Supporting Information

Stereospecific Cross-Coupling of α -(Thiocarbamoyl)organostannanes with Alkenyl, Aryl, and Heteroaryl Iodides

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General Procedures. ^1H and ^{13}C spectra were recorded in CDCl_3 using tetramethylsilane as internal reference. Optical rotations were measured using an Autopol IV automatic polarimeter. The Michigan State University Mass Spectroscopy Facility provided high-resolution mass spectra. All reactions were maintained under an argon atmosphere. Anhydrous solvents were freshly distilled from sodium benzophenone ketyl, except for CH_2Cl_2 , which was distilled from CaH_2 . Extracts were dried over anhydrous Na_2SO_4 and then filtered prior to removal of all volatiles under reduced pressure.

Reagents. Compounds **3**,¹ **4**,² **6**,² **8**,³ **10**,⁴ **12**,⁵ **14**,⁶ and **16**² were prepared following literature procedures. Compounds **20**, **22**, **25**, **27**, **29**, **32**, **34**, **36**, **39**, **41**, **43**, **45**, **47**, and **49** were purchased from Aldrich Chem. Co. and were used as received.

S-[3-Phenyl-1-(tri-*n*-butylstannyl)propyl 1-pyrrolidinecarbothiolate (1). CuTC induced S₂O rearrangement of **3** at rt in THF evolved **1** (95%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.52$; ^1H NMR (300 MHz) δ 7.34-7.14 (m, 5H), 3.54 (t, $J = 6.7$ Hz, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 2.82-2.66 (m, 2H), 2.22-2.06 (m, 2H), 2.02-1.80 (m, 4H), 1.60-1.46 (m, 6H), 1.42-1.26 (m, 6H), 1.02-0.86 (m, 15H); ^{13}C NMR (75 MHz) δ 168.2, 142.4, 128.7, 128.4, 125.8, 47.2, 46.0, 37.6, 36.0, 29.3, 27.6, 26.0, 25.8, 24.8, 13.9, 10.6. HRMS (FAB-CI, NBA) Calcd. for $\text{C}_{26}\text{H}_{45}\text{NOSSn}$ $[\text{M}+\text{H}]^+$ 540.2322, found 540.2325.

O-[3-Hydroxyprop-1(*E*)-enyl] 1-pyrrolidinecarbothioate (2). Following literature procedure,⁷ transmetalation of stannane **8** using *n*-BuLi furnished β -elimination adduct **2** as a colorless oil (91%). TLC (SiO_2): ether, $R_f \sim 0.3$; ^1H NMR (300 MHz) δ 7.50 (dt, $J = 6.4, 1.2$ Hz, 1H), 5.15 (q, $J = 6.4$ Hz, 1H), 4.30 (dd, $J = 7.0, 1.5$ Hz, 2H), 3.75 (t, $J = 6.4$ Hz, 2H), 3.65 (t, $J = 7.0$ Hz, 2H), 2.12-1.90 (m, 4H); ^{13}C NMR (75 MHz) δ 181.8, 140.0, 111.5, 56.8, 52.5, 48.6, 25.9, 24.7. HRMS (FAB-CI, NBA) Calcd. for $\text{C}_8\text{H}_{13}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 188.0745, found 188.0746.

O-[1-Phenethyl-5-phenylpent-2(*E*)-enyl] 1-pyrrolidinecarbothioate (5). Cross-coupling of **3** with iodide **4** as described in the general procedure gave the title adduct as a colorless oil (84%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.34$; ^1H NMR (300 MHz) δ 7.32-7.12 (m, 10H), 5.74 (dt, $J = 15, 6.6$ Hz, 1H), 5.48 (ddt, $J = 15.3, 8.7, 1.2$ Hz, 1H), 4.07 (q, $J = 6.6$ Hz, 1H), 3.51 (t, $J = 6.9$ Hz, 2H), 3.34 (t, $J = 5.4$ Hz, 2H), 2.78-2.54 (m, 4H), 2.42-2.28 (m, 2H), 2.12-1.80 (m, 6H); ^{13}C NMR (75 MHz) δ 165.4, 142.0, 142.0, 131.9, 131.0, 128.7, 128.6, 128.5, 128.5, 126.0, 47.2, 46.9, 46.1, 37.3, 35.8, 34.4, 33.8,

25.8, 24.8. HRMS (FAB-Cl, NBA) Calcd. for $C_{24}H_{29}NOS$ $[M+H]^+$ 380.2048, found 380.2045.

O-[1-Phenethyl-5-phenylpent-2(Z)-enyl] 1-pyrrolidinecarbothioate (7). Cross-coupling of **3** with iodide **6** as described in the general procedure gave the title adduct as a colorless oil (83%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.37$; 1H NMR (300 MHz) δ 7.31-7.11 (m, 10 H), 5.54 (dt, $J = 10.7, 7.3$ Hz, 1H), 5.43 (apparent t, $J = 10.4$ Hz, 1H), 4.45-4.30 (m, 1H), 3.53 (t, $J = 6.7$ Hz, 2H), 3.33 (t, $J = 6.4$ Hz, 2H), 2.84-2.44 (m, 6H), 2.14-1.72 (m, 6H); ^{13}C NMR (75 MHz) δ 165.4, 142.0, 141.9, 131.4, 130.6, 128.8, 128.6, 128.5, 128.4, 126.0, 47.2, 46.1, 42.2, 38.2, 35.8, 33.7, 29.7, 25.8, 24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{24}H_{29}NOS$ $[M+H]^+$: 380.2048, found 380.2045.

O-[1(S)-(2,2-Dimethyl-[1,3]dioxolan-4(R)-yl)-5-phenylpent-2(E)-enyl] 1-pyrrolidinecarbothioate (9). Cross-coupling of **8** with iodide **4** as described in the general procedure gave the title adduct as a colorless oil (82%, >98% d.e.). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.17$; 1H NMR (300 MHz) δ 7.32-7.14 (m, 5H), 5.81 (dt, $J = 15.6, 6.4$ Hz, 1H), 5.57 (dd, $J = 15.3, 8.9$ Hz, 1H), 4.40-4.28 (m, 1H), 4.18 (dd, $J = 8.9, 4.9$ Hz, 1H), 4.02 (dd, $J = 8.6, 6.7$ Hz, 1H), 3.67 (dd, $J = 8.3, 6.7$ Hz, 1H), 3.51 (t, $J = 6.7, 1.2$ Hz, 2H), 3.35 (t, $J = 6.4$ Hz, 2H), 2.70 (t, $J = 7.6$ Hz, 2H), 2.37 (q, $J = 7.3$ Hz, 2H), 2.00-1.80 (m, 4H), 1.40 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz) δ 164.7, 141.9, 134.3, 128.7, 128.5, 126.3, 126.0, 110.0, 78.4, 67.7, 49.2, 47.4, 46.1, 35.6, 34.5, 26.4, 25.8, 25.6, 24.8; $[\alpha]_D^{20} +71.2$ (c 0.5, $CHCl_3$). HRMS (FAB-Cl, NBA) Calcd. for $C_{21}H_{29}NO_3S$ $[M+H]^+$ 376.1946, found 376.1947.

Chiral HPLC: Chiralcel OD (Daicel Chemical Ind. Ltd., 250×4.6 mm); flow rate: 0.5 mL/min.; $\lambda = 254$ nm; eluent: 8% isopropyl alcohol/hexanes; retention time: 14.6 min.

O-(2-Iodo-1-phenethyl-5-phenylpent-2(Z/E)-enyl) 1-pyrrolidinecarbothioate (11). Cross-coupling of **3** with diiodide **10** as described in the general procedure gave **11** as a colorless oil (78%; 4:1 Z/E); 76% yield (9:1 Z/E) at 0°C; 92% yield (4:1 Z/E) at rt using 2.5 equiv of **3** and 1 equiv of **10**.

Z-11: TLC (SiO_2), EtOAc/hexane (1:4), $R_f \sim 0.27$; 1H NMR (300 MHz) δ 7.32-7.10 (m, 10H), 5.99 (t, $J = 7.0$ Hz, 1H), 4.14 (apparent q, $J = 6.4$ Hz, 1H), 3.49 (t, $J = 6.9$ Hz, 2H), 3.42-3.24 (m, 2H), 2.80-2.68 (m, 2H), 2.62-2.40 (m, 4H), 2.16-1.78 (m, 6H); ^{13}C NMR (75 MHz) δ 164.3, 141.4, 141.3, 136.9, 128.7, 128.6, 128.5, 126.2, 126.1, 113.8, 55.5, 47.3, 46.0, 38.2, 37.9, 34.5, 33.5, 25.7, 24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{24}H_{28}INOS$ $[M+H]^+$: 506.1015, found 506.1013.

E-11: TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.3$; 1H NMR (300 MHz) δ 7.32-7.10 (m, 10H), 6.27 (t, $J = 7.3$ Hz, 1H), 4.31 (apparent q, $J = 6.4$ Hz, 1H), 3.51 (t, $J = 6.4$ Hz, 2H), 3.42-3.26 (m, 2H), 2.80-2.38 (m, 26H), 2.10-1.78 (m, 6H); ^{13}C NMR (75 MHz) δ 164.2, 142.8, 141.4, 141.2, 128.8, 128.7, 128.6, 126.2, 126.2, 108.3, 48.5, 47.5, 46.2, 39.0, 35.3, 33.6, 33.3, 25.8, 24.8. HRMS (FAB-I, NBA) Calcd. for $C_{24}H_{28}INOS$ $[M+H]^+$: 506.1015, found 506.1013.

O-(1-Cyclohex-1(E)-enyl-3-phenyl-propyl) 1-pyrrolidinecarbothioate (13). Cross-coupling of **3** with iodide **12** as described in the general procedure gave the title adduct as a colorless oil (73%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.33$; 1H NMR (400 MHz) δ 7.30-7.12 (m, 5H), 5.74 (s, 1H), 4.07 (t, $J = 8.1$ Hz, 1H), 3.50 (t, $J = 6.9$ Hz, 2H), 3.34 (t, $J = 6.4$ Hz, 2H), 2.72-2.54 (m, 2H), 2.12-1.96 (m, 4H), 1.96-1.80 (m, 4H), 1.70-1.48 (m, 4H); ^{13}C NMR (75 MHz) δ 166.0, 142.2, 136.9, 128.6, 128.5, 126.0, 124.8, 51.6, 47.3,

46.1, 36.3, 34.2, 26.1, 25.8, 25.5, 24.8, 23.0, 22.6. HRMS (FAB-Cl, NBA) Calcd. for $C_{20}H_{27}NOS$ $[M+H]^+$: 330.1892, found 330.1893.

O-[1-(6-Oxo-cyclohex-1-enyl)-3-phenylpropyl] 1-pyrrolidinecarbothioate (15). Cross-coupling of **3** with iodide **14** as described in the general procedure gave the title adduct as a colorless oil (66%). TLC (SiO₂): EtOAc/hexane (1:3.3), $R_f \sim 0.15$; ¹H NMR (400 MHz) δ 7.30-7.08 (m, 5H), 6.94 (t, $J = 4$ Hz, 1H), 4.38 (t, $J = 7.7$ Hz, 1H), 3.49 (t, $J = 6.6$ Hz, 2H), 3.40-3.26 (m, 2H), 2.75-2.66 (m, 1H), 2.60-2.48 (m, 1H), 2.44-2.30 (m, 4H), 2.24-2.08 (m, 2H), 2.20-1.78 (m, 6H); ¹³C NMR (75 MHz) δ 198.3, 166.0, 147.4, 141.8, 139.8, 128.6, 128.6, 125.9, 47.3, 45.9, 45.4, 38.9, 36.5, 34.5, 26.2, 25.8, 24.7, 22.9. HRMS (FAB-Cl, NBA) Calcd. for $C_{20}H_{25}NO_2S$ $[M+H]^+$: 344.1684, found 344.1686.

O-[1-(1-Phenethyl-3-phenyl-2(Z)-propenyl) 1-pyrrolidinecarbothioate (17). Cross-coupling of **3** with iodide **16** as described in the general procedure gave the title adduct as a colorless oil (87%). TLC (SiO₂): EtOAc/hexane (1:4), $R_f \sim 0.31$; ¹H NMR (300 MHz) δ 7.44-7.16 (m, 10H), 6.64 (d, $J = 15.6$ Hz, 1H), 6.26 (dd, $J = 15.8, 8.9$ Hz, 1H), 7.33 (apparent q, $J = 7.0$ Hz, 1H), 3.53 (t, $J = 6.7$ Hz, 2H), 3.37 (t, $J = 7.0$ Hz, 2H), 2.90-2.70 (m, 2H), 2.32-2.04 (m, 2H), 2.02-1.80 (m, 4H); ¹³C NMR (75 MHz) δ 165.0, 141.8, 137.1, 131.2, 130.3, 128.7, 128.6, 128.6, 127.7, 126.6, 126.1, 47.3, 47.2, 46.1, 36.9, 33.8, 25.7, 24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{22}H_{25}NOS$ $[M+H]^+$ 352.1735, found 352.1740.

O-1-(tri-*n*-Butylstannyl)propyl 1-pyrrolidinecarbothioate (18). The corresponding α -hydroxystannane⁸ (0.95 mmol; >98% e.e. based on ¹H NMR of the Mosher's ester⁸) was dissolved in CH₂Cl₂ (5 mL) containing DMAP (0.095 mmol) and thiocarbonyldiimidazole (1.41 mmol). After stirring for 3h at room temperature, the reaction mixture was filtered through a small bed of silica gel and the product was eluted with 10% EtOAc/hexane (30 mL). The imidazole in the thiocarbamate was exchanged by stirring in neat pyrrolidine (2 mL) for 2 h at room temperature. The excess pyrrolidine was evaporated in *vacuo*, and the residue was chromatographed using EtOAc/hexane (2:98) to give **18** (81%) as a colorless oil. TLC (SiO₂): EtOAc/hexane (1:4), $R_f \sim 0.66$; ¹H NMR (400 MHz) δ 5.49 (dd, $J = 7.6, 7.5$ Hz, 1H), 3.70 (t, $J = 6.8$ Hz, 2H), 3.55-3.38 (m, 2H), 2.02-1.84 (m, 6H), 1.56-1.40 (m, 6H), 1.34-1.22 (m, 6H), 0.96 (t, $J = 7.3$ Hz, 3H), 0.92-0.82 (m, 15H); ¹³C NMR (100 MHz) δ 185.6, 80.9, 52.0, 47.7, 29.3, 27.9, 27.7, 25.9, 24.8, 13.9, 12.3, 10.3; $[\alpha]_D^{20} +48.1$ (c 2.6, CHCl₃). HRMS (FAB-Cl, NBA) Calcd. for $C_{20}H_{41}NOSSn$ $[M+H]^+$ 464.2009, found 464.2011.

(R)-O-(1-Ethyl-3-phenyl-3(E)-propenyl) 1-pyrrolidinecarbothioate (19). Cross-coupling of **18** with iodide **16** as described in the general procedure gave the title adduct as a colorless oil in 85% yield (90% e.e.) at 23°C; in 76% yield (91% e.e.) at 0°C, and in 70% yield (95% e.e.) at -20°C. TLC (SiO₂): EtOAc/hexane (1:4), $R_f \sim 0.26$; ¹H NMR (100 MHz) δ 7.37 (d, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.19 (t, $J = 7.1$ Hz, 1H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.18 (dd, $J = 15.8, 8.8$ Hz, 1H), 4.18 (dd, $J = 15.6, 7.7$ Hz, 1H), 3.50 (t, $J = 6.8$ Hz, 2H), 3.34 (t, $J = 6.4$ Hz, 2H), 2.00-1.76 (m, 6H), 1.02 (t, $J = 7.3$ Hz, 3H); ¹³C NMR (100 MHz) δ 165.4, 137.3, 131.0, 130.5, 128.7, 127.6, 126.6, 49.1, 47.2, 46.1, 28.5, 25.8, 24.8, 12.2; $[\alpha]_D^{20} +145.2$ (c 0.65, CHCl₃). HRMS (FAB-Cl, NBA) Calcd. for $C_{16}H_{21}NOS$ $[M+H]^+$ 276.1422, found 276.1421.

Chiral HPLC: Chiralpak AD (Daicel Chemical Ind. Ltd., 250 × 4.6 mm); flow rate: 0.5 mL/min.; λ = 254 nm; eluent: 5% isopropyl alcohol/hexanes; retention times: 15.1 min. for (R)-enantiomer and 16.7 min for (S)-enantiomer.

PTC-ether **19** (30 mg) was stirred with oxone[®] (134 mg, 2 equiv) in CH₃CN/H₂O (2 mL, 5:2) at room temperature. After 3 h, the reaction mixture was diluted with ether (10 mL), dried over Na₂SO₄, and all volatiles removed in *vacuo*. The residues was purified by SiO₂ TLC (30% EtOAc/hexanes) to give (R)-1-phenylpent-1(E)-en-3-ol (14 mg, 72%) as a colorless oil, $[\alpha]_D^{20}$ +4.6 (*c* 0.7, CHCl₃); lit.⁹ for *S*-antipode, -5.7 (*c* 100, CHCl₃; 96% ee).

1-phenyl-4-(pyrrolidine-1-carbothioxyloxy)-hex-2(Z)-enoate (21). Cross-coupling of **3** with iodide **20** as described in the general procedure gave the title adduct as a colorless oil (81%). TLC (SiO₂): EtOAc/hexane (1:4), R_f ~ 0.23; ¹H NMR (400 MHz) δ 7.32-7.16 (m, 5H), 6.28 (dd *J* = 11.4, 10.6 Hz, 1H), 5.81 (dd, *J* = 11.4, 0.6 Hz, 1H), 5.25 (dd, *J* = 10.4, 7.3 Hz, 1H), 4.20 (q, *J* = 7.4 Hz, 2H), 3.50 (t, *J* = 6.2 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 2.90-2.75 (m, 1H), 2.75-2.68 (m, 1H), 2.23-2.11 (m, 1H), 2.12-1.99 (m, 1H), 1.98-1.80 (m, 4H); ¹³C NMR (75 MHz) δ 166.0, 164.7, 148.4, 141.8, 128.6, 128.5, 126.1, 120.2, 60.4, 47.2, 46.2, 42.9, 36.7, 33.8, 25.8, 24.8, 14.4. HRMS (FAB-Cl, NBA) Calcd. for C₁₉H₂₅NO₃S [M+H]⁺: 348.1633, found 348.1632.

O-1,3-Diphenylpropyl 1-pyrrolidinecarbothioate (23). Cross-coupling of **3**, added dropwise in THF over 30 min, with iodide **22** as described in the general procedure gave the title adduct as a colorless oil (65%). TLC (SiO₂): EtOAc/hexane (1:4), R_f ~ 0.23; ¹H NMR (400 MHz) δ 7.40-3.10 (m, 10H), 4.64 (dd, *J* = 8.8, 6.9 Hz, 1H), 3.60-3.38 (m, 2H), 3.38-3.22 (m, 2H), 2.74-2.62 (m, 1H), 2.62-2.50 (m, 1H), 2.44-2.32 (m, 1H), 2.32-2.18 (m, 1H), 2.06-1.76 (m, 4H); ¹³C NMR (75 MHz) δ 165.3, 142.6, 141.7, 128.8, 128.6, 128.5, 128.0, 127.4, 126.1, 48.9, 47.3, 46.0, 38.7, 34.1, 25.8, 24.7. HRMS (FAB-Cl, NBA) Calcd. for C₂₀H₂₃NOS [M+H]⁺: 326.1579, found 326.1580.

O-(S)-[[(R)-2,2-Dimethyl-1,3-dioxolan-4-yl]phenyl]methyl 1-pyrrolidinecarbothioate (24). Cross-coupling of **8** with iodide **22** as described in the general procedure gave the title adduct as a colorless oil (63%; >98% d.e.). TLC (SiO₂): EtOAc/hexane (1:4), R_f ~ 0.13; ¹H NMR (300 MHz) δ 7.42-7.22 (m, 5H), 4.77 (d, *J* = 7.0 Hz, 1H), 4.59 (q, *J* = 7.0 Hz, 1H), 4.11 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.78 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.56-3.44 (m, 2H), 3.42-3.26 (m, 2H), 1.98-1.78 (m, 4H), 1.35 (s, 3H), 1.34 (s, 3H); ¹³C NMR (75 MHz) δ 164.3, 139.6, 129.2, 128.6, 127.7, 110.3, 78.8, 68.0, 50.9, 47.6, 46.0, 26.6, 25.9, 25.7, 24.7; $[\alpha]_D^{20}$ +59.1 (*c* 0.6, CHCl₃). HRMS (FAB-Cl, NBA) Calcd. for C₁₇H₂₃NO₃S [M+H]⁺: 322.1477, found 322.1476.

Chiral HPLC: Chiralcel OD (Daicel Chemical Ind. Ltd., 250 × 4.6 mm); flow rate: 0.5 mL/min.; λ = 254 nm; eluent: 8% isopropyl alcohol/hexanes; retention time: 15.2 min.

O-1-(4-Fluorophenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (26). Cross-coupling of **3** with iodide **25** as described in the general procedure gave the title adduct as a colorless oil (70%). TLC (SiO₂): EtOAc/hexane (1:4), R_f ~ 0.3; ¹H NMR (400 MHz) δ 7.36-7.22 (m, 4H), 7.20-7.10 (m, 3H), 7.24-6.96 (m, 2H), 4.61 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.60-3.40 (m, 2H), 3.38-3.22 (m, 2H), 2.72-2.61 (m, 1H), 2.61-2.50 (m, 1H), 2.42-2.28 (m, 1H), 2.28-2.12 (m, 1H), 1.98-1.78 (m, 4H); ¹³C NMR (75 MHz) δ 165.1, 163.6, 160.4, 141.5, 138.6, 138.5, 129.6, 129.5, 128.6, 126.2, 115.7, 115.5, 48.1, 47.3, 46.1,

38.6, 34.1, 25.8, 24.7. HRMS (FAB-CI, NBA) Calcd. for $C_{20}H_{22}FNOS$ $[M+H]^+$ 344.1484, found 344.1485.

O-1-(4-Cyanophenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (28). Cross-coupling of **3** with iodide **27** as described in the general procedure gave the title adduct as a colorless oil (72%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.14$; 1H NMR (300 MHz) δ 7.61 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.32-7.08 (m, 5H), 4.64 (t, $J = 7.6$ Hz, 1H), 3.60-3.40 (m, 2H), 3.40-3.22 (m, 2H), 2.78-2.50 (m, 2H), 2.44-2.12 (m, 2H), 2.02-1.76 (m, 4H); ^{13}C NMR (75 MHz) δ 164.4, 148.9, 140.9, 132.6, 128.8, 128.7, 128.5, 126.4, 119.1, 111.0, 48.4, 47.4, 46.1, 37.7, 33.9, 25.7, 24.7. HRMS (FAB-CI, NBA) Calcd. for $C_{21}H_{22}N_2OS$ $[M+H]^+$ 351.1531, found 351.1530.

O-1-(4-Trifluoromethylphenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (30). Cross-coupling of **3** with iodide **29** as described in the general procedure gave the title adduct as a colorless oil (74%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.31$; 1H NMR (400 MHz) δ 7.57 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 7.32-7.10 (m, 5H), 4.67 (t, $J = 7.9$ Hz, 1H), 3.60-3.38 (m, 2H), 3.38-3.22 (m, 2H), 2.76-2.64 (m, 1H), 2.64-2.50 (m, 1H), 2.42-2.28 (m, 1H), 2.28-2.16 (m, 1H), 2.02-1.78 (m, 4H); ^{13}C NMR (75 MHz) δ 164.6, 147.2, 147.1, 141.2, 128.6, 128.6, 128.4, 126.3, 125.8, 125.7, 125.7, 125.6, 48.3, 47.4, 46.1, 38.1, 34.0, 25.8, 24.7. HRMS (FAB-CI, NBA) Calcd. for $C_{21}H_{22}F_3NOS$ $[M+H]^+$ 394.1453, found 394.1454.

O-(S)-[(R)-2,2-Dimethyl-1,3-dioxolan-4-yl](4-(trifluoromethyl)phenyl)methyl 1-pyrrolidinecarbothioate (31). Cross-coupling of **8** with iodide **29** as described in the general procedure gave the title adduct as a colorless oil (72%; >98% d.e.). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.11$; 1H NMR (300 MHz) δ 7.54 (apparent q, $J = 8.9$ Hz, 4H), 4.38 (d, $J = 7.3$ Hz, 1H), 4.58 (q, $J = 7.3$ Hz, 1H), 4.14 (dd, $J = 8.6, 6.4$ Hz, 1H), 3.78 (dd, $J = 8.6, 6.7$ Hz, 1H), 3.57-3.42 (m, 2H), 3.40-3.26 (m, 2H), 2.00-1.78 (m, 4H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz) δ 163.6, 144.1, 129.5, 125.5, 125.4, 117.6, 110.5, 78.3, 68.1, 50.7, 47.6, 46.1, 26.7, 25.8, 24.7; $[\alpha]_D^{20} +70$ (c 0.5, $CHCl_3$). HRMS (FAB-CI, NBA) Calcd. for $C_{18}H_{22}F_3NO_3S$ $[M+H]^+$ 390.1351, found 390.1349.

Chiral HPLC: Chiralcel OD (Daicel Chemical Ind. Ltd., 250×4.6 mm; flow rate: 0.5 mL/min.; $\lambda = 254$ nm; eluent: 8% isopropyl alcohol/hexanes; retention time: 14.0 min.

O-1-(4-Nitrophenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (33). Cross-coupling of **3** with iodide **32** as described in the general procedure gave the title adduct as a colorless oil (70%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.16$; 1H NMR (400 MHz) δ 8.16 (d, $J = 8.8$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.32-7.08 (m, 5H), 4.68 (t, $J = 7.9$ Hz, 1H), 3.56-3.38 (m, 2H), 3.38-3.22 (m, 2H), 2.76-2.64 (m, 1H), 2.64-2.52 (m, 1H), 2.42-2.28 (m, 1H), 2.28-2.16 (m, 1H), 2.02-1.78 (m, 4H); ^{13}C NMR (100 MHz) δ 164.2, 151.1, 147.0, 140.9, 128.9, 128.7, 128.5, 126.4, 124.0, 48.1, 47.4, 46.1, 37.6, 33.9, 25.7, 24.7. HRMS (FAB-CI, NBA) Calcd. for $C_{20}H_{22}N_2O_3S$ $[M+H]^+$ 371.1430, found 371.1431.

O-1-(2-Chlorophenyl)-3-phenylpropyl pyrrolidine-1-carbothioate (35). Cross-coupling of **3** with iodide **34** as described in the general procedure gave the title adduct as a colorless oil (61%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.31$; 1H NMR (300 MHz) δ 7.45 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.37 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.30-7.08 (m, 7H), 5.16 (t, $J = 7.6$ Hz, 1H), 3.51 (t, $J = 7.0$ Hz, 2H), 3.42-3.26 (m, 2H), 2.82-2.68 (m, 1H), 3.64-2.48 (m, 1H), 2.46-2.22 (m, 2H), 2.02-1.78 (m, 4H); ^{13}C NMR (75 MHz) δ 164.9, 141.7, 139.7, 133.9, 130.1, 129.6, 128.6, 128.5, 128.5, 127.2, 126.0, 47.3, 46.0, 38.4, 33.9, 25.8,

24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{20}H_{22}ClNOS$ $[M+H]^+$ 360.1189, found 360.1191.

O-1-(2-Benzoylphenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (37). Cross-coupling of **3** with iodide **36** as described in the general procedure gave the title adduct as a colorless oil (77%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.27$; 1H NMR (400 MHz) δ 7.84 (apparent d, $J = 6.9$ Hz, 2H), 7.56 (apparent t, $J = 8.4$ Hz, 2H), 7.52-7.38 (m, 3H), 7.32-7.18 (m, 4H), 7.18-7.08 (m, 3H), 4.88 (t, $J = 7.5$ Hz, 1H), 3.42-3.28 (m, 2H), 3.28-3.16 (m, 1H), 3.14-3.02 (m, 1H), 2.82-2.68 (m, 1H), 2.58-2.46 (m, 1H), 2.36-2.24 (m, 2H), 1.92-1.70 (m, 4H); ^{13}C NMR (75 MHz) δ 198.3, 164.6, 142.2, 141.9, 138.6, 138.1, 133.1, 130.7, 130.6, 129.1, 128.9, 128.6, 128.4, 128.4, 126.4, 125.9, 47.1, 46.2, 45.9, 39.2, 34.2, 25.7, 24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{27}H_{27}NO_2S$ $[M+H]^+$: 430.1841, found 430.1836.

O-(S)-(2-Benzoylphenyl)((R)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl 1-pyrrolidinecarbothioate (38). Cross-coupling of **8** with iodide **36** as described in the general procedure gave the title adduct as a colorless oil (75%; >98% d.e.). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.11$; 1H NMR (400 MHz) δ 7.82 (d, $J = 7.1$ Hz, 2H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.50-7.38 (m, 3H), 7.32-7.20 (m, 2H), 5.14 (d, $J = 7.3$ Hz, 1H), 4.61 (q, $J = 6.6$ Hz, 1H), 4.13 (dd, $J = 8.6, 6.2$ Hz, 1H), 3.74 (dd, $J = 8.6, 7.3$ Hz, 1H), 3.38 (t, $J = 6.7$ Hz, 2H), 3.32-3.10 (m, 2H), 1.92-1.70 (m, 4H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz) δ 198.4, 163.8, 139.4, 138.8, 138.1, 133.1, 131.4, 130.8, 130.4, 129.0, 128.2, 126.5, 109.9, 79.1, 68.3, 47.4, 47.2, 45.9, 26.3, 25.9, 25.7, 24.7; $[\alpha]_D^{20} +60$ (c 1.2, $CHCl_3$). HRMS (FAB-Cl, NBA) Calcd. for $C_{24}H_{27}NO_4S$ $[M+H]^+$ 426.1739, found 426.1738.

Chiral HPLC: Chiralcel OD (Daicel Chemical Ind. Ltd., 250×4.6 mm; flow rate: 0.5 mL/min.; $\lambda = 254$ nm; eluent: 8% isopropyl alcohol/hexanes; retention time: 14.8 min.

O-1-(2-Nitrophenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (40). Cross-coupling of **3** with iodide **39** as described in the general procedure gave the title adduct as a colorless oil (72%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.18$; 1H NMR (400 MHz) δ 7.79 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.63 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.54 (dt, $J = 7.5, 1.1$ Hz, 1H), 7.34 (dt, $J = 8.3, 1.3$ Hz, 1H), 7.30-7.12 (m, 5H), 5.23 (t, $J = 7.7$ Hz, 1H), 3.50-3.36 (m, 2H), 3.36-3.20 (m, 2H), 2.98-2.86 (m, 1H), 2.70-2.58 (m, 1H), 2.31 (q, $J = 8.8$ Hz, 2H), 2.00-1.76 (m, 4H); ^{13}C NMR (75 MHz) δ 164.3, 149.6, 141.5, 138.6, 132.9, 130.5, 128.6, 128.5, 127.8, 126.2, 124.4, 47.4, 46.1, 44.3, 38.0, 34.2, 25.8, 24.7. HRMS (FAB-Cl, NBA) Calcd. for $C_{20}H_{22}N_2O_3S$ $[M+H]^+$: 371.1429, found 371.1428.

O-1-(3-Cyanophenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (42). Cross-coupling of **3** with iodide **41** as described in the general procedure gave the title adduct as a colorless oil (64%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.14$; 1H NMR (300 MHz) δ 7.67 (t, $J = 1.8$ Hz, 1H), 7.60 (dt, $J = 7.6, 1.5$ Hz, 1H), 7.52 (dt, $J = 7.9, 1.2$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.32-7.08 (m, 5H), 4.62 (t, $J = 7.9$ Hz, 1H), 3.60-3.40 (m, 2H), 3.40-3.22 (m, 2H), 2.78-2.50 (m, 2H), 2.42-2.12 (m, 2H), 2.02-1.76 (m, 4H); ^{13}C NMR (75 MHz) δ 164.3, 145.0, 141.0, 132.7, 131.6, 130.9, 129.5, 128.7, 128.5, 126.4, 119.0, 112.8, 48.0, 47.4, 46.1, 37.9, 34.0, 25.8, 24.8. HRMS (FAB-Cl, NBA) Calcd. for $C_{21}H_{22}N_2OS$ $[M+H]^+$ 351.1531, found 351.1530.

O-1-(4-Methoxyphenyl)-3-phenylpropyl 1-pyrrolidinecarbothioate (44). Cross-coupling of **3** with iodide **43** as described in the general procedure gave the title adduct as a colorless oil (60%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.29$; 1H NMR (300 MHz) δ

7.32-7.08 (m, 7H), 6.90-6.82 (m, 2H), 4.60 (dd, $J = 9.2, 6.7$ Hz, 1H), 3.80 (s, 3H), 3.56-3.42 (m, 2H), 3.36-3.22 (m, 2H), 2.74-2.48 (m, 2H), 2.42-2.14 (m, 2H), 2.00-1.76 (m, 4H); ^{13}C NMR (75 MHz) δ 165.5, 158.8, 141.8, 134.5, 129.1, 128.6, 128.5, 126.1, 114.2, 55.5, 48.4, 47.3, 46.1, 38.8, 34.2, 25.8, 24.8. HRMS (FAB-ESI, NBA) Calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 356.1684, found 356.1686.

O-1-(1H-Indol-6-yl)-3-phenylpropyl 1-pyrrolidinecarbothioate (46). Cross-coupling of **3** with iodide **45** as described in the general procedure gave the title adduct as a colorless oil (60%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.13$; ^1H NMR (400 MHz) δ 8.16 (br s, 1H), 7.64 (s, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.30-7.08 (m, 7H), 6.55-6.49 (m, 1H), 4.76 (dd, $J = 9.3, 6.2$ Hz, 1H), 3.58-3.40 (m, 2H), 3.38-3.20 (m, 2H), 2.76-2.62 (m, 1H), 2.62-2.52 (m, 1H), 2.52-2.40 (m, 1H), 2.40-2.24 (m, 1H), 1.96-1.74 (m, 4H); ^{13}C NMR (100 MHz) δ 165.8, 142.1, 135.3, 133.6, 128.6, 128.5, 128.2, 125.9, 124.8, 122.3, 120.0, 111.4, 103.0, 49.6, 47.2, 46.0, 39.4, 34.3, 25.8, 24.8. HRMS (FAB-ESI, NBA) Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 365.1688, found 365.1686.

O-3-Phenyl-1-(thiophen-2-yl)propyl 1-pyrrolidinecarbothioate (48). Cross-coupling of **3** with iodide **47** as described in the general procedure gave the title adduct as a colorless oil (61%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.3$; ^1H NMR (300 MHz) δ 7.35-7.13 (m, 6H), 7.04 (dt, $J = 3.6, 0.6$ Hz, 1H), 6.94 (dd, $J = 4.9, 3.4$ Hz, 1H), 4.98 (dd, $J = 8.2, 6.7$ Hz, 1H), 3.52 (t, $J = 6.7$ Hz, 2H), 3.32 (t, $J = 6.7$ Hz, 2H), 2.84-2.58 (m, 2H), 2.50-2.22 (m, 2H), 2.04-1.78 (m, 4H); ^{13}C NMR (75 MHz) δ 164.9, 146.2, 141.5, 128.6, 128.6, 126.9, 126.1, 125.5, 124.6, 47.3, 46.0, 44.2, 39.8, 34.1, 25.8, 25.8, 24.8. HRMS (FAB-ESI, NBA) Calcd. for $\text{C}_{18}\text{H}_{21}\text{NOS}_2$ $[\text{M}+\text{H}]^+$: 332.1143, found 332.1145.

O-1-(1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-3-phenylpropyl 1-pyrrolidinecarbothioate (50). Cross-coupling of **3** with iodide **49** as described in the general procedure gave the title adduct as a colorless oil (68%). TLC (SiO_2): EtOAc/hexane (1:4), $R_f \sim 0.15$; ^1H NMR (300 MHz) δ 7.30-7.08 (m, 6H), 4.33 (t, $J = 7.9$ Hz, 1H), 3.56-3.42 (m, 2H), 3.38-3.28 (m, 2H), 3.33 (s, 3H), 3.31 (s, 3H), 2.80-2.54 (m, 2H), 2.48-2.30 (m, 2H), 2.00-1.74 (m, 4H); ^{13}C NMR (75 MHz) δ 166.0, 162.6, 151.7, 141.3, 141.1, 128.7, 128.6, 126.2, 113.6, 47.4, 46.1, 44.4, 37.2, 34.6, 34.5, 28.1, 25.8, 24.8. HRMS (FAB-ESI, NBA) Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 388.1695, found 388.1697.

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