Generation of cationic 2-azabutadienes from N,S-acetals and their use for the regio- and diastereoselective synthesis of 1,2,3,4-tetrahydroquinolines by intermolecular [4π⁺ + 2π] cycloadditions

Uwe Beifuss a,*, Sabine Ledderhose, b and Vladimir Ondrus a

a Bioorganische Chemie, Institut für Chemie der Universität Hohenheim, Garbenstrasse 30, D-70599 Stuttgart, Germany
b Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany
E-mail: ubeifuss@uni-hohenheim.de

Dedicated to Professor Dr. L. Fisera on the occasion of his 60th birthday
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Abstract
Substituted 1,2,3,4-tetrahydroquinolines and related N-heterocycles are formed highly regio- and diastereoselectively with yields ranging from 57 to 100% by intermolecular polar [4π⁺ + 2π] cycloadditions of cationic 2-azabutadienes and various dienophiles. The cationic 2-azabutadienes can be generated in situ by Lewis acid mediated heterolytic cleavage of N,S-acetals. Best results have been obtained using a new mixed Lewis acid consisting of a mixture of TiCl₄ and PPh₃.

Keywords: N,S-Acetals, cationic 2-azabutadienes, intermolecular [4π⁺ + 2π] cycloadditions, 1,2,3,4-tetrahydroquinolines

Introduction
Tetrahydroquinolines and related ring systems have gained much attention in both natural product synthesis and medical research. Their efficient synthesis can be achieved, for example, by intermolecular cycloadditions of positively charged 2-azabutadienes 1 or neutral 2-azabutadienes 4 with electron-rich alkenes 2 (Scheme 1).¹
Scheme 1

The reactions can be regarded as hetero Diels-Alder reactions with inverse electron demand, with 2-azabutadiene representing the electron-poor and alkene the electron-rich component. 2-azabutadienes can be distinguished by the type of preparation. The majority of reactions so far reported have involved preformed 2-azabutadienes, which are usually obtained by condensation of a primary aromatic amine with a carbonyl compound. Also, there are cycloadditions where the neutral or positively charged 2-azabutadiene is prepared in situ.

Results and Discussion

AM1 calculations indicate that cationic 2-azabutadienes such as 6 - due to their lower LUMO energies - exhibit much higher reactivity than the corresponding neutral 2-azabutadienes like 7 (Figure 1). In addition, the p-atomic orbital coefficients suggest that cationic 2-azabutadienes react much more selectively.

Figure 1. LUMO energies and p-atomic orbital coefficients of 6 and 7 (AM 1).
Mechanistically, these reactions may either be seen to proceed in a concerted manner as polar \([4\pi^+ + 2\pi]\) cycloadditions in terms of hetero Diels Alder reactions with inverse electron demand \(^2\), or as a multi-step process starting with the addition of an alkene 9 to an iminium ion 8 (Figure 2, B) and formation of a carbenium ion 11 as an intermediate and finally undergoing an intramolecular Friedel Crafts reaction.\(^2\)

**Figure 2.** Alternative mechanism for the formation of tetrahydroquinolines 12 from the reaction of cationic 2-azabutadienes 8 with alkenes 9.

As far as we know the first example was reported by Swan, who reacted \(N,N\)-acetal 13 in the presence of benzoic acid with ethyl vinyl ether 14 and obtained the 4-substituted tetrahydroquinoline rac-15 (Scheme 2).\(^5\)

**Scheme 2**

*Shono et al.* demonstrated later that 2-aryl iminium ions may be generated by cleavage of \(N,O\)-acetals with Lewis acids at low temperatures. Here also, reaction with simple and electron-rich olefins leads to regioselective formation of 1,2,3,4-tetrahydroquinolines. For example,
reaction of $N,O$-acetal 16 with silyl enol ether 17 produces the cyclization product $rac$-18 in 61% yield (Scheme 3).

Scheme 3

The same method has also been used recently in the synthesis of 2-difluoromethyl- and 2-trifluoromethyl-substituted quinolines. Altogether, however, the role of $N,O$-acetals in the generation of aryl iminium ions 8 has been limited, since efficient preparation of $N,O$-acetals is only managed by anodic oxidation of tertiary aromatic amines such as $N,N$-dimethylaniline.

Another way of synthesizing tetrahydroquinolines involves the reaction of $N$-(tert-butyldioxymethyl)-anilines, which can be produced by ruthenium-catalyzed oxidation of tertiary $N$-methylanilines and tert-butyl hydroperoxide. But as the reaction of 19 with the $(E)/(Z)$ mixture of crotal trimethylsilane 20 shows that the transformations do not run stereospecifically, i.e. with preservation of the configuration of the dienophilic double bond, since the presumably more stable trans isomer $rac$-21 is obtained in marked excess (de = 88%), which is attributed to the reaction’s involving a cationic multi-step mechanism instead of a polar $[4\pi^+ + 2\pi]$ cycloaddition (Scheme 4).

Scheme 4

Katritzky et al. have reported on a highly efficient approach to tetrahydroquinolines by using $N$-[(benzotriazol-1-yl)methyl]anilines as precursors for the generation of 2-aryl iminium ions.

2-Azabutadienes 8 can also be produced by reaction of aromatic anilines with carbonyl compounds. In particular, Hesse regioselectively reacted primary anilines with aldehydes and alkenes in mixtures of acetic and sulfuric acid to give 1,2,3,4-tetrahydroquinolines (Scheme 5).
The steric course of the transformation remains unknown. If formaldehyde 23 was used as the carbonyl compound the products of the double amino alkylation were isolated, whereas reaction of secondary aromatic amines such as \(N\)-methylaniline 22 with formaldehyde 23 led to tetrahydroquinolines like \(\text{rac-25}\).

\[
\begin{array}{ccc}
\text{Ph} & \text{HCHO} & \text{HOAc, H}_2\text{SO}_4, 23\,^\circ\text{C, 2h} \\
\text{N} & & 67\% \\
\text{22} & \text{23} & \text{24} \\
\end{array}
\]

Scheme 5

\text{Grieco} and \text{Bahsas} demonstrated that cationic 2-azabutadienes like 27 could be generated in considerably milder conditions from anilinium trifluoroacetate 26 and formaldehyde 23 and then reacted with dienophiles. Transformation of 26 with 23 and cyclopentadiene 28 produced the diastereomeric mixture of the pentacycles \(\text{rac-29}\) and \(\text{rac-30}\) (Scheme 6). Here also only the double cyclization products are formed in transformations involving formaldehyde 23. With \text{Grieco} and \text{Bahsas} the synthesis of tetrahydroquinolines can also only be managed if they evade taking formaldehyde 23 as the aldehyde component. Following this method \text{Mellor et al.} have gained access to a large number of polycyclic systems by transforming numerous aromatic and heteroaromatic primary amines with formaldehyde and alkenes. They often selected amines that only allow a single cyclization. Even if few studies have so far been undertaken on the mechanism of the transformation of cationic 2-azabutadienes, the majority of findings indicates that the cyclizations proceed in a stepwise manner. Transformation of 19 and 20 producing \(\text{rac-21}\) favors a multi-step process since it proceeds without preserving the dienophilic double bond configuration. In a number of cases \text{Mellor et al.} also managed to isolate follow-up products of potential intermediates which were then cyclized under reaction conditions to give the final products. From this they concluded that the reactions in these cases proceed stepwise. The present results, though, are insufficient to provide a satisfying answer to the question of which mechanism underlies these cyclizations.
Scheme 6

Of the methods employed to generate cationic 2-azabutadienes the heterolytic cleavage of α-heterosubstituted amines is least subject to constraints on substrate selection. Further advantages are that these reactions can be run in situ under relatively mild conditions and that usually no side products occur with the cycloaddition products. The disadvantage though is that some of the previously employed α-heterosubstituted amines are not easily accessible. According to Shono et al. N,O-acetal 16, for example, can only be efficiently obtained via anodic oxidation of N,N-dimethylaniline in methanol.6a Following previous work by Stewart and Bradley23 we were – in contrast to Shono’s report 6a – able to show that N,O-acetal 16 may very well be produced without being contaminated with the corresponding N,N-acetal 13, though in a yield of just 36% (Scheme 7).

Much better results (69% yield) were achieved when N,N-acetal 13 was obtained by reaction of 22 and 23 (Scheme 8).24

Scheme 7

Scheme 8
Using N,S-acetals 31,25,26 α-aminosulfones 32 27,28 and α-aminonitriles 33 29,30 as substrates for cationic 2-azabutadienes 8 (Figure 3) turned out to be particularly successful.31,32 Here we present a detailed report on the preparation of N,S-acetals, their transformation into the corresponding cationic 2-azabutadienes and their reaction with alkenes to give 1,2,3,4-tetrahydroquinolines.

![Figure 3]

**Figure 3**

Synthesis of N,S-acetal 35a was easily performed by reacting N-methylaniline 22 with formaldehyde 23 and thiophenol 34a in a yield of 84% (Scheme 9).33 The corresponding S-ethyl derivative 35b was produced in a similar way. Due to lower yields of 35b, most studies presented in this paper were undertaken with the S-phenyl derivative 35a.

![Scheme 9]

**Scheme 9**

When N,S-acetal 35a was reacted with styrene 36 and TiCl₄ as a Lewis acid the single cycloadduct produced was the tetrahydroquinoline rac-37 in 61% yield (Scheme 10) (Table 1, Entry 1), which indicates that in 35a the only cleavage taking place is in the C-S bond resulting in the formation of the iminium salt 38; obviously, cleavage of the C-N bond to give 39 does not occur (Scheme 11).
Table 1. Reactions of the N,S-acetals 35a,b with styrene 36 using different Lewis acids

<table>
<thead>
<tr>
<th>Entry</th>
<th>N,S-acetal</th>
<th>Lewis acid</th>
<th>Equiv. (LA)</th>
<th>Equiv. (LA)</th>
<th>T[°C]; t[h]</th>
<th>rac 37 [%]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35a</td>
<td>TiCl4</td>
<td>1.2</td>
<td>1.3</td>
<td>-78; 1</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>35a</td>
<td>SnCl4</td>
<td>1.0</td>
<td>1.5</td>
<td>-78→23; 2; then 23; 2</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>35a</td>
<td>SnCl4</td>
<td>1.0</td>
<td>1.5</td>
<td>23; 1.25</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>35a</td>
<td>SnCl4</td>
<td>2.0</td>
<td>1.5</td>
<td>0;0.25; then 23; 1</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>35a</td>
<td>SnCl4</td>
<td>2.0</td>
<td>3.0</td>
<td>0;0.25; then 23; 1</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>35a</td>
<td>BF3·Et2O</td>
<td>1.0</td>
<td>1.5</td>
<td>-78; 0.25; then 23; 2; then 23; 1</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>35a</td>
<td>(CH3)2S(CH3)BF4</td>
<td>2.0</td>
<td>1.5</td>
<td>23; 24</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>35a</td>
<td>TiCl4 : PPh3 = 1:1</td>
<td>2.0</td>
<td>1.5</td>
<td>0; 0.25; then 23; 96</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>35a</td>
<td>TiCl4 : PPh3 = 2:1</td>
<td>2.0</td>
<td>1.5</td>
<td>0; 0.25; then 23; 72</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>35b</td>
<td>TiCl4 : PPh3 = 2:1</td>
<td>2.0</td>
<td>1.5</td>
<td>0; 0.25; then 23; 72</td>
<td>80</td>
</tr>
</tbody>
</table>

a Isolated Yield.

Scheme 11

If TiCl4 was replaced by SnCl4, tetrahydroquinoline rac-37 was isolated after 1 h at -78 °C, also in 61% yield (Table 1, Entry 2). Performing the reaction with 1.0 equivalents of SnCl4 at higher temperatures (Table 1, Entry 3) raises the yield to 81%. A further increase may be achieved – even though more modestly – by employing 2.0 equivalents of SnCl4 (Table 1, Entry 4). Since both TiCl4 and SnCl4 led to partial decomposition of the N,S-acetal weaker Lewis
acids were also included in this study. Mixtures of TiCl₄ and triphenylphosphine turned out to be particularly promising. In a 1 : 1 ratio they have already been successfully applied as a Lewis acid in a number of cases. ³⁴

If 35a was reacted with styrene (36) and a 1 : 1 mixture of TiCl₄ and triphenylphosphine no formation of rac-37 could be observed (Table 1, Entry 8). On the other hand, rac-37 was isolated in quantitative yield if the reaction was performed with a 2 : 1 mixture of TiCl₄ and triphenylphosphine (Table 1, Entry 9). Since the corresponding transformation with S-ethyl derivative 35b produced tetrahydroquinoline in a yield of no more than 80% (Table 1, Entry 10), S-phenyl-derivative 35a was employed for all transformations with other dienophiles.

Here we found that N,S-acetal 35a may be reacted with a number of dienophiles to give the corresponding tetrahydroquinolines (Table 2). In addition to styrene (36), 35a was also reacted with singly and triply substituted acyclic alkenes 40 and 42, with the allyl ether 44 and the allylsilane 46 (Table 2, Entries 1-5). Furthermore, the cyclic alkenes cyclopentene (48) and cyclopentadiene (28) could be converted into the products 49 and 50 as expected (Table 2, Entries 6, 7). The cycloadducts were obtained in yields ranging from 57 to 100%.

A total surprise, though, was encountered with the products isolated from the reactions of N,S-acetals with enol ethers and silyl enol ethers. While no reaction could be observed between 35a and dihydropyran 51, the transformation with ethyl vinyl ether 14 gave thioether rac-52 as the sole cycloadduct (Scheme 12). The same product was formed by reaction with n-butyl vinyl ether 53.

Transformations of 35a with silyl enol ethers led to correspondingly substituted thioethers; for example, 35a and 54 were converted into rac-55 (Scheme 13).

Faced with these results we assumed that the transformation of the vinyl ethers 56 into the corresponding vinyl sulfides 57 proceed in situ under the influence of Lewis acids in a manner illustrated in Figure 4, which then react with 2-azabutadiene.

In accordance with these findings we expected the formation of the ethyl thio ether 58 when the S-ethyl derivative 35b was reacted with enol ethers such as 53; this assumption turned out to be correct (Scheme 14).
**Table 2.** Reactions of \( N,S\)-acetal 35a with different dienophiles for the regio- and diastereoselective synthesis of 1,2,3,4-tetrahydroquinolines using a 2:1 mixture of TiCl\(_4\) and PPh\(_3\) as Lewis acid

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dienophile (^a)</th>
<th>( t ) [h] (^b)</th>
<th>Product</th>
<th>Yield [%] (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>36 72</td>
<td><img src="Ph" alt="Image" /></td>
<td>37 100</td>
</tr>
<tr>
<td>2</td>
<td>( n)-Bu</td>
<td>40 72</td>
<td><img src="n-Bu" alt="Image" /> 41</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>42 120</td>
<td><img src="n-Bu" alt="Image" /> 43</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>( n)-BuO</td>
<td>44 72</td>
<td><img src="n-BuO" alt="Image" /> 45</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>Me(_3)Si</td>
<td>46 72</td>
<td><img src="Me(_3)Si" alt="Image" /> 47</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>14 120</td>
<td><img src="H" alt="Image" /> 49 (^d)</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>28 48</td>
<td><img src="H" alt="Image" /> 50 (^d)</td>
<td>79</td>
</tr>
</tbody>
</table>

\(^a\) In each case, 1.5 equiv. of the particular dienophile have been used.

\(^b\) All the reactions were performed with 2.0 equiv. of a 2 : 1 mixture of TiCl\(_4\) and triphenylphosphine at 23 °C.

\(^c\) Isolated yield after column chromatography.

\(^d\) Diastereomeric purity was determined by \(^1\)H NMR.
Figure 4. Possible mechanism for the formation of vinyl sulfides 57 by Lewis acid mediated rearrangement of vinyl ethers 56.

According to FMO theory the regioselective formation of the cycloadducts can be interpreted as a result of the most favourable (strong/strong and weak/weak) frontier orbital interactions.
between the LUMO of the diene 6 and the HOMO of the corresponding dienophile (see for example Figure 5). 35

$$E_{\text{HOMO}} = -9.18 \text{ eV}$$

Figure 5. HOMO/LUMO energies and p-atomic orbital coefficients for 6 and 36 from AM1 and PM3 calculations. 20

It has already been mentioned that the reactions discussed here can either proceed in a concerted manner as an intermolecular polar \([4\pi^+ + 2\pi]\) cycloaddition or in a cationic multi-step process.

For elucidating this question the transformations of 35a with \((E)-\) and \((Z)-\)methylstyrene \([(E)-(59)\) and \((Z)-(59)\) resp.] proved to be particularly revealing. GC and GC-MS as well as HPLC studies of the corresponding crude products demonstrate that the reaction of 35a with \((E)-\)methylstyrene \((E)-(59)\) exclusively produced \textit{trans}-derivative \textit{rac}-60 (Scheme 15), whereas reaction of pure \((Z)-\)methylstyrene \((Z)-(59)\) only yields the corresponding \textit{cis}-derivative \textit{rac}-61 (Scheme 16). So, the transformations proceed with preservation of the dienophilic double bond configuration, indicating a concerted process.

Scheme 15
Scheme 16

AM1 and PM3 calculations predict that – independent of the equatorial or axial position of the methyl group at C-3 and the pseudoequatorial and pseudoaxial position of the phenyl group at C-4, respectively - the trans product 60 (Table 3, Entries 1,2) is more stable than the cis product 61 (Table 3, Entries 3,4). In case of a thermodynamically controlled reaction we would expect - regardless of the configuration of the dienophile employed - the products to be formed in proportion to their stabilities and thus the preferred formation of the more stable trans product 60.

Table 3. AM1 und PM3 calculations of 60 and 61

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Geometry/ Substituents</th>
<th>AM1 E[kcal · mol⁻¹]</th>
<th>PM3 E[kcal · mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>trans / 3-Meₐq; 4-Phₐq</td>
<td>48.65</td>
<td>38.20</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>trans / 3-Meₐx; 4-Phₐx</td>
<td>49.21</td>
<td>38.93</td>
</tr>
<tr>
<td>3</td>
<td>61</td>
<td>cis / 3-Meₐq; 4 Phₐx</td>
<td>49.68</td>
<td>39.27</td>
</tr>
<tr>
<td>4</td>
<td>61</td>
<td>cis / 3-Meₐx; 4-Phₐq</td>
<td>50.72</td>
<td>41.06</td>
</tr>
</tbody>
</table>

Isomerization experiments with rac-60 and rac-61 showed that their relative configuration does not alter under reaction conditions, meaning that isomerization does not take place (Table 4).

Table 4. Isomerization experiments with rac-60 and rac-61

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate rac-60 : rac-61 a</th>
<th>T [°C]</th>
<th>t [d]</th>
<th>Product rac-60 : rac-61 a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt; 99 : &lt; 1</td>
<td>23</td>
<td>5</td>
<td>&gt; 99 : &lt; 1</td>
</tr>
<tr>
<td>2</td>
<td>&lt; 1 : &gt; 99</td>
<td>23</td>
<td>5</td>
<td>&lt; 1 : &gt; 99</td>
</tr>
<tr>
<td>3</td>
<td>1.6 : 98.4</td>
<td>23</td>
<td>5</td>
<td>1.6 : 98.4</td>
</tr>
</tbody>
</table>

a The diastereomeric ratio rac-60 : rac-61 was determined by HPLC.
Exclusive formation of the less stable cis product rac-61 from 35a and (Z)-methylstyrene (Z)-(59) is suggestive of a concerted process of the polar [4π+2π] cycloaddition with cationic 2-azabutadienes. This assumption is also supported by the absence of follow-up products of the potential intermediates of an alternative cationic multi-step process. This finding is all the more remarkable as the studies so far published indicate that reactions of this type follow a multi-step cationic mechanism.

It should be noted, though, that exclusive formation of the less stable cis product rac-61 from 35a and (Z)-methylstyrene (Z)-(59) does not offer unambiguous proof of a concerted reaction mechanism. This result could also very well be attributed to the fact that the cyclization of the benzyl cation rac-62 into rac-61 proceeds much quicker than the conversion into the more stable benzyl cation rac-63 by rotation around the C,C single bond (Figure 6). But regardless of the reaction mechanism the method presented here guarantees the regio- and diastereoselective construction of 1,2,3,4-tetrahydroquinolines and related systems.

**Figure 6**

Assignment of the relative configuration of rac-60 and rac-61 was undertaken by ¹H NMR spectroscopy and comparison of the two spectra. The trans arrangement of the protons attached to C-3 and C-4 in rac-60 follows from the signal for 4-H resonating at δ = 3.64 ppm as a doublet with a vicinal coupling constant of ²J₃H,₄H = 8.5 Hz (Figure 7). The value of the coupling constant of J = 8.5 Hz for the vicinal coupling between 2-Hax and 3-H indicates that 3-H is
axially arranged. Altogether, these findings confirm the pseudoequatorial position of the phenyl group at C-4 and the equatorial position of the methyl group at C-3.

Figure 7. The relative configuration of rac-60.

In the $^1$H NMR spectrum of rac-61 the signal for 4-H at $\delta = 3.98$ ppm appears as a doublet with a vicinal coupling constant of $^3J_{3H,4H} = 5.0$ Hz (Figure 8). Comparison to the 8.0 Hz coupling constant for the corresponding coupling in rac-60 provides sound evidence for the cis arrangement of the protons at C-3 and C-4. The equatorial position of 3-H can be derived from the values of the coupling constants of the vicinal couplings between 3-H and the protons at C-2. Accordingly, in rac-61 an axial arrangement is inferred for the methyl group at C-3 and a pseudoequatorial arrangement of the phenyl group at C-4.

Figure 8. Relative configuration of rac-61.

Conclusions

Substituted 1,2,3,4-tetrahydroquinolines can be synthesized by polar $[4\pi^+ + 2\pi]$ cycloadditions of cationic 2-azabutadienes with alkenes. We found that cationic 2-azabutadienes can be generated in situ by Lewis acid mediated heterolytic cleavage of N,S-acetals. Their actions with different dienophiles have been studied and found to yield the corresponding cycloadducts as single
products with yields ranging from 57 to 100%. Best results have been obtained using a new mixed Lewis acid consisting of a mixture of TiCl₄ and PPh₃. Surprisingly little is known about the stereochemistry and mechanism of these \([4\pi^+ + 2\pi]\) cycloadditions. Here we present stereochemical evidence to support a concerted mechanism. We have shown that the reactions of an \(N,S\)-acetal with either (\(E\))- or (\(Z\))-methylstyrene proceed with complete preservation of the stereochemistry of the dienophiles to yield the corresponding diastereomerically pure \textit{trans}- and \textit{cis}-cycloadducts, respectively. These results strongly point to a concerted mechanism being operative in the reactions studied.

**Experimental Section**

**General Procedures.** All moisture-sensitive reactions were performed in dried flasks (140 °C, 2 h) under argon using syringe techniques. Solvents were dried and purified by conventional methods prior to use. Dichloromethane was freshly distilled from P₂O₁₀. Petroleum ether refers to the fraction with b.p. 35-65 °C. Reagents of commercial quality were used from freshly opened containers or purified by common methods. - Melting points: Open capillaries, uncorrected values. - IR: Bruker IFS 25. - UV: Varian Cary 219, Perkin-Elmer Lambda 2, and Perkin-Elmer Lambda 9. - \(^1\)H NMR: Varian FT-80 A (80 MHz), Varian XL-200 (200 MHz), Varian VXR-200 (200 MHz), Bruker AMX-300 (300 MHz). - \(^13\)C NMR: Varian FT-80A (20 MHz), Varian XL-200 (50.3 MHz), Varian VXR-200 (50.3 MHz), Bruker AMX-300 (75.5 MHz); assignment in accordance with DEPT spectra. The signal of tetramethylsilane (\(\delta = 0.00\)) as an internal standard. - MS: Varian MAT 311A, Varian MAT 731 (EI 70 eV). - Analytical HPLC: Kontron 425 with a UV detector.- Silica gel used for column chromatography: Merck Kieselgel 60, 0.040-0.063 mm (230-400 mesh). - TLC analysis: precoated plates, Kieselgel 60 F₂₅₄, Merck; precoated plates, Alugram SIL G/UV₂₅₄, Macherey & Nagel; detection: UV absorption or potassium permanganate solution (1%).

**Methoxymethyl-methyl-phenyl-amine (16).** 24.0 ml (0.30 mol) of 37 % aqueous formaldehyde solution 23 were added to a solution of 21.8 g (0.20 mol) \(N\)-methylaniline 22 in 9.50 g (0.30 mol) methanol at room temp. with stirring. The mixture was heated under reflux until \(N\)-methyleneamine 22 had reacted completely (TLC monitoring, diethyl ether/petroleum ether 1:6). After cooling the reaction mixture was saturated with K₂CO₃ and stirred for 30 min at room temp. The layers were separated and the aqueous layer was extracted with diethyl ether (2 × 25 ml). The combined organic extracts were dried (K₂CO₃). The solvent was removed under reduced pressure and the crude product purified by fractional distillation to yield 16 (10.75 g, 36%) as a colourless liquid, b.p. 91 °C / 7 mbar. \(R_f = 0.32\) (diethyl ether / petroleum ether = 1 : 6). - IR (film): \(\nu = 3094\ cm^{-1}, 3062, 3030\ (C=CH), 2984, 2924, 2894\ (CH), 1602\ (C=C-N), 1504\ (C=C), 1448\ (CH₃), 1230\ (C-O), 1070\ (C-O-C), 752, 694\ (CH). - \(^1\)H NMR (80 MHz, CDCl₃): \(\delta = 3.10\ (s, 3H, NCH₃), 3.30\ (s, 3H, OCH₃), 4.75\ (s, 2H, CH₂), 6.60 - 7.45\ (m,
5H, arom. H). - $^{13}$C NMR (20 MHz, CDCl$_3$): $\delta$ = 38.30 (C-7), 54.25 (C-9), 85.00 (C-8), 113.00 (C-2, C-6), 177.75 (C-4), 128.50 (C-3, C-5), 148.00 (C-1). - MS (70 eV); $m/z$ (%): 151 (44) [M$^+$], 120 (100) [C$_8$H$_{10}$N$^+$], 105 (9) [C$_8$H$_9$+$^-], 91 (3) [C$_7$H$_7$+$^-], 77 (15) [C$_6$H$_5$+$^-], 65 (2) [C$_5$H$_5$+$^-], 51 (7) [C$_4$H$_3$+$^-], 45 (9) [C$_2$H$_7$N$^-$]. - C$_9$H$_{13}$NO (151.2).

$N,N'$-Dimethyl-$N,N'$-diphenyl-methandiamine (13). A solution of 21.4 g (0.20 mol) $N$-methylaniline 22 and 8.00 ml (0.10 mol) 37% aqueous formaldehyde solution 23 was prepared and stirred. After some minutes a slight warming occurred. The mixture was stirred overnight at room temp. until consumption of the aldehyde was completed, as monitored by TLC (diethyl ether/petroleum ether, 1:6). The reaction mixture was extracted with diethyl ether (2 × 25 ml) and the combined organic extracts dried (Na$_2$SO$_4$). The solvent was evaporated. The crude product was purified by fractional distillation to yield 13 (15.67 g, 69%) as a viscous, colorless oil, b.p. 116-120 °C / 0.001 mbar, which solidified in the refrigerator and formed colorless crystals.

\[ R_f = 0.26 \text{ (diethyl ether / petroleum ether = 1 : 6).} \] - IR (KBr) $\nu = 3090$ cm$^{-1}$, 3058, 3026 (C=CH), 2920, 2882, 2814 (CH), 1600 (C=C-N), 1504 (C=C), 1448 (CH$_3$), 750, 692 (CH). - $^1$H NMR (80 MHz, CDCl$_3$): $\delta = 2.85$ (s, 6H, 2 × NCH$_3$), 4.70 (s, 2H, CH$_2$), 6.60 - 7.45 (m, 10H, arom. H). - $^{13}$C NMR (20 MHz, CDCl$_3$): $\delta = 36.06$ (2 × NCH$_3$), 70.11 (CH$_2$), 113.56 (C-2, C-6), 117.68 (C-4), 129.10 (C-3, C-5), 149.11 (C-1). - MS (70 eV); $m/z$ (%): 226 (9) [M +], 120 (100) [C$_8$H$_{10}$N$^+$], 106 (20) [C$_7$H$_8$N$^+$], 91 (17) [C$_6$H$_5$N$^+$], 77 (12) [C$_6$H$_5$+$^-$.] - C$_{15}$H$_{18}$N$_2$ (226.3).

Methyl-phenyl-phenylsulfanylmethyl-amine (35a). An emulsion of $N$-methylaniline 22 (32.2 g, 0.30 mol) and water (66 ml) was prepared and paraformaldehyde 23 (9.00 g, 0.30 mol) was added with stirring. Then a solution of thiophenol 34a (32.4 g, 0.30 mol) in diethyl ether (75 ml) and K$_2$CO$_3$ (41.5 g, 0.30 mol) were added, whereby the mixture warmed. After cooling the reaction mixture was stirred for 48 h at room temp. and monitored by TLC (diethyl ether/petroleum ether, 1:6). The layers were separated and the aqueous layer was extracted with diethyl ether (2 × 75 ml). The combined organic extracts were washed with saturated Na$_2$CO$_3$ (2 × 100 ml) and NaCl (1 × 100 ml) solutions and dried (Na$_2$SO$_4$). The solvent was evaporated and the crude product distilled to yield 35a (57.89 g, 84%) as a colorless oil, b.p. 120 °C/0.001 mbar. To obtain an analytically pure product, 35a was purified by column chromatography (diethyl ether/petroleum ether, 1:15). In addition to 35a, 5% of the minor product diphenylisulfide were isolated and identified by NMR spectroscopy.- $R_f = 0.47$ (diethyl ether/petroleum ether, 1:6). - IR (film): $\nu = 3058$ cm$^{-1}$, 3028 (C=CH), 2940, 2900, 2814 (CH), 1600 (C=C-N), 1504 (C=C), 1478, 1438 (CH$_2$), 746, 692 (CH). - UV (acetonitrile): $\lambda_{max}$ (lg $\varepsilon$ ) = 257 nm (4.23). - $^1$H NMR (80 MHz, CDCl$_3$): $\delta = 2.90$ (s, 3H, NCH$_3$), 4.95 (s, 2H, CH$_2$), 6.60 - 7.55 (m, 10H, aromatic H). - $^{13}$C NMR (20 MHz, CDCl$_3$): $\delta = 38.40$ (NCH$_3$), 61.79 (CH$_2$), 113.89 (C-2', C-6'), 118.20 (C-4'), 127.05 (C-4'), 128.81 (C-3, C-5), 128.96 (C-2, C-6), 132.99 (C-3', C-5'), 135.78 (C-1), 147.11 (C-1'). - MS (70 eV); $m/z$ (%): 229 (8) [M$^+$], 120 (100) [C$_8$H$_{10}$N$^+$], 106 (37) [C$_7$H$_8$N$^+$], 91 (5) [C$_6$H$_5$N$^+$], 77 (20) [C$_5$H$_5$+$^-$.], 65 (6) [C$_4$H$_5$+$^-$.], 51 (6) [C$_4$H$_3$+$^-$.] - C$_{14}$H$_{15}$NS (229.3): calcd. C 73.32, H 6.59, N 6.11, S 13.98; found C 73.37, H 6.68, N 6.19, S 14.03.
**Ethylsulfanylmethyl-methyl-phenyl-amine (35b).** Paraformaldehyde 23 (9.00 g, 0.30 mol) was added to a mixture of N-methylaniline 22 (32.2 g, 0.30 mol) and water (66 ml) under stirring. The reaction mixture was saturated with K$_2$CO$_3$ and warmed. A solution of ethyl mercaptan 34b (18.6 g, 0.30 mol) in diethyl ether (75 ml) was dropped slowly into the warmed mixture and stirred for 12 h at room temp. Monitoring was performed by TLC (diethyl ether/petroleum ether, 1:6). The reaction mixture was extracted with diethyl ether (2 × 75 ml). The combined organic extracts were washed with saturated Na$_2$CO$_3$ (2 × 100 ml) and NaCl (1 × 100 ml) solutions and dried (K$_2$CO$_3$). The solvent was removed under reduced pressure and the crude product purified by fractional distillation to yield 35b (28.94 g, 54%) as a yellow liquid, b.p. 90-95 °C/0.8 mbar. - $R_f = 0.30$ (diethyl ether/petroleum ether, 1:6). - IR (film): $\nu = 3092 \text{ cm}^{-1}$, 3062, 3028 (C=CH), 2966, 2926, 2870 (CH), 1600 (C=C-N), 1504 (C=C), 1480, 1450 (CH$_3$, CH$_2$), 750, 692 (CH). - UV (acetonitrile): $\lambda_{max}$ (lg $\varepsilon$) = 203 nm (4.31), 262 (4.12). - $^1$H NMR (80 MHz, CDCl$_3$): $\delta$ = 1.20 (t, $J = 8.0$ Hz, 3H, CH$_3$), 2.50 (q, $J = 8.0$ Hz, 2H, CH$_2$), 3.00 (s, 3H, NCH$_3$), 4.60 (s, 2H, NCH$_2$S), 6.60-7.35 (m, 5H, aromatic H). - $^{13}$C NMR (50.3 MHz, CDCl$_3$): $\delta$ = 15.08 (C-4), 25.45 (C-3), 37.83 (C-1), 56.48 (C-2), 113.61 (C-2', C-6'), 117.73 (C-4'), 128.84 (C-3', C-5'), 147.85 (C-1'). - MS (70 eV); $m/z$ (%): 181 (6) [M$^+$], 120 (100) [C$_8$H$_{10}$N$^+$], 105 (9) [C$_8$H$_9^+$], 91 (4) [C$_6$H$_5^+$], 77 (16) [C$_6$H$_5$], 65 (2) [C$_4$H$_5$], 51 (6) [C$_4$H$_3^+$]. - C$_{10}$H$_{15}$NS (181.3): calcd. C 66.25, H 8.33; found C 66.23, H 8.28.

**(4RS)-(±)-1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (37) via cyclization of 35a with 36.** 1.14 g (5.00 mmol) of 35a were dissolved in 5 ml dry dichloromethane, treated with the equiv. Lewis acid provided in Table 1 at the given temperature and stirred for 5 min at the reaction temp. Then 1.3 - 3.0 equiv. styrene 36 was added. The mixture was stirred at the temperature and for the time given in Table 1. For work-up the reaction mixture was treated with 5 ml sat. sodium hydrogen carbonate solution: The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 ml). The combined organic layers were dried (Na$_2$SO$_4$) and the solvent removed in vacuo. The crude product was purified by column chromatography on 100 g silica gel (diethyl ether / petroleum ether, 1 : 15) (Table 1, No. 1 - 9).

**General procedure for the synthesis of tetrahydroquinolines**

Triphenylphosphine (1.0 equiv.) in dichloromethane (1 M) was added to a stirred solution of TiCl$_4$ (2.0 equiv.) in dichloromethane (1 ml/1 mmol TiCl$_4$) at 0°C. The solution which turned deep red, was stirred for another 15 min at 0 °C and added dropwise to a solution of methyl-phenyl-phenylsulfanylmethylamine 35a (1.0 equiv) in dichloromethane (5 ml dichloromethane/1 mmol 35a) at 0°C. After 10 min at 0 °C the appropriate dienophile (1.5 equiv.) was added dropwise, the resulting solution was warmed up to room temp. and stirred until completion (TLC). The reaction was quenched by addition of saturated Na$_2$CO$_3$ solution (10 ml/2 mmol TiCl$_4$) and stirred for 20 min. After extraction with dichloromethane (3 × 15 ml/1 mmol 35a) the combined organic layers were dried (Na$_2$SO$_4$), the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel.
(4RS)-(±)-1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (37) by cyclization of 35a and 36: The N,S-acetal 35a (1.14 g, 5.00 mmol) and styrene 36 (0.78 g, 7.5 mmol) were allowed to react in dichloromethane (5 ml) in the presence of a 2:1-mixture of TiCl₄ and triphenylphosphine (2.00 equiv.) as the Lewis acid according to GP for 72 h. After work-up and column chromatography (diethyl ether/petroleum ether, 1:15) 37 (1.11 g, quantitative yield) was obtained as a colourless liquid.

(4RS)-(±)-1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (37) by cyclization of 35b and 36: The N,S-acetal 35b (186 mg, 1.00 mmol) and styrene 36 (150 mg, 1.50 mmol) were reacted in accordance with the General Procedure. The reaction mixture was stirred at room temp. for 72 h. After work-up the crude material was purified by column chromatography on silica gel (diethyl ether/petroleum ether, 1:15) to give 37 (183.5 mg, 80%) as a colorless liquid. - Rf = 0.32 (diethyl ether/petroleum ether, 1:4). - IR (film): ν = 3060 cm⁻¹, 3026 (CH, aromatic), 1602 (C=C-N), 1504 (C=C), 1432 (CH₃), 3.25 (t, J = 6.0 Hz, 2H, 2-H₂), 4.15 (t, J = 5.0 Hz, 1H, 4-H), 6.45-7.50 (m, 9H, aromatic H). - ¹³C NMR (20 MHz, CDCl₃): δ = 31.06 (C-3), 39.15 (NCH₃), 43.36 (C-4), 48.39 (C-2), 110.96 (C-8), 116.21 (C-6), 124.69 (C-4a), 126.04 (C-5), 127.53 (C-7), 128.22 (C-2', C-6'), 128.59 (C-3', C-5'), 129.85 (C-4'), 146.53 (C-1'), 146.78 (C-8a). - MS (70 eV); m/z (%): 223 (100) [M⁺], 208 (30) [M⁺ - CH₃], 193 (8) [M⁺ - CH₂NH₂], 178 (7) [M⁺ - C₂H₂N₂], 165 (14) [M⁺ - C₃H₈N], 152 (13) [M⁺ - C₃H₁₁], 146 (19) [M⁺ - C₆H₁₁], 144 (86) [M⁺ - C₆H₇], 130 (22) [C₉H₈N⁺], 103 (13) [C₈H₇⁺], 77 (23) [C₇H₇⁺], 57 (8) [C₄H₉⁺], 51 (16) [C₄H₇⁺], 41 (20) [C₂H₃N⁺]. - C₁₆H₁₇N (223.3): calcd. C 86.06, H 7.67, N 6.27; found C 85.97, H 7.66, N 6.32.

(4SR)-(±)-1-Methyl-4-pentyl-1,2,3,4-tetrahydroquinoline (41). 1-Heptene 40 (200 mg, 2.00 mmol) was added to a solution of the N,S-acetal 35a (228 mg, 1.00 mmol) and a 2:1-mixture of TiCl₄ and triphenylphosphine in dichloromethane according to the General Procedure. The reaction mixture was stirred for 72 h at room temp. After work-up and column chromatography (diethyl ether/petroleum ether, 1:30) yielded 41 (117.6 mg, 57%) as a colorless oil. - Rf = 0.25 (diethyl ether/petroleum ether, 1:30). - UV (acetonitrile): λmax (lg ε) = 209 nm (4.34), 259 (4.05), 307 (3.43). - IR (film): ν = 3064 cm⁻¹, 3024 (C=C-H), 2952, 2926, 2828 (CH), 1602 (C=C-N), 1504 (C=C), 1466, 1456 (CH₂), 744 (CH). - ¹H NMR (300 MHz, DMSO-d₆): δ = 0.88 (t, J = 7.0 Hz, 3H, 4'-CH₃), 1.20-1.60 (m, 8H, 1'-H₂, 2'-H₂, 3'-H₂, 4'-H₂), 1.68-1.92 (m, 2H, 3'-H₂), 2.65 (m, 1H, 4'-H), 2.80 (s, 3H, NCH₃), 3.06-3.26 (m, 2H, 2-H₂), 6.50 (dt, J = 1.0 Hz, J = 8.0 Hz, 1H, 6-H), 6.52 (d, J = 8.0 Hz, 1H, 8-H), 6.88-7.00 (m, 2H, 5-H, 7-H). - ¹³C NMR (50.3 MHz, DMSO-d₆): δ = 13.87 (C-5'), 22.09 (C-4'), 25.97 (C-3'), 26.01 (C-2'), 31.41 (C-3), 35.49 (C-4), 36.16 (C-1'), 38.52 (NCH₃), 46.91 (C-2), 110.62 (C-8), 115.41 (C-6), 126.41 (C-4a), 126.69 (C-5), 127.98 (C-7), 145.74 (C-8a). - MS (70 eV); m/z (%): 217 (59) [M⁺], 147 (23) [M⁺ - C₃H₁₀], 146 (100) [M⁺ - C₃H₁₁], 91 (4) [C₆H₅⁺], 82 (5) [C₅H₈⁺], 57 (8) [C₄H₉⁺], 43 (5) [C₃H₇⁺]. - C₁₅H₂₃N (217.4): calcd. C 82.89, H 10.67, N 6.44; found C 82.79, H 10.69, N 6.28.
(3RS)-(±)-1,3,4,4-Tetramethyl-1,2,3,4-tetrahydroquinoline (43). In accordance with the General Procedure the N,S-acetal 35a (237 mg, 1.03 mmol) was transformed to the tetrahydroquinoline 43 in the presence of the freshly distilled dienophile methyl-2-butene 42 (110 mg, 1.50 mmol). The reaction mixture was stirred for 120 h at room temp. After work-up the crude material was purified by column chromatography (diethyl ether/petroleum ether, 1:30) to yield the colorless oil 43 (144.4 mg, 74%). - Rf = 0.39 (diethyl ether/petroleum ether, 1:30). - IR (film): ν = 3062 cm⁻¹, 3032 (C=C-H), 2966, 2936, 2882 (CH), 1602 (C=C-N), 1504 (C=C), 1388 [C(CH3)₂], 1374 (CH3), 742 (CH). - ¹H NMR (300 MHz, DMSO-d₆): δ = 0.88 (d, J = 8.0 Hz, 3H, 3'-CH₃eq), 1.07 (s, 3H, 4'-CH₃ax), 1.21 (s, 3H, 4'-CH₃eq), 1.75 (m, 1H, 3'-H ax), 2.82 (s, 3H, NCH3), 2.92 (dd, J = 8.0 Hz, J = 12.0 Hz, 1H, 2'-H₃ax), 3.18 (dd, J = 4.0 Hz, J = 12.0 Hz, 1H, 2'-H₃eq), 6.52 (d, J = 8.0 Hz, 1H, 8-H), 6.54 (dt, J = 1.5 Hz, J = 7.5 Hz, 1H, 6-H), 6.96 (dd, J = 1.5 Hz, J = 7.5 Hz, J = 8.0 Hz, 1H, 7-H), 7.12 (dd, J = 1.5 Hz, J = 7.5 Hz, 1H, 5-H). - ¹³C NMR (50.3 MHz, DMSO-d₆): δ = 13.88 (3'-CH₃), 25.34 (4'-CH₃), 29.07 (4'-CH₃), 34.97 (C-3), 36.70 (C-4), 38.69 (NCH3), 53.77 (C-2), 110.37 (C-8), 115.56 (C-6), 125.57 (C-5), 126.38 (C-7), 130.91 (C-4a), 144.79 (C-8a). - MS (70 eV); m/z (%): 189 (96) [M +], 174 (100) [M+ - CH₃], 159 (22) [M+ - C₂H₆], 144 (61) [M⁺ - C₃H₇], 132 (52) [M⁺ - C₄H₉], 117 (14) [M⁺ - C₅H₁₀N], 91 (9) [C₆H₅N⁺], 77 (9) [C₆H₅⁺], 65 (3) [C₅H₅O⁺], 41 (3) [CH₃CN⁺]. - C_{13}H_{19}N (189.3): calcd. C 82.48, H 10.12, N 7.40; found C 82.32, H 10.06, N 7.45.

(4SR)-(±)-1-Methyl-4-methylbutoxy-1,2,3,4-tetrahydroquinoline (45). In accordance with the General Procedure N,S-acetal 35a (233 mg, 1.02 mmol) and allyl-n-butyl ether 44 (170 mg, 1.50 mmol) were reacted to give tetrahydroquinoline 45. For this purpose the reaction mixture was stirred for 72 h at room temp. After work-up the crude material was purified by column chromatography (diethyl ether/petroleum ether, 1:15) to yield 45 (169.5 mg, 72%) as a colorless oil. - Rf = 0.25 (diethyl ether/petroleum ether, 1:15). - IR (film): ν = 3066 cm⁻¹, 3026 (C=C-H), 2956, 2930, 2864 (CH), 1604 (C=C-N), 1504 (C=C), 1458, 1432 (CH₂), 1322, 1108 (C-O), 746 (CH). - UV (acetonitrile): λ max (lg ε) = 209 nm (4.33), 258 (4.04), 307 (3.41). - ¹H NMR (300 MHz, DMSO-d₆): δ = 0.90 (t, J = 7.5 Hz, 3H, 4'-CH₃), 1.26-1.40 (m, 2H, 3'-H₂), 1.44-1.56 (m, 2H, 2'-H₂), 1.76-1.96 (m, 2H, 2'-H₂), 2.80 (s, 3H, NCH3), 2.93 (m, 1H, 4-H), 3.04-3.20 (m, 2H, 2'-H₂), 3.32-3.48 (m, 4H, 1'-H₂, 4'-CH₂), 6.52 (dt, J = 1.0 Hz, J = 7.5 Hz, 1H, 6-H), 6.56 (d, J = 7.5 Hz, 1H, 8-H), 6.94-7.04 (m, 2H, 5-H, 7-H). - ¹³C NMR (50.3 MHz, DMSO-d₆): δ = 13.72 (C-4'), 18.94 (C-3'), 23.67 (C-2'), 31.39 (C-3), 35.80 (C-4'), 38.69 (NCH₃), 46.73 (C-2), 69.91 (4-CH₂), 74.34 (C-1'), 110.88 (C-8), 115.63 (C-6), 122.41 (C-4a), 127.17 (C-5), 128.67 (C-7), 146.54 (C-8a). - MS (70 eV); m/z (%): 233 (23) [M⁺], 146 (100) [M⁺ - C₅H₁₁O], 132 (6) [M⁺ - C₆H₁₄O], 117 (14) [M⁺ - C₆H₁₀N], 105 (2) [C₇H₇N⁺], 91 (4) [C₆H₅N⁺], 77 (3) [C₆H₅⁺], 69 (5) [C₄H₅O⁺], 60 (2) [C₃H₆O⁺], 55 (9) [C₄H₅⁺], 41 (14) [CH₃CN⁺]. - C_{15}H_{23}NO (233.4): calcd. C 77.21, H 9.93, N 6.00; found C 77.30, H 9.95, N 6.27.

(4SR)-(±)-1-Methyl-4-methyltrimethylsilyl-1,2,3,4-tetrahydroquinoline (47). The N,S-acetal 35a (228 mg, 1.00 mmol) and allyltrimethylsilane 46 (170 mg, 1.50 mmol) were reacted in accordance with the General Procedure. The reaction mixture was stirred for 72 h at room temp. After work-up column chromatography (diethyl ether/petroleum ether, 1:100) yielded 47
(155.6 mg, 67%) as a colorless oil. - \( R_f = 0.22 \) (diethyl ether/petroleum ether, 1:100). - IR (film): \( \nu = 3064 \text{ cm}^{-1}, 3026, 2900, 2874 \) (CH), 1602 (C=C-N), 1450 (C-H), 838 (Si(CH\(_3\))\(_3\)), 742 (CH). - UV (acetonitrile): \( \lambda_{\text{max}} \) (lg \( \varepsilon \)) = 210 nm (4.35), 258 (4.04), 307 (3.45). - \( ^1H \) NMR (300 MHz, DMSO-d\(_6\)): \( \delta = 0.02 \) [s, 9H, Si(CH\(_3\))\(_3\)], 0.78 [d, \( J = 9.5 \) Hz, \( J = 14.5 \) Hz, 1H, CH\(_2\)(Si(CH\(_3\))\(_3\))], 0.90 [dd, \( J = 5.0 \) Hz, \( J = 14.5 \) Hz, 1H, CH\(_2\)(Si(CH\(_3\))\(_3\))], 1.58-1.70 (m, 1H, 3-Hax), 1.84-1.98 (m, 1H, 3-Heq), 2.80 (s, 3H, NCH\(_3\)), 2.88 (dt, \( J = 5.0 \) Hz, \( J = 10.0 \) Hz, 1H, 2-H), 3.12 (dt, \( J = 10.0 \) Hz, \( J = 5.0 \) Hz, 1H, 2-H), 3.18-3.20 (m, 1H, 4-H), 6.50 (dt, \( J = 7.5 \) Hz, 1H, 2-H), 6.52 (d, \( J = 7.5 \) Hz, 1H, 8-H), 6.88-6.98 (m, 2H, 5-H, 7-H). - 13C NMR (50.3 MHz, DMSO-d\(_6\)): \( \delta = 23.60 \) (C-3), 29.86 (C-2), 35.89 (C-1), 36.26 (C-3a), 39.59 (NCH\(_3\)), 41.09 (C-9b), 54.26 (C-4), 111.45 (C-6), 117.09 (C-8), 126.41 (C-9a), 129.40 (C-7), 146.83 (C-5a). - MS (70 eV); \( m/z \) (%): 187 (100) [M\(^+\)], 172 (11) [M\(^+\) - CH\(_3\)], 158 (12) [M\(^+\) - C\(_2\)H\(_5\)], 144 (60) [M\(^+\) - C\(_3\)H\(_7\)], 130 (9) [C\(_8\)H\(_{10}\)N\(^+\)], 115 (6) [C\(_9\)H\(_7\)N\(^+\)], 91 (6) [C\(_6\)H\(_5\)N\(^+\)], 77 (16) [C\(_6\)H\(_5\)Si\(^+\)], 65 (28) [C\(_6\)H\(_5\)\(^+\)], 51 (34) [C\(_6\)H\(_5\)\(^+\)], 42 (49) [C\(_3\)H\(_6\)\(^+\)]. - C\(_{13}\)H\(_{17}\)N \( (187.3): \) calcd. C 83.37, H 9.15, N 7.48; found 83.38, H 9.15, N 7.48.

(3aRS,9bSR)-(±)-5-Methyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta-[c]quinoline (49). According to the General Procedure the N,S-acetal 35a (236 mg, 1.03 mmol) and freshly distilled cyclopentene 48 (100 mg, 1.50 mmol) were allowed to react in dichloromethane (5 ml) in the presence of a 2:1-mixture of TiCl\(_4\) and triphenylphosphine (2.00 equiv.) as the Lewis acid for 20 h. After work-up and column chromatography (diethyl ether/petroleum ether, 1:30) 49 (168.2 mg, 87%) was obtained as a yellow oil. - \( R_f = 0.31 \) (diethyl ether/petroleum ether, 1:30). - IR (film): \( \nu = 3066 \text{ cm}^{-1}, 3048, 2948, 2864 \) (CH), 1602 (C=C-N), 1500 (C=C), 1476, 1450 (C-H), 746 (CH). - UV (acetonitrile): \( \lambda_{\text{max}} \) (lg \( \varepsilon \)) = 210 nm (4.38), 255 (4.00), 303 (3.42). - \( ^1H \) NMR (300 MHz, DMSO-d\(_6\)): \( \delta = 1.30-1.68 \) (m, 4H, 2-H, 3-H), 1.86-1.98 (m, 1H, 1-H), 2.28-2.40 (m, 1H, 1-H), 2.63 (dd, \( J = 10.0 \) Hz, \( J = 11.0 \) Hz, 1H, 4-Hax), 2.78 (s, 3H, NCH\(_3\)), 2.86-3.02 (m, 1H, 9b-H), 2.96 (dd, \( J = 5.0 \) Hz, \( J = 11.0 \) Hz, 1H, 4-Heq), 6.60 (dt, \( J = 1.0 \) Hz, \( J = 7.5 \) Hz, 1H, 8-H), 6.61 (d, \( J = 7.5 \) Hz, 1H, 6-H), 6.94-7.06 (m, 2H, 5-H, 7-H). - 13C NMR (50.3 MHz, CDCl\(_3\)): \( \delta = 23.60 \) (C-3), 29.86 (C-2), 35.89 (C-1), 36.26 (C-3a), 39.59 (NCH\(_3\)), 41.09 (C-9b), 54.26 (C-4), 111.45 (C-6), 117.09 (C-8), 126.41 (C-9a), 129.40 (C-7), 146.83 (C-5a). - MS (70 eV); \( m/z \) (%): 187 (100) [M\(^+\)], 172 (11) [M\(^+\) - CH\(_3\)], 158 (12) [M\(^+\) - C\(_2\)H\(_5\)], 144 (60) [M\(^+\) - C\(_3\)H\(_7\)], 130 (9) [C\(_8\)H\(_{10}\)N\(^+\)], 115 (6) [C\(_9\)H\(_7\)N\(^+\)], 91 (6) [C\(_6\)H\(_5\)N\(^+\)], 77 (16) [C\(_6\)H\(_5\)Si\(^+\)], 65 (28) [C\(_6\)H\(_5\)\(^+\)], 51 (34) [C\(_6\)H\(_5\)\(^+\)], 42 (49) [C\(_3\)H\(_6\)\(^+\)]. - C\(_{13}\)H\(_{17}\)N \( (187.3): \) calcd. C 83.37, H 9.15, N 7.48; found 83.38, H 9.15, N 7.34.

(3aRS,9bSR)-(±)-5-Methyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (50). Freshly distilled cyclopentadiene 28 (100 mg, 1.50 mmol) was added to a solution of N,S-acetal 35a (233 mg, 1.02 mmol) and a 2:1-mixture of TiCl\(_4\) and triphenylphosphine in dichloromethane (5 ml) according to the General Procedure. The reaction mixture was stirred for 48 h at room temp. After work-up column chromatography (diethyl ether/petroleum ether, 1:30) 50 (148.9 mg, 79%) as a greenish oil. - \( R_f = 0.31 \) (diethyl ether/petroleum ether, 1:30). - IR (film): \( \nu = 3054 \text{ cm}^{-1}, 3026, 2844, 2810 \) (CH), 1600 (C=C-N), 1500 (C=C), 1448 (CH\(_2\)), 750, 716, 668 (CH). - UV (acetonitrile): \( \lambda_{\text{max}} \) (lg \( \varepsilon \)) = 210 nm (4.40), 256 (3.96), 302 (3.45). - \( ^1H \)
NMR (300 MHz, DMSO-d6): δ = 2.10 (m, 1H, 3-H), 2.54-2.80 (m, 2H, 3-H, 3a-H), 2.60 (dd, J = 9.0 Hz, J = 11.0 Hz, 1H, 4-Hax), 3.81 (dq, J = 8.0 Hz, J = 2.5 Hz, 1H, 9b-H), 5.62 (dt, J = 8.0 Hz, J = 2.5 Hz, 1H, 2-H), 5.71-5.84 (m, 1H, 1-H), 6.64 (d, J = 8.0 Hz, 1H, 6-H), 6.66 (dt, J = 1.5 Hz, J = 8.0 Hz, 1H, 8-H), 7.01 (ddt, J = 1.0 Hz, J = 1.5 Hz, J = 8.0 Hz, 1H, 7-H), 7.11 (dd, J = 1.0 Hz, J = 8.0 Hz, 1H, 9-H). - 13C NMR (125.7 MHz, DMSO-d6): δ = 35.18 (C-3a), 36.99 (C-3), 39.09 (NCH3), 45.79 (C-9b), 53.56 (C-4), 111.67 (C-6), 117.10 (C-8), 125.55 (C-9a), 126.13 (C-9), 128.18 (C-7), 128.72 (C-1), 135.84 (C-2), 147.71 (C-5a). - MS (70 eV); m/z (%): 185 (100) [M+], 170 (44) [M+ - CH3], 144 (54) [M+ - C3H7], 131 (19) [C9H9N+], 115 (15) [C9H7+], 91 (9) [C6H5N+], 77 (11) [C6H5+], 51 (6) [C4H5+], 42 (9) [C3H6+]. - C13H15N (185.3): calcd. C 84.28, H 8.16, N 7.56; found C 84.10, H 8.27, N 7.50.

(4SR)-(±)-1-Methyl-4-phenylsulfanyl-1,2,3,4-tetrahydroquinoline (52). The N,S-acetal 35a (229 mg, 1.00 mmol) was dissolved in dichloromethane (5 ml), cooled to 0°C and BF3.Et2O (280 mg, 2.00 mmol) was added. Freshly distilled ethyl vinyl ether 14 (290 mg, 3.00 mmol) was slowly added and the reaction mixture was stirred at room temp. for 7 h until completion (TLC). The reaction was worked up as stated in the General Procedure. The residue was purified by column chromatography (diethyl ether/petroleum ether, 1:15) to obtain 52 (123.1 mg, 48%) as a yellow oil. - Rf = 0.32 (diethyl ether/petroleum ether, 1:15). - IR (film): ν = 3052 cm⁻¹ (C=C-H), 2960, 2914, 2874, 2824 (CH), 1600 (C=C-N), 1500 (C=C), 1478, 1452, 1434, 1326, 1312 (CH2), 748, 736, 690 (CH). - UV (acetonitrile): λmax (lg ε) = 210 nm (4.47), 260 (4.19), 322 (3.65). - 1H NMR (200 MHz, CDCl3): δ = 2.04 (dq, J = 13.5 Hz, J = 4.0 Hz, 1H, 3-Heq), 2.18 (ddt, J = 12.0 Hz, J = 13.5 Hz, J = 4.0 Hz, 1H, 3-Hax), 2.90 (s, 3H, NCH3), 3.12 (ddt, J = 1.5 Hz, J = 12.0 Hz, J = 4.0 Hz, 1H, 2-Heq), 3.72 (dt, J = 4.0 Hz, J = 12.0 Hz, 1H, 2-Hax), 4.52 (m, 1H, 4-H), 6.56-6.70 (m, 2H, 6-H, 8-H), 7.06-7.52 (m, 7H, 5-H, 7-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H). - 13C NMR (20 MHz, CDCl3): δ = 26.92 (C-3), 38.95 (NCH3), 46.07 (C-2), 111.35 (C-8), 115.98 (C-6), 119.96 (C-4a), 127.06 (C-5), 128.77 (C-7), 128.96 (C-2', C-6'), 130.57 (C-4'), 132.06 (C-3', C-5'), 135.37 (C-1'), 146.47 (C-8a). - MS (70 eV); m/z (%): 255 (41) [M+], 147 (69) [M+ - C6H6S], 146 (100) [M+ - C6H5S], 131 (73) [C9H9S+], 130 (57) [C9H8N+], 109 (10) [C6H5S+], 91 (13) [C6H5N+], 65 (9) [C6H5+], 51 (6) [C4H5+]. - C16H17NS (255.4): calcd. C 75.25, H 6.71, N 5.48, S 12.56; found C 75.14, H 6.87, N 5.51, S 12.62.

(4SR)-(±)-1,4-Dimethyl-4-phenylsulfanyl-1,2,3,4-tetrahydrochinoline (55). The N,S-acetal 35a (229 mg, 1.00 mmol) and 54 (195 mg, 1.50 mmol) were reacted in the presence of a 2:1-mixture of TiCl4 and triphenylphosphine (2.00 equiv.) as the Lewis acid in accordance with the General Procedure. The reaction mixture was stirred for 24 h and worked up as stated in the General Procedure. After column chromatography (diethyl ether/petroleum ether, 1:30) 55 (104.9 mg, 40%) was obtained as a yellow oil. - Rf = 0.26 (diethyl ether/petroleum ether, 1:30). - IR (film): ν = 3060 cm⁻¹, 3032 (C=C-H), 2958, 2922, 2864 (CH), 1602 (C=C-N), 1502 (C=C), 1330 (CH3), 746, 694 (CH). - UV (acetonitrile): λmax (lg ε) = 221 nm (4.37), 260 (4.03), 322 (3.51). - 1H NMR (200 MHz, DMSO-d6): δ = 1.55 (s, 3H, 4-CH3), 1.80-2.00 (m, 2H, 3-H2), 2.84 (s, 3H, NCH3), 2.84-3.06 (m, 1H, 2-H), 3.06-3.24 (m, 1H, 2-H), 6.46-6.62 (m, 2H, 6-H, 8-H),
6.92-7.30 (m, 2H, 5-H, 7-H), 7.30-7.44 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H). - $^{13}$C NMR (20 MHz, DMSO-$d_6$): δ = 29.75 (4-CH$_3$), 34.47 (C-3), 38.76 (NCH$_3$), 46.76 (C-2), 49.33 (C-4), 111.12 (C-8), 115.29 (C-6), 124.96 (C-4a), 127.28 (C-5), 128.08 (C-4)*, 128.57 (C-2', C-6'), 128.77 (C-7)*, 132.10 (C-1'), 136.55 (C-3', C-5'), 145.66 (C-8a). - MS (70 eV); m/z (%): 269 (22) [M$^+$], 160 (100) [M$^+$ - C$_6$H$_6$S], 144 (41) [M$^+$ - C$_7$H$_9$S], 118 (15) [M$^+$ - C$_4$H$_11$N], 91 (6) [C$_6$H$_5$N$^+$], 77 (6) [C$_6$H$_5$], 65 (12) [C$_5$H$_5$], 51 (4) [C$_4$H$_5$]. - C$_{17}$H$_{19}$NS (269.4): calcd. C 75.79, H 7.11, N 5.20, S 11.90; found C 75.69, H 7.25, N 5.17, S 11.94.

(4SR)-(±)-1-Methyl-4-ethylsulfanyl-1,2,3,4-tetrahydroquinoline (58). The N,S-acetal 35b (185 mg, 1.00 mmol) and freshly destilled $n$-butyl vinyl ether 53 (150 mg, 1.50 mmol) were allowed to react in dichloromethane (5 ml) in the presence of a 2:1-mixture of TiCl$_4$ and triphenylphosphine (2.00 equiv.) according to the General Procedure for 2 h. Work-up was performed in accordance with the General Procedure and the crude material was purified by column chromatography on silica gel (diethyl ether/petroleum ether, 1:30) to yield 58 (84.1 mg, 40%) as a colorless oil. - R$_f$ = 0.32 (diethyl ether/petroleum ether, 1:30). - IR (film): ν = 3060 cm$^{-1}$, 3024 (C=C-H), 2958, 2922, 2868, 2826 (CH), 1604 (C=C-N), 1504 (C=C), 1452, 1436 (CH$_2$), 746 (CH). - UV (acetonitrile): λ$_{max}$ (lg ε) = 261 nm (3.92), 316 (3.36). - $^1$H NMR (200 MHz, DMSO-$d_6$): δ = 1.22 (t, $J$ = 7.0 Hz, 3H, SCH$_2$CH$_3$), 1.93-2.20 (m, 2H, 3-H2), 2.50-2.65 (m, 2H, SCH$_2$CH$_3$), 2.84 (s, 3H, NCH$_3$), 3.16 (dt, $J$ = 11.5 Hz, $J$ = 4.0 Hz, 1H, 2-H eq), 3.48 (dt, $J$ = 4.0 Hz, $J$ = 11.5 Hz, 1H, 2-Hax), 4.10 (t, $J$ = 4.0 Hz, 1H, 4-H), 6.46-6.61 (m, 2H, 6-H, 8-H), 6.95-7.08 (m, 2H, 5-H, 7-H). - $^{13}$C NMR (75.4 MHz, CDCl$_3$): δ = 14.58 (SCH$_2$CH$_3$), 24.11 (SCH$_2$CH$_3$), 26.73 (C-3), 38.42 (NCH$_3$), 40.85 (C-4), 45.82 (C-2), 110.91 (C-8), 115.15 (C-6), 121.24 (C-4a), 127.95 (C-5), 129.77 (C-7), 146.83 (C-8a). - MS (70 eV); m/z (%): 207 (19) [M$^+$], 146 (100) [M$^+$ - C$_6$H$_5$S], 131 (13) [M$^+$ - C$_7$H$_9$S], 130 (12) [C$_9$H$_8$S$^+$], 130 (12) [C$_9$H$_8$N$^+$], 91 (4) [C$_6$H$_5$N$^+$], 77 (5) [C$_6$H$_5$], 55 (2) [C$_4$H$_7$]. - C$_{12}$H$_{17}$NS: calcd. 207.1081; found 207.1081 (MS).

(3RS,4RS)-(±)-trans-1,3-Dimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (60). (E)-Methylstyrene (E)-59 (180 mg, 1.50 mmol) was added to a solution of N,S-acetal 35a (234 mg, 1.02 mmol) and a 2:1-mixture of TiCl$_4$ and triphenylphosphine (2.00 equiv.) according to the General Procedure. The reaction mixture was stirred for 72 h at room temp. Work-up was performed in accordance with the General Procedure and column chromatography (diethyl ether/petroleum ether, 1:30) yielded 60 (181.3 mg, 75%) as a white solid, m.p. 82°C. - IR (KBr): ν = 3058 cm$^{-1}$, 3032 (C=C-H), 2968, 2952, 2894, 2866 (CH), 1598 (C=C-N), 1502 (C=C), 1450 (CH$_2$), 1428 (CH$_2$), 766, 744, 690 (CH). - UV (acetonitrile): λ$_{max}$ (lg ε) = 213 nm (4.45), 261 (3.99), 309 (3.46). - $^1$H NMR (300 MHz, DMSO-$d_6$): δ = 0.83 (d, $J$ = 4.0 Hz, 3H, 3-CH$_3$eq), 2.13 (m, 1H, 3-Hax), 2.68 (s, 3H, NCH$_3$), 2.94 (dd, $J$ = 8.5 Hz, $J$ = 11.0 Hz, 1H, 2-Hax), 3.18 (dd, $J$ = 4.0 Hz, $J$ = 11.0 Hz, 1H, 2-Heq), 3.64 (d, $J$ = 8.5 Hz, 4-Hax), 6.40-6.46 (m, 2H, 6-H, 7-H), 6.64 (d, $J$ = 8.0 Hz, 1H, 8-H), 6.94-7.32 (m, 6H, 5-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H). - $^{13}$C NMR (50.3 MHz, CDCl$_3$): δ = 18.12 (3-CH$_3$), 34.95
(C-3), 39.38 (NCH₃), 51.77 (C-4), 56.69 (C-2), 110.74 (C-8), 116.37 (C-6), 125.38 (C-4a), 126.14 (C-5), 127.18 (C-4'), 128.22 (C-2', C-6'), 129.16 (C-3', C-5'), 130.26 (C-7), 145.68 (C-1'), 146.55 (C-8a). - MS (70 eV); m/z (%): 237 (100) [M+], 222 (16) [M+ - CH₃], 194 (16) [M+ - C₂H₄], 179 (9) [M⁺ - C₃H₈N], 158 (19) [M⁺ - C₅H₅N], 144 (63) [M⁺ - C₆H₇N], 115 (12) [C₆H₇⁺], 91 (27) [C₆H₅⁺], 77 (14) [C₆H₅⁺]. - C₁₇H₁₉N (237.3): calcd. C 86.03, H 8.07, N 5.90; found C 85.89, H 8.06, N 5.81.

(3RS,4SR)-(±)-cis-1,3-Dimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (61). The N,S-acetal 35a (492 mg, 2.15 mmol) and (Z)-methylstyrene (Z)-59 (470 mg, 4.00 mmol) were allowed to react in dichloromethane (5 ml) in accordance with the General Procedure for 72 h at room temp. Work-up was performed in accordance with the General Procedure and the crude material was purified by column chromatography (diethyl ether/petroleum ether, 1:100) to yield 61 (341.3 mg, 67%) as a white solid, m.p. 82°C. The diastereomeric ratio rac-60/rac-61 was determined by analytical HPLC {t_R (rac-60) = 7.60 min, t_R (rac-61) = 9.74 min (rac-60 / rac-61 < 1 : 99) [Merck LiChrospher® 60 RP - select B (5µm); acetonitrile/phosphate buffer (pH 2.13), 62 : 38]} and NMR spectroscopy. - R_f = 0.32 (diethyl ether/petroleum ether, 1:30). - IR (KBr): ν = 3058 cm⁻¹, 3028 (C=C-H), 2952, 2920, 2884 (CH), 1602 (C=C-N), 1506 (C=C), 1450 (CH₃), 1430 (CH₂), 748, 700 (CH). - UV (acetonitrile): λ_max (lg ε) = 211 nm (4.46), 260 (3.96), 311 (3.52). - 1H NMR (200 MHz, DMSO-d₆): δ = 0.70 (d, J = 7.0 Hz, 3H, 3-CH₃ax), 2.26 (m, 1H, 3-Heq), 2.92 (d, J = 11.0 Hz, 1H, 2-Heq), 2.93 (s, 3H, NCH₃), 3.03 (ddd, J = 1.5 Hz, J = 4.5 Hz, J = 11.0 Hz, 1H, 4-Hax), 3.98 (d, J = 5.0 Hz, 1H, 4-Hax), 6.47 (dt, J = 1.0 Hz, J = 7.5 Hz, 1H, 6-H), 6.67 (dd, J = 1.0 Hz, J = 8.0 Hz, 1H, 8-H), 6.74 (dd, J = 2.0 Hz, J = 7.5 Hz, 1H, 5-H), 6.95-7.29 (m, 6H, 7-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H). - 13C NMR (50.3 MHz, DMSO-d₆): δ = 16.04 (3-CH₃), 30.41 (C-3), 38.25 (NCH₃), 47.92 (C-4), 52.49 (C-2), 110.37 (C-8), 115.36 (C-6), 124.53 (C-4a), 125.75 (C-5), 127.30 (C-4'), 127.40 (C-2', C-6'), 129.48 (C-7), 129.52 (C-3', C-5'), 142.73 (C-1'), 145.52 (C-8a). - MS (70 eV); m/z (%): 237 (100) [M⁺], 222 (13) [M⁺ - CH₃], 194 (18) [M⁺ - C₂H₄], 179 (9) [M⁺ - C₃H₈N], 158 (19) [M⁺ - C₅H₅N], 144 (63) [M⁺ - C₆H₇N], 115 (12) [C₆H₇⁺], 91 (31) [C₆H₅⁺], 77 (16) [C₆H₅⁺], 51 (9) [C₄H₃⁺]. - C₁₇H₁₉N (237.3): calcd. C 86.03, H 8.07, N 5.90; found C 85.73, H 8.14, N 5.78.

Isomerization experiments with rac-60 and rac-61. 47.4 mg (0.2 mmol) rac-60, rac-61 or 1.6 : 98.4 - mixture of rac-60/rac-61 were dissolved in 1 ml dry dichloromethane and cooled to 0°C. A 1 M solution of TiCl₄ : triphenylphosphin = 2 : 1 (2.0 Equiv.) was added and the reaction mixture was stirred for 5 days at room temp. The reaction was quenched by addition of 5 ml saturated Na₂CO₃ solution. After extraction with dichloromethane (2 × 15 ml) the combined organic layers were dried (Na₂SO₄). The solvent was removed in vacuo and the residue was purified by column chromatography on 5 g silica gel (diethyl ether / petroleum ether, 1 : 30). The diastereomeric ratio rac-60/rac-61 was determined by analytical HPLC {t_R (rac-60) = 7.60 min, t_R (rac-61) = 9.74 min [Merck LiChrospher® 60 RP - select B (5µm); acetonitrile/phosphate buffer (pH 2.13), 62 : 38]}. - References


20. Calculations were performed using the VAMP and MOPAC 6.0 packages. VAMP (T. Clark, Universität Erlangen-Nürnberg) is a vectorized version of AMPAC and MOPAC. The keyword PRECISE was used throughout.
24. (a) Fröhlich, E. Ber. 1907, 40, 762. (b) Braun, J. Ber. 1908, 41, 2145.

27. Schank, K. *The Chemistry of the Sulphones and Sulphoxides*; Wiley: Chichester, 1988; p 165.


