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Palladium-Catalyzed Direct Regioselective *ortho*-Phosphonation of Aromatic Azo Compounds with Dialkyl Phosphites

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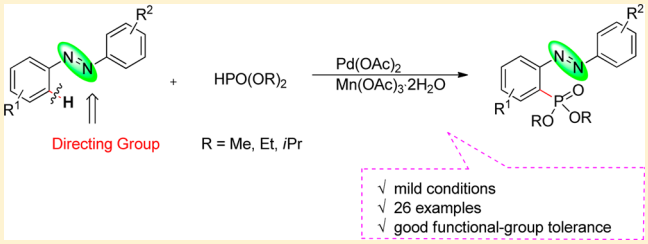
Supporting Information

ABSTRACT: An efficient palladium-catalyzed regioselective C−P bond formation of azo compounds through C−H bond functionalization using dialkyl phosphites as phosphorus source under mild conditions was developed. A series of both symmetrical and unsymmetrical azoarenes were successfully phosphonylated through this procedure with tolerance of a broad range of functional groups.



Carbon−hydrogen bonds are ubiquitous in organic molecules. Hence, transforming C−H bonds into other functional groups is of significant importance in organic synthesis. However, the challenge to functionalize C−H bonds still remains due to the inactive nature of some C−H bonds. This challenge was largely overcome by the introduction of transition metals to activate C−H bonds.[1] Another challenge is the realization of the desired chemoselectivity for substrates containing diverse C−H bonds. The common strategies adopted depend on introducing directing groups, such as pyridine, oxazoline, amide, carbonyl and hydroxyl groups, etc.[2]

Aromatic azo compounds are important building blocks and have been widely applied in such fields as dyes, indicators, nonlinear optics, photochemical switches, and pharmaceuticals due to their unique properties.[3] As a result, great attention has been focused on the functionalization of azoarenes. In recent years, the Pd-catalyzed *ortho*-nitration,[4] acylation,[5] amination,[6] alkoxylation,[7] amidation,[8] halogenation,[9] and acyloxylation[10] of azoarenes using an azo group as a directing group have been achieved, respectively. However, this area is still worth further researching despite these examples.

Aryl phosphonates and their derivatives are important intermediates that are present in many biologically active compounds.[11] Since the pioneering work developed by Hirao and co-workers in 1981,[12] many methods have been developed to construct both C−P bonds,[13] and P−S bonds,[14] among which the $(RO)_2PH(O)/Mn(OAc)_3$ system has recently been successfully introduced to generate phosphonyl radicals for phosphonation of arenes as well as conjugate alkenes/alkynes.[15] Surprisingly, to the best of our knowledge, there has been few reports on the phosphonation of azo compounds, which requires prefunctional azo compounds.[16] Our group has been interested in the synthetic applications of C−H bond functionalization,[17] so we would like to report the first example to access phosphonylated azo compounds via direct transition-metal-catalyzed C−H bond activation. For the overall transformation, the C−P bond was formed with high regioselectivity and good yield.

Our study started from the model reaction of azobenzene (**1a**) with diethyl phosphite (**2a**) to optimize the reaction conditions. A series of experiments were performed to examine the effect of catalyst, oxidant, solvent, and temperature under an air atmosphere (Table 1). It was found that, in the absence of $Pd(OAc)_2$ or oxidant, no desired product was obtained at all (Table 1, entries 1 and 2). This result suggested that the reaction possibly underwent Pd(II) and oxidant cocatalyzed pathways. In the presence of a catalytic amount of $Pd(OAc)_2$ (10 mol %) with $Mn(OAc)_3·2H_2O$ (3.0 equiv) as oxidant and HOAc as a solvent at 80 °C, we were pleased to find that the reaction afforded compound **3aa** in 48% yield (Table 1, entry 3). Then, various Pd catalysts, including $Pd(dppf)Cl_2$, $PdCl_2$, and $PdCl_2(PPh_3)_2$, were employed with no improvement in yield (Table 1, entries 4−6). In an attempt to improve the yield, a series of oxidants, such as $K_2S_2O_8$, $PhI(OAc)_2$, and MnO_2, were tested, and no conversion was observed when $K_2S_2O_8$ was employed (Table 1, entry 9), while a slightly low yield of compound **3aa** was afforded by using $PhI(OAc)_2$ or MnO_2 (Table 1, entries 10−12). The yield was not improved when the temperature was increased even to 110 °C (Table 1, entries 13 and 14). Surprisingly, when it was reduced to 60 °C, the yield of compound **3aa** was increased to 94% (Table 1, entry 15). A better yield (97%) was obtained when the reaction was conducted at room temperature (Table 1, entry 16). For further screening of the amount of $Mn(OAc)_3·2H_2O$, it was found that 2.0 equiv of $Mn(OAc)_3·2H_2O$ was the best (Table 1, entries 17−19). The efforts to enhance the yield proved fruitless by replacing HOAc with other solvents, such as 1,2-DCE, 1,4-dioxane, MeOH, CH_3CN, and DMF (Table 1, entries 20−24).

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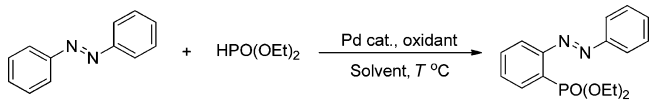
Table 1. Conditions Optimizations for Phosphonation Reaction of Azobenzene[a]



1a 2a 3aa

entry	catalyst	oxidant (equiv)	T (°C)	solvent	yield (%)[b]
1		$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	80	HOAc	0
2	$Pd(OAc)_2$		80	HOAc	0
3	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	80	HOAc	48
4	$Pd(dppf)Cl_2$	$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	80	HOAc	trace
5	$PdCl_2$	$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	80	HOAc	33
6	$PdCl_2(PPh_3)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	80	HOAc	47
7	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	80	HOAc	74
8	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	80	HOAc	60[c]
9	$Pd(OAc)_2$	$K_2S_2O_8$ (3.0)	80	HOAc	0
10	$Pd(OAc)_2$	$PhI(OAc)_2$ (2.0)	80	HOAc	29
11	$Pd(OAc)_2$	MnO_2 (2.0)	80	HOAc	47
12	$Pd(OAc)_2$	MnO_2 (1.0)	80	HOAc	38
13	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	100	HOAc	73
14	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	110	HOAc	63
15	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	60	HOAc	94
16	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	HOAc	97
17	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (3.0)	r.t.	HOAc	74
18	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (1.0)	r.t.	HOAc	65
19	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (0.2)	r.t.	HOAc	trace
20	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	1,2-DCE	23
21	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	1,4-dioxane	0
22	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	MeOH	14
23	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	CH_3CN	0
24	$Pd(OAc)_2$	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	r.t.	DMF	0

[a]Unless otherwise noted, general reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), catalyst (10 mol %), oxidant and solvent (3 mL), 12 h, air. Oxidant was added in three portions. [b]Isolated yield. [c]Oxidant was added in one portion.

With the optimized reaction conditions in hand, the substrate scope of the phosphonation reaction of azo compounds with dialkyl phosphites was then explored, and the results were summarized in Table 2. A broad range of aromatic azo compounds with electron-donating and electron-withdrawing groups worked well with dialkyl phosphites. Azobenzene reacted with dimethyl, diethyl, and diisopropyl H-phosphonate, respectively, affording the desired products in good to excellent yields of 85−97% (**3aa**, **3ab**, **3ac**). Substituents on the aromatic moiety of the aromatic azo compounds had a great influence on the efficiency of this coupling reaction. Generally, electron-rich aromatic azo compounds were more reactive than electron-poor aromatic azo compounds. For example, electron-donating groups (−OMe) on the aromatic ring worked well with dialkyl phosphites, giving the corresponding products in good yield (**3ja**, **3jb**, **3jc**), whereas electron-withdrawing groups (−COOEt, $-OCF_3$) on the aromatic ring had a negative effect on the yield of the reaction (**3la**, **3ka**). The reaction of the azoarenes with methyl substituted in various position of the aromatic moiety with dialkyl phosphites afforded the corresponding products in satisfactory yields of 58−95% (**3ba**, **3bb**, **3bc**, **3ca**, **3cb**, **3da**, **3db**, and **3dc**). Notably, the *ortho*-substituted azobenzene gave a relatively lower product yield than the *para*- or *meta*-substituted azobezene due to steric hindrance (**3ba**, **3ca**, **3da**, **3cb**, and **3db**). The reaction of azoarenes with halogen moieties on the *para* and *meta* positions seemed to be not very efficient, furnishing decreasing yields of phosphonylated products (**3ea**, **3fa**, **3ga**, **3hb**, and **3ib**). Delightedly, the yields of some halo-substituted azoarenes could be increased by raising the temperature (**3ia**, **3ha**). As for the unsymmetrically substituted azoarenes, the reaction proceeded well with good regioselectivity. Two isomers of *ortho*-phosphonation products were isolated in 18% and 61% yields, respectively, and the *ortho*-phosphonation reactions occurred mainly at the unsubstituted phenyl ring rather than at the phenyl ring with an electron-withdrawing substituent (**3na**, **3na′**), which was in accordance with the rule mentioned above, namely, an electron-rich aromatic ring was more reactive than an electron-poor aromatic ring.

In an effort to investigate whether the *ortho*-monophosphonylated aromatic azo compound could be further phosphonylated, compound **3aa** reacted with diethyl phosphite under the same reaction conditions. It turned out that no further reaction was observed (Scheme 1), which may be in part attributed to the increase of steric hindrance and the electron-poor property of the *ortho*-monophosphonylated aromatic azo compound.

It was well established that the $(RO)_2PH(O)/Mn(OAc)_3$ system can generate phosphonyl radicals.[15] Therefore, we proposed that the C−H *ortho*-phosphonation of azo compounds may also involve a radical process. To confirm this hypothesis, a typical radical scavenger, tetramethylpiperidine *N*-oxide (TEMPO), was added to the reaction of azobenzene (**1a**) with diethyl phosphite (**2a**) under the same reaction conditions, and it was found that the reaction was largely suppressed (Scheme 2).

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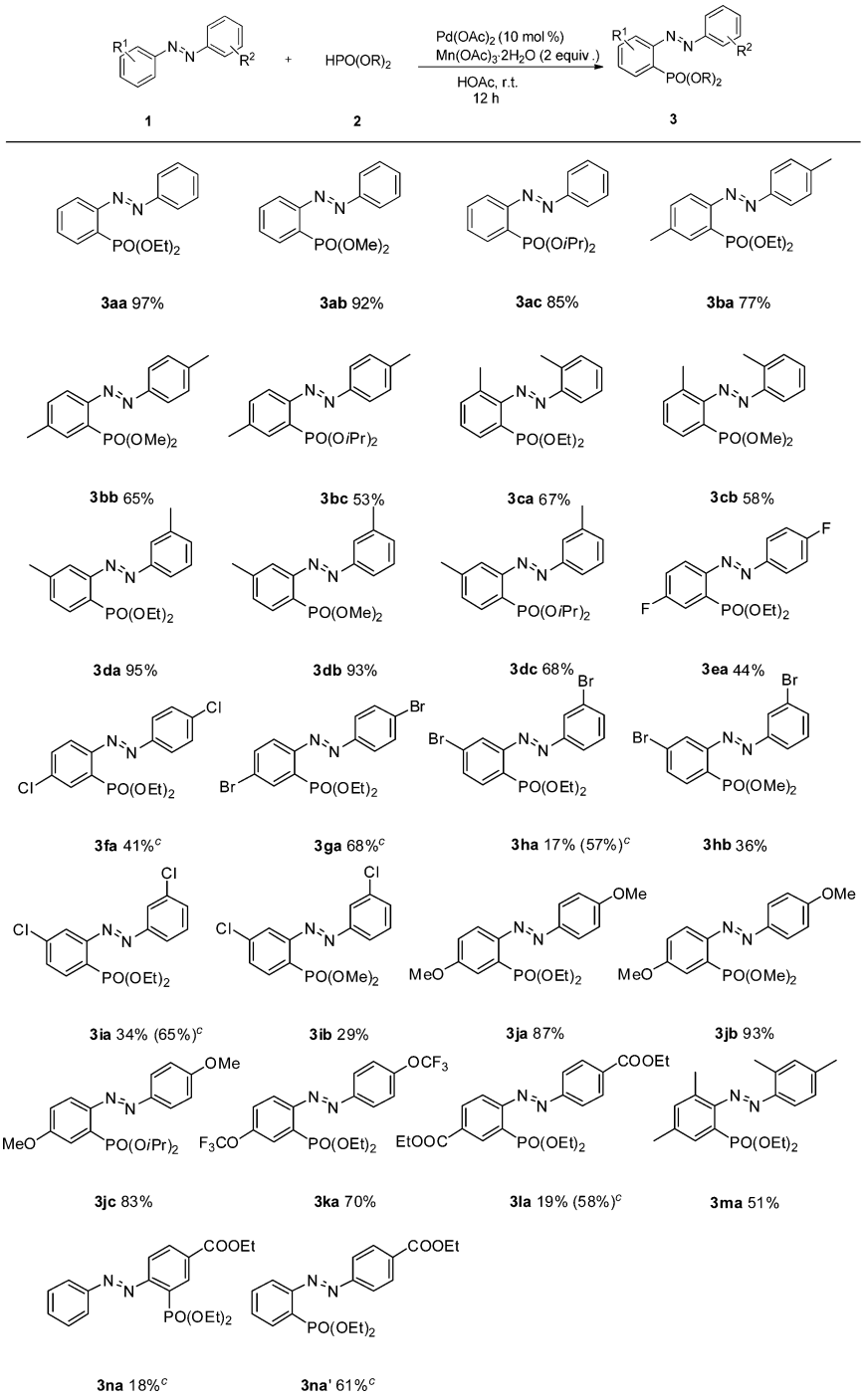
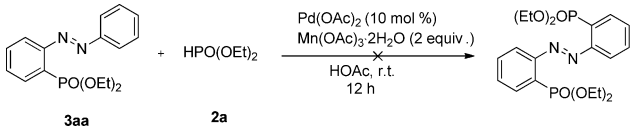
Table 2. *ortho*-Phosphonation of Substituted Azoarenes with Dialkyl Phosphites[a,b,c]

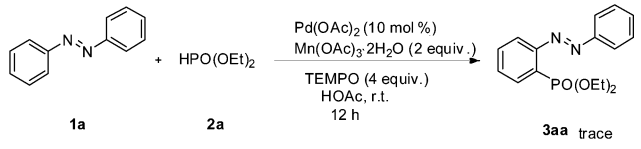


[a]Unless otherwise noted, general reaction conditions: aromatic azo compounds **1** (0.25 mmol), dialkyl phosphites **2** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), $Mn(OAc)_3{\cdot}2H_2O$ (2.0 equiv), and HOAc (3 mL) under air at room temperature for 12 h. $Mn(OAc)_3{\cdot}2H_2O$ was added in three portions. [b]Isolated yield. [c]The yields at 80 °C were shown.

Scheme 1. C−H *ortho*-Phosphonation of Compound 3aa



Scheme 2. Controlled Reaction



On the basis of the experimental result and some previous literatures,[5e,15,18] a plausible mechanism was proposed (Scheme 3). In the first step, azobenzene coordinating with Pd(II) catalyst by sp^2 C−H activation formed the palladacyclic intermediate **A**.[5e] Next, **A** reacting with a phosphonyl radical

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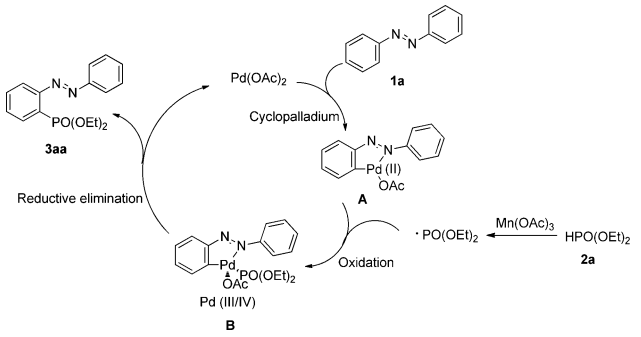
Scheme 3. Proposed Pathways for This Reaction



generated in situ from the oxidation of diethyl phosphite (**2a**) afforded either Pd(III)[19] or Pd(IV)[20] species **B**. Finally, product **3aa** was afforded by the reductive elimination of species **B** with the release of Pd(II) catalyst.

In summary, the Pd(II)-catalyzed C−H *ortho*-phosphonation of azoarenes with dialkyl phosphites using $Mn(OAc)_3$ as oxidant has been developed, which provides an easy access to synthesize *ortho*-dialkylphosphonatodiarylazo compounds in moderate to excellent yields under mild conditions. This reaction further extends the application scope of free-radical-based phosphonation of aromatic ring systems. As well, further studies are ongoing to investigate the properties and synthetic application of these azobenzene derivatives.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz, respectively, using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Aromatic azo compound substrates were prepared according to the literature procedure.[21] Chromatography: Column chromatography was performed with silica gel (200−300 mesh ASTM).

General Experimental Procedures and Characterizations. To a solution of azobenzene (0.25 mmol), dialkyl phosphites (0.5 mmol), and $Pd(OAc)_2$ (0.025 mmol) in HOAc (3 mL) was added $Mn(OAc)_3 \cdot 2H_2O$[22] (0.5 mmol) in three portions. After being stirred at room temperature or 80 °C for 12 h, the mixture was evaporated under vacuum. The corresponding product was isolated by silica gel column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

*(E)-Diethyl (2-(Phenyldiazenyl)phenyl)phosphonate (**3aa**).* Orange red oil. Yield: 97% (77 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16−8.09 (m, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.79−7.75 (m, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.57−7.47 (m, 4H), 4.25−4.09 (m, 4H), 1.28 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.6 (d, J = 5.2 Hz), 152.7 (s), 134.5 (d, J = 7.7 Hz), 133.3 (s), 131.6 (s), 130.3 (d, J = 14.2 Hz), 129.2 (s), 127.0 (s), 123.6 (s), 115.5 (s), 62.3 (d, J = 5.7 Hz), 16.3 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.74 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}N_2O_3P$ 319.1212; Found 319.1206.

*(E)-Dimethyl (2-(Phenyldiazenyl)phenyl)phosphonate (**3ab**).* Orange red oil. Yield: 92% (66 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15−8.08 (m, 1H), 8.02−7.98 (m, 2H), 7.83−7.78 (m, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.58−7.50 (m, 4H), 3.81 (d, J = 11.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 152.6 (d, J = 5.0 Hz), 151.7 (s), 133.6 (d, J = 7.6 Hz), 132.5 (d, J = 2.6 Hz), 130.6 (s), 129.3 (d, J = 14.2 Hz), 128.2 (s), 125.1 (s), 122.6 (s), 114.6 (d, J = 10.7 Hz), 51.8 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.77 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}N_2O_3P$ 291.0899; Found 291.0912.

*(E)-Diisopropyl (2-(Phenyldiazenyl)phenyl)phosphonate (**3ac**).* Orange red oil. Yield: 85% (73 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19−8.13 (m, 1H), 8.02 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), 7.76−7.70 (m, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.56−7.49 (m, 4H), 4.84−4.77 (m, 2H), 1.40−1.32 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.5 (d, J = 5.0 Hz), 152.8 (s), 134.5 (d, J = 7.7 Hz), 133.0 (d, J = 2.5 Hz), 131.4 (s), 130.2 (s), 130.1 (d, J = 6.7 Hz), 129.0 (s), 123.6 (s), 115.4 (d, J = 10.5 Hz), 70.8 (d, J = 5.8 Hz), 24.2 (d, J = 4.0 Hz), 23.8 (d, J = 5.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.37 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}N_2O_3P$ 347.1525; Found 347.1533.

*(E)-Diethyl (5-Methyl-2-(p-tolyldiazenyl)phenyl)phosphonate (**3ba**).* Orange red oil. Yield: 77% (66 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97−7.82 (m, 3H), 7.74−7.67 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 4.28−4.07 (m, 4H), 2.45 (s, 3H), 2.43 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 151.7 (d, J = 4.9 Hz), 150.9 (s), 141.9 (s), 140.7 (d, J = 14.0 Hz), 137.4 (s), 135.1 (d, J = 7.7 Hz), 134.0 (d, J = 2.7 Hz), 129.8 (s), 123.5 (s), 115.3 (d, J = 11.2 Hz), 62.2 (d, J = 5.4 Hz), 21.5 (d, J = 20.1 Hz), 16.4 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.40 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}N_2O_3P$ 347.1525; Found 347.1525.

*(E)-Dimethyl (5-Methyl-2-(p-tolyldiazenyl)phenyl)phosphonate (**3bb**).* Orange red solid, mp: 143−145 °C. Yield: 65% (51 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95−7.87 (m, 3H), 7.74−7.70 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 3.79 (d, J = 11.6 Hz, 6H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 151.7 (d, J = 5.1 Hz), 150.9 (s), 142.1 (s), 140.8 (d, J = 14.2 Hz), 135.1 (d, J = 7.7 Hz), 134.2 (d, J = 2.7 Hz), 129.8 (s), 125.8 (s), 123.5 (s), 115.4 (d, J = 11.4 Hz), 52.7 (d, J = 5.6 Hz), 21.6 (s), 21.4 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.36 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}N_2O_3P$ 319.1212; Found 319.1208.

*(E)-Diisopropyl (5-Methyl-2-(p-tolyldiazenyl)phenyl)phosphonate (**3bc**).* Orange red solid, mp: 92−94 °C. Yield: 53% (50 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 14.8 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.69−7.65 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.8 Hz, 2H), 4.82−4.73 (m, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 1.34 (d, J = 6.0 Hz, 6H), 1.16 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 150.5 (d, J = 4.8 Hz), 149.9 (s), 140.7 (s), 139.4 (d, J = 14.1 Hz), 134.2 (d, J = 8.0 Hz), 132.6 (d, J = 2.8 Hz), 128.7 (d, J = 6.0 Hz), 126.9 (s), 122.5 (s), 114.2 (d, J = 11.1 Hz), 69.6 (d, J = 5.7 Hz), 23.1 (d, J = 4.0 Hz), 22.7 (d, J = 5.0 Hz), 20.4 (d, J = 19.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.03 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}N_2O_3P$ 375.1838; Found 375.1815.

*(E)-Diethyl (3-Methyl-2-(o-tolyldiazenyl)phenyl)phosphonate (**3ca**).* Orange red oil. Yield: 67% (58 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98−7.92 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.42−7.27 (m, 4H), 4.18−4.01 (m, 4H), 2.70 (s, 3H), 2.38 (s, 3H), 1.23 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 154.6 (d, J = 5.9 Hz), 151.2 (s), 138.5 (s), 136.4 (d, J = 2.7 Hz), 132.4 (d, J = 7.9 Hz), 131.5 (s), 131.2 (s), 128.5 (d, J = 10.8 Hz), 127.4 (d, J = 15.3 Hz), 126.5 (s), 116.1 (s), 62.0 (d, J = 5.6 Hz), 19.7 (d, J = 2.0 Hz), 17.8 (s), 16.2 (d, J = 6.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.57 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}N_2O_3P$ 347.1525; Found 347.1526.

*(E)-Dimethyl (3-Methyl-2-(o-tolyldiazenyl)phenyl)phosphonate (**3cb**).* Orange red oil. Yield: 58% (46 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96−7.89 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.41−7.28 (m, 4H), 3.71 (d, J = 11.2 Hz, 6H), 2.71 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 154.6 (d, J = 6.0 Hz), 151.3 (s), 138.5 (s), 136.6 (d, J = 2.7 Hz), 132.5 (d, J = 7.7 Hz), 131.6 (d, J = 1.6 Hz), 131.2 (s), 128.9 (d, J = 11.0 Hz), 127.6 (d, J = 15.4 Hz), 126.7 (s), 123.4 (s), 116.0 (s), 52.6 (d, J = 5.7 Hz), 19.8 (d, J = 2.0 Hz), 17.8 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.51 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}N_2O_3P$ 319.1212; Found 319.1221.

*(E)-Diethyl (4-Methyl-2-(m-tolyldiazenyl)phenyl)phosphonate (**3da**).* Yellow oil. Yield: 95% (82 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04−7.97 (m, 1H), 7.81 (d, J = 9.2 Hz, 2H), 7.54 (d, J = 5.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.38−7.30 (m, 2H), 4.24−4.08 (m, 4H), 2.47 (s, 6H), 1.25 (t, J = 2.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100

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Hz): δ 153.8 (d, J = 5.4 Hz), 152.9 (s), 144.2 (d, J = 2.7 Hz), 138.9 (s), 134.6 (d, J = 8.2 Hz), 132.3 (s), 130.9 (d, J = 14.6 Hz), 129.0 (s), 124.4 (s), 123.8 (s), 120.6 (s), 115.9 (d, J = 11.1 Hz), 62.1 (d, J = 5.6 Hz), 21.7 (s), 21.4 (s), 16.4 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.43 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{24}N_2O_3P$ 347.1525; Found 347.1529.

(E)-Dimethyl (4-Methyl-2-(m-tolyldiazenyl)phenyl)phosphonate (**3db**). Yellow oil. Yield: 93% (74 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02−7.95 (m, 1H), 7.80 (d, J = 10.8 Hz, 2H), 7.57 (s, 1H), 7.44−7.26 (m, 3H), 3.78 (d, J = 11.6 Hz, 6H), 2.47 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.8 (d, J = 5.7 Hz), 152.9 (s), 144.4 (d, J = 2.7 Hz), 139.1 (s), 134.6 (d, J = 7.9 Hz), 132.4 (s), 131.2 (d, J = 14.6 Hz), 129.0 (s), 124.6 (s), 122.7 (s), 120.3 (s), 116.0 (d, J = 11.1 Hz), 52.7 (d, J = 5.7 Hz), 21.7 (s), 21.4 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.48 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}N_2O_3P$ 319.1212; Found 319.1212.

(E)-Diisopropyl (4-Methyl-2-(m-tolyldiazenyl)phenyl)phosphonate (**3dc**). Yellow oil. Yield: 68% (63 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (dd, J_1 = 7.6 Hz, J_2 = 14.0 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 4.8 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.36−7.29 (m, 2H), 4.83−4.73 (m, 2H), 2.46 (s, 6H), 1.34 (d, J = 6.0 Hz, 6H), 1.17 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 150.6 (d, J = 5.3 Hz), 152.9 (s), 143.8 (d, J = 2.7 Hz), 138.9 (s), 134.7 (d, J = 8.2 Hz), 132.1 (s), 130.7 (d, J = 14.7 Hz), 128.9 (s), 126.9 (s), 125.0 (s), 124.1 (s), 120.8 (s), 70.7 (d, J = 5.8 Hz), 24.1 (d, J = 4.0 Hz), 23.8 (d, J = 5.0 Hz), 21.6 (s), 21.3 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.11 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{28}N_2O_3P$ 375.1838; Found 375.1801.

(E)-Diethyl (5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)phosphonate (**3ea**). Yellow oil. Yield: 44% (39 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04−7.98 (m, 2H), 7.87−7.76 (m, 2H), 7.35−7.29 (m, 1H), 7.21 (t, J = 8.4 Hz, 2H), 4.26−4.12 (m, 4H), 1.30 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 166.0 (s), 164.6 (d, J = 19.9 Hz), 163.5 (s), 149.2 (d, J = 3.0 Hz), 125.6 (d, J = 9.0 Hz), 121.2 (d, J = 8.0 Hz), 121.0 (d, J = 8.0 Hz), 120.4 (d, J = 2.8 Hz), 120.1 (d, J = 2.9 Hz), 116.3 (s), 116.1 (s), 62.5 (d, J = 5.7 Hz), 16.4 (d, J = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.23 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}F_2N_2O_3P$ 355.1023; Found 355.1002.

(E)-Diethyl (5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)phosphonate (**3fa**). Yellow oil. Yield: 41% (40 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (dd, J_1 = 2.4 Hz, J_2 = 14.4 Hz, 1H), 7.95 (d, J = 8.8 Hz, 2H), 7.78−7.74 (m, 1H), 7.60 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.50 (d, J = 8.8 Hz, 2H), 4.32−4.09 (m, 4H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 151.5 (d, J = 4.8 Hz), 151.0 (s), 137.9 (s), 137.0 (s), 136.8 (s), 134.2 (d, J = 8.2 Hz), 133.3 (d, J = 2.6 Hz), 129.6 (s), 124.9 (s), 116.9 (d, J = 11.5 Hz), 62.5 (d, J = 5.7 Hz), 16.4 (d, J = 6.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.26 (s). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{17}Cl_2N_2NaO_3P$ 409.0252; Found 409.0244.

(E)-Diethyl (5-Bromo-2-((4-bromophenyl)diazenyl)phenyl)phosphonate (**3ga**). Yellow oil. Yield: 68% (81 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (dd, J_1 = 2.4 Hz, J_2 = 14.4 Hz, 1H), 7.89−7.85 (m, 2H), 7.76 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.70−7.64 (m, 3H), 4.31−4.09 (m, 4H), 1.29 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 151.9 (d, J = 4.8 Hz), 151.4 (s), 137.1 (d, J = 8.2 Hz), 136.3 (d, J = 2.5 Hz), 132.5 (s), 129.8 (s), 126.5 (s), 125.1 (s), 117.1 (d, J = 11.2 Hz), 62.5 (d, J = 5.7 Hz), 16.4 (d, J = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.02 (s). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{17}Br_2N_2NaO_3P$ 496.9241; Found 496.9242.

(E)-Diethyl (4-Bromo-2-((3-bromophenyl)diazenyl)phenyl)phosphonate (**3ha**). Orange red oil. Yield: 57% (71 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14 (t, J = 2.0 Hz, 1H), 8.03−7.94 (m, 2H), 7.91 (dd, J_1 = 1.6 Hz, J_2 = 4.4 Hz, 1H), 7.72−7.68 (m, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 4.29−4.09 (m, 4H), 1.30 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.6 (d, J = 5.4 Hz), 153.3 (s), 135.9 (d, J = 8.4 Hz), 134.6 (s), 133.4 (d, J = 14.6 Hz), 130.6 (s), 128.5 (s), 128.2 (d, J = 3.6 Hz), 125.8 (s), 123.4 (s), 123.2 (s), 118.9 (d, J = 10.8 Hz), 62.5 (d, J = 5.8 Hz), 16.4 (d, J = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.57 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}Br_2N_2O_3P$ 474.9422; Found 474.9419.

(E)-Dimethyl (4-Bromo-2-((3-bromophenyl)diazenyl)phenyl)phosphonate (**3hb**). Orange red oil. Yield: 36% (40 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (t, J = 2.0 Hz, 1H), 8.01−7.92 (m, 3H), 7.73−7.69 (m, 1H), 7.67−7.63 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 3.82 (d, J = 11.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.6 (d, J = 5.7 Hz), 153.3 (s), 135.9 (d, J = 8.3 Hz), 134.7 (s), 133.6 (s), 133.5 (s), 130.6 (d, J = 8.4 Hz), 128.6 (s), 126.3 (s), 123.2 (s), 122.9 (s), 119.0 (d, J = 11.1 Hz), 52.9 (d, J = 5.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 18.53 (s). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{13}Br_2N_2NaO_3P$ 468.8928; Found 468.8931.

(E)-Diethyl (4-Chloro-2-((3-chlorophenyl)diazenyl)phenyl)phosphonate (**3ia**). Orange red oil. Yield: 65% (63 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (dd, J_1 = 8.4 Hz, J_2 = 13.6 Hz, 1H),.7.98 (s, 1H), 7.94−7.89 (m, 1H), 7.76 (dd, J_1 = 2.0 Hz, J_2 = 4.4 Hz, 1H), 7.56−7.52 (m, 1H), 7.51−7.48 (m, 2H), 4.27−4.11 (m, 4H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.8 (d, J = 5.6 Hz), 153.3 (s), 139.9 (d, J = 3.7 Hz), 135.8 (d, J = 8.4 Hz), 135.3 (s), 131.7 (s), 130.4 (d, J = 17.5 Hz), 128.0 (s), 126.1 (s), 122.9 (d, J = 3.1 Hz), 115.9 (d, J = 11.1 Hz), 62.4 (d, J = 5.7 Hz), 16.4 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.40 (s). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{17}Cl_2N_2NaO_3P$ 409.0252; Found 409.0258.

(E)-Dimethyl (4-Chloro-2-((3-chlorophenyl)diazenyl)phenyl)phosphonate (**3ib**). Orange red oil. Yield: 29% (26 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (dd, J_1 = 8.4 Hz, J_2 = 14.0 Hz, 1H), 7.97 (s, 1H), 7.93−7.88 (m, 1H), 7.78 (dd, J_1 = 2.0 Hz, J_2 = 4.4 Hz, 1H), 7.57−7.48 (m, 3H), 3.82 (d, J = 11.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 153.3 (d, J = 5.8 Hz), 153.3 (s), 140.1 (d, J = 3.6 Hz), 135.8 (d, J = 8.3 Hz), 135.3 (s), 131.8 (s), 130.6 (s), 130.4 (d, J = 8.4 Hz), 126.9 (s), 125.0 (s), 123.3 (s), 122.5 (s), 116.0 (d, J = 11.2 Hz) 52.9 (d, J = 5.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 18.35 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}Cl_2N_2O_3P$ 359.0119; Found 359.0124.

(E)-Diethyl (5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)phosphonate (**3ja**). Yellow oil. Yield: 87% (82 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99−7.94 (m, 2H), 7.83 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1H), 7.62 (dd, J_1 = 2.8 Hz, J_2 = 15.6 Hz, 1H), 7.13 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.03−6.99 (m, 2H), 4.25−4.09 (m, 4H), 3.92 (s, 3H), 3.89 (s, 3H), 1.28 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 162.0 (s), 160.7 (d, J = 17.7 Hz), 147.6 (d, J = 4.7 Hz), 147.3 (s), 130.6 (s), 128.8 (s), 125.2 (s), 119.4 (d, J = 2.8 Hz), 118.5 (d, J = 9.0 Hz), 117.1 (d, J = 12.8 Hz), 114.2 (s), 62.2 (d, J = 5.6 Hz), 55.7 (d, J = 26 Hz), 16.4 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.86 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{24}N_2O_5P$ 379.1423; Found 379.1434.

(E)-Dimethyl (5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)phosphonate (**3jb**). Yellow oil. Yield: 93% (81 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98−7.93 (m, 2H), 7.86 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1H), 7.60 (dd, J_1 = 2.8 Hz, J_2 = 15.6 Hz, 1H), 7.15 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.04−6.98 (m, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 3.80 (d, J = 11.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 162.1 (s), 160.8 (d, J = 17.7 Hz), 147.6 (d, J = 4.9 Hz), 147.3 (s), 129.5 (s), 127.7 (s), 125.2 (s), 119.7 (d, J = 2.9 Hz), 118.5 (d, J = 9.0 Hz), 117.1 (d, J = 13.0 Hz), 114.3 (s), 55.9 (s), 55.6 (s), 52.8 (d, J = 5.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.97 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}N_2O_5P$ 351.1110; Found 351.1104.

(E)-Diisopropyl (5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)phosphonate (**3jc**). Yellow oil. Yield: 83% (84 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00−7.95 (m, 2H), 7.81 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1H), 7.66 (dd, J_1 = 2.8 Hz, J_2 = 15.6 Hz, 1H), 7.11 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.03−6.98 (m, 2H), 4.86−4.73 (m, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 1.35 (d, J = 6.0 Hz, 6H), 1.18 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 161.9 (s), 160.7 (d, J = 17.6 Hz), 147.5 (d, J = 4.7 Hz), 147.4 (s), 131.8 (s), 130.0 (s), 125.2 (s), 119.2 (d, J = 2.8 Hz), 118.5 (d, J = 9.1 Hz), 117.0 (d, J = 12.7 Hz), 114.1 (s), 70.9 (d, J = 5.7 Hz), 55.8 (s), 55.6 (s), 24.2 (d, J = 3.9 Hz), 23.8 (d, J = 5.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.47 (s). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{28}N_2O_5P$ 407.1736; Found 407.1738.

(E)-Diethyl(5-(trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)diazenyl)phenyl)phosphonate (**3ka**). Yellow oil. Yield: 70% (85 mg).

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^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08−8.03 (m, 2H), 7.95 (dd, J_1 = 2.0 Hz, J_2 = 14.8 Hz, 1H), 7.86 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1H), 7.51−7.47 (m, 1H), 7.38 (d, J = 8.0 Hz, 2H), 4.30−4.13 (m, 4H), 1.31 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 151.5 (d, J = 1.7 Hz), 151.3 (d, J = 4.6 Hz), 150.6 (s), 150.4 (d, J = 1.7 Hz), 150.2 (d, J = 1.8 Hz), 132.0 (s), 130.2 (s), 126.3 (d, J = 8.2 Hz), 125.2 (d, J = 5.0 Hz), 121.6 (d, J = 3.6 Hz), 121.3 (s), 119.0 (d, J = 4.3 Hz), 117.5 (d, J = 12.2 Hz), 62.6 (d, J = 5.8 Hz), 16.3 (d, J = 6.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.75 (s). HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{18}F_6N_2O_5P$ 487.0858; Found 487.0861.

*(E)-Ethyl 3-(Diethoxyphosphoryl)-4-((4-(ethoxycarbonyl)phenyl)-diazenyl)benzoate (**3la**).* Yellow oil. Yield: 58% (67 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.76 (dd, J_1 = 1.6 Hz, J_2 = 14.4 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.2 Hz, 2H), 7.80 (dd, J_1 = 5.2 Hz, J_2 = 8.4 Hz, 1H), 4.48−4.40 (m, 4H), 4.30−4.14 (m, 4H), 1.46−1.41 (m, 6H), 1.30 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 165.9 (s), 165.2 (s), 155.8 (d, J = 5.5 Hz), 155.0 (s), 135.7 (d, J = 8.6 Hz), 134.5 (d, J = 2.5 Hz), 133.2 (s), 130.7 (s), 123.5 (s), 115.8 (d, J = 10.4 Hz), 62.5 (d, J = 6.7 Hz), 61.7 (s), 61.4 (s), 16.4 (d, J = 6.4 Hz), 14.3 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.01 (s). HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{22}H_{28}N_2O_7P$ 463.1634; Found 463.1642.

*(E)-Diethyl (2-((2,4-Dimethylphenyl)diazenyl)-3,5-dimethyl-phenyl)phosphonate (**3ma**).* Yellow oil. Yield: 51% (47 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 14.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.15 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 4.17−3.98 (m, 4H), 2.66 (s, 3H), 2.49 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 152.2 (d, J = 5.6 Hz), 149.4 (s), 138.4 (s), 137.4 (d, J = 15.4 Hz), 137.2 (d, J = 2.8 Hz), 133.1 (d, J = 8.0 Hz), 131.7 (s), 128.5 (d, J = 11.4 Hz), 127.3 (s), 123.4 (s), 115.9 (s), 61.9 (d, J = 5.5 Hz), 21.4 (s), 21.0 (s), 20.1 (d, J = 2.2 Hz), 17.8 (s), 16.3 (d, J = 6.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 18.27 (s). HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{27}N_2NaO_3P$ 397.1657; Found 397.1664.

*(E)-Ethyl 3-(Diethoxyphosphoryl)-4-(phenyldiazenyl)benzoate (**3na**).* Yellow oil. Yield: 18% (18 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.75 (dd, J_1 = 2.0 Hz, J_2 = 14.4 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 8.06−8.00 (m, 2H), 7.78 (dd, J_1 = 5.2 Hz, J_2 = 8.4 Hz, 1H), 7.58−7.51 (m, 3H), 4.44 (q, J = 7.2 Hz, 2H), 4.29−4.11 (m, 4H), 1.44 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 167.0 (s), 156.1 (s), 154.3 (d, J = 5.0 Hz), 135.6 (d, J = 7.5 Hz), 134.3 (d, J = 2.7 Hz), 131.6 (s), 130.7 (s), 128.8 (s), 124.3 (s), 116.7 (d, J = 10.4 Hz), 63.2 (d, J = 5.8 Hz), 62.3 (s), 30.7 (s), 17.4 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.26 (s). HRMS (ESI-TOF) m/z: [M +Na]$^+$ Calcd for $C_{19}H_{23}N_2NaO_5P$ 413.1242; Found 413.1239.

*(E)-Ethyl 4-((2-(Diethoxyphosphoryl)phenyl)diazenyl)benzoate (**3na′**).* Yellow oil. Yield: 61% (59 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, J = 8.8 Hz, 2H), 8.17−8.10 (m, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.81−7.77 (m, 1H), 7.70−7.64 (m, 1H), 7.61−7.55 (m, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.26−4.11 (m, 4H), 1.43 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 166.0 (s), 155.1 (s), 153.4 (d, J = 5.0 Hz), 134.6 (d, J = 7.5 Hz), 133.3 (d, J = 2.7 Hz), 132.7 (s), 130.9 (d, J = 14.0 Hz), 130.6 (s), 123.3 (s), 115.4 (d, J = 10.4 Hz), 62.3 (d, J = 5.8 Hz), 61.4 (s), 16.4 (d, J = 6.6 Hz), 14.2 (d, J = 20.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.40 (s). HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{24}N_2O_5P$ 391.1423; Found 391.1430.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectral data for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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