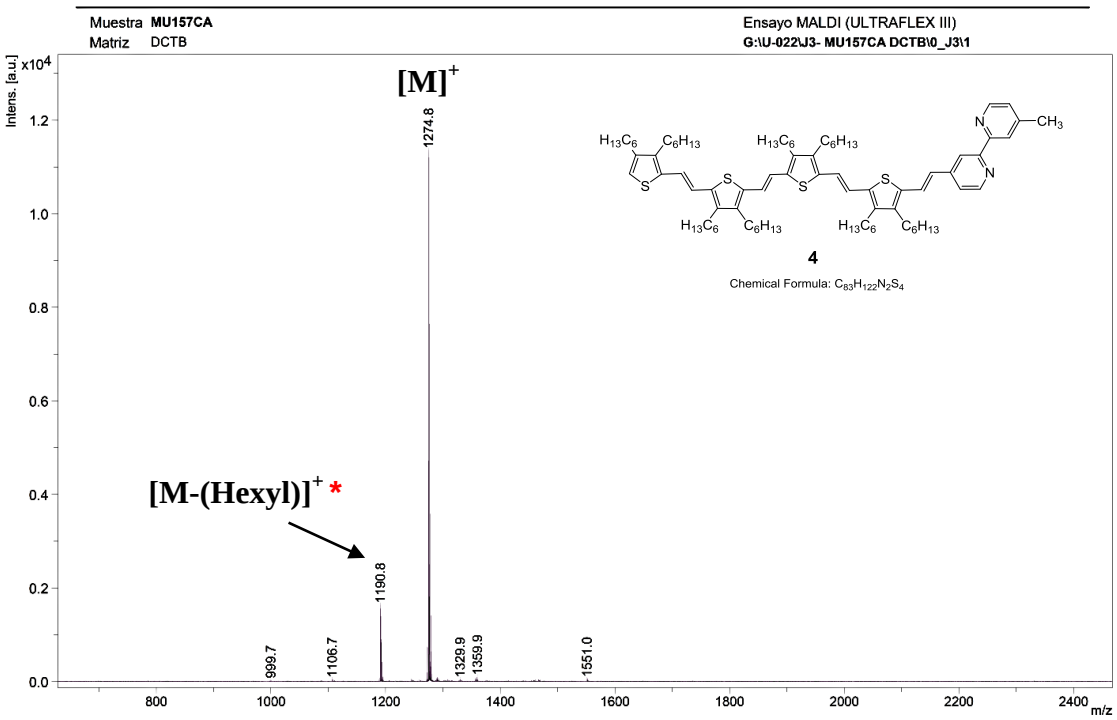


Figure S44. MS spectrum of **4** (MALDI-TOF, matrix: DCTB; *denotes a fragmentation peak).

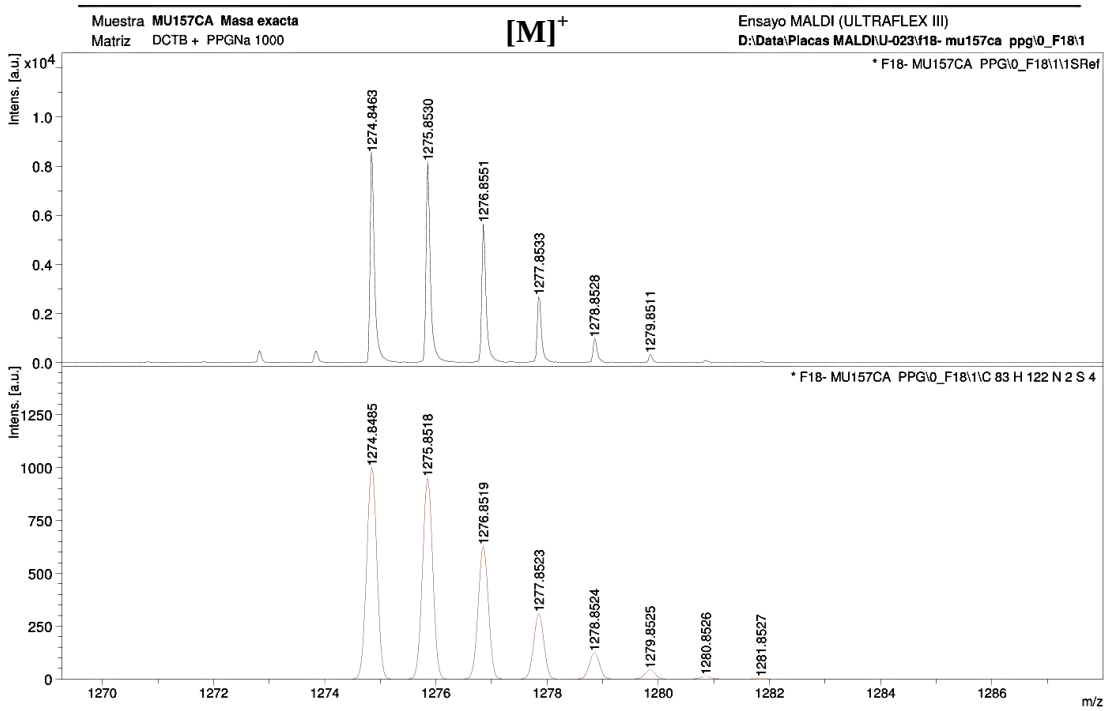


Figure S45. HRMS spectrum of **4** (MALDI-TOF, matrix: DCTB + PPGNa 1000): experimental (top) and theoretical isotopic distribution calculated for [M]+ (bottom).

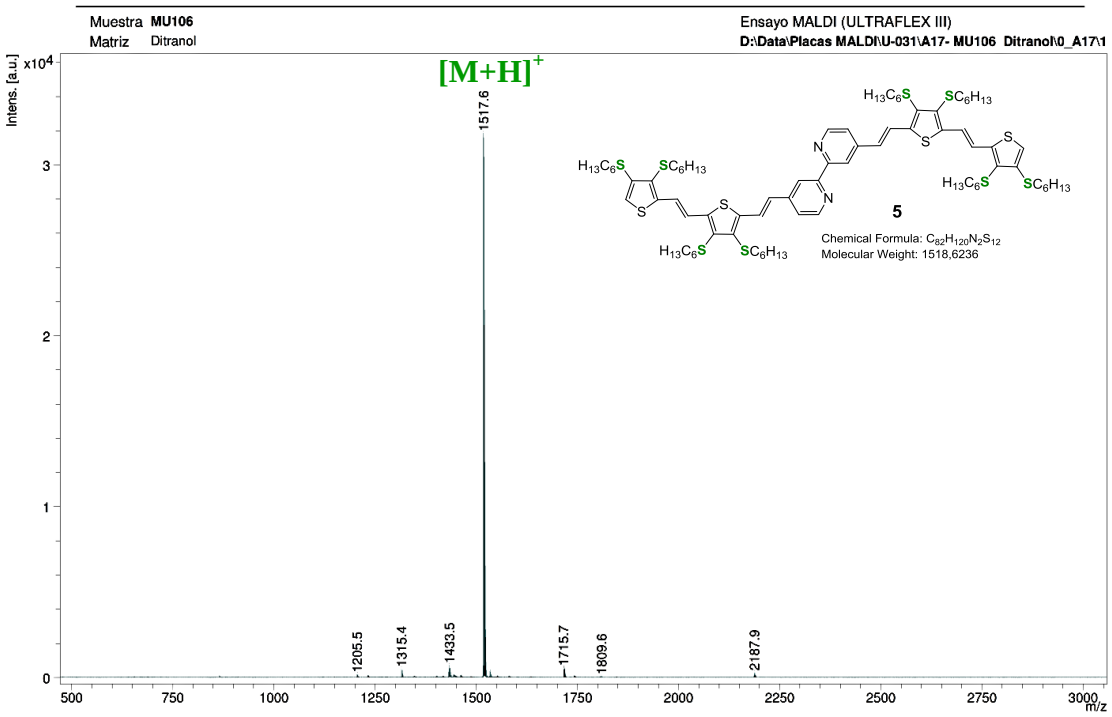


Figure S46. MS spectrum of **5** (MALDI-TOF, matrix: dithranol).

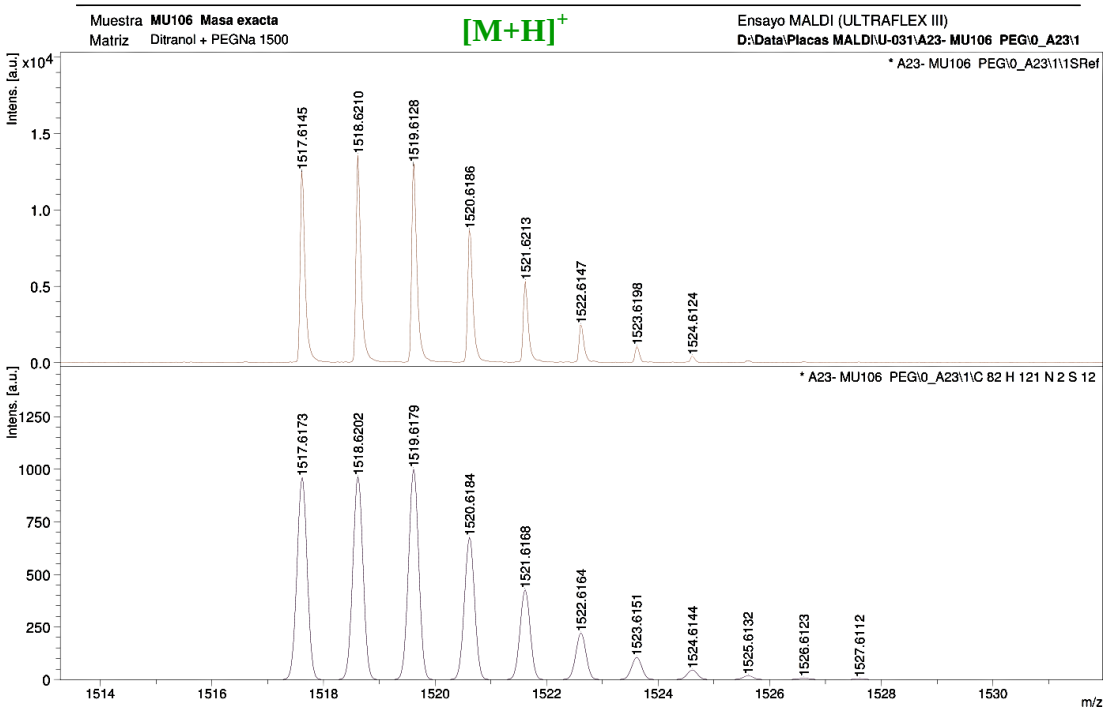


Figure S47. HRMS spectrum of **5** (MALDI-TOF, matrix: dithranol + PEGNa 1500 experimental (top) and theoretical isotopic distribution calculated for [M+H]+ (bottom).

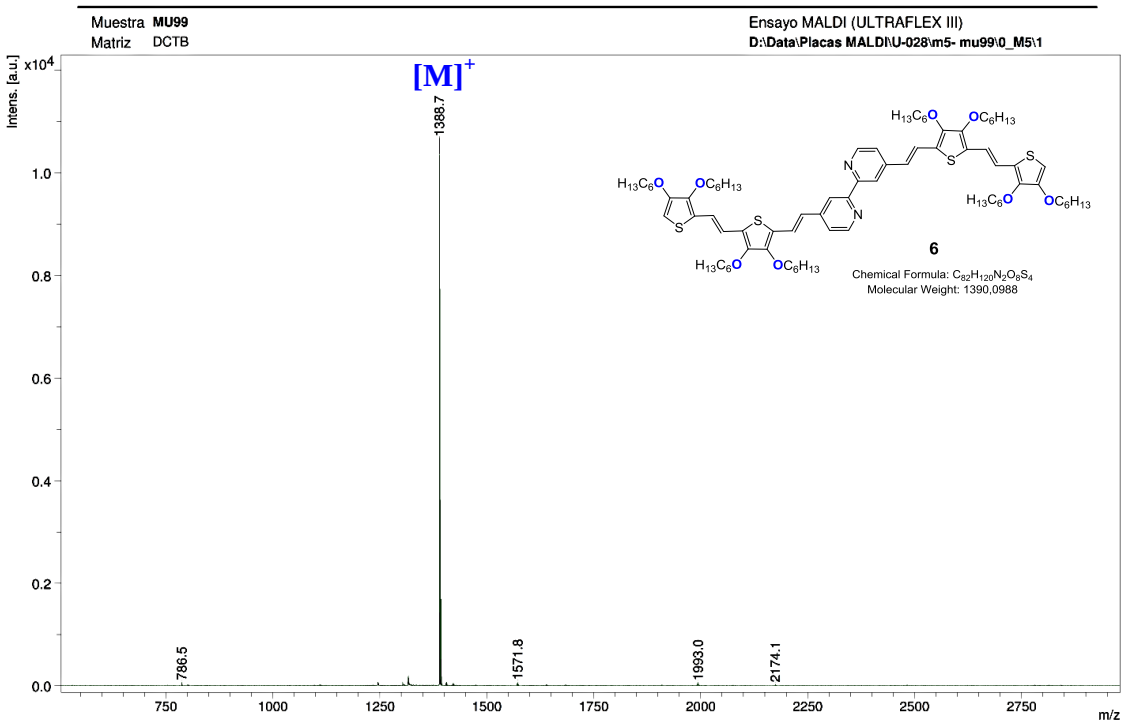


Figure S48. MALDI-TOF mass spectrum of **6** (matrix: DCTB).

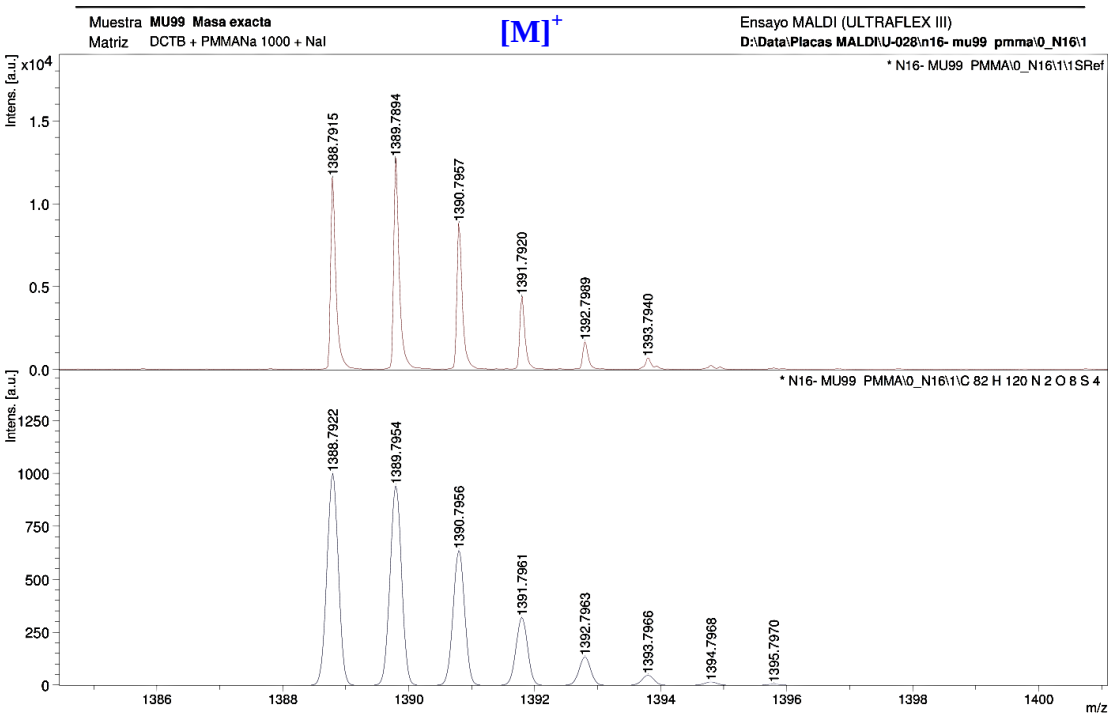


Figure S49. HRMS spectrum of **6** (MALDI-TOF, matrix: DCTB + PMMANa 1000 + NaI): experimental (top) and theoretical isotopic distribution calculated for [M]+ (bottom).

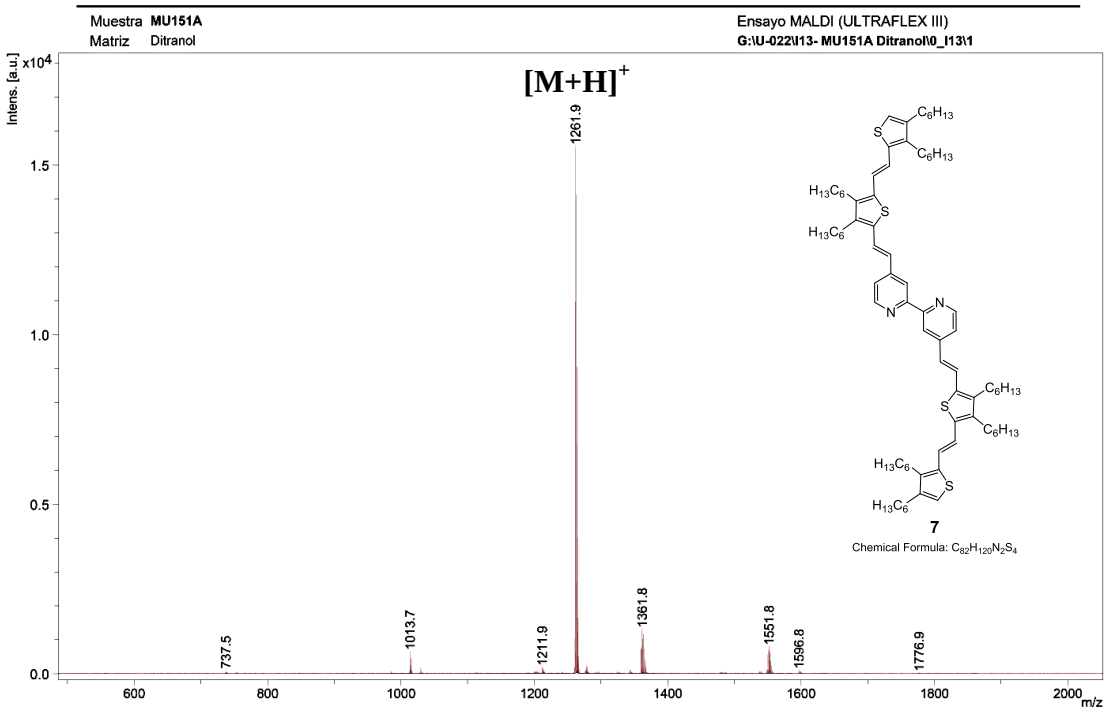


Figure S50. MS spectrum of **7** (MALDI-TOF, matrix: Dithranol).

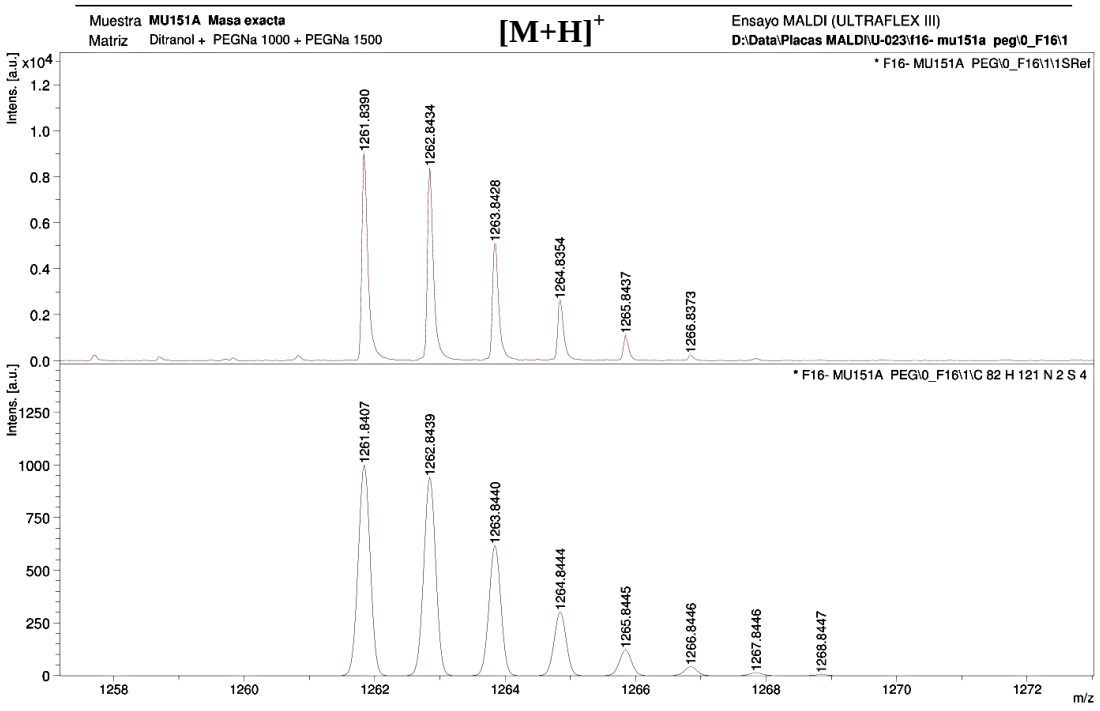


Figure S51. HRMS spectrum of **7** (MALDI-TOF, matrix: Dithranol + PEGNa 1000 + PEGNa 1500) experimental (top) and theoretical isotopic distribution calculated for [M+H]+ (bottom).

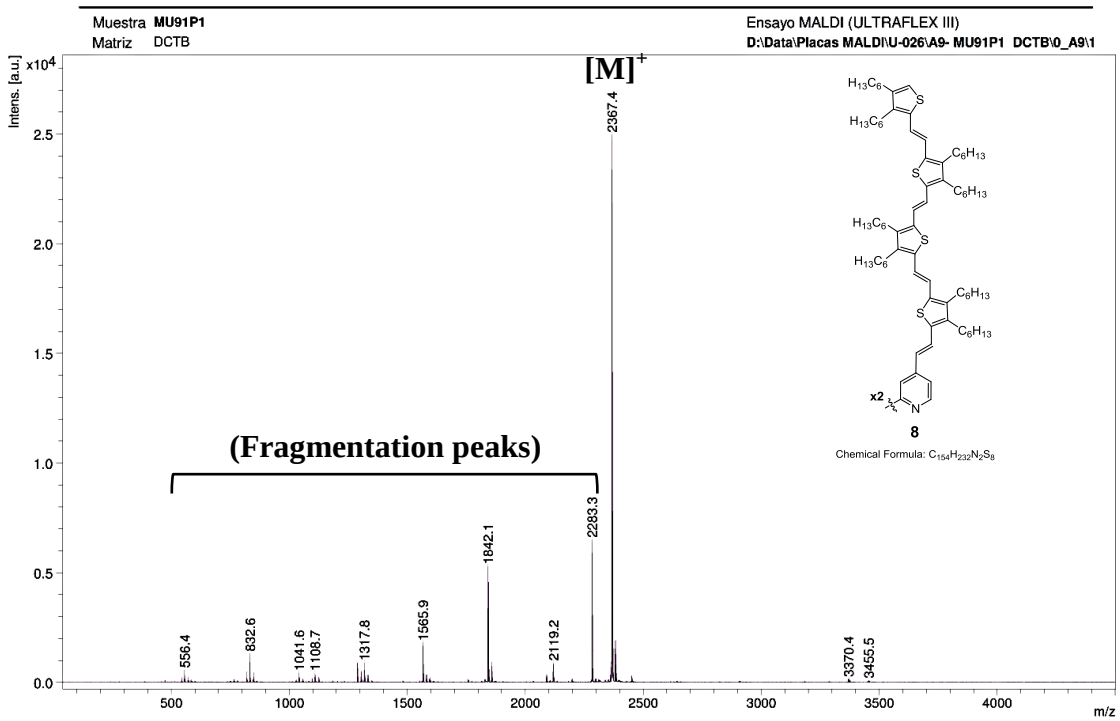


Figure S52. MS spectrum of **8** (MALDI-TOF, matrix: DCTB).

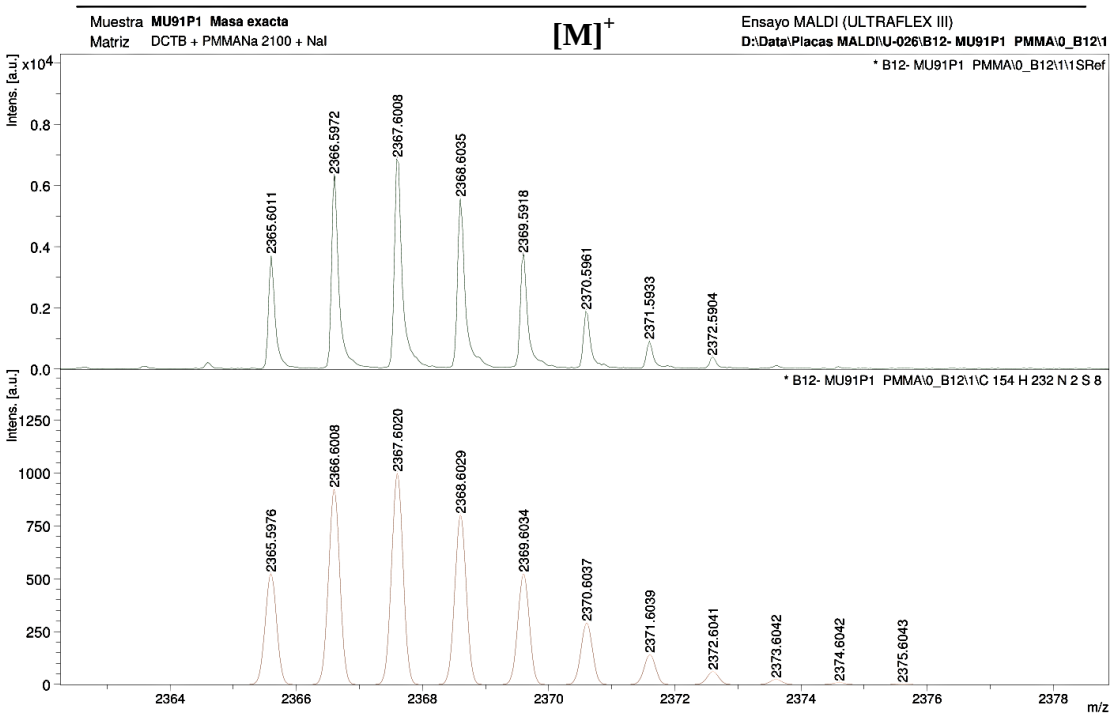


Figure S53. HRMS spectrum of **8** (MALDI-TOF, matrix: DCTB + PMMANa 2100+ NaI): experimental (top) and theoretical isotopic distribution calculated for [M]+ (bottom).

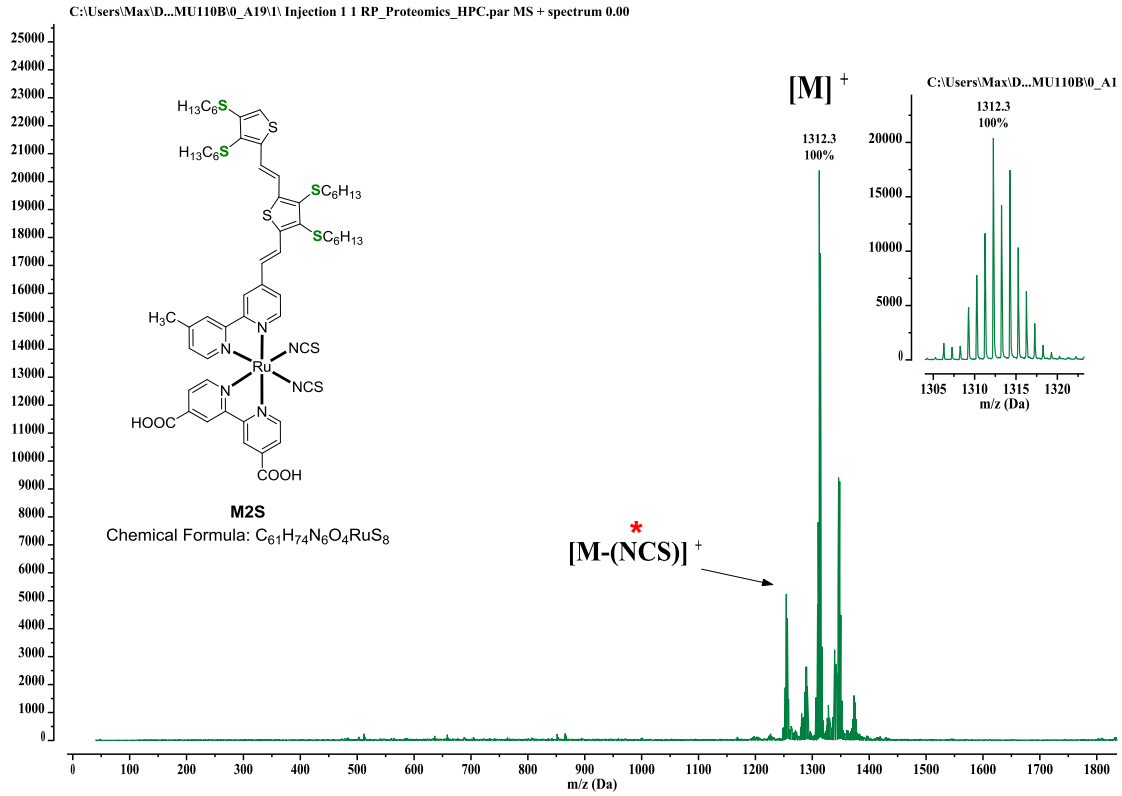


Figure S54. MS spectrum of **M2S** (MALDI-TOF, matrix: DCTB; *denotes a fragmentation peak).

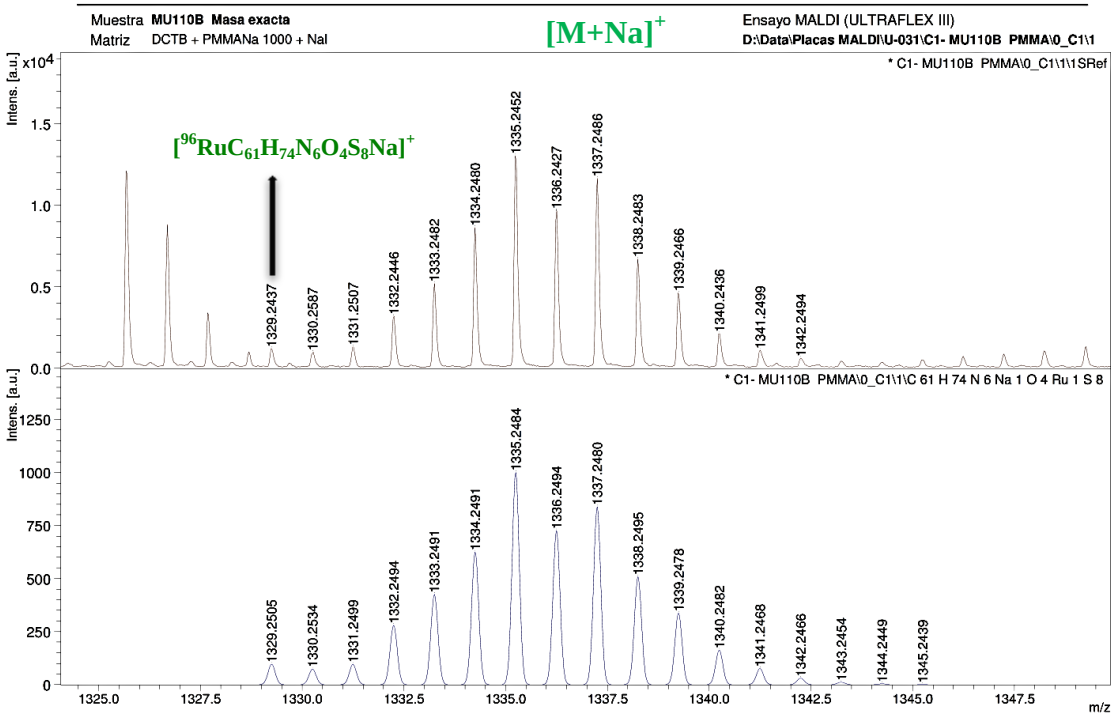


Figure S55. HRMS spectrum of **M2S** (MALDI-TOF, matrix: DCTB+PMMANa+NaI): experimental (top) and theoretical isotopic distribution calculated for [M+Na]+ (bottom).

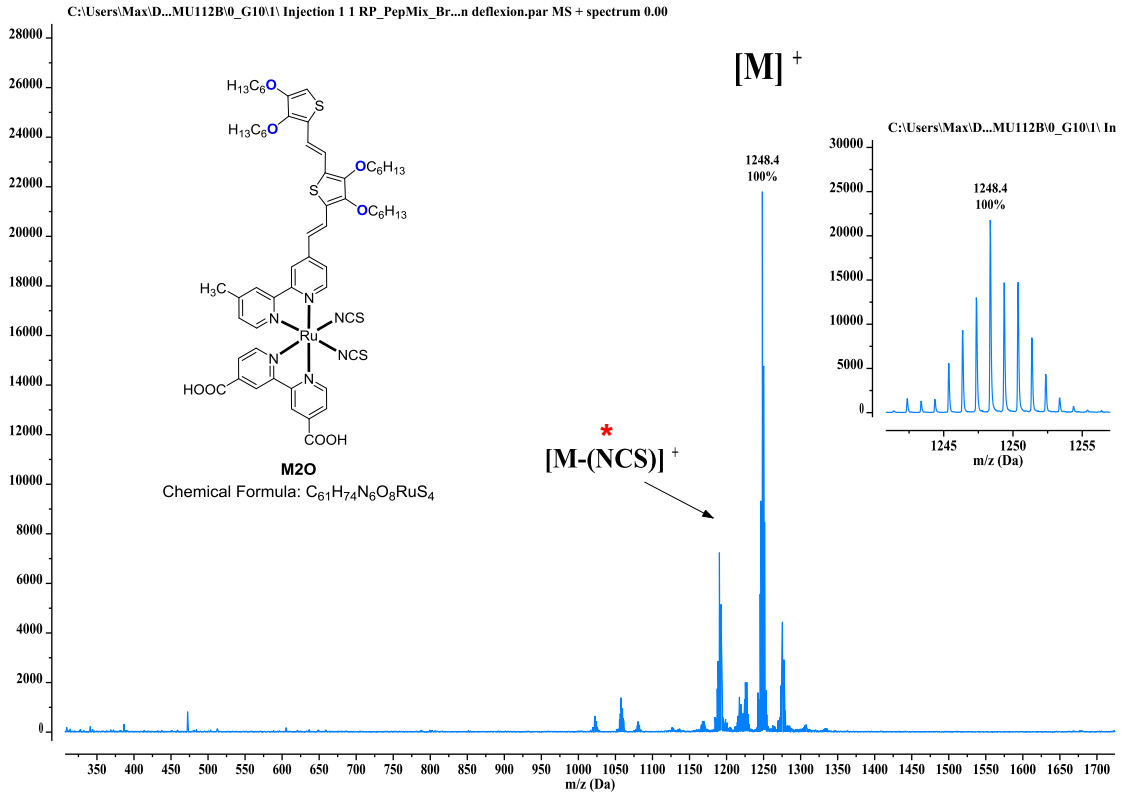


Figure S56. MS spectrum of **M2O** (MALDI-TOF, matrix: dithranol; *denotes a fragmentation peak).

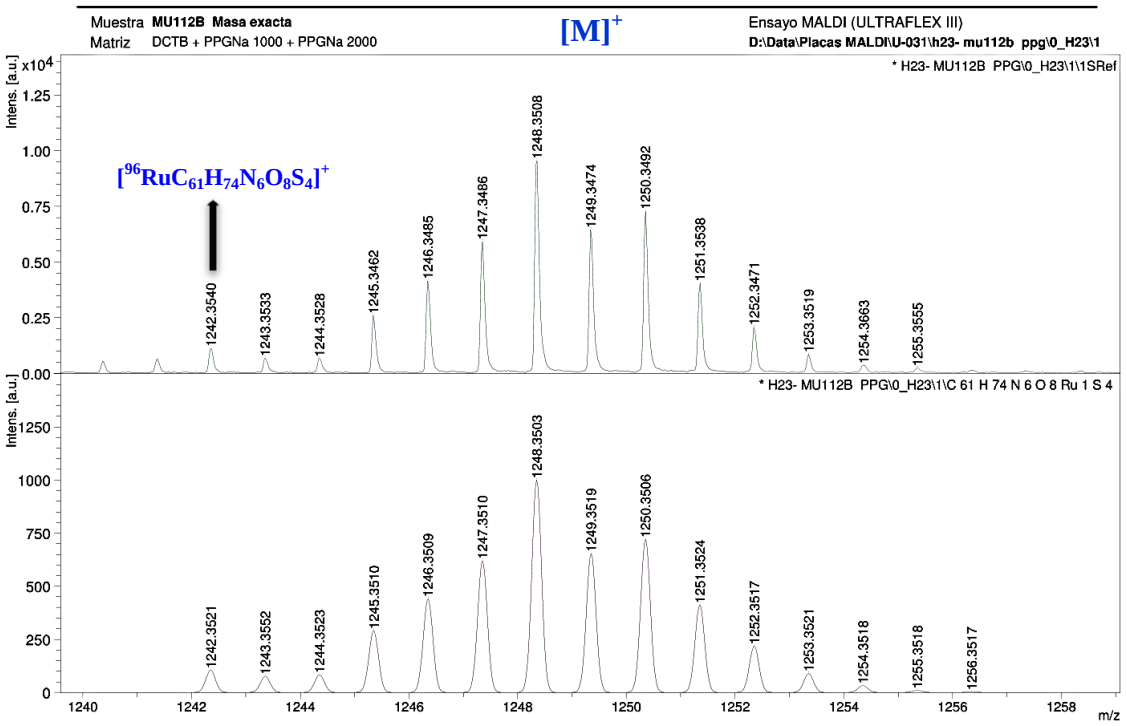


Figure S57. HRMS spectrum of **M2O** (MALDI-TOF, matrix: DCTB+PPGNa+PPGNa2000): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

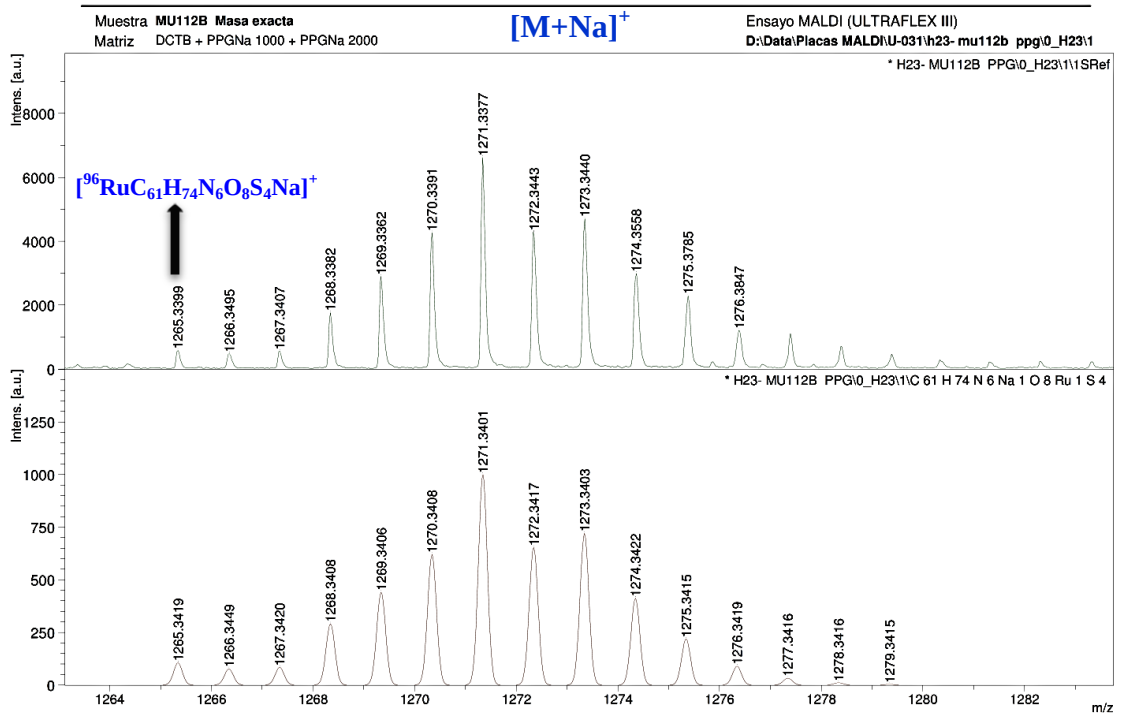


Figure S58. HRMS spectrum of **M2O** (MALDI-TOF, matrix: DCTB + PPGNa + PPGNa 2000) experimental (top) and theoretical isotopic distribution calculated for $[M+Na]^+$ (bottom).

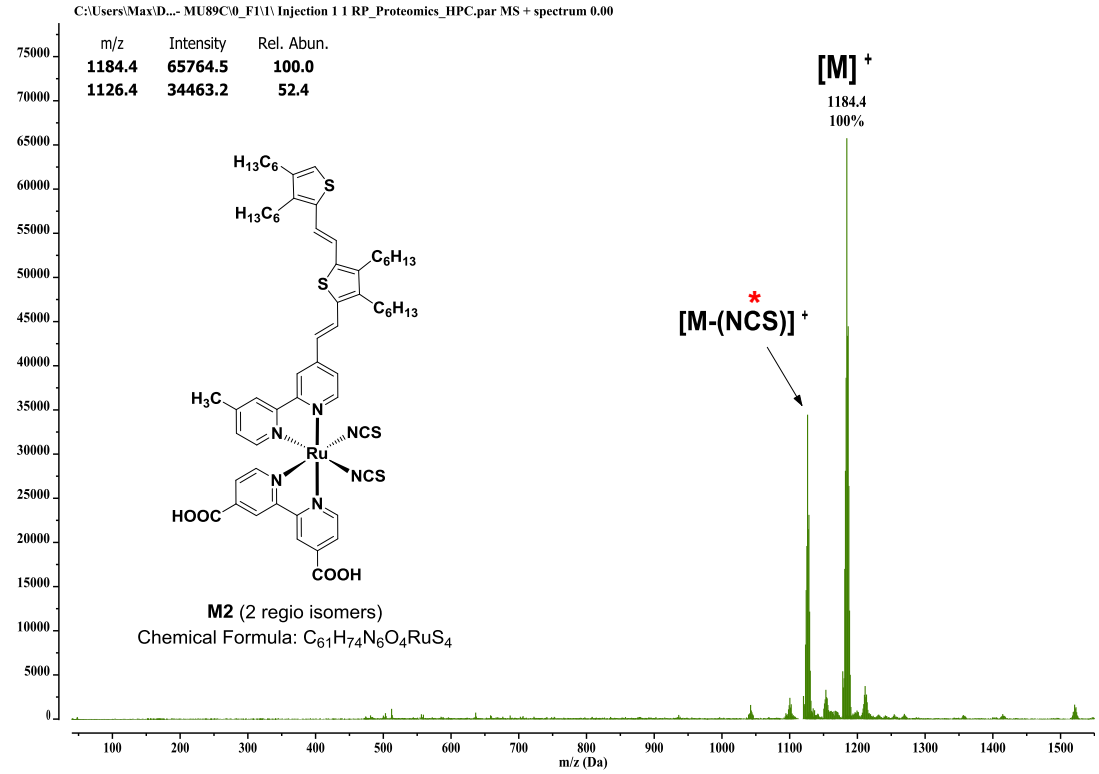


Figure S59. MS spectrum of **M2** (MALDI-TOF, matrix: DCTB; *denotes a fragmentation peak).

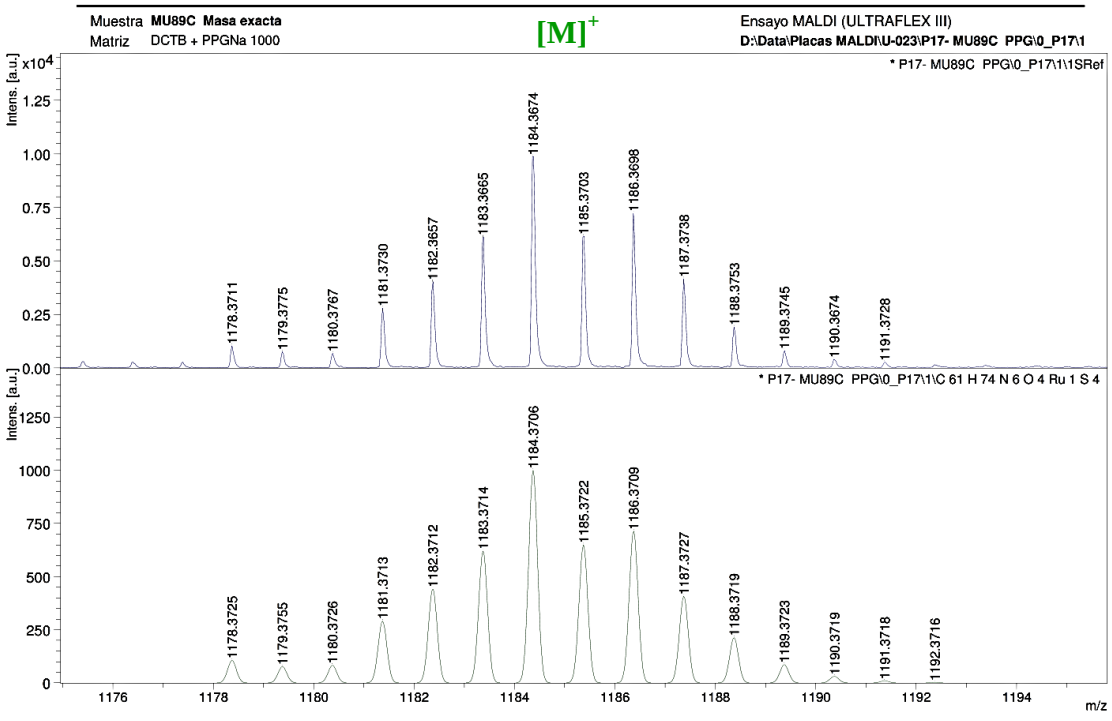


Figure S60. HRMS spectrum of **M2** (MALDI-TOF, matrix: DCTB + PPGNa 1000): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

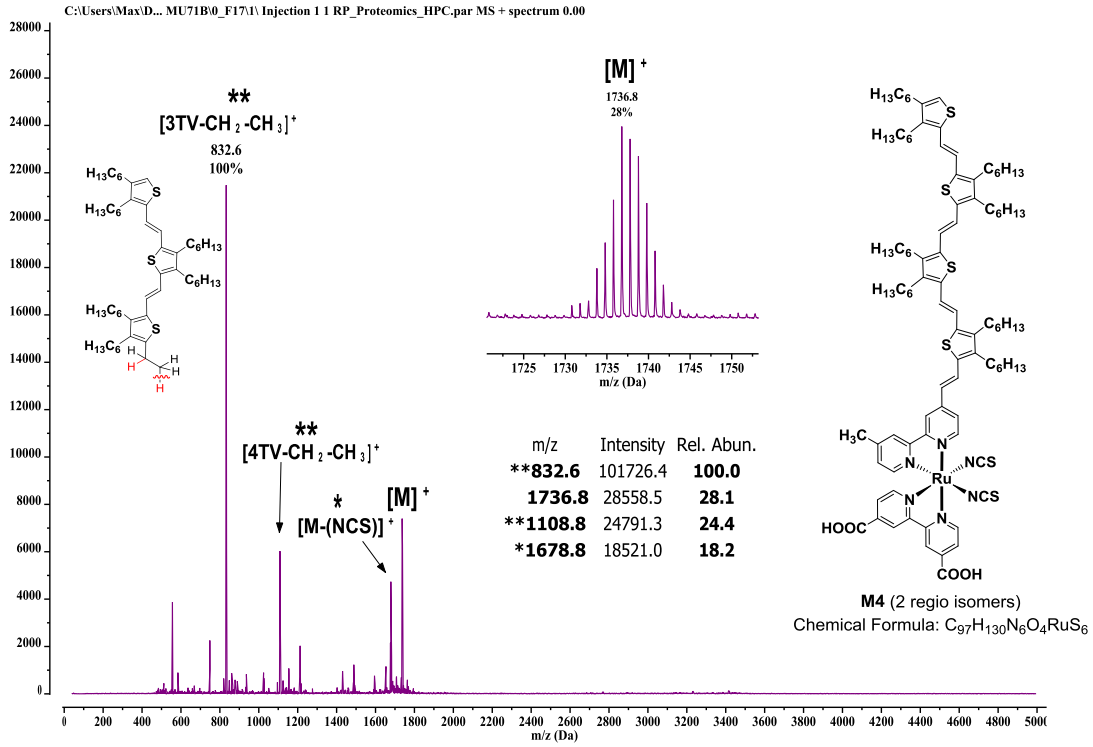


Figure S61. MS spectrum of **M4** (MALDI-TOF, matrix: DCTB; ** denotes fragmentation / recombination species of the 4TV moiety, * denotes the $[M-(NCS)]^+$ fragmentation peak).

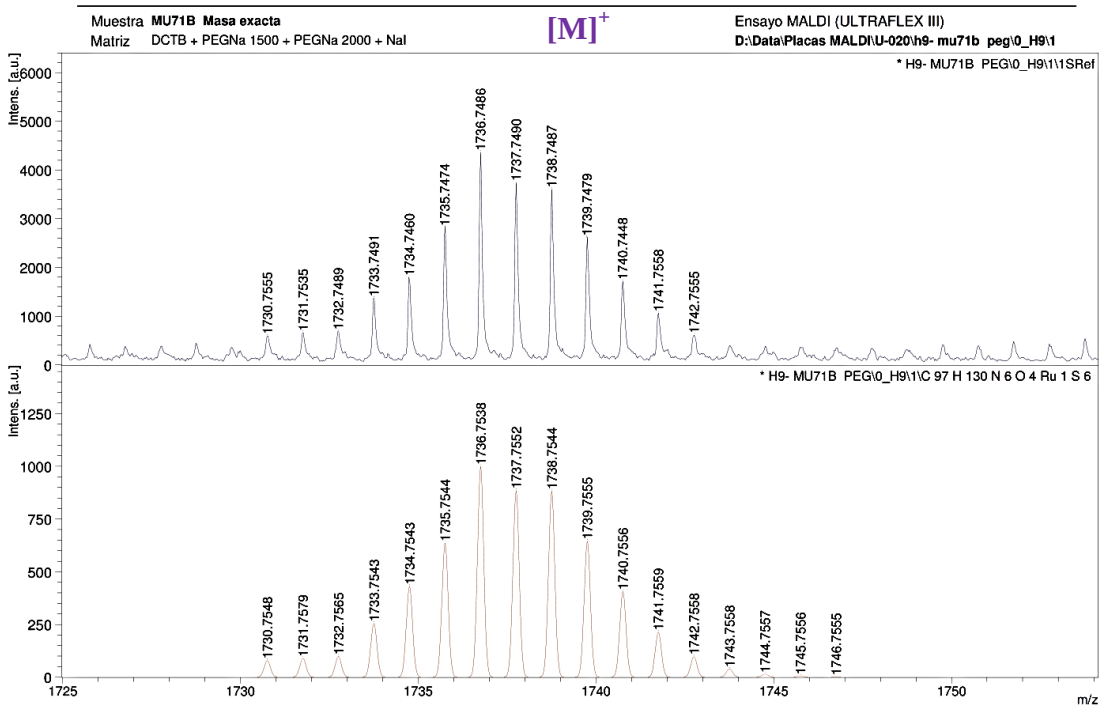


Figure S62. HRMS spectrum of **M4** (MALDI-TOF, matrix: DCTB + PEGNa 1500 + PEGNa 2000 + NaI): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

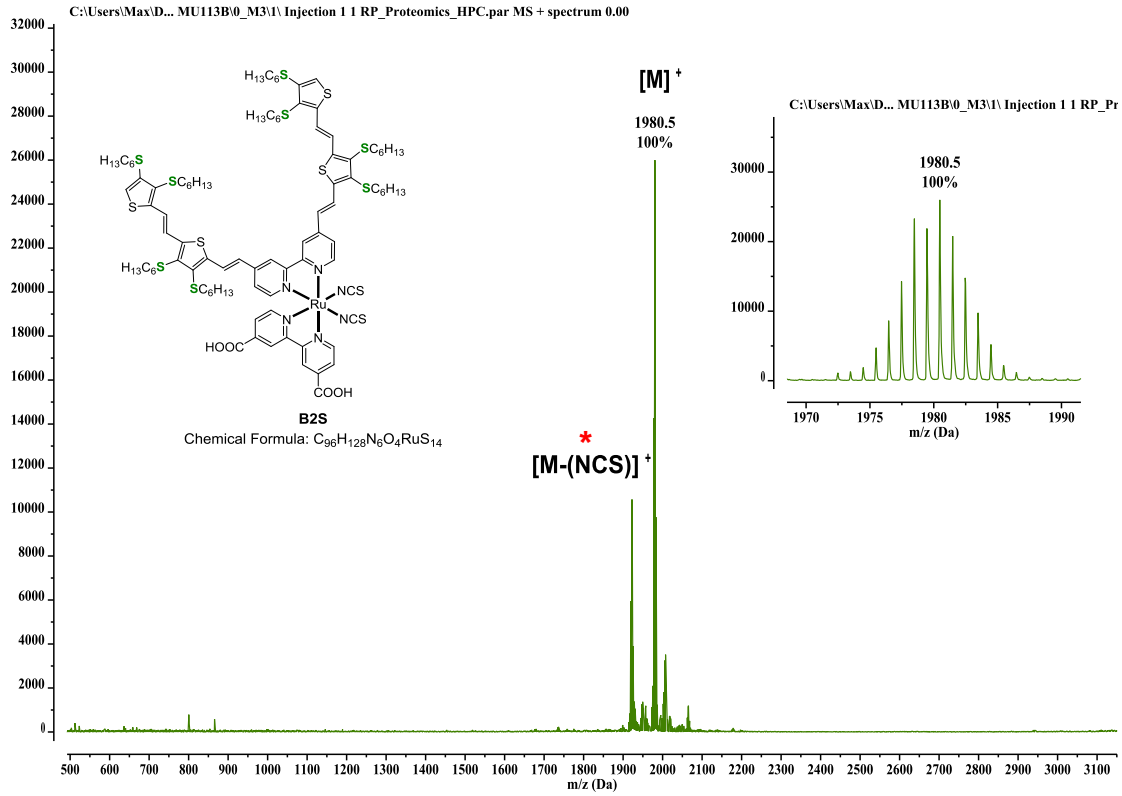


Figure S63. MS spectrum of **B2S** (MALDI-TOF, matrix: DCTB; * denotes a fragmentation peak).

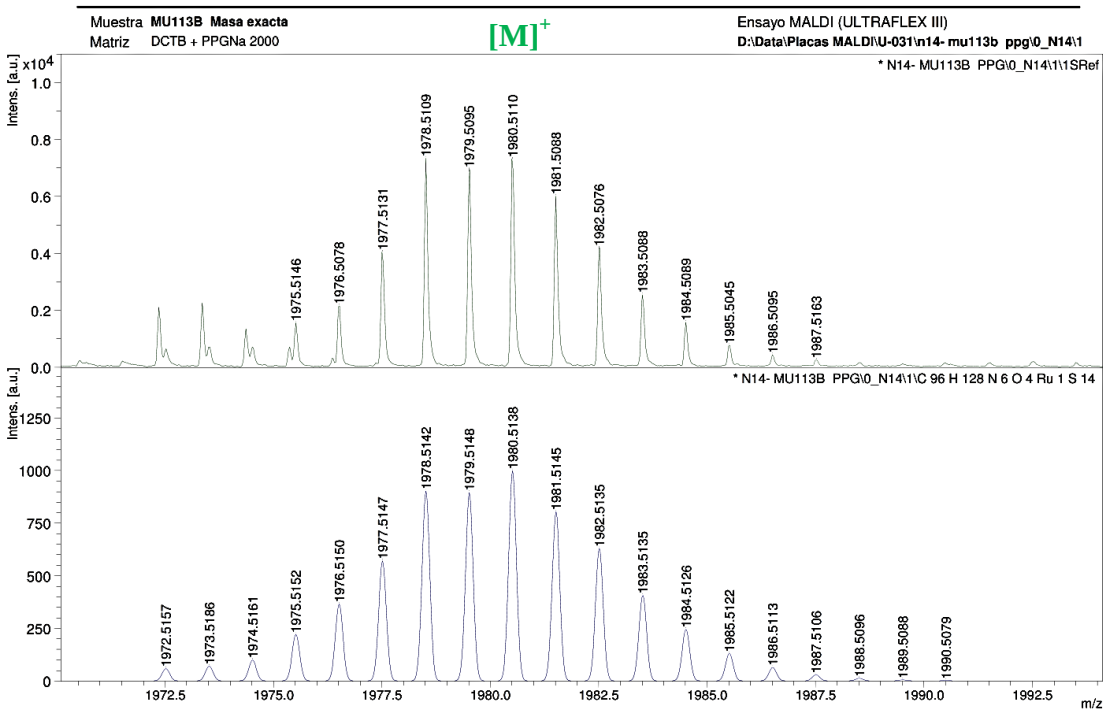


Figure S64. HRMS spectrum of **B2S** (MALDI-TOF, matrix: DCTB+PPGNa 2000): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

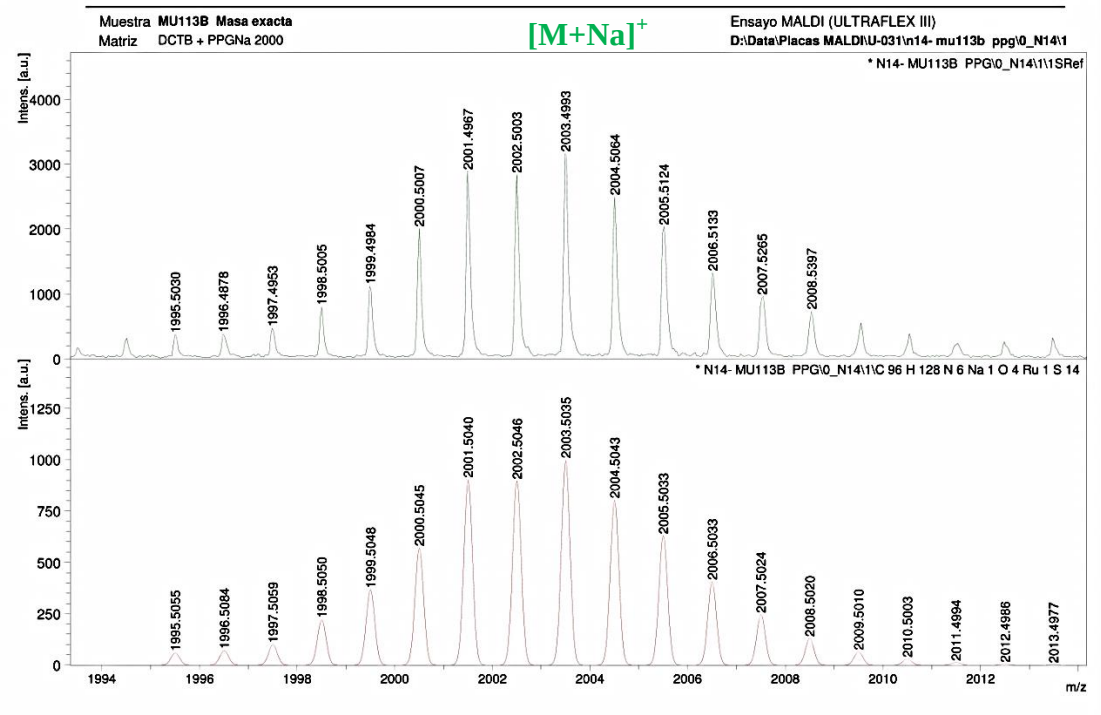


Figure S65. HRMS spectrum of **B2S** (MALDI-TOF, matrix: DCTB+PPGNa 2000): experimental (top) and theoretical isotopic distribution calculated for $[M+Na]^+$ (bottom).

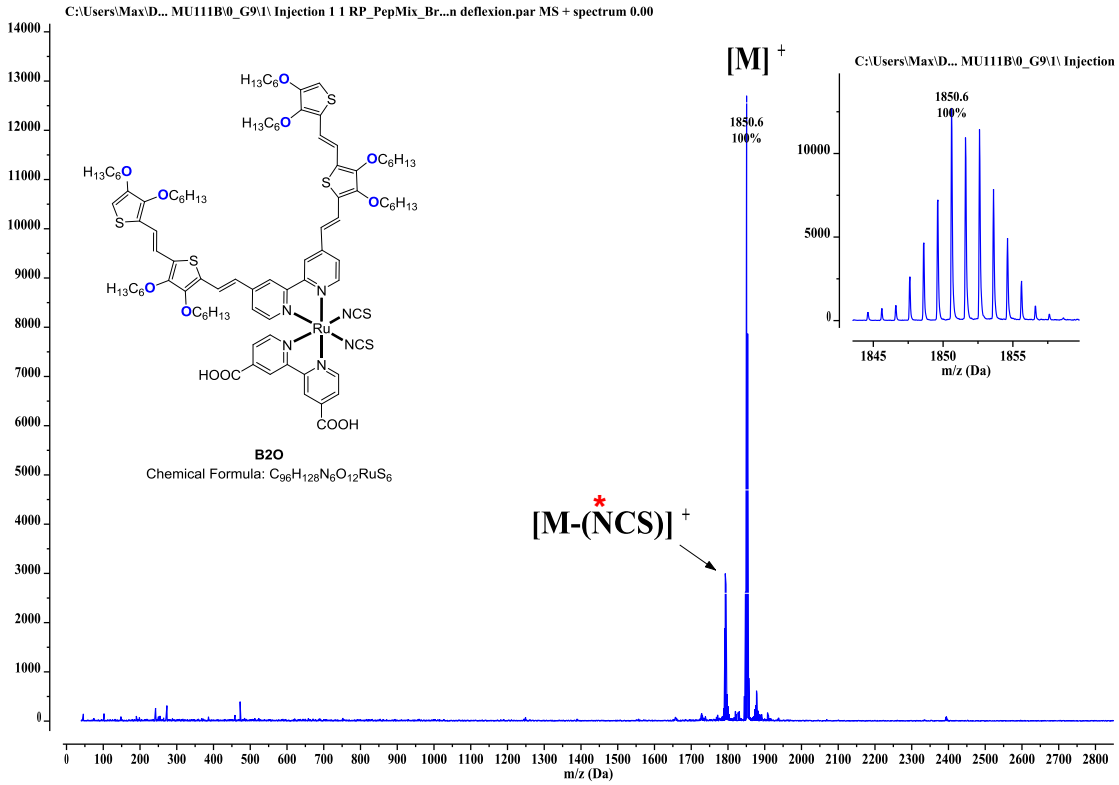


Figure S66. MS spectrum of **B2O** (MALDI-TOF, matrix: DCTB; * denotes a fragmentation peak).

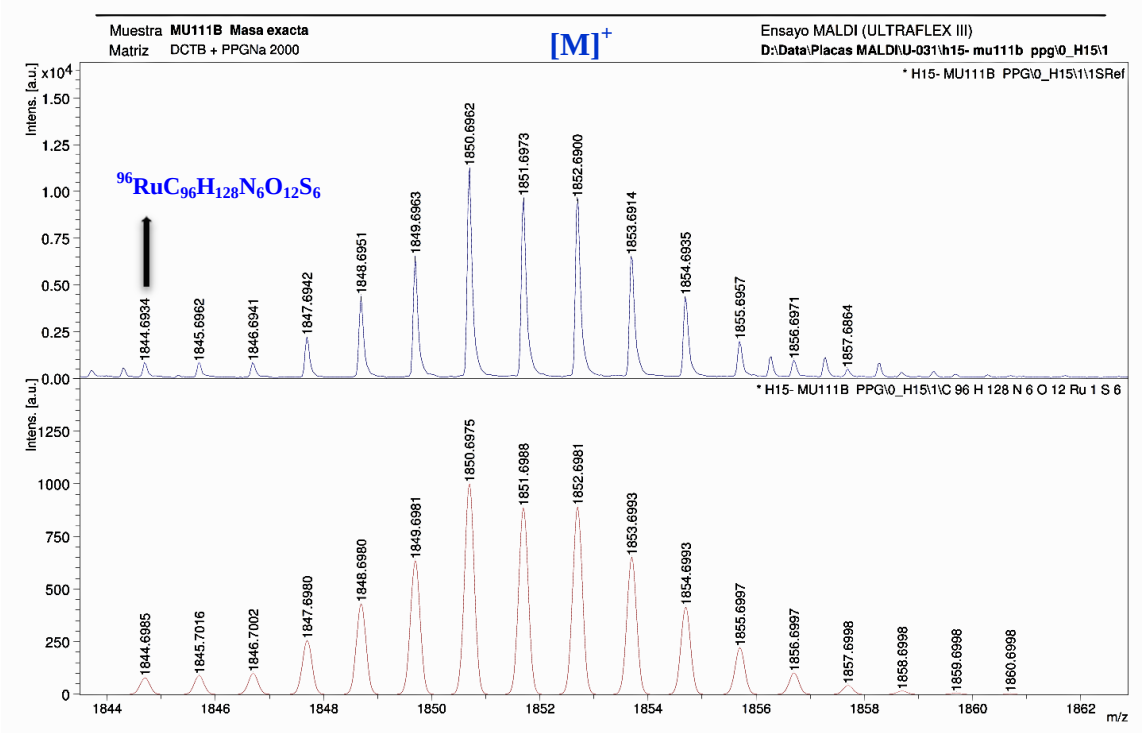


Figure S67. HRMS spectrum of **B2O** (MALDI-TOF, matrix: DCTB + PPGNa 2000): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

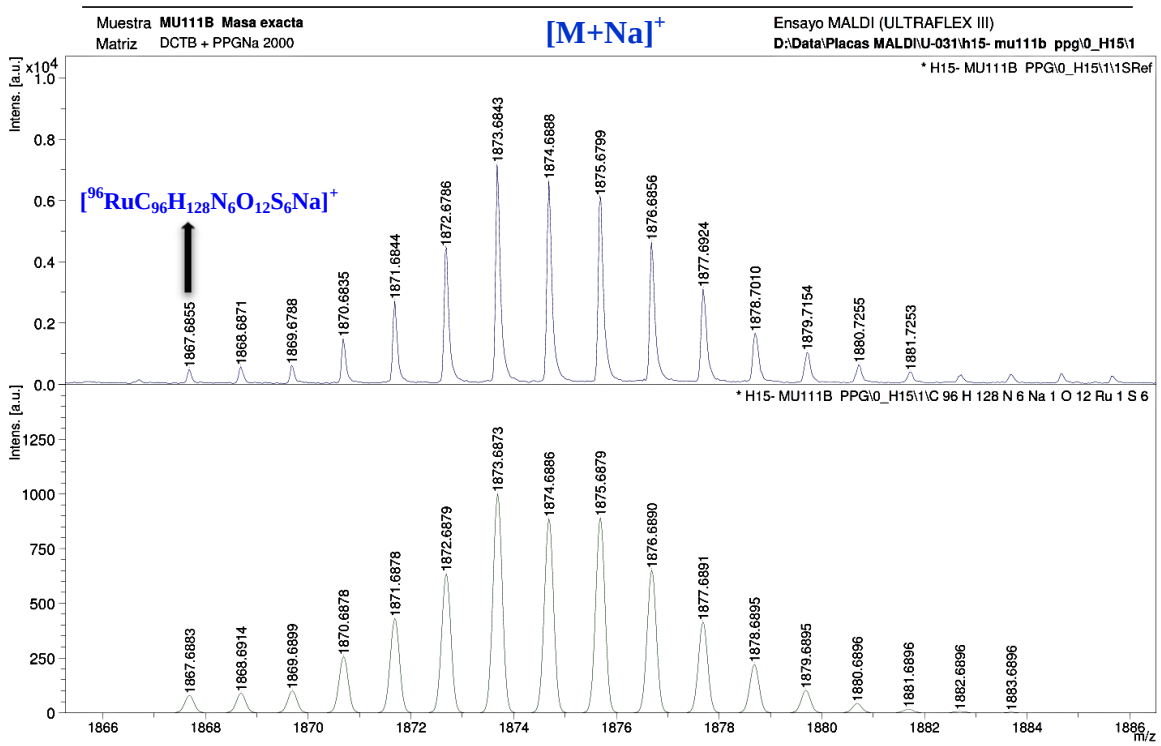


Figure S68. HRMS spectrum of **B2O** (MALDI-TOF, matrix: DCTB + PPGNa 2000): experimental (top) and theoretical isotopic distribution calculated for $[M+Na]^+$ (bottom).

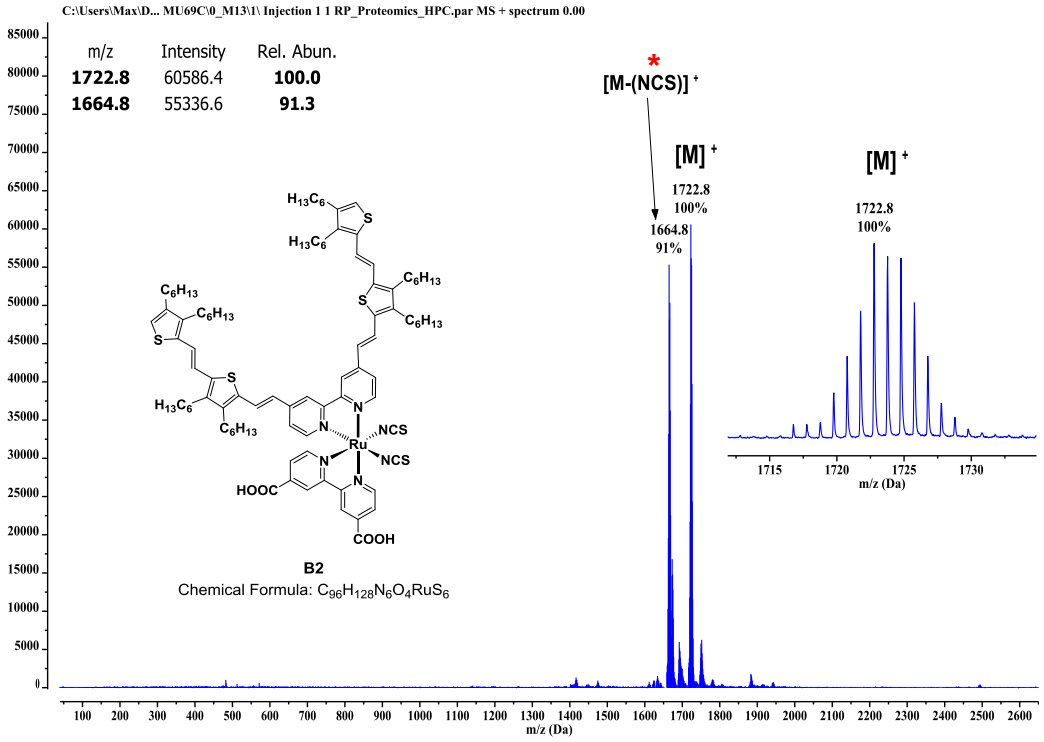


Figure S69. MS spectrum of **B2** (MALDI-TOF, matrix: DCTB).

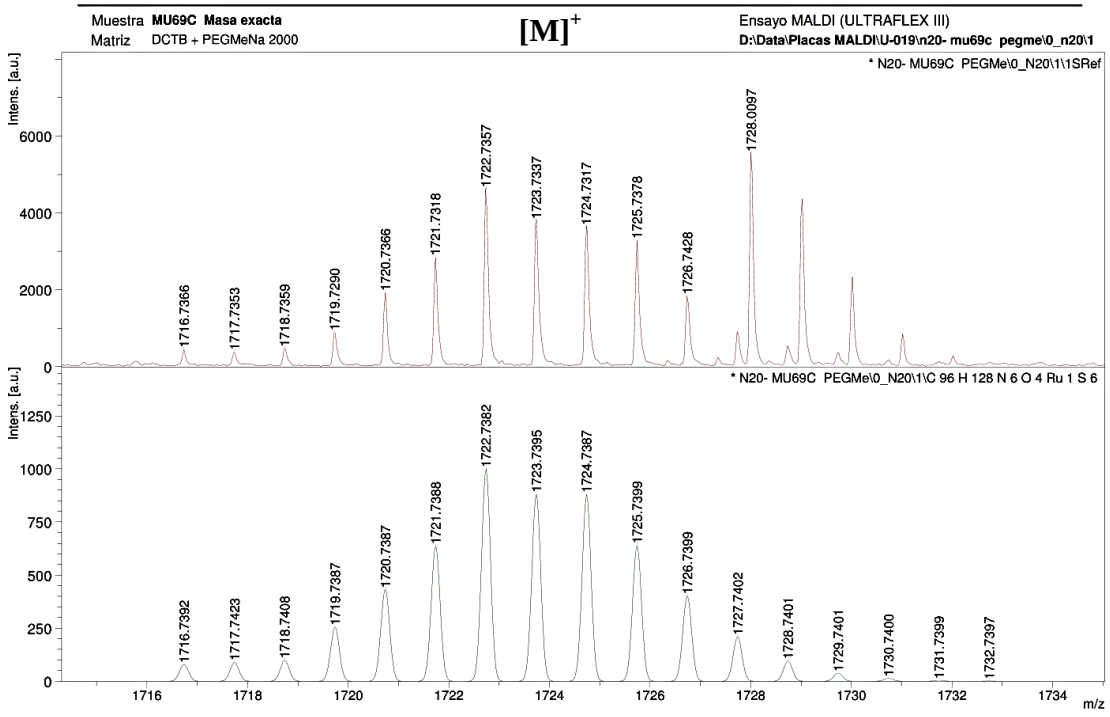


Figure S70. HRMS spectrum of **B2** (MALDI-TOF, matrix: DCTB + PEGMeNa 2000): experimental (top) and theoretical isotopic distribution calculated for $[M]^+$ (bottom).

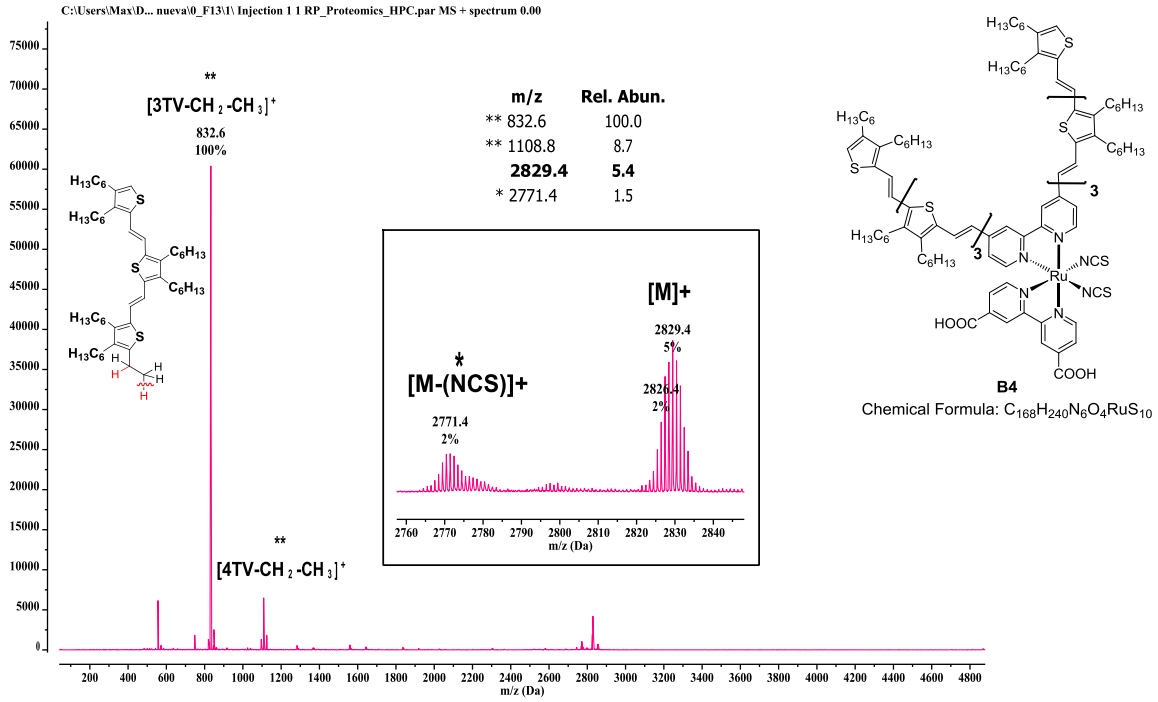


Figure S71. MS spectrum of **B4** (MALDI-TOF, matrix: DCTB); inset: enlargement of the 2760–2845 m/z region (** denotes fragmentation / recombination species of the 4TV moieties); *denotes the M-(NCS)]$^+$ fragmentation peak).

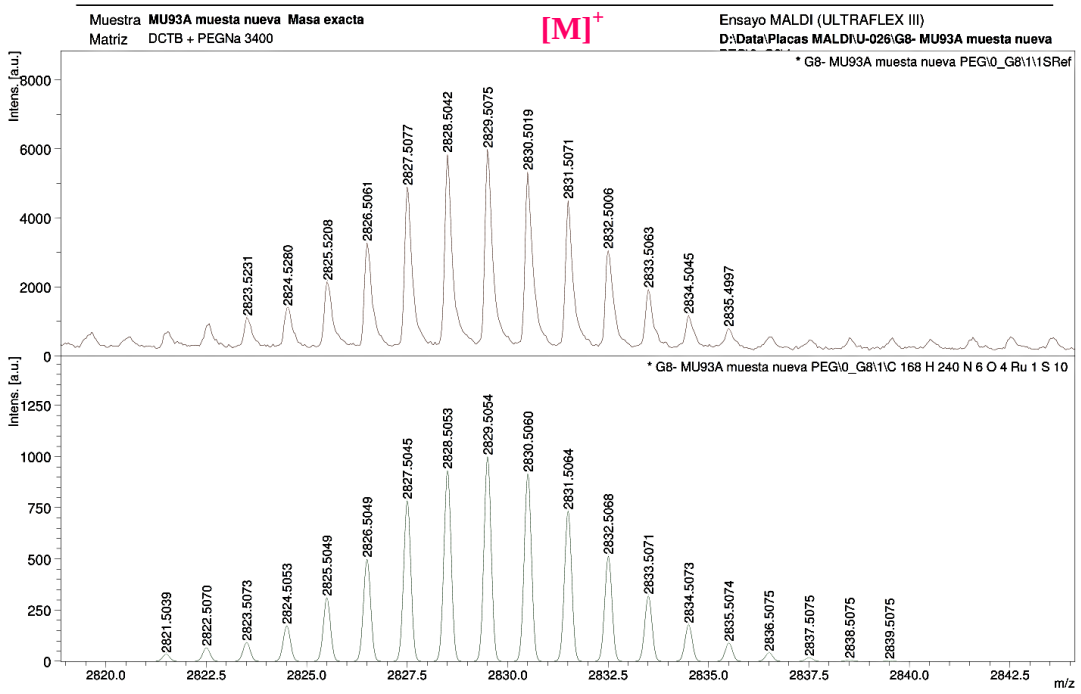


Figure S72. HRMS spectrum of **B4** (MALDI-TOF, matrix: DCTB + PEGNa 3400): experimental (top) and theoretical isotopic distribution calculated for [M]$^+$ (bottom).

V. Device preparation and photovoltaic characterization procedures

- **Photoanode preparation**

A transparent fluorine-doped tin oxide conducting glass (NSG10) was cleaned using ethanol and water followed by an ultrasonic cleaning in Deconnex^{TM} solution for 30 min. The electrodes were then washed with water and ethanol. To remove the organics, a further thermal treatment was done at 500 °C for 30 min. The clean FTO glass were treated twice with $TiCl_4$ (40 mM, 30 min, 75 °C). Two different TiO_2 pastes (transparent layer and scattering layer) were screen printed on to the $TiCl_4$ pre-treated electrode and followed a series sintering step as described elsewhere in the literature (See: Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M. K.; Grätzel, M. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. Thin Solid Films 2008, *516*, 4613-4619). The transparent layer were made with 20 nm TiO_2 particles with a pore diameter of 32 nm, and the scattering layer with 400 nm size particles. The photoanodes were further treated with $TiCl_4$ following the steps described above.

- **Device fabrication**

The TiO_2 electrodes were dried at 500°C for 30 min prior to the sensitization in the dye solution. The dye solutions were composed of 0.2 mM of Ru(II)-complex in a mixture of $CHCl_3$ and EtOH (2:3). When indicated, coadsorbent (CHENO) was incorporated in the dye solution at a concentration of 0.2 mM (i.e. 1 eq/ dye molecule). After 14–18h of dipping, the electrodes were successively washed with a 1:10 mixture of $CHCl_3$ and EtOH, and then EtOH (100 %) to remove the loosely bounded dye molecules. The counter electrodes were made by drop casting of isopropanolic solution of H_2PtCl_6 (5 mM) onto a pre-cleaned FTO glass (TEC7, Solaronix, Switzerland) and the electrodes were fired at 410 °C for 30 min. The sensitized photoanode and counter electrode were melt sealed using a 25 µm polymeric spacer (Surlyn^{TM}, Dupont, USA). The electrolyte in acetonitrile was then injected by the vacuum backfilling process through a hole drilled at the side of the counter electrode. The cell fabrication was completed by melt sealing the hole with a glass and soldering the metal solder to make contacts.

- **Photovoltaic characterization**

A 450W xenon lamp (Oriel, USA) was used as a light source. The spectral output of the lamp was filtered using a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2%. The current-voltage characteristics of the cell were recorded with a Keithley model 2400 digital source meter (Keithley, USA). The photo-active area of 0.159 cm^2 was defined by a black metal mask. The values reported are for the best devices obtained in each configuration. Two cells were made for each conditions.

Table S1. Detailed photovoltaic data of the DSSC devices on [10+5][b] µm thick TiO_2 films using iodine-based liquid electrolytes[c] A, B, or C, under simulated one sun illumination (AM1.5G) and active area of 0.159 cm^{-2}.

Dye	Elect.[c]	Cell	V_{OC} (mV)	J_{SC} (mA/cm²)	F.F.	P_{in} (mW•cm^{-2})	Calcd. η (%)	Average η (%)
M2S	A	#1	581.92	5.66	0.772	96.921	**2.62**	2.33 ± 0.3
		#2	573.79	4.48	0.772	97.793	2.03	
	B	#1	584.27	6.20	0.749	98.063	**2.77**	2.57 ± 0.2
		#2	553.48	5.59	0.735	95.978	2.37	
	C	#1	554.60	5.94	0.745	96.509	**2.54**	2.45 ± 0.1
		#2	556.06	5.51	0.721	94.103	2.35	
M2O	A	#1	532.51	4.03	0.722	98.466	**1.57**	1.46 ± 0.1
		#2	520.43	3.44	0.731	97.928	1.34	
	B	#1	525.60	4.59	0.770	96.643	**1.92**	1.78 ± 0.1
		#2	531.96	3.81	0.773	96.072	1.63	
	C	#1	510.70	4.50	0.756	96.541	**1.80**	1.74 ± 0.1
		#2	495.01	4.41	0.740	96.229	1.68	
B2S	A	#1	551.62	2.60	0.692	96.679	**1.03**	0.89 ± 0.14
		#2	525.72	2.33	0.594	96.876	0.75	
	B	#1	547.18	3.84	0.742	97.864	**1.59**	1.39 ± 0.2
		#2	547.56	2.75	0.748	95.353	1.18	
	C	#1	525.18	3.17	0.765	96.717	**1.32**	1.31 ± 0.02
		#2	530.00	3.09	0.761	96.537	1.29	
B2O	A	#1	555.01	3.91	0.756	96.759	**1.70**	1.61 ± 0.1
		#2	549.81	3.56	0.754	96.889	1.52	
	B	#1	555.26	4.88	0.748	95.733	**2.12**	2.00 ± 0.2
		#2	532.69	4.62	0.739	96.038	1.89	
	C	#1	525.60	4.59	0.770	96.643	**1.92**	1.76 ± 0.2
		#2	532.02	3.99	0.730	96.901	1.60	

[b] The TiO_2 films have a total thickness of 15 µm consisting of a 10 µm thick TiO_2 active layer and an additional 5 µm of scattering layer. [c] Electrolytes are composed of 0.6 M DMII, 0.5 M 4-tertbutyl pyridine, 0.03 M I_2 0.1 M guanidinium thiocyanate, in AcCN and differ only by the concentration of lithium iodide: 0.05 M (A), 0.1 M (B) and 0.2 M (C).

VI. I/V curves and IPCE spectra

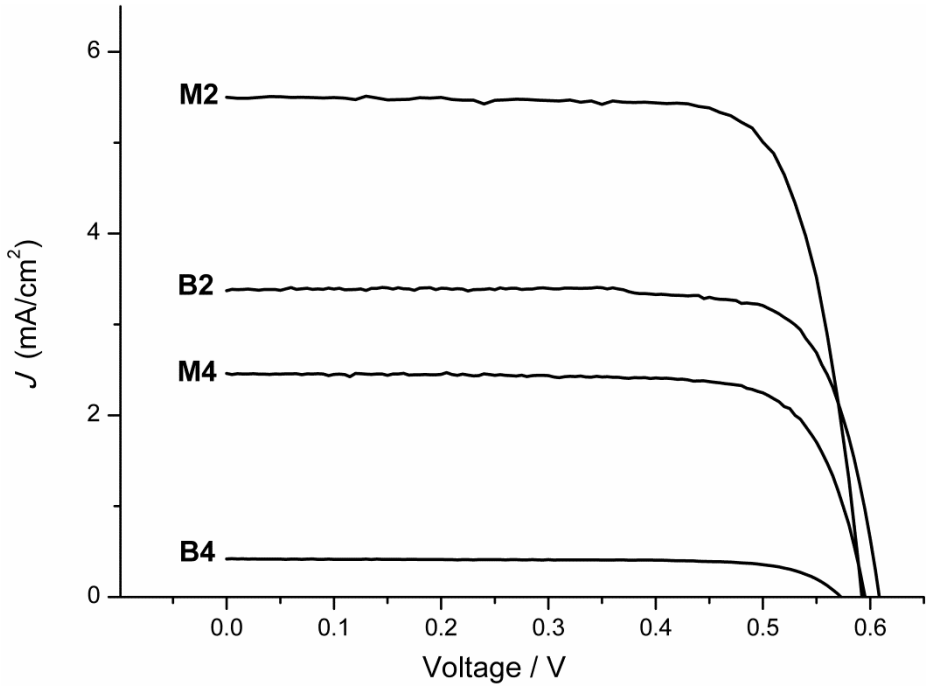


Figure S73. I/V curves under one sun illumination (AM1.5G) of the best DSSC devices made with **M2**, **B2**, **M4** and **B4** ([10+5] µm thick TiO_2 films, electrolyte A).

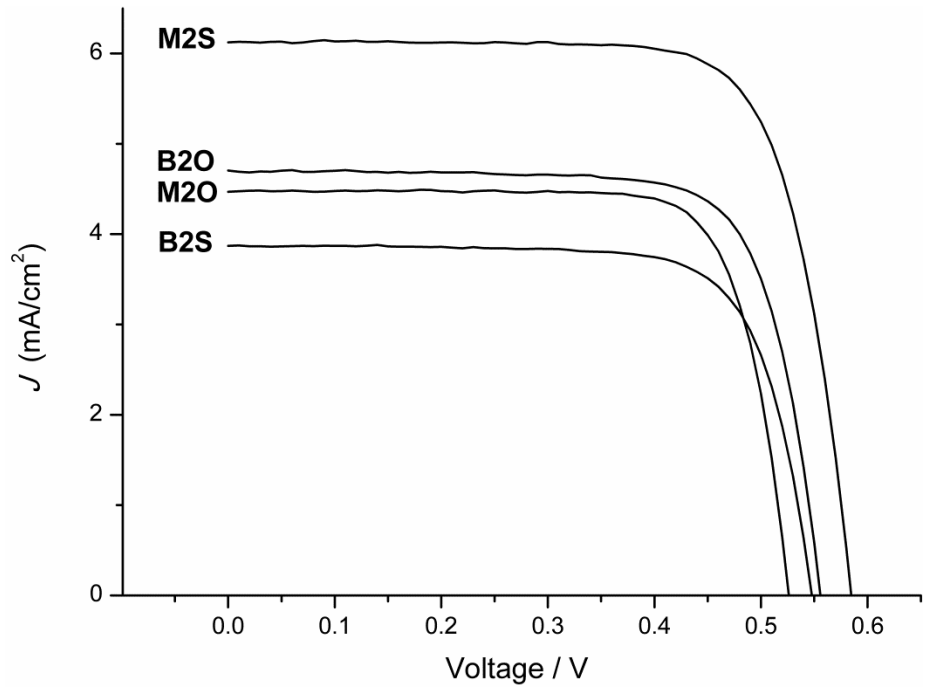


Figure S74. I/V curves under one sun illumination (AM1.5G) of the best DSSC devices made with **M2S**, **M2O**, **B2S** and **B2O** ([10+5] µm thick TiO_2 films, electrolyte B).

Cell Name: MU86_Feb 16#18

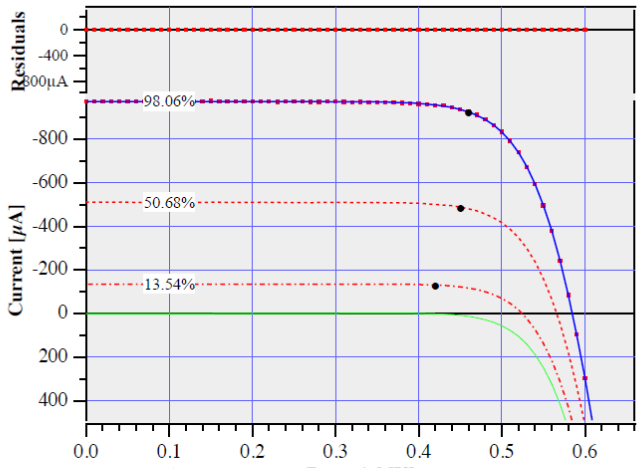
Measurement Date	: Mon, Feb 16, 2015 / 5:03:20 PM
Type of cell	:
Cell Active Area	: 0.16 cm^2
Dye Sensitiser	: Z907
Light Source	: Xe 450W @ AM1.5G
Additional Remarks	: TTFL236
Electrolyte 960	: EMU4
Working Temperature	: 298 K
SemiConductor Layer	: 10+5,+TiCl4
Layer Thickness, Porosity	: 2 µm, 68 %
Working Electrode Glass	: NSG 10Ω/cm
Counter Electrode Type	: Pt
Data File Name	: MU86_Feb 16#18.sIV
Current Compliance	: 2 mA
Settling Time, Voltage Step	: 0.04 s, 10 mV

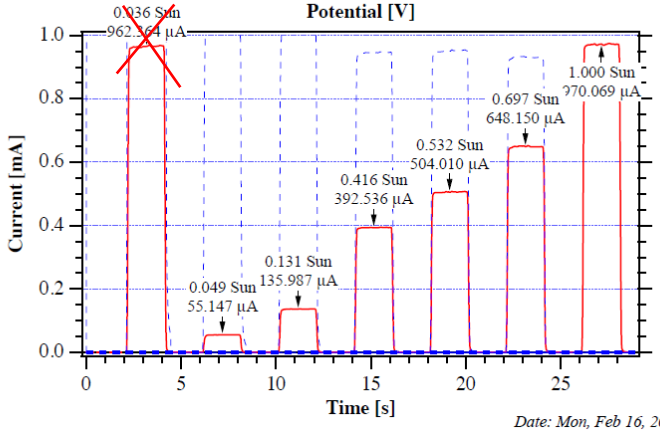
	13.5% Sun	50.7% Sun	98.1% Sun
$Current_{ref}$	-390.649 µA	-1.462 mA	-2.829 mA
$Power_{in}$	13.542 mW/cm^2	50.681 mW/cm^2	98.063 mW/cm^2
Norm. Std. Dev.	0.16	0.12	0.13
Module U_{oc}	523.42 mV	565.29 mV	584.27 mV
Cell U_{oc}	523.42 mV	565.29 mV	584.27 mV
I_{sc}	-135.143 µA	-511.599 µA	-973.470 µA
J_{sc}^{norm}	-819.44 µA/cm^2	-3.36 mA/cm^2	-6.20 mA/cm^2
U_{pmax}	421.06 mV	451.58 mV	461.71 mV
I_{pmax}	-821.2 µA/cm^2	-3.0 mA/cm^2	-5.8 mA/cm^2
$Power_{out}$	345.77 µW/cm^2	1.38 mW/cm^2	2.66 mW/cm^2
Total $Power_{out}$	55.32 µW	220.21 µW	425.95 µW
Fill Factor	0.782	0.761	0.749
Efficiency η	2.55%	2.72%	2.71%

Slope $\partial V_{oc}/\partial \log(I_o)$: 71.098 mV

Calibration File: Solar Lab I:Igor Applications:DataScan Data:cal_Thu, Oct 11, 2001

© RAHB: IVDynamics_Francine Measured by Henry on IV new





Date: Mon, Feb 16, 2015

Cell	Dye/Conc.	Diping Solvent	Diping Time	Film Thickness (µm)	Elect.	V_{OC} (mV)	J_{SC} (mA•cm^{-2})	F.F.	P_{in} (mW•cm^{-2})	η (%) at full sun (uncorrected)	Calculated η at full sun (V_{OC}*J_{SC}*FF)/Pin
MU86	**M2S** / 0.2 mM	$CHCl_3$/EtOH (2:3)	15h	[10+5]	B (EMU4)	584.27	6.20	0.749	98.063	2.71	**2.77%**

Figure S75. I/V curves and current dynamics under diferent light intensities for the best device made with **M2S** on a [10+5] µm thick TiO_2 film and using idodine-based electrolyte B (EMU4).

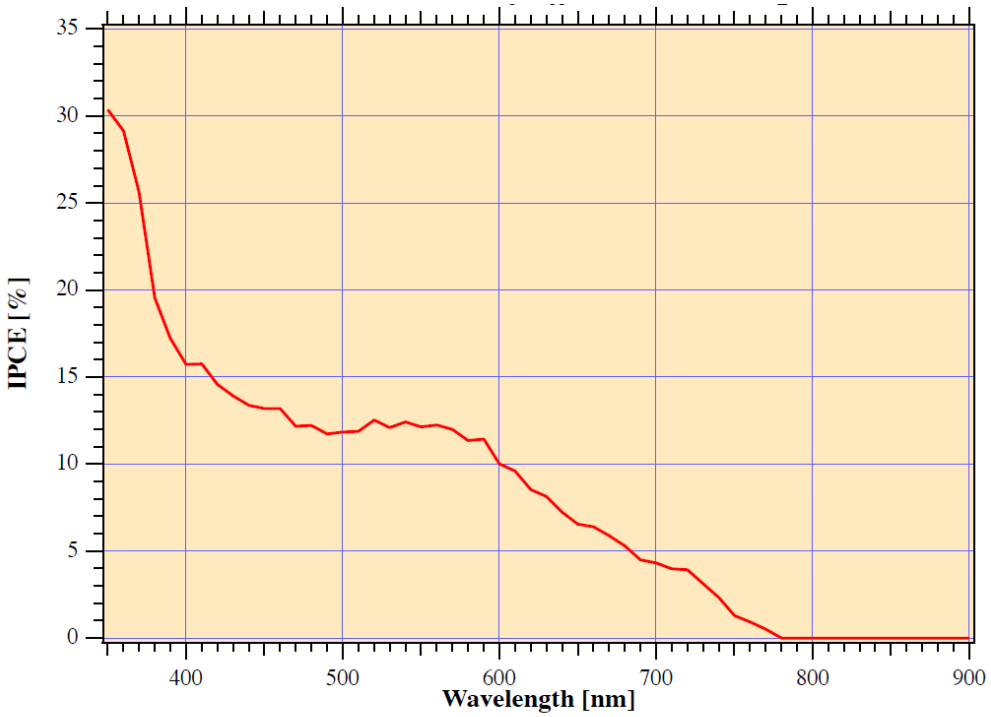


Figure S76. IPCE spectrum of **M2S**/DSSC adsorbed on [10+5] μm thick TiO_2 film and using idodine-based electrolyte A.

VII. Electrochemical voltamograms

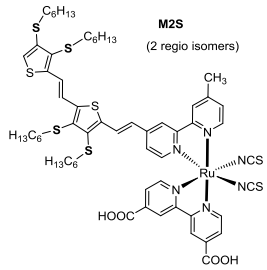
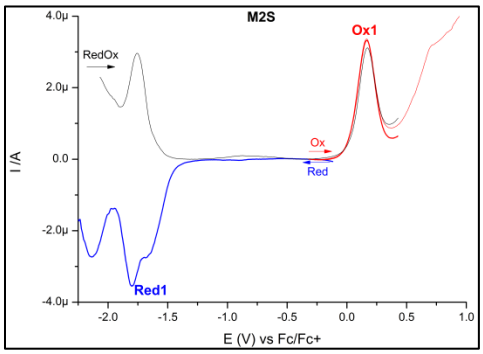
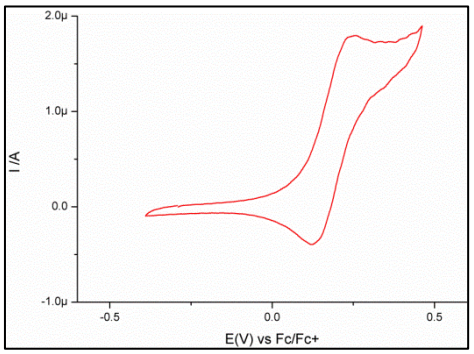
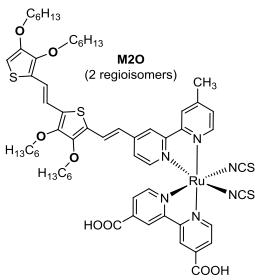
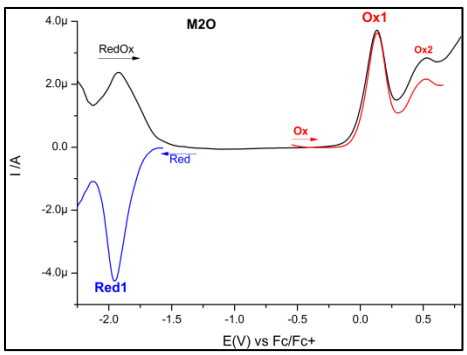
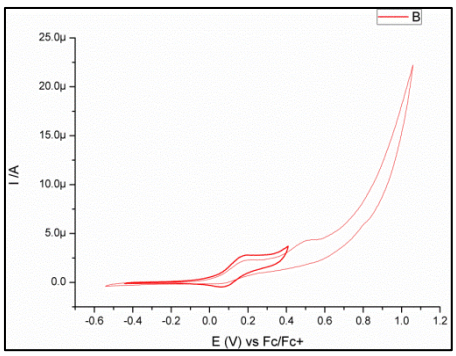
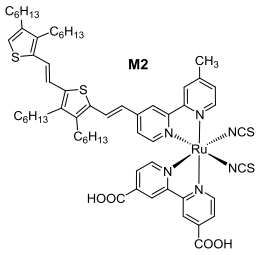
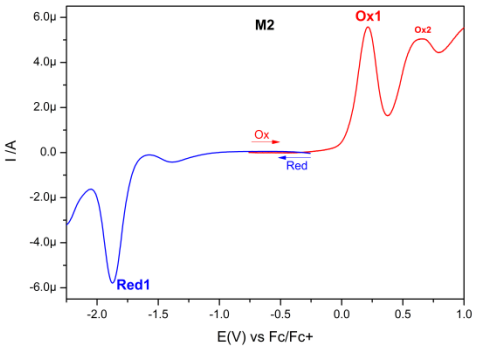
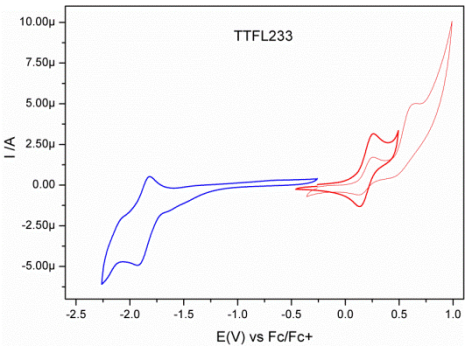
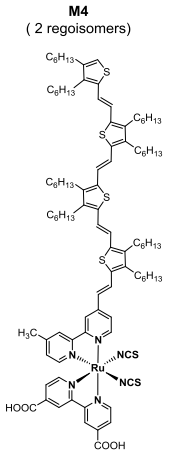
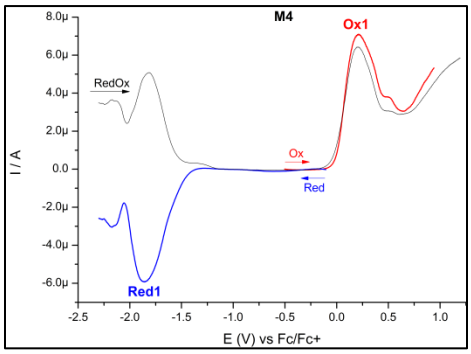
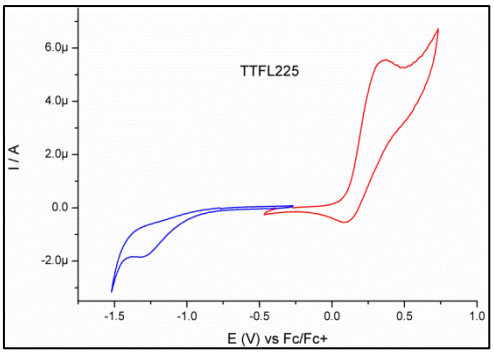
Compound	OSWV	CV
		
		
		
		

Figure S77. OSWV and CV voltamograms of **M**-type complexes.

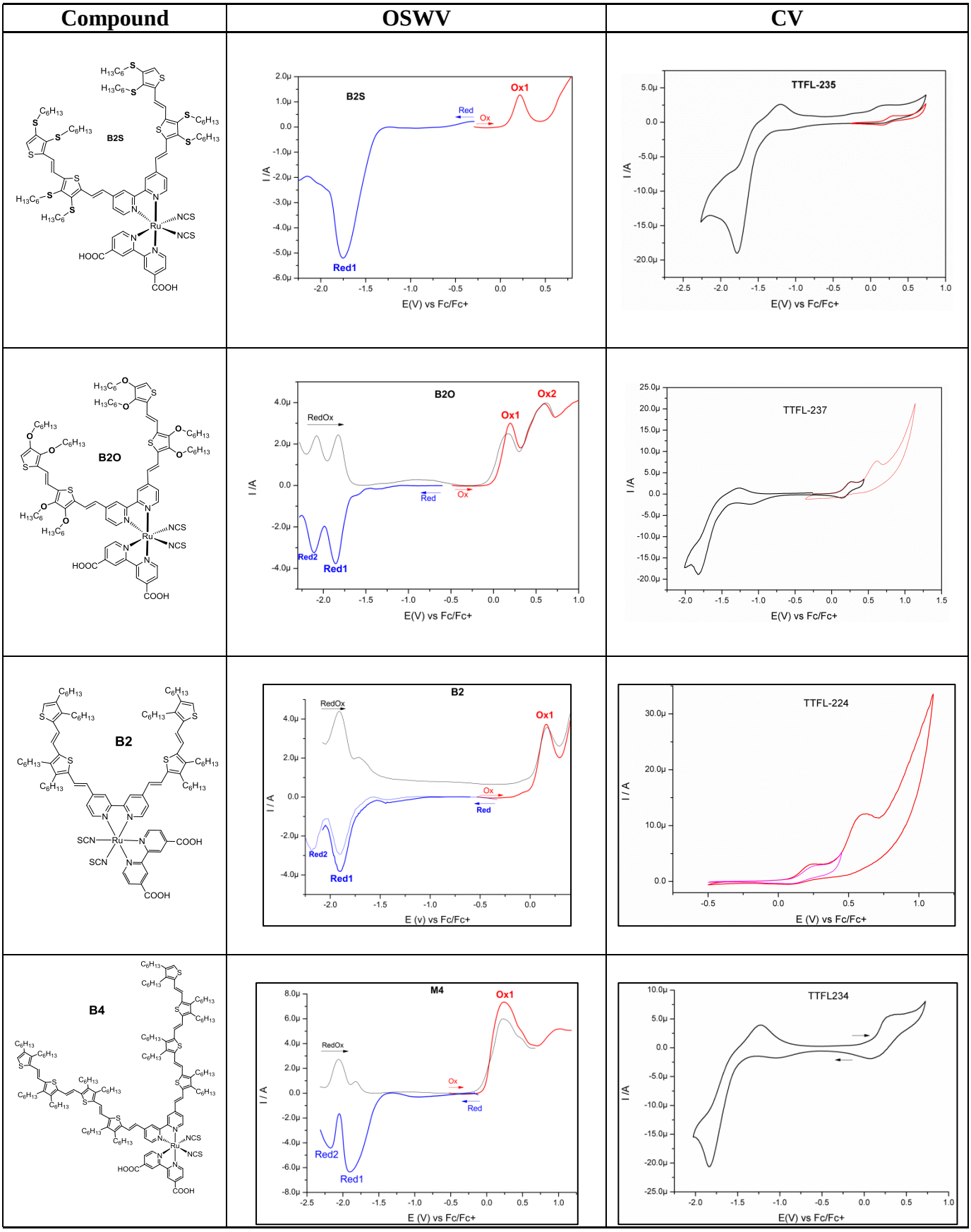
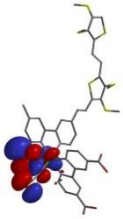
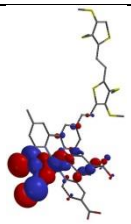
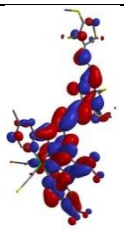
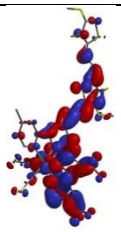
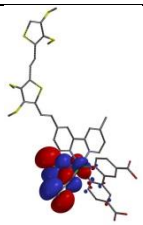
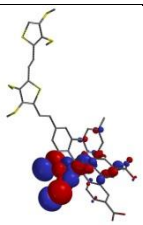
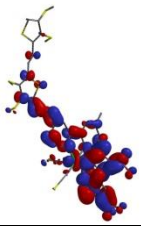
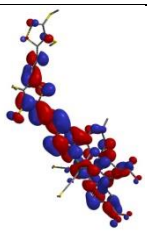
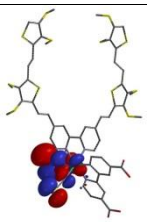
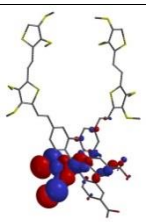
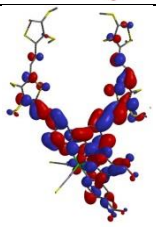
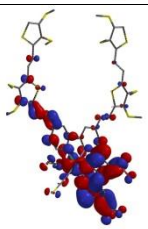
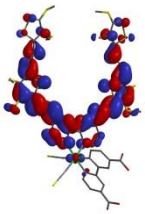
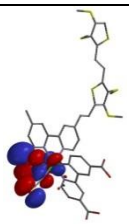
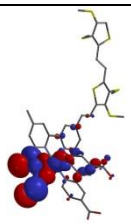
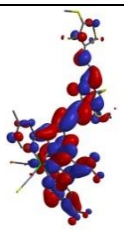
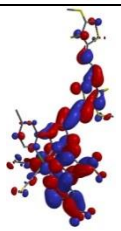
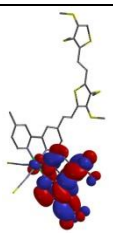
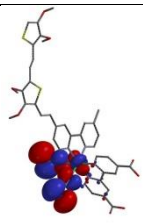
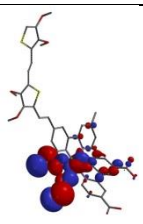
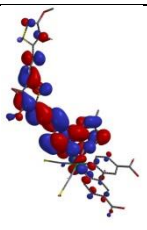
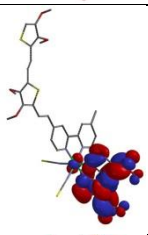
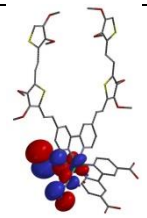
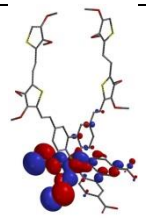
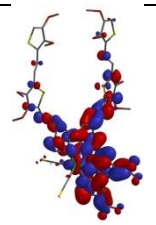
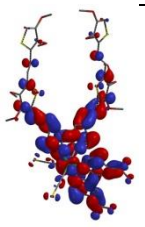
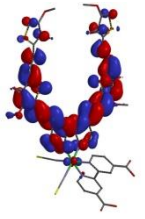
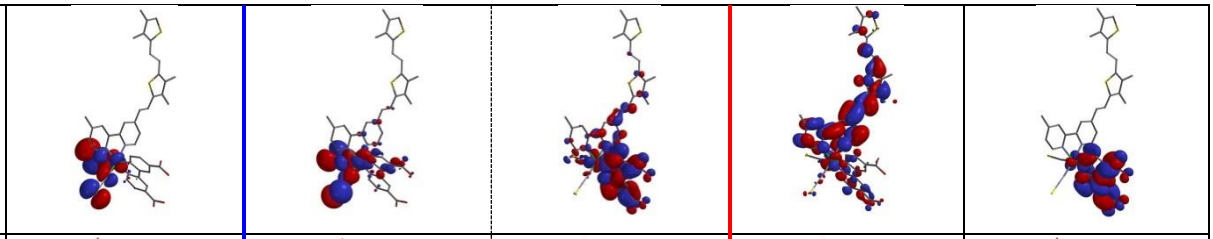
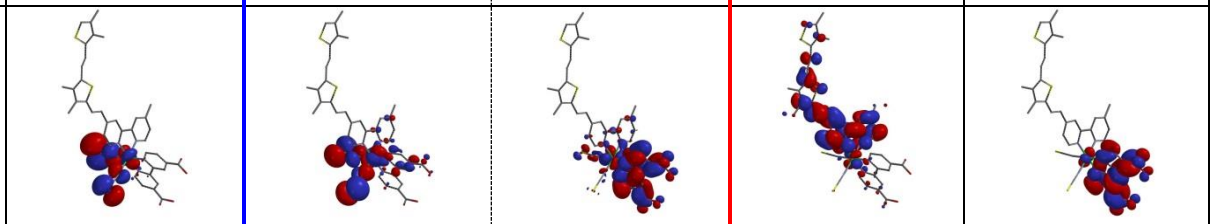
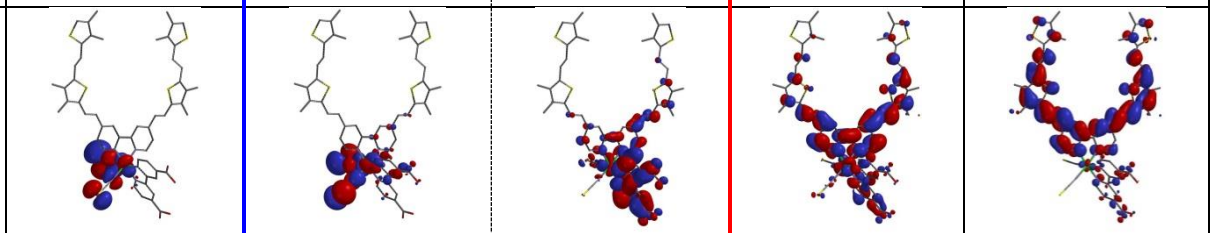
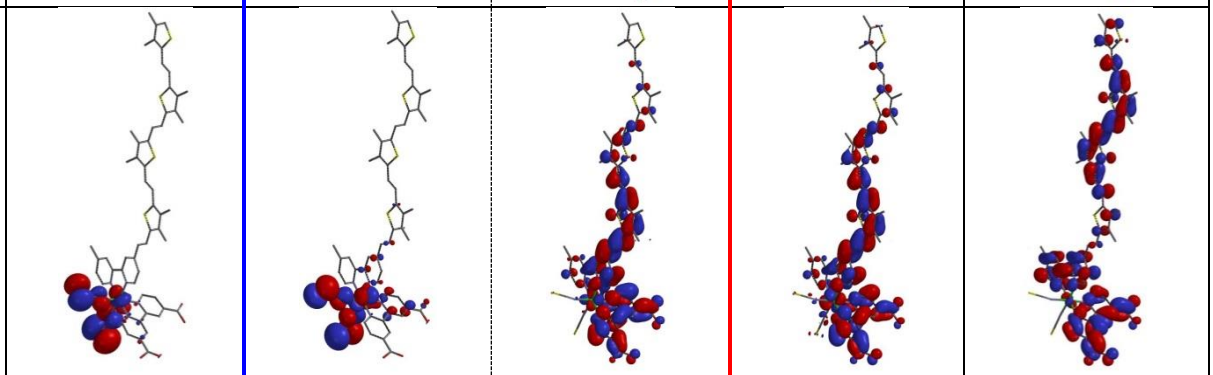
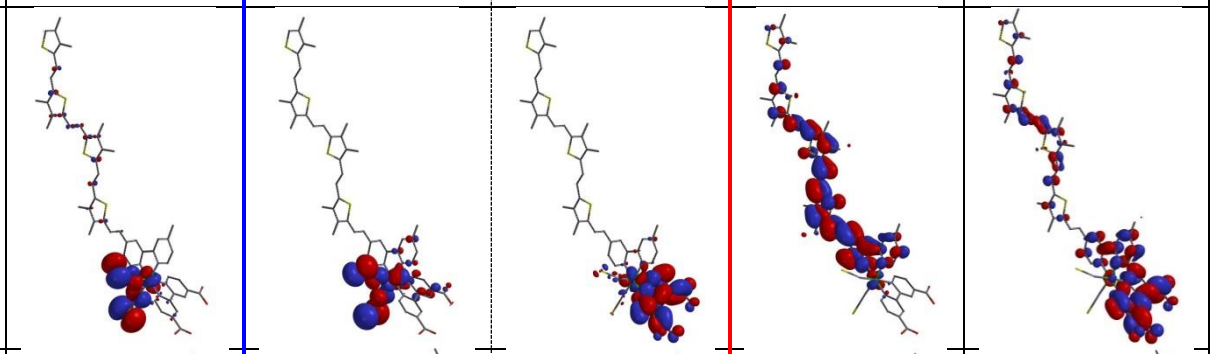


Figure S78. OSWV and CV voltamograms of **B**-type complexes.

VIII. Surfaces of frontier molecular orbitals predicted by DFT calculations

Table S2. . Surfaces of frontier molecular orbitals predicted with DFT calculations at the B3LYP level (6-31G*) in vacuum. To simplify the computations, hexyl chains were replaced with methyl groups. Hydrogen atoms are omitted for sake of clarity.

		HOMO-1	**HOMO**	**LUMO**	LUMO+1	LUMO+2
M2S	[1,3]					
	[1,4]					
B2S						
M2O	[1,3]					
	[1,4]					
B2O						

M2	[1,3]					
	[1,4]					
B2						
M4	[1,3]					
	[1,4]					
B4