Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Smart lanthanide antennas for sensing water

Francisco Fueyo-González,[a,d] Emilio Garcia-Fernandez,[b] David Martinez,[b] Lourdes Infantes,[c] Angel Orte,[b] Juan A. González-Vera,[*a,b] and Rosario Herranz[*a]

[a]Instituto de Química Médica (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain.
[b]Departmento de Fisicoquímica, Unidad de Excelencia de Química aplicada a Biomedicina y Medioambiente, Facultad de Farmacia, Universidad de Granada, Campus Cartuja, 18071, Granada, Spain.
[c]Instituto de Química Física Rocasolano, IQFR-CSIC, Serrano 119, 28006 Madrid, Spain.
[d]Current address: Department of Medicine, Translational Transplant Research Center, Immunology Institute, Icahn School of Medicine at Mount Sinai, New York, USA.

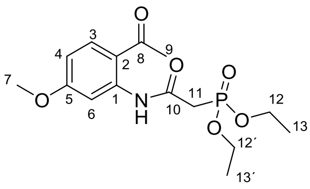
Table of Contents **PAGE**

I. General Methods

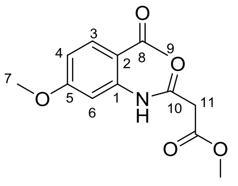
All reagents were of commercial quality. Solvents were dried and purified by standard methods. Analytical TLC was performed on aluminum sheets coated with a 0.2 mm layer of silica gel 60 F_{254}. Silica gel 60 (230-400 mesh) was used for flash chromatography. HPLC-MS was performed on a Sunfire C_{18} (4.6×50 mm, 3.5

µm) column at 30°C, with a flow rate of 1 mL/min and gradient of 0.1% of formic acid in CH_3CN (solvent A) in 0.1% of formic acid in H_2O (solvent B) was used as mobile phase. Electrospray in positive mode was used for ionization. NMR spectra were recorded using Varian Inova or Mercury 400, and Varian Unity 500 spectrometers. The NMR spectra assignments were based on COSY, HSQC, and HMBC spectra. High resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF instrument with an ESI source. MW experiments were carried out in sealed vessels in a MW Emrys^{TM} Synthesizer (Biotage AB), with transversal IR sensor for reaction temperature monitoring. UV-visible spectroscopy measurements were made at 25 ºC on a Lambda 35 Perkin Elmer UV-vis spectrophotometer. Steady-state fluorescence emission spectra were performed at 25 ºC either on a JASCO FP-8300 spectrofluorometer equipped with a 450 W xenon lamp for excitation. Lifetime experiments were acquired in a Varian Cary Eclipse Spectrofluorometer. Starna and Hellma quartz cuvettes of 1 cm path length and several volumes were employed.

II. Experimental Synthetic Methods

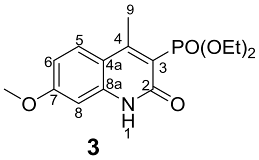


Synthesis of diethyl (2-((2-acetyl-5-methoxyphenyl)amino)-2-oxoethyl)phosphonate (6). HATU (205 mg, 0.54 mmol) and DIPEA (220 µL, 1.23 mmol) were added to a solution of 2-amino-4-methoxy-acetophenone (75 mg, 0.45 mmol) and diethyl phosphonoacetic acid (81 µL, 0.49 mmol) in dry CH_2Cl_2 (5 mL) and the solution was stirred at room temperature for 2 h. After this time the reaction was incomplete, therefore, additional HATU (102 mg, 0.27 mmol) and DIPEA (110 µL, 0.62 mmol) were added and the reaction was stirred again for 45 min. Then, the reaction mixture was evaporated to dryness and the residue was purified by flash chromatography, using a 0-5 % gradient of MeOH in CH_2Cl_2 as eluent, to give the amide **6** as a yellow syrup (124 mg, 80 %). HPLC-MS (30-95% gradient of A in B, 10 min) t_R = 3.35 min. ^{1}H-RMN [$(CD_3)_2CO$, 400 MHz)] δ: 1.18 [dt, 6 H, J = 1 and 7 Hz, CH_3(Et)], 2.49 (s, 3H, CH_3CO), 3.05 (d, 2H, J = 21 Hz, 11-H), 3.75 (s, 3H, OMe), 4.04 [m, 4H, CH_2(Et)], 6.61 (dd, 1H, J = 3 and 9 Hz, 4-H), 7.92 (d, 1H, J = 9 Hz, 3-H), 8.23 (d, 1H, J = 3 Hz, 6-H), 12.06 (s, 1H, CONH). ^{13}C-RMN [$(CD_3)_2CO$, 100 MHz] δ: 15.2 [d, J = 6 Hz, CH_3(Et)], 27.1 (CH_3CO), 37.4 (C_{11}), 54.6 (OMe), 61.9 [d, J = 6.5 Hz, CH_2(Et)], 104.1 (C_4), 107.8 (C_6), 114.9 (C_1), 134.0 (C_3), 142.4 (C_2), 163.2 (CONH), 164.0 (C_5), 200.5 ($COCH_3$). HRMS (ESI) *m/z*: Calc. for $C_{15}H_{22}NO_6P$ ($[M+H]^+$): 344.1185, Found: 344.1177.



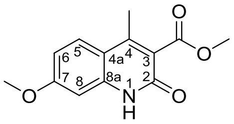
Synthesis of methyl 3-((2-acetyl-5-methoxyphenyl)amino)-3-oxopropanoate (7). Methyl 3-chloro-3-oxopropanoate (74 µL, 0.54 mmol) was added to a solution of 2-amino-4-methoxy-acetophenone (50 mg, 0.3 mmol) in dry CH_2Cl_2 (5 mL) and the solution was stirred at room temperature for 2 h. Then, the reaction mixture was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 (5 mL). The solution was successively washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4 and evaporated to dryness to give the amide **7** as yellow syrup (80 mg, 100%). HPLC-MS (30-95% gradient of A in B, 10 min) t_R = 3.54 min. ^{1}H-RMN (CD_3Cl, 400 MHz) δ: 2.54 (s, 3H, CH_3CO), 3.46 (s, 2H, 11-H), 3.74 (s, 3H, CO_2Me), 3.81 (s, 3H, OMe), 6.58 (dd, 1H, *J*= 2.5 and 9 Hz, 4-H), 7.75 (d, 1H, *J*= 9 Hz, 3-H), 8.33 (d, 1H, *J*= 2.5 Hz, 6-H), 12.35 (s, 1H, NH). ^{13}C-RMN (CD_3Cl, 100 MHz) δ: 28.3 ($\mathit{CH_3}$CO), 45.1 (C_{11}), 52.8 (CO_2Me), 55.8 (OMe), 104.5 (C_4), 110.3 (C_6), 115.7 (C_1), 133.7 (C_3), 143.2 (C_2), 164.9 (C_5 + CONH), 167.8 (CO_2Me), 201.2 (C_8). HRMS (ESI) *m/z*: Calc. for $C_{13}H_{15}NO_5$ ($[M+H]^+$): 266.1023, Found: 266.1015.

Synthesis of diethyl (7-methoxy-4-methyl-2-oxo-1,2-dihydroquinolin-3-yl)phosphonate (3). NaH (5.6 mg, 0.24 mmol) was added to a solution of the amide **6** (45 mg, 0.13 mmol) in dry DMF (3 mL) and the mixture was heated to reflux for 5 h. Then, the mixture was evaporated to dryness under reduced pressure and the residue was purified by flash chromatography, using 0-5 % gradient of MeOH in CH_2Cl_2 to give the 1,2-dihydroquinolin-2-one derivative **3** as solid (13 mg, 30 %). M.p. 195 ºC (EtOH). HPLC-MS (30-95% gradient of A in B, 10 min) t_R = 2.08 min. ^{1}H-RMN (DMSO-d_6, 500 MHz) δ: 1.08 [t, 6H, *J* = 7 Hz, CH_3 (Et)], 2.37 (s, 2H, 4-CH_3), 3.63 [m, 4H, CH_2 (Et)], 3.80 (s, 3H, OMe), 6.82 (m, 2H, 6- and 8-H), 7.61 (d, 1H, *J* = 9 Hz, 5-H) ^{13}C-RMN (DMSO-d_6, 125 MHz) δ: 16.7 [d, *J* = 6.5 Hz, CH_3(Et)], 18.5 (4-CH_3), 55.3 (OMe), 59.1 [d, J = 5.5 Hz, CH_2 (Et)], 98.3 (C_8), 110.3 (C_6), 113.8 (C_3), 117.9 (C_{4a}), 126.2 (C_5), 140.4 (C_{8a}), 147.9 (C_4), 160.9 (C_7), 166.3 (C_2). HRMS (ESI) *m/z*: Calc. for $C_{15}H_{20}NO_5P$ ($[M+H]^+$): 326.1151, Found: 326.1135.



3

Synthesis of methyl 7-methoxy-4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (4). K_2CO_3 (47 mg, 0.33 mmol) was added to a solution of the carboxamide **7** (60 mg, 0.22 mmol) in MeOH (8 mL) and the mixture was heated at 70 ºC by MW irradiation for 30 min. Then, the reaction mixture was cooled at room temperature and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (50 mL) and the solution was successively washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4 and evaporated to dryness, to give the desired 2-oxo-1,2-dihydroquinoline-3-carboxylate **4** as a beige solid (56 mg, 100 %). M. p. 188 ºC (EtOH). HPLC-MS (30-95% gradient of A in B, 10 min) t_R = 2.42 min. ^{1}H-RMN [$(CD_3)_2CO$, 400 MHz] δ: 2.27 (s, 3H, 4-Me), 3.71 (s, 3H, CO_2Me), 3.76 (s, 3H, OMe), 6.74 (d, 1H, *J* = 9 Hz, 6-H), 6.86 (s, 1H, 8-H), 7.62 (d, 1H, *J* = 9 Hz, 5-H). ^{13}C-RMN [$(CD_3)_2CO$, 100 MHz] δ: 14.9 (4-Me), 50.9 (CO_2*Me*), 54.6 (OMe), 97.8 (C_8), 110.6 (C_6), 112.6 (C_{4a}), 123.8 (C_3), 126.5 (C_5), 140.0(C_{8a}), 144.4 (C_4), 158.6 (C_2), 161.8 (C_7), 166.4 (CO_2). HRMS (ESI) *m/z*: Calc. for $C_{13}H_{13}NO_4$ ($[M+H]^+$): 248.0917, Found: 248.0917.



III. Spectroscopy Methods

a. Photophysical properties

Excitation and emission spectra of compounds were determined for 12 µM solutions in solvents of diverse polarity. The spectra were recorded between 300 and 690 nm (0.5 nm increments and 0.1 s integration time) with excitation set at the appropriate excitation wavelength. Slit widths were set to5 nm for excitation and to 5 nm for emission, depending on the observed emission intensity. All the spectra were corrected for background fluorescence by subtracting a blank scan of the solvent solution.

Fluorescence quantum yield determination. Fluorescence quantum yields (Φ) of quinolin-2(1*H*)-one derivatives **1-4** were determined in solvents of different polarity, and calculated using Quinine sulfate dihydrate (in 0.1M H_2SO_4) as reference.[1] Concentration of the sample and the reference was set to assure that the absorbance was less than 0.1 at identical excitation wavelengths. The following equation was used to calculate the quantum yield:

$$\Phi = \frac{I_x A_r n^2{}_x \Phi_r}{A_x I_r n^2{}_r} \qquad \text{(S1)}$$

where x and r denote the sample and standard, respectively, A is the absorption at the excitation wavelength, I is the integrated fluorescence intensity, and n is the refractive index of the solvent.

Fluorescence quantum yields of (Φ) of lanthanide complexes of **1-4** were measured with an integrating sphere on a UV-VIS-NIR Horiba QuantaMaster-8000 (QM-8000) spectrofluorometer.

Fluorescence lifetimes determination. Lifetime experiments lanthanide complexes of **1-4** were acquired in a Varian Cary Eclipse Spectrofluorometer at room temperature using the following conditions: excitation wavelength 320 nm; emission wavelength 545 nm for terbium or 615 nm for europium; excitation slit width 5.0 nm, emission slit width 5.0 nm; total decay time 15.0 ms; delay time 0.1 ms; gate time 0.2 ms; number of cycles 20; PMT detector voltage 600 V.

---

[1] (a) Wuerth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Nat. Protoc.*, **2013**, *8*, 1535-1550 (b) Brouwer, A. M. *Pure Appl. Chem.*, **2011**, *83*, 2213-2228; (c) Rurack, K.; Spieles. M. *Anal. Chem.*, **2011**, *83*, 1232-1242.

Table S1. Photophysical properties of quinolin-2(1*H*)-one derivatives **1**-**4**

Compd[a]	Solvent	λ_{max}^{abs} (nm)	ε ($M^{-1}cm^{-1}$)[b]	λ_{max}^{em} (nm) [c]	Φ_F[d]
1	Toluene	313, 354	3541	421	0.071
	Dioxane	312, 356	3544	421	0.044
	CH_3CN	312, 355	2896	435	0.098
	MeOH	313, 365	3992	440	0.138
	H_2O	313, 354	4168	460	0.403
2	Toluene	308, 361	3727	435	0.059
	Dioxane	308, 359	3723	437	0.043
	CH_3CN	310, 357	2989	458	0.111
	MeOH	310, 356	4849	464	0.095
	H_2O	312, 357	4564	485	0.344
3	Toluene	328, 343	4119	366	0.079
	Dioxane	328, 343	3085	366	0.070
	CH_3CN	326, 340	3394	365	0.120
	MeOH	325, 338	4713	359	0.143
	H_2O	322, 336	5115	358	0.189
4	Toluene	334, 347	3668	408	0.093
	Dioxane	332, 346	3876	408	0.056
	CH_3CN	332, 344	4236	409	0.058
	MeOH	330, 342	4302	415	0.102
	H_2O	330, 342	4334	415	0.115

[a] Measured in duplicate at a 12 μM concentration. [b] For the lower λ_{max}^{abs}. [c] Excited at 320 nm. [d] Calculated with reference to quinine sulfate (in 0.1M H_2SO_4).

b. Lanthanide luminescence sensitization studies Figures S1-S8

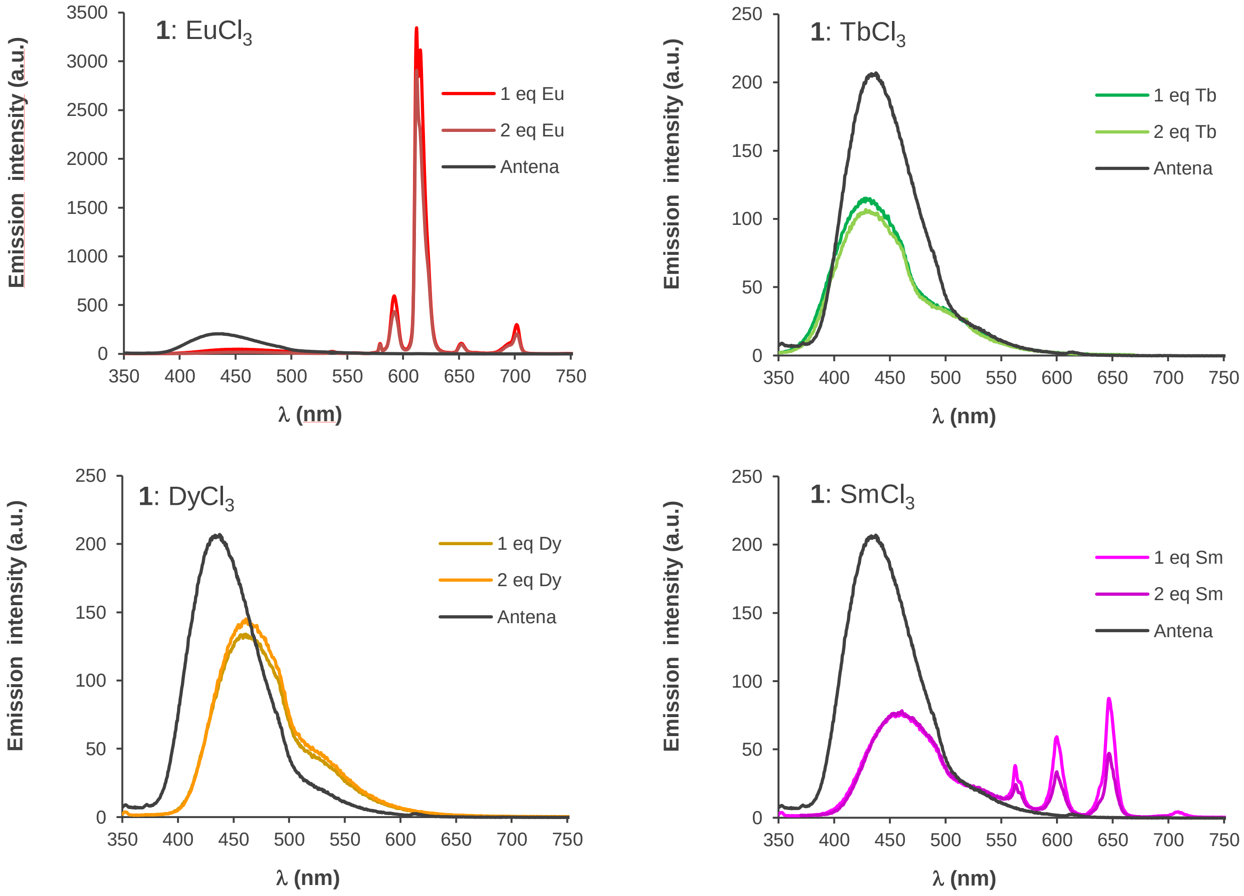


Figure S1. Emission spectra of **1** (54 µM in CH_3CN) and after addition of 1 and 2 equivalents of $EuCl_3$, $TbCl_3$, $DyCl_3$ and $SmCl_3$.

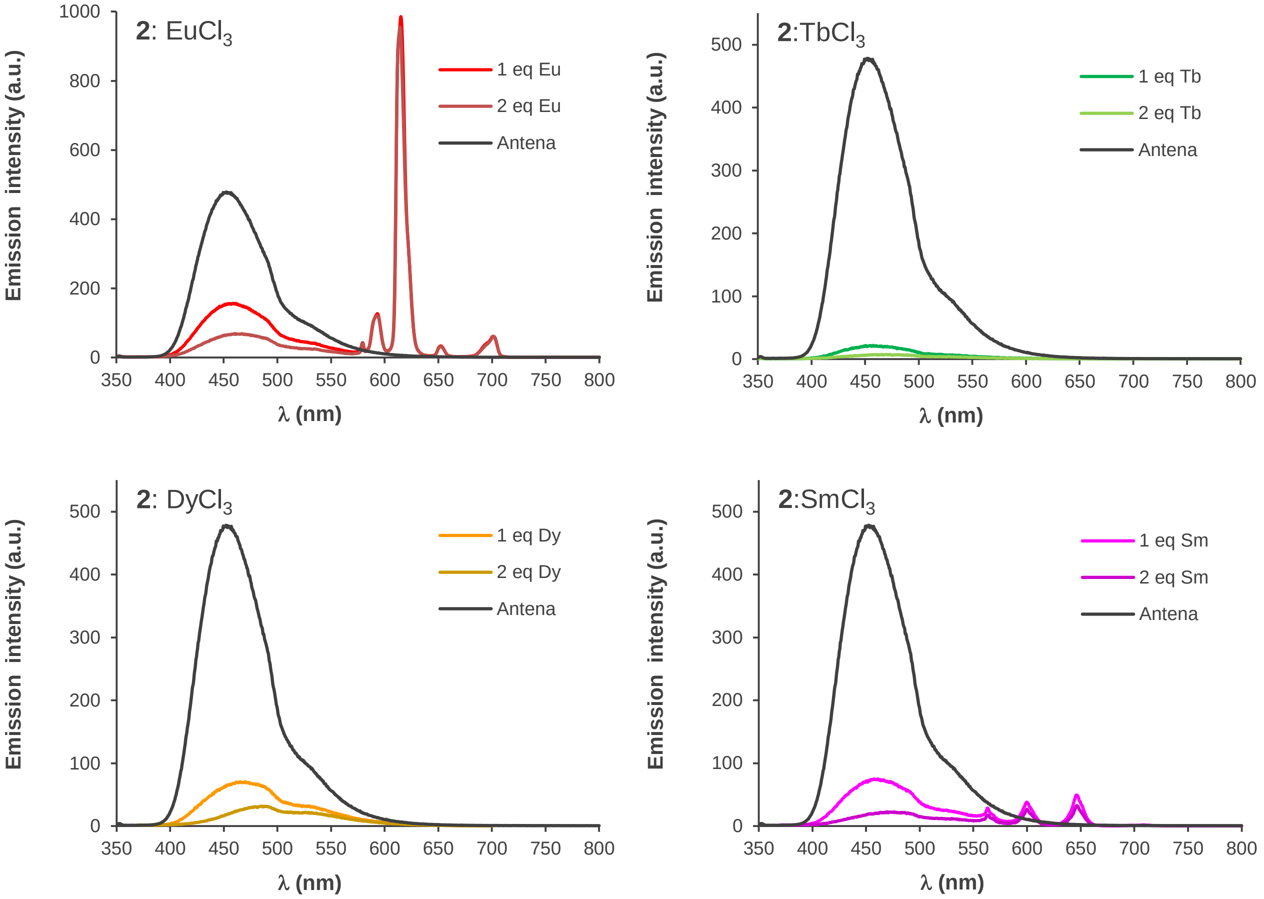


Figure S2. Emission spectra of **2** (54 μM in CH_3CN) and after addition of 1 and 2 equivalents of $EuCl_3$, $TbCl_3$, $DyCl_3$ and $SmCl_3$.

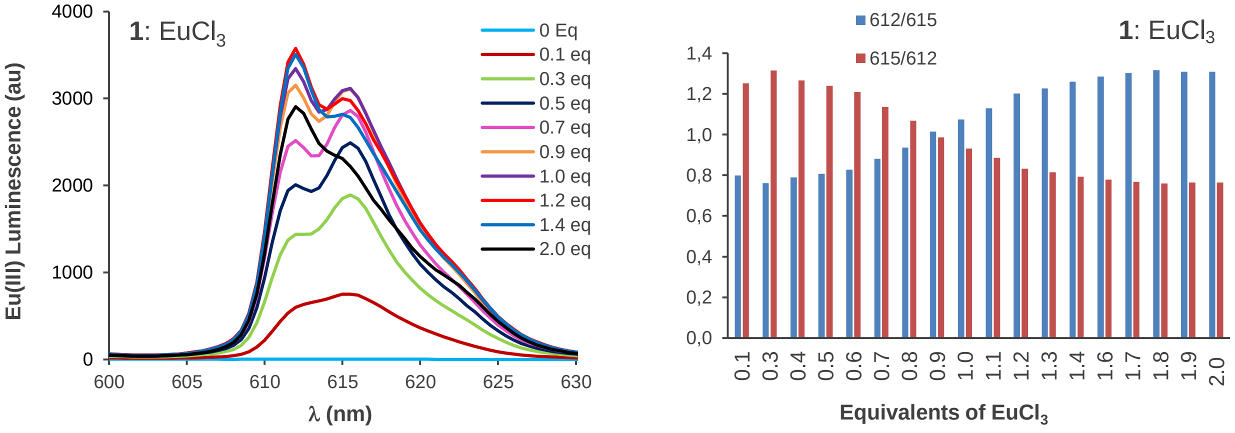


Figure S3. Expansion of the Eu(III) $^5D_0 \rightarrow ^7F_2$ band in the titration spectra of **1** (54 μM) in CH_3CN with increasing equivalents of $EuCl_3$ and the respective I_{612}/I_{615} and I_{615}/I_{616} ratios.

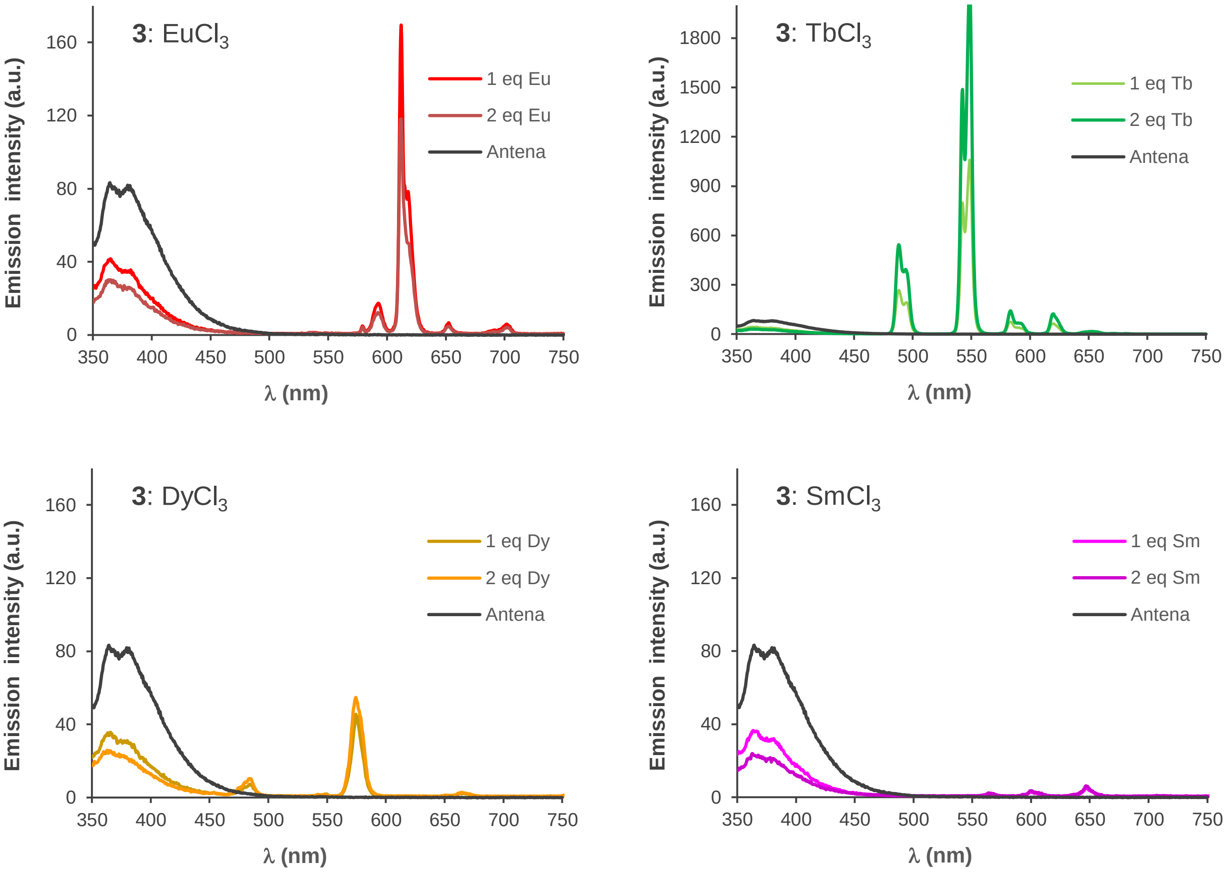


Figure S4. Emission spectra of **3** (54 μM in CH_3CN) and after addition of 1 and 2 equivalents of $EuCl_3$, $TbCl_3$, $DyCl_3$ and $SmCl_3$.

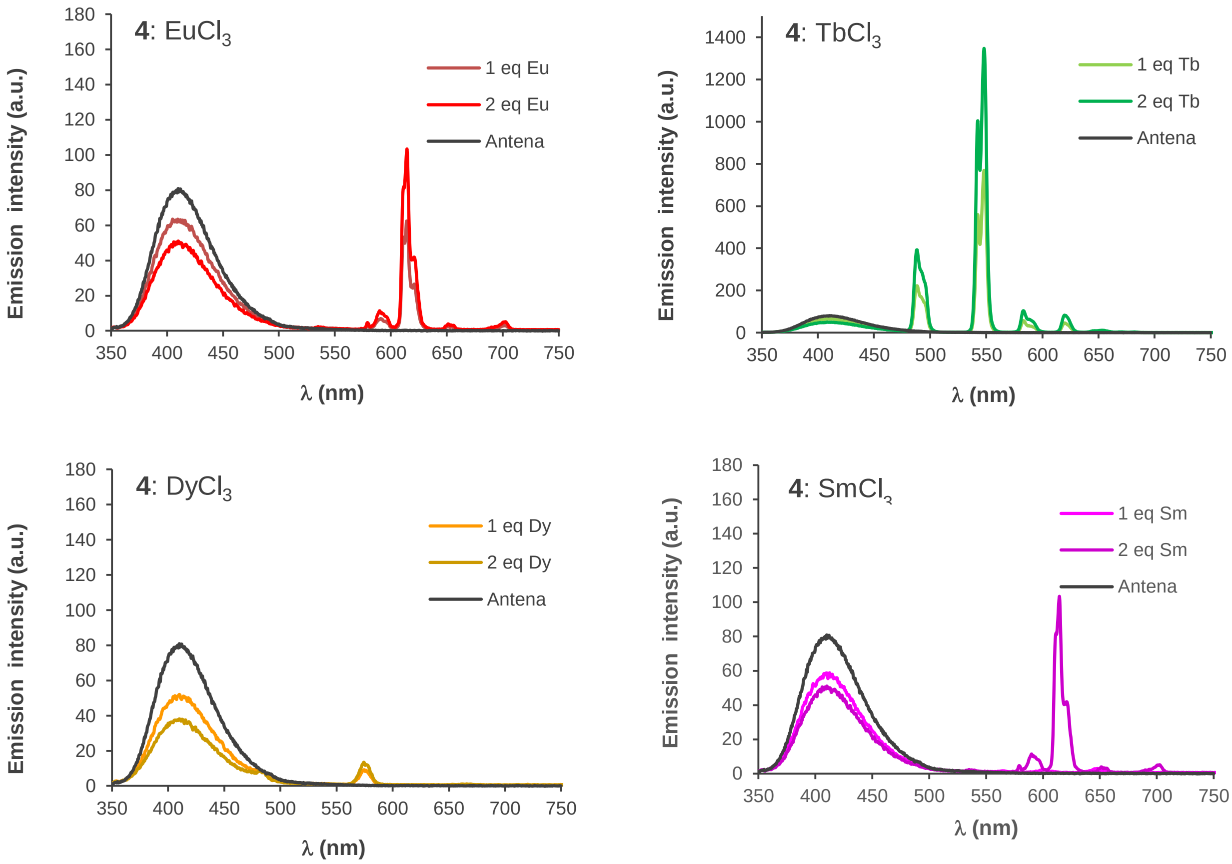


Figure S5 Emission spectra of **4** (54 μM in CH_3CN) and after addition of 1 and 2 equivalents of $EuCl_3$, $TbCl_3$, $DyCl_3$ and $SmCl_3$.

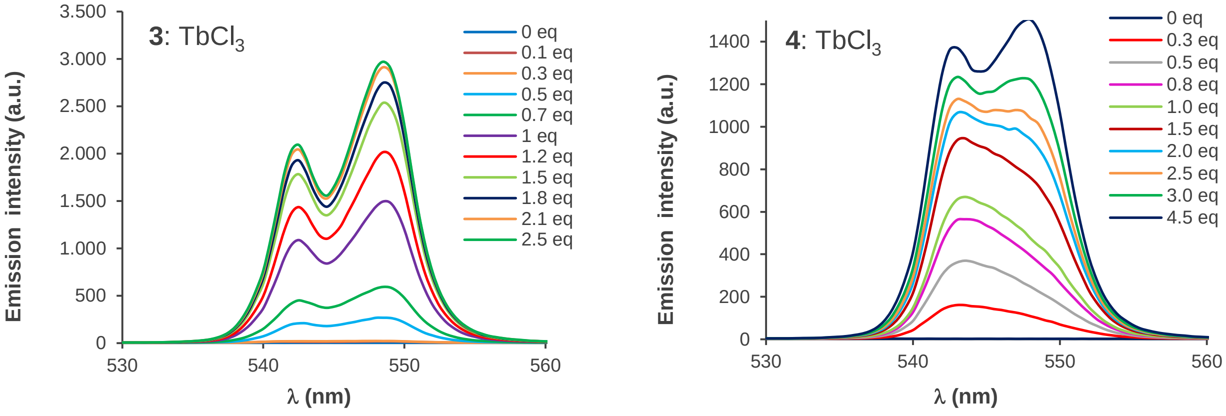


Figure S6. Expansion of the $^5D_4 \rightarrow ^7F_5$ band of Tb(III) in the emission spectra of the titration of **3** and **4** with $TbCl_3$.

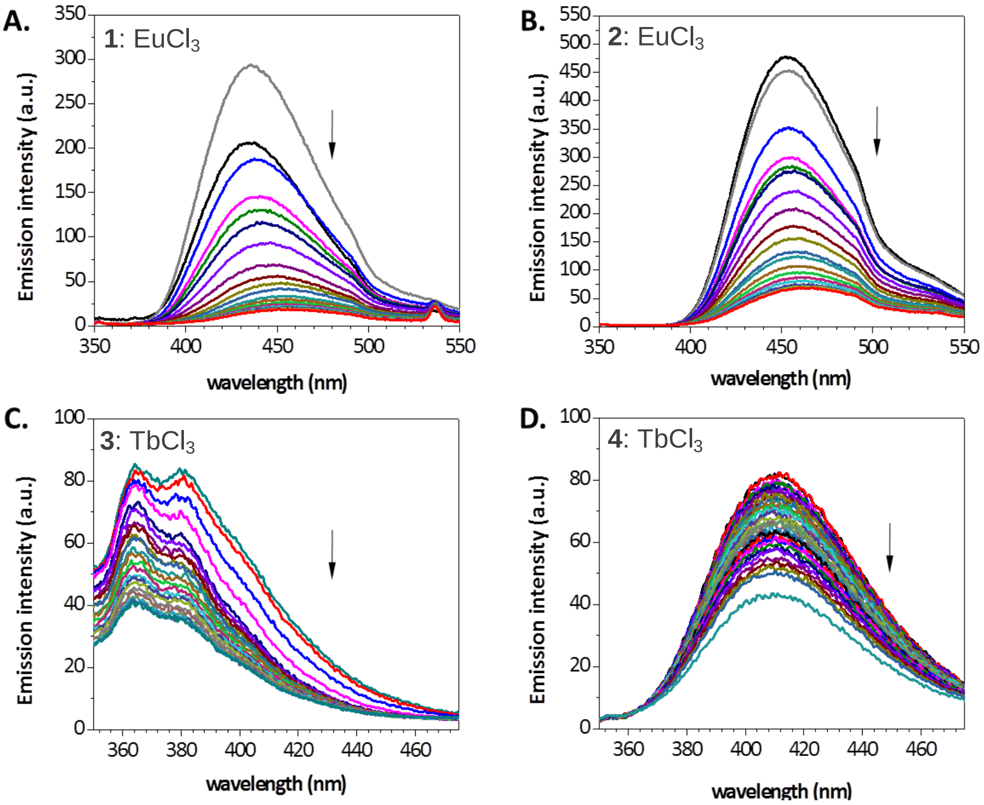


Figure S7. Titration spectra of solutions (54 µM in CH_3CN) of the 8-methoxy-4,5-dihydrocyclopenta[*de*]quinolin-2(1*H*)-ones **1** (A) and **2** (B) with increasing equivalents (0-2) of $EuCl_3$, and solutions (54 µM in CH_3CN) of the carbostyril analogues **3** (C) and **4** (D) with increasing equivalents (0-4) of $TbCl_3$, showing the quenching in the fluorescence of the antenna.

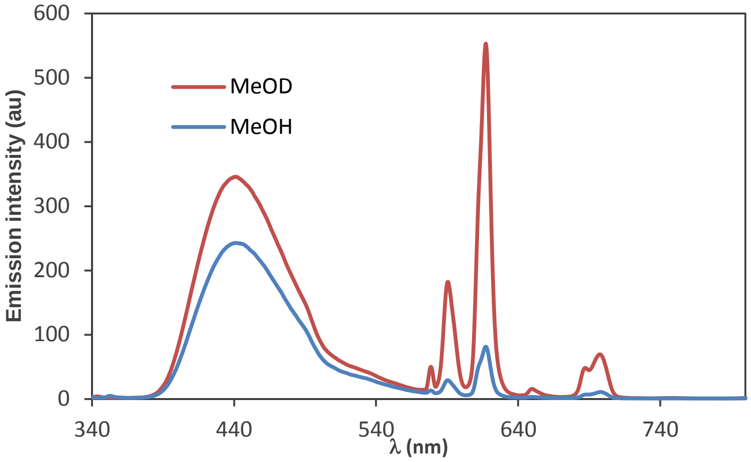


Figure S8. Emission spectra of the complex **Eu^{3+}(1)$_2$Cl$_3$** (50 μM) in MeOH and MeOD.

c. Determination of the number of Eu^{3+}-coordinated methanol molecules for Eu^{3+}(1)$_2$$Cl_3$

Luminescence decay lifetimes (τ) for **Eu^{3+}(1)$_2$**Cl_3 (50 μM) were obtained (λ_{ex} = 320 nm) and the resultant decay curves were fit to monoexponential decay function using the standard curve fitting algorithm of the instrument software to yield lifetime values for the sample with different amounts of MeOH and MeOD. Linear regression of acquired lifetimes allowed to to obtain extrapolated values for the lifetimes in pure MeOH and MeOD (Fig. S8). The number of methanol solvent molecules bound to the central metal, *q*, in the complex **Eu^{3+}(1)$_2$**Cl_3 was calculated from Horrocks and co-workers[2] equation. In this equation, τ^{-1} is the reciprocal lifetime value of either MeOH or MeOD, *A* is an empirical constant (*A* = 2.1 for europium) and *q* has the meaning abovementioned.

$$q = A(\tau_{MeOH}^{-1} - \tau_{MeOD}^{-1}) \qquad \text{(S2)}$$

---

[2] (a) Holz, R. C.; Chang, C. A.: Horrocks, W. D. *Inorg. Chem.*, **1991**, *30*, 3270-3275. (b) Horrocks, W. D.; Sudnick, D. R. *Acc. Chem. Res.*, **1981**, *14*, 384-392.

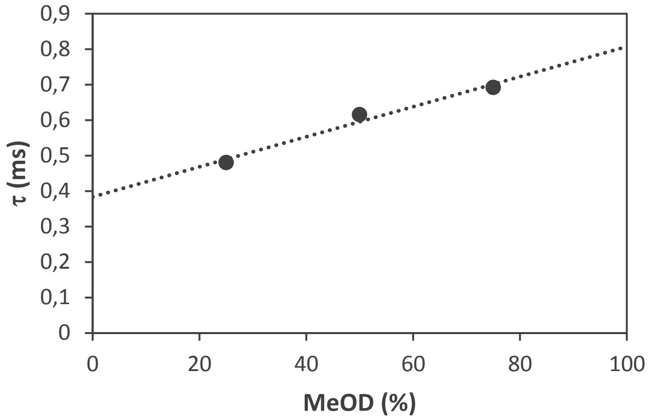


Figure S9. Representative plot of three luminescence decay lifetime measurements of MeOH/MeOD solutions of the complex **Eu^{3+}(1)$_2$**Cl_3 (50 μM) employed to determine the number of bound methanol solvent molecules.

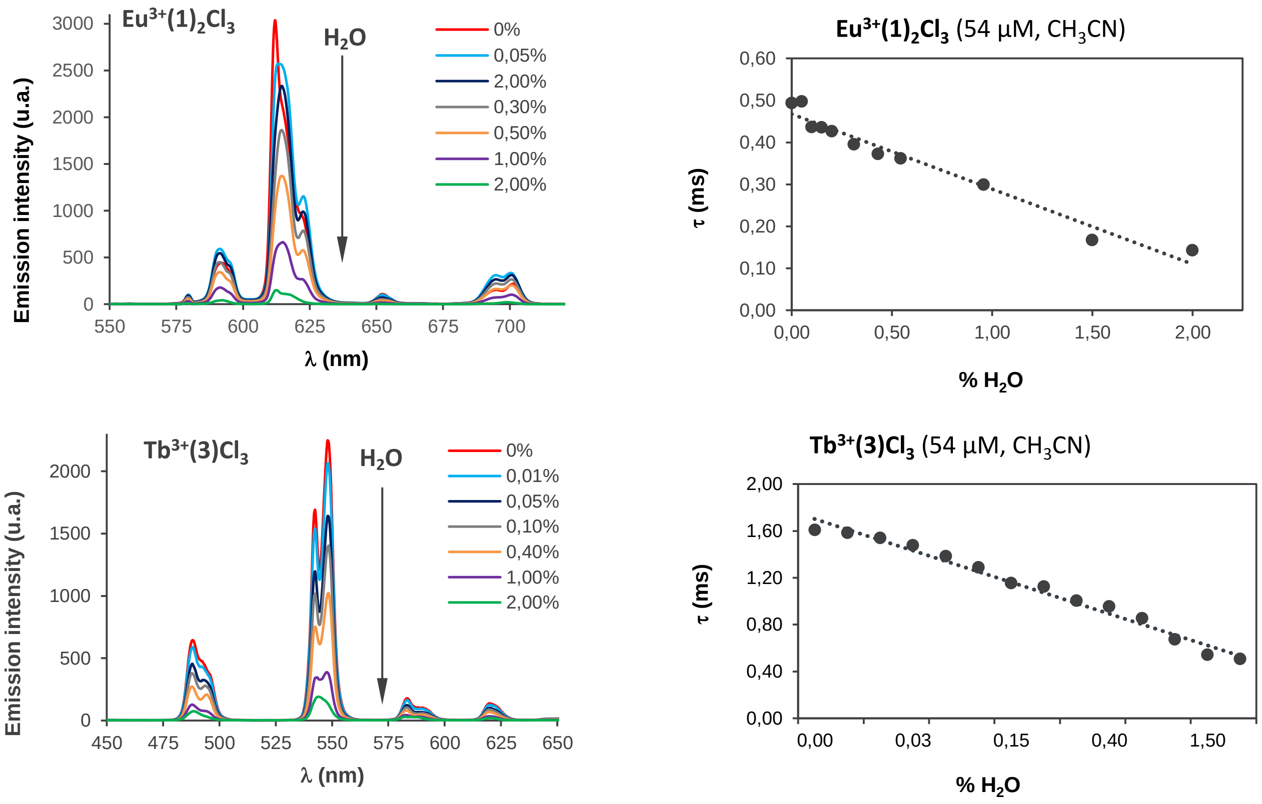


Figure S10. Variations in the emission spectra of the **Eu(1)$_2$Cl$_3$** and **Tb (3)Cl$_3$** complexes by increasing H_2O content and their respective lifetimes.

IV. Binding model and fitting parameters

The titration curves of compounds **1-3** with lanthanides ions (Figures 2E and 2F) were satisfactorily fitted to a binding model that takes into account the possibility of single or multiple binding events for each antenna, as described elsewhere[3]:

$$F = F_{max} \cdot \left\{ \frac{1 + K \cdot \frac{[A]_T}{n_A} + K \cdot [Ln]_T - \sqrt{\left(1 + K \cdot \frac{[A]_T}{n_A} + K \cdot [Ln]_T\right)^2 - 4 \cdot K^2 \cdot \frac{[A]_T}{n_A} \cdot [Ln]_T}}{2 \cdot K} \right\} \qquad \text{(S3)}$$

where F and F_{max} accounts, respectively, for current and maximum luminescence intensity at lanthanide emission wavelength, either 616 nm or 545 nm; K, the apparent binding constant of the antenna-lanthanide complex; $[A]_T$, the total concentration of antenna (54.4 µM); n_A, the number of antenna molecules in the complex; $[Ln]_T$, the total concentration of lanthanide.

Taking into account equation (S3), the following fitting parameters were retrieved, Table S2:

Table S2. Fitting parameters for the titrations of compounds **1-4** to equation S3.

Ln Complex	**K (M^{-n})**	**n_A**	**n_L (1) (2)**	**F_{max}**	**r (3)**
(1)-Eu	$(1.1 \pm 0.8)\times10^6$	1.42 ± 0.07	0.70	$(2.6 \pm 0.2)\times10^4$	0.9934
(2)-Eu	$(3 \pm 2)\times10^6$	1.39 ± 0.04	0.72	$(2.45 \pm 0.08)\times10^4$	0.9953
(3)-Tb	$(2.3 \pm 0.4)\times10^5$	1.0 ± 0.2	1.0	$(1.90 \pm 0.05)\times10^4$	0.9949
(4)-Tb	$(2.8 \pm 0.9)\times10^4$	0.7 ± 0.9	1.43	$(1.4 \pm 0.2)\times10^4$	0.9965

(1) Derived parameters from fitting parameters; (2) Coordination number of lanthanides per antenna molecule; (3) non-linear regression fitting parameter.

However, for the antenna **3** it is necessary to consider a cooperative model derived from the Hill equation[4] for taking into account the initial lag, probably due to the action of a positive cooperative association, according to the following equation:

---

[3] Hahn, L.; Buurma, N. J.; Gade, L. H.; *Chem. Eur. J.*, **2016**, *22*, 6314-6322.

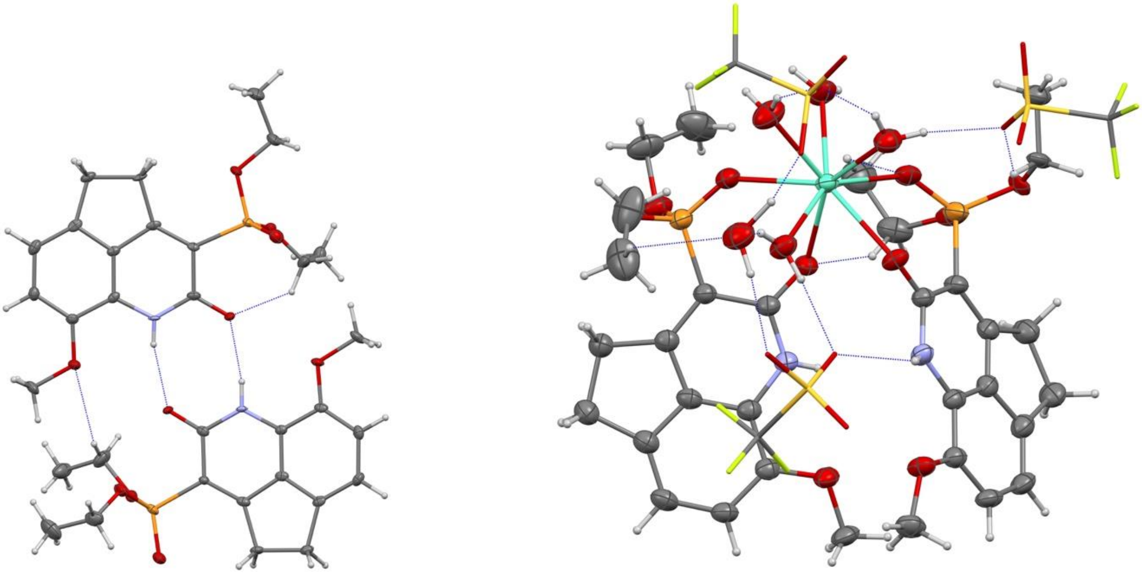
[4] Abeliovich, H. *Biophys. J.* **2005**, *89*, 76-79.

$$\frac{F}{F_{max}} = \frac{[Ln]_T^n}{K_d^n + [Ln]_T^n} \tag{S4}$$

where F and F_{max} accounts, respectively, for current and maximum luminescence intensity at the lanthanide emission wavelength; K_d, the apparent dissociation constant (K_d=1/K) of the antenna-lanthanide complex; n, is the cooperativity factor; $[Ln]_T$, the total concentration of lanthanide. The fitting shown in Figure 2F resulted on a highly positive cooperativity (n = 3.8) and a binding constant K (= 1/ K_d) of 1.9 ×10^4 M^{-n}, two orders of magnitude lower than those of complexes of antennas **1** and **2** with Eu(III).

V. X-Ray Diffraction

X-ray Diffraction data were collected at 100K using the ALBA Synchrotron Radiation Source (BL13 Beamline) for the compounds **1**, Eu(**1**)$_2$(H$_2$O)$_4$ and Eu(**2**)$_2$(H$_2$O)$_4$OTf; and at 120K on a diffractometer using CuKα source for compound **2**, Figure S9and S10. The structures were solved by Patterson method using SIR2014 (compound **1**)[5] and SHELXS (for complexes Eu(**1**)$_2$(H$_2$O)$_4$ and Eu(**2**)$_2$(H$_2$O)$_4$OTf)[6] and by direct methods using SHELXS for compound **2**[4]. All of them were refined with the ShelXL refinement package using Least Squares minimization. Crystal structure of **1** presents two independent molecules that differ mainly in the conformation of the phosphoryl group and a disordered model was observed in one of the ethyl substituents. Compound Eu(**2**)$_2$(H$_2$O)$_4$OTf also presents disorder in three of the four independent ethoxy groups and in one trifluoromethanesulfonate ion.



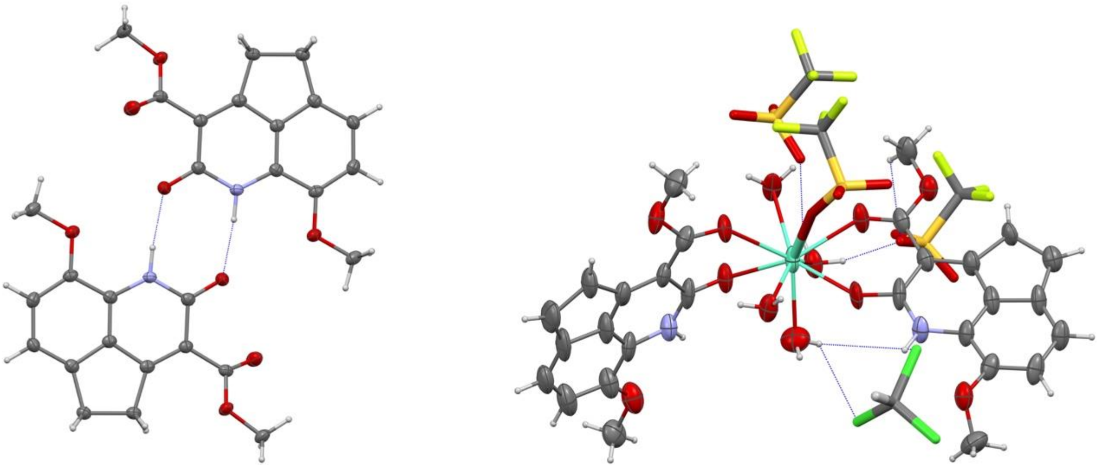
1 Eu(**1**)$_2$(H$_2$O)$_4$

Figure S11. Molecular structure determined by X-ray diffraction of compounds **1** and its europium complexes. Thermal ellipsoids have been set at 50% probability for non-hydrogen atoms. Disordered models observed in compound **1** have been omitted and, the trifluoromethanesulfonate ions and the chloroform molecules have been represented by capped and sticks, for clarity purpose.

---

[5] Burla, M. C.; Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. *J. Appl. Cryst.* **2015**, *48*, 306-309.

[6] Sheldrick, G.M. *Acta Cryst.* **2015**, *C71*, 3-8.

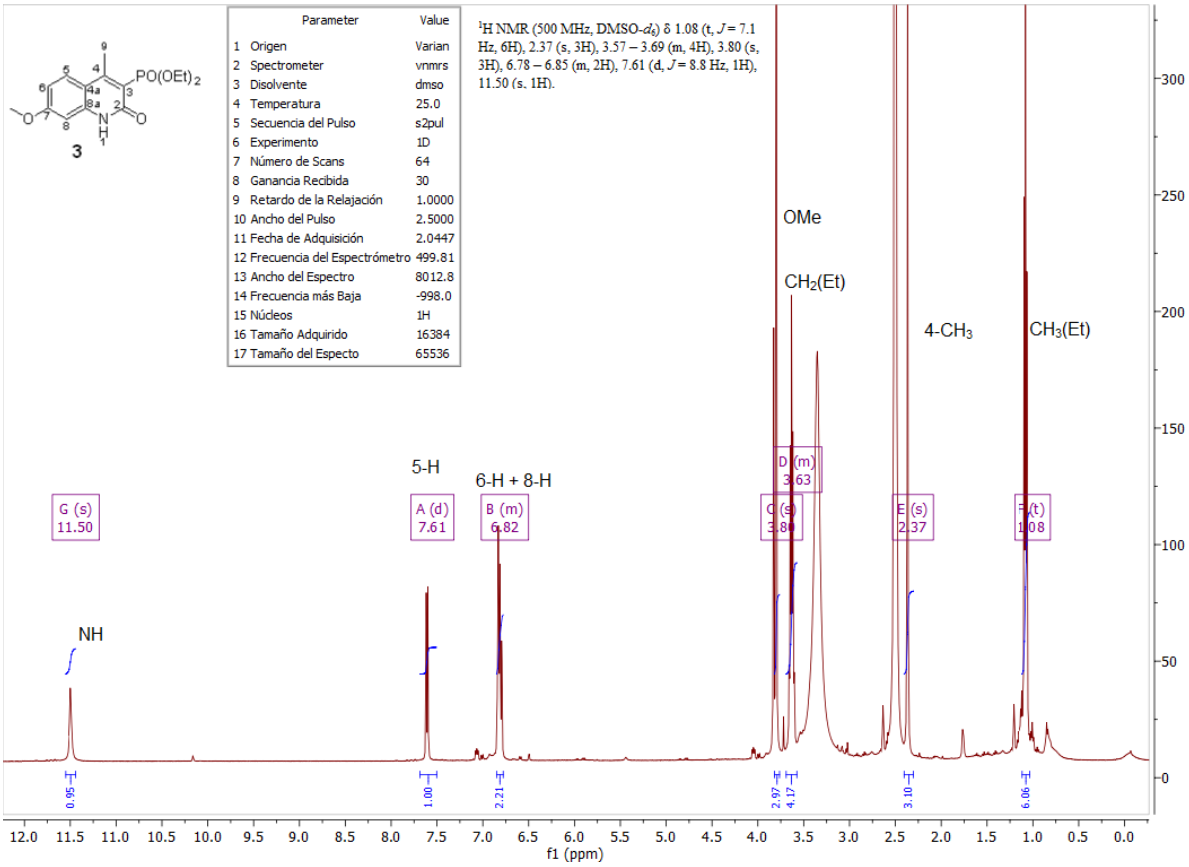


2

Eu(**2**)$_2$(H$_2$O)$_4$OTf

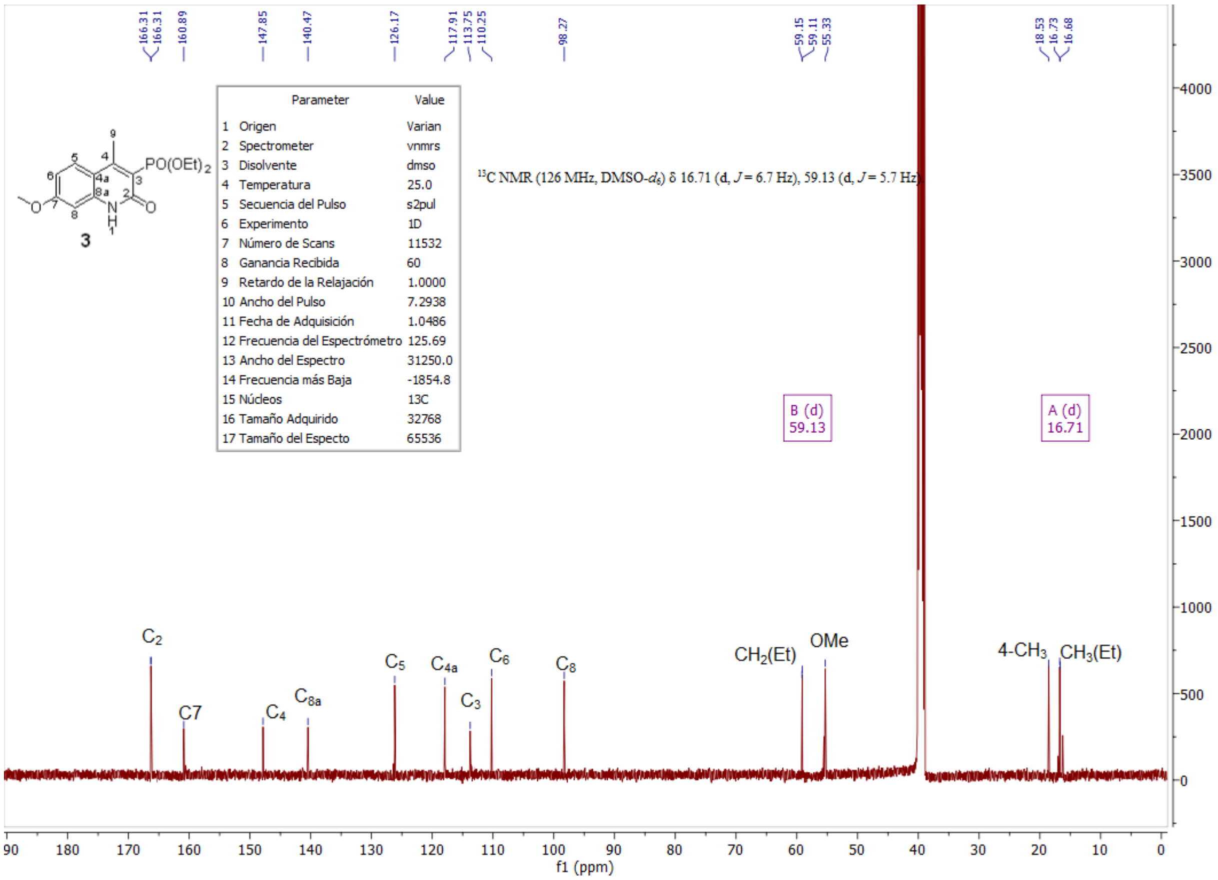
Figure S12. Molecular structures determined by X-ray diffraction of compound **2** and its europium complex. Thermal ellipsoids have been set at 50% probability for non-hydrogen atoms. Disordered models observed in Eu(**2**)$_2$(H$_2$O)$_4$OTf have been omitted and, the trifluoromethanesulfonate anions and the chloroform molecules have been represented by capped and sticks, for clarity purpose.

VI. NMR SPECTRA (^{1}H-NMR AND ^{13}C-NMR) OF 3, 4, 6, AND 7



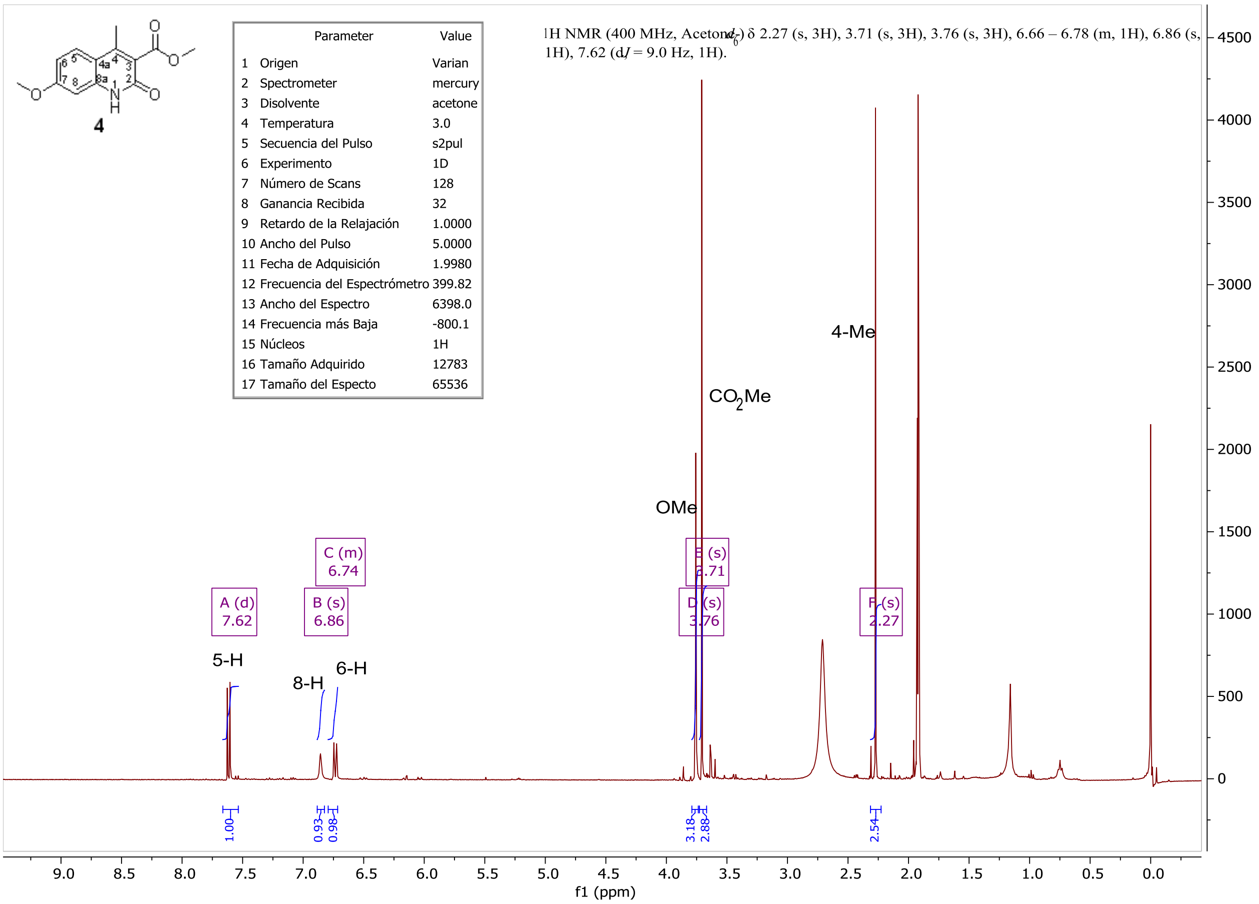
	Parameter	Value
1	Origen	Varian
2	Spectrometer	vnmrs
3	Disolvente	dmso
4	Temperatura	25.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	64
8	Ganancia Recibida	30
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	2.5000
11	Fecha de Adquisición	2.0447
12	Frecuencia del Espectrómetro	499.81
13	Ancho del Espectro	8012.8
14	Frecuencia más Baja	-998.0
15	Núcleos	1H
16	Tamaño Adquirido	16384
17	Tamaño del Especto	65536

^{1}H NMR (500 MHz, DMSO-d_6) δ 1.08 (t, J = 7.1 Hz, 6H), 2.37 (s, 3H), 3.57 – 3.69 (m, 4H), 3.80 (s, 3H), 6.78 – 6.85 (m, 2H), 7.61 (d, J = 8.8 Hz, 1H), 11.50 (s, 1H).



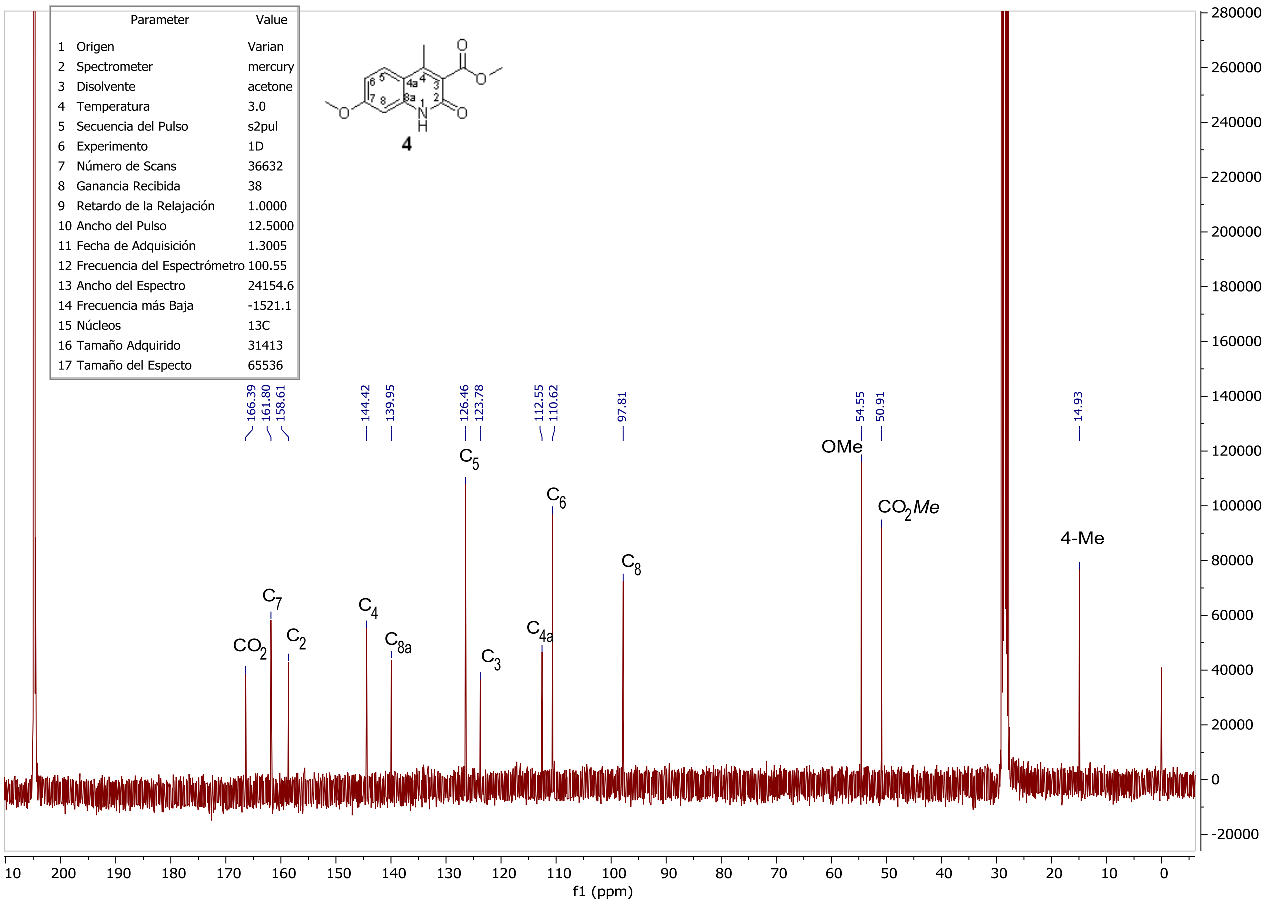
	Parameter	Value
1	Origen	Varian
2	Spectrometer	vnmrs
3	Disolvente	dmso
4	Temperatura	25.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	11532
8	Ganancia Recibida	60
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	7.2938
11	Fecha de Adquisición	1.0486
12	Frecuencia del Espectrómetro	125.69
13	Ancho del Espectro	31250.0
14	Frecuencia más Baja	-1854.8
15	Núcleos	13C
16	Tamaño Adquirido	32768
17	Tamaño del Especto	65536

^{13}C NMR (126 MHz, DMSO-d_6) δ 16.71 (d, J = 6.7 Hz), 59.13 (d, J = 5.7 Hz)

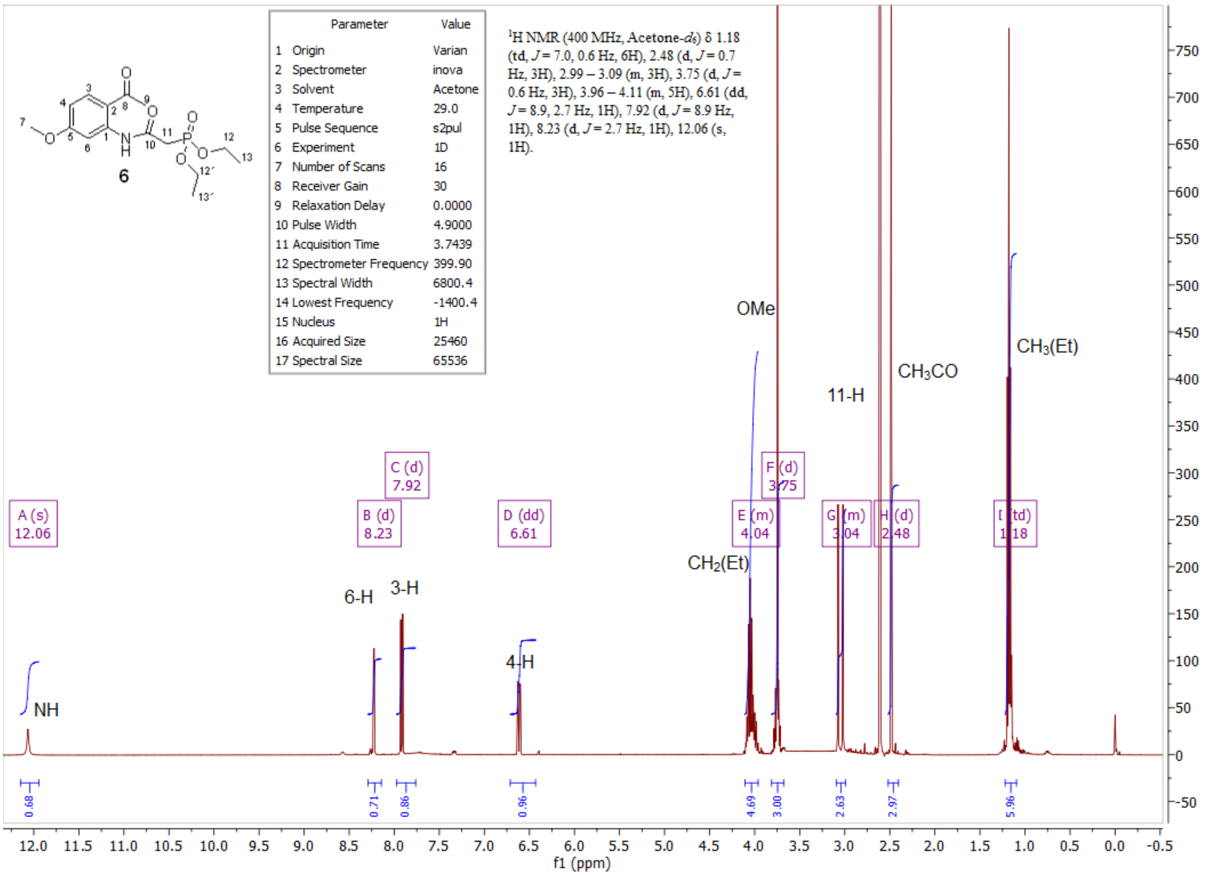


1H NMR (400 MHz, Acetone-d_6) δ 2.27 (s, 3H), 3.71 (s, 3H), 3.76 (s, 3H), 6.66 – 6.78 (m, 1H), 6.86 (s, 1H), 7.62 (d, J = 9.0 Hz, 1H).

	Parameter	Value
1	Origen	Varian
2	Spectrometer	mercury
3	Disolvente	acetone
4	Temperatura	3.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	128
8	Ganancia Recibida	32
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	5.0000
11	Fecha de Adquisición	1.9980
12	Frecuencia del Espectrómetro	399.82
13	Ancho del Espectro	6398.0
14	Frecuencia más Baja	-800.1
15	Núcleos	1H
16	Tamaño Adquirido	12783
17	Tamaño del Especto	65536

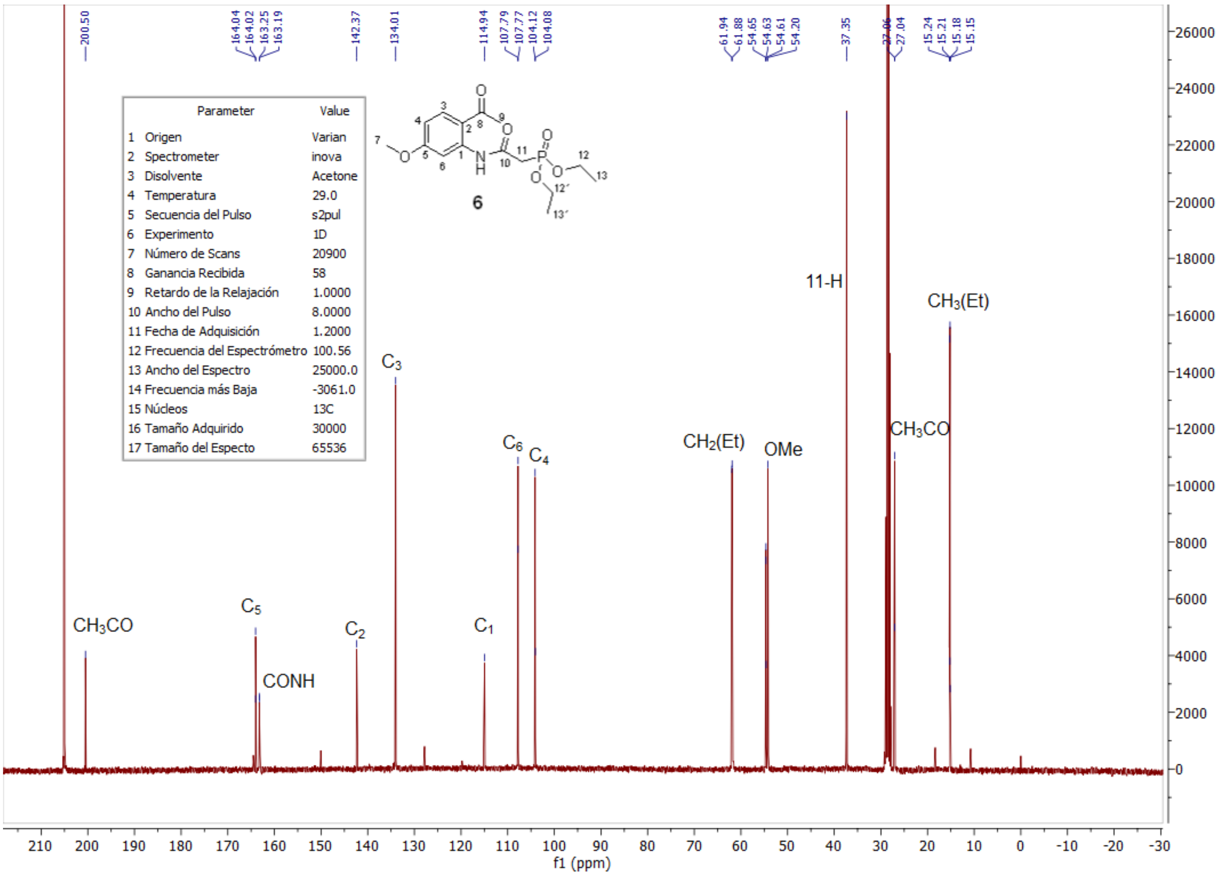


	Parameter	Value
1	Origen	Varian
2	Spectrometer	mercury
3	Disolvente	acetone
4	Temperatura	3.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	36632
8	Ganancia Recibida	38
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	12.5000
11	Fecha de Adquisición	1.3005
12	Frecuencia del Espectrómetro	100.55
13	Ancho del Espectro	24154.6
14	Frecuencia más Baja	-1521.1
15	Núcleos	13C
16	Tamaño Adquirido	31413
17	Tamaño del Especto	65536

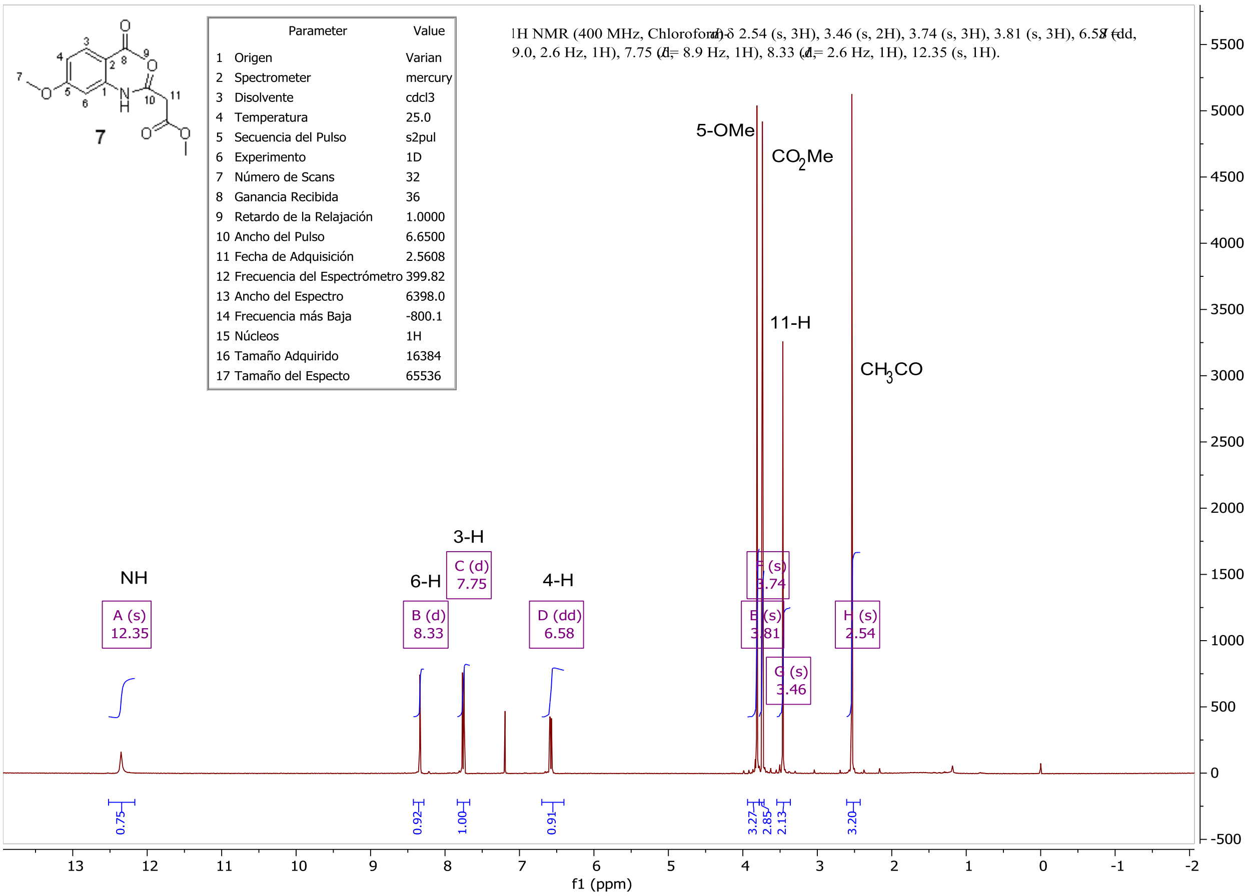


	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	Acetone
4	Temperature	29.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	30
9	Relaxation Delay	0.0000
10	Pulse Width	4.9000
11	Acquisition Time	3.7439
12	Spectrometer Frequency	399.90
13	Spectral Width	6800.4
14	Lowest Frequency	-1400.4
15	Nucleus	1H
16	Acquired Size	25460
17	Spectral Size	65536

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.18 (td, *J* = 7.0, 0.6 Hz, 6H), 2.48 (d, *J* = 0.7 Hz, 3H), 2.99 – 3.09 (m, 3H), 3.75 (d, *J* = 0.6 Hz, 3H), 3.96 – 4.11 (m, 5H), 6.61 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 8.23 (d, *J* = 2.7 Hz, 1H), 12.06 (s, 1H).

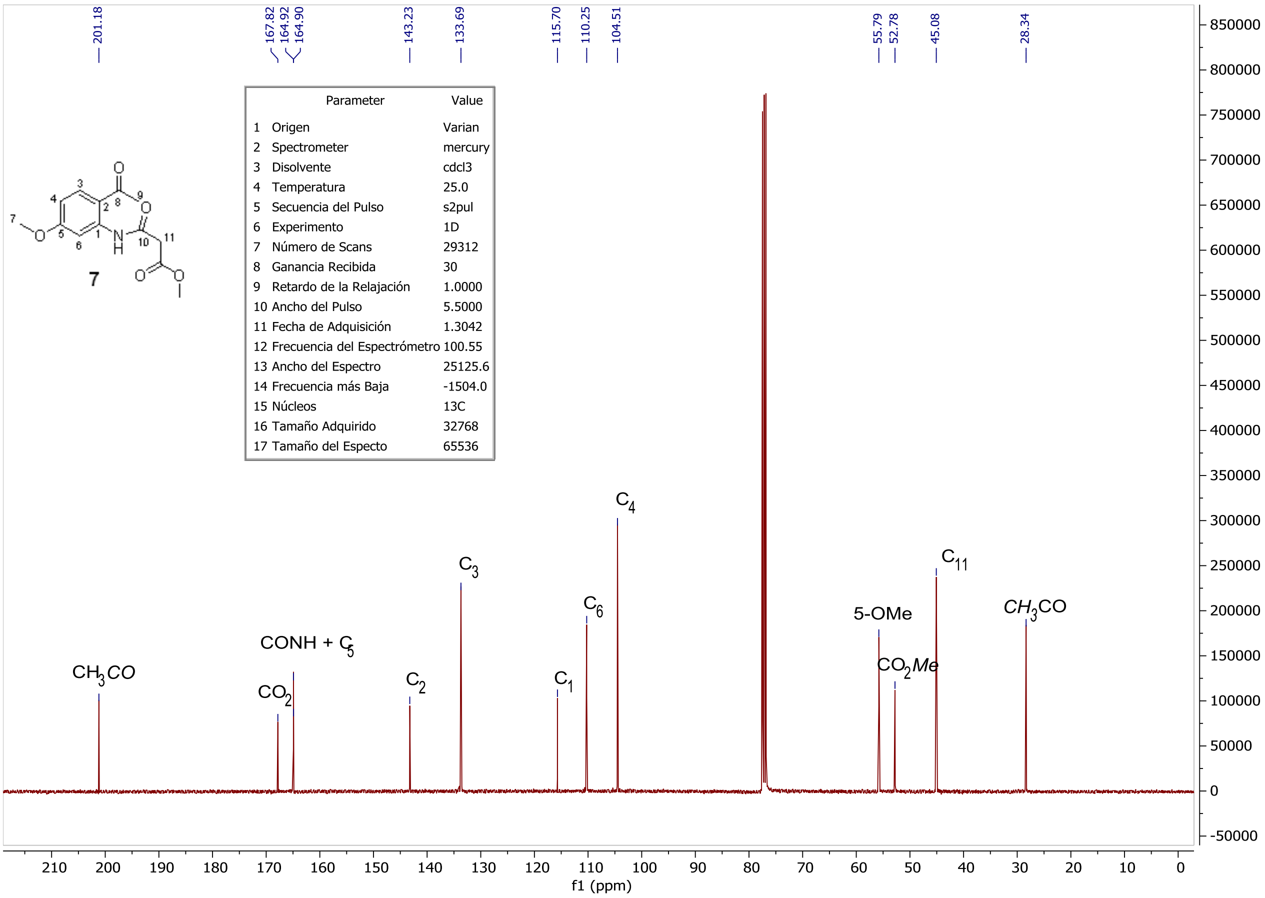


	Parameter	Value
1	Origen	Varian
2	Spectrometer	inova
3	Disolvente	Acetone
4	Temperature	29.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	20900
8	Ganancia Recibida	58
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	8.0000
11	Fecha de Adquisición	1.2000
12	Frecuencia del Espectrómetro	100.56
13	Ancho del Espectro	25000.0
14	Frecuencia más Baja	-3061.0
15	Núcleos	13C
16	Tamaño Adquirido	30000
17	Tamaño del Especto	65536



1H NMR (400 MHz, Chloroform-d) δ 2.54 (s, 3H), 3.46 (s, 2H), 3.74 (s, 3H), 3.81 (s, 3H), 6.58 (dd, J = 9.0, 2.6 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 8.33 (d, J = 2.6 Hz, 1H), 12.35 (s, 1H).

	Parameter	Value
1	Origen	Varian
2	Spectrometer	mercury
3	Disolvente	cdcl3
4	Temperatura	25.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	32
8	Ganancia Recibida	36
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	6.6500
11	Fecha de Adquisición	2.5608
12	Frecuencia del Espectrómetro	399.82
13	Ancho del Espectro	6398.0
14	Frecuencia más Baja	-800.1
15	Núcleos	1H
16	Tamaño Adquirido	16384
17	Tamaño del Especto	65536



	Parameter	Value
1	Origen	Varian
2	Spectrometer	mercury
3	Disolvente	cdcl3
4	Temperatura	25.0
5	Secuencia del Pulso	s2pul
6	Experimento	1D
7	Número de Scans	29312
8	Ganancia Recibida	30
9	Retardo de la Relajación	1.0000
10	Ancho del Pulso	5.5000
11	Fecha de Adquisición	1.3042
12	Frecuencia del Espectrómetro	100.55
13	Ancho del Espectro	25125.6
14	Frecuencia más Baja	-1504.0
15	Núcleos	13C
16	Tamaño Adquirido	32768
17	Tamaño del Especto	65536