Synthesis Y. Su et al. Paper

Trichloroisocyanuric Acid Mediated Oxidative Dehydrogenation of Hydrazines: A Practical Chemical Oxidation To Access Azo Compounds

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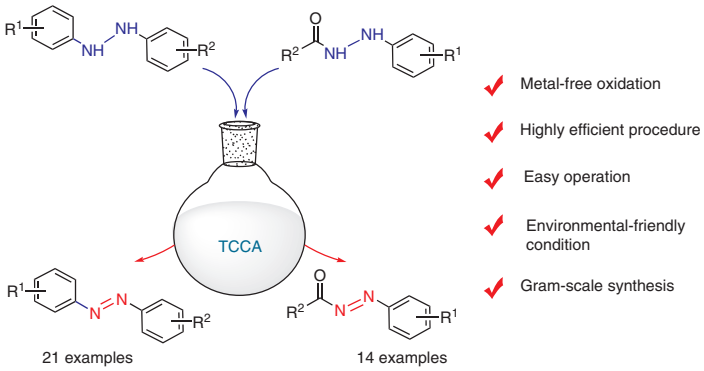

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Abstract A highly efficient, metal-free, chemical oxidation of hydrazines has been implemented using environmentally friendly TCCA as oxidant. This benign protocol provides straightforward access to a wide range of azo compounds in THF in excellent yield. Altogether, 35 azo compounds were obtained in this way and scale-up preparations were performed. Additionally, a plausible mechanism was also proposed. Step-economical process, mild reaction conditions, operational simplicity, high reaction efficiency, and easy scale-up highlight the practicality of this methodology.

Key words trichloroisocyanuric acid, dehydrogenation, hydrazines, azo compound, chemical oxidation

As well known, the azo group is a crucial structural unit distributed in dyes and pigments,[1] pharmaceuticals,[2] food additives,[1c] organic reaction reagents[3] and materials.[2e,4] For instance, methyl red and methyl orange, azobenzene derivatives, are utilized as dyes and indicators; Prontosil,[5] an aromatic azo compound, is not only a simply dye, but also more important it was the first synthetic antibacterial sulfonamide. Furthermore the dialkyl azodicarboxylates, such as diethyl azodicarboxylate (DEAD) and diisopropyl azodicarboxylate (DIAD), are essential reagents in the Mitsunobu reaction[6] and versatile reactants in organic transformations.[7] Doubtlessly, their importance and the utilizations of azo compounds have impelled the development of efficient preparative routes to these privileged compounds.[8] The classical methods for the synthesis of azo compounds include the oxidative coupling reaction of anilines,[9] the coupling reactions of diazonium salts,[10] the Mills reaction,[11] the reductive coupling reaction of nitro compounds,[12] the oxidation of hydrazines and so on (Scheme 1).[1d,13] Among these methods for preparing azo compounds, the straightforward and efficient routes mainly relied on the oxidation of hydrazines.[14] In this regard, various types of oxidants have been involved toward such useful scaffolds, such as hypervalent heavy metallic oxidants,[14a–h] O_2/metal co-oxidant,[12b,14i–k] H_2O_2/heavy metallic salt oxidant,[14l,m] elemental Br_2[14n] or NBS,[14o] hypervalent iodine compounds.[9h,14p] Very recently, several elegant and benign methods to achieving azo compounds have been developed. Balaraman and co-workers realized a photocatalyzed dehydrogenation of diarylhydrazines with dual-transition-metal (Ru and Co) catalysts, thus providing a benign method to azobenzenes.[14x] Afterward, the Fan group also used the organic dye ($Acr-Me^+$) as the photocatalyst to obtaining azobenzenes via an environmentally friendly strategy.[14y] Very recently, the Xia and Wu group reported a photoredox-catalyzed procedure to access azobenzenes from diarylhydrazines using eosin Y as the catalyst. Meanwhile, they also realized the interconversion from azobenzenes to hydrazine derivatives.[14z] Besides the photo-promoted oxidative dehydrogenation of hydrazines, Huang and co-workers employed a novel, green and efficient electrochemical dehydrogenation of hydrazines in an undivided cell to give azo compounds with a broad substrate scope.[14aa] Although many efforts have been devoted to the synthesis of azo compounds, given the importance of azo compounds and the production practicality, it is still actively appealing to develop alternative and environmental friendly approaches for preparing azo compounds.

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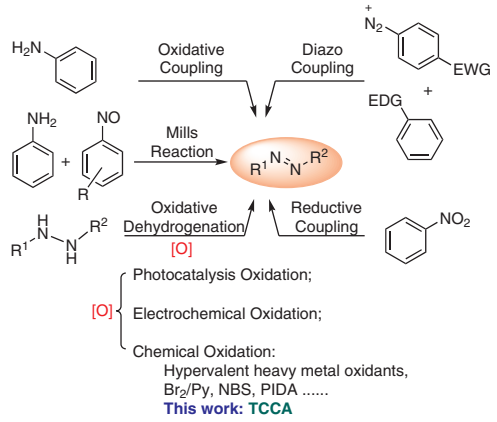
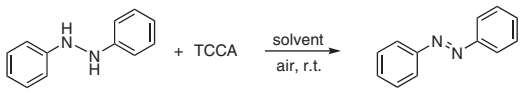


Scheme 1 Classical approaches to the synthesis of azo compounds

Among various categories of oxidants, trichloroisocyanuric acid (TCCA) has emerged as an extremely convenient oxidant as well as a versatile chlorinating reagent or radical initiator in synthesis, due to its stability, commercial availability, cheapness, harmless, easy handling, mild reaction conditions, and environmentally benign attributes.[15] Hence, it has been proved to be an efficient safe alternative to toxic heavy-metal reagents and expensive organometallic catalysts for a wide range of oxidations, such as, transformation of alcohols to carboxyl compounds,[16] oxidative aromatizations via dehydrogenations,[17] asymmetric epoxidations[18] and others. In continuation of our interest in the applications of TCCA in chemical transformations,[19] herein, we report the oxidative dehydrogenation of hydrazines with this benign oxidant to provide azo compounds. The environmental benign reaction conditions, high reaction efficiency, and remarkable practicality on a gram scale are salient features of our investigation.

Our investigation began by optimizing the oxidative dehydrogenation conditions of diphenylhydrazine (**1a**) with TCCA (Table 1). Initially, the model substrate **1a** was treated with 0.34 equiv of TCCA in ethanol (entry 1) at room temperature. Gratifyingly, this dehydrogenation was efficiently accomplished in 18 min to give desired azobenzene **3a** in 52% yield. To improve the yield of **3a**, the amount of TCCA was increased and a modest yield improvement was observed (entries 2–4). What is intriguing is that the conversions (monitored by TLC) under these conditions were almost quantitative and the azo compound was the sole product. We speculated that hypochlorous acid was formed during the aqueous workup, which led to chlorination and/or oxidation of the reaction mixture. Such undesired reactions may cause erosion of the yields. Hence, after completion of the reactions (entries 5–7), we concentrated the reaction mixture to dryness without aqueous workup and purified the crude product directly. To our delight, this variation improved the yield to 85% (entry 6). However, further increasing the amount of TCCA to 2.5 equiv only enhanced the reaction rate without improving the yield (entry 7). With these benign conditions in hand, we set out to further evaluate this reaction by varying the solvent (entries 8–14). As indicated in Table 1, this oxidative dehydrogenation took place in various common solvents to yield the desired azobenzene in moderate to good yields. Toluene, DCM, acetonitrile, and DMF gave **3a** in moderate to good yields (entries 8–11). To our great delight, using aprotic ethers as solvent (entries 12–14), such as Et_2O, THF and methyl *tert*-butyl ether (MTBE), dramatically improved the reaction to generate desired product in excellent yields, especially THF gave the best result of 97% yield (entry 13). Afterwards, several control experiments were performed on this oxidative reaction in THF using 0.34, 1.0, and 1.5 equiv of TCCA to give

Table 1 Optimization of Oxidative Dehydrogenation of **1a** with TCCA[a]



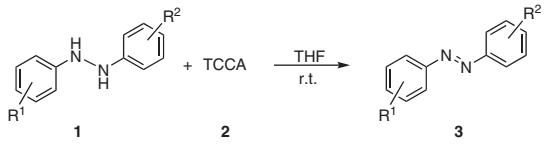
1a **2** **3a**

Entries	Molar ratio of **1a**/**2**	Solvent	Time (min)	Yield (%)[b]
1[c]	1.0:0.34	EtOH	18	52
2[c]	1.0:1.0	EtOH	15	65
3[c]	1.0:1.5	EtOH	9	72
4[c]	1.0:2.0	EtOH	6	78
5	1.0:1.5	EtOH	10	76
6	1.0:2.0	EtOH	6	85
7	1.0:2.5	EtOH	3	84
8	1.0:2.0	toluene	20	65
9	1.0:2.0	DCM	15	66
10	1.0:2.0	MeCN	25	71
11	1.0:2.0	DMF	15	86
12	1.0:2.0	Et_2O	13	91
13	1.0:2.0	THF	15	97
14	1.0:2.0	MTBE	14	91
15	1.0:0.34	THF	42	50
16	1.0:1.0	THF	35	55
17	1.0:1.5	THF	25	76
18[d]	1.0:2.0	THF	32	63
19[e]	1.0:1.0	THF	30	58
20[e]	1.0:2.0	THF	15	95
21[f]	1.0:2.0	THF	16	94

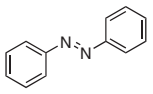
[a] Reaction conditions: **1a** (0.3 mmol), solvent (1.5 mL), r.t., air; concentration of the reaction mixture and direct purification of the crude product by chromatography (silica gel).
[b] Isolated yield.
[c] The reaction were quenched with water.
[d] Et_3N (3.0 equiv) was added and the reaction was carried out at 0 °C.
[e] K_2CO_3 (3.0 equiv) was added.
[f] The reaction was carried out under argon atmosphere.

the desired **3a** in 50%, 55%, and 76% yields (entries 15–17). However, when compared with the conditions using 2.0 equiv of TCCA (entry 13), reducing the ratio of TCCA increased the reaction time and led to unidentified side reactions with a dramatic deterioration in yield. Next the acid binding agents Et_3N and K_2CO_3 were added to try to reduce

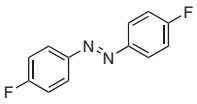
Table 2 Scope of Diphenylhydrazines for Oxidative Dehydrogenation[a,b]



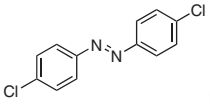
1 2 3



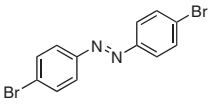
3a
97% yield, 15 min;
Scale-up: 97% yield, 18 min, 954 mg



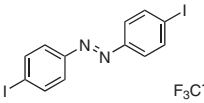
3b
91% yield, 13 min



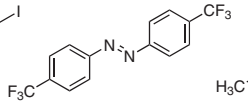
3c
89% yield, 14 min



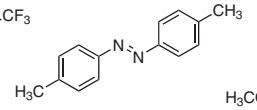
3d
89% yield, 16 min



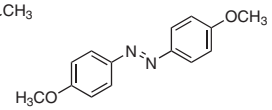
3e
91% yield, 17 min



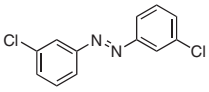
3f
92% yield, 12 min



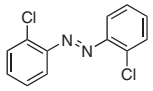
3g
92% yield, 14 min



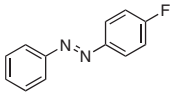
3h
82% yield, 12 min



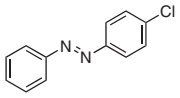
3i
87% yield, 14 min



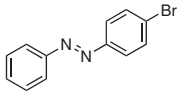
3j[c]
81% yield, 16 min



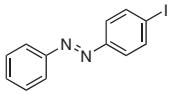
3k
88% yield, 16 min



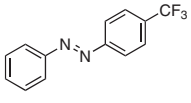
3l
89% yield, 16 min



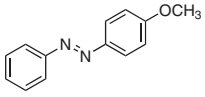
3m
92% yield, 14 min



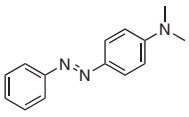
3n
93% yield, 14 min



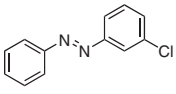
3o
93% yield, 14 min



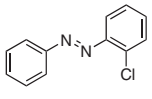
3p
88% yield, 11 min



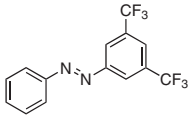
3q
90% yield, 13 min



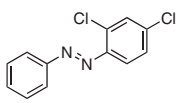
3r
91% yield, 12 min



3s
82% yield, 12 min



3t
93% yield, 14 min



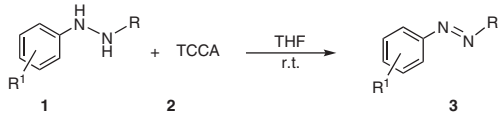
3u
93% yield, 13 min

[a] Reaction conditions: **1** (0.3 mmol), TCCA (**2**; 0.6 mmol), THF (1.5 mL), r.t.
[b] Isolated yield.
[c] The reaction was carried out at –10 °C.

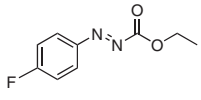
the consumption of TCCA (entries 18–20). Disappointingly, these variations did not decrease the ratio of TCCA. The addition of Et_3N resulted in severe exotherm, which was believed to lead to many side-reactions. Even when the reaction was carried out at 0 °C, this oxidative reaction with 2.0 equiv of TCCA just gave 63% yield of azo compound **3a** after 32 min (entry 18). On the other hand, employing 1.0 or 2.0 equiv of TCCA with 3.0 equiv of inorganic base K_2CO_3 neither improved nor reduced the reaction results (entries 19 and 20). These preliminary results indicate that the addition of base did not improve the reaction or decrease the amount of TCCA. Finally, this oxidative dehydrogenation was carried out under an argon atmosphere in THF (entry 21). The results indicated that oxygen is not responsible for this oxidation. Considering the above investigations, the optimized conditions consisted of performing the oxidative dehydrogenation reaction of hydrazines with TCCA (2.0 equiv) at room temperature using THF as the solvent.

With the optimum reaction conditions in hand, we proceeded to investigate the suitability of substrates. As shown in Table 2, symmetrical substituted diphenylhydrazines bearing substituents with different electronic properties were firstly submitted to the dehydrogenation. As expected, a series of bis(4-substituted phenyl)hydrazines **1a**–**1h** were found to function very well in this reaction and gave excellent yields of the corresponding products **3a**–**3h** (82–97%). In particular, the electron-donating group (Me, OMe) substituted bis(*p*-tolyl)hydrazine (**1g**) and bis(4-methoxyphenyl)hydrazine (**1h**) were also compatible with this protocol and gave the desired products **3g** and **3h** in good

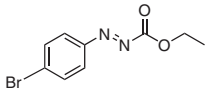
Table 3 Scope of 2-Phenylhydrazine-1-carboxylates for Oxidative Dehydrogenation[a,b]



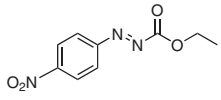
1 2 3



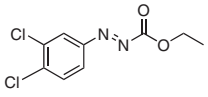
3v
92% yield, 13 min



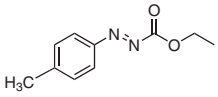
3w
91% yield, 15 min



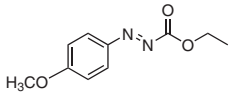
3x
94% yield, 15 min;
Scale-up: 96% yield, 20 min, 950 mg



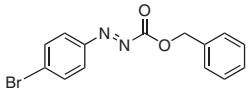
3y
92% yield, 12 min



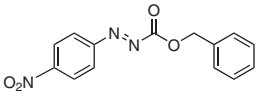
3z[c]
90 % yield, 7 min



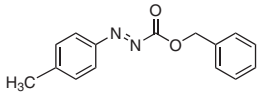
3aa[c]
86% yield, 9 min



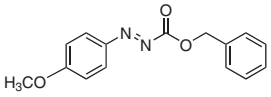
3ab
93% yield, 14 min



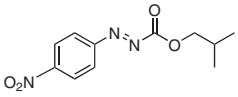
3ac
95% yield, 16 min



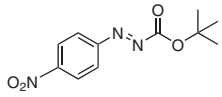
3ad[c]
88% yield, 7 min



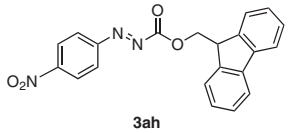
3ae[c]
85% yield, 7 min



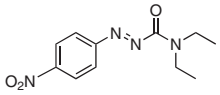
3af
95% yield, 16 min



3ag
95% yield, 16 min



3ah
88% yield, 15 min



3ai
91% yield,13 min

[a] Reaction conditions: **1** (0.3 mmol), TCCA (**2**; 0.6 mmol), THF (1.5 mL), r.t.
[b] Isolated yield
[c] THF was replaced by heptane/EtOH (2:1).

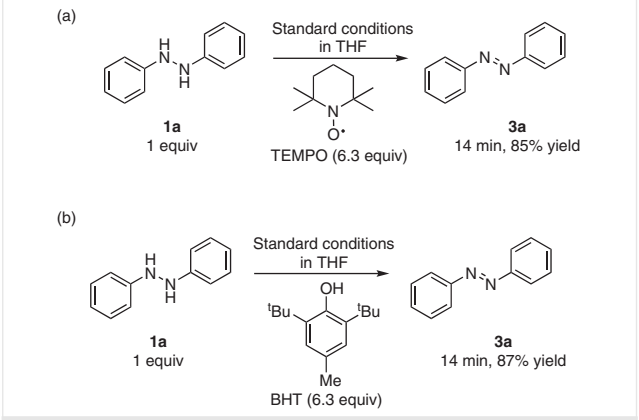
yields without any chlorination byproducts. Electronic effects seemed to have no remarkable influence on these dehydrogenation processes.

Then, hindered bis(3- and 2-chlorophenyl)hydrazines **1i** and **1j** were employed to investigate the hindrance effect on this conversion. Interestingly, bis(3-chlorophenyl)hydrazine (**1i**) was suitable reactant for this reaction, leading to the expected azobenzene **3i** in 87% yield. However, under the standard conditions, substrate **1j** merely gave desired **3j** in very low yield together with some unidentified byproducts. To overcome this problem, the reaction temperature was varied to decrease the reactivity of TCCA. We were pleased to find that when the reaction was carried out at –10 °C, the expected product **3j** was obtained in 81% yield. Furthermore, a wide range of unsymmetrical 1-(substituted phenyl)-2-phenylhydrazines **1k–1u** possessing various substituents on the phenyl ring were employed in this transformation. Unsymmetrical 1-(monosubstituted phenyl)-2-phenylhydrazines, with F, Cl, Br, I, CF_3, Me, and OMe **1k–1s** and even 1-(disubstituted phenyl)-2-phenylhydrazines **1t–1u** both behaved as well as the symmetrical bis(substituted phenyl)hydrazines bearing electron-withdrawing groups, regardless of the position of the substituent in the phenyl ring, see **1r** and **1s**. Notably, 1-(2-chlorophenyl)-2-phenylhydrazine (**1s**) smoothly provided azo compound **3s** in 82% yield without variation of the reaction temperature (compared with **1j**). Additionally, in order to prove the synthetic potential of this transformation, a gram-scale reaction of **1a** in THF was executed to obtain **3a** without reduction in the yield.

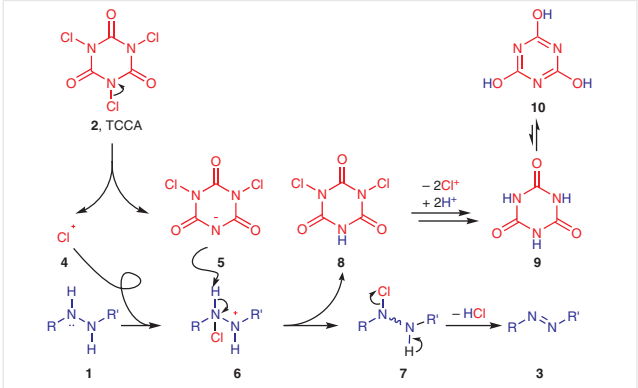
Encouraged by these positive results of oxidative dehydrogenation, we next sought to extend this benign methodology to various substituted 2-phenylhydrazine-2-carboxylates. As shown in Table 3, various alkyl (ethyl, Bn, *i*-Bu, *t*-Bu and 9-fluorenylmethyl) 2-phenylhydrazine-1-carboxylates bearing different substituents in the *para*-position of the phenyl ring **1v–1ah** were studied. It was found that the different alkyl groups were tolerated in this oxidative dehydrogenation and reacted to generate desired azo compounds in excellent yields (91–95% yields). Additionally, 2-phenylhydrazine-1-carboxamide **1ai** was also efficiently dehydrogenated, affording the desired azo compound **3ai** in 91% yield. However, electron-donating substituents (Me, OMe) in the *para*-position of the phenyl ring of 2-phenylhydrazine-1-carboxylates were substantially affected their reactivity. Under the standard conditions, hydrazines **1z**, **1aa**, **1ad** and **1ae** gave complexes instead of the desired products. To avoid this limitation, we adjusted reaction parameters, such as reaction temperature, concentration, and solvent, to decrease the reactivity and oxidation ability of TCCA. Gratifyingly, replacing THF by the co-solvent mixture heptane/EtOH (2:1) resulted in the corresponding azo compounds **3z**, **3aa**, **3ad**, and **3ae** in good yields (85–90% yields). Finally, the gram-scale reaction of representative hydrazine **1x** were also carried out in THF to prepare **3x** in 96% yield.

To gain further insight into the reaction mechanisms of this TCCA-based direct oxidative dehydrogenation of various hydrazines, common control experiments were performed. Firstly, the oxidative dehydrogenations of **1a** worked equally well under an argon atmosphere (Table 1, entry 21). This result indicates that oxygen is not the contributing oxidant in this oxidative dehydrogenation procedure. Then the oxidative dehydrogenation reaction of **1a** was performed in the presence of radical scavengers TEMPO and BHT (Scheme 2), but the reaction retains its reactivity to form **3a**. These results indicate that this oxidative dehydrogenation excludes a radical process. Additionally, the reaction of **1a** under the standard conditions in THF was monitored by ^{1}H NMR spectroscopy. Analysis of this reaction mixture revealed the presence of cyanuric acid.

Based on our control experimental results as well as other reports,[16a,20] the most plausible mechanism is proposed in Scheme 3. Initially, the heterolytic cleavage of TCCA (**2**) gives chlorinium ion (**4**) and dichlorocyanuric acid anion **5**. Subsequent electrophilic addition of hydrazine **1** with in situ formed chlorine cation **4** leads to *N*-chlorohydrazine cation **6**, which transfers a proton to intermediate



Scheme 2 Control experiments



Scheme 3 Plausible reaction mechanism

anion **5** to generate *N*-chlorohydrazine **7** and dichlorocyanuric acid **8**. Final *N*-chlorohydrazine **7** eliminates HCl to produce the desired azo compound **2**. Meanwhile, the intermediate dichlorocyanuric acid **8** takes part in the subsequent similar process to furnish cyanuric acid **10** via isomerization of the isocyanuric acid intermediate **9**.

In conclusion, we have developed an efficient, metal-free, and benign method for the oxidation of hydrazines leading to diverse azo compounds using commercial and environmentally friendly TCCA as chemical oxidant. This oxidative dehydrogenation protocol exhibits a reasonably broad substrate scope and good functional group compatibility. Meanwhile, the gram-scale preparation of azo compounds makes this benign protocol very practical and with more applications in the future. Additional studies on other mild oxidations mediated by TCCA are underway in our group.

All solvents were dried according to standard methods prior to use. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica gel 60 (300–400 mesh). Analytical TLC was performed using silica gel (silica gel 60 F254). TLC plates were analyzed by exposure to UV light. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz or 600 MHz and 100 MHz or 150 MHz, respectively. NMR experiments were carried out in $CDCl_3$ and are reported relative to internal TMS (δ = 0.00 for ^{1}H NMR), residual $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.00 for ^{13}C NMR). Melting points are uncorrected. HRMS were recorded on Q-Exactive and Micro TOF-QII mass instrument (ESI). All starting materials were prepared according to literature procedures: **1a**,[21] **1b–1h**,[13c] **1i–1j**,[22] **1k–1u**,[13c] **1v–1ai**.[23]

Azo Compounds 3; General Procedure

To a 10-mL flame-dried round-bottom flask equipped with a stirrer bar were added hydrazine **1** (0.3 mmol) and THF (1.5 mL). Then TCCA **2** (2.0 equiv) was added in portions and the resulting mixture was stirred at r.t. until all the starting material had been completely consumed (TLC monitoring; for reaction times see Tables 2 and 3). The mixture was evaporated under reduced pressure and the residue was purified by column chromatography (heptane/EtOAc 20:1–3:1) to obtain the desired azo compound **3**.

(*E*)-1,2-Diphenyldiazene (3a)[14aa]

Orange solid; yield: 54 mg (97%); mp 67–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.91 (m, 4 H), 7.55–7.45 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 131.0, 129.1, 122.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{11}N_2$: 183.09167; found: 183.09171.

(*E*)-1,2-Bis(4-fluorophenyl)diazene (3b)[14aa]

Orange solid; yield: 60 mg (91%); mp 100–101 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.89 (m, 4 H), 7.21–7.15 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 250 Hz), 148.9 (d, *J* = 2.0 Hz), 124.8 (d, *J* = 9.0 Hz), 116.0 (d, *J* = 23 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9F_2N_2$: 219.07283; found: 219.07283.

(*E*)-1,2-Bis(4-chlorophenyl)diazene (3c)[14aa]

Orange solid; yield: 67 mg (89%); mp 190–191 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.84 (m, 4 H), 7.50–7.47 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 137.2, 129.4, 124.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9Cl_2N_2$: 251.01373; found: 251.01373.

(*E*)-1,2-Bis(4-bromophenyl)diazene (3d)[14aa]

Orange solid; yield: 91 mg (89%); mp 203–204 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 4 H), 7.65 (d, *J* = 8.4 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 132.4, 125.8, 124.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9Br_2N_2$: 338.91270; found: 338.91272.

(*E*)-1,2-Bis(4-iodophenyl)diazene (3e)

Orange solid; yield: 119 mg (91%); mp >230 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.85 (m, 4 H), 7.66–7.62 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 138.4, 124.5, 98.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9I_2N_2$: 434.88496; found: 434.88495.

(*E*)-1,2-Bis[4-(trifluoromethyl)phenyl]diazene (3f)[14aa]

Orange solid; yield: 88 mg (92%); mp 101–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 4 H), 7.80 (d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 133.0 (q, *J* = 32 Hz), 126.4 (q, *J* = 4 Hz), 123.8 (q, *J* = 270 Hz), 123.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9F_6N_2$: 319.06644; found: 319.09012.

(*E*)-1,2-Di-*p*-tolyldiazene (3g)[14aa]

Orange solid; yield: 59 mg (92%); mp 140–142 °C.

^{1}H NMR 400 MHz, ($CDCl_3$): δ = 7.81 (d, *J* = 8.4 Hz, 4 H), 7.30 (d, *J* = 8.0 Hz, 4 H), 2.42 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.8, 141.2, 129.7, 122.7, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}N_2$: 211.12298; found: 211.12305.

(*E*)-1,2-Bis(4-methoxyphenyl)diazene (3h)[14aa]

Orange solid; yield: 60 mg (82%); mp 163–165 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.8 Hz, 4 H), 7.00 (d, *J* = 9.2 Hz, 4 H), 3.88 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.5, 147.1, 124.3, 114.1, 55.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}N_2O_2$: 243.11280; found: 243.11281.

(*E*)-1,2-Bis(3-chlorophenyl)diazene (3i)[9f]

Orange solid; yield: 66 mg (87%); mp 97–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 2 H), 7.85–7.83 (m, 2 H), 7.48–7.47 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.1, 135.2, 131.2, 130.2, 122.6, 121.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9Cl_2N_2$: 251.01373; found: 251.01382.

(*E*)-1,2-Bis(2-chlorophenyl)diazene (3j)

Orange solid; yield: 62 mg (81%); mp 130–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 2 H), 7.58–7.56 (m, 2 H), 7.44–7.34 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.8, 135.8, 132.2, 130.7, 127.4, 118.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9Cl_2N_2$: 251.01373; found: 251.01384.

(*E*)-1-(4-Fluorophenyl)-2-phenyldiazene (3k)[14aa]

Orange solid; yield: 53 mg (88%); mp 77–79 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94–7.89 (m, 4 H), 7.51–7.43 (m, 3 H), 7.19–7.15 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 250.5 Hz), 152.4, 149.1 (d, *J* = 3.0 Hz), 131.0, 129.1, 124.8 (d, *J* = 9.0 Hz), 122.8, 116.0 (d, *J* = 22.5 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}FN_2$: 201.08225; found: 201.08244.

(*E*)-1-(4-Chlorophenyl)-2-phenyldiazene (3l)[14aa]

Orange solid; yield: 58 mg (89%); mp 86–87 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.84 (m, 4 H), 7.54–7.46 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 150.9, 136.9, 131.2, 129.3, 129.1, 124.1, 122.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}ClN_2$: 217.05270; found: 217.05270.

(*E*)-1-(4-Bromophenyl)-2-phenyldiazene (3m)[14aa]

Orange solid; yield: 72 mg (92%); mp 87–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.90 (m, 2 H), 7.82–7.79 (m, 2 H), 7.67–7.63 (m, 2 H), 7.55–7.47 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 151.3, 132.3, 131.3, 129.1, 125.3, 124.3, 122.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}BrN_2$: 261.00219; found: 261.00217.

(*E*)-1-(4-Iodophenyl)-2-phenyldiazene (3n)[14z]

Orange solid; yield: 87 mg (93%); mp 105–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.83 (m, 4 H), 7.68–7.62 (m, 2 H), 7.54–7.46 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 152.1, 138.6, 131.6, 129.4, 124.7, 123.2, 97.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}IN_2$: 308.98832; found: 308.98822.

(*E*)-1-Phenyl-2-[4-(trifluoromethyl)phenyl]diazene (3o)[14aa]

Orange solid; yield: 70 mg (93%); mp 95–96 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2 H), 7.95–7.93 (m, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.54–7.50 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.4, 152.4, 132.2 (q, *J* = 33 Hz), 131.8, 129.2, 126.3 (q, *J* = 4.5 Hz), 123.9 (q, *J* = 271.5 Hz), 123.2, 123.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}F_3N_2$: 251.07906; found: 251.07856.

(*E*)-1-(4-Methoxyphenyl)-2-phenyldiazene (3p)[14aa]

Orange solid; yield: 56 mg (88%); mp 53–54 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.87 (m, 4 H), 7.52–7.42 (m, 3 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 152.7, 147.0, 130.3, 129.0, 124.7, 122.5, 114.2, 55.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}N_2O$: 213.10224; found: 213.10223.

(*E*)-*N*,*N*-Dimethyl-4-(phenyldiazenyl)aniline (3q)

Orange solid; yield: 61 mg (90%); mp 115–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.83 (m, 4 H), 7.49–7.45 (m, 2 H), 7.39–7.35 (m, 1 H), 6.76 (d, *J* = 9.2 Hz, 2 H), 3.08 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 152.4, 143.6, 129.3, 128.9, 124.9, 122.2, 111.5, 40.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{16}N_3$: 226.13387; found: 226.13398.

(*E*)-1-(3-Chlorophenyl)-2-phenyldiazene (3r)

Orange solid; yield: 59 mg (91%); mp 64–65 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 3 H), 7.83–7.81 (m, 1 H), 7.52–7.46 (m, 3 H), 7.43–7.41 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.4, 152.3, 135.1, 131.5, 130.6, 130.1, 129.1, 123.0, 122.3, 121.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}ClN_2$: 217.05270; found: 217.05273.

(*E*)-1-(2-Chlorophenyl)-2-phenyldiazene (3s)

Orange oil; yield: 53 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.97 (m, 2 H), 7.71–7.69 (m, 1 H), 7.57–7.50 (m, 4 H), 7.42–7.33 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.8, 148.7, 135.3, 131.6, 131.5, 130.7, 129.1, 127.3, 123.3, 117.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}ClN_2$: 217.05270; found: 217.05270.

(*E*)-1-[3,5-Bis(trifluoromethyl)phenyl]-2-phenyldiazene (3t)

Orange solid; yield: 89 mg (93%); mp 70–71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (s, 2 H), 7.99–7.96 (m, 3 H), 7.57–7.55 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 152.0, 132.7 (q, *J* = 34 Hz), 132.5, 129.3, 123.8 (q, *J* = 4 Hz), 123.4, 123.1 (q, *J* = 271 Hz), 123.0 (d, *J* = 4 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9F_6N_2$: 319.06644; found: 319.06644.

(*E*)-1-(2,4-Dichlorophenyl)-2-phenyldiazene (3u)

Orange solid; yield: 70 mg (93%); mp 107–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.94 (m, 2 H), 7.66 (d, *J* = 8.8 Hz, 1 H), 7.56 (d, *J* = 2.4 Hz, 1 H),7.54–7.47 (m, 3 H), 7.30 (dd, *J* = 8.8, 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 147.1, 137.1, 136.2, 131.8, 130.4, 129.2, 127.7, 123.4, 118.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9Cl_2N_2$: 251.01373; found: 251.01375.

Ethyl (*E*)-2-(4-Fluorophenyl)diazene-1-carboxylate (3v)[14i]

Orange oil; yield: 55 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.96 (m, 2 H), 7.27–7.19 (m, 2 H), 4.52 (q, *J* = 7.2 Hz, 2 H), 1.47 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1 (d, *J* = 255 Hz), 161.9, 148.1 (d, *J* = 3 Hz), 126.2 (d, *J* = 9.0 Hz), 116.5 (d, *J* = 23 Hz), 64.5, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{10}FN_2O_2$: 197.07208; found: 197.07207.

Ethyl (*E*)-2-(4-Bromophenyl)diazene-1-carboxylate (3w)[14i]

Orange oil; yield: 70 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.79 (m, 2 H), 7.69–7.67 (m, 2 H), 4.53 (q, *J* = 7.2 Hz, 2 H), 1.47 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 150.2, 132.7, 128.9, 125.1, 64.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{10}BrN_2O_2$: 256.99202; found: 256.99158.

Ethyl (*E*)-2-(4-Nitrophenyl)diazene-1-carboxylate (3x)[14i]

Orange solid; yield: 63 mg (94%); mp 58–59 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42–8.39 (m, 2 H), 8.08–8.04 (m, 2 H), 4.56 (q, *J* = 7.2 Hz, 2 H), 1.49 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 154.2, 150.3, 124.8, 124.2, 65.0, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{10}N_3O_4$: 224.06658; found: 224.06596.

Ethyl (*E*)-2-(3,4-Dichlorophenyl)diazene-1-carboxylate (3y)[14i]

Orange solid; yield: 69 mg (92%); mp 43–44 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 2.4 Hz, 1 H), 7.81 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.64 (d, *J* = 8.8 Hz, 1 H), 4.53 (q, *J* = 7.2 Hz, 2 H), 1.48 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 150.2, 138.1, 134.0, 131.2, 124.6, 123.6, 64.8, 14.1.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_9H_7Cl_2N_2O_2$: 244.98791; found: 244.99680.

Ethyl (*E*)-2-(*p*-Tolyl)diazene-1-carboxylate (3z)[14i]

Orange oil; yield: 52 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 4.52 (q, *J* = 7.2 Hz, 2 H), 2.45 (s, 3 H) 1.47 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 149.8, 145.2, 130.0, 123.9, 64.3, 21.7, 14.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{13}N_2O_2$: 193.09715; found: 193.09712.

Ethyl (*E*)-2-(4-Methoxyphenyl)diazene-1-carboxylate (3aa)[14i]

Orange oil; yield: 54 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 2 H), 7.03–6.99 (m, 2 H), 4.51 (q, *J* = 7.2 Hz, 2 H), 3.91 (s, 3 H) 1.47 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 162.1, 146.1, 126.5, 114.5, 64.2, 55.7, 14.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{13}N_2O_3$: 209.09207; found: 209.09203.

Benzyl (*E*)-2-(4-Bromophenyl)diazene-1-carboxylate (3ab)

Orange solid; yield: 89 mg (93%); mp 75–76 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.75 (m, 2 H), 7.66–7.64 (m, 2 H), 7.49–7.46 (m, 2 H), 7.43–7.35 (m, 3 H), 5.46 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 150.2, 134.2, 132.6, 128.9, 128.9, 128.7, 128.7, 125.1, 70.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{12}BrN_2O_2$: 319.00767; found: 319.00052.

Benzyl (*E*)-2-(4-Nitrophenyl)diazene-1-carboxylate (3ac)

Orange solid; yield: 81 mg (95%); mp 116–118 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.39–8.37 (m, 2 H), 8.05–8.02 (m, 2 H), 7.49–7.48 (m, 2 H), 7.43–7.38 (m, 3 H), 5.49 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.4, 154.2, 150.3, 134.0, 129.1, 128.8, 128.8, 124.8, 124.3, 70.4.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{10}N_3O_4$: 284.06658; found: 284.06772.

Benzyl (*E*)-2-(*p*-Tolyl)diazene-1-carboxylate (3ad)

Orange oil; yield: 68 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2 H), 7.50–7.47 (m, 2 H), 7.42–7.36 (m, 3 H), 7.32–7.29 (m, 2 H), 5.46 (s, 2 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 149.8, 145.3, 134.5, 129.9, 128.8, 128.7, 128.7, 124.0, 69.8, 21.7.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{13}N_2O_2$: 253.09715; found: 253.09718.

Benzyl (*E*)-2-(4-Methoxyphenyl)diazene-1-carboxylate (3ae)

Orange solid; yield: 69 mg (85%); mp 44–45 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.93 (m, 2 H), 7.50–7.47 (m, 2 H), 7.42–7.34 (m, 3 H), 7.00–6.96 (m, 2 H), 5.45 (s, 2 H), 3.88 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.7, 162.0, 146.1, 134.6, 128.7, 128.7, 128.6, 126.5, 114.4, 69.6, 55.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}N_2O_3$: 271.10772; found: 271.10770.

Isobutyl (*E*)-2-(4-Nitrophenyl)diazene-1-carboxylate (3af)

Orange solid; yield: 72 mg (95%); mp 41–43 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.39 (m, 2 H), 8.08–8.05 (m, 2 H), 4.28 (d, *J* = 6.8 Hz, 2 H), 2.21–2.11 (m, 1 H), 1.05 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 154.2, 150.2, 124.8, 124.2, 74.6, 27.8, 18.8.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{11}H_{12}N_3O_4$: 250.08223; found: 250.08266.

tert-Butyl (*E*)-2-(4-Nitrophenyl)diazene-1-carboxylate (3ag)

Orange solid; yield: 72 mg (95%); mp 135–136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41–8.37 (m, 2 H), 8.04–8.01 (m, 2 H), 1.68 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 154.4, 150.1, 124.7, 124.1, 86.1, 27.8.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{11}H_{12}N_3O_4$: 250.08223; found: 250.08490.

9*H*-Fluoren-9-ylmethyl (*E*)-2-(4-Nitrophenyl)diazene-1-carboxylate (3ah)

Orange solid; yield: 99 mg (88%); mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.39 (m, 2 H), 8.11–8.07 (m, 2 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.68–7.61 (m, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 4.75–4.72 (m, 2 H), 4.41 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 154.2, 150.4, 142.8, 141.3, 128.1, 127.3, 125.1, 124.8, 124.4, 120.2, 70.4, 46.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{15}N_3O_4Na$: 396.09548; found: 396.09523.

(*E*)-*N*,*N*-Diethyl-2-(4-nitrophenyl)diazene-1-carboxamide (3ai)

Orange solid; yield: 68 mg (91%); mp 101–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 2 H), 8.04 (d, *J* = 8.8 Hz, 2 H), 3.61 (q, *J* = 6.8 Hz, 2 H), 3.52 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 6.8 Hz, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 154.7, 149.8, 124.7, 123.9, 41.9, 41.7, 14.4, 12.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{15}N_4O_3$: 251.11387; found: 251.11383.

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Supporting Information

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References

(1) (a) Zollinger, H. *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments, 3rd ed*; VHCA/Wiley-VCH: Zürich/Weinheim, **2003**. (b) *Industrial Dyes: Chemistry, Properties, Applications*; Hunger, K., Ed.; Wiley-VCH: Weinheim, **2003**, 20. (c) Chudgar, R. J. *Azo Dyes*, In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: Chichester, **2001**, 425. (d) Merino, E. *Chem. Soc. Rev.* **2011**, *40*, 3835.

(2) (a) Nørager, N. G.; Poulsen, M. H.; Strømgaard, K. *J. Med. Chem.* **2018**, *61*, 8048. (b) Wong, P. T.; Choi, S. K. *Chem. Rev.* **2015**, *115*, 3388. (c) Lee, S. H.; Moroz, E.; Castagner, B.; Leroux, J.-C. *J. Am. Chem. Soc.* **2014**, *136*, 12868. (d) Sandborn, W. J. *Am. J. Gastroenterol.* **2002**, *97*, 2939. (e) DiCesare, N.; Lakowicz, J. R. *Org. Lett.* **2001**, *3*, 3891. (f) Yamaoka, T.; Makita, Y.; Sasatani, H.; Kim, S.-I.; Kimura, Y. *J. Controlled Release* **2000**, *66*, 187. (g) Singh, A. K.; Das, J.; Majumdar, N. *J. Am. Chem. Soc.* **1996**, *118*, 6185.

(3) (a) Tang, S.; Deng, Y.-L.; Li, J.; Wang, W.-X.; Wang, Y.-C.; Li, Z.-Z.; Yuan, L.; Chen, S.-L.; Sheng, R.-L. *Chem. Commun.* **2016**, *52*, 4470. (b) Ibrahim, A. A.; Golonka, A. N.; Lopez, A. M.; Stockdill, J. L. *Org. Lett.* **2014**, *16*, 1072. (c) Larraufie, M.-H.; Courillon, C.; Ollivier, C.; Lacôte, E.; Malacria, M.; Fensterbank, L. *J. Am. Chem. Soc.* **2010**, *132*, 4381. (d) Sha, C.-K.; Hsu, C.-W.; Chen, Y.-T.; Cheng, S.-Y. *Tetrahedron Lett.* **2000**, *41*, 9865.

(4) (a) Hüll, K.; Morstein, J.; Trauner, D. *Chem. Rev.* **2018**, *118*, 10710. (b) Bandara, H. M. D.; Burdette, S. C. *Chem. Soc. Rev.* **2012**, *41*, 1809. (c) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422. (d) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (e) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915. (f) Gorostiza, P.; Isacoff, E. Y. *Science* **2008**, *322*, 395. (g) Banghart, M.; Borges, K.; Isacoff, E.; Trauner, D.; Kramer, R. H. *Nat. Neurosci.* **2004**, *7*, 1381. (h) Bushuyev, O. S.; Tomberg, A.; Friščić, T.; Barrett, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 12556. (i) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Vögtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714. (j) Cisnetti, F.; Ballardini, R.; Credi, A.; Gandolfi, M. T.; Masiero, S.; Negri, F.; Pieraccini, S.; Spada, G. P. *Chem. Eur. J.* **2004**, *10*, 2011. (k) Commins, P.; Garcia-Garibay, M. A. *J. Org. Chem.* **2014**, *79*, 1611.

(5) (a) Arslan, T. *J. Chem. Res.* **2018**, *42*, 267. (b) Gingell, R.; Bridges, J. W. *Xenobiotica* **1973**, *3*, 599.

(6) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. P. *Chem. Rev.* **2009**, *109*, 2551.

(7) (a) Lau, Y.-F.; Chan, C.-M.; Zhou, Z.; Yu, W.-Y. *Org. Biomol. Chem.* **2016**, *14*, 6821. (b) Nair, V.; Biju, A. T.; Mathew, S. C.; Babu, B. P. *Chem. Asian J.* **2008**, *3*, 810.

(8) Ling, Y.; Geng, X.; Jiao, N. *Green Oxidative Synthesis of Azo, Diazo, and Azido Compounds*, In *Green Oxidation in Organic Synthesis*; Jiao, N.; Stahl, S. S., Ed.; John Wiley & Sons: Hoboken, **2019**, 221.

(9) (a) Saha, A.; Payra, S.; Selvaratnam, B.; Bhattacharya, S.; Pal, S.; Koodali, R. T.; Banerjee, S. *ACS Sustainable Chem. Eng.* **2018**, *6*, 11345. (b) John, A. A.; Lin, Q. *J. Org. Chem.* **2017**, *82*, 9873. (c) Dutta, B.; Biswas, S.; Sharma, V.; Savage, N.; Alpay, S.; Suib, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 2171. (d) Seth, K.; Roy, S. R.; Kumar, A.; Chakraborti, A. K. *Catal. Sci. Technol.* **2016**, *6*, 2892. (e) Cai, S.; Rong, H.; Yu, X.; Liu, X.; Wang, D.; He, W.; Li, Y. *ACS Catal.* **2013**, *3*, 478. (f) Zhu, Y.; Shi, Y. *Org. Lett.* **2013**, *15*, 1942. (g) Okumura, S.; Lin, C.-H.; Takeda, Y.; Minakata, S. *J. Org. Chem.* **2013**, *78*, 12090. (h) Monir, K.; Ghosh, M.; Mishra, S.; Majee, A.; Hajra, A. *Eur. J. Org. Chem.* **2014**, *2014*, 1096. (i) Takeda, Y.; Okumura, S.; Minakata, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 7804. (j) Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6174. (k) Grirrane, A.; Corma, A.; García, H. *Science* **2008**, *322*, 1661. (l) Lim, Y.-K.; Lee, K.-S.; Cho, C.-G. *Org. Lett.* **2003**, *5*, 979. (m) Noureldin, N. A.; Bellegarde, J. W. *Synthesis* **1999**, 939. (n) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326. (o) Wawzonek, S.; McIntyre, T. W. *J. Electrochem. Soc.* **1972**, *119*, 1350. (p) Baer, E.; Tosoni, A. L. *J. Am. Chem. Soc.* **1956**, *78*, 2857.

(10) (a) Qiu, J.; Xiao, J.; Tang, B.; Ju, B.; Zhang, S. *Dyes Pigm.* **2019**, *160*, 524. (b) Wang, J.; Wu, B.; Li, S.; Sinawang, G.; Wang, X.; He, Y. *ACS Sustainable Chem. Eng.* **2016**, *4*, 4036. (c) He, Y.; He, W.; Wei, R.; Chen, Z.; Wang, X. *Chem. Commun.* **2012**, *48*, 1036. (d) Dabbagh, H. A.; Teimouri, A.; Chermahini, A. N. *Dyes Pigm.* **2007**, *73*, 239. (e) Barbero, M.; Cadamuro, S.; Dughera, S.; Giaveno, C. *Eur. J. Org. Chem.* **2006**, *2006*, 4884. (f) Tomasulo, M.; Raymo, F. M. *Org. Lett.* **2005**, *7*, 4633. (g) Gung, B. W.; Taylor, R.

T. *J. Chem. Educ.* **2004**, *81*, 1630. (h) Haghbeen, K.; Tan, E. W. *J. Org. Chem.* **1998**, *63*, 4503. (i) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R.; Perracino, P. *Synthesis* **1998**, 1235.

(11) (a) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, *104*, 3315. (b) Tie, C.; Gallucci, J. C.; Parquette, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 1162. (c) Ibne-Rasa, K. M.; Lauro, C. G.; Edwards, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 1165. (d) Ueno, K.; Akiyoshi, S. *J. Am. Chem. Soc.* **1954**, *76*, 3670.

(12) (a) Zhang, Y.-F.; Mellah, M. *ACS Catal.* **2017**, *7*, 8480. (b) Moormann, W.; Langbehn, D.; Herges, R. *Synthesis* **2017**, *49*, 3471. (c) Hu, L.; Cao, X.; Chen, L.; Zheng, J.; Lu, J.; Sun, X.; Gu, H. *Chem. Commun.* **2012**, *48*, 3445. (d) Hu, L.; Cao, X.; Shi, L.; Qi, F.; Guo, Z.; Lu, J.; Gu, H. *Org. Lett.* **2011**, *13*, 5640. (e) Grirrane, A.; Corma, A.; Garcia, H. *Nat. Protoc.* **2010**, *5*, 429. (f) Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 9657. (g) Sakai, N.; Fujii, K.; Nabeshima, S.; Ikeda, R.; Konakahara, T. *Chem. Commun.* **2010**, *46*, 3173. (h) Wada, S.; Urano, M.; Suzuki, H. *J. Org. Chem.* **2002**, *67*, 8254.

(13) (a) Buncel, E. *Acc. Chem. Res.* **1975**, *8*, 132. (b) Zhang, Y.; Huang, C.; Lin, X.; Hu, Q.; Hu, B.; Zhou, Y.; Zhu, G. *Org. Lett.* **2019**, *21*, 2261. (c) Wang, L.; Ishida, A.; Hashidoko, Y.; Hashimoto, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 870. (d) Brenzovich, W. E.; Houk, R. J. T.; Malubay, S. M. A.; Miranda, J. O.; Ross, K. M.; Abelt, C. J. *Dyes Pigm.* **2002**, *52*, 101.

(14) (a) Tirapegui, C.; Acevedo-Fuentes, W.; Dahech, P.; Torrent, C.; Barrias, P.; Rojas-Poblete, M.; Mascayano, C. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 1649. (b) Donck, S.; Gravel, E.; Li, A.; Prakash, P.; Shah, N.; Leroy, J.; Li, H.; Namboothiri, I. N. N.; Doris, E. *Catal. Sci. Technol.* **2015**, *5*, 4542. (c) Gao, W.; He, Z.; Qian, Y.; Zhao, J.; Huang, Y. *Chem. Sci.* **2012**, *3*, 883. (d) Tšubrik, O.; Sillard, R.; Mäeorg, U. *Synthesis* **2006**, 843. (e) Wang, C.-L.; Wang, X.-X.; Wang, X.-Y.; Xiao, J.-P.; Wang, Y.-L. *Synth. Commun.* **1999**, *29*, 3435. (f) LeFevre, G. N.; Crawford, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 1019. (g) Gaviraghi, G.; Pinza, M.; Pifferi, G. *Synthesis* **1981**, 608. (h) Dimroth, K.; Tüncher, W. *Synthesis* **1977**, 339. (i) Kim, M. H.; Kim, J. *J. Org. Chem.* **2018**, *83*, 1673. (j) Hashimoto, T.; Hirose, D.; Taniguchi, T. *Adv. Synth. Catal.* **2015**, *357*, 3346. (k) Company, A.; Yao, S.; Ray, K.; Driess, M. *Chem. Eur. J.* **2010**, *16*, 9669. (l) Trischler, F. *J. Therm. Anal. Calorim.* **1979**, *16*, 119. (m) Drug, E.; Gozin, M. *J. Am. Chem. Soc.* **2007**, *129*, 13784. (n) Jürmann, G.; Tšubrik, O.; Tammeveski, K.; Mäeorg, U. *J. Chem. Res.* **2005**, *2005*, 661. (o) Starr, J. T.; Rai, G. S.; Dang, H.; McNelis, B. J. *Synth. Commun.* **1997**, *27*, 3197. (p) Molina, C. L.; Chow, C. P.; Shea, K. J. *J. Org. Chem.* **2007**, *72*, 6816. (q) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1981**, *46*, 1564. (r) Gephart, R. T. III.; Huang, D. L.; Aguila, M. J. B.; Schmidt, G.; Shahu, A.; Warren, T. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 6488. (s) Church, R. F. R.; Weiss, M. J. *J. Org. Chem.* **1970**, *35*, 2465. (t) Štefane, B.; Polanc, S. *Synlett* **2008**, 1279. (u) Mihara, M.; Nakai, T.; Iwai, T.; Ito, T.; Mizuno, T. *Synlett* **2007**, 2124. (v) Bai, L.-S.; Gao, X.-M.; Zhang, X.; Sun, F.-F.; Ma, N. *Tetrahedron Lett.* **2014**, *55*, 4545. (w) Barth, M.; Shah, S. T. A.; Rademann, J. *Tetrahedron* **2004**, *60*, 8703. (x) Sahoo, M. K.; Saravanakumar, K.; Jaiswal, G.; Balaraman, E. *ACS Catal.* **2018**, *8*, 7727. (y) Lv, H.; Laishram, R. D.; Li, J.; Zhou, Y.; Xu, D.; More, S.; Dai, Y.; Fan, B. *Green Chem.* **2019**, *21*, 4055. (z) Wang, X.; Wang, X.; Xia, C.; Wu, L. *Green Chem.* **2019**, *21*, 4189. (aa) Du, K.-S.; Huang, J.-M. *Green Chem.* **2019**, *21*, 1680.

(15) (a) Tilstam, U.; Weinmann, H. *Org. Process. Res. Dev.* **2002**, *6*, 384. (b) Mendonca, G.; de Mattos, M. *Curr. Org. Synth.* **2013**, *10*, 820. (c) Gaspa, S.; Carraro, M.; Pisano, L.; Porcheddu, A.; De Luca, L. *Eur. J. Org. Chem.* **2019**, *2019*, 3544. (d) Blotny, G. *Tetrahedron* **2006**, *62*, 9507. (e) Barros, J. C. *Synlett* **2005**, 2115.

(16) (a) Gaspa, S.; Porcheddu, A.; De Luca, L. *Adv. Synth. Catal.* **2016**, *358*, 154. (b) Jing, Y.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2014**, *16*, 4932. (c) De Luca, L.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041. (d) De Luca, L.; Giacomelli, G.; Masala, S.; Porcheddu, A. *J. Org. Chem.* **2003**, *68*, 4999.

(17) (a) Viveros-Ceballos, J. L.; Sayago, F. J.; Cativiela, C.; Ordóñez, M. *Eur. J. Org. Chem.* **2015**, *2015*, 1084. (b) Azarifar, D.; Maleki, B. *J. Chin. Chem. Soc.* **2013**, *52*, 1215. (c) Tilstam, U.; Harre, M.; Heckrodt, T.; Weinmann, H. *Tetrahedron Lett.* **2001**, *42*, 5385.

(18) (a) Ye, J.; Wang, Y.; Liu, R.; Zhang, G.; Zhang, Q.; Chen, J.; Liang, X. *Chem. Commun.* **2003**, 2714. (b) Ye, J.; Wang, Y.; Chen, J.; Liang, X. *Adv. Synth. Catal.* **2004**, *346*, 691.

(19) (a) Zhang, W.; Su, Y.; Wang, K.-H.; Wu, L.; Chang, B.; Shi, Y.; Huang, D.; Hu, Y. *Org. Lett.* **2017**, *19*, 376. (b) Wen, L.; Huang, D.; Wang, K.-H.; Wang, Y.; Liu, L.; Yang, Z.; Su, Y.; Hu, Y. *Synthesis* **2018**, *50*, 1979. (c) Su, Y.; Shi, Y.; Chang, B.; Wu, L.; Chong, S.; Zhang, W.; Huang, D.; Wang, K.; Hu, Y. *Chin. J. Org. Chem.* **2018**, *38*, 1454. (d) Su, Y.; Zhao, Y.; Chang, B.; Zhao, X.; Zhang, R.; Liu, X.; Huang, D.; Wang, K.-H.; Huo, C.; Hu, Y. *J. Org. Chem.* **2019**, *84*, 6719.

(20) (a) van Summeren, R. P.; Romaniuk, A.; IJpeij, E. G.; Alsters, P. L. *Catal. Sci. Technol.* **2012**, *2*, 2052. (b) Veisi, H. *Synthesis* **2010**, 2631. (c) Filler, R. *Chem. Rev.* **1963**, *63*, 21.

(21) Zhang, Y.; Tang, Q.; Luo, M. *Org. Biomol. Chem.* **2011**, *9*, 4977.

(22) Khurana, J. M.; Ray, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 407.

(23) Urankar, D.; Steinbücher, M.; Kosjek, J.; Košmrlj, J. *Tetrahedron* **2010**, *66*, 2602.