Electric Supporting information for

Unexpected formation of stannolanes and trigonal bipyramidal tin complexes by radical cyclization reaction

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General

All $^1$H and $^{13}$C NMR spectra were recorded on JEOL JNM-ECA500 Delta2 (500 MHz for $^1$H, 125 MHz for $^{13}$C, and 186 MHz for $^{119}$Sn) spectrometer. All the reactions in this paper were performed under nitrogen atmosphere unless otherwise mentioned. CH$_2$Cl$_2$ was dried over CaH$_2$, and distilled under nitrogen before use. Dry THF was purchased from Kanto Kagaku Co. Ltd. High resolution mass spectra (HRMS) were measured at Integrated Center for Sciences, Ehime University, Matsuyama, Japan.

Preparation of $(3S,3aS)$-methyl 5,5-dibutyl-3-(p-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2a): A mixture of $(S)$-methyl 2-(((4-methyl-N-(prop-2-yn-1-yl)phenylsulfon-amido)(p-tolyl)methyl)acrylate (1a) (256.1 mg, 0.64 mmol), Bu$_3$SnH (0.21 mL, 0.77 mmol), and Et$_3$B in hexane solution (1.0 M, 0.77 mL) in toluene (64 mL) was placed in 100 mL two necked flask and purged by air at room temperature. After stirring for 1 h at room temperature, sat NH$_4$Claq (10 mL) was added. The organic phase was separated and aqueous phase was extracted with EtOAc (3 × 30 mL). The organic phases were combined, washed with brine (10 mL), and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated. The residue was purified by flash chromatography (silica gel/hexane:EtOAc 50:1, 20:1, and 10:1) to give 2a in 80% yield (320.7 mg, 80%). White solid, mp 68–69 ºC; $[\alpha]_D^{+17.1}$ (c 1.01, CHCl$_3$); the enantiomeric purity was determined by HPLC analysis, t$_R$ 63.8 min (($R$)-2a), t$_R$ 79.5 min (($S$)-2a) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80/20, 1.0mL/min] as >99%ee; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.3$ Hz, 2 H), 7.14 (d, $J = 8.0$ Hz, 2 H), 6.99 (d, $J = 7.9$ Hz, 2 H), 6.88 (d, $J = 7.4$ Hz, 2 H), 6.61 (s, 1 H, $J^{119}$Sn–$^1$H = 113.4 Hz), 5.38 (s, 1 H), 4.13 (dd, $J = 13.3, 2.1$ Hz, 1 H), 4.08 (dd, $J = 13.3, 1.3$ Hz, 1 H), 3.44 (s, 3 H), 2.36 (s, 3
H), 2.28 (s, 3 H), 1.49 – 1.02 (m, 12 H), 0.90 (d, J = 13.2 Hz, 1 H), 0.83 (t, J = 7.3 Hz, 3 H), 0.74 (t, J = 7.3 Hz, 3 H), 0.26 (d, J = 13.2 Hz, 1 H, $J^{19}$Sn–H = 54.3 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 175.2 (s), 157.8 (d, $J^{13}$C–$^{119}$Sn = 52.2 Hz), 142.7 (s), 137.2 (s), 136.8 (s), 136.2 (s), 129.2 (s), 128.9 (s), 127.9 (s), 127.5 (s), 69.0 (d, $J^{13}$C–$^{119}$Sn = 15.3 Hz), 68.5 (d, $J^{13}$C–$^{119}$Sn = 32.2 Hz), 52.7 (s), 50.6 (d, $J^{13}$C–$^{119}$Sn = 60.2 Hz), 29.0 (d, $J^{13}$C–$^{119}$Sn = 22.4 Hz), 28.8 (d, $J^{13}$C–$^{119}$Sn = 22.9 Hz), 27.1 (d, $J^{13}$C–$^{119}$Sn = 56.7 Hz), 27.0 (d, $J^{13}$C–$^{119}$Sn = 55.9 Hz), 21.5 (s), 21.2 (s), 13.73 (s), 13.73 (s), 13.67 (d, $J^{13}$C–$^{117}$Sn = 297.4 Hz, $J^{13}$C–$^{119}$Sn = 309.8 Hz), 13.0 (d, $J^{13}$C–$^{117}$Sn = 332.0 Hz, $J^{13}$C–$^{119}$Sn = 350.8 Hz), 12.4 (d, $J^{13}$C–$^{117}$Sn = 322.4 Hz, $J^{13}$C–$^{119}$Sn = 337.2 Hz); $^{119}$Sn NMR (186 MHz, CDCl$_3$) δ 141.6; IR (neat) 2920, 1726, 1614, 1344, 1159, 908 cm$^{-1}$; HRMS (FAB M+1) m/z 632.1856. Calcd for C$_{30}$H$_{42}$NO$_4$SSn m/z 632.1856.

(3S,3aS)-tert-butyl

5,5-dibutyl-3-phenyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carbonyl xylate (2b):

![Image of the compound structure]

Colorless oil; [α]$_D$ +11.3 (c 1.01, CHCl$_3$); the enantiomeric purity was determined by HPLC analysis, $t_R$ 17.8 min ((R)-2b), $t_R$ 34.7 min ((S)-2b) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/PrOH, 88/12, 1.0mL/min] as >99%ee; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, J = 8.3 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 7.18 – 7.12 (m, 3 H), 6.90 (br, 2 H), 6.68 (s, 1 H, $J^{19}$Sn–H = 115.4 Hz), 5.42 (s, 1 H), 4.12 (dd, J = 12.9, 2.0 Hz, 1 H), 4.02 (d, J = 13.0 Hz, 1 H), 2.36 (s, 3 H), 1.36 (s, 9 H), 1.54 – 1.01 (m, 12 H), 0.92 (d, J = 13.3 Hz, 1 H), 0.85 (t, J = 7.3 Hz, 3 H), 0.74 (t, J
\[ \delta = 7.0 \text{ Hz}, 3 \text{ H}, 0.23 \text{ (d, } J = 13.2 \text{ Hz, 1 H, } J^{19}\text{Sn} \text{–}^{1}\text{H} = 53.4 \text{ Hz});^{13}\text{C NMR (CDCl}_3, 126 \text{ MHz}) \delta 173.1, 158.2 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 54.3 \text{ Hz}), 142.6, 138.2, 136.0, 132.9, 128.9, 128.2, 127.9, 127.8, 126.9, 81.20, 69.47 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 16.1 \text{ Hz}), 68.4 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 30.5 \text{ Hz}), 50.4 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 63.2 \text{ Hz}), 28.7 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 22.1 \text{ Hz}), 28.4 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 26.1 \text{ Hz}), 27.5, 26.8 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 56.4 \text{ Hz}), 26.7 (J^{19}\text{Sn} \text{–}^{13}\text{C} = 58.2 \text{ Hz}), 21.2, 13.42, 13.37, 12.8 (J^{117}\text{Sn} \text{–}^{13}\text{C} = 285.0 \text{ Hz}, J^{19}\text{Sn} \text{–}^{13}\text{C} = 304.1 \text{ Hz}), 12.6 (J^{117}\text{Sn} \text{–}^{13}\text{C} = 278.3 \text{ Hz}, J^{19}\text{Sn} \text{–}^{13}\text{C} = 293.5 \text{ Hz}), 12.0 (J^{117}\text{Sn} \text{–}^{13}\text{C} = 320.0 \text{ Hz}, J^{19}\text{Sn} \text{–}^{13}\text{C} = 337.2 \text{ Hz});^{119}\text{Sn} \text{NMR (186 MHz, CDCl}_3) \delta 142.2; \text{ IR (neat) 2922, 1717, 1616, 1343, 1161, 908 cm}^{-1}; \text{ HRMS (FAB}\text{+ M}^+ \text{m/z 660.2185. calcd for C}_{32}\text{H}_{46}\text{NO}_4\text{SSn 660.2170.}

(3S,3aS)-\text{tert-butyl} 5,5-\text{dibutyl-3-(p-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carb oxylate (2c)

\[
\begin{array}{c}
\text{Bu} \\
\text{Sn} \\
\text{N} \\
\text{CO}_{2}\text{Bu} \\
\text{Ts} \\
\text{p-Tol}
\end{array}
\]

Pale yellow oil; [\alpha]_D -1.1 (c 1.06, CHCl}_3); the enantiomeric purity was determined by HPLC analysis, \( t_R \) 23.2 min ((R)-2c), \( t_R \) 47.7 min ((S)-2c) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 96%ee; \(^1\text{H NMR (500 MHz, CDCl}_3) \delta 7.44 \text{ (d, } J = 8.3 \text{ Hz, 2 H), 7.08 \text{ (d, } J = 8.1 \text{ Hz, 2 H), 6.95 \text{ (d, } J = 7.6 \text{ Hz, 2 H), 6.84 \text{ (br, 2 H), 6.56 \text{ (s, 1 H, } J^{19}\text{Sn} \text{–}^{1}\text{H} = 115.4 \text{ Hz), 5.41 \text{ (s, 1 H), 4.14 \text{ (dd, } J = 12.9, 2.1 \text{ Hz, 1 H), 4.01 \text{ (d, } J = 12.9 \text{ Hz, 1 H), 2.34 \text{ (s, 3 H), 2.28 \text{ (s, 3 H), 1.37 \text{ (s, 9 H), 1.54 – 1.00 \text{ (m, 12 H), 0.93 \text{ (d, } J = 11.9 \text{ Hz, 1 H), 0.85 \text{ (t, } J = 7.3 \text{ Hz, 3 H), 0.75 \text{ (t, } J = 7.0 \text{ Hz, 3 H), 0.27 \text{ (d, } J = 13.2 \text{ Hz, 1 H, } J^{19}\text{Sn} \text{–}^{1}\text{H} = 53.2 \text{ Hz});^{13}\text{C NMR (126 MHz, CDCl}_3) \delta 173.7, 158.3 \text{ (J}^{19}\text{Sn} \text{–}^{13}\text{C} = 55.9 \text{ Hz), 142.4, 136.8, 136.4, 128.9,}
\]
128.9, 128.5, 127.8, 127.6, 127.1, 81.2, 69.4 \( (J^{119}\text{Sn}^{13}\text{C} = 16.3 \text{ Hz}) \), 68.2 \( (J^{119}\text{Sn}^{13}\text{C} = 30.4 \text{ Hz}) \), 50.4 \( (J^{119}\text{Sn}^{13}\text{C} = 60.4 \text{ Hz}) \), 28.7, 28.4 \( (J^{119}\text{Sn}^{13}\text{C} = 22.7 \text{ Hz}) \), 27.4, 26.8 \( (J^{119}\text{Sn}^{13}\text{C} = 55.7 \text{ Hz}) \), 26.7 \( (J^{119}\text{Sn}^{13}\text{C} = 56.4 \text{ Hz}) \), 21.1, 20.8, 13.4, 13.3, 12.7 \( (J^{117}\text{Sn}^{13}\text{C} = 330.4 \text{ Hz}) \), \( J^{119}\text{Sn}^{13}\text{C} = 345.6 \text{ Hz} \), 12.5 \( (J^{117}\text{Sn}^{13}\text{C} = 284.6 \text{ Hz}) \), \( J^{119}\text{Sn}^{13}\text{C} = 309.4 \text{ Hz} \), 11.9 (d, \( J^{117}\text{Sn}^{13}\text{C} = 319.6 \text{ Hz} \), \( J^{119}\text{Sn}^{13}\text{C} = 336.6 \text{ Hz} \)); \( ^{119}\text{Sn} \) NMR (186 MHz, CDCl\( _3 \)) \( \delta 140.7 \); IR (neat) 2922, 1717, 1616, 1342, 1161, 909 cm\(^{-1} \);

HRMS (FAB\(^+\) M+1) \( m/z 674.2338 \). calcd for \( \text{C}_{33}\text{H}_{48}\text{NO}_{4}\text{SSn} 674.2326 \).

\((3S,3aS)\)-tert-butyl

\(5,5\)-dibutyl-2-(methylsulfonyl)-3-(p-tolyl)-1,2,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2d)

![Chemical Structure Image]

Colorless oil; \([\alpha]_D^\circ +10.6 \) (c 1.10, CHCl\( _3 \)); the enantiomeric purity was determined by HPLC analysis, \( t_R \) 22.1 min ((\( R \))-2d), \( t_R \) 50.5 min ((\( S \))-2d) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 96%ee;

\(^1\text{H} \) NMR (500 MHz, CDCl\( _3 \)) \( \delta 7.07 \) (d, \( J = 8.0 \text{ Hz} \), 2 H), 6.99 (d, \( J = 7.7 \text{ Hz} \), 2 H), 6.64 (s, 1 H, \( ^{119}\text{Sn}^{13}\text{H} = 115.6 \text{ Hz} \), 5.30 (s, 1 H), 4.20 (dd, \( J = 13.0 \), 1.8 Hz, 1 H), 4.11 (d, \( J = 13.1 \text{ Hz} \), 1 H), 2.62 (s, 3 H), 2.29 (s, 3 H), 1.65–1.05 (m, 12 H), 1.47 (s, 9 H), 0.97 (d, \( J = 13.2 \text{ Hz} \), 1 H), 0.86 (t, \( J = 7.3 \text{ Hz} \), 3 H), 0.78 (t, \( J = 7.0 \text{ Hz} \), 3 H), 0.28 (d, \( J = 13.2 \text{ Hz} \), 1 H, \( ^{119}\text{Sn}^{13}\text{H} = 53.4 \text{ Hz} \)); \(^{13}\text{C} \) NMR (126 MHz, CDCl\( _3 \)) \( \delta 174.1 \), 158.3 \( (J^{119}\text{Sn}^{13}\text{C} = 55.9 \text{ Hz}) \), 137.5, 136.9, 129.1, 128.4 \( (J^{117}\text{Sn}^{13}\text{C} = 335.2 \text{ Hz}) \), \( J^{119}\text{Sn}^{13}\text{C} = 350.6 \text{ Hz} \), 81.8 \( (J^{119}\text{Sn}^{13}\text{C} = 39.5 \text{ Hz}) \), 69.6 \( (J^{119}\text{Sn}^{13}\text{C} = 14.9 \text{ Hz}) \), 68.0 \( (J^{119}\text{Sn}^{13}\text{C} = 30.7 \text{ Hz}) \), 50.8 \( (J^{119}\text{Sn}^{13}\text{C} = 61.3 \text{ Hz}) \), 37.9, 29.1 \( (J^{119}\text{Sn}^{13}\text{C} = 22.2 \text{ Hz}) \),
28.8 ($J^{19}\text{Sn}^{-13}\text{C} = 22.6$ Hz), 27.9, 27.1 ($J^{19}\text{Sn}^{-13}\text{C} = 56.9$ Hz), 27.0 ($J^{19}\text{Sn}^{-13}\text{C} = 56.6$ Hz), 21.2, 13.7, 13.6, 13.1 ($J^{17}\text{Sn}^{-13}\text{C} = 332.0$ Hz, $J^{19}\text{Sn}^{-13}\text{C} = 347.2$ Hz), 12.6 ($J^{17}\text{Sn}^{-13}\text{C} = 290.8$ Hz, $J^{19}\text{Sn}^{-13}\text{C} = 306.5$ Hz), 12.4 ($J^{17}\text{Sn}^{-13}\text{C} = 322.5$ Hz, $J^{19}\text{Sn}^{-13}\text{C} = 339.0$ Hz); $^{119}\text{Sn}$ NMR (186 MHz, CDCl$_3$) $\delta$ 144.8; IR (neat) 1714, 1337, 1155 cm$^{-1}$; HRMS (FAB$^+$ M+1) $m/z$ 598.2013 calcd for C$_{27}$H$_{44}$NO$_4$SSn 598.2013.

(3S,3aS)-*tert*-butyl

5,5-dibutyl-3-(4-chlorophenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2e)

Pale yellow oil; $[\alpha]_D^0 -0.8$ (c 1.05, CHCl$_3$); the enantiomeric purity was determined by HPLC analysis, $t_R$ 13.3 min ((R)-2e), $t_R$ 19.5 min ((S)-2e) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as >99%ee; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.3$ Hz, 2 H), 7.13 (d, $J = 8.1$ Hz, 4 H), 6.90 (br, 2 H), 6.58 (s, 1 H, $J^{19}\text{Sn}^{-1}H = 115.4$ Hz), 5.42 (s, 1 H), 4.12 (dd, $J = 12.9$, 2.0 Hz, 1 H), 4.02 (d, $J = 13.0$ Hz, 1 H), 2.36 (s, 3 H), 1.36 (s, 9 H), 1.54 – 1.00 (m, 12 H), 0.90 (d, $J = 13.2$ Hz, 1 H), 0.85 (t, $J = 7.3$ Hz, 3 H), 0.77 (t, $J = 7.0$ Hz, 3 H), 0.19 (d, $J = 14.2$ Hz, 1 H, $J^{19}\text{Sn}^{-1}H = 53.3$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.2, 157.4 ($J^{19}\text{Sn}^{-13}\text{C} = 55.2$ Hz), 142.6, 138.2, 136.0, 132.9, 129.1, 128.9, 128.2, 127.8, 126.9, 81.2, 69.1 ($J^{19}\text{Sn}^{-13}\text{C} = 17.0$ Hz), 67.5 ($J^{19}\text{Sn}^{-13}\text{C} = 29.6$ Hz), 50.1 ($J^{19}\text{Sn}^{-13}\text{C} = 60.2$ Hz), 28.5 ($J^{19}\text{Sn}^{-13}\text{C} = 22.6$ Hz), 28.3 ($J^{19}\text{Sn}^{-13}\text{C} = 23.1$ Hz), 27.2, 26.6 ($J^{19}\text{Sn}^{-13}\text{C} = 57.7$ Hz), 26.5 ($J^{19}\text{Sn}^{-13}\text{C} = 56.7$ Hz), 21.0, 13.2, 13.1, 12.7 ($J^{17}\text{Sn}^{-13}\text{C} = 333.2$ Hz, $J^{19}\text{Sn}^{-13}\text{C} = 348.6$ Hz), 12.3 ($J^{17}\text{Sn}^{-13}\text{C} = 278.3$ Hz, $J^{19}\text{Sn}^{-13}\text{C} = 280.8$ Hz), 11.9
\( J^{117}\text{Sn–}^{13}\text{C} = 316.4 \text{ Hz}, J^{119}\text{Sn–}^{13}\text{C} = 328.5 \text{ Hz} \); \(^{119}\text{Sn} \text{ NMR} (186 \text{ MHz, CDCl}_3) \delta 140.1; \ \text{IR (neat)} 2922, 1717, 1616, 1343, 1161, 908 \text{ cm}^{-1}; \ \text{HRMS (FAB}^+ \text{ M+1) } m/z 694.1771. \ \text{calcd for } C_{32}H_{45}ClNO_4SSn 694.1780.

\((3S,3aS)\)-\textit{tert}-butyl

\textbf{5,5-dibutyl-3-(4-methoxyphenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2f)}

\[
\begin{align*}
\text{Bu} & \quad \text{Bu} \\
\text{Sn} & \\
\text{CO}_3\text{tBu} & \\
\text{OMe} & \\
\text{Ts} & \quad \text{Ts} \\
\text{N} & \\
\text{Bu} & \quad \text{Bu}
\end{align*}
\]

Colorless oil; \([\alpha]_D +1.4 \text{ (c 1.00, CHCl}_3)\); the enantiomeric purity was determined by HPLC analysis, \( t_R \) 23.7 min ((\(R\))-2f), \( t_R \) 46.6 min ((\(S\))-2f) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 85/15, 1.0mL/min] as 95\%ee;

\(^1\text{H NMR} (500 \text{ MHz, CDCl}_3) \delta 7.42 (d, J = 8.3 \text{ Hz, 2 H}), 7.09 (d, J = 8.2 \text{ Hz, 2 H}), 6.87 (br, 2 H), 6.68 (d, J = 8.3 \text{ Hz, 2 H}), 6.56 (s, 1 H, \( J^{119}\text{Sn–}^{1}\text{H} = 115.4 \text{ Hz} \)), 5.41 (s, 1 H), 4.15 (dd, \( J = 13.0, 2.1 \text{ Hz, 1 H} \)), 3.99 (d, \( J = 13.8 \text{ Hz, 1 H} \)), 2.33 (s, 3 H), 3.76 (s, 3 H), 1.38 (s, 9 H), 1.54 – 1.04 (m, 12 H), 0.91 (d, \( J = 13.3 \text{ Hz, 1 H} \)), 0.85 (t, \( J = 7.3 \text{ Hz, 3 H} \)), 0.76 (t, \( J = 7.1 \text{ Hz, 3 H} \)), 0.28 (d, \( J = 12.7 \text{ Hz, 1 H} \), \( J^{119}\text{Sn–}^{1}\text{H} = 53.2 \text{ Hz} \)); \(^{13}\text{C NMR} (126 \text{ MHz, CDCl}_3) \delta 173.7, 158.3 (J^{119}\text{Sn–}^{13}\text{C} = 55.2 \text{ Hz}), 158.9, 142.4, 136.4, 131.6, 129.0, 128.9, 127.7, 127.1, 113.2, 81.3, 69.5 (J^{119}\text{Sn–}^{13}\text{C} = 16.4 \text{ Hz}), 68.0 (J^{119}\text{Sn–}^{13}\text{C} = 31.9 \text{ Hz}), 55.0, 50.3 (J^{119}\text{Sn–}^{13}\text{C} = 61.4 \text{ Hz}), 28.7 (J^{119}\text{Sn–}^{13}\text{C} = 21.8 \text{ Hz}), 28.5 (J^{119}\text{Sn–}^{13}\text{C} = 22.8 \text{ Hz}), 27.4, 26.8 (J^{119}\text{Sn–}^{13}\text{C} = 57.0 \text{ Hz}), 26.7 (J^{119}\text{Sn–}^{13}\text{C} = 56.7 \text{ Hz}), 21.2, 13.4, 13.3, 12.8 (J^{117}\text{Sn–}^{13}\text{C} = 330.2 \text{ Hz}, J^{119}\text{Sn–}^{13}\text{C} = 346.0 \text{ Hz}), 12.5 (J^{117}\text{Sn–}^{13}\text{C} = 261.2 \text{ Hz}, J^{119}\text{Sn–}^{13}\text{C} = 296.2 \text{ Hz}), 12.0 (J^{117}\text{Sn–}^{13}\text{C} = 319.2 \text{ Hz}, J^{119}\text{Sn–}^{13}\text{C} = 336.8 \text{ Hz}); \ \text{^{119}Sn NMR (186 MHz, CDCl}_3) \delta 140.0; \ \text{IR (neat)
2930, 1719, 1612, 1343, 1247, 1161, 1098, 910 cm\(^{-1}\); HRMS (FAB\(^+\) M+1) \(m/z\) 690.2261. calcld for C\(_{33}\)H\(_{48}\)NO\(_5\)SSn 690.2275.

\((3S,3aS)\)-tert-butyl

5,5-dibutyl-3-(o-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2g)

![Structural formula](image)

Colorless oil; \([\alpha]_D^{16.9}\) (c 1.00, CHCl\(_3\)); the enantiomeric purity was determined by HPLC analysis, \(t_R\) 17.4 min \((R)-2g\), \(t_R\) 19.1 min \((S)-2g\) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 98%ee;

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 8.2\) Hz, 2 H), 7.12 (d, \(J = 8.3\) Hz, 2 H), 7.10 (d, \(J = 8.9\) Hz, 1 H), 7.05 (td, \(J = 7.4\), 1.1 Hz, 1 H), 6.87 (t, \(J = 7.3\) Hz, 1 H), 6.60 (d, \(J = 7.9\) Hz, 1 H), 6.58 (s, 1 H, \(J^{119}\)Sn–1H = 115.4 Hz), 5.83 (s, 1 H), 4.17 (dd, \(J = 12.8\), 2.2 Hz, 1 H), 4.06 (dd, \(J = 12.9\), 0.9 Hz, 1 H), 2.45 (s, 3 H), 2.34 (s, 3 H), 1.37 (s, 9 H), 1.55 – 1.02 (m, 12 H), 0.95 (d, \(J = 13.2\) Hz, 1 H), 0.84 (t, \(J = 7.3\) Hz, 3 H), 0.73 (t, \(J = 7.0\) Hz, 3 H), 0.18 (d, \(J = 13.2\) Hz, 1 H, \(J^{119}\)Sn–1H = 54.2 Hz); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 173.9, 158.0 (\(J^{119}\)Sn–13C = 55.6 Hz), 142.6, 138.0, 136.3, 136.2, 129.7, 129.0, 128.1, 127.2, 127.0, 126.5, 125.8, 81.3, 69.4 (\(J^{119}\)Sn–13C = 17.0 Hz), 64.1 (\(J^{119}\)Sn–13C = 31.0 Hz), 50.6 (\(J^{119}\)Sn–13C = 60.7 Hz), 28.8 (\(J^{119}\)Sn–13C = 22.0 Hz), 28.3 (\(J^{119}\)Sn–13C = 22.8 Hz), 27.5, 26.9 (\(J^{119}\)Sn–13C = 55.3 Hz), 26.7 (\(J^{119}\)Sn–13C = 55.2 Hz), 21.2, 19.7, 13.4, 13.3, 12.7 (\(J^{117}\)Sn–13C = 329.4 Hz, \(J^{119}\)Sn–13C = 345.0 Hz), 12.1 (\(J^{117}\)Sn–13C = 266.8 Hz, \(J^{119}\)Sn–13C = 281.8 Hz), 11.9 (\(J^{117}\)Sn–13C = 324.0 Hz, \(J^{119}\)Sn–13C = 340.0 Hz);

\(^{119}\)Sn NMR (186 MHz, CDCl\(_3\)) \(\delta\) 139.3; IR (neat) 2924, 1717, 1616, 1341, 1159, 908
cm\(^{-1}\); HRMS (FAB\(^{+}\) M+1) \(m/z\) 674.2320. calcd for C\(_{33}\)H\(_{48}\)NO\(_{4}\)SSn 674.2326.

\((3S,3aS)\)-\textit{tert}-butyl

5,5-dibutyl-3-(naphthalen-2-yl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2h)

Pale yellow oil; \([\alpha]_D\) -21.9 (c 1.03, CHCl\(_3\)); the enantiomeric purity was determined by HPLC analysis, \(t_R\) 20.9 min ((R)-2h), \(t_R\) 30.3 min ((S)-2h) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 96\%ee;

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 8.2\) Hz, 2 H), 7.82 – 7.39 (m, 6 H), 7.06 – 6.93 (m, 1 H), 6.90 (d, \(J = 8.0\) Hz, 2 H), 6.63 (s, 1 H, \(J^{119}\)Sn – 1H = 114.6 Hz), 5.61 (s, 1 H), 4.26 (dd, \(J = 13.0\), 2.1 Hz, 1 H), 4.12 (d, \(J = 13.5\) Hz, 1 H), 2.20 (s, 3 H), 1.42 (s, 9 H), 1.56 – 1.02 (m, 12 H), 0.96 (d, \(J = 13.3\) Hz, 1 H), 0.83 (t, \(J = 7.3\) Hz, 3 H), 0.64 – 0.50 (m, 3 H), 0.25 (d, \(J = 13.3\) Hz, 1 H, \(J^{119}\)Sn – 1H = 53.2 Hz); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 173.8, 158.5 (\(J^{119}\)Sn – 13C = 54.6 Hz), 142.6, 136.9, 136.5, 133.1, 132.9, 129.5, 129.0, 128.2, 128.1, 128.0, 127.8, 127.5, 127.2, 126.0, 125.9, 81.8, 69.8 (\(J^{119}\)Sn – 13C = 16.0 Hz), 68.9 (\(J^{119}\)Sn – 13C = 30.7 Hz), 50.9 (\(J^{119}\)Sn – 13C = 61.7 Hz), 29.0 (\(J^{119}\)Sn – 13C = 22.1 Hz), 28.7 (\(J^{119}\)Sn – 13C = 22.6 Hz), 27.8, 27.1 (\(J^{119}\)Sn – 13C = 56.3 Hz), 26.9 (\(J^{119}\)Sn – 13C = 59.5 Hz), 21.4, 17.7, 13.7, 13.4, 13.1 (\(J^{117}\)Sn – 13C = 331.6 Hz, \(J^{119}\)Sn – 13C = 347.1 Hz), 12.2 (\(J^{117}\)Sn – 13C = 319.2 Hz, \(J^{119}\)Sn – 13C = 346.6 Hz); \(^{119}\)Sn NMR (186 MHz, CDCl\(_3\)) \(\delta\) 157.2; IR (neat) 2924, 1716, 1344, 1251, 1139, 665 cm\(^{-1}\); HRMS (FAB\(^{+}\) M+2) \(m/z\) 711.2394. calcd for C\(_{36}\)H\(_{49}\)NO\(_{4}\)SSn 711.2404.
(3S,3aS)-tert-butyl

5,5-dibutyl-3-(4-fluorophenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2i)

Pale yellow oil; [α]D +9.87 (c 1.02, CHCl3); the enantiomeric purity was determined by HPLC analysis, tR 13.7 min ((R)-2i), tR 21.4 min ((S)-2i) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 92%ee;

1H NMR (500 MHz, CDCl3) δ 7.46 (d, J = 8.2 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 6.94 (s, 2 H), 6.85 (t, J = 8.4 Hz, 2H), 6.58 (s, 1 H, J119Sn–1H = 115.1 Hz), 5.45 (s, 1 H), 4.13 (dd, J = 12.9, 2.1 Hz, 1 H), 4.02 (d, J = 13.3 Hz, 1 H), 2.34 (s, 3 H), 1.56–1.03 (m, 12 H), 1.37 (s, 9 H), 0.91 (d, J = 13.1 Hz, 1 H), 0.85 (t, J = 7.3 Hz, 3 H), 0.76 (t, J = 7.0 Hz, 3 H), 0.20 (d, J = 13.3 Hz, 1 H, J119Sn–1H = 52.9 Hz); 13C NMR (126 MHz, CDCl3) δ 173.5, 163.1, 161.1, 157.8 (J119Sn–13C = 54.5 Hz), 142.7, 136.3, 135.6, 135.5, 129.1, 128.2, 127.2, 114.8 (J19F–13C = 21.4 Hz), 81.6, 69.5 (J119Sn–13C = 16.4 Hz), 67.7 (J119Sn–13C = 30.7 Hz), 50.4 (J119Sn–13C = 60.2 Hz), 28.9 (J119Sn–13C = 22.0 Hz), 28.6 (J119Sn–13C = 22.7 Hz), 27.6, 27.0 (J119Sn–13C = 51.6 Hz), 26.9 (d, J = 54.4 Hz), 21.3, 13.5, 13.4, 13.0 (J17Sn–13C = 330.0 Hz, J119Sn–13C = 346.0 Hz), 12.7 (J117Sn–13C = 270.2 Hz, J119Sn–13C = 292.9 Hz), 12.2 (J117Sn–13C = 322.4 Hz, J119Sn–13C = 338.0 Hz); 119Sn NMR (186 MHz, CDCl3) δ 140.6; IR (neat) 2924, 1716, 1508, 1344, 1161 cm−1; HRMS (FAB+ M+1) m/z 678.2072. calcd for C32H45FNO4SSn 678.2075.

(3S,3aS)-tert-butyl

5,5-dibutyl-3-(m-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-car
boxylate (2j)

Pale yellow oil; [α]D −1.84 (c 1.03, CHCl₃); the enantiomeric purity was determined by HPLC analysis, tR 18.6 min ((R)-2j), tR 33.9 min ((S)-2j) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 96%ee;

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 8.3 Hz, 2 H), 7.07 (d, J = 8.4 Hz, 2 H), 7.03 (d, J = 7.5 Hz, 1 H), 6.96 (d, J = 7.6 Hz, 1 H), 6.81 – 6.70 (m, 1 H), 6.67 – 6.58 (m, 1 H), 6.56 (s, 1 H, 3J¹¹⁹Sn–¹H = 115.4 Hz), 5.41 (s, 1 H), 4.18 (dd, J = 12.9, 2.1 Hz, 1 H), 4.01 (dd, J = 12.9, 1.1 Hz, 1 H), 2.32 (s, 3 H), 2.17 (s, 3 H), 1.39 (s, 9 H), 1.54 – 1.04 (m, 12 H), 0.92 (d, J = 13.3 Hz, 1 H), 0.85 (t, J = 7.3 Hz, 3 H), 0.74 (t, J = 7.1 Hz, 3 H), 0.25 (d, J = 13.3 Hz, 1 H, J¹¹⁹Sn–¹H = 53.2 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 158.4 (J¹¹⁹Sn–¹³C = 55.5 Hz), 142.4, 139.14, 137.3, 136.5, 128.9, 128.1, 127.8, 127.7, 127.2, 81.4, 69.5 (J¹¹⁹Sn–¹³C = 16.3 Hz), 68.6 (J¹¹⁹Sn–¹³C = 31.4 Hz), 50.6 (J¹¹⁹Sn–¹³C = 61.7 Hz), 28.9 (J¹¹⁹Sn–¹³C = 22.1 Hz), 28.5 (J¹¹⁹Sn–¹³C = 22.7 Hz), 27.6, 27.0 (J¹¹⁹Sn–¹³C = 55.3 Hz), 26.8 (J¹¹⁹Sn–¹³C = 55.8 Hz), 21.3, 21.2, 13.5, 13.4, 12.9 (J¹¹⁷Sn–¹³C = 330.3 Hz, J¹¹⁹Sn–¹³C = 347.7 Hz), 12.7 (J¹¹⁷Sn–¹³C = 287.9 Hz, J¹¹⁹Sn–¹³C = 302.1 Hz), 12.1 (J¹¹⁷Sn–¹³C = 320.1 Hz, J¹¹⁹Sn–¹³C = 335.4 Hz); ¹¹⁹Sn NMR (186 MHz, CDCl₃) δ 140.3; IR (neat) 2922, 1716, 1344, 1159 cm⁻¹; HRMS (FAB⁺ M+1) m/z 674.2314. calcd for C₃₃H₄₈NO₄SSn 674.2326.

(3S,3aS)-tert-butyl

5,5-dibutyl-2-tosyl-3-(4-(trifluoromethyl)phenyl)-1,2,3,3a,4,5-hexahydrostannol[3,
4-cyprrole-3a-carboxylate (2k)

Pale yellow oil; [α]D +2.24 (c 1.07, CHCl3); the enantiomeric purity was determined by HPLC analysis, tR 8.9 min ((R)-2k), tR 10.3 min ((S)-2k) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 96%ee; 1H NMR (500 MHz, CDCl3) δ 7.44 (d, J = 8.3 Hz, 2 H), 7.40 (d, J = 7.9 Hz, 2 H), 7.09 (dd, J = 8.5, 0.5 Hz, 2 H), 7.11 – 7.03 (m, 2 H), 6.61 (s, 1 H), 5.49 (s, 1 H), 4.16 (dd, J = 13.0, 2.1 Hz, 1 H), 4.08 (dd, J = 12.9, 1.1 Hz, 1 H), 2.33 (s, 3 H), 1.37 (s, 9 H), 1.56 – 0.98 (m, 12 H), 0.92 (d, J = 13.3 Hz, 1 H), 0.85 (t, J = 7.3 Hz, 3 H), 0.72 (t, J = 7.1 Hz, 3 H), 0.12 (d, J = 13.3 Hz, 1 H), 0.12 (d, J = 13.3 Hz, 1 H), 0.85 (t, J = 7.3 Hz, 3 H), 0.72 (t, J = 7.1 Hz, 3 H), 0.12 (d, J = 13.3 Hz, 1 H), J119Sn–J13C = 115.3 Hz), 13C NMR (126 MHz, CDCl3) δ 173.3, 157.5 (J119Sn–13C = 53.6 Hz), 143.8, 142.9, 136.2, 129.6 (q, J19F–13C = 32.3 Hz), 129.1, 128.7, 127.1, 124.9 (q, J19F–13C = 3.8 Hz), 81.8, 69.5 (J119Sn–13C = 16.7 Hz), 67.9 (J119Sn–13C = 29.9 Hz), 50.6 (J119Sn–13C = 54.5 Hz), 28.9 (J119Sn–13C = 22.2 Hz), 28.6 (J119Sn–13C = 23.0 Hz), 27.6, 27.0 (J119Sn–13C = 57.4 Hz), 26.7 (J119Sn–13C = 57.4 Hz), 21.3, 13.6, 13.3, 13.1 (J117Sn–13C = 301.6 Hz, J119Sn–13C = 336.5 Hz), 12.7 (J117Sn–13C = 259.0 Hz, J119Sn–13C = 278.4 Hz), 12.2 (J117Sn–13C = 334.1 Hz, J119Sn–13C = 349.5 Hz); 119Sn NMR (186 MHz, CDCl3) δ 141.1; IR (neat) 2926, 1716, 1508, 1344, 1161 cm−1; HRMS (FAB+ M+1) m/z 728.2054. calcd for C33H43F5NO4SSn 728.2043.

(3R,3aS)-tert-butyl

5,5-dibutyl-3-(furan-2-yl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2l)
Pale yellow oil; [α]D +16.9 (c 1.09, CHCl₃); the enantiomeric purity was determined by HPLC analysis, tR 17.3 min ((R)-2l), tR 23.4 min ((S)-2I) [CHIRALPAK IC (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 88/12, 1.0mL/min] as 87%ee;

H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 8.3 Hz, 2 H), 7.10 (d, J = 8.5 Hz, 2 H), 7.02 (t, J = 1.0 Hz, 1 H), 6.49 (s, 1 H, 3J119Sn-1H = 116.0 Hz), 6.19 (d, J = 1.3 Hz, 2 H), 5.52 (s, 1 H), 4.18 (dd, J = 12.9, 2.1 Hz, 1 H), 3.86 (dd, J = 12.9, 1.3 Hz, 1 H), 2.34 (s, 3 H), 1.45 (s, 9 H), 1.57 – 1.09 (m, 12 H), 1.03 (d, J = 13.1 Hz, 1 H), 0.86 (t, J = 7.3 Hz, 3 H), 0.79 (t, J = 7.2 Hz, 3 H), 0.24 (d, J = 13.1 Hz, 1 H, 3J119Sn-1H = 52.8 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 173.1, 158.6 (3J¹¹⁹Sn-¹³C = 52.2 Hz), 152.0, 142.4, 141.9, 136.2, 129.1, 127.0, 126.3, 109.9, 109.8, 81.8, 69.5 (3J¹¹⁹Sn-¹³C = 17.8 Hz), 62.3 (3J¹¹⁹Sn-¹³C = 34.1 Hz), 49.7 (3J¹¹⁹Sn-¹³C = 62.8 Hz), 28.9 (3J¹¹⁹Sn-¹³C = 19.9 Hz), 28.7 (3J¹¹⁹Sn-¹³C = 22.5 Hz), 27.7, 27.0 (3J¹¹⁹Sn-¹³C = 54.4 Hz), 26.9 (3J¹¹⁹Sn-¹³C = 56.3 Hz), 21.4, 13.6 (3J¹¹⁷Sn-¹³C = 289.1 Hz, J¹¹⁹Sn-¹³C = 309.9 Hz), 13.1 (3J¹¹⁷Sn-¹³C = 333.6 Hz, J¹¹⁹Sn-¹³C = 349.2 Hz), 12.3 (3J¹¹⁷Sn-¹³C = 321.5 Hz, J¹¹⁹Sn-¹³C = 334.8 Hz), 12.2;

¹¹⁹Sn NMR (186 MHz, CDCl₃) δ 141.6; IR (neat) 2928, 1718, 1346, 1161 cm⁻¹; HRMS (FAB⁺ M+1) m/z 650.1963. calcd for C₃₀H₄₄NO₅SSn 650.1962.

(3S,3aS)-tert-butyl

5,5-dibutyl-3-isopropyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannol[3,4-c]pyrrole-3-carboxylate (2m)
Colorless oil; $[\alpha]_D^\circ +9.9$ (c 0.97, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.3$ Hz, 2 H), 7.21 (d, $J = 8.0$ Hz, 2 H), 5.84 (s, 1 H), 4.40 (dd, $J = 15.0$, 1.9 Hz, 1 H), 4.08 (d, $J = 15.2$ Hz, 1 H), 3.34 (d, $J = 9.1$ Hz, 1 H), 2.38 (s, 3 H), 2.29 – 2.18 (m, 1 H), 1.93 (d, $J = 11.6$ Hz, 1 H), 1.38 (s, 9 H), 1.66 – 1.09 (m, 12 H), 1.18 (d, $J = 6.8$ Hz, 3 H), 0.98 (d, $J = 6.5$ Hz, 3 H), 0.88 (t, $J = 7.3$ Hz, 3 H), 0.80 (t, $J = 7.3$ Hz, 3 H), 0.17 (d, $J = 11.7$ Hz, 1 H, $J^{119}$Sn–H = 54.7 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.3, 161.0 ($J^{19}$Sn–$^{13}$C = 39.6 Hz), 143.3, 135.5, 129.4, 128.5, 124.5 ($J^{117}$Sn–$^{13}$C = 310.6 Hz, $J^{119}$Sn–$^{13}$C = 324.6 Hz), 81.7, 79.3 ($J^{119}$Sn–$^{13}$C = 41.0 Hz), 68.8 ($J^{119}$Sn–$^{13}$C = 9.3 Hz), 55.0 ($J^{119}$Sn–$^{13}$C = 53.6 Hz), 31.3, 32.2, 29.1 ($J^{119}$Sn–$^{13}$C = 23.2 Hz), 28.9 ($J^{119}$Sn–$^{13}$C = 20.4 Hz), 27.9, 27.2 ($J^{119}$Sn–$^{13}$C = 51.0 Hz), 27.1 (d, $J^{119}$Sn–$^{13}$C = 58.9 Hz), 21.7, 20.4, 17.6 ($J^{117}$Sn–$^{13}$C = 321.6 Hz, $J^{119}$Sn–$^{13}$C = 336.2 Hz), 13.9,13.7, 12.8 ($J^{117}$Sn–$^{13}$C = 331.0 Hz, $J^{119}$Sn–$^{13}$C = 346.2 Hz), 12.4 ($J^{117}$Sn–$^{13}$C = 314.8 Hz, $J^{119}$Sn–$^{13}$C = 329.4 Hz); $^{119}$Sn NMR (186 MHz, CDCl$_3$) $\delta$ 127.3; IR (neat) 2922, 1716, 1346, 1159 cm$^{-1}$; HRMS (FAB$^+$ M+2) m/z 627.2410. calcd for C$_{29}$H$_{49}$NO$_4$SSn 627.2404.

**(3S,3aS)-tert-butyl**

5,5-dibutyl-3-propyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2n)
Colorless oil; isolated as an inseparable 1:1 mixture of the two diastereomer; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.3$ Hz, 1 H), 7.67 (d, $J = 8.3$ Hz, 1 H), 7.25 (d, $J = 8.8$ Hz, 1 H), 7.23 (d, $J = 8.8$ Hz, 1 H), 6.40 (s, 0.5 H), 6.10 (s, 0.5 H), 4.48 (dd, $J = 5.8$, 4.5 Hz, 0.5 H), 4.40 (dd, $J = 14.6$, 2.1 Hz, 0.5 H), 4.07 (dd, $J = 14.6$, 1.0 Hz, 0.5 H), 3.89 (dd, $J = 13.2$, 1.2 Hz, 0.5 H), 3.33 (dd, $J = 10.4$, 4.5 Hz, 0.5 H), 2.38 (s, 1.5 H), 2.36 (s, 1.5 H), 2.26–2.17 (m, 2 H), 1.40 (s, 4.5 H), 1.25 (s, 4.5 H), 1.67 – 0.96 (m, 15 H), 0.93 – 0.78 (m, 9 H), 0.26 (d, $J = 11.9$ Hz, 0.5 H, $J^{119}$Sn–$^1$H = 54.0 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.0, 171.7, 160.0, 159.9, 143.2, 142.9, 136.9, 135.3, 129.5, 129.4, 127.7, 127.5, 125.4, 124.9, 81.7, 81.2, 72.2, 68.7, 68.6, 64.1, 54.3, 49.8, 35.8, 34.9, 29.2, 29.1, 29.0, 28.8, 27.93, 27.92, 27.63, 27.62, 27.2, 27.1, 27.0, 26.9, 21.6, 21.5, 20.7, 19.6, 18.8, 17.6, 14.5, 14.2, 13.8, 13.75, 13.73, 13.70, 13.1, 13.0, 12.6, 12.5, 12.3; $^{119}$Sn NMR (186 MHz, CDCl$_3$) δ 137.0, 132.7; HRMS (FAB$^+$ M+2) m/z 627.2404. calc for C$_{29}$H$_{49}$NO$_4$SSn 627.2404

Preparation of TBP tin complex (4b): To a solution of 2b (120.0 mg, 0.18 mmol) in ether (20 mL) was added 12 M HCl aq (0.5 mL) and the resulting biphasic mixture was stirred at room temperature for 18 h. The organic phase was separated, washed with brine (10 mL x 2), and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated in vacuo and the residue was purified through flash chromatography (hexane-EtOAc (20:1) to give 4b in 100% yield (123.0 mg, 0.18 mmol).
H), 4.55 (dt, $J = 13.3, 2.0$ Hz, 1 H), 4.07 (d, $J = 13.3$ Hz, 1 H), 2.30 (s, 3 H), 1.58 (s, 9 H), 1.44 – 1.14 (m, 12 H), 1.08 (d, $J = 13.9$ Hz, 1 H), 0.91 (t, $J = 7.3$ Hz, 3 H), 0.88 (t, $J = 7.3$ Hz, 3 H), 0.87 (d, $J = 13.1$ Hz, 1 H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.90 ($J^{119}$Sn–$^{13}$C = 14.9 Hz), 147.23 ($J^{119}$Sn–$^{13}$C = 28.5 Hz), 142.7, 137.1, 136.3, 129.0, 128.3, 128.2, 127.8, 126.7, 110.4, 86.7, 70.9 ($J^{119}$Sn–$^{13}$C = 38.1 Hz), 60.9 ($J^{119}$Sn–$^{13}$C = 19.9 Hz), 52.4, 27.9 ($J^{119}$Sn–$^{13}$C = 25.5 Hz), 27.9 ($J^{119}$Sn–$^{13}$C = 25.5 Hz), 27.6, 26.5 ($J^{117}$Sn–$^{13}$C = 79.0 Hz, $J^{119}$Sn–$^{13}$C = 82.6 Hz), 26.4 ($J^{117}$Sn–$^{13}$C = 76.7 Hz, $J^{119}$Sn–$^{13}$C = 80.1 Hz), 21.3 ($J^{117}$Sn–$^{13}$C = 429.5 Hz, $J^{119}$Sn–$^{13}$C = 459.2 Hz), 21.5, 20.2 ($J^{117}$Sn–$^{13}$C = 439.3 Hz, $J^{119}$Sn–$^{13}$C = 459.9 Hz), 19.8 ($J^{117}$Sn–$^{13}$C = 435.8 Hz, $J^{119}$Sn–$^{13}$C = 455.9 Hz), 13.6, 13.5; $^{119}$Sn NMR (186 MHz, CDCl$_3$) $\delta$ 24.8; IR (neat) 2922, 1659, 1343, 1161, 812 cm$^{-1}$; HRMS (FAB$^+$ M+1) $m/z$ 696.1931. calcd for C$_{32}$H$_{47}$ClNO$_4$SSn 696.1936.

TBP complex (4c)

White solid; mp 92 – 93 ºC; $[\alpha]_D$ = –36.0 (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J = 8.3$ Hz, 2 H), 6.99 (d, $J = 8.0$ Hz, 2 H), 6.91 (br, 2 H), 6.75 (br, 2 H), 5.24 (s, 1 H), 5.10 (s, 1 H), 5.06 (s, 1 H), 4.53 (dt, $J = 13.3, 2.2$ Hz, 1 H), 4.06 (d, $J = 13.4$ Hz, 1 H), 2.32 (s, 3 H), 2.28 (s, 3 H), 1.56 (s, 9 H), 1.40 – 1.12 (m, 12 H), 1.08 (d, $J = 13.9$ Hz, 1 H, $J^{119}$Sn–$^{1}$$H = 67.1$ Hz), 0.90 (t, $J = 7.2$ Hz, 3 H), 0.90 (d, $J = 14.3$ Hz, 1 H, $J^{119}$Sn–$^{1}$H = 72.2 Hz), 0.88 (t, $J = 7.3$ Hz, 1 H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 179.1 ($J^{119}$Sn–$^{13}$C = 16.2 Hz), 147.4 ($J^{119}$Sn–$^{13}$C = 27.9 Hz), 142.7, 142.7, 138.0, 134.0, 129.0,
128.9, 127.9, 126.8, 110.30, 86.7, 70.9 ($J^{119}\text{Sn}–^{13}\text{C} = 39.5$ Hz), 61.0 ($J^{119}\text{Sn}–^{13}\text{C} = 19.8$ Hz), 52.5, 27.91 ($J^{119}\text{Sn}–^{13}\text{C} = 26.8$ Hz), 27.91 ($J^{119}\text{Sn}–^{13}\text{C} = 26.8$ Hz), 27.65, 26.64 ($J^{119}\text{Sn}–^{13}\text{C} = 79.4$ Hz), 26.61 ($J^{119}\text{Sn}–^{13}\text{C} = 77.4$ Hz), 21.5, 21.4 ($J^{117}\text{Sn}–^{13}\text{C} = 430.2$ Hz, $J^{119}\text{Sn}–^{13}\text{C} = 448.0$ Hz), 21.1, 20.3 ($J^{117}\text{Sn}–^{13}\text{C} = 438.0$ Hz, $J^{119}\text{Sn}–^{13}\text{C} = 450.0$ Hz), 13.7, 13.6; $^{119}\text{Sn}$ NMR (186 MHz, CDCl$_3$) δ 25.4; IR (neat) 2924, 1655, 1342, 1159, 907 cm$^{-1}$; HRMS (FAB$^+$ M+1) m/z 710.2088. calcd for C$_{33}$H$_{49}$ClNO$_4$Sn 710.2093.

**TBP complex (4e)**

![TBP complex](image)

Pale yellow oil; $[\alpha]_D$ -50.6 (c 1.01, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.3$ Hz, 1 H), 7.10 (br, 2 H), 7.04 (d, $J = 8.1$ Hz, 2 H), 6.82 (s, 2 H), 5.27 (s, 1 H), 5.10 (s, 1 H), 5.08 (s, 1 H), 4.54 (d, $J = 13.4$ Hz, 1 H), 4.09 (d, $J = 13.4$ Hz, 1 H), 2.34 (s, 3 H), 1.57 (s, 9 H), 1.47 – 1.13 (m, 12 H), 1.02 (d, $J = 13.9$ Hz, 1 H, $J^{119}\text{Sn}–^{1}$H = 73.5 Hz), 0.90 (t, $J = 7.4$ Hz, 3 H), 0.88 (t, $J = 7.3$ Hz, 3 H), 0.87 (d, $J = 14.2$ Hz, 1 H, $J^{119}\text{Sn}–^{1}$H = 72.7 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.5 ($J^{119}\text{Sn}–^{13}$C = 14.4 Hz), 146.8 ($J^{119}\text{Sn}–^{13}$C = 23.5 Hz), 143.1, 136.3, 135.7, 134.1, 129.1, 129.0, 128.5, 126.6, 110.8, 87.0, 70.1 ($J^{119}\text{Sn}–^{13}$C = 42.0 Hz), 60.8 ($J^{119}\text{Sn}–^{13}$C = 19.8 Hz), 52.4, 27.9 ($J^{119}\text{Sn}–^{13}$C = 24.1 Hz), 27.8 ($J^{119}\text{Sn}–^{13}$C = 25.6 Hz), 27.6, 26.56 ($J^{117}\text{Sn}–^{13}$C = 79.6 Hz, $J^{119}\text{Sn}–^{13}$C = 83.0 Hz), 26.53 ($J^{117}\text{Sn}–^{13}$C = 76.1 Hz, $J^{119}\text{Sn}–^{13}$C = 79.8 Hz), 21.6, 21.4 ($J^{117}\text{Sn}–^{13}$C = 442.5 Hz, $J^{119}\text{Sn}–^{13}$C = 468.9 Hz), 20.3 ($J^{117}\text{Sn}–^{13}$C = 440.6 Hz, $J^{119}\text{Sn}–^{13}$C = 460.8 Hz), 19.8 ($J^{117}\text{Sn}–^{13}$C = 446.4 Hz, $J^{119}\text{Sn}–^{13}$C = 466.1 Hz), 13.6, 13.5; $^{119}$Sn NMR (186
MHz, CDCl$_3$) δ 24.7; IR (neat) 2924, 1668, 1344, 1163, 912 cm$^{-1}$; HRMS (FAB$^+$ M+1) m/z 730.1546. calcd for C$_{32}$H$_{46}$Cl$_2$NO$_4$SSn 730.1547.

**TBP complex (4f)**

Colorless oil; [α]$_D$ –50.1 (c 1.02, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.19 (d, J = 8.3 Hz, 2 H), 7.01 (d, J = 8.1 Hz, 2 H), 6.79 (br, 2 H), 6.66 (br, 2 H), 5.24 (s, 1 H), 5.11 (s, 1 H), 5.05 (s, 1 H), 4.53 (dt, J = 13.4, 2.2 Hz, 1 H), 4.04 (d, J = 13.3 Hz, 1 H), 3.77 (s, 3 H), 2.32 (s, 3 H), 1.57 (s, 9 H), 1.41 – 1.16 (m, 12 H), 1.10 (d, J = 13.9 Hz, 1 H, J$^{119}$Sn–1H = 67.9 Hz), 0.91 (t, J = 7.3 Hz, 3 H), 0.90 (d, J = 13.2 Hz, 1 H, J$^{119}$Sn–1H = 66.5 Hz), 0.88 (t, J = 7.3 Hz, 3 H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 179.1 (J$^{119}$Sn–$^{13}$C = 14.9 Hz), 159.5, 147.4 (J$^{119}$Sn–$^{13}$C = 29.6 Hz), 142.7, 136.5, 129.2, 129.0, 126.8, 113.8, 110.3, 86.7, 70.6 (J$^{119}$Sn–$^{13}$C = 39.1 Hz), 61.0 (J$^{119}$Sn–$^{13}$C = 19.4 Hz), 55.2, 52.3, 27.9 (J$^{119}$Sn–$^{13}$C = 27.3 Hz), 27.8 (J$^{119}$Sn–$^{13}$C = 26.6 Hz), 27.6, 26.6 (J$^{117}$Sn–$^{13}$C = 79.1 Hz, J$^{119}$Sn–$^{13}$C = 82.6 Hz), 26.5 (J$^{117}$Sn–$^{13}$C = 76.6 Hz, J$^{119}$Sn–$^{13}$C = 80.3 Hz), 21.4, 21.3 (J$^{117}$Sn–$^{13}$C = 426.8 Hz, J$^{119}$Sn–$^{13}$C = 456.1 Hz), 20.2 (J$^{117}$Sn–$^{13}$C = 439.5 Hz, J$^{119}$Sn–$^{13}$C = 460.1 Hz), 19.8 (J$^{117}$Sn–$^{13}$C = 435.4 Hz, J$^{119}$Sn–$^{13}$C = 455.4 Hz), 13.6, 13.5; $^{119}$Sn NMR (186 MHz, CDCl$_3$) δ 25.1; IR (neat) 2926, 1657, 1342, 1250, 1161, 1098, 910 cm$^{-1}$; HRMS (FAB$^+$ M+1) m/z 726.2025. calcd for C$_{33}$H$_{49}$ClNO$_5$SSn 726.2042.

**TBP complex (4g)**
White solid; mp 84 – 84 ºC; [α]D = 33.6 (c 1.05, CHCl3), 1H NMR (500 MHz, CDCl3) δ 7.16 – 7.09 (m, 3 H), 7.04 (td, J = 7.5, 1.2 Hz, 1 H), 6.96 (d, J = 8.0 Hz, 2 H), 6.73 (t, J = 7.2 Hz, 1 H), 6.42 (d, J = 7.8 Hz, 1 H), 5.61 (s, 1 H), 5.35 (s, 1 H), 5.16 (s, 1 H), 4.56 (dt, J = 13.1, 2.3 Hz, 1 H), 4.05 (d, J = 13.0, 1 H), 2.38 (s, 3 H), 2.29 (s, 3 H), 1.61 (s, 9 H), 1.41 – 1.13 (m, 12 H), 0.97 (d, J = 14.1 Hz, 1 H, J119Sn–1H = 82.8 Hz), 0.90 (t, J = 7.3 Hz, 3 H), 0.89 (t, J = 7.3 Hz, 3 H), 0.68 (d, J = 14.2 Hz, 1 H, J119Sn–1H = 55.3 Hz); 13C NMR (126 MHz, CDCl3) δ 179.2 (J119Sn–13C = 17.6 Hz), 147.7 (J119Sn–13C = 5.3 Hz), 142.5, 137.2, 136.4, 135.3, 130.3, 128.9, 127.6, 127.2, 126.4, 126.2, 111.9, 87.1, 65.9 (J119Sn–13C = 62.4 Hz), 60.0 (J119Sn–13C = 19.7 Hz), 52.1, 27.9 (J119Sn–13C = 28.9 Hz), 27.9 (J119Sn–13C = 24.3 Hz), 27.7, 26.6 (J117Sn–13C = 75.6 Hz, J119Sn–13C = 79.5 Hz), 26.5 (J117Sn–13C = 77.0 Hz, J119Sn–13C = 81.0 Hz), 21.7 (J117Sn–13C = 403.5Hz, J119Sn–13C = 424.7 Hz), 21.3, 21.2 (J117Sn–13C = 441.9 Hz, J119Sn–13C = 462.5 Hz), 19.5, 19.2 (J117Sn–13C = 439.9 Hz, J119Sn–13C = 460.7 Hz), 13.6, 13.5; 119Sn NMR (186 MHz, CDCl3) δ 23.2; IR (neat) 2924, 1667, 1340, 1159, 910 cm−1; HRMS (FAB+ M+1) m/z 710.2109. calcd for C33H46ClNO3SSn 710.2093.

**TBP complex (4h)**
Colorless oil; $[\alpha]_D -61.5$ (c 1.01, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.76 – 7.42 (m, 6 H), 7.10 (d, $J = 6.8$ Hz, 2 H), 6.95 – 6.80 (m, 1 H), 6.73 (d, $J = 8.0$ Hz, 2 H), 5.31 (s, 1 H), 5.26 (s, 1 H), 5.15 (s, 1 H), 4.61 (dd, $J = 13.4$, 1.6 Hz, 1 H), 4.18 (d, $J = 13.5$ Hz, 1 H), 2.13 (s, 3 H), 1.60 (s, 9 H), 1.60 – 1.48 (m, 4 H), 1.38 – 1.17 (m, 8 H), 1.07 (d, $J = 14.0$ Hz, 1 H), 0.97 (dd, $J = 13.9$, 1.4 Hz, 1 H), 0.87 (t, $J = 6.5$ Hz, 3 H), 0.85 (t, $J = 7.3$ Hz, 3 H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 179.0 ($J^{^{119}}$Sn–$^{13}$C = 14.2 Hz), 147.5 ($J^{^{119}}$Sn–$^{13}$C = 27.5 Hz), 142.9, 136.5, 134.4, 133.1, 132.9, 130.1, 128.9, 128.4, 128.0, 127.6, 126.7, 126.5, 125.2, 110.8, 87.0, 71.4 ($J^{^{119}}$Sn–$^{13}$C = 42.5 Hz), 61.1 ($J^{^{119}}$Sn–$^{13}$C = 15.2 Hz), 52.7, 28.1 ($J^{^{119}}$Sn–$^{13}$C = 25.9 Hz), 28.0 ($J^{^{119}}$Sn–$^{13}$C = 27.2 Hz), 27.9, 26.8 ($J^{^{117}}$Sn–$^{13}$C = 78.9 Hz, $J^{^{119}}$Sn–$^{13}$C = 82.9 Hz), 26.7 ($J^{^{117}}$Sn–$^{13}$C = 76.8 Hz, $J^{^{119}}$Sn–$^{13}$C = 80.3 Hz), 21.8, 21.3 ($J^{^{117}}$Sn–$^{13}$C = 409.6 Hz, $J^{^{119}}$Sn–$^{13}$C = 422.4 Hz), 20.6 ($J^{^{117}}$Sn–$^{13}$C = 439.8 Hz, $J^{^{119}}$Sn–$^{13}$C = 459.2 Hz), 19.8 ($J^{^{117}}$Sn–$^{13}$C = 435.2 Hz, $J^{^{119}}$Sn–$^{13}$C = 455.6 Hz), 13.73, 13.73; $^{119}$Sn NMR (186 MHz, CDCl$_3$) $\delta$ 25.67; IR (neat) 2956, 1660, 1342, 1161, 910 cm$^{-1}$; HRMS (FAB$^+$ M+1) $m/z$ 746.2074. calc'd for C$_{36}$H$_{46}$ClNO$_4$SSn 746.2093.

**TBP complex (4i)**

![TBP complex (4i)](image)

Colorless oil; $[\alpha]_D -29.0$ (c 1.10, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.20 (d, $J = 8.3$ Hz, 2 H), 7.03 (d, $J = 8.1$ Hz, 2 H), 6.90 – 6.79 (m, 4 H), 5.27 (s, 1 H), 5.12 (s, 1 H), 5.10 (s, 1 H), 4.55 (dt, $J = 13.4$, 2.2 Hz, 1 H), 4.07 (d, $J = 13.4$ Hz, 1 H), 2.33 (s, 3 H), 1.57 (s, 9 H), 1.39 – 1.19 (m, 12 H), 1.06 (d, $J = 13.9$ Hz, 1 H, $J^{^{119}}$Sn–$^{1}$H = 66.1 Hz),
0.91 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.84 (d, J = 13.9 Hz, 1 H, J$^{119}$Sn–H = 71.0 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.8 (J$^{119}$Sn–$^{13}$C = 14.1 Hz), 163.7, 161.6, 147.2 (J$^{119}$Sn–$^{13}$C = 27.8 Hz), 143.1, 136.6, 133.32, 133.30, 129.7, 129.2, 126.8, 115.4 (J$^{119}$Sn–$^{13}$C = 21.4 Hz), 110.8, 87.0, 70.2 (J$^{119}$Sn–$^{13}$C = 40.7 Hz), 61.0 (J$^{119}$Sn–$^{13}$C = 20.1 Hz), 52.5, 28.0 (J$^{119}$Sn–$^{13}$C = 26.3 Hz), 28.0 (J$^{119}$Sn–$^{13}$C = 26.4 Hz), 27.8, 26.7 (J$^{117}$Sn–$^{13}$C = 78.0 Hz, J$^{119}$Sn–$^{13}$C = 79.8 Hz), 26.6 (J$^{117}$Sn–$^{13}$C = 78.8 Hz, J$^{119}$Sn–$^{13}$C = 82.6 Hz), 21.8 (J$^{117}$Sn–$^{13}$C = 400.6 Hz, J$^{119}$Sn–$^{13}$C = 421.0 Hz), 21.4, 20.4 (J$^{117}$Sn–$^{13}$C = 439.8 Hz, J$^{119}$Sn–$^{13}$C = 460.6 Hz), 20.0 (d, J$^{117}$Sn–$^{13}$C = 436.0 Hz, J$^{119}$Sn–$^{13}$C = 455.4 Hz), 13.8, 13.6; $^{119}$Sn NMR (186 MHz, CDCl$_3$) δ 24.5; IR (neat) 2924, 1658, 1508, 1157 cm$^{-1}$; HRMS (FAB$^+$ M+1) m/z 714.1844. calcld for C$_{32}$H$_{46}$ClFNO$_4$SSn 714.1842.

**TBP complex (4j)**

![TBP complex structure](image)

Pale yellow oil; [α]$_D$ –23.8 (c 1.06, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.17 (d, J = 8.3 Hz, 2 H), 6.98 (d, J = 7.9 Hz, 4 H), 6.73 – 6.46 (m, 2 H), 5.25 (s, 1 H), 5.10 (s, 1 H), 5.06 (s, 1 H), 4.56 (dt, J = 13.4, 2.2 Hz, 1 H), 4.08 (d, J = 13.3 Hz, 1 H), 2.30 (s, 3 H), 2.14 (s, 3 H), 1.58 (s, 9 H), 1.44 – 1.16 (m, 12 H), 1.09 (d, J = 13.9 Hz, 1 H, J$^{119}$Sn–H = 67.7 Hz), 0.92 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.86 (d, J = 13.7 Hz, 1 H, J$^{119}$Sn–H = 70.0 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 179.0 (J$^{119}$Sn–$^{13}$C = 14.8 Hz), 147.3 (J$^{119}$Sn–$^{13}$C = 30.8 Hz), 142.6, 137.9, 136.8, 136.5, 128.9, 128.8, 128.2, 126.7, 110.3, 86.3, 71.0 (J$^{119}$Sn–$^{13}$C = 37.8 Hz), 60.9 (J$^{119}$Sn–$^{13}$C = 19.9 Hz), 52.5, 27.9 (J$^{119}$Sn–$^{13}$C = 27.1 Hz), 27.8 (J$^{119}$Sn–$^{13}$C = 26.0 Hz), 27.6, 26.5 (J$^{117}$Sn–$^{13}$C = 78.3 Hz, J$^{119}$Sn–$^{13}$C = 81.7 Hz), 26.5 (J$^{117}$Sn–$^{13}$C = 75.8 Hz, J$^{119}$Sn–H = 79.5 Hz), 21.5, 21.2
\(J_{117}^{13} \text{Sn} - ^{13}C = 409.3\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 426.1\text{ Hz}\), 21.1, 20.2 \(J_{117}^{13} \text{Sn} - ^{13}C = 440.0\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 458.5\text{ Hz}\), 19.9 \(J_{117}^{13} \text{Sn} - ^{13}C = 435.3.3\text{ Hz}, J_{119}^{13} \text{Sn} - ^{1}H = 458.5\text{ Hz}\), 13.6, 13.5; \(^{119}\text{Sn} NMR (186 MHz, CDCl\text{)} \delta 25.2; IR (neat) 2924, 1658, 1342, 1159 \text{ cm}^{-1}; HRMS (FAB\text{+} M+1) \text{ m/z 710.2103. caleld for C}_{33}H_{46}ClIF_{3}NO_{4}SSn 710.2093.

**TBP complex (4k)**

![TBP complex structure]

Pale yellow oil; \([\alpha]_D^{13} -33.0\text{ (c 1.00, CHCl\text{)};} \ ^{1}H NMR (500 MHz, CDCl\text{)} \text{ } 7.36 \text{ (d, } J = 6.4\text{ Hz, 2 H}), 7.18 \text{ (d, } J = 8.2\text{ Hz, 2 H}), 7.06 - 6.94 \text{ (m, 2 H)}, 6.98 \text{ (d, } J = 8.3\text{ Hz, 2 H}), 5.30 \text{ (s, 1 H)}, 5.15 \text{ (s, 1 H)}, 5.12 \text{ (s, 1 H)}, 4.58 \text{ (d, } J = 13.5\text{ Hz, 1 H}), 4.15 \text{ (d, } J = 13.5\text{ Hz, 1 H)}, 2.29 \text{ (s, 3 H)}, 1.58 \text{ (s, 9 H)}, 1.64 - 1.19 \text{ (m, 12 H)}, 0.99 \text{ (d, } J = 13.9\text{ Hz, 1 H}, J_{119}^{13} \text{Sn} - ^{1}H = 65.6\text{ Hz}), 0.89 \text{ (t, } J = 7.3\text{ Hz, 3 H}), 0.88 \text{ (t, } J = 7.4\text{ Hz, 3 H}), 0.85 \text{ (d, } J = 14.0\text{ Hz, 1 H}, J_{119}^{13} \text{Sn} - ^{1}H = 72.6\text{ Hz}); ^{13}C NMR (126 MHz, CDCl\text{)} \delta 178.2 \text{ (J}_{119}^{13} \text{Sn} - ^{13}C = 14.3\text{ Hz)}, 146.6 \text{ (J}_{119}^{13} \text{Sn} - ^{13}C = 22.5\text{ Hz}), 143.2, 141.2, 136.2, 130.2 \text{ (q, J}_{13}^{19} \text{F} - ^{13}C = 32.6\text{ Hz)}, 129.1, 126.5, 125.2 \text{ (q, J}_{13}^{19} \text{F} - ^{13}C = 3.7\text{ Hz)}, 123.7 \text{ (q, J}_{13}^{19} \text{F} - ^{13}C = 272.3\text{ Hz)}, 111.0, 87.1, 70.1 \text{ (J}_{119}^{13} \text{Sn} - ^{13}C = 43.5\text{ Hz)}, 60.7 \text{ (J}_{119}^{13} \text{Sn} - ^{13}C = 19.6\text{ Hz)}, 52.6, 27.8 \text{ (J}_{119}^{13} \text{Sn} - ^{13}C = 27.0\text{ Hz)}, 27.6, 26.5 \text{ (J}_{117}^{13} \text{Sn} - ^{13}C = 73.4\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 83.2\text{ Hz)}, 26.4 \text{ (J}_{117}^{13} \text{Sn} - ^{13}C = 73.6\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 86.7\text{ Hz)}, 21.7 \text{ (J}_{117}^{13} \text{Sn} - ^{13}C = 398.4\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 416.9\text{ Hz)}, 21.1, 20.4 \text{ (J}_{117}^{13} \text{Sn} - ^{13}C = 441.1\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 461.8\text{ Hz)}, 19.7 \text{ (J}_{117}^{13} \text{Sn} - ^{13}C = 436.9\text{ Hz}, J_{119}^{13} \text{Sn} - ^{13}C = 457.1\text{ Hz}), 13.5, 13.4; ^{119}\text{Sn NMR (186 MHz, CDCl\text{)} } \delta 24.4; IR (neat) 2926, 1668, 1323, 1161 \text{ cm}^{-1}; HRMS (FAB\text{+} M+1) \text{ m/z 764.1808. caleld for C}_{33}H_{46}ClIF_{3}NO_{4}SSn 764.1810.
TBP complex (4l)

Pale yellow oil; $[\alpha]_D^{20} = -34.9$ (c 1.13, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 (d, J = 8.3 Hz, 2 H), 7.09 (d, J = 8.2 Hz, 2 H), 7.05 (d, J = 1.5 Hz, 1 H), 6.19 (dd, J = 3.2, 1.8 Hz, 1 H), 6.13 (d, J = 3.2 Hz, 1 H), 5.18 (s, 1 H), 5.13 (s, 2 H), 4.50 (d, J = 12.9 Hz, 1 H), 3.98 (d, J = 12.8 Hz, 1 H), 2.34 (s, 3 H), 1.73 – 1.58 (m, 4 H), 1.56 (s, 9 H), 1.49 – 1.25 (m, 8 H), 1.25 (d, J = 14.1 Hz, 1 H), 0.95 (t, J = 7.3 Hz, 3 H), 0.90 (t, J = 7.3 Hz, 3 H), 0.66 (d, J = 13.8 Hz, 1 H, $^1$J$_{119}$Sn–$^1$H = 64.3 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.8 ($^1$J$_{119}$Sn–$^{13}$C = 12.0 Hz), 149.7, 147.2 ($^1$J$_{119}$Sn–$^{13}$C = 44.9 Hz), 142.7, 136.2, 129.2, 126.6, 110.5, 109.9, 109.4, 86.5, 64.4 ($^1$J$_{119}$Sn–$^{13}$C = 28.0 Hz), 60.9 ($^1$J$_{119}$Sn–$^{13}$C = 20.3 Hz), 51.8, 27.9 ($^1$J$_{119}$Sn–$^{13}$C = 26.4 Hz), 27.8 ($^1$J$_{119}$Sn–$^{13}$C = 27.2 Hz), 27.5, 26.6 ($^1$J$_{117}$Sn–$^{13}$C = 78.8 Hz, $^1$J$_{119}$Sn–$^{13}$C = 82.6 Hz), 26.5 ($^1$J$_{117}$Sn–$^{13}$C = 77.3 Hz, $^1$J$_{119}$Sn–$^{13}$C = 80.5 Hz), 21.3, 20.7 ($^1$J$_{117}$Sn–$^{13}$C = 402.0 Hz, $^1$J$_{119}$Sn–$^{13}$C = 422.4 Hz), 20.2 ($^1$J$_{117}$Sn–$^{13}$C = 432.4 Hz, $^1$J$_{119}$Sn–$^{13}$C = 452.4 Hz), 19.7 ($^1$J$_{117}$Sn–$^{13}$C = 436.8 Hz, $^1$J$_{119}$Sn–$^{13}$C = 457.2 Hz), 13.6, 13.5; $^{119}$Sn NMR (186 MHz, CDCl$_3$) $\delta$ 28.2; IR (neat) 2942, 1661, 1344, 1161 cm$^{-1}$; HRMS (FAB$^+$ M+1) $m/z$ 686.1730. calcd for C$_{30}$H$_{45}$ClNO$_5$SSn 686.1729.

Radical cyclization of 1c under high Bu$_3$SnH concentration conditions (Scheme 2)

A mixture of 1c (172.0 mg, 0.40 mmol) and AIBN (6.9 mg, 0.04 mmol) in Bu$_3$SnH (0.13 mL, 0.47 mmol) was heated at 110°C for 1.5 h. The reselting reaction mixture was subjected to column chromatography (hexane then hexane-EtOAc 50:1 to 20:1) to give 2c (111.7 mg, 0.17 mmol) and 3c (125.1 mg, 0.17 mmol) in 42% and 44% yield, respectively.
(2S,3S)-tert-butyl

4-methylene-2-(p-tolyl)-1-tosyl-3-((tributylstannyl)methyl)pyrrolidine-3-carboxylate (3c)

Colorless oil; $\alpha_\text{D} = -21.3$ (c 1.04, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J =$ 8.3 Hz, 2 H), 6.95 (d, $J =$ 8.1 Hz, 2 H), 6.90 (d, $J =$ 7.8 Hz, 2 H), 6.82 (d, $J =$ 7.2 Hz, 2 H), 5.17 (s, 2 H), 5.12 (s, 1 H), 4.40 (dt, $J =$ 13.0, 2.2 Hz, 1 H), 3.96 (d, $J =$ 13.0 Hz, 1 H), 2.29 (s, 3 H), 2.27 (s, 3 H), 1.47 (s, 9 H), 1.39 – 1.15 (m, 12 H), 1.00 (d, $J =$ 12.8 Hz, 1 H), 0.82 (t, $J =$ 7.1 Hz, 9 H), 0.76 – 0.59 (m, 6 H), 0.37 (d, $J =$ 13.0 Hz, 1 H, $J^{119}$Sn–$^1$H = 44.9 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.2, 150.0 ($J^{119}$Sn–$^{13}$C = 40.3 Hz), 142.3, 137.5, 136.9 ($J^{119}$Sn–$^{13}$C = 47.4 Hz), 135.4, 128.9, 128.8, 127.0, 109.2, 70.2 ($J^{119}$Sn–$^{13}$C = 19.1 Hz), 61.4 ($J^{119}$Sn–$^{13}$C = 18.9 Hz), 82.1, 52.1, 29.1 ($J^{119}$Sn–$^{13}$C = 19.5 Hz), 27.8, 27.5 ($J^{119}$Sn–$^{13}$C = 60.0 Hz), 21.4, 21.1, 13.8, 12.4 ($J^{117}$Sn–$^{13}$C = 271.2 Hz, $J^{119}$Sn–$^{13}$C = 283.9 Hz), 11.0 ($J^{117}$Sn–$^{13}$C = 315.2 Hz, $J^{119}$Sn–$^{13}$C = 329.9 Hz); $^{119}$Sn NMR (186 MHz, CDCl$_3$) $\delta$ –23.1; IR (neat) 2988, 1716, 1342, 1161, 910 cm$^{-1}$; Anal. Calcd. for C$_{30}$H$_{41}$NO$_4$SSn: C, 57.16; H, 6.56; N, 2.22. Found: C, 57.20; H, 6.57; N, 2.20; HRMS (FAB$^+$ M+1) $m/z$ 732.3100. calcd for C$_{37}$H$_{58}$NO$_4$SSn 732.3109.
checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

No syntax errors found.

CIF dictionary

Please wait while processing ....

Interpreting this report

Structure factor report

**Datablock: I**

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<tr>
<td>Hall group</td>
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<td>C33 H48 Cl N O4 S Sn</td>
</tr>
<tr>
<td>Sum formula</td>
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<td>C33 H48 Cl N O4 S Sn</td>
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<td>0.119, 0.224</td>
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The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

**Alert level C**

**RINTA01_ALERT_3_C** The value of Rint is greater than 0.12

Rint given \quad 0.123

**PLAT094_ALERT_2_C** Ratio of Maximum / Minimum Residual

Density .... \quad 2.08

**PLAT910_ALERT_3_C** Missing # of FCF Reflections Below Th(Min) ..... 1

**PLAT912_ALERT_4_C** Missing # of FCF Reflections Above STh/L= 0.600 \quad 11

**PLAT913_ALERT_3_C** Missing # of Very Strong Reflections in FCF .... 1

**Alert level G**

**REFLT03_ALERT_4_G** Please check that the estimate of the number of Friedel pairs is correct. If it is not, please give the correct count in the

_publ_section_exptl_refinement section of the submitted CIF.

From the CIF: _diffrn_reflns_theta_max \quad 68.18

From the CIF: _reflns_number_total \quad 6254

Count of symmetry unique reflns \quad 3587

Completeness (_total/calc) \quad 174.35%

TEST3: Check Friedels for noncentro structure

Estimate of Friedel pairs measured \quad 2667

Fraction of Friedel pairs measured \quad 0.744
Are heavy atom types Z>Si present  yes
PLAT791_ALERT_4_G Note: The Model has Chirality at C3
  (Verify)  S
PLAT791_ALERT_4_G Note: The Model has Chirality at C4
  (Verify)  S
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max)
  still  80 Perc.

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
  5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  4 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  1 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the “special_details” fields of the CIF. checkCIF was carefully designed to identify
outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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PLATON version of 21/12/2011; check.def file version of 16/12/2011

**Datablock I - ellipsoid plot**
Download CIF editor (pubICIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry
checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

No syntax errors found.

Please wait while processing ....

Datablock: I

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<tr>
<td>Temperature:</td>
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</table>

| Volume          | 1552.1(3)       | 1552.1(3)           |
| Space group     | P 1             | P 1                 |
| Hall group      | P 1             | P 1                 |
| Moiety formula  | C30 H41 N 04 S Sn | C30 H41 N 04 S Sn |
| Sum formula     | C30 H41 N 04 S Sn | C30 H41 N 04 S Sn |
| Mr              | 630.42          | 630.41              |
| Dx, g cm⁻³      | 1.349           | 1.349               |
| Z               | 2               | 2                   |
| Mu (mm⁻¹)       | 0.923           | 0.923               |
| F000            | 652.0           | 652.0               |
| F000'           | 651.17          |                     |
| h, k, lmax      | 11, 12, 25      | 11, 12, 25          |
| Nref            | 7111[ 14222]    | 11472               |
| Tmin, Tmax      | 0.766, 0.912    | 0.661, 0.912        |
The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

**Alert level C**

PLAT220_ALERT_2_C Large Non-Solvent C
Ueq(max)/Ueq(min) ... 3.9 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H
Uiso(max)/Uiso(min) .. 5.0 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C17 --
C22 .. 5.2 su
PLAT234_ALERT_4_C Large Hirshfeld Difference Sn1 --
C11 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C18 --
C19 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 --
C23 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C26 --
C27 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference Sn2 --
C37 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N2 --
C35 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C38 --
C39 .. 0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C51 --
C52 .. 0.18 Ang.
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C15
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C27
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C39
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C43
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C45
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ............. 0.0156 Ang
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C37 ... C38 ... 1.43 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C39 ... C40 ... 1.34 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact H37B ... H13D ... 2.07 Ang.
PLAT910_ALERT_3_C Missing # of FCF Reflections Below Th(Min) ..... 10
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 11
PLAT912_ALERT_4_C Missing # of FCF Reflections Above STh/L= 0.600 67
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 1
PLAT915_ALERT_3_C Low Friedel Pair Coverage ..................... 62 Perc.

⚠️Alert level G

REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel pairs is correct. If it is not, please give the correct count in the _publ_section_exptl_refinement section of the submitted CIF.

- From the CIF: _diffeffl_reflns_theta_max 27.47
- From the CIF: _refinl_number_total 11472
- Count of symmetry unique reflns 7111
Completeness (_total/calc)  161.33%

TEST3: Check Friedels for noncentro structure

Estimate of Friedel pairs measured  4361

Fraction of Friedel pairs measured  0.613

Are heavy atom types Z>Si present  yes

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite  7

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites ....  11

PLAT301_ALERT_3_G Note: Main Residue Disorder ....................
4 Perc.

PLAT791_ALERT_4_G Note: The Model has Chirality at C3
(Verify)  S

PLAT791_ALERT_4_G Note: The Model has Chirality at C4
(Verify)  S

PLAT791_ALERT_4_G Note: The Model has Chirality at C33
(Verify)  S

PLAT791_ALERT_4_G Note: The Model has Chirality at C34
(Verify)  S

PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints ........  143

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PLATON version of 21/12/2011; check.def file version of 16/12/2011

Datablock I - ellipsoid plot
Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications
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