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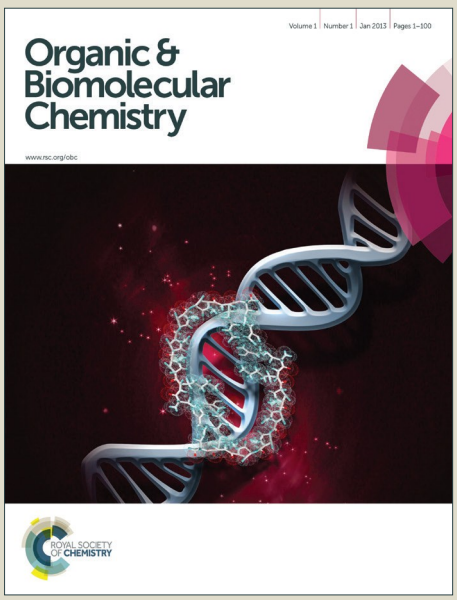

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ARTICLE

Efficient, Versatile and Practical Palladium-Catalyzed Highly Regioselective *ortho*-Halogenation of Azoxybenzenes

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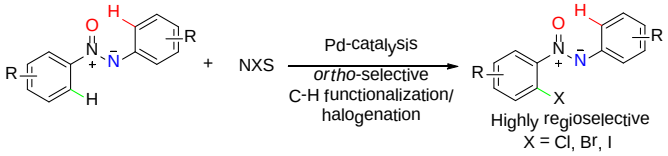
A highly efficient and practical strategy of regio-selective *ortho*-halogenation (I, Br, Cl) of azoxybenzenes with NXS in the presence of palladium catalysts has been developed in good to excellent yields. The reaction proceeded smoothly and could tolerate a variety of functional groups. Moreover, this chemistry is available to the substrate in at least gram scale.

Introduction

Over the past decade, aryl halides are extremely valuable starting materials for constructing complex skeletons in synthetic elaboration due to their role as precursors for synthesis of organometallic reagents,[1] nucleophilic aromatic substitution[2] as well as transition-metal catalyzed cross-coupling reactions.[3] Generally, the most common methods for synthesis of halogenated arenes involved electrophilic aromatic substitution[4] and *ortho*-lithiation followed by a halogen quench[5], which both showed many limitations and suffered from several notable disadvantages.[6,7b] With regard to the development of selectively halogenation reactions, the emergence of direct C-H functionalization/halogenation provides an atom-economic strategy[8,9], which dramatically produced halogenated aromatic products with highly selectivity that would not ordinarily be obtained under traditional conditions. Since the pioneering work of Sanford,[7] Shi[10] and Yu,[11] many groups of Bedford[12] and Xu[13] illustrated the major importance of these *ortho*-selective transformations with the assistance of diverse directing groups. However, although significant progress in C-H bond functionalization/halogenation has been achieved, application of this strategy to create carbon-halogen bonds for more diverse structures is still surprisingly underdeveloped.



Scheme 1 Pd-catalyzed *ortho*-halogenation of azoxybenzenes with NXS.

Owing to their unique structure and liquid crystalline properties[14], azoxy compounds are able to serve as polymer inhibitors, stabilizers, dyes and key materials in electronic devices[15]. Furthermore, it is well known that regioselective control of C-H bond activation of azoxy compounds is an extreme challenge, due to its two different coordinating sites provided by directing groups[16] (N or O). In spite of numerous methods for the synthesis of azoxy compounds being developed[9l,17], exploration in the sterically hindered *ortho*-functionalization of azoxybenzenes is very limited[18]. Recently, Wang[18a] and we[18c,18d] reported *ortho*-acylation of azoxybenzenes respectively, and subsequently a method of alkenylation of azoxy compounds was established[18b]. As far as we know, there is no report on the *ortho*-halogenation of azoxybenzenes, which represent profoundly more desirable target as a synthetically highly important yet unmet goal. Encouraged by our previous research[19] and as part of our ongoing interest in C-H activation, herein we describe a novel and efficient approach to synthesis of a variety of azoxy halides by Pd-catalyzed *ortho*-C-H bond halogenation employing commercially available electrophilic halogenating reagents—particularly N-bromo-, N-chloro-, and N-iodosuccinimide.

Results and discussion

Our initial investigation was carried out by examining azoxybenzene (**1a**, 1.0 equiv.) and NBS (1.1 equiv.) in the presence of 10 mol% $Pd(OAc)_2$ in AcOH at 100 °C for 12 h (Table 1, entry 1). To our delight, the *ortho*-bromo- product was isolated in 87% yield, and further screening of solvents showed no promotion in this reaction (Table 1, entry 2-5). Inspired by the previous discovery of large beneficial effect of Brønsted acids in promoting the electrophilicity of the palladium (II) catalyst[20] and rendering NBS a more effective source of Br^{+}[21], we attempted to improve the desired product yield. Much to our surprise, this reaction was dramatically affected by the addition of Brønsted acids, and the corresponding yield was

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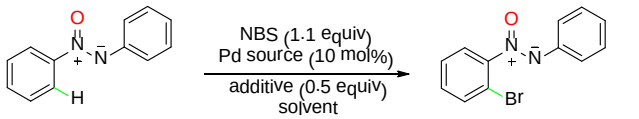
†Electronic Supplementary Information (ESI) available: Details experimental procedures, complete characterization data, copies of NMR spectra for all crucial compounds. CCDC 1054759. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Table 1. Optimization of the reaction condition[a,b]



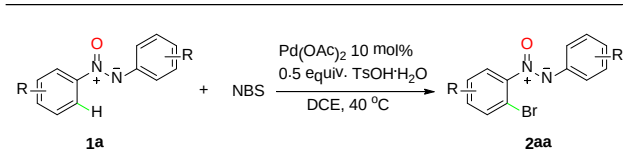
1a 2aa

Entry	Catalyst	Additive	Solvent	Yield [%][b]
1	$Pd(OAc)_2$		AcOH	87%
2	$Pd(OAc)_2$		DCE	18%
3	$Pd(OAc)_2$		DME	n.r.
4	$Pd(OAc)_2$		Toluene	trace
5	$Pd(OAc)_2$		MeCN	55%
6	$Pd(OAc)_2$	AcOH	MeCN	56%
7	$Pd(OAc)_2$	$TsOH·H_2O$	MeCN	58%
8	$Pd(OAc)_2$	AcOH	DCE	30%
9	$Pd(OAc)_2$	$TsOH·H_2O$	DCE	85%
10	$Pd(OAc)_2$	TFA	DCE	69%
11	$Pd(OAc)_2$	$TsOH·H_2O$	DCE	88%[c]
12	$Pd(OAc)_2$	$TsOH·H_2O$	DCE	92%[d]
13	$Pd(OAc)_2$	$TsOH·H_2O$	DCE	97%[e]
14	$Pd(OAc)_2$	$TsOH·H_2O$	DCE	80%[f]
15	$PdCl_2$	$TsOH·H_2O$	DCE	60%
16	$Pd(TFA)_2$	$TsOH·H_2O$	DCE	62%
17	$Pd(PPh_3)_4$	$TsOH·H_2O$	DCE	57%

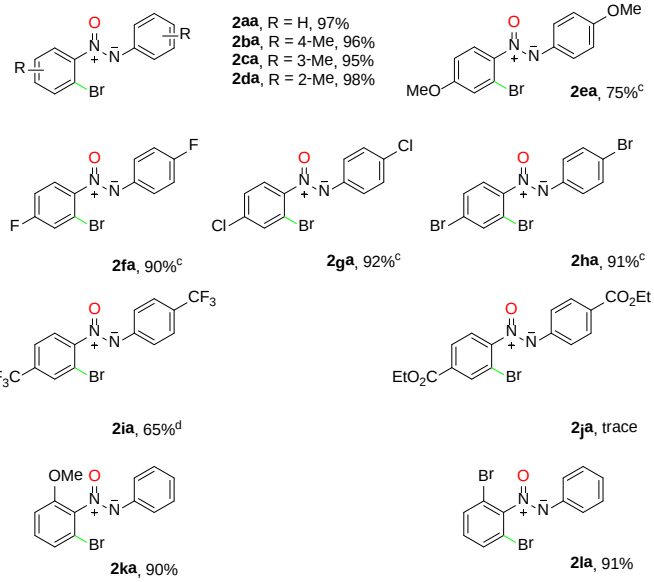
[a] All the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.22 mmol of NBS and 0.1 mmol of acid (if any) in 1.0 mL of solvents at 100 °C under air condition. [b] Isolated yields. [c]At 80 °C. [d]At 60 °C. [e]At 40 °C. [f]At room temperature.

increased to 85% in DCE with *p*-toluenesulfonic acid (PTSA) as an additive contrast to 18% without the acid (Table 1, entry 9). Other

Table 2. Scope of the *ortho*-bromination of azoxybenzene with NBS[a,b]



1a 2aa

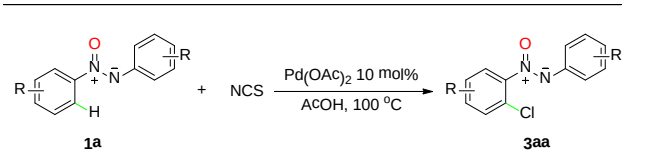


[a] All the reactions were carried out in the presence of 0.2 mmol of **1**, 0.22 mmol of NBS and 0.1 mmol of $TsOH·H_2O$ in 1.0 mL DCE at 40 °C under air condition. [b] Isolated yields. [c] At 80 °C. [d] At 100 °C.

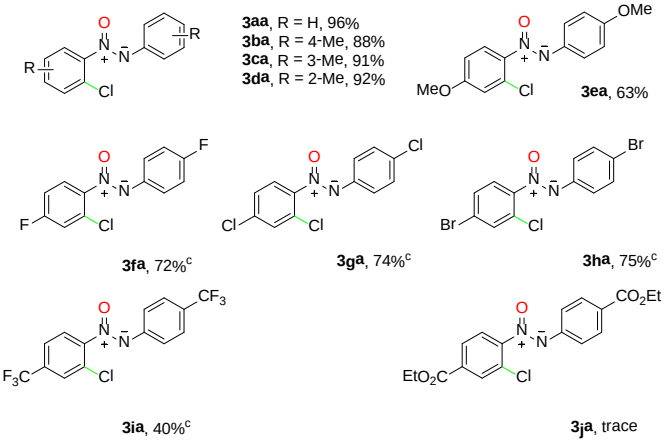
Brønsted acids, including acetic acid and trifluoroacetic acid, also proved to be effective. It was found that the reaction temperature was very crucial to this transformation, and the best result was observed in 97% at 40 °C (Table 1, entry 13), while increasing or lowering the reaction temperature suppressed the efficiency. Subsequently, different Pd catalysts were also investigated, only $Pd(OAc)_2$ facilitated this procedure in any appreciable conversion. Finally, the optimized reaction conditions for the *ortho*-C-H halogenation of azoxy compound were determined to be NBS (1.1 equiv.) with 10 mol% $Pd(OAc)_2$ as the catalyst, 0.5 equiv of PTSA as additive, and DCE as solvent, at 40 °C under air for 12 h.

With a reliable protocol in hand, the scope of the *ortho*-bromination of azoxy compounds was investigated. The results, summarized in Table 2, revealed that the reaction had good compatibility with several functional groups, and good to excellent yields were obtained for most case. For example, nearly quantitative yields were obtained when methyl groups substituted on the substrates, and an interesting regioselectivity could be found in that when a *meta*-substituent existed at aromatic ring due to the steric hindrance (Table 2, **2ba**-**2da**). It is noteworthy that the reaction can tolerate various halogen groups such as fluoro, chloro and bromo, which afford the desired products in good yields under a slight higher temperature and could be used for further transformations into other important skeletons (Table 2, **2fa**-**2ha**). However, in the presence of methoxyl, a strongly electron-donating group, the corresponding product was obtained in a slight lower efficiency along with unidentified by-products (Table 2, **2ea**). Moreover, when trifluoromethyl-substituted azoxy compound was exposed under the reaction condition, the desired bromination product was observed in moderate yield even in high temperature (Table 2, **2ia**). Much to our pleasure, this transformation can also be successfully extended to unsymmetrical azoxybenzene with

Table 3. Scope of the *ortho*-chlorination of azoxybenzene with NCS[a,b]



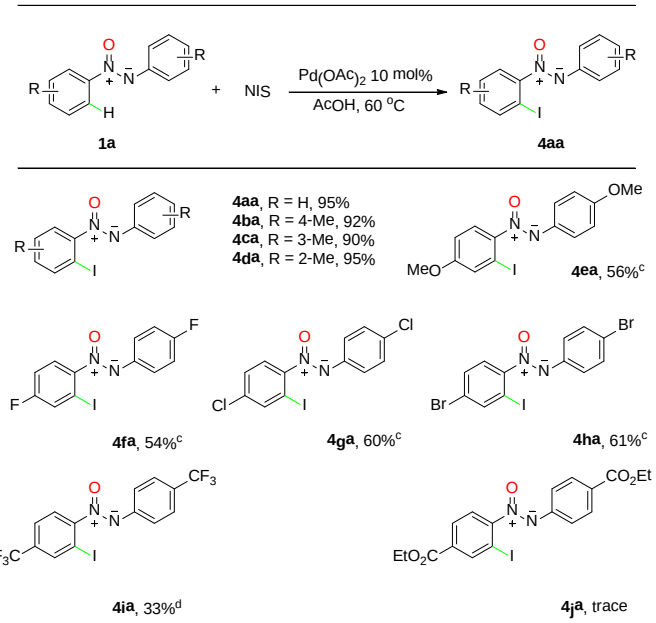
1a 3aa



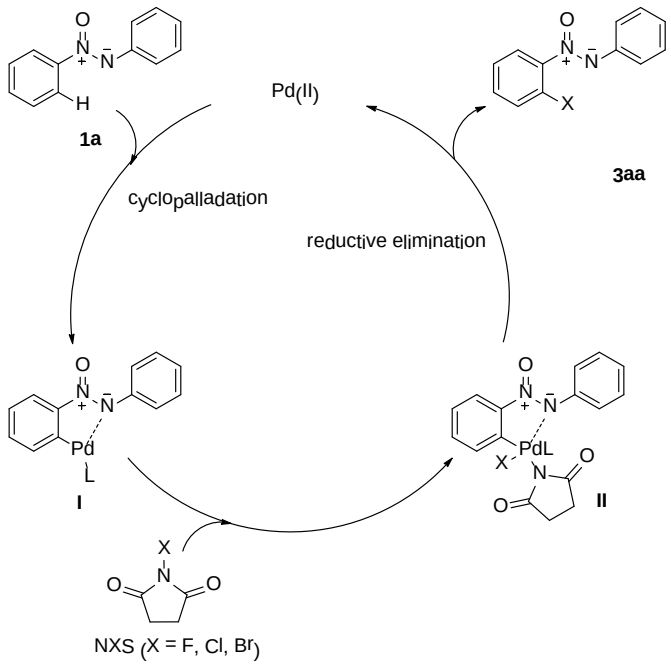
[a] All the reactions were carried out in the presence of 0.2 mmol of **1** and 0.22 mmol of NCS in 1.0 mL AcOH at 100 °C under air condition. [b] Isolated yields. [c] At 120 °C.

excellent yields (Table 2, **2ka**-**2la**), and the desired regioselective products were determined by N-atom assisted in azoxy group (vide

Table 4. Scope of the *ortho*-iodination of azoxybenzene with NIS[a,b]



[a] All the reactions were carried out in the presence of 0.2 mmol of **1** and 0.22 mmol of NIS in 1.0 mL AcOH at 60 °C under air condition. [b] Isolated yields. [c] At 80 °C. [d] At 120 °C.



Scheme 2 Proposed reaction mechanism.

infra).

To additionally establish the power of this strategy, we next examined the chlorination and iodination of azoxy compounds under the same reaction conditions. Although moderate yields were found with simple replacement of NBS by NCS or NIS under otherwise identical conditions,[22] we were pleased to observe that a subtle change of the solvents exerts significant effect on the corresponding *ortho*-chlorination and iodination reactions. Much to our pleasure, azoxybenzene was found to generate the *ortho*-chlorinated and *ortho*-iodinated products in 96% and 95% yields in AcOH, respectively (see Supporting Information (**SI**) for more details). More importantly, for the most of the substrates we employed, moderate to good yields were observed in this reaction and good tolerances to the chemically active functional groups were also revealed (Table 3 and Table 4). Interestingly, high selectivity was found in chlorination and iodination reactions when *meta*-substituted azoxybenzene was involved, which lead to form the single regioselective products in excellent yields. It is important to note that this chemistry was successfully extend to the polyhalogenated aromatic azoxy compounds in spite of relative low efficiency, which was hard to prepare by traditional methods.

A distinctive feature of transition-metal catalyzed C-H functionalization is their limited reacting scale, which is a key restraining factor in the use of many strategies in organic synthesis. For this purpose, the reaction on gram scale was exposed under the established conditions. We are delight to observe that 2.48 g (yield 90 %) of 2-bromo-azoxybenzene, 1.97 g (yield 85 %) of 2-chloro-azoxybenzene and 2.66 g (yield 82 %) of 2-iodo-azoxybenzene were obtained with 10 mmol (1.98 g) of azoxybenzene as the reactant and 5% $Pd(OAc)_2$ as the catalyst, which demonstrates the possibility to use this transformation in general organic synthesis.

Based on our experimental results and previous literature[7,9f], a possible mechanism was proposed to account for this *ortho*-halogenation of azoxy compounds, which was depicted in Scheme 2. Initially, a five-membered palladacycle intermediate **I** was generated with the assistance of N atom by chelation-directed C-H activation, which is generally considered to be a better coordinating atom than O. Oxidative addition of NXS to palladacycle leads to the formation of Pd(IV) complex **II**[7,23], followed by reductive elimination to afford *ortho*-halogenated azoxy compounds and regenerate active Pd(II) to continue the catalytic cycle.

Conclusions

In summary, we have developed an efficient, versatile and practical catalytic system for the synthesis of *ortho*-halogenation of azoxybenzenes via a regio-selective directing-group-assisted strategy. The potential for gram scale functionalization has been demonstrated and different NXS can be employed as effective halogenating reagents in this transformation. Further investigation on the application of this chemistry and other functionalization of azoxy compounds are ongoing in our laboratory.

Experimental

General experimental information

All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DMF, 1, 2-dichloroethane, DMSO, 1, 4- dioxane and CH_3CN were distilled from appropriate drying agents prior to use. All chemicals were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh)

was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker INOVA-400. NMR Spectrums were recorded on a 400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. Azoxybenzenes were prepared from arylamines, according to the literature[1].

General Catalytic Procedure for *Ortho*-Bromination of Azoxybenzenes with NBS.

A mixture of azoxybenzene (39.6 mg, 0.2 mmol, 1.0 equiv), $TsOH\cdot H_2O$ (19.0 mg, 0.1 mmol, 0.5 equiv), NBS (39.2 mg, 0.22 mmol, 1.1 equiv) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %) in DCE (1 mL) was stirred under air at 40 ^{o}C for 12 h followed by cooling. The volatiles removed under reduced pressure. The contents were subjected to flash chromatography to give the corresponding product (97%) as a pale yellow oil. The purified material was dried under an oil-pump vacuum.

2-(2-bromophenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (2aa). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 12.0 Hz, 2 H), 7.71-7.63 (m, 2 H), 7.52-7.42 (m, 4 H), 7.34 (t, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.33, 143.66, 134.03, 130.86, 130.26, 128.77, 128.22, 125.40, 124.81, 115.11. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_9BrN_2ONa^+$: 298.9796, Found $[M+Na]^+$: 298.9744.

2-(2-bromo-4-methylphenyl)-2-oxo-1-(p-tolyl)hydrazin-2-ium-1-ide (2ba). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 8.0 Hz ,2 H), 7.55-7.43 (m, 2 H), 7.29 (d, *J* = 4 Hz ,2 H), 7.22 (d, *J* = 8.0 Hz ,1 H), 2.41 (d, *J* = 8.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.10, 141.52, 141.45, 140.86, 134.21, 129.32, 128.73, 125.52, 124.55, 114.75, 21.61, 20.93. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{13}BrN_2ONa^+$: 327.0103, Found $[M+Na]^+$: 326.9997.

2-(2-bromo-5-methylphenyl)-2-oxo-1-(m-tolyl)hydrazin-2-ium-1-ide (2ca). Deep red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.0 Hz,2 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.40-7.36 (m, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.15-7.13 (m, 1 H), 2.42 (s, 3 H) , 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.11, 143.71, 138.79, 138.57, 133.61, 131.62, 130.98, 128.55, 125.80, 125.29, 122.43, 111.57, 21.43, 20.79. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{14}BrN_2O^+$: 305.0290, Found $[M+H]^+$: 305.0208.

2-(2-bromo-6-methylphenyl)-2-oxo-1-(o-tolyl)hydrazin-2-ium-1-ide (2da). Deep yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18-8.15 (m, 1 H), 7.53 (d, *J* = 4.0 Hz, 1 H), 7.34-7.19 (m, 5 H), 2.44 (s, 3 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.80, 141.96, 134.90, 132.67, 130.96, 130.87, 130.15, 129.95, 129.12, 125.90, 121.60, 115.26, 18.48, 17.19. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{13}BrN_2ONa^+$: 327.0103, Found $[M+Na]^+$: 327.0035.

2-(2-bromo-4-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxohydrazin-2-ium-1-ide (2ea). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 12.0 Hz, 1 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.98 (d, *J* = 12.0 Hz, 2 H), 6.94-6.92 (m, 1 H), 3.88 (s, 3 H), 3.85 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.71, 160.30, 142.97, 137.76, 127.82, 125.91, 118.67, 115.97, 113.70, 113.65, 55.92, 55.51.HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{13}BrN_2O_3Na^+$: 359.0002, Found $[M+Na]^+$: 358.9878.

2-(2-bromo-4-fluorophenyl)-1-(4-fluorophenyl)-2-oxohydrazin-2-ium-1-ide (2fa). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 2 H), 7.68 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H), 7.45 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.92 (d, *J* = 252.0 Hz), 162.16 (d, *J* = 253.0 Hz), 145.82, 140.10(d, *J* = 3.0 Hz), 128.01(d, *J* = 10.0 Hz), 126.36(d, *J* = 9.0 Hz), 121.25(d, *J* = 26.0 Hz), 116.23 (d, *J* = 10.0 Hz), 115.76 (d, *J* = 23.0 Hz), 115.37 (d, *J* = 23.0 Hz). HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7BrF_2N_2ONa^+$: 334.9602, Found $[M+Na]^+$: 334.9737.

2-(2-bromo-4-chlorophenyl)-1-(4-chlorophenyl)-2-oxohydrazin-2-ium-1-ide (2ga). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, *J* = 8.0 Hz, 2 H), 7.72 (s, 1 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.47-7.42 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.68, 141.96, 136.40, 135.90, 133.73, 129.02, 128.42, 126.94, 125.79, 115.97. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7BrCl_2N_2ONa^+$: 366.9017, Found $[M+Na]^+$: 366.9335.

1-(4-bromophenyl)-2-(2,4-dibromophenyl)-2-oxohydrazin-2-ium-1-ide (2ha). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.0 Hz, 2 H), 7.88 (d, *J* = 4.0 Hz, 1 H), 7.63-7.58 (m, 3 H), 7.54 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.09, 142.28, 136.46, 132.02, 131.37, 127.07, 125.98, 124.29, 124.25, 116.13. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7Br_3N_2ONa^+$: 454.8001, Found $[M+Na]^+$: 454.7833.

2-(2-bromo-4-(trifluoromethyl)phenyl)-2-oxo-1-(4-(trifluoromethyl)phenyl)hydrazin-2-ium-1-ide (2ia). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 12.0 Hz, 2 H), 8.01 (s, 1 H), 7.79-7.74 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.06, 145.59, 133.23 (q, $J_{C\text{-}F}$ = 33.0 Hz), 131.62 (q, $J_{C\text{-}F}$ = 33.0 Hz), 131.49 (d, $J_{C\text{-}F}$ = 4.0 Hz), 126.00 (q, $J_{C\text{-}F}$ = 3.0 Hz), 125.57, 125.40, 122.96 (q, $J_{C\text{-}F}$ = 118.0 Hz), 122.95 (q, $J_{C\text{-}F}$ = 118.0 Hz), 115.86. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_7BrF_6N_2ONa^+$: 434.9538, Found $[M+Na]^+$: 434.9381.

2-(2-bromo-6-methoxyphenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (2ka). Pale yellow oil.^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 2 H), 7.51-7.42 (m, 3 H), 7.26-2.25 (m, 2 H), 7.00 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.88, 143.73, 130.59, 130.14, 128.70, 125.48, 125.38, 124.63, 116.46, 111.49, 56.52. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{13}H_{11}BrN_2O_2Na^+$: 328.9902, Found $[M+Na]^+$:328.9902.

2-(2,6-dibromophenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (2la). White solid. ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.54-7.46 (m, 3 H), 7.20 (t, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ :143.40, 132.59, 130.92, 130.57, 128.84, 125.42, 116.65. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_8Br_2N_2ONa^+$: 376.8901, Found $[M+Na]^+$: 376.8903.

General Catalytic Procedure for *Ortho*-Chlorination/Iodination of Azoxybenzenes with NCS/NIS.

A mixture of azoxybenzene (39.6 mg, 0.2 mmol, 1.0 equiv), NCS/NIS (0.22 mmol, 1.1 equiv) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %) in AcOH (1 mL) was stirred under air at 60 ^{o}C or 100 ^{o}C for 12 h as specified in Table 2 and Table 3 followed

by cooling. The volatiles removed under reduced pressure. The contents were subjected to flash chromatography to give the corresponding products (96% and 95%) as pale yellow oil. The purified materials were dried under an oil-pump vacuum.

2-(2-chlorophenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (3aa). Deep red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 2 H), 7.68-7.65 (m, 1 H), 7.53-7.47 (m, 3 H), 7.43-7.38 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.68, 143.70, 130.89, 130.67, 130.22, 128.74, 127.50, 126.74, 125.38, 124.79. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{12}H_9ClN_2ONa^+$: 255.0301, Found [M+Na]$^+$: 255.0212.

2-(2-chloro-4-methylphenyl)-2-oxo-1-(p-tolyl)hydrazin-2-ium-1-ide (3ba). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.32-7.25 (m, 3 H), 7. 17 (d, *J* = 8.0 Hz, 1 H), 2.41 (d, *J* = 4.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.54, 141.66, 141.31, 140.79, 131.15, 129.31, 128.04, 126.40, 125.53, 124.63, 21.57, 21.00. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}ClN_2ONa^+$: 283. 0614, Found [M+Na]$^+$: 283.0519.

2-(2-chloro-5-methylphenyl)-2-oxo-1-(m-tolyl)hydrazin-2-ium-1-ide (3ca). Deep red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 4.0 Hz, 1 H), 7.40-7.37 (m, 2 H),7.26-7.21 (m, 2 H), 2.43 (s, 3 H), 2.40 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.34, 143.65, 138.59, 138.07, 131.41, 131.05, 130.51, 128.56, 125.83, 125.15, 123.47, 122.46, 21.45, 20.78. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}ClN_2ONa^+$: 283.0614, Found [M+Na]$^+$: 283.0512.

2-(2-chloro-6-methylphenyl)-2-oxo-1-(o-tolyl)hydrazin-2-ium-1-ide (3da). Deep red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.10 (d, *J* = 8.0 Hz, 1 H), 7.36-7.27 (m, 5 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 2.43 (s, 3 H), 2.40 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.27, 142.10, 134.69, 132.64, 130.86, 129.63, 129.46, 129.03, 127.83, 126.67, 125.94, 121.58, 18.40, 16.96. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}ClN_2ONa^+$: 283.0614, Found [M+Na]$^+$: 283.0611.

2-(2-chloro-4-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxohydrazin-2-ium-1-ide (3ea). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1 H), 8.27 (s, 1 H), 7.64 (d, *J* = 12.0 Hz, 1 H), 7.00 (d, *J* = 4.0 Hz, 1 H), 6.99 (d, *J* = 0.0 Hz, 1 H), 6.97 (t, *J* = 4.0 Hz, 1 H), 6.89 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H), 3.88 (s, 3 H), 3.85 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.70, 160.38, 141.31, 137.81, 127.83, 126.00, 115.63, 113.69, 113.04, 55.90, 55.50. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}ClN_2O_3Na^+$: 315.0512, Found [M+Na]$^+$: 315.0404.

2-(2-chloro-4-fluorophenyl)-1-(4-fluorophenyl)-2-oxohydrazin-2-ium-1-ide (3fa). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27-8.24 (m, 2 H), 7.72-7.69 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H), 7.29-7.26 (m, 1 H), 7.20-7.15 (m, 2 H), 7.15-7.10 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.90 (d, *J* = 252.0Hz), 162.20 (d, *J* = 253.0 Hz), 144.14, 140.10 (d, *J* = 3.0 Hz), 128.40 (d, *J* = 11.0 Hz), 128.03 (d, *J* = 8.0 Hz), 126.44 (d, *J* = 10.0 Hz), 118.26 (d, *J* = 25.0 Hz), 115.75 (d, *J* = 22.0 Hz), 114.80 (d, J = 22.0Hz). HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{12}H_7ClF_2N_2ONa^+$: 291.0113, Found [M+Na]$^+$: 291.0110.

1-(4-chlorophenyl)-2-(2,4-dichlorophenyl)-2-oxohydrazin-2-ium-1-ide (3ga). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, *J* = 12.0 Hz, 2 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 4.0 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.40 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.00, 141.97, 136.36, 135.91, 130.80, 129.01, 127.92, 127.82, 126.96, 125.86. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{12}H_7Cl_3N_2ONa^+$: 322.9522, Found [M+Na]$^+$: 322.9409.

2-(4-bromo-2-chlorophenyl)-1-(4-bromophenyl)-2-oxohydrazin-2-ium-1-ide (3ha). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (s, 1 H), 8.05 (s, 1H), 7.71 (s, 1 H), 7.63-7.62 (m, 1 H), 7.61-7.59 (m, 1 H), 7.57-7.55 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: ^{13}C NMR (101 MHz, CDCl3) δ: 146.46, 142.33, 133.61, 132.02, 130.76, 127.99, 127.10, 126.03, 124.30, 124.14. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{12}H_7Br_2N_2ONa^+$: 410.8511, Found [M+Na]$^+$: 410.8362.

2-(2-chloro-4-(trifluoromethyl)phenyl)-2-oxo-1-(4-(trifluoromethyl)phenyl)hydrazin-2-ium-1-ide (3ia). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.72 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.38, 145.61, 133.24 (q, $J_{C\text{-}F}$ = 33.0 Hz), 131.67 (q, $J_{C\text{-}F}$ = 33.0 Hz), 128.47 (q, $J_{C\text{-}F}$ = 4.0 Hz), 127.87, 126.02 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.61, 125.53, 124.84 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.02 (q, $J_{C\text{-}F}$ = 105.0 Hz), 123.01 (q, $J_{C\text{-}F}$ = 106.0 Hz). HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_7ClF_6N_2ONa^+$: 391.0049, Found [M+Na]$^+$: 390.9896.

2-(2-iodophenyl)-2-oxo-1-phenylhydrazin-2-ium-1-ide (4aa). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (t, *J* = 8.0 Hz, 2 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.65-7.63 (m, 1 H), 7.53-7.42 (m, *J* = 8.0 Hz, 4 H), 7.21-7.17 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.60, 143.58, 140.42, 130.99, 130.26, 129.07, 128.77, 125.39, 124.32, 87.97. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{12}H_9IN_2ONa^+$: 346.9657, Found [M+Na]$^+$: 346.9650.

2-(2-iodo-4-methylphenyl)-2-oxo-1-(p-tolyl)hydrazin-2-ium-1-ide (4ba). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.0 Hz, 2 H), 7.77 (s, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 4.0 Hz, 1 H), 2.43 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.44, 141.45, 140.79, 140.64, 140.09, 129.56, 129.30, 125.50, 124.02, 87.84, 21.60, 20.67. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}IN_2ONa^+$: 374.9970, Found [M+Na]$^+$: 374.9964.

2-(2-iodo-5-methylphenyl)-2-oxo-1-(m-tolyl)hydrazin-2-ium-1-ide (4ca). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 4.0 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 0.0 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.25 (d, *J* = 4.0 Hz, 1 H), 7.00-6.98 (m, 1H), 2.43 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.47, 143.58, 139.97, 139.71, 138.55, 131.91, 130.99, 128.53, 125.77, 124.93, 122.43, 83.74, 21.46, 20.82. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}IN_2ONa^+$: 374.9970, Found [M+Na]$^+$: 374.9963.

2-(2-iodo-6-methylphenyl)-2-oxo-1-(o-tolyl)hydrazin-2-ium-1-ide (4da). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.31-7.23 (m, 4 H), 7.06-7.01 (m, 1 H), 2.43 (d, *J* = 4.0 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl3) δ : 152.23, 141.82, 137.32, 135.18, 132.02, 131.05, 130.84, 130.20, 129.20, 125.81, 121.67, 88.49, 18.60, 17.54. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{13}IN_2ONa^+$: 374.9970,Found [M+Na]$^+$: 374.9963.

2-(2-iodo-4-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxohydrazin-2-ium-1-ide (4ea). Pale yellow oil. ^{1}H NMR (400

MHz, $CDCl_3$) δ: 8.30 (t, *J* = 4.0 Hz, 1 H), 8.27 (t, *J* = 4.0 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.01-6.99 (m, 1 H), 6.98-6.94 (m, 2 H), 3.86 (s, 3 H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.67, 160.07, 146.25, 137.67, 127.78, 125.27, 125.09, 114.35, 113.69, 88.60, 55.86, 55.49. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{13}IN_2O_3Na^+$: 406.9869, Found $[M+Na]^+$: 406.9860.

2-(4-fluoro-2-iodophenyl)-1-(4-fluorophenyl)-2-oxohydrazin-2-ium-1-ide (4fa). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27-8.23 (m, 2 H), 7.68-7.63 (m, 2 H), 7.22-7.16 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.82 (d, *J* = 252.0Hz), 161.79 (d, *J* = 257.0 Hz), 149.00, 139.96 (d, *J* = 3.0 Hz), 127.95 (d, *J* = 8.0 Hz), 127.32 (d, *J* = 25.0 Hz), 125.68 (d, *J* = 10.0 Hz), 116.04 (d, *J* = 23.0 Hz), 115.72 (d, *J* = 23.0 Hz), 88.35 (d, J = 9.0Hz). HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7F_2IN_2ONa^+$: 382.9464, Found $[M+Na]^+$: 382.9326.

2-(4-chloro-2-iodophenyl)-1-(4-chlorophenyl)-2-oxohydrazin-2-ium-1-ide (4ga). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 2 H), 7.96 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.01, 141.94, 139.93, 136.33, 135.89, 129.19, 129.03, 126.94, 125.19, 88.46. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7Cl_2IN_2ONa^+$: 414.8878, Found $[M+Na]^+$: 414.8710.

2-(4-bromo-2-iodophenyl)-1-(4-bromophenyl)-2-oxohydrazin-2-ium-1-ide (4ha). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 1 H), 8.06 (d, *J* = 8.0 Hz, 2 H), 7.63-7.60 (m, 3 H), 7.52 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.40, 142.56, 142.24, 132.14, 132.02, 127.07, 125.43, 124.38, 124.27, 88.87. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{12}H_7Br_2IN_2ONa^+$: 502.7867, Found $[M+Na]^+$: 502.7859.

2-(2-iodo-4-(trifluoromethyl)phenyl)-2-oxo-1-(4-(trifluoromethyl)phenyl)hydrazin-2-ium-1-ide (4ia). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.0 Hz, 3 H), 7.80-7.75 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.44, 145.55, 137.78 (d, J_{C-F} = 4.0 Hz), 133.12 (q, J_{C-F} = 34.0 Hz), 131.62 (q, J_{C-F} = 32.0 Hz), 126.42 (q, J_{C-F} = 3.0 Hz), 126.03 (q, J_{C-F} = 4.0 Hz), 125.58, 124.72, 122.84 (q, J_{C-F} = 140.0 Hz), 122.83 (q, J_{C-F} = 142.0 Hz), 88.20. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_7F_6IN_2ONa^+$: 482.9405, Found $[M+Na]^+$: 482.9388.

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