CHAPTER-4

A REGIOSELECTIVE RING NITRATION OF *N*-ALKYL ANILINES USING *TERT*-BUTYL NITRITE UNDER MILD CONDITIONS

4.1 Introduction

Nitroarenes are not only important starting materials but also structural units of many natural products and bioactive molecules. In fact, nitroaromatic compounds are one of most used class of compounds in chemical industry. In this context, *N*-alkyl (or benzyl) nitroanilines are the direct source of mono-*N*-alkylated phenylenediamines which are used extensively in the preparation of various bioactive molecules and heterocycles such as benzimidazoles, benzotriazoles, benzodiazepines, etc (Figure 3.1) [1-5]. *N*-Alkyl nitroanilines are typically prepared through a multistep synthesis involving the protection of aniline with acetyl group followed by nitration and then, deprotection of acetyl group followed by alkylation (Scheme 4.1). In fact, recently nitration of *N*-acyl and *N*-sulfonyl anilines has been well explored with different reagents [6-11]. However, despite having wide importance in organic synthesis, direct nitration of *N*-alkyl anilines is yet unexplored.

In 1908, Tingle *et al.,* made a brief study on the direct nitration of *N*-alkyl anilines by using the classical nitration methods [12]. This study demonstrated that *N*-alkyl anilines behave similarly to unprotected anilines and provide tarry oxidation products as well as inconsistent regio-nitrated products for different *N*-alkyl substituents. For example, nitration of *N*-methylaniline provides *m*-nitro *N*-methylaniline while *N*-ethylaniline provides *p*-nitro *N*-ethylaniline in the presence of HNO_3/H_2SO_4 [12].

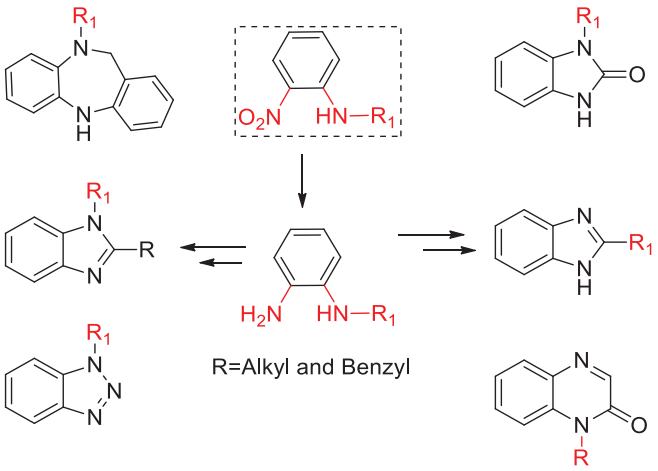
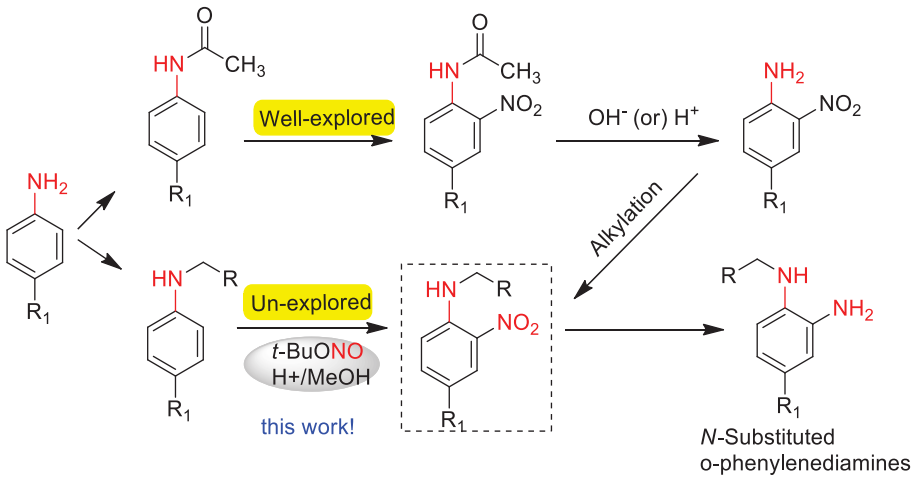


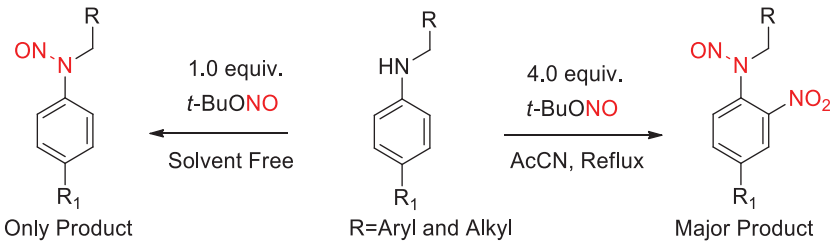
Figure 4.1 Synthetic importance of nitroanilines.



Scheme 4.1 Different approaches for the synthesis of *N*-alkyl nitroanilines.

Aryl *N*-nitrosamines have been recognized as an important starting material in organic synthesis [13] and recently emerged as a traceless directing group for the activation of aryl C-H bonds [14-17]. As discussed in chapter 2, *N*-alkyl anilines undergo *N*-nitrosation efficiently with 1.0 equiv. of *tert*-butyl nitrite (TBN) in a short span of time [18]. However, during the course of this investigation, we had observed that with excess

TBN, *N*-alkyl anilines provide synthetically useful *N*-alkyl *N*-nitroso nitroaniline as the major product (Scheme 4.2). *tert*-Butyl nitrite is a radical nitrating agent that has been explored in the nitration of phenols, azoarenes, arylboronic acids, etc [19]. In fact, recently nitration of acetanilides and sulfonanilides were successfully accomplished by using TBN under mild condition [8]. However, the direct ring nitration of *N*-alkyl anilines using TBN is not known in the literature. Hence, the scope and limitation of this transformation was investigated and reported in this chapter.



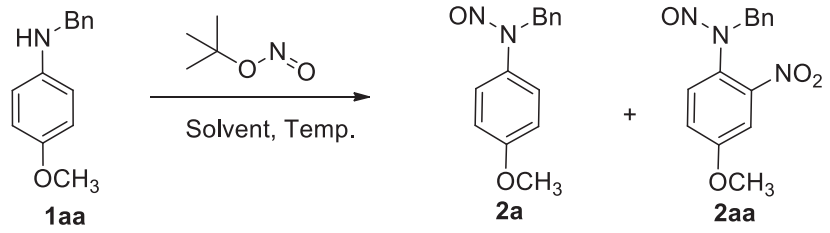
Scheme 4.2 Effect of TBN leads to different products.

4.2 Results and Discussions

4.2.1 Optimization for *N*-nitrosation nitration under different reaction conditions

For the optimization of reaction condition, 4-Methoxy *N*-benzyl aniline **1aa** was chosen as the model substrate and subjected for ring nitration in the presence of different equivalent of TBN at room temperature. Initially, the reaction was attempted with 1 equiv. TBN under solvent free condition as well as in acetonitrile for 10 minutes. Both the reactions provide *N*-nitroso compound **2a** as the only product (as discussed in chapter 2) [18].

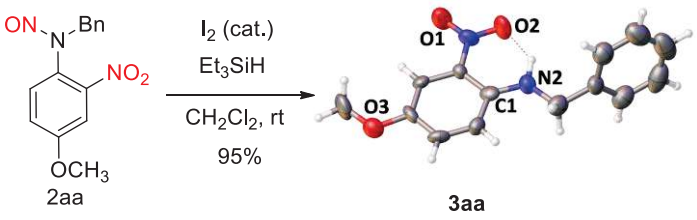
Table 4.1 Initial observations during the *N*-nitrosation reaction.[a,b]



S.No.	Solvent	TBN (equiv.)	Temp. (°C)	Time	Yield (%)[b] 2a	2aa
1	-	1.0	RT	10 min	>95	nd
2	CH_3CN	1.0	RT	10 min	89	nd
3	CH_3CN	2.0	RT	10 min	94	nd
4	CH_3CN	3.0	RT	10 min	>97	nd
5	CH_3CN	3.0	RT	30 min	84	11
6	CH_3CN	3.0	RT	3 h	63	31
7	CH_3CN	3.0	RT	12 h	29	71
8	DCE	3.0	RT	12 h	64	30
9	1,4-dioxane	3.0	RT	12 h	59	35
10	THF	3.0	RT	12 h	75	20
11	MeOH	3.0	RT	12 h	94	nd
12	CH_3CN	3.0	50	3 h	13	80
13	CH_3CN	3.0	80	3 h	15	89
14	**CH_3CN**	**4.0**	**80**	**1h**	**nd**	**94**

[a]Reaction conditions: Aniline **1aa** (1 mmol) and TBN were stirred in acetonitrile (8 mL). [b]Isolated yields.[c]Not detected in TLC.

Further, the amount of TBN was varied from 1.0-3.0 equiv. while the reactions were performed in acetonitrile. Up to 10 minutes, only the *N*-nitroso compound **2a** was observed with 2 and 3 equivalents of TBN. However, when the reaction was allowed to stir for longer time with 3 equiv. of *tert*-butyl nitrite, formation of a new product was observed along *N*-nitrosamine **2a**. It is noteworthy that the yield of new product was increased subsequently with the time. For instance, after 30 mins the new product was formed in 11% yield which was subsequently increased to 71% after 12 h (Table 4.1, entries **5-7**). To our delight, the resulting product has been identified as *N*-nitroso *N*-benzyl 2-nitro 4-methoxyaniline (**2aa**) through NMR and Mass [20]. A selective denitrosation of the product **2aa** using I_2/Et_3SiH [21] gave the *N*-benzyl 2-nitro 4-methoxyaniline (**3aa**) in quantitative yield with the structure confirmed by NMR, Mass and single crystal XRD (Scheme 4.3, Table 4.6).



Scheme 4.3 Denitrosation of *N*-nitrosamine **2aa.**

Understanding the novelty and synthetic utility of this transformation, the reaction was further optimized under different reaction conditions. The reaction was investigated in other solvents such as DCE, 1,4-Dioxane, THF and methanol using 3.0 equivalent TBN for 12 h at room temperature. However, all these solvents provide the desired product **2aa** in a

lower yield when compared with acetonitrile. In fact, only nitrosamine **2a** was detected in methanol. Hence, the reaction was further investigated in elevated temperatures, i.e. 50 °C and 80 °C with 3-4 equiv. of TBN. To our delight, the desired product **2aa** was obtained in 94% yield with 4 equiv. of TBN at 80 °C within 4 h (Table 4.1, entry **14**).

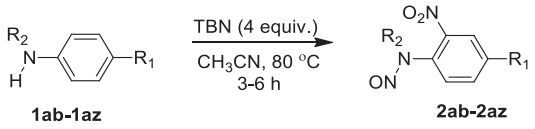
4.3 Substrate Scope

4.3.1 *N*-Nitrosation nitration of *N*-alkyl anilines

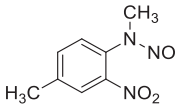
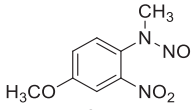
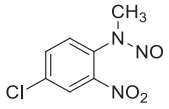
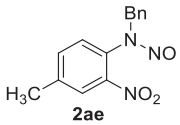
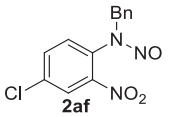
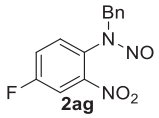
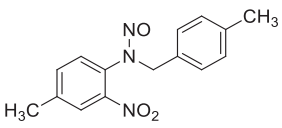
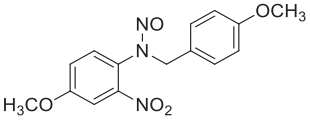
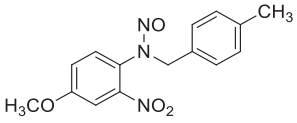
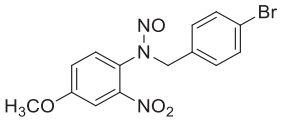
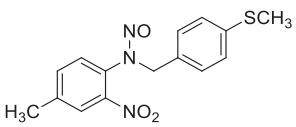
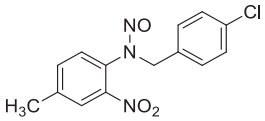
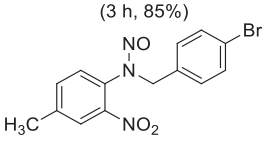
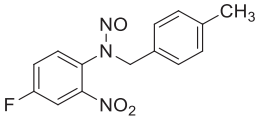
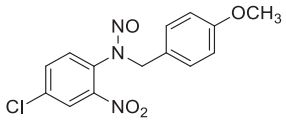
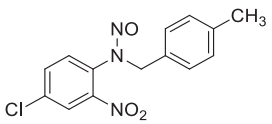
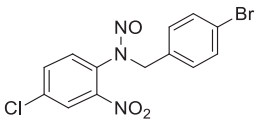
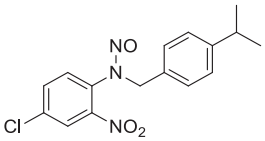
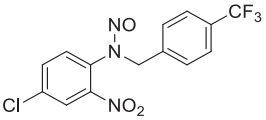
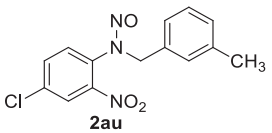
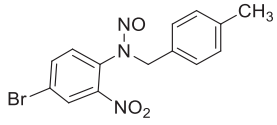
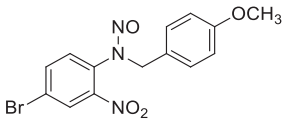
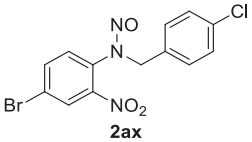
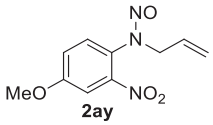
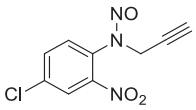
Having established the optimized condition, we further investigated the potential application of this method with different *N*-alkyl and benzyl anilines (Tables 4.2 and 4.3). Initially, the nitration of *p*-substituted *N*-alkyl and benzyl anilines was studied under optimized conditions (Table 4.2). It was observed that nitration of anilines bearing electron donating groups such as methyl and methoxy substituents proceeds faster (*i.e.* in 3 h) than in the case of electron withdrawing groups such as fluorine, chlorine and bromine functionalized anilines (*i.e.* in 6 h).

Nevertheless, both types of anilines provide *o*-nitrated products in comparable yields, *i.e.* 72-84% (Table 4.2, **2ab**-**2az**). However, nitration did not occur with strongly electron withdrawing groups such as with nitro and cyano group substituted anilines. On the other hand, when the substituents present on the benzylic ring (Bn), no influence was observed in the nitration process (Table 4.2, **2ah**-**2ax**). Indeed, the benzylic aromatic ring remained intact during the nitration process even in the presence of strong electron donating groups such as methoxy, which is an important feature of this method (Table 4.2, **2ai**, **2ap** and **2aw**).

Table 4.2 Nitration of various *p*-substituted *N*-alkyl anilines.[a,b]



1ab-1az 2ab-2az

 **2ab** (3 h, 81%)	 **2ac** (3 h, 82%)	 **2ad** (6 h, 80%)	 **2ae** (3 h, 84%)
 **2af** (6 h, 83%)	 **2ag** (6 h, 72%)	 **2ah** (3 h, 83%)	 **2ai** (3 h, 80%)
 **2aj** (3 h, 85%)	 **2ak** (3 h, 84%)	 **2al** (3 h, 79%)	 **2am** (3 h, 81%)
 **2an** (3 h, 83%)	 **2ao** (6 h, 75%)	 **2ap** (6 h, 80%)	 **2aq** (6 h, 80%)
 **2ar** (6 h, 83%)	 **2as** (6 h, 81%)	 **2at** (6 h, 79%)	 **2au** (6 h, 82%)
 **2av** (6 h, 80%)	 **2aw** (6 h, 82%)	 **2ax** (6 h, 83%)	 **2ay** (3 h, 82%)
 **2az** (3 h, 83%)			

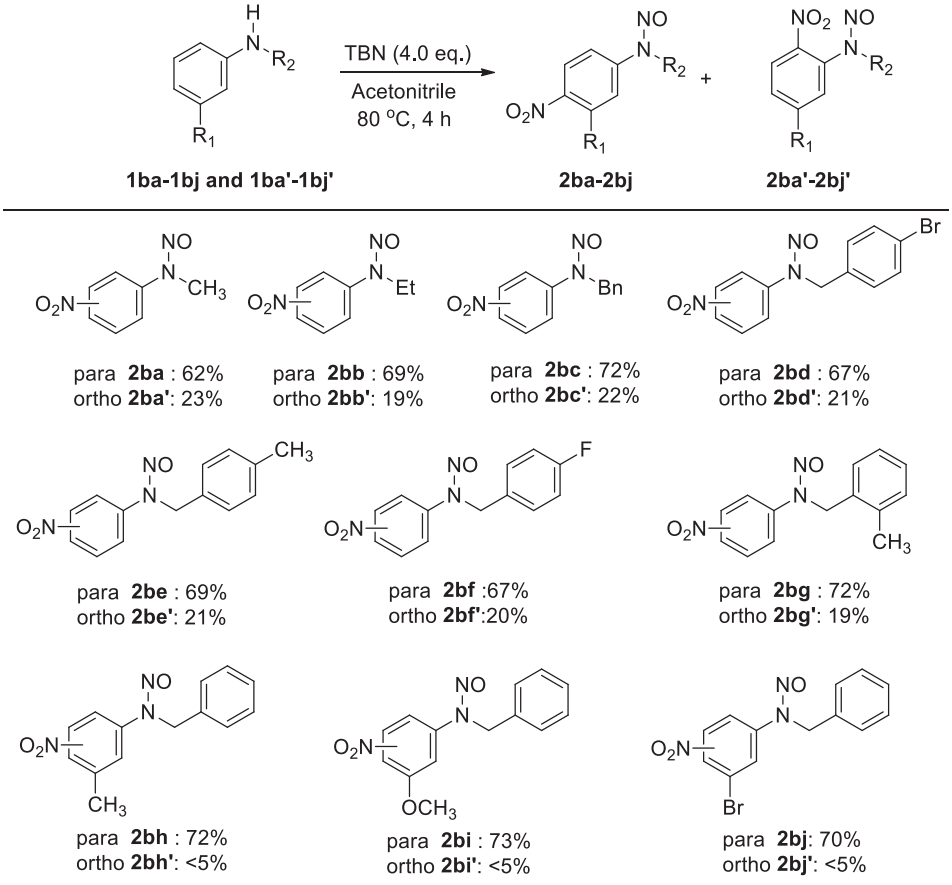
[a]Reaction conditions: Amine (1 mmol) and TBN (4 equiv.) were stirred in acetonitrile (8 mL) at 80 °C. [b]Isolated yields.

In addition, neither over nitrated nor *m*-nitrated products was observed in the reaction which increases the scope of this methodology. To our delight, functionalized anilines bearing sensitive functional groups such as allyl and propargyl underwent nitration under optimized condition and gave the desired products **2ay** and **2az** in >82% yields (Table 4.2). It is notable that *N*-propargyl *o*-nitroanilines have been recently used in the synthesis of biologically important quinoxaline derivatives [22].

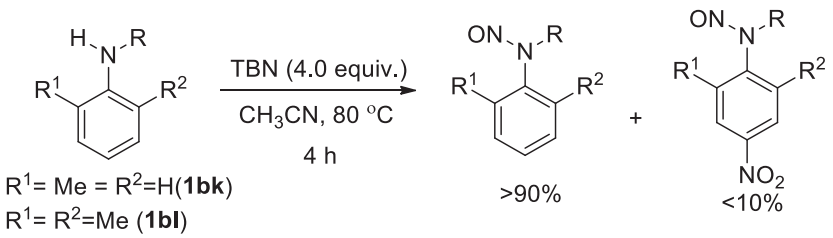
Further, the nitration of unsubstituted *N*-alkyl and benzyl anilines (**1ba**-**1bg**) was attempted under the optimized condition (Table 4.3). To our delight, the nitration reaction proceeds very efficiently and gave the mono-nitrated products (either *o*- or *p*-, but not *m*-) in 85-91% yields. It is also interesting to note that irrespective of the substituent present on the amine, unsubstituted anilines provide *p*-nitro products (**2ba**-**2bg**) in high yields in comparison to *o*-nitro products (**2ba'**-**2bg'**).

Similar to unsubstituted anilines, *m*-functionalized anilines also gave the *p*-nitroaniline products in high yields along with negligible amounts of *o*-nitrated products (Table 4.3, **2bh**-**2bj**). Having studied the nitration of *p*-, *m*- and unsubstituted *N*-alkyl anilines, nitration of *o*-substituted anilines **1bk** and **1bl** was investigated under optimized condition (Scheme 4.4). However, to our surprise, no nitration was observed while *N*-nitrosamine was obtained as the major product. It might be due to some mechanistic aspect related to steric hindrance (vide infra).

Table 4.3 Nitration of various unsubstituted and *m*-substituted *N*-alkyl anilines.[a,b]



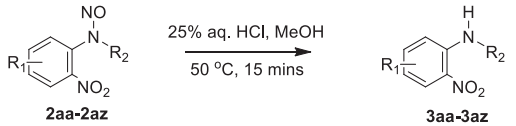
[a]Reaction conditions: secondary amine (1 mmol) and TBN (4 equiv.) were stirred in acetonitrile (8 mL) at 80 °C for 4 h. [b]Isolated yields.



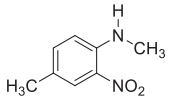
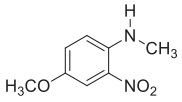
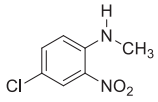
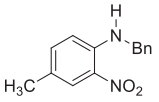
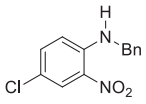
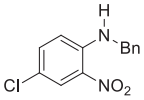
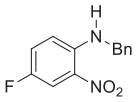
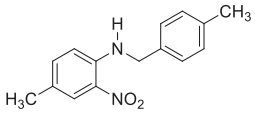
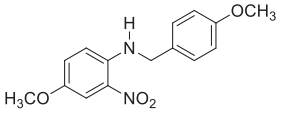
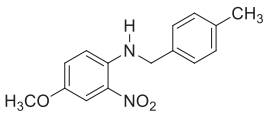
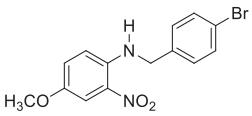
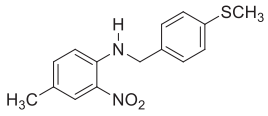
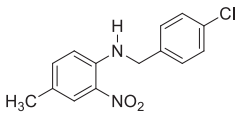
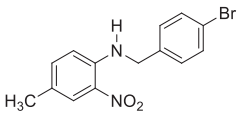
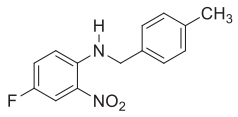
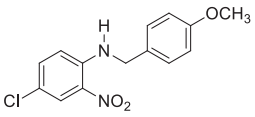
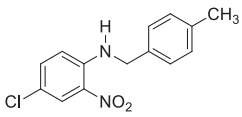
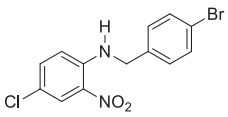
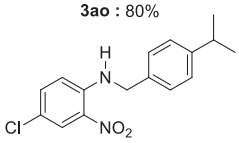
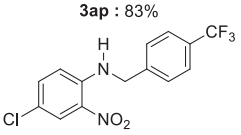
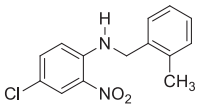
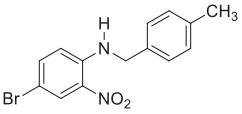
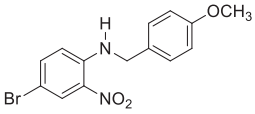
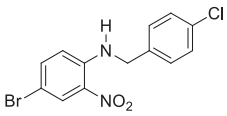
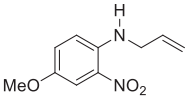
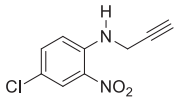
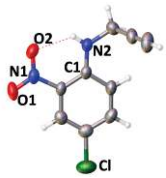
Scheme 4.4 Nitration of *o*-substituted *N*-alkyl anilines.

4.3.2 Synthesis of *N*-alkyl nitroanilines *via* denitrosation

Table 4.4 Denitrosation of *N*-nitrosamines using aq. HCl-methanol.[a,b]



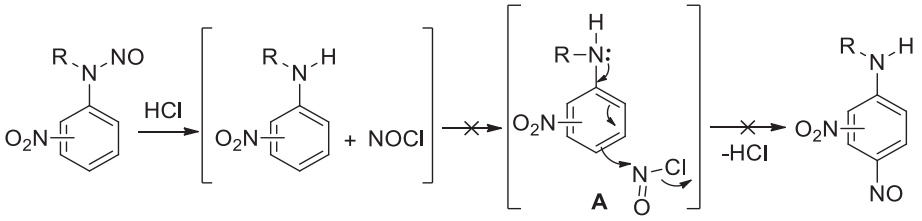
2aa-2az **3aa-3az**

 **3aa** : 85%	 **3ab** : 83%	 **3ac** : 90%	 **3ad** : 83%
 **3ae** : 84%	 **3af** : 83%	 **3ag** : 81%	 **3ah** : 89%
 **3ai** : 87%	 **3aj** : 88%	 **3ak** : 84%	 **3al** : 88%
 **3am** : 81%	 **3an** : 83%	 **3ao** : 80%	 **3ap** : 83%
 **3aq** : 80%	 **3ar** : 83%	 **3as** : 85%	 **3at** : 83%
 **3au** : 87%	 **3av** : 84%	 **3aw** : 81%	 **3ax** : 83%
 **3ay** : 84%	 **3az** : 83%	≡ 	

[a]Reaction conditions: Substituted *N*-nitrosamines (1 mmol) and HCl (2 mL) were stirred in the methanol (5 mL) at 50 °C. [b]Isolated yields.

Having generated a large number of *N*-nitroso *N*-alkyl nitroanilines, a selective denitrosation would be useful to obtain *N*-alkyl nitroanilines that can be used for further applications. Iodine-triethylsilane mediated denitrosation of *N*-nitrosamine is among the best, which shows a remarkable functional group tolerance [19]. However, to make it more convenient, another simple and cost effective method was developed in this study. In this protocol, *N*-nitrosamines (**2aa**-**2bj**) are treated with 25% aqueous HCl in methanol and stirred for 15 min at 50 °C, followed by acid-basic work-up provides the *N*-alkyl nitroanilines (**3aa**-**3bj**) in excellent yields (Table 4.4 and Table 4.5).

Although, *N*-alkyl *N*-nitroso anilines are susceptible for Fischer-Hepp rearrangement in the presence of hydrochloric acid, we haven't observed any such products during the denitrosation. Perhaps, it is due to the presence of strongly electron withdrawing nitro group on the aryl ring. As per the Fisher-Hepp rearrangement mechanism [23], the reaction of *N*-alkyl *N*-nitroso aniline with HCl leads to the formation of nitrosyl chloride and secondary amine, after which the electrophilic nitrosation would takes place as shown in the mechanism (Scheme 4.5).

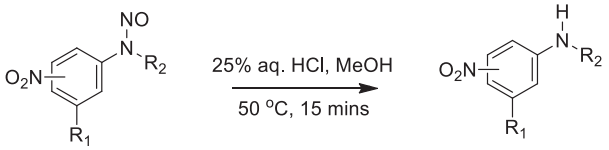


Scheme 4.5 Fisher-Hepp rearrangement reaction mechanism.

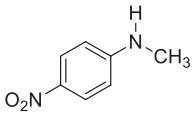
However, nitroarenes are poor substrates for the electrophilic substitution reactions, hence; selective dinitrosation of *N*-nitroso *N*-alkyl nitroanilines was achieved efficiently

without Fisher-Hepp rearrangement. Moreover, this method tolerates many functional groups including allyl, propargyl and benzyl groups. Please see the table 4.6 for crystal parameters of **3az**.

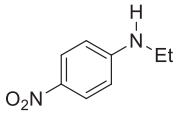
Table 4.5 Denitrosation of unsubstituted and *meta*-substituted *N*-nitrosamines using aq. HCl-methanol.[a,b]



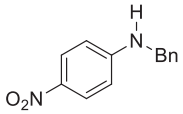
2ba-2bj and 2ba'-2bg' **3ba-3bj 3ba'-3bg'**



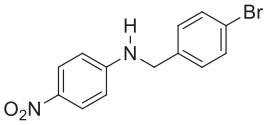
3ba : 82%



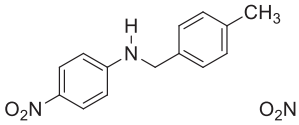
3bb : 84%



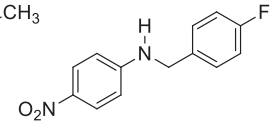
3bc : 83%



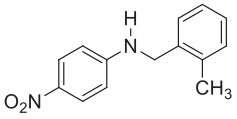
3bd : 81%



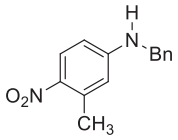
3be : 80%



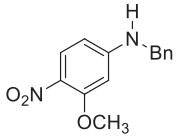
3bf : 79%



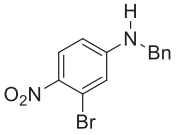
3bg : 78%



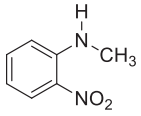
3bh : 80%



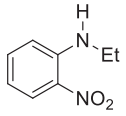
3bi : 80%



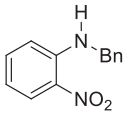
3bj : 80%



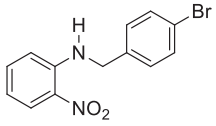
3ba' : 81%



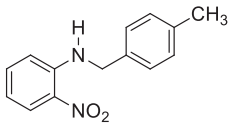
3bb' : 80%



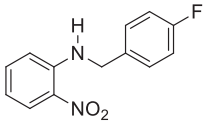
3bc' : 80%



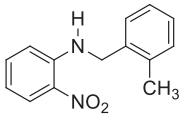
3bd' : 75%



3be' : 78%



3bf' : 72%



3bg' : 74%

[a]Reaction conditions: Substituted *N*-nitrosamines (1 mmol) and HCl (2 mL) were stirred in the methanol (5 mL) at 50 °C. [b]Isolated yields.

Table 4.6 Crystal refinement parameters for **3aa** and **3az**.

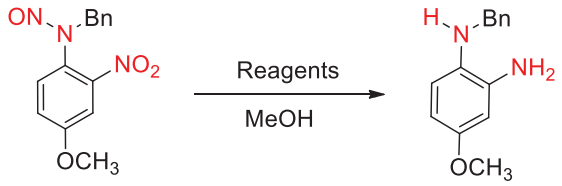
Parameters	3aa	3az
CCDC	1836064	1835907
Empirical formula	$C_{14}H_{14}N_2O_3$	$C_9H_7N_2O_2Cl$
Formula weight	258.27	210.62
Temperature/K	293(2)	295
Crystal system	Orthorhombic	triclinic
Space group	$P2_12_12_1$	P-1
a/Å	a = 7.0221(10)	6.1027(5)
b/Å	b = 19.019(3)	8.5357(9)
c/Å	c = 19.187(3)	10.1750(11)
α/°	90	112.463(10)
β/°	90	95.209(9)
γ/°	90	99.616(8)
Volume/Å^3	2562.6(7) Å^3	475.92(8)
Z	8	2
ρ_{calc} mg/mm^3	1.339	1.470
μ/mm^{-1}	0.096	0.374
F(000)	1088	216.0
Crystal size/mm^3	0.400 × 0.200 × 0.200	0.7 × 0.18 × 0.06
2Θ range for data collection	2.123 to 22.890°	7.5 to 58.04°
Index ranges	-7<=h<=7, -20<=k<=20, -19<=l<=21	-8 ≤ h ≤ 8, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	15169	5163
Independent reflections	3503 [R(int) = 0.0684]	2216[R(int) = 0.0258]
Data/restraints/parameters	3503 / 2 / 353	2216 / 0 / 131
Goodness-of-fit on F^2	1.031	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0629, wR_2 = 0.1278	R_1 = 0.0423, wR_2 = 0.1003
Final R indexes [all data]	R_1 = 0.1453, wR_2 = 0.1658	R_1 = 0.0636, wR_2 = 0.1128
Largest diff. peak/hole / e Å^{-3}	0.203 and -0.227	0.17/-0.28

[a]$R_1=\Sigma||F_o| -|F_c||/\Sigma|F_o|$, [b]$wR_2=|\Sigma_w(|F_o|^2-|F_c|^2)|/\Sigma|w|(F_o)^2|^{1/2}$

4.3.3 Synthesis of *N*-substituted *o*-phenylenediamines

N-Substituted *o*-phenylenediamines have found broad applications in organic synthesis, for instance, in the preparation of various heterocyclic compounds (Figure 1) [1-5]. Hence, a facile method for the one-step procedure i.e. denitrosation of *N*-nitrosamine followed by reduction of the nitro group, was sought. In this context, 4-methoxy *N*-nitroso *N*-benzyl nitroaniline was chosen as a model substrate and subjected for one-pot reduction with different reducing agents (Table 4.7). Initially the reaction was tested with mild reducing system Zn/NH_4Cl and Fe/NH_4Cl in methanol at room temperature. The Zn/NH_4Cl system provides the desired product in 15% while 10% was obtained with Fe/NH_4Cl. Hence, the reduction reaction was investigated at 50 °C with Zn/NH_4Cl in methanol. The yield of the reaction is subsequently increased with increase in temperature and the equivalence of reducing agents. However, the reaction did not reach to completion while only 50% of the conversion was observed. Therefore, the reduction reaction was further investigated with Zn/AcOH and Zn/HCl systems. To our delight, Zn (4 equiv.)/AcOH (1.5 mL) gave the desired product **4aa** in 89% yield within 20 minutes at 50 °C (Table 4.7, entry 8). In fact, other reducing agents such as $NiCl_2/NaBH_4$ and Raney Ni/H_2 were found inferior and gave low yields (Table 4.7). Using the optimized condition, reduction of various *N*-nitroso *N*-alkyl nitroaniline was reduced to *N*-substituted *o*-phenylenediamines (**4aa**-**4al**) in 78-88% yield within 20 min. This one-step reduction reaction proceeds smoothly irrespective of the substituents present on the substrates (Table 4.8).

Table 4.7 Optimization of one step procedure for denitrosation followed by reduction of nitro group in 4-methoxy *N*-nitroso *N*-benzyl nitroaniline.[a,b]

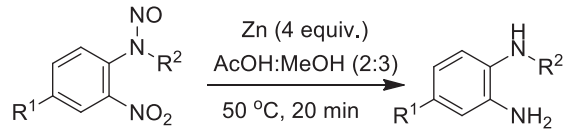


2aa **4aa**

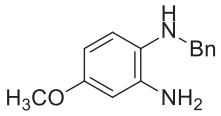
S.No.	Metal (equiv.)	Additive	Temp. (°C)	Time	Yield (%)[b]
1	Zn (2.0)	NH_4Cl (1.0 mL)	RT	1 h	15
2	Fe (2.0)	NH_4Cl (1.0 mL)	RT	1 h	10
3	Zn (2.0)	NH_4Cl (1.0 mL)	50	1 h	30
4	Zn (4.0)	NH_4Cl (2.0 mL)	50	2 h	50
5	Zn (2.0)	AcOH (1.0 mL)	RT	1 h	59
6	Zn (2.0)	HCl (1.0 mL)	RT	1 h	59
7	Zn (4.0)	AcOH (1.0 mL)	50	30 min	72
8	**Zn (4.0)**	**AcOH (1.5 mL)**	**50**	**20 min**	**88**
9	$NiCl_2$ (2.0)	$NaBH_4$ (4.0 eq.)	RT	1 h	35
10	Raney Ni (4 eq.)	H_2 (1 bar)	RT	3 h	<10

[a]Reaction conditions: *N*-nitroso nitroaniline (1 mmol) , Methanol (6 mL). [b]Isolated yields.

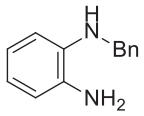
Table 4.8 Denitrosation followed by reduction of nitro group in *N*-nitroso *N*-alkyl nitroaniline.[a,b]



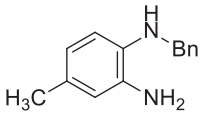
4aa-4al



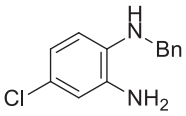
4aa : 88%



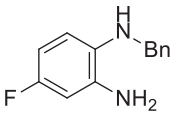
4ab : 85%



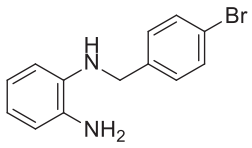
4ac : 83%



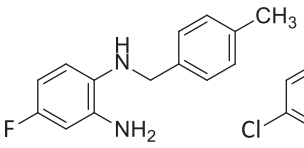
4ad : 82%



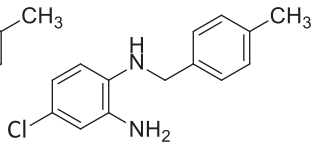
4ae : 79%



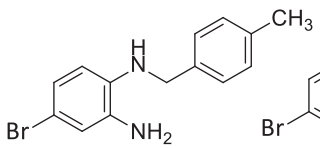
4af : 80%



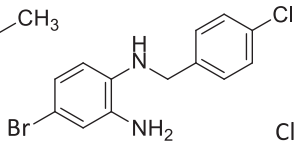
4ag : 80%



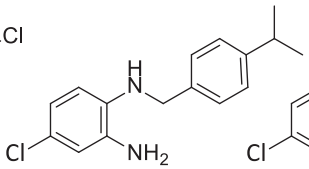
4ah : 82%



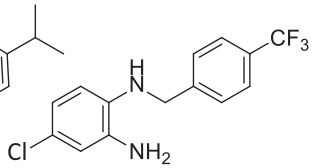
4ai : 85%



4aj : 81%



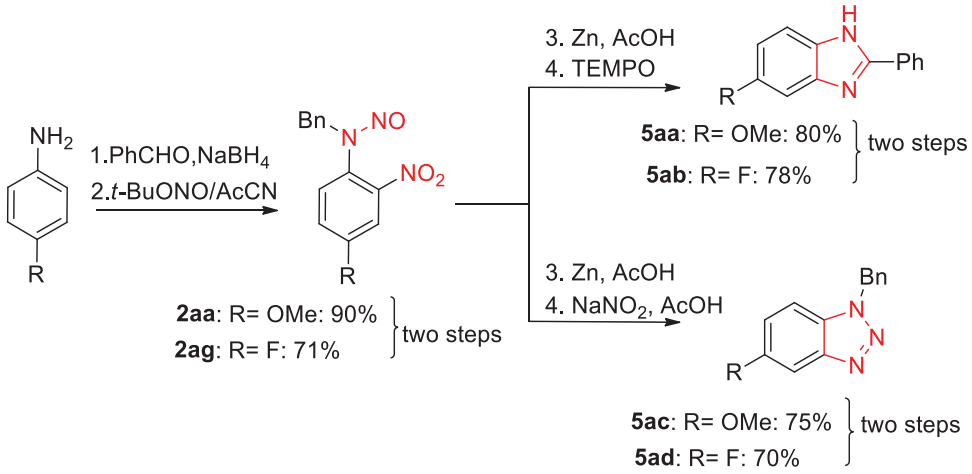
4ak : 80%



4al: 78%

[a]Reaction conditions: Substituted *N*-nitrosamines (1 mmol) and Zn (4 eq.) were stirred in AcOH:MeOH (2:3, 7.5 mL) at 50 °C. [b]Isolated yields.

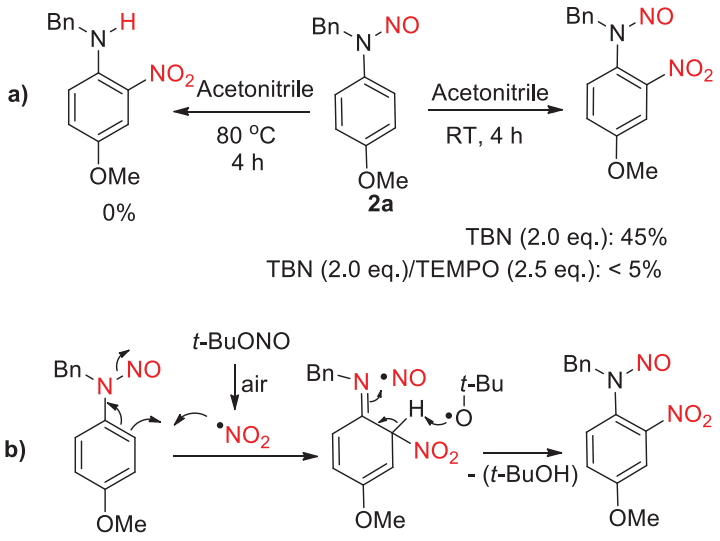
Considering the biological importance of benzimidazoles and benzotriazoles [1-5, 24] synthesis of **5aa-5ad** was demonstrated using the developed methodology as the key steps (Scheme 4.6). *N*-Benzylated *o*-phenylenediamine compounds **4ab** and **4ae** were generated in three steps from corresponding anilines in high yields (>70%) and were subsequently converted into useful benzimidazoles (**5aa** and **5ab**) and benzotriazoles (**5ac** and **5ad**) using literature procedures [25].



Scheme 4.6 Synthesis of benzimidazole and benzotriazoles.

4.4 Control Experiments and Plausible Mechanism

It is well known that unsubstituted *N*-nitroso *N*-alkyl anilines undergo Fischer-Hepp rearrangement in the presence of acid to provide corresponding *p*-nitroso *N*-alkyl anilines, but not nitroanilines [23]. Additionally, it has been also observed that *p*-substituted *N*-nitroso *N*-alkyl anilines undergo preferentially denitrosation rather than Fischer-Hepp rearrangement in the presence of acid [23]. On the other hand, Drake *et al.,* [26] and Welzel [27] have independently found that diaryl *N*-nitrosamines undergo radical dissociation upon heating which leads to ring nitrated product in case of some carbazoles while mixtures of different rearranged products were observed with simple diphenylamine. Thus, to understand the possible ring nitration mechanism, we have carried out a few control experiments (Scheme 4.7, **a**).

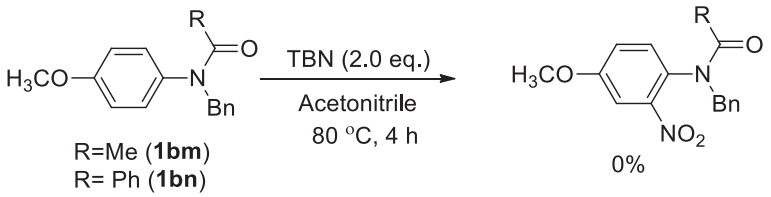


Scheme 4.7 Plausible mechanism for ring nitration reaction.

Initially, *N*-nitrosamine **2a** was refluxed in acetonitrile in the absence of TBN under air in order to understand the possible rearrangements. No reaction was observed while **2a** was recovered in 91% yield which indicates that there is no Fischer-Hepp type rearrangement taking place. On the other hand, from Table 4.1 it is clear that the formation of *N*-nitrosamine is the first step after which the ring nitration takes place. To verify this, nitration of *N*-nitrosamine **2a** was attempted with 2.0 equiv. of TBN at room temperature which provides *o*-nitro compound **2aa** in 45% yield in 4 h. However, no reaction was observed when the nitration of *N*-nitrosamine **2a** was attempted with TBN in the presence of radical scavenger TEMPO. This indicates that the reaction proceeds through a radical mechanism.

Based on these experiments and literature reports, a plausible mechanism is proposed (Scheme 4.7, **b**). TBN provides nitro radical in the presence of air [6, 19] which undergoes substitution on the aryl ring resulting in amine-nitroso (*i.e.* N-N) bond cleavage. Subsequently, the abstraction of a proton by *t*-butoxy radical would result in the formation of *N*-nitrosamine **2aa**.

It is also important to note that the *o*-substituted *N*-alkyl anilines (**1bk** and **1bl**) did not undergo nitration under optimized condition and it provides only the corresponding *N*-nitroso compounds (Scheme 4.4). This observation lends supports to the proposed mechanism, because, sterically hindered *N*-nitrosamines are expected to be more stable where N-N bond cleavage would not occur easily, hence, no nitration takes place. To support further the assumption of N-N bond cleavage, nitration of *N*-acetyl and *N*-benzoyl *N*-benzyl 4-methoxyanilines (**1bm** and **1bn**) was attempted with 2.0 equiv. of TBN at 80 °C (Scheme 4.8). No nitration was observed as there is no possibility of N-CO bond cleavage even at high temperature.



Scheme 4.8 Nitration of *N*-acyl *N*-alkyl anilines with TBN.

4.5 Conclusion

In summary, we have developed a practical method for the regioselective nitration of *N*-alkyl anilines using *tert*-butyl nitrite under metal free condition. The reaction provides synthetically useful *N*-nitroso *N*-alkyl nitroanilines in excellent yields. Simple methods were developed for the conversion of *N*-nitroso *N*-alkyl nitroanilines into *N*-alkyl nitroanilines and *N*-alkyl phenylenediamines using 25% aqueous HCl in methanol and Zn/AcOH respectively. Developed methodologies were validated by demonstrating the synthesis of benzimidazole and benzotriazole derivatives in good yields.

4.6 Experimental Section

4.6.1 General procedure for the synthesis of *N*-alkyl *N*-nitroso nitroanilines

N-Alkyl (or benzyl) aniline (1.0 mmol, 1.0 equiv.) was allowed to stir in acetonitrile (8 mL) approximately for 5 min at room temperature to which *tert*-butyl nitrite (TBN) (0.48 mL, 4.0 equiv.) was added. The reaction was further allowed to stir for 10 minutes at room temperature and then, kept at pre-heated oil bath at 80 °C for 3 h (**1aa-1ac, 1ah-1an, 1ay, 1ba-1bc and 1bg-1bi**) and 6 h (**1ad, 1af, 1ag, 1ao-1ax, 1az, 1bd, 1bf and 1bj**). The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine solution. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2, eluent: Hexane/ethyl acetate) to obtain corresponding pure substituted *N*-alkyl *N*-nitrosamines (**2ab-2bj**). All the *o*-nitro *N*-alkyl *N*-nitroso aniline

compounds showed rotamers in ~ 3:2 ratio as observed by ^{1}H NMRs. Between two isomers, benzylic protons of one isomer appeared as broad signal due to restricted rotation.

4.6.2 General procedure for the denitrosation of *N*-alkyl *N*-nitroso nitroanilines

Substituted *N*-alkyl *N*-nitroso anilines (1.0 mmol, 1.0 equiv.) was allowed to stir in methanol (5 mL) approximately for 5 min at room temperature to which 25% aqueous hydrochloric acid (HCl) (2 mL) was added. The reaction was further allowed to stir for 15-20 minutes at pre-heated oil bath at 50 °C. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with chloroform (50 mL) and washed with sodium bicarbonate solution followed by brine solution. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for short column chromatography purification (SiO_2, eluent: Hexane/ethyl acetate) to obtain *N*-alkyl nitroanilines (**3aa-3bg'**) in high yields.

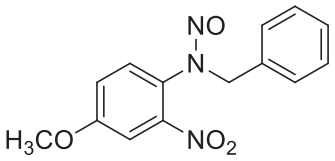
4.6.3 General procedure for the denitrosation followed by reduction of nitro group in *N*-alkyl *N*-nitroso nitroanilines

N-Nitrosamine (1.0 mmol, 1 equiv.) was stirred in MeOH (6 ml) at 50 ºC to which activated zinc dust (4.0 mmol, 4 equiv.) was added portionwise followed by acetic acid (1.5 mL). The reaction mixture was allowed to stir for 20 min at the same temperature. After completion, the reaction mixture was cooled to room temperature and filtered through celite. The filtrated (methanol solution) was evaporated, diluted with chloroform (50 mL) and washed with 1 molar aqueous solution of NaOH and brine. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography

(SiO_2, eluent: Hexane/ethyl acetate) to obtain corresponding pure *N*-Substituted *o*-phenylenediamines (**4aa-4al**).

4.7 Analytical Data of Products

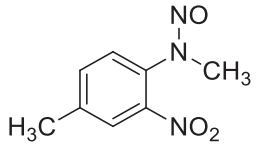
4.7.1 *N*-Nitroso *N*-benzyl-*N*-(4-methoxy-2-nitroaniline) (2aa)



2aa

The compound was obtained as yellow viscous liquid. (Yield: 269 mg, 94%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f= 0.38. IR (neat): 3091, 2845, 1525, 1268, 1067, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.5 Hz, 2H), 7.37 (m, 3H), 7.32-7.26 (m, 3H), 7.12 (m, 4H), 7.00 (dd, *J* = 8.8, 0.62H), 6.49 (d, *J* = 9.1 Hz, 0.62H), 6.05-5.38 (2 brs, 1H), 5.13 (s, 2H), 3.92 (s, 3H), 3.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 160.1, 146.4, 145.8, 133.6, 130.3, 130.2, 129.2, 129.0, 128.9, 128.7, 128.7, 128.0, 127.2, 119.6, 119.4, 110.5, 110.5, 58.0, 56.1, 56.0, 50.3. HRMS: Calc. for $C_{14}H_{14}N_3O_4$ $[M+H]^+$: 288.0984, Obser. 288.0982.

4.7.2 *N*-Nitroso *N*-methyl 4-methyl 2-nitroaniline (2ab)

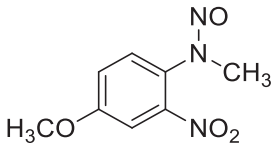


2ab

The compound was obtained as yellow viscous liquid. (Yield: 157 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f= 0.49. IR (neat) 3123, 2783, 1600, 1278, 1056 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.57 (dd, *J* = 15.1,

8.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.28 (s, 0.26H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.21 (s, 0.51H), 3.40 (s, 3H), 2.53 (s, 3H), 2.49 (s, 0.54). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 144.0, 141.4, 140.6, 135.2, 134.6, 133.2, 127.2, 127.0, 125.9, 125.6, 40.5, 35.0, 24.0, 20.9. HRMS: Calc. for $C_8H_{10}N_3O_3$ $[M+H]^+$: 196.0722, Obser. 196.0720.

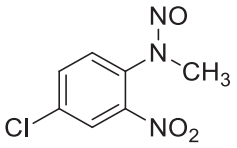
4.7.3 *N*-Nitroso *N*-methyl 4-methoxy 2-nitroaniline (2ac)



2ac

The compound was obtained as yellow viscous liquid. (Yield: 173 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.47. IR (neat): 3023, 2763, 1412, 1268, 1001 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.6 Hz), 7.42 (d, *J* = 8.8 Hz), 7.28 (dd, *J* = 8.7, 2.5 Hz), 7.23 (dd, *J* = 8.7, 2.4 Hz), 7.07 (d, *J* = 8.7 Hz), 4.18 (s), 3.94 (s), 3.90 (s), 3.38 (s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 160.0, 146.1, 145.0, 128.8, 128.5, 128.5, 124.2, 120.2, 119.7, 110.5, 110.3, 56.2, 56.1, 40.6, 35.3. HRMS: Calc. for $C_8H_{10}N_3O_4$ $[M+H]^+$: 212.0671, Obser. 212.0670.

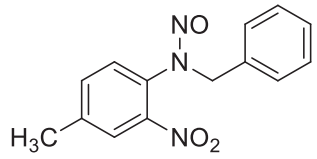
4.7.4 *N*-Nitroso *N*-methyl 4-chloro 2-nitroaniline (2ad)



2ad

The compound was obtained as yellow viscous liquid. (Yield: 172 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.48. IR (neat): 3223, 2343, 1523, 1258, 1008 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (t, *J* = 2.9 Hz), 7.76 (dt, *J* = 13.4, 6.7 Hz), 7.50 (d, *J* = 8.5 Hz), 7.16 (d, *J* = 8.4 Hz), 4.24 (s), 3.40 (s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 135.2, 134.7, 134.3, 134. 0, 128.6, 127.9, 125.9, 125.5, 40.3, 34.7. HRMS: Calc. for $C_7H_7ClN_3O_3$ $[M+H]^+$: 216.0176, Obser. 216.0174.

4.7.5 *N*-Nitroso *N*-benzyl-*N*-(4-methyl-2-nitroaniline) (2ae)

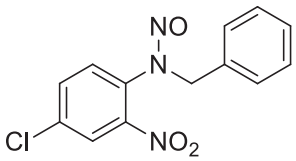


2ae

The compound was obtained as yellow viscous liquid. (Yield: 227 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.39. IR (neat): 3023, 3023, 1560, 1223, 1123, 789 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 11.7, 6.6 Hz, 2H), 7.64 (m 1H), 7.60-7.52 (m, 2H), 7.25 (dd, *J* = 5.9, 2.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 9.3 Hz, 0.51H), 5.94-5.53 (2 brs, 1H), 5.14 (s, 2H), 2.38 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 145.0, 138.6, 137.9, 134.5, 134.0, 133.5,

131.1, 131.0, 130.4, 130.3, 129.6, 129.5, 129.4, 129.2, 129.1, 128.7, 128.3, 127.0, 125.6, 125.3, 57.6, 49.6, 21.1, 21.0. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1031.

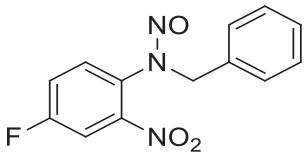
4.7.6 *N*-Nitroso *N*-benzyl-*N*-(4-chloro-2-nitroaniline) (2af)



2af

The compound was obtained as yellow viscous liquid. (Yield: 241 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtO Ac 90:10, R_f= 0.42. IR (neat): 3234, 3123, 1523, 1134, 1000, 973 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 8.03 (s, 1H), 7.57 (d, *J* = 6.6 Hz, 1H), 7.46 (d, *J* = 10.4 Hz, 4H), 7.36 (m, 4H), 7.27 (m, 4H), 7.17-7.06 (m, 3H), 6.56 (t, *J* = 8.5 Hz, 0.65H), 6.00-5.66 (2 brs, 1H), 5.12 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.0, 136.3, 135.3, 134.5, 134.1, 133.9, 133.6, 133.1, 132.9, 132.2, 129.1, 129.1, 128.9, 128.6, 128.3, 125.9, 125.7, 57.7, 49.6. HRMS: Calc. for $C_{13}H_{11}ClN_3O_3$ $[M+H]^+$: 292.0489, Obser. 292.0487.

4.7.7 *N*-Nitroso *N*-benzyl-*N*-(4-fluoro-2-nitroaniline) (2ag)

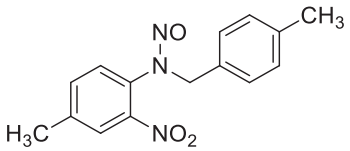


2ag

The compound was obtained as yellow viscous liquid. (Yield: 198 mg, 72%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.52. IR (neat): 3223, 3034, 1458, 1178, 1087 cm^{-1}. ^1H

NMR (500 MHz, $CDCl_3$) δ 7.40-7.35 (dd, *J* = 7.7, 2.8 Hz, 10H), 7.31-7.28 (m, 3H), 7.26-7.22 (m, 2H), 7.17-7.10 (m, 2H), 6.64 (d, *J* = 8.8, 0.65H), 6.06-5.41 (2 brs, 1H), 5.14 (s, 2H). 13C NMR (125 MHz, $CDCl_3$) δ 162.9, 162.5, 160.8, 160.4, 146.4, 146.4, 145.5, 145.4, 133.9 (q, J_{C-F} = 40.0 Hz), 131.0, 130.9, 130.7, 130.7, 130.4, 130.4, 129.1, 129.0, 128.8 (q, J_{C-F} = 35.0 Hz), 128.2, 126.7, 126.7, 121.3, 121.1, 120.9, 120.7, 113.5 (q, J_{C-F} = 40.0 Hz), 57.7, 49.9. HRMS: Calc. for $C_{13}H_{11}FN_3O_3$ $[M+H]^+$: 276.0784, Obser. 276.0782.

4.7.8 *N*-Nitroso *N*--(4-methylbenzyl)-*N*-(4-methyl -2-nitroaniline) (2ah)

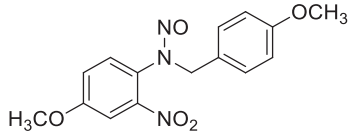


2ah

The compound was obtained as yellow viscous liquid. (Yield: 233 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f= 0.43. IR (neat): 3267, 3156, 1523, 1278, 1007, 985 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.9 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 10.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 11.4, 8.0 Hz, 0.54H), 7.03 (d, *J* = 8.0 Hz, 11H), 6.53 (d, *J* = 8.0 Hz, 3H), 6.01–5.46 (2 brs, 1H), 5.10 (s, 2H), 2.48 (s, 3H), 2.43 (s, 2H), 2.37 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 144.6, 141.3, 140.6,

138.5, 137.7, 134.6, 134.2, 131.8, 131.1, 130.4, 129.5, 129.3, 129.0, 128.7, 128.2, 125.8, 125.6, 57.5, 49.6, 21.0, 20.9, 20.9, 20.8. HRMS: Calc. for $C_{15}H_{16}N_3O_3$ $[M+H]^+$: 286.1192, Obser. 286.1191.

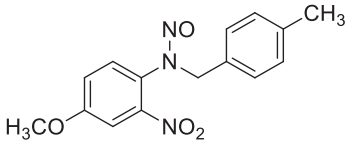
4.7.9 *N*-Nitroso *N*-(4-methoxybenzyl)-*N*-(4-methoxy-2-nitroaniline) (2ai)



2ai

The compound was obtained as yellow viscous liquid. (Yield: 253 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.40, IR (neat): 3123, 2783, 1600, 1278, 1056 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.9 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.13-6.92 (m, 5H), 6.86 (d, *J* = 11.2 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 0.68H), 6.49 (s, 2H), 5.94-5.32 (2 brs, 1H), 5.03 (s, 2H), 3.87 (s, 3H), 3.82 (s, 2H), 3.78 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 160.1, 159.8, 159.3, 146.4, 145.8, 130.6, 130.5, 130.4, 130.1, 127.0, 126.1, 125.5, 119.6, 119.3, 114.3, 114. 1, 110.6, 57.5, 56.2, 56.1, 55.2, 55.2, 49.7. HRMS: Calc. for $C_{15}H_{16}N_3O_5$ $[M+H]^+$: 318.1090, Obser. 318.10989.

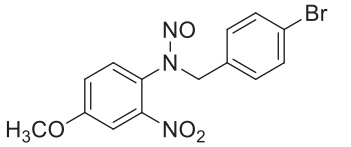
4.7.10 *N*-Nitroso *N*-(4-methylbenzyl)-*N*-(4-methoxy-2-nitroaniline) (2aj)



2aj

The compound was obtained as yellow viscous liquid. (Yield: 255 mg, 85%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.38. IR (neat): 3864, 2921, 1705, 1525, 1115, 830 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.42 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.37-7.20 (m, 1H), 7.07 (dd, *J* = 13.1, 8.4 Hz, 3H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.85-6.76 (m, 2H), 6.50 (d, *J* = 8.0 Hz, 0.59H), 5.90-5.42 (2 brs, 1H), 5.08 (s, 2H), 3.82 (s, 2H), 3.78 (s, 3H), 2.49 (s, 3H), 2.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 159.3, 145.4, 144.7, 141.3, 140.7, 134.6, 134.2, 131.8, 130.5, 130.3, 128.9, 128.6, 128.1, 126.1, 125.9, 125.7, 125.4, 114.2, 114.0, 57.3, 55.2, 55.1, 49.3, 20.9, 20.9. HRMS: Calc. for $C_{15}H_{16}N_3O_4$ $[M+H]^+$: 302.1141, Obser. 302.1140.

4.7.11 *N*-Nitroso *N*-(4-bromobenzyl)-*N*-(4-methyl-2-nitroaniline) (2ak)

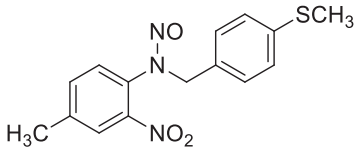


2ak

The compound was obtained as yellow viscous liquid. (Yield: 307 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f= 0.39. IR (neat): 3234, 3012, 1456, 1130, 1090 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 10.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 10.4 Hz, 0.58H), 7.32–

7.23 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 0.58H), 5.71-5.43 (2 brs, 1H), 5.08 (s, 2H), 3.83 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 159.5, 146.2, 145.2, 137.0, 136.5, 133.4, 130.5, 130.4, 130.3, 129.7, 129.5, 128.7, 128.5, 128.3, 125.7, 125.0, 123.8, 122.7, 114.4, 114.2, 57.2, 55.2, 55.2, 49.0. HRMS: Calc. for $C_{14}H_{13}BrN_3O_4$ $[M+H]^+$: 366.0089, Obser. 366.0087.

4.7.12 *N*-Nitroso *N*-(4-thiomethylbenzyl)-*N*-(4-methyl-2-nitroaniline) (2al)

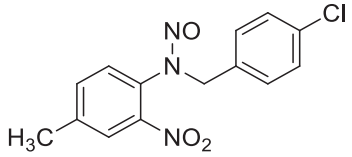


2al

The compound was obtained as yellow viscous liquid. (Yield: 250 mg, 79%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3203, 2783, 1600, 1259, 1116 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 0.57H), 7.30–7.23 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 0.55), 5.89-5.45 (2 brs, 1H), 5.09 (s, 2H), 2.49 (s, 5H), 2.46 (s, 3H), 2.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 144.6, 141.4, 140.8, 139.5, 138.6, 134.6, 134.2, 131.8, 130.6, 130.0, 129.6, 129.3, 128.7, 128.3,

128.0, 126.3, 125.9, 125.7, 57.3, 49.4, 20.9, 20.9, 15.3, 15.3. HRMS: Calc. for $C_{15}H_{16}N_3O_3S$ $[M+H]^+$: 318.0912, Obser. 318.0911.

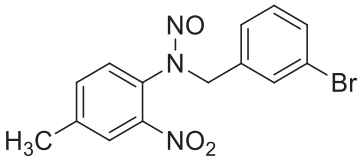
4.7.13 *N*-Nitroso *N*-(4-chlorobenzyl)-*N*-(4-methyl -2-nitroaniline) (2am)



2am

The compound was obtained as yellow viscous liquid. (Yield: 247 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.49. IR (neat): 3380, 2923, 1524, 1346, 1081, 794 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.30–7.23 (m, 4H), 7.07 (t, *J* = 7.6 Hz, 3H), 6.51 (d, *J* = 8.0 Hz, 0.52H), 5.86-5.46 (2 brs, 1H), 5.08 (s, 2H), 2.48 (s, 3H), 2.42 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.6, 141.6, 141.0, 134.7, 134.3, 134.0, 132.8, 132.0, 131.7, 130.5, 130.2, 129.1, 128.9, 128.6, 128.2, 127.8, 126.1, 125.9, 57.0, 49.2, 21.0, 21.0. HRMS: Calc. for $C_{14}H_{13}ClN_3O_3$ $[M+H]^+$: 306.0645, Obser. 306.0643.

4.7.14 *N*-Nitroso *N*--(3-bromobenzyl)-*N*-(4-methyl -2-nitroaniline) (2an)

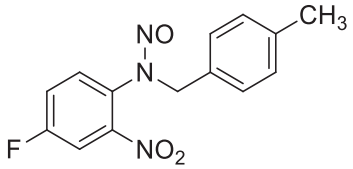


2an

The compound was obtained as yellow viscous liquid. (Yield: 302 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.45. IR (neat): 3834, 2925, 1700, 1524, 1346,

1069, 793 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.49 (dd, *J* = 19.2, 10.0 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.38-7.24 (m, 3H), 7.21-7.06 (m, 3H), 6.55 (d, *J* = 8.0 Hz, 0.42H), 5.91-5.49 (2brs, 1H), 5.09 (s, 2H), 2.51 (s, 3H), 2.45 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.6, 141.7, 141.0, 136.7, 135.9, 134.8, 134.4, 132.0, 131.9, 131.8, 131.6, 131.2, 130.5, 130.3, 130.1, 128.7, 128.2, 127.9, 127.7, 127.3, 126.1, 125.9, 122.9, 122.7, 119.5, 57.1, 49.3, 21.0, 21.0. HRMS: Calc. for $C_{15}H_{16}BrN_3O_3$ $[M+H]^+$: 365.0375, Obser. 365.037.

4.7.15 *N*-Nitroso *N*-(4-methylbenzyl)-*N*-(4-fluoro-2-nitroaniline) (2ao)

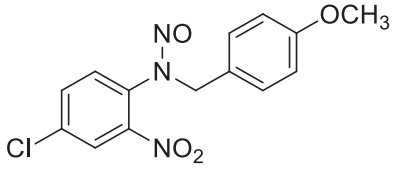


2ao

The compound was obtained as yellow viscous liquid. (Yield: 216 mg, 75%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.52. IR (neat): 3023, 2793, 1406, 1238, 986 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 10.8, 3.0 Hz, 1H), 7.35 (dd, *J* = 12.8, 5.9 Hz, 1H), 7.26-7.17 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.61 (dd, *J* = 8.8, 5.0 Hz, 0.64H), 6.05-5.34 (2brs, 1H), 5.10 (s, 2H), 2.38 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 215.0 Hz), 162.5 (d, $J_{C\text{-}F}$ = 215.0 Hz),

160.9, 160.5, 146.4, 145.4, 138.8, 138.1, 131.2, 131.1, 130.9, 130.7, 130.6, 130.1, 129.7, 129.5, 129.1 128.9, 126.9, 121.2, 121.1 (d, J_{C-F} = 90.0 Hz), 120.9 (d, J_{C-F} = 90.0 Hz), 120.7, 113.5 (d, J_{C-F} = 25.0 Hz), 113.3 (d, J_{C-F} = 50.0 Hz), 57.6, 49.7, 21.1, 21.0. HRMS: Calc. for $C_{14}H_{13}FN_3O_3$ $[M+H]^+$: 290.0941, Obser. 290.0939.

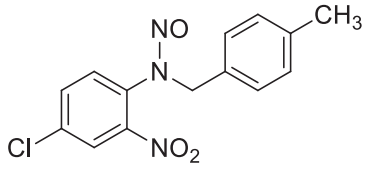
4.7.16 *N*-Nitroso *N*-(4-chlorobenzyl)-*N*-(4-methoxy -2-nitroaniline) (2ap)



2ap

The compound was obtained as yellow viscous liquid. (Yield: 256 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.51. IR (neat): 3023, 2983, 1412, 1118, 1009, 978 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.31-7.28 (m, 1H), 7.27-7.23 (m, 1H), 7.17-7.13 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.9 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 0.54H), 5.93–5.40 (2brs, 1H), 5.07 (s, 2H), 3.92 (s, 3H), 3.86 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 160.1, 146.3, 145.6, 134.6, 133.9, 132.8, 132.1, 130.5, 130.3, 130.1, 129.9, 129.0, 128.8, 126.8, 122.6, 119.6, 119.4, 110.7, 110.7, 57.1, 56.1, 56.0, 49.5. HRMS: Calc. for $C_{14}H_{13}ClN_3O_4$ $[M+H]^+$: 322.0595, Obser. 322.0593.

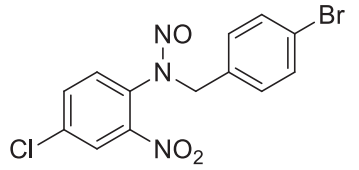
4.7.17 *N*-Nitroso *N*-(4-methylbenzyl)-*N*-(4-chloro -2-nitroaniline) (2aq)



2aq

The compound was obtained as yellow viscous liquid. (Yield: 244 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.53. IR (neat): 3723, 3012, 1435, 1278, 1012, 786 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 14.1 Hz, 1H), 7.59 (d, *J* = 10.9 Hz, 1H), 7.49 (d, *J* = 10.8 Hz, 0.64H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.21-7.16 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 0.65H), 6.02-5.48 (2 brs, 1H), 5.11 (s, 2H), 2.38 (s, 2H), 2.33 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 146.7, 145.1, 138.8, 138.2, 136.3, 135.3, 134.0, 133.5, 133.0, 130.8, 130.2, 130.0, 129.7, 129.6, 129.6, 129.2, 129.2, 129.1, 128.7, 126.9, 125.8, 125.6, 57.5, 49.3, 21.1, 21.1. HRMS: Calc. for $C_{14}H_{13}ClN_3O_3$ $[M+H]^+$: 306.0645, Obser. 306.0643.

4.7.18 *N*-Nitroso *N*-(2-methylbenzyl)-*N*-(4-chloro-2-nitroaniline) (2ar)

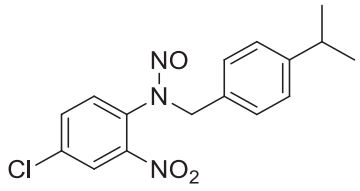


2ar

The compound was obtained as yellow viscous liquid. (Yield: 305 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.52. IR (neat): 3875, 3393, 2319, 1615, 1502, 1139, 789 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H),

7.53 (d, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 9.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.5 Hz, 0.50H), 5.73-5.37 (2 brs, 1H), 4.98 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.0, 136.5, 135.6, 134.3, 133.8, 133.0, 132.8, 132.3, 132.2, 132.1, 130.8, 130.4, 129.8, 128.9, 128.8, 126.1, 125.8, 123.2, 122.4, 57.0, 49.0. HRMS: Calc. for $C_{14}H_{10}BrClN_3O_3$ $[M+H]^+$: 367.9563, Obser. 367.9560.

4.7.19 *N*-Nitroso *N*-(4-isopropylbenzyl)-*N*-(4-chloro-2-nitroaniline) (2as)

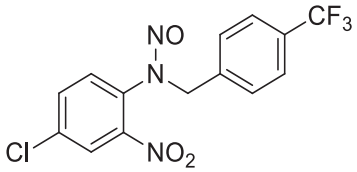


2as

The compound was obtained as yellow viscous liquid. (Yield: 269 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3021, 2456, 1538, 1214, 744, 668 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 9.4, 1.8 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.6 Hz, 0.61H), 7.26 (dd, *J* = 14.4, 8.7 Hz, 6), 7.18 (dd, *J* = 16.7, 8.2 Hz, 3H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 0.58H), 5.91-5.46 (2 brs, 1H), 5.11 (s, 2H), 2.93 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.88 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 149.1, 136.3, 135.3, 134.0,

133.5, 133.1, 131.2, 130.4, 130.2, 129.1, 129.1, 128.6, 127.1, 127.0, 126.9, 125.8, 125.7, 115.6, 57.5, 49.5, 47.0, 33.8, 33.7, 29.6, 23.8, 23.8. HRMS: Calc. for $C_{16}H_{17}ClN_3O_3$ $[M+H]^+$: 334.0958, Obser. 334.0956.

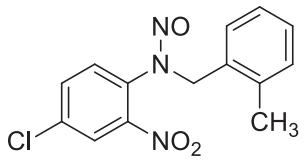
4.7.20 *N*-Nitroso *N*-(4-trifluoromethanebenzyl)-*N*-(4-chloro-2-nitroaniline) (2at)



2at

The compound was obtained as yellow viscous liquid. (Yield: 283 mg, 79%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.55. IR (neat): 3741, 3023, 1600, 1348, 1015, 986 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 2.3 Hz, 1H), 7.67 (t, J = 5.4 Hz, 1H), 7.60 (s, 2H), 7.54 (t, J = 11.1 Hz, 1H), 7.27 (s, 2H), 7.21 (d, J = 8.5 Hz, 1H), 6.65 (d, J = 8.5 Hz, 0.43H), 6.07-5.56 (2 brs, 1H), 5.19 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.0, 138.0, 137.2, 136.7, 135.7, 134.3, 133.8, 132.8, 131.3, 131.2, 130.9, 130.7, 130.6, 130.4, 130.1, 129.7, 129.4, 128.8, 128.6, 127.1, 126.1 (q, J_{C-F} = 15.0 Hz), 126.1, 125.9, 125.9 (q, J_{C-F} = 15.0 Hz), 124.8, 122.6, 115.4, 57.0, 49.2. HRMS: Calc. for $C_{14}H_{10}ClF_3N_3O_3$ $[M+H]^+$: 360.0363, Obser. 360.0360.

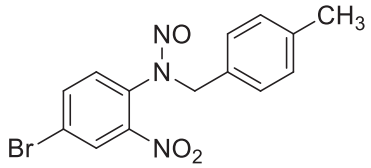
4.7.21 *N*-Nitroso *N*-(2-methylbenzyl)-*N*-(4-chloro-2-nitroaniline) (2au)



2au

The compound was obtained as yellow viscous liquid. (Yield: 250 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.49. IR (neat): 3721, 2429, 1349, 1214, 744 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 14.8 Hz, 1H), 7.52 (dd, *J* = 40.1, 8.5 Hz, 2H), 7.35-7.23 (m, 2H), 7.21 (d, *J* = 14.8 Hz, 1H), 7.14 (m, 4H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 0.64H), 5.94-5.61 (2 brs, 1H), 5.16 (s, 2H), 2.38 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 145.2, 137.7, 136.3, 135.3, 134.0, 133.5, 132.8, 131.5, 131.1, 130.8, 130.7, 130.6, 130.4, 129.2, 129.2, 129.0, 128.9, 128.5, 126.4, 126.4, 125.7, 125.6, 55.5, 47.1, 19.1, 19.0. HRMS: Calc. for $C_{14}H_{13}ClN_3O_3$ $[M+H]^+$: 306.0645, Obser. 306.0643.

4.7.22 *N*-Nitroso *N*-(4-methylbenzyl)-*N*-(4-bromo-2-nitroaniline) (2av)

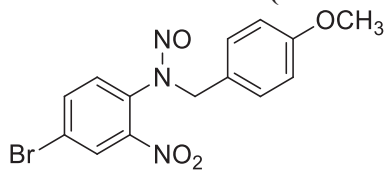


2av

The compound was obtained as yellow viscous liquid. (Yield: 280 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.48. IR (neat): 3423, 2780, 1412, 1289, 1026, 765 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 0.9 Hz, 1H), 7.46-7.35 (m, 4H), 7.34-7.25 (m, 4H), 7.17-7.07

(m, 3H), 6.50 (d, *J* = 8.1 Hz, 0.55H), 6.92-5.47 (2 brs, 1H), 5.15 (s, 2H), 2.49 (s, 3H), 2.44 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 145.3, 144.7, 141.4, 140.7, 134.6, 134.3, 134.2, 133.6, 131.9, 129.2, 128.9, 128.9, 128.8, 128.7, 128.7, 128.4, 128.2, 128.0, 126.0, 125.8, 121.9, 57.8, 49.9, 21.0, 20.9. HRMS: Calc. for $C_{14}H_{13}BrN_3O_3$ $[M+H]^+$: 350.0140, Obser. 350.0138.

4.7.23 *N*-Nitroso *N*-(4-methoxybenzyl)-*N*-(4-bromo-2-nitroaniline) (2aw)

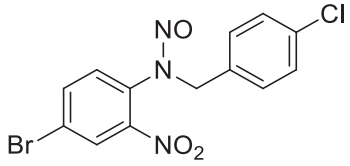


2aw

The compound was obtained as yellow viscous liquid. (Yield: 296 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:10, R_f = 0.49. IR (neat): 3803, 3393, 2916, 1502, 885 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 14.5, 9.3 Hz, 3H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 3H), 7.04 (d, *J* = 8.8 Hz, 0.56H), 6.52 (d, *J* = 8.8 Hz, 0.55H), 6.00-5.36 (2brs, 1H), 5.08 (s, 2H), 3.93 (s, 3H), 3.88 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 60.2, 146.4, 145.7, 134.7, 134.0, 132.8, 132.1, 130.8, 130.5, 130.4, 130.2, 130.0, 129.4, 129.1, 128.9, 126.9, 122.7, 119.7, 119.5, 110.7, 57.2, 56.2, 56.1, 49.6. HRMS: Calc. for

$C_{14}H_{13}BrN_3O_4$ $[M+H]^+$: 366.0089, Obser. 366.0083.

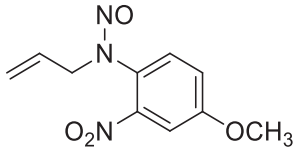
4.7.24 *N*-Nitroso *N*-(4-methoxybenzyl)-*N*-(4-bromo-2-nitroaniline) (2ax)



2ax

The compound was obtained as yellow viscous liquid. (Yield: 305 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.50. IR (neat): 3006, 2983, 1578, 1109, 983 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.4 Hz, 3H), 7.63 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 0.50H), 5.91-5.50 (2 brs, 1H), 5.09 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.1, 136.6, 135.7, 134.3, 133.8, 133.0, 132.8, 132.3, 132.2, 132.1, 130.8, 130.4, 129.9, 129.0, 128.8, 126.1, 125.8, 123.2, 122.5, 57.0, 49.0. HRMS: Calc. for $C_{13}H_{10}BrClN_3O_3$ $[M+H]^+$: 369.9594, Obser. 369.9594.

4.7.25 *N*-Nitroso *N*-allyl-*N*-(4-methoxy-2-nitroaniline) (2ay)

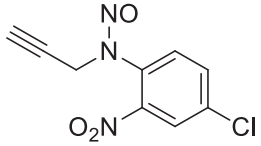


2ay

The compound was obtained as yellow viscous liquid. (Yield: 194 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.51. IR (neat): 3403, 2983, 1660, 1278, 1053 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (t, *J* = 2.7 Hz,

2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.18 (dd, *J* = 9.4, 6.5 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 0.52H), 6.05–5.98 (m, 0.52H), 5.66-5.57 (m, 1H), 5.25 (d, *J* = 14.1 Hz, 1H), 5.11 (t, *J* = 13.7 Hz, 3H), 4.44 (d, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 160.1, 146.5, 145.8, 131.5, 129.8, 129.8, 129.2, 127.2, 123.0, 121.1, 120.4, 119.9, 119.5, 110.5, 110.4, 56.8, 56.2, 56.1, 49.9. HRMS: Calc. for $C_{10}H_{12}N_3O_4$ $[M+H]^+$: 238.0828, Obser. 238.0823.

4.7.26 *N*-Nitroso *N*-propargyl-*N*-(4-methoxy-2-nitroaniline) (2az)

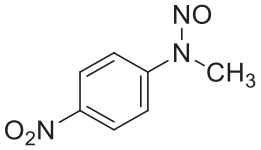


2az

The compound was obtained as yellow viscous liquid. (Yield: 198 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.48. IR (neat): 3423, 2972, 1604, 1171, 1023 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.3 Hz, 1H), 8.16 (d, *J* = 2.3 Hz, 0.33H), 7.81 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.3 Hz, 0.37H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 0.36H), 5.60-5.91 (brs, 1H), 4.71 (d, *J* = 2.6 Hz, 2H), 2.50 (t, *J* = 2.5 Hz, 0.32H), 2.29 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.0, 137.0, 136.3, 134.5, 134.1, 132.1, 131.2, 130.3, 125.9,

125.9, 76.2, 75.7, 75.1, 74.4, 43.1, 36.0. HRMS: Calc. for $C_9H_7ClN_3O_3$ $[M+H]^+$: 240.0176, Obser. 240.0175.

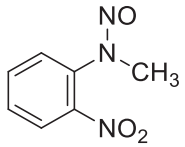
4.7.27 *N*-Nitroso *N*-methyl-*N*-(4-nitroaniline) (2ba)



2ba

The compound was obtained as yellow solid. M.p. 101 °C (Yield: 112 mg, 62%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 90:10, R_f = 0.48. IR (neat): 3021, 2783, 1156, 1118, 1053 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 3.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 145.8, 125.2, 117.8, 30.0. HRMS: Calc. for $C_7H_8N_3O_3$ $[M+H]^+$: 182.0566, Obser. 182.0563.

4.7.28 *N*-Nitroso *N*-methyl -*N*-(2-nitroaniline) (2ba')

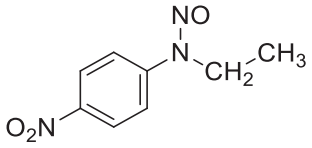


2ba'

The compound was obtained as yellow viscous liquid. (Yield: 41 mg, 23%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.45. IR (neat): 3042, 2984, 1293, 1007, 1053 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.28 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.4 Hz, 0.21H), 7.07 (d, *J* = 8.7 Hz, 0.19H), 4.18 (s, 0.67H), 3.94 (s, 3H), 3.90 (s, 0.64H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 160.0, 146.1, 145.0, 128.8, 128.5, 128.5, 124.2, 120.2, 119.7, 110.5,

110.3, 56.2, 56.1, 40.6, 35.3. HRMS: Calc. for $C_7H_8N_3O_3$ $[M+H]^+$: 182.0566, Obser. 182.0564.

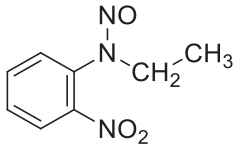
4.7.29 *N*-Nitroso *N*-ethyl-*N*-(4-nitroaniline) (2bb)



2bb

The compound was obtained as yellow solid. M.p. 120 ºC (Yield: 134 mg, 69%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.49. IR (neat): 3231, 2978, 1236, 1008, 987 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 145.8, 125.3, 117.7, 37.9, 11.6. HRMS: Calc. for $C_8H_{10}N_3O_3$ $[M+H]^+$: 196.0722, Obser. 196.0722.

4.7.30 *N*-Nitroso *N*-ethyl -*N*-(2-nitroaniline) (2bb')

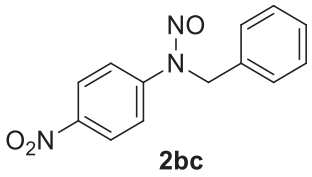


2bb'

The compound was obtained as yellow viscous liquid. (Yield: 37 mg, 19%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:20, R_f = 0.38. IR (neat): 3256, 2987, 1123, 1007, 965 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 16.4, 8.2 Hz, 1H), 7.83-7.74 (m, 2H), 7.68-7.59 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 0.50H), 4.72-4.63 (m, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 1.52 (t, *J* = 7.3 Hz, 1.60H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1,

134.5, 134.4, 133.7, 130.7, 130.3, 129.5, 128.1, 127.4, 125.8, 125.3, 48.9, 41.9, 13.9, 11.3. HRMS: Calc. for $C_8H_{10}N_3O_3$ $[M+H]^+$: 196.0722, Obser. 196.0722.

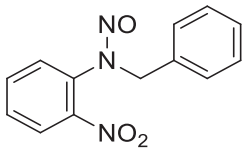
4.7.31 *N*-Nitroso *N*-benzyl-*N*-(4-nitroaniline) (2bc)



2bc

The compound was obtained as yellow solid. M.p. 110 °C (Yield: 179 mg, 72%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.50. IR (neat): 3431, 2965, 1266, 1108, 975 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 9.2 Hz, 2H), 7.32-7.18 (m, 3H), 6.97 (d, *J* = 7.1 Hz, 2H), 5.21 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 145.9, 133.2, 129.1, 128.0, 126.6, 125.2, 118.0, 45.9. HRMS: Calc. for $C_{13}H_{12}N_3O_3$ $[M+H]^+$: 258.0879, Obser. 258.0877.

4.7.32 *N*-Nitroso *N*-benzyl-*N*-(2-nitroaniline) (2bc')

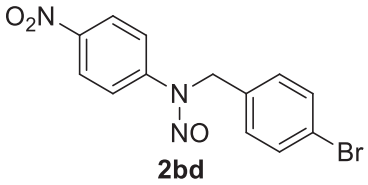


2bc

The compound was obtained as yellow viscous liquid. (Yield: 56 mg, 22%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.44. IR (neat): 3411, 2986, 1136, 975 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58-7.42 (m, 3H), 7.3-7.15 (m, 6H), 7.11-7.00 (m, 2H), 6.54 (dd, *J* = 7.2, 1.9 Hz, 0.46H), 5.90-5.42 (2 brs, 1H),

5.07 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 144.9, 134.5, 134.2, 134.0, 133.6, 133.4, 130.9, 130.4, 129.6, 129.1, 129.1, 128.9, 128.8, 128.6, 128.2, 128.1, 125.7, 125.4, 57.8, 49.8. HRMS: Calc. for $C_{13}H_{12}N_3O_3$ $[M+H]^+$: 258.0879, Obser. 258.0878.

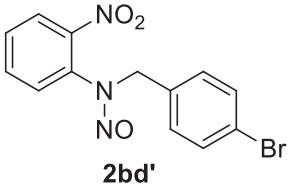
4.7.33 *N*-Nitroso *N*-(*4*-bromobenzyl)-*N*-(4-nitroaniline) (2bd)



2bd

The compound was obtained as yellow liquid. (Yield: 225 mg, 67%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.50. IR (neat): 3341, 2865, 1263, 1138, 975 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.2 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 2H), 7.31 (dd, *J* = 5.9, 1.5 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.28 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.9, 132.2, 132.2, 128.3, 125.3, 122.0, 118.0, 45.3. HRMS: Calc. for $C_{13}H_{11}BrN_3O_3$ $[M+H]^+$: 335.9984, Obser. 335.9982.

4.7.34 *N*-Nitroso *N*-(*4*-bromobenzyl)-*N*-(*2*-nitroaniline) (2bd')

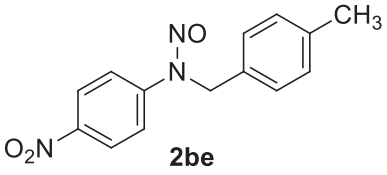


2bd'

The compound was obtained as yellow viscous liquid. (Yield: 80 mg, 21%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.43. IR (neat): 3441, 2945, 1345, 1126, 899 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz,

1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.58 (dt, *J* = 13.9, 7.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 7.2 Hz, 0.38H), 6.95-5.49(2 brs, 1H), 5.11 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 144.7, 134.2, 134.1, 133.8, 133.1, 132.4, 132.0, 131.8, 130.7, 130.5, 130.4, 130.3, 129.7, 128.6, 127.7, 125.7, 125.3, 122.9, 122.1, 57.0, 49.1. HRMS: Calc. for $C_{13}H_{11}BrN_3O_3$ $[M+H]^+$: 335.9984, Obser. 335.9983.

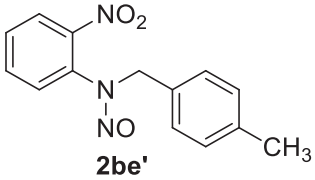
4.7.35 *N*-Nitroso *N*-(4-methylbenzyl) -*N*-(4-nitroaniline) (2be)



2be

The compound was obtained as yellow solid. M.p. 58 °C (Yield: 186 mg, 69%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.51. IR (neat): 3421, 2905, 1513, 1356, 789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.2 Hz, 2H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 145.8, 137.8, 130.2, 129.7, 126.6, 125.1, 118.1, 45.6, 21.0. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1032.

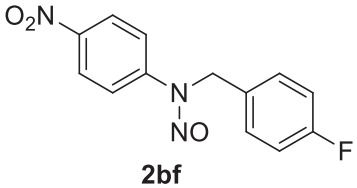
4.7.36 *N*-Nitroso *N*-(4-methylbenzyl)-*N*-(2-nitroaniline) (2be')



2be'

The compound was obtained as yellow viscous liquid. (Yield: 56 mg, 21%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.46. IR (neat): 3445, 3046, 1500, 1136, 790 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.01-7.94 (m, 1H), 7.55 (m, 2H), 7.51-7.42 (m, 2H), 7.18-7.14 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 9.3 Hz, 0.59H), 5.80-5.35 (2 brs, 1H), 5.04 (s, 2H), 2.28 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 148.8, 139.1, 138.7, 137.9, 134.6, 134.0, 133.5, 130.4, 130.3, 129.6, 129.5, 129.4, 129.2, 129.1, 128.7, 128.3, 125.7, 125.3, 57.6, 49.6, 21.19, 21.1. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1032.

4.7.37 *N*-Nitroso *N*-(4-fluorobenzyl)-*N*-(4-nitroaniline) (2bf)

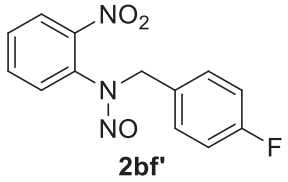


2bf

The compound was obtained as yellow liquid. (Yield: 194 mg, 67%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.48. IR (neat): 3821, 2985, 1531, 1389, 890 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.1 Hz, 2H), 7.81-7.69 (m, 2H), 7.04 (dd, *J* = 12.0, 6.9 Hz, 4H), 5.26 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 161.3,

146.2, 145.9, 128.5 (d, J_{C-F} = 35.0 Hz), 125.2, 121.8, 121.2, 119.6, 118.1, 116.1 (d, J_{C-F} = 90.0 Hz), 45.2. HRMS: Calc. for $C_{13}H_{11}FN_3O_3$ $[M+H]^+$: 276.0784, Obser. 276.0784.

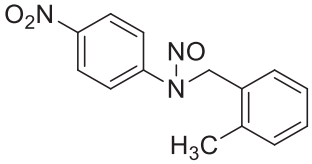
4.7.38 *N*-Nitroso *N*-(*4*-fluorobenzyl)-*N*-(2-nitroaniline) (2bf')



2bf'

The compound was obtained as yellow viscous liquid. (Yield: 55 mg, 20%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.37. IR (neat): 3468, 2890, 1453, 1012, 878 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 8.5 Hz, 1H), 7.63-7.54 (m, 2H), 7.35 (t, *J* = 8.4 Hz, 4H), 7.29-7.24 (m, 1H), 7.16-7.12 (m, 1H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 5.9 Hz, 0.46H), 5.89-5.55 (2 brs, 1H), 5.13 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, J_{C-F} = 249.0 Hz), 161.8 (d, J_{C-F} = 245.0 Hz), 145.7, 144.8, 134.2 (d, J_{C-F} = 30.0 Hz), 133.7, 131.0, 130.9, 130.6, 130.5, 130.5, 129.9, 129.7, 129.2, 129.2, 128.7, 127.9, 125.7, 125.3, 115.9 (q, J_{C-F} = 50.0 Hz), 56.9, 49.0. HRMS: Calc. for $C_{13}H_{11}FN_3O_3$ $[M+H]^+$: 276.0784, Obser. 276.0784.

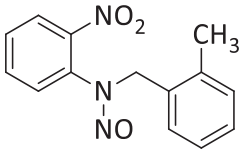
4.7.39 *N*-Nitroso *N*-(2-methylbenzyl)-*N*-(4-nitroaniline) (2bg)



2bg

The compound was obtained as yellow liquid. (Yield: 195 mg, 72%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.49. IR (neat): 3737, 2852, 1525, 1115, 905 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.3 Hz, 2H), 7.62 (d, *J* = 9.2 Hz, 2H), 7.11 (q, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.13 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 145.8, 134.9, 130.7, 130.4, 127.8, 126.3, 125.2, 125.1, 118.1, 44.4, 19.06. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1033.

4.7.40 *N*-Nitroso *N*-(2-methylbenzyl)-*N*-(2-nitroaniline) (2bg')

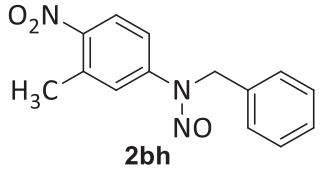


2bg'

The compound was obtained as yellow viscous liquid. (Yield: 51 mg, 19%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.38. IR (neat): 3083, 2895, 1898, 1332, 921 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09-8.01 (m, 1H), 7.66-7.50 (m, 3H), 7.31-7.19 (m, 3H), 7.18-7.07 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.61-6.55 (m, 0.55H), 5.95-5.61 (2 brs, 1H), 5.19 (s, 2H), 2.37 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145., 145.0, 137.7, 136.2, 134.2,

134.0, 133.5, 131.7, 131.1, 130.9, 130.7, 130.6, 130.6, 130.4, 129.5, 129.2, 129.0, 128.2, 127.8, 126.2, 126.2, 125.5, 125.2, 55.6, 47.3, 19.0, 18.9. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1035.

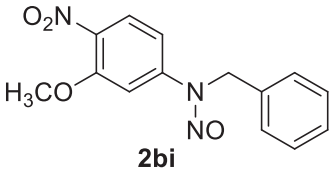
4.7.41 *N*-Nitroso *N*-benzyl-*N*-(2-methyl-4-nitroaniline) (2bh)



2bh

The compound was obtained as yellow viscous liquid. (Yield: 195 mg, 72%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.52. IR (neat): 3821, 2939, 1529, 1131, 811 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.34-7.26 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 2H), 5.27 (s, 2H), 2.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.8, 136.0, 133.3, 129.0, 127.9, 126.5, 126.5, 121.4, 115.9, 45.9, 21.2. HRMS: Calc. for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, Obser. 272.1034.

4.7.42 *N*-Nitroso *N*-benzyl-*N*-(2-methoxy-4-nitroaniline) (2bi)

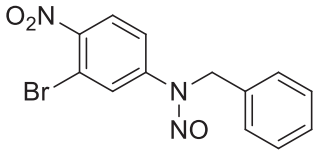


2bi

The compound was obtained as yellow viscous liquid. (Yield: 206 mg, 73%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.51. IR (neat): 3421, 1540, 1466, 1389, 744 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.43-7.24 (m, 4H), 7.08 (t, *J* = 9.9 Hz, 3H), 5.27 (s,

2H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 146.2, 137.2, 133.4, 129.1, 128.0, 127.4, 126.6, 109.0, 102.9, 56.6, 45.9. HRMS: Calc. for $C_{14}H_{14}N_3O_4$ $[M+H]^+$: 288.2787, Obser. 288.2785.

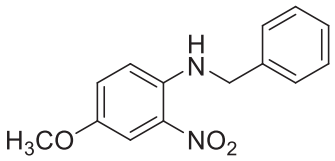
4.7.43 *N*-Nitroso *N*-benzyl-*N*-(2-bromo-4-nitroaniline) (2bj)



2bj

The compound was obtained as yellow viscous liquid. (Yield: 235 mg, 70%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 90:10, R_f = 0.49. IR (neat): 3421, 2985, 1561, 1099, 923 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.2 Hz, 2H), 7.66 (d, *J* = 9.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.12 (dd, *J* = 12.9, 4.9 Hz, 2H), 6.89 (dd, *J* = 7.7, 0.6 Hz, 1H), 5.16 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 146.0, 135.5, 131.3, 130.6, 129.6, 125.3, 125.1, 123.2, 118.0, 45.2. HRMS: Calc. for $C_{14}H_{14}BrN_3O_3$ $[M+H]^+$: 335.9984, Obser. 335.9982.

4.7.44 *N*-Benzyl-4-methoxy-2-nitroaniline (3aa)

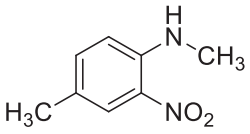


3aa

The compound was obtained as orange solid. M.p. 105 °C. (Yield: 219 mg, 85%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat) 3372, 2923, 2852, 1739, 1464, 1210, 1051, 782 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29

(brs, 1H), 7.57 (d, *J* = 3.0 Hz, 1H), 7.28 (dd, *J* = 12.2, 4.9 Hz, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 9.3, 3.0 Hz, 1H), 6.70 (d, *J* = 9.4 Hz, 1H), 4.47 (d, *J* = 5.7 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 141.1, 137.6, 131.2, 128.8, 127.6, 127.1, 126.9, 115.6, 107.1, 55.8, 47.2. HRMS: Calc. for $C_{14}H_{15}N_2O_3$ $[M+H]^+$: 259.1083, Obser. 259.1077.

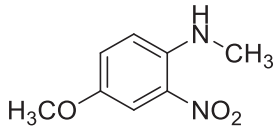
4.7.45 *N*,4-Dimethyl-2-nitroaniline (3ab)



3ab

The compound was obtained as an orange solid. M.p. 85-86 °C (Yield: 137 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.68. IR (neat): 3400, 1640, 1570, 789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (brs, 1H), 7.61 (d, *J* = 2.7 Hz, 1H), 7.18 (dd, *J* = 9.3, 2.8 Hz, 1H), 6.83 (d, *J* = 9.3 Hz, 1H), 3.80 (s, 3H), 3.03 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 142.3, 130.6, 127.4, 114.7, 106.7, 55.7, 29.8. HRMS: Calc. for $C_8H_{11}N_2O_2$ $[M+H]^+$: 167.0821, Obser. 167.0811.

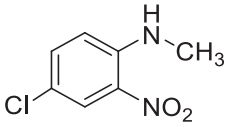
4.7.46 4-Methoxy-*N*-methyl-2-nitroaniline (3ac)



3ac

The title compound was obtained as an orange solid. M.p. 97-98 ºC (Yield: 163 mg, 90%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.64. IR (neat): 3452, 1633, 1566, 1013, 980 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.2 Hz, 1H), 8.03 (brs, 1H), 7.41 (dd, *J* = 9.2, 2.2 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 3.04 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 136.3, 131.5, 125.7, 119.9, 114.7, 29.8. HRMS: Calc. for $C_8H_{11}N_2O_3$ $[M+H]^+$: 183.0770, Obser. 183.0767.

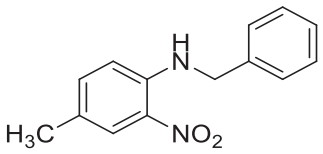
4.7.47 4-Chloro-*N*-methyl-2-nitroaniline (3ad)



3ad

The title compound was obtained as an orange solid. M.p.108-109 ºC (Yield: 154 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3455, 1656, 1557, 1003, 987 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.2 Hz, 1H), 8.03 (brs, 1H), 7.41 (dd, *J* = 9.2, 2.2 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 3.04 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 136.3, 131.5, 125.7, 119.9, 114.7, 29.8. HRMS: Calc. for $C_7H_6ClN_2O_2$ $[M+H]^+$: 187.0274, Obser. 187.0274.

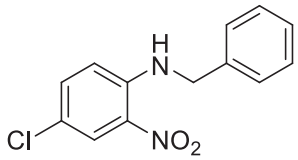
4.7.48 *N*-Benzyl-4-methyl-2-nitroaniline (3ae)



3ae

The title compound was obtained as yellow solid. M.p. 95 °C. (Yield: 203 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 2919, 2328, 1868, 1455, 1221, 867, 760 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (brs, 1H), 7.99 (s, 1H), 7.41-7.16 (m, 6H), 6.72 (d, *J* = 8.7 Hz, 1H), 4.53 (d, *J* = 5.4 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 137.8, 137.8, 132.1, 129.1, 127.8, 127.2, 126.3, 125.5, 114.4, 47.3, 20.1. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser. 243.1122.

4.7.49 *N*-Benzyl-4-chloro-2-nitroaniline (3af)

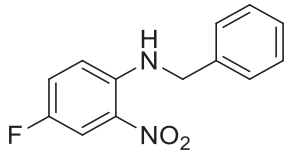


3af

The title compound was obtained as orange solid. M.p. 79 °C. (Yield: 217 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.69. IR (neat): 2917, 1732, 1495, 1350, 985, 886 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 8.12 (d, *J* = 2.5 Hz, 1H), 7.33-7.28 (m, 2H), 7.24 (dd, *J* = 10.8, 7.1 Hz, 4H), 6.70 (d, *J* = 9.2 Hz, 1H), 4.47 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.8, 136.3, 132.0, 129.0, 127.8, 126.9, 125.9, 120.5, 115.6, 47.1. HRMS: Calc. for $C_{13}H_{12}ClN_2O_2$ $[M+H]^+$: 263.0587, Obser.

263.0577.

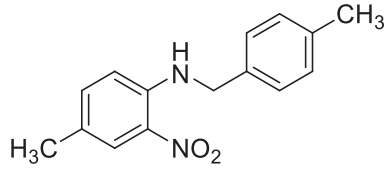
4.7.50 *N*-Benzyl-4-fluoro-2-nitroaniline (3ag)



3ag

The title compound was obtained as orange solid. M.p. 132-133 ºC. (Yield: 199 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.64. IR (neat): 3390, 2916, 2841, 1634, 1430, 1270, 870 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (brs, 1H), 7.89 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.38-7.27 (m, 5H), 7.19-7.13 (m, 1H), 6.77 (dd, *J* = 9.4, 4.5 Hz, 1H), 4.53 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 151.6, 142.3, 137.1, 128.9, 127.7, 126.9, 124.9 (d, J_{C-F} = 245.0 Hz), 115.5 (d, J_{C-F} = 25.0 Hz), 112.1 (d, J_{C-F} = 105.0 Hz), 47.3. HRMS: Calc. for $C_{13}H_{12}FN_2O_2$ $[M+H]^+$: 247.0883 , Obser. 247.0860.

4.7.51 4-Methyl-*N*-(4-methylbenzyl)-2-nitroaniline (3ah)

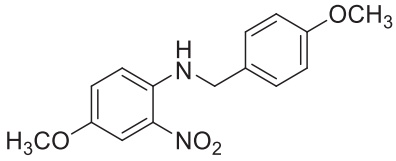


3ah

The title compound was obtained as dark yellow solid. M.p. 110-111 ºC. (Yield: 227 mg, 89%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.69. IR (neat): 3390, 2919, 2851, 1732, 1562, 1455, 921 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (brs, 1H), 7.91 (s, 1H), 7.18-7.12 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 1H), 4.41 (d,

J = 5.6 Hz, 2H), 2.26 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 137.6, 137.2, 134.4, 131.7, 129.5, 126.9, 126.0, 125.1, 114.1, 46.8, 21.0, 19.9. HRMS: Calc. for $C_{15}H_{17}N_2O_2$ $[M+H]^+$: 257.1290, Obser. 257.1289.

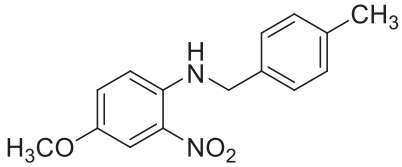
4.7.52 4-Methoxy-*N*-(4-methoxybenzyl)-2-nitroaniline (3ai)



3ai

The title compound was obtained as dark yellow solid. M.p. 107 °C. (Yield: 250 mg, 87%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 2921, 1571, 1513, 1246, 1034 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (brs, 1H), 7.57 (d, *J* = 2.8 Hz, 1H), 7.19 (t, *J* = 4.0 Hz, 4H), 7.03 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9.3 Hz, 1H), 4.40 (d, *J* = 5.5 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 149.8, 141.1, 131.37, 129.5, 128.3, 127.1, 115.6, 114.3, 107.3, 55.8, 55.3, 46.8. HRMS: Calc. for $C_{15}H_{17}N_2O_4$ $[M+H]^+$: 289.1188, Obser. 289.1189.

4.7.53 4-Methoxy-*N*-(4-methylbenzyl)-2-nitroaniline (3aj)

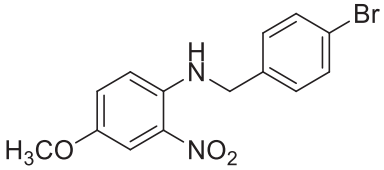


3aj

The title compound was obtained as dark reddish yellow solid. M.p. 143-144 °C. (Yield: 239 mg, 88%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.68. IR (neat)

3378, 2922, 2852, 1730, 1482, 1227, 1032, 932. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 7.63 (d, *J* = 2.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.78 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 5.6 Hz, 2H), 3.78 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 141.2, 137.3, 134.5, 131.2, 129.5, 127.1, 126.9, 115.6, 107.1, 55.8, 47.0, 21.0. HRMS: Calc. for $C_{15}H_{17}N_2O_3$ $[M+H]^+$: 273.1239, Obser. 273.1242.

4.7.54 *N*-(4-Bromobenzyl)-4-methoxy-2-nitroaniline (3ak)

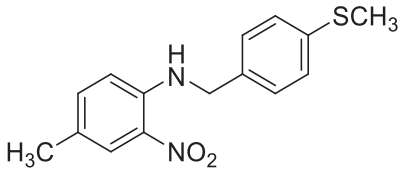


3ak

The title compound was obtained as dark yellow solid. M.p. 133-134 °C. (Yield: 283 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.64. IR (neat): 3326, 2916, 1455, 1101, 980 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.51 (brs, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.32-7.23 (m, 3H), 7.12 (dd, *J* = 9.3, 2.6 Hz, 1H), 6.73 (d, *J* = 9.3 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 140.6, 140.1, 131.5, 130.7, 130.4, 129.9, 127.0, 125.3, 123.0, 115.4, 107.4, 55.8, 46.6. HRMS: Calc. for $C_{14}H_{14}BrN_2O_3$

$[M+H]^+$: 337.0188, Obser. 337.0181.

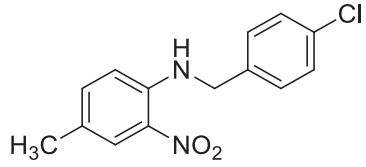
4.7.55 *N*-(4-Thiomethylbenzyl)-4-(methyl)-2-nitroaniline (3al)



3al

The title compound was obtained as yellow solid. M.p.79-80 °C. (Yield: 253 mg, 88%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.68. IR (neat): 2292, 1632, 1493, 1015, 952 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (brs, 1H), 8.01 (d, *J* = 1.1 Hz, 1H), 7.30-7.21 (m, 5H), 6.72 (d, *J* = 8.7 Hz, 1H), 4.51 (d, *J* = 5.7 Hz, 2H), 2.50 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 137.7, 137.6, 134.3, 127.5, 126.9, 126.0, 125.3, 114.1, 46.6, 19.9, 15.8. HRMS: Calc. for $C_{15}H_{16}N_2NaO_2S$ $[M+Na]^+$: 311. 0830, Obser. 311.0854.

4.7.56 *N*-(4-Chlorobenzyl)-4-methyl-2-nitroaniline (3am)

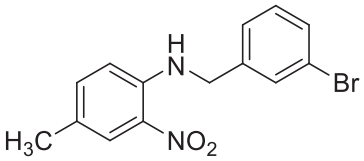


3am

The title compound was obtained as orange solid. M.p. 88-89 °C. (Yield: 223 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3380, 2919, 2850, 1731, 1494, 1287, 1013, 984 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (brs, 1H), 7.57 (s, 1H), 7.22 (dd, *J* = 28.0, 7.6 Hz, 4H), 7.01 (d, *J* = 9.3 Hz, 1H), 6.64 (d, *J* = 9.3 Hz, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 149.9, 140.7, 136.1, 133.3, 131.4, 129.0, 128.2, 127.0, 115.4, 107.2, 55.8, 46.5. HRMS: Calc. for $C_{14}H_{14}ClN_2O_2$ $[M+H]^+$: 277.0744, Obser. 277.0735.

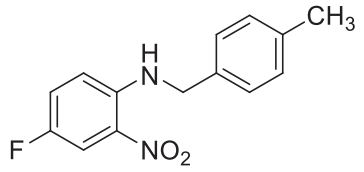
4.7.57 *N*-(3-Bromobenzyl)-4-methyl-2-nitroaniline (3an)



3an

The title compound was obtained as dark yellow solid. M.p. 82-83 ºC. (Yield: 265 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f= 0.69. IR (neat): 3396, 2922, 1715, 1433, 1033, 856 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (brs, 1H), 7.93 (d, *J* = 14.8 Hz, 1H), 7.39-7.32 (m, 2H), 7.19-7.12 (m, 3H), 6.57 (d, *J* = 8.7 Hz, 1H), 4.43 (d, *J* = 5.8 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 140.1, 137.6, 132.0, 130.6, 130.4, 129.8, 126.1, 125.6, 125.3, 122.9, 114.0, 46.4, 19.9. HRMS: Calc. for $C_{14}H_{14}BrN_2O_2$ $[M+H]^+$: 321.0239, Obser. 321.0233.

4.7.58 4-Fluoro-*N*-(4-methylbenzyl)-2-nitroaniline (3ao)

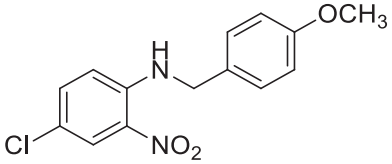


3ao

The title compound was obtained as orange solid. M.p. 143-144 °C. (Yield: 208 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.64. IR (neat): 2921, 1520, 1258, 1014, 793 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (brs, 1H), 7.83 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.18-7.12 (m,

3H), 7.10 (d, J = 8.3 Hz, 3H), 6.72 (dd, J = 9.4, 4.5 Hz, 1H), 4.42 (d, J = 5.6 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 151.6, 142.3, 137.5, 134.0, 129.6, 126.9, 124.9 (d, $J_{C\text{-}F}$ = 95.0 Hz), 115.5 (d, $J_{C\text{-}F}$ = 25.0 Hz), 112.1, 111.9, 47.1, 21.0. HRMS: Calc. for $C_{14}H_{14}FN_2O_2$ $[M+H]^+$: 261.1039, Obser. 261.1037.

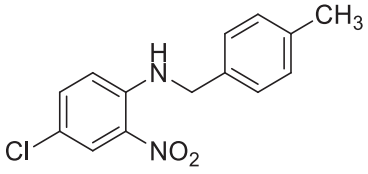
4.7.59 4-Chloro-*N*-(4-methoxybenzyl)-2-nitroaniline (3ap)



3ap

The title compound was obtained as orange solid. M.p. 116-117 °C. (Yield: 242 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 2917, 2849, 1586, 1516, 1403, 1222, 1034 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (brs, 1H), 8.12 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 9.1, 1.9 Hz, 1H), 7.18 (d, J = 8.5 Hz, 3H), 6.83 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 9.2 Hz, 1H), 4.39 (d, J = 5.5 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 143.8, 136.2, 132.0, 128.7, 128.3, 125.9, 120.4, 115.6, 114.4, 55.3, 46.7. HRMS: Calc. for $C_{14}H_{14}ClN_2O_3$ $[M+H]^+$: 293.0693, Obser. 293.0688.

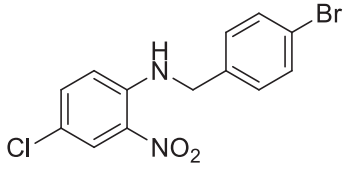
4.7.60 4-Chloro-*N*-(4-methylbenzyl)-2-nitroaniline (3aq)



3aq

The title compound was obtained as orange solid. M.p. 143-145 °C. (Yield: 220 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.70. IR (neat): 3367, 2916, 2848, 1637, 1466, 1030, 929 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (brs, 1H), 8.26 (d, *J* = 2.4 Hz, 1H), 7.36 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.12 (dd, *J* = 20.2, 8.1 Hz, 4H), 6.66 (d, *J* = 9.2 Hz, 1H), 4.42 (d, *J* = 5.6 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.8, 137.6, 133.7, 132.5, 129.6, 128.9, 126.9, 115.9, 106.7, 46.9, 21.0. HRMS: Calc. for $C_{14}H_{14}ClN_2O_2$ $[M+H]^+$: 277.0744, Obser. 277.0739.

4.7.61 *N*-(4-Bromobenzyl)-4-chloro-2-nitroaniline (3ar)

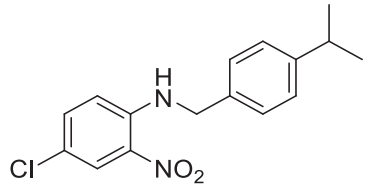


3ar

The title compound was obtained as orange solid. M.p. 140-141 °C (Yield: 281 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3383, 2918, 2849, 1714, 1455, 1258, 983 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (brs, 1H), 8.44 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 1H), 4.75 (d, *J* = 5.7 Hz,

2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 136.3, 135.9, 132.2, 132.1, 128.5, 126.0, 121.7, 120.8, 115.5, 46.5. HRMS: Calc. for $C_{13}H_{11}BrClN_2O_2$ $[M+H]^+$: 340.9692, Obser. 340.9687.

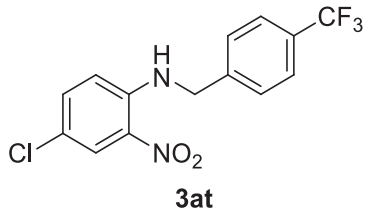
4.7.62 4-Chloro-*N*-(4-isopropylbenzyl)-2-nitroaniline (3as)



3as

The title compound was obtained as yellow-orange solid. M.p. 106 °C (Yield: 258 mg, 85%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 2869, 2360, 1683, 1374, 967 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (brs, 1H), 8.08 (d, *J* = 2.5 Hz, 1H), 7.24-7.19 (m, 1H), 7.18-7.11 (m, 4H), 6.71 (d, *J* = 9.2 Hz, 1H), 4.41 (t, *J* = 9.7 Hz, 2H), 2.86-2.78 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 143.8, 136.2, 134.0, 127.8, 127.0, 127.0, 126.3, 125.8, 120.3, 115.6, 46.9, 33.7, 23.9. HRMS: Calc. for $C_{16}H_{17}ClN_2NaO_2$ $[M+H]^+$: 305.1057, Obser. 305.1046.

4.7.63 4-Chloro-2-nitro-*N*-(4-(trifluoromethyl)benzyl)aniline (3at)

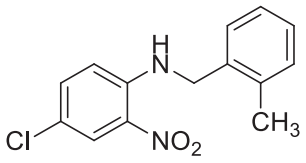


3at

The title compound was obtained as orange solid. M.p. 77-78 °C (Yield: 273 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 3387, 2924,

1615, 1293, 1065, 988 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 8.12 (d, *J* = 2.3 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 9.1, 2.3 Hz, 1H), 6.61 (d, *J* = 9.2 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 141.0, 136.4, 132.3, 130.7 (q, J_{C-F} = 100.0 Hz), 127.3, 126.2 (q, J_{C-F} = 30.0 Hz), 125.2, 123.0, 121.2, 115.6, 46.8. HRMS: Calc. for $C_{14}H_{11}ClF_3N_2O_2$ $[M+H]^+$: 331.0461, Obser. 331.0455.

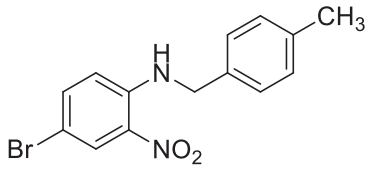
4.7.64 4-Chloro-*N*-(2-methylbenzyl)-2-nitroaniline (3au)



3au

The title compound was obtained as yellowish orange solid. M.p. 107-108 °C. (Yield: 240 mg, 87%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3386, 3103, 3064, 2849, 1915, 1495, 972 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (brs, 1H), 8.12 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.19-7.13 (m, 3H), 7.11 (dd, *J* = 7.3, 3.1 Hz, 1H), 6.70 (d, *J* = 9.2 Hz, 1H), 4.39 (d, *J* = 5.4 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.3, 135.9, 134.3, 131.9, 130.7, 128.0, 127.4, 126.4, 125.9, 120.4, 115.5, 45.4, 18.9. HRMS: Calc. for $C_{14}H_{14}ClN_2O_2$ $[M+H]^+$: 277.0744, Obser. 277.0734.

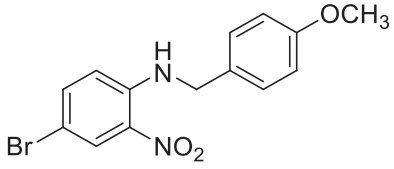
4.7.65 4-Bromo-*N*-(4-methylbenzyl)-2-nitroaniline (3av)



3av

The title compound was obtained as yellow solid. M.p. 101-102 °C. (Yield: 270 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.64. IR (neat): 3378, 3094, 2910, 1618, 1458, 1055, 882 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (brs, 1H), 8.25 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.12 (dd, *J* = 20.3, 8.0 Hz, 4H), 6.65 (d, *J* = 9.2 Hz, 1H), 4.41 (d, *J* = 5.6 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.8, 137.3, 133.7, 132.5, 129.6, 128.8, 126.9, 115.9, 106.7, 46.9, 21.0. HRMS: Calc. for $C_{14}H_{14}BrN_2O_2$ $[M+H]^+$: 321.0239, Obser. 321.0237.

4.7.66 4-Bromo-*N*-(4-methoxybenzyl)-2-nitroaniline (3aw)

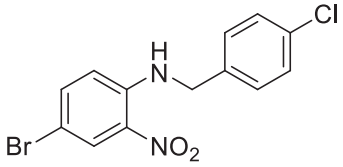


3aw

The title compound was obtained as orange solid. M.p. 122-123 °C. (Yield: 283 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3379, 3095, 2916, 2850, 1620, 1462, 1055, 882 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (brs, 1H), 8.25 (s, 1H), 7.37 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.21-7.11 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 9.2 Hz, 1H), 4.38 (d, *J* = 5.5 Hz, 2H),

3.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 144.0, 138.8, 132.4, 128.8, 128.6, 128.3, 115.9, 114.4, 106.7, 55.3, 46.7. HRMS: Calc. for $C_{14}H_{14}BrN_2O_3$ $[M+H]^+$: 337.0188, Obser. 337.0187.

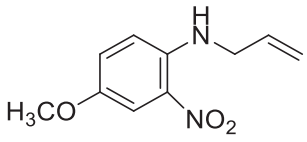
4.7.67 4-Bromo-*N*-(4-chlorobenzyl)-2-nitroaniline (3ax)



3ax

The title compound was obtained as orange solid. M.p. 119-120 °C. (Yield: 283 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 95:5, R_f = 0.66. IR (neat): 3384, 2920, 2850, 1713, 1259, 1069, 889 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (brs, 1H), 8.40 (s, 1H), 7.49 (d, *J* = 9.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.33-7.31 (m, 3H), 6.72 (d, *J* = 9.1 Hz, 1H), 4.57 (d, *J* = 5.7 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 138.9, 135.3, 133.7, 132.7, 129.2, 129.0, 128.2, 115.8, 107.2, 46.5. HRMS: Calc. for $C_{13}H_{11}BrClN_2O_2$ $[M+H]^+$: 340.9692, Obser. 340.9690.

4.7.68 *N*-Allyl-4-methoxy-2-nitroaniline (3ay)

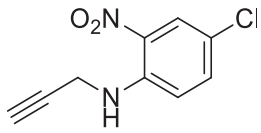


3ay

The title compound was obtained as yellow solid. M.p. 110-111 °C (Yield: 174 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.69. IR (neat): 3381, 2922, 1746, 1505, 1032, 967 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ

8.03 (brs, 1H), 7.54 (d, *J* = 3.0 Hz, 1H), 7.06 (dd, *J* = 9.3, 3.0 Hz, 1H), 6.73 (d, *J* = 9.4 Hz, 1H), 5.87 (ddd, *J* = 22.2, 10.2, 5.0 Hz, 1H), 5.19 (ddd, *J* = 13.8, 11.5, 1.1 Hz, 2H), 3.95–3.83 (m, 2H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 141.2, 133.5, 131.0, 127.1, 116.9, 115.5, 107.0, 55.8, 45.4. HRMS: Calc. for $C_{10}H_{13}N_2O_3$ $[M+H]^+$: 209.0926, Obser. 209.0934.

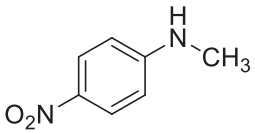
4.7.69 4-Chloro-2-nitro-N-(prop-2-ynyl)aniline (3az)



3az

The title compound was obtained as orange solid. M.p. 155-156 °C. (Yield: 174 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3381, 2922, 2853, 1746, 1455, 1032, 967 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.6 Hz, 1H), 8.01 (brs, 1H), 7.38 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.87 (dd, *J* = 9.1, 2.7 Hz, 1H), 4.05 (dd, *J* = 5.5, 2.6 Hz, 2H), 2.24 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 136.2, 132.6, 121.3, 125.9, 115.4, 78.4, 72.6, 32.6. HRMS: Calc. for $C_9H_8ClN_2O_2$ $[M+H]^+$: 211.0274, Obser. 211.0265.

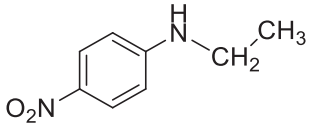
4.7.70 *N*-Methyl-4-nitroaniline (3ba)



3ba

The title compound was obtained as yellow solid. M.p. 149-150°C (Yield: 124 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 3430, 1946, 1450, 1001, 957 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 4.70 (brs, 1H), 2.95 (d, *J* = 4.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 137.8, 126.3, 110.6, 30.0. HRMS: Calc. for $C_7H_9N_2O_2$ $[M+H]^+$: 153.0664, Obser.153.0663.

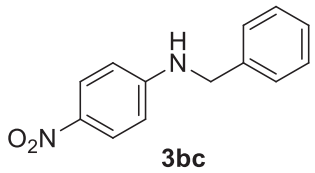
4.7.71 *N*-Ethyl-4-nitroaniline (3bb)



3bb

The title compound was obtained as yellow solid. M.p. 95-96 ºC, (Yield: 139 mg, 84%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3450, 1933, 1560, 1131, 789 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 9.1 Hz, 2H), 4.55 (brs, 1H), 3.32-3.23 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 137.6, 126.4, 110.8, 37.9, 14.3. HRMS: Calc. for $C_7H_9N_2O_2$ $[M+H]^+$: 153.0664, Obser. 153.0662.

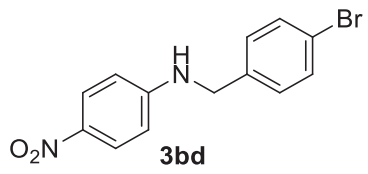
4.7.72 *N*-Benzyl-4-nitroaniline (3bc)



3bc

The title compound was obtained as yellow solid. M.p. 147 °C. (Yield: 189 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.69. IR (neat): 3351, 2921, 2851, 2391, 1906, 1494, 1173, 994 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.05-7.95 (m, 2H), 7.38-7.20 (m, 5H), 6.56-6.44 (m, 2H), 4.81 (brs, 1H), 4.36 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 137.3, 128.9, 127.8, 127.3, 126.3, 111.3, 47.6. HRMS: Calc. for $C_{13}H_{13}N_2O_2$ $[M+H]^+$: 229.0977, Obser. 229.0983.

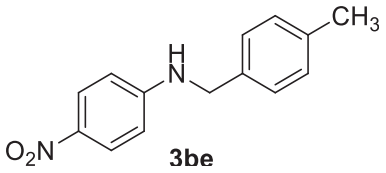
4.7.73 *N*-(4-Bromobenzyl)-4-nitroaniline (3bd)



3bd

The title compound was obtained as yellow solid. M.p.142 °C. (Yield: 247 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.65. IR (neat): 3350, 1915, 1593, 1276, 1102, 819 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 7.96 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 9.2 Hz, 2H), 4.39 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.4, 138.3, 136.4, 131.6, 129.6, 126.4, 120.3, 45.3. HRMS: Calc. for $C_{13}H_{12}BrN_2O_2$ $[M+H]^+$: 307.0082, Obser. 307.0080.

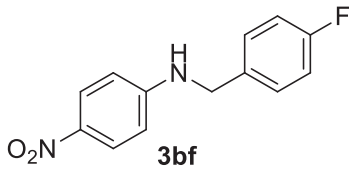
4.7.74 *N*-(4-Methylbenzyl)-4-nitroaniline (3be)



3be

The title compound was obtained as yellow solid. M.p. 178-179 °C (Yield: 193 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3499, 3386, 2919, 2852, 1986, 1454, 1062, 989 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.2 Hz, 2H), 7.19 (s, 2H), 7.17 (s, 2H), 6.54 (d, *J* = 9.2 Hz, 2H), 4.79 (brs, 1H), 4.36 (d, *J* = 5.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 138.3, 137.6, 134.2, 129.6, 127.3, 126.3, 111.2, 47.4, 21.0. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser. 243.1143.

4.7.75 *N*-(4-Fluorobenzyl)-4-nitroaniline (3bf)

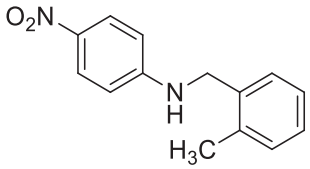


3bf

The title compound was obtained as yellow solid. M.p. 143-144 °C (Yield: 194 mg, 79%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.64. IR (neat): 3499, 3386, 2919, 2852, 1906, 1454, 860 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 7.98 (d, *J* = 9.3 Hz, 1H), 7.41-7.36 (m, 1H), 7.17 (t, *J* = 8.9 Hz, 1H), 6.67 (d, *J* = 9.2 Hz, 1H), 4.41 (d, *J* = 4.1 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.7, 160.8, 154.7 (d, *J* = 50.0 Hz), 136.5, 135.1 (d, *J* = 5.0 Hz), 129.7, 129.6,

128.8, 128.7, 126.6, 115.8 (d, J_{C-F} = 85.0 Hz), 115.2 (d, J_{C-F} = 85.0 Hz), 111.5, 45.5, 45.4. HRMS: Calc. for $C_{13}H_{12}FN_2O_2$ $[M+H]^+$: 247.0883, Obser.247.0903.

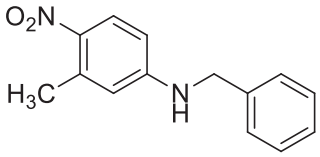
4.7.76 *N*-(2-Methylbenzyl)-2-nitroaniline (3bg)



3bg

The title compound was obtained as yellow solid. M.p.197-198 °C. (Yield: 198 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.68. IR (neat): 3379, 2920, 2850, 1731, 1433, 775 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 9.1 Hz, 2H), 7.20-7.08 (m, 4H), 6.50 (d, J = 9.2 Hz, 2H), 4.58 (brs, 1H), 4.30 (d, J = 5.2 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 138.3, 136.2, 134.9, 130.7, 128.1, 127.9, 126.4, 125.2, 118.2, 111.1, 45.8, 18.9. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser. 243.1132.

4.7.77 *N*-Benzyl-3-methyl-4-nitroaniline (3bh)

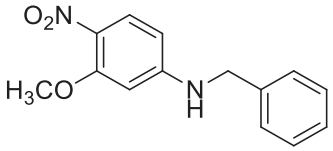


3bh

The title compound was obtained as yellow solid. M.p. 77-78 °C. (Yield: 198 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f= 0.65. IR (neat): 3356, 2993, 1745, 1452, 980 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.0 Hz, 1H), 7.43-7.32 (m, 5H), 6.51-6.41 (m, 2H), 4.77

(brs, 1H), 4.43 (d, *J* = 5.4 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 138.7, 137.8, 137.5, 128.8, 128.3, 127.7, 127.3, 114.6, 109.7, 47.5, 22.4. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser. 243.1130.

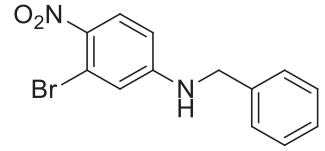
4.7.78 *N*-Benzyl-3-methoxy-4-nitroaniline (3bi)



3bi

The title compound was obtained as yellow solid. M.p. 120.5-123.4 °C. (Yield: 198 mg, 79%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 3543, 2820, 1730, 1443, 789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.1 Hz, 1H), 7.42-7.29 (m, 5H), 6.19 (d, *J* = 9.1 Hz, 1H), 6.11 (s, 1H), 5.09 (brs, 1H), 4.44 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 153.9, 137.3, 129.3, 128.8, 127.7, 127.2, 104.3, 95.1, 56.0, 47.5. HRMS: Calc. for $C_{14}H_{15}N_2O_3$ $[M+H]^+$: 259.1083, Obser. 259.1082.

4.7.79 *N*-Benzyl-3-bromo-4-nitroaniline (3bj)

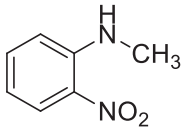


3bj

The title compound was obtained as yellow solid. M.p. 67-69 °C. (Yield: 198 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.65. IR (neat): 3450, 2879, 1729, 1430,789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.1 Hz, 1H), 7.40 (s, 2H), 7.35 (t, *J* = 6.0 Hz, 3H), 6.89 (d, *J*

= 2.3 Hz, 1H), 6.54 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.89 (brs, 1H), 4.42 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 138.1, 136.8, 128.9, 128.9, 127.9, 127.3, 118.0, 117.3, 110.7, 47.5. HRMS: Calc. for $C_{13}H_{12}BrN_2O_2$ $[M+H]^+$: 306.0082, Obser. 306.0080.

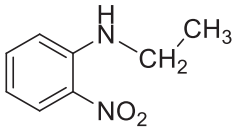
4.7.80 *N*-Methyl-2-nitroaniline (3ba')



3ba'

The title compound was obtained as yellow solid. M.p. 38 °C (Yield: 123 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3447, 1730, 1230, 1084, 789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 1H), 8.06 (brs, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 3.04 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 136.2, 131.8, 126.7, 115.1, 113.3, 29.6. HRMS: Calc. for $C_7H_9N_2O_2$ $[M+H]^+$: 153.0664, Obser. 153.0663.

4.7.81 *N*-Ethyl-4-nitroaniline (3bb')

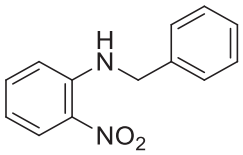


3bb'

The title compound was obtained as red liquid. (Yield: 132 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.65. IR (neat): 3457, 2920, 1640, 1322, 778 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 1H),

8.00 (brs, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.65 (t, *J* = 7.7 Hz, 1H), 3.42-3.31 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 136.1, 131.6, 126.8, 115.0, 113.6, 37.6, 14.3. HRMS: Calc. for $C_7H_9N_2O_2$ $[M+H]^+$: 167.0821, Obser. 167.0811.

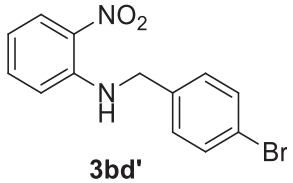
4.7.82 *N*-Benzyl-2-nitroaniline (3bc')



3bc'

The title compound was obtained as yellow solid. M.p. 73-74 ºC (Yield: 182 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.64. IR (neat): 3395, 1614, 1506, 1569, 946 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.31-7.25 (m, 5H), 7.23-7.21 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.58 (t, *J* = 8.3 Hz, 1H), 4.46 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 137.3, 136.1, 132.2, 128.8, 127.6, 126.9, 126.7, 115.6, 114.1, 47.0. HRMS: Calc. for $C_{13}H_{13}N_2O_2$ $[M+H]^+$: 229.0977, Obser. 229.0985.

4.7.83 *N*-(4-Bromobenzyl)-2-nitroaniline (3bd')

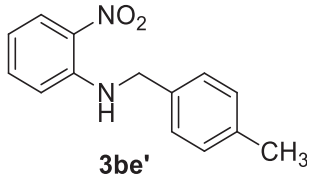


3bd'

The title compound was obtained as yellow solid. M.p. 113-114 °C (Yield: 230 mg, 75%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3378, 1866, 1894,

1496, 1066, 827 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (brs, 1H), 8.10 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 1H), 6.59 (t, *J* = 8.3 Hz, 1H), 4.42 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 136.4, 136.1, 132.3, 131.9, 128.6, 126.8, 121.4, 115.9, 114.0, 46.4. HRMS: Calc. for $C_{13}H_{12}BrN_2O_2$ $[M+H]^+$: 307.0082, Obser. 307.0080.

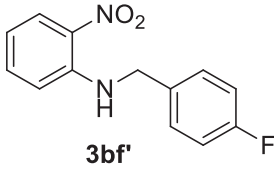
4.7.84 *N*-(4-Methylbenzyl)-2-nitroaniline (3be')



3be'

The title compound was obtained as yellow solid. M.p. 65 °C. (Yield: 188 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.67. IR (neat): 3386, 2920, 2853, 1906, 1434, 1228,986 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (brs, 1H), 8.22 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.41 (t, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.23-7.17 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.68 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 4.53 (d, *J* = 5.7 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 137.3, 136.1, 134.2, 132.1, 129.5, 126.9, 126.7, 115.5, 114.1, 46.8, 21.0. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser. 243.1138.

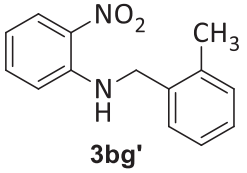
4.7.85 *N*-(4-Fluorobenzyl)-2-nitroaniline (3bf')



3bf'

The title compound was obtained as yellow solid. M.p. 76-77 °C (Yield: 177mg, 72%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.64. IR (neat): 3390, 2920, 1575, 1448, 1023, 991 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (brs, 1H), 7.82 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.33-7.19 (m, 5H), 7.13-7.04 (m, 1H), 6.70 (dd, *J* = 9.4, 4.5 Hz, 1H), 4.46 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 151.6, 142.3, 137.1, 128.9, 127.7, 126.9, 124.9, 124.7, 115.5 (d, J_{C-F} = 30.0 Hz), 112.1 (d, J_{C-F} = 105.0 Hz), 47.3. HRMS: Calc. for $C_{13}H_{12}FN_2O_2$ $[M+H]^+$: 247.0883, Obser. 247.0904.

4.7.86 *N*-(2-Methylbenzyl)-2-nitroaniline (3bg')

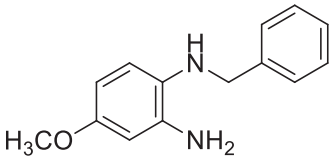


3bg'

The title compound was prepared using the general procedure. The title compound was obtained as yellow solid. M.p. 103-104 °C (Yield: 179mg, 74%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.68. IR (neat): 3379, 2919, 2850, 1713, 1279, 980, 856 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (brs, 1H), 8.09 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.30 (t, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H),

7.15–7.10 (m, 2H), 7.10-7.06 (m, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.57 (t, *J* = 8.3 Hz, 1H), 4.37 (d, *J* = 5.4 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 136.1, 135.9, 134.8, 132.1, 130.6, 127.8, 127.5, 126.8, 126.3, 115.5, 114.0, 45.2, 18.9. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1134, Obser.243.1132.

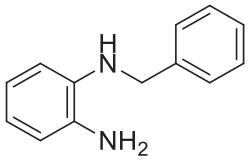
4.7.87 *N*^{1}-Benzyl-4-methoxybenzene-1,2-diamine (4aa)



4aa

The title compound was obtained as white solid. M.p. 53-54 °C (Yield: 200 mg, 88%) The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.38. IR (neat): 3224, 3056, 3035, 1989, 1345, 889 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.37 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 6.36 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.27 (s, 2H), 3.76 (s, 3H), 3.46 (brs, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 139.6, 137.16, 130.6, 128.5, 127.8, 127.1, 114.5, 103.7, 103.1, 55.4, 49.6. HRMS: Calc. for $C_{14}H_{17}N_2O$ $[M+H]^+$: 229.1341, Obser. 229.1340.

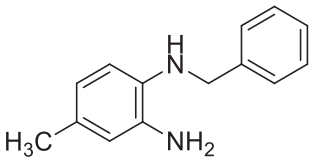
4.7.88 N^1-Benzylbenzene-1,2-diamine (4ab)



4ab

The title compound was obtained as white solid. M.p. 50 °C (Yield: 168 mg, 85%). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 85:15, R_f = 0.39. IR (neat): 3217, 3061, 3029, 1954, 1462, 873 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.86 (td, *J* = 7.7, 1.8 Hz, 1H), 6.81-6.71 (m, 3H), 4.36 (s, 2H), 3.49 (brs, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 137.6, 134.1, 128.5, 127.7, 127.2, 120.7, 118.7, 116.5, 111.9, 48.6. HRMS: Calc. for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1235, Obser. 199.1230.

4.7.89 N^1-Benzyl-4-methylbenzene-1,2-diamine (4ac)

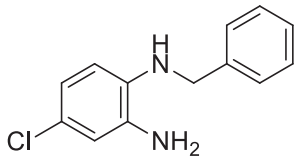


4ac

The title compound was obtained as white solid. M.p. 57-58 °C, (Yield: 175 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.40. IR (neat): 3224, 3056, 3033, 1972, 1450, 878 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.35-7.29 (m, 1H), 6.62 (d, *J* = 10.2 Hz, 3H), 4.33 (s, 2H), 3.28 (brs, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 134.9, 134.5, 128.5, 127.7, 127.1, 126.1, 120.6, 117.2,

112.5, 48.9, 20.5. HRMS: Calc. for $C_{14}H_{17}N_2$ $[M+H]^+$: 213.1392, Obser. 213.1390.

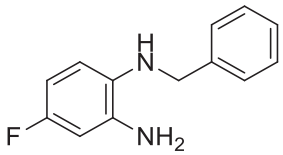
4.7.90 N^1-Benzyl-4-chlorobenzene-1,2-diamine (4ad)



4ad

The title compound was obtained as off-white solid. M.p. 163 °C (Yield: 190 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3254, 3067, 1982, 1475, 875 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 60.2, 7.7 Hz, 4H), 6.74 (d, *J* = 9.7 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.31 (brs, 2H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 135.6, 135.5, 130.0, 129.7, 129.4, 129.3, 129.2, 127.6, 126.4, 125.5, 125.5, 125.5, 124.0, 120.0,119. 116.0, 112.8, 48.6. HRMS: Calc. for $C_{13}H_{14}ClN_2$ $[M+H]^+$: 233.0846, Obser. 233.0843.

4.7.91 N^1-Benzyl-4-fluorobenzene-1,2-diamine (4ae)

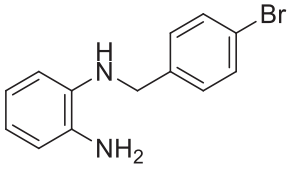


4ae

The title compound was obtained as off-white solid. M.p. 72 °C (Yield: 179 mg, 79%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3350, 3256, 1878, 1375, 950 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.37 (m, 4H), 7.33 (t, *J* = 7.0 Hz, 1H), 6.65-6.60 (m, 1H), 6.53-6.46 (m, 2H), 4.29 (s, 2H), 3.41 (brs, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 158.1, 156.2, 139.2, 136.7 (d, J_{C-F} = 40.0 Hz), 132.8, 128.5, 127.7, 127.3, 113.6 (d, J_{C-F} = 40.0 Hz, 1H), 105.3 (d, J_{C-F} = 85.0 Hz), 103.3 (d, J_{C-F} = 100.0 Hz), 49.2. HRMS: Calc. for $C_{13}H_{14}FN_2$ $[M+H]^+$: 217.1141, Obser. 217.1140.

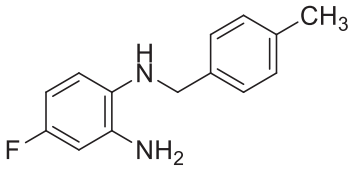
4.7.92 N^1-(4-Bromobenzyl)benzene-1,2-diamine (4af)



4af

The title compound was obtained as dark brown solid. M.p. 85 °C (Yield: 229 mg, 83%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.43. IR (neat): 3375, 3334, 1978, 1390,989 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 9.6 Hz, 3H), 6.77 (dq, J = 16.0, 8.7 Hz, 3H), 6.63 (d, J = 7.8 Hz, 1H), 4.31 (s, 2H), 3.21 (brs, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 137.3, 134.1, 131.6, 129.3, 120.9, 120.7, 119.0, 116.7, 112.0, 47.9. HRMS: Calc. for $C_{13}H_{14}BrN_2$ $[M+H]^+$: 277.0340, Obser. 277.0339.

4.7.93 4-Fluoro-N^1-(4-Methylbenzyl)benzene-1,2-diamine (4ag)

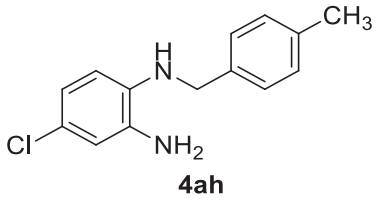


4ag

The title compound was obtained as off-white solid. M.p. 101-103 °C (Yield: 184 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3340, 3356,

1996, 1382, 957 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.67–6.61 (m, 1H), 6.52 (dd, *J* = 13.2, 5.6 Hz, 2H), 4.25 (s, 2H), 3.43 (brs, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 156.1, 136.9, 136.6, 136.5, 136.1, 132.8, 132.8, 129.2, 127.7, 113.4, 113.3, 105.2, 105.1, 103.2, 103.0, 48.9, 21.0. HRMS: Calc. for $C_{14}H_{16}FN_2$ $[M+H]^+$: 231.1298, Obser. 231.1297.

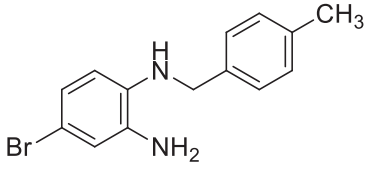
4.7.94 4-Chloro-*N*^{1}-(4-Methylbenzyl)benzene-1,2-diamine (4ah)



4ah

The title compound was obtained as white solid. M.p. 97-98 °C (Yield: 201 mg, 82%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.44. IR (neat): 3457, 3234, 1906, 1453, 980 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.4 Hz, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.79-6.71 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 4.26 (s, 2H), 3.24 (brs, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 135.6, 129.3, 127.7, 123.7, 119.9, 116.1, 113.1, 48.5, 21.1. HRMS: Calc. for $C_{14}H_{16}ClN_2$ $[M+H]^+$: 247.1002, Obser. 247.1000.

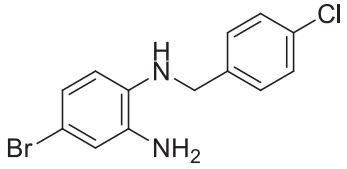
4.7.95 4-Bromo-N^1-(4-methylbenzyl)benzene-1,2-diamine (4ai)



4ai

The title compound was obtained as dark brown solid. M.p. 110-111 °C (Yield: 247 mg, 85%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.42. IR (neat): 3357, 3278, 1978, 1567, 972 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 5.8 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.93–6.89 (m, 1H), 6.86 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 4.26 (s, 2H), 3.38 (brs, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 136.5, 135.7, 135.7, 129.2, 127.6, 122.9, 118.7, 113.1, 110.5, 48.2, 21.0. HRMS: Calc. for $C_{14}H_{16}BrN_2$ $[M+H]^+$: 291.0497, Obser. 291.0492.

4.7.96 4-Bromo-N^1-(4-chlorobenzyl)benzene-1,2-diamine (4aj)

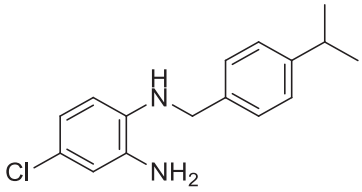


4aj

The title compound was obtained as off-white solid. M.p. 149-150 °C (Yield: 251 mg, 81%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.40. IR (neat): 3387, 3015, 1345, 1037, 1002, 972 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.34-7.15 (m, 2H), 6.74 (d, *J* = 5.6 Hz, 2H), 6.51 (d, *J* = 9.0 Hz, 1H), 4.27 (s, 2H), 3.23 (brs, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 135.5, 131.7, 129.2, 123.9, 121.1, 120.0, 116.2, 113.0, 47.9. HRMS:

Calc. for $C_{14}H_{13}BrClN_2$ $[M+H]^+$: 310.9951, Obser. 310.9949.

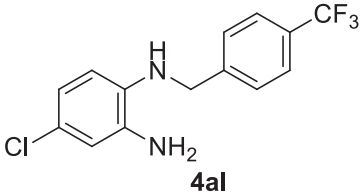
4.7.97 4-Chloro-N^1-(4-isopropylbenzyl)benzene-1,2-diamine (4ak)



4ak

The title compound was obtained as dark brown liquid. (Yield: 219 mg, 80 %). The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc 85:15, R_f= 0.41. IR (neat): 3349, 3256, 1789, 1354, 897 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.73 (d, *J* = 2.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 4.26 (s, 2H), 3.62 (brs, 3H), 4.06-3.08 (m, 1H), 1.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 136.0, 135.7, 135.7, 127.8, 126.6, 123.7, 119.9, 116.0, 113.1, 48.5, 33.8, 23.9. HRMS: Calc. for $C_{16}H_{20}ClN_2$ $[M+H]^+$: 275.1315, Obser. 275.1313.

4.7.98 4-Chloro-N^1-(4-(trifluoromethyl)benzyl)benzene-1,2-diamine (4al)

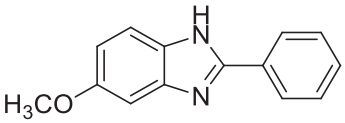


4al

The title compound was obtained as dark brown liquid. (Yield: 234 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 85:15, R_f = 0.44. IR (neat): 3363, 3200, 1889, 1251, 1087 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 60.2, 7.7 Hz, 4H), 6.74 (d, *J* = 9.7 Hz, 2H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.39 (s, 2H), 3.39 (brs, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

143.1, 135.6 (d, J_{C-F} = 50.0 Hz), 130.0 (q, J_{C-F} = 130 Hz), 129.2, 127.6, 126.4 (q, J_{C-F} = 15.0 Hz), 124.0, 120.0, 116.4, 113.0, 48.0. HRMS: Calc. for $C_{14}H_{13}ClF_3N_2$ $[M+H]^+$: 301.0719, Obser.301.0716.

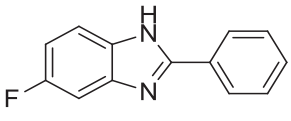
4.7.99 5-Methoxy-2-phenyl-1H-benzo[d]imidazole (5aa)



5aa

The title compound was obtained as white solid. M.p. 142-143 °C. (Yield: 179 mg, 80%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:20, R_f = 0.38. IR (neat): 3674, 3345, 1652, 1558, 1419, 1180, 808, 742 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (brs, 2H), 7.40 (d, J = 8.3 Hz, 1H), 7.25-7.36 (m, 3H), 7.18 (d, J = 14.7 Hz, 1H), 6.93 (s, 1H), 6.82 (dd, J = 24.3, 8.9 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 151.6, 139.1, 134.1, 129.8, 129.0, 128.9, 126.6, 116.0, 112.5, 97.4, 55.6. HRMS: Calc. for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.1028, Obser. 225.1027.

4.7.100 5-Fluoro-2-phenyl-1H-benzo[d]imidazole (5ab)

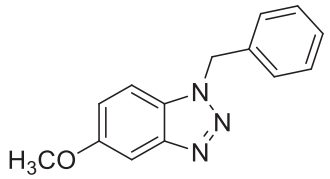


5ab

The title compound was obtained as white solid. M.p. 177-178 °C. (Yield: 165 mg, 78%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:20, R_f = 0.40. IR (neat): 2395, 1772, 1628, 1593, 1499 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ

13.04 (s, 1H), 8.16 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 7.5 Hz, 3H), 7.51 (dd, J = 16.9, 10.1 Hz, 2H), 7.39 (s, 1H), 7.06 (t, J = 9.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.2, 157.3, 152.3 (d, J_{C-F} = 42.5 Hz), 129.7 (d, J_{C-F} = 75.0 Hz), 128.6, 126.1, 109.9 (d, J_{C-F} = 80.0 Hz), 78.8. HRMS: Calc. for $C_{13}H_{10}FN_2$ $[M+H]^+$: 213.0828, Obser. 213.0824.

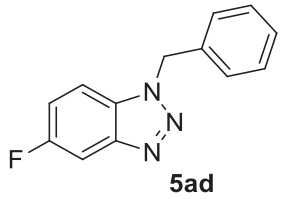
4.7.101 1-Benzyl-5-methoxy-1H-benzo[d][1,2,3]triazole (5ac)



5ac

The title compound was obtained as white solid. M.p. 135-137 °C (Yield: 179 mg, 75%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:20, R_f = 0.39. IR (neat): 3079, 3068, 2942, 2920, 1611, 1463, 1450, 2784, 1250, 1012 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.48-7.33 (m, 3H), 7.27 (t, J = 9.7 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 5.79 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 146.2, 132.6, 129.0, 127.2, 126.6, 123.7, 119.9, 114.2, 109.7, 55.2, 51.8. HRMS: Calc. for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1137, Obser. 240.1132.

4.7.102 1-Benzyl-5-fluoro-1H-benzo[d][1,2,3]triazole (5ad)



5ad

The title compound was obtained as white solid. M.p. 101-103 °C (Yield: 156 mg, 69%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 80:20, R_f = 0.42. IR (neat): 3056, 2903, 2764, 2532, 1120, 1015, 973 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.47-7.40 (m, 1H), 7.39-7.33 (m, 2H), 7.27 (d, J = 10.4 Hz, 2H), 7.02 (t, J = 8.4 Hz, 2H), 5.81 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 161.5, 146.2, 132.5, 130.5 (d, J_{C-F} = 15.0 Hz), 129.3 (d, J_{C-F} = 35.0 Hz), 127.4, 123.9, 120.0, 120.0, 115.9 (d, J_{C-F} = 90.0 Hz), 109.4, 51.3. HRMS: Calc. for $C_{13}H_{12}FN_3$ $[M+H]^+$: 228.0937, Obser. 228.0937.

4.8 Spectral Data of Few Products

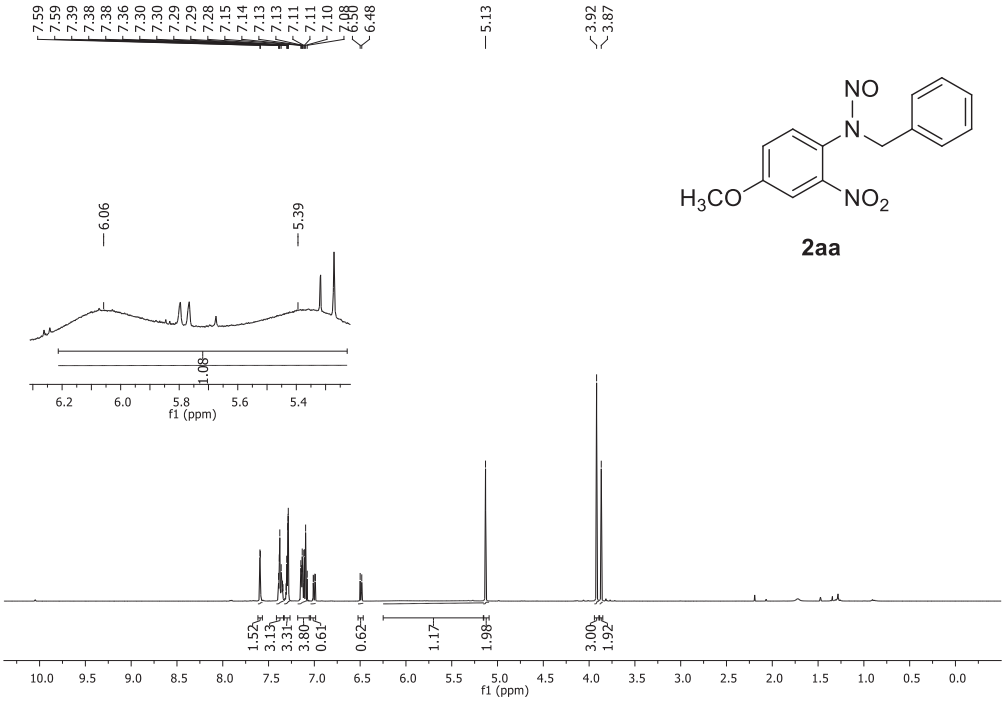


Figure 4.2 ^{1}H NMR of product **2aa** in $CDCl_3$.

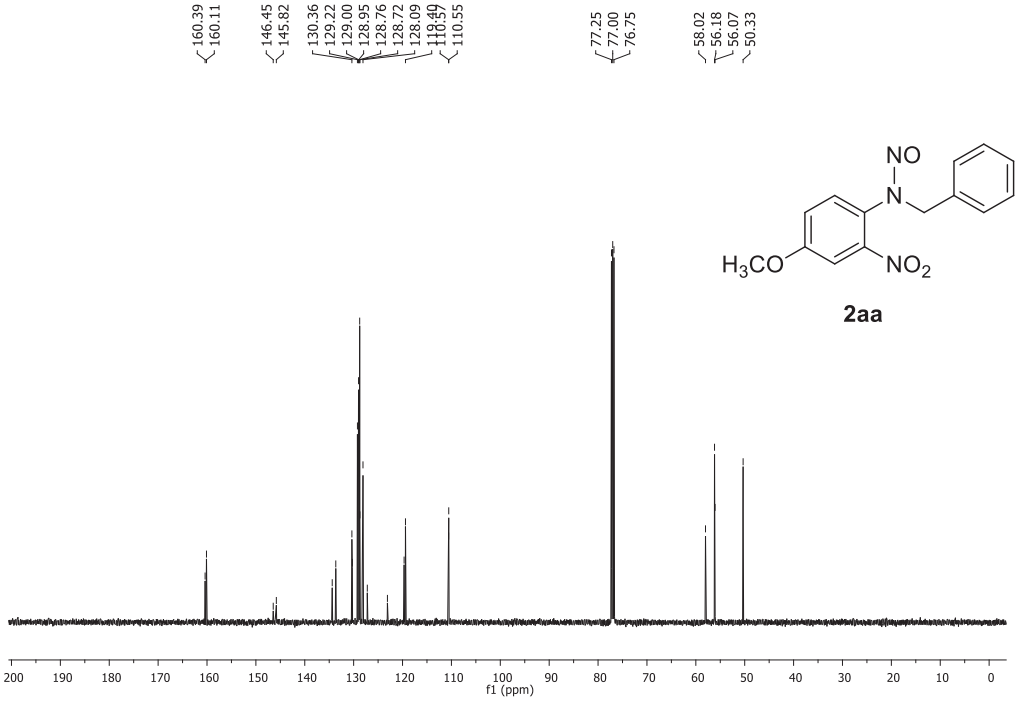


Figure 4.3 ^{13}C NMR of product **2aa** in $CDCl_3$.

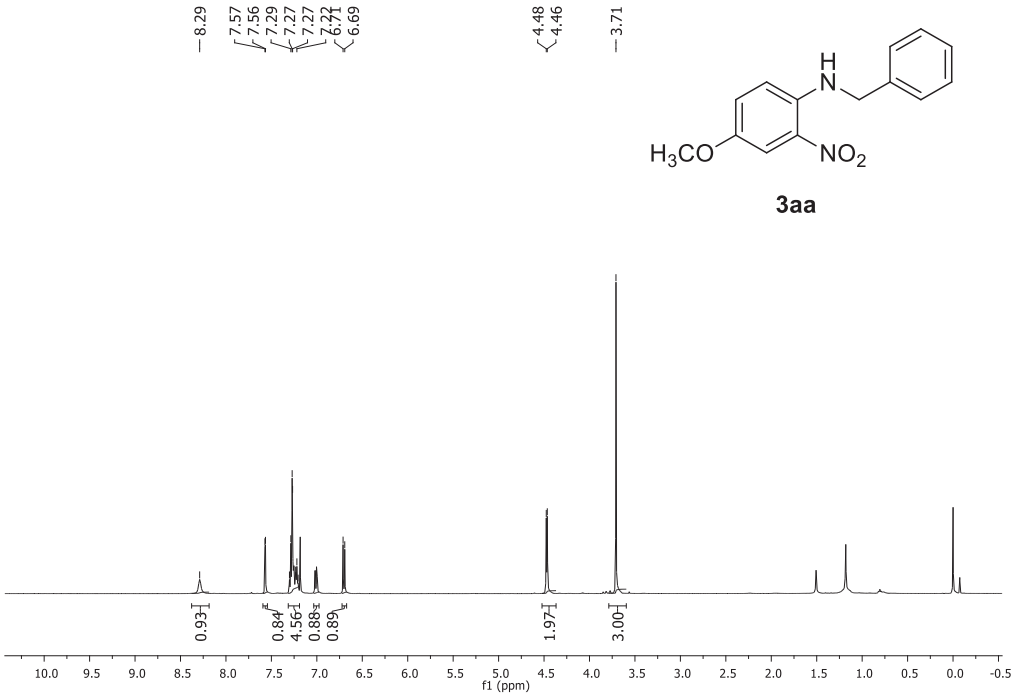


Figure 4.4 ^{1}H NMR of product **3aa** in $CDCl_3$.

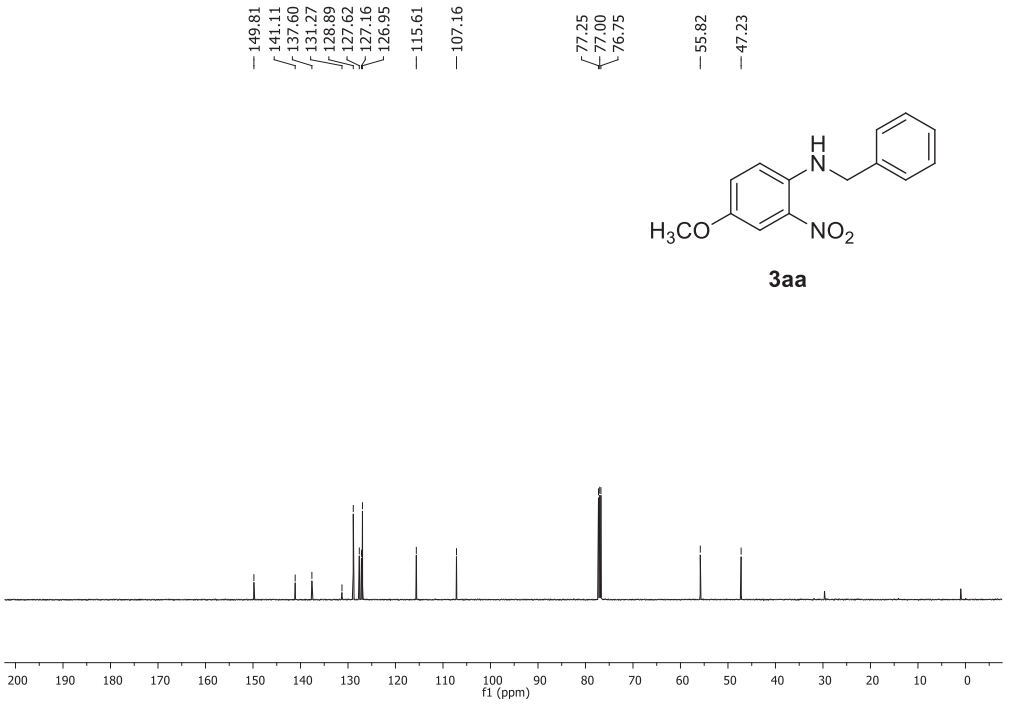


Figure 4.5 ^{13}C NMR of product **3aa** in $CDCl_3$.

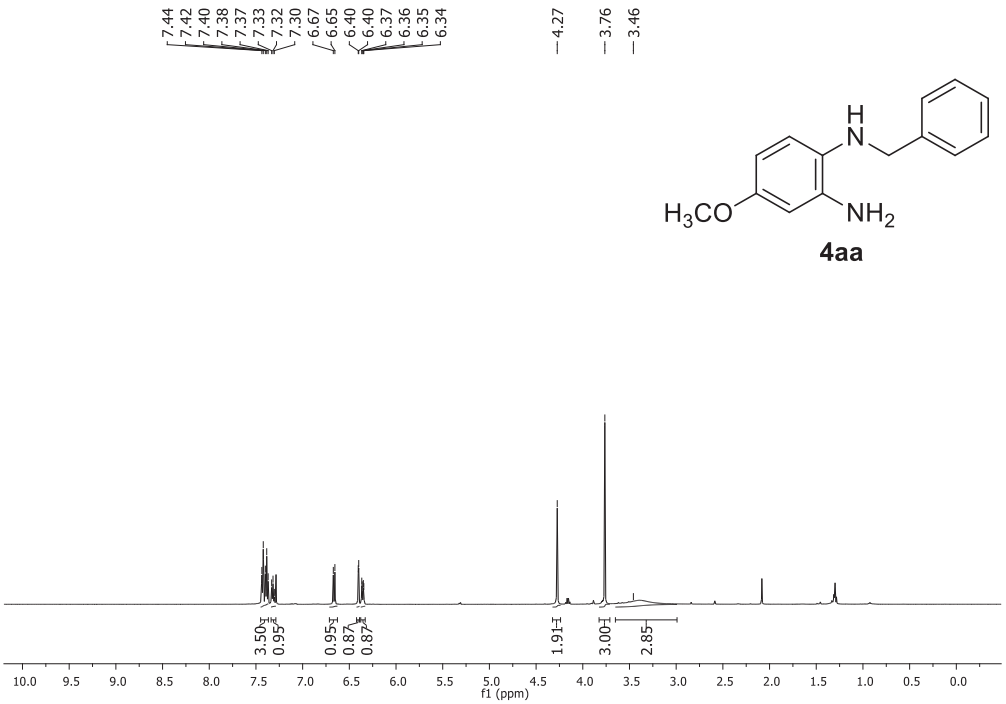


Figure 4.6 ^{1}H NMR of product **4aa** in $CDCl_3$.

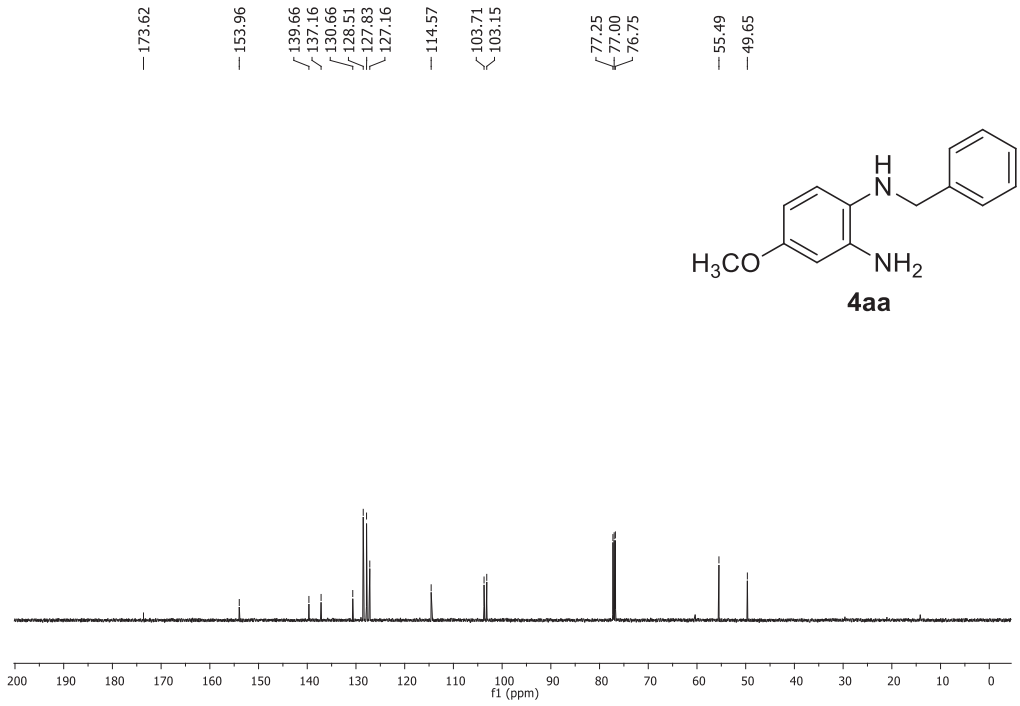


Figure 4.7 ^{13}C NMR of product **4aa** in $CDCl_3$.

4.9 References

[1] A. Orjales, R. Mosquera, L. Labeaga, R. Rodes, "New 2-piperazinylbenzimidazole derivatives as 5-HT3 antagonists. Synthesis and pharmacological evaluation," *Journal of Medicinal Che*mistry, **40**(1997) 586-593.

[2] N. P. Kumar, P. Sharma, S. S. Kumari, U. Brahma, S. Nekkanti, N. Shankaraiah, A. Kamal, "Synthesis of substituted phenanthrene-9-benzimidazole conjugates: Cytotoxicity evaluation and apoptosis inducing studies," *European Journal of Medicinal Chemistry,* **140**(2017) 128-140.

[3] Y. Bansal, O. Silakari, "The therapeutic journey of benzimidazoles: A review," *Bioorganic and Medicinal Chemistry,* **20**(2012) 6208-6236.

[4] S. Oh, S. Kim, S. Kong, G. Yang , N. Lee, D. Han, J. Goo, J. L. Siqueira-Neto, L. H. Freitas-Junior, R. Song, "Synthesis and biological evaluation of 2,3-dihydroimidazo [1,2-a]benzimidazole derivatives against *Leishmania donovani* and *Trypanosoma cruzi*," *European Journal of Medicinal Chemistry,* **84**(2014) 395-403.

[5] J. B. Wright, "The Chemistry of the benzimidazoles," *Chemical Reviews*, **48**(1951) 397-541.

[6] B. Kilpatrick, M. Heller, S. Arns, "Chemoselective nitration of aromatic sulfonamides with *tert*-butyl nitrite," *Chemical Communications*, **49**(2013) 514-516.

[7] Y. X. Li, L. H. Li, Y. F. Yang, H. L. Hua, X. B. Yan, L. B. Zhao, J. B. Zhang, F. J. Ji and Y. M. Liang, "Direct oxidative nitration of aromatic sulfonamides under mild conditions," *Chemical Communications*, **50**(2014) 9936-9938.

[8] U. Kloeckner, B. J. Nachtsheim, "Mild hypervalent iodine mediated oxidative nitration of *N*-aryl sulfonamides," *Chemical Communications*, **50**(2014) 10485-10487.

[9] Y. He, N. N. Zhao, L. Q. Qiu, X. Y. Zhang, X. S. Fan, "Direct amidation of *N*-Boc- and *N*-Cbz-protected amines *via* Rhodium-catalyzed coupling of arylboroxines and carbamates," *Organic Letters*, **18**(2016) 6054-6057.

[10] S. J. S. Dusel, B. Konig, "Visible-light-mediated nitration of protected anilines," *Journal of Organic Chemistry*, **83**(2018) 2802-2807.

[11] G. B. Yan, M. H. Yang, "Recent advances in the synthesis of aromatic nitro compounds," *Organic and Biomolecular Chemistry*, **11**(2013) 2554-2566.

[12] J. B. Tingle, F. C. Blanck, "Studies in nitration, III. Nitration of aniline and of certain of its *N*-alkyl, *N*-aryl and *N*-acyl derivatives," *Journal of American Chemical Society,* **30**(1908) 1395-1412.

[13] J.-P. Anselme, The organic chemistry of *N*-nitrosamines: A brief review, ACS Symposium Series, American Chemical Society, 1979.

[14] T. T. Gao, P. P. Sun, "Palladium-catalyzed *N*-nitroso-directed C-H alkoxylation of arenes and subsequent formation of 2-alkoxy-*N*-alkylarylamines," *Journal of Organic Chemistry,* **79**(2014) 9888-9893.

[15] B. Q. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, "Rhodium(III)-catalyzed *N*-nitroso-directed C-H olefination of arenes. high-yield, versatile coupling under mild conditions," *Journal of American Chemical Society,* **135**(2013) 468-473.

[16] B. Q. Liu, C. Song, C. Sun, S. G. Zhou, J. Zhu, "Rhodium(III)-catalyzed indole synthesis using N-N bond as an internal oxidant," *Journal of American Chemical Society,* **135**(2013) 16625-16631.

[17] C. M. Wang, Y. Huang, "Traceless directing strategy: Efficient synthesis of *N*-alkyl indoles *via* redox-neutral C-H activation,"*Organic Letters*, **15**(2013) 5294-5297.

[18] P. Chaudhary, S. Gupta, N. Muniyappan, S. Sabiah, J. Kandasamy, "An efficient synthesis of *N*-nitrosamines under solvent, metal and acid free conditions using *tert*-butyl nitrite," *Green Chem*istry, **18**(2016) 2323-2330.

[19] P. F. Li, X. D. Jia, "*tert*-Butyl nitrite (TBN) as a versatile reagent in organic synthesis," *Synthesis-Stuttgart*, **50**(2018) 711-722.

[20] Rotamers were observed in ~ 3:2 ratio as per ^{1}H NMR.

[21] P. Chaudhary, R. Korde, S. Gupta, P. Sureshbabu, S. Sabiah, J. Kandasamy, "An efficient metal-free method for the denitrosation of aryl *N*-nitrosamines at room temperature," *Advanced Synthesis and Catalysis*, 360(2018) 556-561.

[22] S. Aichhorn, M. Himmelsbach, W. Schofberger, "Synthesis of quinoxalines or quinolin-8-amines from *N*-propargyl aniline derivatives employing Tin and Indium chlorides," *Organic and Biomolecular Chemistry*, **13**(2015) 9373-9380.

[23] D. L. H. Williams, "The mechanism of the Fischer-Hepp rearrangement of aromatic *N*-nitroso-amines," *Tetrahedron* **31**(1975) 1343-1349.

[24] I. Briguglio, S. Piras, P. Corona, E. Gavini, M. Nieddu, G. Boatto, A. Carta, "Benzotriazole: An overview on its versatile biological behavior," *European Journal of Medicinal Chemistry,* **97**(2015) 612-648.

[25] D. Xue, Y. Q. Long, "Metal-free TEMPO-promoted C(sp^3)-H amination to afford multisubstituted benzimidazoles," *Journal of Organic Chemistry,* **79**(2014) 4727-4734.

[26] N. L. Drake, H. J. S. Winkler, C. M. Kraebel, T. D. Smith, "Fischer-Hepp rearrangements of substituted 9-nitrosocarbazoles," *Journal of Organic Chemistry,* **27**(1962) 1026-1030.

[27] P. Welzel, "Thermal cleavage of some diaryl nitrosamines and nitramines," *Chemical Reports*, **104**(1971) 808-821.