Supporting Information

Design of water-soluble lanthanide luminescent probes for the selective detection of HOCl

Lucile Bridou,[a] Adam Nhari,[b,c] Loeza Collobert,[d] Dina Akl,[a] Salauat R. Kiraev,[a] Kyangwi Patrick Malikidogo,[b],‡ Jennifer K. Molloy,[c] Boris Le Guennic,[e] Maryline Beyler,[d] Raphaël Tripier,[d] Olivier Maury,[a],* Olivier Sénèque,[b],*

[a] CNRS UMR 5182, Laboratoire de Chimie, Univ Lyon, ENS de Lyon, 46 Allée d'Italie, 69007 Lyon, France

[b] Univ. Grenoble Alpes, CNRS, CEA, IRIG, LCBM (UMR 5249), F-38000 Grenoble, France

[c] Univ. Grenoble Alpes, CNRS, DCM (UMR 5250), F-38000 Grenoble, France

[d] Univ Brest, UMR CNRS 6521 CEMCA, 6 avenue Victor le Gorgeu, F-29200, Brest, France

[e] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France

‡ Present address: Faculté des Sciences et Technologies, Université de Goma, B.P. 204 Goma, R. D. Congo.

General Procedures

Synthesis and characterization

Unless stated otherwise, all reactions of air- and/or water sensitive compounds were carried out under an inert gas atmosphere using standard Schlenk techniques. Solvents were purchased from Fisher Scientific, VWR Chemicals or Carlo Erba Reagents and used without further purification. All the solvents used for the synthesis were stored over 3 Å molecular sieves. $CDCl_3$ was supplied by Eurisotop. Starting materials were purchased from Sigma-Aldrich, TCI, Alfa Aesar or Acros Organics and used without further purification. Column chromatography was performed using silica gel (40–63 mm) from VWR Chemicals. Dialysis membranes (cut-off 100-500 Da) were purchased from Repligen.

^1H, ^{13}C and the corresponding two-dimensional nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 500 (500 MHz for ^1H), Bruker Avance 400 (400 MHz), BrukerAMX-3 300 (300 MHz) spectrometers for pyclen-based compounds and on Bruker Avance III 300 MHz or on a Bruker Ascend 400 MHz spectrometers for the tacn-based molecules. The chemical shifts in ppm were referenced to the solvent residual proton signals ($CDCl_3$: 7.26 ppm in ^1H and 77.2 ppm in ^{13}C spectra; DMSO-d_6: 2.50 ppm in ^1H and 39.5 ppm in ^{13}C spectra). The multiplicities

of the signals were abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of doublets), m (multiplet) and br (broad signal).

IR Spectra were recorded on a Spectrum 65, 100 and 400 series FT-IR spectrometer. Typical 8 scans were accumulated for each spectrum (resolution of 1 or 0.5 cm^{-1}).

High resolution mass spectrometry measurements (HRMS) were performed on a Bruker maXis mass spectrometer by the SALSA platform from ICOA laboratory or on a Thermo Scientific LTQ Orbitrap XL spectrometer (ICMG, Grenoble) for pyclen compounds and at the Centre Commun de Spectrometrie de Masse (Villeurbanne, France) with a MicroOTOFQ II (Bruker) using electrospray ionization (ESI) for tacn derivatives.

Analytical HPLC was performed on a Prominence Shimadzu HPLC/LCMS-2020 instrument equipped with UV SPD-20 A detector (254 nm) using a Puriflash prep C_{18AQ} column (5 μm, 250 mm × 4.6 mm, 1 mL/min flow rate) or on an Agilent Infinity 1260 II system equipped with UV-vis (214 and 331 nm) and ESIMS detectors using a Waters XBridge BEH130 C18 column (2.5 μm, 75 mm × 4.6 mm, 1 mL/min flow rate). The method used for the analytical HPLC was the following: elution with 0.1% formic acid in H_2O and CH_3CN (B), gradient: 0→4 min isocratic 5% B, 4→13 min 5→90% B, 13→17 min isocratic 90% B, 17→18 min 90→5% B, 18→30min 5% B; Flow: 1 mL/min. Preparative HPLC separations were performed on a VWR LaPrepΣ system using a Waters XBridge Peptide BEH130 C18 (5 μm, 150 mm × 19 mm column at a flow rate of 14 mL/min) with UV detection at 214 and 331 nm. Pyclen·3HCl was provided by Guerbet (Aulnay-sous-bois, France).

Photophysical measurements

Absorption spectra were recorded on a JASCO V–650 spectrophotometer or on a Varian Cary50 spectrophotometer in diluted solution (*ca*. 1–10 μM), using spectrophotometric grade solvents. Molar extinction coefficients (ε) were precisely determined at least 2–3 times. Emission spectra were measured using a Horiba–Jobin–Yvon Fluorolog-3 fluorometer. For the steady-state luminescence experiments, the sample was excited by unpolarized light from a 450 W Xenon continuous wave (CW) lamp and detected at right angle to measure the dilute solutions in 10×10 mm quartz cuvettes by using a Hamamatsu R928 photomultiplier. Spectra were corrected for both excitation source light–intensity variation and emission spectral responses. Overall luminescence quantum yields were measured for the complexes by using optically dilute method using an external standard. Diluted solutions with an absorbance lower than 0.1 were used and the following equation was employed:

$$\frac{\Phi_{ovl(x)}}{\Phi_{ovl(r)}} = \left[\frac{A_r(\lambda)}{A_x(\lambda)}\right] \times \left[\frac{n_x^2}{n_r^2}\right] \times \left[\frac{D_x}{D_r}\right]$$

Where A is the absorbance at the excitation wavelength λ, n is the refractive index and D is the integrated luminescence intensity, ‘‘r’’ and ‘‘x’’ stand for reference and sample, respectively. The reference is

quinine bisulphate in a 1 *N* aqueous solution of sulphuric acid ($\Phi_{ovl(r)}$ = 54.6%).[25] The reference and sample compounds were excited at the same wavelength. In practice, the absorbance and spectra of a minimum of 5 solutions at different optical densities were measured. The emission area was then plotted as a function of the optical density for both the compound and the reference. Each slope corresponds to the ratio $A_{x/r}(\lambda)/D_{x/r}$ of the equation above and is directly linked to the compound quantum yield.

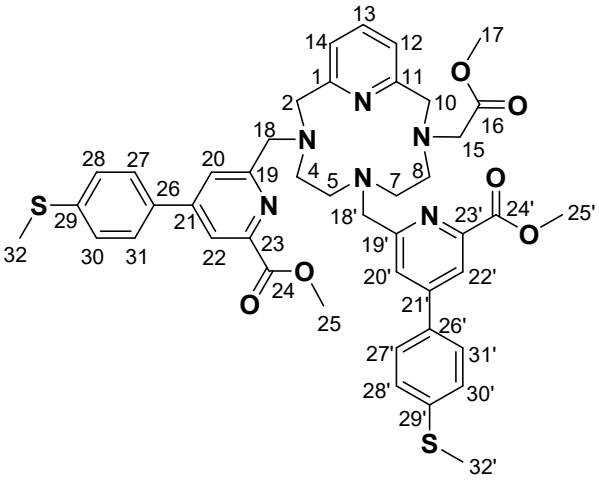
Lanthanide(III) luminescence and phosphorescence lifetimes (τ) were obtained by pulsed excitation with a FL-1040 UP Xenon lamp. Luminescence decay curves were fitted using the mono-exponential equation:

$$I(t) = I_0 \times e^{\frac{-t}{\tau}}$$

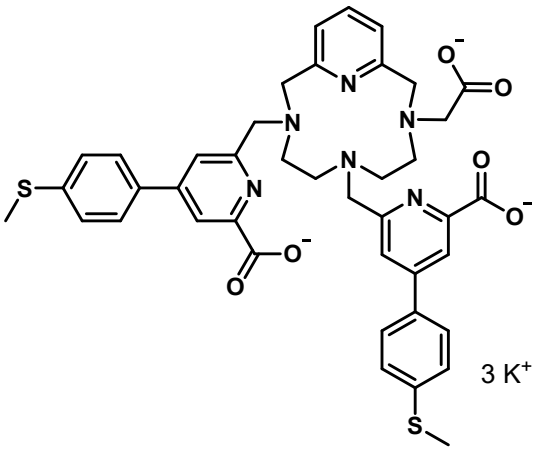
Preparation of oxidants

HOCl: A 1 mM HOCl solution in water was prepared by dilution of a 2% stock solution of NaOCl (its precise concentration was determined by UV-vis absorption with ε = 350 $M^{-1}.cm^{-1}$ at 292 nm). **H_2O_2:** A 10 mM H_2O_2 solution was prepared by dilution of a 30% H_2O_2 stock solution (9.8M). ***t*BuOOH:** 13.5 mg of tert-butyl hydroperoxide was dissolved in 15 mL of degassed deionized water to obtain a 10 mM *t*BuOOH solution. **HO•:** It was generated in situ by adding a 10 mM iron(II) sulfate heptahydrate solution in the cuvette containing the buffered TbL_3 solution, and then an excess of the 10 mM H_2O_2 solution. The HO• was assumed at least equal to the iron concentration. ***t*BuOO•:** It was generated in situ by adding a 10 mM iron(II) sulfate heptahydrate solution in the cuvette containing the buffered TbL_3 solution, and then the 10 mM *t*BuOOH solution. **$O_2^{\bullet-}$:** A 10 mM solution was prepared by dissolving 10.6 mg of KO_2 in 15 mL of DMSO. **$ONOO^-$:** 2 mL of HCl (0.6 mM) was slowly added dropwise to a mixture of 2 mL of $NaNO_2$ (0.6 mM) and 2 mL of H_2O_2 (0.7 mM) at 0°C (ice-bath), and then 2 mL of a cold NaOH solution (1.2 mM) were added. The concentration of $ONOO^-$ was determined using absorption at 302 nm (ε = 1670 $M^{-1}cm^{-1}$). The solution was stored at –20 °C.

Synthesis of the antennae and associated ligands and complexes



Compound L_2'. Potassium carbonate (93 mg, 0.67 mmol, 6 equiv) was added to a solution of compound **1** (31 mg, 0.11 mmol) in acetonitrile (4 mL), which was stirred for 10 min under argon. A solution of compound **2** (83 mg, 0.22 mmol, 2 equiv) in acetonitrile (15 mL) was added to the first solution dropwise. The reaction mixture was stirred under reflux for 24 h. An additional solution of compound **2** (4.1 mg, 0.011 mmol, 0.1 equiv) in acetonitrile (2 mL) was added to the reaction mixture, which was stirred at reflux for 16 h until the full conversion of the starting materials. The resulting suspension was cooled down to room temperature before filtration over a pad of cotton. The filtrate was evaporated on a rotary evaporator and purified on an alumina neutral column (CH_2Cl_2:MeOH 97:3) to give compound **L_2'** (44 mg, 0.054 mmol, 48%) as yellow oil^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H, H22 or H22'), 7.96 (d, J = 1.6 Hz, 1H, H22 or H22'), 7.87 (s, 1H, H20 or H20'), 7.71 (s, 1H, H20 or H20'), 7.58 (m, 5H, H13, H27, H27', H31, H31'), 7.29 (dd, J^3 = 8.5, 5.7 Hz, 4H, H28, H28', H30, H30'), 7.12 (d, J^3 = 7.6 Hz, 1H, H14), 7.07 (d, J^3 = 7.6 Hz, 1H, H12), 4.27 – 4.17 (m, 2H, H10), 4.17 – 4.07 (m, 2H, H2), 4.01 (s, 3H, H25 or H25'), 3.87 (d, J^2 = 8.9 Hz, 2H, H18 or H18'), 3.84 (s, 3H, H25 or H25'), 3.68 (s, 3H, H17), 3.66 (d, J^2 = 7.8, Hz 2H, H18 or H18'), 3.50 (m, 2H, H15), 3.23-3.04 (m, 1H, H4), 2.77 – 2.56 (m, 2H, H4, H8), 2.52 (s, 3H, H32 or H32'), 2.50 (s, 3H, H32 or H32'), 2.47 – 2.39 (m, 1H, H8), 2.27 – 2.20 (m, 1H, H5), 2.10 – 1.98 (m, 2H, H5, H7), 1.92 – 1.81 (m, 1H, H7). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.9 (C16), 166.1, 165.3 (C24, C24'), 160.8 (C11), 159.6, 159.3 (C23, C23'), 158.2 (C1), 150.1, 149.9 (C21, C21'), 147.9, 147.8 (C19, C19'), 141.9, 141.7 (C29, C29'), 138.1 (C13), 132.6, 132.5(C26, C26'), 127.3 (C27, C27', C31, C31'), 126.6 (C28, C28', C30, C30'), 124.3, 124.0 (C20, C20'), 121.7, 121.2 (C22, C22'), 121.0 (C14), 120.7 (C12), 63.1 (C10), 62.6 (C2), 61.5 (C18 or C18'), 59.4 (C18 or C18'), 56.8 (C15), 55.0 (C8), 54.7 (C4), 54.3 (C5, C7), 53.1, 53.0 (C25, C25'), 51.7 (C17), 50.8, 50.6, 15.3 (C32, C32'). ESI-HR-MS (positive, MeOH) m/z calc for $[C_{44}H_{48}N_6O_6S_2+H]^+$: 821.3149, found: 821.3140 $[M+H]^+$; calc for $[C_{44}H_{48}N_6O_6S_2+2H]^{2+}$: 411.1611, found: 411.1612, $[M+2H]^{2+}$. m/z = $[275]^{2+}$, $[382]^{2+}$, $[550]^+$, $[572]^+$: fragmentation



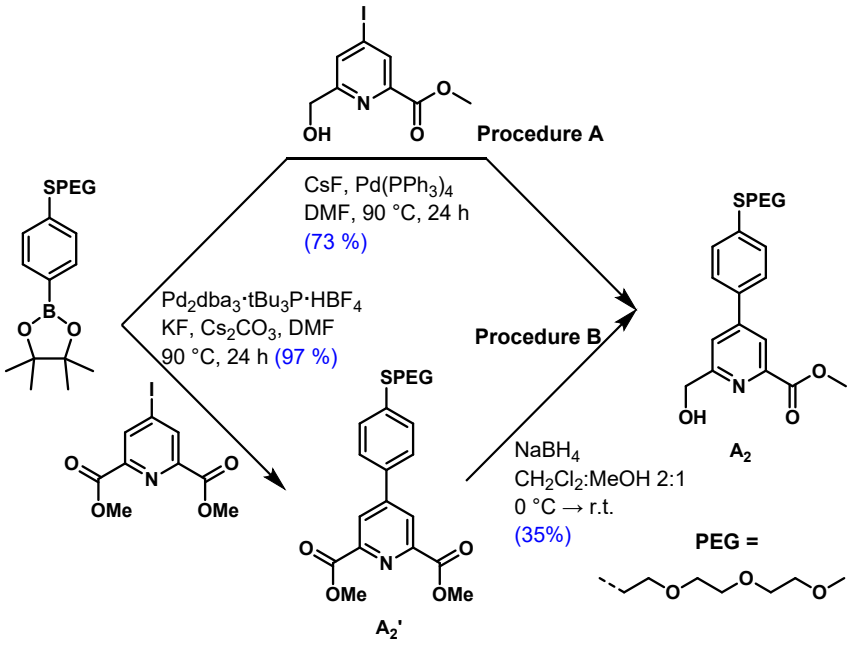
Ligand L_2. A solution of potassium hydroxide (1M, 620 µL) was added to a solution of compound **L_2'** (51 mg, 0.062 mmol) in THF/MeOH (4:1, 4 mL). The reaction mixture was stirred at 70°C for 48 h, and the solvents were evaporated. The residue was dissolved in methanol and the excess salts were centrifuged. The supernatant was evaporated to dryness and the crude was dialyzed. Compound **L_2** was obtained as a white powder (55.2 mg, 0.062 mmol) with 99% yield. Due to its complexity, ^{1}H NMR spectrum could not be described, but is provided in Figure S22. $^{13}C\{^1H\}$ NMR (125 MHz, D_2O): δ 181.4, 178.5, 178.2, 172.4, 172.0, 171.4, 164.7, 159.9, 159.3, 158.8, 157.3, 154.2, 153.6, 150.2, 148.8, 148.1, 147.7, 143.4, 140.3, 140.2, 140.0, 137.9, 133.0, 127.2, 126.9, 126.2, 125.5, 121.9, 120.7, 119.2, 69.4, 63.9, 62.5, 41.6, 41.4, 34.4, 29.6, 23.2, 14.2, 14.1. HRMS (ESI+) m/z calcd for $[C_{41}H_{42}N_6O_6S_2+H]^+$: 779.2680, found: 779.2678, $[M+H]^+$; calcd for $[C_{41}H_{42}N_6O_6S_2+Ca]^{2+}$: 409.1111, found: 409.1116 $[M+Ca]^{2+}$; calcd for $[C_{41}H_{42}N_6O_6S_2+Zn]^{2+}$: 421.0943, found: 421.0950 $[M+Ca]^{2+}$; calcd for $[C_{41}H_{42}N_6O_6S_2+2H]^{2+}$: 390.1373, found: 390.1382 $[M+2H]^{2+}$. m/z = $[261]^{2+}$, $[361]^{2+}$, $[522]^+$: fragmentations.

General procedure for the synthesis of LnL_2 complexes (Ln = Eu, Tb). Compound **L_2** was dissolved in water (C = 0.015–0.022 M). The pH was adjusted to ~6.3 with a solution of HCl (0.5 M). The corresponding 1.1 equiv. of lanthanide trichloride hexahydrate was dissolved in water (C = 0.07 M) and added to the solution. The reaction mixture was stirred at room temperature for 10 minutes and the pH was adjusted to ~6–6.4 with 0.1 M KOH. Then, the reaction mixture was stirred at room temperature (Ln = Tb) or under reflux (Ln =, Eu) or for 48 h and centrifuged. The solid was solubilized in methanol and evaporated on a rotary evaporator. The crude was purified by flash chromatography on C_{18aq} (H_2O:CH_3CN 100:0; 9 minutes, up to 10:90 in 7 minutes, 5 minutes at 10:90 isocratic; up to 0:100 for 5 minutes) and the solvent was evaporated to give **LnL_2** as a white solid.

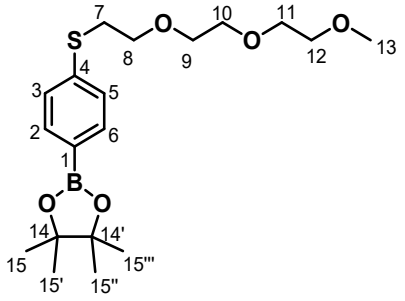
EuL_2 was prepared with general procedure using **L_2** (58 mg, 0.065 mmol) and $EuCl_3.6H_2O$ (28 mg, 0.071 mmol 1.1 equiv.). Yielding the desired complex EuL_2 (51mg, 0.055 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d^6) δ 23.19 (s, 1H), 16.97 (s, 1H), 14.21 (s, 1H), 11.17 (s, 1H), 10.18 (s, 1H), 7.74 – 7.33

(m, 1H), 7.23 (d, J^3= 8.2 Hz, 2H), 2.14 (d, J^3 = 8.6, 2H), 6.74 (d, J^3 = 8.3 Hz, 2H), 6.28 (t, J = 7.2 Hz, 1H), 6.06 (s, 1H), 5.55 (d, J^3 = 7.5 Hz, 1H), 5.33 (s, 2H), 4.96 (s, 1H), 4.48 (s, 1H), 2.82 (s, 1H), 2.19 (s, 3H) 2.04 – 1.93 (m, 1H), 1.61 (s, 1H), 1.45 (s, 1H), 1.23 (s, 3H), 1.09-1.00 (m, 1H), 0.83 (s, 1H), -1.95 (s, 1H), -2.24 (s, 1H), -2.54 (s, 1H), -5.73 (s, 2H), -6.38 (s, 1H), -8.84 (s, 1H), -9.42 (s, 1H).HRMS (ESI+)m/z calcd for $[C_{41}H_{39}N_6O_6S_2Eu+H]^+$: 929.1657, found: 929.1662, $[M+H]^+$; calcd for $[C_{41}H_{39}N_6O_6S_2Eu+2H]^{2+}$: 465.0865, found: 465.0868, $[M+2H]^{2+}$; calcd for $[C_{41}H_{39}N_6O_6S_2Eu+H+Na]^{2+}$: 476.0774, found: 476.0778.

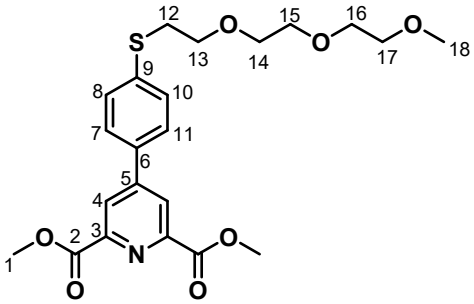
TbL$_2$ was prepared with general procedure using **L$_2$** (60 mg, 0.065 mmol) and $EuCl_3.6H_2O$ (27 mg, 0.073 mmol 1.1 equiv.). Yielding the desired complex **TbL$_2$** (6 mg, 0.013 mmol, 10%). HRMS (ESI+)) m/z calcd for $[C_{41}H_{39}N_6O_6S_2Tb+H]^+$: 9351698, found: 9351704, $[M+H]^+$; $[C_{41}H_{39}N_6O_6S_2Tb+Na]^+$: 957.1518, found: 957.1539, $[M+Na]^+$; calcd for $[C_{41}H_{39}N_6O_6S_2Tb+2H]^{2+}$: 468.0885, found: 468.0889.



Scheme S1. Alternative synthetic pathways to obtain antenna **A$_1$**. Both procedures A and B yield the same molecule according to the characterization data (see below).

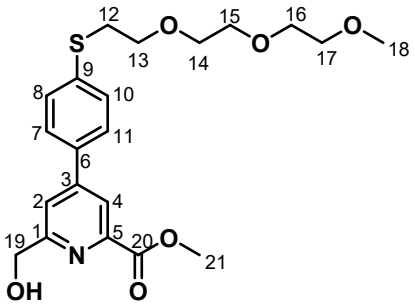


Compound 4. In a Schlenk tube, potassium acetate (1.63 g, 16.6 mmol, 3.9 eq), bis(pinacolato)diboron (1.38 g, 5.43 mmol, 1.3 eq) and $PdCl_2(dppf)_2$ (cat.) were dried under vacuum. Compound **3** (1.43 g, 4.26 mmol, 1 eq) was added to the mixture, which was suspended in DMSO (50 mL) and stirred under argon bubbling for 20 min. The mixture was then stirred at 90°C under argon overnight. The crude was filtered on celite and washed with water. The aqueous layer was extracted with EtOAc, and organic phases washed with water, then brine. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under vacuum. The obtained black oil was purified on silica column using CH_2Cl_2:AcOEt (9:1 to 5:5). Compound **4** was obtained as a yellow oil with 91 % yield (1.48 g, 3.87 mmol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.1 Hz, 2H, $H_{3\text{-}5}$), 7.30 (d, J = 8.1 Hz, 2H, $H_{2\text{-}6}$), 3.67 (t, J = 7.0 Hz, 2H, H_8), 3.62-3.59 (m, 6H, $H_{9\text{-}10\text{-}11}$), 3.52-3.50 (m, 2H, H_{12}), 3.35 (s, 3H, H_{13}), 3.15 (t, J = 7.0 Hz, H_7), 1.32 (s, 12 H, H_{15}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.3 (C_4), 135.2 ($C_{3\text{-}5}$), 127.2 ($C_{2\text{-}6}$), 126.2 (C_1), 83.8 (C_{14}), 72.0 (C_{12}), 70.6 ($C_{10\text{-}11}$), 70.5 (C_9), 69.8 (C_8), 59.1 (C_{13}), 32.0 (C_7), 24.9 (C_{15}).
HRMS (ESI+) m/z: $[C_{19}H_{31}NaO_5S]^+ = [M+Na]^+$ = 405.1880 (cal. 405.1883).



Compound A_2'. Under argon atmosphere, compound **4** (0.92 g, 2.39 mmol, 1.1 equiv.), dimethyl 4-iodo-2,6-pyridinedicarboxylate (0.70 g, 2.18 mmol, 1 equiv.), potassium fluoride (0.41 g, 7.19 mmol, 3.3 equiv.) and a spatula tip of caesium carbonate were dissolved in DMF (20 mL) and the mixture was degassed by purging with argon for at least 30 min. [Pd2dba3*t*Bu3P·HBF4] in catalytic amounts was added, followed by further 15 min of degassing. The mixture was heated to 90 °C for 72 h before it was cooled down and diluted with CH_2Cl_2. The organic phase was washed with water and brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (gradient CH_2Cl_2 → CH_2Cl_2:MeOH 100:1 ratio) to yield **A_2'** as brown solid (0.95 g, 2.12 mmol, 97%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 2H, H_4), 7.68 (d, J = 8.5 Hz, 2H, $H_{8,10}$), 7.46 (d, J = 8.5 Hz, 2H, $H_{7,11}$), 4.05 (s, 6H, H_1), 3.73 (t, J = 6.9 Hz, 2H, H_{13}), 3.67-3.61 (m, 6H, $H_{14\text{–}16}$), 3.55-

3.52 (m, 2H, H_{17}), 3.37 (s, 3H, H_{18}), 3.21 (t, J = 6.9 Hz, 2H, H_{12}). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.4 (C_2), 150.4 z(C_6), 149.0 (C_3), 140.1 (C_9), 133.3 (C_5), 128.8 ($C_{7,11}$), 127.6 ($C_{8,10}$), 125.3 (C_4), 72.1 (C_{17}), 70.7 (br, $C_{15,16}$), 70.6 (C_{14}), 69.9 (C_{13}), 59.2 (C_{18}), 53.4 (C_1), 32.4 (C_{12}).



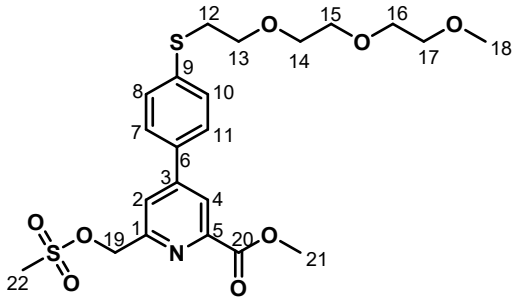
Compound A_2 was prepared via two synthetic pathways, both of which yield the same product according to the chemical characterization data. The full characterization is presented for the batch prepared via procedure A.

Procedure A. In a Schlenk flask, **4** (890 mg, 2.33 mmol, 1.1 eq), KF (450 mg, 7.74 mmol, 3.7 eq) and [$Pd_2(dba)_3$/Bu_3P·HBF_4] (1:1.2) (cat.) were added and dried under vacuum. The monoalcohol **5** (616 mg, 2.10 mmol, 1 eq) and anhydrous DMF (30 mL) were added to the dry mixture. After 20 min of argon bubbling, the reaction mixture was stirred under argon at 90°C during 2 days. The crude was diluted with CH_2Cl_2 and water. Then, the two layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The obtained brown oil was purified on silica column using CH_2Cl_2:Acetone (1:0 to 7:3) as eluent. Compound **A_2** was obtained as a brown oil with 72 % yield (637 mg, 1.51 mmol).

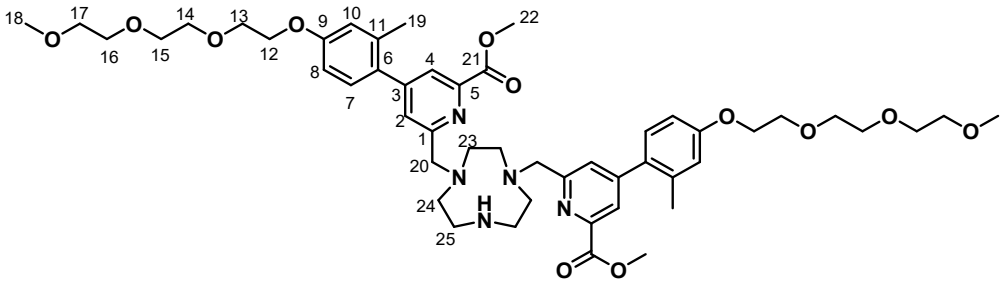
Procedure B. Diester **A_2'** (0.65 g, 1.45 mmol, 1 equiv.) was dissolved in a 2:1 mixture of dichloromethane and methanol (50 mL, previously dried over molecular sieves) and the solution was cooled to 0 °C. $NaBH_4$ (55 mg, 1.45 mmol, 1 equiv.) was added and the mixture was stirred while cooling (1-2 h), until TLC (CH_2Cl_2:EtOAc 2:1) showed appearance of bis-reduced species. The reaction was quenched by the addition of aqueous 1 M HCl (10 mL), the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with a gradient of CH_2Cl_2:EtOAc 2:1 to CH_2Cl_2:EtOAc:MeOH 2:1:0.1 to yield Compound **A_2** (0.21 g, 0.50 mmol, 35%) as yellow oil (recovery of starting material from column).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 1.7 Hz, 1H, H_4), 7.73 (d, J = 1.4 Hz, 1H, H_2), 7.61 (d, J = 8.4 Hz, 2H, $H_{8\text{-}10}$), 7.43 (d, J = 8.4 Hz, 2H, $H_{7\text{-}11}$), 4.90 (s, 2H, H_{19}), 4.01 (s, 3H, H_{21}), 3.72 (t, J = 6.9 Hz, 2H, H_{13}), 3.66-3.62 (m, 6H, $H_{14\text{-}15\text{-}16}$), 3.56-3.52 (m, 2H, H_{17}), 3.36 (s, 3H, H_{18}), 3.19 (t, J = 6.9 Hz, 2H, H_{12}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8 (C_{20}), 161.1 (C_1), 149.7 (C_6), 147.8 (C_5), 139.1 (C_9), 134.4 (C_3), 128.9 ($C_{7\text{-}11}$), 127.6 ($C_{8\text{-}10}$), 121.6 (C_4), 121.2 (C_2), 72.0 (C_{17}), 70.7 ($C_{15\text{-}16}$), 70.6 (C_{14}), 69.9

(C_{13}), 65.0 (C_{19}), 59.2 (C_{18}), 53.1 (C_{21}), 32.5 (C_{12}). HRMS (ESI+) m/z: $[C_{21}H_{28}NO_6S]^+ = [M+H]^+ =$ 422.1632 (cal. 422.1637) ; $[C_{21}H_{27}NNaO_6S]^+ = [M+H]^+ = 444.1451$ (cal. 444.1457).

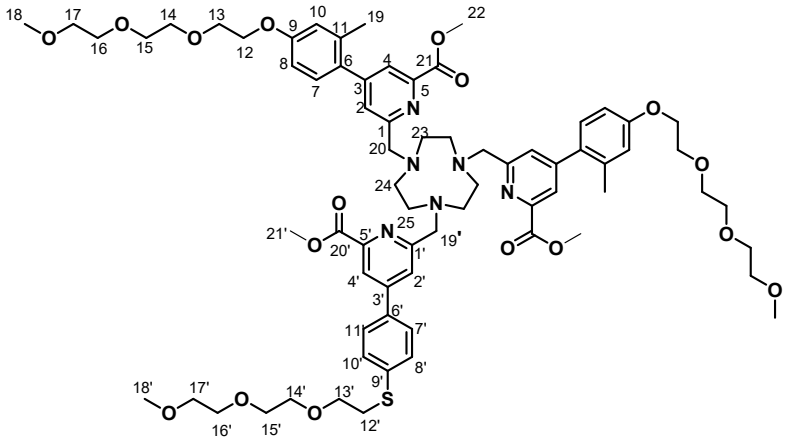


Compound 6. Triethylamine (0.20 mL, 1.48 mmol, 3 eq) was added to a solution of $\mathbf{A_2}$ (0.20 g, 0.47 mmol, 1 eq) in CH_2Cl_2 (10 mL). The mixture was cooled to 0°C in an ice bath. Mesyl chloride (0.11 mL, 1.42 mmol, 3 eq) was added dropwise and the mixture was stirred at room temperature for 30 min. Water was added and the two layers separated. Aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with water, dried over Na_2SO_4 and evaporated. Compound **6** was obtained as a colorless oil with a quantitative yield (0.24 g, 0.47 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, J = 1.6 Hz, 1H, H_4), 7.85 (d, J = 1.6 Hz, 1H, H_2), 7.62 (d, J = 8.4 Hz, 2H, $H_{8\text{-}10}$), 7.45 (d, J = 8.6 Hz, 2H, $H_{7\text{-}11}$), 5.47 (s, 2H, H_{19}), 4.03 (s, 3H, H_{21}), 3.72 (t, J = 6.9 Hz, 2H, H_{13}), 3.66-3.61 (m, 6H, $H_{14\text{-}15\text{-}16}$), 3.55-3.52 (m, 2H, H_{17}), 3.37 (s, 3H, H_{18}), 3.20 (t, J = 6.9 Hz, 2H, H_{12}), 3.16 (s, 3H, H_{22}). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.5 (C_{20}), 155.1 (C_1), 150.4 (C_6), 148.2 (C_5), 139.7 (C_9), 133.8 (C_3), 128.9 ($C_{7,11}$), 127.6 ($C_{8,10}$), 122.6 (C_4), 122.5 (C_2), 72.1 (C_{17}), 71.2 (C_{19}), 70.7 (br, $C_{15,16}$), 70.6 (C_{14}), 69.9 (C_{13}), 59.2 (C_{18}), 53.3 (C_{21}), 38.2 (C_{22}), 32.5 (C_{12}).



Compound 8. In a Schlenk tube, TACN·3HCl (24.1 mg, 0.10 mmol, 1 eq) and DIPEA (51.7 mg, 0.40 mmol, 4 eq) were added and dried under vacuum. Dry mixture of MeOH:$CHCl_3$ 50:50 (14 mL) were added and the solution was stirred for 30 min under argon. Mesylate **7** (101.2 mg, 0.21 mol, 2 eq) was added and the mixture was stirred at 70°C under argon for 24h. The crude was concentrated and purified on neutral alumina column (activity III) using CH_2Cl_2:MeOH (10:0 to 9:1) as eluent. Compound **8** was obtained as a pale brown oil with 43 % yield (40.1 mg, 0.043 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 1.2 Hz, 2H, H_4), 7.35 (d, J = 1.2 Hz, 2H, H_2), 7.09 (d, J = 8.0 Hz, 2H, H_7), 6.81

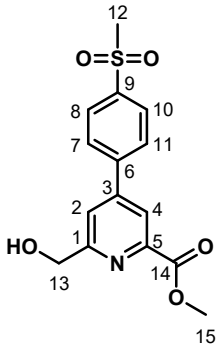
(d, J = 8.0 Hz, 4H, $H_{8,10}$), 4.17–4.11 (m, 4H, H_{12}), 4.07 (s, 4H, H_{22}), 4.05 (s, 6H, H_{20}), 3.89–3.84 (m, 4H, H_{13}), 3.77–3.72 (m, 4H, $H_{14\text{-}15\text{-}16}$), 3.70–3.65 (m, 8H, $H_{14\text{-}15\text{-}16}$), 3.59–3.55 (m, 4H, H_{17}), 3.51 (br, 4H, H_{25}), 3.39 (s, 6H, H_{18}), 3.12 (s, 4H, H_{24}), 2.82 (s, 4H, H_{23}), 2.25 (s, 6H, H_{19}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6 (C_{21}), 159.3 ($C_{1,9}$), 151.8 (C_3), 147.5 (C_5), 136.6 (C_6), 130.6 ($C_{7,11}$), 126.3 (C_2), 125.0 (C_4), 117.1 (C_{10}), 112.5 (C_8), 72.0 (C_{17}), 71.0–70.7 ($C_{14\text{-}15\text{-}16}$), 69.8 ($C_{13}$), 67.6 ($C_{12}$), 60.8 ($C_{22}$), 59.2 ($C_{18}$), 55.3 ($C_{23}$), 53.4 ($C_{20}$), 52.3 ($C_{24}$), 47.0 ($C_{25}$), 20.8 ($C_{19}$). HRMS(ESI+) m/z: $[C_{50}H_{70}N_5NaO_{12}]^{2+}$ = [M+H+Na]$^{2+}$ = 477.7448 (calc. 477.7454), $[C_{50}H_{70}N_5O_{12}]^+$ = [M+H]$^+$ = 932.5009 (calc. 932.5015), $[C_{50}H_{69}N_5NaO_{12}]^+$ = [M+Na]$^+$ = 954.4821 (calc. 954.4835).



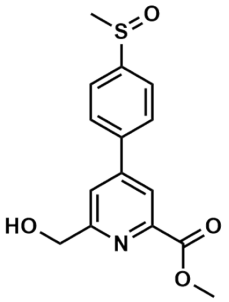
Compound L_3'. In a Schlenk flask, the bis-alkylate **8** (231.6 mg, 0.248 mmol, 1.2 eq) and Na_2CO_3 (255.4 mg, 2.41 mmol, 11 eq) were added and dried under vacuum. Dry MeCN (25 mL) was added and the solution was stirred for 15 min under argon. SPeg-antenna mesylate **6** (106,2 mg, 0.212 mmol, 1.0 eq) was added and the mixture was stirred at 60 °C under argon overnight. The mixture was filtered to remove the salts. The crude was concentrated and purified on silica column using CH_2Cl_2:MeOH (100:0 to 95:5) as eluent. Compound **L_3'** was obtained as a pale brown oil with 24 % yield (69.3 mg, 0.052 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H, $H_{4'}$), 8.06 (s, 1H, $H_{2'}$), 7.92 (s, 2H, H_4), 7.64 (s, 2H, H_2), 7.56 (d, J = 8.3 Hz, 2H, $H_{8',10'}$), 7.38 (d, J = 8.4 Hz, 2H, $H_{7',11'}$), 7.05 (d, 2H, H_7), 6.79 (m, 4H, $H_{8,10}$), 4.20 – 4.10 (m, 4H, H_{12}), 4.00 (s, 6H, $H_{19',20}$), 3.97 (s, 9H, $H_{21',22}$), 3.90 – 3.84 (m, 4H, H_{13}), 3.77 – 3.72 (m, 4H, $H_{14\text{-}15\text{-}16}$), 3.72 – 3.62 (m, 18H, $H_{14\text{-}15\text{-}16\text{-}13'\text{-}14'\text{-}15'\text{-}16'\text{-}17'}$), 3.56 (m, 4H, H_{17}), 3.38 (s, 6H, H_{18}), 3.37 (s, 3H, $H_{18'}$), 3.18 (t, J = 6.9 Hz, 2H, $H_{12'}$), 3.01 (s, 4H, $H_{23\text{-}24\text{-}25}$), 2.95 (s, 8H, $H_{23\text{-}24\text{-}25}$), 2.20 (s, 6H, H_{19}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1 ($C_{21,20'}$), 159.2 ($C_{1,1'}$), 159.1 (C_9), 148.2 ($C_{3,3'}$), 148.0 ($C_{6'}$), 147.3 ($C_{5,5'}$), 136.6 (C_6), 131.7 ($C_{9'}$), 130.7 ($C_{7,11}$), 128.9 ($C_{7',11'}$), 127.5 ($C_{8',10'}$), 127.4 (C_2), 127.1 ($C_{2'}$), 124.8 (C_4), 121.4 ($C_{4'}$), 117.1 (C_{10}), 112.4 (C_8), 72.1 ($C_{17,17'}$), 71.0-70.6 (m, $C_{14\text{-}15\text{-}16\text{-}14'\text{-}15'\text{-}16'}$), 69.8 ($C_{13,13'}$), 67.6 ($C_{12,20\text{-}19'}$), 59.2 ($C_{18\text{-}18'}$), 56.1 ($C_{23\text{-}24\text{-}25}$), 53.0 ($C_{21',22}$), 32.6 ($C_{12'}$), 20.8 ($C_{19}$). HRMS(ESI+) m/z: $[C_{71}H_{96}N_6O_{17}S]^{2+}$ = [M+2H]$^{2+}$ = 668.3282 (calc. 668.3271); $[C_{71}H_{95}N_6O_{17}S]^+$ = [M+H]$^+$ = 1335.6447 (calc. 1335.6469). FT-IR (cm^{-1}, ATR): 1722 [C=O (ester)].

Complex TbL_3. A solution of NaOH (6.6 mg, 0.165 mmol, 12 eq) in water (4 mL) was added to **L_3'** (19.2 mg, 0.014 mmol, 1 eq) dissolved in methanol (1 mL). The reaction mixture was stirred at 70°C for 24 h. After cooling to room temperature, methanol was evaporated. The solution was acidified with 1 M HCl solution to pH 6.5. $TbCl_3.6H_2O$ (6.0 mg, 0.016 mmol, 1.1 eq) was added and pH was adjusted to 6.0 with 1M NaOH solution. The mixture was stirred at room temperature for 3 days. The solution was extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4 and evaporated. **TbL_3** was obtained as a white solid with 93 % yield (18.9 mg, 0.013 mmol). HRMS(ESI+) m/z: $[C_{68}H_{85}N_6Na_2O_{17}STb]^{2+}$ = $[M+2Na]^{2+}$ = 747.2370 (calc. 747.2371). FT-IR (cm^{-1}, ATR): 1648 [C=O (ester)].

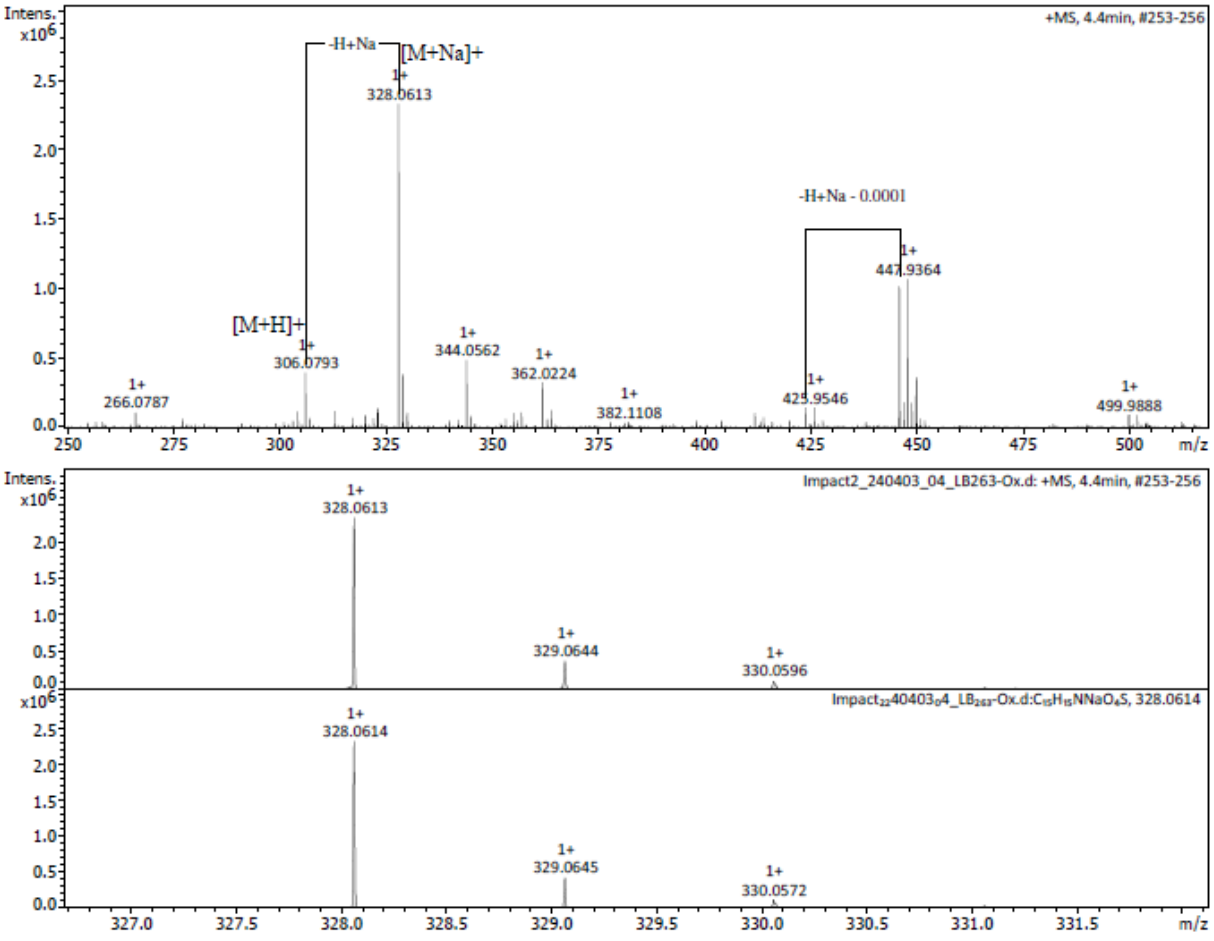
Characterisation of HOCl oxidation products of A_1



Compound A_1^{diox}. A solution of antenna **A_1** (8 mg, 0.028 mmol) was dissolved in a 1:1 mixture of MeOH:HOCl (5% aq. solution), C = 10 mM. The reaction mixture was stirred at room temperature over 72 h. The resulting solution was dried in vacuo and redissolved in CH_2Cl_2 (5 mL), then washed with water (10 mL). The organic phase was collected and dried with Na_2SO_4 and concentrated in vacuo. The isolated beige product (6.3 mg, 71%) was identified as a sulfone antenna **A_1^{diox}** according to the chemical characterisation data. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 1.5 Hz, 1H, H_4), 8.10 (d, J = 8.5 Hz, 2H, $H_{7,11}$), 7.89 (d, J = 8.5 Hz, 2H, $H_{8,10}$), 7.80 (d, J = 1.5 Hz, 1H, H_2), 4.96 (s, 2H, H_{13}), 4.04 (s, 3H, H_{15}), 3.11 (s, 3H, H_{12}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5 (C_{14}), 161.6 (C_1), 148.6 (C_9), 148.3 (C_5), 142.8 (C_3), 141.6 (C_6), 128.6 ($C_{7,11}$), 128.4 ($C_{8,10}$), 122.2 (C_4), 122.0 (C_2), 64.9 (C_{13}), 53.3 (C_{15}), 44.7 (C_{12}). HRMS(ESI+) m/z: $[C_{15}H_{16}NO_5S]^+$ = $[M+H]^+$ = 322.0742 (calc. 322.0744); $[C_{15}H_{15}NNaO_5S]^+$ = $[M+H]^+$ = 344.0560 (calc. 344.0563)

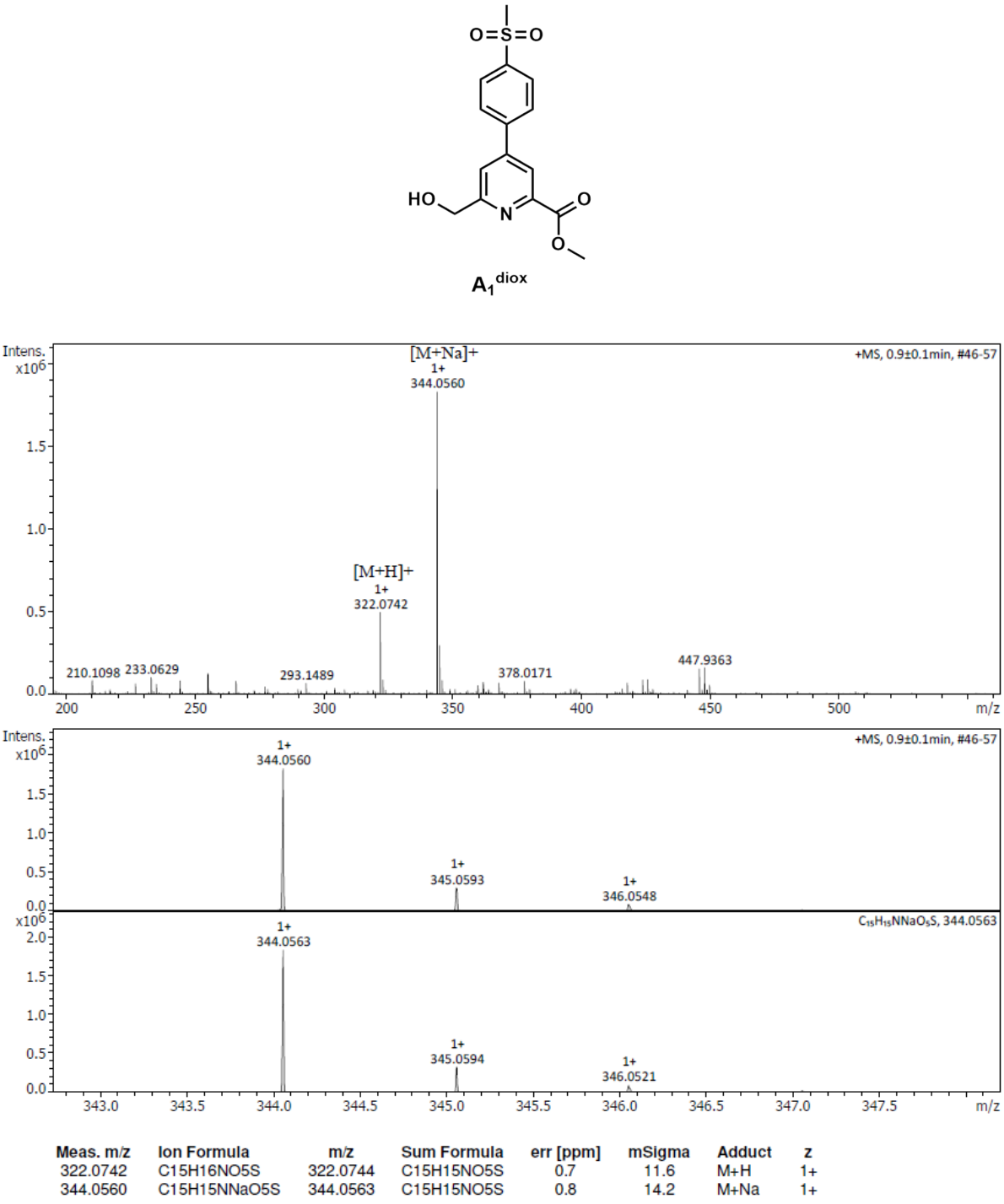


A_1^{ox}



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
306.0793	C15H16NO4S	306.0795	C15H15NO4S	0.5	11.8	M+H	1+
328.0613	C15H15NNaO4S	328.0614	C15H15NO4S	0.4	13.4	M+Na	1+

Figure S1. HRMS spectra of $\mathbf{A_1^{ox}}$ species in MeOH (C = 0.1 mM). Spectra were obtained from a cuvette solution after adding 3 eq. of aq. HOCl, the conversion was observed by UV-Vis.



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
322.0742	C15H16NO5S	322.0744	C15H15NO5S	0.7	11.6	M+H	1+
344.0560	C15H15NNaO5S	344.0563	C15H15NO5S	0.8	14.2	M+Na	1+

Figure S2. HRMS spectra of $\mathbf{A_1}^{\mathbf{diox}}$ species in MeOH (C = 0.1 mM). Spectra were obtained after isolating the in situ synthesised $\mathbf{A_1}^{\mathbf{diox}}$.

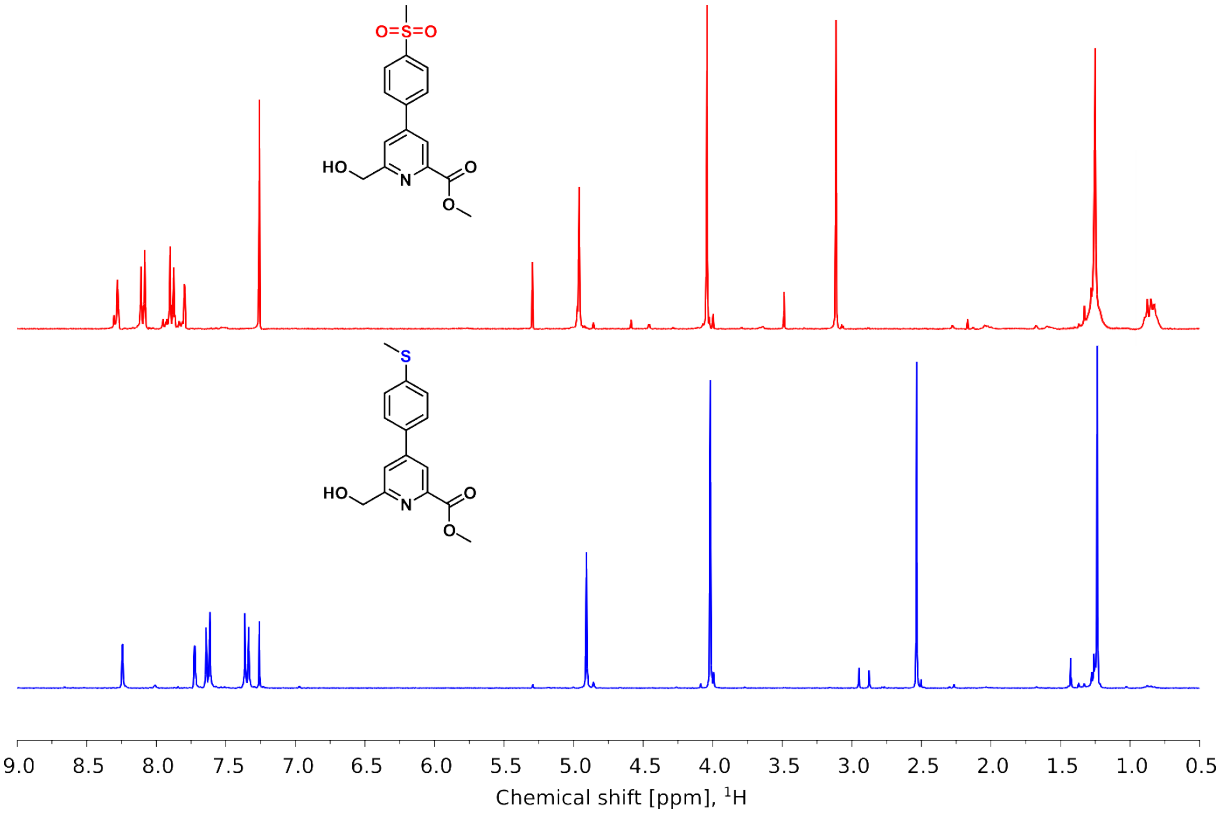


Figure S3. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of antenna $\mathbf{A_1}$ (blue) and isolated $\mathbf{A_1^{diox}}$ (red) from quantitative oxidation of $\mathbf{A_1}$ by HOCl.

Computational details

All (TD-)DFT calculations have been conducted with the Gaussian 16 software (revision A.03),[1] using the PBE0 functional[2] and a 6-311+G(d,p) basis set for all atoms. The ground-state geometry optimizations were followed by frequencies calculations to identify the structures as minima of energy. Solvent effects (methanol) were included through a Polarizable Continuum Model (PCM),[3] and the Linear-Response formalism of PCM was used for TD-DFT calculations.[4] Tight convergence criteria were applied at all steps. We use Le Bahers' dCT model to quantify charge transfer.[5]

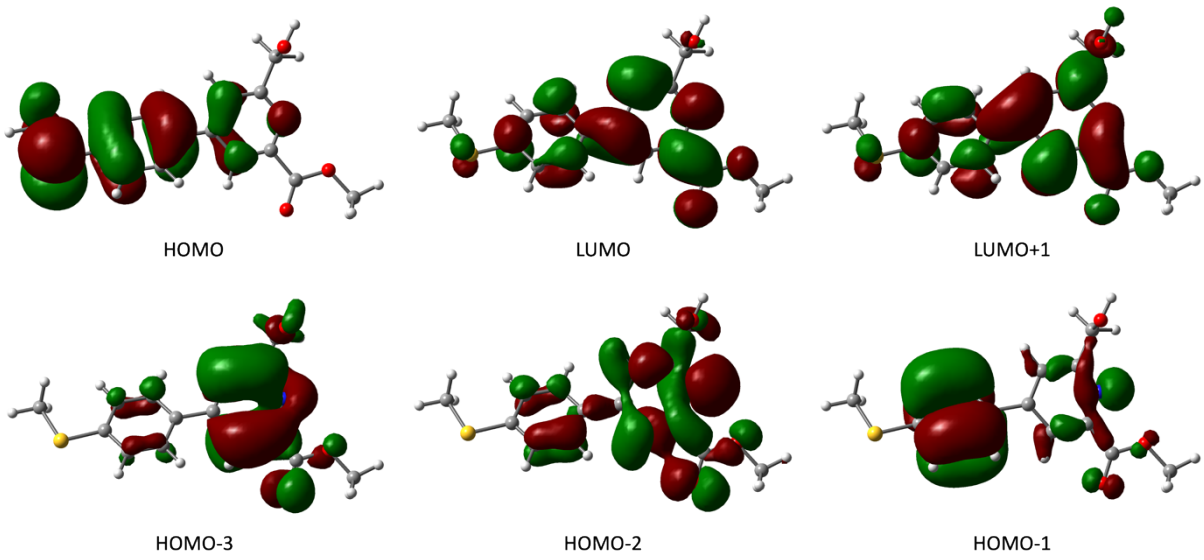


Figure S4. Main molecular orbitals involved in the transitions for $\mathbf{A_1}$.

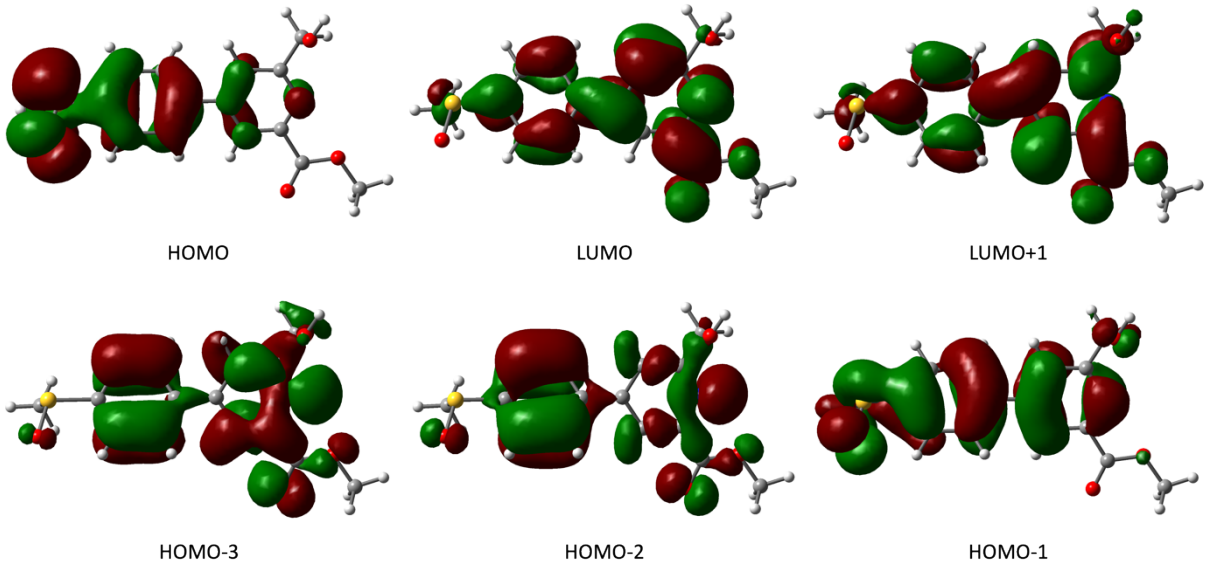


Figure S5. Main molecular orbitals involved in the transitions for $\mathbf{A_1^{ox}}$.

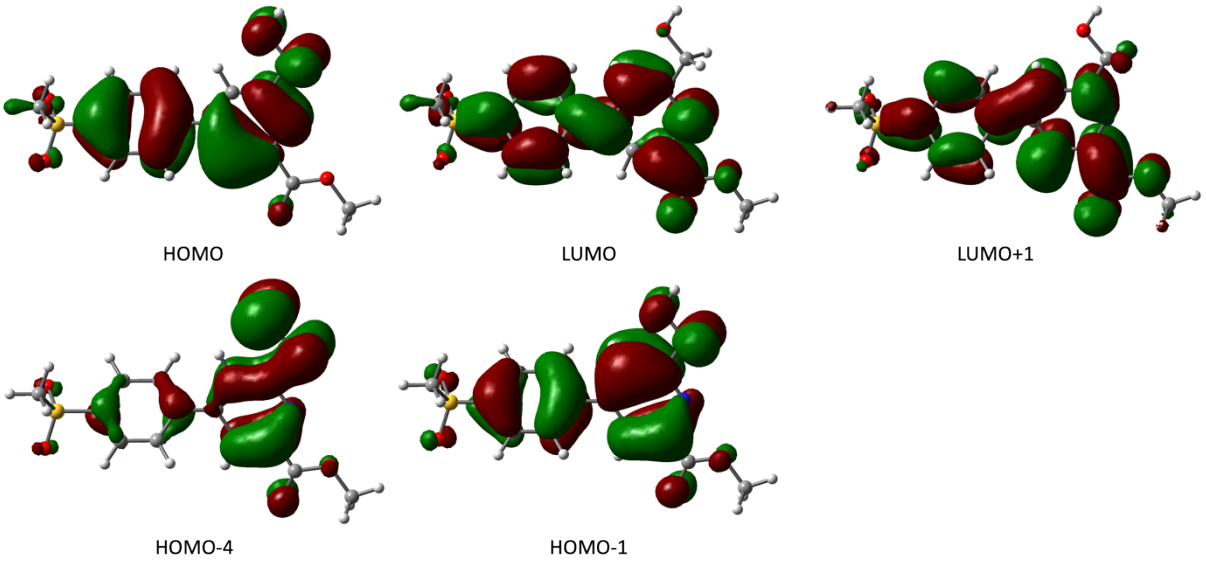


Figure S6. Main molecular orbitals involved in the transitions for $\mathbf{A_1^{diox}}$.

Table S1. Theoretical electronic absorption data obtained for dyes **A_1, A_1^{ox} and A_1^{diox}** in methanol solution. The theoretical values are evaluated at the PCM(MEOH)-PBE0/6-311+G(d,p) level of approximation. Only transitions with f > 0.10 and orbital contributions to the transitions > 10% are given.

	$\lambda_{max}^{calc.}$ (nm)	*f*	Assignment (%)
A_1			
1	336	0.34	HOMO → LUMO (98.3)
2	299	0.29	HOMO → LUMO+1 (96.4)
6	248	0.11	HOMO-3 → LUMO (28.7) HOMO-1 → LUMO (21.5) HOMO-2 → LUMO+1 (10.2)
15	215	0.23	HOMO-4 → LUMO+1 (48.4) HOMO-5 → LUMO+1 (23.1) HOMO-3 → LUMO+1 (11.4)
16	213	0.25	HOMO-3 → LUMO+1 (43.7) HOMO-5 → LUMO+1 (31.0)
A_1^{ox}			
1	294	0.29	HOMO → LUMO (93.3)
5	252	0.24	HOMO-1 → LUMO (53.8) HOMO → LUMO+1 (12.7) HOMO-2 → LUMO+1 (11.1)
11	229	0.31	HOMO-1 → LUMO+1 (53.3) HOMO-4 → LUMO (14.0)
14	221	0.16	HOMO → LUMO+3 (64.9) HOMO-4 → LUMO+1 (10.0)
15	217	0.12	HOMO-4 → LUMO+1 (53.9) HOMO-3 → LUMO+1 (15.6)
A_1^{diox}			
2	271	0.23	HOMO → LUMO (78.2) HOMO-1 → LUMO (11.3)

3	256	0.41	HOMO-1 → LUMO (72.4) HOMO → LUMO (16.4)
8	228	0.37	HOMO-1 → LUMO+1 (82.7) HOMO → LUMO+1 (11.0)
9	225	0.13	HOMO-4 → LUMO (79.2) HOMO → LUMO+1 (13.1)

Table S2. Charge Transfer parameters (distance and amount of charge) determined using Le Bahers' model for the S0-S1 transition of dyes **A_1, A_1^{ox} and A_1^{diox}**. The theoretical values are evaluated at the PCM(MeOH)-PBE0/6-311+G(d,p) level of approximation.

	d_{CT} (Å)	q_{CT} (e)
A_1	6.15	0.80
A_1^{ox}	6.18	0.73
A_1^{diox}	1.68	0.73

HRMS analysis of HOCl oxidation products of LnL_1 and LnL_2 complexes

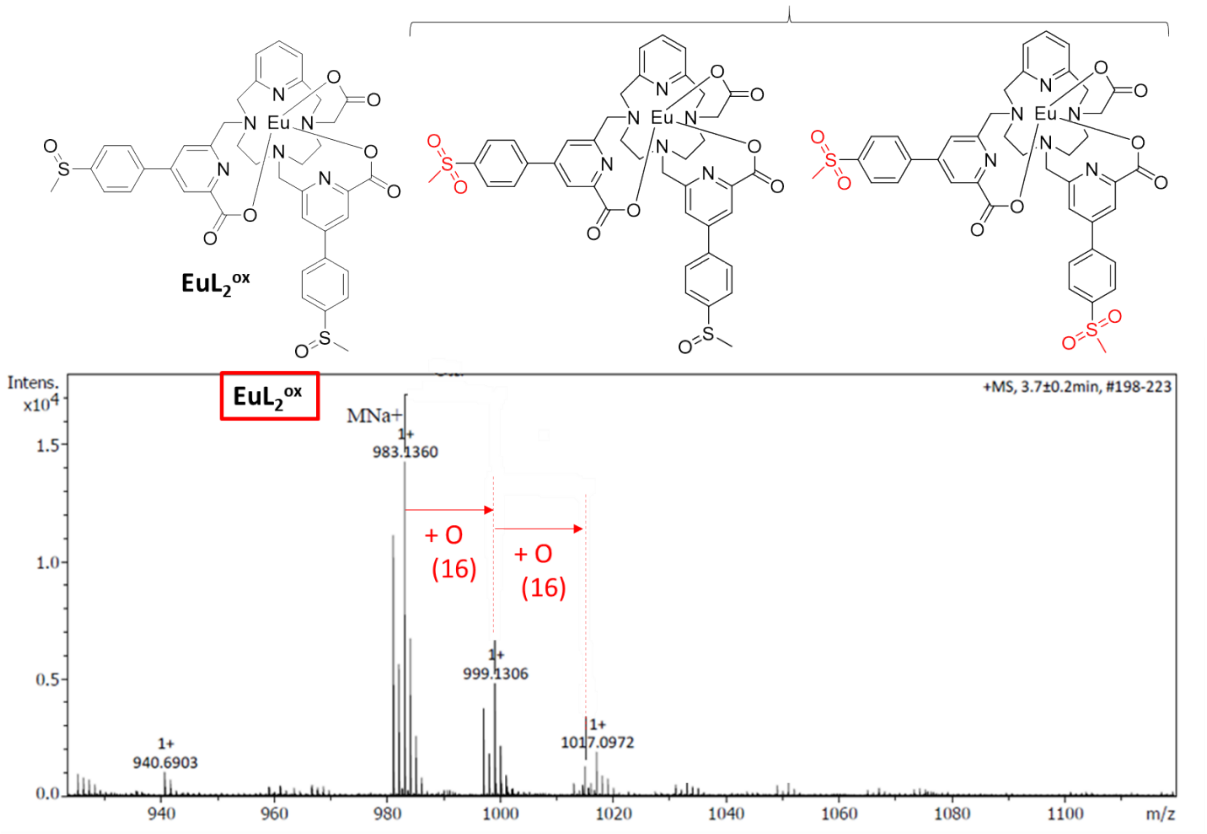
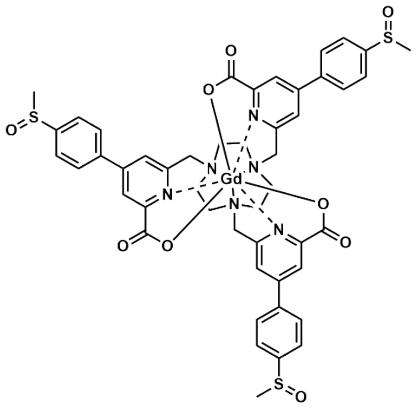
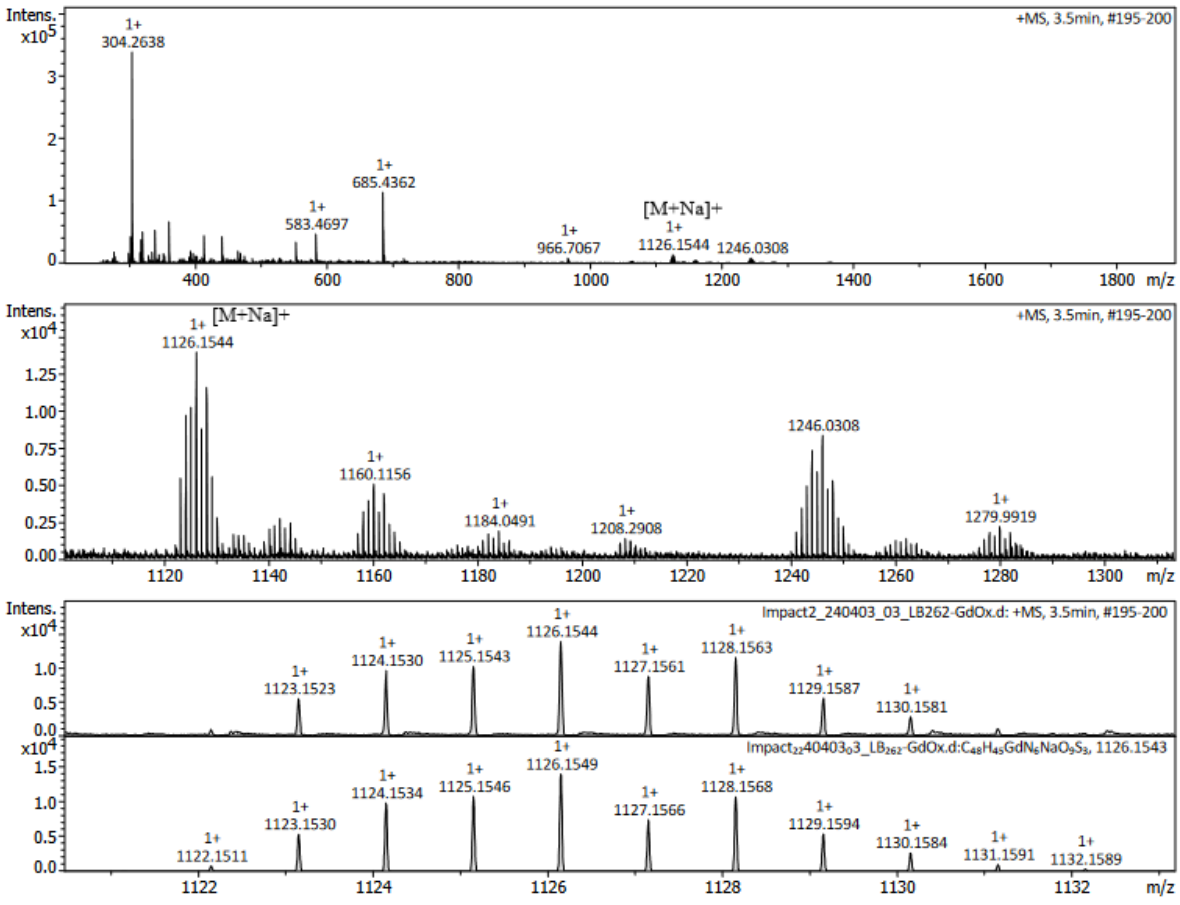


Figure S7. Attributed HRMS spectra of $\mathbf{TbL_1^{Ox}}$ and $\mathbf{EuL_2^{Ox}}$ complexes recorded after adding HOCl to methanol solution (C ≈ 10 µM).

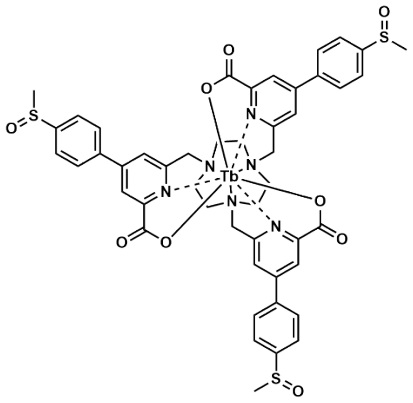


GdL_1^{ox}

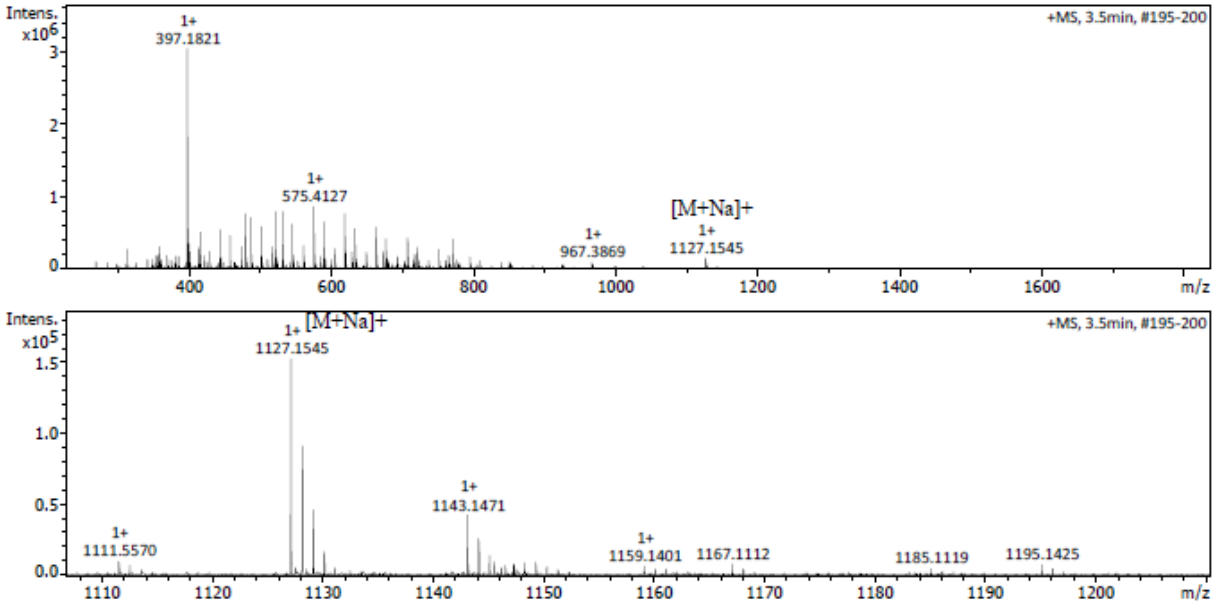


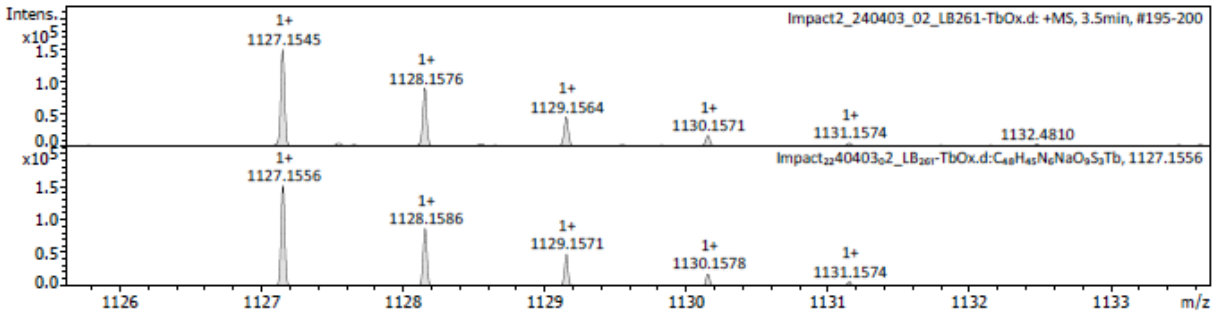
Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
1126.1544	C48H45GdN6NaO9S3	~~1126.1543~~ 1126.1549	C48H45GdN6O9S3	0.4	46.8	M+Na	1+

Figure S8. HRMS spectra of **GdL_1^{ox}** species in MeOH (C = 0.1 mM). Spectra were obtained from a cuvette solution after adding 15 eq. of HOCl, the conversion was observed by UV-Vis.



TbL_1^{ox}





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
1127.1545	C48H45N6NaO9S3Tb	1127.1556	C48H45N6O9S3Tb	0.9	11.4	M+Na	1+

Figure S9. HRMS spectra of **TbL_1^{ox}** species in MeOH (C = 0.1 mM). Spectra were obtained from a cuvette solution after adding 15 eq. of HOCl, the conversion was observed by UV-Vis.

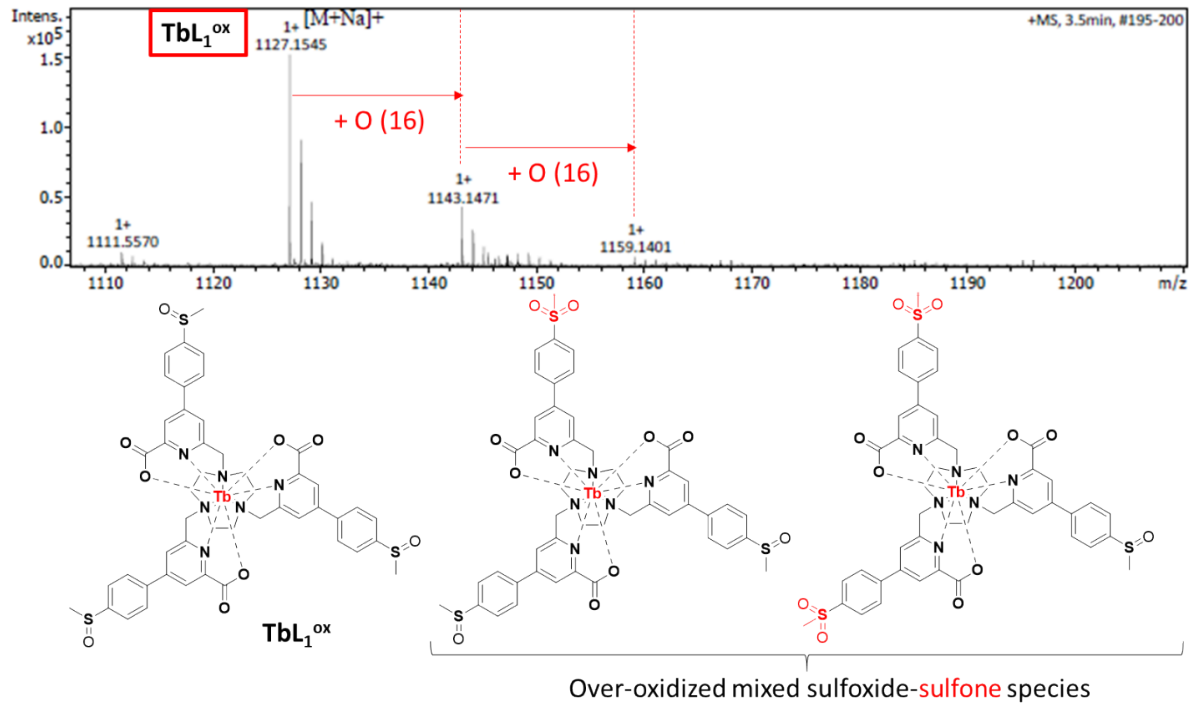


Figure S10. Attributed HRMS spectra of **TbL_1^{ox}** species in MeOH (C = 0.1 mM).

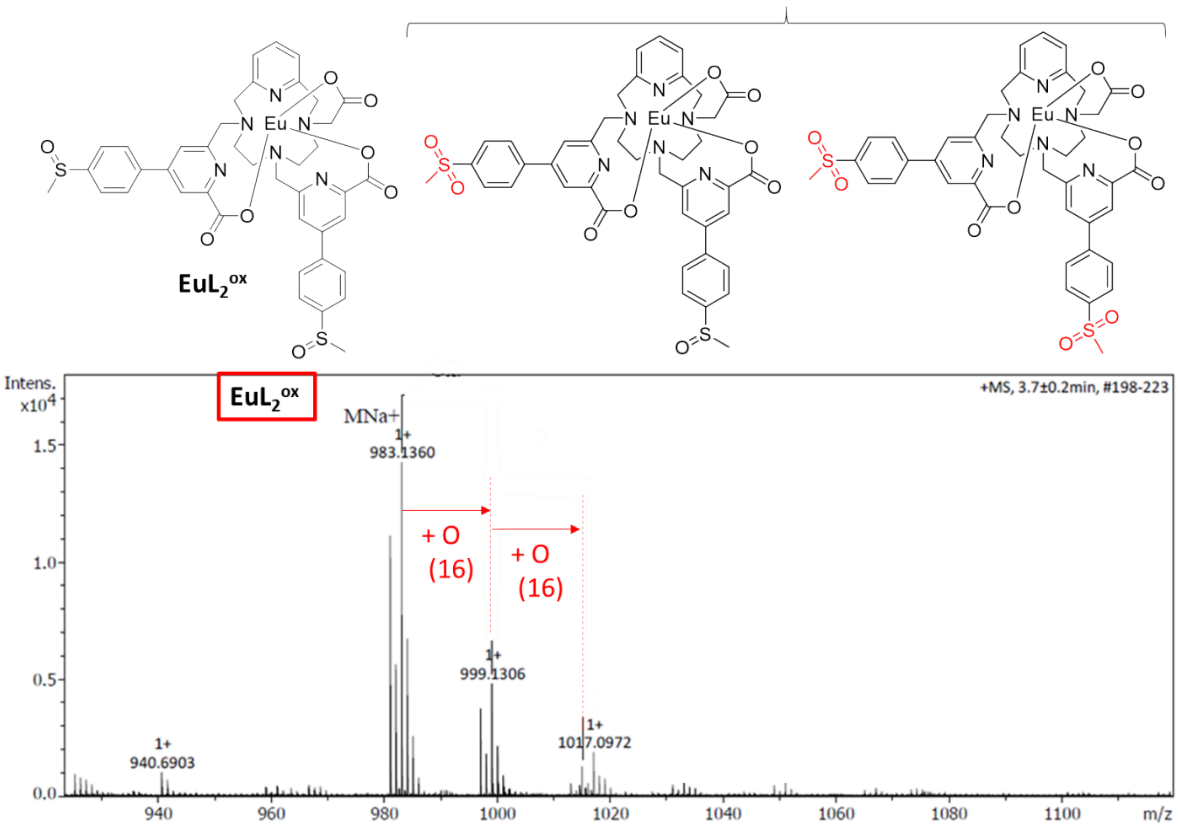


Figure S11. Attributed HRMS spectra of **EuL_2^{ox}** species in MeOH (C = 0.1 mM).

Photophysical Characterization and Titrations

Figure S12. Absorption (black), excitation (blue, λ_{em} = 614 nm for Eu and 541 nm for Tb) and steady-state emission spectra of **LnL_2** (Ln = Tb, green; Ln = Eu, red) in methanol solutions at 293 K before (top, λ_{ex} = 330 nm) and after (bottom, λ_{ex} = 283 nm) addition of excess HOCl.

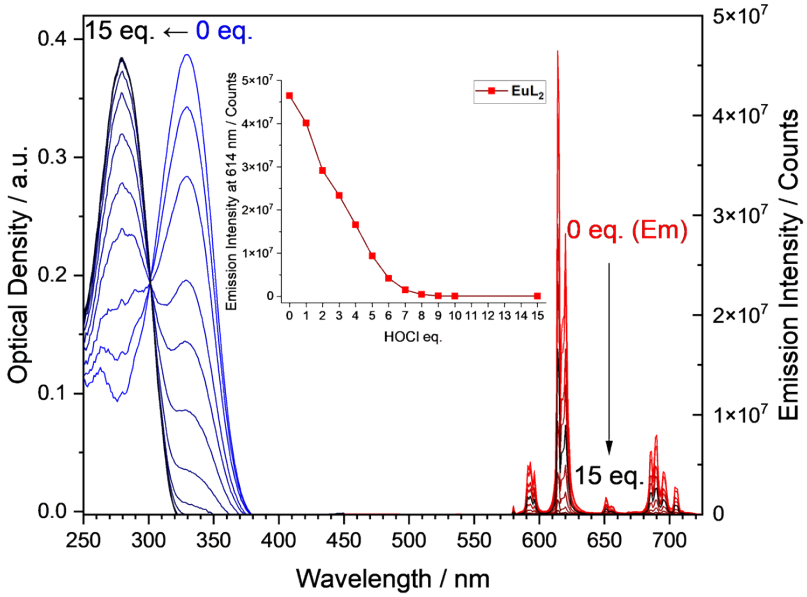


Figure S13. Titration of **EuL_2** by HOCl in MeOH at 293 K. (Left) Evolution of the absorption spectra, (right) evolution of the Eu(III) emission spectra upon 370 nm excitation; (inset) variation of the 614 nm emission intensity with the number of HOCl equivalents.

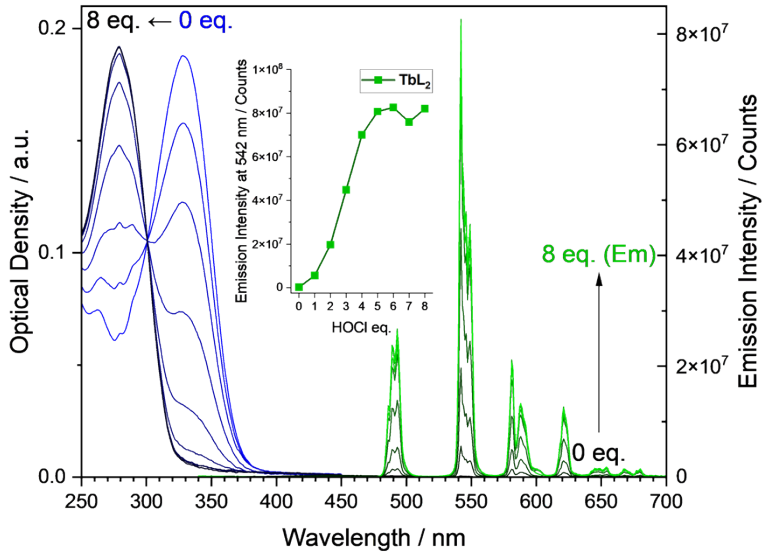


Figure S14. Titration of $\mathbf{TbL_2}$ by HOCl in MeOH at 293 K. (Left) Evolution of the absorption spectra, (right) evolution of the Tb(III) emission spectra upon 301 nm excitation; (inset) variation of the 542 nm emission intensity with the number of HOCl equivalents.

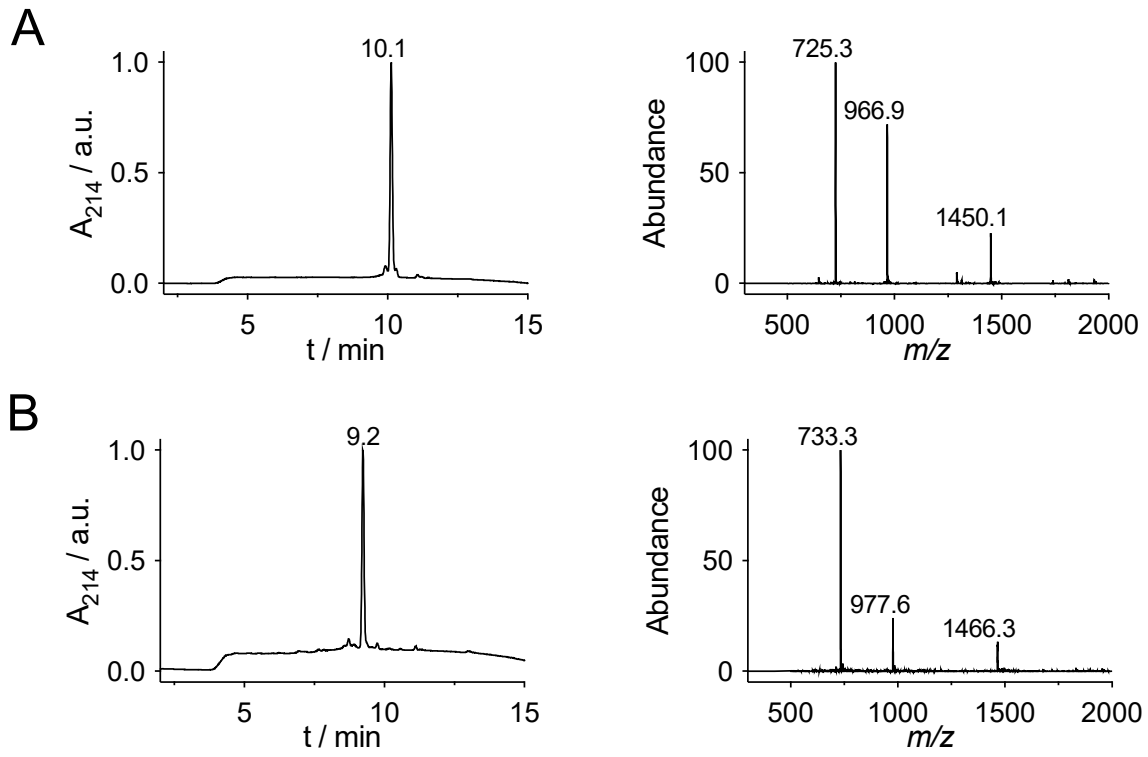


Figure S15. Analytical LCMS analysis of **TbL$_3$** in PBS (A) before and (B) after addition of a 4-fold excess of HOCl: HPLC chromatogram with absorbance monitoring at 214 nm (Right) and LRMS (ESI+) spectrum. (A) calculated peak maximum *m/z* = 725.2 $[M+2H]^{2+}$, 967.0 $[2M+3H]^{3+}$, 1449.5 $[M+H]^{+}$ for M = $C_{68}H_{85}N_6O_{17}STb$ (**TbL$_3$**); (B) calculated peak maximum *m/z* = 733.3 $[M+2H]^{2+}$, 977.7 $[2M+3H]^{3+}$, 1466.4 $[M+H]^{+}$ for M = $C_{68}H_{85}N_6O_{18}STb$ (**TbL$_3^{ox}$**). C18 RP-HPLC, eluting with solvent A = TFA 0.1% in H_2O and solvent B = TFA 0.1% in CH_3CN/H_2O 9:1 v/v. Gradient: 0→2 min 95% A, 2→15 min 5→100% B. Flow: 1 mL/min.

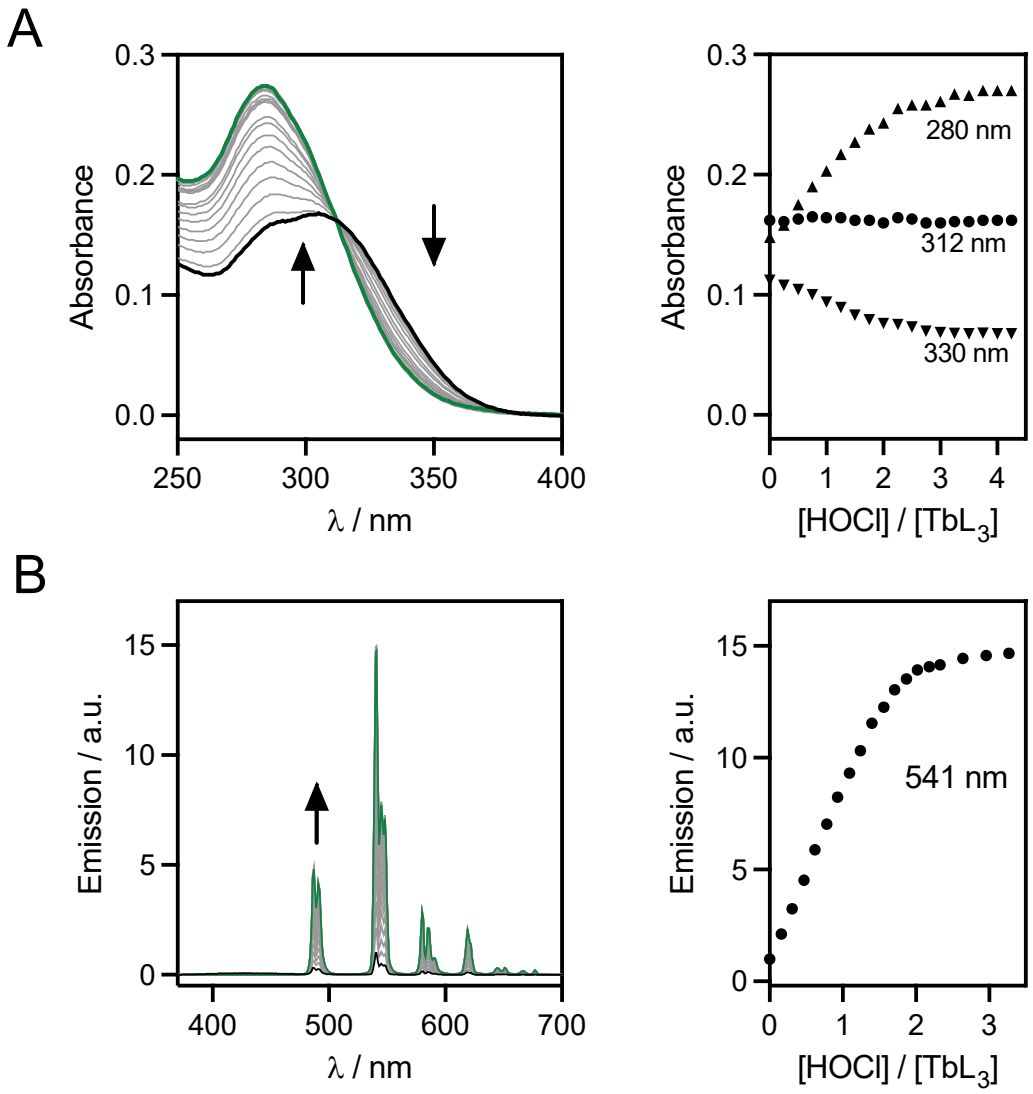


Figure S16. (A) Absorption and (B) emission (λ_{ex} = 298 nm) monitoring of the titration of **TbL_3** 4.5µM in PBS by HOCl.

NMR and FTIR spectra.

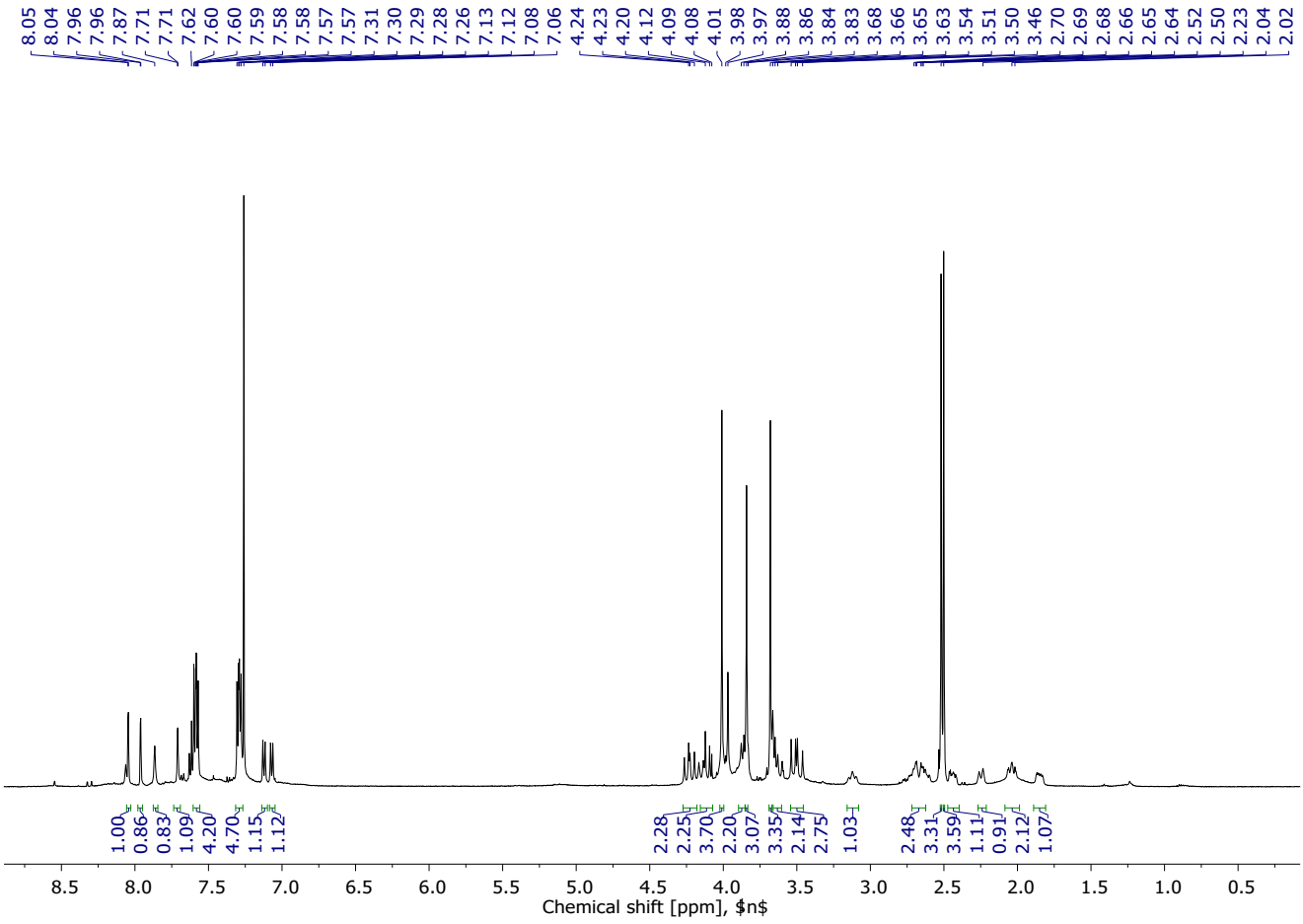


Figure S17. ^{1}H NMR spectrum of compound **L2'** in $CDCl_3$ (500 MHz, 298 K).

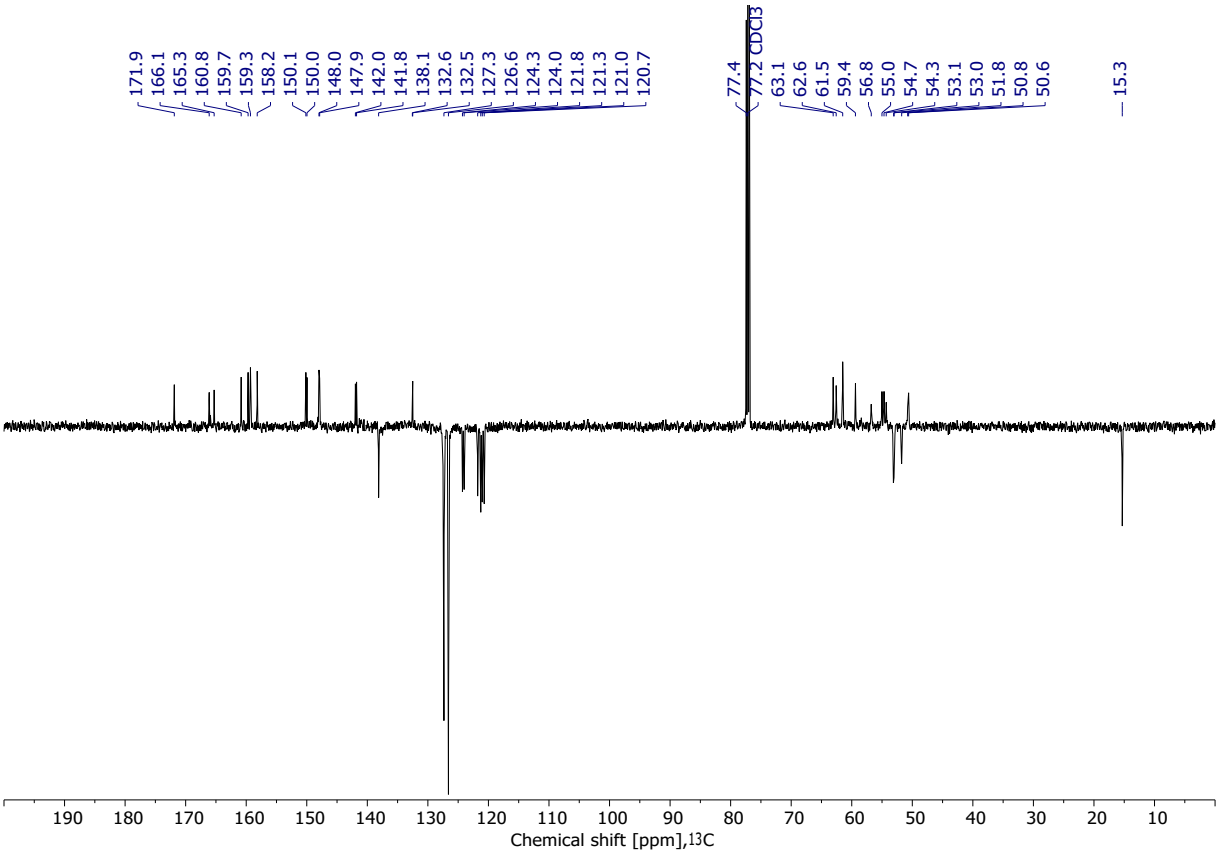


Figure S18. ^{13}C NMR spectrum of compound **L2'** in $CDCl_3$ (125 MHz, 298 K).

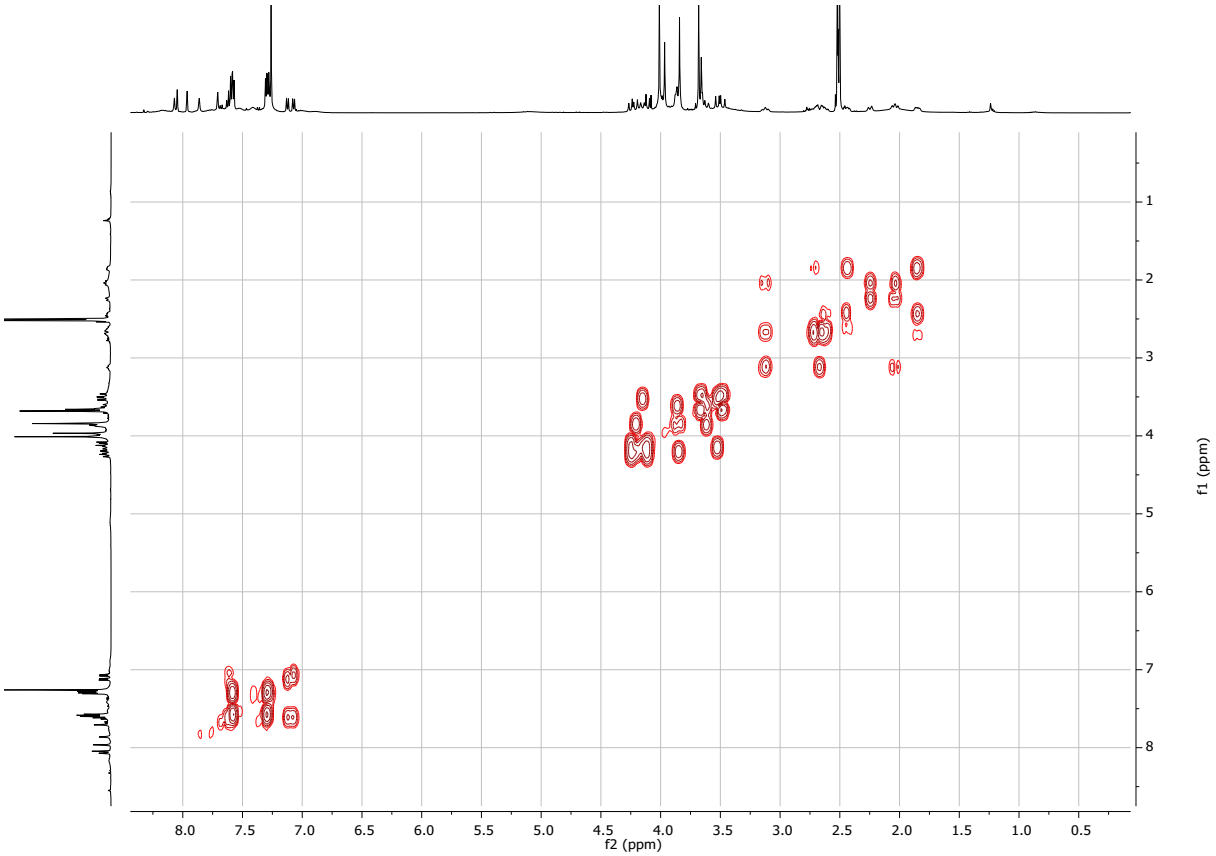


Figure S19. COSY NMR spectrum of compound **L²'** in CDCl3.

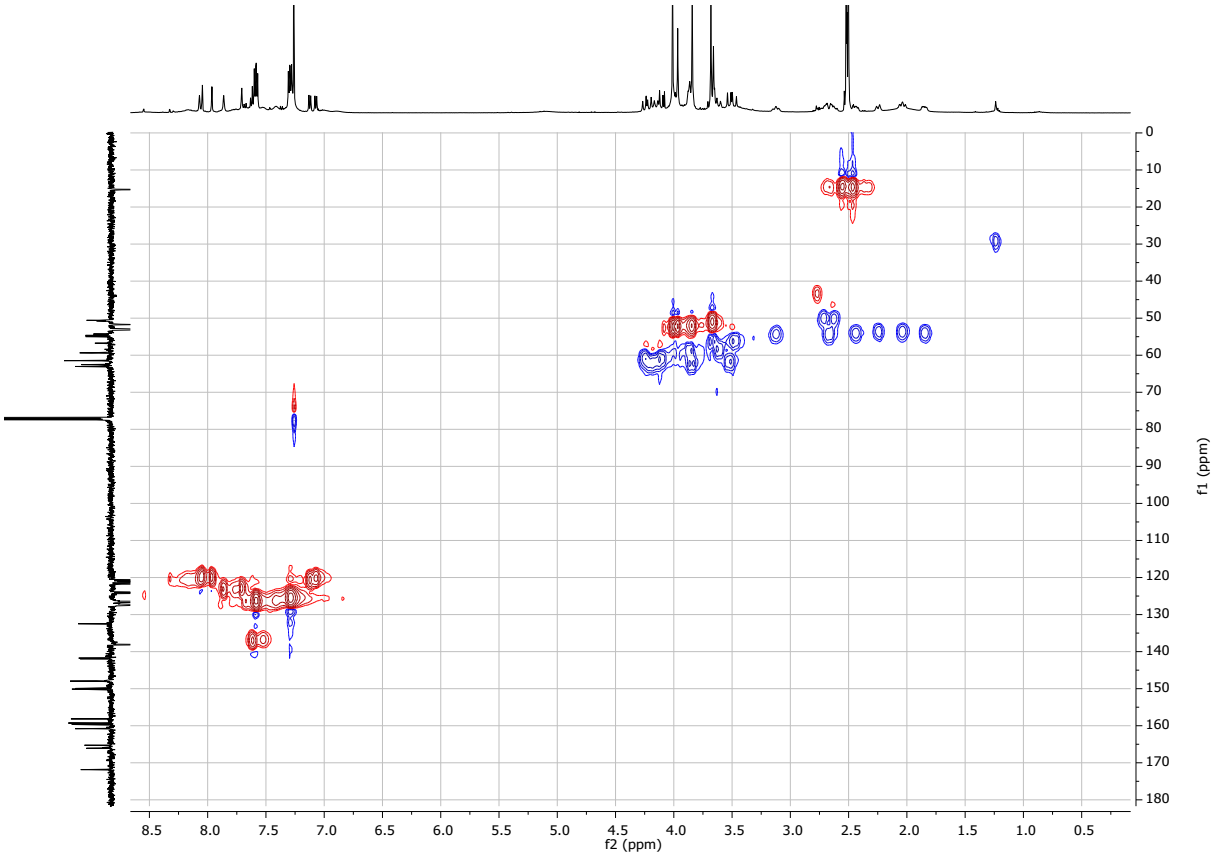


Figure S20. HSQC NMR spectrum of compound **L_2'** in $CDCl_3$.

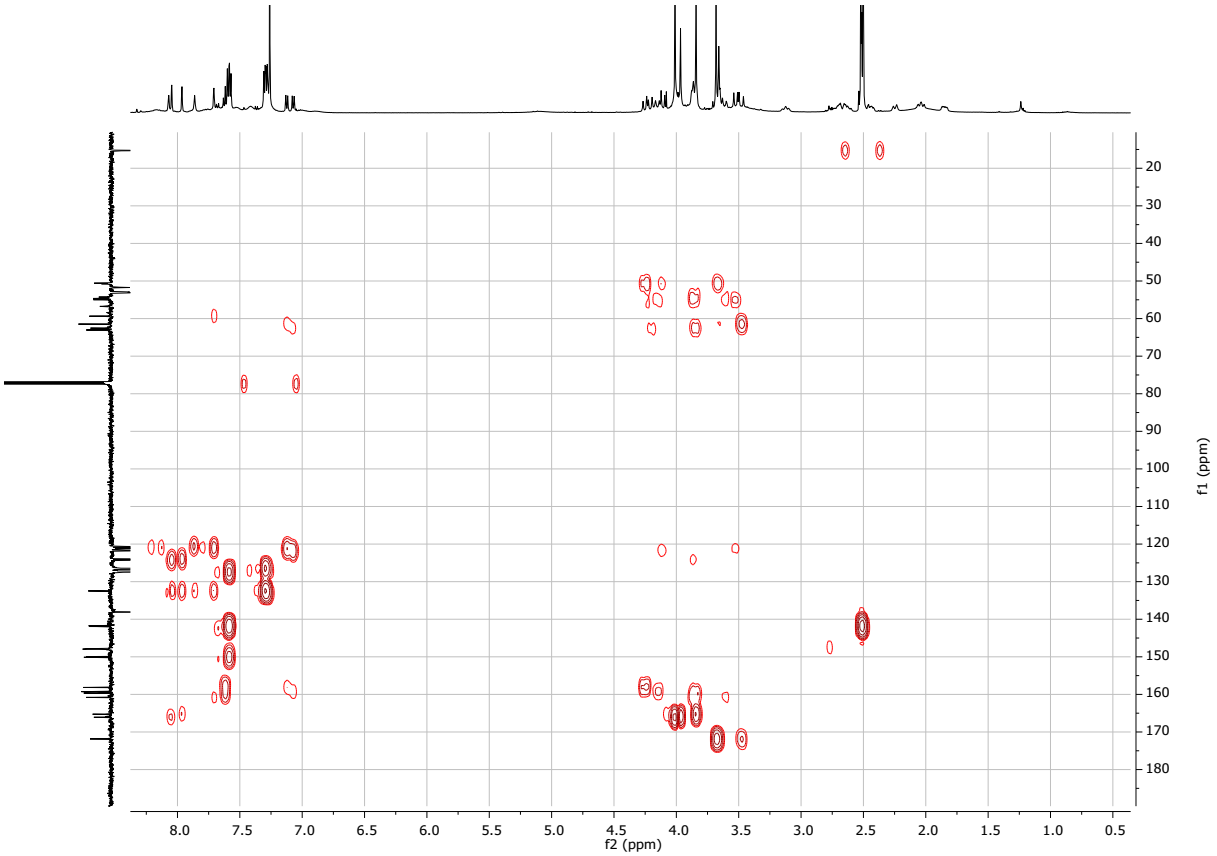


Figure S21. HMBC NMR spectrum of compound **L_2'** in $CDCl_3$.

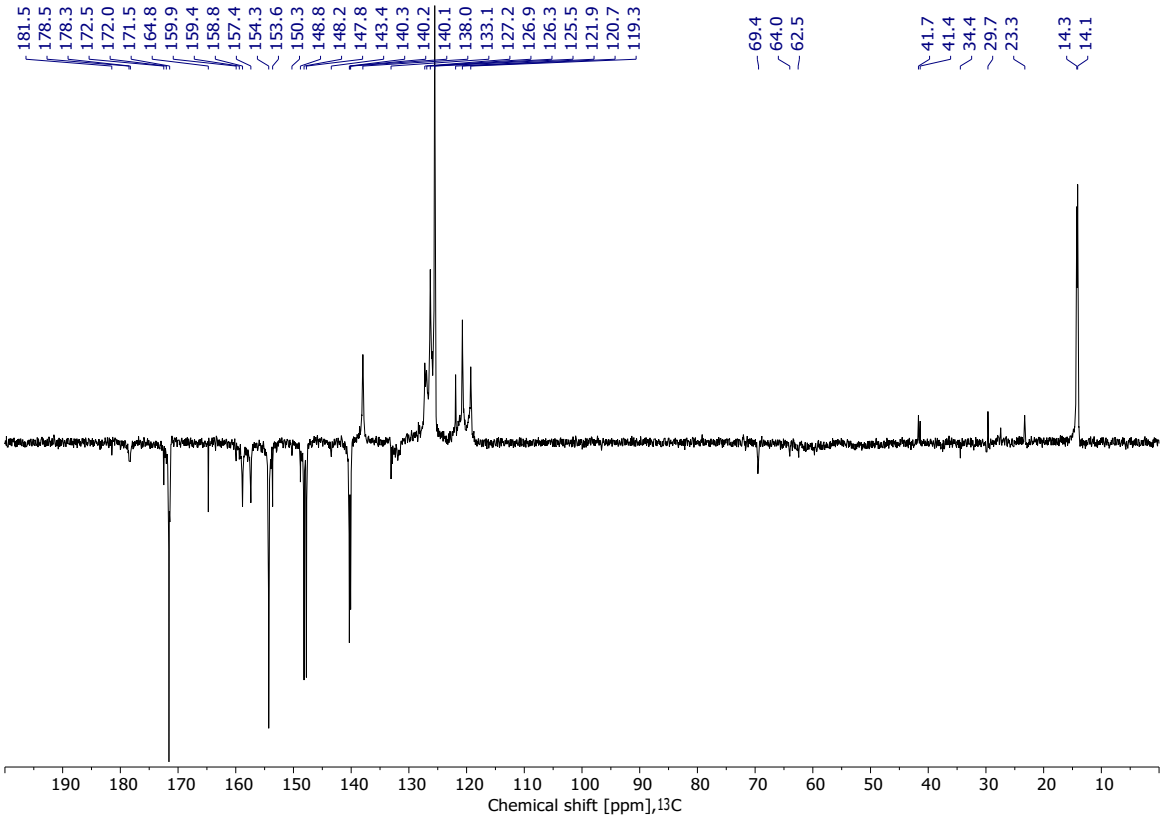


Figure S22. ^{13}C NMR spectrum of compound **L_2** in $CDCl_3$ (125 MHz, 298 K).

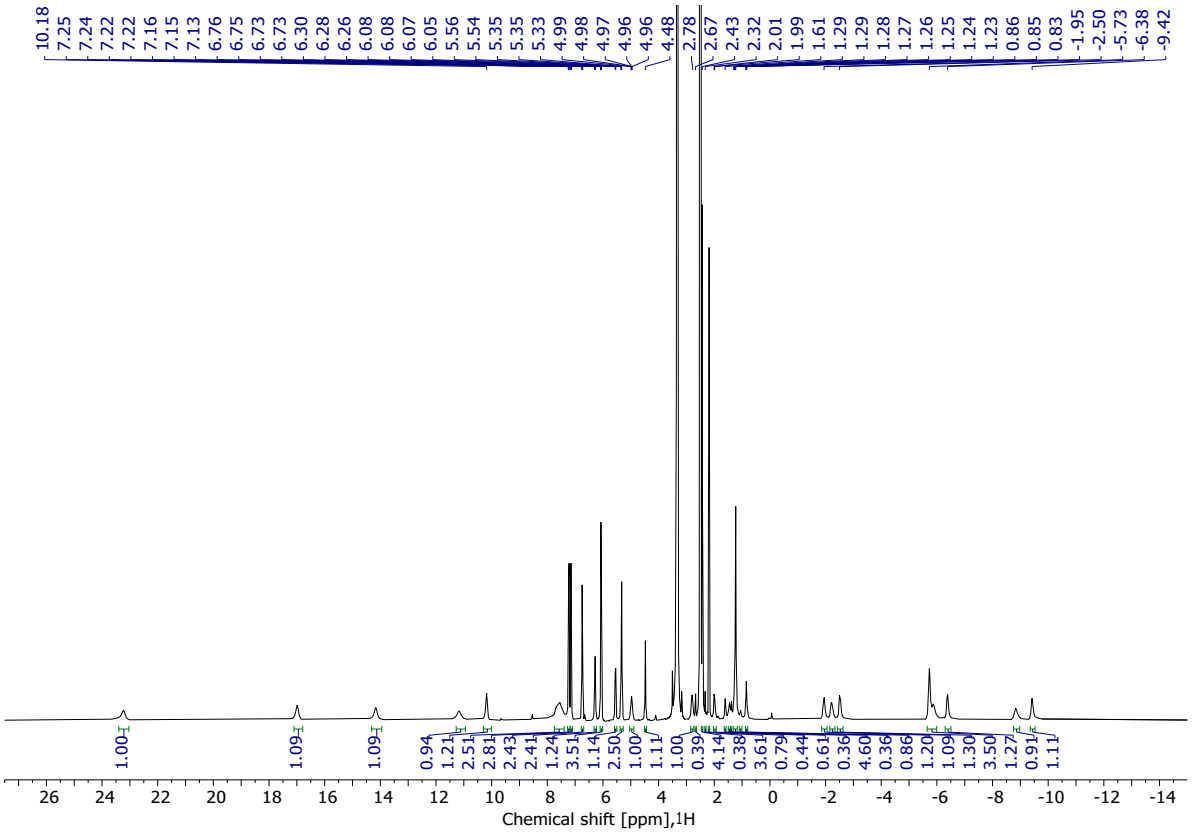


Figure S23. ^{1}H NMR spectrum of compound **EuL_2** in DMSO-d_6 (400 MHz, 298 K).

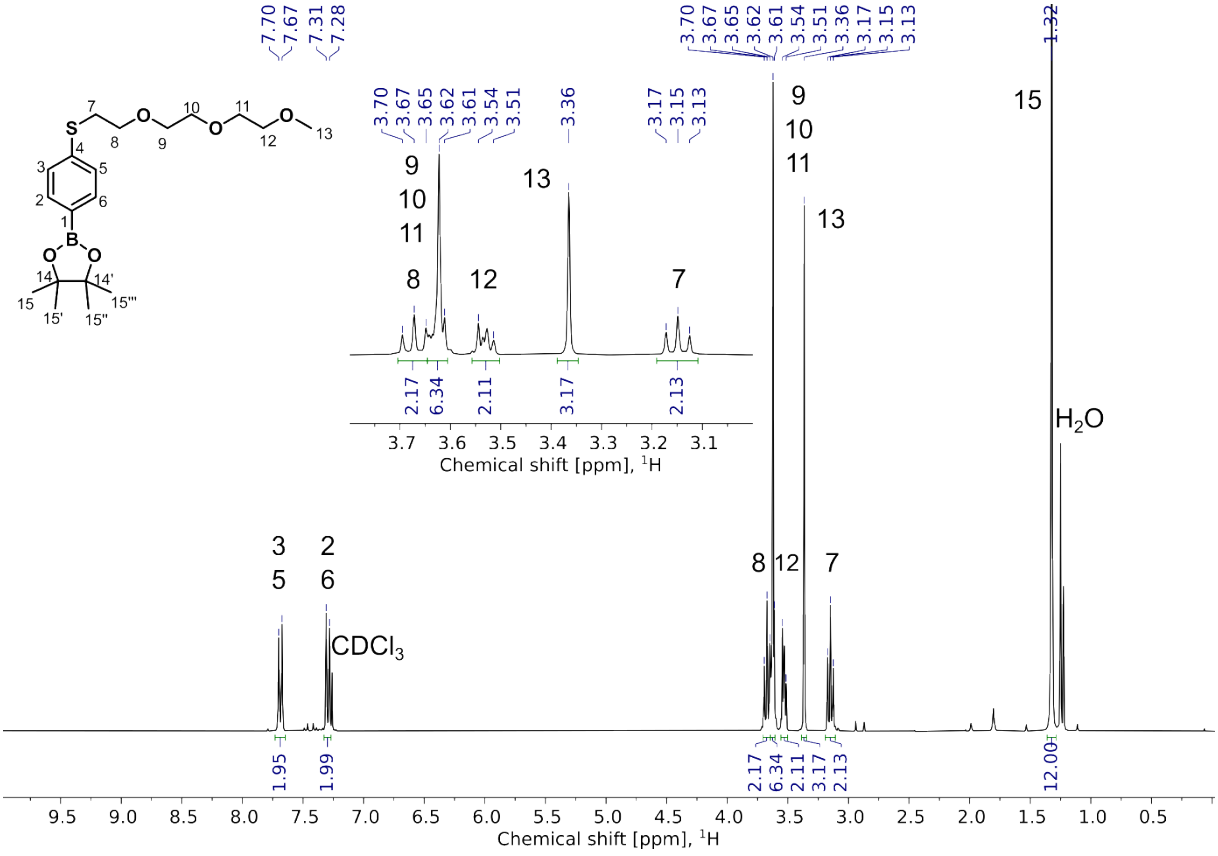


Figure S24. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4**.

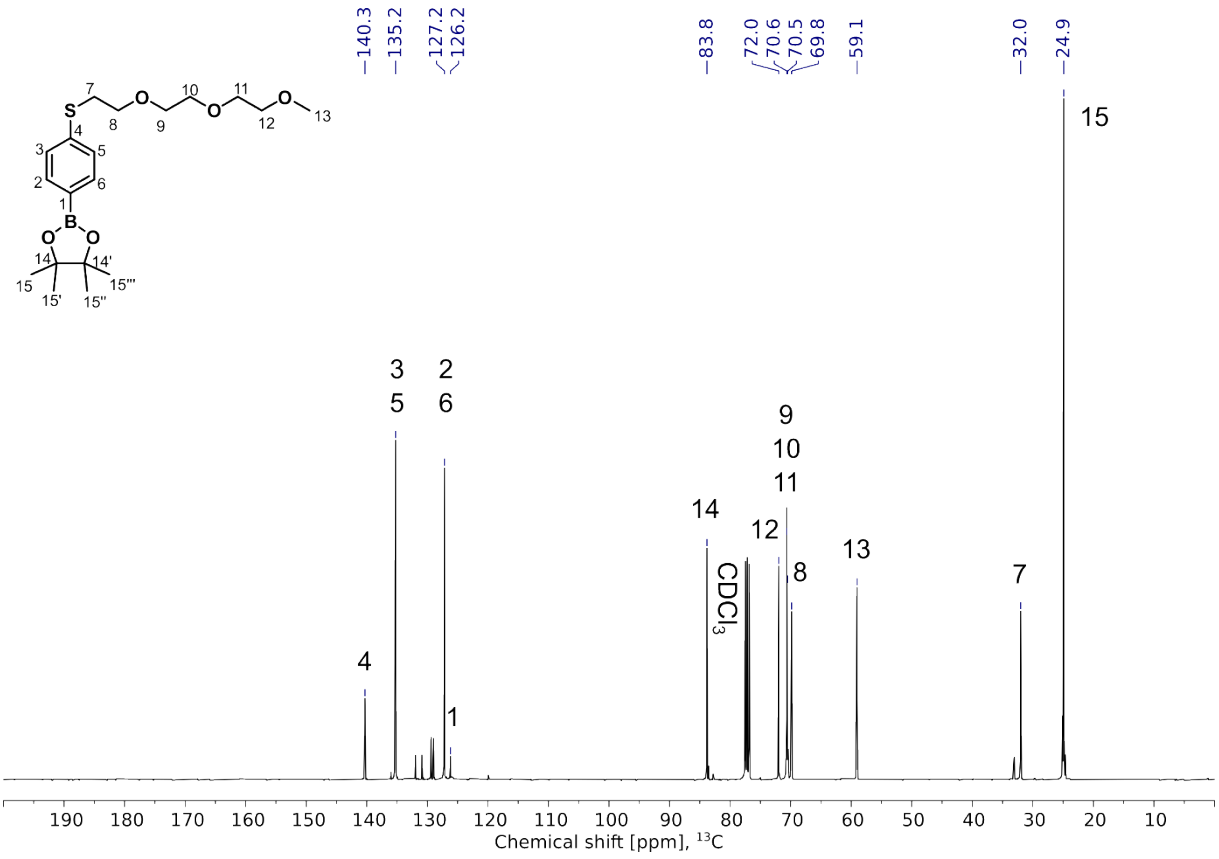


Figure S25. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4**.

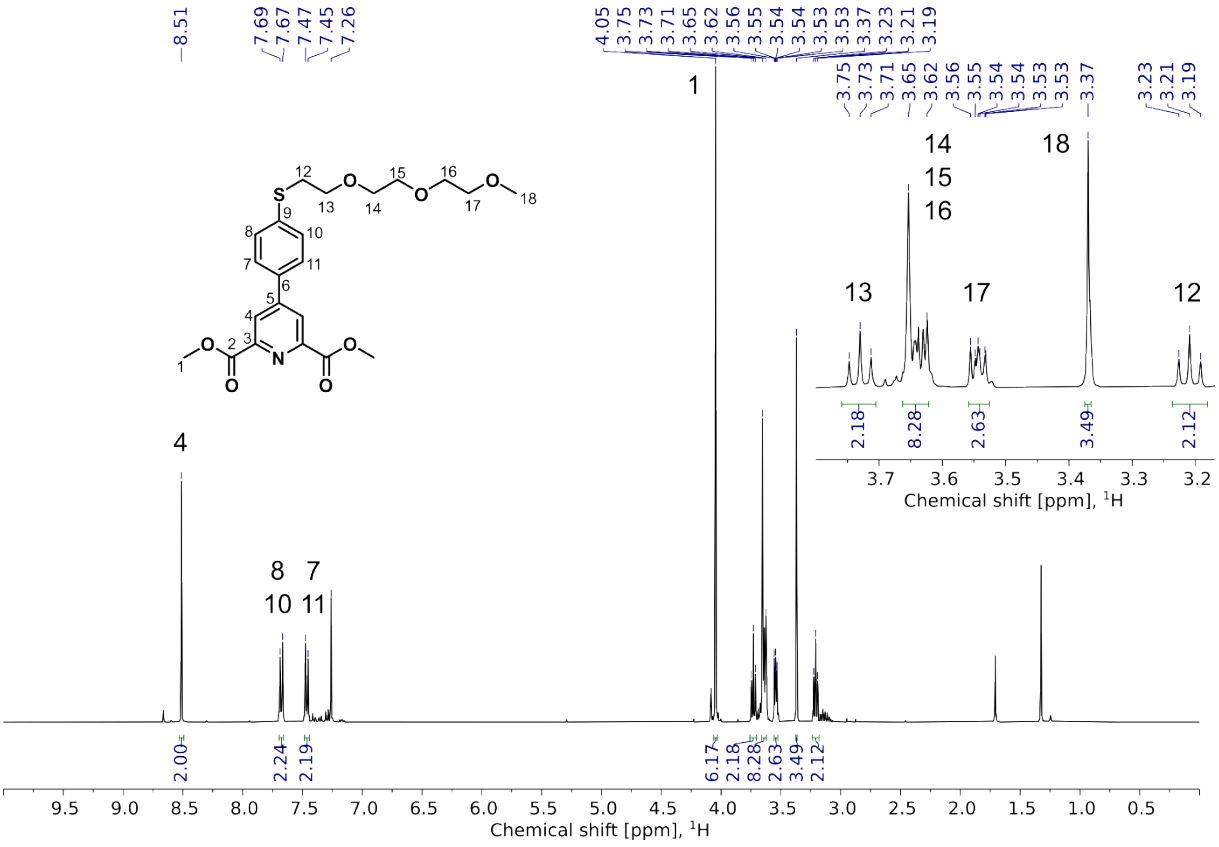


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $\mathbf{A_2'}$.

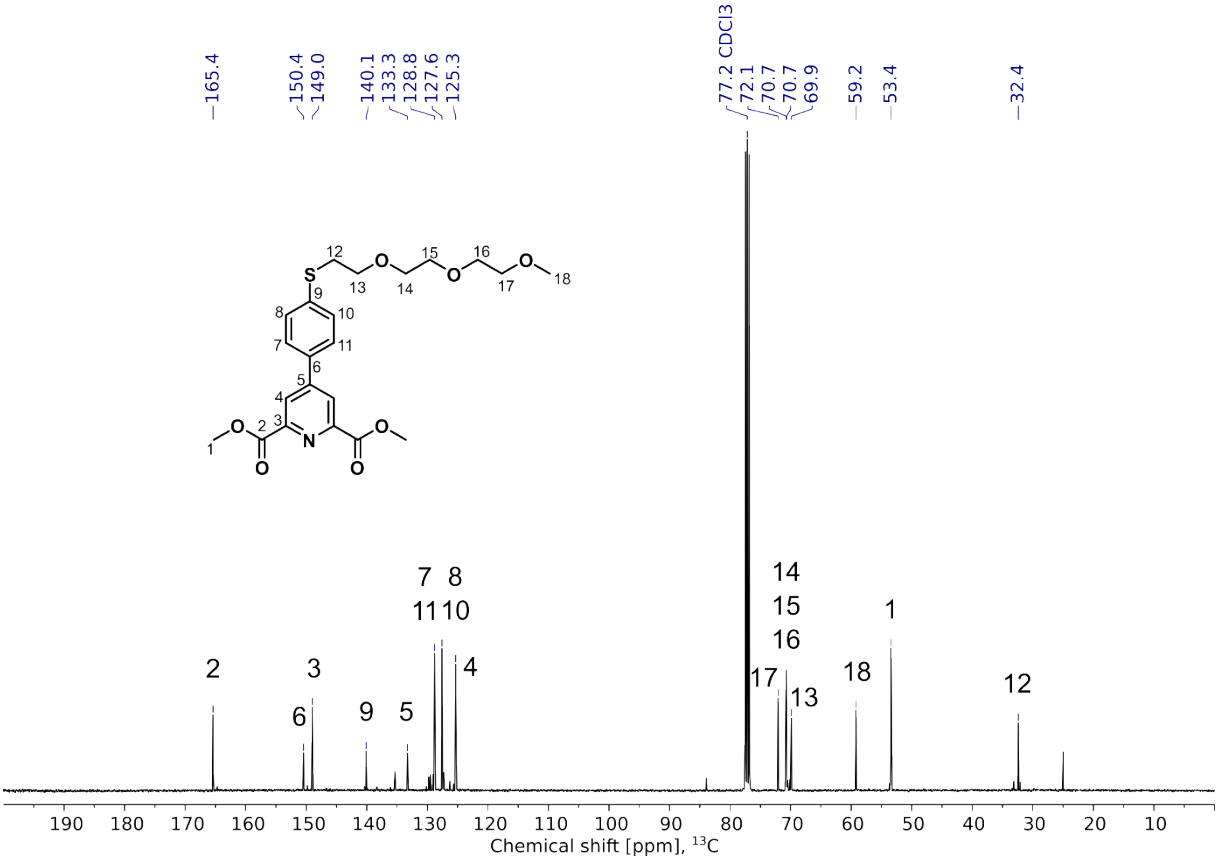


Figure S27. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **A_2'**.

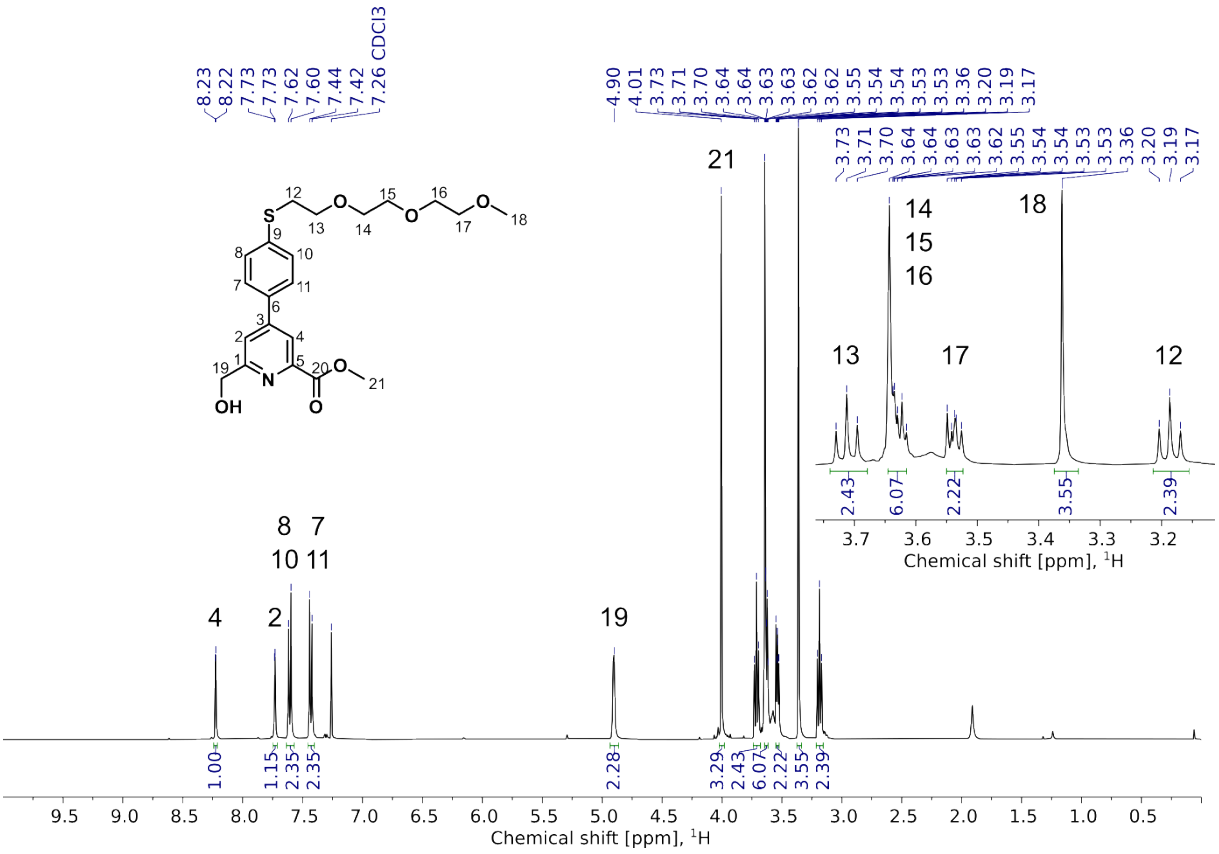


Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **A_2**.

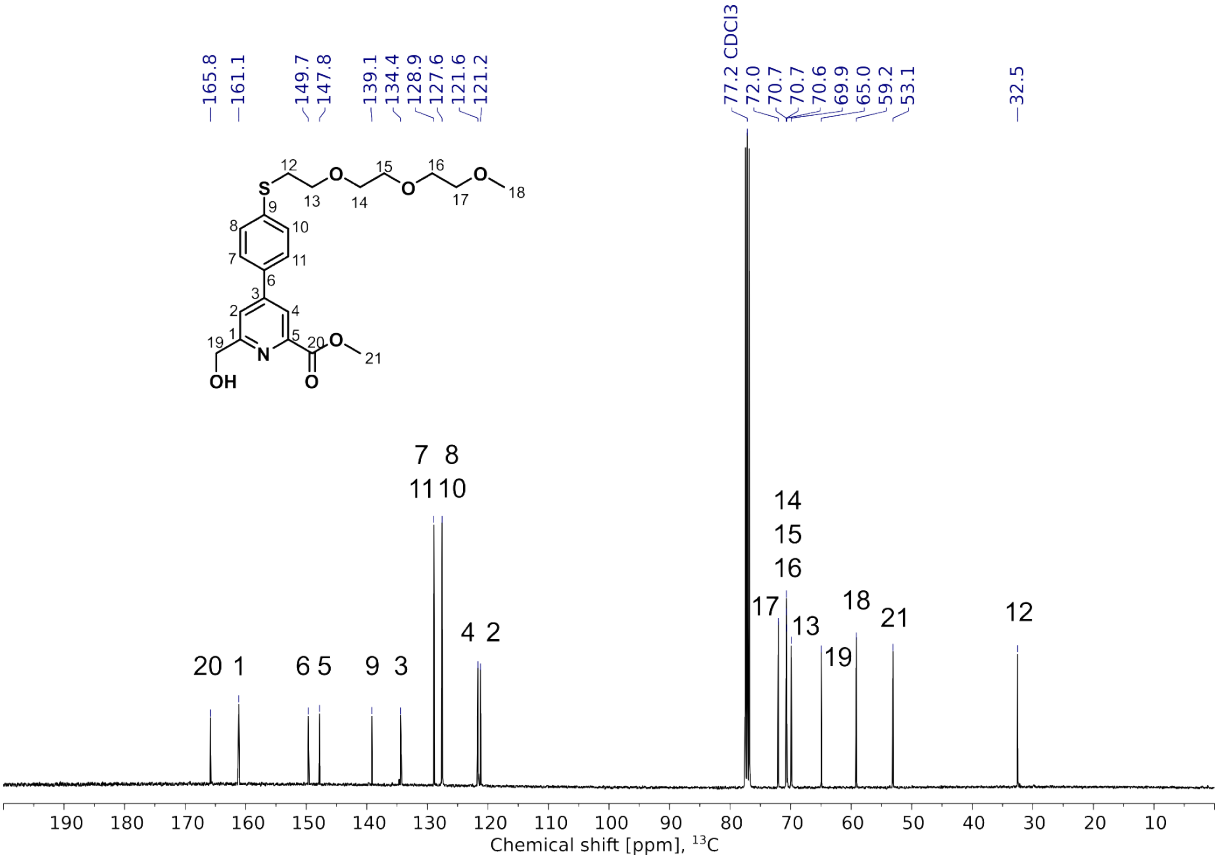


Figure S29. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of $\mathbf{A_2}$.

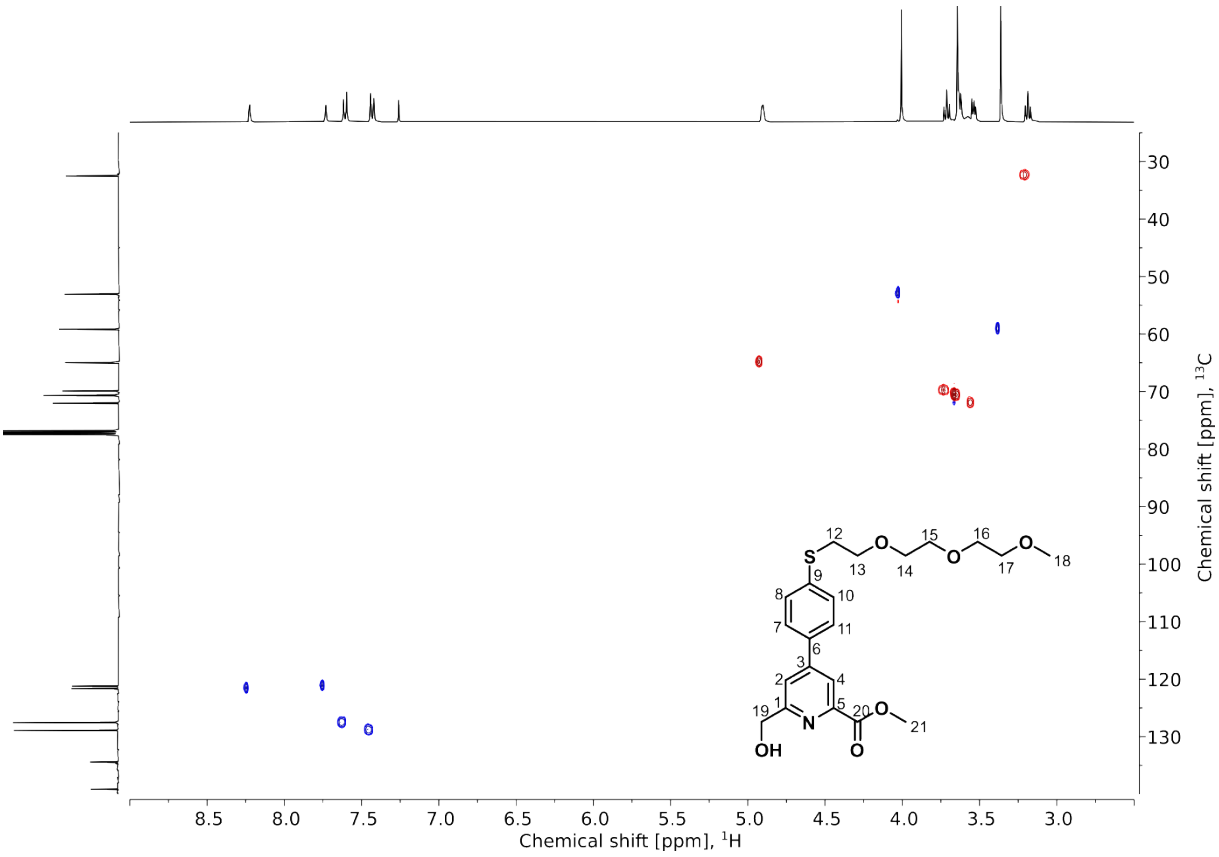


Figure S30. HSQC NMR spectrum ($CDCl_3$) of $\mathbf{A_2}$.

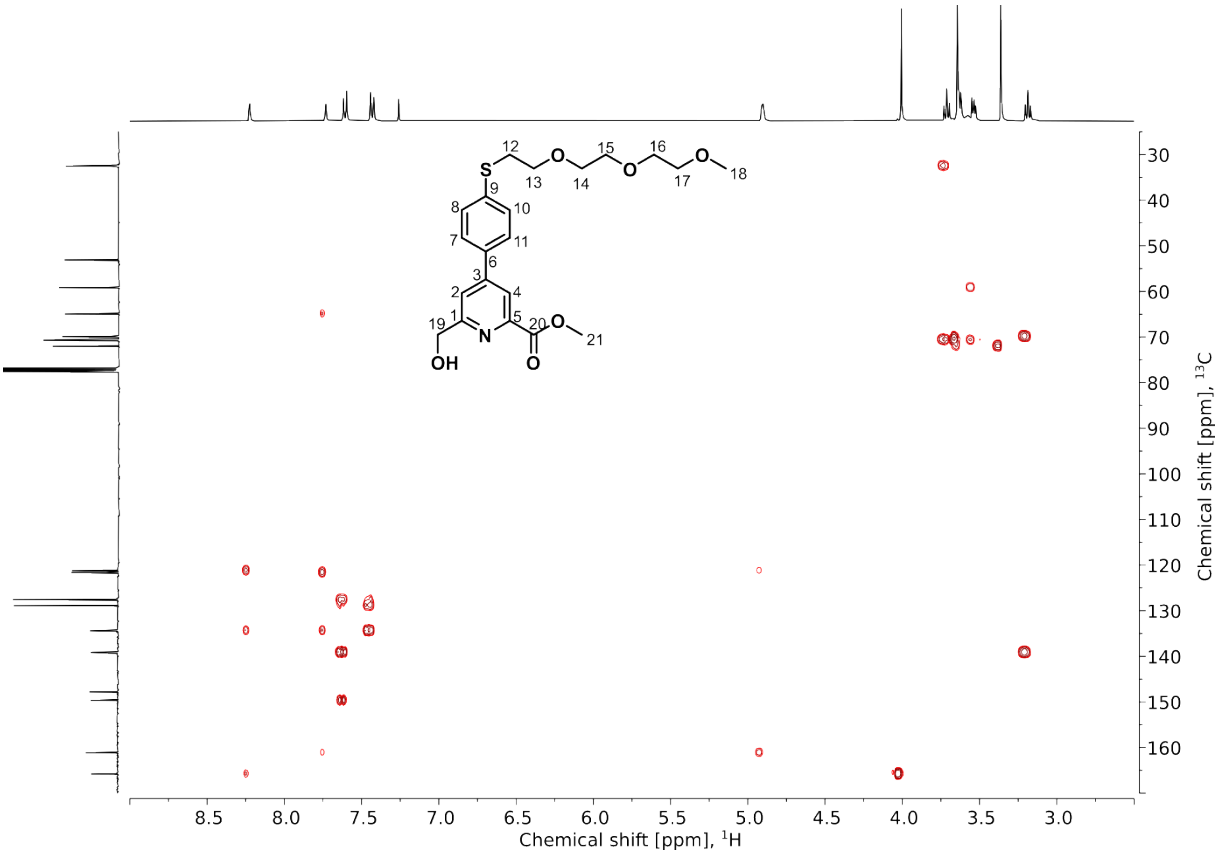


Figure S31. HMBC NMR spectrum ($CDCl_3$) of $\mathbf{A_2}$.

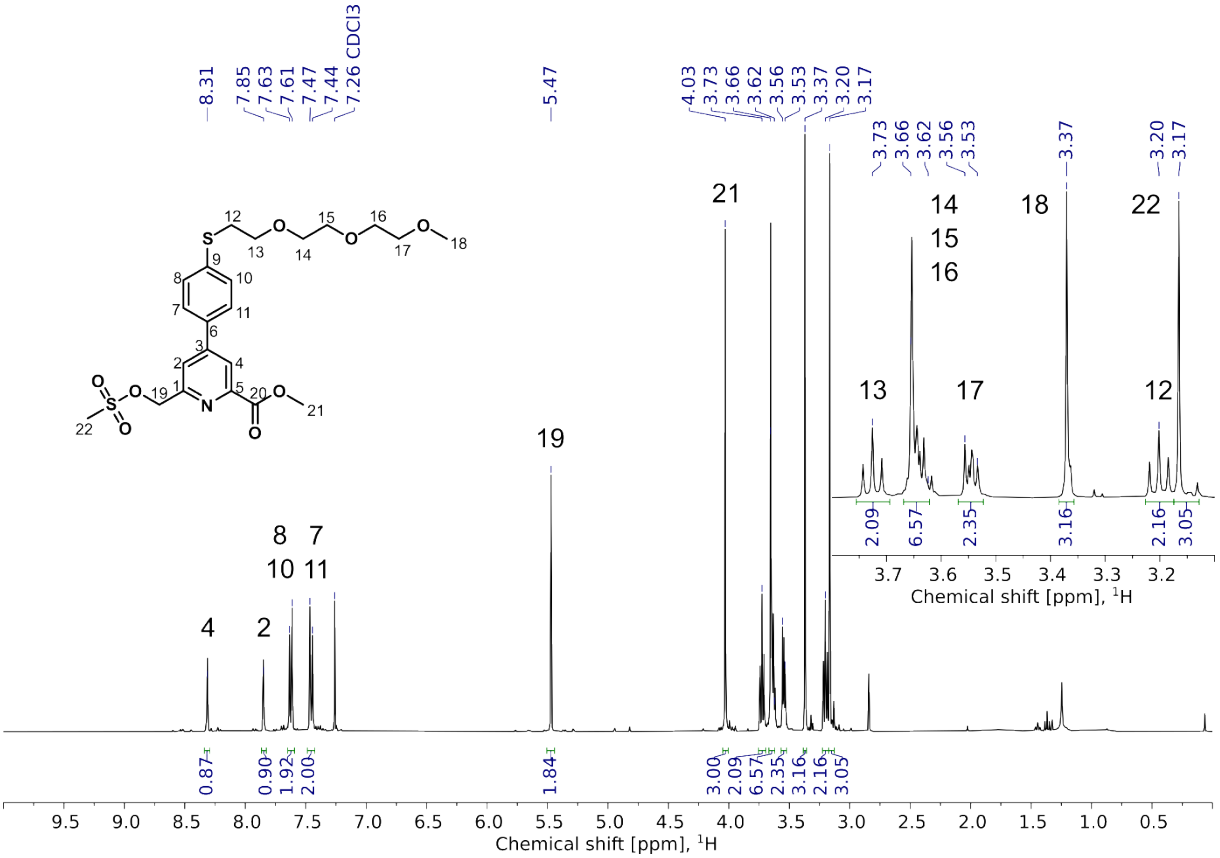


Figure S32. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**.

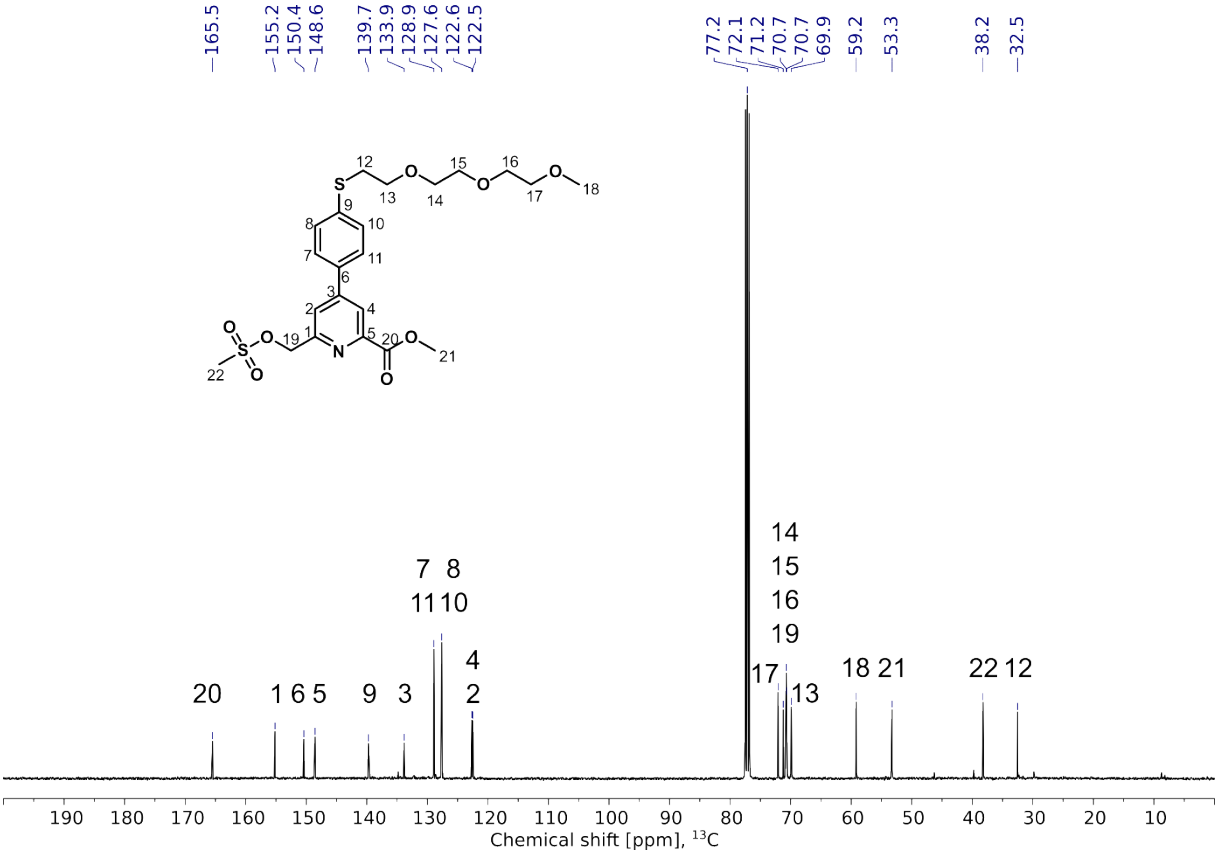


Figure S33. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6**.

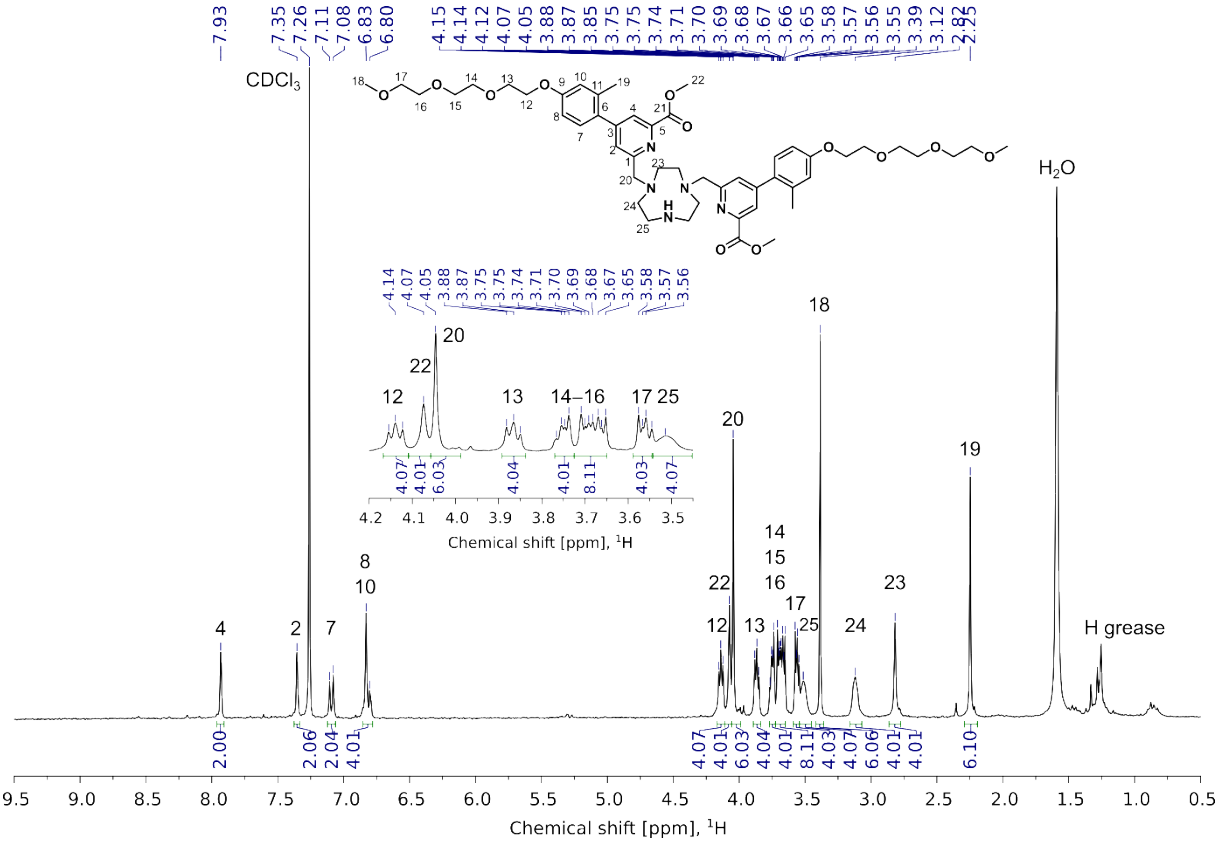


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**.

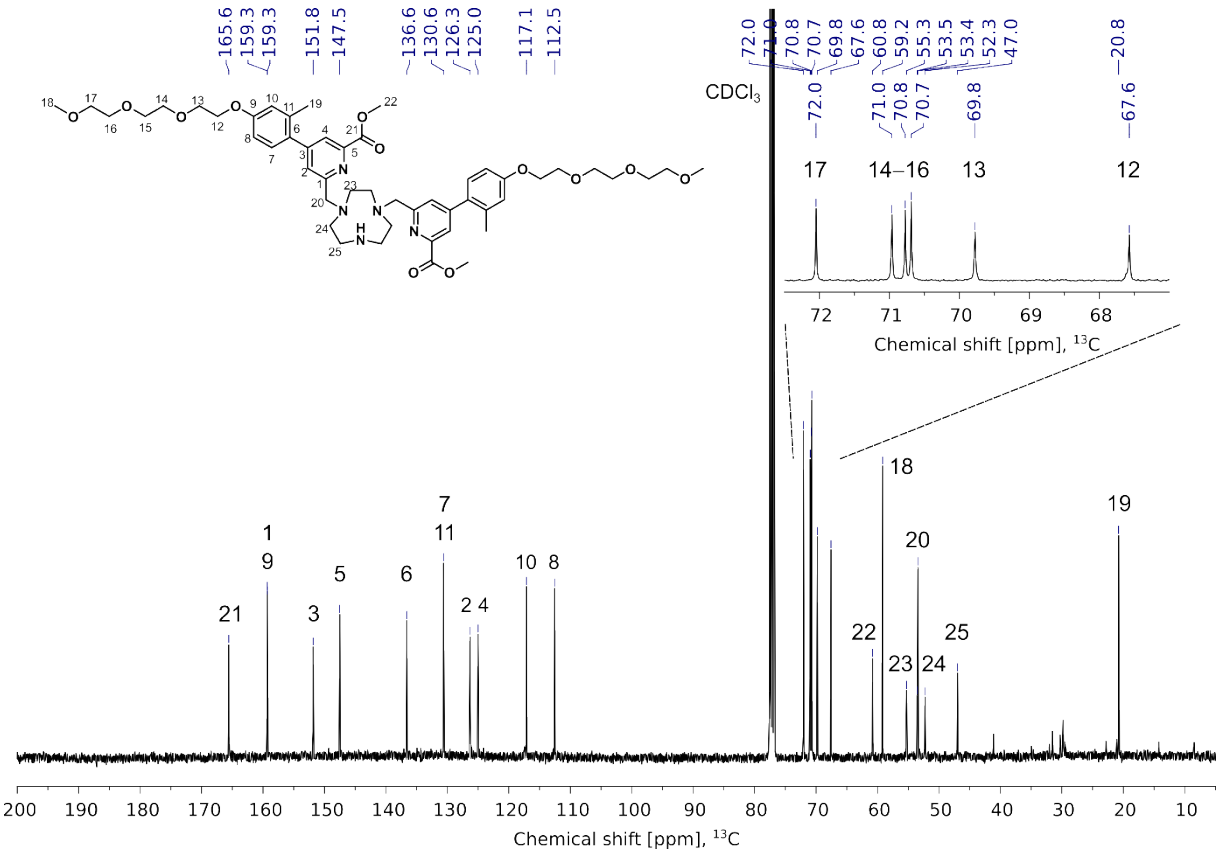


Figure S35. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **8**.

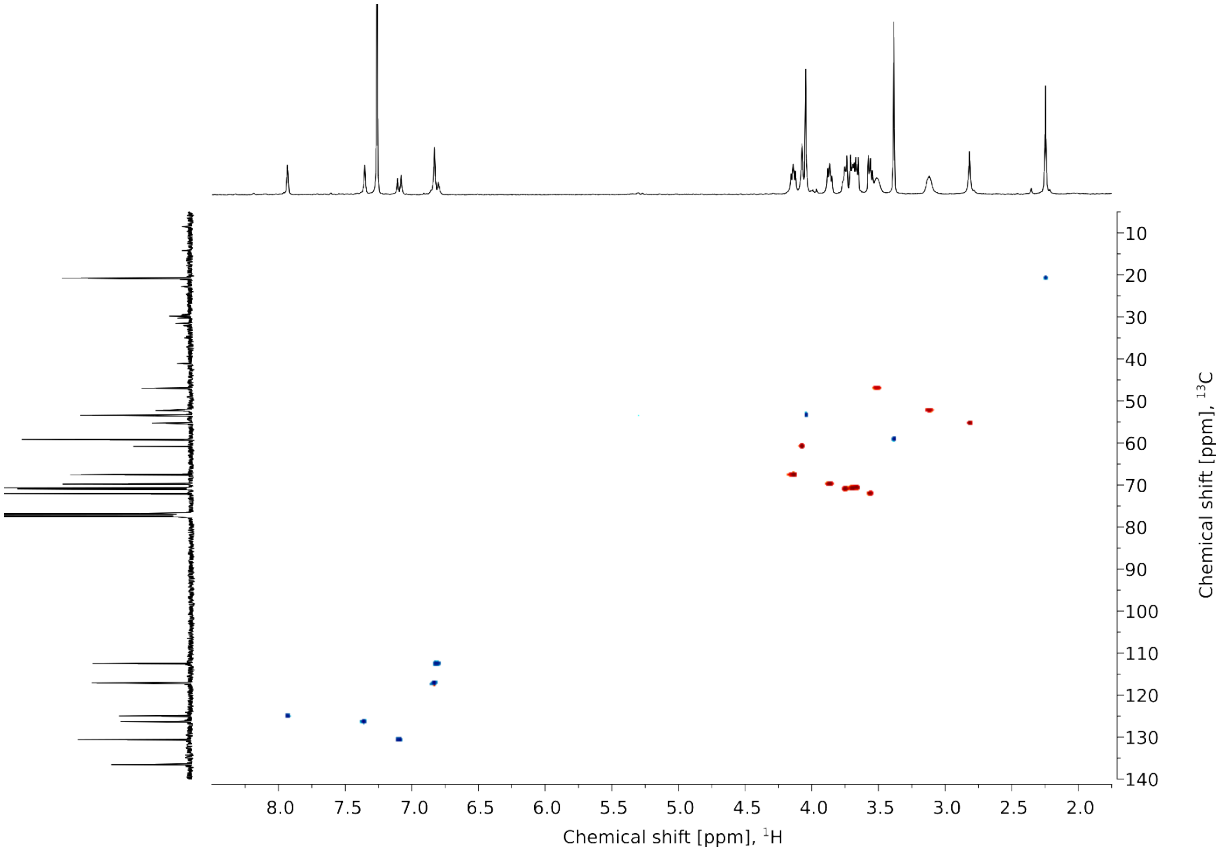


Figure S36. HSQC NMR spectrum ($CDCl_3$) of **8**.

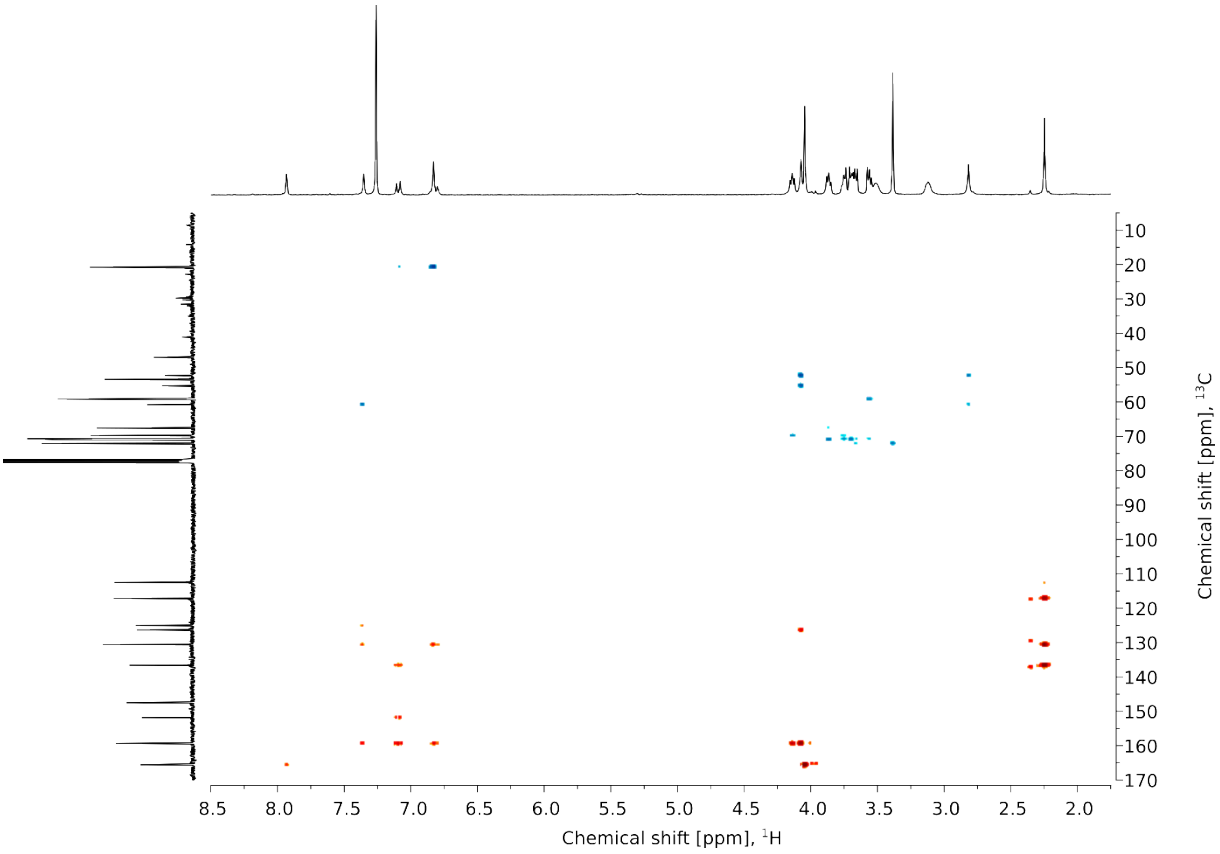


Figure S37. HMBC NMR spectrum ($CDCl_3$) of **8**.

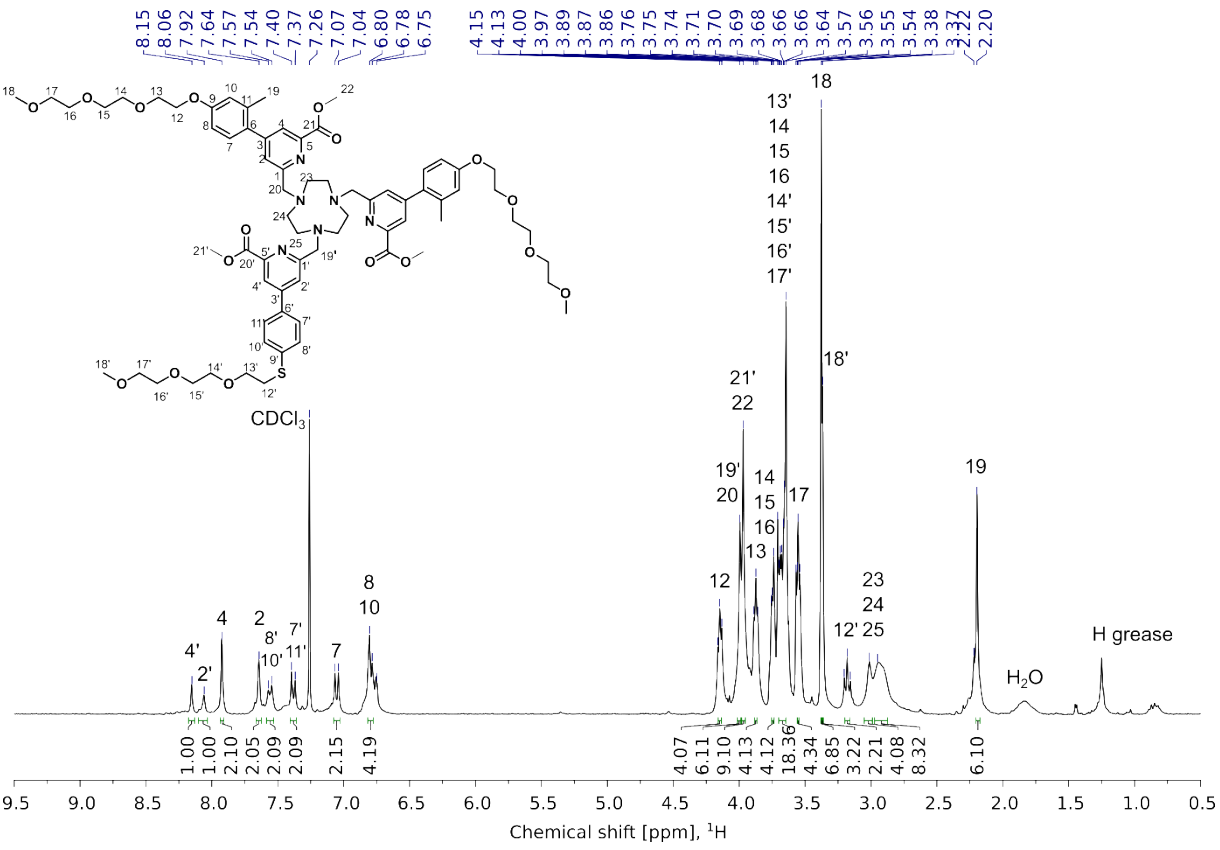


Figure S38. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $\mathbf{L_3'}$.

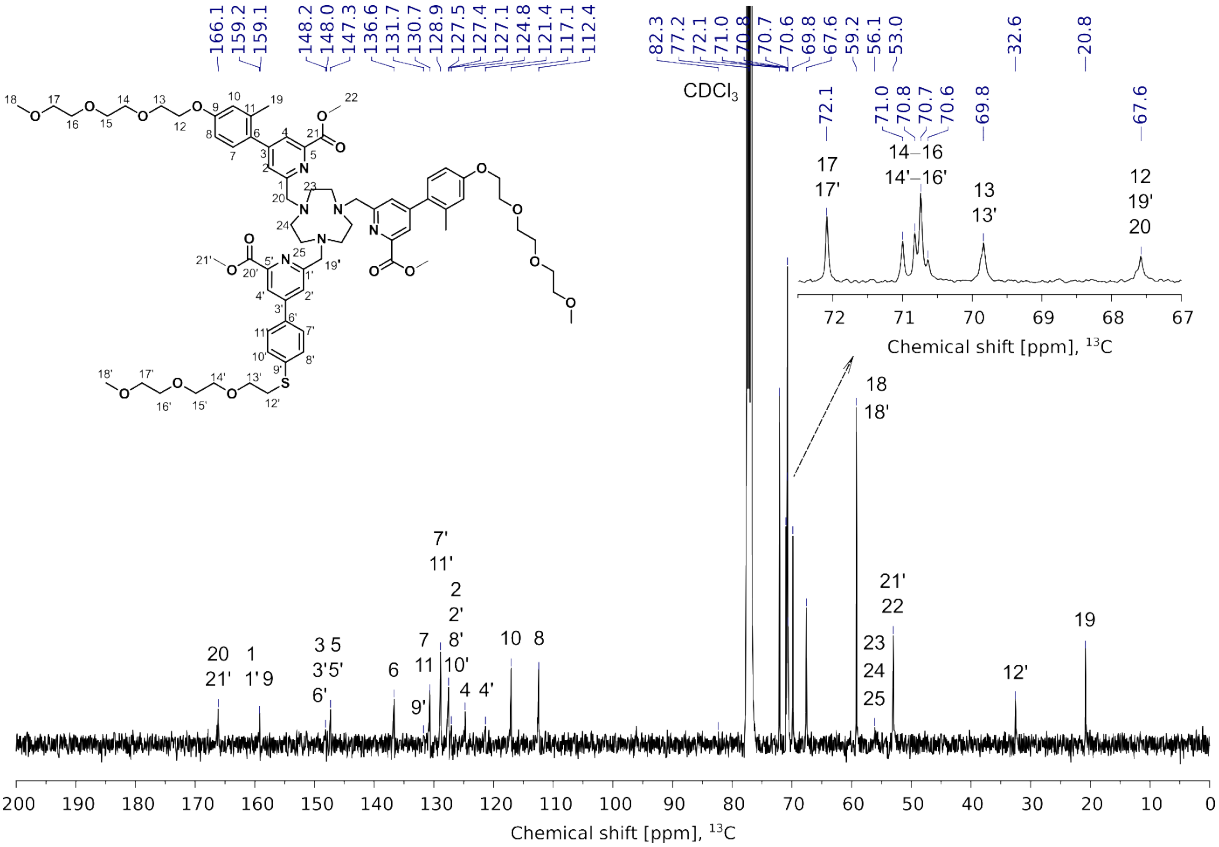


Figure S39. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **L_3'**.

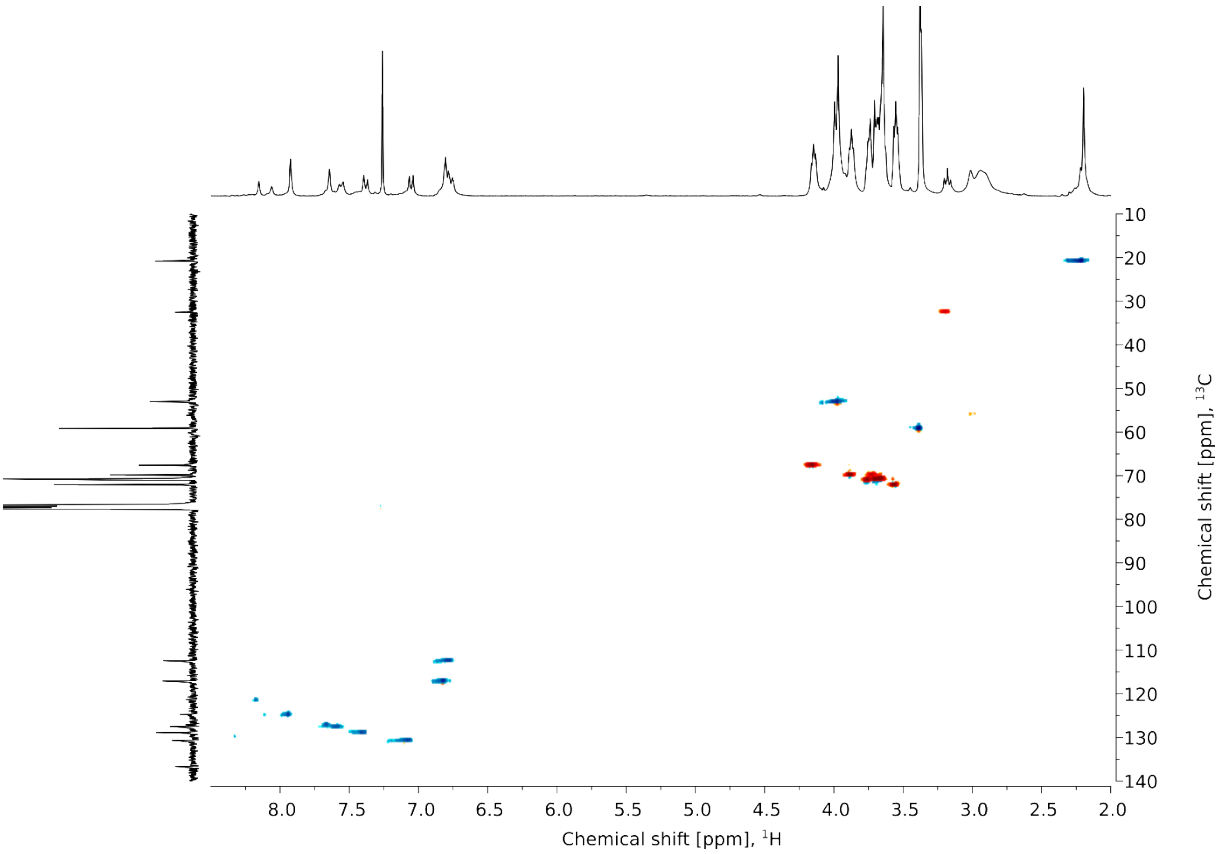


Figure S40. HSQC NMR spectrum ($CDCl_3$) of **L_3'**.

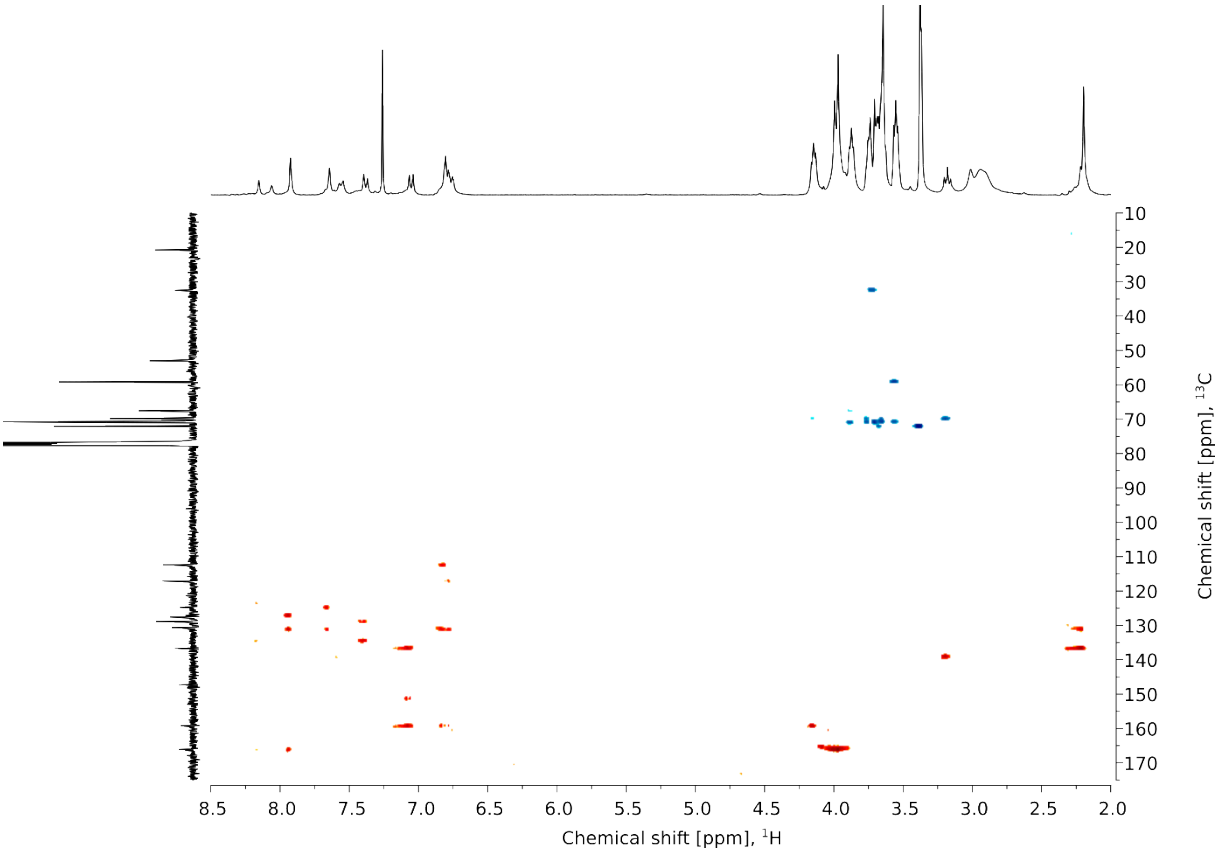


Figure S41. HMBC NMR spectrum ($CDCl_3$) of **L_3'**.

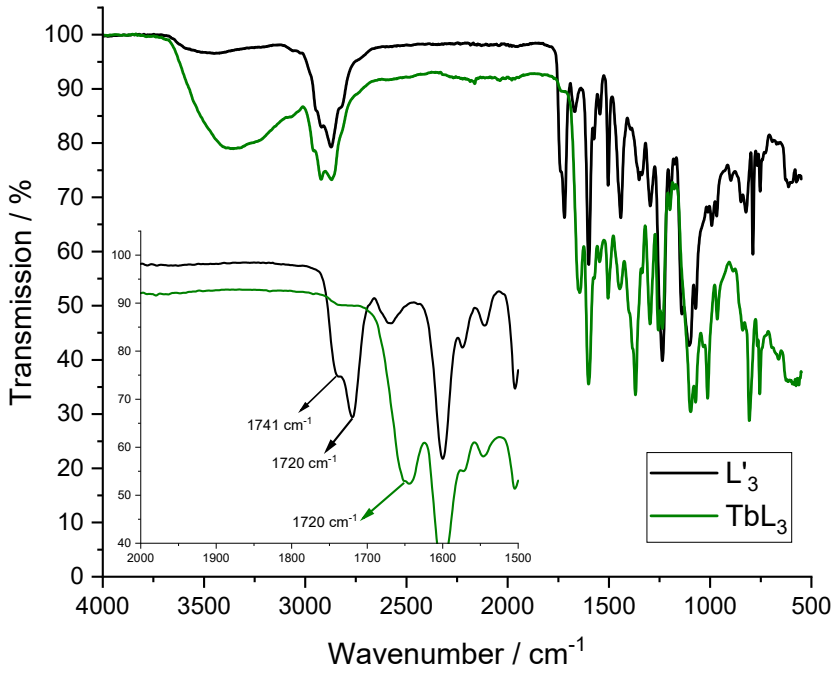


Figure S42. FTIR spectrum of **L'$_3$** and **TbL$_3$**. C=O bonds absorption peaks are indicated in the zoom for the ligand methyl ester in black and for the terbium complex in green.

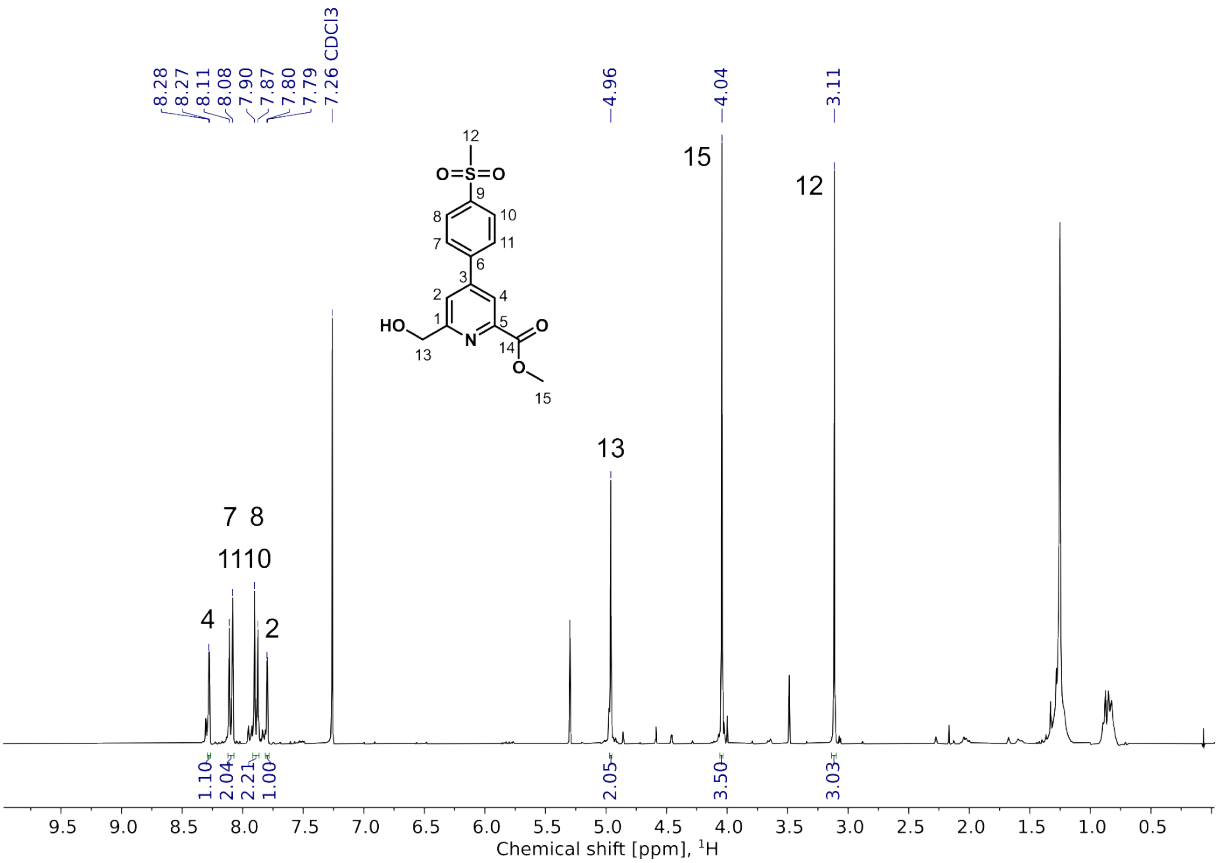


Figure S43. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of $\mathbf{A_1^{diox}}$.

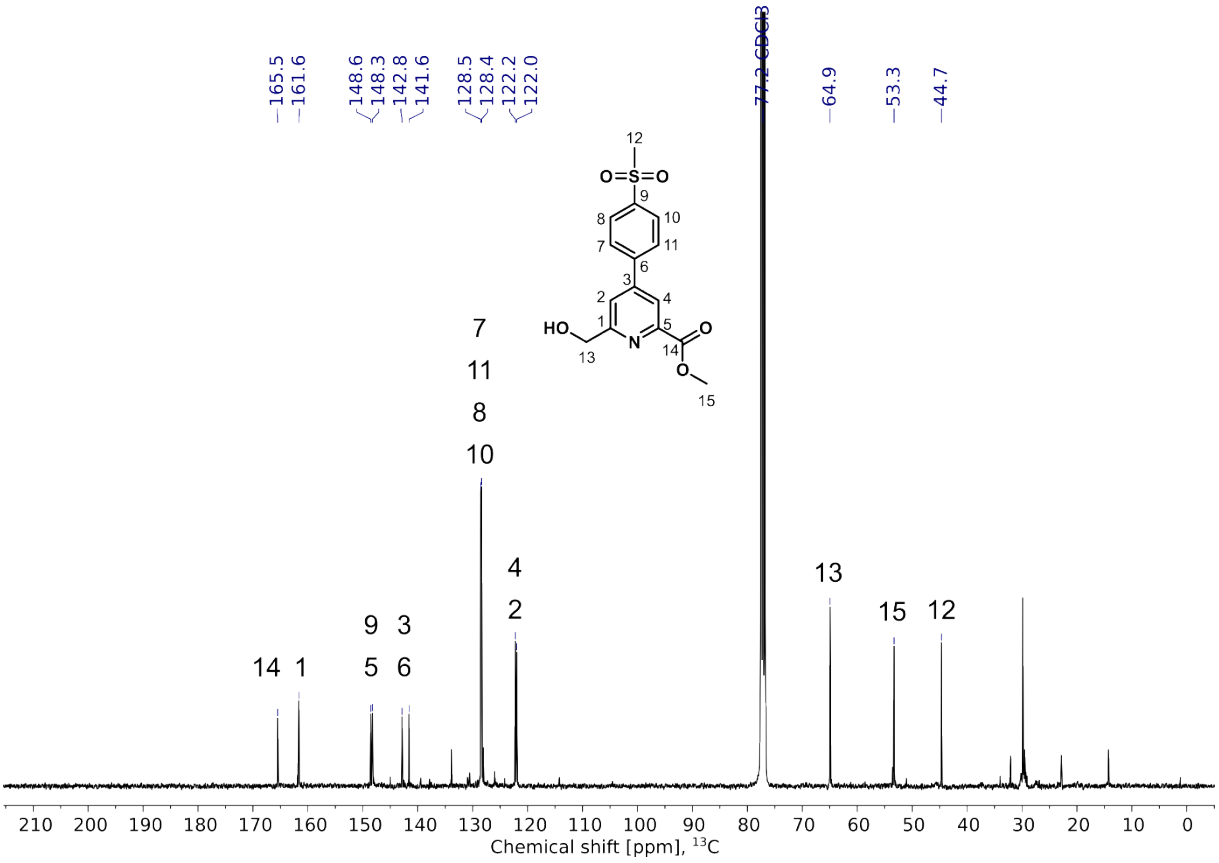


Figure S44. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of $\mathbf{A_1}^{\mathbf{diox}}$.

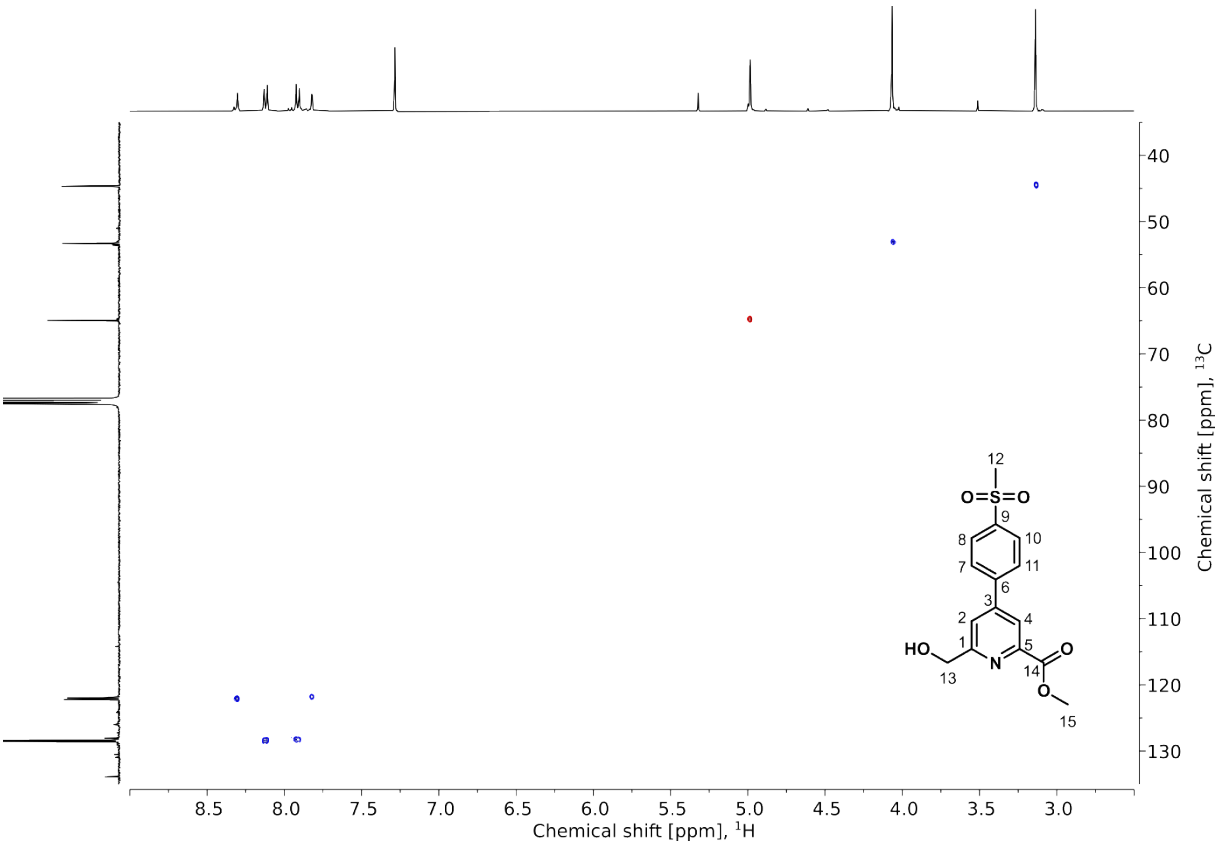


Figure S45. HSQC NMR spectrum ($CDCl_3$) of $\mathbf{A_1}^{\mathbf{diox}}$.

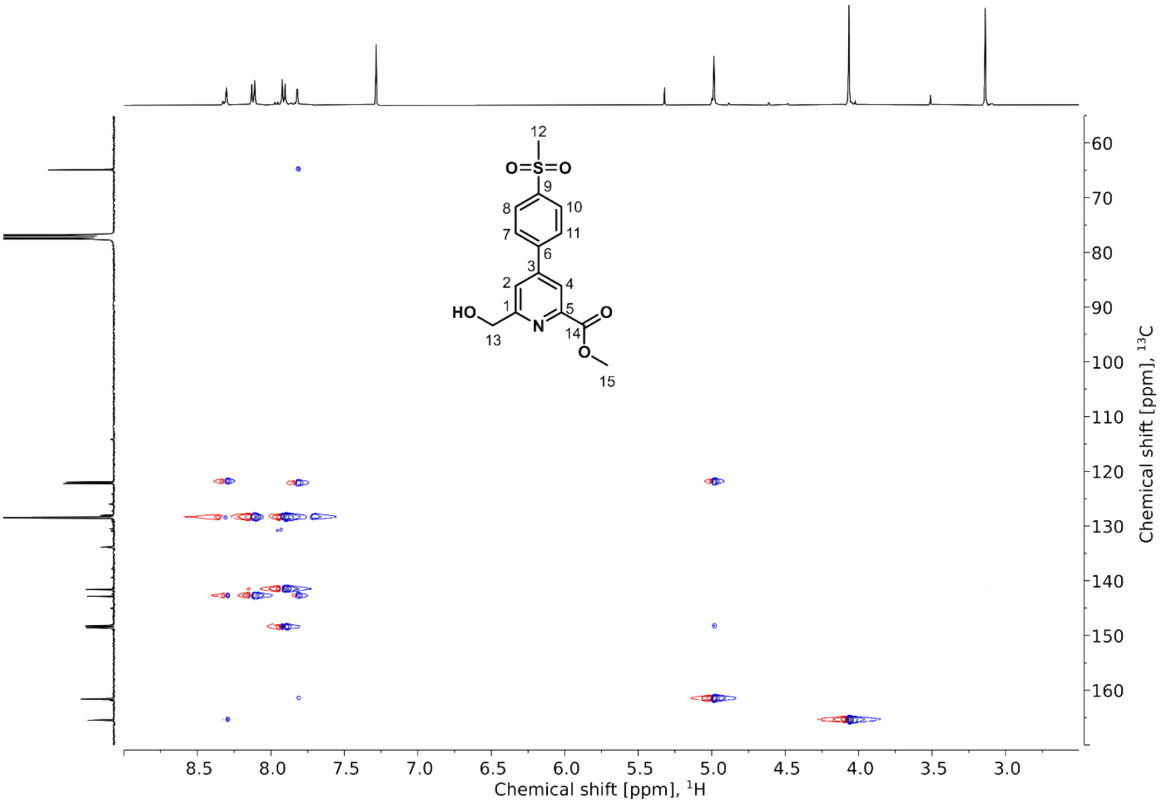


Figure S46. HMBC NMR spectrum ($CDCl_3$) of $\mathbf{A_1}^{\mathbf{diox}}$.

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