Supplementary Material (ESI) for Chemical Communications
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New Directions for the Morita-Baylis-Hillman Reaction; Homologous Aldol Adducts via Epoxide Opening

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Experimental Section

All reactions were carried out in oven-dried glassware under a positive pressure of argon. Concentration of solutions was accomplished using a Buchi rotary evaporator with a water aspirator followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise noted, all reagents and solvents were used without additional purification.

Analytical thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} glass plates. Visualization on TLC was achieved by use of UV light (254 nm), and exposure to basic potassium permanganate or acidic anisaldehyde solution, followed by heating. Flash column chromatography was carried out using Merck 60, 230–400 mesh ASTM silica gel. When needed, additional purification was achieved through use of a CombiFlash Graduate Medium Pressure LC unit.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was recorded on a Varian Fourier Transform 500 (500 MHz) spectrometer. Chemical shifts are reported in units, parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d*. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, are reported in Hertz (Hz).

Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on a Varian Fourier Transform 300 (75 MHz) and was fully decoupled by broad-band decoupling. Chemical shifts are reported in ppm with the centerline of the triplet for chloroform-*d* set at 77.0 ppm.

Infrared (IR) spectra were recorded as thin films on sodium chloride plates using a Perkin-Elmer FT-IR Paragon 1000 Fourier Transform spectrometer with frequencies given in reciprocal centimeters (cm^{-1}).

Mass spectra were obtained on a Jeol model JMS600H mass spectrometer (70 eV).

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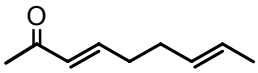
Elemental analyses were performed at Atlantic Microlab Inc. in Norcross, GA.

Compound **7**[1] has been previously reported. All compounds isolated and characterized were colorless oils.

Typical cross-metathesis procedure: To a solution of methyl vinyl ketone (2.8 g, 40 mmol), 1,2-epoxy-5-hexene (3.9 g, 40 mmol) and methylene chloride (120 mL) was added 849 mg of Grubbs 2nd generation catalyst (1 mmol). The reaction mixture was then refluxed under argon for 18 hours. Upon completion of the reaction, the methylene chloride was removed *in vacuo* and the mixture was passed through a short plug of silica gel with 50% ethyl acetate in hexanes. Subsequent column chromatography using 50% ethyl acetate in hexanes provided a brown oil. A distillation under reduced pressure (0.1 mm Hg) at 150^{O}C (bath temperature) afforded 3.25 g (58%) of epoxide **10** as a colorless oil.

Typical epoxidation procedure: To a solution of nona-3,7-dien-2-one (2.7 g, 19.5 mmol) in methylene chloride (65 mL) was added MCPBA (4.8 g, 19.5 mmol). The reaction mixture continued to stir at room temperature for 12 hours. Upon completion of the reaction, the mixture was diluted with methylene chloride, washed with a solution of saturated sodium bisulfite and then with 1 M sodium hydroxide, dried over $MgSO_4$, and filtered through a short pad of Celite. Subsequent purification by column chromatography using 25% ethyl acetate in hexanes provided 2.46 g (82%) of epoxide **4** as a colorless oil.

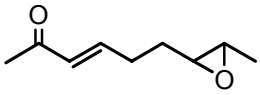
Typical epoxide-opening procedure: To a solution containing epoxide **20** (100 mg, 0.59 mmol) in 24 mL of tert-butanol was added trimethylphosphine (0.05 mL, 0.59 mmol). The reaction mixture continued to stir at room temperature under an argon atmosphere for 18 hours. Subsequent removal of a majority of the tert-butanol *in vacuo* and purification by column chromatography, using 25% ethyl acetate in methylene chloride , yielded 76 mg (76%) of cyclohexenone alcohol **21** as a viscous colorless oil.



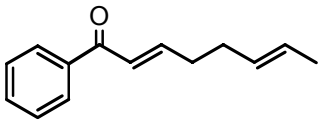
Nona-3,7-dien-2-one: 1-triphenyl-phosphoranylidene-2-propanone (9.7 g, 30.5 mmol) was added to a solution of 4-hexenal[2] (3.0 g, 30.5 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was refluxed under argon for 16 hours. Upon completion of the reaction, the CH_2Cl_2 was removed *in vacuo*. The crude material was washed with pentane and filtered through a short pad of Celite. Purification by column chromatography using 9% ethyl acetate in hexanes afforded 3.16 g (75%) of nona-3,7-dien-2-one as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.79 (dt, J = 16.1, 6.6 Hz, 1H), 6.08 (dt, J = 16.1, 1.5 Hz, 1H), 5.37-5.52 (m, 2H), 2.28 (ddt, J = 6.6, 1.5, 7.3

[1] White, M. C.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 7194.
[2] Aebi, J. D.; Deyo, D. T.; Sun, C. Q.; Guillaume, D.; Dunlap, B.; Rich D. H. *J. Med. Chem.* **1990**, *33*, 999.

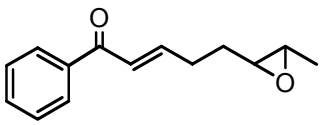
Hz, 2H), 2.24 (s, 3H), 2.16 ddt, *J* = 6.6, 1.5, 7.3 Hz, 2H), 1.65 (dt, *J* = 5.1, 1.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.10, 147.42, 131.16, 129.22, 125.80, 32.09, 30.73, 26.44, 17.52. IR (NaCl, cm^{-1}): 3024, 2919, 2854, 1698, 1678, 1627, 1436, 1360, 1253, 968. HRMS (CI+) Calc'd for $C_9H_{15}O$: 139.11230, Found: 139.11197. Anal. Calc'd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.91; H, 10.29.



Epoxide 4: Epoxide **4** was prepared by the typical epoxidation procedure using nona-3,7-dien-2-one (82% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.81 (dt, *J* = 16.1, 6.6 Hz, 1H), 6.11 (dt, *J* = 16.1, 1.5 Hz, 1H), 2.78 (dq, *J* = 2.2, 5.1 Hz, 1H), 2.66 (ddd, *J* = 6.6, 4.4, 2.2 Hz, 1H), 2.31-2.45 (m, 2H), 2.25 (s, 3H), 1.78 (dddd, *J* = 13.2, 8.8, 7.3, 4.4 Hz, 1H), 1.58-1.66 (m, 1H), 1.30 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.75, 146.45, 131.16, 58.19, 54.01, 30.06, 28.46, 26.38, 17.06. IR (NaCl, cm^{-1}): 2982, 2927, 1697, 1674, 1627, 1434, 1362, 1255, 981. HRMS (CI+) Calc'd for $C_9H_{15}O_2$: 155.1072, Found: 155.1064. Anal. Calc'd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.97; H, 9.16.

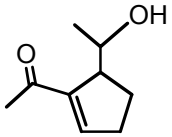


1-Phenyl-octa-2,6-dien-1-one[3]: Phenylcarbonylmethylenetriphenylphosphorane[4] (9.7 g, 30.5 mmol) was added to a solution of 4-hexenal (5.0 g, 50.9 mmol) in THF (200 mL). The reaction mixture was refluxed under argon for 16 hours. Upon completion of the reaction, the THF was removed *in vacuo*. The crude material was washed with pentane and filtered through a short pad of Celite. Purification by column chromatography using 6% ethyl acetate in hexanes afforded 7.3 g (72%) of 1-phenyl-octa-2,6-dien-1-one as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89-7.94 (m, 2H, Aromatic H), 7.52-7.58 (m, 1H, Aromatic H), 7.43-7.49 (m, 2H, Aromatic H), 7.04 (dt, *J* = 15.4, 6.8 Hz, 1H), 6.87 (dt, *J* = 15.4, 1.5 Hz, 1H), 5.40-5.55 (m, 2H), 2.38 (ddd, *J* = 6.8, 1.5, 7.3 Hz, 1H), 2.22 (dt, *J* = 7.3, 7.3 Hz, 2H), 1.66 (dd, *J* = 6.1, 1.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.12, 148.69, 137.58, 132.18, 129.33, 128.12, 128.09, 125.68, 32.36, 30.79, 17.51. IR (NaCl, cm^{-1}): 3058, 3025, 2917, 2853, 1668, 1651, 1621, 1598, 1579, 1447, 1350, 1284, 1227, 1179, 1019, 1002, 967. HRMS (EI+) Calc'd for $C_{14}H_{16}O$: 200.12012, Found: 200.11996. Anal. Calc'd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.84; H, 8.10.

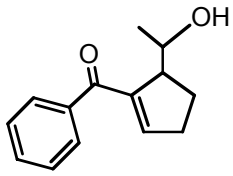


[3] Sasaki, M.; Yudin, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 14242.
[4] Kuroda, H.; Hanaki, E.; Izawa, H.; Kano, M.; Itahashi, H. *Tetrahedron* **2004**, *60*, 1913.

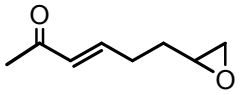
Epoxide 5: Epoxide **5** was prepared by the typical epoxidation procedure with 1-phenyl-octa-2,6-dien-1-one (78% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91-7.95 (m, 2H, Aromatic H), 7.53-7.59 (m, 1H, Aromatic H), 7.44-7.50 (m, 2H, Aromatic H), 7.06 (dt, *J* = 15.4, 6.6 Hz, 1H), 6.93 (dt, *J* = 15.4, 1.5 Hz, 1H), 2.80 (dq, *J* = 2.2, 5.1 Hz, 1H), 2.70 (ddd, *J* = 6.6, 4.4, 2.2 Hz, 1H), 2.41-2.55 (m, 2H), 1.83 (dddd, *J* = 13.2, 8.8, 7.3, 5.1 Hz, 1H), 1.66-1.75 (m, 1H), 1.30 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.78, 147.67, 137.30, 132.22, 128.06, 128.01, 125.81, 58.20, 54.04, 30.16, 28.72, 17.08. IR (NaCl, cm^{-1}): 3058, 2982, 2926, 1668, 1651, 1621, 1597, 1578, 1447, 1380, 1345, 1287, 1225, 1180, 1020, 983. HRMS (EI+) Calc'd for $C_{14}H_{16}O_2$: 216.11503, Found: 216.11500. Anal. Calc'd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.51; H, 7.33.



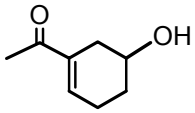
Alcohol 6: (single diastereomer) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dd, *J* = 4.4, 2.9 Hz, 1H), 3.94 (dq, *J* = 2.9, 6.6 Hz, 1H), 3.20-3.27 (m, 1H), 2.53-2.62 (m, 1H), 2.48 (ABdddd, J_{AB} = 19.8 Hz, *J* = 9.5, 5.1, 2.9, 1.5 Hz, 1H), 2.38 (s, 3H), 2.14 (dddd, *J* = 13.2, 9.5, 9.5, 6.6 Hz, 1H), 1.71 (ddt, *J* = 13.2, 9.5, 5.1 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.95, 149.81, 145.63, 68.98, 51.12, 32.38, 26.91, 26.08, 18.90. IR (NaCl, cm^{-1}): 3418, 3057, 2969, 2929, 2839, 1660, 1651, 1614, 1455, 1428, 1372, 1290, 1205, 1128, 1077, 1056, 1000, 975. HRMS (CI+) Calc'd for $C_9H_{15}O_2$: 155.1072, Found: 155.1066. Anal. Calc'd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.39; H, 9.12.



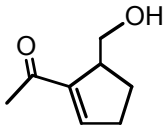
Alcohol 9: (single diastereomer) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73-7.77 (m, 2H, Aromatic H), 7.52-7.58 (m, 1H Aromatic H), 7.42-7.48 (m, 2H, Aromatic H), 6.66 (dd, *J* = 4.4, 2.9 Hz, 1H), 4.08 (dq, *J* = 2.9, 6.6 Hz, 1H), 3.38-3.45 (m, 1H), 2.48-2.67 (m, 2H), 2.20 (dddd, *J* = 13.9, 9.5, 9.5, 5.9 Hz, 1H), 1.85 (ddt, *J* = 13.9, 9.5, 5.9 Hz, 1H), 1.12 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.07, 150.83, 144.27, 138.70, 132.17, 129.04, 128.14, 68.72, 52.42, 32.71, 25.59, 19.46. IR (NaCl, cm^{-1}): 3418, 3060, 2968, 1714, 1634, 1574, 1446, 1352, 1289, 1178, 1130, 1077, 1001, 976. HRMS (CI+) Calc'd for $C_{14}H_{17}O_2$: 217.12286, Found: 217.12297. Anal. Calc'd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.55; H, 7.36.



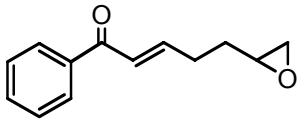
Epoxide 10: Epoxide **10** was prepared by the typical cross-metathesis procedure using 1,2-epoxy-5-hexene and methyl vinyl ketone (58% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (dt, *J* = 16.1, 6.6 Hz, 1H), 6.12 (dt, *J* = 16.1, 1.5 Hz, 1H), 2.95 (ddt, *J* = 7.3, 2.9, 4.4 Hz, 1H), 2.78 (dd, *J* = 5.1, 4.4 Hz, 1H), 2.50 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.34-2.47 (m, 2H), 2.25 (s, 3H), 1.81 (dddd, *J* = 13.2, 8.1, 6.6, 4.4 Hz, 1H), 1.60-1.69 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.52, 146.20, 131.01, 50.73, 46.18, 30.34, 28.24, 26.17. IR (NaCl, cm^{-1}): 2994, 2925, 1697, 1674, 1627, 1431, 1362, 1255, 1201, 981. HRMS (CI+) Calc'd for $C_8H_{13}O_2$: 141.09156, Found: 141.09158. Anal. Calc'd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.36; H, 8.75.



Alcohol 11[5]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.89 (ddd, *J* = 5.9, 4.4, 2.2 Hz, 1H), 4.04 (dddd, *J* = 8.1, 8.1, 5.1, 2.9 Hz, 1H), 2.62 (ABddd, J_{AB} = 17.6 Hz, *J* = 6.6, 2.9, 1.5 Hz, 1H), 2.49 (ABm, J_{AB} = 19.8 Hz, 1H), 2.32 (partly obscured ABm, J_{AB} = 19.8 Hz, 1H), 2.29 (s, 3H), 2.19 (ABddd, J_{AB} = 17.6 Hz, *J* = 6.6, 4.4, 2.2 Hz, 1H), 1.83 (ddddd, *J* = 13.2, 5.9, 5.9, 2.9, 1.5 Hz, 1H), 1.61-1.73 (m, 1H).



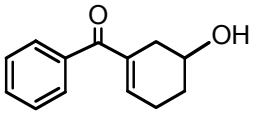
Alcohol 12: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.92 (ddd, *J* = 4.4, 2.9, 2.9 Hz, 1H), 3.61 (ABd, J_{AB} = 11.0 Hz, *J* = 4.4 Hz, 1H), 3.53 (ABd, J_{AB} = 11.0 Hz, *J* = 8.0 Hz, 1H), 3.14 (ddddd, *J* = 8.0, 7.3, 5.9, 4.4, 2.2 Hz), 2.44-2.62 (m, 2H), 2.38 (s, 3H), 2.16 (dddd, *J* = 13.2, 9.5, 9.5, 5.9 Hz, 1H), 1.61 (ddt, *J* = 13.2, 8.8, 5.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 199.12, 148.98, 147.69, 66.34, 47.28, 32.08, 27.32, 26.98. IR (NaCl, cm^{-1}): 3421, 2928, 1703, 1662, 1612, 1430, 1373, 1297, 1256, 1080, 1034. HRMS (CI+) Calc'd for $C_8H_{13}O_2$: 141.09156, Found: 141.09165. Anal. Calc'd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.36; H, 8.82.



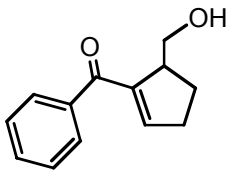
Epoxide 13: Epoxide **13** was prepared by the typical cross-metathesis procedure using 1,2-epoxy-5-hexene and 1-phenylbut-2-en-1-one[6] (55% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91-7.95 (m, 2H, Aromatic H), 7.53-7.59 (m, 1H, Aromatic H), 7.44-7.50 (m, 2H, Aromatic H), 7.07 (dt, *J* = 15.4, 6.6 Hz, 1H), 6.94 (dt, *J* = 15.4, 1.5 Hz, 1H), 2.98

[5] Keay, B. A.; Rajapaksa, D.; Rodrigo, R. *Can. J. Chem.* **1984**, *62*, 1093.
[6] Pitts, M. R.; Harrison, J. R.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 955.

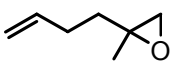
(ddt, J = 6.6, 2.2, 4.4 Hz, 1H), 2.79 (dd, J = 4.4, 4.4 Hz, 1H), 2.44-2.57 (obscured m, 2H), 2.53 (obscured dd, J = 4.4, 2.2 Hz, 1H), 1.86 (dddd, J = 13.9, 8.8, 6.6, 4.4 Hz, 1H), 1.67-1.76 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.01, 147.62, 137.42, 132.34, 128.17, 128.13, 126.02, 51.07, 46.58, 30.70, 28.81. IR (NaCl, cm^{-1}): 3055, 2990, 2923, 1668, 1651, 1621, 1597, 1578, 1447, 1352, 1288, 1224, 1180, 1002, 916. HRMS (CI+) Calc'd for $C_{13}H_{15}O_2$: 203.10721, Found: 203.10713. Anal. Calc'd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.91; H, 6.95.



Alcohol 14: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61-7.65 (m, 2H, Aromatic H), 7.46-7.53 (m, 1H, Aromatic H), 7.39-7.44 (m, 2H, Aromatic H), 6.58 (ddd, J = 5.6, 4.1, 1.5 Hz, 1H), 4.14 (dddd, J = 8.5, 8.5, 4.9, 3.2 Hz, 1H), 2.83 (ABddd, J_{AB} = 15.8 Hz, J = 4.9, 2.9, 1.5 Hz, 1H), 2.50 (ABdddd, J_{AB} = 19.8 Hz, J = 8.1, 6.1, 4.1, 2.4 Hz, 1H), 2.29-2.44 (m, 2H), 1.87-1.95 (m, 1H), 1.69-1.78 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.65, 143.23, 138.32, 135.92, 131.39, 129.04, 127.98, 65.90, 32.77, 29.25, 23.93. IR (NaCl, cm^{-1}): 3418, 3058, 2928, 1634, 1575, 1446, 1267, 1127, 1067, 1000, 958. HRMS (FAB+) Calc'd for $C_{13}H_{14}O_2Na$: 225.0892, Found: 225.0897. Anal. Calc'd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.53; H, 6.93.



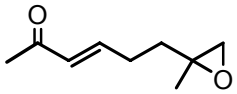
Alcohol 15: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71-7.76 (m, 2H, Aromatic H), 7.52-7.58 (m, 1H, Aromatic H), 7.42-7.48 (m, 2H, Aromatic H), 6.63-6.67 (m, 1H), 3.75 (ABd, J_{AB} = 10.7 Hz, J = 4.1 Hz, 1H), 3.70 (ABd, J_{AB} = 10.7 Hz, J = 7.6 Hz, 1H), 3.29-3.38 (m, 1H), 2.50-2.68 (m, 2H), 2.25 (dddd, J = 13.2, 9.0, 9.0, 6.4 Hz, 1H), 1.77 (ddt, J = 13.2, 9.0, 5.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.27, 150.63, 145.83, 138.78, 132.26, 129.12, 128.22, 66.13, 48.38, 32.55, 27.42. IR (NaCl, cm^{-1}): 3417, 3059, 2929, 1643, 1634, 1598, 1576, 1446, 1431, 1351, 1316, 1285, 1179, 1158, 1130, 1075, 1055, 1028, 975. HRMS (CI+) Calc'd for $C_{13}H_{15}O_2$: 203.10721, Found: 203.10735. Anal. Calc'd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.05; H, 6.86.



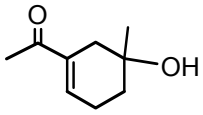
2-But-3-enyl-2-methyl-oxirane[7]: This was prepared by the typical epoxidation procedure using 2-methyl-1,5-hexadiene (73% yield). ^{1}H NMR ($CDCl_3$, 500 MHz):

[7] Larock, R. C.; Leung, W. Y. *J. Org. Chem.* **1990**, *55*, 6244.

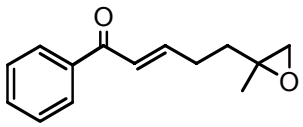
δ5.82 (ddt, J = 16.8, 10.3, 6.6 Hz, 1H), 5.04 (ddt, J = 16.8, 1.5, 1.5 Hz, 1H), 4.97 (dd, J = 10.3, 1.5 Hz, 1H), 2.62 (AB, J_{AB} = 5.1 Hz, 1H), 2.58 (AB, J_{AB} = 5.1 Hz, 1H), 2.13-2.20 (m, 2H), 1.71 (ddd, J = 13.9, 8.8, 6.6 Hz, 1H), 1.60 (ddd, J = 13.9, 8.8, 7.3 Hz, 1H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.54, 114.35, 56.05, 53.27, 35.58, 29.03, 20.51. IR (NaCl, cm^{-1}): 3076, 3040, 2980, 2928, 2858, 1642, 1489, 1450, 1390, 1262, 1108, 1068, 995, 911. HRMS (CI+) Calc'd for $C_7H_{13}O$: 113.09665, Found: 113.09706.



Epoxide 16: Epoxide **16** was prepared by the typical cross-metathesis procedure using 2-but-3-enyl-2-methyl-oxirane and methyl vinyl ketone (62% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.79 (dt, J = 16.1, 6.6 Hz, 1H), 6.09 (dt, J = 16.1, 1.5 Hz, 1H), 2.63 (AB, J_{AB} = 4.4 Hz, 1H), 2.60 (AB, J_{AB} = 4.4 Hz, 1H), 2.33 (ddt, J = 7.3, 1.5, 7.3 Hz, 2H), 2.24 (s, 3H), 1.75 (ABt, J_{AB} = 13.9 Hz, J = 7.3 Hz, 1H), 1.72 (ABt, J_{AB} = 13.9 Hz, J = 7.3 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.08, 146.40, 130.62, 55.28, 52.57, 34.15, 27.21, 25.92, 20.07. IR (NaCl, cm^{-1}): 3039, 2928, 1697, 1674, 1627, 1430, 1391, 1362, 1255, 1190, 981. HRMS (CI+) Calc'd for $C_9H_{15}O_2$: 155.10721, Found: 155.10757. Anal. Calc'd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.96 ; H, 9.24.

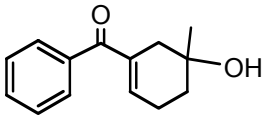


Alcohol 17: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.93 (ddd, J = 6.3, 3.4, 1.7 Hz, 1H), 2.46-2.57 (m, 1H), 2.40 (ABm, J_{AB} = 18.1 Hz, 1H), 2.24-2.37 (obscured m, 2H), 2.31 (s, 3H), 1.72 (dddd, J = 13.2, 6.1, 4.1, 1.7 Hz, 1H), 1.54 (ddd, J = 13.2, 8.8, 6.1 Hz, 1H), 1.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.94, 139.91, 137.42, 68.24, 37.19, 33.78, 29.25, 25.22, 23.93. IR (NaCl, cm^{-1}): 3418, 3051, 2966, 2929, 1667, 1651, 1644, 1634, 1428, 1385, 1250, 1204, 1104, 1078, 1022, 959. HRMS (EI+) Calc'd for $C_9H_{14}O_2$: 154.09938, Found: 154.09941. Anal. Calc'd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.93; H, 9.05.

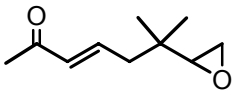


Epoxide 18: Epoxide **18** was prepared by the typical cross-metathesis procedure using 2-but-3-enyl-2-methyl-oxirane and 1-phenylbut-2-en-1-one (48% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90-7.95 (m, 2H, Aromatic H), 7.53-7.59 (m, 1H, Aromatic H), 7.44-7.50 (m, 2H, Aromatic H), 7.05 (dt, J = 15.4, 6.6 Hz, 1H), 6.91 (dt, J = 15.4, 1.5 Hz, 1H), 2.66 (AB, J_{AB} = 5.1 Hz, 1H), 2.62 (AB, J_{AB} = 5.1 Hz, 1H), 2.40-2.47 (m, 2H), 1.77-1.84 (m, 2H), 1.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.95, 148.02, 137.39,

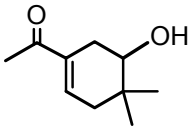
132.27, 128.12, 128.08, 125.71, 55.81, 53.20, 34.60, 27.90, 20.52. IR (NaCl, cm^{-1}): 3039, 2928, 1668, 1651, 1622, 1598, 1578, 1448, 1390, 1336, 1288, 1222, 1180, 1072, 1002. HRMS (CI+) Calc'd for $C_{14}H_{17}O_2$: 217.12286, Found: 217.12279. Anal. Calc'd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.48.



Alcohol 19: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61-7.65 (m, 2H, Aromatic H), 7.47-7.52 (m, 1H, Aromatic H), 7.39-7.44 (m, 2H, Aromatic H), 6.59-6.63 (m, 1H), 2.46-2.61 (m, 3H), 2.28-2.37 (m, 1H), 1.73-1.81 (m, 1H), 1.59-1.67 (m, 1H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.65, 142.78, 138.50, 136.46, 131.42, 129.12, 128.05, 68.42, 38.17, 34.00, 29.29, 24.06. IR (NaCl, cm^{-1}): 3435, 3057, 2964, 2927, 1637, 1597, 1577, 1446, 1421, 1374, 1277, 1254, 1141, 1107, 1027, 1001, 972. HRMS (CI+) Calc'd for $C_{14}H_{17}O_2$: 217.12286, Found: 217.12301. Anal. Calc'd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.58; H, 7.32.

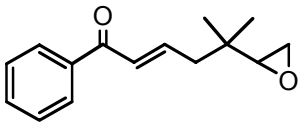


Epoxide 20: Epoxide **20** was prepared by the typical cross-metathesis procedure using 2-(1,1-dimethyl-but-3-enyl)-oxirane[8] and methyl vinyl ketone (64% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.85 (dt, J = 16.1, 8.1 Hz, 1H), 6.10 (d, J = 16.1 Hz, 1H), 2.78 (dd, J = 4.4, 2.9 Hz, 1H), 2.66 (dd, J = 4.4, 4.4 Hz, 1H), 2.61 (dd, J = 4.4, 2.9 Hz, 1H), 2.19-2.29 (obscured m, 2H), 2.25 (obscured s, 3H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.92, 143.28, 132.97, 58.12, 42.77, 42.39, 33.46, 26.09, 22.04. IR (NaCl, cm^{-1}): 3053, 3002, 2965, 2932, 2876, 1697, 1673, 1627, 1473, 1430, 1405, 1364, 1255, 1188, 983, 914. HRMS (CI+) Calc'd for $C_{10}H_{17}O_2$: 169.12286, Found: 169.12258. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.24; H, 9.59.

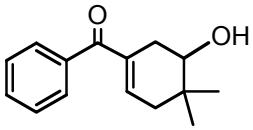


Alcohol 21: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.80-6.85 (m, 1H), 3.60 (dd, J = 5.1, 5.1 Hz, 1H), 2.57 (dm, J = 2.2 Hz, 1H), 2.23-2.32 (obscured m, 2H), 2.30 (s, 3H), 2.05 (dm, J = 2.2 Hz, 1H), 0.95 (s, 3H), 0.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.81, 139.59, 136.13, 73.03, 37.69, 33.14, 29.54, 25.85, 25.13, 22.54. IR (NaCl, cm^{-1}): 3444, 3050, 2956, 1667, 1651, 1470, 1422, 1392, 1354, 1329, 1255, 1199, 1176, 1133, 1056, 1012, 981. HRMS (CI+) Calc'd for $C_{10}H_{17}O_2$: 169.12286, Found: 169.12257. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.50.

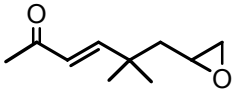
[8] Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6697.



Epoxide 22: Epoxide **22** was prepared by the typical cross-metathesis procedure using 2-(1,1-dimethyl-but-3-enyl)-oxirane[18] and 1-phenylbut-2-en-1-one[16] (52% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91-7.96 (m, 2H, Aromatic H), 7.53-7.59 (m, 1H, Aromatic H), 7.44-7.50 (m, 2H, Aromatic H), 7.09 (dt, J = 15.4, 8.1 Hz, 1H), 6.91 (dt, J = 15.4, 1.5 Hz, 1H), 2.82 (dd, J = 4.4, 2.9 Hz, 1H), 2.67 (dd, J = 4.4, 4.4 Hz, 1H), 2.64 (dd, J = 4.4, 2.9 Hz, 1H), 2.37 (ABdd, J_{AB} = 13.9 Hz, J = 8.1, 1.5 Hz, 1H), 2.31 (ABdd, J_{AB} = 13.9 Hz, J = 8.1, 1.5 Hz, 1H), 0.96 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.15, 145.23, 137.64, 132.53, 128.42, 128.36, 58.87, 43.72, 43.13, 34.20, 22.91, 22.90, 22.43. IR (NaCl, cm^{-1}): 3057, 2965, 2931, 2874, 1668, 1651, 1621, 1598, 1579, 1471, 1448, 1404, 1365, 1348, 1280, 1222, 1180, 1158, 1072, 1011, 983, 914. HRMS (ESI+) Calc'd for $C_{15}H_{18}O_2Na$: 253.12045, Found: 253.12025. Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.05; H, 7.92.



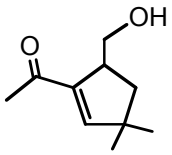
Alcohol 23: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.65 (m, 2H, Aromatic H), 7.48-7.56 (m, 1H, Aromatic H), 7.39-7.44 (m, 2H, Aromatic H), 6.51 (ddd, J = 3.7, 2.2, 1.5 Hz, 1H), 3.70 (dd, J = 5.9, 5.1 Hz, 1H), 2.78 (ABdt, J_{AB} = 18.3 Hz, J = 2.2, 5.1 Hz, 1H), 2.46 (ABddd, J_{AB} = 18.3 Hz, J = 5.9, 3.7, 2.2 Hz, 1H), 2.29 (ABdt, J_{AB} = 19.8 Hz, J = 2.2, 3.7 Hz, 1H), 2.07 (ABdt, J_{AB} = 19.8 Hz, J = 2.2, 4.4 Hz, 1H), 1.00 (s, 3H), 0.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.47, 142.56, 138.33, 135.15, 131.39, 129.06, 127.98, 73.072, 37.81, 33.29, 30.44, 25.96, 22.56. IR (NaCl, cm^{-1}): 3458, 3058, 2957, 1633, 1597, 1577, 1471, 1446, 1422, 1383, 1268, 1200, 1178, 1116, 1057, 982. HRMS (ESI+) Calc'd for $C_{15}H_{18}O_2Na$: 253.12045, Found: 253.12053. Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.95; H, 7.86.



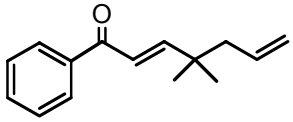
Epoxide 24: Epoxide **24** was prepared by the typical epoxidation procedure with 5,5-dimethyl-octa-3,7-dien-2-one[9] (70% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, J = 16.1 Hz, 1H), 6.06 (d, J = 16.1 Hz, 1H), 2.88 (dddd, J = 6.9, 5.1, 4.8, 2.6 Hz, 1H), 2.74 (dd, J = 5.1, 5.1 Hz, 1H), 2.41 (dd, J = 5.1, 2.6 Hz, 1H), 2.27 (s, 3H), 1.66 (ABd, J_{AB} = 14.3 Hz, J = 4.8 Hz, 1H), 1.55 (ABd, J_{AB} = 14.3 Hz, J = 6.9 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.76, 155.82, 127.53, 48.99, 46.52, 44.89,

[9] Cockerill, S. G.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2101.

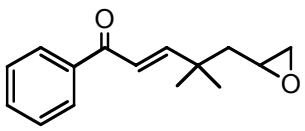
36.56, 27.11, 26.71, 26.48. IR (NaCl, cm^{-1}): 3045, 2965, 2928, 2874, 1698, 1623, 1469, 1426, 1387, 1363, 1301, 1257, 1182, 1134, 986. HRMS (CI+) Calc'd for $C_{10}H_{17}O_2$: 169.1229, Found: 169.1223. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.18; H, 9.66.



Alcohol 25: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.63 (d, J = 1.5 Hz, 1H), 3.57 (ABd, J_{AB} = 11.0 Hz, J = 3.3 Hz, 1H), 3.51 (ABd, J_{AB} = 11.0 Hz, J = 8.8 Hz, 1H), 3.17 (ddddd, J = 8.8, 8.8, 7.7, 3.3, 1.5 Hz, 1H), 2.37 (s, 3H), 1.98 (dd, J = 13.2, 8.8 Hz, 1H), 1.34 (dd, J = 13.2, 7.7 Hz, 1H), 1.17 (s, 3H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.04, 158.23, 144.52, 66.66, 47.18, 44.27, 42.36, 28.45, 27.58, 26.94. IR (NaCl, cm^{-1}): 3428, 3038, 2956, 2866, 1651, 1614, 1464, 1362, 1301, 1201, 1132, 1040, 965. HRMS (CI+) Calc'd for $C_{10}H_{17}O_2$: 169.12286, Found: 169.12279. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.11; H, 9.45.



4,4-Dimethyl-1-phenyl-hepta-2,6-dien-1-one: Sodium hydride (60% in mineral oil, 800 mg, 20 mmol) was added to 60 mL of ethanol and stirred at room temperature for 15 minutes. This was followed by the addition of acetophenone (2.4 g, 20 mmol) and 2,2-dimethyl-4-pentenal (2.5 g, 20 mmol). The reaction mixture then was allowed to stir at room temperature for 5 hours. Upon completion of the aldol reaction, the ethanol was removed *in vacuo*. The crude mixture was diluted with ethyl acetate, washed with water, dried over $MgSO_4$, and filtered through a short pad of Celite. Purification by column chromatography using 6% ethyl acetate in hexanes provided 3.47 g (81%) of 4,4-dimethyl-1-phenyl-hepta-2,6-dien-1-one as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90-7.95 (m, 2H, Aromatic H), 7.53-7.59 (m, 1H, Aromatic H), 7.44-7.50 (m, 2H, Aromatic H), 7.02 (d, J = 15.7 Hz, 1H), 6.76 (d, J = 15.7 Hz, 1H), 5.75 (ddt, J = 16.7, 10.2, 7.3 Hz, 1H), 5.07 (dm, J = 10.2 Hz, 1H), 5.05 (dm, J = 16.7 Hz, 1H), 2.18 (d, J = 7.3 Hz, 2H), 1.13 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.14, 158.00, 138.04, 134.22, 132.45, 128.43, 128.36, 122.18, 117.73, 46.42, 37.07, 26.13. IR (NaCl, cm^{-1}): 3075, 3004, 2963, 2928, 2871, 1673, 1651, 1620, 1598, 1580, 1464, 1448, 1385, 1365, 1329, 1298, 1283, 1221, 1180, 1090, 1035, 1019, 993, 916. HRMS (EI+) Calc'd for $C_{15}H_{18}O$: 214.13577, Found: 214.13550. Anal. Calc'd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.84; H, 8.60.



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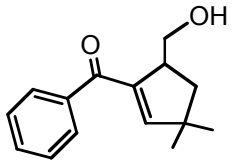
Epoxide 26: Epoxide **26** was prepared by the typical epoxidation procedure with 4,4-dimethyl-1-phenyl-hepta-2,6-dien-1-one (76% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91-7.96 (m, 2H, Aromatic H), 7.54-7.60 (m, 1H, Aromatic H), 7.45-7.51 (m, 2H, Aromatic H), 7.07 (d, J = 15.7 Hz, 1H), 6.86 (d, J = 15.7 Hz, 1H), 2.92 (dddd, J = 7.0, 5.1, 4.8, 2.6 Hz, 1H), 2.75 (dd, J = 4.8, 4.8 Hz, 1H), 2.44 (dd, J = 4.8, 2.6 Hz, 1H), 1.71 (ABd, J_{AB} = 14.3 Hz, J = 5.1 Hz, 1H), 1.62 ABd, J_{AB} = 14.3 Hz, J = 7.0 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.79, 157.08, 137.79, 132.49, 128.35, 128.33, 122.23, 48.94, 46.40, 44.71, 36.81, 26.87, 26.27. IR (NaCl, cm^{-1}): 3054, 2963, 2927, 2872, 1732, 1670, 1650, 1619, 1597, 1578, 1464, 1447, 1426, 1410, 1386, 1366, 1297, 1223, 1180, 1158, 1132, 1091, 1036, 1019, 991, 953. HRMS (FAB+) Calc'd for $C_{15}H_{18}O_2Na$: 253.12045, Found: 253.12044. Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.27; H, 7.85.



Alcohol 27: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70-7.75 (m, 2H, Aromatic H), 7.53-7.58 (m, 1H, Aromatic H), 7.43-7.48 (m, 2H, Aromatic H), 6.39 (d, J = 1.5 Hz, 1H), 3.74 (ABd, J_{AB} = 11.0 Hz, J = 4.4 Hz, 1H), 3.70 (ABd, J_{AB} = 11.0 Hz, J = 8.1 Hz, 1H), 3.37-3.44 (m, 1H), 2.07 (dd, J = 13.2, 8.1 Hz, 1H), 1.55 (dd, J = 13.2, 7.3 Hz, 1H), 1.20 (s, 3H), 1.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.48, 159.47, 142.19, 138.62, 132.07, 128.95, 128.05, 66.95, 47.95, 44.84, 42.09, 28.43, 27.62. IR (NaCl, cm^{-1}): 3418, 3059, 2954, 2863, 1644, 1576, 1446, 1384, 1295, 1212, 1177, 1113, 1044, 1027, 960. HRMS (FAB+) Calc'd for $C_{15}H_{18}O_2Na$: 253.12045, Found: 253.12052. Anal. Calc'd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.98; H, 7.96.