Supporting Information

**Ruthenium-Catalyzed Cyclization of Alkyne-Epoxy Functionalities through
Alternation of the Substituent and Structural Skeleton of Epoxides.**

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(1) General Sections

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula and septa apparatus. Benzene, diethyl ether, tetrahydrofuran and hexane were dried with sodium benzophenone and distilled before use. $\text{TpRuPPh}_3(\text{CH}_3\text{CN})_2\text{PF}_6$ catalyst was prepared by heating $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ with LiPF_6 in CH_3CN .¹ 2-Bromobenzaldehyde was obtained commercially and used without purification. *o*-(2'-Trimethylsilyl-ethynyl)benzaldehyde was obtained by the Sonogashira coupling reaction of 2-bromobenzaldehyde with trimethylsilylacetylene.² (α -Methylbenzyl)triphenyl phosphonium bromide was prepared by heating triphenylphosphine with neat α -bromoethylbenzene.³

(1) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G.

Organometallics **1997**, *16*, 34.

(2) Sonogashira K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(2) Angelis, Y. S.; Orfanopoulos, M. *J. Org. Chem.* **1997**, *62*, 6083.

(2) Spectral data for compound 1a-1g, 2a-2f, 3a-3c, 4a-4c, 5a-5h, 6a-6h and 7a.

1-(*o*-ethynylphenyl)-2-methyl-2-phenyl epoxides (1a). IR (nujol, cm^{-1}): 3330(s), 3100(s), 3065(s), 2258(m), 2119(s), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): (*E/Z* = 1.3), (major-*E*-isomer) δ 7.53 ~ 7.44 (m, 3 H), 7.41 (dt, *J* = 8.0, 1.0 Hz, 3 H),

7.38 (dt, $J = 7.5, 1.0$ Hz, 2 H), 7.25 (d, $J = 7.5$ Hz, 1 H), 4.20 (s, 1 H), 3.25 (s, 1 H), 1.41 (s, 3 H); (selected peaks, minor-*Z*-isomer) δ 7.43 (dt, $J = 7.5, 1.0$ Hz, 3 H), 7.18 (dt, $J = 7.5, 1.0$ Hz, 2 H), 7.13 (dt, $J = 8.0, 1.0$ Hz, 2 H), 4.45 (s, 1 H), 3.42 (s, 1 H), 1.85 (s, 3 H), the remaining peaks are overlapped with those of major isomer; ^{13}C NMR (100 MHz, CDCl_3): (major-*E*-isomer) δ 142.5, 139.5, 132.2, 128.6, 128.4, 127.8, 127.6, 126.7, 125.6, 121.5, 82.4, 81.8, 64.9, 64.0, 17.9; Mass (75 eV, m/z): 234 (M^+); HRMS calcd. for $\text{C}_{17}\text{H}_{14}\text{O}$: 234.1045, Found: 234.1042.

2-Ethyl-3-(2-ethynyl-phenyl)-2-phenyl-oxirane (1b). IR (nujol, cm^{-1}): 3330(s), 3100(s), 3065(s), 2258(m), 2119(s), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): (*E/Z* = 2.5), (major-*E*-isomer) δ 7.57 ~ 7.52 (m, 3 H), 7.39 (dt, $J = 8.0, 1.0$ Hz, 3 H), 7.18 (t, $J = 7.5$ Hz, 2 H), 7.10 (d, $J = 7.5$ Hz, 1 H), 4.24 (s, 1 H), 3.33 (s, 1 H), 1.99 ~ 1.82 (m, 1 H), 1.43 ~ 1.37 (m, 1 H), 0.80 (t, $J = 7.5$ Hz, 3 H); (selected peaks, minor-*Z*-isomer) δ 7.45 (dt, $J = 7.5, 1.0$ Hz, 3 H), 7.31 (t, $J = 7.5$ Hz, 2 H), 7.01 (d, $J = 7.5$ Hz, 2 H), 4.47 (s, 1 H), 3.42 (s, 1 H), 2.21 ~ 2.17 (m, 1 H), 2.10 ~ 1.98 (m, 1 H), 1.02 (t, $J = 7.5$ Hz, 3 H), the remaining peaks are overlapped with those of major isomer; ^{13}C NMR (100 MHz, CDCl_3): (major-*E*-isomer) δ 141.5, 139.3, 132.5, 128.6, 128.4, 127.9, 127.7, 127.4, 126.4, 121.5, 82.5, 81.0, 65.6, 64.6, 24.5, 9.31; Mass (75 eV, m/z): 248 (M^+); HRMS calcd. for $\text{C}_{18}\text{H}_{16}\text{O}$: 248.1201, Found: 248.1206.

3-(2-Ethynyl-phenyl)-2-methyl-2-p-tolyl-oxirane (1c). IR (nujol, cm^{-1}): 3330(s), 3100(s), 3065(s), 2258(m), 2119(s), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 2.6$), (major-*E*-isomer) δ 7.44 ~ 7.38 (m, 3 H), 7.34 ~ 7.25 (m, 2 H), 7.19 (d, $J = 7.5$ Hz, 2 H), 7.11 (d, $J = 7.5$ Hz, 1 H), 4.18 (s, 1 H), 3.23 (s, 1 H), 2.37 (s, 3 H), 1.38 (s, 3 H); (selected peaks, minor-*Z*-isomer) δ 7.51 (d, $J = 8.0$ Hz, 1 H), 7.08 ~ 7.03 (m, 2 H), 6.93 (d, $J = 7.5$ Hz, 1 H), 4.41 (s, 1 H), 3.40 (s, 1 H), 2.19 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): (major-*E*-isomer) δ 139.4, 137.1, 132.2, 129.0, 128.7, 128.3, 127.3, 126.3, 125.3, 120.5, 82.1, 81.1, 65.6, 63.7, 21.1, 17.7; Mass (75 eV, m/z): 248 (M^+); HRMS calcd. for $\text{C}_{18}\text{H}_{16}\text{O}$: 248.1201, Found: 248.1206.

3-(2-Ethynyl-phenyl)-2-(4-fluoro-phenyl)-2-methyl-oxirane (1d). IR (nujol, cm^{-1}): 3330(s), 3100(s), 3065(s), 2258(m), 2119(s), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 1.8$), (major-*E*-isomer) δ 7.53 ~ 7.46 (m, 3 H), 7.42 ~ 7.39 (m, 2 H), 7.32 ~ 7.25 (m, 1 H), 7.06 (t, $J = 7.5$ Hz, 2 H), 4.15 (s, 1 H), 3.24 (s, 1 H), 1.37 (s, 3 H);

(selected peaks, minor-*Z*-isomer) δ 7.31 (d, $J = 8.0$ Hz, 1 H), 7.17 (dt, $J = 7.5, 1.0$ Hz, 2 H), 7.09 ~ 7.02 (m, 2 H), 6.97 (d, $J = 7.5$ Hz, 1 H), 6.78 (t, $J = 8.0$ Hz, 2 H), 4.39 (s, 1 H), 3.39 (s, 1 H), 1.80 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): (major-*E*-isomer) δ 162.1 (d, $J_{\text{CF}} = 244.3$ Hz), 139.0, 138.1, 132.3, 128.8, 127.3 (d, $J_{\text{CF}} = 29.0$ Hz), 127.0, 126.3, 120.5, 115.1 (d, $J_{\text{CF}} = 21.4$ Hz), 82.1, 81.8, 65.6, 63.2, 17.7; Mass (75 eV, m/z): 252 (M^+); HRMS calcd. for $\text{C}_{17}\text{H}_{13}\text{FO}$: 252.0950, Found: 252.0955.

3-(2-Ethynyl-4-fluorophenyl)-2-methyl-2-phenyloxirane (1e). IR (nujol, cm^{-1}): 3250(s), 3100(s), 3050(s), 2250(m), 2100(s), 1625(w), 1250(m); ^1H NMR (600 MHz, CDCl_3): (*E*-form only) δ 7.20 ~ 7.18 (m, 2 H), 7.14 ~ 7.11 (m, 2 H), 7.09 ~ 7.06 (m, 1 H), 7.00 (dd, $J = 8.8, 2.6$ Hz, 1 H), 6.94 (dd, $J = 8.6, 5.7$ Hz, 1 H), 6.74 (dt, $J = 8.8, 2.6$ Hz, 1 H), 4.36 (s, 1 H), 3.43 (s, 1 H), 1.81 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): (*E*-form only) δ 161.0 (d, $J_{\text{CF}} = 244.9$ Hz), 138.0, 134.5, 127.8, 127.7, 127.1, 126.5, 121.6 (d, $J_{\text{CF}} = 9.7$ Hz), 118.5 (d, $J_{\text{CF}} = 23.4$ Hz), 115.6 (d, $J_{\text{CF}} = 21.3$ Hz), 82.8, 80.1, 65.8, 64.1, 25.1; Mass (75 eV, m/z): 252 (M^+); HRMS calcd. for $\text{C}_{17}\text{H}_{13}\text{FO}$: 252.0950, Found: 252.0958.

3-(2-Ethynyl-4-fluorophenyl)-2-methyl-2-p-tolyloxirane (1f). IR (nujol, cm^{-1}): 3250(s), 3100(s), 3050(s), 2250(m), 2100(s), 1625(w), 1250(m); ^1H NMR (600 MHz,

CDCl₃): (*E*-form only) δ 7.38 ~ 7.34 (m, 3 H), 7.21 (dd, J = 9.0, 2.6 Hz, 1 H), 7.18 ~ 7.16 (m, 2 H), 7.11 (dt, J = 8.5, 2.6 Hz, 1 H), 4.07 (s, 1 H), 3.33 (s, 1 H), 2.33 (s, 3 H), 1.33 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): (*E*-form only) δ 162.2 (d, J_{CF} = 244.6 Hz), 139.8, 138.0, 136.2, 129.7, 129.0, 125.9, 122.8, 119.6 (d, J_{CF} = 23.4 Hz), 116.8 (d, J_{CF} = 21.4 Hz), 83.8, 80.5, 65.8, 64.2, 21.5, 18.0; Mass (75 eV, m/z): 266 (M^+); HRMS calcd. for C₁₈H₁₅FO: 266.1107, Found: 266.1110.

3-(2-Ethynyl-5-fluoro-phenyl)-2-methyl-2-phenyl-oxirane (1g). IR (nujol, cm⁻¹): 3250(s), 3100(s), 3050(s), 2250(m), 2100(s), 1625(w), 1250(m); ¹H NMR (600 MHz, CDCl₃): (*E*-form only) δ 7.50 ~ 7.48 (m, 3 H), 7.37 (t, J = 7.4 Hz, 2 H), 7.31 ~ 7.28 (m, 1 H), 7.14 (dd, J = 9.3, 2.6 Hz, 1 H), 6.97 (dt, J = 8.3, 2.7 Hz, 1 H), 4.14 (s, 1 H), 3.19 (s, 1 H), 1.39 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): (*E*-form only) δ 162.7 (d, J_{CF} = 249.6 Hz), 142.2, 141.8, 134.2 (d, J_{CF} = 8.1 Hz), 128.3, 127.5, 125.3, 116.5, 114.7 (d, J_{CF} = 22.5 Hz), 113.9 (d, J_{CF} = 23.7 Hz), 81.9, 80.1, 65.0, 64.0, 17.6; Mass (75 eV, m/z): 252 (M^+); HRMS calcd. for C₁₇H₁₃FO: 252.0950, Found: 252.0956.

2-Methyl-1-phenyl-1H-indene (2a). IR (nujol, cm⁻¹): 3030(s), 3008(s), 3065(s), 2258(m), 1625(m), 1685(s); ¹H NMR (500 MHz, CDCl₃): δ 7.27 ~ 7.25 (m, 3 H), 7.20

(dt, $J = 7.5, 1.5$ Hz, 2 H), 7.10 (d, $J = 8.0$ Hz, 1 H), 7.04 (d, $J = 7.5$ Hz, 1 H), 7.01 (d, $J = 7.5$ Hz, 2 H), 6.53 (s, 1 H), 4.28 (s, 1 H), 1.91 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ 149.9, 148.5, 144.7, 139.7, 128.6, 128.1, 127.1, 127.0, 126.6, 124.1, 123.7, 119.7, 59.3, 15.1; HRMS calcd. for $\text{C}_{16}\text{H}_{14}$: 206.1096, Found: 206.1098.

2-Ethyl-1-phenyl-1H-indene (2b). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 2258(m), 1625(m), 1685(s); ^1H NMR (500 MHz, CDCl_3): δ 7.27 (t, $J = 7.0$ Hz, 2 H), 7.25 (d, $J = 8.0$ Hz, 2 H), 7.20 (t, $J = 7.5$ Hz, 1 H), 7.10 (t, $J = 7.5$ Hz, 1 H), 7.04 (d, $J = 7.5$ Hz, 1 H), 7.01 (d, $J = 7.5$ Hz, 2 H), 6.55 (s, 1 H), 4.37 (s, 1 H), 2.25 ~ 2.20 (m, 2 H), 1.13 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ 156.3, 148.5, 144.6, 139.9, 128.6, 128.2, 126.7, 126.6, 125.1, 124.2, 123.7, 119.9, 58.1, 22.4, 12.8; HRMS calcd. for $\text{C}_{17}\text{H}_{16}$: 220.1252, Found: 220.1256.

2-Methyl-1-p-tolyl-1H-indene (2c). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 2258(m), 1625(m), 1685(s); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.28 ~ 7.21 (m, 2 H), 7.17 (t, $J = 7.5$ Hz, 2 H), 7.06 (t, $J = 7.5$ Hz, 2 H), 6.88 (d, $J = 7.5$ Hz, 2 H), 6.53 (s, 1 H), 4.27 (s, 1 H), 2.29 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 150.5, 149.2,

145.1, 136.9, 136.7, 129.7, 128.2, 127.3, 126.9, 124.4, 123.8, 120.1, 59.3, 21.1, 15.2;
HRMS calcd. for C₁₇H₁₆: 220.1252, Found: 220.1256.

1-(4-Fluoro-phenyl)-2-methyl-1H-indene (2d). IR (nujol, cm⁻¹): 3030(s), 3008(s), 3065(s), 2258(m), 1625(m), 1685(s); ¹H NMR (500 MHz, CDCl₃): δ 7.44 (t, *J* = 7.0 Hz, 2 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.12 (d, *J* = 7.5 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 2 H), 6.93 (d, *J* = 7.5 Hz, 2 H), 6.52 (s, 1 H), 4.26 (s, 1 H), 1.89 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 161.7 (d, *J*_{CF} = 242.8 Hz), 149.6, 148.4, 144.6, 135.3, 129.6 (d, *J*_{CF} = 7.7 Hz), 127.2, 126.8, 124.2, 123.6, 119.9, 115.5 (d, *J*_{CF} = 21.0 Hz), 58.5, 15.0; HRMS calcd. for C₁₆H₁₃F: 224.1001, Found: 224.1005.

5-Fluoro-2-methyl-1-phenyl-1H-indene (2e). IR (nujol, cm⁻¹): 3030(s), 3005(s), 3060(s), 2255(m), 1625(m), 1685(s); ¹H NMR (400 MHz, CDCl₃): δ 7.28 ~ 7.25 (m, 4 H), 7.04 ~ 6.97 (m, 3 H), 6.71 (dt, *J* = 8.8, 2.4 Hz, 1 H), 6.48 (s, 1 H), 4.24 (s, 1 H), 1.90 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 162.5 (d, *J*_{CF} = 240.5 Hz), 152.4, 146.5, 143.8, 139.3, 128.6, 128.0, 126.8, 126.5, 124.3 (d, *J*_{CF} = 9.1 Hz), 110.5 (d, *J*_{CF} = 22.6

Hz), 107.0 (d, $J_{\text{CF}} = 23.1$ Hz), 58.7, 15.3; HRMS calcd. for $\text{C}_{16}\text{H}_{13}\text{F}$: 224.1001, Found: 224.1005.

irradiation	intensity increase
H^1 (δ 4.24)	Me (δ 1.90, 1.5 %), H^4 (δ 7.25, 7.5 %) $\text{H}^{2'}$ (δ 7.01, 1.5 %)
H^3 (δ 6.48)	H^7 (δ 7.27, 2.0 %), Me (2.3 %)
Me (δ 1.90)	H^1 (δ 4.24, 3.4 %), H^3 (5.3 %)

5-Fluoro-2-methyl-1-p-tolyl-1H-indene (2f). IR (nujol, cm^{-1}): 3030(s), 3005(s), 3060(s), 2255(m), 1625(m), 1685(s); ^1H NMR (400 MHz, CDCl_3): δ 7.06 (d, $J = 8.2$ Hz, 2 H), 6.92 (dd, $J = 8.1, 5.1$ Hz, 1 H), 6.92 (dd, $J = 9.0, 2.4$ Hz, 1 H), 6.87 (d, $J = 5.8$ Hz, 2 H), 6.69 (dt, $J = 9.0, 2.4$ Hz, 1 H), 6.46 (s, 1 H), 4.20 (s, 1 H), 2.29 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 162.4 (d, $J_{\text{CF}} = 240.0$ Hz), 152.5, 146.5, 144.0, 136.4, 136.1, 129.4, 127.9, 126.4, 124.2 (d, $J_{\text{CF}} = 9.0$ Hz), 110.5 (d, $J_{\text{CF}} = 22.5$ Hz), 106.9 (d, $J_{\text{CF}} = 23.1$ Hz), 58.3, 21.0, 15.3; HRMS calcd. for $\text{C}_{17}\text{H}_{15}\text{F}$: 238.1158, Found: 238.1160.

2-(2-Ethynyl-hex-1-enyl)-3-isopropyl-oxirane (3a). IR (nujol, cm^{-1}): 2256(m), 1620(w), 1225(m); ^1H NMR (400 MHz, CDCl_3): (*trans/cis* = 1.1), (major-*trans*-isomer) δ 5.36 (d, J = 8.7 Hz, 1 H), 3.17 (s, 1 H), 2.77 (dd, J = 8.6, 4.3 Hz, 1 H), 2.63 (dd, J = 6.8, 1.2 Hz, 1 H), 2.13 (t, J = 7.6 Hz, 2 H), 1.60 ~ 1.54 (m, 1 H), 1.52 ~ 1.44 (m, 2 H), 1.32 ~ 1.25 (m, 2 H), 0.96 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H), 0.86 (t, J = 6.5 Hz, 3 H); (minor-*cis*-isomer) δ 5.54 (d, J = 8.7 Hz, 1 H), 3.89 (dd, J = 8.7, 4.3 Hz, 1 H), 3.63 (dd, J = 8.7, 1.4 Hz, 1 H), 3.17 (s, 1 H), 2.16 (t, J = 7.4 Hz, 2 H), 1.60 ~ 1.54 (m, 1 H), 1.52 ~ 1.44 (m, 2 H), 1.32 ~ 1.25 (m, 2 H), 1.09 (d, J = 6.7 Hz, 3 H), 1.00 (d, J = 6.7 Hz, 3 H), 0.86 (t, J = 6.5 Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*trans*-isomer) δ 135.6, 128.8, 82.9, 81.2, 65.4, 55.5, 36.9, 36.6, 30.5, 30.0, 21.9, 20.2, 18.3; (minor-*cis*-isomer) δ 132.6, 127.6, 82.5, 81.1, 64.8, 55.4, 36.9, 36.6, 30.0, 28.1, 21.8, 18.9, 13.8; Mass (75 eV, m/z): 192 (M^+); HRMS calcd. for $\text{C}_{13}\text{H}_{20}\text{O}$: 192.1514, Found: 192.1520.

2-Butyl-3-(2-ethynyl-oct-1-enyl)-oxirane (3b). IR (nujol, cm^{-1}): 2256(m), 1620(w), 1225(m); ^1H NMR (400 MHz, CDCl_3): (*trans/cis* = 1.1), (major-*trans*-isomer) δ 5.35 (d, J = 2.2 Hz, 1 H), 3.59 (dd, J = 8.8, 2.2 Hz, 1 H), 3.16 (s, 1 H), 2.83 (dt, J = 5.6, 2.2 Hz, 1 H), 2.18 ~ 2.10 (m, 2 H), 1.60 ~ 1.54 (m, 4 H), 1.35 ~ 1.20 (m, 10 H), 0.90 ~ 0.81 (m, 6 H); (minor-*cis*-isomer) δ 5.53 (d, J = 4.3 Hz, 1 H), 3.87 (dd, J = 8.8, 4.3 Hz, 1 H), 3.18 (s, 1 H), 3.10 (dt, J = 5.6, 4.3 Hz, 1 H), 2.18 ~ 2.10 (m, 2 H), 1.60 ~ 1.54 (m, 4 H), 1.35 ~ 1.20 (m, 10 H), 0.90 ~ 0.81 (m, 6 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*trans*-isomer) δ 135.5, 127.9, 82.5, 81.2, 60.2, 56.5, 37.0, 31.9, 31.5, 28.5, 27.8, 26.0, 25.5, 22.5, 14.0, 13.9; Mass (75 eV, m/z): 234 (M^+); HRMS calcd. for $\text{C}_{16}\text{H}_{26}\text{O}$:

234.1984, Found: 234.1987.

2-(2-Ethynyl-oct-1-enyl)-3-phenyl-oxirane (3c). IR (nujol, cm^{-1}): 3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (500 MHz, CDCl_3): (*trans/cis* = 1.1) (major-*trans*-isomer) δ 7.41 ~ 7.25 (m, 5 H), 5.26 (d, J = 9.0 Hz, 1 H), 3.87 (dd, J = 9.0, 2.0 Hz, 1 H), 3.80 (d, J = 2.0 Hz, 1 H), 3.14 (s, 1 H), 2.02 (t, J = 7.0 Hz, 2 H), 1.56 ~ 1.50 (m, 2 H), 1.42 ~ 1.26 (m, 6 H), 0.82 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): (major-*trans*-isomer) δ 136.9, 134.5, 130.2, 128.4, 128.2, 126.3, 82.8, 80.9, 59.1, 57.3, 37.1, 31.5, 28.5, 27.8, 22.5, 14.0; Mass (75 eV, m/z): 254 (M^+); HRMS Calcd For $\text{C}_{18}\text{H}_{22}\text{O}$: 254.1671; Found: 254.1676.

5-butyl-2-isopropyl-phenol. (4a). IR (nujol, cm^{-1}): 3610(s), 1580(m), 1625(w), 1225(m); ^1H NMR (400 MHz, CDCl_3) δ 7.08 (d, J = 8.0 Hz, 1 H), 6.73 (d, J = 8.0 Hz, 1 H), 6.57 (s, 1 H), 4.84 (bs, OH), 3.19 ~ 3.12 (m, 1 H), 2.51 (t, J = 7.6 Hz, 2 H), 1.58 ~ 1.53 (m, 2 H), 1.37 ~ 1.32 (m, 2 H), 1.24 (s, 3 H), 1.23 (s, 3 H), 0.91 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 152.5, 141.6, 131.4, 126.1, 120.9, 115.2, 35.0, 33.4, 26.7, 22.7, 22.6, 22.3, 13.9; HRMS for $\text{C}_{13}\text{H}_{20}\text{O}$: Calcd 192.1514; Found 192.1518.

2-butyl-5-hexylphenol (4b). IR (nujol, cm^{-1}): 3610(s), 1580(m), 1625(w), 1225(m); ^1H NMR (600 MHz, CDCl_3) δ 6.99 (d, $J = 7.6$ Hz, 1 H), 6.67 (d, $J = 7.6$ Hz, 1 H), 6.57 (s, 1 H), 4.66 (bs, OH), 2.54 (t, $J = 7.7$ Hz, 2 H), 2.50 (t, $J = 7.7$ Hz, 2 H), 1.58 ~ 1.56 (m, 4 H), 1.35 ~ 1.22 (m, 8 H), 0.89 ~ 0.83 (m, 6 H); ^{13}C NMR (150 MHz, CDCl_3): δ 153.1, 142.1, 129.8, 125.5, 120.7, 115.1, 35.4, 31.7, 31.5, 31.3, 29.6, 29.5, 29.0, 22.5, 14.0, 14.0; HRMS for $\text{C}_{16}\text{H}_{26}\text{O}$: Calcd 234.1984; Found 234.1988.

4-Hexyl-biphenyl-2-ol (4c). IR (nujol, cm^{-1}): 3610(s), 1580(m), 1625(w), 1225(m); ^1H NMR (600 MHz, CDCl_3) δ 7.48 ~ 7.43 (m, 4 H), 7.37 ~ 7.34 (m, 1 H), 7.13 (d, $J = 8.0$ Hz, 1 H), 6.81 ~ 6.78 (m, 2 H), 5.14 (bs, OH), 2.58 (t, $J = 7.7$ Hz, 2 H), 1.63 ~ 1.59 (m, 2 H), 1.36 ~ 1.28 (m, 6 H), 0.87 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 152.1, 144.5, 137.1, 129.9, 129.2, 129.0, 127.6, 125.3, 121.0, 115.6, 36.6, 31.7, 31.2, 29.0, 22.6, 14.1; HRMS for $\text{C}_{18}\text{H}_{22}\text{O}$: Calcd 254.1671; Found 254.1675.

2-Methyl-3-(2-phenyl-but-1-en-3-ynyl)-2-propyl-oxirane (5a): IR (nujol, cm^{-1}):

3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 0.9$), (major-*Z*-isomer) δ 7.62 ~ 7.58 (m, 2 H), 7.38 ~ 7.30 (m, 3 H), δ 6.27 (d, $J = 8.0$ Hz, 1 H), 3.87 (d, $J = 8.0$ Hz, 1 H), 3.43 (s, 1 H), 1.72 ~ 1.60 (m, 1 H), 1.52 ~ 1.45 (m, 3 H), 1.40 (s, 3 H), 0.97 ~ 0.91 (m, 3 H); (minor-*E*-isomer) δ 7.62 ~ 7.58 (m, 2 H), 7.38 ~ 7.30 (m, 3 H), δ 6.27 (d, $J = 8.0$ Hz, 1 H), 3.89 (d, $J = 8.0$ Hz, 1 H), 3.42 (s, 1 H), 1.72 ~ 1.60 (m, 1 H), 1.52 ~ 1.45 (m, 3 H), 1.33 (s, 3 H), 0.87 ~ 0.84 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*Z*-isomer) δ 136.6, 134.3, 134.1, 128.6, 126.9, 125.9, 84.7, 79.8, 64.0, 62.6, 35.9, 22.1, 18.8, 14.2; Mass (75 eV, m/z): 226 (M^+); HRMS Calcd For $\text{C}_{16}\text{H}_{18}\text{O}$: 226.1358; Found: 226.1360.

2-Methyl-2-pentyl-3-(2-phenylbut-1-en-3-ynyl)-oxirane (5b): IR (nujol, cm^{-1}): 3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 0.9$), (major-*Z*-isomer) δ 7.63 ~ 7.60 (m, 2 H), 7.38 ~ 7.32 (m, 3 H), 6.28 (d, $J = 8.8$ Hz, 1 H), 3.90 (d, $J = 8.8$ Hz, 1 H), 3.44 (s, 1 H), 1.65 ~ 1.32 (m, 4 H), 1.27 (s, 3 H), 1.26 ~ 1.20 (m, 4 H), 0.90 ~ 0.84 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*Z*-isomer) δ 136.7, 134.4, 134.2, 128.4, 127.0, 125.9, 84.7, 79.9, 63.9, 61.7, 38.5, 33.8, 31.7, 25.1, 22.1, 13.9; Mass (75 eV, m/z): 254 (M^+); HRMS Calcd For $\text{C}_{18}\text{H}_{22}\text{O}$: 254.1671; Found: 254.1675.

3-(2-Ethynyl-oct-1-enyl)-2,2-dimethyl-oxirane (5c). IR (nujol, cm^{-1}): 2256(m), 1620(w), 1225(m); ^1H NMR (400 MHz, CDCl_3): δ 5.54 (d, $J = 8.8$ Hz, 1 H), 3.67 (d, $J = 8.8$ Hz, 1 H), 3.18 (s, 1 H), 2.14 (t, $J = 6.9$ Hz, 2 H), 1.55 ~ 1.41 (m, 2 H), 1.35 ~ 1.26 (m, 8 H), 0.87 ~ 0.83 (m, 7 H); ^{13}C NMR (150 MHz, CDCl_3): δ 133.6, 128.6, 82.8, 81.3, 61.9, 60.6, 37.2, 31.5, 28.5, 27.9, 24.7, 22.6, 19.4, 14.1; Mass (75 eV, m/z): 206 (M^+); HRMS calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$: 206.1671, Found: 206.1676.

2-Ethyl-3-(2-ethynyl-oct-1-enyl)-2-methyl-oxirane (5d). IR (nujol, cm^{-1}): 2256(m), 1620(w), 1225(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 1.2$), (major-*E*-isomer) δ 5.56 (d, $J = 8.8$ Hz, 1 H), 3.66 (d, $J = 8.8$ Hz, 1 H), 3.18 (s, 1 H), 2.15 (t, $J = 8.0$ Hz, 2 H), 1.67 ~ 1.59 (m, 2 H), 1.53 ~ 1.43 (m, 4 H), 1.29 ~ 1.25 (m, 4 H), 1.24 (s, 3 H), 0.95 (t, $J = 8.0$ Hz, 3 H), 0.85 (t, $J = 6.0$ Hz, 3 H); (selected peaks, minor-*Z*-isomer) δ 5.56 (d, $J = 8.8$ Hz, 1 H), 3.66 (d, $J = 8.8$ Hz, 1 H), 3.17 (s, 1 H), 2.15 (t, $J = 8.0$ Hz, 2 H), 1.67 ~ 1.59 (m, 2 H), 1.53 ~ 1.43 (m, 4 H), 1.32 (s, 3 H), the rest peaks are overlapped with those of the major isomer; ^{13}C NMR (150 MHz, CDCl_3): (major-*E*-isomer) δ 133.7, 128.4, 82.9, 81.3, 64.0, 62.1, 37.2, 31.5, 28.5, 27.9, 26.7, 22.5, 21.4, 14.0, 9.6; Mass (75 eV, m/z): 220 (M^+); HRMS Calcd For $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827; Found: 220.1832.

2,2-Dimethyl-3-(2-phenyl-but-1-en-3-ynyl)-oxirane (5e): IR (nujol, cm^{-1}): 3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): δ 7.61 ~ 7.58 (m, 2 H), 7.36 ~ 7.29 (m, 3 H), 6.24 (d, $J = 8.8$ Hz, 1 H), 3.89 (d, $J = 8.8$ Hz, 1 H), 3.42 (s, 1 H), 1.43 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 136.6, 134.1, 128.4, 127.2, 125.9, 125.2, 84.6, 79.8, 62.4, 61.3, 24.8, 19.6; Mass (75 eV, m/z): 198 (M^+); HRMS Calcd For $\text{C}_{14}\text{H}_{14}\text{O}$: 198.1045; Found: 198.1050.

2-Ethyl-2-methyl-3-(2-phenyl-but-1-en-3-ynyl)-oxirane (5f): IR (nujol, cm^{-1}): 3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): ($E/Z = 0.6$), (major-*Z*-isomer) δ 7.62 ~ 7.58 (m, 2 H), 7.38 ~ 7.30 (m, 3 H), 6.27 (d, $J = 8.4$ Hz, 1 H), 3.89 (d, $J = 8.4$ Hz, 1 H), 3.44 (s, 1 H), 1.78 ~ 1.62 (m, 1 H), 1.61 ~ 1.54 (m, 1 H), 1.41 (s, 3 H), 1.03 ~ 0.99 (m, 3 H), (minor-*E*-isomer) δ 7.62 ~ 7.58 (m, 2 H), 7.38 ~ 7.30 (m, 3 H), 6.27 (d, $J = 8.4$ Hz, 1 H), 3.89 (d, $J = 8.4$ Hz, 1 H), 3.43 (s, 1 H), 1.78 ~ 1.62 (m, 1 H), 1.61 ~ 1.54 (m, 1 H), 1.33 (s, 3 H), 1.03 ~ 0.99 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*Z*-isomer) δ 136.6, 134.3, 134.0, 128.4, 127.0, 125.9, 84.7, 79.8, 64.8, 62.6, 26.9, 21.5, 9.7; Mass (75 eV, m/z): 212 (M^+); HRMS Calcd For $\text{C}_{15}\text{H}_{16}\text{O}$: 212.1201; Found: 212.1205.

3-(2-Ethynyl-cyclohex-1-enyl)-2,2-dimethyl-oxirane (5g). IR (nujol, cm^{-1}): 2256(m), 1620(w), 1225(m); ^1H NMR (400 MHz, CDCl_3): δ 3.51 (s, 1 H), 3.11 (s, 1 H), 2.42 ~ 2.27 (m, 2 H), 2.16 ~ 2.15 (m, 2 H), 1.58 ~ 1.55 (m, 2 H), 1.36 (s, 3 H), 1.24 ~ 1.22 (m, 2 H), 1.16 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 143.2, 116.2, 83.3, 80.4, 64.9, 59.7, 29.3, 26.3, 24.4, 22.1, 21.5, 19.2; Mass (75 eV, m/z): 176 (M^+); HRMS calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201, Found: 176.1206.

3-(2-Ethynyl-oct-1-enyl)-2-methyl-2-phenyl-oxirane (5h): IR (nujol, cm^{-1}): 3310(s), 3100(s), 3065(s), 2182(m), 1625(w), 1250(m); ^1H NMR (400 MHz, CDCl_3): (*E/Z* = 0.6), (major-*Z*-isomer) δ 7.40 ~ 7.33 (m, 3 H), 7.29 ~ 7.25 (m, 2 H), 5.70 (d, J = 8.4 Hz, 1 H), 3.79 (d, J = 8.4 Hz, 1 H), 3.14 (s, 1 H), 2.20 (t, J = 7.6 Hz, 2 H), 1.66 (s, 3 H), 1.52 ~ 1.45 (m, 2 H), 1.23 ~ 1.15 (m, 6 H), 0.88 ~ 0.81 (m, 3 H), (minor-*E*-isomer) δ 7.40 ~ 7.33 (m, 2 H), 7.29 ~ 7.25 (m, 2 H), 4.99 (d, J = 9.2 Hz, 1 H), 4.02 (d, J = 9.2 Hz, 1 H), 3.22 (s, 1 H), 1.99 (t, J = 6.8 Hz, 2 H), 1.69 (s, 3 H), 1.52 ~ 1.45 (m, 2 H), 1.23 ~ 1.15 (m, 6 H), 0.88 ~ 0.81 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3): (major-*Z*-isomer) δ 142.4, 132.8, 129.3, 128.3, 126.5, 125.1, 83.2, 81.1, 64.2, 62.6, 37.3, 31.5, 28.5, 27.9, 24.7, 22.5, 18.5; Mass (75 eV, m/z): 268 (M^+); HRMS Calcd For $\text{C}_{19}\text{H}_{24}\text{O}$: 268.1827;

Found: 268.1830.

6-Methyl-3-phenyl-6-propyl-cyclohexa-2,4-dienone (6a). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 1705(s), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 7.62 ~ 7.54 (m, 2 H), 7.52 ~ 7.39 (m, 3 H), 6.64 (d, $J = 9.7$ Hz, 1 H), 6.41 (d, $J = 9.6$ Hz, 1 H), 6.29 (s, 1 H), 1.99 ~ 1.94 (m, 1 H), 1.48 ~ 1.40 (m, 1 H), 1.21 (s, 3 H), 1.20 ~ 1.01 (m, 2 H), 0.80 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.7, 152.6, 148.3, 137.8, 129.9, 128.8, 126.6, 121.7, 121.7, 50.6, 43.3, 25.4, 18.4, 14.4; HRMS calcd. for $\text{C}_{16}\text{H}_{18}\text{O}$: 226.1358, Found: 226.1362.

irradiation	intensity increase
H^1 (δ 6.64)	H^2 (δ 6.41, 8.0 %), H^3 (δ 7.54, 7.5 %)
H^2 (δ 6.48)	H^1 (δ 6.64, 10.0 %), H^4 (δ 1.46, 3.3 %)

6-Methyl-6-pentyl-3-phenyl-cyclohexa-2,4-dienone (6b). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 1705(s), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 7.60 ~ 7.51 (m, 2 H), 7.50 ~ 7.35 (m, 3 H), 6.63 (d, $J = 9.7$ Hz, 1 H), 6.40 (d, $J = 9.7$ Hz, 1 H), 6.29 (s, 1 H), 1.99 ~ 1.92 (m, 1 H), 1.50 ~ 1.40 (m, 1 H), 1.20 (s, 3 H), 1.20 ~ 0.98 (m, 6 H), 0.79

(t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.7, 152.5, 148.3, 137.8, 129.9, 128.8, 126.6, 121.7, 121.7, 50.5, 41.0, 32.1, 25.4, 24.7, 22.3, 13.9; HRMS calcd. for $\text{C}_{18}\text{H}_{22}\text{O}$: 254.1671, Found: 254.1675.

3-Hexyl-6,6-dimethyl-cyclohexa-2,4-dienone (6c). IR (nujol, cm^{-1}): 1705(s), 1650(m), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 6.24 (d, $J = 9.6$ Hz, 1 H), 6.03 (d, $J = 9.6$ Hz, 1 H), 5.84 (s, 1 H), 2.28 (t, $J = 7.2$ Hz, 2 H), 1.68 ~ 1.49 (m, 2 H), 1.32 ~ 1.27 (m, 6 H), 1.16 (s, 6 H), 0.85 (t, $J = 6.4$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.7, 157.8, 148.0, 122.1, 122.0, 46.0, 36.4, 31.5, 28.8, 27.5, 25.4, 25.4, 22.4, 14.0; HRMS calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$: 206.1671, Found: 206.1676.

6-Ethyl-3-hexyl-6-methyl-cyclohexa-2,4-dienone (6d). IR (nujol, cm^{-1}): 1705(s), 1650(m), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 6.19 (d, $J = 9.6$ Hz, 1 H), 6.12 (d, $J = 9.6$ Hz, 1 H), 5.82 (s, 1 H), 2.26 (t, $J = 7.2$ Hz, 2 H), 1.90 ~ 1.87 (m, 1 H), 1.51 ~ 1.47 (m, 2 H), 1.43 ~ 1.37 (m, 1 H), 1.29 ~ 1.20 (m, 6 H), 1.10 (s, 3 H), 0.83 (t, $J = 6.8$ Hz, 3 H), 0.62 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.7, 158.0, 147.0, 123.9, 123.9, 50.7, 36.3, 33.7, 31.4, 28.6, 27.4, 24.9, 22.4, 13.9, 9.2; HRMS calcd. for $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827, Found: 220.1831.

6,6-Dimethyl-3-phenyl-cyclohexa-2,4-dienone (6e). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 1705(s), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 7.57 ~ 7.55 (m, 2 H), 7.43 ~ 7.41 (m, 3 H), 6.56 (d, $J = 9.6$ Hz, 1 H), 6.42 (d, $J = 9.6$ Hz, 1 H), 6.29 (s, 1 H), 1.25 (s, 6 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.6, 152.5, 149.0, 137.8, 129.9, 128.8, 126.6, 121.1, 120.3, 46.1, 25.6, 25.6; HRMS calcd. for $\text{C}_{14}\text{H}_{14}\text{O}$: 198.1045, Found: 198.1049.

6-Ethyl-6-methyl-3-phenyl-cyclohexa-2,4-dienone (6f). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 1705(s), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 7.65 ~ 7.53 (m, 2 H), 7.53 ~ 7.19 (m, 3 H), 6.66 (d, $J = 9.7$ Hz, 1 H), 6.38 (d, $J = 9.7$ Hz, 1 H), 6.29 (s, 1 H), 2.12 ~ 1.99 (m, 1 H), 1.52 ~ 1.49 (m, 1 H), 1.20 (s, 3 H), 0.70 (d, $J = 7.4$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.7, 152.6, 147.9, 137.7, 129.8, 128.8, 126.6, 122.1, 121.8, 50.9, 33.8, 24.9, 9.3; HRMS calcd. for $\text{C}_{15}\text{H}_{16}\text{O}$: 212.1201, Found: 212.1205.

3,3-Dimethyl-5,6,7,8-tetrahydro-3H-naphthalen-2-one (6g). IR (nujol, cm^{-1}): 1705(s), 1650(m), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 5.90 (s, 1 H), 5.80 (s, 1 H), 2.54 ~ 2.51 (m, 2 H), 2.40 ~ 2.37 (m, 2 H), 1.66 ~ 1.63 (m, 4 H), 1.13 (s, 6 H); ^{13}C NMR (150 MHz, CDCl_3): δ 205.9, 156.8, 143.0, 129.1, 122.0, 46.3, 30.6, 28.7, 25.7, 25.7, 22.7, 21.8; HRMS calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201, Found: 176.1204.

3-Hexyl-6-methyl-6-phenyl-cyclohexa-2,4-dienone (6h). IR (nujol, cm^{-1}): 3030(s), 3008(s), 3065(s), 1705(s), 1625(m); ^1H NMR (400 MHz, CDCl_3): δ 7.30 ~ 7.10 (m, 5 H), 6.42 (d, $J = 9.5$ Hz, 1 H), 6.22 (d, $J = 9.5$ Hz, 1 H), 5.84 (s, 1 H), 2.35 (t, $J = 8.0$ Hz, 2 H), 1.59 (s, 3 H), 1.58 ~ 1.54 (m, 2 H), 1.40 ~ 1.28 (m, 6 H), 0.89 ~ 0.84 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3): δ 203.0, 157.9, 146.7, 140.7, 128.6, 127.2, 126.6, 122.7, 121.7, 53.5, 36.4, 31.5, 28.8, 27.4, 23.4, 22.5, 14.0; HRMS calcd. for $\text{C}_{19}\text{H}_{24}\text{O}$: 268.1827, Found: 268.1833.

[2-(2-Methyl-propenyl)-phenyl]-acetic acid isobutyl ester (7a). IR (nujol, cm^{-1}): 1720(s), 1625(m), 1320(s); ^1H NMR (400 MHz, CDCl_3): δ 6.13 (d, $J = 11.2$ Hz, 1 H), 5.97 (d, $J = 11.2$ Hz, 1 H), 4.09 (d, $J = 6.6$ Hz, 2 H), 3.13 (s, 2 H), 2.12 (t, $J = 7.8$ Hz, 2

H), 1.90~1.82 (m, 1 H), 1.77 (s, 3 H), 1.72 (s, 3 H), 1.40~1.32 (m, 2 H), 1.30~1.20 (m, 6 H), 0.92~0.75 (m, 9 H); ^{13}C NMR (125 MHz, CDCl_3): δ 171.7, 134.9, 131.9, 124.0, 120.7, 70.7, 38.2, 36.3, 31.7, 29.0, 27.9, 27.7, 26.3, 22.6, 19.1, 19.0, 18.2, 14.0; HRMS calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_2$: 280.2402, Found: 280.2405.