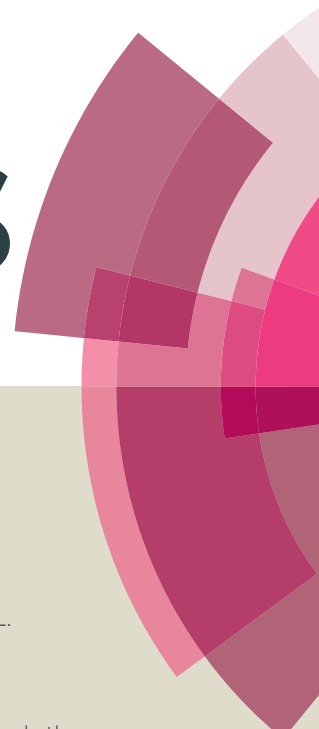


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ARTICLE

# Biphenyl derivatives containing trimethylsilyl benzyl ether or oxime groups as probes for NO<sub>2</sub> detection

Received 00th January 20xx,  
Accepted 00th January 20xx

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Four probes based in the use of a biphenyl moiety and functionalized with trimethylsilyl benzyl ether (**P1** and **P3**) and oxime (**P2** and **P4**) groups have been prepared and tested as optical probes for the detection of NO<sub>2</sub>. Reaction of NO<sub>2</sub> with acetonitrile solutions of **P2-P4** resulted in the formation of aldehydes **7** and **8** with a concomitant redshift of the absorption bands. Probe **P2** displayed a bathochromic shift of 45 nm upon reaction with NO<sub>2</sub> and was able to detect this poisonous gas at concentrations as low as 0.02 ppm. **P2** was highly selective against NO<sub>2</sub> and other gases (i.e. NO, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>) and vapours of organic solvents (i.e. acetone, hexane, chloroform, acetonitrile or toluene) had no effect in the optical properties of the probe.

DOI: 10.1039/x0xx00000x

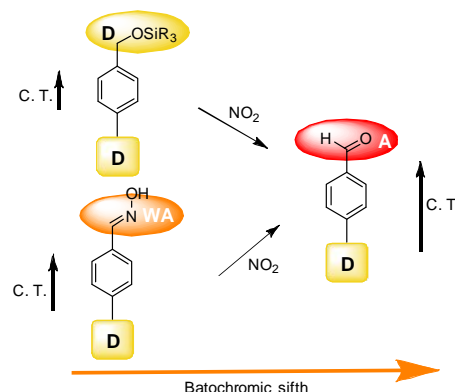
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## Introduction

Nitrogen oxides (NO<sub>x</sub>) are formed in large quantities from fuel combustion in cars, trucks and power plants,<sup>1</sup> they are a major problem in urban areas and are linked to many respiratory diseases.<sup>2</sup> From a chemical point of view NO<sub>x</sub> mainly refers to the sum of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), although other nitrogen species can also be included, such as nitrous and nitric acids. Together with the adverse effects of direct exposure to NO<sub>x</sub> on human health, it is also remarkable its contribution to ground level ozone and fine particle pollution. Hence, strict regulations regarding levels of nitrogen oxides are currently applied by governments and the monitorization of NO<sub>x</sub> levels based in reliable analytical methods is of great interest.<sup>3</sup>

Among NO<sub>x</sub> species, NO<sub>2</sub> causes a range of harmful effects on lungs such as increased inflammation of the airways, worsened cough and wheezing, reduced lung function, increased asthma attacks and increased susceptibility to respiratory infection.<sup>4</sup> All these problems are more important for children and older adults.<sup>5</sup> Due to the ubiquitous presence of NO<sub>2</sub>, the development of selective and sensitive sensing methods for its

detection is a hot area of research.<sup>6</sup> No standards have been agreed upon for nitrogen oxides in indoor air, moreover ASHRAE and the US EPA National Ambient Air Quality Standards list 0.053 ppm as the average 24-hour limit for NO<sub>2</sub> in outdoor air.<sup>7</sup> However, NO<sub>2</sub> levels in certain cities and at certain hours can reach even higher values (near 100 ppm). Laser-based photoacoustic spectroscopy,<sup>8</sup> surface acoustic wave (SAW),<sup>9</sup> transition metal oxide devices,<sup>10</sup> carbon quantum dot-functionalized aerogels,<sup>11</sup> or ozone treated graphene<sup>12</sup> are some reported analytical techniques used to detect/monitor NO<sub>2</sub> levels. However, some of these methods show certain limitations such as lack of specificity, limited selectivity, operational complexity, non-portability, difficulties in real-time monitoring and false positive readings. As an alternative to these instrumental procedures, the development of molecular chemosensors, constructed under the chemodosimeter paradigm, has been gaining interest in recent years. However, the number of publications related with optical probes for NO<sub>2</sub> detection is still relatively scarce.<sup>13</sup>



**Scheme 1.** Sensing protocol used for NO<sub>2</sub> detection.

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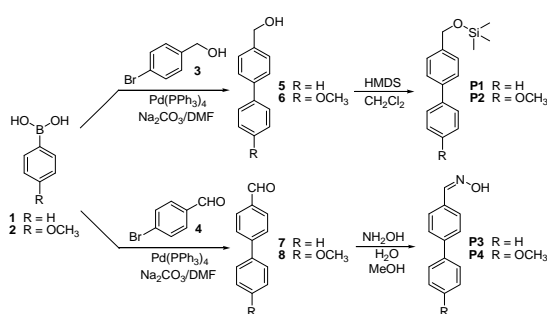
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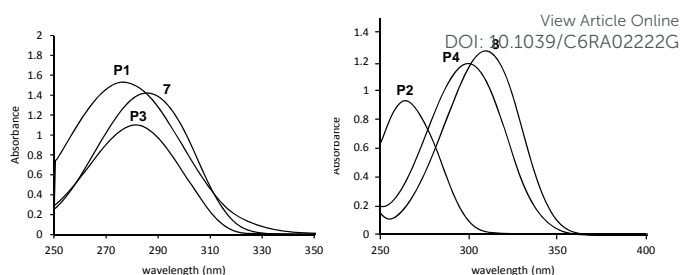
Bearing in mind our interest in the development of chemical sensors for gas detection,<sup>14</sup> we report herein the synthesis and sensing behavior towards NO<sub>2</sub> of four new chemodosimeters based on the biphenyl chromophore. Among the different organic reactions involving NO<sub>2</sub> we decided to explore the utility of the generation of aromatic aldehydes from trimethylsilyl benzyl ethers<sup>15</sup> and oximes<sup>16</sup> in order to prepare suitable chemodosimeters for the detection of this poisonous and pollutant gas. These are reactions with quantitative yields, working at room temperature and at ambient pressure. The synthesized biphenyl probes (*vide infra*) possess electron donor groups (such as methoxide electronically connected with trimethylsilyl) or oxime (weak electron acceptor) moieties. The underlying idea is that, upon NO<sub>2</sub> reaction, the formed aldehyde (an electron acceptor moiety) would change the electronic properties of the chemodosimeter with subsequent shifts of the absorption bands (see Scheme 1).

## Results and discussion

Probes **P1-P4** were prepared following the synthetic pathway depicted in Scheme 2. Pd(0) catalyzed cross-coupling reaction of the appropriate boronic acids (**1** and **2**) with 4-bromohydroxymethylbenzene (**3**) or 4-bromobenzaldehyde (**4**) yielded the corresponding biphenyl derivatives bearing hydroxyl (**5** and **6**) or aldehyde (**7** and **8**) moieties.<sup>17</sup> Transformation of the hydroxyl group into the corresponding trimethylsilyl ether (probes **P1** and **P2**) was carried out using hexamethyldisilazane (HMDS) in dry CH<sub>2</sub>Cl<sub>2</sub>,<sup>18</sup> whereas the probes containing oximes (**P3** and **P4**) were obtained with hydroxylamine hydrochloride in H<sub>2</sub>O/MeOH mixed with sodium carbonate.<sup>19</sup> All compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS (see Supporting Information). Acetonitrile solutions of the four probes (1.0 × 10<sup>-4</sup> M) showed intense absorption bands in the 260–300 nm region with ε values ranging from 6000 to 15000 M<sup>-1</sup> cm<sup>-1</sup>.



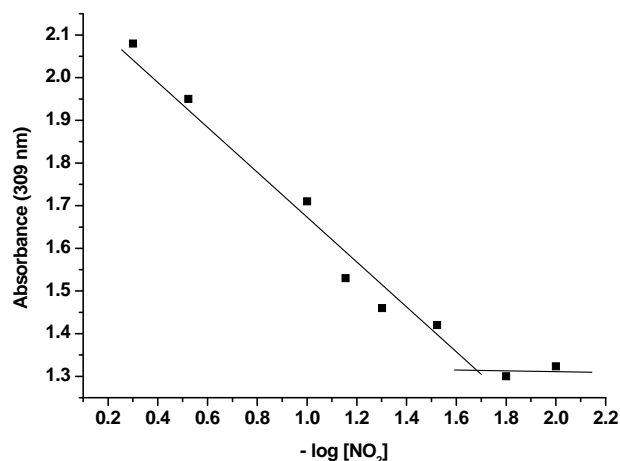
**Scheme 2.** Synthetic pathways used for the preparation of probes **P1-P4**.



**Figure 1.** (Left) UV spectra of probes **P1** and **P3** (1.0 × 10<sup>-4</sup> M in acetonitrile) alone and after bubbling 1 ppm of NO<sub>2</sub> during 5 min. (Right) UV spectra of probes **P2** and **P4** (1.0 × 10<sup>-4</sup> M in acetonitrile) alone and after bubbling 1 ppm of NO<sub>2</sub> during 5 min. The reactions gave aldehydes **7** and **8**, respectively.

In a first step, the absorption changes of probes **P1-P4** (1.0 × 10<sup>-4</sup> M in acetonitrile) after bubbling 1 ppm of NO<sub>2</sub> during 5 min. (obtained from a commercial cylinder), was tested.

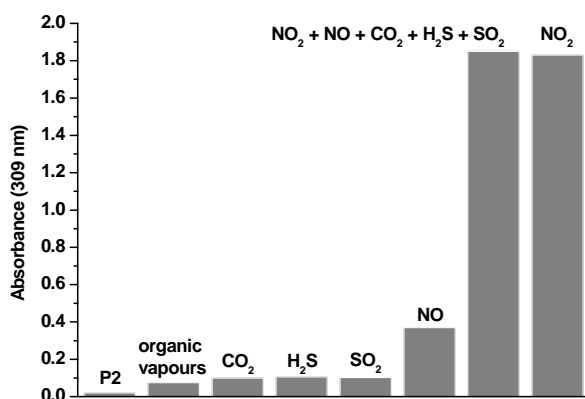
Acetonitrile solutions of **P1** showed an absorption band centered at 277 nm that was redshifted to 285 nm upon bubbling air containing 1 ppm of NO<sub>2</sub> (see Figure 1). Interestingly, the same absorption band centered at 285 nm was observed upon bubbling NO<sub>2</sub> into acetonitrile solutions of probe **P3** (see also Figure 1). The new absorption band, formed upon NO<sub>2</sub> bubbling, was ascribed to the formation of aldehyde **7** as a consequence of the oxidative deprotection of the trimethylsilyl ether moiety in **P1** and of the rupture of the oxime group in **P3**. In fact both, the UV and <sup>1</sup>H NMR spectra of aldehyde **7**, were fully coincident with that obtained after treatment of probes **P1** and **P3** with NO<sub>2</sub>. Optically, the transformation of an electron donor (trimethylsilyl ether in **P1**) or a weak electron acceptor (oxime in **P3**) group into an aldehyde (with a marked ability to attract electronic density) yielding **7**, resulted in a bathochromic shift of the absorption band of **P1** and **P3**. A similar redshifts of the absorption bands of acetonitrile solutions of **P2** and **P4** was observed upon bubbling NO<sub>2</sub> (1 ppm in air) (see Figure 1). These changes were ascribed to the reaction of NO<sub>2</sub> with the probes that yielded in both cases aldehyde **8**. Also in this case it was found that the UV and <sup>1</sup>H NMR spectra of aldehyde **8**, were fully coincident with that obtained after treatment of probes **P2** and **P4** with NO<sub>2</sub>. The best sensing performance, in terms of a larger shift of the absorption band, was obtained for probe **P2**, for which a redshift of 45 nm (from 264 to 309 nm) was observed upon bubbling 1 ppm of NO<sub>2</sub>. For this reason, further detailed studies with **P2** were carried out in order to assess the sensitivity and selectivity of this probe toward NO<sub>2</sub>.



**Figure 2.** Absorbance at 309 nm measured after bubbling increasing quantities of  $\text{NO}_2$  into acetonitrile solutions of probe **P2** ( $1.0 \times 10^{-4}$  M).

The limit of detection (LOD) using **P2** for  $\text{NO}_2$  was determined by UV measurements by bubbling increasing amounts of  $\text{NO}_2$  into an acetonitrile solution of the probe. As shown in Figure 2, the absorbance at 309 nm was gradually enhanced when the concentration of  $\text{NO}_2$  increases. From the titration profile a LOD as low as 0.02 ppm was calculated.

In a second step, the selectivity of **P2** was assessed. This is an important issue in the design of probes for pollutant gases in order to overcome potential interferences or false-positive readings produced by other species. Taking this into account, the potential reactivity of probe **P2** with other hazardous gases (i.e.  $\text{NO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ) or organic vapors (i.e. acetone, hexane, chloroform, acetonitrile, toluene) was tested by bubbling the selected species into acetonitrile solution of **P2** ( $1.0 \times 10^{-4}$  M). None of the gases tested, at concentrations up to 100 ppm, induced changes in the UV spectra of probe **P2** indicating a high selective reaction of **P2** with  $\text{NO}_2$  (see Figure 3).



**Figure 3.** Absorbance at 309 nm of probe **P2** alone and in the presence of selected potential interferents (all compounds at a concentration of 100 ppm).

Competitive studies were also carried out. Thus, Figure 3 shows that the absorption of the band at 309 nm of probe **P2** in the presence of a complex gas mixture ( $\text{NO}_2 + \text{NO} + \text{CO}_2 + \text{H}_2\text{S} + \text{SO}_2$ ) was the same than that observed when  $\text{NO}_2$  was used alone. This result demonstrated a high selective response of probe **P2** toward  $\text{NO}_2$  and suggested its possible use for the detection/monitoring of this poisonous gas.

## Conclusions

Four new biphenyl-based probes **P1-P4** have been synthesized and used for the selective recognition of  $\text{NO}_2$ . For all four probes a bathochromic shift of the absorption bands was observed in the presence of the  $\text{NO}_2$  and ascribed to the generation of an aromatic aldehyde upon reaction of  $\text{NO}_2$  with trimethylsilyl benzyl ether or oxime groups contained in **P1-P2** and **P3-P4**, respectively. Among the prepared chemosensors, **P2** showed the higher shift of the absorption band and for this probe a LOD as low as 0.02 ppm was determined for  $\text{NO}_2$  detection. Moreover, the response of **P2** was highly selective and no reaction was found in the presence of  $\text{NO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  or organic vapors of acetone, hexane, chloroform, acetonitrile or toluene. We believe that these, or similar probes based in the same chemical reaction, can display a large potential as optical probes for the selective detection of  $\text{NO}_2$ .

## Experimental Section

**General remarks:** Dichloromethane and acetonitrile were distilled from  $\text{P}_2\text{O}_5$  under Ar prior to use. Silica gel 60 F254 (Merck) plates were used for TLC. Column chromatography was performed on silica gel.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were determined on a Bruker AV 300 spectrometer. Chemical shifts are reported in parts per million (ppm), calibrated to the solvent peak set. High-resolution mass spectra were recorded in the positive ion mode with a VG-AutoSpec mass spectrometer. Absorption and fluorescence spectra were recorded using a Shimadzu UV-2600 spectrophotometer.

**Synthesis of biphenyl alcohols 5 and 6:** In a typical run, the corresponding boronic acid (**1** for the synthesis of **5**; **2** for the preparation of **6**) (2 mmol) was added, to a solution of **3** (1 mmol) in DMF (20 ml) in the presence of sodium carbonate (6 mmol). Afterward, the flask was evacuated and refilled with argon. Then, tetrakis(triphenylphosphine)palladium(0) was added and the crude obtained heated at 100 °C for 30 minutes with vigorous stirring. The resultant mixture was diluted with  $\text{H}_2\text{O}$  (10 mL) and  $\text{Et}_2\text{O}$  (10 mL), followed by extraction twice with  $\text{Et}_2\text{O}$ . The ethereal extract was collected and the solvent evaporated under vacuum. The final product was isolated by column chromatography on silica, with hexane/ethyl acetate (8:2) as eluent, yielding a colourless solid (65%).

**5:** (65%), colourless solid.  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  (ppm): 7.68 - 7.60 (m, 4H), 7.50 - 7.32 (m, 5H), 5.21 (t,  $J = 5.7$  Hz, 1H),



4.54 (d,  $J = 5.7$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 142.2, 140.5, 138.9, 129.3, 127.6, 127.4, 126.9, 126.7, 62.9.

**6:** (67%), colourless solid.  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  (ppm): 7.50–7.43 (m, 4H), 7.37 (d,  $J = 8.4$  Hz, 2H), 6.91 (d,  $J = 8.7$  Hz, 2H), 5.20 (t,  $J = 5.7$  Hz, 1H), 4.53 (d,  $J = 5.7$  Hz, 2H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 159.1, 132.9, 132.8, 132.7, 127.9, 127.4, 126.2, 114.7, 63.0, 55.6.

**Synthesis of probes P1 and P2:** HDMS (40 mmol) was added to the corresponding alcohol (20 mmol) in dry dichloromethane (20 mL). The mixture was stirred at room temperature for 22 h (full conversion) under argon atmosphere. The solvent was evaporated and the crude was purified by column chromatography on silica using with hexane/ethyl acetate (8:2) as eluent, to give the probes **P1** (90%) or **P2** (93%) as white solids.

**P1:** (90%), white solid, m. p. 158–160°C.  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  (ppm): 7.50 (m, 4H), 7.27 (m, 5H), 4.56 (s, 2H), 0.00 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 140.5, 140.3, 139.2, 129.2, 127.6, 127.3, 126.9, 63.8, -0.1. UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 277$  nm ( $\epsilon = 15300 \text{ M}^{-1}\text{cm}^{-1}$ ).

**P2:** (93%), white solid, m. p. 170–173°C.  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  (ppm): 7.45 (m, 4H), 7.22 (d,  $J = 8.4$  Hz, 2H), 6.88 (d,  $J = 8.5$  Hz, 2H), 4.55 (s, 2H), 3.66 (s, 3H), 0.00 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 139.6, 138.8, 132.6, 129.2, 127.9, 127.3, 126.2, 114.6, 63.8, 0.1. UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 264$  nm ( $\epsilon = 8000 \text{ M}^{-1}\text{cm}^{-1}$ ).

**Synthesis of 7 and 8:** **4** (1.5 mmol) and **1** or **2** for **7** and **8** respectively (3 mmol) were dissolved in DMF (20 mL). Afterward, sodium carbonate (9 mmol) was added to this solution. The crude reaction was stirred under inert atmosphere for 30 min. Then, a catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added and the reaction was stirred at 100 °C for 10 minutes. After this time water (10 mL) was added and the mixture was extracted with ethyl acetate (2 x 20 mL). The organic phase was washed with brine (2 x 20 mL), dried with  $\text{MgSO}_4$  and evaporated to give the product

**7** was purified by silica column chromatography with hexane/ethyl acetate (9:1) to give a white crystalline solid (82%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.06 (s, 1H), 8.01 (m, 2H), 7.92 (d,  $J = 8.3$  Hz, 2H), 7.78 (m, 2H), 7.50 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  193.20, 146.34, 139.27, 135.56, 130.62, 129.60, 129.06, 127.84, 127.60. HRMS (EI):  $m/z$  calc. for  $\text{C}_{13}\text{H}_{10}\text{O}$  182.07  $[\text{M}+1]^+$  found: 183.0797 UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 289$  nm ( $\epsilon = 9500 \text{ M}^{-1}\text{cm}^{-1}$ ).

**8** was purified by silica column chromatography with hexane/ethyl acetate (8:2) to give a white crystalline solid (75%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.03 (s, 1H), 8.01–7.93 (m, 2H), 7.91–7.85 (m, 2H), 7.74 (d,  $J = 9.0$  Hz, 2H), 7.08 (d,  $J = 8.9$  Hz, 2H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 192.9, 160.2, 145.9, 134.8, 131.3, 130.5, 128.7, 127.0, 114.9, 55.6. HRMS (EI):  $m/z$  calc. for  $\text{C}_{14}\text{H}_{12}\text{O}_2$  212.08  $[\text{M}+1]^+$  found: 213.0901. UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 309$  nm ( $\epsilon = 12700 \text{ M}^{-1}\text{cm}^{-1}$ ).

**Synthesis of probes P3 and P4:** The corresponding aldehyde (**7** and **8** for **P3** and **P4** respectively, 2 mmol) and hydroxylamine

hydrochloride (2.2 mmol) were dissolved in methanol/water (1:1, 40 mL). A previously prepared solution of sodium carbonate (2 mmol) in water was slowly added and the reaction was stirred for 3 h at room temperature. Then, methanol was evaporated and the aqueous phase was extracted with ether (4 x 40 mL). The organic phase was washed with brine (1 x 30 mL) and dried with  $\text{MgSO}_4$ . After evaporation of the solvent probes **P3** (99%) and **P4** (77%) were isolated as white solids.

**P3:** (99%), white crystalline solid, m. p. 142–145°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.28 (s, 1H), 8.19 (s, 1H), 7.70 (m, 6H), 7.48 (m, 2H) 7.40 (m, 1H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 148.1, 141.2, 139.8, 132.6, 129.3, 128.1, 127.3, 127.3, 126.9. HRMS (EI):  $m/z$  calc. for  $\text{C}_{13}\text{H}_{11}\text{NO}$  197.08  $[\text{M}+1]^+$  found: 198.0913. UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 282$  nm ( $\epsilon = 5800 \text{ M}^{-1}\text{cm}^{-1}$ ).

**P4:** (77%), white crystalline solid, m. p. 165–167°C.  $^1\text{H}$  NMR (300 MHz, Chloroform- $d$ )  $\delta$  8.09 (s, 1H), 7.50 (m, 5H), 6.92 (d,  $J = 8.9$  Hz, 2H), 5.23 (s, 1H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  (ppm): 159.5, 148.2, 140.9, 134.8, 130.5, 128.7, 128.1, 127.0, 114.9, 55.6. HRMS (EI):  $m/z$  calc. for  $\text{C}_{14}\text{H}_{13}\text{NO}_2$  227.09  $[\text{M}+1]^+$  found: 228.1019. UV-Vis (acetonitrile)  $\lambda_{\text{max}} = 300$  nm ( $\epsilon = 11800 \text{ M}^{-1}\text{cm}^{-1}$ ).

**Limits of detection measurements:** Increasing quantities of  $\text{NO}_2$  gas from commercially available  $\text{NO}_2$  cylinder were bubbled for 5 min through a solution of **P2** in acetonitrile. The UV spectra were recorded in 1-cm path length cells at 25 °C. Representation of the wavelength (nm) vs. concentration of  $\text{NO}_2$  allowed the limit of detection to be calculated by using the equation (1)

$$LOD = 3s_b/m \quad (1)$$

in which  $s_b$  is the standard deviation of blank measurements and  $m$  is the slope of the linear regression plot.

## Acknowledgements

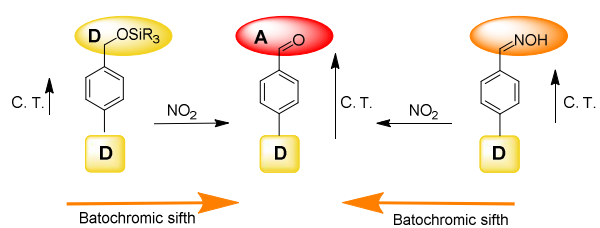
We thank the Spanish Government and FEDER funds (MAT2012-38429-C04) and Generalitat Valenciana (PROMETEOII/2014/047) for support. SCSIE (Universidad de Valencia) is gratefully acknowledged for all the equipment employed.

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DOI: 10.1039/C6RA02222G



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