Supporting Information (5 pages)

Synthesis of Allenes via Palladium-Catalyzed Hydrogen Transfer Reactions: Propargylic Amines As an Allenyl Anion Equivalent

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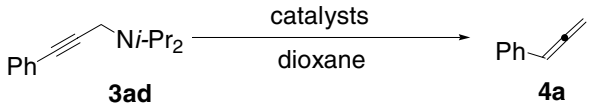
General Information. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) or a VARIAN UNITY-INOVA 400 (400 MHz) spectrometers. The chemical shifts are reported in δ units relative to internal tetramethylsilane. IR spectra were recorded on a Shimadzu FTIR-8200A spectrometer. High-resolution mass spectra (EI and FAB) were recorded on a Jeol JMS-HX110. Most commercially supplied chemicals were used without further purification. The structure of phenylallene **4a** was determined unambiguously by comparison with authentic sample prepared by the literature procedure.[1, 2]

Hydrogen transfer reactions of 3ad under various palladium-catalyzed conditions and plausible mechanisms.

Hydrogen transfer reactions of **3ad** proceeded in the presence of Pd(0) catalysts, such as $Pd_2dba_3{\cdot}CHCl_3$ and Pd_2dba_3 (2.5 mol%), with $(C_6F_5)_3P$ (20 mol%) to give **4a** in 99% yields (entries 1 and 2 in Table 1). In the absence of $(C_6F_5)_3P$ as a ligand, **4a** was obtained in 5% yield (entry 3). A referee pointed out the possibility of Pd (II) as an actual catalyst. We examined the hydrogen transfer reaction of **3ad** using $Pd(OAc)_2/(C_6F_5)_3P$ as catalysts and **4a** was obtained in 95% yield (entry 4). Even in the absence of the ligand, the reaction proceeded to give **4a** in 61% yield along with the recovery of **3ad** in 31% yield (entry 5). Since the oxidative insertion of Pd (0) to a C-H bond adjacent to nitrogen was investigated by Murahashi and the coworkers,[3] we may propose a Pd(0) mechanism as shown in Scheme 1. Oxidative insertion of Pd (0) to **3** would form the Pd (II) complex **7**, which comes to rapid equilibrium with the iminium ion complex **8** assisted by a lone pair electron of the nitrogen. The hydrogen transfer from palladium to alkyne moiety of **8** followed by the rearrangement of a π-bond would give the allenes **4** and the imine **9**, and palladium (0) is regenerated. Since $(C_6F_5)_3P$ is an electron-deficient phosphine and an effective ligand for the Pd(0)-catalyzed reaction, it would be considered that a role of $(C_6F_5)_3P$ is the stabilization of the anionic palladium intermediate **8** in the equilibrium between **7** and **8** to accelerate the generation of allenes **4** in the catalytic cycle (Scheme 1). Although the imine **9** was not detected in the reaction mixture, benzyl benzylideneamine was detected by GC-MS in the case of the reaction of **3ab**. This result strongly supports our proposed mechanism. According to the result obtained from entry 4 in Table 1, an alternative mechanism, in which Pd (II) would be a reactive intermediate through the catalytic cycle, could be envisaged as shown in Scheme 2. The coordination of $Pd(OAc)_2$ with **3** would form the complex **7'**, which comes to rapid equilibrium with the iminium ion complex **8'** assisted by a lone pair electron of the nitrogen. The hydrogen transfer from H-Pd-OAc to alkyne moiety of **8'** followed by the rearrangement of π-bond would give the allenes **4** and the imine **9**, and $Pd(OA)_2$ is regenerated.

Table 1. Hydrogen transfer reactions of **3ad** under various palladium-catalyzed conditions [a]

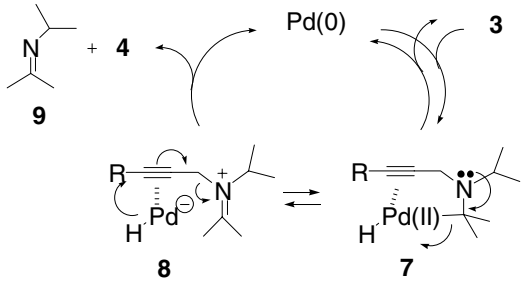


3ad **4a**

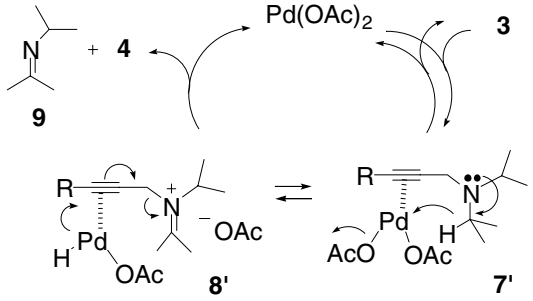
entry	Pd (mol%)	Ligand (mol%)	yield of **4a** / %
1	$Pd_2dba_3{\cdot}CHCl_3$ (2.5)	$(C_6F_5)_3P$ (20)	99
2	Pd_2dba_3 (2.5)	$(C_6F_5)_3P$ (20)	99
3	Pd_2dba_3 (2.5)	none	5 (95) [b]
4	$Pd(OAc)_2$ (5)	$(C_6F_5)_3P$ (20)	95
5	$Pd(OAc)_2$ (5)	none	61 (31) [b]

[a]The reactions were carried out in dioxane at 100°C under Ar for 24 h. The reaction progress was monitored by GC analysis. [b]The recovery of **3ad** after 24 h is indicated in the parentheses.

Scheme 1. The Pd(0) Mechanism



Scheme 2. The Pd(II) Mechanism



Typical procedure for the synthesis of propargylamines by Sonogashira coupling reactions.

A mixture of **1a** (205 mg, 1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), CuI (17 mg, 0.09 mmol), and **2d** (180 mg, 1.3 mmol) was dissolved in acetonitril (5 mL) under Ar and triethylamine (210 μL, 1.5 mmol) was added. The mixture was stirred at 60 °C for 6 h. The reaction progress was monitored by GC. The solvent was removed under the reduced pressure and the residue was purified by silica gel column chromatography with hexane/ethyl acetate (10/1) to give **3ad** (185 mg, 86% yield).

***N,N*-diethyl-3-phenylprop-2-ynylamine (3aa).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.28-7.26 (m, 2H), 3.63 (s, 2H), 2.61 (q, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 128.1, 127.6, 123.2, 84.9, 84.3, 47.3, 41.5, 12.8; IR 2970, 1599, 1489, 1443, 1200, 1092, 1069 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{18}N$: $(M+H)^+$ *m/z* 188.1439, found *m/z* 188.1434.

***N,N*-dibenzyl-3-phenylprop-2-ynylamine (3ab).** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50~7.47 (m, 2H), 7.43~7.41 (m, 3H), 7.34~7.30 (m, 6H), 7.27~7.22 (m, 4H), 3.74 (s, 4H), 3.46 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 131.7, 129.0, 128.2, 127.9, 127.0, 85.8, 84.4, 57.7, 42.1;IR 3028, 2826, 1597, 1489, 1454, 918cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{22}N$: $(M+H)^+$ *m/z* 312.1752, found *m/z* 312.1747. Calcd for $C_{23}H_{21}NNa$: $(M+Na)^+$ *m/z* 334.1572, found *m/z* 334.1566.

***N,N*-diisobutylprop-3-phenylprop-2-ynylamine (3ac).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.31-7.26 (m, 3H), 3.55 (s, 2H), 2.26 (d, *J* = 7.2 Hz, 4H), 1.73, (tsept, *J* = 7.2, 6.4 Hz, 2H), 0.90 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.0, 127.6, 123.5, 85.4, 84.6, 62.7, 43.5, 26.4, 20.9; IR 2953, 2868, 1597, 1489, 1468, 1364, 1072 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{26}N$: $(M+H)^+$ *m/z* 244.2065, found *m/z* 244.2060.

***N,N*-diisopropyl-3-phenylprop-2-ynylamine (3ad).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.28-7.26 (m, 3H), 3.65 (s, 2H), 3.26 (sept, *J* = 6.4 Hz, 2H), 1.15 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.2, 128.0, 127.5, 123.6, 88.9, 83.4, 48.5, 34.8, 20.7; IR 2966, 1598, 1488, 1380, 1203, 1176 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{22}N$: $(M+H)^+$ *m/z* 216.1752, found *m/z* 216.1747.

***cis*-2,6-dimethyl-1-(3-phenyl-prop-2-ynyl)-piperidine (3ae).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43, (m, 2H), 7.32-7.29 (m, 3H), 3.87 (s, 2H), 2.61-2.58 (m, 2H), 1.69-1.62 (m, 4H), 1.42-1.29 (m, 2H), 1.17 (d, *J* = Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 128.1, 127.7, 123.3, 85.0, 83.5, 54.8, 38.1, 35.4, 24.8, 21.1; IR 1926, 1489, 1441, 1317, 1200, 1094, 1059 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{22}N$: $(M+H)^+$ *m/z* 228.1752, found *m/z* 228.1747. Calcd for $C_{16}H_{21}NNa$: $(M+Na)^+$ *m/z* 250.1572, found *m/z* 250.1566.

***N,N*-diisopropyl-3-(3-naphthyl)prop-2-ynylamine (3bd).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.56-7.37 (m, 3H), 3.83 (s, 2H), 3.34 (sept, *J* = 6.8 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.3, 133.0, 130.0, 128.0, 127.9, 126.4, 126.0, 125.0, 121.3, 93.8, 81.6, 48.5, 35.0, 20.8; IR 3057, 2968, 1508, 1458, 1380, 1203, 1176 cm^{-1}; HRMS (FAB) calcd for $C_{19}H_{24}N$: $(M+H)^+$ *m/z* 266.1906, found *m/z* 266.1903. Calcd for $C_{19}H_{23}NNa$: $(M+Na)^+$ *m/z* 288.1728, found *m/z* 288.1723.

***N,N*-diisopropyl-3-(4-methoxypheyl)-prop-2-ynylamine (3cd).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.81, (d, *J* = 8.8Hz, 2H), 3.78 (s, 3H), 3.64 (s, 2H), 3.26 (sept, *J* = 6.8 Hz, 2H), 1.14 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 132.6,115.8, 113.6, 87.3, 83.1, 55.2, 48.4, 34.8, 20.7; IR 2966, 1606, 1508, 1463, 1290, 1247, 1176, 1035 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{24}NO$: $(M+H)^+$ *m/z* 246.1858, found *m/z* 246.1852. Calcd for $C_{16}H_{23}NONa$: $(M+Na)^+$ *m/z* 268.1677, found *m/z* 268.1672.

***N*-4-(3-*N,N*-diisopropylaminoprop-1-ynyl)-phenylacetamide (3dd).** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (bs, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.63 (s, 2H), 3.25 (sept, *J* = 6.4 Hz, 2H), 2.15 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 137.3, 131.9, 119.3, 119.2, 88.4, 83.0, 48.5, 34.8, 24.6,

20.7; IR 3257, 2972, 1664, 1600, 1510, 1373, 1203, 1178, 1029, 839cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{25}N_2O$: $(M+H)^+$ *m/z* 273.1967, found *m/z* 273.1961. Calcd for $C_{17}H_{24}N_2ONa$: $(M+Na)^+$ *m/z* 295.1786, found *m/z* 295.1781.

4-(3-*N,N*-diisopropylaminoprop-1-ynyl)-benzoic acid ethylester (3ed). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 2H), 3.25 (sept, *J* = 6.8 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 131.8, 129.2, 128.2, 92.4, 82.8, 61.0, 48.5, 34.9, 20.7, 14.3; IR 2970, 1720, 1606, 1463, 1365, 1271, 1174, 1105, 1020, 858 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{26}NO_2$: $(M+H)^+$ *m/z* 288.1964, found *m/z* 288.1958. Calcd for $C_{18}H_{25}NO_2Na$: $(M+Na)^+$ *m/z* 310.1783, found *m/z* 310.1778.

***N,N*-diisopropyl-3-(4-nitrophenyl)-prop-2-ynylamine (3fd).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.2 Hz, 2H), 7.52 (d, *J* = 9.2 Hz, 2H), 3.71 (s, 2H), 3.28 (sept, *J* = 6.8 Hz, 2H), 1.17 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 131.9, 130.4, 123.3, 94.8, 82.0, 48.8, 34.9, 20.5; IR 2970, 2229, 1593, 1519, 1342, 1307, 1203, 1194, 1101, 854 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{21}N_2O_2$: $(M+H)^+$ *m/z* 261.1603, found *m/z* 261.1598.

4-(3-*N,N*-diisopropylaminoprop-1-ynyl)-benzaldehyde (3gd). Brown Oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 3.70 (s, 2H), 3.28 (sept, *J* = 6.4 Hz, 2H), 1.17 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 134.9, 131.7, 129.8, 129.3, 93.4, 82.9, 48.7, 34.9, 20.6; IR 2970, 1703, 1602, 1560, 1263, 1301, 1207, 1164, 831 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}NO$: $(M+H)^+$ *m/z* 244.1701, found *m/z* 244.1696.

1-Allenylnaphthalene (4b). White solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.52-7.42 (m, 3H), 6.86 (t, *J* = 6.8 Hz, 1H), 5.20 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.7, 133.7, 129.9, 128.5, 127.3, 125.8, 125.5, 125.4, 125.1, 124.7, 123.3, 90.3, 77.8; IR (KBr) 1940, 1649, 1494, 1392, 1301, 1232, 1101, 987 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{10}$: (M^+) *m/z* 166.0781, found *m/z* 166.0777.

1-Methoxy-4-allenylbenzene (4c). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.11 (t, *J* = 6.8 Hz, 1H), 5.11 (d, *J* = 6.8Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 158.5, 127.6, 125.9, 114.0, 93.3, 78.6, 55.3; IR(neat) 2837, 1942, 1608, 1487, 1247, 1087, 1035 cm^{-1}; MS (EI) *m/z* 146 (M^+), 131 ([M-Me]$^+$), 115 ([M-OMe]$^+$).

4-Allenylacetanilide (4d). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (bs, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.12 (t, *J* = 6.8 Hz, 1H), 5.13 (d, *J* = 6.8 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 168.4, 136.7, 129.8, 127.2, 120.1, 93.3, 78.9, 24.5; IR (KBr) 3057, 1944, 1660, 1602, 1508, 1404, 1369, 1263 cm^{-1}; MS (EI) *m/z* 173 (M^+), 130 ([M-Ac]$^+$), 115 ([M-NHAc]$^+$).

Ethyl 4-allenylbenzoate (4e). Colorless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.19 (d, *J* = 6.8 Hz, 1H), 5.20 (t, *J* = 6.8 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 6.0, Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.6, 166.4, 138.8, 129.8, 128.7, 126.4, 93.6, 79.1, 60.8, 14.2; IR (neat) 3357, 2981, 1940, 1716, 1608, 1517, 1274 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}O_2$: (M^+) *m/z* 188.0837, found *m/z* 188.0843

4-Allenylnitrobenzene (4f). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.24 (t, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 141.2, 126.9, 123.9, 93.0, 79.7; IR (neat) 1938, 1643, 1595, 1471, 1384, 1342, 1139, 858 cm^{-1}; HRMS (EI)

calcd for $C_9H_7NO_2$: (M^+) *m/z* 161.0477, found *m/z* 161.0466.

4-Allenylbenzaldehyde (4g). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.22 (t, *J* = 6.8 Hz, 1H), 5.24 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.7, 191.4, 140.7, 134.8, 130.0, 126.9, 93.6, 79.4; IR (neat) 2734, 1938, 1697, 1602, 1573, 1487, 1438, 1388 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{14}N_2O$: (M^+) *m/z* 144.0575, found *m/z* 144.0576.

1-Phenyl-2,3-butadien-1-ol (6a). Colorless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.25 (m, 5H), 5.45, (q, *J* = 3.6 Hz, 1H), 5.27 (s, 1H), 4.94-4.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 142.2, 128.3, 127.7, 125.9, 95.1, 78.2, 71.9; IR (neat) 3373, 3030, 2891, 1955, 1494, 1454, 1002, 850 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}O$:(M^+) *m/z* 146.0732, found *m/z* 146.0726.

1-Benzyloxy-1-phenyl-2,3-butadiene (6b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.28 (m, 10H), 5.35 (q, *J* = 6.8 Hz, 1H), 4.94 (d, *J* = 7.6 Hz, 1H), 4.88-4.77 (m, 2H), 4.58 (q, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.50, 141.18, 138.08, 128.26, 128.20, 127.65, 127.58, 127.40, 126.50, 92.71, 79.27, 76.46, 70.18; IR (neat) 2868, 1953, 1645, 1519, 1487, 1386, 1276, 1097 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}O$: (M^+) *m/z* 236.1201, found *m/z* 236.1196.

1-(4-Methoxyphenyl)-2,3-butadien-1-ol (6c). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.43 (q, *J* = 6.6 Hz, 1H), 5.23 (s, 1H), 4.93-4.89 (m, 2H), 3.81, (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 159.0, 134.9, 127.2, 113.7, 95.2, 78.0, 71.5, 55.2; IR (neat) 3402, 2837, 1955, 1610, 1585, 1514, 1247, 1174, 1033 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}O_2$: (M^+) *m/z* 176.0838, found *m/z* 176.0832.

1-(3,5-Dimethoxyphenyl)- 2,3-butadien-1-ol (6d). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (d, *J* = 6.0 Hz, 2H), 6.39 (t, *J* = 6.4 Hz, 1H), 5.42 (q, *J* = 6.4 Hz, 1H), 5.21 (s, 1H), 4.95-4.93 (m, 2H), 3.80 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 160.6, 145.2, 103.8, 99.6, 94.9, 78.1, 71.9, 55.3; IR (neat) 3421, 2839, 1955, 1596, 1458, 1296, 1205, 1060 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}O_3$: (M^+) *m/z* 206.0943, found *m/z* 206.0937.

1,2-Nonadien-4-ol (6e). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (q, *J* = 6.8 Hz, 1H), 4.86-4.84 (m, 2H), 4.19-4.14 (m, 1H), 1.58-1.54 (m, 2H), 1.43-1.25 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 206.6, 94.8, 77.3, 69.7, 37.5, 31.7, 25.1, 22.6, 14.1; IR(neat) 3336, 2931, 1955, 1508, 1458, 1022, 842 cm^{-1}. Since the M^+ of **5e** was not detected by the mass spectroscopy, the alcohol **6e** was transformed into the benzoate form and assigned. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 5.27 (t, *J* = 5.1 Hz, 1H), 5.30 (q, *J* = 5.1 Hz, 1H), 4.87-4.81 (m, 2H), 1.83-1.73 (m, 2H), 1.43-1.28 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 94.8, 77.3, 69.7, 37.5, 31.7, 25.1, 22.6, 14.1; MS (EI) *m/z* 244 (M^+), 173 ($[M-C_5H_{11}]^+$), 123 ($[M-OBz]^+$).

1-Allenylcyclohexanol (6f). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (t, *J* = 6.8 Hz, 1H), 4.87 (d, *J* = 6.8Hz, 2H), 1.69-1.59 (m, 4H), 1.47 (t, *J* = 5.2 Hz, 4H), 1.37-1.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 205.9, 99.3, 78.0, 70.4, 38.3, 25.5, 22.6; IR(neat) 3367, 2933, 2856, 1955, 1508, 952cm^{-1}; the M^+ of **6f** was not detected by the mass spectroscopy.

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