

## **Exploiting P-chemistry to modulate the Thermally Activated Delayed Fluorescence of organic fluorophores**

Nicolas Ledos,<sup>a</sup> Denis Jacquemin,<sup>b,c\*</sup> Pierre-Antoine Bouit,<sup>a\*</sup> Muriel Hissler<sup>a\*</sup>

[a] Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes

[b] Nantes Université, CNRS, CEISAM UMR 6230, F-44000 Nantes, France.

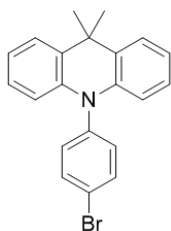
[c] Institut Universitaire de France (IUF), F-75005 Paris, France

E-mail : [Denis.Jacquemin@univ-nantes.fr](mailto:Denis.Jacquemin@univ-nantes.fr), [pierre-antoine.bouit@univ-rennes.fr](mailto:pierre-antoine.bouit@univ-rennes.fr), [muriel.hissler@univ-rennes.fr](mailto:muriel.hissler@univ-rennes.fr)

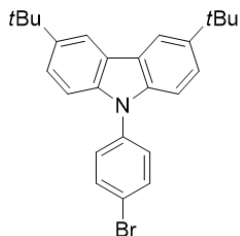
<b>Experimental part</b>	<b>page S1</b>
<b>Spectroscopic data</b>	<b>page S6</b>
<b>Theoretical calculations</b>	<b>page S9</b>
<b>NMR spectra</b>	<b>page S12</b>

## Experimental Part General.

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly purified using MBRAUN SPS-800 drying columns. Separations were performed by gravity column chromatography on silica gel (ACROS Organic Silica gel, for column chromatography, 0.035-0.070mm, 60Å). <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker AV 300 and AV III 400 MHz NMR spectrometers equipped with BBO or BBFO probeheads. Assignment of proton and carbon atoms is based on DPET-135 experiments. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were reported in parts per million (ppm) using residual solvent signal as reference. In the NMR description, C<sub>q</sub> corresponds to quaternary carbon. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO (Scanmat, UMS 2001). UV-Visible spectra were recorded at room temperature (rt) on a Specord 205 UV/Vis/NIR spectrophotometer. The UV-Vis emission spectra measurements were recorded on a FL 920 Edinburgh Instrument equipped with a Hamamatsu R5509-73 photomultiplier for the NIR domain (300-1700 nm) and corrected for the response of the photomultiplier. Relative quantum yields were calculated compared to quinine sulfate (H<sub>2</sub>SO<sub>4</sub>, 0.05 M), φ<sub>ref</sub>= 0.54. The absolute quantum yields were measured with a C9920-03 Hamamatsu. Life-times measurements were conducted with 375 nm diode laser excitation (EPL-series) plugged to a TCSPC pulsed source interface using an Edinburgh FS920 Steady State Fluorimeter combined with a FL920 Fluorescence Lifetime Spectrometer.



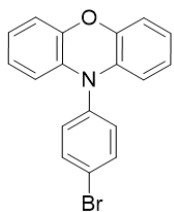
**Compound 1:** Compound 1 was synthesized following a reported procedure.<sup>1</sup>



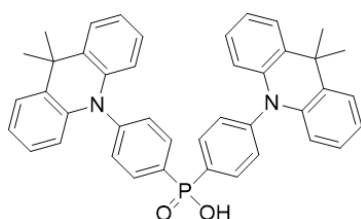
**Compound 2:** A mixture of 3,6-di-*tert*-butyl-9H-carbazole (840 mg, 3.0 mmol), 1-bromo-4-iodobenzene (1.7 g, 6.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.67 g, 12.1 mmol), Cu powder (129 mg, 2.0 mmol), and 18-crown-6 (255 mg, 1.0 mmol) in *o*-dichlorobenzene (15 ml) was degassed with Ar for 30 min while stirring. The reaction mixture was then refluxed under Ar for 12 h. The crude mixture was filtered, and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 ml). The combined filtrates were evaporated to dryness. The residue was purified by silica gel chromatography Heptane/DCM (7/1 v/v) to give compound 2 (1.24 g, 95 %) as a white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.18 (d, *J* = 1.9 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.55 – 7.41 (m, 4H), 7.34 (d, *J* = 8.7 Hz, 2H), 1.47 (s, 18H). NMR data fit with previously reported procedure.<sup>2</sup>

<sup>1</sup> I. S. Park, S. Y. Lee, C. Adachi, T. Yasuda, *Adv. Funct. Mater.* **2016**, *26*, 1813–1821.

<sup>2</sup> Y. Liu, M. Nishiura, Y. Wang, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 5592–5593.

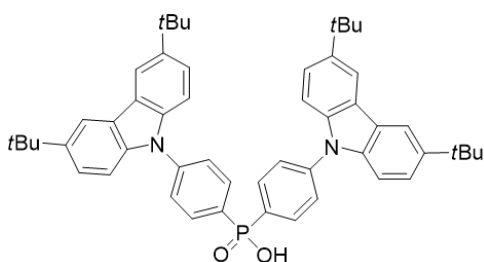


**Compound 3:** A mixture of 10H-phenoxazine (1.5 g, 8.2 mmol), 1-bromo-4-iodobenzene (4.64 g, 16.4 mmol),  $K_2CO_3$  (4.55 g, 33.0 mmol), Cu powder (355 mg, 5.5 mmol), and 18-crown-6 (700 mg, 2.7 mmol) in DMF (50 ml) was degassed with Ar for 30 min while stirring. The reaction mixture was then heated to 140°C under Ar for 12 h. The crude mixture was filtered, and the residue was washed with  $CH_2Cl_2$  (3 x 10 ml). The combined filtrates were evaporated to dryness. The residue was purified by silica gel chromatography Heptane/DCM (15/1 v/v) to give compound **3** (1.46 g, 53 %) as a white solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.72 (d,  $J$  = 8.5 Hz, 2H), 7.24 (d,  $J$  = 8.5 Hz, 2H), 6.73 – 6.49 (m, 6H), 5.91 (dd,  $J$  = 7.8, 1.6 Hz, 2H). NMR data fit with previously reported procedure.<sup>1</sup>



**Compound 4:**  $Pd_2(dba)_3$  (10 mg, 0.01 mmol) and Xantphos (20mg, 0.04mmol) were introduced in a flask under Argon. Toluene (10 mL) was added, and the mixture was stirred at rt for 5 min. Then  $iPr_2EtN$  (228 mg, 1.8 mmol),  $NaH_2PO_2 \cdot H_2O$  (48 mg, 0.045 mmol) and **1** (400mg, 1.1 mmol) were added. The flask was then heated and stirred at 115°C for 60 h. After the reaction, the reaction mixture was allowed to return to rt. The solvent was evaporated, and the residue was dissolved in DCM (50 mL)

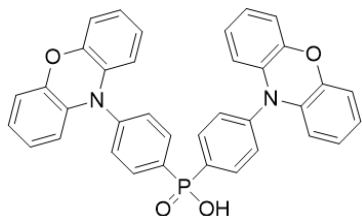
and HCl 10% (50mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $MgSO_4$ . After filtration, the solvent was evaporated, and the residue was washed using AcOEt and was followed by column chromatography on silica gel by using DCM/ $Et_3N$ /MeOH (100/5/5 v/v/v) as eluent. The solvent was evaporated, and the residue was dissolved in DCM (50 mL) and HCl 10% (5mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $MgSO_4$ . After filtration, the solvent was evaporated to afford **4** as a white powder (225 mg, Yield = 79%).  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.17 (dd,  $J$  = 12.2, 8.2 Hz, 4H), 7.60 – 7.34 (m, 8H), 7.07 – 6.79 (m, 8H), 6.37 – 6.20 (m, 4H), 1.64 (s, 12H). Due to solubility issues, no  $^{13}C$  NMR spectra could be recorded.  $^{31}P$  NMR (162 MHz,  $CD_2Cl_2$ )  $\delta$  +31.9 (s). HRMS (ESI,  $CH_2Cl_2$ ):  $[M-H]^-$  ( $C_{42}H_{36}N_2O_2P$ ),  $m/z$  Calcd for: 631.25199,  $m/z$  Found: 631.2518.



**Compound 5:**  $Pd_2(dba)_3$  (5 mg, 0.005 mmol) and Xantphos (10mg, 0.02mmol) were introduced in a flask under Argon. Toluene (10 mL) was added, and the mixture was stirred at rt for 5 min. Then  $iPr_2EtN$  (228 mg, 1.8 mmol),  $NaH_2PO_2 \cdot H_2O$  (39 mg, 0.37 mmol) and **2** (400mg, 0.92 mmol) were added. The flask was then heated and stirred at 115°C for 60h. After the reaction, the reaction mixture

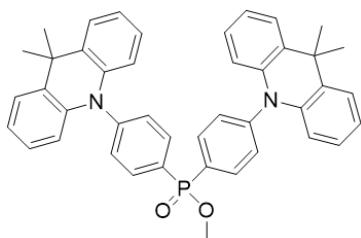
was allowed to return to rt. The solvent was evaporated, and the residue was dissolved in DCM (50 mL) and HCl 10% (50mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $MgSO_4$ . After filtration, the solvent was evaporated, and the residue was washed using cold acetone and was followed by column chromatography on silica gel by using DCM/ $Et_3N$ /MeOH (100/5/5 v/v/v) as eluent. The solvent was evaporated, and the residue was dissolved in DCM (50 mL) and HCl 10% (5mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $MgSO_4$ . After filtration, the solvent was evaporated to afford **5** as a white powder (242 mg, Yield = 85%).  $^1H$  NMR (400 MHz,

DMSO)  $\delta$  8.30 (d,  $J = 1.9$  Hz, 4H), 8.10 (dd,  $J = 11.5, 8.1$  Hz, 4H), 7.85 – 7.77 (m, 4H), 7.51 – 7.38 (m, 8H), 1.41 (s, 36H). Due to solubility issues, no  $^{13}\text{C}$  NMR spectra could be recorded.  $^{31}\text{P}$  NMR (162 MHz, DMSO)  $\delta$  +22.0 (s). HRMS (ESI,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  90/10):  $[\text{M}-\text{H}]^-$  ( $\text{C}_{52}\text{H}_{56}\text{N}_2\text{O}_2\text{P}$ ),  $m/z$  Calcd for: 771.40849,  $m/z$  Found: 771.4079.



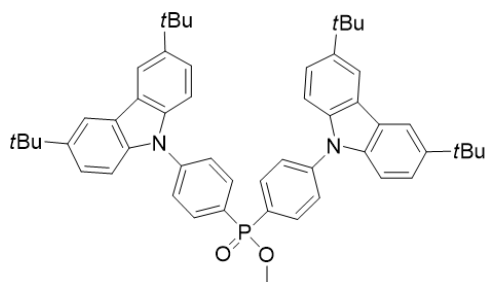
**Compound 6:**  $\text{Pd}_2(\text{dba})_3$  (5 mg, 0.005 mmol) and Xantphos (10mg, 0.02mmol) were introduced in a flask under Argon. Toluene (10 mL) was added, and the mixture was stirred at rt for 5 min. Then  $i\text{Pr}_2\text{EtN}$  (228 mg, 1.8 mmol),  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  (59 mg, 0.56 mmol) and **3** (400mg, 1.18 mmol) were added. The flask was then heated and stirred at  $115^\circ\text{C}$  for 60 h. After the reaction, the reaction mixture was allowed to return to rt. The solvent was

evaporated, and the residue was dissolved in DCM (50 mL) and HCl 10% (50mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $\text{MgSO}_4$ . After filtration, the solvent was evaporated, and the residue was washed using cold acetone and was followed by column chromatography on silica gel by using  $\text{DCM}/\text{Et}_3\text{N}/\text{MeOH}$  (100/5/5 v/v/v) as eluent. The solvent was evaporated, and the residue was dissolved in DCM (50 mL) and HCl 10% (5mL) was added. The mixture was extracted with DCM three times. The combined organic phases were dried over anhydrous  $\text{MgSO}_4$ . After filtration, the solvent was evaporated to afford **6** as a greenish powder (230 mg, Yield = 71%).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.07 (dd,  $J = 11.5, 8.0$  Hz, 4H), 7.58 (dd,  $J = 8.3, 2.5$  Hz, 4H), 6.87 – 6.54 (m, 12H), 5.88 (dd,  $J = 7.5, 1.9$  Hz, 4H). Due to solubility issues, no  $^{13}\text{C}$  NMR spectra could be recorded.  $^{31}\text{P}$  NMR (162 MHz, DMSO)  $\delta$  +21.5 (s). HRMS (ESI,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  90/10):  $[\text{M}-\text{H}]^-$  ( $\text{C}_{36}\text{H}_{24}\text{N}_2\text{O}_4\text{P}$ ),  $m/z$  Calcd for: 579.14792,  $m/z$  Found: 579.1480.



**Compound 7:** A mixture of **4** (90 mg, 0.14 mmol), methanol (6 mg, 0.21 mmol), and DCC (44 mg, 0.21 mmol) was dissolved in 5 mL of toluene and stirred at rt overnight. The solution was cooled to  $0^\circ\text{C}$  to precipitate the resulting DCU and the solution was filtered. Solvent were evaporated. **7** was obtained after chromatography on a silica gel column using  $\text{DCM}/\text{EtOAc}$  (6/1 v/v) as a white powder (52 mg, Yield =

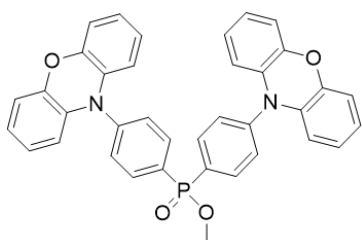
57%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.16 (dd,  $J = 11.8, 8.3$  Hz, 4H), 7.59 – 7.40 (m, 8H), 7.01 – 6.91 (m, 8H), 6.32 – 6.24 (m, 4H), 3.90 (d,  $J = 11.2$  Hz, 3H), 1.68 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  145.8 (d,  $J = 3$  Hz,  $\text{C}_q$ ), 140.9 (s,  $\text{C}_q$ ), 134.9 (d,  $J = 11$  Hz,  $\text{CH}$ ), 131.8 (d,  $J = 14$  Hz,  $\text{CH}$ ), 131.4 (d,  $J = 138$  Hz,  $\text{C}_q$ ), 131.0 (s,  $\text{C}_q$ ), 126.8 (s,  $\text{CH}$ ), 125.7 (s,  $\text{CH}$ ), 121.4 (s,  $\text{CH}$ ), 114.7 (s,  $\text{CH}$ ), 52.2 (d,  $J = 6$  Hz,  $\text{OCH}_3$ ), 36.4 (s,  $\text{C}_q$ ), 31.3 (s,  $\text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  +31.1 (s). HRMS (ESI,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  95/5):  $[\text{M}+\text{H}]^+$  ( $\text{C}_{43}\text{H}_{40}\text{N}_2\text{O}_2\text{P}$ ),  $m/z$  Calcd for: 647.28219,  $m/z$  Found: 647.2817.



**Compound 8:** A mixture of **5** (80 mg, 0.1 mmol), methanol (4.1 mg, 0.15 mmol), and DCC (31 mg, 0.15 mmol) was dissolved in 5 mL of toluene, stirred at rt overnight. The solution was cooled to  $0^\circ\text{C}$  to precipitate the resulting DCU and the solution was filtered. Solvent were evaporated. **8** was obtained after chromatography on a silica gel column using  $\text{DCM}/\text{EtOAc}$  (6/1 v/v) as a white powder (75 mg,

Yield = 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.16 (dd,  $J = 1.8, 0.8$  Hz, 4H), 8.11 (dd,  $J = 11.8, 8.4$  Hz, 4H),

7.78 (dd,  $J = 8.4, 2.9$  Hz, 4H), 7.55 – 7.42 (m, 8H), 3.90 (d,  $J = 11.2$  Hz, 3H), 1.46 (s, 36H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  144.1 (s,  $C_q$ ), 142.4 (d,  $J(\text{C-P}) = 3$  Hz,  $C_q$ ), 139.0 (s,  $C_q$ ), 133.8 (d,  $J(\text{C-P}) = 11$  Hz,  $\text{CH}$ ), 129.7 (d,  $J(\text{C-P}) = 139$  Hz,  $C_q$ ), 126.6 (d,  $J(\text{C-P}) = 13$  Hz,  $\text{CH}$ ), 124.3 (s,  $\text{CH}$ ), 124.2 (s,  $C_q$ ), 116.8 (s,  $\text{CH}$ ), 109.6 (s,  $\text{CH}$ ), 52.1 (d,  $J(\text{C-P}) = 6$  Hz,  $\text{OCH}_3$ ), 35.1 (s,  $C_q$ ), 32.1 (s,  $^t\text{Bu}$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  +30.95 (s). HRMS (ESI,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  10/90):  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{53}\text{H}_{59}\text{N}_2\text{O}_2\text{PNa}$ ),  $m/z$  Calcd for: 809.42064,  $m/z$  Found: 809.4209.



**Compound 9:** A mixture of **6** (80 mg, 0.14 mmol), methanol (6 mg, 0.21 mmol), and DCC (44 mg, 0.21 mmol) was dissolved in 5 mL of toluene, stirred at rt overnight. The solution was cooled to 0°C to precipitate the resulting DCU and the solution was filtered. Solvent were evaporated and **9** was obtained after chromatography on a silica gel column using DCM/EtOAc (6/1 v/v) as a green powder (69 mg, Yield = 83%).  $^1\text{H}$  NMR

(400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.15 – 8.04 (m, 4H), 7.53 (dd,  $J = 8.4, 2.9$  Hz, 4H), 6.74 – 6.56 (m, 12H), 5.96 (dd,  $J = 7.9, 1.4$  Hz, 4H), 3.86 (d,  $J = 11.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  144.0 (s,  $C_q$ ), 143.1 (d,  $J(\text{C-P}) = 3$  Hz,  $C_q$ ), 134.6 (d,  $J(\text{C-P}) = 11$  Hz,  $\text{CH}$ ), 133.8 (s,  $C_q$ ), 131.4 (d,  $J(\text{C-P}) = 138$  Hz,  $C_q$ ), 131.2 (d,  $J(\text{C-P}) = 14$  Hz,  $\text{CH}$ ), 123.3 (s,  $\text{CH}$ ), 121.8 (s,  $\text{CH}$ ), 115.5 (s,  $\text{CH}$ ), 113.4 (s,  $\text{CH}$ ), 51.7 (d,  $J(\text{C-P}) = 6$  Hz,  $\text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  +30.5 (s). HRMS (ESI,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  10/90):  $[\text{M}]^+$  ( $\text{C}_{37}\text{H}_{27}\text{N}_2\text{O}_4\text{P}$ ),  $m/z$  Calcd for: 594.1703,  $m/z$  Found: 594.1707.

### Spectroscopic data

Experimental determination of  $\Delta E_{ST}$ :

The energy of the  $S_1$  state was determined using the fluorescence spectrum band edge at rt in toluene. The energy of the  $T_1$  state was determined using the first peak of the phosphorescence spectrum at 77K (Figure S1). The phosphorescence spectrum is acquired by measuring the compound's luminescence after a delay of 290 ms, effectively eliminating fluorescence signal (in the order of the nanosecond).

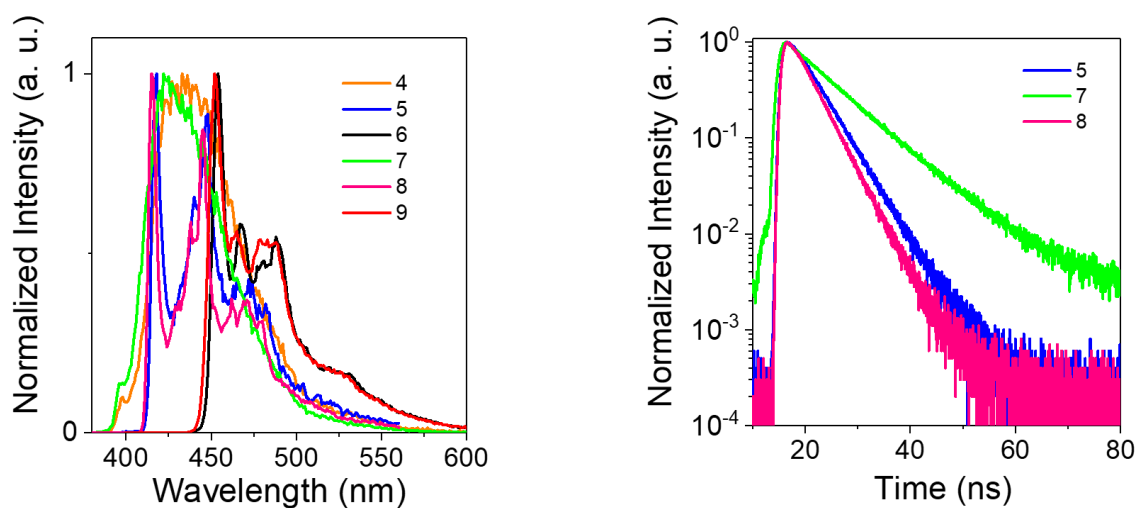


Figure S1: (Left) Phosphorescent spectra of compounds 4-9 (Right) Prompt fluorescence of emitters 5, 7 and 8

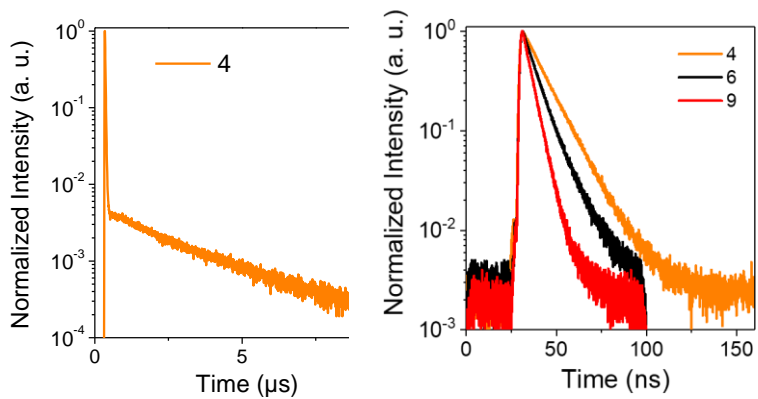


Fig. S2: Luminescence lifetime in presence of oxygen (up) and under inert conditions (bottom) of emitters **4**, **6** and **9**.

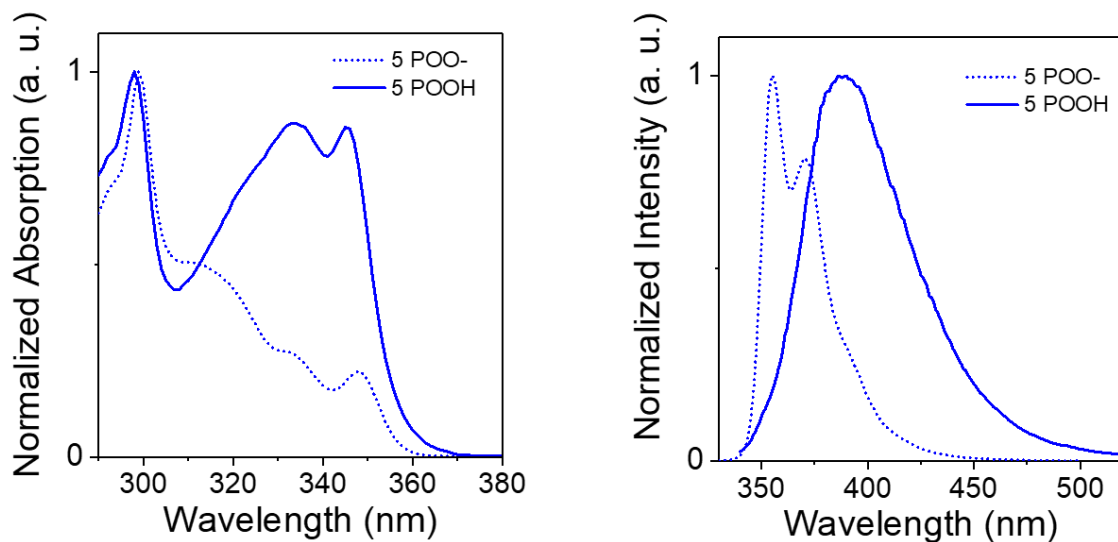


Figure S3: Absorption (left) and fluorescence spectra (right) of emitters **5** in neutral (labeled POOH) and basic media (labeled POO-).

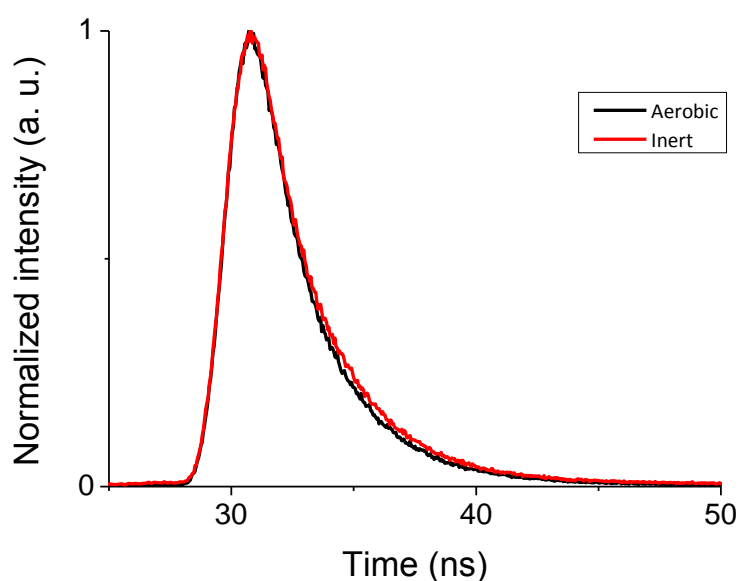


Figure S4: Fluorescence decay of **6** POO<sup>-</sup> in basic media in aerated solution (black) and deaerated solution (dashed).

In this study,  $\phi_{PF}$  and  $\phi_{DF}$  were determined by the method of Nakagawa *et al.*,<sup>3</sup> using total PL quantum efficiency and the ratio between prompt and delayed components which was calculated from transient PL measurements. The intensity ratio between prompt ( $r_1$ ) and delayed ( $r_2$ ) components were determined using emission lifetime ( $\tau_1, \tau_2$ ) and fitting parameter ( $A_1, A_2$ ) as follow.

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

$$r_1 = \frac{A_1 \tau_1}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

$$r_2 = \frac{A_2 \tau_2}{A_1 \tau_1 + A_2 \tau_2} \quad (3)$$

Then,  $\phi_{PF}$  and  $\phi_{DF}$  were determined using intensity ratio ( $r_1, r_2$ ) and total emission quantum yield.

$$\varphi_{PL} = \varphi_{PF} + \varphi_{DF} \quad (4) \quad \varphi_{DF} = \varphi_{PL} \times r_1 \quad (5) \quad \varphi_{PF} = \varphi_{PL} \times r_2 \quad (6)$$

The calculation of  $k_{PF}$ ,  $k_{DF}$ ,  $k_{ISC}$  and  $k_{RISC}$  were determined using the following equation:<sup>4[2]</sup>

$$k_{PF} = \frac{\varphi_{PF}}{\tau_{PF}} \quad (7) \quad k_{DF} = \frac{\varphi_{DF}}{\tau_{DF}} \quad (8)$$

$$k_{ISC} = \frac{\varphi_{DF} \times k_{DF}}{\varphi_{DF} + \varphi_{PF}} \quad (9) \quad k_{RISC} = \frac{\varphi_{DF} \times k_{DF} \times k_{PF}}{k_{ISC} \times \varphi_{PF}} \quad (10)$$

<sup>3</sup> T. Nakagawa, S.-Y. Ku, K.-T. Wong, C. Adachi, *Chem. Commun.* **2012**, 48, 9580

<sup>4</sup> C. Duan, J. Li, C. Han, D. Ding, H. Yang, Y. Wei, H. Xu, *Chemistry of Materials* **2016**, 28, 5667–5679.



### Theoretical calculations

We have performed the DFT and TD-DFT calculations with Gaussian 16.<sup>5</sup> No simplification was made (full structure used), and no symmetry constrain applied. Default Gaussian16 thresholds and algorithms were used but for an improved optimization threshold ( $10^{-5}$  au on average residual forces), a stricter self-consistent field convergence criterion ( $10^{-10}$  a.u.) and the systematic use of the *superfine* DFT integration grid, the denser grid available in Gaussian.

Firstly, the  $S_0$  geometries have been optimized with DFT and the vibrational frequencies have been analytically determined, using the M06-2X *meta*-GGA hybrid exchange-correlation functional.<sup>6</sup> These calculations were performed with the 6-311G(d,p) atomic basis set in solution using the PCM<sup>7</sup> model and selecting toluene as solvent. Secondly, starting from the optimal ground-state geometries, we have used TD-DFT with the same functional and basis set to optimize the  $S_1$  geometry and compute analytically the vibrational frequencies. All optimized structures correspond to true minima of the potential energy surface. Thirdly, the vertical transition energies were determined with TD-DFT and the same functional, but a diffuse-containing basis set, namely 6-311+G(2d,p), in gas-phase as well as in solution using the cLR<sup>2</sup> variant of the PCM,<sup>8</sup> in its *non-equilibrium* limit. Toluene was used as solvent. It should be stressed here that cLR<sup>2</sup>-PCM includes both linear-response and state-specific solvent corrections, and therefore should be well-suited for both local and charge-transfer states, as well as states with a mixed character.

As we are aware of the significant dependency of the TD-DFT results on the selected functional,<sup>9</sup> the obtained transition energies were also computed using CC2<sup>10</sup> with the Turbomole code.<sup>11</sup> The CC2 energies were calculated in gas phase applying the resolution of identity scheme, and using the *aug-cc-pVDZ* atomic basis set. Combining the CC2 and TD-DFT data using a well-known protocol,<sup>12</sup> one can obtain accurate CC2-corrected estimates of the absorption, emission and 0-0 energies that can be straightforwardly compared to experimental values. For the S-T gaps, we used SCS-CC2, which is recommended for these estimates, on the  $S_1$  optimal structures.

---

<sup>5</sup> M. J. Frisch, et al. Gaussian 16, revision A.03; Gaussian Inc.: Wallingford, CT, 2016

<sup>6</sup> Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215–241.

<sup>7</sup> J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, **2005**, *105*, 2999–3094.

<sup>8</sup> C. A. Guido, A. Chrayteh, G. Scamani, B. Mennucci, D. Jacquemin *J. Chem. Theory Comput.*, **2021**, *17*, 5155–5164.

<sup>9</sup> A. D. Laurent, D. Jacquemin, *Int. J. Quantum Chem.*, **2013**, *113*, 2019–2039.

<sup>10</sup> O. Christiansen, H. Koch, P. Jørgensen *Chem. Phys. Lett.*, **1995**, *243*, 409–418.

<sup>11</sup> TURBOMOLE V7.3/V7.5, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007; TURBOMOLE GmbH. <http://www.turbomole.com>.

<sup>12</sup> D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.*, **2015**, *11*, 5340–5359.

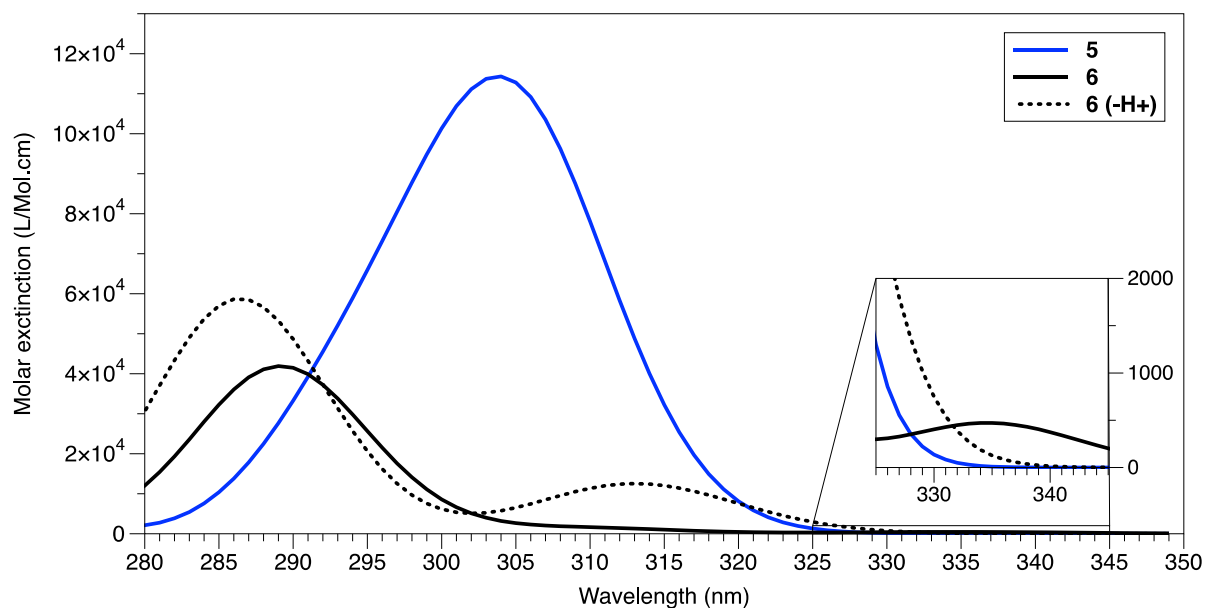


Fig. S5. Simulated UV/Vis spectra using vertical TD-DFT energies. Note the inset on the right with the small extra band of **6**.

Table S1 Summary of key theoretical data: vertical absorption and fluorescence wavelengths, 0-0 energies. All calculations in acetonitrile

Dye	Vert-abs (nm)	Vert-fl (nm)	0-0 (eV)
<b>5</b>	329	375	3.29
<b>6</b>	394	582	2.34
<b>6 (-H<sup>+</sup>)</b>	338	665	3.20

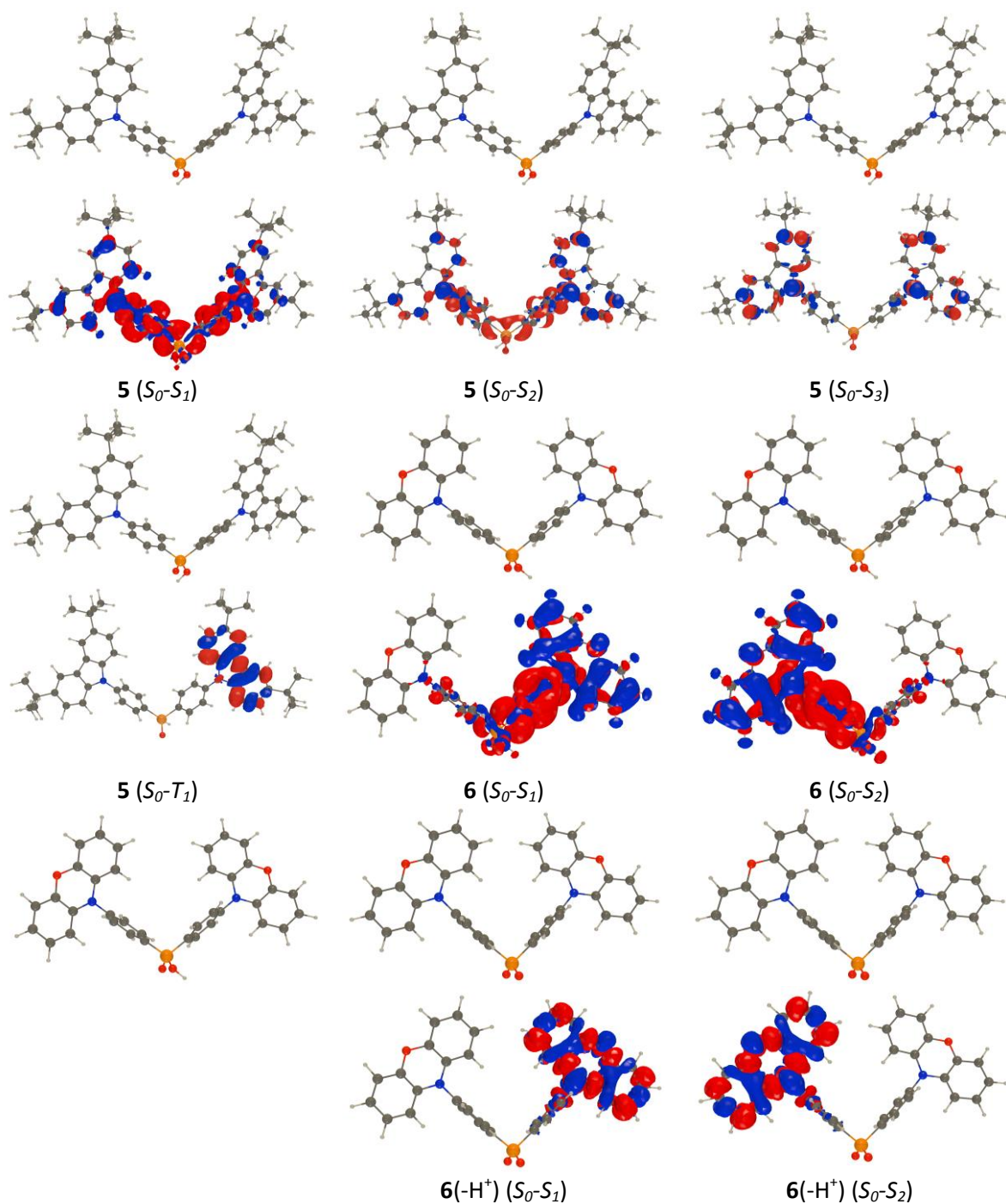


Fig. S6. Structure (top) and electron density difference plot (bottom) corresponding to the lowest excited states of the investigated dyes. The blue and red lobes correspond to decrease and increase of electron density, respectively. Contour threshold 0.001 au.

## NMR spectra

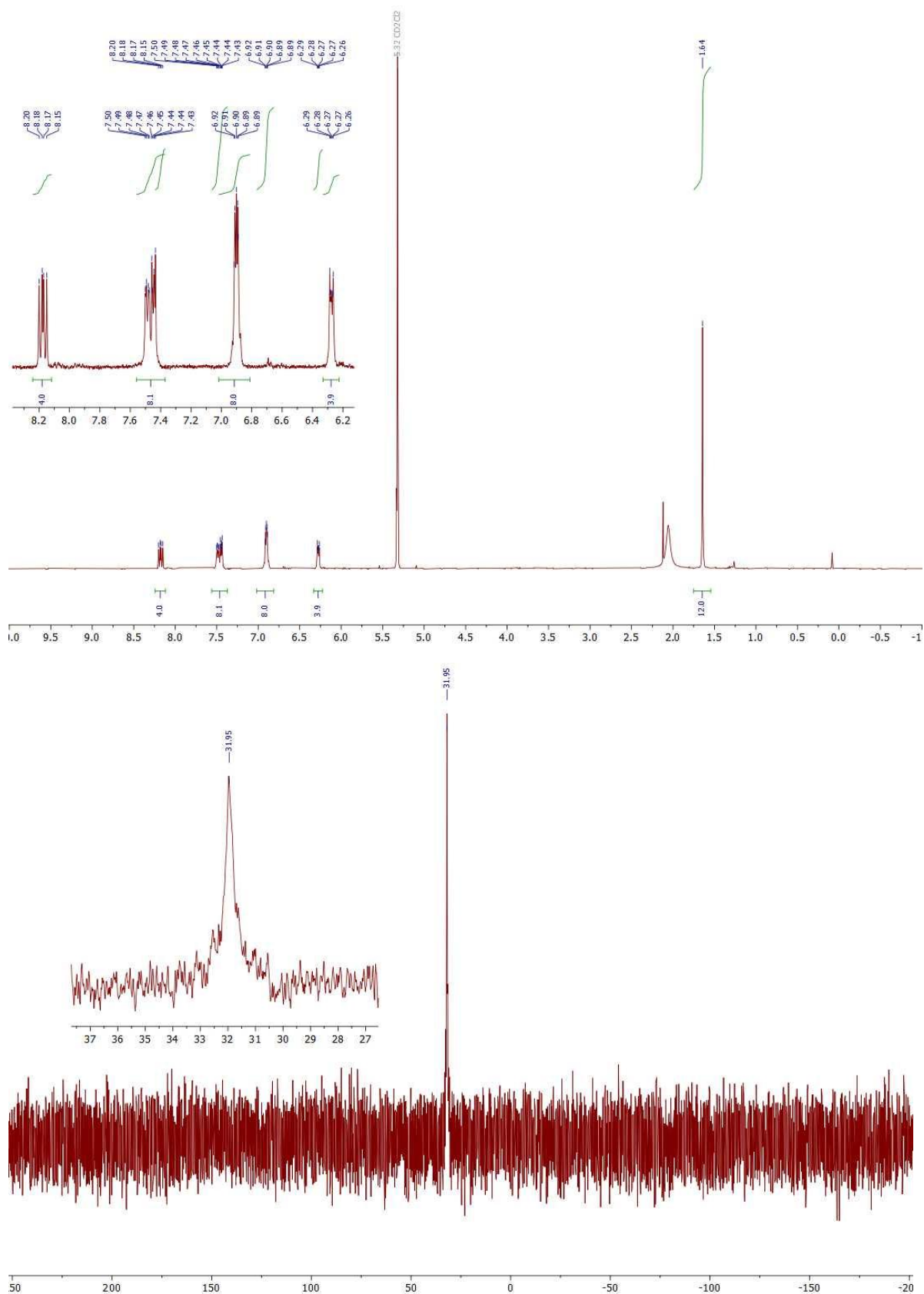


Fig. S7:  $^1\text{H}$  NMR (400 MHz) and  $^{31}\text{P}$  NMR (162 MHz) NMR spectra of **4** in  $\text{CDCl}_3$ .

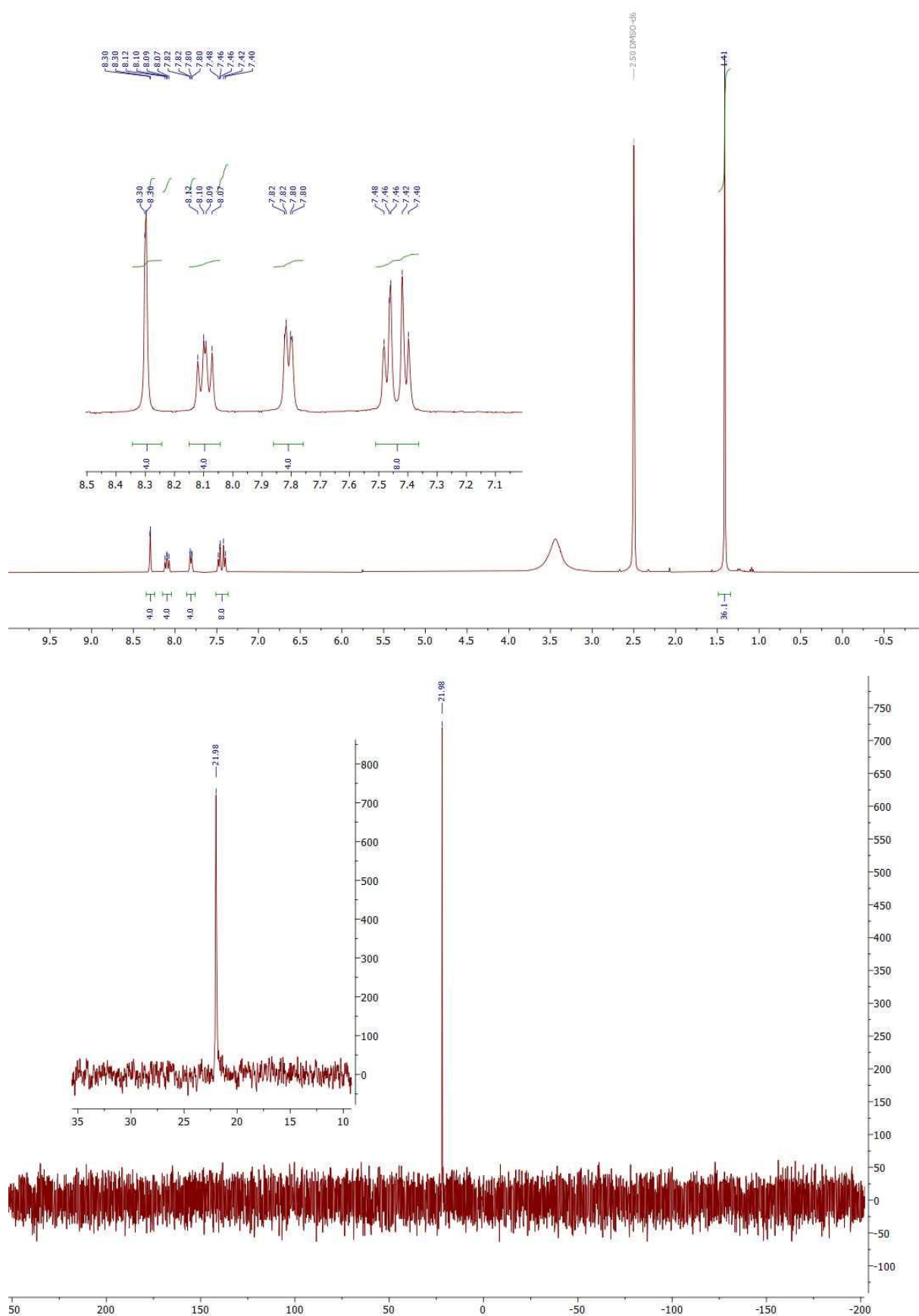


Fig. S8: <sup>1</sup>H NMR (400 MHz) and <sup>31</sup>P NMR (162 MHz) NMR spectra of **5** in DMSO-d<sub>6</sub>.

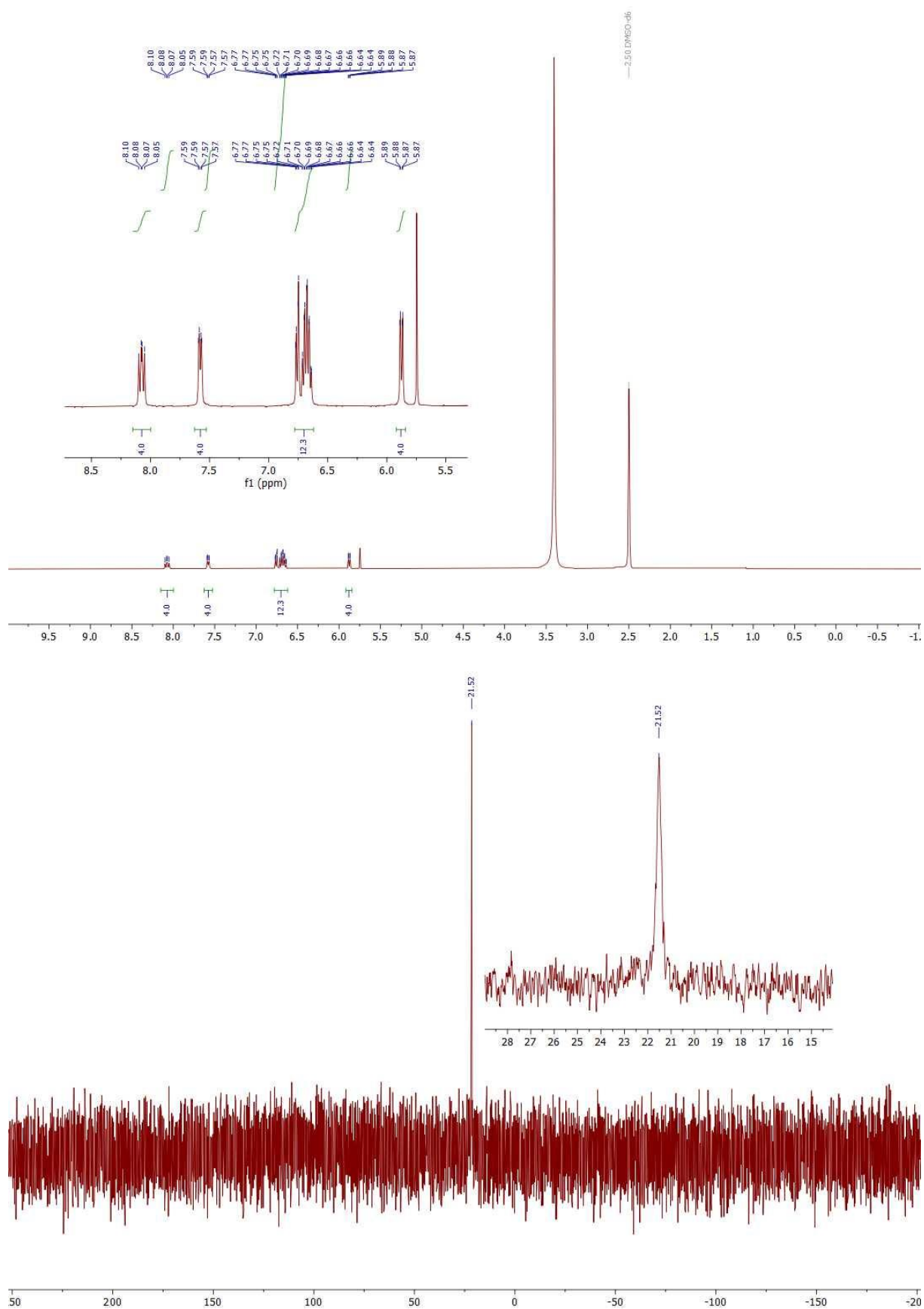
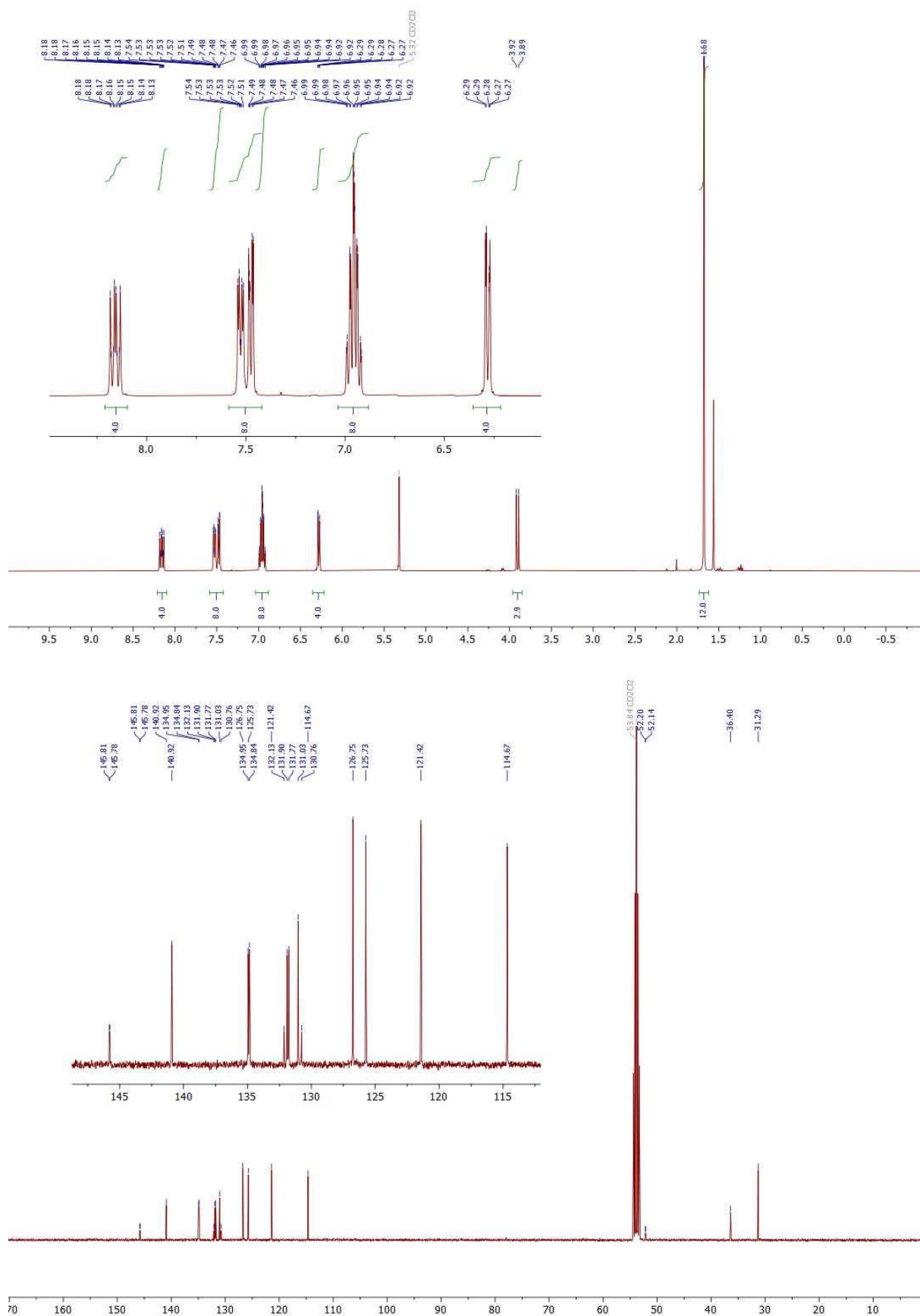


Fig. S9: <sup>1</sup>H NMR (400 MHz) and <sup>31</sup>P NMR (162 MHz) NMR spectra of **6** in DMSO-d<sub>6</sub>.



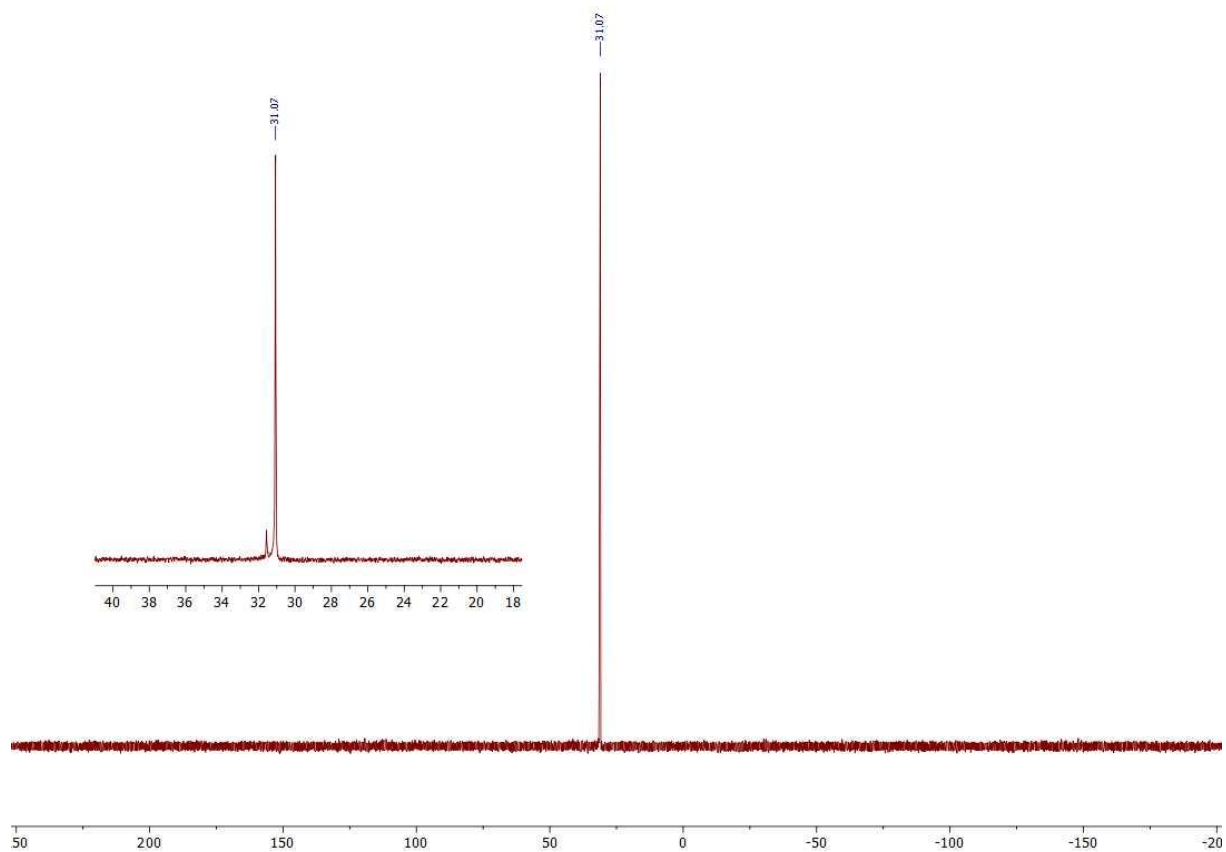
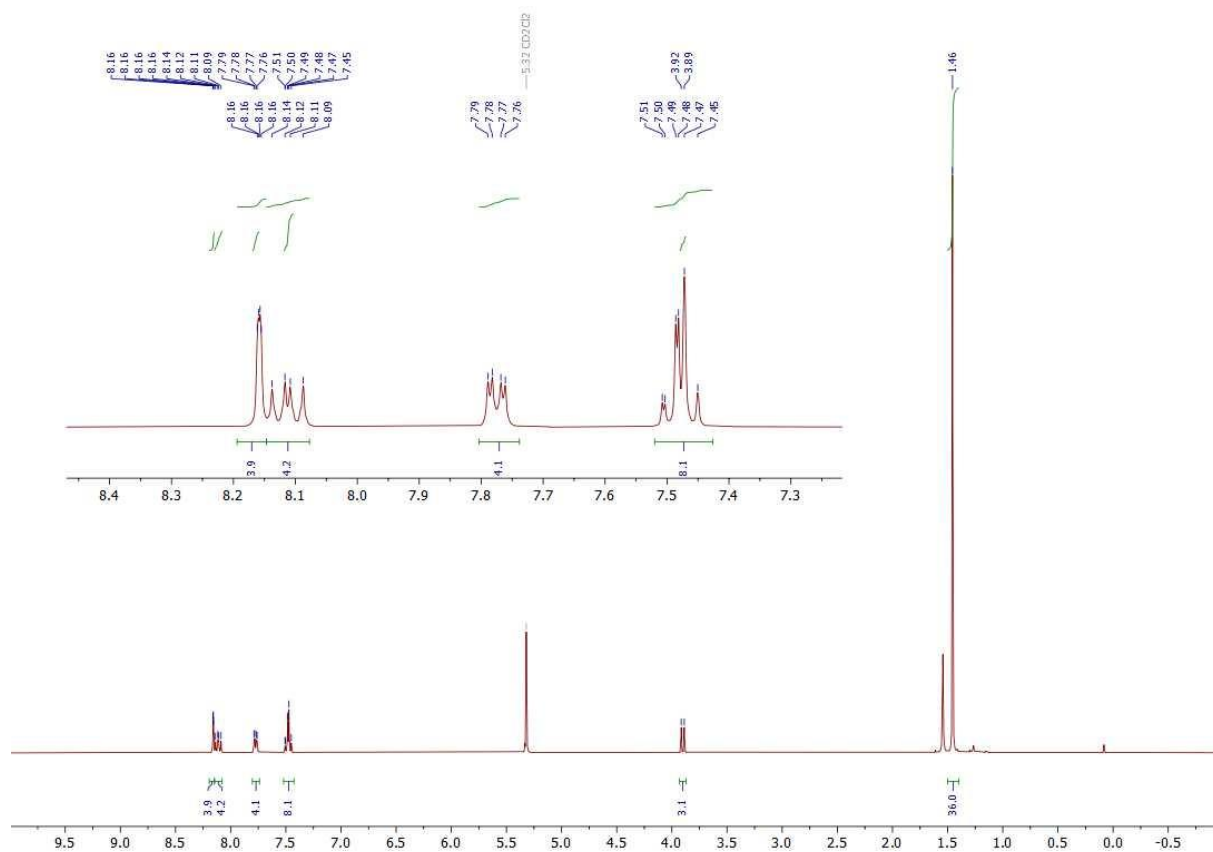


Fig. S10: <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>31</sup>P NMR (162 MHz) NMR spectra of **7** in CD<sub>2</sub>Cl<sub>2</sub>.





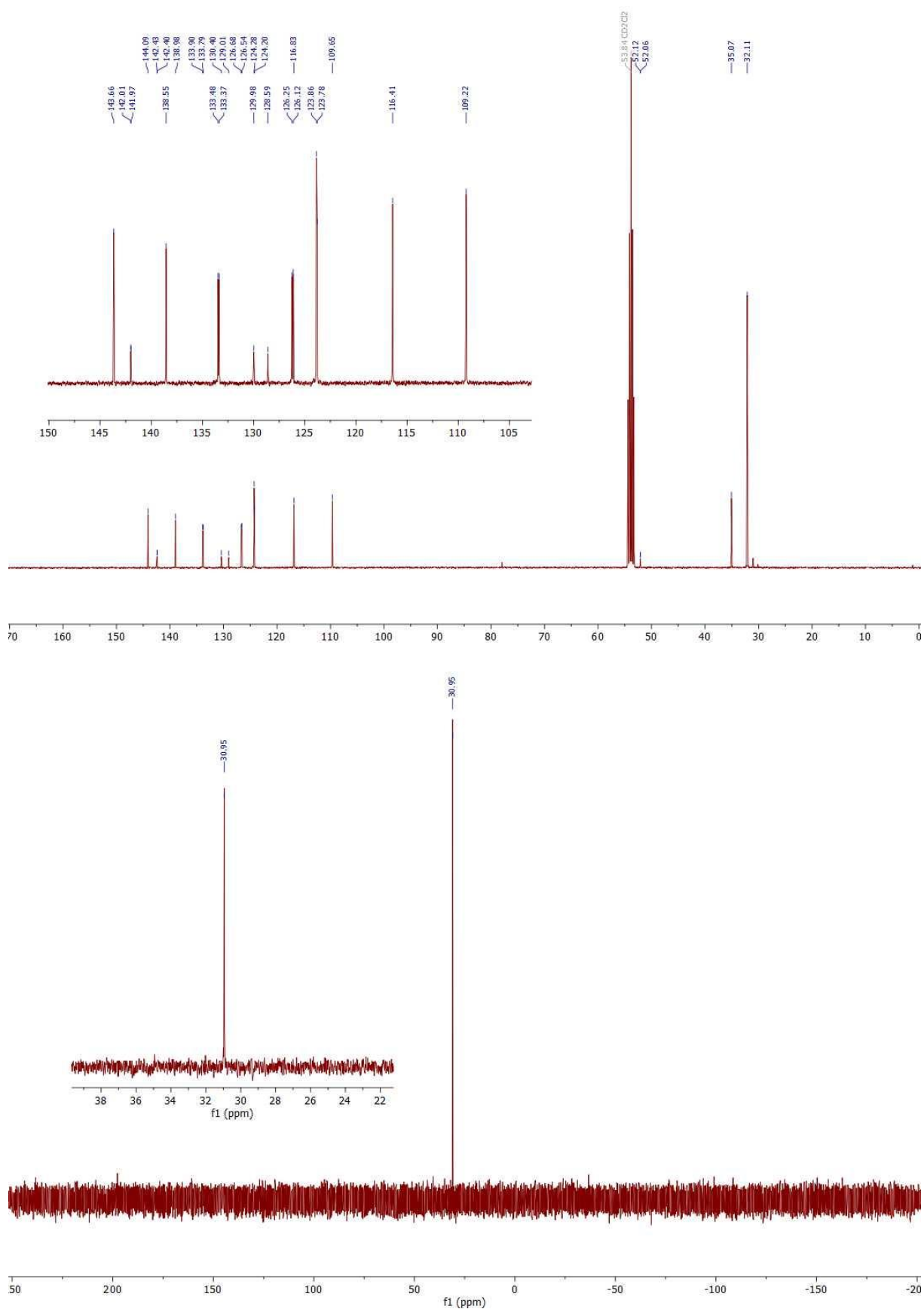
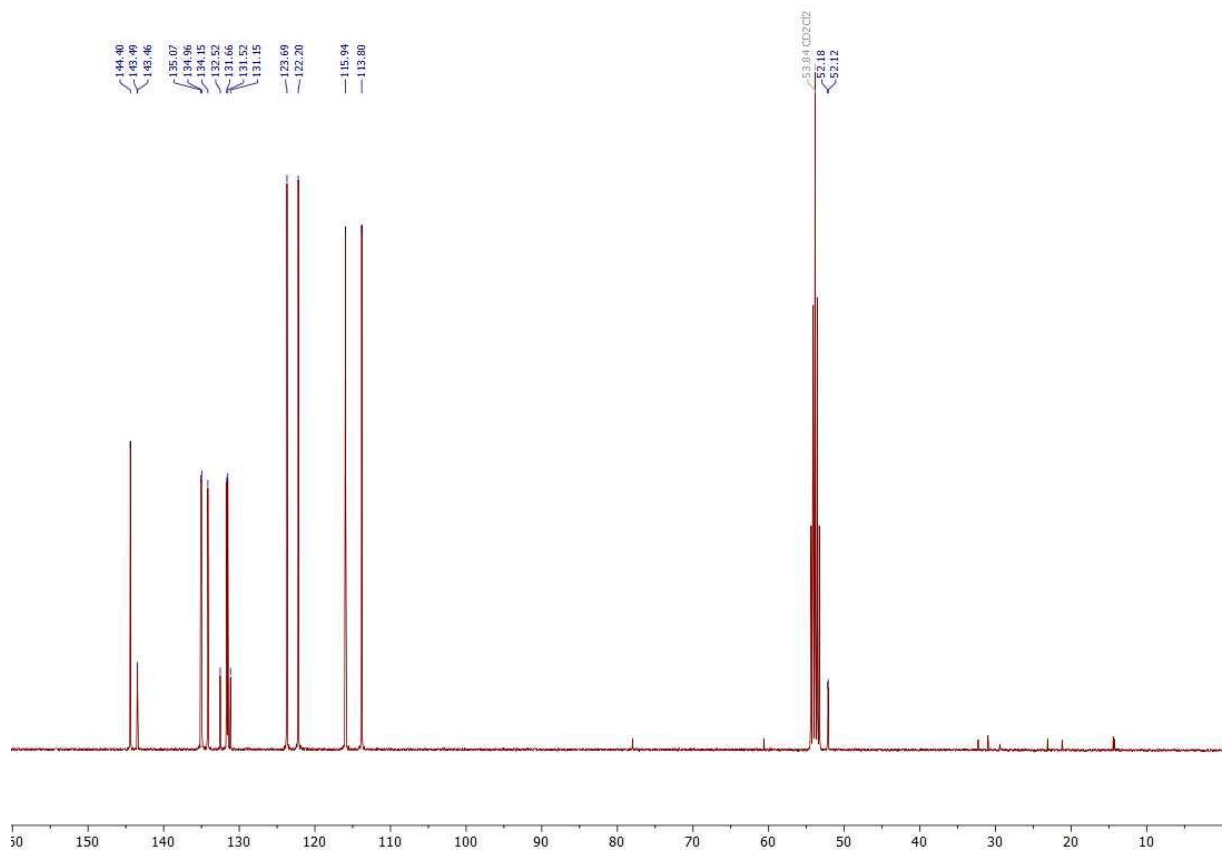
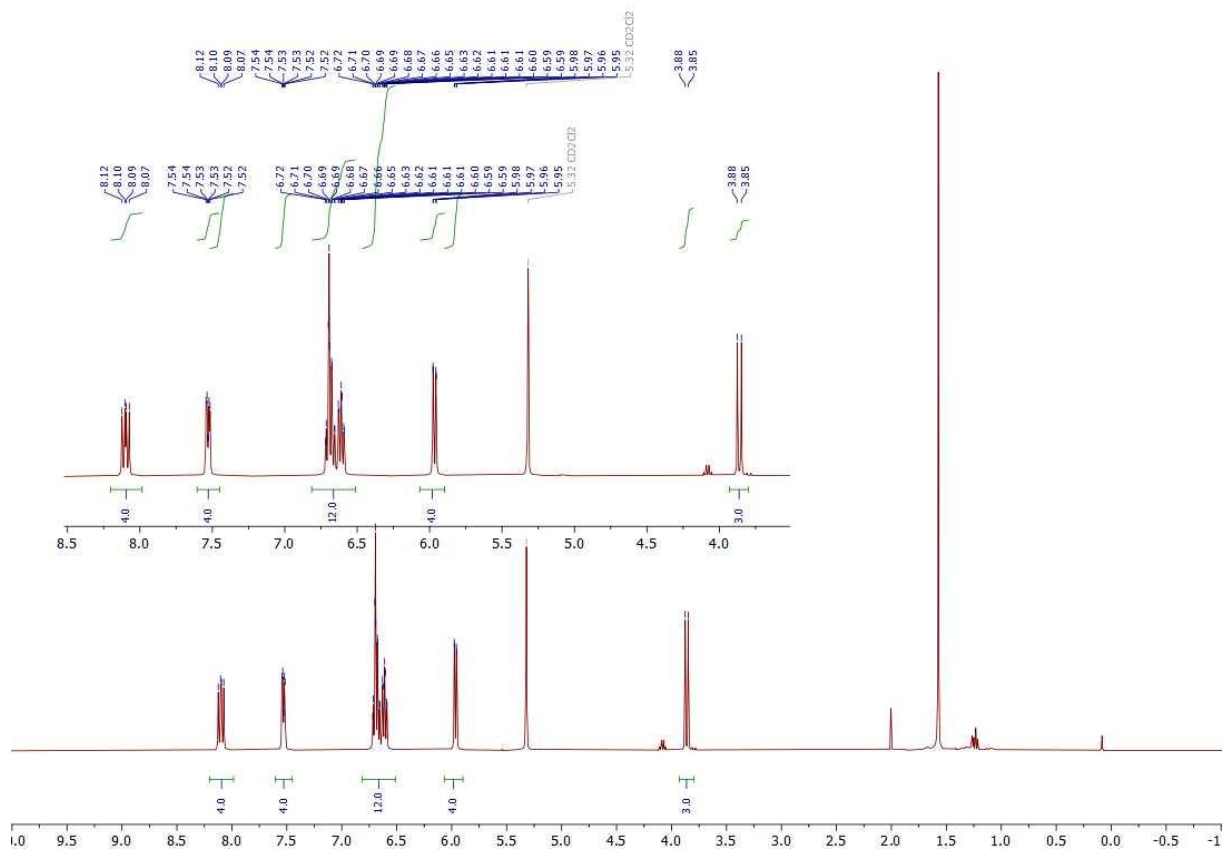


Fig. S11: <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>31</sup>P NMR (162 MHz) NMR spectra of **8** in CD<sub>2</sub>Cl<sub>2</sub>.



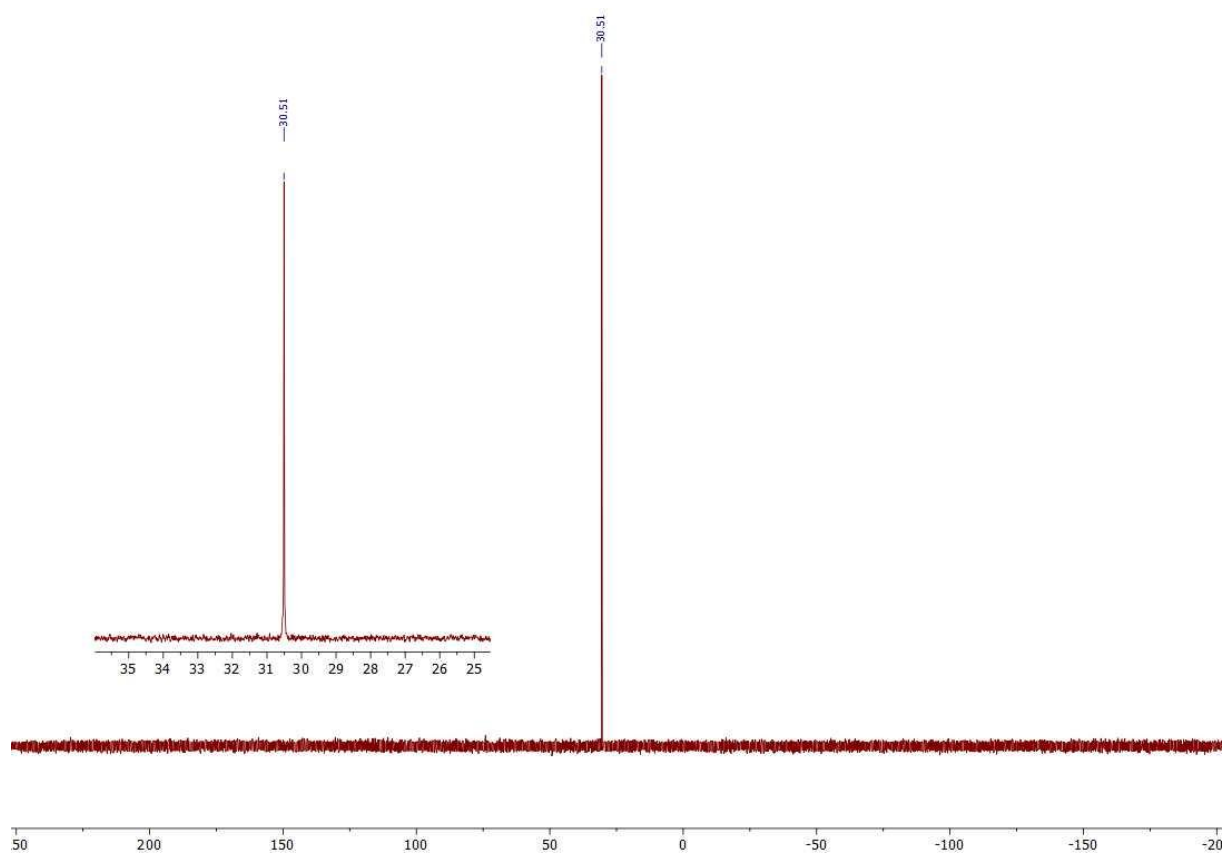


Fig. S12: <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>31</sup>P NMR (162 MHz) NMR spectra of **9** in CD<sub>2</sub>Cl<sub>2</sub>.