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Cp*Rh(III) Catalyzed *Ortho*-Halogenation of *N*-Nitrosoanilines by Solvent-Controlled Regioselective C-H Functionalization

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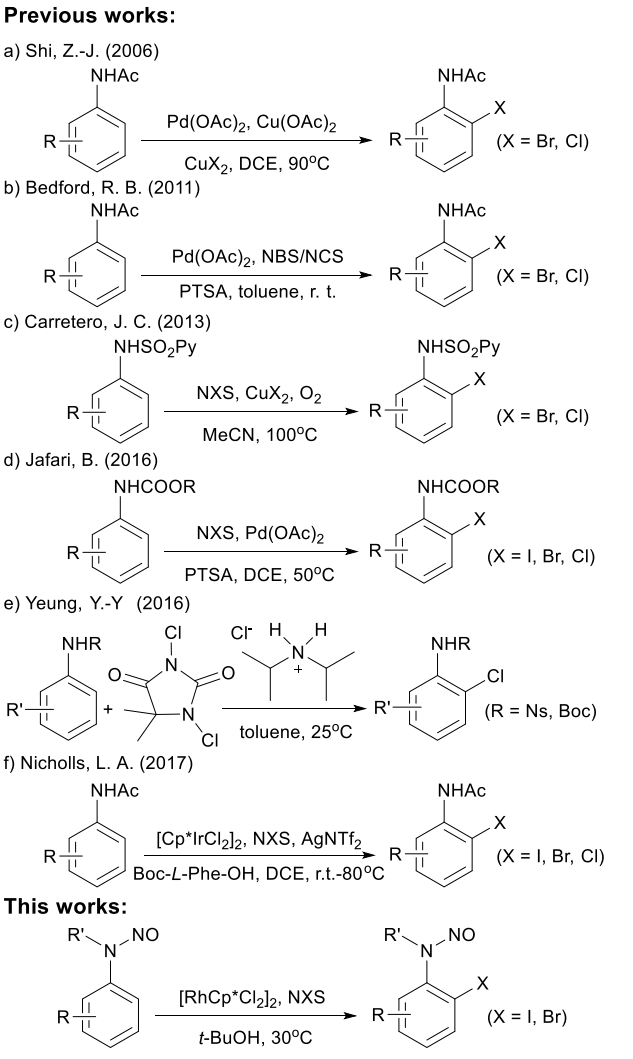
We present a novel, efficient, and regioselective method for the rhodium-catalyzed direct C-H ortho-halogenation of anilines that involves a removable N-nitroso directing group. This method featured mild reaction conditions, wide substrate scope, good functional group tolerance and satisfactory yields. To maintain the high ortho-regioselectivity and conversion, increasing the steric hindrance of the solvent was critical. Preliminary mechanistic studies suggest that C-H activation may be involved in the rate-determining step.

Introduction

In the last decade, substantial progress has been made in the field of transition-metal-catalyzed C-H bond functionalization,[1] which has provided a general and efficient method for regioselective C-X bond formation reactions.[2] Despite these significant advances, the *ortho*-halogenation of electron-rich anilines remains a significant challenge due to poor *ortho*/*para* selectivity, and in most cases only para-halogenated or over-halogenated aniline could be obtained.[3-8] Among the various strategies employed to address these challenges, the use of protecting groups on the amine functional group has proven to be the most successful approach. In 2006, Shi reported the first Palladium-catalyzed *ortho*-halogenation of aniline by use of an acetyl protected amine as a directing group (Scheme 1a).[9] Since then, only very limited types of protecting groups, such as sulfonyl and carbamate, have been used similarly in the *ortho* C-H halogenation of aniline (Scheme 1b-f).[10-14] Other than this advancement in aniline halogenation methods, these reactions still required high reaction temperatures, the directing groups were not easily removable or the substrate scope was limited to para or meta substituted aniline.

The use of a nitroso function as a directing group was first reported by Zhu et al., where they demonstrated successful functionalization of the *ortho* C-H bond by olefination, acylation, cyanation, acyloxylation, alkoxylation and alkynylation.[15] These previous works demonstrated that a nitroso directing group could act as a suitable directing group since it possesses various coordination modes to transition metal centers and is removable. Illuminated by these findings, we envisioned that the *N*-nitroso group could also be employed as a suitable



Scheme 1 *Ortho* C-H Activation/Halogenation of Aniline

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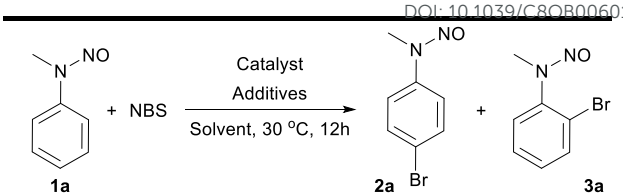
directing group for the C(sp^2)-H halogenation of anilines.[16] In this study, we report a Rh(III)-catalyzed *ortho*-halogenation of anilines by using *N*-nitroso function as the directing group. This reaction exhibits advantages such as high efficiency, broad substrate scope and mild operation conditions, thus providing a complementary protocol for the synthesis of *ortho*-halogenated anilines. To our knowledge, this is the first report of the application of an *N*-nitroso group as a directing group in a regioselective C-H halogenation reaction.

Results and discussion

During initial experiments and following previous work by Glorius et al.[4a], *N*-nitrosoanilines (**1a**) were reacted with inexpensive, commercially available *N*-bromosuccinimide (NBS) as the electrophilic halogen source in the presence of $[Cp^*RhCl_2]_2$, and $AgSbF_6$, with PivOH as the additive and 1,2-dichloroethane as the solvent. However, no desired product was observed, and only the *para*-brominated product (**2a)** was obtained in 36% yield which was likely via an electrophilic substitution pathway (Table 1, Entry 1). The Nuclear Magnetic Resonance (NMR) yield of **2a** and regioselectivity remained essentially unaffected when PivOH was not added to the reaction. As a result, tests were performed under reaction conditions that omitted the PivOH additive. Solvents, however, were observed to critically influence the efficiency and regioselectivity of the reaction. Substituting toluene and 1,4-dioxane for the solvents instead of 1,2-dichloroethane produced similar *para*-brominated products (Table 1, Entries 3-4). However, when MeOH was used as the solvent, the target *ortho*-brominated product (**3a)** was obtained at a 16% yield, although this was accompanied by a 42% yield of the *para*-brominated product (**2a,** Table 1, Entry 5). These findings prompted our exploration of more alcoholic solvents to determine their role in regioselectivity. We observed that alcohol solvents with sterically more hindered OH group produced higher *ortho*-regioselectivity and conversion (Table 1, Entries 5-8). When *t*-BuOH was used as the solvent, total *ortho*-regioselectivity was achieved and the desired product (**3a)** could be produced at an 85% yield (Table 1, Entry 8). Moreover, the best result was obtained when the reaction was performed under air (Table 1, Entry 9). Therefor our reaction could be operated without the protection of inert gas which simplified the procedure. (Table 1, Entry 9).

Further investigations revealed that an Rh(III) catalyst and $AgSbF_6$ were also essential for this reaction. Poor conversions and only *para*-selectivity were observed when [Ru(p-cymene)$Cl_2]_2$ and $[Cp^*IrCl_2]_2$ were used as the catalyst (Table 1, Entries 10-11). When $AgSbF_6$ was replaced with either $AgNTf_2$ or AgOTf, the desired product (**3a)** was only obtained in 79% and 73% yields, respectively (Table 1, Entries 12-13). Control experiments confirmed that the $[Cp^*RhCl_2]_2$ catalyst and $AgSbF_6$ counter anion were both indispensable (Table 1, Entries 14-15). Additionally, either reducing the catalyst loading or increasing reaction temperature resulted in poorer yields (Table 1, Entries 16-17).

Table 1. Reaction Optimization[a]



Entry	Catalyst System	Solvent	Yield (%)[b] 2a	3a
1[c]	$[Cp^*RhCl_2]_2/AgSbF_6$	DCE	36	N.D.
2	$[Cp^*RhCl_2]_2/AgSbF_6$	DCE	35	N.D.
3	$[Cp^*RhCl_2]_2/AgSbF_6$	toluene	26	N.D.
4	$[Cp^*RhCl_2]_2/AgSbF_6$	1,4-dioxane	42	N.D.
5	$[Cp^*RhCl_2]_2/AgSbF_6$	MeOH	42	16
6	$[Cp^*RhCl_2]_2/AgSbF_6$	EtOH	8	47
7	$[Cp^*RhCl_2]_2/AgSbF_6$	^{i}PrOH	3	61
8	$[Cp^*RhCl_2]_2/AgSbF_6$	*t*-BuOH	N.D.	85
9[d]	$[Cp^*RhCl_2]_2/AgSbF_6$	*t*-BuOH	N.D.	91
10[d]	$[RuCl_2(p\text{-cymene})]_2/AgSbF_6$	*t*-BuOH	15	N.D.
11[d]	$[IrCp^*Cl_2]_2/AgSbF_6$	*t*-BuOH	46	N.D.
12[d]	$[Cp^*RhCl_2]_2/AgNTf_2$	*t*-BuOH	N.D.	79
13[d]	$[Cp^*RhCl_2]_2/AgOTf$	*t*-BuOH	N.D.	73
14[d]	$[Cp^*RhCl_2]_2$/-	*t*-BuOH	51	N.D.
15[d]	-/$AgSbF_6$	*t*-BuOH	57	N.D.
16[e]	$[Cp^*RhCl_2]_2/AgSbF_6$	*t*-BuOH	N.D.	67
17[f]	$[Cp^*RhCl_2]_2/AgSbF_6$	*t*-BuOH	N.D.	80
18[g]	$[Cp^*RhCl_2]_2/AgSbF_6$	*t*-BuOH	N.D.	96[h]

[a] Reaction conditions: **1a** (0.20 mmol), NBS (0.24 mmol), catalyst (5 mol%), Ag salt (20 mol%), solvent (1.0 mL), 30 °C, under N_2 for 12 h. [b] Yields were based on ^{1}H NMR analysis of the crude mixture (1,3,5-trimethoxybenzene: internal standard). [c] PivOH (0.22 mmol) was used. [d] Reaction run under air. [e] At 50 °C, under air. [f] catalyst (4 mol%), Ag salt (16 mol%), under air. [g] NIS (0.24 mmol), under air. [h] *ortho*-iodinated product **4a** was obtained. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, PivOH = Pivalic acid, DCE = 1,2-dichloroethane, ^{i}PrOH = isopropanol, *t*-BuOH = *tert*-butyl alcohol, N.D. = not detected.

Finally, the current optimized conditions could extend to *ortho*-iodination by using *N*-Iodosuccinimide (NIS) as the halogen source. Complete *ortho* regioselectivity was obtained and the desired *ortho*-iodinated product was observed at a 96% yield (Table 1, Entry 18). Unfortunately, this reaction failed when *N*-Chlorosuccinimide was used as the chlorine source and only starting materials were observed, even at temperatures up to 120°C.

Once the optimized conditions were determined, we evaluated the substrate scope and functional group tolerance of the reaction (Table 2). We first chose substrate **1a-f,** with different *N*-alkyls substituted on the amino group. Benzyl substituents and different linear-alkyl substituents on *N*-nitrosoaniline like ethyl and *n*-propyl groups reacted well with NBS (**3a**-**3d**) and NIS (**4a**-**4d**) under the optimal conditions, producing the desired products at 80-97% yields. Reactions (to form **3a** and **4a**) were scaled up successfully to a 1 mmol scale. Complete conversion was still observed for reactions, although the yields were slightly lower. The reaction yields decreased when substrate **1e** was used and the halogenated product **3e**-Br and **4e**-**I** were only obtained at 41% and 69% yields, respectively. No product was observed when an *N*-propanenitrile substituent was employed (**3f** and **4f**). In general, similarly good results were achieved when the *N*-nitrosoaniline starting material was substituted with electron-withdrawing or

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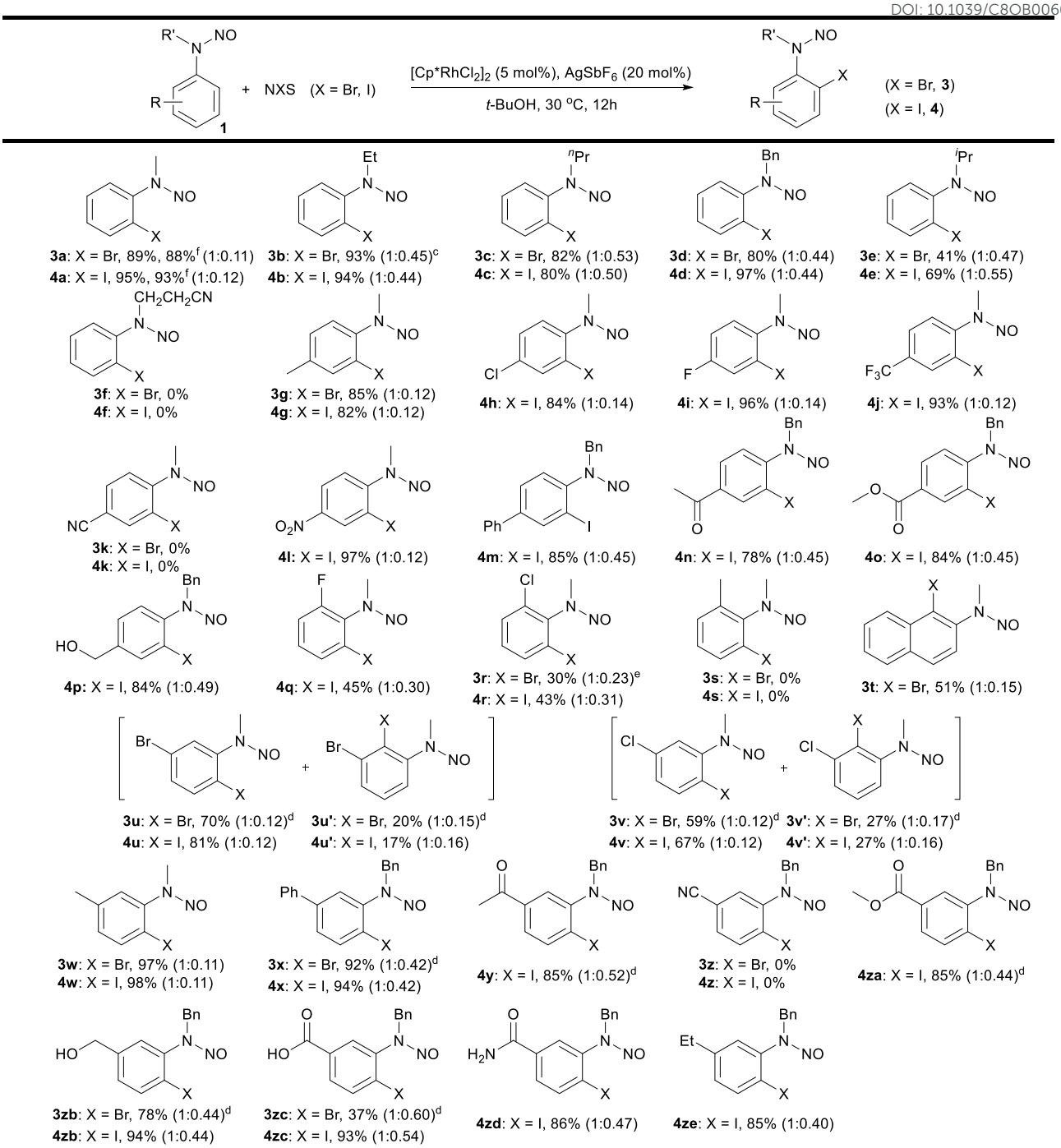
Table 2. Substrate Scope



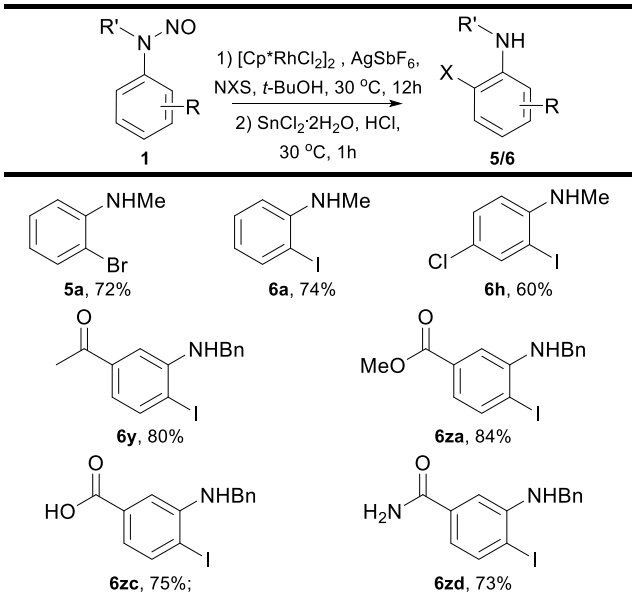
[a] Reraction conditions: **1a** (0.20 mmol), NBS/NIS (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ salt (20 mol%), *t*-BuOH (1.0 mL), 30 °C, under air for 12 h. [b] Yield of isolated product. [c] NBP (0.24 mmol) was used, 40 °C. [d] $Zn(NTf_2)_2$ (20 mol%) was used. [e] NBP (0.24 mmol) was used. [f] The reaction was conducted on a 1 mmol scale with 5 mol% of the catalyst and 20 mol% of $AgNTf_2$.

electron-donating groups at the *para* position, such as methyl groups, halides, or trifluoromethyl groups (**3g** and **4g**-**4j**). Moreover, some synthetically more useful compounds were also tolerated, including *N*-benzyl substituted *N*-nitrosoanilines bearing phenyl, acyl, ester, nitro or benzyl alcohol groups at the *para*-positions of the phenyl ring (**4l**-**4p**). The selectivity of meta-substituted substrates was found to be controlled by steric issues from either *N*- or phenyl ring substituents. For example, when a *meta*-Cl or Br substituted substrate was used, two *ortho*-halogenated regioisomers were obtained and halogenation to the less hindered *ortho*-position was preponderant (**3u**-**3v** and **4u**-**4v**). However, when a *meta*-methyl or *N*-benzyl substituted substrate was used, the less hindered, *ortho*-position halogenated product was observed as a single regioisomer (**3w**-**3x, 3zb**-**3zc**, **4w**-**4y** and **4za**-**4ze**). Further, when substrate **1t** was used, only the more sterically hindered *ortho*-position halogenated regioisomer could be obtained, though the yield was more moderate (**3t**). Some

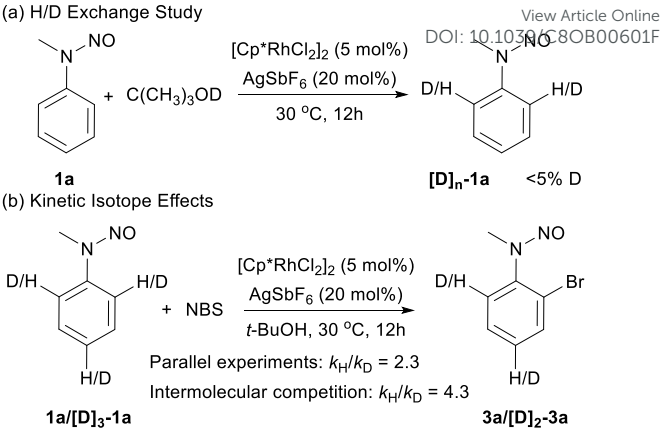
functional groups, especially unprotected benzyl alcohols, carboxylic acids, nitro groups and amides could participate in the reaction smoothly to furnish the desired products efficiently, thus offering a convenient setup for further synthetic transformations. Unfortunately, no product was observed when nitrile substituent was employed, probably due to the competitive coordination between the lone-pair electrons on the cyano group and the Rh(III) catalyst (**3k, 4k, 3z** and **4z**). It must be pointed out that during the bromination process of *meta*-substituted substrates, an addition of 20 mol% $Zn(NTf_2)_2$ was necessary. We speculated that $Zn(NTf_2)_2$ may have acted as a Lewis acid and facilitated activation of the NBS, thus improving the yield. An obvious steric hindrance effect was also observed for the *ortho*-substituted *N*-nitrosoaniline substrates, with markedly decreased yields under the standard reaction conditions (**3r**-**3s** and **4q**-**4s**).

To demonstrate the synthetic utility of this method, a one-pot procedure was tested to remove the directing group under mild conditions at 1 mmol scale. First, we have chosen **4a** as model substrate to investigate the denitrosation process of halogenated N-nitrosamine. After exploring various reaction conditions (see the Supporting Information for details), we were pleased to find that $SnCl_2{\cdot}2H_2O$/HCl system gave the best results and obtained **6a** in 81% yield. Second, a one-pot procedure was tested to remove the directing group under mild conditions at this same scale. When *ortho*-iodination reaction of substrate **4a** completed, $SnCl_2{\cdot}2H_2O$ and HCl (12 N) were subsequently added to the solution. After 1h at 30°C, the desired denitrosation products **6a** could be isolated in 74% yield. Moreover, some synthetically more useful compounds including 4-Cl, 3-Ac, 3-COOMe, 3-COOH and 3-$CONH_2$ substituents at the phenyl ring were tolerated (table 2) and produced moderate to good yield (60%-84%).

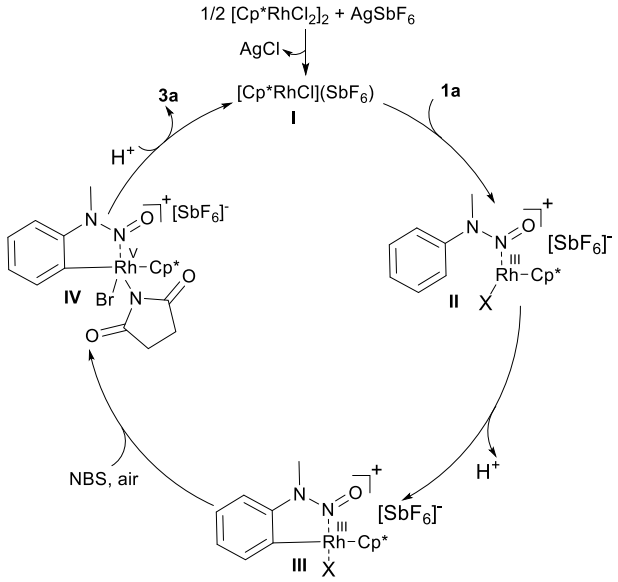
Table 3. Removal of the NO-directing Group with One-pot Procedure



[a] Reaction conditions: **1** (1.0 mmol), NBS/NIS (1.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ salt (20 mol%), *t*-BuOH (5.0 mL), 30 °C, under air for 12 h. Then, MeOH (5.0 mL), $SnCl_2{\cdot}2H_2O$ (2.5 mmol), HCl (12N, 6.0 mL) was added, 30 °C, 1h. [b] Yield of isolated product.



Scheme 2 Preliminary Mechanistic Studies



Scheme 3 Plausible Reaction Mechanis

Lastly, preliminary mechanistic studies were performed to explore the Cp*Rh(III) catalyzed *ortho*-halogenation. No significant H/D exchange was observed, which suggested that the C−H activation step might be irreversible (Scheme 2a). The kinetic isotope effect (KIE) was measured according to the previous work (Scheme 2a),[17] two parallel reactions and intermolecular competition reaction produced KIE values of K_H/K_D = 2.3 and K_H/K_D = 4.3, respectively. This result indicates that the C-H bond-cleavage process is presumably the rate-determining step.

Based on our mechanistic studies and relevant reports, a plausible catalytic cycle was proposed shown in Scheme 3. First, treatment of the dimeric precursor $[RhCp^*Cl_2]_2$ with $AgSbF_6$ generated the active cationic rhodium(III) species **I**, which coordinated to *N*-nitrosoanilines (**1a**) and formed intermediated **II**. Second, an irreversible C-H bond activation

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took place and formed the cyclic rhodium species **III**, which could undergo subsequent N-Br oxidative addition to generate Rh(V) complex **IV**. Lastly, a reductive elimination of the intermediated **IV** liberated the final product **3a** and regenerated the Rh(III) catalyst.

Conclusions

In summary, we have realized a highly efficient rhodium-catalyzed, solvent-controlled regioselective C-H halogenation of anilines by using *N*-nitroso function as a suitable and removable directing group. This reaction features good functional group tolerance, excellent reactivity and easy operation, thus providing a complementary protocol for synthesis of *ortho*-halogenated anilines. Further efforts to explore the synthetic application of this present regioselective halogenation reaction are on-going in our laboratory.

Experimental

All the reactions were carried out under air atmosphere. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All the solvents used for the reactions were dried according to standard procedures. All the reactions were monitored by thin layer chromatography (TLC, Silica gel Merck 60 F_{254}); The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel (particle size 40-63 µm, 230-400 mesh SiliaFlash® P60 (Silicycle Inc.)). NMR spectra were recorded on Bruker Ultrashield™ 500 MHz. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR). High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. The starting materials *N*-nitrosoanilines[15a, 18] were prepared according to the literature procedure.

General procedure for the Cp*Rh(III) Catalyzed *Ortho*-Halogenation of *N*-Nitrosoanilines

1a (27.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgSbF_6$ (13.8 mg, 20 mol %), and NXS (1.2 eq) were weighed into a pressure tube, then *t*-BuOH (1.0 mL) was added under air. The reaction mixture was stirred for 12 h at 30 °C. Purification was performed by flash column chromatography on silica gel using n-hexane and tetrahydrofuran to afford the product **3a** as a pale yellow liquid (38.3 mg, 89%).

Characterization data for the products in Table 2

***N*-(2-Bromophenyl)-*N*-methylnitrous amide (3a).** Pale yellow liquid (89% yield, 38.3 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1: 0.11. ^{1}H NMR (500 MHZ,$CDCl_3$) (*syn* and *anti* isomers) δ 7.75 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H × 0.11), 7.47 (td, *J* = 7.8 Hz, 1.1 Hz, 1H), 7.40-7.38 (m, 1H + 1H × 0.11), 7.36 (td, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.29 (td, *J* = 8.0 Hz, 1.4 Hz, 1H × 0.11), 7.03 (dd, *J* = 1.3 Hz, 1H × 0.11), 4.09 (s, 3H × 0.11), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 141.70, 133.98, 133.69, 131.02, 130.74, 128.72, 128.53, 128.37, 128.34, 120.74, 120.03, 40.05, 35.37. HRMS (ESI) m/z calculated for $C_7H_8BrN_2O$ $[M+H]^+$, 214.9820, found 214.9820.

***N*-(2-Bromophenyl)-*N*-ethylnitrous amide (3b)** Pale yellow liquid (93% yield, 42.6 mg, *syn*:*anti* = 1:0.45). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H × 0.45), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42-7.34 (m, 2H + 1H × 0.45), 7.29 (t, *J* = 7.8 Hz, 1H × 0.45), 6.99 (d, *J* = 7.7 Hz, 1H × 0.45), 4.67-4.64 (m, 1H × 0.45), 4.44-4.42 (m, 1H × 0.45), 4.01 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H × 0.45), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 140.20, 137.64, 133.96, 133.72, 130.90, 130.81, 129.55, 129,29, 128.40 (overlapped), 121.50, 121.40, 48.39, 41.73, 14.11, 11.14. HRMS (ESI) m/z calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9978.

***N*-(2-Bromophenyl)-*N*-propylnitrous amide (3c)** Yellow liquid (82% yield, 40.0 mg, *syn*:*anti* = 1:0.53). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.76 (dd, *J* = 8.5 Hz, 0.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H × 0.53), 7.47 (td, *J* = 7.6 Hz, 0.6 Hz, 1H), 7.41-7.34 (m, 2H + 1H × 0.53), 7.29 (td, *J* = 8.1 Hz, 1.0 Hz, 1H × 0.53), 6.99 (dd, *J* = 7.8 Hz, 0.8 Hz, 1H × 0.53), 4.59-4.54 (m, 1H × 0.53), 4.31-4.28 (m, 1H × 0.53), 3.91 (t, *J* = 7.7 Hz, 2H), 1.83-1.77 (m, 2H × 0.53), 1.54-1.46 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H × 0.53), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 140.58, 137.93, 134.01, 133.76, 130.85, 130.72, 129.38, 129.20, 128.38 (overlapped), 121.36, 121.25, 55.07, 48.20, 21.86, 19.62, 11.57, 11.24. HRMS (ESI) m/z calculated for $C_9H_{12}BrN_2O$ $[M+H]^+$, 243.0128, found 243.0128.

***N*-Benzyl-*N*-(2-bromophenyl)nitrous amide (3d)** Yellow liquid (89% yield, 51.8 mg, *syn*:*anti* = 1:0.44). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.74 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.65 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.44), 7.34-7.29 (m, 3H + 3H × 0.44), 7.26-7.24 (m, 2H + 2H × 0.44), 7.22-7.16 (m, 2H × 0.44), 7.12-7.08 (m, 3H), 6.50 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H × 0.44), 6.07 (d, *J* = 14.5 Hz, 1H × 0.44), 5.21-5.16 (m, 2H + 1H × 0.44). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 140.08, 137.32, 134.59 (overlapped), 133.89, 133.58, 130.91, 130.83, 130.02, 129.78, 129.19, 129.10, 128.85, 128.63, 128.60, 128.23, 128.07, 127.98, 121.28, 121.17, 57.20, 49.57. HRMS (ESI) m/z calculated for $C_{13}H_{12}BrN_2O$ $[M+H]^+$, 291.0127, found 291.0143.

***N*-(2-Bromophenyl)-*N*-isopropylnitrous amide (3e)** Yellow liquid (41% yield, 20.0 mg, *syn*:*anti* = 1:0.47). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.79 (d, *J* = 7.9 Hz, 1H × 0.47), 7.69 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H × 0.47), 7.41-7.33 (m, 1H + 2H × 0.47), 7.29 (td, *J* = 7.9 Hz, 0.7 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.11-5.06 (m, 1H × 0.47), 4.85-4.80 (m, 1H), 1.69 (d, *J* = 6.8 Hz, 6H × 0.47), 1.51 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 137.70, 134.10, 133.79, 130.95, 130.80, 129.98, 129.38, 128.28, 128.07, 124.05, 122.17, 56.82, 48.05, 22.70, 21.52, 19.52. HRMS (ESI) m/z calculated for $C_9H_{12}BrN_2O$ $[M+H]^+$, 243.0128, found 243.0129.

***N*-(2-Bromo-4-methylphenyl)-*N*-methylnitrous amide (3g)** Yellow liquid (85% yield, 38.9 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.55 (s, 1H), 7.49 (s,

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1H × 0.12), 7.28-7.24 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H × 0.12), 6.90 (d, *J* = 8.0 Hz, 1H × 0.12), 4.07 (s, 3H × 0.12), 3.38 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H × 0.12). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 141.38, 139.19 (overlapped), 134.26, 134.08, 129.47, 129.17, 127.96, 127.82, 120.27, 119.70, 40.15, 35.45, 20.96, 20.90. HRMS (ESI) m/z calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9977.

***N*-(2-Bromo-6-chlorophenyl)-*N*-methylnitrous amide (3r)** Yellow liquid (30% yield, 15.0 mg, *syn*:*anti* = 1:0.23). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.68 (dd, *J* = 8.1 Hz, 0.9 Hz, 1H), 7.57-7.53 (m, 1H + 1H× 0.23), 7.44 (dd, *J* = 8.1 Hz, 0.8 Hz, 1H × 0.23), 7.32 (t, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 8.2 Hz, 1H × 0.23), 4.09 (s, 3H× 0.23), 3.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 139.23, 134.49, 132.96, 132.11, 131.88, 131.67, 131.61, 129.62, 129.36, 124.08, 122.31, 38.33, 33.85. HRMS (ESI) m/z calculated for $C_7H_7BrClN_2O$ $[M+H]^+$, 250.9403, found 250.9411.

***N*-(1-Bromonaphthalen-2-yl)-*N*-methylnitrous amide (3t)** Brown liquid (51% yield, 27.0 mg, *syn*:*anti* = 1:0.15). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H × 0.15), 7.97-7.92 (m, 2H), 7.90-7.86 (m, 2H × 0.15), 7.70 (t, *J* = 8.2 Hz, 1H), 7.66-7.61 (m, 1H + 2H × 0.15), 7.47 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H × 0.15), 4.19 (s, 3H × 0.15), 3.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 139.71, 134.30, 134.16, 132.62, 131.71, 129.43, 129.07, 128.47 (overlapped), 128.33, 128.30, 128.13, 127.93, 127.84, 127.69, 124.96, 124.19, 121.53, 120.94, 39.87, 35.56. HRMS (ESI) m/z calculated for $C_{11}H_{10}BrN_2O$ $[M+H]^+$, 264.9971, found 264.9981.

***N*-(2,5-Dibromophenyl)-*N*-methylnitrous amide (3u)** White solid (70% yield, 41.2 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.56-7.52 (m, 1H + 1H × 0.12), 7.49 (dd, *J* = 8.5 Hz, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H × 0.12), 7.17 (d, *J* = 1.9 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.72, 135.03, 134.75, 134.06, 133.66, 131.39, 131.31, 121.70 (overlapped), 119.81, 118.73, 39.86, 35.22. HRMS (ESI) m/z calculated for $C_7H_7Br_2N_2O$ $[M+H]^+$, 294.8899, found 294.8914.

***N*-(2,3-Dibromophenyl)-*N*-methylnitrous amide (3u')** Yellow liquid (20% yield, 11.8 mg, *syn*:*anti* = 1:0.15). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.78-7.76 (m, 1H), 7.70 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H × 0.15), 7.35-7.34 (m, 2H), 7.30-7.26 (m, 1H × 0.15), 6.97 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H × 0.15), 4.10 (s, 3H × 0.15), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.47, 134.73, 134.52, 129.27, 129.05, 127.24, 127.08, 126.92 (overlapped), 123.76 (overlapped), 39.83, 35.29. HRMS (ESI) m/z calculated for $C_7H_7Br_2N_2O$ $[M+H]^+$, 294.8899, found 294.8914.

***N*-(2-Bromo-5-chlorophenyl)-*N*-methylnitrous amide (3v)** White solid (59% yield, 29.4 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.68 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H × 0.12), 7.42 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 7.29 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H × 0.12), 7.03 (d, *J* = 2.4 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.55, 134.76, 134.47, 134.33, 134.28, 131.16, 130.72, 128.58, 128.48, 117.94 (overlapped), 39.83, 35.20. HRMS (ESI) m/z calculated for $C_7H_7BrClN_2O$, $[M+H]^+$, 250.9403, found 250.9412.

***N*-(2-Bromo-3-chlorophenyl)-*N*-methylnitrous amide (3v')** Yellow liquid (27% yield, 13.5 mg, *syn*:*anti* = 1:0.17). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.62 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H), 7.54 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H × 0.17), 7.42 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H × 0.17), 7.31 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 6.94 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H × 0.17), 4.10 (s, 3H × 0.17), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.59, 136.75, 136.65, 131.37, 131.12, 128.98, 128.73, 126.59, 126.46, 121.46 (overlapped), 39.85, 35.31. HRMS (ESI) m/z calculated for $C_7H_7BrClN_2O$ $[M+H]^+$, 250.9403, found 250.9412.

***N*-(2-Bromo-5-methylphenyl)-*N*-methylnitrous amide (3w)** White solid (97% yield, 44.4 mg, *syn*:*anti* = 1:0.11). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H × 0.11), 7.20 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H × 0.11), 6.82 (s, 1H × 0.11), 4.07 (s, 3H × 0.11), 3.38 (s, 3H). 2.37 (s, 3H), 2.31 (s, 3H × 0.11). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 141.33, 139.18, 138.99, 133.54, 133.26, 131.90, 131.54, 128.99, 128.72, 117.04, 116.36, 40.09, 35.38, 20.79 (overlapped). HRMS (ESI) m/z calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9979.

***N*-Benzyl-*N*-(4-bromo-[1,1'-biphenyl]-3-yl)nitrous amide (3x)** Yellow liquid (92% yield, 67.4 mg, *syn*:*anti* = 1:0.42). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H × 0.42), 7.54 (dd, *J* = 8.3 Hz, 2.1 Hz, 1H), 7.43-7.42 (m, 3H + 3H × 0.42), 7.40-7.33 (m, 3H + 3H × 0.42), 7.30-7.27 (m, 3H + 3H × 0.42), 7.25-7.23 (m, 2H × 0.42), 7.18-7.17 (m, 2H), 6.67 (d, *J* = 2.0 Hz, 1H × 0.42). 6.13 (d, *J* = 14.4 Hz, 1H × 0.42), 5.26-5.22 (m, 2H + 1H × 0.42). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 141.72, 141.52, 140.35, 138.61, 138.58, 137.67, 134.67, 134.13, 133.94, 133.76, 129.45, 129.40, 129.32, 129.30, 129.23 (overlapped), 129.08, 128.95, 128.71, 128.57, 128.30 (overlapped), 128.11, 128.07, 126.94, 126.81, 119.93 (overlapped), 57.32, 49.65. HRMS (ESI) m/z calculated for $C_{19}H_{16}BrN_2O$ $[M+H]^+$, 367.0440, found 367.0460.

***N*-Benzyl-*N*-(2-bromo-5-(hydroxymethyl)phenyl)nitrous amide (3zb)** Yellow liquid (78% yield, 50.1 mg, *syn*:*anti* = 1:0.44). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H × 0.44), 7.31-7.30 (m, 1H + 1H × 0.44), 7.26-7.22 (m, 4H + 2H × 0.44), 7.16 (d, *J* = 8.1 Hz, 1H × 0.44), 7.10-7.09 (m, 2H + 2H × 0.44), 6.50 (d, *J* = 0.9 Hz, 1H × 0.44), 5.96 (d, *J* = 14.6 Hz, 1H × 0.44), 5.26 (d, *J* = 14.6 Hz, 1H × 0.44), 5.13 (s, 2H), 4.54 (s, 2H), 4.40 (s, 2H × 0.44). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 141.99, 141.81, 139.98, 137.23, 134.33, 133.82, 133.72, 133.49, 129.21, 129.20, 129.05, 128.99, 128.84, 128.63, 128.00 (overlapped), 127.90, 127.64, 119.61, 119.58, 63.51 (overlapped), 57.37, 49.84. HRMS (ESI) m/z calculated for $C_{14}H_{14}BrN_2O_2$ $[M+H]^+$, 321.0233, found 321.0249.

3-(Benzyl(nitroso)amino)-4-bromobenzoic acid (3zc) White solid (37% yield, 24.8 mg, *syn*:*anti* = 1:0.60). ^{1}H NMR (500 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.86-7.82 (m, 1H + 2H × 0.60), 7.35-7.33 (m, 2H + 3H × 0.60), 7.29-7.23 (m, 1H + 3H × 0.60), 7.15 (d, *J* = 6.8 Hz, 2H), 5.94 (d, *J* = 14.8 Hz, 1H × 0.60), 5.55 (d, *J* = 14.8

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Hz, 1H × 0.60), 5.18 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 166.17, 166.07, 140.18, 137.88, 134.77, 134.20, 134.01 (overlapped), 132.12, 132.04, 132.00, 131.95, 130.20, 130.17, 129.68, 129.28, 129.16, 128.99, 128.91, 128.34, 126.78, 126.49, 57.00, 49.91. HRMS (ESI) m/z calculated for $C_{14}H_{12}BrN_2O_3$ $[M+H]^+$, 335.0025, found 335.0046.

***N*-(2-Iodophenyl)-*N*-methylnitrous amide (4a)** Pale yellow liquid (95% yield, 49.8 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H × 0.12), 7.50 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H × 0.12), 7.34 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.20 (td, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.12), 6.98 (d, *J* = 7.8 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 145.11, 140.32, 140.02, 131.01, 130.92, 129.66, 129.44, 127.96, 127.75, 95.43, 95.17, 40.13, 35.54. HRMS (ESI) m/z calculated for $C_7H_8IN_2O$ $[M+H]^+$, 262.9675, found 262.9688.

***N*-Ethyl-*N*-(2-iodophenyl)nitrous amide (4b)** Pale yellow liquid (94% yield, 52.0 mg, *syn*:*anti* = 1:0.44). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.02 (dd, *J* = 8.0 Hz, 1.1 Hz, 1H), 7.93 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H × 0.44), 7.50 (td, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.43 (td, *J* = 7.6 Hz, 1.1 Hz, 1H × 0.44), 7.30 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.20 (td, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.13 (td, *J* = 7.8 Hz, 1.3 Hz, 1H × 0.44), 6.93 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.44), 4.73-4.66 (m, 1H × 0.44), 4.40-4.33 (m, 1H × 0.44), 3.98 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H × 0.44), 1.08 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.54, 141.63, 140.33, 140.12, 130.93, 130.89, 129.25 (overlapped), 129.04, 128.96, 96.83, 96.41, 48.45, 42.01, 14.30, 11.13. HRMS (ESI) m/z calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9846.

***N*-(2-Iodophenyl)-*N*-propylnitrous amide (4c)** Pale yellow liquid (80% yield, 46.5 mg, *syn*:*anti* = 1:0.50). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H × 0.50), 7.49 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H × 0.50), 7.30 (dd, *J* = 7.7 Hz, 0.7 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.8 Hz, 0.9 Hz, 1H × 0.50), 6.92 (d, *J* = 7.8 Hz, 1H × 0.50), 4.62-4.57 (m, 1H × 0.50), 4.26-4.21 (m, 1H × 0.50), 3.88 (t, *J* = 7.8 Hz, 2H), 1.88-1.75 (m, 2H × 0.50), 1.54-1.46 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H × 0.50), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.91, 141.91, 140.39, 140.17, 130.85 (overlapped), 129.23, 129.21, 128.89 (overlapped), 96.61, 96.22, 55.12, 48.54, 22.00, 19.59, 11.62, 11.29. HRMS (ESI) m/z calculated for $C_9H_{12}IN_2O$ $[M+H]^+$, 290.9989, found 290.9994.

***N*-Benzyl-*N*-(2-iodophenyl)nitrous amide (4d)** Yellow liquid (97% yield, 65.6 mg, *syn*:*anti* = 1:0.44). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.98 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.9 Hz, 0.8 Hz, 1H × 0.44), 7.35-7.31 (m, 2H + 1H × 0.44), 7.27-7.23 (m, 3H + 2H × 0.44), 7.18 (td, *J* = 7.7 Hz, 1.1 Hz, 1H × 0.44), 7.15-7.09 (m, 2H + 2H × 0.44), 7.03 (td, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.44), 6.99 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 6.36 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H × 0.44), 6.08 (d, *J* = 14.5 Hz, 1H × 0.44), 5.14-5.10 (m, 2H + 1H × 0.44). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.39, 141.25, 140.28, 139.98, 134.59, 133.80, 130.96, 130.93, 129.60, 129.46, 129.30, 129.05, 128.92, 128.88, 128.66, 128.64, 128.04 (overlapped), 96.70, 96.14, 57.26, 49.91. HRMS (ESI) m/z calculated for $C_{13}H_{12}IN_2O$ $[M+H]^+$, 338.9988, found 339.0002.

***N*-(2-Iodophenyl)-*N*-isopropylnitrous amide (4e)** Yellow liquid (69% yield, 40.0 mg, *syn*:*anti* = 1:0.55). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.04 (dd, *J* = 7.9 Hz, 0.8 Hz, 1H × 0.55), 7.94 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.49 (td, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.55), 7.42 (td, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.32 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.55), 7.20 (td, *J* = 7.9 Hz, 1.3 Hz, 1H × 0.55), 7.12 (td, *J* = 7.9 Hz, 1.3 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1.1 Hz, 1H), 5.07-5.02 (m, 1H × 0.55), 4.75-4.70 (m, 1H), 1.77 (d, *J* = 6.8 Hz, 6H × 0.55), 1.53 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.12, 141.97, 140.50, 140.26, 130.98, 130.74, 129.11 (overlapped), 128.98, 128.94, 97.19 (overlapped), 56.91, 48.07, 22.84, 21.78, 19.67. HRMS (ESI) m/z calculated for $C_9H_{12}IN_2O$ $[M+H]^+$, 290.9989, found 290.9992.

***N*-(2-Iodo-4-methylphenyl)-*N*-methylnitrous amide (4g)** Yellow liquid (82% yield, 45.3 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.81 (s, 1H), 7.73 (s, 1H × 0.12), 7.29 (d, *J* = 7.9 Hz, 1H), 7.23-7.19 (m, 1H + 1H × 0.12), 6.84 (d, *J* = 8.0 Hz, 1H × 0.12), 4.07 (s, 3H × 0.12), 3.35 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H × 0.12). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.67, 141.46 (overlapped), 140.59, 140.42, 130.44, 130.10, 127.47, 127.18, 95.12, 95.02, 40.23, 35.63, 20.73, 20.68. HRMS (ESI) m/z calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9844.

***N*-(4-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4h)** Yellow liquid (84% yield, 49.8 mg, *syn*:*anti* = 1:0.14). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.00 (d, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H × 0.14), 7.50 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.43 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H × 0.14), 7.28 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H × 0.14), 4.08 (s, 3H × 0.14), 3.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.89, 141.80, 139.66, 139.49, 136.04, 135.92, 129.92, 129.59, 128.43, 128.39, 95.93, 95.49, 39.97, 35.42. HRMS (ESI) m/z calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9295.

***N*-(4-Fluoro-2-iodophenyl)-*N*-methylnitrous amide (4i)** Yellow liquid (96% yield, 53.8 mg, *syn*:*anti* = 1:0.14). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.72 (dd, *J* = 7.6 Hz, 2.2 Hz, 1H), 7.63 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H × 0.14), 7.33-7.30 (m, 1H), 7.21 (td, *J* = 8.7 Hz, 2.4 Hz, 1H), 7.15 (td, *J* = 8.7 Hz, 2.2 Hz, 1H × 0.14), 6.95-6.92 (m, 1H × 0.14), 4.08 (s, 3H × 0.14), 3.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 163.10 (d, $J_{C\text{-}F}$ = 253.5 Hz), 163.07 (d, $J_{C\text{-}F}$ = 253.3 Hz), 141.73 (d, $J_{C\text{-}F}$ = 3.4 Hz), 139.31 (d, $J_{C\text{-}F}$ = 3.8 Hz), 128.90 (d, $J_{C\text{-}F}$ = 8.9 Hz), 128.80 (d, $J_{C\text{-}F}$ = 9.1 Hz), 127.25 (d, $J_{C\text{-}F}$ = 24.7 Hz), 127.19 (d, $J_{C\text{-}F}$ = 24.6 Hz), 116.96 (d, $J_{C\text{-}F}$ = 22.3 Hz), 116.54 (d, $J_{C\text{-}F}$ = 22.3 Hz), 95.55 (d, $J_{C\text{-}F}$ = 8.7 Hz) (overlapped), 40.12, 35.50. HRMS (ESI) m/z calculated for $C_7H_7FIN_2O$ $[M+H]^+$, 280.9581, found 280.9593.

***N*-(2-Iodo-4-(trifluoromethyl)phenyl)-*N*-methylnitrous amide (4j)** Yellow liquid (93% yield, 61.4 mg, *syn*:*anti* = 1:0.12). The ^{13}C NMR data listed here represent peak information only for the major syn isomer. ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.25 (s, 1H), 8.15 (s, 1H × 0.12), 7.78 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H × 0.12), 7.46 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H × 0.12), 4.12 (s, 3H × 0.12), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.11, 137.49 (q, $J_{C\text{-}F}$ = 3.7 Hz),

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132.82 (q, J_{C-F} = 33.2 Hz), 127.97, 126.55 (q, J_{C-F} = 3.5 Hz), 123.52 (q, J_{C-F} = 271.3 Hz), 94.83, 35.30. HRMS (ESI) m/z calculated for $C_8H_7F_3IN_2O$ $[M+H]^+$, 330.9549, found 330.9570.

***N*-(2-Iodo-4-nitrophenyl)-*N*-methylnitrous amide (4l)** Yellow liquid (97% yield, 59.7 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.84 (d, *J* = 2.3 Hz, 1H), 8.73 (d, *J* = 2.3 Hz, 1H × 0.12), 8.37 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 8.30 (dd, *J* = 8.6 Hz, 2.3 Hz, 1H × 0.12), 7.51 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H × 0.12), 4.14 (s, 3H × 0.12), 3.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.23, 147.73, 135.60, 127.82, 124.46, 94.11, 35.37. HRMS (ESI) m/z calculated for $C_7H_7IN_3O_3$ $[M+H]^+$, 307.9527, found 307.9533.

***N*-Benzyl-*N*-(3-iodo-[1,1'-biphenyl]-4-yl)nitrous amide (4m)** Yellow liquid (85% yield, 70.4 mg, *syn*:*anti* = 1:0.45). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.21 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H × 0.45), 7.57-7.54 (m, 2H + 2H × 0.45), 7.50-7.34 (m, 5H + 8H × 0.45), 7.29-7.28 (m, 2H + 1H × 0.45), 7.18-7.17 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H × 0.45), 6.14 (d, *J* = 14.6 Hz, 1H × 0.45), 5.21-5.17 (m, 2H + 1H × 0.45). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 144.11, 144.09, 142.38, 140.14, 138.72, 138.46, 138.39, 138.28, 134.67, 133.89, 129.50, 129.43, 129.32 (overlapped), 129.08, 128.99, 128.92, 128.70, 128.67, 128.47, 128.38, 128.06, 127.68, 127.65, 127.21, 127.19, 97.05, 96.56, 57.36, 49.98. HRMS (ESI) m/z calculated for $C_{19}H_{16}IN_2O$ $[M+H]^+$, 415.0301, found 415.0323.

***N*-(4-Acetyl-2-iodophenyl)-*N*-benzylnitrous amide (4n)** Yellow liquid (78% yield, 59.3 mg, *syn*:*anti* = 1:0.45). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.53 (d, *J* = 1.6 Hz, 1H), 8.42 (d, *J* = 1.4 Hz, 1H × 0.45), 7.91 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H), 7.75 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H × 0.45), 7.35-7.33 (m, 1H + 1H × 0.45), 7.28-7.24 (m, 2H + 4H × 0.45), 7.10-7.08 (m, 3H), 6.48 (d, *J* = 8.2 Hz, 1H × 0.45), 6.10 (d, *J* = 14.6 Hz, 1H × 0.45), 5.20 (d, *J* = 14.6 Hz, 1H × 0.45), 5.14 (s, 2H), 2.61 (s, 3H), 2.54 (s, 3H × 0.45). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 195. 57, 195.51, 146.91, 145.38, 140.31, 139.77, 138.78, 138.62, 134.19, 133.44, 129.67, 129.31, 129.26, 129.21, 128.99, 128.82, 128.81, 128.76, 128.56, 128.22, 96.73, 96.62, 57.03, 49.50, 26.66, 26.58. HRMS (ESI) m/z calculated for $C_{15}H_{14}IN_2O_2$ $[M+H]^+$, 381.0094, found 381.0113.

Methyl 4-(benzyl(nitroso)amino)-3-iodobenzoate (4o) Yellow liquid (84% yield, 66.6 mg, *syn*:*anti* = 1:0.45). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.52 (d, *J* = 1.4 Hz, 1H × 0.45), 8.00 (dd, *J* = 8.2 Hz, 1.7 Hz, 1H), 7.84 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H × 0.45), 7.33-7.32 (m, 1H + 1H × 0.45), 7.26-7.23 (m, 2H + 4H × 0.45), 7.09-7.05 (m, 3H), 6.45 (d, *J* = 8.2 Hz, 1H × 0.45), 6.08 (d, *J* = 14.6 Hz, 1H × 0.45), 5.19 (d, *J* = 14.6 Hz, 1H × 0.45), 5.13 (s, 2H), 3.92 (s, 3H), 3.88 (s, 3H × 0.45). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 164.65 (overlapped), 146.89, 145.36, 141.49, 140.99, 134.18, 133.43, 132.39, 132.24, 130.17, 129.95, 129.42, 129.28, 129.23, 129.08, 128.98, 128.81, 128.75, 128.21, 96.13, 96.07, 57.04, 52.73, 52.66, 49.54. HRMS (ESI) m/z calculated for $C_{15}H_{14}IN_2O_3$ $[M+H]^+$, 397.0043, found 397.0061.

***N*-Benzyl-*N*-(4-(hydroxymethyl)-2-iodophenyl)nitrous amide (4p)** Yellow liquid (84% yield, 61.9 mg, *syn*:*anti* = 1:0.49). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.98 (s, 1H), 7.88 (s, 1H × 0.49), 7.33-7.24 (m, 4H + 5H × 0.49), 7.15-7.10 (m, 2H + 1H × 0.49), 6.95 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H × 0.49), 6.06 (d, *J* = 14.5 Hz, 1H × 0.49), 5.15-5.10 (m, 2H + 1H × 0.49), 4.67 (s, 2H), 4.59 (s, 2H × 0.49). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 144.27, 144.26, 142.33, 140.09, 138.19, 137.94, 134.44, 133.70, 129.34, 129.31 (2C, overlapped), 129.20, 128.89, 128.67 (overlapped), 128.06, 127.14, 127.08, 96.67, 96.10, 63.47, 63.44, 57.38, 50.00. HRMS (ESI) m/z calculated for $C_{14}H_{14}IN_2O_2$ $[M+H]^+$, 369.0094, found 369.0111.

***N*-(2-Fluoro-6-iodophenyl)-*N*-methylnitrous amide (4q)** Yellow liquid (45% yield, 25.4 mg, *syn*:*anti* = 1:0.30). The ^{13}C NMR data listed here represent peak information only for the major syn isomer. ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.68-7.67 (m, 1H × 0.30), 7.28-7.25 (m, 1H), 7.24-7.19 (m, 1H), 7.16-7.14 (m, 2H × 0.30), 4.09 (s, 3H × 0.30), 3.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.01 (d, J_{C-F} = 254.6 Hz), 135.27 (d, J_{C-F} = 3.8 Hz), 133.57 (d, J_{C-F} =13.6 Hz), 132.45 (d, J_{C-F} =8.3 Hz), 117.00 (d, J_{C-F} = 20.4 Hz), 98.09, 34.45. HRMS (ESI) m/z calculated for $C_7H_7FIN_2O$ $[M+H]^+$, 280.9581, found 280.9594.

***N*-(2-Chloro-6-iodophenyl)-*N*-methylnitrous amide (4r)** Yellow liquid (43% yield, 25.5 mg, *syn*:*anti* = 1:0.31). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H × 0.31), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H × 0.31), 7.16 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H × 0.31), 4.10 (s, 3H × 0.31), 3.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.34, 140.50, 138.37, 138.22, 133.53 (overlapped), 132.06, 131.98, 130.53, 130.27, 98.84, 96.69, 38.25, 33.89. HRMS (ESI) m/z calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9298.

***N*-(5-Bromo-2-iodophenyl)-*N*-methylnitrous amide (4u)** White solid (81% yield, 55.2 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H × 0.12), 7.49 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 7.25-7.24 (m, 1H × 0.12), 7.11 (d, *J* = 2.1 Hz, 1H × 0.12), 4.08 (s, 3H × 0.12), 3.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 146.21, 141.29, 141.02, 134.15, 133.95, 131.01, 130.87, 123.01, 122.94, 93.29 (overlapped), 39.95, 35.42. HRMS (ESI) m/z calculated for $C_7H_7BrIN_2O$ $[M+H]^+$, 340.8780, found 340.8795.

***N*-(3-Bromo-2-iodophenyl)-*N*-methylnitrous amide (4u')** White solid (17% yield, 11.7 mg, *syn*:*anti* = 1:0.16). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H × 0.16), 7.38 (t, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H × 0.16), 7.26-7.24 (m, 1H), 6.89 (d, *J* = 7.9 Hz, 1H × 0.16), 4.10 (s, 3H × 0.16), 3.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 147.28, 133.55 (overlapped), 132.11, 132.00, 130.49, 130.20, 126.45, 126.05, 104.46 (overlapped), 39.88, 35.47. HRMS (ESI) m/z calculated for $C_7H_7BrIN_2O$ $[M+H]^+$, 340.8780, found 340.8794.

***N*-(5-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4v)** White solid (67% yield, 39.7 mg, *syn*:*anti* = 1:0.12). ^{1}H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H × 0.12), 7.35 (d, *J* = 2.2 Hz, 1H), 7.21 (dd, *J* = 8.5 Hz, 2.2 Hz, 1H), 7.13 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H × 0.12), 6.98 (d, *J* = 2.2 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 146.09, 141.04,

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140.76, 135.52, 135.43, 131.23, 131.01, 128.20, 128.10, 92.96, 92.35, 39.89, 35.35. HRMS (ESI) m/z calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9295.

***N*-(3-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4v')** White solid (27% yield, 16.0 mg, *syn*:*anti* = 1:0.16). The ^{13}C NMR data listed here represent peak information only for the major syn isomer. ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.59 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H), 7.50 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H × 0.16), 7.45 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H × 0.16), 7.22 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H), 6.85 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.16), 4.11 (s, 3H × 0.16), 3.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.32, 140.81, 130.10, 129.98, 125.98, 101.31, 35.48. HRMS (ESI) m/z calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9296.

***N*-(2-Iodo-5-methylphenyl)-*N*-methylnitrous amide (4w)** White solid (98% yield, 54.1 mg, *syn*:*anti* = 1:0.11). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H × 0.11), 7.15 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H × 0.11), 6.78 (s, 1H × 0.11), 4.07 (s, 3H × 0.11), 3.36 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H × 0.11). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ144.89, 140.21, 139.98, 139.90, 139.62, 132.04, 131.87, 128.75, 128.30, 90.98, 90.75, 40.14, 35.54, 27.65, 20.82. HRMS (ESI) m/z calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9845.

***N*-Benzyl-*N*-(4-iodo-[1,1'-biphenyl]-3-yl)nitrous amide (4x)** Yellow liquid (94% yield, 77.9 mg, *syn*:*anti* = 1:0.42). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H × 0.42), 7.42-7.34 (m, 6H + 8H × 0.42), 7.30-7.28 (m, 3H + 1H × 0.42), 7.21-7.18 (m, 3H + 2H × 0.42), 6.55 (d, *J* = 2.0 Hz, 1H × 0.42), 6.16 (d, *J* = 14.5 Hz, 1H × 0.42), 5.21-5.19 (m, 2H + 1H × 0.42). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.76, 142.53, 142.35, 141.73, 140.51, 140.15, 138.62, 138.60, 134.71, 133.88, 129.52, 129.48, 129.46 (overlapped), 129.08, 128.98, 128.94, 128.73, 128.33, 128.22, 128.14 (overlapped), 128.09 (overlapped), 126.89, 126.75, 94.94, 94.46, 57.36, 49.95. HRMS (ESI) m/z calculated for $C_{19}H_{16}IN_2O$ $[M+H]^+$, 415.0301, found 415.0320.

***N*-(5-Acetyl-2-iodophenyl)-*N*-benzylnitrous amide (4y)** Yellow liquid (85% yield, 64.6 mg, *syn*:*anti* = 1:0.52). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.11 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H × 0.52), 7.69 (dd, *J* = 8.2 Hz, 1.4 Hz, 1H), 7.61 (dd, *J* = 8.3 Hz, 1.4 Hz, 1H × 0.52), 7.47 (d, *J* = 1.4 Hz, 1H), 7.36-7.35 (m, 1H + 1H × 0.52), 7.29-7.26 (m, 2H +4H × 0.52), 7.12-7.11 (m, 2H), 6.82 (d, *J* = 1.4 Hz, 1H × 0.52), 6.12 (d, *J* = 14.5 Hz, 1H × 0.52), 5.19-5.14 (m, 2H + 1H × 0.52), 2.44 (s, 3H), 2.28 (s, 3H × 0.52). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 195.91, 143.79, 141.75, 140.79, 140.41, 137.81, 137.68, 134.27, 133.47, 129.82, 129.81, 129.41, 129.37, 129.08, 129.00, 128.88, 128.82, 128.77, 128.28, 103.40, 103.15, 57.22, 49.61, 26.40, 26.18. HRMS (ESI) m/z calculated for $C_{15}H_{14}IN_2O_2$ $[M+H]^+$, 381.0094, found 381.0106.

Methyl 3-(benzyl(nitroso)amino)-4-iodobenzoate (4za) Yellow liquid (85% yield, 67.4 mg, *syn*:*anti* = 1:0.44). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.08 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 7.97 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H × 0.44), 7.77 (d, *J* = 8.3 Hz, 1H), 7.68-7.67 (m, 1H + 1H × 0.44), 7.34 (br, 1H + 1H × 0.44), 7.29-7.25 (m, 2H + 4H × 0.44), 7.12-7.09 (m, 2H +1H × 0.44), 6.01 (d, *J* = 14.6 Hz, 1H × 0.44), 5.30 (d, *J* = 14.6 Hz, 1H × 0.44), 5.14 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H × 0.44). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 165.38, 165.25, 143.77, 141.71, 140.67, 140.27, 134.11, 133.34, 131.43, 131.34, 131.32, 131.26, 130.11, 129.85, 129.32, 129.28, 128.96, 128.78, 128.75, 128.20, 103.12, 103.01, 57.29, 52.60, 52.46, 49.87. HRMS (ESI) m/z calculated for $C_{15}H_{14}IN_2O_3$ $[M+H]^+$, 397.0043, found 397.0058.

***N*-Benzyl-*N*-(5-(hydroxymethyl)-2-iodophenyl)nitrous amide (4zb)** Yellow liquid (94% yield, 69.2 mg, *syn*:*anti* = 1:0.44). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H × 0.44), 7.32-7.31 (m, 1H + 1H × 0.44), 7.26-7.23 (m, 3H + 2H × 0.44), 7.12-7.09 (m, 2H + 2H × 0.44), 7.01 (br, 1H + 1H × 0.44), 6.38 (s, 1H × 0.44), 6.00 (d, *J* = 14.5 Hz, 1H × 0.44), 5.20 (d, *J* = 14.6 Hz, 1H × 0.44), 5.10 (s, 2H), 4.54 (s, 2H), 4.39 (s, 2H × 0.44). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 143.40, 142.88, 142.71, 141.30, 140.23, 139.93, 134.36, 133.63, 129.35, 129.28, 129.25, 129.16, 128.87, 128.69, 128.65, 128.06, 127.53, 127.41, 94.67, 94.23, 63.59 (overlapped), 57.43, 50.16. HRMS (ESI) m/z calculated for $C_{14}H_{14}IN_2O_2$ $[M+H]^+$, 369.0094, found 369.0108.

3-(Benzyl(nitroso)amino)-4-iodobenzoic acid (4zc) White solid (93% yield, 71.1 mg, *syn*:*anti* = 1:0.54). ^1H NMR (500 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 13.26 (br, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H × 0.54), 7.74-7.71 (m, 2H), 7.64 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H × 0.54), 7.35-7.34 (m, 2H + 1H × 0.54), 7.30-7.23 (m, 1H + 4H × 0.54), 7.15-7.14 (m, 2H), 7.12 (d, *J* = 1.5 Hz, 1H × 0.54), 5.99 (d, *J* = 14.7 Hz, 1H × 0.54), 5.43 (d, *J* = 14.7 Hz, 1H × 0.54), 5.16 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 166.41, 166.29, 143.72, 142.05, 141.12, 140.62, 134.82, 133.95, 132.46, 132.33, 131.70 (overlapped), 129.77, 129.61, 129.45, 129.28, 129.18, 128.99, 128.92, 128.35, 104.63, 104.53, 57.07, 50.10. HRMS (ESI) m/z calculated for $C_{14}H_{12}IN_2O_3$ $[M+H]^+$, 382.9887, found 382.9912.

3-(Benzyl(nitroso)amino)-4-iodobenzamide (4zd) White solid (86% yield, 65.6 mg, *syn*:*anti* = 1:0.47). ^1H NMR (500 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 8.15-8.13 (m, 2H), 8.02-8.00 (m, 2H × 0.47), 7.82 (d, *J* = 1.7, 1H), 7.72 (dd, *J* = 8.1 Hz, 1.4 Hz, 1H), 7.62 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H × 0.47), 7.57 (br, 1H), 7.48 (br, 1H × 0.47), 7.33 (br, 2H + 1H × 0.47), 7.29-7.24 (m, 1H + 5H × 0.47), 7.16-7.15 (m, 2H), 5.90 (d, *J* = 14.7 Hz, 1H × 0.47), 5.53 (d, *J* = 14.7 Hz, 1H × 0.47), 5.17 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) (*syn* and *anti* isomers) δ 166.59, 166.52, 143.53, 141.85, 140.65, 140.05, 135.80, 135.71, 134.74, 133.92, 130.12, 130.01, 129.82, 129.42, 129.11, 128.94, 128.86, 128.29, 128.22, 127.88, 102.18, 102.07, 57.17, 50.18. HRMS (ESI) m/z calculated for $C_{14}H_{13}IN_3O_2$ $[M+H]^+$, 382.0046, found 382.0062.

***N*-Benzyl-*N*-(5-ethyl-2-iodophenyl)nitrous amide (4ze)** Yellow liquid (85% yield, 62.3 mg, *syn*:*anti* = 1:0.40). ^1H NMR (500 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H × 0.40), 7.34-7.33 (m, 1H + 1H × 0.40), 7.28-7.25 (m, 2H + 4H × 0.40), 7.13-7.12 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H × 0.40), 6.81 (s, 1H), 6.15 (s, 1H × 0.40), 6.09 (d, *J* = 14.4 Hz, 1H × 0.40), 5.12-5.10 (m, 2H + 1H × 0.40), 2.55 (q, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.6 Hz, 2H × 0.40), 1.12 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H × 0.40). ^{13}C NMR (125 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 145.84, 145.59, 143.19,

141.15, 139.89, 139.56, 134.67, 133.89, 130.77, 130.75, 129.44, 129.41, 129.32, 128.98, 128.80, 128.58, 127.99 (overlapped), 92.55, 91.93, 57.33, 49.92, 28.06, 27.96, 15.08, 14.83. HRMS (ESI) m/z calculated for $C_{15}H_{16}IN_2O$ $[M+H]^+$,367.0301, found 367.0320.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

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