Supplementary Data

Palladium-Catalyzed Highly Diastereoselective Cyclic Carbopalladation-Carbonylative Esterification Tandem Reaction of Iododienes and Iodoarylalkenes.

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Diastereoselective Tandem Carbonylative Cyclization of 1,1-Disubstituted Alkenes. Preparation of Starting Material. (a) (*Z*)-6-Methyl-1-iodo-3-(*t*-butyldimethylsilyloxy)-1,6-heptadiene (1a). A mixture of methyl 2-(methoxycarbonyl)-4-methyl-4-pentenoate (4.28 g, 20 mmol), NaCl (1.75 mg, 30 mmol), H_2O (1.6 mL, 1.6 g, 90 mmol), and DMSO (25 mL) was stirred at 150 °C under argon for 12 h.[a] The reaction mixture was quenched with H_2O, extracted with *n*-pentane, dried over $MgSO_4$, filtered, and evaporated. Kugelrhor distillation afforded 2.10 g (74%) of methyl 4-methyl-4-pentenoate. To this compound was added a solution of KOH (5.6 g, 100 mmol) in a mixture of MeOH (10 mL)/H_2O (5 mL). After being stirred for 3 h at 23 °C, the reaction mixture was brought to pH = 1 by addition of a 3 M aqueous HCl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated to give 1.69 g (quant) of 4-methyl-4-pentenoic acid: ^{1}H NMR δ 1.75 (s, 3 H), 2.2-2.4 (m, 2 H), 4.71 (s, 1 H), 4.77 (s, 1 H), 10.2 (bs, 1 H); ^{13}C NMR δ 22.50, 32.18, 32.39, 110.48, 143.48, 179.79. This acid (1.69 g, 7.4 mmol) in CH_2Cl_2 (7 mL) was treated with $(COCl)_2$ (2.6 mL, 3.8 g, 30 mmol) at 25 °C.[b] After being stirred for 1 h at this temperature, the reaction mixture was heated at reflux for 30 min, and then treated at 0 °C by a solution of 2-(trimethylsilyl)ethynylzinc bromide in THF, prepared by successive treatment of

trimethylsilylacetylene (588 mg, 6.0 mmol) dissolved in THF with a 2.5 M solution of *n*-BuLi in hexanes 92.4 mL, 6.0 mmol, -78 °C, 1 h) and $ZnBr_2$ (1.35 g, 6.0 mmol, -78 °C) dissolved in THF.[c] After being stirred for 2 h, the reaction mixture was quenched with aqueous HCl, extracted with Et_2O, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (98/2 *n*-pentane-Et_2O) gave 360 mg (46%) of 1-(trimethylsilyl)-6-methyl-6-hepten-1-yn-3-one: ^{1}H NMR δ 0.06 (s, 9 H), 1.56 (s, 3 H), 2.1-2.25 (m, 2 H), 2.45-2.6 (m, 2 H), 4.51 (bs, 1 H), 4.57 (bs, 1 H); ^{13}C NMR δ -0.91, 22.46, 31.39, 43.29, 97.72, 101.72, 110.57, 143.44, 186.92. To this compound (650 mg, 33.5 mmol) were successively added at 0 °C a 0.5 M solution of $CeCl_3$ (60 mL, 30 mmol) in MeOH and $NaBH_4$ (140 mg, 3.7 mmol).[d] The reaction was stirred for 2 min, diluted in Et_2O, washed with H_2O over $MgSO_4$, filtered, and evaporated. Chromatography on silica (95/5 *n*-pentane-Et_2O) afforded 565 mg (86%) of 1-(trimethylsilyl)-methyl-6-hepten-1-yn-3-ol: ^{1}H NMR δ 0.15 (s, 9 H), 1.72 (s, 3 H), 1.75-1.85 (m, 2 H), 2.1-2.2 (m, 2 H), 2.25-2.35 (m, 1 H), 4.1-4.4 (m, 1 H), 4.71 (bs, 2 H); ^{13}C NMR δ -0.19, 22.39, 33.21, 35.47, 62.38, 89.48, 106.58, 110.44, 144.87. A solution of this compound (200 mg, 1.0 mmol) in MeOH was treated with K_2CO_3 (276 mg, 2.0 mmol) for 25 °C for 1 h. After evaporation, the reaction mixture was diluted in Et_2O, washed successively with aqueous HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated to give 124 mg (quant) of 6-methyl-6-hepten-1-yn-3-ol: ^{1}H NMR δ 1.74 (s, 3 H), 1.8-2.0 (m, 2 H), 2.05-2.3 (m, 2 H), 2.45-2.5 (m, 1 H), 4.3-4.5 (m, 1 H), 4.73 (bs, 2 H); ^{13}C NMR δ 22.42, 33.06, 35.38, 61.92, 73.11, 84.66, 110.53, 144.79. To a suspension of MeONa (117 mg, 2.2 mmol) in THF (2 mL) were successively added at -20 °C a 1 M solution of $LiAlH_4$ in THF (1.1 mL, 1.1 mmol, 0 °C, 30 min) and 6-methyl-6-hepten-1-yn-3-ol (124 mg, 1.0 mmol) dissolved in THF.[e] After being stirred for 12 h at 0 °C, the reaction mixture was treated with ethyl acetate (98 μL, 88

mg, 1.0 mmol, 0 °C, 15 min), and I_2 (381 mg, 1.5 mmol, -78 °C) in THF (3 mL). The resulting reaction mixture was warmed to 23 °C, successively treated with conc. NH_4OH and $Na_2S_2O_3$, diluted with Et_2O, and filtered. The resulting reaction mixture was successively washed with aqueous HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. Filtration on silica gel afforded crude (*Z*)-6-methyl-1-iodo-1,6-heptadiene-3-ol. A mixture of this crude compound, imidazole (102 mg, 1.5 mmol), and TBDMSCl (150 mg, 1.0 mmol) in DMF (2 mL) was stirred for 12 h. The resulting reaction mixture was diluted in *n*-pentane, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 120 mg (33%) of **1a**: ^{1}H NMR δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.5-1.7 (m, 2 H), 1.74 (s, 3 H), 2.0-2.25 (m, 2 H), 4.3-4.4 (m, 1 H), 4.72 (s, 2 H), 6.15-6.25 (m, 2 H); ^{13}C NMR δ -4.71, -4.19, 18.08, 22.71, 25.84, 33.02, 34.88, 75.14, 79.82, 109.82, 144.56, 145.50; High-resolution MS calcd for $C_{14}H_{27}IOSi$ (M^++1) 367.0954, found 367.0943.

(b)(*Z*)-2-Methyl-7-iodo-5-(*t*-butyldimethylsilyloxy)-1,6-undecadiene(1b). To 2-heptyn-1-ol (2.24 g, 20 mmol) in CH_2Cl_2 (100 mL) were successively added Celite (10 g) and PCC (12.9 g, 60 mmol).[f] The reaction mixture was stirred for 3 h, diluted with *n*-pentane, and filtered on silica gel to give 1.39 g (63%) of 2-heptynal. To 4-iodo-2-methyl-1-butene (2.64 g, 13.5 mmol) dissolved in Et_2O was added at -78 °C a 1.7 M solution of *t*-BuLi in *n*-pentane (15.9 mL, 27 mmol). After being stirred for 30 min at this temperature, the reaction mixture was warmed to 0 °C and then treated at -78 °C with 2-heptynal (1.39 g, 12.6 mmol) dissolved in Et_2O (10 mL).. The resulting reaction mixture was warmed to 0 °C, quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (85/15 *n*-pentane-Et_2O) afforded 1.59 g (70%) of 2-methyl-1-undecen-6-yn-5-ol: ^{1}H NMR δ 0.91 (t, J = 7.2 Hz, 3 H), 1.3-1.6 (m, 4 H), 1.7-

1.9 (m, 5 H), 2.05-2.3 (m, 5 H), 4.3-4.45 (m, 1 H), 4.72 (s, 2 H); ^{13}C NMR δ 13.50, 18.28, 21.84, 22.41, 30.67, 33.29, 36.00, 62.31, 80.98, 85.62, 110.18, 145.10. To a suspension of MeONa (207 mg, 3.84 mmol) in THF (4 mL) were successively added a 1 M solution of $LiAlH_4$ in THF (1.92 mL, 1.92 mmol, 0 °C, 30 min), 2-methyl-1-undecen-6-yn-5-ol (290 mg, 1.6 mmol, 0 °C, 6 h) dissolved in THF (1 mL), ethyl acetate (0.15 mL, 160 mg, 1.92 mmol), and I_2 (762 mg, 3 mmol, -78 °C) dissolved in THF (5 mL).[e] The reaction mixture was warmed to 23 °C, and successively treated with conc. NH_4OH and $Na_2S_2O_3$. The resulting reaction mixture was diluted with Et_2O, filtered, washed successively with aqueous HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 380 mg (77%) of (*Z*)-2-methyl-7-iodo-1,6-undecadien-5-ol: ^{1}H NMR δ 0.92 (t, J = 7.3 Hz, 3 H), 1.2-1.6 (m, 4 H), 1.6-1.9 (m, 5 H), 2.0-2.25 (m, 3 H), 2.48 (t, J = 7.3 Hz, 2 H), 4.2-4.4 (m, 1 H), 4.74 (s, 1 H), 5.59 (dd, J = 7.6, 1.0 Hz, 1 H); ^{13}C NMR δ 13.80, 21.27, 22.51, 31.22, 33.30, 34.02, 44.98, 76.18, 110.19, 110.24, 136.93, 145.30. A mixture of this alcohol (422 mg, 1.37 mmol), imidazole (184 mg, 1.37 mmol), and TBDMSCl (255 mg, 1.7 mmol) in DMF (5 mL) was stirred for 12 h. The resulting reaction mixture was diluted with *n*-pentane, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 530 mg (92%) of **1b**: ^{1}H NMR δ 0.04 (s, 3 H), 0.09 (s, 3 H), 0.8-0.9 (m, 12 H), 1.2-1.7 (m, 6 H), 1.74 (s, 3 H), 1.95-2.2 (m, 2 H), 2.48 (t, J = 7.2 Hz, 2 H), 4.26 (q, J = 6.3 Hz, 1 H), 4.71 (s, 2 H), 5.52 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ -4.63, -4.05, 13.09, 21.28, 22.71, 25.88, 31.21, 33.24, 35.28, 44.84, 77.30, 107.13, 109.73, 138.30, 145.73.

(c) (*Z*)-2-Methyl-7-iodo-5-(*t*-butyldimethylsilyloxy)-1,6,10-undecatriene (1c). A mixture of 6-hepten-2-yn-1-ol (1.1 g, 10.1 mmol), PCC (6.5 g, 30 mmol), and Celite (6.5 g) was stirred at 20 °C for 3 h. The reaction mixture was diluted with *n*-pentane and filtered on silica gel (95/5 *n*-

pentane-Et_2O) to give 600 mg (55%) of 6-hepten-2-ynal after evaporation. A solution of 4-iodo-2-methyl-1-butene (1.47 mg, 7.5 mmol) in Et_2O (10 mL) was treated at -78 °C with a 1.7 M solution of *t*-BuLi in *n*-pentane (8.82 mL, 15 mmol), stirred for 1 h at this temperature, and warmed to 20 °C. The resulting reaction mixture was treated at -78 °C with 6-hepten-2-ynal (600 mg, 5.55 mmol) dissolved in Et_2O (5 mL), and warmed to 20 °C. The reaction mixture was diluted with Et_2O, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (85/15 *n*-pentane-Et_2O) afforded 475 mg (48%) of 2-methyl-1,10-undecadiene-6-yn-5-ol: ^{1}H NMR δ 1.74 (s, 3 H), 1.75-1.9 (m, 2 H), 2.1-2.4 (m, 8 H), 4.3-4.45 (m, 1 H), 5.0-5.2 (m, 2 H), 5.75-5.95 (m, 1 H); ^{13}C NMR δ 18.41, 22.41, 32.75, 33.22, 35.85, 62.20, 81.51, 84.75, 110.00, 115.59, 136.74, 145.03. To a suspension of MeONa (302 mg, 5.6 mmol) in THF (4 mL) were added at 0 °C a 1 M solution of $LiAlH_4$ in THF (2.8 mL, 2.8 mmol, 30 min) and 2-methyl-1,10-undecadien-6-yn-5-ol (475 mg, 2.67 mmol) dissolved in THF.[e] After 6 h at 0 °C, the reaction mixture was successively treated with ethyl acetate (0.27 mL, 246 mg, 2.8 mmol, 0 °C, 15 min) and I_2 (1.27 g, 5 mmol, -78 °C, 10 min) dissolved in THF. After 30 min at 20 °C, the reaction mixture was quenched with conc. aqueous NH_4OH, treated with aqueous $Na_2S_2O_3$, and diluted with Et_2O. This reaction mixture was decanted, extracted with Et_2O, washed successively with aqueous HCl and $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (90/10 *n*-pentane-Et_2O) gave 495 mg (60%) of (*Z*)-2-methyl-7-iodo-1,6,10-undecatrien-5-ol: ^{1}H NMR δ 1.55-1.85 (m, 5 H), 1.9-2 (m, 1 H), 2.0-2.4 (m, 4 H), 2.58 (t, J = 7.5 Hz, 2 H), 4.2-4.4 (m, 1 H), 4.74 (s, 2 H), 4.95-5.15 (m, 2 H), 5.62 (d, J = 7.5 Hz, 1 H), 5.7-5.85 (m, 1 H). A mixture of (*Z*)-2-methyl-7-iodo-1,6,10-undecatrien-5-ol (495 mg, 1.62 mmol), imidazole (218 mg, 3.2 mmol), *t*-butyldimethylsilyl chloride (285 mg, 1.9 mmol) in DMF (3 mL) was stirred for 3 h. The reaction mixture was diluted with *n*-pentane, washed with

H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 550 mg (87%) of **1c**: ^{1}H NMR δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.55-1.7 (m, 2 H), 1.72 (s, 3 H), 1.95-2.2 (m, 2 H), 2.2-2.35 (m, 2 H), 2.55-2.6 (m, 2 H), 4.2-4.3 (m, 1 H), 4.70 (s, 2 H), 4.95-5.15 (m, 2 H), 5.54 (d, J = 6 Hz, 1 H), 5.65-5.85 (m, 1 H); ^{13}C NMR δ -4.75, -4.07, 17.92, 22.73, 25.82, 33.03, 33.24, 35.23, 44.64, 77.34, 105.71, 109.63, 115.60, 136.21, 138.96, 145.33.

(d) (*Z*)-2,11-Dimethyl-7-iodo-5-(*t*-butyldimethylsilyloxy)-1,6,10-dodecatriene (1d). To a mixture of crushed Mg turnings (5.8 g, 240 mmol), I_2 (one crystal), and $HgCl_2$ (50 mg, 0.1 mmol) in THF (20 mL) was added 10 mL of a mixture of propargyl bromide (9 mL, 14.3 g, 120 mmol) in THF (100 mL). The reaction mixture was heated to reflux to initiate the reaction, and the remaining part of the solution of propargyl bromide in THF was added at such a rate to maintain a slight reflux. After the addition was completed, the reaction mixture was heated at reflux for 30 min, and added to 4-bromo-2-methyl-2-butene (5.2 mL, 6.67 g, 44 mol) dissolved in THF (40 mL) at 25 °C. The resulting reaction was heated at reflux for 2 h, quenched with NH_4Cl, extracted with *n*-pentane, dried over $MgSO_4$, and filtered. Evaporation of the solvent followed by distillation afforded 3.5 g (74%) of 6-methyl-5-hepten-1-yne: ^{1}H NMR δ 1.63 (s, 3 H), 1.71 (s, 3 H), 1.9-2.0 (m, 1 H), 2.1-2.3 (m, 4 H), 5.1-5.25 (m, 1 H); ^{13}C NMR δ 17.73, 18.88, 25.62, 27.22, 68.07, 84.47, 122.52, 133.09. to this compound (1.08 g, 10 mmol) dissolved in Et_2O (15 mL) were successively added at -78 °C a 2.5 M solution of *n*-BuLi in hexanes (4.0 mL, 10 mmol, 30 min) and *N*-formylmorpholine (1.2 mL, 1.38 g, 12 mmol).[c] The reaction was warmed to 0 °C, and added to a mixture of ice (100 g) and conc. aqueous HCl (60 mL). The resulting reaction mixture was extracted at least 5 times with *n*-pentane, washed with $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel

(95/5 *n*-pentane-Et_2O) afforded 910 mg (67%) of 7-methyl-6-octen-2-ynal: ^{1}H NMR δ 1.63 (s, 3 H), 1.71 (s, 3 H), 2.1-2.5 (m, 4 H), 5.0-5.20 (m, 1 H), 9.17 (s, 1 H); ^{13}C NMR δ 17.62, 19.53, 25.48, 26.11, 81.44, 98.83, 121.47, 133.96, 176.98. A solution of 4-iodo-2-methyl-1-butene (1.96 g, 10 mmol) in Et_2O (15 mL) was treated with a 1.7 M solution of *t*-BuLi in *n*-pentane (12.4 mL, 21 mmol, -78 °C), stirred for 30 min at this temperature, and warmed to 0 °C. This reaction mixture was cooled to -78 °C, and treated with 7-methyl-6-octen-2-ynal (910 mg, 6.7 mmol) in Et_2O. The resulting reaction mixture was warmed to 0 °C, quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 1.13 g (82%) of 2,11-dimethyl-1,10-dodecadien-6-yn-5-ol: ^{1}H NMR δ 1.4-2.0 (m, 11 H), 2.0-2.4 (m, 7 H), 4.25-4.45 (m, 1 H), 4.72 (s, 2 H), 5.05-5.25 (m, 1 H); ^{13}C NMR δ 17.72, 19.13, 22.44, 25.61, 27.38, 33.24, 35.93, 62.31, 81.03, 85.50, 110.19, 122.71, 132.91, 145.08. 2,11-Dimethyl-1,10-dodecadien-6-yn-5-ol (1.13 g, 5.5 mmol) was converted into 1.42 g (77%) of (*Z*)-2,11-dimethyl-7-iodo-1,6,10-dodecatrien-5-ol after chromatography on silica gel (95/5 *n*-pentane-Et_2O): ^{1}H NMR δ 1.5-2.0 (m, 11 H), 2.0-2.3 (m, 5 H), 2.51 (5, J = 7.3 Hz, 2 H), 4.30 (q, 7.4 Hz, 1 H), 4.74 (s, 2 H), 5.0-5.15 (m, 1 H), 5.58 (d, J = 7.3 Hz, 1 H); ^{13}C NMR δ17.92, 22.52, 25.64, 27.82, 33.23, 33.98, 45.46, 109.51, 110.18, 121.99, 132.96, 137.25, 145.26. A mixture of this compound (558 mg, 1.67 mmol), imidazole (204 mg, 3 mmol), and TBDMSCl (300 mg, 2.0 mmol), in DMF (4 mL) was stirred for 12 h. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 715 mg (94%) of (*Z*)-2,11-dimethyl-7-iodo-5-(*t*-butyldimethylsilyloxy)-1,6,10-dodecatriene (**1d**): ^{1}H NMR δ 0.04 (s, 3 H), 0.08 (s, 3 H), 0.80 (s, 9 H), 1.5-1.7 (m, 8 H), 1.72 (s, 3 H), 2.0-2.3 (m, 4 H), 2.4-2.5 (m, 2 H), 4.2-4.3 (m, 1 H), 4.71 (s, 2 H), 5.0-5.15 (m, 1 H), 5.52 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ -4.66, -4.03, 17.94, 18.08, 22.73, 25.72, 25.89, 27.73, 33.17, 35.21, 45.35, 77.27, 106.52, 109.74, 122.25, 132.78,

138.64, 145.63.

(e) 2-(4′-Methyl-1′-(*t*-butyldimethylsilyloxy)-4′-pentenyl)-1-iodobenzene (8a). 4-Iodo-2-methyl-1-butene (588 mg, 3.0 mmol) dissolved in Et_2O (6.0 mL) was treated at -78 °C with a 1.7 M solution of *t*-BuLi in *n*-pentane (3.7 mL, 6.3 mmol), stirred for 30 min at this temperature, and warmed to 0 °C. The reaction mixture was treated at -78 °C with $MgBr_2$ (552 mg, 3.0 mmol), warmed to 0 °C, and treated with 2-iodobenzaldehyde (696 mg, 3.0 mmol). The resulting reaction mixture was warmed to 25 °C, quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (85/15 *n*-pentane-Et_2O) afforded 220 mg (24%) of 1-(2′-iodophenyl)-4-penten-1-ol: ^{1}H NMR δ 1.6-2.0 (m, 5 H), 2.05-2.4 (m, 2 H), 2.60 (bs, 1 H), 4.76 (s, 2 H), 4.88 (dd, J = 8.5, 3.5 Hz, 1 H), 6.9-7.0 (m, 1 H), 7.36 (t, J = 7.4 Hz, 1 H), 7.4-7.5 (m, 1 H), 7.79 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 22.03, 46.71, 74.49, 97.06, 114.13, 126.75, 128.47, 128.98, 139.10, 142.36, 145.54. A mixture of this compound (220 mg, 0.72 mmol), imidazole (136 mg, 2 mmol), and TBDMSCl (150 mg, 1.0 mmol) in DMF (2 mL) was stirred for 12 h. The reaction mixture was diluted with *n*-pentane, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 279 mg (93%) of **8a**: ^{1}H NMR δ 0.17 (s, 3 H), 0.23 (s, 3 H), 1.06 (s, 9 H), 1.75-2.05 (m, 5 H), 2.15-2.45 (m, 2 H), 4.87 (s, 2 H), 5.01 (dd, J = 8.2, 3.5 Hz, 1 H), 7.0-7.15 (m, 1 H), 7.4-7.55 (m, 1 H), 7.6-7.7 (m, 1 H), 7.91 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ -4.93, -4.54, 18.14, 22.76, 25.86, 33.96, 37.49, 77.97, 96.89, 109.76, 127.92, 128.17, 128.70, 138.84, 145.66, 147.54.

(f) 2-(4′-Methyl-1′-(methoxymethyloxy)-4′-pentyl)-1-iodobenzene (8b). To a solution of 2-(4′-methyl-1′-(hydroxy)-4′-pentenyl)-1-iodobenzene (140 mg, 0.46 mmol), prepared as above, in CH_2Cl_2 (5 mL) were successively added *i*-Pr_2NEt (1.39 mL, 1.03 g, 8.0 mmol), DMAP (15 mg,

0.12 mmol), and MOMCl (0.30 mL, 322 mg, 2 mmol). The reaction mixture was stirred for 12 h, diluted in Et_2O, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (97/3 *n*-pentane-Et_2O) afforded 150 mg (94%) of **8b**: ^{1}H NMR δ 1.7-1.95 (m, 5 H), 2.05-2.4 (m, 2 H), 3.38 (s, 3 H), 4.49 (d, J = 6.6 Hz, 1 H), 4.56 (d, J = 6.6 Hz, 1 H), 4.73 (s, 2 H), 4.83 (dd, J = 8.2, 4.5 Hz, 1 H), 6.9-7.05 (m, 1 H), 7.3-7.5 (m, 2 H), 7.80 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ22.65, 34.01, 35.30, 55.93, 81.13, 94.85, 98.40, 110.08, 127.48, 128.43, 129.11, 139.29, 144.61, 145.24.

(g) 2-(3′-Methyl-1′-(*t*-butyldimethylsilyloxy)-3′-butenyl)-1-iodobenzene (10). A solution of 2-iodobenzaldehyde (980 mg, 4.2 mmol) in THF (10 mL) was treated at 0 °C with a solution of methallylmagnesium chloride (10 mmol) in THF. After 5 min, the reaction was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered and evaporated. Chromatography on silica gel (85/15 *n*-pentane-Et_2O) afforded 798 mg (66%) of 2-(3′-methyl-1′-(hydroxy)-3′-butenyl)-1-iodobenzene: ^{1}H NMR δ 1.88 (s, 3 H), 2.12 (dd, J = 13.9, 10.1 Hz, 1 H), 2.44 (d, J = 2.4 Hz, 1 H), 2.48 (bd, J = 13.7 Hz, 1 H), 4.9-5.0 (m, 3 H), 6.9-7.0 (m, 1 H), 7.34 (t, J = 7.5 Hz, 1 H), 7.53 (dd, J = 7.8, 1.6 Hz, 1 H), 7.76 (dd, J = 7.9, 1.0 Hz, 1 H); ^{13}C NMR δ 22.03, 46.71, 74.49, 97.06, 114.13, 126.75, 128.47, 128.98, 139.10, 142.36, 145.54. A mixture of this compound (0.80 g, 2.78 mmol), imidazole (340 mg, 5 mmol), and TBDMSCl (525 mg, 3.5 mmol) in DMF (10 mL) was stirred for 12 h. The reaction mixture was diluted with *n*-pentane, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (99/1 *n*-pentane-Et_2O) afforded 1.04 g (93%) of **10**: ^{1}H NMR δ 0.18 (s, 3 H), 0.21 (s, 3 H), 1.04 (s, 9 H), 2.03 (s, 3 H), 2.34 (dd, J = 13.4, 9.1 Hz, 1 H), 2.48 (dd, J = 13.4, 9.1 Hz, 1 H), 4.9-5.05 (m, 2 H), 5.13 (dd, J = 9.1, 2.9 Hz, 1 H), 7.0-7.15 (m, 1 H), 7.4-7.5 (m, 1 H), 7.70 (dd, J = 7.8, 1.6 Hz, 1 H), 7.90 (dd, J = 7.9, 1.0 Hz, 1 H); ^{13}C NMR δ

-4.97, -4.63, 18.16, 23.16, 25.89, 47.82, 77.38, 96.83, 113.78, 127.89, 128.20, 128.74, 138.82, 142.07, 147.41.

Pd-Catalyzed Cyclic Carbopalladation-Carbonylative Esterification Tandem Reaction Under Conditions A. (a) Cyclization of 1b under Conditions A. Representative Procedure. A mixture of **1b** (490 mg, 1.24 mmol), $Cl_2Pd(PPh_3)_2$ (42 mg, 0.062 mmol), Et_3N (0.69 mL, 501 mg, 5.0 mmol), and H_2O (0.25 mL) in a 2:1 mixture of DMF/MeOH (7.4 mL) was stirred under 1 atm of CO at 85 °C (bath temp.). The yellow reaction mixture turned black, and then slowly turned back to its original yellow color. This mixture was then exposed to air for 20-30 sec, flushed with CO, and stirred until it turned black over 0.5 to 1 h. The reaction mixture was evaporated, diluted with Et_2O, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Analysis by NMR spectroscopy indicated that 1-(*t*-butyldimethylsilyl)-4-methyl-4-(methoxycarbonylmethyl)-3-(*n*-butyl)-2-cyclohexene (**2b**) was formed in 84% NMR yield as a 95:5 diastereomeric mixture along with a 5-6% yield of methyl (*Z*)-2-(*n*-butyl)-4-(*t*-butyldimethylsilyloxy)-7-methyl-2,7-octadienoate (**4b**). Chromatography on silica gel (98/2 *n*-pentane-Et_2O) afforded 17 mg (4%) of (**4b**) 343 mg (78%) of **(1S*,4R*)-2b** and 17 mg (4%) of **(1S*,4S*)-2b**. The spectral data for **(1S*,4R*)-2b** are as follows: ^{1}H NMR δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.8-1.0 (m, 12 H), 1.14 (s, 3 H), 1.2-2.0 (m, 10 H), 2.31 (d, J = 13.5 Hz, 1 H), 2.38 (d, J = 13.8 Hz, 1 H), 3.63 (s, 3 H), 4.15-4.25 (m, 1 H), 5.33 (bs, 1 H); ^{13}C NMR δ -4.52, -4.44, 14.06, 18.32, 22.83, 25.52, 25.98, 29.19, 29.92, 30.50, 33.03, 37.33, 44.13, 51.18, 67.90, 126.28, 144.08, 172.28; IR (neat) 1740 (s) cm^{-1}; High-resolution MS calcd for $C_{20}H_{38}O_3Si$ 353.2512, found 353.2515. The spectral data for **(1S*,4S*)-2b** are as follows: ^{1}H NMR δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.8-1.0 (m, 12 H), 1.07 (s, 3 H), 1.2-2.0 (m, 10 H), 2.36 (d, J = 13.5 Hz, 1 H), 2.46 (d, J = 13.5 Hz, 1 H), 3.64 (s, 3 H), 4.15-4.25 (m, 1 H), 5.31 (bs, 1 H); ^{13}C NMR δ

-4.50, -4.46, 14.06, 18.31, 22.85, 25.42, 25.98, 28.98, 29.98, 30.98, 32.65, 37.10, 42.64, 51.23, 67.85, 126.13, 145.00, 172.48. The spectral data for **4b** are as follows: ^{1}H NMR δ 0.03 (s, 3 H), 0.07 (s, 3 H), 0.8-0.95 (m, 12 H), 1.2-1.5 (m, 4 H), 1.5-1.7 (m, 2 H), 1.73 (s, 3 H), 1.9-2.4 (m, 2 H), 3.74 (s, 3 H), 4.65-4.75 (bs, 2 H), 4.85-5.0 (m, 1 H), 5.81 (d, J = 8.4 Hz, 1 H); ^{13}C NMR δ -4.89, -4.40, 13.84, 18.12, 22.18, 22.62, 25.85, 31.02, 33.39, 33.77, 35.84, 51.31, 69.46, 109.55, 130.43, 145.19, 145.90, 168.06; IR (neat) 1722 (s), 1650 (m) cm^{-1}.

(b) Carbonylative Cyclization of 1a. Under Conditions A, **1a** (111 mg, 0.30 mmol) gave 1-(*t*-butyldimethylsilyloxy)-4-methyl-4-(methoxycarbonyl-methyl)-2-cyclohexene in 81% NMR yield as 94:6 mixture of **(1S*,4R*)-2a** and **(1S*,4S*)-2a**. Chromatography on silica gel (98/2 *n*-pentane-Et_2O) afforded 72 mg (81%) of **(1S*,4R*)-2a**: ^{1}H NMR δ 0.07 (s, 6 H), 0.89 (s, 9 H), 1.12 (s, 3 H), 1.55-1.7 (m, 3 H), 1.75-1.85 (m, 1 H), 2.2-2.3 (m, 2 H), 3.64 (s, 3 H), 4.15-4.2 (m, 1 H), 5.5-5.6 (m, 2 H); ^{13}C NMR δ -4.62, -4.54, 18.26, 25.92, 26.47, 29.39, 32.38, 34.41, 46.57, 51.22, 67.14, 130.75, 135.70, 172.02. The following signals were discernible for **(1S*,4S*)-2a**: ^{13}C NMR δ 26.82, 29.21, 29.68, 32.14, 45.11, 66.71, 130.23, 136.30.

(c) Carbonylative Cyclization of 1c. Under Conditions A, **1c** (112 mg, 0.285 mmol) gave 1-(*t*-butyldimethylsilyloxy)-4-methyl-4-(methoxoycarbonyl-methyl)-3-(3′-butenyl)-2-cyclohexene (**2c**) in 65% NMR yield as 85:15 mixture of **(1S*,4R*)-2c** and **(1S*,4S*)-2c**. Chromatography on silica gel (98/2 *n*-pentane-Et_2O) afforded 53 mg (57%) of **(1S*,4R*)-2c**: ^{1}H NMR δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.89 (s, 9 H), 1.14 (s, 3 H), 1.5-1.65 (m, 2 H), 1.65-1.85 (m, 2H), 1.95-2.1 (m, 2 H), 2.1-2.25 (m, 2 H), 2.30 (d, J = 13.8 Hz, 1 H), 2.39 (d, J = 13.8 Hz, 1 H), 3.63 (s, 3 H), 4.1-4.25 (m, 1 H), 4.9-5.1 (m, 2 H), 5.34 (bs, 1 H), 5.75-5.9 (m, 1 H); ^{13}C NMR δ -4.55, -4.44, 18.32, 25.58, 25.98, 29.15, 29.44, 32.27, 33.03, 37.30, 44.12, 51.23, 67.85, 114.58, 126.67, 138.59, 143.15,

172.19; High-resolution MS calcd for $C_{20}H_{36}O_3Si$ (M^++1) 353.2512, found 353.2501. The spectral data for **(1S*,4S*)-2c** are as follows: ^{1}H NMR δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.89 (s, 9 H), 1.08 (s, 3 H), 1.2-1.25 (m, 1 H), 1.5-1.65 (m, 1 H), 1.7-1.85 (m, 1 H), 1.9-2.1 (m, 3 H), 2.1-2.25 (m, 2 H), 2.36 (d, J = 13.3 Hz, 1 H), 2.46 (d, J = 13.3 Hz, 1 H), 3.64 (s, 3 H), 4.1-4.25 (m, 1 H), 4.9-5.1 (m, 2 H), 5.33 (bs, 1 H), 5.75-5.9 (m, 1 H); ^{13}C NMR δ -4.52, -4.48, 18.30, 25.45, 25.97, 28.93, 29.46, 32.65, 32.67, 37.07, 42.64, 51.27, 67.75, 114.64, 126.54, 138.52, 144.05, 172.39.

(d) Carbonylative Cyclization of 1d. Under Conditions A, **1d** (218 mg, 0.49 mmol) gave 1-(*t*-butyldimethylsilyloxy)-4-methyl-4-(methoxycarbonyl-methyl)-3-(4′-methyl-3′-pentenyl)-2-cyclohexene **2d** in 80% NMR yield as 93:7 mixture of **(1S*,4R*)-2d** and **(1S*,4S*)-2d**. Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 134 mg (72%) of **(1S*,4R*)-2d** and 8 mg (4%) of **(1S*,4S*)-2d.** The spectral data for **(1S*,4R*)-2d** are as follows: ^{1}H NMR δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.90 (s, 9 H), 1.14 (s, 3 H), 1.4-1.9 (m, 10 H), 1.9-2.0 (m, 2 H), 2.05-2.2 (m, 2 H), 2.30 (d, J = 13.8 Hz, 1 H), 2.39 (d, J = 13.8 Hz, 1 H), 3.63 (s, 3 H), 4.15-4.25 (m, 1 H), 5.05-5.2 (m, 1 H), 5.36 (s, 1 H); ^{13}C NMR δ -4.56, -4.45, 17.68, 18.30, 25.56, 25.66, 25.96, 26.72, 29.18, 30.09, 33.01, 37.29, 44.11, 51.14, 67.91, 124.33, 126.49, 131.54, 143.61, 172.18. The spectral data for **(1S*,4S*)-2d** are as follows: ^{1}H NMR δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.90 (s, 9 H), 1.07 (s, 3 H), 1.25-1.4 (m, 1 H), 1.5-1.65 (m, 4 H), 1.69 (s, 3 H), 1.7-1.85 (m, 1 H), 1.9-2.0 (m, 3 H), 2.0-2.2 (m, 2 H), 2.36 (d, J = 13.8 Hz, 1 H), 2.46 (d, J = 13.8 Hz, 1 H), 3.64 (s, 3 H), 4.15-4.25 (m, 1 H), 5.05-5.2 (m, 1 H); 5.33 (s, 1 H); ^{13}C NMR δ -4.52, -4.46, 17.74, 18.33, 25.44, 25.69, 25.98, 27.16, 28.98, 30.15, 32.66, 37.08, 42.62, 51.24, 67.88, 124.29, 126.38, 131.68, 144.54, 172.44.

(e) Carbonylative Cyclization of 8a. Under Conditions A, **8a** (148 mg, 0.35 mmol) gave (1R*,4S*)-1-(*t*-butyldimethylsilyloxy)-4-methyl-4-(methoxycarbonylmethyl)-1,2,3,4-

tetrahydronaphthalene (**9a**) in >98% diastereoselectivity: ^{1}H NMR δ 0.16 (s, 3 H), 0.17 (s, 3 H), 0.95 (s, 9 H), 1.39 (s, 3 H), 1.7-2.2 (m, 4 H), 2.55-2.75 (m, 2 H), 3.56 (s, 3 H), 4.7-4.8 (m, 1 H), 7.1-7.25 (m, 3 H), 7.35-7.55 (m, 1 H); ^{13}C NMR δ -4.60, -4.15, 18.15, 25.90, 29.68, 30.05, 32.26, 36.63, 47.12, 51.16, 69.80, 125.99, 126.09, 127.13, 127.25, 139.66, 142.69, 171.92.

(f) Carbonylative Cyclization of 8b. Under Conditions A, **8b** (150 mg, 0.43 mmol) gave a 94% NMR yield of 1-(methoxymethyloxy)-4-methyl-4-(methoxycarbonylmethyl)1,2,3,4-tetrahydronaphthalene **9b** as a 1:1 diastereomeric mixture. Chromatography on silica gel (90/1 *n*-pentane-Et_2O) afforded 92 mg (72%) of a 1:1 diastereomeric mixture of **9b**: ^{1}H NMR δ 1.37 (s, 3 H, minor), 1.44 (s, 3 H, major), 1.6-2.4 (m, 4 H, minor+major), 2.53 (d, J = 14 Hz, 1 H, major), 2.2 (d, J = 14 Hz, 1 H, major), 2.69 (s, 2 H, minor), 3.47 (s, 3 H, major), 3.62 (s, 1 H, minor), 4.6-4.7 (s, 1 H, minor+major), 4.76 (d, J = 6.9 Hz, 1 H, minor+major), 4.84 (d, J = 6.9 Hz, 1 H, minor), 4.87 (d, J = 6.9 Hz, 1 H, major), 7.1-7.4 (m, 4 H, minor+major); ^{13}C NMR δ 25.14, 25.16, 28.76, 29.03, 30.67, 30.69, 36.30, 46.43, 46.92, 51.14, 55.41, 55.46, 72.80, 73.05, 126.01, 126.11, 126.31, 126.38, 127.89, 127.96, 129.08, 129.39, 135.33, 135.65, 143.71, 144.03, 171.74, 171.82.

(g) Carbonylative Cyclization of 10. Under Conditions A, **10**, (217 mg, 0.54 mmol) gave 1-(*t*-butyldimethylsilyloxy)-3-methyl-3-(methoxycarbonylmethyl)-indane (**11**) in 76% yield as 94:6 mixture of diastereomer. Chromatography on silica gel (98/2 *n*-pentane-Et_2O) afforded 135 mg (74%) of **(1R*,3S*)-11**: ^{1}H NMR δ 0.16 (s, 3 H), 0.18 (s, 3 H), 0.94 (s, 9 H), 1.47 (s, 3 H), 1.85 (dd, J = 13.0, 6.6 Hz, 1 H), 2.42 (d, J = 13.9 Hz, 1 H), 2.52 (d, J = 13.9 Hz, 1 H), 2.66 (dd, J = 13.0, 6.8 Hz, 1 H), 3.60 (s, 3 H), 5.27 (t, J = 6.7 Hz, 1 H), 7.1-7.4 (m, 4 H); ^{13}C NMR δ -4.61, -4.42, 18.19, 25.87, 27.47, 44.43, 45.84, 49.53, 51.26, 74.22, 122.53, 124.25, 127.34, 128.04, 144.59, 148.57, 172.03; IR (neat) 1736 cm^{-1}. The following signals were discernible for the minor isomer: ^{1}H NMR

δ 2.1-2.4 (m, 2 H), 3.66 (s, 3 H); ^{13}C NMR δ 26.69, 46.11, 74.42, 122.28, 122.53, 124.42, 128.12.

Synthesis of the p-Nitrobenzoate Derivative. A mixture of **(1S*,4R*)-2b** (86 mg, 0.24 mmol) in THF (1 mL) was treated at 0 °C with a 1 M solution of TBAF in THF (1.0 mL, 1.0 mmol). After being stirred for 2 h at 25 °C, the reaction mixture was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Filtration on silica gel afforded 57.6 mg (quant.) of the deprotected alcohol: ^{1}H NMR δ 0.92 (t, J = 7.1 Hz, 3 H), 1.15 (s, 3 H), 1.2-2.0 (m, 11 H), 2.3-2.45 (m, 2 H), 3.64 (s, 3 H), 4.1-4.25 (bs, 1 H), 5.47 (bs, 1 H); ^{13}C NMR δ 14.03, 22.74, 25.50, 28.54, 29.95, 30.55, 32.24, 37.26, 43.44, 51.23, 66.36, 124.65, 146.21, 172.16. To a solution of the alcohol obtained above (48 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) were successively added *i*-Pr_2NEt (104 μL, 77 mg, 0.6 mmol), DMAP (10 mg, 0.08 mmol), and *p*-nitrobenzoyl chloride (74 mg, 0.4 mmol). The reaction mixture was stirred for 12 h at 23 °C, diluted with Et_2O, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 78 mg (quant) of (1S*,4R*)-1-(*p*-nitrobenzoyloxy)-4-methyl-4-(methoxycarbonyl-methyl)-3-(*n*-butyl)-2-cyclohexene: ^{1}H NMR δ 0.92 (t, J = 7.1 Hz, 3 H), 1.22 (s, 3 H), 1.25-1.5 (m, 4 H), 1.6-2.15 (m, 6 H), 2.35-2.45 (m, 2 H), 3.67 (s, 3 H), 5.45-5.6 (m, 2 H), 8.2-8.35 (m, 4 H); ^{13}C NMR δ 14.02, 22.75, 24.84, 25.43, 30.20, 30.42, 31.98, 37.20, 42.94, 51.35, 70.91, 119.62, 123.39, 130.67, 136.17, 149.63, 150.37, 164.32, 171.89. Recrystallization from MeOH gave colorless crystals, which were analyzed by X-ray crystallography.

Total Synthesis of the Colvin-Raphael Lactone: To **2a** (72 mg, 0.24 mmol) dissolved in THF (2.0 mL) was added a 1 M solution of TBAF in THF (1.0 mL, 1.0 mmol. After being stirred for 1 h at 23 °C, the reaction mixture was diluted with Et_2O, extracted with H_2O, dried over $MgSO_4$, filtered, and evaporated. Filtration of silica gel (95/5 *n*-pentane-Et_2O) afforded 40 mg (90%) of

deprotected **2a**: ^{1}H NMR δ 1.13 (s, 3 H), 1.55-1.7 (m, 3 H), 1.83 (bs, 1 H), 1.85-2.0 (m, 1 H), 2.2-2.3 (m, 2 H), 3.66 (s, 3 H), 4.15-4.2 (m, 1 H), 5.6-5.7 (m, 2 H); ^{13}C NMR δ 26.55, 28.76, 31.74, 34.29, 45.82, 51.28, 65.73, 129.15, 137.25, 171.95. To a mixture of oxalyl chloride (87 μL, 127 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) were successively added at -78 °C methyl sulfoxide (0.14 mL, 156 mg, 2.0 mmol, 10 min) and deprotected (**2a**) (40 mg, 0.22 mmol) in CH_2Cl_2. After being stirred for 1.5 h at -60 °C, the reaction mixture was treated with Et_3N (0.41 mL, 303 mg, 3.0 mmol), warmed to 0 °C, diluted with Et_2O, washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (50/50 *n*-pentane-Et_2O) afforded 37 mg (92%) of 4-methyl-4-(methoxycarbonylmethyl)-2-cyclohexen-1-one: ^{1}H NMR δ 1.27 (s, 3 H), 1.8-2.0 (m, 1 H), 2.0-2.2 (m, 1 H), 2.4-2.6 (m, 4 H), 3.69 (s, 3 H), 5.92 (d, J = 10.3 Hz, 1 H), 6.86 (d, J = 10.3 Hz, 1 H); ^{13}C NMR δ 24.88, 33.90, 34.01, 34.89, 44.66, 51.57, 127.62, 156.78, 171.23, 198.73. Using the reported procedure,[f] this compound (37 mg, 0.20 mmol) was converted into the Colvin-Raphael lactone in 51% yield (17 mg): ^{1}H NMR δ1.15 (s, 3 H), 1.45-1.6 (m, 1 H), 1.6-1.85 (m, 1 H), 1.77 (s, 3 H), 2.0-2.1 (m, 2 H), 2.33 (d, J = 17 Hz, 1 H), 2.43 (d, J = 17 Hz, 1 H), 4.4-4.45 (m, 1 H), 5.5-5.6 (m, 1 H); ^{13}C NMR δ 22.89, 23.50, 26.68, 29.82, 36.50, 42.33, 82.19, 117.30, 141.61, 176.29.

Pd-Catalyzed "Zipper"-Mode Cascade Cyclic Carbopalladation Reaction of 1c. A mixture of **1c** (100 mg, 0.255 mmol), $Pd(OAc)_2$ (2.7 mg, 0.012 mmol), PPh_3 (9.5 mg, 0.036 mmol), Ag_2CO_3 (74 mg, 0.27 mg), and DMF (1 mL) was stirred at 90 °C. After 3.5 h, the reaction mixture was diluted with *n*-pentane, extracted with H_2O, dried over $MgSO_4$, filtered, and evaporated. ^{1}H NMR analysis of the crude reaction mixture showed the formation of **12** in 70% yield: ^{1}H NMR δ 0.0-0.5 (m, 6 H), 0.8-1.1 (m, 12 H), 1.2-2.4 (m, 10 H), 4.1-4.2 (m, 1 H, minor), 4.2-4.3 (m, 1 H, major), 4.64 (s, 1 H), 4.75 (s, 1 H), 5.29 (s, 1 H, major), 5.37 (bs, 1 H, minor); ^{13}C NMR δ -4.60, -

4.46, 14.06, 18.39, 22.34, 24.09, 24.70, 26.03, 29.31, 29.58, 29.71, 32.94, 33.12, 34.12, 34.67, 35.86, 36.15, 36.33, 36.61, 37.16, 48.88, 50.51, 66.88, 68.98, 109.06, 109.36, 124.36, 125.45, 143.68, 144.57, 146.49, 147.1.

(*Z*)-4,4-Bis(methoxycarbony)-7-iodo-1,6-undecadiene (14). To a suspension of NaH (120 mg, 3.0 mmol, 60% dispersion in mineral oil) in THF (20 mL) were successively added at 0 °C methyl 2-(methoxycarbonyl)-4-pentenoate (490 mg, 2.85 mmol, 0 °C, 30 min) dissolved in THF, the mesylate of (*Z*)-3-iodo-2-hepten-1-ol (870 mg, 2.86 mmol, 0 °C), and NaI (30 mg, 0.2 mmol). After being stirred for 3 h at 23 °C, the reaction mixture was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 920 mg (82%) of **14**: ^{1}H NMR δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.2-1.4 (m, 2 H), 1.4-1.55 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2 H), 2.74 (d, *J* = 6.8 Hz, 2 H), 2.79 (t, *J* = 7.6 Hz, 2 H), 3.72 (s, 6 H), 5.0-5.2 (m, 2 H), 5.38 (t, *J* = 6.8 Hz, 1 H), 5.5-5.8 (m, 1 H); ^{13}C NMR δ 13.75, 21.17, 31.34, 37.57, 39.66, 45.20, 52.45, 57.28, 113.13, 119.39, 128.51, 132.11, 170.93; IR (neat) 1736 cm^{-1}.

Carbonylative Cyclization of 14. Under Conditions A, **14** (197 mg, 0.5 mmol) gave a 37% NMR yield of 4,4-bis(methoxycarbonyl)-1-(*n*-butyl)-6-methylene-1-cyclohexene (**16a**) along with a 17% yield of 5,5-bis(methoxycarbonyl)-2-(*n*-butyl)-1-methyl-1,3-cyclohexadiene (**16b**). Chromatography on silica gel (95/5 *n*-pentane-Et_2O) afforded 50 mg (45%) of a 2:1 mixture of **16a** and **16b**. The spectral data for **16a** are as follows: ^{1}H NMR δ 0.89 (t, *J* = 7.1 Hz, 3 H), 1.2-1.45 (m, 4 H), 2.16 (t, *J* = 7.2 Hz, 2 H), 2.65-2.75 (m, 2 H), 2.87 (s, 2 H), 3.70 (s, 6 H), 4.90 (bs, 1 H), 5.03 (bs, 1 H), 5.55-6.05 (m, 1 H); ^{13}C NMR δ 13.92, 22.51, 30.61, 31.73, 32.07, 37.59, 52.60, 54.20, 110.67, 123.07, 136.73, 138.99, 171.39. The following signals were discernible for **16b**: ^{1}H NMR δ 1.77 (s, 3 H), 2.0-2.1 (m, 2 H), 2.72 (s, 2 H), 3.71 (s, 3 H), 5.80 (d, *J* = 9.5 Hz, 1 H), 5.97 (d, *J* =

9.5 Hz, 1 H); ^{13}C NMR δ 13.92, 18.76, 22.10, 30.51, 30.93, 35.94, 52.74, 54.64, 119.76, 126.65, 127.82, 130.73, 171.28, IR (neat) 1736 cm^{-1}; High-resolution MS calcd for $C_{15}H_{22}O_4$ 226.1518, found 266.1515.

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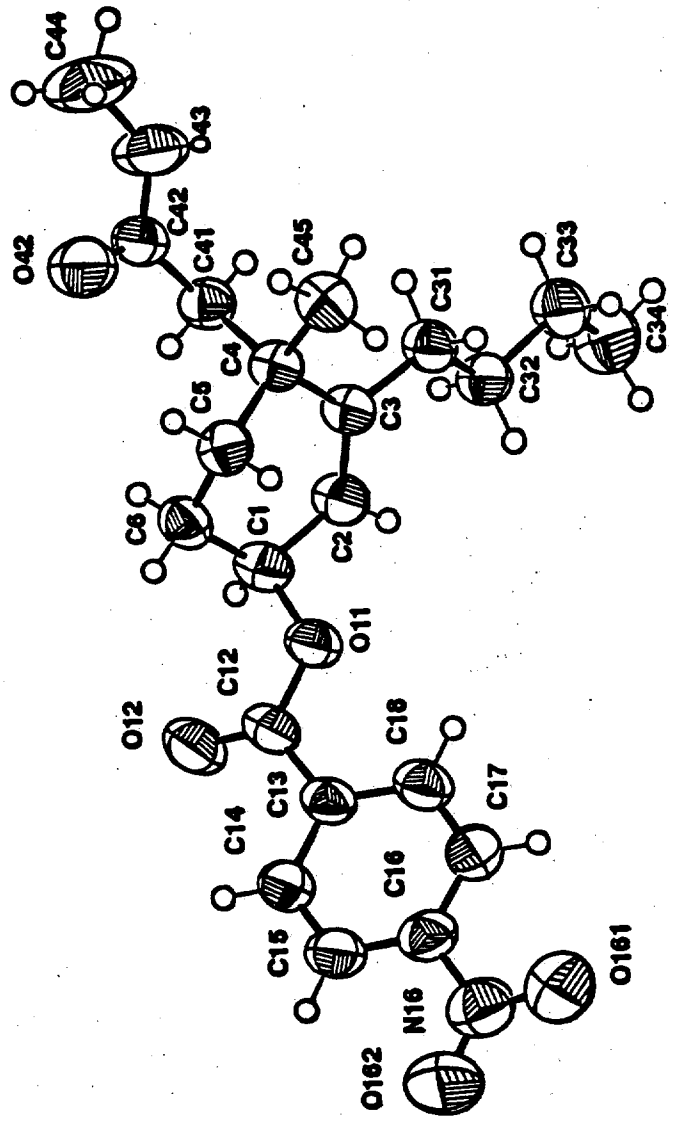
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C42
O42
C41
C45
C31
C33
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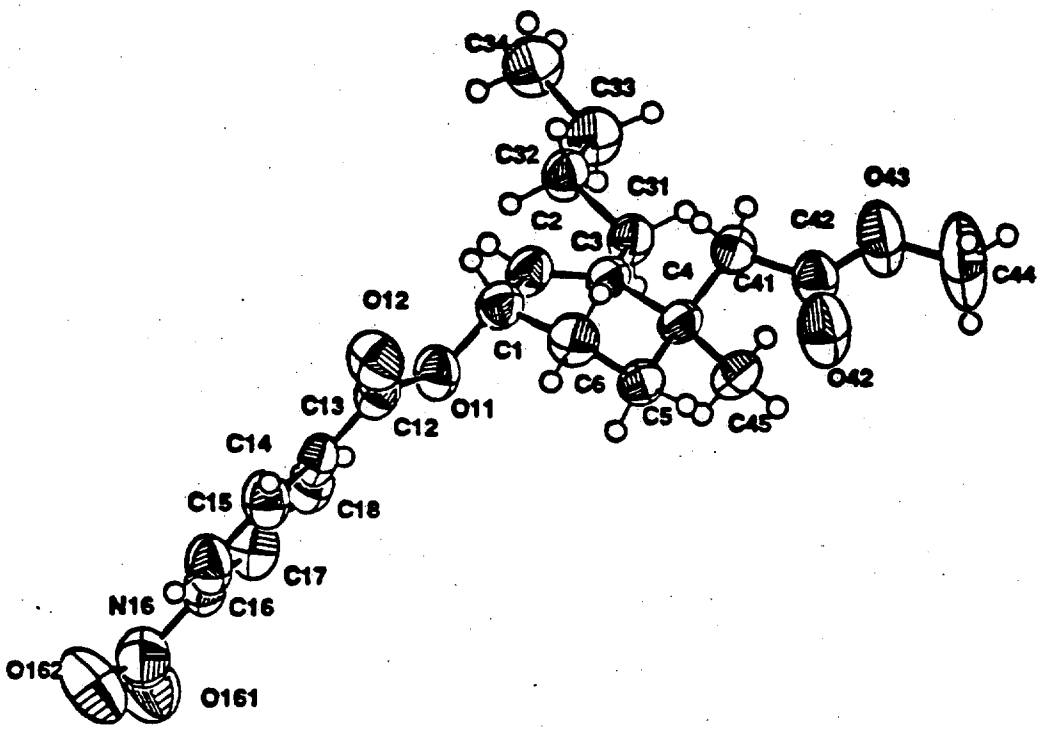
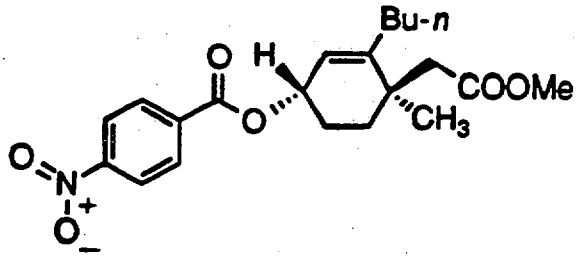
C32
C4
C3
C5
C6
C1
C2
O11
C12
O12
C18
C13
C17
C14
C16
C15
O161
N16
O162

Appendix D: Crystallographic Data for the *p*-Nitrobenzoyl Derivative of 18e





EXPERIMENTAL

DATA COLLECTION

A colorless chunk of $C_{21}H_{27}NO_6$ having approximate dimensions of 0.30 x 0.30 x 0.24 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu K_α radiation (λ = 1.54184 Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $40 < \theta < 47°$, measured by the computer controlled diagonal slit method of centering. The triclinic cell parameters and calculated volume are: a = 5.703(1), b = 14.402(2), c = 14.501(1)Å, α = 117.42(1), β = 93.62(1), γ = 90.85(1)°, V = 1053.9Å^3. For Z = 2 AND F.W. = 389.45 the calculated density is 1.23 g/cm^3. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.73° with a take-off angle of 6.0° indicating moderate crystal quality. There were no systematic absences; the space group was determined to be $P\bar{1}$(# 2).

The data were collected at a temperature of 295 ± 1 K using

the ω-2θ scan technique. The scan rate varied from 2 to 16°/min (in omega). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 148.7°. The scan range (in deg.) was determined as a function of θ to correct for the separation of the Kα doublet(ref 1); the scan width was calculated as follows:

$$\omega \text{ scan width} = 0.73 + 0.200 \tan \theta$$

Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.2 to 2.8 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 25.6.

DATA REDUCTION

A total of 4458 reflections were collected, of which 4278 were unique.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.0 /cm for Cu K radiation. No absorption correction was made. Intensities of

equivalent reflections were averaged. The agreement factor for the averaging was 4.3% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program SHELX-86 (ref 2). The remaining atoms were located using DIRDIF (ref 3)and in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $w=1/[\sigma^2(Fo^2)+(0.0607P)^2+0.2109P]$ where $P=(Fo^2+2Fc^2)/3$

Scattering factors were taken from the "International Tables for Crystallography" (ref 4). 4277 reflections were used in the refinements. However, only reflections with $F_o^2>2\sigma(F_o^2)$ were used in calculating R. The final cycle of refinement included 257 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma\ |Fo - Fc|\ /\ \Sigma\ Fo = 0.051$$

$$R2 = SQRT\ (\ \Sigma\ w\ (\ Fo^2 - Fc^2\ )^2\ /\ \Sigma\ w\ (Fo^2)^2\ ) = 0.119$$

The standard deviation of an observation of unit weight was 1.11. The highest peak in the final difference Fourier had a height of 0.19 e/A^3. The minimum negative peak had a height of -0.16 e/A^3.

Refinement was performed on a pentium PC using SHELX-93 (ref 5). Crystallographic drawings were done using programs ORTEP (ref 6) and/or PLUTON (ref 7).

(1) "CAD4 Operations Manual", Enraf-Nonius, Delft, 1977.

(2) G. M. Sheldrick, SHELXS86. A Program for the Solution of Crystal Structures. Univ. of Gottingen, Germany, 1985

(3).P. T. Beurskens, W. P. Bosman, H. M. Doesburg, Th. E. M. van den Hark, P. A. J. Prick, J. H. Noordick, G. Beurskens, R. O. Gould, and V. Parthasarathi, "Conformation in Biology", edited by R. Srinivasan and R. H. Sarma, pp. 389, New York Adenine Press, 1983.

(4) "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4.

(5) G. M. Sheldrick, SHELXS93. A Program for Crystal Structure Refinement. Univ. of Gottingen, Germany, 1993

(6) C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976)

(7) A. L Spek, PLUTON. Molecular Graphics Program. Univ. of Ultrecht, The Netherlands (1991)

CRYSTALLOGRAPHIC DATA FOR

$C_{21}H_{27}NO_6$

$O_6NC_{21}H_{27}$	formula weight 389.45
a = 5.7034(5)Å	space group $P\bar{1}$ (No. 2)
b = 14.4016(16)Å	T = 295. K
c = 14.5006(9)Å	λ = 1.54184Å
α = 117.417(6)°	ρ_{calc} = 1.227g cm^{-3}
β = 93.622(6)°	μ = 7.04cm^{-1}
γ = 90.854(8)°	$R(F_o)^a$ = 0.051
V = 1053.9(4)Å^3	$R_w(F_o^2)^b$ = 0.119

---

[a] $R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$

[b] $R_w = [\Sigma \, w \, (|F_o^2| - |F_c^2|)^2 / \Sigma \, w \, |F_o^2|^2]^{1/2}$

CRYSTAL DATA AND DATA COLLECTION PARAMETERS for

$C_{21}H_{27}NO_6$

formula	$O_6NC_{21}H_{27}$
formula weight	389.45
space group	$P\bar{1}$ (No. 2)
a, Å	5.7034(5)
b, Å	14.4016(16)
c, Å	14.5006(9)
α, deg	117.417(6)
β, deg	93.622(6)
γ, deg	90.854(8)
V, Å^3	1053.9(4)
Z	2
d_{calc}, g cm^{-3}	1.227
crystal dimensions, mm	0.30x0.30x0.24
temperature, K	295.
radiation (wavelength)	Cu K_α(1.54184Å)
monochromator	graphite
linear abs coef, mm^{-1}	0.704
absorption correction applied	none
diffractometer	Enraf-Nonius CAD4
scan method	ω-2θ
h, k, l range	-7 to 7 -17 to 0 -16 to 18
2θ range, deg	5.38-148.66
scan width, deg	0.73 + 0.20tan(θ)
take-off angle, deg	6.00

DATA TABLE(cont)

programs used	SHELXL-93
F_{000}	416.0
weighting $w=1/[\sigma^2(Fo^2)+(0.0607P)^2+0.2109P]$ where $P=(Fo^2+2Fc^2)/3$	
data collected	4458
unique data	4278
R_{int}	0.043
data used in refinement	4277
cutoff used in R-factor calculations	$F_o^2>2\sigma(F_o^2)$
refined extinction coef	0.0403
number of variables	257
largest shift/esd in final cycle	0.00
$R(F_o)$	0.051
$R_w(F_o^2)$	0.119
goodness of fit	1.111

Table of Bond Distances in Angstroms

for $C_{21}H_{27}NO_6$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O(11)	C(12)	1.337(3)	C(4)	C(45)	1.536(4)
O(11)	C(1)	1.479(3)	C(4)	C(41)	1.547(4)
O(12)	C(12)	1.200(3)	C(5)	C(6)	1.511(4)
O(42)	C(42)	1.187(3)	C(12)	C(13)	1.489(4)
O(43)	C(42)	1.312(4)	C(13)	C(14)	1.381(4)
O(43)	C(44)	1.457(5)	C(13)	C(18)	1.385(4)
O(161)	N(16)	1.213(4)	C(14)	C(15)	1.371(4)
O(162)	N(16)	1.206(4)	C(15)	C(16)	1.361(4)
N(16)	C(16)	1.477(4)	C(16)	C(17)	1.377(4)
C(1)	C(2)	1.500(4)	C(17)	C(18)	1.381(4)
C(1)	C(6)	1.507(4)	C(31)	C(32)	1.524(4)
C(2)	C(3)	1.318(4)	C(32)	C(33)	1.516(4)
C(3)	C(31)	1.521(4)	C(33)	C(34)	1.514(4)
C(3)	C(4)	1.532(4)	C(41)	C(42)	1.497(4)
C(4)	C(5)	1.534(4)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

for $C_{21}H_{27}NO_6$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(12)	O(11)	C(1)	117.0(2)	O(12)	C(12)	O(11)	124.3(3)
C(42)	O(43)	C(44)	115.7(3)	O(12)	C(12)	C(13)	123.7(3)
O(162)	N(16)	O(161)	123.5(4)	O(11)	C(12)	C(13)	112.0(3)
O(162)	N(16)	C(16)	118.2(4)	C(14)	C(13)	C(18)	119.0(3)
O(161)	N(16)	C(16)	118.3(3)	C(14)	C(13)	C(12)	118.7(3)
O(11)	C(1)	C(2)	104.6(2)	C(18)	C(13)	C(12)	122.3(3)
O(11)	C(1)	C(6)	111.5(2)	C(15)	C(14)	C(13)	120.8(3)
C(2)	C(1)	C(6)	113.2(2)	C(16)	C(15)	C(14)	118.9(3)
C(3)	C(2)	C(1)	126.0(3)	C(15)	C(16)	C(17)	122.4(3)
C(2)	C(3)	C(31)	121.2(3)	C(15)	C(16)	N(16)	118.9(3)
C(2)	C(3)	C(4)	121.5(3)	C(17)	C(16)	N(16)	118.6(3)
C(31)	C(3)	C(4)	117.3(2)	C(16)	C(17)	C(18)	118.0(3)
C(3)	C(4)	C(5)	108.7(2)	C(17)	C(18)	C(13)	120.8(3)
C(3)	C(4)	C(45)	111.2(2)	C(3)	C(31)	C(32)	116.3(2)
C(5)	C(4)	C(45)	108.2(2)	C(33)	C(32)	C(31)	113.3(2)
C(3)	C(4)	C(41)	106.6(2)	C(34)	C(33)	C(32)	111.9(3)
C(5)	C(4)	C(41)	112.7(2)	C(42)	C(41)	C(4)	115.2(2)
C(45)	C(4)	C(41)	109.4(2)	O(42)	C(42)	O(43)	122.4(3)
C(6)	C(5)	C(4)	113.2(2)	O(42)	C(42)	C(41)	126.4(3)
C(1)	C(6)	C(5)	111.1(2)	O(43)	C(42)	C(41)	111.2(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C(12)	O(11)	C(1)	C(2)	-156.54	(0.27)
C(12)	O(11)	C(1)	C(6)	80.76	(0.31)
C(1)	O(11)	C(12)	O(12)	-2.30	(0.49)
C(1)	O(11)	C(12)	C(13)	179.31	(0.25)
C(44)	O(43)	C(42)	O(42)	0.87	(0.56)
C(44)	O(43)	C(42)	C(41)	179.70	(0.34)
O(161)	N(16)	C(16)	C(15)	-172.12	(0.38)
O(161)	N(16)	C(16)	C(17)	8.02	(0.56)
O(162)	N(16)	C(16)	C(15)	8.45	(0.56)
O(162)	N(16)	C(16)	C(17)	-171.41	(0.38)
O(11)	C(1)	C(2)	C(3)	-115.30	(0.32)
C(6)	C(1)	C(2)	C(3)	6.24	(0.43)
O(11)	C(1)	C(6)	C(5)	82.63	(0.27)
C(2)	C(1)	C(6)	C(5)	-34.93	(0.33)
C(1)	C(2)	C(3)	C(4)	0.49	(0.47)
C(1)	C(2)	C(3)	C(31)	-179.13	(0.27)
C(2)	C(3)	C(4)	C(5)	21.24	(0.38)
C(2)	C(3)	C(4)	C(41)	-100.52	(0.31)
C(2)	C(3)	C(4)	C(45)	140.31	(0.29)
C(31)	C(3)	C(4)	C(5)	-159.13	(0.25)
C(31)	C(3)	C(4)	C(41)	79.11	(0.30)
C(31)	C(3)	C(4)	C(45)	-40.06	(0.34)
C(2)	C(3)	C(31)	C(32)	16.05	(0.42)
C(4)	C(3)	C(31)	C(32)	-163.58	(0.25)
C(3)	C(4)	C(5)	C(6)	-50.88	(0.33)
C(41)	C(4)	C(5)	C(6)	66.98	(0.32)
C(45)	C(4)	C(5)	C(6)	-171.77	(0.25)
C(3)	C(4)	C(41)	C(42)	-170.10	(0.24)
C(5)	C(4)	C(41)	C(42)	70.79	(0.30)
C(45)	C(4)	C(41)	C(42)	-49.80	(0.33)
C(4)	C(5)	C(6)	C(1)	59.47	(0.33)
O(11)	C(12)	C(13)	C(14)	166.58	(0.29)
O(11)	C(12)	C(13)	C(18)	-13.91	(0.44)
O(12)	C(12)	C(13)	C(14)	-11.82	(0.50)
O(12)	C(12)	C(13)	C(18)	167.69	(0.34)
C(12)	C(13)	C(14)	C(15)	-178.56	(0.31)
C(18)	C(13)	C(14)	C(15)	1.91	(0.48)
C(12)	C(13)	C(18)	C(17)	178.93	(0.30)
C(14)	C(13)	C(18)	C(17)	-1.56	(0.48)
C(13)	C(14)	C(15)	C(16)	-0.97	(0.51)
C(14)	C(15)	C(16)	N(16)	179.79	(0.34)
C(14)	C(15)	C(16)	C(17)	-0.36	(0.53)
N(16)	C(16)	C(17)	C(18)	-179.46	(0.32)
C(15)	C(16)	C(17)	C(18)	0.69	(0.52)
C(16)	C(17)	C(18)	C(13)	0.29	(0.50)

Table of Torsion Angles in Degrees (continued)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C(3)	C(31)	C(32)	C(33)	176.94 (0.28)
C(31)	C(32)	C(33)	C(34)	-174.43 (0.30)
C(4)	C(41)	C(42)	O(42)	-59.46 (0.46)
C(4)	C(41)	C(42)	O(43)	121.76 (0.30)

Table of Atomic Multiplicities

for $C_{21}H_{27}NO_6$

Name	Multiplicity	Name	Multiplicity	Name	Multiplicity
O(11)	1.000	O(12)	1.000	O(42)	1.000
O(43)	1.000	O(161)	1.000	O(162)	1.000
N(16)	1.000	C(1)	1.000	C(2)	1.000
C(3)	1.000	C(4)	1.000	C(5)	1.000
C(6)	1.000	C(12)	1.000	C(13)	1.000
C(14)	1.000	C(15)	1.000	C(16)	1.000
C(17)	1.000	C(18)	1.000	C(31)	1.000
C(32)	1.000	C(33)	1.000	C(34)	1.000
C(41)	1.000	C(42)	1.000	C(44)	1.000
C(45)	1.000	H(1)	1.000	H(2)	1.000
H(14)	1.000	H(15)	1.000	H(17)	1.000
H(18)	1.000	H(5A)	1.000	H(5B)	1.000
H(6A)	1.000	H(6B)	1.000	H(31A)	1.000
H(31B)	1.000	H(32A)	1.000	H(32B)	1.000
H(33A)	1.000	H(33B)	1.000	H(34A)	1.000
H(34B)	1.000	H(34C)	1.000	H(41A)	1.000
H(41B)	1.000	H(44A)	1.000	H(44B)	1.000
H(44C)	1.000	H(45A)	1.000	H(45B)	1.000
H(45C)	1.000				

Positional Parameters and Their Estimated Standard Deviations

for $C_{21}H_{27}NO_6$

Atom	x	y	z	U(Å^2)
O(11)	0.2714(4)	0.7858(2)	0.45893(14)	0.0615(8)
O(12)	0.3227(4)	0.9406(2)	0.6031(2)	0.0790(11)
O(42)	0.0220(5)	0.9310(2)	0.1214(2)	0.0999(14)
O(43)	-0.2865(5)	0.8372(2)	0.0227(2)	0.1048(14)
O(161)	1.1783(6)	0.5859(3)	0.6291(3)	0.1145(15)
O(162)	1.2576(6)	0.7345(3)	0.7611(3)	0.1238(16)
N(16)	1.1408(6)	0.6775(3)	0.6820(3)	0.0840(16)
C(1)	0.0721(5)	0.8249(2)	0.4187(2)	0.0581(13)
C(2)	-0.0686(5)	0.7279(2)	0.3423(2)	0.0594(14)
C(3)	-0.1023(5)	0.6948(2)	0.2410(2)	0.0498(12)
C(4)	0.0060(5)	0.7548(2)	0.1887(2)	0.0492(11)
C(5)	0.2155(5)	0.8244(2)	0.2599(2)	0.0558(14)
C(6)	0.1563(5)	0.8914(2)	0.3708(2)	0.0604(14)
C(12)	0.3760(5)	0.8518(3)	0.5523(2)	0.0592(14)
C(13)	0.5715(5)	0.8033(2)	0.5849(2)	0.0558(12)
C(14)	0.7271(6)	0.8672(3)	0.6681(2)	0.0659(14)
C(15)	0.9130(6)	0.8265(3)	0.6996(2)	0.0704(14)
C(16)	0.9402(6)	0.7214(3)	0.6484(2)	0.0655(14)
C(17)	0.7872(6)	0.6542(3)	0.5664(2)	0.0701(14)
C(18)	0.6015(6)	0.6964(3)	0.5352(2)	0.0661(14)
C(31)	-0.2518(5)	0.5957(2)	0.1715(2)	0.0578(13)
C(32)	-0.4110(5)	0.5544(2)	0.2264(2)	0.0598(14)

Positional Parameters and Their Estimated Standard Deviations (cont.)

for $C_{21}H_{27}NO_6$

Atom	x	y	z	U(Å^2)
C(33)	-0.5640(6)	0.4589(3)	0.1519(3)	0.0740(14)
C(34)	-0.7364(6)	0.4264(3)	0.2083(3)	0.089(2)
C(41)	-0.1920(5)	0.8185(2)	0.1710(2)	0.0562(13)
C(42)	-0.1351(6)	0.8689(3)	0.1044(2)	0.0634(14)
C(44)	-0.2477(10)	0.8821(4)	-0.0473(4)	0.158(3)
C(45)	0.0957(5)	0.6794(2)	0.0834(2)	0.0626(14)

$U_{eq} = (1/3)\Sigma_i\Sigma_j\ U_{ij}a^*_i a^*_j a_i \cdot a_j$

Positional Parameters and Their Estimated Standard Deviations

for $C_{21}H_{27}NO_6$

Atom	x	y	z	U(Å^2)
H(1)	-0.0238(5)	0.8667(2)	0.4761(2)	0.075
H(2)	-0.1384(5)	0.6875(2)	0.3688(2)	0.077
H(14)	0.7055(6)	0.9388(3)	0.7032(2)	0.086
H(15)	1.0187(6)	0.8699(3)	0.7550(2)	0.092
H(17)	0.8082(6)	0.5825(3)	0.5330(2)	0.091
H(18)	0.4954(6)	0.6526(3)	0.4802(2)	0.085
H(5A)	0.3425(5)	0.7803(2)	0.2598(2)	0.072
H(5B)	0.2710(5)	0.8695(2)	0.2318(2)	0.072
H(6A)	0.2947(5)	0.9339(2)	0.4118(2)	0.079
H(6B)	0.0348(5)	0.9383(2)	0.3719(2)	0.079
H(31A)	-0.1477(5)	0.5410(2)	0.1321(2)	0.075
H(31B)	-0.3493(5)	0.6088(2)	0.1218(2)	0.075
H(32A)	-0.3143(5)	0.5368(2)	0.2730(2)	0.078
H(32B)	-0.5114(5)	0.6095(2)	0.2684(2)	0.078
H(33A)	-0.6503(6)	0.4741(3)	0.1010(3)	0.096
H(33B)	-0.4646(6)	0.4013(3)	0.1148(3)	0.096
H(34A)	-0.837(3)	0.3688(12)	0.1583(3)	0.116
H(34B)	-0.830(3)	0.4843(6)	0.2478(15)	0.116
H(34C)	-0.6515(7)	0.4054(17)	0.2543(14)	0.116
H(41A)	-0.3311(5)	0.7723(2)	0.1390(2)	0.073
H(41B)	-0.2304(5)	0.8727(2)	0.2383(2)	0.073
H(44A)	-0.353(5)	0.847(2)	-0.1089(15)	0.205

Positional Parameters and Their Estimated Standard Deviations (cont.)

for $C_{21}H_{27}NO_6$

Atom	x	y	z	U(Å^2)
H(44B)	-0.088(2)	0.873(3)	-0.066(3)	0.205
H(44C)	-0.276(7)	0.9554(8)	-0.0129(12)	0.205
H(45A)	0.178(3)	0.7188(2)	0.0560(7)	0.081
H(45B)	-0.0352(6)	0.6399(11)	0.0355(5)	0.081
H(45C)	0.201(3)	0.6324(10)	0.0929(3)	0.081

Hydrogens included in calculation of structure factors but not refined
$B_{iso}(H)=1.3*B_{iso}(C)$

Anisotropic Temperature Factor Coefficients - U's

for $C_{21}H_{27}NO_6$

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O(11)	0.0715(14)	0.0632(13)	0.0440(11)	-0.0072(11)	-0.0049(10)	0.0214(10)
O(12)	0.086(2)	0.069(2)	0.0587(13)	0.0023(13)	-0.0073(12)	0.0112(12)
O(42)	0.118(2)	0.104(2)	0.093(2)	-0.048(2)	-0.031(2)	0.065(2)
O(43)	0.118(2)	0.129(2)	0.087(2)	-0.045(2)	-0.040(2)	0.074(2)
O(161)	0.131(3)	0.100(2)	0.111(2)	0.022(2)	-0.007(2)	0.049(2)
O(162)	0.118(2)	0.126(3)	0.116(2)	0.000(2)	-0.044(2)	0.053(2)
N(16)	0.086(2)	0.097(3)	0.079(2)	-0.001(2)	0.001(2)	0.050(2)
C(1)	0.055(2)	0.067(2)	0.048(2)	-0.0051(15)	0.0030(13)	0.0232(15)
C(2)	0.060(2)	0.067(2)	0.052(2)	-0.0146(15)	0.0022(14)	0.029(2)
C(3)	0.045(2)	0.059(2)	0.0447(15)	-0.0041(13)	0.0051(12)	0.0235(13)
C(4)	0.0442(15)	0.058(2)	0.0463(15)	-0.0029(13)	0.0076(12)	0.0246(13)
C(5)	0.049(2)	0.063(2)	0.062(2)	-0.0082(14)	0.0037(13)	0.035(2)
C(6)	0.063(2)	0.055(2)	0.057(2)	-0.0117(15)	-0.0035(14)	0.022(2)
C(12)	0.064(2)	0.062(2)	0.043(2)	-0.014(2)	-0.0002(14)	0.018(2)
C(13)	0.068(2)	0.061(2)	0.0379(14)	-0.0132(15)	0.0008(13)	0.0234(14)
C(14)	0.078(2)	0.063(2)	0.054(2)	-0.013(2)	-0.009(2)	0.027(2)
C(15)	0.078(2)	0.077(2)	0.058(2)	-0.020(2)	-0.015(2)	0.036(2)
C(16)	0.073(2)	0.077(2)	0.058(2)	-0.007(2)	0.000(2)	0.042(2)
C(17)	0.087(2)	0.066(2)	0.060(2)	-0.003(2)	0.003(2)	0.032(2)
C(18)	0.079(2)	0.068(2)	0.047(2)	-0.012(2)	0.000(2)	0.024(2)
C(31)	0.059(2)	0.062(2)	0.053(2)	-0.0137(14)	-0.0008(14)	0.0281(15)
C(32)	0.060(2)	0.067(2)	0.059(2)	-0.014(2)	-0.0017(14)	0.036(2)

Anisotropic Temperature Factor Coefficients - U's (Continued)

for $C_{21}H_{27}NO_6$

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C(33)	0.075(2)	0.073(2)	0.077(2)	-0.028(2)	-0.010(2)	0.040(2)
C(34)	0.078(2)	0.099(3)	0.107(3)	-0.031(2)	-0.008(2)	0.064(3)
C(41)	0.053(2)	0.065(2)	0.052(2)	-0.0017(14)	0.0029(13)	0.0286(15)
C(42)	0.071(2)	0.065(2)	0.053(2)	-0.008(2)	-0.006(2)	0.028(2)
C(44)	0.204(6)	0.193(5)	0.120(4)	-0.076(5)	-0.065(4)	0.122(4)
C(45)	0.061(2)	0.069(2)	0.056(2)	-0.001(2)	0.0166(14)	0.026(2)

The form of the anisotropic temperature factor is:

$\exp[-2\pi \{h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c\ U(2,3)\}]$ where a^*, b^*, and c^* are reciprocal lattice constants.

F°obs & F°calc for $C_{21}H_{27}NO_4$

H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc
-7	-2	1	0	0	-6	-4	2	3	3	-6	2	8	0	1	-5	-10	12	-3	0	-5	-4	2	2	1
-7	-2	2	0	0	-6	-4	3	28	25	-6	3	0	-5	1	-5	-9	1	0	0	-5	-4	3	148	156
-7	-2	3	11	10	-6	-4	4	5	8	-6	3	1	0	2	-5	-9	2	1	2	-5	-4	4	3	2
-7	-2	4	9	8	-6	-4	5	-1	0	-6	3	2	5	7	-5	-9	3	0	3	-5	-4	5	10	15
-7	-1	1	0	0	-6	-4	6	12	9	-6	3	3	5	5	-5	-9	4	-3	0	-5	-4	6	26	22
-7	-1	2	-2	3	-6	-4	7	-1	0	-6	3	4	-1	1	-5	-9	5	2	5	-5	-4	7	3	0
-7	-1	3	4	3	-6	-4	8	1	5	-6	3	5	9	4	-5	-9	6	3	5	-5	-4	8	11	13
-7	-1	4	6	3	-6	-4	9	11	11	-6	3	6	4	9	-5	-9	7	10	7	-5	-4	9	1	0
-7	0	1	4	3	-6	-4	10	2	2	-6	3	7	9	8	-5	-9	8	-2	0	-5	-4	10	0	0
-7	0	2	-3	0	-6	-3	1	-6	0	-6	4	0	1	5	-5	-9	9	-5	0	-5	-4	11	6	6
-7	0	3	7	8	-6	-3	2	-4	0	-6	4	1	3	1	-5	-9	10	25	24	-5	-4	12	5	1
-7	0	4	-3	1	-6	-3	3	0	0	-6	4	2	-5	2	-5	-9	11	9	12	-5	-4	13	2	2
-7	1	0	2	1	-6	-3	4	59	51	-6	4	3	5	0	-5	-9	12	-3	0	-5	-3	1	33	36
-7	1	1	3	2	-6	-3	5	-10	1	-6	4	4	3	3	-5	-8	1	15	10	-5	-3	2	80	87
-7	1	2	4	7	-6	-3	6	-6	4	-6	4	5	-1	0	-5	-8	2	2	4	-5	-3	3	9	10
-7	1	3	-1	3	-6	-3	7	52	44	-6	4	6	0	0	-5	-8	3	-8	0	-5	-3	4	0	1
-7	2	0	1	4	-6	-3	8	0	1	-6	4	7	0	3	-5	-8	4	-10	5	-5	-3	5	120	115
-7	2	1	2	0	-6	-3	9	3	0	-6	5	0	-1	1	-5	-8	5	5	6	-5	-3	6	41	30
-7	2	2	1	0	-6	-3	10	2	0	-6	5	1	0	0	-5	-8	6	12	15	-5	-3	7	15	17
-7	3	0	0	2	-6	-2	1	96	95	-6	5	2	-1	1	-5	-8	7	-2	4	-5	-3	8	0	0
-7	3	1	0	1	-6	-2	2	9	7	-6	5	3	0	0	-5	-8	8	12	15	-5	-3	9	7	6
-6	-9	3	7	5	-6	-2	3	61	57	-6	5	4	-2	2	-5	-8	9	2	0	-5	-3	10	0	1
-6	-9	4	5	4	-6	-2	4	0	5	-6	5	5	3	1	-5	-8	10	28	28	-5	-3	11	-4	0
-6	-9	5	2	3	-6	-2	5	9	9	-6	5	6	0	0	-5	-8	11	-9	0	-5	-3	12	-4	0
-6	-9	6	13	8	-6	-2	6	46	42	-6	6	0	0	1	-5	-8	12	1	1	-5	-3	13	17	16
-6	-9	7	3	3	-6	-2	7	7	6	-6	6	1	1	4	-5	-8	13	-1	0	-5	-2	1	-7	7
-6	-8	1	0	0	-6	-2	8	0	2	-6	6	2	2	0	-5	-7	1	12	14	-5	-2	2	-9	0
-6	-8	2	5	4	-6	-2	9	12	7	-6	6	3	12	11	-5	-7	2	8	7	-5	-2	3	-10	1
-6	-8	3	0	0	-6	-2	10	0	1	-6	6	4	-3	1	-5	-7	3	3	5	-5	-2	4	0	0
-6	-8	4	0	2	-6	-1	1	12	6	-6	6	5	4	1	-5	-7	4	-8	0	-5	-2	5	24	22
-6	-8	5	3	1	-6	-1	2	3	3	-6	7	0	3	4	-5	-7	5	10	9	-5	-2	6	2	1
-6	-8	6	11	12	-6	-1	3	8	6	-6	7	1	2	0	-5	-7	6	4	3	-5	-2	7	-3	4
-6	-8	7	-1	0	-6	-1	4	1	11	-6	7	2	6	7	-5	-7	7	-3	2	-5	-2	8	-7	2
-6	-8	8	2	2	-6	-1	5	22	19	-6	7	3	0	1	-5	-7	8	0	6	-5	-2	9	20	13
-6	-8	9	1	0	-6	-1	6	9	8	-6	8	0	2	1	-5	-7	9	17	18	-5	-2	10	-1	2
-6	-7	1	-4	0	-6	-1	7	21	16	-6	8	1	-1	0	-5	-7	10	10	5	-5	-2	11	-1	0
-6	-7	2	2	5	-6	-1	8	3	2	-6	8	2	0	1	-5	-7	11	1	12	-5	-2	12	0	2
-6	-7	3	-5	1	-6	-1	9	0	0	-6	9	0	-1	0	-5	-7	12	1	0	-5	-2	13	1	0
-6	-7	4	0	3	-6	-1	10	2	1	-5	-12	4	5	5	-5	-7	13	-1	1	-5	-1	1	26	21
-6	-7	5	-4	6	-6	0	1	3	6	-5	-12	5	2	2	-5	-6	1	22	20	-5	-1	2	-4	8
-6	-7	6	3	0	-6	0	2	1	0	-5	-12	6	2	2	-5	-6	2	44	38	-5	-1	3	7	5
-6	-7	7	2	0	-6	0	3	-3	2	-5	-12	7	1	1	-5	-6	3	4	0	-5	-1	4	1	2
-6	-7	8	3	0	-6	0	4	0	1	-5	-12	8	0	0	-5	-6	4	-6	2	-5	-1	5	26	29
-6	-7	9	1	1	-6	0	5	11	6	-5	-12	9	28	23	-5	-6	5	-1	0	-5	-1	6	80	77
-6	-7	10	0	2	-6	0	6	3	6	-5	-11	1	22	20	-5	-6	6	15	16	-5	-1	7	-6	1
-6	-6	1	-1	1	-6	0	7	12	7	-5	-11	2	5	2	-5	-6	7	1	3	-5	-1	8	7	2
-6	-6	2	12	13	-6	0	8	0	1	-5	-11	3	23	21	-5	-6	8	7	4	-5	-1	9	1	2
-6	-6	3	6	4	-6	0	9	0	2	-5	-11	4	1	1	-5	-6	9	-2	1	-5	-1	10	6	7
-6	-6	4	5	0	-6	1	0	1	7	-5	-11	5	3	0	-5	-6	10	33	26	-5	-1	11	2	0
-6	-6	5	-1	0	-6	1	1	-4	1	-5	-11	6	9	8	-5	-6	11	-7	0	-5	-1	12	1	0
-6	-6	6	2	5	-6	1	2	2	5	-5	-11	7	6	5	-5	-6	12	2	1	-5	0	1	39	34
-6	-6	7	7	4	-6	1	3	-3	5	-5	-11	8	16	13	-5	-6	13	-1	0	-5	0	2	16	20
-6	-6	8	-3	2	-6	1	4	3	8	-5	-11	9	1	3	-5	-5	1	0	1	-5	0	3	0	4
-6	-6	9	3	6	-6	1	5	1	2	-5	-11	10	1	5	-5	-5	2	82	77	-5	0	4	0	1
-6	-6	10	5	3	-6	1	6	11	13	-5	-11	11	0	1	-5	-5	3	0	0	-5	0	5	49	42
-6	-5	1	3	3	-6	1	7	7	3	-5	-10	1	3	1	-5	-5	4	13	14	-5	0	6	1	2
-6	-5	2	16	17	-6	1	8	-3	0	-5	-10	2	21	17	-5	-5	5	10	3	-5	0	7	0	4
-6	-5	3	6	4	-6	1	9	2	2	-5	-10	3	7	7	-5	-5	6	-4	12	-5	0	8	2	2
-6	-5	4	11	10	-6	2	0	-1	0	-5	-10	4	-3	1	-5	-5	7	0	1	-5	0	9	16	13
-6	-5	5	1	3	-6	2	1	-4	1	-5	-10	5	1	2	-5	-5	8	-1	2	-5	0	10	2	1
-6	-5	6	9	4	-6	2	2	0	5	-5	-10	6	1	0	-5	-5	9	9	10	-5	0	11	0	2
-6	-5	7	18	11	-6	2	3	10	9	-5	-10	7	3	6	-5	-5	10	3	4	-5	0	12	2	1
-6	-5	8	-3	0	-6	2	4	-3	0	-5	-10	8	0	0	-5	-5	11	-2	0	-5	1	0	-1	3
-6	-5	9	1	1	-6	2	5	1	3	-5	-10	9	-2	1	-5	-5	12	-1	3	-5	1	1	12	6
-6	-5	10	-1	0	-6	2	6	0	0	-5	-10	10	-1	1	-5	-5	13	0	0	-5	1	2	-7	1
-6	-4	1	24	26	-6	2	7	-7	0	-5	-10	11	-4	1	-5	-4	1	152	145	-5	1	3	-4	2

Reflections flagged with an asterisk were considered unobserved.

F²obs & F²calc for $C_{21}H_{27}NO_4$

H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc	H	K	L	Obs	Calc
-5	1	4	0	9	-5	7	6	1	1	-4	-11	14	-2	0	-4	-6	6	26	19	-4	-2	12	15	10
-5	1	5	23	19	-5	7	7	-1	0	-4	-10	1	3	7	-4	-6	7	37	34	-4	-2	13	-11	2
-5	1	6	24	24	-5	8	0	-2	3	-4	-10	2	0	23	-4	-6	8	77	91	-4	-2	14	8	7
-5	1	7	2	0	-5	8	1	7	5	-4	-10	3	14	17	-4	-6	9	39	43	-4	-1	1	2	2
-5	1	8	7	7	-5	8	2	8	6	-4	-10	4	46	47	-4	-6	10	35	34	-4	-1	2	281	247
-5	1	9	1	4	-5	8	3	0	0	-4	-10	5	44	45	-4	-6	11	4	5	-4	-1	3	197	171
-5	1	10	0	9	-5	8	4	-2	1	-4	-10	6	-4	0	-4	-6	12	-6	2	-4	-1	4	50	43
-5	1	11	4	3	-5	8	5	-1	0	-4	-10	7	1	6	-4	-6	13	24	24	-4	-1	5	6	2
-5	2	0	0	4	-5	8	6	0	1	-4	-10	8	4	0	-4	-6	14	3	3	-4	-1	6	80	71
-5	2	1	-7	2	-5	9	0	0	0	-4	-10	9	10	8	-4	-6	15	-1	2	-4	-1	7	5	2
-5	2	2	15	15	-5	9	1	2	1	-4	-10	10	0	14	-4	-5	1	28	33	-4	-1	8	22	22
-5	2	3	12	11	-5	9	2	-8	2	-4	-10	11	9	13	-4	-5	2	107	106	-4	-1	9	-2	0
-5	2	4	10	12	-5	9	3	0	0	-4	-10	12	2	2	-4	-5	3	172	181	-4	-1	10	51	41
-5	2	5	23	23	-5	9	4	-1	0	-4	-10	13	-1	0	-4	-5	4	-2	2	-4	-1	11	44	33
-5	2	6	4	2	-5	10	0	-3	1	-4	-10	14	1	3	-4	-5	5	33	28	-4	-1	12	-12	2
-5	2	7	10	13	-5	10	1	7	6	-4	-10	15	0	1	-4	-5	6	4	2	-4	-1	13	3	4
-5	2	8	5	7	-5	10	2	0	0	-4	-9	1	-2	2	-4	-5	7	23	17	-4	-1	14	2	0
-5	2	9	13	12	-5	10	3	2	0	-4	-9	2	-1	3	-4	-5	8	20	12	-4	0	1	58	54
-5	2	10	9	9	-5	11	0	2	3	-4	-9	3	-7	1	-4	-5	9	26	20	-4	0	2	0	0
-5	2	11	8	4	-5	11	1	0	0	-4	-9	4	85	93	-4	-5	10	5	1	-4	0	3	64	61
-5	3	0	-6	1	-4	-14	4	9	7	-4	-9	5	6	7	-4	-5	11	7	5	-4	0	4	42	41
-5	3	1	23	24	-4	-14	5	7	8	-4	-9	6	10	9	-4	-5	12	29	29	-4	0	5	2	6
-5	3	2	2	0	-4	-14	6	16	14	-4	-9	7	-16	0	-4	-5	13	8	11	-4	0	6	35	39
-5	3	3	4	5	-4	-14	7	45	41	-4	-9	8	19	29	-4	-5	14	-3	2	-4	0	7	31	28
-5	3	4	15	10	-4	-14	8	1	0	-4	-9	9	13	17	-4	-5	15	2	1	-4	0	8	42	45
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Reflections flagged with an asterisk were considered unobserved.