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Photoinduced Cleavage of N–N Bonds of Aromatic Hydrazines and Hydrazides by Visible Light

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Abstract

A photocatalytic system involving $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$, visible light, and air has been developed for cleavage of the N–N bonds of hydrazines and hydrazides. This catalytic system is generally effective for N,N-disubstituted hydrazine and hydrazide derivatives, including arylhydrazides, *N*-alkyl-*N*-arylhydrazines, and *N*,*N*-diarylhydrazines. The utility of this cleavage reaction has been demonstrated by synthesizing a variety of secondary aromatic amines.

Keywords

nitrogen–nitrogen bonds; visible light; cleavage; ruthenium; amines

As our society becomes increasingly aware of the issue of environmental sustainability, green chemistry is gaining acceptance in industry and academia. The use of renewable and abundant sources such as visible light is becoming one of the key criteria for developing future ‘green’ methods. As such, the field of visible light photocatalysis has started to attract growing attention from the synthetic organic community.[1] Seminal works from MacMillan, Stephenson, Yoon, and others have shown the versatility of visible light induced reactions in organic synthesis by using ruthenium(II) or iridium(III) complexes or dyes as photocatalysts.[2–6]

Amines are routinely used as a sacrificial oxidant in these processes to reduce photoexcited organometallic complexes to ruthenium(I) or iridium(II) complexes while being oxidized to nitrogen radical cations (Scheme 1). Then carbon radicals generated through reduction by the ruthenium(I) or iridium(II) complexes undergo C–C bond formation in most of the reported reactions. On the other hand, the fate of the nitrogen radical cations is relatively unknown. We recently became interested in harnessing the synthetic potential of these nitrogen radical cations generated by visible light photocatalysis. Hydrazines and hydrazides were chosen initially in our studies because they are more easily oxidized than amines. Furthermore, they are useful precursors to generate amines or amides after cleavage of the N–N bonds.[7] This cleavage is often accomplished under strong reductive,[8] oxidative,[9] or other[10] relatively harsh conditions. Herein, we report cleavage of the N–N bonds of hydrazines and hydrazides using visible light photocatalysis under extremely mild conditions.[11]

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Our preliminary studies focused on the cleavage of the N–N bond of *N*-phenyl-*N*-benzoyl hydrazine (**1a**; Table 1). $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (**3a**)[12,13] was first examined as the photocatalyst using a 13 watt GE compact fluorescent light bulb as the light source. The reactions were carried out under an air atmosphere. Because the photocatalyst **3a** is insoluble or sparingly soluble in most solvents except acetonitrile, the reaction was initially carried out in acetonitrile with 2 mol% of **3a**. It was incomplete after 24 hours, providing 42% of the desired cleavage product, *N*-phenylbenzamide (**2a**) along with 44% of recovered **1a** (Table 1, entry 1). Addition of methanol to the reaction mixture (MeCN–MeOH, 1:1 v/v) greatly facilitated the cleavage and provided **2a** in 71% yield (100% conversion) after 24 hours (entry 2). The ratio of MeCN versus MeOH had little effect on the rate of cleavage, and **2a** was generated in similar yields (entry 3). Reducing the catalyst loading (1 mol% **3a**) reduced the yield of **2a** to 59%, with 6% of recovered **1a** (entry 4). Little or no conversion was observed when the reaction was conducted either in the absence of **3a** or in the dark (entries 5 and 6). Use of degassed MeCN and MeOH dramatically slowed down the reaction, and **2a** was isolated in only 13% yield after 40 hours (entry 7). This result hinted that oxygen might play a significant role in the cleavage of the N–N bond. Use of O_2 in the place of air did not improve the reaction and a lower yield (54% yield, 100% conversion) of **2a** was obtained after 24 hours (entry 8). Because the N–N bond cleavage of some electron-rich hydrazines is known to be realized by simple exposure to light, we subjected *N*-methyl-*N*-phenyl hydrazine (**1b**) to similar studies to those of **1a**. As expected, the cleavage was faster. Using only MeCN and 2 mol% **3a**, the desired cleavage product, *N*-methylaniline was obtained as its *N*-acetyl derivative **2b** in 82% yield after 24 hours (entry 9).[14] The use of MeOH as a co-solvent did not provide any benefit to either the reaction rate or the yield of **2b** (entry 10). The background reaction in the absence of the catalyst **3a** was faster than that of **1a**, yet it was still much slower than the catalyzed reaction (12% conversion after 48 h, entry 11).

We then compared $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (**3a**) against two other known ruthenium complexes (**3b**[4a] and **3c**[15]) and Rose Bengal (**3d**)[16] in the cleavage of the N–N bonds of **1a** and **1b** (Table 2). For hydrazides such as **1a**, among the three ruthenium complexes **3a–c** (entries 1–3), only **3a** showed sufficient efficiency to catalyze the cleavage reaction. Rose Bengal showed similar activity to **3a** but gave more side products (entry 4). For hydrazines such as **1b**, the three ruthenium complexes (**3a–c**) and Rose Bengal (**3d**) all led to completion of the cleavage of the N–N bond. Surprisingly, **3a** was the least active catalyst among the three ruthenium complexes (entry 5). Catalyst **3b** was more active than **3a** and **3c** but also gave more side products than the latter (entries 5–7). Rose Bengal (**3d**) was also more active than **3a** (entry 8). Similar to **1a**, the reaction catalyzed by Rose Bengal (**3d**) gave more side products than **3a**. Overall, **3a** was the optimal catalyst for both the hydrazines and hydrazides.

With the catalyst system optimized, we next applied it to a variety of hydrazine and hydrazide derivatives (Table 3). This catalytic system was found to be generally effective for N,N-disubstituted hydrazine and hydrazide derivatives including arylhydrazides, *N*-alkyl-*N*-arylhydrazines, and *N,N*-diarylhydrazines. Between the two substituents on the nitrogen atom, one needed to be an aryl group while the second could be an aryl, alkyl, or acyl group. Most of the substrates that meet this criterion gave the desired products in satisfactory yields. Electron-withdrawing substituents on the aromatic rings, such as a trifluoromethyl group, had little effect on the cleavage because **1c** behaved very similarly to **1d** (entries 1 and 2). Functional groups such as olefins and Cl were compatible with the reaction conditions (entries 3 and 6). Hydrazide derivatives containing heterocycles worked under the optimized conditions although they were not as effective as their counterparts with only aromatic rings (entry 4). The cleavage of a hydrazine substituted with a biaryl group

and an alkyl group also afforded the desired secondary amine in modest yield (entry 7). In this case, it appeared that the cleavage product decomposed under the cleavage reactions. To our surprise, tetra-substituted hydrazine derivatives were found to be inert under the optimized conditions (entry 8). Trisubstituted hydrazine derivatives, depending on the pattern of substituents, underwent one of the two types of oxidations to give either hydrazones or azo compounds. One was oxidation of N(H)R to form hydrazones (entries 9 and 10). The other was oxidative cleavage of the *N*-Me group followed by oxidation of the forming N–N bonds to provide azo compounds (entry 11).

Secondary aromatic amines are of great interest in many areas of chemistry because of the prevalence of these compounds in pharmaceuticals, materials, etc. Their preparation through nucleophilic amination has been recently popularized by the Goldberg reaction[17] and Buchwald–Hartwig amination.[18] On the other hand, synthesis of the secondary aromatic amines through electrophilic amination has received much less attention. Knochel recently reported an electrophilic amination protocol for the synthesis of diarylamines that involves addition of nucleophilic aryl donors to arylazo tosylates followed by cleavage of N–N bonds (Scheme 2).[7a] Excess allyl iodide (3 equiv) and zinc (10 equiv) were required for the cleavage of the N–N bonds. Separately, Mäeorg reported that a number of alkyl and aromatic nucleophiles were efficiently added to *N*-*tert*-butoxycarbonylaryldiazenes to generate Boc-protected hydrazines.[19] Although *N*-*tert*-butoxycarbonylaryldiazenes are potentially a synthon of 'ArNH(+)', the author did not pursue the further conversion of the addition product, Boc-protected hydrazines, to secondary aromatic amines. We felt that, coupled with Mäeorg's method, our photochemistry could be developed into an efficient electrophilic amination protocol that is complementary to Knochel's. As shown in Table 4, we were able to add a wide variety of nucleophiles, including aryl boronic acids [catalyzed by $Cu(OAc)_2$], alkyl lithiums, aryl lithiums, aryl Grignard reagents, and lithium amide enolates, to *N*-*tert*-butoxycarbonylaryldiazenes. The Boc group of the hydrazines was easily removed by treatment with trifluoroacetic acid (TFA). Some of the deprotected hydrazines were not stable to silica gel chromatography. For those, the deprotected products were directly subjected to the cleavage reactions. In general, the cleavage step worked as well as those in our substrate scope studies (see above) with one exception where the ruthenium catalyst (**3a**) was found to decompose with a substrate containing an iodide group (entry 9).

We thought it likely that several competing reaction pathways would operate under the photocatalytic conditions (Scheme 3). Similar to tertiary amines, hydrazine or hydrazide **1** would reductively quench a photoexcited state $[Ru(bpyrz)_3]^{2+}$*, which is generated by exposure of $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (**3a**) to visible light. Deprotonation of the resulting nitrogen radical cation **6** would produce radical **7**, which could then react with O_2 to form radical **8**. Depending on R^1, two different pathways are proposed to diverge from **8**. When R^1 is H, a rearrangement of **8** to **10** via **9** is proposed. Similar rearrangements have been observed with nitroso oxides.[20] Fragmentation of **10** would provide nitrous acid and amine radical **10**, which could be reduced by ruthenium(I) to afford amine **2**. On the other hand, when R^1 is non-hydrogen, radical **8** would be reduced by ruthenium(I) to yield **12**. Elimination of HOO^- would generate diazenium **13**, which could undergo two different isomerization processes (cf. Table 3). When R^1 is a benzyl group, isomerization of **13** to hydrazone **2l** would be favorable. In contrast, isomerization of **13** to **16** would be favorable when R^1 is a phenyl group. Conversion of **16** into **17** followed by oxidation in situ would provide azobenzene **2m**.

To support the hypothesis that hydrazine or hydrazide **1** would be initially oxidized by a photoexcited state $[Ru(bpyrz)_3]^{2+}$*, we performed two series of fluorescence quenching experiments (Stern–Volmer studies[21]) using substrates **1a** and **1b** (Figure 1). The ratio of the fluorescene intensity without a quencher (I_o) versus that with a quencher (I) was shown to be

first order dependent on the concentration of **1a** or **1b**, indicating that both act as reductive quenchers of the excited state of $[Ru(bpyrz)_3]^{2+}$. Hydrazine **1b** is expected to be a stronger reducing agent than hydrazide **1a** because the latter compound is substituted with a benzoyl group instead of a methyl group. The slope of the line for hydrazine **1b** was larger than that for hydrazide **1a**, which was consistent with this expectation. Furthermore, protonation of hydrazines such as **1b** would remove one of the two lone pairs on the two nitrogen atoms, rendering **1b** an ineffective quencher of $[Ru(bpyrz)_3]^{2+}*$. Indeed, the HCl salt of hydrazine **1b** was found to be inert under the optimized conditions.

In conclusion, we have developed a photocatalytic method for cleavage of the N–N bonds of hydrazines and hydrazides. The method, using 2 mol% ruthenium(II) catalyst, visible light, and air, is operationally very simple. The utility of this method has been demonstrated by the synthesis of secondary aromatic amines through electrophilic amination. Furthermore, this study has shed some light on the fate of nitrogen radical cations generated by quenching the photoexcited state $[Ru(bpyrz)_3]^{2+}*$.

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Anhydrous solvents were purchased and used as received except THF, CH_2Cl_2, Et_2O, and toluene, which were rigorously purged with argon for 2 h and then further purified by passing through two packed columns of neutral alumina (for THF and Et_2O) or through neutral alumina and copper(II) oxide (for toluene and CH_2Cl_2) under argon from a solvent purification system. All new compounds were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy (thin film on NaCl plates), in addition to elemental analysis and/or high resolution mass spectroscopy. Melting points are uncorrected. For starting materials and intermediates, copies of the ^1H and ^{13}C NMR spectra are given in the Supporting Information. Copies of the ^1H and ^{13}C NMR spectra for all the final products are given in the Supporting Information. NMR spectra were recorded in deuterated solvents. All ^1H NMR experiments are reported in δ units in parts per million (ppm) and were measured relative to the signals for residual chloroform (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), CD_3CN (δ = 1.96 ppm), or CD_3OD (δ = 3.34 ppm). All ^{13}C NMR spectra (obtained with ^1H decoupling) are reported in ppm relative to $CDCl_3$ (δ = 77.00 ppm), DMSO-d_6 (δ = 39.51 ppm), CD_3CN (δ = 118.26 ppm), or CD_3OD (δ = 49.86 ppm). The following abbreviations are used to designate multiplicities of NMR signals: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet, and dd (doublet of doublet). Coupling constants (*J* values) are reported in hertz (Hz).

Deprotection of *N*-*tert*-Butoxycarbonyl *N*′,*N*′-Disubstituted Hydrazines and Hydrazides; General Procedure A

To a solution of a Boc-hydrazine or hydrazide derivative (0.3 mmol) in CH_2Cl_2 (5 mL) was added TFA (0.5 mL) at 0 °C. The flask was placed in a fridge until no starting material was observed by TLC. Sat. aq Na_2CO_3 (10 mL) was added and the resulting mixture was stirred at 0 °C for 5 min, then the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic solution was washed with H_2O (1 × 5 mL), brine (1 × 5 mL) and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure to afford the crude N′,N′-disubstituted hydrazine or hydrazide, which was purified by silica gel column chromatography. If the hydrazine or hydrazide was not stable on silica gel, it was then used directly in the next step.

Ruthenium(II)-Catalyzed Photolytic Cleavage of N–N Bonds; General Procedure B

A screw-capped, disposable test tube with a stir bar was charged with $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (2 mol%), substituted hydrazine or hydrazide (0.5 mmol), and solvent (5 mL). A 20-gauge 11/2″ needle was pierced through the Teflon cap of the tube so that the reaction system was exposed to air. The reddish solution was stirred at r.t. under the irradiation of a 13 W GE compact fluorescent light bulb. The reaction was monitored by TLC. When the reaction was complete, the mixture was filtered through a short silica pad and eluted with Et_2O (20 mL) and EtOAc (5 mL). The solution was concentrated under reduced pressure and the residue was purified by silica gel chromatography to afford the product. A photograph of the setup is shown in the Supporting Information.

N-Benzoylaniline (2a)[22]

Following general procedure B, **1a** (106 mg, 0.5 mmol) in MeCN (2.5 mL) and MeOH (2.5 mL) was subjected to the reaction for 12 h. Purification on silica gel column chromatography (hexanes–Et_2O, 5:1) gave the product.

Yield: 70 mg (71%); white crystals; mp 165–166 °C (Lit.[22] 165–167 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.25 (s, 1 H), 7.94–7.97 (m, 2 H), 7.79 (d, J = 8.0 Hz, 2 H), 7.51–7.61 (m, 3 H), 7.35 (t, J = 7.8 Hz, 2 H), 7.10 (t, J = 7.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.6, 139.2, 135.0, 131.6, 128.6, 128.4, 127.7, 123.7, 120.4.

N-Acetyl-*N*-methylaniline (2b)[23]

Following general procedure B, *N*-methyl phenylhydrazine (35 μL, 0.30 mmol) in MeCN (2 mL) and MeOH (1 mL) was subjected to the reaction for 24 h. The crude product was dissolved in EtOAc (5 mL), and AcCl (47 μL, 0.66 mol) was added. The solution was heated at 50 °C for 20 min, and then diluted with Et_2O (60 mL). After washing with sat. aq $NaHCO_3$ (1 × 5 mL), H_2O (1 × 5 mL), and brine (1 × 5 mL), the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexanes–acetone, 4:1) to give the product.

Yield: 37 mg (83%); white crystals; mp 108–109 °C (Lit.[24] 106–108 °C). The ^{1}H and ^{13}C NMR data are consistent with those reported.[23]

N-tert-Butoxycarbonylaniline (2c)[25]

Based on general procedure B, **1c** (103 mg, 0.5 mmol) was subjected to the reaction in MeCN (2.5 mL) and MeOH (2.5 mL) for 24 h. After purification by silica gel column chromatography (hexanes–EtOAc, 10:1), the product was obtained.

Yield: 79 mg (82%); white crystals; mp 140–143 °C (Lit.[26] 134–136 °C). The ^{1}H and ^{13}C NMR data are consistent with those reported.[25]

N-tert-Butoxycarbonyl-4-trifluoromethylaniline (2d)[27]

Based on general procedure B, compound **1d** (122 mg, 0.44 mmol) in MeCN (2.5 mL) and MeOH (2.5 mL) was subjected to the reaction for 28 h. Purification by silica gel column chromatography (hexanes–EtOAc, 20:1) gave the desired product.

Yield: 93 mg (81%); white crystals; mp 120–123 °C (Lit.[27] 121–122 °C). The ^{1}H and ^{13}C NMR data are consistent with those reported.[27]

N-Styrylacetylaniline (2e)[28]

Following the general procedure B, **1e** (101 mg, 0.4 mmol) in MeCN (2.0 mL) and MeOH (2.0 mL) was subjected to the reaction for 10 h. Purification by silica gel column chromatography (hexanes–EtOAc, 6:1) gave the product.

Yield: 51 mg (54%); white crystals; mp 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.52 (m, 2 H), 7.41–7.44 (m, 2 H), 7.27–7.37 (m, 5 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 6.65 (d, *J* = 15.9 Hz, 1 H), 6.39 (dt, *J* = 15.8, 7.3 Hz, 1 H), 3.34 (dd, *J* = 7.3, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 137.6, 136.4, 135.4, 129.0, 128.7, 128.0, 126.4, 124.5, 121.8, 119.9, 41.9.

(*N*-Phenylcarboxamido)pyrazine (2f)[29]

Following general procedure B, compound **1f** (62 mg, 0.29 mmol) in MeCN (1.5 mL) and MeOH (1.5 mL) was irradiated for 28 h. Purification by silica gel column chromatography (hexanes–EtOAc, 2:1) gave the product.

Yield: 27 mg (47%); white crystals; mp 128–130 °C (Lit.[30] 123–125 °C). The ^{1}H and ^{13}C NMR data are consistent with those reported.[29]

N-Benzylaniline (2g)[31]

Based on general procedure B, crude **1g** in MeCN (2.6 mL) and MeOH (1.3 mL) was subjected to the reaction for 24 h. After purified by silica gel column chromatography (hexanes–CH_2Cl_2, 2:1) the product was obtained as a yellow oil (51 mg, 68%). The ^{1}H and ^{13}C NMR data are consistent with those reported.[31]

N-Benzyl-2-chloroaniline (2h)[32]

Following general procedure B, crude **1h** was subjected to the reaction in MeCN (3 mL) and MeOH (1.5 mL) for 15 h. After purification by silica gel column chromatography (hexanes–CH_2Cl_2, 10:1→8:1), the desire product (43 mg, 51%) was obtained as a colorless oil. The ^{1}H and ^{13}C NMR data are consistent with those reported.[32]

N-Butyl-(3′-chlorobiphenyl-4-yl)amine (2i)

Following general procedure B, compound **1i** (87 mg, 0.32 mmol) in MeCN (2.0 mL) and MeOH (1.0 mL) was subjected to the reaction for 15 h. Purification by silica gel column chromatography (hexanes–EtOAc, 50:1) gave the product.

Yield: 31 mg (37%, two steps); colorless oil.

IR (neat): 3416, 3063, 3030, 2962, 2931, 2869, 1615, 1594, 1530, 1478, 1330, 824, 782 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 1.9 Hz, 1 H), 7.40–7.44 (m, 3 H), 7.31 (t, *J* = 7.8 Hz, 1 H), 7.21–7.24 (m, 1 H), 6.65–6.69 (m, 2 H), 3.75 (br s, 1 H), 3.17 (t, *J* = 7.1 Hz, 2 H), 1.60–1.68 (m, 2 H), 1.46 (sext, *J* = 7.4 Hz, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 143.1, 134.5, 129.8, 128.2, 127.9, 126.2, 125.8, 124.2, 112.8, 43.5, 31.6, 20.3, 13.9.

Anal. Calcd for $C_{16}H_{18}ClN$: C, 73.98; H, 6.98; N, 5.39. Found: C, 73.99; H, 7.12; N, 5.51.

2-Methyl-1-methylene-2-phenylhydrazine (2k)[33]

Following general procedure B, compound **1k** (68 mg, 0.5 mmol) in MeCN (2.5 mL) and MeOH (2.5 mL) was subjected to the cleavage reaction for 15 h. After purification by silica gel column chromatography (hexanes–CH_2Cl_2, 2:1), **2k** was isolated as the major product.

Yield: 24 mg (36%); colorless oil. The ^{1}H and ^{13}C NMR data are consistent with those reported.[33]

1-Benzylidene-2-methyl-2-phenylhydrazine (2l)[34]

Following general procedure B, compound **1l** (105 mg, 0.49 mmol) in MeCN (5 mL) was subjected to the cleavage reaction for 36 h. After purification by silica gel chromatography (hexanes–EtOAc, 30:1), **2l** was obtained.

Yield: 91 mg (88%); white crystals; mp 107–109 °C (Lit.[35] 106–107 °C). The ^{1}H and ^{13}C NMR data are consistent with those reported.[34]

Azobenzene (2m)

Following general procedure B, **1m** (67 mg, 0.34 mmol) in MeCN (1.5 mL) and MeOH (1.5 mL) was subjected to the reaction for 2 d. After purification by silica gel column chromatography (hexanes–EtOAc, 100:1), the product was obtained.

Yield: 36 mg (58%); yellow crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.98 (m, 4 H), 7.48–7.57 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 131.0, 129.1, 122.8. NMR spectra are identical to those from an authentic sample.

N-*tert*-Butoxycarbonyl-*N*′-(2-chlorophenyl)-*N*′-(4-fluorophenyl)hydrazine (5n)

Based on the literature procedure,[19b] a solution of **4n** (300 mg, 1.25 mmol), 4-fluorophenylboronic acid (280 mg, 2.0 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (12.5 mg, 0.0625 mmol) in dried MeOH (5 mL) was heated at reflux for 5 min in an atmosphere of N_2. The solution was cooled to r.t. and 100 mg of silica gel was added. After stirring for 5 min, the solvent was removed and the residue was subjected to silica gel column chromatography (hexanes–EtOAc, 25:1) to give the pure product.

Yield: 398 mg (95%); white crystals; mp 107–109 °C.

IR (neat): 3307, 3067, 2983, 2935, 1729, 1708, 1509, 1481, 1370, 1230, 1160, 831 cm^{-1}.

^{1}H NMR (400 MHz, CD_3OD): δ = 7.55 (d, *J* = 7.6 Hz, 1 H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 6.93 (t, *J* = 8.7 Hz, 2 H), 6.65–6.68 (m, 2 H), 1.48/1.37 (rotamers, 2 × s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2 (d, *J* = 240.0 Hz), 154.7, 143.4, 141.7, 131.9, 130.7, 130.2, 128.1, 127.9, 115.36 (d, *J* = 22.5 Hz), 114.7, 81.3, 28.1.

Anal. Calcd for $C_{17}H_{18}ClFN_2O_2$: C, 60.63; H, 5.39; N, 8.32. Found: C, 60.48; H, 5.29; N, 8.24.

N-(2-Chlorophenyl)-*N*-(4-fluorophenyl)hydrazine (1n)

Compound **5n** (110 mg, 0.33 mmol) was subjected to general procedure A to give crude **1n** as a reddish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.50 (m, 1 H), 7.28–7.35 (m, 2H), 7.20–7.24 (m, 1 H), 6.87–6.95 (m, 4 H), 4.23 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (d, *J* = 236.2 Hz), 146.1 (d, *J* = 1.5 Hz), 146.0, 131.9, 131.1, 128.1 (d, *J* = 22.2 Hz), 127.5, 115.7 (d, *J* = 7.5 Hz), 115.2, 115.0.

N-(2-Chlorophenyl)-4-fluoroaniline (2n)[36]

The crude compound **1n** in MeCN (3.0 mL) and MeOH (1.5 mL) was subjected to general procedure B. Purification by silica gel column chromatography (hexanes–CH_2Cl_2, 6:1) gave the product.

Yield: 66 mg (91%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.01–7.17 (m, 6 H), 6.77–6.81 (m, 1 H), 6.01 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0 (d, *J* = 240.7 Hz), 141.0, 137.3 (d, *J* = 2.5 Hz), 129.7, 127.5, 123.2 (d, *J* = 8.0 Hz), 120.8, 120.0, 116.1 (d, *J* = 22.4 Hz), 114.5.

N-*tert*-Butoxycarbonyl-*N*′-(4-trifluoromethylphenyl)-*N*′-(3-chlorophenyl)hydrazine (5o)

This compound was prepared according to the literature procedure.[19b] A mixture of **4o** (300 mg, 1.09 mmol), 3-chlorophenylboronic acid (274 mg, 1.75 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (11 mg, 0.055 mmol) in anhydrous MeOH (5 mL) was heated at reflux for 2 h. The solvent was removed with a rotary evaporator and the residue was purified by silica gel column chromatography (hexanes–EtOAc, 5:1) to give the product.

Yield: 400 mg (95%); white crystals; mp 119–121 °C.

IR (neat): 3284, 3072, 2986, 2936, 1710, 1619, 1597, 1524, 1480, 1372, 1329, 1251, 1163, 1117, 1075, 838 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.6 Hz, 2 H), 7.26 (t, *J* = 8.2 Hz, 1 H), 7.22–7.24 (m, 1 H), 7.13 (d, *J* = 8.6 Hz, 2 H), 7.09–7.11 (m, 2 H), 6.92/6.69 (rotamers, 2 × br s, 1 H), 1.50/1.32 (rotamers, 2 × br s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 148.6, 146.1, 135.0, 130.3, 126.4, 124.3 (q, *J* = 270.5 Hz), 124.5/124.3, 123.9 (q, *J* = 31.7 Hz), 121.4, 119.4/119.1, 116.9, 82.4/82.1, 28.2/28.0.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{18}H_{18}ClF_3N_2O_2$: 385.0925; found: 385.0928.

N′-(4-Trifluoromethylphenyl)-*N*′-(3-chlorophenyl)hydrazine (1o)

According to general procedure A, **5o** (120 mg, 0.31 mmol) afforded crude **1o** after 4 h at r.t.

Yield: 85 mg; yellow oil.

IR (neat): 3359, 3076, 2928, 1620, 1592, 1517, 1478, 1327, 1166, 1117, 1073, 839, 785 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.6 Hz, 2 H), 7.31 (t, *J* = 1.9 Hz, 1 H), 7.28–7.24 (m, 3 H), 7.18–7.15 (m, 1 H), 7.08–7.05 (m, 1 H), 4.20 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 148.8, 135.0, 130.3, 126.2 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 269.4 Hz), 123.7, 122.6 (q, *J* = 32.5 Hz), 121.3, 119.3, 117.0.

N-(3-Chlorophenyl)-4-trifluoromethylaniline (2o)

According to general procedure B, crude **1o** obtained above (ca. 0.31 mmol) in MeCN (1.5 mL) and MeOH (1.5 mL) was subjected to the cleavage reaction for 15 h to give **2o**.

Yield: 73 mg (87%, 2 steps); off-white crystals; mp 60–63 °C.

IR (neat): 3414, 1597, 1584, 1532, 1327, 1117, 1070, 844, 769 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.6 Hz, 2 H), 7.23 (t, *J* = 8.1 Hz, 1 H), 7.13 (t, *J* = 2.1 Hz, 1 H), 7.08 (d, *J* = 8.6 Hz, 2 H), 7.00 (dd, *J* = 8.1, 2.1 Hz, 2 H), 5.92 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 142.7, 135.1, 130.5, 126.8 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 269.2 Hz), 122.6 (q, *J* = 32.6), 122.4, 118.9, 117.2, 116.3.

Anal. Calcd for $C_{13}H_9ClF_3N$: C, 57.47; H, 3.34; N, 5.16. Found: C, 57.71; H, 3.23; N, 5.11.

N-*tert*-Butoxycarbonyl-*N*′-(3-fluorophenyl)-*N*′-phenylhydrazine (5p)

Isopropylmagnesium chloride (2 M in THF, 1.1 mL, 2.2 mmol) was added dropwise to a solution of 1-fluoro-3-iodobenzene (235 μL, 2 mmol) in THF (5 mL) at −20 °C. After 30 min, the solution was cooled to −95 °C and a solution of **4p** (412 mg, 2 mmol) in THF (2 mL) was added. The reaction was quenched with sat. aq NH_4Cl (5 mL) after 5 min. The mixture was extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL) and dried over anhydrous $MgSO_4$. After being concentrated in vacuo, the residue was purified by silica gel column chromatography (hexanes–EtOAc, 20:1) to give **5p**.

Yield: 581 mg (96%); white crystals; mp 123–125 °C.

IR (neat): 3289, 3071, 3040, 3006, 2983, 2936, 1711, 1613, 1594, 1493, 1374, 1252, 1164, 759 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.87/9.46 (rotamers, 2 × br s, 1 H), 7.36 (t, *J* = 7.8 Hz, 2 H), 7.27 (q, *J* = 7.8 Hz, 1 H), 7.16–7.20 (m, 2 H), 7.07–7.12 (m, 1 H), 6.63–6.77 (m, 3 H), 1.42/1.21 (rotamers, 2 × s, 9 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.8 (d, J = 240.3 Hz), 155.1, 148.5 (d, J = 10.1 Hz), 145.1, 130.5 (d, J = 9.8 Hz), 129.2, 123.8, 121.1, 112.3, 107.2 (d, J = 21.0 Hz), 103.0 (d, J = 25.9 Hz), 79.8, 28.4.

Anal. Calcd for $C_{17}H_{19}FN_2O_2$: C, 67.53; H, 6.33; N, 9.27. Found: C, 67.42; H, 6.31; N, 9.18.

N-(3-Fluorophenyl)-*N*-phenylhydrazine (1p)

This crude compound was obtained from compound **5p** (100 mg, 0.33 mol) following general procedure A.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.39 (m, 2 H), 7.27–7.30 (m, 2 H), 7.15–7.21 (m, 1 H), 7.09–7.13 (m, 1 H), 6.90–6.95 (m, 2 H), 6.57–6.62 (m, 1 H), 4.18 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (d, J = 242.0 Hz), 151.0 (d, J = 10.0 Hz), 148.4, 129.8 (d, J = 9.9 Hz), 129.4, 123.8, 121.8, 112.6 (d, J = 2.5 Hz), 107.0 (d, J = 21.4 Hz), 104.3 (d, J = 25.6 Hz).

N-(3-Fluorophenyl)aniline (2p)[37]

Following general procedure B, after 18 h, crude **1p** in MeCN (2.0 mL) and MeOH (1.0 mL) gave the desired product after silica gel column chromatography (hexanes–Et_2O, 8:1).

Yield: 52 mg (84%); yellow oil. The ^{1}H and ^{13}C NMR data are consistent with those reported.[37]

N-*tert*-Butoxycarbonyl-*N*′-(4-trifluoromethylphenyl)-*N*′-phenylhydrazine (5q)

According to the literature procedure,[19a] a solution of phenylmagnesium bromide (3 M in THF, 317 μL, 0.95 mmol) was added drop-wise to a solution of **4o** (200 mg, 0.73 mmol) in anhydrous THF (5 mL) at −100 °C. After 15 min, the reaction was quenched by addition of sat. aq NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 × 20 mL) and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL), and dried over anhydrous $MgSO_4$. After the solvents were removed by rotary evaporation, the residue was purified by silica gel column chromatography (hexanes–EtOAc, 10:1) to give the desired product.

Yield: 246 mg (96%); white crystals; mp 112–115 °C.

IR (neat): 3289, 2988, 2938, 1711, 1622, 1327, 1165, 1117, 1071, 836 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.97/9.55 (rotamers, 2 × br s, 1H), 7.57 (d, J = 8.6, 2 H), 7.41 (t, J = 7.7 Hz, 2 H), 7.26–7.29 (m, 2 H), 7.16–7.21 (m, 1 H), 7.00 (d, J = 8.6 Hz, 2 H), 1.43/1.22 (rotamers, 2 × s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2/155.0, 149.4, 144.6, 129.3, 126.1, 125.1/124.8, 124.5 (q, J = 269.2 Hz), 122.8/122.3, 122.3 (q, J = 32.5 Hz), 115.4/115.2, 82.0/81.5, 28.1/27.9.

Anal. Calcd for $C_{18}H_{19}F_3N_2O_2$: C, 61.36; H, 5.44; N, 7.95. Found: C, 61.39; H, 5.36; N, 7.99.

N-(4-Trifluoromethylphenyl)aniline (2q)[38]

According to general procedure A, **5q** (120 mg, 0.34 mmol) was subjected to the deprotection reaction for 1 h. The crude hydrazine **1q** in MeCN (2.0 mL) and MeOH (1.0 mL) was subjected to the cleavage reaction for 4 h following general procedure B. After purification by silica gel column chromatography (hexanes–EtOAc, 40:1), compound **2q** was obtained.

Yield: 69 mg (85%, two steps); yellow oil.

IR (neat): 3351, 3224, 3066, 3042, 2931, 2858, 1620, 1597, 1517, 1493, 1327, 1280, 1164, 1114, 1070, 839, 702.

The ^{1}H and ^{13}C NMR data are consistent with those reported.[38]

Anal. Calcd for $C_{13}H_{10}F_3N$: C, 65.82; H, 4.25; N, 5.90. Found: C, 65.82; H, 4.27; N, 5.84.

N-tert-Butoxycarbonyl-*N′*-(2-methoxyphenyl)-*N′*-(4-trifluoromethylphenyl)hydrazine (5r)

To a solution of anisole (218 μL, 2 mmol) and TMEDA (362 μL, 2.4 mmol) in THF (10 mL), was added *n*-BuLi (1.6 M in THF, 1.5 mL, 2.4 mmol) at 0 °C. The solution was stirred at r.t. for 2 h, then 1.8 mL of the above solution was added to a solution of **4o** (137 mg, 0.5 mmol) in THF (5 mL) at −78 °C. The reaction was quenched with sat. aq NH_4Cl (5 mL) after 20 min. Purification by silica gel column chromatography (hexanes–Et_2O, 4:1) afforded the desired product.

Yield: 151 mg (79%); yellow oil.

IR (neat): 3371, 3306, 3008, 2981, 2940, 2845, 1734, 1620, 1525, 1501, 1469, 1373, 1329, 1248, 1162, 1117, 1067, 834, 760 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.75/9.27 (2 × br s, 1 H), 7.49 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 6.8 Hz, 1 H), 7.31–7.36 (m, 1 H), 7.14–7.16 (m, 1 H), 7.03 (t, J = 7.6 Hz, 1 H), 6.61 (d, J = 7.8 Hz, 2H), 3.72 (s, 3 H), 1.42 (br s, 9 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.2, 154.6, 150.7, 131.8, 128.6, 127.8, 126.0 (q, J = 3.6 Hz), 125.1 (q, J = 270.2 Hz), 121.1, 118.3 (q, J = 32.0 Hz), 112.8, 112.1, 79.8, 55.5, 28.1.

Anal. Calcd for $C_{19}H_{21}F_3N_2O_3$: C, 59.68; H, 5.54; N, 7.33. Found: C, 59.74; H, 5.48; N, 7.31.

N-(2-Methoxyphenyl)-*N*-(4-trifluoromethylphenyl)hydrazine (1r)

Following general procedure A, compound **5r** (135 mg, 0.35 mmol) afforded crude **1r**.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.40 (m, 2 H), 7.31–7.35 (m, 1 H), 7.26–7.29 (m, 1 H), 6.97–7.07 (m,4 H), 4.29 (br s, 2 H), 3.83 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 153.0, 135.1, 128.6, 128.5, 125.9 (q, J = 3.8 Hz), 125.0 (q, J = 270.5 Hz), 121.3, 119.4 (q, J = 32.2 Hz), 112.8, 112.4, 55.5.

N-(2-Methoxyphenyl)-(4-trifluoromethyl)aniline (2r)

Following general procedure B, crude **1r** in MeCN (2 mL) and MeOH (1 mL) was subjected to the cleavage reaction for 12 h. Another 2 mol% of the catalyst **3a** was added and the reaction was complete after another 12 h. Purification by silica gel column chromatography (hexanes–Et_2O, 10:1) afforded the desired product.

Yield: 61 mg (65%, two steps); pink crystals; mp 60–62 °C.

IR (neat): 3415, 3077, 3009, 2970, 2946, 2845, 1622, 1602, 1533, 1465, 1323, 1246, 1115, 1070, 1029, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.7 Hz, 2 H), 7.36–7.39 (m, 1 H), 7.14 (d, *J* = 8.7 Hz, 2 H), 6.92–7.02 (m, 3 H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 146.3, 130.8, 126.6 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 270.6 Hz), 122.0, 121.7 (q, *J* = 32.7 Hz), 120.7, 117.2, 116.0, 110.8, 55.6.

Anal. Calcd for $C_{14}H_{12}F_3NO$: C, 62.92; H, 4.53; N, 5.24. Found: C, 63.20; H, 4.31; N, 5.33.

N-tert-Butoxycarbonyl-*N*′-(2-bromo-4-methylphenyl)-*N*′-(pyridn-3-yl)hydrazine (5s)

According to the literature procedure,[19a] *i*-PrMgCl·LiCl (1.3 M in THF, 1.5 mL, 2.0 mmol) was added dropwise to a solution of 3-bro-mopyridine (193 μL, 2.0 mmol) in THF (2 mL) at 0 °C. The solution was stirred at r.t. for 30 min, then cooled to −100 °C and a solution of **5i** (598 mg, 2.0 mmol) in THF (5 mL) was added. The reaction was quenched after 20 min with sat. aq NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 × 20 mL) and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL), and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexanes–EtOAc, 5:1→1:1) to give **5s**.

Yield: 277 mg (73%); white crystals; mp 58–61 °C.

IR (neat): 3159, 2978, 2933, 1732, 1581, 1491, 1369, 1242, 1164 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.91/9.49 (rotamers, 2 × br s, 1 H), 8.02 (d, *J* = 4.0 Hz, 1 H), 7.84 (br s, 1 H), 7.55–7.57 (m, 1 H), 7.49 (d, *J* = 7.7 Hz, 1 H), 7.31 (d, *J* = 7.7 Hz, 1 H), 7.22 (dd, *J* = 8.5, 4.7 Hz, 1 H), 6.83 (d, *J* = 7.0 Hz, 1 H), 2.33 (s, 3 H), 1.42 (br s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 143.4, 140.9, 140.1, 139.2, 135.2, 134.2, 131.0, 129.7, 123.2, 122.6, 119.3, 81.6, 28.2, 20.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{21}BrN_3O_2$: 378.0812; found: 378.0812.

N-(2-Bromo-4-methylphenyl)-*N*-(pyridin-3-yl)hydrazine (1s)

Compound **5s** (78 mg, 0.21 mmol) was subjected to general procedure A. Purification by silica gel column chromatography (CH_2Cl_2–Et_2O, 2:1) gave **1s**.

Yield: 24 mg (42%); colorless oil.

IR (neat): 3338, 3310, 3167, 3037, 2959, 2926, 2856, 1584, 1488, 1428, 1319, 1249, 1044, 800, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 2.8 Hz, 1 H), 8.05 (dd, *J* = 4.6, 1.3 Hz, 1 H), 7.52–7.53 (m, 1 H), 7.17–7.22 (m, 3 H), 7.08 (ddd, *J* = 8.4, 4.6, 0.7 Hz, 1 H), 4.19 (s, 2 H), 2.38 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.7, 143.2, 139.8, 139.4, 136.0, 134.8, 130.0, 128.7, 123.1, 122.5, 119.9, 20.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}BrN_3$: 278.0288; found: 278.0287.

N-(Pyridn-3-yl)-2-bromo-4-methylaniline (2s)

Following general procedure B, **1s** (58 mg, 0.21 mmol) in MeCN (2.0 mL) and MeOH (1.0 mL) was subjected to the cleavage reaction for 6 h. After purification by silica gel column chromatography (hexanes–acetone, 4:1) the product was obtained.

Yield: 30 mg (55%); yellow oil.

IR (neat): 3393, 3235, 3032, 2923, 1587, 1517, 1485, 1314, 806, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 8.22 (d, *J* = 4.3 Hz, 1 H), 7.38–7.41 (m, 2 H), 7.20 (dd, *J* = 8.2, 4.6 Hz, 1 H), 7.14 (d, *J* = 8.2 Hz, 1 H), 7.01–7.04 (m, 1 H), 5.90 (s, 1 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 141.0, 139.1, 137.5, 133.5, 132.6, 128.9, 124.8, 123.7, 117.4, 113.8, 20.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{11}BrN_2$: 262.0106; found: 262.0101.

N-*tert*-Butoxycarbonyl-*N*′-(2-byphenyl)-*N*′-phenylhydrazine (5t)

To a solution of 2-bromobiphenyl (259 μL, 1.5 mmol) in THF (5 mL) was added *i*-PrMgCl·LiCl (1.3 M in THF, 1.3 mL, 1.65 mmol) at 0 °C. The solution was stirred at r.t. for 15 h (GC analysis showed incomplete halogen exchange) and cooled to −78 °C. A solution of **4p** (309 mg, 1.5 mmol) in THF (2 mL) was added and the reaction was quenched with sat. aq NH_4Cl (5 mL) after 30 min. The mixture was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL) and then dried over anhydrous $MgSO_4$. After being concentrated in vacuo, the residue was purified by silica gel column chromatography (hexanes–CH_2Cl_2, 3:1→1:1) to give **5t**.

Yield: 270 mg (50%); colorless oil.

IR (neat): 3373, 3320, 3065, 2982, 2934, 1744, 1726, 1706, 1599, 1500, 1477, 1162, 750, 705 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.71/9.08 (2 × s, 1 H), 7.50–7.68 (m, 3 H), 7.41–7.47 (m, 1 H), 7.29–7.33 (m, 2 H), 7.18 (t, *J* = 7.3 Hz, 2 H), 7.07–7.12 (m, 1 H), 6.91–6.99 (m, 2 H), 1.45/1.31 (2 × s, 9 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.6, 146.9, 142.6, 139.4, 136.7, 130.9, 128.8, 128.1, 127.8, 126.7, 126.1, 125.1, 119.3, 114.5, 79.4, 28.2.

Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.50; H, 6.61; N, 7.78.

N-(2-Biphenyl)-*N*-phenylhydrazine (1t)

Following general procedure A, **5t** (180 mg, 0.5 mmol) was treated at 0 °C for 3 h to give crude **1t** (126 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.51 (m, 3 H), 7.32–7.41 (m, 6 H), 7.23–7.28 (m, 2 H), 7.05–7.08 (m, 2 H), 6.81–6.86 (m, 1 H), 3.63 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 146.4, 139.5, 139.1, 131.7, 128.7 (2 × C), 128.6, 128.3, 127.4, 126.9, 126.6, 118.2, 113.8.

N-(2-Biphenyl)aniline (2t)[39]

Following general procedure A, crude **1t** in MeCN (3 mL) and MeOH (1.5 mL) was subjected to the cleavage reaction for 24 h. After purification by silica gel column chromatography (hexanes–Et_2O, 5:1), **2t** was obtained.

Yield: 88 mg (72%, two steps); as yellow oil.

IR (neat): 3409, 3053, 3029, 1584, 1593, 1516, 1503, 1474, 1438, 1314, 747, 705 cm^{-1}.

The ^{1}H and ^{13}C NMR data are consistent with those reported.[39]

N-*tert*-Butoxycarbonyl-*N*′-(2-bromo-4-methylphenyl)-*N*′-butylhydrazine (5u)

According to the literature procedure,[19a] *n*-butylmagnesium bromide (2 M in THF, 0.35 mL, 0.67 mmol) was added to a solution of **4s** (200 mg, 0.67 mmol) in THF (5 mL) at −100 °C. The color of the reactant turned from red to yellow during the addition. The reaction was quenched with sat. aq NH_4Cl (5 mL) after 15 min, the mixture was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL) and then dried over $MgSO_4$. After being concentrated in vacuo, the residue was purified by silica gel column chromatography to give the product.

Yield: 220 mg (92%); yellow oil.

IR (neat): 3247, 2965, 2933, 2874, 1701, 1493, 1371, 1169 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.78/8.40 (rotamers, 2 × s, 1H), 7.36 (s, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 2.96–3.13 (m, 2 H), 2.23/2.17 (rotamers, 2 × s, 3 H), 1.47–1.55 (m, 2 H), 1.26–1.44 (m, 11 H), 0.87 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.4, 147.3, 134.6, 133.4, 128.6, 122.1, 116.9, 78.5, 55.7, 29.2, 28.1, 19.8, 19.5, 14.1.

Anal. Calcd for $C_{16}H_{25}BrN_2O_2$: C, 53.79; H, 7.05; N, 7.84. Found: C, 54.05; H, 7.14; N, 7.82.

N-Butyl-*N*-(2-bromo-4-methylphenyl)hydrazine (1u)

Following general procedure A, **5u** (120 mg, 0.34 mmol) afforded the crude product (85 mg) as a yellow oil that was used directly in the next step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.39 (m, 1 H), 7.18 (d, *J* = 8.1 Hz, 1 H), 7.06–7.10 (m, 1 H), 3.56 (br s, 2 H), 3.01–3.05 (m, 2 H), 2.28 (s, 3 H), 1.60–1.69 (m, 2 H), 1.40 (quin, *J* = 7.4 Hz, 2 H), 0.94 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 134.9, 133.9, 128.6, 120.7, 118.9, 59.6, 29.5, 20.3, 20.1, 14.0.

N-Butyl-2-bromo-4-methylaniline (2u)[40]

Based on general procedure B, compound **1u** (crude, 85 mg, ca. 0.33 mol) in MeCN (2.0 mL) and MeOH (1.0 mL) was subjected to the cleavage reaction for 15 h and then purified by silica gel column chromatography (hexanes–EtOAc, 50:1) to give the desired product.

Yield: 57 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.25 (m, 1 H), 6.97–7.00 (m, 1H), 6.55 (d, *J* = 8.3 Hz, 1 H), 4.10 (br s, 1 H), 3.13 (q, *J* = 6.7 Hz, 2 H), 2.22 (s, 3 H), 1.61–1.68 (m, 2 H), 1.45 (quin, *J* = 7.4 Hz, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 132.7, 128.9, 126.9, 111.2, 109.5, 43.8, 31.4, 20.3, 20.0, 13.9.

MS (CI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{17}BrN_2$: 242; found: 242.

N-tert-Butoxycarbonyl-*N′*-butyl-*N′*-(4-iodophenyl)hydrazine (5v)

According to the literature procedure,[19a] *n*-butylmagnesium chloride (2.0 M in THF, 375 μL, 0.75 mmol) was added dropwise to a solution of **4v** (250 mg, 0.75 mmol) in THF (10 mL) at −100 °C. The solution color turned from orange to green. After 5 min, the reaction was quenched with sat. aq NH_4Cl (5 mL), the mixture was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL), and dried over anhydrous $MgSO_4$. After being concentrated in vacuo, the residue was purified by silica gel column chromatography (hexanes–EtOAc, 100:5) to give the product.

Yield: 280 mg (95%); yellow crystals; mp 72–75 °C.

IR (neat): 3299, 2965, 2934, 2874, 1709, 1590, 1489, 1368, 1251, 1163, 813 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.49 (m, 2 H), 6.56–6.60 (m, 2 H), 6.42/6.23 (rotamers, 2 × br s, 1 H), 3.34–3.48 (m, 2 H), 1.56–1.64 (m, 2 H), 1.32–1.48 (m, 11 H), 0.95 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 149.0, 137.8, 114.8, 81.1, 80.5, 52.1, 28.6, 28.3, 20.2, 14.0.

Anal. Calcd for $C_{15}H_{23}IN_2O_2$: C, 46.16; H, 5.94; N, 7.18. Found: C, 46.36; H, 6.03; N, 7.25.

N-Butyl-*N*-(4-iodophenyl)hydrazine (1v)

Based on general procedure A, **5v** (170 mg, 0.436 mmol) gave the crude product (115 mg, 91%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.49 (m, 2 H), 6.73–6.77 (m, 2 H), 3.54 (br s, 2 H), 3.56 (t, *J* = 7.5 Hz, 2 H), 1.57–1.64 (m, 2 H), 1.38 (sext, *J* = 7.5 Hz, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 137.5, 115.2, 78.8, 55.1, 27.6, 20.1, 14.0.

N-Butyl-4-iodoaniline (2v)[41]

The crude product **1v** (ca. 0.4 mmol) was subjected to the cleavage reaction in MeCN (4.0 mL) following general procedure B. After 10 h, another 2 mmol% of catalyst was added. After another 10 h, the reaction mixture was loaded onto a silica gel column (hexanes–CH_2Cl_2, 3:1→2:1) to give the desired product.

Yield: 23 mg (21%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.42 (m, 2 H), 6.36–6.40 (m, 2 H), 3.63 (br s, 1 H), 3.07 (t, *J* = 7.1 Hz, 2 H), 1.55–1.62 (m, 2 H), 1.42 (sext, *J* = 7.2 Hz, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 149.8, 138.5, 115.6, 76.5, 43.8, 31.9, 20.9, 14.1.

1-(*N*-*tert*-Butoxycarbonylamino-*N*-phenyl-DL-alanyl)pyrrolidine (5w)

Freshly prepared LDA in THF (0.26 M, 1.83 mmol) was added to 1-propionylpyrrolidine (234 mg, 1.83 mmol) in THF (5 mL) at −20 °C. After 1 h, the solution was cooled to −78 °C and a solution of **4p** (170 mg, 0.825 mmol) in THF (2 mL) was added. The reaction was quenched with sat. aq NH_4Cl (5 mL) after 30 min, the mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with H_2O (1 × 5 mL), brine (1 × 5 mL) and then dried over anhydrous $MgSO_4$. After being concentrated in vacuo, the residue was purified by silica gel column chromatography (hexanes–EtOAc, 3:2) to give **5w**.

Yield: 195 mg (71%); colorless oil.

IR (neat): 3472, 3362, 3258, 3065, 2981, 2934, 2881, 1738, 1637, 1456, 1234, 1168, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (br s, 1 H), 7.21–7.31 (m, 2H), 6.79–6.89 (m, 3 H), 4.67 (q, *J* = 6.9 Hz, 1 H), 3.33–3.57 (m, 4H), 1.98–2.06 (m, 2 H), 1.76–1.88 (m, 2 H), 1.43–1.54 (m, 11 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 156.2, 149.6, 129.1, 120.5, 114.2, 79.9, 56.7, 46.1, 45.6, 28.3, 26.2, 23.9, 14.7.

Anal. Calcd for $C_{18}H_{27}N_3O_3$: C, 64.84; H, 8.16; N, 12.6. Found: C, 64.82; H, 8.26; N, 12.33.

1-(*N*-Amino-*N*-phenyl-DL-alanyl)pyrrolidine (1w)

Following general procedure A, **5w** (120 mg, 0.36 mmol) afforded crude **1w** (78 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.28 (m, 2 H), 7.03–7.06 (m, 2 H), 6.79–6.83 (m, 1 H), 4.60 (q, *J* = 6.8 Hz, 1 H), 3.73 (br s, 2 H), 3.40–3.55 (m, 4 H), 1.77–1.95 (m, 4 H), 1.39 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 150.8, 129.1, 118.9, 114.0, 57.4, 46.2, 45.9, 26.2, 24.0, 11.7.

1-(*N*-Phenyl-DL-alanyl)pyrrolidine (2w)[42]

Following general procedure B, crude **1w** in MeCN (2 mL) and MeOH (2 mL) was subjected to the cleavage reaction for 24 h. After purification by silica gel column chromatography (hexanes–EtOAc, 1:1), the product **2w** was obtained.

Yield: 40 mg (51%, two steps); white crystals; mp 111–112 °C (Lit.[42] 113–115 °C).

IR (neat): 3320, 3116, 3050, 2976, 2923, 2872, 2854, 1643, 1427, 1643, 1332, 756, 693 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.19 (m, 2 H), 6.68–6.73 (m, 1 H), 6.56–6.63 (m, 2 H), 4.63 (br s, 1 H), 4.25 (q, *J* = 6.6 Hz, 1 H), 3.44–3.63 (m, 4 H), 1.97–2.03 (m, 2 H), 1.84–1.91 (m, 2 H), 1.38 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 146.7, 129.3, 117.7, 113.5, 50.5, 46.2, 46.0, 26.1, 24.1, 18.0.

MS (CI): *m*/*z* (%) = 219 (100) $[M + H]^+$.

Acknowledgments

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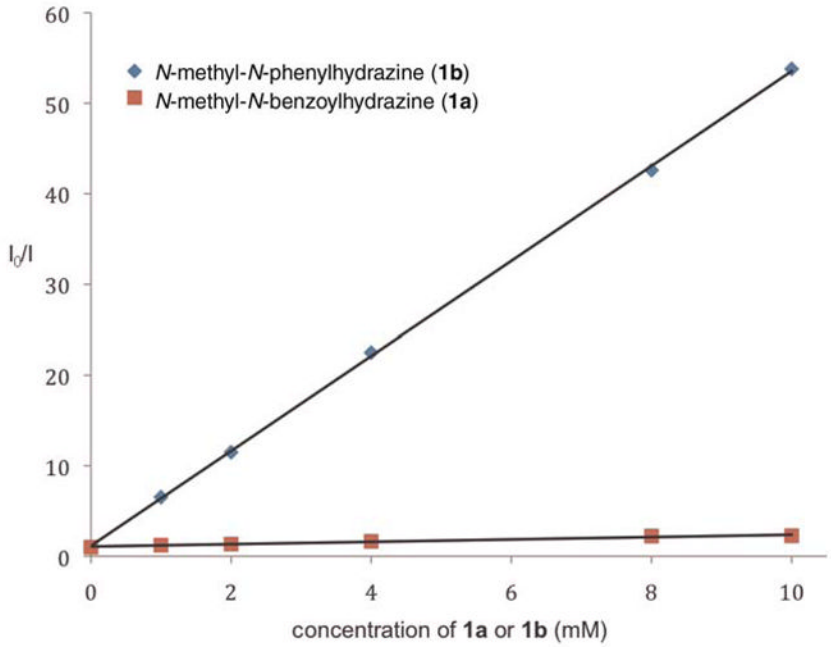
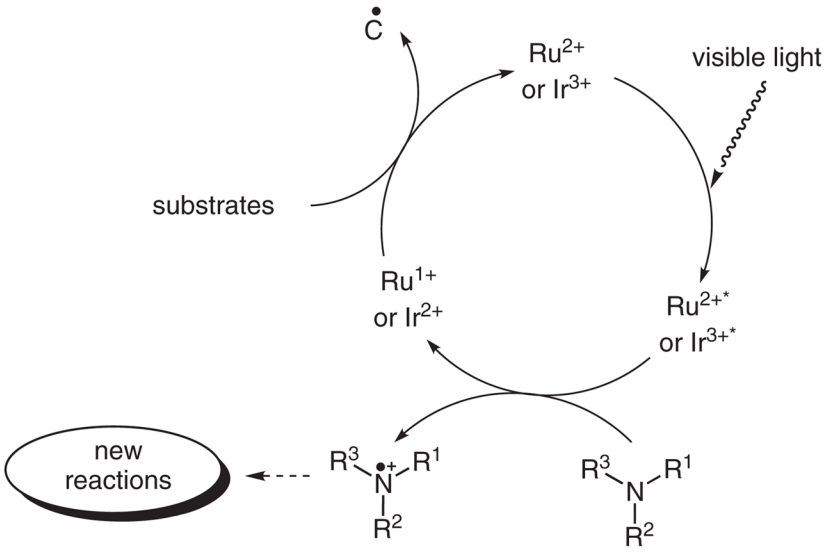
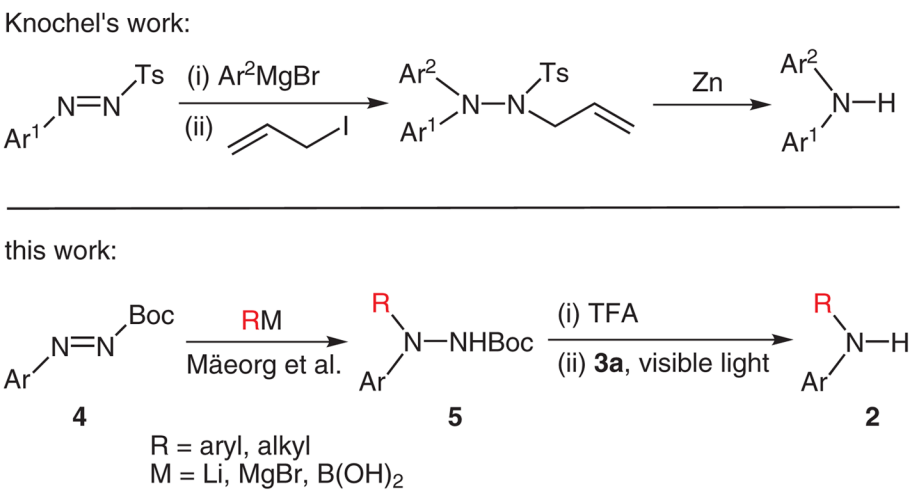


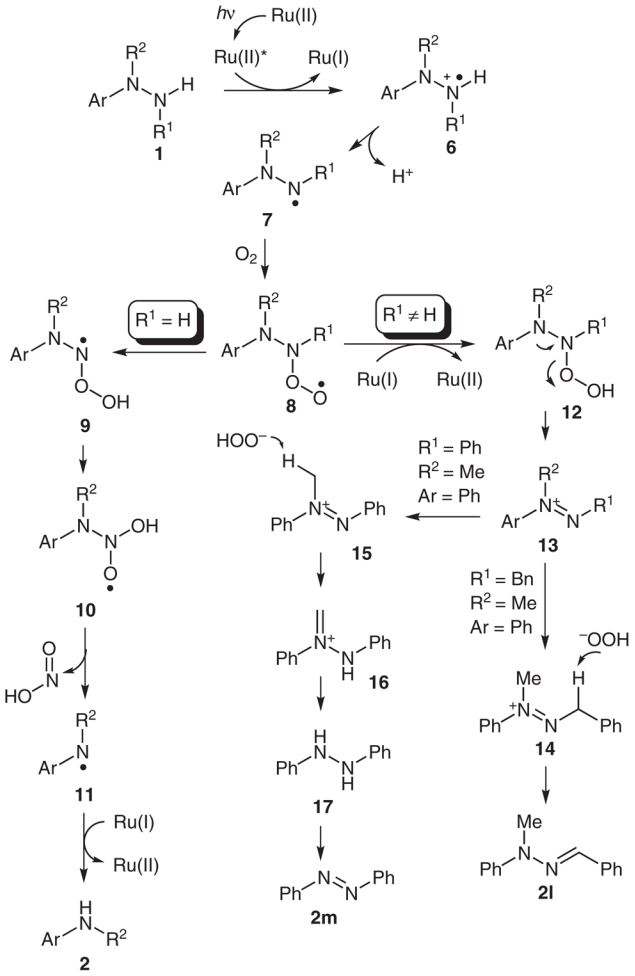
Figure 1.
Fluorescence quenching of $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (**3a**)by hydrazide **1a** and hydrazines **1b**



Scheme 1.
General catalytic cycle for visible light photocatalysis



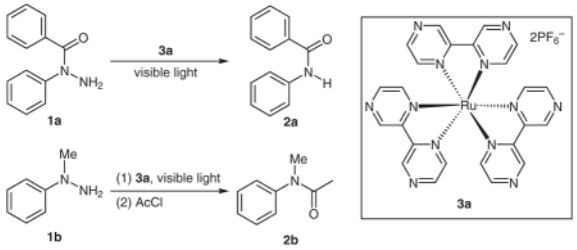
Scheme 2.
Electrophilic amination via aryl azo compounds



Scheme 3.
Proposed pathways

Table 1

Optimization of the Catalyst Systems based on $[Ru(bpyrz)_3](PF_6)_2 \cdot 2H_2O$ (**3a**)



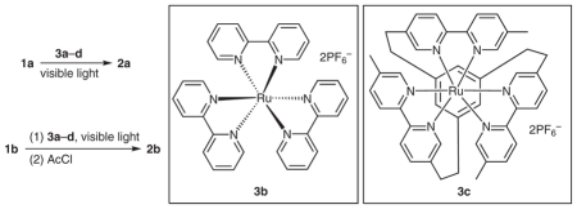
Entry	Substrate	Catalyst (mol%)	Conditions	Time (h)	Yield (%)
1	**1a**	**3a** (2)	air, MeCN	24	42 (44)[a]
2	**1a**	**3a** (2)	air, MeCN–MeOH (1:1)	24	71
3	**1a**	**3a** (2)	air, MeCN–MeOH (2:1)	24	74
4	**1a**	**3a** (1)	air, MeCN–MeOH (1:1)	24	59 (6)[a]
5	**1a**	**3a** (0)	air, MeCN–MeOH (1:1)	120	trace
6[b]	**1a**	**3a** (2)	air, MeCN–MeOH (1:1)	48	0
7	**1a**	**3a** (2)	N_2, degassed MeCN–MeOH (1:1)	40	13
8	**1a**	**3a** (2)	O_2, MeCN–MeOH (1:1)	24	54
9	**1b**	**3a** (2)	air, MeCN	24	82
10	**1b**	**3a** (2)	air, MeCN–MeOH (2:1)	24	83
11	**1b**	**3a** (0)	air, MeCN–MeOH (2:1)	48	12 (88)[a]

[a] Yield of recovered starting material.

[b] No light.

Table 2

Comparison of Ruthenium Catalysts **3a**–**c** and Rose Bengal (**3d**)

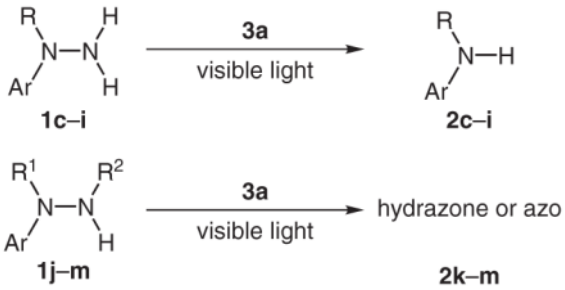


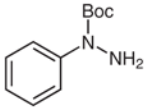
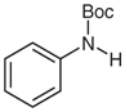
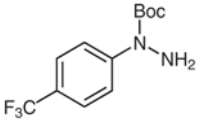
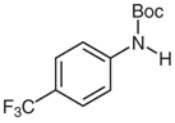
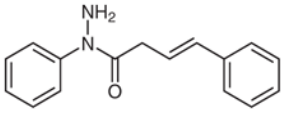
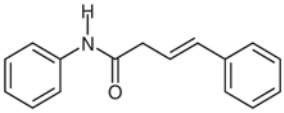
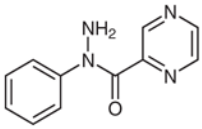
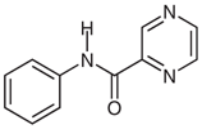
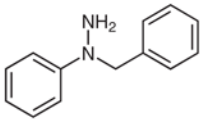
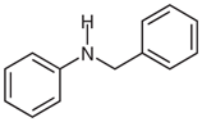
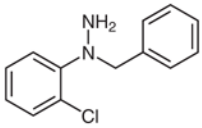
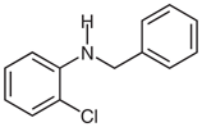
Entry	Substrate	Catalyst (mol%)	Conditions	Time (h)	Yield (%)
1	**1a**	**3a** (2)	air, MeCN–MeOH (1:1)	24	71
2	**1a**	**3b** (2)	air, MeCN–MeOH (1:1)	110	10 (80)[a]
3	**1a**	**3c** (2)	air, MeCN–MeOH (1:1)	110	8 (73)[a]
4	**1a**	**3d** (2)	air, MeCN–MeOH (1:1)	36	49
5	**1b**	**3a** (2)	air, MeCN–MeOH (2:1)	24	83
6	**1b**	**3b** (2)	air, MeCN–MeOH (2:1)	4	65
7	**1b**	**3c** (2)	air, MeCN–MeOH (2:1)	10	85
8	**1b**	**3d** (2)	air, MeCN–MeOH (2:1)	10	56

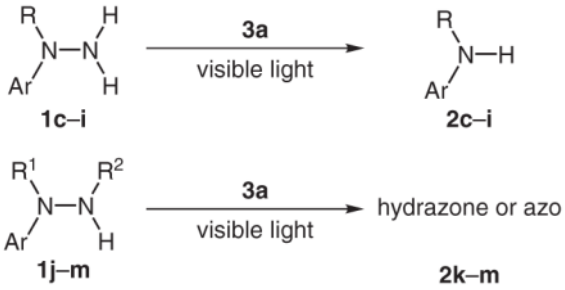
[a]Yield of recovered **1a**.

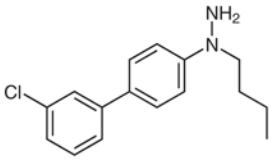
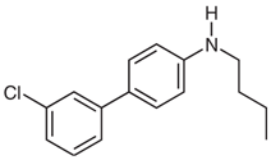
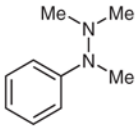
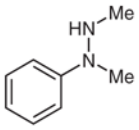
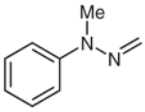
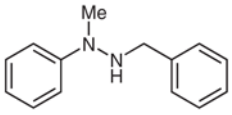
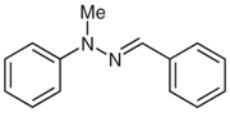
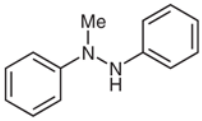
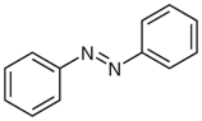
Table 3

Ruthenium(II)-Catalyzed Photoinduced Cleavage of N–N Bonds[a]



Entry	Substrate	Product	Yield (%)
1			82
	1c	**2c**	
2			81
	1d	**2d**	
3			54
	1e	**2e**	
4			47
	1f	**2f**	
5			68[b]
	1g	**2g**	
6			51[b]
	1h	**2h**	



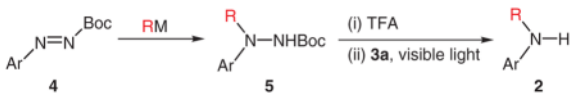
Entry	Substrate	Product	Yield (%)
7	 **1i**	 **2i**	37
8	 **1j**	–	–
9	 **1k**	 **2k**	36
10	 **1l**	 **2l**	88
11	 **1m**	 **2m**	58

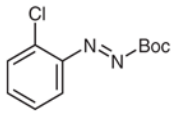
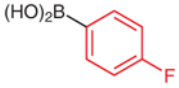
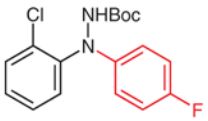
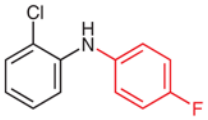
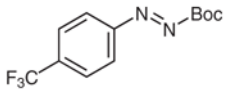
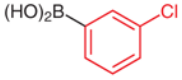
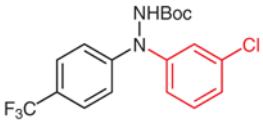
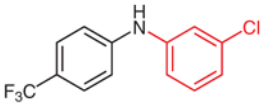
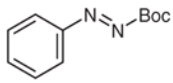
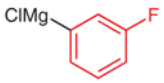
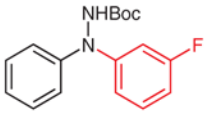
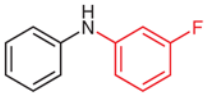
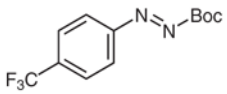
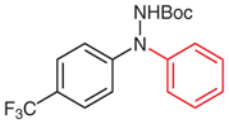
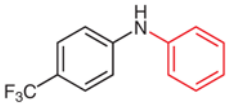
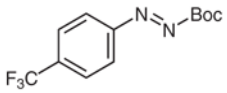
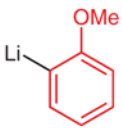
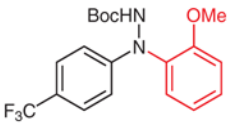
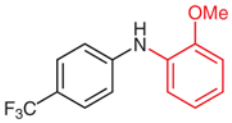
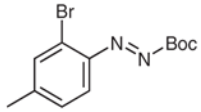
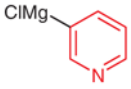
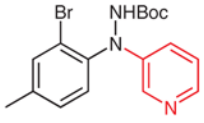
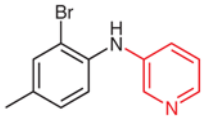
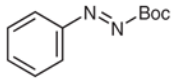
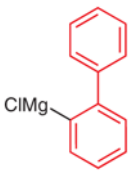
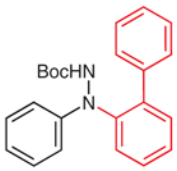
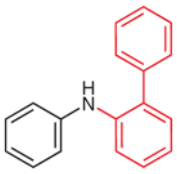
[a]Reactions were performed on 0.3–0.5 mmol scale in 3–5 mL solvent with 2 mol% **3a**. A household 13 W light bulb was used as the light source. Reaction time ranged from 4 to 28 h.

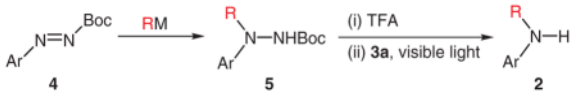
[b]Due to the instability of these hydrazine derivatives, the crude products were subjected to the cleavage reaction directly after Boc-deprotection. The yields given refer to overall yields for the two steps.

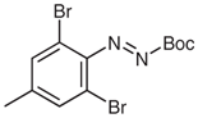
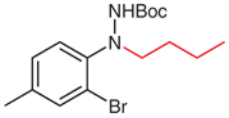
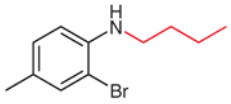
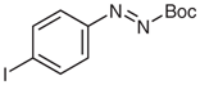
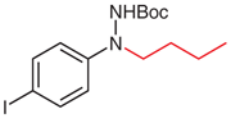
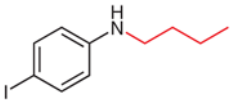
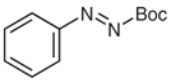
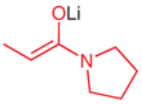
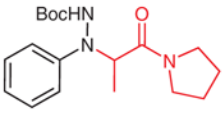
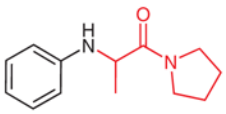
Table 4

Synthesis of Secondary Aromatic Amines[a]



Entry	4	RM	5 (Yield %)	2 (Yield %)
1	 **4n**		 **5n** (95)	 **2n** (91)[b]
2	 **4o**		 **5o** (95)	 **2o** (87)[b]
3	 **4p**		 **5p** (96)	 **2p** (84)[b]
4	 **4q**	PhMgBr	 **5q** (96)	 **2q** (85)[b]
5	 **4r**		 **5r** (79)	 **2r** (65)[b]
6	 **4s**		 **5s** (73)	 **2s** (55)
7	 **4t**		 **5t** (50)	 **2t** (72)[b]



Entry	4	RM	5 (Yield %)	2 (Yield %)
8	 **4u**	BuMgCl	 **5u** (92)	 **2u** (70)[b]
9	 **4v**	BuMgCl	 **5v** (95)	 **2v** (21)[b,c]
10	 **4w**		 **5w** (71)	 **2w** (51)[b]

[a]Reactions were performed on 0.3–0.5 mmol scale in 3–5 mL of MeCN–MeOH (1:1 v/v) with 2 mol% **3a**. A household 13 W light bulb was used as the light source. Reaction time ranged from 15 to 48 h.

[b]Due to the instability of these hydrazine derivatives, the crude products were subjected to the cleavage reaction directly after Boc-deprotection. The yields refer to overall yields for the two steps.

[c]Another 2 mol% of **3a** was added after 10 h; 43% of hydrazine was recovered.