

# An unexpected oxidative C-O bond formation: 11,17a-dihydrobenzo[4,5]oxazolo[3,2-a]dinaphtho[2,1-c:1',2'-e]azepine

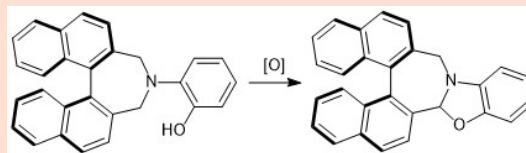
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Phosphoric acids bound to 3,3'-substituted 1,1'-binaphthalene-2,2'-diol (BINOL) have found wide application as effective asymmetric catalysts. In this work, we describe our attempt to construct a new binaphthalene-based phosphoric acid **6**. We found that both the key precursor **2** and the desired product **6** decay rapidly and quantitatively to a stable dihydrooxazole **3** via an O<sub>2</sub>-driven oxidative C-O bond formation.

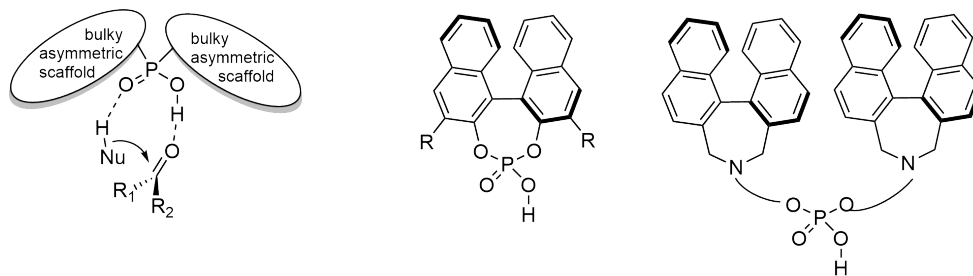


## Introduction

Phosphate esters have been used successfully as organocatalysts [1, 2, 3] in a plethora of transformations including, but not limited to Mannich reactions [4, 5, 6], Friedel-Crafts reactions [7], transfer hydrogenations [8], aza-Diels-Alder reactions [9], Biginelli reactions [10], Pictet-Spengler reactions [11], bromoesterifications [12], alkylation of alpha-diazo esters [13] and hydrophosphonylations [14].

Powerful asymmetric organocatalysts have been designed selecting bulky asymmetric organic residues bound to the remaining two oxygen atoms at the phosphorous center [15] as shown in Fig. 1.

**Figure 1.** Left hand side: Common design for asymmetric phosphate organocatalysts, exemplified for the nucleophilic attack on an activated carbonyl group. Center: Typical implementation of this design using 3,3'-substituted BINOL phosphoesters [5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. Right-hand side: new catalyst design with chiral dinaphthoazepine moieties, this paper.

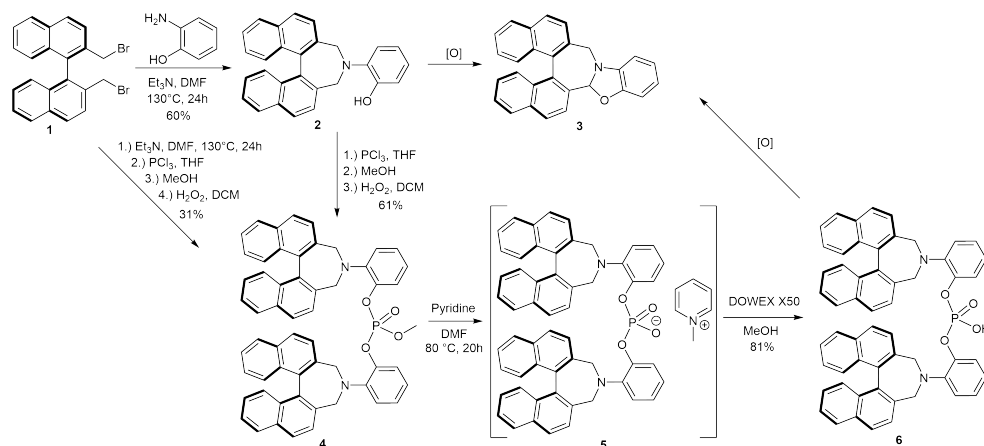


In this work, we aimed to extend this concept to phosphoric acids with pendant sidearms containing two dinaphthoazepine groups.

## Results and discussion

As a chiral precursor, we prepared dibromide (*R*)-**1** in three steps from (*R*)-BINOL according to Bulman Page *et al.* [16] and Rosini *et al.* [17] (Scheme 1). We then attempted to synthesize aminophenol **2** under standard conditions but observed formation of dihydrooxazole **3**, obviously the oxidation product of **2**.

**Figure 2.** Synthesis of chiral phosphate **6**. Both the key intermediate **2** and the free acid **6** decay readily to dihydrooxazole **3**. We did not determine the configuration of the  $sp^3$  carbon in the dihydrooxazole, but we found only one of the two possible diastereomers.



Even when working in an inert atmosphere, this side reaction limited the yield of phenol **2** to 60%. The product had to be kept under argon to prevent further oxidation.

Phenol **2** was converted into methyl phosphate **4** with  $\text{PCl}_3$ , solvolysis and follow-up oxidation in 36% overall yield. Due to the air sensitivity of the phenol, we developed an in-situ protocol to transform dibromide **1** into phosphate ester **4**, but the yield was about as low (31%) as the two-step approach.

Exploiting the alkylating properties of phosphate esters [18], we were able to break the O- $\text{CH}_3$  bond in **4** by transalkylation with an excess of pyridine, yielding the pyridinium salt **5**. Protonation of the crude salt **5** using the cation exchange resin DOWEX X50 afforded the desired free acid **6** in 81% yield (from **4**). However, the acid turned out to be unstable in solution as well. Immediate decomposition to dihydrooxazole **3** was observed.

In summary, our attempts to synthesize the new potential organocatalytic Brønsted acid **6** showed that these compounds are inherently unstable; both phenol **2** and the final product **6** displayed a strong tendency to form dihydrooxazole **3**. While this finding renders free acid **6** unsuitable as a catalyst, the observed oxidative bond formation could be an interesting new way to construct C-O bonds in target molecules.

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## Experimental details

### General

NMR Spectra were recorded on two different Bruker spectrometers (Bruker Biospin, Billerica, MA, USA): A Bruker AVIII 400 spectrometer operating at 400.27 MHz ( $^1\text{H}$ ), 100.66 MHz ( $^{13}\text{C}$ ) and 162.04 MHz ( $^{31}\text{P}$ ) used for standard spectra and a Bruker AVIII 600 operating at 600.25 MHz ( $^1\text{H}$ ), 150.95 MHz ( $^{13}\text{C}$ ) and 242.97 MHz ( $^{31}\text{P}$ ). All NMR spectra were recorded at 298 K unless otherwise specified. Chemical shifts are stated in ppm relative to the solvent residual signals. The solvents were calibrated to 7.24 ( $^1\text{H}$ ) and 77.00 ( $^{13}\text{C}$ ) for  $\text{CDCl}_3$  and 2.50 ( $^1\text{H}$ ) and 39.52 ( $^{13}\text{C}$ ) for  $\text{DMSO-d}_6$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are recorded in a J-modulated mode. HRMS was, unless otherwise noted, acquired on a Bruker Maxis ESI oa-RTOF mass spectrometer (maXis ESI-Qq-TOF mass spectrometer, Bruker Daltonics, Bremen, Germany) using a quadrupole analyzer as ion guide.

Preparative column chromatography was performed on a Biotage Isolera One flash purification system using self-packed  $\text{SiO}_2$  cartridges (Macherey-Nagel silica gel 60M, particle size 40-63  $\mu\text{m}$ ). TLC were performed on Macherey-Nagel TLC aluminium sheets with a 0.20 mm layer of silica gel 60 with F 254 fluorescence indicator. Dry THF was distilled from sodium benzophenone ketyl under argon, dry DCM was distilled from  $\text{CaH}_2$  and DMF was distilled from  $\text{CaH}_2$  under reduced pressure and stored with molecular sieve 4Å.  $\text{PCl}_3$  and  $\text{Et}_3\text{N}$  were distilled and stored under argon prior to use. Other chemicals were bought from Sigma-Aldrich, Acros Organics and Alfa Aesar in reagent grade or better and used as recieved.

### Synthesis

#### *1,17a-Dihydrobenzo[4,5]oxazolo[3,2-a]dinaphtho[2,1-c:1',2'-e]azepine 3:*

In an oven dried Schlenk tube 1.02 g of dibromide **1** (2.32 mmol) and 0.32 g of 2-aminophenol (2.97 mmol, 1.28 equiv.) were dissolved in dry DMF. After the solution was degassed 1.6 mL of  $\text{Et}_3\text{N}$  (1.16 g, 11.5 mmol, 4.95 equiv.) was added by syringe and the mixture was heated to 130  $^\circ\text{C}$ . After 24 h the mixture was cooled to room temperature. Then 25 mL of deionized water was added and the mixture was extracted three times with DCM (50 + 25 + 25 mL). The organic phase was washed twice with brine (25 + 25 mL), once with water (25 mL) and dried with  $\text{MgSO}_4$ . Chromatography yielded 0.582g (65%) of **3** as a white powder.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 8.00 (d,  $J$  = 8.3 Hz, 1H); 7.96 (t,  $J$  = 8.9 Hz, 2H); 7.90 (d,  $J$  = 8.1 Hz, 1H); 7.80 (d,  $J$  = 8.6 Hz, 1H); 7.69 (d,  $J$  = 8.3 Hz, 1H); 7.49 (ddd,  $J$  = 7.9, 6.8, 1.0 Hz, 1H); 7.45 (ddd,  $J$  = 7.9, 6.8, 0.9 Hz, 1H); 7.38 (t,  $J$  = 8.6 Hz, 2H); 7.28 (ddd,  $J$  = 8.2, 6.8, 1.2 Hz, 1H); 7.24 (ddd,  $J$  = 8.2, 6.7, 1.1 Hz, 1H); 6.90 (dd,  $J$  = 7.7, 0.8 Hz, 1H); 6.78 (dt,  $J$  = 7.7, 1.0 Hz, 1H); 6.71 (dt,  $J$  = 7.7, 1.2 Hz, 1H); 6.47 (dd,  $J$  = 7.3, 0.9 Hz, 1H); 6.32 (s, 1H); 4.39 (d,  $J$  = 11.0 Hz, 1H); 3.62 (d,  $J$  = 10.9 Hz, 1H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  = 151.61 ( $\text{C}_q$ ); 137.64 ( $\text{C}_q$ ); 134.15 ( $\text{C}_q$ ); 133.48 ( $\text{C}_q$ ); 133.34 ( $\text{C}_q$ ); 133.32 ( $\text{C}_q$ ); 133.09 ( $\text{C}_q$ ); 131.71 ( $\text{C}_q$ ); 131.13 ( $\text{C}_q$ ); 130.63 ( $\text{C}_q$ ); 129.35 (CH); 129.15 (CH); 128.36 (CH); 128.31 (CH); 127.38 (CH); 127.25 (CH); 127.13 (CH); 126.23 (CH); 126.08 (CH); 125.99 (CH); 125.92 (CH); 121.83 (CH); 121.73 (CH); 119.44 (CH); 107.91 (CH); 107.67 (CH); 95.56 (CH); 48.43 ( $\text{CH}_2$ ) ppm. HRMS:  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{20}\text{NO}$  ( $[\text{M} + \text{H}]^+$ ): 386.1539, found: 386.1539;  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{19}\text{NNaO}$  ( $[\text{M} + \text{Na}]^+$ ): 408.1359; found: 408.1361.

#### *2-(3,5-Dihydro-4H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl)phenol 2:*

In an oven dried Schlenk tube 0.20 g of dibromide **1** (0.45 mmol) and 0.06 g of 2-aminophenol (0.58 mmol, 1.28 equiv.) was dissolved in 10 mL of DMF (abs.). The solution was degassed and 0.32 mL of  $\text{Et}_3\text{N}$  (0.23 g, 2.29 mmol, 5.05 equiv.) was added

by syringe and the mixture was heated to 130 °C. After 24 h refluxing the resulting mixture was cooled to room temperature and approximately 25 mL of water were added. The resulting slurry was filtered and the solid was washed with water. It was dissolved in DCM and washed with 15 mL of water then dried with MgSO<sub>4</sub> and the solvent was removed by rotary evaporation. Flash chromatography on a 25 g column (15-40% EtOAc in heptane) lead to 105 mg (60%) of **2** as a cream-colored foam that was kept under argon. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ = 8.01-7.95 (m, 4H); 7.52-7.45 (m, 6H); 7.29 (ddd, J = 8.4, 6.7, 1.3 Hz, 2H); 7.08 (dt, J = 8.0, 1.4 Hz, 1H); 7.00 (dd, J = 8.0, 1.4 Hz, 1H); 6.83 (dd, J = 7.9, 1.4 Hz, 1H); 6.72 (dt, J = 7.6, 1.6 Hz, 1H); 3.92 (d, J = 12.3 Hz, 2H); 3.74 (d, J = 12.3 Hz, 2H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 101 MHz) δ = 151.86 (C<sub>q</sub>); 138.77 (C<sub>q</sub>); 135.16 (2C<sub>q</sub>); 133.33 (2C<sub>q</sub>); 133.21 (2C<sub>q</sub>); 131.45 (2C<sub>q</sub>); 128.95 (2CH); 128.36 (2CH); 127.69 (2CH); 127.50 (2CH); 126.82 (2CH); 126.01 (2CH); 125.74 (2CH); 124.20 (CH); 119.66 (CH); 114.08 (CH); 55.81 (2CH<sub>2</sub>) ppm. HRMS: calcd. for C<sub>28</sub>H<sub>22</sub>NO ([M + H]<sup>+</sup>): 388.1696; found: 388.1687.

*Bis(2-(3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl)phenyl) methyl phosphate* **4**:

In an oven dried Schlenk tube 100 mg of aminophenol **2** (0.26 mmol) was dissolved in 10 mL of dry THF and 0.18 mL of Et<sub>3</sub>N (130 mg, 1.29 mmol, 5.0 equiv.) was added. The solution was degassed three times by freezing, then it was cooled with an ice bath and 12 μL of PCl<sub>3</sub> (20 mg, 0.14 mmol, 0.54 equiv.) was added. Immediately a white solid was formed. The mixture was stirred for 90 min at 0 °C then the solvent was removed in vacuo and the residue was dissolved in DCM and 0.12 mL of hydrogen peroxide (30% in water, 0.13 g, 3.87 mmol, 14.9 equiv.) was added. The mixture was stirred for an additional h, and then 30 mL of NaHCO<sub>3</sub> solution was added. The organic layer was removed and the aqueous layer was extracted twice with DCM (10 + 5 mL). Removal of the solvent by rotary evaporation gave the crude product. Flash chromatography gave the product in a yield of 67 mg (61%) as a white foam. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz) δ = 7.89 (d, J = 8.1 Hz, 2H); 7.88 (d, J = 8.1 Hz, 2H); 7.82 (d, J = 8.2 Hz, 2H); 7.77 (d, J = 8.2 Hz, 2H); 7.48 (pt, J = 8.7 Hz, 4H); 7.45 (ddd, J = 7.9, 7.0, 0.9 Hz, 4H); 7.43-7.41 (m, 1H); 7.31-7.24 (m, 9H); 6.83-6.73 (m, 4H); 6.69 (d, 7.8 Hz, 1H); 6.64 (m, 1H); 4.02 (d, J = 12.3 Hz, 2H); 3.99 (d, J = 12.3 Hz, 2H); 3.74 (d, J = 11.8 Hz, 3H); 3.71 (d, J = 12.2 Hz, 2H); 3.70 (d, J = 12.2 Hz, 2H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 151 MHz) δ = 143.18 (d, J = 6.7 Hz, C<sub>q</sub>); 143.06 (d, J = 7.0 Hz, C<sub>q</sub>); 142.68 (d, J = 5.9 Hz, C<sub>q</sub>); 142.36 (d, J = 6.1 Hz, C<sub>q</sub>); 134.87 (2C<sub>q</sub>); 134.85 (2C<sub>q</sub>); 133.36 (4C<sub>q</sub>); 133.10 (4C<sub>q</sub>); 131.25 (4C<sub>q</sub>); 128.70 (2CH); 128.69 (2CH); 128.27 (2CH); 128.26 (2CH); 127.60 (2CH); 127.57 (2CH); 127.45 (4CH); 125.84 (2CH); 125.81 (2CH); 125.53 (2CH); 125.51 (2CH); 125.49 (d, J = 1.1 Hz, CH); 125.19 (CH); 122.21 (CH); 121.25 (d, J = 2.6 Hz, CH); 120.97 (d, J = 2.6 Hz, CH); 120.41 (CH); 120.24 (CH); 55.33 (d, J = 6.3 Hz, CH<sub>3</sub>); 53.93 (2CH<sub>2</sub>); 53.84 (2CH<sub>2</sub>) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 243 MHz) δ = 10.64 (s) ppm. HRMS: m/z calcd. for C<sub>57</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>P ([M + H]<sup>+</sup>): 851.3033; found: 851.3034.

*Bis(2-(3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl)phenyl) methyl phosphate* **4** (in situ protocol):

In an oven dried Schlenk tube 0.225 g of dibromide **1** (0.51 mmol) and 0.059 g of 2-aminophenol (0.54 mmol, 1.05 equiv.) was dissolved in 10 mL of dry DMF. The solution was degassed three times by putting it in vacuum. Then 0.40 mL of Et<sub>3</sub>N (0.29 g, 2.86 mmol, 5.6 equiv.) was added with a syringe and the mixture was heated to 130 °C. After 24 h at this temperature the resulting mixture was cooled to room temperature and the solvent was evaporated in vacuo. Then 12 mL of THF was added and the mixture was degassed. The Schlenk tube was then cooled in an ice bath and 0.40 mL of Et<sub>3</sub>N (0.29 g, 2.86 mmol, 5.6 equiv.) and 22 μL of PCl<sub>3</sub> (35 mg, 0.26 mmol,

0.5 equiv.) was added and the mixture was stirred for 90 min. Afterwards the mixture was quenched by adding 0.5 mL of methanol and the precipitate was filtered over a pad of Celite under argon and the solvent was removed. To the residue was added 5 mL of DCM and 0.05 mL of hydrogen peroxide (30% in water, 57 mg, 1.66 mmol, 3.1 equiv.). After 1 h water was added and the mixture was left over night. Extraction with DCM followed by drying with MgSO<sub>4</sub> and removal of the solvent by rotary evaporation gave the crude product. Flash chromatography afforded 68 mg (31%) of **4**.

*Bis(2-(3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl)phenyl) hydrogen phosphate*  
**6**:

In an oven dried Schlenk tube 65 mg of ester **4** (0.08 mmol) was dissolved in 1 mL of DMF and 1 mL of pyridine (12.4 mmol, 162.5 equiv.) was added. The mixture was heated to 80°C and kept at this temperature for 20 h. The resulting solution was then cooled to room temperature and the solvent removed until only a foamy solid was left. The pyridinium salt **5** was identified by NMR: <sup>1</sup>H-NMR: (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 8.86 (d, J = 5.8 Hz, 2H); 7.99 (s, 2H); 7.83 (dd, J = 7.4, 2.2 Hz, 2H); 7.80 (d, J = 8.1 Hz, 4H); 7.67 (d, J = 8.3 Hz, 4H); 7.41-7.34 (pt and ddd overlapping, 8H); 7.19-7.16 (d overlapping with other signal, 9H); 6.68- 6.60 (m, 4H); 6.57 (dd, J = 7.1 Hz, 2.0 Hz, 2H); 4.20 (d, J = 12.3 Hz, 4H); 4.07 (s, 3H); 3.62 (d, J = 12.3 Hz, 4H) ppm. <sup>31</sup>P-NMR: (CDCl<sub>3</sub>, 162 MHz)  $\delta$  = -10.08 (s) ppm.

Then 555 mg DOWEX and 14 mL of methanol was added. Immediately a white solid formed. The solid was decanted and the residue washed with diethyl ether. After evaporation of the solvent, activated charcoal and DCM was added. The mixture was filtrated and the charcoal washed with DCM. This resulted in 44 mg (81%) of amorphous white solid **6** that decomposed in solution. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>, 600 MHz)  $\delta$  = 7.86 (d, J = 8.2 Hz, 4H); 7.82 (d, J = 8.3 Hz, 4H); 7.50-7.44 (m, 6H); 7.42 (d, J = 8.3 Hz, 4H); 7.34 (d, J = 8.3 Hz, 4H); 7.28 (ddd, J = 8.2, 6.8, 1.2 Hz, 4H); 6.94 (pt J = 7.7 Hz, 2H); 6.71 (pt, J = 7.7 Hz, 2H); 6.56 (d, J = 7.7 Hz, 2H); 4.11 (d, J = 12.5 Hz, 4H); 3.74 (d, J = 12.5 Hz, 4H) ppm. <sup>13</sup>C-NMR: (CDCl<sub>3</sub>, 151 MHz)  $\delta$  = 144.91 (d, J = 7.2 Hz, 2C<sub>q</sub>); 137.95 (2C<sub>q</sub>); 135.23 (4C<sub>q</sub>); 135.59 (4C<sub>q</sub>); 131.19 (4C<sub>q</sub>); 130.55 (4C<sub>q</sub>); 129.28 (4CH); 128.37 (4CH); 128.35(2CH); 127.82 (4CH); 127.38 (4CH); 126.29 (4CH); 126.24 (4CH); 124.26 (2CH); 123.40 (d, J = 2.9 Hz, 2CH); 120.23 (2CH); 54.69 (4CH<sub>2</sub>) ppm. <sup>31</sup>P-NMR: (CDCl<sub>3</sub>, 243 MHz)  $\delta$  = 6.88 (s) ppm. HRMS: m/z calcd. for C<sub>56</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>P ([M - H]<sup>-</sup>): 835.2731; found: 835.2731.

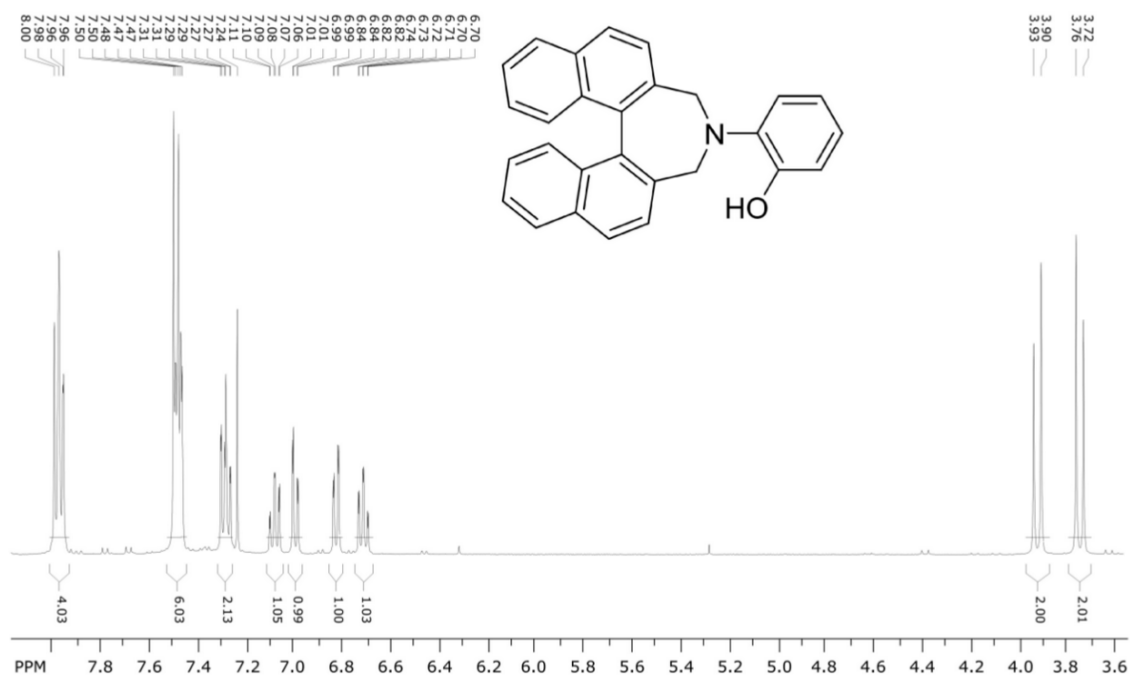
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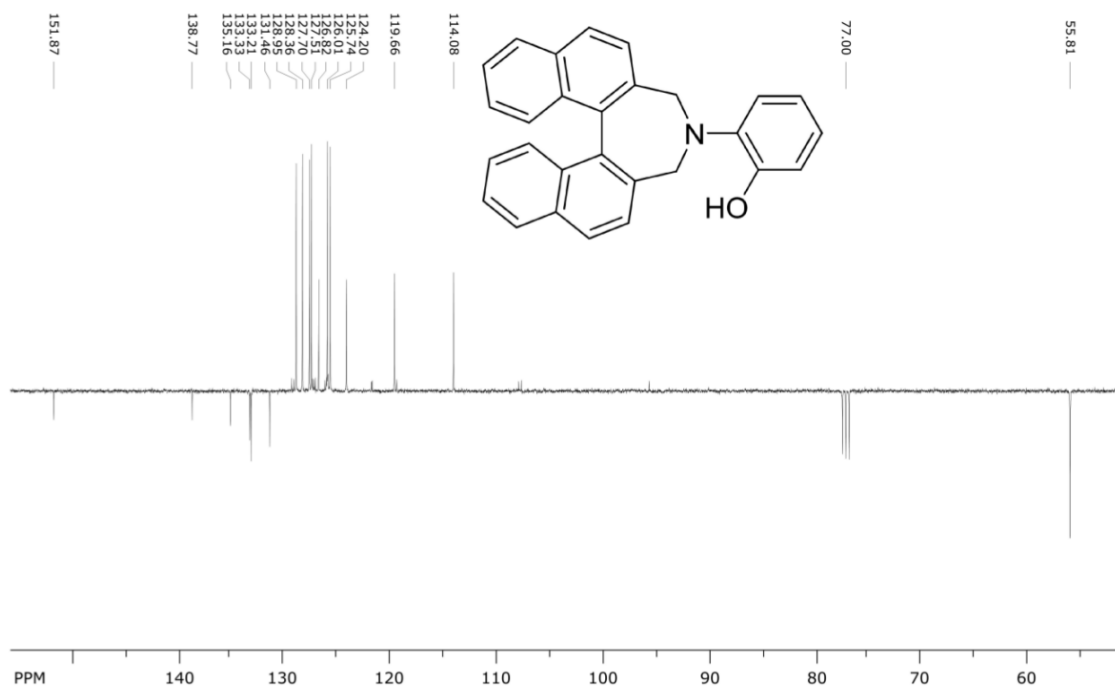
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## Supporting Information

$^1\text{H}$  NMR

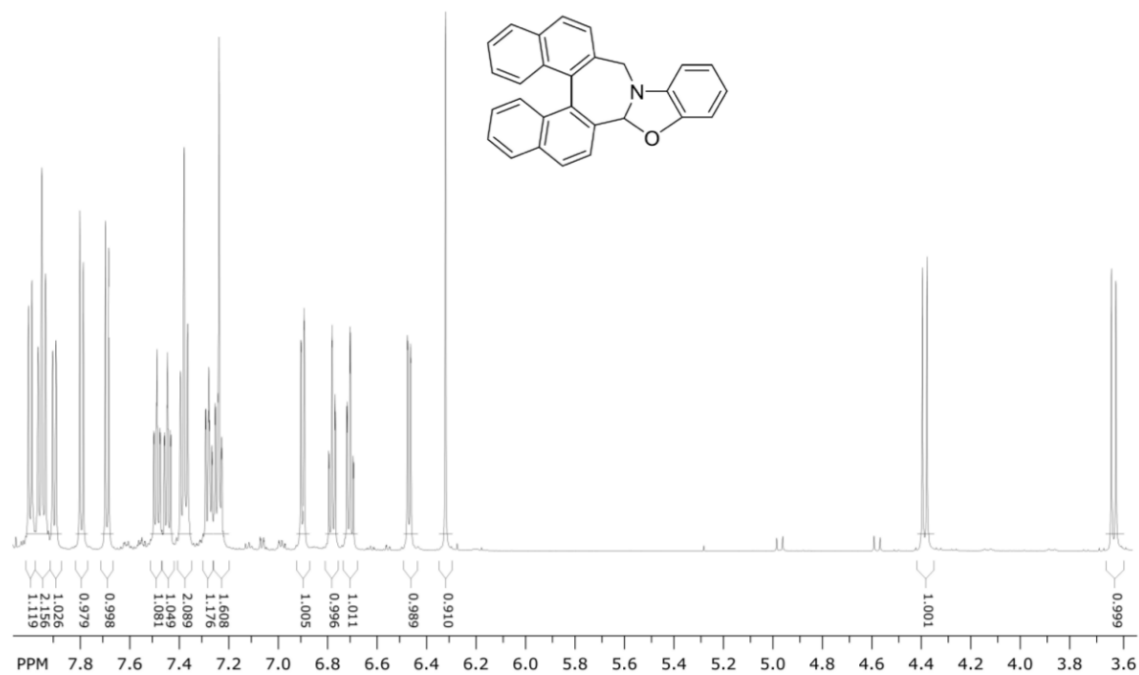


$^{13}\text{C}$  NMR

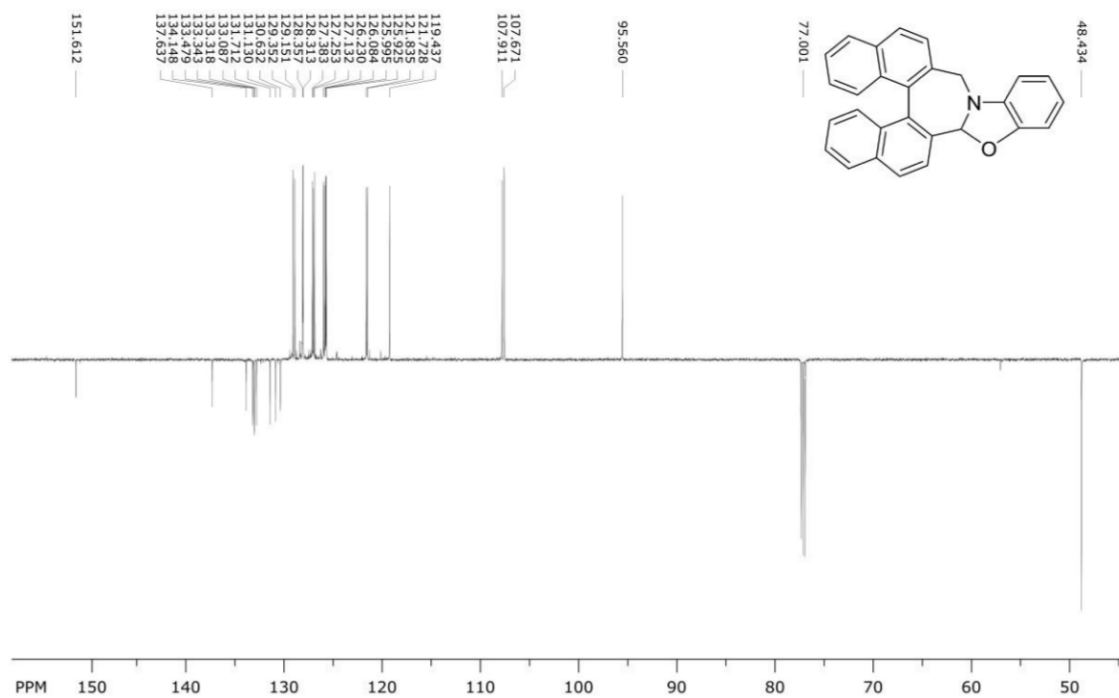


$^1\text{H}$ -NMR spectrum (top) and  $^{13}\text{C}$ -NMR spectrum (bottom) of compound **2**.

$^1\text{H}$  NMR



$^{13}\text{C}$  NMR



$^1\text{H}$ -NMR spectrum (top) and  $^{13}\text{C}$ -NMR spectrum (bottom) of compound **3**.



Chemical structure of compound 10 is shown above the spectrum. The structure is a bis-benzimidazole derivative with a central phosphonate group.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The x-axis represents the chemical shift in PPM, ranging from 3.8 to 7.6. The spectrum shows several peaks corresponding to the protons in the molecule. The integration values are provided below the peaks.

Integration values (from left to right): 4.06, 1.97, 1.03, 8.01, 9.04, 4.02, 0.99, 1.04, 1.09, 2.09, 2.04, 2.04, 2.04.

Chemical structure of compound 10 is shown above the spectrum. The structure is a bis-benzophenone derivative with a central phosphonate group.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The x-axis represents the chemical shift in PPM, ranging from 10 to 15. The spectrum shows several peaks, with the following chemical shifts (ppm) labeled above the corresponding peaks:

- 14.38, 14.34, 14.28, 14.26, 14.20, 14.04, 14.00, 13.96, 13.87, 13.82, 13.77, 13.71, 13.60, 12.70, 12.67, 12.60, 12.45, 12.43, 12.38, 12.34, 12.27, 12.26, 12.22, 12.19, 12.15, 12.12, 12.06, 12.04, 12.01, 11.98, 11.94, 11.91, 11.87, 11.84, 11.81, 11.78, 11.75, 11.72, 11.69, 11.66, 11.63, 11.60, 11.57, 11.54, 11.51, 11.48, 11.45, 11.42, 11.39, 11.36, 11.33, 11.30, 11.27, 11.24, 11.21, 11.18, 11.15, 11.12, 11.09, 11.06, 11.03, 11.00, 10.97, 10.94, 10.91, 10.88, 10.85, 10.82, 10.79, 10.76, 10.73, 10.70, 10.67, 10.64, 10.61, 10.58, 10.55, 10.52, 10.49, 10.46, 10.43, 10.40, 10.37, 10.34, 10.31, 10.28, 10.25, 10.22, 10.19, 10.16, 10.13, 10.10, 10.07, 10.04, 10.01, 9.98, 9.95, 9.92, 9.89, 9.86, 9.83, 9.80, 9.77, 9.74, 9.71, 9.68, 9.65, 9.62, 9.59, 9.56, 9.53, 9.50, 9.47, 9.44, 9.41, 9.38, 9.35, 9.32, 9.29, 9.26, 9.23, 9.20, 9.17, 9.14, 9.11, 9.08, 9.05, 9.02, 8.99, 8.96, 8.93, 8.90, 8.87, 8.84, 8.81, 8.78, 8.75, 8.72, 8.69, 8.66, 8.63, 8.60, 8.57, 8.54, 8.51, 8.48, 8.45, 8.42, 8.39, 8.36, 8.33, 8.30, 8.27, 8.24, 8.21, 8.18, 8.15, 8.12, 8.09, 8.06, 8.03, 8.00, 7.97, 7.94, 7.91, 7.88, 7.85, 7.82, 7.79, 7.76, 7.73, 7.70, 7.67, 7.64, 7.61, 7.58, 7.55, 7.52, 7.49, 7.46, 7.43, 7.40, 7.37, 7.34, 7.31, 7.28, 7.25, 7.22, 7.19, 7.16, 7.13, 7.10, 7.07, 7.04, 7.01, 6.98, 6.95, 6.92, 6.89, 6.86, 6.83, 6.80, 6.77, 6.74, 6.71, 6.68, 6.65, 6.62, 6.59, 6.56, 6.53, 6.50, 6.47, 6.44, 6.41, 6.38, 6.35, 6.32, 6.29, 6.26, 6.23, 6.20, 6.17, 6.14, 6.11, 6.08, 6.05, 6.02, 6.00, 5.97, 5.94, 5.91, 5.88, 5.85, 5.82, 5.79, 5.76, 5.73, 5.70, 5.67, 5.64, 5.61, 5.58, 5.55, 5.52, 5.49, 5.46, 5.43, 5.40, 5.37, 5.34, 5.31, 5.28, 5.25, 5.22, 5.19, 5.16, 5.13, 5.10, 5.07, 5.04, 5.01, 4.98, 4.95, 4.92, 4.89, 4.86, 4.83, 4.80, 4.77, 4.74, 4.71, 4.68, 4.65, 4.62, 4.59, 4.56, 4.53, 4.50, 4.47, 4.44, 4.41, 4.38, 4.35, 4.32, 4.29, 4.26, 4.23, 4.20, 4.17, 4.14, 4.11, 4.08, 4.05, 4.02, 4.00, 3.97, 3.94, 3.91, 3.88, 3.85, 3.82, 3.79, 3.76, 3.73, 3.70, 3.67, 3.64, 3.61, 3.58, 3.55, 3.52, 3.49, 3.46, 3.43, 3.40, 3.37, 3.34, 3.31, 3.28, 3.25, 3.22, 3.19, 3.16, 3.13, 3.10, 3.07, 3.04, 3.01, 2.98, 2.95, 2.92, 2.89, 2.86, 2.83, 2.80, 2.77, 2.74, 2.71, 2.68, 2.65, 2.62, 2.59, 2.56, 2.53, 2.50, 2.47, 2.44, 2.41, 2.38, 2.35, 2.32, 2.29, 2.26, 2.23, 2.20, 2.17, 2.14, 2.11, 2.08, 2.05, 2.02, 2.00, 1.97, 1.94, 1.91, 1.88, 1.85, 1.82, 1.79, 1.76, 1.73, 1.70, 1.67, 1.64, 1.61, 1.58, 1.55, 1.52, 1.49, 1.46, 1.43, 1.40, 1.37, 1.34, 1.31, 1.28, 1.25, 1.22, 1.19, 1.16, 1.13, 1.10, 1.07, 1.04, 1.01, 0.98, 0.95, 0.92, 0.89, 0.86, 0.83, 0.80, 0.77, 0.74, 0.71, 0.68, 0.65, 0.62, 0.59, 0.56, 0.53, 0.50, 0.47, 0.44, 0.41, 0.38, 0.35, 0.32, 0.29, 0.26, 0.23, 0.20, 0.17, 0.14, 0.11, 0.08, 0.05, 0.02, 0.00.

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