Functionalizations of [6]- and [7]-Helicenes at their Most Sterically Hindered Positions

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Experimental Section

THF was distilled from Na/Ph₂CO; CH₂Cl₂, 1,2-dichloroethane, and DMF from CaH₂. (Chloromethylene)dimethylammonium chloride⁴⁷ and *N*-methoxy-*N*-methylacetamide^{26b} were synthesized. The term chromatography refers to flash chromatography on silica gel.⁴⁸

Preparation of methoxylated helicenes 3a and 4a. THF (40 mL) was added under N₂ to a mixture of (+)-**3** (895 mg, 1.86 mmol) and *t*-BuOK (835 mg, 7.46 mmol). The mixture was vigorously stirred for 5 min. MeI (4.64 mL, 74.5 mmol) was added, and stirring was continued for 24 h. The yellow suspension was poured into H₂O (300 mL), extracted with CH₂Cl₂ (50 mL, 2 × 30 mL), the extracts were dried over Na₂SO₄ and filtered. The residue after the solvent had been evaporated was dissolved in a minimal amount of CH₂Cl₂ and chromatographed with 2:1 hexane / EtOAc. The yield of yellow solid was 863 mg (91%). Mp 128–130 °C (recrystallized from cyclohexane). [α]_D +2124 (*c* = 0.011, CH₃CN). IR (CCl₄): 2936, 2831, 1617, 1512, 1461, 1295, 1257, 1201, 1159, 1131 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 8.47 (d, 8.5 Hz, 2H), 8.03 (d, 8.5 Hz, 2H), 7.59 (s, 2H), 6.56 (d, 8.6 Hz, 2H), 5.81 (d, 8.6 Hz, 2H), 4.20 (s, 6H), 3.98 (s, 6H), 2.58 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 153.8, 149.2, 148.2, 130.4, 128.4, 126.0, 125.8, 124.8, 124.4, 119.6, 117.4, 105.6, 101.3, 96.5, 56.3, 56.0, 54.2 ppm. UV-vis (CH₃CN, *c* = 1.36 × 10⁻⁵ M): λ_{max} (log ε) 242 (4.79), 258 (sh, 4.60), 280 (4.42), 294 (4.39), 322 nm (4.50). CD (*c* = 1.36 × 10⁻⁵ M, CH₃CN), nm (Δε): 219 (107), 240 (–280), 257 (–61), 290 (–91), 322 (–68), 348 (380). Anal. calcd for C₃₂H₂₈O₆ C, 75.58; H, 5.55, found C, 75.34; H, 5.45.

The procedure above was applied to 1.10 g (1.86 mmol) of (+)-**4**. The crude product was chromatographed with 3:1 hexane/EtOAc. The yield of yellow solid was 1.03 g (91%). Mp 220–221 °C. [α]_D +2507 (*c* = 0.028, CH₃CN). IR (CCl₄): 2938, 2832, 1611, 1496, 1461, 1381, 1282, 1230, 1110, 1089 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 8.35 (s, 4H), 7.07 (s, 2H), 6.31 (d, 8.6, 2H), 5.71 (d, 8.6 Hz, 2H), 4.25 (s, 6H), 4.11 (s, 6H), 3.85 (s, 6H), 2.53 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 153.2, 147.7, 147.5, 143.6, 127.6, 125.7, 125.2, 124.5, 124.0, 119.7, 119.4, 118.5, 104.0, 101.8, 96.5, 61.3, 55.9, 55.6, 54.1 ppm. UV-vis (CH₃CN, *c* = 9.80 × 10⁻⁶ M): λ_{max} (log ε) 208 (4.90), 253 (4.72), 284 (sh, 4.56), 303 (4.60), 362 nm (4.05). CD (*c* = 9.80 × 10⁻⁶ M, CH₃CN), nm (Δε): 207 (96), 233 (367), 284 (–361), 361 (242), 377 (sh, 221), 404 (sh, 129). Anal. calcd for C₃₈H₃₄O₈ C, 73.77; H, 5.54, found C, 73.72; H, 5.39.

Preparation of bromohelicenes 3b and 4b. A solution of *N*-bromosuccinimide (215 mg, 1.21 mmol) in CH₃CN (10 mL) was added under N₂ to a stirred solution of (+)-**3a** (300 mg, 0.59 mmol) in CH₂Cl₂ (10 mL) and CH₃CN (10 mL). The solution was stirred for 1h, the solvent was evaporated, and the residue was chromatographed with CH₂Cl₂. The yield of yellow solid (mp >250 °C) was 365 mg (93%). [α]_D +2119 (*c* = 0.025, CH₃CN). IR (CCl₄): 2937, 1614, 1511, 1460, 1440, 1332, 1291, 1199, 1161, 1132 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 8.49 (d, 8.5 Hz, 2H), 8.04 (d, 8.5 Hz, 2H), 7.59 (s, 2H), 6.79 (s, 2H), 4.20 (s, 6H), 4.03 (s, 6H), 2.01 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 153.5, 150.7, 147.8, 130.9, 127.5, 125.8, 124.6, 124.0, 120.0 (2 peaks), 109.7, 109.6, 97.4, 59.0, 56.1, 55.9 ppm. UV-vis (CH₃CN, *c* = 8.69 × 10⁻⁶ M): λ_{max} (log ε) 252 (4.80), 286 (sh, 4.49), 329 (4.52), 435 nm (3.52). CD (*c* = 8.69 × 10⁻⁶ M, CH₃CN), nm (Δε): 214 (140), 227 (124), 251 (–324), 308 (sh, 79), 347 (368), 435 (–17). Anal. calcd for C₃₂H₂₆O₆Br₂ C, 57.68; H, 3.93, found C, 57.75; H, 3.93.

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The same procedure applied to (+)-**4a** (400 mg, 0.65 mmol) and *N*-bromosuccinimide (236 mg, 1.33 mmol) gave 436 mg (87%) of a yellow solid (chromatographed with 3:1 hexane/EtOAc). Mp 152–154 °C. $[\alpha]_D^{25} +2370$ ($c = 0.015$, CH₃CN). IR (CCl₄): 2935, 1610, 1582, 1493, 1497, 1426, 1381, 1315, 1280, 1203, 1109, 1097, 983 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 8.41 (d, 8.6 Hz, 2H), 8.36 (d, 8.6 Hz, 2H), 7.03 (s, 2H), 6.49 (s, 2H), 4.23 (s, 6H), 4.14 (s, 6H), 3.85 (s, 6H), 2.03 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 153.6, 150.3, 146.2, 143.4, 126.3, 126.1, 125.8, 123.8, 123.7, 120.7, 120.3, 120.0, 110.6, 108.2, 96.4, 61.4, 58.9, 55.6 ppm. UV-vis (CH₃CN, $c = 9.58 \times 10^{-6}$ M): $\lambda_{\max}$ (log ϵ) 213 (4.82), 257 (4.65), 269 (4.63), 285 (4.67), 304 nm (4.54). CD ($c = 9.58 \times 10^{-6}$ M, CH₃CN), nm ($\Delta\epsilon$): 241 (496), 262 (–148), 287 (–400), 305 (–297), 374 (326). Anal. calcd for C₃₈H₃₂O₈Br₂ C, 58.78; H, 4.15, found C, 58.73; H, 4.03.

Preparation of monoaldehydes 3c and 4c. A solution of (+)-**3a** (51 mg, 0.10 mmol) in 1,2-dichloroethane (3 mL) was added under N₂ to a stirred mixture of (chloromethylene)dimethylammonium chloride (711 mg, 5.0 mmol) in DMF (7 mL). The mixture was stirred at 50 °C for 14 h, poured into H₂O (100 mL), and extracted with CH₂Cl₂ (3 $\times$ 15 mL). The extracts were washed with 1 M HCl (50 mL), brine (20 mL) dried over Na₂SO₄, and filtered. The solvent was evaporated and the residue was chromatographed with 15:1 CH₂Cl₂/EtOAc. The yield of yellow solid (+)-**3c** (mp >240 °C) was 32 mg (59%). $[\alpha]_D^{25} +2646$ ($c = 0.021$, CH₃CN). IR (CCl₄): 2938, 1669, 1600, 1461, 1388, 1298, 1202, 1161, 1134 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 9.62 (s, 1H), 8.52 (d, 8.4 Hz, 1H), 8.48 (d, 8.4 Hz, 1H), 8.09 (d, 8.4 Hz, 1H), 8.01 (d, 8.4 Hz, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 6.97 (s, 1H), 6.49 (d, 8.6 Hz, 1H), 5.78 (d, 8.6 Hz, 1H), 4.23 (s, 3H), 4.21 (s, 3H), 4.04 (s, 3H), 3.94 (s, 3H), 2.58 (s, 3H), 2.05 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) 189.7, 157.4, 156.5, 153.4, 150.5, 148.8, 148.6, 131.1, 130.0, 128.4, 128.1, 126.8, 125.6, 125.3, 125.0, 124.8, 123.9, 122.6, 120.5, 119.6, 118.8, 117.4, 106.0, 101.6, 100.4, 97.3, 97.0, 61.4, 56.3, 56.1 (2 peaks), 56.0, 54.2 ppm. UV-vis (CH₃CN, $c = 1.60 \times 10^{-5}$ M): $\lambda_{\max}$ (log ϵ) 258 (sh, 4.63), 243 (4.69), 314 nm (4.63). CD ($c = 1.60 \times 10^{-5}$ M, CH₃CN), nm ($\Delta\epsilon$): 219 (38), 244 (–75), 269 (–7), 281 (6), 316 (–87), 351 (111). HRMS (FAB) m/z calcd for C₃₃H₂₈O₇ 536.1835, found 536.1862.

Analogously, (+)-**4a** (62 mg, 0.10 mmol) combined with (chloromethylene)dimethylammonium chloride (711 mg, 5.0 mmol) in DMF (7 mL) and CH₂Cl₂ (3 mL) at 25 °C for 24 h gave, after chromatography with 10:1 PhCH₃/EtOAc, 20 mg (32%) of recovered **4a** and 39 mg (60%) of (+)-**4c**, a yellow solid mp 140–142 °C. $[\alpha]_D^{25} +2775$ ($c = 0.019$, CH₃CN). IR (CCl₄): 2938, 1670, 1602, 1495, 1378, 1288, 1203, 1090 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 9.62 (s, 1H), 8.43–8.32 (m, 4H), 7.08 (s, 1H), 7.00 (s, 1H), 6.74 (s, 1H), 6.30 (d, 8.5 Hz, 1H), 5.72 (d, 8.5 Hz, 1H), 4.26 (s, 3H), 4.25 (s, 3H), 4.13 (s, 3H), 4.02 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 2.53 (s, 3H), 2.09 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) 190.0, 155.7, 153.4, 150.1, 148.1, 147.1, 144.3, 143.0, 129.0, 127.4, 126.3, 126.2, 126.1, 124.7, 124.6, 124.4, 124.2, 123.3, 120.6, 120.4, 120.0 (2 peaks), 119.4, 118.4, 103.7, 102.3, 99.5, 96.8, 61.4, 56.1, 55.6, 55.5, 55.4, 54.2 ppm. UV-vis (CH₃CN, $c = 1.02 \times 10^{-5}$ M): $\lambda_{\max}$ (log ϵ) 247 (4.71), 300 nm (4.63). CD ($c = 1.02 \times 10^{-5}$ M, CH₃CN), nm ($\Delta\epsilon$): 232 (68), 303 (–95), 389 (69). HRMS (FAB) m/z calcd for C₃₉H₃₄O₉ 646.2203, found 646.2228.

Preparation of bisaldehydes 3d and 4d. Method A. DMF (1 mL), followed by POCl₃ (1 mL), was added to a solution of **3a** (68 mg, 0.13 mmol) in CH₂Cl₂ (0.5 mL). The reaction mixture was stirred at 50 °C for ca 15 h, cooled, carefully poured into 5% aqueous NaOAc and extracted (2 $\times$) with EtOAc. The combined organic extracts were washed with water and brine, dried over Na₂SO₄ and evaporated. Chromatography (CH₂Cl₂-EtOAc, 95:5) gave 46 mg (61%) of pure **3d**. Its spectroscopic and physical

properties (mp >240 °C, yellow color) were identical to those of a sample prepared by Method B.

Similarly, DMF (2 mL), followed by POCl₃ (2 mL), was added to a solution of **4a** (187 mg, 0.30 mmol) in CH₂Cl₂ (1 mL) and the reaction mixture was heated to 70 °C. After work-up as above, chromatography (toluene-EtOAc, 95:5) gave 178 mg (87%) of pure **4d**. Its spectroscopic and physical properties (mp >240 °C, yellow color) were identical to those of a sample prepared by means of Method B.

Method B. BuLi (2.5 M in hexanes, 0.36 mL, 0.90 mmol) was added to a stirred solution of (+)-**3b** (100 mg, 0.15 mmol) in THF (9 mL) at -78 °C. The solution was stirred at -78 °C for 15 min. Then DMF (0.114 mL, 1.5 mmol), was added, the cooling bath was removed, and the mixture was stirred for 30 min. The reaction mixture was quenched with 1 M HCl (4 mL), poured into H₂O (50 mL), and extracted with Et₂O (30 mL). The extract was washed with saturated aqueous NaHCO₃ (20 mL) and brine (20 mL), dried over Na₂SO₄, and filtered. The solvent was evaporated and the residue was chromatographed. **3c** (28 mg, 35%) was eluted with 15:1 CH₂Cl₂/EtOAc, (+)-**3d** with 5:1 CH₂Cl₂/EtOAc. The yield of a yellow solid (+)-**3d** (mp >240 °C) was 50 mg (59%). [α]_D +3466 (*c* = 0.020, CH₃CN). IR (CCl₄): 2939, 1674, 1608, 1596, 1458, 1393, 1300, 1227, 1205, 1080 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 9.60 (s, 2H), 8.54 (d, 8.5 Hz, 2H), 8.09 (d, 8.5 Hz, 2H), 7.61 (s, 2H), 6.90 (s, 2H), 4.24 (s, 6H), 3.99 (s, 6H), 2.12 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 189.3, 156.5, 156.1, 150.9, 131.8, 130.8, 128.1, 126.1, 124.4, 123.6, 122.5, 120.6, 118.8, 101.0, 97.8, 61.3, 56.1, 56.0 ppm. UV-vis (CH₃CN, *c* = 1.17 × 10⁻⁵ M): λ_{max} (log ϵ) 255 (4.70), 316 (4.74), 3.87 nm (4.14). CD (*c* = 1.17 × 10⁻⁵ M, CH₃CN), nm ($\Delta\epsilon$): 218 (-80), 244 (-28), 268 (74), 324 (-171), 390 (115). HRMS (FAB) *m/z* calcd for C₃₄H₂₈O₈ 564.1782, found 564.1763.

Similarly, (+)-**4b** (117 mg, 0.15 mmol) gave 19 mg (20%) of **4a** (eluted with CH₂Cl₂), 52 mg (54%) of **4c** (eluted with 30:1 CH₂Cl₂/EtOAc), and 21 mg (21%) of (+)-**4d** (eluted with 10:1 CH₂Cl₂/EtOAc). Mp >240 °C. [α]_D: +3348 (*c* = 0.021, CH₃CN). IR (CCl₄): 2935, 1670, 1601, 1491, 1375, 1291, 1204, 1120, 1090 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 9.60 (s, 2H), 8.41 (d, 8.6 Hz, 2H), 8.38 (d, 8.6 Hz, 2H), 7.02 (s, 2H), 6.73 (s, 2H), 4.27 (s, 6H), 4.06 (s, 6H), 3.89 (s, 6H), 2.15 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 189.8, 156.0, 155.2, 150.5, 143.8, 129.3, 126.7, 126.2, 125.8, 124.5, 123.5, 120.8, 120.4, 119.8, 99.3, 97.1, 61.5, 61.3, 56.0, 55.5 ppm. UV-vis (CH₃CN, *c* = 9.29 × 10⁻⁶ M): λ_{max} (log ϵ) 225 (4.76), 250 (4.73), 307 nm (4.77). CD (*c* = 9.29 × 10⁻⁶ M, CH₃CN), nm ($\Delta\epsilon$): 230 (62), 243 (-10), 268 (92), 313 (-141), 369 (57), 416 (89). HRMS (FAB) *m/z* calcd for C₄₀H₃₄O₁₀ 674.2152, found 674.2175.

Preparation of monoacetyl derivatives 3e and 4e. AlCl₃ (16 mg, 0.12 mmol) was added to a stirred solution of (+)-**3a** (51 mg, 0.10 mmol) and AcCl (0.6 mL, 8.5 mmol) in CH₂Cl₂ (3 mL) cooled in an ice bath. The mixture was stirred for 15 min in a closed flask at 0 °C. Then AlCl₃ (3 × 16 mg) was added in three portions in 15 min intervals. The reaction mixture was carefully poured into H₂O (50 mL) and extracted with EtOAc (20, 5 mL). The extracts were washed with H₂O (50 mL) and saturated aqueous NaHCO₃ (30 mL), dried over Na₂SO₄, and filtered. The solvent was evaporated and the residue was chromatographed with 10:1 CH₂Cl₂/EtOAc. The yield of yellow solid (+)-**3e** (mp >240 °C) was 44 mg (80%). [α]_D +2417 (*c* = 0.021, CH₃CN). IR (CCl₄): 2937, 1656, 1607, 1461, 1382, 1300, 1219, 1132, 1074 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 8.50 (d, 8.4 Hz, 1H), 8.48 (d, 8.4 Hz, 1H), 8.07 (d, 8.5 Hz, 1H), 8.01 (d, 8.5 Hz, 1H), 7.57 (s, 2H), 7.06 (s, 1H), 6.50 (d, 8.6 Hz, 1H), 5.81 (d, 8.6 Hz, 1H), 4.22 (s, 3H), 4.20 (s, 3H), 4.03 (s, 3H), 3.94 (s, 3H), 2.59 (s, 3H), 2.08 (s, 3H), 1.97 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) 198.9, 155.7, 153.8, 153.7, 150.0, 148.7, 148.3, 131.0, 128.8, 128.1, 126.4, 125.6, 125.2, 125.0,

124.7, 124.1, 124.0, 120.2, 119.7, 119.1, 117.4, 105.5, 104.5, 101.5, 97.0, 96.7, 60.0, 56.1, 56.0 (3 peaks), 55.8, 54.2, 30.8 ppm. UV-vis (CH₃CN, $c = 8.41 \times 10^{-6}$ M): $\lambda_{\max}$ (log ϵ) 242 (4.74), 307 (4.60), 384 (sh, 3.99). CD ($c = 8.41 \times 10^{-6}$ M, CH₃CN), nm ($\Delta\epsilon$): 218 (52), 244 (–69), 311 (–87), 348 (117). Anal. calcd for C₃₄H₃₀O₇ C, 74.17; H, 5.49, found C, 73.77; H, 5.55.

Similarly, (+)-**4a** (62 mg, 0.10 mmol) and AcCl (0.6 mL, 8.5 mmol) in CH₂Cl₂ (3 mL) with AlCl₃ (3 × 16 mg) at 0 °C gave a mixture of **4a** (22 mg, 36%) and **4e** (35 mg, 53%), which was separated by column chromatography. (**4a** eluted with 30:1 CH₂Cl₂/EtOAc, (+)-**4e** eluted with 20:1 CH₂Cl₂/EtOAc). Mp of (+)-**4e** >240 °C. [α]_D +2927 ($c = 0.021$, CH₃CN). IR (CCl₄): 2938, 1657, 1606, 1495, 1375, 1289, 1230, 1089 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.38–8.34 (m, 4H), 7.04 (s, 1H), 7.01 (s, 1H), 6.88 (s, 1H), 6.31 (d, 8.6 Hz, 1H), 5.73 (d, 8.6 Hz, 1H), 4.26 (s, 3H), 4.25 (s, 3H), 4.12 (s, 3H), 4.04 (s, 3H), 4.00 (s, 3H), 3.84 (s, 3H), 2.55 (s, 3H), 2.11 (s, 3H), 2.01 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) 198.4, 155.0, 153.0, 152.2, 149.7, 148.1, 147.1, 144.2, 143.0, 128.0, 127.4, 126.5, 126.2, 126.1, 126.0, 125.0, 124.8, 124.5, 124.3, 124.2, 120.3, 120.0, 119.6, 118.3, 103.9, 103.4, 102.2, 96.8, 96.6, 61.4 (2 peaks), 59.8, 56.0, 55.5, 54.2, 30.8 ppm. UV-vis (CH₃CN, $c = 8.41 \times 10^{-6}$ M): $\lambda_{\max}$ (log ϵ) 207 (4.79), 251 (4.70), 303 nm (4.68). CD ($c = 8.41 \times 10^{-6}$ M, CH₃CN), nm ($\Delta\epsilon$): 231 (190), 249 (132), 303 (–321), 387 (257). HRMS (FAB) m/z calcd for C₄₀H₃₆O₉ 660.2358, found 660.2358.

A better way to prepare 4e: **4a** (185 mg, 0.31 mmol) was dissolved in CH₂Cl₂ (9 mL) and Ac₂O (2 mL) was added. The solution was cooled to 0 °C, and AlCl₃ (10 × 50 mg, 10 × 0.37 mmol) was added in portions at 5 min. intervals. The reaction was stirred for 5 more min, carefully quenched with water, and extracted with EtOAc. Washing with 1 M HCl and brine, drying over Na₂SO₄, evaporation, and chromatography gave unreacted **4a** (61 mg, 33%) and **4e** (130 mg, 63%, 94% based on recovered starting material).

Preparation of bisacetyl derivatives 3f and 4f. Method A. AlCl₃ (160 mg, 1.2 mmol) was added to a stirred solution of (+)-**3a** (51 mg, 0.10 mmol) and AcCl (0.6 mL, 8.5 mmol) in CH₂Cl₂ (3 mL). The mixture was stirred in a closed flask for 15 min at 25 °C, then AcCl (6 × 0.3 mL) and AlCl₃ (6 × 106 mg) were added at 10 min intervals. The reaction mixture was carefully poured into H₂O (50 mL) and extracted with EtOAc (20 mL, then 5 mL). The extracts were washed with H₂O (50 mL) and saturated aqueous NaHCO₃ (30 mL), dried over Na₂SO₄, and filtered. The solvent was evaporated and the residue was chromatographed with 5:1 CH₂Cl₂/EtOAc. The yield of yellow solid (+)-**3f** (mp >240 °C) was 49 mg (83%). [α]_D +2787 ($c = 0.023$, CH₃CN). IR (CCl₄): 2937, 1663, 1609, 1595, 1458, 1385, 1303, 1220, 1132, 1074 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.51 (d, 8.4 Hz, 2H), 8.06 (d, 8.4 Hz, 2H), 7.56 (s, 2H), 7.00 (s, 2H), 4.23 (s, 6H), 3.99 (s, 6H), 2.06 (s, 6H), 2.04 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 198.4, 155.6, 153.1, 150.1, 131.5, 129.6, 128.6, 125.8, 124.3, 120.4, 119.1, 104.8, 97.2, 60.0, 56.1, 55.8, 30.7 ppm. UV-vis (CH₃CN, $c = 8.66 \times 10^{-6}$ M): $\lambda_{\max}$ (log ϵ) 254 (4.69), 309 (4.72), 387 nm (sh, 4.04). CD ($c = 8.66 \times 10^{-6}$ M, CH₃CN), nm ($\Delta\epsilon$): 212 (–28), 264 (39), 317 (–161), 375 (122). Anal. calcd for C₃₆H₃₂O₈ C, 72.96; H, 5.44, found C, 72.65; H, 5.51.

Similarly, (+)-**4a** (62 mg, 0.10 mmol) and AcCl (0.6 mL, then 3 × 0.3 mL) in CH₂Cl₂ (3 mL) combined with AlCl₃ (160 mg, then 3 × 106 mg) gave, after chromatography with 10:1 CH₂Cl₂/EtOAc, 56 mg (80%) of yellow solid (+)-**4f**. Mp >240 °C. [α]_D +3127 ($c = 0.018$, CH₃CN). IR (CCl₄): 2937, 1658, 1603, 1490, 1378, 1295, 1204, 1097 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.37 (d, 8.6 Hz, 2H), 8.34 (d, 8.6 Hz, 2H), 6.99 (s, 2H), 6.86 (s, 2H), 4.26 (s, 6H), 4.06 (s, 6H), 3.89 (s, 6H), 2.09 (s, 6H), 2.07 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 198.3, 154.9, 151.7, 150.0, 143.5, 128.1, 126.4, 126.3, 125.7,

124.8, 120.6, 120.1, 120.0, 103.3, 97.0, 61.4, 59.8, 55.8, 55.4, 30.8 ppm. UV-vis (CH₃CN, $c = 1.11 \times 10^{-5}$ M): $\lambda_{\max}$ (log ϵ) 229 (4.70), 251 (4.72), 308 (4.77), 372 nm (sh, 4.17). CD ($c = 1.11 \times 10^{-5}$ M, CH₃CN), nm ($\Delta\epsilon$): 228 (187), 266 (255), 308 (–445), 398 (326). HRMS (FAB) m/z calcd for C₄₂H₃₈O₁₀ 702.2463, found 702.2493.

Method B. BuLi (2.5 M in hexanes, 0.120 mL, 0.3 mmol) was added to a stirred solution of **3b** (33 mg, 0.05 mmol) in THF (3 mL) at –78 °C. The mixture was stirred at –78 °C for 15 min, then *N*-methoxy-*N*-methylacetamide (0.053 mL, 0.5 mmol) was added, and the cooling bath was removed. The reaction mixture was stirred at 25 °C for 2 h, quenched with 1 M HCl (4 mL), poured into H₂O (50 mL), and extracted with CH₂Cl₂ (4 × 15 mL). The extracts were dried over Na₂SO₄ and filtered, and the solvent was evaporated. The residue when chromatographed with 20:1 CH₂Cl₂/EtOAc yielded 10 mg (40%) of **3a**, 10 mg (37%) of **3e**, and 5 mg (17%) of **3f**.

The same procedure applied to **4b** (39 mg, 0.05 mmol) followed by chromatography with 10:1 CH₂Cl₂/EtOAc gave 19 mg (61%) of **4a** 8 mg (24%) of **4e**, and 3 mg (9%) of **4f**.

Preparation of acetylenes from the acetylderivatives. PCl₃ (55 μ L) was added to monoacetyl derivative (–)-**3e** (57 mg, 0.1 mmol) dissolved in dry benzene (1 mL), and the solution was stirred for about 5 min. at ambient temperature. A suspension of PCl₅ (30 mg, 0.14 mmol) in benzene (1 mL) was added via syringe. The reaction mixture was stirred overnight (ca. 20 h), poured into water, and extracted with EtOAc. The organic layer was washed with more water and brine, dried over Na₂SO₄ and evaporated. Chromatography with toluene gave 33 mg (56%) of (–)-**3h**. Mp 240–241 °C. [α]_D: –2305 ($c = 1.1 \times 10^{-4}$, CH₃CN). IR (film, NaCl): 2998, 2935, 2832, 1609, 1456, 1297, 1204, 1158, 1130, 1073 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.49 (d, 8.4 Hz, 1H), 8.46 (d, 8.4 Hz, 1H), 8.06 (d, 8.4 Hz, 1H), 7.99 (d, 8.4 Hz, 1H), 7.58 (s, 1H), 7.57 (s, 1H), 6.73 (s, 1H), 6.56 (d, 8.5 Hz, 1H), 5.87 (d, 8.5 Hz, 1H), 5.37 (d, 0.7 Hz, 1H), 5.04 (d, 0.7 Hz, 1H), 4.21 (s, 3H), 4.20 (s, 3H), 4.02 (s, 3H), 3.95 (s, 3H), 2.61 (s, 3H), 1.93 ppm (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 153.9, 150.1, 149.5, 149.4, 148.6, 135.9, 131.1, 129.3, 129.2, 128.9, 128.5, 126.5, 126.3, 125.9, 125.8, 125.6, 125.3, 124.9, 124.5, 120.4, 120.2, 120.0, 118.2, 117.3, 106.8, 105.9, 102.1, 97.6, 97.2, 59.5, 56.7, 56.6, 56.4, 54.9 ppm. UV-vis ($c = 1.94 \times 10^{-4}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 432 (3.33), 324 (4.43), 298 (4.48), 247 (4.75), 205 nm (4.74). CD ($c = 1.94 \times 10^{-4}$ M, CH₃CN) nm ($\Delta\epsilon$): 351 (–137), 298 (64), 245 (94), 220 (–50). HRMS (FAB) m/z calcd for C₃₄H₂₉ClO₆ 568.1653, found 568.1667.

A solution of lithium diisopropylamide (LDA, 290 μ L, 0.29 mmol), freshly prepared by adding *n*-BuLi (2.2 mL, 1.6 M in hexane, 3.5 mmol) to diisopropylamine (0.5 mL, 3.5 mmol) in dry THF (0.8 mL) at 0 °C and stirring the mixture for 2 h at 0 °C, was added to (–)-**3h** (33 mg, 0.06 mmol) in dry THF (1.5 mL) at –78 °C, and the mixture was stirred at ambient temperature for 2 h. After the reaction had been carefully quenched with 1 M HCl, the mixture was extracted with EtOAc, and the organic layer was washed with more 1 M HCl, water and brine and dried over Na₂SO₄. Chromatography on silica gel (toluene : EtOAc 99 : 1) gave 25 mg (82%) of (–)-**3i**. Mp >260 °C (darkens above 240 °C). [α]_D: –2533 ($c = 0.94 \times 10^{-4}$, CH₃CN). IR (film, NaCl): 3285, 2935, 2831, 2100 (w), 1608, 1458, 1298, 1203, 1133, 1073 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.49 (d, 8.4 Hz, 1H), 8.45 (d, 8.4 Hz, 1H), 8.06 (d, 8.4 Hz, 1H), 7.98 (d, 8.4 Hz, 1H), 7.63 (s, 1H), 7.55 (s, 1H), 6.62 (d, 8.5 Hz, 1H), 6.61 (s, 1H), 5.83 (d, 8.5 Hz, 1H), 4.20 (s, 6H), 4.02 (s, 3H), 3.99 (s, 3H), 2.95 (s, 1H), 2.58 (s, 3H), 2.09 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 155.0, 154.6, 153.8, 150.1, 149.4, 149.2, 131.2, 128.5, 126.9, 126.6, 126.2, 125.5, 125.2, 124.5, 120.6, 119.9, 119.6, 117.9, 109.1, 108.2, 106.7, 101.8, 97.8, 97.0, 81.7, 79.2, 60.1, 56.9, 56.5, 56.4, 56.2, 54.6 ppm. UV-vis ($c = 1.8 \times 10^{-4}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 434

(3.33), 377 (3.97), 326 (4.42), 298 (4.51), 247 (4.74), 206 nm (4.68). CD ($c = 1.8 \times 10^{-4}$ M, CH₃CN) nm ($\Delta\epsilon$): 353 (–124), 298 (74), 245 (104), 212 (–46). HRMS (FAB) m/z calcd for C₃₄H₂₈O₆ 532.1886, found 532.1888.

Similarly, (–)-**4e** (185 mg, 0.28 mmol) in dry benzene (3 mL), PCl₃ (150 μ L) and a suspension of PCl₅ (80 mg, 0.38 mmol) in benzene (3 mL), stirred for ca. 16 h, gave (after chromatography with toluene-EtOAc, 99 : 1) 122 mg (64%) of (–)-**4h**. Mp 127 °C. $[\alpha]_D$: –2639 ($c = 0.80 \times 10^{-4}$, CH₃CN). IR (KBr): 2932, 2830, 1607, 1286, 1209, 1091 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.33 (m, 4H), 7.03 (s, 1H), 7.02 (s, 1H), 6.56 (s, 1H), 6.33 (d, 8.5 Hz, 1H), 5.72 (d, 8.5 Hz, 1H), 5.46 (s, 1H), 5.23 (s, 1H), 4.24 (s, 3H), 4.23 (s, 3H), 4.11 (s, 3H), 4.04 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.55 (s, 3H), 1.94 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 154.3, 153.4, 149.9, 148.4, 147.9, 147.7, 144.4, 143.4, 135.7, 127.9, 127.3, 126.5, 126.4, 126.1, 125.4, 125.3, 125.1, 124.8, 124.6, 124.5, 121.3, 120.5, 120.4, 120.3, 119.8, 118.5, 117.7, 105.6, 104.5, 102.4, 97.1, 96.9, 61.8, 59.2, 56.4, 56.0, 55.9, 55.8, 54.7 ppm. UV-vis ($c = 1.18 \times 10^{-4}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 366 (4.00), 303 (4.59), 255 (4.63), 211 nm (4.76). CD ($c = 1.18 \times 10^{-4}$ M, CH₃CN) nm ($\Delta\epsilon$): 382 (–93), 300 (116), 272 (sh, 24), 245 (sh, –66), 236 (–72). HRMS (FAB) m/z calcd for C₄₀H₃₅ClO₈ 678.2020, found 678.2021. A solution of LDA prepared as above (700 μ L, 0.7 mmol), added to (+)-**4h** (95 mg, 0.14 mmol) in dry THF (3 mL), gave 72 mg (80%) of (+)-**4i**. Mp 290 °C decomp. $[\alpha]_D$: +3031 ($c = 4.3 \times 10^{-4}$, CH₃CN). IR (KBr): 3290, 2932, 2100 (w), 1607, 1456, 1284, 1234, 1204, 1118, 1083 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.36 (m, 4H), 7.12 (s, 1H), 7.01 (s, 1H), 6.37 (s, 1H), 6.30 (d, 8.5 Hz, 1H), 5.70 (d, 8.5 Hz, 1H), 4.25 (s, 3H), 4.21 (s, 3H), 4.15 (s, 3H), 4.10 (s, 3H), 3.86 (s, 6H), 3.01 (s, 1H), 2.53 (s, 3H), 2.10 ppm (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 154.3, 154.0, 153.0, 149.8, 148.3, 147.6, 144.5, 143.4, 127.8, 127.0, 126.3, 126.1, 125.4, 125.2, 124.6, 120.7, 120.6, 120.4, 119.7, 118.5, 109.2, 107.9, 104.1, 102.1, 96.9, 81.9, 79.3, 61.8, 60.1, 56.4, 55.9, 54.6 ppm. UV-vis ($c = 5.68 \times 10^{-5}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 362 (4.04), 297 (4.57), 288 (4.57), 249 nm (4.58). CD ($c = 5.685 \times 10^{-5}$ M, CH₃CN) nm ($\Delta\epsilon$): 383 (41), 362 (31), 319 (–4), 281 (–4), 238 (1). HRMS (FAB) m/z calcd for C₄₀H₃₄O₈ 642.2254, found 642.2255.

Similarly, bisacetyl derivative (–)-**3f** (49 mg, 0.083 mmol) in benzene (2 mL), PCl₃ (72 μ L), and PCl₅ (43 mg, 0.206 mmol, added as a solid) gave 29 mg (56%) of (–)-**3j**. Mp 200–201 °C. $[\alpha]_D$: –2374 ($c = 0.808 \times 10^{-4}$, CH₃CN). IR (film, NaCl): 2931, 1609, 1457, 1299, 1205, 1159, 1128, 1082 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.47 (d, 8.5 Hz, 2H), 8.00 (d, 8.5 Hz, 2H), 7.55 (s, 2H), 6.71 (s, 2H), 5.38 (d, 0.7 Hz, 2H), 5.04 (d, 0.7 Hz, 2H), 4.20 (s, 6H), 3.97 (s, 6H), 1.98 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 154.7, 150.1, 149.0, 136.2, 131.5, 127.0, 125.9, 125.1, 124.9, 124.7, 120.4, 120.2, 117.2, 106.4, 97.6, 59.3, 56.4, 56.1 ppm. UV-vis ($c = 1.28 \times 10^{-4}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 435 (3.30), 280 (sh, 3.92), 327 (4.40), 301 (4.53), 250 (4.71), 206 nm (4.70). CD ($c = 1.28 \times 10^{-4}$ M, CH₃CN) nm ($\Delta\epsilon$): 351 (–129), 302 (99), 250 (46), 230 (–28), 216 (–37). HRMS (FAB) m/z calcd for C₃₆H₃₀Cl₂O₆ 628.1419, found 628.1434. The procedure above, applied to 10 molar equivalents (800 μ L, 0.8 mmol) of the ca. 1 M solution of LDA and (+)-**3j** (50 mg, 0.08 mmol) in dry THF (1.5 mL), gave 43 mg (97%) of (+)-**3k**. Decomposes at temperatures higher than 260 °C without melting. $[\alpha]_D$: +3075 ($c = 1.2 \times 10^{-4}$, CH₃CN). IR (film, NaCl): 3283, 3268, 2935, 2840, 2100 (w), 1612, 1457, 1300, 1203, 1160, 1135, 1078 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 8.47 (d, 8.5 Hz, 2H), 8.03 (d, 8.5 Hz, 2H), 7.59 (s, 2H), 6.66 (s, 2H), 4.20 (s, 6H), 4.02 (s, 6H), 2.96 (s, 2H), 2.12 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 154.6, 154.2, 150.5, 131.5, 128.1, 127.6, 126.2, 124.9, 124.6, 120.4, 119.5, 109.5, 108.0, 97.9, 81.8, 79.1, 60.1, 56.4, 56.3 ppm. UV-vis ($c = 2.1 \times 10^{-4}$ M, CH₃CN) $\lambda_{\max}$ (log ϵ): 370 (sh, 4.01), 327 (4.40), 301 (4.63), 248 (4.76), 208 nm (4.65). CD ($c = 2.1 \times 10^{-4}$ M, CH₃CN) nm

($\Delta\epsilon$): 360 (133), 301 (–133), 278 (–68), 265 (–46), 246 (–21), 229 (16), 216 (13). HRMS (FAB) m/z calcd for $C_{36}H_{28}O_6$ 556.1886, found 556.1890.

The same procedure applied to bisacetyl derivative (+)-**4f** (331 mg, 0.47 mmol) in benzene (5 mL), PCl_3 (410 μ L) and PCl_5 (245 mg, 1.18 mmol) in benzene (5 mL) gave 150 mg (43%) of (+)-**4j**. Mp very broad, starting at 122 °C. $[\alpha]_D$: +3046 ($c = 0.64 \times 10^{-4}$, CH_3CN). IR (KBr): 2930, 2832, 1606, 1290, 1211, 1096 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ 8.32 (m, 4H), 6.98 (s, 2H), 6.58 (s, 2H), 5.46 (s, 2H), 5.21 (s, 2H), 4.23 (s, 6H), 4.04 (s, 6H), 3.89 (s, 6H), 1.99 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 150.0, 147.6, 143.7, 135.8, 127.2, 126.3, 126.2, 125.3, 125.0, 124.4, 120.8, 120.7, 120.3, 117.6, 105.6, 97.0, 61.8, 59.3, 55.9, 55.8 ppm. UV-vis ($c = 8.6 \times 10^{-5}$ M, CH_3CN) λ_{max} (log ϵ): 383 (sh, 3.92), 371 (plateau, 3.99), 304 (4.64), 250 (4.65), 213 nm (4.70). CD ($c = 8.6 \times 10^{-5}$ M, CH_3CN) nm ($\Delta\epsilon$): 385 (119), 298 (–142), 253 (62), 224 (41). HRMS (FAB) m/z calcd for $C_{42}H_{36}Cl_2O_8$ 738.1787, found 738.1802. As above, using 10 molar equivalents (2 mL, 2 mmol) of the ca. 1 M LDA solution, applied to (–)-**4j** (150 mg, 0.2 mmol) in dry THF (3mL), the yield of (–)-**4k** was 100 mg (74%). Mp 266 °C decomp. $[\alpha]_D$: –3081 ($c = 0.82 \times 10^{-4}$, CH_3CN). IR (KBr): 3286, 2934, 2840, 2100 (w), 1607, 1456, 1360, 1292, 1208, 1121, 1089 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, 8.6 Hz, 2H), 8.35 (d, 8.6 Hz, 2H), 7.07 (s, 2H), 6.36 (s, 2H), 4.22 (s, 6H), 4.14 (s, 6H), 3.86 (s, 6H), 3.00 (s, 2H), 2.15 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.8, 152.6, 149.8, 143.8, 126.7, 126.5, 126.3, 125.6, 124.3, 120.8, 120.4, 120.2, 108.9, 107.6, 96.8, 81.8, 79.0, 61.7, 59.9, 55.9, 55.7 ppm. UV-vis ($c = 1.23 \times 10^{-4}$ M, CH_3CN) λ_{max} (log ϵ): 371 (3.97), 338 (sh, 4.31), 306 (4.62), 2.95 (4.67), 259 (4.60), 239 nm (4.70). CD ($c = 1.23 \times 10^{-4}$ M, CH_3CN) nm ($\Delta\epsilon$): 389 (–112), 322 (sh, 64), 295 (141), 250 (–121). HRMS (FAB) m/z calcd for $C_{42}H_{34}O_8$ 666.2254, found 666.2238.

Preparation of the acetylenes from the corresponding aldehydes. Lithium bis(trimethylsilyl)amide (0.28 mL of 1.0 M solution in hexane) was added to a suspension, cooled to –78 °C, of (chloromethyl)triphenylphosphonium chloride (104 mg, 0.3 mmol) in THF (1.5 mL). The cooling bath was removed, and the reaction mixture was stirred at ambient temperature for 30 min. Then a solution of aldehyde **3c** (53 mg, 0.1 mmol) in THF (1.5 mL) was added via a cannula, and the mixture was refluxed for 1 h. After it had been cooled, the reaction mixture was diluted with hexane and EtOAc (80 : 20) and filtered through a plug of silica gel soaked with the same solvent mixture. The silica gel was then washed with more of the solvent. After evaporation and vacuum drying, the product was dissolved in THF (2.5 mL), and MeLi (0.6 mL) was added at –78 °C. The reaction mixture was stirred at ambient temperature for 1 h and carefully quenched with 1 M HCl. Extraction with EtOAc, washing with water and brine, drying over Na_2SO_4 , and chromatography (hexane–EtOAc, 90 : 10) gave 38 mg (72%) of **3i** whose spectroscopic and physical properties were identical to those of **3i** prepared by the method described above.

The same procedure applied to **3d** (20 mg, 0.035 mmol), $(ClCH_2PPh_3)^+ Cl^-$ (37 mg, 0.107 mmol), $LiN(Si(CH_3)_3)_2$ (0.1 mL), and MeLi (0.4 mL) gave 11 mg (56%) of **3k**.

Similarly, **4c** (36 mg, 0.056 mmol), $(ClCH_2PPh_3)^+ Cl^-$ (58 mg, 0.167 mmol), $LiN(Si(CH_3)_3)_2$ (0.156 mL), and MeLi (0.33 mL) gave 27 mg (76%) of **4i**.

Finally, **4d** (46 mg, 0.068 mmol), $(ClCH_2PPh_3)^+ Cl^-$ (71 mg, 0.204 mmol), $LiN(Si(CH_3)_3)_2$ (0.19 mL), and MeLi (0.625 mL) gave 24 mg (53%) of **4k**.

Cleavage of 1, ω -methoxyl groups. Aldehyde (–)-**3c** (31 mg, 0.056 mmol) and Bu_4NI (217 mg, 0.587 mmol) were dissolved in dry CH_2Cl_2 (2 mL), cooled to –78 °C, and 1 M BBr_3 in CH_2Cl_2 (62 μ L) was added. The reaction mixture was stirred at that temperature for 10 min, then at 25 °C for 90 min, and then quenched with 1 M HCl. After extraction with CH_2Cl_2 (3 $\times$), washing with water, drying (Na_2SO_4) and

evaporation, the residue was dissolved in the minimal amount of CH_2Cl_2 , loaded on a column of silica gel, and the yellow product was eluted first with CH_2Cl_2 , then with CH_2Cl_2 -EtOAc (99 : 1). Obtained was 11 mg (37%) of yellow product (–)-**5c**. $[\alpha]_{\text{D}}^{\text{20}}$: –3284 ($c = 1.935 \times 10^{-4}$, CH_3CN). IR (film, NaCl): 3583, 2927, 2829, 1602, 1457, 1308, 1231, 1129 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 11.13 (s, 1H), 9.38 (s, 1H), 8.48 (d, 8.4 Hz, 1H), 8.43 (d, 8.4 Hz, 1H), 8.05 (d, 8.4 Hz, 1H), 8.00 (d, 8.4 Hz, 1H), 7.57 (s, 1H), 7.52 (s, 1H), 6.51 (d, 8.5 Hz, 1H), 6.51 (s, 1H), 5.85 (d, 8.5 Hz, 1H), 4.22 (s, 3H), 4.20 (s, 3H), 4.02 (s, 3H), 3.93 (s, 3H), 2.64 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 194.2, 158.2, 156.3, 154.2, 149.4, 149.0, 147.6, 131.2, 129.7, 128.6, 127.1, 126.3, 126.1, 125.9, 124.5, 121.1, 119.9, 118.1, 116.8, 112.5, 106.3, 105.4, 101.8, 97.3, 96.8, 57.0, 56.6, 56.3, 54.8 ppm. UV-vis ($c = 3.7 \times 10^{-4}$ M, CH_3CN) λ_{max} (log ϵ): 410 (3.84), 319 (4.53), 261 (4.57), 247 nm (4.59). CD ($c = 3.7 \times 10^{-4}$ M, CH_3CN) nm ($\Delta\epsilon$): 443 (–26), 418 (sh, –39), 389 (–49), 353 (–88), 318 (108), 264 (–22), 245 (7), 218 (–47). HRMS (FAB) m/z calcd for $\text{C}_{32}\text{H}_{26}\text{O}_7$ 522.1679, found 522.1697.

The same procedure applied to bisaldehyde (+)-**3d** (30 mg, 53 μmol), Bu_4NI (196 mg, 0.53 mmol) in dry CH_2Cl_2 (2 mL), and 1 M BBr_3 in CH_2Cl_2 (106 μL , 106 μmol) gave 16 mg (58%) of (+)-**5d**. The compound decomposes without melting at temperatures higher than 200 °C. $[\alpha]_{\text{D}}^{\text{20}}$: +4781 ($c = 0.61 \times 10^{-4}$, CH_3CN). IR (film, NaCl): 2936, 2835, 1603, 1509, 1406, 1323, 1232, 1151, 1129, 1076 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 11.21 (s, 2H), 9.41 (s, 2H), 8.44 (d, 8.5 Hz, 2H), 8.03 (d, 8.5 Hz, 2H), 7.51 (s, 2H), 6.47 (s, 2H), 4.22 (s, 6H), 3.96 ppm (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.7, 157.9, 155.3, 148.0, 131.9, 131.6, 129.4, 126.9, 125.5, 125.1, 120.7, 116.8, 112.4, 105.4, 56.7, 56.5 ppm. UV-vis ($c = 1.14 \times 10^{-4}$ M, CH_3CN) λ_{max} (log ϵ): 414 (4.07), 322 (4.58), 260 (4.57), 223 nm (4.53). CD ($c = 1.14 \times 10^{-4}$ M, CH_3CN) nm ($\Delta\epsilon$): 455 (66), 428 (86), 406 (77), 331 (–153), 325 (–151), 265 (53), 245 (–11), 227 (–51). HRMS (FAB) m/z calcd for $\text{C}_{32}\text{H}_{24}\text{O}_8$ 536.1471, found 536.1484.

Similarly, (–)-**4c** (100 mg, 0.155 mmol) and Bu_4NI (600 mg, 1.62 mmol) in dry CH_2Cl_2 (5 mL), and 1 M BBr_3 in CH_2Cl_2 (170 μL , 0.17 mmol) gave 65 mg (66%) of (–)-**6c**. Analytically pure material was obtained by recrystallization from hexane. The compound decomposes without melting at temperatures higher than 140 °C. $[\alpha]_{\text{D}}^{\text{20}}$: –3750 ($c = 1.976 \times 10^{-4}$, CH_3CN). IR (film, NaCl): 3582, 2837, 2833, 1602, 1333, 1291, 1233, 1090 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 10.93 (s, 1H), 9.42 (s, 1H), 8.35 (m, 4H), 7.01 (s, 1H), 7.00 (s, 1H), 6.33 (d, 8.5 Hz, 1H), 6.31 (s, 1H), 5.75 (d, 8.5 Hz, 1H), 4.26 (s, 3H), 4.23 (s, 3H), 4.12 (s, 3H), 4.05 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 2.54 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 194.2, 157.2, 154.2, 154.1, 148.2, 147.7, 147.0, 144.7, 143.7, 130.2, 128.0, 127.3, 126.8, 126.3, 125.8, 125.3, 125.1, 124.3, 121.1, 120.7, 120.3, 119.7, 119.0, 118.2, 113.5, 104.2, 102.7, 96.7, 96.6, 61.9, 61.8, 56.7, 56.3, 56.1, 54.7 ppm. UV-vis ($c = 3.12 \times 10^{-4}$ M, CH_3CN) λ_{max} (log ϵ): 457 (plateau, 3.36), 366 (sh, 4.01), 322 (sh, 4.44), 306 (4.54), 254 (4.59), 209 nm (4.71). CD ($c = 3.12 \times 10^{-4}$ M, CH_3CN) nm ($\Delta\epsilon$): 469 (sh, –30), 440 (–48), 426 (–51), 389 (–35), 325 (42), 307 (62), 265 (16), 253 (–7), 231 (–55), 206 (18). HRMS (FAB) m/z calcd for $\text{C}_{38}\text{H}_{32}\text{O}_9$ 632.2046, found 632.2031. Crystals of **6c** were grown from a CH_2Cl_2 -hexane solution.

The same procedure applied to (+)-**4d** (45 mg, 67 μmol) and Bu_4NI (246 mg, 0.67 mmol) in dry CH_2Cl_2 (2 mL), and 1 M BBr_3 in CH_2Cl_2 (147 μL , 147 μmol) gave 20 mg (47%) of (+)-**6d**. Mp >260 °C. $[\alpha]_{\text{D}}^{\text{20}}$: +5319 ($c = 0.90 \times 10^{-4}$, CH_3CN). IR (film, NaCl): 2940, 2836, 1621, 1603, 1410, 1335, 1302, 1235, 1094 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 11.01 (s, 2H), 9.43 (s, 2H), 8.39 (d, 8.6 Hz, 2H), 8.34 (d, 8.6 Hz, 2H), 6.96 (s, 2H), 6.36 (s, 2H), 4.25 (s, 6H), 4.07 (s, 6H), 3.91 ppm (s, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 194.5, 158.0, 154.3, 147.3, 144.6, 130.3, 128.1, 127.5, 126.0, 121.7, 120.2, 118.3, 113.6, 104.0, 96.4, 61.7, 56.4, 55.9 ppm. UV-vis ($c = 1.40 \times 10^{-4}$ M, CH_3CN) λ_{max} (log ϵ): 459 (3.74), 405

(plateau, 3.94), 316 (4.70), 260 (sh, 4.60), 244 nm (4.68). CD ($c = 1.40 \times 10^{-4}$ M, CH₃CN) nm ($\Delta\epsilon$): 454 (81), 434 (68), 370 (65), 314 (–154), 274 (59), 247 (–60), 222 (43). HRMS (FAB) m/z calcd for C₄₀H₃₅ClO₈ 646.1839, found 646.1864.

BBr₃ (1.0 M in CH₂Cl₂, 0.200 mL, 0.20 mmol) was added at –78 °C to a stirred solution of (+)-**3f** (59 mg, 0.10 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at –78 °C for 15 min, then at 25 °C for 45 min, and quenched with 1 M HCl (4 mL). It was poured into 1 M HCl (50 mL), and extracted with CH₂Cl₂ (4 × 5 mL). The extracts were dried over Na₂SO₄, filtered, and the solvent was evaporated. The residue was dissolved in a minimal amount of CH₂Cl₂ and chromatographed with 1:3 hexane/EtOAc. The yield of orange-yellow solid (+)-**5f** (mp >240 °C) was 50 mg (89%). [α]_D: +4825 ($c = 0.021$, CH₃CN). IR (CCl₄): 2938, 1605, 1512, 1462, 1363, 1330, 1233, 1135 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 12.56 (s, 2H), 8.41 (d, 8.5 Hz, 2H), 8.00 (d, 8.5 Hz, 2H), 7.44 (s, 2H), 6.58 (s, 6H), 4.19 (s, 6H), 3.93 (s, 6H), 2.42 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 201.5, 157.5, 156.5, 146.7, 131.4, 131.0, 129.2, 126.6, 125.2, 125.1, 120.4, 117.2, 110.7, 102.9, 96.6, 56.2, 56.0, 26.5 ppm. UV-vis (CH₃CN, $c = 1.30 \times 10^{-5}$ M): $\lambda_{\max}$ (log ϵ) 251 (4.65), 263 (4.65), 318 (5.63), 405 nm (4.13). CD ($c = 1.30 \times 10^{-5}$ M, CH₃CN), nm ($\Delta\epsilon$): 224 (–31), 237 (14), 265 (37), 328 (–178), 383 (91), 400 (87), 425 (79), 454 (68). HRMS (FAB) m/z calcd for C₃₄H₂₈O₈ 564.1782, found 564.1808. Racemic **5f** (mp >240 °C) was prepared from racemic **3**. Its ¹H and ¹³C NMR spectra were identical to those of optically active **5f**. Crystals for X-ray diffraction analysis were grown by allowing a solution in CH₂Cl₂ to evaporate slowly at room temperature. The crystals were yellow-orange.

The same procedure applied to (+)-**4f** (70 mg, 0.10 mmol) gave 50 mg (75%) of orange-yellow solid (+)-**6f**. Mp >240 °C. [α]_D: +4919 ($c = 0.017$, CH₃CN). IR (KBr): 2936, 1603, 1415, 1374, 1307, 1234, 1107, 983, 823 cm^{–1}. ¹H NMR (CDCl₃, 400 MHz) δ 12.39 (s, 2H), 8.36 (d, 8.6 Hz, 2H), 8.31 (d, 8.6 Hz, 2H), 6.94 (s, 2H), 6.43 (s, 2H), 4.25 (s, 6H), 4.05 (s, 6H), 3.87 (s, 6H), 2.48 ppm (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) 201.7, 157.0, 155.1, 145.7, 144.1, 129.7, 127.3, 127.2, 125.7, 125.5, 121.1, 119.6, 118.2, 111.7, 101.9, 95.2, 61.3, 55.8, 55.5, 26.8 ppm. UV-vis (CH₃CN, $c = 9.77 \times 10^{-6}$ M): $\lambda_{\max}$ (log ϵ) 239 (4.71), 310 (4.72), 395 (sh, 4.06), 452 nm (sh, 3.70). CD ($c = 9.77 \times 10^{-6}$ M, CH₃CN), nm ($\Delta\epsilon$): 227 (50), 247 (–41), 267 (55), 313 (–158), 367 (69), 429 (88), 450 (84). HRMS (FAB) m/z calcd for C₄₀H₃₄O₁₀ 674.2150, found 674.2197. Racemic **6f** (mp >240 °C) was prepared from racemic **4**. Its ¹H and ¹³C NMR spectra were identical to those of nonracemic **4f**. Crystals for X-ray diffraction analysis were grown by allowing a solution in EtOAc to evaporate slowly at room temperature. The crystals were yellow-orange.

4g: BuLi (81 μ L, 1.6 M, in hexane, 0.129 mmol) was added slowly to **4b** (33.4 mg, 0.043 mmol) in Et₂O (3 mL) cooled to –78 °C. During 40 min, the mixture was stirred and warmed to –20 °C, and then ClP(O)Ph₂ (33 μ L, 0.17 mmol) was added. The mixture was stirred overnight (–20 °C to 25 °C, 10 h), then poured into Et₂O (30 mL) and H₂O (30 mL). The ether layer was washed with saturated aqueous NaHCO₃ (30 mL) and dried over Na₂SO₄. Chromatography on silica gel, eluting with EtOAc/MeOH (9:1) gave pure **4g**, a golden yellow solid (29.5 mg, a 67% yield). ¹H NMR (CDCl₃) δ 8.23 (d, 8.5 Hz, 2H), 8.15 (d, 8.5 Hz, 2H), 7.73–7.56 (m, 8H), 7.14–6.98 (m, 8H), 6.88 (s, 2H), 6.78–6.71 (m, 4H), 4.13 (s, 6H), 3.92 (s, 6H), 3.62 (s, 6H), 0.98 ppm (s, 6H); ¹³C NMR (CDCl₃) δ 154.6, 152.0, 150.2, 150.0, 144.2, 133.7, 133.6, 132.3, 131.5, 131.3, 131.1, 128.7, 128.6, 128.4, 128.2, 128.0, 126.8, 125.9, 125.7, 125.2, 122.0, 119.6, 108.5, 108.4, 97.7, 61.9, 58.0, 55.9 ppm; ³¹P NMR (CDCl₃) δ 27.44 ppm (s); IR (NaCl) 3055.1, 2937.6, 2838.6, 1607.6, 1514.8, 1490.0, 1452.9, 1378.7, 1316.8, 1279.7, 1205.5, 1094.1, 982.8, 828.1, 723.0, 698.2 cm^{–1}; HRMS (FAB) m/z calcd for C₆₂H₅₃O₁₀P₂: 1019.3116, found: 1019.3115.

3g: Similarly, a solution of **3b** (73.3 mg, 0.11 mmol) in Et₂O (5 mL), treated with BuLi (206 μ L, 1.6 M, in hexane, 0.33 mmol) and ClP(O)Ph₂ (84 μ L, 0.44 mmol), gave 51.2 mg of **3g**, a golden yellow solid (51% yield). ¹H NMR (CDCl₃) δ 8.39 (d, 8.4 Hz, 2H), 7.90 (d, 8.4 Hz, 2H), 7.51 (s, 2H), 7.46–7.12 (m, 20H), 6.97 (d, 13.2 Hz, 2H), 4.19 (s, 6H), 3.77 (s, 6H), 1.13 ppm (s, 6H); ¹³C NMR (CDCl₃) δ 149.7, 135.7, 134.3, 134.0, 132.6, 132.4, 132.3, 131.8, 131.5, 131.3, 131.1, 130.8, 129.5, 128.5, 128.2, 128.0, 127.9, 127.7, 125.6, 124.0, 120.3, 119.1, 119.0, 118.4, 117.0, 108.6, 108.5, 98.6, 58.2, 55.9, 55.7 ppm; ³¹P NMR (CDCl₃) δ 27.88 ppm (s); IR (NaCl) 3055.8, 3001.5, 2960.7, 2933.6, 2838.5, 2213.6, 1615.8, 1588.7, 1513.9, 1446.8, 1337.3, 1296.6, 1228.7, 1201.5, 1160.7, 1113.2, 1072.4, 1031.7, 1004.5, 909.4, 848.3, 726.0, 698.9 cm⁻¹; HRMS (FAB) *m/z* calcd for C₅₆H₄₇O₈P₂: 909.2748, found: 909.2791.

8a: NaH (2.28 g, 57 mmol), followed by DMF (70 mL), was added to a sample under argon of (±)-**4**^{19d} that had been prepared from 8.00 g (9.50 mmol) of the corresponding helicenebisquinone and dried in a vacuum at 100 °C, but not purified by chromatography. The mixture was stirred at 25 °C for 30 min, which gave a deep red solution, and after PhCH₂Br (18.1 mL, 152 mmol) had slowly been syringed in, the mixture was stirred at 25 °C for 10 h, and the mixture was then carefully poured into H₂O (900 mL) plus 1N HCl (100 mL) in a 2 L separatory funnel. Extraction with Et₂O (300 mL), washing with H₂O (300 mL) and brine (300 mL), drying over Na₂SO₄, and chromatography on silica gel (eluting with with 5:1:1 hexane/CH₂Cl₂/EtOAc), followed by drying under a vacuum, gave 5.98 g of pure product, an 82% overall yield. ¹H NMR (CDCl₃) δ 8.24 (d, 8.6 Hz, 2H), 7.92 (d, 8.6 Hz, 2H), 7.13 (s, 2H), 7.07–7.05 (m, 6H), 6.49 (d, 6.0 Hz, 2H), 6.48 (d, 7.4 Hz, 2H), 6.34 (d, 8.5 Hz, 2H), 5.85 (d, 8.5 Hz, 2H), 4.18 (s, 6H), 4.01 (d, 12.0 Hz, 2H), 3.91 (s, 6H), 3.90 (s, 6H), 3.58 ppm (d, 12.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 153.9, 148.5, 147.6, 143.9, 137.8, 127.9, 126.9, 126.6, 126.4, 125.5, 125.0, 124.4, 120.5, 119.7, 119.4, 104.6, 104.3, 97.0, 69.3, 61.5, 56.5, 56.0 ppm; IR (NaCl) 2938.1, 2836.2, 1613.6, 1498.1, 1382.6, 1200.7, 1233.2, 1110.9, 1083.0, 737.3 cm⁻¹. HRMS (FAB) *m/z* calcd for C₅₀H₄₂O₈: 770.2880, found: 770.2891.

7a: Similarly, helicene (+)-[6]-bisquinone (1.05 g, 2.34 mmol), gave 1.32 g of golden yellow solid (+)-**7a** (an 85% yield). m.p. 128–130°C; [α]_D +1309° (0.0191, CH₂Cl₂); ¹H NMR (CDCl₃) δ 8.19 (d, 8.4 Hz, 2H), 8.00 (d, 8.4 Hz, 2H), 7.27 (s, 2H), 7.07–7.04 (m, 6H), 6.53 (d, 8.7 Hz, 2H); 6.32 (d, 6.8 Hz, 4H), 5.88 (d, 8.7 Hz, 2H), 4.02 (d, 12.3 Hz, 2H), 3.99 (s, 6H), 3.80 (s, 6H), 3.70 ppm (d, 12.3 Hz, 2H); ¹³C NMR (CDCl₃) δ 153.8, 148.7, 148.6, 139.5, 137.2, 130.3, 129.0, 128.8, 128.7, 128.4, 128.3, 128.1, 127.9, 127.7, 127.5, 127.2, 126.5, 126.4, 125.5, 125.3, 125.0, 124.9, 120.1, 117.9, 105.8, 103.2, 96.0, 94.0, 68.8, 56.8, 55.3 ppm; IR (NaCl) 3063.4, 3031.3, 2999.2, 2935.1, 2826.0, 1684.1, 1613.6, 1530.2, 1510.9, 1453.2, 1427.5, 1376.2, 1292.8, 1260.7, 1222.2, 1158.1, 1132.4, 1105.6, 1067.8, 1017.8, 909.2, 838.8, 733.4, 696.8 cm⁻¹; HRMS (FAB) *m/z* calcd for C₄₄H₃₆O₆: 660.2512, found: 660.2524.

8b: A solution of NBS (2.90 g, 16.3 mmol) in MeCN (100 mL) was added by cannula to a dried sample of **8a** (6.11 g, 7.95 mmol) in 1:1 MeCN/CH₂Cl₂ (200 mL). The reaction mixture, initially orange-red, immediately darkened. After it had stirred at 25 °C for 2 h, TLC analysis showed a single product to have formed. The solvent was evaporated, and chromatography on silica gel (eluting with 7:3 hexane/EtOAc), gave 6.91 g (a 96% yield) of pure product, a bright yellow solid. ¹H NMR (CDCl₃) δ 8.35 (d, 8.7 Hz, 2H), 8.03 (d, 8.7 Hz, 2H), 7.10–7.06 (m, 8H), 6.57 (s, 2H), 6.50 (d, 6.2 Hz, 2H), 6.49 (d, 7.4 Hz, 2H), 4.21 (s, 6H), 3.92 (s, 6H), 3.65 (s, 6H), 3.45 (d, 11.4 Hz, 2H), 2.96 ppm (d, 11.4 Hz, 2H); ¹³C NMR (CDCl₃) δ 154.2, 151.0, 145.3, 143.6, 137.3, 127.7, 127.1, 126.9, 126.8, 126.6, 124.1, 124.0, 121.8, 121.5, 120.1, 111.4, 108.8, 96.8, 73.6, 61.2, 56.1, 56.0, 53.8 ppm; IR (NaCl) 2937.9, 2835.7, 1607.5, 1493.6, 1456.3, 1382.1, 1313.1, 1279.6, 1202.4,

1129.8, 1017.0, 822.3, 734.7 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{50}\text{H}_{40}\text{O}_8^{79}\text{Br}_2$: 926.1090, found: 926.1119.

7b: Similarly, (+)-**7a** (508 mg, 0.77 mmol) and NBS (274 mg, 1.54 mmol) gave 585 mg (a 93% yield) of (+)-**7b**, a yellow solid. $[\alpha]_{\text{D}}^{20} +2025^\circ$ (0.023, CH_2Cl_2); ^1H NMR (CDCl_3) δ 8.16 (d, 8.4 Hz, 2H), 7.92 (d, 8.4 Hz, 2H), 7.37 (s, 2H), 7.43–7.01 (m, 6H), 6.82 (s, 2H), 6.40 (d, 7.1 Hz, 4H), 4.04 (s, 6H), 4.00 (s, 6H), 3.44 (d, 10.3 Hz, 2H), 2.76 ppm (d, 10.3 Hz, 2H); ^{13}C NMR (CDCl_3) δ 153.7, 150.9, 146.3, 136.2, 130.7, 129.4, 128.6, 128.4, 127.8, 127.6, 127.2, 127.0, 125.5, 125.0, 120.4, 109.7, 96.8, 72.1, 55.8, 55.5 ppm; IR (NaCl) 3033.2, 2938.1, 2836.2, 1601.5, 1613.6, 1511.7, 1457.3, 1335.1, 1207.5, 1192.4, 1131.3, 1070.2, 1029.4, 839.2, 696.6 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{44}\text{H}_{34}\text{O}_6^{79}\text{Br}_2$: 816.0722, found: 816.0712.

8c and 8d: A suspension of 10% Pd/C powder (135 mg) in a solution of **8b** (236 mg, 0.255 mmol) in EtOAc (21 mL) was vigorously stirred under hydrogen [$P(\text{H}_2) = 2.5$ atm] at 25 $^\circ\text{C}$ for 30 min. Filtration, washing with CH_2Cl_2 (3×10 mL), and chromatography on silica gel (eluting with 7:3 hexane/EtOAc) gave 236 mg (85%) of pure **8c**, an orange red solid. ^1H NMR (CDCl_3) δ 8.44 (unresolved dd, 4H), 7.09 (s, 2H), 6.50 (s, 2H), 4.29 (s, 6H), 4.18 (s, 6H), 4.00 (s, 2H), 3.88 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 153.9, 148.5, 144.5, 141.2, 127.3, 126.5, 125.6, 124.6, 124.2, 121.3, 120.5, 117.7, 108.1, 104.1, 96.92, 61.85, 56.10 ppm; IR (NaCl) 3508.7, 2938.1, 2829.4, 1654.3, 1606.8, 1491.3, 1430.2, 1382.6, 1267.2, 1097.3, 1009.0, 770.1 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{36}\text{H}_{28}\text{O}_8^{79}\text{Br}_2$: 746.0151, found: 746.0160.

Further elution (with the same eluent) gave the mono-bromo derivative (**8d**, 29 mg). This compound could be prepared in a practical yield (64%) by increasing the amount of palladium to 1.0 eq, the hydrogen pressure (to 4 atm), and the reaction time (to 6 h). ^1H NMR (CDCl_3) δ 8.51–8.42 (two sets of dd, 4H), 7.20 (s, 1H), 7.05 (s, 1H), 6.50 (s, 1H), 6.36 (d, 8.5 Hz, 1H), 5.92 (d, 8.5 Hz, 1H), 4.29 (s, 3H), 4.28 (s, 3H), 4.20 (s, 3H), 4.12 (s, 3H), 3.95 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.87 (s, 3H), 2.08 ppm (s, 1H); ^{13}C NMR (CDCl_3) δ 154.0, 153.2, 148.6, 148.3, 145.1, 144.4, 143.9, 141.2, 127.9, 127.5, 126.7, 126.4, 124.7, 124.4, 124.3, 124.2, 124.1, 121.1, 120.7, 118.0, 117.8, 109.4, 108.2, 105.6, 104.5, 97.6, 97.3, 61.8, 56.3, 56.2, 56.1 ppm; IR (NaCl) 3513.0, 3426.6, 2994.5, 2936.9, 2833.2, 1652.2, 1606.1, 1496.6, 1456.3, 1433.3, 1381.4, 1292.6, 1270.6, 1234.4, 1184.7, 1156.9, 1106.9, 1088.7, 1004.8, 978.5, 909.6, 825.5, 786.0, 734.0 cm^{-1} ; LRMS (APCI+) m/z : calcd for $\text{C}_{36}\text{H}_{29}\text{O}_8^{79}\text{Br}$: 668.1, found: 668.2.

7c and 7d: The procedure is similar to the preparation of **8c**, except that the hydrogen pressure is 4 atm and the reaction time is 5 h. Starting from (+)-**7b** (88 mg, 0.108 mmol), the product was isolated as a light-yellow solid in 81% yield (55.7 mg). $[\alpha]_{\text{D}}^{20} +1635^\circ$ (1.9×10^{-4} , CH_2Cl_2); ^1H NMR (CDCl_3) δ 8.46 (d, 8.4 Hz, 2H), 8.11 (d, 8.4 Hz, 2H), 7.51 (s, 2H), 6.74 (s, 2H), 4.18 (s, 6H), 4.14 (s, 6H), 3.98 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 154.4, 148.6, 142.0, 131.2, 127.4, 127.0, 126.0, 124.8, 120.6, 117.3, 113.0, 107.0, 97.1, 56.8, 56.3 ppm; IR (NaCl) 3510.9, 2960.8, 2926.0, 2831.7, 1615.8, 1588.7, 1507.2, 1459.6, 1357.7, 1310.2, 1249.1, 1201.5, 1133.6, 1079.2, 1018.1, 909.5, 838.7, 779.9, 730.8 cm^{-1} . LRMS (APCI+) m/z calcd for $\text{C}_{30}\text{H}_{22}\text{O}_6^{79}\text{Br}_2$: 636.0, found: 637.5.

When the reaction time was extended to 10 h, 81 mg (0.099 mmol) of (+)-**7b** gave 24.9 mg (57% yield) of (+)-**7d**. $[\alpha]_{\text{D}}^{20} +1907^\circ$ (0.088, CH_2Cl_2); ^1H NMR (CDCl_3) δ 8.53 (d, 8.4 Hz, 1H), 8.49 (d, 8.5 Hz, 1H), 8.12 (d, 8.5 Hz, 1H), 8.07 (d, 8.4 Hz, 1H), 7.61 (s, 1H), 7.56 (s, 1H), 6.73 (s, 1H), 6.62 (d, 8.5 Hz, 1H), 6.00 (d, 8.5 Hz, 1H), 4.20 (s, 3H), 4.15 (s, 3H), 4.10 (s, 1H), 4.00 (s, 3H), 3.95 (s, 3H), 3.46 ppm (s, 1H); ^{13}C NMR (CDCl_3) δ 153.7, 153.3, 148.6, 148.3, 145.5, 142.5, 131.3, 127.2, 126.7, 125.9, 125.4, 125.3, 124.9, 124.8, 122.8, 120.9, 120.3, 116.4, 116.2, 109.2, 108.1, 107.1, 103.0, 97.3, 97.2, 56.4, 56.3, 55.9 ppm; IR (NaCl) 3513.0, 3226.6, 2994.5, 2936.9, 2833.2, 1652.2, 1606.1, 1496.6, 1456.3, 1433.3, 1381.4,

1292.6, 1270.6, 1234.4, 1106.9, 1088.7, 1004.8, 909.6, 825.5, 734.8 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{O}_6^{79}\text{Br}$: 558.0678, found: 558.0671.

8e: The procedure is similar to the preparation of **4g**. A solution of **8b** (87.1 mg, 0.094 mmol) treated with BuLi (175.9 μL , 1.6 M in hexane, 0.281 mmol) and $\text{CIP}(\text{O})\text{Ph}_2$ (71.6 μL , 0.375 mmol) gave 68 mg of **8e** (62% yield). ^1H NMR (CDCl_3) δ 8.40 (d, 8.7 Hz, 2H), 8.08 (d, 8.7 Hz, 2H), 7.43–6.76 (m, 28H), 6.65 (d, $^3J_{\text{PH}}$ 13.3 Hz, 2H), 5.83 (d, 6.8 Hz, 4H), 4.01 (s, 6H), 3.80 (s, 6H), 3.39 (s, 6H), 2.60 (d, 12.0 Hz, 2H), 2.33 ppm (d, 12.0 Hz, 2H); ^{13}C NMR (CDCl_3) δ 154.0, 151.7, 132.4, 132.1, 131.9, 131.7, 131.6, 131.4, 129.0, 128.6, 128.4, 128.1, 126.9, 125.3, 120.3, 104.8, 104.7, 97.9, 71.5, 69.2, 68.5, 62.8, 54.2, 31.8, 19.3, 13.9 ppm; ^{31}P NMR (CDCl_3) δ 26.25 ppm (s); IR (NaCl) 3055.1, 3005.6, 2937.6, 2838.6, 1607.6, 1564.3, 1514.8, 1490.0, 1452.9, 1434.4, 1381.6, 1317.9, 1204.5, 1097.7, 980.6, 840.8, 826.0, 728.5 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{74}\text{H}_{61}\text{O}_{10}\text{P}_2$: 1171.3742, found: 1171.3718.

7e: Similarly, **7b** (406 mg, 0.496 mmol), BuLi (930 μL , 1.6 M in hexane, 1.488 mmol), and $\text{CIP}(\text{O})\text{Ph}_2$ (380 μL , 1.984 mmol) gave 374 mg of **7e** (71% yield), a golden yellow solid. ^1H NMR (CDCl_3) δ 7.75 (d, 8.5 Hz, 2H), 7.66 (s, 2H), 7.58 (d, 8.5 Hz, 2H), 7.44–6.83 (m, 26H), 6.58 (d, $^3J_{\text{PH}}$ 13.5 Hz, 2H), 5.84 (d, 7.7 Hz, 4H), 4.12 (s, 6H), 3.91 (s, 6H), 2.96 (d, 11.4 Hz, 2H), 2.45 ppm (d, 11.4 Hz, 2H); ^{13}C NMR (CDCl_3) δ 154.8, 153.7, 150.8, 150.6, 135.8, 135.6, 134.8, 134.2, 131.8, 131.6, 131.4, 131.0, 130.7, 130.4, 130.1, 128.2, 128.0, 127.7, 127.6, 126.5, 125.9, 125.3, 124.7, 120.5, 119.9, 118.2, 116.8, 108.2, 108.0, 98.1, 73.4, 55.6 ppm; ^{31}P NMR (CDCl_3) δ 26.10 ppm (s); IR (NaCl) 3053.9, 3003.9, 2960.2, 2935.2, 2835.4, 1611.8, 1588.6, 1511.9, 1455.7, 1412.0, 1337.1, 1293.4, 1199.8, 1162.3, 1118.6, 1074.9, 1006.3, 912.6, 843.9, 731.6, 694.1, 644.0 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{68}\text{H}_{55}\text{O}_8\text{P}_2$: 1061.3374, found: 1061.3392.

8f: A mixture of **8e** (68 mg, 0.058 mmol) dissolved in 1:1 THF/MeOH (4 mL), 10% Pd/C (123 mg, 0.116 mmol), and HCO_2NH_4 (146 mg, 2.32 mmol) sealed with a Teflon cap in a pressure tube was stirred vigorously overnight (10 h). The Pd/C was filtered and washed with THF (about 15 mL) until the filtrate was colorless. After excess HCO_2NH_4 had been removed by extracting the filtrates plus Et_2O (45 mL) with H_2O (80 mL), chromatography on silica gel (eluting with EtOAc) gave 48.9 mg (85% yield) of **8f**. ^1H NMR (CDCl_3) δ 9.85 (s, 2H), 8.49 (d, 8.7 Hz, 2H), 8.40 (d, 8.7 Hz, 2H), 7.88–7.14 (m, 22H), 6.08 (d, $^3J_{\text{PH}}$ 12.6 Hz, 2H), 4.24 (s, 6H), 3.73 (s, 6H), 3.72 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 155.8, 154.9, 146.3, 146.1, 143.7, 133.7, 133.3, 132.6, 132.4, 131.4, 131.2, 131.0, 128.3, 128.2, 128.0, 126.7, 126.0, 125.7, 121.1, 120.0, 119.7, 105.4, 105.2, 101.0, 99.5, 96.7, 61.3, 56.1, 55.4 ppm; ^{31}P NMR (CDCl_3) δ 37.94 ppm (s); IR (NaCl) 3430.7, 3053.1, 2999.1, 2933.2, 2831.2, 1608.3, 1572.3, 1494.4, 1458.4, 1404.4, 1380.5, 1314.5, 1278.5, 1242.6, 1206.6, 1116.7, 1006.7, 978.8, 834.9, 733.0 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{60}\text{H}_{49}\text{O}_{10}\text{P}_2$: 991.2803, found: 991.2784.

7f: Similarly, 322 mg, 0.303 mmol of **7e** gave 222 mg (83% yield) of **7f**, a pale yellow solid. ^1H NMR (CDCl_3) δ 10.15 (s, 2H), 8.43 (d, 8.4 Hz, 2H), 7.98 (d, 8.4 Hz, 2H), 7.68 (s, 2H), 7.51–7.18 (m, 20H), 6.21 (d, $^3J_{\text{PH}}$ 13.1 Hz, 2H), 4.19 (s, 6H), 3.72 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 156.1, 155.9, 147.3, 147.1, 133.5, 132.6, 132.4, 132.0, 131.7, 131.5, 131.3, 130.7, 130.1, 129.9, 128.4, 128.3, 128.1, 126.0, 125.8, 124.6, 120.0, 118.5, 118.3, 106.2, 106.0, 100.5, 99.1, 97.0, 56.4, 55.8 ppm; ^{31}P NMR (CDCl_3) δ 39.48 ppm (s); IR (NaCl) 3057.3, 3000.9, 2937.6, 2831.9, 1606.3, 1507.7, 1451.3, 14002.0, 1296.3, 1233.0, 1197.7, 1162.5, 1127.3, 1070.9, 1000.5, 859.6, 837.5, 732.8, 697.6 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{54}\text{H}_{43}\text{O}_8\text{P}_2$: 881.2435, found: 881.2406.

8g: After **8f** (5.1 mg, 0.0051 mmol) dissolved in toluene (3 mL) had stirred for 10 min with Bu_3N (490 μL , 2.06 mmol), Cl_3SiH (208 μL , 2.06 mmol) was slowly added, and the mixture under argon was refluxed for 20 h. It was then cooled to 25 $^\circ\text{C}$ and, after 3

mL of a degassed 30% solution of NaOH in H₂O had been added, stirred at 60 °C for 10 min. A quick workup with Et₂O (30 mL) and H₂O (50 mL), then brine (40 mL) and Na₂SO₄, followed by chromatography on a short silica gel column, gave first with hexane as the eluent Bu₃N, then with CH₂Cl₂/hexane (8:2) as the eluent 4.5 mg (91% yield) of **8g**, a bright yellow solid. ¹H NMR (CDCl₃) δ 8.52 (d, 8.7 Hz, 2H), 8.40 (d, 8.7 Hz, 2H), 7.44–7.37 (m, 10H), 7.26 (s, 2H), 7.05–6.85 (m, 10H), 6.07 (d, ³J_{PH} 3.9 Hz, 2H), 4.86 (d, ⁴J_{PH} 5.5 Hz, 2H), 4.19 (s, 6H), 3.93 (s, 6H), 3.59 ppm (s, 6H); ¹³C NMR (CDCl₃) δ 153.7, 148.4, 147.6, 144.1, 136.7, 133.7, 133.5, 133.2, 133.0, 130.9, 128.4, 128.1, 127.4, 126.1, 125.5, 125.1, 120.7, 120.6, 117.6, 112.7, 108.9, 97.6, 61.3, 55.8, 53.9 ppm; ³¹P NMR (CDCl₃) δ –26.91 ppm (s); IR (NaCl) 3506.0, 3371.3, 3057.0, 2960.7, 2935.1, 2870.9, 2832.4, 1716.2, 1652.1, 1607.1, 1498.1, 1459.6, 1433.9, 1376.2, 1312.1, 1286.4, 1260.7, 1233.1, 1203.0, 1093.9, 1017.0, 978.5, 830.9, 734.7, 696.2 cm^{–1}; LRMS (APCI+) *m/z* calcd for C₆₀H₄₉O₈P₂: 958.3, found: 959.3.

7g: Similarly, **7f** (32 mg, 0.036 mmol), HSiCl₃ (367 μL) in a mixture of toluene (4 mL) and Bu₃N (866 μL) gave 29.3 mg (95% yield) of **7g**, a golden yellow solid. ¹H NMR (CDCl₃) δ 8.48 (d, 8.4 Hz, 2H), 8.04 (d, 8.4 Hz, 2H), 7.66 (s, 2H), 7.34–6.89 (m, 20H), 6.35 (d, ³J_{PH} 3.7 Hz, 2H), 5.46 (d, ⁴J_{PH} 7.8 Hz, 2H), 4.21 (s, 6H), 3.73 ppm (s, 6H); ¹³C NMR (CDCl₃) δ 154.7, 150.5, 150.2, 148.1, 136.4, 135.9, 133.6, 133.3, 133.0, 132.7, 131.0, 128.4, 128.3, 128.2, 128.1, 127.2, 126.0, 125.0, 124.5, 120.3, 116.3, 111.2, 109.6, 97.0, 56.0, 55.9 ppm; ³¹P NMR (CDCl₃) δ –30.40 ppm (s); IR (NaCl) 3506.0, 3384.1, 3069.8, 3050.5, 2999.2, 2960.7, 2933.1, 2832.4, 1607.1, 1510.9, 1453.2, 1433.9, 1414.7, 1305.6, 1260.7, 1228.7, 1199.6, 1160.1, 1132.2, 1074.2, 1025.9, 1001.0, 842.8, 802.4, 743.1, 696.0 cm^{–1}; HRMS (FAB) *m/z* calcd for C₅₄H₄₃O₆P₂: 849.2537, found: 849.2490.

12. After NaH (475 mg, 60% dispersion in mineral oil, 11.9 mmol) had been vigorously stirred at 25 °C for 30 min with **4** (1.4g, 2.4 mmol) dissolved in THF (25 mL), ClP(O)(OEt)₂ (2.7 mL, 19 mmol) was syringed in, and stirring was continued for another 8 h. Dilution with Et₂O (250 mL), washing with 10% NaOH (3 × 100 mL), H₂O (150 mL) and brine (150 mL), and drying (MgSO₄, then high vacuum), gave **10**, a viscous yellow-brown oil (1.86 g, a 91% yield), which was used directly in the next step.

After LDA (340 μL, 1.8 M, in heptane/THF/ethylbenzene, (20:40:15) 0.613 mmol) had been added to a solution at –55 °C of **10** (106 mg, 0.123 mmol) in THF (2 mL), the mixture was stirred and gradually warmed to 25 °C during 4 h. It was then poured into saturated aqueous NH₄Cl (60 mL) and CH₂Cl₂ (30 mL), dried (Na₂SO₄), and chromatographed (7:3 EtOAc/CH₂Cl₂ eluting a yellow band), giving 104 mg (98% yield) of **12**, a thick yellow oil, which solidifies upon standing at 25 °C. ¹H NMR (CDCl₃) δ 8.77 (s, 2H), 8.43 (d, 8.7 Hz, 2H), 8.37 (d, 8.7 Hz, 2H), 7.09 (s, 2H), 6.23 (d, 14.3 Hz, 2H), 4.24 (s, 6H), 4.23–4.17 (m, 4H), 4.09 (s, 6H), 3.83 (s, 6H), 3.68–3.52 (m, 2H), 3.50–3.32 (m, 2H), 1.50 (t, 7.0 Hz, 6H), 0.95 ppm (t, 7.0 Hz, 6H); ¹³C NMR (CDCl₃) δ 155.6, 152.1, 152.0, 147.1, 146.9, 143.8, 128.4, 127.8, 126.6, 125.6, 125.3, 120.8, 119.7, 118.4, 103.7, 103.6, 100.2, 97.7, 96.6, 62.0 (d, ²J_{PC} 50 Hz), 62.2 (d, ²J_{PC} 48 Hz), 61.3, 55.8, 16.5 (d, ³J_{PC} 6 Hz), 15.9 (d, ³J_{PC} 6 Hz) ppm; ³¹P NMR (CDCl₃) δ 24.14 ppm (s); IR (NaCl) 3460.6, 2979.8, 2923.9, 1606.5, 1382.9, 1315.8, 1282.3, 1209.5, 1109.0, 1064.2, 1019.5, 963.6, 846.2 cm^{–1}; HRMS (FAB) *m/z* calcd for C₄₄H₂₈O₁₄P₂: 863.2599, found: 863.2579.

11: The procedure is similar to the preparation of **12**. Reaction of (+)-**3** (107 mg, 0.223 mmol) with NaH (45 mg, 60% dispersion in mineral oil, 1.12 mmol) and ClP(O)(OEt)₂ (258 μL, 1.78 mmol) gave (+)-**9** as a yellow oil that solidifies upon addition of Et₂O (146 mg, an 87% yield). [α]_D^{+1395°} (0.232, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, 8.4 Hz, 2H), 8.00 (d, 8.4 Hz, 2H), 7.55 (s, 2H), 6.52 (d, 8.8 Hz, 2H), 6.34 (dd, 8.8 Hz, 1.6 Hz, 2H), 4.16 (s, 6H), 3.97 (s, 6H), 3.51–3.40 (two sets of unresolved ddt,

4H), 2.70–2.62 (unresolved ddt, 2H), 2.50–2.44 (unresolved ddt, 2H), 1.09 (ddd, 6.5 Hz, 6.5 Hz, 1.2 Hz, 6H), 0.38 (ddd, 6.5 Hz, 6.5 Hz, 1.1 Hz, 6H); ^{13}C NMR (CDCl_3) δ 153.6, 151.6, 139.9, 130.8, 127.1, 125.9, 125.4, 120.0, 119.6, 119.5, 113.5, 105.1, 97.1, 63.2 (d, $^2J_{\text{PC}}$ 24.4 Hz), 63.1 (d, $^2J_{\text{PC}}$ 24.7 Hz), 56.0, 55.8, 15.7 (d, $^3J_{\text{PC}}$ 8.0 Hz), 15.1 (d, $^3J_{\text{PC}}$ 7.6 Hz) ppm; IR (NaCl) 2981.3, 2939.4, 2909.4, 2837.5, 1614.5, 1512.6, 1458.6, 1425.9, 1386.7, 1296.7, 1242.8, 1218.1, 1158.8, 1128.9, 1033.0, 997.0, 889.1 805.1 cm^{-1} ; ^{31}P NMR (CDCl_3) δ -6.58 ppm (s); HRMS (FAB) m/z calcd for $\text{C}_{38}\text{H}_{43}\text{O}_{12}\text{P}_2$: 753.2232, found: 753.2208.

As in the preparation of **12**, 63 mg (a 100% yield) of (+)-**11** was obtained as a yellow solid from (+)-**9** (64 mg, 0.084 mmol) and LDA (234 μL , 1.8 M in heptane/THF/ethylbenzene (20:40:15), 0.42 mmol). $[\alpha]_{\text{D}}^{+2229^\circ}$ (0.472, CH_2Cl_2); ^1H NMR (CDCl_3) δ 9.51 (s, 2H), 8.47 (d, 8.4 Hz, 2H), 8.02 (d, 8.4 Hz, 2H), 7.64 (s, 2H), 6.41 (d, 14.2 Hz, 2H), 4.21 (s, 6H), 4.01–3.95 (m, 2H), 3.89 (s, 6H), 3.73–3.65 (m, 4H), 3.56–3.50 (m, 2H), 1.38 (t, 7.0 Hz, 6H), 1.01 ppm (t, 7.0 Hz, 6H); ^{13}C NMR (CDCl_3) δ 156.2, 154.6, 147.2 (68.4 Hz), 130.7, 130.1 (33 Hz), 126.0, 125.8, 124.6, 120.0, 117.2 (62.4 Hz), 104.2, 97.9, 96.8, 95.5, 61.7, 56.0, 16.4, 15.9, ppm; ^{31}P NMR (CDCl_3) δ 25.51 ppm (s); IR (NaCl) 3058.9, 2985.0, 2935.7, 1610.8, 1512.2, 1456.7, 1407.4, 1296.5, 1241.1, 1204.1, 1160.9, 1136.3, 1074.7, 1019.2, 969.9, 865.2, 840.5, 772.7, 729.6 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{38}\text{H}_{43}\text{O}_{12}\text{P}_2$: 753.2232, found: 753.2241.

14: K_2CO_3 (151 mg, 1.09 mmol) and then $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ (235 mg, 0.546 mmol) dissolved in MeCN (4 mL) in drops were added to a solution at 25 $^\circ\text{C}$ of **8c** (97 mg, 0.13 mmol) in a mixture of MeCN (4 mL) and MeOH (16 mL). The progress of the reaction was monitored by TLC (1:1 hexane/EtOAc) at 2 min intervals. Upon completion of reaction (ca. 20 min), the mixture was poured into H_2O (80 mL) and Et_2O (40 mL). The ether layer was washed with brine (30 mL), dried over Na_2SO_4 , and concentrated. Silica gel flash chromatography, eluting with 6:4 hexane/EtOAc, gave 58 mg (55% yield) of **14**, a yellow solid. ^1H NMR (CDCl_3) δ 8.38 (d, 8.8 Hz, 2H), 8.31 (d, 8.8 Hz, 2H), 7.01 (s, 2H), 6.87 (s, 2H), 6.87 (s, 2H), 4.16 (s, 6H), 4.14 (s, 6H), 3.57 (s, 6H), 2.55 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 176.8, 160.3, 144.9, 140.6, 137.1, 128.4, 127.5, 127.0, 126.1, 125.6, 122.7, 121.5, 120.2, 102.0, 96.3, 61.0, 56.1, 50.8 ppm; IR (NaCl) 2938.1, 2849.8, 1667.8, 1654.3, 1600.0, 1464.1, 1382.6, 1294.3, 1267.2, 1219.6, 1090.6, 1009.0 cm^{-1} ; LRMS (APCI+) m/z calcd for $\text{C}_{37}\text{H}_{32}\text{O}_{10}^{79}\text{Br}_2$: 806.0, found: 806.2.

13: The procedure was similar to that used to prepare **14**, except that the solvent system was 2:1:1 MeOH/MeCN/ $\text{HC}(\text{OMe})_3$ (4 mL), the chromatography was performed on basic Al_2O_3 , and the eluent was 55:45 hexane/EtOAc. Thus substrate **7c** (7.7 mg, 0.0121 mmol), $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ (22 mg, 0.051 mmol), and K_2CO_3 (14 mg, 0.10 mmol) gave 4.9 mg (58% yield) of orange-colored **13**. ^1H NMR (CDCl_3) δ 8.34 (d, 8.6 Hz, 2H), 7.81 (d, 8.6 Hz, 2H), 7.19 (s, 2H), 7.16 9s, 2H), 4.16 (s, 6H), 3.54 (s, 6H), 2.88 ppm (s, 6H); IR (NaCl) 3059.8, 2935.3, 2854.3, 1655.9, 1596.6, 1515.7, 1459.6, 1384.9, 1310.2, 1254.2, 1229.2, 1135.8, 1023.8, 855.7 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{32}\text{H}_{26}\text{O}_8^{79}\text{Br}_2$: 695.9994, found: 696.0012.

16: $\text{Ti}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (321 mg, 0.723 mmol) dissolved in 1:1 MeOH/ $\text{HC}(\text{OMe})_3$ (10 mL) was slowly added to a solution at -30 $^\circ\text{C}$ of **6f** (232 mg, 0.344 mmol) in CH_2Cl_2 (15 mL) and 1:1 MeOH/ $\text{HC}(\text{OMe})_3$ (25 mL), and the solution was stirred for 1 h during which time the temperature was gradually increased to -10 $^\circ\text{C}$. Workup with Et_2O (120 mL), H_2O (100 mL), and saturated NaHCO_3 (120 mL), drying over Na_2SO_4 , and chromatography on basic Al_2O_3 , eluting with 1:1 hexane/ Et_2O gave 239 mg (94% yield) of **16**, an orange yellow solid. ^1H NMR (CDCl_3) δ 8.37 (d, 8.8 Hz, 2H), 8.31 (d, 8.8 Hz, 2H), 7.15 (s, 2H), 6.97 (s, 2H), 4.24 (s, 6H), 4.14 (s, 6H), 3.60 (s, 6H), 2.63 (s, 6H), 1.98 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 195.6, 183.2, 158.8, 145.3, 142.8, 140.8, 140.1, 128.5, 126.9,

126.0, 125.9, 121.7, 120.4, 102.8, 94.4, 61.6, 56.6, 53.8, 50.6, 30.1 ppm; IR (NaCl) 2944.9, 2836.2, 1695.1, 1667.9, 1593.2, 1552.4, 1498.1, 1464.1, 1382.6, 1355.5, 1253.6, 1192.4, 1117.7, 1083.8, 975.1, 825.6, 737.3 cm^{-1} ; LRMS (APCI+) m/z calcd for $\text{C}_{42}\text{H}_{38}\text{O}_{12}$: 734.2, found: 735.6.

15: Similarly, (+)-**5f** (24.3 mg, 0.0431 mmol) and $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (40 mg, 0.09 mmol) gave 26.1 mg (97% yield) of (+)-**15**, an orange yellow solid. $[\alpha]_{\text{D}}^{+1937^\circ}$ (0.185, CH_2Cl_2); ^1H NMR (CDCl_3) δ 8.33 (d, 8.6 Hz, 2H), 7.87 (d, 8.6 Hz, 2H), 7.43 (s, 2H), 7.06 (s, 2H), 4.14 (s, 6H), 3.61 (s, 6H), 2.68 (s, 6H), 2.17 ppm (s, 6H); ^{13}C NMR (CDCl_3) δ 195.9, 182.9, 159.3, 142.5, 142.2, 140.3, 131.8, 131.0, 127.0, 126.4, 125.3, 121.3, 101.6, 94.1, 56.4, 51.1, 51.0, 31.1 ppm; IR (NaCl) 2991.3, 2940.4, 2832.8, 1695.1, 1666.7, 1598.8, 1508.3, 1457.3, 1389.4, 1344.1, 1253.5, 1235.2, 1208.2, 1117.7, 1044.1, 846.0 cm^{-1} ; LRMS (APCI+) m/z calcd for $\text{C}_{36}\text{H}_{32}\text{O}_{10}$: 624.6, found: 625.8.

Figure 1. 400MHz ^1H NMR spectrum of **3a** in CDCl_3 .

Figure 2. 75 MHz ^{13}C NMR spectrum of **3a** in CDCl_3 .

Figure 4. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.36×10^{-5} M solution of **3a** in CH_3CN .

Figure 5. 400MHz ^1H NMR spectrum of 4a in CDCl_3 .

Figure 6. 75 MHz ^{13}C NMR spectrum of **4a** in CDCl_3 .

Figure 8. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 9.80×10^{-6} M solution of **4a** in CH_3CN .

Figure 9. 400MHz ^1H NMR spectrum of **3b** in CDCl_3 .

Figure 10. 75 MHz ^{13}C NMR spectrum of **3b** in CDCl_3 .

Figure 12. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 8.96×10^{-6} M solution of **3b** in CH_3CN .

Figure 13. 400MHz ^1H NMR spectrum of **4b** in CDCl_3 .

Figure 14. 75 MHz ^{13}C NMR spectrum of **4b** in CDCl_3 .

Figure 15. IR spectrum of 4b in CCl_4 .

Figure 16. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 9.58×10^{-6} M solution of **4b** in CH_3CN .

Figure 17. 400MHz ^1H NMR spectrum of 3c in CDCl_3 .

Figure 19. IR spectrum of 3c in CCl_4 .

Figure 20. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.60×10^{-5} M solution of **3c** in CH_3CN .

Figure 21. 400MHz ^1H NMR spectrum of **4c** in CDCl_3 .

Figure 22. 75 MHz ^{13}C NMR spectrum of 4c in CDCl_3 .

Figure 24. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.02×10^{-5} M solution of **4c** in CH_3CN .

Figure 25. 400MHz ^1H NMR spectrum of **3d** in CDCl_3 .

Figure 26. 75 MHz ^{13}C NMR spectrum of 3d in CDCl_3 .

Figure 27. IR spectrum of 3d in CCl₄.

Figure 28. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.17×10^{-5} M solution of **3d** in CH_3CN .

Figure 29. 400MHz ^1H NMR spectrum of **4d** in CDCl_3 .

Figure 30. 75 MHz ^{13}C NMR spectrum of **4d** in CDCl_3 .

Figure 31. IR spectrum of **4d** in CCl_4 .

Figure 32. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 9.29×10^{-6} M solution of **4d** in CH_3CN .

Figure 33. 400MHz ^1H NMR spectrum of **3e** in CDCl_3 .

Figure 34. 75 MHz ^{13}C NMR spectrum of 3e in CDCl_3 .

Figure 35. IR spectrum of 3e in CCl₄.

Figure 36. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 8.41×10^{-6} M solution of **3e** in CH_3CN .

Figure 37. 400MHz ^1H NMR spectrum of **4e** in CDCl_3 .

Figure 38. 75 MHz ^{13}C NMR spectrum of **4e** in CDCl_3 .

Figure 39. IR spectrum of 4e in CCl₄.

Figure 40. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 8.41×10^{-6} M solution of **4e** in CH_3CN .

Figure 41. 400MHz ^1H NMR spectrum of 3f in CDCl_3 .

Figure 42. 75 MHz ^{13}C NMR spectrum of **3f** in CDCl_3 .

Figure 43. IR spectrum of 3f in CCl₄.

Figure 44. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 8.66×10^{-6} M solution of **3f** in CH_3CN .

Figure 45. 400MHz ^1H NMR spectrum of **4f** in CDCl_3 .

Figure 47. IR spectrum of 4f in CCl_4 .

Figure 48. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.11×10^{-5} M solution of **4f** in CH_3CN .

Figure 49. 400MHz ^1H NMR spectrum of **3h** in CDCl_3 .

Figure 50. 100 MHz ^{13}C NMR spectrum of 3h in CDCl_3 .

Figure 51. IR spectrum of 3h as a film on NaCl.

Figure 52. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.94×10^{-4} M solution of **3h** in CH_3CN .

Figure 53. 400MHz ^1H NMR spectrum of **3i** in CDCl_3 .

Figure 54. 75 MHz ^{13}C NMR spectrum of **3i** in CDCl_3 .

Figure 55. IR spectrum of 3i as a film on NaCl.

Figure 56. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.8×10^{-4} M solution of **3i** in CH_3CN .

Figure 57. 400MHz ^1H NMR spectrum of **4h** in CDCl_3 .

Figure 58. 75 MHz ^{13}C NMR spectrum of **4h** in CDCl_3 .

Figure 59. IR spectrum of 4h in KBr.

Figure 60. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.18×10^{-4} M solution of **4h** in CH_3CN .

Figure 61. 400MHz ^1H NMR spectrum of 4i in CDCl_3 .

Figure 62. 75 MHz ^{13}C NMR spectrum of **4i** in CDCl_3 .

Figure 63. IR spectrum of 4i in KBr.

Figure 64. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 5.68×10^{-5} M solution of **4i** in CH_3CN .

Figure 65. 400MHz ^1H NMR spectrum of **3j** in CDCl_3 .

Figure 66. 75 MHz ^{13}C NMR spectrum of **3j** in CDCl_3 .

Figure 67. IR spectrum of 3j as a film on NaCl.

Figure 68. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.28×10^{-4} M solution of **3j** in CH_3CN .

Figure 69. 400MHz ^1H NMR spectrum of 3k in CDCl_3 .

Figure 70. 75 MHz ^{13}C NMR spectrum of **3k** in CDCl_3 .

Figure 71. IR spectrum of 3k as a film on NaCl.

Figure 72. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 2.1×10^{-4} M solution of **3k** in CH_3CN .

Figure 73. 400MHz ^1H NMR spectrum of 4j in CDCl_3 .

Figure 74. 75 MHz ^{13}C NMR spectrum of **4j** in CDCl_3 .

Figure 75. IR spectrum of 4j in KBr.

Figure 76. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 8.6×10^{-5} M solution of **4j** in CH_3CN .

Figure 77. 400MHz ^1H NMR spectrum of 4k in CDCl_3 .

Figure 79. IR spectrum of 4k in KBr.

Figure 80. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.23×10^{-4} M solution of **4k** in CH_3CN .

Figure 81. 400MHz ^1H NMR spectrum of 5c in CDCl_3 .

Figure 82. 100 MHz ^{13}C NMR spectrum of **5c** in CDCl_3 .

Figure 83. IR spectrum of 5c as a film on NaCl.

Figure 84. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 3.7×10^{-4} M solution of 5c in CH_3CN .

Figure 85. 400MHz ^1H NMR spectrum of 5d in CDCl_3 .

Figure 86. 100 MHz ^{13}C NMR spectrum of **5d** in CDCl_3 .

Figure 87. IR spectrum of 5d as a film on NaCl.

Figure 88. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.14×10^{-4} M solution of **5d** in CH_3CN .

Figure 89. 400MHz ^1H NMR spectrum of **6c** in CDCl_3 .

Figure 90. 100 MHz ^{13}C NMR spectrum of **6c** in CDCl_3 .

Figure 91. IR spectrum of 6c as a film on NaCl.

Figure 92. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 3.12×10^{-4} M solution of **6c** in CH_3CN .

Figure 93. 400MHz ^1H NMR spectrum of **6d** in CDCl_3 .

Figure 94. 75 MHz ^{13}C NMR spectrum of **6d** in CDCl_3 .

Figure 95. IR spectrum of **6d** as a film on NaCl.

Figure 96. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.40×10^{-4} M solution of **6d** in CH_3CN .

Figure 97. 400MHz ^1H NMR spectrum of 5f in CDCl_3 .

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Figure 98. 75 MHz ^{13}C NMR spectrum of 5f in CDCl_3 .

Figure 99. IR spectrum of **5f** in CCl_4 .

Figure 100. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 1.30×10^{-5} M solution of 5f in CH_3CN .

Figure 101. 400MHz ^1H NMR spectrum of **6f** in CDCl_3 .

Figure 102. 75 MHz ^{13}C NMR spectrum of **6f** in CDCl_3 .

Figure 103. IR spectrum of 6f in KBr.

Figure 104. CD (upper curve, ordinate on right) and UV-vis absorption (lower curve, ordinate on left) spectra of a 9.77×10^{-6} M solution of **6f** in CH_3CN .

Figure 105. 300MHz ^1H NMR spectrum of 3g in CDCl_3 .

Figure 106. 75 MHz ^{13}C NMR spectrum of **3g** in CDCl_3 .

Figure 107. IR spectrum of 3g as a film on NaCl.

Figure 108. 300MHz ^1H NMR spectrum of **4g** in CDCl_3 .

Figure 109. 75 MHz ^{13}C NMR spectrum of **4g** in CDCl_3 .

Figure 110. IR spectrum of **4g** as a film on NaCl.

Figure 111. 300MHz ^1H NMR spectrum of **7a** in CDCl_3 .

Figure 112. 75 MHz ^{13}C NMR spectrum of **7a** in CDCl_3 .

Figure 113. IR spectrum of 7a as a film on NaCl.

Figure 114. 300MHz ^1H NMR spectrum of **7b** in CDCl_3 .

Figure 115. 75 MHz ^{13}C NMR spectrum of **7b** in CDCl_3 .

Figure 116. IR spectrum of 7b as a film on NaCl.

Figure 117. 300MHz ^1H NMR spectrum of 7c in CDCl_3 .

Figure 118. 75 MHz ^{13}C NMR spectrum of 7c in CDCl_3 .

Figure 119. IR spectrum of 7c as a film on NaCl.

Figure 120. 300MHz ^1H NMR spectrum of 7d in CDCl_3 .

Figure 121. 75 MHz ^{13}C NMR spectrum of **7d** in CDCl_3 .

Figure 122. IR spectrum of 7d as a film on NaCl.

Figure 123. 300MHz ^1H NMR spectrum of **7e** in CDCl_3 .

Figure 124. 75 MHz ^{13}C NMR spectrum of **7e** in CDCl_3 .

Figure 125. IR spectrum of 7e as a film on NaCl.

Figure 126. 300MHz ^1H NMR spectrum of **7f** in CDCl_3 .

Figure 127. 75 MHz ^{13}C NMR spectrum of **7f** in CDCl_3 .

Figure 128. IR spectrum of 7f as a film on NaCl.

Figure 129. 300MHz ^1H NMR spectrum of 7g in CDCl_3 .

Figure 130. 75 MHz ^{13}C NMR spectrum of 7g in CDCl_3 .

Figure 131. IR spectrum of 7g as a film on NaCl.

Figure 132. 300MHz ^1H NMR spectrum of 8a in CDCl_3 .

Figure 133. 75 MHz ^{13}C NMR spectrum of 8a in CDCl_3 .

Figure 134. IR spectrum of 8a as a film on NaCl.

Figure 135. 300MHz ^1H NMR spectrum of **8b** in CDCl_3 .

Figure 136. 75 MHz ^{13}C NMR spectrum of **8b** in CDCl_3 .

Figure 137. IR spectrum of 8b as a film on NaCl.

Figure 138. 400MHz ^1H NMR spectrum of 8c in CDCl_3 .

Figure 139. 75 MHz ^{13}C NMR spectrum of 8c in CDCl_3 .

Figure 140. IR spectrum of 8c as a film on NaCl.

Figure 141. 300MHz ^1H NMR spectrum of 8d in CDCl_3 .

Figure 142. 75 MHz ^{13}C NMR spectrum of **8d** in CDCl_3 .

Figure 144. 300MHz ^1H NMR spectrum of **8e** in CDCl_3 .

Figure 145. 75 MHz ^{13}C NMR spectrum of **8e** in CDCl_3 .

Figure 146. IR spectrum of 8e as a film on NaCl.

Figure 147. 300MHz ^1H NMR spectrum of **8f** in CDCl_3 .

Figure 148. 75 MHz ^{13}C NMR spectrum of **8f** in CDCl_3 .

Figure 149. IR spectrum of 8f as a film on NaCl.

Figure 150. 300MHz ^1H NMR spectrum of 8g in CDCl_3 .

Figure 151. 75 MHz ^{13}C NMR spectrum of 8g in CDCl_3 .

Figure 152. IR spectrum of 8g as a film on NaCl.

Figure 153. 400MHz ^1H NMR spectrum of **9** in CDCl_3 .

Figure 154. 75 MHz ^{13}C NMR spectrum of **9** in CDCl_3 .

Figure 155. IR spectrum of 9 as a film on NaCl.

Figure 156. 300MHz ^1H NMR spectrum of **11** in CDCl_3 .

Figure 157. 75 MHz ^{13}C NMR spectrum of **11** in CDCl_3 .

Figure 158. IR spectrum of **11** as a film on NaCl.

Figure 159. 300MHz ^1H NMR spectrum of 12 in CDCl_3 .

Figure 160. 75 MHz ^{13}C NMR spectrum of 12 in CDCl_3 .

Figure 161. IR spectrum of **12** as a film on NaCl.

Figure 162. 300MHz ^1H NMR spectrum of 13 in CDCl_3 .

Figure 164. 300MHz ^1H NMR spectrum of **14** in CDCl_3 .

Figure 165. 75 MHz ^{13}C NMR spectrum of **14** in CDCl_3 .

Figure 166. IR spectrum of 14 as a film on NaCl.

Figure 167. 300MHz ^1H NMR spectrum of **15** in CDCl_3 .

Figure 168. 75 MHz ^{13}C NMR spectrum of **15** in CDCl_3 .

Figure 169. IR spectrum of 15 as a film on NaCl.

Figure 170. 300MHz ^1H NMR spectrum of **16** in CD_2Cl_2 .

Figure 171. 75 MHz ^{13}C NMR spectrum of **16** in CD_2Cl_2 .

Figure 172. IR spectrum of 16 as a film on NaCl.