Supporting Information

Total Diastereofacial Selective Iodofunctionalization of Terpene Derivatives Based on Ipy₂BF₄

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General. Unless noted, all reactions were carried out under an atmosphere of dry nitrogen using oven-dried glassware and syringes. Temperatures are reported as bath temperatures; baths were prepared cooling ethanol or acetone by means of liquid nitrogen or a cryocool. Dichloromethane, methanol and acetonitrile were continuously refluxed and freshly distilled from calcium hydride under nitrogen. Ether was refluxed and distilled from sodium. Solvents used in extraction and purification were distilled prior to use. Compounds were visualized on analytical thin-layer chromatograms (TLC) by UV light (254 nm) and/or by staining with a Ce/Mo reagent (prepared by solving phosphomolybdic acid (2 g), cerium(IV) sulfate (1 g), and concentrated sulfuric acid (10 mL) in water (90 mL)) and subsequent heating. Silica gel 60 (230-400 mesh) was used for flash chromatography. NMR spectra were recorded at 400, 300, and 200 MHz for proton frequency and 100, 75, and 50 MHz for carbon frequency using the DEPT pulse

sequence with tetramethylsilane ($\delta = 0.0$, $^1\text{H-NMR}$) and CDCl_3 ($\delta = 77.0$, $^{13}\text{C-NMR}$) as references. Elemental analyses were performed by the Microanalytical Laboratory, Universidad de Oviedo. Melting points were obtained with open capillary tubes and are uncorrected. For optical rotations sample concentrations are given in g/100mL. Commercially available starting materials were used without further purification. Acetonides **1** were obtained as described in previous works (see ref 5 in text).

General procedure for the iodofunctionalization of acetonides. A solution of IPy_2BF_4 (0.41 g, 1.1 mmol) and the corresponding nucleophile (excess) in dried CH_2Cl_2 (20 mL) was treated under nitrogen atmosphere at the required temperature (see below) with a 54% solution of HBF_4 in ether (0.20 mL, 1.5 mmol). The colour of the mixture turns into red. A solution of the corresponding acetonide (1 mmol) in dried CH_2Cl_2 (10 mL) was slowly added to the resulting mixture at the same temperature and the reaction was monitored by TLC. The reaction mixture was quenched with a 5% solution of sodium thiosulfate pentahydrate (20 mL) and extracted with CH_2Cl_2 (2x10mL). The combined organic layers were washed with water (2x10mL) and dried over anhydrous Na_2SO_4 . The solvents were removed under vacuum and the residue was purified by flash chromatography (SiO_2 , hexane/ethyl acetate mixtures) or recrystallization to afford compounds **2**, **3**, or **4**.

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*S*,2*S*)-1-iodo-2-methoxy-2-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2a): Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at $-60\text{ }^\circ\text{C}$ was followed by addition of a solution of acetonide **1a** (0.33 g, 1 mmol) in dichloromethane (10 mL) at $-60\text{ }^\circ\text{C}$ and stirring was continued for 4h while the temperature raised $-30\text{ }^\circ\text{C}$. Work-up as

described above yielded **2a** (0.41 g) as white solid. Mp 82-84 °C (decompose, hexane). $[\alpha]_D^{20} = +50.3$ ($c = 0.86$, dichloromethane). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.40\text{--}7.20$ (m, 5H; ArH), 4.42 (d, $J = 6.7$ Hz, 1H; CHOMe), 4.12 (d, $J = 6.7$ Hz, 1H; CHI), 3.69 (d, $J = 7.9$ Hz, 1H; OCHCH_2), 3.67 (s, 1H; OCHCHI), 3.30 (s, 3H; OMe), 2.40-1.25 (m, 6H; aliphatic ring), 1.46, 1.42, 1.24, 1.14, 0.89 (5s, 15H; 5x Me). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 139.8, 128.1, 127.8, 127.4, 101.1, 87.9, 71.3, 65.6, 57.7, 48.2, 45.3, 39.3, 39.2, 34.9, 34.0, 28.0, 26.6, 25.2, 24.0, 22.7, 20.7$. HRMS (70 EV, EI): calcd. for $\text{C}_{22}\text{H}_{30}\text{IO}_3$ ($[M-15]^+$): 469.1240, found 469.1237. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ (484.4): C 57.03, H 6.87; found C 57.28, H 6.84.

(1*R*,2*R*,3*R*,7*S*,9*R*)-3-[(1*R*,2*R*)-1-iodo-2-methoxy-2-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (*ent*-2a): A procedure analogous to that described for **2a** yielded *ent*-**2a** (0.40 g). $[\alpha]_D^{20} = -50.3$ ($c = 0.86$, dichloromethane).

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*S*,2*S*)-2-Acetoxy-1-iodo-2-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2b): Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 1:2 mixture of dichloromethane:acetic acid (15 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at room temperature was followed by addition of a solution of acetone **1a** (0.33 g, 1 mmol) in dichloromethane (5 mL) at room temperature and stirring was continued for 10 min. Work-up as described above with an additional washing of the organic layer with a saturated solution of Na_2CO_3 , yielded **2b** (0.31 g) as a white solid. Mp 99-101 °C (decompose, hexane). $[\alpha]_D^{20} = +19.5$ ($c = 0.63$, dichloromethane). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.45\text{--}7.28$ (m, 5H; ArH), 6.08 (d, $J = 5.6$ Hz, 1H; CHOAc), 4.27 (dd, $J = 5.6, 1.5$ Hz, 1H; CHI), 3.69 (d, $J = 8.2$ Hz, 1H; OCHCH_2), 3.38 (d, $J = 1.5$ Hz, 1H; OCHCHI), 2.45-1.15 (m, 6H; aliphatic ring), 2.17 (s, 1H; MeCO), 1.44, 1.42, 1.22, 1.12, 0.89 (5s, 15H; 5x Me). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 169.5, 138.8, 128.4, 128.3, 126.9, 101.3, 79.8, 71.4, 65.8, 48.3, 45.5,$

39.5, 39.4, 34.0, 32.4, 28.0, 26.9, 25.2, 24.0, 22.7, 20.9, 20.4. HRMS (70 EV, EI): calcd. for $C_{23}H_{30}IO_4$ ($[M-15]^+$): 497.1189, found 497.1186. Elemental analysis calcd (%) for $C_{24}H_{33}IO_4$ (512.4): C 56.17, H 6.49; found C 56.17, H 6.52.

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*S*,2*S*)-2-azido-1-iodo-2-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2c): Reaction of IPy₂BF₄ (0.56 g, 1.5 mmol) in dichloromethane (20 mL) with trimethylsilylazide (0.14 g, 0.16 mL, 1.20 mmol) and boron trifluoride diethyl etherate (0.21 g, 0.19 mL, 1.5 mmol) at –60 °C was followed by addition of a solution of acetonide **1a** (0.33 g, 1 mmol) in dichloromethane (10 mL) at at –60 °C and stirring was continued for 4h. Work-up as described above yielded **2c** (0.39 g) as a white solid. Mp 149-151 °C (CH₂Cl₂/CHCl₃ 1:10). $[\alpha]_D^{20} = +47.9$ ($c = 0.42$, dichloromethane). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.45$ -7.30 (m, 5H; ArH), 4.92 (d, $J = 6.5$ Hz, 1H; CHN₃), 4.17 (d, $J = 6.5$ Hz, 1H; CHI), 3.70 (d, $J = 8.3$ Hz, 1H; OCHCH₂), 3.51 (s, 1H; OCHCHI), 2.40-1.00 (m, 6H; aliphatic ring), 1.48, 1.42, 1.23, 1.12, 0.88 (5s, 15H; 5x Me). ¹³C NMR (75 MHz, CDCl₃): $\delta = 138.3$, 128.7, 128.5, 127.3, 101.4, 71.6, 71.4, 66.2, 48.3, 45.4, 39.5, 39.4, 34.1, 33.2, 28.0, 26.8, 25.3, 24.0, 22.7, 20.8. HRMS (70 EV, EI): calcd. for $C_{21}H_{27}IN_3O_2$ ($[M-15]^+$): 480.1148, found 480.1154. Elemental analysis calcd (%) for $C_{22}H_{30}IN_3O_2$ (495.4): C 53.34, H 6.10; found C 53.26, H 5.96.

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*S*,2*S*)-2-Hydroxy-1-iodo-2-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2d): Reaction of IPy₂BF₄ (0.41 g, 1.1 mmol) and acetonide **1a** (0.33 g, 1 mmol) in a 1:1 mixture of dichloromethane:acetonitrile (30 mL) containing water (1.8 mL) with a 54% solution of HBF₄ in diethyl ether (0.20 mL, 1.5 mmol) at room temperature for 90 min. Work-up as described above yielded **2d** (0.31) as a white solid. Mp 114-116 °C (hexane). $[\alpha]_D^{20} = +38.6$ ($c = 0.07$, dichloromethane). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.50$ -7.20 (m, 5H;

ArH), 5.27 (s, 1H; *CHOH*), 4.37 (s, 1H; *CHI*), 3.63 (d, $J = 7.8$ Hz, 1H; *OCHCH₂*), 3.24 (s, 1H; *OCHCHI*), 2.87 (br s, 1H; OH), 2.40-0.70 (m, 6H; aliphatic ring), 1.49, 1.39, 1.18, 1.02, 0.82 (5s, 15H; 5x Me). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 141.0, 128.4, 127.4, 126.0, 101.4, 81.0, 71.2, 65.4, 48.3, 44.5, 39.2, 39.1, 38.1, 34.1, 27.8, 27.6, 24.6, 23.9, 22.6, 20.7$. HRMS (70 EV, EI): calcd. for $\text{C}_{21}\text{H}_{28}\text{IO}_3$ ($[M-15]^+$): 455.1083, found 455.1084. Elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{31}\text{IO}_3$ (470.4): C 56.17, H 6.64; found C 56.17, H 6.66.

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*S*)-2-Iodo-1-methoxy-1-phenylethyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2e). Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at -60°C was followed by addition of a solution of acetone **1b** (0.33 g, 1 mmol) in dichloromethane (10 mL) at -60°C and stirring was continued for 4h while the temperature raised -30°C . Work-up as described above yielded **2e** (0.34 g) as a white solid. Mp $127-128^\circ\text{C}$ ($\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 1:10). $[\alpha]_{\text{D}}^{20} = -13.1$ ($c = 0.58$, dichloromethane). ^1H NMR (200 MHz, CDCl_3): $\delta = 7.60-7.15$ (m, 5H; ArH), 4.42 (s, 1H, *OCHCOMe*), 4.03 (d, $J = 11.3$ Hz, 1H; *CHHI*), 3.72 (d, $J = 11.3$ Hz, 1H; *CHHI*), 3.56 (d, $J = 7.9$ Hz, 1H; *OCHCH₂*), 3.42 (s, 3H; OMe), 2.50-1.70 (m, 6H; aliphatic ring), 1.54, 1.36, 1.27, 0.85, 0.45 (5s, 15H; 5x Me). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 140.0, 128.2, 127.1, 126.8, 100.6, 80.4, 72.8, 72.3, 50.4, 49.7, 47.0, 39.3, 39.2, 35.2, 28.3, 27.8, 26.8, 24.4, 22.8, 22.2, 17.2$. HRMS (70 EV, EI): calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_3$ ($[M-128]^+$): 356.2351, found 356.2359. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ (484.4): C 57.03, H 6.87; found C 57.26, H 6.82.

(1*S*,2*S*,3*S*,7*R*,9*S*)-3-[(1*R*)-1-iodo-2-methoxy-2-methylpropyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2f): Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution

of HBF₄ in diethyl ether (0.20 mL, 1.5 mmol) at –60 °C was followed by addition of a solution of acetonide **1c** (0.33 g, 1 mmol) in dichloromethane (10 mL) at –60 °C and stirring was continued for 4h while the temperature raised –30 °C. Work-up as described above yielded **2f** (0.36 g) as a white solid. Mp 72-74 °C (decompose, CH₂Cl₂/CHCl₃ 1:10). $[\alpha]_D^{20} = -3.5$ ($c = 0.68$, dichloromethane). ¹H NMR (400 MHz, CDCl₃): $\delta = 4.03$ (s, 1H; CHI), 3.75 (d, $J = 8.3$ Hz, 1H; OCHCH₂), 3.47 (s, 1H; OCHCHI), 3.20 (s, 3H; OMe), 2.40 (ddt, $J = 14.6, 8.3, 1.8$ Hz, 1H; OCHCHH), 2.12-2.04 (m, 1H; CHHCH), 1.90-1.84 (m, 1H; CH₂CHCH₂), 1.76 (dd, $J = 14.6, 4.0$ Hz, 1H; OCHCHH), 1.72-1.62 (m, 2H; MeCCH and CHHCH), 1.39, 1.38, 1.33, 1.32, 1.27, 1.24, 0.93 (7s, 21H; 7xMe). ¹³C NMR (75 MHz, CDCl₃): $\delta = 100.9, 77.4, 71.2, 66.2, 49.7, 48.4, 45.6, 42.6, 39.4, 39.3, 34.6, 28.1, 27.4, 25.8, 25.7, 24.2, 22.8, 21.9, 20.9$. HRMS (70 EV, EI): calcd. for C₁₉H₃₃IO₃ ([M]⁺): 436.1474, found 436.1477. Elemental analysis calcd (%) for C₁₉H₃₃IO₃ (436.4): C 52.30, H 7.62; found C 52.42, H 7.56.

(1S,2S,3S,7R,9S)-3-[(1R,2S)-2-Iodo-1-methoxy-1-methylpropyl]-2,5,5,10,10-pentamethyl-4,6-dioxatricycle[7.1.1.0^{2,7}]undecane (2g): Reaction of IPy₂BF₄ (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF₄ in diethyl ether (0.20 mL, 1.5 mmol) at –60 °C was followed by addition of a solution of acetonide **1d** (0.33 g, 1 mmol) in dichloromethane (10 mL) at –60 °C and stirring was continued for 4h while the temperature raised –30 °C. Work-up as described above yielded **2g** (0.32 g) as a colourless oil. $R_f = 0.30$ (Hexane/Ether 20:1). $[\alpha]_D^{20} = -42.0$ ($c = 1.0$, dichloromethane). ¹H NMR (400 MHz, CDCl₃): $\delta = 5.02$ (q, $J = 6.8$ Hz, 1H; CHI), 4.07 (s, 1H; OCHCOMe), 3.74 (dd, $J = 8.6, 1.8$ Hz, 1H; OCHCH₂), 3.38 (s, 3H; OMe), 2.44 (ddt, $J = 14.4, 8.6, 2.0$ Hz, 1H; OCHCHH), 2.24-2.14 (m, 2H; MeCCH and CHHCH), 1.99 (d, $J = 6.8$ Hz, 3H; MeCHI), 1.92-1.86 (m, 1H; CH₂CHCH₂), 1.79 (ddd, $J = 14.4, 3.8, 1.8$ Hz, 1H; OCHCHH), 1.60 (dd, $J = 10.0, 9.0$

Hz, 1H; *CHHCH*), 1.38, 1.34, 1.33, 1.30, 1.25, 0.98 (s, 3H; Me). ^{13}C NMR (75 MHz, CDCl_3): δ = 100.5, 80.6, 72.7, 71.7, 52.1, 50.3, 47.6, 42.5, 39.8, 39.3, 35.4, 28.4, 27.3, 26.5, 25.2, 24.6, 23.0, 21.5, 21.2. HRMS (70 EV, EI): calcd. for $\text{C}_{19}\text{H}_{33}\text{IO}_3$ ($[M]^+$): 436.1474, found 436.1473; elemental analysis calcd (%) for $\text{C}_{19}\text{H}_{33}\text{IO}_3$ (436.4): C 52.30, H 7.62; found C 52.41, H 7.55.

(1*S*,2*S*,4*R*,7*R*,8*S*)-8-[(1*S*,2*S*)-1-iodo-2-methoxy-2-phenylethyl]-3,3,7,10,10-pentamethyl-9,11-dioxatricycle[5.4.0.0^{2,4}]undecane (2h). Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at $-60\text{ }^\circ\text{C}$ was followed by addition of a solution of acetone **1e** (0.33 g, 1 mmol) in dichloromethane (10 mL) at $-60\text{ }^\circ\text{C}$ and stirring was continued for 4h while the temperature raised $-30\text{ }^\circ\text{C}$. Work-up as described above yielded **2h** (0.40 g) as a white solid. Mp $86\text{--}88\text{ }^\circ\text{C}$ (decompose, hexane). $[\alpha]_{\text{D}}^{20} = +71.5$ ($c = 0.44$, dichloromethane). ^1H NMR (300 MHz, CDCl_3): δ = 7.50–7.20 (m, 5H; ArH), 4.33 (d, $J = 8.3\text{ Hz}$, 1H; *CHOMe*), 4.19 (d, $J = 8.3\text{ Hz}$, 1H; *CHI*), 3.80 (s, 1H; *OCHCHI*), 3.54 (d, $J = 2.6\text{ Hz}$, 1H; *OCHCH*), 3.23 (s, 3H; *OMe*), 2.20–0.60 (m, 6H; aliphatic ring), 1.61, 1.48, 1.04, 0.91, 0.74 (5s, 15H; 5x Me). ^{13}C NMR (75 MHz, CDCl_3): δ = 140.2, 128.1, 128.0, 127.8, 100.4, 86.3, 74.9, 68.8, 57.5, 36.5, 36.2, 29.3, 29.2, 29.0, 26.3, 25.7, 23.6, 22.0, 16.6, 15.3, 15.2. HRMS (70 EV, EI): calcd. for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ ($[M]^+$): 484.1474, found 484.1469. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ (484.4): C 57.03, H 6.87; found C 57.33, H 6.71.

(1*S*,3*S*,5*R*,7*R*,11*S*)-11-[(1*S*,2*S*)-1-iodo-2-methoxy-2-phenylethyl]-1,4,4,9,9-pentamethyl-8,10-dioxatricycle[5.4.0.0^{3,5}]undecane (2i). Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at $-60\text{ }^\circ\text{C}$ was followed by addition of a solution of acetone **1f** (0.33 g, 1 mmol) in dichloromethane (10 mL) at $-60\text{ }^\circ\text{C}$ and

stirring was continued for 4h while the temperature raised $-30\text{ }^{\circ}\text{C}$. Work-up as described above yielded **2i** (0.37 g) as a white solid. Mp $112\text{--}114\text{ }^{\circ}\text{C}$ (hexane). $[\alpha]_{\text{D}}^{20} = +58.9$ ($c = 0.36$, dichloromethane). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.50\text{--}7.20$ (m, 5H; ArH), 4.38 (d, $J = 8.3$ Hz, 1H; CHOMe), 4.25 (d, $J = 8.3$ Hz, 1H; CHI), 3.75 (s, 1H; OCHCHI), 3.56 (m, 1H; OCHCH_2), 3.27 (s, 3H; OMe), 2.00–0.25 (m, 6H; aliphatic ring), 1.46, 1.44, 1.00, 0.96, 0.92 (5s, 15H; 5x Me). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 140.2, 128.1, 127.8, 100.5, 86.8, 74.1, 65.8, 57.7, 39.2, 35.2, 28.1, 26.8, 25.8, 23.4, 22.8, 22.6, 17.9, 17.7, 17.4, 14.3$. HRMS (70 EV, EI): calcd. for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ ($[M]^+$): 484.1474, found 484.1467. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{IO}_3$ (484.4): C 57.03, H 6.87; found C 56.98, H 6.85

(1*S*,3*S*,5*R*,7*R*,11*S*)-11-[(1*R*)-1-iodo-2-methoxy-2-methylpropyl]-1,4,4,9,9-pentamethyl-8,10-dioxatricycle[5.4.0.0^{3,5}]undecane (2j). Reaction of IPy_2BF_4 (0.41 g, 1.1 mmol) in a 2:1 mixture of dichloromethane:methanol (30 mL) with a 54% solution of HBF_4 in diethyl ether (0.20 mL, 1.5 mmol) at $-60\text{ }^{\circ}\text{C}$ was followed by addition of a solution of acetone **1g** (0.33 g, 1 mmol) in dichloromethane (10 mL) at $-60\text{ }^{\circ}\text{C}$ and stirring was continued for 4h while the temperature raised $-30\text{ }^{\circ}\text{C}$. Work-up as described above yielded **2j** (0.33 g) as a white solid. Mp $77\text{--}79\text{ }^{\circ}\text{C}$ (decompose, $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 1:10). $[\alpha]_{\text{D}}^{20} = -20.0$ ($c = 0.24$, dichloromethane). ^1H NMR (400 MHz, CDCl_3): $\delta = 4.19$ (s, 1H; CHI), 3.59 (apparent t, $J = 2.7$ Hz, 1H; OCHCH_2), 3.44 (s, 1H; OCHCHI), 3.29 (s, 3H; OMe), 1.92 (ddd, $J = 14.5, 6.7, 3.2$ Hz 1H; OCHCHH), 1.66 (dd, $J = 15.4, 7.5$ Hz, 1H; CCHH), 1.42, 1.41, 1.40, 1.39, 1.05, 0.98, 0.96 (7s, 21H; 7xMe), 0.84 (ddd, $J = 14.5, 9.3, 2.3$ Hz, 1H; OCHCHH), 0.73 (td, $J = 9.3, 6.7$ Hz, 1H; OCHCH_2CH), 0.62 (td, $J = 9.3, 7.5$ Hz, 1H; CCH_2CH), 0.38 (dd, $J = 15.4, 9.3$ Hz, 1H; CCHH). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 100.4, 77.2, 74.0, 66.0, 50.2, 42.8, 39.4, 28.2, 26.7, 26.5, 26.0, 23.5, 22.9, 22.6, 21.4, 18.0, 17.8, 17.7, 14.3$. HRMS (70 EV, EI): calcd.

for $C_{19}H_{33}IO_3$ ($[M]^+$): 436.1474, found 436.1472. Elemental analysis calcd (%) for $C_{19}H_{33}IO_3$ (436.4): C 52.30, H 7.62; found C 52.45, H 7.49.

(1*R*,2*S*,9*S*,10*R*,11*R*,15*S*,17*R*)-10-Iodo-13,13,18,18-tetramethyl-9-phenyl-12,14-dioxa-3,5,7-pentacyclo[15.1.1.0^{2,11}.0^{2,15}.0^{3,8}]nonadecatriene (3): To a solution of IPy_2BF_4 (0.29 g, 0.77 mmol) and acetone **1h** (0.27 g, 0.7 mmol) in dried dichloromethane (30 mL) was added a 54% solution of HBF_4 in diethyl ether (0.10 mL, 0.77 mmol) at room temperature and stirring was continued for 30 min at the same temperature. Work-up as described above yielded **3** (0.25 g) as a slightly orange solid. Mp 112-114 °C (hexane). $[\alpha]_D^{20} +10.0$ ($c=0.09$, dichloromethane). 1H NMR (200 MHz, $CDCl_3$): δ = 7.61 (d, $J=7.4$ Hz, 1H; CHCC), 7.36-7.20 (m, 5H; PhH), 7.11 (t, $J=7.4$ Hz, 1H; CHCHCC), 6.99 (t, $J=7.4$ Hz, 1H; CHCHCCH), 6.70 (d, $J=7.4$ Hz, 1H; CHCCH), 4.91 (d, $J=8.5$ Hz, 1H; OCHCH₂), 4.86 (d, $J=10.5$ Hz, 1H; CHI), 4.75 (s, 1H; OCHCHI), 4.45 (d, $J=10.5$ Hz, 1H; PhCH), 2.80-2.75 (m, 1H; CHHCO), 2.41-2.39 (m, 1H; CHHCH), 2.22-2.20 (m, 1H; CHC), 2.08-2.03 (m, 2H; CHHCO and CHCH₂), 1.82 (d, $J=10.4$ Hz, 1H; CHHCH), 1.44, 1.23, 1.11, 1.05 (4s, 12H; 4x Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =144.6, 140.3, 138.7, 130.1, 129.4, 129.2, 128.4, 126.8, 126.0, 124.8, 101.4, 75.5, 68.2, 54.0, 53.9, 51.4, 40.0, 39.8, 37.1, 35.5, 28.8, 28.6, 27.7, 24.4, 23.3. HRMS (70 EV, EI): calcd. for $C_{24}H_{25}IO$ ($[M-58]^+$): 456.0950, found 456.0957. Elemental analysis calcd (%) for $C_{27}H_{31}IO_2$ (514.4): C 63.04, H 6.07; found C 63.17, H 5.92.

[1*R*,2*S*,5*R*,6*R*,7*S*,11*S*,13*R*]-6-Iodo-9,9,14,14-tetramethyl-5-phenyl-4,8,10-trioxatetracyclo[11.1.1.0^{2,7}.0^{2,11}]pentadecane (4): To a solution of IPy_2BF_4 (0.29 g, 0.77 mmol) and acetone **1i** (0.27 g, 0.7 mmol) in dried dichloromethane (30 mL) was added a 54% solution of HBF_4 in diethyl ether (0.10 mL, 0.77 mmol) at -40 °C and stirring was continued for 12 h while the temperature raised to room temperature. Work-

up as described above yielded **4** (0.13 g) as a colorless oil. R_f = 0.24 (Hexane/Ethyl Acetate 20:1). $[\alpha]_D^{20} = -39.5$ ($c = 2.1$, dichloromethane). ^1H NMR (300 MHz, CDCl_3): δ = 7.50-7.20 (m, 5H; ArH), 5.28 (d, $J = 10.6$ Hz, 1H; PhCH), 4.77 (dd, $J = 10.6, 2.8$ Hz, 1H; CH I), 4.27 (d, $J = 2.8$ Hz, 1H; OCHCHI), 4.03 (s, 2H; CH_2O), 3.93 (d, $J = 7.9$ Hz, 1H; OCHCH₂), 2.40-1.80 (m, 6H; aliphatic ring), 1.48, 1.43, 1.28, 0.75 (4s, 12H; 4x Me). ^{13}C NMR (75 MHz, CDCl_3): δ = 141.5, 128.5, 127.8, 127.7, 99.9, 82.4, 78.6, 76.4, 66.6, 56.5, 45.1, 39.4, 39.0, 33.4, 28.7, 26.6, 25.6, 25.3, 23.4, 23.3. HRMS (70 EV, EI): calcd. for $\text{C}_{22}\text{H}_{29}\text{O}_3$ ($[M-127]^+$): 341.2117, found 341.2110. Elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{29}\text{IO}_3$ (468.4): C 56.42, H 6.24; found C 56.50, H 6.13.

Figure1: X-ray crystal structure of **2a** (ORTEP, thermal ellipsoids with 25% probability)

Figure2: X-ray crystal structure of **2e** (ORTEP, thermal ellipsoids with 25% probability)