Asymmetric Brønsted Acid Catalyzed Carbonyl Activation – Organocatalytic Domino Electrocyclization-Halogenation Reaction

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Supporting information

General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. 2,4,4,6-Tetrabromo-2,5-cyclohexadiene-1-one (TBCHD) was recrystallized from hexane/CH₂Cl₂ mixture prior to use. Solvents for chromatography were technical grade and distilled prior to use. The chloroform used in reactions was reagent grade and distilled from CaH₂. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063-0.2 mm). Solvent mixtures are understood as volume/volume.

¹H-NMR and ¹³C-NMR were recorded on a Bruker AM 250 spectrometer in CDCl₃. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 μm, lot # 28089-U, Supelco). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm⁻¹). Optical rotations were measured on a Perkin Elmer 241 polarimeter. The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. CHIRALCEL OD-H or CHIRALPAK AD-H; eluent: hexane/2-propanol). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances. The yields and enantiomeric excesses are given in table.

Preparation of the substrates: The preparation of substrate 1a was reported.[¹] Preparation of the other substrates followed the same strategy and general procedures described in the same paper.[¹]

Preparation of catalysts: The chiral N-triflyl phosphoramidate 3a-3j were prepared according to the procedure of Yamamoto, et al.[²]
**General procedure for Nazarov-halogenation reaction.** The substrate (50 mg) and brominating agent (2 equiv.) were suspended in chloroform (0.1 M) in a screw-capped test-tube and allowed to stir at 0 °C for 10 min. The catalyst (5 mol%) was added to the reaction mixture. The reaction was stirred at 0 °C for 2 h and then allowed to warm to 5 or 10 °C for 60 h (see table). The reaction mixture was purified by column chromatography on silica gel (ethyl acetate/hexane) which was neutralized with triethylamine prior to use to afford the product. The racemic compounds were prepared by using achiral catalyst A (10 mol%) at 0 °C to room temperature for overnight.

![Achiral catalyst A](image)

**Physical data:**

(5S,6R)-6-bromo-6-methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta-[b]pyran-7(2H)-one 5a

$$\text{PhOPO}$$

$$\text{PhO}^+\text{NHSO}_2\text{CF}_3$$

$$\text{achiral catalyst A}$$

$${}^1\text{H-NMR}$$ (250 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ 7.32-7.21 (m, 3H), 7.03 (d, $J = 7.1$ Hz, 2H), 4.45 (s, 1H), 4.28-4.09 (m, 2H), 2.14 (t, $J = 6.7$ Hz, 2H), 2.02-1.84 (m, 2H), 1.21 (s, 3H); $^{13}{\text{C-NMR}}$ (63 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ 195.17, 149.00, 141.93, 136.81, 129.01, 128.20, 67.32, 60.92, 59.69, 24.84, 22.47, 21.50; IR (CHCl$_3$): $\tilde{\nu}$ = 3023, 2928, 2884, 1719, 1646, 1595, 1493, 1455, 1435, 1403, 1375, 1305, 1184, 1109, 1049, 988, 754, 703, 667 cm$^{-1}$; EI-MS: m/z (relative intensity) = 308 (46) [C$_{15}$H$_{15}$BrO$_2$]$^+$, 306 (50) [C$_{15}$H$_{15}$BrO$_2$]$^{+}$, 227 (100) [M-Br]$^+$, 199 (22), 171 (20), 143 (35), 142 (29), 141 (45), 129 (45), 128 (76), 127 (20), 115 (85), 105 (56), 91 (33), 77 (28), 66 (15), 65 (16); [$\alpha$]$_D$ = +71.1 (c = 1.0 in CHCl$_3$); HPLC conditions: OD-H column, n-hexane/2-propanol = 95/5, flow rate = 1 mL min$^{-1}$, major enantiomer: $t_R = 16.04$ min; minor enantiomer: $t_R = 13.03$ min.

(5S,6R)-6-bromo-5-(4-fluorophenyl)-6-methyl-3,4,5,6-tetrahydro-cyclopenta[b]pyran-7(2H)-one 5b

$${}^1\text{H-NMR}$$ (250 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ 7.10-6.93 (m, 4H), 4.44 (s, 1H), 4.28-4.09 (m, 2H), 2.13 (t, $J = 6.0$ Hz, 2H), 2.04-1.84 (m, 2H), 1.20 (s, 3H); $^{13}{\text{C-NMR}}$ (63 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ 194.95, 162.50 (d, $J_{C-F} = 247.8$ Hz), 149.07, 141.49, 132.53 (d, $J_{C-F} = 3.3$ Hz), 116.21, 115.87, 67.33, 60.17, 59.39, 24.89, 22.39, 21.45; IR (neat): $\tilde{\nu}$ = 2926, 1723, 1648, 1601, 1508, 1435, 1375, 1303, 1271, 1229, 1159, 1109, 1048, 988, 842, 758 cm$^{-1}$; EI-MS: m/z (relative intensity) = 326 (42) [C$_{15}$H$_{14}$BrFO$_2$]$^{+}$, 324 (58) [C$_{15}$H$_{14}$BrFO$_2$]$^{+}$, 245 (100) [M-}
Br\]^+, 217 (24), 189 (27), 161 (42), 160 (30), 159 (41), 147 (45), 146 (80), 133 (96), 123 (76), 109 (43); [α]_{D}^{RT} = +59.3 (c = 1.0 in CHCl₃); HPLC conditions: OD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min⁻¹, major enantiomer: t_R = 28.94 min; minor enantiomer: t_R = 25.13 min.

(5S,6R)-6-bromo-5-(4-chlorophenyl)-6-methyl-3,4,5,6-tetrahydro-cyclopenta[b]pyran-7(2H)-one 5c

\(^1\)H-NMR (250 MHz, CDCl₃, 25 °C, TMS): δ 7.28 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 4.43 (s, 1H), 4.28-4.08 (m, 2H), 2.12 (t, J = 6.3 Hz, 2H), 2.03-1.85 (m, 2H), 1.21 (s, 3H); 13C-NMR (63 MHz, CDCl₃, 25 °C, TMS): δ 194.84, 149.15, 141.28, 135.28, 134.17, 129.27, 67.35, 60.27, 59.14, 24.93, 22.38, 21.43; IR (neat): ν ~ = 2926, 1726, 1649, 1594, 1489, 1434, 1409, 1374, 1302, 1270, 1184, 1110, 1091, 1048, 1014, 988, 841, 813, 757 cm⁻¹; EI-MS: m/z (relative intensity) = 344 (15) [C₁₅H₁₄\(^{81}\)Br\(^{37}\)ClO₂]\(^+\), 342 (50) [C₁₅H₁₄\(^{81}\)Br\(^{35}\)ClO₂]\(^+\) and [C₁₅H₁₄\(^{79}\)Br\(^{37}\)ClO₂]\(^+\), 340 (30) [C₁₅H₁₄\(^{79}\)Br\(^{35}\)ClO₂]\(^+\), 263 (34), 262 (24), 261 (94) [M-Br]^\(+\), 233 (19), 205 (17), 177 (17), 163 (15), 142 (40), 141 (75), 139 (60), 128 (35), 127 (32), 125 (19), 114 (25), 115 (100), 111 (22), 77 (24); [α]_{D}^{RT} = +100.1 (c = 1.0 in CHCl₃); HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min⁻¹, major enantiomer: t_R = 22.54 min; minor enantiomer: t_R = 26.29 min.

(5S,6R)-6-bromo-5-(4-bromophenyl)-6-methyl-3,4,5,6-tetrahydro-cyclopenta[b]pyran-7(2H)-one 5d

\(^1\)H-NMR (250 MHz, CDCl₃, 25 °C, TMS): δ 7.43 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 4.41 (s, 1H), 4.27-4.08 (m, 2H), 2.12 (t, J = 6.2 Hz, 2H), 2.05-1.83 (m, 2H), 1.20 (s, 3H); 13C-NMR (63 MHz, CDCl₃, 25 °C, TMS): δ 194.80, 149.13, 141.35, 135.77, 132.21, 122.24, 67.36, 60.29, 59.10, 24.97, 22.38, 21.41; IR (CHCl₃): ν ~ = 2925, 1720, 1648, 1592, 1486, 1271, 1184, 1109, 1048, 1014, 988, 841, 813, 755 cm⁻¹; EI-MS: m/z (relative intensity) = 388 (24) [C₁₅H₁₄\(^{81}\)Br\(^{35}\)Br₂O₂]\(^+\), 386 (45) [C₁₅H₁₄\(^{81}\)Br\(^{37}\)Br₂O₂]\(^+\), 384 (22) [C₁₅H₁₄\(^{79}\)Br\(^{35}\)Br₂O₂]\(^+\), 307 (57) [M-Br]^\(+\), 305 (62) [M-Br]^\(+\), 277 (13), 249 (8), 198 (21), 185 (17), 183 (22), 170 (28), 155 (23), 142 (44), 141 (70), 128 (43), 127 (20), 115 (100), 111 (17), 102 (14), 89 (13), 77 (21); [α]_{D}^{RT} = +94.7 (c = 1.0 in CHCl₃); HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min⁻¹, major enantiomer: t_R = 33.92 min; minor enantiomer: t_R = 29.25 min.
(5S,6R)-6-bromo-6-methyl-5-(4-(trifluoromethyl)phenyl)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one 5e

$^1$H-NMR (250 MHz, CDCl$_3$, 25 °C, TMS): δ 7.57 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.52 (s, 1H), 4.32-4.09 (m, 2H), 2.20-2.07 (m, 2H), 2.04-1.86 (m, 2H), 1.20 (s, 3H); $^{13}$C-NMR (63 MHz, CDCl$_3$, 25 °C, TMS): δ 194.64, 149.34, 140.87, 131.34, 130.82, 130.30, 126.02 (CF$_3$, q, J = 3.7 Hz), 121.74, 67.38, 60.60, 58.75, 24.99, 22.39, 21.40; IR (neat): ν = 2925, 1724, 1649, 1434, 1325, 1271, 1166, 1067, 1048, 988, 851 cm$^{-1}$; EI-MS: m/z (relative intensity) = 376 (54) [C$_{16}$H$_{14}$BrF$_3$O$_2$]$,^•$, 374 (56) [C$_{16}$H$_{14}$BrF$_3$O$_2$]$^•$, 296 (23), 295 (100) [M-Br]$^+$, 294 (18), 267 (23), 239 (23), 211 (23), 197 (26), 191 (22), 173 (39), 159 (17), 142 (29), 141 (57), 128 (29), 115 (61), 94 (15), 79 (21), 69 (27); [α]$_D^{37}$ = +59.8 (c = 1.0 in CHCl$_3$); HPLC conditions: OD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min$^{-1}$, major enantiomer: t$_R$ = 30.38 min; minor enantiomer: t$_R$ = 22.01 min.

(5S,6R)-6-bromo-6-methyl-5-p-tolyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one 5f

$^1$H-NMR (250 MHz, CDCl$_3$, 25 °C, TMS): δ 7.10 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 4.41 (s, 1H), 4.28-4.06 (m, 2H), 2.27 (s, 3H), 2.13 (t, J = 6.3 Hz, 2H), 2.00-1.82 (m, 2H), 1.20 (s, 3H); $^{13}$C-NMR (63 MHz, CDCl$_3$, 25 °C, TMS): δ 195.31, 148.87, 142.22, 137.99, 133.72, 129.69, 67.31, 60.57, 59.89, 24.83, 22.46, 21.51, 21.17; IR (neat): ν = 2924, 1720, 1648, 1512, 1442, 1402, 1373, 1304, 1277, 1177, 1109, 1048, 987, 831, 814 cm$^{-1}$; EI-MS: m/z (relative intensity) = 322 (33) [C$_{16}$H$_{17}$BrO$_2$]$^•$, 320 (32) [C$_{16}$H$_{17}$BrO$_2$]$^•$, 241 (100) [M-Br]$^+$, 213 (23), 185 (22), 157 (21), 156 (20), 142 (37), 141 (56), 129 (33), 128 (47), 119 (49), 115 (58), 111 (18), 91 (34), 77 (21), 65 (22); [α]$_D^{37}$ = +41.5 (c = 1.0 in CHCl$_3$); HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min$^{-1}$, major enantiomer: t$_R$ = 17.89 min; minor enantiomer: t$_R$ = 22.47 min.

(5S,6R)-6-bromo-5-(4-methoxyphenyl)-6-methyl-3,4,5,6-tetrahydro-cyclopenta[b]pyran-7(2H)-one 5g

$^1$H-NMR (250 MHz, CDCl$_3$, 25 °C, TMS): δ 6.95 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.39 (s, 1H), 4.27-4.07 (m, 2H), 3.74 (s, 3H), 2.13 (t, J = 6.7 Hz, 2H), 2.05-1.83 (m, 2H), 1.21 (s, 3H); $^{13}$C-NMR (63 MHz, CDCl$_3$, 25 °C, TMS): δ 195.32, 159.45, 148.84, 142.16, 128.74, 114.37, 67.30, 60.20, 60.03, 55.35, 24.83, 22.45, 21.52; IR (neat): ν =
2929, 1714, 1649, 1512, 1455, 1379, 1302, 1248, 1177, 1110, 1048, 988, 839, 736 cm⁻¹; EI-MS: m/z (relative intensity) = 338 (31) \[C_{16}H_{17}^{81}BrO_3\]^+, 336 (28) \[C_{16}H_{17}^{79}BrO_3\]^+, 258 (22), 257 (100) \[M-Br\]^+, 256 (31), 229 (29), 201 (16), 172 (14), 158 (17), 141 (14), 135 (44), 129 (26), 128 (32), 115 (40), 111 (31), 103 (20), 91 (17), 77 (27); \([\alpha]_D^{20} = +50.3 (c = 1.0 \text{ in CHCl}_3)\); HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min⁻¹, major enantiomer: \(t_R = 26.90 \text{ min}\); minor enantiomer: \(t_R = 33.65 \text{ min}\).

\((5S,6R)-6\text{-bromo-6-methyl-5-(naphthalen-1-yl)-3,4,5,6-tetrahydro-cyclopenta}[b]pyran-7(2H)-one 5h\)

\[\begin{align*}
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Br}
\end{align*}\]

\(^1\text{H}-\text{NMR} (250 \text{ MHz, CDCl}_3, 25 \degree \text{C}, \text{TMS}): \delta 8.32 (d, J = 8.3 \text{ Hz, 1H}), 7.85 (d, J = 7.8 \text{ Hz, 1H}), 7.75 (d, J = 8.3 \text{ Hz, 1H}), 7.64-7.55 (m, 1H), 7.54-7.46 (m, 1H), 7.35 (t, J = 7.8 \text{ Hz, 1H}), 6.89 (dd, J = 7.1, 1.1 \text{ Hz, 1H}), 5.26 (s, 1H), 4.37-4.14 (m, 2H), 2.36-1.93 (m, 4H), 1.12 (s, 3H); \(^{13}\text{C}-\text{NMR} (63 \text{ MHz, CDCl}_3, 25 \degree \text{C}, \text{TMS}): \delta 195.52, 149.49, 141.91, 134.14, 133.28, 129.10, 128.71, 127.17, 126.30, 125.33, 125.28, 123.97, 67.40, 59.41, 55.75, 23.50, 22.84, 21.59; \text{IR (CHCl}_3): \tilde{\nu} = 2925, 1719, 1649, 1441, 1402, 1182, 1109, 1050, 986, 803, 785, 755 \text{ cm}^{-1}; \text{EI-MS: m/z (relative intensity) = 358 (58) \[C_{19}H_{17}^{81}BrO_2\]^+, 356 (64) \[C_{19}H_{17}^{79}BrO_2\]^+, 278 (34), 277 (93) \[M-Br\]^+, 276 (25), 249 (51), 233 (17), 231 (18), 221 (39), 205 (20), 195 (31), 191 (41), 179 (34), 178 (54), 165 (100), 155 (25), 152 (40), 127 (42); \([\alpha]_D^{20} = –32.0 (c = 1.0 \text{ in CHCl}_3); \text{HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min}^{-1}, \text{ major enantiomer: } t_R = 21.68 \text{ min}; \text{ minor enantiomer: } t_R = 23.91 \text{ min.}\)

\((5S,6R)-6\text{-bromo-6-methyl-5-(naphthalen-2-yl)-3,4,5,6-tetrahydro-cyclopenta}[b]pyran-7(2H)-one 5i\)

\[\begin{align*}
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Br}
\end{align*}\]

\(^1\text{H}-\text{NMR} (250 \text{ MHz, CDCl}_3, 25 \degree \text{C}, \text{TMS}): \delta 7.81-7.71 (m, 3H), 7.54 (s, 1H), 7.39 (m, 2H), 7.09 (d, J = 8.7 \text{ Hz, 1H}), 4.61 (s, 1H), 4.31-4.10 (m, 2H), 2.15 (t, J = 6.5 \text{ Hz, 2H}), 2.02-1.87 (m, 2H), 1.24 (s, 3H); \(^{13}\text{C}-\text{NMR} (63 \text{ MHz, CDCl}_3, 25 \degree \text{C}, \text{TMS}): \delta 195.22, 149.10, 141.98, 134.30, 133.44, 133.05, 128.85, 127.86, 127.80, 126.72, 126.50, 67.39, 61.09, 59.68, 24.84, 22.54, 21.52; \text{IR (CHCl}_3): \tilde{\nu} = 2925, 1719, 1647, 1435, 1420, 1375, 1270, 1185, 1109, 1048, 755 \text{ cm}^{-1}. \text{EI-MS: m/z (relative intensity) = 358 (52) \[C_{19}H_{17}^{81}BrO_2\]^*, 356 (59) \[C_{19}H_{17}^{79}BrO_2\]^*, 278 (44), 277 (100) \[M-Br\]^*, 276 (46), 250(22), 249 (63), 235 (16), 221 (56), 192 (28), 191 (37), 179 (34), 178 (66), 165 (72), 155 (28), 152 (34), 141 (19), 127
(34), 115 (17); \([\alpha]_D^{RT} = +111.1 \ (c = 1.0 \text{ in CHCl}_3); \) HPLC conditions: OD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min\(^{-1}\), major enantiomer: \(t_R = 33.86 \text{ min}\); minor enantiomer: \(t_R = 38.68 \text{ min}\).

**5j**

**5S,6R)-5-(1,3-benzodioxol-5-yl)-6-bromo-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one**

\(\text{H-NMR (250 MHz, CDCl}_3, 25 \text{ °C, TMS): } \delta 6.73 \ (d, J = 8.1 \text{ Hz, 1H}), 6.60-6.41 \ (m, 2H), 5.91 \ (s, 2H), 4.36 \ (s, 1H), 4.28-4.02 \ (m, 2H), 2.15 \ (t, J = 6.3 \text{ Hz, 2H}), 2.02-1.87 \ (m, 2H), 1.25 \ (s, 3H); \)**

\(\text{13C-NMR (63 MHz, CDCl}_3, 25 \text{ °C, TMS): } \delta 195.12, 148.96, 148.28, 147.54, 141.79, 130.52, 108.68, 101.38, 67.31, 60.60, 59.80, 24.64, 22.43, 21.49; \)**

\(\text{IR (CHCl}_3): \nu \sim = 2925, 1719, 1647, 1595, 1502, 1487, 1436, 1234, 1189, 1109, 1039, 929, 756 \text{ cm}^{-1}; \)**

**EI-MS: m/z (relative intensity) = 352 (72) [C\(_{16}H\(_{15}\)\(_{81}BrO\(_4\)\)]^+, 350 (69) [C\(_{16}H\(_{15}\)\(_{79}BrO\(_4\)\)]^+, 272 (25), 271 (76) [M-Br]^+, 270 (43), 243 (100), 228 (16), 215 (48), 186 (28), 157 (22), 149 (56), 129 (48), 128 (74), 127 (27), 115 (53), 111 (28), 103 (35), 102 (42), 77 (35); \([\alpha]_D^{RT} = +54.0 \ (c = 1.0 \text{ in CHCl}_3); \)**

HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min\(^{-1}\), major enantiomer: \(t_R = 38.57 \text{ min}\); minor enantiomer: \(t_R = 59.78 \text{ min}\).

**5k**

**5S,6R)-6-bromo-5-(naphthalen-2-yl)-6-propyl-3,4,5,6-tetrahydro-cyclopenta[b]pyran-7(2H)-one**

\(\text{H-NMR (250 MHz, CDCl}_3, 25 \text{ °C, TMS): } \delta 7.83 \ (m, 3H), 7.57 \ (s, 1H), 7.50-7.39 \ (m, 2H), 7.11 \ (d, J = 8.6 \text{ Hz, 1H}), 4.54 \ (s, 1H), 4.30-4.05 \ (m, 2H), 2.24-1.62 \ (m, 5H), 1.52-1.38 \ (m, 1H), 1.28-1.92 \ (m, 2H), 0.40 \ (t, J = 7.3 \text{ Hz, 3H}); \)**

\(\text{13C-NMR (63 MHz, CDCl}_3, 25 \text{ °C, TMS): } \delta 194.97, 148.74, 142.25, 134.39, 133.30, 132.97, 128.57, 127.86, 127.80, 126.65, 126.48, 67.33, 66.40, 61.11, 37.12, 22.38, 21.55, 18.83, 13.99; \)**

\(\text{IR (neat): } \nu \sim = 2960, 2928, 2871, 1715, 1650, 1595, 1455, 1433, 1271, 1231, 1112, 1066, 859, 820, 754 \text{ cm}^{-1}; \)**

**EI-MS: m/z (relative intensity) = 386 (13) [C\(_{21}H\(_{21}\)\(_{81}BrO\(_2\)\)]^+, 384 (21) [C\(_{21}H\(_{21}\)\(_{79}BrO\(_2\)\)]^+, 306 (32), 305 (100) [M-Br]^+, 277 (19), 275 (15), 264 (26), 263 (29), 247 (8), 235 (13), 207 (13), 191 (26), 179 (20), 178 (39), 165 (45), 155 (38), 152 (24), 141 (17), 128 (22), 127 (21), 115 (12), 111 (17); \([\alpha]_D^{RT} = +84.0 \ (c = 1.0 \text{ in CHCl}_3); \)**

HPLC conditions: AD-H column, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min\(^{-1}\), major enantiomer: \(t_R = 21.13 \text{ min}\); minor enantiomer: \(t_R = 23.88 \text{ min}\).
(5S,6R)-6-bromo-5-(3-bromophenyl)-6-propyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one 5l

\[
\begin{align*}
\text{H-NMR (250 MHz, CDCl}_3, 25 \, ^\circ\text{C, TMS): } & \delta 7.72-7.61 (m, 1H), 7.19 (s, 1H), 7.15 (d, J = 7.8 \, \text{Hz, } 1H), 6.99 (d, J = 7.2 \, \text{Hz, } 1H), 4.34 (s, 1H), \\
& 4.29-4.04 (m, 2H), 2.20-1.79 (m, 4H), 1.77-1.59 (m, 1H), 1.54-1.37 (m, 1H), 1.15-0.95 (m, 2H), 0.53 (t, J = 7.2 \, \text{Hz, } 3H); \\
\text{C-NMR (63 MHz, CDCl}_3, 25 \, ^\circ\text{C, TMS): } & \delta 193.41, 147.87, 140.22, 138.22, 129.29, \\
& 129.26, 121.89, 66.24, 64.54, 59.50, 36.03, 21.20, 20.38, 17.73, 12.90; \\
\text{IR (neat): } & \tilde{\nu} = 2960, 2928, 1722, 1650, 1590, 1566, 1474, 1432, 1402, 1292, 1269, 1171, 1113, 1071, 912, 793, 738, \\
& 698, 680 \, \text{cm}^{-1}; \\
\text{EI-MS: } & m/z \text{ (relative intensity) } = 416 (2) [\text{C}_{17}\text{H}_{18}^{81}\text{Br}_2\text{O}_2]^+, 414 (2) [\text{C}_{17}\text{H}_{18}^{81}\text{Br}_7\text{Br}_2\text{O}_2]^+, 374 (5), 372 (8), 335 (20) [\text{M-Br}]^+, 333 (20) [\text{M-Br}]^+, 307 (5), 305 (6), \\
& 303 (6), 293 (6), 291 (7), 193 (11), 169 (21), 165 (21), 153 (19), 141 (63), 128 (58), 115 (100), \\
& 102 (13), 91 (30), 77 (46); [\alpha]_D^{20} = +96.0 (c = 1.0 \text{ in CHCl}_3); \\
\text{HPLC conditions: } & \text{AD-H column, } n-\text{hexane/2-propanol } = 95/5, \text{ flow rate } = 0.6 \text{ mL min}^{-1}, \text{ major enantiomer: } t_R = 15.74 \text{ min; } \\
& \text{minor enantiomer: } t_R = 21.83 \text{ min.}
\end{align*}

References:


Chromatogram: WI_549R1_F2_ADH_955_flow06_2
Method: HPLC1_ADH_955_flow06_1aq_45
Data file: WI_549R1_F2_ADH_955_flow06_2.DAT
Date: 7/21/2007 12:41:12 PM

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Data file: WI_549R4_F2_ADH_955_flow06_1.DAT
Date: 9/2/2007 6:03:52 PM

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