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# 1,1-, 1,2-, and 1,4-Eliminations from the Corresponding Dihalogenated Compounds Using $Bu_3SnSiMe_3$-$F^-$

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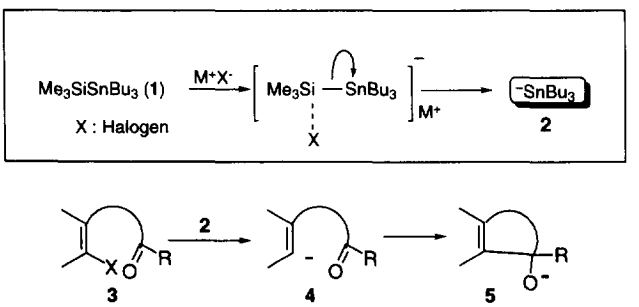
**Abstract**: The stannyl anion **2**, generated from $Me_3SiSnBu_3$ (**1**)[6] in the presence of $R_4NX$, CsF or TASF $[(Et_2N)_3SSiMe_3F_2]$[7] in DMF under very mild conditions,[8] was used for 1,1-, 1,2-, or 1,4- elimination of an aryl or vinyl halide with an appropriate leaving group at the α-, β-, or δ-position of halogen. Thus, alkylidene carbene **8** is generated from 1,1-dihalo-alkene **6** or **7** and benzyne **10** is generated from 1,2-dibromobenzene **9** and an *o*-quinodimethane **12** was produced from α,α'-dibromoxylene **11a**.


Stannyl anion, which is usually prepared from $R_3SnCl$ and Na[1a] or Li,[1b] from $R_3SnSnR_3$ and RLi[2] or from $R_3SnH$ and LDA,[2] is useful for synthetic organic chemistry. It has been used for the protection of the carbonyl group,[2,3] transformation of the carbonyl group,[4] and formation of an alkene.[5] Recently, we found that the stannyl anion **2** was generated from $Me_3SiSnBu_3$ (**1**)[6] in the presence of $R_4NX$, CsF or TASF $[(Et_2N)_3SSiMe_3F_2]$[7] in DMF under very mild conditions.[8]

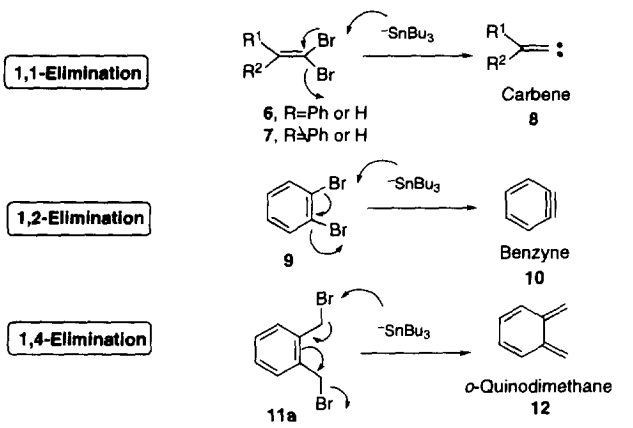
**Scheme 1**




Using this stannyl anion, we developed a novel cyclization of an aryl or vinyl halide and the carbonyl group in a tether. The total syntheses of the natural products acorone,[9a] coniceine[9b] and (-)-cepharotaxine,[9c] were also achieved using this novel cyclization. Furthermore, we previously reported the generation of allyl and benzyl anion[9d] from $Me_3SiSnBu_3$ and CsF or TASF. The first step in these reactions is believed to proceed by an electron transfer from the stannyl anion **2** to an aryl or vinyl halide **3**. As a result, an aryl or vinyl anion **4** is produced, which then attacks the carbonyl carbon in a tether to produce the cyclized product. If an

aryl or vinyl halide with an appropriate leaving group at the α-, β-, or δ-position of halogen is treated with $Bu_3SnSiMe_3$-$F^-$, 1,1-, 1,2-, or 1,4- elimination occurs. Thus, alkylidene carbene **8** is generated from 1,1-dihalo-alkene **6** or **7** and benzyne **10** is generated from 1,2-dibromobenzene **9**. An *o*-quinodimethane **12** is formed from α,α'-dibromoxylene (Scheme 2).[10] We report here the generation of the reactive intermediates alkylidene carbene, benzyne, and *o*-quinodimethane from the corresponding dihalogenated compounds.

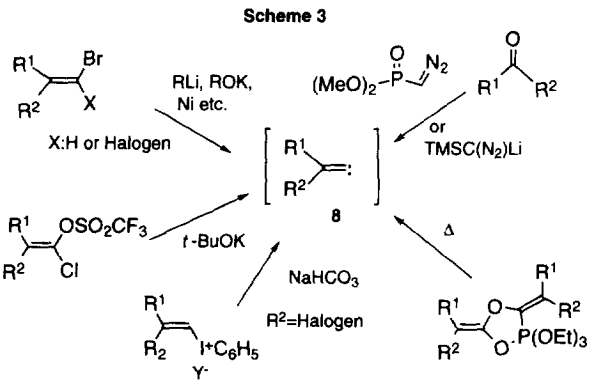
**Scheme 2**

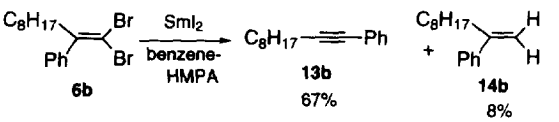



## Generation of alkylidene carbene from 1,1-dihalo alkene

There are many methods for generating alkylidene carbene,[11,12] which is a very reactive intermediate in the synthetic organic chemistry. Representative methods for generating alkylidene carbene are shown in Scheme 3. In many cases, alkylidene carbene is produced by α-elimination. Recently, an elegant method for

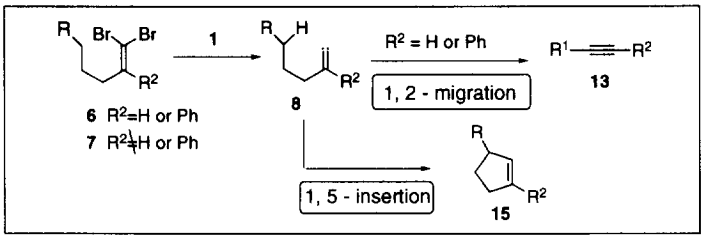
**Scheme 3**



generating alkylidene carbene from 1, 1-dibromoalkene **6b** using $SmI_2$ was reported by Tani (Scheme 3).[13] If the substituent $R^2$ on the alkene of alkylidene carbene **8** is hydrogen or a phenyl group, 1,2-migration occurs to give alkyne **13**. On the other hand, when $R^2$ of **8** is not hydrogen or a phenyl group, an 1,5-insertion reaction proceeds to give cyclopentene derivative **15** (Scheme 4). To determine whether or not an

**Scheme 4**




**Scheme 5**

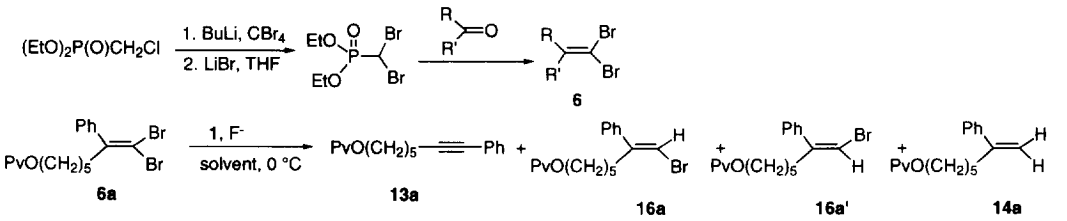


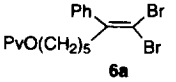
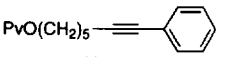
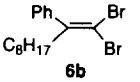
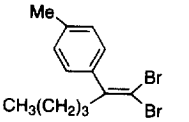
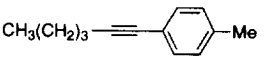
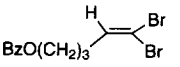
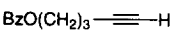

**Table 1** Reaction of **6a** with 1-$F^-$ under various conditions

| Run | $F^-$ | Solvent | Yield (%) | | | |
|---|---|---|---|---|---|---|
| | | | **13a** | **16a** | **16a'** | **14a*** |
| 1 | CsF (3 eq) | DMF | 36 | 32 | 11 | 2 |
| 2 | TASF (3 eq) | DMF | 74 | 5 | 2 | 7 |
| 3 | TASF (2 eq) | THF | 74 | — | — | — |
| 4 | TASF (3 eq) | THF | 57 | — | — | — |

* Yields were calculated from NMR

alkylidene carbene **8** is produced by α-elimination of 1,1-dibromoalkene using stannyl anion generated from $Me_3SiSnBu_3$ and $F^-$, we attempted to form alkyne **13** from 1,1-dibromo alkene **6**. The starting 1,1-dibromoalkenes **6** were prepared from ketones by the method of Savigac and Corey.[14] To a DMF solution of dibromoalkene **6a** and CsF (3 equiv.) was added $Me_3SiSnBu_3$ (3 equiv.), and the solution was stirred at room temperature for 3 hr. The desired alkyne **13a** was obtained in 36% yield along with the dehaloganation products **16a**, **16a'** and **14a** in 32 %, 11 % and 2 % yields, respectively. Although the yield was moderate, the results indicate that α-elimination occurs from the 1,1-dibromoalkene using the stannyl anion generated from $Me_3SiSnBu_3$ and CsF to give the alkylidene carbene. To improve the yield of **13a**, the reactions were carried out under various conditions. The results are shown in Table 1. The use of TASF instead of CsF improved the yield of the desired alkyne **13a** to 74 %. (Table 1, run 2). THF can also be used as the solvent (run 3). Under similar conditions, compounds **6b**, **6c** and **6d** were treated with $Me_3SiSnBu_3$ and TASF to give the desired alkynes **13b**, **13c** and **13d**, in 90 %, 76 %, and 76 % yields, respectively.

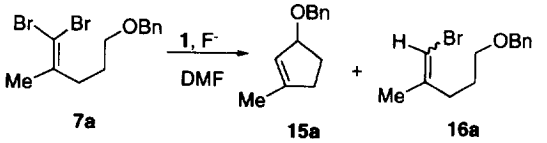
**Table 2** Formation of Alkyne **13** from **6** by 1,1-Elimination

| Run | Substrate | Product | Yield (%) |
|---|---|---|---|
| 1 |  **6a** |  **13a** | 74 |
| 2 |  **6b** |  **13b** | 90 |
| 3 |  **6c** |  **13c** | 76 |
| 4 |  **6d** |  **13d** | 76 |

The reactions were carried out using **1** (3 equiv.) and TASF(3 equiv.) in DMF at 0 °C.

We next examined the 1,5-insertion reaction[15] of alkylidene carbene generated from 1,1-dihaloalkene **7** and $Me_3SiSnBu_3$-$F^-$. It is generally accepted that the 1,5-insertion reaction of alkylidene carbene into the C-H bond is accelerated when a hetero atom is connected to the carbon in the C-H bond. When a DMF solution of 1,1-dibromoalkene **7a**, $Me_3SiSnBu_3$ (2 equiv.) and TASF (2 equiv.) was stirred at 0 ℃ for 1 h, the cyclopentene derivative **15a** was obtained in 65 % yield along with the dehalognenation product **16a** in 16 % yield. To improve the yield of the desired cyclopentene derivative **15a**, the reaction was carried out under various conditions. The results are shown in Table 3. The use of TASF as $F^-$ is superior to that of CsF for generating alkylidene carbene, and the yield of the desired alkyne **15a** was improved to 75 % by the addition of MS4A to the DMF solution.

**Scheme 6**




**7a** **15a** **16a**

**Table 3** Reaction of **7a** with **1** and $F^-$ under various conditions

| Run | 1 | $F^-$ | Conditions | Yields(%) 15a | 16a |
|---|---|---|---|---|---|
| 1 | 2 eq | TASF (2 eq) | 0 °C, 1 h | 65 | 16 |
| 2 | 2 eq | CsF (2 eq) | 0 °C, 1 h | 44 | 36 |
| 3 | 1.5 eq | TASF (1.5 eq) | 0 °C, 1 h | 59 | 23 |
| 4 | 2 eq | TASF (2 eq) | 60 °C, 0.5 h | 57 | 16 |
| 5 | 2 eq | TASF (2 eq) | 0 °C, 1 h* | 75 | 25 |

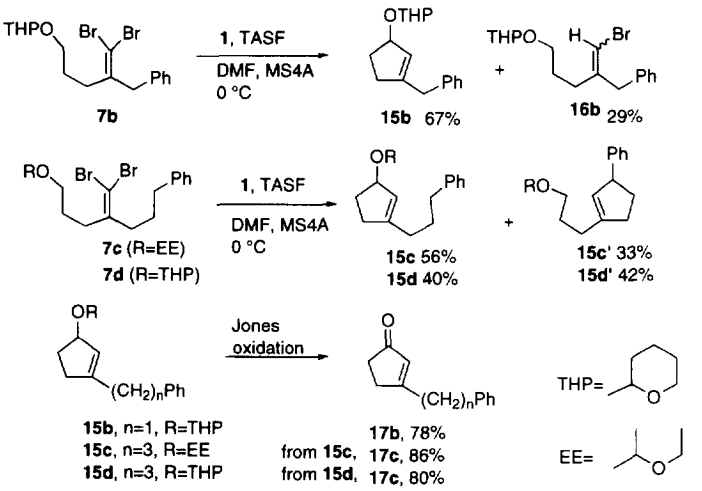
*MS4A was added.

It was tried to synthesize cyclopentenone[16] using this reaction. For this purpose, the hydroxy group was protected by DHP (dihydropyrane). Treatment of compound **7b** with $Me_3SiSnBu_3$ and TASF in the presence of MS4A at 0 ℃ gave cyclopentenol derivative **15b** in 67 % yield. Jones oxidation of **15b** without removal of the protecting group proceeded smoothly to give cyclopentenone derivative **17b** in 78 % yield.

We next examined which C-H bonds, a C-H bond bearing a hetero atom and that bearing a phenyl group, accelerated the C-H insertion reaction[17]. A DMF solution of compound **7c**, $Me_3SiSnBu_3$ and TASF was stirred in the presence of MS4A at 0 ℃ to give **15c** and **15c'** in 56 % and 33 % yields, respectively. In a similar manner, dibromoalkene **7d** gave **15d** and **15d'** in 40% and 42% yields, respectively. These results indicates that the reaction rates for the insertion of alkylidene carbene into a C-H bond bearing oxygen and into a C-H bond in a benzylic position are almost the same. The former product **15c** was converted into cyclopentenone **17c** in 86 % yield by Jones oxidation.

These results indicate that α-elimination from 1,1-dibromoalkene occurs to produce alkylidene carbene, which affords the alkyne *via* 1,2-migration or the cyclopentene derivative *via* C-H insertion reaction.

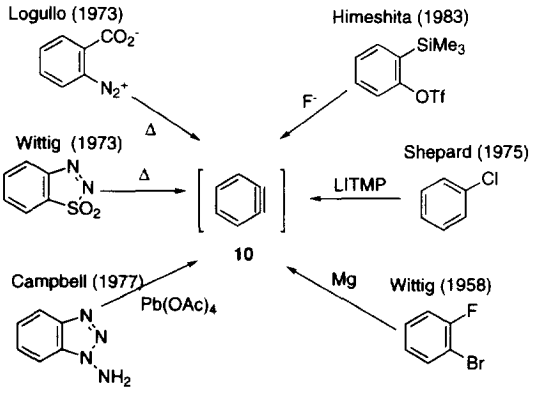
**Scheme 7**




## Generation of benzyne from 1,2-dibromobenzene using $Me_3SiSnBu_3$-$F^-$

Since α-elimination of 1,1-dibromoalkene proceeded to produce alkylidene carbene, we next tried to generate benzyne from 1,2-dibromobenzyne using $Me_3SiSnBu_3$ and $F^-$. There are many methods for

**Scheme 8**



generating benzyne[18,19] including dehydrohalogenation of halobenzene, thermal decomposition of diazo-compoud, and β-elimination of 1,2-dihalobenzene by a strong base. Since the stannyl anion generated from $Me_3SiSnBu_3$ and $F^-$ has a high nucleophilicity and a low basicity, we expected benzyne would be generated from dibromobenzene using $Me_3SiSnBu_3$-$F^-$ under mild conditions, and would give the adduct *via* [2+4] cycloaddition. When a DMF solution of 1,2-dibromobenzene **9**, $Me_3SiSnBu_3$ and CsF was stirred in the presence of furan **18a** as the diene at 0 ℃, the cycloadduct **19a**[20] was obtained in 13 % yield. Although this yield is low, it means that 1,2-elimination occurs from dibromobenzene by the stannyl anion to give benzyne, which reacts with furan to produce **19a**. Furan derivative **18b** was used as a diene and the reaction was carried out under various conditions (Table 4). As a result, the desired cycloadduct **19b** was obtained in 44 % yield when THF was used as a solvent and TASF as $F^-$ (Table 4, Run 4). On the other hand, when furan derivative **18c**, which has an electron-withdrawing group at the 2-position was used for this reaction, none of the adduct was obtained. These results indicate that 1,2-elimination of 1,2-dibromobenzene occurs to give benzyne using $Me_3SiSnBu_3$ and $F^-$ under very mild conditions.

**Scheme 9**

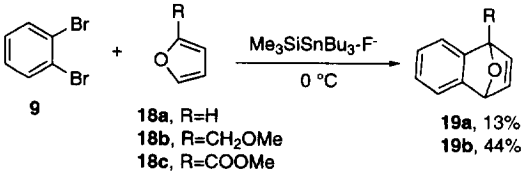


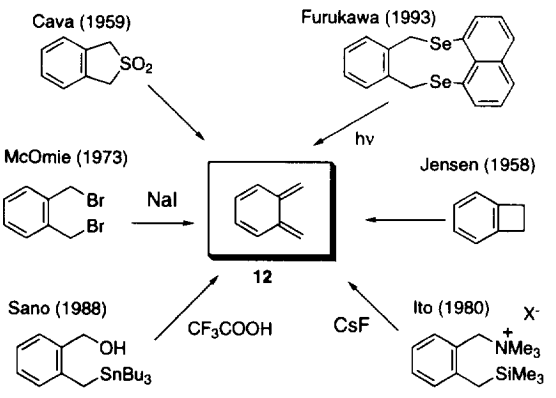

**Table 4** Reaction of **9** and **18** in the presence of **1** and $F^-$

| Run | Diene | $F^-$ | Solvent | Conditions | **19** (%) |
|---|---|---|---|---|---|
| 1 | **18a** | TASF | DMF | 0 °C | 13 |
| 2 | **18b** | CsF | DMF | 0 °C-rt | 17 |
| 3 | **18b** | TASF | THF | -30 °C | 30 |
| 4 | **18b** | TASF | THF | 0 °C-rt | 44 |
| 5 | **18b** | TASF | DMF | 0 °C-rt | 20 |

### Generation of *o*-quinodimethane from α, α'-dibromoxylene using $Me_3SiSnBu_3$-$F^-$

The above result prompted us to produce *o*-quinodimethane **12** from α,α'-dibromoxylene **11a**. [4+2] Cycloaddition of *o*-quinodimethane to an olefin is a convenient method for synthesizing the tetrahydronaphthalene.[21a-21e] There are many procedures for generating *o*-quinodimethane.[21]

**Scheme 10**




When a THF solution of α,α'-dibromoxylene **11a**, dimethyl fumarate (**20a**, 2 eq.), $Me_3SiSnBu_3$ (2 eq.), and TASF (2 eq.) was stirred at 30 ℃ for 1h, the desired tetrahydronaphthalene derivative **21a**[21l] was

obtained in 25% yield along with the *o*-quinodimethane dimer **22**[22] in 24% yield (Table 5, Run 1). The formation of *o*-quinodimethane dimer **22** indicates that *o*-quinodimethane **12** is generated from **11a** and $Me_3SiSnBu_3$ in the presence of TASF and the reaction of the generated **12** with **20a** proceeds *via* [4+2] cycloaddition. The yield was improved when the reaction was carried out in DMF in the presence of CsF instead of TASF (Run 2). The use of 3 eq. of $Me_3SiSnBu_3$ and CsF increased the yield of the desired product **21a** (93% yield, Run 5). $CH_2Cl_2$ can be used as a solvent, but longer reaction times are required (Run 6).

**Scheme 11**

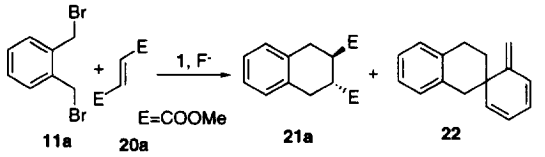
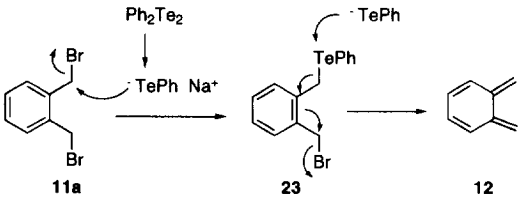



**Table 5** Reaction of **11a** with **20a** under various conditions

| Run | $F^-$ (eq.) | Solvent | Temp | time (h) | Yield (%) **21a** | Yield (%) **22** |
|---|---|---|---|---|---|---|
| 1 | TASF (2.0) | THF | 0 °C | 1 | 25 | 24 |
| 2 | CsF (2.0) | DMF | 0 °C | 1 | 40 | —* |
| 3 | CsF (1.1) | DMF | rt | 2 | 58 | — |
| 4 | CsF (2.0) | DMF | rt | 1 | 73 | — |
| 5 | CsF (3.0) | DMF | rt | 1 | 93 | — |
| 6 | CsF (3.0) | $CH_2Cl_2$ | rt | 120 | 78 | — |

* A trace amount of **22** was obtained.

**Scheme 12**




Professor Sonoda[23] reported the formation of *o*-quinodimethane from α,α'-dibromoxylene using $Ph_2Te_2$ and $NaBH_4$ (Scheme 12). In this reaction, two equivalents of $TePh^-$ are required. However, in our present reaction, the use of 1.1 equivalents of stannyl anion gave the desired cyclized product **21a** in 58 % yield (Run 3). This means that only one equivalent stannyl anion is required for the generation of *o*-quinodimethane by the stannyl anion. The effect of the leaving group was examined and the results are shown in Table 6. For the formation of *o*-quinodimethane **12** from **11** and stannyl anion generated from $Me_3SiSnBu_3$ and CsF, the reactivity of the triflate as the leaving group is the same as that of the bromide (Table 6, Runs 1 and 2) However, the reaction of **11d** with $Me_3SiSnBu_3$ in the presence of CsF did not give the desired product, and the stannylated compound **24**, the dehalogenation product **25** and the Michael addition product **26** were obtained in 10%, 25%, and 18% yields, respectively.

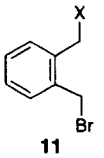
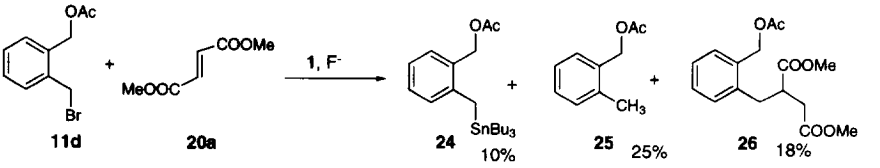


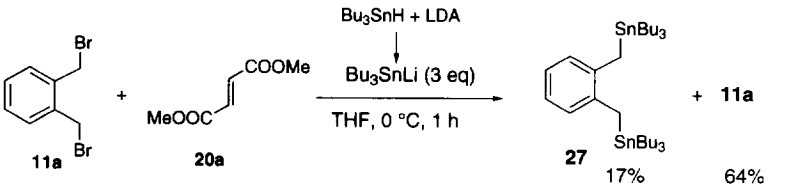

**Table 6** Reaction of **11** with **20a**

| Run | X | | **21a** (%) | **22** (%) |
|---|---|---|---|---|
| 1 | Br | **11a** | 73 | trace |
| 2 | OTf | **11b** | 70 | 8 |
| 3 | $OCOCF_3$ | **11c** | 56 | trace |
| 4 | $OCOCH_3$ | **11d** | — | — |

**Scheme 13**

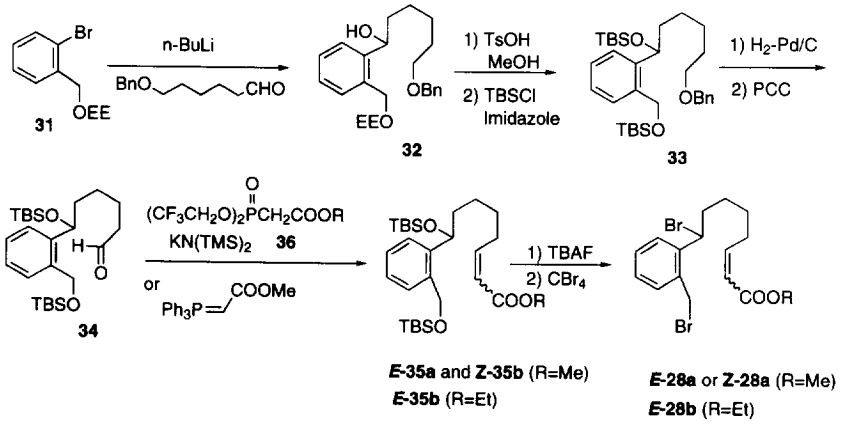



**Scheme 14**



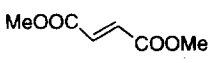
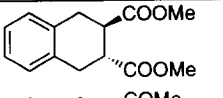
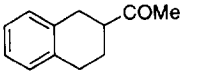
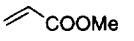
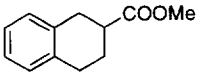
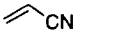
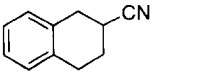
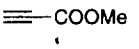
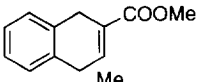
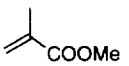
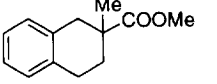
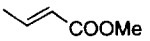
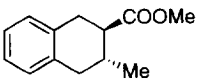
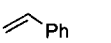
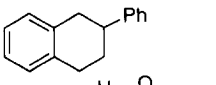
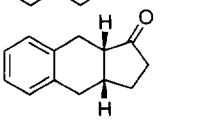

On the other hand, the reaction of α,α'-dibromoxylene with **20a** using stannyl lithium prepared from $Bu_3SnH$ and LDA did not give the [4+2] cycloadduct and only a small amount of di-stannylated product **27** was obtained. Based on the above results, the reaction of **11** with various dienophiles **20** was carried out in the presence of $Me_3SiSnBu_3$ and CsF. The results are summarized in Table 7. The yields of the [4+2] cyclization products **21a-21d** were good to moderate (Runs 1~5). The reaction of **11a** with methyl propiolate **20e**, styrene **20h** and cyclopentenone **20i** as the dienophiles afforded the desired cyclized products **21e, 21h**, and **21i**, respectively.

**Scheme 16**



**Scheme 15**


**Table 7** [4+2] Coupling between **11a** and **20** in the presence of **1** and TASF

| Run | Dienophiles (**20**) | | **1** (eq) | | | Yield (%) **21** | Yield (%) **22** |
|---|---|---|---|---|---|---|---|
| 1 |  | **20a** | 3 |  | **21a** | 93 | trace |
| 2 |  | **20b** | 3 |  | **21b** | 86 | trace |
| 3 |  | **20c** | 3 |  | **21c** | 87 | trace |
| 4 |  | **20d** | 2 |  | **21d** | 59 | 1 |
| 5 |  | **20e** | 2 |  | **21e** | 36 | 20 |
| 6 |  | **20f** | 2 |  | **21f** | 45 | 5 |
| 7 |  | **20g** | 2 |  | **21g** | 15 | 22 |
| 8 |  | **20h** | 3 |  | **21h** | 30 | 14 |
| 9 |  | **20i** | 3 |  | **21i** | 22 | 6 |

We next carried out the intramolecular cyclization reaction. The starting materials **28** were prepared from *o*-bromobenzyl alcohol derivative **31** (Scheme 6). For the *E*- and *Z*-α,β-unsaturated esters, ***E*-28a** and ***Z*-28a**, were prepared by Wittig reactions to aldehyde **34**, respectively (Scheme 16). The ethyl ester ***E*-28b** was prepared from aldehyde **34** and the corresponding Wittig reagent **36b** (R=Et). The reaction of ***E*-28a** with $Me_3SiSnBu_3$ in the presence of CsF proceeded smoothly to give the tricyclic ester **29a** in high yield. The corresponding ethyl ester of **29b** was obtained in 81% yield from ***E*-28b** and $Me_3SiSnBu_3$ in the presence of CsF. The stereochemistry of **29b** was determined by comparison with reported spectral data.[24] The reaction of the ***Z*-28** with stannyl anion also gave the desired product **30** in 61% yield as a single isomer, the stereochemistry of which was determined by X-ray analysis. The results are shown in Fig 1.

**Scheme 17**

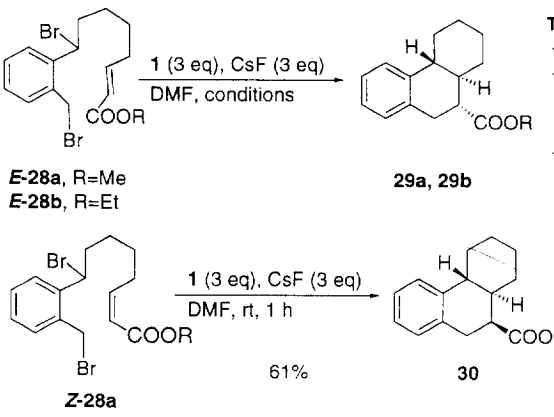
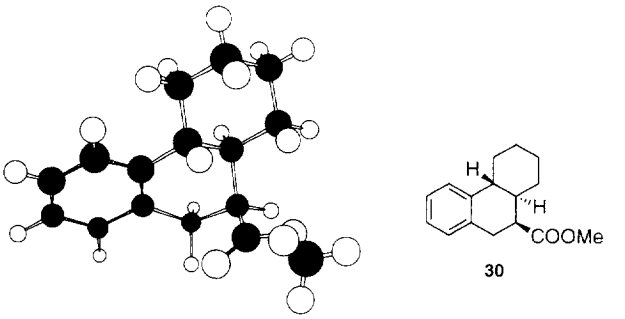



**Table 9** Intramolecular cyclization of ***E*-28**

| Run | | Conditions | Yield (%) |
|---|---|---|---|
| 1 | ***E*-28a** | rt, 1 h | 83 |
| 2 | ***E*-28b** | 0 °C, 0.25 h | 81 |
| 3 | ***E*-28b** | -20 °C, 1 h | 77 |

**Figure 1** X ray Crystal Structure of **30**




We have successfully generated alkylidene carbene, benzyne and *o*-quinodimethane from the corresponding dihalogenated compounds by 1,1-, 1,2, and 1,4-elimination using $Me_3SiSnBu_3$ and $F^-$ under very mild conditions.

The notable features of the formation of these reactive intermediates are as follows. The starting materials are readily available and the reaction procedure is very simple. In a typical procedure, to the DMF solution of substrate and CsF or TASF was added $Me_3SiSnBu_3$ at 0 ℃ or at room temperature. The reaction time is very short. This procedure is useful for the synthesis of various naturally occurring substrates and biologically active substances.

## EXPERIMENTAL SECTION

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, and all the reaction solutions were degassed through freeze-pump-thaw cycle. Solvents were distilled under an argon atmosphere from sodium benzophenone ketyl (THF) or $CaH_2$(DMF and $CH_2Cl_2$). All other reagents and solvents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (70-230 mesh, 60 Å), and flash chromatography was performed on silica gel 60 (230-400 mesh, 60 Å). Melting points are uncorrected.

**General Procedure for the Synthesis of 1,1-Dibromoalkene.** To a suspension of LiBr (6 equiv.) and diisopropylamine (3 equiv.) was added BuLi (1.59 N hexane solution) at 0 ℃ for 40 min. To this solution was added dibromomethane diethylphosphonate (3 equiv.) in THF at -78 ℃ and the solution was stirred at -78 ℃ for 30 min. A THF solution of an aldehyde or ketone (1 equiv.) was added at -78 ℃ and the solution was stirred at -78 ℃ for 2 h. The solution was allowed to stand at 0 ℃ and then water was added. The organic layer was extracted with ether. The organic layer was washed with brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel to give dibromoalkene **6**.

**7,7-Dibromo-6-phenyl-6-heptyl pivaloate (6a).** IR (neat) ν 1727, 1654, 1154 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.18 (s, 9 H), 1.31 - 1.46 (m, 4 H), 1.59 (tt, *J* = 6.8, 6.8 Hz, 2 H), 2.59 (t, *J* = 7.3 Hz, 2 H), 4.01 (t, *J* = 6.8 Hz, 2 H), 7.13 - 7.18 (m, 2 H), 7.28 - 7.40 (m, 3 H); MS (EI, *m/z*) 433, 431, 429, 331, 329, 327, 215, 249, 169, 128, 115, 57 (base); HRMS *m/z* calcd for $C_{18}H_{24}O_2Br_2$ 432.0122, found 432.0100. 434.0102, found 434.0093.

**1,1-Dibromo-2-phenyl-1-decene (6b).** IR (neat) ν 1654, 1458 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3 H), 1.16 - 1.43 (m, 12 H), 2.57 (t, *J* = 7.4 Hz, 2 H), 7.15 - 7.18 (m, 2 H), 7.30 - 7.40 (m, 3 H); MS (EI, *m/z*) 375, 373, 371, 277, 275, 273, 213, 115 (base); HRMS *m/z* calcd for $C_{16}H_{22}Br_2$ 376.0048, found 376.0042. 372.0088, found 372.0071.

**1,1-dibromo-2-(4-methylphenyl)-1-pentene (6c).** IR (neat) ν 1647 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 0.89 (m, 3 H), 1.23-1.40 (m, 4 H), 2.36 (s, 3 H), 2.56 (m, 2 H), 7.06 (d, *J*=8.5 Hz, 2 H), 7.17 ( d, *J*=8.5 Hz, 2 H); MS (EI, *m/z*) 334, 332, 330 ( $M^+$), 292, 290, 288, 278, 276, 274, 129 (base).

**5,5-dibromo-4-heptenyl benzoate (6d).** IR (neat) ν 1654, 1154 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.92 (tt, *J* = 6.3, 7.4 Hz, 2 H), 2.29 (dt, *J* = 7.4, 7.4 Hz, 2 H), 4.34 (t, *J* = 6.3 Hz, 2 H), 6.47 (t, *J* = 7.4 Hz, 1 H), 7.40 - 7.50 (m, 2 H), 7.54 - 7.60 (m, 1 H), 8.01 - 8.10 (m, 2 H); MS (EI, *m/z*) 350, 348, 346, 269, 267, 228, 226, 224, 105 (base); HRMS *m/z* calcd for $C_{12}H_{12}O_2Br_2$ 349.9157, found 349.9161. 347.9184 found 347.9158. 345.9233, found 345.9204.

**5-Benzyloxy-1,1-dibromo-2-methylpentene (7a).** 93%; IR (neat) ν 1738, 1252, 1150 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.72 - 1.83 (m, 2 H), 1.89 (s, 3 H), 2.36 - 2.42 (m, 2 H), 3.49 (t, *J* =6.3 Hz, 2 H), 4.51 (s, 2 H), 7.23 - 7.38 (m, 5 H); MS (EI, *m/z*) 350, 348, 346, 269, 267, 259, 257, 255, 242, 240, 238, 187, 65 (base); Anal. Calcd for $C_{13}H_{16}OBr_2$ : C, 44.85; H, 4.63; Br, 45.91. Found: C, 44.19; H, 4.53; Br, 46.25.

**1,1-Dibromo-2-benzylpropenyl 3,4,5,6-tetrahydropyran-2-yl ether (7b).** 73%; IR (neat) ν 1496, 1035, 1120 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.42 - 1.88 (m, 10 H) 2.25 - 2.32 (m, 2 H), 3.31 - 3.39 (m, 1 H), 3.40 - 3.49 (m, 1 H), 3.67 (s, 1 H), 3.62 - 3.73 (m, 1 H), 3.78 - 3.82 (m, 1 H), 4.52 - 4.54 (m,1 H), 7.12 - 7.32 (m, 5 H); MS (EI, *m/z*) 318, 316, 314, 237, 235, 156, 91 (base); HRMS *m/z* calcd for $C_{11}H_{12}Br_2O$ 318.9306, found 318.9314.

**3-Dibromomethylene-1-phenylhexyl(1'-ethoxyethyl)ether (7c).** 99%; IR (neat) ν 1496, 1058 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.13 (t, *J* =7.1 Hz, 3 H), 1.22 (d, *J* =5.2 Hz, 3 H), 1.56 - 1.79 (m, 4 H), 2.20 - 2.28 (m, 4 H), 2.57 (t, *J* =7.7 Hz, 2 H), 3.27 - 3.62 (m, 4 H), 4.59 (q, *J* =5.2 Hz, 1 H), 7.06 - 7.13 (m, 3 H), 7.18 - 7.27 (m, 2 H); MS (EI, *m/z*) 391, 389, 387 ($M^+$-OEt), 355, 353 ($M^+$-Br), 346, 344, 342, 265, 263, 183, 155, 141, 104, 91 (base); HRMS m/z calcd for $C_{16}H_{21}OBr_2$ ($M^+$-OEt) 386.9959, found 386.9950.

**3-Dibromomethylene-1-phenylhexyl (3,4,5,6-tetrahydropyran-2-yl) ether (7c).** 99%; IR (neat) ν 1496, 1035, 1120 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.46 - 1.63 (m, 4 H), 1.64 - 1.86 (m, 6 H), 2.30 (ddd, *J* = 8.1, 8.1, 13.4 Hz, 2 H), 2.36 (ddd, *J* =7.9 7.9 13.4 Hz, 2 H), 2.64 (t, *J* =7.7 Hz, 2 H), 3.38 (ddd, *J* =6.3, 6.3, 9.8 Hz, 1 H), 3.45 - 3.55 (m, 1 H), 3.73 (ddd, *J* =6.4, 6.4, 9.8 Hz, 1 H), 3.80 - 3.90 (m, 1 H), 4.57 (brt, *J* =3.1 Hz, 1 H), 7.14 - 7.23 (m, 3 H), 7.25 - 7.31 (m, 2 H)

**General Procedure for the Synthesis of Alkyne.** To a solution of $Me_3SiSnBu_3$ (3 equiv.) and 1,1-dibromoalkene **6** (1 equiv.) in THF or DMF (ca 0.25 M solution) was added TASF (3 equiv.) at 0 ℃ and the solution was stirred at the same temperature for an apropriate hour. To this solution ethyl acetate was added and the orgabic layer was washed with brine, dried over $Na_2SO_4$, and concentrated. The residue was purified by silica gel column chromatography to give the desired alkyne **13**.

**7-Phenyl-6-heptynyl pivaloate (13a).** IR (neat) ν 2233, 1727, 1154 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ1.19 (s, 9 H), 1.48 - 1.74 (m, 6 H), 2.43 (t, *J* = 6.8 z, 2 H), 4.08 (t, *J* = 6.2 Hz, 2 H), 7.22 - 7.23 (m, 3 H), 7.34 - 7.72 (m, 2 H); MS (EI, *m/z*) 214, 157, 143, 129, 117 (base); HRMS *m/z* calcd for $C_{18}H_{24}O_2$ 272.1776, found 272.1765.

**1-phenyldecyne (13b).** IR (neat) ν 2238 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.9 Hz, 3 H), 1.22 - 1.34 (m, 8 H), 1.39 - 1.47 (m, 2 H), 1.60 (tt, *J* = 7.3, 7.3 Hz, 2 H), 2.40 (t, *J* = 7.2 Hz, 2 H), 7.21 - 7.33 (m, 3 H), 7.36 - 7.43 (m, 2 H); MS (EI, *m/z*) 214, 157, 143, 129, 117 (base); HRMS *m/z* calcd for $C_{16}H_{22}$ 214.3537, found 214.3529.

**1-(4-methylphenyl)-1-hexyne(13c).** IR (neat) ν 2238, 1617 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.18 Hz, 3 H), 1.14-1.65 (m, 4 H), 2.33 (s, 3 H), 2.40 (t, *J*=7.0 Hz, 2 H), 7.09 (d, *J*=8.1 Hz, 2 H), 7.29 (d, *J*=8.1 Hz, 2 H); MS (EI, *m/z*) 172, 157, 143, 129, 91, 43.

**4-Pentynyl benzoate (13d).** IR (neat) ν 3300, 2119, 1718, 1274 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.99 (t, *J* = 2.8 Hz, 1 H), 2.01 (tt, *J* = 6.4, 6.4 Hz, 2 H), 2.39 (dt, *J* = 2.8, 7.1 Hz, 2 H), 4.43 (t, *J* = 6.2 Hz, 2 H), 7.41 - 7.47 (m, 2 H), 7.51 - 7.59 (m, 1 H) 7.97 - 8.06 (m, 2 H); MS (EI, *m/z*) 188, 187, 160, 146, 123, 105 (base); HRMS *m/z* calcd for $C_{12}H_{12}O_2$ 188.2272, found 188.2291.

**General Procedure for the Synthesis of Cyclopentene Derivatives (15).** To a DMF solution (ca 0.25 M solution) of **7** (1 equiv), TASF or CsF (2 equiv.) in the presence of MS4A was added $Me_3SiSnBu_3$ (2 equiv.) and the solution was stirred at 0 ℃ for 1 h. Water was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by chromatography on silica gel to give the desired cyclopentene derivative **15**.

**3-Methyl-2-cyclopentenyl benzyl ether (15a).** IR (neat) ν 1654, 732 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.78 (s, 3 H), 1.91 (ddd, *J* =9.1, 7.3, 12.9 Hz, 2 H), 2.08 - 2.16 (m, 1 H), 2.21 (ddd, *J* =8.8, 7.3 12.9 Hz, 1 H), 2.52 - 2.36 (m, 1 H), 4.47 (d, *J*=11.7 Hz, 1 H), 4.57 -4.65 (m, 1 H), 5.50 - 5.55 (m, 1 H), 7.21 - 7.62 (m, 5 H); MS (EI, *m/z*) 188, 187, 173, 97, 81, 77 (base); HRMS *m/z* calcd for $C_{13}H_{16}O$ 188.2719, found 188.2699.

**3-Phenetyl-2-cyclopentenyl tetrahydropyran-2-yl ether (15b).** IR (neat) ν 1495, 1112, 1029 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.47 - 1.64 (m, 4 H) 1.65 - 1.96 (m, 3 H), 2.07 - 2.50 (m, 3 H), 3.36 (d, *J* =5.8 Hz, 1 H), 3.41 - 3.54 (m, 1 H), 3.49 (d, *J* =5.8 Hz, 1 H), 3.85-3.95 (m, 1 H), 4.62 - 4.69 (m, 1 H), 4.77 - 4.87 (m, 1 H), 5.46 - 5.53 (m, 1 H), 7.15-7.35 (m, 5 H); MS (EI, *m/z*) 258, 173, 167, 157, 91, 85 (base); HRMS *m/z* calcd for $C_{17}H_{22}O_2$ 258.1620, found 258.1638.

**1-Bromo-2-benzylpropenyl 3,4,5,6-tetrahydropyran-2-yl ether (16b)** IR (neat) ν 1496, 1035, 1120 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.40 - 1.61 (m, 5 H) 1.61 - 1.90 (m, 4 H), 2.62 - 2.18 (m, 1 H), 2.55 (dddd, *J* =8.3, 8.3, 13, 13 Hz, 1 H), 3.29 - 3.55 (m, 3 H), 3.60 - 3.92 (m, 3 H), 4.52 (Brt, 3/7 H), 4.58 (brt, 4/7 H), 5.99 (brs, 4/7 H), 6.10 (brs, 3/7 H), 7.12 - 7.35 (m, 5 H); MS (EI, *m/z*) 340, 338, 259, 236, 1547, 129, 91 (base); HRMS *m/z* calcd for $C_{17}H_{23}O_2Br$ 338. 0881, found 338.0867. 340.0843, found 340.0852.

**1-(3-Phenylpropyl)-3-(ethoxyethyloxy)cyclopent-1-ene (15c).** IR (neat) ν 1601, 1123, 1031, 1496 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.21 (t, *J* =7.1 Hz, 3 H), 1.31 (d, *J* =5.4 Hz, 3 H), 1.67 - 1.88 (m, 3 H), 2.07 - 2.33 (m, 4 H), 2.36 - 2.48 (m, 1 H), 2.62 (t, *J* =7.5 Hz, 2 H), 3.41 - 3.55 (m, 1 H), 3.56 - 3.72 (m, 1 H), 4.76 (q, *J* =5.2 Hz, 1 H), 4.72 - 7.82 (m, 1 H), 5.44 - 5.50 (m, 1 H), 7.16 - 7.25 (m, 3 H), 7.26 - 7.34 (m, 2 H); MS (EI, *m/z*) 228 ($M^+$), 185, 156, 104, 91, 73 (base); HRMS *m/z* calcd for $C_{16}H_{20}O$ ($M^+$-EtOH) 228.1520, found 228.1517.

**1-(3-ethoxyethyloxypropyl)-3-phenylcyclopent-1-ene (15c').** IR (neat) ν 1603, 1132, 1089 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.21 (t, *J* =7.1 Hz, 3 H), 1.31 (d, *J* =5.3 Hz, 3 H), 1.69 -1.85 (m, 3 H), 2.24 (brt, *J* =7.7 Hz, 2 H), 2.31 - 2.49 (m, 3 H), 3.41 - 3.55 (m, 2 H), 3.54 - 3.73 (m, 2 H), 3.82 - 3.93 (m, 1 H), 4.69 (q, *J* =5.4 Hz, 1 H), 5.39 - 5.45 (m, 1 H), 7.14 - 7.17 (m, 3 H), 7.18 - 7.34 (m, 2 H); MS (EI, *m/z*) 228 ($M^+$), 185, 156, 104, 91, 73 (base); HRMS *m/z* calcd for $C_{16}H_{20}O$ ($M^+$-EtOH) 228.1525, found 228.1520.

**3-(3-Phenylpropyl)-2-cyclopentenyl tetrahydropyran-2-yl ether (15d).** IR (neat) n 1653, 1496, 1133, 1112 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) d 1.39 - 1.63 (m, 4 H), 1.64 - 1.98 (m, 5 H), 2.02 - 2.49 (m, 5 H), 2.61 (t, *J* =7.8 Hz, 2 H), 3.39 - 3.58 (m, 1 H), 3.81 - 3.96 (m, 1 H), 4.61 - 4.72 (m, 1 H), 4.74 - 4.87 (m, 1 H), 5.47 - 5.53 (m, 1 H), 7.16 - 7.37 (m, 5 H); MS (EI, *m/z*) 287, 203, 185, 143, 85 (base).

**3-(3-phenylcyclopentenyl)propyl tetrahydropyran-2-yl ether (15d').** IR (neat) n 1653, 1136, 1119, 1033 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) d 1.48 - 1.69 (m, 5 H), 1.70 - 1.91 (m, 5 H), 2.25 (brt, J =8.0 Hz, 2 H), 2.32 - 2.49 (m, 3 H), 3.43 (ddd, *J* =6.6, 6.6, 9.6 Hz, 1 H), 3.46 - 3.54 (m, 1 H), 3.75 (ddd, *J* =6.6, 6.6, 9.6 Hz, 1/2 H), 3.78 (ddd, *J* =6.6, 6.6, 9.6 Hz, 1/H), 3.84 - 3.94 (m, H), 4.56 - 4.62 (m, 1 H), 5.40 - 5.45 (m, 1 H), 7.14 - 7.20 (m, 3 H), 7.25 - 7.33 (m, 2 H); MS (EI, *m/z*) 286, 173, 167, 157, 91, 85 (base).

**General Procedure for the Synthesis of Cyclopentenone (17).** To an acetone solution of **15** was added Jones reagent at 0 ℃ and the solution was stirred at room temperature for 30 min. To this solution was added isopropanol until the acetone solution changed to green. Ethyl acetate was added and the organic layer was washed with sat. $NaHCO_3$ and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by silica gel chromatography to give the desired product **17**.

**3-Phenethyl-2-cyclopentenone (17b).** IR (neat) ν 1706, 1674, 1616, 1495, 1182 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2.40 - 2.45 (m, 2 H), 2.55 - 2.62 (m, 2 H), 3.73 (brs, 2 H), 5.91 (m, 1 H), 7.17 - 7.40 (m, 5 H); MS (EI, *m/z*) 172, 157, 129, 115, 53 (base); HRMS *m/z* calcd for $C_{12}H_{12}O$ 172.0888, found 172.0903.

**3-Phenylpropyl-2-cyclopentenone (17c).** IR (neat) ν 1707, 1675, 1615, 1496, 1182 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.93 (tt, *J* =7.7, 7.7 Hz, 2 H), 2.38 - 2.46 (m, 4 H), 2.53 - 2.60 (m, H), 2.68 (t, *J* =7.7 Hz, 2 H), 5.97 (m, 1 H), 7.14 - 7.35 (m, 5 H); MS (EI, *m/z*) 200, 109, 96, 91 (base); HRMS m/z calcd for $C_{14}H_{16}O$ 200.1202, found 200.1209.

**Generation of Benzyne from 1,2-Dibromobenzene**. To a solution of 1,2-dibromobenzene (1 equiv.), furan **18** (2 equiv.), and CsF (2 equiv.) was added $Me_3SiSnBu_3$ (2 equiv.) at 0 ℃ and the solution was stirred at the same temperature for 1h. Water was added and the aqueous layer was extracted with diethyl ether. The organic layer was washed with brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by silica gel chromatography to give the desired coupling product **19**.

**1,4-Dihydro-1,4-epoxynaphthalene (19a).**[20]

**1-Benzyloxymethyl-1,4-dihydro-1,4-epoxynaphtalene (19b).** IR (neat) ν 3117, 3065, 3032, 1149 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 4.26 (dd, $J$ = 11.1, 22.6 Hz, 2 H), 4.74 (dd, $J$ = 12.4, 15.2Hz, 2 H), 5.71 (d, $J$ = 1.8 Hz, 1 H), 6.91 - 7.43 (m, 11 H); MS (EI, *m/z*) 263, 143, 77 (base); HRMS *m/z* Calcd for $C_{13}H_{16}O_2$, 264.3270, found 264.3281.

**General Procedure for the Generation of *o*-quinodimethane followed by Coupling Reaction.** To a solution of α,α'-dibromo-*o*-xylene (11a, 1 equiv.), dienophile (2 equiv.), and CsF (3 equiv.) in DMF (ca. 0.25 M solution) was added $Me_3SiSnBu_3$ (3 equiv.) at 0 ℃ and the solution was stirred at room temperature. Water was added and the aqueous layer was extracted with diethyl ether. The organic layer was washed with brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by silica gel chromatography to give the desired coupling product **21**.

**trans-2,3-Dicarbomethoxy-1,2,3,4-tetrahydronaphtalene (21a).**[21i] **2'-Methyl-1',2',3',4'-tetrahydronaphthone (21b).**[25] **2-Carbomethoxy-1,2,3,4-tetrahydronaphthalene (21c).**[21g] **2-Cyano-1,2,3,4-tetrahydronaphthalene (21d).**[21g] **2-Carbomethoxy-2-methyl-1,2,3,4-tetrahydronaphthalene (21f).**[26] **2-Carbomethoxy-3-methyl-1,2,3,4-tetrahydronaphthalene (21g).**[21i] **2-Phenyl-1,2,3,4-tetrahydronaphthalene (22h).**[27]

**2-Carbomethoxy-1,4-dihydronaphthalene (21e).** IR (neat) ν 1715, 1662, 1270, 1235 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 3.57 - 3.69 (m, 4 H), 3.81 (s, 3 H), 7.13 - 7.21 (m, 5 H); MS (EI, *m/z*) 188, 173, 157, 129 (base); HRMS *m/z* calcd for $C_{12}H_{12}O_2$ 188.0879, found 188.0858.

**2,3,3a,4,9,9a-Hexahydro-1H-benz[f]indene-1-one (21i).** mp 55 - 55.5 ℃; IR (KBr) ν 1738, 1252, 1150 $cm^{-1}$; 1H-NMR ($CDCl_3$) δ 1.53 - 1.71 (m, 1 H), 2.03 - 2.38 (m, 3 H), 2.44 - 2.65 (m, 2 H), 2.72 - 2.97 (m, 4 H), 7.08 - 7.15 (m, 4 H); MS (EI, *m/z*) 186, 158, 129 (base); HRMS *m/z* calcd for $C_{13}H_{14}O$ 186.0999, found 186.1022. Anal. Calcd for $C_{13}H_{14}O$ : C, 83.83; H, 7.58. Found: C, 83.95; H, 7.73.

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