Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Intramolecular hydrogen-bonding activation in cysteines. New effective radical scavenging

Luisa Haya,[a] Iñaki Osante,[b] Ana M. Mainar,[a] Carlos Cativiela,[b] Jose S. Urieta*,[a]

[a] *Group of Applied Thermodynamics and Surfaces (GATHERS), Aragon Institute for Engineering Research (I3A), Facultad de Ciencias, Universidad de Zaragoza, Zaragoza 50009, Spain. Fax: +34 976 761 202; Tel: +34 976 761 298; E-mail: urieta@unizar.es.*

[b] *Amino Acids & Peptides Group, Department of Organic Chemistry, Instituto de Síntesis Química y Catalisis Homogénea. Universidad de Zaragoza-CSIC, 50009 Zaragoza. Spain. Fax:+ 34 976 761210; Tel: +34 976 761210; E-mail: cativiela@ unizar.es.*

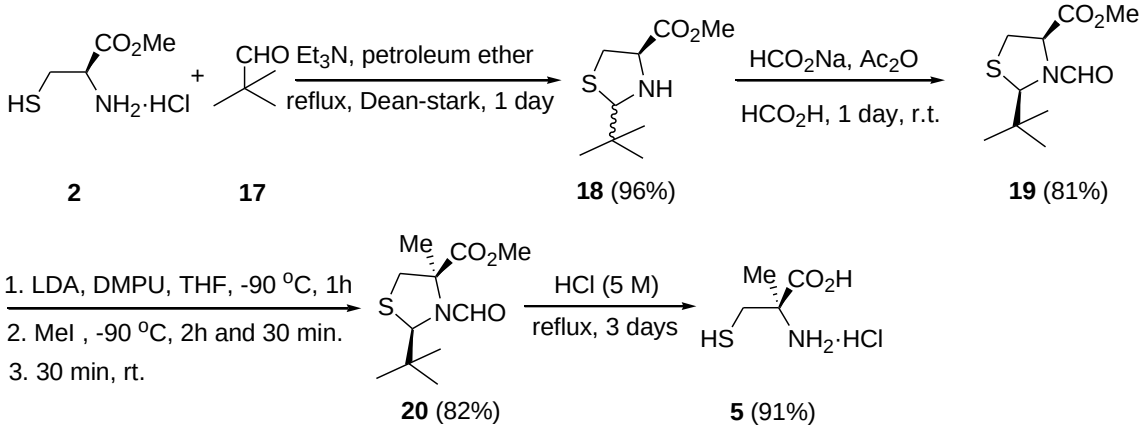
Supporting Information

EXPERIMENTAL SECTION

General: All commercial materials were used as received without further purification. Melting points were registered in a Gallenkamp apparatus and are uncorrected. Flash chromatography was performed using 230–400 mesh Silica Flash 60_ silica gel. Thin layer chromatography was performed with pre-coated TLC sheets of silica gel (60 F254, Merck). NMR spectra were recorded with a Bruker AV-400 (400 MHz for 1H, and 100 MHz for 13C and calibrated with $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in parts per million. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br s = broad singlet, q = quartet and m = multiplet. Coupling constants (J) are given in Hz. High resolution mass spectra (HRMS) were obtained in a Bruker Microtof-Q. The optical rotations $[\alpha]_D$ have been determined in a Jaco P-1020 polarimeter.

Syntheses: The first goal has been the synthesis of (*R*)-*N*-acetyl-2-methylcysteine methyl ester **15** starting from the α-methylcysteine in enantiopure form. Among the methodologies reported to synthesize quaternary cysteines, the most versatile procedure is the self reproduction of quirality from thiazolidines. This procedure allows obtain α-methylcysteine with good yields as mentioned above. The synthesis started with the reaction of the (*R*)-cysteine methyl ester chlorhydrate **2** with trimethylacetaldehyde **17** in the presence of Et_3N under reflux for 24 hours to yield the thiazolidine **18** in 96% as a diastereomeric mixture 66:34. Next, the protection reaction of the amine group of the thiazolidine **18** was carried out with sodium formiate using acetic anhydride in formic acid at room temperature for a day, affording the thiazolidine **19** with good yield 81%. Therefore, the known thiazolidine **19** was treated sequentially with LDA and DMPU as co-solvent at -90 ºC and the electrophile MeI for 2 hours and 30 minutes at room temperature to give the corresponding thiazolidine 20 in 82% as a single diastereomer. The optical rotation was identical to the known compound described in the literature. Finally, (2*R*, 4*R*)-thiazolidine **20** was heated under reflux in 5 M HCl to remove the protecting groups, giving the desired (*R*)-2-methylcysteine 5 in 91% as chlorhydrate form and the spectroscopic data and the rotation matched with that reported previously (Scheme 1). The next step was the thiol group protection of the (*R*)-2-methylcysteine **5**. Among the large number of thiol protecting groups, the election was the trityl which is stable in basic conditions and certain acidic conditions. Thus, the treatment of the (*R*)-2-methylcysteine **5** with TrOH using $BF_3{\cdot}OEt_2$ as a Lewis acid in acetic acid under reflux gave the corresponding (*R*)-*S*-Trityl-2-methylcysteine **21** in 97% yield.18g. Then, it was carried out the carboxylic acid protection of the (*R*)-*S*-Trityl-2-methylcysteine **21** with $SOCl_2$ under reflux in MeOH to obtain the corresponding methyl esters, that was treated with sodium acetate and acetic anhydride in $CHCl_3$ without purification affording the (*R*)-*N*-acetyl-*S*-trityl-2-methylcysteine methyl ester **22** in two steps with good yields. Finally, it was performed the trityl group removing reaction of the cysteine **22**. The reaction was carried out under mild conditions using Et_3SiH and TFA in dichloromethane at 0 ºC for 1 hour giving the desired compound (*R*)-*N*-acetyl-2-methylcysteine methyl ester **15** after purification by flash chromatography with excellent yields. On the other hand, the synthesis of *N*-acetyl-*L*-cysteine methyl ester **6** started from the commercially available (*R*)-*S*-trityl-cysteine **23**, that was converted into the methyl ester by treatment with $SOCl_2$ under reflux in MeOH. Then, the amine was protected as a *N*-acetyl group with sodium acetate and acetic anhydride in $CHCl_3$ and finally the trityl group was removed using Et_3SiH and TFA in dichloromethane at 0 ºC for 3 hours affording the *N*-acetyl-*L*-cysteine methyl ester **6** with good yield (Scheme 1).

Preparation of (*R*)-2-methylcysteine hydrochloride 5.



(2*R*, 4*R*)-2-*tert*-butyl-3-formyl-1,3-thiazolidine-4-carboxylate methyl ester 19.[1,2]

Over a solution of (2*RS*, 4*R*)-2-*tert*-butyl-1,3-thiazolidine-4-carboxylate methyl ester **18** (10.20 g, 50.30 mmol) in formic acid (80 mL) and sodium formate (4.10 g, 60.00 mmol) at 0-5 °C, was added dropwise acetic anhydride (14.30 mL, 151.00 mmol) over 1 h. The reaction mixture was warmed to room temperature and then stirred 3 days. The solvents were removed *in vacuo* and the residue was then carefully neutralised with saturated solution of $KHCO_3$ (30 mL) and extracted with ether (3 × 30 mL). The combined ether extracts were dried, and evaporated *in vacuo* to leave a white solid. Recrystalization from hexane-ether gave (2*R*, 4*R*)-2-*tert*-butyl-3-formyl-1,3-thiazolidine-4-carboxylate methyl ester **19** (9.40 g, 40.80 mmol) as white crystals. Yield: 81%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.32 (s, 1H, C*H*O), 8.25 (s, 1H, C*H*O), 5.23 (s, 1H, C*H*C(CH$_3$)$_3$), 4.85 (t, 1H, *J* = 8.5 Hz, C*H*CO$_2$CH$_3$), 4.77 (dd, 1H, *J* = 8.7, 7.3 Hz, C*H*CO$_2$CH$_3$), 4.72 (s, 1H, C*H*C(CH$_3$)$_3$), 3.78 (s, 3H, CO$_2$C*H*$_3$), 3.73 (s, 3H, CO$_2$C*H*$_3$), 3.40 (dd, 1H, *J* = 11.9, 7.2 Hz, C*H*H), 3.29 (dd, 1H, *J* = 11.8, 8.4 Hz, C*H*H), 3.28 (dd, 1H, *J* = 11.7, 8.4 Hz, C*H*H), 3.23 (dd, 1H, *J* = 11.7, 9.1 Hz, C*H*H), 0.99 (s, 9H, C(C*H*$_3$)$_3$), 0.93 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.94 (*C*O), 163.85 (*C*HO), 162.58 (*C*HO), 75.00 (*C*HC(CH$_3$)$_3$), 71.43 (*C*HC(CH$_3$)$_3$); 63.68 (*C*HCO$_2$CH$_3$), 61.39 (*C*HCO$_2$CH$_3$), 53.00 (CO$_2$*C*H$_3$), 52.58 (CO$_2$*C*H$_3$), 38.52 (*C*(CH$_3$)$_3$), 32.79 (*C*H$_2$), 31.94 (*C*H$_2$), 26.70 (C(*C*H$_3$)$_3$), 26.26 (C(*C*H$_3$)$_3$); Mp : 76 ºC (hexane/ether); IR (KBr): υ = 2959-2870 (C-H), 1749 (C=O), 1667 (C=O), 1364 (CH$_3$), 1201 (C-O), 1177 (C-O) cm^{-1}; $[\alpha]_D^{24}$: -130.8 (c = 1.00; $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{10}H_{18}NO_3S[M+H]^+$: 232.1002; found 232.0983.

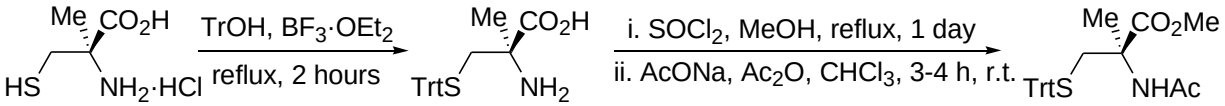
(2*R*, 4*R*)-2-*tert*-butyl-3-formyl-4-methyl-1,3-thiazolidine-4-carboxylate methyl ester 20.[1]

Over a solution of LDA in dry THF (70 mL) at -78 °C and under argon atmosphere [prepared from ^{i}Pr$_2$NH (6.60 mL, 46.90 mmol) and *n*-BuLi (26.80 mL of a solution 1.4 M, 37.50 mmol)], was added DMPU (21.60 mL, 178.20 mmol) and the reaction mixture was then stirred at -78 °C for 1 h. Next, a solution of (2*R*, 4*R*)-2-*tert*-butyl-3-formyl-1,3-thiazolidine-4-carboxylate methyl ester **19** (7.21 g, 31.20 mmol) in dry THF (30 mL) was added over 10 min, keeping the internal temperature at -90 °C. The resulting solution was stirred for 45 minutos at -90 °C and then CH_3I (2.30 mL, 37.50 mmol) was added dropwise over 5 min. The mixture was stirred for 3 h at -90 °C and then warmed to room temperature. The solvents were removed *in vacuo* to leave an oily residue which was partitioned between a saturated solution of NH_4Cl (30 mL) and ether (30 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 30 mL), and the combined ether extracts were then dried over magnesium sulphate anhydrous, filtered and evaporated *in vacuo* to leave and oil. The oil was purified by flash chromatography on silicagel (10% hexane: ethyl acetate), to give the (2*R*, 4*R*)-2-*tert*-butyl-3-formyl-4-methyl-1,3-thiazolidine-4-carboxylate methyl ester **5** (6.26 g, 25.50 mmol). Yield: 82%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = δ 8.39 (s, 1H, C*H*O), 8.27 (s, 1H, C*H*O), 5.28 (s, 1H, C*H*CO$_2$CH$_3$), 4.65 (s, 1H, C*H*CO$_2$CH$_3$), 3.81 (s, 3H, CO$_2$C*H*$_3$), 3.75 (s, 3H, CO$_2$C*H*$_3$), 3.62 (d, 1H, *J* = 12.3 Hz, C*H*H), 3.30 (d, 1H, *J* = 12.3 Hz, C*H*H), 2.85 (d, 1H, *J* = 12.3 Hz, C*H*H), 2.71 (d, 1H, *J* = 12.3 Hz, C*H*H), 1.77 (s, 3H, C*H*$_3$), 1.74 (s, 3H, C*H*$_3$), 1.05 (s, 9H, C(C*H*$_3$)$_3$), 0.94 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 173.04 (*C*O), 171.99 (*C*O), 162.80 (*C*HO), 161.09 (*C*HO), 74.28 (*C*HC(CH$_3$)$_3$), 71.76 (*C*HC(CH$_3$)$_3$), 69.99 (*C*CO$_2$CH$_3$), 69.82 (*C*HCO$_2$CH$_3$), 53.19 (CO$_2$*C*H$_3$), 52.73 (CO$_2$*C*H$_3$), 42.09 (*C*H$_2$), 41.46 (*C*H$_2$), 40.23 (*C*(CH$_3$)$_3$), 39.41 (*C*(CH$_3$)$_3$), 28.14 (*C*H$_3$), 27.04 (C(*C*H$_3$)$_3$), 26.62 (C(*C*H$_3$)$_3$), 20.59 (*C*H$_3$); IR (Nujol): υ = 2924-2854 (C-H), 1748 (C=O), 1671 (C=O), 1456 (C-N), 1330 (CH$_3$), 1196 (C-O) cm^{-1}; $[\alpha]_D^{24}$: -100.3 (c = 0.92; $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{11}H_{19}NO_3S[M+Na]^+$: 268.0978; found 268.0981.

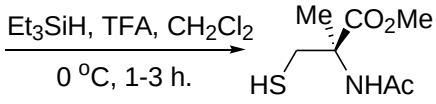
(*R*)-2-methylcysteine hydrochloride 5.[1]

A solution of HCl (5M) (100 ml) was added to (2*R*, 4*R*)-2-*tert*-butyl-3-formyl-4-methyl-1,3-thiazolidine-4-carboxylate methyl ester **20** (5.85 g, 23.90 mmol) and the resulting solution was then heated under reflux in argon atmosphere for 3 days. Next, the reaction solution was washed with ethyl acetate (3 × 30 mL), and then the aqueous layer was evaporated *in vacuo* to give (*R*)-2-methylcysteine hydrochloride **5** (3.73 g, 21.70 mmol) as an oil. Yield: 91%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 3.13 (d, 1H, *J* = 15.1 Hz, C*H*H), 2.87 (d, 1H, *J* = 15.1 Hz, C*H*H), 1.56 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.62 (*C*O), 61.30 (*C*(CO$_2$H)), 30.13 (*C*H$_2$), 21.12 (*C*H$_3$); IR (Nujol): υ = 2934 (C-H), 1734 (CO), 1506 (C-N), 1216 (C-O) cm^{-1}; $[\alpha]_D^{24}$: +7.8 (c = 0.49; H_2O); HRMS (ESI) *m/z* calcd for) $C_4H_{10}NO_2S[M-Cl]^+$: 136.0427; found 136.0422.

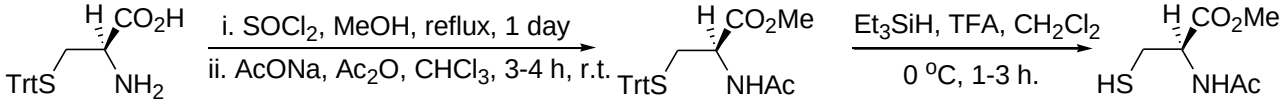
Preparation of (*R*)-*N*-acetyl-cysteine methyl esters.



5 **21**(97%) **22**(56%)



15 (98%)



23 **24**(80%) **6** (86%)

(*R*)-*S*-trityl-2-methylcysteine 21.[3]

Over a solution of (*R*)-2-methylcysteine hydrochloride **5** (1.7 g, 9.8 mmol) in acetic acid (25 mL) at 80ºC, under argon atmosphere, was added TrtOH (2.9 g, 10.8 mmol) in portions for 1 hour. Next, it was added $BF_3{\cdot}OEt_2$ (1.4 mL, 10.8 mmol) and the reaction mixture was stirred for 2 hours. After this time, the reaction was cooled at 0 °C and treated with a saturated solution of sodium acetate (100 mL) and ethyl acetate (30 mL) for 12 hours, affording an off-white solid after filtration which was crystalized with the solvent mixture ether/ethyl acetate 0.75/0.25 v/v, obtaining (*R*)-*S*-trityl-2-methylcysteine **21** (1.4 g, 3.7 mmol). The mother liquors was separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over magnesium sulphate anhydrous, filtered and evaporated *in vacuo*. The oily residue was crystalized with ether/ethyl acetate 0.75/0.25 v/v, obtaining a second portion of (*R*)-*S*-trityl-2-methylcysteine **21 (**2.2 g, 5.8 mmol) as a off-white solid. Global yield: 97%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.36-7.22 (m, 15H, Ar-*H*), 2.43 (d, 1H, *J* = 11.6 Hz, C*H*H), 2.34 (d, 1H, *J* = 11.6 Hz, C*H*H), 1.51 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 170.74 (CO), 144.29 (Ar-*C*), 129.18 (Ar-*C*), 128.08 (Ar-*C*), 126.79 (Ar-*C*), 65.70 (*C*(CO_2H), S*C*Ph_3), 59.00 (*C*H_2), 22.32 (*C*H_3); Mp : 223-225 ºC (ether/ethyl acetate); IR (KBr): υ = 2924 (Ar-H), 2854 (C-H), 1701 (CO), 1636 (CO), 1577 (NH_2), 1458 (C-N), 1445 (C-N), 1394 (CH_3, CH_2), 1364 (CH_3, CH_2), 1273 (C-O), 1228 (C-O) cm^{-1}; $[\alpha]_D^{24}$: + 54.56 (c = 0.13; CH_3OH); HRMS (ESI) *m/z* calcd for $C_{23}H_{23}NO_2S$ $[M+Na]^+$: 400.1342; found 400.1345.

(*R*)-*N*-acetyl-*S*-trityl-2-methylcysteine methyl ester 22.

Over a solution of (*R*)-*S*-trityl-2-methylcysteine **21** (0.51 g, 1.36 mmol) in MeOH (20 mL) was added $SOCl_2$ (0.29 mL, 4.08 mmol) in portions for 1 hour and the reaction mixture was stirred under reflux for 1 day. After this time, the solvent was evaporated *in vacuo* to obtain an oily yellow residue. Without purification, the residue obtained was dissolved in $CHCl_3$ (10 mL), was treated with sodium acetate (0.33 g, 4.08 mmol) and Ac_2O (0.39 mL, 4.08 mmol) and the resultant reaction mixture was stirred for 4 hours. Then, the reaction was quenched with H_2O (20 mL) and the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ (2 × 20 mL) and the final organic layer was dried over magnesium sulfate, filtered and evaporated *in vacuo*. The oil was purified by flash chromatography on silicagel (70% hexane: ethyl acetate), to afford (*R*)-*N*-acetyl-*S*-trityl-2-methylcysteine methyl ester **22** (0.33 g, 0.76 mmol) as an oil. Yield: 56% (2 steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44-7.43 (m, 6H, Ar-*H*), 7.42-7.27 (m, 6H, Ar-*H*), 7.24-7.19 (m, 3H, Ar-*H*), 6.12 (s, 1H, N*H*), 3.67 (s, 3H, CO_2CH_3), 3.02 (d, 1H, *J* = 11.8 Hz, C*H*H), 2.74 (d, 1H, *J* = 11.8 Hz, C*H*H), 1.94 (s, 3H, NHCOCH_3), 1.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 173.29 (*C*O_2CH_3), 169.28 (NH*C*OCH_3) 144.38 (Ar-*C*), 129.40 (Ar-*C*), 127.82 (Ar-*C*), 126.67 (Ar-*C*), 66.43 (S*C*Ph_3), 58.94 (*C*(CO_2H), 52.70 (CO_2CH_3), 37.79 (*C*H_2), 23.45 (CO*C*H_3), 22.80 (*C*H_3); Mp : 223-225 ºC (ether/ethyl acetate); IR (Nujol): υ = 3280 (N-H), 3069-2944 (C-H), 1747 (CO_2CH_3), 1653 (NHCOCH_3), 1553 (NH), 1489 (C-N), 1444 (C-N), 1433 (CH_3, CH_2), 1226 (C-O), 1221 (C-O) cm^{-1}; $[\alpha]_D^{24}$: - 2.0 (c = 0.5; $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{26}H_{27}NO_3S$ $[M+Na]^+$: 456.1604; found 456.1591.

(*R*)-*N*-acetyl-*S*-trityl-cysteine methyl ester 24.

Over a solution of (*R*)-*S*-trityl-cysteine **23** (1.47 g, 4.06 mmol) in MeOH (50 mL) was added $SOCl_2$ (0.88 mL, 12.17 mmol) in portions for 1 hour and the reaction mixture was stirred under reflux for 1 day. After this time, the solvent was evaporated *in vacuo* to obtain an oily yellow residue. Without purification, the residue obtained was dissolved in $CHCl_3$ (30 mL), was treated with sodium acetate (1.0 g, 12.16 mmol) and Ac_2O (1.15 mL, 12.16 mmol) and the resultant reaction mixture was stirred for 2 hours. Then, the reaction was quenched with H_2O (40 mL) and the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ (2 × 30 mL) and the final organic layer was dried over magnesium sulfate, filtered and evaporated *in vacuo*. The oil was purified by flash chromatography on silicagel (80% hexane: ethyl acetate), to afford (*R*)-*N*-acetyl-*S*-trityl-cysteine methyl ester **24** (1.36 g, 3.25 mmol) as an off-white solid. Yield: 80% (2 steps). Physical and spectral properties were in accordance with the literature.[4]

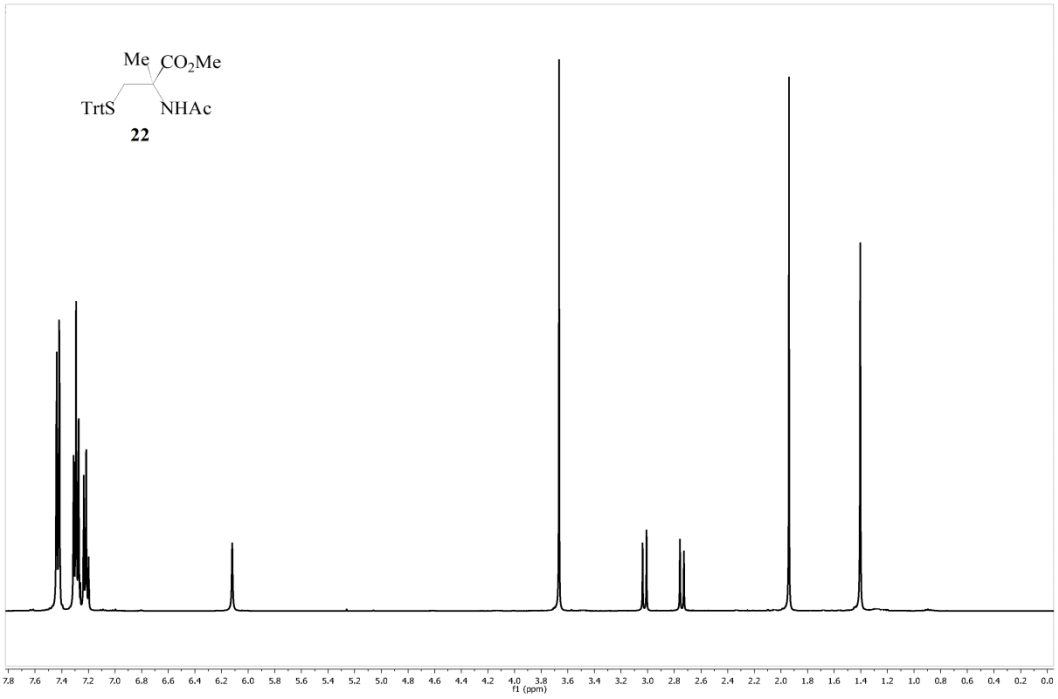
***N*-acetyl-*L*-cysteine methyl ester 6.**

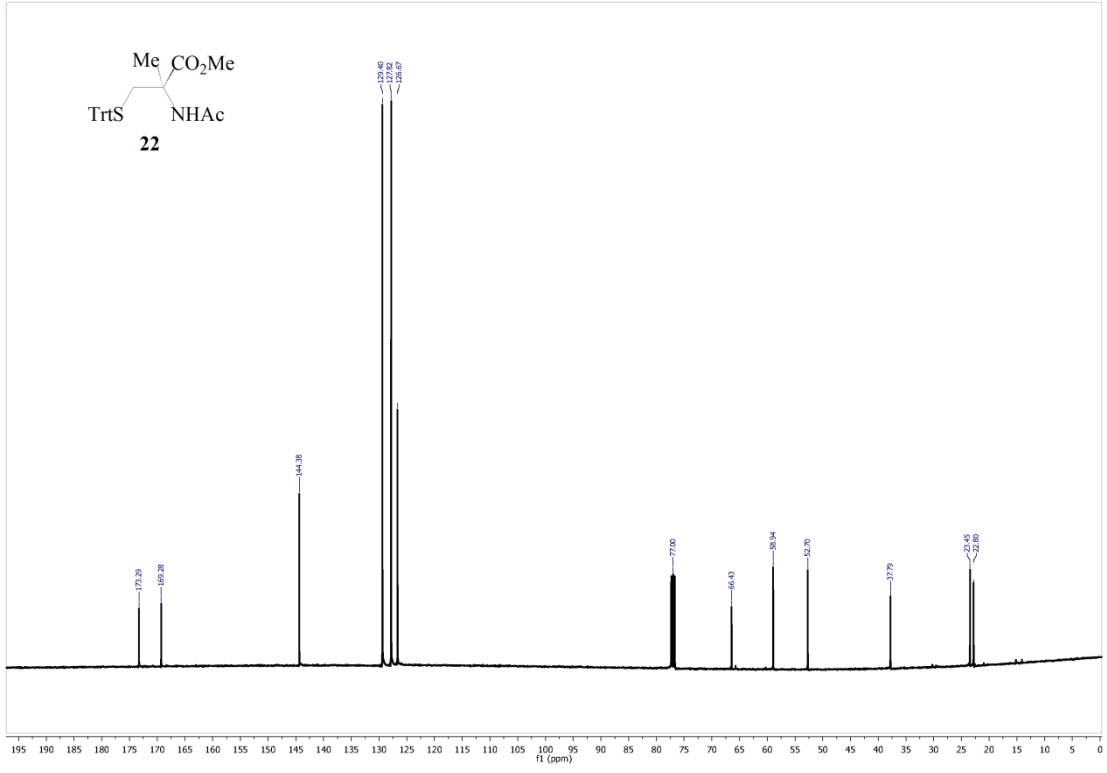
To a stirred solution of (*R*)-*N*-acetyl-*S*-trityl-cysteine methyl ester **24** (1.07 mg, 2.55 mmol) in dichloromethane (70 mL) at 0 °C was added triethylsilane (0.49 mL, 0.31 mmol) followed by trifluoroacetic acid (1.4 mL, approx. 2% v/v) and the resultant solution was stirred for 3 h. Saturated aqueous $NaHCO_3$ (20 mL) was added and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over magnesium sulphate anhydrous, filtered, and concentrated under *vacuum* to give the crude product. Purification by flash cromatography on silicagel (20% hexane: ethyl acetate) afforded *N*-acetyl-*L*-cysteine methyl ester **6** (391 mg, 2.20 mmol) as an oil. Yield: 86%. Physical and spectral properties were in accordance with the literature.[5]

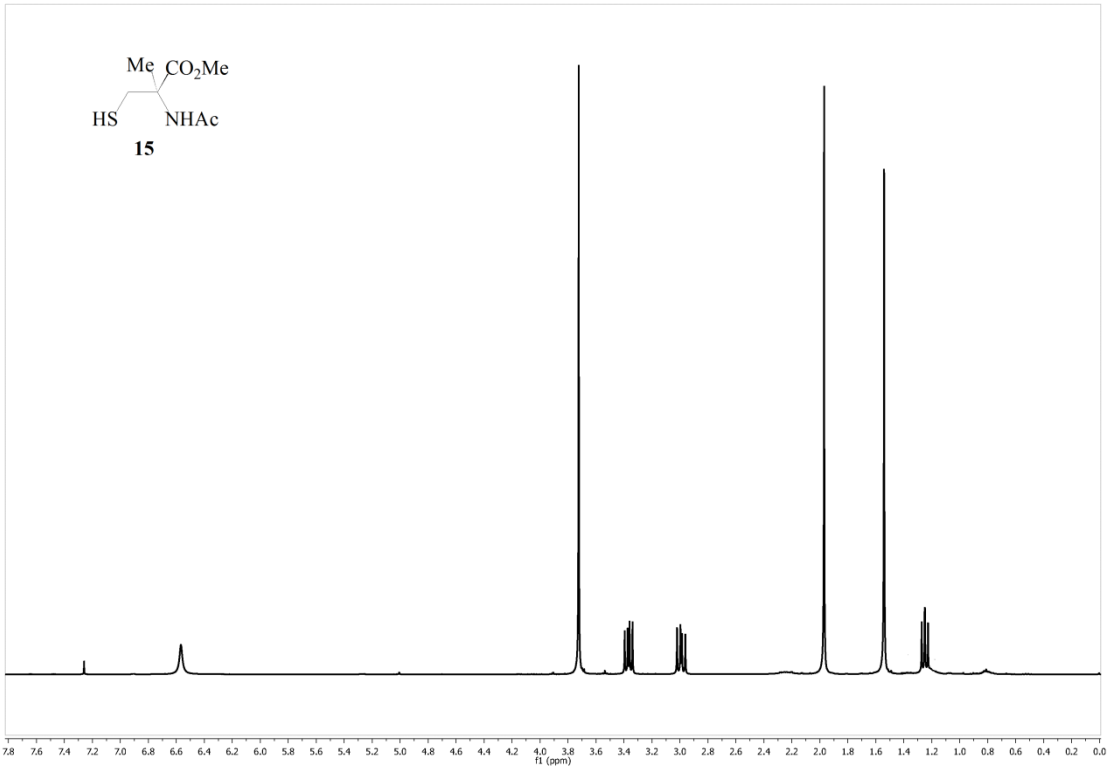
(*R*)-*N*-acetyl-2-methylcysteine methyl ester 15.

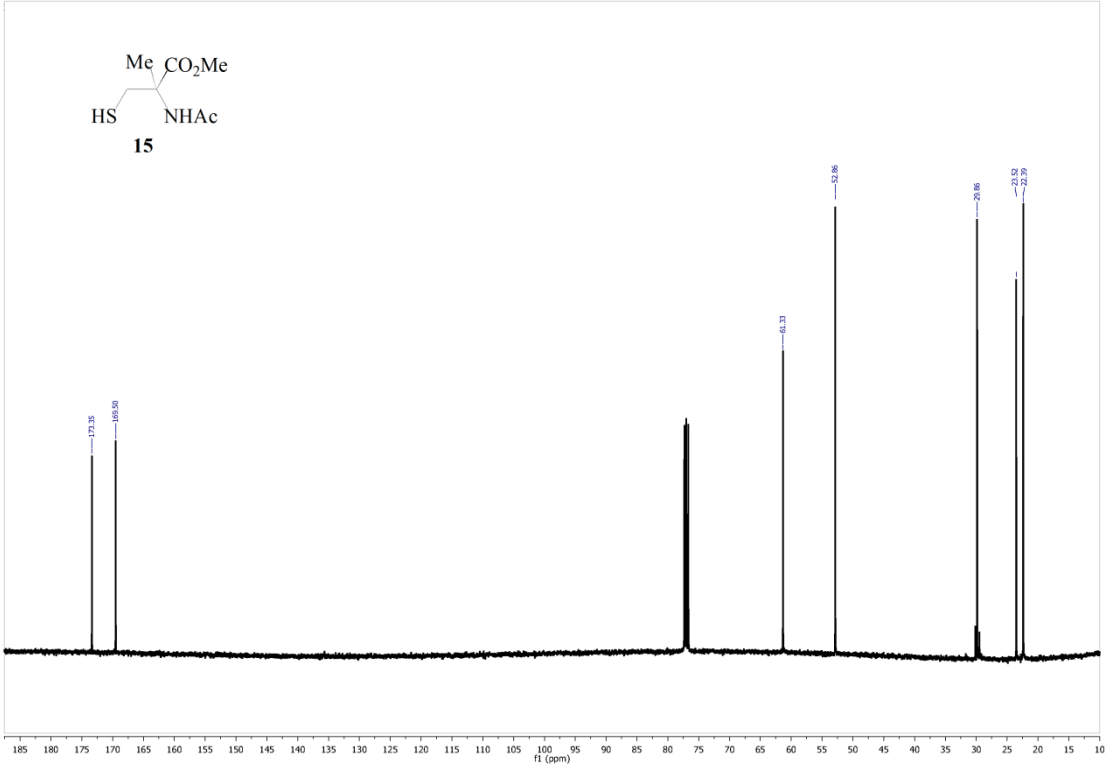
To a stirred solution of (*R*)-*N*-acetyl-*S*-trityl-2-methylcysteine methyl ester **22** (337.6 mg, 0.78 mmol) in dichloromethane (19 mL) at 0 °C was added triethylsilane (0.15 mL, 0.93 mmol) followed by trifluoroacetic acid (0.2 mL, approx. 2% v/v) and the resultant solution was stirred for 1 h. Saturated aqueous $NaHCO_3$ (20 mL) was added and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over magnesium sulphate anhydrous, filtered, and concentrated under *vacuum* to give the crude product. Purification by flash cromatography on silicagel (80% hexane: ethyl acetate) afforded (*R*)-*N*-acetyl-2-methylcysteine methyl ester **15** (145.8 mg, 0.76 mmol) as an oil. Yield: 98%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.57 (s, 1H, N*H*), 3.72 (s, 3H, CO_2CH_3), 3.37 (dd, 1H, *J* = 14.0, 8.5 Hz, C*H*H), 2.99 (dd, 1H, *J* = 14.0, 9.7 Hz, C*H*H), 1.97 (s, 3H, $COCH_3$), 1.54 (s, 3H, CH_3), 1.25 (dd, 1H, *J* = 9.6, 8.5 Hz, S*H*); ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 173.35 (CO_2CH_3), 169.50 ($NHCOCH_3$), 61.32 ($C(CO_2H)$, 52.86 (CO_2CH_3), 29.86 (CH_2) 23.52 ($COCH_3$), 22.39 (CH_3); Mp : 223-225 ºC (ether/ethyl acetate); IR (Nujol): υ = 3361-3192 (N-H), 3054-2952 (C-H), 2546 (S-H), 1735 (CO_2CH_3), 1653 ($NHCOCH_3$), 1540 (NH), 1546 (NH), 1436 (C-N), 1373 (CH_3, CH_2), 1307 (CH_3, CH_2), 1239 (C-O), 1119 (C-O) cm^{-1}; $[\alpha]_D^{24}$: + 9.9 (c = 0.55; $CHCl_3$); HRMS (ESI) *m/z* calcd for) $C_7H_{13}NO_3S$ $[M+Na]^+$: 214.0508; found 214.0506.

NMR Spectra


Me
CO2Me
TrtS
NHAc
22
f1 (ppm)


Me
CO2Me
TrtS
NHAc
22
129.40
127.82
126.97
144.38
171.29
169.28
77.00
66.43
58.94
52.70
37.79
23.45
22.80
f1 (ppm)


Me
CO2Me
HS
NHAc
15
f1 (ppm)


Me
CO2Me
HS
NHAc
15
173.35
169.50
61.33
52.86
29.86
23.52
23.29
f1 (ppm)

Cartesian Coordinates for Optimized Geometries in Gas Phase Phase at B3lyp/6-31+G(d,p) Level:

***Cysteine* (1)**

N	-0.067274	1.675287	-0.503395
C	-0.218836	0.232901	-0.460115
C	-1.630123	-0.082112	0.020662
O	-2.241940	0.566305	0.842112
C	0.757888	-0.546520	0.467227
S	2.531023	-0.349652	0.021066
O	-2.114267	-1.221052	-0.527726
H	-0.308325	2.104652	0.385845
H	0.873874	1.939029	-0.775845
H	-0.104001	-0.161378	-1.474555
H	0.615422	-0.250867	1.510768
H	0.565133	-1.620997	0.391359
H	2.719340	0.851367	0.604439
H	-2.990814	-1.382017	-0.137034

***Cysteine radical cation* (1)**

N	-0.240103	1.734765	-0.362480
C	-0.260031	0.354894	-0.491649
C	-1.624497	-0.175528	0.006821
O	-2.314054	0.456719	0.766979
C	0.843528	-0.441633	0.506080
S	2.538739	-0.327616	-0.000894
O	-1.871453	-1.383319	-0.494415
H	-0.882556	2.174398	0.295015
H	0.346431	2.325723	-0.939510
H	-0.016319	0.021611	-1.501711
H	0.673174	-0.065465	1.515004
H	0.553109	-1.490920	0.418748
H	2.851580	0.827177	0.629894
H	-2.734462	-1.707619	-0.173809

(*R*)-cysteine methyl ester (2)

N	0.630553	1.750642	-0.556436
C	0.243390	0.353409	-0.459153
C	-1.194368	0.300220	0.050483
O	-1.638232	1.028838	0.914685
C	1.094888	-0.539889	0.484991
S	2.869286	-0.657828	0.013153
O	-1.896520	-0.690153	-0.532523
H	0.494463	2.235947	0.326522
H	1.594159	1.846026	-0.860379
H	0.273369	-0.086940	-1.460072
H	1.021181	-0.186474	1.517521
H	0.727031	-1.570378	0.454188
H	3.263928	0.515632	0.547086
C	-3.254919	-0.858400	-0.073529
H	-3.830206	0.051150	-0.259386
H	-3.652680	-1.692385	-0.650368
H	-3.269619	-1.083341	0.995439

(*R*)-cysteine methyl ester *radical cation* (2)

N	0.560295	1.865387	-0.414272
C	0.234048	0.520497	-0.498755
C	-1.211409	0.323419	0.033504
O	-1.694428	1.097195	0.827615
C	1.138962	-0.465171	0.517603
S	2.813534	-0.740159	-0.002791
O	-1.751719	-0.764790	-0.478773
H	0.056732	2.446912	0.253867
H	1.233208	2.301977	-1.032692
H	0.381954	0.115090	-1.500572
H	1.066507	-0.030245	1.514696
H	0.627709	-1.428790	0.468914
H	3.372392	0.353937	0.562349
C	-3.127028	-1.074022	-0.075170
H	-3.784252	-0.263578	-0.391404
H	-3.364351	-2.000510	-0.592174
H	-3.166776	-1.197550	1.007753

(*R*)-*N*-acetylcysteine (3)

C	-0.500371	-0.178491	0.157061
C	-1.133114	-1.558888	-0.032797
O	-0.788262	-2.374387	-0.861747
C	-1.463215	0.893596	-0.402732
S	-0.955448	2.618968	-0.046517
O	-2.167348	-1.755346	0.812868
H	-0.339151	-0.003061	1.224180
H	-1.592548	0.759746	-1.481582
H	-2.442851	0.782672	0.068435
H	0.253025	2.542781	-0.639583
H	-2.542508	-2.632770	0.623084
N	0.797881	-0.142049	-0.485100
H	0.842503	-0.534289	-1.417376
C	1.964967	-0.135511	0.253421
C	3.239763	-0.340081	-0.543960
O	1.975431	0.039693	1.465376
H	3.952949	0.441117	-0.270084
H	3.677819	-1.301579	-0.258594
H	3.086027	-0.327195	-1.626444

(*R*)-*N*-acetylcysteine *radical cation* (3)

C	-0.530353	-0.134925	0.140989
C	-1.335245	-1.426825	-0.052217
O	-1.024093	-2.346140	-0.782134
C	-1.329181	1.068394	-0.406176
S	-0.591415	2.699397	0.002422
O	-2.457767	-1.413599	0.689276
H	-0.371250	-0.003572	1.214439
H	-1.453578	0.988089	-1.489359
H	-2.321899	1.082816	0.047059
H	0.542212	2.554445	-0.711777
H	-2.950831	-2.237829	0.527379
N	0.774257	-0.247510	-0.471193
H	0.816542	-0.376178	-1.473569
C	1.925405	-0.387285	0.248761
C	3.192638	-0.566127	-0.560075
O	1.940676	-0.358309	1.484839
H	3.897291	0.224788	-0.288583
H	3.647803	-1.523468	-0.290347
H	3.026437	-0.541871	-1.639184

(*R*)-*S*-methylcysteine (4)

N	-0.725548	1.820278	-0.168763
C	-0.705629	0.391080	-0.436497
C	0.458538	-0.407331	0.212995
S	2.059682	0.117116	-0.523158
C	3.211569	-0.569708	0.716862
C	-2.008395	-0.210621	0.074488
O	-2.633330	0.199341	1.029151
O	-2.378004	-1.304152	-0.631458
H	0.202282	2.219351	-0.277375
H	-1.055809	1.998900	0.776499
H	-0.668067	0.226466	-1.519809
H	0.321604	-1.481707	0.051148
H	0.477904	-0.205861	1.290052
H	4.220470	-0.317013	0.382761
H	3.042699	-0.124972	1.701445
H	3.123918	-1.657695	0.779074
H	-3.186909	-1.655298	-0.220561

(*R*)-*S*-methylcysteine *radical cation* (4)

N	-0.002123	1.244314	-0.758754
C	-0.660842	-0.064263	-0.634465
C	0.357182	-0.955678	0.108369
S	1.973909	-0.275732	-0.481345
C	2.823812	0.190162	1.055294
C	-1.975389	0.066949	0.141611
O	-2.256023	1.058605	0.775304
O	-2.707616	-1.044795	0.050658
H	-0.090171	1.703505	-1.661740
H	-0.244729	1.885683	-0.000316
H	-0.861092	-0.466932	-1.630820
H	0.286266	-2.018704	-0.130037
H	0.305727	-0.822279	1.192197
H	3.769203	0.653575	0.768020
H	2.216818	0.890908	1.632453
H	3.017585	-0.714550	1.639963
H	-3.526755	-0.943207	0.570533

(*R*)-2-methylcysteine hydrochloride (5)

N	0.037561	1.240505	1.184714
C	0.222790	0.024774	0.402545
C	1.613972	0.126932	-0.237645
O	2.177464	1.170048	-0.494513
C	-0.749307	-0.116574	-0.822944
S	-2.541385	-0.086414	-0.404776
O	2.134450	-1.077677	-0.571336
H	0.285807	2.071323	0.654712
H	-0.919708	1.312506	1.515874
H	-0.555051	0.675160	-1.551623
H	-0.585292	-1.076496	-1.320931
H	-2.680882	1.253935	-0.371039
H	2.981065	-0.906827	-1.018856
C	0.106620	-1.189257	1.337312
H	0.257331	-2.127731	0.799078
H	0.845707	-1.114644	2.138381
H	-0.889503	-1.202370	1.789015

(*R*)-2-methylcysteine hydrochloride *radical cation* (5)

N	0.245275	1.708305	0.329063
C	0.292130	0.326963	0.395377
C	1.622113	-0.121411	-0.269770
O	2.238466	0.603514	-1.013042
C	-0.835907	-0.376903	-0.738483
S	-2.545773	-0.285147	-0.312868
O	1.938601	-1.372959	0.057716
H	0.849465	2.193198	-0.332814
H	-0.368032	2.252053	0.924786
H	-0.605790	0.090993	-1.694788
H	-0.543161	-1.428441	-0.718488
H	-2.822751	0.904413	-0.892506
H	2.772364	-1.624535	-0.382284
C	0.004118	-0.243080	1.786242
H	-0.067083	-1.330823	1.754531
H	0.819315	0.028938	2.462527
H	-0.930141	0.160567	2.183885

***N*-acetyl-*L*-cysteine methyl ester (6)**

C	-0.145097	0.231790	0.094061
C	-1.496492	-0.423423	-0.213140
O	-1.686698	-1.214811	-1.115456
C	-0.161154	1.679372	-0.444923
S	1.301394	2.678994	0.030826
O	-2.454554	0.022763	0.615239
H	0.013711	0.244949	1.175009
H	-0.269194	1.676650	-1.534378
H	-1.017463	2.212288	-0.024159
H	2.223726	1.855072	-0.506418
N	0.922830	-0.557206	-0.489232
H	0.769725	-0.870752	-1.439725
C	1.772016	-1.311884	0.294182
C	2.685494	-2.258950	-0.462921
O	1.807764	-1.212175	1.514629
H	3.718086	-2.063129	-0.162512
H	2.445894	-3.284683	-0.167121
H	2.604033	-2.172371	-1.549862
C	-3.784514	-0.497121	0.394385
H	-3.786876	-1.583008	0.509858
H	-4.406596	-0.026027	1.154029
H	-4.130770	-0.237368	-0.608467

***N*-acetyl-*L*-cysteine methyl ester *radical cation* (6)**

C	0.308308	0.055323	-0.283520
C	1.730653	-0.490721	-0.024121
O	1.926545	-1.632930	0.332365
C	0.053045	1.336980	0.538031
S	-1.485519	2.172825	-0.027388
O	2.646763	0.434070	-0.261997
H	0.246578	0.301169	-1.352050
H	-0.014118	1.123872	1.606196
H	0.865967	2.043405	0.357548
H	-2.206598	2.078961	1.109701
N	-0.605463	-1.036409	0.020494
H	-0.140353	-1.903483	0.287425
C	-1.933490	-1.006113	-0.106643
C	-2.718917	-2.273629	0.101385
O	-2.568164	0.047163	-0.400796
H	-3.451570	-2.117396	0.897497
H	-3.269909	-2.496273	-0.817020
H	-2.074270	-3.119018	0.350675
C	4.044564	0.033468	-0.105309
H	4.268062	-0.777995	-0.798688
H	4.618232	0.925800	-0.344305
H	4.218392	-0.287647	0.922256

(*R*)-*S*-methylcysteine methyl ester (7)

C	0.114313	0.447221	-0.223681
C	-1.352258	0.540340	0.228451
S	-2.285374	-0.969031	-0.251232
C	-3.966641	-0.402167	0.185304
C	0.840837	1.737634	0.186061
O	1.563482	1.861988	1.148426
O	0.536773	2.755093	-0.652606
H	0.161160	0.378190	-1.313913
H	-1.809592	1.411685	-0.247924
H	-1.406705	0.674931	1.315952
H	-4.643824	-1.228893	-0.041112
H	-4.043963	-0.167764	1.250809
H	-4.260917	0.467294	-0.409245
H	1.011625	3.544119	-0.339771
N	0.769454	-0.718406	0.325209
H	0.504198	-1.025882	1.250067
C	1.943185	-1.182217	-0.216623
C	2.616593	-2.314507	0.534073
O	2.408361	-0.705422	-1.247128
H	2.939048	-3.069095	-0.186724
H	3.510630	-1.921423	1.028817
H	1.973048	-2.780921	1.285238

(*R*)-*S*-methyl-2-methylcysteine (8)

N	-0.538250	0.302368	1.737807
C	-0.655273	0.360964	0.283893
C	0.514280	-0.350247	-0.477122
S	2.143051	0.446510	-0.141484
C	3.228322	-1.023457	-0.191663
C	-1.904350	-0.449149	-0.090873
O	-2.368787	-1.348346	0.578556
O	-2.416840	-0.108247	-1.296481
H	0.404334	0.558212	2.020414
H	-0.745787	-0.632879	2.078516
H	0.325409	-0.344012	-1.555106
H	0.576557	-1.388735	-0.136180
H	4.243117	-0.668382	0.002938
H	2.951792	-1.746647	0.580348
H	3.206221	-1.499972	-1.175099
H	-3.166542	-0.704534	-1.464724
C	-0.783310	1.831831	-0.152529
H	-0.847653	1.928720	-1.238665
H	-1.670631	2.278918	0.301957
H	0.089115	2.391671	0.197850

(*R*)-*S*-methylcysteine methyl ester (9)

N	-0.027161	2.037486	-0.240898
C	-0.237998	0.610488	-0.440681
C	0.798545	-0.327354	0.234271
S	2.449869	-0.101273	-0.542829
C	3.499717	-0.905230	0.717215
C	-1.611071	0.250932	0.118729
O	-2.097101	0.753559	1.111658
O	-2.201608	-0.727014	-0.593873
H	0.947261	2.280860	-0.394744
H	-0.286050	2.300267	0.707229
H	-0.248433	0.395156	-1.514950
H	0.491885	-1.373774	0.128708
H	0.868463	-0.080598	1.299661
H	4.530303	-0.832304	0.362195
H	3.420182	-0.394985	1.681136
H	3.241537	-1.961386	0.832606
C	-3.483043	-1.178832	-0.107994
H	-4.196142	-0.351640	-0.100035
H	-3.798337	-1.954533	-0.804765
H	-3.385676	-1.581486	0.902993

(*R*)-*S*-methylcysteine methyl ester *radical cation* (7)

C	0.783773	-0.110498	0.207314
C	0.172292	-1.158211	-0.757913
S	-1.647181	-1.268310	-0.678135
C	-1.957701	-2.152347	0.874877
C	2.318246	-0.137206	0.109701
O	2.976307	0.827508	-0.200221
O	2.798029	-1.347285	0.412370
H	0.512640	-0.377907	1.236390
H	0.585097	-2.146831	-0.538249
H	0.398418	-0.901394	-1.796650
H	-3.042261	-2.211618	0.981860
H	-1.535638	-3.158964	0.807559
H	-1.537209	-1.606095	1.720530
H	3.771423	-1.333058	0.356651
N	0.368398	1.253795	-0.061206
H	1.113494	1.897663	-0.318663
C	-0.882407	1.694799	0.144621
C	-1.172876	3.163717	0.019095
O	-1.805217	0.891742	0.445166
H	-1.894747	3.315852	-0.788606
H	-1.641517	3.507628	0.945633
H	-0.274500	3.753881	-0.172538

(*R*)-*S*-methyl-2-methylcysteine *radical cation* (8)

N	0.207917	1.296556	0.998914
C	0.550869	0.036789	0.468560
C	-0.469619	-0.392884	-0.778116
S	-2.147344	-0.713887	-0.301558
C	-2.821902	0.958875	-0.222500
C	1.890190	0.199296	-0.314848
O	2.334428	1.278921	-0.621416
O	2.431079	-0.983854	-0.614975
H	-0.079995	1.359046	1.967818
H	0.711737	2.100685	0.630993
H	-0.063927	-1.319349	-1.190102
H	-0.423708	0.411934	-1.514993
H	-3.834563	0.897973	0.178144
H	-2.173864	1.557188	0.436638
H	-2.831484	1.416991	-1.215866
H	3.260892	-0.843192	-1.107944
C	0.586182	-1.066211	1.534524
H	0.751968	-2.045218	1.083042
H	1.400708	-0.873043	2.238353
H	-0.354063	-1.092438	2.091842

(*R*)-*S*-methylcysteine methyl ester *radical cation* (9)

N	0.588264	1.423763	-0.545817
C	-0.195097	0.189641	-0.716586
C	0.691847	-0.925505	-0.124176
S	2.398126	-0.298113	-0.471939
C	3.165412	-0.222179	1.173604
C	-1.535085	0.307209	0.023404
O	-1.719792	1.158874	0.868979
O	-2.383193	-0.635439	-0.356296
H	0.607420	2.055889	-1.342003
H	0.348770	1.923640	0.314041
H	-0.369948	0.012725	-1.780514
H	0.552106	-1.906611	-0.582032
H	0.574678	-1.010429	0.959442
H	4.160947	0.204916	1.041164
H	2.571751	0.399639	1.846971
H	3.249325	-1.238229	1.571388
C	-3.689849	-0.653269	0.297379
H	-4.203475	0.289872	0.107426
H	-4.217925	-1.488022	-0.157496
H	-3.561001	-0.802781	1.370144

(*R*)-*N*-acetyl-2-methylcysteine (10)

C	-0.529326	-0.164789	0.169364
C	-1.712297	-1.106128	-0.124614
O	-1.611799	-2.248534	-0.528028
C	-0.653234	1.048688	-0.821073
S	0.005236	2.680690	-0.300805
O	-2.903912	-0.529624	0.125235
H	-0.201872	0.753679	-1.771336
H	-1.710653	1.252763	-1.000480
H	1.262618	2.253152	-0.054139
H	-3.593327	-1.185226	-0.075607
N	0.656839	-0.986873	-0.109680
H	0.445413	-1.933971	-0.401252
C	1.961769	-0.624933	0.034183
C	2.974077	-1.724038	-0.244831
O	2.329192	0.503634	0.367707
H	3.688577	-1.358442	-0.986984
H	3.530525	-1.924053	0.675671
H	2.528473	-2.656629	-0.600992
C	-0.594767	0.238418	1.657853
H	-0.661540	-0.656559	2.284498
H	0.306735	0.790858	1.922054
H	-1.461780	0.874388	1.844610

(*R*)-2-methylcysteine methyl ester (11)

N	-0.636313	1.745134	0.421712
C	1.227096	0.348268	-0.153144
O	1.665426	1.186146	-0.916169
C	-1.002637	-0.535650	-0.648390
S	-2.826705	-0.596262	-0.402193
O	1.932125	-0.725059	0.252192
H	-0.415719	2.226605	-0.445820
H	-1.631035	1.815294	0.614349
H	-0.807850	-0.189789	-1.667106
H	-0.669031	-1.575147	-0.577949
H	-3.121625	0.540772	-1.063469
C	3.273539	-0.832543	-0.268774
H	3.866268	0.033519	0.033537
H	3.677627	-1.747525	0.162867
H	3.253715	-0.892813	-1.359388
C	-0.316200	-0.237834	1.797184
H	0.004327	-1.281635	1.824218
H	0.302274	0.342554	2.485865
H	-1.354157	-0.182438	2.138148
C	-0.215753	0.348787	0.381402

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (12)

C	-0.043943	-0.115849	-0.202516
C	1.306274	-0.687394	0.255982
S	2.699712	0.371227	-0.308709
C	4.085790	-0.716545	0.174997
C	-1.166743	-1.050256	0.282313
O	-1.807474	-0.894734	1.299250
O	-1.312695	-2.092336	-0.556242
H	-0.084335	-0.091428	-1.294536
H	1.423044	-1.688178	-0.169095
H	1.330311	-0.772542	1.349428
H	5.004869	-0.194908	-0.101608
H	4.095177	-0.894862	1.254041
H	4.047619	-1.670326	-0.358866
N	-0.240246	1.231989	0.286556
H	0.181451	1.488591	1.167685
C	-1.234571	2.024181	-0.228538
C	-1.443437	3.359263	0.460033
O	-1.907262	1.667678	-1.191644
H	-1.530224	4.136645	-0.302494
H	-2.389669	3.323455	1.009321
H	-0.640440	3.620742	1.154882
C	-2.335406	-3.048565	-0.206545
H	-3.310124	-2.557174	-0.172955
H	-2.308973	-3.800655	-0.994063
H	-2.120707	-3.496796	0.766453

(*R*)-*N*-acetyl-2-methylcysteine *radical cation* (10)

C	0.665921	-0.030669	0.216560
C	2.041816	0.554338	-0.194693
O	2.207869	1.723340	-0.457250
C	0.373718	-1.253832	-0.692052
S	-1.152118	-2.146294	-0.180108
O	2.997327	-0.378390	-0.183412
H	0.279767	-0.956797	-1.737791
H	1.191728	-1.970569	-0.596675
H	-1.826774	-2.067251	-1.346131
H	3.853426	0.032790	-0.404260
N	-0.278560	1.069617	-0.018323
H	0.173764	1.965759	-0.193754
C	-1.611117	1.019378	0.006280
C	-2.389297	2.301130	-0.142514
O	-2.269101	-0.051546	0.149905
H	-3.071906	2.210747	-0.991431
H	-2.995350	2.447256	0.756367
H	-1.735914	3.164754	-0.282816
C	0.721977	-0.401139	1.717404
H	1.048323	0.461387	2.303789
H	-0.265946	-0.697163	2.079045
H	1.425829	-1.220005	1.883804

(*R*)-2-methylcysteine methyl ester *radical cation* (11)

N	-0.514821	1.867062	0.003510
C	1.252844	0.305251	-0.215114
O	1.704511	0.978767	-1.115019
C	-1.063105	-0.562542	-0.643661
S	-2.779324	-0.762345	-0.274803
O	1.830318	-0.716525	0.388191
H	0.001754	2.328206	-0.744172
H	-1.250287	2.374244	0.481495
H	-0.879322	-0.248928	-1.670447
H	-0.562346	-1.504263	-0.411734
H	-3.259673	0.219430	-1.070076
C	3.185678	-1.059328	-0.048800
H	3.848297	-0.213299	0.135659
H	3.462860	-1.918308	0.557494
H	3.172387	-1.306754	-1.110978
C	-0.417039	0.226417	1.813218
H	-0.251964	-0.835412	1.998122
H	0.282772	0.795637	2.431207
H	-1.436391	0.482347	2.112235
C	-0.180675	0.566410	0.340706

(*R*)-*N*-acetyl-2-methylcysteine methyl ester *radical cation* (12)

C	-0.416609	-0.038753	-0.380881
C	0.130977	-1.475605	-0.304409
S	1.958314	-1.265155	-0.327847
C	2.529014	-2.649650	0.694215
C	-1.829541	0.054251	0.212175
O	-2.045718	0.592268	1.279014
O	-2.715819	-0.544396	-0.569032
H	-0.415041	0.319880	-1.413516
H	-0.182838	-2.117922	-1.131791
H	-0.134497	-1.954143	0.643253
H	3.619683	-2.619496	0.701807
H	2.139743	-2.557881	1.712196
H	2.183975	-3.589535	0.249610
N	0.484989	0.823587	0.391906
H	0.210923	0.939980	1.369347
C	1.109756	1.943891	-0.230700
C	1.677937	2.968461	0.712693
O	1.154592	1.995771	-1.443350
H	2.386828	3.594815	0.171308
H	0.866568	3.603618	1.088316
H	2.169362	2.505234	1.573659
C	-4.106110	-0.533694	-0.121000
H	-4.454186	0.497065	-0.044580
H	-4.651165	-1.076282	-0.889883
H	-4.184286	-1.030511	0.846876

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine (13)

C	0.109481	-0.444868	0.311062
C	-1.330218	-0.642007	-0.226677
S	-2.520834	0.589053	0.458352
C	-3.871797	0.374534	-0.753541
C	0.963999	-1.452593	-0.503078
O	1.174248	-1.351009	-1.691421
O	1.356841	-2.519575	0.223610
H	-1.667838	-1.651118	0.027913
H	-1.317916	-0.537413	-1.315357
H	-4.661770	1.073090	-0.468882
H	-3.535532	0.610131	-1.766811
H	-4.272144	-0.642104	-0.720595
H	1.868119	-3.092093	-0.373456
N	0.552040	0.903580	-0.044006
H	-0.163514	1.579570	-0.275524
C	1.862532	1.280656	0.010001
C	2.161694	2.716701	-0.376914
O	2.748468	0.491927	0.336106
H	2.787582	3.165987	0.398157
H	2.737780	2.711880	-1.307258
H	1.265715	3.327536	-0.518564
C	0.195332	-0.678102	1.829773
H	1.229815	-0.584324	2.163024
H	-0.415126	0.066277	2.348386
H	-0.168684	-1.674010	2.093266

(*R*)-*S*-methyl-2-methylcysteine methyl ester (14)

N	0.074638	1.513538	1.240139
C	-0.220662	0.666207	0.086388
C	0.785364	-0.517343	-0.101852
S	2.496667	0.076144	-0.448104
C	3.453766	-1.293149	0.292784
C	-1.567059	-0.018652	0.383252
O	-1.961647	-0.278004	1.503145
O	-2.235709	-0.361669	-0.733489
H	1.061832	1.756879	1.249050
H	-0.153886	1.028733	2.104380
H	0.458307	-1.167612	-0.919922
H	0.817301	-1.102586	0.823006
H	4.509401	-1.046724	0.156215
H	3.247167	-1.387113	1.362425
H	3.246831	-2.240782	-0.211361
C	-0.284147	1.542542	-1.176182
H	-0.467939	0.948092	-2.073845
H	-1.074254	2.289933	-1.071971
H	0.664610	2.074297	-1.297755
C	-3.477507	-1.068181	-0.533615
H	-4.171847	-0.455486	0.045486
H	-3.867288	-1.254265	-1.533760
H	-3.299074	-2.007588	-0.005150

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine *radical cation* (13)

C	0.949877	-0.118983	0.641891
C	-0.235950	-1.062217	0.953948
S	-1.366214	-1.288425	-0.471676
C	-3.002298	-1.329294	0.309473
C	1.664049	-0.479123	-0.688118
O	2.045835	0.335903	-1.489452
O	1.834770	-1.810527	-0.797128
H	-0.808090	-0.673067	1.799092
H	0.151895	-2.052415	1.203418
H	-3.722686	-1.534595	-0.484099
H	-3.031922	-2.128853	1.054454
H	-3.211074	-0.358744	0.763857
H	2.332544	-1.999915	-1.613544
N	0.536332	1.287186	0.581402
H	1.258688	1.953719	0.824627
C	-0.538896	1.803193	-0.041667
C	-0.629074	3.302283	-0.165799
O	-1.470827	1.106202	-0.513465
H	-0.333388	3.575520	-1.184622
H	-1.663406	3.617841	-0.019112
H	0.020394	3.818714	0.544682
C	1.980247	-0.251834	1.788000
H	2.828949	0.418412	1.619188
H	1.515024	0.004095	2.744140
H	2.362228	-1.272988	1.838916

(*R*)-*S*-methyl-2-methylcysteine methyl ester *radical cation* (14)

N	-0.396977	1.627091	0.616840
C	0.114181	0.317218	0.544375
C	-0.707791	-0.590734	-0.587314
S	-2.395881	-0.951625	-0.181872
C	-3.217161	0.574591	-0.690949
C	1.519228	0.396112	-0.145090
O	1.855086	1.364547	-0.789528
O	2.218142	-0.710367	0.047594
H	-0.799685	1.954164	1.486428
H	0.060725	2.328706	0.038685
H	-0.174479	-1.541703	-0.646761
H	-0.641089	-0.048697	-1.533041
H	-4.262934	0.514488	-0.386846
H	-2.713654	1.417017	-0.192634
H	-3.142282	0.709360	-1.773704
C	0.115354	-0.392657	1.902803
H	0.417296	-1.435641	1.801080
H	0.821601	0.101510	2.575922
H	-0.878437	-0.358938	2.357417
C	3.552819	-0.755542	-0.549798
H	4.166731	0.039132	-0.124629
H	3.941344	-1.736893	-0.287839
H	3.472190	-0.633512	-1.630703

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (15)

C	-0.206959	0.002276	0.180137
C	-1.582244	-0.645984	-0.097628
O	-1.739073	-1.787425	-0.491845
C	-0.057145	1.211148	-0.808532
S	0.990276	2.633999	-0.308068
O	-2.594027	0.192904	0.158877
H	0.286157	0.820611	-1.769707
H	-1.038288	1.665044	-0.960575
H	2.104641	1.909711	-0.064852
N	0.753735	-1.072154	-0.112387
H	0.320376	-1.941806	-0.400888
C	2.107201	-1.032592	0.024353
C	2.826254	-2.341239	-0.262533
O	2.738173	-0.026361	0.356895
H	3.603124	-2.154975	-1.008701
H	3.324385	-2.670670	0.654212
H	2.168586	-3.139508	-0.616655
C	-0.155823	0.407464	1.668135
H	-0.421439	-0.448209	2.297172
H	0.852346	0.734672	1.922223
H	-0.848927	1.227370	1.864099
C	-3.925204	-0.326800	-0.052789
H	-4.096702	-1.194779	0.587294
H	-4.595872	0.489224	0.212132
H	-4.056007	-0.614175	-1.098230

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine methyl ester (16)

C	-0.010787	-0.186581	0.364084
C	-1.299820	-0.846697	-0.184459
S	-2.838190	-0.027430	0.420274
C	-4.011206	-0.684179	-0.817600
C	1.144270	-0.907489	-0.385743
O	1.311987	-0.820103	-1.583918
O	1.863193	-1.705711	0.417767
H	-1.312431	-1.899779	0.112496
H	-1.286432	-0.787742	-1.276416
H	-4.989970	-0.263264	-0.576733
H	-3.730924	-0.379357	-1.829423
H	-4.073073	-1.774096	-0.760784
N	-0.002932	1.217071	-0.054896
H	-0.891759	1.625815	-0.311084
C	1.120809	1.989273	-0.023929
C	0.954454	3.428711	-0.475215
O	2.209214	1.538926	0.332628
H	1.373806	4.087186	0.289810
H	1.534889	3.573501	-1.391355
H	-0.084831	3.710783	-0.665492
C	0.093805	-0.306134	1.894045
H	1.035169	0.124796	2.237771
H	-0.735966	0.233301	2.359601
H	0.052825	-1.351539	2.209335
C	2.967381	-2.389255	-0.208924
H	3.424994	-2.982909	0.581747
H	2.610407	-3.028876	-1.019531
H	3.676272	-1.659231	-0.605432

(*R*)-*N*-acetyl-2-methylcysteine methyl ester *radical cation* (15)

C	0.300702	-0.049630	0.276137
C	1.704694	0.519721	-0.076989
O	1.883509	1.696124	-0.315524
C	0.028076	-1.264982	-0.645985
S	-1.535359	-2.131891	-0.205782
O	2.636490	-0.420987	-0.042294
H	-0.014242	-0.965754	-1.694435
H	0.829276	-1.994500	-0.514379
H	-2.154418	-2.042650	-1.401299
N	-0.616343	1.065450	0.003829
H	-0.136153	1.952232	-0.147665
C	-1.947908	1.038916	-0.037335
C	-2.695291	2.334816	-0.220868
O	-2.633102	-0.019986	0.070351
H	-3.333367	2.259732	-1.105172
H	-3.345429	2.488405	0.645291
H	-2.020140	3.187023	-0.322443
C	0.283859	-0.422977	1.776043
H	0.591933	0.435549	2.378063
H	-0.721403	-0.710992	2.094392
H	0.972610	-1.248328	1.971100
C	4.012446	0.006270	-0.288940
H	4.306823	0.735525	0.466564
H	4.604699	-0.902579	-0.212020
H	4.085324	0.444426	-1.284931

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine methyl ester *radical cation* (16)

C	-0.419852	-0.514542	0.874242
C	0.116004	0.905471	1.162422
S	0.600946	1.806377	-0.357846
C	2.066549	2.733490	0.172243
C	-1.497973	-0.541114	-0.246206
O	-1.575287	-1.425780	-1.065956
O	-2.328176	0.500165	-0.135378
H	0.980259	0.852627	1.828534
H	-0.673040	1.494176	1.635169
H	2.375403	3.344973	-0.677210
H	1.806452	3.376264	1.017483
H	2.861123	2.034114	0.439666
N	0.654670	-1.445032	0.504432
H	0.455720	-2.418004	0.702034
C	1.687511	-1.227351	-0.327793
C	2.534497	-2.409479	-0.724052
O	1.992149	-0.095891	-0.782217
H	2.245690	-2.709011	-1.737316
H	3.584437	-2.112388	-0.747455
H	2.405138	-3.259135	-0.049917
C	-1.067303	-1.051521	2.171799
H	-1.437987	-2.070118	2.020158
H	-0.335639	-1.061343	2.984744
H	-1.912964	-0.424642	2.461002
C	-3.443267	0.545217	-1.074748
H	-3.987818	1.452826	-0.823473
H	-3.062299	0.582335	-2.096173
H	-4.068786	-0.338463	-0.941759

Cartesian Coordinates for Optimized Geometries in Methanol at B3lyp/6-31+G(d,p) Level and PCM Solvation Model:

Cysteine (1)

N	-0.071026	1.705486	-0.445396
C	-0.220340	0.257614	-0.437955
C	-1.638437	-0.092319	0.001078
O	-2.335429	0.594532	0.723262
C	0.756053	-0.532455	0.478170
S	2.526193	-0.350433	0.013355
O	-2.026497	-1.294412	-0.468557
H	-0.183740	2.088457	0.490765
H	0.854701	1.958897	-0.779593
H	-0.089220	-0.107337	-1.461270
H	0.632114	-0.234081	1.522820
H	0.553959	-1.604038	0.403242
H	2.733399	0.864826	0.557524
H	-2.911364	-1.496195	-0.114802

Cysteine *radical cation* (1)

N	-0.216979	1.727236	-0.366748
C	-0.261255	0.347301	-0.477396
C	-1.628541	-0.166973	-0.002299
O	-2.354170	0.471878	0.726907
C	0.844898	-0.429910	0.522013
S	2.535324	-0.336896	-0.003018
O	-1.869617	-1.386436	-0.478584
H	-0.804630	2.194202	0.320161
H	0.465442	2.281137	-0.872282
H	-0.014187	0.005015	-1.482754
H	0.696503	-0.026734	1.522488
H	0.547248	-1.477799	0.462845
H	2.850488	0.844698	0.567793
H	-2.727504	-1.706880	-0.143226

(*R*)-cysteine methyl ester (2)

N	0.666479	1.789680	-0.498511
C	0.247502	0.394903	-0.446309
C	-1.205424	0.336068	0.021068
O	-1.712292	1.128277	0.795702
C	1.070559	-0.534634	0.486613
S	2.842065	-0.691548	0.014267
O	-1.844063	-0.727811	-0.487309
H	0.632503	2.212087	0.426905
H	1.622261	1.854272	-0.838261
H	0.293578	-0.016333	-1.458893
H	1.011419	-0.191524	1.523129
H	0.675602	-1.553196	0.441551
H	3.272075	0.475188	0.533588
C	-3.210022	-0.937593	-0.053952
H	-3.829216	-0.086275	-0.342654
H	-3.537302	-1.841349	-0.564605
H	-3.244152	-1.072057	1.028875

(*R*)-cysteine methyl ester *radical cation* (2)

N	0.570684	1.869905	-0.409447
C	0.226005	0.530544	-0.481626
C	-1.217248	0.339031	0.017242
O	-1.754242	1.121365	0.774145
C	1.144054	-0.437640	0.538241
S	2.802823	-0.753085	-0.005626
O	-1.736363	-0.774616	-0.473303
H	0.118271	2.465483	0.280406
H	1.341885	2.252297	-0.944978
H	0.382515	0.117535	-1.477765
H	1.106701	0.026537	1.522425
H	0.616898	-1.392817	0.525869
H	3.392913	0.344781	0.511936
C	-3.094628	-1.105889	-0.063406
H	-3.771140	-0.302854	-0.357505
H	-3.329253	-2.027450	-0.590594
H	-3.123003	-1.253750	1.016909

(*R*)-*N*-acetylcysteine (3)

C	-0.530353	-0.134925	0.140989
C	-1.335245	-1.426825	-0.052217
O	-1.024093	-2.346140	-0.782134
C	-1.329181	1.068394	-0.406176
S	-0.591415	2.699397	0.002422
O	-2.457767	-1.413599	0.689276
H	-0.371250	-0.003572	1.214439
H	-1.453578	0.988089	-1.489359
H	-2.321899	1.082816	0.047059
H	0.542212	2.554445	-0.711777
H	-2.950831	-2.237829	0.527379
N	0.774257	-0.247510	-0.471193
H	0.816542	-0.376178	-1.473569
C	1.925405	-0.387285	0.248761
C	3.192638	-0.566127	-0.560075
O	1.940676	-0.358309	1.484839
H	3.897291	0.224788	-0.288583
H	3.647803	-1.523468	-0.290347
H	3.026437	-0.541871	-1.639184

(*R*)-*N*-acetylcysteine *radical cation* (3)

C	0.690154	0.040231	-0.285019
C	2.113793	-0.487692	-0.060343
O	2.355176	-1.583939	0.399474
C	0.476975	1.351635	0.511455
S	-1.112202	2.144587	0.065800
O	3.024958	0.406409	-0.442159
H	0.586719	0.258970	-1.354259
H	0.502519	1.177948	1.587321
H	1.250570	2.068293	0.232013
H	-1.803996	1.868673	1.190206
H	3.918421	0.046616	-0.292224
N	-0.224239	-1.026089	0.079655
H	0.202077	-1.856221	0.482931
C	-1.538546	-1.000228	-0.145100
C	-2.354618	-2.226604	0.153776
O	-2.117204	0.027099	-0.603469
H	-3.063201	-1.992720	0.952886
H	-2.927464	-2.491675	-0.738383
H	-1.730725	-3.071257	0.449745

(*R*)-*S*-methylcysteine (4)

N	-0.752115	1.833807	-0.147098
C	-0.711332	0.401087	-0.420857
C	0.459394	-0.380889	0.232975
S	2.059831	0.138278	-0.511811
C	3.218992	-0.589037	0.700409
C	-2.014206	-0.227085	0.059575
O	-2.708620	0.214016	0.955503
O	-2.299406	-1.364979	-0.601031
H	0.155604	2.247048	-0.345994
H	-0.949186	1.993334	0.838990
H	-0.660399	0.251597	-1.505304
H	0.330797	-1.456931	0.084291
H	0.486665	-0.170210	1.307345
H	4.226652	-0.346678	0.356247
H	3.064919	-0.157074	1.692175
H	3.107897	-1.675024	0.743224
H	-3.108325	-1.751923	-0.220706

(*R*)-2-methylcysteine hydrochloride (5)

N	0.045818	1.613191	0.612812
C	0.224895	0.186155	0.351994
C	1.625268	0.008716	-0.253256
O	2.288054	0.902730	-0.745249
C	-0.749733	-0.397097	-0.728923
S	-2.541024	-0.226617	-0.342058
O	2.035294	-1.274956	-0.240626
H	0.183324	2.160402	-0.233860
H	-0.900030	1.783137	0.945702
H	-0.567711	0.076703	-1.696936
H	-0.580731	-1.470510	-0.842614
H	-2.694213	1.043923	-0.762908
H	2.899595	-1.324289	-0.686343
C	0.101974	-0.577960	1.681431
H	0.225415	-1.653139	1.536697
H	0.855605	-0.226159	2.390839
H	-0.886815	-0.397602	2.112201

***N*-acetyl-*L*-cysteine methyl ester (6)**

C	-0.149542	0.223436	0.084802
C	-1.486824	-0.472094	-0.218543
O	-1.643128	-1.351096	-1.044923
C	-0.187795	1.672180	-0.444572
S	1.241157	2.699304	0.082254
O	-2.465719	0.037037	0.539266
H	-0.018490	0.237555	1.169044
H	-0.260044	1.682656	-1.535549
H	-1.066092	2.181677	-0.044033
H	2.196960	2.000282	-0.561134
N	0.957366	-0.524597	-0.470591
H	1.015278	-0.603121	-1.477230
C	1.782408	-1.306395	0.283980
C	2.831154	-2.087939	-0.479296
O	1.692787	-1.368736	1.515938
H	3.818251	-1.829186	-0.086393
H	2.671647	-3.155237	-0.300050
H	2.814288	-1.901328	-1.555347
C	-3.797177	-0.498705	0.337677
H	-3.805750	-1.568145	0.555441
H	-4.431914	0.041655	1.037321
H	-4.119083	-0.324032	-0.690526

(*R*)-*S*-methylcysteine *radical cation* (4)

N	0.005503	1.337897	-0.576799
C	-0.646968	0.028375	-0.587654
C	0.365106	-0.927817	0.073195
S	1.968048	-0.221798	-0.511597
C	2.884985	0.076071	1.024182
C	-1.999124	0.042133	0.123314
O	-2.427026	0.992294	0.745055
O	-2.629823	-1.129610	-0.015504
H	-0.143998	1.920370	-1.395351
H	-0.110410	1.868619	0.284811
H	-0.806875	-0.268834	-1.627219
H	0.277013	-1.967911	-0.241132
H	0.344029	-0.868406	1.163340
H	3.833519	0.531985	0.738848
H	2.324757	0.739747	1.685228
H	3.062247	-0.885377	1.513811
H	-3.476775	-1.100740	0.466181

(*R*)-2-methylcysteine hydrochloride *radical cation* (5)

N	0.240244	1.680127	0.451310
C	0.284365	0.296034	0.398908
C	1.624953	-0.103266	-0.262797
O	2.269981	0.666059	-0.942041
C	-0.829682	-0.281353	-0.784388
S	-2.538947	-0.278270	-0.332362
O	1.939640	-1.372747	-0.018652
H	0.805361	2.224832	-0.196149
H	-0.437041	2.170136	1.024973
H	-0.630977	0.306335	-1.678108
H	-0.527226	-1.322497	-0.907054
H	-2.832704	0.989215	-0.690400
H	2.772131	-1.594574	-0.475483
C	-0.016950	-0.379381	1.740527
H	-0.092096	-1.460170	1.618568
H	0.787637	-0.157354	2.445503
H	-0.956730	-0.003183	2.148799

***N*-acetyl-*L*-cysteine methyl ester *radical cation* (6)**

C	0.305716	0.040771	-0.260557
C	1.725557	-0.492018	-0.002900
O	1.945772	-1.597782	0.452583
C	0.077484	1.351850	0.530197
S	-1.502458	2.146913	0.055816
O	2.638081	0.403517	-0.349963
H	0.223503	0.258508	-1.331630
H	0.082410	1.179459	1.606590
H	0.857471	2.066484	0.264177
H	-2.214006	1.872287	1.167832
N	-0.618309	-1.024308	0.085273
H	-0.197708	-1.854890	0.494570
C	-1.928023	-0.997175	-0.162095
C	-2.751797	-2.221991	0.122736
O	-2.498950	0.031056	-0.629110
H	-3.437705	-2.001673	0.945527
H	-3.349568	-2.455876	-0.761429
H	-2.131353	-3.081246	0.381309
C	4.033009	0.030369	-0.168770
H	4.259920	-0.844753	-0.778823
H	4.600736	0.895834	-0.502315
H	4.222898	-0.179752	0.884470

(*R*)-*S*-methylcysteine methyl ester (7)

C	0.119890	0.455407	-0.199586
C	-1.343609	0.525963	0.266781
S	-2.285083	-0.946182	-0.308737
C	-3.958096	-0.445215	0.232223
C	0.837682	1.761583	0.176446
O	1.630501	1.893606	1.085621
O	0.458195	2.767639	-0.633091
H	0.150003	0.381476	-1.290660
H	-1.804443	1.423087	-0.152171
H	-1.394723	0.586673	1.359421
H	-4.632799	-1.256380	-0.049291
H	-3.993940	-0.311872	1.316149
H	-4.273145	0.473215	-0.269023
H	0.905882	3.584724	-0.349265
N	0.799211	-0.696490	0.353061
H	0.483939	-1.062257	1.241141
C	1.945342	-1.187632	-0.194332
C	2.579870	-2.362488	0.517456
O	2.431721	-0.701507	-1.223442
H	2.678677	-3.190911	-0.189451
H	3.585994	-2.076942	0.838123
H	2.011599	-2.700077	1.386762

(*R*)-*S*-methyl-2-methylcysteine (8)

N	-0.516948	0.274456	1.739549
C	-0.652866	0.349940	0.283383
C	0.510164	-0.350677	-0.493242
S	2.144434	0.445461	-0.173277
C	3.224936	-1.030753	-0.134816
C	-1.918062	-0.434143	-0.094027
O	-2.467662	-1.248286	0.624827
O	-2.342872	-0.166057	-1.343168
H	0.420440	0.576612	1.997820
H	-0.623383	-0.688214	2.052200
H	0.310643	-0.337737	-1.567721
H	0.585613	-1.391255	-0.163813
H	4.239891	-0.668369	0.043086
H	2.937021	-1.703762	0.676115
H	3.198424	-1.559683	-1.089948
H	-3.113745	-0.730287	-1.532068
C	-0.785108	1.828181	-0.129891
H	-0.846015	1.938558	-1.214590
H	-1.676565	2.269189	0.323886
H	0.085251	2.385835	0.228916

(*R*)-*S*-methylcysteine methyl ester (9)

N	-0.027764	2.068412	-0.222547
C	-0.241493	0.638519	-0.431231
C	0.789384	-0.300692	0.247547
S	2.444034	-0.098441	-0.532669
C	3.483355	-0.940053	0.713848
C	-1.624963	0.271172	0.098858
O	-2.173560	0.832842	1.030713
O	-2.146875	-0.772026	-0.560345
H	0.935646	2.307084	-0.445027
H	-0.177772	2.298596	0.758027
H	-0.238206	0.435726	-1.507674
H	0.476943	-1.344870	0.151682
H	0.869971	-0.049086	1.310380
H	4.512675	-0.887943	0.352745
H	3.415915	-0.434406	1.680163
H	3.194299	-1.988422	0.818962
C	-3.428570	-1.262031	-0.097137
H	-4.182679	-0.477810	-0.184661
H	-3.667815	-2.099923	-0.749337
H	-3.351988	-1.590776	0.941030

(*R*)-*S*-methylcysteine methyl ester *radical cation* (7)

C	-0.777990	-0.090700	-0.200935
C	-0.179161	-1.125307	0.787709
S	1.629713	-1.291629	0.675362
C	1.879851	-2.210517	-0.863412
C	-2.308940	-0.111261	-0.108805
O	-2.974584	0.852392	0.206988
O	-2.794744	-1.312760	-0.422690
H	-0.509837	-0.378940	-1.223805
H	-0.614814	-2.109843	0.601053
H	-0.377130	-0.830844	1.820651
H	2.958579	-2.304177	-0.992123
H	1.425423	-3.199343	-0.761630
H	1.448434	-1.670864	-1.707444
H	-3.766729	-1.299539	-0.351799
N	-0.344556	1.270052	0.044945
H	-1.061536	1.925901	0.341451
C	0.910413	1.687922	-0.162974
C	1.221898	3.149567	-0.005001
O	1.818273	0.875748	-0.486450
H	1.909807	3.274034	0.836177
H	1.729996	3.498277	-0.907673
H	0.326295	3.749763	0.162464

(*R*)-*S*-methyl-2-methylcysteine *radical cation* (8)

N	0.235946	1.299140	1.008659
C	0.562353	0.049675	0.472088
C	-0.476620	-0.378621	-0.778975
S	-2.144603	-0.716594	-0.303133
C	-2.841218	0.948271	-0.222909
C	1.894310	0.195053	-0.310187
O	2.355767	1.267321	-0.636927
O	2.432522	-0.991097	-0.595749
H	-0.209396	1.377333	1.913630
H	0.641091	2.136464	0.603958
H	-0.062288	-1.299699	-1.192243
H	-0.435214	0.433126	-1.506438
H	-3.860702	0.863031	0.152949
H	-2.228986	1.552275	0.460468
H	-2.832542	1.410898	-1.212654
H	3.249130	-0.858854	-1.111450
C	0.582685	-1.059455	1.531901
H	0.719917	-2.037098	1.069346
H	1.402427	-0.882244	2.232687
H	-0.356787	-1.063048	2.089165

(*R*)-*S*-methylcysteine methyl ester *radical cation* (9)

N	0.603899	1.482514	-0.423261
C	-0.186403	0.269864	-0.642875
C	0.682557	-0.874548	-0.087885
S	2.382415	-0.282347	-0.499276
C	3.230792	-0.322535	1.102561
C	-1.559354	0.340262	0.028485
O	-1.875434	1.208776	0.819104
O	-2.325376	-0.678975	-0.352216
H	0.566397	2.182165	-1.158843
H	0.492233	1.903017	0.497764
H	-0.328276	0.138156	-1.717754
H	0.501943	-1.845135	-0.550206
H	0.606873	-0.962268	0.998094
H	4.243673	0.043740	0.933692
H	2.710550	0.308275	1.825056
H	3.257535	-1.357568	1.454204
C	-3.650620	-0.765418	0.238024
H	-4.226282	0.125847	-0.015842
H	-4.098555	-1.654175	-0.201037
H	-3.567373	-0.866256	1.321156

(*R*)-*N*-acetyl-2-methylcysteine (10)

C	-0.543962	-0.140811	0.171935
C	-1.749881	-1.058922	-0.126142
O	-1.663276	-2.194894	-0.555686
C	-0.657732	1.072891	-0.812744
S	0.114048	2.668612	-0.321615
O	-2.918228	-0.465965	0.150555
H	-0.263766	0.762097	-1.782419
H	-1.709974	1.330710	-0.942608
H	1.335269	2.158610	-0.046668
H	-3.640726	-1.085993	-0.053857
N	0.628338	-0.980686	-0.118808
H	0.395444	-1.914823	-0.436802
C	1.938906	-0.676438	0.043385
C	2.910873	-1.800926	-0.259654
O	2.351371	0.434586	0.413078
H	3.633640	-1.449256	-1.000858
H	3.462305	-2.040061	0.654595
H	2.429729	-2.708447	-0.630484
C	-0.598253	0.251853	1.663143
H	-0.677791	-0.645574	2.283366
H	0.311399	0.787356	1.933325
H	-1.457306	0.896688	1.856798

(*R*)-2-methylcysteine methyl ester (11)

N	-0.664532	1.805939	0.106285
C	1.242315	0.351493	-0.168165
O	1.761165	1.160439	-0.917872
C	-0.977910	-0.627216	-0.561586
S	-2.802657	-0.682831	-0.317769
O	1.867009	-0.745779	0.282352
H	-0.533800	2.089685	-0.861967
H	-1.655478	1.879657	0.323631
H	-0.786316	-0.448950	-1.622881
H	-0.624910	-1.632654	-0.319995
H	-3.123877	0.335218	-1.139551
C	3.225584	-0.954964	-0.170977
H	3.860706	-0.128160	0.152324
H	3.542446	-1.886852	0.293912
H	3.250047	-1.038465	-1.259185
C	-0.331301	0.093198	1.808612
H	-0.017150	-0.932510	2.011515
H	0.287022	0.776635	2.396561
H	-1.370736	0.208051	2.129229
C	-0.218540	0.428287	0.312263

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (12)

C	-0.077119	-0.113326	-0.169449
C	1.270230	-0.692553	0.290419
S	2.671464	0.315679	-0.346266
C	4.058493	-0.736704	0.212043
C	-1.211292	-1.055847	0.273050
O	-1.931264	-0.876938	1.236273
O	-1.281534	-2.118072	-0.539032
H	-0.102169	-0.072674	-1.261894
H	1.365934	-1.709971	-0.095443
H	1.318101	-0.730571	1.384134
H	4.976984	-0.234419	-0.098634
H	4.057800	-0.837100	1.300121
H	4.013961	-1.723492	-0.255148
N	-0.277750	1.227685	0.339807
H	0.172146	1.486528	1.207146
C	-1.183242	2.080621	-0.212228
C	-1.324339	3.433286	0.452098
O	-1.845541	1.767233	-1.210223
H	-1.131616	4.211848	-0.291324
H	-2.356184	3.550121	0.795931
H	-0.648753	3.573171	1.298809
C	-2.277411	-3.120992	-0.220510
H	-3.275036	-2.679589	-0.254555
H	-2.168904	-3.886251	-0.986723
H	-2.086638	-3.536948	0.770501

(*R*)-*N*-acetyl-2-methylcysteine *radical cation* (10)

C	0.663675	-0.023295	0.215979
C	2.043349	0.548468	-0.190103
O	2.217127	1.702686	-0.523333
C	0.397358	-1.267350	-0.676569
S	-1.157815	-2.133869	-0.237903
O	3.002473	-0.372041	-0.099705
H	0.357917	-0.996011	-1.731249
H	1.194472	-1.995189	-0.518628
H	-1.821164	-1.937869	-1.394786
H	3.859358	0.025533	-0.339890
N	-0.284444	1.060989	-0.054470
H	0.148914	1.944605	-0.311564
C	-1.612737	1.009024	0.033751
C	-2.397933	2.275323	-0.180628
O	-2.252069	-0.052647	0.290666
H	-3.077669	2.130293	-1.024092
H	-3.000406	2.467943	0.710952
H	-1.749539	3.131653	-0.372082
C	0.697787	-0.366396	1.722959
H	0.999138	0.512515	2.297162
H	-0.292069	-0.673577	2.066418
H	1.407963	-1.173531	1.912137

(*R*)-2-methylcysteine methyl ester *radical cation* (11)

N	-0.521541	1.872560	0.022246
C	1.258368	0.322666	-0.194689
O	1.760297	1.026251	-1.048838
C	-1.059393	-0.527069	-0.673051
S	-2.766091	-0.772266	-0.280433
O	1.811819	-0.734245	0.374702
H	-0.041078	2.347119	-0.739007
H	-1.313656	2.335046	0.454871
H	-0.911367	-0.170782	-1.690251
H	-0.544113	-1.471878	-0.493845
H	-3.277142	0.257153	-0.987351
C	3.154329	-1.091026	-0.063530
H	3.837319	-0.266799	0.144402
H	3.414539	-1.971035	0.519712
H	3.141409	-1.316476	-1.130613
C	-0.426467	0.199876	1.796965
H	-0.268316	-0.866360	1.959438
H	0.266490	0.760228	2.429219
H	-1.448772	0.455297	2.082300
C	-0.180836	0.565682	0.330211

(*R*)-*N*-acetyl-2-methylcysteine methyl ester *radical cation* (12)

C	0.336588	-0.104195	0.298401
C	-0.276822	-1.494987	0.089907
S	-2.054217	-1.283801	0.478913
C	-2.858707	-2.401872	-0.682038
C	1.790233	-0.025302	-0.191814
O	2.192463	0.802164	-0.983786
O	2.527841	-0.973856	0.383012
H	0.340022	0.150103	1.362518
H	0.135580	-2.259011	0.753638
H	-0.193629	-1.834178	-0.945432
H	-3.922268	-2.406506	-0.444976
H	-2.690764	-2.041170	-1.701687
H	-2.427111	-3.401578	-0.570208
N	-0.519182	0.870985	-0.364635
H	-0.593730	0.810215	-1.375813
C	-0.788892	2.109689	0.210985
C	-1.472296	3.107615	-0.688511
O	-0.482158	2.338202	1.376471
H	-2.046628	3.804796	-0.077800
H	-0.706089	3.672538	-1.231592
H	-2.125674	2.627558	-1.420852
C	3.938743	-1.010657	0.036661
H	4.414708	-0.074508	0.332097
H	4.346619	-1.847541	0.599282
H	4.052445	-1.170617	-1.036464

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine (13)

C	0.115035	-0.447325	0.297367
C	-1.326851	-0.644908	-0.238142
S	-2.521716	0.569362	0.470857
C	-3.854705	0.416889	-0.771765
C	0.962095	-1.478982	-0.489826
O	1.222464	-1.380610	-1.672828
O	1.297852	-2.552161	0.245820
H	-1.659400	-1.658704	-0.000299
H	-1.326833	-0.520040	-1.324169
H	-4.645073	1.105064	-0.465110
H	-3.496010	0.699408	-1.764274
H	-4.253923	-0.599647	-0.790969
H	1.769961	-3.178396	-0.331610
N	0.566846	0.893304	-0.081167
H	-0.150660	1.571825	-0.303991
C	1.861710	1.293100	-0.005537
C	2.140458	2.739800	-0.354838
O	2.765754	0.512225	0.324505
H	2.565918	3.236896	0.522009
H	2.889025	2.771713	-1.151275
H	1.251564	3.286625	-0.677007
C	0.190401	-0.650586	1.821540
H	1.222921	-0.572426	2.164777
H	-0.402466	0.120722	2.319896
H	-0.202902	-1.629541	2.103708

(*R*)-*S*-methyl-2-methylcysteine methyl ester (14)

N	0.348929	-0.561128	1.706879
C	-0.164821	0.223086	0.582820
C	0.698663	0.116119	-0.721840
S	2.469340	0.572510	-0.508952
C	3.276201	-1.072392	-0.492699
C	-1.532442	-0.368746	0.203803
O	-1.903579	-1.489271	0.509685
O	-2.252545	0.464749	-0.560625
H	1.316381	-0.295617	1.879033
H	0.329707	-1.555103	1.490628
H	0.286678	0.778117	-1.487561
H	0.672167	-0.905904	-1.111833
H	4.347688	-0.888292	-0.386637
H	2.934565	-1.678938	0.348034
H	3.095975	-1.599224	-1.432489
C	-0.293009	1.689524	1.029234
H	-0.662952	2.323400	0.220831
H	-0.972143	1.768549	1.882397
H	0.689340	2.058507	1.339642
C	-3.525269	-0.028160	-1.042220
H	-4.182621	-0.256254	-0.201119
H	-3.937272	0.780806	-1.642868
H	-3.376404	-0.922720	-1.650048

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine *radical cation* (13)

C	0.945630	-0.070214	0.655564
C	-0.149308	-1.122402	0.964286
S	-1.296433	-1.424524	-0.428921
C	-2.926492	-1.347251	0.355551
C	1.674018	-0.345035	-0.684077
O	2.040781	0.513224	-1.454201
O	1.890580	-1.659247	-0.850675
H	-0.724159	-0.806425	1.835900
H	0.320454	-2.085529	1.173542
H	-3.659756	-1.504827	-0.435993
H	-2.997716	-2.145268	1.098921
H	-3.068910	-0.371379	0.821686
H	2.393823	-1.800752	-1.673060
N	0.409060	1.289530	0.641714
H	0.922461	1.979946	1.174495
C	-0.610806	1.738860	-0.104713
C	-0.924182	3.211647	-0.064019
O	-1.314563	0.986530	-0.825621
H	-0.822121	3.614649	-1.075268
H	-1.962979	3.343506	0.248505
H	-0.265190	3.760288	0.610894
C	1.999003	-0.142761	1.785822
H	2.779944	0.606157	1.627192
H	1.518499	0.043676	2.749949
H	2.463605	-1.129498	1.807456

(*R*)-*S*-methyl-2-methylcysteine methyl ester *radical cation* (14)

N	-0.379768	1.641324	0.607062
C	0.125903	0.339230	0.542066
C	-0.711779	-0.596043	-0.574950
S	-2.392750	-0.951888	-0.160155
C	-3.222966	0.553352	-0.718380
C	1.522478	0.402738	-0.140342
O	1.884842	1.358380	-0.797447
O	2.215850	-0.707325	0.063669
H	-0.931878	1.946312	1.398244
H	-0.008169	2.349455	-0.017237
H	-0.173394	-1.544432	-0.612687
H	-0.647862	-0.070569	-1.528604
H	-4.275721	0.471677	-0.448077
H	-2.764745	1.414899	-0.213832
H	-3.109975	0.670599	-1.798643
C	0.119000	-0.361897	1.905390
H	0.412473	-1.407024	1.805940
H	0.818983	0.138079	2.579500
H	-0.880581	-0.318112	2.343921
C	3.531175	-0.783294	-0.554954
H	4.168411	0.008036	-0.158393
H	3.913412	-1.764394	-0.282871
H	3.433035	-0.686539	-1.636984

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (15)

C	-0.214884	0.017354	0.181020
C	-1.593155	-0.630943	-0.104474
O	-1.740136	-1.764215	-0.531353
C	-0.083076	1.231485	-0.797038
S	1.049459	2.605764	-0.331440
O	-2.597987	0.194711	0.181200
H	0.196342	0.849277	-1.781139
H	-1.053636	1.721663	-0.887426
H	2.120940	1.825351	-0.064747
N	0.751281	-1.049545	-0.127933
H	0.318390	-1.907414	-0.452354
C	2.095846	-1.044309	0.036539
C	2.795804	-2.353188	-0.277654
O	2.745584	-0.056334	0.416321
H	3.581657	-2.162877	-1.013620
H	3.277101	-2.717782	0.634875
H	2.126989	-3.127821	-0.658551
C	-0.164628	0.405242	1.672941
H	-0.422590	-0.458663	2.292419
H	0.839733	0.738086	1.933823
H	-0.868719	1.213495	1.878514
C	-3.941360	-0.305723	-0.037798
H	-4.115057	-1.187923	0.580474
H	-4.599251	0.509073	0.257514
H	-4.079177	-0.552667	-1.091761

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine methyl ester (16)

C	0.013188	-0.165596	0.340049
C	-1.268923	-0.843353	-0.207660
S	-2.816845	-0.069662	0.433584
C	-3.991978	-0.704436	-0.815461
C	1.175364	-0.898331	-0.381833
O	1.413425	-0.770180	-1.568720
O	1.818393	-1.753016	0.419893
H	-1.257191	-1.901890	0.065491
H	-1.279447	-0.761237	-1.297857
H	-4.975299	-0.314883	-0.543907
H	-3.727532	-0.350260	-1.814496
H	-4.023396	-1.796204	-0.799454
N	0.013938	1.232577	-0.099981
H	-0.878382	1.625454	-0.371965
C	1.099508	2.043491	-0.029962
C	0.892395	3.480140	-0.463144
O	2.202400	1.629794	0.355904
H	1.154162	4.139613	0.369293
H	1.574995	3.700076	-1.289009
H	-0.130746	3.694541	-0.779795
C	0.098941	-0.261881	1.873574
H	1.040894	0.158376	2.228507
H	-0.724770	0.302872	2.318168
H	0.029499	-1.300359	2.203954
C	2.869290	-2.542085	-0.186913
H	3.253240	-3.171887	0.613601
H	2.462358	-3.150870	-0.996494
H	3.653099	-1.887273	-0.572023

(*R*)-*N*-acetyl-2-methylcysteine methyl ester *radical cation* (15)

C	0.300209	-0.036105	0.262936
C	1.702282	0.523628	-0.094399
O	1.889191	1.679040	-0.427382
C	0.056879	-1.281704	-0.633179
S	-1.531645	-2.121823	-0.269411
O	2.640282	-0.401852	0.038559
H	0.075078	-1.019655	-1.690665
H	0.833677	-2.019670	-0.428763
H	-2.147759	-1.894313	-1.446844
N	-0.626674	1.055487	-0.049268
H	-0.172024	1.929959	-0.302589
C	-1.956938	1.021310	0.002598
C	-2.720523	2.294252	-0.247969
O	-2.616124	-0.030560	0.251801
H	-3.362768	2.154096	-1.121269
H	-3.361178	2.493729	0.614899
H	-2.056349	3.144290	-0.411044
C	0.269918	-0.373491	1.770315
H	0.550257	0.506828	2.353230
H	-0.733221	-0.678161	2.075356
H	0.970748	-1.181079	1.989834
C	4.012148	0.002720	-0.229515
H	4.304199	0.789670	0.466890
H	4.605119	-0.895447	-0.073592
H	4.096615	0.353817	-1.258544

(*R*)-*N*-acetyl-*S*-methyl-2-methylcysteine methyl ester *radical cation* (16)

C	-0.409299	-0.466765	0.950114
C	0.099370	0.970378	1.233408
S	0.655588	1.875653	-0.255530
C	2.353949	2.342518	0.165381
C	-1.476512	-0.525610	-0.175237
O	-1.681382	-1.508601	-0.855009
O	-2.168490	0.613467	-0.241846
H	0.922593	0.932459	1.948474
H	-0.714011	1.567952	1.649271
H	2.762477	2.858776	-0.703742
H	2.330246	3.016252	1.026086
H	2.942222	1.452435	0.392587
N	0.689808	-1.369227	0.611053
H	0.804068	-2.192039	1.188891
C	1.483124	-1.251201	-0.463910
C	2.476108	-2.347287	-0.744390
O	1.417958	-0.259191	-1.234255
H	2.244498	-2.781500	-1.721060
H	3.477555	-1.913296	-0.797489
H	2.454803	-3.133581	0.012176
C	-1.070209	-0.999815	2.240801
H	-1.420728	-2.024061	2.088059
H	-0.349333	-0.987191	3.062700
H	-1.923609	-0.376680	2.514116
C	-3.261912	0.664380	-1.197742
H	-3.685730	1.660433	-1.090610
H	-2.876314	0.510823	-2.206481
H	-3.999206	-0.101630	-0.953536

Cartesian Coordinates for Optimized Geometries in Heptane at B3lyp/6-31+G(d,p) Level and PCM Solvation Model:

(*R*)-*N*-acetyl-2-methylcysteine (10)

C	-0.532996	-0.159229	0.169975
C	-1.722079	-1.095077	-0.125247
O	-1.623567	-2.237237	-0.532552
C	-0.654592	1.054017	-0.818831
S	0.031202	2.678262	-0.304662
O	-2.906690	-0.513246	0.128271
H	-0.216190	0.755886	-1.773864
H	-1.711053	1.271183	-0.986622
H	1.279612	2.230671	-0.047353
H	-3.607648	-1.157433	-0.072322
N	0.650459	-0.985051	-0.111636
H	0.434408	-1.930371	-0.406249
C	1.956769	-0.637213	0.035360
C	2.959027	-1.742868	-0.247517
O	2.335294	0.488799	0.375373
H	3.677938	-1.380987	-0.987235
H	3.511699	-1.953861	0.672856
H	2.504675	-2.668683	-0.609054
C	-0.596737	0.240281	1.659424
H	-0.666246	-0.655777	2.283810
H	0.306148	0.788996	1.926345
H	-1.462437	0.877536	1.848025

***N*-acetyl-*L*-cysteine methyl ester (6)**

C	-0.146703	0.231557	0.090606
C	-1.497916	-0.425170	-0.220029
O	-1.686650	-1.216192	-1.124118
C	-0.160360	1.679029	-0.447542
S	1.297521	2.679515	0.043985
O	-2.453380	0.018133	0.609313
H	0.002805	0.245025	1.172388
H	-0.256349	1.679472	-1.537684
H	-1.020474	2.211193	-0.034336
H	2.228673	1.876821	-0.509419
N	0.928052	-0.553985	-0.482775
H	0.824498	-0.816396	-1.454775
C	1.770002	-1.315699	0.293166
C	2.708103	-2.232663	-0.468241
O	1.781416	-1.247270	1.519950
H	3.734509	-2.021530	-0.156878
H	2.485529	-3.267142	-0.190466
H	2.633487	-2.131248	-1.553998
C	-3.787700	-0.497895	0.392681
H	-3.792672	-1.583118	0.511519
H	-4.405313	-0.023260	1.153303
H	-4.135047	-0.236476	-0.608989

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (15)

C	-0.209494	0.007162	0.180135
C	-1.585922	-0.641493	-0.099663
O	-1.738901	-1.781783	-0.501625
C	-0.066255	1.218101	-0.804455
S	1.009418	2.625439	-0.314612
O	-2.594946	0.193637	0.163796
H	0.255605	0.830745	-1.774033
H	-1.044498	1.684190	-0.935253
H	2.110347	1.882898	-0.063989
N	0.753328	-1.064456	-0.118312
H	0.320140	-1.931654	-0.414933
C	2.104188	-1.036311	0.027326
C	2.815794	-2.345991	-0.267003
O	2.741629	-0.035483	0.373989
H	3.600698	-2.158559	-1.004424
H	3.302093	-2.690401	0.650665
H	2.154529	-3.134003	-0.635822
C	-0.158710	0.406406	1.669501
H	-0.421323	-0.452091	2.295465
H	0.847967	0.736145	1.925802
H	-0.855752	1.222223	1.868670
C	-3.931393	-0.319290	-0.048403
H	-4.104399	-1.188762	0.588608
H	-4.596469	0.498696	0.222900
H	-4.064415	-0.597734	-1.095582

(*R*)-*N*-acetylcysteine (3)

C	-0.491298	-0.197844	0.149504
C	-1.038223	-1.615355	-0.046794
O	-0.625496	-2.416360	-0.859561
C	-1.512346	0.819953	-0.405994
S	-1.112403	2.568340	-0.020104
O	-2.074955	-1.862829	0.778976
H	-0.349898	-0.025279	1.219464
H	-1.623925	0.696453	-1.487712
H	-2.487552	0.644316	0.053475
H	0.098110	2.584234	-0.613244
H	-2.400688	-2.762086	0.598092
N	0.806253	-0.070051	-0.479531
H	0.870954	-0.350237	-1.449841
C	1.970944	-0.049266	0.253438
C	3.251530	-0.124725	-0.554604
O	1.976428	0.037222	1.478697
H	3.928725	0.662629	-0.215171
H	3.733952	-1.086328	-0.353070
H	3.093545	-0.027632	-1.631812

Cartesian Coordinates for Optimized Geometries in DMSO at B3lyp/6-31+G(d,p) Level and PCM Solvation Model:

(*R*)-*N*-acetyl-2-methylcysteine (10)

C	-0.544598	-0.139662	0.172012
C	-1.751492	-1.056646	-0.126113
O	-1.665872	-2.192089	-0.557288
C	-0.657978	1.074216	-0.812293
S	0.119209	2.667947	-0.322806
O	-2.919037	-0.463186	0.152322
H	-0.267098	0.762633	-1.782952
H	-1.709909	1.334585	-0.939514
H	1.338873	2.154209	-0.047691
H	-3.642403	-1.082138	-0.052381
N	0.626903	-0.980431	-0.119572
H	0.392891	-1.913641	-0.439506
C	1.937771	-0.678826	0.043959
C	2.907936	-1.804389	-0.260613
O	2.352131	0.430879	0.416067
H	3.632276	-1.452332	-1.000098
H	3.457717	-2.046912	0.653750
H	2.425470	-2.710029	-0.634252
C	-0.598064	0.252653	1.663312
H	-0.678130	-0.644825	2.283362
H	0.312046	0.787384	1.933442
H	-1.456634	0.898026	1.857344

***N*-acetyl-*L*-cysteine methyl ester (6)**

C	-0.150704	0.221924	0.084965
C	-1.488001	-0.474196	-0.217176
O	-1.643531	-1.357848	-1.038767
C	-0.189146	1.670840	-0.443988
S	1.240956	2.697122	0.081497
O	-2.467680	0.039528	0.536392
H	-0.019362	0.236056	1.169207
H	-0.262452	1.681888	-1.534849
H	-1.066807	2.180434	-0.042266
H	2.195066	2.001988	-0.568552
N	0.956159	-0.525949	-0.470597
H	1.015874	-0.602265	-1.477297
C	1.784423	-1.304057	0.283676
C	2.835346	-2.082422	-0.479734
O	1.695921	-1.366030	1.515981
H	3.821931	-1.818370	-0.089035
H	2.680993	-3.150083	-0.298189
H	2.815880	-1.897867	-1.556072
C	-3.799273	-0.496403	0.335797
H	-3.809010	-1.564515	0.559922
H	-4.434720	0.048562	1.031196
H	-4.119339	-0.327460	-0.693917

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (15)

C	-0.215070	0.017682	0.181112
C	-1.593387	-0.630581	-0.104590
O	-1.740211	-1.763512	-0.532492
C	-0.083642	1.231910	-0.796765
S	1.050794	2.605056	-0.332135
O	-2.598118	0.194712	0.181986
H	0.194327	0.849836	-1.781310
H	-1.053910	1.722890	-0.885822
H	2.121320	1.823409	-0.065089
N	0.751178	-1.049063	-0.128233
H	0.318293	-1.906490	-0.453881
C	2.095523	-1.044568	0.036948
C	2.795235	-2.353281	-0.278203
O	2.745585	-0.057113	0.418083
H	3.580532	-2.162735	-1.014719
H	3.277137	-2.718239	0.633859
H	2.126158	-3.127743	-0.658920
C	-0.164773	0.405190	1.673116
H	-0.422486	-0.458930	2.292371
H	0.839509	0.738196	1.934092
H	-0.869141	1.213137	1.878965
C	-3.941633	-0.305301	-0.037495
H	-4.115387	-1.188123	0.579856
H	-4.599374	0.509252	0.258781
H	-4.079504	-0.550920	-1.091752

(*R*)-*N*-acetylcysteine (3)

C	-0.531249	-0.133831	0.140671
C	-1.339480	-1.423775	-0.052426
O	-1.026769	-2.347456	-0.776162
C	-1.326246	1.072459	-0.405387
S	-0.582219	2.700546	0.003718
O	-2.466154	-1.403862	0.682482
H	-0.372006	-0.003777	1.214310
H	-1.451576	0.993501	-1.488526
H	-2.318584	1.090080	0.048484
H	0.548229	2.554262	-0.715204
H	-2.960945	-2.227253	0.521498
N	0.773192	-0.249586	-0.471187
H	0.815984	-0.372010	-1.474332
C	1.923833	-0.392629	0.248339
C	3.191020	-0.570939	-0.560563
O	1.938949	-0.367349	1.484748
H	3.896935	0.217832	-0.286124
H	3.644406	-1.530027	-0.294013
H	3.025227	-0.542622	-1.639610

Cartesian Coordinates for Optimized Geometries in Water at B3lyp/6-31+G(d,p) Level and PCM Solvation Model:

(*R*)-*N*-acetyl-2-methylcysteine (10)

C	-0.545223	-0.138529	0.172091
C	-1.753071	-1.054403	-0.126084
O	-1.668423	-2.189316	-0.558875
C	-0.658222	1.075531	-0.811843
S	0.124296	2.667278	-0.323990
O	-2.919833	-0.460461	0.154072
H	-0.270401	0.763176	-1.783469
H	-1.709837	1.338415	-0.936443
H	1.342421	2.149866	-0.048748
H	-3.644035	-1.078370	-0.050925
N	0.625489	-0.980172	-0.120331
H	0.390378	-1.912453	-0.442203
C	1.936650	-0.681172	0.044533
C	2.905042	-1.807784	-0.261572
O	2.352868	0.427209	0.419049
H	3.631000	-1.455301	-0.999268
H	3.453111	-2.053732	0.652915
H	2.421296	-2.711524	-0.638096
C	-0.597879	0.253446	1.663480
H	-0.678452	-0.644080	2.283364
H	0.312674	0.787431	1.933553
H	-1.455979	0.899340	1.857880

***N*-acetyl-*L*-cysteine methyl ester (6)**

C	-0.151931	0.220368	0.085205
C	-1.489355	-0.476212	-0.215667
O	-1.644143	-1.364566	-1.032369
C	-0.190428	1.669438	-0.443313
S	1.241103	2.694666	0.080483
O	-2.469764	0.042255	0.533497
H	-0.020191	0.234454	1.169437
H	-0.265017	1.681057	-1.534046
H	-1.067294	2.179293	-0.040261
H	2.193266	2.003138	-0.576210
N	0.954730	-0.527524	-0.470614
H	1.015723	-0.602231	-1.477354
C	1.786487	-1.301619	0.283405
C	2.839223	-2.077213	-0.480244
O	1.699630	-1.362619	1.516094
H	3.825439	-1.807739	-0.092280
H	2.690046	-3.145112	-0.295827
H	2.816721	-1.895232	-1.556936
C	-3.801564	-0.493867	0.333946
H	-3.812399	-1.560630	0.564313
H	-4.437612	0.055641	1.025183
H	-4.119814	-0.330550	-0.697213

(*R*)-*N*-acetyl-2-methylcysteine methyl ester (15)

C	-0.215245	0.017987	0.181203
C	-1.593603	-0.630245	-0.104696
O	-1.740278	-1.762845	-0.533587
C	-0.084178	1.232304	-0.796508
S	1.052038	2.604391	-0.332798
O	-2.598240	0.194699	0.182750
H	0.192434	0.850354	-1.781466
H	-1.054171	1.724033	-0.884321
H	2.121678	1.821596	-0.065439
N	0.751085	-1.048611	-0.128510
H	0.318209	-1.905617	-0.455326
C	2.095221	-1.044807	0.037341
C	2.794714	-2.353354	-0.278726
O	2.745580	-0.057842	0.419761
H	3.579455	-2.162576	-1.015794
H	3.277229	-2.718634	0.632879
H	2.125393	-3.127672	-0.659242
C	-0.164907	0.405141	1.673284
H	-0.422375	-0.459185	2.292330
H	0.839299	0.738309	1.934344
H	-0.869543	1.212793	1.879396
C	-3.941887	-0.304909	-0.037213
H	-4.115703	-1.188333	0.579244
H	-4.599489	0.509407	0.259987
H	-4.079799	-0.549252	-1.091753

(*R*)-*N*-acetylcysteine (3)

C	-0.532367	-0.132315	0.140527
C	-1.345499	-1.419304	-0.052399
O	-1.032334	-2.347787	-0.769797
C	-1.322121	1.077869	-0.404350
S	-0.569515	2.702124	0.004530
O	-2.476328	-1.391259	0.675704
H	-0.372672	-0.003769	1.214339
H	-1.448969	1.000164	-1.487372
H	-2.313841	1.100119	0.050593
H	0.557155	2.552917	-0.719679
H	-2.973747	-2.213269	0.515677
N	0.771690	-0.252958	-0.471139
H	0.814699	-0.370455	-1.474874
C	1.921797	-0.399679	0.247947
C	3.188586	-0.579844	-0.561061
O	1.936983	-0.376717	1.484624
H	3.897026	0.205791	-0.284164
H	3.638688	-1.541245	-0.297225
H	3.023134	-0.547797	-1.640032

Table 1 Gas-phase Gibbs energies, G_g°, calculated at M06-2X/6-31+G(d,p) level and PCM solvation energies, $\Delta\Delta G_{solv}^\circ$ of the species involved in the oxidation processes,

Compound	[a] G_g°		[b] $\Delta\Delta G_{solv}^\circ$
	Red	Ox	
1	-721.7	-721.4	-195.5
2	-761.0	-760.6	-190.0
3	-874.3	-874.0	-170.3
4	-761.0	-760.7	-185.4
5	-761.0	-760.7	-190.0
6	-913.5	-913.2	-159.8
7	-913.6	-913.3	-158.3
8	-800.2	-799.9	-181.6
9	-800.2	-799.9	-173.1
10	-913.6	-913.2	-170.1
11	-800.2	-799.9	-179.6
12	-952.8	-952.5	-179.9
13	-952.8	-952.5	-159.5
14	-839.5	-839.2	-167.7
15	-952.8	-952.5	-164.8
16	-992.1	-991.8	-153.9

[a] G_g° are in atomic units, Hartree [b] $\Delta\Delta G_{solv}^\circ$ are in kJ mol^{-1} [b]The values of the electron spin operator ‹S^2› for the radical cations were between 0.75 and 0.76 at UB3LYP level.

REFERENCIAS

[1] Pattenden, G.; Thom, S. M.; Jones, M. F. *Tetrahedron* **1993**, *49*, 2131-2138.
[2] Mulqueen, G. C.; Pattenden, G.; Whiting, D. A. *Tetrahedron* **1993**, *49*, 5359-5364
[3] Singh, S.; Rao, S. J.; Pennington, M. W. *J. Org. Chem.* **2004**, *69*, 4551-4554.
[4] Kupchan, S. M.; Giacobbe, T. J.; Krull, I. S.; Thomas, A. M.; Eakin, M. A.; Fessler, D. C. *J. Org. Chem.* **1970**, *35*, 3539-3543.
[5] Geiwiz, J.; Goetschi, E.; Hebeisen, P. *Synthesis* **2003**, 1698-1704.