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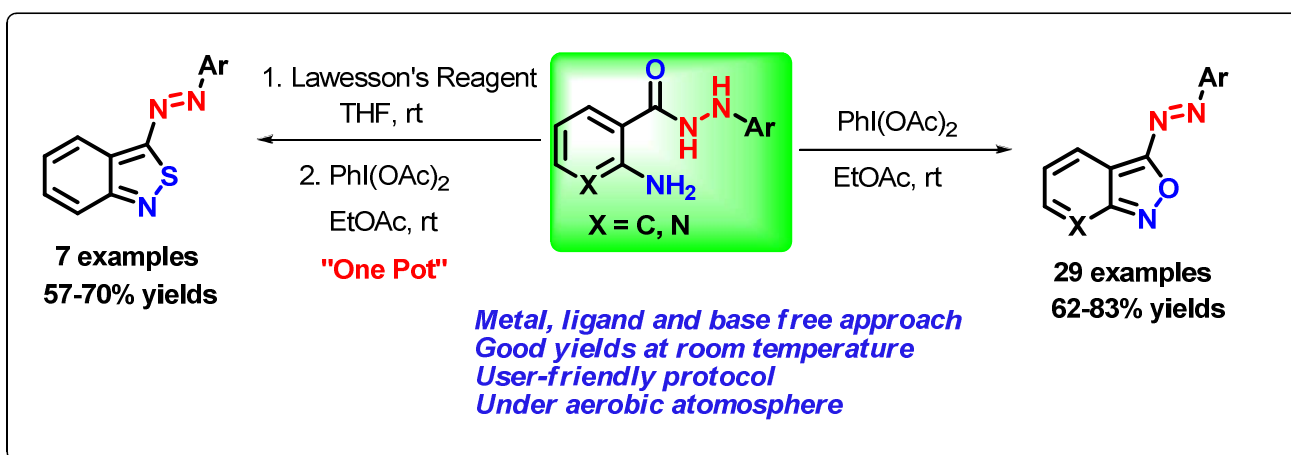
Substrate Controlled Synthesis of Benzisoxazole and Benzisothiazole derivatives via $\text{PhI}(\text{OAc})_2$ -Mediated Oxidation followed by Intramolecular Oxidative O-N/S-N Bond Formation

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ABSTRACT: A phenyliodine(III) diacetate (PIDA)-mediated, highly efficient and tandem approach for the synthesis of aryldiazenylisoxazolo(isothiazolo)arenes from simple 2-amino-*N'*-arylbenzohydrazides has been developed. The reaction proceeds *via* formation of (*E*)-(2-aminoaryl)(aryldiazenyl)methanone as the key intermediate followed by intramolecular oxidative O-N/S-N bond formation in one pot at room temperature. The quiet different reactivity of the

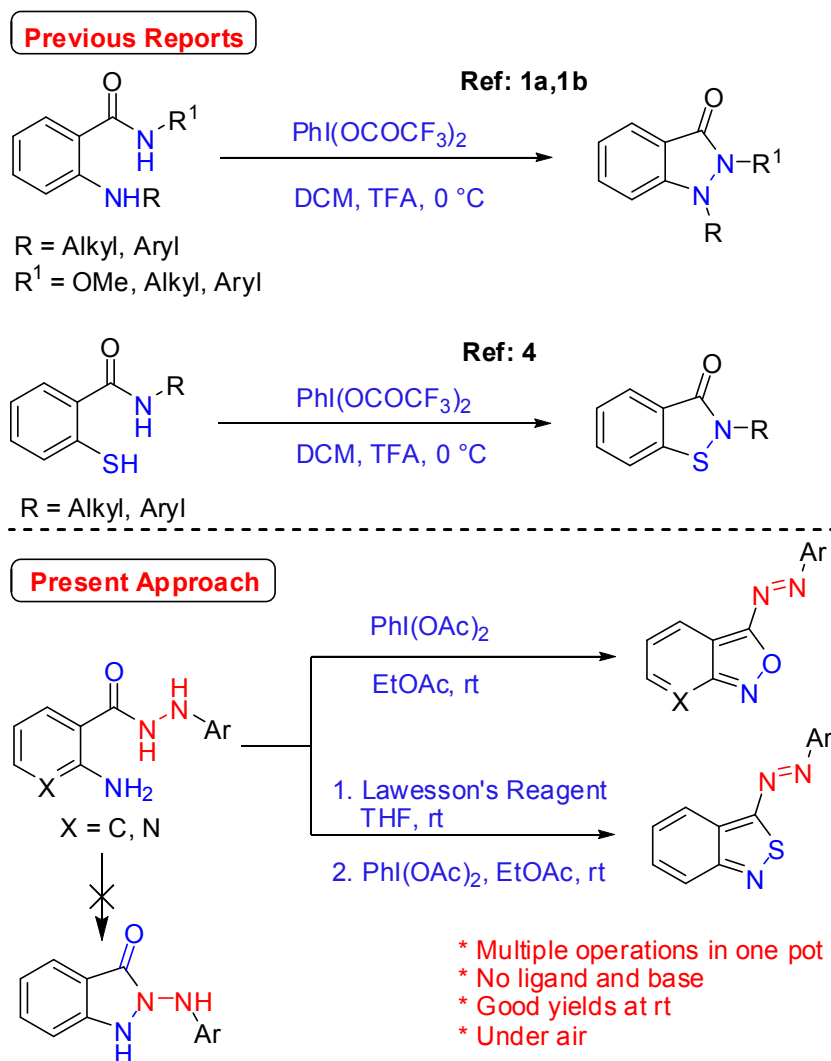
substrate is due to the formation of diazo intermediate which encounters a nucleophilic attack by carbonyl oxygen on electrophilic amine to produce isoxazole products as compare to the previous reports^{1a,1b,4} in which *N*-acylnitrenium ion intermediate is intramolecularly trapped by amine group.

INTRODUCTION

Direct construction of N-X (X = N, O, S) bond is an interesting approach for the synthesis of diverse heterocyclic compounds.¹⁻⁵ N-X bond formations are relatively less explored as compared to C-C and C-X bond formations. Various metal-catalyzed approaches are reported for the formation of N-X bond,^{2,3a-3c,5} however, in view of cost and environmental concerns of metal usage, the development of eco-friendly protocols are still highly desirable. Metal-free approaches for the construction of N-X bond has attracted a great attention due to their practical applicability and green chemistry aspects.^{1,3d,4} Recently, environmentally benign iodine(III) reagents⁶ emerged as inexpensive and efficient oxidizing agents which were successfully used for various intramolecular oxidative cyclizations.^{4,7} Tellitu *et al.*, reported the synthesis of indazolone and benzisothiazolone derivatives by using iodine(III) reagent *via* direct construction of intramolecular oxidative N-N/N-S bond formation from anthranilamide and 2-mercaptoamide derivatives as the starting substrates *via* formation of an *N*-acylnitrenium ion intermediate,^{1a,1b,4} which is stabilized by electron-donating effect of a proper neighbouring groups.^{1a} When we conducted the experiment with 2-amino-*N'*-phenylbenzohydrazides (**1a**) instead of anthranilamide the course of reaction was changed and finally delivered the corresponding benzisoxazole (**2a**)⁸ as product (Scheme 1) and laid the foundation of present work.

In line with the initial observations and continuation to our research on the development of mild and eco-friendly protocols,⁹ we herein present an unprecedented, tandem approach for the

synthesis of aryldiazenylisoxazolo(isothiazolo)arenes from 2-amino-*N'*-arylarylhydrazides by using PIDA as an external oxidant in an industrially acceptable and recommended green solvent *i.e.* ethyl acetate (EtOAc)¹⁰ at room temperature.



Scheme1. Direct N-X (X = N, S, O) bond annulation strategies to access heterocyclic compounds

Benzisoxazoles and benzisothiazoles are very prominent scaffolds found in various biologically active compounds and drugs (Fig 1).¹¹ On the other hand, aromatic azo compounds have broad applications in the field of technical devices such as non-linear optical devices, chemosensors, protein probes and molecular machines.¹² Moreover, the azo group is also utilized as the directing group for *ortho* C-H functionalization of organic compounds.¹³ The biological

applications of these scaffolds as well as synthetic utility of azo compounds prompted us to further investigate and optimize the synthetic methodology.

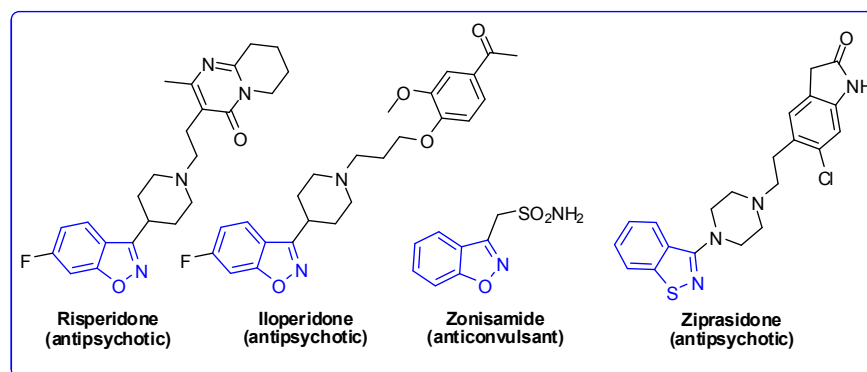


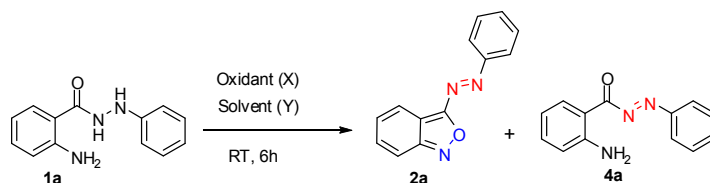
Fig. 1: Representative compounds of biological significance.

RESULTS AND DISCUSSION

We initiated our studies by choosing 2-amino-*N'*-phenylbenzohydrazide (**1a**) as a model substrate. Based on the previous methodologies,^{1a,1b,4} we carried out the reaction of **1a** in dichloromethane (DCM) by using PIFA (Phenyliodotrifluoroacetate) (1.5 equiv., 0.01 M) as an oxidant and trifluoroacetic acid (3 equiv.) as an additive at 0 °C. The reaction failed to give the expected indazolone product. When we carried the same reaction without TFA at room temperature, surprisingly, (*E*)-(2-aminophenyl)(phenyldiazenyl)methanone (**4a**) was formed in 20% yield (Table 1, entry 2). When we used the 3 equiv of PIFA (0.01 M), the reaction delivered the unexpected (*E*)-3-(phenyldiazenyl)benzo[*c*]isoxazole (**2a**) in 15% yield along with **4a** (Table 1, entry 3). This interesting result motivated us to optimize the reaction condition to improve the yield of annulated product **2a**. When we switched the oxidant from PIFA to PIDA (phenyliodoacetate) (3 equiv., 0.01 M), the yield of the benzisoxazole product **2a** and the diazo product **4a** increased to 35% and 40% yields respectively (Table 1, entry 4). We performed the same reaction in DCM with 0.1 M dilution of PIDA (3 equiv.), no change in the yield of **2a** and **4a** were observed (Table 1, entry 5). Next, we started optimization of solvents by keeping PIDA

(3 equiv., 0.1 M) as an oxidant. We screened the reaction in various solvents such as DCE, IPA, THF, ACN and EtOAc (Table 1, entries 6-10). Interestingly, EtOAc was found to be the best solvent and furnished the product **2a** in 80% yield with complete conversion of the intermediate product **4a** (entry 10). Other oxidants like PhI(OPiv)₂, PhIO and I₂ were also screened (Table 1, entries 11-13), however, they failed to improve the yield of **2a**. By decreasing the amount of PIDA (1.5 equiv., 0.1 M) in the reaction, only oxidized intermediate **4a** was formed in 90% yield (entry 14).

Table 1. Optimization of reaction conditions for 1a.^a

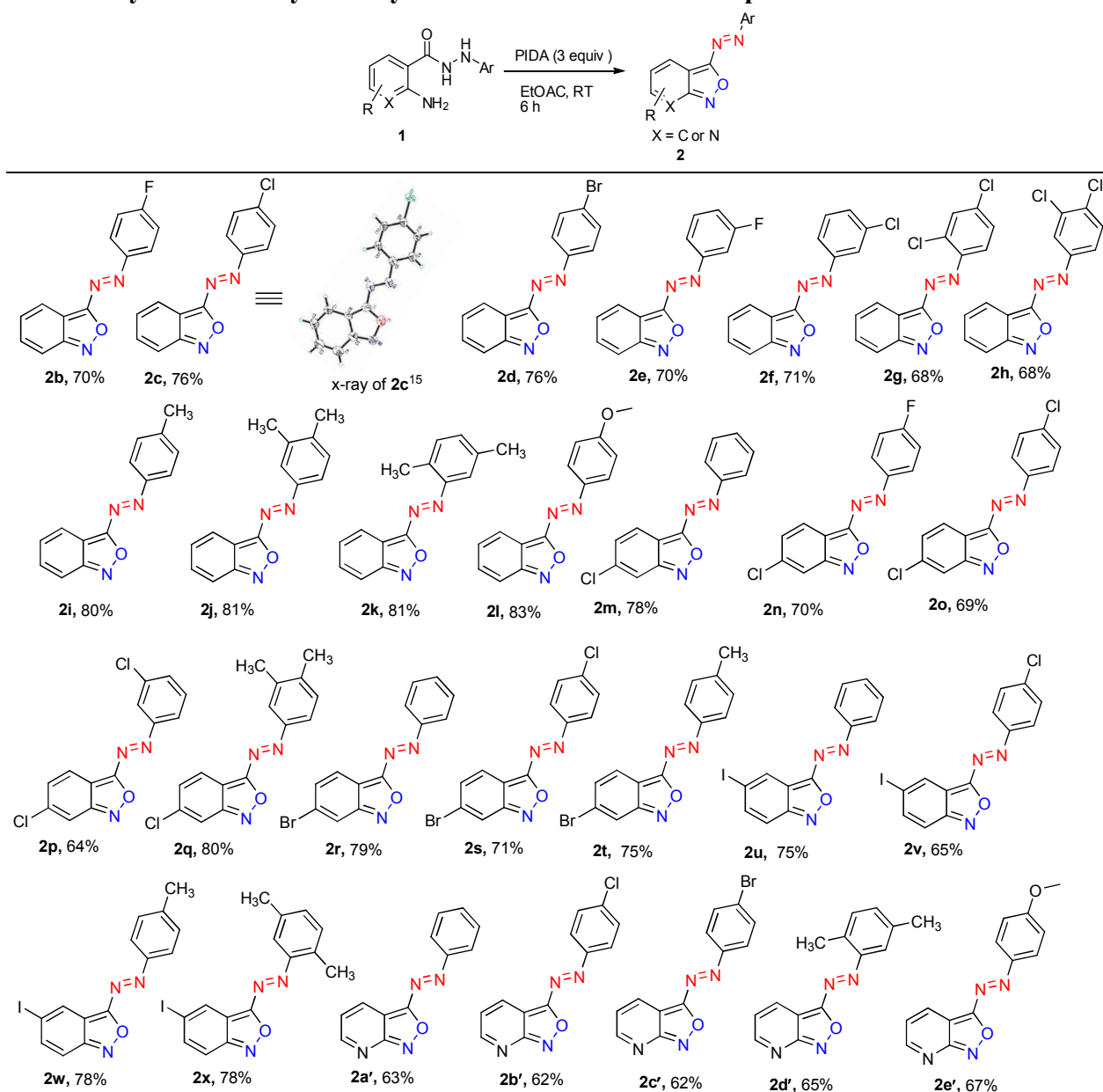


Entry	Oxidant (X) (equiv., Conc.)	Solvent (Y)	Yield ^b (%) 2a/4a
1	PIFA (1.5, 0.01 M) ^c	DCM	0/0
2	PIFA (1.5, 0.01 M)	DCM	0/20
3	PIFA (3.0, 0.01 M)	DCM	15/20
4	PIDA (3.0, 0.01 M)	DCM	35/40
5	PIDA (3.0, 0.1 M)	DCM	35/40
6	PIDA (3.0, 0.1 M)	DCE	30/50
7	PIDA (3.0, 0.1 M)	IPA	32/41
8	PIDA (3.0, 0.1 M)	THF	65/10
9	PIDA (3.0, 0.1 M)	ACN	70/10
10	PIDA (3.0, 0.1 M)	EtOAc	80/0
11	PhI(OPiv) ₂ (3.0, 0.1 M)	EtOAc	35/40
12	PhIO (3.0, 0.1 M)	EtOAc	0/20
13	I ₂ (3.0, 0. M)	EtOAc	0/0

14	PIDA (1.5, 0.1 M)	EtOAc	0/90
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^a Reaction conditions: **1a** (1 equiv.), oxidant (X) (equiv., Conc.) at RT, 6 h, under air. ^b Isolated yields. ^c Reaction carried out at 0° C by using trifluoroacetic acid (TFA) (3 equiv.) as additive. ^d Abbreviations used in the table: PIFA = Phenyliodine(III) bis(trifluoroacetate); PIDA = Phenyliodine(III) diacetate; DCM = Dichloromethane; DCE = Dichloroethane; THF = Tetrahydrofuran; IPA = Isopropylalcohol; ACN = Acetonitrile

With the optimal conditions (Table 1, entry 10) in hand, we next probed the scope and generality of this intramolecular oxidative O-N bond formation approach to a variety of 2-amino-*N'*-arylarlylhydrazides. The arylhydrazides containing electron withdrawing groups (3-F, 3-Cl, 4-Cl, 4-Br, 2,4-dichloro, and 3,4-dichloro) underwent a smooth reaction and yielded the corresponding products in good yields (Table 2, **2b-2h**). The structure of **2c** was confirmed by X-ray diffraction analysis¹⁴ (see supporting information). Similarly, the arylhydrazides bearing electron-donating groups (CH₃, and OCH₃) are well tolerated in the reaction and afforded the desired products in excellent yields (**2i-2l**). Next we demonstrated the reaction by using different substituents such as Cl, Br and I on the aryl ring of arylhydrazides (derived from isatoic anhydride) (**1m-1x**; see experimental section) and they successfully furnished the desired products in good yields (**2m-2x**).

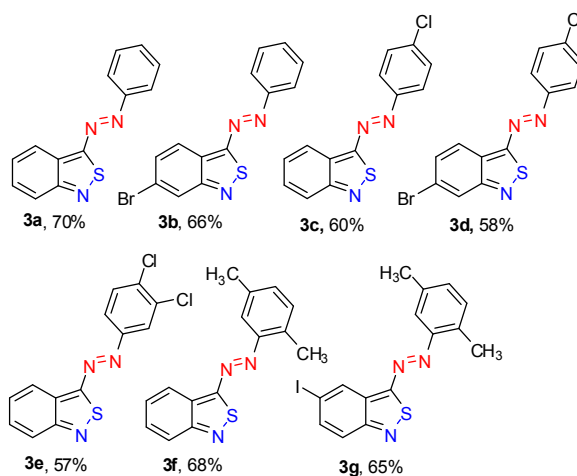
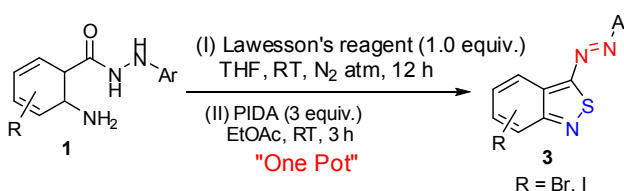
Table 2. Synthesis of aryldiazenylisoxazoloarenes under the optimum reaction conditions.^{a,b}

^a Reaction conditions: **1** (1 equiv.), PIDA (3 equiv., 0.1 M) at RT, 6 h, under air. ^b Isolated yields.

To expand the scope of present approach, we studied the reaction of 2-amino-*N*-phenylnicotinohydrazide (**1a'**) (derived from 2-aminonicotinic acid and phenylhydrazine; see the

supporting information) as diversified substrates under identical reaction conditions. Pleasingly, the corresponding product (*E*)-3-(phenyldiazenyl)isoxazolo[3,4-*b*]pyridine (**2a'**) was formed in 63% yield. Likewise, various electron-withdrawing and electron-donating groups such as Cl, Br, CH₃, and OCH₃ containing nicotinohydrazides are employed in the reaction and afforded the respective products in moderate to good yields (**Table 2, 2b'-2e'**).

Table 3. Synthesis of aryldiazenylbenzothiazoles under the optimum reaction conditions.^{a,b}



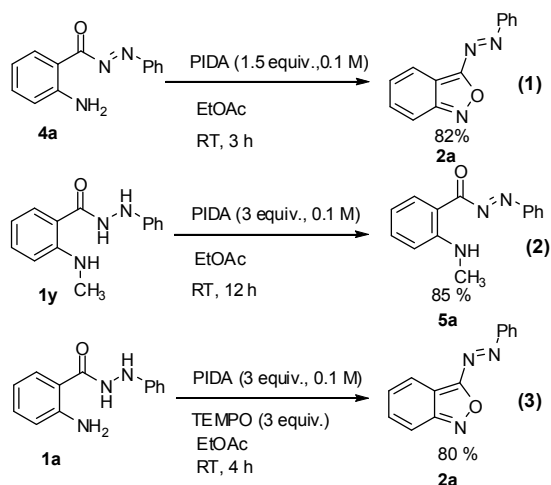
^a Reaction conditions: (A) **1** (1 equiv.), Lawesson's Reagent (1 equiv.), THF, RT, N₂ atm, 12 h; (B) PIDA (3 equiv., 0.1 M), EtOAc, RT, 3 h, under air. ^b Isolated yields.

Additionally, in order to check the versatility of the reaction, the present method was extended for the synthesis of biologically significant aryldiazenylbenzothiazole scaffold from the reaction of 2-amino-*N'*-arylhazides. In this transformation, benzohydrazides were converted to benzothiohydrazides by using Lawesson's reagent (1 equiv.) in THF under N₂ atmosphere at room temperature. After removal of THF under vacuum, the reaction mixture was

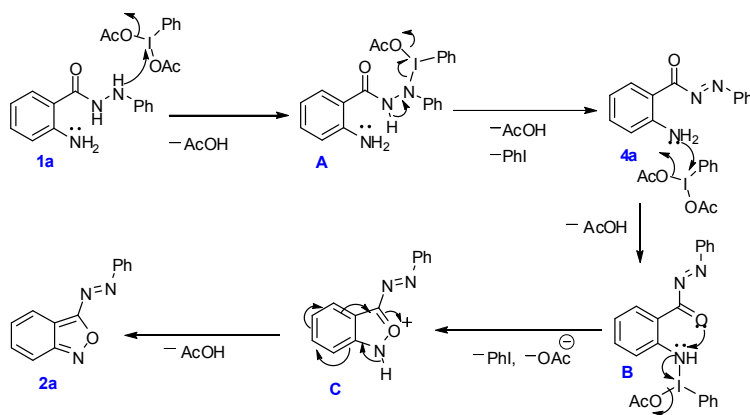
1
2
3 directly subjected to oxidative intramolecular S-N bond formation by using standard reaction
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5 conditions and yielded the respective aryldiazenylbenzothiazoles in moderate to good yields
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7 (Table 3, **3a-3g**). Notably, to the best of our knowledge this is the first approach to synthesize
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9 aryldiazenylbenzothiazoles from arylhydrazides in one pot proving the practical application of
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11 the methodology.
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14
15 Furthermore, in order to investigate the reaction mechanism, few control experiments were
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17 performed (Scheme 2). The reaction of intermediate **4a** with PIDA (1.5 equiv.) under similar
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19 conditions produced the desired product **2a** in 82% yield within 3 h (Scheme 2, eqn (1)). It is
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21 evident that the reaction proceeds *via* formation of intermediate **4a**. When the reaction was
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23 carried out by using 2-(methyldiamino)-*N'*-phenylbenzohydrazide (**1y**) under identical reaction
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25 conditions, only oxidized product **5a** was formed in 85% yield (Scheme 2, eqn (2)). Moreover,
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27 when the reaction of **1a** was performed in the presence of radical inhibitor such as TEMPO
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29 (2,2,6,6-tetramethylpiperidine 1-oxyl) under similar conditions, no significant effect was observed
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31 on the yield of desired product (Scheme 2, eqn (3)), which indicates the absence of radical
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33 mechanism. These results collectively suggest that the formation of **4a** is a prerequisite to getting
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35 the oxidative annulated product (**2a**). The set of experiments also justified the importance of
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37 oxidant and its stoichiometric amount in present methodology.
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Scheme 2. Controlled experiments.



Based on the control experiments and previous literature reports,^{1c,14} a presumptive mechanism is proposed (Scheme 3). Initially, the reaction of **1a** with $\text{PhI}(\text{OCOCH}_3)_2$ (PIDA) gives the iodinated intermediate **A** with the removal of acetic acid. The intermediate **A** is further converted into an azo intermediate **4a** via removal of iodobenzene and acetic acid. The reaction of **4a** with another mole of PIDA gives the iodinated intermediate **B** with the removal of acetic acid, which upon subsequent oxidative O-N bond forming annulation with the loss of iodobenzene and acetic acid delivered the desired benzisoxazole product (**2a**).



Scheme 3. Plausible reaction mechanism

In summary, we have developed a practical, mild and efficient protocol for the synthesis of

aryldiazenylisoxazoloarenes from the reaction of 2-amino-*N'*-arylarylhydrazides. Additionally, we also demonstrated the synthesis of aryldiazenylbenzisothiazoles in one pot by using suitable thiation agent (Lawesson's reagent) followed by our standard reaction conditions. The present work offers an efficient method to access highly interesting diazo group containing arylisoxazoles and benzisothiazoles in good yields. Multiple operations in one pot by using mild reaction conditions at room temperature under aerobic condition are the attractive feature of the present methodology. Further, diazo directed C-H functionalization of these compounds is underway in our laboratory.

Experimental section

General Information. Melting points were determined on a capillary melting point apparatus and are uncorrected. All the compounds were fully characterized by ^1H , ^{13}C , IR, and HRMS analysis. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 / $\text{DMSO}-d_6$ and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 / $\text{DMSO}-d_6$ using TMS as internal standard. Multiplicities are reported as follows: singlet (s), doublet (d), broad singlet (br s), doublet of doublets (dd), triplet (t), doublet of doublet of doublet (ddd), doublet of triplet (dt) and multiplet (m). Chemical shift and coupling constants are reported in parts per million (ppm) relative to residual signal of TMS in deuterated solvents and Hertz, respectively. IR spectra were recorded using FT-IR spectrophotometer and values reported in cm^{-1} . HRMS were recorded using Q-TOF mass spectrometer. Column chromatography was performed over silica gel (60–120 Mesh) and EtOAc-hexane as eluent. All chemicals and reagents were purchased from commercial sources and used without further purification.

General experimental procedure for the preparation of 1d, 1e, 1g, 1h, 1j, 1k, 1l, 1n-1q, and 1s-1x and 1a'-1e'

2-amino-*N'*-arylbenzohydrazides 1a, 1b, 1c, 1f, 1i, 1m, 1r and 1y were known and they were prepared by known literature procedure.^{16a} The substrates 1d, 1e, 1g, 1h, 1j, 1k, 1l, 1n-1q, 1s-1x and 1a'-1e' were unknown and prepared from known literature procedure¹⁶ as given below.

In a 50 mL round-bottom flask, a suspension of isatoic anhydride (1.0 equiv.) in THF (20 mL) was treated by slow addition of 1.2 equiv of phenylhydrazines. The reaction mixture was refluxed overnight (12 h). The completion of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and concentrated under vacuum. 2-Amino-*N'*-arylbenzohydrazides (**1**) were obtained as solids after being crystallized from ethanol.

Experimental procedure for the preparation of 1a'-1e':

To a solution of 2-aminonicotinic acid (1 equiv.) in dry THF (20 mL) at 0 °C placed into a 50 mL of round bottom flask, 1,1'-carbonyldiimidazole (CDI)(1.1 equiv.) was added. The suspension was stirred for 2 h at room temperature. Eventually, the precipitate thinned out and *N,N'*-diisopropylethylamine (DIPEA)(1.2 equiv.) was added, which caused the precipitate to fully dissolve, followed by the addition of phenylhydrazines. The mixture was stirred at rt for 24 h. The reaction was carefully quenched with water (20 mL) and extracted with EtOAc (3x20 mL). The organic layer was dried over anhydrous Na₂SO₄. The organic solvent was removed under reduced pressure and crude residue was crystallized from ethanol to give the desired products (**1a'-1e'**).

Experimental procedure for the synthesis of (*E*)-(2-aminophenyl)(phenyldiazenyl)methanone intermediate(4a):

To a well stirred solution of phenyliodine(III) diacetate (PIDA) (637 mg, 1.5 equiv., 0.1 M) in ethylacetate (20 mL), 2-amino-*N'*-phenylbenzohydrazide (**1a**) (300 mg, 1.0 equiv) was added at

room temperature. The resulting mixture was allowed to stir for 30 min. After completion of the reaction (monitored by TLC), EtOAc was evaporated under reduced pressure and residue was purified by column chromatography on silica gel (60-120 mesh) eluting with hexane: EtOAc (97: 3) to afford the red colour solid product **4a** (90%).

Experimental procedure for the synthesis of aryldiazenylisoxazoloarenes (2a-2x and 2a' - 2e'):

To a well stirred solution of PIDA (3.0 equiv., 0.1 M) in ethylacetate (40 mL), 2-amino-*N'*-arylbzenzohydrazides (**1**) (1.0 equiv.) was added at room temperature. The resulting mixture was allowed to stir for 6 h. The completion of the reaction was monitored by TLC. The reaction mixture was quenched with water and extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. Evaporation of solvent under reduced pressure gave a crude product which was purified by silica gel (60-120 mesh) column chromatography by using hexane: EtOAc (98: 2) as an eluent to afford the red colour solid products (2a-2x and 2a' -2e').

Experimental procedure for the synthesis of aryldiazenylbenzothiazoles (3a-3g):

To a solution of **1** (1 equiv.) in THF (25 mL) was added the lawesson's reagent (1 equiv.) and the reaction mixture was stirred for 24 h at rt under N₂ ballon. After complete conversion of **1**, the solvent was evaporated under reduced pressure and the crude residue was directly subjected for similar experimental procedure as mentioned above. The completion of the reaction was monitored by TLC. The reaction mixture was quenched with water and extracted with EtOAc (20x3 mL). The organic layer was washed with brine and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (60-120 mesh) column chromatography by using hexane: EtOAc (99: 1) as an eluent to afford the red colour solid products (**3a-3g**).

2-amino-N'-(4-bromophenyl)benzohydrazide (1d): White solid (314 mg, 56%); mp 198-200 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3391, 3019, 1669, 1422, 1289, 1215, 1065, 758, 668; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.09 (s, 1H), 7.97 (s, 1H), 7.64 (d, 1H, J = 7.60 Hz), 7.29 (d, 2H, J = 8.56 Hz), 7.20-7.16 (m, 1H), 6.74-6.71 (m, 3H), 6.56-6.52 (m, 1H), 6.36 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.8, 149.9 (C), 149.20 (C), 132.2 (CH), 131.3 (2xCH), 127.9 (CH), 116.4 (CH), 114.7 (CH), 114.2 (2xCH), 112.5 (C), 109.2 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{12}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 306.0242, found: 306.0242.

2-amino-N'-(3-fluorophenyl)benzohydrazide (1e): White solid (225 mg, 50%); mp 164-166 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 3019, 1634, 1403, 1216, 1067, 770, 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.09 (s, 1H), 8.07 (s, 1H), 7.65 (d, 1H, J = 7.44 Hz), 7.21-7.13 (m, 2H), 6.73 (d, 1H, J = 7.76 Hz), 6.61 (d, 1H, J = 7.78 Hz), 6.55 (t, 1H, J = 7.95 Hz), 6.51-6.45 (m, 2H), 6.38 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.8, 163.1 (d, J = 238.72 Hz, C), 152.1 (d, J = 10.20 Hz, C), 149.9 (C), 132.2 (CH), 130.3 (d, J = 9.88 Hz, CH), 128.0 (CH), 116.4 (CH), 114.7 (CH), 112.5 (C), 108.2 (CH), 104.5 (d, J = 21.20 Hz, CH), 98.6 (d J = 25.46 Hz, CH) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{12}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 246.1043, found: 246.1040.

2-amino-N'-(2,4-dichlorophenyl)benzohydrazide (1g): White solid (271 mg, 50%); mp 197-200 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 3019, 1639, 1384, 1215, 1155, 1068, 770, 668; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.23 (s, 1H), 7.67-7.65 (m, 2H), 7.43 (d, 1H, J = 2.32 Hz), 7.23-7.17 (m, 2H), 6.86-6.78 (m, 1H), 6.73 (d, 1H, J = 7.76), 6.55 (t, 1H, J = 7.18 Hz), 6.40 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.6, 150.0 (C), 144.3 (C), 132.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 121.9 (C), 117.7 (C), 116.4 (CH), 114.6 (CH), 114.0 (CH), 112.1 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 296.0357, found: 296.0346.

2-amino-N'-(3,4-dichlorophenyl)benzohydrazide (1h): White solid (271 mg, 50%); mp 171-173 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3390, 3019, 1646, 1404, 1215, 1065, 770, 668; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.14 (s, 1H), 8.21 (s, 1H), 7.64 (dd, 1H, J = 7.88, 1.15 Hz), 7.36 (d, 1H, J = 8.72 Hz), 7.21-7.17 (m, 1H), 6.91 (d, 1H, J = 2.61 Hz), 6.77-6.72 (m, 2H), 6.57-6.53 (m, 1H), 6.39 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.8, 150.07 (C), 150.00 (C), 132.4 (CH), 131.1 (C), 130.6 (CH), 128.0 (CH), 119.2 (C), 116.4 (CH), 114.7 (CH), 113.1 (CH), 112.5 (CH), 112.2 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 296.0357, found: 296.0346.

2-amino-N'-(3,4-dimethylphenyl)benzohydrazide (1j): White solid (281 mg, 60%); mp 188-190 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3389, 3019, 1634, 1403, 1215, 1155, 1068, 758, 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.02 (s, 1H), 7.65 (d, 1H, J = 7.8 Hz), 7.48 (s, 1H), 7.19-7.15 (m, 1H), 6.90 (d, 1H, J = 7.8 Hz), 6.72 (d, 1H, J = 8.24 Hz), 6.60 (s, 1H), 6.56-6.52 (m, 2H), 6.35 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.7, 149.8 (C), 147.8 (C), 136.0 (C), 132.0 (CH), 129.6 (CH), 127.9 (CH), 126.0 (C), 116.3 (CH), 114.7 (CH), 114.0 (CH), 112.9 (C), 110.0 (CH), 19.7 (CH₃), 18.4 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 256.1450, found: 256.1449.

2-amino-N'-(2,5-dimethylphenyl)benzohydrazide (1k): White solid (281 mg, 60%); mp 164-166 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3425, 1618, 1584, 1404, 1216, 1066, 764, 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.08 (s, 1H), 7.68 (dd, 1H, J = 7.92, 1.2 Hz), 7.21-7.16 (m, 1H), 7.04 (br s, 1H), 6.89 (d, 1H, J = 7.48 Hz), 6.73 (dd, 1H, J = 8.24, 0.84 Hz), 6.58-6.53 (m, 2H), 6.49 (d, 1H, J = 7.28 Hz), 6.39 (br s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.6, 149.9 (C), 146.9 (C), 135.2 (C), 132.1 (CH), 129.9 (CH), 127.9 (CH), 119.4 (CH), 119.0 (C), 116.4 (CH), 114.7 (CH), 112.8 (C), 111.8 (CH), 21.1 (CH₃), 16.8 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 256.1450; found: 256.1438.

2-amino-N'-(4-methoxyphenyl)benzohydrazide (1l): White solid (307 mg, 65%); mp 150-152 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3378, 3019, 2932, 1634, 1585, 1508, 1404, 1215, 1156, 1068, 1030, 757, 668; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.06 (d, 1H, J = 2.6 Hz), 7.64 (d, 1H, J = 7.12 Hz), 7.44 (d, 1H, J = 2.84 Hz), 7.19-7.15 (m, 1H), 6.79-6.74 (m, 4H), 6.72-6.70 (m, 1H), 6.54 (t, 1H, J = 7.8 Hz), 6.35 (br s, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 166.8, 152.7 (C), 149.8 (C), 143.6 (C), 132.1 (CH), 127.9 (CH), 116.3 (CH), 114.7 (CH), 114.2 (2xCH), 113.8 (2xCH), 112.9 (C), 55.2 ppm; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 258.1243, found: 258.1225.

2-amino-4-chloro-N'-(4-fluorophenyl)benzohydrazide (1n): White solid (212 mg, 50%); mp 160-162 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3378, 1636, 1507, 1403, 1218, 1065, 771; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.15 (s, 1H), 7.75 (s, 1H), 7.65 (d, 1H, J = 8.46 Hz), 7.00-6.96 (m, 2H), 6.79-6.76 (m, 3H), 6.62 (s, 2H), 6.56 (dd, 1H, J = 8.41, 2.01 Hz) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 168.1, 155.9 (d, J = 232 Hz, C), 151.1 (C), 146.1 (C), 136.7 (C), 129.8 (CH), 115.2 (d, J = 10.38 Hz, 2xCH), 115.0 (CH), 114.3 (CH), 113.5 (d, J = 7.50 Hz, 2xCH), 111.4 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{ClFN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 280.0653; found: 280.0653.

2-amino-4-chloro-N'-(4-chlorophenyl)benzohydrazide (1o): White solid (251 mg, 56%); mp 172-174 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3377, 3019, 1631, 1385, 1215, 1155, 1068, 927, 758, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.17 (s, 1H), 7.97 (s, 1H), 7.66 (d, 1H, J = 8.32 Hz), 7.17 (d, 2H, J = 8.30), 6.79-6.76 (m, 3H), 6.63 (br s, 2H), 6.56 (d, 1H, J = 7.66 Hz) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.0, 151.2 (C), 148.6 (C), 136.8 (C), 129.8 (CH), 128.5 (2xCH), 121.8 (C), 115.1 (CH), 114.3 (CH), 113.7 (2xCH), 111.3 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 296.0357, found: 296.0346.

2-amino-4-chloro-N'-(3-chlorophenyl)benzohydrazide (1p): White solid (246 mg, 55%); mp 200-202 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3366, 3019, 1625, 1404, 1215, 1066, 849, 769, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.17 (s, 1H), 8.09 (s, 1H), 7.66 (d, 1H, J = 8.44 Hz), 7.15 (t, 1H, J = 7.90 Hz), 6.80 (d, 1H, J = 1.30 Hz), 6.73-6.71 (m, 3H), 6.64 (br s, 2H), 6.57 (d, 1H, J = 7.90 Hz) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.0, 151.2 (2xC), 136.8 (C), 133.4 (C), 130.4 (CH), 129.8 (CH), 118.0 (CH), 115.2 (CH), 114.4 (CH), 111.5 (CH), 111.1 (C), 110.8 (CH) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 296.0357; found: 296.0346.

2-amino-4-chloro-N'-(3,4-dimethylphenyl)benzohydrazide (1q): White solid (263 mg, 60%); mp 187-189 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3385, 3019, 1613, 1492, 1404, 1215, 1154, 1068, 769, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.10 (d, 1H, J = 2.03 Hz), 7.65 (d, 1H, J = 8.38 Hz), 7.50 (d, 1H, J = 2.03 Hz), 6.89 (d, 1H, J = 7.94 Hz), 6.78 (d, 1H, J = 1.77 Hz), 6.61 (br s, 2H), 6.59-6.50 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.0, 151.1 (C), 147.7 (C), 136.6 (C), 136.1 (C), 129.8 (CH), 129.6 (CH), 126.1 (C), 115.1 (CH), 114.4 (CH), 114.0 (CH), 111.6 (C), 110.0 (CH), 19.7 (CH₃), 18.4 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 290.1060; found: 290.1053.

2-amino-4-bromo-N'-(4-chlorophenyl)benzohydrazide (1s): White solid (229 mg, 55%); mp 185-187 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3379, 3019, 1636, 1403, 1215, 1066, 758, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.17 (s, 1H), 7.97 (s, 1H), 7.57 (d, 1H, J = 8.44 Hz), 7.17 (d, 2H, J = 8.64 Hz), 6.96 (d, 1H, J = 1.24 Hz), 6.77 (d, 2H, J = 8.64 Hz), 6.69 (d, 1H, J = 8.28 Hz), 6.60 (br s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.7, 151.4 (C), 148.8 (C), 130.3 (CH), 128.9 (2xCH), 126.3 (C), 122.5 (C), 118.6 (CH), 117.9 (CH), 114.2 (2xCH), 112.1 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{BrClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 339.9852, found: 339.9848.

2-amino-4-bromo-N'-p-tolylbenzohydrazide (1t): White solid (224 mg, 57%); mp 189-191 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3449, 3390, 3354, 3287, 3021, 1654, 1607, 1492, 1216, 1062, 907, 761, 669; ^1H NMR (400 MHz,

DMSO- d_6): δ = 10.11 (s, 1H), 7.59-7.56 (m, 2H), 6.96-6.94 (m, 3H), 6.69-6.67 (m, 3H), 6.58 (br s, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.2 (C), 151.2 (C), 147.4 (C), 129.9 (CH), 129.2 (2xCH), 127.4 (C), 125.7 (C), 118.2 (CH), 117.4 (CH), 112.7 (2xCH), 112.1 (C), 20.2 (CH₃) ppm; HRMS (ESI): calcd for C₁₄H₁₄BrN₃O [M+H]⁺ 320.0398, found: 320.0389.

2-amino-5-iodo-*N'*-phenylbenzohydrazide (*Iu*): White solid (210 mg, 58%); mp 218-220 °C; IR FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3402, 1638, 1403, 1217, 1155, 1068, 771, 668; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.16 (s, 1H), 7.93 (d, 1H, J = 1.92 Hz), 7.75 (br s, 1H), 7.44 (dd, 1H, J = 8.68, 1.96 Hz), 7.16-7.12 (m, 2H), 6.76 (d, 2H, J = 7.68 Hz), 6.72-6.69 (m, 1H), 6.59 (d, 1H, J = 8.72 Hz), 6.51 (br s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.0, 149.7 (C), 149.6 (C), 140.6 (CH), 136.1 (CH), 129.2 (2xCH), 119.4 (CH), 119.3 (CH), 115.7 (C), 112.7 (2xCH), 75.2 (C) ppm; HRMS (ESI): calcd for C₁₃H₁₂IN₃O [M+H]⁺ 354.0103, found: 354.0102.

2-amino-*N'*-(4-chlorophenyl)-5-iodobenzohydrazide (*Iv*): White solid (219 mg, 55%); mp 178-180 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 1650, 1403, 1216, 1066, 770, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.18 (s, 1H), 7.95-7.92 (m, 2H), 7.44 (dd, 1H, J = 8.68, 1.40 Hz), 7.18 (d, 2H, J = 8.68 Hz), 6.77 (d, 2H, J = 8.68 Hz), 6.59 (d, 1H, J = 8.72 Hz), 6.52 (br s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 167.5, 149.4 (C), 148.5 (C), 140.2 (CH), 135.7 (CH), 128.5 (2xCH), 121.8 (C), 118.9 (CH), 114.9 (C), 113.7 (2xCH), 74.7 (C) ppm; HRMS (ESI): calcd for C₁₃H₁₁ClIN₃O [M+H]⁺ 387.9714, found: 387.9711.

2-amino-5-iodo-*N'*-*p*-tolylbenzohydrazide (*Iw*): White solid (219 mg, 58%); mp 176-178 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3847, 3744, 3738, 3669, 3391, 1654, 1403, 1217, 1063, 771, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.13 (s, 1H), 7.91 (s, 1H), 7.57 (s, 1H), 7.43 (d, 1H, J = 7.64 Hz), 6.96 (d, 2H, J = 7.96 Hz), 6.68 (d, 2H, J = 8.00 Hz), 6.58 (d, 1H, J = 8.64 Hz), 6.50 (br s, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 167.5, 149.3 (C), 147.3 (C), 140.1 (CH), 135.7 (CH), 129.1 (2xCH), 127.3 (C), 118.9 (CH), 115.3 (C), 112.6 (2xCH), 74.8 (C), 20.1 (CH₃) ppm; HRMS (ESI): calcd for C₁₄H₁₄IN₃O [M+H]⁺ 368.0260, found: 368.0244.

2-amino-*N'*-(2,5-dimethylphenyl)-5-iodobenzohydrazide (*Ix*): White solid (235 mg, 60%); mp 172-174 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3398, 2927, 1637, 1403, 1218, 1067, 771, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 10.18 (s, 1H), 7.96 (s, 1H), 7.44 (d, 1H, J = 8.60 Hz), 7.04 (s, 1H), 6.89 (d, 1H, J = 7.24 Hz), 6.61-6.48 (m, 5H), 2.17 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 167.4, 149.4 (C), 146.7 (C), 140.1 (C), 135.7 (CH), 135.3

(CH), 129.9 (CH), 119.5 (CH), 119.0 (C), 119.0 (CH), 115.2 (C), 111.7 (CH), 74.8 (C), 21.2 (CH₃), 16.8 (CH₃) ppm; HRMS (ESI): calcd for C₁₅H₁₆IN₃O [M+H]⁺ 382.0416, found: 382.0410.

2-amino-N'-phenylnicotinohydrazide(1a'): White solid (272 mg, 55%); mp 158-160 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3398, 1639, 1403, 1219, 1065, 771; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.27 (d, 1H, *J* = 1.88 Hz), 8.12-8.05 (m, 2H), 7.83 (d, 1H, *J* = 2.08 Hz), 7.15 (t, 2H, *J* = 8.12 Hz), 7.00 (br s, 2H), 6.78 (d, 2H, *J* = 7.76 Hz), 6.72 (t, 1H, *J* = 7.28 Hz), 6.63 (dd, 1H, *J* = 7.64, 4.8 Hz) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 167.6, 158.8 (C), 151.7 (CH), 149.5 (C), 136.4 (CH), 128.7 (2xCH), 118.7 (CH), 112.3 (2xCH), 111.4 (CH), 107.8 (C) ppm; HRMS (ESI): calcd for C₁₂H₁₂N₄O [M+H]⁺ 229.1089, found: 229.1088.

2-amino-N'-(4-chlorophenyl)nicotinohydrazide(1b'): White solid (295 mg, 52%); mp 220-222 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1637, 1403, 1216, 1068, 771, 668; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.30 (d, 1H, *J* = 2.28 Hz), 8.12 (dd, 1H, *J* = 4.76, 1.72 Hz), 8.06-8.02 (m, 2H), 7.20-7.16 (m, 2H), 7.00 (br s, 2H), 6.80-6.76 (m, 2H), 6.62 (dd, 1H, *J* = 7.68, 4.76 Hz) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 167.6, 158.8 (C), 151.9 (CH), 148.5 (C), 136.4 (CH), 128.5 (2xCH), 121.9 (C), 113.7 (2xCH), 111.4 (CH), 107.6 (C) ppm; HRMS (ESI): calcd for C₁₂H₁₁ClN₄O [M+H]⁺ 263.0700, found: 263.0690.

2-amino-N'-(4-bromophenyl)nicotinohydrazide(1c'): White solid (345 mg, 52%); mp 216-218 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 3019, 1639, 1404, 1215, 1063, 928, 757, 669; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.29 (d, 1H, *J* = 2.40 Hz), 8.12 (dd, 1H, *J* = 4.76, 1.72 Hz), 8.05-8.03 (m, 2H), 7.30-7.28 (m, 2H), 6.99 (br s, 2H), 6.74-6.72 (m, 2H), 6.62 (dd, 1H, *J* = 7.72, 4.8 Hz) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 167.6, 158.8 (C), 151.9 (CH), 148.9 (C), 136.4 (CH), 131.3 (2xCH), 114.3 (2xCH), 114.4 (CH), 109.4 (C), 107.6 (C) ppm; HRMS (ESI): calcd for C₁₂H₁₁BrN₄O [M+H]⁺ 307.0194, found: 307.0191.

2-amino-N'-(4-methoxyphenyl)nicotinohydrazide (1e'): White solid (337 mg, 60%); mp 149-151 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3745, 3393, 3019, 1633, 1403, 1215, 1155, 1068, 769, 669; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.26 (d, 1H, *J* = 3.04 Hz), 8.11 (dd, 1H, *J* = 4.72, 1.60 Hz), 8.04 (dd, 1H, *J* = 7.68, 1.52 Hz), 7.52 (d, 1H, *J* = 3.16 Hz), 6.99 (br s, 2H), 6.79-6.74 (m, 4H), 6.61 (dd, 1H, *J* = 7.68, 4.80 Hz), 3.65 (s, 3H) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 167.6, 158.7 (C), 152.8 (CH), 151.6 (C), 143.3 (CH), 136.3 (C), 114.2 (2xCH), 113.8 (2xCH), 111.4 (CH), 107.9 (C), 55.2 ppm; HRMS (ESI): calcd for C₁₃H₁₄N₄O₂ [M+H]⁺ 259.1195; found: 259.1191.

(E)-3-(*phenyldiazenyl*)benzo[*c*]isoxazole (**2a**): Red solid (235 mg, 80%); mp 90-92 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 3018, 1654, 1384, 1216, 1084, 770, 669; ^1H NMR (400 MHz, DMSO- d_6): δ = 8.10-8.04 (m, 3H), 7.78 (d, 1H, J = 9.00 Hz), 7.67-7.66 (m, 3H), 7.59-7.55 (m, 1H), 7.43-7.40 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6): δ = 166.9 (C), 157.9 (C), 152.7 (C), 133.6 (CH), 132.3 (CH), 129.7 (2xCH), 129.5 (CH), 123.3 (2xCH), 121.4 (CH), 115.5 (CH), 108.7 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 224.0824, found: 224.0824.

(E)-3-((4-fluorophenyl)diazenyl)benzo[*c*]isoxazole (**2b**): Red solid (205 mg, 70%); mp 158-159 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 3019, 2400, 1592, 1496, 1384, 1215, 1070, 929, 846, 757, 669; ^1H NMR (400 MHz, CDCl_3): δ = 8.02-7.96 (m, 3H), 7.59 (d, 1H, J = 8.92 Hz), 7.36-7.32 (m, 1H), 7.21-7.15 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.4 (C), 165.7 (d, J = 254.57 Hz) (C), 158.5 (C), 150.1 (C), 131.6 (CH), 128.6 (CH), 125.9 (d, J = 9.03 Hz, 2xCH), 121.8 (CH), 116.7 (d, J = 23.09 Hz, 2xCH), 116.0 (CH), 109.8 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_8\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 242.0730, found: 242.0726.

(E)-3-((4-chlorophenyl)diazenyl)benzo[*c*]isoxazole (**2c**): Red solid (224 mg, 76%); mp 140-141 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3746, 3686, 3400, 3019, 2400, 1614, 1385, 1215, 1085, 929, 757, 669; ^1H NMR (400 MHz, CDCl_3): δ = 8.04-7.97 (m, 3H), 7.66 (d, 1H, J = 8.96 Hz), 7.52 (d, 2H, J = 10.56 Hz), 7.43-7.39 (m, 1H), 7.29-7.25 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.4 (C), 158.5 (C), 151.8 (C), 139.3 (C), 131.6 (CH), 129.8 (2xCH), 128.8 (CH), 124.8 (2xCH), 121.8 (CH), 116.1 (CH), 110.0 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_8\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 258.0434, found: 258.0434.

(E)-3-((4-bromophenyl)diazenyl)benzo[*c*]isoxazole (**2d**): Red solid (224 mg, 76%); mp 156-158 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 3019, 1614, 1385, 1215, 1067, 758, 669; ^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, 1H, J = 7.68 Hz), 7.86 (d, 2H, J = 6.72 Hz), 7.65-7.64 (m, 3H), 7.37 (s, 1H), 7.25-7.23 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.4 (C), 158.6 (C), 152.1 (C), 132.8 (2xCH), 131.6 (CH), 128.9 (CH), 127.9 (CH), 125 (2xCH), 121.8 (CH), 116.1 (CH), 110.0 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_8\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 301.9929, found: 301.9923.

(E)-3-((3-fluorophenyl)diazenyl)benzo[*c*]isoxazole (**2e**): Red solid (206 mg, 70%); mp 135-137 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3392, 1619, 1387, 1068, 770; ^1H NMR (400 MHz, DMSO- d_6): δ = 8.13 (d, 1H, J = 8.72 Hz), 7.98-7.95 (m, 1H), 7.85-7.80 (m, 2H), 7.75-7.69 (m, 1H), 7.62-7.51 (m, 2H), 7.48-7.44 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ = 166.7 (C), 162.7 (d, J = 247.37 Hz, C), 158.0 (C), 154.1 (d, J = 8.89 Hz, C), 132.5 (2xCH), 131.6 (d,

$J = 8.57$ Hz, CH), 130.0 (CH), 121.3 (d, $J = 11.03$ Hz, CH), 120.2 (d, $J = 22.09$ Hz, CH), 115.7 (CH), 109.5 (C), 108.2 (d, $J = 22.93$ Hz, CH) ppm; HRMS (ESI): calcd for $C_{13}H_8FN_3O$ $[M+H]^+$ 242.0730, found: 242.0726.

(E)-3-((3-chlorophenyl)diazenyl)benzo[*c*]isoxazole (**2f**): Red solid (206 mg, 71%); mp 155-156 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3401, 3019, 1613, 1385, 1215, 1068, 930, 757, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.06$ -8.02 (m, 2H), 7.96-7.93 (m, 1H), 7.68 (d, 1H, $J = 9.04$ Hz), 7.53-7.48 (m, 2H), 7.45-7.41 (m, 1H), 7.31-7.26 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.3$ (C), 158.6 (C), 154.1 (C), 135.7 (C), 132.6 (CH), 131.7 (CH), 130.5 (CH), 129.1 (CH), 123.1 (CH), 122.5 (CH), 121.7, 116.2 (CH), 110.2 (C) ppm; HRMS (ESI): calcd for $C_{13}H_8\text{ClN}_3\text{O}$ $[M+H]^+$ 258.0434, found: 258.0433.

(E)-3-((2,4-dichlorophenyl)diazenyl)benzo[*c*]isoxazole (**2g**): Red solid (201 mg, 68%); mp 174-176 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3400, 1636, 1403, 1217, 1068, 840, 771, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.13$ (m, 1H), 7.88 (d, 1H, $J = 8.8$ Hz), 7.69 (d, 1H, $J = 9.00$ Hz), 7.63 (d, 1H, $J = 2.16$ Hz), 7.46-7.42 (m, 1H), 7.37-7.31 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.6$ (C), 158.6 (C), 147.9 (C), 139.6 (C), 138.5 (C), 131.8 (CH), 131.0 (CH), 129.9 (CH), 128.2 (CH), 122.5 (CH), 117.7 (CH), 116.1 (CH), 108.3 (C) ppm; HRMS (ESI): calcd for $C_{13}H_7\text{Cl}_2\text{N}_3\text{O}$ $[M+H]^+$ 292.0044 ; found: 292.0042.

(E)-3-((3,4-dichlorophenyl)diazenyl)benzo[*c*]isoxazole (**2h**): Red solid (201 mg, 68%); mp 158-160 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3853, 3745, 3400, 3019, 2400, 1615, 1385, 1215, 1083, 758, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.13$ (d, 1H, $J = 2.12$ Hz), 8.03 (d, 1H, $J = 8.68$ Hz), 7.90 (dd, 1H, $J = 8.56, 2.16$ Hz), 7.68 (d, 1H, $J = 9.04$ Hz), 7.63 (d, 1H, $J = 8.56$ Hz), 7.45-7.41 (m, 1H), 7.32-7.28 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.2$ (C), 158.6 (C), 152.3 (C), 137.1 (C), 134.1 (C), 131.7 (CH), 131.3 (CH), 129.4 (CH), 124.6 (CH), 123.2 (CH), 121.7 (CH), 116.3 (CH), 110.5 (C) ppm; HRMS (ESI): calcd for $C_{13}H_7\text{Cl}_2\text{N}_3\text{O}$ $[M+H]^+$ 292.0044, found: 292.0045.

(E)-3-(*p*-tolyl)diazenyl)benzo[*c*]isoxazole (**2i**): Red solid (236 mg, 80%); mp 130-132 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3400, 3019, 1600, 1385, 1215, 1070, 757, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.06$ (dt, 1H, $J = 8.72, 1.0$ Hz), 7.95 (d, 2H, $J = 8.32$ Hz), 7.65 (dd, 1H, $J = 9.04, 0.72$ Hz), 7.40 (ddd, 1H, $J = 10.2, 6.44, 1.0$ Hz), 7.35 (d, 2H, $J = 8.08$ Hz), 7.26-7.22 (m, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.8$ (C), 158.5 (C), 151.8 (C), 144.4 (C), 131.5 (CH), 130.2 (2xCH), 128.2 (CH), 123.8 (2xCH), 122.0 (CH), 115.9 (CH), 109.5 (C), 21.9 (CH_3) ppm; HRMS (ESI): calcd for $C_{14}H_{11}\text{N}_3\text{O}$ $[M+H]^+$ 238.0980, found: 238.0975.

(E)-3-((3,4-dimethylphenyl)diazenyl)benzo[*c*]isoxazole (**2j**): Red solid (237 mg, 81%); mp 154-155 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3395, 1613, 1388, 1073, 760; ^1H NMR (400 MHz, CDCl_3): δ = 8.09 (d, 1H, J = 8.64 Hz), 7.85 (s, 1H), 7.82 (d, 1H, J = 8.12 Hz), 7.65 (d, 1H, J = 8.96 Hz), 7.42-7.39 (m, 1H), 7.32 (d, 1H, J = 7.96 Hz), 7.26-7.22 (m, 1H), 2.38 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ = 167.2 (C), 157.9 (C), 151.3 (C), 143.7 (C), 138.1 (C), 132.3 (CH), 130.8 (CH), 129.1 (CH), 123.9 (CH), 121.5 (CH), 121.4 (CH), 115.4 (CH), 108.3 (C), 19.7 (CH₃), 19.3 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 252.1137, found: 252.1135.

(E)-3-((2,5-dimethylphenyl)diazenyl)benzo[*c*]isoxazole (**2k**): Red solid (237 mg, 81%); mp 148-150 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3417, 1639, 1403, 1069, 757; ^1H NMR (400 MHz, CDCl_3): δ = 8.03 (d, 1H, J = 8.68 Hz), 7.68 (d, 2H, J = 8.72 Hz), 7.43 (ddd, 1H, J = 9.0, 6.48, 0.92 Hz), 7.29-7.27 (m, 3H), 2.77 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 168.6 (C), 158.5 (C), 151.5 (C), 138.0 (C), 136.6 (C), 134.5 (CH), 131.5 (CH), 131.4 (CH), 128.5 (CH), 122.1 (CH), 115.9 (CH), 115.1 (CH), 107.9 (C), 21.0 (CH₃), 17.6 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 252.1137, found: 252.1132.

(E)-3-((4-methoxyphenyl)diazenyl)benzo[*c*]isoxazole (**2l**): Red solid (243 mg, 83%); mp 120-122 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3409, 1638, 1403, 1068, 760; ^1H NMR (400 MHz, CDCl_3): δ = 8.07-8.03 (m, 3H), 7.63 (d, 1H, J = 9.05 Hz), 7.41-7.37 (m, 1H), 7.24-7.18 (m, 1H), 7.07-7.03 (m, 2H), 3.93 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.9 (C), 164.1 (C), 158.6 (C), 148.2 (C), 131.5 (CH), 127.8 (CH), 126.1 (2xCH), 122.1 (CH), 115.8 (CH), 114.8 (2xCH), 109.4 (C), 55.9 ppm; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 254.0930, found: 254.0915.

(E)-6-chloro-3-(phenyldiazenyl)benzo[*c*]isoxazole (**2m**): Red solid (230 mg, 78%); mp 119-121 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1643, 1403, 1069, 770; ^1H NMR (400 MHz, CDCl_3): δ = 8.05-8.00 (m, 3H), 7.66 (dd, 1H, J = 1.36, 0.8 Hz), 7.60-7.54 (m, 3H), 7.17 (dd, 1H, J = 9.12, 1.56 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 168.0 (C), 158.6 (C), 153.4 (C), 137.9 (C), 133.6 (CH), 130.2 (CH), 129.6 (2xCH), 123.9 (2xCH), 123.3 (CH), 114.5 (CH), 107.3 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_8\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 258.0434, found: 258.0428.

(E)-6-chloro-3-((4-fluorophenyl)diazenyl)benzo[*c*]isoxazole (**2n**): Red solid (206 mg, 70%); mp 170-172 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3403, 2922, 2314, 1642, 1402, 1069, 766; ^1H NMR (400 MHz, CDCl_3): δ = 8.10-8.07 (m, 2H), 8.00 (d, 1H, J = 9.04 Hz), 7.67 (s, 1H), 7.26 (br t, 2H), 7.18 (dd, 1H, J = 9.08, 1.44 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.8 (C), 167.3 (C), 158.6 (C), 150.1 (C), 138.0 (C), 130.2 (CH), 126.2 (d, J = 8.98 Hz, 2xCH), 123.1

(CH), 116.8 (d, $J = 23.0$ Hz, 2xCH), 114.6 (CH), 107.8 (C) ppm; HRMS (ESI): calcd for $C_{13}H_7ClFN_3O$ $[M+H]^+$ 276.0340; found: 276.0330.

(E)-6-chloro-3-((4-chlorophenyl)diazenyl)benzo[*c*]isoxazole (**2o**): Red solid (203 mg, 69%); mp 165-166 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3400, 3019, 2399, 1613, 1385, 1215, 1084, 928, 757, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.99$ (d, 3H, $J = 8.8$ Hz), 7.67 (s, 1H), 7.54 (d, 2H, $J = 8.8$ Hz), 7.19 (dd, 1H, $J = 9.12, 1.36$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.8$ (C), 158.6 (C), 151.7 (C), 139.9 (C), 138.0 (C), 130.5 (CH), 130.0 (2xCH), 125.0 (2xCH), 123.1 (CH), 114.6 (CH), 108.0 (C) ppm; HRMS (ESI): calcd for $C_{13}H_7Cl_2N_3O$ $[M+H]^+$ 292.0044, found: 292.0044.

(E)-6-chloro-3-((3-chlorophenyl)diazenyl)benzo[*c*]isoxazole (**2p**): Red solid (188 mg, 64%); mp 175-176 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3401, 2922, 1644, 1403, 1068, 840, 767; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.04$ -7.96 (m, 3H), 7.70 (d, 1H, $J = 0.64$ Hz), 7.56-7.50 (m, 2H), 7.22 (dd, 1H, $J = 9.08, 1.48$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.7$ (C), 158.7 (C), 154.1 (C), 138.1 (C), 135.8 (C), 133.1 (CH), 130.8 (CH), 130.6 (CH), 123.2 (CH), 123.0 (CH), 122.7 (CH), 114.7 (CH), 108.3 (C) ppm; HRMS (ESI): calcd for $C_{13}H_7Cl_2N_3O$ $[M+H]^+$ 292.0044; found: 292.0041

(E)-6-chloro-3-((3,4-dimethylphenyl)diazenyl)benzo[*c*]isoxazole (**2q**): Red solid (234 mg, 80%); mp 158-160 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3394, 1619, 1386, 1300, 1045, 776; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.98$ (d, 1H, $J = 9.12$ Hz), 7.78-7.75 (m, 2H), 7.61 (s, 1H), 7.28 (d, 1H, $J = 8.00$ Hz), 7.11 (dd, 1H, $J = 9.08, 1.48$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.2$ (C), 158.5 (C), 152.0 (C), 143.9 (C), 138.1 (C), 137.8 (C), 130.8 (CH), 129.7 (CH), 124.4 (CH), 123.5 (CH), 122.1 (CH), 114.3 (CH), 107.3 (C), 20.3 (CH_3), 19.9 (CH_3) ppm; HRMS (ESI): calcd for $C_{15}H_{12}ClN_3O$ $[M+H]^+$ 286.0747, found: 286.0734

(E)-6-bromo-3-(phenyldiazenyl)benzo[*c*]isoxazole (**2r**): Red solid (233 mg, 79%); mp 120-122 °C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3409, 1634, 1403, 1216, 1069, 770, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.07$ -8.03 (m, 2H), 7.95 (dd, 1H, $J = 9.08, 0.72$ Hz), 7.88 (br t, 1H), 7.60-7.54 (m, 3H), 7.31 (dd, 1H, $J = 9.08, 1.44$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.1$ (C), 159.0 (C), 153.4 (C), 133.7 (CH), 132.5 (CH), 129.6 (2xCH), 126.4 (C), 123.9 (2xCH), 123.2 (CH), 118.1 (CH), 107.8 (C) ppm; HRMS (ESI): calcd for $C_{13}H_8BrN_3O$ $[M+H]^+$ 301.9929, found: 301.9922.

(E)-6-bromo-3-((4-chlorophenyl)diazenyl)benzo[*c*]isoxazole(**2s**): Red solid (209 mg, 71%); mp 210-212°C; FT-IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) 3409, 1639, 1403, 1216, 1091, 840, 771, 669; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.98$ (dt, 2H, $J =$

9.48, 2.6 Hz), 7.91 (dd, 1H, $J = 9.08, 0.72$ Hz), 7.88 (br t, 1H), 7.53 (dt, 2H, $J = 9.48, 2.60$ Hz), 7.31 (dd, 1H, $J = 9.08, 1.4$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 167.9$ (C), 159.0 (C), 151.7 (C), 139.9 (C), 132.7 (CH), 130.0 (2xCH), 126.5 (C), 125.0 (2xCH), 123.0 (CH), 118.1 (CH), 108.1 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_7\text{BrClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 335.9539, found: 335.9546.

(E)-6-bromo-3-(*p*-tolylidiazenyl)benzo[*c*]isoxazole (**2t**): Red solid (221 mg, 75%); mp 138-140 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1636, 1403, 1069, 768; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.95$ -7.92 (m, 3H), 7.85 (s, 1H), 7.35 (d, 2H, $J = 8.2$ Hz), 7.27 (dd, 1H, $J = 9.08, 1.32$ Hz), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.3$ (C), 158.9 (C), 151.7 (C), 145.1 (C), 132.0 (CH), 130.3 (2xCH), 126.3 (C), 124.0 (2xCH), 123.4 (CH), 117.9 (CH), 107.6 (C), 21.9 (CH_3) ppm; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 316.0085, found: 316.0072.

(E)-5-iodo-3-(phenylidiazenyl)benzo[*c*]isoxazole (**2u**): Red solid (222 mg, 75%); mp 138-140 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1642, 1401, 1217, 1071, 769; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.54$ (br t, 1H), 8.09-8.04 (m, 2H), 7.63-7.54 (m, 4H), 7.43 (dd, 1H, $J = 9.32, 0.8$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.4$ (C), 156.9 (C), 153.5 (C), 140.3 (CH), 133.6 (CH), 131.0 (CH), 129.6 (2xCH), 123.9 (2xCH), 117.3 (CH), 110.8 (C), 94.2 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_8\text{IN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 349.9790, found: 349.9795.

(E)-3-((4-chlorophenyl)diazenyl)-5-iodobenzo[*c*]isoxazole (**2v**): Red solid (191 mg, 65%); mp 185-187 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1637, 1403, 1068, 841, 760; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.52$ (s, 1H), 8.02 (dt, 2H, $J = 9.44, 2.64$ Hz), 7.63 (dd, 1H, $J = 9.32, 1.48$ Hz), 7.54 (dt, 2H, $J = 9.48, 2.64$ Hz), 7.44 (dd, 1H, $J = 9.32, 0.8$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.2$ (C), 157.0 (C), 151.9 (C), 140.4 (CH), 139.8 (C), 130.9 (CH), 130.0 (2xCH), 125.0 (2xCH), 117.4 (CH), 111.0 (C), 94.6 (C) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_7\text{ClIN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 383.9401, found: 383.9402.

(E)-5-iodo-3-(*p*-tolylidiazenyl)benzo[*c*]isoxazole (**2w**): Red solid (229 mg, 78%); mp 142-144 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 1644, 1403, 1068, 760; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.52$ (s, 1H), 7.96 (d, 2H, $J = 8.32$ Hz), 7.60 (dd, 1H, $J = 9.32, 1.44$ Hz), 7.41 (dd, 1H, $J = 9.32, 0.76$ Hz), 7.35 (d, 2H, $J = 8.16$ Hz), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.6$ (C), 156.9 (C), 151.8 (C), 145.0 (C), 140.2 (CH), 131.1 (CH), 130.3 (2xCH), 124.0 (2xCH), 117.3 (CH), 110.6 (C), 93.7 (C), 22.0 (CH_3) ppm; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{10}\text{IN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 363.9947, found: 363.9939.

(E)-3-((2,5-dimethylphenyl)diazenyl)-5-iodobenzo[*c*]isoxazole (**2x**): Red solid (229 mg, 78%); mp 190-192 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3409, 1640, 1403, 1219, 1068, 771; ^1H NMR (400 MHz, CDCl_3): δ = 8.49 (s, 1H), 7.66 (s, 1H), 7.61 (dd, 1H, J = 9.28, 1.4 Hz), 7.43 (d, 1H, J = 9.28 Hz), 7.29 (br s, 2H), 2.74 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 167.3 (C), 156.9 (C), 151.6 (C), 140.2 (CH), 138.4 (C), 136.7 (C), 135.0 (CH), 131.7 (CH), 131.3 (CH), 117.3 (CH), 115.2 (CH), 109.8 (C), 94.0 (C), 21.1 (CH_3), 17.7 (CH_3) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{IN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 378.0103, found: 378.0103.

(E)-3-(phenyldiazenyl)isoxazolo[3,4-*b*]pyridine (**2a'**): Red solid (184 mg, 63%); mp 120-122 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3410, 1633, 1404, 1217, 1070, 771; ^1H NMR (400 MHz, CDCl_3): δ = 8.88 (dd, 1H, J = 3.88, 1.76 Hz), 8.43 (dd, 1H, J = 8.64, 1.72 Hz), 8.08-8.04 (m, 2H), 7.62-7.55 (m, 3H), 7.23 (dd, 1H, J = 8.60, 3.90 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 168.2 (C), 166.3 (C), 158.6 (CH), 153.2 (C), 134.0 (CH), 131.7 (CH), 129.6 (2xCH), 124.0 (2xCH), 123.8 (CH), 101.9 (C) ppm; HRMS (ESI): calcd for $\text{C}_{12}\text{H}_8\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$ 225.0776, found: 225.0772.

(E)-3-((4-chlorophenyl)diazenyl)isoxazolo[3,4-*b*]pyridine (**2b'**): Red solid (182 mg, 62%); mp 179-181 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 2922, 1644, 1403, 1068, 835, 771; ^1H NMR (400 MHz, CDCl_3): δ = 8.90 (dd, 1H, J = 3.72, 1.56 Hz), 8.42 (dd, 1H, J = 8.64, 1.6 Hz), 8.02 (d, 2H, J = 8.72 Hz), 7.56 (dd, 2H, J = 8.72 Hz), 7.26-7.23 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 168.1 (C), 166.4 (C), 158.6 (CH), 151.7 (C), 140.3 (C), 131.6 (CH), 130.1 (2xCH), 125.2 (2xCH), 124.0 (CH), 102.3 (C) ppm; HRMS (ESI): calcd for $\text{C}_{12}\text{H}_7\text{ClN}_4\text{O}$ $[\text{M}+\text{H}]^+$ 259.0387, found: 259.0395.

(E)-3-((4-bromophenyl)diazenyl)isoxazolo[3,4-*b*]pyridine (**2c'**): Red solid (181 mg, 62%); mp 180-182 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3401, 1644, 1403, 1068, 838, 770; ^1H NMR (400 MHz, CDCl_3): δ = 8.89 (dd, 1H, J = 3.88, 1.72 Hz), 8.41 (dd, 1H, J = 8.64, 1.72 Hz), 7.95-7.91 (m, 2H), 7.74-7.70 (m, 2H), 7.26-7.22 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 168.1 (C), 166.4 (C), 158.7 (CH), 152.0 (C), 133.1 (2xCH), 131.6 (CH), 129.1 (C), 125.3 (2xCH), 124.0 (CH), 102.3 (C) ppm; HRMS (ESI): calcd for $\text{C}_{12}\text{H}_7\text{BrN}_4\text{O}$ $[\text{M}+\text{H}]^+$ 302.9881, found: 302.9873.

(E)-3-((2,5-dimethylphenyl)diazenyl)isoxazolo[3,4-*b*]pyridine (**2d'**): Red solid (192 mg, 65%); mp 165-167 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 1636, 1403, 1217, 1068, 840, 771, 669; ^1H NMR (400 MHz, CDCl_3): δ = 8.87 (dd, 1H, J = 3.88, 1.72 Hz), 8.34 (dd, 1H, J = 8.6, 1.72 Hz), 7.68 (s, 1H), 7.33-7.28 (m, 2H), 7.21 (dd, 1H, J = 8.6, 3.92 Hz), 2.74 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 169.1 (C), 166.3 (C), 158.4 (CH), 151.4 (C), 138.7

(C), 136.8 (C), 135.5 (CH), 131.8 (CH), 131.7 (CH), 123.7 (CH), 115.2 (CH), 100.9 (C), 21.0 (CH₃), 17.6 (CH₃) ppm; HRMS (ESI): calcd for C₁₄H₁₂N₄O [M+H]⁺ 253.1089, found: 253.1086.

(E)-3-((4-methoxyphenyl)diazanyl)isoxazolo[3,4-*b*]pyridine (**2e'**): Red solid (198 mg, 67%); mp 165-167 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 1637, 1403, 1217, 1069, 771; ¹H NMR (400 MHz, CDCl₃): δ = 8.85 (dd, 1H, *J* = 3.88, 1.72 Hz), 8.41 (dd, 1H, *J* = 8.6, 1.72 Hz), 8.05 (dt, 2H, *J* = 10.2, 3.16 Hz), 7.16 (dd, 1H, *J* = 8.64, 3.92 Hz), 7.07-7.03 (m, 2H), 3.94 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 168.7 (C), 166.3 (C), 164.8 (C), 158.4 (CH), 148.0 (C), 132.1 (CH), 126.5 (2xCH), 123.0 (CH), 115.0 (2xCH), 101.5 (C), 56.0 ppm; HRMS (ESI): calcd for C₁₃H₁₀N₄O₂ [M+H]⁺ 255.0882, found: 255.0878

(E)-3-(phenyldiazanyl)benzo[*c*]isothiazole (**3a**): Red solid (220 mg, 70%); mp 96-98 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 2923, 1639, 1385, 1219, 1154, 1068, 771; ¹H NMR (400 MHz, CDCl₃): δ = 8.28-8.26 (m, 1H), 8.02-7.99 (m, 2H), 7.78 (d, 1H, *J* = 8.96 Hz), 7.58-7.52 (m, 3H), 7.51-7.46 (m, 1H), 7.40-7.36 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 173.2 (C), 162.8 (C), 152.6 (C), 132.5 (CH), 131.6 (C), 129.6 (CH), 129.4 (2xCH), 126.7 (CH), 123.6 (2xCH), 122.8 (CH), 121.2 (CH) ppm; HRMS (ESI): calcd for C₁₃H₉N₃S [M+H]⁺ 240.0595; found: 240.0582.

(E)-6-bromo-3-(phenyldiazanyl)benzo[*c*]isothiazole (**3b**): Red solid (205 mg, 66%); mp 116-118 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 2922, 1638, 1385, 1218, 1153, 1068, 771; ¹H NMR (400 MHz, CDCl₃): δ = 8.11 (dd, 1H, *J* = 9.04, 0.36 Hz), 8.00-7.98 (m, 3H), 7.56-7.54 (m, 3H), 7.44 (dd, 1H, *J* = 9.04, 1.56 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 174.0 (C), 162.6 (C), 152.4 (C), 132.9 (CH), 130.3 (CH), 129.9 (C), 129.5 (2xCH), 124.9 (CH), 123.7 (2xCH), 121.9 (CH) ppm; HRMS (ESI): calcd for C₁₃H₈BrN₃S [M+H]⁺ 317.9701; found: 317.9687.

(E)-3-((4-chlorophenyl)diazanyl)benzo[*c*]isothiazole (**3c**): Red solid (186 mg, 60%); mp 135-138 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 2921, 1639, 1385, 1218, 1153, 1068, 772; ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (d, 1H, *J* = 8.56 Hz), 7.96-7.94 (m, 2H), 7.78 (d, 1H, *J* = 8.92 Hz), 7.52-7.48 (m, 3H), 7.42-7.37 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 172.9 (C), 162.8 (C), 150.9 (C), 138.5 (C), 131.7 (C), 129.8 (2xCH), 129.7 (CH), 127.0 (CH), 124.7 (2xCH), 122.9 (CH), 121.1 (CH) ppm; HRMS (ESI): calcd for C₁₃H₈ClN₃S [M+H]⁺ 274.0206, found: 274.0199.

(E)-6-bromo-3-((4-chlorophenyl)diazanyl)benzo[*c*]isothiazole (**3d**): Red solid (179 mg, 58%); mp 162-168 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3399, 2922, 1639, 1385, 1218, 1154, 1068, 771, 669; ¹H NMR (400 MHz, CDCl₃): δ = 8.09 (dd, 1H, *J* = 9.04, 0.48 Hz), 7.99 (d, 1H, *J* = 1.00 Hz), 7.95-7.92 (m, 2H), 7.53-7.50 (m, 2H), 7.45 (dd, 1H, *J* = 9.04,

1.56 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 173.7 (C), 162.6 (C), 150.8 (C), 139.0 (C), 130.5 (CH), 129.8 (2xCH), 129.3 (C), 127.5 (C), 125.0 (CH), 124.9 (2xCH), 121.8 (CH) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_7\text{BrClN}_3\text{S}$ $[\text{M}+\text{H}]^+$ 351.9311; found: 351.9303.

(E)-3-((3,4-dichlorophenyl)diazenyl)benzo[*c*]isothiazole (**3e**): Red solid (176 mg, 57%); mp 150-152 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3396, 3019, 2920, 1638, 1385, 1216, 1154, 1067, 771, 669; ^1H NMR (400 MHz, CDCl_3): δ = 8.25 (d, 1H, J = 8.56 Hz), 8.10 (d, 1H, J = 2.2 Hz), 7.86 (dd, 1H, J = 8.56, 2.24 Hz), 7.79 (d, 1H, J = 8.92 Hz), 7.63 (d, 1H, J = 8.56 Hz), 7.53-7.48 (m, 1H), 7.44-7.40 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 172.4 (C), 162.9 (C), 151.4 (C), 136.4 (C), 134.0 (C), 131.9 (C), 131.3 (CH), 129.8 (CH), 127.4 (CH), 124.2 (CH), 123.4 (CH), 122.9 (CH), 121.1 (CH) ppm; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_7\text{Cl}_2\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ 307.9816; found: 307.9807.

(E)-3-((2,5-dimethylphenyl)diazenyl)benzo[*c*]isothiazole (**3f**): Red solid (212 mg, 68%); mp 124-126 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3847, 3744, 3669, 3392, 2923, 1638, 1385, 1218, 1155, 1068, 772, 669; ^1H NMR (400 MHz, CDCl_3): δ = 8.30-8.27 (m, 1H), 7.76 (d, 1H, J = 8.96 Hz), 7.67 (br s, 1H), 7.49-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.24 (s, 2H), 2.67 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 174.2 (C), 162.9 (C), 150.4 (C), 137.0 (C), 136.4 (C), 133.7 (CH), 131.5 (CH), 131.1 (C), 129.5 (CH), 126.5 (CH), 122.7 (CH), 121.3 (CH), 116.2 (CH), 21.1 (CH₃), 17.2 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ 268.0908; found: 268.0902.

(E)-3-((2,5-dimethylphenyl)diazenyl)-5-iodobenzo[*c*]isothiazole (**3g**): Red solid (199 mg, 65%); mp 197-199 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3400, 3019, 2344, 1638, 1385, 1216, 1068, 769, 668; ^1H NMR (400 MHz, CDCl_3): δ = 8.75 (s, 1H), 7.70-7.68 (m, 2H), 7.51 (d, 1H, J = 9.24 Hz), 7.28 (s, 2H), 2.69 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 173.3 (C), 161.1 (C), 150.4 (C), 138.1 (CH), 137.4 (C), 136.5 (C), 134.1 (CH), 132.4 (C), 131.6 (CH), 130.4 (CH), 123.8 (CH), 116.2 (CH), 93.1 (C), 21.1 (CH₃), 17.2 (CH₃) ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{IN}_3\text{S}$ $[\text{M}+\text{H}]^+$ 393.9875; found: 393.9867.

(E)-(2-aminophenyl)(phenyldiazenyl)methanone (**4a**): Red solid (267 mg, 90%); mp 90-92 °C; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) 3372, 3018, 2925, 2856, 1617, 1389, 1216, 1072, 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.96 (dt, 2H, J = 6.5, 1.26 Hz), 7.72-7.64 (m, 3H), 7.40-7.35 (m, 2H), 7.31 (br s, 2H), 6.92 (d, 1H, J = 8.35 Hz), 6.54-6.50 (m, 1H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 182.9, 153.0 (C), 151.4 (C), 136.0 (CH), 133.3 (CH), 131.5 (CH), 129.7

(2xCH), 122.9 (2xCH), 116.9 (CH), 114.6 (CH), 109.1 (C) ppm; HRMS (ESI): calcd for C₁₃H₁₁N₃O [M+H]⁺ 226.0980, found: 226.0972

(E)-(2-(methylamino)phenyl)(phenyldiazenyl)methanone (**5a**): Red solid (266 mg, 90%); mp 85-87 °C; FT-IR (KBr, ν_{max}/cm⁻¹) 3407, 2938, 2088, 1723, 1638, 1593, 1404, 1385, 1238, 1217, 1149, 1069, 917, 668, 599; ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (br s, 1H), 8.01-7.98 (m, 2H), 7.79 (dd, 1H, *J* = 8.12, 1.56 Hz), 7.60-7.53 (m, 3H), 7.48-7.44 (m, 1H), 6.77 (d, 1H, *J* = 8.56 Hz), 6.60-6.56 (m, 1H), 3.01 (d, 3H, *J* = 5.08 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 183.0, 153.6 (C), 152.3 (C), 136.7 (CH), 133.2 (CH), 133.1 (CH), 129.4 (3xCH), 123.7 (CH), 114.3 (CH), 111.5 (C), 111.3 (CH), 29.6 (CH₃) ppm; HRMS (ESI): calcd for C₁₄H₁₃N₃O [M+H]⁺ 240.1137, found: 240.1133.

ASSOCIATED CONTENT

Supporting Information

¹H and ¹³C spectra of all compounds and X-ray crystallographic data for compound **2c**. This material is available free of charge via the internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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