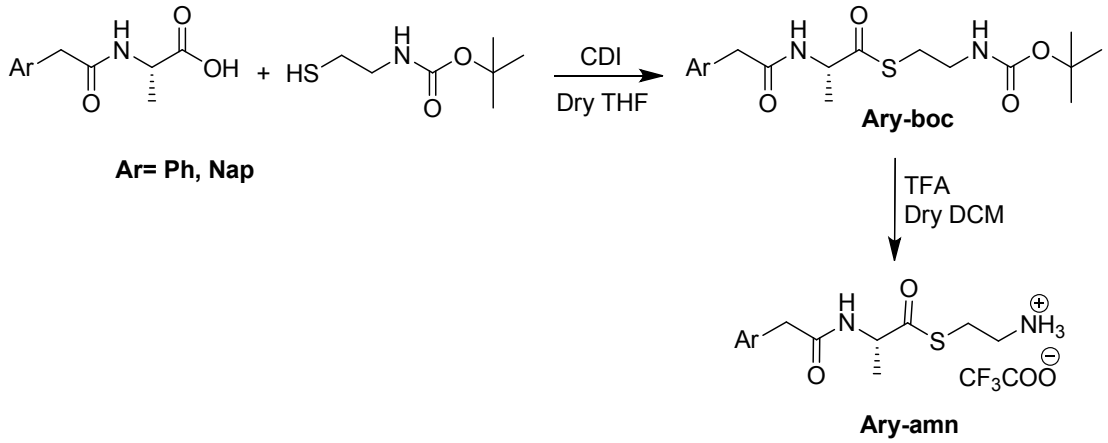
Supporting information

Materials and methods

1-Naphthylacetic acid (1-NAA) and phenylacetic acid were purchased from Spectrochem, 1,1-Carbonyldiimidazole (CDI) was purchased from Alfa Aesar, 2-(boc-amino)ethanethiol was obtained from Sigma, sodium hydrogen diphosphate, sodium dihydrogen phosphate and triethylamine were obtained from Merck. All solvents used in the synthesis were purified, dried, or distilled, as required. ^{1}H NMR spectra were recorded by using Bruker AVANCE III Ultra shield (400 MHz) spectrometer. Mass spectra were recorded in ESI-MS mode on MicroTOF-Q-II instrument manufactured by Bruker Daltonics. UV-vis absorption spectra were recorded on PerkinElmer Lambda 25. Fluorescence spectra were recorded on a Horiba Jobin Yvon Fluorolog 3-111 instrument. Powedered X-ray diffraction was recorded on Rigaku SmartLab, Automated Multipurpose X-ray Diffractometer.

5.4.1. Synthesis and characterizations



Scheme S1. Synthetic protocol for preparing **Ary-amn** compounds

General procedure for the synthesis of alanine thioesters (Ary-boc)

Arylacetic acid and (1 eq., 3.87 mmol) and CDI (1.1 eq., 4.26 mmol) were dissolved in dry THF and stirred for 10 min. THF solution of 2-(boc-amino)ethanethiol (1.1 eq., 4.26 mmol) was added to the activated acid at 0 °C. The reaction mixture was stirred for 1 h at RT and

monitored by TLC (eluent phase was 4:6 v/v hexane:ethyl acetate). THF was removed and the reaction mixture was directly loaded into the column (stationary phase was silica 100-200 mesh and eluent phase was hexane/ethyl acetate) for purification.

(S)-S-(2-((tert-butoxycarbonyl) amino) ethyl) 2-(2-phenylacetamido) propanethiolate (Ph-boc) :

White solid (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)= 7.35-7.25 (5H, Ph-H), 6.07-6.06 (1H, NH), 4.82 (1H, N-H), 4.69-4.62 (1H, C-H), 3.58 (2H, Ph-CH_2), 3.22 (2H, CH_2-N) 2.96-2.93 (2H, CH_2-S) 1.41 (9H, $C(CH_3)_3$), 1.30-1.28 (3H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm)= 200.66, 170.68, 155.75, 134.28, 129.47, 129.03, 127.49, 79.54, 55.17, 43.51, 40.00, 28.99, 28.38, 18.54. Calculated mass. $C_{18}H_{26}N_2O_4S$+H: 367.1686. Found: 367.1706

(S)-S-(2-((tert-butoxycarbonyl) amino) ethyl) 2-(2-(naphthalen-1-yl) acetamido) propanethiolate (Nap-boc) :

White solid (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)= 7.95-7.42 (7H, Nap-H), 5.72-5.70 (1H, NH), 4.68 (1H, N-H), 4.66-4.61 (1H, C-H), 4.06 (2H, Nap-CH_2), 3.17 (2H, CH_2-N) 2.92-2.87 (2H, CH_2-S) 1.42(9H, $C(CH_3)_3$), 1.18-1.16 (3H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm)= 200.44, 170.62, 155.69, 134.00, 132.05, 130.50, 128.83, 128.72, 128.43, 126.79, 126.28, 125.67, 123.92, 79.60, 55.12, 41.60, 39.93, 29.00, 28.38, 18.37. Calculated mass $C_{22}H_{28}N_20_4S$+Na: 439.1662. Found: 439.1682

General procedure for the synthesis of alanine thioester ammonium salts (Ary-amn) :

Trifluoroacetic acid (TFA) was added drop wise to dichloromethane (DCM) solution of **Ph-boc** or **Nap-boc** at 0 °C. Reaction mixture was stirred for 3 h at RT. The formation of alanine thioester ammonium salts was monitored by TLC (eluent phase was 4:6 v/v hexane: ethyl acetate). After completion of reaction, DCM and trifluoroacetic acid were removed *in vacuo*.

(S)-2-((2-(2-phenylacetamido)propanoyl)thio)ethanaminium (Ph-amn) :

Yellow gum (95%). ^{1}H NMR (400 MHz, D_2O) δ(ppm) = 7.33-7.23 (5H, Ph-H), 4.45-4.40 (1H, C-H), 3.62-3.53 (2H, Ph-CH_2), 3.06-2.01 (2H, CH_2-N), 3.06-3.01 (2H, CH_2-S), 1.32-1.30 (3H, CH_3) Calculated mass $C_{13}H_{19}N_2O_2S$. 267.1162. Found: 267.1178 by ESI-MS.

(S)-2-((2-(2-(naphthalen-1-yl)acetamido)propanoyl)thio)ethanaminium (Nap-amn) :

Yellow gum (93%). ^{1}H NMR (400 MHz, D_2O) δ(ppm)= 7.98-7.45 (7H, Nap-H), 4.50-4.45(1H, C-H), 4.16-4.07 (2H, Nap-CH_2), 3.06-3.00 (2H, CH_2-N), 3.06-3.00 (2H, CH_2-S), 1.35-1.33 (3H, CH_3). Calculated mass $C_{17}H_{21}N_20_2S$: 317.1318. Found: 317.1315 by ESI-MS.

(S)-2-(2-(2-phenylacetamido)propanamido)ethanethiolate (Ph-S) :

^{1}H NMR (400 MHz, 1 M phosphate buffer in D_2O, pD = 8) δ (ppm)= 7.31-7.20 (5H, ph-H), 4.14-4.09 (1H, C-H), 3.53 (2H, Ph-CH_2), 3.12-3.08 (2H, CH_2-N) 2.39-2.35 (2H, CH_2-S), 1.25-1.23 (3H, CH_3).

(S)-2-(2-(2-(naphthalen-1-yl)acetamido)propanamido)ethanethiolate (Nap-S) :

^{1}H NMR (400 MHz, 0.1 M NaOD,) δ (ppm)= 7.93-7.41 (7H, Nap-H), 4.21-4.16 (1H, C-H), 4.07 (2H, Nap-CH_2), 3.11-3.07 (2H, CH_2-N) 2.37-2.33 (2H, CH_2-S), 1.28-1.26 (3H, CH_3).

DTNB (5,5(-Dithiobis-(2-nitrobenzoic acid)) assay for thiolate detection

Stock solution of DTNB reagent (0.002 M in 0.05 M sodium acetate) was prepared. 0.5 mL of DTNB reagent from stock solution was diluted with 1.5 mL of water and 0.5 mL of 1 M carbonate buffer (pH=9). This solution was used as a working reagent. 8 mg of **Ph-amn** was dissolved in 1 mL of water and basified by 1 mL of 1 M carbonate buffer (pH=9). 10 µL aliquots of basic **Ph-amn** solution were added to 3 mL of DTNB working reagent at different time points and the absorbance at 412 nm was recorded. At 635 min past pH-increase, 3.5 µL of 3% H_2O_2 was added to the residual basic **Ph-amn** solution, and again 10 µL aliquots were

removed and added to working reagent at different time points. The absorbance values of the resulting solutions were recorded at 412 nm.

Turbidity measurements

To the acidic solution of **Ph-amn** (8 mg/mL), 1 M carbonate buffer (pH=9) of 1 mL was added. This time point was treated as time t=0. The absorbance at 600 nm was recorded for this mixture over a period of time. 3.5 µL of 3% H_2O_2 was added to the basic **Ph-amn** solution at 635 min, and absorbance at 600 nm was recorded at different time intervals upto 730 min since the increase of solution pH.

Intra and inter molecular S-to-N acyl transfer by NMR

Sample I: 200 µL of 1 M phosphate buffer made in D_2O, pD=8.0 was added to 200 µL of deuterated aqueous solution of **Ph-amn** (containing 5 mg compound) followed by addition of 1-hexylamine (2 mg in 100 µL D_2O).

Sample II: Solutions of **Ph-amn** (5 mg dissolved in 300 µL D_2O) and 1-hexylamine (2 mg in 100 µL D_2O) were pre-mixed before 200 µL of 1 M phosphate buffer made in D_2O, pD=8.0 was added to this mixture.

For both the samples, ^1H NMR spectra were recorded immediately after addition of phosphate buffer as well as at 4 h after the addition.

Detection of acrylates using Ph-S

In five different vials, 500 µL of 1 M carbonate buffer (pH=9) was added to a 450 µL aqueous solution of **Ph-amn** (17 mg, 0.064 M final concentration) and stirred for 15 min. Separately, 1 M solutions of different analytes *viz*. acrylamide, acrylonitrile, methyl acrylate, ethyl acrylate and methyl methacrylate were prepared in de-aerated water obtained by N_2 purging for 30 min. 50 µL of analyte solution was added to basic **Ph-amn** solution present in different vials and stirred. Under these conditions, the analyte and **Ph-amn** were equimolar. In control vial, only 50 µL of water was added. For these samples turbidity was measured by

UV-vis spectroscopy at 600 nm. Before the measurement precipitate was well dispersed by mechanical agitation using a pipette.

Kinetic experiment for detection of acrylamide by Ph-S

500 µL of 1 M carbonate buffer (pH=9) was added to a 450 µL aqueous solution of **Ph-amn** (17 mg, 0.064 M) and stirred for 15 min. 50 µL of 14 mM acrylamide solution was added to basic **Ph-amn** solution and stirred. For this mixture, we recorded the absorbance at 600 nm at every 30 min interval upto 240 min past the addition of acrylamide solution.

Fluorescence experiment for detection of acrylamide by Nap-S

1 mM solution of **Nap-amn** was prepared in 1:1 v/v of acetonitrile and water mixture. A 1 mL aliquot of this solution followed by 10 µL of triethylamine was poured in each of the six separate vials. After 30 min, 40 µL of acrylamide solution (0.28, 0.14, 0.070 or 0.035 mM) was added to each vial and stirred for 1 h. Fluorescence spectra for these samples were recorded between 295-500 nm while exciting the samples at 285 nm (keeping the excitation and emission slit width = 3 mm each).

For kinetic experiments, 0.225 mM acrylamide solution was used and fluorescence intensity at 339 nm was monitored every 10 min from 0 to 240 min.

Powder X-ray diffraction (PXRD) of Nap-S+AM adduct

Nap-amn (30 mg/mL) was dissolved in 1.5 mL of water and acetonitrile mixture (1:1 v/v). 20 µL of triethylamine was added to acidic solution of **Nap-amn** and stirred. After 30 min, 6.7 mg of **AM** was added to this solution and stirred for 1 h. The precipitate formed in the vial was separated from the supernatant, carefully washed with water (2 x 2 mL) and lyophilized for 24 h. The dried sample was placed on a sample holder and diffraction data was collected in a 2θ range of 5–100˚.

Scanning Electron Microscopy:

For SEM, precipitates obtained upon addition of different acrylates (0.064 M) to **Ph-S** (0.064 M) were separated out and dried inside vacuum desicator for 24 h. The dried samples were spread on carbon tape and gold coated for 120 s. The images were taken on Carl Zeiss (Ultraplus) FE-SEM used at 5 kV accelerating voltage.

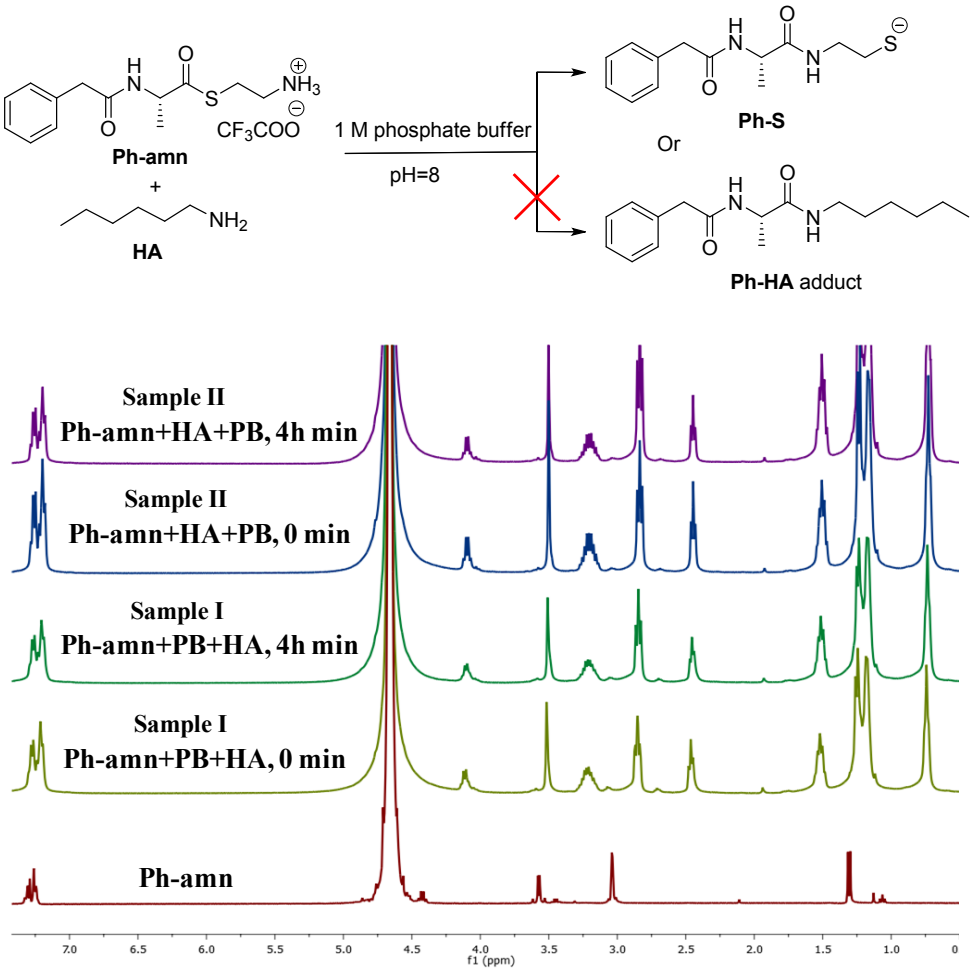


Figure S1. ^{1}H NMR experiment to investigate influence of externally added HA on showing similar spectra for both samples. **HA**: hexylamine, PB: 1M phosphate buffer of pD=8.

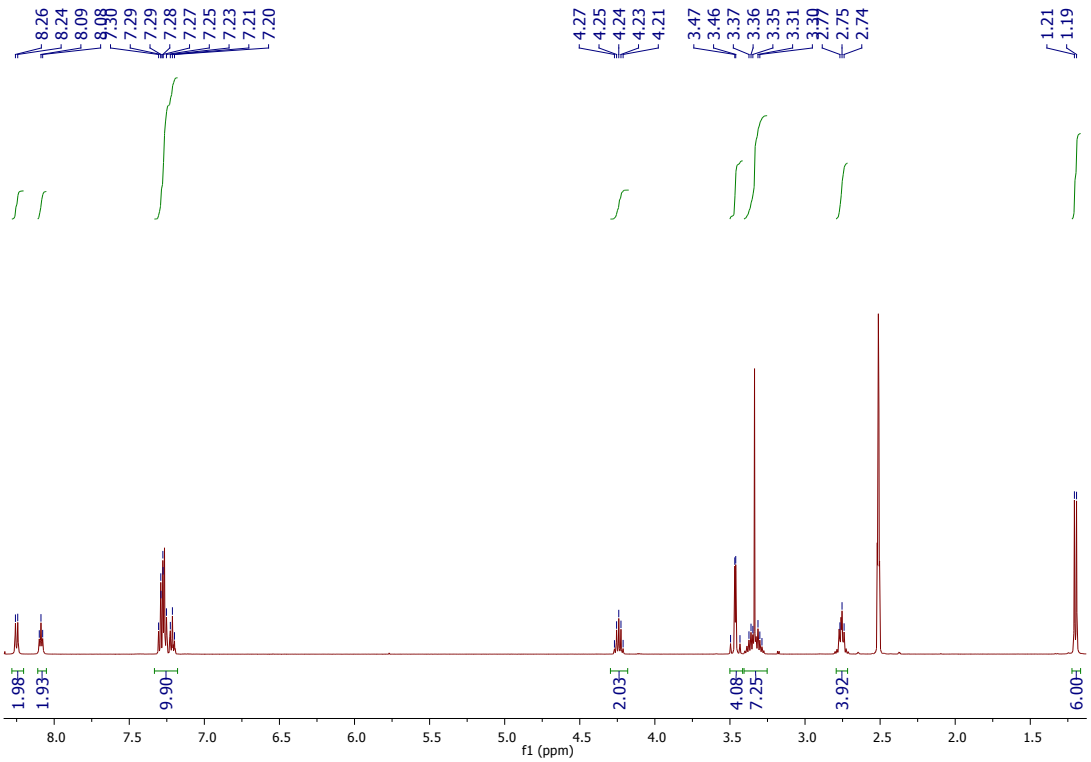


Figure S2. ^{1}H NMR (400 MHz) spectrum in d^{6}-DMSO of **Ph-SS-Ph** formed by oxidation of **Ph-S** by H_2O_2.

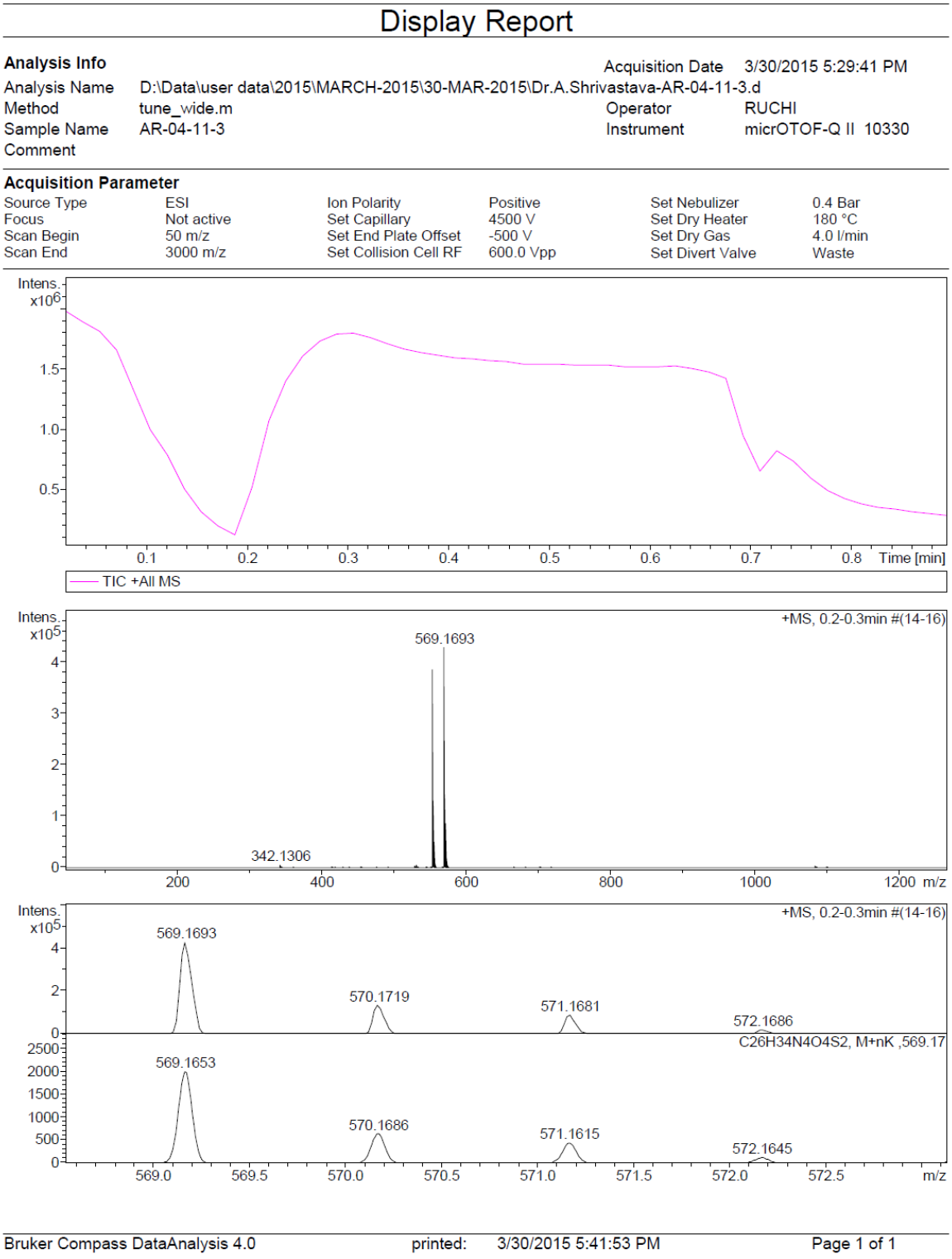


Figure S3. High resolution ESI-MS spectrum of **Ph-SS-Ph.** Calculated mass for $C_{26}H_{34}N_40_4S_2$+K: 569.1653, found: 569.1693

(a)

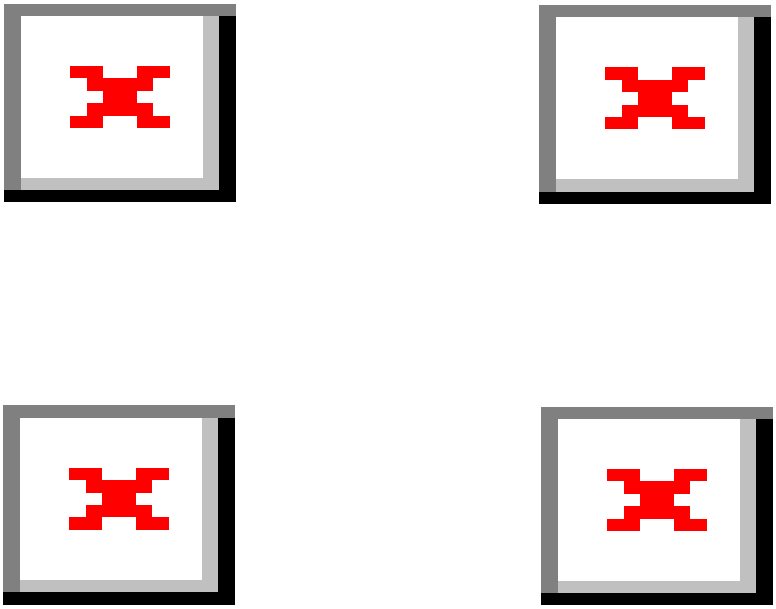


Figure S4. SEM images of precipitated Michael adducts formed by reaction of **Ph-S** with (a) **AN**; (b) **MA**; (c) **EA**, and (d) **MM**.

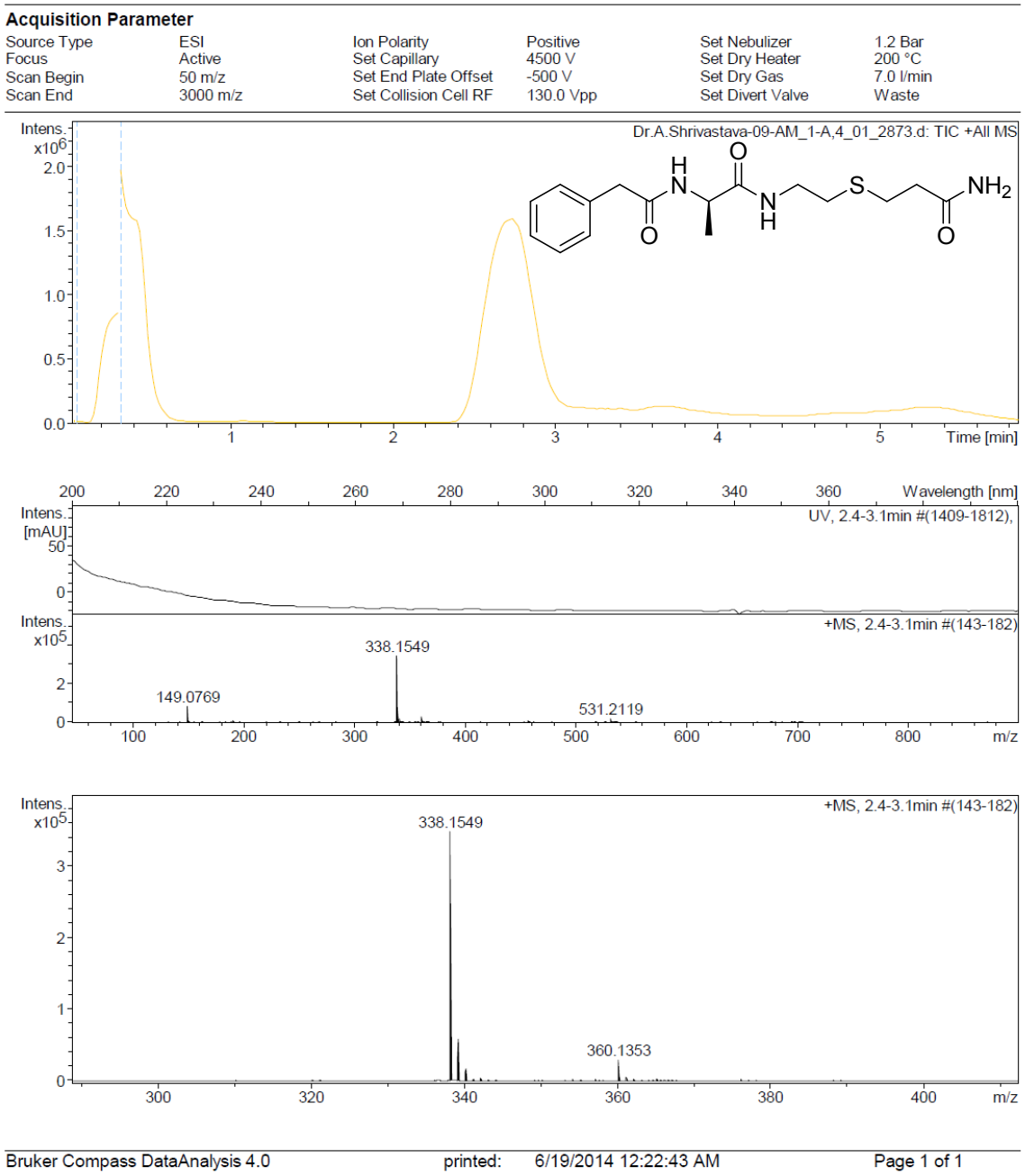


Figure S5. High resolution ESI-MS spectrum of **Ph-S+AM** Michael adduct**.** Calculated mass for $C_{16}H_{23}N_30_3S$+H: 338.1538, found: 338.1549

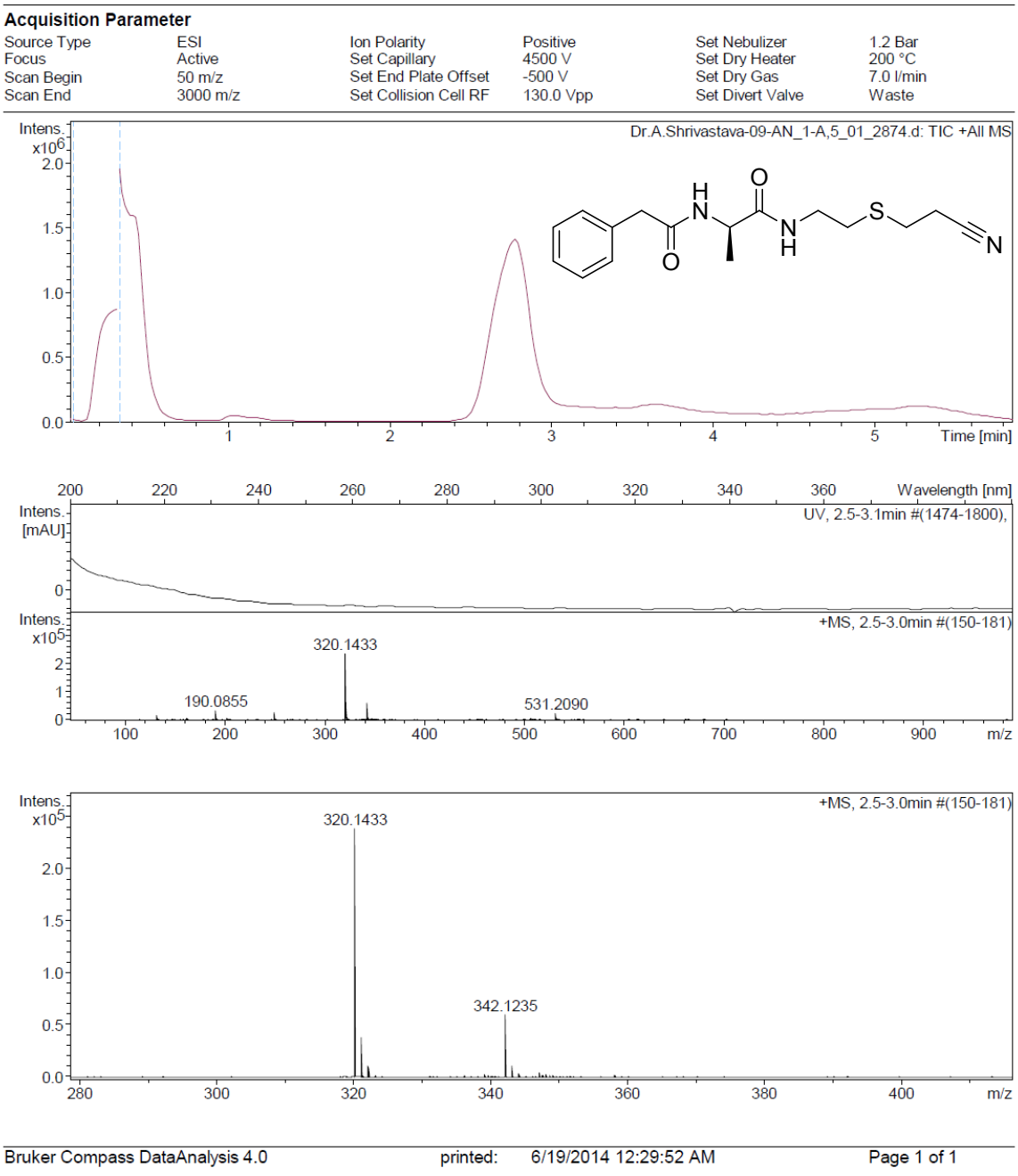


Figure S6. High resolution ESI-MS spectrum of **Ph-S+AN** adduct**.** Calculated mass for $C_{16}H_{21}N_30_2S$+H: 320.1433, found: 320.1433

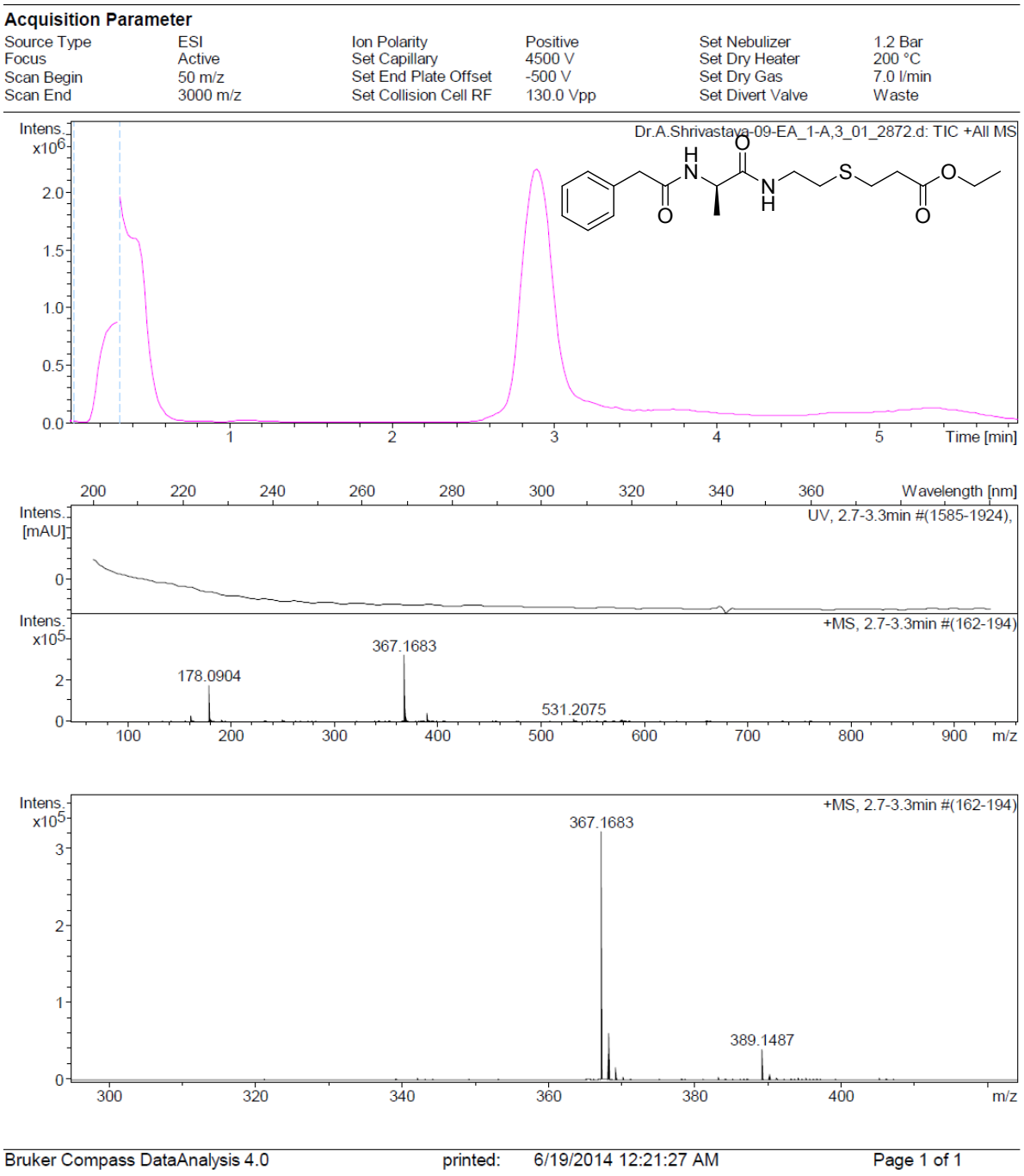


Figure S7. High resolution ESI-MS spectrum of **Ph-S+EA** adduct**.** Calculated mass for $C_{18}H_{26}N_20_4S$+H: 367.1692, found: 367.1683

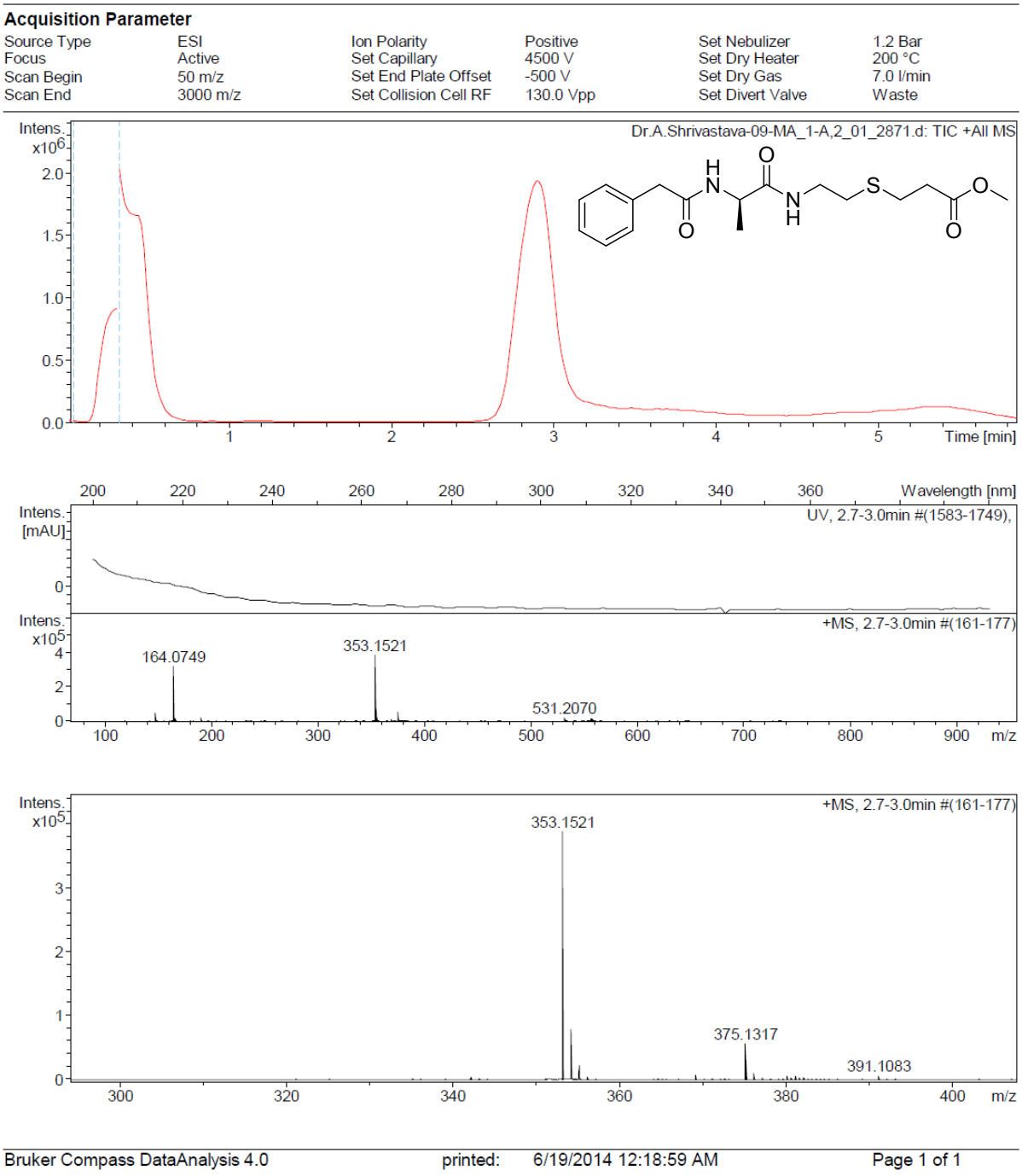


Figure S8. High resolution ESI-MS spectrum of **Ph-S+MA** adduct**.** Calculated mass for $C_{17}H_{24}N_20_4S+H$: 353.1535, found: 353.1521

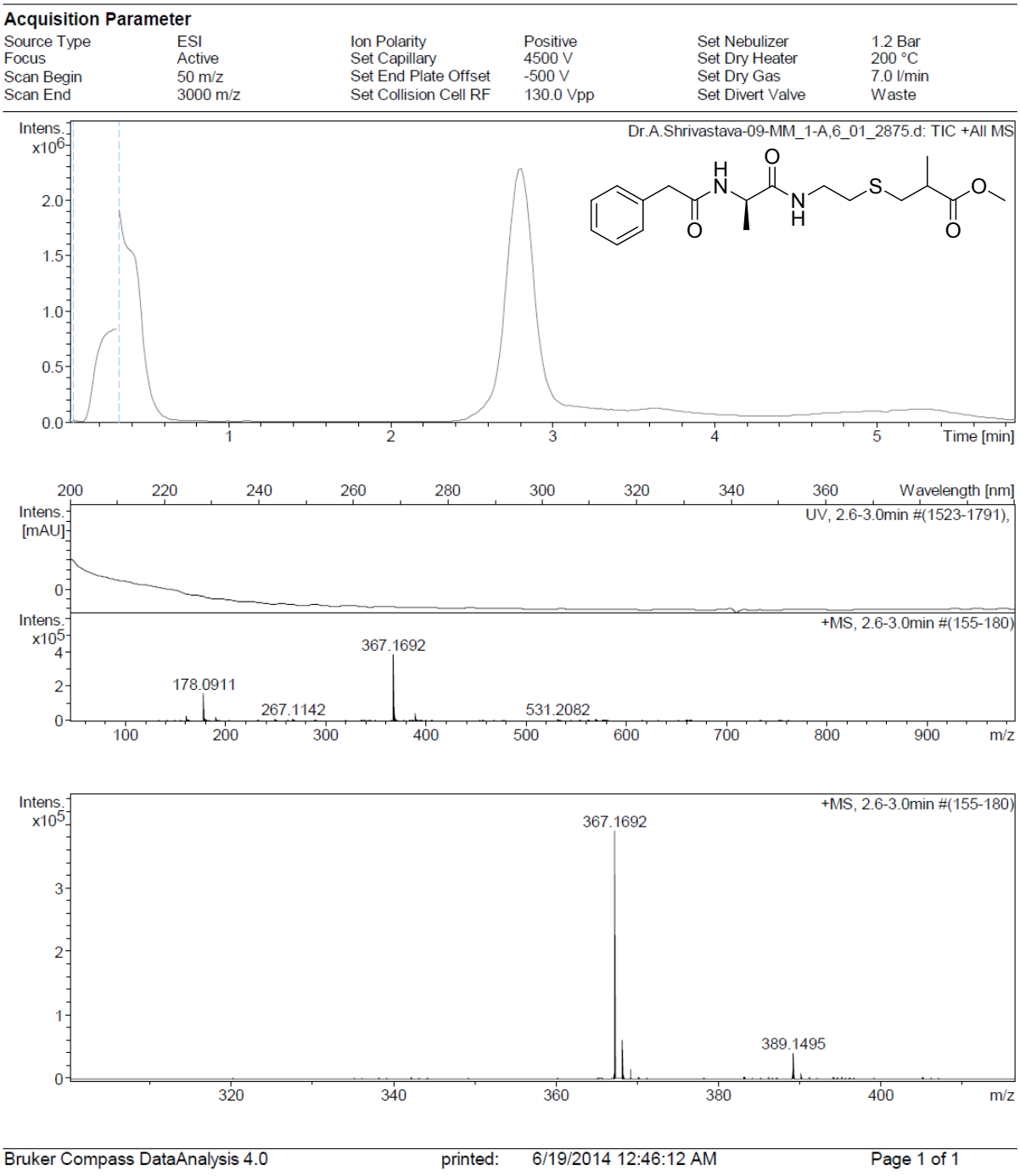


Figure S9. High resolution ESI-MS spectrum of **Ph-S+MM** adduct**.** Calculated mass for $C_{18}H_{26}N_20_4S$+H: 367.1692, found: 367.1

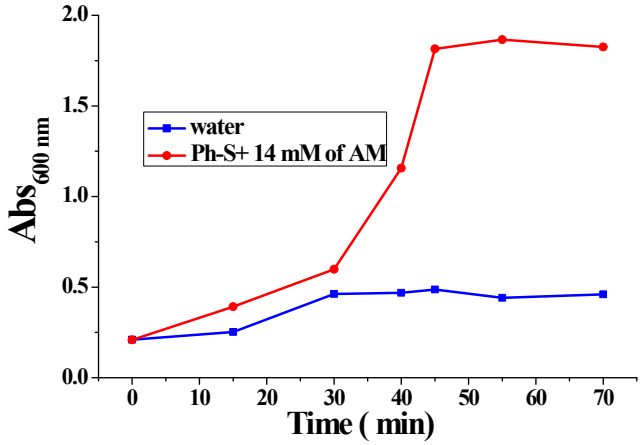
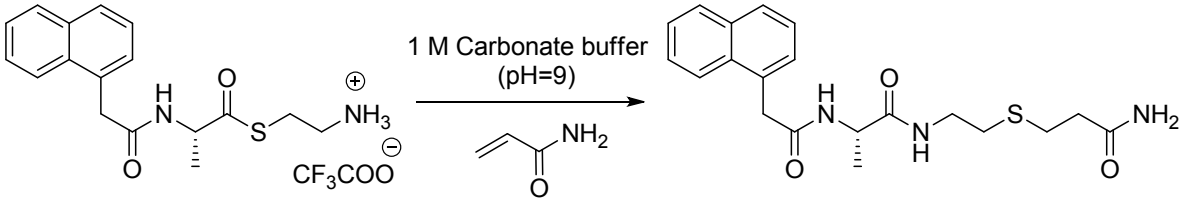


Figure S10. Turbidity increasing with time for 14 mM **AM** containing **Ph-S** (64 mM) sample. Turbidity value saturated in about 45 min after the addition of **AM**.



Scheme S2. Reaction between Michael acceptor (**AM)** and Michael donor (**Nap-S).**

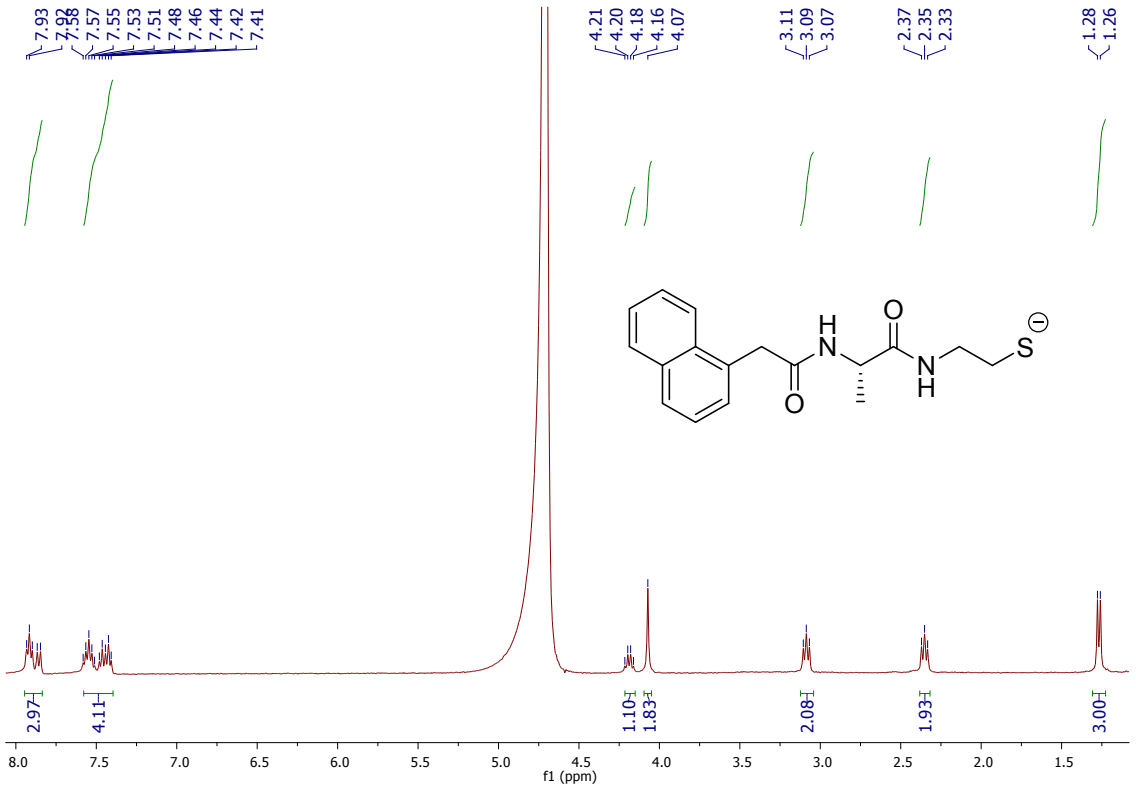


Figure S11. ^{1}H NMR (400 MHz) spectrum of **Nap-S** in 0.1 M NaOD.

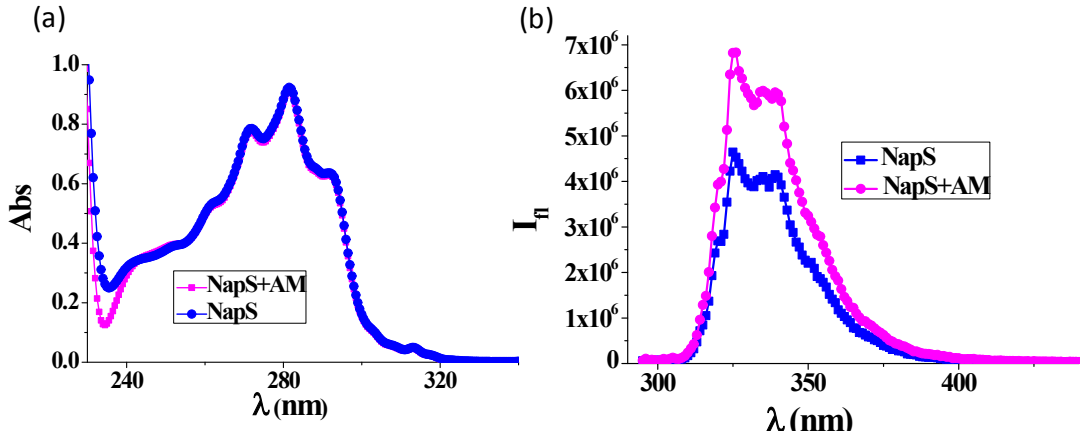


Figure S12. (a) UV-vis spectra for **Nap-S** (blue symbols) and **Nap-S+AM** (pink symbols). (b) The corresponding fluorescence spectra for these samples. **Nap-S** and **Nap-S+AM** were present at same concentration (0.2 mM) in these samples.

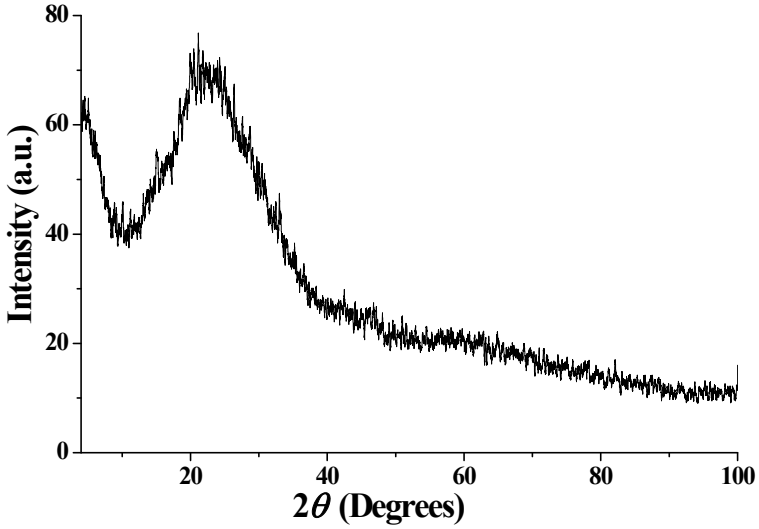
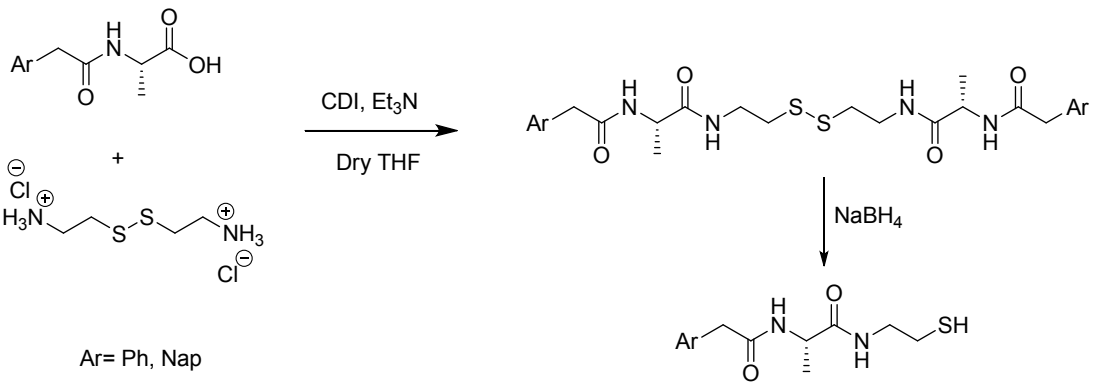


Figure S13. Powder X-ray diffraction pattern for the adduct **Nap-S+AM**.



Scheme S3. Protocol for the synthesis of Aryl thiol compounds.

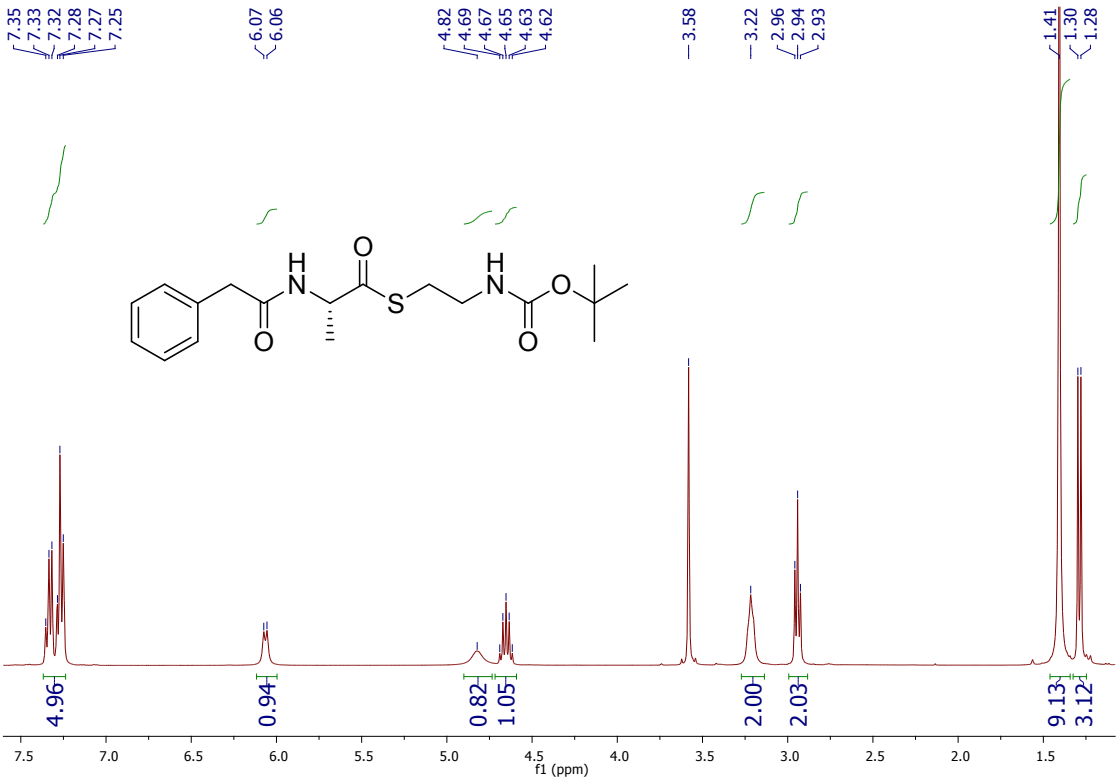


Figure S14. ^{1}H NMR (400 MHz) spectrum of **Ph-boc** in $CDCl_3$.

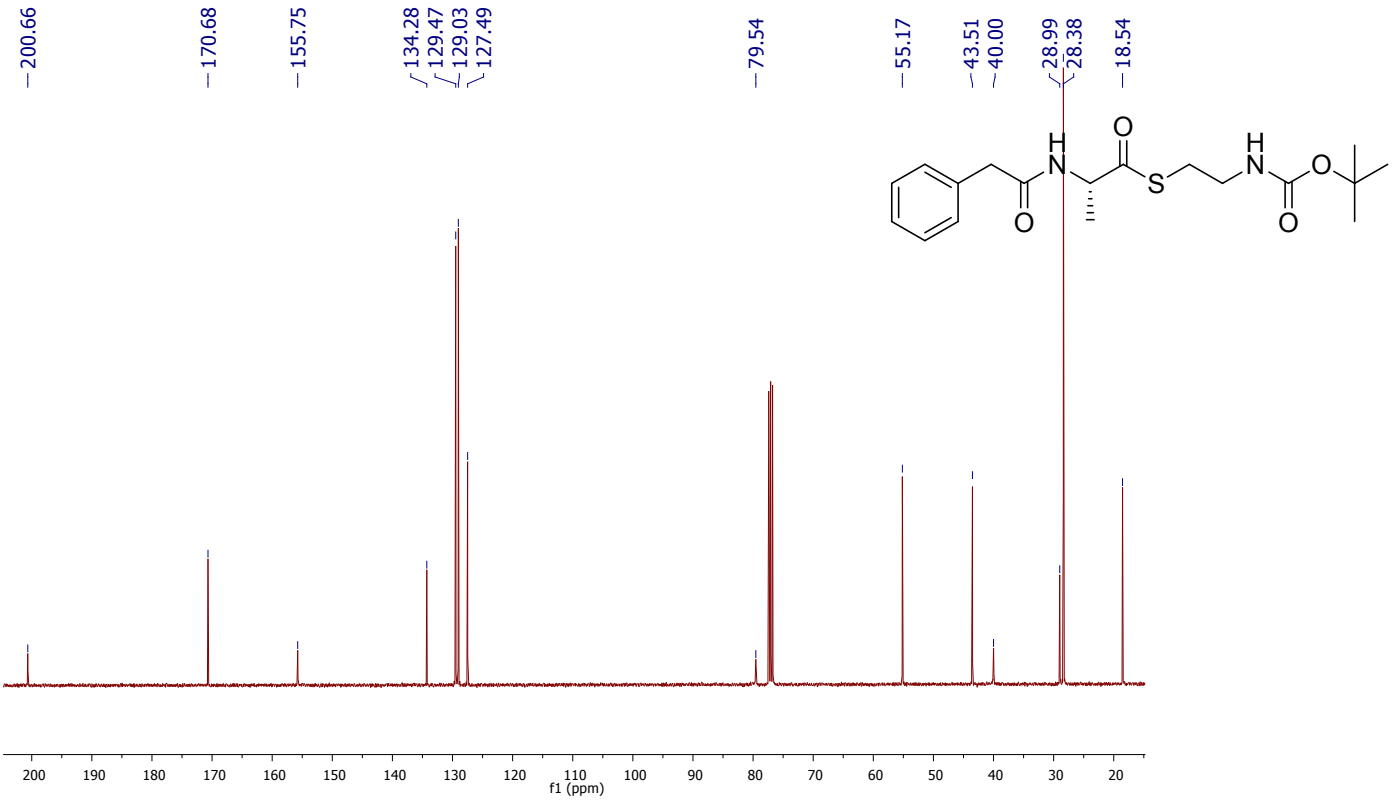


Figure S15. Broadband decoupled ^{13}C NMR (100 MHz) spectrum of **Ph-boc** in $CDCl_3$.

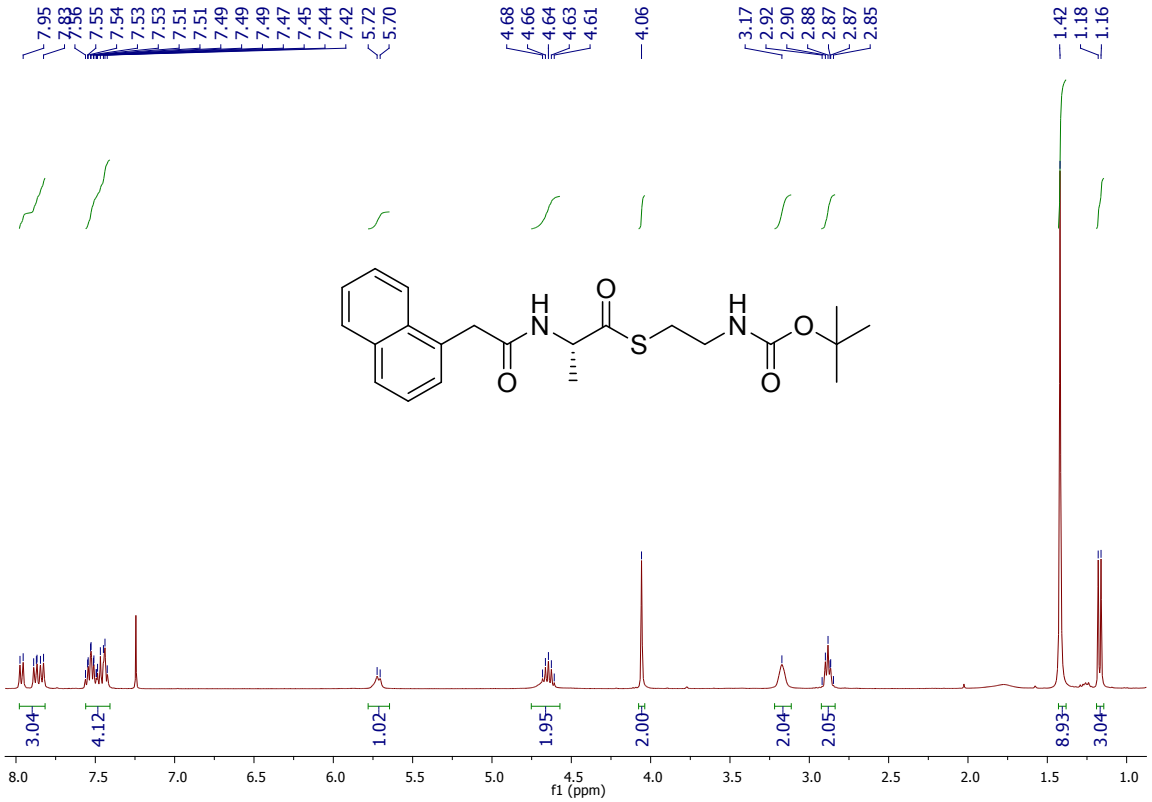


Figure S16. ^{1}H NMR (400 MHz) spectrum of **Nap-boc** in $CDCl_3$.

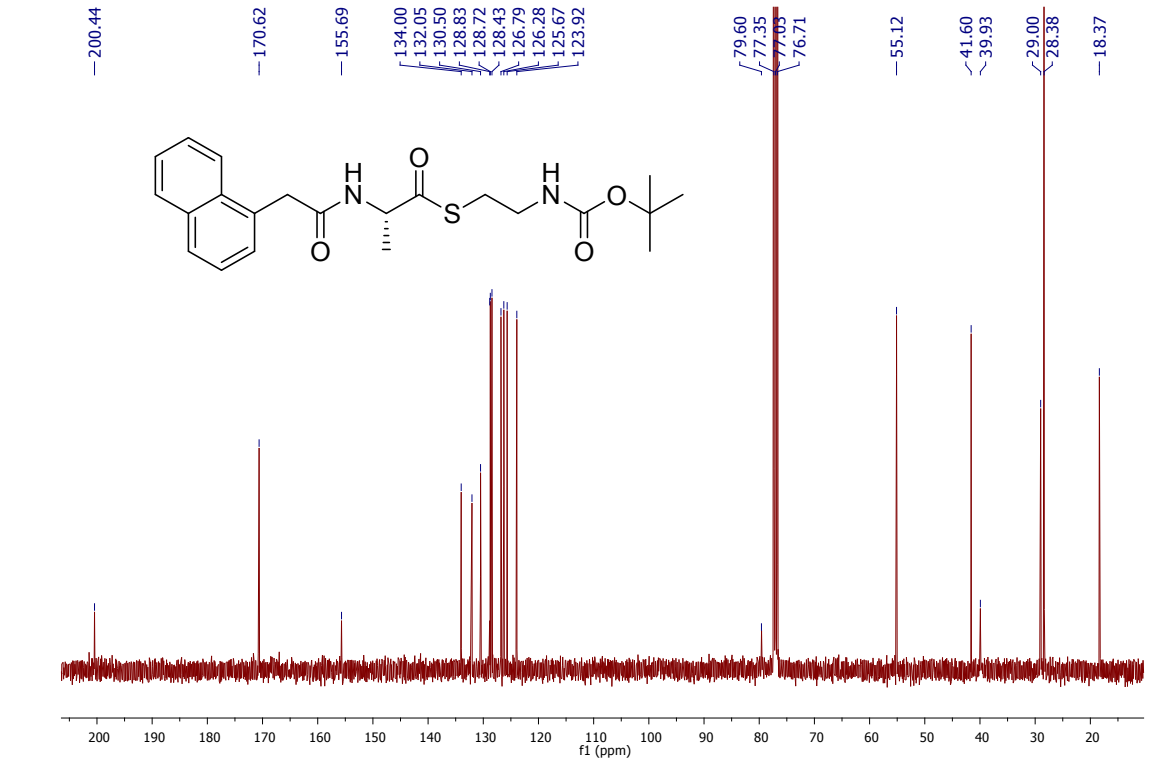


Figure S17. Broadband decoupled ^{13}C NMR (100 MHz) spectrum of **Nap-boc** in $CDCl_3$.

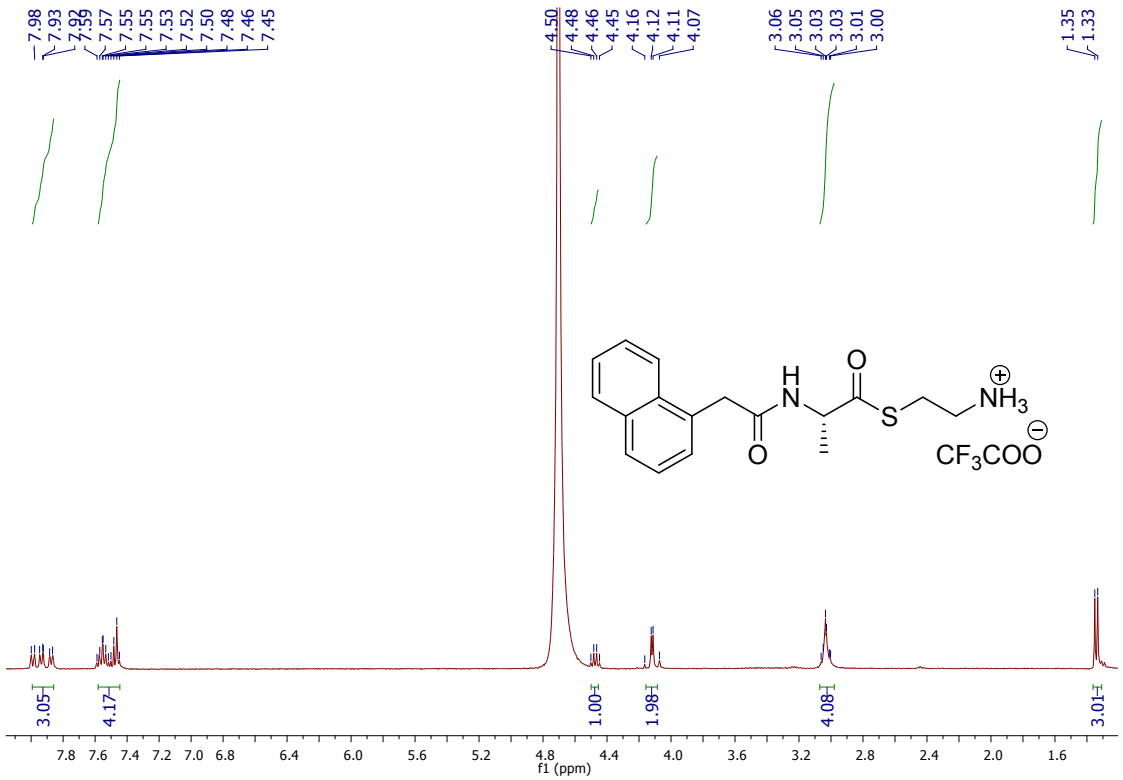


Figure S18. ^{1}H NMR (400 MHz) spectrum of **Nap-amn** in D_2O.

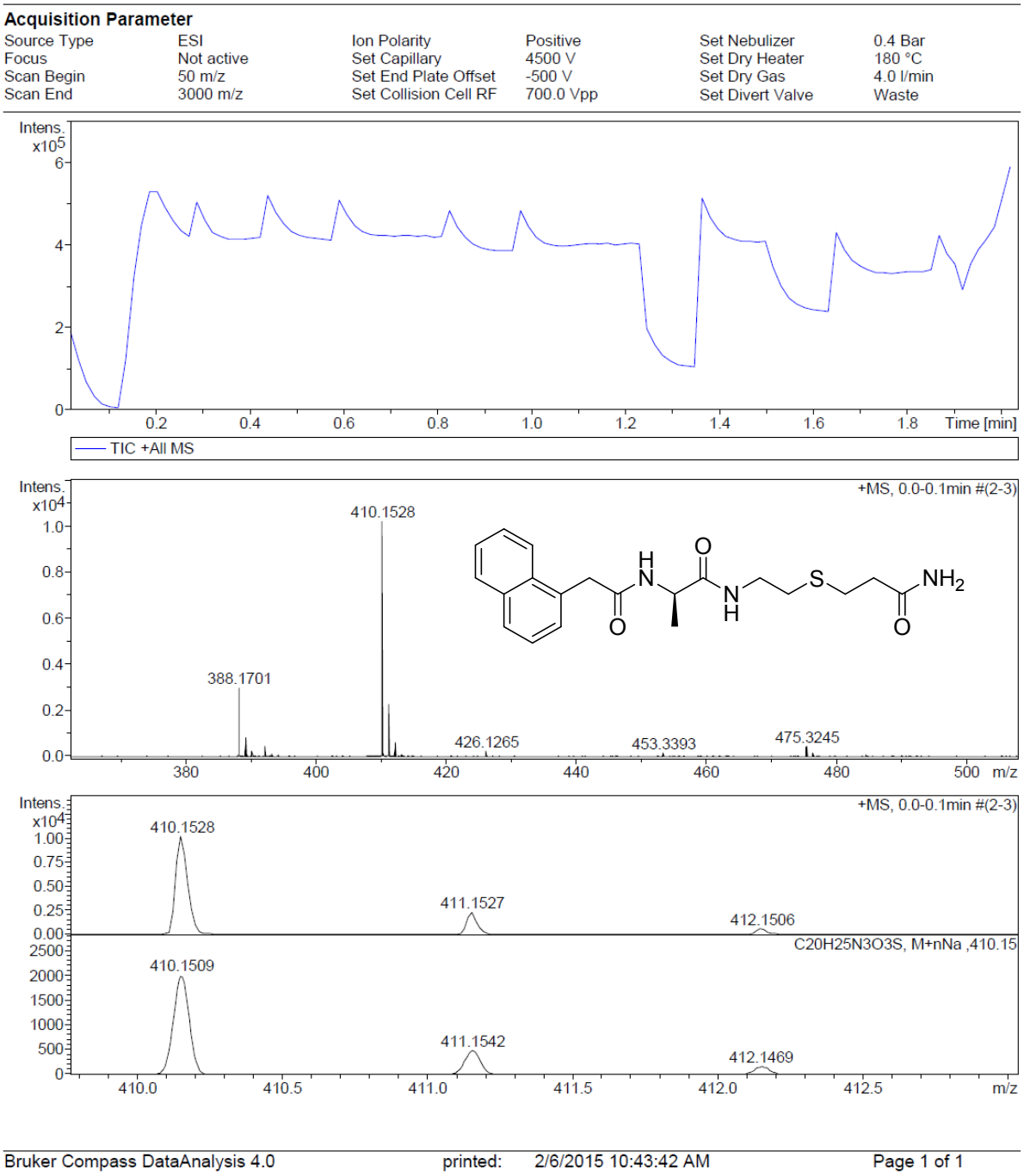


Figure S19. High resolution ESI-MS spectrum of **Nap-S+AM** adduct**.** Calculated mass for $C_{20}H_{25}N_30_30_3S$+Na: 410.1528, found: 410.1509