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Synthesis of Functionalized Azobiphenyl- and Azoterphenyl- Ditopic Linkers: Modular Building Blocks for Photoresponsive Smart Materials

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Modular synthesis of structurally diverse functionalized azobiphenyls and azoterphenyls for the realization of optically switchable materials has been described. The corresponding synthesis of azobiphenyls and azoterphenyls by stepwise Mills/Suzuki-Miyaura cross-coupling reaction, proceeds with high yields and provides facile access to a library of functionalized building blocks. The synthetic methods described herein allow combining several distinct functional groups within a single unit, each intended for a specific task, such as 1) the –N=N– azobenzene core as a photoswitchable moiety, 2) aryls and heteroaryls, functionalized with carboxylic acids or pyridine at its peripheries, as coordinating moieties and 3) varying substitution, size and length of the backbone for adaptability to specific applications. These specifically designed azobiphenyls and azoterphenyls provide modular bricks, potentially useful for the assembly of a variety of polymers, molecular containers and coordination networks, offering a high degree of molecular functionality. Once integrated into materials, the azobenzene system, as a side group on the organic linker backbone, can be exploited for remotely controlling the structural, mechanical or physical properties, thus being applicable for a broad variety of 'smart' applications.

Introduction

Synthetic photoswitchable compounds are versatile intermediates and precursors for developing stimuli-responsive materials, with remote controlled capability for switching them on and off. Smart materials are being developed for manifold applications, such as optical sensing, memories, filters, switches, and molecular machines and are emerging research fields in the biological[1] and materials science[2] communities. Embedded into materials such as polymers,[3] liquid crystals,[4] porous frameworks,[5] and molecular machines,[6] stimuli-responsive units undergo reversible rearrangements in their geometry, polarity and electronic states by external stimuli (e.g. photons, electrons, chemicals, or mechanical forces).[7] Among the stimuli-responsive molecular switches are photoswitchable units – such as spiropyrans (SP),[8] diarylethenes (DAE),[9] azobenzenes (ABs) and stilbenes,[10] (Figure 1)-that have attracted enormous interest, both of experimental and theoretical nature, for their potential applications in materials and life sciences.[11] Prominent among such photoswitchable units are azobenzenes which, when embedded into proteins and peptides, allow conformational control,[12] optical cell signaling,[13] cancer chemotherapy[14] antibiotic treatment,[15] and *in vivo* neuronal activity control.[16] Photostatins (PSTs)-azobenzene analogs of the microtubule inhibitor stilbenoid combretastatin A-4 (CA-4)-allow a strict and precise optical control of *in vivo* mitosis with single-cell spatial precision and are widely investigated in cell biology research and precision targeted chemotherapeutics.[14] As the photophysical, pharmacodynamic, and pharmacokinetic properties of azobenzenes have become established, they are being applied to a wide range of *in vivo* photo-pharmacological targets.

Ensuing the holistic approach of functional molecules for functional materials-from synthesis to function-based on incorporation of azobenzene moieties as molecular switches in the construction of optoelectronic devices, we have been involved in the design and fabrication of various functional nanosystems, such as nanoporous crystalline solids with controlled diffusion properties,[17] nanoscopic films,[18] frameworks,[19] and surface-mounted hybrid systems.[20] These 'smart' material applications are based on well-designed functional organic linkers that have defined characteristic features, imparting desired functions once assembled into materials. In a recent investigation, we have demonstrated the use of model azobenzene-functionalized linkers in optically triggered dynamic molecular separation

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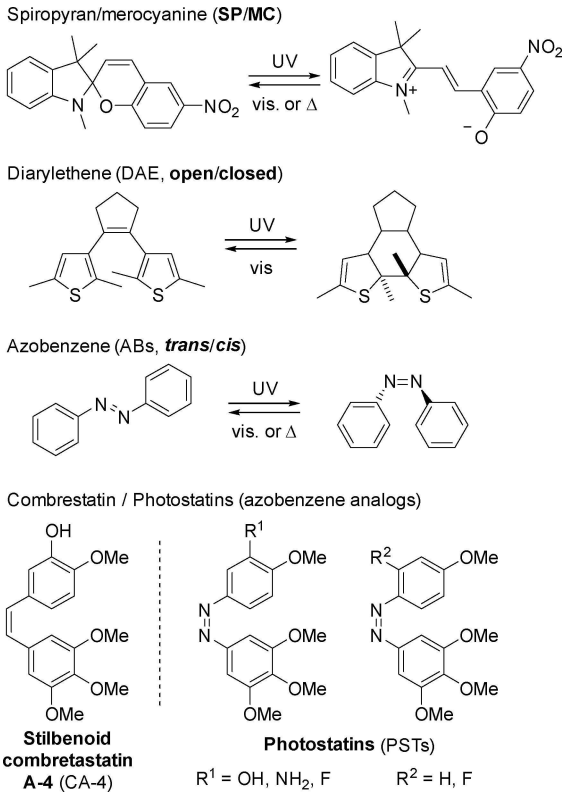


Figure 1. Various photoswitchable chromophores used in functional materials and chemotherapeutics.

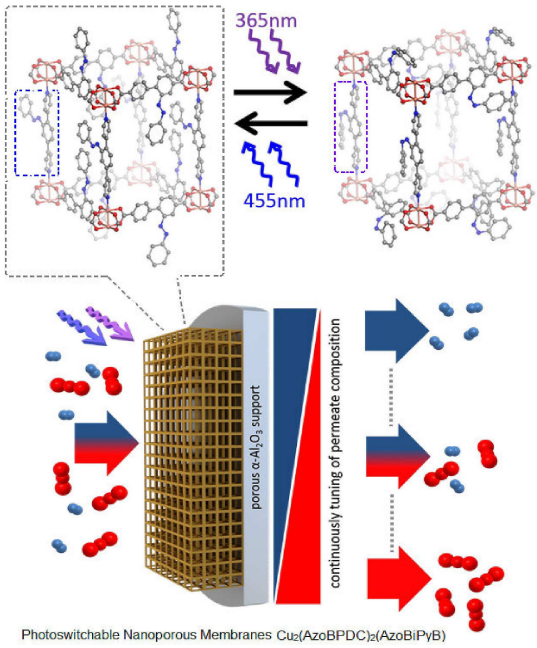


Figure 2. Schematic representation of a MOF membrane with tunable and remotely controllable molecular selectivity. Adapted with permission.[21] Copyright 2016, Nature Publishing Group.

by designed nanoporous membranes containing selective photoresponsive azobenzene side-groups on the linker backbone (Figure 2).[21] By irradiation of a membrane with light of specific wavelengths the incorporated photoswitches can be targeted, thereby remote controlling the membrane's permeability and selectivity, allowing a fine dynamic tuning of the material properties. The key prerequisite is the use of rationally designed organic linkers with functional features fulfilling all the crucial requirements, namely the coordinating end-groups for the connection to the metal nodes of the metal-organic frameworks (MOFs) and the azobenzene side-chain for the light-triggered activation of the photo-responsive devices. Thus, the permeation of the membrane is a consequence of the azobenzene moiety switching, remotely triggered by non-invasive light stimuli. This material exhibits remarkable photostability and undergoes reversible molecular motion (*trans* to *cis* isomerization) that can be repeated without loss of responsiveness.

Studying small azobenzene derivatives and their photoresponsive properties in solution is rather easy, but transforming small molecules into practically useful functional switches in solid-state materials still bears many challenges that need to be overcome.[17] The successful demonstration of nanoporous membrane applications represents a pioneering example and prompted us to develop a straightforward and efficient synthetic strategy to access more structurally diverse building blocks for the synthesis of novel smart materials. Herein we report the details of the synthetic endeavors for the preparation of a series of azobenzene functionalized biphenyls and terphenyls. These model photoswitchable ditopic linkers-bearing both an azobenzene moiety and coordinating functional end-groups (carboxylic acids or pyridines) for connecting to metal nodes-have enormous potential for materials and can be used for the construction of complex structures and the exploration of their properties and functional applications.

Results and Discussion

Designing libraries of diverse classes of molecules suitable for the development of novel responsive materials, we focused on the modular synthesis of linkers incorporating the popular light-responsive azobenzene photoswitch. Although several strategies for the synthesis and functionalization of aryl-substituted diazene (–N=N–) derivatives have been reported,[22] the modulation of synthetic methods for introducing multiple functional groups in a single unit, each with a defined specific function, still remains a challenging task but is crucial for material design.[23] Selective functionalization of such building blocks is one issue that has to be addressed.[24] The coordinative incorporation of stimuli responsive elements into complex systems, to ensure appropriate grafting of the building blocks,-and furthermore being able to control their responsive functions-is another aspect that requires special consideration. We aimed to install azobenzene units as side-groups at predefined positions of the linker backbone. The strategy we present here for the synthesis of the diazene (–N=N–) bond relies on the Mills reaction,[25] which involves two complemen-

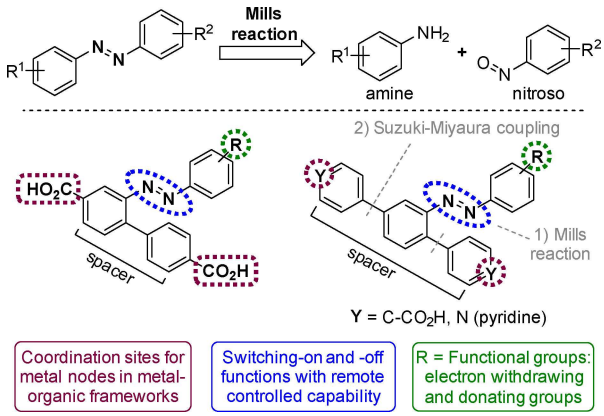
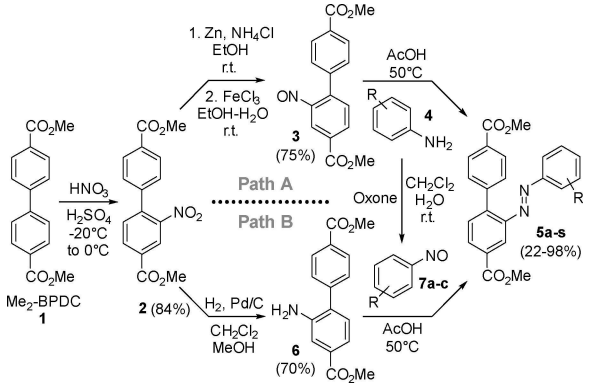


Figure 3. Mills reaction as a key step in the linker synthesis (top). Generic formula of the target functionalized azobiphenyl- and azoterphenyl- ditopic organic linkers as smart building blocks (bottom).

tary partners, an aromatic amine and a nitrosoarene, which react to form the azobenzene moiety (Figure 3). From a mechanistic point of view, the Mills reaction is comparable to the condensation reaction of an amine with an aldehyde, leading to the imine bond formation. The reaction proceeds under acidic conditions with a nucleophilic attack on the nitroso group by the aromatic amine, followed by dehydration of the intermediate. In addition to being rather easy to handle (simple procedure and purification), the Mills reaction proved excellent functional group compatibility. All this contributes to the versatility of these reactions, which overcomes many of the limitations associated with other procedures. For coordinative incorporation into metal organic frameworks (MOFs), azobenzene linkers bearing carboxylic acid groups at the terminal positions were proposed, as these are likeliest to facilitate metal-ligand bond coordination to metal centers.

Synthesis of the functionalized azobenzene linkers parted from commercially available, non-functionalized dimethyl [1,1′-biphenyl]-4,4′-dicarboxylate **1** (Me_2BPDC, Scheme 1), which was selectively mono-nitrated to obtain the nitro-biphenyl-dicarboxylate **2**. To ensure only one phenyl ring of the biphenyl-dicarboxylate **1** is nitrated, exactly 1 equivalent of the diluted nitric acid was added at −20 °C. The reaction mixture was



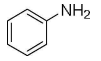
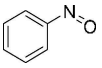
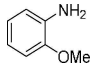
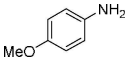
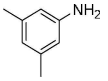
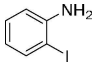
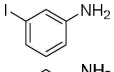
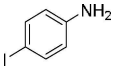
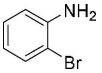
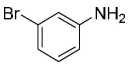
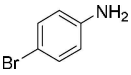
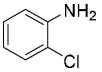
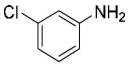
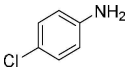
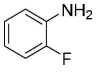
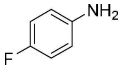
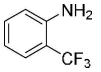
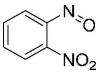
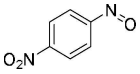
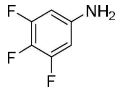
Scheme 1. Modular synthesis of azobenzene-substituted dimethyl 2-(aryldiazenyl)-biphenyl dicarboxylates **5 a–s** with two alternative pathways.

stirred and allowed to warm to 0 °C. Using this procedure, only the monosubstituted biphenyl-dicarboxylate **2** was isolated in 84% yield. Following path A (Scheme 1, upper part), the nitro-derivative **2** was transformed to the nitroso-derivative **3** in 75% yield, in a two-step/one-pot reaction (reduction by zinc, followed by oxidation with iron(III) chloride). Dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate **3** was coupled to the desired substituted anilines **4** in acetic acid at 40 °C, obtaining the linker precursors **5** (dimethyl ester derivatives).

The electronic effect of the substituents plays an important role on the overall yield of the Mills reaction products. Thus, depending on the substitution of the anilines, the advancement of the reaction varied from fairly good to very low yields (see Table 1, around 80% for *para*-methoxy or *para*-fluoro substituents, and around 20% for *ortho*-iodo substituent). In some cases, when the aniline bears a strong electron-withdrawing group such as *ortho*- or *para*-nitroaniline, the reaction failed. To achieve the synthesis of linker precursors with electron-withdrawing substitution patterns and improve the overall yields, an alternate synthetic route (Path B) was also devised (Scheme 1, lower part). Due to the mechanism of the azo-bond formation the reaction of anilines with electron-withdrawing substituents, such as a nitro group, is disfavored and sometimes impossible. The strategy to overcome this reactivity problem consisted in an inversion of the reaction partners. The nitro compound **2** was therefore reduced to the corresponding amino derivative **6** (instead of being reduced to the nitroso compound **3**) and was then subjected to the azo-coupling reaction with substituted nitrosophenyls **7** to yield the dicarboxylic acid linker precursors **5**. This alternate synthetic route couples nitrosophenyls **7**-obtained by oxidation of the corresponding anilines **4** with oxone-to the amine-functionalized linker backbone **6**, making the synthesis of azobenzenes with very strong electron-withdrawing substituents possible. Using the Mills reaction, a library of 19 analogues was obtained, substituted with various electron-withdrawing and electron-donating groups at the *ortho*-, *meta*-, and *para*-positions of the azobenzene side-chain of the resulting azobiphenyls. X-ray diffraction on monocrystals was done for the analogue **5 g** (with iodine on *para* position of the azobenzene side-chain), showing the structure – and especially the *trans* configuration of the azo bond-of the diester derivative (Figure 4). In the last step, the linker precursors **5 a-s** were saponified in aqueous potassium hydroxide solution to obtain the desired substituted azobenzene-functionalized biphenyl dicarboxylic acids **8 a-s** in good to excellent yields (Figure 5).

Selective substitution patterns of the azobenzene ring system influence the spectroscopic properties and isomerization mechanism, and trigger variations in the absorption, emission, thermal stability and photochemical properties of ABs in solution.[22] In the case of the final dicarboxylic acid linkers **8 a-s**, the wavelength of maximum absorption (λ_{max}) in the 320–370 nm region-corresponding to the $\pi \rightarrow \pi^*$ transition in the *trans* state – is shifted from one linker to another analogue (Figure 5). Likewise, the irradiation wavelength for isomerization between the *cis* and the *trans* isomers depends on the substituents of the aromatic rings.[7c] However, a comprehensive

Table 1. Mills reaction. Amino- and nitroso- reaction partners for the synthesis of substituted azobenzene-functionalized biphenyls **5a–s**

Entry	Linker backbone	Reaction partner	Path	**Product** (yield in %)
1	Nitroso **3**		A	**5a** (76)
2	Amino **6**		B	**5a** (66)
3	Nitroso **3**		A	**5b** (60)
4	Nitroso **3**		A	**5c** (78)
5	Nitroso **3**		A	**5d** (36)
6	Nitroso **3**		A	**5e** (22)
7	Nitroso **3**		A	**5f** (67)
8	Nitroso **3**		A	**5g** (73)
9	Nitroso **3**		A	**5h** (26)
10	Nitroso **3**		A	**5i** (58)
11	Nitroso **3**		A	**5j** (62)
12	Nitroso **3**		A	**5k** (40)
13	Nitroso **3**		A	**5l** (46)
14	Nitroso **3**		A	**5m** (73)
15	Nitroso **3**		A	**5n** (52)
16	Nitroso **3**		A	**5o** (81)
17	Nitroso **3**		A	**5p** (60)
18	Amino **6**		B	**5q** (98)
19	Amino **6**		B	**5r** (81)
20	Nitroso **3**		A	**5s** (81)

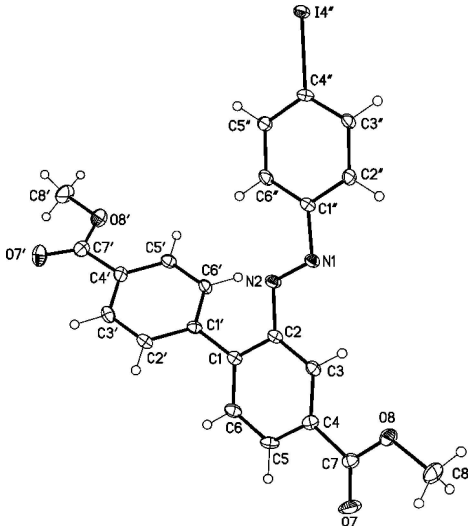


Figure 4. Crystal structure of **5g** (displacement parameters are drawn at 50% probability level).

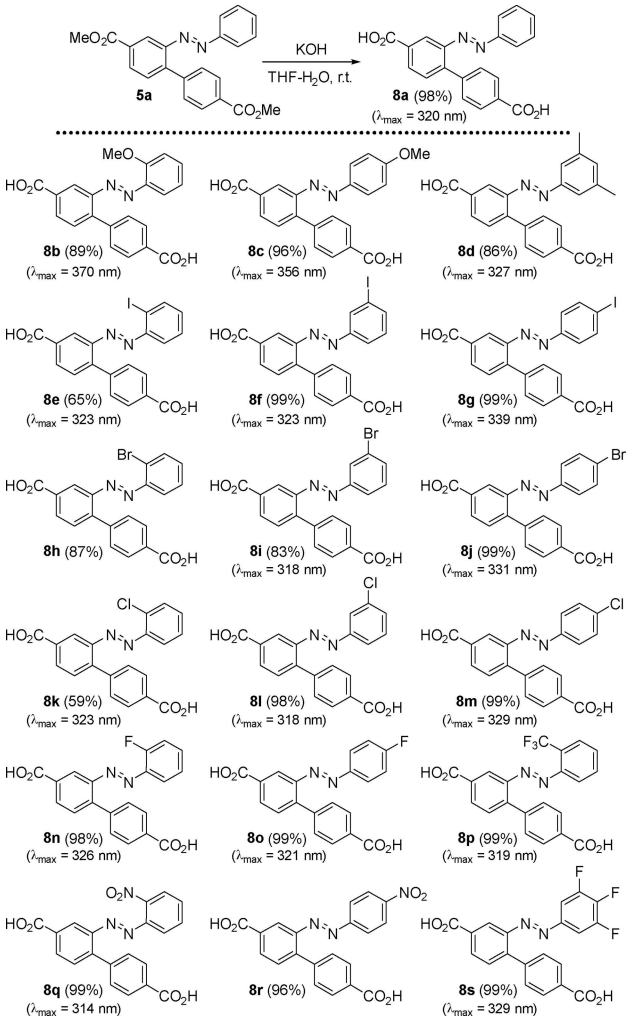
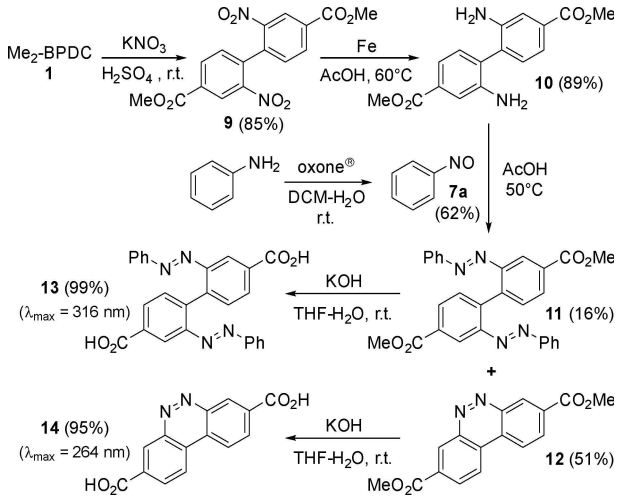
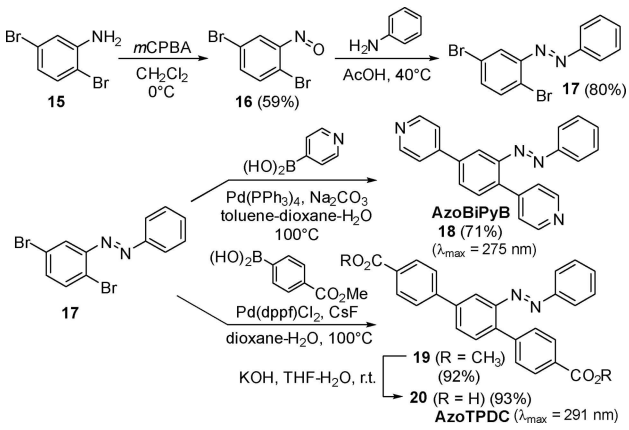


Figure 5. Saponification reaction (top) and structures of azobenzene-functionalized biphenyl-dicarboxylic acid analogues **8a-s** obtained from their corresponding dimethyl ester precursors **5a–s**.

study on the structure-property relationship, physical-chemical parameters of the azobenzene photoswitching was not further investigated in this work. To be applicable into interesting applications, such as optical devices-where a long lifetime is a prerequisite-stabilization of such isomers is necessary, however, this still remains a challenging task. As an example, incorporation of fluorinated azobenzene side groups into MOF thin-



Scheme 2. Synthesis of 2,2′-bis(phenyldiazenyl)-biphenyl dicarboxylic acid **13** and its fused tricyclic cinnoline-like dicarboxylic acid analogue **14**.



Scheme 3. Multi-step synthesis of azobenzene-functionalized terphenyl linker analogues, bispyridine derivative **AzoBiPyB 18** and dicarboxylic acid derivative **AzoTPDC 20** by stepwise Mills reaction/Suzuki-Miyaura cross-coupling reaction.

films enables light-induced switching of the permeation and selection factor; depending on the light irradiated on the membrane, green or violet light (avoiding destructive and bio-incompatible UV light), the membranes can be reversibly modulated.[26]

Exploiting the Mills reaction protocol, with some modifications, open up the possibility of obtaining the symmetrical product **11**, bearing two photoswitchable azobenzene units grafted as side groups to the biphenyl backbone (Scheme 2). Interestingly, the fused tricyclic by-product **12** (benzo[*c*]cinnoline core) was obtained as the main product of the reaction in 51% yield, while the expected bis(azobenzene) derivative **11** was isolated in only 16% yield. As for previously synthesized linker analogues, the last step consisted of a saponification reaction under basic conditions, and led to the final ditopic dicarboxylic acids **13** and **14** in good yields.

Azobenzene derivatives have previously been incorporated into various photochromic macromolecular assemblies.[27] Referring to the MOFs key features such as controlled structures, pore sizes, topologies, and hence the material's properties (e.g. trapping and targeted release of guest molecules, gas separation),[20,21] usually rely on the length of the linker's backbone which are used as spacer groups.[28] Combining both properties, the linker's fixed backbone length and the azobenzene side group's reversibly controllable conformation allows for a flexible and reversibly tunable photoresponsive smart MOF materials. Hence, the size, shape, porosity, and ultimately functions of the pore aperture depend on the *cis*/*trans* isomer ratio of the azobenzene unit attached to the framework's organic linkers.[29–31] In order to synthesize longer backbones with three consecutive aromatic rings-terphenyl linkers-bearing an azobenzene as a side group, a stepwise Mills/Suzuki-Miyaura cross-coupling protocol was used. As a key intermediate, the 2,5-dibromo-azobenzene **17** was prepared in two steps by subjecting 2,5-dibromoaniline **15** to oxidation with *m*CPBA to obtain the nitroso derivative **16** in 59% yield. The intermediate **16** was further transformed under our optimized Mills reaction conditions to obtain the azo-coupled product 2,5-dibromoazobenzene **17** in 80% yield (Scheme 3). After the successful Mills reaction, with the necessary building blocks-including the pre-formed azobenzene-in hand, we extended the synthetic utility of our modular protocol by synthesizing two different classes of model ditopic organic linkers: pyridine-ended terphenyl and carboxylate-grafted terphenyl-based building blocks. Di-bromo functionalized azobenzene **17** was transformed by Pd-catalyzed two-fold Suzuki-Miyaura cross-coupling reaction, using the pyridine or carboxylic ester functionalized aromatic boronic acids. Pyridine, as an aromatic nitrogen-containing heterocycle, can coordinate with most transition metals to form complexes and various coordination networks.[32,33] To incorporate the two different coordination sites-either pyridine or carboxylic acid-at the peripheries of the final products, the corresponding boronic acids were used as coupling reaction partners. These reactions were performed in a biphasic mixture with the Pd-catalyst (i.e. $Pd(PPh_3)_4$ or $Pd(dppf)Cl_2$) and the base (sodium carbonate or cesium fluoride) to obtain the azoterphenyl building blocks azobenzene-bipyridinebenzene (AzoBiPyB **18**) and azobenzene-terphenyldicarboxylic acid (AzoTPDC **20**). Amongst others, both terphenyl linkers **18** and **20** were recently embedded into different photoswitchable azobenzene-containing pillar-layered MOF structures, to study the impact of the light-induced *cis*-to-*trans* isomerization on the adsorption properties of the materials.[34] The whole synthetic sequence from dibromoaniline **15** can be carried out on a multi-gram scale, which demonstrates their generality, practicality and applicability to larger scale production.

These model ditopic organic linkers grafted with azobenzene units as side groups, can strongly bind/coordinate to metals and therefore constitute efficient building units for the construction of photo-responsive nanostructured materials. These 'smart' materials, with remotely controllable structural and mechanical properties are useful tools for the realization of a broad variety of applications.

Conclusions

In summary, a number of diverse functionalized azobiphenyl and azoterphenyl ditopic building blocks were synthesized, based on Mills and Suzuki-Miyaura cross-coupling reactions. This versatile class of azobenzene-functionalized molecules combines several distinct groups in a single molecular unit: 1) photoswitchable azobenzene moiety with various substitution patterns on the aromatic rings; 2) aryls and hetero-aryls blocks functionalized with carboxylic acids or pyridine at its peripheries and 3) variable lengths of the linker backbone. This library of azobenzenes provides modular building units (ditopic functional organic linkers) from which a variety of complex nanoporous materials can be assembled. The azobenzene units impart photosensitivity to the objects made from the resulting complex materials, allowing to remotely control their structural, mechanical and electrical behavior without the need for direct contact with the material. Incorporating structurally diverse azoarene-based tunable building blocks in the development of more ambitious adaptive photoswitchable materials, such as SURMOFs, Liquid Crystals (LCs) and 3D-printed objects, is currently under investigation and we believe that may serve to highlight the immense potential of light-responsive materials and to broaden its implementation in a wide variety of fascinating applications.

Experimental Section

General Methods: Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AC 300, Bruker Avance AM 400, and Bruker Avance 500 spectrometers. Proton (^{1}H) and carbon (^{13}C) chemical shifts (δ) are expressed in parts-per-million [ppm] referenced to the NMR solvent residual peak. All couplings constants (J) are absolute values and expressed in Hertz [Hz]. The description of signal coupling are as follow: s = singlet, b-s = broad singlet, d = doublet, t = triplet, m = multiplet. High resolution mass spectroscopy (HRMS) spectra were recorded with a Finnigan MAT 90 (70 eV) spectrometer. Infrared (IR) spectra were recorded with a Bruker Alpha IR spectrometer by attenuated total reflection (ATR method); absorption is given in wave numbers ($\tilde{\nu}$) [cm^{-1}] and was measured in the range from 3600 cm^{-1} to 500 cm^{-1}. Ultraviolet-visible (UV/Vis) absorption spectra were recorded on a *Varian* Cary 300 spectrometer; absorption is given in wavelengths (λ) [nm] and was measured in the range from 225 nm to 600 nm. Melting points (m.p. in °C) were obtained in a Cambridge Instruments device, model OptiMelt MPA 100. Elemental analysis (EA) was done with an Elementar vario MICRO instrument. The weight scale used was a Sartorius M2P. Calculated (Calcd) and measured (Found) values for carbon, hydrogen and nitrogen are indicated in fractions of 100% mass. Solvents, reagents and chemicals were purchased from standard chemical suppliers. Crude compounds were purified by flash chromatography. For the stationary phase of the column, silica gel, produced by Merck (silica gel 60, 0.040×0.063 mm, 260–400 mesh ASTM), and sea sand by Riedel de Haën (baked out and washed with hydrochloric acid) were used.

Crystal Structure Determination: The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123 (2) K using Cu–Kα radiation (λ = 1.54178 Å.) Direct Methods (SHELXS-97)[35] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[36] Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied. Compound 5 g: red crystals, $C_{22}H_{36}IN_2O_4$, M_r = 500.27, crystal size 0.20×0.18×0.08 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 8.3625(4) Å, b = 6.5846 (3) Å, c = 35.4737(15) Å, β = 96.274(1)°, V = 1941.61(15) Å^3, Z = 4, ρ = 1.711 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 13.237 mm^{-1}, F (000) = 992, $2\theta_{max}$ = 144.4°, 27458 reflections, of which 3806 were independent (R_{int} = 0.028), 265 parameters, R_1 = 0.021 (for 3780 I > 2σ(I)), wR_2 = 0.049 (all data), S = 1.18, largest diff. peak/hole = 0.560/−0.448 e Å^{-3}. CCDC 1877297 (5 g) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Dimethyl 2-nitro-[1,1′-biphenyl]-4,4′-dicarboxylate (2): Dimethyl [1,1′-biphenyl]-4,4′-dicarboxylate (**1**) (2.00 g, 7.40 mmol, 1 equiv.) was dissolved in concentrated sulfuric acid (10 mL), cooled on an ice bath, and 66% HNO_3 (508 µL, 7.40 mmol, 1 equiv.) dissolved in concentrated sulfuric acid (3 mL) was then added drop-wise to this solution. The reaction mixture was stirred at ~5 °C additional 15 minutes and poured slowly onto ice-water slurry with stirring. The resulting white solid collected by filtration was washed with water and then dried under vacuum. Dimethyl 2-nitro-[1,1′-biphenyl]-4,4′-dicarboxylate (**2**) was obtained as a white-yellow solid in 84% yield (2.22 g). m.p.: 163–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.56 (d, 1H, J = 1.5 Hz, *CH*), 8.30 (dd, 1H, J = 8.0 Hz, 1.5 Hz, *CH*), 8.13–8.11 (m, 2H, *CH*), 7.54 (d, 1H, J = 8.0 Hz, *CH*), 7.41–7.40 (m, 2H, *CH*), 4.00 (s, 3H, CO_2CH_3), 3.95 (s, 3H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 166.6 (1 C, CO_2CH_3), 164.8 (1 C, CO_2CH_3), 149.1 (1 C, *Cq*), 141.2 (1 C, *Cq*), 139.6 (1 C, *Cq*), 133.3 (1 C, *CH*), 132.2 (1 C, *CH*), 131.2 (1 C, *Cq*), 130.6 (1 C, *Cq*), 130.2 (2 C, *CH*), 128.0 (2 C, *CH*), 125.6 (1 C, *CH*), 53.0 (1 C, CO_2CH_3), 52.5 (1 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2952, 1717, 1607, 1530, 1432, 1356, 1282, 1185, 1149, 1116, 1021, 1005, 972, 921, 874, 856, 821, 769, 755, 704, 535, 487, 416 cm^{-1}. FAB (*m/z*, Matrix: 3-NBA): 316 (100) [M + H]$^+$, 154 (28) [M + H−OCH_3]$^+$. HRMS–FAB (*m/z*): [M + H]$^+$ calcd for $C_{16}H_{14}NO_6$, 316.0816; found, 316.0814. EA ($C_{16}H_{13}NO_6$): Calcd C 60.95; H 4.16; N 4.44. Found C 60.72; H 4.15; N 4.51.

Dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (3): Dimethyl 2-nitro-[1,1′-biphenyl]-4,4′-dicarboxylate (**2**) (1.500 g, 4.76 mmol, 1.00 equiv.) was added to a solution of ammonium chloride (407 mg, 7.61 mmol, 1.60 equiv.) in methoxyethanol (37 mL) and the mixture was stirred until all solid dissolved. Then, zinc powder (715 mg, 10.9 mmol, 2.30 equiv.) was slowly added and the reaction mixture was stirred at room temperature for 5 minutes. It was then cooled to 0 °C and a cold solution of iron(III) chloride (2.32 g, 14.3 mmol, 3.00 equiv.) in an ethanol/water mixture (5/1, 60 mL) was added. The reaction mixture was stirred for 3 h at 0 °C and then diluted with water and extracted with ethyl acetate. The combined organic layers were then washed with brine, dried with sodium sulfate and the solvent removed under reduced pressure. The product was then recrystallized from ethanol/*n*-hexane. Dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) was obtained as an off-white solid in 75% yield (1.05 g). m.p.: 150.6–153.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.45 (dd, 1H, J = 8.0 Hz, 1.5 Hz, *CH*), 8.21–8.20 (m, 2H, *CH*), 7.90 (d, 1H, J = 8.0 Hz, *CH*), 7.79–7.77 (m, 2H, *CH*), 6.88 (d, 1H, J = 1.5 Hz, *CH*), 3.97 (s, 3H, CO_2CH_3), 3.95 (s, 3H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 166.8 (1 C, CO_2CH_3), 165.8 (1 C, CO_2CH_3), 162.0 (1 C, *Cq*), 148.5 (1 C, *Cq*), 141.0 (1 C, *Cq*), 135.7 (1 C, *CH*), 132.6 (1 C, *CH*), 131.6 (2 C, *CH*), 130.7 (1 C, *Cq*), 130.0 (1 C, *Cq*), 129.6 (2 C, *CH*), 107.7 (1 C, *CH*), 52.8 (1 C, CO_2CH_3), 52.5 (1 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2956, 1732, 1715, 1609, 1492, 1392, 1266, 1175, 1104, 1021 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 264 nm. EI (*m/z*, 70 eV, 110 °C): 299 (39) [M]$^+$, 284 (9) [M-CH_3]$^+$, 268 (9) [M–OCH_3]$^+$, 240 (100) [M–CO_2CH_3]$^+$. HRMS-EI (*m/z*): [M]$^+$ calcd for, 299.0794;

found, 299.0792. EA ($C_{16}H_{13}NO_5$): Calcd C 64.21; H 4.38; N 4.68. Found C 64.00; H 4.41; N 4.69.

Dimethyl 2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 a): [following Path A] Aniline (0.545 g, 5.85 mmol, 2.5 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (0.700 g, 2.34 mmol, 1 equiv.) in ethyl acetate/acetic acid (1/1, 60 mL) and the mixture was stirred at 60 °C for 18 h. The reaction mixture was cooled down to room temperature, concentrated under reduced pressure and filtered off. The solid was washed with a few milliliters of acetic acid and air-dried for 3 h. Dimethyl 2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 a**) was obtained as an orange solid in 76% yield (665 mg). **[following Path B]** Nitrosobenzene (**7 a**) (0.185 g, 1.5 mmol) was added to a solution of dimethyl 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate (**6**) (0.285 g, 1 mmol) in glacial acetic acid (15 mL) and the mixture was stirred at 40 °C for 96 h. The solvent was evaporated to dryness and the residue was purified with column chromatography (silica gel, dichloromethane). Dimethyl 2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 a**) was obtained as an orange solid in 66% yield (247 mg). m.p.: 183–185 °C; ^{1}H NMR (500 MHz, $CDCl_3$,ppm) δ = 8.43 (d, 1H, J = 1.5 Hz, C*H*), 8.22 (dd, 1H, J = 8.0 Hz, 1.5 Hz, C*H*), 8.13–8.12 (m, 2H, C*H*), 7.81–7.79 (m, 2H, C*H*), 7.67 (d, 1H, J = 8.0 Hz, C*H*), 7.58–7.56 (m, 2H, C*H*), 7.49–7.47 (m, 3H, C*H*), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 167.1 (1 C, CO_2CH_3), 166.6 (1 C, CO_2CH_3), 152.7 (1 C, *C*q), 149.7 (1 C, *C*q), 144.1 (1 C, *C*q), 142.8 (1 C, *C*q), 131.7 (1 C, *C*H), 131.4 (1 C, *C*H), 131.0 (2 C, *C*H), 130.9 (1 C, *C*H), 130.8 (1 C, *C*q), 129.6 (1 C, *C*q), 129.4 (2 C, *C*H), 129.1 (2 C, *C*H), 123.6 (2 C, *C*H), 117.7 (1 C, *C*H), 52.6 (1 C, CO_2CH_3), 52.4 (1 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2956, 1731, 1717, 1605, 1432, 1280, 1238, 1187, 1102 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 219, 280, 323, 452 nm. EI (*m/z*, 70 eV, 120 °C): 374 (30) $[M]^+$, 359 (23) $[M\text{-}CH_3]^+$, 343 (4) $[M\text{–}OCH_3]^+$, 315 (11) $[M\text{-}CO_2CH_3]^+$, 270 (88) $[MH\text{–}N{=}NC_6H_5]^+$, 239 (100) $[MH\text{–}CO_2CH_3\text{–}N{=}NC_6H_5]^+$. HRMS-EI *(m/z)*: $[M]^+$ calcd for $C_{22}H_{18}N_2O_4$, 374.1267; found, 374.1265. EA ($C_{22}H_{18}N_2O_4$): Calcd C 70.58; H 4.85; N 7.48. Found C 70.12; H 4.78; N 7.17.

Dimethyl 2-((2-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 b): 2-anisidine (150%L, 165 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (0.200 g, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL) and the solution was heated to 60 °C under constant stirring. After 24 h, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 15% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((2-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 b**) was obtained as an orange solid in 60% yield (162 mg). m.p.: 178.5–179.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.35 (s, 1H, CH), 8.19 (d, 1H, J = 8.1 Hz, CH), 8.12–8.10 (m, 2H, CH), 7.65 (d, 1H, J = 7.9 Hz, CH), 7.57–7.55 (m, 2H, CH), 7.46 (t, 1H, J = 7.8.0 Hz, CH), 7.37 (d, 1H, J = 8.0 Hz, CH), 7.12 (d, 1H, J = 8.4 Hz, CH), 6.94 (t, 1H, J = 7.6 Hz, CH), 4.06 (s, 3H, OCH_3), 3.97 (s, 3H, CO_2CH_3), 3.95 (s, 3H, CO_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.4 (CO_2CH_3), 157.6 (Cq), 150.4 (Cq), 143.5 (Cq), 142.7 (Cq), 142.1 (Cq), 133.2 (CH), 130.9 (CH), 130.7 (3 C, CH, Cq), 130.7 (CH), 129.4 (Cq), 129.0 (2 C, CH), 120.8 (CH), 118.1 (CH), 117.3 (CH), 112.8 (CH), 56.3 (OCH_3), 52.3 (CO_2CH_3), 52.2 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2945, 2832, 1715, 1589, 1484, 1437, 1382, 1276, 1241, 1208, 1159, 1137, 1115, 1104, 1042, 1025, 1000, 927, 842, 781, 759, 749, 703, 573, 516, 485, 420, 385 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 405 (100) $[M+H]^+$, 373 (8), 273 (13), 242 (13), 195 (13), 166 (25). HRMS ($C_{23}H_{21}N_2O_5$): Calc.: 405.1445; Found: 405.1446. EA ($C_{23}H_{21}N_2O_5$): Calcd C 68.31; H 4.98; N 6.93. Found C 67.89; H 4.97; N 6.87.

Dimethyl 2-((4-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 c): 4-anisidine (165 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 28 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 15% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((4-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 c**) was obtained as a yellow solid in 78% yield (213 mg). m.p.: 169.3–170.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.41 (s, 1H, CH), 8.19 (d, 1H, J = 8.0 Hz, CH), 8.13–8.11 (m, 2H, CH), 7.81–7.78 (m, 2H, CH), 7.65 (d, 1H, J = 8.1 Hz, CH), 7.57–7.59 (m, 2H, CH), 7.00–6.88 (m, 2H, CH), 3.98 (s, 3H, CO_2CH_3), 3.96 (s, 3H, CO_2CH_3), 3.88 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.2 (CO_2CH_3), 166.7 (CO_2CH_3), 162.6 (Cq), 149.8 (Cq), 147.3 (Cq), 143.6 (Cq), 143.0 (Cq), 130.9 (3 C, CH), 130.8 (Cq), 130.7 (CH), 129.5 (Cq), 129.1 (2 C, CH), 125.5 (2 C, CH), 117.7 (CH), 114.5 (2 C, CH), 55.8 (OCH_3), 52.5 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2943, 1717, 1600, 1579, 1498, 1457, 1435, 1383, 1281, 1247, 1212, 1181, 1144, 1112, 1029, 1001, 924, 861, 840, 779, 755, 702, 636, 592, 540, 519, 472, 428 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 405 (100) $[M+H]^+$. HRMS ($C_{23}H_{21}N_2O_5$): Calc.: 405.1445; Found: 405.1447. EA ($C_{23}H_{21}N_2O_5$): Calcd C 68.31; H 4.98; N 6.93. Found C 68.00; H 4.99; N 6.91.

Dimethyl 2-((3,5-dimethylphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 d): 3,5-dimethylaniline (162 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 10% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((3,5-dimethylphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 d**) was obtained as an orange solid in 36% yield (97 mg). m.p.: 177.5–177.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.38 (s, 1H, CH), 8.20 (d, 1H, J = 8.1 Hz, CH), 8.12 (d, 2H, J = 8.1 Hz, CH), 7.66 (d, 1H, J = 8.0 Hz, CH), 7.57 (d, 2H, J = 8.2 Hz, CH), 7.42 (s, 2H, CH), 7.12 (s, 1H, CH), 3.98 (s, 3H, CO_2CH_3), 3.96 (s, 3H, CO_2CH_3), 2.38 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.6 (CO_2CH_3), 153.0 (Cq), 149.9 (Cq), 143.7 (Cq), 142.8 (Cq), 139.0 (2 C, Cq), 133.4 (CH), 131.1 (CH), 131.0 (CH), 131.0 (2 C, CH), 130.8 (Cq), 129.6 (Cq), 129.1 (2 C, CH), 121.4 (2 C, CH), 117.8 (CH), 52.5 (CO_2CH_3), 52.4 (CO_2CH_3), 21.4 (2 C, CH_3). IR (ATR, $\tilde{\nu}$) = 2947, 1719, 1604, 1429, 1375, 1278, 1226, 1192, 1169, 1142, 1112, 1023, 996, 961, 932, 909, 861, 840, 820, 780, 760, 743, 703, 685, 603, 577, 481, 383 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 403 (100) $[M+H]^+$, 371 (14) $[M-HOCH_3]^+$, 269 (7), 166 (8). HRMS ($C_{24}H_{23}N_2O_4$): Calc.: 403.1652; Found: 403.1654. EA ($C_{24}H_{23}N_2O_4$): Calcd C 71.63; H 5.51; N 6.96. Found C 71.37; H 5.52; N 6.93.

Dimethyl 2-((2-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 e): 2-iodoaniline (293 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 25 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 15% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((2-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 e**) was obtained as an orange solid in 22% yield (73 mg). m.p.: 230.6–233.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.53 (s, 1H, CH), 8.25 (d, 1H, J = 8.2 Hz, CH), 8.15–8.13 (m, 2H, CH), 8.05 (d, 1H, J = 7.8 Hz, CH), 7.68 (d, 1H, J = 8.1 Hz, CH), 7.59–7.57 (m, 2H, CH), 7.38–7.28 (m, 2 H), 7.18–7.14 (m, 1H, CH), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.4 (CO_2CH_3), 151.2 (Cq), 149.2 (Cq), 144.4 (Cq), 142.5 (Cq), 140.0 (CH), 132.7 (CH), 131.7 (CH), 130.9 (CH), 130.8 (2 C, CH), 129.6 (Cq), 129.1 (2 C, CH), 129.0 (CH), 118.5 (CH),

117.6 (CH), 103.4 (Cq, 2 C), 52.5 (CO_2CH_3), 52.2 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2945, 1713, 1604, 1566, 1434, 1383, 1273, 1231, 1211, 1168, 1134, 1103, 1020, 993, 928, 842, 805, 780, 758, 741, 702, 603, 557, 541, 474, 443 cm^{-1}.FAB (Matrix: 3-NBA), *m/z* (%): 501 (90) $[M+H]^+$, 195 (100), 165 (70). HRMS ($C_{22}H_{18}{}^{127}IN_2O_4$): Calc.: 501.0306; Found: 501.0308.

Dimethyl 2-((3-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5f): 3-iodoaniline (160 %L, 293 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 26 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 12% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((3-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5f**) was obtained as an orange solid in 67% yield (224 mg). m.p.: 187.1–187.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 8.40 (s, 1H, CH), 8.24 (dd, 1H, *J* = 8.1 Hz, *J* = 1.6 Hz, CH), 8.16 (s, 1H), 8.15 − 8.14 (m, 2H, CH), 7.79 (d, 1H, *J* = 7.8 Hz, CH), 7.73 (d, 1H, *J* = 8.0 Hz, CH), 7.68 (d, 1H, *J* = 8.1 Hz, CH), 7.58−7.56 (m, 2H, CH), 7.25−7.20 (m, 1H, CH), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.4 (CO_2CH_3), 153.5 (Cq), 149.3 (Cq), 144.4 (Cq), 142.5 (Cq), 140.2 (CH), 133.0 (CH), 131.8 (CH), 131.2 (CH), 130.9 (2 C, CH), 130.9 (CH), 130.8 (Cq), 129.8 (Cq), 129.2 (2 C, CH), 122.4 (CH), 117.7 (CH), 94.6 (Cq), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2952, 1717, 1604, 1565, 1431, 1282, 1235, 1196, 1100, 1024, 1002, 917, 873, 844, 806, 785, 775, 758, 737, 701, 674, 644, 597, 554, 471, 433 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 201 (37) $[M+H]^+$. HRMS ($C_{22}H_{18}{}^{127}IN_2O_4$): Calc.: 501.0306; Found: 501.0306. EA ($C_{22}H_{18}{}^{127}IN_2O_4$): Calcd C 52.82; H 3.43; N 5.60. Found C 52.68; H 3.53; N 5.61.

Dimethyl 2-((4-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5g): 4-iodoaniline (293 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 28 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product washed with more acetic anhydride. The residue was purified with column chromatography (silica gel, 10% ethyl acetate in cyclohexane). Dimethyl 2-((4-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5g**) was obtained as an orange solid in 73% yield (247 mg). m.p.: 190.0–193.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.42 (s, 1H, CH), 8.22 (d, 1H, *J* = 8.1 Hz, CH), 8.11 (d, 2H, *J* = 8.0 Hz, CH), 7.83 (d, 2H, *J* = 8.3 Hz, CH), 7.67 (d, 1H, *J* = 8.2 Hz, CH), 7.55−7.49 (m, 4H, CH), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.5 (CO_2CH_3), 152.0 (Cq), 149.4 (Cq), 144.4 (Cq), 142.6 (Cq), 138.7 (2 C, CH), 131.7 (CH), 131.1 (CH), 130.9 (2 C, CH), 130.8 (Cq), 129.7 (Cq), 129.1 (2 C, CH), 125.0 (2 C, CH), 117.6 (CH), 98.7 (Cq), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2953, 1721, 1607, 1562, 1474, 1434, 1391, 1278, 1209, 1181, 1110, 1051, 1000, 864, 828, 777, 756, 739, 699, 628, 542, 467 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 501 (100) $[M+H]^+$. HRMS ($C_{22}H_{18}{}^{127}IN_2O_4$): Calc.: 501.0306; Found: 501.0307. EA ($C_{22}H_{18}{}^{127}IN_2O_4$): Calcd C 52.82; H 3.43; N 5.60. Found C 53.47; H 3.55; N 5.30.

Dimethyl 2-((2-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5h): 2-bromoaniline (150 %L, 229 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 10% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((2-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5h**) was obtained as an orange solid in 26% yield (79 mg). m.p.: 218.7–220.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.48 (s, 1H, CH), 8.25 (d, 1H, *J* = 8.1 Hz, CH), 8.15–8.13 (m, 2H, CH), 7.79–7.76 (m, 1H, CH), 7.68 (d, 1H, *J* = 8.1 Hz, CH), 7.59–7.57 (m, 2H, CH), 7.35–7.29 (m, 3H, CH), 4.00 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3). NMR contains slight impurities. ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.5 (CO_2CH_3), 149.6 (2 C, Cq), 144.4 (Cq), 142.5 (Cq), 133.9 (CH), 132.4 (CH), 131.7 (CH), 130.9 (CH), 130.8 (Cq), 130.8 (2 C, CH), 129.6 (Cq), 129.0 (2 C, CH), 128.0 (CH), 126.6 (Cq), 118.2 (CH), 118.0 (CH), 52.5 (CO_2CH_3), 52.2 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2946, 1717, 1604, 1456, 1384, 1274, 1211, 1168, 1134, 1104, 1041, 1024, 993, 929, 843, 806, 780, 759, 742, 702, 602, 559, 542, 475, 411 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 453 (30) $[M+H]^+$, 316 (27), 300 (100), 268 (27), 238 (27), 165 (39). HRMS ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calc.: 453.0444; Found: 453.0446. EA ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calcd C 58.29; H 3.78; N 6.18. Found C 57.52; H 3.81; N 6.05.

Dimethyl 2-((3-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5i): 3-bromoaniline (150 µL, 230 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 28 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product washed with more acetic anhydride. The residue was purified with column chromatography (silica gel, 30% ethyl acetate in cyclohexane). Dimethyl 2-((3-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5i**) was obtained as an orange solid in 58% yield (175 mg). m.p.: 183.8–186.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.41 (s, 1H, CH), 8.25 (d, 1H, *J* = 8.1 Hz, CH), 8.15–8.13 (m, 2H, CH), 7.95 (s, 1H, CH), 7.73 (d, 1H, *J* = 8.5 Hz, CH), 7.69 (d, 1H, *J* = 8.1 Hz, CH), 7.61 (d, 1H, *J* = 7.9 Hz, CH), 7.58−7.56 (m, 2H, CH), 7.37 (t, 1H, *J* = 8.0 Hz, CH), 4.00 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3). Spectrum contains ca. 10% impurities assumed to origin in the isomerism (E/Z) of the compound. ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.9 (CO_2CH_3), 166.3 (CO_2CH_3), 153.5 (Cq), 149.2 (Cq), 144.3 (Cq), 142.5 (Cq), 134.2 (CH), 131.7 (CH), 131.0 (CH), 130.8 (Cq), 130.7 (2 C, CH), 130.7 (Cq), 130.5 (CH), 129.0 (2 C, CH), 126.5 (CH), 123.3 (Cq), 122.0 (CH), 117.5 (CH), 52.5 (CO_2CH_3), 52.2 (CO_2CH_3). Spectrum contains ca. 10% impurities assumed to origin in the isomerism (E/Z) of the compound. IR (ATR, $\tilde{\nu}$) = 2956, 1715, 1604, 1571, 1431, 1383, 1281, 1235, 1196, 1151, 1101, 1025, 1003, 917, 845, 843, 808, 784, 775, 757, 737, 700, 673, 748, 598, 554, 474, 437 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 453 (100) $[M+H]^+$, 453 (80). HRMS ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calc.: 453.0444; Found: 453.0446. EA ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calcd C 58.29; H 3.78; N 6.18. Found C 58.16; H 3.82; N 5.96.

Dimethyl 2-((4-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5j): 4-bromoaniline (230 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product was washed with more acetic anhydride. Dimethyl 2-((4-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5j**) was obtained as an orange solid in 62% yield (188 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.43 (s, 1H, CH), 8.24 (d, 1H, *J* = 8.1 Hz, CH), 8.14−8.12 (m, 2H, CH), 7.72−7.61 (m, 5H, CH), 7.57−7.55 (m, 2H, CH), 4.00 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.9 (CO_2CH_3), 166.3 (CO_2CH_3), 151.3 (Cq), 149.3 (Cq), 144.2 (Cq), 142.5 (Cq), 132.5 (2 C, CH), 131.5 (CH), 131.0 (CH), 130.7 (Cq), 130.7 (2 C, CH), 129.6 (Cq), 129.0 (2 C, CH), 126.1 (Cq), 124.8 (2 C, CH), 117.5 (CH), 52.5 (CO_2CH_3), 52.2 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2947, 1717, 1603, 1570, 1475,

1434, 1279, 1192, 1107, 1064, 1001, 874, 833, 778, 755, 199, 598, 526, 488, 469, 415 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 453 (25) $[M+H]^+$, 271 (41), 261 (53), 239 (41), 217 (59), 195 (100). HRMS ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calc. 453.0444; Found. 453.0446. EA ($C_{22}H_{18}{}^{79}BrN_2O_4$): Calcd C 58.29; H 3.78; N 6.18. Found C 58.21; H 3.84; N 5.90.

Dimethyl 2-((2-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5k): 2-chloroaniline (140 %L, 171 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 30 % ethyl acetate in cyclohexane). Dimethyl 2-((2-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5k**) was obtained as an orange solid in 40 % yield (108 mg). m.p.: 197.2–200.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.43 (d, 1H, *J* = 1.4 Hz, CH), 8.24 (dd, 1H, *J* = 8.1 Hz, *J* = 1.7 Hz, CH), 8.15−8.11 (m, 2H, CH), 7.67 (d, 1H, *J* = 8.1 Hz, CH), 7.59−7.56 (m, 2H, CH), 7.45−7.35 (m, 2H, CH), 7.30 − 7.23 (m, 2H, CH), 3.99 (s, 3H, CO_2CH_3), 3.96 (s, 3H, CO_2CH_3). This spectrum contains around 10 % impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.5 (CO_2CH_3), 149.8 (Cq), 148.7 (Cq), 144.5 (Cq), 142.7 (Cq), 136.3 (Cq), 132.4 (CH), 131.8 (CH), 131.1 (CH), 131.0 (CH), 130.9 (3 C, CH, Cq), 129.7 (Cq), 129.2 (2 C, CH), 127.5 (CH), 118.2 (CH), 117.9 (CH), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). This spectrum contains around 10 % impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$) = 2947, 1719, 1604, 1438, 1275, 1228, 1211, 1169, 1113, 1059, 1024, 994, 930, 943, 780, 760, 743, 703, 603, 562, 480 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 409 (100) $[M+H]^+$, 377 (17), 361 (9). EA ($C_{22}H_{18}ClN_2O_4$): Calcd C 64.63; H 4.19; N 6.85. Found C 63.85; H 4.29; N 6.68.

Dimethyl 2-((3-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5l): 3-chloroaniline (140 %L, 171 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 28 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product washed with more acetic anhydride. The residue was purified with column chromatography (silica gel, 30 % ethyl acetate in cyclohexane). Dimethyl 2-((3-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5l**) was obtained as an orange solid in 46 % yield (125 mg). m.p.: 177.2–179.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.41 (s, 1H, CH), 8.25 (d, 1H, *J* = 8.1 Hz, CH), 8.15−8.12 (m, 2H, CH), 7.78 (s, 1H, CH), 7.71−7.66 (m, 2H, CH), 7.58−7.56 (m, 2H, CH), 7.47−7.40 (m, 2H, CH), 4.00 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3). This spectrum contains around 5 % impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.9 (CO_2CH_3), 166.3 (CO_2CH_3), 153.3 (Cq), 149.2 (Cq), 144.3 (Cq), 142.4 (Cq), 135.2 (Cq), 131.7 (CH), 131.2 (CH), 131.0 (CH), 130.7 (2 C, CH), 130.7 (Cq), 130.2 (CH), 129.6 (Cq), 129.0 (2 C, CH), 123.4 (CH), 121.7 (CH), 117.5 (CH), 52.5 (CO_2CH_3), 52.2 (CO_2CH_3). This spectrum contains around 5 % impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$) = 2957, 1716, 1605, 1432, 1384, 1281, 1235, 1198, 1151, 1102, 1068, 1026, 1003, 917, 876, 843, 811, 785, 756, 738, 701, 674, 599, 554, 476 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 409 (100) $[M+H]^+$. HRMS ($C_{22}H_{18}ClN_2O_4$): Calc.: 409.0950; Found: 409.0952. EA ($C_{22}H_{18}ClN_2O_4$): Calcd C 64.63; H 4.19; N 6.85. Found C 64.19; H 4.18; N 6.62.

Dimethyl 2-((4-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5m): 4-chloraniline (171 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product washed with acetic anhydride. Dimethyl 2-((4-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5m**) was obtained as an orange solid in 73 % yield (201 mg). m.p.: 167.5–170.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.43 (s, 1H, CH), 8.23 (dd, 1H, *J* = 8.1 Hz, *J* = 1.7 Hz, CH), 8.14−8.12 (m, 2H, CH), 7.75−7.73 (m, 2H, CH), 7.66 (d, 1H, *J* = 8.0 Hz, CH), 7.57−7.55 (m, 2H, CH), 7.47−7.46 (m, 2H, CH), 3.99 (s, 3H, CH_3), 3.97 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.9 (CO_2CH_3), 166.3 (CO_2CH_3), 150.9 (Cq), 149.3 (Cq), 144.2 (Cq), 142.5 (Cq), 137.6 (Cq), 131.4 (CH), 130.9 (CH), 130.7 (2 C, CH), 130.7 (Cq), 129.6 (Cq), 129.5 (2 C, CH), 129.0 (2 C, CH), 124.6 (2 C, CH), 117.5 (CH), 52.4 (CO_2CH_3), 52.2 (CO_2CH_3). 130.2 (CH), 127.2 (CH) are impurities and not part of the product spectrum. IR (ATR, $\tilde{\nu}$) = 2952, 1716, 1603, 1482, 1431, 1276, 1187, 1101, 1026, 1007, 914, 875, 833, 778, 756, 699, 596, 541, 492, 433, 389 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 409 (100) $[M+H]^+$, 393 (15) $[M-O]^+$, 377 (15) $[M-HOCH_3]^+$. HRMS ($C_{22}H_{18}{}^{35}ClN_2O_4$): Calc.: 409.0950; Found: 409.0951. EA ($C_{22}H_{18}{}^{35}ClN_2O_4$): Calcd C 64.63; H 4.19; N 6.85. Found C 64.67; H 4.30; N 6.34.

Dimethyl 2-((2-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5n): 2-fluoroaniline (130 %L, 149 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure and 1.0 mL acetic anhydride was added. The suspension was filtered and the product washed with some more acetic anhydride. The residue was purified with column chromatography (silica gel, 30 % ethyl acetate in cyclohexane). Dimethyl 2-((2-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5n**) was obtained as an orange solid in 52 % yield (137 mg). m.p.: 182.2–183.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.42 (s, 1H, CH), 8.24 (d, 1H, *J* = 8.1 Hz, CH), 8.14−8.12 (d, 2H, *J* = 8.2 Hz, CH), 7.68 (d, 1H, *J* = 8.1 Hz, CH), 7.58−7.56 (m, 2H, CH), 7.48−7.38 (m, 2H, CH), 7.32−7.25 (m, 1H), 7.15 (t, 1H, *J* = 7.7 Hz, CH), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ = -123.31 (CF). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.5 (CO_2CH_3), 160.6 (d, *J* = 259 Hz, Cq), 149.9 (Cq), 144.4 (Cq), 142.7 (Cq), 140.8 (d, *J* = 6.6 Hz, Cq), 133.3 (d, *J* = 8.4 Hz, CH), 131.8 (CH), 131.1 (CH), 130.9 (2 C, CH), 129.7 (Cq), 129.2 (2 C, CH), 124.5 (d, *J* = 3.8 Hz, CH), 118.1 (CH), 117.8 (CH), 117.4 (d, *J* = 19.9 Hz, CH), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2951, 1719, 1604, 1589, 1482, 1434, 1279, 1241, 1188, 1103, 1026, 993, 911, 878, 847, 829, 787, 758, 700, 609, 569, 482, 454 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 409 (100) $[M+H]^+$, 377 (17), 361 (9). HRMS ($C_{22}H_{18}FN_2O_4$): Calc.: 393.1245; Found: 393.1244. EA ($C_{22}H_{18}FN_2O_4$): Calcd C 67.34; H 4.37; N 7.14. Found C 67.07; H 4.33; N 7.05.

Dimethyl 2-((4-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5o): 4-fluoroaniline (130 %L, 149 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure and 1.0 mL of acetic anhydride was added to the product. The suspension was filtered and the product washed with acetic anhydride and cyclohexane. Dimethyl 2-((4-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5o**) was obtained as an orange solid in 81 % yield (214 mg). m.p.: 206.7–208.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.43 (s, 1H, CH), 8.23 (d, 1H, *J* = 7.8 Hz, CH), 8.14−8.12 (m, 2H, CH), 7.83−7.80 (m, 2H, CH), 7.67 (d, 1H, *J* = 7.9 Hz, CH), 7.58−7.56 (m, 2H, CH), 7.19−7.15 (m, 2H, CH), 3.99 (s,

3H, CH_3), 3.97 (s, 3H, CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ = -108.12 (CF). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.5 (CO_2CH_3), 164.8 (d, J = 253.4 Hz, Cq), 149.4 (d, J = 3.0 Hz, Cq), 149.5 (Cq), 144.2 (Cq), 142.8 (Cq), 131.4 (CH), 131.1 (CH), 130.9 (2 C, CH), 130.8 (Cq), 129.7 (Cq), 129.2 (2 C, CH), 125.6 (2 C, d, J = 9.1 Hz, CH), 117.7 (CH), 116.4 (2 C, d, J = 22.9 Hz, CH), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2954, 1716, 1594, 1500, 1432, 1277, 1228, 1187, 1144, 1102, 1025, 1007, 987, 914, 874, 839, 785, 757, 741, 700, 598, 534, 499, 462, 413, 387 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 393 (100) $[M+H]^+$. HRMS ($C_{22}H_{18}FN_2O_4$): Calc.: 393.1245; Found: 393.1246. EA ($C_{22}H_{18}FN_2O_4$): Calcd C 67.34; H 4.37; N 7.14. Found C 66.92; H 4.42; N 6.82.

Dimethyl 2-((2-(trifluoromethyl)phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 p): 3-aminobenzo-1-trifluoride (170 %L, 215 mg, 1.34 mmol, 2.00 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (200 mg, 0.668 mmol, 1.00 equiv.) in acetic acid (5 mL), and the solution was heated at 40 °C under constant stirring. After 24 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 12% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((2-(trifluoromethyl)phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 p**) was obtained as a bright orange solid in 60% yield (177 mg). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.44 (s, 1H, CH), 8.26 (d, 1H, J = 8.1 Hz, CH), 8.13 (m, 3H, CH), 7.89 (d, 1H, J = 8.0 Hz, CH), 7.73 (d, 1H, J = 7.9 Hz, CH), 7.70 (d, 1H, J = 8.1 Hz, CH), 7.61 (d, 1H, J = 7.9 Hz, CH), 7.57 (d, 2H, J = 8.2 Hz, CH), 4.00 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ = −62.85 (CF_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.4 (CO_2CH_3), 152.6 (Cq), 149.3 (Cq), 144.7 (Cq), 142.5 (Cq), 132.0 (CH), 131.2 (CH), 130.9 (2 C, CH), 130.9 (2 C, Cq), 130.0 (CH), 129.9 (Cq), 129.2 (2 C, CH), 127.2 (q, J = 3.7 Hz, CH), 125.1 (CH), 121.8 (q, J = 3.9 Hz, CH), 117.6 (CH), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2957, 1727, 1606, 1432, 1328, 1278, 1238, 1188, 1120, 1059, 992, 913, 866, 844, 805, 776, 755, 739, 689, 649, 606, 496, 467 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 443 (93) $[M+H]^+$, 427 (15), 411 (13), 383 (6), 269 (7). HRMS ($C_{23}H_{18}F_3N_2O_4$): Calc.: 443.1213; Found: 443.1212. EA ($C_{23}H_{18}F_3N_2O_4$): Calcd C 62.44; H 3.87; N 6.33. Found C 62.34; H 3.89; N 6.31.

Dimethyl 2-((2-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 q): 1-nitro-2-nitrosobenzene (**7 b**) (160 mg, 1.05 mmol, 1.50 equiv.) was added to a solution of dimethyl 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate (**6**) (200 mg, 0.702 mmol, 1.00 equiv.) in acetic acid (10 mL), and the solution was heated at 40 °C under constant stirring. After 68 hours, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 15 to 75% ethyl acetate in cyclohexane) and recrystallized from isopropanol/*n*-hexane. Dimethyl 2-((2-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 q**) was obtained as an off-yellow solid in 98% yield (289 mg). m.p.: 203.6–206.6 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.35 (d, 1H, J = 1.7 Hz, CH), 8.28 (dd, 1H, J = 8.1 Hz, J = 1.8 Hz, CH), 8.12−8.15 (m, 2H, CH), 7.94 (dd, J = 1H, 7.8 Hz, J = 1.6 Hz, CH), 7.68 (d, 1H, J = 8.1 Hz, CH), 7.65–7.56 (m, 4H, CH), 7.34 (dd, 1H, J = 7.8 Hz, J = 1.6 Hz, CH), 3.98 (s, 3H, CO_2CH_3), 3.96 (s, 3H, CO_2CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 167.0 (CO_2CH_3), 166.3 (CO_2CH_3), 149.5 (Cq), 147.7 (Cq), 145.6 (Cq), 145.1 (Cq), 142.4 (Cq), 133.3 (CH), 132.6 (CH), 131.2 (CH), 131.1 (Cq), 131.0 (CH), 130.8 (2 C, CH), 129.9 (Cq), 129.3 (2 C, CH), 124.4 (CH), 118.8 (CH), 118.0 (CH), 52.7 (CO_2CH_3), 52.4 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3091, 2921, 2842, 1714, 1601, 1519, 1429, 1344, 1281, 1212, 1185, 1107, 995, 961, 925, 869, 750, 788, 759, 732, 707, 693, 608, 492, 472, 417 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 420 (22) $[M+H]^+$, 388 (22) $[M-HOCH_3]^+$, 371 (22) $[M-HCOOCH_3]^+$, 327 (39), 277 (33), 239 (44), 217 (50), 195 (61), 165 (100). HRMS ($C_{22}H_{18}N_3O_6$): Calc. 420.1190; Found. 420.1192. EA ($C_{22}H_{18}N_3O_6$): Calcd C 63.01; H 4.09; N 10.02. Found C 62.67; H 4.30; N 9.94.

Dimethyl 2-((4-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 r): 1-nitro-4-nitrosobenzene (**7 c**) (233 mg, 1.5 mmol, 1.40 equiv.) was added to a solution of dimethyl 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate (**6**) (313 mg, 1.1 mmol, 1.00 equiv.) in acetic acid (30 mL), and the reaction mixture was heated at 75 °C for 24 h. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. A small amount of acetic acid was added and the suspension was filtered off; the solid obtained was washed with a few milliliters of acetic acid and dried in the vacuum-oven at 40 °C overnight. Dimethyl 2-((4-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 r**) was obtained as a red-orange solid in 81% yield (0.373 g). ^1H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.47 (d, 1H, J = 1.5 Hz, *CH*), 8.36−8.34 (m, 2H, *CH*), 8.28 (dd, 1H, J = 8.0 Hz, 1.5 Hz, *CH*), 8.15−8.13 (m, 2H, *CH*), 7.91−7.89 (m, 2H, *CH*), 7.71 (d, 1H, J = 8.0 Hz, *CH*), 7.56−7.54 (m, 2H, *CH*), 4.00 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3). This spectrum contains around 7% impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 167.0 (1 C, CO_2CH_3), 166.3 (1 C, CO_2CH_3), 155.6 (1 C, *Cq*), 149.3 (1 C, *Cq*), 149.1 (1 C, *Cq*), 145.3 (1 C, *Cq*), 142.3 (1 C, *Cq*), 132.6 (1 C, *CH*), 131.4 (1 C, *CH*), 130.9 (3 C, *CH* and *Cq*), 130.0 (1 C, *Cq*), 129.3 (2 C, *CH*), 125.0 (2 C, *CH*), 124.1 (2 C, *CH*), 117.5 (1 C, *CH*), 52.7 (1 C, CO_2CH_3), 52.5 (1 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3004, 2948, 2842, 1716, 1606, 1525, 1433, 1341, 1283, 1105 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 274, 335 nm. APCI (*m/z*): 420 (100) $[M+H]^+$, 286 (27) $[M+H-NC_6H_4NO_2]^+$. HRMS–APCI (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{18}N_3O_6$, 420.1196; found, 420.1185. EA ($C_{22}H_{17}N_3O_6$): Calcd C 63.01; H 4.09; N 10.02. Found C 62.12; H 3.95; N 10.28.

Dimethyl 2-((3,4,5-triluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (5 s): 3,4,5-trifluoroaniline (295 mg, 2.01 mmol, 2 equiv.) was added to a solution of dimethyl 2-nitroso-[1,1′-biphenyl]-4,4′-dicarboxylate (**3**) (0.300 g, 1.00 mmol, 1 equiv.) in acetic acid (15 mL) and the reaction mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature, concentrated under reduced pressure and filtered off; the solid obtained was washed with a few milliliters of acetic acid and dried. Dimethyl 2-((3,4,5-triluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5 s**) was obtained as a red-orange solid in 81% yield (0.346 g). ^1H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.40 (s, 1H, *CH*), 8.25 (d, 1H, J = 8.0 Hz, *CH*), 8.14−8.13 (m, 2H, *CH*), 7.68 (d, 1H, J = 8.0 Hz, *CH*), 7.53−7.52 (m, 2H, *CH*), 7.45 (t, 2H, J = 6.5 Hz, *CH*), 3.99 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3). ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ = -132.23 (dd, 2F, J = 20.2 Hz, 8.0 Hz, *CF*), −154.81 (t, 1F, J = 20.2 Hz, *CF*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 166.9 (1 C, CO_2CH_3), 166.3 (1 C, CO_2CH_3), 151.7 (ddd, 2 C, J = 251 Hz, 11.0 Hz, 4.0 Hz, *CF*), 148.8 (1 C, *Cq*), 147.5 (dt, 1 C, J = 6.4 Hz, 4.0 Hz, *Cq*), 144.9 (1 C, *Cq*), 142.3 (1 C, *Cq*), 142.0 (dt, 1 C, J = 256 Hz, 16.0 Hz, *CF*), 132.3 (1 C, *CH*), 131.3 (1 C, *CH*), 130.8 (1 C, *Cq*), 130.8 (2 C, *CH*), 130.0 (1 C, *Cq*), 129.3 (2 C, *CH*), 117.6 (1 C, *CH*), 108.0 (dd, 2 C, J = 17.5 Hz, 5.0 Hz, CH), 52.7 (1 C, CO_2CH_3), 52.5 (1 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3079, 2959, 1723, 1605, 1511, 1435, 1345, 1284, 1231, 1142, 1048 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 278, 321, 449 nm. EI (*m/z*, 70 eV, 150 °C): 428 (100) $[M]^+$, 413 (78) $[M-CH_3]^+$, 369 (33) $[M-CO_2CH_3]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{22}H_{15}F_3N_2O_4$, 428.0984; found, 428.0980.

Dimethyl 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate (6): A solution of dimethyl 2-nitro-[1,1′-biphenyl]-4,4′-dicarboxylate (**2**) (2.20 g, 6.98 mmol, 1 equiv.) in dichloromethane (25 mL) was diluted with methanol (25 mL). To this solution, 10% Pd/C (250 mg) was added and the reaction mixture was stirred under a hydrogen atmosphere of 3 bars for 18 h on a hydrogenation apparatus. The reaction mixture was filtered through celite, washed with methanol and the filtrate was concentrated under reduced pressure. Dimethyl 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate (**6**) was obtained as a pale

yellow solid in 70% yield (1.73 g). m.p.: 160–161 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 8.14–8.11 (m, 2H, *CH*), 7.56–7.54 (m, 2H, *CH*), 7.48 (dd, 1H, *J* = 7.8 Hz, *J* = 1.2 Hz, *CH*), 7.45 (d, 1H, *J* = 1.2 Hz, *CH*), 7.18 (d, 1H, *J* = 7.8 Hz, *CH*), 3.95 (s, 3H, CO_2CH_3), 3.91 (s, 3H, CO_2CH_3), 3.88 (b-s, 2H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 167.1 (CO_2CH_3), 166.9 (CO_2CH_3), 143.7 (*Cq*), 143.5 (*Cq*), 130.9 (*CH*), 130.6 (*CH*), 130.5 (*Cq*), 130.4 (2 C, *CH*), 129.6 (*Cq*), 129.0 (2 C, *CH*), 119.9 (*Cq*), 116.8 (*CH*), 52.4 (CO_2CH_3), 52.3 (CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3456, 3364, 2950, 1702, 1621, 1603, 1573, 1434, 1399, 1333, 1298, 1246, 1186, 1102, 1020, 997, 907, 866, 827, 797, 778, 759, 703, 561, 462 cm^{-1}. FAB (Matrix: 3-NBA), *m/z* (%): 286 (100) $[M+H]^+$, 285 (90) $[M]^+$, 154 (22) $[M\text{-}HOCH_3]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{16}H_{15}NO_4$, 285.0996; found, 285.0997. EA ($C_{16}H_{15}NO_4$): Calcd C 67.36; H 5.30; N 4.91. Found C: 67.25; H 5.30; N 4.84.

Nitrosobenzene (7a): Aniline (1.200 g, 12.89 mmol, 1 equiv.) was dissolved in 40 mL of dichloromethane. To this solution Oxone® (15.848 g, 25.77 mmol, 2 equiv.) dissolved in water (150 mL) was added and the reaction mixture was stirred at room temperature for 2 h. After separation of the layers, the aqueous phase (orange) was extracted with dichloromethane. Combined organic layers (green) were washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, water, brine, then dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude product (0.854 g) showed expected signals (^{1}H and ^{13}C NMR), and was applied in the next step without further purification. Nitrosobenzene (**7a**) was obtained as a green oil in 62% yield (854 mg). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.91-7.89 (m, 2H, $C^{2/6}H$), 7.71 (t, 1H, *J* = 7.5 Hz, C^4H), 7.62 (t, 2H, *J* = 7.5 Hz, $C^{3/5}$H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 166.0 (1 C, C^1), 135.7 (1 C, C^4), 129.4 (2 C, $C^{3/5}$H), 121.1 (2 C, $C^{2/6}$H).

1-nitro-2-nitrosobenzene (7b): A suspension of Oxone® (2.00 g, 3.26 mmol, 1.50 equiv.) in concentrated sulfuric acid (3 mL) was poured on 14 mg of ice and stirred until all ice dissolved. 2-nitroaniline (300 mg, 2.17 mmol, 1.00 equiv.) was added and the reaction mixture was stirred at room temperature. After 17 hours, the mixture was extracted with dichloromethane. The combined organic layers were washed with saturated $NaHCO_3$ and brine, then dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, 80% ethyl acetate in cyclohexane). 1-nitro-2-nitrosobenzene (**7b**) was obtained as a light-yellow solid in 59% yield (195 mg). m.p.: 123.6–124.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 8.10 (dd, 1H, *J* = 8.0 Hz, *J* = 0.6 Hz, CH), 7.84 (td, 1H, *J* = 8.0 Hz, *J* = 0.6 Hz, CH), 7.67 (td, 1H, *J* = 7.9 Hz, *J* = 0.6 Hz, CH), 6.48 (dd, 1H, *J* = 7.9 Hz, *J* = 0.6 Hz, CH). This spectrum contains around 20% impurities due to non-reacted starting material nitroaniline. ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 155.4 (*Cq*), 150.3 (*Cq*), 135.3 (*CH*), 133.3 (*CH*), 124.4 (*CH*), 110.5 (*CH*). This spectrum contains around 20% impurities due to non-reacted starting material nitroaniline. IR (ATR, $\tilde{\nu}$) = 3092, 2873, 1603, 1586, 1524, 1349, 1291, 1206, 1169, 1148, 1088, 965, 885, 869, 831, 782, 741, 697, 668, 619, 579, 519, 493, 408, 389 cm^{-1}. MS (EI *m/z*, 70 eV, 80 °C): 152 (100) $[M]^+$, 138 (2), 100 (4), 94 (10), 92 (12), 76 (34). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_6H_4N_2O_3$, 152.0216; found, 152.0218. EA ($C_6H_4N_2O_3$): Calcd C 47.38; H 2.65; N 18.42. Found C 47.55; H 2.79; N 18.24.

1-nitro-4-nitrosobenzene (7c): A solution of Oxone® (10.241 g, 16.65 mmol, 2 equiv.) in water (40 mL) was added under Argon and over a period of 15 minutes to a solution of 4-nitroaniline (1.150 g, 8.33 mmol, 1 equiv.) in water (40 mL) and the mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with dichloromethane. Combined organic layers were washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, water, brine, then dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude product was purified by chromatography (0 to 60% DCM in *n*-Hexane). 1-nitro-4-nitrosobenzene (**7c**) was obtained as a yellow solid in 58% yield (0.732 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.53–8.50 (m, 2H, *CH*), 8.07–8.04 (m, 2H, *CH*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 162.6 (1 C, C^4-NO), 150.6 (1 C, C^1-NO_2), 125.6 (2 C, *CH*), 121.5 (2 C, *CH*). IR (ATR, $\tilde{\nu}$) = 3108, 3076, 1616, 1524, 1482, 1417, 1348, 1285, 1107 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 194, 282 nm. EI (*m/z*, 70 eV, 70 °C): 152 (100) $[M]^+$, 136 (1) $[M-O]^+$, 122 (45) $[M-NO]^+$, 106 (7) $[M-NO_2]^+$, 76 (84) $[M-NO-NO_2]^+$. HRMS–EI *(m/z)*: $[M]^+$ Calcd for $C_6H_4N_2O_3$, 152.0222; found, 152.0216. EA ($C_6H_4N_2O_3$): Calcd C 47.38; H 2.65; N 18.42. Found C 47.45; H 2.57; N 18.31.

Saponification procedure (A): Saponification of azobenzene-biphenyldicarboxylates (**5**) was done under the same reaction conditions and procedure: the azobenzene-biphenyldicarboxylate (**5a-s**) were dissolved in THF and added to an aqueous solution of potassium hydroxide. That biphasic solution was refluxed until no more starting material could be detected on TLC. The organic solvent was removed under reduced pressure and the aqueous phase acidified with 1 N HCl to pH 2. The precipitate was filtered off and washed with 1 N HCl. The product were then dried in a vacuum-oven at 40 °C for 3 h to yield the dicarboxylic acid linkers (**8a-s**).

2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8a): Dimethyl 2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5a**) (1.000 g, 2.67 mmol, 1 equiv.) was dissolved (suspended) in THF (30 mL). An aqueous solution of potassium hydroxide (1.499 g, 26.71 mmol, 10 equiv./30 mL) was added and the reaction mixture was stirred at 75 °C for 18 h. The THF was evaporated under reduced pressure, then 1 M HCl aqueous solution was slowly added until pH 1. The solid obtained was filtered off, washed with water and a small amount of methanol, and dried in the vacuum-oven for 3 h at 40 °C. 2-(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8a**) was obtained as a red-orange solid in 98% yield (0.909 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ = 13.21 (b-s, 2H, CO_2H), 8.27 (d, 1H, *J* = 1.5 Hz, *CH*), 8.20 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz, *CH*), 8.06–8.04 (m, 2H, *CH*), 7.83 (d, 1H, *J* = 8.0 Hz, *CH*), 7.79–7.77 (m, 2H, *CH*), 7.66–7.64 (m, 2H, *CH*), 7.60–7.58 (m, 3H, *CH*). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ = 167.1 (1 C, CO_2H), 166.6 (1 C, CO_2H), 152.1 (1 C, *Cq*-N=N), 148.6 (1 C, *Cq*-N=N), 143.3 (1 C, *Cq*), 141.6 (1 C, *Cq*), 131.9 (*CH*), 131.5 (*CH*), 131.4 (*CH*), 131.3 (1 C, *Cq*), 130.9 (2 C, *CH*), 130.2 (1 C, *Cq*), 129.6 (2 C, *CH*), 128.8 (2 C, *CH*), 123.0 (2 C, *CH*), 116.6 (1 C, *CH*). IR (ATR, $\tilde{\nu}$) = 1679, 1603, 1553, 1421, 1291, 1238, 1189, 1127, 1004 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 275, 320 nm. EI (*m/z*, 70 eV, 220 °C): 346 (15) $[M]^+$, 301 (8) $[M-CO_2H]^+$, 300 (14) $[M-H-CO_2H]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{20}H_{14}N_2O_4$, 346.0954; found, 346.0952. EA ($C_{20}H_{14}N_2O_4$): Calcd C 69.36; H 4.07; N 8.09. Found C 65.38; H 3.93; N 7.37.

2-((2-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8b): An aqueous solution of potassium hydroxide (164 mg, 2.92 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((2-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5b**) (118 mg, 0.292 mmol, 1.00 equiv.) in THF (8 mL), following the general procedure A. 2-((2-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8b**) was obtained as an orange solid in 89% yield (98 mg). m.p.: 332.5–339.5 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.24 (b-s, 2H, CO_2H), 8.18 (s, 1H), 8.17 (d, 1H, *J* = 8.1 Hz, CH), 8.05–8.03 (m, 2H, CH), 7.80 (d, 1H, *J* = 7.8 Hz, CH), 7.65–7.63 (m, 2H, CH), 7.56–7.52 (m, 1H, CH), 7.31 (d, 1H, *J* = 8.3 Hz, CH), 7.25 (d, 1H, *J* = 7.8 Hz, CH), 6.99 (t, 1H, *J* = 7.6 Hz, CH), 4.00 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.6 (CO_2H), 157.2 (Cq), 149.2 (Cq), 143.1 (Cq), 141.8 (Cq), 141.5 (Cq), 133.7 (CH), 131.4 (CH), 131.3 (Cq), 131.1 (Cq), 130.8 (2 C, CH), 130.1 (CH), 128.8 (2 C, CH), 120.6 (CH), 116.9 (CH), 116.5 (CH), 113.6 (CH), 56.1 (OCH_3). IR (ATR, $\tilde{\nu}$) = 2817, 2525, 1920, 1677, 1592, 1485, 1416, 1279, 1243, 1185, 1157, 1125, 1043, 1022, 1004, 911, 866, 837, 758, 738, 698, 672, 652, 538, 479, 431 cm^{-1}. UV/Vis (DMSO), λ_{max} = 267, 280, 370 nm. APCI (*m/z*): 377 (100) $[M+H]^+$.

2-((4-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8c): An aqueous solution of potassium hydroxide (258 mg, 4.60 mmol, 10 equiv./4 mL) was added to a solution of dimethyl 2-((4-methoxy-phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5c**) (186 mg, 0.460 mmol, 1.00 equiv.) in THF (13 mL), following the general procedure A. 2-((4-methoxyphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8c**) was obtained as a brown-yellow solid in 96% yield (166 mg). m.p.: 339.3–342.8 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.22 (b-s, 2H, CO_2H), 8.25 (s, 1H, CH), 8.14 (d, 1H, J = 8.1 Hz, CH), 8.03–8.05 (m, 2H, CH), 7.81–7.75 (m, 3H, CH), 7.64–7.62 (m, 2H, CH), 7.14–7.12 (m, 2H, CH), 3.85 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.6 (CO_2H), 162.4 (Cq), 148.7 (Cq), 146.5 (Cq), 142.8 (Cq), 141.9 (Cq), 131.3 (CH), 131.3 (Cq), 130.8 (3 C, CH), 130.1 (Cq), 128.8 (2 C, CH), 125.0 (2 C, CH), 116.6 (CH), 114.8 (2 C, CH), 55.7 (OCH_3). IR (ATR, $\tilde{\nu}$) = 2834, 2542, 1681, 1600, 1580, 1501, 1418, 1292, 1255, 1182, 1138, 1027, 1004, 918, 870, 829, 758, 741, 698, 670, 602, 535, 500, 469 cm^{-1}. UV/Vis (MeOH), λ_{max} = 193, 248, 283, 356 nm. APCI (*m/z*): 377 (100) $[M+H]^+$.

2-((3,5-dimethylphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8d): An aqueous solution of potassium hydroxide (90 mg, 1.62 mmol, 10 equiv./2 mL) was added to a solution of dimethyl 2-((3,5-dimethylphenyl)diazenyl)-[1,1′- biphenyl]-4,4′-dicarboxylate (**5d**) (65 mg, 0.162 mmol, 1.00 equiv.) in THF (5 mL), following the general procedure A. 2-((3,5-dimethylphenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8d**) was obtained as a brown-yellow solid in 86% yield (52 mg). m.p.: 337.4–339.2 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.20 (b-s, 2H, CO_2H), 8.21 (d, 1H, J = 1.8 Hz, CH), 8.17 (dd, 1H, J = 8.0 Hz, J = 1.8 Hz, CH), 8.05–8.03 (m, 2H, CH), 7.81 (d, 1H, J = 8.0 Hz, CH), 7.64–7.62 (m, 2H, CH), 7.38 (s, 2H, CH), 7.20 (s, 1H, CH), 2.33 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.6 (CO_2H), 152.4 (Cq), 148.8 (Cq), 143.0 (Cq), 141.6 (Cq), 138.8 (Cq, 2 C), 133.3 (CH), 131.4 (CH), 131.3 (Cq), 131.3 (CH), 130.9 (2 C, CH), 130.2 (Cq), 128.8 (2 C, CH), 120.8 (2 C, CH), 116.7 (CH), 20.8 (2 C, CH_3). IR (ATR, $\tilde{\nu}$) = 2860, 2658, 2529, 1678, 1602, 1552, 1491, 1418, 1282, 1236, 1184, 1120, 1005, 909, 852, 839, 801, 781, 759, 739, 700, 681, 661, 611, 537, 476, 430 cm^{-1}. UV/Vis (MeOH), λ_{max} = 195, 244, 277, 327, 440 nm. FAB (Matrix: 3-NBA), *m/z* (%): 375 (100) $[M+H]^+$. HRMS ($C_{22}H_{19}N_2O_4$): Calcd. 375.1339; Found. 375.1338.

2-((2-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8e): An aqueous solution of potassium hydroxide (55 mg, 0.98 mmol, 10 equiv./1 mL) was added to a solution of dimethyl 2-((2-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5e**) (49 mg, 98 %mol, 1.00 equiv.) in THF (3 mL), following the general procedure A. 2-((2-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8e**) was obtained as a red solid in 65% yield (30 mg). m.p. 349.9–360.5 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.24 (b-s, 2H, CO_2H), 8.36 (s, 1H, CH), 8.23 (d, 1H, J = 8.1 Hz, CH), 8.12 (d, 1H, J = 7.8 Hz, CH), 8.07–8.05 (m, 2H, CH), 7.84 (d, 1H, J = 8.1 Hz, CH), 7.68–7.66 (m, 2H, CH), 7.54–7.47 (m, 1H, CH), 7.30 (t, 1H, J = 7.6 Hz, CH), 7.26 (d, J = 7.8 Hz, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.5 (CO_2H), 151.0 (Cq), 148.4 (Cq), 143.8 (Cq), 141.5 (Cq), 139.9 (Cq), 133.3 (Cq), 132.0 (CH), 131.6 (CH), 131.5 (Cq), 131.0 (2 C, CH), 130.3 (Cq), 129.4 (CH), 128.8 (2 C, CH), 117.4 (CH), 117.2 (CH), 103.1 (Cq). IR (ATR, $\tilde{\nu}$) = 2811, 2529, 1679, 1601, 1570, 1454, 1415, 1282, 1125, 1018, 1003, 915, 865, 840, 758, 737, 698, 682, 658, 609, 537, 477, 440, 415 cm^{-1}. UV/Vis (MeOH), λ_{max} = 195, 256, 323, 469 nm. FAB (Matrix: 3-NBA), *m/z* (%): 473 (90) $[M+H]^+$, 462 (100). HRMS ($C_{20}H_{14}O_4N_2{}^{127}I$) Calc.: 472.9993; Found: 472.9995.

2-((3-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8f): An aqueous solution of potassium hydroxide (184 mg, 3.28 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((3-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5f**) (164 mg, 0.328 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((3-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8f**) was obtained as a red solid in 99% yield (154 mg). m.p.: 341.3–344.6 °C (decomposition). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ = 13.25 (b-s, 2H, CO_2H), 8.25 (s, 1H, CH), 8.20 (d, 1H, J = 8.1 Hz, CH), 8.08–8.02 (m, 3H, CH), 7.91 (d, 1H, J = 7.7 Hz, CH), 7.85–7.79 (m, 2H, CH), 7.65–7.63 (m, 2H, CH), 7.38 (t, 1H, J = 7.8 Hz, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.5 (CO_2H), 152.9 (Cq), 148.3 (Cq), 143.5 (Cq), 141.4 (Cq), 140.0 (CH), 131.9 (CH), 131.5 (CH), 131.4 (CH), 131.3 (Cq), 130.9 (2 C, CH), 130.8 (CH), 130.3 (Cq), 128.7 (2 C, CH), 123.1 (CH), 116.6 (CH), 95.5 (Cq). IR (ATR, $\tilde{\nu}$) = 2811, 2541, 1679, 1601, 1568, 1457, 1415, 1284, 1186, 1125, 1004, 992, 915, 866, 840, 781, 759, 738, 702, 675, 661, 606, 538, 476, 431 cm^{-1}. UV/Vis (MeOH), λ_{max} = 196, 272, 323 nm. FAB (Matrix: 3-NBA), *m/z* (%): 473 (0) $[M+H]^+$. HRMS ($C_{20}H_{14}{}^{127}IN_2O_4$): Calc.: 472.9993; Found: 473.0005.

2-((4-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8g): An aqueous solution of potassium hydroxide (224 mg, 4.00 mmol, 10 equiv./4 mL) was added to a solution of dimethyl 2-((4-iodophenyl)diazenyl)-[1,1′-biphenyl]- 4,4′-dicarboxylate (**5g**) (200 mg, 0.400 mmol, 1.00 equiv.) in THF (11 mL), following the general procedure A. 2-((4-iodophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8g**) was obtained as a red solid in 99% yield (187 mg). m.p.: 345.4–348.1 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.17 (b-s, 2H, CO_2H), 8.26 (d, 1H, J = 1.6 Hz, CH), 8.20 (dd, 1H, J = 8.0 Hz, J = 1.7 Hz, CH), 8.06–8.04 (m, 2H, CH), 7.98–7.96 (m, 2H, CH), 7.82 (d, 1H, J = 8.0 Hz, CH), 7.64–7.62 (m, 2H, CH), 7.55–7.53 (m, 2H, CH). This spectrum contains around 20% impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.5 (CO_2H), 151.4 (Cq), 148.6 (Cq), 143.4 (Cq), 141.5 (Cq), 138.6 (2 C, CH), 131.7 (CH), 131.5 (CH), 131.4 (Cq), 130.9 (2 C, CH), 130.2 (Cq), 128.8 (2 C, CH), 124.7 (2 C, CH), 116.6 (CH), 99.7 (Cq). This spectrum contains around 20% impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$) = 2527, 1679, 1602, 1577, 1474, 1418, 1286, 1126, 1052, 1003, 917, 871, 823, 758, 738, 684, 658, 602, 536, 486, 410 cm^{-1}. UV/Vis (MeOH), λ_{max} = 196, 273, 339, 653 nm. APCI (*m/z*): 473 (100) $[M+H]^+$, 346 (13), 243 (13).

2-((2-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8h): An aqueous solution of potassium hydroxide (61 mg, 1.08 mmol, 10 equiv./1 mL) was added to a solution of dimethyl 2-((2-bromophenyl)diazenyl)-[1,1′-biphenyl]- 4,4′-dicarboxylate (**5h**) (49 mg, 108 %mol, 1.00 equiv.) in THF (3 mL), following the general procedure A. 2-((2-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8h**) was obtained as a red solid in 87% yield (40 mg). 1H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.25 (b-s, 2H, CO_2H), 8.30 (s, 1H, CH), 8.23 (d, 1H, J = 8.1 Hz, CH), 8.07–8.05 (m, 2H, CH), 7.93–7.89 (m, 1H, CH), 7.85 (d, 1H, J = 8.1 Hz, CH), 7.68–7.66 (m, 2H, CH), 7.51–7.48 (m, 2H, CH), 7.34–7.31 (m, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.1 (CO_2H), 166.5 (CO_2H), 149.0 (Cq), 148.7 (Cq), 143.8 (Cq), 141.5 (Cq), 133.9 (CH), 133.3 (CH), 132.0 (CH), 131.6 (CH), 131.4 (Cq), 131.0 (2 C, CH), 130.3 (Cq), 128.9 (2 C, CH), 128.8 (CH), 125.2 (Cq), 117.9 (CH), 117.0 (CH). IR (ATR, $\tilde{\nu}$) = 1686, 1603, 1419, 1288, 1127, 1043, 1005, 924, 841, 761, 739, 691, 549 cm^{-1}. APCI (*m/z*): 425/427 (1/1) $[M+H]^+$, 365 (100).

2-((3-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8i): An aqueous solution of potassium hydroxide (196 mg, 3.49 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((3-bromophenyl)diazenyl)-[1,1′-biphenyl]- 4,4′-dicarboxylate (**5i**) (158 mg, 0.349 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((3-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8i**) was obtained as a red solid in 83% yield (123 mg). m.p.: 348.0–349.3 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ = 13.23 (b-s, 2H, CO_2H), 8.26 (s, 1H, CH), 8.21 (d, 1H, J = 8.1 Hz, CH), 8.06–8.04 (d, 2H, J = 8.1 Hz, CH), 7.86–7.79 (m,

3H, CH), 7.76 (d, 1H, J=7.9 Hz, CH), 7.64–7.63 (d, 2H, J=8.1 Hz, CH), 7.58–7.53 (m, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ= 167.1 (CO_2H), 166.5 (CO_2H), 153.1 (Cq), 148.3 (Cq), 143.6 (Cq), 141.5 (Cq), 134.3 (Cq), 132.0 (CH), 131.6 (CH), 131.5 (CH), 131.4 (CH), 130.9 (2 C, CH), 130.3 (Cq), 128.8 (2 C, CH), 124.9 (CH), 122.8 (CH), 122.5 (Cq), 116.6 (CH). IR (ATR, $\tilde{\nu}$)=2542, 1680, 1601, 1417, 1285, 1187, 1125, 1005, 868, 840, 780, 758, 728, 697, 665, 539, 473 cm^{-1}. UV/Vis (MeOH), λ_{max}=195, 270, 318, 447 nm. APCI (*m/z*): 425/427 (4/4) [M+H]$^+$, 365 (100).

2-((4-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8j): An aqueous solution of potassium hydroxide (161 mg, 2.87 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((4-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5j**) (130 mg, 0.287 mmol, 1.00 equiv.) in THF (8 mL), following the general procedure A. 2-((4-bromophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8j**) was obtained as a dark red solid in 99% yield (122 mg). m.p.: 332.3–335.8 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.26 (b-s, 2H, CO_2H), 8.26 (s, 1H, CH), 8.19 (d, 1H, J=8.0 Hz, CH), 8.05–8.03 (m, 2H, CH), 7.83 (d, 1H, J=8.1 Hz, CH), 7.80–7.77 (m, 2H, CH), 7.70–7.68 (m, 2H, CH), 7.63–7.61 (m, 2H, CH). This spectrum contains impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 150.9 (Cq), 148.5 (Cq), 143.4 (Cq), 141.5 (Cq), 132.7 (2 C, CH), 131.8 (CH), 131.5 (CH), 131.4 (Cq), 130.9 (2 C, CH), 130.3 (Cq), 128.9 (2 C, CH), 125.5 (Cq), 124.8 (2 C, CH), 116.6 (CH). This spectrum contains impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$)=2535, 1680, 1602, 1571, 1477, 1418, 1286, 1126, 1067, 1005, 916, 871, 826, 758, 739, 688, 659, 602, 536, 487, 417 cm^{-1}. UV/Vis (MeOH), λ_{max}=164, 276, 331 nm. APCI (*m/z*): 425/427 (98/100) [M+H]$^+$, 346 (22), 243 (13).

2-((2-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8k): An aqueous solution of potassium hydroxide (78 mg, 1.39 mmol, 10 equiv./1 mL) was added to a solution of dimethyl 2-((2-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5k**) (57 mg, 0.139 mmol, 1.00 equiv.) in THF (4 mL), following the general procedure A. 2-((2-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8k**) was obtained as a deep red solid in 59% yield (31 mg). m.p.: 360.5–368.7 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.25 (b-s, 2H, CO_2H), 8.28 (d, 1H, J=1.6 Hz, CH), 8.22 (dd, 1H, J=8.0 Hz, J=1.7 Hz, CH), 8.06–8.04 (m, 2H, CH), 7.84 (d, 1H, J=8.0 Hz, CH), 7.74 (dd, 1H, J=8.0 Hz, J=1.1 Hz, CH), 7.67–7.65 (m, 2H, CH), 7.57 (td, 1H, J=7.7 Hz, J=1.6 Hz, CH), 7.42–7.49 (m, 1H, CH), 7.35 (dd, 1H, J=8.1 Hz, J=1.5 Hz, CH). This spectrum contains around 5% impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 148.8 (Cq), 147.9 (Cq), 143.8 (Cq), 141.5 (Cq), 134.5 (Cq), 133.2 (CH), 132.1 (CH), 131.6 (CH), 131.4 (Cq), 131.0 (2 C, CH), 130.9 (CH), 130.3 (Cq), 128.9 (2 C, CH), 128.2 (CH), 117.7 (CH), 116.9 (CH). This spectrum contains around 5% impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$)=2835, 2540, 1678, 1601, 1462, 1419, 1286, 1188, 1122, 1057, 1004, 915, 867, 840, 782, 759, 738, 700, 665, 609, 539, 483, 450, 418 cm^{-1}. UV/Vis (MeOH), λ_{max}=269, 323 nm. APCI (*m/z*): 381/383 (100/36) [M+H]$^+$, 255 (12), 254 (13).

2-((3-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8l): An aqueous solution of potassium hydroxide (187 mg, 3.33 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((3-chlorophenyl)diazenyl)-[1,1′-biphenyl]- 4,4′-dicarboxylate (**5l**) (136 mg, 0.333 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((3-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8l**) was obtained as a deep red solid in 98% yield (124 mg). m.p.: 371.1–373.5 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.23 (b-s, 2H, CO_2H), 8.28 (d, 1H, J=1.7 Hz, CH), 8.22 (dd, 1H, J=8.0 Hz, J=1.8 Hz, CH), 8.05–8.03 (m, 2H, CH), 7.85 (d, 1H, J=8.0 Hz, CH), 7.80–7.76 (m, 1H, CH), 7.74 (s, 1H, CH), 7.68–7.62 (m, 4H, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 153.0 (Cq), 148.4 (Cq), 143.7 (Cq), 141.5 (Cq), 134.2 (Cq), 132.0 (CH), 131.5 (CH), 131.4 (2 C, CH), 131.4 (Cq), 131.0 (2 C, CH), 130.3 (Cq), 128.8 (2 C, CH), 122.3 (CH), 122.0 (CH), 116.6 (CH). IR (ATR, $\tilde{\nu}$)=2536, 1677, 1601, 1418, 1286, 1188, 1125, 1067, 1005, 869, 839, 784, 758, 737, 699, 671, 607, 539, 475, 399 cm^{-1}. UV/Vis (MeOH), λ_{max}=196, 264, 318 nm. APCI (*m/z*): 381/383 (100/35) [M+H]$^+$, 255 (14), 254 (13).

2-((4-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8m): An aqueous solution of potassium hydroxide (198 mg, 3.52 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((4-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5m**) (144 mg, 0.352 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((4-chlorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8m**) was obtained as a dark red solid in 99% yield (132 mg). m.p.: 367.4–369.9 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.27 (b-s, 2H, CO_2H), 8.28 (d, 1H, J=1.7 Hz, CH), 8.21 (dd, 1H, J=8.0 Hz, J=1.8 Hz, CH), 8.07–8.05 (m, 2H, CH), 7.83 (d, 1H, J=8.0 Hz, CH), 7.81–7.77 (m, 2H, CH), 7.70–7.62 (m, 4H, CH). This spectrum contains around 20% impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 150.6 (Cq), 148.5 (Cq), 143.5 (Cq), 141.5 (Cq), 136.5 (Cq), 131.7 (CH), 131.5 (CH), 131.4 (Cq), 130.9 (2 C, CH), 130.2 (Cq), 129.8 (2 C, CH), 128.9 (2 C, CH), 124.6 (2 C, CH), 116.6 (CH). This spectrum contains around 20% impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$)=2528, 1680, 1602, 1573, 1480, 1419, 1286, 1126, 1088, 1006, 917, 870, 830, 780, 758, 740, 697, 662, 601, 537, 434, 338 cm^{-1}. UV/Vis (MeOH), λ_{max}=195, 277, 329, 447 nm. APCI (*m/z*): 381/383 (100/47) [M+H]$^+$.

2-((2-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8n): An aqueous solution of potassium hydroxide (205 mg, 3.64 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((2-fluorophenyl)diazenyl)-[1,1′-biphenyl]- 4,4′-dicarboxylate (**5n**) (143 mg, 0.162 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((2-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8n**) was obtained as a deep red solid in 98% yield (130 mg). m.p.: 374.5–375.3 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.28 (b-s, 2H, CO_2H), 8.26 (d, 1H, J=1.7 Hz, CH), 8.22 (dd, 1H, J=8.0 Hz, J=1.7 Hz, CH), 8.06–8.04 (m, 2H, CH), 7.85 (d, 1H, J=8.0 Hz, CH), 7.70–7.60 (m, 1H, CH), 7.57–7.50 (m, 3H, CH), 7.40 (td, 1H, J=7.9 Hz, J=1.7 Hz, CH), 7.33–7.29 (m, 1H, CH). ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ=-124.18 (CF). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 159.7 (d, J=256.8 Hz, Cq), 148.8 (Cq), 143.7 (Cq), 141.5 (Cq), 139.9 (d, J=6.6 Hz, Cq), 134.1 (d, J=8.4 Hz, CH), 131.9 (CH), 131.6 (CH), 131.4 (Cq), 130.9 (2 C, CH), 130.3 (Cq), 128.8 (2 C, CH), 125.2 (d, J=3.6 Hz, CH), 117.6 (CH), 117.5 (d, J=19.7 Hz, CH), 116.7 (CH). IR (ATR, $\tilde{\nu}$)=2527, 1677, 1601, 1482, 1419, 1288, 1223, 1152, 1127, 1004, 917, 869, 839, 758, 740, 698, 670, 610, 544, 497, 465 cm^{-1}. UV/Vis (MeOH), λ_{max}=196, 273, 326, 452 nm. APCI (*m/z*): 365 (100) [M+H]$^+$.

2-((4-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8o): An aqueous solution of potassium hydroxide (200 mg, 3.57 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((4-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5o**) (140 mg, 0.357 mmol, 1.00 equiv.) in 10.0 mL THF, following the general procedure A. 2-((4-fluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8o**) was obtained as a dark yellow solid in 99% yield (130 mg). m.p.: 358.7–363.4 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.22 (b-s, 2H, CO_2H), 8.26 (d, 1H, J=1.7 Hz, CH), 8.18 (dd, 1H, J=8.0 Hz, J=1.8 Hz, CH), 8.04 (d, 2H, J=8.5 Hz, CH), 7.85 (d, 1H, J=5.3 Hz, CH), 7.83 (d, 1H, J=3.5 Hz, CH),

7.81 (d, 1H, J=6.3 Hz, CH), 7.63 (d, 2H, J=8.5 Hz, CH), 7.42 (t, 2H, J=8.8 Hz, CH). ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ=-108.20 (CF). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 164.0 (d, J=251 Hz, Cq), 148.9 (d, J=2.9 Hz, Cq), 148.5 (Cq), 143.3 (Cq), 141.6 (Cq), 131.5 (CH), 131.4 (CH), 131.3 (CH), 130.8 (2 C, CH), 130.2 (Cq), 128.8 (2 C, CH), 125.3 (d, 2 C, J=9.3 Hz, CH), 116.7 (Cq), 116.6 (d, 2 C, J=23.2 Hz, CH). IR (ATR, $\tilde{\nu}$)=2528, 1682, 1592, 1499, 1419, 1287, 1231, 1128, 1004, 917, 871, 836, 758, 741, 698, 667, 601, 538, 496, 466, 412 cm^{-1}. UV/Vis (MeOH), λ_{max}=169, 272, 321, 446 nm. APCI (*m/z*): 365 (100) $[M+H]^+$.

2-((2-(trifluoromethyl)phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8p): An aqueous solution of potassium hydroxide (185 mg, 3.30 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((2-(trifluoromethyl)phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5p**) (146 mg, 0.330 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((2-(trifluoromethyl)phenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8p**) was obtained as a bright orange solid in 99% yield (135 mg). m.p.: 341.9–345.1 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.27 (b-s, 2H, CO_2H), 8.31 (d, 1H, J=1.6 Hz, CH), 8.22 (dd, 1H, J=8.1 Hz, J=1.7 Hz, CH), 8.07–8.02 (m, 4H, CH), 7.93 (d, 1H, J=8.0 Hz, CH), 7.88 – 7.79 (m, 2H, CH), 7.67–7.65 (m, 2H, CH). ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ=−61.44 (CF_3). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.5 (CO_2H), 152.1 (Cq), 148.3 (Cq), 143.8 (Cq), 141.4 (Cq), 132.1 (CH), 131.5 (Cq), 131.4 (CH), 131.0 (CH), 131.0 (2 C, CH), 130.3 (Cq), 130.3 (d, J=32.3 Hz, Cq), 128.7 (2 C, CH), 128.0 (d, J=3.6 Hz, CH), 126.6 (CH), 123.7 (d, J=272.6 Hz, Cq), 119.6 (d, J=4.1 Hz, CH), 116.6 (CH). IR (ATR, $\tilde{\nu}$)=2862, 2541, 1683, 1602, 1573, 1554, 1420, 1326, 1285, 1169, 1119, 1061, 1004, 906, 868, 841, 801, 759, 689, 661, 608, 534, 479, 394 cm^{-1}. UV/Vis (MeOH), λ_{max}=195, 271, 319, 445 nm. FAB (Matrix: 3-NBA), *m/z* (%): 415 (100) $[M+H]^+$. HRMS ($C_{21}H_{14}O_4N_2F_3$) Calc. 415.0900; Found. 415.0902.

2-((2-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8q): An aqueous solution of potassium hydroxide (183 mg, 3.27 mmol, 10 equiv./3 mL) was added to a solution of dimethyl 2-((2-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5q**) (235 mg, 0.327 mmol, 1.00 equiv.) in THF (10 mL), following the general procedure A. 2-((2-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8q**) was obtained as a deep red solid in 99% yield (127 mg). m.p.: 337.4–339.2 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ=13.29 (b-s, 2H, CO_2H), 8.24 (dd, 1H, J=8.0 Hz, J=1.7 Hz, CH), 8.17 (d, 1H, J=1.7 Hz, CH), 8.15 (dd, 1H, J=8.0 Hz, J=1.3 Hz, CH), 8.07–8.05 (m, 2H, CH), 7.89–7.82 (m, 2H, CH), 7.77 (td, 1H, J=7.8 Hz, J=1.4 Hz, CH), 7.67–7.65 (m, 2H, CH), 7.44 (dd, 1H, J=7.9 Hz, J=1.3 Hz, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ=167.1 (CO_2H), 166.4 (CO_2H), 148.7 (Cq), 147.1 (Cq), 144.4 (Cq), 144.0 (Cq), 141.2 (Cq), 134.0 (CH), 132.5 (CH), 132.0 (CH), 131.7 (CH), 131.5 (Cq), 130.9 (2 C, CH), 130.4 (Cq), 128.9 (2 C, CH), 124.4 (CH), 118.4 (CH), 116.9 (CH). IR (ATR, $\tilde{\nu}$)=2811, 2530, 1680, 1600, 1524, 1416, 1340, 1283, 1122, 1003, 918, 866, 840, 805, 778, 759, 730, 690, 662, 610, 533, 482, 415 cm^{-1}. UV/Vis (MeOH), λ_{max}=194, 255, 314 nm. APCI (*m/z*): 392 (12) $[M+H]^+$, 374 (100), 328 (20), 271 (10), 254 (82).

2-((4-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8r): Dimethyl 2-((4-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5r**) (250 mg, 596 %mol, 1.00 equiv.) was dissolved (suspended) in THF (10 mL). An aqueous solution of potassium hydroxide (334 mg, 6.0 mmol, 10.0 equiv./10 mL) was added and the reaction mixture was stirred at 75 °C for 24 h. The THF was evaporated under reduced pressure, then 1 M HCl aqueous solution was slowly added until pH 1. The solid obtained was filtrated and washed with water and a small amount of methanol. The solid was dried in the vacuum-oven for 3 h at 40 °C. 2-((4-nitrophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8r**) was obtained as a red-orange solid in 96% yield (0.223 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ=13.14 (b-s, 2H, CO_2H), 8.42–8.40 (m, 2H, CH), 8.29 (d, 1H, J=1.5 Hz, CH), 8.24 (dd, 1H, J=8.0 Hz, 1.5 Hz, CH), 8.06–8.04 (m, 2H, CH), 7.96–7.94 (m, 2H, CH), 7.86 (d, 1H, J=8.0 Hz, CH), 7.66–7.64 (m, 2H, CH). This spectrum contains around 7% impurities due to inseparable side-product. ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ=167.1 (1 C, CO_2H), 166.4 (1 C, CO_2H), 155.1 (1 C, Cq), 148.7 (1 C, Cq), 148.6 (1 C, Cq), 144.1 (1 C, Cq), 141.3 (1 C, Cq), 132.5 (1 C, CH), 131.7 (1 C, CH), 131.4 (1 C, Cq), 131.0 (2 C, CH), 130.4 (1 C, Cq), 128.9 (2 C, CH), 125.2 (2 C, CH), 123.9 (2 C, CH), 116.6 (1 C, CH). This spectrum contains around 7% impurities due to inseparable side-product. IR (ATR, $\tilde{\nu}$)=1680, 1602, 1524, 1419, 1344, 1285, 1104 cm^{-1}. APCI (*m/z*)=392 (100) $[M+H]^+$. HRMS–APCI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{14}N_3O_6$, 392.0883; found, 392.0868. EA ($C_{20}H_{13}N_3O_6$): Calcd C 61.38; H 3.35; N 10.74. Found C 59.33; H 3.45; N 10.36.

2-((3,4,5-trifluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (8s): Dimethyl 2-((3,4,5-trifluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**5s**) (0.215 g, 0.50 mmol, 1 equiv.) was dissolved in THF (20 mL). An aqueous solution of potassium hydroxide (0.169 g, 3.01 mmol, 6 eq/15 mL H_2O) was added and the reaction mixture was heated at 45 °C for 48 h. The THF was evaporated under reduced pressure, then HCl aqueous solution was added until pH 1. The suspension was filtrated, washed with water and dried in the vacuum-oven at 45 °C for 3 h. 2-((3,4,5-trifluorophenyl)diazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**8s**) was obtained as a red-orange solid in 99% yield (0.200 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ=13.23 (b-s, 2H, CO_2H), 8.24 (d, 1H, J=1.5 Hz, CH), 8.17 (dd, 1H, J=8.0 Hz, 1.5 Hz, CH), 8.05 (m, 2H, CH), 7.81 (d, 1H, J=8.0 Hz, CH), 7.63 (m, 2H, CH), 7.49 (m, 2H, CH). This spectrum contains around 10% impurities due to inseparable isomer and side-product. ^{19}F NMR (470 MHz, DMSO-d_6, ppm) δ=-132.87 (dd, 2F, J=21.2 Hz, 8.0 Hz, CF), −155.89 (tt, 1F, J=21.2 Hz, 6.6 Hz, CF). This spectrum shows signals at −126.84 and −130.89 ppm corresponding to the cis-isomer. ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ=167.1 (1 C, CO_2H), 166.4 (1 C, CO_2H), 151.5 (d, 2 C, CF), 147.9 (1 C, Cq), 143.9 (1 C, Cq), 141.3 (1 C, Cq), 137.5 (1 C, Cq), 132.4 (1 C, CH), 131.7 (1 C, CH), 131.0 (2 C, CH), 130.4 (1 C, Cq), 129.6 (1 C, Cq), 129.1 (1 C, Cq), 128.9 (2 C, CH), 116.6 (1 C, CH), 108.0–107.9 (m, 2 C, CH). IR (ATR, $\tilde{\nu}$)=2956, 1731, 1717, 1605, 1432, 1280, 1207, 1187, 1103 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max}=195, 273, 329 nm. EI (*m/z*, 70 eV, 220 °C): 400 (100) $[M]^+$, 398 (29) $[M-2H]^+$, 355 (47) $[M\text{-}CO_2H]^+$, 269 (27) $[M\text{-}C_6H_2F_3]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{11}F_3N_2O_4$, 400.0671; found, 400.0667. EA ($C_{20}H_{11}F_3N_2O_4$): Calcd C 60.01; H 2.77; N 7.00. Found C 62.56; H 4.91; N 4.95.

Dimethyl 2,2′-dinitro-[1,1′-biphenyl]-4,4′-dicarboxylate (9): Dimethyl [1,1′-biphenyl]-4,4′-dicarboxylate (**1**) (5.00 g, 18.5 mmol, 1.00 equiv.) was dissolved in sulfuric acid (55 mL) under vigorous stirring. The mixture was cooled down to 0 °C and a solution of potassium nitrate (3.74 g, 37.0 mmol, 2.00 equiv.) in sulfuric acid (15 mL) was slowly added to the mixture. The reaction was stirred at 0 °C for 1 h, then at room temperature for 30 minutes. The mixture was poured into 200 mL of crushed ice, and extracted with ethyl acetate. The organic phases were collected, washed with saturated $NaHCO_3$ solution, then with brine, dried over magnesium sulfate and concentrated under reduced pressure. The residue was recrystallized in isopropanol/*n*-hexane. Dimethyl 2,2′-dinitro-[1,1′-biphenyl]-4,4′-dicarboxylate (**9**) was obtained as a pale yellow solid in 85% yield (5.665 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ=8.90 (d, 2H, J=1.5 Hz, CH), 8.37 (dd, 2H, J=8.0 Hz, 1.5 Hz, CH), 7.40 (d, 2H, J=8.0 Hz, CH), 4.02 (s, 6H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ=164.7 (CO_2CH_3), 147.0 (2 C, Cq), 137.8 (2 C, Cq), 134.4 (2 C, CH), 132.0 (2 C, Cq), 131.0 (2 C, CH), 126.2 (2 C, CH), 53.1 (2 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$)=3091, 2955, 1721, 1617, 1525, 1482, 1342, 1309, 1285, 1114 cm^{-1}. EI (*m/z*, 70 eV, 130 °C): 360 (2) $[M]^+$, 329 (13) $[M\text{–}OCH_3]^+$,

314 (100) $[M–NO_2]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{16}H_{12}N_2O_8$, 360.0594; found, 360.0593. EA ($C_{16}H_{12}N_2O_8$): Calcd C 53.34; H 3.36; N 7.78. Found C 51.19; H 3.26; N 7.50.

Dimethyl 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylate (10): Dimethyl 2,2′-dinitro-[1,1′-biphenyl]-4,4′-dicarboxylate (**9**) (2.00 g, 5.66 mmol, 1.00 equiv.) was dissolved in acetic acid (50 mL) at 40 °C, then iron powder (3.41 g, 61.06 mmol, 11.0 equiv.) was added and the reaction was stirred at 60 °C overnight. The reaction mixture was filtrated, the filtrate was evaporated and the residue was treated with $NaHCO_3$ solution and extracted several times with dichloromethane. The organic layers were combined, washed with water and brine, dried over magnesium sulfate and concentrated under reduced pressure. Dimethyl 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylate (**10**) was obtained as a yellow solid in 89% yield (1.484 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) $\delta = 7.49$ (dd, 2H, $J =$ 7.5 Hz, $J = 1.5$ Hz, *CH*), 7.47 (d, 2H, $J = 1.5$ Hz, *CH*), 7.18 (d, 2H, $J =$ 7.5 Hz, *CH*), 3.92 (s, 6H, CO_2CH_3), 3.88 (b-s, 4H, $ArNH_2$). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) $\delta = 7.44$ (d, 2H, $J = 1.5$ Hz, *CH*), 7.23 (dd, 2H, $J = 8.0$ Hz, 1.5 Hz, *CH*), 7.08 (d, 2H, $J = 7.5$ Hz, *CH*), 5.02 (b-s, 4H, $ArNH_2$), 3.83 (s, 6H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) $\delta =$ 167.2 (2 C, CO_2CH_3), 144.1 (2 C, *Cq*), 131.1 (2 C, *Cq*), 131.0 (2 C, *CH*), 128.2 (2 C, *Cq*), 120.0 (2 C, *CH*), 116.7 (2 C, *CH*), 52.3 (2 C, CO_2CH_3). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) $\delta = 166.6$ (2 C, CO_2CH_3), 145.6 (2 C, *Cq*), 130.8 (2 C, *CH*), 129.7 (2 C, *Cq*), 127.6 (2 C, *Cq*), 117.2 (2 C, *CH*), 115.9 (2 C, *CH*), 52.0 (2 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3446, 3357, 2948, 1698, 1613, 1562, 1419, 1298, 1231, 1103 cm^{-1}. EI (*m/z*, 70 eV, 120 °C): 300 (100) $[M]^+$, 284 (4) $[M–NH_2]^+$, 269 (14) $[M–OCH_3]^+$, 241 (6) $[M–CO_2CH_3]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for, 300.1110; found, 300.1111. EA ($C_{16}H_{16}N_2O_4$): Calcd C 63.99; H 5.37; N 9.33. Found C 63.79; H 5.30; N 9.32.

Dimethyl 2,2′-bis(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (11): A solution of nitrosobenzene (**7a**) (0.750 g, 7.00 mmol, 4 equiv.) in acetic acid (5 mL) was added to a solution of dimethyl 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylate (**10**) (0.500 g, 1.67 mmol, 1 equiv.) in acetic acid (30 mL) and the reaction mixture was stirred at 50 °C for 48 h. The reaction mixture was cooled to room temperature and the suspension was filtered off; the filtrate was concentrated under reduced pressure and the residue was purified with column chromatography (50 to 100% DCM in *n*-hexane). Dimethyl 2,2′-bis(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**11**) was obtained as a red-orange solid in 16% yield (0.191 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) $\delta = 8.44$ (d, 2H, $J = 1.5$ Hz, *CH*), 8.24 (dd, 2H, $J = 8.0$ Hz, 1.5 Hz, *CH*), 7.70 (d, 2H, $J = 8.0$ Hz, *CH*), 7.49–7.47 (m, 4H, *CH*), 7.36–7.30 (m, 6H, *CH*), 4.01 (s, 6H, CO_2CH_3). This spectrum contains around 8% impurities due to isomerization under the conditions of the measurement. ^{13}C NMR (125 MHz, $CDCl_3$, ppm) $\delta = 166.8$ (2 C, CO_2CH_3), 152.5 (2 C, *Cq*), 150.6 (2 C, *Cq*), 142.3 (2 C, *Cq*), 131.9 (2 C, *CH*), 131.4 (2 C, *CH*), 131.1 (2 C, *Cq*), 130.7 (2 C, *CH*), 129.0 (4 C, *CH*), 123.3 (4 C, *CH*), 116.9 (2 C, *CH*), 52.6 (2 C, CO_2CH_3). This spectrum contains around 8% impurities due to isomerization under the conditions of the measurement. IR (ATR, $\tilde{\nu}$) = 2953, 1725, 1602, 1433, 1288, 1240, 1208, 1118, 1097 cm^{-1}. UV/Vis (CH_2Cl_2), $\lambda_{max} = 232$, 269, 317, 447 nm. EI (*m/z*, 70 eV, 170 °C): 478 (72) $[M]^+$, 447 (100) $[M–OCH_3]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{28}H_{22}N_4O_4$, 478.1641; found, 478.1635. EA ($C_{28}H_{22}N_4O_4$): Calcd C 70.28; H 4.63; N 11.71. Found C 70.13; H 4.64; N 11.56.

Dimethyl benzo[*c*]cinnoline-3,8-dicarboxylate (12): The product (**12**) was obtained as a side-product during the synthesis of (**11**). The reaction mixture was cooled to room temperature and the suspension was filtered off; the solid obtained was washed with a few milliliters of acetic acid and dried in the vacuum-oven at 40 °C overnight. Dimethyl benzo[*c*]cinnoline-3,8-dicarboxylate (**12**) was obtained as a slight green solid in 51% yield (0.254 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) $\delta = 9.46$ (s, 2H, *CH*), 8.67 (d, 2H, $J = 8.0$ Hz, *CH*), 8.57 (d, 2H, $J = 8.0$ Hz, *CH*), 4.08 (s, 6H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) $\delta = 166.0$ (2 C, CO_2CH_3), 145.2 (2 C, *Cq*), 133.7 (2 C, *CH*), 132.1 (2 C, *Cq*), 131.9 (2 C, *CH*), 123.3 (2 C, *Cq*), 122.6 (2 C, *CH*), 53.0 (2 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 3060, 1580, 1524, 1481, 1451, 1346, 1298, 1219, 1150, 1070 cm^{-1}. UV/Vis (MeOH), $\lambda_{max} = 230$, 319, 712 nm. EI (*m/z*, 70 eV, 140 °C): 296 (100) $[M]^+$, 265 (14) $[M–OCH_3]^+$, 237 (43) $[M–CO_2CH_3]^+$, 209 (21) $[M–N_2–CO_2CH_3]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{16}H_{12}N_2O_4$, 296.0797; found, 296.0791. EA ($C_{16}H_{12}N_2O_4$): Calcd C 64.86; H 4.08; N 9.46. Found C 64.24; H 3.98; N 9.35.

2,2′-bis(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (13): Dimethyl 2,2′-bis(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylate (**11**) (0.090 g, 0.19 mmol, 1 equiv.) was dissolved in THF (15 mL). An aqueous solution of potassium hydroxide (0.106 g, 1.88 mmol, 10 equiv./10 mL H_2O) was added and the reaction mixture was heated at 45 °C for 48 h. The THF was evaporated under reduced pressure, then HCl aqueous solution was added until pH 1. The suspension was filtrated, washed with water and dried in the vacuum-oven at 45 °C for 3 h. 2,2′-bis(phenyldiazenyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid (**13**) was obtained as a red-orange solid in 99% yield (0.085 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) $\delta = 13.43$ (b-s, 2H, CO_2H), 8.25 (s, 2H, *CH*), 8.24 (dd, 2H, $J = 8.0$ Hz, 1.5 Hz, *CH*), 7.90 (d, 2H, $J = 8.0$ Hz, *CH*), 7.43–7.39 (m, 10H, *CH*). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) $\delta = 166.7$ (2 C, CO_2H), 151.7 (2 C, *Cq*), 149.8 (2 C, *Cq*), 141.4 (2 C, *Cq*), 132.0 (2 C, *CH*), 131.9 (2 C, *Cq*), 131.7 (2 C, *CH*), 131.1 (2 C, *CH*), 129.2 (4 C, *CH*), 122.5 (4 C, *CH*), 115.6 (2 C, *CH*). EI (*m/z*, 70 eV, 210 °C): 345 (86) $[M-C_6H_5N_2]^+$. IR (ATR, $\tilde{\nu}$) = 2845, 1687, 1603, 1482, 1421, 1292, 1243, 1147, 1128, 1001 cm^{-1}. UV/Vis (MeOH), $\lambda_{max} = 230$, 319, 449 nm. FAB (*m/z*): 451 $[MH]^+$, 345 $[M-C_6H_5N_2]^+$. HRMS–FAB *(m/z)*: [M + H]+ calcd for $C_{18}H_{19}N_4O_4$, 451.1401; found, 451.1400. EA ($C_{26}H_{18}N_4O_4$): Calcd C 69.33; H 4.03; N 12.44. Found C 67.38; H 4.73; N 10.54.

Benzo[*c*]cinnoline-3,8-dicarboxylic acid (14): Dimethyl benzo[c] cinnoline-3,8-dicarboxylate (**12**) (0.149 g, 0.50 mmol, 1 equiv.) was dissolved in THF (35 mL). An aqueous solution of potassium hydroxide (0.282 g, 5.03 mmol, 10 equiv./20 mL H_2O) was added and the reaction mixture was heated at 45 °C for 48 h. The THF was evaporated under reduced pressure, then HCl aqueous solution was added until pH 1. The suspension was filtrated, washed with water and dried in the vacuum-oven at 45 °C for 3 h. Benzo[*c*] cinnoline-3,8-dicarboxylic acid (**14**) was obtained as a pale green solid in 95% yield (0.128 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) $\delta =$ 13.71 (b-s, 2H, CO_2H), 9.17 (d, 2H, $J = 1.5$ Hz, *CH*), 9.04 (d, 2H, $J =$ 8.5 Hz, *CH*), 8.50 (dd, 2H, $J = 8.5$ Hz, 1.5 Hz, *CH*). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) $\delta = 166.3$ (2 C, CO_2H), 144.6 (2 C, *Cq*), 132.8 (2 C, *Cq*), 132.0 (2 C, *CH*), 131.7 (2 C, *CH*), 123.9 (2 C, *CH*), 122.7 (2 C, *Cq*). IR (ATR, $\tilde{\nu}$) = 1682, 1617, 1542, 1475, 1423, 1369, 1285, 1147, 1123 cm^{-1}. UV/Vis (CH_2Cl_2), $\lambda_{max} = 217$, 264, 279 nm. EI (*m/z*, 70 eV, 220 °C): 268 (57) $[M]^+$, 240 (13) $[M–N_2]^+$, 223 (16) $[M-CO_2H]^+$. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{14}H_8N_2O_4$, 268.0484; found, 268.0477.

1,4-dibromo-2-nitrosobenzene (16): 2,5-dibromoaniline (**15**) (2.51 g, 10.00 mmol, 1 equiv.) was added at 0 °C under argon to a solution of 3-chloroperoxybenzoic acid (*m*-CPBA) (70-75%) (4.76 g, 20.00 mmol, 2 equiv.) in dry dichloromethane (60 mL) and the reaction mixture was stirred at 0 °C for 1 h. A solution of sodium carbonate (2.33 g, 22.00 mmol, 2.2 equiv.) in water (250 mL) was added and the reaction mixture was allowed to room temperature. Organic layer was separated, washed with water and brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 10% *n*-hexane in dichloromethane) to give 1,4-dibromo-2-nitrosobenzene (**16**) as a yellow solid in 59% yield (1.57 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) $\delta = 7.88$ (d, 1H, $J = 8.5$ Hz, C^6H), 7.65 (dd, 1H, $J = 8.5$ Hz, 2.5 Hz, C^5H), 6.33 (d, 1H, $J = 2.5$ Hz, C^3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) $\delta = 160.2$ (1 C, C^2q), 138.7 (1 C, C^5H), 136.8

(1 C, C^6H), 131.6 (1 C, C^4q), 122.4 (1 C, C^1q), 112.8 (1 C, C^3H). IR (ATR, $\tilde{\nu}$) = 3076, 1566, 1454, 1383, 1260, 1190 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 238, 291, 368 nm. EI (*m/z*, 70 eV, 50 °C): 265 $[M]^+$, 235 $[M-NO]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_6H_3Br_2NO$, 262.8581; found, 262.8584. EA ($C_6H_3Br_2NO$): Calcd C 27.20; H 1.14; N 5.29. Found C 27.24; H 1.11; N 5.44.

1-(2,5-dibromophenyl)-2-phenyldiazene (17): Aniline (320 µL, 3.51 mmol, 1 equiv.) was added to a solution of 1,4-dibromo-2-nitrosobenzene (**16**) (1.03 g, 3.86 mmol, 1.1 equiv.) in acetic acid (25 mL) and the reaction mixture was stirred at 40 °C for 24 h. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. Acetic acid (5 mL) was added to the residue and the suspension was filtered off; the solid obtained was washed with a few milliliters of acetic acid and dried in the vacuum-oven at 45 °C for 3 h. 1-(2,5-dibromophenyl)-2-phenyldiazene (**17**) was obtained as a red-orange solid in 80% yield (0.87 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00–7.98 (m, 2H, *CH*), 7.83 (d, 1H, *J* = 2.5 Hz, *CH*), 7.62 (d, 1H, *J* = 8.5 Hz, *CH*), 7.55–7.53 (m, 3H, *CH*), 7.44 (dd, 1H, *J* = 8.5 Hz, 2.5 Hz, *CH*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 152.5 (1 C, *Cq*), 150.3 (1 C, *Cq*), 135.0 (1 C, *CH*), 134.5 (1 C, *CH*), 132.3 (1 C, *CH*), 129.4 (2 C, *CH*), 124.6 (1 C, *Cq*), 123.8 (2 C, *CH*), 122.2 (1 C, *Cq*), 121.2 (1 C, *CH*). IR (ATR, $\tilde{\nu}$) = 3080, 1484, 1443, 1368, 1307, 1287, 1068, 1032 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 323 nm. EI (*m/z*, 70 eV, 70 °C): 340 $[M]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{12}H_8Br_2N_2$, 337.9054; found, 337.9053. EA ($C_{12}H_8Br_2N_2$): Calcd C 42.39; H 2.37; N 8.24. Found C 41.49; H 2.19; N 8.02.

4,4′-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (AzoBiPyB) (18): 1-(2,5-dibromophenyl)-2-phenyldiazene (**17**) (0.500 g, 1.47 mmol, 1 equiv.), 4-pyridylboronic acid (0.723 g, 5.88 mmol, 4.00 equiv.), tetrakis(triphenylphosphine)palladium(0) (170 mg, 0.15 mmol, 0.10 equiv.) and sodium carbonate (1.247 g, 11.76 mmol, 8 equiv.) were added in a degassed mixture of toluene-dioxane-water (50 mL, 2/2/1) and the mixture was heated at 85 °C for 72 h under argon. The reaction mixture was cooled to room temperature, organic solvents were removed under reduced pressure. The resulting aqueous suspension was extracted with dichloromethane. The organic phase was washed with water, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 25% dichloromethane in ethyl acetate). 4,4′-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (AzoBiPyB) (**18**) was obtained as a red solid in 71% yield (0.350 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.74 (d, 2H, *J* = 6.0 Hz, *CH*), 8.71 (d, 2H, *J* = 6.0 Hz, *CH*), 8.09 (d, 1H, *J* = 2.0 Hz, *CH*), 7.87 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz, *CH*), 7.83–7.81 (m, 2H, *CH*), 7.71 (d, 1H, *J* = 8.0 Hz, *CH*), 7.64 (d, 2H, *J* = 6.0 Hz, *CH*), 7.53–7.50 (m, 3H, *CH*), 7.46 (d, 2H, *J* = 6.0 Hz, *CH*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 152.7 (1 C, *Cq*), 150.6 (2 C, *CH*), 150.0 (1 C, *Cq*), 149.3 (2 C, *CH*), 147.3 (1 C, *Cq*), 146.4 (1 C, *Cq*), 139.6 (1 C, *Cq*), 139.0 (1 C, *Cq*), 131.9 (1 C, *CH*), 131.4 (1 C, *CH*), 129.5 (2 C, *CH*), 129.4 (1 C, *CH*), 125.7 (2 C, *CH*), 123.6 (2 C, *CH*), 121.8 (2 C, *CH*), 114.9 (1 C, *CH*). IR (ATR, $\tilde{\nu}$) = 3025, 1589, 1546, 1467, 1381, 1201, 1152 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 275, 323 nm. EI (*m/z*, 70 eV, 150 °C): 336 $[M]^+$, 231 $[M\text{-}C_6H_5N_2]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{22}H_{16}N_4$, 336.1375; found, 336.1374. EA ($C_{22}H_{16}N_4$): Calcd C 78.55; H 4.79; N 16.66. Found C 78.06; H 4.69; N 16.09.

Dimethyl 2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate (19): 1-(2,5-dibromophenyl)-2-phenyldiazene (**17**) (0.510 g, 1.50 mmol, 1 equiv.), 4-(methoxycarbonyl)phenylboronic acid (1.350 g, 7.50 mmol, 5.00 equiv.), tetrakis(triphenylphosphine)palladium(0) (173 mg, 0.15 mmol, 0.10 equiv.) and sodium carbonate (1.908 g, 18.00 mmol, 12 equiv.) were added in a degassed mixture of toluene-dioxane-water (75 mL, 2/2/1) and the mixture was heated at 85 °C for 72 h under argon. The reaction mixture was cooled to room temperature, organic solvents were removed under reduced pressure. The resulting aqueous suspension was extracted with dichloromethane. The organic phase was washed with water, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 70 to 100% dichloromethane in *n*-hexane). Dimethyl 2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate (**19**) was obtained as an orange solid in 92% yield (0.622 g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.17–8.15 (m, 2H, *CH*), 8.14–8.12 (m, 2H, *CH*), 8.05 (d, 1H, *J* = 2.0 Hz, *CH*), 7.84 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz, *CH*), 7.82–7.78 (m, 4H, *CH*), 7.70 (d, 1H, *J* = 8.0 Hz, *CH*), 7.61–7.59 (m, 2H, *CH*), 7.51–7.47 (m, 3H, *CH*), 3.97 (s, 3H, CO_2CH_3), 3.96 (s, 3H, CO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 167.3 (1 C, CO_2CH_3), 167.1 (1 C, CO_2CH_3), 152.8 (1 C, *Cq*), 150.0 (1 C, *Cq*), 144.6 (1 C, *Cq*), 143.2 (1 C, *Cq*), 140.7 (1 C, *Cq*), 139.9 (1 C, *Cq*), 131.6 (1 C, *CH*), 131.5 (1 C, *CH*), 131.0 (2 C, *CH*), 130.4 (2 C, *CH*), 129.6 (1 C, *CH*), 129.4 (2 C, *CH*), 129.2 (1 C, *Cq*), 129.1 (2 C, *CH*), 128.5 (1 C, *Cq*), 127.3 (2 C, *CH*), 123.5 (2 C, *CH*), 114.9 (1 C, *CH*), 52.4 (2 C, CO_2CH_3). IR (ATR, $\tilde{\nu}$) = 2949, 1718, 1607, 1436, 1274, 1187, 1103, 1018 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 455, 296 nm. EI (*m/z*, 70 eV, 220 °C): 450 (94) $[M]^+$, 435 (100) $[M\text{–}CH_3]^+$, 391 (60) $[M\text{-}CO_2CH_3]^+$. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{28}H_{22}N_2O_4$, 450.1580; found, 450.1577. EA ($C_{28}H_{22}N_2O_4$): Calcd C 74.65; H 4.92; N 6.22. Found C 74.88; H 4.85; N 6.31.

2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid (AzoTPDC) (20): Dimethyl 2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate (**19**) (200 mg, 444 %mol, 1.00 equiv.) was dissolved in THF (12 mL). An aqueous solution of potassium hydroxide (249 mg, 4.44 mmol, 10.0 equiv./12 mL) was added and the reaction mixture was stirred at 75 °C for 24 h. The THF was evaporated under reduced pressure, then 1 M HCl aqueous solution was slowly added until pH 1. The aqueous mixture was extracted several times with ethyl acetate; the organic layers were combined, washed with water, brine, dried over magnesium sulfate and evaporated under reduced pressure. 2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid (AzoTPDC) (**20**) was obtained as a red-orange solid in 93% yield (0.175 g). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ = 13.04 (b-s, 2H, CO_2H), 8.09–8.02 (m, 6H, *CH*), 7.93–7.92 (m, 2H, *CH*), 7.83–7.78 (m, 3H, *CH*), 7.66–7.64 (m, 2H, *CH*), 7.59–7.57 (m, 3H, *CH*). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ = 167.2 (1 C, CO_2H), 167.0 (1 C, CO_2H), 152.2 (1 C, *Cq*), 149.3 (1 C, *Cq*), 143.0 (1 C, *Cq*), 142.0 (1 C, *Cq*), 139.7 (1 C, *Cq*), 139.1 (1 C, *Cq*), 131.7 (1 C, *CH*), 131.7 (1 C, *CH*), 130.8 (2 C, *CH*), 130.2 (1 C, *Cq*), 130.1 (2 C, *CH*), 129.8 (1 C, *Cq*), 129.7 (1 C, *CH*), 129.5 (2 C, *CH*), 128.8 (2 C, *CH*), 127.0 (2 C, *CH*), 122.9 (2 C, *CH*), 114.0 (1 C, *CH*). This spectrum shows additional signals corresponding to the *cis* isomer, due to isomerization under the conditions of the measurement: 167.0 (1 C, CO_2H), 166.9 (1 C, CO_2H), 153.1 (1 C, *Cq*), 152.0 (1 C, *Cq*), 142.5 (1 C, *Cq*), 141.4 (1 C, *Cq*), 138.9 (1 C, *Cq*), 131.5 (1 C, *Cq*), 131.0 (1 C, *CH*), 129.9 (2 C, *CH*), 129.4 (2 C, *CH*), 129.0 (2 C, *CH*), 127.8 (1 C, *CH*), 127.1 (1 C, *CH*), 126.7 (2 C, *CH*), 126.2 (2 C, *CH*), 119.5 (2 C, *CH*), 117.6 (1 C, *CH*). IR (ATR, $\tilde{\nu}$) = 2920, 2874, 1683, 1606, 1422, 1317, 1289, 1179, 1128, 1019 cm^{-1}. UV/Vis (CH_2Cl_2), λ_{max} = 291 nm. EI (*m/z*, 70 eV, 220 °C): 284 $[M\text{–}C_6H_4CO_2H\text{–}OH]^+$. EA ($C_{26}H_{18}N_2O_4$): Calcd C 73.92; H 4.30; N 6.63. Found C 74.35; H 4.49; N 6.52.

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Conflict of interest

The authors declare no conflict of interest.

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