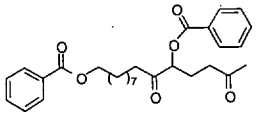
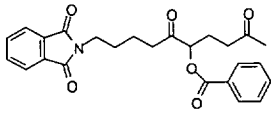
1st enantiomer: 6.83 min (major).
2nd enantiomer: 9.19 min

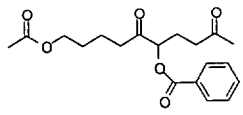


1, 11-Di(benzoyloxy)-pentadecan-10, 14-dione (**75**)

Yellow oil, R_f = 0.20 (2/1 petroleum ether/ether). IR (thin film): 2928, 2855, 1717, 1452, 1371, 1315, 1275, 1176, 1114, 1070, 1026, 712 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 8.07-8.02 (m, 4H), 7.62-7.52 (m, 2H), 7.49-7.41 (m, 4H), 5.25 (dd, J_1=8.1 Hz, J_2=4.4 Hz, 1H), 4.30 (t, J=6.7 Hz, 2H), 2.66-2.44 (m, 4H), 2.30-2.22 (m, 1H), 2.18-2.06 (m, 1H), 2.16 (s, 3H), 1.80-1.70 (m, 2H), 1.62-1.58 (m, 2H), 1.43-1.23 (m, 10H). ^{13}C NMR (75MHz, $CDCl_3$): δ 207.1, 207.0, 166.7, 165.9, 133.5, 132.8, 130.5, 129.8, 129.5, 129.2, 128.5, 128.3, 77.7, 65.1, 38.7, 38.6, 30.1, 29.4, 29.3, 29.2, 29.1, 28.7, 26.0, 24.2, 23.1. HRMS: Calc'd for $C_{29}H_{36}O_6$-$C_6H_5CO_2H$: 358.2144. Found: 358.2143.
Non-Racemic (TBPVI-27): Separated on Chiralpak AD Column (90:10 heptane:isopropanol, 1 mL/min., 254 nm detection)
1st enantiomer: 17.26 min (major).
2nd enantiomer: 24.91 min



1-Phthalimido-6-benzoyloxydodecan-5, 9-dione (**76**)
Yellow oil, R_f = 0.13 (1/1 petroleum ether/ether). IR (neat): 2933, 2868, 1772, 1713, 1466, 1451, 1438, 1398, 1372, 1273, 1113, 1071 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 8.03 (d, J=7.9, 2H), 7.84-7.81 (m, 2H), 7.71-7.68 (m, 2H), 7.59 (t, J=6.8, 1H), 7.46 (t, J=7.6, 2H), 5.24 (dd, J_1=7.9 Hz, J_2=4.5 Hz, 1H), 3.69 (t, J=6.6 Hz, 2H), 2.72-2.64 (m, 4H), 2.29-2.20 (m, 1H) 2.16 (s, 3H), 2.12-2.07 (m, 1H), 1.72-1.64 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ 207.0, 206.4, 168.4, 165.9, 133.9, 133.5, 132.1, 130.1, 129.8, 128.5, 123.2, 77.6, 38.5, 37.9, 37.4, 30.1, 27.8, 24.2, 20.1. Anal. Calc'd for $C_{25}H_{25}NO_6$: C, 68.95; H, 5.79; N, 3.22. Found: C, 68.76; H, 5.71; N, 3.06.
Non-Racemic (TBPVI-43): Separated on Chiralcel OD Column (90:10 heptane:isopropanol, 1 mL/min., 254 nm detection)
1st enantiomer: 41.83 min (major).
2nd enantiomer: 48.01 min

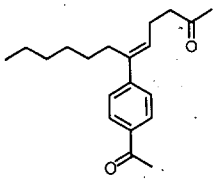


1-Acetoxy-6-benzoyloxydodecan-59-iodine (**77**)
Yellow oil, R_f = 0.18 (1/1 petroleum ether/ether). IR (neat): 3064, 2924, 2853, 1722, 1680, 1602, 1452, 1367, 1316, 1272, 1247, 1112 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 8.06 (dd, J_1=8.2, J_2=1.1, 2H), 7.61 (t, J=7.3, 1H), 7.47 (t, J=7.8, 2H), 5.24 (dd, J_1=8.1 Hz,

J_2=4.4 Hz, 1H), 4.06 (t, J=6.0 Hz, 2H), 2.67-2.59 (m, 4H), 2.30-2.22 (m, 1H) 2.17 (s, 3H), 2.15-2.05 (m, 1H), 2.03 (s, 3H), 1.71-1.61 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ 207.0, 206.5, 171.2, 166.0, 133.6, 129.8, 129.1, 128.6, 77.7, 64.1, 38.6, 38.1, 30.1, 27.9, 24.2, 21.0, 19.6. Anal. Calc'd for $C_{19}H_{26}O_6$: C, 65.50; H, 6.94. Found: C, 65.64; H 7.17.
Non-Racemic (TBPVI-38): Separated on Chiralpak AD Column (90:10 heptane:isopropanol, 1 mL/min., 254 nm detection)
1st enantiomer: 15.36 min (major).
2nd enantiomer: 20.13 min

Experimental Details for Equation 11: Cross Coupling Reaction of Vinyl Chloride 15

Following the published procedure, vinyl chloride **15** (22 mg, 0.1 mmol) *p*-acetylbenzeneboronic acid (33 mg, 0.2 mmol), potassium fluoride (20 mg, 0.33 mmol) and Pd_2dba_3•$CHCl_3$ (2.6 mg, 0.0025 mmol) were added to a test tube. The tube was sealed and placed under argon. THF (0.25 mL) was added to the test tube purged with argon for 5 min. Then, tri-*t*-butylphosphine (2.6 mg, 0.0015 mL, 0.006 mmol) was added, and the reaction stirred at rt for 16 h. The reaction was next poured into ether (25 mL), and extracted three times with water then the organic layer was dried over magnesium sulfate. The ether was removed by rotary evaporation to give a crude material that was purified by silica gel chromatography (10/1 petroleum ether/ethyl acetate) to give 22 mg **78** (73%) as the *E* isomer.

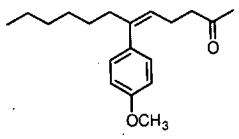


E-6-(4-Acetyl-phenyl)-dodec-5-en-2-one (**78**)
Colorless oil. R_f = 0.17 (15:1 petroleum ether/ether). IR (neat): 2957, 2929, 2858, 2358, 1719, 1687, 1456, 1361, 1264, 1162, 1123, 1100 cm^{-1}. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.99-7.97 (m, 1H), 7.60-7.57 (m, 1H), 7.51-7.47 (m, 2H), 5.55 (t, J=7.7, 1H), 2.63 (s, 3H), 2.52 (t, J=7.3, 2H), 2.37-2.29 (m, 4H), 2.17 (s, 3H), 1.58-1.52 (m, 2H), 1.35-1.27 (m, 6H), 0.91 (t, J=6.9, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.5, 198.2, 137.1, 135.4, 133.1, 128.6, 128.3, 125.9, 42.9, 33.6, 31.6, 30.0, 28.4, 27.2, 26.6, 22.6, 22.5, 14.0.
HRMS: Calc'd for $C_{20}H_{28}O_2$: 300.2089. Found: 300.2095.

Experimental Details for Equation 12: Cross Coupling Reaction of Vinyl Bromide 40 to form 79a.

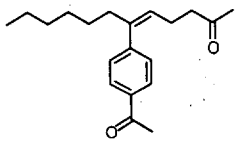
Following the published procedure,[v] vinyl bromide **40** (26 mg, 0.10 mmol) *p*-methoxybenzeneboronic acid (31 mg, 0.2 mmol), potassium fluoride (20 mg, 0.33 mmol) and Pd_2dba_3•$CHCl_3$ (2.6 mg, 0.0025 mmol) were added to a test tube. The tube was sealed and placed under argon. THF (0.4 mL) was added an the test tube purged with argon for 5 min. Then, tri-*t*-butylphosphine (1.2 mg, 0.0015 mL, 0.006 mmol) was added, and the reaction stirred at rt for 16 h. The reaction was next poured into ether (25 mL), and extracted three times with water then the organic layer was dried over magnesium

sulfate. The ether was removed by rotary evaporation to give a crude material that was purified by silica gel chromatography (8/1 petroleum ether/ether) to give 21 mg **79a** (71%) as the *Z* isomer. The other isomer was observed in the crude reaction mixture but not isolated.



Z-6-(4-Methoxy-phenyl)-dodec-5-en-2-one (**79a**)
Colorless oil. R_f = 0.32 (8/1 petroleum ether/ethyl ether). IR (neat): 2956, 2928, 2856, 1717, 1608, 1511, 1465, 1361, 1288, 1246, 1176, 1160 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 7.07 (d, J=8.5, 2H), 6.89 (d, J=8.8, 2H), 5.36 (t, J=7.2, 1H), 3.83 (s, 3H), 2.43 (t, J=7.4, 2H), 2.29 (t, J=6.6, 2H), 2.25 (q, J=7.3, 2H), 2.10 (s, 3H), 1.31-1.24 (m, 8H), 0.87 (t, J=7.1, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.7, 158.1, 142.1, 133.2, 129.3, 124.5, 113.4, 55.2, 44.1, 39.4, 31.6, 29.8, 28.8, 28.0, 23.4, 22.6, 14.1. Anal. Calc'd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.30; H, 9.69.

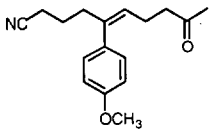
Experimental Details for Equation 12: Cross Coupling Reaction of Vinyl Bromide 40 to Form **79b.**
Following the published procedure, vinyl bromide **40** (26 mg, 0.1 mmol) *p*-acetylbenzeneboronic acid (33 mg, 0.2 mmol), potassium fluoride (20 mg, 0.33 mmol) and Pd_2dba_3•$CHCl_3$ (2.6 mg, 0.0025 mmol) were added to a test tube. The tube was sealed and placed under argon. THF (0.25 mL) was added to the test tube purged with argon for 5 min. Then, tri-*t*-butylphosphine (2.6 mg, 0.0015 mL, 0.006 mmol) was added, and the reaction stirred at rt for 16 h. The reaction was next poured into ether (25 mL), and extracted three times with water then the organic layer was dried over magnesium sulfate. The ether was removed by rotary evaporation to give a crude material that was purified by silica gel chromatography (10/1 petroleum ether/ethyl acetate) to give 23 mg **79b** (73%) as the *Z* isomer. The other isomer was observed in the crude reaction mixture but not isolated.



Z-6-(4-Acetyl-phenyl)-dodec-5-en-2-one (**79b**)
Colorless oil. R_f = 0.25 (15:1 petroleum ether/ether). IR (neat): 2930, 2858, 2362, 2339, 1719, 1656, 1460, 1430, 1382, 1228, 1162, 1120 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.61-7.58 (m, 1H), 7.51-7.48 (m, 1H), 5.68 (t, J=6.8, 1H), 2.64 (s, 3H), 2.56 (t, J=7.2, 2H), 2.45-2.40 (m, 4H), 2.17 (s, 3H), 1.54 (quint., J=7.2, 2H), 1.34-1.27 (m, 6H), 0.90 (t, J=6.8, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.0, 198.2, 137.1, 133.1, 129.8, 128.6, 128.3, 126.4, 42.2, 41.4, 31.5, 29.8, 28.0 (x2), 26.6, 25.6, 22.5, 14.0. HRMS: Calc'd for $C_{20}H_{28}O_2$: 300.2089. Found: 300.2090.

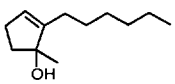
Experimental Details for Equation 13: Cross Coupling Reaction of Vinyl Bromide 42

Following the published procedure, vinyl bromide **42** (48.8 mg, 0.20 mmol) *p*-methoxybenzeneboronic acid (62 mg, 0.4 mmol), potassium fluoride (40 mg, 0.66 mmol) and Pd_2dba_3•$CHCl_3$ (5.2 mg, 0.005 mmol) were added to a test tube. The tube was sealed and placed under argon. THF (0.8 mL) was added to the test tube purged with argon for 5 min. Then, tri-*t*-butylphosphine (2.4 mg, 0.003 mL, 0.012 mmol) was added, and the reaction stirred at rt for 16 h. The reaction was next poured into ether (25 mL), and extracted three times with water then the organic layer was dried over magnesium sulfate. The ether was removed by rotary evaporation to give a crude material that was purified by silica gel chromatography (4/1 petroleum ether/ethyl acetate) to give 30 mg **80** (63%) as the *Z* isomer. The other isomer was observed in the crude reaction mixture but not isolated.



Z-5-(4-Methoxy-phenyl)-9-oxo-dec-5-enenitrile (**80**)

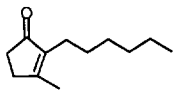
Colorless oil. R_f = 0.43 (2/1 petroleum ether/ethyl acetate). IR (neat): 2938, 2839, 1715, 1652, 1608, 1512, 1456, 1442, 1362, 1247, 1178, 1162 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 7.07 (d, J=8.8, 2H), 6.90 (d, J=8.8, 2H), 5.46 (t, J=7.3, 1H), 3.83 (s, 3H), 2.52-2.41 (m, 4H), 2.35-2.26 (m, 4H), 2.09 (s, 3H), 1.63 (quint, J=7.2, 2H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.2, 158.5, 139.1, 131.5, 129.3, 127.0, 119.6, 113.8, 55.2, 43.6, 37.9, 29.8, 23.4, 23.2, 16.2. HRMS:. Calc'd for $C_{17}H_{21}NO_2$: 271.1572. Found: 271.1574.



2-Hexyl-1-methyl-cyclopent-2-enol (**81**)

Chromium (II) chloride (342 mg, 2.78 mmol) and nickel (II) chloride (145 mmol, 1.12 mmol) were weighed out in a flask in a drybox and placed under argon. To this flask a solution of the vinyl bromide **40** (145 mg, 0.56 mmol) in DMF (2 mL) was added, and the reaction stirred overnight at room temperature. The crude reaction mixture was then applied directly to a silica gel column (2/1 petroleum ether/ethyl ether) to give 71 mg product (70%).

Colorless oil. R_f = 0.40 (2/1 petroleum ether/ethyl ether). IR (neat) : 3364, 3048, 2958, 2927, 2856, 1458, 1365, 1177, 1111, 1082, 964, 918 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.45-5.44 (m, 1H), 2.39-2.31 (m, 1H), 2.22-2.15 (m, 1H), 2.11-2.00 (m, 2H), 1.97-1.92 (m, 1H), 1.54-1.43 (m, 2H), 1.38-1.21 (m, 11H), 0.91 (t, J=6.9, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 149.1, 124.8, 83.9, 41.0, 31.8, 29.5, 28.5, 28.1, 25.8, 25.5, 22.6, 14.1. Anal. Calc'd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.26; H, 11.99.



2-n-Hexyl-3-methyl-cyclopent-2-enone (**82**)
To a solution of **81** (50 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added pyridinium dichromate (71 mg, 0.33 mmol). The reaction was stirred for 1 h, then ether (20 mL) was added and the mixture filtered through a pad of Celite. The solvent was then evaporated by simple distillation and the residue was purified by silica gel chromatography (3/1 petroleum ether/ethyl ether) to give 30 mg product (63%).
Colorless oil. R_f = 0.26 (3/1 petroleum ether/ethyl ether). IR (neat): 2956, 2927, 2857, 2361, 1700, 1648, 1443, 1409, 1385, 1340, 1177, 1072 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 2.51-2.49 (m, 2H), 2.39-2.37 (m, 2H), 2.18 (t, J=7.3, 2H), 2.07 (s, 3H), 1.39-1.32 (m, 2H), 1.31-1.28 (m, 6H), 0.89 (t, J=6.8, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 209.7, 170.0, 140.8, 34.3, 31.7, 31.3, 29.3, 28.4, 23.0, 22.6, 17.2, 14.1. Anal. Calc'd for $C_{12}H_{20}O$: C, 79.94; H, 11.18: C, 80.00; H, 11.26

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[i] For the diketones, see: Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836.
[ii] Moshe Portnoy, Final Report, Stanford University, 1997.
[iii] Satoh, Y.; Serizawa, H.; Hara, S.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 5225.
[iiii] Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.