





Article

# C–O Coupling of Hydrazones with Diacetyliminoxyl Radical Leading to Azo Oxime Ethers—Novel Antifungal Agents

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**Abstract:** Selective oxidative C–O coupling of hydrazones with diacetyliminoxyl is demonstrated, in which diacetyliminoxyl plays a dual role. It is an oxidant (hydrogen atom acceptor) and an O-partner for the oxidative coupling. The reaction is completed within 15–30 min at room temperature, is compatible with a broad scope of hydrazones, provides high yields in most cases, and requires no additives, which makes it robust and practical. The proposed reaction leads to the novel structural family of azo compounds, azo oxime ethers, which were discovered to be highly potent fungicides against a broad spectrum of phytopathogenic fungi (*Venturia inaequalis*, *Rhizoctonia solani*, *Fusarium oxysporum*, *Fusarium moniliforme*, *Bipolaris sorokiniana*, *Sclerotinia sclerotiorum*).

**Keywords:** oxime radicals; C–O coupling; fungicidal compounds; crop protection; new modes of action



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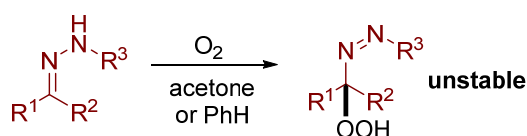
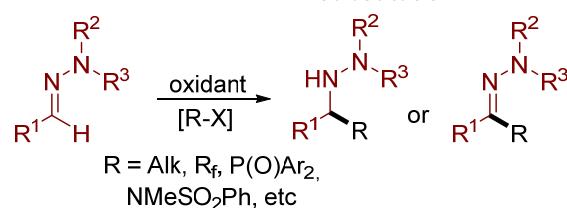
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## 1. Introduction

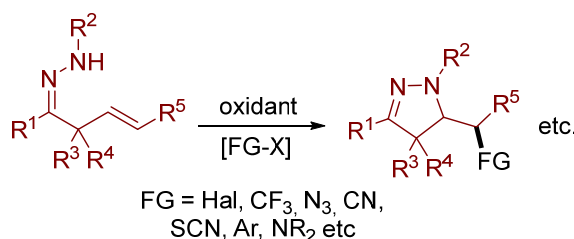
The functionalization of organic compounds employing free radicals has emerged as a powerful tool in modern organic chemistry [1,2]. In particular, *N*-oxyl radicals [3] have gained much attention as key agents in oxidative functionalization due to their mild conditions of generation, relatively high stability combined with high reactivity towards organic substrates, and outstanding structural diversity, allowing for control of their properties. However, *N*-oxyl radicals are usually generated *in situ* from corresponding *N*-hydroxy compounds and thus their usage demands oxidants or catalysts and other additives. Frequently, these additional reagents contain transition-metal salts, pose limitations on the substrate scope, and do not correspond to the principles of green chemistry. The peculiar feature of the present work is the use of diacetyliminoxyl [4] as a single ready-to-use free-radical reagent which plays the role of both oxidant and coupling partner for the oxidative functionalization reaction of hydrazones (Scheme 1C). Previously, free-radical chemistry of hydrazones was associated mainly with addition and hydrogen substitution reactions of aldehyde hydrazones [5–7] (Scheme 1A) and cyclizations of hydrazone-derived *N*-radicals [7–9] (Scheme 1B). However, ionic mechanisms were proposed for oxidative cyclizations of  $\alpha,\beta$ -unsaturated *N*-tosylhydrazones in some cases [8,10]. It should also be noted that in some functionalizations of type A (Scheme 1A), an additional synthetic step of chelate complex formation was necessary for effective radical functionalization of hydrazones [11–13]. Hydrazones are reported to undergo peroxidation by *t*-BuOOH in the presence of cobalt–salen complexes with the formation of geminal azoperoxides and geminal azoxyperoxides [14]. Unstable geminal azohydroperoxides [15] are formed as a result of hydrazone autoxidation by molecular oxygen [16–19]. In general, free-radical

functionalization of hydrazones with the formation of azocompounds is less developed compared to methods based on electrophilic attack of hydrazone carbon atoms, such as Michael-type reactions [20–23], chlorination [24], alkoxylation, or cyanation [25]. Geminal azoacetates are synthesized by the oxidation of hydrazones with  $\text{Pb}(\text{OAc})_4$  [26–28]. In the present work (Scheme 1C), diacetyliminoxyl was used as the only necessary reagent for high-yielding oxidative C–O coupling with the broad scope of both ketohydrazones and aldehyde-derived hydrazones at room temperature. It should be noted that none of the products of oxidative functionalization of hydrazones mentioned above were considered as fungicidal compounds. Unexpectedly, synthesized C–O coupling products were discovered as a new structural family of fungicides with activity against phytopathogenic fungi at the level of commercially used crop-protection compounds. This finding is very important in the light of the continuous development of strains of phytopathogenic fungi which are resistant against known synthetic fungicide types [29–31].

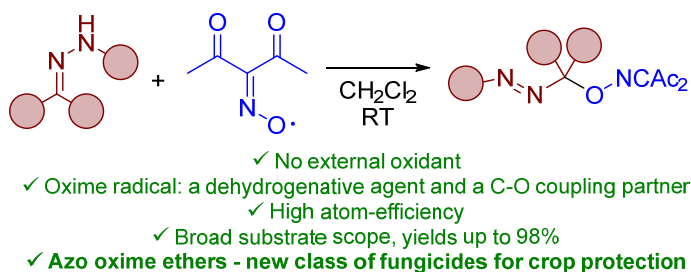
### A. Radical addition and H-atom substitution



### B. Oxidative cyclization of $\beta,\gamma$ -unsaturated hydrazones



### C. This work: selective dehydrogenation and oxidative C–O coupling



Scheme 1. Radical functionalization of hydrazones.

## 2. Results and Discussion

Hydrazone **2aa** was used for the initial experiments with diacetyliminoxyl **1** (Table 1).  $\text{CH}_2\text{Cl}_2$  was used as a solvent because it is a convenient medium for the synthesis and storage of diacetyliminoxyl **1**. The reaction of **2aa** with two equivalents of diacetyliminoxyl under air afforded C–O coupling product **3aa** with an 85% yield (Table 1, entry 1), along with diacetyl oxime **1-H**. The reaction completed in 15 min, as evidenced by the disappearance of the dark red color characteristic of diacetyliminoxyl (for UV-Vis spectrum of **1**,

see [32]) and TLC. To check the possible involvement of oxygen as an oxidant [18] in the discovered process, or its possible negative impact on the yield, an experiment under argon was conducted (Table 1, entry 2). However, carrying out the reaction under inert conditions did not lead to a significant change in the yield of **3aa**. The increase in the amount of **1** above the stoichiometric ratio increased the yield of **3aa** by 10% (entry 3 compared to entry 1). Finally, the reaction with excess of hydrazone **2aa** resulted in almost the same yield as in the case of the stoichiometric amount of **2aa** (entry 4).

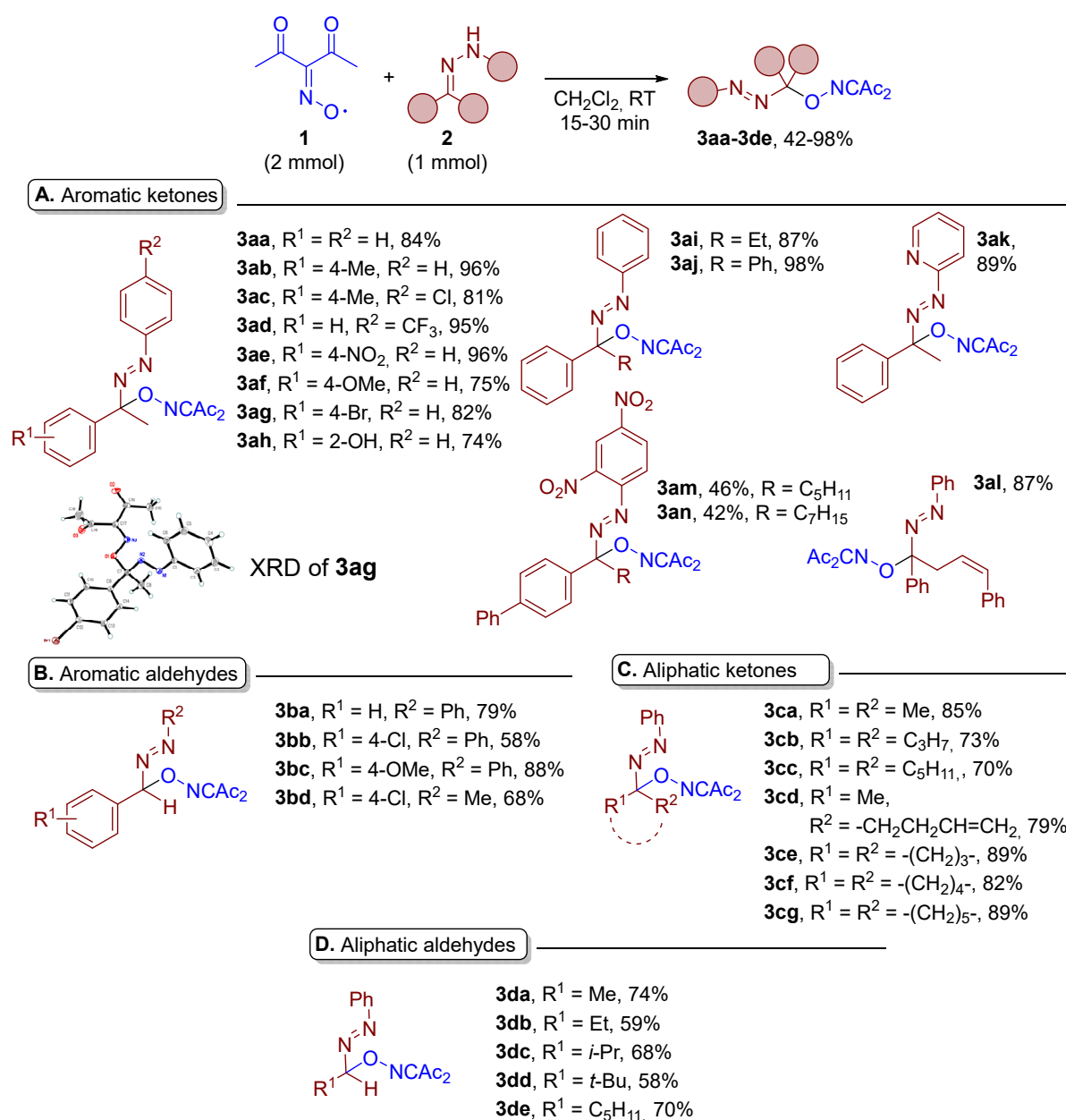
**Table 1.** Screening of the reaction parameters.

Run	Conditions	Yield <b>3aa</b> , % <sup>a</sup>	Yield <b>1-H</b> , % <sup>a</sup>
1	<b>1</b> (2 mmol), <b>2aa</b> (1 mmol), air	85 (84)	86 (82)
2	<b>1</b> (2 mmol), <b>2aa</b> (1 mmol), Argon	79	79
3	<b>1</b> (3 mmol), <b>2aa</b> (1 mmol), air	95	96
4	<b>1</b> (2 mmol), <b>2aa</b> (2 mmol), air	83 <sup>b</sup>	85 <sup>b</sup>

<sup>a</sup> Yields were determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields are given in parentheses. <sup>b</sup> Yields are based on **1** because **2aa** was used in excess. According to the reaction stoichiometry, 100% corresponds to 1 mmol of **3aa** or **1-H**

The conditions of entry 1 of Table 1 were used to test the scope of the discovered C–O coupling (Scheme 2). The discovered C–O coupling is compatible with a wide range of hydrazones derived from aromatic ketones (Scheme 2A), aromatic aldehydes (Scheme 2B), aliphatic ketones (Scheme 2C), and aliphatic aldehydes (Scheme 2D).

Good yields of C–O coupling products **3aa–3ah** (74–96%) were observed for *N*-arylhydrazones of methylalkylketones containing electron-donating or electron-withdrawing substituents at benzene rings. The structure of **3ag** was unambiguously confirmed by XRD analysis (see the ESI). The replacement of a methyl group by ethyl did not affect the reaction yield significantly (product **3ai** compared to **3aa**, yields 84–87%). Hydrazone of benzophenone gave an almost quantitative yield of **3aj** despite steric hindrance and the expected low energy of the formed C–O bond [33] due to the steric and electronic effects of phenyl rings. 2-Pyridyl moiety at the nitrogen atom of ketohydrazone was also tolerated (product **3ak**). The reaction took place even in the case of bulky biphenylalkyl hydrazones with long-chain alkyl groups and a 2,4-dinitrophenyl group at the nitrogen atom, albeit with moderate yields of 42–46% (products **3am**, **3an**). The reaction of diacetylinoxyl with  $\beta,\gamma$ -unsaturated phenylhydrazone **2al** delivered the C–O coupling product **3al** at 87% with the intact double C=C bond, despite the possible radical cyclization reactions typical of  $\beta,\gamma$ -unsaturated phenylhydrazones [9]. Moreover, diacetylinoxyl **1** is known to undergo addition to C=C double bonds at room temperature [34]. Hydrazones derived from aromatic aldehydes also furnish C–O coupling products (**3ba–3bd**) in moderate to high yields. Of note, **3bd** was obtained at a 68% yield employing *N*-methyl-substituted hydrazone **2bd**. The reaction proceeded with high yields with acetone phenylhydrazone (product **3ca**), and somewhat lower yields were obtained with higher homologues of acetone (products **3cd**, **3cd**). As in the case of unsaturated hydrazone **2al**, allylacetone phenylhydrazone **2cd** underwent oxidative C–O coupling with the formation of product **3cd** containing intact C=C bond. Cyclic phenylhydrazones with ring sizes of 4–6 furnished the corresponding products **3ce–3cg** at a 82–89% yield. The hydrazones of aldehydes reacted smoothly with diacetylinoxyl, providing azocompounds **3da–3de** with a 58–74% yield.

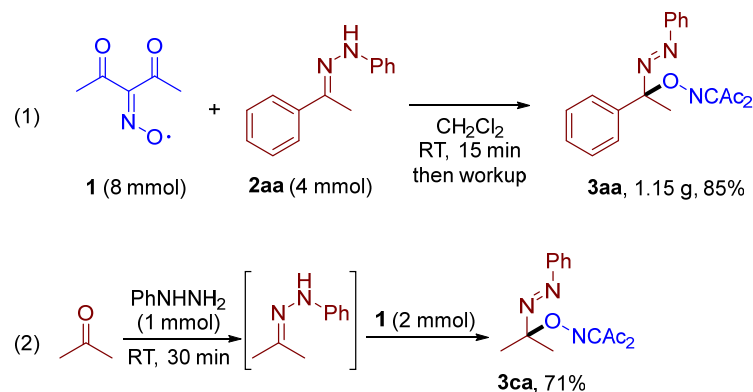


**Scheme 2.** Oxidative C–O coupling of various hydrazones **2** with diacetyliminoxyl **1**.

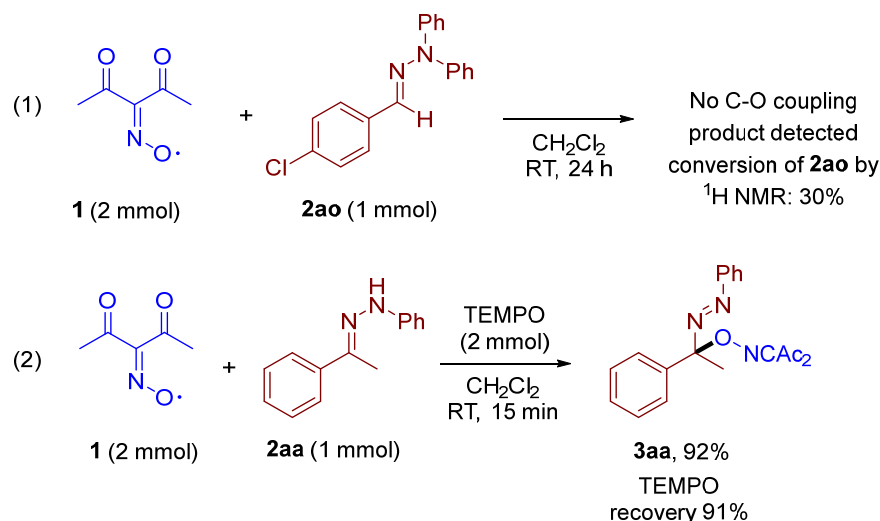
Scheme 3 demonstrates the practical applicability of the developed protocol for the synthesis at a 4 mmol scale without chromatographic purification or recrystallization (Scheme 3, (1)). Due to the instability of some phenylhydrazones in their pure form, we developed a one-pot procedure delivering the in situ generation of hydrazone that was sequentially added to the solution of diacetyliminoxyl (Scheme 3, (2)). Employing this protocol, the corresponding C–O coupling product **3ca** was obtained at a yield of 71%.

Control experiments were conducted to support the plausible reaction mechanism (Scheme 4). *N,N*-diphenyl phenylhydrazone **2ao** was introduced in the reaction with diacetyliminoxyl at standard reaction conditions (Scheme 4, (1)). There was no C–O coupling product observed by <sup>1</sup>H-NMR monitoring of the crude reaction mixture after 24 h, indicating that hydrogen atom abstraction from the nitrogen atom is a possible crucial step rather than the addition of an oxime radical at the C=N double bond. The experiment with TEMPO (Scheme 4, (2)) is a typical control reaction which is usually employed to intercept possible C-centered radical intermediates. The introduction of two equivalents of TEMPO into the reaction of diacetyliminoxyl **1** with hydrazone **2aa** did not lead to

significant changes; product **3aa** was obtained without yield loss (Scheme 4, (2)). Moreover, no formation of a TEMPO adduct with C-centered radical was observed (TEMPO recovery 91%), highlighting the exceptionally high efficiency of diacetyliminoxyl in scavenging stabilized C-centered radicals [33].

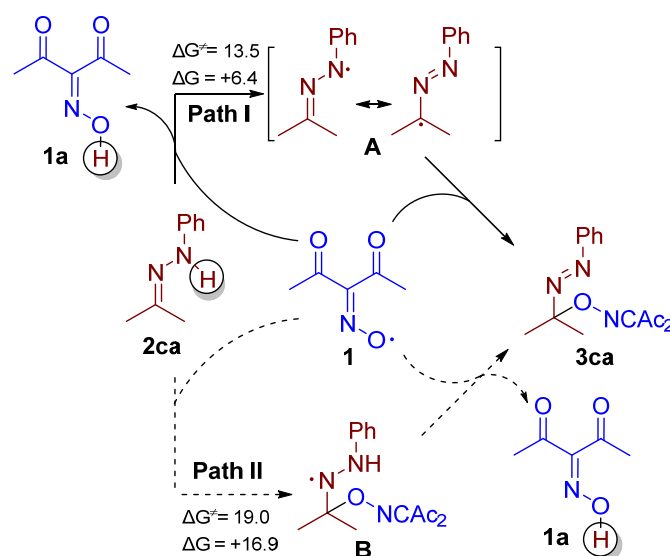


**Scheme 3.** Gram-scale synthesis of **3aa** (1) and developed one-pot procedure for the synthesis of **3ca** (2).



**Scheme 4.** Control experiments: (1) reaction of **1** with *N,N*-disubstituted hydrazone, (2) TEMPO scavenging experiment.

Two possible reaction pathways can be proposed for the discovered C–O coupling of diacetyliminoxyl with hydrazones (Scheme 5). In path I, the hydrogen atom abstraction from hydrazone **2ca** by diacetyliminoxyl **1** is followed by the coupling of the resultant hydrazyl radical **A** with **1**. In path II, diacetyliminoxyl is added to hydrazone **2ca** first, then hydrogen atom from adduct **B** is abstracted. In both cases, the first stage is expected to be rate determining, whereas the second is expected to be very fast or even barrierless. In order to evaluate which path is more plausible, DFT calculations were performed by employing the low-cost but robust B97-3c composite method [35]. The calculations revealed that path I is favored, both kinetically and thermodynamically, compared to path II; however, both pathways demonstrate activation barriers less than  $20 \text{ kcal}\cdot\text{mol}^{-1}$ , which are acceptable for room temperature reactions. The fact that path I is energetically more favored than path II is in agreement with the published data on C–O coupling of diacetyliminoxyl with pyrazolones, isoxazolones, and phenols [33]. However, it should be noted that diacetyliminoxyl addition reactions to  $\pi$ -systems were reported recently [34].



**Scheme 5.** Possible reaction pathway of the oxidative C–O coupling of diacetylliminoxyl with hydrazones ( $\Delta G$  and  $\Delta G^\ddagger$  values are calculated by B97-3c composite DFT method [35] and given in kcal·mol<sup>-1</sup>).

### 3. In Vitro Fungicidal Activity of the Synthesized Azo Compounds

In the second part of our research, the synthesized azo oxime ethers **3** were discovered as a new class of fungicides. Fungal diseases of agricultural crops represents one of the major threats to crop production [36–39]. Phytopathogenic fungi contribute significantly to reductions in crop yield [37–40] and produce mycotoxins, which can be extremely dangerous food contaminants [41–46] (for example, aflatoxins produced by *Aspergillus* genus, trichothecenes by *Fusarium* species, and ergot alkaloids produced by fungi of *Claviceps* genus). Fungicides remain the most effective tool for crop protection against fungal diseases [47]; however, fungicidal resistance development against known active compound classes [29–31,48] is a serious threat to crop production, forcing scientists to search for new types of fungicides. Currently, despite the large number of fungicidal compounds used in agriculture, most of them belong to a limited number of classes and share a common mode of action. Namely, succinate dehydrogenase inhibitors (SDHIs), demethylation inhibitors (DMIs, imidazoles and triazoles), quinone outside inhibitors (QoI, or strobilurins), and quinone inside inhibitors (QiI) dominate the fungicide global market and development [49–51]. Thus, the discovery of novel antifungal agents with unforeseen modes of action is a primary scientific goal [52–58].

Synthesized products **3** were tested for fungicidal activity at concentrations of 10–30  $\mu\text{g}/\text{mL}$  against six phytopathogenic fungi from different taxonomic classes: *V. i.*—*Venturia inaequalis*, *R. s.*—*Rhizoctonia solani*, *F. o.*—*Fusarium oxysporum*, *F. m.*—*Fusarium moniliforme*, *B. s.*—*Bipolaris sorokiniana*, *S. s.*—*Sclerotinia sclerotiorum* (Table 2). Triadimefon and kresoxim-methyl—commercially available fungicides—were used as reference compounds.

**Table 2.** In vitro fungicidal activity of the synthesized azo oxime ethers **3**.

Compound	C, mg/L	Mycelium Growth Inhibition (%)					
		<i>V. i.</i>	<i>R. s.</i>	<i>F. o.</i>	<i>F. m.</i>	<i>B. s.</i>	<i>S. s.</i>
 3aa	30	78	44	51	81	57	47

Table 2. Cont.

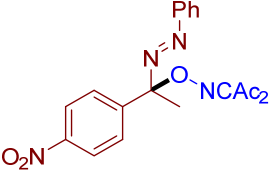
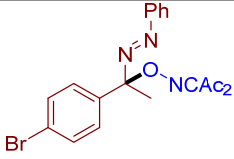
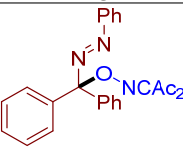
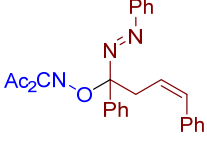
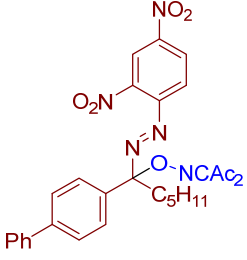
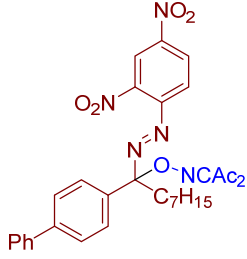
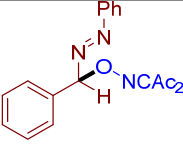
Compound	C, mg/L	Mycelium Growth Inhibition (%)					
		<i>V. i.</i>	<i>R. s.</i>	<i>F. o.</i>	<i>F. m.</i>	<i>B. s.</i>	<i>S. s.</i>
 3ae	30	64	32	55	56	52	18
 3ag	30	49	36	35	26	53	9
 3aj	30	29	42	23	20	24	15
 3al	30	11	41	6	18	17	8
 3am	30	8	34	29	24	26	16
 3an	30	18	22	3	4	10	6
 3ba	30	76	83	34	96	86	97

Table 2. Cont.

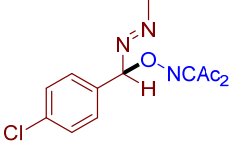
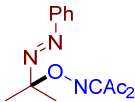
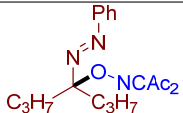
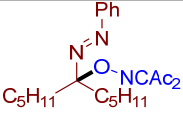
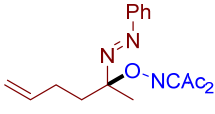
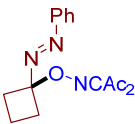
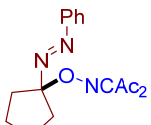
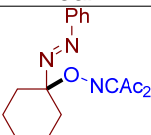
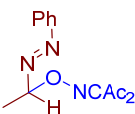
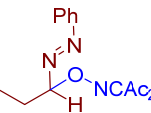
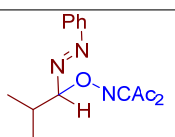
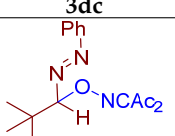
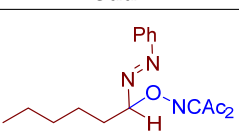
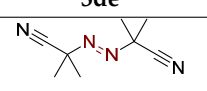
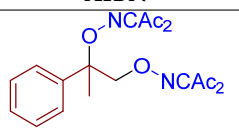
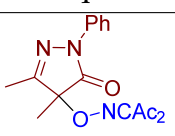
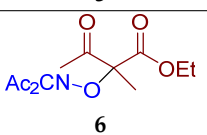
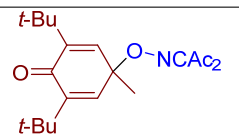
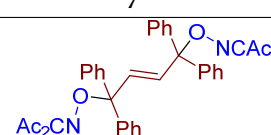
	Compound	C, mg/L	Mycelium Growth Inhibition (%)					
			V. i.	R. s.	F. o.	F. m.	B. s.	S. s.
9		30	38	34	16	21	18	23
	<b>3bd</b>							
10		30	100	85	92	100	66	99
	<b>3ca</b>	10	100	82	88	96	53	97
11		30	16	54	27	48	65	16
	<b>3cb</b>							
12		30	18	15	6	7	23	6
	<b>3cc</b>							
13		30	100	69	78	96	55	86
	<b>3cd</b>	10	71	60	77	92	47	62
14		30	100	92	94	99	84	98
	<b>3ce</b>	10	100	78	92	99	65	100
15		30	98	58	88	98	61	97
	<b>3cf</b>	10	77	71	77	96	35	81
16		30	51	45	63	89	46	39
	<b>3cg</b>							
17		30	100	100	94	100	92	100
	<b>3da</b>	10	100	85	90	100	86	100
18		30	100	100	94	100	84	100
	<b>3db</b>	10	100	94	88	98	67	97



Table 2. Cont.

	Compound	C, mg/L	Mycelium Growth Inhibition (%)					
			V. i.	R. s.	F. o.	F. m.	B. s.	S. s.
19		30	100	98	90	97	70	94
		10	100	78	94	98	75	100
20		30	100	49	30	94	56	81
21		30	84	86	87	93	70	68
		10	81	72	85	89	58	67
22	 AIBN	30	6	19	0	14	21	2
23		30	8	53	18	27	47	11
24		30	60	100	55	65	55	17
25		30	0	17	3	14	8	3
26		30	10	8	21	37	62	19
27		30	6	28	5	16	21	6
28	Triadimefon	30	70	62	65	86	71	71
		10	49	58	62	82	64	63
29	Kresoxim-methyl	10	100	100	65	64	58	54

The data on fungicidal activity exceeding the standard (triadimefon) are highlighted in green.

As can be seen from Table 2, compounds **3da** and **3dc** exhibit the greatest activity against phytopathogenic fungi. In general, azo oxime ethers with small aliphatic substituents at the quaternary carbon atom (**3ca–cg** and **3da–de**) possess a higher activity compared to azo oxime ethers bearing aromatic substituents at the quaternary center (**3aa**, **3ae**, **3ag**, and **3ba**). Compounds **3aj**, **3al**, **3am**, and **3an** with bulky substituents at quater-

nary carbon atom do not show significant fungicidal activity, as well as azo oxime ether **3bd** with a Me substituent at the nitrogen atom. Aldehyde-derived azo oxime ethers (**3ba** and **3da–de**), in general, are superior to ketone derivatives (**3aa**, **3ae**, **3ag**, and **3ca–cg**). In the series of long-chain alkyl or cyclic azo compounds, activity decreases with increasing alkyl chain (**3ca**, **3cb**, **3cc**) or ring size (**3ce**, **3cf**, **3cg**). AIBN, an alkyl azo derivative frequently used as a radical initiator taken for comparison, does not show significant activity. Compounds with a diacetyl oxime moiety, obtained by oxidative C–O coupling of diacetylinoxyl with alkenes [34], pyrazolones [33], phenols [33], and dicarbonyl compounds [59], were also tested for fungicidal activity. None of them show essential mycelium growth inhibition, indicating that diacetyl oxime moiety itself is not sufficient for the manifestation of the observed fungicidal activity. It is noteworthy that the activity of the synthesized azo compounds in the present study was not predictable due to their structural novelty. The closest related fungicidal compounds are generally diaryl azo derivatives [60–62] and substituted oxime derivatives with a RO–N=C–N=N–Ar fragment at the oxime moiety [63]. In contrast to these fungicides, the azo oxime ethers reported in the present work contain a tertiary C(sp<sup>3</sup>) atom at the azo group. The activity of the azo oxime ethers **3ca**, **3cd–cf**, and **3da–de** is comparable to that of triadimefon and kresoxim-methyl, which are commercially available fungicides widely used in crop protection.

EC<sub>50</sub> values were measured for the most promising azo compounds, **3ca** and **3da**, and reference compound kresoxim-methyl (Table 3).

**Table 3.** EC<sub>50</sub> Values for mycelium growth inhibition by the most active azo oxime ethers **3ca** and **3da** in comparison with kresoxim-methyl.

Compound	EC <sub>50</sub> (mg/L)					
	<i>V. i.</i>	<i>R. s.</i>	<i>F. o.</i>	<i>F. m.</i>	<i>B. s.</i>	<i>S. s.</i>
<b>3ca</b>	0.77	1.3	0.44	0.45	3.3	2.1
<b>3da</b>	1.7	1.3	0.37	0.41	0.94	1.0
Reference compound (kresoxim-methyl)	0.16	0.053	0.45	1.0	4.1	0.30

Synthesized azo compounds **3ca** and **3da** have a similar activity spectrum that greatly differs from that of kresoxim-methyl. Overall, the EC<sub>50</sub> values of **3ca** and **3da** are comparable to those of kresoxim-methyl; however, at higher concentrations, these azo compounds demonstrate stronger mycelium growth inhibition (Table 2).

#### 4. Materials and Methods

In all experiments RT stands for 22–25 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE II 300 and Bruker Fourier 300HD (300.13 for <sup>1</sup>H and 75.47 MHz for <sup>13</sup>C, respectively) spectrometers in CDCl<sub>3</sub>. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: <sup>1</sup>H (CDCl<sub>3</sub> δ = 7.26 ppm); <sup>13</sup>C (CDCl<sub>3</sub> δ = 77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). FT-IR spectra were recorded on Bruker Alpha instrument. High resolution mass spectra (HR-MS) were measured on a Bruker maXis instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage—4500 V); mass range from *m/z* 50 to *m/z* 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for all acetonitrile solutions (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Phenylhydrazine 97%, *p*-tolylhydrazine hydrochloride 98%, 4-chlorophenylhydrazine hydrochloride 97%, 4-(trifluoromethyl) phenylhydrazine 96%, 2-hydrazinopyridine 98%, 2,4-dinitrophenylhydrazine 97%, methylhydrazine 98%, acetophenone 98%, 4-methylacetophenone 95%, 4-nitroacetophenone 98%, 4-methoxyacetophenone 98%, 4-bromoacetophenone 98%,

2-hydroxyacetophenone 98%, propiophenone 99%, benzophenone 99%, benzaldehyde 98%, 4-chlorobenzaldehyde 98%, 4-methoxybenzaldehyde 99%, 4-heptanone 98%, 6-undecanone 97%, 5-hexen-2-one 98%, cyclobutanone 98%, cyclopentanone 99%, cyclohexanone 99%, acetaldehyde 99.5%, propionaldehyde 98%, isobutyraldehyde 99+%, pivaldehyde 96%, hexanal 96%. Hydrazones **2** were synthesized by condensation with the corresponding carbonyl compounds [64–69]. Ketones and corresponding hydrazones **2l–n** were synthesized according to published procedures [70–73]. Compounds **4** and **8** [34], **5** [4,33], **7** [33], and **6** [59] with a diacetyl oxime moiety were synthesized by oxidative C–O coupling according to published procedures. CH<sub>2</sub>Cl<sub>2</sub> was distilled prior to use. Acetone was distilled over KMnO<sub>4</sub>. The preparation of diacetylinoxyl radical is described earlier in [4]. Then, Pb(OAc)<sub>4</sub> (469 mg, 1.0 mmol) was added to a stirred solution of diacetyl oxime (258 mg, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) with vigorous stirring. Stirring was continued for 10 min; then, the reaction mixture was chromatographed on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The fraction corresponding to the dark-red spot was collected, so that the volume of the fraction was 50 mL.

#### General reaction conditions for Table 1

Hydrazone **2aa** (1–2 mmol) was added to a stirred solution of diacetylinoxyl radical **1** (2–3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), prepared as described earlier in [4], at room temperature. The reaction mixture was stirred for 15 min under air (entries 1, 3, 4) or under argon (entry 2) atmosphere, until the dark red color of diacetylinoxyl disappeared. After that, the reaction mixture was rotary evaporated under a water-jet vacuum. Yields were determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

#### Experimental details for Scheme 2

Hydrazone **2** (1 mmol, 134–460 mg) was added to a stirred solution of diacetylinoxyl **1** (2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at room temperature. The reaction mixture was stirred at RT for 15–30 min until the red color of diacetylinoxyl disappeared. After that, the reaction mixture was rotary evaporated under a water-jet vacuum. C–O coupling products **3** were isolated by column chromatography on silica gel.

**(E)-3-((1-phenyl-1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3aa**, was synthesized as a yellow oil (84%, purified by column chromatography with DCM as eluent). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>): δ = 7.81–7.69 (m, 2H), 7.56–7.43 (m, 5H), 7.43–7.28 (m, 3H), 2.48 (s, 3H), 2.27 (s, 3H), 2.05 (s, 3H). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>): δ = 198.8, 194.7, 156.6, 151.6, 139.4, 131.6, 129.2, 128.7, 128.6, 126.5, 122.9, 105.2, 30.5, 25.9, 23.8. FT-IR (thin layer): ν<sub>max</sub> = 1725, 1690, 1363, 960, 695. HR-MS (ESI): *m/z* = 360.1313, calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 360.1319.

**(E)-3-((1-(phenyldiazenyl)-1-(*p*-tolyl)ethoxy)imino)pentane-2,4-dione, 3ab**, was synthesized as a yellow oil (96%, purified by column chromatography with DCM as eluent). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>): δ = 7.81–7.71 (m, 2H), 7.54–7.44 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.49 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>): δ = 198.7, 194.7, 156.5, 151.6, 138.6, 136.4, 131.4, 129.24, 129.18, 126.5, 122.8, 105.2, 30.5, 25.8, 23.5, 21.2. FT-IR (thin layer): ν<sub>max</sub> = 1725, 1687, 1363, 1305, 968. HR-MS (ESI): *m/z* = 352.1654, calcd. for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>+H<sup>+</sup>: 352.1656.

**(E)-3-((1-((4-chlorophenyl)diazenyl)-1-(*p*-tolyl)ethoxy)imino)pentane-2,4-dione, 3ac**, was synthesized as a yellow oil (81%, purified by column chromatography with DCM as eluent). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>): δ = 7.70 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>): δ = 198.6, 194.6, 156.7, 149.9, 138.7, 137.5, 136.2, 129.4, 129.3, 126.4, 124.1, 105.3, 30.5, 25.8, 23.4, 21.2. FT-IR (thin layer): ν<sub>max</sub> = 1726, 1690, 1362, 1300, 1088, 959. HR-MS (ESI): *m/z* = 386.1252, 388.1230, calcd. for C<sub>20</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>3</sub>+H<sup>+</sup>: 386.1266, 388.1238.

**(E)-3-((1-phenyl-1-((4-(trifluoromethyl)phenyl)diazenyl)ethoxy)imino)pentane-2,4-dione, 3ad**, was synthesized as a yellow oil (95%, purified by column chromatography with DCM as eluent). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.58–7.49 (m, 2H), 7.47–7.32 (m, 3H), 2.49 (s, 3H), 2.29 (s, 3H), 2.10 (s, 3H). <sup>13</sup>C NMR

(75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.5, 194.5, 156.7, 153.3, 138.8, 132.89 (q,  $J$  = 32.7 Hz), 128.9, 128.7, 126.42 (q,  $J$  = 3.6 Hz), 123.84 (q,  $J$  = 272.5 Hz), 123.0, 105.5, 30.5, 25.7, 23.6. **FT-IR** (thin layer):  $\nu_{\max}$  = 1726, 1692, 1364, 1324, 1169, 1131, 1066, 959. **HR-MS** (ESI):  $m/z$  = 428.1198, calcd. for C<sub>20</sub>H<sub>18</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 428.1192.

**(E)-3-((1-(4-nitrophenyl)-1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3ae**, was synthesized as a yellow oil (98%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.25 (d,  $J$  = 8.9 Hz, 2H), 7.81–7.67 (m, 4H), 7.56–7.45 (m, 3H), 2.48 (s, 3H), 2.24 (s, 3H), 2.03 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.2, 194.3, 157.1, 151.3, 148.0, 146.6, 132.2, 129.4, 127.8, 123.8, 123.0, 104.1, 30.4, 25.9, 24.4. **FT-IR** (thin layer):  $\nu_{\max}$  = 1727, 1693, 1605, 1522, 1350, 1300, 1142, 1109, 1079, 1067, 958, 855, 769, 758, 693. **HR-MS** (ESI):  $m/z$  = 405.1161, calcd. for C<sub>19</sub>H<sub>18</sub>N<sub>4</sub>O<sub>5</sub>+Na<sup>+</sup>: 405.1169.

**(E)-3-((1-(4-methoxyphenyl)-1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3af**, was synthesized as a yellow oil (75%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.80–7.67 (m, 2H), 7.55–7.38 (m, 5H), 6.95–6.82 (m, 2H), 3.80 (s, 3H), 2.47 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.8, 194.7, 159.9, 156.5, 151.6, 131.4, 129.2, 128.0, 122.8, 113.9, 105.1, 55.4, 30.5, 25.8, 23.3. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1690, 1608, 1514, 1363, 1303, 1253, 1185, 1109, 1030, 960, 834, 769. **HR-MS** (ESI):  $m/z$  = 390.1423, calcd. for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>+Na<sup>+</sup>: 390.1424.

**(E)-3-((1-(4-bromophenyl)-1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3ag**, was synthesized as yellow crystals (82%, purified by column chromatography with DCM as eluent). Mp = 90–91 °C. **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81–7.70 (m, 2H), 7.55–7.45 (m, 5H), 7.44–7.35 (m, 2H), 2.47 (s, 3H), 2.27 (s, 3H), 2.01 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.6, 194.6, 156.8, 151.4, 138.6, 131.8, 129.3, 128.4, 123.1, 122.9, 104.6, 102.8, 30.5, 25.9, 23.8. **FT-IR** (thin layer):  $\nu_{\max}$  = 1773, 1484, 1397, 1362, 1302, 1135, 1078, 1010, 966, 920, 828, 685, 550. **HR-MS** (ESI):  $m/z$  = 416.0608, 418.0592, calcd. for C<sub>19</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>3</sub>+H<sup>+</sup>: 416.0604, 418.0585. Single crystal X-ray analysis is available (see Supplementary Figure S1, page S15).

**(E)-3-((1-(2-hydroxyphenyl)-1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3ah**, was synthesized as a pale yellow solid (74%, purified by column chromatography with DCM as eluent) Mp = 103–104 °C. **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.16 (s, 1H), 7.74–7.71 (m, 2H), 7.54–7.49 (m, 3H), 7.36–7.27 (m, 2H), 6.97–6.90 (m, 2H), 2.46 (s, 3H), 2.25 (s, 3H), 2.09 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.2, 194.4, 157.0, 155.4, 150.9, 132.5, 131.3, 129.6, 127.3, 124.0, 123.0, 120.3, 118.5, 106.9, 30.6, 25.9, 22.8. **FT-IR** (thin layer):  $\nu_{\max}$  = 1727, 1692, 1483, 1458, 1364, 1299, 1246, 1201, 1105, 957, 939, 76. **HR-MS** (ESI):  $m/z$  = 376.1260, calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>+Na<sup>+</sup> = 376.1268.

**(E)-3-((1-phenyl-1-(phenyldiazenyl)propoxy)imino)pentane-2,4-dione, 3ai**, was synthesized as a yellow oil (87%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85–7.69 (m, 2H), 7.57–7.53 (m, 2H), 7.51–7.47 (m, 3H), 7.44–7.30 (m, 3H), 2.52 (s, 3H), 2.60–2.35 (m, 2H), 2.23 (s, 3H), 0.88 (t,  $J$  = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.8, 194.7, 156.7, 151.6, 138.2, 131.4, 129.2, 128.5, 128.3, 126.9, 122.8, 106.9, 31.1, 30.3, 25.8, 7.7. **FT-IR** (thin layer):  $\nu_{\max}$  = 2979, 1726, 1691, 1450, 1363, 1296, 1138, 1070, 963, 763, 699, 691. **HR-MS** (ESI):  $m/z$  = 374.1472, calcd. for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 374.1475.

**(E)-3-((diphenyl(phenyldiazenyl)methoxy)imino)pentane-2,4-dione, 3aj**, was synthesized as a slightly yellow solid (98%, purified by column chromatography with DCM as eluent). Mp = 103–104 °C. **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.86–7.75 (m, 2H), 7.58–7.45 (m, 7H), 7.43–7.30 (m, 6H), 2.56 (s, 3H), 2.05 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.7, 194.7, 156.3, 151.5, 139.9, 131.6, 129.3, 128.6, 128.4, 128.0, 123.0, 105.6, 30.1, 25.7. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1686, 1300, 1013, 976, 941, 762, 695. **HR-MS** (ESI):  $m/z$  = 422.1461, calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 422.1475.

**(E)-3-((1-phenyl-1-(pyridin-2-yl)diazenyl)ethoxy)imino)pentane-2,4-dione, 3ak**, was synthesized as a yellow oil (89%, purified by column chromatography with PE/EtOAc = 2/5 as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.70 (d,  $J$  = 4.2 Hz, 1H), 7.85 (td,  $J$  = 7.7, 1.8 Hz, 1H), 7.60–7.48 (m, 3H), 7.46–7.29 (m, 4H), 2.48 (s, 3H), 2.28 (s, 3H), 2.12 (s, 3H). **<sup>13</sup>C NMR**

(75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.6, 194.6, 162.2, 156.8, 149.6, 138.6, 138.5, 129.0, 128.7, 126.5, 125.8, 114.3, 106.0, 30.6, 25.9, 23.5. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1690, 1583, 1455, 1425, 1363, 1299, 1261, 1194, 1145, 1119, 1069, 955, 791, 770, 699. **HR-MS** (ESI):  $m/z$  = 339.1448, calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>+H<sup>+</sup>: 339.1452.

**3-(((Z)-1,4-diphenyl-1-(E)-phenyldiazenyl)but-3-en-1-yl)oxy)imino)pentane-2,4-dione, 3al**, was synthesized as a slightly yellow viscous gum (87%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79–7.70 (m, 2H), 7.58–7.45 (m, 5H), 7.45–7.17 (m, 8H), 6.54 (d,  $J$  = 11.8 Hz, 1H), 5.58 (dt,  $J$  = 11.8, 7.2 Hz, 1H), 3.57 (dd,  $J$  = 7.2, 1.8 Hz, 2H), 2.50 (s, 3H), 1.98 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.6, 194.7, 156.6, 151.5, 137.3, 137.2, 132.5, 131.6, 129.2, 128.74, 128.67, 128.61, 128.4, 127.0, 126.9, 124.9, 122.9, 106.3, 36.2, 30.3, 25.6. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1690, 1600, 1494, 1449, 1363, 1301, 1193, 1059, 1018, 1003, 950, 765, 699. **HR-MS** (ESI):  $m/z$  = 462.1781, calcd. for C<sub>27</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 462.1788.

**(E)-3-(((1-([1,1'-biphenyl]-4-yl)-1-((2,4-dinitrophenyl)diazenyl)hexyl)oxy)imino)pentane-2,4-dione, 3am**, was synthesized as a viscous orange gum (46%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.83 (d,  $J$  = 2.3 Hz, 1H), 8.51 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.73–7.56 (m, 6H), 7.52–7.41 (m, 3H), 7.41–7.32 (m, 1H), 2.60–2.47 (m, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.42–1.20 (m, 6H), 0.94–0.77 (m, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.5, 194.4, 157.1, 148.6, 148.1, 146.1, 141.7, 140.2, 135.6, 129.0, 128.4, 127.9, 127.5, 127.18, 127.15, 120.5, 120.3, 108.1, 37.3, 31.8, 30.2, 25.8, 22.6, 22.4, 14.0. **FT-IR** (thin layer):  $\nu_{\max}$  = 3103, 2957, 2931, 2869, 1726, 1692, 1608, 1536, 1487, 1346, 1298, 1147, 954, 836, 766, 744, 698. **HR-MS** (ESI):  $m/z$  = 582.1955, calcd. for C<sub>29</sub>H<sub>29</sub>N<sub>5</sub>O<sub>7</sub>+Na<sup>+</sup>: 582.1959.

**(E)-3-(((1-([1,1'-biphenyl]-4-yl)-1-((2,4-dinitrophenyl)diazenyl)octyl)oxy)imino)pentane-2,4-dione, 3an**, was synthesized as a viscous orange gum (42%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.82 (d,  $J$  = 2.3 Hz, 1H), 8.51 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.78–7.55 (m, 6H), 7.54–7.40 (m, 3H), 7.39–7.29 (m, 1H), 2.66–2.49 (m, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.55–1.09 (m, 10H), 0.86 (t,  $J$  = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.5, 194.4, 157.1, 148.6, 148.1, 146.1, 141.8, 140.2, 135.6, 129.0, 128.4, 127.9, 127.5, 127.2, 120.5, 120.3, 108.1, 37.4, 31.8, 30.3, 29.6, 29.1, 25.8, 23.0, 22.7, 14.2. **FT-IR** (thin layer):  $\nu_{\max}$  = 1724, 1691, 1607, 1545, 1541, 1346, 1297, 1194, 1146, 963, 835, 766, 747, 698. **HR-MS** (ESI):  $m/z$  = 605.2712, calcd. for C<sub>31</sub>H<sub>33</sub>N<sub>5</sub>O<sub>7</sub>+H<sup>+</sup>: 605.2718.

**(E)-3-((phenyl(phenyldiazenyl)methoxy)imino)pentane-2,4-dione, 3ba**, was synthesized as a yellow oil (79%, purified by column chromatography with DCM as eluent). **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79–7.76 (m, 2H), 7.55–7.51 (m, 2H), 7.50–7.47 (m, 3H), 7.44–7.39 (m, 3H), 6.50 (s, 1H), 2.46 (s, 3H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.9, 194.4, 157.2, 151.6, 134.4, 131.9, 130.7, 129.8, 129.3, 129.0, 127.9, 123.7, 107.3, 30.6, 25.9. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1693, 1453, 1419, 1360, 1195, 1098, 1019, 952, 766, 695. **HR-MS** (ESI):  $m/z$  = 346.1162 calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup> = 346.1162.

**(E)-3-(((4-chlorophenyl)(phenyldiazenyl)methoxy)imino)pentane-2,4-dione, 3bb**, was synthesized as a yellow powder (58%, purified by column chromatography with DCM as eluent). Mp = 49–50 °C. **<sup>1</sup>H NMR** (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.84–7.69 (m, 2H), 7.57–7.42 (m, 5H), 7.42–7.35 (m, 2H), 6.45 (s, 1H), 2.45 (s, 3H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.7, 194.3, 157.3, 151.4, 135.9, 132.9, 132.1, 129.3, 129.23, 129.19, 123.1, 106.5, 30.6, 26.0. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1697, 1488, 1413, 1363, 1296, 1091, 1049, 1019, 939, 821, 768, 691. **HR-MS** (ESI):  $m/z$  = 380.0770, calcd. for C<sub>18</sub>H<sub>16</sub>ClN<sub>3</sub>O<sub>3</sub>+Na<sup>+</sup>: 380.0772.

**(E)-3-(((4-methoxyphenyl)(phenyldiazenyl)methoxy)imino)pentane-2,4-dione, 3bc**, was synthesized as a yellow solid (88%, purified by column chromatography with DCM as eluent). Mp = 69–70 °C. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81–7.69 (m, 2H), 7.51–7.38 (m, 5H), 6.98–6.89 (m, 2H), 6.44 (s, 1H), 3.81 (s, 3H), 2.45 (s, 3H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (76 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.0, 194.5, 160.8, 157.0, 151.5, 131.8, 129.3, 129.2, 126.6, 123.0, 114.4, 107.2, 55.4, 30.6, 25.9. **FT-IR** (thin layer):  $\nu_{\max}$  = 1725, 1692, 1515, 1360, 1300, 1253, 1027, 951. **HR-MS** (ESI):  $m/z$  = 376.1261 calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>+Na<sup>+</sup> = 376.1268.

**(E)-3-(((4-chlorophenyl)(methyldiazenyl)methoxy)imino)pentane-2,4-dione, 3bd**, was synthesized as a yellow oil (68%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz, DMSO- $d_6$ ):  $\delta$  = 7.53 (d,  $J$  = 8.6 Hz, 2H), 7.47 (d,  $J$  = 8.6 Hz, 1H), 6.36 (s, 1H), 3.85 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C NMR}$  (75.47 MHz, DMSO- $d_6$ ):  $\delta$  = 198.2, 193.7, 156.9, 134.5, 133.1, 129.5, 128.9, 104.5, 57.0, 30.1, 25.6. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 1727, 1693, 1493, 1363, 1298, 1090, 977, 950. **HR-MS** (ESI):  $m/z$  = 318.0611, calcd. for  $\text{C}_{13}\text{H}_{14}\text{ClN}_3\text{O}_3+\text{Na}^+$ : 318.0616.

**(E)-3-(((2-(phenyldiazenyl)propan-2-yl)oxy)imino)pentane-2,4-dione, 3ca**, was synthesized as a yellow oil (85%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76–7.67 (m, 2H), 7.52–7.43 (m, 3H), 2.44 (s, 3H), 2.35 (s, 3H), 1.62 (s, 6H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.9, 194.8, 156.3, 151.6, 131.3, 129.2, 122.6, 104.7, 30.6, 25.8, 23.5. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 1726, 1690, 1384, 1303, 1196, 1173, 1145, 1070, 963, 767, 691. **HR-MS** (ESI):  $m/z$  = 298.1160, calcd. for  $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_3+\text{Na}^+$ : 298.1162.

**(E)-3-(((4-(phenyldiazenyl)heptan-4-yl)oxy)imino)pentane-2,4-dione, 3cb**, was synthesized as a yellow oil (73%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.75–7.63 (m, 2H), 7.54–7.41 (m, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.15–1.91 (m, 4H), 1.55–1.19 (m, 4H), 0.90 (t,  $J$  = 7.3 Hz, 6H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 199.0, 194.8, 156.2, 151.6, 131.2, 129.2, 122.5, 107.5, 37.2, 30.4, 25.8, 16.3, 14.6. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 2964, 2934, 2875, 1726, 1690, 1363, 1303, 960, 768, 691. **HR-MS** (ESI):  $m/z$  = 354.1782, calcd. for  $\text{C}_{18}\text{H}_{25}\text{N}_3\text{O}_3+\text{Na}^+$ : 354.1788.

**(E)-3-(((6-(phenyldiazenyl)undecan-6-yl)oxy)imino)pentane-2,4-dione, 3cc**, was synthesized as a yellow oil (70%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.73–7.64 (m, 2H), 7.53–7.42 (m, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.13–1.93 (m, 4H), 1.49–1.18 (m, 12H), 0.86 (t,  $J$  = 6.8 Hz, 6H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.9, 194.8, 156.3, 151.7, 131.1, 129.2, 122.5, 107.6, 34.8, 32.2, 30.4, 25.8, 22.5, 22.4, 14.1. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 2957, 2932, 2870, 1727, 1692, 1363, 1301, 960, 767. **HR-MS** (ESI):  $m/z$  = 410.2402, calcd. For  $\text{C}_{22}\text{H}_{33}\text{N}_3\text{O}_3+\text{Na}^+$ : 410.2414.

**(E)-3-(((2-(phenyldiazenyl)hex-5-en-2-yl)oxy)imino)pentane-2,4-dione, 3cd**, was synthesized as a slightly yellow viscous gum (79%, purified by column chromatography with PE/EA = 10/1 as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76–7.66 (m, 2H), 7.54–7.44 (m, 3H), 5.93–5.62 (m, 1H), 5.21–4.77 (m, 2H), 2.45 (s, 3H), 2.35 (s, 3H), 2.27–1.98 (m, 4H), 1.63 (s, 3H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.9, 194.8, 156.4, 151.6, 137.7, 131.4, 129.2, 122.6, 115.1, 106.0, 36.4, 30.5, 27.4, 25.9, 21.4. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 1726, 1690, 1420, 1367, 1303, 982, 960, 826. **HR-MS** (ESI):  $m/z$  = 338.1475, calcd. for  $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_3+\text{Na}^+$ : 338.1475.

**(E)-3-(((1-(phenyldiazenyl)cyclobutoxy)imino)pentane-2,4-dione, 3ce**, was synthesized as a slightly yellow viscous gum (89%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81–7.70 (m, 2H), 7.56–7.42 (m, 3H), 2.69–2.50 (m, 4H), 2.46 (s, 3H), 2.35 (s, 3H), 2.09–1.84 (m, 2H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.7, 194.7, 157.3, 151.7, 131.4, 129.2, 122.8, 105.2, 31.9, 30.7, 25.9, 12.0. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 1727, 1690, 1364, 1304, 1251, 1143, 954, 768, 690. **HR-MS** (ESI):  $m/z$  = 310.1163, calcd. for  $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3+\text{Na}^+$ : 310.1162.

**(E)-3-(((1-(phenyldiazenyl)cyclopentyl)oxy)imino)pentane-2,4-dione, 3cf**, was synthesized as a slightly yellow viscous gum (82%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78–7.63 (m, 2H), 7.55–7.40 (m, 3H), 2.44 (s, 3H), 2.35 (s, 3H), 2.30–2.12 (m, 4H), 1.96–1.81 (m, 4H).  $^{13}\text{C NMR}$  (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.8, 194.8, 156.8, 151.7, 131.2, 129.2, 122.6, 115.6, 36.4, 30.5, 25.9, 24.8. **FT-IR** (thin layer):  $\nu_{\text{max}}$  = 2959, 1725, 1685, 1363, 1302, 1188, 959, 766, 690. **HR-MS** (ESI):  $m/z$  = 340.1059, calcd. for  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_3+\text{K}^+$ : 340.1058.

**(E)-3-(((1-(phenyldiazenyl)cyclohexyl)oxy)imino)pentane-2,4-dione, 3cg**, was synthesized as a slightly yellow viscous gum (89%, purified by column chromatography with DCM as eluent).  $^1\text{H NMR}$  (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.74–7.64 (m, 2H), 7.55–7.39 (m, 3H), 2.46 (s, 3H), 2.45 (s, 3H), 2.19–2.06 (m, 2H), 1.92–1.68 (m, 5H), 1.67–1.46 (m, 2H), 1.45–1.27 (m, 1H).

$^{13}\text{C}$  NMR (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.9, 194.8, 156.6, 151.7, 131.2, 129.2, 122.6, 105.2, 32.1, 30.6, 25.9, 25.0, 21.9$ . FT-IR (thin layer):  $\nu_{\text{max}} = 2938, 2863, 1727, 1689, 1599, 1450, 1420, 1363, 1304, 1275, 1256, 1195, 1159, 1146, 1069, 1023, 983, 960, 928, 911, 766, 691$ . HR-MS (ESI):  $m/z = 316.1654$ , calcd. for  $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_3 + \text{H}^+$ : 316.1656.

**(E)-3-((1-(phenyldiazenyl)ethoxy)imino)pentane-2,4-dione, 3da**, was synthesized as a pale brown gum (74%, purified by column chromatography with DCM as eluent).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79\text{--}7.69$  (m, 2H), 7.54–7.44 (m, 3H), 5.67 (q,  $J = 6.3$  Hz, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 1.59 (d,  $J = 6.3$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 198.2, 194.5, 156.8, 151.5, 131.7, 129.3, 122.8, 103.5, 30.6, 25.9, 17.5$ . FT-IR (thin layer):  $\nu_{\text{max}} = 1727, 1691, 1365, 1299, 1107, 1088, 1060, 965, 770, 691$ . HR-MS (ESI):  $m/z = 300.0733$ , calcd. for  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_3 + \text{K}^+$ : 300.0745.

**(E)-3-((1-(phenyldiazenyl)propoxy)imino)pentane-2,4-dione, 3db**, was synthesized as a pale yellow gum (59%, purified by column chromatography with DCM as eluent).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.83\text{--}7.64$  (m, 2H), 7.60–7.39 (m, 3H), 5.55–5.41 (m, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 2.15–1.88 (m, 2H), 1.05 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 198.2, 194.6, 156.9, 151.5, 131.6, 129.3, 122.8, 107.9, 30.6, 25.9, 25.3, 8.7$ . FT-IR (thin layer):  $\nu_{\text{max}} = 1726, 1691, 1363, 1301, 1022, 988, 950, 769, 691$ . HR-MS (ESI):  $m/z = 298.1152$ , calcd. for  $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_3 + \text{Na}^+$ : 298.1162.

**(E)-3-((2-methyl-1-(phenyldiazenyl)propoxy)imino)pentane-2,4-dione, 3dc**, was synthesized as a yellow gum (68%, purified by column chromatography with DCM as eluent).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 7.77\text{--}7.68$  (m, 2H), 7.62–7.49 (m, 3H), 5.42 (d,  $J = 5.5$  Hz, 1H), 2.40 (s, 3H), 2.39–2.28 (m, 1H), 2.26 (s, 3H), 0.99 (t,  $J = 7.5$  Hz, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 198.3, 193.7, 156.7, 150.9, 131.8, 129.4, 122.3, 109.1, 31.1, 30.0, 25.5, 17.5, 16.6$ . FT-IR (thin layer):  $\nu_{\text{max}} = 2970, 1726, 1691, 1364, 1299, 1020, 998, 959, 769, 691$ . HR-MS (ESI):  $m/z = 290.1500$ , calcd. For  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3 + \text{H}^+$ : 290.1499.

**(E)-3-((2,2-dimethyl-1-(phenyldiazenyl)propoxy)imino)pentane-2,4-dione, 3dd**, was synthesized as a pale yellow gum (21%, purified by column chromatography with DCM as eluent).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.80\text{--}7.69$  (m, 2H), 7.53–7.44 (m, 3H), 5.27 (s, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 1.08 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.1, 194.5, 156.8, 151.6, 131.6, 129.3, 122.9, 112.1, 36.0, 30.4, 25.7$ . FT-IR (thin layer):  $\nu_{\text{max}} = 2973, 1727, 1693, 1365, 1300, 1021, 999, 959$ . HR-MS (ESI):  $m/z = 326.1474$ , calcd. for  $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_3 + \text{Na}^+$ : 326.1475.

**(E)-3-(((1-(phenyldiazenyl)hexyl)oxy)imino)pentane-2,4-dione, 3de**, was synthesized as a yellow gum (70%, purified by column chromatography with DCM as eluent).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.80\text{--}7.67$  (m, 2H), 7.55–7.42 (m, 3H), 5.55 (dd,  $J = 7.7, 5.1$  Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 2.11–1.76 (m, 2H), 1.55–1.40 (m, 2H), 1.40–1.23 (m, 4H), 0.89 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.2, 194.6, 156.8, 151.5, 131.6, 129.2, 122.8, 107.0, 31.8, 31.6, 30.6, 25.9, 23.9, 22.5, 14.1$ . FT-IR (thin layer):  $\nu_{\text{max}} = 2956, 2931, 1727, 1691, 1363, 1299, 964$ . HR-MS (ESI):  $m/z = 318.1810$ , calcd. for  $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_3 + \text{H}^+$ : 318.1812.

#### Experimental details for gram-scale synthesis of 3aa (Scheme 3)

Hydrazone **2aa** (4 mmol, 840 mg) was added to a stirred solution of diacetyliminoxyl **1** (8 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 mL) at room temperature. The reaction mixture was stirred at RT for 15 min, then rotary evaporated under a water-jet vacuum to an approximate volume of 40 mL. The reaction mixture was successively washed with 50 mL of saturated solution of  $\text{NaHCO}_3$ , 50 mL of water, dried over  $\text{MgSO}_4$ , and rotatory evaporated under a water-jet vacuum. The obtained C–O coupling product **3aa** (1.15 g, 3.41 mmol) was analytically pure, which was further confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

#### Experimental details for one-pot procedure for the synthesis of 3ca (Scheme 3)

Phenylhydrazine (1 mmol, 108 mg) was dissolved in acetone (5 mL) and stirred at room temperature for 30 min. Then, the resulting solution was added dropwise to a stirred solution of diacetyliminoxyl **1** (2 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL). The obtained reaction mixture was stirred at RT for 15 min, and was then rotary evaporated under a water-jet vacuum.

The C–O coupling product **3ca** was purified by column chromatography on silica gel as described in the experimental details of Scheme 2.

**Experimental details for reaction of 1 with *N,N*-disubstituted hydrazone 2ao (Scheme 4)**

Hydrazone **2ao** (1 mmol, 306 mg) was added to a stirred solution of diacetylinoxyl **1** (2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at room temperature. The reaction mixture was stirred at RT for 24 h and analyzed by <sup>1</sup>H-NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

**Experimental details for TEMPO scavenging experiment (Scheme 4).**

TEMPO (2 mmol, 312 mg) and hydrazone **2aa** (1 mmol, 210 mg) were added to a stirred solution of diacetylinoxyl radical **2** (2 mmol) in DCM (50 mL). The reaction mixture was stirred for 15 min at room temperature and was then rotary evaporated under water-jet vacuum. Column chromatography on silica gel afforded **3aa** (310 mg, 0.92 mmol, 92%) and TEMPO (284 mg, 1.81 mmol, 91% recovery).

**Fungicidal activity tests (experimental details for Tables 2 and 3).** The standard poison food technique [58,74–78] was used for fungicidal activity measurements against six phytopathogenic fungi of different taxonomic classes: *V.i.*—*Venturia inaequalis* MRA-16-2, *R.s.*—*Rhizoctonia solani* 100063, *F.o.*—*Fusarium oxysporum* FO-8, *F.m.*—*Fusarium moniliforme* 100146, *B.s.*—*Bipolaris sorokiniana* MRB(V)-1, *S.s.*—*Sclerotinia sclerotiorum* 100033. The strains used in this work were obtained from the collection of the All-Russian Research Institute for Phytopathology (B. Vyazemy, Moscow reg., Russia). The tested substances were dissolved in acetone (concentration 1 mg/mL) and introduced into liquid sugar-potato agar at 50–55 °C, so that the final substance concentration in the nutrient medium was 10 mg/L, and mixed thoroughly. Then, the agar containing the tested substance was poured into sterile Petri dishes. After the cooling of agar to room temperature, pieces of mycelium from the peripheral growth zone of a 3–5 day old culture of the fungus were transferred to test Petri dishes using a needle. A colony grown in the same medium without the addition of a fungicidal substance (same volume of acetone without any substance was added) was used as a control. The diameters of the formed fungal colonies were measured 72 h after inoculation. Each experiment was repeated 3 times, except for tests with *V.i.* culture which were conducted in 5 replicates. The suppression of mycelium growth in comparison with the control was calculated as  $((D_c - D_s)/D_c) \times 100\%$ , where  $D_c$  is an average fungus colony diameter in control medium, and  $D_s$  is an average fungus colony diameter in the presence of the tested substance. Serial two-fold dilution experiments were conducted for EC<sub>50</sub> determination.

**Computational details (Scheme 5).** DFT calculations were conducted by the B97-3c composite method [35] including D3 dispersion correction [79,80], as implemented in the Orca 5.0.4 program [81]. The main conformers of diacetylinoxyl **1** and hydrazone **2ca** were considered in all calculations. The presented results correspond to 218.15 K and 1 atm. See the supporting information for the cartesian coordinates and energy values of optimized structures of **1a**, **1**, **2ca**, **A**, **B**, and transition states for path I and path II. Optimized geometries were visualized by the Avogadro 1.2 program [82].

## 5. Conclusions

In summary, we have disclosed the oxidative C–O coupling of hydrazones with diacetylinoxyl as a ready-to-use radical reagent playing two roles: the role of a hydrogen atom acceptor and the role of a partner for the C–O coupling. The developed protocol is compatible with both aromatic and aliphatic keto- and aldehyde-derived hydrazones. Synthesized azo oxime ethers were discovered as a novel structural fungicide type with activity against phytopathogenic fungi that is comparable to the activity of commercial fungicides (triadimefon and kresoxim-methyl).

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28237863/s1>, <sup>1</sup>H and <sup>13</sup>C NMR spectra of the synthesized compounds, XRD of **3ag**, computational details. References [83–86] are cited in the supplementary materials.



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