Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 61 (2005) 10262–10276

# Direct alkenylation of arylamines at the *ortho*-position with magnesium alkylidene carbenoids and some theoretical studies of the reactions

Tsuyoshi Satoh,[a,*] Yumi Ogino[a] and Kaori Ando[b,*]

[a]*Department of Chemistry, Faculty of Science, Tokyo University of Science; Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
[b]*College of Education, University of the Ryukyus, Nishihara-cho, Okinawa 903-0213, Japan*

Received 22 July 2005; accepted 5 August 2005

Available online 12 September 2005

**Abstract**—1-Chlorovinyl *p*-tolyl sulfoxides were synthesized from ketones and chloromethyl *p*-tolyl sulfoxide in high yields. Treatment of the sulfoxides with isopropylmagnesium chloride at −78 °C in toluene gave magnesium alkylidene carbenoids (α-chloro alkenylmagnesium chlorides), which were treated with *N*-lithio arylamines to afford *ortho*-alkenylated arylamines in moderate yields. The reaction, in some cases, proceeded in a highly stereospecific manner at the carbon bearing the chlorine and the sulfinyl group. The structures of the α-chloro alkenylmagnesium chlorides and the reactivity of the *N*-lithio *meta*-substituted anilines were studied at the B3LYP and MP2 levels of theory with the 6-31(+)G* basis set. This reaction offers a quite novel and direct alkenylation of arylamines at the *ortho*-position of the aromatic ring.


## 1. Introduction

Arylamines, including anilines, are undoubtedly one of the most important and fundamental compounds in organic chemistry. Arylamines have been widely used as the material for medicine, dyes, and other chemical products. In view of this importance of arylamines, innumerable studies are still being actively carried out concerning their chemistry and synthesis.[1]

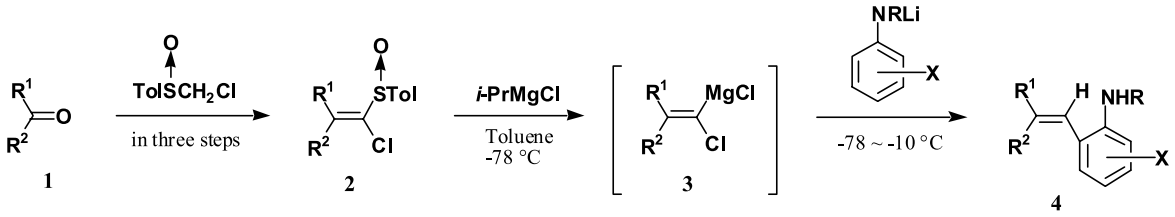
The alkylation of the aromatic ring of arylamines is quite important chemistry for the synthesis of derivatives of arylamines. However, direct alkylation of arylamines having a free amino group is not a so easily accessible process. For example, under normal Friedel–Crafts alkylation conditions, the reaction is inhibited by complex formation of the amino group with the acid catalyst. An even more difficult process is the direct alkenylation of the arylamines. To the best of our knowledge, only two reports concerning the direct alkenylation of arylamines on the aromatic ring have been published so far by Sartori et al.[2] and Yamaguchi et al.[3] Sartori's group synthesized 1,1-diarylethylenes directly from substituted anilines and phenylacetylene in the presence of montmorillonite KSF.[2] Yamaguchi's group synthesized *ortho*-vinylated anilines directly from anilines with ethyne in the presence of $SnCl_4$–$Bu_3N$.[3]

We recently reported a new method for the generation of magnesium alkylidene carbenoids **3** from 1-chlorovinyl *p*-tolyl sulfoxides **2**, which were synthesized from ketones **1** and chloromethyl *p*-tolyl sulfoxide in three steps in high yields,[4] with a Grignard reagent[5] via a sulfoxide–magnesium exchange reaction.[6] From the generated magnesium alkylidene carbenoids **3**, a new method for the synthesis of *tetra*-substituted olefins[7] and allenes[8] was realized.

In continuation of our interest in the development of new synthetic methods by utilizing the generated magnesium alkylidene carbenoids **3** in organic synthesis, we investigated the reaction of **3** with *N*-lithio amines and found that the reaction with *N*-lithio arylamines gave *ortho*-alkenylated arylamines **4** in moderate to good yields (Scheme 1).[9] In this paper we describe in detail the direct alkenylation of arylamines at the *ortho*-position with magnesium alkylidene carbenoids and theoretical studies of the reaction.

*Keywords*: Sulfoxide–magnesium exchange reaction; Magnesium alkylidene carbenoid; Alkenylation; *ortho*-Alkenylated arylamine; Theoretical study.
* Corresponding authors. Tel.: +81 3 5228 8272; fax: +81 3 3235 2214; e-mail: tsatoh@ch.kagu.tus.ac.jp

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.08.035




**Scheme 1.**

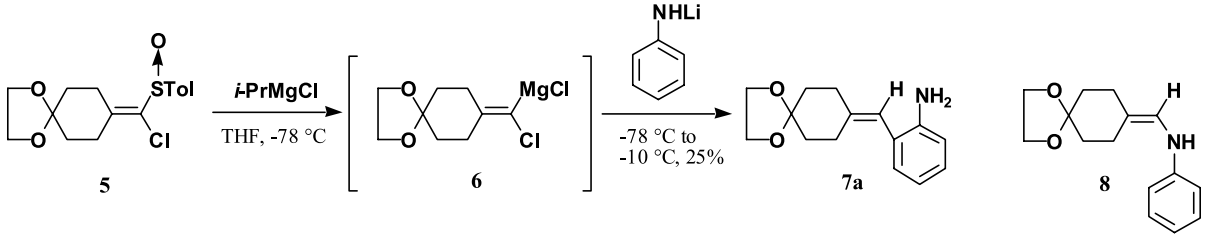
## 2. Results and discussion

### 2.1. Direct *ortho*-alkenylation of arylamines including aniline with the magnesium alkylidene carbenoid 6

1-Chlorovinyl *p*-tolyl sulfoxide **5**, which was synthesized from 1,4-cyclohexanedione mono ethylene ketal and chloromethyl *p*-tolyl sulfoxide in high yield,[4,7] in dry THF was treated with *t*-BuMgCl (0.12 equiv) at −78 °C to remove a trace of moisture in the reaction mixture. After 10 min, *i*-PrMgCl (2.8 equiv) was added to the reaction mixture. The sulfoxide–magnesium exchange reaction took place instantaneously to give the magnesium alkylidene carbenoid **6**.[8b] First, reaction of **6** with *N*-lithio piperidine and *N*-lithio *n*-hexylamine was investigated, however, only a rather complex mixture was obtained with these *N*-lithio alkylamines.

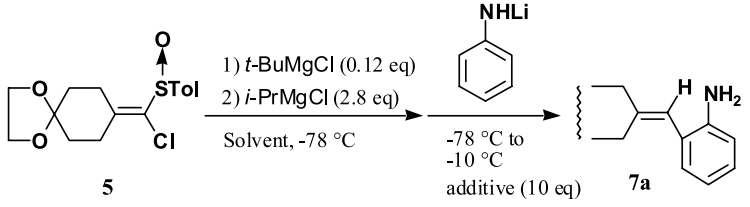
Next, the reaction was investigated with *N*-litho arylamines. *N*-litho aniline (3 equiv), which was generated from aniline and *n*-BuLi in THF at −78 °C, was added to the solution of the magnesium alkylidene carbenoid **6**, generated as above, through a cannula at −78 °C and the temperature of the reaction mixture was gradually allowed to warm to −10 °C. We obtained a colorless crystalline product in 25% yield. The product showed $C_{15}H_{19}NO_2$ as the molecular formula and N–H absorption on its IR spectrum. At this stage two products, alkenyl aniline **7a** and enamine **8**, were expected to be produced. $^1$H NMR showed two NH protons and only four aromatic protons ($\delta$ 6.69 (1H, d), 6.73 (1H, t), 6.98 (1H, d), 7.06 (1H, t)). From the coupling pattern of these aromatic protons and the $^{13}$C NMR, the structure of the product was unambiguously determined to be the *ortho*-alkenylated aniline **7a** (Scheme 2).

We were somewhat surprised and pleased by this result because no report has been published on the reaction of anilines with alkylidene carbenes (or carbenoids).[10] In addition, this reaction was recognized to be a quite novel and direct alkenylation of arylamines on the aromatic ring.




**Scheme 2.**

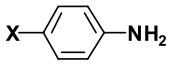
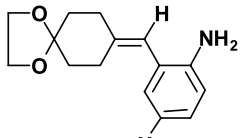
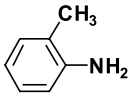
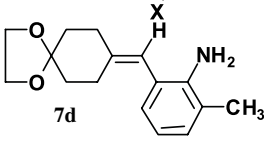
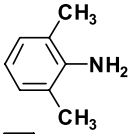
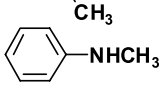
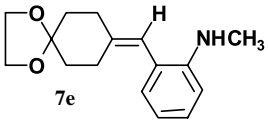
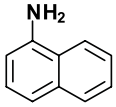
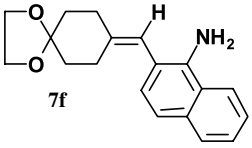
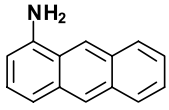
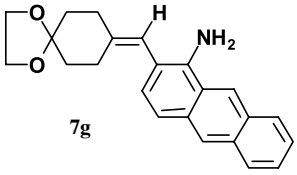
**Table 1**. Conditions for the *ortho*-alkenylation of aniline




| Entry | Solvent | Additive | Yield of **7a** % |
|---|---|---|---|
| 1 | THF | No | 25 |
| 2 | CPME[a] | No | 9 |
| 3 | Toluene | No | 49 |
| 4 | Toluene | DMPU[b] | 14 |
| 5 | Toluene | HMPA | 14 |
| 6 | Toluene | 12-Crown-6 | 16 |
| 7 | Toluene | TMEDA | 25 |
| 8 | Toluene | DME | 37 |
| 9 | Toluene | CPME[a] | 40 |

[a] Cyclopentyl methyl ether.
[b] 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)pyrimidinone.

**Table 2**. Synthesis of *ortho*-alkenylated arylamines **7** by the reaction of magnesium alkylidene carbenoid **6** with *N*-lithio arylamines

| Entry | Arylamine[a] | *ortho*-Alkenylated arylamine **7** | (Yield, %) |
|---|---|---|---|
| 1 |  |  **7b** X=$OCH_3$ **7c** X=Cl | (44) (28) |
| 2 | | | |
| 3 |  |  **7d** | (32) |
| 4 |  | —[b] | |
| 5 |  |  **7e** | (38) |
| 6 |  |  **7f** | (66) |
| 7 |  |  **7g** | (60) |

[a] Three equivalents of *N*-lithio arylamines were reacted with **6**.
[b] No *para*-alkenylated product was obtained.

First of all, we investigated the best conditions for this *ortho*-alkenylation and the results are summarized in Table 1.

The use of cyclopentyl methyl ether (CPME) as a solvent gave a miserable yield (entry 2). As shown in entry 3, toluene was found to be a good solvent for the reaction and 49% yield of **7a** was obtained. Encouraged by this result, several reaction conditions were investigated in toluene in the presence of an additive. However, the additives investigated were found to be ineffective (entries 4–9). We decided to use toluene as the solvent without any additive throughout this study.

Next, we investigated the generality of this reaction of the magnesium alkylidene carbenoid **6** with other *N*-lithio arylamines under the conditions described above and the results are summarized in Table 2. The reaction with the aniline having an electron-donating group ($OCH_3$) at the 4-position gave a similar yield of **7b** (entry 1), however, the aniline having an electron-withdrawing group (Cl) gave **7c** in markedly diminished yield (entry 2). The reaction with *ortho*-toluidine gave the *ortho*-alkenylated aniline **7d** (entry 3). Interestingly, 2,6-dimethylaniline gave no *para*-alkenylated aniline. This result indicated that this reaction only gives *ortho*-alkenylated products.

*N*-Methylaniline gave an *ortho*-alkenylated product **7e** in 38% yield (entry 5). Interestingly, the reaction with 1-aminonaphthalene and 1-aminoanthracene gave much better yields of the *ortho*-alkenylated aryl amines **7f** and **7g**, respectively, (entries 6 and 7).

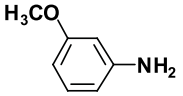
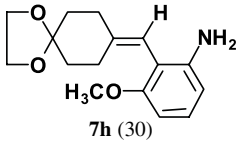
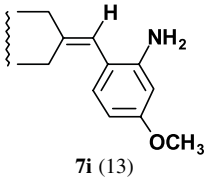
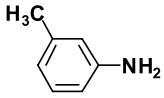
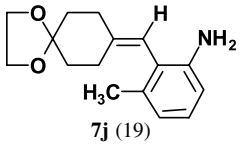
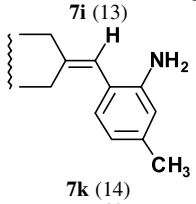
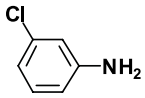
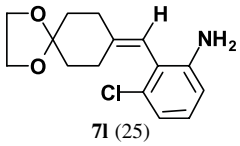
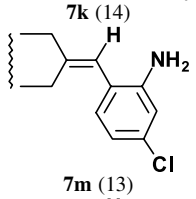
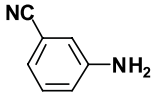
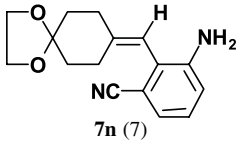
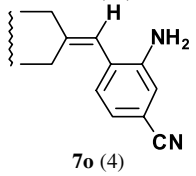
The reaction of the magnesium alkylidene carbenoid **6** with *meta*-substituted anilines is quite interesting because the regioisomers are expected to be obtained. We investigated the reaction with four *meta*-substituted anilines and the results are summarized in Table 3.

The reaction with *meta*-anisidine gave two products and the main product was found to have the alkenyl group at a more hindered position **7h** (entry 1). In the previous communication, we reported that the reason for this regioselectivity may be the chelation of the magnesium alkylidene carbenoid **6** between the amino group and the methoxy group.[9] However, all other *meta*-substituted anilines, even *meta*-methylaniline, which has no ability for the chelation, gave more hindered alkenylated compounds as main products (entries 2–4), although the yields were not satisfactory. The theoretical study for this regioselectivity is discussed later (vide infra).

## 2.2. Study for the reaction mechanism

At this stage, we investigated the mechanism of this reaction

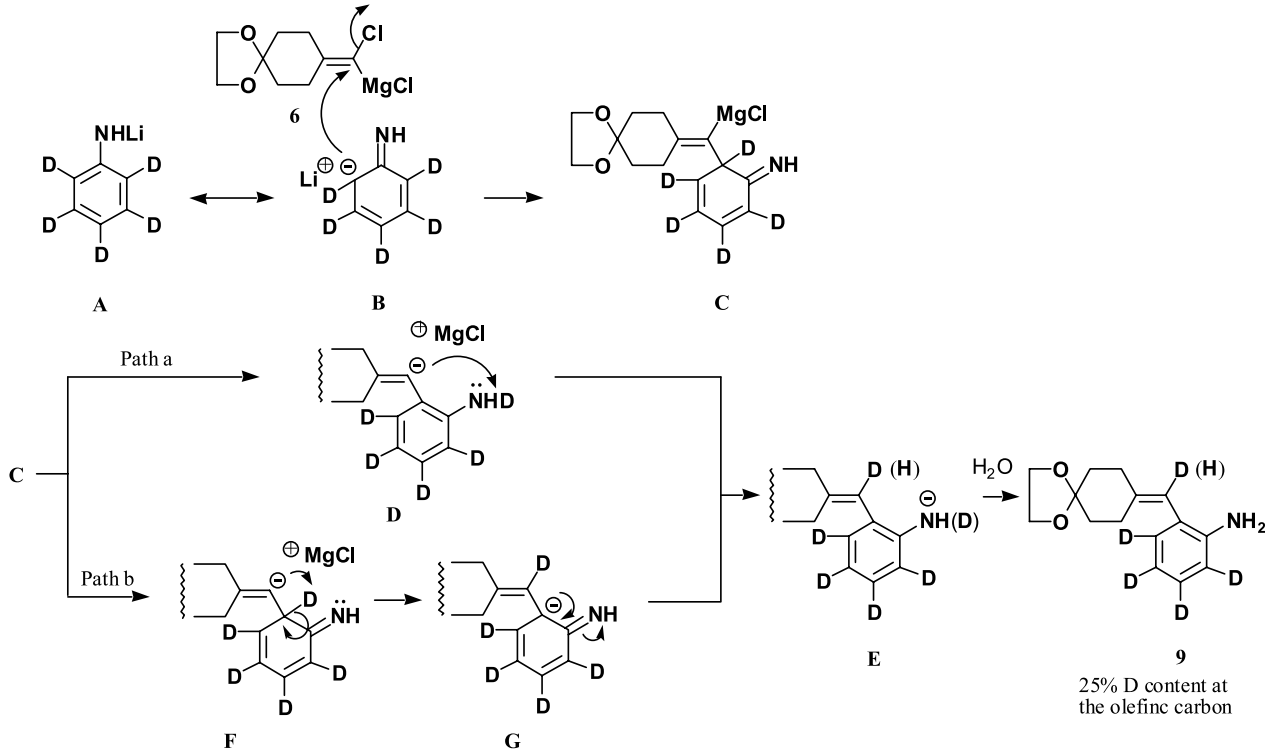
**Table 3**. Synthesis of *ortho*-alkenylated arylamines **7** by the reaction of magnesium alkylidene carbenoid **6** with *meta*-substituted *N*-lithio anilines

| Entry | *meta*-Substituted anilin[a] | *ortho*-Alkenylated arylamine **7** | (Yield, %) |
|---|---|---|---|
| 1 |  |  **7h** (30) |  **7i** (13) |
| 2 |  |  **7j** (19) |  **7k** (14) |
| 3 |  |  **7l** (25) |  **7m** (13) |
| 4 |  |  **7n** (7) |  **7o** (4) |

[a] Three equivalents of *meta*-substituted *N*-lithio aniline was reacted with **6**.

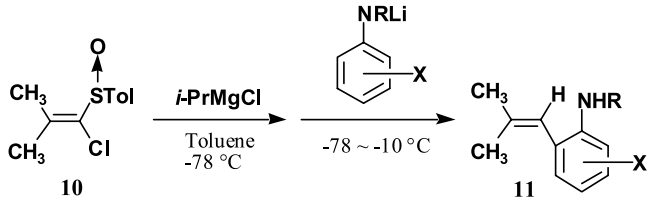
by using aniline-2,3,4,5,6-$d_5$ (Scheme 3). The reaction of the magnesium alkylidene carbenoid **6** with *N*-lithio aniline-2,3,4,5,6-$d_5$ **A** was carried out in toluene and *ortho*-alkenylated aniline **9** was obtained. The deuterium incorporation of **9** at the olefinic carbon was measured by $^1$H NMR and the deuterium incorporation was found to be 25%. From this result, we propose the mechanism of this reaction as follows (Scheme 3).

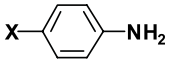
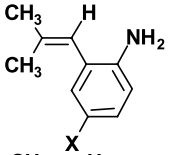
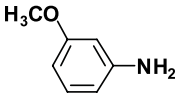
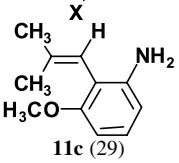
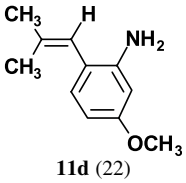
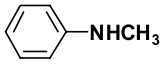
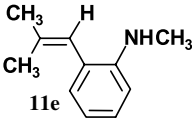
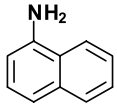
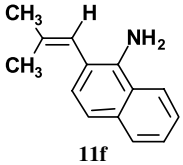
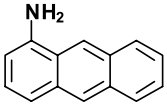
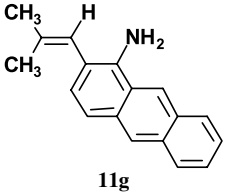
The *N*-lithio arylamine **A** is present in the resonance form,




**Scheme 3.**

**Table 4**. Synthesis of *ortho*-alkenylated arylamines by the reaction of magnesium alkylidene carbenoid derived from **10** with *N*-lithio arylamines




| Entry | Arylamine[a] | *ortho*-Alkenylated arylamine | | (Yield, %) |
|---|---|---|---|---|
| 1 |  |  | **11a** X=H | (43) |
| 2 | | | **11b** X=$OCH_3$ | (43) |
| 3 |  |  **11c** (29) |  **11d** (22) | |
| 4 |  |  **11e** | | (46) |
| 5 |  |  **11f** | | (81) |
| 6 |  |  **11g** | | (79) |

[a] Three equivalents of *N*-lithio arylamine was reacted with the carbenoid derived from **10**.

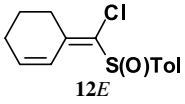
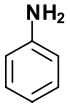
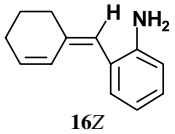
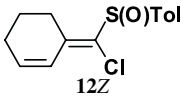
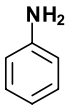
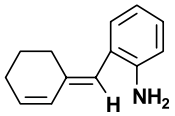
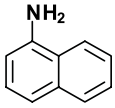
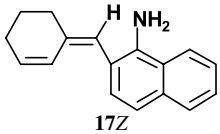
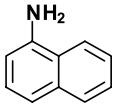
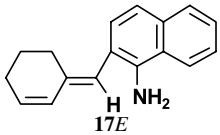
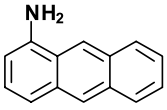
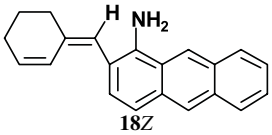
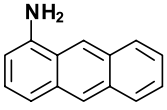
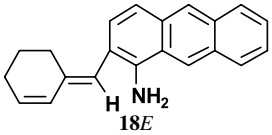
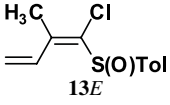
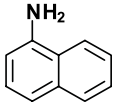
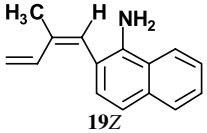
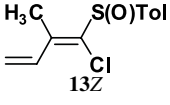
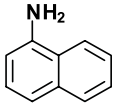
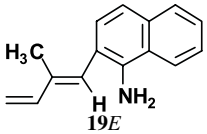
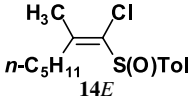
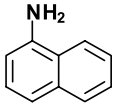
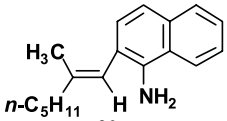
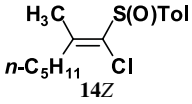
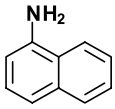
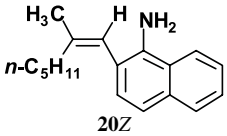
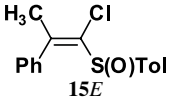
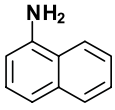
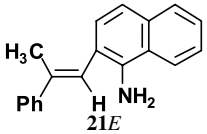
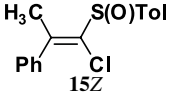
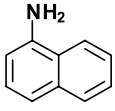
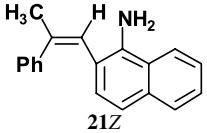
lithium α-imino carbanion **B**. The reaction of **B** with the magnesium alkylidene carbenoid **6** takes place with inversion of the configuration at the carbenoid carbon to give the intermediate **C**. The inversion of the configuration in the reaction of lithium alkylidene carbenoids with alkyllithium has been reported by Walborsky et al.[11] Oku et al.[12] and Narasaka et al.[13] We will discuss later the structure of the carbenoid and the reaction by B3LYP and MP2 calculations (vide infra).

Two pathways (path a and b) were postulated for the mechanism from the intermediate **C** to the product **9**. Thus, the intermediate **C** is first aromatized (intermolecular transfer of the deuterium from the carbon to the nitrogen was presumed to be take place) to give the alkenylmagnesium **D**. Then the alkenyl anion picks up the proton or deuterium on the nitrogen to give **E**, which was treated with water to afford **9** (path a). Less than 50% deuterium incorporation on the olefinic carbon was anticipated in path a. The other mechanism (path b) is as follows: the alkenyl anion first picks up the deuterium on the carbon next to the imine **F** to give an anion having deuterium on the olefinic carbon **G**. The intermediate **G** is aromatized to give **E**. Close to 100% deuterium incorporation was expected in path b. As described above, because the obtained *ortho*-alkenylated aniline **9** had 25% of deuterium on the olefinic carbon, this reaction was proved to proceed via path a.

### 2.3. Synthesis of the aryl amines having 2-methyl-1-propene at the *ortho*-position

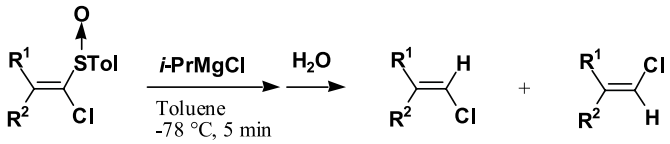
To investigate the generality of this reaction, we further studied this reaction using 1-chlorovinyl *p*-tolyl sulfoxide **10** derived from acetone and the results are summarized in Table 4. Entries 1 and 2 show that quite similar yields were obtained with aniline and *p*-anisidine. The reaction with *m*-anisidine gave two products and the main product was again found to be the more sterically hindered **11c** (entry 3). *N*-methylaniline gave better yield compared with the result in Table 2, entry 5. Again, much better yields were obtained from the reaction of the magnesium alkylidene carbenoid with 1-aminonaphthalene and 1-aminoanthracene (entries 5 and 6).

**Table 5**. The reaction of the magnesium alkylidene carbenoids derived from *E*- and *Z*-1-chlorovinyl *p*-tolyl sulfoxides with *N*-lithio aniline, *N*-lithio 1-aminonaphthalene and *N*-lithio 1-aminoanthracene

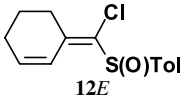
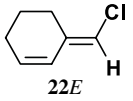
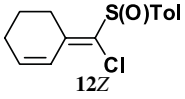
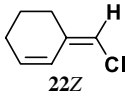
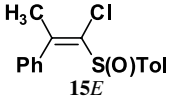
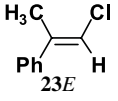
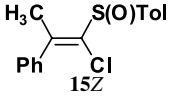
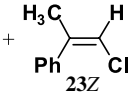
| Entry | Arylamine[a] | | Product | *E*/*Z*[b] | (Yield, %) |
|---|---|---|---|---|---|
| 1 |  **12***E* |  |  **16***Z* | 6:94 | (53) |
| 2 |  **12***Z* |  |  **16***E* | 94:6 | (46) |
| 3 | **12***E* |  |  **17***Z* | 3:97 | (65) |
| 4 | **12***Z* |  |  **17***E* | 95:5 | (71) |
| 5 | **12***E* |  |  **18***Z* | 22:78 | (69) |
| 6 | **12***Z* |  |  **18***E* | 84:16 | (66) |
| 7 |  **13***E* |  |  **19***Z* | 4:96 | (68) |
| 8 |  **13***Z* |  |  **19***E* | 94:6 | (62) |
| 9 |  **14***E* |  |  **20***E* | 44:56 | (54) |
| 10 |  **14***Z* |  |  **20***Z* | 34:66 | (55) |
| 11 |  **15***E* |  |  **21***E* | 6:94 | (61) |
| 12 |  **15***Z* |  |  **21***Z* | 25:75 | (45) |

[a] Three equivalents of *N*-lithio aniline, *N*-lithio 1-aminonaphthalene and *N*-lithio 1-aminoanthracene were reacted with the magnesium alkylidene carbenoids.
[b] The ratio of *E*/*Z* was determined from their $^1$H NMR.

**Table 6**. Quenching of the magnesium alkylidene carbenoid derived from **12** and **15** with water




**12** and **15**

| Entry | 1-Chlorovinyl *p*-tolyl sulfoxide | Alkenylchloride |
|---|---|---|
| 1 |  **12***E* |  **22***E* |
| 2 |  **12***Z* |  **22***Z* |
| 3 |  **15***E* |  **23***E* |
| 4 |  **15***Z* | **23***E* +  **23***Z* **23***E*:**23***Z*=35:65 |

## 2.4. Stereochemistry of the reaction

Next, we investigated the stereochemistry of these reactions. First of all, stereoisomers of the 1-chlorovinyl *p*-tolyl sufoxides (**12**–**15**) were synthesized from unsymmetrical ketones (2-cyclohexenone, methyl vinyl ketone, 2-heptanone, and acetophenone) and the reaction was carried out with aniline, 1-aminonaphthalene and 1-aminoanthracene. The results are summarized in Table 5. Quite interestingly, the reaction of the magnesium alkylidene carbenoids derived from **12***E* and **12***Z* with aniline and 1-aminonaphthalene gave *Z-ortho*-alkenylated arylamines **16***Z* and **17***Z*, and *E-ortho*-alkenylated arylamines **16***E* and **17***E*, respectively, with high stereospecificity (entries 1–4). The reaction of **12***E* and **12***Z* with 1-aminoanthracene gave also the *ortho*-alkenylated 1-aminoanthracenes, **18***Z* and **18***E*, stereospecifically although the stereospecificity was somewhat lower (entries 5 and 6). The 1-chlorovinyl *p*-tolyl sulfoxide derived from methyl vinyl ketone **13** showed again quite high stereospecificity with 1-aminonaphthalene to give **19***Z* and **19***E* (entries 7 and 8).

Further, this reaction was carried out with the 1-chlorovinyl *p*-tolyl sulfoxides derived from unsymmetrical dialkyl ketone (2-heptanone) **14** and alkyl aryl ketone (acetophenone) **15** with 1-aminonaphthalene. Quite interestingly, both vinyl sulfoxides **14***E* and **14***Z* gave mainly *Z*-isomer **20***Z* (entries 9 and 10), namely, the reactions with **14** show stereoselectivity. The reaction with **15***E* and **15***Z* showed also stereoselectivity. In this case, **15***E* exclusively gave **21***Z*

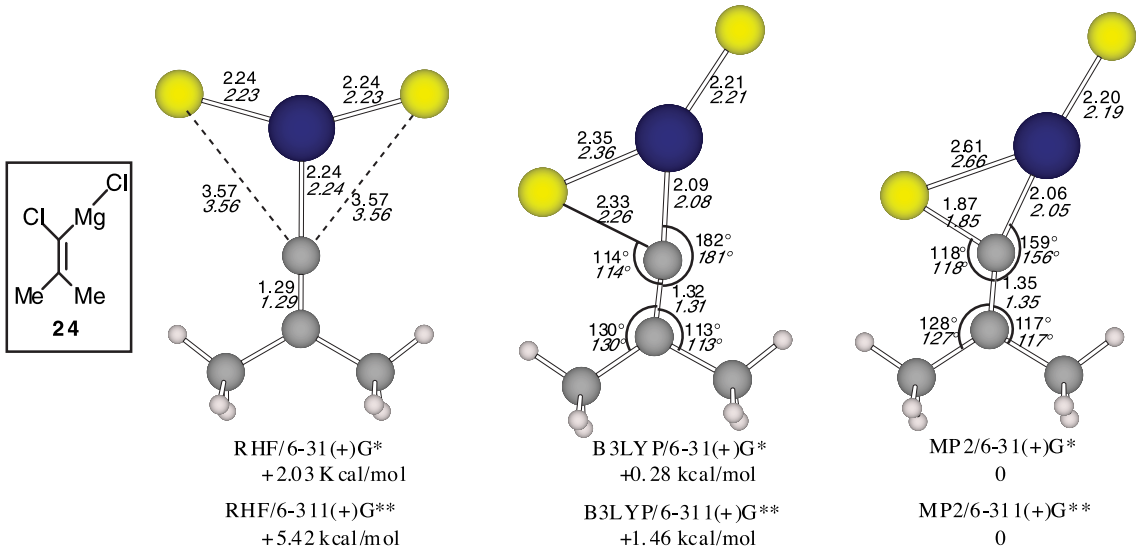



**Figure 1.** Geometries of 1-chloro-2-methylpropenylmagnesium chloride **24** optimized at the RHF, B3LYP, and MP2 levels of theory with the 6-31(+)G* and 6-311(+)G** basis sets. The energies of these geometries were calculated at the CCSD(T) method with the corresponding basis set.

in high stereoselectivity (entry 11). The reaction with **15***Z* gave **21***Z*, however, the selectivity was lower than the reaction with **15***E* (entry 12).

The stereospecificity and the stereoselectivity mentioned above are explained as follows. If the configuration of the magnesium alkylidene carbenoids generated from 1-chlorovinyl *p*-tolyl sulfoxides derived from α,β-unsaturated ketones is stable enough in the reaction conditions, the *N*-lithio arylamine attacks backside to the chlorine atom to give the product stereospecifically. On the other hand, if the configuration of the magnesium alkylidene carbenoids generated from the 1-chlorovinyl *p*-tolyl sulfoxide derived from dialkyl ketone or alkyl aryl ketone is not stable under the reaction conditions, both isomers of the magnesium alkylidene carbenoids are present in equilibrium before the alkenylation and from the more stable isomer the main product is produced.

In order to obtain the information on the stability of the magnesium alkylidene carbenoids, we treated **12** and **15** with *i*-PrMgCl at −78 °C for 5 min and the generated magnesium alkylidene carbenoids were quenched with water. The results are summarized in Table 6. As anticipated, the reaction of **12***E* and **12***Z* gave **22***E* and **22***Z*, respectively, without any presence of the isomer (entries 1 and 2). These results imply that the configuration of the generated magnesium alkylidene carbenoids is stable for at least 5 min. The reaction of **15***E* gave **23***E* exclusively, however, **15***Z* gave a mixture of **23***E* and **23***Z*. These results imply that the magnesium alkylidene carbenoid generated from **15***E* and **15***Z* is unstable.[7] These results are consistent with the stereospecificity and the stereoselectivity shown in Table 5. We studied the stability for the geometry of the magnesium alkylidene carbenoids by calculation and will discuss this later (vide infra).

### 2.5. Theoretical studies for the α-chloro alkenylmagnesium chlorides and the reactivity of the *N*-lithio *meta*-substituted anilines

To better understand these substitution reactions of the magnesium alkylidene carbenoids (α-chloro alkenylmagnesium chlorides), we studied them computationally. All calculations were performed using the Gaussian 98 program.[14] The frequency calculations on the optimized structures gave only harmonic frequencies and confirmed that they are minima. The structures of the α-chloro alkenylmagnesium chlorides were first studied using the RHF, B3LYP, and MP2 levels of theory with the 6-31(+)G*[15] basis set. The obtained geometries of 1-chloro-2-methylpropenyl-magnesium chloride **24** are shown in Figure 1.

The magnesium atom interacts with the vinyl chloride strongly at the RHF level and the structure is a complex of the alkenyl carbene with $MgCl_2$ rather than the α-chloro alkenylmagnesium chloride. This structure is not compatible with our experimental results. On the other hand, both the B3LYP and MP2 geometries are the α-halo alkenylmagnesium chloride where the C–Cl bond is bridged by the magnesium atom. The $^{13}C$ NMR study[16,17] of the α-bromo alkyllithium compounds showed considerable weakening of the C–Br bonds and the theoretical studies reported a bridging geometry for $H_2CLiCl$,[18] $CH_2$=FLi,[19] and RR′C=CLiX (X=Cl, Br).[13]

In order to know, which α-chloro alkenylmagnesium chloride structure is more reliable, the energies were computed using a higher level of the correlation method, CCSD(T)/6-31(+)G*, on these geometries. The relative energies are +2.03, 0.28, and 0 kcal/mol, respectively. Although the Cl–Mg distance of the MP2 geometry is longer than that of the B3LYP by 0.26 Å, those CCSD(T) energies are not much different. The MP2 geometry was reoptimized with constraining the Cl–Mg distance to 2.45, 2.50, and 2.55 Å at the MP2/6-31(+)G* level and the relative CCSD(T) energies were −0.09, −0.13 and −0.08 kcal/mol, respectively. Therefore, the real structure seems to be between the B3LYP structure and the MP2 structure and is closer to the latter. To see the basis set effects, the structures were also calculated using 6-311(+)G**. Since the geometries are almost the same as the 6-31(+)G* basis for all the RHF, B3LYP, and MP2 levels of theory, the 6-31(+)G* basis set is as good as the 6-311(+)G** basis set for the structure of α-chloro alkenylmagnesium chloride.

Stereospecific formation of the alkenyl aniline was observed when the conjugated α-chloro alkenylmagnesium chlorides were used. Therefore, the structures of the conjugated α-chloro alkenylmagnesium chlorides were further studied. The optimized structures for *E*- and *Z*-1-chloro-2-methyl-1, 3-butadienylmagnesium chloride **25** are shown in Figure 2. There are three characteristic differences between **24** (see Fig. 1) and **25**. The distances between the Mg and the vinyl-Cl is much longer, the C–Cl bond is shorter, and the C=C–

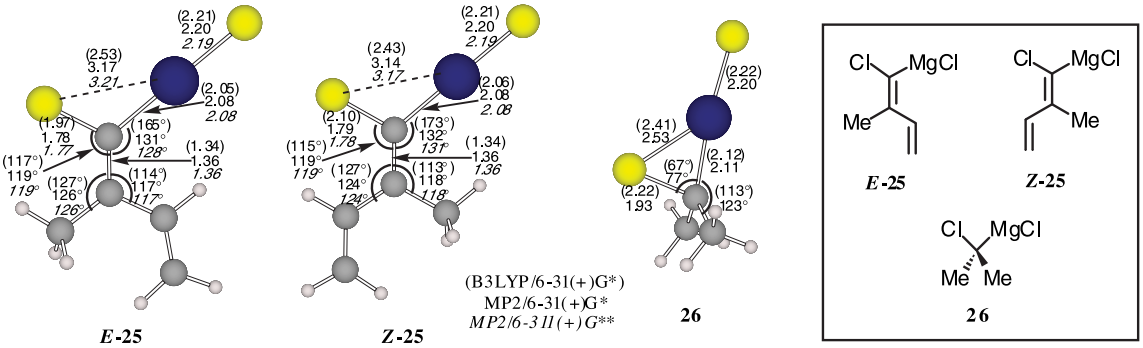



**Figure 2.** Geometries of *E*-**25**, *Z*-**25**, and **26** optimized at the B3LYP/6-31(+)G*, and MP2/6-31(+)G*, and MP2/6-311(+)G**.

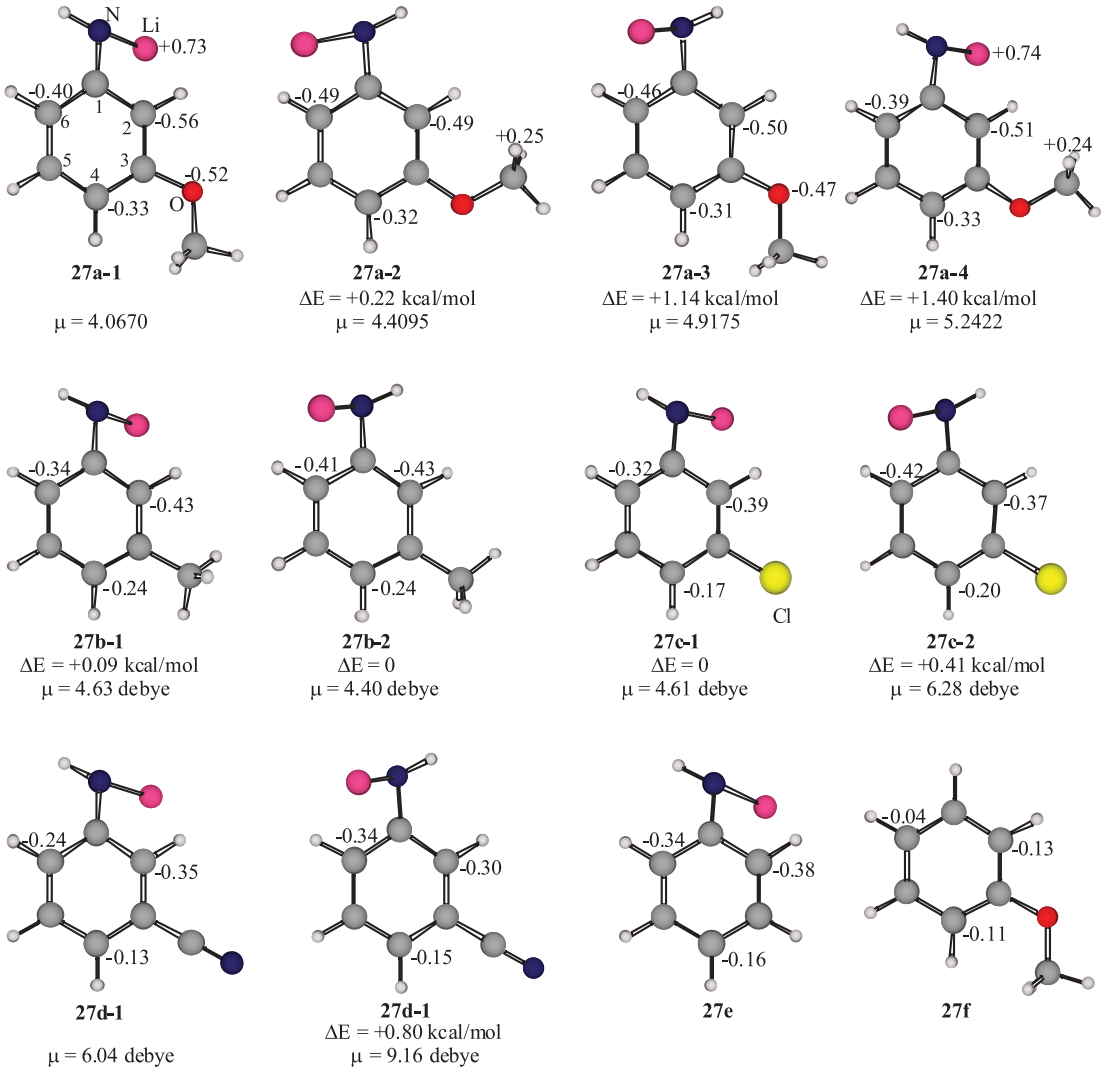



**Figure 3.** Optimized structures of *N*-lithio *meta*-substituted anilines **27** at the MP2/6-31(+)G* level of theory. Atomic charges with hydrogens summed into heavy atoms were calculated using the CHelpG scheme of Breneman (MP2/6-31(+)G* density=MP2 pop=CHelpG).

Mg angle is smaller in **25** at both the B3LYP and MP2 levels of theory. Thus, the conjugated systems are geometrically stabilized. The charges computed by natural population analysis (MP2/6-31(+)G* density=MP2 pop=NPA) show a more negative charge on the vinyl-Cl in **24** and the alkyl-Cl in 2-chloro-2-propanylmagnesium chloride **26** than on the vinyl-Cl in **25** (the values are as follows: *E*-**25**, −0.06; *Z*-**25**, −0.07; **24**, −0.18; **26**, −0.22).[20] In these cases, the Mg–Cl distances correspond to the amount of the negative charge on the vinyl-Cl. That is, the shorter the Mg–Cl distances, the more negative charge on the Cl. Only a small amount of the negative charge is placed on the vinyl-Cl due to the charge delocalization in the conjugated systems **25**. Thus, the interaction between the Mg and the Cl is weaker in **25** than those in **24** and **26**. This weaker interaction increases the geometrical stabilization, and, therefore, stereospecific reaction can be expected.

For the reaction with *meta*-substituted anilines, the more hindered alkenylated compounds were obtained as main products. To see the reactivity of these *N*-lithio *meta*-substituted anilines **27**, the electrostatic potential-derived charges using the CHelpG scheme of Breneman (MP2/6-31(+)G* density=MP2 pop=CHelpG) were calculated with the structures optimized at the MP2/6-31(+)G* level. The results are shown in Figure 3.

Four conformers **27a-1**–**27a-4** were obtained for *N*-lithio *meta*-anisidine. The more negative atom charge (−0.56) was found on the carbon-2 in the most stable conformer **27a-1**. The same value (−0.49) was obtained on both the carbon-2 and the carbon-6 in **27a-2**, which is 0.22 kcal/mol less stable than **27a-1**. In the other two conformers (**27a-3** and **27a-4**), the more negative charge was also found on the carbon-2. Thus, the obtained product selectivity corresponds well to the negative charges on both the carbon-2 and the carbon-6, and the conformer stability.

There are two conformers for *N*-lithio *meta*-methylaniline (**27b-1** and **27b-2**). Although the more negative charge was found on the carbon-2 in both conformers, the difference is small in the more stable **27b-2**. Therefore, the less selective formation of **7j** was found (see Table 3, entry 2). There are also two conformers for both *N*-lithio *meta*-chloroaniline and *N*-lithio *meta*-cyanoaniline (**27c** and **27d**). The more negative charges were found on the carbon-2 in the more

stable conformers **27c**-**1** and **27d**-**1**. Compared to **27a**, the less negative charges found in **27c** and **27d** are thought to be a reason for the lower product yields. In these cases, all the more stable conformers have smaller dipole moment. Since the reaction was performed in toluene with low polarity ($\varepsilon=2.379$), the conformers with lower dipole moment are stabilized. In fact, the energy differences are in proportion to the differences of the dipole moment in **27b–d**.

For **27a**, not only the dipole moment, but also the MeO conformation is important for the conformer stability. The electrostatic interaction of the lithium with the carbon-2 and the oxygen stabilizes **27a**-**1**. On the other hand, this stabilization was reduced in **27a**-**4** due to the electrostatic interaction between the negative carbon-2 and the positive methyl group. The electrostatic repulsion between the carbon-2 and the oxygen destabilizes **27a**-**3** compared with **27a**-**2**. Furthermore, the dipole moment increases in the order of **27a**-**1**, **27a**-**2**, **27a**-**3**, and **27a**-**4**. Thus, the energy differences of these conformers can be explained on the basis of the dipole moment and the electrostatic interaction. The electrostatic potential-derived charges were also calculated for *N*-lithio aniline **27e** and anisole **27f**. The strongly electron-donating lithioamino group increases the negative charge on both the ortho positions with the lithium side more. Thus, the CHelpG results explain the experimental reactivity and the selectivity very well.

## 3. Experimental

### 3.1. General

All melting points are uncorrected. $^1$H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (Merck) 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, toluene was distilled from $CaH_2$ and THF was distilled from diphenylketyl.

**5**,[7] **10**,[21] **12***E*,[4] **12***Z*,[4] **15***E*,[7] and **15***Z*[7] are known compounds.

**3.1.1. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)phenylamine (7a).** To a solution of **5** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.036 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.84 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **6**. *n*-BuLi (0.93 mmol) was added to a solution of aniline (0.082 mL; 0.90 mmol) in 4 mL of dry toluene in an another flame-dried flask at −78 °C under argon atmosphere to give the lithium anilide. This solution was added to a solution of the carbenoid **6** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq $NH_4Cl$ and the whole was extracted with $CHCl_3$. 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 **7a** (35.9 mg; 49%) as colorless needles; mp 118–119 °C (AcOEt/hexane); IR (KBr) 3464 (NH), 3371 (NH), 2946, 2894, 1631, 1491, 1454, 1116, 1079, 1029, 904, 754 cm$^{-1}$; $^1$H NMR $\delta$ 1.67 (2H, t, $J$=6.4 Hz), 1.80 (2H, t, $J$=6.4 Hz), 2.35 (2H, t, $J$=6.6 Hz), 2.46 (2H, dt, $J$=6.4 Hz), 3.67 (2H, br s), 3.98 (4H, s), 6.09 (1H, s), 6.69 (1H, d, $J$=8.0 Hz), 6.73 (1H, t, $J$=7.5 Hz), 6.98 (1H, d, $J$=7.4 Hz), 7.06 (1H, t, $J$=7.0 Hz). $^{13}$C NMR $\delta$ 26.3, 33.6, 35.5, 36.3, 64.4 (2C), 108.7, 115.0, 118.0, 119.2, 123.6, 127.7, 130.1, 142.4, 144.3. MS *m*/*z* (%) 245 ($M^+$, 100), 200 (30), 183 (19), 159 (27), 144 (44), 130 (39), 107 (70), 106 (45). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N 5.71. Found: C, 72.99; H, 7.75; N, 5.48.

**3.1.2. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-4-methoxyphenylamine (7b).** Colorless oil; IR (neat) 3445 (NH), 3362 (NH), 2948, 1604, 1498, 1274, 1239, 1120, 1082, 1035 cm$^{-1}$; $^1$H NMR $\delta$ 1.67 (2H, t, $J$=6.4 Hz), 1.80 (2H, t, $J$=6.6 Hz), 2.37 (2H, t, $J$=6.1 Hz), 2.45 (2H, t, $J$=6.1 Hz), 3.43 (2H, br s), 3.74 (3H, s), 3.98 (4H, m), 6.09 (1H, s), 6.58 (1H, d, $J$=2.8 Hz), 6.65 (1H, s), 6.67 (1H, d, $J$=2.8 Hz). MS *m*/*z* (%) 275 ($M^+$, 100), 230 (22), 212 (8), 189 (15), 174 (22), 160 (16), 137 (55), 122 (15), 117 (8). Calcd for $C_{16}H_{21}NO_3$: *M*, 275.1520. Found: *m*/*z* 275.1523.

**3.1.3. 4-Chloro-2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)phenylamine (7c).** Colorless oil; IR (neat) 3469 (NH), 3369 (NH), 2951, 2884, 1615, 1488, 1275, 1248, 1120, 1082, 1033 cm$^{-1}$; $^1$H NMR $\delta$ 1.67 (2H, t, $J$=6.6 Hz), 1.79 (2H, t, $J$=6.6 Hz), 2.33 (2H, t, $J$=6.6 Hz), 2.45 (2H, t, $J$=6.6 Hz), 3.66 (2H, br s), 3.98 (4H, s), 6.01 (1H, s), 6.61 (1H, d, $J$=8.5 Hz), 6.94 (1H, d, $J$=2.4 Hz), 7.00 (1H, dd, $J$=8.4, 2.5 Hz). MS *m*/*z* (%) 279 ($M^+$, 98), 234 (28), 218 (14), 193 (20), 178 (22), 164 (36), 158 (28), 141 (100), 130 (12), 121 (18), 95 (20), 86 (12), 77 (10), 55 (12), 42 (12). Calcd for $C_{15}H_{18}ClNO_2$: *M*, 279.1025. Found: *m*/*z* 279.1025.

**3.1.4. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-6-methylphenylamine (7d).** Colorless crystals; mp 105–106 °C (AcOEt/hexane); IR (KBr) 3454 (NH), 3369 (NH), 2954, 2879, 2853, 1625, 1588, 1477, 1464, 1119, 1083, 1031, 919, 751 cm$^{-1}$; $^1$H NMR $\delta$ 1.66 (2H, t, $J$=6.6 Hz), 1.80 (2H, t, $J$=6.4 Hz), 2.18 (3H, s), 2.35 (2H, t, $J$=6.4 Hz), 2.46 (2H, t, $J$=6.4 Hz), 3.65 (2H, br s), 3.98 (4H, m), 6.11 (1H, s), 6.67 (1H, t, $J$=7.3 Hz), 6.87 (1H, d, $J$=7.3 Hz), 6.97 (1H, d, $J$=7.3 Hz). MS *m*/*z* (%) 259 ($M^+$, 100), 214 (28), 196 (12), 186 (6), 173 (33), 158 (46), 144 (36), 130 (10), 121 (62), 99 (6). Calcd for $C_{16}H_{21}NO_2$: *M*, 259.1570. Found: *m*/*z* 259.1570. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N 5.40. Found: C, 73.97; H, 8.12; N, 5.37.

**3.1.5. [2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)phenyl]methylamine (7e).** Colorless crystals; mp 70–71 °C (hexane); IR (KBr) 3424 (NH), 2947, 2884, 2813, 1601, 1578, 1507, 1166, 1120, 1082, 1034, 909, 749 cm$^{-1}$; $^1$H NMR $\delta$ 1.65 (2H, t, $J$=6.6 Hz), 1.80 (2H, t, $J$=6.6 Hz), 2.33 (2H, t, $J$=6.6 Hz), 2.45 (2H, t, $J$=6.6 Hz), 2.86 (3H, s), 3.79 (1H, br s), 3.98 (4H, m), 6.03 (1H, s), 6.62 (1H, d, $J$=8.3 Hz), 6.68 (1H, dt, $J$=7.4, 0.9 Hz), 6.96 (1H, d, $J$=

7.4 Hz), 7.18 (1H, dt, $J$=8.3, 1.2 Hz). MS $m/z$ (%) 259 ($M^+$, 100), 214 (24), 173 (24), 158 (50), 144 (28), 130 (18), 120 (42), 99 (11), 91 (11), 77 (6). Calcd for $C_{16}H_{21}NO_2$: $M$, 259.1571. Found: $m/z$ 259.1574. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.67; H, 7.89; N, 5.40.

**3.1.6. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl) naphthalen-1-ylamine (7f).** Colorless needles; mp 123–124 °C (AcOEt/hexane); IR (KBr) 3472 (NH), 3383 (NH), 2948, 2883, 1615, 1566, 1432, 1403, 1120, 1080, 1033, 758, 735 $cm^{-1}$; $^1H$ NMR $\delta$ 1.67 (1H, t, $J$=6.4 Hz), 1.84 (1H, t, $J$=6.4 Hz), 2.35 (2H, t, $J$=6.6 Hz), 2.52 (2H, t, $J$=6.5 Hz), 3.96–4.00 (4H, m), 4.21 (2H, br s), 6.28 (1H, s), 7.15 (1H, d, $J$=8.6 Hz), 7.27 (1H, d, $J$=8.3 Hz), 7.41–7.44 (2H, m), 7.76–7.77 (1H, m), 7.81–7.82 (1H, m). MS $m/z$ (%) 295 ($M^+$, 100), 250 (20), 234 (6), 232 (8), 208 (10), 194 (20), 180 (35), 156 (82). Calcd for $C_{19}H_{21}NO_2$: $M$, 295.1570. Found: $m/z$ 295.1562. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.15; H, 7.16; N, 4.75.

**3.1.7. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl) anthracen-1-ylamine (7g).** Colorless amorphous; IR (KBr) 3469 (NH), 3390 (NH), 2944, 2879, 1610, 1428, 1383, 1119, 1087, 1035, 909, 870, 737 $cm^{-1}$; $^1H$ NMR $\delta$ 1.70 (2H, t, $J$=6.6 Hz), 1.86 (2H, t, $J$=6.4 Hz), 2.39 (2H, t, $J$=6.1 Hz), 2.54 (2H, t, $J$=6.1 Hz), 3.97–4.01 (4H, m), 4.36 (2H, br s), 6.32 (1H, s), 7.16 (1H, d, $J$=8.6 Hz), 7.41–7.46 (3H, m), 7.95–7.97 (1H, m), 7.98–8.0 (1H, m), 8.34 (1H, s), 8.38 (1H, s). MS $m/z$ (%) 345 ($M^+$, 100), 300 (15), 243 (15), 206 (60), 193 (6). Calcd for $C_{23}H_{23}NO_2$: $M$, 345.1717. Found: $m/z$ 345.1707.

**3.1.8. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-3-methoxyphenylamine (7h).** Colorless oil; IR (neat) 3469 (NH), 3371 (NH), 2949, 2886, 2838, 1615, 1471, 1258, 1210, 1122, 1081, 1034 $cm^{-1}$; $^1H$ NMR $\delta$ 1.67 (2H, t, $J$=6.4 Hz), 1.81 (2H, t, $J$=6.4 Hz), 2.15 (2H, t, $J$=6.4 Hz), 2.49 (2H, t, $J$=6.4 Hz), 3.69 (2H, br s), 3.76 (3H, s), 3.97 (4H, m), 5.88 (1H, s), 6.31 (1H, d, $J$=8.2 Hz), 6.36 (1H, d, $J$=8.3 Hz), 7.02 (1H, t, $J$=8.2 Hz). MS $m/z$ (%) 275 ($M^+$, 100), 230 (26), 213 (16), 189 (34), 174 (40), 160 (24), 136 (63), 130 (10), 117 (8), 106 (15). Calcd for $C_{16}H_{21}NO_3$: $M$, 275.1520. Found: $m/z$ 275.1520.

**3.1.9. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-5-methoxyphenylamine (7i).** Colorless crystals; mp 87–88 °C (AcOEt/hexane); IR (KBr) 3466 (NH), 3363 (NH), 2953, 2901, 1599, 1622, 1578, 1506, 1209, 1081, 1030, 903 $cm^{-1}$; $^1H$ NMR $\delta$ 1.66 (2H, t, $J$=6.4 Hz), 1.79 (2H, t, $J$=6.6 Hz), 2.35 (2H, t, $J$=6.6 Hz), 2.44 (2H, t, $J$=6.6 Hz), 3.69 (2H, br s), 3.76 (3H, s), 3.97–3.99 (4H, m), 6.03 (1H, s), 6.26 (1H, d, $J$=2.7 Hz), 6.31 (1H, dd, $J$=8.2, 2.7 Hz), 6.88 (1H, d, $J$=8.2 Hz). MS $m/z$ (%) 275 ($M^+$, 100), 230 (26), 214 (20), 189 (30), 174 (22), 160 (23), 136 (75), 130 (6), 117 (8). Calcd for $C_{16}H_{21}NO_3$: $M$, 275.1521. Found: $m/z$ 275.1525. Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.74; H, 7.54; N, 5.13.

**3.1.10. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-3-methylphenylamine (7j) and 2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)-5-methylphenylamine (7k).** The reaction gave an inseparable mixture of **7j** and **7k**. Colorless oil; IR (neat) 3468 (NH), 3370 (NH), 2948, 2884, 1610, 1466, 1120, 1083, 757 $cm^{-1}$; $^1H$ NMR (vinylic proton and aromatic protons of **7j**) $\delta$ 5.95 (s), 6.55 (d, $J$=7.9 Hz), 6.60 (d, $J$=7.3 Hz), 6.96 (t, $J$=7.8 Hz); $^1H$ NMR (vinylic proton and aromatic protons of **7k**) $\delta$ 6.06 (s), 6.52 (s), 6.55 (d, $J$=7.9 Hz), 6.86 (d, $J$=7.7 Hz). MS $m/z$ (%) 259 ($M^+$, 100), 214 (38), 173 (30), 158 (54), 144 (48), 120 (80). Calcd for $C_{16}H_{21}NO_2$: $M$, 259.1572. Found: $m/z$ 259.1577.

**3.1.11. 3-Chloro-2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)phenylamine (7l).** Colorless oil; IR (neat) 3474 (NH), 3368 (NH), 2952, 2884, 1615, 1471, 1447, 1120, 1083, 1034, 908 $cm^{-1}$; $^1H$ NMR $\delta$ 1.65–1.70 (2H, m), 1.78–1.84 (2H, m), 2.12–2.16 (2H, m), 2.48–2.52 (2H, m), 3.79 (2H, br s), 3.95–4.00 (4H, m), 5.92 (1H, s), 6.58 (1H, d, $J$=8.0 Hz), 6.77 (1H, d, $J$=8.0 Hz), 6.97 (1H, t, $J$=8.0 Hz). MS $m/z$ (%) 279 ($M^+$, 100), 234 (26), 218 (18), 193 (28), 178 (32), 164 (42), 158 (23), 141 (73). Calcd for $C_{15}H_{18}ClNO_2$: $M$, 279.1024. Found: $m/z$ 279.1018.

**3.1.12. 5-Chloro-2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)phenylamine (7m).** Colorless oil; IR (neat) 3469 (NH), 3371 (NH), 2948, 2883, 1608, 1466, 1120, 1083, 1034, 908, 758 $cm^{-1}$; $^1H$ NMR $\delta$ 1.65 (2H, t, $J$=6.6 Hz), 1.79 (2H, t, $J$=6.6 Hz), 2.31 (2H, t, $J$=6.6 Hz), 2.44 (2H, t, $J$=6.6 Hz), 3.73 (2H, br s), 3.98 (4H, m), 6.00 (1H, s), 6.67 (1H, s), 6.68 (1H, d, $J$=8.3 Hz), 6.87 (1H, d, $J$=8.3 Hz). MS $m/z$ (%) 279 ($M^+$, 100), 250 (8), 234 (26), 220 (8), 217 (20), 193 (26), 178 (29), 164 (38), 158 (20), 141 (65). Calcd for $C_{15}H_{18}ClNO_2$: $M$, 279.1024. Found: $m/z$ 279.1022.

**3.1.13. 3-Amino-2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)benzonitrile (7n).** Colorless oil; IR (neat) 3472 (NH), 3369 (NH), 2953, 2885, 2272 (CN), 1621, 1463, 1121, 1084, 1033, 909 $cm^{-1}$; $^1H$ NMR $\delta$ 1.68–1.84 (4H, m), 2.21 (2H, m), 2.58 (2H, m), 3.88 (2H, br s), 3.95–3.99 (4H, m), 6.06 (1H, s), 6.86 (1H, dd, $J$=7.8, 0.9 Hz), 7.04 (1H, dd, $J$=7.8, 0.9 Hz), 7.12 (1H, t, $J$=7.8 Hz). MS $m/z$ (%) 270 ($M^+$, 100), 241 (22), 225 (40), 209 (28), 197 (38), 169 (32), 155 (40), 131 (23), 99 (34). Calcd for $C_{16}H_{18}N_2O_2$: $M$, 270.1367. Found: $m/z$ 270.1362.

**3.1.14. 3-Amino-4-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)benzonitrile (7o).** Colorless oil; IR (neat) 3475 (NH), 3370 (NH), 2953, 2923, 2874, 2229 (CN), 1627, 1424, 1117, 1083, 1032, 909 $cm^{-1}$; $^1H$ NMR $\delta$ 1.67 (2H, t, $J$=6.6 Hz), 1.81 (2H, t, $J$=6.6 Hz), 2.31 (2H, t, $J$=6.4 Hz), 2.47 (2H, t, $J$=6.4 Hz), 3.87 (2H, br s), 3.97–4.00 (4H, m), 6.03 (1H, s), 6.92 (1H, d, $J$=1.2 Hz), 6.99 (1H, dd, $J$=7.6, 1.2 Hz), 7.03 (1H, d, $J$=7.6 Hz). MS $m/z$ (%) 270 ($M^+$, 100), 257 (10), 241 (15), 225 (28), 208 (30), 197 (19), 183 (23), 169 (52), 155 (57), 132 (99), 99 (40), 86 (44). Calcd for $C_{16}H_{18}N_2O_2$: $M$, 270.1367. Found: $m/z$ 270.1370.

**3.1.15. 2-(2-Methylpropenyl)phenylamine (11a).** Colorless oil; IR (neat) 3466 (NH), 3376 (NH), 3022, 2968, 2930, 2855, 1615, 1491, 1454, 1299, 750 $cm^{-1}$; $^1H$ NMR $\delta$ 1.71 (3H, s), 1.91 (3H, s), 3.66 (2H, br s), 6.06 (1H, s), 6.69 (1H, d, $J$=7.6 Hz), 6.73 (1H, t, $J$=7.6 Hz), 7.00 (1H, d, $J$=7.6 Hz), 7.05 (1H, t, $J$=7.6 Hz). MS $m/z$ (%) 147 ($M^+$, 100), 117 (30), 106 (30), 91 (11), 77 (13), 65 (11). Calcd for $C_{10}H_{13}N$: $M$, 147.1047. Found: $m/z$ 147.1049.

**3.1.16. 4-Methoxy-2-(2-methylpropenyl)phenylamine (11b).** Colorless oil; IR (neat) 3440 (NH), 3363 (NH), 2929, 2852, 1603, 1497 $cm^{-1}$; $^1H$ NMR $\delta$ 1.73 (3H, d, $J$= 1.2 Hz), 1.91 (3H, d, $J$=1.2 Hz), 3.43 (2H, br s), 3.74 (3H, s), 6.06 (1H, br s), 6.61 (1H, m), 6.65 (2H, m). MS $m/z$ (%) 177 ($M^+$, 100), 162 (85), 147 (18), 134 (8), 117 (12), 91 (8). Calcd for $C_{11}H_{15}NO$: $M$, 177.1152. Found: $m/z$ 117.1154.

**3.1.17. 3-Methoxy-2-(2-methylpropenyl)phenylamine (11c).** Colorless oil; IR (neat) 3462 (NH), 3376 (NH), 2930, 2852, 1618, 1506, 1294, 1205, 1168, 1030 $cm^{-1}$; $^1H$ NMR $\delta$ 1.59 (3H, s), 1.94 (3H, d, $J$=1.3 Hz), 3.71 (2H, br s), 3.78 (3H, s), 5.91 (1H, br s), 6.32 (1H, d, $J$=8.0 Hz), 6.37 (1H, d, $J$=8.0 Hz), 7.02 (1H, t, $J$=8.0 Hz). MS $m/z$ (%) 177 ($M^+$, 80), 162 (100), 147 (30), 131 (12), 117 (8), 106 (16), 91 (10), 77 (18), 65 (6). Calcd for $C_{11}H_{15}NO$: $M$, 177.1153. Found: $m/z$ 117.1153.

**3.1.18. 5-Methoxy-2-(2-methylpropenyl)phenylamine (11d).** Colorless oil; IR (neat) 3473 (NH), 3377 (NH), 2932, 2836, 1612, 1468, 1257, 1129, 1092, 1055, 770 $cm^{-1}$; $^1H$ NMR $\delta$ 1.70 (3H, s), 1.89 (3H, s), 3.70 (2H, br s), 3.76 (3H, s), 5.99 (1H, s), 6.26 (1H, d, $J$=2.8 Hz), 6.31 (1H, dd, $J$=8.3, 2.8 Hz), 6.90 (1H, d, $J$=8.3 Hz). MS $m/z$ (%) 178 (12), 177 ($M^+$, 100), 162 (66), 136 (48), 131 (10), 117 (10), 91 (8). Calcd for $C_{11}H_{15}NO$: $M$, 177.1152. Found: $m/z$ 177.1150.

**3.1.19. *N*-Methyl-*N*-[2-(2-methylpropenyl)phenyl]amine (11e).** Colorless oil; IR (neat) 3429 (NH), 2911, 2814, 1602, 1578, 1506, 1459, 748 $cm^{-1}$; $^1H$ NMR $\delta$ 1.69 (3H, d, $J$= 0.9 Hz), 1.91 (3H, d, $J$=1.3 Hz), 2.85 (3H, s), 3.76 (1H, br s), 6.00 (1H, br s), 6.61 (1H, d, $J$=7.3 Hz), 6.68 (1H, t, $J$= 7.3 Hz), 6.98 (1H, d, $J$=7.3 Hz), 7.16 (1H, t, $J$=7.3 Hz). MS $m/z$ (%) 161 ($M^+$, 100), 146 (84), 131 (36), 118 (58), 115 (12), 91 (16), 77 (12), 65 (6). Calcd for $C_{11}H_{15}N$: $M$, 161.1204. Found: $m/z$ 161.1206.

**3.1.20. 2-(2-Methylpropenyl)naphthalen-1-ylamine (11f).** Colorless oil; IR (neat) 3469 (NH), 3383 (NH), 3054, 2929, 1610, 1565, 1507, 1430, 1400 $cm^{-1}$; $^1H$ NMR $\delta$ 1.72 (3H, s), 1.97 (3H, d, $J$=1.2 Hz), 4.20 (2H, br s), 6.25 (1H, s), 7.17 (1H, d, $J$=8.3 Hz), 7.27 (1H, d, $J$=8.3 Hz), 7.41–7.44 (2H, m), 7.77 (1H, dd, $J$=6.6, 2.5 Hz), 7.81–7.83 (1H, m). MS $m/z$ (%) 197 ($M^+$, 100) 182 (85), 167 (30), 156 (22), 90 (6), 28 (24). Calcd for $C_{14}H_{15}N$: $M$, 197.1204. Found: $m/z$ 197.1211.

**3.1.21. 2-(2-Methylpropenyl)anthracen-1-ylamine (11g).** Colorless crystals; mp 98–100 °C (hexane); IR (KBr) 3469 (NH), 3383 (NH), 3050, 2960, 2926, 1617, 1527, 1402, 1387, 891, 873, 735 $cm^{-1}$; $^1H$ NMR $\delta$ 1.75 (3H, s), 2.00 (3H, d, $J$=1.2 Hz), 4.34 (2H, br s), 6.30 (1H, s), 7.19 (1H, d, $J$=8.5 Hz), 7.41–7.46 (3H, m), 7.95–7.97 (1H, m), 7.99 (1H, m), 8.34 (1H, s), 8.39 (1H, s). MS $m/z$ (%) 247 ($M^+$, 100), 232 (26), 217 (20), 202 (6), 115 (8), 28 (24). Calcd for $C_{18}H_{17}N$: $M$, 247.1360. Found: $m/z$ 247.1370. Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.69; H, 6.87; N, 5.57.

**3.1.22. (*E*)-1-Chloro-2-methyl-1-(*p*-tolylsulfinyl)-1,3-butadiene (13*E*) and (*Z*)-1-chloro-2-methyl-1-(*p*-tolylsulfinyl)-1,3-butadiene (13*Z*).** A solution of chloromethyl *p*-tolyl sulfoxide (1.0 g; 5.3 mmol) in dry THF (5 mL) was added dropwise to a solution of LDA (7.95 mmol) in 20 mL of THF at −78 °C. The solution was stirred at −78 °C for 10 min, then methyl vinyl ketone (0.648 mL: 7.95 mmol) was added. The reaction mixture was stirred for 10 min and the reaction was quenched by satd aq $NH_4Cl$. The whole was extracted with $CHCl_3$. The organic layer was washed once with water and dried over $MgSO_4$. The solvent was evaporated to leave the adducts as colorless crystals. The adducts were dissolved in a mixture of acetic anhydride (11.2 mL) and pyridine (21.4 mL). 4-Dimethylaminopyridine (108 mg; 0.88 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 15 h. The acetic anhydride and pyridine were evaporated under vacuum and the residue was purified by silica gel column chromatography to give the acetate (1.21 g; 76%) as a colorless oil (a mixture of two diastereomers); IR (neat) 2995, 2945, 1739 (CO), 1370, 1239 (COC), 1092, 1065 (SO) $cm^{-1}$.

A solution of the acetate (205 mg; 0.68 mmol) in dry THF (4 mL) was added dropwise to a solution of *N*-lithio 2-piperidone [1.7 mmol; prepared from *n*-BuLi (1.7 mmol) and 2-piperidone (169 mg; 1.7 mmol) in THF (4 mL) at 0 °C] in THF at 25 °C. The mixture was stirred at 25 °C for 30 min. The reaction was quenched by satd aq $NH_4Cl$ and the whole was extracted with $CHCl_3$ and the organic layer was washed three times with water. The organic layer was dried over $MgSO_4$. The solvent was evaporated to leave colorless crystals, which were purified by silica gel column chromatography to give **13***E* (79 mg; 48%) and **13***Z* (79 mg; 48%).

Compound **13***E*: Colorless needles; mp 103–104 °C (AcOEt/hexane); IR (KBr) 3095, 3053, 3024, 2918, 1555, 1494, 1417, 1086, 1059 (SO), 922, 899, 807 $cm^{-1}$; $^1H$ NMR $\delta$ 2.13 (3H, s), 2.41 (3H, s), 5.50 (1H, d, $J$=11.0 Hz), 5.63 (1H, d, $J$=16.8 Hz), 7.30 (2H, d, $J$=7.9 Hz), 7.47 (1H, dd, $J$=16.8, 11.0 Hz), 7.48 (2H, d, $J$=7.9 Hz). MS $m/z$ (%) 240 ($M^+$, 15), 223 (12), 205 (10), 188 (16), 175 (18), 157 (25), 139 (46), 124 (46), 117 (52), 105 (25), 89 (72), 77 (20), 65 (100). Calcd for $C_{12}H_{13}ClOS$: $M$, 240.0374. Found: $m/z$ 240.0369. Anal. Calcd for $C_{12}H_{13}ClOS$: C, 59.87; H, 5.44; Cl, 14.73; S, 13.32. Found: C, 59.89; H, 5.29; Cl, 14.73; S, 13.09.

Compound **13***Z*: Colorless crystals; mp 77–78 °C (AcOEt/hexane); IR (KBr) 3050, 3002, 2957, 1564, 1492, 1447, 1418, 1087, 1060 (SO), 939, 891, 810 $cm^{-1}$; $^1H$ NMR $\delta$ 2.40 (3H, s), 2.41 (3H, s), 5.56 (1H, d, $J$=11.0 Hz), 5.69 (1H, d, $J$=17.4 Hz), 6.93 (1H, dd, $J$=17.4, 11.0 Hz), 7.31 (2H, d, $J$=8.3 Hz), 7.49 (2H, d, $J$=8.3 Hz). MS $m/z$ (%) 240 ($M^+$, 20), 223 (22), 192 (15), 187 (15), 177 (22), 157 (65), 139 (45), 123 (55), 105 (30), 91 (40), 77 (20), 65 (100). Calcd for $C_{12}H_{13}ClOS$: $M$, 240.0374. Found: $m/z$ 240.0371. Anal. Calcd for $C_{12}H_{13}ClOS$: C, 59.87; H, 5.44; Cl, 14.73; S, 13.32. Found: C, 59.92; H, 5.21; Cl, 14.62; S, 13.08.

**3.1.23. (*E*)-1-Chloro-2-methyl-1-(*p*-tolylsulfinyl)-1-heptene (14*E*) and (*Z*)-1-chloro-2-methyl-1-(*p*-tolylsulfinyl)-1-heptene (14*Z*).** These compounds were synthesized from chloromethyl *p*-tolyl sulfoxide and 2-heptanone in a similar way as described above. The acetates were isolated by silica

gel column chromatography to give more polar acetate-P (55%) as a colorless oil and less polar acetate-L (39%) as colorless crystals.

Acetate-P; IR (neat) 2956, 2870, 1732 (CO), 1494, 1461, 1369, 1243 (COC), 1154, 1093, 1066 (SO), 1018, 820, 516 $cm^{-1}$; $^1H$ NMR $\delta$ 0.89 (3H, t, $J$=7.0 Hz), 1.20–1.43 (6H, m), 1.71 (3H, s), 1.87–1.93 (1H, m), 2.14 (3H, s), 2.17–2.20 (1H, m), 2.42 (3H, s), 5.25 (1H, s), 7.33 (2H, d, $J$=8.3 Hz), 7.47 (2H, d, $J$=8.3 Hz). MS $m/z$ (%) 344 ($M^+$, 2), 205 (32), 140 (87), 139 (36), 109 (26), 91 (16), 65 (6), 43 (100). Calcd for $C_{17}H_{25}ClO_3S$: $M$, 344.1213. Found: $m/z$ 344.1216.

Acetate-L: Colorless crystals; mp 64–65 °C (AcOEt/hexane); IR (KBr) 2950, 2931, 1726 (CO), 1242 (COC), 1087, 1463 (SO), 515 $cm^{-1}$; $^1H$ NMR $\delta$ 0.92 (3H, t, $J$=7.0 Hz), 1.33–1.48 (6H, m), 1.61 (3H, s), 1.99–2.06 (1H, m), 2.09 (3H, s), 2.35–2.40 (1H, m), 2.42 (3H, s), 5.38 (1H, s), 7.33 (2H, d, $J$=8.0 Hz), 7.47 (2H, d, $J$=8.0 Hz). MS $m/z$ (%) 344 ($M^+$, 2), 205 (32), 140 (50), 139 (33), 109 (25), 91 (15), 65 (6), 43 (100). Calcd for $C_{17}H_{25}ClO_3S$: $M$, 344.1231. Found: $m/z$ 344.1233. Anal. Calcd for $C_{17}H_{25}ClO_3S$: C, 59.20; H, 7.31; Cl, 10.28; S, 9.3. Found: C, 59.18; H, 7.36; Cl, 10.15; S, 9.23.

Treatment of the acetate-L and acetate-P with *N*-lithio 2-piperidone in THF at 25 °C gave **14***Z* (93%) and **14***E* (96%), respectively.

Compound **14***E*: Colorless oil; IR (neat) 2957, 2929, 2860, 1493, 1456, 1088, 1061 (SO), 808 $cm^{-1}$; $^1H$ NMR $\delta$ 0.87 (3H, t, $J$=7.0 Hz), 1.26–1.31 (4H, m), 1.45–1.50 (2H, m), 2.31 (3H, s), 2.33 (2H, t, $J$=8.0 Hz), 2.41 (3H, s), 7.30 (2H, d, $J$=7.9 Hz), 7.46 (2H, d, $J$=7.9 Hz). MS $m/z$ (%) 284 ($M^+$, 26), 267 (100), 211 (24), 175 (32), 140 (36), 139 (26), 123 (21), 91 (36), 89 (17), 65 (17). Calcd for $C_{15}H_{21}ClO_3S$: $M$, 284.1002. Found: $m/z$ 284.0994.

Compound **14***Z*: Colorless oil; IR (neat) 2957, 2929, 2861, 1493, 1456, 1088, 1062 (SO), 808 $cm^{-1}$; $^1H$ NMR $\delta$ 0.94 (3H, t, $J$=6.6 Hz), 1.38–1.41 (4H, m), 1.50–1.59 (2H, m), 2.00 (3H, s), 2.41 (3H, s), 2.73 (2H, t, $J$=7.9 Hz), 7.31 (2H, d, $J$=7.9 Hz), 7.49 (2H, d, $J$=8.2 Hz). MS $m/z$ (%) 284 ($M^+$, 85), 267 (100), 211 (75), 175 (56), 140 (90), 139 (63), 123 (56), 91 (72), 89 (68), 55 (42), 41 (42). Calcd for $C_{15}H_{21}ClOS$: $M$, 284.1001. Found: $m/z$ 284.0993.

**3.1.24. (*Z*)-2-(Cyclohex-2-enylidenemethyl)phenylamine (16*Z*).** Colorless oil; IR (neat) 3467 (NH), 3376 (NH), 3030, 2932, 2829, 1615, 1489, 1453, 747 $cm^{-1}$; $^1H$ NMR $\delta$ 1.81 (2H, quintet, $J$=6.2 Hz), 2.18–2.20 (2H, m), 2.48 (2H, t, $J$=6.0 Hz), 3.69 (2H, br s), 5.87–5.91 (1H, m), 6.01 (1H, s), 6.35 (1H, d, $J$=10.8 Hz), 6.69 (1H, d, $J$=7.6 Hz), 6.73 (1H, t, $J$=7.3 Hz), 7.04–7.07 (2H, m). MS $m/z$ (%) 185 ($M^+$, 100), 170 (15), 157 (64), 143 (14), 130 (34), 115 (10), 106 (52), 91 (13), 77 (14). Calcd for $C_{13}H_{15}N$: $M$, 185.1204. Found: $m/z$ 185.1210.

**3.1.25. (*E*)-2-(Cyclohex-2-enylidenemethyl)phenylamine (16*E*).** Colorless oil; IR (neat) 3461 (NH), 3375 (NH), 3021, 2931, 2862, 2829, 1615, 1489, 1454 $cm^{-1}$; $^1H$ NMR $\delta$ 1.68 (2H, quintet, $J$=6.2 Hz), 2.16–2.19 (2H, m), 2.47 (2H, dt, $J$=6.3, 1.5 Hz), 3.69 (2H, br s), 5.88–5.91 (1H, m), 6.10 (1H, s), 6.25 (1H, d, $J$=10.0 Hz), 6.69 (1H, d, $J$=8.0 Hz), 6.74 (1H, t, $J$=7.5 Hz), 7.04–7.07 (2H, m). MS $m/z$ (%) 185 ($M^+$, 100), 170 (13), 157 (63), 143 (13), 130 (33), 115 (10), 106 (52), 91 (12), 77 (12). Calcd for $C_{13}H_{15}N$: $M$, 185.1204. Found: $m/z$ 185.1212.

**3.1.26. (*Z*)-2-(Cyclohex-2-enylidenemethyl)naphthalen-1-ylamine (17*Z*).** Colorless crystals; mp 71–73 °C (hexane); IR (KBr) 3478 (NH), 3392 (NH), 2928, 2856, 2822, 1614, 1403, 790, 736 $cm^{-1}$; $^1H$ NMR $\delta$ 1.84 (2H, quintet, $J$=6.2 Hz), 2.20–2.21 (2H, m), 2.53 (2H, t, $J$=6.3 Hz), 4.16 (2H, br s), 5.88–5.91 (1H, m), 6.18 (1H, s), 6.32 (1H, dd, $J$=10.0, 0.9 Hz), 7.23 (1H, d, $J$=8.3 Hz), 7.26 (1H, d, $J$=8.3 Hz), 7.40–7.43 (2H, m), 7.74–7.76 (1H, m), 7.78–7.80 (1H, m). MS $m/z$ (%) 235 ($M^+$, 100), 220 (10), 207 (42), 193 (8), 180 (30), 167 (6), 156 (18), 143 (6). Calcd for $C_{17}H_{17}N$: $M$, 235.1359. Found: $m/z$ 235.1353.

**3.1.27. (*E*)-2-(Cyclohex-2-enylidenemethyl)naphthalen-1-ylamine (17*E*).** Colorless oil; IR (neat) 3472 (NH), 3385 (NH), 3054, 3021, 2930, 2862, 2829, 1615, 1403, 806, 758, 737 $cm^{-1}$; $^1H$ NMR $\delta$ 1.68 (2H, quintet, $J$=6.2 Hz), 2.17–2.20 (2H, m), 2.46 (2H, t, $J$=6.2 Hz), 4.18 (2H, br s), 5.90–5.93 (1H, m), 6.29 (1H, s), 6.31 (1H, d, $J$=10.1 Hz), 7.22 (1H, d, $J$=8.6 Hz), 7.26 (1H, d, $J$=8.6 Hz), 7.39–7.43 (2H, m), 7.74–7.76 (1H, m), 7.79–7.80 (1H, m). MS $m/z$ (%) 235 ($M^+$, 100), 220 (10), 207 (44), 193 (8), 180 (30), 167 (8), 156 (18), 143 (6). Calcd for $C_{17}H_{17}N$: $M$, 235.1360. Found: $m/z$ 235.1366.

**3.1.28. (*Z*)-2-(Cyclohex-2-enylidenemethyl)athracen-1-ylamine (18*Z*).** Colorless amorphous; IR (KBr) 3456 (NH), 3382 (NH), 2929, 2858, 1618, 875, 738 $cm^{-1}$; $^1H$ NMR $\delta$ 1.85 (2H, quintet, $J$=6.2 Hz), 2.21–2.23 (2H, m), 2.55 (2H, t, $J$=5.9 Hz), 4.34 (2H, br s), 5.91–5.94 (1H, m), 6.22 (1H, s), 6.37 (1H, dd, $J$=10.0, 0.9 Hz), 7.24 (1H, dd, $J$=8.7, 1.9 Hz), 7.40–7.43 (3H, m), 7.93–7.97 (2H, m), 8.31 (1H, s), 8.34 (1H, s). MS $m/z$ (%) 285 ($M^+$, 100), 257 (16), 230 (16), 206 (10), 193 (6). Calcd for $C_{21}H_{19}N$: $M$, 285.1516. Found: $m/z$ 285.1509.

**3.1.29. (*E*)-2-(Cyclohex-2-enylidenemethyl)athracen-1-ylamine (18*E*).** Colorless crystals; mp 114–115 °C (hexane); IR (KBr) 3462 (NH), 3389 (NH), 2928, 2827, 1613, 869, 737 $cm^{-1}$; $^1H$ NMR $\delta$ 1.71 (2H, quintet, $J$=6.1 Hz), 2.19–2.21 (2H, m), 2.49 (2H, t, $J$=6.0 Hz), 4.35 (2H, br s), 5.91–5.95 (1H, m), 6.33–6.34 (2H, m), 7.24 (1H, d, $J$=8.5 Hz), 7.41–7.43 (3H, m), 7.93–7.97 (2H, m), 8.31 (1H, m), 8.35 (1H, s). MS $m/z$ (%) 285 ($M^+$, 100), 256 (18), 230 (18), 206 (10). Calcd for $C_{21}H_{19}N$: $M$, 285.1517. Found: $m/z$ 285.1521. Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 87.79; H, 6.44; N, 4.86.

**3.1.30. (*Z*)-2-(2-Methylbuta-1,3-dienyl)naphthalen-1-ylamine (19*Z*).** Colorless crystals; mp 51–52 °C (hexane); IR (KBr) 3476 (NH), 3391 (NH), 3055, 2979, 2930, 1618, 1404, 900, 810, 762, 738 $cm^{-1}$; $^1H$ NMR $\delta$ 2.07 (3H, s), 4.21 (2H, br s), 5.14 (1H, d, $J$=10.7 Hz), 5.36 (1H, d, $J$=17.4), 6.47 (1H, s), 6.65 (1H, dd, $J$=17.4, 10.7 Hz), 7.19 (1H, d, $J$=8.3 Hz), 7.26 (1H, d, $J$=8.3 Hz), 7.41–7.45 (2H, m), 7.75–7.77 (1H, m), 7.79–7.81 (1H, m). MS $m/z$ (%) 209 ($M^+$, 100), 194 (84), 178 (20), 165 (12), 152 (8), 139 (6), 96

(12). Calcd for $C_{15}H_{15}N$: *M*, 209.1204. Found: *m/z* 209.1207. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.85; H, 7.24; N, 6.69.

**3.1.31. (*E*)-2-(2-Methylbuta-1,3-dienyl)naphthalen-1-ylamine (19*E*).** Colorless oil; IR (neat) 3474 (NH), 3388 (NH), 3055, 2918, 1615, 1403, 902, 797, 760, 737 $cm^{-1}$; $^1H$ NMR $\delta$ 1.89 (3H, s), 4.22 (2H, br s), 5.16 (1H, d, $J$=10.7 Hz), 5.33 (1H, d, $J$=17.4 Hz), 6.55 (1H, s), 6.66 (1H, dd, $J$=17.4, 10.7 Hz), 7.21 (1H, d, $J$=8.2 Hz), 7.28 (1H, d, $J$=8.2 Hz), 7.42–7.46 (2H, m), 7.77–7.78 (1H, m), 7.81–7.83 (1H, m). MS *m/z* (%) 209 ($M^+$, 100), 194 (88), 178 (20), 165 (14), 152 (10), 139 (6), 115 (6), 96 (14). Calcd for $C_{15}H_{15}N$: *M*, 209.1203. Found: *m/z* 209.1203.

**3.1.32. (*Z*)-2-(2-Methylhept-1-enyl)naphthalen-1-ylamine (20*Z*).** Colorless oil; IR (neat) 3467 (NH), 3386 (NH), 2927, 2857, 1611, 1400, 1380 $cm^{-1}$; $^1H$ NMR $\delta$ 0.81 (3H, t, $J$=6.9 Hz), 1.13–1.23 (4H, m), 1.42 (2H, quintet, $J$=7.6 Hz), 1.94 (3H, s), 2.07 (2H, t, $J$=7.8 Hz), 4.17 (2H, br s), 6.23 (1H, s), 7.14 (1H, d, $J$=8.3 Hz), 7.26 (1H, d, $J$=9.2 Hz), 7.40–7.45 (2H, m), 7.76 (1H, m), 7.81 (1H, d, $J$=7.3 Hz). MS *m/z* (%) 253 ($M^+$, 100), 196 (50), 182 (54), 167 (12), 156 (23), 143 (23). Calcd for $C_{18}H_{23}N$: *M*, 253.1828. Found: *m/z* 253.1822.

**3.1.33. (*E*)-2-(2-Methylhept-1-enyl)naphthalen-1-ylamine (20*E*).** Colorless oil; IR (neat) 3472 (NH), 3384 (NH), 2928, 2856, 1615, 1403, 800, 760, 734 $cm^{-1}$; $^1H$ NMR $\delta$ 0.94 (3H, t, $J$=6.4 Hz), 1.38 (4H, m), 1.57 (2H, t, $J$=6.7 Hz), 1.69 (3H, s), 2.24 (2H, t, $J$=7.5 Hz), 4.18 (2H, br s), 6.25 (1H, s), 7.17 (1H, d, $J$=8.3 Hz), 7.27 (1H, d, $J$=8.3 Hz), 7.40–7.45 (2H, m), 7.76 (1H, d, $J$=8.0 Hz), 7.81 (1H, d, $J$=7.7 Hz). MS *m/z* (%) 253 ($M^+$, 100), 238 (6), 196 (53), 182 (61), 167 (13), 156 (25), 143 (23). Calcd for $C_{18}H_{23}N$: *M*, 253.1829. Found: *m/z* 253.1837.

**3.1.34. (*Z*)-2-(2-Phenylpropenyl)naphthalen-1-ylamine (21*Z*).** Colorless crystals; mp 110–112 °C (AcOEt/hexane); IR (KBr) 3487 (NH), 3391 (NH), 2965, 2926, 2869, 1614, 1406, 804, 760, 748, 696 $cm^{-1}$; $^1H$ NMR $\delta$ 2.32 (3H, s), 4.24 (2H, br s), 6.55 (1H, s), 6.86 (1H, d, $J$=8.6 Hz), 7.02 (1H, d, $J$=8.6 Hz), 7.13–7.20 (5H, m), 7.36–7.42 (2H, m), 7.65–7.67 (1H, m), 7.76 (1H, d, $J$=8.0 Hz). MS *m/z* (%) 259 ($M^+$, 92), 244 (100), 215 (8), 182 (11), 167 (10), 156 (18), 121 (12). Calcd for $C_{19}H_{17}N$: *M*, 259.1359. Found: *m/z* 259.1355. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.82; H, 6.58; N, 5.48.

**3.1.35. (*E*)-2-(2-Phenylpropenyl)naphthalen-1-ylamine (21*E*).** Colorless amorphous; IR (KBr) 3484 (NH), 3399 (NH), 3049, 2919, 2851, 1608, 1404, 761, 740, 697 $cm^{-1}$; $^1H$ NMR $\delta$ 2.16 (3H, s), 4.27 (2H, br s), 6.90 (1H, s), 7.28 (1H, d, $J$=8.3 Hz), 7.32–7.34 (2H, m), 7.40 (2H, t, $J$=7.6 Hz), 7.44–7.48 (2H, m), 7.61 (2H, d, $J$=8.0 Hz), 7.79–7.81 (1H, m), 7.84–7.86 (1H, m). MS *m/z* (%) 259 ($M^+$, 92), 244 (100), 215 (8), 182 (11), 167 (8), 156 (17), 122 (8), 121 (9). Calcd for $C_{19}H_{17}N$: *M*, 259.1360. Found: *m/z* 259.1364.

**3.1.36. (*E*)-3-Cholromethylenecyclohexene (22*E*).** To a solution of **12** (80 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.036 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.84 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid. After 5 min, the reaction was quenched by satd aq $NH_4Cl$ and the whole was extract with $CHCl_3$. 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 19.7 mg (51%) of **22*E*** as a colorless oil; IR (neat) 2941, 2867, 2834, 1694, 835, 795, 755 $cm^{-1}$; $^1H$ NMR $\delta$ 1.71 (2H, quintet, $J$=6.3 Hz), 2.11–2.15 (2H, m), 2.46 (2H, dt, $J$=6.3, 2.1 Hz), 5.83–5.87 (1H, m), 5.91 (1H, s), 6.06 (1H, dt, $J$=10.1, 2.0 Hz). MS *m/z* (%) 128 ($M^+$, 40), 113 (6), 93 (100), 79 (82), 77 (66). Calcd for $C_7H_9Cl$: *M*, 128.0393. Found: *m/z* 128.0390.

**3.1.37. (*Z*)-3-Cholromethylenecyclohexene (22*Z*).** Colorless oil; IR (neat) 2940, 2866, 2832, 818, 758, 731 $cm^{-1}$; $^1H$ NMR $\delta$ 1.70–1.75 (2H, m), 2.16–2.20 (2H, m), 2.30–2.33 (2H, m), 5.72 (1H, s), 6.01–6.05 (1H, m), 6.55–6.58 (1H, m). MS *m/z* (%) 128 ($M^+$, 32) 113 (9), 93 (67), 83 (100), 79 (47), 77 (46). Calcd for $C_7H_9Cl$: *M*, 128.0393. Found: *m/z* 128.0391.

**3.1.38. (*E*)-(2-Chloro-1-methylvinyl)benzene (23*E*).** Colorless oil; IR (neat) 3080, 3059, 2923, 1494, 1443, 801, 749, 695 $cm^{-1}$; $^1H$ NMR $\delta$ 2.20 (3H, d, $J$=1.2 Hz), 6.32 (1H, q, $J$=1.4 Hz), 7.27–7.31 (1H, m), 7.32–7.34 (4H, m). MS *m/z* (%) 152 ($M^+$, 100), 115 (56), 103 (33), 91 (47), 78 (42). Calcd for $C_9H_9Cl$: *M*, 152.0393. Found: *m/z* 152.0397.

**3.1.39. (*Z*)-(2-Chloro-1-methylvinyl)benzene (23*Z*).** Colorless oil; IR (neat) 3059, 2970, 2916, 1494, 1442, 835, 762, 697 $cm^{-1}$; $^1H$ NMR $\delta$ 2.09 (3H, d, $J$=1.5 Hz), 6.11 (1H, q, $J$=1.5 Hz), 7.28–7.32 (1H, m), 7.37–7.38 (4H, m). MS *m/z* (%) 152 ($M^+$, 100) 115 (56), 103 (33), 91 (18), 78 (43). Calcd for $C_9H_9Cl$: *M*, 152.0393. Found: *m/z* 152.0390.

## Acknowledgements

This work was supported by a grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan to promote multi-disciplinary research project, which is gratefully acknowledged.

## References and notes

1. Barton, D. H. R.; Ollis, W. D. In Sutherland, I. O., Ed.; Comprehensive Organic Chemistry; Pergamon: Oxford, 1979; Vol. 2, pp 131–184.
2. Arienti, A.; Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron* **1997**, *53*, 3795–3804.
3. (a) Yamaguchi, M.; Arisawa, M.; Hirama, M. *Chem. Commun.* **1998**, 1399–1400. (b) Yamaguchi, M.; Arisawa, M. *Farumashia* **1999**, *35*, 145–149.
4. Satoh, T.; Kawashima, T.; Takahashi, S.; Sakai, K. *Tetrahedron* **2003**, *59*, 9599–9607.

5. Satoh, T.; Takano, K.; Someya, H.; Matsuda, K. *Tetrahedron Lett.* **1995**, *36*, 7097–7100.
6. (a) Satoh, T. *J. Synth. Org. Chem. Jpn.* **1996**, *54*, 481–489. (b) Satoh, T. *J. Synth. Org. Chem. Jpn.* **2003**, *61*, 98–110. (c) Satoh, T. *Chem. Rec.* **2004**, *3*, 329–341.
7. Satoh, T.; Takano, K.; Ota, H.; Someya, H.; Matsuda, K.; Koyama, M. *Tetrahedron* **1998**, *54*, 5557–5574.
8. (a) Satoh, T.; Sakamoto, T.; Watanabe, M. *Tetrahedron Lett.* **2002**, *43*, 2043–2046. (b) Satoh, T.; Sakamoto, T.; Watanabe, M.; Takano, K. *Chem. Pharm. Bull.* **2003**, *51*, 966–970.
9. Preliminary results of this study was reported as a communication: Satoh, T.; Ogino, Y.; Nakamura, M. *Tetrahedron Lett.* **2004**, *45*, 5785–5789.
10. (a) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405. (b) Oku, A.; Harada, T. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 736–755. (c) Oku, A. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 710–723. (d) Kirmse, W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1164–1170.
11. (a) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035–5037. (b) Walborsky, H. M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, *26*, 2743–2746. (c) Rachon, J.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 7435–7436. (d) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546–555.
12. (a) Harada, T.; Nozaki, Y.; Yamaura, Y.; Oku, A. *J. Am. Chem. Soc.* **1985**, *107*, 2189–2190. (b) Oku, A.; Harada, T.; Hattori, K.; Nozaki, Y.; Yamaura, Y. *J. Org. Chem.* **1988**, *53*, 3089–3098.
13. Yanagisawa, H.; Miura, K.; Kitamura, M.; Narasaka, K.; Ando, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2009–2026.
14. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; G. Petersson, A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng. C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian Inc., Pittsburgh PA, 1998.
15. For both Mg and Li, the 6-31G* basis set was used.
16. Seebach, D.; Siegel, H.; Müllen, K.; Hiltbrunner, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 784–785.
17. (a) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046–2053. (b) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308–337.
18. Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467–6475.
19. (a) Pelter, A.; Kvicala, J.; Parry, D. E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2681–2682. (b) Wang, B.; Deng, C. *Chem. Phys. Lett.* **1988**, *147*, 99–104.
20. The electrostatic potential-derived charges using the CHelpG scheme of Breneman: *E*-**25**, −0.118; *Z*-**25**, −0.138; **24**, −0.141; **26**, −0.28. The Mulliken charges: *E*-**25**, +0.13; *Z*-**25**, +0.14; **24**, −0.11; **26**, −0.19.
21. Satoh, T.; Ota, H. *Tetrahedron* **2000**, *56*, 5113–5122.