Supporting Information

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Alkene-Directed Regioselective Nickel-Catalyzed Cross-Coupling of Cyclic Anhydrides with Diorganozinc Reagents

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General Methods. All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Tetrahydrofuran, diethylether, and dichloromethane were degassed with argon and passed through two columns of neutral alumina. Column chromatography was performed on EM Science silica gel 60 (230-400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light, KMnO₄, aqueous ceric ammonium molybdate, or bromocresol green dips followed by heating.

Anhydrides 1 and 14 were purchased from Aldrich Chemical Co. and used without further purification. Anhydrides 2b, 2c, 2e, 2j, 2k were prepared by literature methods.¹ Anhydride 8 was prepared by hydrogenation of 2a (H₂, 10% Pd/C, EtOAc). Ni(COD)₂ was purchased from Strem Chemical, Inc. and used without further purification.

Infrared spectra were obtained on a Nicolet Avatar 320 FT-IR spectrometer. ¹H NMR and spectra were recorded on a Varian 300 or 400MHz spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from an internal standard [tetramethylsilane (TMS) or deuterated chloroform (CDCl₃)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ¹³C NMR were recorded on a Varian 300, 400, or 500 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from CDCl₃ taken as 77.0 ppm. Mass spectra were obtained on Fisons VG Autospec. Analytical gas chromatography (GC) was performed on a Varian Cp 3800 gas chromatograph equipped with a flame ionization detector using a Chromopack Cp Wax 52 CB (30 m X 0.32 mm) capillary column.

General procedure for the ring-opening cross-metathesis of cis-5-Norbornene-endoc-2,3-dicarboxylic anhydride. A flame-dried round bottom flask was charged with Grubbs 1st generation catalyst (0.1 eq) in an inert atmosphere (N₂) glove box and sealed with a septum. Upon removal from the glove box, CH₂Cl₂ was added via syringe and the solution was stirred at ambient temperature for 5 min. Cis-5-Norbornene-endoc-2,3-dicarboxylic anhydride in CH₂Cl₂ was added via cannula to the Grubbs 1st generation catalyst in CH₂Cl₂. Terminal olefin was added dropwise via syringe, and the reaction was allowed to stir overnight. The reaction was concentrated and the resulting residue was purified by column chromatography (CH₂Cl₂) to separate recovered catalyst from the mixture.

General procedure for the alkene-directed nickel-catalyzed regioselective cross-coupling of succinic anhydrides. A flame-dried round bottom flask was charged with Ni(COD)_2 (0.1 eq) in an inert atmosphere (N_2) glove box and sealed with a septum. Upon removal from the glove box and placed under Ar, 0.5 mL THF was added via syringe and the solution was allowed to stir at ambient temperature for 5 min. The solution was then cooled to 0 °C in an ice bath at which point diethyl zinc (1.7 eq) was added via syringe. Anhydride (1 eq) in THF (0.5 mL) was then added via cannula and the reaction was allowed to stir for the time indicated. The reaction was then diluted with 10 mL of ether and quenched with 10 mL 1M HCl. The layers were separated and the aqueous layer was extracted with ether (2 X 10 mL) and the combined organic extracts were washed with brine, dried over MgSO_4, filtered, and concentrated in vacuo. The corresponding methyl ester was generated by treatment with TMSCHN_2 (2.0 M in Et_2O) in 1:1 PhH:MeOH at room temperature and purified by column chromatography.

General procedure for the monoreduction of terminal olefin. A vial was charged with RuHCl(PPh_3)_3:PhMe adduct (0.1 eq) in an inert atmosphere (N_2) glove box and sealed with a septum. Upon removal from the glove box anhydride, dissolved in ethyl acetate/benzene (1:1, 0.1M) with a septum. Upon removal from the glove box anhydride, dissolved in ethyl acetate/benzene (1:1, 0.1M) was added to the vial. The reaction was placed under H_2 (500 psi), in a parr bomb, with a needle placed through the septum. The reaction mixture was further purified by column chromatography (CH_2Cl_2) to separate recovered catalyst from the mixture. The product was further purified by column chromatography (10:1 Hex/EtOAc) providing 2.134 g (61%) of anhydride 2a as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.34 (ddd, 2H, J = 8.2, 5.1, 2.1 Hz), 7.00 (dd, 2H, J = 8.8, 8.6 Hz), 6.48 (d, 1H, J = 15.8 Hz), 6.20 (dd, 1H, J = 17.8, 7.9 Hz), 6.03-5.89 (m, 1H), 5.21 (dd, 1H, J = 17.2, 1.3 Hz), 5.16 (dd, 1H, J = 11.0, 0.7 Hz), 3.59-3.49 (m, 2H), 3.21-3.00 (m, 2H), 2.13 (ddd, 1H, J = 12.8, 5.5, 5.5 Hz), 1.55 (ddd, 1H, 12.8, 12.8, 12.8 Hz); ^13C NMR (75 MHz, CDCl_3) δ 170.7, 170.5, 162.4 (d, J_CF = 247 Hz), 134.7, 132.8 (d, J_CF = 3 Hz), 131.0, 128.0 (d, J_CF = 8 Hz), 126.2, (d, J_CF = 2 Hz), 117.4, 115.5 (d, J_CF = 22 Hz), 49.8, 49.4, 46.7, 46.1, 36.5; IR (NaCl, neat) 2983, 1854, 1775, 1642, 1600, 1509, 1225, 1206 cm^-1; HRMS (FAB+) calcd for C_{12}H_{15}O_3F, 286.1005. Found 286.0994.

(3aR,4S,6R,6aS)-4-(4-fluorostyryl)-6-vinyltetrahydro-1H-cyclopenta[c|furan-1,3(3aH)-dione (2a). According to the general procedure, 2.0 g (12.18 mmol) cis-5-norbornene-endo-2,3-dicarboxylic anhydride (1) in 60 mL CH_2Cl_2 was added via cannula to 0.501 g Grubbs 1st generation catalyst (0.609 mmol) i in 37 mL CH_2Cl_2. 4-fluorostyrene (2.184 mL, 18.28 mmol) was added via syringe and the reaction was stirred overnight. The reaction was then concentrated and purified by column chromatography (CH_2Cl_2) to separate recovered catalyst from the mixture. The product was further purified by column chromatography (10:1 Hex/EtOAc) providing 2.134 g (61%) of anhydride 2a as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.34 (ddd, 2H, J = 8.2, 5.1, 2.1 Hz), 7.00 (dd, 2H, J = 8.8, 8.6 Hz), 6.48 (d, 1H, J = 15.8 Hz), 6.20 (dd, 1H, J = 17.8, 7.9 Hz), 6.03-5.89 (m, 1H), 5.21 (dd, 1H, J = 17.2, 1.3 Hz), 5.16 (dd, 1H, J = 11.0, 0.7 Hz), 3.59-3.49 (m, 2H), 3.21-3.00 (m, 2H), 2.13 (ddd, 1H, J = 12.8, 5.5, 5.5 Hz), 1.55 (ddd, 1H, 12.8, 12.8, 12.8 Hz); ^13C NMR (75 MHz, CDCl_3) δ 170.7, 170.5, 162.4 (d, J_CF = 247 Hz), 134.7, 132.8 (d, J_CF = 3 Hz), 131.0, 128.0 (d, J_CF = 8 Hz), 126.2, (d, J_CF = 2 Hz), 117.4, 115.5 (d, J_CF = 22 Hz), 49.8, 49.4, 46.7, 46.1, 36.5; IR (NaCl, neat) 2983, 1854, 1775, 1642, 1600, 1509, 1225, 1206 cm^-1; HRMS (FAB+) calcd for C_{12}H_{15}O_3F, 286.1005. Found 286.0994.
CH₂Cl₂. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography providing 0.465 g (25 %) of anhydride 2d as a yellow oil. Rf = 0.353 (85:15 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 5.99-5.85 (m, 1H), 5.61-5.43 (m, 2H), 5.15 (dd, 1H, J = 13.4, 2.6, 1.3 Hz), 5.14 (ddd, 1H, J = 14.0, 2.4, 1.1 Hz), 3.45 (qnt, 2H, J = 8.1 Hz), 3.01-2.89 (m, 2H), 2.06-1.95 (m, 3H), 1.39 (ddd, 1H, J = 12.8, 12.8, 12.8 Hz), 1.39-1.23 (m, 4H), 0.87 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 170.7, 170.5, 134.9, 133.4, 126.1, 116.8, 49.5, 49.4, 146.5, 36.5, 32.1, 31.3, 22.1, 13.9; IR (NaCl, neat) 2958, 2928, 1729, 1652, 1287, 1124 cm⁻¹; HRMS (FAB+) calcd for C₁₅H₂₃O₃, 249.1491, Found 249.1488.

(3aR,4S,6R,6aS)-4-((E)-5-oxohex-1-enyl)-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (2f). According to the general procedure, 2.0 g (12.18 mmol) cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (1) in 60 mL CH₂Cl₂ and 4.24 mL (36.6 mmol) 5-hexen-2-one were added via cannula to 0.517 g (0.609 mmol) Grubbs 2nd generation catalyst in 60 mL CH₂Cl₂. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography (8:2 Hex/EtOAc) providing 0.7346 g (0.465 m) 2f, δ 5.15 (ddd, 1H, J = 13.4, 2.6, 1.3 Hz), 5.12 (dd, 1H, J = 16.5, 1.0 Hz), 3.52-3.41 (m, 2H), 3.04-2.89 (m, 2H), 2.49 (t, 2H, J = 7.3 Hz), 2.29-2.20 (m, 2H), 2.10 (s, 3H), 1.96 (ddd, 1H, J = 12.4, 5.5, 5.5 Hz), 1.36 (dd, 1H, J = 13.2, 13.2, 13.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 208.1, 170.7, 170.6, 134.8, 131.4, 127.3, 117.0, 49.5, 49.4, 46.4, 45.5, 42.9, 36.2, 26.3; IR (NaCl, neat) 2960, 2923, 1854, 1775, 1644, 1418, 1362, 1326, 1259, 1206, 1163 cm⁻¹; HRMS (FAB+) calcd for C₁₅H₁₉O₄, 263.1283, Found 263.1274.

(3aR,4S,6R,6aS)-4-((E)-3-phenylprop-1-enyl)-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (2g). According to the general procedure, 1.5 g (9.14 mmol) cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (1) in 45 mL CH₂Cl₂ and 6.05 mL (45.7 mmol) allyl benzene were added via cannula to 0.376 g (0.457 mmol) Grubbs 1st generation catalyst in 45 mL CH₂Cl₂. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography providing 1.686 g (65 %) of anhydride 2g as a yellow oil. Rf = 0.66 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.19 (m, 5H) 5.95 (ddd, 1H, J = 16.6, 10.6, 7.5 Hz), 5.80-5.58 (m, 2H), 5.19 (dd, 1H, J = 9.5, 1.3 Hz), 5.17 (dd, 1H, J = 16.6, 0.9 Hz), 3.47 (dd, 1H, J = 13.3, 8.2 Hz), 3.46 (dd, 2H, J = 13.4, 8.1 Hz), 3.40 (d, 2H, J = 6.1 Hz), 3.06-2.92 (m, 2H), 2.05 (ddd, 1H, J = 12.6, 5.5, 5.5 Hz), 1.46 (ddd, 1H, J = 13.0, 13.0, 13.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 170.6, 139.9, 134.9, 132.0, 128.6, 128.4, 127.8, 126.1, 117.3, 49.5, 49.4, 46.6, 45.7, 38.9, 36.3; IR (NaCl, neat) 3084, 3027, 2960, 1854, 1775, 1642, 1602, 1495, 1453 cm⁻¹; HRMS (FAB+) calcd for C₁₈H₁₉O₃, 283.1334, Found 283.1324.
dicarboxylic anhydride (I) in 60 mL CH₂Cl₂ and 9.68 mL (60.9 mmol) allyltrimethylsilane were added via cannula to 0.501 g (0.609 mmol) Grubbs 1ˢᵗ generation catalyst in 60 mL CH₂Cl₂. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography (95:5 Hex/EtOAc) providing 0.136 mg (4 %) of anhydride 2h as a yellow oil. RF = 0.69 (65:35 Hex/EtOAc), ¹H NMR (300 MHz, CDCl₃) δ 5.94 (ddd, 1H, J = 17.0, 9.3, 7.5 Hz), 5.63 (ddd, 1H, J = 10.8, 9.7, 9.0 Hz), 5.25 (dd, 1H, J = 10.1, 8.6 Hz), 5.18 (dd, 1H, 9.7, 0.9 Hz), 5.17 (dd, 1H, J = 16.1, 0.9 Hz), 3.50 (dd, 1H, J = 8.5, 8.5 Hz) 3.38 (dd, 1H, J = 9.3, 9.3 Hz) 3.21 (ddt, 1H, J = 18.6, 12.6, 5.5 Hz) 3.05-2.93 (m, 1H), 1.97 (ddd, 1H, J = 13.0, 11.3, 5.5 Hz), 1.52 (d, 2H, J = 9.1 Hz), 1.36 (ddd, 1H, J = 12.9, 12.9, 12.9 Hz), 0.03 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 170.4, 135.0, 129.4, 123.2, 117.1, 49.5, 49.2, 46.8, 40.3, 37.5, 19.2, -1.9; IR (NaCl, neat) 3082, 2955, 2896, 1854,1776, 1643, 11420, 1324,1248, 1204, 1147 cm⁻¹. HRMS (FAB+) calcd for C₁₅H₂₃O₃Si, 279.1416, Found 279.1508.

(3aR,4S,6R,6aS)-4-((E)-3-(trimethylsilyl)prop-1-enyl)-6-vinyltetracyclo[4.1.1.0²⁷.⁵]octa-2,6-diene (2i). According to the general procedure, 2.0 g (12.18 mmol) cis-5-Norbornene-endo-2,3-dicarboxylic anhydride (I) in 60 mL CH₂Cl₂ and 9.68 mL (60.9 mmol) allyltrimethylsilane were added via cannula to 0.501 g (0.609 mmol) Grubbs 1ˢᵗ generation catalyst in 60 mL CH₂Cl₂. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography (95:5 Hex/EtOAc) providing 0.410 mg (12 %) of anhydride 4i as a yellow oil. RF = 0.66 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 5.94 (ddd, 1H, J = 17.4, 9.7, 7.5 Hz) 5.57 (ddd, 1H, J = 15.8, 8.1, 8.1 Hz), 5.31 (dd, 1H, J = 15.1, 8 Hz), 5.17 (dd, 1H, J = 11.2, 1.1 Hz), 5.16 (dd, 1H, J = 15.0, 1.3 Hz), 3.48 (dd, 1H, J = 15.9, 7.7 Hz), 3.40 (dd, 1H, J = 16.7, 8.2 Hz), 3.05-2.90 (m, 2H), 1.98 (ddd, 1H, J = 12.7, 11.4, 5.5 Hz), 1.49 (d, 2H, J = 8.2 Hz), 1.40 (ddd, 1H, J = 12.8, 12.8, 12.8 Hz), -0.4 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 170.6, 135.1, 129.1, 124.5, 117.0, 49.6, 49.5, 46.3, 46.3, 37.0, 22.9, -2.04; IR (NaCl, neat) 3082, 3012, 2955, 2896, 1854,1776, 1643, 1420, 1324,1248, 1204, 1147 cm⁻¹. HRMS (FAB+) calcd for C₁₅H₂₃O₃Si, 279.1416, Found 279.1534.

(3aR,4S,6R,6aS)-4-((E)-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (2l). According to the general procedure, 1.20 g (7.31 mmol) allyloxy(tert-butyldimethylsilyl) anhydride were added via cannula to 0.301 g (0.366 mmol) Grubbs 1ˢᵗ generation catalyst. The reaction was stirred overnight. The reaction was concentrated and purified by column chromatography (95:5 Hex/EtOAc) providing 340 mg (14 %) of anhydride 2l as a yellow oil. RF = 0.66 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 5.93 (ddd, 1H, J = 17.4, 9.5, 7.5 Hz), 5.78 (dd, 1H, 15.4, 7.2 Hz), 5.68 (dt, 1H, J = 15.4, 4.4 Hz), 5.18 (dd, 1H, J = 10.9, 0.8 Hz), 5.17 (dd, 1H, J = 16.1, 0.8 Hz), 4.16 (d, 2H, J = 4.4 Hz), 3.43 (dd, 1H, 5.8, 5.8 Hz), 3.49 (dd, 1H, J = 8.4, 8.4 Hz), 3.46 (dd, 1H, J = 8.1, 8.1 Hz), 3.06-2.93 (m, 2H), 2.04 (ddd, 1H, J = 12.8, 5.5, 5.5 Hz) 1.41 (ddd, 1H, J = 12.8, 12.8, 12.8 Hz), 0.90 (s, 9H), 0.07 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 170.5, 170.2, 134.7, 132.2, 126.5, 117.1, 63.4, 49.5,
49.4, 46.6, 45.4, 36.4, 26.0, 18.5, -5.1; IR (NaCl, neat) 2955, 2930, 2858, 1855, 1776, 1718, 1472, 1463, 1362, 1256, 1206; HRMS (FAB+) calcd for C_{18}H_{29}O_4Si, 337.1835, Found 337.1829.

(1R,2S,3R,5S)-methyl 5-(4-fluorostyryl)-2-propionyl-3-vinylcyclopentane-carboxylate (3a). According to the general procedure, 2.88 mg (0.01048 mmol) Ni(COD)_2 in 0.5 mL THF was treated with 0.018 mL (0.178 mmol) of Et_2Zn at 0 °C. 30.0 mg (0.105 mmol) of anhydride 2a in 0.5 mL in THF was added via cannula and the reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 34.5 mg (99 %) of methyl ester 3a as an oil. Rf = 0.67 (65:35 Hex/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.28 (dd, 2H, J = 8.7, 5.4 Hz), 6.95 (dd, 2H, J = 8.8, 8.8 Hz), 6.36 (d, 1H, J = 15.7 Hz), 6.22 (dd, 1H, J = 16, 8.3 Hz), 5.91 (dd, 1H, J = 17.1, 9.7, 9.7 Hz), 5.07 (dd, 1H, J = 17, 1.1 Hz), 4.99 (dd, 1H, J = 10.1, 1.9 Hz), 3.62 (s, 3H), 3.39 (dd, 1H, J = 9.1, 6.4 Hz), 3.15 (dd, 1H, J = 8.4, 6.8 Hz), 3.11-2.97 (m, 2H), 2.54-2.38 (m, 2H), 2.20-2.01 (m, 2H), 1.01 (t, 3H, J = 7.3 Hz); ^13C NMR (75 MHz, CDCl_3) δ 210.4, 172.9, 161.9 (d, ^1J_CF = 245 Hz), 139.2 133.7 4^J_CF = 2 Hz), 129.6, 129.3 (d, 6^J_CF = 2 Hz), 127.5 (d, 3^J_CF = 7 Hz), 115.9, 115.2 (d, 2^J_CF = 22 Hz), 58.1, 51.6, 51.5, 46.0, 45.0, 37.7, 37.6, 7.4; IR (NaCl, neat) 2925, 1733, 1683, 1652, 1641, 1509, 1549, 1225, 1158 cm^{-1}; HRMS (FAB+) calcd for C_{20}H_{24}FO_3, 331.1709, Found 331.1700.

(3aR,4S,6S,6aS)-4-((E)-2-cyclohexylvinyl)-6-ethyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (4). A round bottom flask was charged with 0.134 g (0.424 mmol) of the ketoacid derivative of 3a in 2 mL CH_2Cl_2 and 3 mL 0.5 M NaHCO_3. A solution of 0.257 g (1.01 mmol) of I_2 and 0.272 mg (1.64 mmol) KI in 2 mL water was added dropwise to the reaction mixture and the resulting deep red biphasic mixture was stirred in the dark for 17 h. The reaction was quenched with 15 mL of sat. NaHSO_3. The organic layer was separated and the aqueous layer extracted with DCM. The organic layers were combined, washed with sat. NaHCO_3, brine, dried over MgSO_4, filtered and concentrated in vacuo to provide a colorless oil, which was purified by column chromatography to provide 0.122 g (65 %) of desired product. Rf = 0.48 (65:35 Hex/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.35 (ddd, 2H, J = 8.8, 5.5, 2.2 Hz), 6.99 (ddd, 2H, J = 8.6, 6.8, 2.0 Hz), 6.50 (ddd, 1H, J = 15.7, 7.3 Hz), 6.41 (d, 1H, J = 15.7 Hz), 4.12 (ddd, 1H, J = 7.3, 3.6, 3.6 Hz), 3.31 (dd, 2H, 1H, J = 10.2, 6.4, Hz), 3.20-3.05 (m, 2H), 2.89-2.78 (m, 1H), 2.35-2.25 (m, 1H), 2.00 (dq, 1H, J = 14.3, 6.4 Hz), 1.98 (dq, 1H, J = 14.4, 7.3 Hz), 1.63 (dd, 2H, J = 12.8, 9.9 Hz), 1.03 (t, 3H, J = 7.5 Hz); ^13C NMR (100 MHz, CDCl_3) δ 174.2, 162.2 (d, ^1J_CF = 247 Hz), 133.1 (d, 6^J_CF = 3 Hz), 130.1, 127.9 (d, 3^J_CF = 8 Hz), 127.3 (d, 4^J_CF = 2 Hz), 117.9, 115.3 (d, 2^J_CF = 21 Hz), 86.0, 53.8, 51.6, 50.3, 50.2, 37.9, 30.8, 10.3, 8.1; IR (NaCl, neat) 2972, 2938, 1765, 1600, 1508, 1461, 1330, 1298, 1224, 1158 cm^{-1}; HRMS (FAB+) calcd for C_{19}H_{24}F_3O_3I, 443.0520. Found 443.0511.
(1R,2S,3R,5S)-methyl 2-propionyl-5-styryl-3-vinylcyclopentane-carboxylate (3b). According to the general procedure, 4.1 mg (0.014 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.026 mL (0.253 mmol) of Et₂Zn at 0 °C. 40.0 mg (0.149 mmol) of anhydride 2b in 0.5 mL in THF was added via cannula and the reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 39.9 mg (86 %) of methyl ester 3b as an oil. Rf = 0.62 (65:35 Hex/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, 2H, J = 8.3 Hz), 7.26, (t, 2H, J = 7.8 Hz), 7.17 (t, 1H, J = 7.3 Hz), 6.40 (d, 1H, J = 15.8 Hz), 6.27 (dd, 1H, J = 15.7, 8.3 Hz), 5.92 (dd, 1H, J = 17.1, 9.8, 9.8 Hz), 5.06 (dd, 1H, J = 17.0, 0.9 Hz), 4.98 (dd, 1H, J = 10.0, 0.9 Hz), 3.61 (s, 3H), 3.37 (dd, 1H, J = 9.4, 6.8 Hz), 3.13 (dd, 1H, J = 8.3, 8.3 Hz), 3.07 (dd, 1H, J = 9.4, 8.9, 8.3 Hz), 3.00 (dd, 1H, J = 8.5, 8.5, 8.5 Hz), 2.53-2.35 (m, 2H), 2.18-2.03 (m, 2H), 1.0 (t, 3H, J = 2.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 201.5, 173.2, 139.5, 137.3, 131.0, 129.8, 128.4, 127.1, 126.2, 115.8, 58.2, 51.4, 45.8, 45.2, 37.7, 37.4, 7.3; IR (NaCl, neat) 2936, 1735, 1711, 1493, 1435, 1383, 1198, 1173 cm⁻¹; HRMS (FAB+) calcd for C₂₀H₂₅O₃, 313.1804, Found 313.1808.

(1R,2S,3R,5S)-methyl 5-(4-methoxystyril)-2-propionyl-3-vinylcyclopentane-carboxylate (3c). According to the general procedure, 4.31 mg (0.017 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.034 mL (0.335 mmol) of Et₂Zn at 0 °C. 50.0 mg (0.168 mmol) of anhydride 2c in 0.5 mL in THF was added via cannula and the reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 55 mg (96 %) of methyl ester 3c as an oil. Rf = 0.55 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.26 (d, 2H, J = 8.8 Hz), 6.82 (d, 2H, J = 8.7 Hz), 6.36 (d, 1H, J = 16 Hz), 6.13 (dd, 1H, J = 15.8, 8.4 Hz), 5.95 (dd, 1H, J = 17.0, 9.6, 9.6 Hz), 5.07 (dd, 1H, J = 16.8, 1.7 Hz), 4.99 (dd, 1H, J = 10.0, 1.9 Hz), 3.79 (s, 3H), 3.64 (s, 3H), 3.39 (dd, 1H, J = 9.4, 6.6 Hz), 3.14 (m, 2H), 3.00 (dd, 1H, J = 10.3, 8.3 Hz), 2.6-2.3 (m, 2H), 2.19-2.04 (m, 2H), 1.01 (t, 3H, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 210.5, 173.3, 158.9, 139.7, 130.4, 127.5, 127.3, 115.7, 113.8, 58.3, 55.3, 51.4, 45.8, 45.3, 37.8, 37.3, 7.3; IR (NaCl, neat) 2937, 2836, 2359, 1734, 1711, 1639, 1607, 1577, 1512, 1461, 1435, 1421, 1384, 1360, 1300, 1250, 1197, 1175 cm⁻¹; HRMS (FAB+) calcd for C₂₁H₂₆O₄, 342.1831. Found 342.1844.

(1R,2S,3R,5S)-methyl 5-((E)-hex-1-enyl)-2-propionyl-3-vinylcyclopentane-carboxylate (3d). According to the general procedure, 3.32 mg (0.012 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.021 mL (0.205 mmol) of Et₂Zn at 0 °C. 30.0 mg (0.121 mmol) of anhydride 2d in 0.5 mL in THF was added via cannula and the reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 35.0 mg (99 %) of methyl ester 3d as an oil. Rf = 0.50 (85:15 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 5.95 (ddd, 1H, J = 17.0, 9.8, 9.8 Hz), 5.51-5.39 (m, 2H), 5.03 (dd, 1H, J = 17, 1.9 Hz), 4.96 (dd, 1H, J = 10.0, 1.9 Hz), 3.67 (s, 3H),
the reaction was stirred for 4 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 35.5 mg (50 %) of methyl ester 3f as an oil. Mixture of cis and trans isomers, major isomer reported: Rf = 0.67 (65:35 Hex/ EtOAc); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.91 (ddd, 1H, \(J = 17.3, 9.8, 9.8 \text{ Hz}\)), 5.94-5.31 (m, 2H), 5.00 (dd, 1H, \(J = 17.1, 2.0 \text{ Hz}\)), 4.96 (dd, 1H, \(J = 10.1, 2.0 \text{ Hz}\)), 3.63 (s, 3H), 3.34 (ddd, 1H, \(J = 16.2, 9.6, 6.6 \text{ Hz}\)), 3.09-2.98 (m, 2H), 2.53-2.22 (m, 7H), 2.13 (d, 3H), 2.06 (ddd, 1H, \(J = 16.2, 13.8, 8.1 \text{ Hz}\)), 1.98-1.86 (m, 1H), 0.99 (t, 3H, \(J = 7.2\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 210.6, 208.6, 173.7, 140.0, 130.6, 130.3, 115.9, 58.6, 51.4, 45.9, 45.0, 43.5, 37.9, 37.4, 30.2, 26.8, 22.1, 7.5; IR (NaCl, neat) 2936, 1733, 1714, 1639, 1437, 1361, 1198, 1166; HRMS (FAB+) calcd for C\(_{20}\)H\(_{31}\)O\(_3\), 319.2273. Found 319.2264.

(1R,2S,3R,5S)-methyl 5-((E)-5-oxohex-1-enyl)-2-propionyl-3-vinylcyclopentanecarboxylate (3g). According to the general procedure, 2.92 mg (0.01063 mmol) Ni(COD)\(_2\) in 0.5 mL THF was treated with 0.019 mL (0.181 mmol) of Et\(_2\)Zn at 0 °C. 30.0 mg (0.106 mmol) of anhydride 2g in 0.5 mL in THF was added via cannula and the reaction was stirred for 4 h at 0 °C. Upon work-up, the acid was converted to the

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S-7
corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 33 mg (95 %) of methyl ester 3g as an oil. Rf = 0.60 (65:35 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.19-7.14 (m, 3H), 5.94 (ddd, 1H, J = 17.3, 9.6, 9.6 Hz), 5.67-5.56 (m, 2H), 5.04 (dd, 1H, J = 18.4, 1.9 Hz), 4.97 (dd, 1H, J = 10.0, 1.9 Hz), 3.61 (s, 3H), 3.32 (d, 2H, J = 5.6 Hz), 3.09-2.99 (m, 2H), 2.85 (ddd, 1H, J = 14.9, 10.4, 7.9), 2.48 (dq, 1H, J = 17.9, 7.4 Hz), 2.38 (dq, 1H, J = 17.9, 7.2 Hz), 2.14-1.95 (m, 2H), 1.00 (t, 3H, J = 7.2 Hz); 13C NMR (75 MHz, CDCl₃) δ 210.4, 173.4, 140.6, 139.8, 130.9, 130.6, 128.5, 128.3, 125.9, 115.6, 58.4, 51.3, 51.2, 45.6, 44.7, 38.9, 37.7, 37.2, 7.3 ; IR (NaCl, neat) 3026, 2976, 2948, 1735, 1712, 1495, 1453, 1435, 1198, 1168 cm⁻¹; HRMS (FAB+) calcld for C_{21}H_{23}O₃, 327.1960, Found 327.1971.

(1R,2S,3R,5S)-methyl 2-propionyl-5-((Z)-3-(trimethylsilyl)prop-1-enyl)-3-vinylcyclopentanecarboxylate (3h). According to the general procedure, 3.78 mg (0.015 mmol) Ni(acac)₂ and 41 mg (0.147 mmol) of anhydride 2h in 1.5 mL THF were treated with 0.026 mL (0.250 mmol) of Et₂Zn at 0 °C and the reaction was stirred for 30 min at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 32 mg (66 %) of methyl ester 3h as an oil. Rf = 0.76 (65:35 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 5.98 (ddd, 1H, J = 17.2, 9.7, 9.7 Hz), 5.47-5.38 (m, 1H), 5.22 (dd, 1H, J = 9.9, 9.7 Hz), 5.02 (dd, 1H, J = 17.2, 1.8 Hz), 4.94 (dd, 1H, J = 10.0, 1.8 Hz), 3.68 (s, 3H), 3.35 (dd, 1H, J = 9.9, 6.4 Hz), 3.14-2.94 (m, 3H), 2.47 (dq, 1H, J = 18.5, 7.7 Hz), 2.34 (dq, 1H, J = 17.9, 7.1 Hz), 2.08 (ddd, 1H, J = 10.6, 7.9, 7.9, 7.9 Hz), 1.97-1.86 (m, 1H), 1.51 (dd, 1H, J = 14.1, 10.0 Hz), 1.42 (dd, 1H, J = 13.9, 5.8 Hz), 0.98 (t, 3H, J = 7.1 Hz), -0.04 (s, 9H); 13C NMR (75 MHz, CDCl₃) δ 210.0, 173.8, 140.3, 127.4, 126.4, 115.3, 58.9, 51.2, 50.6, 45.6, 39.4, 38.6, 36.9, 18.9, 7.3, -1.9; IR (NaCl, neat) 3074, 2953, 1736, 1713, 1641, 1435, 1381, 1248, 1198, 1166 cm⁻¹; HRMS (FAB+) calcld for C_{18}H_{30}O₃Si, 323.2042. Found 323.2250.

(1R,2S,3R,5S)-methyl 2-propionyl-5-((E)-3-(trimethylsilyl)prop-1-enyl)-3-vinylcyclopentanecarboxylate (3i). According to the general procedure, 8.8 mg (0.034 mmol) Ni(acac)₂ and 95 mg (0.341 mmol) of anhydride 2i in 3.4 mL THF was treated with 0.059 mL (0.580 mmol) of Et₂Zn at 0 °C. The reaction was stirred for 30 min at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 28 mg (70 %) of methyl ester 3i as an oil. Rf = 0.79 (65:35 Hex/EtOAc); 1H NMR (400 MHz, CDCl₃) δ 5.97 (ddd, 1H, J = 17.2, 9.9, 9.7 Hz), 5.45 (ddd, 1H, J = 15.2, 8.0, 8.0 Hz), 5.21 (dd, 1H, J = 15.0, 8.0 Hz), 5.00 (dd, 1H, J = 17.0, 1.8 Hz), 4.92 (dd, 1H, J = 10.1, 1.7 Hz), 3.66 (s, 3H), 3.31 (dd, 1H, J = 10.2, 6.6 Hz), 3.10 (ddd, 1H, J = 18.1, 8.8, 8.8, 8.8 Hz), 2.94 (dd, 1H, J = 7.1, 7.1 Hz), 2.73 (ddd, 1H, J = 15.6, 11.2, 7.7 Hz), 2.46 (dq, 1H, J = 17.2, 7.3 Hz), 2.31 (dq, 1H, J = 17.7, 7.1 Hz), 2.05 (ddd, 1H, J = 16.1, 13.0, 8.0 Hz), 1.95 (dd, 1H, J = 11.7, 8.9 Hz), 1.38 (d, 2H, J = 7.9 Hz), 0.96 (t, 3H, J = 7.1 Hz), -0.053 (s, 9H); 13C NMR (75 MHz, CDCl₃) δ 209.8, 173.8, 140.6, 128.3, 127.1, 115.2, 59.0, 51.2, 51.0, 45.8, 45.3, 38.3, 36.6, 22.7, 7.3, -2.1; IR (NaCl, neat) 3074, 2953, 1737, 1714,
(1R,2S,3R,5S)-methyl 2-propionyl-5-((Z)-3-(tributylstannyl)-prop-1-enyl)-3-vinylcyclopentanecarboxylate (3j). According to the general procedure, 1.91 mg (0.00695 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.012 mL (0.118 mmol) of Et₂Zn at 0 °C. 30.0 mg (0.108 mmol) of anhydride 2j in 0.5 mL in THF was added via cannula and the reaction was stirred overnight at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 39.9 mg (64 %) of methyl ester 3j as an oil. Rf = 0.82 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 6.00 (dd, 1H, J = 17.1, 9.7, 9.7 Hz), 5.57 (dd, 1H, J = 9.7, 9.7 Hz), 5.25 (dd, 1H, J = 16.6, 1.8 Hz), 5.01 (dd, 1H, J = 10.6, 9.3 Hz), 4.95 (dd, 1H, J = 9.9, 1.9 Hz), 3.69 (s, 3H), 3.35 (dd, 1H, J = 9.8, 6.2 Hz), 3.16-2.95 (m, 3H), 2.48 (dq, 1H, J = 17.9, 7.3 Hz), 2.34 (dq, 1H, J = 17.9, 7.1 Hz), 2.14-2.04 (m, 1H), 1.92 (dd, 1H, J = 12.1, 10.8, 8.8 Hz), 1.71 (m, 2H), 1.53-1.42 (m, 6H), 1.36-1.24 (m, 1H), 0.99 (t, 3H, J = 7.3 Hz), 0.91-0.86 (t, 9H, J = 7.3 Hz), 0.89-0.83 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.9, 173.9, 140.5, 130.4, 122.9, 115.3, 59.1, 51.3, 50.4, 45.5, 38.6, 36.7, 29.2, 28.9, 27.4, 14.1, 13.7, 9.2, 7.3; HRMS (FAB+) calcd for C₂₇H₄₇O₃Sn, 539.2592. Found 539.2601.

(1R,2S,3R,5S)-methyl 2-propionyl-5-((E)-3-(tributylstannyl)-prop-1-enyl)-3-vinylcyclopentanecarboxylate (3k). According to the general procedure, 2.99 mg (0.01088 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.019 mL (0.185 mmol) of Et₂Zn at 0 °C. 53.9 mg (0.109 mmol) of anhydride 2k in 0.5 mL in THF was added via cannula and the reaction was stirred for 12 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 39.9 mg (68 %) of methyl ester 3k as an oil. Rf = 0.90 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 6.00 (ddd, 1H, J = 17.0, 9.8, 9.8 Hz), 5.61 (dd, 1H, J = 15.5, 8.8, 8.8 Hz), 5.16 (dd, 1H, J = 15.0, 8.6 Hz), 5.01 (dd, 1H, J = 17.0, 1.9 Hz), 4.93 (dd, 1H, J = 10.0, 2.1 Hz), 3.70 (s, 3H), 3.34 (dd, 1H, J = 10.4, 6.6 Hz), 3.09 (dd, 1H, J = 8.8, 8.8, 8.8 Hz), 2.92 (dd, 1H, J = 6.8, 6.8 Hz), 2.71 (ddd, 1H, J = 15.5, 11.5, 7.8 Hz), 2.47 (dq, 1H, J = 17.9, 7.2 Hz), 2.31 (dq, 1H, J = 17.7, 7.2 Hz), 2.08-1.91 (m, 2H), 1.67 (dd, 1H, J = 10.7, 8.7 Hz), 1.68 (dd, 1H, J = 10.7, 8.7 Hz), 1.50-1.42 (m, 6H), 1.33-1.24 (m, 6H), 0.98 (t, 3H, J = 7.2 Hz), 0.90-0.60 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 209.9, 173.9, 140.7, 131.6, 123.6, 115.1, 59.1, 51.3, 51.0, 46.1, 45.3, 38.6, 36.6, 29.1, 27.3, 14.3, 13.7, 9.1, 7.3; IR (NaCl, neat) 2955, 2927, 2871, 2853, 1737, 1714, 1461, 1434, 1377, 1197, 1166 cm⁻¹; HRMS (FAB+) calcd for C₂₇H₄₇O₃Sn, 539.2592, Found 539.2611.

(1R,2S,3R,5S)-methyl 5-((E)-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-2-propionyl-3-vinylcyclopentanecarboxylate (3l). According to the general procedure, 2.45 mg (0.0089 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.016 mL Et₂Zn at 0 °C. 30.0 mg (0.089 mmol) of anhydride 2l in 0.5 mL in THF was added via cannula and the
reaction was stirred for 12 h at 0 °C. The reaction was quenched with 10 mL 1M AcOH and 10 mL ether. The layers were separated and the aqueous layer was extracted with ether (2 x 10 mL) and combined organics were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 25 mg (73 %) of methyl ester 3l as an oil in an 80:20 mixture of regioisomers. Rf = 0.70 (65:35 Hex/EtOAc); Mixture of inseparable regioisomers. See attached spectra for 1H NMR (300 MHz, CDCl₃); 13C NMR (75 MHz, CDCl₃) δ 210.3, 210.0, 174.3, 173.65, 140.9, 140.3, 137.1, 129.9, 116.0, 115.8, 115.5, 63.9, 59.6, 58.9, 51.5, 51.8, 51.1, 49.3, 45.7, 45.2, 44.9, 42.4, 38.0, 37.9, 37.2, 36.7, 35.3, 26.2, 7.6; IR (NaCl, neat) 2950, 1735, 1712, 1165 cm⁻¹; HRMS (FAB+) calcd for C₁₉H₂₁O₄; Found 267.1596, Found 267.1401.

(1R,2S,3R,5S)-methyl 2-acetyl-5-(4-fluorostyryl)-3-vinylcyclopentanecarboxylate (5a). According to the general procedure, 2.88 mg (0.01048 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.089 mL (1.0 M solution in hexane, 0.186 mmol) of Me₂Zn at 0 °C. 30.0 mg (0.105 mmol) of anhydride 2a in 0.5 mL in THF was added via cannula and the reaction was stirred for 15 min at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 31 mg (94 %) of methyl ester 5a as an oil. Rf = 0.52 (65:35 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 7.28 (dd, 2H, J = 8.8, 5.7 Hz) 6.96 (dd, 2H, J = 8.6, 8.6 Hz) 6.37 (d, 1H, J = 15.8 Hz) 6.17 (dd, 1H, J = 15.9, 8.2 Hz), 6.00 (dd, 1H, J = 17, 9.7, 9.7 Hz), 5.10 (ddd, 1H, J = 17, 1.8, 1.1 Hz), 5.02 (dd, 1H, J = 10.1, 1.8 Hz) 3.63 (s, 3H) 3.41 (dd, 1H, J = 9.6, 6.6 Hz), 3.14 (dd, 1H, J = 9.5, 9.5 Hz), 3.11-2.95 (m, 2H), 2.22-2.01 (m, 2H), 2.15 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 207.5, 173.0, 161.9 (d, JCF = 245 Hz), 139.4, 133.3 (d, JC₅ = 3 Hz), 129.7, 129.3 (d, JC₅ = 2 Hz), 127.5 (d, JC₅ = 8 Hz), 115.9, 115.2 (d, JC₅ = 22 Hz), 59.4, 51.5, 51.4, 45.5, 45.0, 37.7, 31.6; IR (NaCl, neat) 2953, 1733, 1709, 1642, 1602, 1509, 1436, 1357, 1225 cm⁻¹; HRMS (FAB+) calcd for C₁₉H₂₁O₄, Found 210.1596, Found 210.1401.

(1R,2S,3R,5S)-methyl 5-(4-fluorostyryl)-2-isobutyryl-3-vinylcyclopentanecarboxylate (5b). According to the general procedure, 2.88 mg (0.023 mmol) Ni(COD)₂ in 0.5 mL THF was treated with 0.178 mL (1.0 M solution in toluene, 0.178 mmol) of t-PrZn at 0 °C. 30.0 mg (0.105 mmol) of anhydride 2a in 0.5 mL in THF was treated with 0.089 mL (1.0 M solution in hexane, 0.186 mmol) of t-PrZn at 0 °C. The reaction was stirred for 12 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 20 mg (55 %) of methyl ester 5b as an oil. Rf = 0.64 (65:35 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 7.29 (dd, 2H, J = 7.1, 5.5, 2.2 Hz), 6.97 (dd, 2H, J = 9.6, 5.0, 2.8 Hz), 6.37 (d, 1H, J = 15.9 Hz), 6.21 (dd, 1H, J = 15.9, 8.3 Hz), 5.90 (ddd, 1H, J = 17.0, 9.7, 9.7 Hz), 5.06 (dd, 1H, J = 16.8, 1.8 Hz), 4.99 (dd, 1H, J = 9.8, 1.8 Hz), 3.63 (s, 3H), 3.18-2.97 (m, 4H), 2.68 (ddd, 1H, J = 13.7, 6.7, 6.7 Hz), 2.20-2.01 (m, 2H), 1.13 (d, 3H, J = 7.1 Hz), 1.00 (d, 3H, J = 6.7 Hz); 13C NMR (75 MHz, CDCl₃) δ 213.8, 173.1, 162.0 (d,
$^{1}J_{CF} = 246$ Hz, 139.6, 133.3 (d, $^{4}J_{CF} = 3$ Hz), 129.7, 127.6 (d, $^{3}J_{CF} = 8$ Hz), 115.7, 115.3 (d, $^{2}J_{CF} = 22$ Hz), 56.4, 51.5, 51.4, 46.2, 45.1, 41.3, 37.7, 19.2, 16.7; IR (NaCl, neat) 3073, 2970, 2935, 2873, 1735, 1709, 1653, 1637, 1616, 1602, 1559, 1509, 1466, 1458, 1436 cm$^{-1}$; HRMS (FAB+) calcd for C$_{21}$H$_{26}$F$_{3}$O$_{3}$, 345.1866. Found 345.1868.

![Structural formula](image)

(1R,2S,3R,5S)-methyl 2-benzoyl-5-(4-fluorostyryl)-3-vinylcyclopentanecarboxylate (5c). According to the general procedure, 2.88 mg (0.01048 mmol) Ni(COD)$_{2}$ in 0.5 mL THF was treated with 0.039 mg (0.178 mmol) of Et$_{2}$Zn at 0 °C. 30.0 mg (0.105 mmol) of anhydride 2a in 0.5 mL in THF was added via cannula and the reaction was stirred for 15 min at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/ EtOAc) providing 34 mg (86 %) of methyl ester 5c as an oil. Rf $= 0.59$ (65:35 Hex/EtOAc); $^{1}$H NMR (300 MHz, CDCl$_{3}$) δ 7.89 (d, 2H, $J = 7.2$ Hz), 7.54 (t, 2H, $J = 7.7$ Hz), 7.44 (t, 2H, $J = 7.5$ Hz), 7.32 (dd, 2H, $J = 8.5$, 5.9 Hz), 6.98 (dd, 2H, $J = 8.7$, 8.7 Hz) 6.44 (d, 1H, $J = 15.7$ Hz), 6.27 (dd, 1H, $J = 15.7$, 8.0 Hz), 5.86 (ddd, 1H, 16.9, 9.7, 9.7 Hz), 3.73 (d, 1H, $J = 16.1$ Hz), 4.69 (d, 1H, $J = 8.6$ Hz), 4.24 (dd, 1H, $J = 9.7$, 6.6 Hz), 3.68 (s, 3H), 3.31-3.24 (m, 2H), 3.12 (ddd, 1H, $J = 17.4$, 8.8, 8.8 Hz), 2.24 (apt t, 2H, $J = 9.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_{3}$) δ 199.3, 172.2, 161.1 (d, $^{1}J_{CF} = 246$ Hz), 138.8, 137.5, 133.3, 132.7, 129.9, 129.2, 128.3, 127.6 (d, $^{3}J_{CF} = 8$ Hz), 115.7, 115.2 (d, $^{2}J_{CF} = 22$ Hz), 54.5, 51.8, 51.5, 46.9, 45.4, 38.2; IR (NaCl, neat) 3070, 2949, 1733, 1679, 1640, 1598, 1581, 1448, 1436, 1385, 1342, 1223, 1175, 1158 cm$^{-1}$; HRMS (FAB+) calcd for C$_{24}$H$_{26}$F$_{3}$O$_{3}$, 379.1709. Found 379.1695.

![Structural formula](image)

(1R,2S,3R,5S)-methyl 2-(4-ethoxy-4-oxobutanoyl)-5-(4-fluorostyryl)-3-vinylcyclopentanecarboxylate (5d). According to the general procedure, 3.36 mg (0.012 mmol) Ni(COD)$_{2}$ in 0.75 mL THF was treated with 0.016 mL i-Pr$_{2}$Zn (0.550 mmol) at 0 °C. 35 mg (0.122 mmol) of anhydride 2a in 0.5 mL in THF was added via cannula and the reaction was stirred for 12 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 39 mg (79 %) of methyl ester 5d as an oil. Rf $= 0.50$ (65:35 Hex/EtOAc); $^{1}$H NMR (300 MHz, CDCl$_{3}$) δ 7.23 (dd, 2H, $J = 8.3$, 5.6 Hz), 6.96 (t, 2H, $J = 8.7$ Hz), 6.36 (d, 1H, $J = 15.7$ Hz), 6.17 (dd, 1H, $J = 15.7$, 8.3 Hz), 5.97 (ddd, 1H, $J = 17.0$, 9.6, 9.6 Hz), 5.10 (dd, 1H, $J = 17.0$, 1.2 Hz), 5.02 (dd, 1H, $J = 9.8$, 1.1 Hz), 4.12 (q, 2H, $J = 7.0$ Hz), 3.61 (s, 3H), 3.44 (dd, 1H, $J = 9.1$, 6.6 Hz), 3.18 (dd, 1H, $J = 8.3$, 8.3 Hz), 3.13-2.99 (m, 2H), 2.84-2.59 (m, 3H), 2.49 (ddd, 1H, $J = 13.0$, 6.4, 6.4 Hz), 2.16 (ddd, 1H, $J = 13.2$, 8.1, 8.1 Hz), 2.05 (ddd, 1H, $J = 13.0$, 10.0, 10.0 Hz), 1.24 (t, 3H, $J = 7.3$ Hz); $^{13}$C NMR (75 MHz, CDCl$_{3}$) δ 208.2, 173.1, 172.9, 162.0 (d, $^{1}J_{CF} = 246$ Hz), 139.3, 133.4 (d, $^{4}J_{CF} = 3$ Hz), 129.8, 129.5, 127.6 (d, $^{3}J_{CF} = 9$ Hz), 116.2, 115.3 (d, $^{2}J_{CF} = 21$ Hz), 60.5, 58.5, 51.5, 51.4, 45.8, 44.9, 38.9, 37.6, 28.0, 14.2; IR (NaCl, neat) 2965, 2933, 2878, 1853, 1778, 1602, 1510, 1461, 1223, 1209, 1159, 1078, 1051 cm$^{-1}$; HRMS (FAB+) calcd for C$_{25}$H$_{28}$F$_{2}$O$_{3}$, 403.1921. Found 403.1931.
(3αS,4αS,6αS,6αR)-4-ethyl-6-(4-fluorostyryl)tetrahydro-1H-cyclopenta[1,3(3αH)]dione (10a). According to the general procedure, 0.300 g (1.048 mmol) of anhydride 2a and 29 mg (0.031 mmol) RuHCl(PPh₃)₃ was treated with 5.24 mL ethyl acetate and 5.24 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.285 g (94%) as a white solid. Rf = 0.393 (85:15 Hex/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (ddd, 2H, J = 8.9, 5.3, 2.1 Hz), 7.00 (ddd, 2H, J = 8.6, 8.6, 2.0 Hz), 6.45 (d, 1H, J = 15.8 Hz), 6.20 (dd, 1H, J = 15.8, 7.9 Hz), 3.53 (dd, 1H, J = 8.8, 8.5 Hz), 3.48 (dd, 1H, J = 8.8, 8.5 Hz), 3.08 (dddd, 1H, J = 14.0, 8.5, 5.5, 5.5 Hz), 2.32–2.21 (m, 1H), 2.18 (ddd, 1H, J = 12.3, 5.5, 5.5 Hz), 1.82 (ddq, 1H, J = 14.3, 7.5, 7.5 Hz), 1.47 (ddq, 1H, J = 14.9, 7.4, 7.4 Hz), 1.24 (ddd, 1H, J = 12.8, 12.8, 12.8 Hz), 1.06 (t, 3H, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 171.0, 136.7, 131.8, 128.5, 127.6, 126.9, 126.4, 50.0, 48.2, 46.1, 45.7, 37.2, 23.8, 13.2; IR (NaCl, neat) 3082, 2964, 2932, 2876, 1852, 1779, 1506, 1494, 1457, 1162, 1137; HRMS (FAB+) calcd for C₁₇H₁₇FO₃ 288.1154. Found 288.1162.

(3αS,4αS,6αS,6αR)-4-ethyl-6-styryltetrahydro-1H-cyclopenta[c]furan-1,3(3αH)-dione (10b). According to the general procedure, 0.100 g (0.373 mmol) of anhydride 2b and 10.7 mg (0.011 mmol) RuHCl(PPh₃)₃ was treated with 1.9 mL ethyl acetate and 1.9 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.086 g (85%) as a white solid. Rf = 0.67 (65:35 Hex/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, 2H, J = 7.9 Hz), 7.29 (t, 2H, J = 7.2 Hz), 7.24–7.20 (m, 1H), 6.48 (d, 1H, J = 16.0 Hz), 6.27 (ddd, 1H, J = 15.7, 7.9 Hz), 3.51 (t, 1H, J = 8.4 Hz), 3.44 (t, 1H, J = 9.1 Hz), 3.10–3.01 (m, 1H), 2.29–2.19 (m, 1H), 2.18–2.12 (m, 1H), 1.80 (ddq, 1H, J = 12.0, 2.7 Hz), 1.44 (ddq, 1H, J = 12.7 Hz), 1.22 (q, 1H, J = 1.27 Hz), 1.04 (t, 3H, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 171.0, 136.7, 131.8, 128.5, 127.6, 126.4, 50.0, 48.2, 46.1, 45.6, 37.3, 23.8, 13.2; IR (NaCl, neat) 3082, 2964, 2932, 2876, 1852, 1779, 1506, 1494, 1457, 1449, 1208; HRMS (FAB+) calcd for C₁₇H₁₉O₃, 271.1334, Found 271.1322.

(3αS,4αS,6αS,6αR)-4-ethyl-6-(4-methoxystyryl)tetrahydro-1H-cyclopenta[c]furan-1,3(3αH)-dione (10c). According to the general procedure, 0.100 g (0.335 mmol) of anhydride 2c and 9.3 mg (0.011 mmol) RuHCl(PPh₃)₃ was treated with 1.7 mL ethyl acetate and 1.7 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.069 g (69%) as a white solid. Rf = 0.52 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, 2H, J = 8.5 Hz), 6.85 (d, 2H, J = 8.3 Hz), 6.43 (d, 1H, J = 15.8), 6.13 (dd, 1H, J = 15.8, 8.1 Hz), 3.81 (s, 3H), 3.47 (dd, 1H, J = 8.9, 8.4 Hz), 3.45 (dd, 1H, J = 8.7, 8.6 Hz), 3.06 (ddt, 1H, J = 18.4, 7.9, 5.8 Hz), 2.30–2.21 (m, 1H), 2.15 (dt, 1H, J = 12.8, 5.3 Hz), 1.82 (dq, 1H, J = 14.1, 7.1 Hz), 1.41 (dq, 1H, J = 15.1, 7.7 Hz), 1.23 (ddd, 1H, J = 8.7, 7.8, 7.8 Hz), 1.06 (t, 3H, J = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 171.0, 159.2, 131.3, 129.5, 127.6, 124.6, 114.0,
(3aR,4S,6S,6aS)-4-((E)-2-cyclohexyvinyl)-6-ethyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (10e). According to the general procedure, 0.030 g (0.109 mmol) of anhydride 2e and 3.2 mg (0.003 mmol) RuHCl(PPh₃)₃ was treated with 0.5 mL ethyl acetate and 0.5 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.027 g (89 %) 10e as a white solid. Rf = 0.60 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 5.50 (dd, 1H, J = 15.5, 7.1 Hz), 5.44 (dd, 1H, J = 16.2, 7.5 Hz), 3.43-3.38 (m, 2H), 2.90-2.82 (m, 1H), 2.22-2.09 (m, 2H), 2.04 (dd, 1H, J = 12.6, 5.4, 5.4 Hz), 2.00-1.92 (m, 1H), 1.78-1.59 (m, 7H), 1.42 (ddq, 1H, J = 14.5, 7.2, 7.2 Hz) 1.27-1.16 (m, 3H), 1.16-0.95 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 171.4, 170.9, 138.9, 138.9, 124.3, 49.7, 48.3, 45.8, 45.5, 40.4, 37.2, 32.8, 32.8, 26.1, 25.9, 23.6, 13.1; IR (NaCl, neat) 2928, 2853, 1777, 1731, 1449, 1205, 918; HRMS (FAB+) calcd for C₁₇H₂₃O₃, 277.1804. Found 277.1793.

(3aS,4S,6S,6aR)-4-ethyl-6-((E)-3-phenylprop-1-enyl)tetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (10g). According to the general procedure, 0.100 g (0.356 mmol) of anhydride 2g and 9.7 mg (0.011 mmol) RuHCl(PPh₃)₃ was treated with 1.8 mL ethyl acetate and 1.8 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.041 g (40 %) 10g as a white solid. Rf = 0.66 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.53-7.19 (m, 5H), 5.72 (dd, 1H, J = 15.2, 7.1, 5.7 Hz), 5.63 (dd, 1H, J = 15.4, 6.2 Hz) 3.43 (dd, 2H, J = 13.1, 8.0 Hz), 3.43 (m, 2H), 2.97-2.86 (m, 1H), 2.25-2.13 (m, 1H), 2.09 (dd, 1H, J = 18.7, 5.4, 5.4 Hz), 1.79 (ddq, 1H, J = 15.1, 8.5, 8.5 Hz), 1.43 (ddq, 1H, J = 15.7, 9.0, 9.0 Hz), 1.14 (ddq, 1H, J = 13.9, 13.9, 13.9 Hz), 1.03 (t, 3H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 171.2, 170.9, 140.0, 131.6, 128.6, 128.4, 128.3, 126.1, 49.7, 48.3, 45.8, 45.5, 39.0, 37.1, 23.7, 13.2.

(3aR,4S,6S,6aS)-4-((E)-3-(benzoyloxy)prop-1-enyl)-6-ethyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (10m). According to the general procedure, 0.119 g (0.381 mmol) of anhydride 2m and 10.6 mg (0.011 mmol) RuHCl(PPh₃)₃ was treated with 1.9 mL ethyl acetate and 1.9 mL benzene and was allowed to react under hydrogen pressure for 12 h. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.036 g (35 %) 10m as a white solid. Rf = 0.36 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.27 (m, 5H), 5.85 (dd, 1H, J = 15.5, 7.3 Hz), 5.71 (dt, 1H, J = 15.5, 5.8 Hz), 4.52 (s, 2H), 4.03 (d, 2H, J = 5.7 Hz), 3.49-3.44 (m, 2H), 3.00-2.89 (m, 1H), 2.27-2.04 (m, 2H), 1.86-1.72 (m, 1H), 1.51-1.36 (m, 1H), 1.15 (dd, 1H, J = 12.8, 12.8, 12.8 Hz), 1.04 (t, 3H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 171.3, 171.1, 138.5, 130.7, 129.8, 128.6, 128.1, 127.8, 72.3, 70.4, 49.9, 48.5, 45.8, 37.1, 23.9, 12.9; IR (NaCl, neat) 2962, 1852, 1778, 1205, 917 cm⁻¹.

55.3, 50.0, 48.3, 46.3, 45.6, 37.4, 23.8, 13.2; IR (NaCl, neat) 3034, 2963, 2935, 2877, 1851, 1778, 1653, 1607, 1512, 1464, 1458, 1250 cm⁻¹; HRMS (FAB+) calcd for C₁₈H₂₁O₄, 301.1440. Found 301.1433.
(1S,2R,3S,5S)-methyl 5-ethyl-2-propionyl-3-styrylcyclopentancarboxylate (11a). According to the general procedure, 2.67 mg (0.010 mmol) Ni(acac)₂ and 30 mg (0.104 mmol) of anhydride 10a in 1.0 mL in THF was treated with 0.021 mL (0.208 mmol) of Et₂Zn at 0 °C. The reaction was stirred for 1 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 76.0 mg (96 %) of methyl ester 11a as an oil. Rf = 0.75 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.28 (dd, 2H, J = 8.7, 5.5, 2.2 Hz), 6.95 (dd, 2H, J = 8.6, 6.6, 2.0 Hz), 6.40 (dd, 1H, J = 15.7, 8.0 Hz), 6.32 (d, 1H, J = 15.6 Hz), 3.75 (s, 3H), 3.39 (m, 2H), 3.02 (dd, 1H, J = 6.2, 6.2 Hz), 2.46 (dq, 1H, J = 17.6, 7.3 Hz), 2.29 (dq, 1H, J = 17.4, 7.1 Hz), 2.19 (dd, J = 12.5, 8.0, 8.0 Hz), 2.10-1.97 (m, 1H), 1.77 (dd, 1H, J = 12.6, 7.9, 7.9 Hz), 1.48-1.29 (m, 2H), 0.93 (t, 3H, J = 7.5 Hz), 0.91 (t, 3H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 209.8, 174.3, 137.1, 132.8, 130.4, 128.4, 127.1, 126.2, 115.3 (d, JₐCF = 2 Hz), 129.9, 127.7 (d, JₐCF = 8 Hz), 115.3 (d, JₐCF = 21 Hz), 59.9, 51.2, 50.0, 44.7, 44.0, 38.1, 36.2, 23.7, 12.9, 7.5; IR (NaCl, neat) 2961, 2877, 1731, 1711, 1602, 1509, 1460, 1437, 1226, 1200, 1158 cm⁻¹; HRMS (FAB+) calcd for C₂₀H₂₅O₃F, 332.1788. Found 332.1775.

(1S,2R,3S,5S)-methyl 5-ethyl-2-propionyl-3-styrylcyclopentancarboxylate (11b). According to the general procedure, 6.14 mg (0.024 mmol) Ni(acac)₂ and 64 mg (0.239 mmol) of anhydride 10b in 2.4 mL in THF was treated with 0.049 mL (0.478 mmol) of Et₂Zn at 0 °C. The reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 34 mg (86 %) of methyl ester 11b as an oil. Rf = 0.68 (65:35 Hex/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.33 (dd, 2H, J = 8.6, 1.6 Hz), 7.26 (dt, 2H, J = 8.2, 1.1 Hz), 7.18 (dddd, 1H, J = 8.2, 8.2, 1.5, 1.5 Hz; 6.47 (dd, 1H, J = 15.7, 8.6 Hz), 6.37 (d, 1H, J = 16.0 Hz), 3.75 (s, 3H), 3.39-3.25 (m, 2H), 3.02 (dd, 1H, J = 6.4, 6.4 Hz), 2.48 (dq, 1H, J = 17.6, 7.3 Hz), 2.30 (dq, 1H, J = 17.6, 7.4 Hz), 2.20 (ddd, 1H, J = 15.0, 7.5, 7.5 Hz), 2.11-1.97 (m, 1H), 1.79 (dd, 1H, J = 19.6, 12.3, 7.7 Hz), 1.49-1.26 (m, 2H), 0.93 (t, 3H, J = 7.3 Hz), 0.92 (t, 3H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 209.8, 174.3, 137.1, 132.8, 130.4, 128.4, 127.1, 126.2, 59.9, 51.2, 49.0, 44.6, 44.0, 38.1, 36.1, 23.7, 12.8, 7.5; IR (NaCl, neat) 3025, 2959, 2876, 1733, 1710, 1598, 1577, 1493, 1460, 1148, 1435, 1200, 1173; HRMS (FAB+) calcd for C₂₀H₂₅O₃, 315.1960. Found 315.1970.

(1S,2R,3S,5S)-methyl 5-ethyl-3-(4-methoxystyryl)-2-propionylcyclopentancarboxylate (11c). According to the general procedure, 5.92 mg (0.023 mmol) Ni(acac)₂ and 69.0 mg (0.230 mmol) of anhydride 10c in 2.3 mL in THF was treated with 0.047 mL (0.461 mmol) of Et₂Zn at 0 °C. The reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 76.0 mg (96 %) of methyl ester 11c as an
oil. Rf = 0.68 (65:35 Hex/EtOAc); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26 (dd, 2H, $J =$ 8.8, 2.2 Hz), 6.80 (d, 2H, $J =$ 8.7, 2.0 Hz), 6.32-6.30 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 3.35 (dd, 1H, $J =$ 10.5, 6.2 Hz), 3.31-3.24 (m, 1H), 3.01 (dd, 1H, $J =$ 6.4, 6.4 Hz), 2.47 (dq, 1H, $J =$ 17.5, 7.3 Hz), 2.29 (dq, 1H, $J =$ 17.6, 7.4 Hz), 2.18 (ddd, 1H, $J =$ 15.0, 12.4, 7.3, 7.3 Hz), 2.09-1.97 (m, 1H), 1.77 (ddd, 1H, $J =$ 12.1, 7.7, 7.7 Hz), 1.51-1.27 (m, 2H), 0.92 (t, 3H, $J =$ 7.3 Hz), 0.91 (t, 3H, $J =$ 7.3 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.0, 174.3, 158.8, 130.6, 130.0, 129.8, 127.3, 113.8, 59.9, 55.2, 51.2, 49.1, 44.6, 44.1, 38.2 36.2, 23.7, 12.8, 7.5; IR (NaCl, neat) 2059, 2876, 2837, 1733, 1710, 1607, 1577, 1511, 1462, 1435, 1299, 1249, 1200, 1174, 1024 cm$^{-1}$; HRMS (FAB+) calcd for C$_{21}$H$_{29}$O$_4$, 345.2066. Found 345.2057.

(1S,2R,3S,5S)-methyl 3-((E)-2-cyclohexylvinyl)-5-ethyl-2-propionyl-cyclopentanecarboxylate (11e). According to the general procedure, 5.29 mg (0.021 mmol) Ni(acac)$_2$ and 57 mg (0.206 mmol) of anhydride 10c in 2.0 mL in THF was treated with 0.042 mL (0.412 mmol) of Et$_2$Zn at 0 $^\circ$C. The reaction was stirred for 3 h at 0 $^\circ$C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 51 mg (77 %) of methyl ester 11e as an oil. Rf = 0.68 (65:35 Hex/EtOAc); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.58 (ddd, 1H, $J =$ 15.4, 9.7, 0.9 Hz), 5.30 (dd, 1H, $J =$ 15.4, 7.0 Hz), 3.71 (s, 3H), 3.26 (dd, 1H, $J =$ 10.6, 6.5 Hz), 3.04 (ddddd, 1H, $J =$ 9.9, 9.1, 8.2, 8.2 Hz), 2.93 (dd, 1H, $J =$ 6.6, 6.6 Hz), 2.48 (dq, 1H, $J =$ 17.7, 7.3 Hz), 2.26 (dq, 1H, $J =$ 17.7, 7.3 Hz), 2.10 (dt, 1H, $J =$ 12.5, 7.5 Hz), 2.02-1.83 (m, 2H), 1.70-1.58 (m, 7H), 1.45-1.26 (m, 3H), 1.27-1.10 (m, 3H), 0.96 (t, 3H, $J =$ 7.3 Hz), 0.89 (t, 3H, $J =$ 7.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.0, 174.3, 137.6, 130.1, 59.6, 51.1, 48.9, 44.5, 43.8, 40.4, 38.3, 36.3, 33.1, 26.1, 25.9, 23.6, 12.8, 7.3; IR (NaCl, neat) 2925, 2851, 1780, 1737, 1713, 1460, 1448, 1434, 1412, 1377, 1198, 1165 cm$^{-1}$; HRMS (FAB+) calcd for C$_{20}$H$_{33}$O$_3$, 321.2430. Found 321.2444.

(1S,2R,3S,5S)-methyl 5-ethyl-3-((E)-3-phenylprop-1-enyl)-2-propionyl-cyclopentanecarboxylate (11g). According to the general procedure, 3.06 mg (0.012 mmol) Ni(acac)$_2$ and 34 mg (0.119 mmol) of anhydride 10g in 1.2 mL in THF was treated with 0.024 mL (0.238 mmol) of Et$_2$Zn at 0 $^\circ$C. The reaction was stirred for 3 h at 0 $^\circ$C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 36 mg (92 %) of methyl ester 11g as an oil. Rf = 0.63 (65:35 Hex/EtOAc); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29-7.24 (m, 2H), 7.19-7.12 (m, 3H), 5.79 (dd, 1H, $J =$ 15.0, 9.6 Hz), 5.56 (ddd, 1H, $J =$ 13.9, 6.8, 6.8 Hz), 3.72 (s, 3H), 3.27 (dd, 2H, $J =$ 14.3, 6.8 Hz), 3.18-3.06 (m, 1H), 2.96 (dd, 1H, $J =$ 16.6, 6.6 Hz), 2.45 (dq, 1H, $J =$ 17.8, 7.3 Hz), 2.26 (dq, 1H, $J =$ 17.9, 7.1 Hz), 2.13 (dt, 1H, $J =$ 12.7, 7.7 Hz), 2.04-1.90 (m, 1H), 1.71 (dt, 1H, $J =$ 12.1, 8.1 Hz), 1.47-1.25 (m, 3H), 0.94 (t, 3H, $J =$ 7.3 Hz), 0.91 (t, 3H, $J =$ 7.5 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 209.9, 174.4, 140.7, 133.8, 130.2, 128.4, 128.3, 125.9, 59.5, 51.2, 49.0, 44.5, 43.6, 38.9, 38.2, 36.3, 23.6, 12.9, 7.3; IR (NaCl, neat) 2961, 1770, 1731, 1454, 1203, 1171, 950; HRMS (FAB+) calcd for C$_{21}$H$_{29}$O$_3$, 329.2117. Found 329.2096.
(1S,2R,3S,5S)-methyl 3-((E)-3-(benzyloxy)prop-1-enyl)-5-ethyl-2-propionylcyclopentanecarboxylate (11m). According to the general procedure, .97 mg (0.004 mmol) Ni(acac)\textsubscript{2} and 12 mg (0.038 mmol) of anhydride 10m in 0.4 mL in THF was treated with 0.008 mL (0.076 mmol) of Et\textsubscript{2}Zn at 0 °C. The reaction was stirred for 3 h at 0 °C. The reaction was quenched with 10 mL 1M AcOH and 10 mL ether. The layers were separated and the aqueous layer was extracted with ether (2 x 10 mL) and combined organics were washed with brine, dried over MgSO\textsubscript{4}, filtered, and concentrated in vacuo. The acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 19.5 mg (65 %) of methyl ester 11m as an oil. Rf = 0.60 (65:35 Hex/EtOAc); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36-7.26 (m, 5H), 5.96 (dd, 1H, \(J = 15.5, 9.7\) Hz), 5.62 (ddd, 1H, \(J = 12.8, 6.4, 6.4\) Hz), 4.45 (s, 2H), 3.94 (d, 2H, 6.4 Hz), 3.72 (s, 3H), 3.30 (dd, 1H, \(J = 7.7, 6.4\) Hz), 3.09-2.97 (m, 1H), 2.96 (dd, 1H, \(J = 6.4, 6.4\) Hz), 2.47 (dq, 1H, 17.9, 7.5 Hz), 2.30 (dq, 1H, 17.4, 7.4 Hz), 2.20-1.97 (m, 2H), 1.75-1.65 (m, 1H), 1.55 (ddd, 1H, \(J = 11.7, 8.0, 8.0\) Hz), 1.30-1.12 (m, 2H), 0.82 (t, 3H, \(J = 7.1\) Hz), 0.74 (t, 3H, \(J = 7.3\) Hz); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 209.8, 174.3, 138.3, 136.8, 128.4, 127.7, 127.5, 127.4, 72.0, 70.6, 59.6, 51.2, 49.0, 44.6, 43.4, 38.0, 36.3, 23.7, 12.9, 7.5; IR (NaCl, neat) 2932, 2874, 2360, 2344, 1735, 1731, 1461, 1453, 1434, 1195, 1165 cm\textsuperscript{-1}; HRMS (FAB+) calcd for C\textsubscript{22}H\textsubscript{30}O\textsubscript{3}Na, 381.2036. Found 381.2031.

(3aR,4R,6R,6aS)-4-allyl-6-vinyltetrahydro-1H-cyclopenta[c]furan-1,3(3aH)-dione (12). 1.0 g (3.59 mmol) of anhydride 4k in 36 mL of chloroform was treated with 1.4 mL trifluoroacetic acid and allowed to stir overnight. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 0.700 g (94 %) of anhydride 12 as a colorless oil. Rf = 0.63 (65:35); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 5.96-5.77 (m, 2H), 5.16-5.01 (m, 4H), 3.49 (dd, 1H, \(J = 8.2, 8.2\) Hz), 3.43 (dd, 1H, \(J = 8.2, 8.2\) Hz), 2.98-2.87 (m, 1H), 2.55 (ddd, 1H, \(J = 13.9, 6.2, 6.2\) Hz), 2.40-2.26 (m, 1H), 2.15-2.03 (m, 2H), 1.16 (ddd, 1H, \(J = 12.8, 12.8, 12.8\) Hz); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) 171.2, 170.8, 136.0, 135.0, 116.8, 116.6, 49.4, 48.1, 46.3, 43.1, 36.3, 34.5; IR (NaCl, neat) 3079, 2978, 2923, 2850, 1855, 1772, 1642, 1456, 1440, 1418, 1338, 1320, 1259, 1206 cm\textsuperscript{-1}; HRMS (FAB+) calcd for C\textsubscript{12}H\textsubscript{13}O\textsubscript{3}, 207.1015. Found 207.1009.

(1R,2S,3R,5R)-methyl 5-allyl-2-propionyl-3-vinylcyclopentane-carboxylate (13). According to the general procedure, 6.35 mg (0.023 mmol) Ni(COD)\textsubscript{2} in 1.0 mL THF was treated with 0.040 mL (0.392 mmol) of Et\textsubscript{2}Zn at 0 °C. 47.6 mg (0.231 mmol) of anhydride 12 in 1.3 mL in THF was added via cannula and the reaction was stirred for 12 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 19.5 mg (45 %) of methyl ester 13 as an oil. Rf = 0.67 (65:35 Hex/EtOAc); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 6.01 (ddd, 1H, \(J = 18.3, 17.6, 10.2\) Hz), 5.84-5.70 (m, 1H), 5.05-4.92 (m, 4H), 3.72 (s, 3H), 3.31 (dd, 1H, \(J = 10.4, 6.6\) Hz), 3.17-3.04 (m, 1H), 3.00-2.96 (m, 1H), 2.49 (dq, 1H, \(J = 18.7, 7.9\) Hz), 2.31 (dq, 1H, \(J = 17.4, 7.3\) Hz), 2.24-2.06 (m, 4H), 1.82-1.72 (m, 1H),
0.98 (t, 3H, J = 7.3 Hz); 13C NMR (75 MHz, CDCl3) 210.0, 174.2, 141.0, 137.1, 115.9, 115.4, 59.6, 51.5, 49.3, 45.2, 42.4, 38.0, 36.7, 35.3, 7.6; IR (NaCl, neat) 2976, 2949, 1733, 1712, 1435, 1196, 1166, 914 cm⁻¹; HRMS (FAB+) calcd for C₁₅H₂₃O₃, 251.1647, Found 251.1638.

**Methyl 3-propionyloct-5-enoate (S1).** According to the general procedure, 3.7 mg (0.014 mmol) Ni(acac)₂, 5.0 mg (0.017 mmol) pyphos, and 0.030 g (0.143 mmol) of 2-octen-1-ylsuccinic anhydride (1) in 1.0 mL THF was treated with 0.260 mL (0.285 mmol) of 15 wt% Et₂Zn in toluene at 0 °C. The reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 36 mg (>99 %) of methyl ester as an oil. The mixture of cis/trans was subjected to hydrogenation conditions to obtain 36 mg (>99 %) of reduced ketoester. Rf = 0.89 (65:35 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 3.64 (s, 3H), 2.96 (dddd, 1H, J = 10.3, 10.3, 7.1, 7.1 Hz), 2.76 (dd, 1H, J = 16.8, 10.0 Hz), 2.56 (dq, 2H, J = 7.3, 2.9 Hz), 2.51 (ddd, 1H, J = 16.85, 4.3 Hz), 2.34 (dd, 1H, J = 16.85, 4.3 Hz), 1.60-1.54 (m, 1H), 1.41-1.34 (m, 1H), 1.31-1.20 (m, 12H), 1.06 (t, 3H, J = 7.2 Hz), 0.87 (t, 3H, J = 6.7 Hz); 13C NMR (75 MHz, CDCl₃) δ 213.8, 173.1, 51.7, 47.0, 35.7, 35.1, 31.8, 31.7, 29.6, 29.3, 29.2, 27.0, 22.6, 14.1, 7.6; IR (NaCl, neat) 2927, 2856, 1740, 1716, 1460, 1438, 1201, 1176 cm⁻¹; HRMS (FAB+) calcd for C₁₅H₂₃O₃, 257.2101, Found 257.2111.

**Methyl 4-propionylhept-6-enoate (17).** According to the general procedure, 5 mg (0.019 mmol) Ni(acac)₂, 3.7 mg (0.023 mmol) bipy, and 0.030 g (0.20 mmol) of anhydride 16 in 1.0 mL THF was treated with 0.350 mL (0.390 mmol) of Et₂Zn (15 wt% in toluene) at 0 °C. The reaction was stirred for 3 h at 0 °C. Upon work-up, the acid was converted to the corresponding methyl ester. The reaction was concentrated and purified by column chromatography (9:1 Hex/EtOAc) providing 39.0 mg (>99 %) of methyl ester 17 as an oil. Rf = 0.4 (90:10 Hex/EtOAc); 1H NMR (300 MHz, CDCl₃) δ 5.69 (dddd, 1H, J = 10.2, 10.2, 7.1, 7.1 Hz), 5.07-5.00 (m, 2H), 3.64 (s, 3H), 2.64 (dddd, 1H, J = 11.5, 8.1, 6.3, 5.3 Hz), 2.46 (dq, 2H, J = 7.3, 5.0 Hz), 2.38-2.13 (m, 5H), 2.00-1.65 (m, 2H), 1.03 (t, 3H, J = 7.3 Hz); 13C NMR (75 MHz, CDCl₃) δ 213.6, 173.5, 135.0, 117.2, 51.6, 50.3, 35.9, 35.8, 31.5, 25.8, 7.4; IR (NaCl, neat) 2974, 2939, 1737, 1713, 1642, 1438, 1377, 1198, 1171 cm⁻¹; HRMS (FAB+) calcd for C₁₁H₁₉O₃, 199.1334, Found 199.1297.

**Structural Assignments:**

Based on the crystal structure data (vide infra), we have unambiguously assigned the structure of 3a. The structure of compounds 3b-l was based on analogy to the parent compound 3a. In order to provide further evidence for the change in regiochemistry, the following control experiments were completed:

- **2a** was subjected to Pd/C and H₂ and the doubly reduced anhydride subjected to the standard reaction conditions to provide a 1:1 mixture of regioisomers A and B.
(eq 1).

- the major regioisomer from alkylation of 2a affords A when subjected to hydrogenation (eq 2).
- the major regioisomer from alkylation of 10a affords B when subjected to hydrogenation (eq 3).
- based on this control experiment, the regiochemistry of compounds 11b-11m was assigned by analogy.

\[
\text{(1)}
\]

\[
\text{(2)}
\]

\[
\text{(3)}
\]

- iodolactonization of ketoacid derived from 2e provides C as the major product (eq 4).

\[
\text{(4)}
\]

(C). A round bottom flask was charged with 0.030 g (0.099 mmol) of the ketoacid derivative of 3a in 2 mL CH₂Cl₂ and 3 mL 0.5 M NaHCO₃. A solution of 0.060 g (0.235 mmol) of I₂ and 0.062 mg (0.380 mmol) KI in 2 mL water was added dropwise to the
reaction mixture and the resulting deep red biphasic mixture was stirred in the dark for 17 h. The reaction was quenched with 15 mL of sat. NaHSO₃. The organic layer was separated and the aqueous layer extracted with DCM. The organic layers were combined, washed with sat. NaHCO₃, brine, dried over MgSO₄, filtered and concentrated in vacuo to provide an oil, which was purified by column chromatography to provide a white solid. ¹H NMR (400 MHz, CDCl₃) δ 5.76-5.68 (dd, 1H, J = 15.5, 8.2 Hz), 5.51-5.37 (dd, 1H, J = 15.4, 6.5 Hz), 4.10-4.05 (m, 1H), 3.38-3.21 (m, 3H), 3.10-3.02 (m, 1H), 2.94-2.71 (m, 2H), 2.22-2.12 (m, 1H), 2.03-1.88 (m, 4H), 1.72-1.59 (m, 6H), 1.31-1.06 (m, 4H), 1.00 (t, 3H, J = 7.4 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 174.5, 138.7, 124.9, 117.8, 86.2, 53.9, 51.6, 50.5, 50.4, 40.7, 38.3, 33.2, 31.1, 26.3, 26.2, 10.6, 8.3.

• alkylation of 12 or treatment of 3k with TFA both afford 13 as the major regioisomer (eq 5).
Spectral Data for 2a
Spectral Data for 2d
Spectral Data for 2f
Spectral Data for 2g
Spectral Data for 2h
Spectral Data for 2i
Spectral Data for 21
Spectral Data for 3a

![Spectral Data Diagram]
Spectral Data for 3b
Spectral Data for 3c
Spectral Data for 3d
Spectral Data for 3e
Spectral Data for 3f
Spectral Data for 3g
Spectral Data for 3h
Spectral Data for 3i
Spectral Data for 3j
Spectral Data for 3k
Spectral Data for 31

H
H
TBSO

S-38
Spectral Data for 5a
Spectral Data for 5b
Spectral Data for 5c
Spectral Data for 5d
Spectral Data for 10a
Spectral Data for 10b

[Chemical Structure Image]

S-44
Spectral Data for 10c
Spectral Data for 10e
Spectral Data for 10g
Spectral Data for **10m**
Spectral Data for 11a

![Spectral Data Diagram]
Spectral Data for 11b
Spectral Data for 11c
Spectral Data for 11e

\[
\begin{align*}
\text{H}_3C\text{O}_2\text{Me} & \\
\text{H} & \\
\text{HOEt} & \\
\end{align*}
\]

S-52
Spectral Data for 11g
Spectral Data for 11m
Spectral Data for 12
Spectral Data for 13
Spectral Data for H$_2$-15:

![Spectral Data Diagram]

S-57
Spectral Data for 17
Spectral Data for 4
Crystal structure of 4.