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Cyclopropylation of arylamines at the 2-position with cyclopropylmagnesium carbenoids

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ABSTRACT

Direct cyclopropylation of arylamines at the 2-position with 1-chlorocyclopropyl phenyl sulfoxides was achieved. The reaction of *N*-lithio arylamines with cyclopropylmagnesium carbenoids, which are generated from 1-chlorocyclopropyl phenyl sulfoxides with *i*-PrMgCl via the sulfoxide–magnesium exchange reaction, is the key of this procedure. This method offers an unprecedented way for the synthesis of arylamines having a cyclopropane ring at the 2-position directly from arylamines.

1. Introduction

Arylamines are obviously one of the most important and fundamental compounds in organic, synthetic organic, and medicinal chemistry. Arylamines have long been widely used as the materials for dyes, medicine, and other chemical products. In view of the importance of arylamines, innumerable studies have been carried out concerning their chemistry and synthesis.[1]

Concerning the alkylation of the aromatic ring of arylamines under the Friedel–Crafts-type reaction, as the treatment of an arylamine with Lewis acid results in the formation of inactive complex, direct alkylation of arylamine is known to be difficult.[2] An even more difficult process is the direct cyclopropylation of the aromatic ring under the Friedel–Crafts-type conditions. As the cyclopropyl carbocations that were generated under the Friedel–Crafts-type conditions were known to be rearranged spontaneously to their corresponding allylic cations,[3] direct cyclopropylation of aromatic ring of the arylamines has not been reported yet. On the other hand, some direct *N*-cyclopropylation of arylamines was reported by the reaction of arylamines with 1-bromoethoxycyclopropane,[4] [(1-ethoxycyclopropyl)oxy]trimethylsilane,[5] and cyclopropylbismuth reagent.[6]

Recently, we are investigating the chemistry and synthetic uses of cyclopropylmagnesium carbenoids and some new synthetic methods have appeared.[7] In 2006, we reported that the reaction of cyclopropylmagnesium carbenoid, generated from 1-chlorocyclopropyl phenyl sulfoxide with *i*-PrMgCl, with *N*-lithio arylamines gave α-amino-substituted cyclopropylmagnesiums.[8] Protonation of the α-amino-substituted cyclopropylmagnesium intermediates gave *N*-cyclopropylated arylamines in good yields.[8]

In continuation of our study for the reaction of the cyclopropylmagnesium carbenoids with arylamines, we found that the reaction of *N*-lithio arylamines with cyclopropylmagnesium carbenoids having at least one methyl group on the cyclopropane ring gave 2-cyclopropylated arylamines. As no report has been published concerning direct cyclopropylation of arylamines on the aromatic ring, we were highly interested in this reaction and investigated it in detail. In this paper, we report, in detail, the reaction of *N*-lithio arylamines with cyclopropylmagnesium carbenoids having various substituents **2**, derived from 1-chlorocyclopropyl phenyl sulfoxides **1** with *i*-PrMgCl, to give 2-cyclopropylated arylamines **3** and/or *N*-cyclopropylated arylamines **4** (Scheme 1).[9]

2. Results and discussion

2.1. Synthesis of 1-chlorocyclopropyl phenyl sulfoxides 1

At first, various 1-chlorocyclopropyl phenyl sulfoxides **1a–f** were synthesized as shown in Scheme 2. 1-Chlorocyclopropyl phenyl sulfoxide **1a** was synthesized from commercially available cyclopropyl phenyl sulfide as reported previously in almost quantitative

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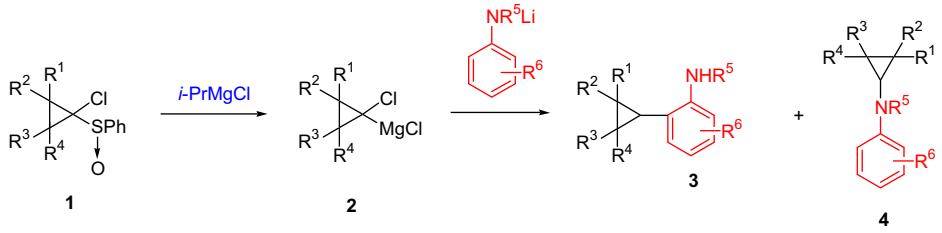
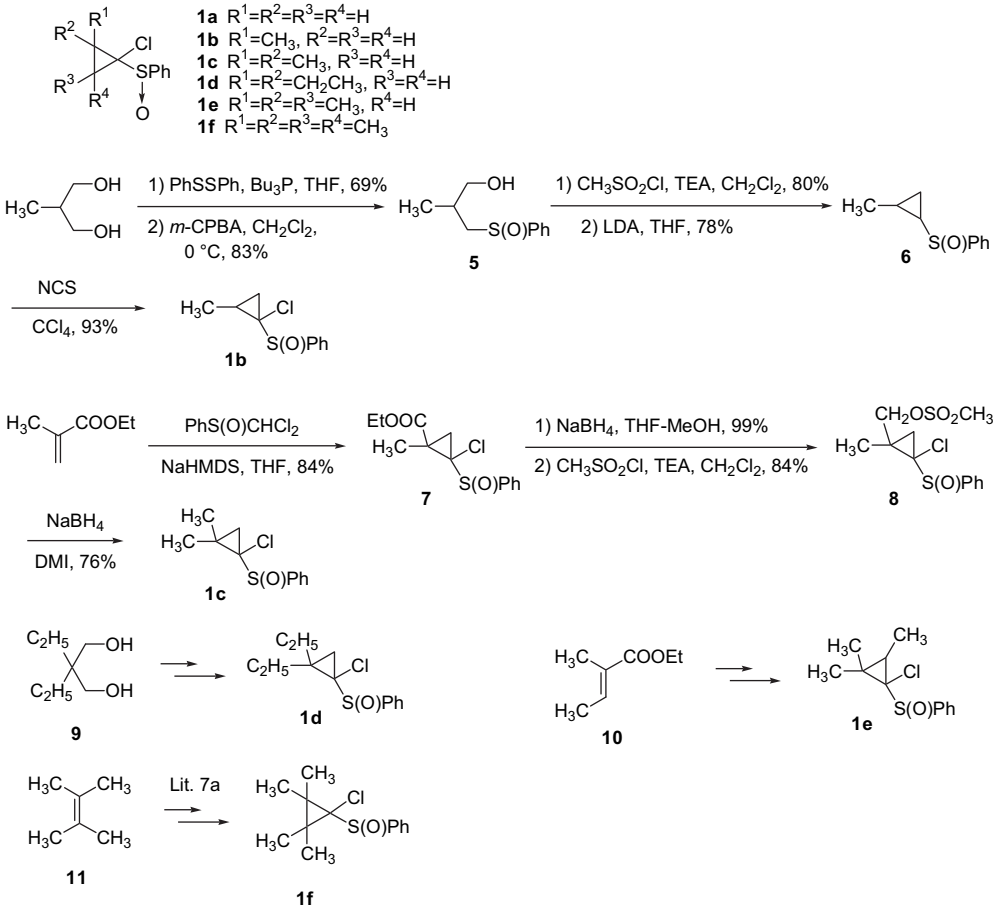


Scheme 1.



Scheme 2. Synthesis of 1-chlorocyclopropyl phenyl sulfoxides **1a**–**f**.

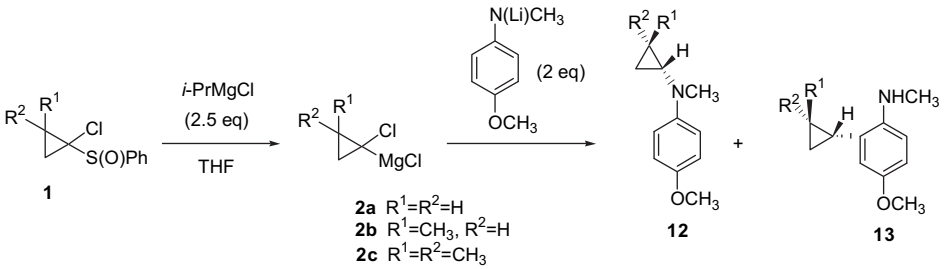
yield.[8] 1-Chloro-2-methylcyclopropyl phenyl sulfoxide **1b** was synthesized from commercially available 2-methyl-1,3-propanediol as follows. Thus, one hydroxyl group of the diol was converted to sulfide group under the conventional reaction to give hydroxyl-sulfide, which was oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to give sulfoxide **5**. The hydroxyl group of **5** was treated with methanesulfonyl chloride and the resultant mesylate was treated with 2.5 equiv of LDA to give cyclopropyl phenyl sulfoxide **6** as 1:1 mixture of two diastereomers. Finally, sulfoxide **6** was chlorinated with NCS to afford the desired product **1b** as 1:1 mixture of two diastereomers.

1-Chloro-2,2-dimethylcyclopropyl phenyl sulfoxide **1c** was synthesized from ethyl 2-methylacrylate. Thus, the reaction of ethyl 2-methylacrylate with dichloromethyl phenyl sulfoxide in the presence of NaHMDS afforded cyclopropane **7** as a single diastereomer.[10] The ester group of **7** was reduced with $NaBH_4$ in THF with methanol[11] and the resultant hydroxyl group was mesylated to give **8** in good yield. Finally, the mesyloxy group of **8** was reduced with $NaBH_4$ in 1,3-dimethyl-2-imidazolidinone (DMI) at 70 °C to give the desired product **1c** in 76%.

1-Chloro-2,2-diethylcyclporopyl phenyl sulfoxide **1d** was synthesized from 2,2-diethyl-1,3-propanediol **9** in the same way described for the synthesis of **1b**. 1-Chloro-2,2,3-trimethylcyclopropyl phenyl sulfoxide **1e** was synthesized from ethyl 2-methylbut-2-enoate **10** in the same way described for the synthesis of **1c**. 1-Chloro-2,2,3,3-tetramethylcyclopropyl phenyl sulfoxide **1f** was synthesized from 2,3-dimethyl-2-butene **11**.[7a]

2.2. Reaction of cyclopropylmagnesium carbenoids 2 with *N*-lithio non-substituted arylamines and *N*-lithio *para*-substituted arylamines

As reported previously,[8] to a solution of *i*-PrMgCl (2.5 equiv) in THF at −78 °C was added a solution of **1a** in THF and the reaction mixture was stirred at the temperature for 10 min to generate cyclopropylmagnesium carbenoid **2a** (Scheme 3). To this was added a solution of *N*-lithio *N*-methyl *p*-anisidine (2 equiv), generated from *N*-methyl *p*-anisidine with *n*-BuLi, through a cannula and the reaction mixture was slowly allowed to warm to −40 °C for over 1 h



Entry	2	Conditions	12 / Yield%	13 / Yield%
1	**2a**	-78 ~ -40 °C	**12a** 82	0[a)]
2	**2b**	-78 ~ 0 °C	**12b** 25	**13b** 16[a)]
3	**2c**	-78 ~ 0 °C	0	**13c** 59[a)]
4	**2c**	-78 ~ 0 °C	0	**13c** 60[b)]

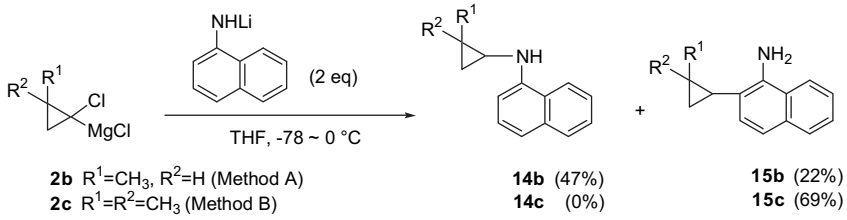
a) Method A: A solution of *N*-lithio arylamine was added to a solution of the cyclopropylmagnesium carbenoid through a cannular.
b) Method B: The cyclopropylmagnesium carbenoid was generated in the presence of *N*-lithio arylamine.

Scheme 3. Reaction of cyclopropylmagnesium carbenoids **2a**–**c**, derived from **1a**–**c** with *i*-PrMgCl, with *N*-lithio *N*-methyl *p*-anisidine giving *N*-cyclopropylated and *C*-cyclopropylated *N*-methyl *p*-anisidine **12** and **13**, respectively.

(**Method A**). This reaction gave *N*-cyclopropyl *N*-methyl *p*-anisidine **12a** in 82% yield (see entry 1 in Scheme 3).[8]

To investigate the generality of this reaction, we carried out this reaction with cyclopropylmagnesium carbenoid having a methyl group on the cyclopropane ring **2b**, generated from **1b** with *i*-PrMgCl, with *N*-lithio *N*-methyl *p*-anisidine. This reaction gave the expected *N*-cyclopropylated compound **12b** (25%) and, somewhat surprisingly, 2-cyclopropylated *N*-methyl *p*-anisidine **13b** in 16% yield (entry 2 in Scheme 3). Interestingly, **12b** and **13b** were obtained as single diastereomers and the structure was determined to be as shown in Scheme 3 by NOESY experiment. Further, the reaction was carried out with cyclopropylmagnesium carbenoid a similar yield (60%; entry 4 in Scheme 3). Despite the yield was similar, the operation became easier by using Method B. In some cases, we used both the Methods A and B, and the better yield will be reported.

As described above, although the real reason is still not clear, the reaction with cyclopropylmagnesium carbenoid having one methyl group on the cyclopropane ring **2b** gave both *N*-cyclopropylated arylamine **12b** and *C*-cyclopropylated arylamine **13b**. In addition, very interestingly, the reaction with cyclopropylmagnesium carbenoid having geminal methyl groups **2c** gave only *C*-cyclopropylated arylamine **13c**. These results were reproduced in the reaction of **2b** and **2c** with *N*-lithio 1-naphthylamine (Scheme 4).



Scheme 4. Reaction of cyclopropylmagnesium carbenoids **2b** and **2c** with *N*-lithio 1-naphthylamine giving *N*-cyclopropylated and *C*-cyclopropylated naphthylamines, **14** and **15**, respectively.

having geminal dimethyl groups on the cyclopropane ring **2c**. Quite surprisingly, this reaction only gave 2-cyclopropylated *N*-methyl *p*-anisidine **13c** in 59% yield (entry 3 in Scheme 3).

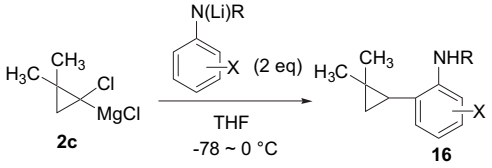
As transfer of a solution of *N*-lithio *N*-methyl *p*-anisidine in THF to the solution of cyclopropylmagnesium carbenoid through a cannula was a bother, we tried to generate the cyclopropylmagnesium carbenoid in the presence of *N*-lithio *N*-methyl *p*-anisidine. Thus, a solution of 1-chloro-2,2-dimethylcyclopropyl phenyl sulfoxide **1c** in THF was added to a solution of *N*-lithio *N*-methyl *p*-anisidine at −78 °C. After 10 min, *i*-PrMgCl (2.5 equiv) was added to the reaction mixture to generate the cyclopropylmagnesium carbenoid **2c** and the temperature of the reaction mixture was slowly allowed to warm to 0 °C (**Method B**). From this treatment, **13c** was obtained in

Thus, the reaction of cyclopropylmagnesium carbenoid **2b** with *N*-lithio 1-naphthylamine gave a mixture of both the *N*-cyclopropylated 1-naphthylamine **14b** (47%) and *C*-cyclopropylated 1-naphthylamine **15b** (22%). The reaction of **2c** with *N*-lithio 1-naphthylamine again gave only *C*-cyclopropylated 1-naphthylamine **15c** (69%) as a single product. As mentioned above, no report was published concerning direct cyclopropylation of arylamines on the aromatic ring. The results described above are the first examples of direct cyclopropylation of arylamines on the aromatic ring at the 2-position.

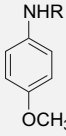
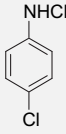
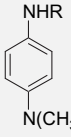
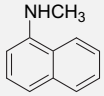
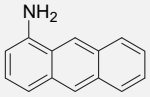
As we were highly interested in the direct cyclopropylation of arylamines at the 2-position, generality of this reaction was investigated by using cyclopropylmagnesium carbenoid **2c** with

various *N*-lithio non-substituted and *para*-substituted arylamines. The results are summarized in Table 1. *N*-Methylaniline and *N*-phenylaniline (diphenylamine) gave moderate yields of the desired 2-cyclopropylated products **16a** and **16b** (entries 1 and 2). The Method B was effective in the case of the reaction with *N*-phenylaniline (compare entries 2 and 3). *p*-Anisidine and its derivatives gave variable yields (entries 4–6).

Table 1
Reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio arylamines giving 2-cyclopropylated arylamines **16**



2c **16**

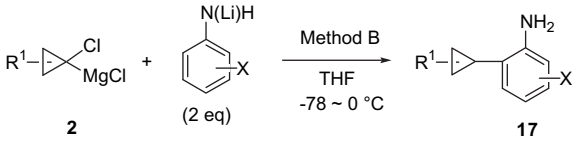
Entry	Arylamine		**16**/Yield/%
1		R=CH_3	**16a**/40[a]
2		R=Ph	**16b**/50[a]
3		R=Ph	**16b**/69[b]
4		R=H	**16c**/26[a]
5		R=CH_3	**13c**/59[a]
6		R=Bn	**16d**/22[a]
7			**16e**/9[a]
8		R=H	**16f**/58[b]
9		R=CH_3	**16g**/64[a]
10			**16h**/22[a]
11			**16i**/70[a]

[a] The reaction was conducted under Method A.
[b] The reaction was conducted under Method B. In this experiment both the methods were applied and the better yields were shown in this table.

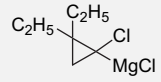
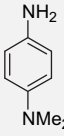
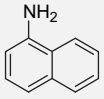
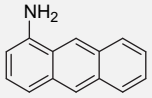
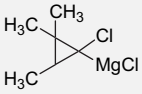
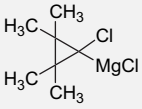
N-Methyl *p*-chloroaniline gave the desired product **16e** in only 9% with corresponding *N*-cyclopropylated compound (15%). This result suggested that the presence of an electron-withdrawing group on the aromatic ring retard the *C*-cyclopropylation. In contrast to this, it was suggested that the presence of an electron-donating group (dimethylamino group) on the aromatic ring activated the *C*-cyclopropylation (entries 8 and 9). Interestingly, 1-aminoanthracene gave the best yield in Table 1 (entry 11).

Table 2 shows the results for the reaction of cyclopropylmagnesium carbenoids having geminal ethyl groups **2d**, trimethyl groups **2e** and tetramethyl groups **2f** with 4-(dimethylamino)aniline, 1-naphthylamine, and 1-aminoanthracene. As shown in Table 2, the yields were about 40 to 65%, except in the case of 4-(dimethylamino)aniline with **2f** (entry 7). The reaction of 1-naphthylamine and 1-aminoanthracene again gave somewhat better yields compared with that of the aniline derivatives.

Table 2
Reaction of cyclopropylmagnesium carbenoids **2d–f** with *N*-lithio arylamines under Method B giving 2-cyclopropylated arylamines **17**



2 **17**

Entry	**2**	Arylamine	**17**/Yield/%
1	 **2d**	 4-(dimethylamino)aniline	**17a**/35
2	**2d**	 1-naphthylamine	**17b**/55
3	**2d**	 1-aminoanthracene	**17c**/38
4	 **2e**	4-(Dimethylamino)aniline	**17d**/44
5	**2e**	1-Naphthylamine	**17e**/47
6	**2e**	1-Aminoanthracene	**17f**/65
7	 **2f**	4-(Dimethylamino)aniline	**17g**/15
8	**2f**	1-Naphthylamine	**17h**/43
9	**2f**	1-Aminoanthracene	**17i**/56

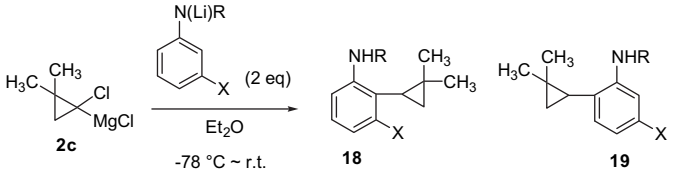
2.3. Reaction of cyclopropylmagnesium carbenoid 2c with *meta*-substituted arylamines, *ortho*-substituted arylamines, and nitrogen-containing heterocyclic compounds

We next investigated the reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio *meta*-substituted arylamines. The reaction must be interesting because two regioisomers would be expected to be formed. We studied the reactivity and regioselectivity of the reaction of cyclopropylmagnesium carbenoid **2c** with eight *N*-lithio *meta*-substituted arylamines under Method B and the results are summarized in Table 3.

The reaction with *N*-lithio *m*-anisidine gave, as expected, two *C*-cyclopropylated arylamines **18a** and **19a** and the main product was proved to be 2-cyclopropylated *m*-anisidine **18a** (entry 1). The reaction with *N*-lithio *N*-methyl *m*-anisidine again gave 2-cyclopropylated *N*-methyl *m*-anisidine **18b** as the main product (entry 2). The yield was found to be higher when the nitrogen of *N*-lithio *m*-anisidine has a methyl group.

The results shown in entries 3–6 indicate that the reaction of *m*-methylaniline and even *m*-chloroaniline showed the similar regioselectivity, except the result in entry 3. The yields were again better when the nitrogen of *N*-lithio anilines has a methyl group. *N*-Lithio anilines having a trifluoromethyl group at the *meta*-position showed quite low reactivity toward **2c** (entries 7 and 8). From these results, it was implied that the presence of a strong electron-withdrawing group on the aromatic ring retards the cyclopropylation.

Table 3
Reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio *meta*-substituted arylamines under Method B giving 2-cyclopropylated arylamines **18** and **19**



Entry	Arylamine		**18**/Yield/%	**19**/Yield/%
	X	R		
1	OCH_3	H	**18a**/23	**19a**/17
2	OCH_3	CH_3	**18b**/52	**19b**/21
3	CH_3	H	**18c**/16	**19c**/21
4	CH_3	CH_3	**18d**/23	**19d**/19
5	Cl	H	**18e**/17	**19e**/8
6	Cl	CH_3	**18f** 29	**19f**/16
7	CF_3	H	**18g**/0	**19g**/9
8	CF_3	CH_3	Complex mixture	

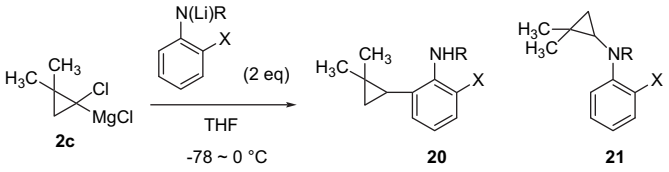
Cyclopropylmagnesium carbenoid **2c** was generated from **1c** with 3 equiv of *i*-PrMgCl in diethyl ether at −78 °C.

The regioselectivity mentioned above is quite interesting. It is usually said that electrophilic aromatic substitution (such as Friedel–Crafts-type alkylation) of *meta*-substituted aromatic compounds at the 2-position is very difficult because of the position is too hindered.[12] However, as shown in Table 3, our reaction of **2c** with *N*-lithio *meta*-substituted anilines gave 2-substituted products selectively as a main product.

We have observed the similar phenomena in our study for the reaction of magnesium alkylidene carbenoids with *N*-lithio *meta*-substituted arylamines.[13] The reaction gave 2-alkenylated arylamines as the main products. In order to have the better understanding of these phenomena, the electrostatic potential-derived charges of some *N*-lithio *meta*-substituted arylamines were calculated and it was found that the carbon at the 2-position has more negative atom charge (for details, see Ref. 13). The regioselectivity observed in the presented reactions could again be rationalized from the charge of the *N*-lithio *meta*-substituted arylamines.

Next, the reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio *ortho*-substituted arylamines was investigated and the results are summarized in Table 4. Very interestingly, as shown in Table 4, the reactions of **2c** with *N*-lithio *ortho*-substituted arylamines without substituent on the nitrogen gave 6-cyclopropylated products **20a** and **20b** as only isolable products, though the yields were variable (entries 1 and 2). On the other hand, the reactions of **2c** with *N*-lithio *ortho*-substituted amines with a methyl group on the nitrogen gave *N*-cyclopropylated products **21a-c** in up to 42% yield (entries 3–5).

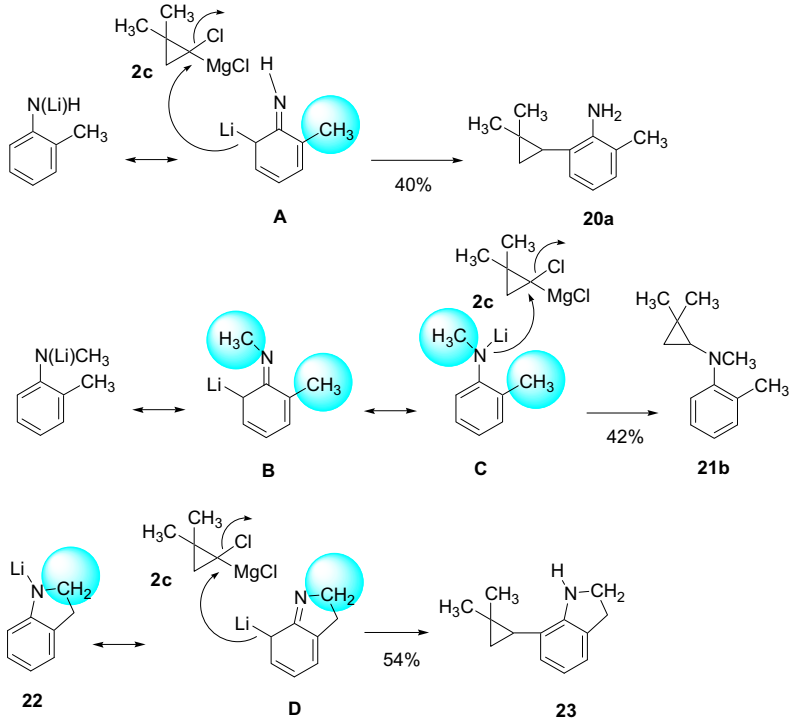
Table 4
Reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio *ortho*-substituted arylamines under Method B giving 2-cyclopropylated arylamines **20** or *N*-cyclopropylated arylamine **21**



Entry	Arylamine		**20**/Yield/%	**21**/Yield/%
	X	R		
1	CH_3	H	**20a**/40	0
2	Cl	H	**20b**/14	0
3	OCH_3	CH_3	0	**21a**/37
4	CH_3	CH_3	0	**21b**/42
5	Cl	CH_3	0	**21c**/22

Cyclopropylmagnesium carbenoid **2c** was generated from **1c** with 2.5 equiv of *i*-PrMgCl in THF at −78 °C.

These quite interesting differences for the selective *C*- and *N*-cyclopropylation described in Table 4, and the mechanism of this reaction are explained as follows (Scheme 5). Thus, *N*-lithio

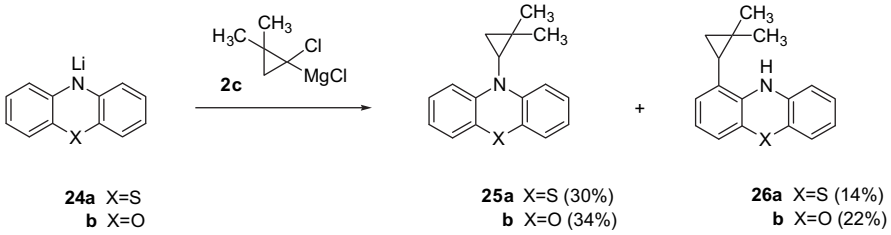


Scheme 5. Reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio 2-methylanilines and *N*-lithio indoline **22** giving *N*-cyclopropylated and *C*-cyclopropylated products **21b** and **23**, respectively. Rationalization for the *N*- and C-cyclopropylation.

o-toluidine is present in the resonance form, lithium α-imino carbanion **A**. The carbanion attacks at the carbenoid carbon of **2c** to give *ortho*-cyclopropylated *o*-toluidine **20a**. On the other hand, *N*-lithio *N*-methyl *o*-toluidine is present in the resonance form, lithium α-imino carbanion **B**, in which the methyl group on the nitrogen must be placed away from the methyl group on the aromatic ring. As the result, the carbanion is highly hindered by the methyl group on the nitrogen and the attack of the carbanion to the carbenoid carbon must be prevented. This case, *N*-lithio form **C** reacts with **2c** to give *N*-cyclopropylated product **21b**.

The evidence for this assumption is obtained from the reaction of *N*-lithio indoline **22** with cyclopropylmagnesium carbenoid **2c**. This reaction gave *ortho*-cyclopropylated indoline **23** in 54% yield without any *N*-cyclopropylated compound. *N*-Lithio indoline **22** has alkyl groups on the nitrogen and on the aromatic ring at the *ortho*-position; however, as the alkyl groups are bound, the carbanionic carbon in the resonance form **D** is not hindered by the alkyl group. From resonance form **D**, *C*-cyclopropylated product **23** was formed.

Finally, the reaction of **2c** with *N*-lithio phenothiazine and *N*-lithio phenoxazine was investigated (Scheme 6). These reactions gave a mixture of *N*- and *C*-cyclopropylated compounds **25** and **26** in 40–50% yields and the main products were found to be *N*-cyclopropylated ones **25**.



24a X=S
b X=O

25a X=S (30%)
b X=O (34%)

26a X=S (14%)
b X=O (22%)

Scheme 6. Reaction of cyclopropylmagnesium carbenoid **2c** with *N*-lithio phenothiazine and *N*-lithio phenoxazine.

In conclusion, we found, for the first time, the reaction of cyclopropylmagnesium carbenoids **2**, generated from 1-chlorocyclopropyl phenyl sulfoxides **1** with *i*-PrMgCl, with *N*-lithio arylamines gave 2-cyclopropylated arylamines **3** in moderate yields. We are still uncertain of the reason why the *C*-cyclopropylation needs at least one substituent on the cyclopropane ring; however, the chemistry described in this paper contributes to a synthesis of 2-cyclopropylated arylamines directly from arylamines and to the chemistry of cyclopropanes.[14]

3. Experimental

3.1. General

Melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 500 and BRUKER UltraShield 400, 300 spectrometer. IR spectra were recorded on a Perkin–Elmer spectrum One FTIR instrument. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion with JEOL JMS-SX102A. Silica gel 60N (KANTO CHEMICAL) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent and reagent, diethyl ether, and THF were distilled from diphenylketyl.

*3.1.1. 1-Chloro-2-methylcyclopropyl phenyl sulfoxide (**1b**).* To a solution of 2-methyl-1,3-propanediol (1.8 g; 20 mmol) and diphenyl disulfide (2.4 g; 11 mmol) in 100 ml of THF was added with stirring tributylphosphine (2.43 g; 12 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h. After removal of the solvent in vacuo, the product was purified by silica gel column chromatography to afford a sulfide (2.52 g; 69%) as colorless oil. IR (neat) 3366 (OH), 2959, 2926, 1584, 1481, 1439, 1026, 739 cm^{-1}; ^{1}H NMR δ 1.05 (3H, d, J=6.7 Hz), 1.56 (1H, br s), 1.91–2.00 (1H, m), 2.85 (1H, dd, J=12.9, 9.8 Hz), 3.07 (1H, dd, J=12.9, 9.8 Hz), 3.59–3.62 (2H, m), 7.16–7.18 (1H, m), 7.22 (2H, d, J=7.3 Hz), 7.30–7.35 (2H, m); MS *m*/*z* (%) 182 (M^+, 69), 123 (39), 111 (15), 110 (100). Calcd for $C_{10}H_{14}OS$: *M*, 182.0764. Found: *m*/*z* 182.0761.

To a solution of the sulfide (2.41 g; 13.2 mmol) in 50 ml of CH_2Cl_2 at 0 °C was added *m*-chloroperbenzoic acid (70% purity; 3.58 g; 14.5 mmol) and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with aq Na_2SO_3 and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was washed with 5% aq NaOH followed by brine. The product was purified by silica gel column chromatography to give sulfoxide **5** as colorless oil (about 1:1.3 mixture of two diastereomers). IR (neat) 3401 (OH), 2969, 2928, 1647, 1444, 1018 (SO), 752 cm^{-1}; MS *m*/*z* (%) 198 (M^+, 2), 126 (100), 110 (20). Calcd for $C_{10}H_{14}O_2S$: *M*, 198.0714. Found: *m*/*z* 198.0719.

To a solution of **5** (2.2 g; 11.1 mmol) in 27 ml of CH_2Cl_2 at 0 °C was added triethylamine (1.84 ml; 13.2 mmol) dropwise with stirring. After 10 min, methanesulfonyl chloride (1.5 ml; 13.2 mmol) was added and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with water and the whole was extracted with $CHCl_3$. The product was purified by short pad of silica gel to give mesylate (2.43 g; 80%) as colorless oil and it was used without further purification.

To a solution of LDA (31.5 mmol) in 30 ml of THF at 0 °C was added a solution of the mesylate (3.5 g; 12.7 mmol) in 30 ml of THF dropwise with stirring. The reaction mixture was stirred at 0 °C for 30 min and the reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$ and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford cyclopropane **6** (1.78 g; 78%).

To a solution of **6** (1.78 g; 9.9 mmol) in 30 ml of CCl_4 was added *N*-chlorosuccinimide (1.47 g; 11 mmol) and the reaction mixture was stirred at room temperature for overnight. The precipitate was filtered off and the solvent was removed to give a residue, which was purified by silica gel column chromatography to give **1b** as colorless oil (1:1 mixture of two diastereomers). IR (neat) 3061, 2968, 1444, 1306, 1088, 1056 (SO), 749 cm^{-1}; ^{1}H NMR δ 0.81 (0.5H, dd, J=7.7, 6.6 Hz), 0.99 (0.5H, dd, J=7.7, 6.7 Hz), 1.20 (1.5H, d, J=6.1 Hz), 1.29 (1.5H, d, J=6.1 Hz), 1.74–1.78 (1H, m), 1.82–1.94 (1H, m), 7.51–7.58 (3H, m), 7.69–7.70 (2H, m). MS *m*/*z* (%) 214 (M^+, 11), 126 (100), 89 (21), 78 (53), 77 (22), 53 (51). Calcd for $C_{10}H_{11}ClOS$: *M*, 214.0219. Found: *m*/*z* 214.0213.

*3.1.2. 1-Chloro-2,2-dimethylcyclopropyl phenyl sulfoxide (**1c**).* To a solution of ethyl 2-methylacrylate (1.38 ml; 9.6 mmol) and dichloromethyl phenyl sulfoxide (2.0 g; 9.6 mmol) in 24 ml of THF at −78 °C was added a solution of NaHMDS (2.0 mol/L solution; 7.2 ml; 14.4 mmol) dropwise with stirring. The temperature of the

reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched by adding satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to give cyclopropylsulfoxide **7** (2.32 g; 84%) as colorless oil. IR (neat) 2982, 1728 (CO), 1445, 1305, 1180, 1096, 1057 (SO), 858, 748 cm^{-1}; ^1H NMR δ 1.34 (3H, t, J=7.0 Hz), 1.40 (1H, d, J=7.3 Hz), 1.56 (3H, s), 2.67 (1H, d, J=7.3 Hz), 4.27 (2H, q, J=7.0 Hz), 7.51–7.55 (3H, m), 7.65–7.69 (2H, m). MS m/z (%) 286 (M^+, 9), 241 (24), 161 (65), 133 (100), 126 (54), 105 (25). Calcd for $C_{13}H_{15}ClO_3S$: M, 286.0430. Found: m/z 286.0429.

To a solution of **7** (2.86 g; 10 mmol) in 25 ml of THF was added $NaBH_4$ (0.43 g; 11.5 mmol) and the mixture was heated at reflux for 30 min. During this heating, methanol (2.5 ml) was added dropwise to the reaction mixture. The reaction was quenched by adding satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to give an alcohol (2.44 g; 99%) as crystals. ^1H NMR δ 1.20 (1H, d, J=7.3 Hz), 1.48 (3H, s), 1.95 (1H, d, J=7.3 Hz), 2.63 (1H, t, J=5.8 Hz, OH), 3.86 (1H, m), 4.10 (1H, m), 7.54 (3H, m), 7.81 (2H, m).

To a solution of the alcohol (2.44 g; 9.98 mmol) in 20 ml of CH_2Cl_2 was added triethylamine (1.1 ml; 10.3 mmol) at 0 °C with stirring. After 10 min, methanesulfonyl chloride (11 mmol) was added to the reaction mixture and the whole mixture was stirred at 0 °C for 30 min. The reaction was quenched by adding satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford mesylate **8** (2.43 g; 84%) as colorless oil. The mesylate was used immediately in the next step.

To a solution of **8** (71 mg; 0.24 mmol) in 0.8 ml of 1,3-dimethyl-2-imidazolidinone was added $NaBH_4$ (11 mg; 0.3 mmol) and the reaction mixture was stirred and heated at 70 °C for 30 min. The reaction was quenched by adding satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to give **1c** (42 mg; 76%) as colorless crystals. Mp. 66–70 °C (AcOEt–hexane); IR (KBr) 3069, 2959, 1478, 1086, 1049 (SO), 753 cm^{-1}; ^1H NMR δ 1.33 (1H, d, J=6.8 Hz), 1.35 (3H, s), 1.58 (3H, s), 1.90 (1H, d, J=6.8 Hz), 7.24–7.56 (3H, m), 7.64–7.67 (2H, m). MS m/z (%) 228 (M^+, 5), 211 (12), 170 (7), 126 (100), 103 (29). Calcd for $C_{11}H_{13}ClOS$: M, 228.0374. Found; m/z 228.0368. Anal. Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; Cl, 15.50; S, 14.02. Found: C, 57.77; H, 5.68; Cl, 15.44; S, 14.00.

*3.1.3. 1-Chloro-2,2-diethylcyclopropyl phenyl sulfoxide (**1d**).* Colorless crystals; mp 100–101 °C (AcOEt–hexane); IR (KBr) 3061, 2972, 1443, 1089, 1055 (SO), 748, 691 cm^{-1}; ^1H NMR δ 1.02 (3H, t, J=7.0 Hz), 1.11 (1H, d, J=6.9 Hz), 1.12 (3H, t, J=7.0 Hz), 1.44 (1H, d, J=6.9 Hz), 1.70 (2H, m), 1.95 (2H, m), 7.51–7.55 (3H, m), 7.64–7.69 (2H, m). Anal. calcd for $C_{13}H_{17}ClOS$: C, 60.80; H, 6.67; Cl, 13.81; S, 12.49. Found; C, 60.83; H, 6.70; Cl, 13.67; S, 12.42.

*3.1.4. 1-Chloro-2,2,3-trimethylcyclopropyl phenyl sulfoxide (**1e**).* Colorless crystals; mp 54.5–55 °C (AcOEt–hexane); IR (KBr) 3063, 2962, 2929, 1442, 1078, 1054 (SO), 749, 689 cm^{-1}; ^1H NMR δ 1.14 (3H, s), 1.20 (3H, d, J=6.0 Hz), 1.56 (3H, s), 1.94 (1H, q, J=6.0 Hz), 7.51–7.62 (3H, m), 7.64–7.67 (2H, m). Anal. calcd for $C_{12}H_{15}ClOS$: C, 59.37; H, 6.23; Cl, 14.60; S, 13.21. Found; C, 59.36; H, 6.24; Cl, 14.47; S, 13.13.

*3.1.5. 1-Chloro-2,2,3,3-tetramethylcyclohexyl phenyl sulfoxide (**1f**).* Colorless crystals; mp 103–105 °C (AcOEt–hexane); IR (KBr) 3071, 2994, 2958, 2923, 1442, 1380, 1085, 1052 (SO), 754, 688 cm^{-1}; ^1H NMR δ 1.17, 1.30, 1.57, 1.70 (each 3H, s), 7.50–7.55 (3H, m), 7.60–7.64 (2H, m). Anal. calcd for $C_{13}H_{17}ClOS$: C, 60.80; H, 6.67; Cl, 13.81; S, 12.49. Found; C, 60.82; H, 6.73; Cl, 13.78; S, 12.56.

*3.1.6. N-(2-Methylcyclopropyl)-N-methyl-para-anisidine (**12b**) and N-Methyl-2-(2-methylcyclopropyl)-para-anisidine (**13b**).* To a solution of *i*-PrMgCl (1.0 mol/L; 0.5 mmol) in 0.5 ml of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added a solution of **1b** (36.4 mg, 0.2 mmol) in 0.8 ml of dry THF dropwise with stirring and the reaction mixture was stirred for 10 min to give cyclopropylmagnesium carbenoid **2b**. In another flame-dried flask, *n*-BuLi (0.4 mmol) was added to a solution of *N*-methyl *p*-anisidine (0.4 mmol) in 0.5 ml of dry THF at −78 °C to give *N*-lithio *N*-methyl *p*-anisidine. This solution was added to the solution of **2b** through a cannula. The temperature of the reaction mixture was slowly allowed to warm to 0 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with AcOEt. The organic layer was washed once with water and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **12b** (9.5 mg, 25%) and **13b** (6.1 mg, 16%). **12b:** Colorless oil; IR (neat) 2928, 1512, 1246, 1044, 819 cm^{-1}; ^1H NMR δ 0.53 (1H, q, J=5.8 Hz), 0.75 (1H, m), 0.88–0.96 (1H, m), 1.16 (3H, d, J=6.4 Hz), 1.95 (1H, m), 2.89 (3H, s), 3.77 (3H, s), 6.84 (2H, d, J=9.2 Hz), 6.89 (2H, d, J=9.2 Hz). MS m/z (%) 191 (M^+, 34), 190 (20), 176 (100), 160 (15), 135 (18), 121 (19). Calcd for $C_{12}H_{17}NO$: M, 191.1309. Found: m/z 191.1310. **13b**: Colorless oil; IR (neat) 3430 (NH), 2952, 1506, 1419, 1286, 1219, 1154, 1035, 798, 757 cm^{-1}; ^1H NMR δ 0.64 (1H, m), 0.77 (1H, m), 0.92–0.99 (1H, m), 1.25 (3H, d, J=6.1 Hz), 1.30–1.34 (1H, m), 2.89 (3H, s), 3.74 (3H, s), 6.54 (1H, d, J=8.6 Hz), 6.65 (1H, d, J=2.7 Hz), 6.72 (1H, dd, J=8.6, 2.7 Hz). MS m/z (%) 191 (M^+, 78), 176 (100), 160 (28), 148 (13), 136 (12). Calcd for $C_{12}H_{17}NO$: M, 191.1309. Found: m/z 191.1302.

*3.1.7. N-Methyl-2-(2,2-dimethylcyclopropyl)-para-anisidine (**13c**)*

3.1.7.1. Method A. To a solution of *i*-PrMgCl (1.0 mol/L; 0.5 mmol) in 0.5 ml of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added a solution of **1c** (45.7 mg, 0.2 mmol) in 0.8 ml of dry THF dropwise with stirring and the reaction mixture was stirred for 10 min to give cyclopropylmagnesium carbenoid **2c**. In another flame-dried flask, *n*-BuLi (0.4 mmol) was added to a solution of *N*-methyl *p*-anisidine (54.8 mg, 0.4 mmol) in 0.5 ml of dry THF at −78 °C under argon atmosphere to give *N*-lithio *N*-methyl *p*-anisidine. This solution was added to a solution of the magnesium cyclopropylidene **2c** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to 0 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with ethyl acetate. The organic layer was washed once with water and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **13c** (24.2 mg, 59%) as a colorless oil; IR (neat) 3431 (NH), 2938, 1510, 1452, 1285, 1216, 1168, 1053, 1033, 800 cm^{-1}; ^1H NMR δ 0.74 (1H, m), 0.76 (3H, s), 0.79–0.83 (1H, m), 1.30 (3H, s), 1.49 (1H, dd, J=8.3, 5.8 Hz), 2.88 (3H, s), 3.61 (1H, br s), 3.74 (3H, s), 6.55 (1H, d, J=8.6 Hz), 6.62 (1H, d, J=3.1 Hz), 6.72 (1H, dd, J=8.6, 3.1 Hz). MS m/z (%) 205 (M^+, 100), 190 (67), 175 (18), 174 (23), 162 (28), 160 (27), 150 (32), 148 (27). Calcd for $C_{13}H_{19}NO$: M, 205.1465. Found: m/z 205.1452.

3.1.7.2. Method B. To a solution of *N*-methyl *p*-anisidine (0.4 mmol) in 0.5 ml of dry THF in a flame-dried flask at 0 °C under argon atmosphere was added *n*-BuLi (0.4 mmol) dropwise with stirring. The reaction mixture was cooled to −78 °C and a solution of **1c** (45.7 mg, 0.2 mmol) in 0.8 ml of dry THF was added dropwise with stirring. After 10 min, *i*-PrMgCl (1.0 mol/L; 0.5 mmol) was added to the reaction mixture and the temperature of the reaction mixture was slowly allowed to warm to 0 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with AcOEt. The organic layer was washed once with water and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **13c** (24.5 mg, 60%).

*3.1.8. N-Cyclopropyl-N-(4-methoxyphenyl)methylamine (**12a**).* Colorless oil; IR (neat) 3004, 2933, 1513, 1455, 1361, 1245, 1040, 818 cm^{-1}; ^1H NMR δ 0.58 (2H, m), 0.77 (2H, m), 2.27 (1H, m), 2.29 (3H, s), 3.77 (3H, s), 6.84 (2H, d, J=9.2 Hz), 6.97 (2H, d, J=9.2 Hz). MS m/z (%) 177(M^+, 100), 176(60), 162(80), 146(18), 134(16), 121(57). Calcd for $C_{11}H_{15}NO$: M, 177.1154. Found: m/z 177.1135.

*3.1.9. N-(2-Methylcyclopropyl)naphtalen-1-ylamine (**14b**).* Yellow oil; IR (neat) 3403 (NH), 2951, 1732, 1582, 1523, 1448, 1406, 1096, 770 cm^{-1}; ^1H NMR δ 0.60 (1H, m), 0.78–0.84 (1H, m), 0.94–1.01 (1H, m), 1.22 (3H, d, J=6.0 Hz), 2.22–2.27 (1H, m), 4.81 (1H, br s), 6.93 (1H, dd, J=9.0, 1.0 Hz), 7.25 (1H, d, J=9.0 Hz), 7.39–7.45 (3H, m), 7.69 (1H, d, J=7.0 Hz), 7.78 (1H, d, J=7.0 Hz). This product is somewhat unstable and reliable data for the mass spectrum could not be obtained.

*3.1.10. 2-(2-Methylcyclopropyl)naphthalen-1-ylamine (**15b**).* Yellow crystals; mp 100–101 °C (hexane); IR (KBr) 3435 (NH), 3341 (NH), 3054, 2948, 1620, 1400, 806, 799, 739 cm^{-1}; ^1H NMR δ 0.71–0.78 (1H, m), 0.85–0.91 (1H, m), 1.02–1.12 (1H, m), 1.32 (3H, d, J=5.9 Hz), 1.51–1.57 (1H, m), 4.43 (2H, br s), 7.23–7.24 (2H, m), 7.36–7.45 (2H, m), 7.73–7.81 (2H, m). MS m/z (%) 197 (M^+, 100), 182 (63), 165 (20), 156 (12). Calcd for $C_{14}H_{15}N$: M, 197.1204. Found: m/z 197.1206.

*3.1.11. 2-(2,2-Dimethylcyclopropyl)naphthalen-1-ylamine (**15c**).* Colorless crystals; mp 188–189 °C (AcOEt–hexane); IR (KBr) 3300 (NH), 3196 (NH), 2950, 1634, 1393, 1365, 1090, 806, 745 cm^{-1}; ^1H NMR δ 0.82 (3H, s), 0.83–0.89 (1H, m), 0.92 (1H, dd, J=8.6, 4.5 Hz), 1.36 (3H, s), 1.72 (1H, dd, J=8.6, 5.8 Hz), 4.32 (2H, br s), 7.18 (1H, d, J=11.0 Hz), 7.25 (1H, d, J=12.0 Hz), 7.36–7.46 (2H, m), 7.75–7.82 (2H, m). Anal. calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found; C, 85.32; H, 8.06; N, 6.59.

*3.1.12. N-[2-(2,2-Dimethylcyclopropyl)phenyl]methyl-amine (**16a**).* Colorless oil; IR (neat) 3443 (NH), 3066, 2939, 1606, 1582, 1514, 1461, 1321, 1166, 746 cm^{-1}; ^1H NMR δ 0.73–0.76 (1H, m), 0.76 (3H, s), 0.81 (1H, dd, J=8.3, 4.3 Hz), 1.31 (3H, s), 1.46 (1H, dd, J=8.3, 5.8 Hz), 2.91 (3H, s), 3.93 (1H, br s), 6.61 (1H, d, J=7.9 Hz), 6.65 (1H, dt, J=7.3, 0.9 Hz), 6.97 (1H, d, J=7.3 Hz), 7.15 (1H, m). MS m/z (%) 175 (M^+, 100), 160 (73), 132 (57), 130 (34), 120 (58), 118 (58), 91 (28). Calcd for $C_{12}H_{17}N$: M, 175.1359. Found: m/z 175.1351.

*3.1.13. N-[2-(2,2-Dimethylcyclopropyl)phenyl]phenylamine (**16b**).* Colorless oil; IR (neat) 3427 (NH), 3043, 2940, 1596, 1515, 1497, 1456, 1316, 746 cm^{-1}; ^1H NMR δ 0.81–0.82 (1H, m), 0.81 (3H, s), 0.87 (1H, dd, J=8.6, 6.6 Hz), 1.32 (3H, s), 1.65 (1H, dd, J=8.6, 6.1 Hz), 5.82 (1H, br s), 6.86 (1H, t, J=7.3 Hz), 6.94 (1H, dt, J=6.4, 0.90 Hz), 7.08–7.14 (4H, m), 7.24–7.29 (3H, m). MS m/z (%) 237 (M^+, 100), 222 (48), 194 (40), 182 (50), 180 (75). Calcd for $C_{17}H_{19}N$: M, 237.1517. Found: m/z 237.1519.

*3.1.14. 2-(2,2-Dimethylcylcopropyl)-4-methoxyphenylamine (**16c**).* Colorless oil; IR (neat) 3448 (NH), 3368 (NH), 2941, 1603, 1498, 1283, 1164, 1052, 1035, 810 cm^{-1}; ^1H NMR δ 0.74–0.76 (1H, m), 0.80–0.82 (1H, m), 0.81 (3H, s), 1.31 (3H, s), 1.57 (1H, dd, J=8.3, 5.8 Hz), 3.53 (2H, br s), 3.74 (3H, s), 6.59 (1H, s), 6.62–6.63 (2H, m). MS m/z (%) 191 (M^+, 100), 176 (61), 161 (19), 160 (19), 136 (37), 134 (18). Calcd for $C_{12}H_{17}NO$: M, 191.1308. Found: m/z 191.1308.

*3.1.15. Benzyl-[2-(2,2-dimethylcyclopropyl)phenyl]methylamine (**16d**).* Colorless oil; IR (neat) 3444 (NH), 2939, 1509, 1454, 1286, 1216, 1053, 699 cm^{-1}; ^1H NMR δ 0.74–0.77 (1H, m), 0.79 (3H, s), 0.79–0.81 (1H, m), 1.21 (3H, s), 1.51 (1H, dd, J=8.2, 5.5 Hz), 3.69 (3H, s), 3.95 (1H, br s), 4.32 (1H, d, J=13.8 Hz), 4.37 (1H, d, J=13.8 Hz), 6.54 (1H, d, J=8.6 Hz), 6.64 (1H, d, J=2.5 Hz), 6.67 (1H, dd, J=8.6, 2.5 Hz), 7.28 (1H, m), 7.36–7.40 (4H, m). MS m/z (%) 281 (M^+, 45), 190 (100), 148 (35), 91 (52). Calcd for $C_{19}H_{23}NO$: M, 281.1778. Found: m/z 281.1782.

*3.1.16. [4-Chloro-2-(2,2-dimethylcyclopropyl)phenyl]methylamine (**16e**).* Colorless oil; IR (neat) 3446 (NH), 2926, 1601, 1510, 1408, 1322, 1165, 805 cm^{-1}; ^1H NMR δ 0.73–0.76 (1H, m), 0.76 (3H, s), 0.83 (1H, dd, J=8.3, 6.5 Hz), 1.30 (3H, s), 1.41 (1H, dd, J=8.3, 5.5 Hz), 2.89 (3H, s), 3.90 (1H, br s), 6.50 (1H, d, J=8.6 Hz), 6.92 (1H, d, J=2.5 Hz), 7.08 (1H, dd, J=8.6, 2.5 Hz). MS m/z (%) 209 (M^+, 100), 194 (52), 174 (38), 159 (40), 154 (74), 152 (43), 117 (38). Calcd for $C_{12}H_{16}NCl$: M, 209.0971. Found: m/z 209.0971.

*3.1.17. 2-(2,2-Dimethylcyclopropyl)-N^4,N^4-dimethylbenzene-1,4-diamine (**16f**).* Colorless oil; IR (neat) 3449 (NH), 3364 (NH), 2926, 2856, 1603, 1508 cm^{-1}; ^1H NMR δ 0.66–0.74 (2H, m), 0.75 (3H, s), 1.23 (3H, s), 1.49–1.52 (1H, m), 2.72 (6H, s), 3.24 (2H, br s), 6.45 (1H, d, J=2.4 Hz), 6.50 (1H, dd, J=8.4, 6.5 Hz), 6.55 (1H, d, J=8.4 Hz). MS m/z (%) 204(M^+, 100), 203 (26), 187 (5), 173 (5), 160 (5), 159 (4), 149 (4). Calcd for $C_{13}H_{20}N_2$: M, 204.1626. Found: m/z 204.1633.

*3.1.18. 2-(2,2-Dimethylcyclopropyl)-N^1,N^4,N^4-trimethylbenzene-1,4-diamine (**16g**).* Colorless oil; IR (neat) 3429 (NH), 3061, 2940, 1515, 1312, 1226, 799, 355 cm^{-1}; ^1H NMR δ 0.73–0.77 (1H, m), 0.77 (3H, s), 0.79–0.82 (1H, m), 1.30 (3H, s), 1.48–1.52 (1H, m), 2.81 (6H, s), 2.88 (3H, s), 3.40 (1H, br s), 6.56–6.62 (2H, m), 6.69 (1H, m). MS m/z (%) 218 (M^+, 100), 203 (22), 188 (12), 173 (17), 160 (21), 146 (8), 117 (8). Calcd for $C_{14}H_{22}N_2$: M, 218.1781. Found: m/z 218.1781.

*3.1.19. [2-(2,2-Dimethylcyclopropyl)naphthalen-1-yl]methylamine (**16h**).* Yellow oil; IR (neat) 3388 (NH), 3057, 2941, 2885, 1613, 1568, 1509, 1450, 1376, 1122, 830, 807, 748 cm^{-1}; ^1H NMR δ 0.79 (3H, s), 0.87–0.98 (2H, m), 1.37 (3H, s), 1.85 (1H, dd, J=8.4, 6.0 Hz), 3.03 (3H, d, J=1.9 Hz), 3.91 (1H, br s), 7.19 (1H, d, J=8.4 Hz), 7.35–7.48 (3H, m), 7.79 (1H, d, J=4.1 Hz), 8.13 (1H, d, J=8.4 Hz). MS m/z (%) 225 (M^+, 43), 210 (100), 195 (19), 180 (36), 168 (66), 141 (11), 115 (10), 28 (22). Calcd for $C_{16}H_{19}N$: M, 225.1517. Found: m/z 225.1516.

*3.1.20. 2-(2,2-Dimethylcyclopropyl)anthracen-1-ylamine (**16i**).* Orange crystals; mp 120 °C (Hexane); IR (KBr) 3412 (NH), 3326 (NH), 2932, 1623, 1376, 877, 738 cm^{-1}; ^1H NMR δ 0.84–0.88 (1H, m), 0.87 (3H, s), 0.94 (1H, dd, J=8.6, 4.3 Hz), 1.39 (3H, s), 1.77 (1H, dd, J=8.6, 6.0 Hz), 4.45 (2H, br s), 7.18–7.39 (2H, m), 7.40–7.44 (2H, m), 7.94–7.99 (2H, m), 8.33 (2H, d, J=6.0 Hz). Anal. calcd for $C_{19}H_{19}N$: C, 86.31; H, 7.33; N, 5.36. Found; C, 86.54; H, 7.24; N, 5.26.

*3.1.21. 2-(2,2-Diethylcyclopropyl)-N^4,N^4-dimethylbenzene-1,4-diamine (**17a**).* Colorless oil; IR (neat) 3500 (NH), 3359 (NH), 2961, 1604, 1506, 1457, 1427, 806 cm^{-1}; ^1H NMR δ 0.73–0.80 (3H, m), 0.84 (3H, s), 1.02 (3H, t, J=7.4 Hz), 1.26–1.43 (2H, m), 1.62–1.74 (2H, m), 2.81 (6H, s), 3.48 (2H, br s), 6.54–6.64 (3H,m). MS m/z (%) 232 (M^+, 100), 203 (26), 159 (12), 149 (17). Calcd for $C_{15}H_{24}N_2$: M, 232.1938. Found: m/z 232.1938.

*3.1.22. 2-(2,2-Diethylcyclopropyl)naphtalen-1-ylamine (**17b**).* Colorless crystals; mp 37.5–38.0 °C (AcOEt–hexane); IR (KBr) 3439 (NH), 3342 (NH), 2956, 1626, 1397, 1372, 807, 744 cm^{-1}; ^1H NMR δ 0.75–0.80 (1H, m), 0.78 (3H, s), 0.82–0.87 (2H, m), 1.06–1.09 (3H, m), 1.34–1.43 (2H, m), 1.71–1.80 (2H, m), 4.37 (2H, br s), 7.16–7.24 (2H, m), 7.35–7.43 (2H,m), 7.73–7.77 (2H, m). Anal. calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found; C, 85.28; H, 8.78; N, 5.79.

*3.1.23. 2-(2,2-Diethyl-cyclopropyl)-anthracen-1-ylamine (**17c**).* Colorless oil; IR (neat) 3476 (NH), 3395 (NH), 3053, 2961, 2932, 1726, 1622, 1429, 1382, 870, 737 cm^{-1}; ^1H NMR δ 0.77–0.82 (1H, m), 0.80 (3H, s), 0.83–0.93 (2H, m), 1.11 (3H, t, J=7.4 Hz), 1.40 (2H, d, J=4.3 Hz), 1.77–1.86 (2H, m), 4.55 (2H, br s), 7.22 (2H, t, J=8.6 Hz),

7.39–7.93 (2H, m), 7.94–8.00 (2H,m), 8.34 (2H, d, *J*=8.0 Hz). MS *m/z* (%) 232 (M^+, 100), 203 (26), 159 (12), 149 (17). Calcd for $C_{15}H_{24}N_2$: *M*, 289.1830. Found: *m/z* 289.1825.

*3.1.24. N^4,N^4-Dimethyl-2-(2,2,3-trimethylcyclopropyl)benzene-1,4-diamine (**17d**).* Colorless oil; IR (neat) 3445 (NH), 3358 (NH), 2939, 2866, 1603, 1508, 1376, 1340, 804 cm^{-1}; ^1H NMR δ 0.81 (3H, s), 1.00 (1H, q, *J*=6.0 Hz), 1.18 (1H, d, *J*=6.0 Hz), 1.23 (3H, d, *J*=6.0 Hz), 1.27 (3H, s), 2.81 (6H, s), 3.32 (2H, br s), 6.56–6.65 (3H, m). MS *m/z* (%) 218 (M^+, 100), 203 (22), 187 (10), 174 (11), 160 (19), 149 (15). Calcd for $C_{14}H_{22}N_2$: *M*, 218.1782. Found: *m/z* 218.1782.

*3.1.25. 2-(2,2,3-Trimethylcyclopropyl)naphtalen-1-ylamine (**17e**).* Colorless oil; IR (neat) 3476 (NH), 3391 (NH), 3055, 2940, 1614, 1401, 805, 751 cm^{-1}; ^1H NMR δ 0.80 (3H, s), 1.11 (1H, q, *J*=6.0 Hz), 1.29 (3H, d, *J*=6.0 Hz), 1.34 (4H, m), 4.26 (2H, br s), 7.19–7.24 (2H, m), 7.26–7.45 (2H, m), 7.74–7.82 (2H, m). MS *m/z* (%) 225 (M^+, 100), 210 (80), 194 (21), 182 (44), 180 (27), 156 (28), 143 (22), 127 (7), 115 (7). Calcd for $C_{16}H_{19}N$: *M*, 225.1517. Found: *m/z* 225.1517.

*3.1.26. 2-(2,2,3-Trimethylcyclopropyl)anthracen-1-ylamine (**17f**).* Colorless oil; IR (neat) 3456 (NH), 3390 (NH), 2927, 2863, 1609, 1381, 868, 737 cm^{-1}; ^1H NMR δ 0.84 (3H, s), 1.10 (1H, q, *J*=6.0 Hz), 1.30 (3H, d, *J*=6.0 Hz), 1.36 (4H, m), 4.40 (2H, br s), 7.23 (1H, s), 7.28–7.44 (3H, m), 7.92–8.00 (2H, m), 8.33 (2H, d, *J*=6.7 Hz). MS *m/z* (%) 275 (M^+, 100), 260 (55), 244 (17), 232 (24), 217 (20), 193 (18), 178 (9), 165 (9), 115 (8). Calcd for $C_{20}H_{21}N$: *M*, 275.1673. Found: *m/z* 275.1672.

*3.1.27. N^4,N^4-Dimethyl-2-(2,2,3,3-tetramethylcyclopropyl)benzene-1,4-diamine (**17g**).* Colorless oil; IR (neat) 3456 (NH), 3361 (NH), 2936, 2788, 1602, 1505, 800 cm^{-1}; ^1H NMR δ 1.01 (6H, s), 1.25 (1H, s), 1.29 (6H, s), 2.80 (6H, s), 3.46 (2H, br s), 6.57–6.66 (3H, m). MS *m/z* (%) 232 (M^+, 100), 217 (35), 201 (10), 189 (12), 174 (18), 160 (17), 149 (10), 130 (8). Calcd for $C_{15}H_{24}N_2$: *M*, 232.1937. Found: *m/z* 232.1937.

*3.1.28. 2-(2,2,3,3-Tetramethylcyclopropyl)naphtalen-1-ylamine (**17h**).* Colorless crystal; mp 76–77 °C (AcOEt–hexane); IR (KBr) 3447 (NH), 3379 (NH), 2934, 1618, 1394, 805, 760 cm^{-1}; ^1H NMR δ 1.02 (6H, s), 1.36 (6H, s), 1.39 (1H, s), 4.27 (2H, br s), 7.20–7.25 (2H, m), 7.26–7.45 (2H, m), 7.74–7.82 (2H, m). Anal. calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found; C, 85.23; H, 8.81; N, 5.78.

*3.1.29. 2-(2,2,3,3-Tetramethylcyclopropyl)anthracen-1-ylamine (**17i**).* Colorless oil; IR (neat) 3429 (NH), 3360 (NH), 2938, 1607, 1378, 876, 741 cm^{-1}; ^1H NMR δ 1.05 (6H, s), 1.39 (6H, s), 1.45 (1H, s), 4.42 (2H, br s), 7.26 (1H, s), 7.40–7.44 (3H, m), 7.93–8.01 (2H, m), 8.34 (2H, d, *J*=10.3 Hz). MS *m/z* (%) 289 (M^+, 100), 246 (32), 232 (27), 204 (18), 165 (13), 115 (7). Calcd for $C_{21}H_{23}N$: *M*, 289.1828. Found: *m/z* 289.1825.

*3.1.30. 2-(2,2-Dimethylcyclopropyl)-3-methoxyphenylamine (**18a**).* Yellow oil; IR (neat) 3482 (NH), 3385 (NH), 2952, 1612, 1468, 1256, 1132, 1096, 766 cm^{-1}; ^1H NMR δ 0.67–0.72 (1H, m), 0.85 (3H, s), 0.91 (1H, dd, *J*=8.6, 4.1 Hz), 1.25 (3H, s), 1.30 (1H, dd, *J*=8.6, 6.4 Hz), 3.76 (3H, s), 3.89 (2H, br s), 6.29 (1H, d, *J*=8.2 Hz), 6.32 (1H, d, *J*=8.2 Hz), 6.96 (1H, t, *J*=8.2 Hz). MS *m/z* (%) 191 (M^+, 100), 176 (97), 160 (25), 148 (26), 136 (84), 123 (24), 106 (28). Calcd for $C_{12}H_{17}NO$: *M*, 191.0310. Found: *m/z* 191.1309.

*3.1.31. [2-(2,2-Dimethylcyclopropyl)-3-methoxyphenyl]methylamine (**18b**).* Yellow oil; IR (neat) 3450 (NH), 2952, 2833, 1599, 1475, 1255, 1163, 1115, 762 cm^{-1}; ^1H NMR δ 0.66 (1H, br s), 0.81 (3H, s), 0.91 (1H, dd, *J*=8.7, 6.3 Hz), 1.19–1.24 (1H, m), 1.28 (3H, s), 2.87 (3H, s), 3.77 (3H, s), 4.23 (1H, br s), 6.29 (2H, d, *J*=8.3 Hz), 7.09 (1H, t, *J*=8.3 Hz). MS *m/z* (%) 206 (16), 205 (M^+, 100), 190 (75), 174 (18), 150 (74), 148 (86), 133 (22), 118 (15), 106 (11), 91 (21). Calcd for $C_{13}H_{19}NO$: *M*, 205.1466. Found: *m/z* 205.1464.

*3.1.32. 2-(2,2-Dimethylcyclopropyl)-3-methylphenylamine (**18c**).* Colorless oil; IR (neat) 3547 (NH), 2923, 2852, 1651, 1215, 929, 758 cm^{-1}; ^1H NMR δ 0.67 (1H, dd, *J*=6.5, 4.3 Hz), 0.88 (3H, s), 0.95–1.01 (1H, m), 1.31 (3H, s), 1.46 (1H, t, *J*=6.5 Hz), 2.29 (3H, s), 3.89 (2H, brs, NH_2), 6.51 (1H, d, *J*=7.5 Hz), 6.58 (1H, d, *J*=7.5 Hz), 6.92 (1H, t, *J*=7.5 Hz). MS *m/z* (%) 175 (M^+, 100), 160 (88), 149 (53), 145 (39), 132 (80), 120 (90), 91 (33), 57 (40), 43 (33). Calcd for $C_{12}H_{17}N$: *M*, 175.1361. Found: *m/z* 175.1359.

*3.1.33. [2-(2,2-Dimethylcyclopropyl)-3-methylphenyl]methylamine (**18d**).* Colorless oil; IR (neat) 3458 (NH), 2925, 2812, 1583, 1470, 1278, 1158, 767 cm^{-1}; ^1H NMR δ 0.55–0.65 (1H, m), 0.82 (3H, s), 0.96–0.98 (1H, m), 1.31 (3H, s), 1.33–1.42 (1H, m), 2.29 (3H, s), 2.86 (3H, s), 4.09 (1H, br s), 6.42–6.54 (2H, m), 7.01–7.06 (1H, m). MS *m/z* (%) 189 (M^+, 100), 174 (88), 158 (22), 146 (80), 134 (60), 132 (82), 120 (58). Calcd for $C_{13}H_{19}N$: *M*, 189.1517. Found: *m/z* 189.1517.

*3.1.34. 3-Chloro-2-(2,2-dimethylcycloprpyl)phenylamine (**18e**).* Colorless oil; IR (neat) 3394 (NH), 2923, 1610, 1446, 1296, 1123, 761 cm^{-1}; ^1H NMR δ 0.69 (1H, m), 0.91 (3H, s), 0.93–1.01 (1H, m), 1.32 (3H, s), 1.50 (1H, m), 3.98 (2H, br s), 6.53 (1H, d, *J*=7.9 Hz), 6.76 (1H, d, *J*=7.9 Hz), 6.91 (1H, t, *J*=7.9 Hz). MS *m/z* (%) 197 (M^+, 28), 195 (92), 180 (85), 140 (100), 130 (24), 117 (35). Calcd for $C_{11}H_{14}ClN$: *M*, 195.0815. Found: *m/z* 195.0815.

*3.1.35. [3-Chloro-2-(2,2-dimethylcyclopropyl)phenyl]methylamine (**18f**).* Colorless oil; IR (neat) 3458 (NH), 2954, 2867, 1592, 1455, 1312, 1127, 756 cm^{-1}; ^1H NMR δ 0.86 (3H, s), 0.96–1.02 (1H, m), 1.31 (3H, s), 1.38–1.41 (1H, m), 1.52–1.55 (1H, m), 2.85 (3H, s), 4.34 (1H, br s), 6.46 (1H, d, *J*=8.2 Hz), 6.71 (1H, d, *J*=8.2 Hz), 7.02 (1H, t, *J*=8.2 Hz). MS *m/z* (%) 211 (M^+, 28), 209 (90), 194 (51), 166 (66), 154 (100), 152 (64), 131 (30), 117 (40). Calcd for $C_{12}H_{16}ClN$: *M*, 209.0971. Found: *m/z* 209.0973.

*3.1.36. 2-(2,2-Dimethylcyclopropyl)-5-methoxyphenylamine (**19a**).* Colorless oil; IR (neat) 3476 (NH), 3380 (NH), 2940, 1622, 1512, 1446, 1294, 1212, 1030, 839 cm^{-1}; ^1H NMR δ 0.69 (1H, dd, *J*=5.5, 4.7 Hz), 0.78 (1H, dd, *J*=8.5, 4.5 Hz), 0.81 (3H, s), 1.30 (3H, s), 1.47 (1H, dd, *J*=8.5, 5.7 Hz), 3.74 (3H, s), 3.77 (2H, br s), 6.25–6.27 (2H, m), 6.85–6.87 (1H, m). MS *m/z* (%) 191 (M^+, 68), 176 (100), 161 (15), 136 (20), 123 (11). Calcd for $C_{12}H_{17}NO$: *M*, 191.1310. Found: *m/z* 191.1313.

*3.1.37. 2-(2,2-Dimethylcyclopropyl)-5-methoxyphenylamine (**19b**).* Yellow oil; IR (neat) 3444 (NH), 2939, 1619, 1584, 1521, 1455, 1212, 1172, 1043, 829 cm^{-1}; ^1H NMR δ 0.68 (1H, t, *J*=5.2 Hz), 0.76 (3H, s), 0.78–0.81 (1H, m), 1.28 (3H, s), 1.38 (1H, dd, *J*=8.0, 5.2 Hz), 2.89 (3H, s), 3.79 (3H, s), 3.96 (1H, br s), 6.18–6.20 (2H, m), 6.86 (1H, d, *J*=8.3 Hz). MS *m/z* (%) 205 (M^+, 74), 190 (100), 174 (16), 160 (28), 148 (42), 133 (12), 117 (11), 91 (16). Calcd for $C_{13}H_{19}NO$: *M*, 205.1465. Found: *m/z* 205.1462.

*3.1.38. 2-(2,2-Dimethylcyclopropyl)-5-methylphenylamine (**19c**).* Colorless oil; IR (neat) 3472 (NH), 3379 (NH), 2940, 1623, 1513, 1445, 1296, 1209, 1036, 805 cm^{-1}; ^1H NMR δ 0.70–0.72 (1H, m), 0.76–0.81 (1H, m), 0.81 (3H, s), 1.29 (3H, s), 1.50 (1H, dd, *J*=8.2, 6.0 Hz), 2.24 (3H, s), 3.71 (2H, br s), 6.50–6.52 (2H, m), 6.83–6.86 (1H, m). MS *m/z* (%) 175 (M^+, 81), 160 (100), 145 (42), 132 (21), 120 (59), 117 (10), 91 (19), 77 (3). Calcd for $C_{12}H_{17}N$: *M*, 175.1361. Found: *m/z* 175.1360.

*3.1.39. [2-(2,2-Dimethylcyclopropyl)-5-methylphenyl]methylamine (**19d**).* Colorless oil; IR (neat) 3443 (NH), 2937, 1579, 1522, 1445, 1302, 842, 804 cm^{-1}; ^1H NMR δ 0.69–0.72 (1H, m), 0.76 (3H, s),

0.76–0.82 (1H, m), 1.28 (3H, s), 1.41 (1H, dd, *J*=8.3, 6.0 Hz), 2.31 (3H, s), 2.89 (3H, s), 3.89 (1H, br s), 6.42–6.48 (2H, m), 6.83–6.85 (1H, m). MS *m/z* (%) 189 (M^+, 93), 174 (100), 159 (30), 144 (34), 134 (44), 132 (62), 117 (17), 91 (10), 77 (8). Calcd for $C_{13}H_{19}N$: *M*, 189.1517. Found: *m/z* 189.1518.

*3.1.40. 5-Chloro-2-(2,2-dimethylcyclopropyl)phenylamine (**19e**).* Colorless oil; IR (neat) 3485 (NH), 3394 (NH), 2942, 1615, 1494, 1418, 1197, 1099, 901, 803 cm^{-1}; ^1H NMR δ 0.70–0.74 (1H, m), 0.80 (3H, s), 0.80–0.84 (1H, m), 1.30 (3H, s), 1.47 (1H, dd, *J*=8.4, 5.8 Hz), 3.83 (2H, br s), 6.63–6.64 (2H, m), 6.85–6.89 (1H, m). MS *m/z* (%) 195 (M^+, 97), 180 (96), 160 (31), 145 (100), 140 (82), 130 (29), 117 (23), 77 (10). Calcd for $C_{11}H_{14}ClN$: *M*, 195.0815. Found: *m/z* 195.0817.

*3.1.41. [5-Chloro-2-(2,2-dimethylcyclopropyl)phenyl]methylamine (**19f**).* Colorless oil; IR (neat) 3448 (NH), 2925, 1598, 1511, 1407, 1278, 884 cm^{-1}; ^1H NMR δ 0.69–0.74 (1H, m), 0.74 (3H, s), 0.81 (1H, dd, *J*=8.4, 4.5 Hz), 1.25 (3H, s), 1.38 (1H, dd, *J*=8.4, 5.8 Hz), 2.88 (3H, m), 4.00 (1H, br s), 6.53–6.61 (2H, m), 6.84–6.89 (1H, m). MS *m/z* (%) 211 (M^+, 32), 209 (100), 194 (79), 166 (38), 159 (48), 154 (79), 117 (32). Calcd for $C_{12}H_{16}ClN$: *M*, 209.0971. Found: *m/z* 209.0971.

*3.1.42. 2-(2,2-Dimethylcyclopropyl)-5-trifluoromethylphenylamine (**19g**).* Colorless oil; IR (neat) 3489 (NH), 3400 (NH), 2945, 1623, 1435, 1336, 1164, 1120, 818 cm^{-1}; ^1H NMR δ 0.78–0.82 (1H, m), 0.80 (3H, s), 0.88 (1H, dd, *J*=10.4, 4.6 Hz), 1.33 (3H, s), 1.51–1.53 (1H, m), 3.93 (2H, br s), 6.89–6.93 (2H, m), 7.03–7.25 (1H, m). MS *m/z* (%) 229 (M^+, 81), 214 (96), 186 (28), 174 (100), 166 (17), 145 (24). Calcd for $C_{12}H_{14}NF_3$: *M*, 229.1079. Found: *m/z* 229.1076.

*3.1.43. 2-(2,2-Dimethylcyclopropyl)-6-methylphenylamine (**20a**).* Colorless oil; IR (neat) 3482 (NH), 3395 (NH), 2940, 1614, 1465, 1275, 1123, 872, 746 cm^{-1}; ^1H NMR δ 0.75–0.77 (1H, m), 0.80–0.83 (1H, m), 0.80 (3H, s), 1.32 (3H, s), 1.53–1.55 (1H, m), 2.19 (3H, s), 3.74 (2H, br s), 6.63 (1H, t, *J*=7.6 Hz), 6.86 (1H, d, *J*=7.6 Hz), 6.93 (1H, d, *J*=7.6 Hz). MS *m/z* (%) 176 (M^+, 12), 175 (84), 160 (100), 145 (51), 120 (67), 117 (15), 91 (13). Calcd for $C_{12}H_{17}N$: *M*, 175.1361. Found: *m/z* 175.1361.

*3.1.44. 2-Chloro-6-(2,2-dimethylcyclopropyl)phenylamine (**20b**).* Colorless oil; IR (neat) 3491 (NH), 3395 (NH), 2943, 1611, 1455, 1279, 1073, 857, 762 cm^{-1}; ^1H NMR δ 0.75–0.78 (1H, m), 0.80 (3H, s), 0.84–0.86 (1H, m), 1.32 (3H, s), 1.52–1.57 (1H, m), 4.17 (2H, br s), 6.61 (1H, t, *J*=7.7 Hz), 6.88 (1H, d, *J*=7.7 Hz), 7.12 (1H, d, *J*=7.7 Hz). MS *m/z* (%) 195 (M^+, 45), 180 (100), 160 (18), 144 (35), 127 (30). Calcd for $C_{11}H_{14}NCl$: *M*, 195.0815. Found: *m/z* 195.0824.

*3.1.45. (2,2-Dimethylcyclopropyl)-(2-methoxyphenyl)methylamine (**21a**).* Colorless oil; IR (neat) 3065, 2946, 1595, 1503, 1273, 1113, 1030, 743 cm^{-1}; ^1H NMR δ 0.30–0.33 (1H, m), 0.60 (1H, dd, *J*=7.0, 4.6 Hz), 1.00 (3H, s), 1.12 (3H, s), 2.14 (1H, dd, *J*=7.0, 4.0 Hz), 2.86 (3H, s), 3.82 (3H, s), 6.83–6.92 (3H, m), 7.09–7.13 (1H, m). MS *m/z* (%) 205 (M^+, 10), 190 (100), 174 (75), 134 (22), 121 (12). Calcd for $C_{13}H_{19}NO$: *M*, 205.1467. Found: *m/z* 205.1467.

*3.1.46. (2,2-Dimethylcyclopropyl)methyl-o-tolylamine (**21b**).* Colorless oil; IR (neat) 3066, 2945, 2867, 1599, 1494, 1370, 1300, 1213, 1107, 984, 842, 761 cm^{-1}; ^1H NMR δ 0.12–0.15 (1H, m), 0.53 (1H, dd, *J*=6.9, 4.5 Hz), 1.04 (3H, s), 1.08 (3H, s), 2.20–2.23 (1H, m), 2.24 (3H, s), 2.66 (3H, s), 6.89–6.94 (1H, m), 7.10–7.20 (3H, m). MS *m/z* (%) 189 (M^+, 20), 174 (100), 144 (15), 132 (28), 118 (9), 91 (14). Calcd for $C_{13}H_{19}N$: *M*, 189.1518. Found: *m/z* 189.1516.

*3.1.47. (2-Chloro-phenyl)-(2,2-dimethylcyclopropyl)methylamine (**21c**).* Colorless oil; IR (neat) 3067, 2947, 1589, 1484, 1441, 1122, 1052, 983, 876, 753 cm^{-1}; ^1H NMR δ 0.20–0.23 (1H, m), 0.57 (1H, dd, *J*=7.0, 4.5 Hz), 1.04 (3H, s), 1.09 (3H, s), 2.24 (1H, dd, *J*=7.0, 4.0 Hz), 2.84 (3H, s), 6.88–6.92 (1H, m), 7.15–7.19 (1H, m), 7.22–7.24 (1H, m), 7.28–7.30 (1H, m). MS *m/z* (%) 209 (M^+, 4), 194 (100), (174 91), 158 (21), 144 (20), 138 (11), 111 (10). Calcd for $C_{12}H_{16}NCl$: *M*, 209.0971. Found: *m/z* 209.0969.

*3.1.48. 7-(2,2-Dimethylcyclopropyl)-2,3-dihydro-1H-indole (**23**).* Colorless oil; IR (neat) 3394 (NH), 3060, 2941, 2864, 1726, 1598, 1453, 1257, 1028, 746 cm^{-1}; ^1H NMR δ 0.73–0.76 (2H, m), 0.82 (3H, s), 1.26 (3H, s), 1.51–1.56 (1H, m), 3.06 (2H, t, *J*=8.4 Hz), 3.52–3.61 (2H, m), 3.72 (1H, br s), 6.64 (1H, t, *J*=7.4 Hz), 6.76 (1H, d, *J*=7.4 Hz), 6.98 (1H, d, *J*=7.4 Hz). MS *m/z* (%) 187 (M^+, 82), 172 (100), 157 (20), 144 (18), 132 (31), 117 (10), 91 (5). Calcd for $C_{13}H_{17}N$: *M*, 187.1361. Found: *m/z* 187.1362.

*3.1.49. 10-(2,2-Dimethylcyclopropyl)-10H-phenothiazine (**25a**).* Colorless oil; IR (neat) 3066, 2948, 1573, 1461, 1372, 1309, 1236, 1127, 1038, 909, 748 cm^{-1}; ^1H NMR δ 0.47–0.50 (1H, m), 1.02 (3H, s), 1.05 (1H, dd, *J*=6.9, 5.2 Hz), 1.33 (3H, s), 2.64 (1H, dd, *J*=6.9, 4.0 Hz), 6.90–6.94 (2H, m), 7.05–7.18 (6H, m). MS *m/z* (%) 267 (M^+, 100), 252 (70), 236 (17), 223 (17), 198 (65), 154 (9), 119 (7). Calcd for $C_{17}H_{17}NS$: *M*, 267.1082. Found: *m/z* 267.1085.

*3.1.50. 10-(2,2-Dimethylcyclopropyl)-10H-phenoxazine (**25b**).* Colorless oil; IR (neat) 3065, 2927, 1482, 1338, 1293, 1268, 745 cm^{-1}; ^1H NMR δ 0.55–0.56 (1H, m), 1.04 (1H, dd, *J*=7.1, 5.2 Hz), 1.07 (3H, s), 1.31 (3H, s), 2.17 (1H, dd, *J*=7.1, 4.0 Hz), 6.77–6.78 (5H, m), 6.89–6.92 (3H, m). MS *m/z* (%) 251 (M^+, 100), 250 (33), 236 (65), 220 (31), 183 (23), 182 (86). Calcd for $C_{17}H_{17}NO$: *M*, 251.1310. Found: *m/z* 251.1319.

*3.1.51. 1-(2,2-Dimethylcyclopropyl)-10H-phenothiazine (**26a**).* Yellow oil; IR (neat) 3395 (NH), 2947, 2926, 1568, 1475, 1434, 1292, 1123, 884, 741 cm^{-1}; ^1H NMR δ 0.73–0.77 (1H, m), 0.79 (3H, s), 0.93 (1H, dd, *J*=8.5, 4.6 Hz), 1.40 (3H, s), 1.54 (1H, m), 6.19 (1H, br s), 6.57 (1H, m), 6.82–6.89 (3H, m), 7.01–7.04 (2H, m). MS *m/z* (%) 267 (M^+, 100), 252 (26), 273 (20), 224 (42), 211 (63). Calcd for $C_{17}H_{17}NS$: *M*, 267.1082. Found: *m/z* 267.1083.

*3.1.52. 1-(2,2-Dimethylcyclopropyl)-10H-phenoxazine (**26b**).* Colorless oil; IR (neat) 3429 (NH), 3063, 2941, 1497, 1467, 1411, 1287, 742 cm^{-1}; ^1H NMR δ 0.70–0.73 (1H, m), 0.83–0.86 (1H, m), 0.86 (3H, s), 1.33 (3H, s), 1.41 (1H, dd, *J*=8.5, 5.8 Hz), 5.22 (1H, br s), 6.41–6.42 (1H, m), 6.54–6.59 (3H, m), 6.62–6.68 (2H, m), 6.72–6.76 (1H, m). MS *m/z* (%) 251 (M^+, 100), 236 (56), 221 (28), 220 (19), 208 (68), 207 (32), 196 (38), 195 (94). Calcd for $C_{17}H_{17}NO$: *M*, 251.1308. Found: *m/z* 251.1308.

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