Supporting Information

For

Convenient thioacid precursor, α-methylphenacyl thioester

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General Methods
Analytical thin layer chromatography (TLC) was performed using Merck KGaA TLC 60F-254 plates (0.25 mm), and visualization was accomplished with a 2.5% solution of p-anisaldehyde in AcOH/H₂SO₄/H₂O, and a 1% solution of ninhydrin in EtOH, followed by heating or UV irradiation (254 nm). Silica gel column chromatography was performed on FUJI SILYSIA CHEMICAL Ltd. Silica Gel PSQ60B 46-50 μm (spherical, neutral). Specific rotations were measured on an automatic polarimeter with a path length of 50 mm in the solvent specified. Concentrations are given in g/100 mL. Optical rotations were measured on a JASCO P-2200 photoelectric polarimeter. ¹H and ¹³C NMR spectra were recorded on a JEOL Ltd. JNM-ECP400 series (400 MHz). ¹H NMR data are reported as follows: chemical shift in parts per million (ppm) downfield or upfield from tetramethylsilane (δ 0.00) or CDCl₃ (δ 7.26), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Chemical shifts in ¹³C NMR are reported in ppm downfield or upfield from CDCl₃ (δ 77.36). High-resolution mass spectra (HRMS) were recorded on a JEOL Ltd. AccuTOFCS JIMS-T100CS with an electrospray ionization (ESI) source coupled.

General procedure for preparation of S-phenacyl thioacetates.
To a phenacyl bromide in DMF (1.0 M) was added S-potassium thioacetate (1.05 equiv.) at 0 °C. The reaction mixture was stirred for 30 min, and the reaction was quenched with water. The mixture was extracted with CH₂Cl₂, and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo to give an S-phenacyl thioacetate.

S-Phenacyl thioacetate (2a). Phenacyl bromide (1a, 1.1 g, 5.7 mmol) was used as a bromide. Yellow solid. Data were in agreement with a known literature.[¹]

S-α-Methylphenacyl thioacetate (2b). 2-Bromopropiophenone (1b, 14 g, 66 mmol) was used as a bromide. Brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J₀,m = 7.6 Hz, 2H, Ar-Hₜ), 7.51 (t, Jₚ,m = 7.6 Hz, 1H, Ar-Hₚ), 7.40 (dd, J₀,m = 7.6 Hz, Jₚ,p = 7.6 Hz, 2H, Ar-Hₚm), 5.23 (q, Jₚ,β = 7.2 Hz, 1H, CH), 2.30 (s, 3H, CH₃), 1.49 (d, Jₚ,β = 7.2 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 194.0, 134.9, 133.6, 128.7, 128.6, 42.4, 30.3, 17.8; ESIHRMS: m/z calcd. for C₁₁H₁₂O₂SNa (M + Na)+ 231.0456, found 231.0462.
**S-α,α-Dimethylphenacyl thioacetate (2c).** 2-Bromo-2-methylpropiophenone[2] (1c, 15 g, 66 mmol) was used as a bromide. Brown oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J_{\alpha,m} = 7.6$ Hz, 2H, Ar-H$_{\alpha}$), 7.44 (t, $J_{m,p} = 7.2$ Hz, 1H, Ar-H$_p$), 7.36 (dd, $J_{\alpha,m} = 7.6$ Hz, $J_{m,p} = 7.2$ Hz, 2H, Ar-H$_m$), 2.11 (s, 3H, CH$_3$), 1.70 (s, $J = 7.2$ Hz, 6H, CH$_3$ x 2); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.8, 194.2, 136.3, 131.7, 129.4, 128.8, 128.2, 127.8, 55.5, 30.2, 26.9; ESIHRMS: $m/z$ calcd. for C$_{12}$H$_{10}$O$_2$SNa (M + Na)$^+$ 245.0613, found 245.0626.

**Phenacylthiol (3a).** 2a (0.23 g, 1.2 mmol) in MeOH (2.4 mL) were degassed, and NaOMe (12 mg, 0.23 mmol) was added at room temperature. The reaction mixture was degassed again and stirred for 30 min, and the reaction was quenched with HCl aq. (3.0 M, 10 mL). The mixture was extracted with CH$_2$Cl$_2$ (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo to give the title compound as a yellow oil. Data were in agreement with a known literature.[1]

**α-Methylphenacylthiol (3b).** To a degassed solution of 2b (14 mL, 66 mmol) in MeCN (66 mL) was added H$_2$NNH$_2$·H$_2$O (3.4 mL, 66 mmol) at 0°C. The reaction mixture was degassed again and stirred for 15 min. Then, the reaction was quenched with HCl aq. (1.0 M, 300 mL). The mixture was extracted with CH$_2$Cl$_2$ (100 mL x 3), and the combined organic layer was washed with brine (300 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo to give the title compound as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J_{\alpha,m} = 7.2$ Hz, 2H, Ar-H$_{\alpha}$); 7.53 (t, $J_{m,p} = 7.2$ Hz, 1H, Ar-H$_p$); 7.43 (dd, $J_{\alpha,m} = 7.2$ Hz, $J_{m,p} = 7.2$ Hz, 2H, Ar-H$_m$); 4.36 (qd, $J_{\alpha,\beta} = 6.6$ Hz, $J_{\alpha,SH} = 9.5$ Hz, 1H, CH$_2$); 2.00 (d, $J_{\alpha,SH} = 9.5$ Hz, 1H, SH); 1.58 (d, $J_{\alpha,\beta} = 6.6$ Hz, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.7, 134.8, 133.4, 128.8, 128.7, 36.7, 21.0; FABHRMS: $m/z$ calcd. for C$_9$H$_{11}$OS (M + H)$^+$ 167.0531, found 167.0522.

**α,α-Dimethylphenacylthiol (3e).** To a degassed solution of 2c (15 g, 66 mmol) in MeCN (66 mL) was added H$_2$NNH$_2$·H$_2$O (3.4 mL, 66 mmol) at 0°C. The reaction mixture was degassed again and stirred for 15 min. Then, the reaction was quenched with HCl aq. (1.0 M, 300 mL). The mixture was extracted with CH$_2$Cl$_2$ (100 mL x 3), and the combined organic layer was washed with brine (300 mL).
mL), dried over Na₂SO₄, and concentrated in vacuo to give the title compound as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, Jₐ,m = 7.6 Hz, 2H, Ar-Hₙ), 7.42 (t, Jₘ,p = 7.6 Hz, 1H, Ar-Hₚ), 7.35 (dd, Jₐ,m = 7.6 Hz, Jₘ,p = 7.6 Hz, 2H, Ar-Hₙ), 2.30 (s, 1H, SH), 1.62 (s, 6H, CH₃ x 2); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 136.5, 131.7, 129.3, 128.1, 49.0, 30.2. Data were in agreement with a known literature.¹⁹

![Chemical structure](image)

**S-Phenacyl N-tert-butoxycarbonyl-l-thiotryptophanate (4a).** To Boc-l-Trp-OH (199 mg, 0.66 mmol) and phenacylthiol (120 mg, 0.79 mmol) in CH₂Cl₂ (1.3 mL) were added EDCI (151 mg, 0.79 mmol) and DMAP (8 mg, 0.06 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (10 mL). The mixture was extracted with CH₂Cl₂ (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a yellow foam (244 mg, 85%). [α]°D = -75.2 (c = 0.75, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.72 (br s, 1H, NHₙ), 7.93 (d, Jₐ,m = 7.6 Hz, 2H, Ar-Hₙ), 7.65-7.52 (m, 2H, Ar-H, In-H), 7.45 (dd, Jₐ,m = 7.6 Hz, Jₘ,p = 7.6 Hz, 2H, Ar-Hₙ), 7.33 (d, Jₐ,e = 8.0 Hz, Hₖ), 7.19 (dd, Jₑ,f = 8.0 Hz, Jₖ,g = 8.0 Hz, 1H, Hⱼ), 7.12 (dd, Jₖ,e = 8.0 Hz, Jₑ,f = 8.0 Hz, 1H, Hₖ), 7.01 (s, 1H, Hₕ), 5.29 (br d, Jₐ, NH = 8.0 Hz, 1H, NH), 4.77 (td, Jₐ, NH = 8.0 Hz, Jₐ,β = 4.8 Hz, 1H, Hₐ), 4.35 & 4.12 (ABq, J = 16.0 Hz, 1H each, CH₂-α), 3.32 (d, Jₐ,β = 4.8 Hz, 2H, CH₂β), 1.44 (s, 9 H, 'Bu); ¹³C NMR (100MHz, CDCl₃) δ 201.1, 193.7, 155.6, 136.4, 135.7, 133.9, 127.7, 123.7, 122.2, 119.6, 118.6, 111.7, 109.1, 80.6, 61.1, 36.9, 28.5, 28.0; ESIHRMS: m/z calcd. for C₂₉H₃₅N₂O₃SNa (M + Na)+ 461.1511, found 461.1512.

![Chemical structure](image)

**S-α-Methylphenacyl N-tert-butoxycarbonyl-l-thiotryptophanate (4b).** To Boc-l-Trp-OH (599 mg, 2.0 mmol) and α-methylphenacylthiol (399 mg, 2.4 mmol) in CH₂Cl₂ (4.0 mL) were added EDCI (364 mg, 1.9 mmol) and DMAP (24 mg, 0.2 mmol) at room temperature. The reaction mixture

SI-6
was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH₂Cl₂ (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the title compound as a yellow foam (840 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ 8.91 (br s, 0.5H each, NH₂), 7.96 (d, Jₐ,m = 7.2 Hz, 2H, Ar-Hₐ), 7.60 (t, Jₐ,p = 7.2 Hz, 1H, Ar-Hₚ), 7.55 (d, Jₐ,¢ = 6.8 Hz, 1H, H¢), 7.43 (dd, Jₐ,m = 7.2 Hz, Jₐ,p = 7.2 Hz, 2H, Ar-Hₚ), 7.34 (dd, Jₐ,¢ = 6.8 Hz, Jₐ,c = 7.2 Hz, 1H, H¢), 7.16 (d, Jₐ,g = 7.2 Hz, 1H, Hg), 7.14 (dd, Jₐ,c = 7.2 Hz, Jₐ,g = 7.2 Hz, 1H, Hg), 6.93 (s, 0.5H each, Hβ), 5.45-5.25 (br d, Jₐ,NH = 10.8 Hz, 1H, NH), 5.21 (q, Jₐ,e = 4.9 Hz, 1H, Hα), 4.70 (ddd, Jₐ,a = 4.8 Hz each, Jₐ,NH = 10.8 Hz, 1H, Hα), 3.31 & 3.29 (dd, Jₐ,a = 4.8 Hz, Jₐ,b = 12.8 Hz, 2H, CH₂β), 1.50 (d, Jₐ,e = 4.9 Hz, 3H, CH₃β), 1.46&1.39 (s, 4.5H each, 'Bu); ¹³C NMR (100MHz, CDCl₃) δ 200.1, 200.8, 198.3, 198.1, 155.6, 155.5, 136.5, 135.1, 133.9, 127.6, 122.3, 119.7, 118.7, 118.7, 111.8, 109.1, 80.7, 77.8, 77.6, 77.5, 77.2, 61.3, 61.2, 61.1, 42.8, 42.7, 28.4, 17.8, 17.5; ESIHRMS: m/z calcd. for C₂₅H₃₂N₂O₄SNa (M + Na)⁺ 475.1668, found 475.1692.

**S-(α,α-Dimethylphenacyl) N-tert-butoxycarbonyl-L-thiotryptophanate** (4c). To Boc-L-Trp-OH (500 mg, 1.6 mmol) and α,α-dimethylphenacylthiol (356 mg, 1.9 mmol) in CH₂Cl₂ (3.2 mL) were added EDCI (364 mg, 1.9 mmol) and DMAP (24 mg, 0.2 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH₂Cl₂ (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a greenish foam (745 mg, 97%). [α]Dᵇ = -52.1 (c = 1.23, CHCl₃); ¹H NMR (400 MHz CDCl₃) δ 8.46 (br s, 1H, NHₐ), 8.02 (d, Jₐ,m = 8.0 Hz, 2H, Ar-Hₐ), 7.54-7.44 (m, 2H, Ar-H, In-H), 7.34 (ddd, Jₐ,m = 8.0 Hz, Jₐ,p = 7.6 Hz, 2H, Ar-Hₚ), 7.32 (dd, Jₐ,¢ = 8.0 Hz, 1H, H¢), 7.18 (dd, Jₐ,g = 8.0 Hz, Jₐ,c = 7.6 Hz, 1H, Hg), 7.11 (dd, Jₐ,c = 7.6 Hz, Jₐ,¢ = 8.0 Hz, 1H, H¢), 6.60 (s, 1H, Hβ), 4.98 (br d, Jₐ,NH = 8.4 Hz, 1H, NH), 4.53 (td, Jₐ,e = 7.2 Hz, Jₐ,NH = 8.4 Hz, 1H, Hα), 2.99 (d, Jₐ,a = 7.2 Hz, 2H, CH₂β), 1.70 (s, 6H, CH₃β x 2), 1.43 (s, 9H, 'Bu); ¹³C NMR (100MHz, CDCl₃) δ 201.2, 200.5, 155.2, 136.2, 136.2, 129.1, 127.7, 122.2, 119, 7, 118.6, 111.5, 109.1, 80.4, 60.7, 55.1, 28.4, 28.2, 27.4, 27.0; ESIHRMS: m/z calcd. for C₂₅H₃₂N₂O₄SNa (M + Na)⁺ 489.1824, found 489.1804.
General procedure for deprotection followed by benzylation in Table 1.

Thiotryptophanates (0.12 mmol) in 90% AcOH aq. (0.1 M) was degassed, and 50 equiv. of freshly washed Zn was added to the solution. The mixture was degassed again and stirred, followed by concentration under high vacuum. The residue was suspended in CHCl₃/MeOH (5/1), and then filtrated through silicagel pad. The filtrate was concentrated in vacuo. The residue was suspended in CHCl₃/MeOH (5/1), and then filtration through a silica gel pad. The filtrate was concentrated in vacuo. To the residue in DMF (0.1 M) were added 3.0 equiv. of Cs₂CO₃ and BnBr, and the reaction mixture was stirred for 30 min. The reaction was quenched with water (10 mL). The mixture was extracted with CH₂Cl₂ (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding benzyl thioester.

\[
\begin{align*}
\text{S-Benzy1 N-tert-butoxycarbonyl-l-thiotryptophanate (5). Colorless solid; mp: } & 127.5-130.0 \degree C; \\
\left[\alpha\right]_D^{20} & = -53.6 \, (c = 0.53, \text{CHCl}_3); \ 
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \delta 8.19 \, (\text{br s, } 1H, \text{NH}), 7.57 \, (\text{br }, 1H, \text{In-H}), 7.34 \, (d, J_{d,e} = 8.0 \, Hz, 1H, H_d), 7.31-7.17 \, (m, 6H, \text{In-H, Ar-H x5}), 7.12 \, (dd, J_{d,e} = 8.0 \, Hz, J_{e,f} = 7.2 \, Hz, 1H, H_e), 6.82 \, (s, 1H, H_b), 5.06 \, (br d, J_{a,NH} = 8.0 \, Hz, NH), 4.73 \, (ddd, J_{a,b} = 8.0 \, Hz, J_{a,b} = 5.6 \, Hz each, 1H, H_a), 4.10 & 4.04 \, (ABq, J = 12.4 \, Hz, 1H each, CH₂Ph), 3.36 & 3.33 & 3.28 & 3.25 \, (ddd, J_{a,b} = 5.6 \, Hz each, J_{b,b} = 17.6 \, Hz, 2H, CH₂β), 1.42 \, (s, 9H, ‘Bu); \ 
\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \delta 201.4, 155.3, 137.3, 136.2, 128.6, 127.1, 122.3, 119.8, 118.9, 111.3, 109.6, 80.4, 65.4, 60.6, 33.5, 28.4, 28.2; \ 
\text{ESIHRMS: } m/z \ \text{calcd. for } C_{23}H_{26}N_{2}O_{3}SNa (M + Na)^+ 433.1562, \ \text{found 433.1567.}
\end{align*}
\]

General procedure for preparation of S-α-Methylphenacetyl thioester 7a-i (Table 2) To a carboxylic acid and 1.2 equiv. of α-methylphenacetylthiol in CH₂Cl₂ (0.5 M) were added 1.2 equiv. of EDCI and 0.1 equiv. of DMAP at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH₂Cl₂ (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding Mpa thioester.
S-α-Methylphenacly thiobenzoate (7a). Benzoic acid (6a, 168 mg, 1.4 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (335 mg, 90%). 1H NMR (400 MHz, CDCl3) δ 8.00 (d, J_α,m = 7.6 Hz, 2H, Ar-Hα), 7.89 (d, J_α,m = 7.7 Hz, 2H, Ar-Hα), 7.48 (t, J_α,p = 7.7 Hz, 1H, Ar-Hp), 7.46 (t, J_m,p = 7.2 Hz, 1H, Ar-Hp), 7.38 (dd, J_α,m = 7.6 Hz, J_m,p = 7.7 Hz, 2H, Ar-Hm), 7.33 (dd, J_α,m = 7.7 Hz, J_m,p = 7.2 Hz, 2H, Ar-Hm), 5.46 (q, J_α,β = 7.0 Hz, 1H, Hα), 1.16 (d, J_α,β = 7.0 Hz, 3H, CH3), 0.82 (t, J = 6.8 Hz, 3H, CH3β); 13C NMR (100 MHz, CDCl3) δ 197.4, 190.0, 136.2, 135.0, 134.0, 133.6, 128.9, 128.8, 128.7, 127.5, 42.5, 17.7; ESIHRMS: m/z calcd. for C16H14O2SNa (M + Na)+ 293.0613, found 293.0616.

S-α-Methylphenacly thiodoecanoate (7b). Capric acid (6b, 219 mg, 1.3 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 19/1) to afford the title compound as a yellow syrup (377 mg, 92%). 1H NMR (400 MHz, CDCl3) δ 7.90 (d, J_α,m = 7.6 Hz, 2H, Ar-Hα), 7.49 (t, J_α,p = 7.2 Hz, 1H, Ar-Hp), 7.38 (dd, J_α,m = 7.6 Hz, J_m,p = 7.2 Hz, 2H, Ar-Hm), 5.23 (q, J_α,β = 7.0 Hz, 1H, Hα), 2.49 (t, J_α,β = 7.6 Hz, 2H, COCH2), 1.59 (t, J_α,β = 6.8 Hz, 2H, CH2), 1.49 (d, J_α,β = 7.0 Hz, 3H, CH3), 1.29-1.10 (m, 12H, CH2 x6), 0.82 (t, J = 6.8 Hz, 3H, CH3β); 13C NMR (100 MHz, CDCl3) δ 197.6, 197.2, 135.0, 133.4, 128.7, 128.6, 43.7, 41.9, 31.9, 29.4, 29.3, 29.2, 28.9, 25.6, 22.7, 17.7, 14.2; ESIHRMS: m/z calcd. for C19H23O2SNa (M + Na)+ 343.1708, found 343.1705.

S-α-Methylphenacly N-tert-butoxycarbonyl-l-thiophenylalainate (7c). Boc-l-Phe-OH (6c, 99 mg, 0.37 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (147 mg, 95%). 1H NMR (400 MHz, CDCl3) δ 7.93 (d, J_α,m = 7.6 Hz, 2H, Ar-Hα), 7.52 (t, J_α,p = 7.6 Hz, 1H, Ar-Hp), 7.42 (dd, J_α,m = 7.6 Hz, J_m,p = 7.6 Hz, 2H, Ar-Hm), 7.23-7.13 (m, 3H, Ar-H), 7.08 (dd, J_α,m = 9.6 Hz, J_m,p = 9.6 Hz, 2H, Ar-Hm), 5.21 (q, J_α,β = 6.8 Hz, 1H, Hα), 5.04 & 4.99 (br d, J_α,αNH = 8.0 Hz, 0.5H each, NH), 4.63 (td, J_α,β = 6.8 Hz, J_α,αNH = 8.0 Hz, 1H, Hα), 3.15-2.95 (m, 2H, CH2β), 1.49
Purification was performed by chromatography (20 g, hexane/EtOAc = 9/1) to afford the title compound as a white foam (1.1 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J_{o.m} = 7.2$ Hz, 2H, Ar-H$_o$), 7.41 (t, $J_{m,p} = 7.2$ Hz, 1H, Ar-H$_m$), 7.29 (dd, $J_{o.m} = 7.2$ Hz, $J_{m,p} = 7.2$ Hz, 2H, Ar-H$_m$), 5.73 & 5.64 (br d, $J_{a,NH} = 10.8$ Hz, 0.5H each, NH), 5.11 (q, $J_{a',b'} = 6.4$ Hz, 1H, H$_a$), 3.87 (ddd, $J_{a,b} = 17.2$ Hz, $J_{a,NH} = 10.8$ Hz each, 2H, CH$_2$), 1.37 (d, $J_{a',b'} = 6.4$ Hz, 3H, H$_a$), 1.28 & 1.20 (s, 4.5H each, 'Bu); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.8, 197.6, 155.8, 134.7, 133.7, 133.5, 128.8, 128.7, 128.5, 80.2, 50.2, 42.2, 42.0, 28.3, 17.7; ESIHRMS: $m/z$ calcd. for C$_{16}$H$_{27}$NO$_2$SNa (M + Na)$^+$ 346.1589, found 346.1583.

S-$\alpha$-Methylphenacyl $N$-tert-butoxycarbonylthioglycinate (7d). Boc-Gly-OH (6d, 604 mg, 3.5 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (20 g, hexane/EtOAc = 9/1) to afford the title compound as a white foam (1.1 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 & 7.92 (d, $J_{o.m} = 6.8$ Hz, 1H each, Ar-H$_o$), 7.50 & 7.48 (t, $J_{m,p} = 7.2$ Hz, 0.5H each, Ar-H$_m$), 7.39 & 7.37 (dd, $J_{o.m} = 6.8$ Hz, $J_{m,p} = 7.2$ Hz, 1H each, Ar-H$_m$), 7.30-7.12 (m, 5H, Ar-H), 5.59 & 5.56 (br d, $J_{a,NH} = 8.0$ Hz, 0.5H each, NH), 5.23 (q, $J_{a',b'} = 7.2$ Hz, 1H, H$_a$), 4.51 & 4.49 (ddd, $J_{a,NH} = 8.0$ Hz, $J_{a,b} = 8.0$ Hz each, 0.5H each, H$_a$), 4.44 & 4.38 (ABq, $J = 12.4$ Hz, 1H each, CH$_3$Ph), 3.93 & 3.60 (dd, $J_{a,b} = 8.0$ Hz, $J_{b,b} = 11.2$ Hz, 1H each, CH$_3$), 1.52 (d, $J_{a',b'} = 7.2$ Hz, 3H, CH$_3$), 1.44 & 1.38 (s, 4.5H each, 'Bu); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.7, 199.1, 197.4, 155.3, 155.2, 135.0, 134.9, 133.7, 133.6, 133.52, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.5, 80.6, 80.5, 73.5, 73.4, 73.3, 60.7, 60.5, 42.6, 42.4, 28.4, 18.0, 18.0, 17.6, 17.6; ESIHRMS: $m/z$ calcd. for C$_{23}$H$_{29}$NO$_2$SNa (M + Na)$^+$ 466.1664, found 466.1664.
S-α-Methylphenacyl N-tert-butoxycarbonyl-O-benzyl-L-thioreonate (7f). Boc-L-Thr-OH (6f, 312 mg, 1.5 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (523 mg, 99%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 & 7.94 (d, \(J_{o,m} = 7.6\) Hz, 1H each, Ar-H\(_\alpha\)), 7.54 & 7.49 (t, \(J_{m,p} = 7.2\) Hz, 0.5H each, Ar-H\(_p\)), 7.42 & 7.37 (dd, \(J_{o,m} = 7.6\) Hz, \(J_{m,p} = 7.2\) Hz, 1H each, Ar-H\(_m\)), 7.35-7.05 (m, 5H, Ar-H), 5.42 & 5.41 (br, 0.5H each, NH), 5.24 (q, \(J_{\alpha,\beta'} = 6.4\) Hz, 1H, H\(_a\)), 4.55-4.23 (m, 4H, CH\(_2\)Ph, H\(_\alpha\), H\(_\beta\)), 1.54 (d, \(J_{\alpha,\beta'} = 6.4\) Hz, 3H, CH\(_3\)\(_\beta\)), 1.47 & 1.40 (s, 4.5H each, 'Bu), 1.23 (m, 3H, CH\(_3\)\(_\alpha\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.8, 200.3, 197.7, 197.5, 155.9, 155.8, 137.8, 137.7, 135.1, 134.9, 133.7, 133.6, 80.6, 80.6, 74.9, 74.4, 71.6, 65.2, 65.1, 42.5, 42.4, 28.4, 28.3, 18.0, 17.5, 16.9, 16.7; ESIHRMS: \(m/z\) calcd. for C\(_{23}\)H\(_{29}\)NO\(_3\)SNa (M + Na\(^+\)) 480.1821, found 480.1850.

S-α-Methylphenacyl N-fluorenymethyloxycarbonyl-L-thirophtanate (7g). Fmoc-L-Trp-OH (6g, 500 mg, 1.2 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a white foam (662 mg, 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.16 (br, 1H, NH\(_a\)), 8.00-7.92 (m, 2H, Ar-H), 7.79-7.72 (m, 2H, Fm-H), 7.63-7.10 (m, 13H, Ar-H x 3, Fm-H x 6, In-H x 4), 6.88 & 6.83 (s, 0.5H each, H\(_b\)), 5.32 (br d, \(J_{\alpha,NH} = 7.6\) Hz, 1H, NH), 5.21 (q, \(J_{\alpha,\beta'} = 7.2\) Hz, 1H, H\(_a\)), 4.82 (ddd, \(J_{\alpha,NH} = 7.6\) Hz, \(J_{\alpha,\beta} = 5.6\) Hz each, 1H, H\(_a\)), 4.35 (dd, \(J_{c',\gamma'} = 7.2\) Hz each, 2H, CH\(_2\)\(_\gamma\)), 4.17 & 4.11 (t, \(J_{c',\gamma'} = 7.2\) Hz, 1H, H\(_c\)), 3.30 (ddd, \(J_{\alpha,\beta} = 5.6\) Hz each, \(J_{\beta,\beta'} = 15.6\) Hz, 2H, CH\(_2\)\(_\beta\)), 1.51 & 1.48 (d, \(J_{\alpha,\beta'} = 7.2\) Hz, 1H each, CH\(_2\)\(_\beta\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.6, 155.9, 143.8, 143.7, 141.4, 136.2, 135.1, 135.0, 133.7, 128.9, 128.8, 127.9, 127.2, 125.5, 123.4, 122.5, 118.6, 118.5, 111.5, 111.5,
3.0 action mixture was stirred for 100.43. Purification of the 100 g, hexane/EtOAc = 227 in ash chromatography (silica gel 20, 85 mmol)

To a tam £ 12 (100 & 1.91 Hz (0.81 g, residue by fl washed with brine (**100 mL). The mixture was extracted with CH2Cl2 (30 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na2SO4, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 19/1 to 9/1) gave a yellow foam (0.81 g, 74%). 1H NMR (400 MHz, CDCl3) δ 7.92 (d, 2H, Ar-Hα), 7.73 (d, 2H, Ar-Hβ), 7.60 (d, 2H, Ar-Hγ), 7.54 (t, 2H, Ar-Hδ), 7.43 (dd, 2H, Ar-Hε), 7.38 (dd, 2H, Ar-Hζ), 7.30 (dd, 2H, Ar-Hη), 7.20 (m, 2H, Ar-Hτ), 5.19 (q, Jα,β = 7.2 Hz, 2H, Ar-Hθ), 5.10-5.00 (m, 1H, NH), 4.35-4.21 (m, 1H, Ar-Hω), 4.15 (t, Jα,β = 5.6 Hz, 2H, Hβ), 3.52 (d, Jα,β = 5.6 Hz, 2H, Hγ), 2.58-2.48 (m, 2H, CH2γ), 2.17-2.05 & 1.91-1.78 (m, 2H, CH2β), 1.53 (d, Jα,β = 7.2 Hz, 3H, CH3β), 1.41 (s, 9H, 'Bu); 13C NMR (100 MHz, CDCl3) δ 199.9, 198.1, 151.1, 145.3, 141.2, 135.0, 133.7, 128.8, 128.6, 127.9, 127.2, 124.7, 120.0, 80.8, 59.8, 46.7, 42.7, 39.8, 32.4, 28.4, 27.7, 17.6; ESIHRMS: m/z calcd. for C33H35NO6SNa (M + Na)+ 612.1854, found 612.1836.

Sα-α-Methylphenaclyl Sα-9-fluorenylmethyl N-tert-butoxycarbonyl-L-dithioglutamate (7h). To a Boc-L-Glu(OH)-SMpa (S3, 0.74 g, 1.86 mmol) and 9-fluorenylmethylthiol (0.47 g, 2.23 mmol) in CH2Cl2 (4.0 mL) were added EDCI (0.43 g, 2.23 mmol) and DMAP (23 mg, 0.19 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (100 mL). The mixture was extracted with CH2Cl2 (30 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na2SO4, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 19/1 to 9/1) gave a yellow foam (0.81 g, 74%). 1H NMR (400 MHz, CDCl3) δ 7.92 (d, 2H, Ar-Hα), 7.73 (d, 2H, Ar-Hβ), 7.60 (d, 2H, Ar-Hγ), 7.54 (t, 2H, Ar-Hδ), 7.43 (dd, 2H, Ar-Hε), 7.38 (dd, 2H, Ar-Hζ), 7.30 (dd, 2H, Ar-Hη), 7.20 (m, 2H, Ar-Hτ), 5.19 (q, Jα,β = 7.2 Hz, 2H, Ar-Hθ), 5.10-5.00 (m, 1H, NH), 4.35-4.21 (m, 1H, Ar-Hω), 4.15 (t, Jα,β = 5.6 Hz, 2H, Hβ), 3.52 (d, Jα,β = 5.6 Hz, 2H, Hγ), 2.58-2.48 (m, 2H, CH2γ), 2.17-2.05 & 1.91-1.78 (m, 2H, CH2β), 1.53 (d, Jα,β = 7.2 Hz, 3H, CH3β), 1.41 (s, 9H, 'Bu); 13C NMR (100 MHz, CDCl3) δ 199.9, 198.1, 151.1, 145.3, 141.2, 135.0, 133.7, 128.8, 128.6, 127.9, 127.2, 124.7, 120.0, 80.8, 59.8, 46.7, 42.7, 39.8, 32.4, 28.4, 27.7, 17.6; ESIHRMS: m/z calcd. for C33H35NO6SNa (M + Na)+ 612.1854, found 612.1836.
at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (10 mL). The mixture was extracted with CH₂Cl₂ (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 10 g, hexane/EtOAc = 9/1 to 2/1) gave a colorless foam (93 mg, 77%). 1H NMR (400 MHz, CDCl₃) δ 7.94 & 7.92 (d, J₀,m = 7.6 Hz, 1H each, Ar-H₀), 7.61 & 7.57 (d, J₀,b = 7.2 Hz, 1H each, H₀), 7.53 (t, Jₚ,m = 7.2 Hz, 1H, Ar-Hₚ), 7.44 (dd, Jₚ,m = 7.6 Hz, Jₚ,p = 7.2 Hz, 2H, Ar-Hₚ), 7.38 (dd, Jₚ,b = 7.6 Hz, Jₚ,d = 7.2 Hz, 2H, Hₚ), 7.30 (dd, Jₚ,b = 7.6 Hz, Jₚ,c = 7.2 Hz, 2H, Hₚ), 6.08 (s, 2H, Ar-H), 5.71 & 5.76 (br d, Jₚ,NH = 8.4 Hz, 0.5H each, NH), 5.21 (q, Jₚ',β' = 6.8 Hz, 1H, Hₚ'), 4.50-4.32 (m, 3H, Hₚ, CH₂f), 4.25 & 4.21 (ABq, J = 12.4 Hz, 2H, CH₂Ph), 4.15 (t, Jₚ,e,f = 6.8 Hz, 1H, Hₚ), 3.77 (s, 9H, OCH₃ x 3), 2.68 & 2.52 (m, 2H, CH₂γ), 1.54 (d, Jₚ',β' = 6.4 Hz, 3H, CH₃β'); 13C NMR (100 MHz, CDCl₃) δ 199.6, 199.5, 199.1, 197.5, 197.2, 161.0, 159.2, 156.0, 155.8, 143.9, 143.8, 143.7, 143.7, 141.4, 141.3, 135.0, 134.8, 133.7, 128.8, 128.6, 127.8, 127.2, 125.2, 125.2, 120.1, 120.1, 104.5, 90.6, 67.4, 67.3, 60.5, 60.5, 55.9, 55.4, 47.2, 47.2, 42.9, 42.7, 39.4, 27.8, 27.7, 22.5, 17.8, 17.6; ESIHRMS: m/z calcd. for C₃₉H₃₉N₉O₈S₂Na (M + Na)⁺ 736.2015, found 762.2008.

Scheme SI-1. Preparations of Mpa thioesters 7h and 7i.

7h

Sα-α-Methylphenacyl Oα-allyl N-tert-butoxycarbonyl-l-α-thioglutamate (S2). To a Boc-l-Glu(OAll)-OH[6] (2.0 g, 6.9 mmol) and methylphenacylthiol (1.4 g, 8.3 mmol) in CH₂Cl₂ (13 mL) were added EDCI (1.6 g, 8.3 mmol) and DMAP (85 mg, 0.69 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (100 mL). The
mixture was extracted with CH₂Cl₂ (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 19/1 to 9/1) gave a yellow syrup (2.2 g, 72%).

1H NMR (400 MHz, CDCl₃) δ 7.93 (d, J₀,m = 7.2 Hz, 2H, Ar-H₀), 7.56 & 7.55 (t, Jm,p = 7.2 Hz, 0.5H each, Ar-Hₚ), 7.44 (dd, J₀,m = 7.2 Hz, Jm,p = 7.2 Hz, 2H, Ar-Hₚ), 5.87 (m, 1H, Hₜ), 5.37-5.12 (m, 4H, CH₂γ', Hα', NH), 4.53-4.66 (m, 2H, CH₂α'), 4.45-4.30 (m, 1H, Hα), 2.46-2.35 (m, 2H, CH₂β), 2.23-2.11 & 1.96-1.85 (m, 1H each, CH₂β), 1.53 (d, Jα',β' = 6.8 Hz, 3H, CH₃β'), 1.43 & 1.37 (s, 4.5H each, t-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 200.1, 197.6, 172.4, 155.2, 134.9, 133.7, 132.0, 128.8, 128.6, 118.6, 80.7, 65.6, 60.0, 42.7, 42.6, 30.2, 28.4, 27.5, 27.3, 17.8, 17.6; ESIHRMS: m/z calcd. for C₂₂H₂₆NO₅SNa (M + Na)⁺ 458.1613, found 458.1628.

**Sα-α-Methylphenacly N-tert-butoxycarbonyl-1-α-thioglutamate (S3).**

Triphenylphosphine (286 mg, 1.1 mmol) and palladium (II) acetate (49 mg, 0.21 mmol) in CH₂Cl₂ (9.0 mL) were added to Boc-ℓ-Glu(OAl₃)-Smpa (S2, 1.9 g, 4.36 mmol). The mixture was degassed, and then phenylsilane (0.27 mL, 2.2 mmol) was added. After stirring for 1 h, the resulting solution was concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20 g, CHCl₃/MeOH = 39/1 to 19/1) gave a yellow form (1.65 g, 96%). 1H NMR (400 MHz, CDCl₃) δ 8.38 (br, 1H, CO₂H), 7.93 (d, J₀,m = 7.2 Hz, 2H, Ar-H₀), 7.55 (t, Jm,p = 7.2 Hz, 1H, Ar-Hₚ), 7.44 (dd, J₀,m = 7.2 Hz, Jm,p = 7.2 Hz, 2H, Ar-Hₚ), 5.33-5.22 (br m, 1H, NH), 5.21 (q, Jα',β' = 6.8 Hz, 1H, Hα'), 4.45-4.09 (m, 1H, Hₜ), 2.53-2.33 (m, 2H, CH₂β), 2.24-2.05 & 1.98-1.81 (m, 1H each, CH₂β), 1.52 (d, Jα',β' = 6.8 Hz, 3H, CH₃β'), 1.42 & 1.40 (s, 4.5H each, t-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 200.8, 197.5, 197.2, 155.3, 134.9, 133.7, 128.8, 128.7, 80.9, 59.9, 42.8, 30.1, 28.4, 27.3, 17.8, 17.6; ESIHRMS: m/z calcd. for C₁₀H₁₅NO₅SNa (M + Na)⁺ 418.1300, found 418.1312.

**Sα-α-Methylphenacly O-tert-butyl N-(9-fluorenylmethyloxycarbonyl)-1-α-thioglutamate (S5).**

To a Fmoc-ℓ-Glu(OBu)-OH·H₂O (1.0 g, 2.3 mmol) and α-methylphenacylthiol (0.47 g, 2.8 mmol) in CH₂Cl₂ (4.7 mL) were added EDCI (0.54 g, 2.8 mmol) and DMAP (29 mg, 0.23 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water.
(100 mL). The mixture was extracted with CH₂Cl₂ (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20g, hexane/EtOAc = 9/1 to 4/1) gave a yellow foam (1.3 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 & 7.92 (d, Jₓₑₘ = 8.0 Hz, 1H each, Ar-Hₓ), 7.74 & 7.73 (d, Jₓₑₙ = 8.0 Hz, 1H each, Hₘ), 7.61 & 7.55 (d, Jₓₑₙ = 7.6 Hz, 1H each, Hₘ), 7.53 & 7.51 (t, Jₓₑₙ = 7.6 Hz, 0.5H each, Ar-Hₘ), 7.43 (dd, Jₓₑₘ = 8.0 Hz, Jₓₑₙ = 7.6 Hz, 2H, Ar-Hₓ), 7.37 (dd, Jₓₑₙ = 7.6 Hz, Jₓₑₙ = 8.0 Hz, 2H, Hₘ), 7.29 (dd, Jₓₑₙ = 7.6 Hz, Jₓₑₙ = 7.6 Hz, 2H, Hₘ), 7.29 & 7.12 (m, 4.5H each, Ar), 5.21 & 5.19 (q, Jₓₑₙ = 6.8 Hz, 1H, Hₓ), 4.53-4.42 (m, 2H, ArH), 4.32 (t, Jₓₑₙ = 6.8 Hz, 0.5H each, Hₓ), 2.38-2.23 (m, 2H, CH₂₂), 2.15 & 1.93 (dt, Jₓₑₙ = 6.8 Hz, Jₓₑₙ = 6.8 Hz, 1H each, CH₂₂), 1.55 & 1.54 (d, Jₓₑₙ = 6.0 Hz, 1.5H each, CH₃₂), 1.45 & 1.44 (s, 4.5H each, 1Bu); ¹³C NMR (100 MHz, CDCl₃) δ 200.0, 199.4, 197.6, 197.2, 172.4, 172.3 156.0, 155.9, 143.9, 143.9, 143.7, 143.7, 141.4, 141.3, 135.0, 134.9, 133.7, 128.8, 128.8, 128.7, 127.9, 127.8, 127.2, 127.2, 125.2, 125.1, 120.1, 120.1, 81.2, 67.3, 67.3, 60.7, 60.7, 47.2, 47.2, 42.8, 42.6, 31.5, 28.2, 27.4, 27.2, 17.8, 17.6; ESIHRMS: m/z calcd. for C₃₃H₃₅NO₉SNa (M + Na)⁺ 596.2083, found 596.2106.

S*-α-Methylphenacyl N-fluorenylmethoxy carbonyl-1-α-thioglutamate (S6). To a solution of Fmoc-L-Glu(OtBu)-SMpa (S5, 115 mg, 0.20 mmol) in 40% TFA/CH₂Cl₂ (1.0 mL) was added EtSiH (38 µL, 0.24 mmol), and the reaction mixture was stirred for 1 h. The solution was concentrated in vacuo, and the residual TFA was removed by azeotropic distillation with toluene in vacuo which gave a colourless form (quantitative yield). ¹H NMR (400 MHz, CDCl₃) δ 8.43 (br, 1H, CO₂H), 7.93 & 7.91 (d, Jₓₑₙ = 8.4 Hz, 1H each, Ar-Hₓ), 7.72 (d, Jₓₑₙ = 7.2 Hz, 2H, Hₘ), 7.61-7.50 (m, 3H, Ar-H, Fm-H x 2), 7.45-7.23 (m, 6H, ArH x 2, FmH x 4), 5.80 & 5.73 (br d, Jₓₑₙ = 6.8 Hz, 0.5H each, NH), 5.21 (q, Jₓₑₙ = 6.8 Hz, 1H, Hₓ), 4.53-4.30 (m, 3H, CH₂₂, Hₓ), 4.18 & 4.14 (t, Jₓₑₙ = 6.8 Hz, 0.5H each, Hₓ), 2.46-2.28 (m, 2H, CH₂₂), 2.26-2.13 & 1.95-1.82 (m, 1H each, CH₂₂), 1.52 (d, Jₓₑₙ = 6.8 Hz, 3H, CH₃₂); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 199.3, 197.8, 197.4, 177.9, 177.8 156.2, 156.1, 143.8, 143.8, 143.7, 143.7, 141.4, 134.9, 134.9, 134.8, 133.8, 128.9, 128.7, 127.9, 127.2, 125.2, 125.1, 120.1, 67.4, 67.3, 60.4, 60.3, 47.2, 43.2, 43.0, 30.1, 27.4, 27.2, 17.7, 17.6; ESIHRMS: m/z calcd. for C₂₉H₂₃NO₉SNa (M + Na)⁺ 540.1457, found 540.1449.
General procedure for deprotection followed by derivatization to S-benzyl thioesters 8a-i (Table 2). S-α-Methylphenacyl thioesters in 90% AcOH aq. (0.1 M) was degassed, and 50 equiv. of freshly washed Zn was added to the solution. The mixture was degassed again and stirred at room temperature, followed by concentration under high vacuum. The residue was suspended in CHCl₃/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated in vacuo. To the residue in DMF (0.1 M) were added 3.0 equiv. of Cs₂CO₃ and BnBr, and the reaction mixture was stirred for 30 min. The reaction was quenched with water (10 mL). The mixture was extracted with CH₂Cl₂ (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding benzyl thioester.

S-Benzyl thiobenzoate (8a). BzSMpa (7a, 60 mg, 0.22 mmol) was used as a S-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 19/1) to afford the title compound as a colorless syrup (41 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, Jₒ,m = 7.6 Hz, 2H, S⁻Bn(Ar-H)), 7.57 (t, Jₘ,p = 7.3 Hz, 1H, S⁻Bn(Ar-H)), 7.50-7.20 (m, 7H, the other Ar-H), 4.38-4.28 (m, 2H, CH₂Ph); ¹³C NMR (100 MHz, CDCl₃) δ 191.4, 137.6, 136.9, 133.5, 129.1, 128.7, 127.4, 127.4, 33.1; Anal. Calcd for (C₁₄H₁₂O₂S): C, 73.65; H, 5.30; O, 7.01; S, 14.04. Found: C, 73.37; H, 5.39.

S-Benzyl thiodecanoate (8b). C₉H₁₉COSMpa (7b, 50 mg, 0.16 mmol) was used as a S-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/toluene = 4/1) to give the title compound as a colorless syrup (40 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.17 (m, 5H, Ar-H), 4.24-4.16 (m, 2H, CH₂Ph), 2.56 (t, Jₐ,β = 7.6 Hz, 2H, CH₂β), 1.67 (m, 2H, CH₂), 1.38-1.16 (m, 12H, CH₂), 0.88 (t, J = 7.0 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 137.9, 128.9, 128.7, 127.2, 43.9, 33.2, 31.9, 29.5, 29.3, 29.0, 25.7, 22.8, 14.2; ESIHRMS: m/z calcd. for C₁₇H₂₆O₂SNa (M + Na)⁺ 301.1602, found 301.1621.
S-Benzy l N-ter t-butoxycar bonyl-l-thiophenylalaninate (8c). Boc-l-Phe-SMpa (7e, 55 mg, 0.13 mmol) was used as a S-α-methylphenacyl thio ester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless solid (41 mg, 83%). [α]D 20 = -11.0 (c = 0.36, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.34-7.21 (m, 8H, Ar-H), 7.14-7.04 (m, 2H, Ar-H), 4.89 (br d, JαNH = 4.0 Hz, 1H, NH), 4.65 (ddd, Jαβ = 6.4 Hz each, JαNH = 4.0 Hz, 1H, Hα), 4.17 & 4.04 (ABq, J = 13.6 Hz, 1H each, CH2Ph), 3.11 (dd, Jαβ = 6.4 Hz, Jββ = 19.2 Hz, 2H, CH2β), 1.43 & 1.39 (s, 4.5H each, 'Bu); 13C NMR (100 MHz, CDCl3) δ 200.5, 155.0, 137.2, 135.5, 129.5, 129.0, 128.9, 128.7, 127.4, 127.1, 80.5, 38.4, 33.4, 28.5, 28.4; ESIHRMS: m/z calcd. for C25H28NO3SNa (M + Na)+ 394.1453, found 394.1479.

S-Benzy l N-ter t-butoxycar bonylthioglycine (8d). Boc-Gly-SMpa (7d, 183 mg, 0.57 mmol) was used as a S-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 19/1) to afford the title compound as a yellow foam (132 mg, 83%). mp: 72.4-76.3 °C; 1H NMR (400 MHz, CDCl3) δ 7.38-7.21 (m, 5H, Ar-H), 5.10 (br d, JαNH = 6.2 Hz, NH), 4.15 & 4.12 (ABq, J = 12.4 Hz, 2H, CH2Ph), 4.05 (d, JαNH = 6.2 Hz, 2H, CH2α), 1.45 (s, 9H, 'Bu); 13C NMR (100 MHz, CDCl3), δ 197.8, 137.1, 129.0, 128.7, 127.5, 127.0, 80.5, 50.3, 33.0, 28.4; ESIHRMS: m/z calcd. for C16H19NO3SNa (M + Na)+ 304.0984, found 304.0996.

S-Benzy l N-ter t-butoxycar bonyl-O-benzy l-l-thioserinate (8e). Boc-l-Ser(OBn)-SMpa (7e, 61 mg, 0.14 mmol) was used as a S-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless oil (43 mg, 78%). [α]D 20 = -1.7 (c = 0.53, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.38-7.17 (m, 10H, Ar-H), 5.49 (br d, JαNH = 8.8 Hz, 1H, NH), 4.49 (ddd, JαNH = 8.8 Hz, Jαβ = 3.6 Hz each, 1H, Hα), 4.47-4.42 (m, 2H, SCH2Ph), 4.19 & 4.08 (ABq, J = 14.0 Hz, 1H each, OCH2Ph), 4.00 & 3.98 (dd, Jαβ = 3.6 Hz, Jββ = 9.6 Hz, 1H, CH2β), 3.67 & 3.64 (dd, Jαβ = 3.6 Hz, Jββ = 9.6 Hz, 1H, CH2β), 1.46 (s, 9H, 'Bu); 13C NMR(100 MHz, CDCl3) δ 200.2, 155.4, 137.5, 137.2, 129.0, 128.7, 128.5, 127.9, 127.7, 127.4, 80.5, 73.5, 70.4, 60.4, 33.6, 28.4; ESIHRMS: m/z calcd. for C32H32NO3SNa (M + Na)+ 424.1559, found 424.1572.
**S-Benzyl N-tert-butoxycarbonyl-O-benzyl-L-thiothreonate (8f).** Boc-L-Thr(OBn)-SMpa (7f, 51 mg, 0.11 mmol) was used as a S-α-methylphenaclyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless solid (33 mg, 73%). mp: 90.2-93.2 °C; [α]D20 = -17.0 (c = 0.48, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.40-7.05 (m, 10H, Ar-H), 5.42 (br d, J = 9.2 Hz, 1H, NH), 4.43 & 4.30 (ABq, J = 11.6 Hz, 1H each, SCh2Ph), 4.33-4.25 (m, 2H, Hα, Hβ), 4.20 & 4.03 (ABq, J = 13.6 Hz, 1H each, OCH2Ph), 1.46 (s, 9H, 3Bu), 1.24 (d, Jβγ = 6.0 Hz, CH3γ); 13C NMR (100 MHz, CDCl3) δ 201.3, 156.0, 137.9, 129.0, 128.7, 128.4, 127.8, 127.3, 80.4, 74.8, 71.7, 65.1, 33.6, 28.4, 16.9; ESIHRMS: m/z calcd. for C23H29NO3SNa (M + Na)+ 438.1715, found 438.1725.

**S-Benzyl N-fluorenlymethyloxycarbonyl-L-thiotryptophanate (8g).** Fmoc-L-Trp-SMpa (7g, 80 mg, 0.09 mmol) was used as a S-α-Methylphenaclyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 2/1) to afford the title compound as a white foam (43 mg, 85%). [α]D20 = -47.9 (c = 0.50, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.03 (br, 1H, NHα), 7.75 (d, Jc′,d′ = 7.2 Hz, 2H, Hd′), 7.59 (d, Jd,e = 7.6 Hz, 1H, Hδ), 7.52 (dd, Jb,c′ = 7.6 Hz, Jc′,d′ = 7.2 Hz, 2H, Hc′), 7.43-7.18 (m, 11H, Fm-H x4, InH x2, Ar-H x5), 7.15 (dd, Jd,e = 7.6 Hz, Jc,f = 7.2 Hz, 1H, Hδ), 6.79 (s, 1H, Hb), 5.32 (br d, Jα,NH = 8.8 Hz, 1H, NH), 4.82 (ddd, Jα,NH = 8.8 Hz, Jα,β = 5.2 Hz each, 1H, Hα), 4.35 (dd, Jc,f = 7.2 Hz each, 2H, CH2f), 4.18 (t, Jc,f = 7.2 Hz, 1H, Hc′), 4.11 & 4.07 (ABq, J = 13.6 Hz, 1H each, CH3Ph), 3.34 (ddd, Jα,β = 5.2 Hz each, Jβ,γ = 14.8 Hz, 2H, CH2γ); 13C NMR (100 MHz, CDCl3) δ 200.7, 155.8, 143.9, 143.8, 141.4, 137.1, 136.2, 129.1, 128.7, 127.8, 127.4, 127.2, 125.2, 123.3, 122.5, 120.0, 118.7, 111.4, 109.4, 67.3, 61.1, 47.2, 33.6, 28.2; ESIHRMS: m/z calcd. for C33H28N2O3SNa (M + Na)+ 555.1719, found 555.1709.
**S~a~-Benzyl S~a~9-fluorenylmethyl N-tert-butoxycarbonyl-l-dithioglutamate (8h).**

Boc-L-Glu(SFm)-SMpa (7h, 110 mg, 0.19 mmol) was used as a S-α-Methylphenacetyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/Acetone = 9/1 to 4/1) to afford the title compound as a colourless foam (79 mg, 78%). [α]D = 3.26 (c = 0.31, CHCl3);

1H NMR (400 MHz, CDCl3) δ 7.75 (s, Jcd = 7.6 Hz, 2H, Hα), 7.62 (d, Jab = 7.2 Hz, 2H, Hα), 7.34 (dd, Jbc = 7.2 Hz, Jcd = 7.6 Hz, 2H, Hβ), 7.31 (dd, Jab = 7.2 Hz, Jbc = 7.2 Hz, 2H, Hα), 7.30-7.22 (m, 5H, Ar-H), 5.09 (br, 1H, NH), 4.36-4.26 (m, 1H, Hα), 4.16 (t, Jbc = 5.6 Hz, 1H, Hα), 4.19-4.04 (m, 2H, CH3Ph), 3.53 (d, Jef = 5.6 Hz, 2H, CH2β), 2.65-2.48 (m, 2H, CH2β), 2.22-1.7 & 2.04-1.80 (m, 1H each, CH2β), 1.43 (s, 9H, 'Bu); 13C NMR (100 MHz, CDCl3) δ 200.1, 198.1, 155.2, 145.4, 141.2, 137.0, 129.0, 128.7, 127.9, 127.2, 124.7, 124.7, 124.7, 120.0, 80.6, 59.8, 46.8, 40.0, 33.4, 32.4, 28.4, 28.1; ESIHRMS: m/z calcd. for C31H33NO8S2Na (M + Na)+ 570.1749, found 570.1771

![Structure of 8h](image)

**S~a~-Benzyl S~a~2,4,6-trimethoxybenzyl N-(9-fluorenylmethoxycarbonyl)-l-dithioglutamate (8i).**

Fmoc-L-Glu(STmob)-SMpa (7i, 50 mg, 0.07 mmol) was used as a S-α-Methylphenacetyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 2/1) to afford the title compound as a colorless solid (38 mg, 81%). mp: 103.0-106.2 °C; [α]D = -3.0 (c = 0.43, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.74 (s, Jcd = 7.2 Hz, 2H, Hα), 7.60 (d, Jab = 7.2 Hz, 2H, Hα), 7.38 (dd, Jbc = 6.8 Hz, Jcd = 7.2 Hz, 2H, Hβ), 7.29 (m, 7H, Fm-H, Ar-H x 5), 6.08 (s, 2H, Ar-H), 5.58 (br d, JαNH = 8.4 Hz, 0.5H each, NH), 4.50-4.35 (m, 3H, Hα, CH2β), 4.26-4.18 (m, 3H, CH2Ph, Hα), 4.13 & 4.09 (ABq, J = 13.6 Hz, 2H, CH2Ph), 3.77 (s, 9H, OCH3 x 3), 2.70-2.54 (m, 2H, CH2β), 2.32-2.23 & 2.10-1.98 (m, 1H each, CH2β); 13C NMR (100 MHz, CDCl3) δ 199.9, 199.6, 161.0, 159.2, 155.9, 143.9, 143.8, 143.7, 141.3, 136.8, 129.0, 128.8, 127.8, 127.5, 127.2, 125.2
Purification of the residue was extracted with CHCl₃. The mixture was stirred for further 1 h, quenched with water (20 mL), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. The solution was concentrated in vacuo, and the residual TFA was removed by azeotropic distillation with toluene in vacuo. In another flask, Boc-L-Trp-OH (667 mg, 2.2 mmol), and N-methylmorpholine (192 µL, 1.8 mmol) were suspended in CH₂Cl₂ (3.0 mL), and HOBT·H₂O (355 mg, 2.6 mmol) and EDCI (336 mg, 1.8 mmol) were added. The reaction mixture was stirred for 15 min, and it was added to a solution of the residue in CH₂Cl₂ (3.0 mL). The reaction mixture was stirred for further 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH₂Cl₂ (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash.
chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to 1/1) gave an orange foam (588 mg, 82%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.92 (br s, 1H, NH\(_2\)), 7.95 & 7.94 (d, \(J_{oo}=7.6\) Hz, 1H each, Ar-H\(_o\)), 7.59 (t, \(J_{mp}=7.6\) Hz, 1H, Ar-H\(_p\)), 7.58 (d, \(J_{dx}=6.8\) Hz, 1H, H\(_d\)), 7.46 (dd, \(J_{om}=7.6\) Hz, \(J_{mp}=7.6\) Hz, 2H, Ar-H\(_m\)), 7.32 (dd, \(J_{dx}=6.8\) Hz, \(J_{ef}=8.0\) Hz, 1H, H\(_e\)), 7.16 (dd, \(J_{ef}=8.0\) Hz, \(J_{fg}=7.6\) Hz, 1H, H\(_f\)), 7.09 & 7.08 (d, \(J_{fg}=7.6\) Hz, 0.5H each, H\(_g\)), 7.00 (s, 1H, H\(_b\)), 6.59 (br s, 1H, NH), 5.21 & 5.20 (q, \(J_{e^-f^-}=6.8\) Hz, 0.5H each, H\(_e^\alpha\)), 5.12 (br s, 1H, NH), 4.51 (m, 1H, H\(_o\)), 4.04 (m, 2H, CH\(_2e\)), 3.21 (m, 2H, CH\(_2d\)), 1.49 (d, \(J_{e^-d^-}=6.8\) Hz, 3H, CH\(_3\beta\)), 1.39 (s, 9H, 'Bu'); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 195.8, 172.4, 172.4, 156.5, 155.6, 136.3, 134.8, 133.9, 128.9, 128.7, 127.6, 123.7, 123.6, 119.8, 118.7, 111.4, 110.2, 110.0, 55.4, 55.3, 55.2, 48.9, 42.5, 28.4, 28.0, 17.9, 17.8; ESIHRMS: \(m/z\) calcd. for C\(_{52}H\(_{49}\)N\(_8\)O\(_{20}\)S\(_{17}\)Na (M + Na)\(^+\) 532.1882, found 532.1895.

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\text{S-\(\alpha\)-Methylphenacetyl N\(^*=\)benzoxycarbonyl-N\(^*=\)tert-butoxycarbonyl-L-lysyl-L-tryptophan thio glycinate (10). Boc-L-Trp-Gly-SMpa (9, 526 mg, 1.1 mmol) was dissolved in 40\% TFA/CH\(_2\)Cl\(_2\) (11 mL), and the solution was stirred for 20 min. The solution was concentrated \textit{in vacuo}, and the residual TFA was removed by azotropic distillation with toluene \textit{in vacuo}. In another flask, Cbz-L-Lys(Boc)-OH (605 mg, 1.6 mmol), and N-methylmorpholine (140 \(\mu\)L, 1.3 mmol) were suspended in CH\(_2\)Cl\(_2\) (2.1 mL), and HOBT\cdot H\(_2\)O (258 mg, 1.9 mmol) and EDCI (244 mg, 1.3 mmol) were added. The reaction mixture was stirred for 10 min, and it was added to a solution of the residue in CH\(_2\)Cl\(_2\) (1 mL). The reaction mixture was stirred for further 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH\(_2\)Cl\(_2\) (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na\(_2\)SO\(_4\), and concentrated \textit{in vacuo}. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to 1/1) gave an orange foam (662 mg, 86\%).}
ure was extracted with EtOAc (7 mL, 1 H, CH$_2$Br), 1.49 (d, $J_{\alpha-\beta} = 6.8$ Hz, 3H, CH$_3$Br), 1.39 (s, 9H, 'Bu), 1.38-1.27 (m, 4H, CH$_2$-x2). 0.16-1.03 (m, 2H, CH$_2$); $^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 198.0, 197.7, 172.0, 156.9, 156.7, 156.6, 136.3, 136.0, 134.7, 134.0, 133.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.6, 124.0, 123.7, 122.2, 119.8, 118.4, 118.3, 111.6, 110.0, 79.5, 77.3, 67.4, 67.3, 54.0, 49.1, 42.6, 29.8, 28.5, 18.1; ESIHRMS: m/z calcd. for C$_{41}$H$_{49}$N$_3$O$_8$SNa (M + Na)$^+$ 794.3186, found 794.3200.

$S$-Benzy1 $N^\alpha$-benzyloxycarbonyl-$N^\beta$-tert-butoxycarbonyl-$L$-lysyl-$L$-tryptophenylthioglycinate (II). Cbz-L-Lys(Boc)-L-Trp-Gly-SMpa (10, 62 mg, 0.08 mmol) in 90% AcOH (0.8 mL) was degassed, and freshly washed Zn (268 mg, 4.1 mmol) was added to the solution. The mixture was degassed again and stirred for 1 h at 40 °C, followed by concentration under high vacuum. The residue was suspended in CHCl$_3$/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated in vacuo. To the residue in DMF (0.8 ml) were added Cs$_2$CO$_3$ (79 mg, 0.25 mmol) and BnBr, and the reaction mixture was stirred for 15 min. The reaction was quenched with water (10 mL). The mixture was extracted with EtOAc (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 10 g, CHCl$_3$ to CHCl$_3$/EtOAc = 1/1) gave the title compound as a colorless solid (50 mg, 89%). mp: 132.8-138.8 °C; [$\alpha$]$_{D}^{20}$ = -25.1 (c = 0.63, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (br, 1H, NH$_a$), 7.53 (d, $J_{d,e} = 7.8$ Hz, 1H, H$_d$), 7.37-7.16 (m, 11H, In-H), Ar-H x10), 7.12 (dd, $J_{d,e} = 7.8$ Hz, $J_{e,f} = 7.7$ Hz, 1H, H$_e$), 7.05 (dd, $J_{e,f} = 7.7$ Hz, $J_{f,g} = 7.0$ Hz 1H, H$_f$), 6.94 (s, 1H, H$_g$), 6.87 (br, 1H, NH), 5.73 (br, 1H, NH), 4.97 & 4.92 (ABq, $J = 12.0$ Hz, 1H each, PhCH$_2$)$_2$, 4.82 (m, 1H, H$_a$), 4.71 (br, 1H, NH), 4.16-3.87 (m, 5H, CH$_2$Ph, CH$_2$-$\alpha$, H$_d$), 3.32-3.17 (m, 2H, CH$_2$-$\beta$), 3.30-2.87 (m, 2H, CH$_2$-Br), 1.40 (s, 9H, 'Bu), 1.32-1.20 (m, 4H, CH$_2$ x2), 1.15-1.00 (m, 2H, CH$_2$); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.6, 172.1, 171.9, 156.8, 156.6, 137.1, 136.7, 136.1, 129.0, 128.6, 128.4, 128.2, 127.5, 123.6, 122.1, 119.7, 118.5, 111.5, 110.0, 79.5, 77.3, 67.3, 55.8, 53.9, 49.0, 39.6, 33.0, 31.2, 29.7, 28.5, 27.3, 22.1; ESIHRMS: m/z calcd. for C$_{39}$H$_{47}$N$_3$O$_8$SNa (M + Na)$^+$ 752.3094, found 752.3100.

SI-22
**Oα- Allyl Oβ-(9-fluorenylmethyl) N-tert-butoxycarbonyl-L-glutamate (13).**

To Boc-L-Glu(OFm)-OH[5] (12, 1.4 g, 3.3 mmol) in DMF (6.6 mL) were added AllBr (0.34 mL, 4.0 mmol) and K₂CO₃ (0.55 g, 4.0 mmol) at room temperature. The reaction mixture was stirred for 3 h, and then poured to water (100 mL). The mixture was extracted with CH₂Cl₂ (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification of the residue by flash chromatography (silica gel 10 g, hexane/EtOAc = 9/1 to 4/1) gave the title compound as a colorless syrup (1.5 g, 97%). [α]²⁰₀ = 5.9 (c = 0.78, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, Jₐ,a = 7.2 Hz, 2H, Hₐ), 7.57 (d, Jₐ,b = 7.6 Hz, 2H, Hₐ), 7.38 (dd, Jₐ,c = 7.2 Hz, Jₐ,b = 7.6 Hz, 2H, Hₐ), 7.30 (dd, Jₐ,d = 7.2 Hz, Jₐ,b = 7.2 Hz, 2H, Hₐ), 5.90 (dddd, Jₐ,β = 5.2 Hz each, Jₐ,γ(Ε) = 16.8 Hz, Jₐ,γ(Ζ) = 10.4 Hz, 1H, Hₜ), 5.38 (dddd, Jₐ,γ(Ε) = 16.8 Hz, Jₐ,γ(Ζ) = 10.4 Hz, Jₐ,φ = 1.2 Hz, 2H, CH₂ₕ), 5.30-5.18 (br, 1H, NH), 4.63 (dd, Jₐ,φ = 5.2 Hz each, 2H, CH₂ₐ), 4.4-4.33 (m, 3H, CH₂ₕ, Hₗ), 4.19 (t, Jₜ,f = 6.8 Hz, 1H, Hₗ), 2.49 (td, Jₜ,γ = 6.8 Hz, Jₜ,γ = 16.0 Hz, 2H, CH₂ₕ), 2.21 & 1.97 (dddd, Jₜ,φ = 20.8 Hz, Jₜ,φ = 6.8 Hz each, 1H each, CH₂ₕ), 1.41 (s, 9H, βBu); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 171.9, 155.5, 143.8, 143.8, 141.4, 131.6, 127.9, 127.2, 125.1, 120.1, 119.0, 80.1, 66.6, 66.1, 53.1, 46.9, 30.4, 28.4, 27.8; ESI-HRMS: m/z calcd. for C₂₇H₃₃NO₆Na (M + Na)⁺ 488.2049, found 488.2053.

**Oα-Allyl N-tert-butoxycarbonyl-L-glutamic acid (14).** Boc-L-Glu(OFm)-OAll (13, 0.89 g, 1.9 mmol) was added 20% piperidine in DMF (7.3 mL) at room temperature, and the reaction mixture was stirred 20 min, followed by concentration under high vacuum. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to EtOAc) gave the title compound as a colorless syrup (470 mg, 85%). [α]²⁰₀ = 1.5 (c = 1.55, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 9.30-8.30 (br, 1H, CO₂H), 5.88 (ddddd, Jₐ,β = 5.6 Hz each, Jₐ,γ(Ε) = 17.2 Hz, Jₐ,γ(Ζ) = 10.8 Hz, 1H, Hₜ), 5.28 (dddd, Jₐ,γ(Ε) = 17.2 Hz, Jₐ,γ(Ζ) = 10.8 Hz, Jₐ,φ = 1.6 Hz, 2H, CH₂ₕ), 5.22-5.16 (br d, Jₐ,NH = 8.0 Hz, 1H, NH), 4.61 (dd, Jₐ,φ = 5.6 Hz each, 2H, CH₂ₐ), 4.35 (ddd, Jₐ,NH = 8.0 Hz, Jₐ,β = 6.8 Hz).
Hz each, 1H, Hα), 2.44 (td, Jβ,γ = 6.8 Hz each, Jβ,δ = 7.2 Hz, 2H, CH₂β), 2.18 & 1.95 (tdd, Jα,γ = 6.8 Hz, Jβ,γ = 14.4 Hz, 1H each, CH₂γ), 1.44 (s, 9H, 'Bu); ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 172.0, 155.6, 131.5, 119.1, 80.3, 66.2, 52.9, 30.2, 28.3, 27.7; ESI-HRMS: m/z calcd. for C₁₃H₂₃NO₆Na (M + Na)⁺ 310.1267, found 310.1251.

Oα-allyl Sα-α-methylphenacyl N-tert-butoxycarbonyl-l-γ-thioglutamate (15).

To Boc-l-Glu(OH)-OAll (14, 710 mg, 2.5 mmol) and S-α-methylphenacylthiol (500 mg, 3.0 mmol) in CH₂Cl₂ (5.0 mL) were added EDCI (570 mg, 3.0 mmol) and DMAP (30 mg, 0.25 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (30 mL). The mixture was extracted with CH₂Cl₂ (15 mL × 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 9/1) gave a yellow syrup (2.3 mL) were added. After stirring for 1 h, the resulting solution was concentrated in vacuo. Purification of the residue by flash chromatography (silica gel

Sα-α-Methylphenacyl N-tert-butoxycarbonyl-l-γ-thioglutamic acid (16). Triphenylphosphine (29 mg, 0.11 mmol) and palladium (II) acetate (5.0 mg, 0.02 mmol) in CH₂Cl₂ (2.3 mL) were added to a solution of Boc-l-Glu(SMpa)-OAll (15, 490 mg, 1.1 mmol) in CH₂Cl₂ (2.3 mL). The mixture was degassed, and then phenylsilane (0.07 mL, 0.56 mmol) was added. After stirring for 1 h, the resulting solution was concentrated in vacuo. Purification of the residue by flash chromatography (silica gel
15 g. CHCl₃/EtOAc = 9/1 to 4/1) gave a yellow form (436 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, Jₐₘ = 8.0 Hz, 2H, Ar-Hₐ), 7.55 (t, Jₐₚ = 7.6 Hz, 1H, Ar-Hₐ), 7.43 (dd, Jₐₘ = 8.0 Hz, Jₐₚ = 7.6 Hz, 2H, Ar-Hₐ), 5.32 (br, 1H, NH), 5.25 (q, Jₐₐ = 6.8 Hz, 1H, Hₐ), 4.36-4.09 (m, 1H, Hₐ), 2.78-2.55 (m, 2H, CH₂), 2.30-2.13 & 2.09-2.00 (m, 1H each, CH₂), 1.51 (d, Jₐₐ = 6.8 Hz, 3H, CH₃), 1.39 (s, 9H, 'Bu); ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 197.5, 197.2, 197.1, 197.1, 155.9, 155.8, 134.9, 133.8, 128.8, 128.6, 80.5, 80.4, 42.5, 39.7, 39.6, 29.8, 28.4, 27.8, 17.8, 17.8; ESIHRMS: m/z calcd. for C₁₉H₂₅NO₃SNa (M + Na)⁺ 418.1301, found 418.1329.

**Ethyl N-tert-butoxycarbonyl-L-3α-methylphenacetyl-γ-thioglutamylglycinate (17).**

Boc-L-Glu(Smpa)-OH (16, 210 mg, 0.52 mmol), and HOBt.H₂O (120 mg, 0.79 mmol) were suspended in CH₂Cl₂ (5.0 mL), and EDCI (120 mg, 0.63 mmol) and N-methylmorpholine (68 µL, 0.63 mmol) were added. The mixture was stirred for 10 min, and then H₂N-Gly-OEt·HCl (88 mg, 0.63 mmol) was added. The reaction mixture was stirred for further 3 h, and then quenched with water (20 mL). The mixture was extracted with CH₂Cl₂ (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel 15 g, hexane/EtOAc = 4/1 to 1/1) gave a yellow foam (210 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, Jₐₘ = 7.2 Hz, 2H, Ar-Hₐ), 7.53 (t, Jₐₚ = 7.2 Hz, 1H, Ar-Hₐ), 7.42 (dd, Jₐₘ = 7.2 Hz, Jₐₚ = 7.2 Hz, 2H, Ar-Hₐ), 6.99 (br, 1H, NH), 5.41 (br, 1H, NH), 5.23 (q, 1H, Jₐₐ = 6.8 Hz, Hₐ), 4.27-4.16 (m, 1H, Hₐ), 4.14 (q, Jₐₐ = 6.8 Hz, 2H, CH₂), 3.87-4.03 (m, 2H, CH₂), 2.68 (m, 2H, CH₂), 2.14 & 1.95 (m, 1H each, CH₂), 1.50 (d, Jₐₐ = 6.8 Hz, 3H, CH₃), 1.37 (s, 9H, 'Bu), 1.21 (t, Jₐₐ = 6.8 Hz, 3H, CH₃); ¹³C NMR (100MHz, CDCl₃) δ 197.4, 197.3, 197.3, 171.7, 169.6, 169.6, 155.7, 134.9, 134.9, 133.6, 128.8, 128.6, 80.3, 61.5, 53.4, 53.2, 41.1, 39.7, 39.5, 28.4, 28.1, 17.8, 17.7, 14.2; ESIHRMS: m/z calcd. for C₂₂H₃₂N₅O₅SNa (M + Na)⁺ 503.1828, found 503.1851.
Ethyl N-tert-Butyloxycarbonyl-L-tryptophanyl-S-α-methylphenacyl-L-thioglutamylglycinate (18). Boc-L-Glu(SMpa)-Gly-OEt (17, 87 mg, 0.18 mmol) was dissolved in 40% TFA/CH₂Cl₂ (0.9 mL), and the solution was stirred for 15 min. The solution was concentrated in vacuo, and the residual TFA was removed by azeotropic distillation with toluene in vacuo. In another flask, Boc-L-Trp-OH (66 mg, 0.22 mmol) and N-methylmorpholine (24 µL, 0.22 mmol) were suspended in CH₂Cl₂/DMF (1/1, 1.0 mL), and HOBt·H₂O (42 mg, 0.27 mmol) and EDCI (42 mg, 0.22 mmol) were added. The reaction mixture was stirred for 10 min, and it was added to a solution of the residue in CH₂Cl₂/DMF (1/1, 1.0 mL). The reaction mixture was stirred for further 1 h, and then quenched with water (10 mL). The mixture was extracted with CH₂Cl₂ (5 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (10 g, CHCl₃ to CHCl₃/MeOH = 9/1) gave a colorless form (87 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.73 & 8.59 (br, 0.5H each, NH₂), 7.98 & 7.94 (d, Jₐ,m = 7.2 Hz, 1H each, Ar-H₂), 7.64-7.54 (m, 2H, Ar-H, In-H), 7.48 & 7.45 (dd, Jₐ,m = 7.2 Hz, Jₐ,p = 7.6 Hz, 1H each, Ar-Hₘ), 7.30 (m, 1H, In-H), 7.16-7.03 (m, 2H, In-H), 6.99-6.82 (m, 3H, In-H, NH x 2), 5.30 & 5.28 (br, 1H, NH), 5.19 & 5.18 (q, Jₐ−,p− = 6.8 Hz, 0.5H each, Hₐ−), 4.49-4.40 (m, 1H, Hₐ), 4.38-4.26 (m, 1H, Hₐ'), 4.13 & 4.12 (q, Jₐ,b = 7.2 Hz, 1H each, CH₃), 3.90-3.60 (m, 2H, CH₃ₚ'), 3.35-3.23 & 3.19-3.08 (m, 1H each, CH₂p), 2.50-2.38 & 2.27-2.18 (m, 1H each, CH₂β'), 2.10-1.98 & 1.97-1.76 (m, 1H each, CH₂p'), 1.50 & 1.49 (d, Jₐ−,p− = 6.8 Hz, 1.5H each, CH₃p−), 1.40 (s, 9H, 3Bu), 1.23 & 1.22 (t, Jₐ,b = 7.2 Hz, 1.5H each, CH₂b); ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 198.2, 197.9, 197.8, 172.5, 172.4, 171.0, 170.9, 169.5, 162.9, 156.0, 156.0, 155.9, 136.3, 136.3, 135.1, 134.9, 133.8, 133.8, 129.0, 128.9, 128.7, 128.7, 127.5, 127.4, 126.7, 126.1, 123.6, 123.5, 122.2, 119.7, 118.7, 118.6, 111.6, 111.6, 109.7, 80.6, 61.5, 61.5, 56.0, 52.3, 52.1, 43.0, 43.0, 41.3, 39.1, 39.0, 36.7, 31.6, 28.4, 28.0, 27.9, 27.3, 17.5, 17.5, 14.2; ESIHRMS: m/z calcd. for C₃₄H₄₂N₂O₂SNa (M + Na)⁺ 689.2621, found 689.2614.
Ethyl \(N\text{-tert-butoxycarbonyl-L-tryptophanyl-S\text{-benzyl-L-\(\gamma\)thioglutamylglycinate} (19)}\)

Boc-L-Trp-L-Glu(SMpa)-Gly-OEt (18, 40 mg, 0.06 mmol) in 90% AcOH (0.6 mL) was degassed, and freshly washed Zn (198 mg, 3.0 mmol) was added to the solution. The mixture was degassed again and stirred for 6 h at 40 °C, followed by concentration under high vacuum. The residue was suspended in CHCl\(_3\)/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated in vacuo. To the residue in DMF (0.6 mL) were added Cs\(_2\)CO\(_3\) (60 mg, 0.18 mmol) and BnBr, and the reaction mixture was stirred for 15 min. The reaction was quenched with water (10 mL). The mixture was extracted with EtO\(_2\)BnBr, and the reaction mixture was stirred for 15 min. The reaction was quenched with water (10 mL). The mixture was extracted with EtOAc (5 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na\(_2\)SO\(_4\), and concentrated in vacuo. Purification of the residue by silica gel column chromatography (10 g, CHCl\(_3\) to CHCl\(_3\)/MeOH = 9/1) gave the title compound as a white foam (30 mg, 79%). \([\alpha]^{20}_D = -41.3\) (c = 0.45, CHCl\(_3\)) \(1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05-8.00 (br, 1H, NH), 7.90 (d, \(J_{a,e} = 7.6\) Hz, 1H, \(H_d\)), 7.35-7.23 (m, 6H, In-H, Ar-H x 5), 7.15 (dd, \(J_{d,e} = 7.6\) Hz, \(J_{a,f} = 7.2\) Hz, 1H, \(H_e\)), 7.09 (dd, \(J_{d,e} = 7.2\) Hz, \(J_{f,e} = 7.6\) Hz, 1H, \(H_j\)), 6.97 (m, 1H, In-H), 6.90-6.79 (m, 2H, NH x 2), 5.16 (br d, \(J_{a,NH} = 5.6\) Hz, 1H, NH), 4.41 (ddd, \(J_{a,b} = 5.6\) Hz each, \(J_{a,NH} = 5.6\) Hz, 1H, \(H_a\)), 4.33 (ddd, \(J_{a',b'} = 7.6\) Hz each, \(J_{a',NH} = 6.4\) Hz, 1H, \(H_{a'}\)), 4.16 (q, \(J_{a,b} = 7.2\) Hz, 2H, CH\(_2\)), 4.06 & 4.02 (ABq, \(J = 14.0\) Hz, 1H each, CH\(_3\)Ph), 3.90 & 3.71 (dd, \(J_{a',NH} = 6.0\) Hz, \(J_{a',a''} = 18.0\) Hz, 1H, CH\(_{2\alpha'}\)), 3.32 & 3.14 (dd, \(J_{a,b} = 5.6\) Hz, \(J_{\beta,\beta} = 14.4\) Hz, 1H each, CH\(_{3\beta}\)), 2.49 & 2.20 (td, \(J_{\beta',\gamma'} = 6.8\) Hz, \(J_{\gamma',\gamma'} = 16.4\) Hz, 1H each, CH\(_{2\gamma}\)), 1.98 & 1.87 (ddt, \(J_{a',\beta'} = 7.6\) Hz, \(J_{\beta',\gamma'} = 6.8\) Hz, \(J_{\beta',\beta'} = 12.8\) Hz, 1H each, CH\(_{3\beta}\)), 1.42 (s, 9H, \(\text{Bu}\)), 1.25 (t, \(J_{a,b} = 7.2\) Hz, 3H, CH\(_3a\)); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.4, 172.3, 171.0, 169.5, 137.6, 136.2, 129.0, 128.8, 127.5, 127.4, 123.4, 122.4, 119.9, 118.9, 111.4, 110.0, 80.6, 61.5, 55.7, 52.5, 41.3, 39.2, 33.4, 29.8, 29.7, 28.4, 28.0, 27.1, 14.2; ESIHRMS: m/z calcd. for C\(_{32}\)H\(_{40}\)N\(_4\)O\(_3\)-SNa (M + Na\(^+\)) \({\text{647.2516, found 647.2533.}}\)

References


$S$-α-Methylphenacyl thioacetate (2b) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl thioacetate (2b) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α,α-Dimethylphenacyl thioacetate (2c) $^1$H NMR (400 MHz, CDCl$_3$)
$\text{S-}\alpha,\alpha\text{-Dimethylphenacyl thioacetate (2c) }^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$

![S-\alpha,\alpha-Dimethylphenacyl thioacetate (2c) 13C NMR (100 MHz, CDCl₃)](image-url)
\( \alpha \)-Methylphenacylthiol (3b) \(^1\)H NMR (400 MHz, CDCl\(_3\))
α-Methylphenacylthiol (3b) $^{13}$C NMR (100 MHz, CDCl$_3$)
α,α-Dimethylphenacylthiol (3c) $^1$H NMR (400 MHz, CDCl$_3$)
\( \alpha,\alpha\)-Dimethylphenacylthiol (3c) \(^{13}\)C NMR (100 MHz, CDCl\(_3\))
S-Phe

\textit{N-}tert-butoxycarbonyl-\textit{l}-thiotryptophanate (4a) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})
S-Phenacyl N-tert-butoxycarbonyl-L-thiotryptophanate (4a) $^{13}$C NMR (100 MHz, CDCl$_3$)
$S$-\(\alpha\)-Methylphenacyl $N$-\textit{tert}-butoxycarbonyl-\textit{l}-thiotryptophanate (4b) \(^1\)H NMR (400 MHz, CDCl\(_3\))
S-α-Methylphenacyl N-tert-butoxycarbonyl-l-thiotryptophanate (4b) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-(α,α-Dimethylphenacyl) N-tert-butoxycarbonyl-L-thiotryptophanate (4c) ^1H NMR (400 MHz, CDCl_3)
S-(α,α-Dimethylphenacyl) N-tert-butoxycarbonyl-L-thiotryptophanate (4c) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonyl-L-thiaproline (5a-c) $^1$H NMR (400 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonyl-L-thiotryptophanate (5a-c) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl thiobenzoate (7a) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl thiobenzoate (7a) $^{13}$C NMR (100 MHz, CDCl₃)
S-α-Methylphenacyl thiodecanoate (7b) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl thiodecanoate (7b) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacetyl N-tert-butoxycarbonyl-L-thiophenylalainate (7c) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl N-tert-butoxycarbonyl-L-thiophenylalainate (7c) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl N-tert-butoxycarbonyl-thioglycinate (7d) \(^1\)H NMR (400 MHz, CDCl\(_3\))
S-α-Methylenacyl N-tert-butoxycarbonylthioglycinate (7d) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl *N*-tert-butoxycarbonyl-O-benzyl-L-thioserinate (7e) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl N-tert-butoxycarbonyl-O-benzyl-L-thioserinate (7e) $^1$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenaclyl N-tert-butoxycarbonyl-O-benzyl-L-thiothreonate (7f) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl N-tert-butoxycarbonyl-O-benzyl-L-thiothreonate (7f) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl N-fluorenymethoxy carbonyl-L-thiotryptophanate (7g) $^1$H NMR (400 MHz, CDCl$_3$)
S-α-Methylphenacyl N-fluorenlymethoxy carbonyl-L-thiotryptophanate (7g) $^{13}$C NMR (100 MHz, CDCl$_3$)

![Chemical Structure](image)
$S^\alpha-\alpha$-Methylphenacyl $S^\gamma-9$-fluorenymethyl $N$-tert-butoxycarbonyl-1-dithioglutamate (7h) $^1$H NMR (400 MHz, CDCl$_3$)
$S^\alpha-\alpha$-Methylphenacetyl $S^\alpha-9$-fluorenylmethyl N-tert-butoxycarbonyl-l-dithioglutamate (7h) $^{13}$C NMR (100 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

Single Pulse with Broadband Decoupling

119.868 198.148
155.068
141.199
134.866
133.668
128.839
122.665
119.713
116.994
80.799
59.810
48.237
39.770
32.394
22.966
17.934

O
S

BocHN

O
S

Ph

7h

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$\alpha$-Methylphenacyl $\alpha$-2,4,6-trimethoxybenzyl N-(9-fluorenmethyloxycarbonyl)-L-dithioglutamate (7i) $^1$H NMR (400 MHz, CDCl$_3$)
$S\alpha$-Methylphenacyl $S\alpha$-2,4,6-trimethoxybenzyl N-(9-fluorenylmethyloxycarbonyl)-l-dithioglutamate (7i) $^{13}$C NMR (100 MHz, CDCl₃)
\textit{S}^{\alpha,\alpha}\text{-Methylphenacyl} \text{O}^{\alpha}\text{-allyl} \text{N-tert-butoxycarbonyl-1,\alpha-thioglutamate (S2) $^1$H NMR (400 MHz, CDCl$_3$)}

\begin{align*}
S^\alpha\alpha\text{-Methylphenacyl} \text{O}^\alpha\text{-allyl} \text{N-tert-butoxycarbonyl-1,\alpha-thioglutamate (S2) $^1$H NMR (400 MHz, CDCl$_3$)}
\end{align*}
$S^{\alpha,\alpha}$-Methylphenacyl $O^{\alpha}$-allyl N-tert-butoxycarbonyl-l-$\alpha$-thioglutamate (S2) $^{13}$C NMR (100 MHz, CDCl$_3$)
$S^\alpha-\alpha$-Methylphenacyl $N$-tert-butoxycarbonyl-L-$\alpha$-thioglutamate (S3) $^1$H NMR (400 MHz, CDCl$_3$)
$S\alpha$-Methylphenacly $N\text{-}[\text{tert-butoxycarbonyl-L-}\alpha\text{-thioglutamate}}$ (S3) $^{13}$C NMR (100 MHz, CDCl$_3$)

14HT3-142-1,13c
Single Pulse with Broadband Decoupling
$S^\alpha$-$\alpha$-Methylphenacyl $O^{\text{t}-\text{tert}}$-butyl N-(9-fluorenylmethoxy carbonyl)-l-$\alpha$-thioglutamate (S5) $^1$H NMR (400 MHz, CDCl$_3$)
$\alpha$-Methylphenacyl O-tert-butyl N-(9-fluorenylmethyloxycarbonyl)-l-\(\alpha\)-thioglutamate (S5) $^{13}$C NMR (100 MHz, CDCl$_3$)
$S^\alpha$-α-Methylphenacyl $N$-fluorenlymethyloxycarbonyl-$l$-$\alpha$-thioglutamate (S6) $^1$H NMR (400 MHz, CDCl$_3$)
S6-4-Methylphenacyl N-fluorenylmethyloxycarbonyl-\(\alpha\)-thioglutamate (S6)

\(^{13}C\) NMR (100 MHz, CDCl\(_3\))
S-Benzyl thiobenzoate (8a) $^1$H NMR (400 MHz, CDCl$_3$)
S-Benzyl thiobenzoate (8a) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl thiodecanoate (8b) $^1$H NMR (400 MHz, CDCl$_3$)
$S$-Benzyl thiodecanoate (8b) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonyl-L-thiophenylalaninate (8c) $^1$H NMR (400 MHz, CDCl$_3$)
S-Benzyl N-terti-butoxycarbonyl-L-thiophenylalaninate (8c) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonylthioglycinate (8d) $^1$H NMR (400 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonylthioglycinate (8d) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonyl-O-benzyl-L-thioserinate (8e) \(^1\)H NMR (400 MHz, CDCl\(_3\))
S-Benzyl \(N\)-\textit{tert} butoxycarbonyl-\(O\)-benzyl-\textit{L}-thioserinate (8e) \(^{13}\)C NMR (100 MHz, CDCl\(_3\))
S-Benzyl N-tert-butoxycarbonyl-O-benzyl-L-thiothreonate (8f) $^1$H NMR (400 MHz, CDCl$_3$)
S-Benzyl N-tert-butoxycarbonyl-O-benzyl-L-thiothreonate (8f) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-Benzyl N-fluorenlymethyloxycarbonyl-L-thiotryptophanate (8g) $^1$H NMR (400 MHz, CDCl$_3$)

![NMR Spectrum](image-url)
S-Benzyl N-fluorenlymethoxy carbonyl-L-thiotryptophanate (8g) $^{13}$C NMR (100 MHz, CDCl$_3$)
$\alpha$-Benzyl $\gamma$-9-fluorenylmethyl N-tert-butoxycarbonyl-L-dithioglutamate (8h)  

$^1$H NMR (400 MHz, CDCl$_3$)
$\alpha$-Benzyl $\gamma$-9-fluorenylmethyl N-tert-butoxycarbonyl-L-dithioglutamate (8h)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$S^\alpha$-Benzyl $S\gamma$-2,4,6-trimethoxybenzyl $N$-((9-fluorenylmethyloxycarbonyl)-1-dithioglutamate (8i) $^1$H NMR (400 MHz, CDCl$_3$)
$S^\alpha$-Benzyl $S^\varphi$-2,4,6-trimethoxybenzyl $N$-($9$-fluorenylmethyloxycarbonyl)-l-dithioglutamate ($8i$) $^{13}$C NMR (100 MHz, CDCl$_3$)

![NMR spectrum of 8i]
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$\text{S}^\alpha\text{-Cyanoethyl S}^\gamma(2,4,6\text{-trimethoxybenzyl})\text{ N-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8j) }^1\text{H NMR (400 MHz, CDCl}_3)$
$S$-Cyanoethyl $S$-(2,4,6-trimethoxybenzyl) N-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8j) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl N-tert-butoxycarbonyl-L-tryptophanylthioglycinate (9) \(^1\)H NMR (400 MHz, CDCl\(_3\))
S-α-Methylphenacyl N-tert-butoxycarbonyl-L-tryptophanylthioglycinate (9) $^{13}$C NMR (100 MHz, CDCl$_3$)
S-α-Methylphenacyl N*-benzyloxycarbonyl-N*-tert-butoxycarbonyl-L-lysyl-L-tryptophanylthioglycinate (10) $^1$H NMR (400 MHz, CDCl$_3$)
$S\alpha$-Methylphenacyl $N\alpha$-benzyloxy carbonyl-$N\varepsilon$-tert-butoxycarbonyl-$\varepsilon$-lysyl-$\varepsilon$-tryptophanyl thioglycinate (10) $^{13}$C NMR (100 MHz, CDCl₃)
S-Benzyl-N\textsuperscript{\(\alpha\)}-benzyloxycarbonyl-N\textsuperscript{\(\epsilon\)}-tert-butoxycarbonyl-L-lysyl-L-tryptophenylthioglycinate (11) \(^1\)H NMR (400 MHz, CDCl\textsubscript{3})
S-BenzylNα-benzylxycarbonyl-Nα-tert-butoxycarbonyl-L-lysyl-L-tryptophenylthioglycinate (11) $^{13}$C NMR (100 MHz, CDCl$_3$)

![Chemical Structure](image)
$O^\alpha$-Allyl $O^\gamma$-(9-fluorenymethyl) $N$-tert-butoxycarbonyl-$L$-glutamate (13) $^1$H NMR (400 MHz, CDCl$_3$)
O₉-Allyl O₇-(9-fluorenylmethyl) N-tert-butoxycarbonyl-L-glutamate (13) $^{13}$C NMR (100 MHz, CDCl₃)
O\textsuperscript{\alpha}-Allyl N-tert-butoxycarbonyl-L-glutamic acid (14) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})
O-\textit{Allyl} \textit{N-tert-butoxycarbonyl-\textit{l}}-\textit{glutamic acid (14)} \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})
O\textsuperscript{\alpha}-Allyl S\textsuperscript{\gamma}-methylphenacyl N-tert-butoxycarbonyl-L-\textgamma-thioglutamate (15) $^1$H NMR (400 MHz, CDCl\textsubscript{3})
O\textsuperscript{\alpha}-Allyl S\textsuperscript{\gamma}-\alpha-methylphenacyl N-tert-butoxycarbonyl-L-\gamma-thioglutamate (15) \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})
$S\alpha$-Methylphenacyl N-tert-butoxycarbonyl-1-$\gamma$-thioglutamic acid (16) $^1$H NMR (400 MHz, CDCl$_3$)
$S^{\gamma}\alpha$-Methylphenacyl N-\textit{tert}-butoxycarbonyl-$\textit{L}$-$\gamma$-thioglutamic acid (16) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethyl N-tert-butoxycarbonyl-1-S\(^\gamma\)-α-methylphenacyl-\(\gamma\)-thioglutamylglycinate (17) \(^1\)H NMR (400 MHz, CDCl\(_3\))
Ethyl N-tert-butoxycarbonyl-l-S\textsuperscript{-}\textalpha-methylphenacyl-\textgamma-thioglutamylglycinate (17) $^{13}$C NMR (100 MHz, CDCl\textsubscript{3})
Ethyl \( N \)-tert-Butoxycarbonyl-L-tryptophan-L-\( \alpha \)-methylphenacyl-L-\( \gamma \)-thioglutamylglycinate (18) \( ^1 \)H NMR (400 MHz, CDCl\(_3\))
Ethyl N-tert-Butoxycarbonyl-L-tryptophanyl-Sx-α-methylphenacyl-L-γ-thioglutamylglycinate (18) $^{13}$C NMR (100 MHz, CDCl$_3$)

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Ethyl N-tert-butoxycarbonyl-L-tryptophanyl-S\(^{\gamma}\)-benzyl-L-\(\gamma\)-thioglutamylglycinate (19) \(^1\)H NMR (400 MHz, CDCl\(_3\))
Ethyl \( N\text{-}t\text{e}r\text{-}t\text{e}r\text{b}o\text{xycarbonyl-l\text{-}tryptophanyl-S\text{\textgreek{}}-benzyl-l\text{-}\text{\greek{}}\text{thioglutamy}lgy}l\text{cinate (19)} \) \(^{13}\text{C NMR (100 MHz, CDCl}_3\)