

Supporting Information

Manganese Catalysed Sulfenylation of *N*-methyl Amides with Arenesulfonyl Hydrazides

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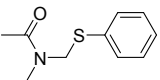
1. General information

Sulfonyl hydrazides were prepared from the corresponding sulfonyl chlorides and hydrazine according to the literature procedure.¹ DTBP (98%) and Manganese (II) acetate powder (99.99% trace metals basis) were purchased from Sigma–Aldrich. Commercially available reagents were used as received without purification. Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin–layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400M spectrometer. The chemical shift references were as follows: (¹H) CDCl₃, 7.26 ppm (CHCl₃); (¹³C) CDCl₃, 77.00 ppm (CDCl₃). HRMS spectra were carried out at Micromass GCT (TOF MS EI⁺).

2. General procedure

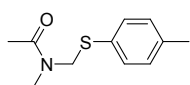
To a Schlenk tube equipped with a magnetic stir bar were added Mn(OAc)₂ (2 mg, 0.01 mmol) and arenesulfonyl hydrazide (0.5 mmol), *N,N*-dimethylacetamide (2.0 mL, 15–25 mmol) and DTBP (5.5 M in decane, 1 mmol, 0.2 mL) were added. The vial was sealed and the resulting reaction mixture was kept stirring at the 120°C for 8 h. After required reaction time, the mixture was cooled down to room temperature, diluted in ethyl acetate, and washed with brine. The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated in *vacuo*, and the resulting residue was purified by silica gel column chromatography (2:1 hexane/ethyl acetate) to afford the product. The rotamer ratios were determined based on the integrations of methylene peaks on each NMR spectrum.

3. Characterisation data

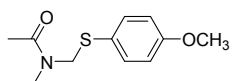
 *N*-methyl-*N*-(*p*-tolylthiomethyl)acetamide (**1a**): Colorless oil. Yield: 83 mg (86%).
IR (film) 2927, 1656 (C=O), 1476, 1393, 1259, 1014, 744, 694 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.48 (m, 2H), 7.22–7.35 (m, 3H), 4.88 and 4.64 (2×s, 2H, ratio=1.87:2), 2.97 and 2.96 (2×s, 3H), 2.01 and 1.63 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.6 and 170.4, 134.8 and 133.8, 132.2 and 131.4, 129.2 and 128.8, 127.10, 57.7 and 51.5, 35.0 and 32.7,

1) *Organic Syntheses*, Coll. Vol. 5, p.1055 (1973); Vol. 40, p.93 (1960).

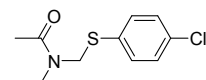
21.7 and 20.5. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₀H₁₃NOS] 195.0718, found 195.0709.



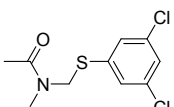
N-methyl-*N*-(*p*-tolylthiomethyl)acetamide (**1b**): Colorless oil. Yield: 94 mg (91%). ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.36 (m, 2H), 7.07-7.14 (m, 2H), 4.82 and 4.59 (2×s, 2H, ratio=1.55:2), 2.97 and 2.95 (2×s, 3H), 2.33 and 2.30 (2×s, 3H), 2.00 and 1.61 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 139.3 and 137.5, 135.2 and 132.2, 130.2 and 130.1, 129.8 and 128.7, 58.00 and 52.3, 35.3 and 32.8, 21.9 and 21.2, 21.1 and 20.7. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₁H₁₅NOS] 209.0874, found 209.0871.



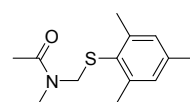
N-((4-methoxyphenylsulfanyl)methyl)-*N*-methylacetamide (**1c**): Colorless oil. Yield: 99 mg (88%). IR (film) 2938, 1658 (C=O), 1493, 1392, 1246, 1173, 1028, 829 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.38 (m, 2H), 6.78-6.83 (m, 2H), 4.72 and 4.51 (2×s, 2H, ratio=1.22:2), 3.76 and 3.74 (2×s, 3H), 2.93 (s, 3H), 1.96 and 1.56 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.5 and 170.4, 160.5 and 159.5, 137.0 and 134.8, 124.0 and 122.5, 114.8 and 114.4, 58.1 and 55.2, 55.1 and 53.0, 35.2 and 32.6, 21.7 and 20.5. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₁H₁₅NO₂S] 225.0823, found 225.0819.



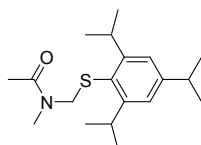
N-((4-chlorophenylsulfanyl)methyl)-*N*-methylacetamide (**1d**): Colorless oil. Yield: 97 mg (85%). IR (film) 2929, 1655 (C=O), 1476, 1391, 1261, 1094, 1012, 820 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.41 (m, 2H), 7.23-7.32 (m, 2H), 4.86 and 4.64 (2×s, 2H, ratio=2:1.5), 2.99 and 2.95 (2×s, 3H), 2.02 and 1.70 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.7 and 170.4, 136.1 and 135.3, 133.2 and 132.7, 132.5 and 131.0, 129.5 and 129.1, 57.7 and 51.6, 35.1 and 32.8, 21.8 and 20.8. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₀H₁₂³⁵ClNOS] 229.0328, found 229.0329.



N-((3,5-dichlorophenylsulfanyl)methyl)-*N*-methylacetamide (**1e**): Colorless oil. Yield: 111 mg (85%). IR (film) 3064, 2929, 1657 (C=O), 1567, 1556, 1260, 1100, 1016, 849, 797, 668 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (2×d, *J* = 4.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 2H), 4.91 and 4.77 (2×s, 2H, ratio=2:0.86), 3.04 and 2.96 (2×s, 3H), 2.07 and 1.92 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.8 and 170.3, 137.9 and 136.5, 135.3 and 135.0, 131.2 and 128.5, 128.5 and 128.4, 126.9 and 126.8, 57.2 and 51.1, 35.1 and 33.2, 21.8 and 21.0. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₀H₁₁³⁵Cl₂NOS] 262.9938, found 262.9930.

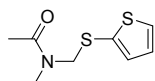


N-(mesitylthiomethyl)-*N*-methylacetamide (**1f**): Colorless oil. Yield: 100 mg (85%). IR (film) 2922, 1652 (C=O), 1463, 1392, 1259, 1012, 852 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 6.90 (d, *J* = 9.0 Hz, 2H), 4.55 and 4.44 (2×s, 2H, ratio=0.86:2), 2.92 and 2.91 (2×s, 3H), 2.49 and 2.45 (2×s, 6H), 2.24 and 2.23 (2×s, 3H), 1.99 and 1.62 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 143.3 and 142.9, 139.3 and 138.5, 129.3 and 129.0, 128.6 and 127.5, 56.4 and 52.6, 36.0 and 33.2, 22.0, 21.8 and 21.7, 21.0 and 20.2. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₃H₁₉NOS] 237.1187, found 237.1184.

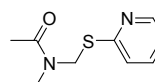


N-methyl-*N*-((2,4,6-triisopropylphenylsulfanyl)methyl)acetamide (**1g**): Colorless oil. Yield: 129 mg (80%). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (2×s, 2H), 4.55 and 4.42 (2×s, 2H, ratio=0.79:2), 3.94 and 3.84 (2×m, 2H), 2.96 and 2.94 (2×s, 3H),

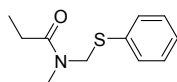
2.90 and 2.86 (2×m, 1H), 2.05 and 1.60 (2×s, 3H), 1.24 and 1.22 (2×m, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 153.3 and 153.0, 150.8 and 150.0, 126.9 and 125.9, 122.0 and 121.8, 58.4 and 54.6, 36.3 and 34.3, 34.2 and 33.3, 31.6 and 29.7, 24.4 and 24.3, 23.9 and 21.8, 20.3. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₉H₃₁NOS] 321.2126, found 321.2120.



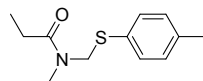
N-methyl-*N*-((thiophen-2-ylthio)methyl)acetamide (**1h**): Colorless oil. Yield: 82 mg (82%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (2×dd, *J* = 5.2, 1.2 Hz, 1H), 6.99 (2×ddd, *J* = 14.7, 5.4, 3.6 Hz, 2H) 4.69 and 4.54 (2×s, 2H, ratio=1.27:2), 3.02 and 2.99 (2×s, 3H), 2.03 and 1.61 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.7 and 170.6, 136.8 and 135.2, 131.8 and 130.6, 129.9 and 128.2, 127.7, 59.4 and 55.6, 35.5 and 32.6, 21.8 and 20.3. HRMS (TOF MS EI⁺) *m/z* calcd for [C₈H₁₁NOS₂] 201.0282, found 201.0291.



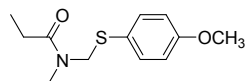
N-methyl-*N*-((pyridin-2-ylthio)methyl)acetamide (**1i**): Colorless oil. Yield: 82 mg (84%). ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.44 (2×m, 2H), 7.08 (2×td, *J* = 9.1, 0.9 Hz, 2H), 5.15 and 5.13 (2×s, 2H, ratio=2:1.51), 2.96 and 2.83 (2×s, 3H), 2.11 and 1.95 (2×s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.0 and 170.6, 157.3 and 155.8, 148.9 and 148.7, 136.2 and 136.0, 122.9 and 122.2, 120.1 and 119.6, 51.0 and 46.7, 35.5 and 32.7, 21.5 and 21.2. HRMS (TOF MS EI⁺) *m/z* calcd for [C₉H₁₂N₂OS] 196.0670, found 196.0671.



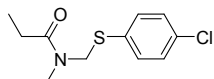
N-methyl-*N*-(phenylsulfanylmethyl)propionamide (**1j**): Colorless oil. Yield: 90 mg (86%). IR (film) 3057, 2978, 1659 (C=O), 1472, 1396, 1258, 1063, 746, 693 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.46 (m, 2H), 7.20-7.32 (m, 3H), 4.88 and 4.64 (2×s, 2H, ratio=2:1.77), 2.94 (s, 3H), 2.23 and 1.89 (2×q, *J* = 7.4 Hz, 2H), 1.02 and 0.89 (2×t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8 and 173.7, 134.6 and 133.8, 132.4 and 131.5, 129.1 and 128.8, 128.7 and 128.6, 127.0 and 126.1, 56.5 and 51.8, 34.2 and 33.0, 26.6 and 25.5, 9.0 and 8.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₁H₁₅NOS] 209.0874, found 209.0866.



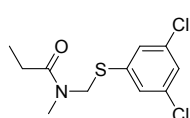
N-methyl-*N*-(*p*-tolylthiomethyl)propionamide (**1k**): Colorless oil. Yield: 95 mg (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 16.5, 7.9 Hz, 2H), 4.82 and 4.59 (2×s, 2H, ratio=1.92:2), 2.94 (d, *J* = 1.1 Hz, 3H), 2.31 and 2.28 (2×s, 3H), 2.22 and 1.87 (2×q, *J* = 7.4 Hz, 2H), 1.02 and 0.88 (2×t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8 and 173.7, 139.0 and 137.3, 134.8 and 132.2, 130.1 and 129.9, 129.6 and 128.7, 56.8 and 52.4, 34.3 and 33.0, 26.7 and 25.5, 21.0 and 20.9, 9.0 and 8.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₂H₁₇NOS] 223.1031, found 223.1028.



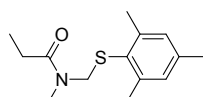
N-((4-methoxyphenylsulfanyl)methyl)-*N*-methylpropionamide (**1l**): Colorless oil. Yield: 101 mg (85%). IR (film) 2937, 1656 (C=O), 1591, 1493, 1246, 1181, 1060, 1029, 828 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 6.7 Hz, 2H), 6.79-6.83 (m, 2H), 4.75 and 4.54 (2×s, 2H, ratio=1.56:2), 3.76 (s, 3H), 2.93 (s, 3H), 2.21 and 1.83 (2×d, *J* = 7.0 Hz, 2H), 1.00 and 0.87 (2×t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8 and 173.68, 160.4 and 159.5, 136.9 and 134.8, 124.0 and 122.7, 114.7 and 114.4, 57.1 and 55.2, 55.2 and 53.3, 34.4 and 33.0, 26.7 and 25.5, 9.1 and 8.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₂H₁₇NO₂S] 239.0980, found 239.0971.



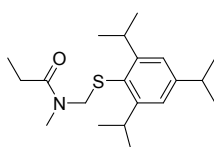
N-((4-chlorophenylsulfanyl)methyl)-*N*-methylpropionamide (**1m**): Colorless oil. Yield: 102 mg (84%). IR (film) 2938, 1651 (C=O), 1476, 1394, 1259, 1094, 1012, 818 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.31 (dd, $J = 4.6, 3.6$ Hz, 2H), 7.14-7.22 (m, 2H), 4.80 and 4.58 (2 \times s, 2H, ratio=2:1.2), 2.89 and 2.87 (2 \times s, 3H), 2.17 and 1.88 (2 \times q, $J = 7.4$ Hz, 2H), 0.96 and 0.86 (2 \times t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6 and 173.4, 135.6 and 134.8, 132.9 and 132.6, 132.2 and 130.9, 129.2 and 128.7, 56.4 and 51.6, 33.9 and 32.9, 26.5 and 25.4, 8.8 and 8.7. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_{11}\text{H}_{14}^{35}\text{Cl}\text{NOS}]$ 243.0485, found 243.0486.



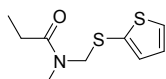
N-((3,5-dichlorophenylsulfanyl)methyl)-*N*-ethylpropionamide (**1n**): Colorless oil. Yield: 117 mg (85%). IR (film) 2938, 1659 (C=O), 1556, 1402, 1254, 1064, 797, 669 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.30 (m, 2H), 7.14 (t, $J = 1.7$ Hz, 1H), 4.89 and 4.75 (2 \times s, 2H, ratio=2:0.65.), 2.98 and 2.93 (2 \times s, 3H), 2.27 and 2.14 (2 \times q, $J = 7.4$ Hz, 2H), 1.05 and 1.00 (2 \times t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7 and 173.2, 162.1, 137.5 and 136.4, 134.9 and 134.6, 130.7 and 128.2, 128.0 and 126.5, 55.9 and 50.9, 33.9 and 33.1, 26.5 and 25.6, 8.8 and 8.7. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_{11}\text{H}_{13}^{35}\text{Cl}_2\text{NOS}]$ 277.0095, found 277.0084.



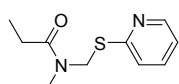
N-(mesitylthiomethyl)-*N*-methylpropionamide (**1o**): Colorless oil. Yield: 108 mg (82%). IR (film) 2936, 1660 (C=O), 1462, 1394, 1258, 1202, 1057, 890, 851, 671 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 6.93 and 6.90 (2 \times s, 2H), 4.58 and 4.46 (2 \times s, 2H, ratio=1.18:2), 2.93 and 2.91 (2 \times s, 3H), 2.51 and 2.47 (2 \times s, 6H), 2.25 and 2.24 (2 \times s, 3H), 1.93 (q, $J = 7.4$ Hz, 2H), 1.06 and 0.92 (2 \times t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7 and 173.5, 143.2 and 142.9, 139.1 and 138.4, 129.2 and 128.9, 128.5 and 127.6, 55.4 and 52.7, 35.1 and 33.5, 26.7 and 25.1, 21.9 and 21.8, 21.0 and 20.9, 9.1 and 9.0. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_{14}\text{H}_{21}\text{NOS}]$ 251.1344, found 251.1337.



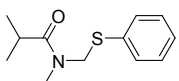
N-methyl-*N*-((2,4,6-triisopropylphenylsulfanyl)methyl)propionamide (**1p**): Colorless oil. Yield: 134mg (80%). IR (film) 2961, 1663 (C=O), 1462, 1393, 1258, 1059, 878 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.02 and 7.00 (2 \times s, 2H), 4.56 and 4.43 (2 \times s, 2H, ratio=0.92:2), 3.93 and 3.84 (2 \times dd, $J = 13.7, 6.9$ Hz, 2H), 2.96 and 2.94 (2 \times s, 3H), 2.83-2.87 and 2.87-2.90 (2 \times m, 1H), 2.29 and 1.83 (2 \times q, $J = 7.4$ Hz, 2H), 1.21-1.23 and 1.23-1.25 (2 \times m, 18H), 1.10 and 0.86 (2 \times t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6 and 173.4, 153.3 and 153.0, 150.6 and 149.8, 126.9 and 125.9, 121.9 and 121.7, 57.3 and 54.8, 35.4 and 34.3, 34.2 and 33.5, 31.5 and 26.7, 25.2 and 24.4, 24.3 and 23.9, 9.1 and 8.9. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_{20}\text{H}_{23}\text{NOS}]$ 335.2283, found 335.2277.



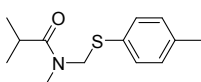
N-methyl-*N*-((thiophen-2-ylthio)methyl)propionamide (**1q**): Colorless oil. Yield: 86 mg (81%). IR (film) 2936, 1659 (C=O), 1462, 1396, 1259, 1061, 847, 705 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.40 and 7.34 (2 \times dd, $J = 5.4, 1.1$ Hz, 1H), 7.11 and 6.96 (2 \times ddd, $J = 13.5, 3.5, 1.1$ Hz, 2H), 4.69 and 4.54 (2 \times s, 2H, ratio=1.94:2), 2.98 (s, 3H), 2.26 and 1.82 (2 \times q, $J = 7.4$ Hz, 2H), 1.03 and 0.89 (2 \times t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9 and 173.7, 136.6 and 135.1, 131.8 and 131.6, 130.4 and 130.0, 128.0 and 127.6, 58.3 and 55.8, 34.7 and 32.8, 26.7 and 25.3, 9.0 and 8.9. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_9\text{H}_{13}\text{NOS}_2]$ 215.0439, found 215.0432.



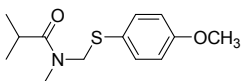
N-methyl-*N*-((pyridin-2-ylthio)methyl)propionamide (**1r**): Colorless oil. Yield: 87 mg (84%). ¹H NMR (400 MHz, CDCl₃) δ 8.34-8.37 and 7.40-7.47 (2×m, *J* = 5.4, 1.1 Hz, 2H), 7.14 and 6.95 (2×ddd, *J* = 13.0, 8.1, 0.8 Hz, 3H), 5.22 and 5.20 (2×s, 2H, ratio=2:1.31), 3.00 and 2.90 (2×s, 3H), 2.45 and 2.25 (2×q, *J* = 7.4 Hz, 2H), 1.08 and 1.05 (2×t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 174.3 and 173.9, 157.6 and 156.2, 149.1 and 148.9, 136.2 and 136.0, 123.0 and 122.4, 120.2 and 119.7, 50.3 and 47.2, 34.7 and 33.1, 26.5 and 26.1, 9.1 and 8.7. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₀H₁₄N₂OS] 210.0827, found 210.0837.



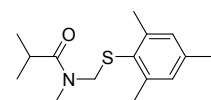
N-methyl-*N*-(phenylsulfanylmethyl)isobutyramide (**1s**): Colorless oil. Yield: 91 mg (82%). IR (film) 2968, 1655 (C=O), 1473, 1396, 1248, 1083, 745, 692 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.12-7.24 (m, 3H), 4.83 and 4.63 (2×s, 2H, ratio=2:1.46), 2.95 and 2.91 (2×s, 3H), 2.62 and 2.23 (2×dd, *J* = 13.5, 6.7 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4 and 177.2, 134.8 and 133.5, 132.3 and 131.8, 129.3 and 128.8, 128.8 and 128.7, 127.2 and 126.7, 56.4 and 51.7, 34.0 and 33.1, 30.5 and 29.9, 19.3 and 18.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₂H₁₇NOS] 223.1031, found 223.1025.



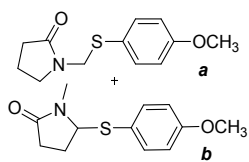
N-methyl-*N*-(*p*-tolylthiomethyl)isobutyramide (**1t**): Colorless oil. Yield: 100 mg (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.36 (m, 2H), 7.13 and 7.07 (2×d, *J* = 8 Hz, 2H), 4.84 and 4.64 (2×s, 2H, ratio=2:2.05), 3.01 and 2.97 (2×s, 3H), 2.69 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.32 and 2.30 (2×s, 3H), 0.98 (d, *J* = 4 Hz, 3H), 0.85 (d, *J* = 4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4 and 177.1, 139.1 and 137.4, 135.1 and 132.5, 130.1 and 129.8, 129.6 and 128.5, 56.5 and 52.4, 34.1 and 33.1, 30.5, 29.9 and 29.7, 21.1 and 21.0, 19.2 and 19.0. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₃H₁₉NOS] 237.1187, found 237.1182.



N-((4-methoxyphenylsulfanyl)methyl)-*N*-methylisobutyramide (**1u**): Colorless oil. Yield: 101 mg (80%). IR (film) 2967, 1651 (C=O), 1591, 1494, 1246, 1172, 1085, 1030, 828 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.41 (m, 2H), 6.79-6.86 (m, 2H), 4.77 and 4.59 (2×s, 2H, ratio=1.84:2), 3.77 (d, *J* = 8 Hz, 3H), 3.01 and 2.97 (2×s, 3H), 2.68 and 2.24 (2×dt, *J* = 13.5, 6.7 Hz, 1H), 0.97 (d, *J* = 4 Hz, 3H), 0.84 (d, *J* = 4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4 and 177.0, 160.4 and 159.6, 137.0 and 135.0, 123.8 and 122.5, 114.9 and 114.4, 56.7 and 55.3, 55.2 and 53.1, 34.2 and 33.1, 30.4 and 29.9, 19.2 and 18.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₃H₁₉NO₂S] 253.1136, found 253.1137.



N-(mesitylthiomethyl)-*N*-methylisobutyramide (**1v**): Colorless oil. Yield: 108 mg (82%). ¹H NMR (400 MHz, CDCl₃) δ 6.93 and 6.90 (2×s, 2H), 4.60 and 4.50 (2×s, 2H, ratio=1.31:2), 3.00 and 2.94 (2×s, 3H), 2.69 (dt, *J* = 13.5, 6.8 Hz, 1H), 2.52 and 2.47 (2×s, 6H), 2.24 (s, 3H), 1.00 and 0.87 (2×d, *J* = 4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 177.3 and 176.9, 143.2 and 142.9, 139.2 and 138.3, 129.5 and 128.9, 128.2 and 127.4, 55.0 and 52.5, 35.0 and 33.6, 30.4 and 29.7, 29.67, 21.9 and 20.9, 19.3 and 18.9. HRMS (TOF MS EI⁺) *m/z* calcd for [C₁₅H₂₃NOS] 265.1500, found 265.1495.



1-((4-methoxyphenyl)sulfanyl)methylpyrrolidin-2-one (**a**)

and 5-(4-methoxyphenyl)-1-methylpyrrolidin-2-one(**b**) (**1v**) **a/b=2:1**.

Colorless oil. Yield: 92 mg (78%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.7$ Hz, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 8.7$ Hz, 2H), 4.65 (dd, $J = 8.4, 2.0$ Hz, 1H), 4.61 (s, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 2.96 (s, 3H), 2.42 (ddd, $J = 18.9, 13.9, 8.9$ Hz, 2H), 2.24 (t, $J = 8.1$ Hz, 2H), 2.17 – 2.09 (m, 2H), 1.97 (ddt, $J = 22.8, 15.3, 5.2$ Hz, 3H), 1.60 – 1.44 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 174.7, 174.4, 160.6, 159.5, 137.4, 134.4, 123.5, 120.1, 114.8, 114.5, 77.3, 77.0, 76.7, 69.3, 55.2, 55.1, 48.1, 45.8, 30.7, 29.0, 27.8, 26.1, 17.5. HRMS (TOF MS EI^+) m/z calcd for $[\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S}]$ 237.0823, found 237.0822.

4. ¹H and ¹³C NMR Spectra

