# Organic & Biomolecular Chemistry

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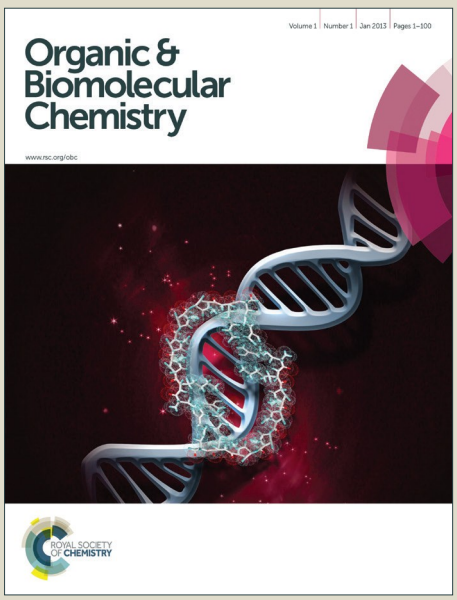





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Paper

# Palladium-catalyzed direct *ortho*-ethoxycarbonylation of azobenzenes and azoxybenzenes with diethyl azodicarboxylate

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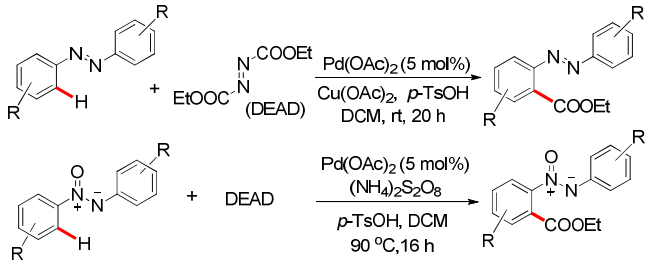
**The palladium-catalyzed direct *ortho*-ethoxycarbonylation of azobenzenes and azoxybenzenes with diethyl azodicarboxylate (DEAD) was developed. In the presence of $Cu(OAc)_2$ or $(NH_4)_2S_2O_8$ as oxidant, this protocol allowed using both electron-deficient and electron-rich azobenzenes and azoxybenzenes to produce the corresponding products in moderate to good yields.**

Aromatic azo compounds, as important building blocks, are widely used in many fields, such as industrial dyes, indicators, photochemical switches and protein probes.[1] As a result, great deals of attentions have been focused on the modification and functionalization of these compounds. As an important tool in regio-specific aromatic ring functionalization, there are a few of the examples of C−H activation directed by the azo group have been reported recently. Transition-metal-catalyzed *ortho*-acyloxylation,[2] halogenation,[3] arylation,[4] alkoxylation,[5] acylation,[6] amination,[7] amidation,[8] nitration,[9] phosphonation,[10] sulfonylation[11] and cyclization[12] of azobenzenes have been developed. Azoxy compounds are also important materials and useful intermediates in organic synthesis. An *ortho*-acylation of azoxybenzenes with α-oxocarboxylic acids by Pd-catalyzed C–H activation followed by decarboxylation and acylation,[13a] and other functionalizations have been reported.[13b,c] However, Pd-catalyzed direct C−H activation and ethoxycarbonylation of azobenzenes and azoxybenzenes has not yet been explored. To develop a highly efficient and simple method to access ortho-ethoxycarbonylation of azo and azoxy compounds is desirable.

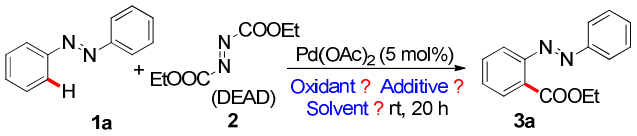
It is well known that esters are very useful commodity chemicals and vital synthetic building blocks, and they have been widely used as pharmaceutical industrial products, natural products and functional materials. Additionally, esters also serve as valuable intermediates in organic synthesis.[14] In 1980, Fujiwara first reported Pd-promoted one-step carboxylation of aromatic compounds utilizing CO and alcohols as the sources of ester groups.[15a] Subsequently, many efforts have been devoted to develop efficient C–H carboxylation reactions by using CO and $CO_2$ as the carboxylation reagent.[15b-h] However, the necessity to handle hazardous gas (CO) which is often in high pressure and the usage of pre-functionalized substrates restricting its application in organic synthesis. Therefore, the development of safe, easy handled and environmentally friendly CO-free strategies for alkoxycarbonylation is attracting widespread attention.[16] Recently, various carboxylation regents have been developed for the direct C–H carboxylation, such as azodicarboxylates,[17] alkyl chloroformates,[18] diaziridinone,[19] glyoxylates,[20] α-keto esters[21] and carbazates.[22] Among the above carboxylation reagents, azodicarboxylates are especially promising alkoxycarbonyl surrogates because they are readily available and are widely used in organic chemistry, but rarely used in the construction of esters. In 2008, Yu and co-workers developed the Pd-catalyzed oxidative ethoxycarboxylation of aromatic C–H bond with diethyl azodicarboxylate (DEAD).[17a] Most recently, Pd-catalyzed direct *ortho*-C–H ethoxycarboxylation of anilides was accomplished by You.[17b] Herein, we wish to report a Pd-catalyzed direct *ortho*-ethoxycarboxylation of azobenzenes and azoxybenzenes with diethyl azodicarboxylate (DEAD) under mild reaction conditions, providing the corresponding products in moderate to good yields (Scheme 1).




**Scheme 1** Alkoxycarbonylation of azobenzenes and azoxybenzenes with diethyl azodicarboxylate.

We initiated our studies by using azobenzene (**1a**) as substrate and diethyl azodicarboxylate (**2**) as ethoxycarbonylation reagent. The results are assembled in Table 1. In the presence of a catalytic amount of $Pd(OAc)_2$ (5 mol%) and $K_2S_2O_8$ (1.0 equiv) as oxidant, the model reaction carried out in dichloromethane (DCM) at ambient temperature for 20 h generated the desired product **3a** in 40% yield (Table 1, entry 1). A slightly low yield of **3a** was obtained when the oxidant was switched to $(NH_4)_2S_2O_8$ (Table 1, entry 2). Gratifyingly, the use of $Cu(OAc)_2$ gave **3a** in 61% yield (Table 1, entry 3). Inspired by this result, various oxidants, such as BQ (*p*-benzoquinone), TBHP (*tert*-butyl hydroperoxide, 70% aqueous solution), $Ag_2CO_3$ and $PhI(OAc)_2$ were screened, but did not enhance the yield of product **3a** (Table 1, entries 4−7). Then, other Cu salts, including CuCl and $Cu(CF_3CO_2)_2$ were employed with no improvement of product yields (Table 1, entries 8 and 9). Among all of the examined oxidants, $Cu(OAc)_2$ proved to be the best one for this transformation. Some common additives, such as *p*-TsOH

**Table 1** Optimization of the reaction conditions[a]



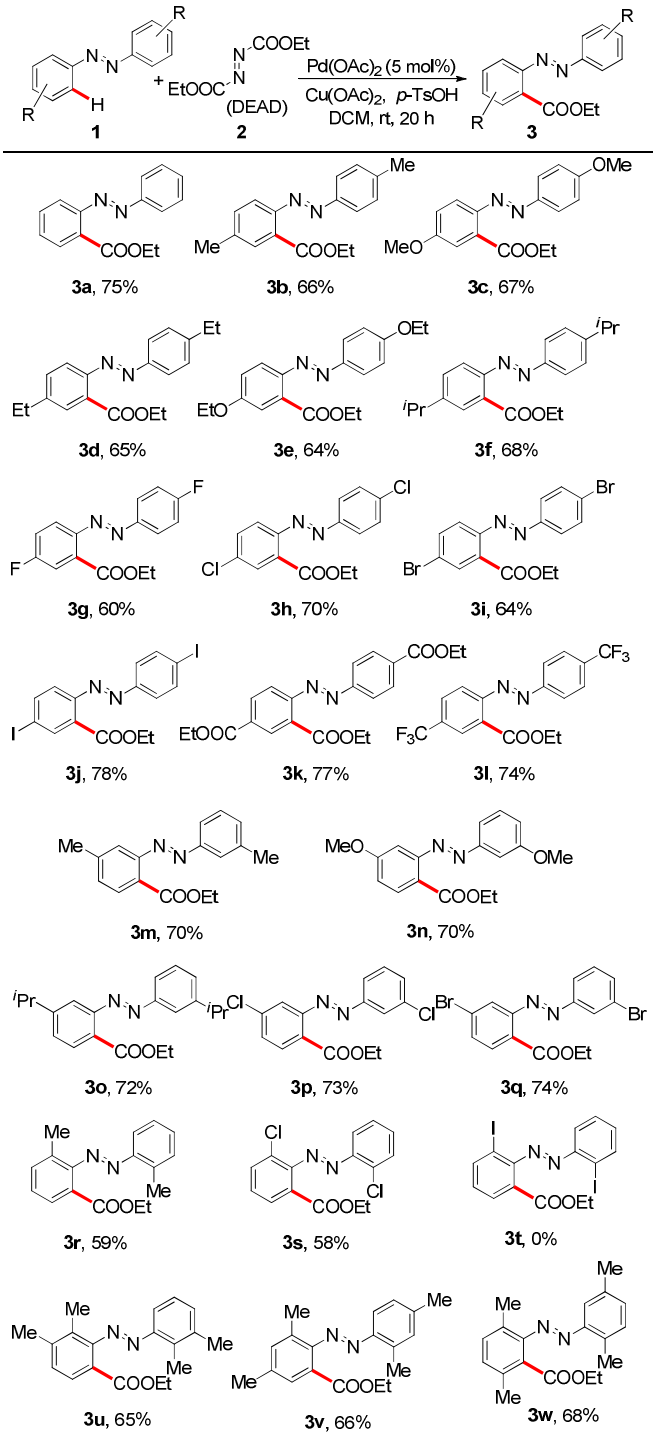

1a 2 3a

| Entry | Oxidant | Additive | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $K_2S_2O_8$ | – | DCM | 40 |
| 2 | $(NH_4)_2S_2O_8$ | – | DCM | 33 |
| 3 | $Cu(OAc)_2$ | – | DCM | 61 |
| 4 | BQ | – | DCM | 42 |
| 5 | TBHP | – | DCM | 39 |
| 6 | $Ag_2CO_3$ | – | DCM | 27 |
| 7 | $PhI(OAc)_2$ | – | DCM | 23 |
| 8 | CuCl | – | DCM | 43 |
| 9 | $Cu(CF_3COO)_2$ | – | DCM | 22 |
| 10 | ***$Cu(OAc)_2$*** | ***p-TsOH*** | ***DCM*** | ***75*** |
| 11 | $Cu(OAc)_2$ | HOAc | DCM | 53 |
| 12 | $Cu(OAc)_2$ | $CH_3CO_2H$ | DCM | 26 |
| 13 | $Cu(OAc)_2$ | $CH_3SO_3H$ | DCM | 60 |
| 14 | $Cu(OAc)_2$ | *p*-TsOH | DCM | 72[c] |
| 15 | $Cu(OAc)_2$ | *p*-TsOH | DCM | 53[d] |
| 16 | $Cu(OAc)_2$ | *p*-TsOH | DCM | 51[e] |
| 17 | $Cu(OAc)_2$ | *p*-TsOH | DCM | 73[f] |
| 18 | $Cu(OAc)_2$ | *p*-TsOH | $CH_3OH$ | 0 |
| 19 | $Cu(OAc)_2$ | *p*-TsOH | DMF | 17 |
| 20 | $Cu(OAc)_2$ | *p*-TsOH | DMSO | 22 |
| 21 | $Cu(OAc)_2$ | *p*-TsOH | DMA | 12 |
| 22 | $Cu(OAc)_2$ | *p*-TsOH | DCE | 43 |
| 23 | $Cu(OAc)_2$ | *p*-TsOH | DME | trace |
| 24 | $Cu(OAc)_2$ | *p*-TsOH | THF | trace |
| 25 | $Cu(OAc)_2$ | *p*-TsOH | Toluene | 53 |
| 26 | $Cu(OAc)_2$ | *p*-TsOH | $CH_3CN$ | 50 |
| 27 | $Cu(OAc)_2$ | *p*-TsOH | 1,4-Dioxane | trace |
| 28 | $Cu(OAc)_2$ | *p*-TsOH | HOAc | trace |

[a] *Reaction conditions*: azobenzene (**1a**, 0.20 mmol), diethyl azodicarboxylate (**2**, 0.50 mmol), $Pd(OAc)_2$ (5 mol%), oxidant (0.20 mmol), additive (0.40 mmol) at room temperature under air for 20 h. [b] Isolated yield. [c] 30 h. [d] 12 h. [e] **1a**/**2** = 1:1. [f] **1a**/**2** = 1:3.

(*p*-toluenesulfonic acid), HOAc, $CH_3CO_2H$ and $CH_3SO_3H$ were added to the reaction. In the presence of *p*-TsOH, the yield of **3a** was increased to 75% (Table 1, entry 10). However, the addition of HOAc, $CH_3CO_2H$ and $CH_3SO_3H$ to the reaction resulted in a reduced yield of **3a** (Table 1, entries 11–13). Prolonging the reaction time from 20 h to 30 h did not improve the yield of **3a** (Table 1, entry 14). However, shorting the time to 12 h resulted in a decrease of the product yield (Table 1, entry 15). Changing the **1a**/**2** molar ratio from 1/2.5 to 1/1 reduced the yield of **3a** from 73% to 51% (Table 1, entry 10 vs entry 16). Increasing the loading of **2** to 3 equiv did not provide the improved yield of **3a** (Table 1, entry 17). Moreover, further investigation of the solvents and reaction temperature demonstrated that DCM was the best reaction medium among the tested solvents (Table 1, entries 18–28), and the best result was obtained when the model reaction was performed at room temperature. Finally, the optimized reaction conditions for the Pd-catalyzed *ortho*-ethoxycarbonylation of **1a** with **2** were identified as follows:

**Table 2** The scope of the ethoxycarbonylation of azobenzenes with diethyl azodicarboxylate (**2**)[a,b]




[a] *Reaction conditions*: azobenzene (**1**, 0.20 mmol), diethyl azodicarboxylate (**2**, 0.50 mmol), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (0.20 mmol), *p*-TsOH (0.40 mmol) in DCM (2.0 mL) at room temperature under air for 20 h. [b] Isolated yield.

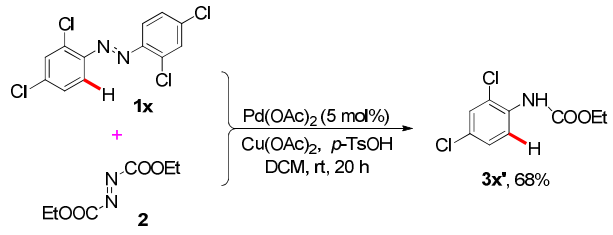
$Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (1 equiv) as the oxidant, *p*-TsOH (2 equiv) as the additive, in DCM at room temperature under air for 20 h.

To explore the applicability of this reaction, various aromatic

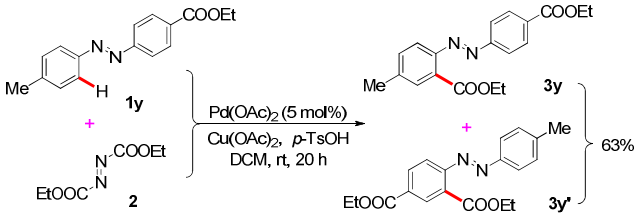
azo compounds were investigated under the optimized reaction conditions. As can be seen from Table 2, the reactions of azobenzenes (**1**) with diethyl azodicarboxylate (**2**) proceeded well and generated the corresponding ethoxycarbonylation products in good yields. The reactions indicated wide functional group tolerance and broad range of azobenzenes bearing substituents on the benzene rings. The substrates (azobenzenes) with both electron-donating and electron-withdrawing groups on the benzene rings reacted with diethyl azodicarboxylate well, providing the corresponding products in good yields. The reactions did not show the obvious electronic effect. For example, the reactions of azobenzenes with the electron-donating groups, such as Me, MeO, Et, EtO, and $^{i}$Pr, on the *para*-positions of azo units generated the corresponding products (**3b**–**f**) in 64–68% yields. On the other hand, azobenzenes with the electron-withdrawing substituents, including F, Cl, Br, I, COOEt, and $CF_3$ on their *para*-positions reacted with **2** smoothly to provide the desired products (**3g**–**l**) in 60–78% yields. It should be noted that *meta*-substituted azobenzenes worked well in the reaction to give the *ortho*-ethoxycarboxylation products (**3m**–**q**) in good yields (70–74%). Notably, the *ortho*-substituted azobenzenes gave relatively lower product yields than their *para*- or *meta*-substituted azobezenes due to the steric hindrance (**3r** and **3s**). However, 1,2-bis(2-iodophenyl)diazene failed to react with **2** under the present reaction conditions, and none of the desired product **3t** was detected. Furthermore, tetra-substituted azobenzenes showed good reactivity and provided desired products (**3u**–**3w**) in 65–68% yields. Especially, when 1,2-bis(2,5-dimethylphenyl)diazene reacted with **2**, the desired product **3w** was obtained in 68% yield.

It should be noted that the reaction of 1,2-bis(2,4-dichlorophenyl)diazene (**1x**) with **2** did not provide the desired product, but gave the product **3x'** in 68% yield (Scheme 2).

When unsymmetrical azobenzene, such as (*E*)-ethyl 2-((4-(ethoxycarbonyl)phenyl)diazenyl)-5-methylbenzoate (**1y**) was employed to react with **2**, a mixture of two inseparable isomers (**3y** and **3y'**) was obtained in a moderate yield (Scheme 3) with a ratio of **3y**:**3y'** (1.24:1 from $^{1}$H NMR in Supporting Information).

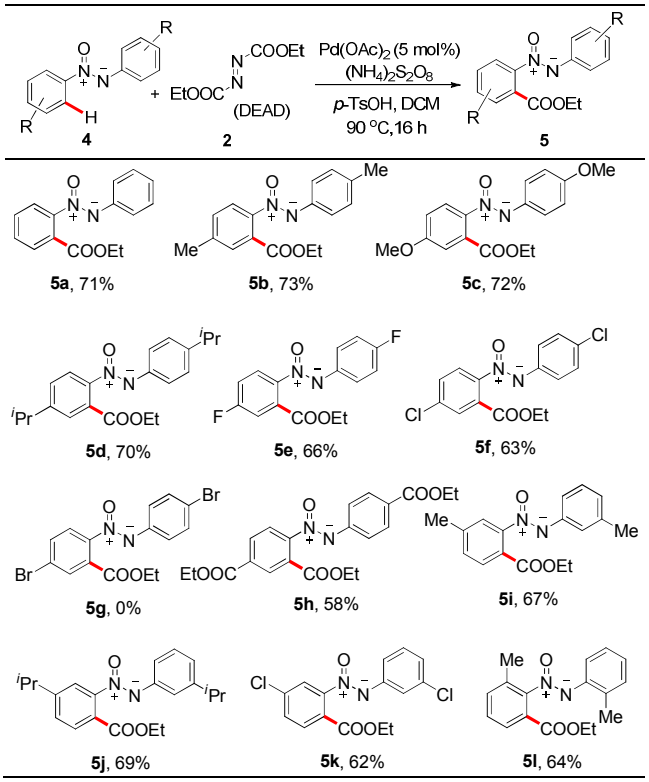



**Scheme 2** Reaction of 1,2-bis(2,4-dichlorophenyl)diazene with diethyl azodicarboxylate (**2**).




**Scheme 3** Reaction of (*E*)-ethyl 2-((4-(ethoxycarbonyl)phenyl)diazenyl)-5-methylbenzoate (**1y**) with diethyl azodicarboxylate (**2**).

**Table 3** The scope of the ethoxycarbonylation of azoxybenzenes with diethyl azodicarboxylate (**2**) [a,b]




[a] *Reaction conditions*: azoxybenzene (**4**, 0.20 mmol), diethyl azodicarboxylate (**2**, 0.50 mmol), $Pd(OAc)_2$ (5 mol%), $(NH_4)_2S_2O_8$ (0.30 mmol), *p*-TsOH (0.40 mmol) in DCM (2.0 mL) at 90 °C under air for 16 h. [b] Isolated yields.

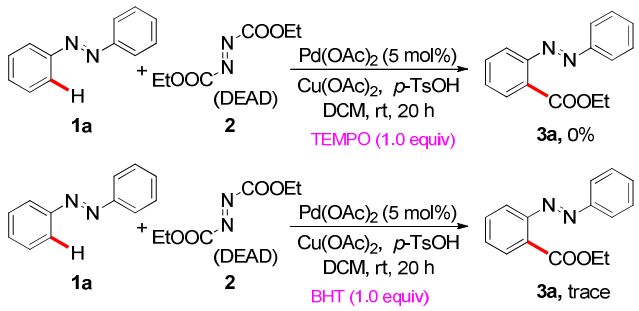
Next, the optimization of the reaction conditions was investigated for the reaction of azoxybenzene (**4a**) with diethyl azodicarboxylate (**2**). The results presented in Table S1 and S2 (Supporting Information) indicated that the optimized reaction conditions were involved in $Pd(OAc)_2$ (5 mol%), $(NH_4)_2S_2O_8$ (1.5 equiv), *p*-TsOH (2 equiv) in DCM at 90 °C under air for 16 h.

In order to explore the scope and generality of azoxybenzenes in the reaction with **2** under the optimized reaction conditions, a variety of substituents on the aromatic moiety in the azoxybenzenes were examined, as shown in Table 3. Generally, electron-rich azoxybenzenes were more suitable substrates, and gave higher product yields than that of electron-poor azoxybenzenes.

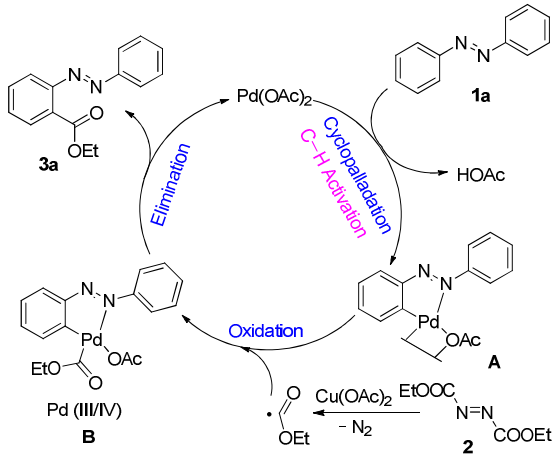
As can be seen in Table 3, higher product yields were obtained from the reactions of diethyl azodicarboxylate with *para*-substituted azoxybenzenes containing methyl, methoxy, and *iso*-propyl groups (**5b**–**d**) in comparison with that from the reactions of **2** with azoxybenzenes bearing fluoro, chloro and ethoxycarbonyl groups at the *para*-positions (**5e**, **5f**, and **5h**). Surprisingly, azoxybenzene with bromo substituent at the *para*-position do not react with **2** under the present reaction conditions and no product **5g** was isolated. Meanwhile, *meta*-substituted (Me, *iso*-Pr, and Cl) azoxybenzenes also proved to be the good substrates for this reaction and gave the corresponding products **5i**–**k** in 62–69% yields. It is important to note that methyl substituted azoxybenzene at the *ortho*-position provided the desired product **5l** in 64% yield.

When typical radical scavengers, TEMPO (2,2,6,6-

tetramethyl-1-piperidinyloxy) and BHT (2,6-di-(*tert*-butyl)-4-methylphenol) were added to the reaction mixture, and the reaction was suppressed completely (Scheme 4). It proposed that the C−H *ortho*-ethoxycarbonylation of azo and azoxy compounds may involve a radical pathway. On the basis of the control experiments in Scheme 3 and in combination with previous related studies,[6d,23] a plausible reaction mechanism of this Pd-catalyzed ethoxycarbonylation of aromatic azo compounds is proposed in Scheme 5. Initially, a five-member cyclopalladated intermediate **A** was generated through Pd(II)-catalyzed *ortho*-selective C–H bond activation of azobenzene (**1a**) and its coordination. Subsequently, **A** reacted with the ethoxyacyl radical generated from the decomposition of diethyl azodicarboxylate (DEAD, **2**) to produce either Pd(IV) or Pd(III) species **B**.[6a,23b,23c,24] Finally, the intermediate **B** underwent reductive elimination to afford the desired product **3a**. Meanwhile, a Pd(II) species is regenerated for the next catalytic cycle.




**Scheme 4** The control experiments.




**Scheme 5** The proposed reaction mechanism.

In conclusion, we developed a Pd(II)-catalyzed *ortho*-ethoxycarbonylation of azobenzenes and azoxybenzenes with diethyl azodicarboxylate. The reactions of diethyl azodicarboxylate with a variety of azo and azoxy compounds proceeded smoothly to generate the corresponding ethoxycarbonylation products in moderate to good yields. The reaction is highly efficient and well tolerated. Further investigations into the reaction mechanism and the application of azobenzene and azoxybenzene derivatives are currently underway.

## Experimental Section

All $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

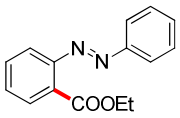
Azobenzenes were prepared from arylamines using CuBr as catalyst.[25] Azoxybenzenes were prepared from arylamines in the presence of $SeO_2/H_2O_2$/MeOH system,[26] and which must be recrystallized from ethanol before use. The chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China. Products were purified by flash chromatography on 100–200 mesh silica gels, $SiO_2$.

**Typical procedure for the ethoxycarbonylation of azobenzenes with diethyl azodicarboxylate**

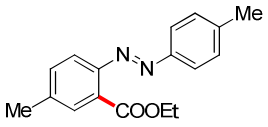
A 10 mL of reaction tube equipped with a stir bar was charged with a mixture of azobenzene (**1a**, 36.4 mg, 0.20 mmol), diethyl azodicarboxylate (DEAD, **2**, 87 mg, 0.50 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Cu(OAc)_2$ (36.4 mg, 0.20 mmol), *p*-toluenesulfonic acid (76 mg, 0.40 mmol) and dichloromethane (DCM, 2.0 mL). After the reaction mixture was stirred at room temperature for 20 h, it was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:50, v/v), affording the desired product **3a** as a yellow liquid.

**Typical procedure for the ethoxycarbonylation of azoxybenzenes with diethyl azodicarboxylate**

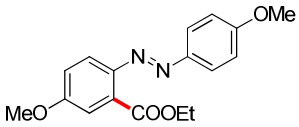
A 10 mL of reaction tube equipped with a stir bar was charged with a mixture of azoxybenzene (**4a**, 39.6 mg, 0.20 mmol), diethyl azodicarboxylate (DEAD, **2**, 87 mg, 0.50 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $(NH_4)_2S_2O_8$ (68.4 mg, 0.30 mmol), *p*-toluenesulfonic acid (76 mg, 0.40 mmol) and dichloromethane (DCM, 2.0 mL). After the reaction mixture was stirred at 90 °C for 16 h, it was cooled to room temperature and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:50, v/v), affording the desired product **5a** as a yellow liquid.



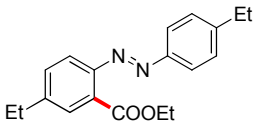

**(*E*)-Ethyl 2-(phenyldiazenyl)benzoate (3a)**[27]
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 6.8 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.63–7.57 (m, 2H), 7.54–7.48 (m, 4H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.38, 152.54, 151.93, 131.70, 131.29, 129.63, 129.57, 128.99, 123.10, 118.59, 61.26, 14.22. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{15}N_2O_2$: 255.1134, Found: 255.1133.



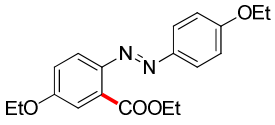
**(*E*)-Ethyl 5-methyl-2-(*p*-tolyldiazenyl)benzoate (3b)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, $J$ = 8.2 Hz, 2H), 7.60 (s, 1H), 7.58 (d, $J$ = 8.2 Hz, 1H), 7.38 (d, $J$ = 8.1 Hz, 1H), 7.31 (d, $J$ = 8.1 Hz, 2H), 4.39 (q, $J$ =7.1 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 1.33 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.87, 150.62, 149.49, 141.58, 139.94, 132.10, 129.77, 129.53, 129.16, 122.93, 118.59, 61.14, 21.31, 21.01, 14.18. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_2$: 283.1447, Found: 283.1444.



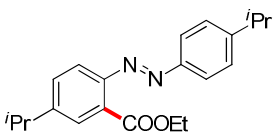
**(*E*)-Ethyl 5-methoxy-2-((4-methoxyphenyl)diazenyl)benzoate (3c)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J$ = 8.4 Hz, 2H), 7.73 (d, $J$ = 8.8 H, 1H), 7.24 (s, 1H), 7.06 (d, $J$ = 8.6 Hz, 1H), 6.99 (d, $J$ = 8.5 Hz, 2H), 4.41 (q, $J$ = 6.9 Hz, 2H), 3.88 (s, 3H ), 3.86 (s, 3H), 1.34 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.93, 161.88, 160.52, 146.95, 145.05, 131.46, 124.68, 120.28, 117.23, 114.07, 113.51, 61.32, 55.61, 55.42, 14.27. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_4$: 315.1345, Found: 315.1343.



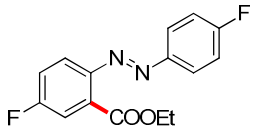
**(*E*)-Ethyl 5-ethyl-2-((4-ethylphenyl)diazenyl)benzoate (3d)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, $J$ = 8.1 Hz, 2H), 7.63 (s, 1H), 7.60 (d, $J$ = 8.2 Hz, 1H), 7.41 (d, $J$ = 8.0 Hz, 1H), 7.34 (d, $J$ = 8.1 Hz, 2H), 4.39 (q, $J$ = 7.1 Hz, 2H), 2.78–2.72 (m, 4H ), 1.35–1.28 (m, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.05, 150.89, 149.80, 147.90, 146.24, 131.02, 129.29, 128.72, 128.41, 123.11, 118.80, 61.21, 28.74, 28.48, 15.23, 15.13, 14.27. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2O_2$: 311.1760 Found: 311.1763.



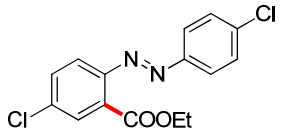
**(*E*)-Ethyl 5-ethoxy-2-((4-ethoxyphenyl)diazenyl)benzoate (3e)**
Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, $J$ = 8.8 Hz, 2H), 7.72 (d, $J$ = 8.9 Hz, 1H), 7.23–7.22 (m, 1H), 7.06 (dd, $J$ = 8.9 Hz, 2.7 Hz, 1H), 6.98 (d, $J$ = 8.9 Hz, 2H), 4.40 (q, $J$ = 7.1 Hz, 2H), 4.15–4.09 (m, 4H ), 1.46 (t, $J$ = 6.9 Hz, 6H), 1.34 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.97, 161.26, 159.89, 146.84, 144.97, 131.36, 124.67, 120.24, 117.67, 114.53, 114.07, 63.95, 63.69, 61.29, 14.63, 14.57, 14.26. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2O_4$: 343.1658, Found: 343.1655.



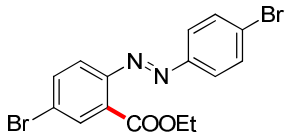
**(*E*)-Ethyl 5-(*iso*-propyl)-2-((4-(*iso*-propyl)phenyl)diazenyl)benzoate (3f)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, $J$ = 8.3 Hz, 2H), 7.65–7.64 (m, 1H), 7.60 (d, $J$ = 8.2 Hz, 1H), 7.44 (dd, $J$ = 8.3 Hz, 1.7 Hz, 1H), 7.38 (d, $J$ = 8.3 Hz, 2H), 4.40 (q, $J$ = 7.1 Hz, 2H), 3.06–2.97 (m, 2H), 1.36–1.31 (m, 15H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.15, 152.46, 150.95, 150.80, 149.91, 129.62, 129.22, 127.35, 126.97, 123.09, 118.85, 61.21, 34.05, 33.88, 23.71, 23.62, 14.27. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{27}N_2O_2$: 339.2073, Found: 339.2067.



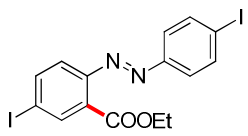
**(*E*)-Ethyl 5-fluoro-2-((4-fluorophenyl)diazenyl)benzoate (3g)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.70–7.67 (m, 1H), 7.51 (dd, $J$ = 8.4 Hz, 2.7 Hz, 1H), 7.30–7.25 (m, 1H), 7.22–7.18 (m, 2H), 4.41 (q, $J$ = 7.1 Hz, 2H), 1.35 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.22 (d, $J_{C-F}$ = 2.4 Hz), 164.65 (d, $J_{C-F}$ = 251.4 Hz), 163.12 (d, $J_{C-F}$ = 250.7 Hz), 149.02 (d, $J_{C-F}$ = 3.0 Hz), 147.77 (dd, $J_{C-F}$ = 3.3 Hz, 0.7 Hz), 131.67 (d, $J_{C-F}$ = 7.8 Hz), 125.23 (d, $J_{C-F}$ = 9.0 Hz), 120.51 (d, $J_{C-F}$=8.5Hz), 118.72 (d, $J_{C-F}$ = 22.6 Hz), 116.53 (d, $J_{C-F}$ = 24.5 Hz), 116.12 (d, $J_{C-F}$ = 22.8 Hz), 61.74, 14.27. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}F_2N_2O_2$: 291.0945, Found: 291.0947.



**(*E*)-Ethyl 5-chloro-2-((4-chlorophenyl)diazenyl)benzoate (3h)**
Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, $J$ = 8.6 Hz, 2H), 7.81–7.80 (m, 1H), 7.61–7.59 (m, 1H), 7.54 (dd, $J$ = 8.6 Hz, 2.1 Hz, 1H), 7.49 (d, $J$ = 8.6 Hz, 2H), 4.40 (q, $J$ = 7.1 Hz, 2H), 1.35 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.96, 150.70, 149.60, 137.64, 136.04, 131.72, 130.91, 129.60, 129.34, 124.40, 119.64, 61.70, 14.21. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Cl_2N_2O_2$: 323.0354, Found: 323.0346.

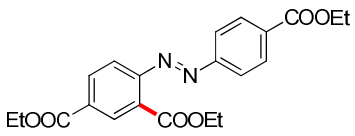


**(*E*)-Ethyl 5-bromo-2-((4-bromophenyl)diazenyl)benzoate (3i)**
Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.97–7.96 (m, 1H), 7.78 (d, $J$ = 8.6 Hz, 2H), 7.70 (dd, $J$ = 8.6 Hz, 2.0 Hz, 1H), 7.66 (d, $J$ = 8.6 Hz, 2H), 7.51 (d, $J$ = 8.5 Hz, 1H), 4.39 (q, $J$ = 7.1 Hz, 2H), 1.34 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.83, 151.10, 150.07, 134.76, 132.57, 132.38, 131.05, 126.24, 124.63, 124.19, 119.83, 61.74, 14.25. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Br_2N_2O_2$: 410.9344, Found: 410.9345.



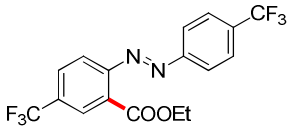
**(*E*)-Ethyl 5-iodo-2-((4-iodophenyl)diazenyl)benzoate (3j)**
Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.16–8.15 (m, 1H), 7.92–7.90 (m, 1H), 7.87 (d, $J$ = 8.5 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz,

2H), 7.35 (d, $J$ = 8.4 Hz, 2H), 4.38 (q, $J$ = 7.1 Hz, 2H), 1.34 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.68, 151.66, 150.66, 140.71, 138.40, 131.01, 124.68, 124.41, 119.85, 98.67, 95.84, 61.70, 14.24. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}I_2N_2O_2$: 506.9066, Found: 506.9073.



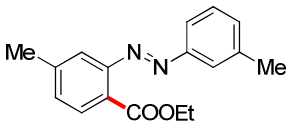

**(*E*)-Diethyl 4-((4-(ethoxycarbonyl)phenyl)diazenyl)isophthalate (3k)**

Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.54–8.53 (m, 1H), 8.26 (dd, $J$ = 8.3 Hz, 1.3 Hz, 1H), 8.21 (d, $J$ = 8.4 Hz, 2H), 7.97 (d, $J$ = 8.4 Hz, 2H), 7.60 (d, $J$ = 8.3 Hz, 1H), 4.46–4.38 (m, 6H), 1.44 (t, $J$ = 7.1 Hz, 3H), 1.43 (t, $J$ = 7.1 Hz, 3H), 1.33 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.23, 165.70, 165.02, 154.70, 154.37, 132.97, 131.72, 131.28, 130.51, 129.00, 123.03, 118.41, 61.67,. 61.47, 61.25, 14.20, 14.18. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{23}N_2O_6$: 399.1556, Found: 399.1561.



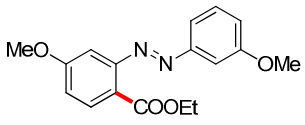

**(*E*)-Ethyl 5-(trifluoromethyl)-2-((4-(trifluoromethyl)phenyl)diazenyl)benzoate (3l)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.04 (d, $J$ = 8.2 Hz, 2H), 7.87 (d, $J$ = 8.2 Hz, 1H), 7.82 (d, $J$ = 8.3 Hz, 2H), 7.65 (d, $J$ = 8.3 Hz, 1H), 4.43 (q, $J$ = 7.1 Hz, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H ). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.44, 153.99, 153.84, 133.19 (q, $J_{C-F}$ = 32.5 Hz), 131.55 (q, $J_{C-F}$ = 33.2 Hz), 129.30, 128.82 (q, $J_{C-F}$ = 3.5 Hz), 127.29 (q, $J_{C-F}$ = 3.7 Hz), 126.33 (q, $J_{C-F}$ = 3.8 Hz), 123.61 (q, $J_{C-F}$ = 270.8 Hz), 123.48, 123.24 (q, $J_{C-F}$ = 271.1 Hz), 118.86, 61.89, 14.13. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{13}F_6N_2O_2$: 391.0881, Found: 391.0879.



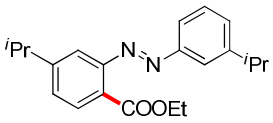

**(*E*)-Ethyl 4-methyl-2-(*m*-tolyldiazenyl)benzoate (3m)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, $J$ = 7.8 Hz, 1H), 7.75 (s, 2H), 7.44–7.40 (m, 1H), 7.34–7.29 (m, 3H), 4.38 (q, $J$ = 7.1 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 3H), 1.33 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.24, 152.69, 152.50, 142.66, 138.86, 131.99, 130.02, 129.97, 128.80, 125.66, 123.27, 120.64, 118.67, 61.08, 21.36, 21.22, 14.23. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_2$: 283.1447, Found: 283.1449.



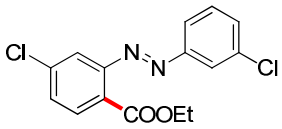

**(*E*)-Ethyl 4-methoxy-2-((3-methoxyphenyl)diazenyl)benzoate (3n)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, $J$ = 8.4 Hz, 1H), 7.59 (d, $J$ = 7.8 Hz, 1H), 7.48 (s, 1H), 7.46–7.42 (m, 1H), 7.08 (dd, $J$ = 8.1 Hz, 2.0 Hz, 1H), 7.02–6.99 (m, 2H), 4.35 (q, $J$ = 7.1 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 1.31 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.56, 162.50, 160.23, 154.49, 153.70, 131.97, 129.68, 120.63, 118.12, 117.22, 115.38, 106.33, 102.30, 60.95, 55.55, 55.33, 14.27. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_4$: 315.1345, Found: 315.1348.



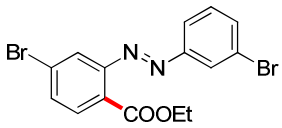

**(*E*)-Ethyl 4-(*iso*-propyl)-2-((3-(*iso*-propyl)phenyl)diazenyl)benzoate (3o)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.81 (d, $J$ = 7.9 Hz, 1H), 7.77 (d, $J$ = 7.6 Hz, 1H), 7.47–7.43 (m, 2H), 7.39–7.36 (m, 2H), 4.37 (q, $J$ = 7.1 Hz, 2H), 3.08–3.01 (m, 2H), 1.35–1.31 (m, 15H). $^{13}$C NMR (100 MHz, CDCl3): δ 164.47, 153.36, 152.76, 152.52, 149.89, 129.95, 129.54, 128.87, 127.48, 125.99, 121.32, 120.39, 116.57, 61.06, 34.14, 33.97, 23.78, 23.53, 14.23. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{27}N_2O_2$: 339.2073, Found: 339.2068.



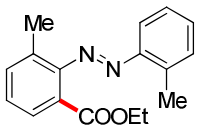

**(*E*)-Ethyl 4-chloro-2-((3-chlorophenyl)diazenyl)benzoate (3p)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.86–7.83 (m, 2H), 7.56–7.55 (m, 1H), 7.49–7.48 (m, 2H), 7.47–7.46 (m, 1H), 4.40 (q, $J$ = 7.1 Hz, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.10, 153.04, 152.26, 138.12, 135.18, 131.47, 131.26, 130.14, 129.78, 127.75, 122.81, 122.14, 117.95, 61.62, 14.22. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Cl_2N_2O_2$: 323.0354, Found: 323.0353.



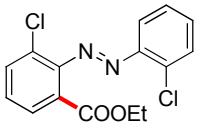

**(*E*)-Ethyl 4-bromo-2-((3-bromophenyl)diazenyl)benzoate (3q)**

Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.89 (d, $J$ = 7.6 Hz, 1H), 7.76 (d, $J$ = 8.2 Hz, 1H), 7.71–7.70 (m, 1H), 7.64–7.62 (m, 2H), 7.43–7.39 (m, 1H), 4.40 (q, $J$ = 7.1 Hz, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl3): δ 166.23, 153.09, 152.05, 134.39, 132.79, 131.35, 130.44, 128.30, 126.32, 125.02, 123.37, 123.10, 120.86, 61.66, 14.26. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Br_2N_2O_2$: 410.9344, Found: 410.9342.

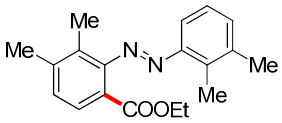



**(*E*)-Ethyl 3-methyl-2-(*o*-tolyldiazenyl)benzoate (3r)**

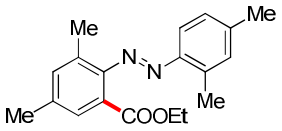
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J$ = 8.0 Hz, 1H), 7.53 (d, $J$ = 7.4 Hz, 1H), 7.42–7.38 (m, 2H), 7.35 (d, $J$ = 7.8 Hz, 2H), 7.32–7.29 (m, 1H), 4.16 (q, $J$ = 7.1 Hz, 2H), 2.66 (s, 3H ), 2.55 (s, 3H), 1.10 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.63, 151.50, 150.49, 138.48, 134.75, 133.17, 131.34, 131.24, 128.34, 127.38, 126.25, 124.08, 115.81, 60.82, 17.86, 17.31, 13.87. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_2$: 283.1447, Found: 283.1443.



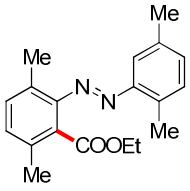
**(*E*)-Ethyl 3-chloro-2-((2-chlorophenyl)diazenyl)benzoate (3s)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.83–7.82 (m, 1H), 7.67–7.63 (m, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.49–7.45 (m, 1H), 7.42–7.38 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.56, 149.76, 148.31, 136.02, 132.78, 132.72, 130.83, 130.73, 129.36, 128.60, 127.29, 125.57, 118.03, 61.45, 13.82. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{13}Cl_2N_2O_2$: 323.0354, Found: 323.0349.



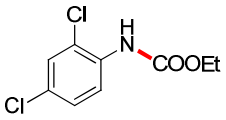
**(*E*)-Ethyl 2-((2,3-dimethylphenyl)diazenyl)-3,4-dimethylbenzoate (3u)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.24–7.18 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.76, 152.09, 150.66, 140.86, 138.25, 137.36, 133.27, 132.52, 129.47, 126.90, 125.60, 121.67, 113.45, 60.66, 19.99, 19.79, 13.88, 13.73, 13.10. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2O_2$: 311.1760, Found: 311.1761.



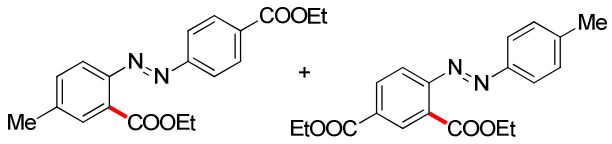
**(*E*)-Ethyl 2-((2,4-dimethylphenyl)diazenyl)-3,5-dimethylbenzoate (3v)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.28 (s, 1H), 7.21(s, 1H), 7.15(s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.62(s, 3H), 2.55(s, 3H), 2.40(s, 6H), 1.10 (t, *J* = 7.1 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.21, 149.01, 148.67, 141.58, 138.69, 138.41, 135.39, 133.59, 131.73, 127.70, 127.03, 124.17, 115.71, 60.73, 21.28, 20.88, 17.85, 17.28, 13.92. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2O_2$: 311.1760, Found: 311.1764.



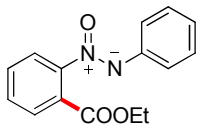
**(*E*)-Ethyl 2-((2,5-dimethylphenyl)diazenyl)-3,6-dimethylbenzoate (3w)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.28–7.26 (m, 1H), 7.24–7.19(m, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 2.63 (s, 3H), 2.39 (s, 6H), 1.18 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.09, 150.53, 148.91, 135.81, 135.49, 133.80, 133.75, 132.05, 131.76, 131.49, 131.07, 124.75, 116.11, 60.60, 20.89, 18.76, 18.08, 17.07, 13.98. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2O_2$: 311.1760, Found: 311.1761.



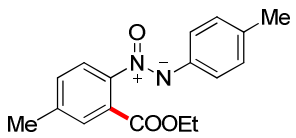
**Ethyl (2,4-dichlorophenyl)carbamate (3x')**[28]
Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.9 Hz, 1H), 7.36–7.35 (m, 1H), 7.24 (dd, *J* = 8.9 Hz, 2.2 Hz, 1H), 7.07 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 152.94, 133.54, 128.57, 127.94, 127.76, 122.34, 120.50, 61.63, 14.32. HRMS (ESI) $[M+H]^+$ Calcd. for $C_9H_{10}Cl_2NO_2$: 234.0089, Found: 234.0080.



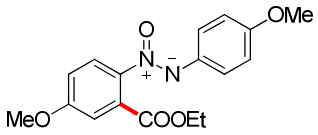
**(*E*)-Ethyl 2-((4-(ethoxycarbonyl)phenyl)diazenyl)-5-methylbenzoate (3y) + (*E*)-diethyl 4-(p-tolyldiazenyl)isophthalate (3y')**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.51–8.50 (m, 1H), 8.25 (dd, *J* = 8.3 Hz, 1.5 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.62–7.61 (m, 1H), 7.60–7.59 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.46–4.37 (m, 6H), 2.47 (s, 3H), 2.46 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 6H), 1.36–1.31 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.74, 166.71,166.00, 165.33, 155.01, 154.89, 150.79, 149.31, 142.82, 141.33, 132.98, 132.34, 131.29, 131.04, 130.54, 130.11, 130.09, 129.85, 128.64, 123.47, 122.83, 118.89, 61.64, 61.47, 61.26, 21.57, 21.29, 14.36, 14.30. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{19}H_{21}N_2O_4$: 341.1501, Found: 341.1498.



**2-(2-(Ethoxycarbonyl)phenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (5a)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.86–7.82 (m, 2H), 7.63–7.59 (m, 1H), 7.57–7.53 (m, 1H), 7.50–7.46 (m, 2H), 7.42–7.39 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.67, 143.84, 131.875, 130.16, 129.95, 129.87, 128.65, 128.61, 126.85, 125.18, 123.70, 61.74, 13.83. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{15}N_2O_3$: 271.1083, Found: 271.1083.

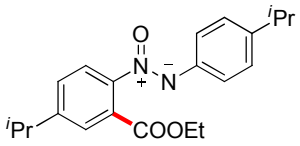


**2-(2-(Ethoxycarbonyl)-4-methylphenyl)-2-oxo-1-(*p*-tolyl)hydrazin-2-ium-1-ide (5b)**
Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.58 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.26 (q, *J* =7.1 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.24, 141.70, 140.73, 140.36, 131.95, 130.09 ,129.18, 127.71, 126.92, 125.31, 123.56, 61.64, 21.43, 20.95, 13.86. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_3$: 299.1396, Found: 299.1398.



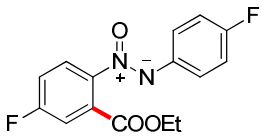
**2-(2-(Ethoxycarbonyl)-4-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxohydrazin-2-ium-1-ide (5c)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, $J$ = 9.0 Hz, 2H), 7.85 (d, $J$ = 8.9 Hz, 1H), 7.18–7.17 (m, 1H), 7.03 (dd, $J$ = 8.9 Hz, 2.6 Hz 1H), 6.94 (d, $J$ = 9.0 Hz, 2H), 4.25 (q, $J$ = 7.1 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 1.15 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.34, 160.48, 160.42, 141.23, 137.84, 128.91, 127.48., 125.18, 116.36 ,114.12, 113.61, 61.73, 55.78, 55.34, 13.84. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_5$: 331.1294, Found: 331.1299.



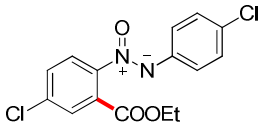
**2-(Ethoxycarbonyl)-4-(*iso*-propyl)phenyl)-1-(4-*iso*-propyl)phenyl)-2-oxohydrazin-2-ium-1-ide (5d)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, $J$ = 8.4 Hz, 2H), 7.79 (d, $J$ = 8.2 Hz, 2H), 7.65–7.64 (m, 1H), 7.45 (dd, $J$ = 8.3 Hz, 1.6 Hz, 1H), 7.33 (d, $J$ = 8.5 Hz, 2H), 4.28 (q, $J$ = 7.1 Hz, 2H), 3.06–2.94 (m, 2H), 1.31–1.28 (m, 12H), 1.18 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.32, 151.50, 151.14, 146.28, 141.94, 129.55,127.77, 126.94, 126.53, 125.41, 123.69, 61.66, 34.04, 33.83, 23.63, 23.54, 13.86. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{27}N_2O_3$: 355.2022, Found: 355.2021.



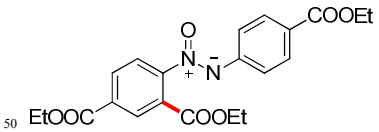
**2-(2-(Ethoxycarbonyl)-4-fluorophenyl)-1-(4-fluorophenyl)-2-oxohydrazin-2-ium-1-ide (5e)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.24–8.20 (m 2H), 7.91–7.88 (m, 1H), 7.50 (dd, $J$ = 8.1 Hz, 2.7 Hz 1H), 7.33–7.28 (m, 1H), 7.19–7.14 (m, 2H), 4.29 (q, $J$ =7.1 Hz, 2H), 1.19 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.56 (d, $J_{C-F}$ = 2.1 Hz), 163.90 (d, $J_{C-F}$ = 4.4 Hz), 162.64 (d, $J_{C-F}$ = 4.9 Hz), 140.17 (d, $J_{C-F}$ = 3.3 Hz), 129.26 (d, $J_{C-F}$ = 7.9 Hz), 127.69 (d, $J_{C-F}$ = 8.5 Hz), 125.94 (d, $J_{C-F}$ = 8.7 Hz), 118.40 (d, $J_{C-F}$ = 23.0 Hz), 116.94 (d, $J_{C-F}$ = 25.1 Hz), 115.61 (d, $J_{C-F}$ = 22.4 Hz), 62.13, 13.81. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}F_2N_2O_3$: 307.0894, Found: 307.0889.



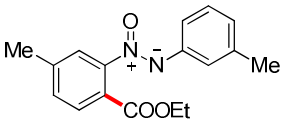
**2-(4-Chloro-2-(ethoxycarbonyl)phenyl)-1-(4-chlorophenyl)-2-oxohydrazin-2-ium-1-ide (5f)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, $J$ = 8.8 Hz, 2H), 7.83 (d, $J$ = 8.6 Hz, 1H), 7.78–7.77 (m, 1H), 7.58 (dd, $J$ = 8.6 Hz, 2.1 Hz 1H), 7.45 (d, $J$ =8.8 Hz, 2H), 4.29 (q, $J$ =7.1 Hz, 2H), 1.20 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.51, 146.33, 142.05, 136.55, 135.52, 131.53, 129.86, 128.90, 128.52, 126.67, 125.10, 62.17, 13.85. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Cl_2N_2O_3$: 339.0303, Found: 339.0297.



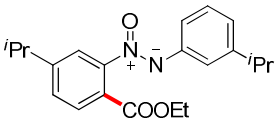
**2-(2,4-Bis(ethoxycarbonyl)phenyl)-1-(4-(ethoxycarbonyl)phenyl)-2-oxohydrazin-2-ium-1-ide (5h)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.50–8.49 (m, 1H), 8.29 (dd, $J$ = 8.2 Hz, 1.6 Hz, 1H), 8.17–8.12 (m, 4H), 7.92 (d, $J$ = 8.3 Hz, 1H), 4.47–4.38 (m, 4H), 4.30 (q, $J$ = 7.1 Hz, 2H), 1.43 (t, $J$ = 6.9 Hz, 3H), 1.42 (t, $J$ = 6.9 Hz, 3H), 1.20 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.53, 164.72, 164.23, 150.54, 146.60, 132.91, 132.50, 131.40, 131.24, 130.06, 127.10, 124.87, 123.99 ,62.13, 61.81, 61.14, 14.17, 14.12, 13.85. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{23}N_2O_7$: 415.1505, Found: 415.1493.



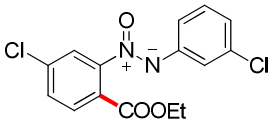
**2-(2-(Ethoxycarbonyl)-5-methylphenyl)-2-oxo-1-(*m*-tolyl)hydrazin-2-ium-1-ide (5i)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.96–7.95 (m, 2H), 7.77 (d, $J$ = 7.9 Hz, 1H), 7.60 (s, 1H), 7.37–7.35 (m, 2H), 7.23 (d, $J$ = 7.5 Hz, 1H), 4.26 (q, $J$ = 7.1 Hz, 2H), 2.47 (s, 3H), 2.43 (s, 3H), 1.17 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.43, 143.14, 138.36, 130.60, 130.56, 130.19, 129.68, 128.38, 127.73, 125.65, 124.20, 123.51, 122.21, 61.54, 21.32, 21.22, 13.85. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_3$: 299.1396, Found: 299.1389.



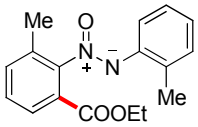
**2-(2-(ethoxycarbonyl)-5-(*iso*-propyl)phenyl)-1-(3-*iso*-propyl)phenyl-2-oxohydrazin-2-ium-1-ide (5j)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $J$ = 8.0 Hz, 1H), 7.96 (s, 1H), 7.81 (d, $J$ = 8.0 Hz 1H), 7.66 (s, 1H), 7.43–7.39 (m, 2H), 7.31–7.29 (m, 1H), 4.27 (q, $J$ = 7.1 Hz, 2H), 3.07–2.96 (m, 2H), 1.32–1.29 (m, 12H), 1.16 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.50, 153.93, 149.39, 148.81, 143.96, 130.31, 128.45, 128.17, 128.10, 123.83, 123.64, 122.34, 121.78, 61.53, 34.01, 34.00, 23.77, 23.40, 13.83. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{21}H_{27}N_2O_3$: 355.2022, Found: 355.2017.



**2-(5-Chloro-2-(ethoxycarbonyl)phenyl)-1-(3-chlorophenyl)-2-oxohydrazin-2-ium-1-ide (5k)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.96–7.94 (m, 1H), 7.83–7.81 (m, 2H), 7.56 (dd, $J$ = 8.3 Hz, 1.8 Hz 1H), 7.43–7.42 (m, 2H), 4.29 (q, $J$ = 7.1 Hz, 2H), 1.20 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.48, 148.81, 144.36, 137.94, 134.38, 131.38, 130.50, 130.07, 129.69, 124.95, 124.90, 124.23, 123.68, 62.04, 13.84. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{15}H_{13}Cl_2N_2O_3$: 339.0303, Found: 339.0304.




**2-(2-(Ethoxycarbonyl)-6-methylphenyl)-2-oxo-1-(*o*-tolyl)hydrazin-2-ium-1-ide (5l)**

Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, $J$ = 7.7 Hz 1H), 7.90 (d, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 7.5 Hz, 1H), 7.45–7.41 (m, 1H), 7.35–7.28 (m, 3H), 4.31 (q, $J$ = 7.1 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 1.24 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.27, 148.39, 142.10, 135.14, 135.12, 131.55, 130.61, 128.92, 128.71, 128.63, 125.79, 124.54, 121.77, 61.58, 18.22, 16.78, 13.89. HRMS (ESI) $[M+H]^+$ Calcd. for $C_{17}H_{19}N_2O_3$: 299.1396, Found: 299.1389.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here].

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