Synthesis of Functionalized Diaryldiazenes by Formal [3+3] Cyclizations of 1,3-Bis(silyloxy)-1,3-butadienes with 2-Aryldiazenyl-3-silyloxy-2-en-1-ones

Jennifer Hefner[a], Simone Ladzik[a], Martin Hein[a], Manuela Harms[b], Michael Lalk[b], Nazken Kelzhanova[a], Amanzhan T. Saginayev[c], Qamar Rahman[d], Alexander Villinger[a], Christine Fischer[e], and Peter Langer[a,e]

[a] Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
[b] Institut für Pharmazie, Ernst-Moritz-Arndt-Universität Greifswald, F.-L.-Jahn-Str. 17, 17487 Greifswald, Germany
[c] Atyrau Institute of Oil and Gas, Atyrau, Republic of Kazakhstan
[d] Amity University, Lucknow Campus, Viraj Khand-5, Gomti Nagar, Lucknow – 226010, India
[e] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Reprint requests to Prof. Peter Langer. Fax: +381 4986412. E-mail: peter.langer@uni-rostock.de

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The formal [3+3] cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 2-aryldiazenyl-3-silyloxy-2-en-1-ones afforded a variety of functionalized diaryl-diazenes.

Key words: Azo Compounds, Cyclizations, Diazenes, Silyl Enol Ethers, Salicylates

Introduction

In 1995, 800.000 t of organic dyes were produced every year. Half of this amount is based on azo compounds which can be used to realize various kinds of colors and show excellent pigment properties [1]. Chrysoidin, developed in 1875, represents the first synthetic azo dye which is still used today for coloring paper (Fig. 1). The bis-azo dyes Naphthol Blueblack 6B and Kongo Red are used for textiles [1]. Azo dyes are also used in analytical chemistry. For example, methyl orange is used as an indicator. The use of azo compounds, such as Butter Yellow or Brown FK (E154), as food dyes is limited by their toxicity. For example, Druckrey was the first to show that Butter Yellow can cause liver cancer. This resulted in prohibition of this dye for food industries as early as in 1938 [2, 3]. More recently, diaryl-diazenes have been shown to be interesting lead structures in medicinal chemistry. Pharmacologically active derivatives include, for example, the salicylate-derived diazene **A** (Fig. 1) which exhibits anti-cancer, cytotoxic, apoptosis-inducing, antiallergic, antihistaminic, and protein-binding activity. It inhibits the release of leukotriene B_4, thromboxane B_2, and prostaglandin and shows interesting transport properties *in vivo* [4]. Diazene **B**, the dye Alizarin Yellow R, shows inhibition of amyloid fibril formation [5 – 9].

Diaryl-diazenes have been prepared by electrophilic substitution reactions of benzene derivatives with aryldiazonium salts. Despite the general usefulness of this method, the synthesis of highly substituted and functionalized derivatives is problematic, due to the formation of mixtures of *ortho/para* regioisomeres and due to the limited availability of the required starting materials. Instead of the formation of a C–N bond, diaryl-diazenes have also been prepared by formation of two C–C bonds based on cyclization reactions of diazene-containing building blocks. The cyclization of 2-aryldiazenyl-1,3-diones with guanidine [10], sulfuryl diamide [11], hydroxylamine [12], hydrazines [13, 14], hydrazides [15], and anilines [16] afforded various aryl-hetaryl-diazenes [18 – 21]. Recently, we reported preliminary results [22] related to the first synthesis of functionalized diaryl-diazenes, containing two benzene moieties, based on a building

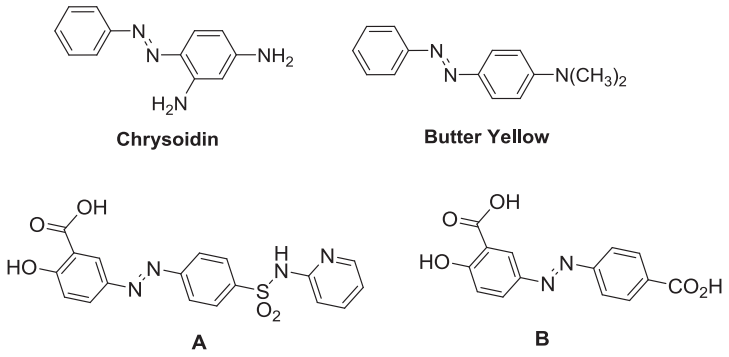


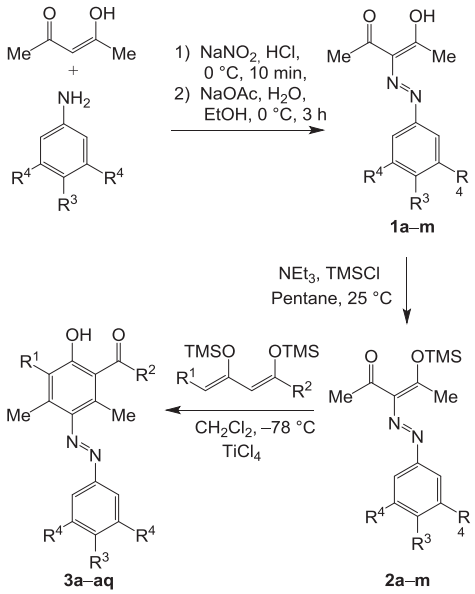
Fig. 1. Important diaryl-diazenes.

block approach. These reactions, which rely on the formal [3+3] cyclization of 2-aryldiazenyl-3-silyloxy-2-en-1-ones with 1,3-bis(silyloxy)-1,3-butadienes [23], allow for a convenient synthesis of salicylate-derived diazenes which are not readily available by other methods. Herein, we wish to report full details and a study related to the preparative scope.

Results and Discussion

Synthesis

The reaction of pentane-2,4-dione with various anilines, following a known procedure [17], afforded the 2-aryldiazenyl-1,3-diones **1a**–**m** (Scheme 1, Tables 1A and 1B). Derivatives **1c**–**e**, **g**, **m** are new. The silylation of **1a**–**m** gave the 2-aryldiazenyl-3-silyloxy-2-en-1-ones **2a**–**m**. The $TiCl_4$-mediated reaction of various 1,3-bis(trimethylsilyloxy)-1,3-butadienes with **2a**–**m**, readily available from the corresponding 1,3-dicarbonyl compounds [24 – 28], afforded the diaryldiazenes **3a**–**ao**. During the optimization, it proved to be important to carry out the reaction in a highly concentrated solution. The products are formed by $TiCl_4$-mediated attack of the terminal carbon atom of the 1,3-bis(trimethylsilyloxy)-1,3-butadiene onto the 3-silyloxy-2-en-1-one, cyclization *via* the central carbon atom of the diene onto the carbonyl group, and aromatization. The yields of the products were in the range of 12 – 66 %. The low yields can be explained by incomplete conversion and by $TiCl_4$-mediated oxidative dimerization of the diene, which is a known process [27, 28]. In addition, the difficult chromatographic purification resulted in a decrease of the yield in many cases. The base-mediated cyclization of **3h** afforded chromane **4** in 76 % yield (Scheme 2).



Scheme 1. Synthesis of diaryl-diazenes **3a**–**aq**.

Solid-state structures

The structures of several products in the solid state were studied by X-ray crystal structure analyses. Table 2 shows crystal data. All compounds show intramolecular hydrogen bonds also contained in Table 2. For those compounds, where the hydroxyl protons were not refined freely, the distances to the carbonyl oxygen atoms are given without standard deviation. The distances d(O–H···O) are in the range of 1.65 – 1.95 Å, the distances d(O···O) are in the range of 2.512 – 2.621 Å. The values are similar to that reported for salicylic acid (d(O···O) = 2.590 – 2.620 Å; d(O–H···O) = 1.690 – 1.704 Å) [29, 30]. In Table 2 only the

Table 1A. Synthesis of **3a–v**.

3	R^1	R^2	R^3	R^4	Yield (%) (**3**)[a]	M. p. (°C)	λ_{max} (nm)
a	H	OMe	H	H	66	82	228, 335, 457
b	H	OEt	H	H	60	66 – 67	
c	Me	OMe	H	H	50	88 – 90	226, 338, 457
d	Et	OMe	H	H	51	75 – 77	227, 340, 467
e	OMe	OMe	H	H	41	79 – 80	227, 338, 459
f	*n*Undec	OMe	H	H	35		
g	H	O*i*Pr	H	H	46		
h	$(CH_2)_3Cl$	OMe	H	H	41	86 – 87	
i	H	OMe	H	Me	31	140 – 143	232, 335, 457
j	H	OMe	Et	H	33	74 – 75	245, 335, 453
k	Me	OMe	Et	H	30		
l	H	OMe	*i*Pr	H	32		231, 340, 455
m	Me	OMe	*i*Pr	H	31	82 – 84	
n	H	OEt	*i*Pr	H	41	49 – 50	
o	H	O*i*Pr	*i*Pr	H	60		
p	$(CH_2)_3Cl$	OMe	*i*Pr	H	30	62 – 64	
q	H	OMe	*t*Bu	H	41	70 – 72	230, 335, 453
r	Me	OMe	*t*Bu	H	30	137 – 139	
s	H	OEt	*t*Bu	H	37	62 – 64	
t	H	O*i*Pr	*t*Bu	H	31	97	
u	H	OEt	*n*-Dec	H	23	42 – 43	245, 337, 450
v	$Ph(CH_2)_2$	OMe	OMe	H	31		

[a] Isolated yields.

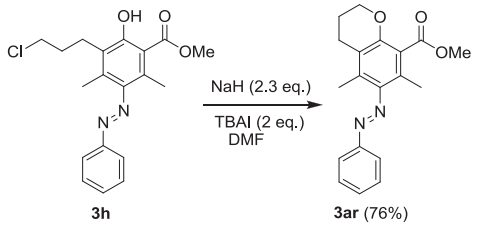
Table 1B. Synthesis of **3w–aq**.

3	R^1	R^2	R^3	R^4	Yield (%) (**3**)[a]	M. p. (°C)	λ_{max} (nm)
w	Me	OMe	OMe	H	36	131 – 132	
x	H	OEt	OMe	H	31	77 – 78	245, 340, 444
y	H	$(CH_2)_2OMe$	OMe	H	33	77 – 79	
z	$(CH_2)_3Cl$	OMe	OMe	H	22	95 – 96	
aa	H	OEt	SMe	H	38	85 – 87	245, 356, 451
ab	Me	OMe	SMe	H	55	91 – 93	
ac	Et	OMe	SMe	H	39	86 – 88	
ad	H	$(CH_2)_2OMe$	SMe	H	32	85 – 86	
ae	Allyl	OMe	SMe	H	30	61 – 63	
af	$(CH_2)_3Cl$	OMe	SMe	H	39	125 – 127	
ag	*n*Pr	OMe	SMe	H	22	80 – 82	
ah	H	OMe	COOEt	H	11	122 – 123	245, 348, 468
ai	H	OMe	Cl	H	44	95 – 98	230, 340, 456
aj	Me	OMe	Cl	H	35	121 – 122	
ak	OMe	OMe	Cl	H	32	96 – 98	
al	H	OEt	Cl	H	40	99 – 100	
am	Et	OMe	Cl	H	47	61 – 63	
an	H	OMe	Br	H	20	111 – 113	231, 341, 461
ao	$(CH_2)_3Cl$	OMe	Br	H	21	107 – 109	
ap	H	OEt	OCF_3	H	12	56 – 57	245, 339, 453
aq	H	OEt	-O-CH_2-O		24	116 – 117	245, 354, 446

[a] Isolated yields.

distances between the hydrogen donor and acceptor oxygens are given because the determination of the exact positions of the hydrogen atoms is unreliable (see also the section *Crystal Structure Determination*).

The bond lengths of the azo group are in the range of d(N–N) = 1.207 – 1.259 Å (for comparison: d_{cov}(N=N) = 1.20 Å; d_{cov}(N≡N) = 1.10 Å [31]) as also reported [36, 37] for azo-benzene (d(N–N) = 1.171 – 1.243 Å) (Table 3). The C–N bond lengths are also in the range as reported for azo-benzene (d(C–N) = 1.433 – 1.472 Å) [32]. In all cases, the azo group exists in the thermodynamically favored *E*-configuration ((C–N–N–C) ∼ 180°). The torsion angles to the azo-phenyl group are quite different



Scheme 2. Synthesis of chroman **3ar**.

and vary in the range of (N1–N2–C–C) = 0.2 – 26.8°. The largest angle is observed for diazene **3d**. The azo phenyl moiety and the salicylate moiety are orthogonal to each other (= 90°) (Fig. 2). This structure is stabilized in the crystal lattice by intermolecular short contacts between a hydrogen atom of the azophenyl group and an oxygen atom of the hydroxyl group of a neighboring molecule (d(C–H···O) ∼ 2.5 Å) with a distance of the hydrogen donor and acceptor atoms (d(C15···O3*) = 3.257 Å. Related structures are found for derivatives **3am** and **3q** (Figs. 3, 4). Table 3 shows selected bond lengths and torsion angles (d in Å, in deg).

To study the importance of π stacking in the crystal structures, the shortest intermolecular distance between the phenyl groups were inspected for all compounds (Table 4). The angles between the planes of the rings were not taken into consideration. The shortest distance d_{min} = 3.645 Å is observed for derivative **3a** (Fig. 5). In general, the π stacking is stronger for derivatives containing a hydrogen atom located next to the hydroxyl group (**3a**, **3i**, **3q**, **3an**) as compared to those containing a hydrogen atom next to an alkyl group located (**3d**, **3am**), presumably due to the steric effect of the latter. However, for all products the π-stacking effects are not predominant for the structure of the crystal lattice because of the relatively large distances [33 – 37]. The intra- and intermolecular hydrogen bonds are more relevant (*vide infra*).

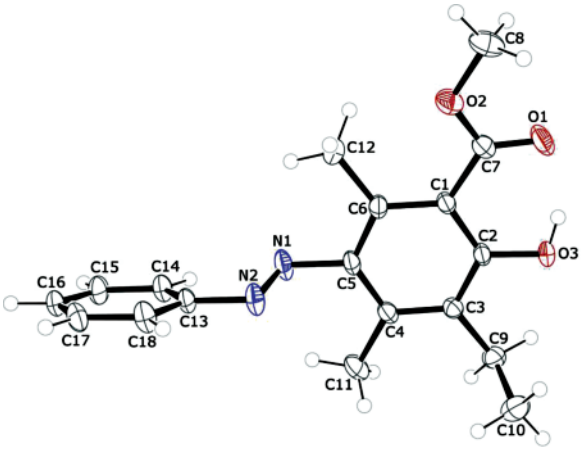


Fig. 2. ORTEP plot of the molecular structure of **3d** in the solid (displacement ellipsoids at the 50 % probability level; hydrogen atoms as spheres with arbitrary radius).

The structure of **3an** is shown in Fig. 6. The unit cell contains two independent molecules, with the second molecule disordered. The structural parameters of both molecules differ greatly from each other and are discussed separately. In both molecules intramolecular hydrogen bonds were found. In molecule 1 the distance between the hydrogen donor and acceptor oxygen atoms is d(O3···O1) = 2.528 Å. For molecule 2 (disordered) the values are d(O6a···O4a) = 2.668 Å (major occupancy) and d(O6b···O4b) = 2.49 Å (minor occupancy). The difference of the d(O···O) values for the two molecules of **3an** is due to the carboxyl group, which is not in the aromatic ring plane for molecule 2 [molecule 1: (C2–C1–C7–O1) = +4.9°, molecule 2: (C18a–C17a–C23a–O4a) = +31.1° (major occupancy) and (C18b–C17b–C23b–O4b) = −16°

	Crystal system	Space group	Z	Intramolecular hydrogen bonds d(O···O) (Å)
3a	orthorhombic	*Pbca*	8	2.517(2)
3d	monoclinic	$P2_1/n$	4	2.542(2)
3am	monoclinic	$P2_1/n$	4	2.541(3)
3q	monoclinic	$P2_1/n$	8	2.513(4)[a] and 2.512(4)[a]
3an	triclinic	$P\bar{1}$	4	2.528(3)[a,b], 2.668(10)[a,b] (major occupancy) and 2.49(3)[a,b](minor occupancy)
3i	triclinic	$P\bar{1}$	2	2.523(1)

Table 2. Overview of crystal structure analyses.

[a] Two symmetry-independent molecules per cell unit; [b] the difference between the d(O···O) values for the 2 molecules of **3an** is due to the carboxyl group, which is not in the aromatic ring plane for the second (disordered) molecule.

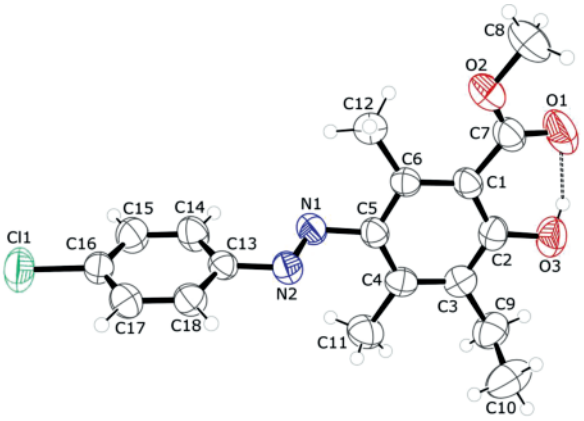


Fig. 3. ORTEP plot of the molecular structure of **3am** in the solid (displacement ellipsoids at the 50 % probability level; hydrogen atoms as spheres with arbitrary radius).

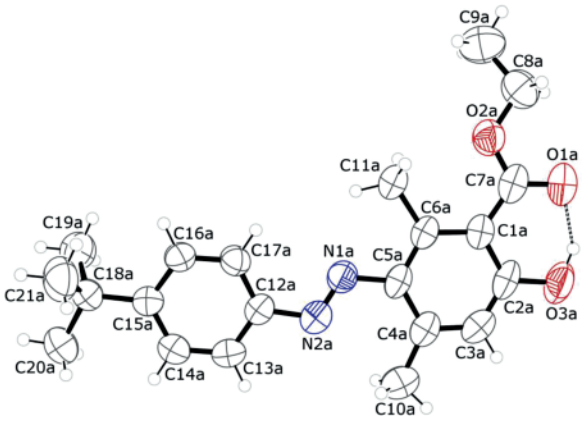


Fig. 4. ORTEP plot of the molecular structure of **3q** in the solid (displacement ellipsoids at the 50 % probability level; hydrogen atoms as spheres with arbitrary radius).

	d(N–N)	*d*(C–N1)	*d*(N2–C)	(C–N–N–C)	(N1–N2–C–C)
3a	1.259(2)[a]	1.425(2)[a]	1.439(2)[a]	−178.7(1)[a]	+0.2(3)[a]
	1.21(1)[a]	1.459(8)[a]	1.47(1)[a]	+178.7(5)[a]	−11(1)[a]
3d	1.216(2)	1.448(2)	1.443(3)	−179.6(1)	+26.8(2)
3am	1.233(2)	1.440(2)	1.436(2)	−177.0(1)	+16.0(3)
3q	1.216(3)[b]	1.418(3)[b]	1.436(3)[b]	−179.0(2)[b]	−9.0(4)[b]
	1.207(3)[b]	1.423(4)[b]	1.451(4)[b]	+179.6(2)[b]	−5.3(5)[b]
3an	1.229(2)[b]	1.419(3)[b]	1.425(3)[b]	−177.0(2)[b]	−5.0(4)[b]
	1.238(3)[a,b]	1.431(3)[a,b]	1.438(3)[a,b]	−179.6(3)[a,b]	+3.1(4)[a,b]
	1.237(9)[a,b]	1.417(7)[a,b]	1.424(7)[a,b]	+180(1)[a,b]	−1(2)[a,b]
3i	1.254(1)	1.421(1)	1.431(1)	−179.47(8)	−20.9(1)

[a] Disordered; [b] two symmetry-independent molecules per cell unit.

Table 3. Selected bond lengths (Å) and dihedral angles (deg).

Table 4. π-Stacking effects.

Compound	d_{min} (stacking) (Å)	Compound	d_{min} (stacking) (Å)
3a	3.645	**3q**	3.743
3d	4.978	**3an**	3.849
3am	4.303	**3i**	3.691

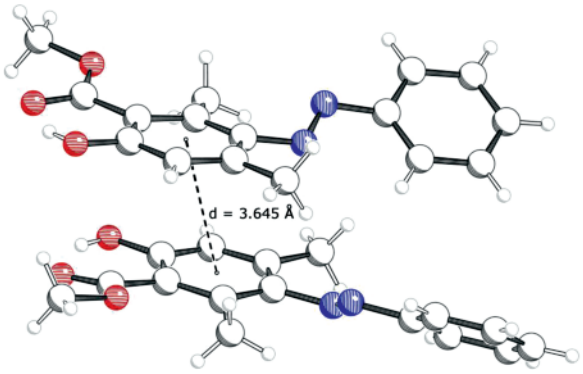


Fig. 5. π-Stacking of **3a** (the disorder of the molecules is not shown).

(minor occupancy)]. The N–N bond lengths of the azophenyl moiety are *d*(N1–N2) = 1.229 Å, *d*(N3a–N4a) = 1.238 (major occupancy) and *d*(N3b–N4b) = 1.237 Å (minor occupancy) for molecules 1 and 2, respectively. The torsion angles of the azophenyl moieties are (N1–N2–C11–C12) = –5.0°, (N3a–N4a–C27a–C28a) = 3.1° (major occupancy) and (N3b–N4b–C27b–C28b) = –0.7° (minor occupancy) for molecules 1 and 2, respectively. In addition to intramolecular hydrogen bonds, intermolecular hydrogen bonds are observed in the range of 2.3 to 2.5 Å [distances between the hydrogen donor and acceptor oxygens: *d*(O4a···O3) = 3.133 Å (*d*(O4b···O3) = 3.138 Å for minor occupancy of molecule 2) and *d*(O1···O6a) = 3.024 Å (*d*(O1···O6b) = 2.926 Å for minor occupancy of molecule 2)]. The distance between the carbonyl oxygen atoms (*d*(O1···O4a) = 2.787 Å

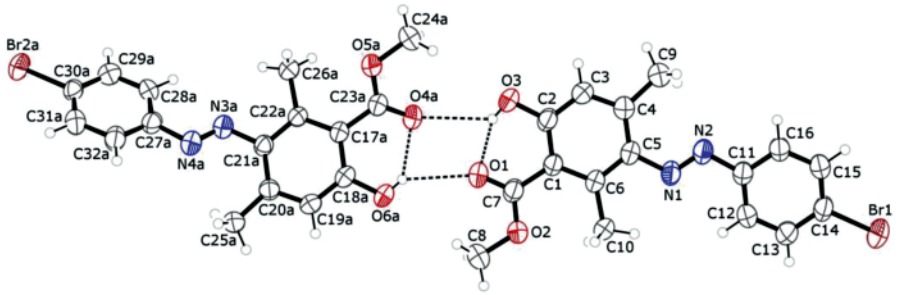


Fig. 6. Dimer formation of **3an** without showing the disorder of molecule 2 (displacement ellipsoids at the 50% probability level; hydrogen atoms as spheres with arbitrary radius).

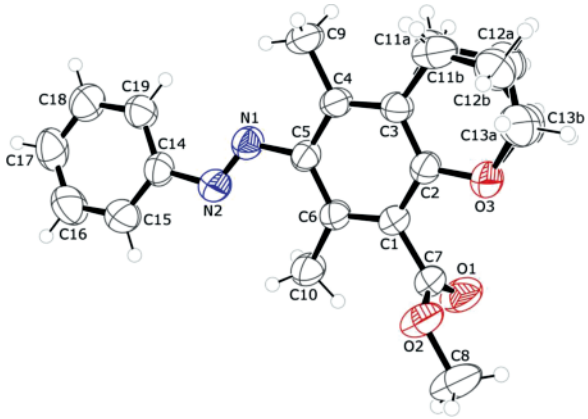


Fig. 7. ORTEP plot of the molecular structure of **3ar** in the crystal showing the disordered heterocyclic ring (displacement ellipsoids at the 50% probability level; hydrogen atoms as spheres with arbitrary radius).

and d(O1···O4b) = 2.756 Å) is shorther than the sum of the van der Waals radii (r_{vdW}(O) = 1.5 Å, d_{vdW}(O···O) = 3.0 Å [38]).

The structure of **3ar** was also studied by X-ray crystal structure analysis (Fig. 7). The heterocyclic ring is disordered in the solid state.

The puckering parameters [39] of the sequence O3–C2–C3–C11a–C12a–C13a (heterocyclic ring) are Q = 0.478(7) Å, θ = 128.2(7)° and ϕ = 85.4(9)°. This results in a conformation between $^6H_5$ (H = semi-chair) and $^6S_5$ (S = screw-boat) [40]. For the sequence O3–C2–C3–C11b–C12b–C13b the values are Q = 0.494(9) Å, θ = 51,7(1)° and ϕ = 273.3(1)°. Weak intermolecular O···H interactions are observed between O1 and a proton of the methyl group C10** (H10a**) (distance between hydrogen donor and acceptor atom: d(O1···C10**) = 3.514 Å; ** = neighboring molecule 2). The distance between the oxygen atoms O(1) is d(O1···O1**) = 3.628 Å. Weak interactions are also observed between another proton of the methyl group C10 (H10c) and carbon atoms C15* and C16* of the azophenyl moiety of another neighboring molecule (distances between hydrogen donor and acceptor atoms: d(C10···C15*) = 3.748 Å and d(C10···C16*) = 3.582 Å; * = neighboring molecule 1). Layers are formed in the crystal lattice as depicted in Fig. 8.

Spectroscopic studies

For all products, intramolecular hydrogen bonds are present in solution as indicated by the low-field shifts in the ^{1}H NMR spectra in the range of δ = 11.09 – 11.51 ppm ($CDCl_3$). UV/Vis spectroscopic studies were carried out in dichloromethane. All products show three bands. The spectrum of **3a** is discussed in detail as an representative example for all other derivatives (Fig. 9). The first absorption (λ = 228 nm, ε_{max} = 18468) with a shoulder at λ = 250 nm and the second absorption (λ = 334 nm, ε_{max} = 16 195) can be assigned to the $\pi \rightarrow \pi^*$ transitions of the molecule. Azo compounds usually exhibit low lying (n,π^*)-electronic states which are coupled to other (lower) energy states. The weak third absorption located at λ = 457 nm (ε_{max} = 568) can be assigned to such coupled $n \rightarrow \pi^*$ transitions. A systematic influence of the substituents on the absorptions was not observed.

Pharmacological activity

The cytotoxicity of three derivatives were studied using the immortalized human keratinocyte cell line

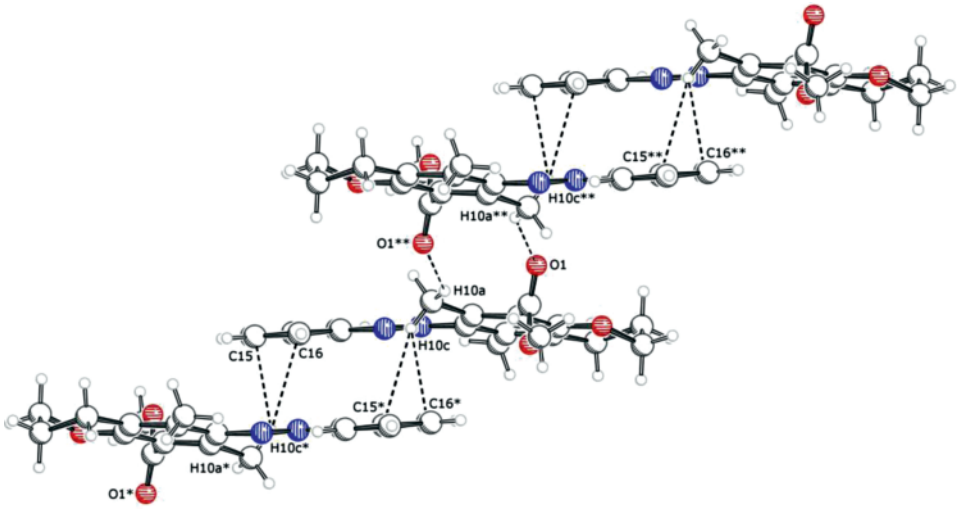


Fig. 8. Layers of **3ar** formed in the crystal (dashed lines show weak intermolecular interactions; the disorder of the dihydropyrane rings is not shown).

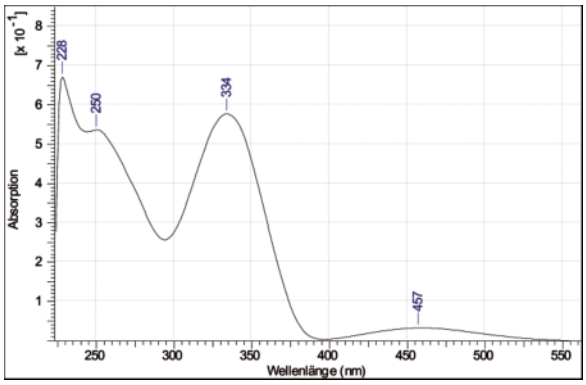


Fig. 9. UV/Vis spectrum of **3a** (1.0 mg in 100 mL of dichloromethane).

HaCaT. The incubation with the test compounds was carried out for three days, with several parallel experiments and the results confirmed by two independent screenings. At a high concentration of 100 μM all compounds showed a weak (**3al**) or strong (**3e** and **3am**) cytotoxicity. The IC_{50} values of **3e** and **3am** were 44.5 μM und 63.8 μM, respectively. At lower concentrations ($< 12.5\ \mu$M) the compounds proved to be non-toxic. The presence of chlorine atoms plays a minor role for the cytotoxicity. In contrast, the presence of the substituent located next to the hydroxyl groups, as present in case of **3e** and **3am**, seems to be advantageous for the cytotoxicity.

Conclusions

In conclusion, we have reported formal [3 + 3] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes with readily available 2-aryldiazenyl-3-silyloxy-2-en-1-ones. These reactions provided a convenient approach to various functionalized diaryl-diazenes which are not readily available by other methods. The structures in solution and in the solid state were studied in detail.

Experimental Section

General comments

All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents were used as indicated. Mass spectrometric data (MS) were obtained by electron impact ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative-scale chromatography silica gel 60 (0.063 – 0.200 mm, 70 – 230 mesh) was used.

General procedure for the synthesis of 3-aryldiazenyl-4-hydroxy-pent-3-en-2-ones ***1a–m***

To a solution of the aniline (0.02 mol) in 4.3 mL of hydrochloric acid was slowly added 0.02 mol of $NaNO_3$ (dissolved in 2.4 mL of water) at −5 °C. To the mixture was added 0.15 mol of NaOAc dissolved in 75 mL of water and

75 mL of ethanol at 0 °C. Subsequently, 0.02 mol of acetylacetone was added, and the solution was stirred for 15 min. A precipitate formed which was filtered off, washed with ice-cold water, and dissolved in ether or dichloromethane. The solution was dried (Na_2SO_4), filtered, and the solvent of the filtrate was removed *in vacuo* to give **1a**–**m**. The synthesis of **1a**, **b**, **h**–**k** has been previously reported [17].

*3-(4-iso-Propylphenyldiazenyl)-4-hydroxy-pent-3-en-2-one (**1c**)*

Starting with 4-isopropylaniline (2.7 g, 20.0 mmol), sodium nitrite (1.38 g, 20.0 mmol) and acetylacetone (2.0 g, 20.0 mmol), **1c** was isolated as a yellow solid (4.08 g, 83 %); m. p.: 62 – 64 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (d, $^3J = 6.92$ Hz, 6H, $CH(CH_3)_2$), 2.45 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.84 – 3.01 (sept, $^3J = 6.89$ Hz, 1H, CH), 7.24 – 7.28 (m, 2H, Ar), 7.33 – 7.37 (m, 2H, Ar), 14.81 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 23.9$ ($CH(CH_3)_2$), 26.6, 31.6 (CH_3), 33.7 (CH), 116.4, 127.6 (CH_{Ar}), 132.9, 139.4, 147.1 (C_{Ar}/C–N), 197.1, 197.7 ppm (CO/COH). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3330$ (w), 3043 (w), 2959 (w), 1676 (s), 829 (m), 792 (m). – MS (GC, 70 eV): m/z (%) = 246 (100) $[M]^+$, 231 (32), 134 (48), 120 (55), 91 (35), 43 (80). – HRMS (EI): $m/z = 246.135907$ (calcd. 246.13628 for $C_{14}H_{18}N_2O_2$, $[M]^+$). – Anal. for $C_{14}H_{18}N_2O_2$ (246.30): calcd. C 68.27, H 7.37, N 11.37; found C 68.11, H 7.29, N 11.22.

*3-(4-tert-Butylphenyldiazenyl)-4-hydroxy-pent-3-en-2-one (**1d**)*

Starting with 4-tert-butylaniline (3.0 g, 20.0 mmol), sodium nitrite (1.38 g, 20.0 mmol) and acetylacetone (2.0 g, 20.0 mmol), **1c** was isolated as a yellow solid (4.74 g, 91 %); m. p.: 81 – 82 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9H, $C(CH_3)_3$), 2.48 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 7.33 – 7.36 (m, 2H, Ar), 7.41 – 7.45 (m, 2H, Ar), 14.80 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 26.6$ (CH_3), 31.3 ($C(CH_3)_3$), 31.6 (CH_3), 34.6 ($C(CH_3)_3$), 116.0, 126.5 (CH_{Ar}), 133.0, 139.1, 149.3 (C_{Ar}/C–N), 197.0, 197.7 ppm (CO/COH). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2960$ (w), 1666 (s), 1618 (m), 1519 (s), 1186 (s), 835 (s), 748 (m). – MS (GC, 70 eV): m/z (%) = 260 (73) $[M]^+$, 245 (100), 134 (40), 43 (66). – HRMS (EI): $m/z = 260.15183$ (calcd. 260.15139 for $C_{15}H_{20}N_2O_2$, $[M]^+$). – Anal. for $C_{15}H_{20}N_2O_2$ (260.33): calcd. C 69.20, H 7.74, N 10.76; found C 69.40, H 7.94, N 10.41.

*3-(4′-n-Decyl)phenyldiazenyl-4-hydroxy-pent-3-en-2-one (**1e**)*

Starting with 4-decylaniline (4.67 g, 20.0 mmol), sodium nitrite (1.38 g, 20.0 mmol) and acetylacetone (2.0 g, 20.0 mmol), **1e** was isolated as a yellow solid (2.4 g, 35 %); m. p.: 61 – 62 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (t, $^3J = 6.7$ Hz, 3H, CH_2CH_3), 1.24 – 1.33 (m, 14H, 7 × CH_2), 1.55 – 1.68 (m, 2H, CH_2), 2.47 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.60 (t, $^3J = 7.7$ Hz, 2H, CH_2Ar), 7.20 (d, $^3J = 8.5$ Hz, 2H, ArH), 7.32 (d, $^3J = 8.5$ Hz, 2H, ArH), 14.81 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.1$ (CH_2CH_3), 22.7 (CH_2CH_3), 26.6 (CH_3), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (br) (CH_2), 31.4 (CH_2), 31.6 (CH_3), 31.9 (CH_2), 35.4 (CH_2), 116.3 (CH_{Ar}), 129.6 (CH_{Ar}), 132.9 (*n*-Dec), 139.4 (C_{Ar}N=N), 141.1 (C-3), 197.1, 197.7 ppm (COH, C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3064$ (w), 2953 (w), 2919 (s), 2847 (m), 1667 (s), 1621 (m), 1585 (w), 1495 (s), 1464 (w), 1426 (w), 1371 (m), 1351 (m), 1321 (m), 1311 (w), 1270 (m), 1195 (s), 1176 (s), 1166 (s), 1115 (w), 1055 (m), 1024 (w). – MS (GC, 70 eV): m/z (%) = 344 (100) $[M]^+$, 217 (39), 106 (66), 43 (56). – Anal. for $C_{21}H_{32}N_2O_2$(344.20): calcd. C 73.22, H 9.36, N 8.13; found C 73.37, H 9.21, N 8.23.

*3-(4′-Methylthio)phenyldiazenyl-4-hydroxy-pent-3-en-2-one (**1g**)*

Starting with 4-methylthioaniline (2.78 g, 20.0 mmol), sodium nitrite (1.38 g, 20.0 mmol) and acetylacetone (2.0 g, 20.0 mmol), **1g** was isolated as a red-brown solid (4.2 g, 84 %); m. p.: 115 – 116 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.46$ (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.59 (s, 3H, SCH_3), 7.26 – 7.25 (m, 4H, ArH), 14.80 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 16.3$ (SCH_3), 26.6 (CH_3), 31.6 (CH_3), 116.8 (CH_{Ar}), 128.0 (CH_{Ar}), 133.1 ($C_{Ar}SCH_3$), 136.1 (C_{Ar}N=N), 139.1 (C-3), 197.0, 197.9 ppm (COH, C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3312$ (w), 3232 (w), 2979 (w), 2916 (w), 1666 (s), 1621 (s), 1572 (m), 1510 (s), 1493 (m), 1411 (m), 1364 (m), 1345 (m), 1325 (m), 1314 (s), 1300 (s), 1266 (s), 1202 (s), 1184 (s), 1166 (s), 1119 (w), 1107 (w), 1088 (m), 1049 (w), 1023 (m). – MS (GC, 70 eV): m/z (%) = 250 (69) $[M]^+$, 138 (100), 43 (25). – Anal. for $C_{12}H_{14}N_2O_2S$ (250.08): calcd. C 57.58, H 5.64, N 11.19, S 12.81; found C 57.82, H 5.83, N 11.18, S 12.97.

*3-((3,5-Dimethylphenyl)diazenyl)-4-hydroxy-pent-3-en-2-one (**1m**)*

Starting with 3,5-dimethylaniline (2.42 g, 20.0 mmol), sodium nitrite (1.38 g, 20.0 mmol) and acetylacetone (2.0 g, 20.0 mmol), **1m** was isolated as a yellow solid (3.76 g, 81 %); m. p.: 91 – 92 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.35$ (s, 6H, CH_3), 2.50 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 6.85 (s, 1H, Ar), 7.03 (s, 2H, Ar), 14.71 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, CDCl3): $\delta = 21.4$, 26.7, 31.6 (CH_3), 114.1, 127.8 (CH_{Ar}), 133.0, 139.5, 141.5 (C_{Ar}/CN), 197.2, 197.8 ppm (CO/COH). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3360$ (w), 2921 (w), 1673 (s), 1519 (s), 1450 (m), 1183 (s), 787 (m). – MS (GC, 70 eV): m/z (%) = 232 (100) $[M]^+$, 121 (55),

120 (59), 105 (35), 43 (83). – HRMS (EI): $m/z = 232.12046$ (calcd. 232.12063 for $C_{13}H_{16}N_2O_2$, $[M]^+$). – Anal. for $C_{13}H_{16}N_2O_2$ (232.28): calcd. C 67.22, H 4.94, N 12.06; found C 66.52, H 6.83, N 11.97.

General procedure for the synthesis of 3-aryldiazenyl-4-trimethylsilyloxy-pent-3-en-2-ones ***2a–m***

To a pentane or dichloromethane solution of 1.0 mmol of **1** was added 1.6 mmol of triethylamine. The solution was stirred for 1 – 2 h, and then 1.8 mmol TMSCl was added. The stirring was continued for 3 d. After filtration under argon atmosphere, the solvent was removed *in vacuo* to give **2a–m**. Due to their unstable nature, **2a–m** were characterized only by ^{1}H NMR spectroscopy and used directly after their preparation.

*3-(Phenyldiazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2a**)*

Starting with **1a** (3.063 g, 15.0 mmol), NEt_3 (1.973 g, 19.5 mmol) and Me_3SiCl (2.444 g, 22.5 mmol) in CH_2Cl_2 (30 mL) **2a** was isolated as an orange-yellow solid (3.814 g, 92 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.09$ (s, 9H, $Si(CH_3)_3$), 2.34 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.01 – 7.10 (m, 3H, ArH), 7.15 – 7.20 ppm (m, 2H, ArH).

*3-(4′-Ethyl)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2b**)*

Starting with **1b** (3.2 g, 13.8 mmol), NEt_3 (3.1 mL, 22.1 mmol) and Me_3SiCl (3.2 mL, 24.8 mmol) in CH_2Cl_2 (30 mL), **2b** was isolated as a brown solid (3.25 g, 77 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.05 - 0.16$ (m, 9H, $Si(CH_3)_3$), 1.07 – 1.17 (m, 3H, CH_2CH_3), 2.37, 2.49 (s, 3H, CH_3), 2.55 (q, $^3J = 8.2$ Hz, 2H, CH_2CH_3), 6.92 – 7.15 ppm (m, 4H, ArH).

*3-((4-iso-Propylphenyl)diazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2c**)*

Starting with **1c** (2.461 g, 10.0 mmol), NEt_3 (1.315 g, 13.0 mmol) and Me_3SiCl (1.630 g, 15.0 mmol) in CH_2Cl_2 (20 mL), **2c** was isolated as an orange-yellow solid (2.962 g, 93 %). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.16$ (s, 9H, $Si(CH_3)_3$), 1.19 (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 2.41 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 3.02 (sept, $^3J = 6.9$ Hz, 1H, CH), 7.03 – 7.06 (m, 2H, ArH), 7.17 – 7.21 ppm (m, 2H, ArH).

*3-((4-tert-Butylphenyl)diazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2d**)*

Starting with **1d** (2.603 g, 10.0 mmol), NEt_3 (1.315 g, 13.0 mmol) and Me_3SiCl (1.630 g, 15.0 mmol) in CH_2Cl_2 (20 mL), **2d** was isolated as an orange-yellow solid (3.026 g, 91 %). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H, $Si(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 2.44 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.30 – 7.33 (m, 2H, Ar), 7.38 – 7.42 ppm (m, 2H, Ar).

*3-(4′-n-Decyl)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2e**)*

Starting with **1e** (2.5 g, 7.3 mmol), NEt_3 (1.6 mL, 11.7 mmol) and Me_3SiCl (1.7 mL, 13.1 mmol) in CH_2Cl_2 (40 mL), **2j** was isolated as a yellow solid (0.96 g, 32 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.00 - 0.32$ (m, 9H, $Si(CH_3)_3$), 0.87 (t, $^3J = 7.0$ Hz, 3H, CH_2CH_3), 1.18 – 1.35 (m, 16H, 8 × CH_2), 1.52 – 1.67 (m, 2H, CH_2Ar), 2.47, 2.59 (s, 3H, CH_3), 7.20, 7.32 ppm (d, $^3J = 8.5$ Hz, 2H, ArH).

*3-(4′-Methoxy)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2f**)*

Starting with **1f** (3.2 g, 13.7 mmol), NEt_3 (3.0 mL, 21.9 mmol) and Me_3SiCl (3.2 mL, 24.6 mmol) in CH_2Cl_2 (30 mL), **2b** was isolated as a slightly yellow solid (3.6 g, 86 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.12 - 0.15$ (m, 9H, $Si(CH_3)_3$), 2.36, 2.49 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 6.84, 7.26 ppm (d, $^3J = 8.7$ Hz, 2H, ArH).

*3-(4′-Methylthio)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2g**)*

Starting with **1g** (3.5 g, 14.0 mmol), NEt_3 (3.1 mL, 22.4 mmol) and Me_3SiCl (3.2 mL, 25.2 mmol) in pentane (50 mL), **2g** was isolated as a brown solid (4.2 g, 93 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.22$ (s, 9H, $Si(CH_3)_3$), 2.46, 2.47, 2.49 (s, 3H, 2 × CH_3, SCH_3), 7.11, 7.28 ppm (d, $^3J = 8.7$ Hz, 2H, ArH).

*3-(4′-Ethoxycarbonyl)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2h**)*

Starting with **1h** (3.0 g, 8.6 mmol), NEt_3 (1.9 mL, 13.8 mmol) and Me_3SiCl (1.98 mL, 15.5 mmol) in CH_2Cl_2 (50 mL), **2d** was isolated as a yellow solid (1.0 g, 33 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H, $Si(CH_3)_3$), 1.38 – 1.41 (m, 3H, OCH_2CH_3), 2.50, 2.60 (s, 3H, CH_3), 4.37 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 7.42, 8.08 ppm (d, $^3J = 8.8$ Hz, 2H, Ar).

*3-((4-Chlorophenyl)diazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2i**)*

Starting with **1i** (2.506 g, 10.5 mmol), NEt_3 (1.381 g, 13.7 mmol) and Me_3SiCl (1.717 g, 15.8 mmol) in CH_2Cl_2 (20 mL), **2i** was isolated as an orange-yellow solid (2.938 g, 90 %). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.14$ (s, 6H, $Si(CH_3)_2$), 0.16 (s, 3H, $SiCH_3$), 2.39 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 7.17 – 7.18 (m, 2H, Ar), 7.25 – 7.27 ppm (m, 2H, Ar).

*3-((4-Bromophenyl)diazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2j**)*

Starting with **1j** (2.831 g, 10.0 mmol), NEt_3 (1.315 g, 13.0 mmol) and Me_3SiCl (1.630 g, 15.0 mmol) in CH_2Cl_2 (20 mL), **2j** was isolated as an orange-yellow solid (3.127 g, 88 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H, $Si(CH_3)_3$), 2.44 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.23 – 7.25 (m, 2H, Ar), 7.47 – 7.50 ppm (m, 2H, Ar).

*3-(4′-Trifluoromethoxy)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2k**)*

Starting with **1k** (3.0 g, 10.4 mmol), NEt_3 (2.3 mL, 16.7 mmol) and Me_3SiCl (2.4 mL, 18.7 mmol) in CH_2Cl_2 (40 mL), **2k** was isolated as a yellow solid (1.25 g, 42 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9H, $Si(CH_3)_3$), 2.48, 2.60 (s, 3H, CH_3), 7.26, 7.42 ppm (d, $^3J = 8.8$ Hz, 2H, ArH). – ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -58.1$ ppm (OCF_3).

*3-(3′-4′Dioxolo)phenyldiazenyl-4-trimethylsilyloxy-pent-3-en-2-one (**2l**)*

Starting with **1l** (3.0 g, 12.1 mmol), NEt_3 (2.7 mL, 19.4 mmol) and Me_3SiCl (2.8 mL, 21.8 mmol) in CH_2Cl_2 (60 mL), **2l** was isolated as a brown solid (1.42 g, 37 %). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.02 - 0.25$ (m, 9H, $Si(CH_3)_3$), 2.44, 2.57 (s, 3H, CH_3), 5.99 (s, 2H, CH_2), 6.71 – 6.80 (m, 2H, ArH), 7.05 ppm (s, 1H, ArH).

*3-((3,5-Dimethylphenyl)diazenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**2m**)*

Starting with **1m** (2.323 g, 10.0 mmol), NEt_3 (1.315 g, 13.0 mmol) and Me_3SiCl (1.630 g, 15.0 mmol) in CH_2Cl_2 (20 mL), **2m** was isolated as an orange-yellow solid (2.740 g, 90 %). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.06$ (s, 6H, $Si(CH_3)_2$), 0.15 (s, 3H, $SiCH_3$, 2.35 (s, 6H, CH_3), 2.49 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 6.85 (s, 1H, Ar), 7.03 ppm (s, 2H, Ar).

*General procedure for the synthesis of diaryl-diazenes **3a–aq***

To a CH_2Cl_2 solution (3 ml) of 1.0 mmol of **2a–m** was added 1.5 mmol of the 1,3-bis(silyl enol ether). The solution was cooled to −78 °C and 1.1 mmol $TiCl_4$ was added. The mixture was stirred overnight and was then allowed to warm up to room temperature and poured into an aqueous solution of hydrochloric acid (10 %) and extracted with CH_2Cl_2 three times. The collected organic layers were dried with Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (heptanes-ethyl acetate) to give products **3a–aq**.

*Methyl 4,6-dimethyl-5-phenyldiazenyl-salicylate (**3a**)*

Starting with **2a** (276 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3a** was isolated as a red solid (188 mg, 66 %); m. p.: 82 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.31$ (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 6.78 (s, 1H, Ar), 7.49 – 7.56 (m, 3H, N=NAr), 7.86 – 7.89 (m, 2H, N=NAr), 11.23 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.3$, 20.5 (CH_3), 52.2 (OCH_3), 111.4 (CAr), 118.3, 122.4, 129.1, 130.9 (CH_{Ar}) 136.8, 137.3 ($C_{Ar}CH_3$), 145.4, 152.6 ($C_{ArN=N}$), 161.7 ($C_{Ar}OH$), 172.0 ppm ($COOCH_3$). – IR (KBr, cm^{-1}): $\tilde{\nu} = 3018$ (w), 2964 (w), 1620 (s), 1445 (s), 1239 (s), 1083 (m), 689 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon) = 228$ (4.27), 335 (4.21), 457 (2.75). – MS (GC, 70 eV): m/z (%) = 284 (99) $[M]^+$, 179 (100), 147 (91), 77 (59). – HRMS (EI): $m/z = 284.11567$ (calcd. 284.11554 for $C_{16}H_{16}N_2O_3$, $[M]^+$). – Anal. for $C_{16}H_{16}N_2O_3$ (284.31): calcd. C 67.59, H 5.67, N 9.85; found C 66.97, H 5.89, N 9.29.

*Ethyl 4,6-dimethyl-5-phenyldiazenyl-salicylate (**3b**)*

Starting with **2a** (276 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3b** was isolated as a red solid (179 mg, 60 %); m. p.: 66 – 67 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.44$ (t, $^3J = 7.1$ Hz, 3H, CH_2CH_3), 2.31 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.47 (q, $^3J = 7.1$ Hz, 2H, CH_2), 6.78 (s, 1H, Ar), 7.48 – 7.57 (m, 3H, N=NAr), 7.85 – 7.89 (m, 2H, N=NAr), 11.31 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 17.4, 20.5 (CH_3), 61.8 (CH2), 111.6 (C_{Ar}), 118.3, 122.4, 129.1, 130.9 (CH_{Ar}) 136.8, 137.3 ($C_{Ar}CH_3$), 145.4, 152.6 ($C_{ArN=N}$), 161.8 ($C_{Ar}OH$), 171.6 ppm ($COOCH_2CH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2989$ (w), 2935 (w), 1644 (s), 1471 (m), 1243 (s), 1083 (m), 690 (s). – MS (GC, 70 eV): m/z (%) = 298 (100) $[M]^+$, 193 (57), 147 (72), 77 (58). – HRMS (EI): $m/z = 298.13163$ (calcd. 298.13119 for $C_{17}H_{18}N_2O_3$, $[M]^+$). – Anal. for $C_{17}H_{18}N_2O_3$ (298.34): calcd. C 68.44, H 6.08, N 9.39; found C 68.11, H 6.10, N 9.14.

*Methyl 3,4,6-trimethyl-5-phenyldiazenyl-salicylate (**3c**)*

Starting with **2a** (276 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3c** was isolated as a red solid (149 mg, 50 %); m. p.: 88 – 90 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.18$ (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 7.50 – 7.57 ppm (m, 3H, N=NAr), 7.89 – 7.91 (m, 2H, N=NAr), 11.51 (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.7$, 15.8, 17.3 (CH_3), 52.2 (OCH_3), 110.6 (C_{Ar}), 122.5 (CH_{Ar}), 123.9 (C_{Ar}), 129.1 (CH_{Ar}), 130.2 ($C_{Ar}CH_3$), 131.1 (CH_{Ar}), 135.8 ($C_{Ar}CH_3$), 146.3, 152.5 ($C_{ArN=N}$), 159.7 ($C_{Ar}OH$), 172.7 ppm ($COOCH_3$). – IR

(ATR, cm^{-1}): $\tilde{\nu}$ = 3036 (w), 2958 (w), 1650 (s), 1438 (m), 1208 (s), 1100 (m), 805 (m), 688 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 226 (4.09), 338 (3.90), 457 (2.82). – MS (EI, 70 eV): m/z (%) = 298 (92) $[M]^+$, 266 (48) $[M]^+$, 256 (37), 193 (79), 161 (91), 77 (44). – HRMS (EI): m/z = 298.13183 (calcd. 298.13119 for $C_{17}H_{18}N_2O_3$, $[M]^+$). – Anal. for $C_{17}H_{18}N_2O_3$ (298.34): calcd. C 68.44, H 6.08, N 9.39; found C 67.98, H 6.05, N 9.08.

*Methyl 3-methoxy-4,6-dimethyl-5-phenyldiazenyl-salicylate (**3d**)*

Starting with **2a** (276 mg, 1.0 mmol), **4d** (436 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3d** was isolated as a red solid (128 mg, 41 %); m. p.: 75 – 77 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 7.50 – 7.58 (m, 3H, N=NAr), 7.86 – 7.90 (m, 2H, N=NAr), 11.09 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 12.3, 16.8 (CH_3), 52.4, 60.3 (OCH_3), 112.4 (C_{Ar}), 122.5, 129.1 (CH_{Ar}), 129.6, 129.8 (C_{Ar}), 131.1 (CH_{Ar}), 145.2 (C_{Ar}), 145.4, 152.5 ($C_{ArN=N}$), 155.0 ($C_{Ar}OH$), 172.0 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2999 (w), 2964 (w), 1659 (s), 1436 (s), 1205 (s), 1115 (m), 1066 (m), 691 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 227 (4.10), 340 (3.97), 467 (2.38). – MS (GC, 70 eV): m/z (%) = 314 (100) $[M]^+$, 282 (37), 209 (68), 177 (83), 77 (73). – HRMS (EI): m/z = 314.12618 (calcd. 314.12611 for $C_{17}H_{18}N_2O_4$, $[M]^+$). – Anal. for $C_{17}H_{18}N_2O_4$ (314.34): calcd. C 64.96, H 5.77, N 8.91; found C 63.86, H 5.93, N 8.73.

*Methyl 4,6-dimethyl-3-ethyl-5-phenyldiazenyl-salicylate (**3e**)*

Starting with **2a** (276 mg, 1.0 mmol), **4e** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3e** was isolated as a red solid (159 mg, 51 %); m. p.: 79 – 80 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 2.21 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.78 (q, ^3J = 7.5 Hz, 2H, CH_2CH_3), 3.97 (s, 3H, OCH_3), 7.51 – 7.57 (m, 2H, N=NAr), 7.88 – 7.92 (m, 3H, N=NAr), 11.47 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.2, 14.9, 17.4 (CH_3), 19.4 (CH_2), 52.2 (OCH_3), 110.8 (C_{Ar}), 122.5, 129.1 (CH_{Ar}), 129.8, 130.0 (C_{Ar}), 131.1 (CH_{Ar}), 135.2 (C_{Ar}), 146.5, 152.5 ($C_{ArN=N}$), 159.6 ($C_{Ar}OH$), 172.7 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3024 (w), 2965 (w), 1652 (s), 1438 (s), 1205 (m), 1035 (m), 766 (s), 689 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 227 (4.21), 338 (4.05), 459 (2.38). – MS (GC, 70 eV): m/z (%) = 312 (100) $[M]^+$, 280 (56), 207 (87), 175 (50), 77 (60). – HRMS (EI): m/z = 312.14677 (calcd. 312.14684 for $C_{18}H_{20}N_2O_3$, $[M]^+$). – Anal. for $C_{18}H_{20}N_2O_3$ (312.36): calcd. C 69.21, H 6.45, N 8.97; found C 68.45, H 6.52, N 8.67.

*Methyl 4,6-dimethyl-5-phenyldiazenyl-3-undecyl-salicylate (**3f**)*

Starting with **2a** (276 mg, 1.0 mmol), **4j** (622 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3f** was isolated as a red oil (154 mg, 35 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 – 0.91 (m, 3H, $(CH_2)_9CH_3$), 1.27 (s, 18H, $(CH_2)_9CH_3$), 2.20 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.71 – 2.76 (m, 2H, CH_2Ar), 3.97 (s, 3H, OCH_3), 7.52 – 7.55 (m, 3H, N=NAr), 7.88 – 7.91 (m, 2H, N=NAr), 11.44 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.1, 15.2, 17.4 (CH_3), 22.7, 26.2, 29.0, 29.3, 29.6, 29.6, 29.7, 30.0, 31.9 (CH_2), 52.2 (OCH_3), 110.8 (C_{Ar}), 122.5 (CH_{Ar}), 128.7 (C_{Ar}), 129.1 (CH_{Ar}), 129.9 ($C_{Ar}CH_3$), 131.1 (CH_{Ar}), 135.4 ($C_{Ar}CH_3$), 146.5, 152.5 ($C_{ArN=N}$), 159.7 ($C_{Ar}OH$), 172.7 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3020 (w), 2922 (s), 1656 (s), 1439 (s), 1206 (m), 766 (m), 690 (m). – MS (EI, 70 eV): m/z (%) = 438 (100) $[M]^+$, 406 (33), 333 (64), 116 (27). – HRMS ((+)-ESI): m/z = 439.29588 (calcd. 439.29552 for $C_{27}H_{39}N_2O_3$, $[M+H]^+$).

*iso-Propyl-4,6-dimethyl-5-phenyldiazenyl-salicylate (**3g**)*

Starting with **2a** (276 mg, 1.0 mmol), **4g** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3g** was isolated as a red oil (145 mg, 46 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.43 (d, ^3J = 6.3 Hz, 6H, $CH(CH_3)_2$), 2.32 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 5.28 – 5.43 (sept, ^3J = 6.3 Hz, 1H, CH), 6.77 (s, 1H, Ar), 7.48 – 7.57 (m, 3H, N=NAr), 7.85 – 7.89 (m, 2H, N=NAr), 11.33 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.5, 20.5 (CH_3), 21.9 ($CH(CH_3)_2$), 69.9 (CH_{iPr}), 111.9 (C_{Ar}), 118.2, 122.4, 129.1, 130.8 (CH_{Ar}) 136.6, 137.2 ($C_{Ar}CH_3$), 145.4, 152.7 ($C_{ArN=N}$), 161.7 ($C_{Ar}OH$), 171.0 ppm ($COOiPr$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3060 (w), 2979 (w), 1651 (s), 1448 (m), 1235 (s), 1101 (s), 764 (s), 686 (s). – MS (GC, 70 eV): m/z (%) = 312 (85) $[M]^+$, 252 (41), 165 (100), 147 (70), 77 (58). – HRMS (EI): m/z = 312.14668 (calcd. 312.14684 for $C_{18}H_{20}N_2O_3$, $[M]^+$). – Anal. for $C_{18}H_{20}N_2O_3$ (312.36): calcd. C 69.21, H 6.45, N 8.97; found C 69.70, H 6.62, N 8.66.

*Methyl 3-(3-chloropropyl)-4,6-dimethyl-5-phenyldiazenyl-salicylate (**3h**)*

Starting with **2a** (276 mg, 1.0 mmol), **4h** (506 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3h** was isolated as a red solid (148 mg, 41 %); m. p.: 86 – 87 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97 – 2.09 (m, 2H, CH_2), 2.21, 2.39 (s, 3H, CH_3), 2.90 (m, ^3J = 7.9 Hz, 2H, $ArCH_2$), 2.63 (m, ^3J = 6.6 Hz, 2H,

CH_2Cl), 3.97 (s, 3H, OCH_3), 7.51 – 7.57 (m, 3H, N=NAr), 7.87 – 7.91 (m, 2H, N=NAr), 11.51 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.2, 17.4 (CH_3), 23.7, 31.8, 45.2 (CH_2), 52.3 (OCH_3), 110.9 (C_{Ar}), 122.5 (CH_{Ar}), 126.7 (C_{Ar}), 129.2 (CH_{Ar}), 130.5 ($C_{Ar}CH_3$), 131.2 (CH_{Ar}), 135.6 ($C_{Ar}CH_3$), 146.6, 152.4 ($C_{ArN=N}$), 159.7 ($C_{Ar}OH$), 172.6 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3012 (w), 2960 (w), 1652 (s), 1435 (s), 1208 (s), 767 (m), 691 (m). – HRMS ((+)-ESI): m/z = 361.13137 (calcd. 361.13135 for $C_{19}H_{21}ClN_2O_3$, [M+H; ^{35}Cl]$^+$). – Anal. for $C_{19}H_{21}ClN_2O_3$ (360.83): calcd. C 63.24, H 5.87, N 7.76; found C 63.36, H 6.00, N 7.12.

*Methyl 4,6-dimethyl-5-((3,5-dimethylphenyl)diazenyl)-salicylate (**3i**)*

Starting with **2m** (305 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3i** was isolated as a red solid (97 mg, 30 %); m. p.: 140 – 143 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H, CH_3), 2.43 (s, 6H, CH_3), 2.59 (s, 3H, CH_3), 3.98 (s, 3H, OCH_3), 6.77 (s, 1H, Ar), 7.15 (s, 1H, N=NAr), 7.48 (s, 2H, N=NAr), 11.19 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.3, 20.3, 21.3 (CH_3), 52.3 (OCH_3), 111.4 (C_{Ar}), 114.1, 118.2, 120.2, 132.6 (CH_{Ar}), 136.2, 137.2, 138.8 ($C_{Ar}CH_3$), 145.7, 152.8 ($C_{ArN=N}$), 161.6 ($C_{Ar}OH$), 172.1 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3003 (w), 2954 (w), 1647 (s), 1444 (s), 1243 (m), 805 (m), 683 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 232 (4.26), 335 (4.19), 457 (2.91). – HRMS ((+)-ESI): m/z = 335.13728 (calcd. 335.13661 for $C_{18}H_{20}N_2O_3Na$, [M+Na]$^+$). – Anal. for $C_{18}H_{20}N_2O_3$ (312.36): calcd. C 69.21, H 6.45, N 8.97; found C 69.50, H 6.74, N 9.11.

*Methyl 4,6-dimethyl-5-(4′-ethylphenyl)diazenyl-salicylate (**3j**)*

Starting with **2b** (305 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3j** was isolated as a red solid (104 mg, 33 %); m. p.: 74 – 75 °C. – ^{1}H NMR (300 MHz, $CDCl_3$):δ = 1.29 (t, ^3J = 7.7 Hz, 3H, CH_2CH_3), 2.27 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.74 (q, ^3J = 7.6 Hz, 2H, CH_2), 3.97 (s, 3H, OCH_3), 6.76 (s, 1H, H-5), 7.35 (d, ^3J = 8.5 Hz, 2H, $CH_{Ar'}$), 7.80 (d, ^3J = 8.5 Hz, 2H, $CH_{Ar'}$), 11.17 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$):δ = 15.5 (CH_2CH_3), 17.2, 20.3 (CH_3), 28.8 (CH_2), 52.2 (OCH_3), 111.4 (C-3), 118.2 (CH_{Ar}), 122.5, 128.6 ($CH_{Ar'}$), 136.2, 137.3 ($C_{Ar}CH_3$), 145.7 (C-1′), 147.8 (C-1), 150.9 (C-4′), 161.5 (COH), 172.1 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2960 (w), 2924 (w), 2873 (w), 1666 (s), 1560 (m), 1554 (m), 1517 (w), 1503 (w), 1477 (w), 1440 (s), 1342 (m), 1329 (m), 1309 (s), 1259 (m), 1212 (w), 1195 (m), 1158 (s), 1079 (s), 1029 (m), 1012 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 245, 335, 453. – MS (EI, 70 eV): m/z (%) = 312 (100) [M]$^+$, 297 (24), 281 (22), 280 (68), 279 (73), 252 (28), 251 (55), 223 (21), 179 (98), 149 (21), 147 (89), 105 (55), 91 (40), 77 (29). HRMS (EI): m/z = 312.146649 (calcd. 312.14684 for $C_{18}H_{20}N_2O_3$, [M]$^+$).

*Methyl 5-(4′-ethylphenyl)diazenyl-3,4,6-trimethyl-salicylate (**3k**)*

Starting with **2b** (305 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3k** was isolated as a red oil (92 mg, 30 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 7.6 Hz, 3H, CH_2CH_3), 2.14 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.74 (q, ^3J = 7.6 Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 7.36 (d, ^3J = 8.3 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.3 Hz, 2H, $CH_{Ar'}$), 11.47 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 11.7 (CH_2CH_3), 15.5, 15.7, 17.2 (CH_3),28.8 (CH_2), 52.2 (OCH_3), 110.6 (C-3), 122.6 ($CH_{Ar'}$), 123.8 ($C_{Ar}CH_3$), 128.6 ($CH_{Ar'}$), 130.0, 135.7 ($C_{Ar}CH_3$), 146.5 (C-1′), 148.0 (C-1), 150.8 (C-4′), 159.5 (COH), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3026 (w), 2962 (w), 2930 (w), 2872 (w), 1731 (w), 1653 (s), 1598 (m), 1562 (m), 1515 (m), 1437 (s), 1393 (w), 1378 (w), 1350 (s), 1312 (s), 1258 (s), 1209 (s), 1176 (s), 1150 (m), 1104 (s), 1049 (w), 1031 (m), 1012 (m). – MS (GC, 70 eV): m/z (%) = 326 (100) [M]$^+$, 294 (54), 293 (40), 265 (33), 193 (73), 161 (67), 105 (35), 79 (29), 77 (34). – HRMS (EI): m/z = 326.162149 (calcd. 326.16249 for $C_{19}H_{22}N_2O_3$, [M]$^+$).

*Methyl 4,6-dimethyl-5-((4-iso-propylphenyl)diazenyl)-salicylate (**3l**)*

Starting with **2c** (319 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3l** was isolated as a red oil (104 mg, 32 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (d, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.28 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.90 – 3.06 (m, 1H, CH), 3.98 (s, 3H, OCH_3), 6.77 (s, 1H, Ar), 7.37 – 7.40 (m, 2H, N=NAr), 7.81 – 7.84 (m, 2H, N=NAr), 11.19 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.2, 20.3 (CH_3), 23.8 ($CH(CH_3)_2$), 34.1 (CH_{iPr}), 52.2 (OCH_3), 111.4 (C_{Ar}), 118.2, 122.5, 127.1 (CH_{Ar}) 136.2, 137.2 ($C_{Ar}CH_3$), 145.6 ($C_{ArN=N}$), 150.9 (C_{AriPr}), 152.3 ($C_{ArN=N}$), 161.5 ($C_{Ar}OH$), 172.0 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2958 (m), 1661 (s), 1439 (m), 1350 (m), 1235 (m), 1160 (s), 802 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 231 (4.43), 340 (4.35), 455 (3.03). – HRMS ((+)-ESI): m/z = 327.17067 (calcd. 327.17032 for $C_{19}H_{22}N_2O_3$, [M+H]$^+$). – Anal. for $C_{19}H_{22}N_2O_3$ (326.39): calcd. C 69.92, H 6.79, N 8.85; found C 69.44, H 6.36, N 8.33.

*Methyl 3,4,6-trimethyl-5-((4-iso-propylphenyl)diazenyl)-salicylate (**3m**)*

Starting with **2c** (319 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3m** was isolated as a red solid (105 mg, 31 %); m. p.: 82 – 84 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.32$ (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 2.14 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.02 (sept, $^3J = 6.9$ Hz, 1H, CH), 3.97 (s, 3H, OCH_3), 7.38 – 7.42 (m, 2H, N=NAr), 7.83 – 7.86 (m, 2H, N=NAr), 11.49 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 11.7$, 15.7, 17.3 (CH_3), 23.9 ($CH(CH_3)_2$), 34.2 (CH_{iPr}), 52.2 (OCH_3), 110.6 (C_{Ar}), 122.6 (CH_{Ar}), 123.8 (C_{Ar}), 127.2 (CH_{Ar}), 129.8, 135.7 ($C_{Ar}CH_3$), 146.5, 150.9 ($C_{ArN=N}$), 152.5 (C_{AriPr}), 159.5 ($C_{Ar}OH$), 172.7 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3029$ (w), 2962 (m), 1648 (s), 1434 (m), 1210 (s), 1099 (m), 805 (m). – MS (GC, 70 eV): m/z (%) = 240 (62) $[M]^+$, 177 (100), 164 (46), 161 (69), 149 (45). – HRMS (EI): $m/z =$ 340.178041(calcd. 340.17814 for $C_{20}H_{24}N_2O_3$, $[M]^+$). – Anal. for $C_{20}H_{24}N_2O_3$ (340.42): calcd. C 70.56, H 7.11, N 8.23; found C 69.8, H 7.10, N 7.63.

*Ethyl 4,6-dimethyl-5-((4-iso-propylphenyl)diazenyl)-salicylate (**3n**)*

Starting with **2c** (319 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3n** was isolated as a red solid (140 mg, 41 %); m. p.: 49 – 50 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.44 (t, $^3J = 7.1$ Hz , 3H, CH_2CH_3), 2.28 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.01 (sept, $^3J = 6.9$ Hz, 1H, CH), 4.46 (q, $^3J = 7.1$ Hz, 2H, CH_2CH_3), 6.77 (s, 1H, Ar), 7.37 – 7.41 (m, 2H, N=NAr), 7.81 – 7.84 (m, 2H, N=NAr), 11.28 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 17.4, 20.3 (CH_3), 23.9 ($CH(CH_3)_2$), 34.2 (CH_{iPr}), 61.7 (CH_2), 111.5 (C_{Ar}), 118.1, 122.5, 127.1 (CH_{Ar}), 136.1, 137.2 ($C_{Ar}CH_3$), 145.7 ($C_{ArN=N}$), 151.0 (C_{AriPr}), 152.4 ($C_{ArN=N}$), 161.6 ($C_{Ar}OH$), 171.6 ppm ($COOCH_2CH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2958$ (m), 2927 (m), 1650 (s), 1446 (m), 1239 (s), 1079 (m), 801 (s). – MS (EI, 70 eV): m/z (%) = 340 (100) $[M]^+$, 294 (31), 293 (32), 251 (41), 193 (57), 147 (44). – HRMS (EI): $m/z = 340.17896$ (calcd. 340.17814 for $C_{20}H_{24}N_2O_3$, $[M]^+$). – Anal. for $C_{20}H_{24}N_2O_3$ (340.42): calcd. C 70.56, H 7.11, N 8.23; found C 69.34, H 7.60, N 7.97.

*Iso-Propyl 4,6-dimethyl-5-((4-iso-propylphenyl)diazenyl)-salicylate (**3o**)*

Starting with **2c** (319 mg, 1.0 mmol), **4g** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3o** was isolated as a red oil (211 mg, 60 %). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.32$ (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.42 (d, $^3J = 6.3$ Hz, 6H, $CH(CH_3)_2$), 2.28 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.01 (sept, $^3J = 6.9$ Hz, 1H, CH), 5.35 (sept, $^3J = 6.3$ Hz, 1H, CH), 6.77 (s, 1H, Ar), 7.37 – 7.41 (m, 2H, N=NAr), 7.81 – 7.84 (m, 2H, N=NAr), 11.30 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.5$, 20.3 (CH_3), 21.9, 23.9 ($CH(CH_3)_2$), 34.1, 69.9 (CH_{iPr}), 111.9 (C_{Ar}), 118.1, 122.5, 127.1 (CH_{Ar}), 135.9, 137.1 ($C_{Ar}CH_3$), 145.7, 151.0 ($C_{ArN=N}$), 152.3 (C_{AriPr}), 161.5 ($C_{Ar}OH$), 171.1 ppm ($COOiPr$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3028$ (w), 2961 (m), 1653 (s), 1451 (m), 1236 (s), 1102 (s), 840 (m), 803 (m). – MS (EI, 70 eV): m/z (%) = 354 (100) $[M]^+$, 311 (42), 294 (61), 251 (60), 165 (91), 147 (55). – HRMS (EI): $m/z = 354.19379$ (calcd. 354.19379 for $C_{21}H_{26}N_2O_3$, $[M]^+$). – Anal. for $C_{21}H_{26}N_2O_3$ (354.44): calcd. C 71.16, H 7.39, N 7.90; found C 71.00, H 7.51, N 7.68.

*Ethyl 3-(3-chloropropyl)-4,6-dimethyl-5-((4-isopropyl-phenyl)diazenyl)-salicylate (**3p**)*

Starting with **2c** (319 mg, 1.0 mmol), **4h** (506 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3p** was isolated as a red solid (121 mg, 30 %); m. p.: 62 – 64 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.32$ (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.97 – 2.09 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.87 – 2.93 (m, 2H, ArCH2), 3.02 (sept, $^3J = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.63 (t, $^3J =$ 6.6 Hz, 2H, CH_2Cl), 3.97 (s, 3H, OCH_3), 7.39 – 7.42 (m, 2H, N=NAr), 7.83 – 7.86 (m, 2H, N=NAr), 11.48 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.1$, 17.3 (CH_3), 23.7 (CH_2), 23.9 (CH_3), 31.8 (CH_2), 34.2 (CH), 45.1 (CH_2), 52.2 (OCH_3), 110.9 (C_{Ar}), 122.6 (CH_{Ar}), 126.6 (C_{Ar}), 127.2 (CH_{Ar}) 130.2, 135.5 ($C_{Ar}CH_3$), 146.7, 150.8 ($C_{ArN=N}$), 152.7 (C_{AriPr}), 159.5 ($C_{Ar}OH$), 172.6 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3027$ (w), 2955 (m), 1651 (s), 1437 (s), 1213 (m), 1100 (m), 806 (m). – MS (EI, 70 eV): m/z (%) = 404 (27) [M; ^{37}Cl]$^+$, 402 (81) [M; ^{35}Cl]$^+$, 255 (90), 219 (56), 120 (100), 119 (83), 91 (81). – HRMS ((+)-ESI): $m/z = 403.1788$ (calcd. 403.1783 for $C_{22}H_{28}ClN_2O_3$, [M+H; ^{35}Cl]$^+$). – Anal. for $C_{22}H_{28}ClN_2O_3$ (402.91): calcd. C 65.58, H 6.75, N 6.95; found C 64.10, H 6.80, N 6.57.

*Methyl 4,6-dimethyl-5-((4-tertbutylphenyl)diazenyl)-salicylate (**3q**)*

Starting with **2d** (333 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3q** was isolated as a red solid (140 mg, 41 %); m. p.: 70 – 72 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.93$ (s, 9H, $C(CH_3)_3$), 2.28 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 6.78 (s, 1H, Ar), 7.54 – 7.58 (m, 2H, N=NAr), 7.81 – 7.85 (m, 2H, N=NAr), 11.18 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.2$, 20.3 (CH_3), 31.3 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 52.2 (OCH_3), 111.4 (C_{Ar}),

118.2, 122.2, 126.0 (CH_{Ar}), 136.1, 137.2 ($C_{Ar}CH_3$), 145.7, 150.5 ($C_{ArN=N}$), 154.6 (C_{Ar}), 161.5 ($C_{Ar}OH$), 172.0 ppm ($COOCH_3$). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 2957 (w), 1666 (s), 1446 (s), 1245 (s), 1078 (m), 839 (m), 807 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon) = 230$ (4.20), 335 (4.15), 453 (2.98). – MS (EI, 70 eV): m/z (%) = 340 (100) $[M]^+$, 179 (79), 163 (40), 147 (40), 134 (86). – HRMS (EI): m/z = 340.178405 (calcd. 340.17814 for $C_{20}H_{24}N_2O_3$, $[M]^+$). – Anal. for $C_{20}H_{24}N_2O_3$ (340.42): calcd. C 70.56, H 7.11, N 8.23; found C 69.29, H 7.13, N 7.85.

*Methyl 3,4,6-trimethyl-5-((4-tert-butylphenyl)diazenyl)-salicylate (**3r**)*

Starting with **2d** (333 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3r** was isolated as a red solid (106 mg, 30 %); m. p.: 137 – 139 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 9H, $C(CH_3)_3$), 2.15 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 7.56 – 7.59 (m, 2H, N=NAr), 7.83 – 7.87 (m, 2H, N=NAr), 11.49 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 11.7, 15.7, 17.3 (CH_3), 31.3 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 52.2 (OCH_3), 110.6 (C_{Ar}), 122.3 (CH_{Ar}), 123.8 (C_{Ar}), 126.1 (CH_{Ar}), 130.0, 135.7 ($C_{Ar}CH_3$), 146.5, 150.3 ($C_{ArN=N}$), 154.8 (C_{Ar}), 159.6 ($C_{Ar}OH$), 172.7 ppm ($COOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2966 (m), 1651 (s), 1435 (m), 1260 (s), 1102 (s), 805 (s). – HRMS ((+)-ESI): m/z = 355.20203 (calcd. 355.20162 for $C_{21}H_{27}N_2O_3$, $[M+H]^+$). – Anal. for $C_{21}H_{27}N_2O_3$ (354.44): calcd. C 71.16, H 7.39, N 7.90; found C 71.44, H 7.41, N 7.58.

*Ethyl 4,6-dimethyl-5-((4-tert-butylphenyl)diazenyl)-salicylate (**3s**)*

Starting with **2d** (333 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3s** was isolated as a red solid (130 mg, 37 %); m. p.: 62 – 64 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 9H, $C(CH_3)_3$), 1.44 (t, ^3J = 7.1 Hz, 2H, CH_2CH_3), 2.28 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 4.46 (q, ^3J = 7.1 Hz, 2H, CH_2CH_3), 6.77 (s, 1H, Ar), 7.54 – 7.58 (m, 2H, N=NAr), 7.81 – 7.85 (m, 2H, N=NAr), 11.28 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 17.4, 20.3, 31.3 (CH_3), 35.0 (C_{tBut}), 61.7 (CH_2), 111.5 (C_{Ar}), 118.1, 122.2, 126.0 (CH_{Ar}), 136.1, 137.2 ($C_{Ar}CH_3$), 145.7, 150.5 ($C_{ArN=N}$), 154.6 (C_{Ar}), 161.6 ($C_{Ar}OH$), 171.6 ppm ($COOCH_2CH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2975 (w), 2953 (w), 1651 (s), 1473 (m), 1242 (s), 1084 (m), 806 (m). – MS (EI, 70 eV): m/z (%) = 354 (100) $[M]^+$, 308 (37), 251 (41), 193 (77), 147 (43). – HRMS (EI): m/z = 354.193642 (calcd. 354.19379 for $C_{21}H_{26}N_2O_3$, $[M]^+$). – Anal. for $C_{21}H_{26}N_2O_3$ (354.44): calcd. C 71.16, H 7.39, N 7.90; found C 71.25, H 7.64, N 7.80.

*iso-Propyl 4,6-dimethyl-5-((4-tert-butylphenyl)diazenyl)-salicylate (**3t**)*

Starting with **2d** (333 mg, 1.0 mmol), **4g** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3t** was isolated as a red solid (114 mg, 31 %); m. p.: 97 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 9H, $C(CH_3)_3$), 1.42 (d, ^3J = 6.3 Hz, 6H, $CH(CH_3)_2$), 2.28 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 5.28 – 5.43 (sept, ^3J = 6.3 Hz, 1H, CH), 6.77 (s, 1H, Ar), 7.54 – 7.57 (m, 2H, N=NAr), 7.81 – 7.84 (m, 2H, N=NAr), 11.30 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.5, 20.2, 21.9, 31.3 (CH_3), 35.0 (C_{tBu}), 69.9 (CH_{iPr}), 111.9 (C_{Ar}), 118.1, 122.2, 126.0 (CH_{Ar}), 135.9, 137.1 ($C_{Ar}CH_3$), 145.7, 150.6 ($C_{ArN=N}$), 154.5 (C_{Ar}), 161.5 ($C_{Ar}OH$), 171.1 ppm ($COOiPr$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 2964 (m), 1660 (s), 1460 (m), 1213 (m), 1099 (s), 800 (m). – MS (EI, 70 eV): m/z (%) = 368 (100) $[M]^+$, 308 (37), 251 (31), 165 (89), 147 (39). – HRMS (EI): m/z = 368.20992 (calcd. 368.20944 for $C_{22}H_{28}N_2O_3$, $[M]^+$). – Anal. for $C_{22}H_{28}N_2O_3$ (368.47): calcd. C 71.71, H 7.66, N 7.60; found C 71.82, H 7.82, N 7.02.

*Ethyl 4,6-dimethyl-5-(4′-n-decylphenyl)diazenyl-salicylate (**3u**)*

Starting with **2e** (417 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3u** was isolated as a red solid (100 mg, 23 %); m. p.: 42 – 43 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 1.24 – 1.55 (m, 19H, OCH_2CH_3, 8 × CH_2), 1.61 – 1.70 (m, 2H, CH_2Ar), 2.26 (CH_3), 2.27 (CH_3), 4.44 (q, ^3J = 7.2 Hz, 2H, OCH_2), 6.75 (s, 1H, H-5), 7.31 (d, ^3J = 8.5 Hz, 2H, $CH_{Ar'}$), 7.78 (d, ^3J = 8.5 Hz, 2H, $CH_{Ar'}$), 11.24 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.1, 14.2 (CH_2CH_3), 17.4, 20.3 (CH_3) 22.7, 29.3, 29.3, 29.5, 29.6, 29.6, 31.4, 31.9, 35.9 (CH_2), 61.7 (OCH_2), 111.6 (C-3), 118.2 (CH_{Ar}), 122.4, 129.1 ($CH_{Ar'}$), 136.1, 137.2 ($C_{Ar}CH_3$), 145.7 (C-1′), 146.6 (C-1) 150.9 ($C_{Ar}C_{10}H_{21}$), 161.6 (COH), 171.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2997 (w), 2949 (w), 2918 (s), 2847 (m), 1910 (w), 1647 (s), 1601 (w), 1567 (m), 1465 (m), 1444 (w), 1428 (w), 1399 (w), 1374 (m), 1344 (s), 1309 (m), 1244 (s), 1182 (w), 1167 (m), 1146 (w), 1112 (w), 1080 (m), 1048 (w), 1032 (w), 1011 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 245, 337, 450. – HRMS ((+)-ESI): m/z = 439.29545 (calcd. 439.29552 for $C_{27}H_{39}N_2O_3$, $[M+H]^+$).

*Methyl 4,6-dimethyl-3-(2-phenylethyl)-5-(4′-methoxy-phenyl)diazenyl-salicylate (**3v**)*

Starting with **2f** (306 mg, 1.0 mmol), **4i** (547 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3v** was isolated as a red oil (100 mg, 23 %). – ^{1}H

NMR (300 MHz, $CDCl_3$): $\delta = 2.10$ (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.78 – 2.84 (m, 2H, CH_2), 2.99 – 3.05 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.03 (d, $^3J = 9.1$ Hz, 2H, CH_{Ar}), 7.16 – 7.32 (m, 5H, Ar), 7.88 (d, $^3J = 9.1$ Hz, 2H, $CH_{Ar'}$), 11.46 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.0$, 17.4 (CH_3), 28.7, 35.0 (CH_2), 52.2, 55.6 (OCH_3), 110.9 (C-3), 114.2, 124.3 ($CH_{Ar'}$), 125.8 (CH_{Ar}), 127.4 (CH_2Ar), 128.3, 128.4 (CH_{Ar}), 129.8, 135.4 ($C_{Ar}CH_3$), 142.4 (C_{Ar}), 146.6 (C-1), 146.9 (C-1′), 159.4, 162.2 (C-O), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} =$ 3060 (w), 3024 (w), 3000 (w), 2950 (w), 2837 (w), 1731 (w), 1653 (s), 1599 (s), 1583 (m), 1562 (w), 1502 (s), 1438 (s), 1392 (m), 1353 (m), 1312 (m), 1296 (w), 1247 (s), 1209 (s), 1176 (m), 1141 (s), 1103 (w), 1029 (s). – MS (EI, 70 eV): m/z (%) = 418 (40) $[M]^+$, 295 (31), 267 (50), 176 (100), 123 (63), 122 (32), 108 (69), 107 (38), 92 (22), 91 (81) 77 (39), 69 (22), 65 (24), 57 (21), 44 (22), 43 (21). – HRMS (EI): $m/z = 418.189312$ (calcd. 418.18871 for $C_{25}H_{26}N_2O_4$, $[M]^+$).

*Methyl 5-(4′-methoxyphenyl)diazenyl-3,4,6-trimethyl-salicylate (**3w**)*

Starting with **2f** (306 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3w** was isolated as a red solid (118 mg, 36 %); m. p.: 131 – 132 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.13$ (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.02 (d, $^3J = 8.9$ Hz, 2H, $CH_{Ar'}$) 7.88 (d, $^3J = 8.9$ Hz, 2H, $CH_{Ar'}$), 11.44 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 11.7$, 15.6, 17.2 (CH_3), 52.1, 55.6 (OCH_3), 110.5 (C-3), 114.2, 123.7 ($C_{Ar}CH_3$), 124.3 ($CH_{Ar'}$), 129.6, 135.6 ($C_{Ar}CH_3$), 146.4 (C-1′), 146.9 (C-1), 159.3, 162.2 (C–O), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3016$ (w), 2958 (w), 2842 (w), 2743 (w), 2581 (w), 1649 (m), 1600 (m), 1582 (m), 1503 (m), 1442 (m), 1429 (m), 1398 (m), 1362 (m), 1311 (m), 1297 (m), 1251 (s), 1212 (s), 1199 (m), 1179 (m), 1145 (m), 1099 (m), 1047 (w), 1020 (s). – MS (EI, 70 eV): m/z (%) = 328 (100) $[M]^+$, 296 (64), 295 (38), 268 (21), 240 (26), 193 (66), 161 (81), 135 (26), 108 (27), 107 (96), 105 (27), 92 (49), 91 (24), 79 (27), 78 (24), 77 (86), 64 (23). – HRMS (EI): $m/z = 328.141857$ (calcd. 328.14176 for $C_{18}H_{20}N_2O_4$, $[M]^+$).

*Ethyl 4,6-dimethyl-5-(4′-methoxyphenyl)diazenyl-salicylate (**3x**)*

Starting with **2f** (306 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3x** was isolated as a red solid (101 mg, 31 %); m. p.: 77 – 78 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (t, $^3J = 7.2$ Hz, 3H, OCH_2CH_3), 2.26 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 4.44 (q, $^3J = 7.2$ Hz, 2H, OCH_2), 6.75 (s, 1H, H-5), 7.01 (d, $^3J = 9.1$ Hz, 2H, $CH_{Ar'}$), 7.86 (d, $^3J = 9.1$ Hz, 2H, $CH_{Ar'}$), 11.22 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 17.3 (CH_3) 20.2 (OCH_2CH_3), 55.6 (OCH_3), 61.7 (OCH_2), 111.5 (C-3), 114.2 ($CH_{Ar'}$) 118.1 (CH_{Ar}), 124.2 ($CH_{Ar'}$), 135.7, 137.2 ($C_{Ar}CH_3$), 145.6 (C-1), 147.0 (C-1′), 161.4, 162.0 (C–O), 171.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3002$ (w), 2966 (w), 2924 (w), 2870 (w), 2834 (w), 1661 (s), 1603 (m), 1583 (m), 1558 (m), 1504 (m), 1469 (m), 1449 (m), 1395 (m), 1369 (m), 1338 (m), 1234 (s), 1198 (w), 1181 (m), 1162 (m), 1147 (m), 1103 (m), 1079 (m), 1051 (w), 1030 (m), 1017 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log \varepsilon) = 245, 340, 444$. – MS (EI, 70 eV): m/z (%) = 328 (100) $[M]^+$, 299 (29), 283 (21), 282 (70), 281 (61), 254 (27), 193 (35), 165 (24), 147 (41), 107 (60), 77 (22). – HRMS (EI): $m/z = 328.141515$ (calcd. 328.14176 for $C_{18}H_{20}N_2O_4$, $[M]^+$).

*Methoxyethyl 4,6-dimethyl-5-(4′-methoxyphenyl)diazenyl-salicylate (**3y**)*

Starting with **2f** (306 mg, 1.0 mmol), **4k** (457 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3y** was isolated as a red solid (117 mg, 33 %); m. p.: 77 – 79 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.26$ (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 3.40 (s, 3H, CH_2OCH_3), 3.72 (t, $^3J = 4.7$ Hz, 2H, CH_2), 3.88 (s, 3H, OCH_3), 4.52 (t, $^3J = 4.7$ Hz, 2H, CH_2), 6.75 (s, 1H, H-5), 7.01 (d, $^3J = 9.1$ Hz, 2H, $CH_{Ar'}$), 7.86 (d, $^3J = 9.1$ Hz, 2H, $CH_{Ar'}$), 10.85 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.2$ 20.2 (CH_3), 55.6, 58.9 (OCH_3), 64.3, 70.0 (CH_2), 111.7 (C-3), 114.2 ($CH_{Ar'}$), 118.1 (CH_{Ar}), 124.2 ($CH_{Ar'}$), 135.9, 137.2 ($C_{Ar}CH_3$), 145.7 (C-1′), 147.0 (C-1), 161.0, 162.0 (C–O), 171.0 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2981$ (w), 2925 (w), 2884 (w), 2842 (w), 2813 (w), 1650 (m), 1600 (m), 1582 (m), 1556 (m), 1502 (m), 1468 (m), 1456 (w), 1435 (m), 1410 (m), 1382 (m), 1375 (m), 1345 (m), 1305 (s), 1243 (s), 1198 (m), 1180 (m), 1166 (m), 1143 (w), 1129 (m), 1099 (m), 1079 (m), 1055 (w), 1026 (s). – MS (EI, 70 eV): m/z (%) = 358 (100) $[M]^+$, 299 (25), 282 (71), 281 (53), 254 (27), 163 (28), 147 (36), 107 (46), 59 (32). – HRMS (EI): $m/z = 358.151695$ (calcd. 358.15232 for $C_{19}H_{22}N_2O_5$, $[M]^+$).

*Methyl 3-(n-chloropropyl)-4,6-dimethyl-5-(4′-methoxy-phenyl)diazenyl-salicylate (**3z**)*

Starting with **2f** (490 mg, 1.6 mmol), **4h** (805 mg, 2.4 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3z** was isolated as a red solid (137 mg, 22 %); m. p.: 95 – 96 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.97 – 2.06$ (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.71 (s, 3H, CH_3), 2.88 (t, $^3J = 7.6$ Hz, 2H, CH_2Ar), 3.61 (t, $^3J = 7.0$ Hz, 2H, CH_2Cl), 3.90 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.03 (d, $^3J = 8.8$ Hz, 2H, $CH_{Ar'}$), 7.88 (d, $^3J = 8.8$ Hz, 2H, $CH_{Ar'}$),

11.45 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.1, 17.3 (CH_3), 23.7, 31.8, 45.2 (CH_2), 52.2, 55.6 (OCH_3), 110.9 (C-3), 114.2, 124.4 ($CH_{Ar'}$), 126.5 (C-5), 130.0, 135.5 ($C_{Ar}CH_3$), 146.7 (C-1′), 146.9 (C-1), 159.4, 162.3 (C–O), 172.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3014 (w), 2 959 (w), 2870 (w), 2836 (w), 1651 (s), 1602 (m), 1585 (m), 1574 (w), 1564 (w), 1558 (w), 1504 (m), 1454 (m), 1435 (m), 1395 (m), 1360 (m), 1309 (m), 1294 (w), 1267 (w), 1247 (s), 1227 (w), 1211 (s), 1176 (m), 1141 (s), 1103 (w), 1088 (w), 1071 (w), 1048 (w), 1026 (s). – HRMS ((+)-ESI): m/z = 391.14194 (calcd. 391.14191 for $C_{20}H_{24}ClN_2O_3S$, [M+H; ^{35}Cl]$^+$).

*Ethyl 4,6-dimethyl-5-(4′-methylthiophenyl)diazenyl-salicylate (**3aa**)*

Starting with **2g** (323 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3aa** was isolated as a red solid (132 mg, 38 %); m. p.: 85 – 87 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, ^3J = 7.2 Hz, 3H, OCH_2CH_3), 2.28 (s, 3H, SCH_3), 2.55 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 4.45 (q, ^3J = 7.2 Hz, 2H, OCH_2), 6.75 (s, 1H, H-5), 7.34 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 7.80 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 11.25 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (SCH_3), 15.4, 17.4 (CH_3), 20.5 (OCH_2CH_3), 61.8 (OCH_2), 111.6 (C-3), 118.2 (CH_{Ar}), 122.9, 126.1 ($CH_{Ar'}$), 136.6, 137.3 ($C_{Ar}CH_3$), 142.8 (C-1), 145.5 (C-1′), 150.0 ($C_{Ar}SCH_3$), 161.7 (COH), 171.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2960 (w), 2913 (w), 1909 (w), 1659 (m), 1651 (m), 1585 (m), 1556 (m), 1464 (m), 1444 (m), 1429 (m), 1393 (m), 1368 (m), 1336 (m), 1306 (m), 1249 (s), 1218 (w), 1198 (w), 1163 (m), 1106 (w), 1079 (m), 1050 (w), 1008 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 245, 356, 451. – MS (EI, 70 eV): m/z (%) = 344 (100) [M]$^+$, 315 (30), 298 (52), 297 (61), 251 (36), 193 (39), 165 (36), 163 (34), 147 (67), 139 (33), 124 (50), 123 (52), 91 (26), 45 (30), 44 (42), 43 (26). – HRMS ((+)-ESI): m/z = 367.10852 (calcd. 367.10868 for $C_{18}H_{20}N_2O_3S$, [M+Na]$^+$).

*Methyl 5-(4′-methylthiophenyl)diazenyl-3,4,6-trimethyl-salicylate (**3ab**)*

Starting with **2g** (323 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ab** was isolated as a red solid (190 mg, 55 %); m. p.: 91 – 93 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 3H, CH_3), 2.23 (s, 3H, SCH_3), 2.39 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 7.36 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 11.48 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.7 (SCH_3), 15.4, 15.8, 17.3 (CH_3), 52.2 (OCH_3), 110.6 (C-3), 123.0 ($CH_{Ar'}$), 123.8 ($C_{Ar}CH_3$), 126.0 ($CH_{Ar'}$), 130.1, 135.8 ($C_{Ar}CH_3$), 143.1 (C-1), 146.3 (C-1′), 149.8 ($C_{Ar}SCH_3$), 159.6 (COH), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3016 (w), 2956 (w), 2922 (w), 2851 (w), 1650 (s), 1599 (w), 1586 (w), 1563 (w), 1487 (w), 1441 (m), 1332 (m), 1354 (m), 1314 (m), 1255 (s), 1213 (s), 1198 (m), 1177 (w), 1151 (m), 1001 (w), 1088 (m), 1030 (m), 1007 (m). – MS (EI, 70 eV): m/z (%) = 344 (100) [M]$^+$, 312 (68), 311 (32), 265 (24), 193 (63), 161 (83), 139 (23), 124 (30), 123 (34). – HRMS (EI): m/z = 344.11891 (calcd. 344.11891 for $C_{18}H_{20}N_2O_3S$, [M]$^+$).

*Methyl 4,6-dimethyl-3-ethyl-5-(4′-methylthiophenyl)-diazenyl-salicylate (**3ac**)*

Starting with **2g** (323 mg, 1.0 mmol), **4e** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ac** was isolated as a red solid (140 mg, 39 %); m. p.: 86 – 88 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 2.18 (s, 3H, SCH_3), 2.37 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.76 (q, ^3J = 7.6 Hz, 2H, CH_2), 3.95 (s, 3H, OCH_3), 7.36 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 11.42 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2 (CH_2CH_3), 14.9 (SCH_3), 15.3, 17.4 (CH_3), 19.4 (CH_2), 52.2 (OCH_3), 110.9 (C-3), 122.9, 126.0 ($CH_{Ar'}$), 129.8, 130.0 ($C_{Ar}CH_3$), 135.2 (C-1), 143.1 (C-1′), 146.5 (C-5), 149.8 ($C_{Ar}SCH_3$), 159.4 (COH), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3013 (w), 2971 (w), 2954 (w), 2931 (w), 2872 (w), 1648 (s), 1586 (m), 1564 (m), 1488 (m), 1440 (m), 1429 (m), 1393 (m), 1360 (s), 1317 (s), 1290 (w), 1270 (m), 1239 (w), 1212 (s), 1198 (s), 1177 (w), 1153 (m), 1108 (m), 1086 (m), 1048 (w), 1035 (m), 1007 (w). – MS (EI, 70 eV): m/z (%) = 358 (100) [M]$^+$, 327 (25), 326 (80), 325 (49), 311 (25), 279 (35), 207 (78), 191 (27), 175 (45), 139 (31), 124 (33), 123 (34). – HRMS (EI): m/z = 358.135016 (calcd. 358.13456 for $C_{19}H_{22}N_2O_3S$, [M]$^+$).

*2-Methoxyethyl 4,6-dimethyl-5-(4′-methylthiophenyl)-diazenyl-salicylate (**3ad**)*

Starting with **2g** (323 mg, 1.0 mmol), **4k** (457 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ad** was isolated as a red solid (120 mg, 32 %); m. p.: 85 – 86 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, SCH_3), 2.54 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.72 (t, ^3J = 4.7 Hz, 2H, CH_2), 4.52 (t, ^3J = 4.7 Hz, 2H, CH_2), 6.75 (s, 1H, H-5), 7.34 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 7.80 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 10.88 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (SCH_3), 17.2, 20.5 (CH_3), 58.9 (OCH_3), 64.3, 70.0 (CH_2), 111.8 (C-3), 118.2 (CH_{Ar}), 122.9, 126.0 ($CH_{Ar'}$), 136.8, 137.4 ($C_{Ar}CH_3$), 142.8 (C-1), 145.5 (C-1′), 150.0 ($C_{Ar}SCH_3$), 161.2 (COH), 170.9 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3009 (w), 2964 (w), 2914 (w), 2879 (w), 2850 (w), 2809 (w), 2736 (w), 1657 (s), 1598 (w), 1587 (w), 1574 (m), 1568 (m), 1475 (m), 1449 (m), 1435 (m), 1386 (s), 1375 (s), 1348 (s),

1310 (s), 1254 (s), 1227 (w), 1197 (m), 1168 (s), 1130 (s), 1085 (s), 1029 (s). – MS (EI, 70 eV): m/z (%) = 374 (100) $[M]^+$, 315 (30), 298 (62), 297 (45), 251 (38), 223 (21), 163 (24), 147 (44), 124 (21), 123 (26), 59 (42). – HRMS ((+)-ESI): m/z = 397.1192 (calcd. 397.11925 for $C_{19}H_{22}N_2O_4S$, $[M+Na]^+$).

*Methyl 3-allyl-4,6-dimethyl-5-(4′-methylthiophenyl)-diazenyl-salicylate (**3ae**)*

Starting with **2g** (323 mg, 1.0 mmol), **4l** (451 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ae** was isolated as a red solid (110 mg, 30 %); m. p.: 61 – 63 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3H, SCH_3), 2.39 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.51 (d, ^3J = 5.9 Hz, 2H, CH_2Ar), 3.96 (s, 3H, OCH_3), 4.92 – 5.02 (m, 2H, CH_2=CH), 5.89 – 6.02 (m, 1H, CH=CH_2), 7.36 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 11.46 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2 (SCH_3), 15.3, 17.4 (CH_3), 30.2 (CH_2Ar), 52.2 (OCH_3), 111.0 (C-3), 114.8 (*C*H_2=CH), 123.0 ($CH_{Ar'}$), 125.2 ($C_{Ar}CH_3$), 126.0 ($CH_{Ar'}$), 130.8 ($C_{Ar}CH_3$), 135.4 (*C*H=CH_2), 136.3 (C-5), 143.2 (C-1), 146.5 (C-1′), 149.8 ($C_{Ar}SCH_3$), 159.5 (COH), 172.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3067 (w), 2960 (w), 2924 (w), 1731 (w), 1656 (s), 1584 (m), 1556 (m), 1487 (w), 1435 (s), 1390 (m), 1356 (s), 1310 (m), 1257 (s), 1214 (m), 1197 (m), 1175 (m), 1151 (w), 1088 (s), 1023 (s). – GC-MS (EI, 70 eV): m/z (%) = 370 (100) $[M]^+$, 338 (30), 337 (33), 323 (43), 291 (22), 219 (45), 187 (23), 139 (27), 124 (25), 123 (24). – HRMS ((+)-ESI): m/z = 371.1426 (calcd. 371.14239 for $C_{20}H_{23}N_2O_3S$, $[M+H]^+$).

*Methyl 3-(n-chlorpropyl)-4,6-dimethyl-5-(4′-methylthio-phenyl)diazenyl-salicylate (**3af**)*

Starting with **2g** (323 mg, 1.0 mmol), **4h** (506 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3af** was isolated as a red solid (315 mg, 39 %); m. p.: 125 – 127 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 – 2.06 (m, 2H, CH_2), 2.19 (s, 3H, SCH_3), 2.36 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.88 (t, ^3J = 7.6 Hz, 2H, CH_2Ar), 3.61 (t, ^3J = 6.6 Hz, 2H, CH_2Cl), 3.96 (s, 3H, OCH_3), 7.36 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.7 Hz, 2H, $CH_{Ar'}$), 11.48 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2 (SCH_3), 15.3, 17.4 (CH_3) 23.7 (CH_2Ar), 31.8 (CH_2), 45.1 (CH_2Cl), 52.3 (OCH_3), 110.9 (C-3), 123.0, 126.0 ($CH_{Ar'}$), 126.6, 130.5 ($C_{Ar}CH_3$), 135.6 (C-5), 143.3 (C-1), 146.5 (C-1′), 149.8 ($C_{Ar}SCH_3$), 159.6 (COH), 172.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2959 (w), 2921 (w), 2869 (w), 1934 (w), 1705 (w), 1651 (s), 1586 (m), 1563 (m), 1490 (w), 1432 (s), 1396 (s), 1359 (s), 1316 (s), 1294 (w), 1266 (m), 1247 (m), 1211 (s), 1176 (m), 1141 (m), 1087 (s), 1049 (w), 1030 (m). – HRMS ((+)-ESI): m/z = 407.11897 (calcd. 407.11907 for $C_{20}H_{24}N_2O_3ClS$, $[M+H; ^{35}Cl]^+$).

*Methyl 4,6-dimethyl-3-(n-propyl)-5-(4′-methylthiophenyl)-diazenyl-salicylate (**3ag**)*

Starting with **2g** (323 mg, 1.0 mmol), **4f** (454 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ag** was isolated as a red solid (82 mg, 22 %); m. p.: 80 – 82 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3), 1.50 – 1.59 (m, 2H, CH_2CH$_3$), 2.17 (s, 3H, SCH_3), 2.36 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.70 (t, ^3J = 8.1 Hz, 2H, CH_2Ar), 3.95 (s, 3H, OCH_3), 7.36 (d, ^3J = 8.6 Hz, 2H, $CH_{Ar'}$), 7.82 (d, ^3J = 8.6 Hz, 2H, $CH_{Ar'}$), 11.41 ppm (s, 1H, OH).). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_2CH_3), 15.2, 15.4 (CH_3), 17.4 (SCH_3), 22.2, 28.2 (CH_2), 52.2 (OCH_3), 110.8 (C-3), 122.9, 126.1 ($CH_{Ar'}$), 128.4, 129.8 ($C_{Ar}CH_3$), 135.6 (C-5), 143.1 (C-1), 146.5 (C-1′), 149.9 ($C_{Ar}SCH_3$), 159.6 (COH), 172.7 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2956 (m), 2927 (w), 2867 (w), 1715 (w), 1651 (s), 1584 (m), 1555 (m), 1489 (w), 1430 (s), 1388 (m), 1360 (s), 1312 (m), 1255 (s), 1211 (s), 1196 (w), 1172 (m), 1148 (w), 1113 (m), 1089 (m), 1037 (m), 1007 (w). – MS (EI, 70 eV): m/z (%) = 372 (100) $[M]^+$, 340 (51), 339 (28), 325 (23), 293 (24), 221 (48), 205 (31), 189 (25), 139 (33), 124 (37). – HRMS (EI): m/z = 372.15009 (calcd. 372.15021 for $C_{20}H_{24}N_2O_3S$, $[M]^+$).

*Ethyl 4,6-dimethyl-5-(4′-ethoxycarbonylphenyl)diazenyl-salicylate (**3ah**)*

Starting with **2h** (350 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ah** was isolated as a red solid (40 mg, 11 %); m. p.: 122 – 123 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, ^3J = 7.2 Hz, 3H, OCH_2CH_3), 2.36 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 4.41 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.77 (s, 1H, H-5), 7.86 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 8.18 (d, ^3J = 8.9 Hz, 2H, $CH_{Ar'}$), 11.28 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.3 (OCH_2CH_3), 17.5, 21.2 (CH_3), 52.4 (OCH_3), 61.3 (OCH_2), 118.6 (CH_{Ar}), 122.2, 130.6 ($CH_{Ar'}$), 132.0 (C-3), 137.7, 138.2 ($C_{Ar}CH_3$), 145.3 (C-1′), 155.2 (C-1), 157.1 ($C_{Ar}COOEt$), 162.4 (COH), 166.1, 172.0 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2963 (w), 2924 (w), 2906 (w), 2874 (w), 2849 (w), 1711 (s), 1667 (s), 1644 (w), 1601 (w), 1566 (m), 1501 (w), 1470 (w), 1435 (s), 1407 (w), 1392 (w), 1361 (s), 1310 (m), 1275 (s), 1243 (s), 1221 (m), 1198 (m), 1161 (m), 1142 (m), 1129 (m), 1105 (w), 1092 (m), 1082 (m), 1009 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon)$ = 245, 348, 468. – MS (EI, 70 eV): m/z (%) = 356 (65) $[M]^+$, 179 (100), 147 (76), 120 (27). – HRMS (EI): m/z = 356.136569 (calcd. 356.13667 for $C_{19}H_{20}N_2O_5$, $[M]^+$).

*Methyl 5-((4-chlorophenyl)diazenyl)-4,6-dimethyl-salicylate (**3ai**)*

Starting with **2i** (311 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ai** was isolated as a red solid (140 mg, 44 %); m. p.: 95 – 98 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.32$ (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 6.77 (s, 1H, Ar), 7.47 – 7.51 (m, 2H, N=NAr), 7.79 – 7.82 (m, 2H, N=NAr), 11.25 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.3, 20.8 (CH_3), 52.3 (OCH_3), 111.6 (C_{Ar}), 118.4, 123.6, 129.3 (CH_{Ar}), 136.8 (C_{Ar}), 137.5, 137.6 ($C_{Ar}CH_3$), 145.0, 151.0 ($C_{ArN=N}$), 162.0 ($C_{Ar}OH$), 171.9 ppm (*C*$OOCH_3$). – IR (KBr, cm^{-1}): $\tilde{\nu} = 2992$ (w), 2955 (w), 1668 (s), 1444 (s), 1239 (m), 1089 (s), 833 (s). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log \varepsilon) = 230$ (3.86), 340 (3.79), 456 (1.76). – MS (GC, 70 eV): m/z (%) = 320 (29) [M; ^{37}Cl]$^+$, 318 77) ([M; ^{35}Cl]$^+$, 179 (100), 147 (97), 111 (46). – HRMS (EI): m/z = 318.07708 (calcd. 318.07657 for $C_{16}H_{15}ClN_2O_3$, [M; ^{35}Cl]$^+$). – Anal. for $C_{16}H_{15}ClN_2O_3$ (318.75): calcd. C 60.29, H 4.74, N 8.79; found C 60.42, H 4.98, N 8.04.

*Methyl 5-((4-chlorophenyl)diazenyl)-3,4,6-trimethyl-salicylate (**3aj**)*

Starting with **2i** (311 mg, 1.0 mmol), **4c** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3aj** was isolated as a red solid (115 mg, 35 %); m. p.: 121 – 122 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.18$ (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 7.48 – 7.52 (m, 2H, N=NAr), 7.81 – 7.85 (m, 2H, N=NAr), 11.53 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 11.7$, 15.9, 17.4 (CH_3), 52.3 (OCH_3), 110.7 (C_{Ar}), 123.7 (CH_{Ar}), 124.0 (C_{Ar}), 129.4 (CH_{Ar}), 130.8 (C_{Ar}), 136.0, 137.0 ($C_{Ar}CH_3$), 146.0, 150.9 ($C_{ArN=N}$), 159.9 ($C_{Ar}OH$), 172.6 ppm (*C*$OOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2992 (w), 2961 (w), 1656 (s), 1438 (s), 1213 (s), 1085 (m), 833 (m), 802 (m). – MS (EI, 70 eV): m/z (%) = 334 (33) [M; ^{37}Cl]$^+$, 332 (100) [M; ^{35}Cl]$^+$, 300 (52), 193 (95), 161 (78). – HRMS (EI): m/z = 332.09240 (calcd. 332.09222 for $C_{17}H_{17}ClN_2O_3$, [M; ^{35}Cl]$^+$). – Anal. for $C_{17}H_{17}ClN_2O_3$ (332.78): calcd. C 61.36, H 5.15, N 8.42; found C 60.78, H 5.17, N 8.17.

*Methyl 5-((4-chlorophenyl)diazenyl)-3-methoxy-4,6-dimethyl-salicylate (**3ak**)*

Starting with **2i** (311 mg, 1.0 mmol), **4d** (436 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ak** was isolated as a red solid (111 mg, 32 %); m. p.: 96 – 98 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.24$ (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 7.48 – 7.52 (m, 2H, N=NAr), 7.80 – 7.84 (m, 2H, N=NAr), 11.10 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 12.5$, 16.9 (CH_3), 52.4, 60.3 (OCH_3), 112.5 (C_{Ar}), 123.7, 129.4 (CH_{Ar}), 130.0, 130.3, 137.1, 145.1 (CAr), 145.2, 150.9 ($C_{ArN=N}$), 155.3 ($C_{Ar}OH$), 171.9 ppm (*C*$OOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3031$ (w), 2943 (w), 1654 (s), 1438 (s), 1217 (m), 1114 (m), 1071 (m), 834 (m), 802 (m). – MS (EI,): m/z (%) = 348 (34) [M; ^{35}Cl]$^+$, 315 (22), 256 (25), 111 (29). – HRMS ((+)-ESI): m/z = 349.09504 (calcd. 349.09496 for $C_{17}H_{18}ClN_2O_4$, [M+H; ^{35}Cl]$^+$). – Anal. for $C_{17}H_{18}ClN_2O_4$ (348.78): calcd. C 58.54, H 4.91, N 8.03; found C 58.79, H 5.23, N 7.52.

*Ethyl 5-((4-chlorophenyl)diazenyl)-4,6-dimethyl-salicylate (**3al**)*

Starting with **2i** (311 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3al** was isolated as a red solid (133 mg, 40 %); m. p.: 99 – 100 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.44$ (t, $^3J = 7.1$ Hz, 3H, CH_2CH_3), 2.32 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 4.47 (q, $^3J = 7.1$ Hz, 2H, CH_2CH_3), 6.77 (s, 1H, Ar), 7.47 – 7.50 (m, 2H, N=NAr), 7.79 – 7.82 (m, 2H, N=NAr), 11.33 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 17.5, 20.8 (CH_3), 61.9 (CH_2), 111.7 (C_{Ar}), 118.4, 123.6, 129.3 (CH_{Ar}), 136.8 (C_{Ar}), 137.4, 137.6 ($C_{Ar}CH_3$), 145.0, 151.0 ($C_{ArN=N}$), 162.1 ($C_{Ar}OH$), 171.5 ppm (*C*OOEt). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2970$ (w), 2926 (w), 1659 (s), 1467 (m), 1245 (s), 1083 (m), 804 (s). – MS (GC, 70 eV): m/z (%) = 334 (39) [M; ^{37}Cl]$^+$, 332 (100) [M; ^{35}Cl]$^+$, 286 (46), 193 (64), 147 (88), 111 (53). – HRMS (EI): m/z = 332.09166 (calcd. 332.09222 for $C_{17}H_{17}ClN_2O_3$, [M; ^{35}Cl]$^+$). – Anal. for $C_{17}H_{17}ClN_2O_3$ (332.78): calcd. C 61.36, H 5.15, N 8.42; found C 62.00, H 4.97, N 7.90.

*Methyl 5-((4-chlorophenyl)diazenyl)-3-ethyl-4,6-dimethyl-salicylate (**3am**)*

Starting with **2i** (311 mg, 1.0 mmol), **4f** (433 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3am** was isolated as a red solid (162 mg, 47 %); m. p.: 61 – 63 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.15$ (t, $^3J = 7.5$ Hz, 3H, CH_2CH_3), 2.21 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.77 (q, $^3J = 7.5$ Hz, 2H, CH_2CH_3), 3.97 (s, 3H, OCH_3), 7.49 – 7.52 (m, 2H, N=NAr), 7.81 – 7.85 (m, 2H, N=NAr), 11.48 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.2$, 15.1, 17.5 (CH_3), 19.4 (CH_2), 52.2 (OCH_3), 111.0 (C_{Ar}), 123.7, 129.4 (CH_{Ar}), 130.0, 130.6 (C_{Ar}), 135.4, 137.0 ($C_{Ar}CH_3$), 146.2, 150.9 ($C_{ArN=N}$), 159.8 ($C_{Ar}OH$), 172.6 ppm (*C*$OOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2948 (w), 1653 (s), 1434 (s), 1207 (m), 1086 (m), 805 (m). – MS (GC, 70 eV): m/z (%) = 348 (13) [M; ^{37}Cl]$^+$, 346 (37) [M; ^{35}Cl]$^+$, 314 (23), 207 (100), 175 (20). – HRMS (EI): m/z = 346.10780 (calcd. 346.10787 for

$C_{18}H_{19}ClN_2O_3$, [M; $^{35}Cl]^+$). – Anal. for $C_{18}H_{19}ClN_2O_3$ (346.81): calcd. C 62.34, H 5.52, N 8.08; found C 61.41, H 5.78, N 7.74.

*Methyl 5-((4-bromophenyl)diazenyl)-4,6-dimethyl-salicylate (**3an**)*

Starting with **2j** (355 mg, 1.0 mmol), **4a** (391 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3an** was isolated as a red solid (73 mg, 20 %); m. p.: 111 – 113 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.32$ (s, 3H, CH^3), 2.62 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 6.79 (s, 1H, Ar), 7.63 – 7.67 (m, 2H, N=NAr), 7.71 – 7.75 (m, 2H, N=NAr), 11.24 ppm (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.4$, 20.9 (CH_3), 52.3 (OCH_3), 111.6 (C_{Ar}), 118.5, 123.9 (CH_{Ar}), 125.2 (C_{Ar}), 132.3 (CH_{Ar}), 137.5, 137.7 ($C_{Ar}CH_3$), 145.0, 151.4 ($C_{ArN=N}$), 162.0 ($C_{Ar}OH$), 172.0 ppm ($COOCH_3$). – IR (KBr, cm^{-1}): $\tilde{\nu} = 3037$ (w), 2959 (w), 1663 (s), 1442 (s), 1235 (m), 1083 (m), 834 (s), 806 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon) = 231$ (4.12), 341 (4.11), 461 (3.15). – MS (EI, 70 eV): m/z (%) = 364 (26) [M; ^{81}Br]$^+$, 362 (27) [M; ^{79}Br]$^+$, 173 (100), 112 (76). – HRMS (EI): $m/z = 362.02605$ (calcd. 362.02606 for $C_{16}H_{15}BrN_2O_3$, [M; ^{79}Br]$^+$). – Anal. for $C_{16}H_{15}BrN_2O_3$ (363.21): calcd. C 52.91, H 4.16, N 7.71; found C 52.16, H 4.17, N 7.42.

*Methyl 3-(n-chloropropyl)-4,6-dimethyl-5-(4′-bromophenyl)diazenyl-salicylate (**3ao**)*

Starting with **2j** (355 mg, 1.0 mmol), **4h** (506 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ao** was isolated as a red solid (83 mg, 21 %); m. p.: 107 – 109 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.97 – 2.06 (m, 2H, CH_2), 2.21, 2.39 (s, 3H, CH_3), 2.89 (t, $^3J = 7.6$ Hz, 2H, CH_2), 3.61 (t, $^3J = 6.6$ Hz, 2H, CH_2), 3.97 (s, 3H, OCH_3), 7.66, 7.75 (d, $^3J = 8.9$ Hz, 2H, $CH_{Ar'}$), 11.51 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 15.3$, 17.5 (CH_3), 23.7, 31.8, 45.1 (CH_2), 52.3 (OCH_3), 111.1 (C-3), 124.0, 125.6, 126.8 ($C_{Ar}CH_3$), 131.1 (C-1), 132.4 ($CH_{Ar'}$), 135.8 (C-1′), 146.3 (C-5), 151.2 (C-4′), 160.0 (COH), 172.5 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2957$ (w), 2928 (w), 2870 (w), 1899 (w), 1738 (w), 1715 (w), 1651 (s), 1594 (m), 1558 (m), 1489 (w), 1435 (s), 1392 (m), 1356 (s), 1310 (m), 1295 (m), 1268 (m), 1247 (m), 1228 (w), 1211 (s), 1173 (m), 1143 (m), 1090 (m), 1064 (m), 1028 (m), 1006 (m). – MS (EI, 70 eV): m/z (%) = 442 (15) [M; ^{81}Br, ^{37}Cl]$^+$, 440 (60) [M; ^{81}Br, ^{35}Cl]$^+$, 438 (45) [M; ^{79}Br, ^{37}Cl]$^+$, 408 (30), 07 (22), 406 (24), 405 (21), 404 (44), 403 (24), 402 (56), 387 (26), 373 (42), 371 (46), 327 (32), 323 (26), 257 (23), 255 (75), 239 (22), 235 (36), 223 (32), 219 (100), 204 (50), 191 (23), 187 (23), 173 (48), 171 (51), 92 (29), 91 (33), 65 (28), 43 (28). – HRMS (EI): $m/z = 440.031848$ (calcd. 440.03199 for $C_{19}H_{20}N_2O_3Cl^{81}Br$, [M; ^{81}Br, ^{35}Cl]$^+$), 438.033671 (calcd. 438.03403 for $C_{19}H_{20}N_2O_3ClBr$, [M; ^{79}Br, ^{37}Cl]$^+$).

*Ethyl 4,6-dimethyl-5-(4′-trifluoromethoxyphenyl)diazenyl-salicylate (**3ap**)*

Starting with **2k** (360 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3ap** was isolated as a red solid (45 mg, 12 %); m. p.: 56 – 57 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.44$ (t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 2.32 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 4.46 (q, $^3J = 7.2$ Hz, 2H, OCH_2), 6.76 (s, 1H, H-5), 7.35 (d, $^3J = 8.9$ Hz, 2H, $CH_{Ar'}$), 7.89 (d, $^3J =$ 8.9 Hz, 2H, $CH_{Ar'}$), 11.30 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$ (OCH_2CH_3), 17.5, 20.8 (CH_3), 61.9 (OCH_2), 111.8 (C-3), 118.4 (CH_{Ar}), 118.7 ($C_{Ar}CH_3$), 121.4 ($CH_{Ar'}$), 122.1 ($C_{Ar}CH_3$), 123.9 ($CH_{Ar'}$), 137.4, (C-1), 137.7 (C-1′), 145.0 ($C_{Ar}OCF_3$), 150.8 ($J_{C,F}$ =2.2 Hz, OCF_3), 162.1 (COH), 171.5 ppm (C=O). – ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -57.73$ ppm (CF_3). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2952$ (w), 2931 (w), 2906 (w), 2854 (w), 1909 (w), 1651 (m), 1592 (w), 1564 (m), 1498 (w), 1475 (m), 1449 (m), 1430 (m), 1397 (m), 1374 (m), 1349 (m), 1304 (w), 1245 (s), 1212 (s), 1199 (s), 1156 (s), 1096 (m), 1081 (m), 1028 (w), 1011 (m). – UV/Vis (CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon) = 245$, 339, 453. – MS (GC, 70 eV): m/z (%) = 382 (100) [M]$^+$, 353 (25), 336 (42), 335 (46), 193 (43), 165 (28), 147 (61), 95 (26), 91 (24). – HRMS (EI): $m/z = 382.113612$ (calcd. 382.11349 for $C_{18}H_{17}F_3N_2O_4$, [M]$^+$).

*Ethyl 4,6-dimethyl-5-(3′,4′dioxolophenyl)diazenyl-salicylate (**3aq**)*

Starting with **2l** (320 mg, 1.0 mmol), **4b** (412 mg, 1.5 mmol) and $TiCl_4$ (0.12 mL, 1.1 mmol) in 3 mL of CH_2Cl_2, **3aq** was isolated as a red solid (82 mg, 24 %); m. p.: 116 – 117 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (t, $^3J = 7.2$ Hz, 3H, OCH_2CH_3), 2.26 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 4.44 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 6.06 (s, 2H, CH_2), 6.75 (s, 1H, H-5), 6.94 (d, $^3J = 8.3$ Hz, 1H, H-2′), 7.35 (d, $^3J = 1.7$ Hz, 1H, H-5′), 7.53 (dd, $^3J = 6.2$ Hz, 1H, H-6′), 11.23 ppm (s, 1H, OH). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$ (OCH_2CH_3), 17.4, 20.4 (CH_3),61.7 (OCH_2), 98.3 ($CH_{Ar'}$), 101.9 (CH_2), 107.9 (CH_{Ar}), 111.6 (C-3), 118.2, 123.3 ($CH_{Ar'}$), 136.2, 137.3 ($C_{Ar}CH_3$), 145.3 (C-1′), 148.6 (C-1), 148.8 (C-3′), 150.2 (C-4′), 161.5 (COH), 171.6 ppm (C=O). – IR (ATR, cm^{-1}): $\tilde{\nu} = 2993$ (w), 2970 (w), 2928 (w), 2901 (w), 1650 (s), 1598 (m), 1565 (m), 1538 (w), 1506 (w), 1481 (w), 1469 (s), 1435 (m), 1417 (m), 1399 (m), 1371 (s), 1346 (s), 1308 (s), 1239 (s), 1220 (m), 1164 (m), 1128 (w), 1110 (w), 1077 (m), 1030 (m), 1014 (m). – UV/Vis

(CH_2Cl_2, nm): $\lambda_{max}(\log\varepsilon) = 245, 354, 446$. – HRMS ((+)-ESI): $m/z = 343.12871$ (calcd. 343.12885 for $C_{18}H_{19}N_2O_5$, $[M+H]^+$).

*Synthesis of methyl 5,7-dimethyl-6-phenyldiazenyl-chroman-8-carboxylate (**3ar**)*

Compound **3h** (1.0 equiv.) was dissolved in DMF (15 mL per mmol), and TBAI (2.0 equiv.) and NaH (60% dispersion in mineral oil, 2.3 equiv.) were added under argon atmosphere. After stirring for 20 h, ethyl acetate (5 mL) and ice-cold water (5 mL) were added, and the mixture was neutralized by hydrochloric acid (10%). The mixture was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (heptane-EtOAc = 10 : 1 → 3 : 1). Starting with **3h** (0.100 g, 0.28 mmol), TBAI (0.222 g, 0.42 mmol) and NaH (60%, 0.017 g, 0.416 mmol) in DMF (4.0 mL), **3ar** was isolated as a red solid (0.068 g, 76%; m. p. 124 – 125 °C. – $R_f = 0.17$ (*n*-heptane-EtOAc = 3 : 1). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.04 - 2.11$ (m, 2H, OCH_2CH_2), 2.24 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.71 (t, $^3J = 6.6$ Hz, 2H, ($C_{Ar}CH_2$), 3.92 (s, 3H, OCH_3), 4.18 – 4.21 (t, 2H, OCH_2), 7.50 (m, 3H, (N=NAr), 7.85 – 7.88 ppm (m, 2H, N=NAr). – ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 14.2$, 15.9 (CH_3), 22.0, 22.6 (CH_2), 52.2 (OCH_3), 66.3 (OCH_2), 119.9 (C_{Ar}), 122.4 (CH_{Ar}), 122.5, 126.5 (C_{Ar}), 129.0, 130.8 (CH_{Ar}), 133.0 ($C_{Ar}CH_3$), 145.1, 151.6 ($C_{Ar}N$=N), 152.7 ($C_{Ar}O$), 168.9 ppm (*C*$OOCH_3$). – IR (ATR, cm^{-1}): $\tilde{\nu} = 3061$ (w), 2935 (w), 1728 (s), 1568 (m), 1436 (m), 1275 (s), 1117 (m), 690 (s). – MS (GC, 70 eV): m/z (%) = 324 (100) $[M]^+$, 309 (32), 293 (20), 219 (97), 191 (24), 77 (35).– HRMS (EI): $m/z = 324.14641$ (calcd. 324.14684 for $C_{19}H_{20}N_2O_3$, $[M]^+$). – Anal. for $C_{19}H_{20}N_2O_3$(324.37): calcd. C 70.35, H 6.21, N 8.64; found C 69.95, H 6.31, N 8.52.

Crystal structure determinations [41]

Suitable single crystals were cooled to 173(2) K (**3a**, **3d**, **3i**) or 298(2) K (**3an**, **3q**, **3am**, **3ar**) for the measurements. The data were collected on a Bruker-Nonius Apex-X8 CCD diffractometer using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The structures were solved by Direct Methods (SHELXS-97) [42 – 44] and refined by full-matrix least squares procedures (SHELXL-97, SHELXL-2013) [42 – 44]. Semi-empirical absorption corrections were applied (SADABS) [45]. All non hydrogen atoms were refined anisotropically (exception: **3a**: The atoms of the minor part of the disordered azo-benzene group were refined isotropically). Hydrogen atoms bound to carbon atoms were included in the refinement at calculated positions using a riding model, while hydrogen atoms bound to oxygen atoms were refined freely (exceptions: **3a**: The hydrogen atom of the hydroxyl group (H1) was included in the refinement at a calculated position using a riding model, but the torsion angle of the OH group was allowed to refine; **3q**: The hydrogen atom of the hydroxyl group O3b–H3b was included in the refinement at a calculated position using a riding model, but the torsion angle of the OH group was allowed to refine). Torsion angles of all methyl groups were allowed to refine (exception: **3q**: The torsion angles of all methyl groups were refined in idealized staggered geometry).

Cytotoxic experiments

The experiments were carried out following the procedure previously reported [46].

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