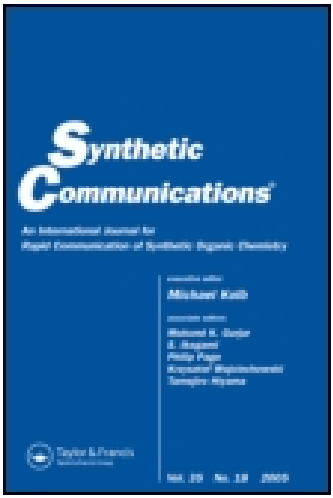

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Preparation of 4-Arylcyclopentenes by Sequential Diallylation of Arylaldehydes and Ring-Closing Metathesis

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Preparation of 4-Arylcyclopentenes by Sequential Diallylation of Arylaldehydes and Ring-Closing Metathesis

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Abstract: Allylsilane diallylation of aryl aldehydes followed by ring closure metathesis leads to 4-arylcyclopentenes in good yields.

Keywords: Aldehydes, allylation, cyclization, cyclopentenes, metathesis

The formation of five-membered carbocycles has been intensely studied in recent years[1] and, in particular, substituted cyclopentenes, such as 4-arylcyclopentenes **3**, are important building blocks used in organic synthesis. These compounds have seldom been prepared and usualy as by-products in the

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course of the Heck reaction of halobenzenes with cyclopentene.[2] Compound **3** can be subjected to a wide variety of additional chemical transformations to give potential intermediates as cyclopentadienes and precursors for the synthesis of natural products and biologically active compounds.

As part of our research program on allylsilane chemistry [preparation of 1-aryl-2,5-divinylcyclopentanes by double allylation of aryl aldehydes or corresponding acetals with 1,8-bis(trimethylsilyl)-2,6-octadiene (BISTRO)],[3] we report herein the diallylation of aryl aldehydes followed by a ring-closure metathesis.

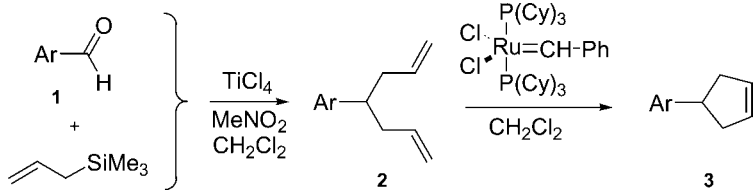
Titanium tetrachloride–mediated double allylation reaction of *p*-anisaldehyde has been observed by Albaugh–Robertson and Katzenellenbogen[4] and some years after, Mayr and Gorath showed that the formation of the $2+1$ product takes place when 2 equiv. of allylsilane per mol of benzaldehyde dimethyl acetal are used.[5]

We have observed that benzaldehyde, naphthaldehydes, and benzaldehydes substituted by electron-donor groups twice undergo allylation by treatment with allylsilane and titanium tetrachloride, giving rise to 1,6-heptadien-4-yl-substituted arene compounds **2** (Scheme 1 and Table 1). The diallylation of phthalaldehyde leads to **2j**, resulting from a single allylation of each carbonyl moiety in modest yield. This moderate yield may be explained by the instability in a reaction conditions of the product.

Having the required precursors in hand, we attempted the cyclisation by ring-closing metathesis.[6] The reaction occurs smoothly, giving rise to 4-aryl cyclopentenes **3** in good yields by using Grubbs's first-generation ruthenium catalyst $(PCy_3)_2(Cl)_2Ru=CHPh$.[7] In the case of **2h** and **2i**, only aryl cyclopentenes **3h** and **3i**, respectively, are obtained in spite of the possibility of formation of 3-oxaoctene derivatives. Finally, the isobenzofurane **2j** gave almost no product formation.

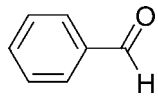
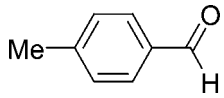
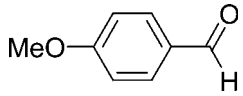
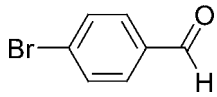
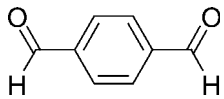
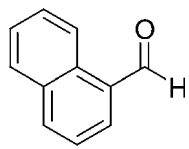
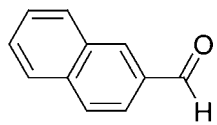
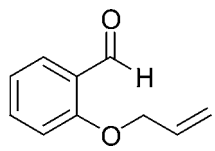
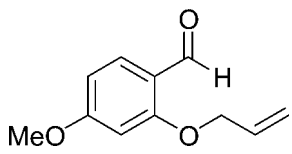
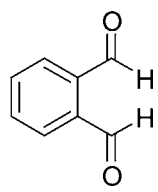
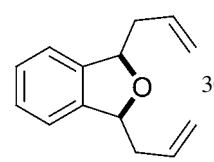
EXPERIMENTAL

CH_2Cl_2 was distilled on P_2O_5. All reactions were run under argon. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in a $CDCl_3$ solution. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$.



Scheme 1.

Table 1. Synthesis of 4-arylcyclopentenes

Entry	1	Yield of **2** (%)	Yield of **3** (%)
a		74	80
b		85	88
c		85	85
d		95	93
e		85	92
f		88	74
g		75	89
h		35	75
i		76	80
j	 	30	—

Double Allylation of Aryl Aldehydes, Typical Procedure

A flame-dried, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a thermometer, and an argon outlet was charged with anhydrous CH_2Cl_2 (20 mL) and $MeNO_2$ (1.2 mL, 20 mmol). The solution was cooled at $-60\,^{\circ}C$ and $TiCl_4$ (1 mL, 8.1 mmol) and then aldehyde (5.0 mmol) in CH_2Cl_2 (2 mL) were added. After 15 min of stirring, the mixture was cooled at $-90\,^{\circ}C$ and allyltrimethylsilane (2.4 mL, 15 mmol, 3 equiv.) in CH_2Cl_2 (2 mL) was slowly added. The mixture was stirred at $-85\,^{\circ}C$ for 3 h and then warmed to $-60\,^{\circ}C$. After completion of the reaction (TLC; 5–15 h), the mixture was poured into a saturated solution of NH_4Cl. After the usual workup, the crude product was purified by flash chromatography on silica gel (petroleum ether then petroleum ether–ether 25 : 1).

4-Phenyl-1,6-heptadiene, 2a.[8] According to the general procedure with benzaldehyde. **2a**, colorless oil; IR 3062, 1640, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ7.38–7.21 (5H, m), 5.74 (2H, ddt, $J = 17.2$, 10.2, 7.0 Hz), 5.04 (2H, br d, $J = 17.2$ Hz), 4.93 (2H, br d, $J = 10.4$ Hz), 2.79 (1H, m), 2.45 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.8 (s), 136.9 (d)(2C), 128.4 (d)(2C), 127.9 (d)(2C), 126.2 (d), 116.2 (t)(2C), 45.7 (d), 40.4 (t)(2C); MS m/z 131 (100), 91 (50).

4-(*p*-Tolyl)-1,6-heptadiene, 2b.[9] According to the general procedure with *p*-tolualdehyde. **2b**, colorless oil; IR 3073, 1640, 911, 813 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.21–7.08 (4H, m), 5.72 (2H, ddt, $J = 17.2$, 10.2, 7.0 Hz), 5.04 (2H, br d, $J = 17.2$ Hz), 4.93 (2H, br d, $J = 10.4$ Hz), 2.74 (1H, m), 2.45 (4H, m), 2.37 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.7 (s), 137.1 (d)(2C), 135.6 (s), 129.1 (d)(2C), 127.7 (d)(2C), 116.1 (t)(2C), 45.3 (d), 40.5 (t)(2C), 21.2 (q); MS m/z 186 (3), 145 (100), 130 (15).

4-(*p*-Anisyl)-1,6-heptadiene, 2c.[5,10] According to the general procedure with *p*-anisaldehyde. **2c**, colorless oil; IR 3073, 1637, 1247, 1037, 912, 830 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.15 (2H, d, $J = 8.7$), 6.91 (2H, d, $J = 8.7$ Hz), 5.75 (2H, ddt, $J = 17.0$, 10.2, 6.9 Hz), 5.04 (2H, br d, $J = 17.0$ Hz), 5.01 (2H, br d, $J = 10.2$ Hz), 3.84 (3H, s), 2.76 (1H, m), 2.44 (4H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.0 (s), 137.0 (d)(2C), 136.7 (s), 128.6 (d)(2C), 116.1 (t)(2C), 113.7 (d)(2C), 55.2 (q), 44.8 (d), 40.6 (t)(2C); MS m/z 161 (100), 146 (8), 119 (9), 91 (16).

4-(*p*-Bromophenyl)-1,6-heptadiene, 2d. According to the general procedure with *p*-bromobenzaldehyde. **2d**, colorless oil; IR 3073, 1640, 813 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37 (2H, d, $J = 8.3$ Hz), 7.0 (2H, d, $J = 8.3$ Hz), 5.60 (2H, ddt, $J = 17.2$, 10.4, 7.1 Hz), 4.95 (2H, br d, $J = 17.2$ Hz), 4.93 (2H, br d, $J = 10.4$ Hz), 2.66 (1H, m), 2.31 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.6 (s), 136.4 (d)(2C), 131.4 (d)(2C), 129.6

(d)(2C), 119.8 (s), 116.5 (t)(2C), 45.2 (d), 40.2 (t)(2C); MS m/z 211 (73), 209 (73), 130 (100) 129 (73). Anal. calcd. for $C_{13}H_{15}Br$: C, 62.17; H, 6.02. Found: C, 62.25; H, 5.98.

1,4-*bis*(1,6-Heptadien-4-yl)benzene, 2e. According to the general procedure with terephthalaldehyde (0.335 g, 2.5 mmol). **2e**, pale yellow; IR 3045, 1647, 914, 839 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24 (4H, br s), 5.74 (4H, ddt, $J = 17.2$, 10.0, 7.0 Hz), 5.04 (4H, br d, $J = 17.2$ Hz), 5.00 (4H, br d, $J = 10.0$ Hz), 2.76 (2H, m), 2.46 (8H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.4 (s)(2C), 137.0 (d)(4C), 127.6 (d)(4C), 116.0 (t)(4C), 45.3 (d)(2C), 40.4 (t)(4C); MS m/z 225 (64), 183 (90), 141 (100), 129 (32), 67 (43). Anal. calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.01; H, 9.78.

1-(1,6-Heptadien-4-yl)naphthalene, 2f. According to the general procedure with 1-naphthaldehyde and 15 h at rt. **2f**, pale yellow oil; IR 3047, 1639, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.20 (1H, d, $J = 8.3$ Hz), 7.93 (1H, d, $J = 7.7$ Hz), 7.79 (1H, d, $J = 8.3$ Hz), 7.75 (4H, m), 5.79 (2H, m), 5.10 (2H, d, $J = 18.0$ Hz), 5.02 (2H, d, $J = 10$ Hz), 3.77 (1H, t, $J = 9.0$ Hz), 2.64 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.6 (s), 136.8 (d)(2C), 134.1 (s), 132.1 (s), 129.1 (d), 126.7 (d), 125.9 (d), 125.5 (d), 125.4 (d), 123.8 (d), 123.3 (d), 116.5 (t)(2C), 39.6 (t)(2C), 38.9 (d)(br. signal); MS m/z 222 (27), 181 (100), 166 (29), 153 (11). Anal. calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.78; H, 8.21.

2-(1,6-Heptadien-4-yl)naphthalene, 2g. According to the general procedure with 2-naphthaldehyde. **2g**, colorless oil; IR 3052, 1639 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.85 (2H, m), 7.65 (s), 7.49 (2H, m), 7.39 (1H, m), 5.75 (2H, ddt, $J = 17.2$, 10.1, 7.0 Hz), 5.06 (2H, br. d, $J = 17.2$ Hz), 5.0 (2H, br. d, $J = 10.1$ Hz), 2.96 (1H, quint., $J = 7.2$ Hz), 2.54 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.2 (s), 136.8 (d)(2C), 133.6 (s), 132.4 (s), 128.0 (d), 127.7 (d)(2C), 126.4 (d), 126.2 (d), 126.0 (d), 125.3 (d), 116.3 (t)(2C), 45.9 (d), 40.4 (t)(2C). Anal. calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.90; H, 8.18.

1-(1,6-Heptadien-4-yl)-2-allyloxybenzene, 2h. According to the general procedure with 2-allyloxybenzaldehyde.[11] **2h**, pale yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ; 7.15 (2H, $J = 7.0$ Hz), 6.96 (1H, d, $J = 7.4$ Hz), 6.86 (1H, d, $J = 8.5$ Hz), 6.09 (1H, ddt, $J = 17.2$, 10.6, 4.9 Hz), 5.74 (2H, ddt, $J = 17.2$, 10.0, 7.0 Hz), 5.45 (1H, br. d, $J = 17.2$ Hz), 5.29 (1H, br. d, $J = 10.6$ Hz), 5.00 (2H, br. d, $J = 17.2$ Hz), 4.94 (1H, br. d, $J = 10.0$ Hz), 4.55 (2H, br. d, $J = 4.9$ Hz), 3.34 (1H, quint. $J = 7.1$ Hz), 2.44 (4H, t, $J = 7.1$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.4 (s), 137.4 (d)(2C), 133.7 (d), 133.1 (s), 128.1 (d), 126.9 (d), 120.7 (d), 116.9 (t), 115.8 (t)(2C), 112.0 (d), 68.9 (t), 38.8 (t)(2C), 37.8 (d). Anal. calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.01; H, 8.78.

1-(1,6-Heptadien-4-yl)-2-allyloxy-4-methoxybenzene, 2i. According to the general procedure with 2-allyloxy-4-methoxybenzaldehyde.[12] **2i**, pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.06 (1H, d, $J = 8.1$ Hz), 6.50 (1H, d, $J = 8.1$ Hz), 6.48 (1H, s), 6.09 (1H, m), 5.75 (2H, m), 5.47 (1H, br. d, $J = 18.1$ Hz), 5.30 (1H, br. d, $J = 10.2$ Hz), 5.01 (2H, br. d, $J = 18.0$ Hz), 4.96 (2H, br. d, $J = 11.3$ Hz), 4.55 (2H, br. s), 3.80 (3H, s), 3.27 (1H, quint., $J = 7.2$ Hz), 2.44 (4H, br. t, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.8 (s), 157.2 (s), 137.4 (d)(2C), 133.5 (d), 128.3 (d), 125.4 (s), 116.9 (t), 115.7 (t)(2C), 104.3 (d), 99.8 (d), 68.8 (t), 55.2 (q), 38.9 (t)(2C), 37.4 (t). Anal. calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.88; H, 8.65.

(*R,S*)-1,3-Diallyl-1,3-dihydro-isobenzofuran 2j.[13] According to the general procedure with phthalaldehyde (0.335 g, 2.5 mmol) and 2 h at $-60\,^\circ$C. Colorless oil; IR 3070, 1640, 1044, 994, 912, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 (2H, m), 7.22 (2H, m), 5.89 (2H, ddt, $J = 17.3$, 10.2, 6.9 Hz), 5.38 (2H, br. t, $J = 4.9$ Hz), 5.17 (2H, br. d, $J = 17.3$ Hz), 5.12 (2H, br. d, $J = 10.2$ Hz), 2.63 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.9 (s), 134.1 (d), 127.5 (d), 121.4 (d), 117.7 (t), 82.5 (d), 41.1 (t); MS m/z 159 (100), 131 (92), 91 (27), 77 (9).

Preparation of Aryl Cyclopentenes, Typical Procedure

Diallyl derivatives **2** (5 mmol) in CH_2Cl_2 (50 mL) was stirred in presence of $(PCy_3)_2(Cl)_2Ru = CHPh$ (206 mg, 0.025 mmol, 0.05 equiv.). After completion of the reaction (TLC), the solvent was evaporated and the crude product was purified by flash chromatography on silica gel (petroleum ether then petroleum ether–ether 25 : 1).

4-Phenylcyclopentene 3a.[14] Precursor **2a** was reacted as indicated in the general procedure. **3a** colorless oil; IR 3058, 3024, 1601, 836, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.22 (5H, m), 5.86 (2H, s), 3.54 (1H, tt, $J = 9.1$, 6.9 Hz), 2.90 (2H, dd, $J = 14.4$, 9.1 Hz), 2.54 (2H, dd, $J = 14.4$, 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6 (s), 130.0 (d)(2C), 128.5 (d)(2C), 127.0 (d)(2C), 125.9 (d), 43.3 (d), 41.5 (t)(2C); MS m/z 144 (96), 129 (100).

4-*p*-Tolylcyclopentene, 3b. Colorless oil; IR 3049, 1613, 813 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20 (2H, ½AA′BB′, $J = 8.1$ Hz), 7.15 (2H, ½AA′BB′, $J = 8.1$ Hz), 5.83 (2H, s), 3.48 (1H, tt, $J = 8.9$, 7.0 Hz), 2.85 (2H, dd, $J = 14.4$, 8.9 Hz), 2.48 (2H, dd, $J = 14.4$, 7.0 Hz), 2.37 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.5 (s), 135.4 (s), 130.0 (d)(2C), 129.2 (d)(2C), 126.9 (d)(2C), 43.0 (d), 41.5 (t)(2C), 21.1 (q); MS m/z 158 (74), 143 (100), 128 (47). Anal. calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.97; H, 8.85.

4-*p*-Anisylcyclopentene 3c.[14] Colorless oil; IR 3052, 1613, 1242, 1040, 826 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.20 (2H, ½AA′BB′, $J = 8.7$ Hz), 6.86 (2H, ½AA′BB′, $J = 8.7$ Hz), 5.79 (2H, s), 3.80 (3H, s), 3.44 (1H, tt, $J = 8.9$, 7.0 Hz), 2.82 (2H, dd, $J = 14.3$, 8.9 Hz), 2.43 (2H, dd, $J = 14.3$, 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.8 (s), 139.7 (s), 130.0 (d)(2C), 127.9 (d)(2C), 113.9 (d)(2C), 55.4 (q), 42.6 (d), 41.6 (t)(2C); MS m/z 174 (100), 159 (58), 144 (33).

4-(*p*-Bromophenyl)cyclopentene 3d. Colorless oil; IR 3052, 1072, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50 (2H, ½AA′BB′, $J = 8.3$ Hz), 7.23 (2H, ½AA′BB′, $J = 8.3$ Hz), 5.89 (2H, s), 3.52 (1H, tt, $J = 9.2$, 6.5 Hz), 2.93 (2H, dd, $J = 14.2$, 9.2 Hz), 2.50 (2H, dd, $J = 14.3$, 8.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.6 (s), 131.5 (d)(2C), 129.8 (d)(2C), 128.7 (d)(2C), 119.5 (s), 42.6 (d), 41.3 (t); MS m/z 224 (69), 222 (74), 143 (100), 128 (83), 115 (31). Anal. calcd. for $C_{11}H_{11}Br$: C, 59.22; H, 4.97. Found: C, 59.33; H, 4.86.

1,4-bis(Cyclopent-3-enyl)benzene 3e. Colorless oil; IR 3052, 1618, 838, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24 (4H, s), 5.81 (4H, s), 3.50 (2H, tt, $J = 8.9$, 7.2 Hz), 2.86 (4H, dd, $J = 14.4$, 8.9 Hz), 2.50 (4H, dd, $J = 14.4$, 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9 (s), 130.0 (d), 127.1 (d), 43.0 (d), 41.4 (t); MS m/z 210 (100), 143 (99), 128 (38), 115 (21). Anal. calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.43; H, 8.58.

4-(1-Naphthyl)cyclopentene 3f. Colorless oil; IR 3048, 1614, 1596, 777, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.35 (1H, m), 8.11 (1H, m), 7.96 (1H, m), 7.73 (2H, m), 7.67 (2H, m), 6.14 (2H, s), 3.21 (1H, m), 3.21 (2H, m), 2.94 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.8 (s), 134.3 (s), 131.8 (s), 130.0 (d), 129.0 (d), 126.6 (d), 125.6 (d)(2C), 125.4 (d), 123.9 (d), 123.4 (d), 40.7 (t), 39.1 (d); MS m/z 194 (100), 179 (19), 165 (19), 153 (9), 128 (6). Anal. calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.68; H, 7.18.

4-(2-Naphthyl)cyclopentene 3g. Colorless oil; IR 3051, 1600, 852, 815, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.87 (3H, m), 7.75 (1H, s), 7.50 (3H, m), 5.93 (2H, s), 3.72 (1H, tt, $J = 9.4$, 6.7 Hz), 3.02 (2H, dd, $J = 14.7$, 9.4 Hz), 2.66 (2H, dd, $J = 14.7$, 6.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.0 (s), 133.7 (s), 132.2 (s), 130.0 (d)(2C), 128.3 (d), 127.7 (d), 125.95 (d), 125.9 (d), 125.2 (d), 125.0 (d), 43.4 (d), 41.5 (t); MS m/z 194 (100), 179 (45), 165 (19), 152 (11), 128 (29). Anal. calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.78; H, 7.22.

1-Allyloxy-2-(cyclopent-3-enyl)benzene 3h. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.17 (2H, m), 6.98–6.87 (2H, m), 6.11 (1H, ddt, $J = 17.1$, 10.6, 4.9), 5.86 (2H, m), 5.48 (1H, br. d, $J = 17.1$ Hz), 5.31 (1H, br. d, $J = 10.6$ Hz), 4.59 (2H, dd, $J = 4.9$, 1.5 Hz), 3.91 (1H, tt, $J = 9.1$, 6.9 Hz),

2.82 (2H, dd, $J = 14.3$, 9.1 Hz), 2.53 (2H, dd, $J = 14.3$, 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.3 (s), 135.6 (s), 133.7 (d), 130.1 (d)(2C), 127.5 (d), 126.8 (d), 120.9 (d), 116.8 (t), 111.9 (d), 68.9 (t), 39.9 (t)(2C), 36.9 (d). Anal. calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.02; H, 8.12.

2-Allyloxy-1-(cyclopent-3-enyl)-4-methoxybenzene 3i. Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (1H, d, $J = 8.8$ Hz), 6.43 (2H, br. s), 6.04 (1H, ddt, $J = 15.5$, 10.6, 5.3 Hz), 5.76 (2H, s), 5.45 (1H, br. d, $J = 15.5$ Hz), 5.25 (1H, br. d, $J = 10.6$ Hz), 4.52 (2H, d, $J = 5.3$ Hz), 3.77 (3H, s), 2.72 (2H, dd, $J = 14.2$, 8.4 Hz), 2.42 (2H, dd, $J = 14.2$, 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.9 (s), 157.2 (s), 133.6 (d), 130.2 (d)(2C), 128.0 (s), 127.8 (d), 117.0 (t), 104.4 (d), 100.0 (d), 69.0 (t), 55.5 (q), 39.9 (t)(2C), 36.3 (d). Anal. calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.28; H, 7.78.

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