Synthesis A. Purkait, C. K. Jana Special Topic

N-Aminations of Benzylamines and Alicyclic Amines with Nitrosoarenes to Hydrazones and Hydrazides

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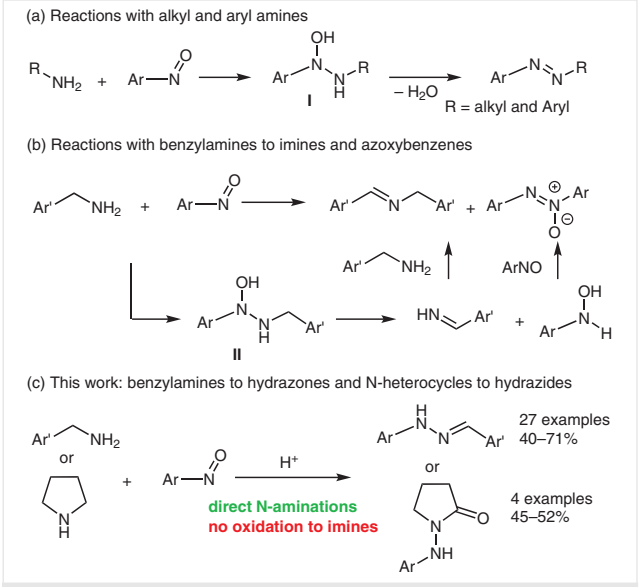
Abstract Unlike other alkylamines, benzylamines upon reaction with a nitrosoarene undergo oxidation to the corresponding imines. A direct amination of benzylamines, which was difficult to achieve due to its facile oxidation, to the corresponding hydrazones is reported. A wide variety of benzylamines and N-heterocycles were reacted with nitrosoarenes to provide structurally diverse hydrazones and hydrazides, respectively. Moreover, the direct N-amination reaction was applied to the one-pot synthesis of triazoles.

Key words N-amination, hydrazones, nitrosoarenes, triazoles, benzylamines

Nitrosoarenes are widely used in organic synthesis to incorporate the amine functionality into molecules.[1] The nitroso group participates in various C–N bond-forming process, such as N-nitroso aldol reactions,[2] annulation reactions,[3] cycloaddition reactions,[4] and nitroso-ene reactions.[5] Furthermore, the nitroso functionality has recently been efficiently reacted with donor–acceptor cyclopropanes to provide different heterocycles.[6] In addition to these C–N bond forming reactions, nitrosoarenes react with alkyl- and arylamines to provide the corresponding azo derivatives forming a N=N bond (Scheme 1a).[1a,7,8] Interestingly, a similar reaction of nitrosoarenes with benzylamines does not provide the desired azo derivative;[7a] the reaction produces azoxy derivatives and the corresponding aldehyde. A careful analysis of the mechanistic rationalization revealed that the elimination of water involving N–H cleavage of initial N-hydroxyhydrazine derivative **I** provide the azo compound for alkyl- or arylamines (Scheme 1b). In contrast, elimination of hydroxylamine occurs (from **II**) involving the cleavage of the activated benzylic C–H bond of the benzylamine to provide the corresponding imine derivative. Then the imine on subsequent reaction with water or another molecule of benzylamine produces an aldehyde and/or imine, respectively. Hydroxylamine also reacts with another molecule of nitrosoarene to provide the observed azoxyarene. We anticipated that developing reaction conditions that facilitate the dehydration of *N*-hydroxyhydrazine derivative **II** instead of elimination of *N*-arylhydroxylamine would provide the possibility of forming the corresponding azo compounds or their tautomers. To our surprise, to the best our knowledge, there are no previous reports of the reaction of nitrosoarenes and benzylamines providing a benzyl-aryl azo compounds or their tautomers. Herein, we report the first example of Brønsted acid mediated direct N-amination of benzylamines using nitrosoarenes to provide the corresponding hydrazones. Similar N-amination of N-heterocycles provided corresponding hydrazide derivatives (Scheme 1c).



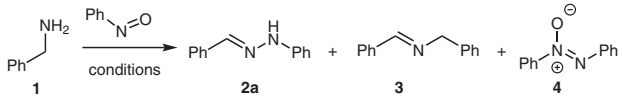
Scheme 1 Reaction of amines with nitrosoarenes

The hydrazones are an important class of compounds that find application in organic synthesis, medicinal chemistry, and supramolecular chemistry including metal and

covalent organic frameworks.[9] Hydrazone derivatives are also found as a key unit of fluorescent chemosensors.[10] The classical condensation of arylhydrazines with an aldehyde and coupling of hydrazines with an alcohol are mainly used for the synthesis of hydrazone derivatives.[11] However, the synthetic utility of these methods are greatly restricted because of the limited availability of arylhydrazines due to their inherent instability issues and difficulties in their synthesis.[12] Therefore, the development of an alternative method for the synthesis of arylhydrazones from readily available starting material is essential.[13]

Based on our hypothesis, nitrosobenzene was reacted with benzylamine in the presence of 2,4-dichlorobenzoic acid (DCBA), which is used to facilitate dehydration (Table 1, entry 1). As expected the desired hydrazone **2a** was formed in 20% yield along with the oxidized product **3** and azoxybenzene **4**. With this initial result in hand, further experiments were carried out to optimize the reaction conditions towards better yields of the hydrazone. The yield of the reaction improved slightly when the reaction was carried out in the presence of acetic acid (entry 2). The reaction at a lower temperature in refluxing dichloromethane gave a similar yield (entry 3). However, the yield of the product significantly increases with increasing reaction time (entry 7). The poor yields were obtained when the reaction was carried out either in the absence of acid or in the presence of higher amount of acetic acid (2 equiv) (entries 9 and 10).

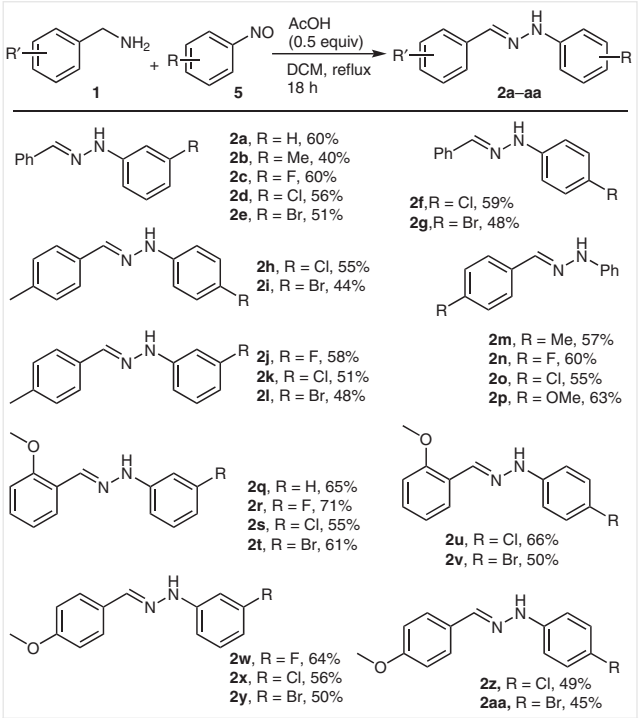
Table 1 Optimization of Reaction Conditions[a]



Entry	Conditions	**2a**[b] (%)	**3**[c] (%)	**4**[c] (%)
1[d]	DCBA (0.6 equiv), toluene, reflux, 8 h	20	27	21
2[d]	AcOH (0.6 equiv), toluene, reflux, 8 h	30	24	20
3[e]	AcOH (0.6 equiv), DCM, reflux, 8 h	38	36	17
4[e]	AcOH (0.6 equiv), DCM, reflux, 15 h	41	33	16
5	AcOH (0.6 equiv), DCM, reflux, 15 h	53	nd	nd
6	AcOH (0.5 equiv), DCM, reflux, 15 h	56	nd	nd
7	AcOH (0.5 equiv), DCM, reflux, 18 h	60	9	11
8[f]	AcOH (0.5 equiv), DCM, reflux, 18 h	55	nd	nd
9	DCM, reflux, 18 h	36	nd	nd
10	AcOH (2.0 equiv), DCM, reflux, 18 h	47	nd	nd

[a] Reaction conditions: benzylamine (0.37 mmol), nitrosobenzene (0.37 mmol), solvent (3.0 mL), unless otherwise stated.
[b] Isolated yield calculated with respect to nitrosobenzene.
[c] Isolated yield of **3** and **4** were calculated with respect to benzylamine and nitrosobenzene, respectively, considering maximum possible yield as 50%; nd = not determined.
[d] Benzylamine (4 equiv) was used.
[e] Benzylamine (2 equiv) was used.
[f] Nitrosobenzene (1.5 equiv) was used.

Next, we investigated the substrate scope of this reaction using the optimal reaction condition. Reactions of benzylamine with various nitrosoarenes were studied first (Scheme 2). Nitrosoarenes containing both electron-donating and electron-withdrawing groups participated in the N-amination reaction with benzylamines to give the corresponding hydrazones **2a–aa** in moderate to good yields. The reaction with halogen-substituted nitrosoarenes provided the better yields of the desired hydrazones **2c–e** as compared to the hydrazone **2b** that is obtained from the reaction with methyl-substituted nitrosoarene. The reactions of various benzylamines with nitrosobenzene were investigated next. The studies revealed that the benzylamines containing Me, OMe, Cl, F, etc. gave the desired products in good yields.

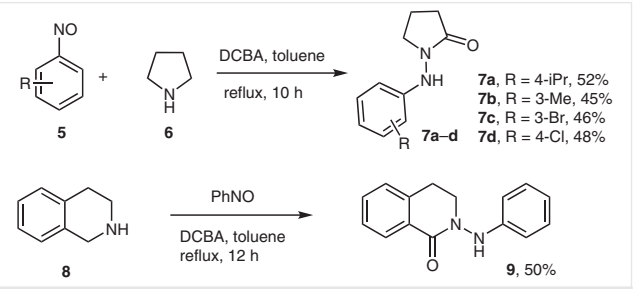


Scheme 2 Substrate scope of the N-amination reaction

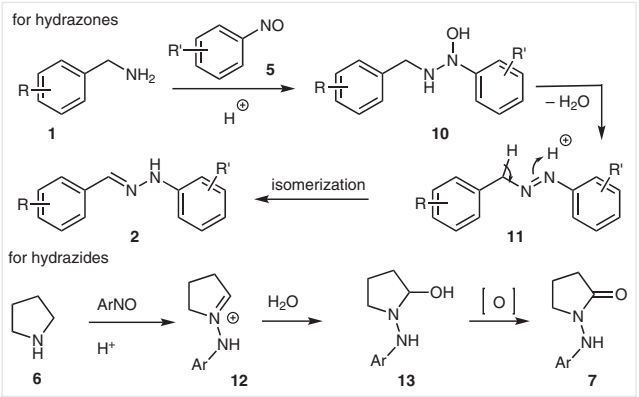
The electron-donating group in the benzylamine makes it more nucleophilic and an electron-withdrawing group makes the nitrosoarene more electrophilic. Therefore, benzylamines with electron-donating groups (Me, OMe) reacted efficiently with the nitrosoarene having electron-withdrawing groups (Cl, F, Br, etc.) to provide the desired hydrazones **2h–aa** in good yields.

The reactions of alicyclic amines with the nitrosoarene were tested next. Accordingly, pyrrolidine was reacted with an nitrosoarene under standard conditions. Surprisingly, the reaction of pyrrolidine with various nitrosoarenes provided hydrazide derivatives **7a–d** in 45–52% yields (Scheme 3). The structure of the **7b** was confirmed from the X-ray

structure (Figure 1). A similar result was also observed for the tetrahydroisoquinoline, which gave the corresponding hydrazide **9** in 50% yield.



Scheme 3 N-Amination of N-heterocycles to hydrazides



Scheme 4 Proposed mechanism of N-amination reaction

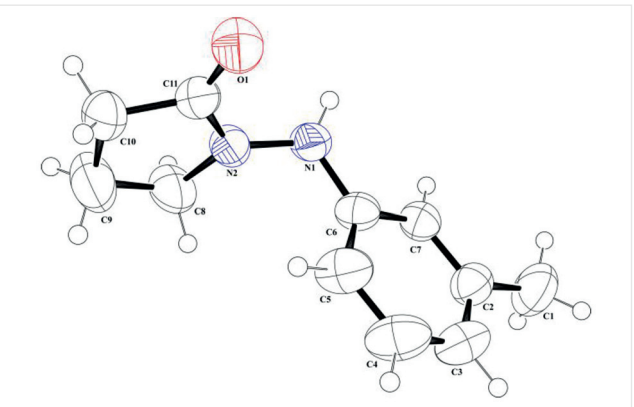
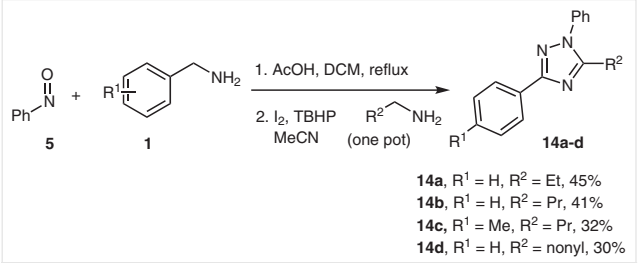


Figure 1 ORTEP diagram of **7b** (with ellipsoid contour 35%)



Scheme 5 Direct synthesis of triazoles starting from nitrosoarenes and amines

A plausible mechanism for the formation of hydrazones and hydrazides is presented in Scheme 4. Analogous to the reaction of amines with carbonyl compounds, nucleophilic addition of amines **1** to the nitrosoarenes **5** occurs to provide hydroxylamine derivative **10**.[1a,7a] Acid-mediated dehydration of **10** produces the corresponding arylazoalkanes derivative **11**, which isomerizes readily to provide the observed hydrazone **2**.[14] A similar intermediate **12** is formed from the reaction of nitrosoarene and N-heterocycles. The iminium intermediate **12** is trapped by H_2O to provide the corresponding hemiaminal **13** which upon subsequent oxidation gives the hydrazide **7**.[15]

Hydrazones are reacted with primary amines in the presence of iodine and *tert*-butyl hydroperoxide (TBHP) for the synthesis of triazoles;[16] they are an important scaffold in biological, pharmaceuticals, and medicinal chemistry.[17] Therefore, we wanted to employ our N-amination reaction for the synthesis of triazoles directly starting from amines and nitrosoarenes. Accordingly, benzylamines were N-aminated under standard conditions to give the corresponding hydrazones that were further reacted with alkylamines in the presence of iodine and TBHP in the same pot to provide the corresponding triazoles **14a–d** with acceptable yields (Scheme 5).

In summary, we have developed an unprecedented N-amination reaction of benzylamines and N-heterocycles with the nitrosoarenes to provide hydrazones and hydrazides, respectively. The use of Brønsted acid facilitated dehydration reaction in comparison to undesired hydroxylamine elimination to achieve the difficult N-amination of benzylamines. A wide range of benzylamines and N-heterocycles reacted efficiently with the readily available nitrosoarenes to provide the corresponding hydrazone and hydrazide derivatives, respectively. This unconventional method for hydrazone synthesis does not involve hydrazines and thus issues relating to the preparation and the stability of hydrazines can be avoided. Moreover, this N-amination reaction was successfully applied in a one-pot synthesis of triazoles.

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (DCM) was freshly distilled from P_2O_5. Commercial grade xylene, benzene, and toluene were distilled over CaH_2 before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck, and Spectrochem. ^1H and ^{13}C NMR spectroscopy: Varian Mercury plus 400 MHz, Bruker 600 MHz (at 298 K), and reported relative to TMS δ = 0 (^1H), δ = 0 (^{13}C), which was used as the inner reference.

Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^1H) = 7.26, δ (^{13}C) = 77.23) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60–120 under gravity. IR: spectra were recorded on a Perkin Elmer Instrument at r.t. as a KBr pellet (IR Grade). MS (ESI-HRMS): mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m*/*z* (% of basis peak). Nitrosoarenes are prepared according to the known procedures.

Hydrazone Derivatives 2; General Procedure I

Freshly prepared nitrosoarene **5** (1 equiv) and AcOH (0.5 equiv) were successively added to a solution of benzylamine **1** (1 equiv) in DCM (3–4 mL); the mixture was refluxed for 15–24 h under an argon atmosphere. The solvent was evaporated under reduced pressure and the crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

(*E*)-1-Benzylidene-2-phenylhydrazine (2a)[13c]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2a** (44 mg, 60%) as a white solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 3 H), 7.40–7.37 (m, 2 H), 7.33–7.28 (m, 3 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 6.89 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.8, 137.5, 135.5, 129.5 (2 C), 128.8 (2 C), 128.6, 126.4 (2 C), 120.3, 112.9 (2 C).

(*E*)-1-Benzylidene-2-(*m*-tolyl)hydrazine (2b)

According to GP I: 1-methyl-3-nitrosobenzene[18a] (45 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2b** (31 mg, 40%) as a yellow gum.

FTIR (KBr): 2956, 2924, 2854, 1587, 1490, 1464, 1376, 1262, 1209, 1097, 1020, 802, 691 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.66 (s, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.32–7.29 (m, 1 H), 7.17 (t, *J* = 7.8, Hz, 1 H), 6.98 (s, 1 H), 6.91 (d, *J* = 7.8 Hz, 1 H), 6.71 (d, *J* = 7.2 Hz, 1 H), 2.36 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.8, 139.4, 137.3, 135.5, 129.4, 128.8 (2 C), 128.6, 126.4 (2 C), 121.2, 113.6, 110.2, 21.9.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{15}N_2$: 211.1230; found: 211.1230.

(*E*)-1-Benzylidene-2-(3-fluorophenyl)hydrazine (2c)

According to GP I: 1-fluoro-3-nitrosobenzene[18b] (46 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2c** (48 mg, 60%) as white solid; mp 113–114 °C.

FTIR (KBr): 3317, 2960, 2924, 1615, 1518, 1490, 1443, 1263, 1070, 798, 679 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.70 (s, 1 H), 7.67–7.66 (m, 2 H), 7.40–7.37 (m, 2 H), 7.33–7.31 (m, 1 H), 7.21–7.18 (m, 1 H), 6.96–6.93 (m, 1 H), 6.78–6.77 (m, 1 H), 6.57–6.54 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.0, 163.4, 146.6, 146.5, 138.3, 135.1, 130.63, 130.57, 129.0, 128.9 (2 C), 126.5 (2 C), 108.43, 108.41, 106.8, 106.7, 100.3, 100.2.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{12}N_2F$: 215.0979; found: 215.0979.

(*E*)-1-Benzylidene-2-(3-chlorophenyl)hydrazine (2d)[18c]

According to GP I: 1-chloro-3-nitrosobenzene[3h] (53 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2d** (48 mg, 56%) as a white solid.

FTIR (KBr): 3323, 2958, 2918, 1592, 1508, 1483, 1300, 1129, 1091, 991, 852, 694 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.67–7.66 (m, 3 H), 7.40–7.38 (m, 2 H), 7.34–7.31 (m, 1 H), 7.19–7.16 (m, 2 H), 6.92–6.90 (m, 1 H), 6.83 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.9, 138.5, 135.4, 135.0, 130.5, 129.0, 128.9 (2 C), 126.5 (2 C), 120.1, 112.9, 111.1.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{12}N_2Cl$: 231.0684; found: 231.0684.

(*E*)-1-Benzylidene-2-(3-bromophenyl)hydrazine (2e)[18d]

According to GP I: 1-bromo-3-nitrosobenzene[3h] (69 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2e** (52 mg, 51%) as a white solid.

FTIR (KBr): 3322, 2956, 2923, 2855, 1589, 1567, 1478, 1287, 1240, 1131, 984, 776, 694 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.67–7.66 (m, 3 H), 7.60 (s, 1 H), 7.40–7.38 (m, 2 H), 7.35–7.32 (m, 2 H), 7.13–7.10 (m, 1 H), 6.99–6.95 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.0, 138.6, 135.0, 130.7, 129.0, 128.9 (2 C), 126.6 (2 C), 123.5, 123.0, 115.8, 111.5.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{12}N_2Br$: 275.0178; found: 275.0178.

(*E*)-1-Benzylidene-2-(4-chlorophenyl)hydrazine (2f)[13c]

According to GP I: 1-chloro-4-nitrosobenzene[3h] (53 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2f** (50 mg, 59%) as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.65 (d, *J* = 7.2 Hz, 2 H), 7.40–7.36 (m, 2 H), 7.33–7.29 (m, 1 H), 7.23 (d, *J* = 8.8 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H).

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{12}N_2Cl$: 231.0684; found: 231.0684.

(*E*)-1-Benzylidene-2-(4-bromophenyl)hydrazine (2g)

According to GP I: 1-bromo-4-nitrosobenzene[3h] (69 mg, 0.37 mmol), benzylamine (40 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2g** (49 mg, 48%) as a white solid; mp 125 °C.

FTIR (KBr): 3339, 2962, 2923, 2853, 1650, 1484, 1401, 1257, 1067, 1027, 812, 691 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.65 (d, *J* = 7.2 Hz, 2 H), 7.39–7.35 (m, 4 H), 7.33–7.30 (m, 1 H), 7.00 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.9, 138.2, 135.2, 132.3 (2 C), 128.91, 128.86 (2 C), 126.5 (2 C), 114.5 (2 C), 112.0.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{12}N_2Br$: 275.0178; found: 275.0167.

(*E*)-1-(4-Chlorophenyl)-2-(4-methylbenzylidene)hydrazine (2h)

According to GP I: 1-chloro-4-nitrosobenzene (53 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2h** (50 mg, 55%) as a white solid; mp 155–156 °C.

FTIR (KBr): 3320, 2960, 2923, 2856, 1598, 1500, 1408, 1253, 1092, 827 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.65 (s, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 2.37 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.6, 139.0, 138.4, 132.4, 129.6 (3 C), 129.4, 126.4 (3 C), 124.6, 114.0, 21.6.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N_2Cl$: 245.0840; found: 245.0840.

(*E*)-1-(4-Bromophenyl)-2-(4-methylbenzylidene)hydrazine (2i)

According to GP I: 1-bromo-4-nitrosobenzene (69 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2i** (47 mg, 44%) as a white solid; mp 160–162 °C.

FTIR (KBr): 2923, 2854, 1592, 1501, 1402, 1248, 1068, 820 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 2.37 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.0, 139.0, 138.5, 132.4, 132.2 (2 C), 129.6 (2 C), 126.4 (2 C), 114.5 (2 C), 111.8, 21.6.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N_2Br$: 289.0335; found: 289.0333.

(*E*)-1-(3-Fluorophenyl)-2-(4-methylbenzylidene)hydrazine (2j)

According to GP I: 1-fluoro-3-nitrosobenzene (46 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2j** (49 mg, 58%) as a white solid; mp 111–113 °C.

FTIR (KBr): 3319, 2960, 1613, 1589, 1490, 1257, 1140, 764, 515 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 1 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.21–7.15 (m, 3 H), 6.95–6.91 (m, 1 H), 6.77–6.75 (m, 1 H), 6.56–6.51 (m, 1 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.9, 146.7, 139.1, 138.7, 132.4, 130.6, 130.5, 129.6 (2 C), 126.5 (2 C), 108.43, 108.41, 106.7, 106.5, 100.4, 100.1, 21.6.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N_2F$: 229.1136; found: 229.1147.

(*E*)-1-(3-Chlorophenyl)-2-(4-methylbenzylidene)hydrazine (2k)

According to GP I: 1-chloro-3-nitrosobenzene (53 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2k** (46 mg, 51%) as a white solid; mp 116–118 °C.

FTIR (KBr): 3312, 2924, 2854, 1592, 1501, 1482, 1241, 1131, 1090, 991, 856, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.50 (s, 1 H), 7.21–7.15 (m, 4 H), 6.91–6.89 (m, 1 H), 6.84–6.82 (m, 1 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.1, 139.1, 138.9, 135.3, 132.4, 130.4, 129.6 (2 C), 126.5 (2 C), 120.0, 112.9, 111.1, 21.6.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N_2Cl$: 245.0840; found: 245.0840.

(*E*)-1-(3-Bromophenyl)-2-(4-methylbenzylidene)hydrazine (2l)

According to GP I: 1-bromo-3-nitrosobenzene (69 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2l** (51 mg, 48%) as a white solid; mp 116–118 °C.

FTIR (KBr): 3313, 3029, 2950, 2912, 1589, 1497, 1238, 1130, 1063, 988, 817, 682 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 2.0 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.10 (t, *J* = 8.0 Hz, 1 H), 6.98–6.93 (m, 2 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.2, 139.2, 138.9, 132.3, 130.7, 129.6 (2 C), 126.6 (2 C), 123.5, 122.9, 115.8, 111.5, 21.6.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N_2Br$: 289.0335; found: 289.0337.

(*E*)-1-(4-Methylbenzylidene)-2-phenylhydrazine (2m)[13c]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), 4-methylbenzylamine (45 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2m** (44 mg, 57%) as a white solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.68 (s, 1 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.0, 138.7, 137.7, 132.7, 129.54 (2 C), 129.49 (2 C), 126.4 (2 C), 120.1, 112.9 (2 C), 21.6.

(*E*)-1-(4-Fluorobenzylidene)-2-phenylhydrazine (2n)[13c]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), 4-fluorobenzylamine (46 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2n** (47 mg, 60%) as a white solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 3 H), 7.30–7.27 (m, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 7.08–7.05 (m, 2 H), 6.90–6.87 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3, 161.8, 144.8, 136.3, 131.7, 129.5 (2 C), 128.0, 127.9, 120.4, 116.0, 115.8, 112.9 (2 C).

(*E*)-1-(4-Chlorobenzylidene)-2-phenylhydrazine (2o)[13c]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), 4-chlorobenzylamine (53 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:15) gave **2o** (47 mg, 55%) as a white solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.64 (s, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 9.0 Hz, 2 H), 7.30–7.27 (m, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 6.90–6.88 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.6, 136.0, 134.2, 134.0, 129.5 (2 C), 129.0 (2 C), 127.5 (2 C), 120.6, 113.0 (2 C).

(*E*)-1-(4-Methoxybenzylidene)-2-phenylhydrazine (2p)[13c]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2p** (53 mg, 63%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (s, 1 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.28 (t, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 6.91 (d, *J* = 9.0 Hz, 2 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 3.84 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.2, 145.2, 137.6, 129.5 (2 C), 128.3, 127.8 (2 C), 120.0, 114.3 (2 C), 112.9 (2 C), 55.5.

(*E*)-1-(2-Methoxybenzylidene)-2-phenylhydrazine (2q)[18e]

According to GP I: nitrosobenzene (40 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2q** (54 mg, 65%) as a yellow gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 8.00–7.98 (m, 1 H), 7.30–7.27 (m, 3 H), 7.11 (d, *J* = 7.6 Hz, 2 H), 6.99 (t, *J* = 7.6 Hz, 1 H), 6.91–6.85 (m, 2 H), 3.87 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.2, 145.0, 133.7, 129.8, 129.5 (2 C), 126.1, 124.0, 121.2, 120.2, 113.0 (2 C), 111.2, 55.6.

(*E*)-1-(3-Fluorophenyl)-2-(2-methoxybenzylidene)hydrazine (2r)

According to GP I: 1-fluoro-3-nitrosobenzene (46 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol mmol) in DCM (4 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2r** (64 mg, 71%) as a yellow gum.

FTIR (KBr): 2926, 2847, 1613, 1601, 1518, 1486, 1288, 1248, 1139, 1023, 756, 683 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 8.00–7.98 (m, 1 H), 7.67 (s, 1 H), 7.32–7.28 (m, 1 H), 7.21–7.15 (m, 1 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 6.95–6.92 (m, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 6.77–6.75 (m, 1 H), 6.56–6.51 (m, 1 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 163.0, 157.2, 146.9, 146.8, 134.5, 130.6, 130.5, 130.0, 126.1, 123.7, 121.2, 111.2, 108.40, 108.38, 106.6, 106.3, 100.3, 100.0, 55.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}FN_2O$: 245.1085; found: 245.1100.

(*E*)-1-(3-Chlorophenyl)-2-(2-methoxybenzylidene)hydrazine (2s)

According to GP I: 1-chloro-3-nitrosobenzene (53 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2s** (53 mg, 55%) as a yellow gum.

FTIR (KBr): 3068, 2956, 2924, 2849, 1597, 1518, 1478, 1326, 1241, 1095, 1020, 853, 756, 606 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 8.00–7.97 (m, 1 H), 7.32–7.27 (m, 1 H), 7.18–7.14 (m, 2 H), 7.02–6.98 (m, 1 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 6.82–6.80 (m, 1 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.3, 146.2, 135.4, 134.7, 130.4, 130.1, 126.1, 123.7, 121.2, 119.9, 112.9, 111.2, 111.0, 55.8.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}ClN_2O$: 261.0789; found: 261.0788.

(*E*)-1-(3-Bromophenyl)-2-(2-methoxybenzylidene)hydrazine (2t)

According to GP I: 1-bromo-3-nitrosobenzene (69 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2t** (69 mg, 61%) as a yellow gum.

FTIR (KBr): 2960, 2916, 2848, 1639, 1598, 1466, 1249, 1103, 1022, 753, 674 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.99–7.98 (m, 1 H), 7.33 (t, *J* = 1.8 Hz, 1 H), 7.31–7.28 (m, 1 H), 7.11–7.08 (m, 1 H), 7.01–6.99 (m, 1 H), 6.96–6.93 (m, 2 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.2, 146.3, 134.7, 130.7, 130.1, 126.1, 123.6, 123.5, 122.8, 121.2, 115.7, 111.4, 111.1, 55.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}BrN_2O$: 305.0284; found: 305.0279.

(*E*)-1-(4-Chlorophenyl)-2-(2-methoxybenzylidene)hydrazine (2u)

According to GP I: 1-chloro-4-nitrosobenzene (53 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2u** (64 mg, 66%) as a yellow gum.

FTIR (KBr): 3080, 2960, 2924, 2852, 1599, 1490, 1437, 1242, 1092, 1019, 822, 756, 606 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.98–7.96 (m, 1 H), 7.30–7.27 (m, 1 H), 7.22–7.19 (m, 2 H), 7.04–7.02 (m, 2 H), 7.00–6.98 (m, 1 H), 6.90–6.88 (m, 1 H), 3.86 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.1, 143.7, 134.2, 130.0, 129.3 (2 C), 125.9, 124.5, 123.7, 121.1, 113.9 (2 C), 111.1, 55.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}ClN_2O$: 261.0789; found: 261.0787.

(*E*)-1-(4-Bromophenyl)-2-(2-methoxybenzylidene)hydrazine (2v)

According to GP I: 1-bromo-4-nitrosobenzene (69 mg, 0.37 mmol), 2-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2v** (56 mg, 50%) as a yellow gum.

FTIR (KBr): 2958, 2924, 2849, 1598, 1488, 1437, 1243, 1070, 1020, 822, 755, 606 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.98–7.95 (m, 1 H), 7.36–7.33 (m, 2 H), 7.31–7.27 (m, 1 H), 7.01–6.97 (m, 3 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.2, 144.2, 134.4, 132.2 (2 C), 130.0, 126.0, 123.8, 121.2, 114.5 (2 C), 111.8, 111.2, 55.78.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}BrN_2O$: 305.0284; found: 305.0293.

(*E*)-1-(3-Fluorophenyl)-2-(4-methoxybenzylidene)hydrazine (2w)

According to GP I: 1-fluoro-3-nitrosobenzene (46 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2w** (58 mg, 64%) as a white solid; mp 120–122 °C.

FTIR (KBr): 3310, 2964, 2921, 2837, 1614, 1495, 1413, 1261, 1175, 917, 840, 687 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (s, 1 H), 7.60 (d, *J* = 9.0 Hz, 2 H), 7.20–7.16 (m, 1 H), 6.92 (d, *J* = 9.0 Hz, 3 H), 6.75–6.74 (m, 1 H), 6.55–6.52 (m, 1 H), 3.84 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.0, 163.4, 160.4, 146.9, 146.8, 138.4, 130.6, 130.5, 127.94 (2 C), 127.90, 114.3 (2 C), 108.31, 108.29, 106.5, 106.3, 100.2, 100.0, 55.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}FN_2O$: 245.1085; found: 245.1085.

(*E*)-1-(3-Chlorophenyl)-2-(4-methoxybenzylidene)hydrazine (2x)

According to GP I: 1-chloro-3-nitrosobenzene (53 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2x** (54 mg, 56%) as a white solid; mp 132–133 °C.

FTIR (KBr): 3313, 2964, 2922, 2831, 1594, 1485, 1295, 1251, 1172, 1026, 917, 767, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 3 H), 7.18–7.14 (m, 2 H), 6.93–6.90 (m, 2 H), 6.90–6.87 (m, 1 H), 6.83–6.80 (m, 1 H), 3.84 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5, 146.3, 138.7, 135.3, 130.4, 128.0 (2 C), 127.9, 119.8, 114.4 (2 C), 112.8, 111.0, 55.5.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}ClN_2O$: 261.0789; found: 261.0788.

(*E*)-1-(3-Bromophenyl)-2-(4-methoxybenzylidene)hydrazine (2y)

According to GP I: 1-bromo-3-nitrosobenzene (69 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (4 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2y** (56 mg, 50%) as a white solid; mp 132–133 °C.

FTIR (KBr): 3300, 2960, 2926, 2839, 1592, 1500, 1415, 1290, 1170, 1023, 840, 675 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1 H), 7.60–7.57 (m, 2 H), 7.31 (t, *J* = 2.0 Hz, 1 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.97–6.90 (m, 4 H), 3.84 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5, 146.4, 138.7, 130.7, 128.0 (2 C), 127.9, 123.5, 122.7, 115.7, 114.4 (2 C), 111.4, 55.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}BrN_2O$: 305.0284; found: 305.0280.

(*E*)-1-(4-Chlorophenyl)-2-(4-methoxybenzylidene)hydrazine (2z)[18f]

According to GP I: 1-chloro-4-nitrosobenzene (53 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2z** (47 mg, 49%) as a white solid.

FTIR (KBr): 3310, 2958, 2925, 2839, 1606, 1488, 1459, 1411, 1252, 1171, 1092, 915, 818, 646 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 9.0 Hz, 2 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 3.84 (s, 3 H).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}ClN_2O$: 261.0789; found: 261.0788.

(*E*)-1-(4-Bromophenyl)-2-(4-methoxybenzylidene)hydrazine (2aa)[18f]

According to GP I: 1-bromo-4-nitrosobenzene (69 mg, 0.37 mmol), 4-methoxybenzylamine (51 mg, 0.37 mmol), and AcOH (11 μL, 0.19 mmol) in DCM (3 mL) were refluxed for 18 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:10) gave **2aa** (51 mg, 45%) as a white solid.

FTIR (KBr): 3307, 2962, 2928, 2829, 1604, 1505, 1486, 1407, 1252, 1172, 1024, 818, 642 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.58 (d, *J* = 8.8 Hz, 2 H), 7.46 (s, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.4, 144.2, 138.3, 132.2 (2 C), 128.0, 127.9 (2 C), 114.43 (2 C), 114.37 (2 C), 111.7, 55.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}BrN_2O$: 305.0284; found: 305.0292.

Hydrazide Derivatives 7 and 9; General Procedure II

Freshly prepared nitrosoarene **5** (1 equiv) and 2,4-dichlorobenzoic acid (0.5 equiv) were successively added to a solution of cyclic secondary amine **6** or **8** (4 equiv) in toluene (3 mL). The mixture was refluxed for 10–12 h under an argon atmosphere. The solvent was evaporated under reduced pressure and crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

1-[(4-Isopropylphenyl)amino]pyrrolidin-2-one (7a)

According to GP II: 1-isopropyl-4-nitrosobenzene (37 mg, 0.25 mmol), pyrrolidine (82 μL, 1.00 mmol), and DCBA (24 mg, 0.12 mmol) in toluene (3 mL) were refluxed for 10 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:3) gave **7a** (29 mg, 52%) as a brown gum.

FTIR (KBr): 2962, 2924, 2853, 1696, 1589, 1514, 1455, 210, 1099, 803, 608 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.04 (s, 1 H), 3.63–3.60 (m, 2 H), 2.87–2.80 (m, 1 H), 2.48 (t, *J* = 8.0 Hz, 2 H), 2.18–2.11 (m, 2 H), 1.20 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.1, 144.1, 142.5, 127.5 (2 C), 114.2 (2 C), 48.5, 33.6, 29.2, 24.4 (2 C), 16.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}N_2O$: 219.1492; found: 219.1502.

1-(*m*-Tolylamino)pyrrolidin-2-one (7b)

According to GP II: 1-methyl-3-nitrosobenzene (30 mg, 0.25 mmol), pyrrolidine (82 μL, 1.00 mmol), and DCBA (24 mg, 0.12 mmol) in toluene (3 mL) were refluxed for 10 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:3) gave **7b** (21 mg, 45%) as a white solid; mp 123–125 °C.

FTIR (KBr): 2956, 2923, 2854, 1697, 1609, 1490, 1415, 1264, 1381, 1019, 777, 541 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.10 (m, 1 H), 6.73 (d, *J* = 7.6 Hz, 1 H), 6.57–6.55 (m, 2 H), 6.03 (s, 1 H), 3.63–3.60 (m, 2 H), 2.49 (t, *J* = 8.0 Hz, 2 H), 2.29 (s, 3 H), 2.19–2.12 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.2, 146.3, 139.5, 129.4, 122.6, 114.6, 111.0, 48.5, 29.1, 21.8, 16.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{15}N_2O$: 191.1179; found: 191.1179.

1-[(3-Bromophenyl)amino]pyrrolidin-2-one (7c)

According to GP II: 1-bromo-3-nitrosobenzene (46 mg, 0.25 mmol), pyrrolidine (82 μL, 1.00 mmol), and DCBA (24 mg, 0.12 mmol) in toluene (3 mL) were refluxed for 10 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:3) gave **7c** (29 mg, 46%) as a light yellow gum.

FTIR (KBr): 2963, 2925, 2851, 1699, 1595, 1524, 1476, 1294, 1262, 1096, 1021, 801, 682 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (t, *J* = 8.0 Hz, 1 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 6.85 (s, 1 H), 6.66 (d, *J* = 8.8 Hz, 1 H), 6.25 (s, 1 H), 3.62–3.58 (m, 2 H), 2.52–2.47 (m, 2 H), 2.21–2.13 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.4, 147.8, 130.9, 124.4, 123.5, 116.4, 112.4, 48.4, 29.0, 16.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{12}N_2BrO$: 255.0128; found: 255.0124.

1-[(4-Chlorophenyl)amino]pyrrolidin-2-one (7d)

According to GP II: 1-chloro-4-nitrosobenzene (35 mg, 0.25 mmol), pyrrolidine (82 μL, 1.00 mmol), and DCBA (24 mg, 0.12 mmol) in toluene (3 mL) were refluxed for 10 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:3) gave **7d** (25 mg, 48%) as a light yellow gum.

FTIR (KBr): 2960, 2924, 2853, 1696, 1596, 1491, 1417, 1261, 1091, 1020, 822, 630 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 6.12 (s, 1 H), 3.62–3.58 (m, 2 H), 2.51–2.47 (m, 2 H), 2.22–2.12 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.3, 145.0, 129.5 (2 C), 126.5, 115.1 (2 C), 48.4, 29.0, 16.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{12}N_2ClO$: 211.0633; found: 211.0634.

2-(Phenylamino)-3,4-dihydroisoquinolin-1(2*H*)-one (9)

According to GP II: nitrosobenzene (27 mg, 0.25 mmol), tetrahydroisoquinoline (0.13 mL, 1.00 mmol), and DCBA (24 mg, 0.12 mmol) in toluene (3 mL) were refluxed for 12 h. Column chromatography of crude product (silica gel, EtOAc/hexane, 1:3) gave **9** (30 mg, 50%) as a white solid; mp 155–156 °C.

FTIR (KBr): 2956, 2925, 2854, 1599, 1464, 1211, 1071, 1019, 719, 606 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.6 Hz, 1 H), 7.49–7.46 (m, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.28 (s, 1 H), 7.24 (s, 1 H), 7.00 (s, 1 H), 6.96–6.91 (m, 3 H), 3.87 (t, *J* = 6.8 Hz, 2 H), 3.26–3.23 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.1, 147.1, 138.2, 132.5, 129.5 (2 C), 128.7, 128.6, 127.5, 127.4, 121.9, 114.4 (2 C), 49.8, 28.6.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}N_2O$: 239.1179; found: 239.1178.

One-Pot Synthesis of Triazoles 14; General Procedure III

Freshly prepared nitrosoarenes (1 equiv), and AcOH were successively added to a solution of benzylamines (1 equiv) in DCM (3–4 mL). The mixture was refluxed for 18 h under an argon atmosphere. The mixture was evaporated to dryness, and MeCN (2 mL) was added. Next, primary amine (3 equiv), molecular I_2 (20 mol%), and aq TBHP (3 equiv) were added successively and the mixture was refluxed at 90 °C for an additional 4 h. The mixture was cooled to r.t., water (15 mL) was added to the mixture, and it was extracted with DCM (3 × 30 mL). The combined organic layers were washed with 10% $Na_2S_2O_3$ solution, dried (anhyd Na_2SO_4), and concentrated in vacuo to provide crude product that was purified by column chromatography (silica gel) to give analytically pure product.

5-Ethyl-1,3-diphenyl-1*H*-1,2,4-triazole (14a)[16]

According to GP III: nitrosobenzene (50 mg, 0.47 mmol), benzylamine (50 mg, 0.47 mmol), and AcOH (14 μL, 0.24 mmol) in DCM (4 mL) were refluxed for 18 h. The mixture was evaporated to dryness and diluted with MeCN (2 mL). $PrNH_2$ (83 mg, 1.41 mmol), I_2 (24 mg, 0.094 mmol), and aq TBHP (127 mg, 1.41 mmol) were added and the mixture was heated at 90 °C for an additional 4 h. The crude product was purifying by column chromatography (silica gel, EtOAc/hexane, 1:10) to give **14a** (53 mg, 45%) as a yellow gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.16 (m, 2 H), 7.52–7.36 (m, 8 H), 2.87–2.82 (m, 2 H), 1.35 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.5, 158.0, 137.7, 131.1, 129.5 (2 C), 129.3, 129.0, 128.6 (2 C), 126.5 (2 C), 125.2 (2 C), 20.3, 12.5.

1,3-Diphenyl-5-propyl-1*H*-1,2,4-triazole (14b)[16]

According to GP III: nitrosobenzene (50 mg, 0.47 mmol), benzylamine (50 mg, 0.47 mmol), and AcOH (14 μL, 0.24 mmol) in DCM (4 mL) were refluxed for 18 h. The mixture was evaporated to dryness and diluted with MeCN (2 mL). $BuNH_2$ (0.10 g, 1.41 mmol), I_2 (24 mg, 0.094 mmol), and aq TBHP (127 mg, 1.41 mmol) were added and the mixture was heated at 90 °C for an additional 4 h. The crude product was purifying by column chromatography (silica gel, EtOAc/hexane, 1:10) to give **14b** (51 mg, 41%) as a yellow gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.17 (m, 2 H), 7.52–7.36 (m, 8 H), 2.80 (t, *J* = 7.6 Hz, 2 H), 1.86–1.77 (m, 2 H), 0.98–0.94 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.5, 157.0, 137.7, 131.1, 129.5 (2 C), 129.3, 129.0, 128.6 (2 C), 126.5 (2 C), 125.3 (2 C), 28.6, 21.5, 13.9.

1-Phenyl-5-propyl-3-(*p*-tolyl)-1*H*-1,2,4-triazole (14c)

According to GP III: nitrosobenzene (50 mg, 0.47 mmol), 4-methylbenzylamine (57 mg, 0.47 mmol), and AcOH (14 μL, 0.24 mmol) in DCM (4 mL) were refluxed for 18 h. The mixture was evaporated to dryness and diluted with MeCN (2 mL). $BuNH_2$ (0.10 g, 1.41 mmol), I_2 (24 mg, 0.094 mmol), and aq TBHP (127 mg, 1.41 mmol) were added and the mixture was heated at 90 °C for an additional 4 h. The crude product was purifying by column chromatography (silica gel, EtOAc/hexane, 1:10) to give **14c** (42 mg, 32%) as a yellow gum.

FTIR (KBr): 2960, 2926, 2854, 1639, 1598, 1501, 1468, 1347, 1111, 1020, 831, 751, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.54–7.44 (m, 5 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.82–2.78 (m, 2 H), 2.39 (s, 3 H), 1.86–1.77 (m, 2 H), 0.98–0.94 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.7, 157.0, 139.3, 137.88, 129.6 (2 C), 129.4 (2 C), 129.1, 128.4, 126.6 (2 C), 125.5 (2 C), 28.7, 21.7, 21.6, 14.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}N_3$: 278.1651; found: 278.1656.

5-Nonyl-1,3-diphenyl-1*H*-1,2,4-triazole (14d)

According to GP III: nitrosobenzene (50 mg, 0.47 mmol), benzylamine (50 mg, 0.47 mmol), and AcOH (14 μL, 0.24 mmol) in DCM (4 mL) were refluxed for 18 h. The mixture was evaporated to dryness and diluted with MeCN (2 mL). Decylamine (0.22 g, 1.41 mmol), I_2 (24 mg, 0.094 mmol), and aq TBHP (127 mg, 1.41 mmol) were added and the mixture was heated at 90 °C for an additional 4 h. The crude product was purifying by column chromatography (silica gel, EtOAc/hexane, 1:15) to give **14d** (49 mg, 30%) as a yellow gum.

FTIR (KBr): 3066, 2954, 2925, 2854, 1645, 1599, 1500, 1466, 1354, 1173, 1070, 1022, 763, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.15 (m, 2 H), 7.54–7.37 (m, 8 H), 2.84–2.80 (m, 2 H), 1.81–1.74 (m, 2 H), 1.35–1.23 (m, 12 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.6, 157.3, 137.8, 131.2, 129.6 (2 C), 129.3, 129.1, 128.7 (2 C), 126.6 (2 C), 125.4 (2 C), 32.0, 29.5, 29.38, 29.36, 29.3, 28.2, 26.8, 22.8, 14.3.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{30}N_3$: 348.2434; found: 348.2434.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610701. X-ray data and copies of NMR spectra are included.

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