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Umpolung of Reactivity of Allylsilane, Allylgermane, and Allylstannane *via* Their Reaction with Thallium (III) Salt: A New Allylation Reaction for Aromatic Compounds[1]

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A new direct allylation of aromatic compounds has been developed. A mixture of allylsilane, allylgermane, or allylstannane and thallium (III) trifluoroacetate was allowed to react with an aromatic compound, a nucleophile, to give allylation product(s) in good yields *via* an allylcationic species. Thus, the usefulness of these allylmetal compounds as allyl cation equivalents was established.

Keywords——allylation of aromatic compounds; allylsilane; allylstannane; thallium (III) trifluoroacetate; umpolung

Direct allylation of aromatic compounds using the Friedel–Crafts reaction has been shown to be fruitless,[2] because of the intervention of a redox reaction through intermolecular hydride shift[3] and instability of the product under the reaction conditions.[2a,3] Reaction of allyl alcohol and benzene in the presence of a Lewis acid catalyst such as $AlCl_3$, $ZnCl_2$, or $FeCl_3$ resulted in the formation of allylbenzene in only up to 15% yield, accompanied with several products including *n*-propylbenzene, 1,1- and 1,2-diphenylpropane, 1,1-diphenyl-1-propene, and 2-chloro-1-phenylpropane.[3,4] Similar results were obtained from the Friedel–Crafts reaction between allyl halides and benzene.[3,5] Allylbenzene has been obtained by the reaction of allyl diphenyl phosphate with benzene in the presence of boron trifluoride etherate in 57% yield.[6]

In searching for a mild and general method for achieving the direct allylation of aromatic compounds, we focused our attention on the allylmetal compounds; allylsilane, allylgermane, and allylstannane (**1**) bearing a highly nucleophilic double bond[7] act as equivalent species of the allyl anion (**2**), transfer the allyl group to various kinds of electrophiles (carbonyl compound, α,β-enone, acetal, acid chloride, α-nitro olefin, epoxide, *etc.*) in the presence of Lewis acid catalysts, and produce allylation products (**3**).[8] In order to use these reagents (**1**) for the allylation of nucleophiles such as aromatic compounds, their polarity must be reversed, as they usually act as equivalent species of the allyl cation (**4**) (Chart 1).

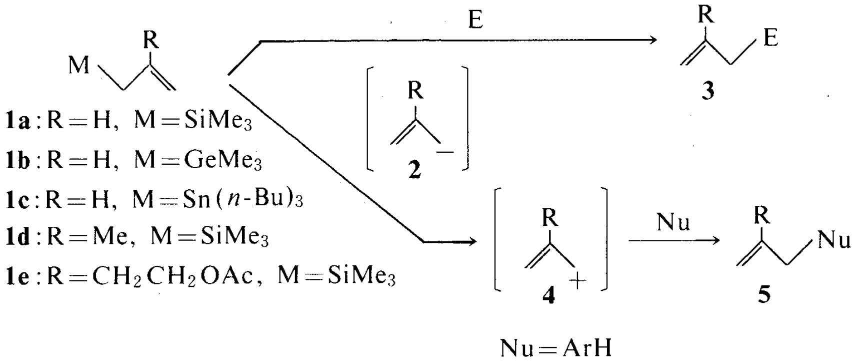


Chart 1

We wish to report our approach to this problem, that is, umpolung of reactivity of allylmetal compounds (**1**). The overall sequence is shown in Chart 2. Allylmetal compound (**1**) was converted to the highly reactive allylorganothallium species **7** by the action of thallium (III) salts (**6**), and subjected to an electrophilic aromatic substitution to give the product **5** (Chart 2).

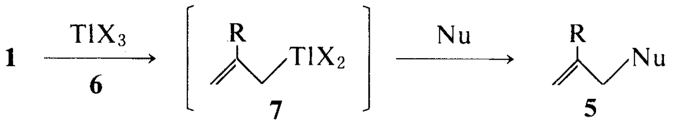


Chart 2

Results and Discussion

Thallium (III) salts have been shown to be strong oxidizing reagents. They oxidize a variety of substances including olefins, carbonyl compounds, and aromatic compounds.[9] Treatment of allyltrimethylsilane (**1a**) with thallium (III) acetate (TTA) (**6**, X=OAc) in benzene at room temperature afforded no allylation product. However, the usage of a more powerful oxidizing reagent, thallium (III) nitrate (TTN) (**6**, X=ONO_2) or thallium (III) trifluoroacetate (TTFA) (**6**, X=$OCOCF_3$), instead of TTA resulted in the formation of the desired allylbenzene in 23 or 70% yield, respectively. The results of allylation of aromatic compounds using allylsilane (**1a**) are summarized in Table I.

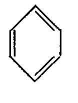
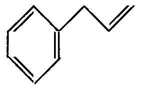
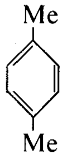
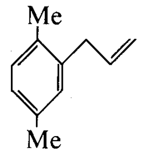
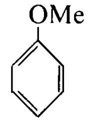
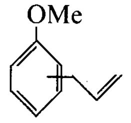
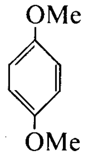
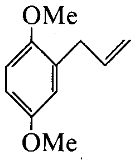
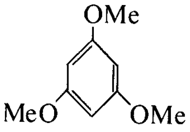
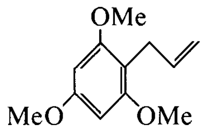
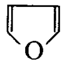
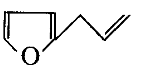
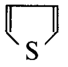
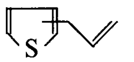
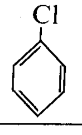
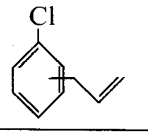
The amount of the aromatic compound used in this reaction has a major effect on the yield of the product; treatment of **1a** with 1.2, 2, 10, and 100 equivalents of *p*-xylene afforded 2-allyl-1,4-dimethylbenzene in 15, 23, 76, and 84% yields, respectively (runs 4—7). In the reaction, the presence of a large excess of aromatic compound is desirable to obtain the allylation product in higher yield; isolation of the product, however, becomes more difficult. The usage of an excess amount of allylsilane (**1a**) relative to the thallium (III) salt (**6**) in the allylation of *p*-dimethoxybenzene had little effect on the yield of the product (runs 9—11). In the case of furan, the use of an excess amount of **1a** relative to **6** was rather detrimental to the reaction and decreased the yield significantly.

As can be seen in Table I, the allylation reaction for various kinds of aromatic compounds proceeded smoothly. The yield in the reaction was found to be much higher than that in the normal Friedel–Crafts allylation reaction.[2] This fact may be attributed to the milder reaction conditions (lower temperature and shorter time) in our case. As expected, electron density on the aromatic ring was shown to have a significant effect on the yield: an electron-deficient aromatic compound such as chlorobenzene gave poor results. As was observed in the usual electrophilic aromatic substitution reaction, a mixture of regio-isomeric products was obtained from the reactions with anisole, chlorobenzene, and thiophene. On the other hand, 2-allylfuran was obtained as the sole product from the reaction with furan.

Allylation reaction of aromatic compounds with substituted allylsilanes proceeded in a similar manner, as shown in Table II. The chemoselectivity of the reaction is noteworthy: allylsilane (**1e**), containing an acetoxy group in the molecule, on treatment with *p*-dimethoxybenzene or furan, produced the corresponding allylation products without affecting the acetoxy group. Allylsilane (**1e**) was prepared as follows: disilylation of 3-methyl-3-penten-1-ol (**8**) *via* its dilithio derivative,[10] which was prepared by treatment of **9** with 2 eq of *n*-BuLi in refluxing hexane in the presence of tetramethylethylenediamine (TMEDA), and successive selective protodesilyltion using 10% H_2SO_4 in tetrahydrofuran afforded the alcohol (**9**) in 38% yield. Acetylation of **10** gave the allylsilane (**1e**).

In the allylation reaction, both allyltrimethylgermane (**1b**) and allyltri-*n*-butylstannane (**1c**) were found to be as useful as allylsilane (**1a**), and the results for allylation of anisole and *p*-dimethoxybenzene are summarized in Table III. It should be emphasized that the ratios of

TABLE I. Allylation of Aromatic Compounds using **1a** and TTFA

Run	Aromatic compd.	**6**	Molar ratio **1a**:**6**:aromatic compd.	Method[a]	Reaction conditions[b]	Product	Yield[c] %
1		TTA	1:1:100	A[d]	RT/2 h		(0)
2		TTN	1:1:100	A[d]	RT/2 h		(23)
3		TTFA	1.2:1:100	A	0°C/5 h RT/30 min		56(70)
4		TTFA	1:1:1.2	B	0°C/2 h		(15)
5		TTFA	1:1:2	B	0°C/3 h		(23)
6		TTFA	1:1:10	B	0°C/2 h RT/30 min		67(76)
7		TTFA	1:1:100	B	RT/30 min		(84)
8		TTFA	1:1:100	A[d]	RT/30 min		53(76)[e]
9		TTFA	1:1:10	B	RT/45 min		46(56)
10		TTFA	1.5:1:10	B	0°C/30 min RT/1 h		(58)
11		TTFA	2:1:10	B	0°C/30 min RT/1 h		(52)
12		TTFA	1.5:1:10	B	RT/1.5 h		53
13		TTFA	1:1:100	C	0°C/1 h		(89)
14		TTFA	1.5:1:100	C	0°C/1 h		(69)
15		TTFA	2:1:100	C	0°C/1 h		(44)
16		TTFA	1:1:100	C	0°C/1 h		41(45)[f]
17		TTFA	1:1:100	B	RT/1 h		(19)[g]

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a) See experimental section.
b) RT: room temperature.
c) Isolated yield and GLC yield (shown in parentheses) based on the thallium (III) salt.
d) The reaction was carried out without dichloromethane.
e) The ratio of *o*- to *p*-isomer is 1:1.7.
f) The ratio of 2- to 3-allylthiophene is 1:0.9.
g) The ratio of *o*- to *p*-isomer is 1:0.7.

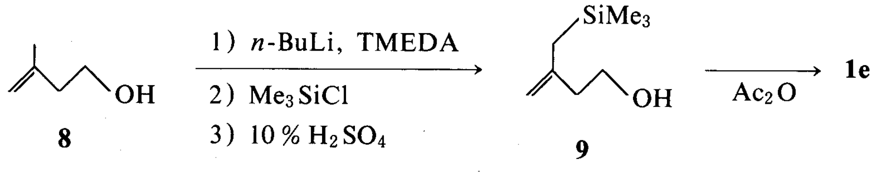
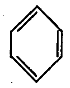
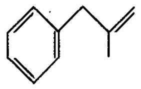
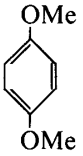
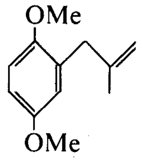
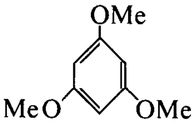
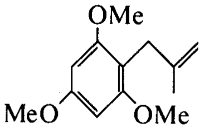
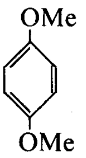
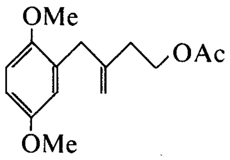
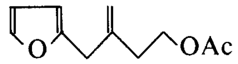
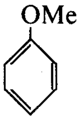
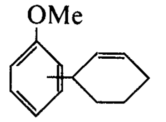


Chart 3

TABLE II. Allylation of Aromatic Compounds using Substituted Allylsilanes and TTFA

Run	Aromatic compd.	1	Molar ratio 1:TTFA:aromatic compd.	Method[a]	Reaction conditions[b]	Product	Yield[c] %
18		**1d**	1:1:100	A	RT/30 min		28(34)
19		**1d**	1:1:10	B	RT/1 h		59(83)
20		**1d**	1.5:1:10	B	RT/45 min		54
21		**1e**	1:1:50	A	RT/2 h		42
22		**1e**	1:1:100	C	0°C/2 h		45
23		**1f**[d]	1:1:100	A	0°C/2 h		23[e]

a) See experimental section

b) RT: room temperature.

c) Isolated yield and GLC yield (shown in parentheses) based on the thallium (III) salt.

d) **1f**: 3-(trimethylsilyl)cyclohexene.

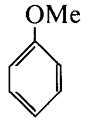
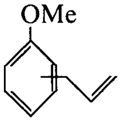
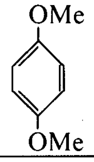
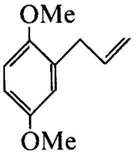
e) The ratio of *o*- to *p*-isomer is 1:3.

o- to *p*-isomers in the product mixture obtained from the reaction of anisole with **1a**, **1b**, or **1c** were within the range of 1:1.7—1.9, probably showing the presence of common reactive intermediate in the allylation reaction using **1a**, **1b**, or **1c**.

Then the regioselectivity in the allylation reaction using non-symmetrical allylsilane was investigated. Allylsilanes have been shown to react with electrophiles accompanied by allylic rearrangement.[11] In our reaction, however, an aromatic compound was introduced into both reactive sites of allylsilane. Thus, a mixture of *E*- and *Z*-isomers of crotyltrimethylsilane (**10**) on treatment with TTFA and *p*-dimethoxybenzene afforded a 19% yield of a mixture of products (**11** and **12**) in a ratio of 1:3.3.

Allylation of aromatic compounds using allylsilane (**1a**) and thallium (III) salt (**6**) could occur as shown in Chart 5. The first step is believed to be the rapid formation of a π-complex **13** as in the reaction of simple olefins with thallium (III) salt.[12] Then its conversion to a reactive allyl organothallium compound or an equivalent species such as allyl cation[13] seems to occur *via* a transient intermediate **14**[14] by a one-electron transfer process.[15] Such a transmetalation reaction of allylsilane (**1a**) with thallium (III) salt seems to be supported by the following fact: mercury (II) and thallium (III) are isoelectronic, and a stable allylmercuric chloride has been isolated from the transmetalation reaction of allylsilane with mercuric chloride.[16]

TABLE III. Allylation of Aromatic Compounds using **1b** or **1c** and TTFA

Run	Aromatic compd.	1	Molar ratio **1**:TTFA:aromatic compd.	Method[a]	Reaction conditions[b]	Product	Yield[c] %
24		**1b**	1:1:100	B	0°C/30 min RT/30 min		(84)[d]
25		**1b**	1:1:10	B	0°C/30 min RT/30 min		68
26		**1c**	1:1:100	A	0°C/30 min RT/30 min		(70)[e]
27		**1c**	1:1:10	A	0°C/1 h RT/1 h		40
28		**1b**	1:1:10	B	0°C/30 min RT/1 h		40(41)
29		**1c**	1:1:10	A	0°C/1 h RT/1 h		40(52)

a) See experimental section.
b) RT: room temperature.
c) Isolated yield and GLC yield (shown in parentheses) based on the thallium (III) salt.
d) The ratio of *o*- to *p*-isomer is 1:1.9.
e) The ratio of *o*- to *p*-isomer is 1:1.8.

Thus, we have developed a new method for the direct allylation of aromatic compounds using allylsilane, allylgermane, or allylstannane (**1**) and thallium (III) salt. The most important feature of this reaction lies in the establishment of the usefulness of allylmetal compounds (**1**) as allyl cation equivalents.

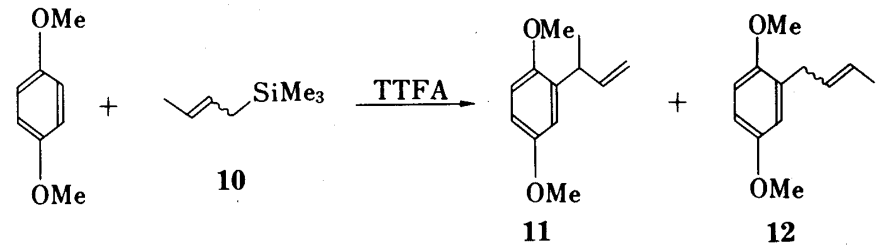


Chart 4

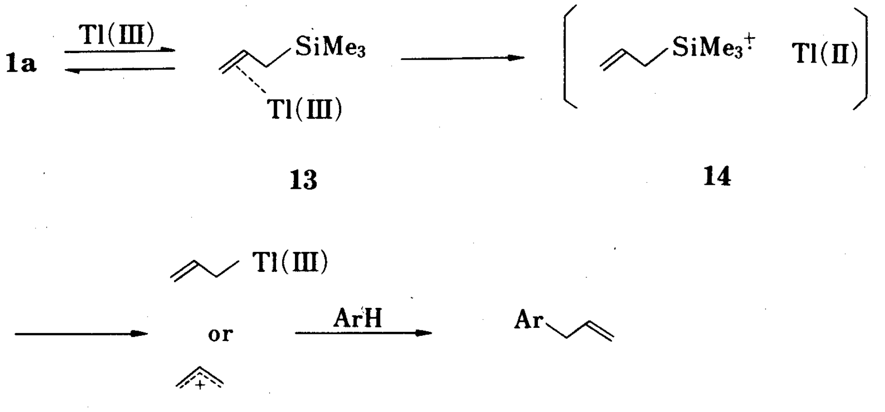


Chart 5

Experimental

Infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating IR spectrophotometer. ^{1}H-Nuclear magnetic resonance (PMR) spectra were obtained with JEOL JNM-FX100 and JEOL JNM-PMX60 spectrometers. ^{13}C-Nuclear magnetic resonance (CMR) spectrum was taken on a JEOL JNM-FX100 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a JEOL JMS-OISG double-focusing mass spectrometer. Analytical gas chromatography was performed on a Shimadzu GC-4CM gas chromatograph with a column of 20% Silicone DC-200 on Celite 545 (1 m). Preparative gas chromatography was performed on a Varian Aerograph Model 920 gas chromatograph with a column of 10% Silicone DC-200 on Chromosorb W (1 m).

Materials——Allyltrimethylsilane (**1a**) is commercially available (Shin-etsu Silicon Chem.). Allylmetal compounds (**1b**—**1d**) were prepared by the method described previously.[17)] Preparation of 3-(trimethylsilyl) cyclohexene (**1f**) was reported previously.[18)] A mixture of *trans*- and *cis*-2-butenyltrimethylsilanes (**10**)[19)] was prepared by the condensation[20)] of trichlorosilane with 1-chloro-2-butene (*E* and *Z* mixture) in the presence of triethylamine and cuprous chloride followed by methylation with methylmagnesium bromide in ether.

Synthesis of 2-(2-Acetoxyethyl)-2-propenyltrimethylsilane (1e)——To a solution of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (20 g, 170 mmol) in hexane (160 ml) was added dropwise a hexane solution of *n*-butyllithium (1.5 M solution, 113 ml; 170 mmol) followed by 3-methyl-3-buten-1-ol (**8**) (7.6 g, 86 mmol) in nitrogen. The mixture was heated at 60°C for 6 h. The resulting red solution was cooled to −78°C and treated with trimethylchlorosilane (28 g, 258 mmol). The reaction temperature was raised to room temperature and the mixture was stirred for 4 h. After addition of ice to the mixture, extraction with ether, drying of the extract with Na_2SO_4 and then concentration *in vacuo* afforded a crude oil (18 g), which was treated with 10% aqueous H_2SO_4 (15 ml) in tetrahydrofuran (100 ml) at 0°C for 20 min. Extraction of the mixture with ether and then usual work-up gave a crude product which was purified by silica gel column chromatography using hexane–ethyl acetate (9:1) to give the alcohol (**9**) (5.2 g, 38%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 3450, 1630, 1250, 1155, 1045. MS *m/e*: 158 (M^+), 143, 103, 73, 69. High resolution MS: Found 158.1102. Calcd for $C_8H_{18}OSi$ (M^+) 158.1127. PMR ($CDCl_3$) δ: 0.04 (9H, s, $SiMe_3$), 1.54 (2H, s, CH_2Si), 2.22 (2H, t, $J=6$ Hz), 3.68 (2H, t, $J=6$ Hz, CH_2O), 4.64 (2H, br s, $C=CH_2$). CMR ($CDCl_3$) δ: 143.7 (s), 109.2 (t), 60.2 (t), 41.2 (t), 26.7 (t), −1.3 (q).

After treatment of the alcohol (**9**) (1.3 g, 8.2 mmol) with acetic anhydride (1 g, 9.4 mmol) and pyridine (0.2 ml) under reflux for 1 h, the crude product was chromatographed on silica gel with hexane–ethyl acetate (20:1) to give the acetate (**1e**) (1.18 g, 75%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1230, 1035, 970. MS *m/e*: 200 (M^+), 133, 117, 73 (base peak). High resolution MS: Found 200.1232. Calcd for $C_{10}H_{20}O_2Si$ (M^+) 200.1232. PMR ($CDCl_3$) δ: 0.02 (9H, s, $SiMe_3$), 1.54 (2H, s, CH_2Si), 2.02 (3H, s, COMe), 2.27 (2H, t, $J=6$ Hz), 4.16 (2H, t, $J=6$ Hz, CH_2O), 4.61 (2H, m, $C=CH_2$).

General Procedure for Allylation Reaction of Aromatic Compounds——Method A: A Typical Example: 1-Phenyl-2-propene (Run 3): Allyltrimethylsilane (**1a**) (1.37 g, 12 mmol) was added dropwise to a stirred suspension of thallium (III) trifluoroacetate (**6**) (5.44 g, 10 mmol) in dichloromethane (30 ml) and benzene (78 g, 1 mol) at 0°C in nitrogen. After being stirred for 5 h at 0°C then for 30 min at room temperature, the reaction mixture was poured into water and extracted with pentane. The extract was washed with aqueous sodium hydrogen carbonate and then with brine. Careful distillation afforded phenyl-2-propene[17,21)] (664 mg, 56%): bp 156—157°C. In a separate experiment, the yield of the product was analyzed by gas-chromatography using bromobenzene as an internal standard.

Method B: A Typical Example: 1-(2,5-Dimethylphenyl)-2-propene (Run 6): A solution of allyltrimethylsilane (**1a**) (21 mg, 0.18 mmol) in 1,4-dimethylbenzene (191 mg, 1.8 mmol) was added dropwise to a stirred suspension of thallium (III) trifluoroacetate (**6**) (98 mg, 0.18 mmol) in dichloromethane (0.5 ml) at 0°C in nitrogen. After being stirred for 2 h at 0°C then for 30 min at room temperature, a usual work-up and purification of the resulting crude product by silica gel column chromatography using pentane as the eluting solvent afforded 1-(2,5-dimethylphenyl)-2-propene[17,21)] (17.5 mg, 67%). In a separate experiment, the yield of the product was analyzed by gas-chromatography with 1-methylnaphthalene as an internal standard.

Method C: A Typical Example: 2-(2-Propenyl)furan (Run 14): Thallium (III) trifluoroacetate (**6**) (516 mg, 0.95 mmol) was added in one portion to a stirred solution of allyltrimethylsilane (**1a**) (163 mg, 1.43 mmol) in furan (6.5 g, 95 mmol) at 0°C in nitrogen. After being stirred for 1 h at 0°C, the reaction mixture was poured into water and extracted with pentane. The extract was washed with aqueous sodium hydrogen carbonate and then with brine. After the addition of bromobenzene (7.2 mg) the reaction mixture was analyzed by gas-chromatography, which showed the formation of 2-(2-propenyl)furan[17,21)] in 69% yield. Its structure was assigned on the basis of spectral data obtained for a pure sample isolated by preparative gas chromatography.

1-(2-Methoxyphenyl)-2-propene, 1-(4-Methoxyphenyl)-2-propene, and 1-(2,5-Dimethoxyphenyl)-2-propene——These compounds were reported recently by ourselves.[17,21)]

1-(2,4,6-Trimethoxyphenyl)-2-propene——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1600, 1500, 1460, 950, 910. MS *m/e*: 208 (M^+, base peak), 193, 181, 179. PMR ($CDCl_3$) δ: 3.31 (2H, dt, $J=6$, 1.5 Hz, CH_2), 3.76 (6H, s, 2×OMe), 3.77 (3H, s, OMe), 4.75—5.05 (2H, m, C=CH$_2$), 5.65—6.1 (1H, m, CH=C), 6.11 (2H, s, aromatic H). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69,21; H, 7.74. Found: C, 68.94; H, 7.83.

2-(2-Propenyl)thiophene[22]———MS *m/e*: 124 (M$^+$, base peak), 97, 91, 79, 53, 45. PMR (CDCl$_3$) δ: 3.57 (2H, dq, J=6.5, 1 Hz, CH$_2$).

3-(2-Propenyl)thiophene[23]———MS *m/e*: 124 (M$^+$, base peak), 97, 91, 79, 77, 53, 51, 45. PMR (CDCl$_3$) δ: 3.39 (2H, d, J=6.5 Hz, CH$_2$).

2-(2-Propenyl)chlorobenzene[24]———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1495, 1090, 1015, 990, 915. MS *m/e*: 152 (M$^+$), 125, 117 (base peak), 116, 115, 91, 89, 63. PMR (CDCl$_3$) δ: 3.50 (2H, d, J=6 Hz, CH$_2$), 4.9—5.2 (2H, m, C=CH$_2$),, 5.7—6.2 (1H, m, C=CH), 7.0—7.4 (4H, m, aromatic H).

4-(2-Propenyl)chlorobenzene[25]———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1595, 1490, 1090, 1015, 995, 920, 835. MS *m/e*: 152 (M$^+$), 125, 117 (base peak), 116, 115, 91, 89, 63. PMR (CDCl$_3$) δ: 3.32 (2H, d, J=6 Hz, CH$_2$), 4.9—5.2 (2H, m, C=CH$_2$), 5.6—6.2 (1H, m, C=CH), 7.0—7.3 (4H, aromatic H).

1-Phenyl-2-methyl-2-propene[22]———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1645, 1605, 1500, 1460, 1000, 920. PMR (CDCl$_3$) δ: 1.62 (3H, s, Me), 3.27 (2H, s, CH$_2$), 4.5—4.85 (2H, m, C=CH$_2$), 7.15 (5H, s, aromatic H).

1-(2,5-Dimethoxyphenyl)-2-methyl-2-propene———Reported recently by ourselves.[17,21]

1-(2,4,6-Trimethoxyphenyl)-2-methyl-2-propene———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1600, 1500, 950, 890. MS *m/e*: 222 (M$^+$, base peak), 207, 191, 181. PMR (CDCl$_3$) δ: 1.76 (3H, s, C-Me), 3.26 (2H, s, CH$_2$), 3.76 (6H, s, 2×OMe), 3.78 (3H, s, OMe), 4.44, 4.62 (each 1H, m, C=CH$_2$), 6.12 (2H, s, aromatic H). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24 ; H, 8.16. Found: C, 70.30; H, 8.17.

4-Acetoxy-2-(2,5-dimethoxyphenylmethyl)-1-propene———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1725, 1640, 1500, 1200, 1040, 895. MS *m/e*: 264 (M$^+$), 204, 189, 173 (base peak), 161, 121, 91. High resolution MS: Found 264.1377. Calcd for $C_{15}H_{20}O_4$ (M$^+$) 264.1362. PMR (CDCl$_3$) δ: 2.04 (3H, s, COMe), 2.34 (2H, t, J=6 Hz, CH$_2$), 3.35 (2H, s, CH$_2$) 3.75, 3.76 (each 3H, s, 2×OMe), 4.19 (2H, t, J=6 Hz, OCH$_2$), 4.79, 4.85 (each 1H, br s, C=CH$_2$), 6.6—6.9 (3H, m, aromatic H).

3-[2-(2-Acetoxyethyl)-2-propenyl]furan———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1730, 1645, 1595, 1510, 1210, 1030, 890. MS *m/e*: 194 (M$^+$), 134 (base peak), 119, 105, 91, 81. High resolution MS: Found 134.0730. Calcd for $C_9H_{10}O$ [(M−AcOH)$^+$] 134.0731. PMR (CDCl$_3$) δ: 2.04 (3H, s, COMe), 2.36 (2H, t, J=6 Hz, CH$_2$), 3.40 (2H, s, CH$_2$), 4.90 (2H, m, C=CH$_2$), 6.05, 6.28, 7.30 (each 1H, m, aromatic H).

3-(2-Methoxyphenyl)cyclohexene———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1600, 1490, 1110, 1020, 835. MS *m/e*: 188 (M$^+$, base peak), 173, 160, 159, 129, 115, 91. High resolution MS: Found 188.1189. Calcd for $C_{13}H_{16}O$ (M$^+$) 188.1200. PMR (CDCl$_3$) δ: 1.2—2.2 (6H, m), 3.80 (3H, s, OMe), *ca.* 3.85 (1H, m), 5.5—6.0 (2H, m, CH=CH), 6.7—7.3 (4H, m, aromatic H).

3-(4-Methoxyphenyl)cyclohexene———IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1650, 1610, 1510, 1110, 1070, 1020, 900, 870, 830. MS *m/e*: 188 (M$^+$, base peak), 173, 159, 145, 129, 115, 91. High resolution MS: Found 188.1194. Calcd for $C_{13}H_{16}O$ (M$^+$) 188.1200. PMR (CDCl$_3$) δ: 1.3—2.2 (6H, m), 3.32 (1H, m), 3.77 (3H, s, OMe), 5.5—6.0 (2H, m, CH=CH), 6.7—7.2 (4H, aromatic H).

Allylation of 1,4-Dimethoxybenzene using 2-Butenyltrimethylsilane (10)———Thallium (III) trifluoroacetate (**6**) (277 mg, 0.51 mmol) was added in one portion to a stirred solution of 1,4-dimethoxybenzene (1.4 g, 10.2 mmol) and 2-butenyltrimethylsilane (**10**) (a mixture of *E*- and *Z*-isomers) (65 mg, 0.51 mmol) in dichloromethane (5 ml) at 0°C in nitrogen. The reaction mixture was stirred for 10 min at 0°C then for 2.5 h at room temperature. After a usual work-up, the resulting crude product was purified by preparative thin-layer chromatography (TLC) [hexane–chloroform (5:1)] to give a mixture of products (**11** and **12**) (18.2 mg, 19%), and their ratio was determined by gas-chromatography to be 1:3.3. Compound **11** was isolated by preparative gas-chromatography. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1645, 1505, 920. MS *m/e*: 192 (M$^+$), 177, 161, 149, 121, 91 (base peak), 77. High resolution MS: Found 192.1140. Calcd for $C_{12}H_{16}O_2$ (M$^+$) 192.1150. PMR (CDCl$_3$) δ: 1.30 (3H, d, J=7 Hz, C-Me), 3.76, 3.78 (each 3H, s, 2×OMe), 3.9 (1H, m), 4.9—5.2 (2H, m, C=CH$_2$) 5.8—6.2 (1H, m, CH=C), 6.5—6.9 (3H, m, aromatic H). A mixture of *E*- and *Z*-isomers of **12** containing a small amount of **11** was obtained by preparative gas-chromatography. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1635, 1605, 1590, 1505, 920. MS *m/e*: 192 (M$^+$), 177, 161, 149, 119, 83, 73 (base peak). High resolution MS: Found 192.1110. Calcd for $C_{12}H_{16}O_2$ (M$^+$) 192.1150. PMR (CDCl$_3$) δ: 1.66 (3H, C-Me), 3.26 (2H, CH$_2$), 3.74, 3.76 (total 6H, OMe) 5.4—5.6 (2H, CH=CH), 6.5—6.9 (3H, aromatic H).

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