CHAPTER III

Preparation of Some Novel Cyclic Vinylsilanes by Wurtz-Fittig Coupling Reaction
Introduction

Vinylsilanes are versatile synthetic building blocks in organic synthesis. The compounds are anionic synthons. The silyl group behaves as a masking agent for the vinylic anion. The silyl group is normally stable to various organic reagents in neutral or basic media conditions. After the completion of a series of steps, the silyl group may be de-protected with well known de-protecting agents (Chapter I). This allows the silyl group to behave as a ‘ferryman’ in organic synthesis.

In recent years, vinylsilanes have played an increasing role in the domain of organic synthesis. Vinylsilanes are known to undergo a variety of stereo- specific and regio-selective transformations. The reactions include halogenations, oxidations, Friedel-Crafts acylations and as nucleophiles in capturing a carbocation in intra- or inter-molecular reactions.

The notable reactivity of vinylsilanes towards electrophiles is due to the stabilizing effects of C–Si bond on the \( \beta \)-carbocation. In addition to these classical applications, vinylsilanes bearing heteroatom (e. g. alkoxyvinylsilanes or halosilanes) are suitable for use in various processes, such as the Tamao-Fleming oxidation and the Hiyama–Denmark cross coupling reactions.

Our laboratory has been involved in the synthesis and reactions of simple and substituted cyclic vinyl silanes. Some of the cyclic vinylsilanes prepared over the last three and a half decades include simple five- to eight-membered (medium-sized rings), ten- and twelve-membered (large rings) cyclic vinylsilanes. In addition, we have also been successful in preparing some novel 1,2-bis(trimethylsilyl)cycloalkenes, 1,3-(bis)-trimethysilylcycloalkenes, 2-trimethylsilyl-1-halocyclopentenes, \( \alpha \)-amino(trimethylsilyl)-cycloalkenes and \( \alpha \)-trimethylsilyl-\( \alpha,\beta \)-unsaturated cyclic ketones by the simple Wurtz-Fittig
coupling reaction of the corresponding halocycloalkenes with sodium and chlorotrimethylsilane in different anhydrous solvents.\textsuperscript{155-159}

One of the anionic synthons earlier prepared by us: 1-bromo-2-trimethylsilylcyclopentene has been used as the starting material in the first step of the total synthesis of columbetdione.\textsuperscript{243}

In further continuation of our studies, directed towards the synthesis and reactions of some novel cyclic vinylsilanes, we chose to synthesize 2-trimethylsilyl-1,3,3-trimethylcyclopentene 35 and 2-trimethylsilyl-1,3,3-trimethylcyclohexene 36.

The five- and six-membered 1,3,3-trimethylcycloalkanyl- group is the basic fundamental unit in many natural products\textsuperscript{215} like: capnellane, taiwaniaquinoid, actinidiolide, heydechenone, and labdane diterpene group of compounds. The corresponding unsaturated cyclohexenyl-moiety is part of the carotenoid group of tetraterpenoids and also in the $\beta$-carotene oxidised Vitamin - A and related group of compounds.

Paquette has reported the preparation of 35 by the tosyl hydrazone route, and isolation using preparative VPC.\textsuperscript{231} To our knowledge, the compound 2 has not been reported, but its corresponding vinylstannane has been synthesized (Figure III.1).\textsuperscript{232}

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{figure3-1.png}
\caption{Figure III. 1}
\end{figure}

In this chapter, we report the successful synthesis of (1) some novel cyclic vinylsilanes: 35 and 36 and (2) a new class of novel spiro[m,n]alkenylsilanes.

The chapter is sub-divided into two parts: Part A and Part B.
Part A describes the synthesis of the five- and six-membered 2-trimethylsilyl-1,3,3-trimethylcycloalkenes 35 and 36.

Part B describes the preparation of some novel spiro[m,n]alkenylsilanes.

Part A: Synthesis of five- and six-membered 2-trimethylsilyl-1,3,3-trimethylcycloalkenes 35 and 36

This section involves the preparation of five- and six-membered 2-trimethylsilyl-1,3,3-trimethylcycloalkenes 35/36 employing the Wurtz-Fittig coupling reaction. The synopsis for the synthesis of the five- and six-membered 2-trimethylsilyl-1,3,3-trimethylcycloalkenes is reasoned from the retrosynthetic analysis of compounds such as capnellene, hirsutene, and the Vitamin-A and related group of compounds. The retrosynthetic analysis clearly shows that the basic cyclic vinylic anionic synthons are as shown in Figure III. 2.

![Chemical Structure](image)

Figure III. 2

Present work

From the retrosynthetic analysis above, we prepared the starting materials the cyclic vinylhalides as given in Chapter II. The cyclic vinylhalides are the starting materials for the Wurtz–Fittig coupling reactions. Therefore cyclic vinylhalides 10, 14, 22-25 (prepared in Chapter II) were subjected to the Wurtz–Fittig coupling reaction with sodium and chlorotrimethylsilane in refluxing anhydrous ether as solvent. The methodology involved using protocols well established in our laboratory over the last three decades. All reactions were followed using gas chromatography. After completion of the reaction, as indicated by
the chromatograms of aliquots, the mixtures were worked up and distilled to isolate pure 35 and 36 (Scheme III. 1).

![Scheme III. 1 Wurtz-Fittig coupling to 1,3,3-trimethyl-2-trimethylsilylcycloalkenes.](image)

Each reaction was carried out a minimum of five times for each cyclic vinylhalide substrate 10, 14, 22 and 25 and the yields of the products 35/36 are averaged and shown in the Table III. 1.

The hindered cyclic vinylhalides 10, 14, 22-25 showed differences in reactivity with sodium metal in the Wurtz–Fittig reaction.

The five- membered cyclic vinylhalides 2-chloro-1,3,3-trimethylcyclopentene (10), 2-bromo-1,3,3-trimethylcyclopentene (22) and 2-iodo-1,3,3-trimethylcyclopentene (24) reacted smoothly under the conditions used to form 35 in good to excellent yields. Among all the five-membered cyclic vinyl halides, the 2-iodo-1,3,3-trimethylcyclopentene (24) was found to be the best substrate for the preparation of 2-trimethylsilyl-1,3,3-trimethylcyclopentene (35) with the highest isolated yield of 81-83%.

In case of the six-membered ring system, the 2-chloro-1,3,3-trimethylcyclohexene (14) was found to be the best substrate with isolated yields of 2-trimethylsilyl-1,3,3-trimethylcyclohexene (36) in the range 75-77%.
The other six-membered cyclic vinylhalides 23 and 25 did not give satisfactory yields, under our reaction conditions. Change of metal to potassium or lithium also did not improve the yields of products. The yields for all the substrates are as indicated in Table III. 1.

Table III. 1. Synthesis of 2-trimethylsilyl-1,3,3-trimethylcycloalkenes using sodium metal in different solvents

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Halogen</th>
<th>Ring size</th>
<th>Solvent</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Cl</td>
<td>5</td>
<td>ether</td>
<td>35</td>
<td>73–76</td>
</tr>
<tr>
<td>14</td>
<td>Cl</td>
<td>6</td>
<td>ether</td>
<td>36</td>
<td>75–77</td>
</tr>
<tr>
<td>22</td>
<td>Br</td>
<td>5</td>
<td>ether</td>
<td>35</td>
<td>72–74</td>
</tr>
<tr>
<td>23</td>
<td>Br</td>
<td>6</td>
<td>ether</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>24</td>
<td>I</td>
<td>5</td>
<td>ether</td>
<td>35</td>
<td>81–83</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>ether</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>THF</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>benzene</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>HMPA</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>ether</td>
<td>36</td>
<td>&lt;10</td>
</tr>
<tr>
<td>25</td>
<td>I</td>
<td>6</td>
<td>benzene</td>
<td>36</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

Although the cyclic vinylhalides 23 and 25 could be prepared in large quantities, their Wurtz-Fittig couplings proceeded in low and inconsistent yields (Table III. 1). On the other hand, although the Wurtz-Fittig coupling reaction of cyclic vinylchloride 14 took place in good yields, the preparation of 14 proved difficult because of low yields in both gem-chlorination (42% yield) and dehydrochlorination steps (40% Yield). As a consequence we were not able to prepare 36 in large quantities (1 g scale). 36 could be prepared only in 0.2 g scales.
The differences in reactivity of the 14, 23 and 25 may be rationalized based on the mechanism of the Wurtz-Fittig reaction that the initial electron transfer leading to the formation of vinylic anion in case of 23 and 25 is too rapid as they disappeared after a short induction period leading to a mixture of undesired products which we did not try to isolate whereas controlled transfer of electron was observed in case of 14 which led to the desired product 36.

In case the five-membered ring though the Wurtz-Fittig reaction is fast with 22 and 24 when compared to 10, we could isolate the desired 35 in all the cases. This desired reactivity could be attributed to the ring size and strain presumably favouring the Wurtz-Fittig product. In case of six-membered system, ring size and strain coupled with rapid reactivity of 23 and 25 did not favour the Wurtz-Fittig product.

From our studies we identified the best suitable vinylhalide equivalent for the preparation of 35 and 36. 2-Iodo-1,3,3-trimethylcyclopentene 24 was the best starting material for 35 and 2-chloro-1,3,3-trimethylcyclohexene 14 was found to be the best substrate for the preparation of 36.
**Part B: Preparation of some novel spirocyclic vinylsilanes**

Spirocycles are important compounds with diverse properties. They are found to occur as subunits in many natural products.\(^{221}\) To our knowledge, there is only one report for the preparation of a spirocycloalkenylsilane in the literature by Paquette\(^{226}\) for the synthesis of 6-trimethylsilyl-spiro[4,5]dec-6-ene. This prompted us to explore the synthesis of some novel spirocyclic vinylsilanes by Wurtz-Fittig coupling reactions.

During our earlier course of study, in the synthesis of five- and six-membered 2-trimethylsilylcycloalkenones, we found 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene to be highly unstable even to the mildest acidic medium (Figure III.3).\(^{157}\) In our laboratory conditions, the chlorotrimethylsilane has tendency to hydrolyze to trimethylsilanol and HCl, This trace HCl is sufficient to cleave the ketal.

![Figure III. 3](image)

The 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene could not be isolated during the experimental conditions of our work up, even though the compound has been isolated by Yus.\(^{233}\)

Therefore, we chose to prepare the corresponding carbon equivalents 6-trimethylsilyl-spiro[4,5]dec-6-ene \((37)\), 7-trimethylsilylspirol[5,5]undec-7-ene \((38)\), 6-trimethylsilylspirol[4,6]undec-6-ene \((39)\) and 7-trimethylsilylspirol[5,6]dodec-7-ene \((40)\) which are the spiranyl- equivalent compounds. These novel spirocycloalkenylsilanes we expected to be very stable.

The scope and utility of the Wurtz–Fittig coupling reaction was therefore extended to spirocyclic vinyl halides \(31-34\), prepared in Chapter 2-Part B.
The spirocycloalkenyliodides 31-34 were subjected to the Wurtz – Fittig coupling reaction employing sodium and chlorotrimethylsilane in anhydrous ether as solvent. The reactions were followed using gas chromatography. After completion of the reaction, as indicated by aliquot samples, the mixtures were worked up and distilled to isolate the novel spirocyclic vinylsilanes 37 - 39 (Scheme III. 2).

![Scheme III. 2 Synthesis of some novel spirocyclic vinylsilanes](image)

A literature survey indicates there are no precedents for the conversion of spirocycloalkenyliodides to spirocycloalkenylians through the Wurtz-Fittig reaction. Hence, this is the first application of Wurtz-Fittig coupling conditions for the preparation of spirocyclic vinylsilanes and is being reported for the first instance of time in this thesis.

We screened the alkali metals Li, Na and K as electron sources for the formation of cyclic vinyl anion. The comparative reactivity of spirocyclic vinyl iodides 31-34 with alkali metals was studied. We isolated the novel spirocycloalkenylians 37-39 Wurtz-Fittig products in the case of 31-33, whereas from 7-iodo-spiro[5,6]dodec-7-ene 34 we did not isolate the Wurtz-Fittig coupling product 40 even after suitable additives known to stabilize organometal species (LiBr, TMEDA, HMPA). Though we could observe the complete disappearance of the starting material 34, the required 7-trimethylsilylspiro[5,6]dodec-7-ene 40 was not identified when followed on GC-MS. This may be attributed to the electronic factors of the 34 and inherent ring strain of the system or as noted earlier the vinylmetal
species formed from 34 might be unstable. The reactions were repeated 10 times for each substrate and the range of isolated yields is indicated in Table III. 3.

From these studies, the lithium metal was found to be the best electron source for the preparation of novel spirocycloalkenylsilanes 37-39 employing the Wurtz – Fittig coupling reaction (Table III. 4).

Table III. 3. Effect of metal for the Wurtz-Fittig coupling reactions of 31-34

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>Lithium</td>
<td>37</td>
<td>81-84</td>
</tr>
<tr>
<td>31</td>
<td>Sodium</td>
<td>37</td>
<td>67-72</td>
</tr>
<tr>
<td>31</td>
<td>Potassium</td>
<td>37</td>
<td>63-67</td>
</tr>
<tr>
<td>32</td>
<td>Lithium</td>
<td>38</td>
<td>67-72</td>
</tr>
<tr>
<td>32</td>
<td>Sodium</td>
<td>38</td>
<td>61-63</td>
</tr>
<tr>
<td>32</td>
<td>Potassium</td>
<td>38</td>
<td>57-61</td>
</tr>
<tr>
<td>33</td>
<td>Lithium</td>
<td>39</td>
<td>84-88</td>
</tr>
<tr>
<td>33</td>
<td>Sodium</td>
<td>39</td>
<td>71-75</td>
</tr>
<tr>
<td>33</td>
<td>Potassium</td>
<td>39</td>
<td>69-73</td>
</tr>
<tr>
<td>34</td>
<td>Lithium</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>Sodium</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>Potassium</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>

The best results with lithium metal can be attributed to the greater solubility of the spirocycloalkenyllithium ion pairs in anhydrous ether solvent and also more controlled
reactivity due to their covalent nature originating from the polarizing power of the lithium ion. This observation is also in good conformity with the HSAB theory.\textsuperscript{234}

Table III. 4: Synthesis of spirocyclic vinyl silanes 37-39 with Li/TMS-Cl

<table>
<thead>
<tr>
<th>Reactant Sl. No</th>
<th>Starting Material</th>
<th>Product</th>
<th>Sl. No.</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>![I]</td>
<td>![SiMe3]</td>
<td>37</td>
<td>81-84</td>
</tr>
<tr>
<td>32</td>
<td>![I]</td>
<td>![SiMe3]</td>
<td>38</td>
<td>67-72</td>
</tr>
<tr>
<td>33</td>
<td>![I]</td>
<td>![SiMe3]</td>
<td>39</td>
<td>84-88</td>
</tr>
<tr>
<td>34</td>
<td>![I]</td>
<td>![SiMe3]</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>

The spiranyl cyclic vinylsilanes 37-39 may serve as starting materials in the synthesis of the muscone related group of compounds (Figure III. 3).\textsuperscript{235}
Mechanism for the Wurtz-Fittig Coupling reaction

The electron transfer from the metal surface to the carbon-halogen bond is well documented in the literature.\textsuperscript{236} The electron transfer reactions are found to proceed through the reactive intermediates such as radicals, anions and radical anions.

In all of our Wurtz-Fittig coupling reactions there is formation of an intense blue colouration during the silylation step. Even though some reactions have been carried out by us to study the exact mechanism of the reactions, it is hereby proposed that the intense blue colouration is due to the formation of a complex which has the vinylic anion surrounded by a sheath of the ether solvent.

The anion is formed by a single electron transfer (SET), followed by a second electron transfer (referred to as double electron transfer-DET).\textsuperscript{236c} The anion with the Na\textsuperscript{+} as the counter cation is then quenched by the chlorotrimethylsilane to form the 2-trimethylsilyl-1,3,3-trimethylcycloalkenes (Scheme III. 3).

\begin{center}
\textbf{Scheme III. 3}
\end{center}

The reason for the formation of blue colour is not clearly understood and requires further study. Earlier studies using tri-$n$-butyltinhydride for formation of free radical did not give the deep blue colour which may suggest that free radicals may not be involved in forming the blue colour.\textsuperscript{158a}
Conclusion

In this chapter the preparation of (i) some highly substituted cyclic vinylsilanes and (ii) some spirocycloalkenylsilanes employing the Wurtz-Fittig coupling reaction is reported. 2-Trimethylsilyl-1,3,3-trimethylcycloalkenes and spirocycloalkenylsilanes are important anionic synthons which may find use in organic syntheses.
**Experimental Section**

**General procedure for the synthesis of 2-trimethylsilyl-1,3,3-trimethylcycloalkenes (35/36):**

To a suspension of finely cut sodium pieces (5 molar equivalents) and chlorotrimethylsilane (3 molar equivalents) in dry ether (10 mL) was added 2-halo-1,3,3-trimethylcycloalkene [(3.2 g (13.5 mmol) of 24; or 0.22 g (1.3 mmol) of 14] in 10 mL of anhydrous ether. The mixture was refluxed with efficient stirring on an oil bath at 45° - 50°C, when a deep navy-blue colouration developed. Monitoring the reaction by GC indicated that the reactants required 6-8 hours for complete conversion to products. The mixture was then cooled, the precipitated solids and remaining sodium were removed by filtering through a plug of glass wool and washed with ether (2 x 5mL). Saturated sodium bicarbonate solution (15 mL) was added to the combined filtrate, the layers were separated, and the organic layer was successively washed with water (3 x 10 mL), brine (15 mL), dried (an. Na₂CO₃), concentrated on a rotary evaporator and distilled under reduce pressure to isolate 35 and 36. The yields of isolated products are given in Table I.

**2-Trimethylsilyl-1,3,3-trimethylcyclopentene 35**

Light yellow oil, Yield 1.9 g, 81 - 83 %; b. p. 65–70 °C/4 mm. IR 2958, 2866, 1647 (v_C=C), 1458, 1377, 1261, 1095, 1016, 802. \(^1\)H NMR 2.19 (t, 2H, J = 7.2), 1.70 (s, 3H), 1.50 (t, 2H, J = 7.2), 0.98 (s, 6H), 0.08 (s, 9H); \(^1\)C NMR 149.6, 142.7, 51.7, 41.8, 39.0, 28.8, 28.7, 17.9, 1.5; GC-MS: m/z (relative intensity): 182 (13, M⁺), 167 (72), 108 (28), 93 (25), 73 (100%, base peak), 74 (46), 59 (58), 45 (62).
IR spectrum of 2-trimethylsilyl-1,3,3-trimethylcyclopentene 35

$^1H$ NMR spectrum of 2-trimethylsilylcyclopentene 35
$^{13}$C NMR  spectrum of 2-trimethylsilylcyclopentene 35$^{211}$

![$^{13}$C NMR spectrum of 2-trimethylsilylcyclopentene 35$^{211}$]

GC-MS spectrum of 2-trimethylsilylcyclopentene 35$^{211}$

2-Trimethylsilyl-1,3,3-trimethylcyclohexene 36

Light yellow oil, Yield 0.2 g, 78-81 %, b. p. 77–80 °C/2mm, IR 2950, 2866, 1649 (ν$_{νυν}$), 1581, 1452, 1456, 1255, 1095, 1051, 840, 808, 761; $^1$H NMR 1.92 (t, 2H, $J = 8$), 1.75 (s, 3H), 1.59-1.53 (m, 2H), 1.36-1.33 (m, 2H), 1.05 (s, 6H), 0.22 (s, 9H); $^{13}$C NMR 142.8, 139.1, 41.3, 35.5, 34.6, 29.5, 24.7, 19.3, 3.8; GC-MS: m/z (relative intensity): 196 (3, M$^+$), 181(8), 123 (10), 122 (31), 107 (25), 73 (100%, base peak), 59 (15), 45 (24), 43 (15)  Anal. Calcd. for C$_{12}$H$_{24}$Si: C, 73.38; H, 12.32 Found: C, 73.58; H, 12.42. %.
IR spectrum of 2-trimethylsilyl-1,3,3-trimethylcyclohexene 36

$^1$H NMR spectrum of 2-trimethylsilyl-1,3,3-trimethylcyclohexene 36
$^{13}$C NMR spectrum of 2-trimethylsilyl-1,3,3-trimethylcyclohexene 36

GC-MS spectrum of 2-trimethylsilyl-1,3,3-trimethylcyclohexene 36
**General procedure for the preparation of spirocycloalkenylsilanes 37 – 39**

To a suspension of finely cut metal pieces (5 mol equivalents) and chlorotrimethylsilane (3 mol equivalents) in 10 mL of anhydrous ether, was added 31 – 34 (5 mmol) in dry ether (5 mL). The mixture was refluxed with efficient stirring on an oil bath at 45- 50 °C. The progress of the reaction was followed by GC. The mixture was cooled; the precipitated solids and remaining metal pieces were removed by filtering on a plug of glass wool and washed with ether (2 x 10 mL). The combined organic extract was washed with saturated sodium bicarbonate (15 mL), saturated sodium chloride (10 mL) and dried (an. Na₂CO₃). Concentration under vacuum and distillation yielded 37-39

**6-Trimethylsilylspiro[4.5]dec-6-ene 37**²²⁶

Light yellow liquid, Yield 0.65 g, 81-83%; b.p. 75-78°C/1 mm; IR 2952, 2929, 2871, 1595 (υCO), 1445, 1406, 1249, 1054, 1002, 943, 836, 754, 684, 634 ; ¹H NMR 6.03 (t, 1H, J = 3.6), 2.03-1.90 (m, 2H), 1.66-1.65 (m, 6H), 1.59-1.56 (m, 2H), 1.44-1.40 (m, 2H), 1.39-1.37 (m, 2H), 0.10 (s, 9H); ¹³C NMR 146.1, 137.5, 46.4, 39.0, 35.2, 27.1, 24.0, 19.2, 1.4; GC-MS: m/e (rel. intensity): 208 (2), 193 (9), 165 (3), 134 (100), 119 (9), 105 (10), 91 (22), 73 (86), 59 (35), 44 (17).
IR spectrum of 6-trimethylsilylspiro[4,5]dec-6-ene (37)²²⁶

¹H NMR spectrum of 6-trimethylsilylspiro[4,5]dec-6-ene (37)²²⁶
$^{13}$C NMR spectrum of 6-trimethylsilylspiro[4,5]dec-6-ene 37

GC-MS spectrum of 6-trimethylsilylspiro[4,5]dec-6-ene 37
7-Trimethylsilylsilo[5,5]undec-7-ene 38

Yield 0.5 g, 63-65%; b.p. 89-93°C/1 mm; IR: 2932, 2854, 1643 (v=C=O), 1450, 1249, 1151, 1091, 840, 688; 1H NMR 5.98 (t, 1H, J = 3.6), 2.04-2.00 (m, 2H), 1.59-1.53 (m, 4H), 1.47-1.41(m, 6H), 1.27-1.25 (m, 4H) 1.31 (s, 9H); 13C NMR 149.0, 137.3, 38.6, 36.8, 30.9, 26.8, 22.1, 22.0, 19.2; GC-MS: m/e (rel. intensity): 222 (12), 207 (16), 179 (4), 148 (90), 139 (14), 119 (8), 105 (7), 91 (11), 73 (100), 59 (32), 45 (12); Anal. calcd. for C14H28Si: C, 75.59%; H, 11.78%. Found: C, 75.72%, H, 12.25%

IR spectrum of 7-trimethylsilylsilo[5,5]undec-7-ene 38
$^1$H NMR spectrum of 7-trimethylsilylspiro[5,5]undec-7-ene 38

$^{13}$C NMR spectrum of 7-trimethylsilylspiro[5,5]undec-7-ene 38

GC-MS spectrum of 7-trimethylsilylspiro[5,5]undec-7-ene 38
6-Trimethylsilylspiro[4,6]undec-6-ene 39

Light yellow oil, Yield 0.6 g, 75-77%; b.p. 72-75°C/0.8 mm IR 2921, 2858, 1645, 1446, 1247, 1151, 1099, 960, 931, 837, 754; \(^1\)H NMR  6.13 (t, 1H, \( J = 6.4\) Hz), 2.21-2.16 (m, 2H), 1.86-1.82 (m, 2H), 1.68-1.54 (m, 8H), 1.48-1.42 (m, 4H), 0.10 (s, 9H); 153.5, 141.7, 51.7, 37.6, 36.5, 30.5, 27.3, 26.6, 23.5, 2.1; GC-MS: m/e (rel. intensity) 222 (0.3), 207 (0.8), 179 (0.5), 148 (30), 133 (6), 91 (13), 73 (100), 59 (33.6), 45 (28) Anal. calcd. for C\(_{14}\)H\(_{26}\)Si: C, 75.59%; H, 11.78%. Found: C, 75.92%, H, 12.38%.

*IR spectrum of 6-trimethylsilylspiro[4,6]undec-6-ene 39*

![](https://example.com/ir_spectrum.png)

*\(^1\)H NMR spectrum of 6-trimethylsilylspiro[4,6]undec-6-ene 39*

![](https://example.com/nmr_spectrum.png)
$^{13}$C NMR spectrum of 6-trimethylsilylspiro[4.6]undec-6-ene 39

GC-MS spectrum of 6-trimethylsilylspiro[4.6]undec-6-ene 39