INTRAMOLECULAR DIELS-ALDER REACTION OF FURANS WITH ALLENYL ETHERS : HIGH EFFECT OF THE CHAIN LENGTH ON THE STRUCTURE AND REACTIVITY OF THE CYCLOADDUCTS

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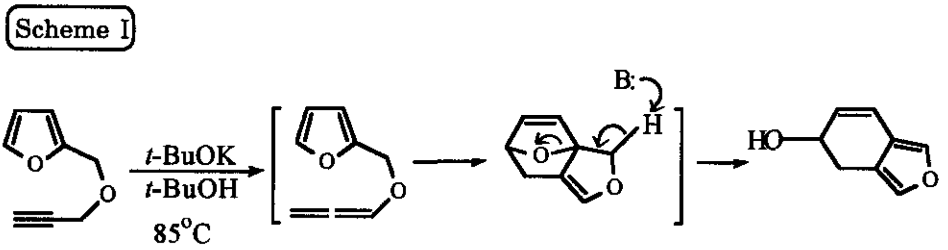
Abstract-The structure and reactivity of the cycloadducts of the title reaction were found to be highly dependent on the chain length between the furan diene and the allenyl ether dienophile. Reaction of the propargyl ether (**2**) with *t*-BuOK in *t*-BuOH at 85 °C for 3 h gave a mixture of the cycloadducts (**3**) and (**4**) in 90% yield, which were transferred to the benzo derivatives (**5**), (**6**) and (**7**). Treatment of the propargyl ether (**8**) with *t*-BuOK in *t*-BuOH at 85 °C for 5 h gave the products (**9**) and (**10**) in a ratio of 8:1 in 65% yield, no detectable amount of the cycloadduct (**8b**) was obtained. Refluxing of the propargyl ether (**13**) with *t*-BuOK in *t*-BuOH at 85 °C for 4 h gave the allenyl ether (**14**). Heating **14** in DMSO at 150 °C for 12 h stilll did not give **15**.

The intramolecular Diels-Alder reaction has been a central topic in modern organic synthesis.[1] The vast majority of the work reported in this area has dealt with reactions utilizing ethylenic and acetylenic dienophiles. However, the intramolecular Diels-Alder reaction of allene has received less attention.[2] Several years ago, Kanematsu *et al.* demonstrated that the allene unit is a versatile synthon as a dienophile in the intramolecular cycloaddition due to the absence of unfavorable nonbonded interactions in the transition state.[3] Afterward, they developed a furan ring transfer reaction *via* the intramolecular Diels-Alder reaction of furan as a diene and allenyl ether as a dienophile.[4] For the purpose of furan ring transfer reaction, in all of their cases there were only one carbon atom and one oxygen atom connection between the furan diene and the allene dienophile for the cycloaddition. In these cases, the cycloadducts were not isolated under the reaction conditions but were further transferred to the isobenzofuran precursors *via* ring opening of the bridged oxygen ring of the cycloadducts (**Scheme I**).

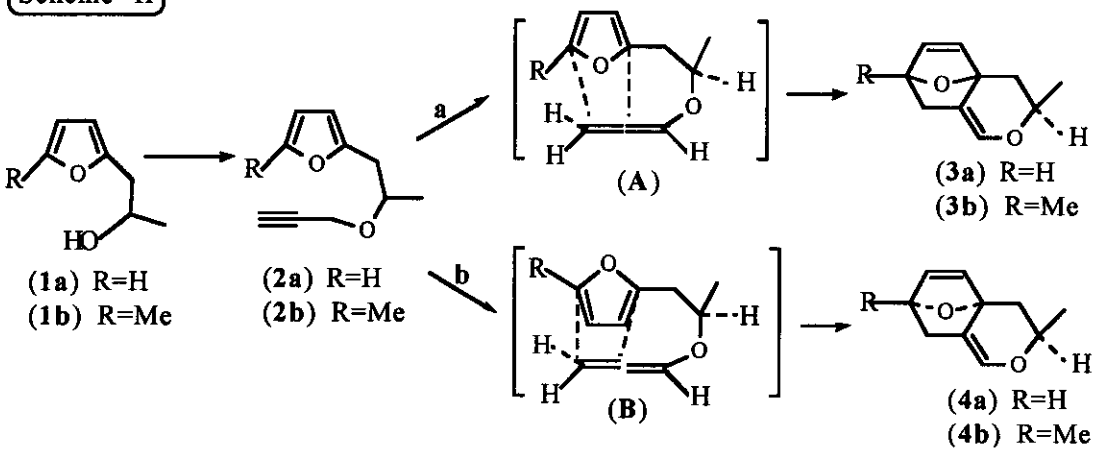


The effect of the chain length between diene and dienophile upon the reactivity of the intramolecular Diels-Alder reaction itself was extensively studied.[1] Recently, Grubbs *et al.* reported an example of the effect of the chain length upon the structure of the cycloadducts of the intramolecular Diels-Alder reaction of α,β-unsaturated ester dienophiles with cyclopentadiene.[5] In this paper we report the high effect of the chain length upon the reactivity of the cycloadducts and hence the structure of the reaction products of the intramolecular Diels-Alder reaction of furans with allenyl ethers.

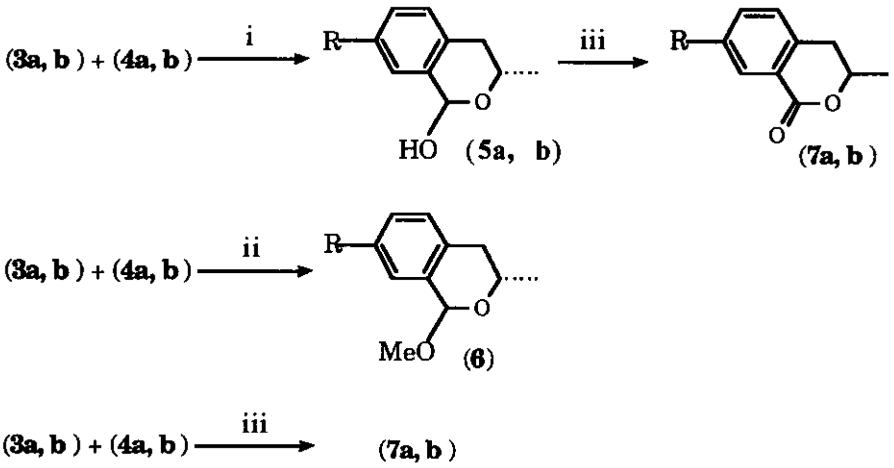
Metallation of furan and 2-methylfuran with *n*-BuLi in dry THF at room temperature followed by addition of propylene oxide gave **1a** and **1b** in 90% yields respectively. Propynylation of the alcohols **(1a)** and **(1b)** gave the corresponding acetylenic compounds **(2a)** and **(2b)** in 70-75% yields. Refluxing the propargyl ether **(2a)** with *t*-BuOK (3 equiv.) in *t*-BuOH for 4 h gave a mixture of the intramolecular cycloadducts **(3a)** and **(4a)** (7 : 1)[6] in 90% yield *via* the allenyl ether intermediate. Reaction of **2b** under the same reaction conditions gave a mixture of the cycloadducts **(3b)** and **(4b)** (7 : 3) in 90% yield. In these cases, we isolated the intramolecular cycloadducts without further ring opening of the bridged oxygen ring. Both compounds **(3a)** and **(3b)** possessed the methyl group *cis* to the bridged oxygen atom revealed down field shift in their nmr spectra with repect to those of **4a** and **4b**.

These experiments suggest that the intramolecular Diels-Alder reaction of substrates bearing an alkyl substituent at the homofurfurylic position proceeds *via* both diastereoisomeric transition states (**Scheme II**). The major stereoisomers, **(3a)** and **(3b)**, are formed through path **a** whereas the minor isomers, **(4a)** and **(4b)**, are formed through path **b**. Further chemical transformations for the cycloadducts **(3a)** and **(4a)** as well as **(3b** and **(4b)** were carried out. Reaction of the mixture[7] of **3a** and **4a** with catalytic amount of *p*-toluenesulfonic acid (PTSA) in aqueous THF and methanol gave **5a** and **6a** as the major products respectively. The stereochemistry of **5a** and **6a** was assigned based on mechanistic consideration. The nucleophiles, H_2O or MeOH, approach to the oxonium ion from the less hindered side, opposite to the methyl group. Oxidation of **5a** with PCC in CH_2Cl_2 gave the benzolactone **(7a)** in 90% yield. Oxidation of the mixture of **3a** and **4a** with PCC in CH_2Cl_2 also directly gave **7a** in 60% yield. The same transformation reactions were also carried out for the mixture of **3b** and **4b** (**Scheme III**). A mechanism was proposed for the direct oxidation of the mixture of **3a** and **4a** with PCC in CH_2Cl_2 to give **7a** (**Scheme IV**).

Scheme II

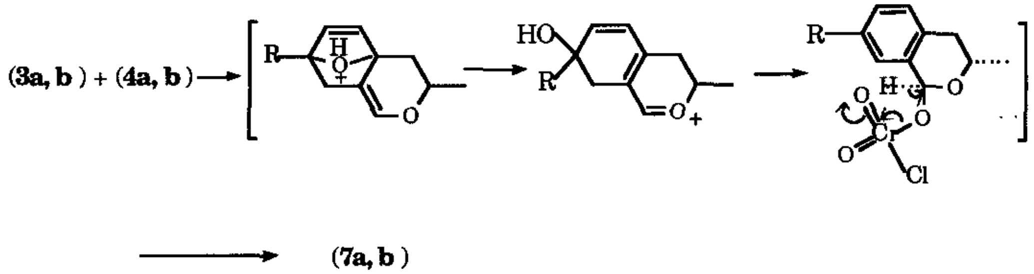


Scheme III



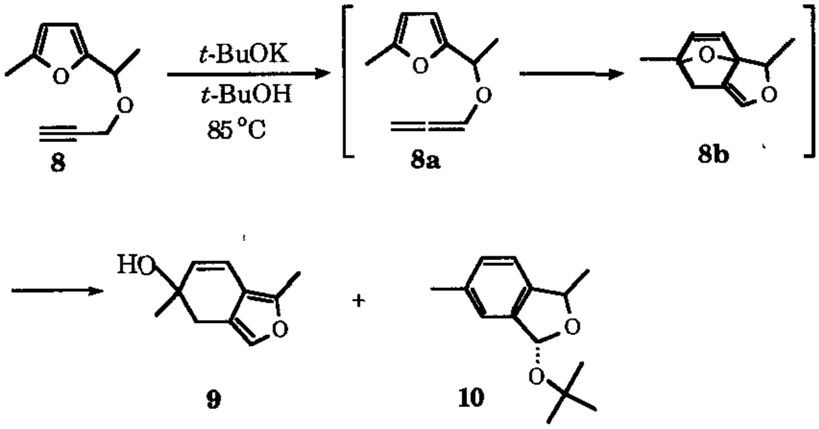
i) PTSA/H_2O-THF, room temperature; **ii)** PTSA/MeOH, room temperature; **iii)** PCC/CH_2Cl_2, room temperature.

Scheme IV



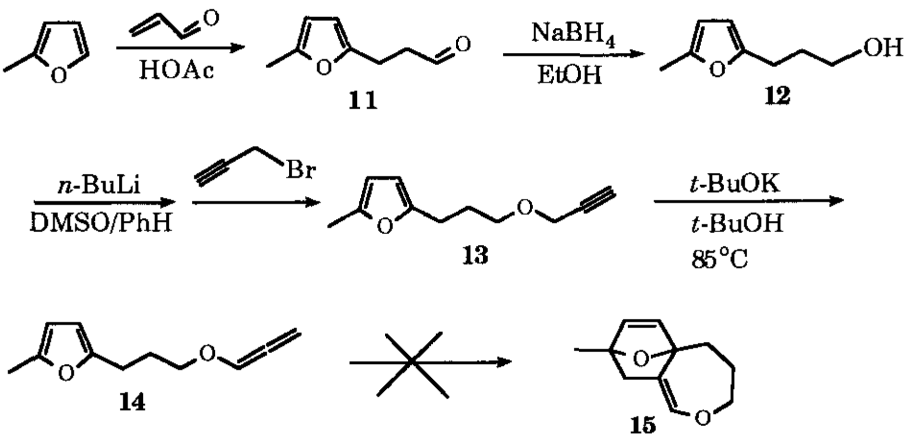
In order to understand the effect of the chain length on the nature of the intramolecular Diels-Alder reaction, we accomplished the intramolecular cycloaddition by varying the chain length. Metallation of 2-methylfuran with *n*-BuLi in dry THF at 25 °C followed by addition of acetaldehyde, then propynylation of the reaction mixture with propargyl bromide in dry DMSO and benzene at 25 °C gave **8** in 67% yield. Refluxing the propargyl ether **(8)** with *t*-BuOK in *t*-BuOH at 85 °C for 5 h gave the products **(9)** and **(10)** in a ratio of 8 : 1 in 65% yield, presumably *via* the intermediates **(8a)** and **(8b)** (**Scheme V**). No detectable amount of the cycloadduct **(8b)** was obtained. We propose here that the cycloadduct **(8b)**, possessing the 3, 10-dioxatricyclo[5. 2. 1. $0^{1,5}$]deca-4,8-diene structure, is highly strained and under the reaction conditions it easily undergoes ring opening of the bridged oxygen atom. On the other hand, in the case of the intramolecular Diels-Alder reaction of **2**, the cycloadducts **(3)** and **(4)** are not highly strained and therefore can be isolated without further ring opening of the bridged oxygen atom. Thus, we found that the structure and reactivity of the cycloadducts of the intramolecular Diels-Alder reaction were highly dependent on the chain length between the furan diene and the allenyl ether dienophle.

Scheme V



For the further study of the effect of the chain length on the nature of the title reaction, compound **(13)** was prepared. Reaction of 2-methylfuran with acrolein in the presence of glacial acetic acid at 80 °C for 10 h gave the Michael adduct **(11)** in 85% yield. Reduction of **11** with sodium borohydride in ethanol at 25 °C gave **12** in 90% yield. Reaction of the alcohol **(12)** with *n*-BuLi in dry DMSO and benzene followed by addition of propargyl bromide at room temperature for 2 h gave **13** in 75% yield. Treatment of the propargyl ether **(13)** with *t*-BuOK in *t*-BuOH at 85 °C for 4 h gave the allenyl ether **(14)** in 80% yield. No detectable amount of the cycloadduct **(15)** was obtained (**Scheme VI**). Prolong the reaction time for 24 h at 85 °C did not give the cycloadduct **(15)**. Heating the allenyl ether **(14)** in DMSO at 150 °C for 12 h still did not give the cycloadduct **(15)**.

Scheme VI



According to these results of the intramolecular Diels-Alder reaction of furans with allenyl ethers, we found the high effect of the chain length on the reactivity of the cycloaddition reaction and the structure and reactivity of the cycloadducts.

EXPERIMENTAL

Grneral. Infrared spectra were recorded on a Hitachi Model 260-50 spectrophotometer. ^{1}H Nmr spectra were measured on a JEOL FX-100FT spectrometer or a Varian EM-360L spectrometer, with TMS as internal standard. ^{13}C Nmr spectra were recorded on a JEOL FX-100FT or Brucker AM-400FT spectrometer with the center line of internal $CDCl_3$ (76.9 ppm) as referance. Mass spectra were taken on a JEOL JMS-D-100 mass spectrometer. High resolution mass values were taken on a JEOL TMS-D-300 mass spectrometer. For thin-layer chromatographic (tlc) analysis, Merck precoated tlc plates (Kieselgel 60 F_{254}, 0.2 mm) were used, and column chromatography was done by using Merck Kieselgel 60 (70-200 mesh) as the stationary phase.

Preparation of 1-(2-Furyl)-2-propanol (1a) and 1-(5-Methyl-2-furyl)-2-propanol (1b)

To a solution of furan (2.00 g, 29.4 mmol) in dry THF (50 ml) was added *n*-BuLi (22 ml, 35 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added dry propylene oxide (2.56 g, 4.41 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 4 h. After addition of saturated NH_4Cl (20 ml) and extraction with ether (5 x 20 ml), the organic layer was washed with brine, dried over $MgSO_4$, evaporated and the residue was purified by distillation to give **1a** (2.7 g, 72%, oil), bp 129-130 °C (760 mmHg); ir (neat) 3500-3200, 1610, 1100 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.34 (*m*, 1H), 6.32 (*m*, 1H), 6.12 (*m*, 1H), 4.12 (*m*, 1H), 2.80 (*d*, J = 6.4 Hz, 2H), 2.28 (*br s*, 1H), 1.21 (*d*, J = 6.2 Hz, 3H); ms m/z 126 (M^+, base), 81, 45. Hrms calcd for $C_7H_{10}O_2$ 126.0681, found 126.0662.

1b: 70% yield, oil, bp 142-143 °C (760 mmHg). Spectral data for **1b**: Ir (neat) 3500-3200, 1610, 1100 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 5.97-5.86 (*m*, 2H), 4.07 (*m*, 1H), 2.70 (*d*, J = 6.1 Hz, 2H) 2.28 (*s*, 3H), 2.06 (*br s*, 1H) 1.22 (*d*, J = 6.1 Hz, 3H); ms m/z 140 (M^+, base), 96. Hrms calcd for $C_8H_{12}O_2$ 140.0837, found 140.0852.

Preparation of Propargyl Ethers (2a) and (2b)

To a solution of compound **(1a)** (2.00 g, 15.9 mmol) in dry benzene (25 ml) and dry dimethyl sulfoxide (25 ml) was added *n*-BuLi (20 ml, 32 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min. To this solution was added dry propargyl bromide (4.72 g, 39.8 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 3 h. After addition of saturated NH_4Cl (30 ml) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, evaporated and the residue was purifed by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **2a** (1.82 g, 72%, oil), bp 143-144 °C (760 mmHg); ir (neat) 3300, 2120, 1610, 1080 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.30 (*m*, 1H), 6,29 (*m*, 1H), 6.08 (*m*, 1H), 4.15 (*d*, J = 2.4 Hz, 2H), 3.95 (*m*, 1H), 2.98-2.60 (doublet of AB*q*, 2H), 2.40 (*t*, J = 2.4 Hz, 1H), 1.19 (*d*, J = 6.1 Hz, 3H); ^{13}C nmr, δ 151.99 (*s*), 140.56 (*d*), 109.80 (*d*), 106.29 (*d*), 79.80 (*d*), 73.65 (*d*), 72.95 (*d*), 55.37 (*t*), 34.69 (*t*), 19.16 (*q*); ms m/z 164 (M^+, 20), 83 (base), 81, 43, 39. Hrms calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0823.

2b: 70% yield, oil, bp 157-158 °C (760 mmHg). Spectral data for **2b**: Ir (neat) 3300, 2120, 1610, 1080 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 5.94 (*m*, 1H), 5.85 (*m*, 1H), 4.15 (*d*, J = 2.4 Hz, 2H), 3.91 (*m*, 1H), 2.96-2.56 (doublet of AB*q*, 2H), 2.39 (*t*, J = 2.4 Hz, 1H), 2.25 (*s*, 3H), 1.19 (*d*, J = 6.1 Hz, 3H); ^{13}C nmr, δ 150.29 (*s*), 150.12 (*s*), 107.05 (*d*), 105.76 (*d*), 80.04 (*d*), 73.65 (*d*), 73.36 (*d*), 55.66

(*t*), 35.04 (*t*), 19.39 (*q*), 13.42 (*q*); ms m/z 178 (M^+, 33), 135, 95, 83 (base), 43. Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0985.

Intramolecular Diels-Alder Reactions of 2a and 2b

Compound **(2a)** (1.03 g, 6.28 mmol) was dissolved in *tert*-butanol (60 ml) in a round-bottomed flask. Potassium *tert*-butoxide (1.41 g, 12.6 mmol) was added to the solution, and the reaction mixture was refluxed at 85 °C for 4 h. After cooling, saturated NH_4Cl (50 ml) was added; the reaction mixture was extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give the cycloadducts **(3a)** and **(4a)** in a ratio of 7:1 in 90% yield (0.92 g). The ^1H and ^{13}C nmr spectral data for **3a** and **4a** are reported by assignment of the spectra of the mixture form of **3a** and **4a**. Spectral data for **3a** (oil): Ir(neat) 3060, 2930, 1690, 1140, 1120 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 6.38-6.16 (*m*, 3H), 5.04 (*m*, 1H), 3.92 (*m*, 1H), 2.53-2.28 (*m*, 2H), 1.96-1.83 (*m*, 2H), 1.40 (*d*, J = 6.3 Hz, 3H); ^{13}C nmr δ 137.13 (*d*), 135.53 (*d*), 134.89 (*d*), 110.97 (*s*), 82.76 (*s*), 78.07 (*d*), 69.59 (*d*), 34.43 (*t*), 28.77 (*t*), 21.05 (*q*); ms m/z 164 (M^+, base), 135, 94, 91, 66. Spectral data for **4a** (oil): Ir(neat) 3060, 2930, 1690, 1140, 1120 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 6.37-6.15 (*m*, 3H), 5.02 (*m*, 1H), 4.15 (*m*, 1H), 2.52-2.30 (*m*, 2H), 1.94-1.82 (*m*, 2H), 1.32 (*d*, J = 6.2 Hz, 3H); ^{13}C nmr δ 137.78 (*d*), 136.11 (*d*), 134.88 (*d*), 110.97 (*s*), 82.75 (*s*), 78.13 (*d*), 69.94 (*d*), 35.24 (*t*), 29.30 (*t*), 19.51 (*q*); ms m/z 164 (M^+, base), 135, 94. Hrms calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0816.

The same reaction conditions and procedure were applied to the intramolecular Diels-Alder reaction of **2b** to give **3b** and **4b** in a ratio of 7:3 in 90% yield. The ^1H and ^{13}C nmr spectral data for **3b** and **4b** are reported by assignment of the spectra of the mixture form of **3b** and **4b**. Spectral data for **3b** (oil): Ir(neat) 3060, 2930, 1690, 1140, 1120 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 6.34-6.14 (*m*, 3H), 3.90 (*m*, 1H), 2.30-2.18 (*m*, 2H), 2.00-1.85 (*m*, 2H), 1.62 (*s*, 3H), 1.38 (*d*, J = 6.3 Hz, 3H); ^{13}C nmr, δ 137.70 (*d*), 136.66 (*d*), 136.02 (*d*), 113.75 (*s*), 85.60 (*s*), 82.84 (*s*), 69.35 (*d*), 35.25 (*t*), 34.54 (*t*), 20.88 (*q*), 18.45 (*q*); ms m/z 178 (M^+, 72), 163, 135 (base). Spectral data for **4b** (oil): Ir(neat) 3060, 2970, 1690, 1140, 1120 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 6.38-6.14 (*m*, 3H), 4.15 (*m*, 1H), 2.40-2.18 (*m*, 2H), 2.04-1.86 (*m*, 2H), 1.62 (*s*, 3H), 1.29 (*d*, J = 6.3 Hz, 3H); ^{13}C nmr δ 138.73 (*d*), 136.77 (*d*), 136.10 (*d*), 116.50 (*s*), 85.70 (*s*), 81.11 (*s*), 69.58 (*d*), 35.38 (*t*), 34.85 (*t*), 20.87 (*q*), 19.28 (*q*); ms m/z 178 (M^+, 70), 163, 135 (base). Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0971.

Formation of 5 from 3 and 4

To a solution of the mixture of **3a** and **4a** (0.100 g, 0.56 mmol) in THF (7 ml) was added H_2O (3 ml). A catalytic amount of PTSA (5 mg) was added and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was extracted with ether and the organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 1/1 as eluent) to give **5a** (oil) in 70% yield (0.070 g). Spectral data for **5a**: Ir(neat) 3600-3100, 1600, 1050 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.29-7.13 (*m*, 4H), 6.05 (*s*, 1H), 4.49-4.05 (*m*, 1H), 3.18 (*s*, 1H), 2.68 (*m*, 2H), 1.35 (*d*, J = 6.2 Hz, 3H); ms m/z 164 (M^+, 5), 163, 147 (base). Hrms calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0853. **5b**: 70% yield (oil). Spectral data for **5b**: Ir(neat) 3600-3100, 1600, 1050 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.30-7.00 (*m*, 3H), 6.00 (*s*, 1H), 4.50-4.08 (*m*, 1H), 3.25 (brs, 1H), 2.60 (*m*, 2H), 2.33 (*s*, 3H) 1.35 (*d*, J = 6.2 Hz, 3H); ms m/z 178 (M^+, 6), 177, 161 (base). Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.1012.

Formation of 6 from 3 and 4

To a solution of the mixture of **3a** and **4a** (0.200 g, 1.12 mmol) in methanol (20 ml) was added a catalytic amount of PTSA (5 mg). The reaction mixture was stirred at room temperature for 10 min. The solvent was evaporated and ether (50 ml) was added. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **6a** (oil) in 80% yield (0.16 g). Spectral data for **6a**: Ir(neat) 1090, 1050, 740 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.27-7.13 (*m*, 4H), 5.55 (*s*, 1H), 4.28 (*m*, 1H), 3.55 (*s*, 3H), 2.69 (*m*, 2H), 1.37 (*d*, J = 6.1 Hz, 3H); ^{13}C nmr δ 134.00 (*s*,) 133.53 (*s*), 127.91 (*d*), 127.73 (*d*), 127.03 (*d*), 125.92 (*d*), 98.38 (*d*), 62.93 (*d*), 54.90 (*q*), 35.57 (*t*), 21.10 (*q*); ms m/z 178 (M^+, 28), 147 (base), 119. Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0978. **6b:** 80% yield. Spectral data for **6b** (oil): Ir(neat) 1090, 1050 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 7.10-6.98 (*m*, 3H), 5.42 (*s*, 1H), 4.20 (*m*, 1H), 3.52 (*s*, 3H), 2.60 (*m*, 2H), 2.26 (*s*, 3H) 1.30 (*d*, J = 6.2 Hz, 3H); ms m/z 192 (M^+,76), 161 (base), 148, 133. Hrms calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1162.

Oxidation of 5 with PCC

To a solution of **5a** (0.13 g, 0.79 mmol) in CH_2Cl_2 (30 ml) was added pyridinium chlorochromate (PCC) (0.51 g, 2.4 mmol). The reaction mixture was stirred at room temperature for 2 h and filtered through Celite. The solvent was evaporated and the crude product was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **7a** (oil) in 90% yield (0.117 g). Spectral data for **7a**: Ir(neat) 1720, 1610, 1280, 1120, 740 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 8.20 (*m*, 1H), 7.72-7.25 (*m*, 3H), 4.75 (*m*, 1H), 2.96 (*m*, 2H), 1.54 (*d*, J = 6 Hz, 3H); ^{13}C nmr δ 164.71 (*s*,) 138.59 (*s*), 124.50 (*s*), 133.09 (*d*), 129.48 (*d*), 126.97 (*d*), 74.62 (*d*), 34.49 (*t*), 20.55 (*q*); ms m/z 162 (M^+, 50), 118 (base). Hrms calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0665. **7b:** 90% yield. Spectral data for **7b** (oil): Ir(neat) 1720, 1610, 1280, 1040, 770 cm^{-1}; ^1H nmr ($CDCl_3$, 100 MHz) δ 8.03 (*s*, 1H), 7.45 (*d*, J = 8 Hz, 1H), 7.20 (*d*, J = 8 Hz, 1H), 4.75 (*m*, 1H), 2.96 (*m*, 2H), 2.44 (*s*, 3H), 1.56 (*d*, J= 6.4 Hz, 3H); ^{13}C nmr δ 165.14 (*s*,) 136.76 (*s*), 135.66 (*s*), 134.00 (*d*), 129.78 (*d*), 126.79 (*d*), 124.09 (*s*), 74.80 (*d*), 34.13 (*t*), 20.61 (*q*); ms m/z 176 (M^+, 66), 132 (base), 104. Hrms calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0823.

Formation of the δ-Lactone (7) from the Oxidation of 3 and 4 with PCC

To a solution of the mixture of **3a** and **4a** (0.15 g, 0.92 mmol) in CH_2Cl_2 (10 ml) was added pyridinium chlorochromate (PCC) (0.80 g, 3.7 mmol). The reaction mixture was stirred at room temperature for 2 h and filtered through Celite. The solvent was evaporated and the crude product was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **7a** (oil) in 60% yield (0.090 g). The same reation conditions and procedure were applied to the oxidation of the mixture of **3b** and **4b** to give **7b** in 65% yield.

Preparation of 1-(5-Methyl-2-furyl) ethyl Propargyl Ether (8)

To a solution of 2-methylfuran (2.00 g, 24.4 mmol) in dry THF (50 ml) was added *n*-BuLi (11.7 ml , 29.2 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added dry acetaldehyde (1.07 g, 24.4 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 4 h. The solvent was changed to benzene and DMSO. Thus, THF was evaporated and dry benzene (20 ml) and dry DMSO (20 ml) was added. To this solution was added propargyl bromide (8.7 g, 73 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 6 h. After addition of saturated NH_4Cl (20 ml) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **8** (oil) (2.6 g, 67%); ir (neat) 3300, 2120, 1560, 1090 cm^{-1}; ^1H nmr δ 6.14 (*d*, J = 3 Hz , 1H), 5.86 (*d* , J = 3 Hz, 1H), 4.60 (*q* , J = 6 Hz, 1H), 4.06 and 3.94 (AB*q*, J = 16 Hz, J = 2 Hz, 2H), 2.38 (*t*, J = 2 Hz, 1H), 2.24 (*s*, 3H), 1.49 (*d*, J = 6 Hz, 3H); ^{13}C nmr δ 152.01 (*s*,) 151.95 (*s*), 108.77 (*d*), 105.72 (*d*), 79.75 (*d*), 73.95 (*s*), 68.92 (*d*), 54.94 (*t*), 19.28 (*q*), 13.34 (*q*); ms m/z 164 (M^+, 12), 109 (base). Hrms calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0826.

Intramolecular Diels-Alder Reaction of 8

Compound **(8)** (2.00 g, 12.2 mmol) was dissolved in *tert*-butanol (100 ml) in a round-bottomed flask. Potassium *tert*-butoxide (4.10 g, 36.6 mmol) was added to the solution, and the reaction mixture was refluxed at 85 °C for 5 h. After cooling, saturated NH_4Cl (20 ml) was added; the reaction mixture was extracted with ether. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 1/1 as eluent) to give **9** (1.1 g, 56%) and **10** (0.20 g, 7 %). Spectral data for **9** (oil): Ir (neat) 3500-3200, 1650, 1110 cm^{-1}; ^1H nmr δ 7.05-7.00 (*m*, 1H), 6.38-6.28 (*m*, 1H) , 5.72-5.62 (*m*, 1H), 2.60-2.80 (*m*, 2H), 2.37 (brs, 1H), 2.24 (*s*, 3H), 1.37 (*s*, 3H); ^{13}C nmr δ 145.86 (*s*,) 135.62 (*d*), 132.83 (*d*), 118.65 (*d*), 118.43 (*s*), 115.43 (*s*), 69.70 (*s*), 34.34 (*t*), 28.22 (*q*), 11.63 (*q*); ms m/z 164 (M^+, 4), 163, 147, 146 (base). Hrms calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0864. Spectral data for **10** (oil): Ir (neat) 1380, 1010, 810 cm^{-1}; ^1H nmr δ 7.10-6.95 (*m*, 3H), 6.29 (*s*, 1H) , 5.15 (*q* , J = 6.6 Hz, 1H), 2.34 (*s*, 3H), 1.51 (*d*, J = 6.6 Hz, 3H), 1.37 (*s*, 9H); ^{13}C nms δ 141.52 (*s*,) 139.24 (*s*), 137.30 (*s*), 129.68 (*d*), 123.14 (*d*), 120.56 (*d*), 100.37

(*d*), 79.15 (*d*), 74.73 (*s*), 29.03 (*q*, 3C), 23.95 (*q*), 21.18 (*q*); ms m/z 220 (M^+, 1), 163, 147 (base). Hrms calcd for $C_{14}H_{20}O_2$ 220.1464, found 220.1475.

Preparation of 3-(5-Methyl-2-furyl)propionaldehyde (11)

To the mixture of 2-methylfuran (6.0 g, 73 mmol) and acrolein (8.2 g, 146 mmol) was added glacial acetic acid (3.0 ml, 47 mmol). The reaction mixture was heated at 80 °C for 10 h. After cooling, saturated Na_2CO_3 (50 ml) was added and the reaction mixture was extracted with ether. The combined organic layer was washed with saturated NH_4Cl and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **11** (8.6 g, 85%). Spectral data for **11** (oil): Ir (neat) 1730, 1570 cm^{-1}; ^1H nmr δ 9.78 (*t*, J = 1 Hz, 1H), 5.80 (*s*, 2H) , 2.69-2.95 (*m* , 4H), 2.25 (*s*, 3H); ms m/z 138 (M^+, 100), 95, 82.

3-(5-Methyl-2-furyl)-1-propanol (12)

To a solution of **11** (2.60 g, 18.8 mmol) in absolute ethanol (50 ml) was added $NaBH_4$ (0.40 g, 10.6 mmol) and the reaction mixture was stirred at room temperature for 0.5 h. After evaporation of the solvent, saturated NH_4Cl (50 ml) was added, and the mixture was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **12** (oil) (2.4 g, 90%) : Ir (neat) 3500-3200, 1570 cm^{-1}; ^1H nmr δ 5.85 (*s*, 2H), 3.65 (*t*, J = 6 Hz, 2H) , 2.65 (*t* , J = 7 Hz, 2H), 2.25 (*s*, 3H), 2.18 (*brs*, 1H), 2.00-1.70 (*m*, 2H); ms m/z 140 (M^+, 100), 139, 122.

3-(5-Methyl-2-furyl)propyl Propargyl Ether (13)

To the mixture of **12** (3.0 g, 21 mmol) in dry DMSO (25 ml) and benzene (25 ml) was added *n*-BuLi (15 ml, 43 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min. To this solution was added dry propargyl bromide (4.6 g, 38.3 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 3 h. After addition of saturated NH_4Cl (30 ml) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give **13** (oil) (4.76 g, 75%): Ir (neat) 3300, 2150, 1570, 1050 cm^{-1}; ^1H nmr δ 5.85 (*s*, 2H), 4.15 (*d*, J = 2 Hz, 2H) , 3.54 (*t* , J = 6 Hz, 2H), 2.68 (t, J = 7 Hz, 2H), 2.42 (*t*, J = 2 Hz, 1H), 2.25 (*s*, 3H), 1.85 (*m*, 2H); ms m/z 178 (M^+, 100), 140, 122. Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0982.

Formation of 3-(5-Methyl-2-furyl)propyl Allenyl Ether (14) from 13

Compound **(13)** (1.3 g, 7.3 mmol) was dissolved in *tert*-butanol (60 ml) in a round-bottomed flask. Potassium *tert*-butoxide (2.46 g, 23.0 mmol) was added to the solution and the reaction mixture was refluxed at 85 °C for 4 h. After cooling, saturated NH_4Cl (50 ml) was added; the reaction mixture was extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated and the residue was purified by column chromatography (with *n*-hexane/ether = 4/1 as eluent) to give the allenyl ether **(14**)(oil) (0.90 g, 70%): Ir (neat) 1950, 1570, 1200 cm^{-1}; ^1H nmr δ 6.70 (*t*, J = 6 Hz, 1H) 5.85 (*s*, 2H), 5.35 (*d*, J = 6 Hz, 2H) , 3.54 (*t* , J = 6 Hz, 2H), 2.60 (*t*, J = 7 Hz, 2H), 2.25 (*s*, 3H), 1.90 (*m*, 2H); ^{13}C nmr δ 200.97 (*s*) 153.16 (*s*), 149.94 (*s*), 121.35 (*d*), 105.59 (*d*), 105.47 (*d*), 90.23 (*t*), 67.62 (*t*), 27.77 (*t*), 24.55 (*t*), 13.42 (*q*); ms m/z 178 (M^+, 11), 139 (base), 122, 94. Hrms calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0967.

When the same procedure but prolonged reaction time (24 h) was applied for the reaction of compound **(13)**, the allenyl ether **(14)** was still obtained as the major product. No detectable amount of the intramolecular cycloadduct **(15)** was obtained.

Attempted Intramolecular Diels-Alder Reaction of 14

Compound **(14)** (0.78 g, 4.4 mmol) was dissolved in dry DMSO (25 ml) in a round-bottomed flask. The solution was heated at 150 °C for 12 h. Starting compound **(14)** was recovered and no detectable amount of the expected cycloadduct **(15)** was obtained.

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6. The ratio of the cycloadducts (**3a**) and (**4a**) was determined by the nmr spectrum of the crude product.
7. Since the separation of epimer (**3a**) and (**4a**) (the same **3b** and **4b**) was difficult, the chemical transformations were carried out without separation.

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