SUPPORTING INFORMATION

Benzotriazolyl-mediated 1,2-Shifts of Electron-rich Heterocycles.

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General. Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in CDCl_3 , acetone- d_6 or DMSO- d_6 as solvents with TMS as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C (75 MHz). THF was dried over sodium / benzophenone and used freshly distilled. Column chromatography was conducted on silica gel 200–425 meshes.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(methylthio)-2-(2-thienyl)-2-propanol (3a) (one diastereomer): microcrystals from acetone-diethyl ether (41%); mp 138–139 °C; ^1H NMR (CDCl_3): δ 7.95 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.45–7.40 (m, 1H), 7.35–7.29 (m, 1H), 7.00 (dd, J = 4.7, 1.4 Hz, 1H), 6.76–6.68 (m, 2H), 6.03 (s, 1H), 4.09 (s, 1H), 2.02 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (CDCl_3): δ 148.3, 145.6, 132.8, 127.3, 126.7, 124.8, 124.1, 123.9, 119.7, 111.9, 77.4, 75.7, 29.0, 14.7. **(Mixture of two diastereomers):** colorless oil (82%); ^1H NMR (CDCl_3): δ 8.06 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.47–7.30 (m, 4H), 7.28–7.25 (m, 1H), 7.01 (dd, J = 4.6, 1.6 Hz, 1H), 6.97–6.95 (m, 2H), 6.73–6.68 (m, 2H), 6.07 (s, 1H), 6.02 (s, 1H), 3.88 (s, 1H), 3.29 (s, 1H), 2.02 (s, 3H), 1.94 (s, 3H), 1.84 (s, 3H), 1.57 (s, 1H), (double set of signals); ^{13}C NMR (CDCl_3): δ 148.8, 148.3, 146.2, 145.6, 132.8, 132.5, 127.3, 127.2, 127.1, 126.7, 124.9, 124.8, 124.2, 124.1, 123.9, 123.8, 119.7, 119.7, 112.9, 112.1, 77.3, 77.3, 77.1, 75.8, 29.0, 28.8, 14.9, 14.7, (double set of signals). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{OS}_2$: C, 55.06; H, 4.95; N, 13.76. Found: C, 55.25; H, 5.14; N, 13.85.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(methylthio)-2-(3-thienyl)-2-propanol (3b) (mixture of two diastereomers): microcrystals from diethyl ether (88 %), mp 118–122 °C; ^1H NMR (CDCl_3): δ 8.03 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.83 (d, J =

8.1 Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.45–7.35 (m, 3H), 7.33–7.26 (m, 3H), 7.10 (dd, $J = 4.7, 1.7$ Hz, 1H), 7.05 (dd, $J = 5.0, 3.0$ Hz, 1H), 6.91 (dd, $J = 3.0, 1.4$ Hz, 1H), 6.83 (dd, $J = 5.1, 1.4$ Hz, 1H), 6.07 (s, 1H), 6.04 (s, 1H), 3.74 (s, 1H), 3.30 (s, 1H), 1.93 (s, 3H), 1.91 (s, 3H), 1.78 (s, 3H), 1.50 (s, 3H), (double set of signals); ^{13}C NMR (CDCl_3): δ 146.3, 145.7, 145.6, 145.3, 132.6, 132.5, 127.3, 127.1, 126.3, 126.0, 125.3, 124.9, 124.2, 124.0, 121.6, 121.2, 119.8, 119.7, 112.8, 112.1, 76.9, 75.7, 28.2, 28.0, 14.7, 14.6, (double set of signals). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{OS}_2$: C, 55.06; H, 4.95; N, 13.76. Found: C, 55.35; H, 5.03; N, 13.80.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(1-methyl-1*H*-indol-3-yl)-1-(methylthio)-2-propanol (3c) (one diastereomer): microcrystals from acetone–diethyl ether (41 %), mp 186–187 °C; ^1H NMR (CDCl_3): δ 8.07–8.04 (m, 1H), 7.90–7.86 (m, 2H), 7.43–7.24 (m, 4H), 7.21–7.16 (m, 1H), 7.07 (s, 1H), 6.42 (s, 1H), 3.74 (s, 3H), 3.11 (s, 1H), 1.75 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (CDCl_3): δ 146.3, 137.6, 132.8, 127.1, 126.8, 124.9, 124.1, 121.8, 120.1, 119.8, 119.6, 118.3, 112.8, 109.8, 76.7, 75.7, 32.8, 27.5, 14.7. **(Mixture of two diastereomers):** colorless oil (82 %); ^1H NMR (CDCl_3): δ 8.06–8.03 (m, 1H), 7.92–7.86 (m, 3H), 7.78–7.74 (m, 1H), 7.56–7.53 (m, 1H), 7.42–7.32 (m, 3H), 7.31–7.23 (m, 4H), 7.22–7.15 (m, 3H), 7.10–7.04 (m, 2H), 6.78 (s, 1H), 6.40 (s, 1H), 6.35 (s, 1H), 3.72 (s, 3H), 3.64 (s, 1H), 3.53 (s, 3H), 3.13 (s, 1H), 2.05 (s, 3H), 1.86 (s, 3H), 1.74 (s, 3H), 1.56 (3H), (double set of signals); ^{13}C NMR (CDCl_3): δ 146.3, 145.5, 137.6, 137.3, 133.2, 132.8, 127.1, 127.0, 126.8, 126.7, 124.9, 124.7, 124.1, 123.8, 121.8, 121.6, 120.1, 119.9, 119.8, 119.6, 119.6, 119.3, 118.3, 118.0, 112.8, 111.6, 109.8, 109.6, 76.7, 75.7, 74.3, 32.8, 32.6, 27.5, 27.5, 14.7 (double set of signals). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{OS}$: C, 64.75; H, 5.72; N, 15.90. Found: C, 64.94; H, 5.84; N, 15.70.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(2-furyl)-1-(methylthio)-2-propanol (3d) (first diastereomer): microcrystals from acetone–diethyl ether (37%), mp 127–128 °C; ¹H NMR (CDCl₃): δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45–7.39 (m, 1H), 7.35–7.29 (m, 1H), 7.13 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.13 (s, 1H), 6.08 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.03 (dd, *J* = 3.4, 0.8 Hz, 1H), 3.96 (s, 1H), 1.96 (s, 3H), 1.87 (s, 3H); ¹³C NMR (CDCl₃): δ 155.5, 145.6, 141.9, 132.8, 127.3, 124.1, 119.8, 111.4, 110.4, 106.7, 75.3, 73.7, 25.2, 14.7. Anal. Calcd for C₁₄H₁₅N₃O₂S: C, 58.11; H, 5.23; N, 14.52. Found: C, 58.25; H, 5.42; N, 14.63. **(Second diastereomer):** colorless oil (35 %); ¹H NMR (CDCl₃): δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.49–7.33 (m, 3H), 6.40–6.36 (m, 2H), 6.25 (s, 1H), 3.37 (s, 1H), 1.84 (s, 3H), 1.46 (s, 3H); ¹³C NMR (CDCl₃): δ 155.9, 146.1, 141.9, 132.3, 127.1, 124.1, 119.4, 113.3, 110.5, 106.5, 75.4, 74.9, 25.7, 14.5.

2-(1-Benzofuran-2-yl)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-(methylthio)-2-propanol (3e) (mixture of two diastereomers): microcrystals from diethyl ether (75 %), mp 141–142 °C; ¹H NMR (CDCl₃): δ 8.07–8.02 (m, 2H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.57–7.54 (m, 1H), 7.49–7.20 (m, 9H), 7.16–7.05 (m, 2H), 6.85 (s, 1H), 6.46 (s, 1H), 6.41 (s, 1H), 6.27 (s, 1H), 4.41 (s, 1H), 3.89 (s, 1H), 1.98 (s, 3H), 1.96 (s, 3H), 1.84 (s, 3H), 1.46 (s, 3H), (double set of signals); ¹³C NMR (DMSO-*d*₆): δ 160.4, 160.0, 154.2, 154.1, 146.0, 145.5, 132.4, 132.2, 127.9, 127.5, 126.9, 126.6, 124.1, 124.1, 124.0, 123.8, 122.9, 122.7, 121.1, 121.0, 119.1, 118.9, 114.3, 114.3, 111.2, 110.9, 103.3, 102.9, 74.6, 74.5, 74.4, 25.6, 25.4, 14.0, 13.9, (double set of signals). Anal. Calcd for C₁₈H₁₇N₃O₂S: C, 63.70; H, 5.05; N, 12.38. Found: C, 63.68; H, 5.04; N, 12.36.

2-(1-Benzothiophen-2-yl)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-(methylthio)-2-

propanol (3f) (mixture of two diastereomers): microcrystals from diethyl ether–acetone (94 %), mp 139–140 °C; ¹H NMR (CDCl₃): δ 8.06 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.83–7.70 (m, 3H), 7.62–7.59 (m, 1H), 7.52–7.49 (m, 1H), 7.47–7.14 (m, 9H), 7.02 (s, 1H), 6.17 (s, 1H), 6.11 (s, 1H), 4.37 (s, 1H), 3.64 (s, 1H), 2.05 (s, 3H), 1.94 (s, 3H), 1.82 (s, 3H), 1.5 (s, 3H), (double set of signals); ¹³C NMR (CDCl₃): δ 149.4, 149.1, 146.3, 145.4, 139.6, 139.3, 139.2, 139.0, 132.9, 132.5, 127.5, 127.4, 124.4, 124.4, 124.3, 124.2, 124.2, 124.2, 123.6, 123.5, 122.3, 122.0, 120.7, 120.6, 119.8, 119.8, 113.0, 111.6, 77.7, 77.7, 76.7, 74.6, 29.1, 28.8, 14.9, 14.7, (double set of signals). Anal. Calcd for C₁₈H₁₇N₃OS₂: C, 60.82; H, 4.82; N, 11.82. Found: C, 60.77; H, 4.74; N, 11.77.

2-(1-Benzothiophen-3-yl)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-(methylthio)-2-

propanol (3g) (first diastereomer): microcrystals from diethyl ether–acetone (20%); mp 159–160 °C; ¹H NMR (CDCl₃): δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.41–7.36 (m, 1H), 7.33–7.24 (m, 3H) 7.21 (s, 1H), 6.47 (s, 1H), 4.01 (s, 1H), 2.12 (s, 3H), 1.89 (s, 3H); ¹³C NMR (CDCl₃): δ 145.4, 141.3, 138.6, 135.7, 132.9, 127.3, 124.0, 124.0, 123.2, 123.1, 119.9, 111.0, 78.1, 73.1, 26.8, 14.7. Anal. Calcd for C₁₈H₁₇N₃OS₂: C, 60.82; H, 4.82; N, 11.82. Found: C, 60.92; H, 4.78; N, 11.65. **(Second diastereomer):** colorless oil (20%); δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.41–7.33 (m, 2H), 7.30–7.25 (m, 2H), 7.23 (s, 1H), 6.49 (s, 1H), 5.41 (s, 1H), 2.09 (s, 3H), 1.80 (s, 3H); ¹³C NMR (CDCl₃): δ 145.5, 140.7, 139.2, 136.0, 132.5, 126.6, 123.6, 123.6, 123.6, 122.6, 119.1, 112.7, 77.1, 74.5, 26.5, 14.3.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(methylthio)-1-phenyl-1-(2-thienyl)-1-ethanol

(3h) (mixture of two diastereomers): microcrystals from diethyl ether (75%); mp 182–183 °C; ¹H NMR (CDCl₃): δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.93–7.83 (m, 3H), 7.79–7.76 (m, 2H), 7.54–7.26 (m, 11H), 7.05–6.95 (m, 5H), 6.73 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.67 (s, 1H), 6.62 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.56 (s, 1H), 4.92 (s, 1H), 4.57 (s, 1H), 1.95 (s, 3H), 1.82 (s, 3H), (double set of signals); ¹³C NMR (DMSO-*d*₆): δ 149.9, 149.1, 145.7, 145.4, 144.0, 143.2, 132.7, 132.1, 128.0, 127.4, 127.2, 127.0, 126.7, 126.6, 126.2, 125.8, 125.4, 125.3, 124.7, 124.4, 123.8, 123.8, 119.5, 118.9, 118.8, 114.9, 114.4, 111.6, 80.3, 80.2, 75.8, 75.5, 14.1, 14.0, (double set of signals). Anal. Calcd for C₁₉H₁₇N₃OS₂: C, 62.10; H, 4.66; N, 11.43. Found: C, 62.35; H, 4.30; N, 11.33.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(2-furyl)-2-(methylthio)-1-phenyl-1-ethanol (3i)

(mixture of two diastereoisomers): microcrystals from diethyl ether–acetone (40%); mp 170–172 °C; ¹H NMR (CDCl₃): δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.95–7.88 (m, 2H), 7.83–7.76 (m, 3H), 7.50–7.28 (m, 10H), 7.03–6.99 (m, 4H), 6.74 (s, 1H), 6.63 (d, *J* = 3.3, Hz 1H), 6.56 (s, 1H), 6.46 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.14 (d, *J* = 3.3 Hz, 1H), 6.01 (dd, *J* = 3.3, 1.9 Hz, 1H), 4.70 (s, 1H), 4.32 (s, 1H), 1.92 (s, 3H), 1.81 (s, 3H), (double sets of signals); ¹³C NMR (CDCl₃): δ 155.0, 155.0, 145.7, 145.4, 142.2, 142.1, 140.5, 140.4, 133.1, 132.7, 128.4, 128.2, 128.0, 127.8, 127.6, 127.4, 125.6, 124.7, 124.3, 124.0, 120.0, 119.8, 111.9, 111.1, 110.9, 110.4, 107.5, 107.4, 79.7, 79.1, 73.1, 72.6, 14.7 (double sets of signals). Anal. Calcd for C₁₉H₁₇N₃O₂S: C, 64.94; H, 4.88; N, 11.96. Found: C, 65.05; H, 4.85; N, 12.01.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(1-methyl-1*H*-indol-3-yl)-2-(methylthio)-1-

phenyl-1-ethanol (3j) (one diastereomer): microcrystals from diethyl ether (36%); mp

119–120 °C; ^1H NMR (CDCl_3): δ 7.79 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.67–7.64 (m, 2H), 7.41–7.25 (m, 7H), 7.15–7.04 (m, 2H), 6.88–6.82 (m, 1H), 6.69 (s, 1H), 3.64 (s, 3H), 3.58 (s, 1H), 1.72 (s, 3H); ^{13}C NMR (CDCl_3): δ 146.1, 143.0, 137.0, 133.0, 128.0, 127.6, 127.2, 127.0, 126.4, 125.7, 124.1, 121.9, 120.7, 119.7, 119.4, 117.1, 112.9, 109.3, 80.0, 75.3, 32.8, 14.7. (**Mixture of two diastereomers**): colorless oil (72%); ^1H NMR ($\text{DMSO}-d_6$ – CDCl_3): δ 8.35 (d, J = 8.4 Hz, 1H), 7.96–7.84 (m, 2H), 7.83 (d, J = 8.2 Hz, 1H), 7.70–7.67 (m, 3H), 7.48–7.10 (m, 15H), 7.03–6.98 (m, 1H), 6.93–6.85 (m, 5H), 6.77–6.73 (m, 2H), 5.81 (s, 1H), 5.54 (s, 1H), 3.86 (s, 3H), 3.62 (s, 3H), 1.84 (s, 3H), 1.70 (s, 3H), (double set of signals); ^{13}C NMR ($\text{DMSO}-d_6$ – CDCl_3): δ 145.6, 145.5, 143.2, 142.7, 136.6, 136.3, 132.5, 131.8, 127.2, 126.9, 126.6, 126.6, 126.4, 126.1, 125.9, 125.9, 125.7, 125.4, 125.1, 123.3, 123.1, 121.1, 121.0, 120.9, 120.7, 118.6, 118.5, 118.3, 118.3, 117.1, 117.0, 114.2, 113.5, 108.7, 108.4, 78.7, 78.6, 76.0, 75.1, 32.4, 32.2, 14.0, 13.7, (double set of signals). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{OS}$: C, 69.54; H, 5.35; N, 13.52. Found: C, 69.83; H, 5.49; N, 13.94.

1-(1-Benzofuran-2-yl)-2-(1*H*-1,2,3-benzotriazol-1-yl)-2-(methylthio)-1-phenyl-1-ethanol (3k) (mixture of two diastereomers): microcrystals from diethyl ether (70%); mp 88–90 °C; ^1H NMR (CDCl_3): δ 7.97–7.88 (m, 5H), 7.82 (d, J = 8.4 Hz, 1H), 7.61–7.59 (m, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.51–7.36 (m, 7H), 7.34–7.27 (m, 5H), 7.17 (d, J = 8.1 Hz, 1H), 7.11–7.08 (m, 1H), 7.05–6.98 (m, 5H), 6.88 (s, 1H), 6.71 (s, 1H), 6.64 (s, 1H), 5.10 (s, 1H), 4.68 (s, 1H), 1.95 (s, 3H), 1.85 (s, 3H), (double set of signals); ^{13}C NMR (CDCl_3): δ 157.7, 157.6, 154.8, 154.4, 145.6, 145.2, 140.2, 140.1, 133.2, 132.9, 128.5, 128.4, 128.1, 128.1, 128.0, 127.8, 127.6, 127.5, 125.6, 124.7, 124.5, 124.4, 124.2, 124.2, 123.2, 122.8, 121.5, 121.3, 120.1, 119.9, 111.5, 111.3, 110.8, 110.7, 104.3, 104.1,

80.0, 79.3, 72.2, 71.8, 14.8, 14.8, (double set of signals). Anal. Calcd for $C_{23}H_{19}N_3O_2S$: C, 68.81; H, 4.77; N, 10.47. Found: C, 68.74; H, 4.79; N, 10.51.

1-(1-Benzothiophen-2-yl)-2-(1*H*-1,2,3-benzotriazol-1-yl)-2-(methylthio)-1-phenyl-1-ethanol (3l) (mixture of two diastereomers): microcrystals from diethyl ether (98%); mp 165–166 °C; 1H NMR ($CDCl_3$): δ 8.01–7.90 (m, 3H), 7.84–7.75 (m, 5H), 7.55–7.29 (m, 15H), 7.19–7.13 (m, 2H), 7.09 (s, 1H), 7.05–6.97 (m, 2H), 6.77 (s, 1H), 6.65 (s, 1H), 5.31 (s, 1H), 4.83 (s, 1H), 1.97 (s, 3H), 1.84 (s, 3H), (double set of signals); ^{13}C NMR ($CDCl_3$): δ 149.1, 148.7, 145.5, 145.4, 141.9, 141.7, 139.6, 139.3, 139.3, 139.0, 133.3, 132.7, 128.45, 128.2, 128.0, 128.0, 127.8, 127.7, 125.5, 124.7, 124.6, 124.5, 124.5, 124.3, 124.2, 124.1, 123.9, 123.6, 122.2, 122.0, 121.8, 120.8, 120.2, 120.0, 111.5, 111.0, 81.5, 81.2, 74.0, 72.8, 14.9, 14.8, (double set of signals). Anal. Calcd for $C_{23}H_{19}N_3OS_2$: C, 66.16; H, 4.59; N, 10.06. Found: C, 66.05; H, 4.51; N, 10.10.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(methylthio)-1-phenyl-1-(3-thienyl)-1-ethanol (3m) (mixture of two diastereomers): microcrystals from diethyl ether–hexane (50%); mp 189–190 °C; 1H NMR ($DMSO-d_6$): δ 8.40 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.89–7.83 (m, 4H), 7.53–7.45 (m, 3H), 7.43–7.29 (m, 4H), 7.23–7.15 (m, 3H), 7.11–7.06 (m, 3H), 7.00–6.94 (m, 3H), 6.84–6.78 (m, 3H), 3.38 (s, 1H), 1.80 (s, 3H), 1.72 (s, 3H), (double set of signals); ^{13}C NMR ($DMSO-d_6$): δ 146.4, 145.9, 145.6, 145.6, 144.3, 143.5, 132.6, 132.2, 127.9, 127.5, 127.3, 127.1, 126.7, 126.5, 126.4, 126.4, 126.0, 125.5, 125.3, 125.3, 123.8, 123.7, 122.0, 121.4, 118.8, 118.7, 115.0, 114.9, 80.3, 80.3, 75.6, 75.1, 13.9, 13.9, (double set of signals). Anal. Calcd for $C_{19}H_{17}N_3OS_2$: C, 62.10; H, 4.66; N, 11.43. Found: C, 61.77; H, 4.87; N, 11.23.

(±)-1-(Methylthio)-1-(2-thienyl)acetone (4a): colorless oil (60%); ^1H NMR (CDCl_3): δ 7.29 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.09–7.07 (m, 1H), 6.99 (dd, $J = 5.1, 3.6$ Hz, 1H), 4.78 (s, 1H), 2.32 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (CDCl_3): δ 201.1, 137.7, 127.0, 126.8, 126.1, 54.6, 26.6, 14.0. Anal. Calcd for $\text{C}_8\text{H}_{10}\text{OS}_2$: C, 51.58; H, 5.41; Found: C, 51.85; H, 5.60. The spectral data of this compound is identical to that reported in the literature.ⁱ⁾

(±)-1-(Methylthio)-1-(3-thienyl)acetone (4b): colorless oil (64%); ^1H NMR (CDCl_3): δ 7.36–7.31 (m, 2H), 7.08–7.06 (m, 1H), 4.58 (s, 1H), 2.25 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (CDCl_3): δ 202.3, 135.3, 127.3, 126.2, 123.6, 55.4, 26.6, 14.0. Anal. Calcd for $\text{C}_8\text{H}_{10}\text{OS}_2$: C, 51.58; H, 5.41; Found: C, 51.83; H, 5.48.

(±)-1-(1-Benzofuran-2-yl)-1-(methylthio)acetone (4e): colorless oil (40%); ^1H NMR (CDCl_3): δ 7.57–7.54 (m, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.31–7.19 (m, 2H), 6.87 (s, 1H), 4.66 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (CDCl_3): δ 199.6, 154.8, 150.7, 128.0, 124.5, 123.0, 121.0, 111.2, 106.4, 52.6, 27.1, 13.8. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}$: C, 65.43; H, 5.49; Found: C, 65.73; H, 5.50;

(±)-1-(1-Benzothiophen-2-yl)-1-(methylthio)acetone (4f): colorless oil (40%); ^1H NMR (CDCl_3): δ 7.80–7.77 (m, 1H), 1.74–7.70 (m, 1H), 7.35–7.30 (m, 3H), 4.81 (s, 1H), 2.36 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (CDCl_3): δ 200.8, 139.9, 139.2, 138.9, 124.5, 124.4, 124.0, 123.5, 122.2, 55.3, 27.0, 14.1. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{OS}_2$: C, 60.98; H, 5.12; Found: C, 60.75; H, 5.09;

ⁱ⁾ Tamura, Y.; Dae Choi, H.; Mizutani, M.; Ueda, Y.; Ishibashi, H. *Chem. Pharm. Bull.* **1982**, *30*, 3574.

(±)-1-(1-Benzothiophen-3-yl)-1-(methylthio)acetone (4g): yellow oil (71%); ^1H NMR (CDCl_3): δ 7.88–7.85 (m, 1H), 7.79–7.76 (m, 1H), 7.66 (s, 1H), 7.40–7.37 (m, 1H), 4.81 (s, 1H), 2.22 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (CDCl_3): δ 202.0, 140.2, 137.4, 128.9, 125.6, 124.8, 124.4, 122.9, 121.7, 53.9, 26.4, 14.1. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{OS}_2$: C, 60.98; H, 5.12; Found: C, 60.80; H, 5.09;

(±)-2-(Methylthio)-2-phenyl-1-(2-thienyl)-1-ethanone (4h): colorless oil (40%); ^1H NMR (CDCl_3): δ 7.98–7.95 (m, 2H), 7.52–7.48 (m, 1H), 7.42–7.37 (m, 2H), 7.24–7.22 (m, 1H), 7.09–7.08 (m, 1H), 6.93–6.89 (m, 1H), 5.71 (d, $J = 1.1$ Hz, 1H), 1.99 (d, $J = 1.6$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 192.5, 138.3, 135.2, 133.4, 128.8, 128.7, 127.3, 126.5, 126.4, 47.9, 13.6. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}_2$: C, 62.87; H, 4.87; Found: C, 62.94; H, 5.06.

(±)-1-(2-Furyl)-2-(methylthio)-2-phenyl-1-ethanone (4i): yellow oil (23%); ^1H NMR (CDCl_3): δ 8.02–7.99 (m, 2H), 7.60–7.55 (m, 1H), 7.49–7.42 (m, 3H), 6.59–6.57 (m, 1H), 6.38–6.36 (m, 1H), 5.57 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (CDCl_3): δ 191.2, 148.3, 142.6, 135.3, 133.4, 128.7, 110.7, 110.0, 46.1, 13.2. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: C, 67.22; H, 5.21; Found: C, 67.10; H, 5.39;

(±)-1-(1-Benzofuran-2-yl)-2-(methylthio)-2-phenyl-1-ethanone (4k): yellow oil (46%); ^1H NMR (CDCl_3): δ 7.97–7.95 (m, 2H), 7.49–7.45 (m, 2H), 7.40–7.35 (m, 3H), 7.22–7.10 (m, 2H), 6.92 (s, 1H), 5.59 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (CDCl_3): δ 190.8, 154.8, 151.1, 135.1, 133.5, 128.7, 128.7, 128.2, 124.4, 122.9, 121.1, 111.2, 107.0, 46.1, 13.3. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$: C, 72.31; H, 5.00; Found: C, 72.27; H, 5.30.

(±)-1-(1-Benzothiophen-2-yl)-2-(methylthio)-2-phenyl-1-ethanone (4l): yellow microcrystals from diethyl ether- hexane to give (40%); mp 71–72 °C; ^1H NMR (CDCl_3):

δ 8.06 (d, J = 7.3 Hz, 2H), 7.80–7.77 (m, 1H), 7.72–7.69 (m, 1H), 7.59–7.54 (m, 1H), 7.49–7.45 (m, 2H), 7.40 (s, 1H), 7.34–7.26 (m, 2H), 5.80 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (CDCl_3): δ 192.4, 140.2, 139.6, 139.2, 135.2, 133.5, 128.8, 128.7, 124.4, 124.3, 124.3, 123.6, 122.2, 48.7, 13.7. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{OS}_2$: C, 68.42; H, 4.73; Found: C, 68.17; H, 4.72.

($\pm$)-2-(Methylthio)-2-phenyl-1-(3-thienyl)-1-ethanone (4m): colorless oil (71%); ^1H NMR δ 8.00 (d, J = 8.2 Hz, 2H), 7.57–7.52 (m, 1H), 7.47–7.42 (m, 3H), 7.32–7.30 (m, 1H), 7.18 (d, J = 5.1 Hz, 1H), 5.57 (s, 1H), 2.01 (s, 3H); ^{13}C NMR δ 193.7, 135.8, 135.7, 133.2, 128.7, 128.6, 127.9, 126.0, 124.0, 48.8, 13.6. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}_2$: C, 62.87; H, 4.87; Found: C, 62.79; H, 4.87.