Supporting information
Photoredox Synthesis of 6-and 7-Membered Ring Scaffolds via N-Centered Radicals

William Boiledieu, Maxime De Abreu, Claire Cuyamendous, Diana Lamaa, Philippe Belmont and Etienne Brachet

Université Paris Cité, UMR 8038 CNRS, Faculté de Pharmacie, F-75006 Paris, France.
etienne.brachet@u-paris.fr

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General Informations

$^1$H NMR, $^{13}$C NMR, $^{31}$P NMR and $^{19}$F NMR spectra were recorded on Bruker Avance 300 or 400 MHz spectrometers. For the $^1$H NMR, the peak due to residual CDCl$_3$ was used as internal reference (fixed at 7.26 ppm). NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, bs = broad signal), and coupling constants $J$ (Hz) and number of protons (for $^1$H NMR). For the $^{13}$C NMR, the triplet due to residual CDCl$_3$ was used as internal reference (fixed at 77.16 ppm). Mass spectra were obtained by positive electrospray ionization method. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254. Visualization was accomplished with short wavelength UV light (254 and 365 nm). Standard flash chromatography was performed using silica gel of particle size 40–63 μm. Photocatalysts were purchased from Aldrich, TCI, and used without any further purification or synthesized as reported in literature. All other commercially available reagents and solvents were used without further purification.
Description of the Visible-Light catalysis apparatus

Our Visible-Light catalysis apparatus consists in an aluminium block in which circulates the cooling fluid linked to the cooling system set at 20°C. The block contains 6 holes and each hole contain a 18W 455 nm LED Cree® XLamp® XT-E Royal Blue LEDs (λ = 455 nm (± 5 nm), 12 V, 1.5 A. The sample are irradiated with a LED through the vial’s plane bottom side at a distance of 1 cm. The vials used are WICOM 20mm Crimp Top Vial, 5ml, 38.5mm x 22.0mm, clear. This apparatus is installed on a magnetic stirrer, as shown on the following scheme and picture.

![Figure 1 - Sketch of the Visible Light catalysis apparatus](image)
Figure 2 - Picture of the Visible Light catalysis apparatus
Protocol of cyclic voltammetry experiments

The redox potentials have been measured by cyclic voltammetry using a glassy-carbon electrode in a $10^{-3}$ M solution of phosphonohydrazones (1 eq.) with 3 eq. of potassium hydroxide, in degassed mixture of methanol. Scan rate: 0.1 V/s, Saturated Calomel Electrode (SCE) used as reference electrode, platinum wire as counter electrode and LiClO$_4$ (0.05 M) as the supporting electrolyte. The cyclic voltammogram were treated using Nova 1.6 software. In the presence of 3 eq. of base, it is worth noting that the oxidation potential corresponds to the anionic form of the starting material.
The redox potentials have also been measured in the absence of KOH (base), using a glassy carbon electrode in a 10^{-3}M solution of phosphonohydrazone (1 eq.), in degassed mixture of methanol. Scan rate: 0.1 V/s, Saturated Calomel Electrode (SCE) used as reference electrode, platinum wire as counter electrode and LiClO\(_4\) (0.05 M) as the supporting electrolyte. Without base, no oxidation potentials are observed under \(E_{\text{Ox}} = 0.77\)V vs. SCE which is the potential of the used photocatalyst thus indicates that the base is crucial to have cyclisation. The base is generating the N-anion intermediate which has a lower oxidation potential, this N-anion can be oxidized by the photocatalyst.
Optimization of the reaction conditions

![Chemical structures and conditions](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>V_{(solvent)}</th>
<th>Photocat. (PC)</th>
<th>PC %</th>
<th>Base</th>
<th>Base eq.</th>
<th>Light</th>
<th>Ratio (6MR):(7MR)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$(PF$_6$)$_2$</td>
<td>2,5</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>35% (isolated)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpz)$_2$(PF$_6$)$_2$</td>
<td>2,5</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Fukuzumi</td>
<td>5</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>(Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$</td>
<td>2</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>20% (isolated)</td>
</tr>
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<td>1 mL</td>
<td>Ru(phen)$_3$(PF$_6$)$_2$</td>
<td>2,5</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>26% (NMR)</td>
</tr>
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<td>Rhodamine</td>
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<td>tBuONa</td>
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<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Eosine Y</td>
<td>5</td>
<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>20% (NMR)</td>
</tr>
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<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
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<td>tBuONa</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>40% (NMR)</td>
</tr>
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<td>tBuONa</td>
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<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN</td>
<td>2 mL</td>
<td>Ru cat. on Silica</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>Eosine Y</td>
<td>5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>(Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$</td>
<td>1</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>(Ir[dF(CF$_3$)ppy]$_2$(bpy))PF$_6$</td>
<td>1</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>Ir(p-F-ppy)$_3$</td>
<td>1</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Solvent</td>
<td>Volume</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>Conc.</td>
<td>Base</td>
<td>Volume</td>
<td>LED</td>
<td>Ratio</td>
<td>Yields (NMR)</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------</td>
<td>--------------------------</td>
<td>-------</td>
<td>------------</td>
<td>--------</td>
<td>-----------</td>
<td>-------</td>
<td>--------------</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>NaOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>40%</td>
</tr>
<tr>
<td>Methanol</td>
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<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>K$_2$CO$_3$</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>35% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>Pyridine</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>LiOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>38% (NMR)</td>
</tr>
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<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>46% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
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<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>CsOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>46% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
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<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>Cs$_2$CO$_3$</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>36% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>Na Acetate</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>NaHCO$_3$</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>LiHMDS</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>2.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>34% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>46% (NMR)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>5.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>38% (NMR)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>DMSO</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>DMF</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>THF</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (4:1)</td>
<td>0,6 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:4)</td>
<td>50% (NMR)</td>
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<td>Acetone</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>2,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Toluene</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H$_2$O (9:1)</td>
<td>0,5 mL</td>
<td>Ru(bpy)$_2$Cl$_2$6H$_2$O</td>
<td>2,5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:5)</td>
<td>56% (NMR)</td>
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<tr>
<td>H₂O</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>-----------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>----------</td>
<td>------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MeCN/MeOH (4:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H₂O (1:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1) 40% (NMR)</td>
<td></td>
</tr>
<tr>
<td>EtCN/H₂O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1) 28% (NMR)</td>
<td></td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H₂O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1) 14% (NMR)</td>
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</tr>
<tr>
<td>PhCN/H₂O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>MeNO₂/H₂O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>EtCN/H₂O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>DMSO/H₂O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H₂O (16:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1) 40% (NMR)</td>
<td></td>
</tr>
<tr>
<td>Butanone</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1) 48% (NMR)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>3 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>5 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>MeCN/H₂O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)₂Cl₂6H₂O</td>
<td>2.5</td>
<td>KOH</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:3) 62% (NMR)</td>
<td></td>
</tr>
</tbody>
</table>

**Photocatalyst additional 2.5 eq. added at mid time of the reaction**

<p>| PhCN/H₂O (9:1) | 0.5 mL | Ru(bpy)₂Cl₂6H₂O | 2.5 | KOH | 3.0 | Blue LED | (0:1) 27% (NMR) |             |
| EtCN/H₂O (9:1) | 0.5 mL | Ru(bpy)₂Cl₂6H₂O | 2.5 | KOH | 3.0 | Blue LED | (0:1) 30% (NMR) |             |
| EtCN/H₂O (9:1) | 0.5 mL | Ru(bpy)₂Cl₂6H₂O | 2.5 | KOH | 3.0 | Blue LED | (0:1) 21% (NMR) |             |
| H₂O/MeCN (1:2) | 0.5 mL | Ru(bpy)₂Cl₂6H₂O | 2.5 | KOH | 3.0 | Blue LED | (0:1) 16% (NMR) |             |
| MeCN/H₂O (9:1) | 2 mL   | Ru(bpy)₂Cl₂6H₂O | 2.5 | KOH | 3.0 | Blue LED | (1:3) 62% (NMR) |             |</p>
<table>
<thead>
<tr>
<th>Additive or Modification</th>
<th>Solvent</th>
<th>V_{(solvent)}</th>
<th>Photocat. (PC)</th>
<th>PC %</th>
<th>Base eq.</th>
<th>Light</th>
<th>Ratio (6MR):(7MR)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Sieve</td>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Without Light</td>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>No light</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>H2O 0.050 mL</td>
<td>Methanol/H_2O</td>
<td>1 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Without PhotoCat.</td>
<td>Methanol</td>
<td>1 mL</td>
<td>No photocatalyst !</td>
<td>0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>White LED Light</td>
<td>Methanol</td>
<td>1 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>White LED</td>
<td>(1:1)</td>
<td>48% (NMR)</td>
</tr>
<tr>
<td>KOH solution in MeOH</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>38% (NMR)</td>
</tr>
<tr>
<td>Hantzsch Ester 2eq.</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>18-Crown Ether 2eq.</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>44% (NMR)</td>
</tr>
<tr>
<td>Thiophenol 2eq.</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>silica 20 mg</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>17% (NMR)</td>
</tr>
<tr>
<td>Degas.</td>
<td>Methanol</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>50% (NMR)</td>
</tr>
<tr>
<td>silica 200 mg</td>
<td>MeCN</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>2 eq. Photocat.</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:1)</td>
<td>46% (NMR)</td>
</tr>
<tr>
<td>silica 200 mg</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>5.0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>silica 5 mg</td>
<td>MeCN</td>
<td>2 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>silica 50 mg</td>
<td>MeCN</td>
<td>2 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>silica 800 mg</td>
<td>MeCN</td>
<td>2 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>silica 100 mg</td>
<td>MeCN/H_2O (9:1)</td>
<td>2 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>NaClO4</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>15% (NMR)</td>
</tr>
<tr>
<td>Benzyl-N+Et3Cl-</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>15% (NMR)</td>
</tr>
<tr>
<td>Cyclohexadiene</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>25% (NMR)</td>
</tr>
<tr>
<td>Base 1eq./4h (x2)</td>
<td>MeCN/H_2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)_2Cl_2 6H_2O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(1:4)</td>
<td>65% (NMR)</td>
</tr>
<tr>
<td>Other Photocatalyst</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$(PF$_6$)$_2$</td>
<td>2,5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>(0:4)</td>
<td>48% (NMR)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>----------------</td>
<td>--------</td>
<td>------------------------</td>
<td>-----</td>
<td>-----</td>
<td>----------</td>
<td>-------</td>
<td>----------</td>
</tr>
<tr>
<td>Diphenyl Sulfide</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Other Photocatalyst</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Eosine Y</td>
<td>5.0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Other Photocatalyst</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>(Ir[dF(CF$_3$)ppy]$_2$(dtbppy))PF$_6$</td>
<td>1.0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Other Photocatalyst</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>(Ir[dF(CF$_3$)ppy]$_2$(bpy))PF$_6$</td>
<td>1.0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Other Photocatalyst</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ir(p-F-ppy)$_3$</td>
<td>1.0</td>
<td>3.0</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>Other PC / 1,5eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$(PF$_6$)$_2$</td>
<td>2.5</td>
<td>1.5</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>40% (NMR)</td>
</tr>
<tr>
<td>Other PC / 1eq./ 3W LED</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$(PF$_6$)$_2$</td>
<td>2.5</td>
<td>1.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>40% (NMR)</td>
</tr>
<tr>
<td>Other PC / 0,5eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$(PF$_6$)$_2$</td>
<td>2.5</td>
<td>0.5</td>
<td>Blue LED</td>
<td>/</td>
<td>0%</td>
</tr>
<tr>
<td>1,5eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>1.5</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>65% (NMR)</td>
</tr>
<tr>
<td>1eq. Base / 3W LED</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>1.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>30% (NMR)</td>
</tr>
<tr>
<td>0,5eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>0.5</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>15% (NMR)</td>
</tr>
<tr>
<td>at 0°C / 1eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>1.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>% (NMR)</td>
</tr>
<tr>
<td>at 40°C / 1eq. Base</td>
<td>MeCN/H2O (9:1)</td>
<td>0.5 mL</td>
<td>Ru(bpy)$_3$Cl$_2$6H$_2$O</td>
<td>2.5</td>
<td>1.0</td>
<td>Blue LED</td>
<td>(0:1)</td>
<td>47% (NMR)</td>
</tr>
</tbody>
</table>
**Study of water effect**

In order to understand the role of water, particularly for the protonation of the final compound, we have conducted two different deuteration reactions on compound 2:

- For the first one we have used ACN and deuterated water.

\[
\begin{align*}
\text{Ru(bpy)}_2\text{Cl}_2\cdot\text{6H}_2\text{O} & \quad \text{KOH 1.5 eq} \\
\text{MeCN:}D_2\text{O (9:1)} & \quad 20 \degree \text{C, 24h} \\
\text{blue LED} & \quad 26 \degree \text{C, 24h} \\
\hline
\text{2b-d} & \quad \text{(12\% deuteration)} \\
\text{2a-d} & \quad \text{(16\% deuteration)}
\end{align*}
\]

- For the second one, we have used, both, deuterated ACN and water.

\[
\begin{align*}
\text{Ru(bpy)}_2\text{Cl}_2\cdot\text{6H}_2\text{O} & \quad \text{KOH 1.5 eq} \\
\text{CD}_3\text{CN:}D_2\text{O (9:1)} & \quad 20 \degree \text{C, 24h} \\
\text{blue LED} & \quad 26 \degree \text{C, 24h} \\
\hline
\text{2b-d} & \quad \text{(57\% deuteration)} \\
\text{2a-d} & \quad \text{(69\% deuteration)}
\end{align*}
\]

- The first trial (only D$_2$O) gave us between 12\% and 16\% deuteration yield for both 7-endo and 6-exo compounds (2a and 2b). However, the second trial (with ACN-$d_3$ and D$_2$O) gave us a 69\% for the 7-endo(2a) and a 57\% for the 6-exo (2b). This seems to indicate that deuteration (protonation in the mechanism) may come from ACN-$d_3$ and D$_2$O.
All the aldehydes have been obtained by Heck reaction following the protocol described on the article from W. Zhang et al. *Tetrahedron*, 2019, 75, 2, 269-277; or by Barluenga reaction following the protocol described on the article from D. Lamaa et al. *J. Org. Chem.* 2020, 85, 21, 13664-13673.
General Procedure A: for the synthesis of phosphonohydrazones and characterization

To an oven-dried sealable glass vial were added aldehyde (1 equiv.), phosphonohydrazine (1.5 equiv.) and MeOH (0.8 M). The vial was sealed with 20mm crimp caps with silicone/PTFE septum and stirred at r.t. (for 2 to 4 hours) until completion of the reaction checked by TLC.

- In case of precipitation of phosphonohydrazone: Reaction medium was filtered using a Büchner funnel. The solid product was then dried under vacuum, characterized and used without any further purification.

- In case of no precipitation of phosphonohydrazone: the mixture was concentrated. The crude product was purified by silica gel column chromatography eluting with a cyclohexane/ethyl acetate mixture to afford the desired pur phosphonohydrazone.
List of phosphonohydrazones:

2', 75%
3', 47%
5', 54%
6', 57%
7', 56%
8', 53%
9', 77%
10', 68%
11', 60%
12', 78%
13', 86%
14', 46%
15', 54%
16', 34%
17', 65%
18', 72%
19', 82%
20', 55%
21', 87%
22', 38%
23', 81%
24', 78%
25', 74%
26', 88%
27', 65%
28', 31%
Diethyl (2-((E)-2-((E)-4-methylstyryl)benzylidene)hydrazineyl)phosphonate (2′):

The white solid (8.5 mmol, 3.2 g, 75% yield) was obtained following the general procedure A after 5 h starting from the aldehyde 2 (2.5 g, 11.3 mmol).

\[ R_f = 0.28 \text{ (Cyclohexane:Ethyl Acetate, 3:7) } \]

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \delta 8.40 (d, J = 28.2 Hz, NH), 8.24 (s, 1H), 7.73 (dd, J = 7.7, 1.5 Hz, 1H), 7.64 (d, J = 16.2 Hz, 1H), 7.61 – 7.58 (dd, J = 7.7, 1.2 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.29 – 7.23 (m, 1H, overlapped with CDCl}_3), 7.18 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 16.1 Hz, 1H), 4.29 – 4.11 (m, 4H), 2.37 (s, 3H), 1.33 (td, J = 7.1, 0.9 Hz, 6H). \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \delta 144.1 (d, J_{C-P} = 19.4 \text{ Hz, CN}), 137.8, 136.7, 134.7, 131.7, 131.6, 129.4 (2C), 129.2, 127.7, 127.4, 126.7 (2C), 126.6, 125.1, 63.4 (d, J_{C-P} = 5.7 \text{ Hz, 2C}), 21.3, 16.2 (d, J_{C-P} = 6.8 \text{ Hz, 2C}). \]

\[ ^31P \text{ NMR (121 MHz, CDCl}_3 \delta 1.95. \]

\[ \text{HR-MS (ESI) m/z: [M + K]+ Calcd for C}_{20}\text{H}_{25}\text{KN}_2\text{O}_3\text{P 411.1234; Found 411.1234.} \]

Diethyl(1(E)-2-(2-(1-phenylvinyl)benzylidene)hydrazineyl)phosphonate (3′):
The pale-yellow solid (0.80 mmol, 280 mg, 47 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 3 (350 mg, 1.7 mmol).

\( R_f = 0.24 \) (Cyclohexane:Ethyl Acetate, 5:5)

\( ^1H\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.00 – 7.93 (m, 1H), 7.68 (s, 1H), 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 5H, overlapped with CDCl\(_3\)), 7.24 – 7.20 (m, 1H), 6.86 (d, \( J = 27.4 \) Hz, NH), 5.87 (d, \( J = 0.7 \) Hz, 1H), 5.22 (d, \( J = 0.7 \) Hz, 1H), 4.19 – 3.99 (m, 4H), 1.30 (t, \( J = 7.1 \) Hz, 6H).

\( ^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 147.1, 143.7 (d, \( J_{C-P} = 18.5 \) Hz, CN), 141.2, 140.6, 132.3, 130.3, 129.2, 128.5 (2C), 128.0, 127.8, 126.7 (2C), 125.7, 116.7, 63.3 (d, \( J_{C-P} = 5.5 \) Hz, 2C), 16.3 (d, \( J_{C-P} = 6.9 \) Hz, 2C).

\( ^{31}P\) NMR (121 MHz, CDCl\(_3\)) \( \delta \) 1.10.

HR-MS (ESI) \( m/z \): [M + H]+ Calcd for C\(_{19}\)H\(_{24}\)N\(_2\)O\(_3\)P 359.1519; Found 359.1513.

Diethyl(2-((E)-2-((E)-1-phenylpent-1-en-1-yl)benzylidene)hydrazineyl) phosphonate (4’):

The pale-yellow solid (0.4 mmol, 158 mg, 47 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 4 (210 mg, 0.8 mmol).

\( R_f = 0.54 \) (Cyclohexane:Ethyl Acetate, 4:6)

\( ^1H\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.02 – 7.98 (m, 1H), 7.66 (s, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.22 (m, 3H), 7.22 – 7.15 (m, 3H), 7.13 – 7.09 (m, 1H), 6.75 (d, \( J = 27.7 \) Hz,
NH), 6.31 (t, J = 7.4 Hz, 1H), 4.22 – 4.02 (m, 4H), 1.89 (q, J = 7.3 Hz, 2H), 1.42 (h, J = 7.3 Hz, 2H), 1.31 (td, J = 7.1, 0.9 Hz, 6H), 0.85 (t, J = 7.4 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.6 (d, $J_{C-P} = 18.3$ Hz, CN), 141.4, 139.4, 138.5, 132.5, 131.5, 130.5, 129.4, 128.4 (2C), 127.5, 127.1, 126.3 (2C), 125.5, 63.4 (d, $J_{C-P} = 5.6$ Hz, 2C), 32.0, 22.6, 16.1 (d, $J_{C-P} = 6.8$ Hz, 2C), 13.9.

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 0.96.

HR-MS (ESI) m/z: [M + H]+ Calcd for C$_{22}$H$_{30}$N$_2$O$_3$P 401.1989; Found 401.1992.

Tetraethyl(4,4'-bis(4-methoxyphenyl)-4',5,5'-tetrahydro-3H,3'H-[5,5'-bibenzo[d][1,2]diazepine]-3,3'-diyl)bis(phosphonate) (5'):

The pale-yellow solid (0.9 mmol, 357 mg, 54 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 5 (400 mg, 1.7 mmol).

R$_f$ = 0.28 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.18 (s, 1H), 7.84 (d, J = 27.4 Hz, 1H), 7.72 (dd, J = 7.7, 1.4 Hz, 1H), 7.57 (dd, J = 7.8, 1.2 Hz, 1H), 7.55 – 7.46 (m, included 7.52 (d, J = 16.1 Hz, 1H) + 7.48 (d, J = 8.5 Hz, 2H)), 7.33 (td, J = 7.4, 1.3 Hz, 1H), 7.25 (td, J = 7.5, 1.3 Hz, 1H, overlap with CDCl$_3$), 6.95 – 6.88 (m, 3H), 4.27 – 4.12 (m, 4H), 3.83 (s, 3H), 1.33 (td, J = 7.1, 0.9 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.5, 144.0 (d, $J_{C-P} = 19.1$ Hz, CN), 136.9, 131.5, 131.3, 130.2, 129.3, 128.0 (2C), 127.6, 127.2, 126.5, 123.9, 114.1 (2C), 63.5 (d, $J_{C-P} = 5.7$ Hz, 2C), 55.3, 16.2 (d, $J_{C-P} = 6.8$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.55.
**HR-MS (ESI) m/z:** [M + Na]+ Calcd for C_{20}H_{25}N_{2}NaO_{4}P 411.1444; Found 411.1446.

Diethyl(2-((E)-2-((E)-3,5-dimethoxystyryl)benzyldene)hydrazineyl) phosphonate (6’):

![Chemical structure](image)

The brown oil (4.4 mmol, 1.85 g, 59 % yield) was obtained following the general procedure A after 10 h starting from the aldehyde 6 (2 g, 7.5 mmol).

**Rf** = 0.33 (Cyclohexane:Ethyl Acetate, 5:5)

**\(^1\)H NMR** (300 MHz, CDCl\(_3\)) \(\delta\) 8.29 (d, \(J = 28.3\) Hz, NH), 8.21 (s, 1H), 7.72 (dd, \(J = 7.5, 1.5\) Hz, 1H), 7.66 (d, \(J = 16.1\) Hz, 1H), 7.60 – 7.55 (m, 1H), 7.37 – 7.23 (m, 2H), 6.89 (d, \(J = 16.0\) Hz, 1H), 6.70 (d, \(J = 2.2\) Hz, 2H), 6.41 (t, \(J = 2.2\) Hz, 1H), 4.27 – 4.08 (m, 4H), 3.83 (s, 6H), 1.31 (t, \(J = 7.1\) Hz, 6H).

**\(^{13}\)C NMR** (75 MHz, CDCl\(_3\)) \(\delta\) 161.1 (2C), 143.9 (d, \(J_{C-P} = 19.3\) Hz, CN), 139.4, 136.4, 131.9, 131.7, 129.3, 127.7, 127.7, 126.8, 126.6, 104.9 (2C), 100.2, 63.5 (d, \(J_{C-P} = 5.7\) Hz, 2C), 55.4, 16.2 (d, \(J_{C-P} = 6.8\) Hz, 2C).

**\(^{31}\)P NMR** (121 MHz, CDCl\(_3\)) \(\delta\) 1.80.

**HR-MS (ESI) m/z:** [M + Na]+ Calcd for C_{21}H_{27}N_{2}NaO_{5}P 441.1550; Found 441.1552.
Diethyl(2-((E)-2-((E)-3,4,5-trimethoxystyryl)benzylidene)hydrazineyl)phosphonate (7):

The white solid (1.5 mmol, 653 mg, 56 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 7 (1.2 g, 2.7 mmol).

\( R_f = 0.28 \) (Cyclohexane:Ethyl Acetate, 1:9)

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \( \delta \) 8.10 (s, 1H), 7.73 (d, \( J = 7.2 \) Hz, 1H), 7.59 – 7.51 (m, 2H), 7.39 – 7.28 (m, 2H), 6.88 (d, \( J = 16.0 \) Hz, 1H), 6.76 (s, 2H), 4.27 – 4.11 (m, 4H), 3.93 (s, 6H), 3.88 (s, 3H), 1.33 (t, \( J = 7.0 \) Hz, 6H).

\(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) \( \delta \) 153.5 (2C), 143.9 (d, \( J_{C-P} = 19.1 \) Hz, CN), 138.3, 136.5, 133.1, 132.0, 131.5, 129.3, 127.7, 127.6, 126.8, 125.5, 103.9 (2C), 63.5 (d, \( J_{C-P} = 5.5 \) Hz, 2C), 61.0, 56.3 (2C), 16.2 (d, \( J_{C-P} = 6.9 \) Hz, 2C).

\(^{31}\text{P NMR}\) (121 MHz, CDCl\(_3\)) \( \delta \) 1.10.

HR-MS (ESI) \( m/z \): [M + H]+ Calcd for C\(_{22}\)H\(_{30}\)N\(_2\)O\(_6\)P 449.1836; Found 449.1836.

Diethyl (2-((E)-2-((E)-4-fluorostyryl)benzylidene)hydrazineyl)phosphonate (8'):
The pale yellow solid (0.66 mmol, 247 mg, 53 % yield) was obtained following the general procedure A after 6 h starting from the aldehyde 8 (280 mg, 1.2 mmol).

Rf = 0.32 (Cyclohexane:Ethyl Acetate, 4:6)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.08 (s, 1H), 7.72 – 7.68 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 (s, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H), 7.06 (t, \(J = 8.7\) Hz, 2H), 6.92 (d, \(J = 16.1\) Hz, 1H), 4.29 – 4.10 (m, 4H), 1.34 (t, \(J = 7.1\) Hz, 6H) 7.72 – 7.68 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.5 (d, \(J_{CF} = 247.6\) Hz, 1C), 144.2 (d, \(J_{CP} = 19.5\) Hz, CN), 136.4, 133.7 (d, \(J_{CF} = 3.3\) Hz, 1C), 131.7, 130.4, 129.2, 128.3 (d, \(J_{CF} = 8.0\) Hz, 2C), 127.9, 127.6, 126.7, 126.3 (d, \(J_{CF} = 2.29\) Hz, 1C), 115.6 (d, \(J_{CF} = 21.6\) Hz, 2C), 63.5 (d, \(J_{CP} = 5.7\) Hz, 2C), 16.2 (d, \(J_{CP} = 6.8\) Hz, 2C).

\(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \(\delta\) 1.05.

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -113.71.

HR-MS (ESI) \(m/z\): [M + Na]+ Calcd for \(C_{19}H_{22}FN_2NaO_3P\) 399.1244; Found 399.1247.

Methyl4-((E)-2-((E)-(2-(diethoxyphosphoryl)hydrazineylidene)methyl)styryl) benzoate (9’):
The white solid (0.72 mmol, 301 mg, 77 % yield) was obtained following the general procedure A after 2 h starting from the aldehyde 9 (250 mg, 0.9 mmol).

\[ \text{Rf} = 0.26 \text{ (Cyclohexane:Ethyl Acetate, 4:6)} \]

\[ ^1H \text{ NMR (300 MHz, CDCl}_3\] \( \delta \) 8.15 (s, 1H), 8.06 – 8.00 (m, 2H), 7.86 (d, \( J = 16.2 \text{ Hz, 1H} \)), 7.69 (dd, \( J = 7.5, 1.7 \text{ Hz, 1H} \)), 7.64 – 7.57 (m, 3H), 7.33 (pd, \( J = 7.3, 1.6 \text{ Hz, 2H} \)), 6.99 (d, \( J = 16.2 \text{ Hz, 1H} \)), 4.27 – 4.11 (m, 4H), 3.93 (s, 3H), 1.32 (td, \( J = 7.1, 0.9 \text{ Hz, 6H} \)).

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3\] \( \delta \) 166.9, 143.9 (d, \( J_{CP} = 19.0 \text{ Hz, CN} \)), 141.9, 136.0, 131.8, 130.5, 130.0 (2C), 129.3, 129.1, 129.1, 128.3, 128.1, 126.9, 126.6 (2C), 63.5 (d, \( J_{CP} = 5.7 \text{ Hz, 2C} \)), 52.1, 16.2 (d, \( J_{CP} = 6.8 \text{ Hz, 2C} \)).

\[ ^{31}P \text{ NMR (121 MHz, CDCl}_3\] \( \delta \) 1.45.

\[ \text{HR-MS (ESI) m/z: [M + Na]+ Calcd for C}_{21}\text{H}_{25}\text{N}_{2}\text{NaO}_{5}\text{P 439.1393; Found 439.1394.} \]

Diethyl(2-(((E))-2-(((E))-4-cyanostyryl)benzylidene)hydrazineyl)phosphonate (10'):

The white solid (0.73 mmol, 278 mg, 68 % yield) was obtained following the general procedure A after 15 h starting from the aldehyde 10 (250 mg, 1.1 mmol).

\[ \text{Rf} = 0.25 \text{ (Cyclohexane:Ethyl Acetate, 5:5)} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\] \( \delta \) 8.07 (s, 1H), 7.69-7.58 (m,6H), 7.63 (d, \( J = 4.7 \text{ Hz, 6H} \)), 7.40 – 7.31 (m, 2H), 6.95 (d, \( J = 16.1 \text{ Hz, 1H} \)), 4.30 – 4.08 (m, 4H), 1.32 (t, \( J = 7.1 \text{ Hz, 6H} \)).
\[ ^{13}\text{C NMR} \ (75 \text{ MHz}, \text{CDCl}_3) \delta \ 143.9 \ (d, J_{C-P} = 18.7 \text{ Hz}, \text{CN}), \ 142.0, \ 135.6, \ 132.5 \ (2\text{C}), \ 131.7, \ 130.6, \ 129.6, \ 129.5, \ 128.7, \ 128.5, \ 127.2 \ (2\text{C}), \ 127.0, \ 119.0, \ 110.9, \ 63.6 \ (d, J_{C-P} = 5.6 \text{ Hz}, \ 2\text{C}), \ 16.2 \ (d, J_{C-P} = 6.8 \text{ Hz}, \ 2\text{C}). \]

\[ ^{31}\text{P NMR} \ (121 \text{ MHz}, \text{CDCl}_3) \delta \ 1.19. \]

HR-MS (ESI) \( m/z \): \[ [M + \text{Na}]^+ \text{ Calcd for } \text{C}_{20}\text{H}_{22}\text{N}_{3}\text{NaO}_{3}\text{P} \ 406.1291; \text{ Found } 406.1291. \]

Diethyl (2-((E)-2-((E)-2-nitrostyryl)benzylidene)hydrazineyl)phosphonate (11'):

The yellow solid (1.2 mmol, 484 mg, 60 % yield) was obtained following the general procedure A after 16 h starting from the aldehyde 11 (500 mg, 2.0 mmol).

\( R_f = 0.20 \) (Cyclohexane:Ethyl Acetate, 5:5)

\[ ^{1}\text{H NMR} \ (300 \text{ MHz}, \text{CDCl}_3) \delta \ 8.06 \ (s, \text{1H}), \ 8.00 \ (d, J = 7.9 \text{ Hz}, \text{1H}), \ 7.88 \ (d, J = 7.3 \text{ Hz}, \text{1H}), \ 7.75 - 7.58 \ (m, \text{4H}), \ 7.48 - 7.41 \ (m, \text{2H}), \ 7.37 \ (t, J = 7.0 \text{ Hz}, \text{2H}), \ 7.07 \ (d, J = 27.1 \text{ Hz}, \text{1H}, \text{NH}), \ 4.29 - 4.10 \ (m, \text{4H}), \ 1.33 \ (t, J = 7.1 \text{ Hz}, \text{6H}). \]

\[ ^{13}\text{C NMR} \ (101 \text{ MHz}, \text{CDCl}_3) \delta \ 148.0, \ 144.2 \ (d, J_{C-P} = 19.0 \text{ Hz}, \text{CN}), \ 135.8, \ 133.3, \ 133.2, \ 132.0, \ 131.7, \ 129.5, \ 129.0, \ 128.5, \ 128.3, \ 128.2, \ 127.6, \ 126.8, \ 124.7, \ 63.5 \ (d, J_{C-P} = 5.5 \text{ Hz}, \ 2\text{C}), \ 16.2 \ (d, J_{C-P} = 6.9 \text{ Hz}, \ 2\text{C}). \]

\[ ^{31}\text{P NMR} \ (121 \text{ MHz}, \text{CDCl}_3) \delta \ 1.50. \]

HR-MS (ESI) \( m/z \): \[ [M + K]^+ \text{ Calcd for } \text{C}_{19}\text{H}_{22}\text{KN}_{3}\text{O}_{5}\text{P} \ 442.0929; \text{ Found } 442.0929. \]
Diethyl(2-((E)-2-((E)-2-(pyridin-2-yl)vinyl)benzylidene)hydrazineyl) phosphonate (12’):

The orange oil (2.4 mmol, 869 mg, 78 % yield) was obtained following the general procedure A after 22 h starting from the aldehyde 12 (650 mg, 3.1 mmol).

\[ R_f = 0.72 \text{ (Methanol:Ethyl Acetate, 1:9)} \]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 8.63 – 8.57 (m, 1H), 8.24 (s, 1H), 8.12 (d, \(J = 15.9\) Hz, 1H), 7.79 (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.72 – 7.60 (m, 2H), 7.44 (d, \(J = 7.9\) Hz, 1H), 7.33 (pd, \(J = 7.3, 1.5\) Hz, 2H), 7.18 (ddd, \(J = 7.5, 4.9, 1.1\) Hz, 1H), 7.04 (d, \(J = 15.9\) Hz, 1H), 4.27 – 4.11 (m, 4H), 1.33 (td, \(J = 7.1, 0.9\) Hz, 6H).

\(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) 155.4, 149.4, 143.2 (d, \(J_{C-P} = 18.9\) Hz, CN), 136.8, 135.7, 132.1, 130.8, 130.1, 129.4, 128.3, 127.4, 126.9, 122.4, 122.4, 63.5 (d, \(J_{C-P} = 5.7\) Hz, 2C), 16.2 (d, \(J_{C-P} = 6.8\) Hz, 2C).

\(^{31}\text{P NMR}\) (121 MHz, CDCl\(_3\)) \(\delta\) 1.16.

**HR-MS (ESI) m/z**: [M + H]+ Calcd for C\(_{18}\)H\(_{23}\)N\(_3\)O\(_3\)P 360.1472; Found 360.1475.

diethyl(2-((E)-2-((E)-2-(pyridin-4-yl)vinyl)benzylidene)hydrazineyl) phosphonate (13’):
The brown solid (1.6 mmol, 587 mg, 86 % yield) was obtained following the general procedure A after 22 h starting from the aldehyde 13 (400 mg, 1.9 mmol).

Rf = 0.42 (Methanol:Ethyl Acetate, 1:9)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, $J = 5.3$ Hz, 2H), 8.12 – 8.02 (m, 2H), 7.71 – 7.59 (m, 2H), 7.48 (m, $J = 5.7$ Hz, 2H), 7.38 (m, $J = 6.5$, 4.2, 2.4 Hz, 2H), 6.90 (d, $J = 16.2$ Hz, 1H), 4.28 – 4.09 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.6 (2C), 145.4, 144.1 (d, $J_{C-P} = 19.9$ Hz, CN), 135.1, 132.3, 131.9, 129.2, 128.6, 128.3, 128.3, 126.9, 126.9, 121.3 (2C), 63.4 (d, $J_{C-P} = 5.7$ Hz, 2C), 16.2 (d, $J_{C-P} = 6.8$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.40.

HR-MS (ESI) m/z: [M + H]+ Calcd for C$_{18}$H$_{23}$N$_{3}$O$_{3}$P 360.1472; Found 360.1472.

Diethyl (2-((E)-2-((E)-hex-1-en-1-yl)benzylidene)hydrazineyl)phosphonate (14$'$):

The yellow oil (1.2 mmol, 406 mg, 46 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 14 (500 mg, 2.6 mmol).
Rf = 0.23 (Cyclohexane:Ethyl Acetate, 5:5)

1H NMR (300 MHz, CDCl₃) δ 8.11 (s, 1H), 7.76 (dd, J = 7.7, 1.5 Hz, 1H), 7.66 (d, J = 27.2 Hz, NH), 7.39 (dd, J = 7.7, 1.3 Hz, 1H), 7.27 (td, J = 7.5, 1.6 Hz, 1H), 7.20 (td, J = 7.5, 1.5 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 15.6, 6.9 Hz, 1H), 4.30 – 4.11 (m, 4H), 2.24 (qd, J = 7.2, 1.4 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.43 – 1.34 (m, 8H), 0.94 (t, J = 7.2 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 143.4 (d, J_C-P = 18.8 Hz, CN), 137.3, 135.2, 130.8, 129.2, 126.9 (d, J_C-P = 3.3 Hz, 1C), 126.6, 126.5, 63.4 (d, J_C-P = 5.6 Hz, 2C), 33.0, 31.4, 22.3, 16.2 (d, J_C-P = 6.9 Hz, 2C), 14.0.

31P NMR (162 MHz, CDCl₃) δ 1.70.

HR-MS (ESI) m/z: [M + H]+ Calcd for C₁₇H₂₈N₂O₃P 339.1832; Found 339.1837.

Diethyl(2-((E)-2-((E)-oct-1-en-1-yl)benzylidene)hydrazineyl)phosphonate (15'):

The pale-yellow solid (0.8 mmol, 293 mg, 54 % yield) was obtained following the general procedure A after 16 h starting from the aldehyde 15 (300 mg, 1.4 mmol).

Rf = 0.24 (Cyclohexane:EtOAc, 5:5)

1H NMR (300 MHz, CDCl₃) δ 8.10 (s, 1H), 7.76 (dd, J = 7.7, 1.5 Hz, 1H), 7.55 (d, J = 27.5 Hz, NH), 7.39 (dd, J = 7.7, 1.5 Hz, 1H), 7.28 (td, J = 7.4, 1.5 Hz, 1H), 7.21 (td, J = 7.4, 1.4 Hz, 1H), 6.74 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 15.6, 6.9 Hz, 1H), 4.30 – 4.11 (m, 4H), 2.23 (qd, J = 7.3, 1.5 Hz, 2H), 1.47 (m, 2H), 1.37 (td, J = 7.1, 0.9 Hz, 8H), 1.34 – 1.29 (m, 4H), 0.94 – 0.86 (m, 3H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.4 (d, $J_{C-P} = 18.7$ Hz, CN), 137.3, 135.3, 130.9, 129.3, 127.0, 126.9, 126.6, 126.4, 63.5 (d, $J_{C-P} = 5.7$ Hz, 2C), 33.4, 31.8, 29.3, 29.0, 22.7, 16.2 (d, $J_{C-P} = 6.9$ Hz, 2C), 14.1.

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.31.

HR-MS (ESI) $m/z$: [M + H]+ Calcd for C$_{19}$H$_{32}$N$_2$O$_3$P 367.2145; Found 367.2146.

Diethyl($E$)-(2-(2-methyl-1-phenylprop-1-en-1-yl)benzylidene)hydrazineyl)phosphonate (16‘):

The pale-yellow solid (0.29 mmol, 112 mg, 34 % yield) was obtained following the general procedure A after 6 h starting from the aldehyde 16 (200 mg, 0.85 mmol).

Rf = 0.27 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.98 – 7.94 (m, 2H), 7.32 – 7.20 (m, 4H, overlapped with CDCl$_3$), 7.19 – 7.09 (m, 4H), 4.28 – 4.12 (m, 4H), 1.96 (s, 3H), 1.66 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.3 (d, $J_{C-P} = 18.4$ Hz, CN), 142.9, 142.1, 134.0, 133.5, 132.2, 130.5, 129.5 (2C), 129.3, 128.0 (2C), 126.9, 126.3, 125.5, 63.4 (d, $J_{C-P} = 5.6$ Hz, 2C), 22.7, 21.9, 16.2 (d, $J_{C-P} = 6.9$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.29.

HR-MS (ESI) $m/z$: [M + H]+ Calcd for C$_{21}$H$_{28}$N$_2$O$_3$P 387.1832; Found 387.1836.
Diethyl(2-((E)-(1-((E)-4-methylstyril)naphthalen-2-yl)methylene)hydrazineyl) phosphonate (17'):

\[
\text{H}^\text{NMR} (300 MHz, CDCl}_3 \ \delta 8.25 (s, 1H), 8.15 - 8.07 (m, 2H), 7.87 - 7.80 (m, 1H),
7.75 (d, J = 8.7 Hz, 1H), 7.55 - 7.46 (m, 5H), 7.24 (d, J = 7.9 Hz, 2H, overlapped with CDCl}_3),
7.17 (d, J = 27.3 Hz, NH), 6.67 (d, J = 16.4 Hz, 1H), 4.26 - 4.12 (m, 4H), 2.41 (s, 3H), 1.36 (t, J = 7.1, 6H).
\]

\[
\text{C}^\text{NMR} (101 MHz, CDCl}_3 \ \delta 144.6 (d, J_{CP} = 18.5 Hz, CN), 138.4, 137.9, 135.7,
133.9, 133.8, 132.3, 129.6 (2C), 129.4, 128.3, 127.6, 126.7, 126.6 (2C), 126.4,
125.6, 123.4, 122.5, 63.5 (d, J_{CP} = 5.6 Hz, 2C), 21.3, 16.2 (d, J_{CP} = 6.8 Hz, 2C).
\]

\[
\text{P}^\text{NMR} (121 MHz, CDCl}_3 \ \delta 1.27.
\]

\[
\text{HR-MS (ESI)} m/z: [M + H]^+ \text{ Calcd for } C_{24}H_{28}N_2O_3P 423.1832; \text{ Found } 423.1837.
\]

Diethyl(2-((E)-3,4,5-trimethoxy-2-((E)-4-methylstyril)benzylidene) hydrazineyl) phosphonate (18'):
The white solid (1.0 mmol, 480 mg, 72 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 18 (450 mg, 1.4 mmol).

Rf = 0.20 (Cyclohexane:Ethyl Acetate, 5:5)

\( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.98 (s, 1H), 7.40 (d, \( J = 8.1 \) Hz, 2H), 7.22 (d, \( J = 11.4 \) Hz, 2H), 7.20 – 7.12 (m, 2H), 6.68 – 6.56 (m, 1H), 4.28 – 4.13 (m, 4H), 3.95 – 3.90 (m, 6H), 3.83 (s, 3H), 2.38 (s, 3H), 1.37 (t, \( J = 7.1 \) Hz, 6H).

\( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 152.6, 151.7, 144.5 (d, \( J_{C-P} = 18.5 \) Hz, CN), 143.4, 137.8, 135.6, 134.7, 129.4 (2C), 127.8, 126.5 (2C), 125.6, 120.3, 105.2, 63.3 (d, \( J_{C-P} = 5.2 \) Hz, 2C), 61.0, 60.9, 56.0, 21.2, 16.2 (d, \( J_{C-P} = 6.7 \) Hz, 2C).

\( ^{31}P \) NMR (121 MHz, CDCl\(_3\)) \( \delta \) 1.80.

HR-MS (ESI) \( m/z \): [M + K]+ Calcd for C\(_{23}\)H\(_{31}\)KN\(_2\)O\(_6\)P 501.1551; Found 501.1553.

Diethyl(2-((E)-2-((E)-4-methylstyryl)-5-(trifluoromethyl)benzylidene)hydrazineyl)phosphonate (19'):

![Chemical structure of 19']

The yellow solid (0.41 mmol, 603 mg, 82 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 19 (500 mg, 1.7 mmol).

Rf = 0.34 (Cyclohexane:Ethyl Acetate, 5:5)

\( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.17 (s, 1H), 7.98 (s, 1H), 7.83 (d, \( J = 27.6 \) Hz, NH), 7.68 (d, \( J = 8.1 \) Hz, 1H), 7.59 – 7.51 (m, 2H), 7.45 (d, \( J = 8.1 \) Hz, 2H), 7.19 (d, \( J = 8.2 \) Hz, 2H), 7.01 (d, \( J = 16.2 \) Hz, 1H), 4.28 – 4.13 (m, 4H), 2.38 (s, 3H), 1.35 (tt, \( J = 7.1, 0.8 \) Hz, 6H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.4 (d, $J_{C-P} = 19.2$ Hz, CN), 139.8, 138.6, 134.0, 134.0, 131.9, 129.5 (2C), 129.4 (q, $J_{C-F} = 32.7$ Hz, 1C), 127.1, 126.9 (2C), 125.5 (q, $J_{C-F} = 3.4$ Hz, 1C), 124.4 (q, $J_{C-F} = 3.8$ Hz, 1C), 124.0 (q, $J_{C-F} = 270$ Hz, CF$_3$), 123.6, 63.7 (d, $J_{C-P} = 5.7$ Hz, 2C), 21.4, 16.2 (d, $J_{C-P} = 6.8$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 0.96.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -62.66.

HR-MS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{21}$H$_{25}$F$_3$N$_2$O$_3$P 441.1549; Found 441.1550.

Diethyl (2-((E)-5-fluoro-2-((E)-4-methylstyrlyl)benzylidene)hydrazineyl) phosphonate (20'):

The pale yellow solid (1.1 mmol, 430 mg, 55% yield) was obtained following the general procedure A after 22 h starting from the aldehyde 20 (500 mg, 2 mmol).

$R_f$ = 0.28 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.08 (s, 1H), 7.56 – 7.46 (m, 2H), 7.43 – 7.36 (m, 3H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.04 (td, $J = 8.4$, 2.7 Hz, 1H), 6.86 (d, $J = 16.1$ Hz, 1H), 4.31 – 4.07 (m, 4H), 2.37 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.1 (d, $J_{C-P} = 246.5$ Hz, CN), 142.5 (d, $J_{C-P} = 19.8$ Hz, 1C), 137.9, 134.5, 133.6 (d, $J_{C-P} = 7.7$ Hz, 1C), 132.9 (d, $J_{C-P} = 3.1$ Hz, 1C), 131.9, 129.5 (2C), 128.5 (d, $J_{C-P} = 7.9$ Hz, 1C), 126.7 (2C), 123.7, 116.5 (d, $J_{C-P} = 22.1$ Hz, 1C), 113.1 (d, $J_{C-P} = 22.9$ Hz, 1C), 63.6 (d, $J_{C-P} = 5.7$ Hz, 2C), 21.3, 16.2 (d, $J_{C-P} = 6.8$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 0.57.
$^{19}$F NMR (282 MHz, CDCl$_3$) δ -114.40.

HR-MS (ESI) $m/z$: [M + Na]+ Calcd for C$_{20}$H$_{24}$FN$_2$NaO$_3$P 413.1401; Found 413.1407.

Diethyl(2-((E)-1-methyl-2-((E)-4-methylstyrlyl)-1H-indol-3-yl)methylene) hydrazineyl)phosphonate (21'):

The yellow solid (0.87 mmol, 370 mg, 87 % yield) was obtained following the general procedure A after 26 h starting from the aldehyde 21 (275 mg, 1.0 mmol).

$R_f$ = 0.29 (Cyclohexane:Ethyl Acetate, 4:6)

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.33 (d, $J = 7.8$ Hz, 1H), 8.11 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 4.4$ Hz, 2H), 7.25 – 7.19 (m, 3H, overlap with CDCl$_3$), 7.13 (d, $J = 16.2$ Hz, 1H), 6.91 (d, $J = 16.5$ Hz, 1H), 6.56 (d, $J = 25.8$ Hz, N-H), 4.24 (m, 4H), 3.79 (s, 3H), 2.40 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 141.7 (d, $J_{C,P} = 19.6$ Hz, CN), 139.6, 138.8, 137.9, 136.9, 133.8, 129.6 (2C), 126.8 (2C), 125.5, 123.3, 122.5, 121.2, 115.0, 109.7, 109.1, 63.3 (d, $J_{C,P} = 5.6$ Hz, 2C), 30.8, 21.4, 16.3 (d, $J_{C,P} = 7.0$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.83.

HR-MS (ESI) $m/z$: [M + H]+ Calcd for C$_{23}$H$_{29}$N$_3$O$_3$P 426.1941; Found 426.1944.
Diethyl(2-((E)-3,4,5-trimethoxy-2-((E)-3,4,5-trimethoxystyryl)benzylidene)hydrazineyl)phosphonate (22'):

The pale-yellow solid (0.8 mmol, 415 mg, 38 % yield) was obtained following the general procedure A after 28 h starting from the aldehyde 22 (800 mg, 2.0 mmol).

\[ R_f = 0.37 \text{ (Cyclohexane:Ethyl Acetate, 2:8)} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta 8.01 \text{ (s, 1H)}, 7.27 \text{ (s, 1H, overlap with CDCl}_3\text{), 7.12 \text{ (d, } J = 15.8 \text{ Hz, 1H), 6.73 \text{ (s, 2H), 6.57 \text{ (d, } J = 16.2 \text{ Hz, 1H), 4.27 - 4.13 \text{ (m, 4H), 3.92 \text{ (s, 12H), 3.88 \text{ (s, 3H), 3.84 \text{ (s, 3H), 1.36 \text{ (t, } J = 7.1 \text{ Hz, 6H).} \text{}})} \]

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3\text{) } \delta 153.5 \text{ (2C), 152.8, 151.8, 144.2 \text{ (d, } J_{C-P} = 18.5 \text{ Hz, CN), 143.5, 138.2, 135.6, 133.2, 127.8, 125.3, 120.7, 105.1, 103.7 \text{ (2C), 63.4 \text{ (d, } J_{C-P} = 5.5 \text{ Hz, 2C), 61.1, 61.0 \text{ (2C), 56.2 \text{ (2C), 56.0, 16.2 \text{ (d, } J_{C-P} = 6.8 \text{ Hz, 2C)} \text{}})} \]

\[ ^{31}P \text{ NMR (121 MHz, CDCl}_3\text{) } \delta 2.88. \]

\[ \text{HR-MS (ESI) } m/z: \text{ [M + H]+ Calcd for C}_{25}\text{H}_{36}\text{N}_2\text{O}_{9}\text{P 539.2153; Found 539.2156.} \]

Methyl4-((E)-6-((E)-(2-diethoxyphosphoryl)hydrazineylidene)methyl)-2,3,4-trimethoxystyryl)benzoate (23'):
The white solid (0.68 mmol, 344 mg, 81 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 23 (300 mg, 0.8 mmol).

**Rf** = 0.41 (Cyclohexane : Ethyl Acetate, 5:5)

**1H NMR** (300 MHz, CDCl₃) δ 8.05 (s, 1H), 8.02 (s, 1H), 8.00 (s, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 16.4 Hz, 1H), 7.23 (s, 1H), 6.85 (d, J = 26.1 Hz, NH), 6.73 (d, J = 16.4 Hz, 1H), 4.19 (m, 4H), 3.93 (s, 3H), 3.92 (s, 6H), 3.85 (s, 3H), 1.35 (t, J = 7.1 Hz, 6H).

**13C NMR** (75 MHz, CDCl₃) δ 166.9, 153.2, 152.0, 143.9 (d, J<sub>C-P</sub> = 17.7 Hz, CN), 143.5, 141.8, 134.4, 130.1 (2C), 129.2, 127.9, 126.4 (2C), 124.8, 124.1, 105.4, 63.5 (d, J<sub>C-P</sub> = 5.6 Hz, 2C), 61.1, 61.0, 56.1, 52.2, 16.2 (d, J<sub>C-P</sub> = 6.7 Hz, 2C).

**31P NMR** (121 MHz, CDCl₃) δ 1.24.

**HR-MS (ESI)** m/z: [M + H]+ Calcd for C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>O<sub>8</sub>P 507.1891; Found 507.1889.

**Diethyl(2-((E)-2-((E)-4-cyanostyryl)-3,4,5-trimethoxybenzylidene)hydrazineyl)phosphonate (24):**

![Image of the compound structure]

The pale yellow solid (0.72 mmol, 343 mg, 78 % yield) was obtained following the general procedure A after 2 h starting from the aldehyde 2’ (300 mg, 0.9 mmol).

**Rf** = 0.28 (Cyclohexane:Ethyl Acetate, 7:3)
$^1$H NMR (300 MHz, CDCl$_3$) δ 7.99 (s, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 16.4 Hz, 1H), 7.21 (s, 1H), 7.11-6.88 (bs, NH), 6.75 (d, J = 16.4 Hz, 1H), 4.28-4.05 (m, 4H), 3.92 (s, 6H), 3.85 (s, 3H), 1.35 (t, J = 7.1 Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.3, 152.1, 144.0 (d, $J_{C-P} = 18.3$ Hz, CN), 143.4, 142.2, 133.1, 132.5 (2C), 128.2, 127.0 (2C), 125.5, 124.0, 119.0, 110.7, 105.5, 63.4 (d, $J_{C-P} = 5.6$ Hz, 2C), 61.1, 60.9, 56.0, 16.2 (d, $J_{C-P} = 6.5$ Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.72.

HR-MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{23}$H$_{29}$N$_3$O$_6$P 474.1789; Found 474.178.

Diethyl(2-((E)-3,4,5-trimethoxy-2-((E)-2-(pyridin-2-yl)vinyl)benzylidene)hydrazineyl)phosphonate (25’):

The pale yellow solid (0.62 mmol, 280 mg, 78 % yield) was obtained following the general procedure A after 5 h starting from the aldehyde 25 (240 mg, 0.8 mmol).

R$_f$ = 0.32 (Methanol:Ethyl Acetate, 1:9)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, J = 4.7 Hz, 1H), 8.11 (s, 1H), 7.75 (d, J = 16.2 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.26 (s, 1H, overlap with CDCl$_3$), 7.20 – 7.13 (m, 1H), 6.85 (d, J = 16.1 Hz, 1H), 4.24 – 4.12 (m, 4H), 3.91 (s, 6H), 3.86 (s, 3H), 1.35 (t, J = 7.0 Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 155.6, 153.1, 152.2, 149.7, 143.7 (d, $J_{C-P} = 18.1$ Hz, CN), 143.5, 136.6, 134.5, 128.2 (d, $J_{C-P} = 3.9$ Hz, 1C), 125.5, 124.6 (d, $J_{C-P} = 1.7$ Hz, 1C), 122.3, 122.2, 105.1, 63.5 (d, $J_{C-P} = 5.5$ Hz, 2C), 61.0 (d, $J_{C-P} = 7.5$ Hz, 2C), 56.0, 16.2 (d, $J_{C-P} = 6.8$ Hz, 2C).
$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.49.

**HR-MS (ESI) $m/z$:** [M + H]$^+$ Calcd for C$_{21}$H$_{29}$N$_3$O$_6$P 450.1789; Found 450.1785.

Diethyl(2-((E)-3,4,5-trimethoxy-2-((E)-2-(pyridin-4-yl)vinyl)benzylidene) hydrazineyl)phosphonate (26‘):

![Chemical Structure](image)

The pale yellow solid (0.48 mmol, 216 mg, 88% yield) was obtained following the general procedure A after 3 h starting from the aldehyde 26 (166mg, 0.55 mmol).

**Rf** = 0.45 (Methanol:Ethyl Acetate, 1:9)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J$ = 5.9 Hz, 2H), 8.08 (s, 1H), 8.04-7.79 (bs, 1H, NH), 7.47 (d, $J$ = 16.5 Hz, 1H), 7.32 (d, $J$ = 5.9 Hz, 2H), 7.23 (s, 1H), 6.67 (d, $J$ = 16.4 Hz, 1H), 4.28-4.09 (m, 4H), 3.93 – 3.89 (m, 6H, included 3.92 (s, 3H) + 3.91 (s, 3H)), 3.85 (s, 3H), 1.34 (t, $J$ = 7.1 Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.4, 152.1, 149.9 (2C), 145.0, 143.7 (d, $J_{C,P}$ = 19.0 Hz, 1C), 143.3, 132.2, 128.4, 126.4, 123.7, 120.9 (2C), 105.4, 63.4 (d, $J_{C,P}$ = 5.6 Hz, 2C), 61.1, 61.0, 56.1, 16.2 (d, $J_{C,P}$ = 6.7 Hz, 2C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.64.

**HR-MS (ESI) $m/z$:** [M + H]$^+$ Calcd for C$_{21}$H$_{29}$N$_3$O$_6$P 450.1789; Found 450.1793.
Diethyl(E)-(2-((2-(1-(3,4,5-trimethoxyphenyl)vinyl)benzofuran-3-yl)methylene)hydrazineyl)phosphonate (27’):

The yellow oil (0.26 mmol, 127 mg, 65 % yield) was obtained following the general procedure A after 5 h starting from the aldehyde 27 (145 mg, 0.4 mmol).

Rf = 0.24 (Cyclohexane : Ethyl Acetate, 3:7)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.25 – 8.21 (m, 1H), 7.54 (s, 1H), 7.50 – 7.45 (m, 1H), 7.37 (td, $J = 8.2, 7.7, 1.6$ Hz, 1H), 7.31 (td, $J = 7.4, 1.2$ Hz, 1H), 6.78 (d, $J = 26.9$ Hz, NH), 6.60 (s, 2H), 5.77 (dd, $J = 25.1, 0.9$ Hz, 2H), 4.32 – 4.08 (m, 4H), 3.90 (s, 3H), 3.83 (s, 6H), 1.37 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.1, 154.2, 153.4 (2C), 138.9, 138.8, 138.7 (d, $J_{C-P} = 5.5$ Hz, CN), 134.1, 126.3, 125.8, 123.7, 123.6, 119.5, 114.6, 111.0, 105.3 (2C), 76.7, 63.4 (d, $J_{C-P} = 5.4$ Hz, 2C), 61.0, 56.3, 16.2 (d, $J_{C-P} = 7.0$ Hz, 2C).

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 1.01.

HR-MS (ESI) m/z: [M + H]+ Calcd for C$_{24}$H$_{28}$N$_2$O$_7$P 487.1629; Found 487.1633.

Diethyl (E)-(2-((2-(1-(pyridin-3-yl)vinyl)pyridin-3-yl)methylene)hydrazineyl) phosphonate (28’):
The pale-yellow solid (156 mg with 83% of mass purity, 0.36 mmol adjusted to account for inseparable starting material, 30 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 28 (250 mg, 1.2 mmol).

\[ \textbf{Rf} = 0.28 \text{ (Methanol:Ethyl Acetate, 1:9)} \]

\textbf{\( ^1H \text{ NMR} \)} (300 MHz, CDCl\textsubscript{3}) \( \delta \) 8.57 (dd, \( J = 4.7, 1.7 \text{ Hz}, 1\text{H} \)), 8.55 – 8.51 (bs, 1H), 8.49 – 8.45 (bs, 1H), 8.39 (d, \( J = 28.4 \text{ Hz}, 1\text{H}, \text{NH} \)), 8.27 (dd, \( J = 8.0, 1.7 \text{ Hz}, 1\text{H} \)), 7.86 (s, 1H), 7.58 – 7.52 (m, 1H), 7.28 (dd, \( J = 8.0, 4.7 \text{ Hz}, 1\text{H}, \) overlapped with CDCl\textsubscript{3}), 7.21 (dd, \( J = 8.0, 4.7 \text{ Hz}, 1\text{H} \)), 6.02 (s, 1H), 5.41 (s, 1H), 4.19 – 3.98 (m, 4H, overlapped with hydrazine), 1.33 – 1.25 (m, 6H, overlapped with hydrazine).

\textbf{\( ^{13}C \text{ NMR} \)} (101 MHz, CDCl\textsubscript{3}) \( \delta \) 157.0, 149.8, 148.9, 147.9, 143.6, 141.2 (d, \( J_{C,P} = 19.3 \text{ Hz}, \text{CN} \)), 135.3, 134.3, 134.0, 129.1, 123.4, 123.1, 120.0, 63.4 (d, \( J_{C,P} = 5.5 \text{ Hz}, 2\text{C} \)), 16.13 (d, \( J_{C,P} = 6.8 \text{ Hz}, 2\text{C} \)).

\textbf{\( ^{31}P \text{ NMR} \)} (121 MHz, CDCl\textsubscript{3}) \( \delta \) 5.56.

\textbf{HR-MS (ESI) m/z:} [M + H]+ Calcd for C\textsubscript{17}H\textsubscript{22}N\textsubscript{4}O\textsubscript{3}P 361.1424; Found 361.1426.
To an oven-dried sealable glass vial were added phosphonohydrazone (1 equiv.), potassium hydroxide (1.5 equiv.), Ru(bpy)$_3$Cl$_2$.6H$_2$O as a photocatalyst (2.5 mol%) and a mix of MeCN and H$_2$O (9:1) (1.7 M). The vial was sealed with 20mm crimp caps with silicone/PTFE septum and the mixture was stirred under blue LED irradiation at 20 °C. After completion of the reaction checked by TLC, the resulting suspension was extracted with EtOAc (3 x 50 mL), washed with brine (50 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude mixture of 6- and 7-member ring product was purified by silica gel column chromatography eluting with a cyclohexane/ethyl acetate mixture to afford the desired products.
Diethyl (4-(p-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (2a):

The brown oil (0.15 mmol, 56 mg, 50% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 2' (112 mg, 0.3 mmol).

\[ \text{Rf} = 0.44 \text{ (Cyclohexane:Ethyl Acetate, 3:7)} \]

\[ ^{1} \text{H NMR} \ (300 \text{ MHz, CDCl}_3) \delta 7.46 \text{ (s, 1H)}, 7.21 - 7.15 \text{ (m, 1H)}, 7.14 - 7.07 \text{ (m, 2H)}, 7.02 - 6.97 \text{ (m, 1H)}, 6.91 - 6.84 \text{ (m, 4H)}, 6.15 \text{ (td, J = 6.4, 2.0 Hz, 1H)}, 4.31 - 4.01 \text{ (m, 4H)}, 3.61 \text{ (ddd, J = 15.7, 6.2, 3.1 Hz, 1H)}, 3.42 \text{ (dd, J = 15.4, 1.7 Hz, 1H)}, 2.14 \text{ (s, 3H)}, 1.35 \text{ (dtd, J = 10.0, 7.1, 1.0 Hz, 6H)}. \]

\[ ^{13} \text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta 140.7 \text{ (d, J}_{C,P} = 16.9 \text{ Hz, CN)}, 138.3, 136.7, 135.8, 132.5, 131.5, 130.1, 129.1, 128.7 \text{ (2C)}, 126.4, 125.9 \text{ (2C)}, 63.9 \text{ (d, J}_{C,P} = 6.0 \text{ Hz, 1C)}, 63.3 \text{ (d, J}_{C,P} = 5.8 \text{ Hz, 1C)}, 61.8 \text{ (d, J}_{C,P} = 10.4 \text{ Hz, 1C)}, 41.9 \text{ (d, J}_{C,P} = 5.3 \text{ Hz, 1C)}, 20.9, 16.2 \text{ (d, J}_{C,P} = 7.7 \text{ Hz, 1C)}, 16.1 \text{ (d, J}_{C,P} = 7.8 \text{ Hz, 1C}). \]

\[ ^{31} \text{P NMR} \ (121 \text{ MHz, CDCl}_3) \delta 2.95. \]

\[ \text{HR-MS (ESI) m/z: [M + H]+ Calcd for C}_{20}\text{H}_{26}\text{N}_{2}\text{O}_{3}\text{P 373.1676; Found 373.1679.} \]

Diethyl (1-(4-methylbenzyl)phthalazin-2(1H)-yl)phosphonate (2b):
The brown oil (0.03 mmol, 11.2 mg, 10% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 2’ (112mg, 0.3 mmol).

\[ \text{Rf} = 0.56 \text{ (Cyclohexane:Ethyl Acetate, 3:7)} \]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta 7.69\) (s, 1H), 7.31 – 7.24 (m, 1H), 7.22 – 7.12 (m, 2H), 6.95 (d, \(J = 7.8\) Hz, 2H), 6.74 (d, \(J = 7.5\) Hz, 2H), 6.40 (d, \(J = 7.5\) Hz, 1H), 5.22 (ddd, \(J = 8.9, 5.2, 2.5\) Hz, 1H), 4.32 – 4.14 (m, 2H), 4.12 – 3.98 (m, 1H), 3.98 – 3.84 (m, 1H), 2.96 (dd, \(J = 12.7, 5.2\) Hz, 1H), 2.87 (dd, \(J = 12.8, 9.8\) Hz, 1H), 2.27 (s, 3H), 1.40 (tt, \(J = 7.1, 1.0\) Hz, 3H), 1.24 (tt, \(J = 7.1, 1.0\) Hz, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta 142.9\) (d, \(J_{C-P} = 12.6\) Hz, CN), 142.8, 135.9, 133.2, 131.7 (d, \(J_{C-P} = 6.5\) Hz, 1C), 130.5, 129.9 (2C), 128.7 (2C), 127.9, 126.8 (d, \(J_{C-P} = 1.1\) Hz, 1C), 123.0, 123.6 (d, \(J_{C-P} = 1.7\) Hz, 1C), 63.9 (d, \(J_{C-P} = 6.3\) Hz, 1C), 63.1 (d, \(J_{C-P} = 5.7\) Hz, 1C), 55.8 (d, \(J_{C-P} = 8.7\) Hz, 1C), 41.1, 21.1, 16.3 (d, \(J_{C-P} = 7.2\) Hz, 1C), 15.9 (d, \(J_{C-P} = 7.0\) Hz, 1C).

\(^{31}\text{P NMR}\) (121 MHz, CDCl\(_3\)) \(\delta 1.78\).

\text{HR-MS (ESI) m/z: [M + H]+ Calcd for C}_{20}\text{H}_{26}\text{N}_{2}\text{O}_{3}\text{P 373.1676; Found 373.1676.} \]

Diethyl(5-phenyl-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (3a):

The brown oil (0.15 mmol, 54 mg, 50 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 3’ (108 mg, 0.3 mmol).

\[ \text{Rf} = 0.33 \text{ (Cyclohexane:Ethyl Acetate, 5:5)} \]
**1H NMR** (400 MHz, CDCl$_3$) δ 7.53 – 7.49 (m, 2H), 7.38 (t, $J$ = 7.4 Hz, 1H), 7.31 (t, $J$ = 7.4 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.16 (t, $J$ = 7.3 Hz, 1H), 6.98 (d, $J$ = 7.5 Hz, 2H), 4.81 (dt, $J$ = 13.2, 6.2 Hz, 1H), 4.74 – 4.68 (m, 1H), 4.14 – 4.03 (m, 1H), 4.02 – 3.90 (m, 1H), 3.60 (dd, $J$ = 13.7, 2.2 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.12 – 3.00 (m, 1H), 1.29 (t, $J$ = 7.1 Hz, 3H), 1.00 (t, $J$ = 7.1 Hz, 3H).

**13C NMR** (75 MHz, CDCl$_3$) δ 142.6, 141.7, 141.0 (d, $J_{C-P}$ = 17.8 Hz, CN), 133.5, 132.3, 130.5, 129.2, 128.5 (2C), 128.4 (2C), 127.3, 126.5, 63.4 (d, $J_{C-P}$ = 5.9 Hz, 1C), 62.5 (d, $J_{C-P}$ = 5.4 Hz, 1C), 53.5 (d, $J_{C-P}$ = 5.8 Hz, 1C), 52.7 (d, $J_{C-P}$ = 8.9 Hz, 1C), 16.2 (d, $J_{C-P}$ = 7.0 Hz, 1C), 16.0 (d, $J_{C-P}$ = 7.5 Hz, 1C).

**31P NMR** (121 MHz, CDCl$_3$) δ 3.67.

**HR-MS (ESI) m/z:** [M + H]$^+$ Calcd for C$_{19}$H$_{24}$N$_2$O$_3$P 359.1519; Found 359.1522.

**Diethyl (5-phenyl-4-propyl-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (4a):**

Enantiomers’ pair (S, S) or (R, R) – Dia syn:

The brown oil (0.03 mmol, 13 mg, 22 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 4' (60 mg, 0.15 mmol).

R$_f$ = 0.36 (Cyclohexane:Ethyl Acetate, 7:3)

**1H NMR** (300 MHz, CDCl$_3$) δ 7.54 – 7.48 (m, 2H), 7.42 (td, $J$ = 7.4, 1.6 Hz, 1H), 7.36 (td, $J$ = 7.3, 1.7 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.14 – 7.07 (m, 1H), 6.94 – 6.90 (m, 2H), 5.11 – 4.97 (m, 1H), 4.58 (t, $J$ = 4.4 Hz, 1H), 4.17 – 4.03 (m, 2H), 3.16 – 3.03 (m, 1H), 2.82 – 2.68 (m, 1H), 1.52 – 1.34 (m, 3H), 1.30 (td, $J$
= 7.1, 1.0 Hz, 3H), 1.27 – 1.14 (m, 1H), 0.93 (td, J = 7.1, 1.1 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.5, 139.9 (d, $J_{CP}$ = 17.9 Hz, CN), 139.1, 133.6, 132.2, 131.4, 129.6, 128.4 (2C), 128.0 (2C), 127.3, 126.3, 64.0 (d, $J = 6.8$ Hz, 1C), 62.0 (d, $J_{CP}$ = 5.5 Hz, 1C), 62.0 (d, $J_{CP}$ = 9.0 Hz, 1C), 56.6 (d, $J_{CP}$ = 6.5 Hz, 1C), 33.6, 19.3, 16.2 (d, $J_{CP}$ = 6.8 Hz, 1C), 15.9 (d, $J_{CP}$ = 7.7 Hz, 1C), 13.9.

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 2.77.

NOESY: A correlation is observed between the two vicinal protons of the 7 members ring

HR-MS (ESI) m/z: [M + H]+$^+$ Calcd for C$_{22}$H$_{30}$N$_2$O$_3$P 401.1989; Found 401.1992.

Enantiomers’ pair (R, S) or (S, R) – Dia anti:

The brown oil (0.03 mmol, 12 mg, 20 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 4’ (60 mg, 0.15 mmol).

R$_f$ = 0.30 (Cyclohexane:Ethyl Acetate, 7:3)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.21 (m, 4H, overlapped with CDCl$_3$), 7.18 (td, J = 7.5, 1.3 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.33 – 4.18 (m, 3H), 4.18 – 4.01 (m, 2H), 1.59 – 1.41 (m, 2H), 1.40 – 1.31 (m, included 1.37 (td, J = 7.1, 1.1 Hz, 3H) + 1.34 (td, J = 7.1, 1.0 Hz, 3H)), 1.30 – 1.06 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.4 (d, $J_{CP}$ = 16.3 Hz, CN), 141.3, 141.1, 140.3, 132.0, 131.8, 129.0, 129.0 (2C), 128.9 (2C), 128.6, 127.2, 126.6, 64.1 (d, $J = 6.4$ Hz, 1C), 63.2 (d, $J_{CP}$ = 5.9 Hz, 1C), 62.9 (d, $J_{CP}$ = 8.5 Hz, 1C), 55.7 (d, $J_{CP}$ = 3.9 Hz, 1C), 31.7, 20.1, 16.2 (d, $J_{CP}$ = 7.1 Hz, 2C), 14.0.
$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.98.

**NOESY:** No correlation observed between the two vicinal protons of the 7 members ring

**HR-MS (ESI) $m/z$:** [M + H]$^+$ Calcd for C$_{22}$H$_{30}$N$_2$O$_3$P 401.1989; Found 401.1992.

Diethyl(4-(4-methoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (5a):

The brown oil (0.054 mmol, 21 mg, 18 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazine 5′ (117 mg, 0.3 mmol).

**Rf** = 0.39 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.11 (m, 2H), 7.05 – 6.98 (m, 1H), 6.91 (d, $J = 8.6$ Hz, 2H), 6.60 (d, $J = 8.7$ Hz, 2H), 6.12 (t, $J = 5.7$ Hz, 1H), 4.26 – 4.06 (m, 4H), 3.65 (s, 3H), 3.62 – 3.54 (m, 1H), 3.43 (d, $J = 15.5$ Hz, 1H), 1.39-1.30 (m, 6H, included 1.36 (t, $J = 7.0$ Hz, 3H) + 1.33 (t, $J = 7.0$ Hz, 3H)).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.11 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.9, 141.0 (d, $J_{C,P} = 16.6$ Hz, CN), 138.4, 132.3, 131.8, 131.7, 130.1, 129.3, 127.2 (2C), 126.5, 113.4 (2C), 64.0 (d, $J_{C,P} = 6.0$ Hz, 1C), 63.4 (d, $J_{C,P} = 5.8$ Hz, 1C), 61.4 (d, $J_{C,P} = 10.2$ Hz, 1C), 55.0, 42.0 (d, $J_{C,P} = 5.3$ Hz, 1C), 16.2 (d, $J_{C,P} = 7.1$ Hz, 1C), 16.1 (d, $J_{C,P} = 7.3$ Hz, 1C).

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 2.84.

**HR-MS (ESI) $m/z$:** [M + Na]$^+$ Calcd for C$_{20}$H$_{25}$N$_2$NaO$_4$P 411.1444; Found 411.1446.
Tetraethyl(4,4'-bis(4-methoxyphenyl)-4',5,5'-tetrahydro-3H,3'H-[5,5'-bibenzo[d][1,2]diazepine]-3,3'-diyl)bis(phosphonate) (XI):

The brown oil (0.015 mmol, 12 mg, 10% yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 5’ (117 mg, 0.3 mmol).

Rf = 0.22 (Cyclohexane:Ethyl Acetate, 2:8)

$^1$H NMR (300 MHz, CDCl3) $\delta$ 7.74 (d, $J = 8.7$ Hz, 2H), 7.50 – 7.43 (m, 2H), 7.30 (d, $J = 7.3$ Hz, 2H), 7.16 (d, $J = 7.7$ Hz, 2H), 7.01 (dd, $J = 8.6$, 2.6 Hz, 2H), 6.92 (d, $J = 8.3$ Hz, 2H), 6.81 (s, 2H), 6.60 (dd, $J = 8.4$, 2.8 Hz, 2H), 6.40 (dd, $J = 8.4$, 1.9 Hz, 2H), 5.29 (d, $J = 4.3$ Hz, 2H), 4.19 – 4.07 (m, 4H), 3.81 (s, 6H), 3.77 – 3.68 (m, 2H), 3.65 – 3.55 (m, 2H), 3.52 (s, 2H), 1.34 (t, $J = 7.0$ Hz, 6H), 1.02 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl3) $\delta$ 158.88, 142.26 (d, $J = 11.4$ Hz), 135.20, 131.41, 129.55, 128.90, 127.66 (2C), 125.43, 124.29 (2C), 113.32, 112.24, 63.84 (d, $J = 6.4$ Hz), 62.47 (d, $J = 5.7$ Hz), 55.66, 55.06, 16.28 (d, $J = 7.7$ Hz), 15.68 (d, $J = 7.6$ Hz).

$^{31}$P NMR (162 MHz, CDCl3) $\delta$ 2.60.

HR-MS (ESI) $m/z$: [M + H]+ Calcd for C$_{40}$H$_{49}$N$_{4}$O$_{8}$P$_{2}$ 775.3020; Found 775.3015.
diethyl(4-(3,5-dimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (6a):

The brown oil (0.07 mmol, 28 mg, 22% yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 6' (125 mg, 0.3 mmol).

**Rf** = 0.40 (Cyclohexane : Ethyl Acetate, 5:5)

**1H NMR** (300 MHz, CDCl₃) δ 7.49 (s, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.10 (m, 2H), 7.03 – 6.98 (m, 1H), 6.18 (d, J = 2.1 Hz, 2H), 6.16-6.11 (m, 1H), 6.10 (t, J = 2.2 Hz, 1H), 4.29 – 4.06 (m, 4H), 3.63 – 3.53 (m, 7H), 3.41 (dd, J = 15.5, 1.7 Hz, 1H), 1.41-1.31 (m, 6H, included 1.38 (td, J = 7.0, 0.9 Hz, 3H) + 1.34 (td, J = 7.1, 1.0 Hz, 3H))

**13C NMR** (101 MHz, CDCl₃) δ 160.4 (2C), 142.3, 140.8 (d, J_C-P = 16.8 Hz, CN), 138.1, 132.4, 131.5, 130.1, 129.2, 126.5, 104.4 (2C), 98.7, 64.0 (d, J = 6.0 Hz, 1C), 63.4 (d, J_C-P = 5.8 Hz, 1C), 62.2 (d, J_C-P = 10.5 Hz, 1C), 55.2 (2C), 41.8 (d, J_C-P = 5.3 Hz, 1C), 16.2 (d, J_C-P = 7.2 Hz, 1C), 16.1 (d, J_C-P = 7.4 Hz, 1C).

**31P NMR** (121 MHz, CDCl₃) δ 2.76.

**HR-MS (ESI) m/z:** [M + Na]+ Calcd for C₂₁H₂₇N₂NaO₅P 441.1550; Found 441.1556.

Diethyl (1-(3,5-dimethoxybenzyl)phthalazin-2(1H)-yl)phosphonate (6b):
The brown oil (0.07 mmol, 28 mg, 22 % yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 6’ (125 mg, 0.3 mmol).

$R_f = 0.30$ (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.71 (s, 1H), 7.32 – 7.27 (m, 1H), 7.23 – 7.16 (m, 2H), 6.49 (d, $J = 7.8$ Hz, 1H), 6.27 (t, $J = 2.3$ Hz, 1H), 6.00 (d, $J = 2.3$ Hz, 2H), 5.31 – 5.23 (m, 1H), 4.33 – 4.19 (m, 2H), 4.11 – 4.02 (m, 1H), 3.98 – 3.88 (m, 1H), 3.65 (s, 6H), 2.95 (dd, $J = 12.6, 5.2$ Hz, 1H), 2.86 (dd, $J = 12.5, 9.6$ Hz, 1H), 1.41 (td, $J = 7.0, 0.8$ Hz, 3H), 1.26 (td, $J = 7.1, 0.8$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.4 (2C), 142.9 (d, $J_{C,P} = 12.2$ Hz, CN), 138.5, 131.6 (d, $J_{C,P} = 6.4$ Hz, 1C), 130.5, 127.9, 126.9, 125.0, 123.6, 107.7 (2C), 99.3, 63.9 (d, $J_{C,P} = 6.3$ Hz, 1C), 63.2 (d, $J_{C,P} = 5.4$ Hz, 1C), 55.5 (d, $J_{C,P} = 8.6$ Hz, 1C), 55.3 (2C), 41.6, 16.3 (d, $J_{C,P} = 7.1$ Hz, 1C), 15.9 (d, $J_{C,P} = 7.0$ Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.75.

HR-MS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{21}$H$_{28}$N$_2$O$_5$P 419.1730; Found 419.1727.

Diethyl(4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (7a):

The brown oil (0.021 mmol, 10 mg, 7 % yield) was obtained following the general procedure B after 27 h starting from the phosphonohydrazone 7’ (135mg, 0.3 mmol).

$R_f = 0.35$ (Cyclohexane:Ethyl Acetate, 1:9)
**1H NMR** (300 MHz, CDCl$_3$) δ 7.49 (s, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 – 6.99 (m, 1H), 6.24 (s, 2H), 6.12 (t, $J = 6.0$ Hz, 1H), 4.28 – 4.07 (m, 4H), 3.70 (s, 3H), 3.66 (s, 6H), 3.57 (ddd, $J = 15.4$, 6.0, 3.3 Hz, 1H), 3.44 (dd, $J = 15.6$, 1.6 Hz, 1H), 1.39 (td, $J = 7.1$, 1.0 Hz, 3H), 1.33 (td, $J = 7.1$, 1.0 Hz, 3H).

**13C NMR** (75 MHz, CDCl$_3$) δ 152.8 (3C), 140.8 (d, $J_{C-P} = 16.6$ Hz, CN), 138.2, 136.4, 135.5, 132.5, 131.5, 130.1, 129.3, 126.6, 103.8 (2C), 64.1 (d, $J_{C-P} = 6.2$ Hz, 1C), 63.4 (d, $J_{C-P} = 6.0$ Hz, 1C), 62.1 (d, $J_{C-P} = 10.4$ Hz, 1C), 60.8, 55.9, 41.9 (d, $J_{C-P} = 5.6$ Hz, 1C), 16.3 (d, $J_{C-P} = 7.5$ Hz, 1C), 16.1 (d, $J_{C-P} = 7.5$ Hz, 1C).

**31P NMR** (121 MHz, CDCl$_3$) δ 2.83.

**HR-MS (ESI)** $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{30}$N$_2$O$_6$P 449.1836; Found 449.1833.

Diethyl(1-(3,4,5-trimethoxybenzyl)phthalazin-2(1H)-yl)phosphonate (7b):

The brown oil (0.045 mmol, 20 mg, 15 % yield) was obtained following the general procedure B after 27 h starting from the phosphonohydrazone 7' (135 mg, 0.3 mmol).

$R_f = 0.45$ (Cyclohexane:Ethyl Acetate, 1:9)

**1H NMR** (400 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.24 – 7.16 (m, 2H), 6.49 (d, $J = 7.4$ Hz, 1H), 6.03 (s, 2H), 5.26 (td, $J = 6.0$, 5.4, 2.4 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.09 – 4.03 (m, 1H), 3.97 – 3.88 (m, 1H), 3.79 (s, 3H), 3.67 (s, 6H), 2.96 – 2.81 (m, 2H), 1.42 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.0$ Hz, 3H).

**13C NMR** (75 MHz, CDCl$_3$) δ 152.8 (2C), 142.7 (d, $J_{C-P} = 12.6$ Hz, CN), 136.7, 131.9, 131.5 (d, $J_{C-P} = 6.5$ Hz, 1C), 130.5, 127.9, 127.1, 125.0, 123.7, 107.0 (2C), 64.0 (d, $J_{C-P} = 6.4$ Hz, 1C), 63.2 (d, $J_{C-P} = 5.8$ Hz, 1C), 60.9, 56.0, 55.6 (d, $J_{C-P} = 8.7$ Hz, 1C), 41.7, 16.3 (d, $J_{C-P} = 7.1$ Hz, 1C), 15.9 (d, $J_{C-P} = 7.1$ Hz, 1C).
$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.68.

HR-MS (ESI) $m/z$: [M + Na]$^+$ Calcd for $C_{22}H_{29}N_2NaO_6P$ 471.1655; Found 471.1656.

Diethyl(4-(4-fluorophenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (8a):

The brown oil (0.12 mmol, 45 mg, 40 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 8' (113 mg, 0.3 mmol).

$R_f$ = 0.43 (Cyclohexane:Ethyl Acetate, 4:6)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.48 (s, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 7.01 – 6.92 (m, 3H), 6.81 – 6.72 (m, 2H), 6.17 (t, $J$ = 6.7 Hz, 1H), 4.28 – 4.06 (m, 4H), 3.58 (ddd, $J$ = 15.7, 6.2, 3.1 Hz, 1H), 3.48 – 3.40 (m, 1H), 1.7 Hz, 1H), 1.41-1.31 (m, 6H, included 1.38 (td, $J$ = 7.0, 0.9 Hz, 3H) + 1.34 (td, $J$ = 7.0, 1.0 Hz, 3H)).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.3 (d, $J_{CF}$ = 244.8 Hz, 1C), 140.9 (d, $J_{CP}$ = 16.7 Hz, CN), 138.0, 135.5 (d, $J_{CF}$ = 3.2 Hz, 1C), 132.3, 131.6, 130.0, 129.3, 127.7 (d, $J_{CF}$ = 8.0 Hz, 2C), 126.6, 114.9 (d, $J_{CF}$ = 21.4 Hz, 2C), 64.1 (d, $J$ = 6.1 Hz, 1C), 63.5 (d, $J$ = 5.8 Hz, 1C), 61.5 (d, $J$ = 10.5 Hz, 1C), 41.9 (d, $J_{CP}$ = 5.3 Hz, 1C), 16.2 (d, $J_{CP}$ = 7.1 Hz, 1C), 16.1 (d, $J_{CP}$ = 7.3 Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 2.65.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -116.53.

HR-MS (ESI) $m/z$: [M + H]$^+$ Calcd for $C_{19}H_{23}FNo_3P$ 377.1425; Found 377.1423.
Diethyl (1-(4-fluorobenzyl)phthalazin-2(1H)-yl)phosphonate (8b):

The brown oil (0.015 mmol, 6 mg, 5% yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 8' (113 mg, 0.3 mmol).

Rf = 0.59 (Cyclohexane:Ethyl Acetate, 4:6)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.35 – 7.28 (m, 1H, overlap with CDCl$_3$), 7.22 – 7.12 (m, 2H), 6.89 – 6.77 (m, 4H), 6.44 (d, $J$ = 8.1 Hz, 1H), 5.28 – 5.20 (m, 1H), 4.11 – 3.99 (m, 1H), 3.99 – 3.87 (m, 1H), 3.01 – 2.85 (m, 2H), 1.42 (t, $J$ = 7.1 Hz, 3H), 1.25 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.8 (d, $J_{C-F}$ = 244.6 Hz, 1C), 142.7 (d, $J_{C-P}$ = 12.7 Hz, CN), 132.1 (d, $J_{C-F}$ = 1.1 Hz, 1C), 131.4 (t, $J_{C-F}$ = 7.9 Hz, 2C), 131.3, 130.6, 128.1, 126.7 (d, $J_{C-F}$ = 1.3 Hz, 1C), 125.1, 123.7 (d, $J_{C-F}$ = 2.8 Hz, 1C), 114.9 (d, $J_{C-F}$ = 21.2 Hz, 2C), 64.0 (d, $J_{C-P}$ = 6.5 Hz, 1C), 63.2 (d, $J_{C-P}$ = 5.7 Hz, 1C), 55.7 (d, $J_{C-P}$ = 8.6 Hz, 1C), 40.9, 16.3 (d, $J_{C-P}$ = 7.1 Hz, 1C), 16.0 (d, $J_{C-P}$ = 7.0 Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.62.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -116.39.

HR-MS (ESI) m/z: [M + H$^+$] Calcd for C$_{19}$H$_{23}$FN$_2$O$_3$P 377.1425; Found 377.1426.

Methyl4-((2-(diethoxyphosphoryl)-1,2-dihydropthalazin-1-yl)methyl)benzoate (9b):
The brown oil (0.072 mmol, 30 mg, 24 % yield) was obtained following the general procedure B after 15 h starting from the phosphonohydrazone 9’ (125 mg, 0.3 mmol).

**Rf** = 0.49 (Cyclohexane:Ethyl Acetate, 4:6)

**1H NMR** (300 MHz, CDCl₃) δ 7.84 – 7.79 (m, 2H), 7.64 (s, 1H), 7.32 – 7.25 (m, 1H, overlapped with CDCl₃), 7.22 – 7.12 (m, 2H), 6.96 – 6.89 (m, 2H), 6.39 (dd, **J** = 7.5, 0.5 Hz, 1H), 5.30 (ddd, **J** = 8.2, 5.5, 2.4 Hz, 1H), 4.36 – 4.17 (m, 2H), 4.12 – 3.99 (m, 1H), 3.98 – 3.89 (m, 1H), 3.88 (s, 3H), 3.08 – 2.94 (m, 2H), 1.41 (td, **J** = 7.1, 1.0 Hz, 3H), 1.24 (td, **J** = 7.1, 0.9 Hz, 3H).

**13C NMR** (101 MHz, CDCl₃) δ 167.1, 142.7 (d, **J**<sub>C-P</sub> = 12.6 Hz, CN), 141.9, 131.1 (d, **J**<sub>C-P</sub> = 6.6 Hz, 1C), 130.7, 130.1 (2C), 129.3 (2C), 128.4, 128.2, 126.6, 125.2, 123.6 (d, **J**<sub>C-P</sub> = 1.7 Hz, 1C), 64.1 (d, **J**<sub>C-P</sub> = 6.5 Hz, 1C), 63.2 (d, **J**<sub>C-P</sub> = 5.8 Hz, 1C), 55.5 (d, **J**<sub>C-P</sub> = 8.8 Hz, 1C), 52.0, 41.7, 16.3 (d, **J**<sub>C-P</sub> = 7.1 Hz, 1C), 15.9 (d, **J**<sub>C-P</sub> = 7.0 Hz, 1C).

**31P NMR** (121 MHz, CDCl₃) δ 1.49.

**HR-MS (ESI) m/z:** [M + K]+ Calcd for C<sub>21</sub>H<sub>25</sub>KN<sub>2</sub>O<sub>5</sub>P 455.1133; Found 455.1131.

Diethyl (1-(4-cyanobenzyl)phthalazin-2(1H)-yl)phosphonate (10b):

The brown oil (0.13 mmol, 50 mg, 44 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 10’ (114 mg, 0.3 mmol).

**Rf** = 0.44 (Cyclohexane:Ethyl Acetate, 5:5)

**1H NMR** (300 MHz, CDCl₃) δ 7.61 (s, 1H), 7.46 – 7.41 (m, 2H), 7.36-7.29 (m, 1H), 7.26 – 7.18 (m, 2H, overlapped with CDCl₃), 7.01 – 6.95 (m, 2H), 6.50 – 6.45 (m,
1H), 5.33 (td, J = 6.9, 2.5 Hz, 1H), 4.33 – 4.19 (m, 2H), 4.12 – 3.98 (m, 1H), 3.98 – 3.84 (m, 1H), 3.01 (d, J = 6.9 Hz, 2H), 1.42 (td, J = 7.1, 1.0 Hz, 3H), 1.24 (td, J = 7.1, 0.9 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.6 (d, $J_{C-P} = 12.5$ Hz, CN), 142.1, 131.8 (2C), 130.9, 130.9 (2C), 130.8, 128.4, 126.4 (d, $J_{C-P} = 1.2$ Hz, 1C), 125.3, 123.6 (d, $J_{C-P} = 1.7$ Hz, 1C), 118.9, 110.5, 64.2 (d, $J_{C-P} = 6.6$ Hz, 1C), 63.3 (d, $J_{C-P} = 5.8$ Hz, 1C), 55.3 (d, $J_{C-P} = 9.0$ Hz, 1C), 42.1, 16.3 (d, $J_{C-P} = 7.0$ Hz, 1C), 15.9 (d, $J_{C-P} = 7.0$ Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.33.

HR-MS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{20}$H$_{22}$N$_3$NaO$_3$P 406.1291; Found 406.1291.

Diethyl (1-(2-nitrobenzyl)phthalazin-2(1H)-yl)phosphonate (11b):

The brown oil (0.075 mmol, 30 mg, 25 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 11’ (121 mg, 0.3 mmol).

$R_f$ = 0.51 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.81 (s, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.34 (dd, J = 12.6, 7.3 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.62 (d, J = 7.1 Hz, 1H), 5.46 (td, J = 7.5, 3.2 Hz, 1H), 4.21 – 4.07 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.80 (m, 1H), 3.46 (dd, J = 13.0, 7.8 Hz, 1H), 3.17 (dd, J = 13.1, 7.0 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.7, 143.6 (d, $J_{C-P} = 12.3$ Hz, CN), 134.0, 132.7, 131.8, 131.2, 131.1 (d, $J_{C-P} = 5.9$ Hz, 1C), 128.4, 127.8, 125.9 (d, $J_{C-P} = 1.3$ Hz, 1C), 125.3, 124.7, 123.6 (d, $J_{C-P} = 1.8$ Hz, 1C), 64.1 (d, $J_{C-P} = 6.5$ Hz, 1C), 63.1 (d, $J_{C-P} =$
The brown oil (0.14 mmol, 50 mg, 46 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 12’ (108 mg, 0.3 mmol).

**RF** = 0.69 (Methanol:Ethyl Acetate, 1:9)

**1H NMR** (300 MHz, CDCl₃) δ 8.47 (d, J = 5.1 Hz, 1H), 7.76 (s, 1H), 7.49 (td, J = 7.7, 1.7 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.24 – 7.07 (m, 3H), 6.89 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 5.55 (ddd, J = 8.7, 5.8, 2.7 Hz, 1H), 4.30 – 4.16 (m, 2H), 4.10 – 3.97 (m, 1H), 3.97 – 3.83 (m, 1H), 3.21 (dd, J = 12.7, 5.5 Hz, 1H), 3.11 (dd, J = 12.7, 9.2 Hz, 1H), 1.39 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H).

**13C NMR** (75 MHz, CDCl₃) δ 156.8, 149.2, 143.3 (d, J_C-P = 12.4 Hz, CN), 136.0, 131.8 (d, J_C-P = 6.3 Hz, 1C), 130.7, 128.0, 126.1 (d, J_C-P = 1.1 Hz, 1C), 125.2, 124.5, 123.6 (d, J_C-P = 1.7 Hz, 1C), 121.5, 63.9 (d, J_C-P = 6.3 Hz, 1C), 63.2 (d, J_C-P = 5.7 Hz, 1C), 54.6 (d, J_C-P = 8.8 Hz, 1C), 43.3, 16.2 (d, J_C-P = 7.1 Hz, 1C), 15.9 (d, J_C-P = 7.0 Hz, 1C).

**31P NMR** (121 MHz, CDCl₃) δ 1.58.

**HR-MS (ESI) m/z**: [M + H]+ Calcd for C₁₈H₂₃N₃O₃P 360.1472; Found 360.1477.
Diethyl (1-(pyridin-4-ylmethyl)phthalazin-2(1H)-yl)phosphonate (13b):

The brown oil (0.14 mmol, 49 mg, 45 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 13' (108 mg, 0.3 mmol).

\[
R_f = 0.36 \text{ (Methanol:Ethyl Acetate, 1:9)}
\]

\[\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.51 – 8.29 \text{ (m, 2H), 7.63 (s, 1H), 7.33 (td, } J = 7.5, 1.2 \text{ Hz, 1H), 7.25 – 7.15 \text{ (m, 2H), 6.92 – 6.78 \text{ (m, 2H), 6.54 (d, } J = 7.5 \text{ Hz, 1H), 5.36 (td, } J = 7.0, 2.2 \text{ Hz, 1H), 4.35 – 4.20 \text{ (m, 2H), 4.12 – 4.02 (m, 1H), 3.98 – 3.85 \text{ (m, 1H), 2.97 (d, } J = 7.0 \text{ Hz, 2H), 1.42 (td, } J = 7.1, 1.0 \text{ Hz, 3H), 1.25 (td, } J = 7.1, 1.0 \text{ Hz, 3H).}
\]

\[\text{C NMR (75 MHz, CDCl}_3\text{)} \delta 149.4 \text{ (2C), 145.6, 142.8 (d, } J_{C-P} = 12.5 \text{ Hz, CN), 131.0, 130.8 (d, } J_{C-P} = 6.5 \text{ Hz, 1C), 128.4, 126.5 (d, } J_{C-P} = 1.1 \text{ Hz, 1C), 125.4 (2C), 125.3, 123.6 (d, } J_{C-P} = 1.7 \text{ Hz, 1C), 64.2 (d, } J_{C-P} = 6.5 \text{ Hz, 1C), 63.3 (d, } J_{C-P} = 5.8 \text{ Hz, 1C), 55.0 (d, } J_{C-P} = 8.9 \text{ Hz, 1C), 41.3, 16.3 (d, } J_{C-P} = 7.0 \text{ Hz, 1C), 15.9 (d, } J_{C-P} = 7.0 \text{ Hz, 1C).}
\]

\[\text{P NMR (121 MHz, CDCl}_3\text{)} \delta 1.34.
\]

HR-MS (ESI) \textit{m/z}: [M + H]+ Calcd for C\textsubscript{18}H\textsubscript{23}N\textsubscript{3}O\textsubscript{3}P 360.1472; Found 360.1474.

Diethyl (1-pentylphthalazin-2(1H)-yl)phosphonate (14b):

The brown oil (0.09 mmol, 30 mg, 30 % yield) was obtained following the general procedure B after 19 h starting from the phosphonohydrazone 14' (102 mg, 0.3 mmol).
\[ R_f = 0.54 \text{ (Cyclohexane:Ethyl Acetate, 5:5)} \]

**1H NMR** (400 MHz, CDCl\(_3\)) \( \delta 7.49 \text{ (s, 1H)}, 7.38 - 7.34 \text{ (m, 1H)}, 7.30 \text{ (dd, } J = 5.7, 3.2 \text{ Hz, 2H}), 7.21 - 7.15 \text{ (m, 1H)}, 4.88 - 4.79 \text{ (m, 1H)}, 4.29 - 4.17 \text{ (m, 2H)}, 4.17 - 4.11 \text{ (m, 1H)}, 4.11 - 4.02 \text{ (m, 1H)}, 3.24 - 3.06 \text{ (m, 2H)}, 1.36 \text{ (dt, } J = 14.8, 7.1 \text{ Hz, 6H}), 1.30 - 1.21 \text{ (m, 3H)}, 1.21 - 1.10 \text{ (m, 3H)}, 0.76 \text{ (t, } J = 6.9 \text{ Hz, 3H}).

**13C NMR** (101 MHz, CDCl\(_3\)) \( \delta 140.3 \text{ (d, } J = 17.4 \text{ Hz, CN)}, 137.8, 132.9, 131.8, 130.2, 129.3, 126.6, 63.8 \text{ (d, } J = 6.2 \text{ Hz, 1C)}, 63.1 \text{ (d, } J = 5.8 \text{ Hz, 1C)}, 57.2 \text{ (d, } J = 9.3 \text{ Hz, 1C)}, 41.0 \text{ (d, } J = 5.6 \text{ Hz, 1C)}, 30.5, 27.9, 22.4, 16.2 \text{ (d, } J = 7.2 \text{ Hz, 1C)}, 16.1 \text{ (d, } J = 7.4 \text{ Hz, 1C)}, 13.9.

**31P NMR** (121 MHz, CDCl\(_3\)) \( \delta 2.82.

**HR-MS (ESI)** \( m/z \): [M + Na]+ Calcd for C\(_{17}\)H\(_{27}\)N\(_2\)NaO\(_3\)P 361.1652; Found 361.1652.

**Diethyl (1-heptylphthalazin-2(1H)-yl)phosphonate (15b):**

![Diagram of Diethyl (1-heptylphthalazin-2(1H)-yl)phosphonate (15b)](image)

The brown oil (0.14 mmol, 53 mg, 48% yield) was obtained following the general procedure B after 15 h starting from the phosphonohydrazone 15’ (110 mg, 0.3 mmol).

\[ R_f = 0.57 \text{ (Cyclohexane:EtOAc, 4:6)} \]

**1H NMR** (300 MHz, CDCl\(_3\)) \( \delta 7.45 \text{ (s, 1H)}, 7.34 - 7.30 \text{ (m, 1H)}, 7.33 - 7.21 \text{ (m, 2H)}, 7.18 - 7.11 \text{ (m, 1H)}, 4.87 - 4.76 \text{ (m, 1H)}, 4.29 - 3.97 \text{ (m, 4H)}, 3.20 - 3.04 \text{ (m, 1H)}, 3.12 - 3.03 \text{ (m, 3H)}, 1.38 - 1.32 \text{ (m, 3H)}, 1.33 \text{ (dt, } J = 10.7, 7.1, 1.0 \text{ Hz, 3H}), 1.27 - 1.18 \text{ (m, 3H)}, 1.18 - 1.07 \text{ (m, 7H)}, 0.77 \text{ (t, } J = 6.8 \text{ Hz, 3H}).

**13C NMR** (75 MHz, CDCl\(_3\)) \( \delta 140.2 \text{ (d, } J_{C-P} = 17.3 \text{ Hz, CN)}, 137.8, 132.9, 131.8, 130.2, 129.3, 126.6, 63.8 \text{ (d, } J_{C-P} = 6.3 \text{ Hz, 1C)}, 63.1 \text{ (d, } J_{C-P} = 5.8 \text{ Hz, 1C)}, 57.2 \text{ (d, } J_{C-P} = 9.3 \text{ Hz, 1C)}, 41.0 \text{ (d, } J_{C-P} = 5.6 \text{ Hz, 1C)}, 31.6, 30.8, 28.9, 25.6, 22.4, 16.2 \text{ (d, } J_{C-P} = 7.8 \text{ Hz, 1C)}, 16.1 \text{ (d, } J_{C-P} = 7.9 \text{ Hz, 1C}), 14.0.

**31P NMR** (121 MHz, CDCl\(_3\)) \( \delta 2.73.

**HR-MS (ESI)** \( m/z \): [M + H]+ Calcd for C\(_{19}\)H\(_{32}\)N\(_2\)O\(_3\)P 367.2145; Found 367.2147.
Diethyl(2-(p-tolyl)-1,2-dihydro-3H-naphtho[2,1-d][1,2]diazepin-3-yl) phosphonate (17a):

The brown oil (0.15 mmol, 60 mg, 49 % yield) was obtained following the general procedure B after 7 h starting from the phosphonohydrazone 17’ (123 mg, 0.3 mmol).

$R_f = 0.37$ (Cyclohexane:Ethyl Acetate, 5:5)

$^1H$ NMR (300 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.5$ Hz, 1H), 7.71 (dd, $J = 7.9$, 1.2 Hz, 1H), 7.59 (t, $J = 4.2$ Hz, 2H), 7.53 (ddd, $J = 6.8$, 8.5, 1.5 Hz, 1H), 7.45 (ddd, $J = 6.9$, 7.9, 1.1 Hz, 1H), 7.26 (d, $J = 8.5$ Hz, 1H, overlapped with CDCl$_3$), 6.87 (d, $J = 8.1$ Hz, 2H), 6.73 (d, $J = 8.2$ Hz, 2H), 6.32 (t, $J = 6.2$ Hz, 1H), 4.64 (ddd, $J = 16.2$, 6.6, 2.8 Hz, 1H), 4.33 - 4.08 (m, 4H), 3.37 (d, $J = 16.1$ Hz, 1H), 2.04 (s, 3H), 1.38 (tdd, $J = 7.1$, 1.7, 1.0 Hz, 6H).

$^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 141.6 (d, $J_{C,P} = 16.8$ Hz, CN), 136.3, 135.8, 135.3, 133.1, 131.9, 129.9, 128.6, 128.6 (2C), 128.4, 127.0, 126.8, 126.5, 125.6 (2C), 123.9, 64.1 (d, $J_{C,P} = 6.1$ Hz, 1C), 63.4 (d, $J_{C,P} = 5.8$ Hz, 1C), 62.1 (d, $J_{C,P} = 10.0$ Hz, 1C), 35.1 (d, $J_{C,P} = 5.1$ Hz, 1C), 20.8, 16.3 (d, $J_{C,P} = 7.1$ Hz, 1C), 16.1 (d, $J_{C,P} = 7.3$ Hz, 1C).

$^{31}P$ NMR (121 MHz, CDCl$_3$) $\delta$ 2.50.

HR-MS (ESI) $m/z$: [M + H]+ Calcd for C$_{24}$H$_{28}$N$_2$O$_3$P 423.1832; Found 423.1838.
Diethyl(6,7,8-trimethoxy-4-(p-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (18a):

The brown oil (0.18 mmol, 83 mg, 60 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 18’ (139 mg, 0.3 mmol).

Rf = 0.35 (Cyclohexane:Ethyl Acetate, 5:5)

\[ \text{H NMR (300 MHz, CDCl}_3\text{)} \delta 7.35 (s, 1H), 6.89 (s, 4H), 6.48 (s, 1H), 6.08 (t, J = 6.1 Hz, 1H), 4.26 – 4.04 (m, 5H), 3.79 (s, 3H), 3.77 (s, 3H), 3.67 (s, 3H), 2.91 (dd, J = 15.8, 1.9 Hz, 1H), 2.17 (s, 3H), 1.35 (dtd, J = 8.7, 7.1, 1.0 Hz, 6H).

\[ \text{C NMR (101 MHz, CDCl}_3\text{)} \delta 151.5, 151.3, 143.0, 140.3 (d, J_{C\text{-}}P = 18.3 \text{ Hz, CN}), 137.2, 135.9, 128.7 (2C), 128.4, 125.8 (2C), 125.0, 110.1, 63.8 (d, J_{C\text{-}}P = 5.8 \text{ Hz, 1C}), 63.3 (d, J_{C\text{-}}P = 5.6 \text{ Hz, 1C}), 62.2 (d, J_{C\text{-}}P = 10.0 \text{ Hz, 1C}), 60.9, 60.7, 55.9, 32.7 (d, J_{C\text{-}}P = 5.1 \text{ Hz, 1C}), 20.9, 16.2 (d, J_{C\text{-}}P = 7.6 \text{ Hz, 1C}), 16.1 (d, J_{C\text{-}}P = 7.8 \text{ Hz, 1C}).

\[ \text{P NMR (121 MHz, CDCl}_3\text{)} \delta 2.90.

HR-MS (ESI) m/z: [M + H]^+ Calcd for C_{23}H_{32}N_{2}O_{6}P 463.1993; Found 463.1995.

Diethyl (4-(p-tolyl)-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (19a):
The brown oil (0.14 mmol, 60 mg, 47 % yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 19’ (128 mg, 0.3 mmol).

R_f = 0.38 (Cyclohexane:Ethyl Acetate, 5:5)

_H NMR_ (300 MHz, CDCl_3) δ 7.48 (s, 1H), 7.43 (s, 1H), 7.33 (d, _J_ = 7.9 Hz, 1H), 7.10 (d, _J_ = 7.9 Hz, 1H), 6.89 (d, _J_ = 8.4 Hz, 2H), 6.84 (d, _J_ = 8.3 Hz, 2H), 6.20 (t, _J_ = 5.8 Hz, 1H), 4.28 – 4.04 (m, 4H), 3.67 (ddd, _J_ = 15.7, 6.3, 3.0 Hz, 1H), 3.40 (d, _J_ = 15.7 Hz, 1H), 2.15 (s, 3H), 1.40 – 1.30 (m, 6H, included 1.37 (td, _J_ = 7.1, 1.0 Hz, 1H), 1.34 (td, _J_ = 7.1, 1.0 Hz, 1H)).

_C NMR_ (101 MHz, CDCl_3) δ 142.0, 138.5 (d, _J_ _C-P_ = 17.0 Hz, CN), 136.2, 136.2, 133.0, 130.7, 129.0 (q, _J_ _C-F_ = 32.8 Hz, 1C), 128.9 (2C), 127.9 (q, _J_ _C-F_ = 3.7 Hz, 1C), 125.6 (2C), 125.3 (q, _J_ _C-F_ = 3.4 Hz, 1C), 123.8 (q, _J_ _C-F_ = 272.3 Hz, CF_3), 64.1 (d, _J_ _C-P_ = 6.0 Hz, 1C), 63.6 (d, _J_ _C-P_ = 5.8 Hz, 1C), 61.9 (d, _J_ _C-P_ = 10.5 Hz, 1C), 41.8 (d, _J_ _C-P_ = 5.3 Hz, 1C), 20.9, 16.2 (d, _J_ _C-P_ = 7.2 Hz, 1C), 16.1 (d, _J_ _C-P_ = 7.4 Hz, 1C).

_P NMR_ (121 MHz, CDCl_3) δ 2.29.

_F NMR_ (282 MHz, CDCl_3) δ -62.54.

HR-MS (ESI) _m/z_: [M + H]+ Calcd for C_{21}H_{25}F_{3}N_{2}O_{3}P 441.1549; Found 441.1553.

Diethyl(8-fluoro-4-(p-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (20a):

![Diethyl(8-fluoro-4-(p-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate](image)

The brown oil PC-195 RM7 (0.1 mmol, 40 mg, 34% yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 20’ (117mg, 0.3 mmol).

R_f = 0.44 (Cyclohexane:Ethyl Acetate, 5:5)
$^1$H NMR (300 MHz, CDCl$_3$) δ 7.38 (s, 1H), 6.95 – 6.83 (m, 6H), 6.79 (td, $J = 8.3$, 2.6 Hz, 1H), 6.14 (t, $J = 6.1$ Hz, 1H), 4.29 – 4.03 (m, 4H), 3.57 (ddd, $J = 15.5$, 6.3, 3.1 Hz, 1H), 3.36 (d, $J = 15.3$ Hz, 1H), 2.17 (s, 3H), 1.35 (dtd, $J = 11.4$, 7.1, 0.9 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.2 (d, $J_{C-F} = 244.9$ Hz, 1C), 138.7 (dd, $J_{C-F,C-P} = 17.0$, 1.9 Hz, CN), 136.5, 136.0, 134.1 (d, $J_{C-F} = 7.0$ Hz, 1C), 134.1 (d, $J_{C-F} = 3.2$ Hz, 1C), 131.7 (d, $J_{C-F} = 7.9$ Hz, 1C), 128.8 (2C), 125.7 (2C), 117.3 (d, $J_{C-F} = 22.0$ Hz, 1C), 116.0 (d, $J_{C-F} = 21.3$ Hz, 1C), 64.0 (d, $J_{C-P} = 6.0$ Hz, 1C), 63.5 (d, $J_{C-P} = 5.8$ Hz, 1C), 62.1 (d, $J_{C-P} = 10.4$ Hz, 1C), 41.1 (d, $J_{C-P} = 5.2$ Hz, 1C), 20.9, 16.2 (d, $J_{C-P} = 7.1$ Hz, 1C), 16.1 (d, $J_{C-P} = 7.3$ Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 2.45.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ -116.89.

HR-MS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{20}$H$_{25}$FN$_2$O$_3$P 391.1581; Found 391.1583.

Diethyl(6-methyl-4-(p-tolyl)-5,6-dihydro-[1,2]diazepino[5,4-b]indol-3(4H)-yl) phosphonate (21a):

The brown oil (0.18 mmol, 76 mg, 59 % yield) was obtained following the general procedure B after 20 h starting from the phosphonohydrazone 21’ (128 mg, 0.3 mmol).

$R_f$ = 0.38 (Cyclohexane:Ethyl Acetate, 2:8)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (s, 1H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.35 – 7.30 (m, 1H), 7.37 – 7.26 (m, 1H, overlapped with CDCl$_3$), 7.21 – 7.15 (m, 1H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.94 (d, $J = 8.1$ Hz, 2H), 6.15-6.05 (m, 1H), 4.39 – 4.26 (m, 2H), 4.17 – 4.02 (m, 1H), 4.02 – 3.93 (m, 1H), 3.93 – 3.86 (m, 1H), 3.83 (s, 3H), 3.58 (dd, $J = 17.4$, 5.1 Hz, 1H), 2.20 (s, 3H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H).
**13C NMR** (101 MHz, CDCl$_3$) $\delta$ 141.9, 141.8, 136.6 (d, $J_{C-P} = 7.5$ Hz, CN), 134.3, 128.8 (2C), 127.0 (2C), 126.4, 122.4, 121.1, 117.6, 109.4, 108.8, 64.4 (d, $J_{C-P} = 6.8$ Hz, 1C), 62.9 (d, $J_{C-P} = 5.9$ Hz, 1C), 55.5 (d, $J_{C-P} = 9.0$ Hz, 1C), 33.0 (d, $J_{C-P} = 5.8$ Hz, 1C), 30.4, 20.9, 16.3 (d, $J_{C-P} = 6.9$ Hz, 1C), 16.0 (d, $J_{C-P} = 7.3$ Hz, 1C).

**31P NMR** (121 MHz, CDCl$_3$) $\delta$ 4.49.

**HR-MS (ESI) m/z:** [M + H$^+$] Calcd for C$_{23}$H$_{27}$N$_3$O$_3$P 424.1784; Found 424.1785.

**Diethyl(6,7,8-trimethoxy-4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (22a):**

![Chemical Structure](image)

The brown oil (0.19 mmol, 101 mg, 63 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 22' (162 mg, 0.3 mmol).

**Rf** = 0.40 (Cyclohexane:Ethyl Acetate, 2:8)

**1H NMR** (300 MHz, CDCl$_3$) $\delta$ 7.35 (s, 1H), 6.47 (s, 1H), 6.29 – 6.28 (m, 2H, included 6.28 (s, 1H) + 6.28 (s, 1H)), 6.08 (t, $J = 6.0$ Hz, 1H), 4.28 – 4.07 (m, 5H), 3.79 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.71 – 3.69 (m, 9H, included 3.70 (s, 3H) + 3.70 (s, 6H)), 2.91 (dd, $J = 15.8$, 1.8 Hz, 1H), 1.45-1.30 (m, 6H).

**13C NMR** (101 MHz, CDCl$_3$) $\delta$ 152.7 (2C), 151.6, 151.2, 143.3, 140.3 (d, $J_{C-P} = 16.8$ Hz, CN), 136.2, 135.6, 128.1, 125.2, 110.3, 103.2 (2C), 64.1 (d, $J_{C-P} = 6.2$ Hz, 1C), 63.3 (d, $J_{C-P} = 5.8$ Hz, 1C), 62.2 (d, $J_{C-P} = 10.0$ Hz, 1C), 61.1, 60.8, 60.8, 56.0, 55.8 (2C), 32.4 (d, $J_{C-P} = 5.2$ Hz, 1C), 16.3 (d, $J_{C-P} = 7.2$ Hz, 1C), 16.1 (d, $J_{C-P} = 7.3$ Hz, 1C).

**31P NMR** (121 MHz, CDCl$_3$) $\delta$ 2.82.

**HR-MS (ESI) m/z:** [M + H$^+$] Calcd for C$_{25}$H$_{36}$N$_2$O$_9$P 539.2153; Found 539.2153.
Methyl 4-((2-(diethoxyphosphoryl)-6,7,8-trimethoxy-1,2-dihydropthalazin-1-yl)methyl)benzoate (23b):

The brown oil (0.06 mmol, 32 mg, 21 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 23’ (152 mg, 0.3 mmol).

Rf = 0.57 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.83 – 7.76 (m, 2H), 7.40 (s, 1H), 7.01 – 6.96 (m, 2H), 6.44 (s, 1H), 5.63 – 5.56 (m, 1H), 4.27 – 4.14 (m, 2H), 4.12 – 3.97 (m, 1H), 3.96 – 3.89 (m, 1H), 3.87 (s, 6H), 3.75 (s, 3H), 3.62 (s, 3H), 3.03 – 2.89 (m, 2H), 1.40 (td, $J = 7.1, 1.0$ Hz, 3H), 1.25 (td, $J = 7.1, 0.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.2, 153.5, 148.9, 144.0, 142.5, 142.3 (d, $J_{C-P} = 12.5$ Hz, CN), 130.3 (2C), 129.0 (2C), 128.1, 119.9 (d, $J_{C-P} = 1.6$ Hz, 1C), 117.3 (d, $J_{C-P} = 6.6$ Hz, 1C), 103.6, 64.0 (d, $J_{C-P} = 6.4$ Hz, 1C), 63.1 (d, $J_{C-P} = 5.8$ Hz, 1C), 60.8, 60.5, 56.1, 52.0, 49.8 (d, $J_{C-P} = 9.5$ Hz, 1C), 41.3, 16.3 (d, $J_{C-P} = 7.1$ Hz), 15.9 (d, $J_{C-P} = 7.0$ Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 1.69.

HR-MS (ESI) m/z: [M + H]+$^+$ Calcd for C$_{24}$H$_{32}$N$_2$O$_8$P 507.1891; Found 507.1897.

Diethyl(1-(4-cyanobenzyl)-6,7,8-trimethoxypthalazin-2(1H)-yl) phosphonate (24b):
The brown oil (0.22 mmol, 104 mg, 73 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 24’ (142 mg, 0.3 mmol).

Rf = 0.29 (Cyclohexane:Ethyl Acetate, 5:5)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.40 (d, J = 8.4 Hz, 2H), 7.37 (s, 1H), 7.02 (d, J = 8.4 Hz, 2H), 6.44 (s, 1H), 5.65-5.52 (m, 1H), 4.26 – 4.15 (m, 2H), 4.09 – 3.99 (m, 1H), 3.97 – 3.88 (m, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H), 2.98 (dd, J = 13.1, 6.8 Hz, 1H), 2.91 (dd, J = 13.2, 5.6 Hz, 1H), 1.40 (td, J = 7.1, 1.0 Hz, 3H), 1.24 (td, J = 7.1, 0.9 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.6, 148.7, 144.0, 142.7, 142.2 (d, $J_{C-P} = 12.4$ Hz, CN), 131.4 (2C), 131.0 (2C), 119.8, 119.1, 116.9 (d, $J_{C-P} = 6.7$ Hz, 1C), 110.0, 103.7, 64.1 (d, $J_{C-P} = 6.5$ Hz, 1C), 63.2 (d, $J_{C-P} = 5.8$ Hz, 1C), 60.8, 60.7, 56.1, 49.8 (d, $J_{C-P} = 9.6$ Hz, 1C), 41.6, 16.3 (d, $J_{C-P} = 7.0$ Hz, 1C), 16.0 (d, $J_{C-P} = 7.0$ Hz, 1C).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 1.56.

HR-MS (ESI) m/z: [M + Na]+ Calcd for C$_{23}$H$_{28}$N$_3$NaO$_6$P 496.1608; Found 496.1615.

Diethyl(6,7,8-trimethoxy-4-(pyridin-2-yl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (25a):

The brown oil (0.06 mmol, 26 mg, 19 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 25’ (135 mg, 0.3 mmol).

Rf = 0.68 (Methanol:Ethyl Acetate, 1:9)

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.34 (d, J = 4.8 Hz, 1H), 7.40 (td, J = 7.8, 1.8 Hz, 1H), 7.34 (s, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.91 (dd, J = 7.5, 4.8 Hz, 1H), 6.41 (s, 1H),
6.17 (t, \(J = 6.2\) Hz, 1H), 4.46 (ddd, \(J = 15.7, 6.5, 3.1\) Hz, 1H), 4.31 – 4.07 (m, 4H), 3.80 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 2.89 (dd, \(J = 15.7, 1.7\) Hz, 1H), 1.42 – 1.32 (m, 6H).

\[ ^{13}C\text{ NMR} (75\text{ MHz, CDCl}_3) \delta 159.0, 151.5, 151.4, 149.0, 143.1, 140.6 (d, \(J_{C-P} = 16.9\) Hz, CN), 136.0, 128.0, 125.6, 121.3, 120.7, 110.1, 64.1 (d, \(J_{C-P} = 6.0\) Hz, 1C), 63.9 (d, \(J_{C-P} = 9.8\) Hz, 1C), 63.4 (d, \(J_{C-P} = 5.9\) Hz, 1C), 60.9, 60.7, 55.9, 32.1 (d, \(J_{C-P} = 4.8\) Hz, 1C), 16.3 (d, \(J_{C-P} = 7.1\) Hz, 1C), 16.1 (d, \(J_{C-P} = 7.1\) Hz, 1C).

\[ ^{31}P\text{ NMR} (121\text{ MHz, CDCl}_3) \delta 2.81. \]

\[ \text{HR-MS (ESI) } m/z: [M + H]^+ \text{ Calcd for } C_{21}H_{29}N_3O_6P 450.1789; \text{ Found 450.1796.} \]

Diethyl(6,7,8-trimethoxy-1-(pyridin-2-ylmethyl)phthalazin-2(1H)-yl) phosphonate (25b):

The brown oil (0.4 mmol, 60 mg, 45 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 25’ (135 mg, 0.3 mmol).

\[ R_f = 0.51 \text{ (Methanol:Ethyl Acetate, 1:9)} \]

\[ ^{1}H\text{ NMR} (300\text{ MHz, CDCl}_3) \delta 8.39 – 8.35 (m, 1H), 7.61 (s, 1H), 7.49 (td, \(J = 7.6, 1.7\) Hz, 1H), 7.10 – 7.02 (m, 2H), 6.52 (s, 1H), 5.67 (ddd, \(J = 7.6, 6.1, 3.1\) Hz, 1H), 4.23 – 4.12 (m, 2H), 4.08 – 3.98 (m, 1H), 3.97 – 3.88 (m, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.61 (s, 3H), 3.12 (dd, \(J = 12.7, 6.1\) Hz, 1H), 3.04 (dd, \(J = 12.7, 7.9\) Hz, 1H), 1.36 (td, \(J = 7.0, 0.7\) Hz, 3H), 1.26 – 1.20 (m, 3H, overlapped with vacuum grease).

\[ ^{13}C\text{ NMR} (101\text{ MHz, CDCl}_3) \delta 157.2, 153.3, 148.7, 143.9, 143.0 (d, \(J_{C-P} = 12.3\) Hz, CN), 135.7, 124.7, 121.3, 119.8, 117.9, 117.9, 103.8, 63.8 (d, \(J_{C-P} = 6.0\) Hz, 1C),
63.1 (d, \( J_{C,P} = 5.6 \text{ Hz}, 1\text{C} \)), 60.7, 60.6, 56.1, 49.3 (d, \( J_{C,P} = 9.2 \text{ Hz}, 1\text{C} \)), 43.2, 16.2 (d, \( J_{C,P} = 7.3 \text{ Hz}, 1\text{C} \)), 16.0 (d, \( J_{C,P} = 7.0 \text{ Hz}, 1\text{C} \)).

\( ^{31}\text{P} \text{ NMR} \) (121 MHz, CDCl\(_3\)) \( \delta \) 1.65.

\( \text{HR-MS (ESI)} \ m/z: [M + H]^+ \) Calcd for C\(_{21}\)H\(_{29}\)N\(_3\)O\(_6\)P 450.1788; Found 450.1793.

Diethyl(6,7,8-trimethoxy-1-(pyridin-4-ylmethyl)phthalazin-2(1H)-yl)phosphonate (26b):

The brown oil (0.14 mmol, 64 mg, 47\% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 26' (135 mg, 0.3 mmol).

\( RF = 0.5 \) (Methanol:Ethyl Acetate, 1:9)

\( ^{1}\text{H} \text{ NMR} \) (300 MHz, CDCl\(_3\)) \( \delta \) 8.34 (bs, 2H), 7.38 (s, 1H), 6.89 (d, \( J = 5.6 \text{ Hz}, 2\text{H} \)), 6.44 (s, 1H), 5.60 (ddd, \( J = 7.1, 5.6, 2.8 \text{ Hz}, 1\text{H} \)), 4.27 – 4.14 (m, 2H), 4.08 – 4.00 (m, 1H), 3.97 – 3.88 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 2.94 (dd, \( J = 13.0, 6.9 \text{ Hz}, 1\text{H} \)), 2.86 (dd, \( J = 12.9, 5.3 \text{ Hz}, 1\text{H} \)), 1.40 (td, \( J = 7.0, 1.0 \text{ Hz}, 3\text{H} \)), 1.24 (td, \( J = 6.7, 6.0, 0.9 \text{ Hz}, 3\text{H} \), overlapped with vacuum grease).

\( ^{13}\text{C} \text{ NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 153.7, 148.83 (d, \( J_{C,P} = 19.1 \text{ Hz}, \text{CN} \)), 148.67 (d, \( J_{C,P} = 11.0 \text{ Hz}, 1\text{C} \)), 147.0, 144.0, 142.3 (d, \( J_{C,P} = 12.4 \text{ Hz}, 1\text{C} \)), 126.2, 119.7 (d, \( J_{C,P} = 1.7 \text{ Hz}, 1\text{C} \)), 116.4 (d, \( J_{C,P} = 6.7 \text{ Hz}, 1\text{C} \)), 103.8, 64.2 (d, \( J_{C,P} = 6.5 \text{ Hz}, 1\text{C} \)), 63.2 (d, \( J_{C,P} = 5.8 \text{ Hz}, 1\text{C} \)), 60.8, 60.7, 56.1, 49.5 (d, \( J_{C,P} = 9.6 \text{ Hz}, 1\text{C} \)), 41.2, 16.3 (d, \( J_{C,P} = 7.0 \text{ Hz}, 1\text{C} \)), 15.9 (d, \( J_{C,P} = 7.0 \text{ Hz}, 1\text{C} \)).

\( ^{31}\text{P} \text{ NMR} \) (121 MHz, CDCl\(_3\)) \( \delta \) 1.72.

\( \text{HR-MS (ESI)} \ m/z: [M + H]^+ \) Calcd for C\(_{21}\)H\(_{29}\)N\(_3\)O\(_6\)P 450.1788; Found 450.1787.
Diethyl(4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzofuro[3,2-d][1,2]55 diazepin-3-yl)phosphonate (27a):

The brown oil (0.03 mmol, 16 mg, 22 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 27' (73 mg, 0.15 mmol).

R<sub>f</sub> = 0.28 (Cyclohexane:Ethyl Acetate, 2:8)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.98 (d, J = 1.2 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.33 (m, 2H), 6.32 (s, 2H), 4.68 – 4.61 (m, 1H), 4.19 – 4.05 (m, 2H), 4.02 – 3.85 (m, 4H), 3.81 (s, 3H), 3.78 (s, 6H), 1.28 (td, J = 7.1, 0.9 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.6, 154.4, 153.4 (2C), 137.5, 126.2 (2C), 125.2, 123.7, 118.5, 112.0 (2C), 111.6, 105.6 (2C), 63.5 (d, J<sub>C,P</sub> = 5.9 Hz, 1C), 63.5 (d, J<sub>C,P</sub> = 6.2 Hz, 1C), 61.2 (d, J<sub>C,P</sub> = 11.7 Hz, 1C), 60.8, 56.2, 48.5 (d, J<sub>C,P</sub> = 5.1 Hz, 1C), 16.1 (d, J<sub>C,P</sub> = 3.4 Hz, 1C), 16.1 (d, J<sub>C,P</sub> = 3.5 Hz, 1C).

<sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ 5.08.

HR-MS (ESI) m/z: [M + H]+ Calcd for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>P 487.1629; Found 487.1628.

Diethyl(9-(pyridin-3-yl)-8,9-dihydro-7H-pyrido[3,2-d][1,2]diazepin-7-yl) phosphonate (28a):
The brown oil (0.06 mmol, 22.5 mg, 50 % yield) was obtained following the general procedure B after 7 h starting from the phosphonohydrazone 28′ (54 mg with 83% of mass purity, 0.12 mmol (adjusted to account for inseparable starting material)).

**Rf = 0.25 (Methanol:Ethyl Acetate, 1:9)**

**1H NMR** (300 MHz, CDCl₃) δ 8.57-8.45 (m, 2H, included 8.53 (dd, J = 4.8, 1.6 Hz, 1H) + 8.51 – 8.48 (m, 1H)), 8.02 (s, 1H), 7.85 (dd, J = 7.9, 1.5 Hz, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 (dd, J = 7.9, 4.7 Hz, 1H), 5.02 (dd, J = 5.1, 3.4 Hz, 1H), 4.85 (dt, J = 14.1, 6.2 Hz, 1H), 4.20 – 3.93 (m, 2H), 3.68 – 3.56 (m, 2H), 3.55 – 3.40 (m, 1H), 1.30 (td, J = 7.1, 0.9 Hz, 3H), 1.10 (td, J = 7.1, 1.0 Hz, 3H).

**13C NMR** (75 MHz, CDCl₃) δ 158.8, 149.4, 146.5, 145.1, 140.9, 139.4, 138.4 (d, J_{C-P} = 17.2 Hz, CN), 138.0, 127.4, 124.5, 123.0, 63.9 (d, J_{C-P} = 6.2 Hz, 1C), 63.6 (d, J_{C-P} = 6.1 Hz, 1C), 54.5 (d, J_{C-P} = 5.2 Hz, 1C), 50.7 (d, J_{C-P} = 9.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.8 Hz, 1C), 16.0 (d, J_{C-P} = 7.5 Hz, 1C).

**31P NMR** (121 MHz, CDCl₃) δ 2.98.

**HR-MS (ESI) m/z:** [M + H]+ Calcd for C₁₇H₂₂N₄O₃P 361.1424; Found 361.1423.
NMR Spectrum
31P dec 1H

8'

\[ \begin{align*}
\text{N} & \quad \text{O} \\
\text{OEt} & \quad \text{OEt} \\
\text{F} & \quad \text{F}
\end{align*} \]
4a- dia syn
4a- dia syn
4a- dia syn
4a - dia syn

NOESY - A correlation is observed between the two vicinal protons of the 7 members ring
4a- diaanti
4a- dia anti
4a- dia anti
NOESY - No correlation observed between the two vicinal protons of the 7 members ring

4a- dia anti
5a
31P dec 1H

![Chemical Structure](image)

8a

![NMR Spectrum](image)
9b
10b
13b
14b
31P dec 1H

19a

\[
\text{CF}_3
\]

\[
\text{N} \rightarrow \equiv \text{N}
\]

\[
\text{O} \rightarrow \text{OEt}
\]

\[
\text{O} \rightarrow \text{OEt}
\]

\[
\text{CH}_3
\]

\[
\text{f1 (ppm)}
\]

226
20a
21a
23b
25b

overlapped with grease