Tetrahedron 72 (2016) 2186–2195

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Regioselectivity of the *ortho*- and *para*-semidine, and diphenyline rearrangements

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ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form 2 March 2016
Accepted 4 March 2016
Available online 8 March 2016

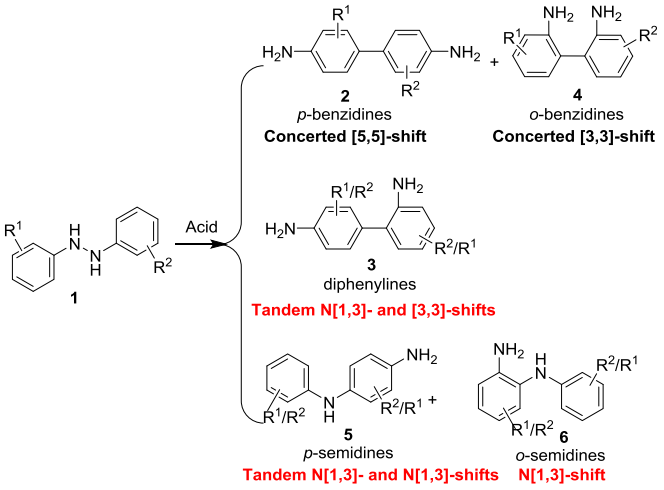
Keywords:
Regioselectivity
N[1,3]-Sigmatropic shift
Semidine
Rearrangement
Diphenyline

ABSTRACT

The regioselectivity of the *o*-semidine, *p*-semidine, and diphenyline rearrangements of unsymmetrical *N*,*N*′-diarylhydrazines was studied experimentally. The results indicate that their electron-rich nitrogen atom is first protonated and then the electron-poor non-protonated nitrogen atom undergoes an *N*[1,3]-sigmatropic shift to the *ortho*-position of the electron-rich aryl rings, generating key intermediates. The intermediates can undergo (1) a direct proton transfer to give *o*-semidines, (2) a second *N*[1,3]-shift of the electron-poor nitrogen atom and then proton transfer to furnish *p*-semidines, and (3) a [3,3]-sigmatropic shift and subsequent proton transfer to yield diphenylines. It is the first *N*[1,3]-sigmatropic shift step that plays an important role in controlling the regioselectivity in the three rearrangements, further determining the structures of *o*-semidines, *p*-semidines, and diphenylines. The current results provide new insights into the *o*/*p*-semidine and diphenyline rearrangements and useful information for controlling and predicting the structures of the rearrangement products.

1. Introduction

The acid-catalyzed benzidine rearrangements have been studied extensively for more than 150 years.[1] Numerous examples have demonstrated that the benzidine rearrangements of *N*,*N*′-diarylhydrazines **1** gave five types of products, namely *p*-benzidines **2**, diphenylines **3**,[2,3] *o*-benzidines **4**, *p*-semidines **5**, and *o*-semidines **6** (Scheme 1).[4] The product distribution was dependent on the substituents on the two aryl rings. A large amount of work has been devoted to the mechanisms of the benzidine rearrangements. For *o*-benzidine and *p*-benzidine rearrangements, concerted [3,3]- and [5,5]-sigmatropic shifts were proposed, respectively, on the basis of kinetic isotope effect (KIE) results on nitrogen and carbon atoms.[5–7] Very recently, we proposed the formation mechanisms for *o*-semidines, *p*-semidines, and diphenylines on the basis of combined experimental and computational investigation.[8] We proposed the *N*[1,3]-sigmatropic shift for the *o*-semidine rearrangement, the tandem *N*[1,3]/*N*[1,3]-sigmatropic shifts for the *p*-semidine rearrangement, and tandem *N*[1,3]/[3,3]-sigmatropic shifts for the diphenyline rearrangement.[8] Our proposed mechanisms are in good agreement with the Shine's KIE results.[5c,e,7]



Scheme 1. The rearrangement products and their established mechanisms in the benzidine rearrangement of *N*,*N*′-diarylhydrazines.

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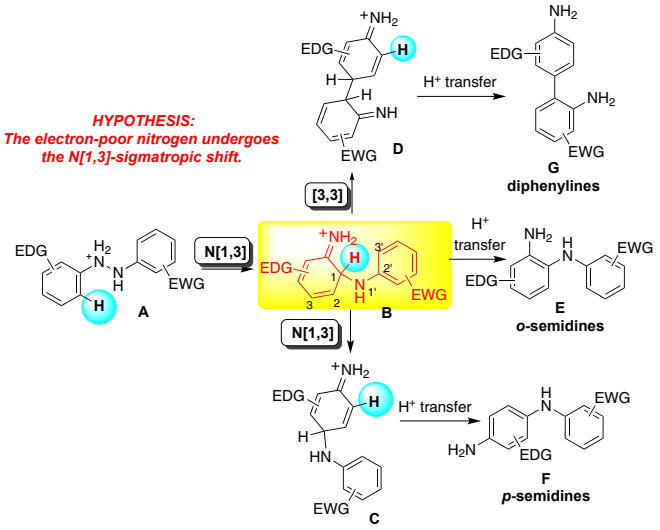
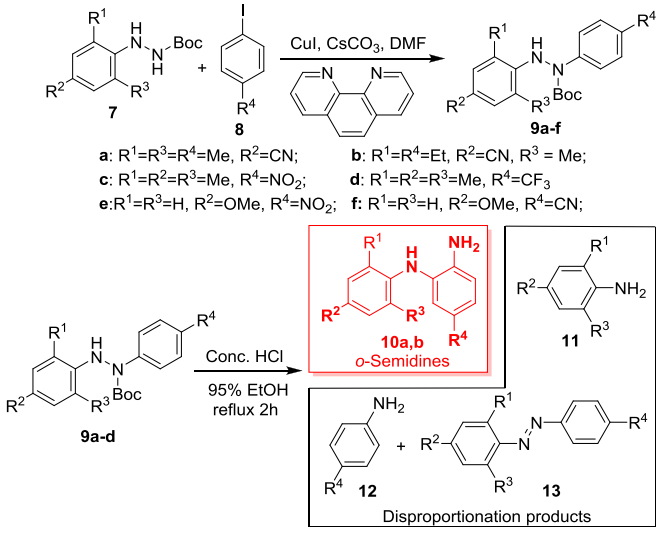


Scheme 2. Hypothesized regioselectivity of the *o*/*p*-semidine and diphenyline rearrangements.



Scheme 3. Regioselectivity in the *o*-semidine rearrangement of 2,4,4′,6-tetrasubstituted *N,N*′-diarylhydrazines **9a**–**d**.

The rearrangements of *N,N*′-diarylhydrazines have still been widely applied recently in the preparation of biaryl compounds, such as biphenyl-based cyclophanes[9] and 2,2′-diamino-1,1′-biaryl-type asymmetric catalytic ligands[10] via *p*-benzidine and *o*-benzidine rearrangements. However, the *o*-semidine, *p*-semidine, and/or diphenyline products have been obtained in considerable yields, even as major products, from certain substituted *N,N*′-diarylhydrazines,[8,11] providing valuable and metal-free alternative synthetic routes to certain aminodiarylamines and diaminobiaryls, especially halogen-substituted ones. Some halogen-substituted aminodiarylamines and diaminobiaryls, especially bromo substituted ones, are challenging to be accessed via Ullman or Suzuki coupling reactions due to the chemoselective or regioselective control of two halo groups. Thus, the *o*-semidine, *p*-semidine, and diphenyline rearrangements provide a good choice for their preparation. A survey on previously reported and our recent results indicates that the *o*-semidine, *p*-semidine, and diphenyline rearrangements show some regioselectivity.[8,11] To apply these rearrangements efficiently in synthesis of aminodiarylamines and diaminobiaryls, herein, we present our studies on the regioselectivity of the *o*-semidine, *p*-semidine, and diphenyline rearrangements of unsymmetrical *N,N*′-diarylhydrazines.

2. Results and discussion

2.1. Hypothesis on the regioselectivity

After carefully analyzing the formation mechanisms of *o*-semidines, *p*-semidines, and diphenylines, we can find that all of these three rearrangements start from the first *N*[1,3] sigmatropic shift, however, the competition among the subsequent proton transfer, the second *N*[1,3] sigmatropic shift, and [3,3] sigmatropic shift decides the product distribution. The product distribution (chemoselectivity) is controlled by the properties of substituents of *N,N*′-diarylhydrazines. From above analysis, we can suggest that the first *N*[1,3] sigmatropic shift plays an important role in controlling the regioselectivity of the *o*-semidine, *p*-semidine, and diphenyline rearrangements.

According to our formation mechanisms of *o*-semidines, *p*-semidines, and diphenylines,[8] one of two nitrogen atoms in hydrazines is protonated under acidic conditions, and the other nitrogen atom undergoes the *N*[1,3] sigmatropic shift. Thus, the protonation should determine the regioselectivity. Although the protonation is reversible, the following *N*[1,3] sigmatropic shift is generally rate-determining step in the rearrangements.[8] There is no regioselective issue in rearrangements of symmetric *N,N*′-diarylhydrazines. Unsymmetrical *N,N*′-diarylhydrazines would show the regioselectivity in the rearrangements. Since two electronically different nitrogen atoms are present in the unsymmetrical *N,N*′-diarylhydrazines ($R^1 \neq R^2$, Scheme 1), we rationalize that the electron-rich nitrogen atom is protonated favorably and the electron-poor one undergoes the rearrangements for unsymmetrical *N,N*′-diarylhydrazines. Thus, we herein hypothesize that the basicity (electron density) of the nitrogen atoms controls the regioselectivity in the *o*-semidine, *p*-semidine, and diphenyline rearrangements of unsymmetrical *N,N*′-diarylhydrazines.

The electron-rich nitrogen rather than the electron-poor one of unsymmetrical *N,N*′-diarylhydrazines should be protonated to give intermediates **A**, in accordance with calculated results,[8] weakening the N—N bond. Subsequently, the electron-poor nitrogen atom should undergo an *N*[1,3]-sigmatropic shift to the *ortho*-position of the electron-rich aryl rings to form intermediates **B**. The intermediates **B** might evolve toward three directions: (1) the direct proton transfer to afford *o*-semidines **E**; (2) a second *N*[1,3]-sigmatropic shift to give intermediates **C**, and then proton transfer to afford *p*-semidines **F**; (3) a [3,3]-sigmatropic shift to give intermediates **D** and then proton transfer to yield diphenylines **G**. Next, the experimental verification of this hypothesis on the regioselectivity of the *o*-semidine, *p*-semidine, and diphenyline rearrangements will be presented.

2.2. Regioselectivity of *o*-semidine rearrangements

To study the regioselectivity of the *o*-semidine rearrangements, we designed 2,4,4′,6-tetrasubstituted *N,N*′-diarylhydrazines **9**, two nitrogen atoms with different electron densities, since they could only undergo the pericyclic *o*-semidine rearrangements, if possible. *N,N*-Diarylhydrazines **9** were readily synthesized from 2,4,6-trisubstituted *N*′-Boc-*N*-arylhydrazines **7** and 4-substituted iodobenzenes **8** via the Cu(I)-catalyzed coupling reaction.[12] Under the acidic conditions, the Boc group of **9** would be deprotected first to release the free hydrazines $Ar^1NH—NHAr^2$, which would undergo the *o*-semidine rearrangements. Upon reflux in 95% ethanol for 2 h in the presence of concentrated HCl, the *N,N*′-diarylhydrazines from **9a** and **9b** underwent the acid-catalyzed rearrangement to afford the *o*-semidine-type products **10a** and **10b** in 35% and 16% yields,

respectively, accompanied with the disproportionation products **11a**, **12a**,**b** and **13a**,**b** (Table 1, entries 1 and 2). Delightly, the obtained *o*-semidines **10a** and **10b** were generated by the *N*[1,3]-sigmatropic shift of the electron-poor 2,6-dialkyl-4-cyanophenylamino nitrogen atom to the electron-rich 4-alkyl phenyl rings, agreeing well with our hypothesis (Scheme 3).

Table 1
Acid-catalyzed rearrangement of *N,N′*-diarylhydrazines **9**

Entry	9	Isolated yield (%)				Total[a]
		10	**11**	**12**	**13**	
1	**a**	35	17	8	22	74
2	**b**	16	29	17	38	83
3	**c**	—	14	29	35	64
4	**d**	—	16	28	37	65

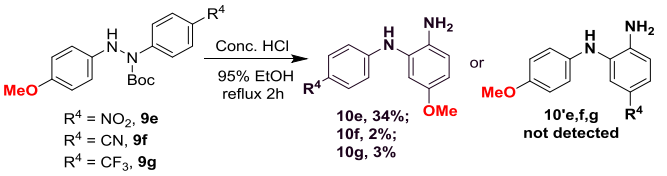
[a] Theoretically, the yields of **11** and **12** should be the same. However, since the R_f values of **11** and **12** are very close, to get the pure products by column chromatography, we only collected the purest parts, and discarded the mixed products. The total yield should be the sum of the yields of **10**, **11** (or **12**) and **13**. Herein, only the higher yields of **11** or **12** were included in the corresponding the total yields. The yields of **13** are generally higher than corresponding those of **11** and **12** possibly because of loss during purification (disposal of inseparable mixture and loss from silica gel absorption) and additional generation of **13** from direct air oxidation of **9**.

Does there exist the possibility that the electron-rich nitrogen would shift to the electron-poor aryl ring? To answer this question, we designed *N,N′*-diarylhydrazines **9c**,**d**, which each have an electron-rich 2,4,6-trisubstituted phenylamino nitrogen and an electron-poor 4-substituted phenylamino nitrogen. Since the reactive sites on the electron-rich trisubstituted phenyls are blocked, if possible, the *o*-semidine rearrangement could only occur via the *N*[1,3]-sigmatropic shift of the electron-rich nitrogen to the electron-poor phenyl ring. However, when **9c**,**d** were subjected to the standard conditions, the corresponding *o*-semidine products **10c**,**d** were not observed; instead, only disproportionation products **11c** and **12c**,**d** were isolated. The absence of the *o*-semidine-type products eliminates the possibility that the electron-rich nitrogen atom would undergo the *N*[1,3]-sigmatropic shift, confirming our hypothesis from a negative side.

The above four reactions in entries 1–4 in Table 1 were carefully designed with 2,4,6-trisubstituted phenyl groups, only to probe the regioselectivity of the *N*[1,3]-sigmatropic shift in the *o*-semidine rearrangements with one possibility. After shedding light on the regioselectivity of 2,4,4′,6-tetrasubstituted *N,N′*-diarylhydrazines **9a**–**d**, we tested it in other more common *o*-semidine rearrangements of 4,4′-disubstituted *N,N*-diarylhydrazines **9e**,**f**,**g** with two different types of *ortho*-positions. The two *para*-substituted aryls in *N,N*-diarylhydrazines **9e**,**f**,**g** were introduced only to facilitate the *o*-semidine rearrangements and to avoid the *p*-semidine and diphenyline rearrangements. They might undergo two different competitive *N*[1,3]-sigmatropic shifts with two different possibilities. However, as predicted, the reactions of *N*-(4-methoxyphenyl)-*N*-(4-nitrophenyl)hydrazine (**9e**), *N*-(4-methoxyphenyl)-*N*-(4-cyanophenyl)hydrazine (**9f**) and *N*-(4-methoxyphenyl)-*N*-(4-trifluoromethylphenyl)hydrazine (**9g**) smoothly gave the desired products **10e**, **10f**, and **10g** in 34%, 2%,[13a] and 3%[13b] yields, respectively, together with the disproportionation products **13e**, **13f**, **13g**, and the corresponding substituted anilines (Scheme 4). The undesired *o*-semidines **10′e**, **10′f**, or **10′g** involving an electron-rich $MeOC_6H_4NH$ shift was not detected.

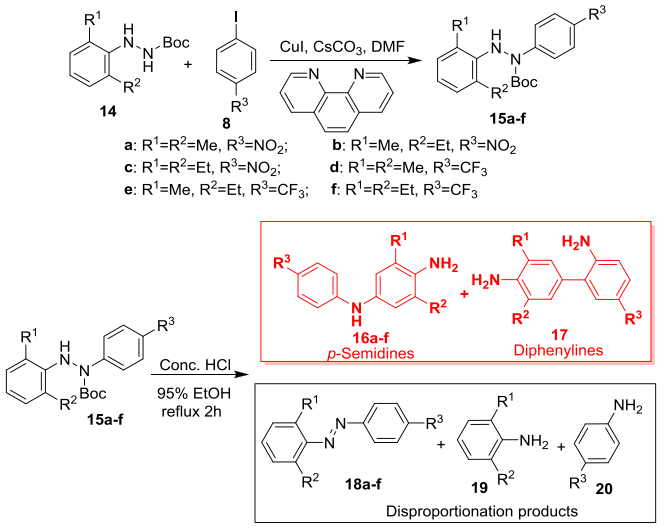
2.3. Regioselectivity of *p*-semidine rearrangements

In our previous report,[8] the *p*-semidine rearrangement mechanism is proposed as tandem *N*[1,3]- and *N*[1,3]-sigmatropic shifts of



Scheme 4. Regioselectivity in the *o*-semidine rearrangement of 4,4′-disubstituted *N,N′*-diarylhydrazines **9e**–**g**.

the same nitrogen atom in *N,N′*-diarylhydrazines. To observe the regioselectivity in the *p*-semidine rearrangements, various 2,4′,6-trisubstituted *N,N′*-diarylhydrazines **15** were designed and prepared from 2,6-disubstituted *N′*-Boc-*N*-arylhydrazines **14** and 4-substituted iodobenzenes **8** via the similar Cu(I)-catalyzed coupling reaction (Scheme 5).[12] In the current design, the 2,6-disubstituted aryls are electron-rich, while the 4-substituted aryls are electron-poor. Thus, we supposed that when the electron-rich 2,6-disubstituted phenylamino nitrogen was protonated, the electron-poor 4-subsstituted phenylamino nitrogen should undergo an *N*[1,3]-sigmatropic shift. Since the two *ortho* reactive sites of the electron-rich aryls were blocked, the first *N*[1,3]-sigmatropic shift intermediates cannot stop and would further undergo the second *N*[1,3]-sigmatropic shift to generate the *p*-semidine products. *N,N′*-Diarylhydrazines **15a**–**c** were first examined, and the expected *p*-semidines **16a**–**c** were isolated in less than 5% yields, proving that it was the electron-poor 4-nitrophenylamino nitrogen atom that underwent tandem *N*[1,3]- and *N*[1,3]-sigmatropic shifts (Table 2, entries 1–3). In the reactions of *N,N′*-diarylhydrazines **15d**–**f**, similar results were also observed. The electron-poor 4-trifluoromethylphenylamino nitrogen underwent tandem *N*[1,3]- and *N*[1,3]-sigmatropic shifts, yielding *p*-semidines **16d-f** in higher 16–18% yields (Table 2, entries 4–6). In all the cases, the diphenyline products **17**, the disproportionation products such as azobenzenes **18** and the corresponding arylamines **19** and **20** were obtained in variable yields (Table 2). All the above reaction mixtures were subjected to the LC-MS analysis without the observation of the corresponding *o*-semidines generated from 2,4-disubstituted phenylamino group shift, because the electron-rich 2,4-disubstituted phenylamino nitrogen did not undergo the *N*[1,3]-sigmatropic shift. The diphenyline rearrangements will also be discussed in the next section.



Scheme 5. Regioselectivity in the *p*-semidine and diphenyline rearrangements of 2,4′,6-trisubstituted *N,N′*-diarylhydrazines **15**.

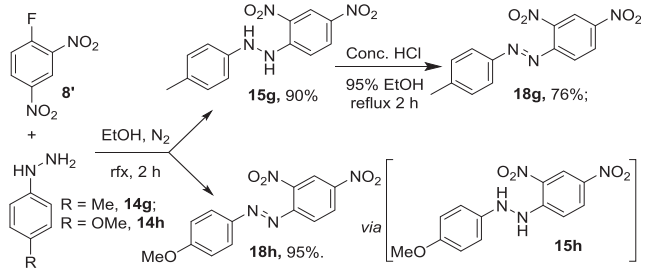
Table 2
Acid-catalyzed rearrangement of 2,4′,6-trisubstituted *N,N′*-diaryl hydrazines **15**

Entry	15	Isolated yield (%)					Total[b]
		16	**17**	**18**	**19**	**20**	
1	**a**	5	5	24	10	18	52
2	**b**	3[a]	3	26	11	20	52
3	**c**	4	4[a]	27	10	25	60
4	**d**	18	21	10	6	9	58
5	**e**	18	10	12	6	10	50
6	**f**	16	14	15	8	12	57

[a] The crude product was reacted with Ac_2O to afford the acetylated product for convenient separation.
[b] Theoretically, the yields of **19** and **20** should be the same. However, since the R_f values of **19** and **20** are very close, to get the pure products by column chromatography, we only collected the purest parts, and discarded the mixed products. The total yield should be the sum of the yields of **16**, **17**, **18**, and **19** (or **20**). Herein, only the higher yields of **19** or **20** were included in the corresponding the total yields. The yields of **18** are generally higher than corresponding those of **19** and **20** possibly because of loss during purification (disposal of inseparable mixture and loss from silica gel absorption) and additional generation of **18** from direct air oxidation of **15**.

It is very interesting that the 4-trifluoromethyl group behaved better than the 4-nitro group in facilitating the *p*-semidine and diphenyline rearrangements (Table 2, entries 1–3 vs entries 4–6). However, the opposite phenomenon was observed in the *o*-semidine rearrangement (Scheme 4, **9e** vs **9g**). The reason is not completely clear now. The current experimental results seemingly indicate that the stronger electron-withdrawing nitro group (Hammett constant −0.78) could promote the first *N*[1,3]-sigmatropic shift (from **A** to **B**), but is unfavorable for the subsequent *N*[1,3]- (from **B** to **C**) and [3,3]-sigmatropic shifts (from **B** to **D**). However, the less strong electron-withdrawing trifluoromethyl group (Hammett constant −0.54) is favorable for both the *N*[1,3]- (from **B** to **C**) and [3,3]-sigmatropic shifts (from **B** to **D**). Of course, it should be also favorable for the first *N*[1,3]-sigmatropic shift in *N,N′*-diarylhydrazines **15**, but not in *N,N′*-diarylhydrazines **9**, related to the electron densities of the other aryl groups in *N,N′*-diarylhydrazines.

To further observe the regioselectivity in the *p*-semidine rearrangements with opposite electron densities in the two aryl groups, *N*-(4-methylphenyl)-*N*-(2,4-dinitrophenyl)hydrazine (**15g**) and *N*-(4-methoxyphenyl)-*N*-(2,4-dinitrophenyl)hydrazine (**15h**) were also designed (Scheme 6).[14] However, only **15g** was successfully synthesized. It failed to undergo the *N*[1,3]-sigmatropic shift, but was smoothly converted into the corresponding azo compound **18g** in 76% yield under standard conditions. In the reaction of **8′** and **14h**, only **18h** was obtained unexpectedly in 95% yield, probably via hydrazine **15h**. It deserves mention that hydrazines **15g** and **15h** are sensitive to air oxidation, and the adventitious oxygen in the reaction vessels or the oxygen in air caused the predominant formation of azo compounds **18g** and **18h**, respectively.



Scheme 6. Preparation and reactions of *N*-aryl-*N*-(2,4-dinitrophenyl)hydrazines **15g**,**h**.

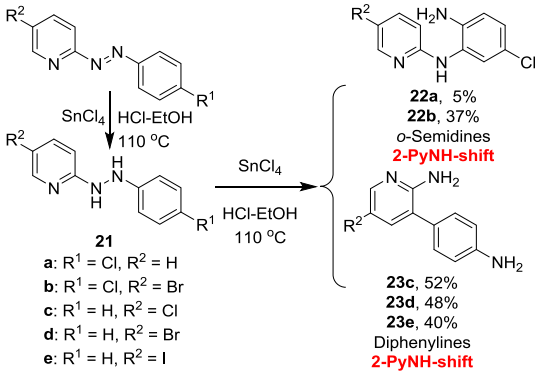
2.4. Regioselectivity of diphenyline rearrangements

In Table 2, the diphenyline products **17** were generated. On the basis of proposed formation mechanism, tandem *N*[1,3] and [3,3]-sigmatropic shifts, comparing the experimentally obtained structures **17a**–**f** with the hypothetically predicted structures **G** in Scheme 2 clearly indicated that it was the electron-poor arylamino nitrogen atom that underwent the *N*[1,3]-sigmatropic shift followed by [3,3] sigmatropic shift.

2.5. Application of our regioselective rule on explanation of reported results

Finally, the regioselectivity of the *o*-semidine, *p*-semidine, and dipenyline rearrangements was investigated and summarized. No matter in the *o*-semidine, *p*-semidine or dipenyline rearrangements, a general regioselectivity is observed that the electron-poor arylamino nitrogen atom undergoes the *N*[1,3]-sigmatropic shift to the electron-rich aryl rings because all three rearrangements start from the same *N*[1,3]-sigmatropic shift, and the electron-rich nitrogen is protonated and the electron poor nitrogen undergoes the *N*[1,3]-sigmatropic shift. Our regioselective rule demonstrates as a general rule to predict the products in the *o*-semidine, *p*-semidine or dipenyline rearrangements of the *N,N′*-diarylhydrazines with two obviously different aryl groups in electron density.

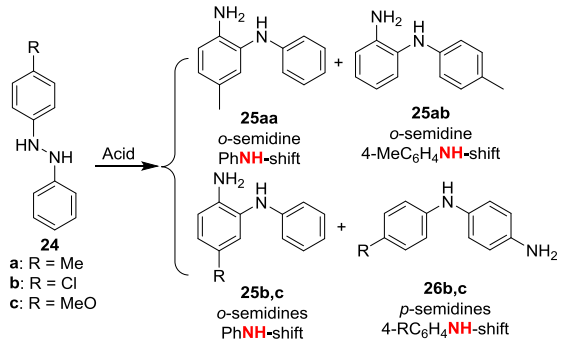
The *N,N′*-diarylhydrazines with an electron-rich aryl and an electron-poor aryl generally show excellent regiospecificity of the *N*[1,3]-sigmatropic shift in the *o*-semidine, *p*-semidine, and diphenyline rearrangements. That is, obviously electron-poor arylamino nitrogen atom undergoes the sigmatropic shift(s). For instance, *N*-(4-chlorophenyl)-*N′*-pydin-2-ylhydrazine (**21a**) and *N*-(4-chlorophenyl)-*N′*-(5-bromopydin-2-yl)hydrazine (**21b**) underwent *o*-semidine rearrangements to afford *o*-semidine products **22a** and **22b** in 5% and 37% yields, respectively, through the *N*[1,3]-sigmatropic shift of the electron-poor pyridine-2-ylamino nitrogen. The diarylhydrazine **21b** with more electron deficient 5-bromopyridin-2-yl group gave higher yield of the *o*-semidine product. However, *N*-phenyl-*N′*-(5-halopydin-2-yl)hydrazines **21c**–**e** underwent diphenyline rearrangement to give rise to the corresponding products diphenylines **23c**–**e** in 52–40% yields through the tandem *N*[1,3]- and [3,3]-sigmatropic shifts of the electron-poor 5-halopyridine-2-ylamino nitrogen (Scheme 7).[11d]



Scheme 7. Good regioselectivity in *o*-semidine and diphenyline rearrangements of *N,N′*-diarylhydrazines with two aryls possessing obvious difference in electron density.

In the cases that the two nitrogens of *N,N′*-diarylhydrazines show little difference in electron density, it is possible that both of the nitrogen atoms may be protonated, resulting in both of the

nitrogen atoms can undergo the *N*[1,3]-sigmatropic shift. For example, in the reaction of *N*-(4-methylphenyl)-*N*′-phenylhydrazine (**24a**) (Scheme 8),[11c] both the relatively electron-rich 4-methylphenylamino and relatively electron poor phenylamino nitrogen atoms underwent the *N*[1,3]-shift in the *o*-semidine rearrangement to afford two different *o*-semidine products **25aa** and **25ab**. However, in the reaction of *N*-(4-chlorophenyl)-*N*′-phenylhydrazine (**24b**) (Scheme 8),[11a] the relatively electron-rich phenylamino nitrogen atom underwent the *N*[1,3]-shift in the *o*-semidine rearrangement to afford **25b**, and the relatively electron-poor 4-chlorophenyl nitrogen atom underwent tandem *N*[1,3]- and *N*[1,3]-sigmatropic shifts in the *p*-semidine rearrangement to produce **26b**. In the reaction of *N*-(4-methoxyphenyl)-*N*′-phenylhydrazine (**24c**) (Scheme 8),[11b] the relatively electron-poor phenyl nitrogen atom underwent the *N*[1,3]-shift in the *o*-semidine rearrangement to afford **25c**, and the relatively electron-rich 4-methoxyphenyl nitrogen atom underwent tandem *N*[1,3]- and *N*[1,3]-sigmatropic shifts in the *p*-semidine rearrangement to produce **26c**. In these cases, the poor regioselectivity was mainly caused by the little electron density difference, namely, slight difference in basicity of the two nitrogen atoms of *N,N*′-diarylhydrazines **24a**–**c**. It is a pity that the yields of **25** and **26** were not reported in the literature.[11a–c]



Scheme 8. Poor regioselectivity in *o*/*p*-semidine rearrangements of *N,N*′-diarylhydrazines with two aryls possessing unobvious difference in electron density.

3. Conclusion

The regioselectivity of the *o*-semidine, *p*-semidine, and diphenyline rearrangements of unsymmetrical *N,N*′-diarylhydrazines was studied by a series of designed substrates. The designed and employed substrates possess two distinctly different nitrogen atoms in electron density. The results indicate that the electron-rich nitrogen atom is first protonated and then the electron-poor non-protonated nitrogen atom undergoes an *N*[1,3]-sigmatropic shift to the *ortho*-position of the electron-rich aryl rings, generating key intermediates **B**. The intermediates can undergo (1) direct proton transfer to give the *o*-semidines, (2) a second *N*[1,3]-sigmatropic shift of the electron-poor nitrogen atom and then proton transfer to furnish *p*-semidines, and (3) a [3,3]-sigmatropic shift and subsequent proton transfer to yield diphenylines. It is the first *N*[1,3]-sigmatropic shift step (basicity of the nitrogen atom) that plays an important role in controlling the regioselectivity, further determining the structures of *o*-semidines, *p*-semidines, and diphenylines. The current results provide new insights into the *o*/*p*-semidine and diphenyline rearrangements and useful information for predicting the structures of the rearrangement products, especially for the unsymmetrical *N,N*′-diarylhydrazines with two electronically distinctly different aryls.

4. Experimental section

4.1. General information

Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. ^{1}H NMR, ^{13}C NMR, and ^{11}F NMR spectra were recorded on a Bruker 300 MHz or 400 MHz spectrometer with TMS as an internal standard or $BF_3{\cdot}OEt_2$ as an external standard in the $CDCl_3$ solution. IR spectra were taken on a Nicolet 370 MCT FT-IR spectrometer in KBr. HRMS data were obtained with an Agilent LC/MSD TOF mass spectrometer. Products were purified on column chromatography using silica gel (200–300 mesh) (Yantai Chemical Co.). TLC separations were performed on silica gel G plates with petroleum ether/ethyl acetate, and the plates were visualized with UV light.

4.2. Typical procedure for synthesis of aryl hydrazines

To a mixture of concentrated HCl (50 mL) and water (40 mL) was added 2,6-dimethylaniline (24.2 g, 0.2 mol) under vigorous stirring. The resulting mixture was cooled to −4 °C, and a solution of $NaNO_2$ (15.2 g, 0.22 mol) in water (30 mL) was added dropwise to maintain temperature below 0 °C. After addition of the sodium nitrite solution, the reaction mixture was stirred for 30 min. A solution of stannous dichloride hydrate (112.8 g, 0.5 mol) in 160 mL of 6 mol/L hydrochloric acid was added over a period of 1.5 h, during which the temperature of the reaction mixture was maintained below 5 °C. The yellowish slurry was allowed to stand overnight at room temperature and stirring was continued for another 22 h. And then the mixture was cooled by ice-water for 1 h. The pale yellow tin complex salt was collected by filtration, dried on the funnel and washed with brine (50 mL), and ether (2×50 mL). The dry complex salt was stirred in water (100 mL), and slurry was stirred vigorously while it was treated with 10 mol/L NaOH (100 mL). The temperature of the mixture was maintained below 15 °C. The crude hydrazine was extracted from the mixture with ether (2×200 mL), and the etheral solution was washed with water (200 mL) and dried over Na_2SO_4. The dried etheral solution was diluted with ether to 500 mL. The diluted solution was treated with 4.8 mol/L HCl in 1,4-dioxane (50 mL) until precipitation of the hydrazine hydrochloride was complete. The filtered hydrochloride was washed with ether (50 mL), dried over Na_2SO_4, and recrystallized from ethanol to afford 2,6-dimethylphenylhydrazine hydrochloride salt as colorless crystals 21.9 g in 63% yield.

4.2.1. 2,6-Dimethylphenylhydrazine hydrochloride salt. Colorless crystals, mp 210–212 °C dec (Lit.[15] 211 °C dec), ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.39 (s, 6H), 6.71 (br s, 1H), 7.08 (s, 3H), 9.82 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 140.6, 134.9, 128.6, 126.9, 18.0.

4.2.2. 2-Ethyl-6-Methylphenylhydrazine hydrochloride salt.[16] Prepared according to the typical procedure from 2-ethyl-6-methylaniline (27.0 g, 0.2 mol), and recrystallized from ethanol to afford 2-ethyl-6-methylphenylhydrazine hydrochloride salt as colorless crystals 24.7 g in 66% yield, mp 200–202 °C dec. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.15 (t, J=7.5 Hz, 3H), 2.40 (s, 3H), 2.77 (q, J=7.5 Hz, 2H), 6.71 (br s, 1H), 7.10–7.17 (m, 3H), 9.76 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 140.7, 140.0, 135.1, 128.6, 127.3, 126.6, 23.6, 18.1, 15.1.

4.2.3. 2,6-Diethylphenyl hydrazine hydrochloride salt. Prepared according to the typical procedure from 2,6-diethylaniline (29.9 g, 0.2 mol), and recrystallized from a mixture of ethanol and diethyl ether to afford 2,6-diethylphenyl hydrazine hydrochloride salt as colorless crystals 18.0 g in 45% yield, mp 170–172 °C dec (Lit.[17] 176–177 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.17 (t, J=7.5 Hz, 6H), 2.77 (q, J=7.5 Hz, 4H), 6.70 (br s, 1H), 7.11–7.23 (m, 3H), 9.75 (s,

3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 140.8, 139.4, 127.5, 126.4, 23.6, 14.9.

4.2.4. 2,4,6-Trimethylphenylhydrazine hydrochloride salt.[12] Prepared according to the typical procedure from 2,4,6-trimethylaniline (27.0 g, 0.2 mol), and recrystallized from 95% ethanol to afford 2,4,6-trimethylphenylhydrazine hydrochloride salt as colorless crystals 20.3 g in 45% yield, mp 195–197 °C dec. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.21 (s, 3H), 2.35 (s, 6H), 6.62 (br s, 1H), 6.88 (s, 2H), 9.73 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 138.0, 136.1, 134.9, 129.1, 20.5, 17.9.

4.2.5. 4-Cyano-2,6-dimethylphenylhydrazine. Prepared according to the typical procedure from 4-cyano-2,6-dimethylaniline (8.33 g, 57 mmol), however, the hydrazine did not convert into hydrochloride with HCl in 1,4-dioxane. The crude product was purified by Al_2O_3 column chromatography with petroleum ether/ethyl acetate to afford 4-cyano-2,6-dimethylphenylhydrazine as orange crystals 4.02 g in 44% yield, mp 100–100.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.34 (s, 6H), 3.66 (s, 2H), 5.28 (s, 1H), 7.22 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.3, 132.8, 127.6, 119.7, 103.9, 18.7. IR (KBr) ν (cm^{-1}): 3356, 3303, 2961, 2919, 2218. HRMS (ESI) calcd for $C_9H_{11}N_3$ $[M+H]^+$ *m/z*: 162.1026, found 162.1032.

4.2.6. 4-Cyano-2-ethyl-6-methylphenylhydrazine. Prepared according to the typical procedure from 4-cyano-2-ethyl-6-methylaniline (12.9 g, 80 mmol), however, the hydrazine did not convert into hydrochloride with HCl in 1,4-dioxane. The crude product was purified by Al_2O_3 column chromatography with petroleum ether/ethyl acetate to afford 4-cyano-2-ethyl-6-methylphenylhydrazine as orange crystals 8.5 g in 61% yield, mp 56–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.24 (t, *J*=7.5 Hz, 3H), 2.37 (s, 3H), 2.7 (q, *J*=7.5 Hz, 2H), 3.66 (br s, 2H), 5.22 (br s, 1H), 7.27 (s, 1H), 7.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.7, 133.4, 132.6, 130.7, 128.6, 119.7, 104.0, 24.5, 18.8, 14.0. IR (KBr) ν (cm^{-1}): 3364, 2968, 2932, 2876, 2218. HRMS (ESI) calcd for $C_{10}H_{13}N_3$ $[M+H]^+$ *m/z*: 176.1182, found 176.1184.

4.3. General procedure for synthesis of *N′*-Boc-*N*-arylhydrazines 7 and 14

To a mixture of an arylhydrazine hydrochloride salt (10 mmol) and triethylamine (1.5 mL, 1.09 g, 11 mmol) or to a solution of an arylhydrazine (10 mmol) in THF (30 mL) was added dropwise a solution of $(Boc)_2O$ (2.41 g, 11 mmol) in THF (20 mL) under stirring in an ice-water bath. The resulting mixture was stirred at room temperature for 2–3 h, filtered, and washed with diethyl ether. The filtrate was then washed successively with saturated sodium bicarbonate and brine. The organic layer was dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure, and purified by flash silica gel chromatography with a mixture of petroleum ether and ethyl acetate as an eluent to afford the desired product.

*4.3.1. N′-Boc-N-(4-cyano-2,6-dimethylphenyl)hydrazine (**7a**).* Colorless crystals, 2.38 g, yield 91%, mp 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.41 (s, 9H), 2.36 (s, 6H), 5.90 (s, 1H), 6.51 (s, 1H), 7.24 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.0, 148.6, 132.8, 127.5, 119.5, 104.9, 81.4, 28.13, 18.6. IR (KBr) ν (cm^{-1}): 3357, 2979, 2930, 2220, 1717. HRMS (ESI) calcd for $C_{14}H_{19}N_3O_2$ $[M+Na]^+$ *m/z*: 262.1550, found 262.1559.

*4.3.2. N′-Boc-N-(4-cyano-2-ethyl-6-methylphenyl)hydrazine (**7b**).* Colorless crystals, 1.92 g, yield 70%, mp 136–136.5 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (t, *J*=7.5 Hz, 3H), 1.40 (s, 9H), 2.38 (s, 3H), 2.76 (q, *J*=7.5 Hz, 2H), 5.93 (d, *J*=2.4 Hz, 1H), 6.38 (s, 1H), 7.26 (s, 1H), 7.29 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.0, 148.1, 133.1, 132.7, 130.7, 127.8, 119.6, 105.0, 81.3, 28.1, 24.3, 18.9, 13.5. IR (KBr) ν (cm^{-1}): 3347, 2971, 2927, 2222, 1711. HRMS (ESI) calcd for $C_{15}H_{21}N_3O_2$ $[M+H]^+$ *m/z*: 276.1707, found 276.1712.

*4.3.3. N′-Boc-N-(2,4,6-trimethylphenyl)hydrazine (**7c**).* Colorless crystals, 2.43 g, yield 98%, mp 99.5–100.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.41 (s, 9H), 2.22 (s, 3H), 2.34 (s, 6H), 5.64 (br s, 1H), 6.27 (s, 1H), 6.80 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 156.2, 141.6, 132.2, 129.5, 128.0, 80.5, 28.2, 20.5, 18.3. IR (KBr) ν (cm^{-1}): 3365, 2975, 2858, 1701, 1485, 1457, 1367, 1160, 852. HRMS (ESI) calcd for $C_{14}H_{22}N_2O_2$ $[M+Na]^+$ *m/z*: 273.1573, found 273.1563.

*4.3.4. N′-Boc-N-(2,6-dimethylphenyl)hydrazine (**14a**).* Colorless crystals, 2.15 g, yield 92%, mp 74–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.41 (s, 9H), 2.35 (s, 6H), 5.72 (s, 1H), 6.51 (s, 1H), 6.83 (t, *J*=7.3 Hz, 1H), 6.97 (d, *J*=7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.1, 144.1, 128.9, 127.9, 122.8, 80.4, 28.1, 18.4. IR (KBr) ν (cm^{-1}): 3367, 3309, 2974, 1688, 1509, 1476, 1300, 1163. HRMS (ESI) calcd for $C_{12}H_{20}N_2O_2$ $[M+Na]^+$ *m/z*: 259.1417, found 259.1410.

*4.3.5. N′-Boc-N-(2-ethyl-6-methylphenyl)hydrazine (**14b**).* Colorless crystals (The crude material was purified by flash silica gel column chromatography to afford an oil, which was solidified as colorless crystals upon storage), 2.35 g, yield 94%, mp 60–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23 (t, *J*=7.5 Hz, 3H), 1.41 (s, 9H), 2.36 (s, 3H), 2.77 (q, *J*=7.5 Hz, 2H), 5.76 (s, 1H), 6.41 (s, 1H), 6.88–7.01 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 156.1, 143.5, 133.8, 128.8, 128.4, 126.7, 123.0, 80.4, 28.1, 24.4, 18.6, 14.4. IR (KBr) ν (cm^{-1}): 3340, 2975, 2932, 2873, 1700, 1595, 1466, 1367, 1164, 759. HRMS (ESI) calcd for $C_{14}H_{22}N_2O_2$ $[M+H]^+$ *m/z*: 251.1754, found 251.1745.

*4.3.6. N′-Boc-N-(2,6-diethylphenyl)hydrazine (**14c**).* Colorless crystals (The crude material was purified by flash silica gel column chromatography to afford as oil, which solidified as colorless crystals upon storage), 2.62 g, yield 99%, mp 45–46 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23 (t, *J*=7.5 Hz, 6H), 1.39 (s, 9H), 2.76 (q, *J*=7.5 Hz, 4H), 5.77 (s, 1H), 6.40 (s, 1H), 6.93–7.03 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 156.1, 143.0, 134.5, 126.7, 123.5, 80.6, 28.2, 24.6, 14.5. IR (KBr) ν (cm^{-1}): 3338, 2967, 2933, 2874, 1702, 1594, 1456, 1366, 1162, 760. HRMS (ESI) calcd for $C_{15}H_{24}N_2O_2$ $[M+Na]^+$ *m/z*: 287.1730, found 287.1715.

4.4. General procedure for the synthesis of *N*-Boc-*N,N′*-diaryl hydrazines 9 and 15

To a round-bottom flask were charged with an *N′*-Boc-*N*-aryl hydrazine **7** or **14** (48 mmol), 4-substituent iodobenzene **8** (40 mmol), CuI (0.78 g, 4 mmol), 1,10-phenanthroline (1.44 g, 8 mmol), Cs_2CO_3 (15.64 g, 48 mmol) and 40 mL of dry DMF at room temperature. The reaction mixture was degassed, charged with N_2 gas and heated to 80 °C. After 4–5 h, the resulting mixture was cooled to room temperature, diluted with ethyl acetate (100 mL), filtered. The filtrate was then washed twice with brine (2×100 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered, concentrated under reduced pressure, The residue was purified by flash chromatography with a mixture of petroleum ether and ethyl acetate as an eluent to afford the desired product, which was recrystallized from a mixture of petroleum ether and ethyl acetate to give the desired crystals **9** or **15**.

The analytical data of compounds **9a**,**b** and **15a**–**f** are identical with those reported in our group.[8]

*4.4.1. tert-Butyl 2-(4-cyano-2,6-dimethylphenyl)-1-(4-methylphenyl)hydrazinecarboxylate (**9a**).* Colorless crystals, 4.50 g, yield 32%, mp 157–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.33 (s, 9H),

2.23 (s, 6H), 2.32 (s, 3H), 6.43 (s, 1H), 7.14 (d, J=8.7 Hz, 2H), 7.21 (s, 2H), 7.47 (d, J=8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.1, 148.0, 140.4, 134.3, 133.2, 128.9, 125.6, 121.6, 119.6, 103.7, 82.5, 27.9, 20.7, 19.0. IR (KBr) ν (cm^{-1}): 3356, 2977, 2926, 2218, 1717.

*4.4.2. tert-Butyl 2-(4-cyano-2-ethyl-6-methylphenyl)-1-(4-ethylphenyl)hydrazinecarboxylate (**9b**).* Colorless crystals, 5.62 g, yield 37%, mp 164–164.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.20 (t, J=7.5 Hz, 3H), 1.23 (t, J=7.5 Hz, 3H), 1.33 (s, 9H), 2.24 (s, 3H), 2.59 (q, J=7.5 Hz, 2H), 2.64 (q, J=7.5 Hz, 2H), 6.45 (d, J=4.1 Hz, 1H), 7.17 (d, J=8.6 Hz, 2H), 7.23 (s, 1H), 7.28 (s, 1H), 7.49 (d, J=8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.1, 147.6, 140.5, 140.5, 133.1, 131.5, 130.8, 127.6, 126.0, 121.6, 119.7, 103.8, 82.3, 28.0, 27.8, 24.3, 19.4, 15.3, 13.6, 8.7.

*4.4.3. tert-Butyl 2-(2,4,6-trimethylphenyl)-1-(4-nitrophenyl)hydrazinecarboxylate (**9c**).* Orange crystals, 2.53 g, yield 17%, mp 127–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (s, 9H), 2.14 (s, 6H), 2.22 (s, 3), 6.20 (s, 1H), 6.77 (s, 2H), 8.03–8.08 (m, 2H), 8.19–8.24 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.4, 149.5, 142.9, 140.7, 131.1, 130.3, 124.9, 124.1, 119.9, 83.6, 27.7, 20.3, 18.9. IR (KBr) ν (cm^{-1}): 3358, 2978, 2928, 2857, 1720, 1591, 1511, 1455, 1308. HRMS (ESI) calcd for $C_{20}H_{25}N_3O_4$ $[M+H]^+$ m/z: 372.1918, found 372.1927.

*4.4.4. tert-Butyl 2-(2,4,6-trimethylphenyl)-1-(4-trifluoromethylphenyl) hydrazinecarboxylate (**9d**).* Colorless crystals, 6.15 g, yield 39%, mp 101–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 9H), 2.15 (s, 6H), 2.21 (s, 3H), 6.17 (s, 1H), 6.76 (s, 2H), 7.57 (d, J=8.6 Hz, 2H), 7.90 (d, J=8.6 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.9, 146.8, 141.0, 130.8, 130.4, 130.1, 125.5 (q, J_1=3.7 Hz), 125.3 (q, J_2=32.5 Hz), 125.2, 124.3 (q, J_3=270 Hz), 120.8, 120.1, 82.7, 27.7, 20.2, 18.9. IR (KBr) ν (cm^{-1}): 3338, 2980, 1701, 1617, 1522, 1487, 1457, 1322. HRMS (ESI) calcd for $C_{21}H_{25}F_3N_2O_2$ $[M+H]^+$ m/z: 395.1941, found 395.1958.

*4.4.5. tert-Butyl 2-(4-methoxyphenyl)-1-(4-nitrophenyl)hydrazine-1-carboxylate (**9e**).* This reaction was performed on 5-mmol scale, and the product was inseparable from its another isomers, with a ratio 2:3 and a total yield 0.674 g (38%). For detail, see the ^{1}H and ^{13}C NMR spectra in ESI. Yellow oil, 0.27 g, yield 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=9.4, 2H), 7.70 (d, J=9.3, 2H), 6.84 (d, J=8.9, 2H), 6.72 (d, J=8.9, 2H), 6.30 (s, 1H), 3.79 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 153.1, 151.9, 148.6, 143.3, 125.9, 124.4, 114.7, 114.5, 83.7, 55.6, 27.9. IR (KBr) ν (cm^{-1}): 3359, 2978, 2932, 1721, 1590, 1514, 1476, 1308. HRMS (ESI) calcd for $C_{18}H_{22}N_3O_5$ $[M+H]^+$ m/z: 360.1554, found 360.1543.

*4.4.6. tert-Butyl 1-(4-cyanophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (**9f**).* This reaction was performed on 5-mmol scale. Yellowish crystals, mp 127–129 °C, 0.48 g, yield 28%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.9 Hz, 2H), 7.59 (d, J=8.9 Hz, 2H), 6.81 (d, J=8.9 Hz, 2H), 6.68 (d, J=8.9 Hz, 2H), 6.23 (s, 1H), 3.76 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.8, 153.2, 146.8, 141.0, 132.7, 120.4, 119.0, 114.7, 114.5, 106.7, 83.4, 55.6, 27.9. IR (KBr) ν (cm^{-1}): 3356, 2977, 2926, 2218, 1717. HRMS (ESI) calcd for $C_{19}H_{22}N_3O_3$ $[M+H]^+$ m/z: 340.1656, found 340.1652.

*4.4.7. tert-Butyl 2-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl) hydrazine-1-carboxylate (**9g**).* This reaction was performed on 5-mmol scale. Yellowish crystals, mp 79–81 °C, 0.42 g, yield 22%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J=8.6 Hz, 2H), 7.59 (d, J=8.6 Hz, 2H), 6.84 (d, J=8.9 Hz, 2H), 6.74 (d, J=8.9 Hz, 2H), 6.30 (s, 1H), 3.79 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 154.7, 153.5, 145.9, 141.4, 125.7 (q, J_{C-F}=31 Hz), 125.6 (q, J_{C-F}=3.8 Hz), 124.6 (q, J_{C-F}=270 Hz), 120.6, 114.7, 114.5, 83.0, 55.6, 28.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ −62.0. IR (KBr) ν (cm^{-1}): 1715. HRMS (ESI) calcd for $C_{14}H_{12}F_3N_2O$ $[M+H\text{-}^t BuOH\text{-}CO]^+$ m/z: 281.0896, found 281.0900.

*4.4.8. tert-Butyl 2-(2,6-dimethylphenyl)-1-(4-nitrophenyl)hydrazinecarboxylate (**15a**).* Orange crystals, 2.57 g, yield 18%, mp 153–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.27 (s, 9H), 2.17 (s, 6H), 6.27 (s, 1H), 6.82 (t, J=7.4 Hz, 1H), 6.97 (d, J=7.4 Hz, 2H), 8.07–8.12 (m, 2H), 8.19–8.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.3, 149.3, 143.3, 142.8, 129.7, 124.8, 124.1, 121.9, 119.7, 83.7, 27.6, 19.0.

*4.4.9. tert-Butyl 2-(2-ethyl-6-methylphenyl)-1-(4-nitrophenyl)hydrazinecarboxylate (**15b**).* Orange crystals, 2.38 g, yield 16%, mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, J=7.5 Hz, 3H), 1.26 (s, 9H), 2.15 (s, 3H), 2.56 (q, J=7.5 Hz, 2H), 6.34 (s, 1H), 6.85–7.03 (m, 3H), 8.06–8.12 (m, 2H), 8.20–8.25 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.4, 149.4, 143.0, 142.8, 131.2, 129.8, 127.3, 125.3, 124.1, 122.1, 119.8, 83.7, 27.6, 24.7, 19.5, 14.2.

*4.4.10. tert-Butyl 2-(2,6-diethylphenyl)-1-(4-nitrophenyl)hydrazinecarboxylate (**15c**).* Orange crystals, 2.00 g, yield 13%, mp 164–165 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15 (t, J=7.5 Hz, 6H), 1.26 (s, 9H), 2.52 (q, J=7.5 Hz, 4H), 6.37 (s, 1H), 6.94–7.04 (m, 3H), 8.07–8.12 (m, 2H), 8.21–8.26 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.5, 149.4, 143.2, 142.3, 131.9, 127.3, 124.1, 122.6, 120.1, 83.8, 27.7, 24.9, 14.4.

*4.4.11. tert-Butyl 2-(2,6-dimethylphenyl)-1-[4-(trifluoromethyl)phenyl]hydrazinecarboxylate (**15d**).* Colorless crystals, 5.63 g, yield 37%, mp 105–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (s, 9H), 2.19 (s, 6H), 6.23 (s, 1H), 6.80 (t, J=7.5 Hz, 1H), 6.95 (d, J=7.5 Hz, 2H), 7.59 (d, J=8.7 Hz, 2H), 7.95 (d, J=8.7 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.8, 146.7, 143.6, 129.6, 125.3 (q, J_1=3.8 Hz), 125.2 (q, J_2=32.5 Hz), 125.0, 124.3 (q, J_3=270 Hz), 121.6, 120.4, 82.8, 27.6, 18.9.

*4.4.12. tert-Butyl 2-(2-ethyl-6-methylphenyl)-1-(4-trifluoromethylphenyl)hydrazinecarboxylate (**15e**).* Colorless crystals, 7.10 g, yield 45%, mp 121–121.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.18 (t, J=7.5 Hz, 3H), 1.28 (s, 9H), 2.17 (s, 3H), 2.56 (q, J=7.5 Hz, 2H), 6.30 (s, 1H), 6.84–7.02 (m, 3H), 7.58–7.61 (m, 2H), 7.93–7.96 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.9, 146.6, 143.0, 131.4, 129.7, 127.2, 125.5, 125.5 (q, J_2=32.5 Hz), 125.4 (q, J_3=3.7 Hz), 124.3 (q, J_1=270 Hz), 122.0, 120.7, 83.0, 27.7, 24.7, 19.5, 14.3.

*4.4.13. tert-Butyl 2-(2,6-diethylphenyl)-1-[4-(trifluoromethyl)phenyl]hydrazinecarboxylate (**15f**).* Colorless crystals, 4.41 g, yield 27%, mp 83–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15 (t, J=7.5 Hz, 6H), 1.27 (s, 9H), 2.54 (q, J=7.5 Hz, 4H), 6.34 (s, 1H), 6.90–7.03 (m, 3H), 7.58–7.61 (m, 2H), 7.92–7.95 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 154.1, 146.7, 142.5, 132.1, 127.3, 125.7 (q, J_2=32.3 Hz), 125.4 (q, J_3=3.7 Hz), 124.3 (q, J_1=270 Hz), 122.4, 120.9, 83.0, 27.8, 24.9, 14.5.

4.5. General procedure for the acid-catalyzed rearrangements of *N,N′*-diarylhydrazines 9 and 15

To a round bottom flask were charged with an *N,N′*-diaryl hydrazine (**9** or **15**, 1 mmol), 95% ethanol (10 mL), and conc. HCl (0.5 mL) under nitrogen at room temperature. The reaction mixture was refluxed for 2 h, then cooled to room temperature, neutralized with solid $NaHCO_3$, filtered, concentrated. The residue was purified by flash column chromatography.

The analytical data of compounds **10a**,**b**, **13**, **16**, **17**, and **18** are identical with those reported in our group.[8]

*4.5.1. 4-[(2-Amino-5-methylphenyl)amino]-3,5-dimethylbenzonitrile (**10a**).* Pink crystals, 88 mg, yield 35%, mp 133–134 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.13 (s, 9H), 3.65 (s, 2H), 5.02 (s, 1H), 6.17 (s,

1H), 6.70 (s, 2H), 7.36 (d, J=0.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.5, 135.4, 132.5, 131.3, 131.2, 129.0, 123.7, 119.6, 119.3, 116.3, 105.4, 20.6, 18.5.

*4.5.2. 4-[(2-Amino-5-ethylphenyl)amino]-3-ethyl-5-methylbenzonitrile (**10b**).* Pink oil, 45 mg, yield 16%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.07 (t, J_1=7.6 Hz, 3H), 1.17 (t, J_2=7.5 Hz, 3H), 2.08 (s, 3H), 2.40 (q, J_1=7.6 Hz, 2H), 2.53 (q, J_2=7.5 Hz, 2H), 3.64 (s, 2H), 5.10 (s, 1H), 6.15 (s, 1H), 6.68–6.75 (m, 2H), 7.35 (s, 1H), 7.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.8, 137.3, 135.8, 135.2, 132.5, 132.1, 131.9, 130.5, 122.1, 119.7, 117.6, 116.4, 105.9, 28.1, 24.4, 18.6, 16.0, 13.8.

*4.5.3. 5-Methoxy-N^1-(4-nitrophenyl)benzene-1,2-diamine (**10e**).* This reaction was performed on 0.75-mmol scale. Yellow crystals, 65 mg, yield 34%, mp 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, J=9.2, 2H), 7.32 (d, J=8.8, 1H), 7.03 (d, J=2.8, 1H), 6.87 (dd, J=8.8, 2.8, 1H), 6.80 (d, J=9.2, 2H), 6.15 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 150.6, 139.8, 129.6, 129.2, 126.2, 125.8, 115.5, 113.8, 113.3, 55.8. IR (KBr) ν (cm^{-1}): 3363, 2962, 1301. HRMS (ESI) calcd for $C_{13}H_{14}N_3O_3$ $[M+H]^+$ m/z: 260.1030, found 260.1037.

*4.5.4. 3,5-Dimethyl-N^1-(4-nitrophenyl)benzene-1,4-diamine (**16a**).* Orange crystals, 13 mg, yield 5%, mp 193–195 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.20 (s, 6H), 3.63 (s, 2H), 6.04 (s, 1H), 6.71 (d, J=9.2 Hz, 2H), 6.83 (s, 2H), 8.07 (d, J=9.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.4, 141.0, 138.6, 129.0, 126.4, 124.8, 122.8, 112.3, 17.7.

*4.5.5. N-(2-Ethyl-6-methyl-4-[(4-nitrophenyl)amino]phenyl)-acetamide (**16b**).* The isolated mixture (36 mg) of *p*-semidine and *p*-nitroaniline in 5 mL of $(Ac)_2O$ was stirred at room temperature for 12 h. The resulting mixture was diluted with water (50 mL), and extracted with ethyl acetate (2×50 mL). The organic layer was washed with saturated $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography with a mixture of petroleum ether and ethyl acetate as an eluent to afford **16b**. Yellow solid, 9 mg, yield 3%, mp 256–259 °C, ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.10 (t, J=7.5 Hz, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 2.52 (q, J=7.5 Hz, 2H), 6.93 (s, 1H), 6.96 (s, 1H), 7.04 (d, J=9.2 Hz, 2H), 8.08 (d, J=9.2 Hz, 2H), 9.14 (s, 1H), 9.22 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 168.5, 151.0, 142.3, 138.2, 137.7, 136.9, 130.5, 126.2, 120.0, 118.5, 113.2, 24.4, 22.5, 18.2, 14.4.

*4.5.6. 3,5-Diethyl-N^1-(4-nitrophenyl)benzene-1,4-diamine (**16c**).* Red oil, 12 mg, yield 4%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.26 (t, J_1=7.5 Hz, 6H), 2.54 (q, J_1=7.5 Hz, 4H), 3.69 (s, 2H), 6.19 (s, 1H), 6.70–6.85 (m, 2H), 6.85 (s, 2H), 8.03–8.08 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.5, 139.7, 138.4, 129.5, 128.8, 126.3, 122.3, 112.2, 24.2, 12.8.

*4.5.7. 3,5-Dimethyl-N^1-[4-(trifluoromethyl)phenyl]benzene-1,4-diamine (**16d**).* Colorless crystals, 50 mg, yield 18%, mp 115–117 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.18 (s, 6H), 3.54 (br s, 2H), 5.63 (br s, 1H), 6.79 (d, J=8.4 Hz, 2H), 6.80 (s, 2H), 7.38 (d, J=8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.4, 139.9, 130.9, 126.5 (q, J=3.5 Hz), 124.9 (q, J=270.4 Hz), 124.0, 122.8, 119.6 (q, J=32.3 Hz), 113.3, 17.7.

*4.5.8. 3-Ethyl-5-methyl-N^1-[4-(trifluoromethyl)phenyl]benzene-1,4-diamine (**16e**).* Yellowish oil, 53 mg, yield 18%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (t, J_1=7.5 Hz, 3H), 2.18 (s, 3H), 2.52 (q, J_1=7.5 Hz, 2H), 3.60 (br s, 2H), 5.65 (s, 1H), 6.80 (d, J_2=8.4 Hz, 2H), 6.81 (s, 2H), 7.38 (d, J_2=8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.4, 139.3, 131.1, 128.6, 126.5 (d, J=3.7 Hz), 124.9 (d, J=270.4 Hz), 123.8, 123.1, 121.9, 119.6 (q, J=32.4 Hz), 113.3, 24.2, 17.8, 13.0.

*4.5.9. 3,5-Diethyl-N^1-[4-(trifluoromethyl)phenyl]benzene-1,4-diamine (**16f**).* Yellow oil, 49 mg, yield 16%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.26 (t, J_1=7.5 Hz, 6H), 2.54 (q, J_1=7.5 Hz, 4H), 3.63 (br s, 2H), 5.69 (s, 1H), 6.82 (d, J_2=8.4 Hz, 2H), 6.84 (s, 2H), 7.39 (d, J_2=8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.4, 138.7, 131.3, 128.9, 126.6 (q, J=3.5 Hz), 124.9 (q, J=270.3 Hz), 121.7, 119.7 (q, J=33.1 Hz), 113.3, 24.3, 13.0.

*4.5.10. 3′,5′-Dimethyl-5-nitro-1,1′-biphenyl-2,4′-diamine (**17a**).* Yellowish crystals, 13 mg, yield 5%, mp 186–188 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.23 (s, 6H), 3.73 (s, 2H), 4.54 (s, 2H), 6.67 (q, J_1=2.6 Hz, 1H), 7.01 (s, 2H), 8.01 (dd, J_1=2.6 Hz, J_2=2.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.1, 142.9, 139.2, 128.6, 127.1, 126.7, 126.2, 124.5, 122.3, 113.6, 17.7.

*4.5.11. 3′-Ethyl-5′-methyl-5-nitro-1,1′-biphenyl-2,4′-diamine (**17b**).* Brown crystals, 8 mg, yield 3%, mp 131–133 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, J_1=7.5 Hz, 3H), 2.34 (s, 3H), 2.58 (q, J_1=7.5 Hz, 2H), 3.77 (s, 2H), 4.55 (s, 2H), 6.68 (dt, J_2=1.6 Hz, J_3=2.7 Hz, 1H), 7.02 (s, 2H), 8.00 (d, J_3=2.7 Hz,1H), 8.03 (d, J_2=1.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.3, 142.3, 138.9, 128.4, 128.0, 127.1, 126.7, 126.5, 126.2, 124.4, 122.5, 113.5, 24.2, 17.7, 12.9.

*4.5.12. N,N′-(3′,5′-Diethyl-5-nitro-1,1′-biphenyl-2,4′-diyl)diacetamide (**17c′**).* The isolated mixture (48 mg) of diphenyline and *p*-nitroaniline in 5 mL of $(Ac)_2O$ was stirred at room temperature for 12 h. The resulting mixture was diluted with water (50 mL), and extracted with ethyl acetate (2×50 mL). The organic layer was washed with saturated $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash chromatography with a mixture of petroleum ether and ethyl acetate as an eluent to afford **17c′**. Yellowish solid, 15 mg, yield 4%, mp 230–232 °C, ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.17(t, J_1=7.5 Hz, 6H), 2.03 (s, 3H), 2.10 (s, 3H), 2.59 (q, J_1=7.5 Hz, 4H), 7.23 (s, 2H), 7.99 (d, J_3=8.9 Hz, 1H), 8.12 (d, J_2=2.6 Hz, 1H), 8.22 (dd, J_2=2.6 Hz, J_3=8.9 Hz, 1H), 9.34 (s, 1H), 9.68 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 169.1, 168.8, 143.9, 142.0, 141.3, 135.2, 135.1, 134.5, 126.4, 126.0, 125.3, 122.8, 24.4, 23.4, 22.6, 14.8.

*4.5.13. 3′,5′-Dimethyl-5-trifluoromethyl-1,1′-biphenyl-2,4′-diamine (**17d**).* Colorless Crystals, 59 mg, yield 21%, mp 74–75 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.23 (s, 6H), 3.70 (br s, 2H), 4.06 (br s, 2H), 6.73 (d, J=9.0 Hz, 1H), 7.02 (s, 2H), 7.32 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.8, 142.4, 128.6, 127.5, 127.5 (q, J=3.6 Hz), 127.3, 124.9 (q, J=270.6 Hz), 124.7 (q, J=3.6 Hz), 122.11, 120.0 (q, J=32.4 Hz), 114.4, 17.6.

*4.5.14. 3′-Ethyl-5′-methyl-5-trifluoromethyl-1,1′-biphenyl-2,4′-diamine (**17e**).* Yellowish oil, 29 mg, yield 10%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (t, J_1=7.5 Hz, 3H), 2.23 (s, 3H), 2.58 (q, J_1=7.5 Hz, 2H), 3.72 (br s, 2H), 4.08 (s, 2H), 6.75 (d, J_2=8.4 Hz, 1H), 7.03 (s, 2H), 7.33 (d, J_2=8.4 Hz, 1H), 7.34 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.8, 141.8, 128.4, 127.8, 127.6, 127.4 (q, J=3.6 Hz), 127.4, 126.5, 124.9 (d, J=270.7 Hz), 124.7 (q, J=3.7 Hz), 122.3, 119.8 (q, J=32.3 Hz), 114.4, 24.2, 17.6, 12.9.

*4.5.15. 3′,5′-Diethyl-5-trifluoromethyl-1,1′-biphenyl-2,4′-diamine (**17f**).* Yellowish oil, 43 mg, yield 14%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, J_1=7.5 Hz, 6H), 2.58 (q, J_1=7.5 Hz, 4H), 3.77 (br s, 2H), 4.09 (br

s, 2H), 6.75 (d, J_2=8.1 Hz, 1H), 7.04 (s, 2H), 7.33 (d, J_2=8.1 Hz, 1H), 7.35 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 141.3, 128.1, 127.8, 127.6, 127.5 (q, J=3.7 Hz), 126.4, 124.9 (q, J=270.7 Hz), 124.8 (q, J=3.7 Hz), 120.0 (q, J=32.4 Hz), 114.5, 24.3, 13.0.

*4.5.16. 3,5-Dimethyl-4-(p-tolyldiazenyl)benzonitrile (**13a**).* Yellow solid, 55 mg, yield 22%, mp 134–135 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.26 (s, 6H), 2.46 (s, 3H), 7.35 (m, 2H), 7.40 (s, 2H), 7.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.9, 150.5, 142.9, 132.4, 131.0, 129.9, 122.7, 118.9, 110.6, 21.5, 18.1.

*4.5.17. 3-Ethyl-4-[(4-ethylphenyl)diazenyl]-5-methylbenzonitrile (**13b**).* Orange crystals, 105 mg, yield 38%, mp 51–53 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.14 (t, J_1=7.5 Hz, 3H), 1.31 (t, J_2=7.6 Hz, 3H), 2.24 (s, 3H), 2.63 (q, J_2=7.6 Hz, 2H), 2.76 (q, J_1=7.5 Hz, 2H), 7.38 (d, J=8.4 Hz, 2H), 7.41 (s, 1H), 7.44 (s, 1H), 7.85 (d, J=8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.9, 150.7, 149.1, 137.5, 132.4, 130.9, 130.1, 128.7, 122.9, 118.9, 110.8, 28.9, 24.5, 18.2, 15.3, 14.8.

*4.5.18. 1-Mesityl-2-(4-nitrophenyl)diazene (**13c**).* Red solid, 94 mg, yield 35%, mp 103–105 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H), 2.47 (s, 6H), 6.98 (s, 2H), 7.95 (d, J=9.0 Hz, 2H), 8.36 (d, J=9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 148.4, 147.9, 140.8, 133.3, 130.4, 124.7, 122.9, 21.2, 19.9.

*4.5.19. 1-Mesityl-2-[4-(trifluoromethyl)phenyl]diazene (**13d**).* Red oil, 108 mg, yield 37%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 2.42 (s, 6H), 6.96 (s, 1H), 6.97 (s, 1H), 7.77 (dd, J=0.6 Hz, 9.0 Hz, 2H), 7.94 (dd, J=0.6 Hz, 9.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.8, 148.3, 139.7, 132.4, 131.9 (q, J_1=32.8 Hz), 130.2, 126.3 (q, J_2=3.8 Hz), 124.0 (q, J_3=273.4 Hz), 122.6, 21.2, 19.5. IR (KBr) ν (cm^{-1}): 2956, 2923, 2851, 1322.

*4.5.20. 1-(4-Methoxyphenyl)-2-(4-nitrophenyl)diazene (**13e**).* Red crystals, mp152–153 °C. Lit.[18] 154–155 °C. 17 mg, yield 9%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: (400 MHz, $CDCl_3$) 8.35 (d, J=9.0 Hz, 2H), 7.97 (d, J=9.0 Hz, 2H), 7.97 (d, J=9.0 Hz, 2H), 7.04 (d, J=9.0 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.3, 156.0, 148.2, 146.9, 125.6, 124.7, 123.1, 114.4, 55.7.

*4.5.21. 4-[(4-Methoxyphenyl)diazenyl]benzonitrile (**13f**).* Red crystals, mp 140–141 °C. Lit.[19] 143.5 °C. 58 mg, yield 24%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J=9.1 Hz, 2H), 7.97 (d, J=7.7 Hz, 2H), 7.82 (d, J=8.7 Hz, 2H), 7.06 (d, J=9.1 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.1, 154.8, 146.9, 133.2, 125.5, 123.1, 118.7, 114.4, 113.2, 55.7.

*4.5.22. 1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)diazene (**13g**).* This reaction was performed on a 0.5-mmol scale. Known compound.[20] Red crystals, mp 104–106 °C. 7 mg, yield 5%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J=8.7 Hz, 4H), 7.75 (d, J=8.3 Hz, 2H), 7.03 (d, J=8.9 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.7, 154.6, 146.9, 131.2 (q, J_{C-F}=32.4 Hz), 126.2 (q, J_{C-F}=3.6 Hz), 124.0 (q, J_{C-F}=250.5 Hz), 114.8, 114.3, 55.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ −62.4.

*4.5.23. 1-(2-Ethyl-6-methylphenyl)-2-(4-nitrophenyl)diazene (**18b**).* Red oil, 70 mg, yield 26%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.20 (t, J=7.5 Hz, 3H), 2.40 (s, 3H), 2.83 (q, J=7.5 Hz, 2H), 7.13–7.28 (m, 3H), 7.97 (d, J=8.7 Hz, 2H), 8.37 (d, J=8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.7, 150.1, 148.7, 139.5, 130.6, 129.9, 129.6, 127.8, 124.8, 123.0, 25.5, 19.8, 15.8.

*4.5.24. 1-(2,6-Diethylphenyl)-2-(4-nitrophenyl)diazene (**18c**).* Red oil, 76 mg, yield 27%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, J=7.5 Hz, 6H), 2.77 (q, J=7.5 Hz, 4H), 7.18–7.32 (m, 3H), 7.99 (d, J=9.9 Hz, 2H), 8.41 (d, J=9.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.7, 150.1, 148.7, 137.7, 129.8, 127.9, 124.8, 123.0, 25.6, 15.7.

*4.5.25. 1-(2-Ethyl-6-methylphenyl)-2-[4-(trifluoromethyl)phenyl]diazene (**18e**).* Red oil, 35 mg, yield 12%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.18 (t, J_1=7.5 Hz, 3H), 2.36 (s, 3H), 2.78 (q, J_1=7.5 Hz, 2H), 7.13–7.25 (m, 3H), 7.79 (d, J_2=8.2 Hz, 2H), 7.97 (d, J_2=8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.6, 150.7, 138.5, 132.3 (q, J_1=32.8 Hz), 123, 130.0, 129.1, 127.7, 126.4 (q, J_2=3.8 Hz), 123.9 (q, J_3=273.4 Hz), 122.7, 25.3, 19.4, 15.7.

*4.5.26. 1-(2,6-Diethylphenyl)-2-[4-(trifluoromethyl)phenyl]diazene (**18f**).* Red oil, 46 mg, yield 15%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.17 (t, J_1=7.5 Hz, 6H), 2.72 (q, J_1=7.5 Hz, 4H), 7.16–7.26 (m, 3H), 7.80 (d, J_2=8.2 Hz, 2H), 7.97 (d, J_2=8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.5, 150.7, 137.0, 132.4 (q, J_1=32.8 Hz), 129.1, 127.7, 126.4 (q, J_2=3.8 Hz), 123.9 (q, J_3=272.2 Hz), 122.7, 25.3, 15.6.

Acknowledgements

This work was supported in part by the National Basic Research Program of China (No. 2013CB328905), the National Natural Science Foundation of China (Nos. 21372025 and 21172017) and specialized Research Fund for the Doctoral Program of Higher Education, Ministry of Education of China (No. 20110010110011).

Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra for all products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.03.019. These data include MOL files and InChiKeys of the most important compounds described in this article.

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13. (a) **4-[(2-Amino-5-methoxyphenyl)amino]benzonitrile (10f)**: This product was obtained as a mixture with 4-aminobenzonitrile (**12f**) and 4-methoxyaniline (**13f**). According to the ratios (**10f**:**12f**:**13f**=0.04:1.00:0.85) from the ^{1}H NMR spectrum of the three compounds and the total mass (122 mg), the yields of **10f**, **12f**, and **13f** were calculated to be 2%, 54%, and 24%, respectively. However, different attempts on purification including acetylation with Ac_2O failed. But **10f** was identified by the characteristic peaks in the ^{1}H NMR spectrum of the mixtures. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.11 (d, J=2.3 Hz, 1H), 6.91 (dd, J=2.3, 8.5 Hz, 1H), 6.04 (s, 1H). Compound **10f** was also identified by the *characteristic peaks* of its acetylated product Ac-**10f** in the ^{1}H NMR spectrum of the mixtures. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J=8.8 Hz, 1H), 7.49 (d, J=8.8 Hz, 2H), 7.22 (d, J=2.4 Hz, 1H), 7.07 (dd, J=8.8, 2.5 Hz, 1H), 6.96 (d, J=8.8 Hz, 2H), 6.44 (s, 1H). (b) **5-Methoxy-*N*^{1}-(4-(trifluoromethyl)phenyl) benzene-1,2-diamine (10g)**: Similar to **10f**, this product was inseparable from 4-methoxyaniline and 4-trifluoromethylaniline, and the yield was calculated as 3% according to the method as mentioned above. For the characteristic peaks: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J=2.1 Hz, 1H), 6.95 (d, J=8.8 Hz, 1H), 6.92 (dd, J=8.5, 2.2 Hz, 1H), 5.63 (s, 1H). Compound **10g** was also identified by the *characteristic peaks* of its acetylated product Ac-**10g** in the ^{1}H NMR spectrum of the mixtures. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J=9.0 Hz, 1H), 6.92 (d, J=2.9 Hz, 1H), 6.81 (dd, J=9.0, 2.9 Hz, 1H), 3.78 (s, 3H), 2.22 (s, 3H). For the spectra of the mixtures of the two products **10f** and **10g**, see Supplementary data.
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