Monomeric Ti(IV)-based complexes incorporating luminescent nitrogen ligands : synthesis, structural characterization, emission spectroscopy and cytotoxic activities

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Supporting Information

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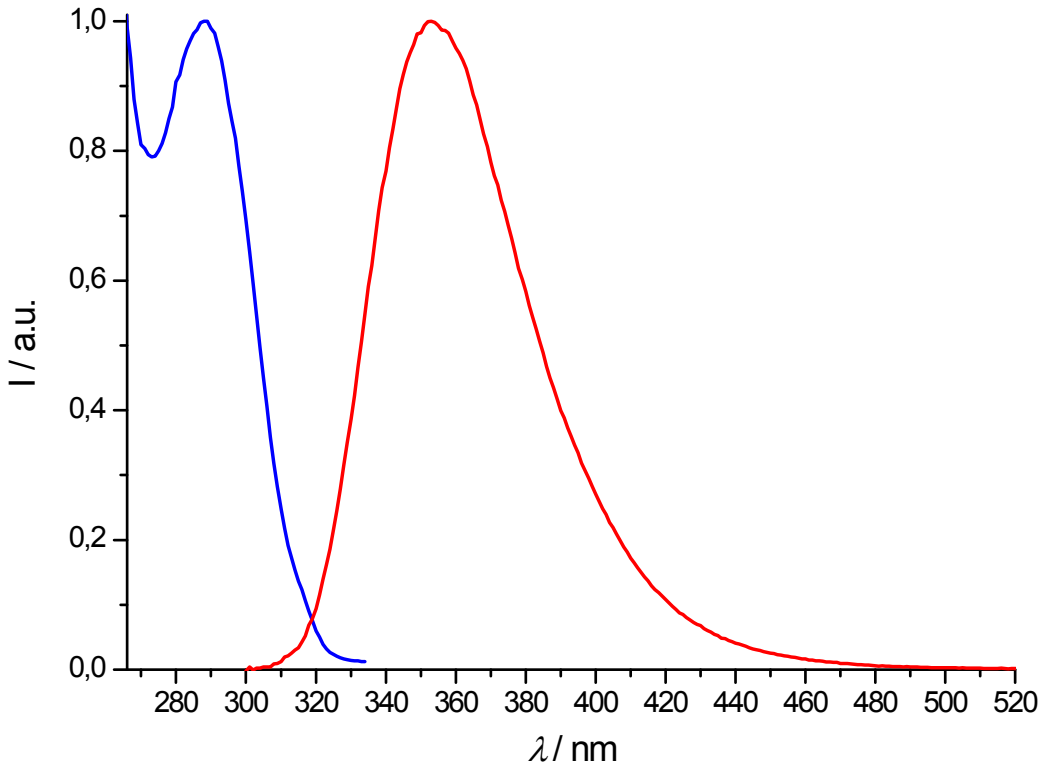

Figure S1. Normalized excitation spectrum (λ_{em} = 350 nm, blue) and emission spectrum (λ_{exc} = 290 nm, red) of compound **1**-H_2 recorded at room temperature in CH_2Cl_2 (concentration 2.95 μM).

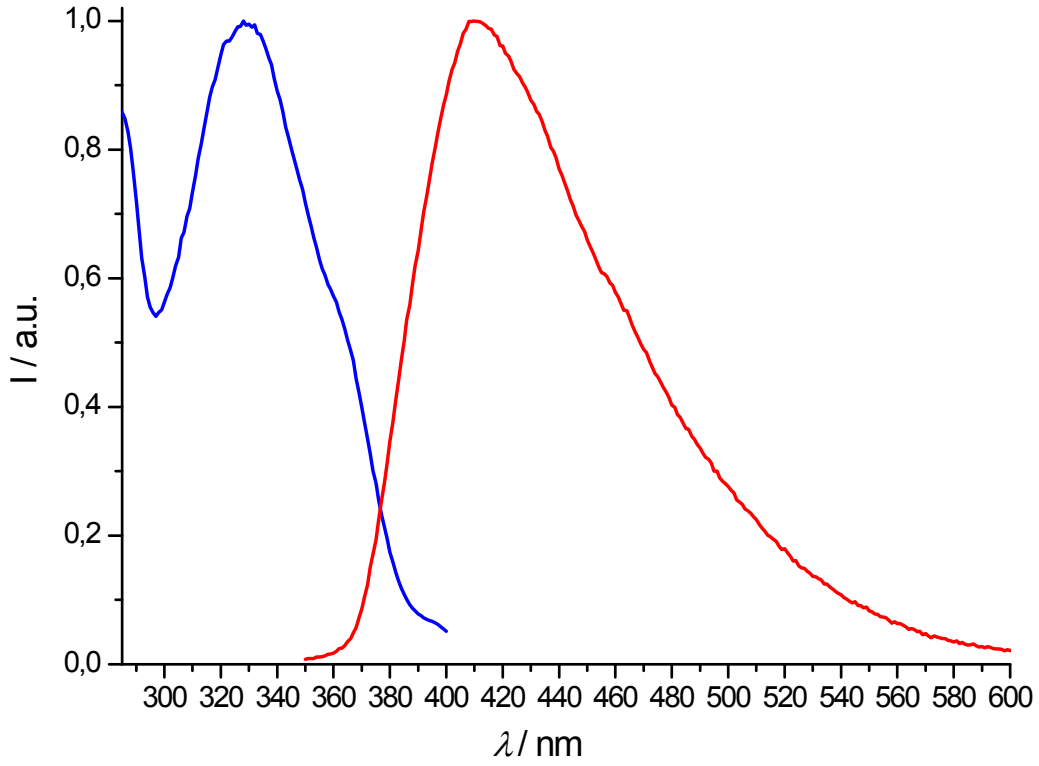

Figure S2. Normalized excitation spectrum (λ_{em} = 411 nm, blue) and emission spectrum (λ_{exc} = 332 nm, red) of compound **2c** recorded at room temperature in CH_2Cl_2 (concentration 3.14 μM).

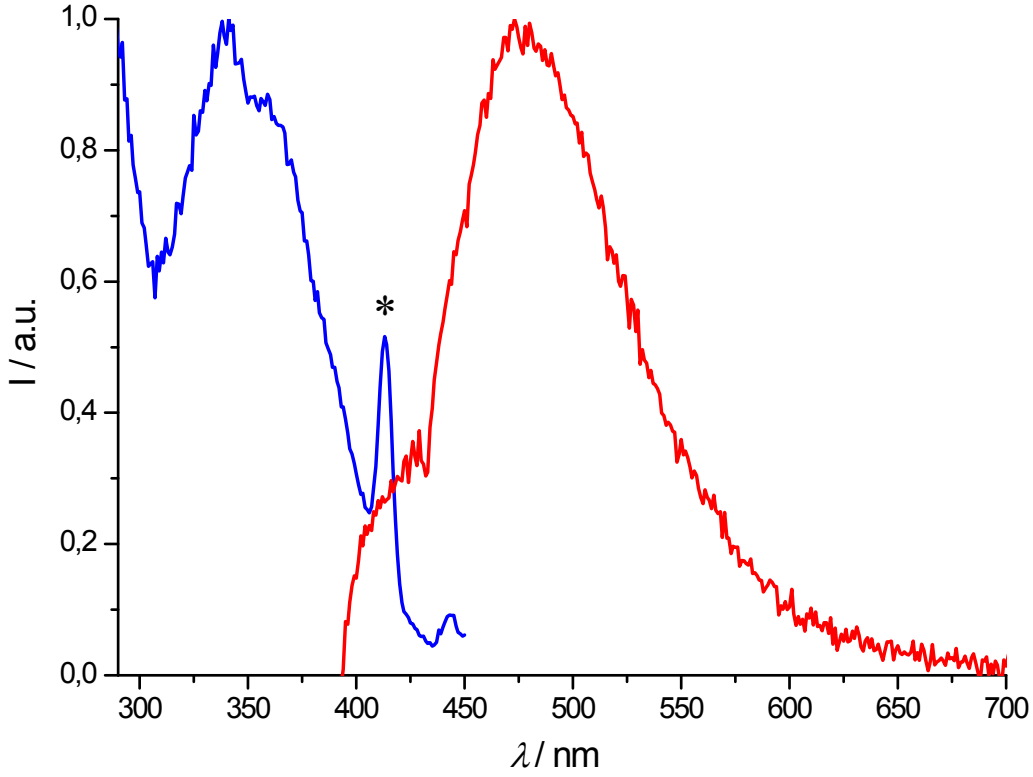

Figure S3. Normalized excitation spectrum (raw, λ_{em} = 473 nm, blue) and emission spectrum (λ_{exc} = 380 nm, red) of compound [Ti(**1**)$_2$(**2c**)] recorded at room temperature in CH_2Cl_2 (concentration 1.67 µM; * = artifact).

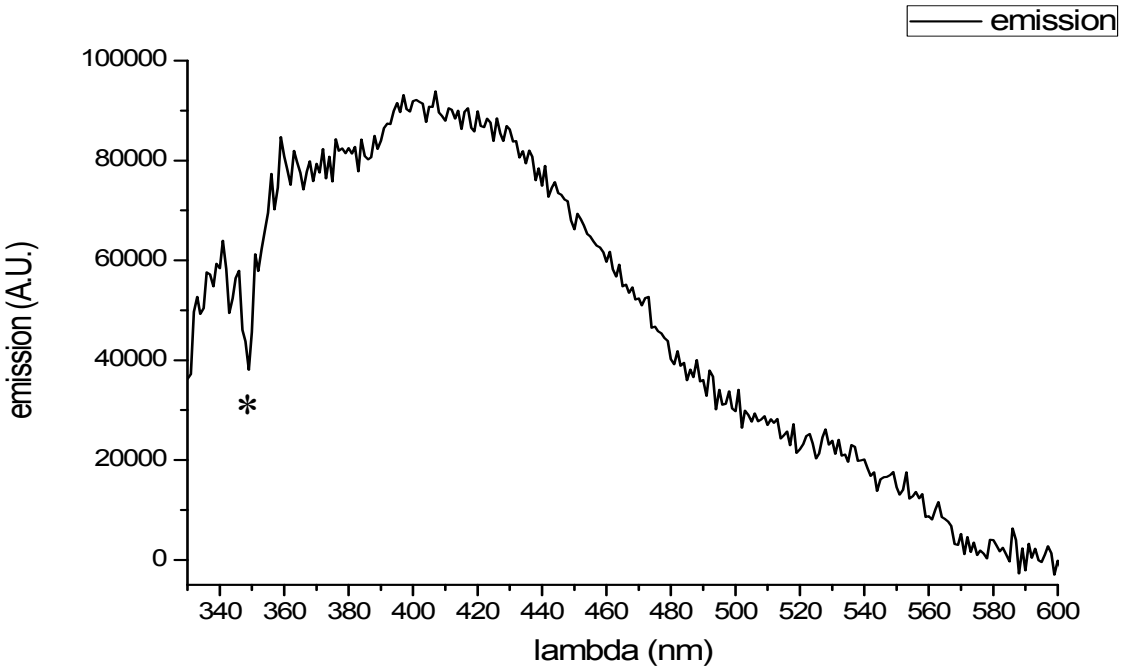

Figure S4. Emission spectrum (λ_{exc} = 315 nm) of compound **2b** recorded at room temperature in CH_2Cl_2 (concentration 1.81 μM; * = artifact).

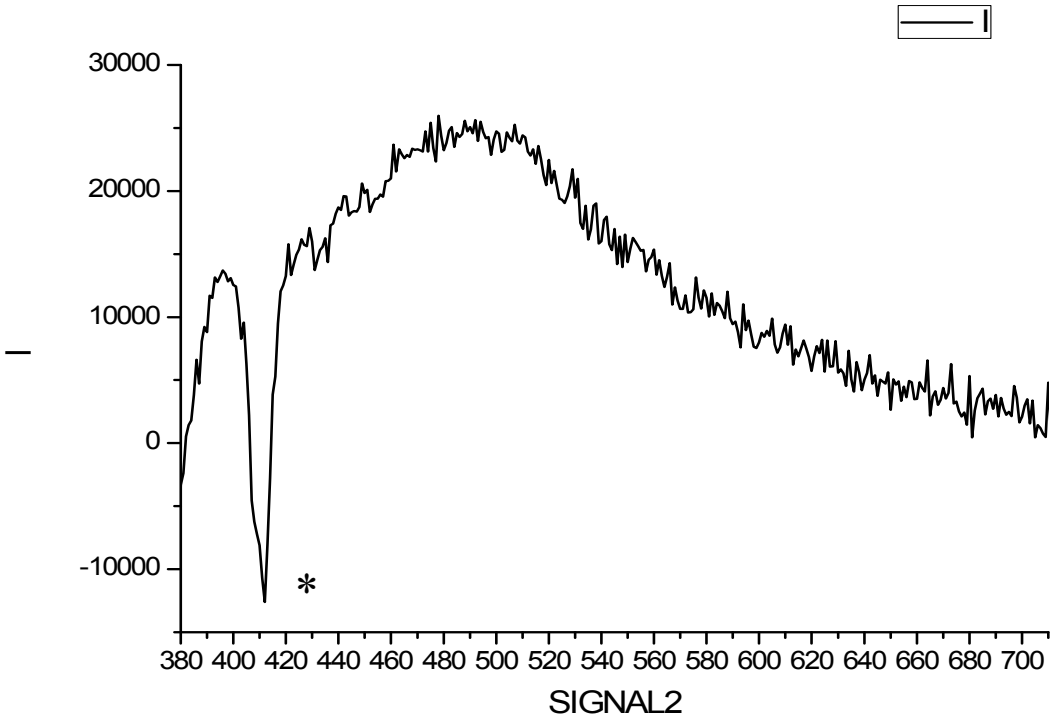

Figure S5. Emission spectrum (λ_{exc} = 365 nm) of compound [Ti(**1**)$_2$(**2d**)] recorded at room temperature in CH_2Cl_2 (concentration 2.25 μM; * = artifact).

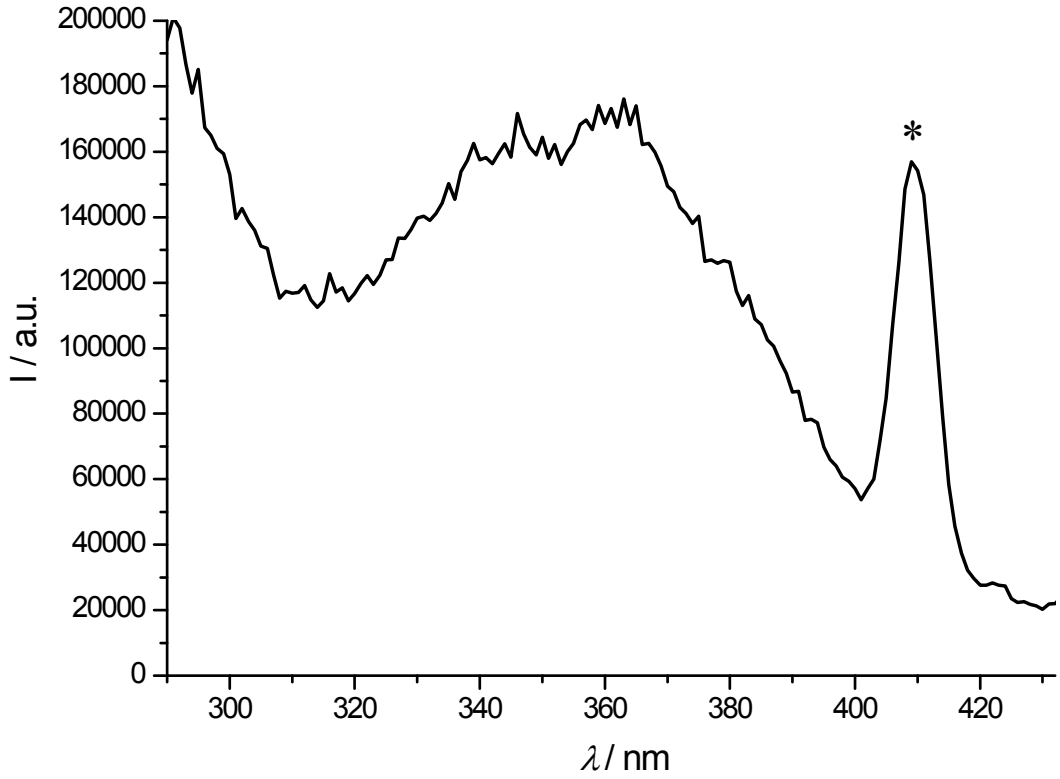

Figure S6. Excitation spectrum (raw, λ_{em} = 468 nm) of compound [Ti(**1**)$_2$(**2d**)] recorded at room temperature in CH_2Cl_2 (concentration 2.25 μM; * = artifact).

Table S1. Fitted lifetimes determined from the luminescence decay spectra

compounds	λ_{LED} / nm	λ_{em} / nm	lifetime / ns
1-H_2	296	350	$\tau = 0.52$
2b	296	395	$\tau_1 = 1.6$ (50%)
			$\tau_2 = 0.14$ (17%)
			$\tau_3 = 8.5$ (33%)
2c	340	411	$\tau_1 = 0.09$ (86%)
			$\tau_2 = 1.5$ (14%)
2d	375	525	$\tau_1 = 0.12$ (96%)
			$\tau_2 = 3.6$ (4%)
3c	375	473	$\tau_1 = 0.5$ (41%)
			$\tau_2 = 1.6$ (54%)
			$\tau_3 = 6.1$ (5%)
3d	375	468	$\tau_1 = 2.1$ (40%)
			$\tau_2 = 8.9$ (28%)
			$\tau_3 = 0.34$ (32%)

The luminescence decays were collected by a time-correlated single-photon-counting technique. The excitation source was a NanoLED-370 electroluminescent diode (Horiba Jobin Yvon) emitting at 375 nm and operated at a 1 MHz repetition rate. The bandpass of the emission double-grating monochromator was set at 2 nm for the measurements. The instrument response function was collected using a dilute scattering solution of Ludox (Sigma-Aldrich). The theoretical luminescence decays were assumed to be exponentials, or the sums of two or three exponentials. They were iteratively reconvoluted with the measured instrument response prior to fitting with the measured luminescence decays using the least-squares method of Fluorescence Decay Analysis Software DAS6 (Horiba Jobin Yvon). The goodness of fit was evaluated by the X2 criterion, the randomness of the residuals, and their autocorrelation.

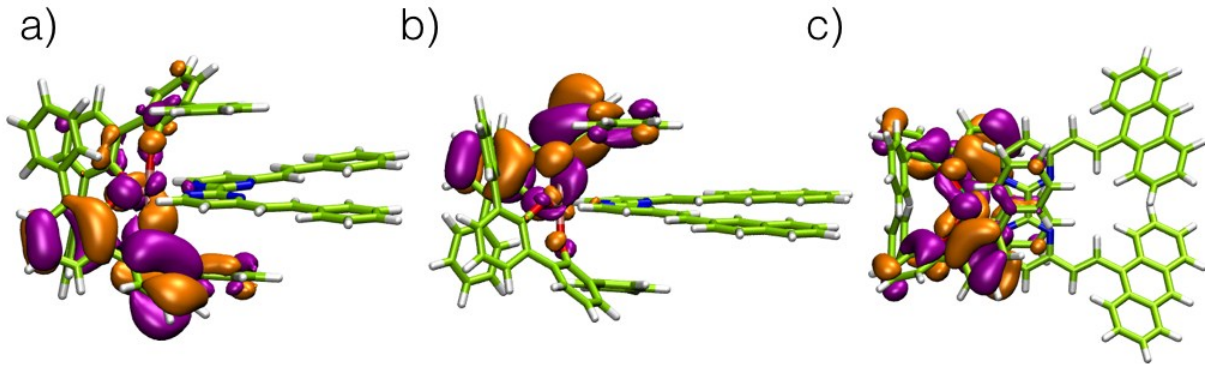

Figure S7. The HOMOs-1 are all centered on the biphenolato ligands.

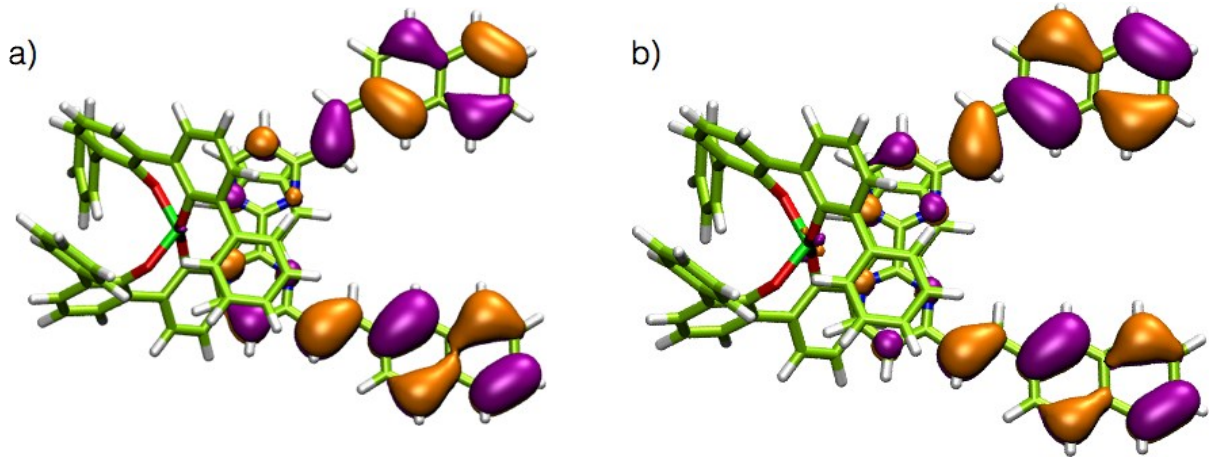

Figure S8. HOMO-6 (a) and HOMO-7 (b) representations of the [Ti(**1**)$_2$(**2c**)] complex.

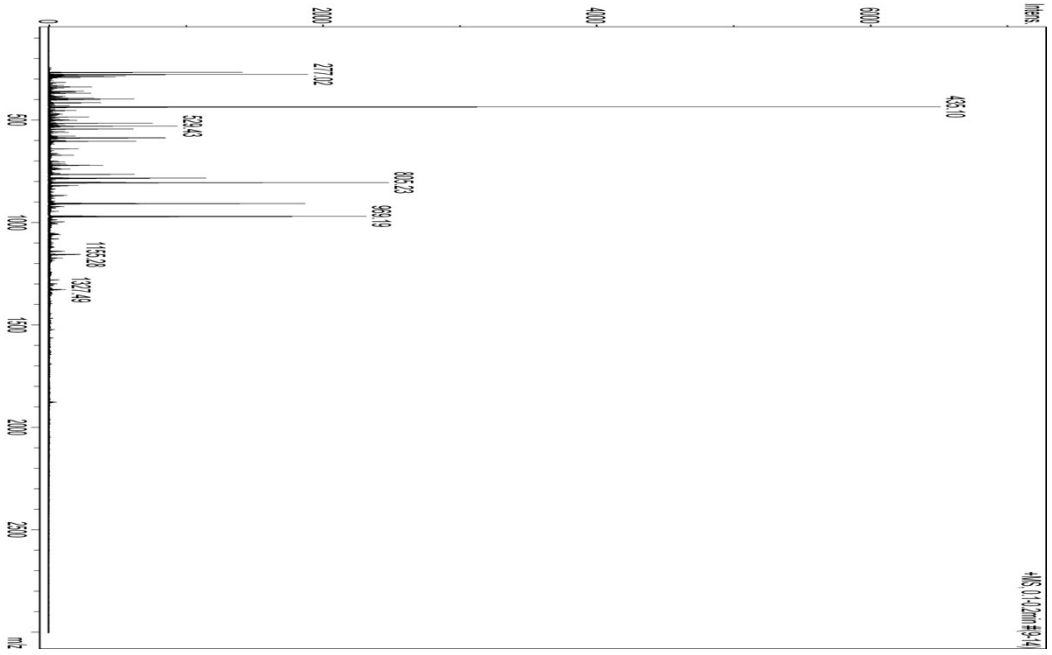

Figure S9. ES-MS of an aliquot of the solution of the [Ti(**1**)$_2$(**2a**)] complex in DMSO-d$_6$ with D_2O revealing the formation of unknown hydrolytic products ([Ti(**1**)$_2$(**2a**)] = 906.27 g.mol^{-1}, **1**-H_2 = 338.13 g.mol^{-1}, **2a** = 186.09 g.mol^{-1}).

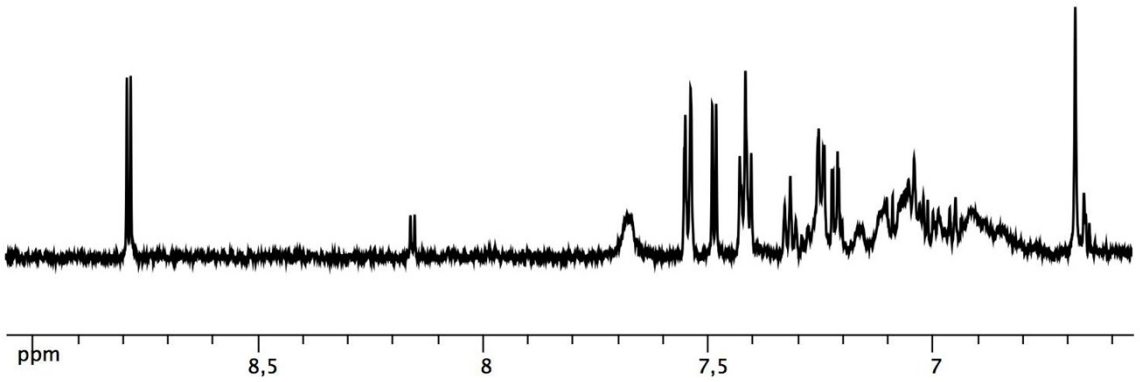

Figure S10. Aromatic region of the ^{1}H NMR spectrum of the solution of the [Ti(**1**)$_2$(**2a**)] complex in DMSO-d_6 with D_2O revealing the presence of large signals of unknown species.