Pyridine-Based Small-Molecule Fluorescent Probes as Optical Sensors for Benzene and Gasoline Adulteration

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Abstract: Here we present simple fluorophores based on the pyridine core, obtained with straightforward synthetic methodologies. These compounds present in solution absorption maxima in the UV region and fluorescence emission of between 300 and 450 nm, depending on the solvent and chemical structure of the fluorophore. The nature of the solvent was shown to play a fundamental role in their excite-state deactivation, which allowed successful exploration of these compounds as optical sensors for benzene and fuel adulteration in gasoline. In ethanolic solution, upon the addition of benzene, in general the fluorophores presented fluorescence quenching, where a linear correlation between the emission intensity and the amount of benzene (quencher) was observed. In addition, the application of an optical sensor for the detection of fuel adulteration in commercial standard and premium gasoline was successfully presented and discussed. Theoretical calculations were also applied to better understand the solvent–fluorophore interactions.

Keywords: organylethynylpyridine; fuel adulterants; benzene sensing; commercial gasoline; optical sensor

1. Introduction

Although renewable fuels have been widely used in our daily lives, petroleum-based fuels are still an energy source of global importance. In this context, the high dependence on these fuels makes their illegal adulteration a highly lucrative endeavor. The addition of industrial solvents as adulterants in petroleum-based fuels is stimulated by price disparities, usually caused by different taxation between them. However, illegal adulteration can have several impacts, such as increased toxic emissions and vehicle malfunctions [1–4].

Fuel adulteration, especially of commercial gasoline, involves the addition of organic solvents, methanol, or ethanol in concentrations higher than those established by current legislation. Thus, numerous analytical techniques have been used in the literature to evaluate and detect possible adulterations in fuels. Approaches based on simple physicochemical methods can be carried out, such as relative density measurements and evaporation/distillation methods. However, more complex analytical methods such as techniques based on the use of chemiresistors [5] and gas chromatography–mass spectrometry [6] (GC–MS) can be used to obtain more reliable results. These techniques usually require experienced professionals for the operation and data processing; in addition, they are dangerous techniques using flammable systems, expensive, and time-consuming. This makes it extremely important to develop new and easy-to-implement technologies to monitor fuel compliance. Other strategies employed are based on polymeric electronic gas sensors [7], polydiacetylene (PDA) paper-based colorimetric sensors [8–10], optical fiber sensors [11], membrane-type surface stress sensors [12], and quartz crystal microbalance (QCM) sensors [13–15]. In this way, a promising and easy-to-execute alternative is based on the use of organic dyes as optical sensors or marking materials. This technique
is based on the absorption and/or emission properties obtained according to changes in dye concentration. Some fluorescent compounds have already been reported in the literature, such as rhodamine [16], polymethine [17,18], squaraine [19], anthraquinone [20], 4-dimethylamino-4-nitrostilbene [21], and 2,1,3-benzothiadiazole (BTD) derivatives [22].

Based on the photophysical properties of pyridine-based compounds, our proposal presents differences concerning the chemosensors presented in the literature for this application, such as the investigated fuel (diesel, kerosene, and jet fuel) or even the identification methodology (test strip) [23,24]. However, taking the adulteration in gasoline using ethanol into account, similar studies can be found, using flavonoid dyes [25], Rhodamine 800, and Atto 680 dyes [26] (Figure 1). In addition, UV-Vis studies have also been reported using pyridinium N-phenolate betaine dyes (Figure 1) [27–29].

In this context, recently described BTD derivatives (Figure 1) [22] were used as solvatochromic dyes in a similar way to the one presented here, being easy to perform and with high linearity, as well as showing low sensitivity to concentration by fluorescence spectroscopy. However, the fluorescent compounds used as fuel sensors still represent a small group of structures, usually formed by complex and/or expensive molecules, and obtained through multiple reaction steps. In this way, the use of small fluorescent molecules as chemosensors could become a cheap and easily obtainable alternative in the evaluation of possible fuel adulteration.

In general, the incorporation of a nitrogen atom in polycyclic aromatic structures can induce or improve their electromagnetic, physicochemical, optical, and structural properties [30–32]. Through chemical modification/doping of the π-conjugated system with nitrogen, it is possible to control the main characteristics of the electronic structure, including the band gap, optical absorption spectra, photoluminescence, and redox behavior. As these parameters can be easily adjusted, many heteroaromatic compounds have been applied as NIR-active dyes [33], two-photon absorbers [34], and fluorescence sensors [35]. In addition, nitrogen doping is employed as a means of band-gap adjustment in perovskite solar cells [39], hole-transport material in perovskite solar cells [40–42], and as an optical sensor that can be used as a fluorescent

![Figure 1. Chemical structure of selected optical sensors for fuel adulteration.](image-url)
probe for the detection of nitroaromatic explosives [43,44]. Recently, the electronic behavior of small molecules has also been studied in ITIC, a new generation of non-fullerene electron-accepting small molecules for organic photovoltaics (OPVs), due to nitrogen substitution/insertion in different positions of the molecule [45]. In addition, small nitrogen compounds from 2-N-aminoquinazolines were also evaluated as fluorophores in solution and solid state [46]. Our research group has focused attention on the influence of chalcogens on the reactivity and properties of organochalcogen compounds [47–49]. Finally, we demonstrate here the photophysical characterization of 2-aryl-3-(organylethynyl)pyridine derivatives (Figure 1), recently described by us as substrates in visible-light-promoted selenocyclization reactions for the formation of Se-functionalized benzo[h]quinolines [50]. In addition, to broaden the scope of application of these compounds, based on their electronic features, they were successfully employed as optical sensors for the detection of fuel adulteration in commercial standard and premium gasoline. It should be noted that the application of small molecules is often not explored in depth, leaving a barrier of knowledge behind molecules of “greater complexity”.

2. Materials and Methods

2.1. General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Compounds 1,4-dioxane and Et$_3$N (triethylamine) were purified and dried under classical methods [51]. Solvents used in liquid–liquid extraction and as eluents for chromatographic purification were distilled before use. Reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F$_{254}$ aluminum sheets, and visualization of the spots was carried out under UV light (254 nm) and stained with iodine or with a mixture of 5% vanillin in 10% H$_2$SO$_4$ using heat as developing agent. Column chromatography was performed on silica gel (230–400 mesh). Some $^1$H NMR spectra were obtained on a Bruker Avance III HD 400 MHz (Billerica, MA, EUA) employing a direct broadband probe at 400 MHz. The spectra were recorded in CDCl$_3$ solutions. The chemical shifts are reported in ppm and referenced to tetramethylsilane (TMS) as the internal reference. Coupling constants (J) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), t (triplet), quint (quintuplet), and m (multiplet). Some $^{13}$C{$^1$H} NMR spectra were obtained on a Bruker Avance III HD 400 MHz employing a direct broadband probe at 100 MHz. The chemical shifts are reported in ppm, referenced to the solvent peak of CDCl$_3$ (δ 77.0 ppm). Melting points were recorded on Buchi Melting Point M-560 equipment (Flawil, Switzerland). High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF spectrometer (Milford, MA, EUA), using Atmospheric Pressure Chemical Ionization (APCI).

2.2. Synthesis

2.2.1. General Procedure for the Synthesis of Starting Materials 1a–e

The 2-chloro-3-(organylethynyl)pyridines 1a–e were prepared according to published procedures [52–55] (Scheme 1). PdCl$_2$(PPh$_3$)$_2$ (5 mol%, 0.105 g) and triethylamine (8.0 mL) were added to a 50.0 mL two-mouthed flask equipped with magnetic stirring and reflux system under argon atmosphere. After that, the respective 3-bromo-2-chloropyridine 4 (3.0 mmol) was added, followed by the addition of organylacetylene 5 (3.3 mmol), and the mixture was stirred for 5 min at room temperature. Then CuI (2 mol%, 0.011 g) was added, and the temperature was increased to 65 °C (oil bath). The reaction remained under magnetic stirring for 24 h. After that, the reaction was extracted with ethyl acetate, and the organic phase was washed with aqueous HCl 1% solution until complete neutralization of the aqueous phase. The organic phase was separated, dried over MgSO$_4$, filtered, and the solvent evaporated under reduced pressure. The crude material was further purified by column chromatography (hexanes/ethyl acetate) on silica gel.
2.2.2. General Procedure for the Synthesis of 2-aryl-3-(organylethynyl)pyridines 3a–k

The 2-aryl-3-(organylethynyl)pyridines 3a–k were prepared according to a published procedure, with minor changes [56]. In a dried sealed Schlenk tube under argon atmosphere, the appropriate 2-aryl-3-(organylethynyl)pyridine 1 (2.0 mmol), aryl boronic acid k (2.0 equiv, 4.0 mmol), Pd(PPh3)4 (5 mol%, 0.115 g), K3PO4 (2.0 equiv, 2.0 mmol), and 1,4-dioxane (8.0 mL) were added (Scheme 2). The mixture remained under magnetic stirring for 24 h at 90 °C (oil bath). After that, the reaction was extracted with ethyl acetate, and the organic phase was washed with a saturated aqueous NaCl solution. The organic phase was separated, dried over MgSO4, filtered, and the solvent evaporated under reduced pressure. The crude material was further purified by column chromatography (hexanes/ethyl acetate) on silica gel. The yield was 51–91%.

2-Phenyl-(phenylethynyl)pyridine (3a) [54,55]: purified by column chromatography (hexane/ethanol acetate = 95:5); yield: 0.458 g (85%); yellowish solid, m.p: 121–123 °C; 1H NMR (CDCl3, 400 MHz) δ (ppm) = 8.62 (dd, J = 4.8 and 1.7 Hz, 1H); 7.90 (dd, J = 7.8 and 1.8 Hz, 1H); 7.74–7.38 (m, 2H); 7.24 (dd, J = 7.8 and 4.8 Hz, 1H); 2.42 (s, 3H). 13C{1H} NMR (CDCl3, 100 MHz) δ (ppm) = 159.6, 148.4, 140.8, 138.8, 136.5, 131.3, 129.3, 128.5, 128.3, 122.9, 121.1, 117.9, 94.5, 87.5.

3-(Phenylethynyl)-2-(4-tolyl)pyridine (3b) [54]: purified by column chromatography (hexane/ethanol acetate = 95:5); yield: 0.458 g (85%); yellowish oil; 1H NMR (CDCl3, 400 MHz) δ (ppm) = 8.64 (dd, J = 4.8 and 1.7 Hz, 1H); 8.03–8.00 (m, 2H); 7.93 (dd, J = 7.8 and 1.7 Hz, 1H); 7.52–7.31 (m, 5H); 7.34–7.31 (m, 3H); 7.25 (dd, J = 7.8 and 4.8 Hz, 1H). 13C{1H} NMR (CDCl3, 100 MHz) δ (ppm) = 159.4, 148.4, 140.8, 138.8, 136.5, 131.3, 129.2, 128.6, 128.5, 128.3, 122.9, 121.4, 117.6, 94.4, 87.6, 21.4.

2-(4-Chlorophenyl)-3-(phenylethynyl)pyridine (3c) [54,55]: purified by column chromatography (hexane/ethanol acetate = 95:5); yield: 0.458 g (85%); white solid, m.p: 121–123 °C; 1H NMR (CDCl3, 400 MHz) δ (ppm) = 8.64 (dd, J = 4.8 and 1.7 Hz, 1H); 7.90 (dd, J = 7.8 and 1.8 Hz, 1H); 7.74–7.38 (m, 2H); 7.24 (dd, J = 7.8 and 4.8 Hz, 1H). 13C{1H} NMR (CDCl3, 100 MHz) δ (ppm) = 158.1, 148.5, 140.9, 137.7, 134.9, 131.3, 130.7, 128.8, 128.4, 128.0, 122.5, 121.6, 117.7, 94.9, 87.0.

2-(4-Methoxyphenyl)-3-(phenylethynyl)pyridine (3d) [54,55]: purified by column chromatography (hexane/ethanol acetate = 90:10); yield: 0.445 g (78%); yellowish oil; 1H NMR (CDCl3, 400 MHz) δ (ppm) = 8.60 (dd, J = 4.8 and 1.7 Hz, 1H); 8.03 (d, J = 8.6 Hz, 2H); 7.89 (dd, J = 7.8 and 1.5 Hz, 1H); 7.45–7.41 (m, 2H); 7.34–7.30 (m, 3H); 7.18 (dd, J = 7.8 and 4.8 Hz, 1H); 7.01 (d, J = 8.6 Hz, 2H); 3.86 (s, 3H). 13C{1H} NMR (CDCl3, 100 MHz) δ (ppm) = 160.2, 159.0, 148.4, 140.8, 131.9, 131.3, 130.7, 128.5, 128.3, 122.9, 120.8, 117.2, 113.2, 94.3, 87.7, 55.3.

2-(Naphthalen-2-yl)-3-(phenylethynyl)pyridine (3e): purified by column chromatography (hexane/ethanol acetate = 95:5); yield: 0.336 g (55%); yellowish solid, m.p: 76–78 °C; 1H NMR (CDCl3, 400 MHz) δ (ppm) = 8.69 (dd, J = 4.8 and 1.7 Hz, 1H); 8.60 (s, 1H); 8.16 (dd, J = 8.6 and 1.7 Hz, 1H); 7.98–7.89 (m, 4H); 7.55–7.49 (m, 2H); 7.40–7.36 (m, 2H); 7.31–7.24 (m,
4H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 159.3, 148.6, 140.9, 136.7, 133.4, 133.0, 131.4, 129.1, 128.6, 128.4, 127.6, 127.4, 126.9, 126.6, 126.1, 122.7, 121.4, 118.1, 94.8, 87.6. HRMS (APCI-QTOF) calculated mass for C\(_{23}\)H\(_{16}\)N + [M + H]\(^{+}\): 306.1283, found: 306.1272.

2-(2-Chlorophenyl)-3-(phenylethynyl)pyridine (3g): purified by column chromatography (hexane/ethyl acetate = 95:5); yield: 0.324 g (56%); yellowish oil; $^{1}$H NMR (CDCl\(_3\), 400 MHz) δ (ppm) = 7.45–7.36 (m, 3H); 7.13 (dd, J = 7.8 and 1.7 Hz, 1H); 7.41 (d, J = 7.5 Hz, 1H); 7.33–7.24 (m, 3H); 7.21–7.14 (m, 6H); 2.26 (s, 3H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 161.8, 147.7, 139.4, 138.9, 135.9, 131.1, 129.8, 129.1, 128.3, 128.1, 128.0, 125.1, 122.4, 121.3, 119.4, 94.5, 86.5, 19.4.

2-(2-Chlorophenyl)-3-(phenylethynyl)pyridine (3h): purified by column chromatography (hexane/ethyl acetate = 95:5); yield: 0.484 g (90%); yellow solid, m.p: 65–67 °C; $^{1}$H NMR (CDCl\(_3\), 400 MHz) δ (ppm) = 8.61 (dd, J = 4.8 and 1.7 Hz, 1H); 8.03–8.00 (m, 2H); 7.89 (dd, J = 7.8 and 1.7 Hz, 1H); 7.50–7.40 (m, 3H); 7.28 (d, J = 8.0 Hz, 2H); 7.20 (dd, J = 7.8 and 4.8 Hz, 1H); 7.11 (d, J = 8.0 Hz, 1H); 2.33 (s, 3H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 159.3, 148.0, 139.1, 138.8, 133.0, 131.3, 130.9, 129.6, 129.4, 128.5, 128.2, 126.4, 122.4, 122.2, 120.1, 95.0, 86.0. HRMS (APCI-QTOF) calculated mass for C\(_{19}\)H\(_{13}\)ClN + [M + H]\(^{+}\): 290.0737, found: 290.0731.

2-Phenyl-3-(4-tolyl)pyridine (3i): purified by column chromatography (hexane/ethyl acetate = 95:5); yield: 0.399 g (69%); yellow solid, m.p: 89–91 °C; $^{1}$H NMR (CDCl\(_3\), 400 MHz) δ (ppm) = 8.66 (dd, J = 4.8 and 1.7 Hz, 1H); 8.00–7.98 (m, 2H); 7.92 (dd, J = 7.8 and 1.7 Hz, 1H); 7.51–7.44 (m, 3H); 7.32–7.25 (m, 5H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 159.8, 144.7, 140.7, 139.3, 134.7, 132.4, 129.3, 128.8, 127.8, 121.4, 119.7, 118.1, 94.8, 86.8, 21.5. HRMS (APCI-QTOF) calculated mass for C\(_{20}\)H\(_{16}\)N + [M + H]\(^{+}\): 270.1283, found: 270.1272.

3-(4-Chlorophenylethenyl)-2-phenylpyridine (3j): purified by column chromatography (hexane/ethyl acetate = 95:5); yield: 0.268 g (51%); yellowish oil; $^{1}$H NMR (CDCl\(_3\), 400 MHz) δ (ppm) = 8.56 (dd, J = 4.8 and 1.7 Hz, 1H); 7.96–7.93 (m, 2H); 7.77 (dd, J = 7.8 and 1.7 Hz, 1H); 7.45–7.36 (m, 3H); 7.13 (dd, J = 7.8 and 4.8 Hz, 1H); 2.33 (t, J = 7.0 Hz, 2H); 1.51 (quint, J = 7.0 Hz, 2H); 1.37–1.21 (m, 6H); 0.88 (t, J = 7.0 Hz, 3H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 159.3, 147.7, 140.9, 139.4, 129.1, 128.4, 127.6, 121.1, 118.5, 96.1, 78.4, 31.2, 28.4, 28.1, 22.4, 19.5, 14.0. HRMS (APCI-QTOF) calculated mass for C\(_{19}\)H\(_{22}\)N + [M + H]\(^{+}\): 264.1752, found: 264.1730.

6-Methyl-2-phenyl-3-(phenylethynyl)pyridine (3k): purified by column chromatography (hexane/ethyl acetate = 95:5); yield: 0.360 g (67%); yellowish solid, m.p: 101–103 °C; $^{1}$H NMR (CDCl\(_3\), 400 MHz) δ (ppm) = 8.01–7.98 (m, 2H); 7.78 (d, J = 7.9 Hz, 1H); 7.49–7.34 (m, 5H); 7.29–7.26 (m, 3H); 7.06 (d, J = 7.9 Hz, 1H); 2.61 (s, 3H). $^{13}$C\(^{1}H\) NMR (CDCl\(_3\), 100 MHz) δ (ppm) = 159.0, 157.6, 140.7, 139.5, 131.2, 129.3, 128.6, 128.3, 128.2, 127.8, 123.0, 121.1, 114.7, 93.6, 87.7, 24.7. HRMS (APCI-QTOF) calculated mass for C\(_{20}\)H\(_{16}\)N + [M + H]\(^{+}\): 270.1283, found: 270.1269.

2.3. Photochemical Characterization

Spectroscopic-grade solvents benzene, ethanol, dichloromethane, and hexane were used for photophysical characterization. UV-Vis absorption spectra in solution (10\(^{-5}\) mol·L\(^{-1}\)) were acquired on a Shimadzu UV-2450 spectrophotometer (Kyoto, Japan) and steady-state fluorescence spectra were obtained on a Shimadzu spectrofluorometer model RF-5301PC. The maximum absorption wavelength was used as the excitation wavelength to acquire the respective fluorescence emission spectra. All measurements were performed at room temperature (25 °C). Based on the emission intensities in benzene and ethanol, additional...
exploratory fluorescence titrations were performed in ethanol at different amounts of benzene. In this way, ethanolic solutions of selected synthesized compounds at a concentration of $\sim 10^{-5}$ M were prepared. To this solution, amounts of 10% benzene (v/v) were added up to 100% benzene (v/v). For these experiments, the absorption maxima in ethanol were used as excitation wavelengths.

2.4. Fuel Adulteration Sensing

Brazilian commercial gasoline (standard or premium) was previously treated as described in the literature [22]. This procedure is essential since commercial gasoline in Brazil presents 27% (standard) or 25% (premium) of anhydrous ethanol. Briefly, the ethanol content was removed by the salting-out methodology. A second treatment was necessary since commercial gasoline presents tagging dyes, which are added for fiscal and security purposes and must be removed before experiments. In this sense, the samples were passed in a column containing silica 60 (230–400 mesh), collected in an Pyrex® narrow-mouth graduated Erlenmeyer flask (Corning, EUA), and kept under stirring in presence of activated charcoal for 2 h. The mixture was filtered to produce colorless gasoline, which was stored at 4 °C. Solutions of selected synthesized compounds at a concentration of $\sim 10^{-5}$ M were prepared using the treated standard and premium types of gasoline (4 mL). To this solution, amounts of 5% ethanol (v/v) were added up to 50% ethanol in gasoline (v/v). For these experiments, the absorption maxima in gasoline were used as excitation wavelengths.

2.5. Theoretical Calculations

All Density Functional Theory calculations used in this work were performed with the quantum chemistry package ORCA v5.0.3 [57–59]. The compounds 3a, 3e, 3f, and 3j were chosen as models for the calculations. The initial molecular geometries for the molecules were obtained by conformational sampling performed by the semiempirical CREST software [60] with the ALPB implicit solvation module [61] active to simulate benzene and ethanol environments. The most stable conformers were subsequently reoptimized using the ωB97X-D3/Def2-TZVP [63] level of theory with tight convergence criteria and the Conductor-like Polarizable Continuum Model (CPCM) [64] implicit solvation active. The resulting relaxed geometries have no imaginary vibrational modes (3a, 3e, and 3f), or the imaginary vibrational mode remaining (3f) is less than $-20$ cm$^{-1}$, which is characteristic of numerical noise and not the formation of a saddle-point. Absorption spectra, from which the electronic density difference was obtained, used the same ωB97X-D3/Def2-TZVP level of theory for the first 80 electronic transitions with Tamm–Dancoff approximation active [65].

3. Results and Discussion

3.1. Synthesis

The synthesis of 2-aryl-3-(organylethynyl)pyridines 3 is little explored in the literature. We found two protocols starting from halopyridines (Scheme 3). The first, described by Shibata and coworkers [66], adopts two distinct Suzuki-type cross-coupling reactions using 3-organylethynyl-2-chloropyridines 1 (obtained by Sonogashira-type cross-coupling reactions) and aryl boronic acids 2 (1.2–1.5 equiv) (Scheme 3a). The second, described by Shestakov and coworkers [67], presents an inverse reaction proposal, initially obtaining 4 by a Suzuki-type cross-coupling reaction. Then, these 2-aryl-3-bromopyridines 4 were used together with organylacetylenes 5 in a Sonogashira-type cross-coupling reaction to give 3 (Scheme 3b).
and arylboronic acids

Reaction conditions: the mixture of 2-chloro-3-(organylethynyl)pyridines 1 (2.0 equiv) as a base in 1,4-dioxane at 90 °C for 24 h to give the 3-(organylethynyl)-2-chloropyridines 3a–h (Scheme 1). The next synthesis step consists of a Suzuki-type cross-coupling reaction, based on the literature. Thus, the reaction was between 3-(organylethynyl)-2-chloropyridines 1 and arylboronic acids 2 (2.0 equiv), using Pd(PPh3)4 (5 mol%) as a catalyst and K3PO4 (2.0 equiv) as a base in 1,4-dioxane at 90 °C under an argon atmosphere in a sealed flask. By this method, eleven 2-aryl-3-(organylethynyl)pyridines 3 were obtained in 55–91% yield after 24 h of reaction (Scheme 2, Figure 2).

\[
\begin{align*}
\text{Ar} & \quad \text{HO} \quad \text{B-OR} \\
\text{N} \quad \text{Cl} & \quad + \quad \text{R} \\
\text{1} & \quad \text{2 (1.2-1.5 equiv)} \\
\quad & \quad \text{Pd(PPh3)4 (5 mol%), K3PO4 (2.0 equiv), 1,4-dioxane (8 mL) at 90 °C for 24 h} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ar} & \quad \text{HO} \quad \text{B-OR} \\
\text{N} \quad \text{Cl} & \quad + \quad \text{R} \\
\text{1} & \quad \text{2 (1.2-1.5 equiv)} \\
\quad & \quad \text{Pd(PPh3)4 (5 mol%), K3PO4 (2.0 equiv), 1,4-dioxane (8 mL) at 90 °C for 24 h} \\
\end{align*}
\]

Scheme 3. Synthetic routes by (a) Suzuki-type and (b) Sonogashira-type cross-couplings for the synthesis of 2-aryl-3-(organylethynyl)pyridines 3 described in the literature. Condition I: \( (\text{AMPHOS})_2\text{PdCl}_2 \) (5 mol%), K2CO3 (2.0 equiv), toluene:H2O (10:1), 100 °C. Condition II: PEPSSI-IPr (5 mol%), BuOK (1.3 equiv), FrOH, 40–60 °C.

To begin our studies, we performed the synthesis of commercially unavailable 3-organylthethyl-2-chloropyridines 1. For this, based on a procedure described in the literature, a Sonogashira-type cross-coupling reaction was promoted using the respective organylacetylene 5 (1.1 equiv), PdCl2(PPh3)2 (5 mol%), CuI (2 mol%) in triethylamine under an argon atmosphere at 65 °C for 24 h to give the 3-(organylthethyl)-2-chloropyridines 1a–h (Scheme 1). The next synthesis step consists of a Suzuki-type cross-coupling reaction, based on the literature. Thus, the reaction was between 3-(organylthethyl)-2-chloropyridines 1 and arylboronic acids 2 (2.0 equiv), using Pd(PPh3)4 (5 mol%) as a catalyst and K3PO4 (2.0 equiv) as a base in 1,4-dioxane at 90 °C under an argon atmosphere in a sealed flask. By this method, eleven 2-aryl-3-(organylthethyl)pyridines 3 were obtained in 55–91% yield after 24 h of reaction (Scheme 2, Figure 2).

Figure 2. Investigation on the scope of the substrates 2-aryl-3-(organylthethyl)pyridines 3a–k. 
1 Reaction conditions: the mixture of 2-chloro-3-(organylthethyl)pyridines 1a–f (2.0 mmol), aryl boronic acids 2a–q (4.0 mmol), Pd(PPh3)4 (5 mol%), K3PO4 (2.0 equiv), 1,4-dioxane (8 mL) at 90 °C (oil bath) under an argon atmosphere was kept under magnetic stirring for 24 h in a sealed flask.
2 Isolated yields.

The Suzuki-type cross-coupling reaction was tolerant of a variety of neutral, electron-donating, and electron-withdrawing substituents at the aromatic ring of the 3-phenylethynyl and 2-aryl moieties of pyridines, allowing the synthesis of several 2-aryl-3-(organylthethyl) pyridines 3 in moderate to excellent yields (Figure 2, 3a–i). It should be noted that a bulky...
boronic acid (naphthalen-2-ylboronic acid) could also be used; in this case, 3e was obtained in 55% yield. We also prepared a derivative containing an aliphatic chain (oct-1-yne) in the 3-ethynyl portion of pyridine, giving 3j in 51% yield under standard reaction conditions (Figure 2, 3j). Finally, we evaluated the insertion of a methyl group attached to the pyridine core, giving 3k in 67% yield (Figure 2, 3k).

3.2. Photophysics and Optical Sensing

The photophysical characterization in solution was performed using benzene, ethanol, dichloromethane, and hexane. The choice of solvents was based on the possible interactions that could occur with the fluorophores, comprising aromatic, non-polar, polar protic, and aprotic solvents. Figures 3 and 4 present the photophysical characterization of selected compounds, which were chosen based on their electronic properties. The relevant photophysical data are highlighted in Table 1. It can be observed that the main absorption bands are located between 250 and 350 nm, with maxima around 300 nm. These compounds presented different shapes and intensities based on their electronic structure. No significant solvatochromic effect was observed for these compounds, indicating an almost absent charge-transfer character in the ground state. A particular behavior was observed in compound 3j (Figure 3e), where there is a large variation in the absorption maximum position depending on the solvent, indicating that the phenyl group attached to the triple bond, absent in this derivative, plays an important role in the location of the absorption maxima of these compounds. Finally, the high molar absorptivity coefficient values (ε~10^4 cm⁻¹·M⁻¹) indicate that the observed electronic transitions are spin and symmetry-allowed 1π-π* transitions. In general, the other derivatives presented similar photophysical behavior (Figures S23–S28).

Figure 3. UV-Vis absorption spectra of the pyridine-based fluorophores (a) 3a, (b) 3d, (c) 3e, (d) 3f, and (e) 3j in solution [~10⁻⁵ M] in benzene (black), ethanol (red), hexane (blue), and dichloromethane (magenta).
these compounds in the excited state show a very interesting behavior. Once again, the other derivatives presented similar photophysical behavior (Figures S23–S28).

Figure 3. UV-Vis absorption spectra of the pyridine-based fluorophores (a) 3a, (b) 3d, (c) 3e, (d) 3f, and (e) 3j in solution [~10^−5 M] in benzene (black), ethanol (red), hexane (blue), and dichloromethane (magenta).

Figure 4. Steady-state fluorescence emission spectra of the pyridine-based fluorophores (a) 3a, (b) 3d, (c) 3e, (d) 3f, and (e) 3j in solution [~10^−5 M] in benzene (black), ethanol (red), hexane (blue), and dichloromethane (magenta).

Table 1. Photophysical data of pyridine-based fluorophores 3a–3k in solution, where λ_{abs} and λ_{em} are the absorption and emission maxima (nm), respectively, ε is the molar extinction coefficient (M^−1·cm^−1), and Δλ_{ST} is the Stokes shift (nm/cm^−1).

<table>
<thead>
<tr>
<th>Fluorophores</th>
<th>3a</th>
<th>3b</th>
<th>3c</th>
<th>3d</th>
<th>3e</th>
<th>3f</th>
<th>3g</th>
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<td>72/6452</td>
<td>62/5640</td>
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The fluorescence emission spectra of the selected compounds are presented in Figure 4. The relevant data are also summarized in Table 1. The spectra were acquired using the absorption maxima as excitation wavelengths. The compounds present fluorescence emission between 300 and 450 nm, with maxima depending on their electronic structure, as well as the environment polarity. Although the ground-state results do not present very significant photophysical differences between the fluorophores and studied solvents, these compounds in the excited state show a very interesting behavior. Once again, the other derivatives presented similar photophysical behavior (Figures S23–S28).
A significant variation in the maxima location could be observed as a function of the polarity of the medium, especially when comparing the same fluorophore. For instance, in hexane the emission maxima lie with higher energies. On the other hand, in highly polar solvents, the emission maxima shift to longer wavelengths (positive solvatochromism), suggesting that these compounds are more polar in the excited state. Moreover, in benzene and dichloromethane, these values tend to be similar, indicating that regardless of the lower polarity of benzene, more effective interaction with this solvent compensates for the higher polarity of dichloromethane. Finally, in ethanol, a solvent that exhibits more specific and strong interactions such as hydrogen bonding with fluorophores, the emission maxima values are also shifted towards the red, as expected. An exception to these observations is found in compound 3j, probably due to its lower π-conjugation provided by the absence of the phenyl linked to the double bond. In this case, no clear tendency is observed between the location of the emission maxima toward the solvent, indicating a diverse polarity of this derivative in comparison with its analogs. A relatively large Stokes shift indicates significant energy loss in the excited state. Based on these results, we can conclude that the electronic structure of these fluorophores, which is relatively simple, affects their photophysical properties in the excited state.

We would like to highlight that the most significant photophysical behavior in these compounds was the relative emission intensity as a function of the solvent. In ethanol, it was observed that the fluorescence intensity was 2-fold (3d), 3-fold (3a–3c, and 3k), 5-6-fold (3e, and 3g–3h), and even 39-fold (3f) higher if compared to the intensity in benzene. Similarly, the fluorescence intensities change depending on whether ethanol or hexane are used. Intensities of 2-fold (3g and 3h), 3-fold (3e and 3i), 4-fold (3d), and 5-fold (3f) higher were also observed in ethanol if compared to hexane. On the contrary, intensities of 2-fold (3a–3b, and 3k) and 5-fold (3j) higher were also observed in hexane if compared to ethanol. These observations allowed us to investigate some selected compounds for optical sensing. Benzene is recognized as one of the contaminants with the clearest evidence of carcinogenicity [68]. This compound is classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer [69], and as highlighted by Lachenmeier et al., since the early 1990s, concerns about benzene contamination of food have been raised. In this way, since this compound can be found in processed foods and beverages [70,71], its detection is worth investigating.

Regarding the spectrophotometric titrations in ethanol, upon the addition of benzene, in general, the fluorophores presented fluorescence quenching (Figures S29–S34). However, as presented in Figure 4, three fluorophores (3c, 3e, and 3i) showed a linear correlation between the emission intensity and the amount of benzene (quencher). Fluorophores 3c and 3i presented linearity in the studied concentration range of benzene (0–80% benzene), with R² values around 0.993 (3c) and 0.989 (3i). It is worth mentioning that compound 3e showed two linear correlations, the first in the range of 10 to 45% of added benzene (R² = 0.991) and the second in the range of 30 to 80% of benzene (R² = 0.985). Based on this behavior, the respective Stern–Volmer quenching constants (KSV) were calculated from the above titration experiments [72]. In this proposal, since the fluorophore concentration was constant in all mixtures, the benzene molecule was taken as the quencher. From the linear Stern–Volmer plots (Figure 5, bottom), the KSV constants were obtained as the slope of the linear plot with values around 0.05 M⁻¹ (Table 2). In addition, the respective bimolecular quenching rate constants (kq = KSV/τ₀) were obtained, using a fluorescence lifetime of benzene in ethanol of around 10 ns [73]. Values around 5 × 10⁶ M⁻¹⋅s⁻¹ were obtained, which are three orders of magnitude smaller than the diffusion rate constants (kdiff ~10⁹ M⁻¹⋅s⁻¹), according to the Smoluchowski–Stokes–Einstein theory [74], suggesting a dynamic mechanism (collisional quenching). Finally, the respective limits of detection (LOD) were also calculated.
with limits of detection (LOD) of ~4% for both commercial standard and premium gasoline. This application is particularly interesting in our country since Brazilian gasoline presents possible to observe a linear correlation in the range of 0–40% of added anhydrous ethanol premium (types of gasoline showed that by adding ethanol into the gasoline, the fluorophores presented fluorescence quenching (Figures S29–S34). Lachenmeier et al., since the early 1990s, concerns about benzene contamination of food (Group 1) by the International Agency for Research on Cancer [69], and as highlighted by evidence of carcinogenicity [68]. This compound is classified as carcinogenic to humans beverages [70,71], its detection is worth investigating.

Regarding the spectrophotometric titrations in ethanol, upon the addition of benzene (v/v). Below are presented the respective plots of $F_0/F$ vs. [quencher], according to Stern–Volmer Equation.

<table>
<thead>
<tr>
<th>Fluorophores</th>
<th>Range (Benzene %)</th>
<th>$K_{SV}$ (M$^{-1}$)</th>
<th>$k_q$ (M$^{-1}$s$^{-1}$)</th>
<th>LOD $^1$ (Benzene %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3c</td>
<td>0–80</td>
<td>0.090</td>
<td>9.0 × 10$^6$</td>
<td>4.6</td>
</tr>
<tr>
<td>3e</td>
<td>10–45</td>
<td>0.021</td>
<td>2.1 × 10$^6$</td>
<td>6.0</td>
</tr>
<tr>
<td>3e</td>
<td>30–80</td>
<td>0.054</td>
<td>5.4 × 10$^6$</td>
<td>12.1</td>
</tr>
<tr>
<td>3i</td>
<td>0–80</td>
<td>0.051</td>
<td>5.1 × 10$^6$</td>
<td>7.4</td>
</tr>
</tbody>
</table>

$^1$ from [78].

On the other hand, fuel adulteration, particularly of commercial gasoline, is one of the major illegal practices nowadays involving the addition of organic solvents or alcohol in different amounts than those recommended by the legislation [22]. Again, in this specific issue, it is desirable to develop sensors for fuel-quality monitoring. As already observed in this investigation, the good solubility of the fluorophores in hexane, as well as their tailored intensity in this solvent and ethanol, allowed us to explore their ability to sense gasoline. This application is particularly interesting in our country since Brazilian gasoline presents 27% of anhydrous ethanol for standard and 25% for premium types of gasoline [76]. In this way, fluorophore 3f was chosen as a model, and its photophysical behavior was first investigated in real samples of commercial gasoline and anhydrous ethanol, as shown in Figure 6a. It can be observed that 3f presented a similar behavior if compared to hexane/ethanol, with increased emission in anhydrous ethanol (4-fold) if compared to commercial common gasoline (Figure 6a).

Fluorescence titrations of anhydrous ethanol in commercial standard (Figure 6b) and premium (Figure 6c) types of gasoline showed that by adding ethanol into the gasoline, the fluorescence emission intensity increases, as expected. Dilution effects were excluded since the addition of the respective gasoline into the initial samples (control experiment) led to different results, where there was no observed increase in fluorescence. These preliminary results corroborate the potential application of this fluorophore as fuel optical sensors for adulteration by the addition of ethanol. In addition, in both gasoline samples it was possible to observe a linear correlation in the range of 0–40% of added anhydrous ethanol with limits of detection (LOD) of ~4% for both commercial standard and premium gasoline.
This latter seems to be an interesting result since adulterated gasoline presents in general a higher percentage of anhydrous ethanol than recommended by the Brazilian legislation.

Figure 6. (a) Steady-state fluorescence emission spectra of 3f in anhydrous ethanol and commercial standard gasoline [~10^{-5} M]. Fluorescence titration of 3f in commercial (b) standard and (c) premium types of gasoline upon different amounts of anhydrous ethanol. (d) Linear correlation between fluorescence intensity vs. (%) ethanol for 3f in commercial standard gasoline (R^2 = 0.984) and premium gasoline (R^2 = 0.985).

3.3. Theoretical Calculations

As stated in the “computational details” section, the lowest conformers were obtained from a conformational sampling and were reoptimized using the density functional theory with implicit benzene and ethanol solvation. The change in the solvation environment does not significantly affect the resulting optimized geometries since the ground states obtained for the studied compounds have negligible differences under benzene and ethanol, with root-mean-square deviations (RMSD) of only ~0.04 Å. In addition, the resulting geometries have nearly identical frontier orbital features under benzene and ethanol, with immediately distinguishable π-conjugation spreading linearly through the triple bond over the molecule and a much smaller electronic probability density spreading to the lateral substituents (Figure 7). The HOMO–LUMO gaps under CPCM are also quite similar, with ethanol affording a slightly greater stabilization and, consequently, a larger H–L gap by about 0.03 eV when compared to benzene, as depicted in Figure 7.

When optimized to the first excited state (S1), under CPCM, the geometric results remained mostly solvent-agnostic with benzene and ethanol generating compatible displacements. Compound 3a optimized to S1 experienced only a small displacement in benzene, showing RMSD = 0.27 Å (ethanol = 0.32 Å) compared to S0. Compound 3c afforded S1 in benzene with RMSD equal to 0.55 Å (ethanol = 0.49 Å). Additionally, for compound 3f an RMSD equal to 0.45 Å (ethanol = 0.52 Å) was found, while compound 3j showed the smallest displacements of the series with an RMSD equal to 0.26 Å (ethanol = 0.28 Å), as summarized in Figure 8.
As depicted in Figure 8, the addition of intermolecular interactions shows an immediate qualitative, the emission intensity experimentally observed. The test wrongly generates important non-covalent interactions such as solvation models [64] and the fact that the continuum scheme cannot correctly describe by implicit solvation with CPCM does not match the diversity of results observed in our experimental results. These discrepancies underline the shortcomings of using implicit solvation models [64] and the fact that the continuum scheme cannot correctly describe important non-covalent interactions such as π-stacking [77] that may be active in a real chemical environment.

Since the theoretical study of an emission spectra using explicit solvent molecules is computationally too demanding, even on a supercomputer, as the systems easily reach hundreds of atoms, a crude test simulating emission spectra for 3f and 3j using a simple vertical gradient approach [78] with the CPCM method is unable to reproduce, even qualitatively, the emission intensity experimentally observed. The test wrongly generates approximately the same intensity for 3f and 3j in both solvation schemes (Figures S35), an indication that the model is missing important components, probably from the absence of intermolecular interactions. Even though the simulation of emission spectra with explicit solvation is prohibitive due to computational costs, a nanocluster for absorption study with an arbitrary number of explicit solvent molecules was built using the CREST software and the procedure for optimization of non-covalent interactions. The new models, despite being quite large, were calculated using analytic TDDFT to identify the different effects using explicit solvation with intermolecular interactions on the first electronic transition. As depicted in Figure 8, the addition of intermolecular interactions shows an immediate impact on the electronic density difference for all systems, with a visually more remarkable change in molecule 3a with benzene, in which the charge transfer to the left side of the molecule appears inhibited while the right side sees an increase in electronic density.

**Figure 7.** Optimized geometries for 3a, 3e, 3f, and 3j. Since the geometries using CPCM to simulate benzene and ethanol are virtually identical, only the benzene results are shown. Isosurface = 0.05 e/Å³.

**Figure 8.** Superposition of S₀ (blue) and S₁ (red) optimized geometries for 3a, 3e, 3f, and 3j. The results depicted are using implicit benzene solvation.
4. Conclusions

In conclusion, a new and efficient protocol was successfully developed for the synthesis of 2-aryl-3-(organylethynyl)pyridines. The reaction showed high selectivity leading to the formation of eleven derivatives with good to moderate yields (55–91%); of these, six derivatives were unpublished in the literature. It is worth noting that these small molecules are easily prepared, expanding the scope of this class of N-derivatives of great synthetic relevance and wide photophysical potential. The photophysical characterization of these compounds showed that the solvent seems to affect their excite-state deactivation. Based on these results, the photophysical properties of these compounds were evaluated in ethanol with different amounts of benzene, where a linear correlation between the emission intensity and the amount of benzene (quencher) was obtained. In this investigation, the observed fluorescence quenching could be related to a dynamic mechanism (collisional quenching). These compounds were also investigated in real samples, using commercial standard and premium gasoline with different amounts of anhydrous ethanol. The studied compounds showed, in both gasoline samples, a linear correlation in the range of 0–40% of added ethanol. This latter seems to be an interesting result since adulterated gasoline presents in general a higher percentage of anhydrous ethanol than that recommended by the Brazilian legislation. Theoretical calculations using TDDFT showed that while the implicit conductor-like polarizable continuum model was unable to reproduce the experimental solvent effects, there is strong evidence that intermolecular interactions are preponderant factors that explain the experimental diversity on the emission spectra.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/photochem3010008/s1, Figures S1–S35: Spectroscopic characterization of compounds 3a to 3k, additional photophysical data and additional theoretical data.


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Conflicts of Interest: The authors declare no conflict of interest.

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