Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

Highly Enantioselective Zinc-Binol-Catalyzed Alkynylation of *N*-Sulfonyl Aldimines

Dr. G. Blay, Dr. L. Cardona, Mrs. E. Climent, Prof. Dr. J. R. Pedro
Departament de Química Orgànica, Facultat de Química, Universitat de València, Dr. Moliner 59, E-46100 Burjassot (València), Spain
Fax: (+34)963544328
E-mail: jose.r.pedro@uv.es

General Procedures. Enantioselective addition reactions were carried out under nitrogen in round bottom flasks oven-dried overnight at 120 °C. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm.

Materials. Dimethylzinc, 2 M solution in toluene, and alkynes were purchased from Aldrich and used without further purification. Toluene was distilled from CaH_2 and stored on 4 Å molecular sieves. *N*-sulfonyl aldimines were prepared from the corresponding aldehyde and the sulfonamide following a general protocol.[1]

Instrumentation. ^{1}H NMR were run at 300 MHz for ^{1}H and at 50 MHz for ^{13}C NMR in a Bruker Avance 300 spectrometer in the deuterated solvents as stated, using residual non-deuterated solvent as internal standard. Chemical shifts (δ) are reported in ppm. The carbon type was determined by DEPT experiments. Specific optical rotations were measured in a Perkin-Elmer polarimeter using sodium light (D line 589 nm). Mass spectra were recorded on a Fisons Instruments VG Autospec GC 8000 series at 70 eV ionizing voltage (EI). Chiral HPLC analyses were performed in a Hitachi Elite Lachrom instrument equipped with a Hitachi UV diode-array L-4500 detector using chiral stationary columns from Daicel. Retention times are given in min.

General experimental procedure for the enantioselective alkynylation:

a) Concentrated conditions (Tables 3 and 4)

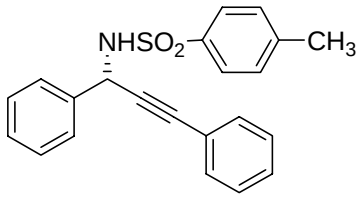
A 2 M solution of Me_2Zn in toluene (0.375 mL, 0.75 mmol) was added dropwise to pure alkyne **1** (0.9 mmol) at room temperature under argon. After stirring for 1 h, a solution of ligand **L6** (17.7 mg, 0.025 mmol) in toluene (0.1 mL) was added via syringe. After 15 min, a solution of imine **2** (0.125 mmol) in toluene (0.225 mL) was added via syringe and the solution was stirred until the reaction was complete (TLC). The reaction mixture was quenched with 1 M aqueous HCl (15 mL), extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded compound **3**.

b) Diluted conditions (Tables 1 and 2, and racemics)

A 2 M solution of Me_2Zn in toluene (0.375 mL, 0.75 mmol) was added dropwise to a solution of alkyne **1** (0.9 mmol) in toluene (0.25 mL) at room temperature under argon. After stirring for 1h, a solution of the ligand **L** (0.025 mmol) in toluene (0.5 mL) was added via syringe. After 15 min, a solution of imine **2** (0.125 mmol) in toluene (0.25 mL) was added via syringe and the solution was stirred until the reaction was complete (TLC). Work up as described above gave compound **3**.

This procedure was also used for the preparation of racemic **3**, with ligand (±)**L1**.

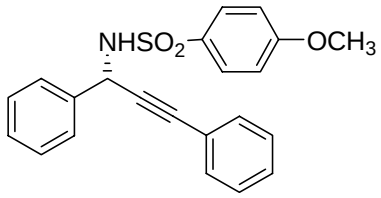
(*S*)-1,3-Diphenyl-*N*-tosylprop-2-yn-1-amine (3aa).[2]



Prepared starting from phenylacetylene (**1a**, 97 μL, 0.9 mmol) and imine **2a (**32.3 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3aa**. Yield 38.5 mg (0.107 mmol, 85 %); mp 214-215 °C; enantiomeric excess (98%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 80:20, 0.3 mL/min, major enantiomer t_r = 23.4 min, minor enantiomer t_r = 27.5 min;

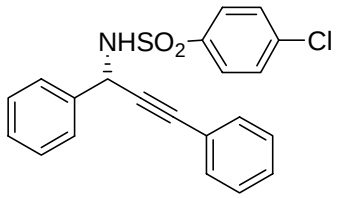
$[\alpha]_D^{25}$ –90.7 (*c* 1.0, $CHCl_3$, ee 98%); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 4.82 (d, *J* = 9.0 Hz, 1H), 5.50 (d, *J* = 9.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.15-7.29 (m, 8H), 7.49 (d, *J* = 8.0, 1.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 49.8 (CH), 85.4 (C), 86.7 (C), 121.9 (C), 127.3 (CH), 127.5 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.6 (CH), 131.6 (CH), 137.32 (C), 137.34 (C), 143.6 (C); ^{1}H NMR (DMSO) δ 2.31 (s, 3H), 5.48 (d, *J* = 9.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.28-7.42 (m, 8H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 8.70 (d, J = 9.0 Hz, 1H); ^{13}C NMR (DMSO) δ 20.9 (CH_3), 48.6 (CH), 85.0 (C), 86.9 (C), 121.5 (C), 126.9 (CH), 127.1 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 129.3 (CH), 131.1 (CH), 138.1 (C), 138.3 (C), 142.6 (C); MS (EI) 361 (M^+, 0.3), 222 (20), 206 (100), 191 (24) 105 (2), 91 (3); HRMS 361.114372, $C_{22}H_{19}NO_2S$ requires 361.11365.

(*S*)-*N*- (4-Methoxyphenylsulfonyl)-1,3-diphenylprop-2-yn-1-amine (3ab).



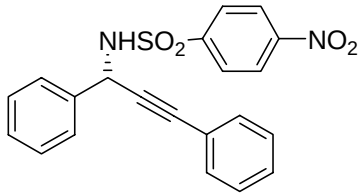
Prepared starting from phenylacetylene (**1a**, 97 μL, 0.9 mmol) and imine **2b (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ab**. Yield 40.5 mg (0.107 mmol, 86 %); mp 185-186 °C; enantiomeric excess (90%) was determined by HPLC (Chiralpack AD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 22.1 min, minor enantiomer t_r = 26.8 min; $[\alpha]_D^{25}$ –78.5 (*c* 0.4, $CHCl_3$, ee 90%); ^{1}H NMR (DMSO) δ 3.75 (s, 3H), 5.45 (d, *J* = 9.6 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 7.11 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.31-7.41 (m, 6H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 8.62 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (DMSO) δ 49.0 (CH), 55.9 (CH_3), 85.4 (C), 87.4 (C), 114.4 (CH), 122.0 (C), 127.5 (CH), 128.3 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 129.4 (CH), 131.6 (CH), 133.0 (C), 138.8 (C), 162.6 (C); MS (EI) 377 (M^+, 0.1), 206 (100), 191 (42), 155 (18), 77 (19); HRMS 377.108772, $C_{22}H_{19}NO_3S$ requires 377.10856

(*S*)-*N*- (4-Chlorophenylsulfonyl)-1,3-diphenylprop-2-yn-1-amine (3ac).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2c (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ac**. Yield 38.9 mg (0.102 mmol, 82%); mp 148-149 °C, enantiomeric excess (89%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 11.3 min, minor enantiomer t_r = 13.6 min; $[\alpha]_D^{25}$ –62.7 (*c* 1.2, $CHCl_3$, ee 89%); ^{1}H NMR ($CDCl_3$) δ 5.04 (d, *J* = 9.0 Hz, 1H), 5.51 (d, *J* = 9.0 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.17-7.33 (m, 8H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 49.9 (CH), 85.1 (C), 87.1 (C), 121.6 (C), 127.3 (CH), 128.3 (CH), 128.6 (CH), 128.8 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 131.5 (CH), 137.0 (C), 138.9 (C), 139.3 (C); MS (EI) 380 (M^+ – 1, 0.2), 222 (17), 206 (100), 191 (42), 189 (13), 178 (20); HRMS 380.0511, $C_{21}H_{15}ClNO_2S$ requires 380.0590;

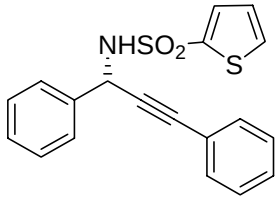
(*S*)-*N*- (4-Nitrophenylsulfonyl)-1,3-diphenylprop-2-yn-1-amine (3ad).[2]



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2c (**36.3 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 80:20 to 70:30) afforded **3ad**. Yield 38.2 mg (0.097 mmol, 78%); mp 158-159 °C; enantiomeric excess (87%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 80:20, 0.5 mL/min, major enantiomer t_r = 25.0 min, minor enantiomer t_r = 30.7 min; $[\alpha]_D^{25}$ –64.6 (*c* 0.7, $CHCl_3$, ee 87%); ^{1}H NMR ($CDCl_3$) δ 5.20 (d, *J* = 9.0 Hz, 1H), 5.65 (d, *J* = 9.0 Hz, 1H), 7.09 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.21-7.38 (m, 6H), 7.52-7.55 (m, 2H), 8.07 (d, *J* = 9.0 Hz, 2H), 8.20 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 50.1 (CH),

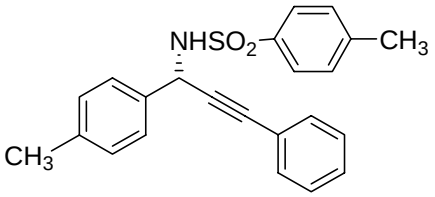
84.7 (C), 87.5 (C), 121.2 (C), 124.0 (CH), 127.4 (CH), 128.4 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 131.3 (CH), 136.5 (C), 146.1 (C), 149.8 (C); ^{1}H NMR (DMSO) δ 5.60 (d, *J* = 9.0 Hz, 1H), 7.08 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.25-7.40 (m, 6H), 7.51 (d, J = 8.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 9.18 (d, *J* = 9.0 Hz, 1H) ^{13}C NMR (DMSO) δ 48.9 (CH), 85.6 (C), 86.4 (C), 121.1 (C), 124.2 (CH), 127.2 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH),128.9 (CH), 131.0 (CH), 137.6 (C); MS (EI) 392 (M+, 0.1), 222 (19), 206 (100), 191 (49), 189 (16), 178 (28); HRMS 392.0832, $C_{21}H_{16}N_2O_4S$ requires 392.0831;

(*S*)-1,3-Diphenyl-*N*- (thien-2-ylsulfonyl)prop-2-yn-1-amine (3ae).



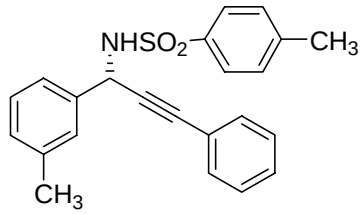
Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2e (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ae**. Yield 36.2 mg (0.102 mmol, 82%); mp 142-143 °C, enantiomeric excess (91%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 14.1 min, minor enantiomer t_r = 18.1min; $[\alpha]_D^{25}$ –57.5 (*c* 1.1, $CHCl_3$, ee 91%); ^{1}H NMR ($CDCl_3$) δ 5.11 (d, *J* = 9.0 Hz, 1H), 5.62 (d, *J* = 9.0 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.9 Hz, 1H), 7.24-7.40 (m, 8H), 7.54-7.58 (m, 3H), 7.69 (dd, *J* = 3.9, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 50.0 (CH), 85.1 (C), 86.6 (C), 121.9 (C), 127.3 (CH), 127.4 (CH), 128.2 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 131.6 (CH), 132.3 (CH), 132.9 (CH), 137.2 (C), 141.1 (C); MS (EI) 353 (M^+, 0.3), 288 (43), 207 (18), 206 (100), 191 (94), 184 (68), 178 (47), HRMS 353.054446, $C_{19}H_{15}NO_2S_2$ requires 353.05442;

(*S*)-3-Phenyl-1- (*p*-tolyl)-*N*-tosylprop-2-yn-1-amine (3af).[2,3]



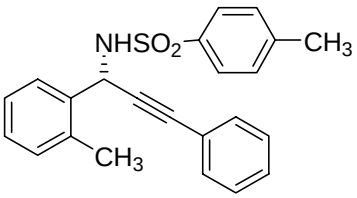
Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2f (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded **3af**. Yield 38.9 mg (0.103 mmol, 93%); mp 225-226 °C; enantiomeric excess (92%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 11.9 min, minor enantiomer t_r = 14.2 min; $[\alpha]_D^{25}$ –82.2 (*c* 1.0, $CHCl_3$, ee 92%); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.27 (s, 3H), 4.83 (d, *J* = 9.0 Hz, 1H), 5.45 (d, *J* = 9.0 Hz, 1H), 7.02-7.09 (m, 4H), 7.14-7.21 (m, 5H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.1 (CH_3), 21.4 (CH_3), 49.5 (CH), 85.6 (C), 86.5 (C), 122.0 (C), 127.2 (CH), 127.5 (CH), 128.1 (CH), 128.5 (CH), 129.4 (CH), 129.5 (CH), 131.5 (CH), 134.4 (C), 137.4 (C), 138.3 (C), 143.5 (C); MS (EI) 375 (M^+, 0.2), 360 (0.1), 310 (5), 236 (16), 220 (100); HRMS 375.1308, $C_{23}H_{21}NO_2S$ requires 375.1293;

(*S*)-3-Phenyl-1- (*m*-tolyl)-*N*-tosylprop-2-yn-1-amine (3ag).



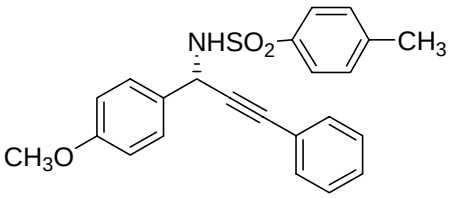
Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2g (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ag**. Yield 40.8 mg (0.109 mmol, 87%); mp 186-187 °C; enantiomeric excess (95%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 9.9 min, minor enantiomer t_r = 12.9 min; $[\alpha]_D^{25}$ –80.4 (*c* 1.3, $CHCl_3$, ee 95%); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.34 (s, 3H), 4.90 (d, *J* = 9.0 Hz, 1H), 5.52 (d, *J* = 9.0 Hz, 1H), 7.10-7.13 (m, 3H), 7.21-7.36 (m, 8H), 7.81 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3), 21.4 (CH_3), 49.8 (CH), 85.6 (C), 86.5 (C), 122.0 (C), 124.3 (CH), 127.5 (CH), 128.0 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 129.2 (CH), 129.5 (CH), 131.5 (CH), 137.2 (C), 137.4 (C), 138.5 (C), 143.5 (C); MS (EI) 375 (M^+, 0.5), 360 (0.3), 310 (5), 236 (18), 220 (100); HRMS 375.1302, $C_{23}H_{21}NO_2S$ requires 375.1293;

(*S*)-3-Phenyl-1- (*o*-tolyl)-*N*-tosylprop-2-yn-1-amine (3ah).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2h (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ah**. Yield 37.5 mg (0.100 mmol, 80%); mp 219-220 °C; enantiomeric excess (99%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 8.1 min, minor enantiomer t_r = 12.0 min; $[\alpha]_D^{25}$ –72.2 (*c* 1.0, $CHCl_3$, ee 99%); ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 2.49 (s, 3H), 4.74 (d, *J* = 9.0 Hz, 1H), 5.70 (d, *J* = 9.0 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.17-7.29 (m, 8H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.1 (CH_3), 21.4 (CH_3), 47.6 (CH), 85.6 (C), 86.6 (C), 122.0 (C), 126.3 (CH), 127.4 (CH), 127.6 (CH), 128.0 (CH), 128.5 (CH), 128.8 (CH), 129.5 (CH), 131.1 (CH), 131.5 (CH), 135.2 (C), 136.5 (C), 137.4 (C), 143.5 (C); MS (EI) 375 (M^+, 2), 360 (9), 236 (32), 220 (100); HRMS 375.1298, $C_{23}H_{21}NO_2S$ requires 375.1293.

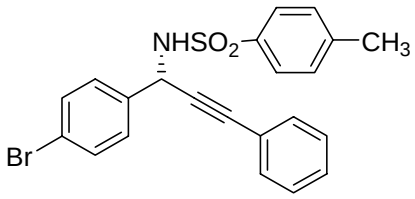
(*S*)-1- (4-Methoxyphenyl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3ai).[2]



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2i (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ai**. Yield 37.6 mg (0.096 mmol, 77%); mp 194-195 °C; enantiomeric excess (87%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 22.1 min, minor enantiomer t_r = 26.8 min; $[\alpha]_D^{25}$ –64.9 (*c* 1.0, $CHCl_3$, ee 87%); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.80 (s, 3H), 4.90 (d, *J* = 9.0 Hz, 1H), 5.51 (d, *J* = 9.0 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.11 (dd, *J* = 9.0, 3.0 Hz, 2H), 7.22-7.30 (m, 5H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H);

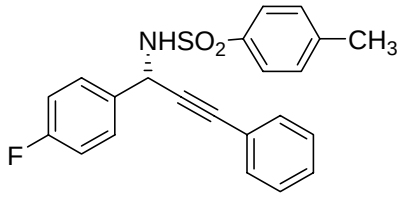
^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 49.3 (CH), 55.3 (CH_3), 85.7 (C), 86.5 (C), 114.0 (CH), 122.0 (C), 127.5 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 129.5 (C), 129.6 (CH), 131.5 (CH), 137.4 (C), 143.5 (C), 159.7 (C); MS (EI) 391 (M^+, 1), 326 (12), 289 (17), 236 (100), 221 (52); HRMS 391.1243, $C_{23}H_{21}NO_3S$ requires 391.1242.

(*S*)-1- (4-Bromophenyl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3aj).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2c (**42.3 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded **3aj**. Yield 47.1 mg (0.107 mmol, 86%);mp 231-232 °C; enantiomeric excess (100%) was determined by HPLC (Chiralcel AS-H), hexane:*i*-PrOH 85:15, 1.0 mL/min, major enantiomer t_r = 35.1 min, minor enantiomer t_r = 41.7 min; $[\alpha]_D^{25}$ –77.0 (*c* 0.23, $CHCl_3$, ee 100%); ^{1}H NMR (DMSO) δ 2.31 (s, 3H), 5.49 (d, *J* = 9.0 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.30-7.36 (m, 5H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 8.74 (d, J = 9.3 Hz, 1H); ^{13}C NMR (DMSO) δ 20.8 (CH_3), 48.1 (CH), 85.2 (C), 86.4 (C), 121.1 (C), 121.3 (C), 126.8 (CH), 128.4 (CH), 128.7 (CH), 129.3 (CH), 129.4 (CH), 131.2 (CH), 131.4 (CH), 137.8 (C), 138.0 (C), 142.7 (C); MS (EI) 441, 439 (M^+, 0.1), 360 (4), 284 (72), 91 (100); HRMS 439.0256, $C_{22}H_{18}BrNO_2S$ requires 439.0242.

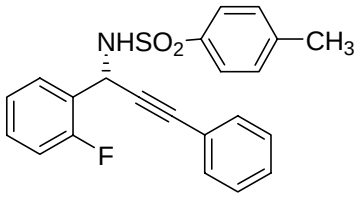
(*S*)-1- (4-Fluorophenyl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3ak).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2k (**33.0 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded **3ak**. Yield 40.7 mg (0.107 mmol, 86%); mp 214-215 °C;

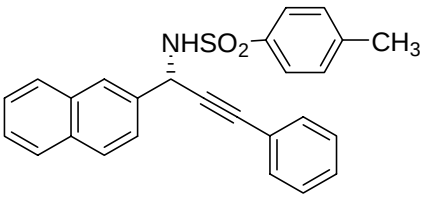
enantiomeric excess (90%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 0.7 mL/min, major enantiomer t_r = 29.5 min, minor enantiomer t_r = 32.7 min; $[\alpha]_D^{25}$ –105.8 (*c* 0.2, $CHCl_3$, ee 90%); ^{1}H NMR (DMSO) δ 2.31 (s, 3H), 5.50 (d, *J* = 6.9 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.21 (t, *J* = 8.9 Hz, 2H), 7.29-7.35 (m, 5H), 7.53 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (DMSO) δ 20.8 (CH_3), 48.0 (CH), 85.1 (C), 86.7 (C), 115.2 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 121.4 (C), 126.9 (CH), 128.4 (CH), 128.7 (CH), 129.2 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 129.3 (CH), 131.1 (CH), 134.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 138.1 (C), 142.7 (C), 161.6 (d, $^1J_{C\text{-}F}$ = 243 Hz); MS (EI) 379 (M^+, 0.3), 314 (7), 274 (6), 240 (20), 224 (100); HRMS 379.1045, $C_{22}H_{18}FNO_2S$ requires 379.1042.

(*S*)-1- (2-Fluorophenyl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3al).



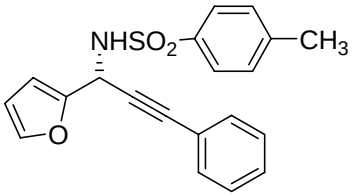
Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2l (**32.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3al**. Yield 36.9 mg (0.097 mmol, 78%); mp 211-212 °C; enantiomeric excess (88%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 1.0 mL/min, major enantiomer t_r = 20.2 min, minor enantiomer t_r = 25.2 min; $[\alpha]_D^{25}$ –38.2 (*c* 0.2, $CHCl_3$, ee 88%); ^{1}H NMR (DMSO) δ 2.29 (s, 3H), 5.65 (d, *J* = 9.0 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.20-7.38 (m, 8H), 7.62 (td, *J* = 7.8, 1.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 8.76 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (DMSO) δ 20.8 (CH_3), 42.7 (CH), 84.7 (C), 85.8 (C), 115.5 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 121.2 (C), 124.6 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.4 (d, $^2J_{C\text{-}F}$ = 13.5 Hz), 126.8 (CH), 128.4 (CH), 127.8 (CH), 129.1 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 129.3 (CH), 130.4 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 131.2 (CH), 137.9 (C), 142.7 (C), 158.9 (d, $^1J_{C\text{-}F}$ = 146 Hz); MS (EI) 379 (M^+, 0.3), 314 (3), 274 (4), 240 (13), 224 (100); HRMS 379.1054, $C_{22}H_{18}FNO_2S$ requires 379.1042.

(*S*)-1- (Naphthalen-2-yl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3am).[2]



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2m (**38.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3am**. Yield 41.6 mg (0.101 mmol, 81%); mp 214-215 °C; enantiomeric excess (84%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 0.5 mL/min, major enantiomer t_r = 83.4 min, minor enantiomer t_r = 92.8 min; $[\alpha]_D^{25}$ –64.7 (*c* 0.5, $CHCl_3$, ee 84%); ^{1}H NMR (DMSO) δ 2.27 (s, 3H), 5.65 (d, *J* = 9.3 Hz, 1H), 7.11-7.14 (m, 2H), 7.30-7-36 (m, 5H), 7.54 (d, *J* = 9.3 Hz, 1H), 7.54 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.90-7.98 (m, 4H), 8.81 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (DMSO) δ 20.8 (CH_3), 48.9 (CH), 85.3 (C), 86.8 (C), 121.5 (C), 125.3 (CH), 125.6 (CH), 126.3 (CH), 126.4 (CH), 126.9 (CH), 127.5 (CH), 127.9 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.3 (CH), 131.2 (CH), 132.4 (C), 132.5 (C), 135.7 (C), 138.1 (C), 142.6 (C); MS (EI) 411 (M^+, 6), 346 (6), 309 (2), 272 (11), 256 (100); HRMS 411.1298, $C_{26}H_{21}NO_2S$ requires 411.1293.

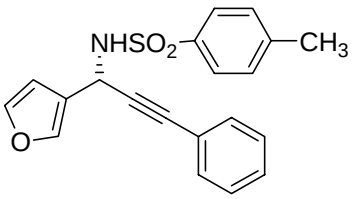
(*R*)-1- (Furan-2-yl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3an).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2n (**30.0 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3an**. Yield 32.9 mg (0.094 mmol, 74%); mp 185-186 °C; enantiomeric excess (91%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 12.7 min, minor enantiomer t_r = 14.8 min; $[\alpha]_D^{25}$ –61.1 (*c* 1.1, $CHCl_3$, ee 91%); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 5.01 (d, *J* = 9.3 Hz, 1H), 5.53 (d, *J* = 9.3 Hz, 1H), 6.22 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.14-7.27 (m, 6H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 44.9 (CH), 83.4 (C), 85.3 (C), 108.4 (CH), 110.4 (CH),

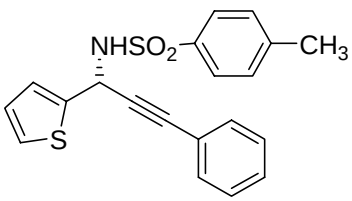
121.7 (C), 127.4 (CH), 128.1 (CH), 128.7 (CH), 129.5 (CH), 131.6 (CH), 137.3 (C), 143.2 (CH), 143.6 (C), 149.5 (C); MS (EI) 351 (M^+, 0.4), 303 (2), 286 (9), 246 (21), 212 (31), 196 (100); HRMS 351.0928, $C_{20}H_{17}NO_3S$ requires 351.0929.

(*R*)-1- (Furan-3-yl)-3-phenyl-*N*-tosylprop-2-yn-1-amine (3ao).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2o (**30.0 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded **3ao**. Yield 33.6 mg (0.094 mmol, 75%); mp 160-161 °C; enantiomeric excess (64%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 12.0 min, minor enantiomer t_r = 13.7 min; $[\alpha]_D^{25}$ –65.3 (*c* 1.1, $CHCl_3$, ee 64%); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 4.84 (d, *J* = 9.3 Hz, 1H), 5.38 (dd, *J* = 9.3, 0.9 Hz, 1H), 6.39 (d, *J* = 1.2 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.15-7.23 (m, 5H), 7.31 (t, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 0.9 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 42.5 (CH), 84.8 (C), 85.0 (C), 109.5 (CH), 121.7 (C), 123.8 (C), 127.5 (CH), 128.1 (CH), 128.7 (CH), 129.6 (CH), 131.5 (CH), 137.3 (C), 140.8 (CH), 143.7 (C), 143.9 (CH); MS (EI) 351 (M^+, 6), 286 (2), 212 (6), 196 (100); HRMS 351.0927, $C_{20}H_{17}NO_3S$ requires 351.0929.

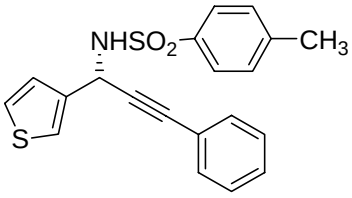
(*R*)–3-Phenyl-1- (thien-2-yl)-*N*-tosylprop-2-yn-1-amine (3ap).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2p (**33.1 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ap**. Yield 33.0 mg (0.090 mmol, 72%); mp 206-207 °C; enantiomeric excess (78%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 12.6 min, minor enantiomer t_r = 14.3 min;

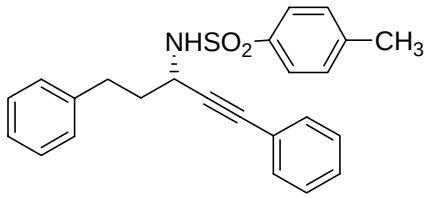
$[\alpha]_D^{25}$ –84.0 (*c* 0.5, $CHCl_3$, ee 78%); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 4.98 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 9.3 Hz, 1H), 6.87 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.07 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.11 (dt, *J* = 3.6, 1.2 Hz, 1H), 7.16-7.24 (m, 6H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 45.8 (CH), 85.2 (C), 85.8 (C), 121.6 (C), 126.3 (CH), 126.4 (CH), 126.9 (CH), 127.5 (CH), 128.1 (CH), 128.8 (CH), 129.6 (CH), 131.6 (CH), 137.2 (C), 141.4 (C), 143.7 (C); MS (EI) 367 (M^+, 0.2), 302 (5), 262 (10), 228 (17), 212 (100); HRMS 367.0700, $C_{20}H_{17}NO_2S_2$ requires 367.0701.

(*R*)-3-Phenyl-1- (thien-3-yl)-*N*-tosylprop-2-yn-1-amine (3aq).



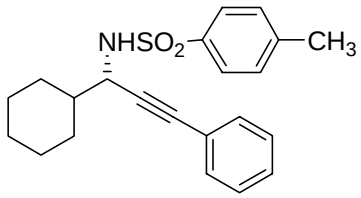
Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2q (**33.1 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3aq**. Yield 34.4 mg (0.094 mmol, 75%); mp 193-194 °C; enantiomeric excess (81%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 13.0 min, minor enantiomer t_r = 15.0 min; $[\alpha]_D^{25}$ –45.7 (*c* 0.8, $CHCl_3$, ee 81%); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 4.92 (d, *J* = 9.0 Hz, 1H), 5.50 (d, *J* = 9.0 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.15-7.24 (m, 6H), 7.32 (m, 1H), 7.74 (d, *J* = 8.4 Hz, 2H);^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 45.8 (CH), 85.5 (C), 121.8 (C), 123.4 (CH), 126.7 (CH), 126.8 (CH), 127.5 (CH), 128.1 (CH), 128.6 (CH), 129.6 (CH), 131.5 (CH), 137.3 (C), 138.6 (C), 143.6 (C); ^{1}H NMR (DMSO) δ 2.08 (s, 3H), 5.54 (s, 1H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.23-7.42 (m, 9H), 7.32 (m, 1H), 7.70 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.92 (dd, J = 5.0, 1.4 Hz, 1H), 9.04 (s, 1H); ^{13}C NMR (DMSO) δ 30.6 (CH_3), 48.8 (CH), 84.8 (C), 86.8 (C), 121.6 (C), 127.0 (CH),127.5 (CH), 128.0 (CH), 128.5 (CH), 128.7 (CH), 131.3 (CH), 132.2 (CH), 132.7 (CH), 138.3 (C), 141.7 (C); MS (EI) 367 (M^+, 6), 302 (5), 262 (2), 228 (14), 212 (100); HRMS 367.0703, $C_{20}H_{17}NO_2S_2$ requires 367.0701.

(*S*)-1,5-Diphenyl-*N*-tosylpent-1-yn-3-amine (3ar).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2r (**35.9 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ar**. Yield 41.7 mg (0.107 mmol, 86%);mp 173-174 °C; enantiomeric excess (18%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, minor enantiomer t_r = 13.5 min, major enantiomer t_r = 20.5 min; $[\alpha]_D^{25}$ –10.7 (*c* 1.1, $CHCl_3$, ee 18%); ^{1}H NMR ($CDCl_3$) δ 1.98 (m, 2H), 2.24 (s, 3H), 2.75 (t, *J* = 7.8 Hz, 2H), 4.20 (t, *J* = 6.9 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.10-7.24 (m, 10H), 7.15-7.25 (m, 8H), 7.71 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 31.7 (CH_2), 38.2 (CH_2), 45.7 (CH), 84.7 (C), 86.8 (C), 122.0 (C), 126.1 (CH), 127.4 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.5 (CH), 131.4 (CH), 137.2 (C), 140.6 (C), 143.5 (C); MS (EI) 389 (M^+, 2), 284 (100), 234 (58); HRMS 389.1453, $C_{24}H_{23}NO_2S$ requires 389.1450.

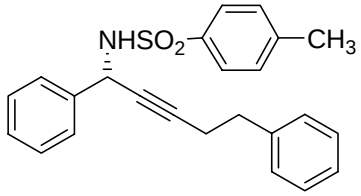
(*S*)-1-Cyclohexyl-3-phenyl-*N*-tosylprop-2-yn-1-amine (3as).



Prepared starting from phenylacetylene (**1a**, 0.97 μL, 0.9 mmol) and imine **2q (**33.1 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3as**. Yield 38.6 mg (0.105 mmol, 84%); mp 205-206 °C; enantiomeric excess (38%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 1.0 mL/min, minor enantiomer t_r = 10.0 min, major enantiomer t_r = 11.6 min; $[\alpha]_D^{25}$ –29.6 (*c* 1.1, $CHCl_3$, ee 38%); ^{1}H NMR ($CDCl_3$) δ 1.02-1.24 (m, 5H), 1.41-1.85 (m, 6H), 2.25 (s, 3H), 4.02 (m, 1H), 6.96 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.12-7.22 (m, 5H), 7.73 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 25.7 (CH_2), 25.8 (CH_2), 26.1

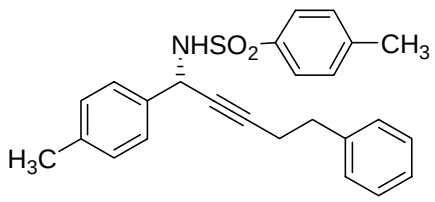
(CH_2), 28.4 (CH_2), 29.1 (CH_2), 43.2 (CH), 51.3 (CH), 85.1 (C), 86.2 (C), 122.2 (C), 127.4 (CH), 128.0 (CH), 128.2 (CH), 129.5 (CH), 131.4 (CH), 137.3 (C), 143.4 (C); MS (EI) 367 (M^+, 1), 284 (100); HRMS 367.1616, $C_{22}H_{25}NO_2S$ requires 367.1606.

(*S*)-1,5-Diphenyl-*N*-tosylpent-2-yn-1-amine (3ba).



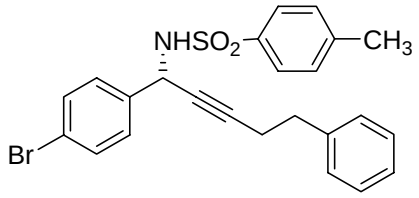
Prepared starting from 4-phenyl-1-butyne (**1b**, 0.127 mL, 0.9 mmol) and imine **2a (**32.3 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3ba**. Yield 36.8 mg (0.095 mmol, 75%); mp 153-154 °C; enantiomeric excess (90%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 13.0 min, minor enantiomer t_r = 18.0 min; $[\alpha]_D^{25}$ –42.7 (*c* 1.5, $CHCl_3$, ee 90%); ^{1}H NMR ($CDCl_3$) δ 2.18 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 3H), 2.53 (t, *J* = 7.8 Hz, 2H), 4.78 (d, *J* = 8.7 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 7.14-7.30 (m, 10H), 7.66 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.6 (CH_2), 21.5 (CH_3), 34.5 (CH_2), 49.3 (CH), 86.6 (C), 126.4 (CH), 127.2 (CH), 127.5 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.3 (CH), 137.4 (C),137.8 (C), 140.3 (C), 143.3 (C); ^{13}C NMR (DMSO) δ 20.0 (CH_2), 20.9 (CH_3), 33.9 (CH_2), 48.4 (CH), 78.0 (C), 85.6 (C), 126.1 (CH), 126.9 (CH), 127.0 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 129.2 (CH), 138.4 (C),138.7 (C), 140.3 (C), 142.4 (C); MS (EI) 389 (M^+, 0.2), 260 (3), 234 (70), 91 (100); HRMS 389.1455, $C_{24}H_{23}NO_2S$ requires 389.1450.

(*S*)-5-Phenyl-1- (*p*-tolyl)-*N*-tosylpent-2-yn-1-amine (3bf).



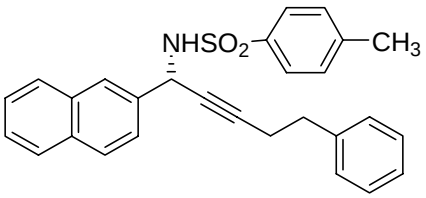
Prepared starting from 4-phenyl-1-butyne (**1b**, 0.127 mL, 0.9 mmol) and imine **2f (**33.5 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3bf**. Yield 40.3 mg (0.100 mmol, 80%); mp 135-136 °C; enantiomeric excess (93%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 14.3 min, minor enantiomer t_r = 17.4 min; $[\alpha]_D^{25}$ –40.2 (*c* 1.1, $CHCl_3$, ee 93%); ^{1}H NMR ($CDCl_3$) δ 2.25 (m, 2H), 2.32 (s, 3H), 2.41 (s, 3H) 2.61 (t, *J* = 7.5 Hz, 2H), 4.68 (d, *J* = 8.7 Hz, 1H), 5.23 (d, *J* = 8.7 Hz, 1H), 7.10 (t, *J* = 8.1 Hz, 4H), 7.23-7.31 (m, 7H), 7.74 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_2), 21.1 (CH_3),21.5 (CH_3), 34.6 (CH_2), 49.2 (CH), 77.7 (C), 86.4 (C), 126.4 (CH), 127.1 (CH), 127.5 (CH), 128.3 (CH), 128.4 (CH), 129.2 (CH), 129.3 (CH), 134.9 (C), 137.5 (C), 138.1 (C), 140.3 (C), 143.3 (C); MS (EI) 403 (M^+, 0.1), 273 (2), 248 (100); HRMS 403.1601, $C_{25}H_{25}NO_2S$ requires 403.1606.

(*S*)-1- (4-Bromophenyl)-5-phenyl-*N*-tosylpent-2-yn-1-amine (3bj).



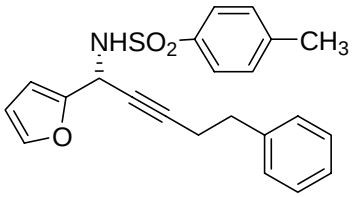
Prepared starting from 4-phenyl-1-butyne (**1b**, 0.127 mL, 0.9 mmol) and imine **2j (**42.3 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure 3bj. Yield 41.0 mg (0.087 mmol, 70%); mp 203-204 °C; enantiomeric excess (100%) was determined by HPLC (Chiralcel AS-H), hexane:*i*-PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 7.5 min, minor enantiomer t_r = 10.1 min; $[\alpha]_D^{25}$ –9.0 (*c* 0.8, $CHCl_3$, ee 100%); ^{1}H NMR ($CDCl_3$) δ 2.21 (m, 2H), 2.35 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H), 4.63 (d, *J* = 8.7 Hz, 1H), 5.13 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 8.4, 2H), 7.17-7.25 (m, 5H), 7.32 (d, *J* = 8.7, 2H), 7.64 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.6 (CH_2), 21.6 (CH_3), 34.4 (CH_2), 48.9 (CH), 77.2 (C), 87.1 (C), 122.3 (C), 126.5 (CH), 127.5 (CH), 128.4 (CH), 128.5 (CH), 129.0 (CH), 129.5 (CH), 131.6 (CH), 136.9 (C),137.3 (C), 140.1 (C), 143.5 (C); MS (EI) 469, 467 (M^+, 0.2), 339, 337 (4), 314, 312 (100); HRMS 467.0542, $C_{24}H_{22}BrNO_2S$ requires 467.0555.

(*S*)-1- (Naphthalen-2-yl)-5-phenyl-*N*-tosylpent-2-yn-1-amine (3bn).



Prepared starting from 4-phenyl-1-butyne (**1b**, 0.127 mL, 0.9 mmol) and imine **2n (**38.6 mg, 0.125 mmol). Purification by flash column chromatography (hexane/CH_2Cl_2 4:6 to 3:7) afforded pure **3bn**. Yield 40.7 mg (0.093 mmol, 74%); mp 108-112 °C; enantiomeric excess (87%) was determined by HPLC (Chiralpack AD-H), hexane:*i*-PrOH 95:5, 1.0 mL/min, major enantiomer t_r = 48.4 min, minor enantiomer t_r = 63.6 min; $[\alpha]_D^{27}$ –34.9 (*c* 0.5, $CHCl_3$, ee 87%); ^{1}H NMR ($CDCl_3$) δ 2.24 (m, 2H), 2.30 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 4.77 (d, *J* = 9.0 Hz, 1H), 5.36 (d, *J* = 9.0 Hz, 1H), 7.06-7.22 (m, 7H), 7.39-7.42 (m, 3H), 7.64-7.71 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_2), 21.5 (CH_3), 34.6 (CH_2), 49.6 (CH), 77.5 (C), 86.9 (C), 125.1 (CH), 126.1 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 127.5 (CH), 127.6 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.3 (CH), 132.9 (C), 133.0 (C), 135.0 (C), 137.4 (C), 140.3 (C),143.3 (C); MS (EI) 439 (M^+, 1), 309 (9), 284 (56), 91 (100); HRMS 439.1605, $C_{28}H_{25}NO_2S$ requires 439.1606.

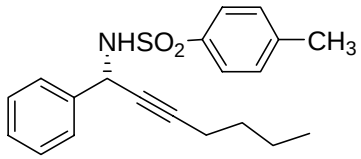
(*R*)-1- (Furan-2-yl)-5-phenyl-*N*-tosylpent-2-yn-1-amine (3bo).



Prepared starting from 4-phenyl-1-butyne (**1b**, 0.127 mL, 0.9 mmol) and imine **2o (**30.0 mg, 0.125 mmol). Purification by flash column chromatography (hexane/diethyl ether 90:10 to 80:20) afforded pure **3bo**. Yield 38.8 mg (0.102 mmol, 82%); mp 138-139 °C, enantiomeric excess (99%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, minor enantiomer t_r = 16.0 min, major enantiomer t_r = 17.3 min; $[\alpha]_D^{25}$ –23.0 (*c* 1.4, $CHCl_3$, ee 99%); ^{1}H NMR ($CDCl_3$) δ 2.20 (m, 2H), 2.32 (s, 3H),

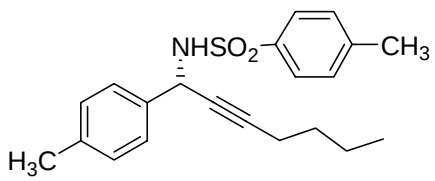
2.56 (t, J = 7.5 Hz, 2H), 4.84 (d, J = 8.7 Hz, 1H), 5.25 (m, 1H), 6.14 (m, 2H), 7.05 (d, J = 7.5, 2H), 7.14-7.24 (m, 6H), 7.65 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_2), 21.5 (CH_3), 34.4 (CH_2), 43.6 (CH), 75.6 (C), 85.5 (C), 108.1 (CH), 110.3 (CH), 126.4 (CH), 127.4 (CH), 128.3 (CH), 128.4 (CH), 129.4 (CH), 137.4 (C), 140.2 (C),142.9 (CH), 143.3 (C), 150.0 (C); MS (EI) 379 (M^+, 0.2), 249 (4), 224 (100); HRMS 379.1253, $C_{22}H_{21}NO_3S$ requires 379.1242.

(*S*)-1-Phenyl-*N*-tosylhept-2-yn-1-amine (3ca).[4]



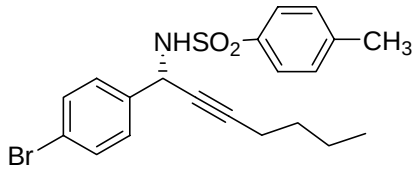
Prepared starting from 1-hexyne (**1c**, 103 μL, 0.9 mmol) and imine **2a (**32.4 mg, 0.125 mmol). Purification by flash column chromatography (hexane:EtOAc 95:5 to 85:15) afforded pure **3ca**. Yield 35.3 g (0.103 mmol, 82%); mp 103-106 °C, enantiomeric excess (81%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 0.5 mL/min, major enantiomer t_r = 14.4 min, minor enantiomer t_r = 16.7 min; $[\alpha]_D^{25}$ –41.6 (*c* 0.7, $CHCl_3$, ee 81%); ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 6.9 Hz, 3H), 1.20 (m, 4H), 1.89 (m, 2H), 2.35 (s, 3H), 4.80 (d, J = 9.0 Hz, 1H), 5.22 (dt, J = 9.0, 1.9 Hz, 1H), 7.19-7.24 (m, 5H), 7.39 (m, 2H), 7.70 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 18.2 (CH_2), 21.5 (CH_3), 21.9 (CH_2), 30.3 (CH_2), 49.4 (CH), 77.2 (C), 87.5 (C), 127.2 (CH), 127.5 (CH), 128.2 (CH), 128.5 (CH), 129.4 (CH), 137.5 (C), 138.1 (C), 143.3 (C); MS (EI) 299 (M^+-42, 3), 259 (2), 202 (6), 186 (100); HRMS 299.0956, $C_{17}H_{17}NO_2S$ requires 299.0980.

(*S*)-1- (*p*-Tolyl)-*N*-tosylhept-2-yn-1-amine (3cf).



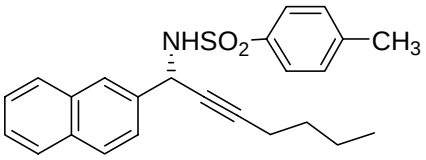
Prepared starting from 1-hexyne (**1c**, 103 μL, 0.9 mmol) and imine **2f (**34.0 mg, 0.125 mmol). Purification by flash column chromatography (hexane:EtOAc 95:5 to 90:10) afforded pure **3cf**. Yield 19.9 mg (0.056 mmol, 45%); mp 133-136 °C; enantiomeric excess (89%) was determined by HPLC (Chiralpack AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, major enantiomer t_r = 17.7 min, minor enantiomer t_r = 20.3 min; $[\alpha]_D^{25}$ –43.1 (*c* 0.8, $CHCl_3$, ee 89%); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.1 Hz, 3H), 1.27 (m, 4H), 1.96 (m, 2H), 2.32 (s, 3H), 2.43 (s, 3H), 4.76 (d, *J* = 9.0 Hz, 1H), 5.26 (d, *J* = 9.0 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 18.2 (CH_2), 21.1 (CH_3), 21.5 (CH_3), 21.9 (CH_2), 30.3 (CH_2), 49.2 (CH), 76.7 (C), 87.2 (C), 127.1 (CH), 127.5 (CH), 129.2 (CH), 129.4 (CH), 135.2 (C), 135.6 (C), 138.0 (C), 143.2 (C); MS (EI) 313 (M^+-42, 2), 273 (2), 216 (5), 200 (100); HRMS 313.1127, $C_{18}H_{19}NO_2S$ requires 313.1137.

(*S*)-1- (*p*-Bromophenyl)-*N*-tosylhept-2-yn-1-amine (3cj).



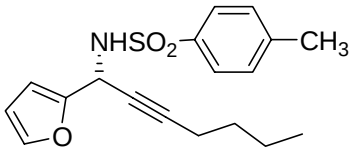
Prepared starting from 1-hexyne (**1c**, 103 μL, 0.9 mmol) and imine **2j (**42.2 mg, 0.125 mmol). Purification by flash column chromatography (hexane:EtOAc 95:5 to 90:10) afforded pure **3cj**. Yield 26.3 mg (0.062 mmol, 50%); mp 136-138 °C; enantiomeric excess (93%) was determined by HPLC (Chiralcel AD-H), hexane:*i*-PrOH 98:2, 0.7 mL/min, minor enantiomer t_r = 62.6 min, major enantiomer t_r = 65.8 min; $[\alpha]_D^{25}$ –39.4 (*c* 0.4, $CHCl_3$, ee 93%); MS (EI) 379, 377 (M^+-42, 3), 282, 280 (5), 266, 264 (100); HRMS 377.0083, $C_{17}H_{16}BrNO_2S$ requires 377.0085; ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 6.9 Hz, 3H), 1.19 (m, 4H), 1.90 (m, 2H), 2.36 (s, 3H), 4.81 (d, *J* = 9.0 Hz, 1H), 5.16 (dt, *J* = 9.0, 1.9 Hz, 1H), 7.19-7.27 (m, 4H), 7.35 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 18.2 (CH_2), 21.5 (CH_3), 21.9 (CH_2), 30.3 (CH_2), 48.9 (CH), 76.1 (C), 87.9 (C), 122.3 (C), 127.4 (CH), 129.0 (CH), 129.4 (CH), 131.6 (CH), 137.2 (C), 137.3 (C), 143.5 (C); MS (EI) 379, 377 (M^+-42, 3), 282, 280 (5), 266, 264 (100); HRMS 377.0083, $C_{17}H_{16}BrNO_2S$ requires 377.0085.

(*S*)-1- (Naphthalen-2-yl)-*N*-tosylhept-2-yn-1-amine (3cn).



Prepared starting from 1-hexyne (**1c**, 103 μL, 0.9 mmol) and imine **2n (**38.6 mg, 0.125 mmol). Purification by flash column chromatography (hexane:EtOAc 95:5 to 85:15) afforded pure **3cn**. Yield 34.5 mg (0.088 mmol, 71%); mp 127-135 °C; enantiomeric excess (76%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 0.7 mL/min, major enantiomer t_r = 16.5 min, minor enantiomer t_r = 19.2 min; $[\alpha]_D^{27}$ –35.0 (*c* 0.5, $CHCl_3$, ee 76%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.32 (m, 4H), 2.02 (m, 2H), 2.38 (s, 3H), 5.00 (d, *J* = 9.0 Hz, 1H), 5.45 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.46-7.49 (m, 2H), 7.54 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.74-7.85 (m, 5H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 18.2 (CH_2), 21.4 (CH_3), 21.9 (CH_2), 30.3 (CH_2), 49.6 (CH), 76.5 (C), 87.7 (C), 125.1 (CH), 126.1 (CH), 126.2 (CH), 126.3 (CH), 127.4 (CH), 127.5 (CH), 128.1 (CH), 128.5 (CH), 129.3 (CH), 132.9 (C), 133.0 (C), 135.3 (C), 137.4 (C), 143.3 (C); MS (EI) 391 (M^+, 4), 349 (3), 309 (13), 236 (100); HRMS 391.1606, $C_{24}H_{25}NO_2S$ requires 391.1606.

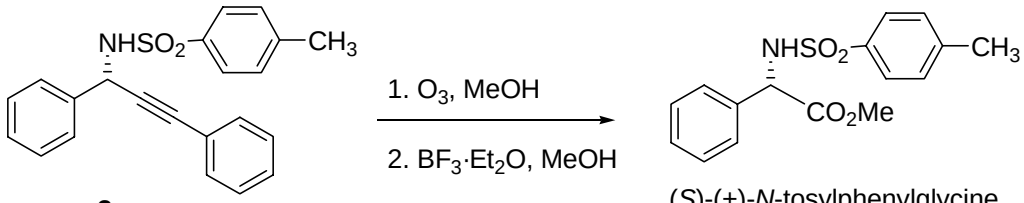
(*R*)-1- (Furan-2-yl)-*N*-tosylhept-2-yn-1-amine (3co).



Prepared starting from 1-hexyne (**1c**, 103 μL, 0.9 mmol) and imine **2o (**31.1 mg, 0.125 mmol). Purification by flash column chromatography (hexane:EtOAc 95:5 to 80:20) afforded pure **3co**. Yield 35.0 mg (0.106 mmol, 85%); mp 80-83 °C; enantiomeric excess (93%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 0.6 mL/min, major enantiomer t_r = 13.4 min, minor enantiomer t_r = 15.2 min; $[\alpha]_D^{25}$ –29.4 (*c* 0.4, $CHCl_3$, ee 93%); ^{1}H NMR ($CDCl_3$) δ 0.78 (t, *J* = 7.1, 3H), 1.21 (m, 4H), 1.91 (m, 2H), 2.34 (s, 3H), 4.92 (d, *J* = 8.7 Hz, 1H), 5.27 (td, *J* = 1.8, 8.7 Hz, 1H), 6.18 (m, 1H), 6.20 (m, 1H), 7.19 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 18.1 (CH_2), 21.5 (CH_3), 21.8 (CH_2), 30.2 (CH_2), 43.6 (CH), 74.6 (C), 86.3 (C), 108.0 (CH), 110.3 (CH), 127.4 (CH), 129.3 (CH), 137.5 (C),

142.9 (CH), 143.3 (C), 150.3 (C); MS (EI) 331 (M^+, 0.1), 289 (2), 192 (4), 176 (100); HRMS 331.1237, $C_{18}H_{21}NO_3S$ requires 331.1242.

Determination of the absolute configuration of compound 3aa

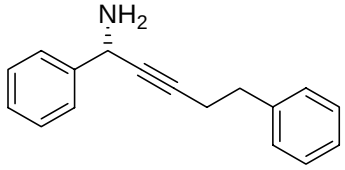


3aa
(98% ee)

(*S*)-(+)-*N*-tosylphenylglycine methyl ester

Ozone enriched oxygen was bubbled through a solution of tosyl aldimine **3aa** (33.8 mg, 0.094 mmol, 98% ee) in MeOH (20 mL) at – 40 ºC for 45 min. The excess ozone was removed by bubbling nitrogen for 5 min. The resulting solution was allowed to reach rt, $BF_3{\cdot}Et_2O$ (0.35 mL) was added and the mixture was heated at reflux temperature for 3.5 h. After cooling to rt, saturated aqueous $NaHCO_3$ (10 mL) was added, the organic solvent was removed under reduced pressure, and the resulting aqueous solution was extracted with dichloromethane (3 × 15 mL), washed with brine (10 mL) and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash chromatography eluting with hexane-EtOAc (8:2) gave 19.6 mg (66%) of (*S*)-(+)-*N*-tosylphenylglycine methyl ester:[5] $[\alpha]^{25}_D$ = + 105.6 (*c* 0.77, $CHCl_3$), Lit.[5a] $[\alpha]^{25}_D$ = + 103; ^{1}H NMR δ 2.38 (s, 3H), 3.57 (s, 3H), 5.06 (d, *J* = 6.9 Hz, 2H), 5.70 (d, *J* = 7.9 Hz, 1H), 7.30-7.15 (m, 7H), 7.62 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR δ 21.5 (CH_3), 53.0 (CH), 59.3 (CH_3), 127.1 (CH), 127.2 (CH), 128.6 (CH), 128.8 (CH), 129.5 (CH), 135.2 (C), 136.8 (C), 143.5 (C), 170.5 (C).

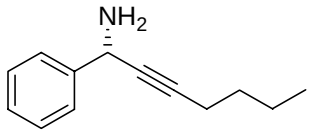
(*S*)-1,5-Diphenylpent-2-yn-1-amine (4ba).



Tosyl amine **3ba** (25.0 mg, 0.065 mmol, 63% ee) dry THF (1 mL) was added to a 0.1 M THF solution of SmI_2 (7.8 mL, 0.78 mmol) and HMPA (0.5 mL) at rt under nitrogen.

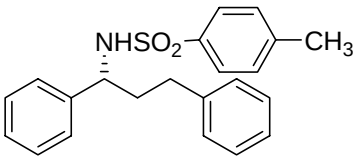
The solution was heated at 60 ºC for 5h until the purple color of the solution disappeared. The reaction was cooled at rt and quenched with satd aqueous NaCl (30 mL) and extracted with diethyl ether (3 ×15 mL). The organic layer was washed with brine (3 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography eluting with hexane-EtOAc (6:4, containing 10 drops Et_3N for 100 mL of eluent) gave amine **4ba**. Yield 11.0 mg (0.047 mmol, 72%); an oil; enantiomeric excess (63%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1.0 mL/min, minor enantiomer t_r = 17.5 min, major enantiomer t_r = 24.5 min; $[\alpha]_D^{25}$ –7.3 (*c* 0.4, $CHCl_3$, ee 63%); ^{1}H NMR ($CDCl_3$) δ 2.54 (td, *J* = 7.5, 2.1 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 3.15 (br s, 2H), 4.80 (s, 1H), 7.15-7.40 (m, 8H), 7.46 (dd, *J* = 8.4, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_2), 34.7 (CH_2), 47.2 (CH), 85.1 (C), 126.3 (CH), 126.9 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 129.7 (C), 140.6 (C); MS (EI) 235 (M^+, 76), 234 (100), 218 (47), 156 (87), 144 (96), 91 (67); HRMS 235.1360, $C_{17}H_{17}N$ requires 235.1361.

(*S*)-1-Phenylhept-2-yn-1-amine (4ca).



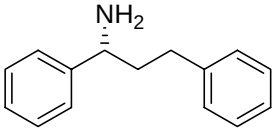
The same procedure described above was followed, but the mixture was stirred at rt overnight. From compound **3ca** (25.0 mg, 0.073 mmol, 81% ee) after chromatography eluting with hexane-EtOAc (6:4, containing 10 drops Et_3N for 100 mL of eluent) was obtained amine **4ca**. Yield 9.7 mg (0.052 mmol, 71%); an oil; enantiomeric excess (81%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 0.5 mL/min, minor enantiomer t_r = 15.8 min, major enantiomer t_r = 16.7 min; $[\alpha]_D^{25}$ –12.2 (*c* 0.5, $CHCl_3$, ee 81%); ^{1}H NMR ($CDCl_3$) δ 0.914 (t, *J* = 7.2 Hz, 3H), 1.35-1.56 (m, 4H), 2.24 (td, *J* = 6.9 2.1 Hz, 2H), 2.69 (br s, 2H), 4.79 (s, 1H), 7.24-7.39 (m, 8H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 18.5 (CH_2), 22.0 (CH_2), 30.8 (CH_2), 47.5 (CH), 85.4 (C), 126.8 (CH), 127.6 (CH), 128.5 (CH), 142.2 (C); MS (EI) 187 (M^+, 17), 186 (25), 170 (23), 158 (15), 144 (100), 130 (52), 109 (68); HRMS 187.1360, $C_{13}H_{17}N$ requires 187.1361.

(*R*)-1,3-Diphenyl-*N*-tosylpropan-1-amine (5aa).



A solution of compound **3aa** (28 mg, 0.077 mmol, 97% ee) in abs EtOH (7 mL) was stirred under hydrogen (balloon) in the presence of 5% $Pd/CaCO_3$ (10 mg) for 1.5 h. After this time, the mixture was filtered through a short pad of silica gel, eluting with EtOAc, and the solvent was removed under reduced pressure to give compound **5aa**. Yield 28 mg (0.077 mmol, 100%); mp 111-112 °C; enantiomeric excess (97%) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 85:15, 1.0 mL/min, major enantiomer t_r = 11.0 min, minor enantiomer t_r = 19.4 min; $[\alpha]_D^{25}$ +11.9 (*c* 1.1, $CHCl_3$, ee 97%); ^{1}H NMR ($CDCl_3$) δ 1.70-2.10 (m, 2H), 2.25 (s, 3H), 2.30-2.57 (m, 2H), 4.18 (q, *J* = 6.6 Hz, 1H), 5.26 (d, *J* = 6.6 Hz, 1H), 6.80-7.45 (m, 12H), 7.43 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 32.0 (CH_2), 38.9 (CH_2), 57.8 (CH), 125.9 (CH), 126.5 (CH), 127.0 (CH), 127.4 (CH), 128.34 (CH), 128.35 (CH), 128.4 (CH), 129.3 (CH), 137.5 (C), 140.6 (C), 140.9 (C), 142.9 (C); MS (EI) 365 (M^+, 0.1), 260 (100), 194 (77), 155 (65), 91 (79); HRMS 365.1459, $C_{22}H_{23}NO_2S$ requires 365.1450.

(*R*)-1,3-Diphenylpropan-1-amine (6aa).[6]



The same procedure described above at 70 ºC was followed. From compound **5aa** (26 mg, 0.071 mmol, 97% ee) after chromatography eluting with hexane-EtOAc (5:5, containing 10 drops Et_3N for 100 mL of eluent) was obtained amine **6aa**. Yield 12.5 mg (0.059 mmol, 83%); $[\alpha]_D^{25}$ +9.1 (c 0.5, CHCl3, ee 97%), Lit.[6b] $[\alpha]_D^{25}$ +11.9 (c 1.0); ^{1}H NMR ($CDCl_3$) δ 1.90-2.10 (m, 2H), 2.42-2.57 (m, 2H), 2.65 (br s, 2H), 3.86 (t, *J* = 7.0 Hz, 1H), 7.05-7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 32.6 (CH_2), 40.2 (CH_2), 55.7 (CH), 125.8 (CH), 126.5 (CH), 127.3 (CH), 128.34 (CH), 128.35 (CH), 128.6 (CH), 141.59 (C), 141.60 (C), 144.56 (C); MS (EI) 211 (M^+, 0.8), 194 (7), 178 (3), 106 (100), 91 (29); HRMS 211.1361, $C_{15}H_{17}N$ requires 211.1361. Determination of the ee: Tosyl

chloride (9.0 mg, 0.043 mmol) was added to a solution of compound **6aa** (8.0 mg, 0.034 mmol) and pyridine (4 drops) in CH_2Cl_2 (1 mL) at rt. After 48, the mixture was diluted with EtOAc (30 mL), washed with 2M HCl (2 × 7 mL) and brine (3 x 7 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue chromatographed on silica gel eluting with hexane-EtOAc (8:2) to give the corresponding tosyl imine **5aa** (9.2 mg, 0.026 mmol, 77%) which was analyzed by HPLC as described above (97% ee).

References

[1] (a) L. C. Vishwakarma, O. D. Stringer, F. A. Davis, *Org. Synth.* **1987**, *66*, 203. (b) J. Esquivias, R. Gómez Arrayás, J. C. Carretero, *Angew. Chem. Int. Ed*. **2006**, *45*, 629.

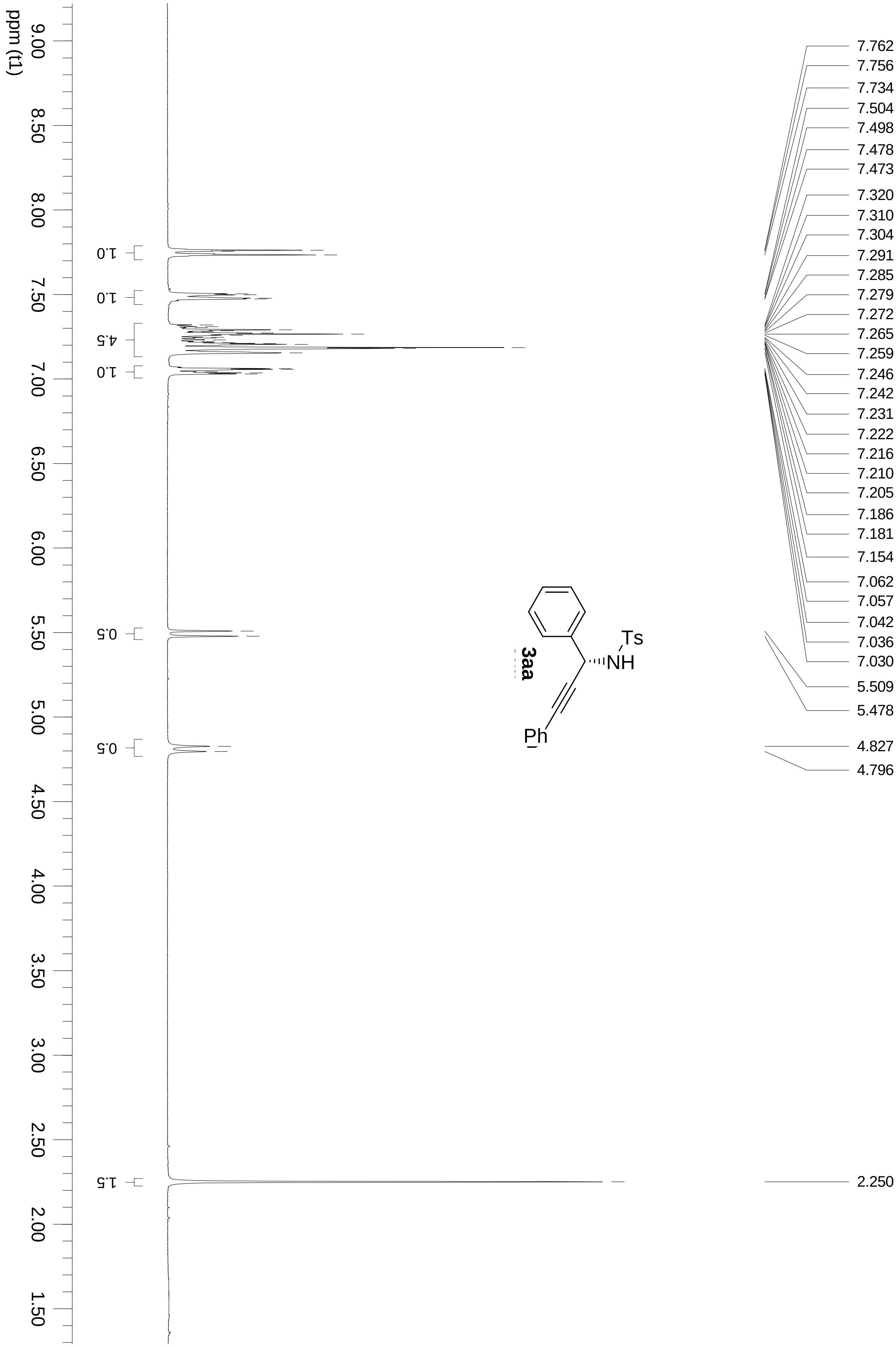
[2] L. Zani, S. Alesi, P. G. Cozzi, C. Bolm, *J. Org. Chem.* **2006**, *71*, 1558.

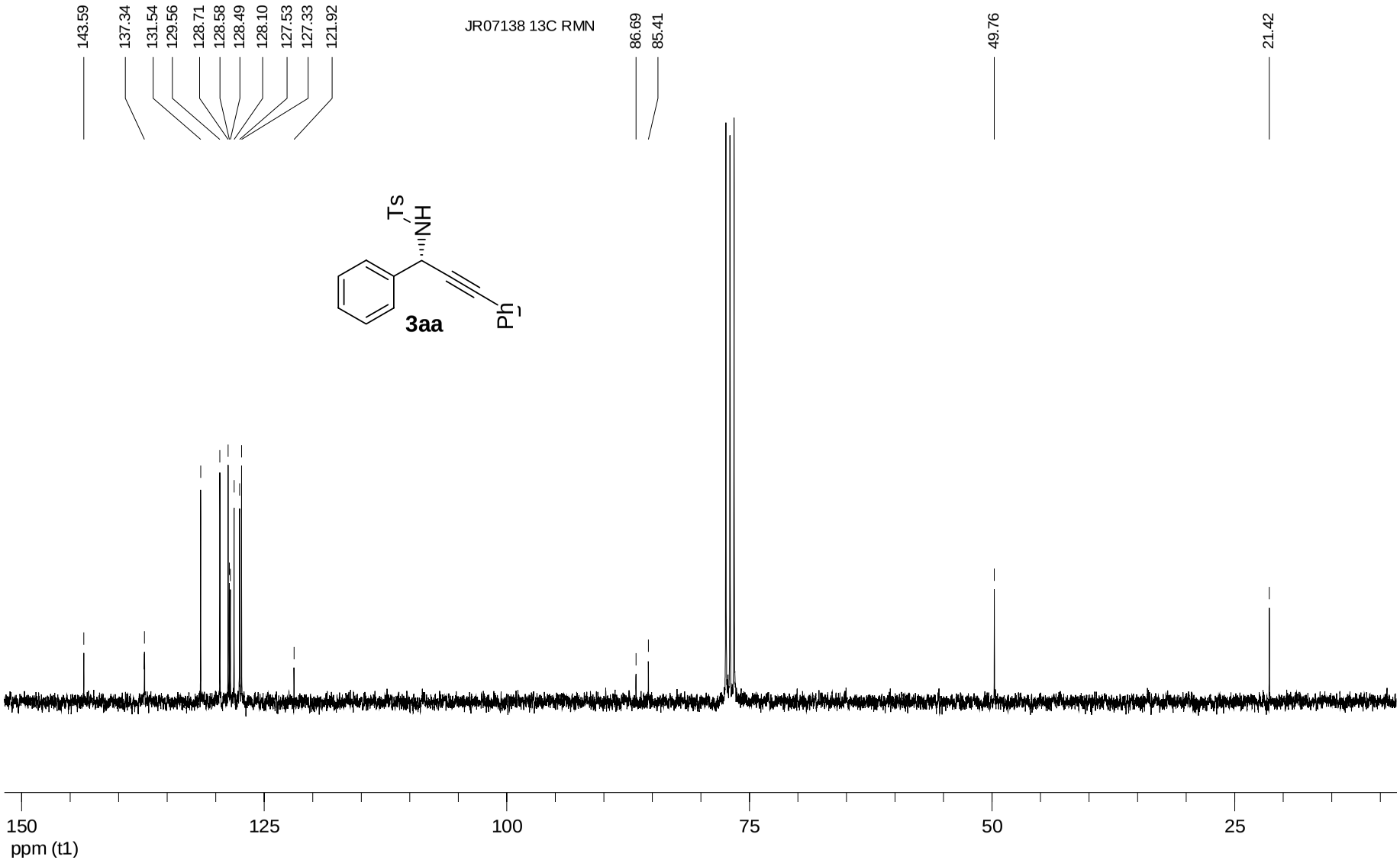
[3] K. Y. Lee, C. G. Lee, J. E. Na, J. N. Kim, *Tetrahedron Lett.* **2005**, *46*, 69.

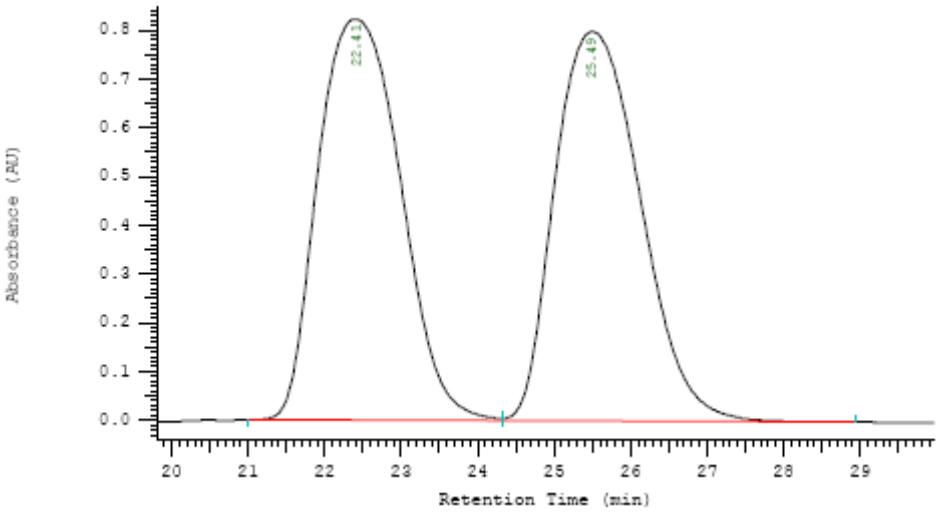
[4] J. Sisko, S. M. Weinreb, *J. Org. Chem.* **1990**, *55*, 393.

[5] (a) M. Ordóñez, R. De la Cruz-Cordero, M. Fernández-Zertuche, M. A. Muñoz-Hernández, O. García-Barradas, *Tetrahedron: Asymmetry* **2004**, *15*, 3035. (b) M. Shi, Y. M. Xu, Y. L. Shi, *Chem. Eur. J.* **2005**, *11*, 1794.

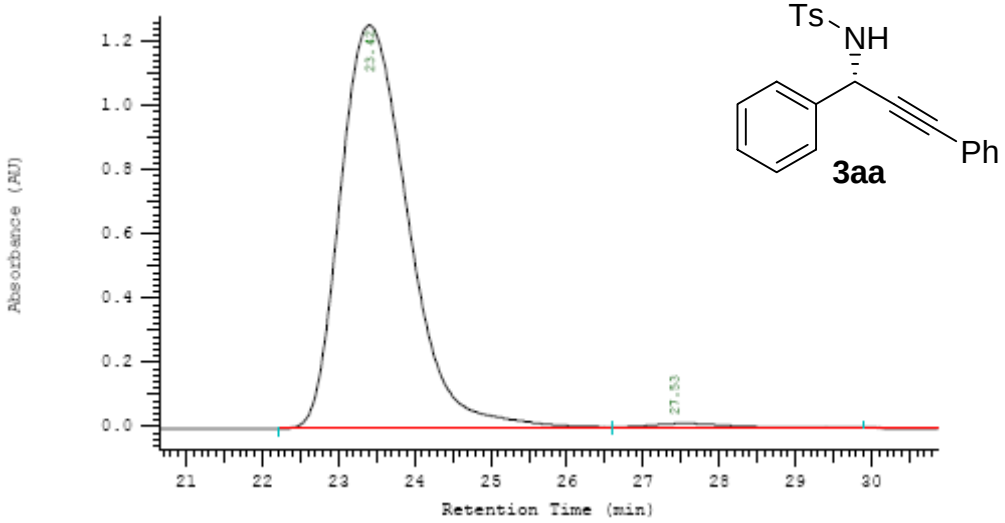
[6] (a) P. Horrillo-Martínez, K. C. Hultzsch, A. Gil, V. Branchadell, *Eur. J. Org. Chem.* **2007**, 3311, racemic. (b) V. Ghislandi, *Farmaco Ed. Sc.* **1965**, *20*, 860.


ppm (t1)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.0
1.0
4.5
1.0
0.5
0.5
1.5
7.762
7.756
7.734
7.504
7.498
7.478
7.473
7.320
7.310
7.304
7.291
7.285
7.279
7.272
7.265
7.259
7.246
7.242
7.231
7.222
7.216
7.210
7.205
7.186
7.181
7.154
7.062
7.057
7.042
7.036
7.030
5.509
5.478
4.827
4.796
2.250
Ts
NH
Ph
3aa


143.59
137.34
131.54
129.56
128.71
128.58
128.49
128.10
127.53
127.33
121.92
JR07138 13C RMN
86.69
85.41
49.76
21.42
Ts
NH
Ph
3aa
150
125
100
75
50
25
ppm (t1)

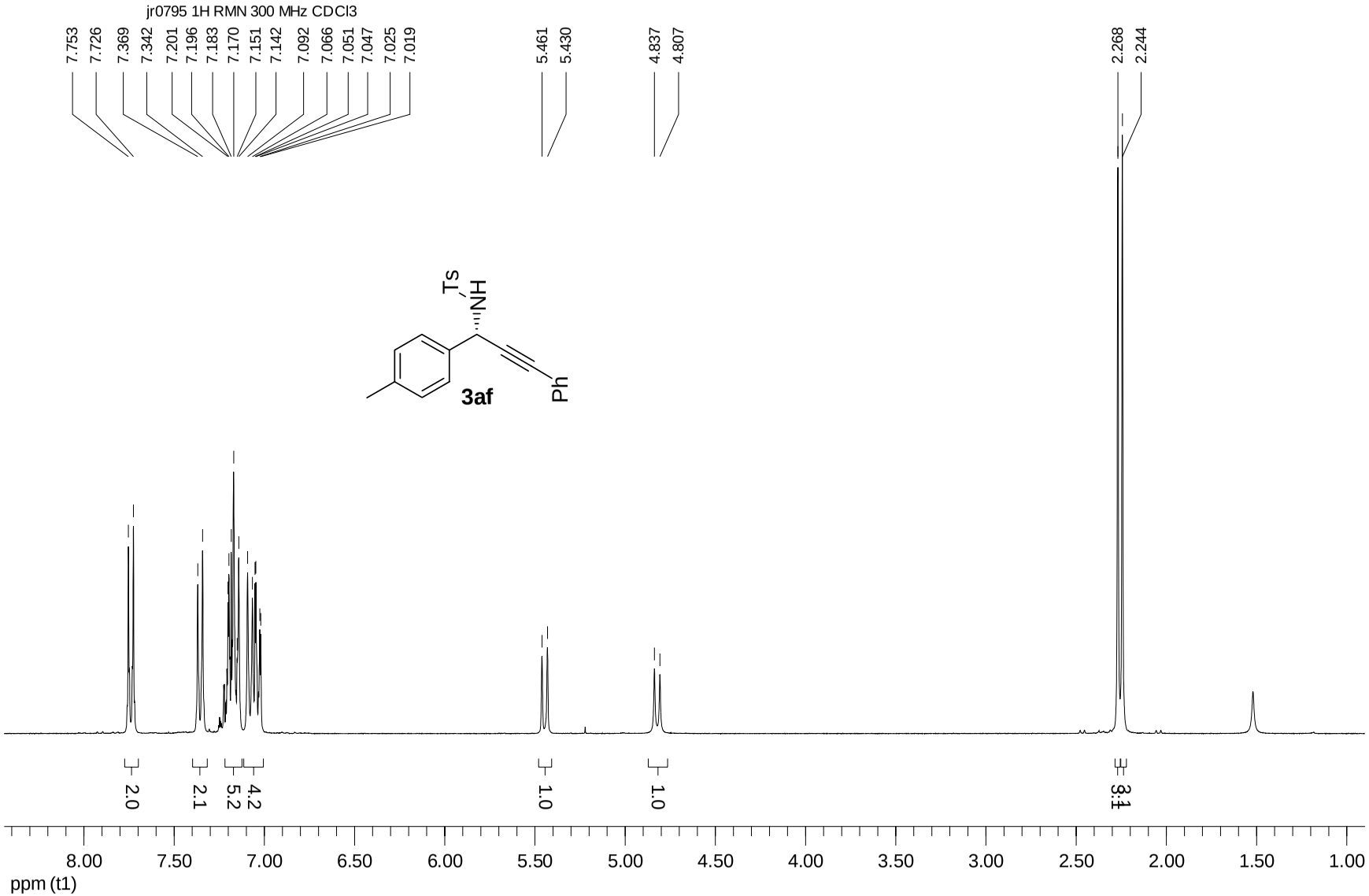


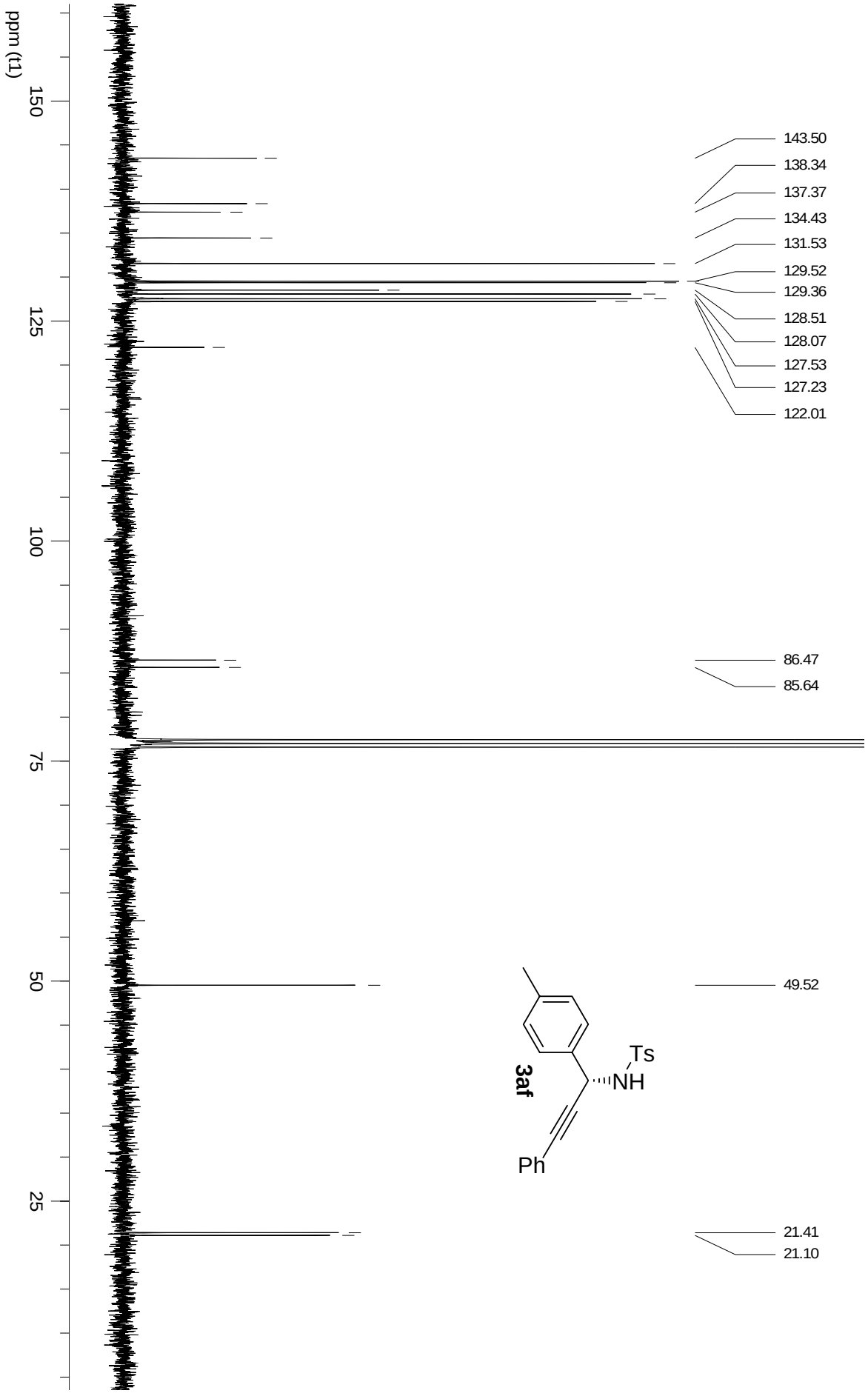
RT	Area	Area %
22.41	30765171	49.808
25.49	31001824	50.192
	61766995	100.000

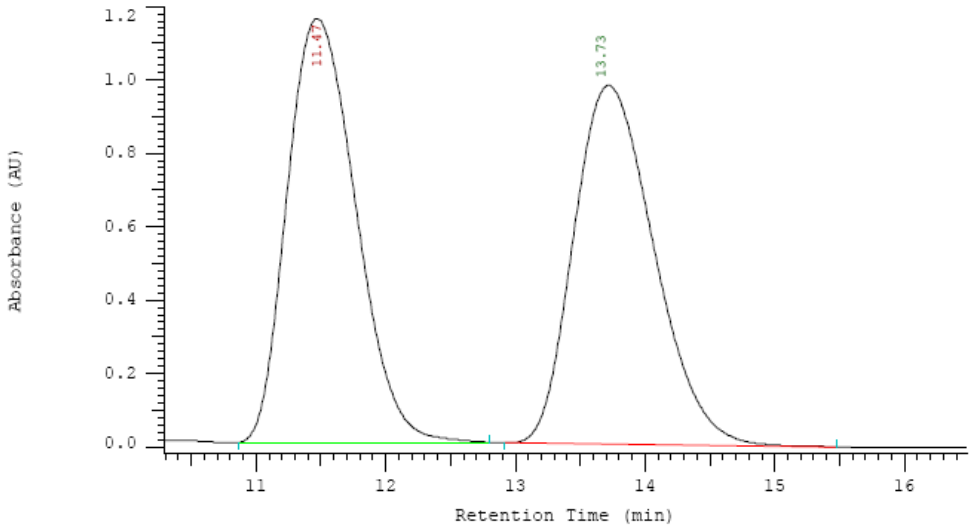


3aa

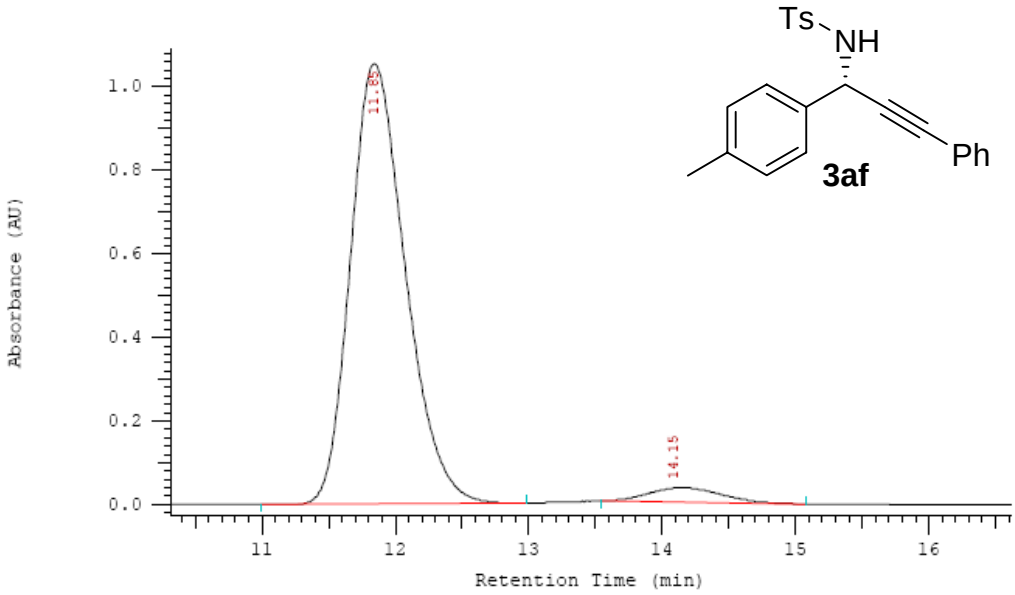
RT	Area	Area %
23.42	38914051	98.975
27.53	402970	1.025
	39317021	100.000


jr0795 1H RMN 300 MHz CDCl3
7.753
7.726
7.369
7.342
7.201
7.196
7.183
7.170
7.151
7.142
7.092
7.066
7.051
7.047
7.025
7.019
5.461
5.430
4.837
4.807
2.268
2.244
Ts
HN
Ph
3af
2.0
2.1
5.2
4.2
1.0
1.0
3.1
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (t1)


ppm (t1)
150
125
100
75
50
25
143.50
138.34
137.37
134.43
131.53
129.52
129.36
128.51
128.07
127.53
127.23
122.01
86.47
85.64
49.52
21.41
21.10
3af
Ts
NH
Ph

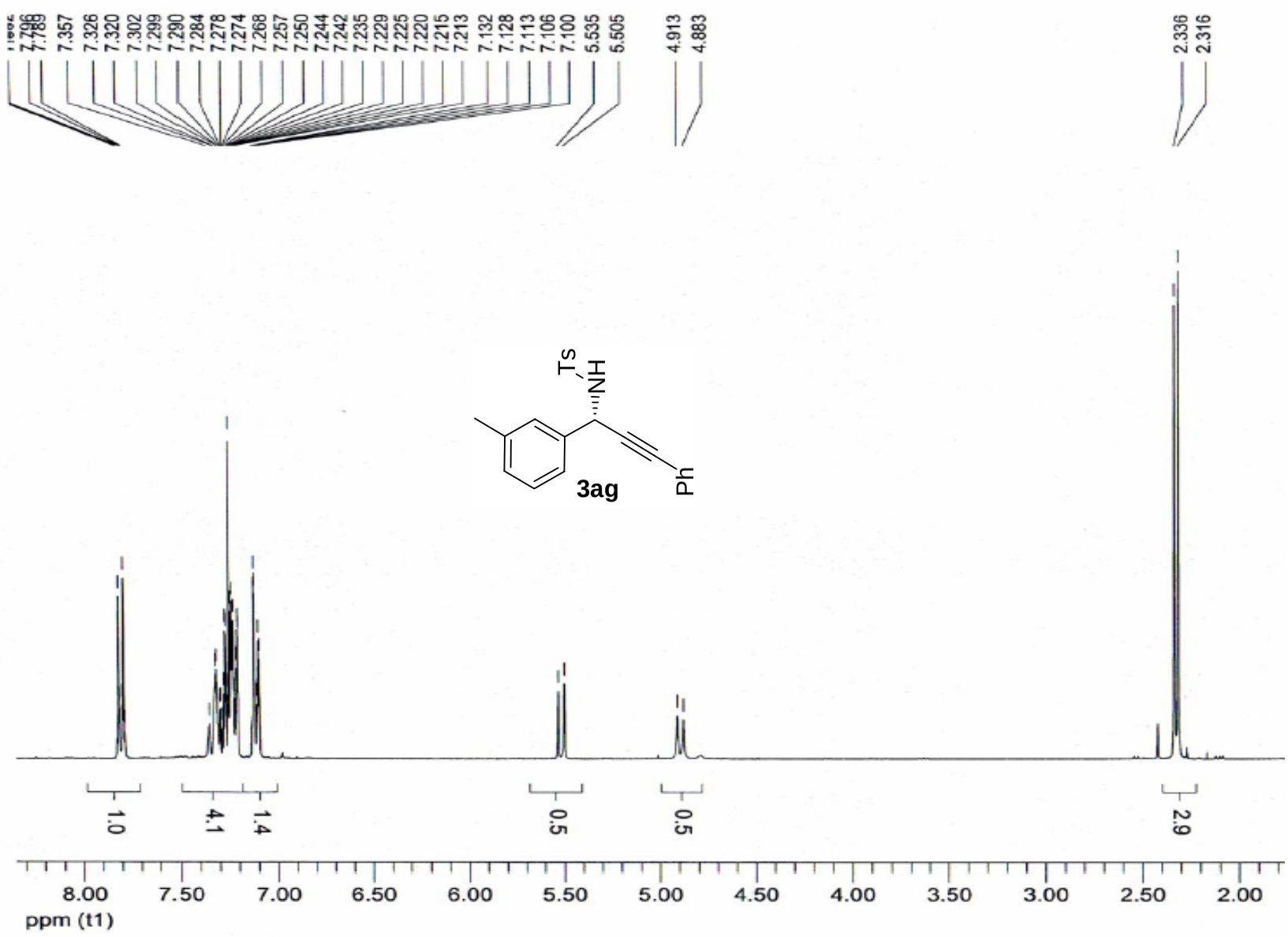


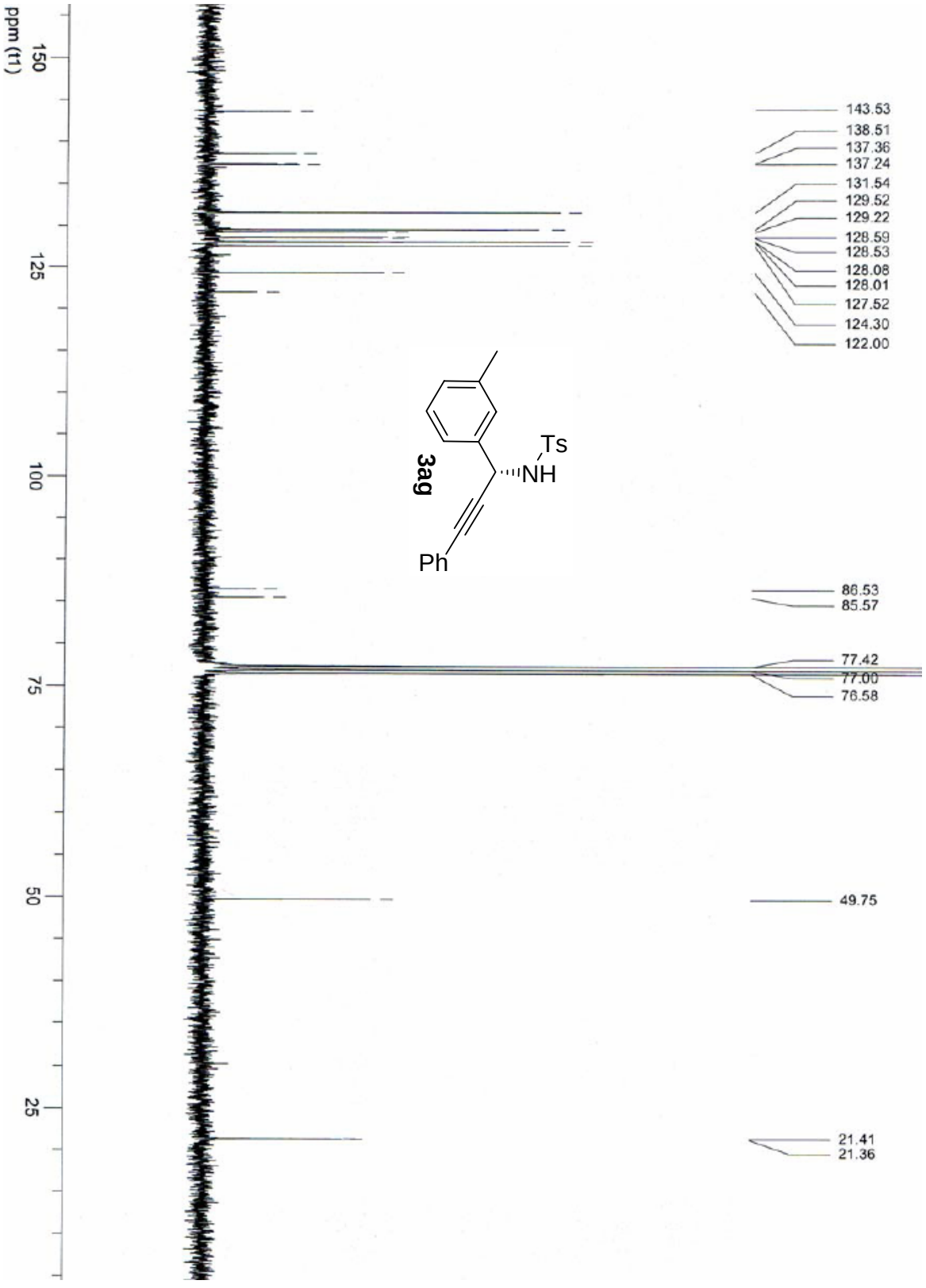
RT	Area	Area %
11.47	21171219	50.193
13.73	21008230	49.807
	42179449	100.000

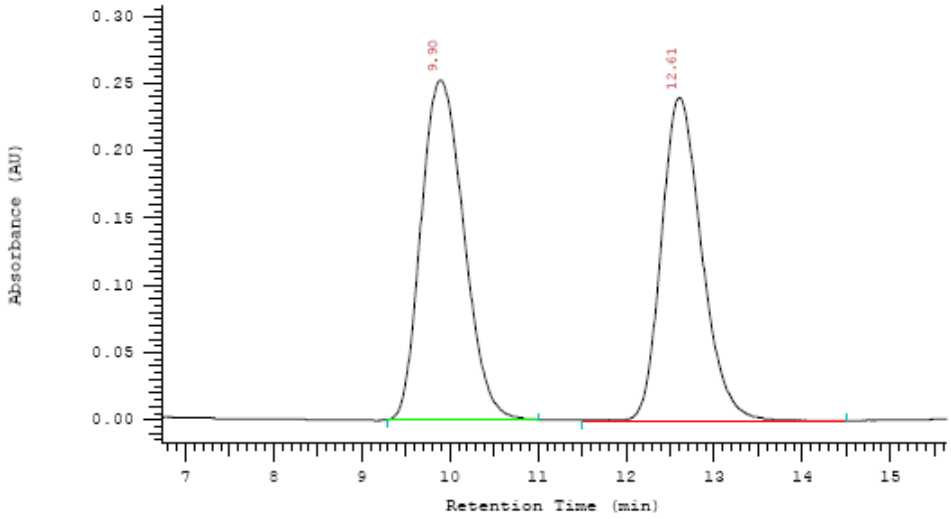


3af

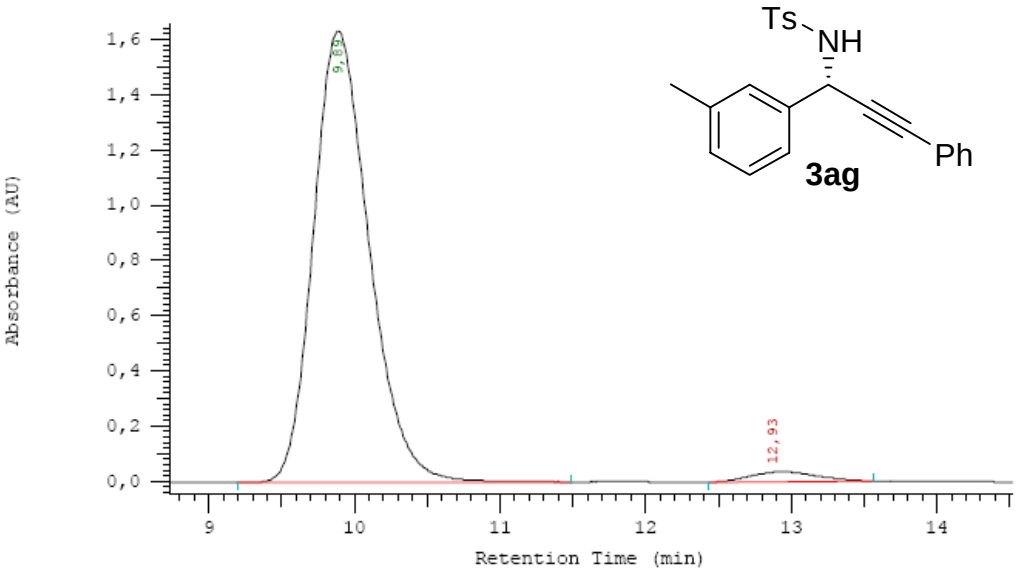
RT	Area	Area %
11.85	14998409	95.830
14.15	652590	4.170
	15650999	100.000


7.357
7.326
7.320
7.302
7.299
7.290
7.284
7.278
7.274
7.268
7.257
7.250
7.244
7.242
7.235
7.229
7.225
7.220
7.215
7.213
7.132
7.128
7.113
7.106
7.100
5.535
5.505
4.913
4.883
2.336
2.316
Ts
HN
Ph
3ag
1.0
4.1
1.4
0.5
0.5
2.9
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)

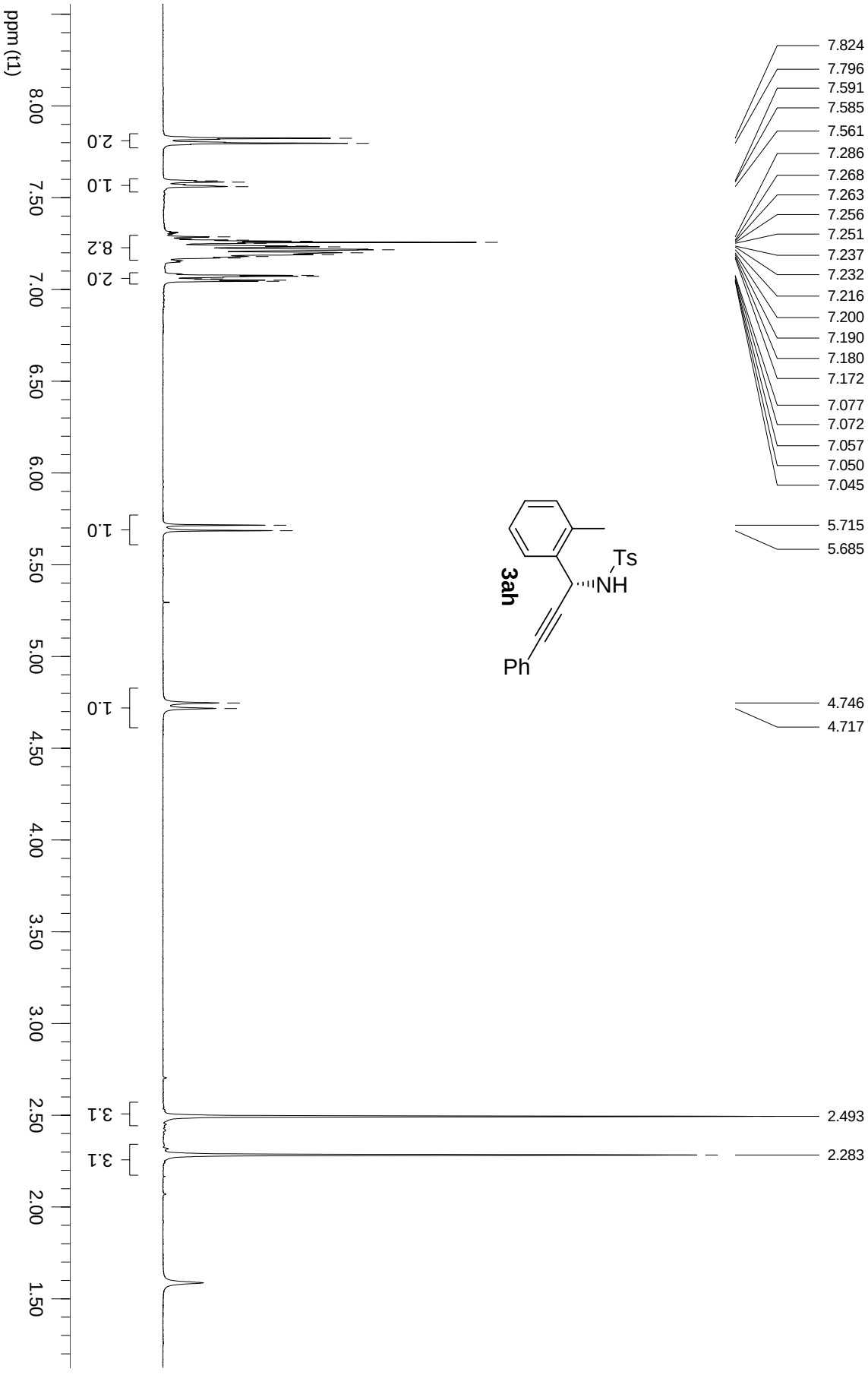

ppm (t1)
150
125
100
75
50
25
143.53
138.51
137.36
137.24
131.54
129.52
129.22
128.59
128.53
128.08
128.01
127.52
124.30
122.00
86.53
85.57
77.42
77.00
76.58
49.75
21.41
21.36
3ag
Ts
NH
Ph

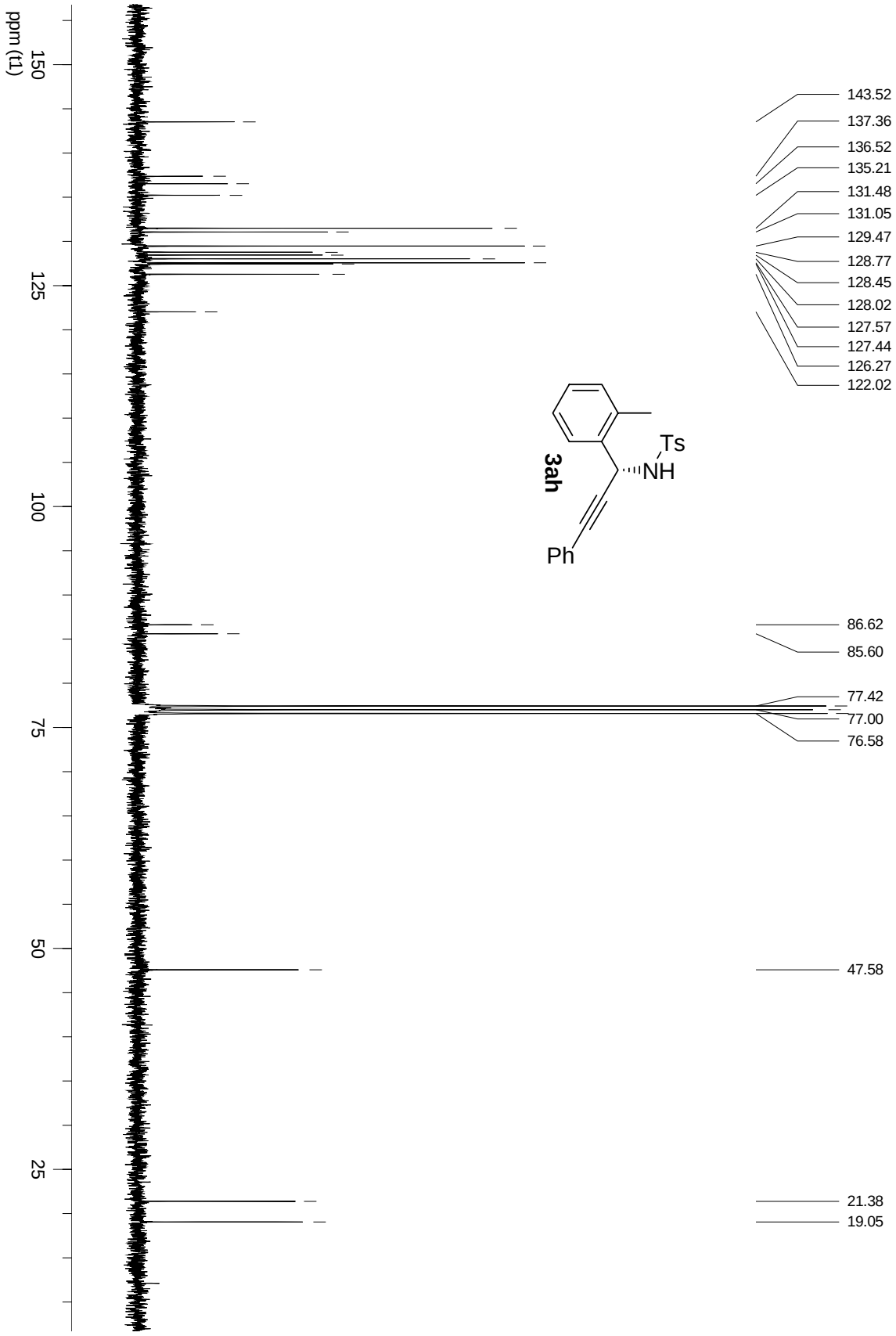


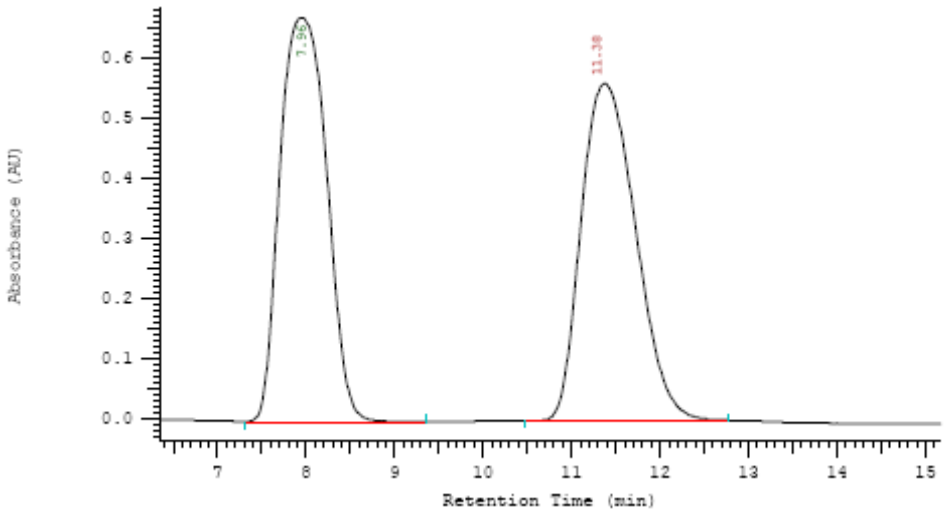
RT	Area	Area %
9.90	4206750	52.734
12.61	3770580	47.266
	7977330	100.000



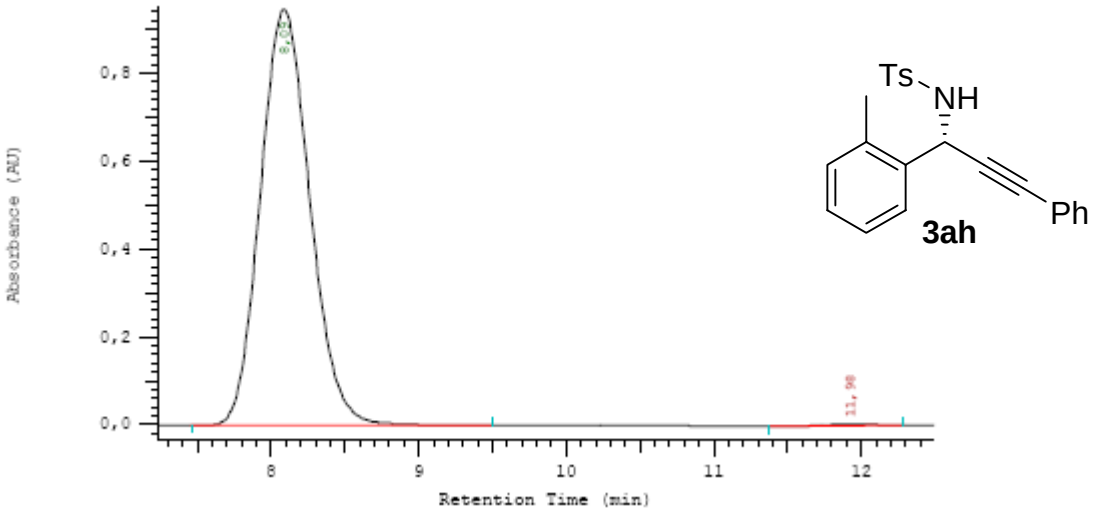
RT	Area	Area %
9,89	21647169	97,397
12,93	578515	2,603
	22225684	100,000


ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
2.0
1.0
8.2
2.0
1.0
1.0
3.1
3.1
7.824
7.796
7.591
7.585
7.561
7.286
7.268
7.263
7.256
7.251
7.237
7.232
7.216
7.200
7.190
7.180
7.172
7.077
7.072
7.057
7.050
7.045
5.715
5.685
4.746
4.717
2.493
2.283
3ah
Ts
NH
Ph


ppm (t1)
150
125
100
75
50
25
143.52
137.36
136.52
135.21
131.48
131.05
129.47
128.77
128.45
128.02
127.57
127.44
126.27
122.02
Ts
NH
3ah
Ph
86.62
85.60
77.42
77.00
76.58
47.58
21.38
19.05

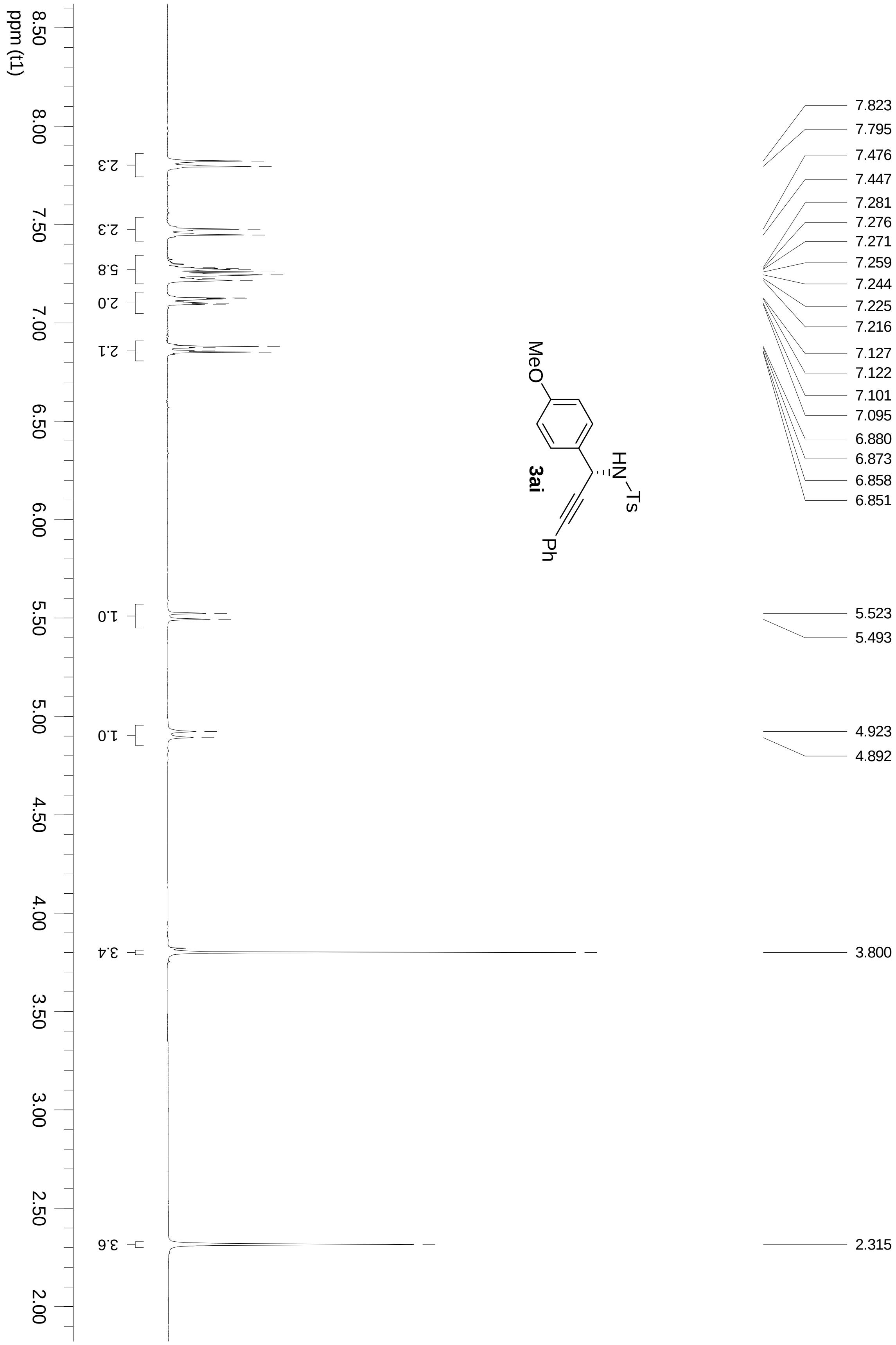


RT	Area	Area %
7.96	12242150	50.718
11.38	11895300	49.282
	24137450	100.000

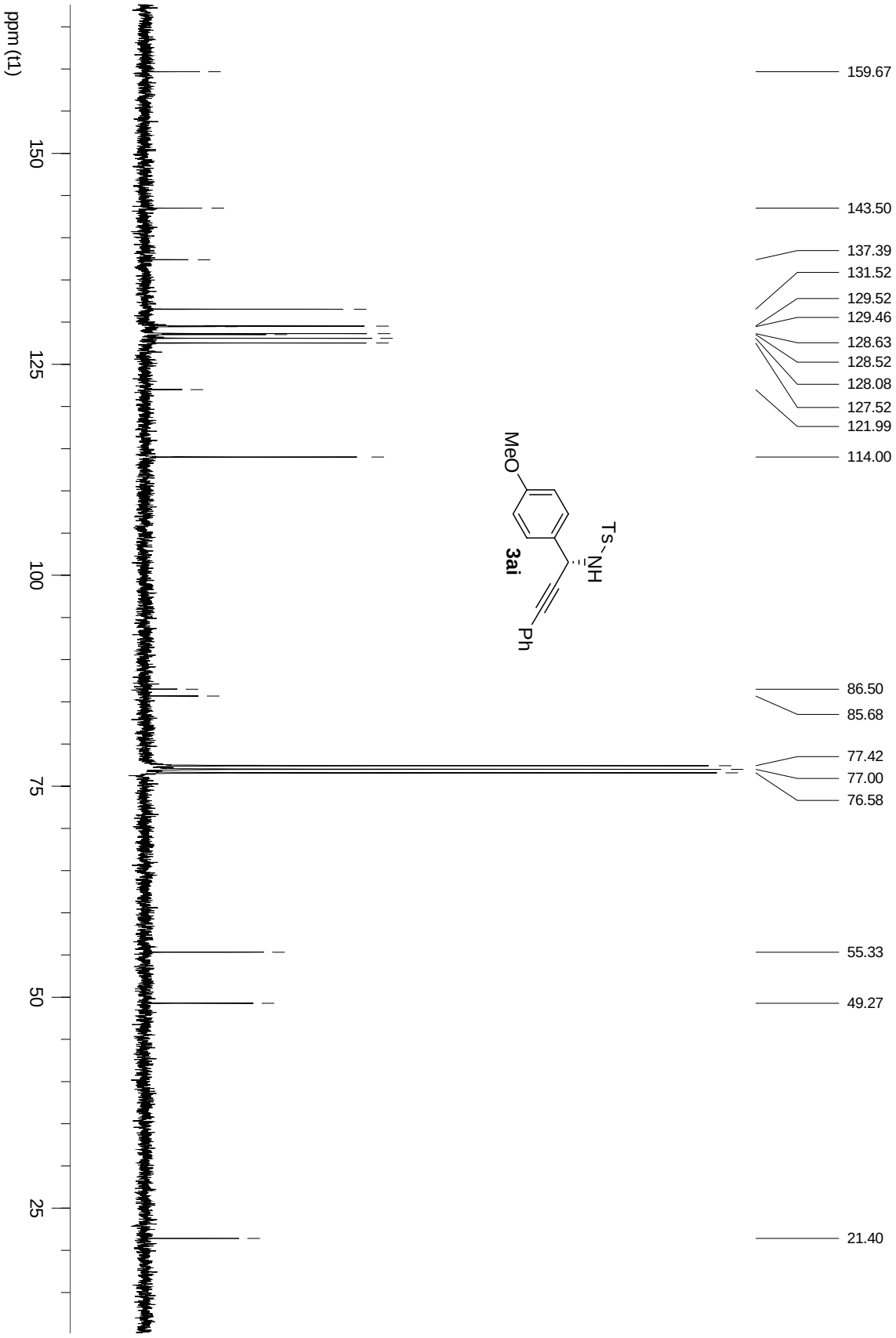


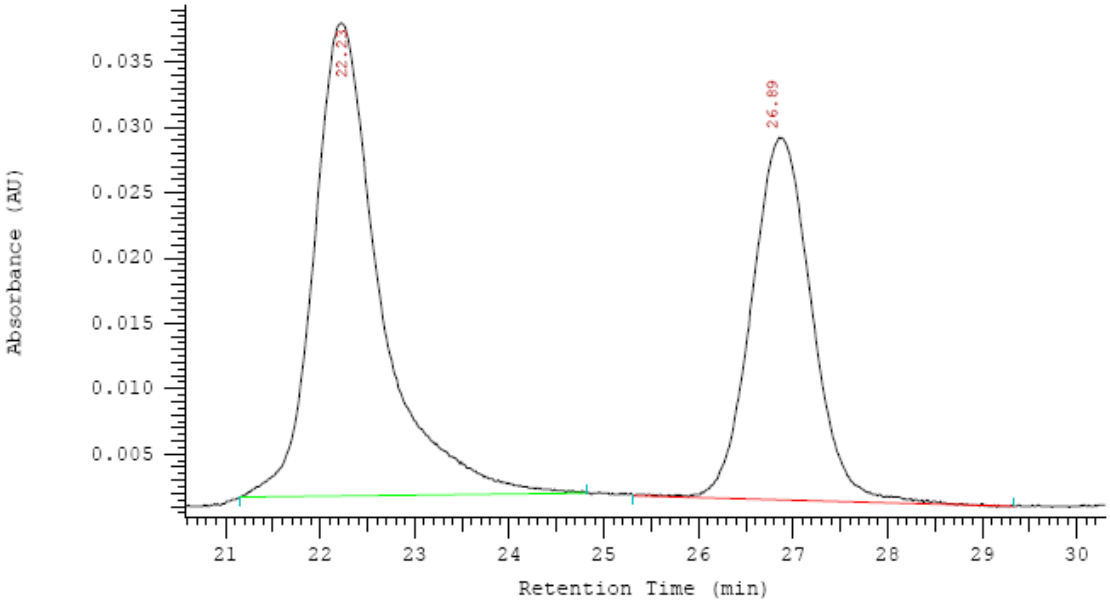
3ah

RT	Area	Area %
8,09	11028980	99,487
11,98	56875	0,513
	11085855	100,000

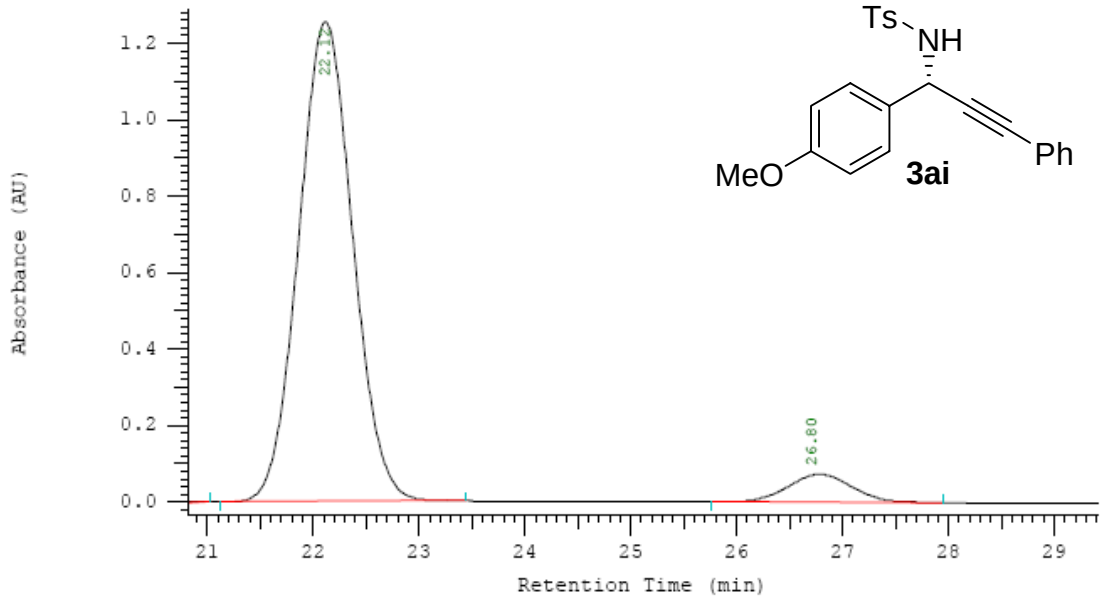


ppm (t1)
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
2.3
2.3
5.8
2.0
2.1
1.0
1.0
3.4
3.6
MeO
HN
Ts
Ph
3ai
7.823
7.795
7.476
7.447
7.281
7.276
7.271
7.259
7.244
7.225
7.216
7.127
7.122
7.101
7.095
6.880
6.873
6.858
6.851
5.523
5.493
4.923
4.892
3.800
2.315

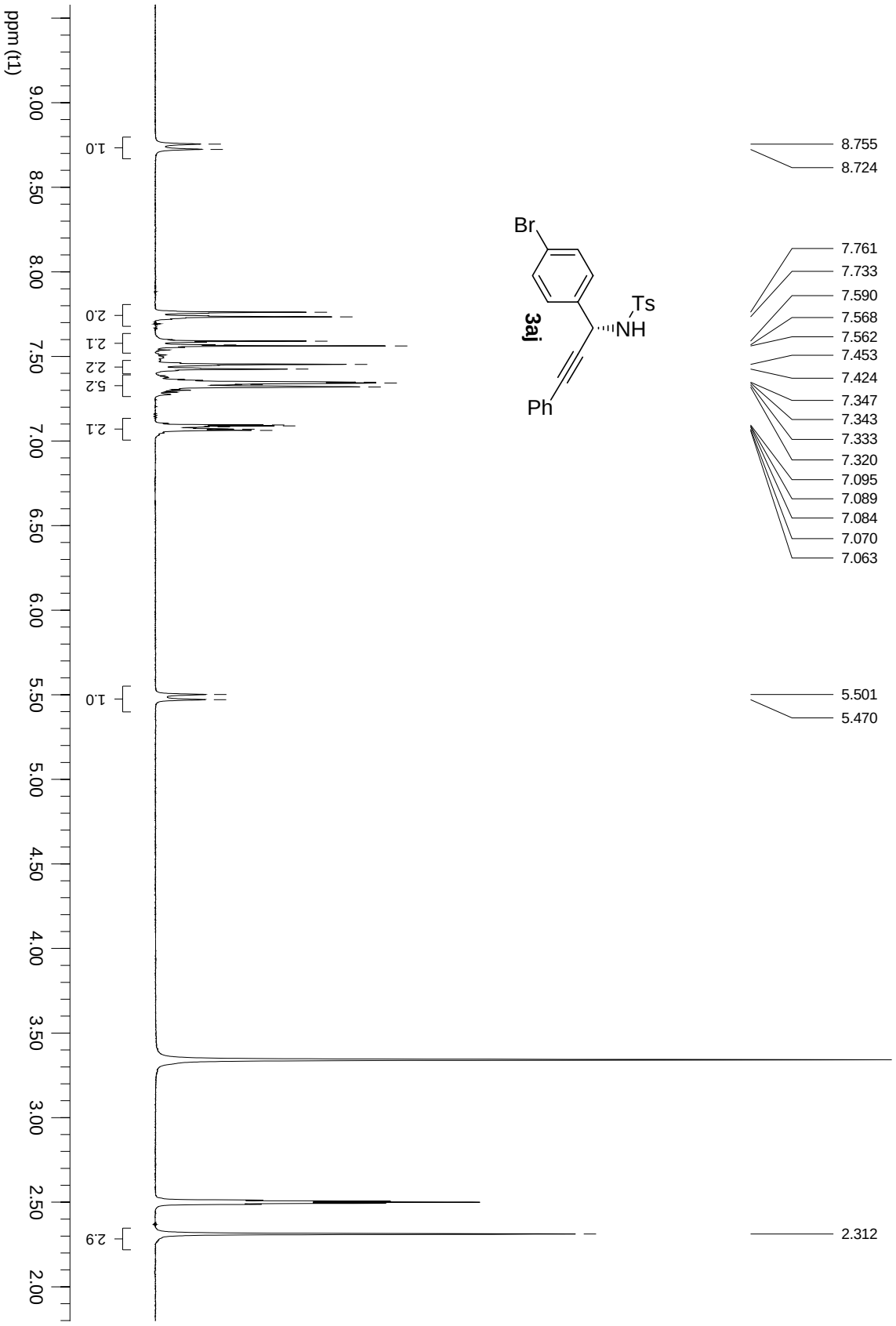

ppm (t1)
150
125
100
75
50
25
159.67
143.50
137.39
131.52
129.52
129.46
128.63
128.52
128.08
127.52
121.99
114.00
86.50
85.68
77.42
77.00
76.58
55.33
49.27
21.40
MeO
Ts
NH
Ph
3ai

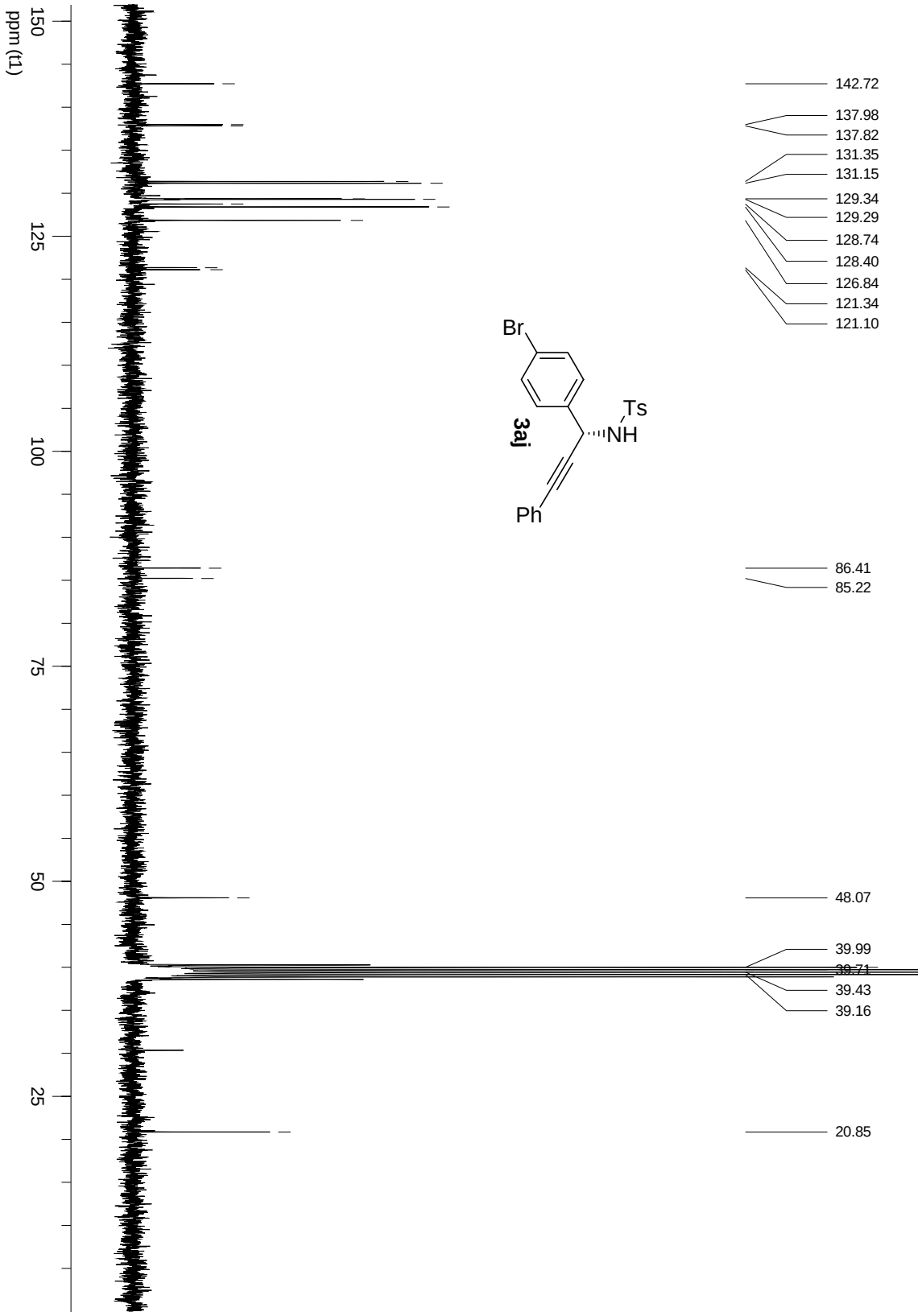


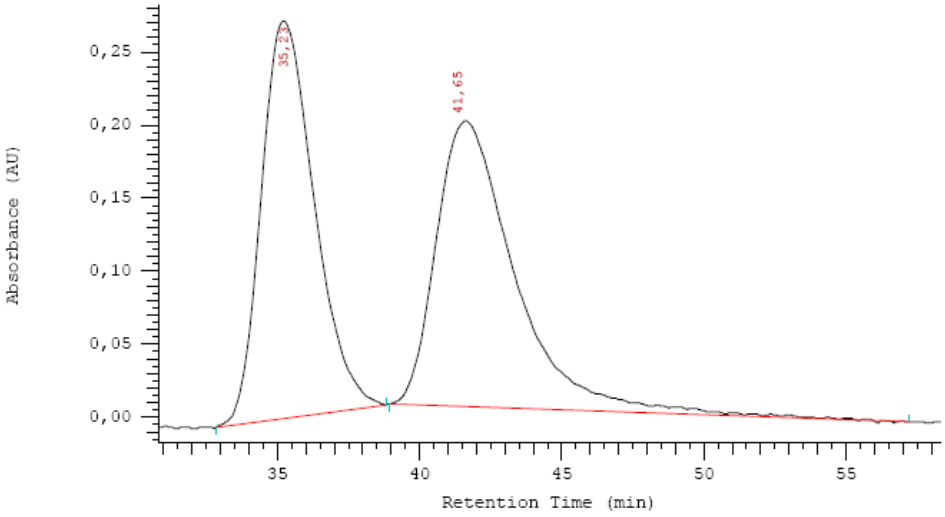
RT	Area	Area %
22.23	870970	58.987
26.89	605585	41.013
	1476555	100.000



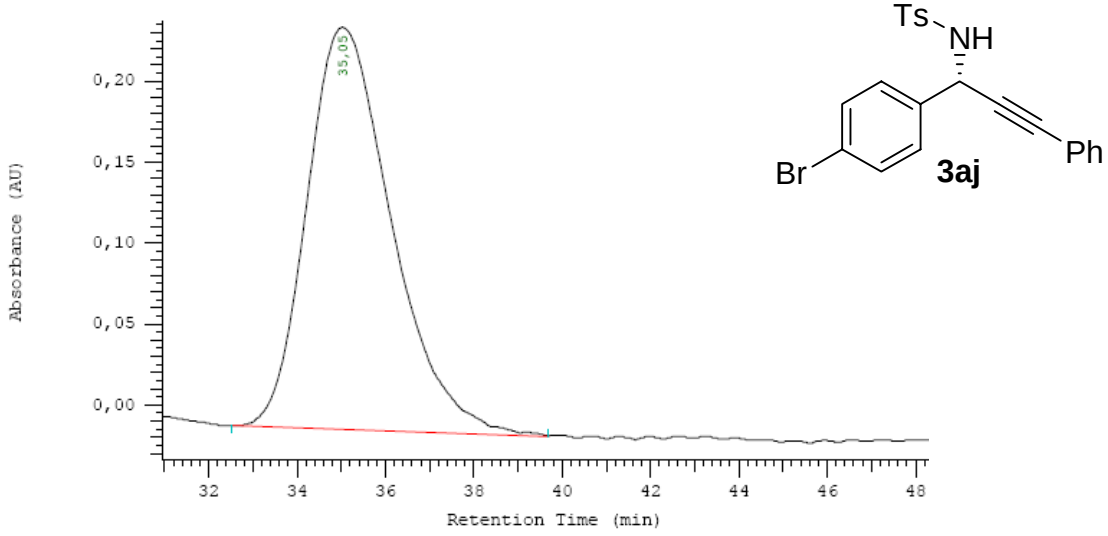
RT	Area	Area %
22.12	22080974	93.609
26.80	1507500	6.391
	23588474	100.000


ppm (t1)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.0
2.0
2.1
2.2
5.2
2.1
1.0
2.9
Br
Ts
NH
Ph
3aj
8.755
8.724
7.761
7.733
7.590
7.568
7.562
7.453
7.424
7.347
7.343
7.333
7.320
7.095
7.089
7.084
7.070
7.063
5.501
5.470
2.312


ppm (t1)
150
125
100
75
50
25
142.72
137.98
137.82
131.35
131.15
129.34
129.29
128.74
128.40
126.84
121.34
121.10
Br
Ts
NH
3aj
Ph
86.41
85.22
48.07
39.99
39.71
39.43
39.16
20.85

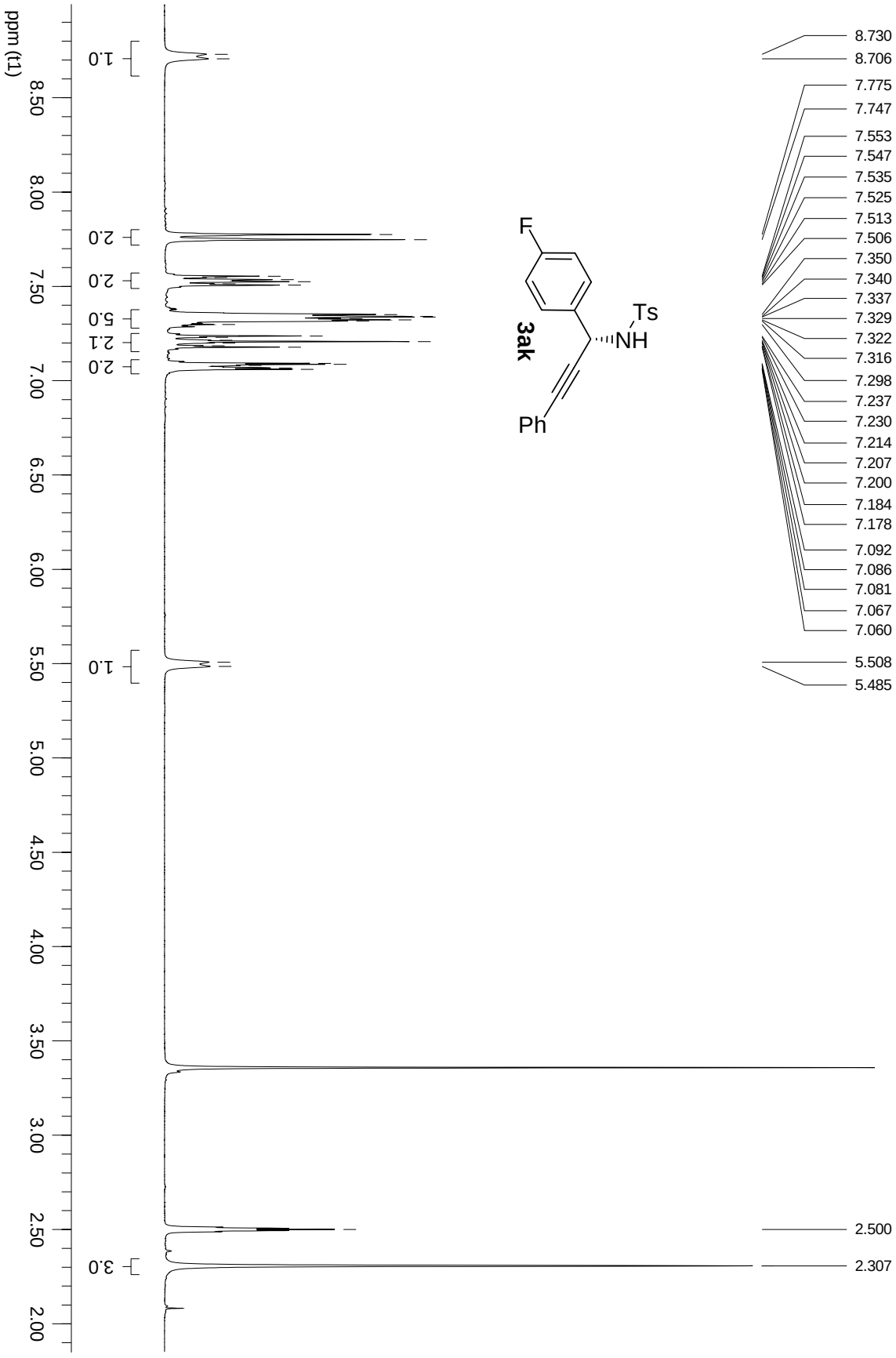


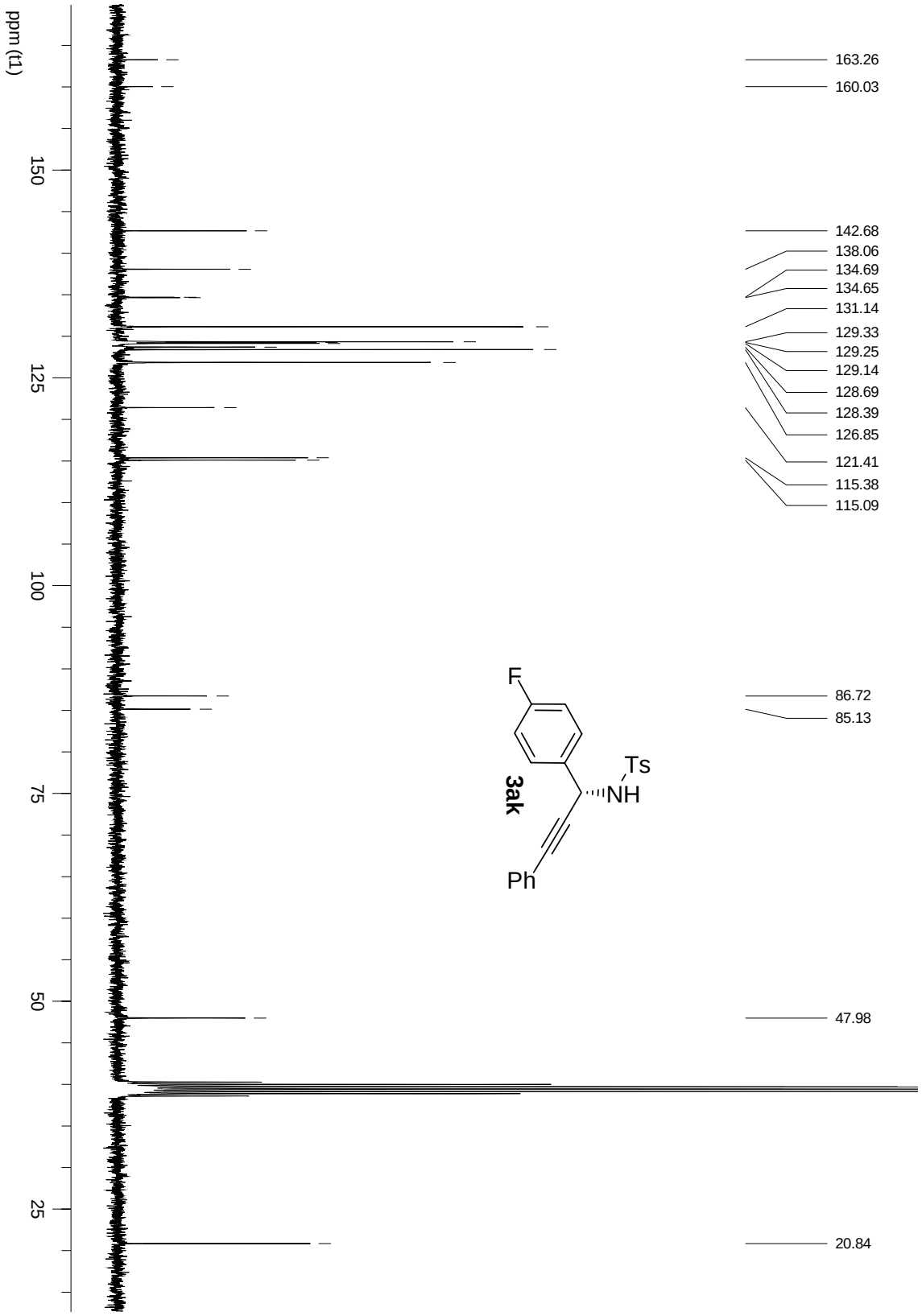
RT	Area	Area %
35,23	17363075	48,334
41,65	18560350	51,666
	35923425	100,000

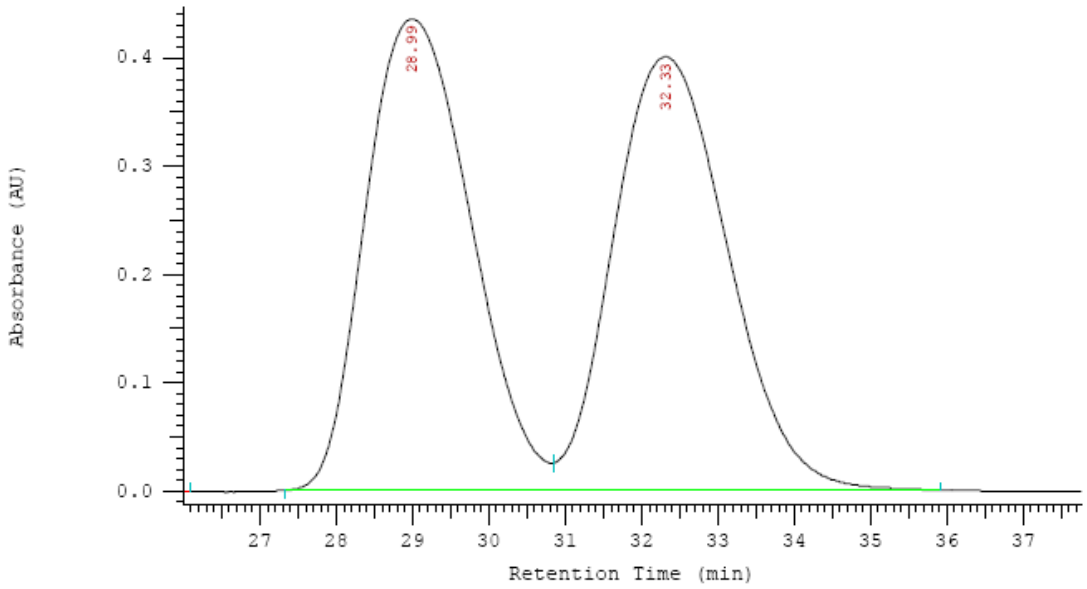


3aj

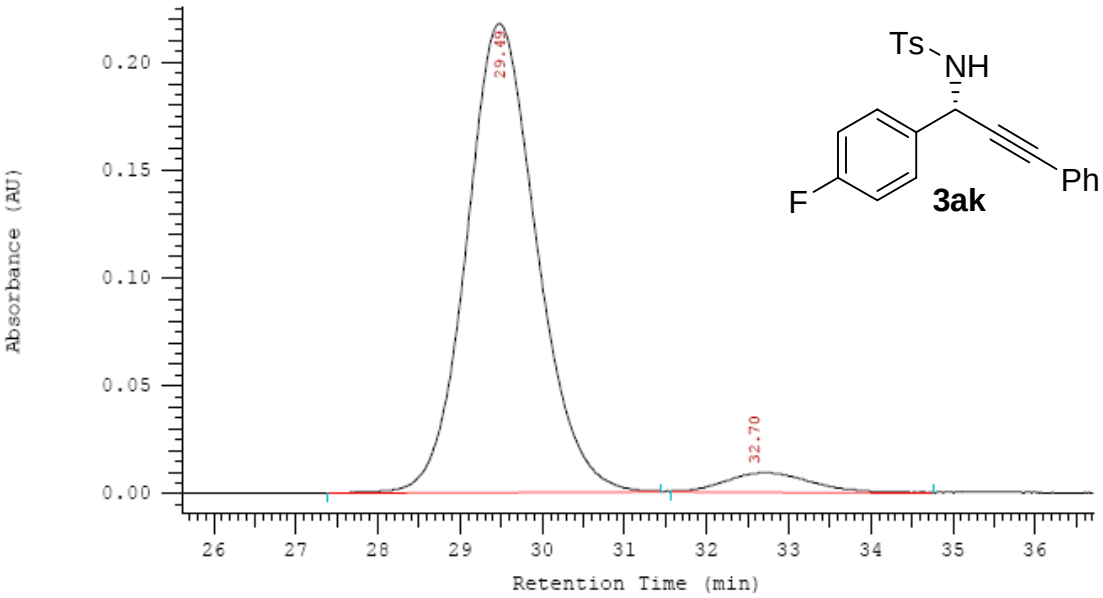
RT	Area	Area %
35,05	16392700	100,000
	16392700	100,000


ppm (t1)
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.0
2.0
2.0
5.0
2.1
2.0
1.0
3.0
F
Ts
NH
Ph
3ak
8.730
8.706
7.775
7.747
7.553
7.547
7.535
7.525
7.513
7.506
7.350
7.340
7.337
7.329
7.322
7.316
7.298
7.237
7.230
7.214
7.207
7.200
7.184
7.178
7.092
7.086
7.081
7.067
7.060
5.508
5.485
2.500
2.307

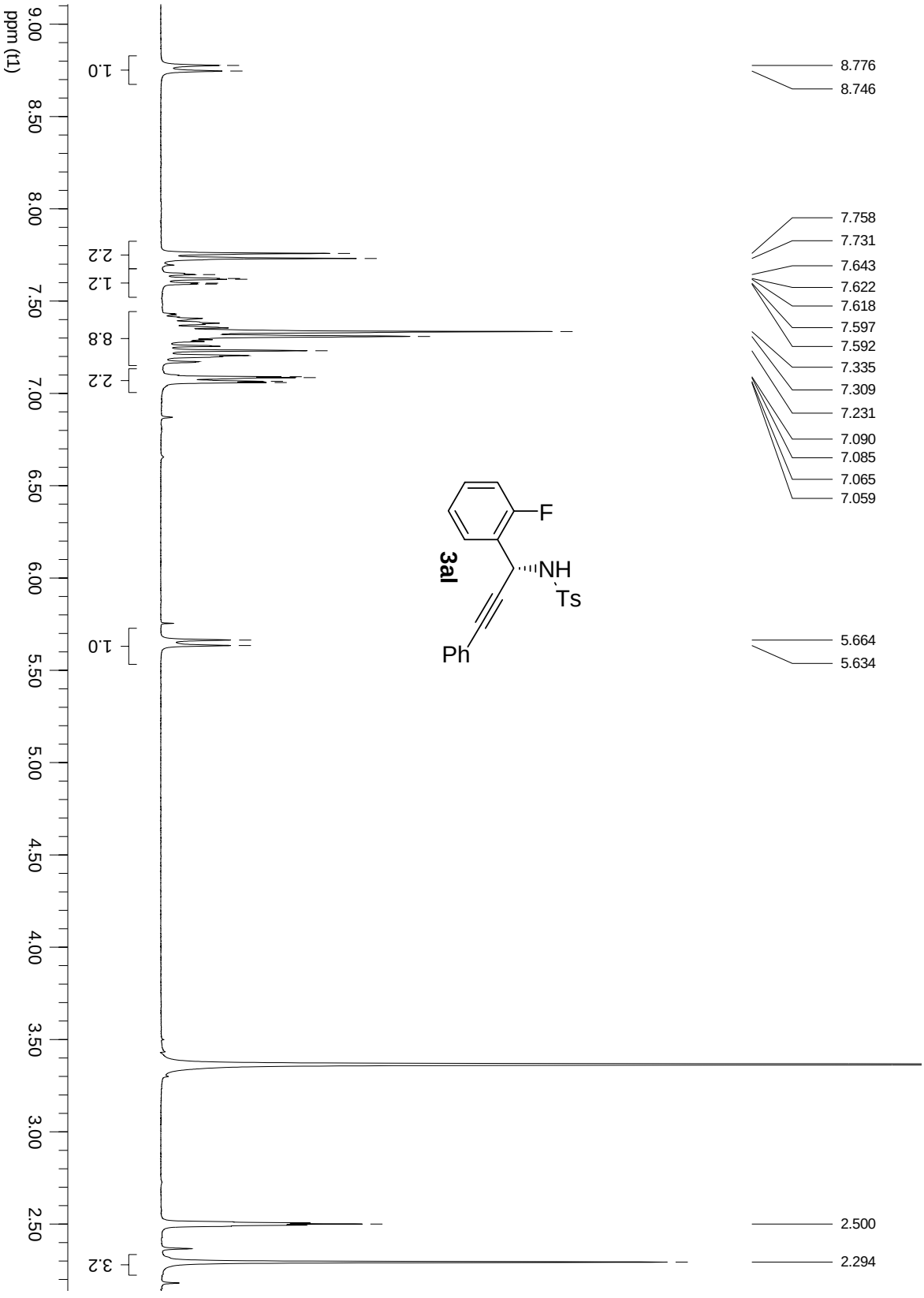

ppm (t1)
150
125
100
75
50
25
163.26
160.03
142.68
138.06
134.69
134.65
131.14
129.33
129.25
129.14
128.69
128.39
126.85
121.41
115.38
115.09
86.72
85.13
47.98
20.84
F
Ts
NH
Ph
3ak

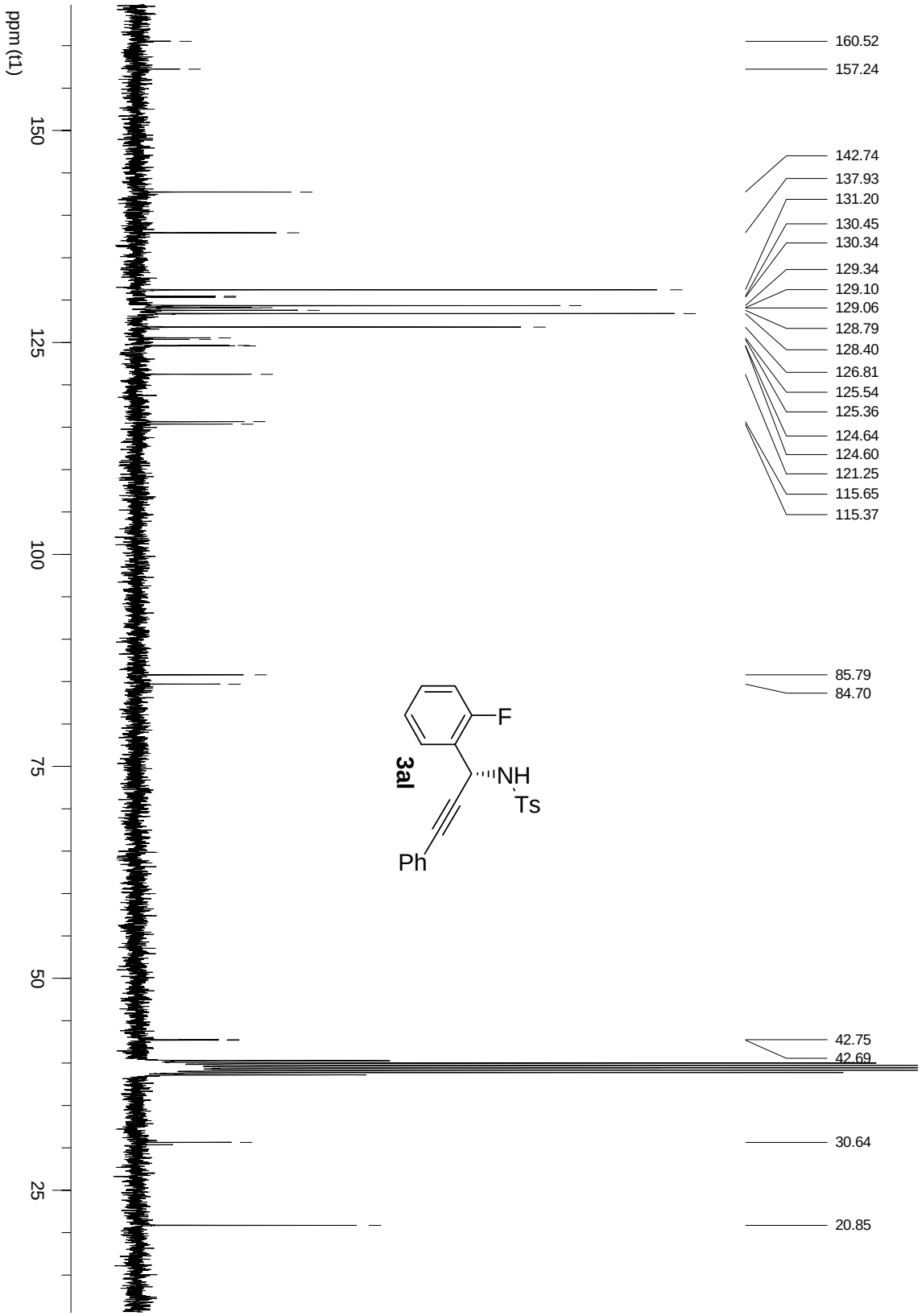


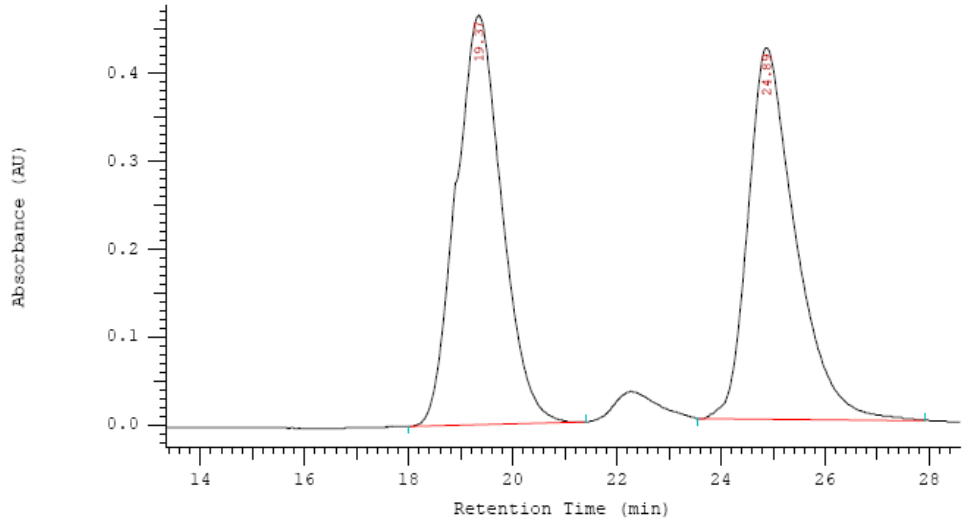
RT	Area	Area %
28.99	20771416	49.869
32.33	20880395	50.131
	41651811	100.000



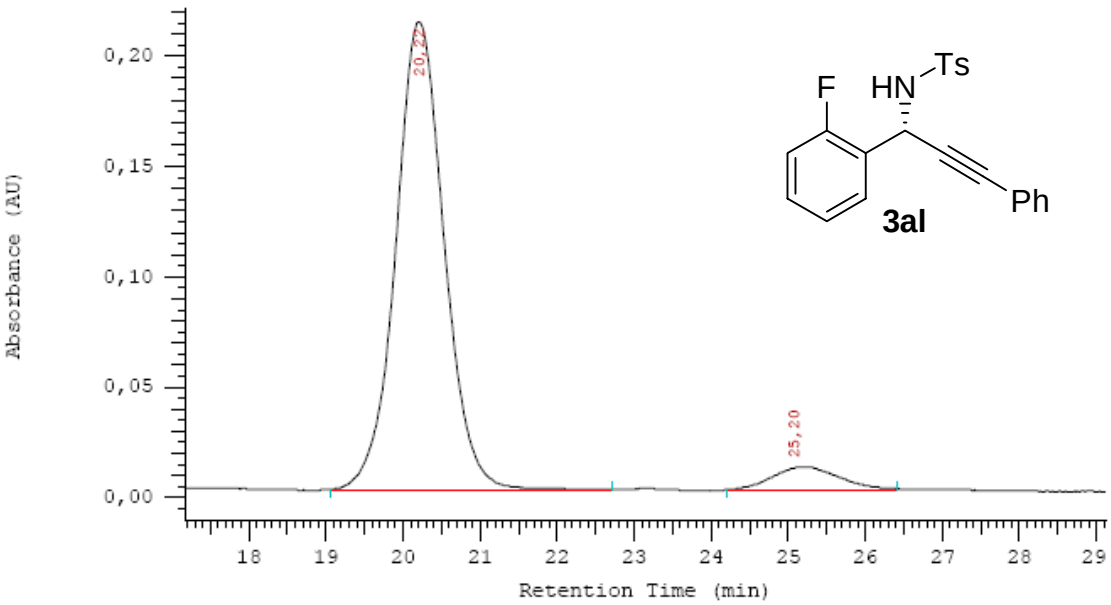
RT	Area	Area %
29.49	6383750	95.355
32.70	310970	4.645
	6694720	100.000


ppm (t1)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
1.0
2.2
1.2
8.8
2.2
1.0
3.2
8.776
8.746
7.758
7.731
7.643
7.622
7.618
7.597
7.592
7.335
7.309
7.231
7.090
7.085
7.065
7.059
5.664
5.634
2.500
2.294
3al
F
NH
Ts
Ph

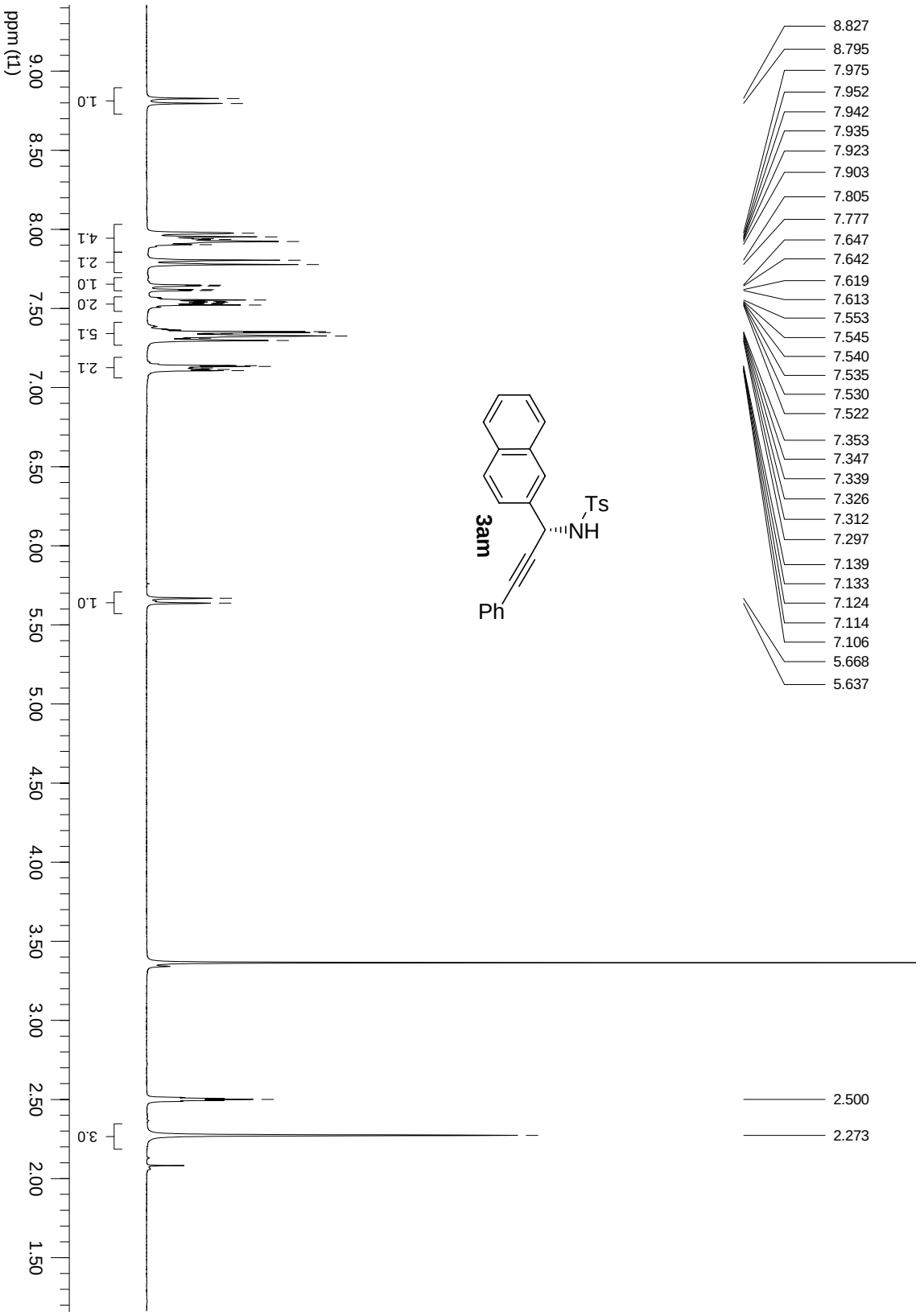

ppm (t1)
150
125
100
75
50
25
160.52
157.24
142.74
137.93
131.20
130.45
130.34
129.34
129.10
129.06
128.79
128.40
126.81
125.54
125.36
124.64
124.60
121.25
115.65
115.37
85.79
84.70
42.75
42.69
30.64
20.85
F
NH
Ts
Ph
3al

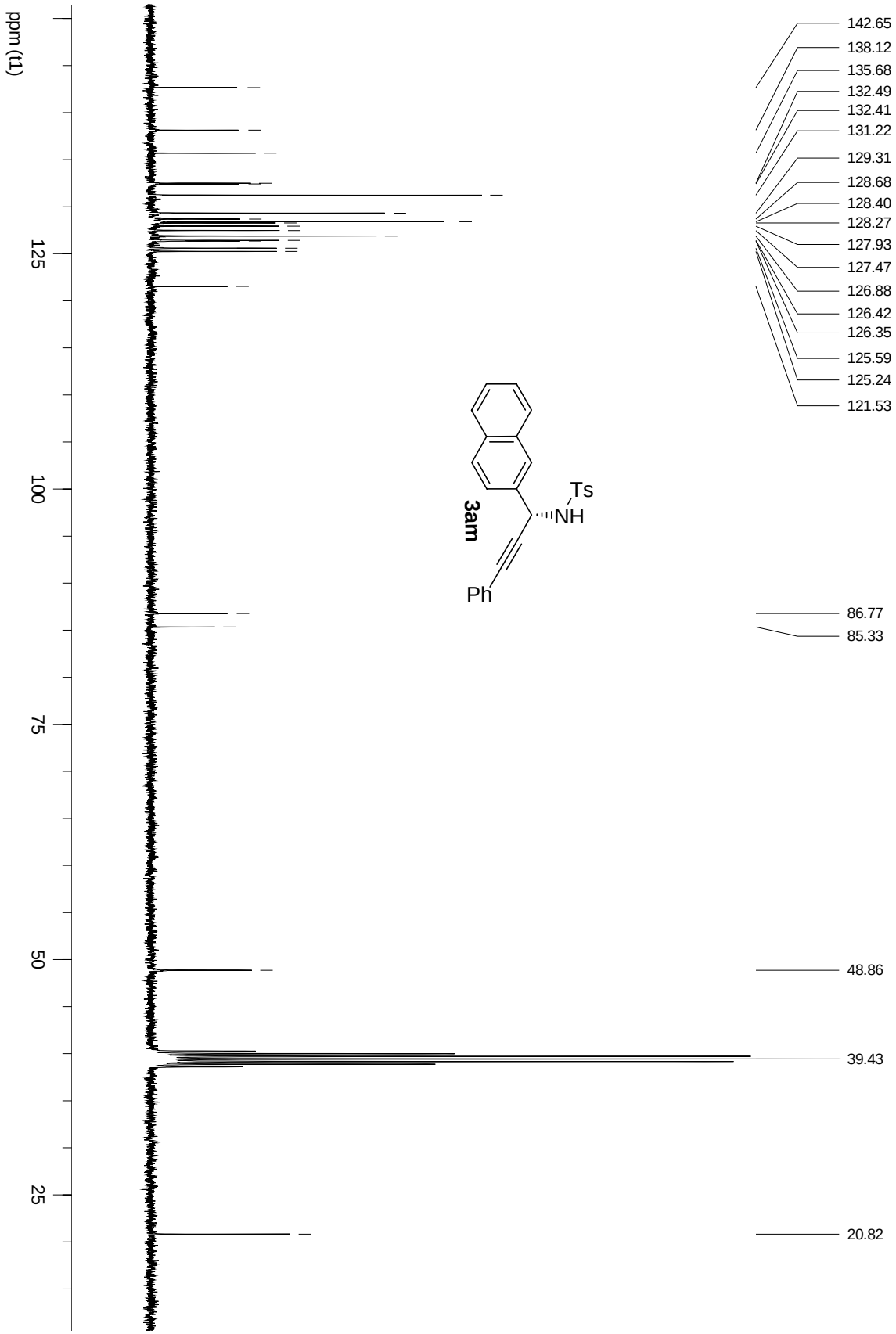


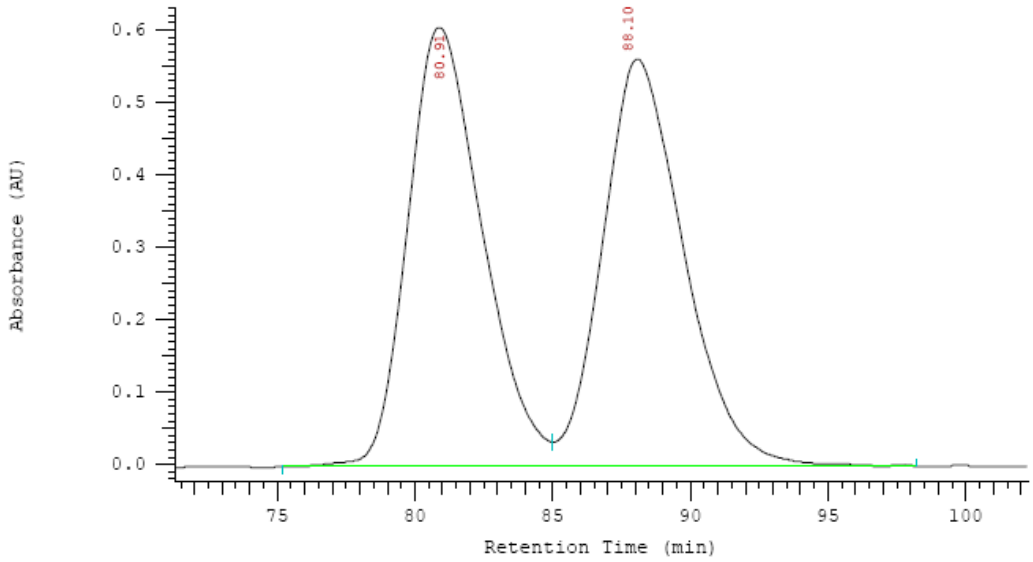
RT	Area	Area %
19.36	5541715	51.724
24.89	5172340	48.276
	10714055	100.000



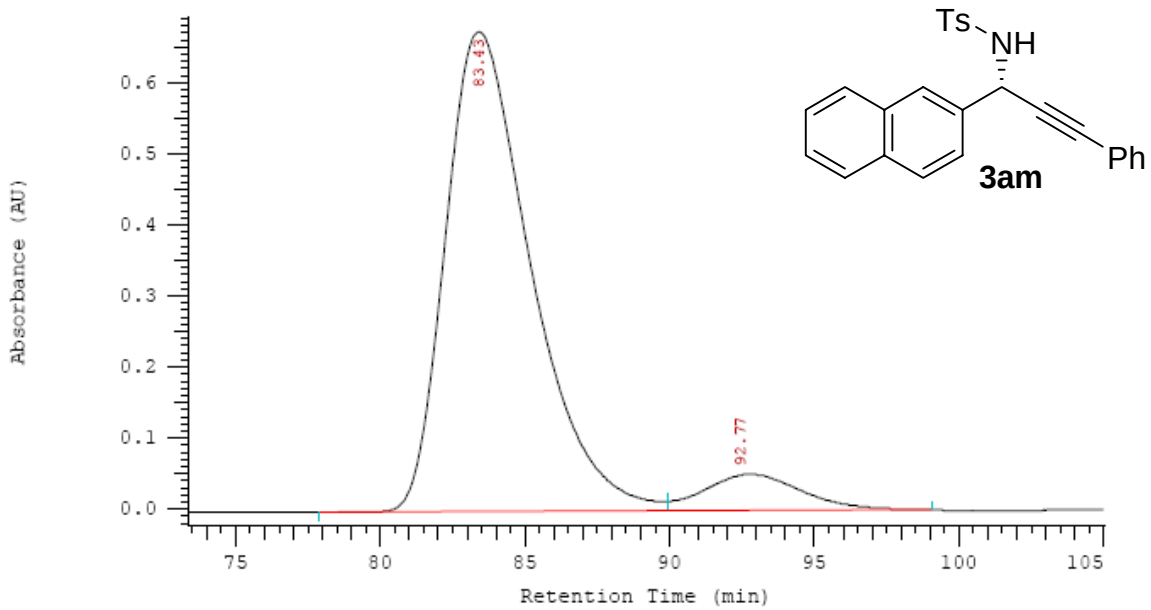
RT	Area	Area %
20,22	4557400	93,800
25,20	301240	6,200
	4858640	100,000


ppm (t1)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.0
4.1
2.1
1.0
2.0
5.1
2.1
1.0
3.0
3am
Ts
NH
Ph
8.827
8.795
7.975
7.952
7.942
7.935
7.923
7.903
7.805
7.777
7.647
7.642
7.619
7.613
7.553
7.545
7.540
7.535
7.530
7.522
7.353
7.347
7.339
7.326
7.312
7.297
7.139
7.133
7.124
7.114
7.106
5.668
5.637
2.500
2.273

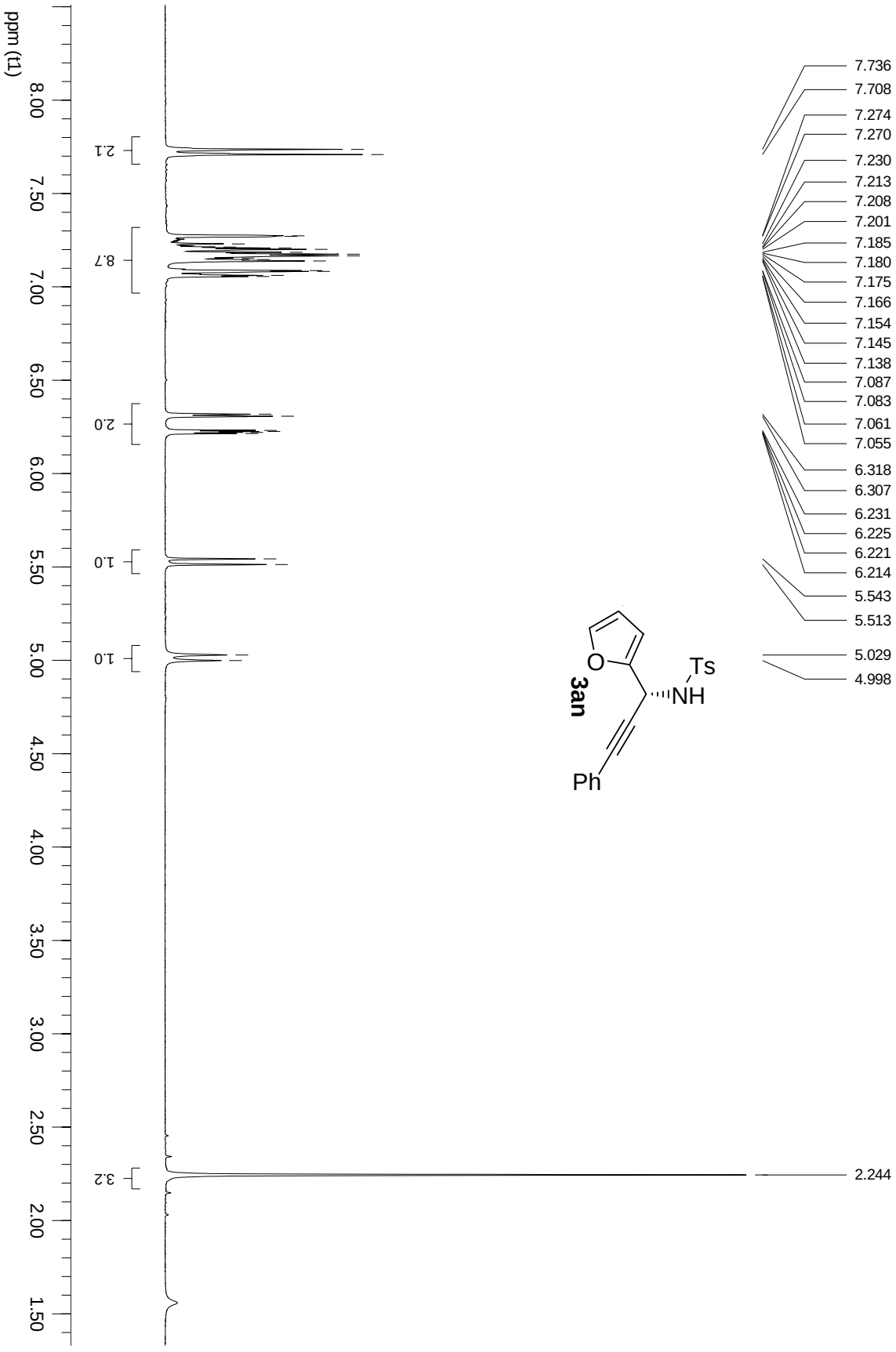

ppm (t1)
125
100
75
50
25
142.65
138.12
135.68
132.49
132.41
131.22
129.31
128.68
128.40
128.27
127.93
127.47
126.88
126.42
126.35
125.59
125.24
121.53
Ts
NH
3am
Ph
86.77
85.33
48.86
39.43
20.82

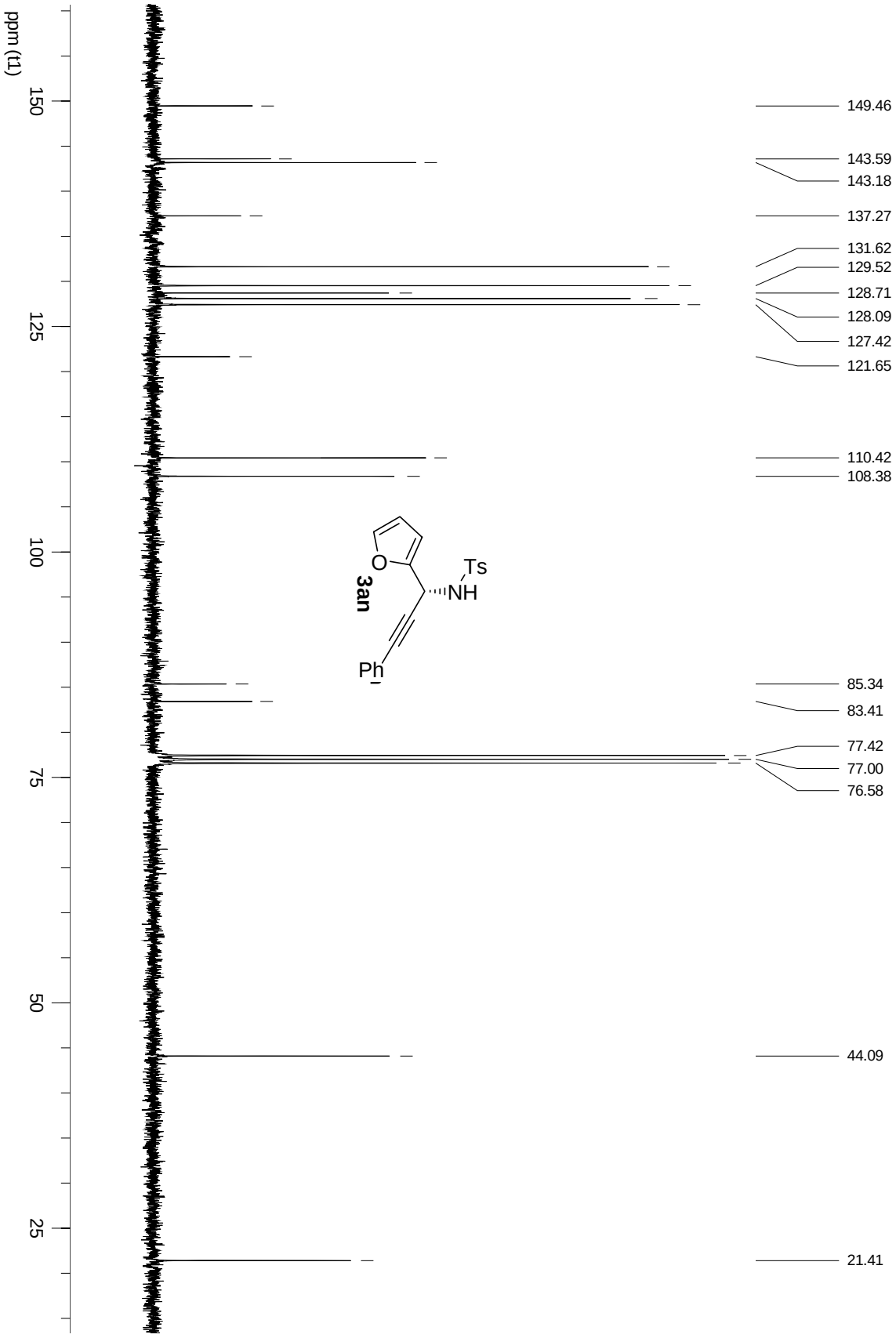


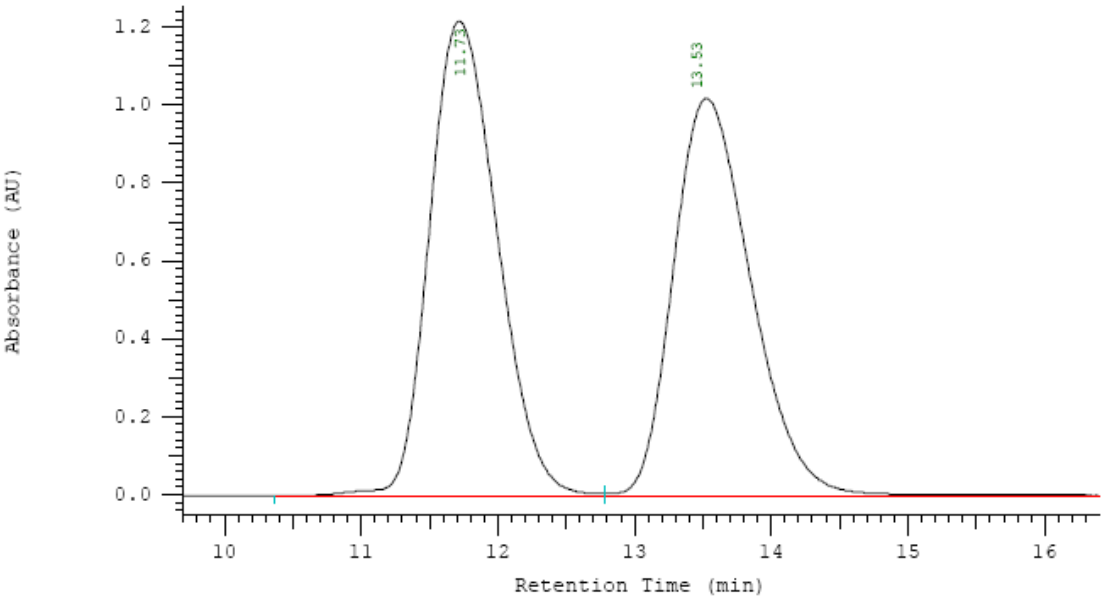
RT	Area	Area %
80.91	54929900	49.578
88.10	55865056	50.422
	1.107E+08	100.000



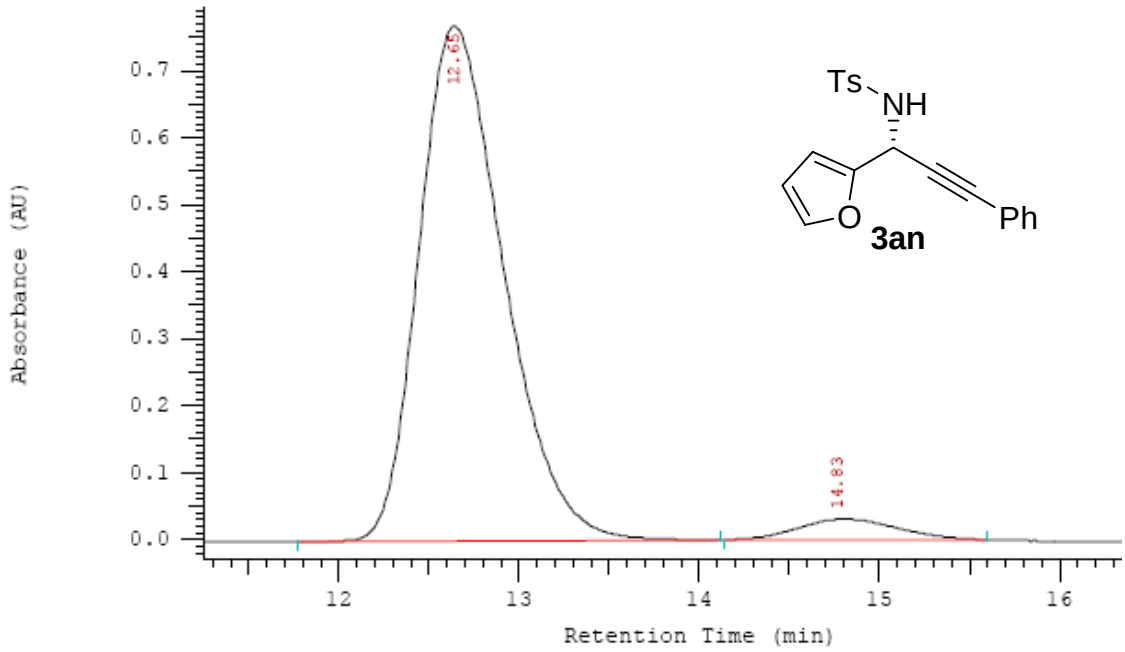
RT	Area	Area %
83.43	68397184	92.026
92.77	5926573	7.974
	74323757	100.000


ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
2.1
8.7
2.0
1.0
1.0
3.2
7.736
7.708
7.274
7.270
7.230
7.213
7.208
7.201
7.185
7.180
7.175
7.166
7.154
7.145
7.138
7.087
7.083
7.061
7.055
6.318
6.307
6.231
6.225
6.221
6.214
5.543
5.513
5.029
4.998
2.244
O
Ts
NH
Ph
3an

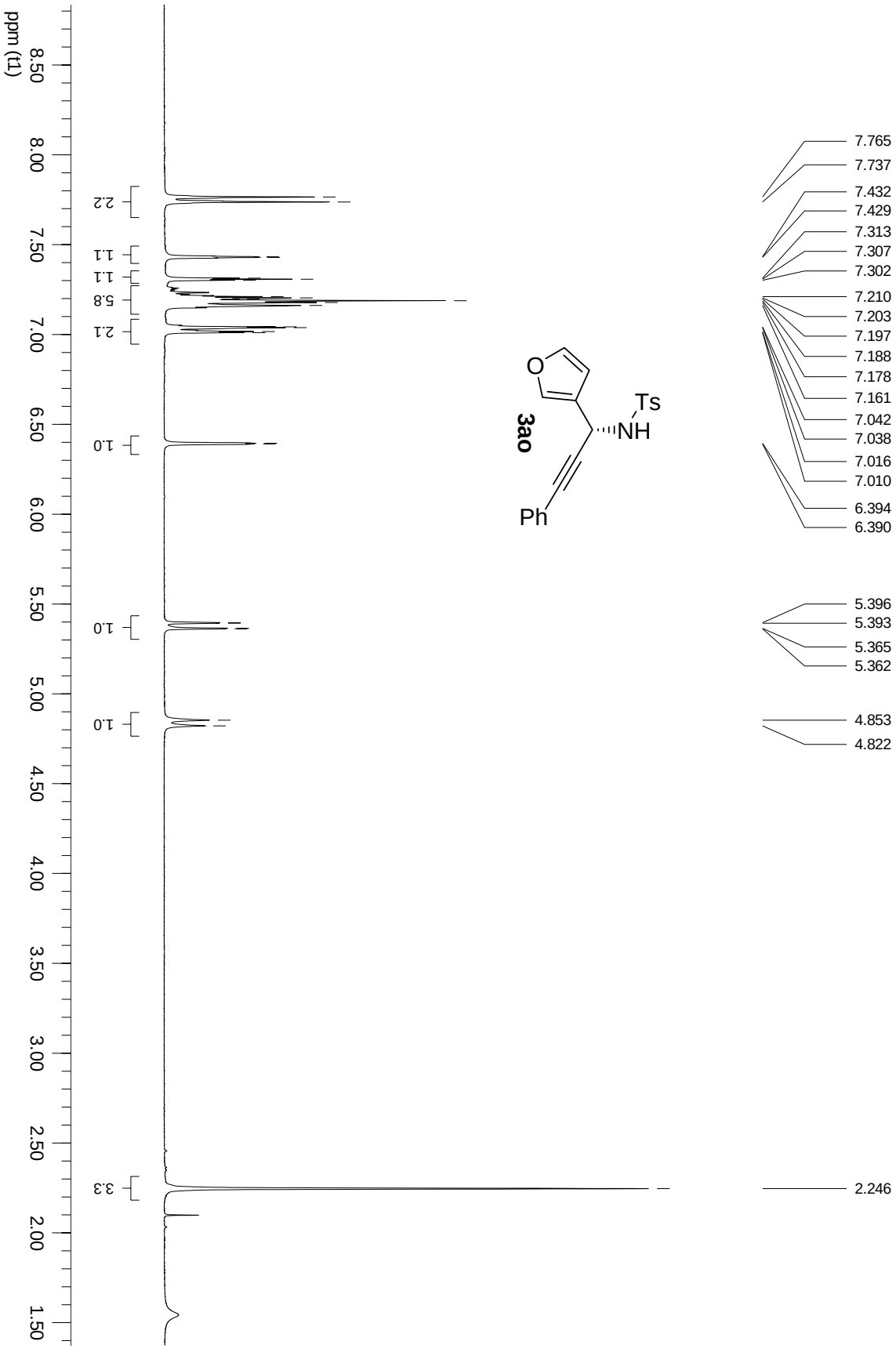

ppm (t1)
150
125
100
75
50
25
149.46
143.59
143.18
137.27
131.62
129.52
128.71
128.09
127.42
121.65
110.42
108.38
85.34
83.41
77.42
77.00
76.58
44.09
21.41
O
Ts
NH
3an
Ph

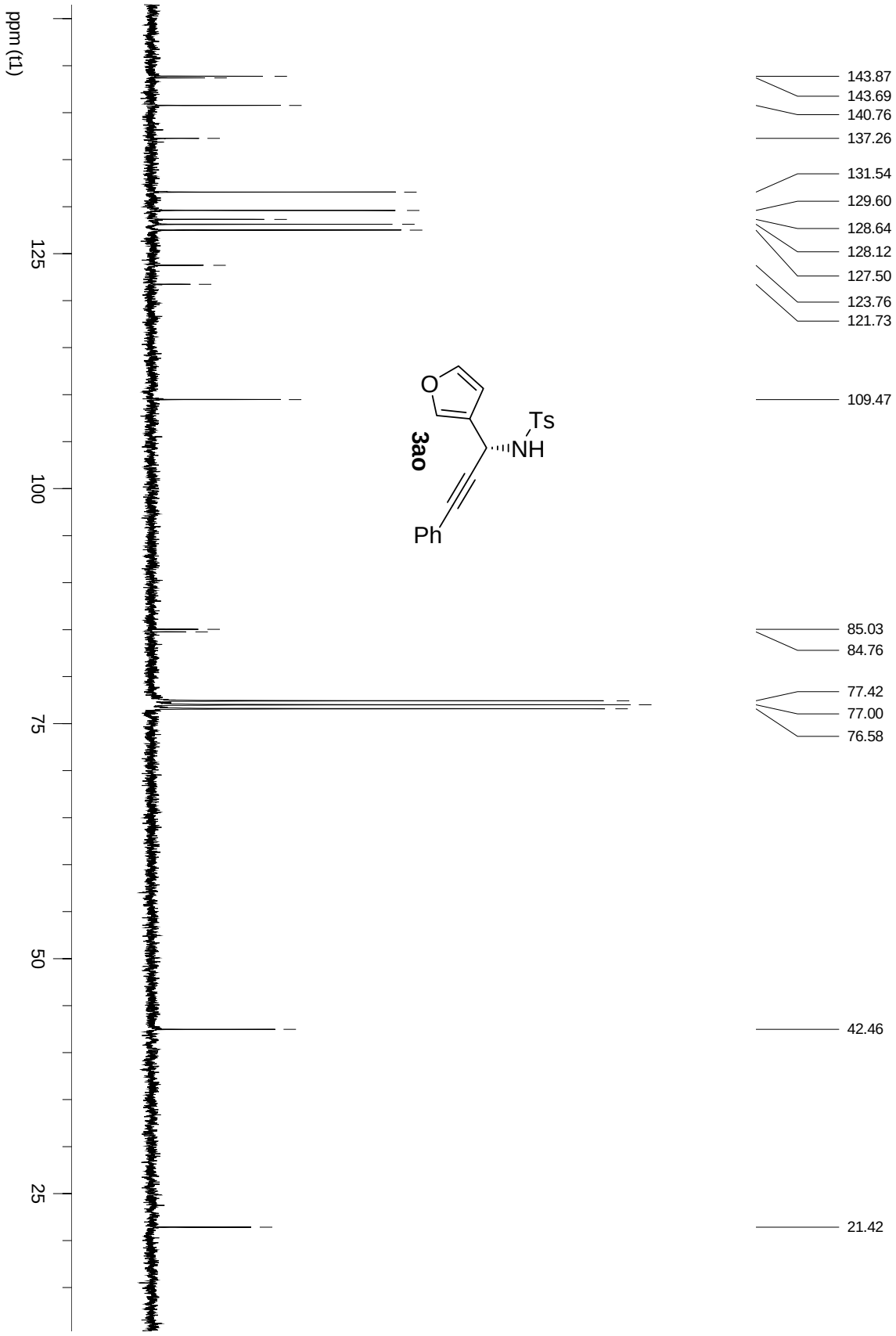


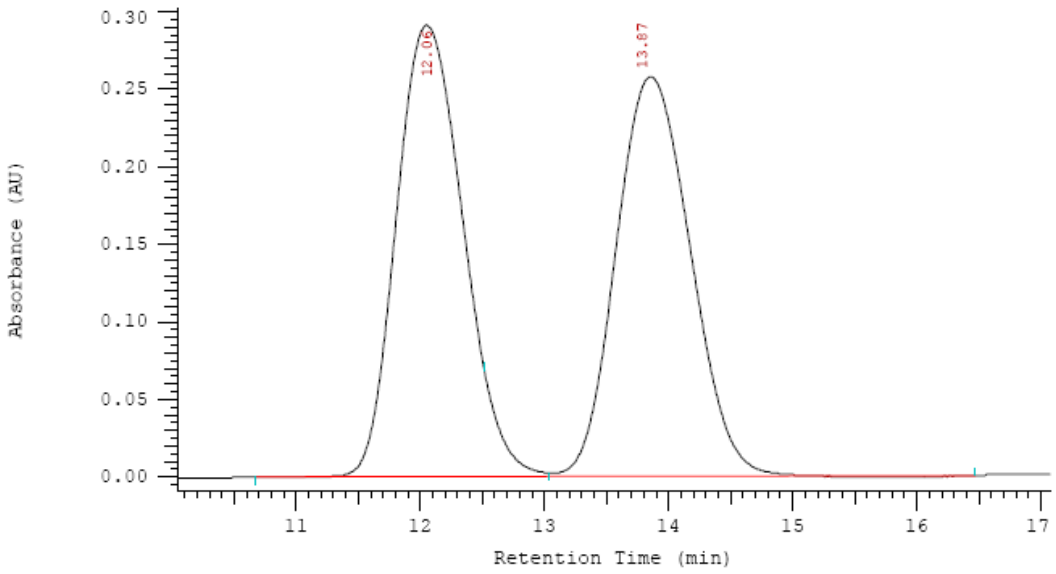
RT	Area	Area %
11.73	20897870	51.115
13.53	19986470	48.885
	40884340	100.000



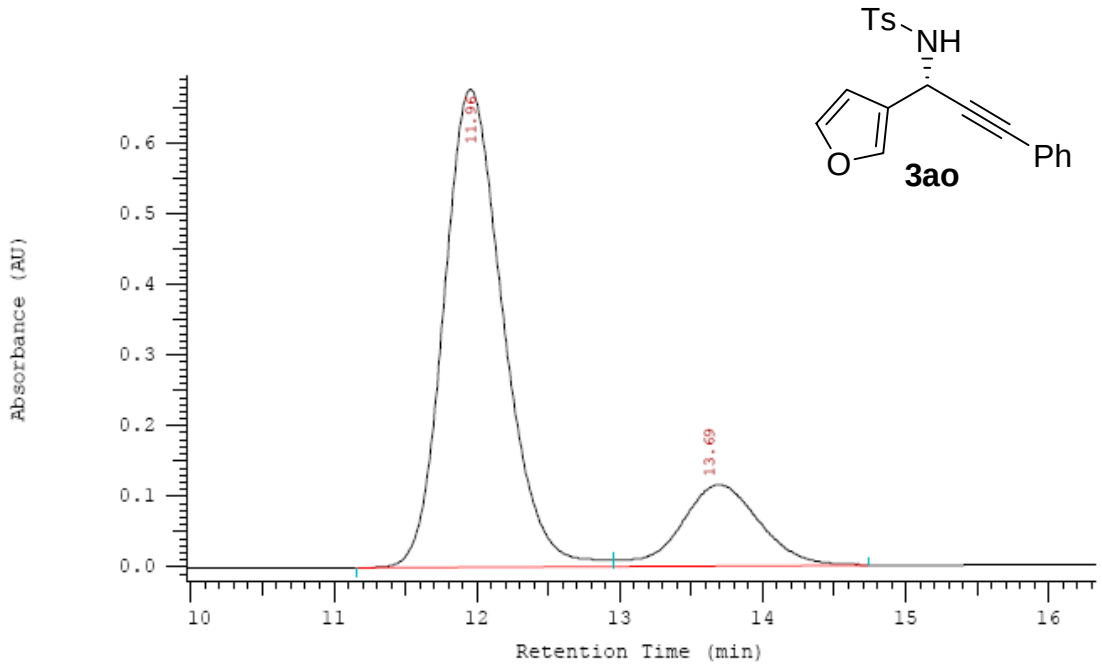
RT	Area	Area %
12.65	12502089	95.418
14.83	600325	4.582
	13102414	100.000


ppm (t1)
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
2.2
1.1
1.1
5.8
2.1
1.0
1.0
1.0
3.3
3ao
O
Ts
NH
Ph
7.765
7.737
7.432
7.429
7.313
7.307
7.302
7.210
7.203
7.197
7.188
7.178
7.161
7.042
7.038
7.016
7.010
6.394
6.390
5.396
5.393
5.365
5.362
4.853
4.822
2.246


ppm (t1)
125
100
75
50
25
143.87
143.69
140.76
137.26
131.54
129.60
128.64
128.12
127.50
123.76
121.73
109.47
85.03
84.76
77.42
77.00
76.58
42.46
21.42
O
Ts
NH
Ph
3ao

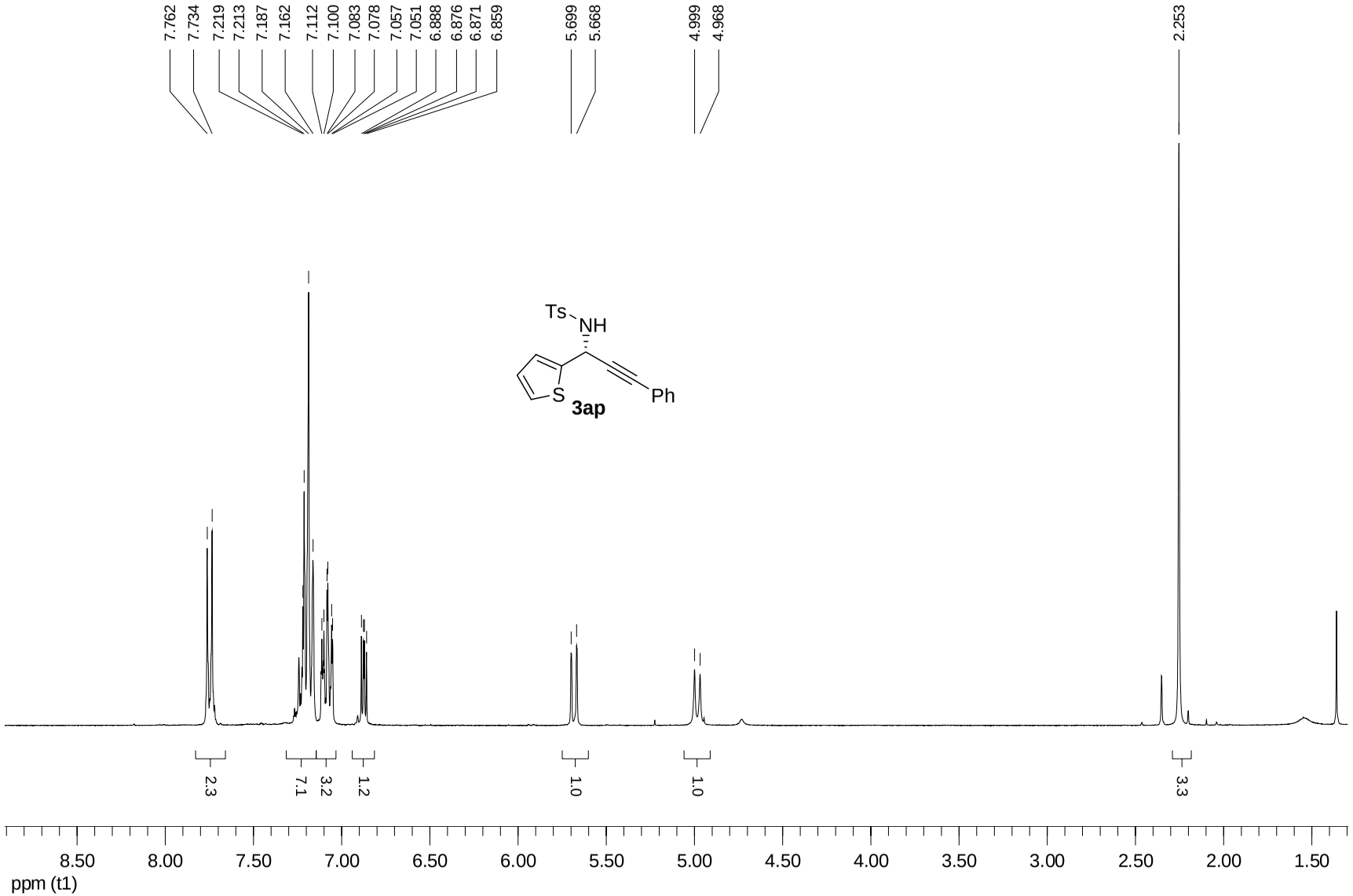


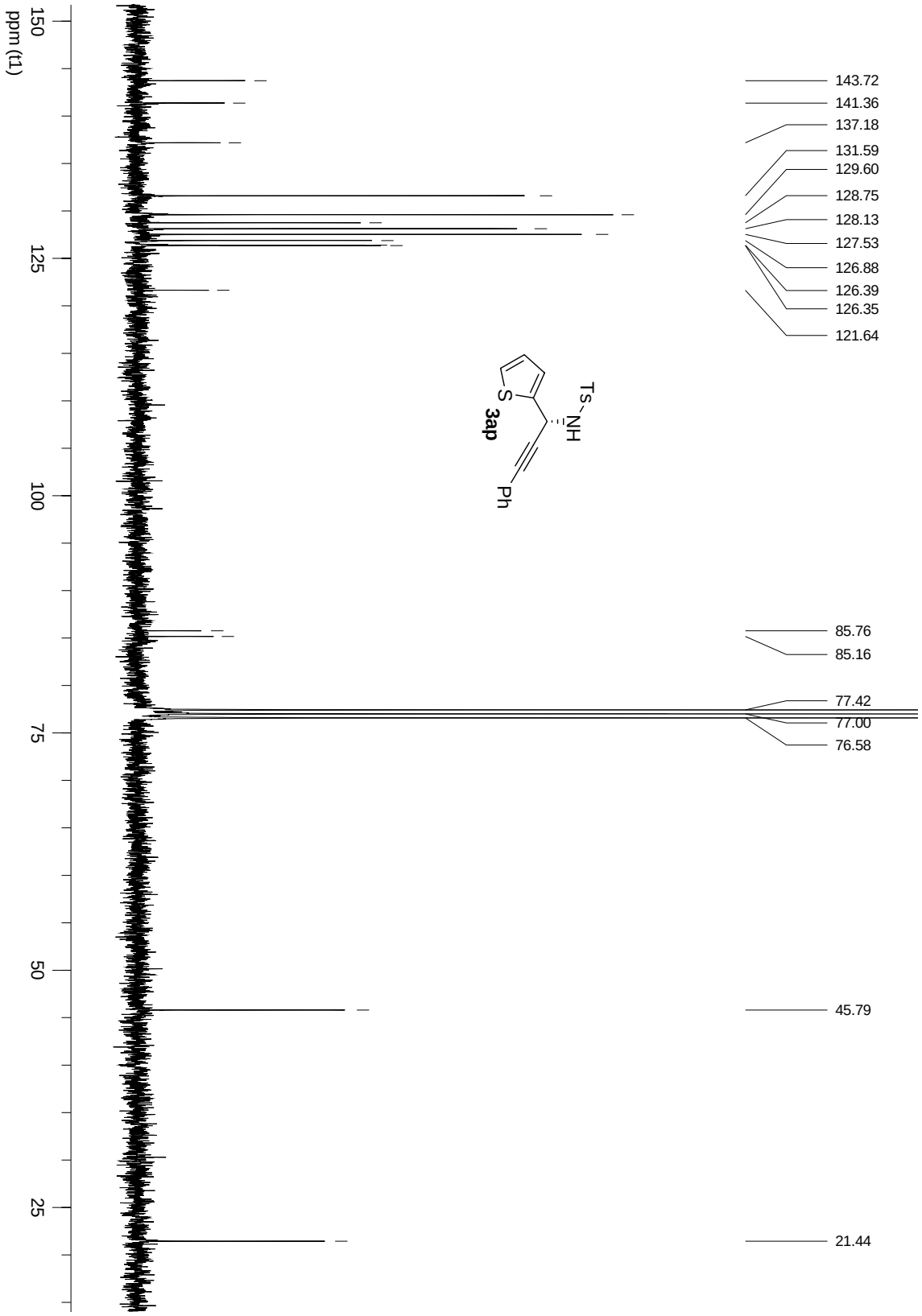
RT	Area	Area %
12.06	5108140	49.105
13.87	5294297	50.895
	10402437	100.000

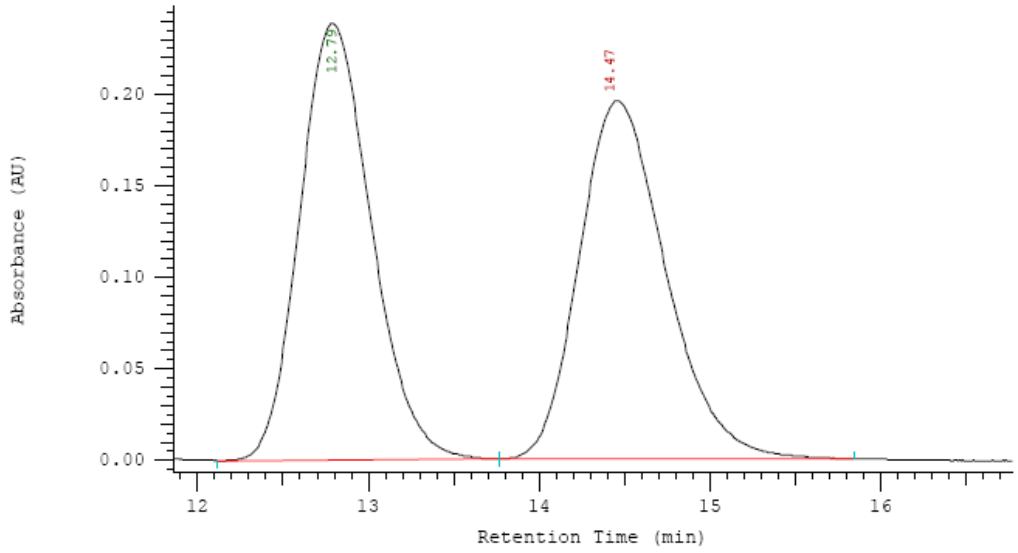


3ao

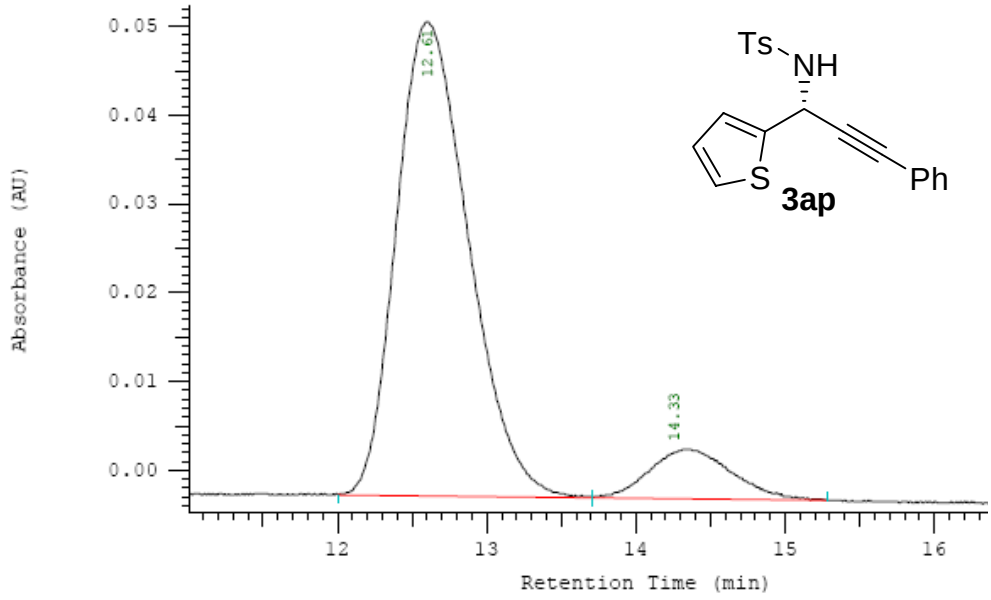
RT	Area	Area %
11.96	9689202	81.797
13.69	2156287	18.203
	11845489	100.000


7.762
7.734
7.219
7.213
7.187
7.162
7.112
7.100
7.083
7.078
7.057
7.051
6.888
6.876
6.871
6.859
5.699
5.668
4.999
4.968
2.253
Ts
NH
S
Ph
3ap
2.3
7.1
3.2
1.2
1.0
1.0
3.3
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)

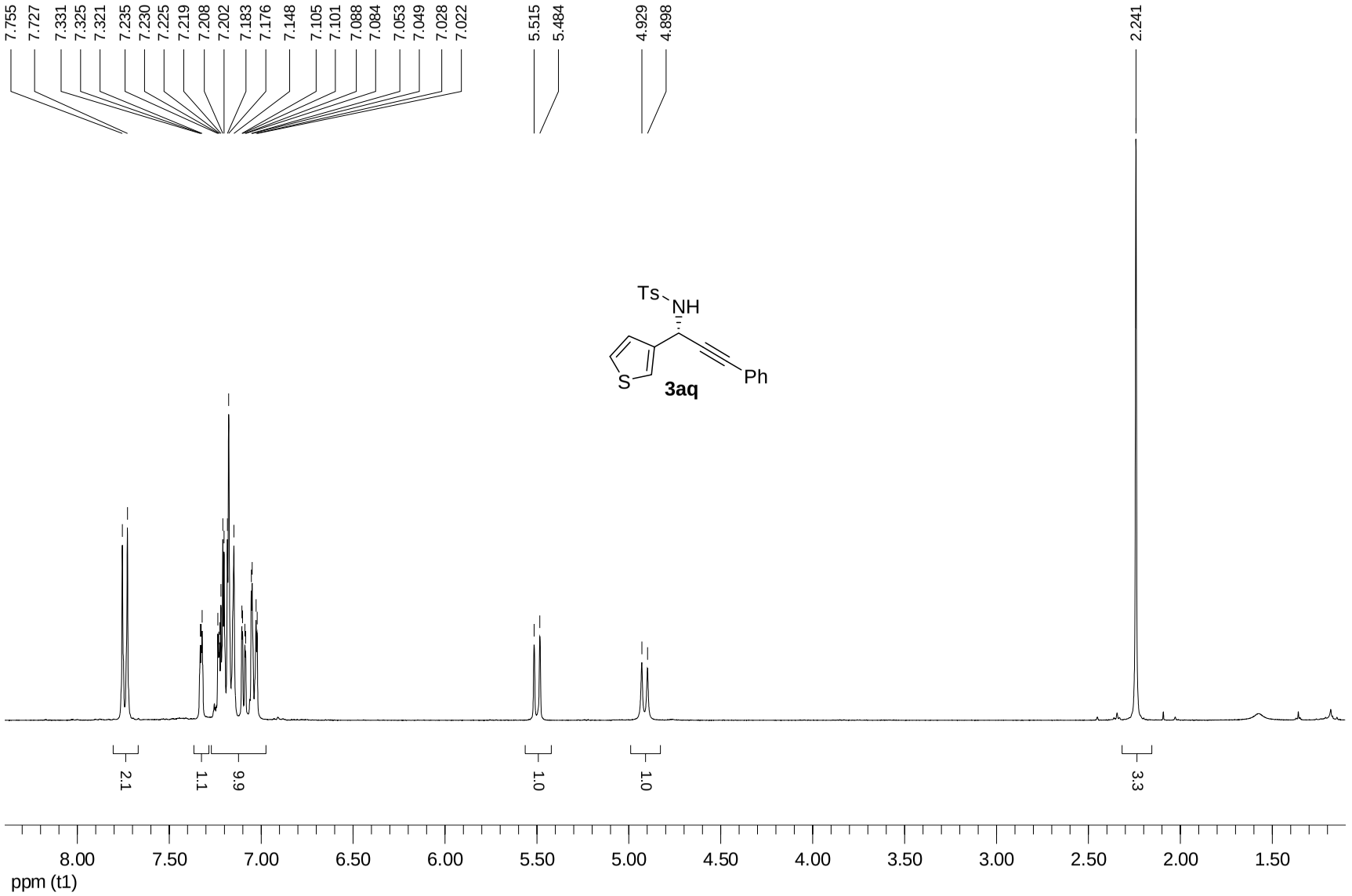

ppm (t1)
150
125
100
75
50
25
143.72
141.36
137.18
131.59
129.60
128.75
128.13
127.53
126.88
126.39
126.35
121.64
85.76
85.16
77.42
77.00
76.58
45.79
21.44
S
Ts
NH
Ph
3ap

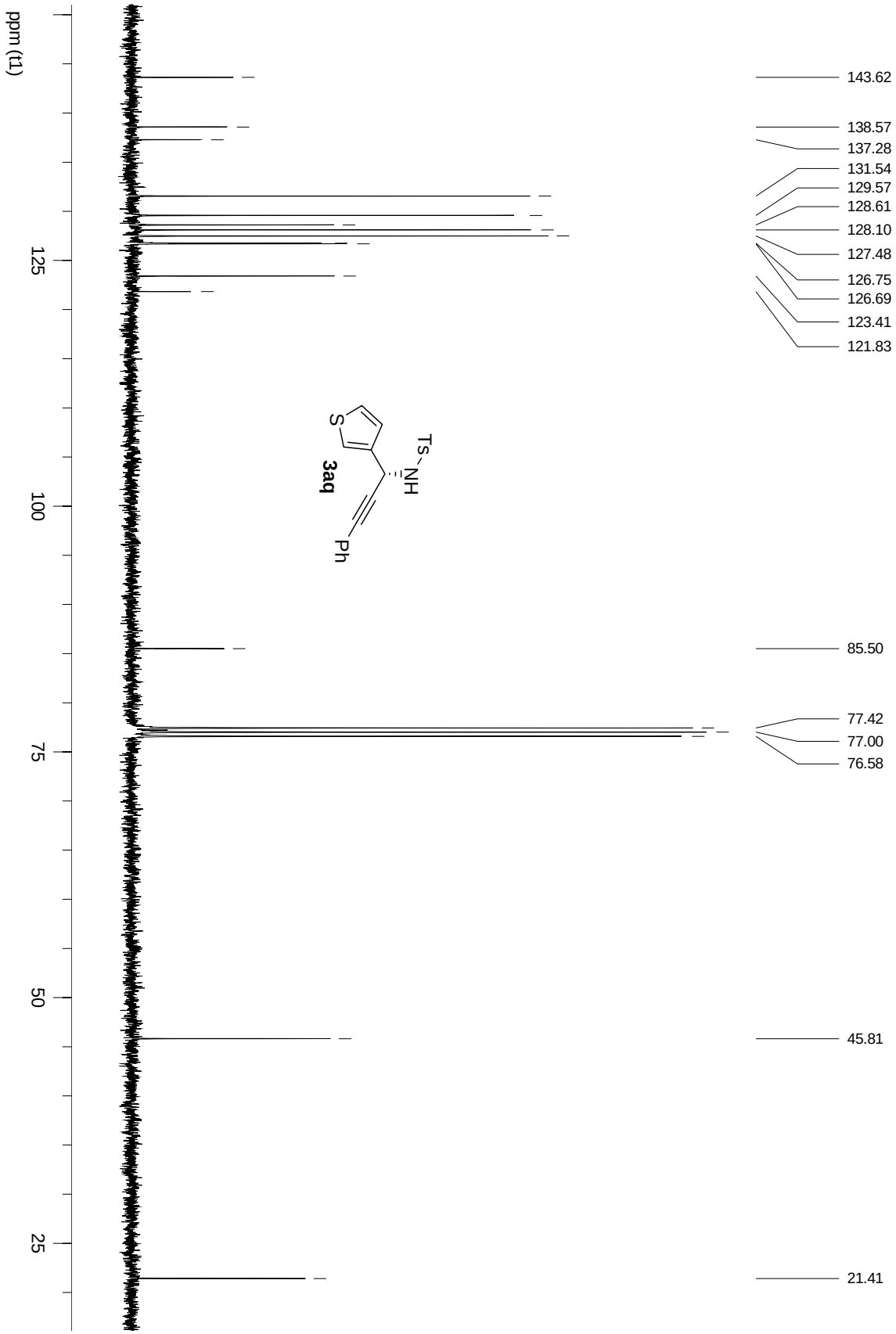


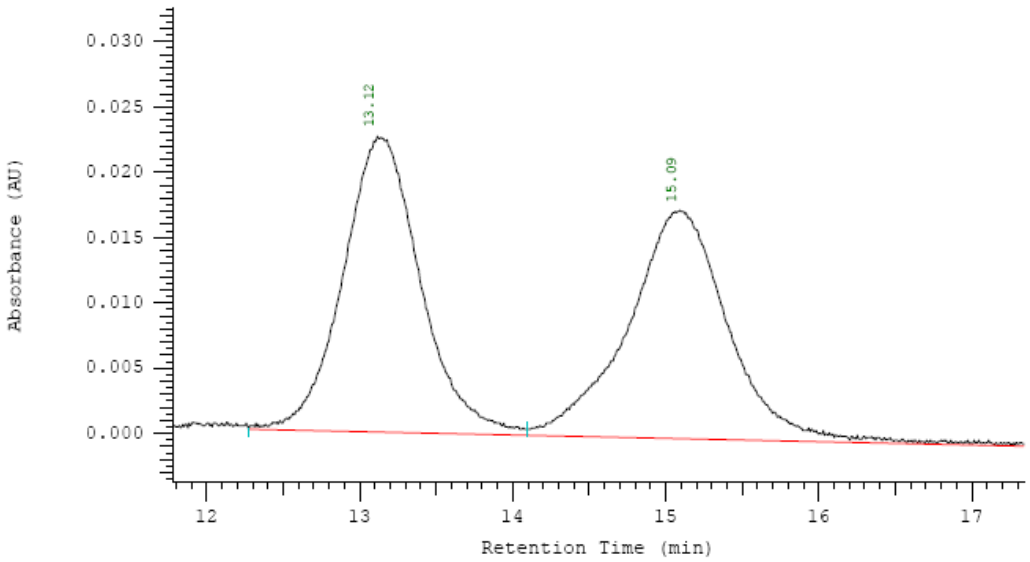
RT	Area	Area %
12.79	3498158	49.879
14.47	3515102	50.121
	7013260	100.000



RT	Area	Area %
12.61	891750	89.305
14.33	106789	10.695
	998539	100.000

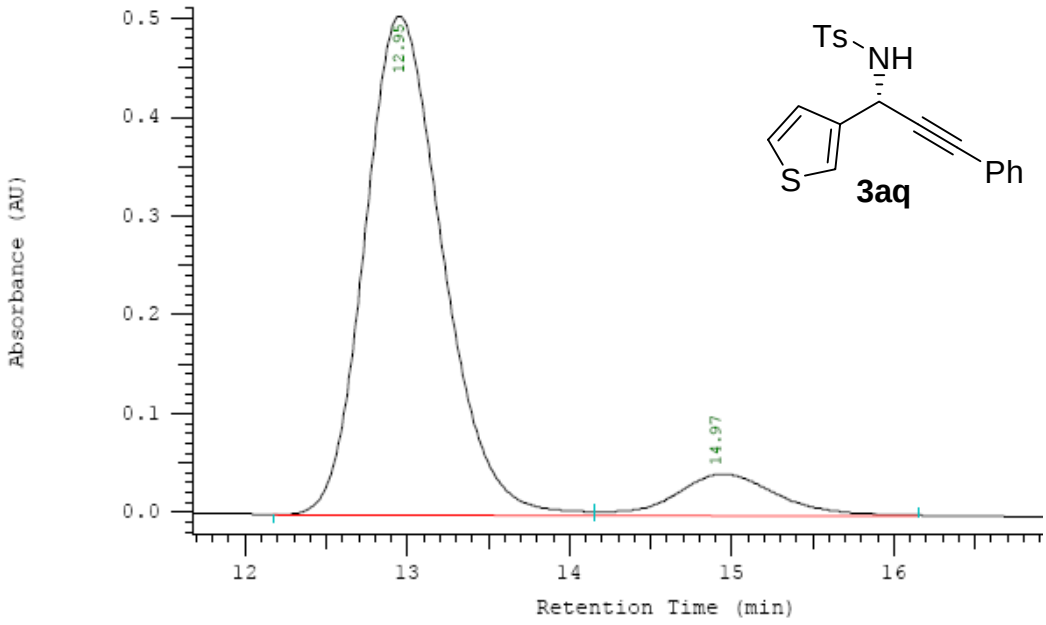

7.755
7.727
7.331
7.325
7.321
7.235
7.230
7.225
7.219
7.208
7.202
7.183
7.176
7.148
7.105
7.101
7.088
7.084
7.053
7.049
7.028
7.022
5.515
5.484
4.929
4.898
2.241
Ts
NH
S
Ph
3aq
2.1
1.1
9.9
1.0
1.0
3.3
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)


ppm (t1)
125
100
75
50
25
143.62
138.57
137.28
131.54
129.57
128.61
128.10
127.48
126.75
126.69
123.41
121.83
85.50
77.42
77.00
76.58
45.81
21.41
S
Ts
NH
Ph
3aq

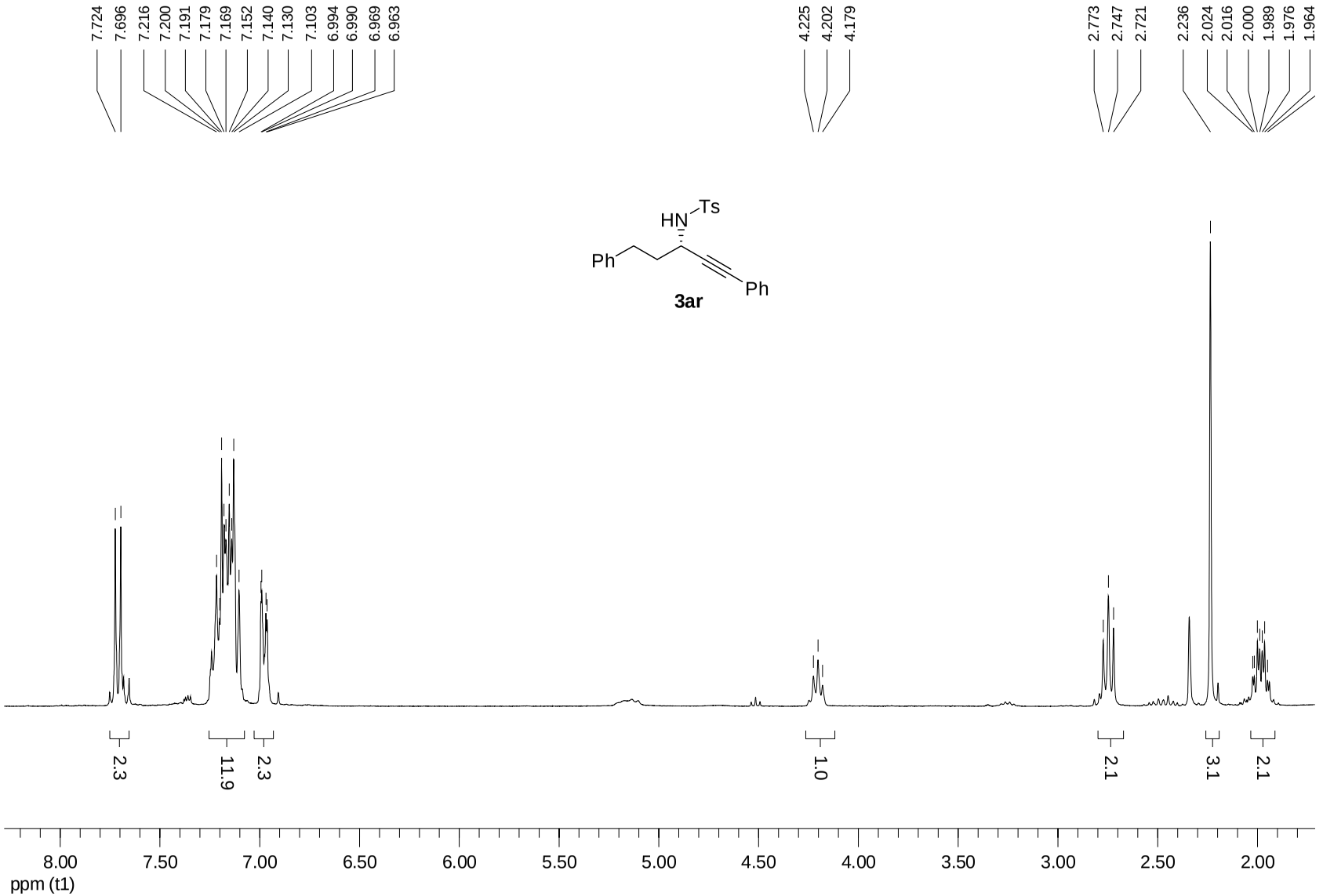


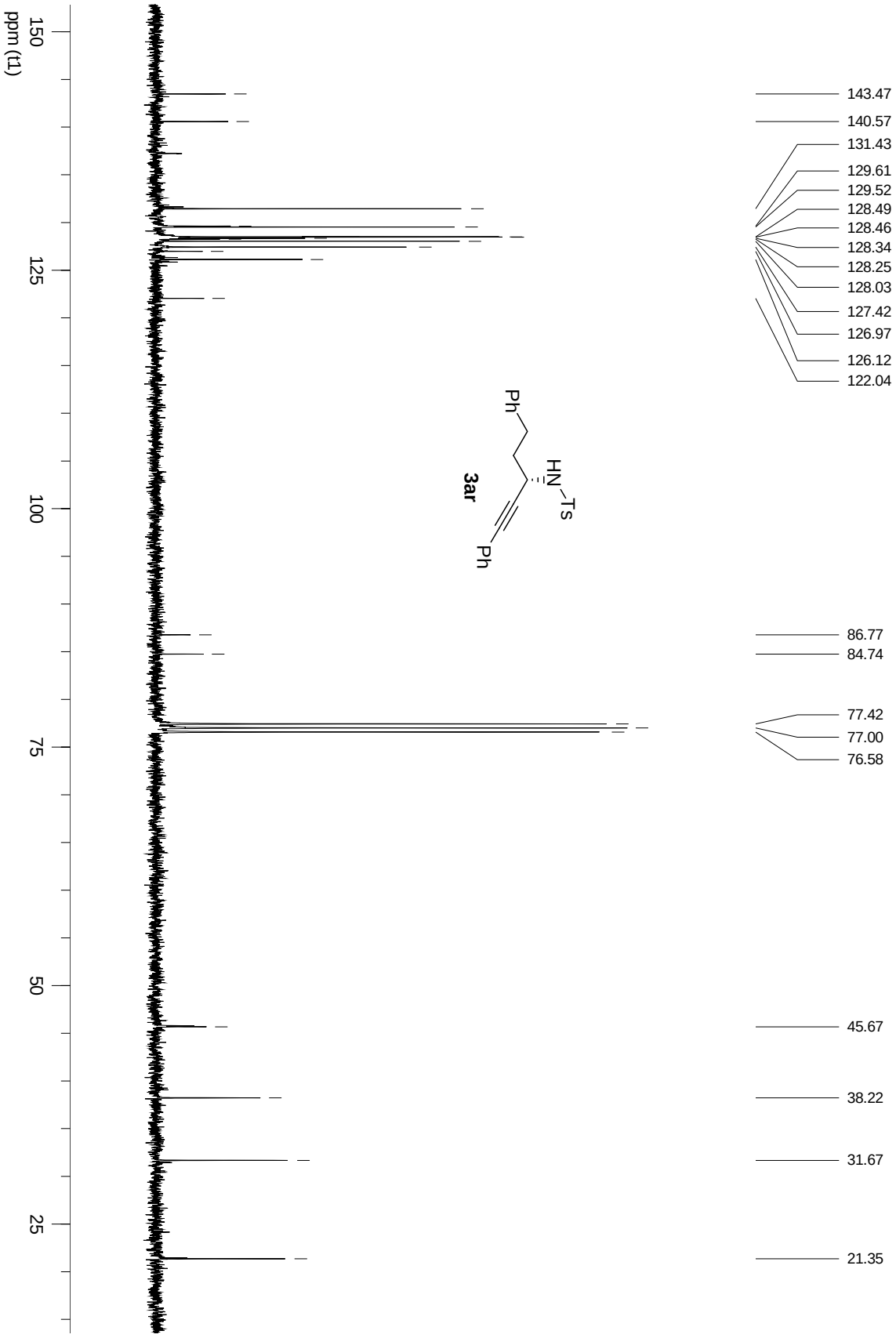
tiofe

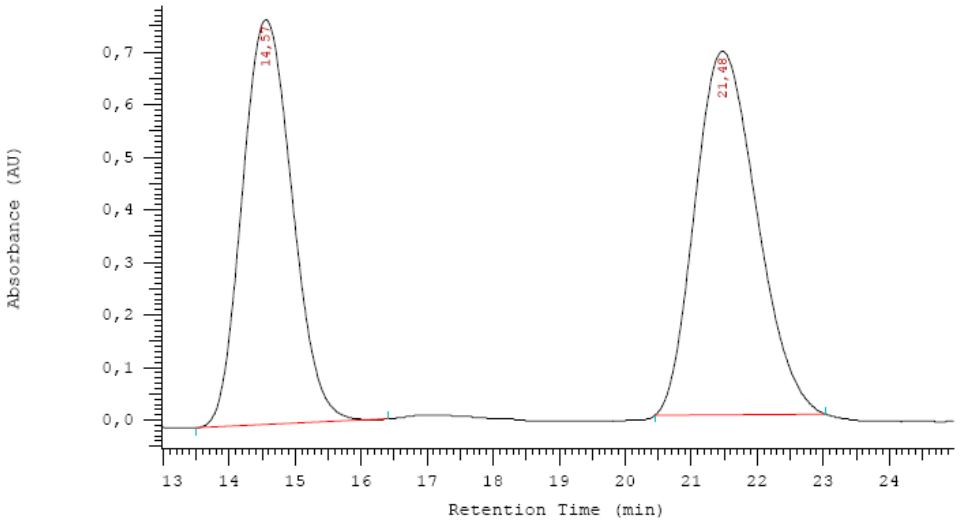
RT	Area	Area %
13.15	693545	50.552
15.10	678409	49.448
	1371954	100.000



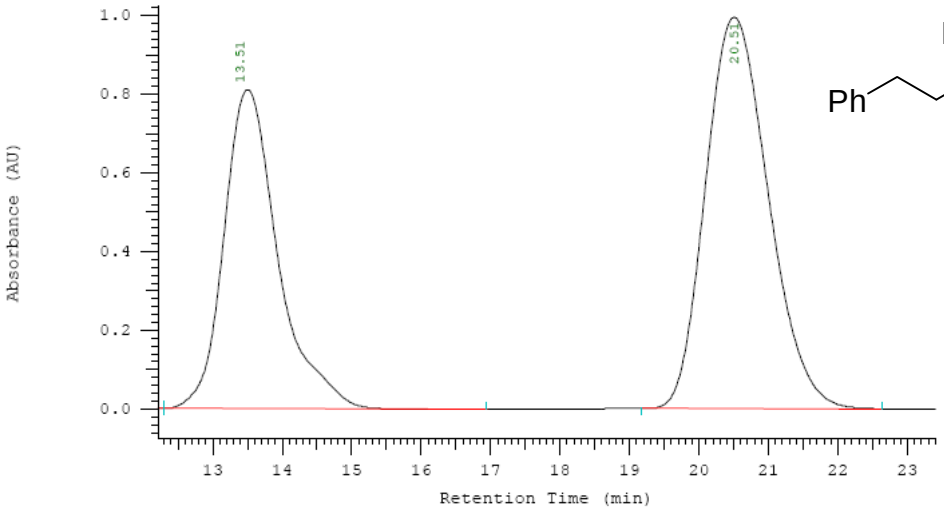
RT	Area	Area %
12.95	8417287	90.351
14.97	898892	9.649
	9316179	100.000

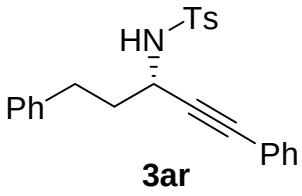

7.724
7.696
7.216
7.200
7.191
7.179
7.169
7.152
7.140
7.130
7.103
6.994
6.990
6.969
6.963
4.225
4.202
4.179
2.773
2.747
2.721
2.236
2.024
2.016
2.000
1.989
1.976
1.964
HN
Ts
Ph
Ph
3ar
2.3
11.9
2.3
1.0
2.1
3.1
2.1
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)


ppm (t1)
150
125
100
75
50
25
143.47
140.57
131.43
129.61
129.52
128.49
128.46
128.34
128.25
128.03
127.42
126.97
126.12
122.04
Ph
HN
Ts
Ph
3ar
86.77
84.74
77.42
77.00
76.58
45.67
38.22
31.67
21.35



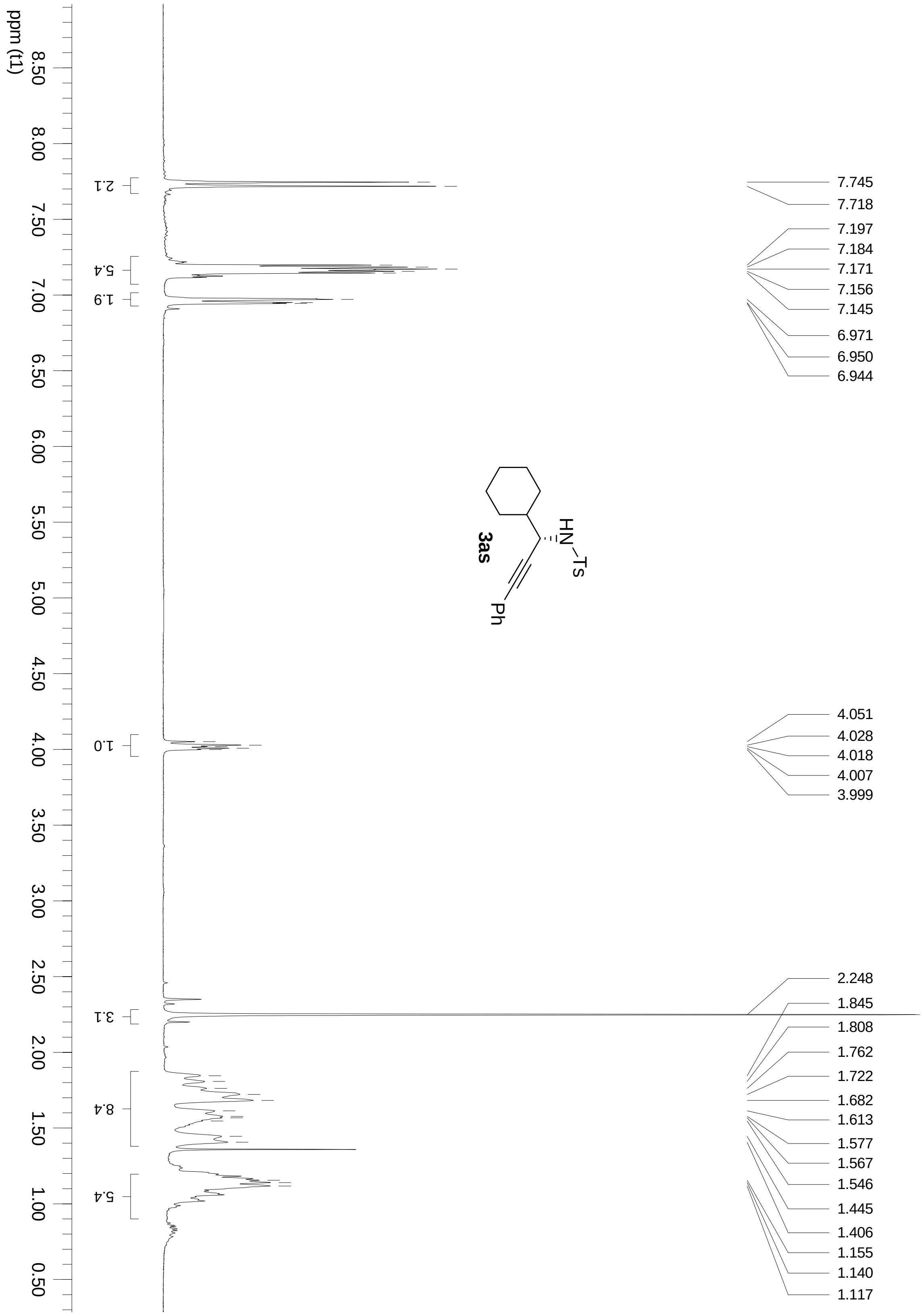
RT	Area	Area %
14,57	20042110	47,226
21,48	22396185	52,774
	42438295	100,000



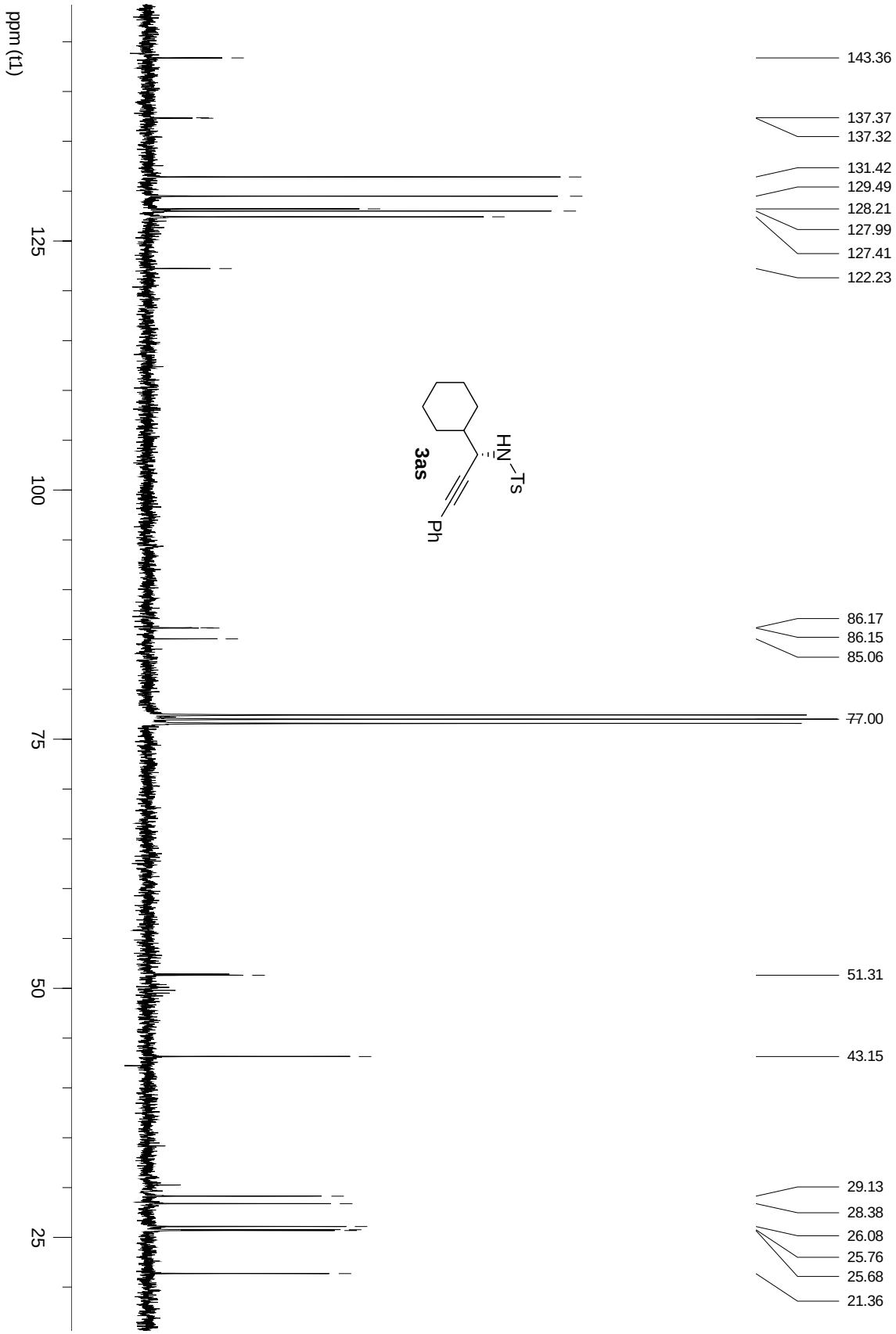


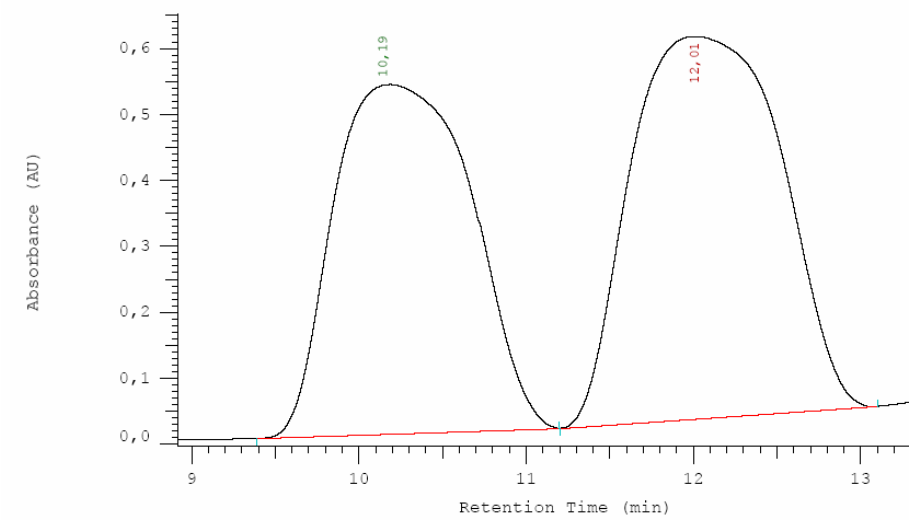
3ar

RT	Area	Area %
13.51	21644649	41.109
20.51	31007136	58.891
	52651785	100.000

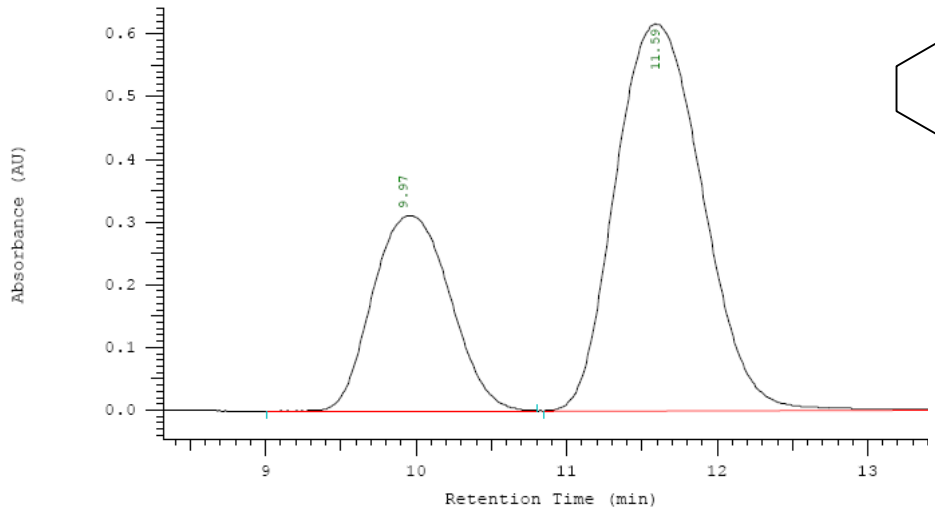


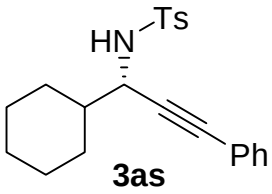
ppm (t1)
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
2.1
5.4
1.9
1.0
3.1
8.4
5.4
7.745
7.718
7.197
7.184
7.171
7.156
7.145
6.971
6.950
6.944
4.051
4.028
4.018
4.007
3.999
2.248
1.845
1.808
1.762
1.722
1.682
1.613
1.577
1.567
1.546
1.445
1.406
1.155
1.140
1.117
HN
Ts
Ph
3as


ppm (t1)
125
100
75
50
25
143.36
137.37
137.32
131.42
129.49
128.21
127.99
127.41
122.23
86.17
86.15
85.06
77.00
51.31
43.15
29.13
28.38
26.08
25.76
25.68
21.36
3as
HN
Ts
Ph



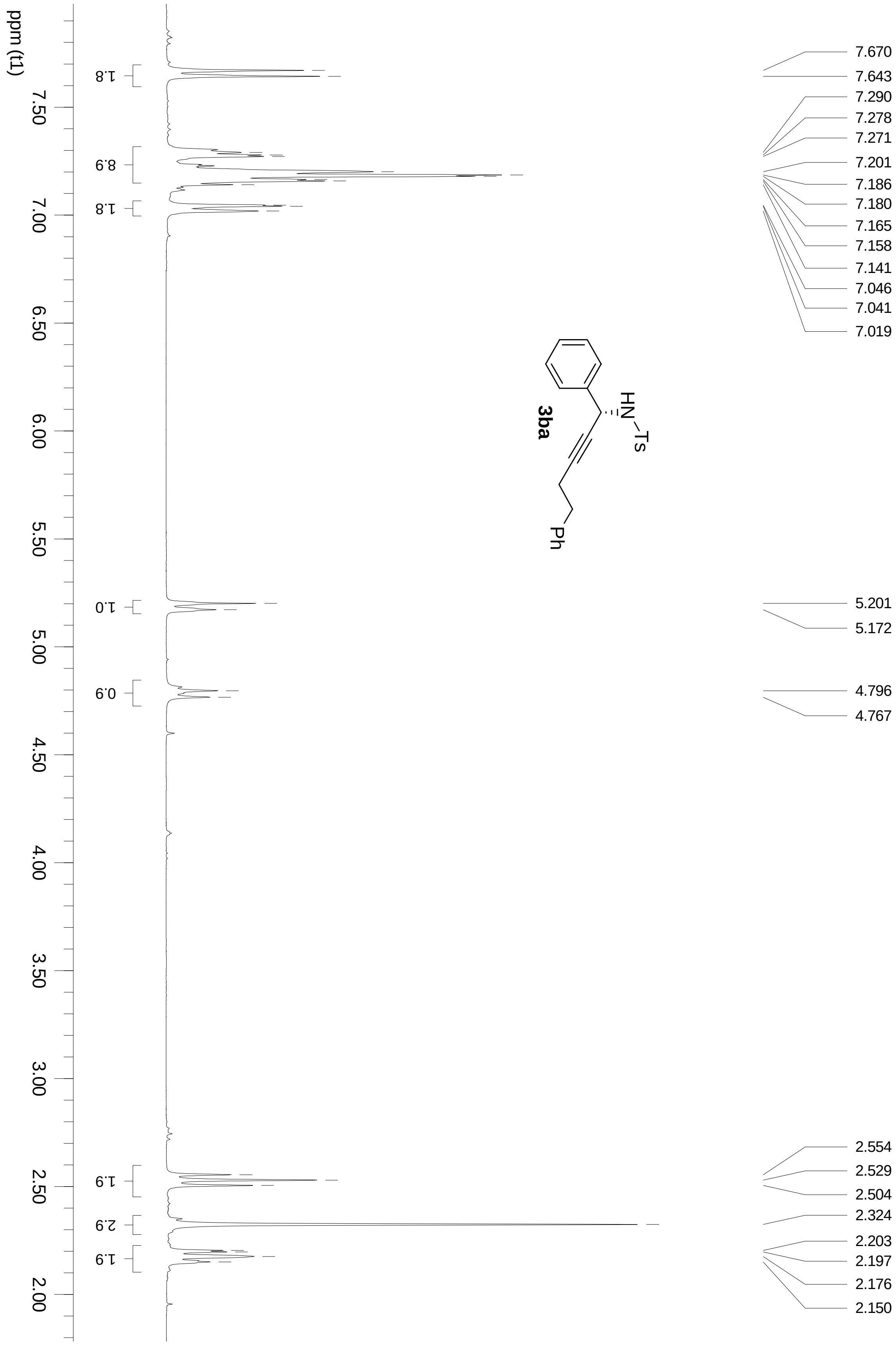
RT	Area	Area %
10,19	15257560	45,650
12,01	18165635	54,350
	33423195	100,000



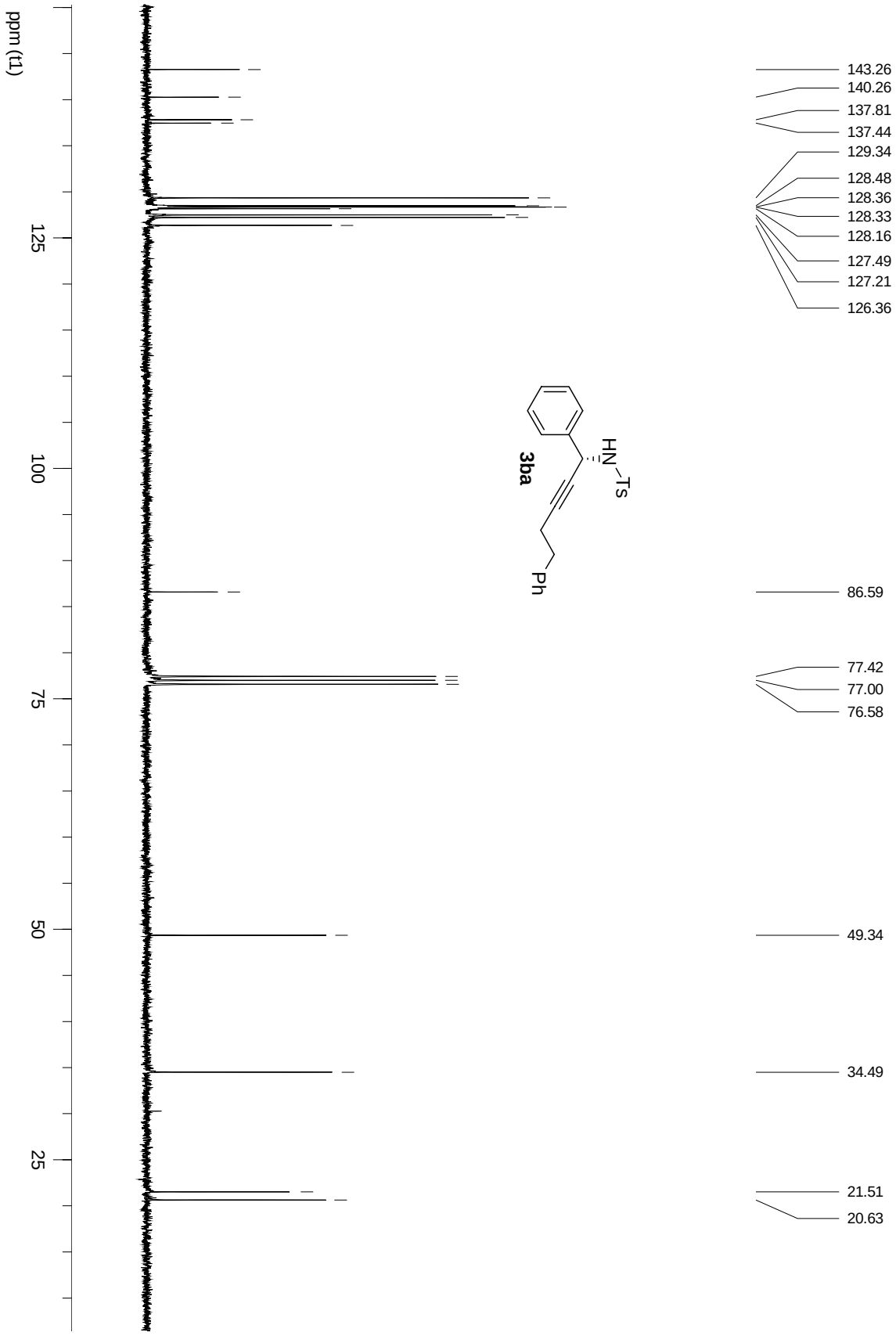


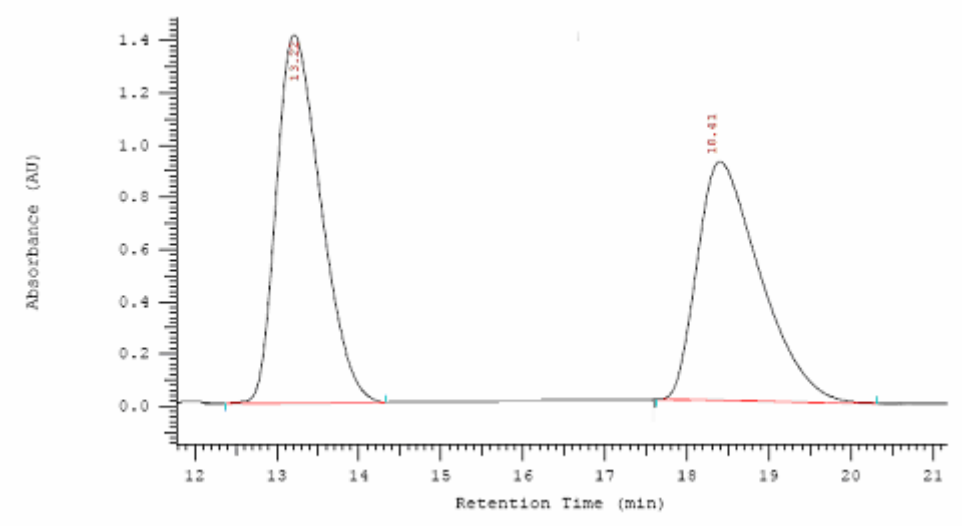
3as

RT	Area	Area %
9.97	5557404	31.041
11.59	12346169	68.959
	17903573	100.000

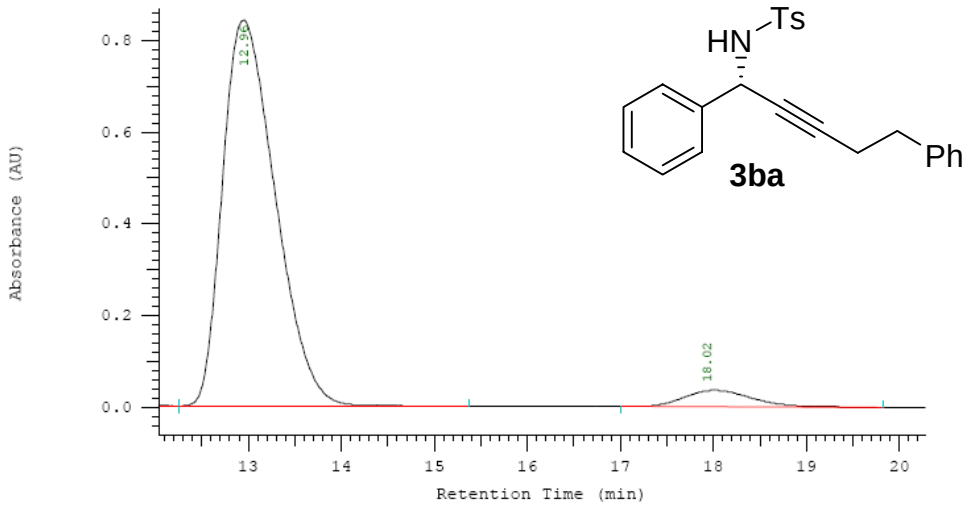


ppm (t1)
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.8
8.9
1.8
1.0
0.9
1.9
2.9
1.9
7.670
7.643
7.290
7.278
7.271
7.201
7.186
7.180
7.165
7.158
7.141
7.046
7.041
7.019
5.201
5.172
4.796
4.767
2.554
2.529
2.504
2.324
2.203
2.197
2.176
2.150
HN
Ts
Ph
3ba

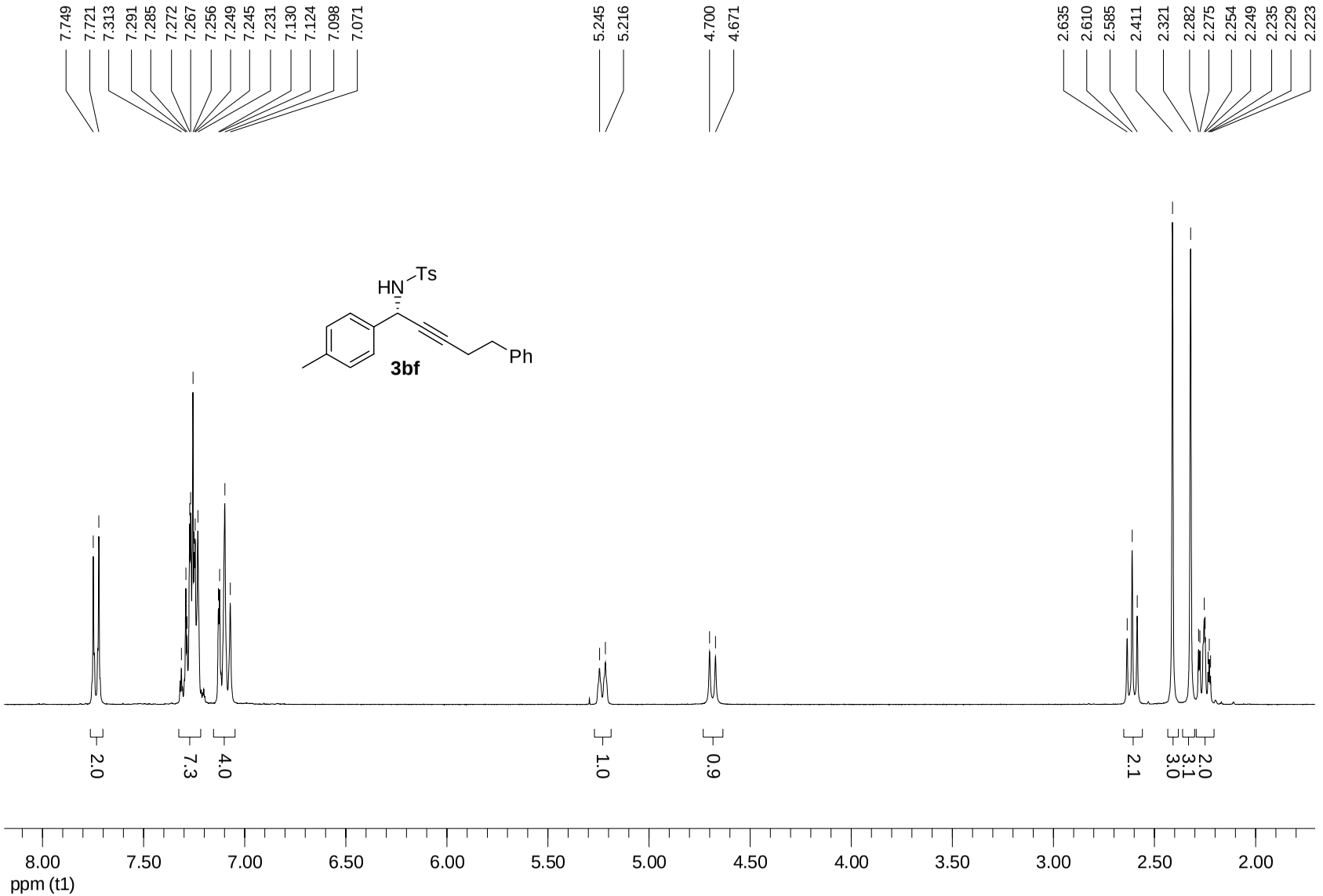

ppm (t1)
125
100
75
50
25
143.26
140.26
137.81
137.44
129.34
128.48
128.36
128.33
128.16
127.49
127.21
126.36
HN
Ts
3ba
Ph
86.59
77.42
77.00
76.58
49.34
34.49
21.51
20.63

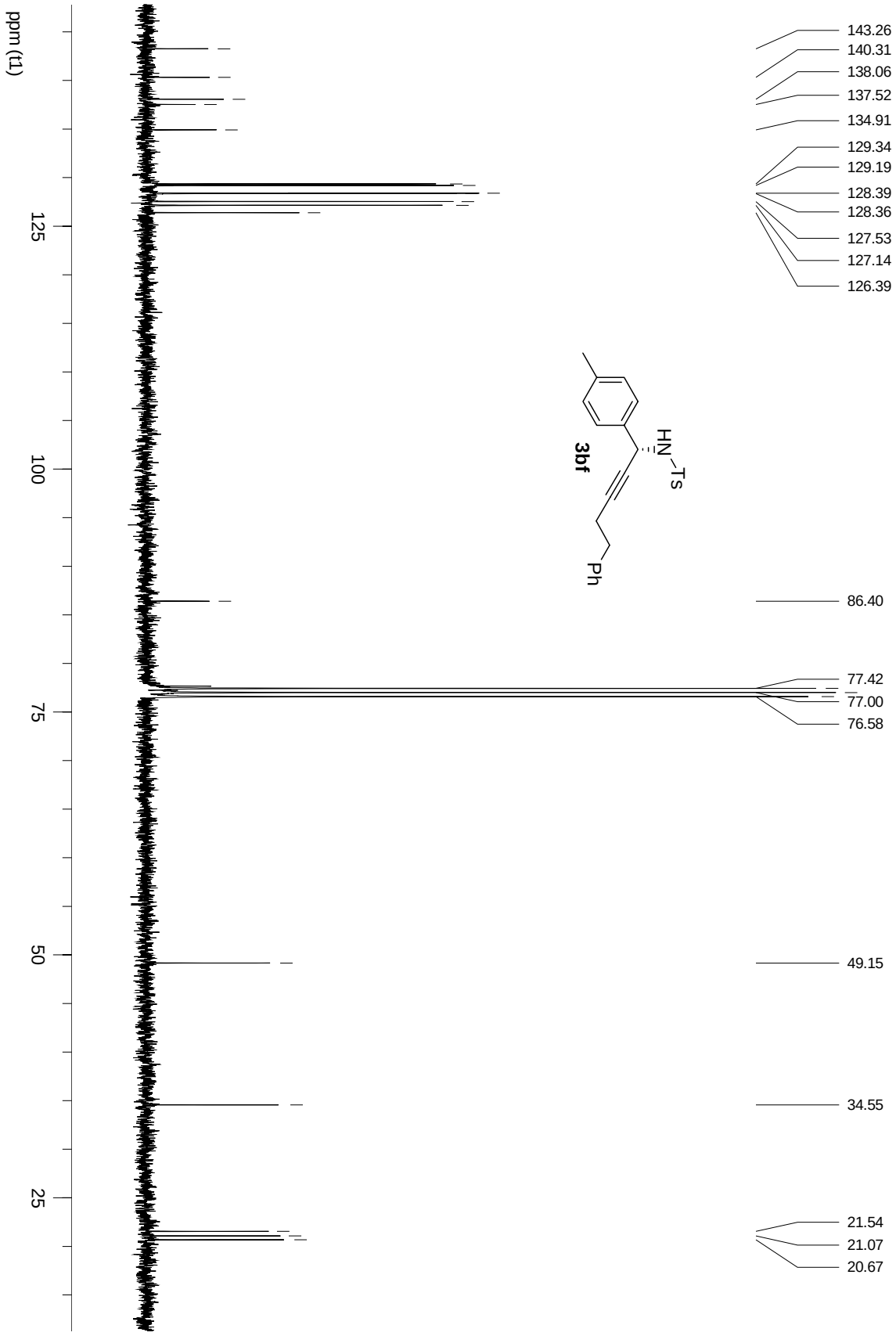


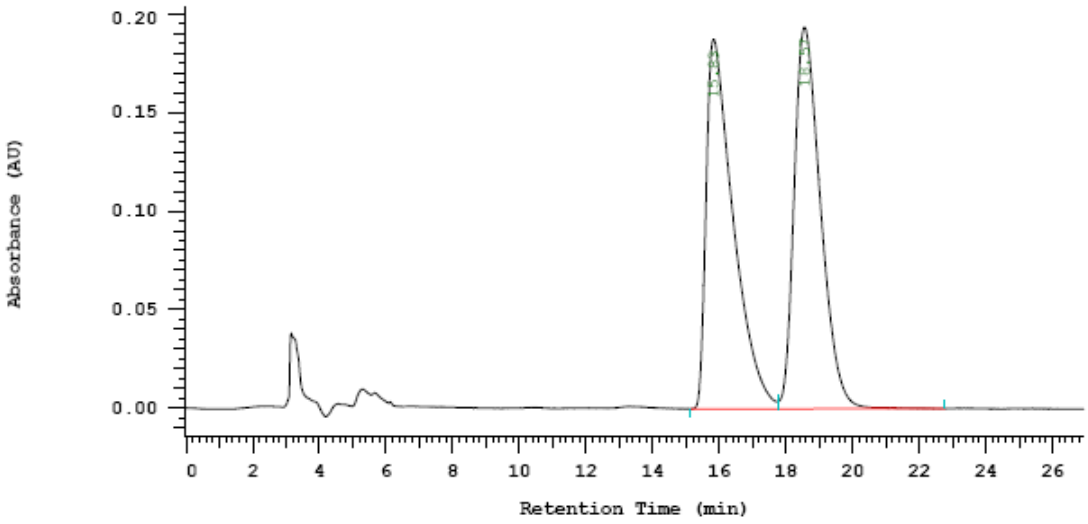
RT	Area	Area %
13.23	1143740	49.951
18.40	1146005	50.049
	2289745	100.000



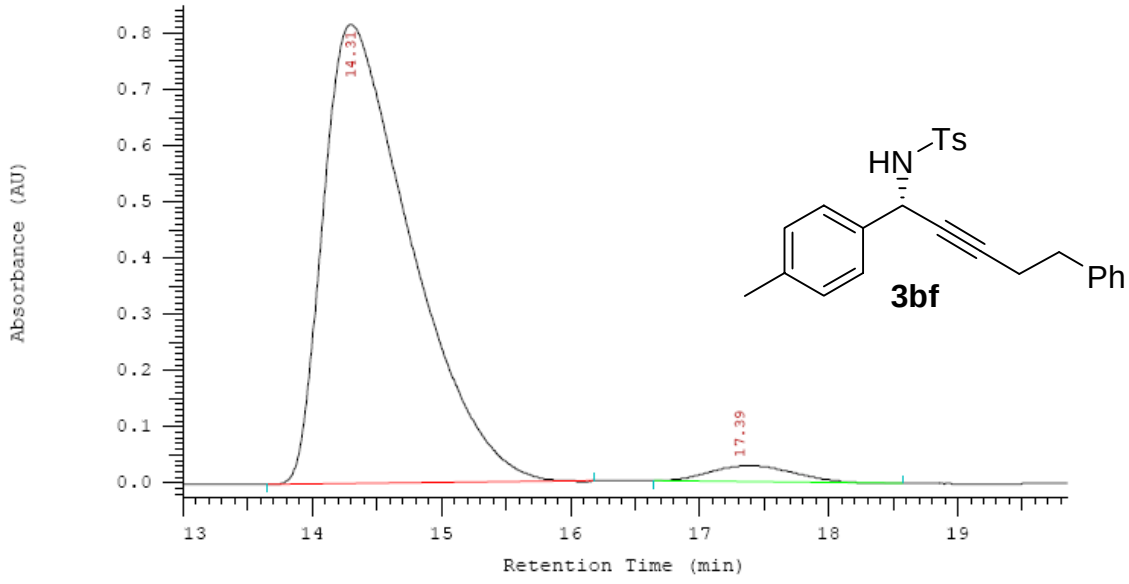
RT	Area	Area %
12.96	16445180	94.789
18.02	904150	5.211
	17349330	100.000


7.749
7.721
7.313
7.291
7.285
7.272
7.267
7.256
7.249
7.245
7.231
7.130
7.124
7.098
7.071
5.245
5.216
4.700
4.671
2.635
2.610
2.585
2.411
2.321
2.282
2.275
2.254
2.249
2.235
2.229
2.223
HN
Ts
Ph
3bf
2.0
7.3
4.0
1.0
0.9
2.1
3.0
3.1
2.0
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)

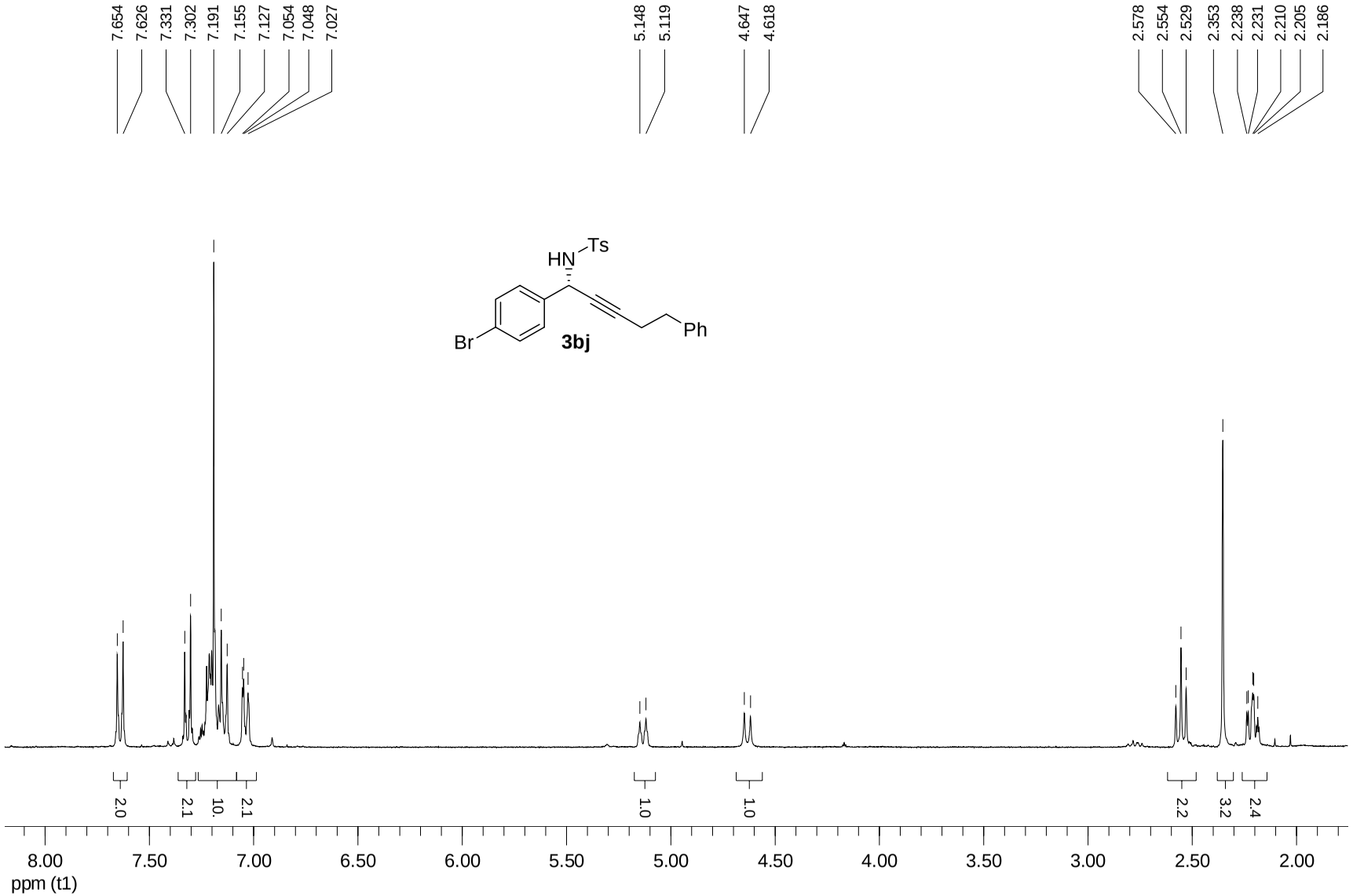

ppm (t1)
125
100
75
50
25
143.26
140.31
138.06
137.52
134.91
129.34
129.19
128.39
128.36
127.53
127.14
126.39
HN
Ts
Ph
3bf
86.40
77.42
77.00
76.58
49.15
34.55
21.54
21.07
20.67

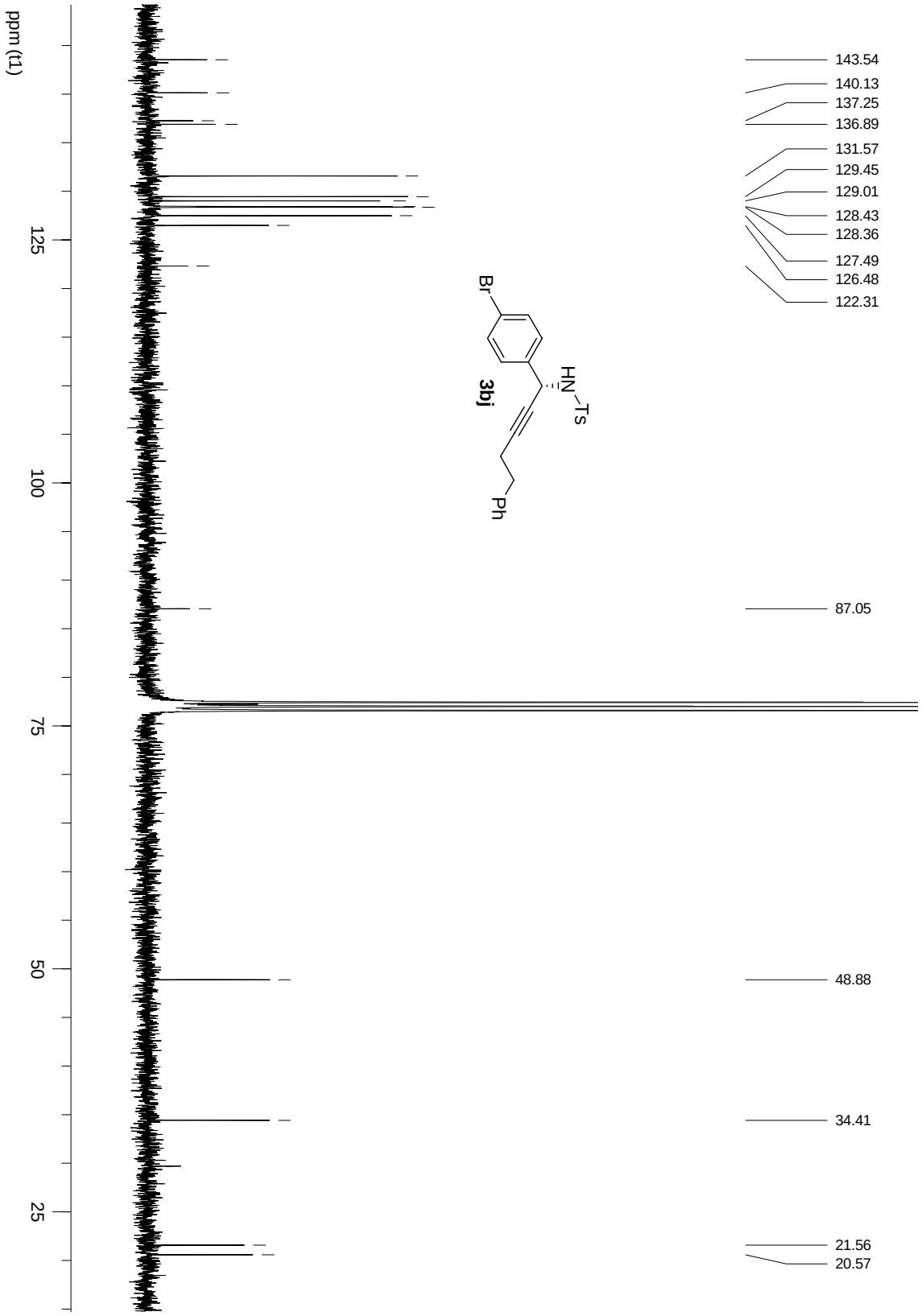


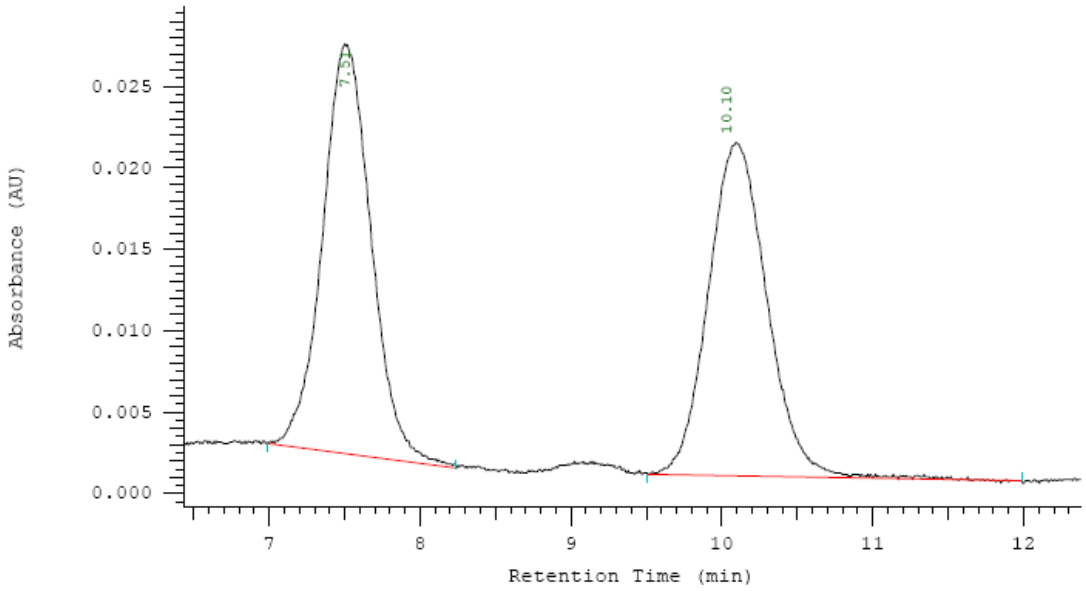
No.	RT	Area	Area %
1	15.83	5288654	49.916
2	18.57	5306465	50.084
		10595119	100.000



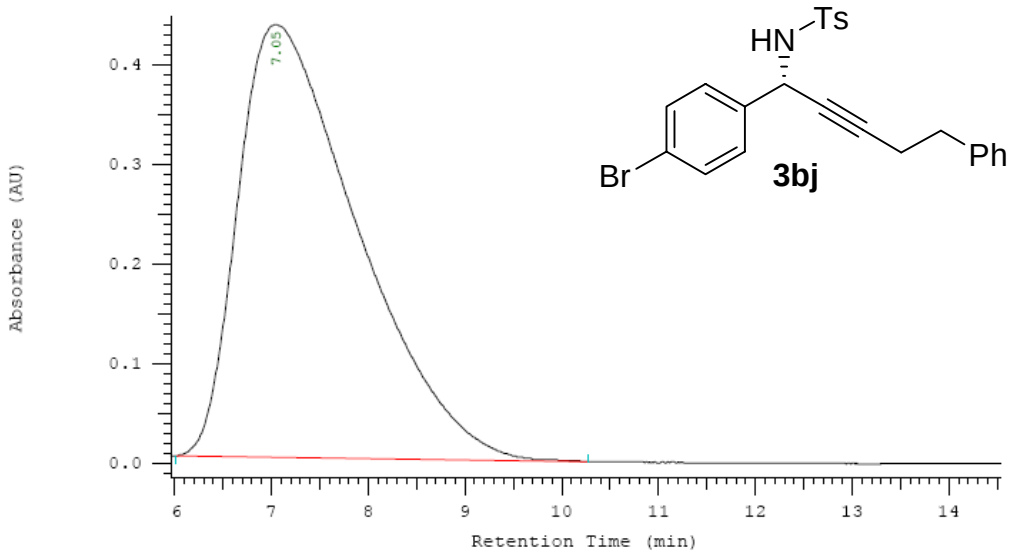
RT	Area	Area %
14.31	19243040	96.644
17.39	668310	3.356
	19911350	100.000


7.654
7.626
7.331
7.302
7.191
7.155
7.127
7.054
7.048
7.027
5.148
5.119
4.647
4.618
2.578
2.554
2.529
2.353
2.238
2.231
2.210
2.205
2.186
HN
Ts
Br
Ph
3bj
2.0
2.1
10.
2.1
1.0
1.0
2.2
3.2
2.4
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)


ppm (t1)
125
100
75
50
25
143.54
140.13
137.25
136.89
131.57
129.45
129.01
128.43
128.36
127.49
126.48
122.31
87.05
48.88
34.41
21.56
20.57
Br
HN
Ts
Ph
3bj

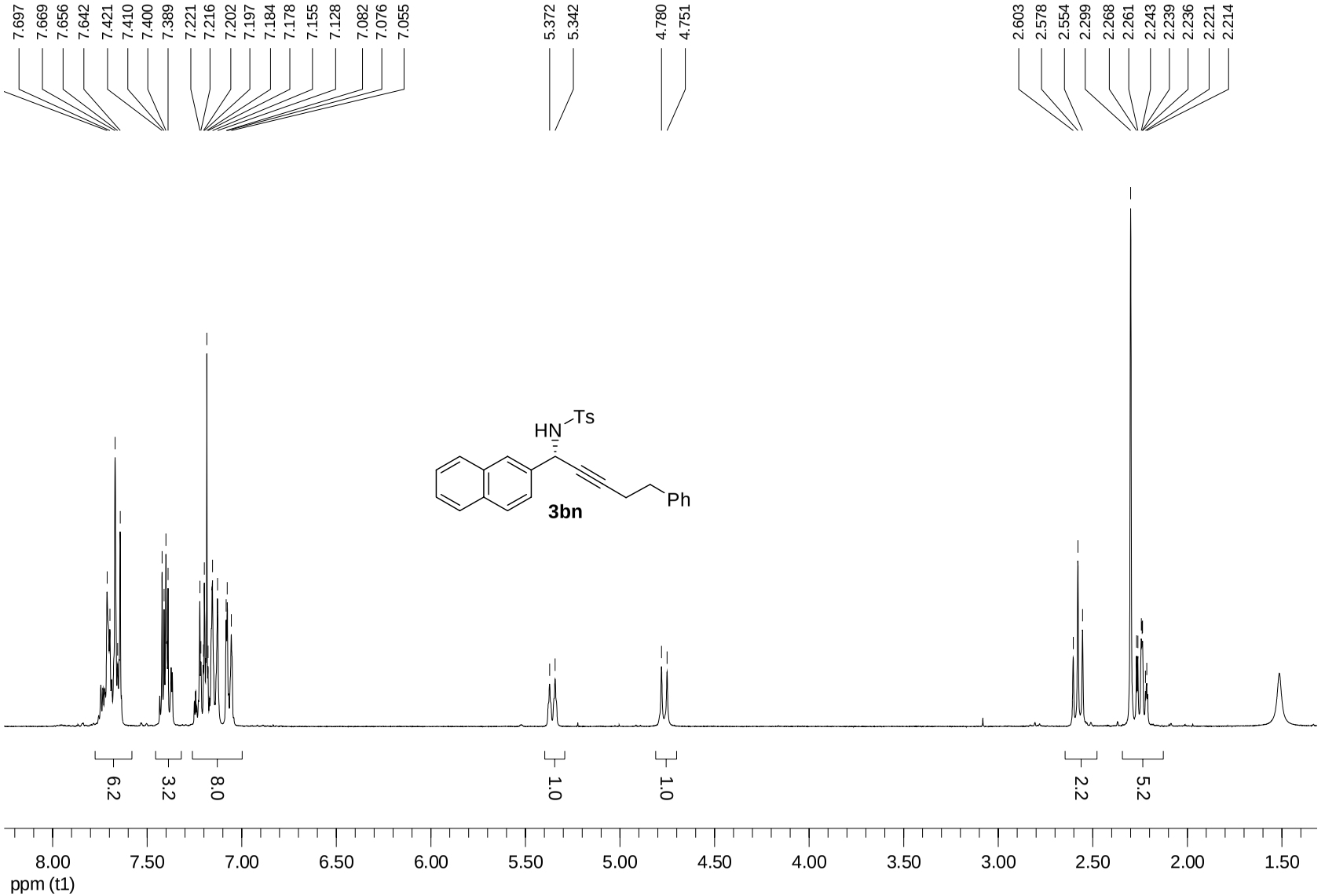


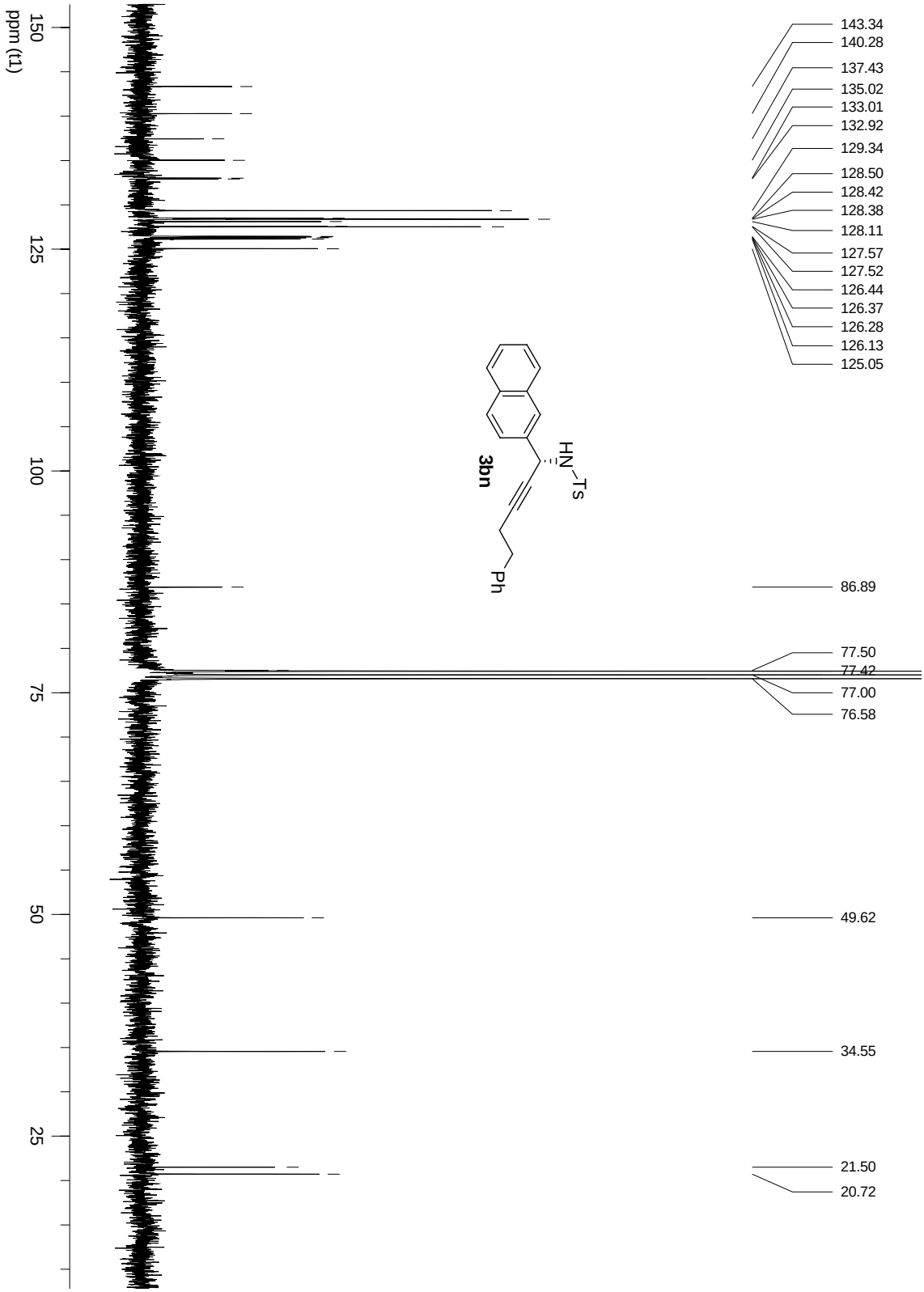
RT	Area	Area %
7.51	280930	50.439
10.10	276045	49.561
	556975	100.000

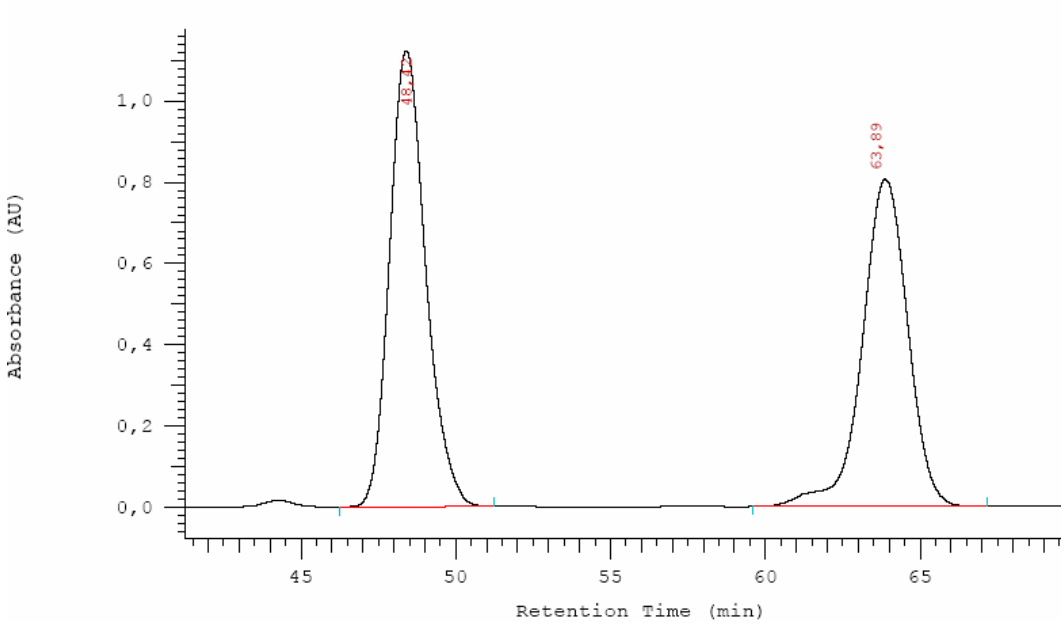


3bj

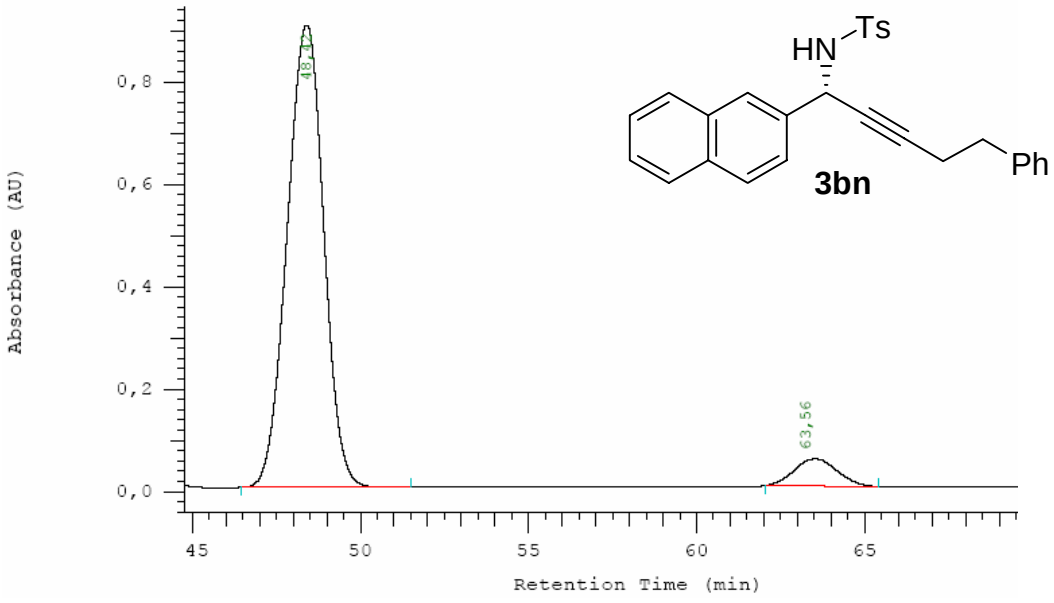
RT	Area	Area %
7.05	18576145	100.000
	18576145	100.000


7.697
7.669
7.656
7.642
7.421
7.410
7.400
7.389
7.221
7.216
7.202
7.197
7.184
7.178
7.155
7.128
7.082
7.076
7.055
5.372
5.342
4.780
4.751
2.603
2.578
2.554
2.299
2.268
2.261
2.243
2.239
2.236
2.221
2.214
HN
Ts
Ph
3bn
6.2
3.2
8.0
1.0
1.0
2.2
5.2
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)

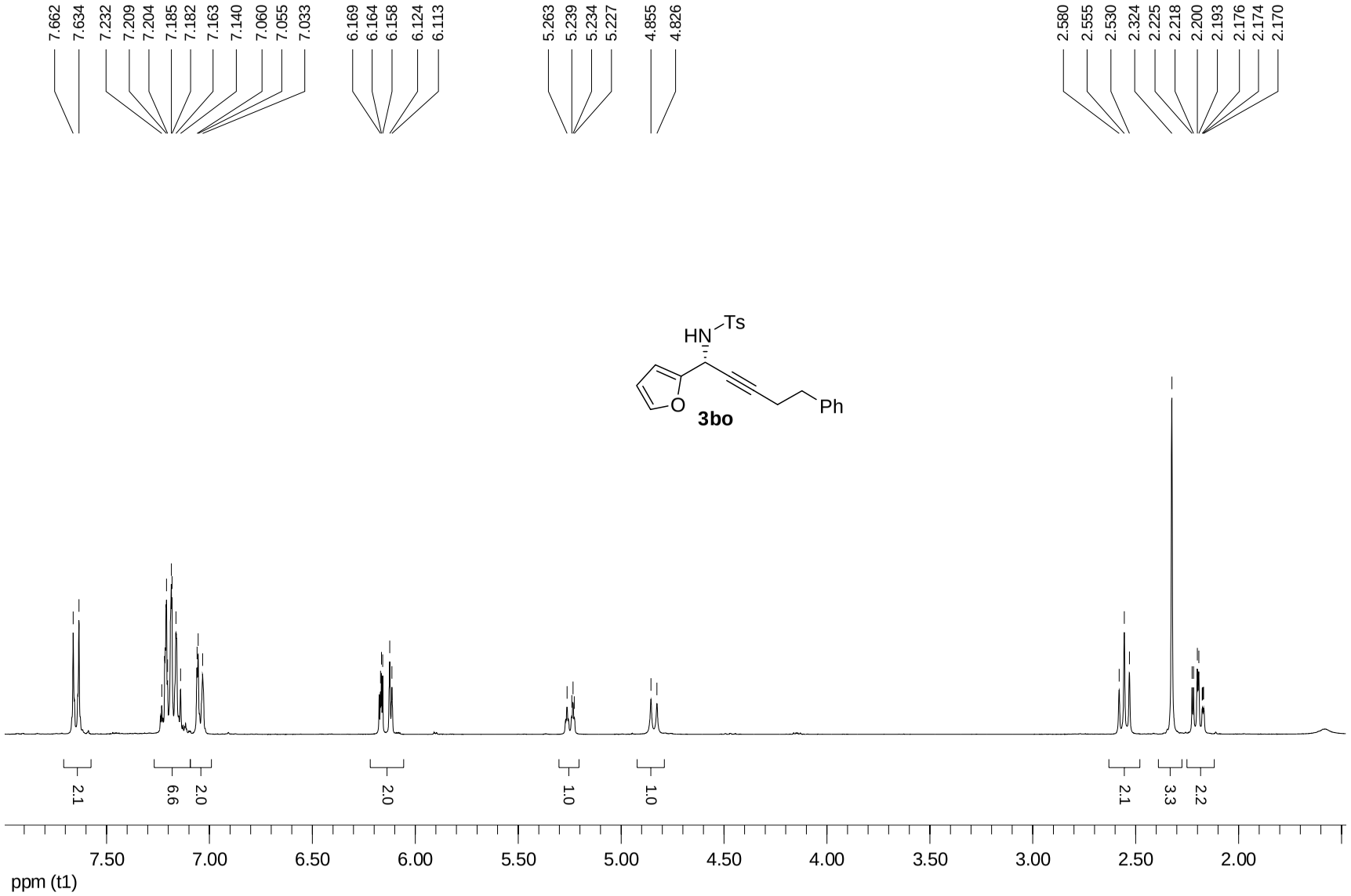

ppm (t1)
150
125
100
75
50
25
143.34
140.28
137.43
135.02
133.01
132.92
129.34
128.50
128.42
128.38
128.11
127.57
127.52
126.44
126.37
126.28
126.13
125.05
HN
Ts
3bn
Ph
86.89
77.50
77.42
77.00
76.58
49.62
34.55
21.50
20.72

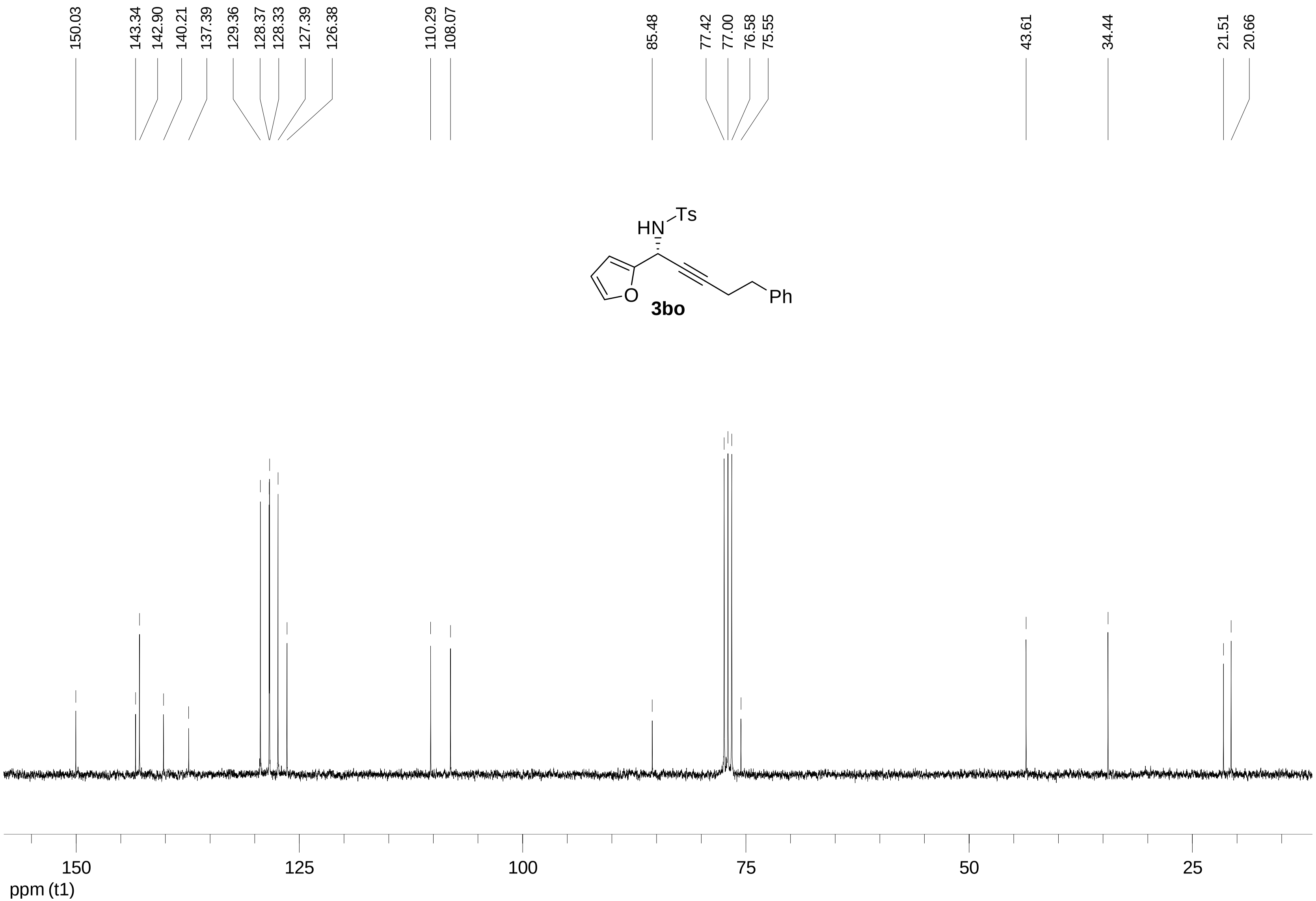


No.	RT	Area	Area %
1	48,42	44455580	52,308
2	63,89	40532502	47,692
		84988082	100,000

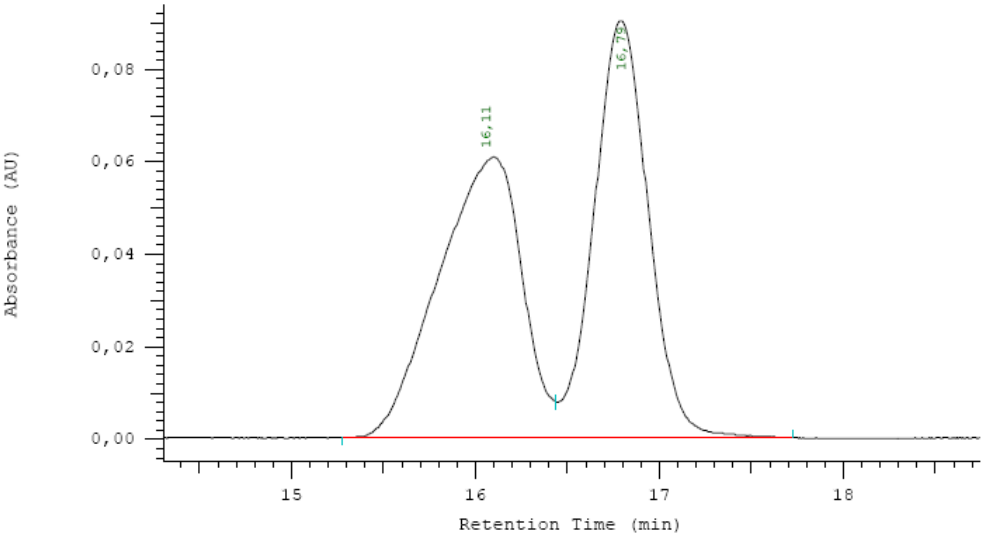


No.	RT	Area	Area %
1	48,42	33233504	93,435
2	63,56	2335075	6,565
		35568579	100,000

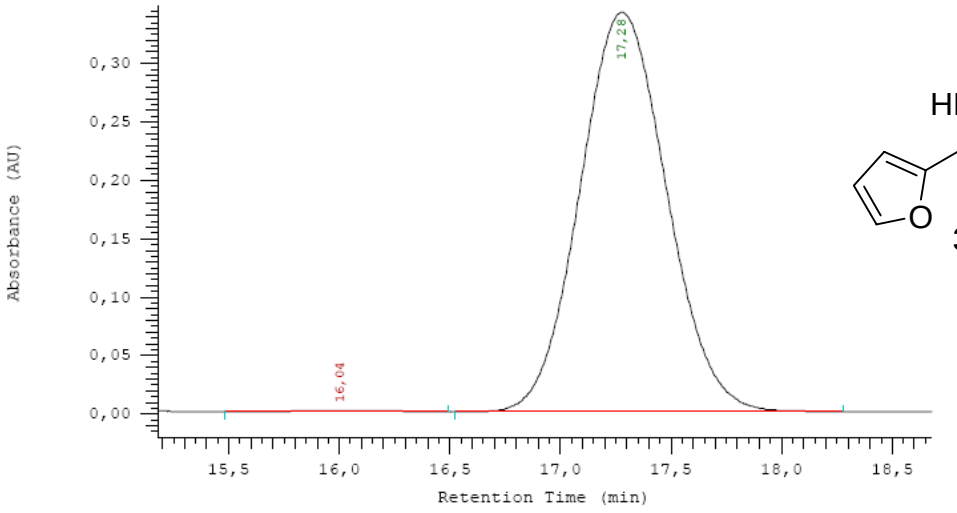

7.662
7.634
7.232
7.209
7.204
7.185
7.182
7.163
7.140
7.060
7.055
7.033
6.169
6.164
6.158
6.124
6.113
5.263
5.239
5.234
5.227
4.855
4.826
2.580
2.555
2.530
2.324
2.225
2.218
2.200
2.193
2.176
2.174
2.170
HN
Ts
O
Ph
3bo
2.1
6.6
2.0
2.0
1.0
1.0
2.1
3.3
2.2
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)

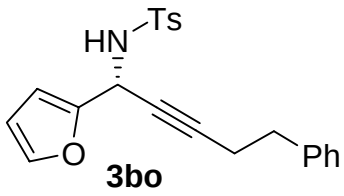

150.03
143.34
142.90
140.21
137.39
129.36
128.37
128.33
127.39
126.38
110.29
108.07
85.48
77.42
77.00
76.58
75.55
43.61
34.44
21.51
20.66
HN
Ts
O
Ph
150
125
100
75
50
25
ppm (t1)

3bo



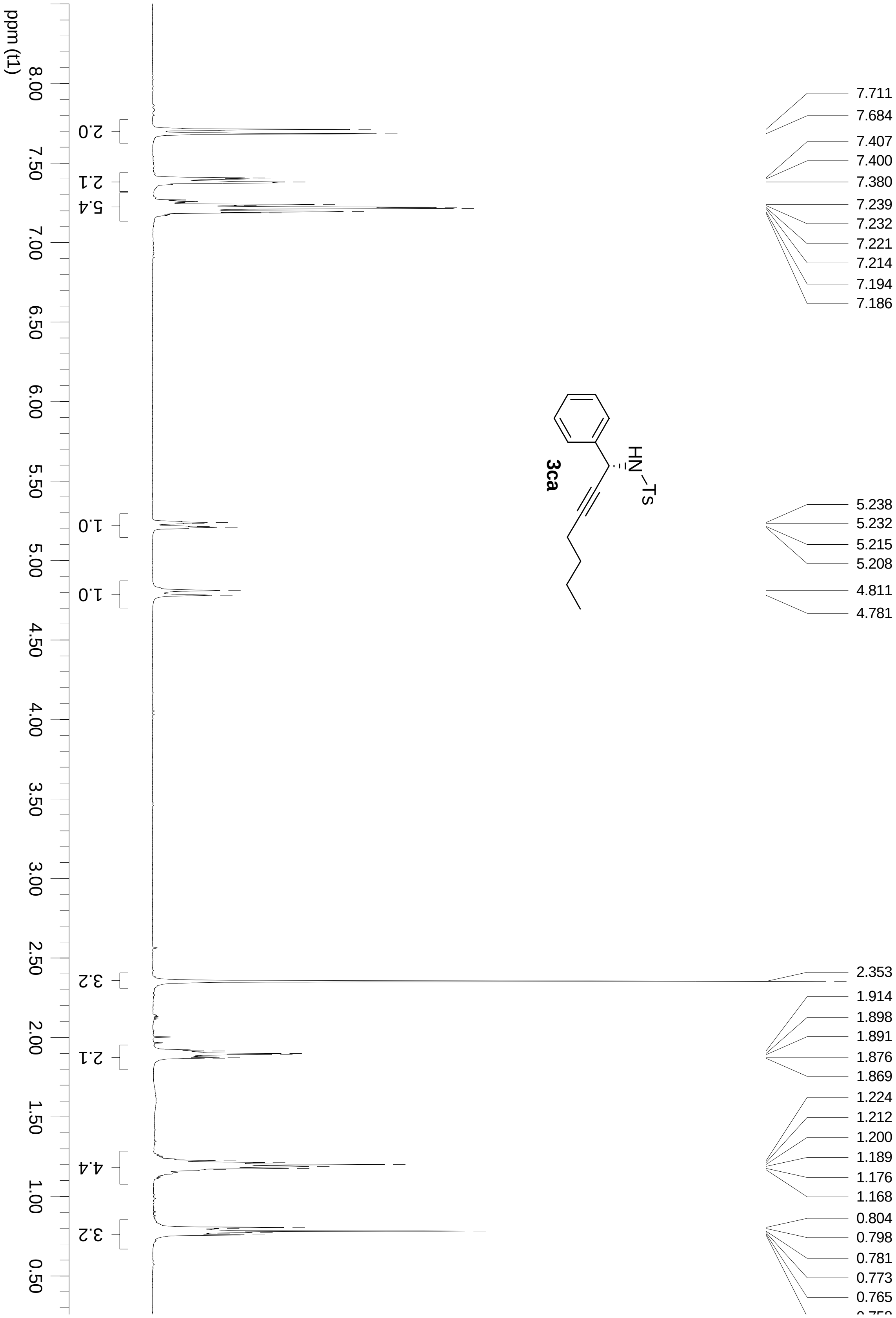
RT	Area	Area %
15,79	1168395	50,986
16,58	1123184	49,014
	2291579	100,000



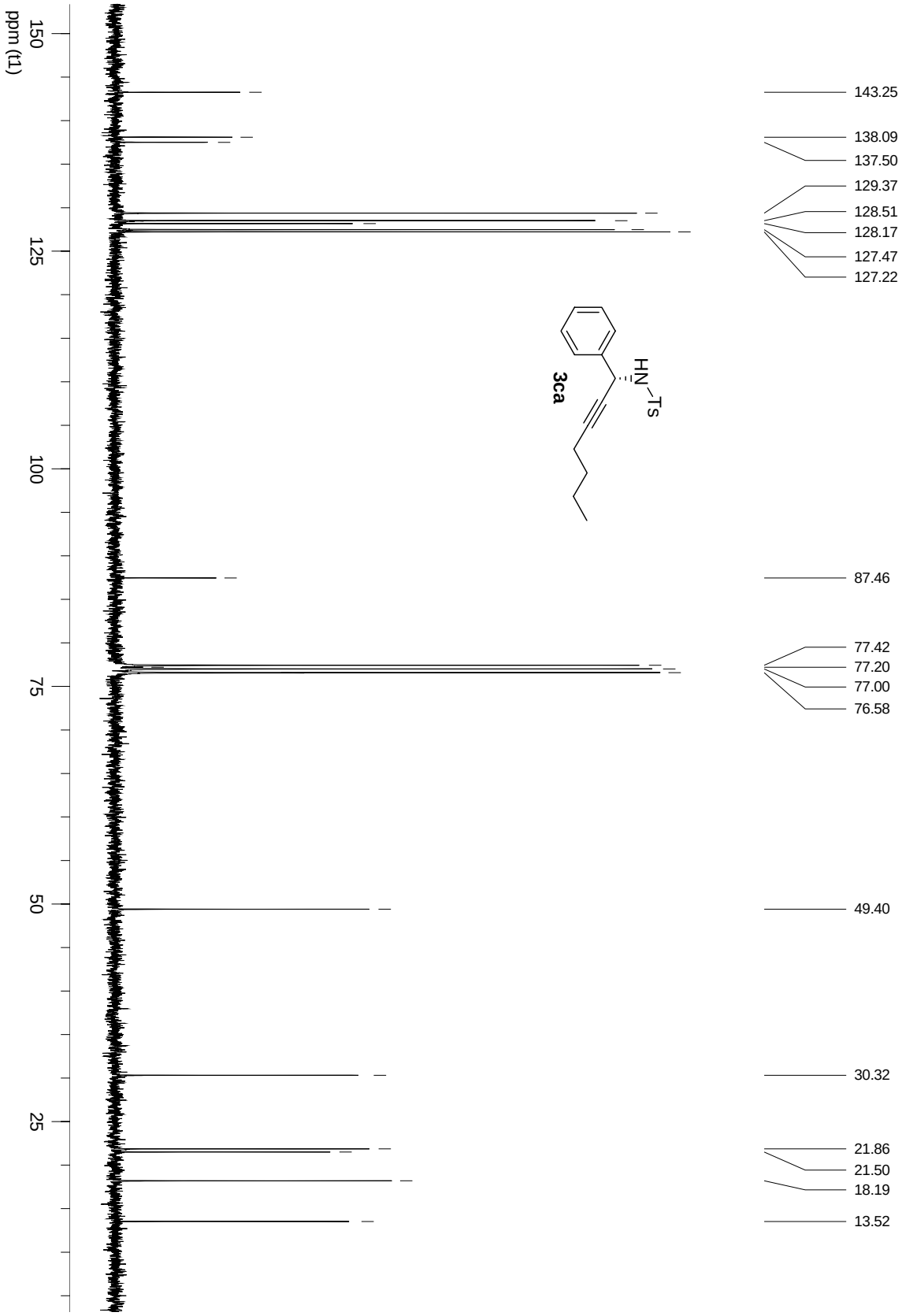


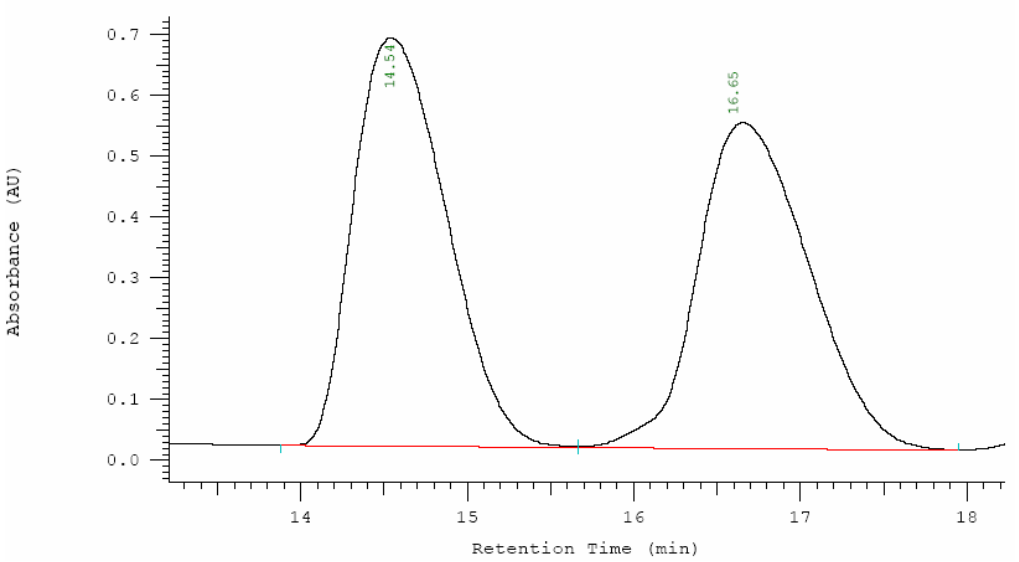
3bo

RT	Area	Area %
16,04	20010	0,426
17,28	4678040	99,574
	4698050	100,000

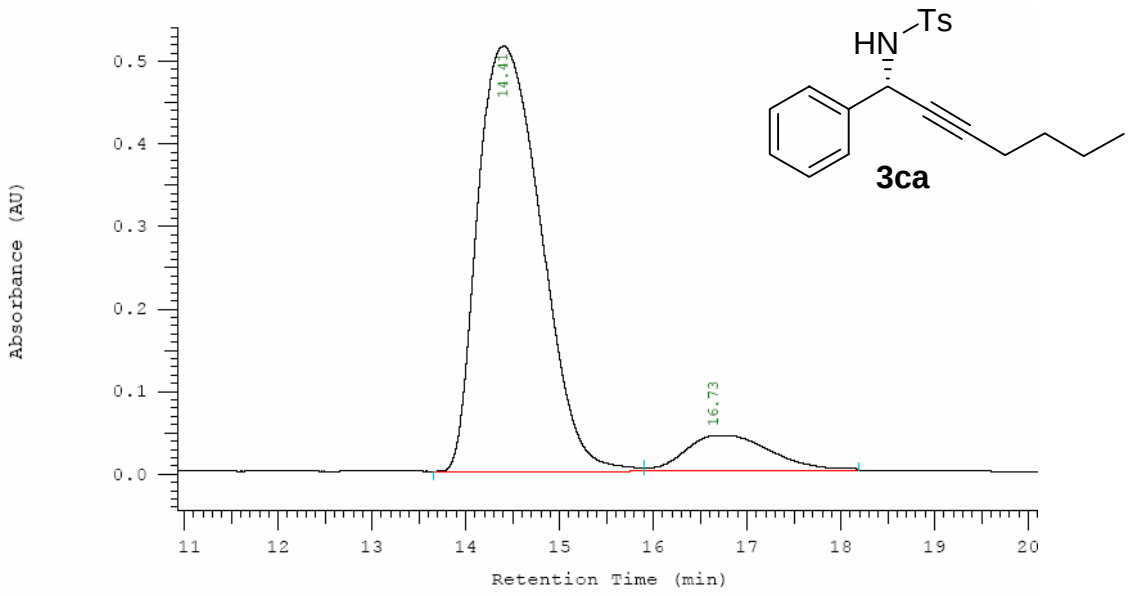


ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
2.0
2.1
5.4
1.0
1.0
3.2
2.1
4.4
3.2
7.711
7.684
7.407
7.400
7.380
7.239
7.232
7.221
7.214
7.194
7.186
5.238
5.232
5.215
5.208
4.811
4.781
2.353
1.914
1.898
1.891
1.876
1.869
1.224
1.212
1.200
1.189
1.176
1.168
0.804
0.798
0.781
0.773
0.765
HN
Ts
3ca

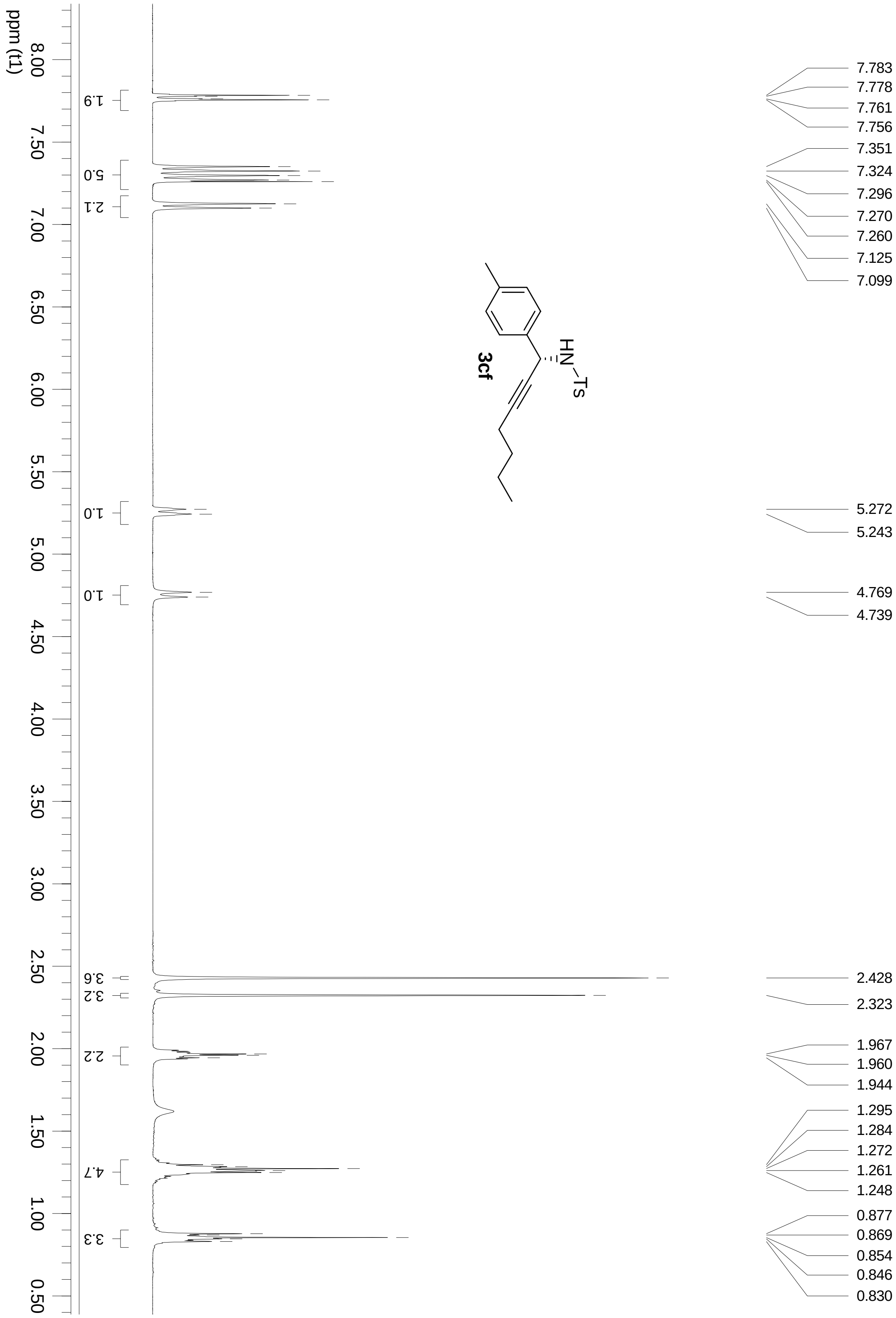

ppm (t1)
150
125
100
75
50
25
143.25
138.09
137.50
129.37
128.51
128.17
127.47
127.22
87.46
77.42
77.20
77.00
76.58
49.40
30.32
21.86
21.50
18.19
13.52
HN
Ts
3ca



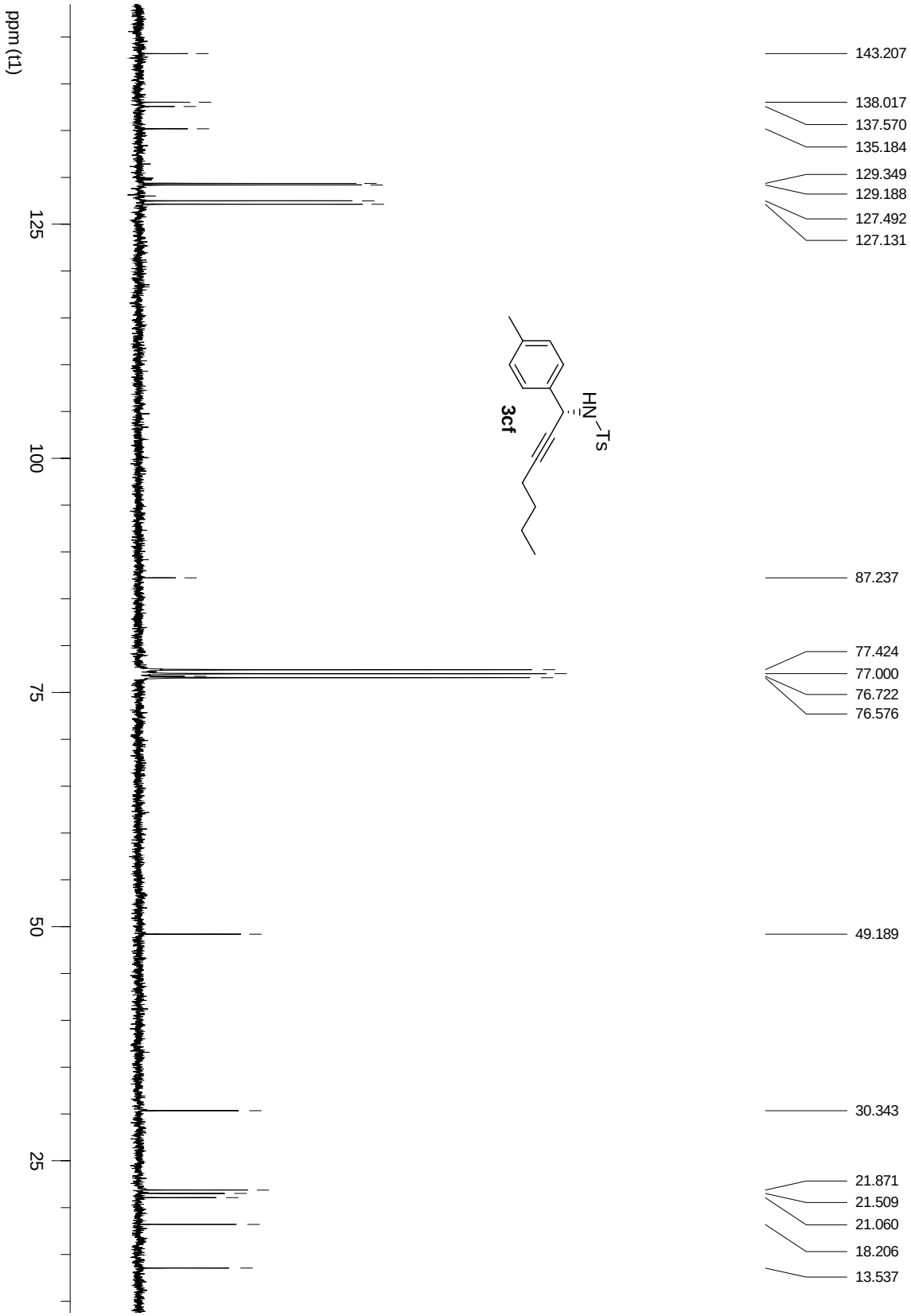
No.	RT	Area	Area %
1	14.54	12999644	51.098
2	16.65	12441075	48.902
		25440719	100.000

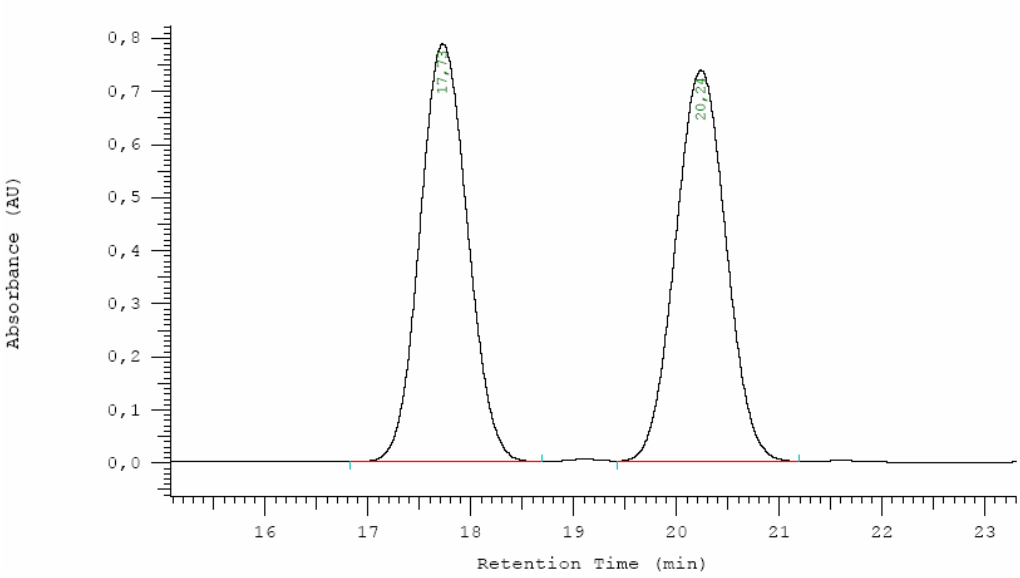


No.	RT	Area	Area %
1	14.40	3956598	90.484
2	16.73	416101	9.516
		4372699	100.000

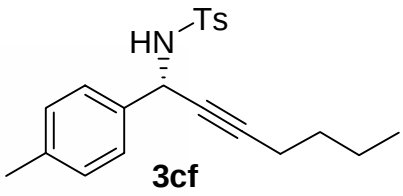


7.783
7.778
7.761
7.756
7.351
7.324
7.296
7.270
7.260
7.125
7.099
5.272
5.243
4.769
4.739
2.428
2.323
1.967
1.960
1.944
1.295
1.284
1.272
1.261
1.248
0.877
0.869
0.854
0.846
0.830
HN
Ts
3cf
ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
1.9
5.0
2.1
1.0
1.0
3.6
3.2
2.2
4.7
3.3

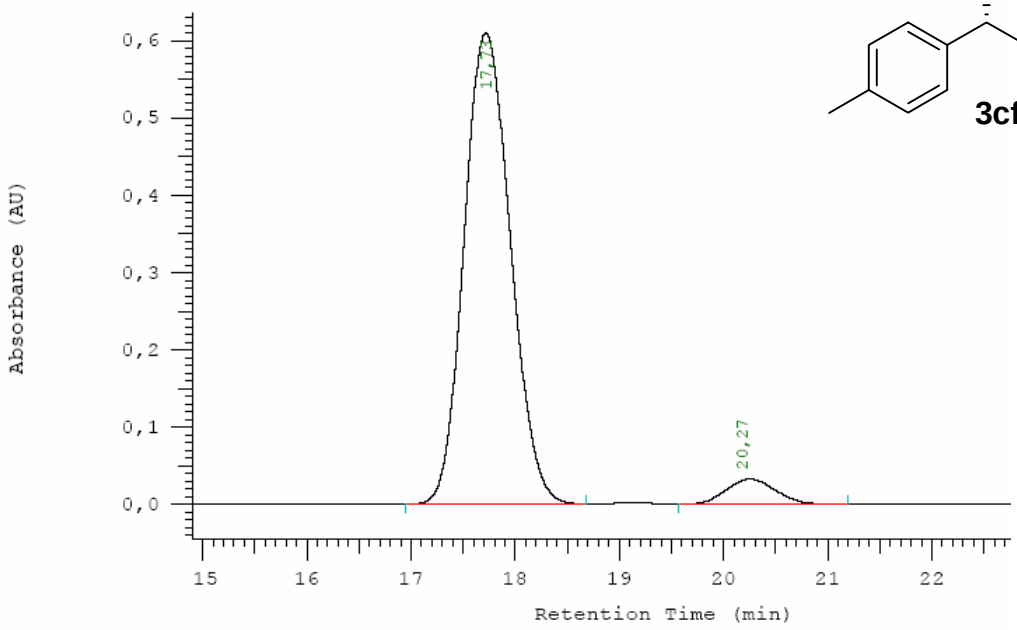

ppm (t1)
125
100
75
50
25
143.207
138.017
137.570
135.184
129.349
129.188
127.492
127.131
87.237
77.424
77.000
76.722
76.576
49.189
30.343
21.871
21.509
21.060
18.206
13.537
HN
Ts
3cf



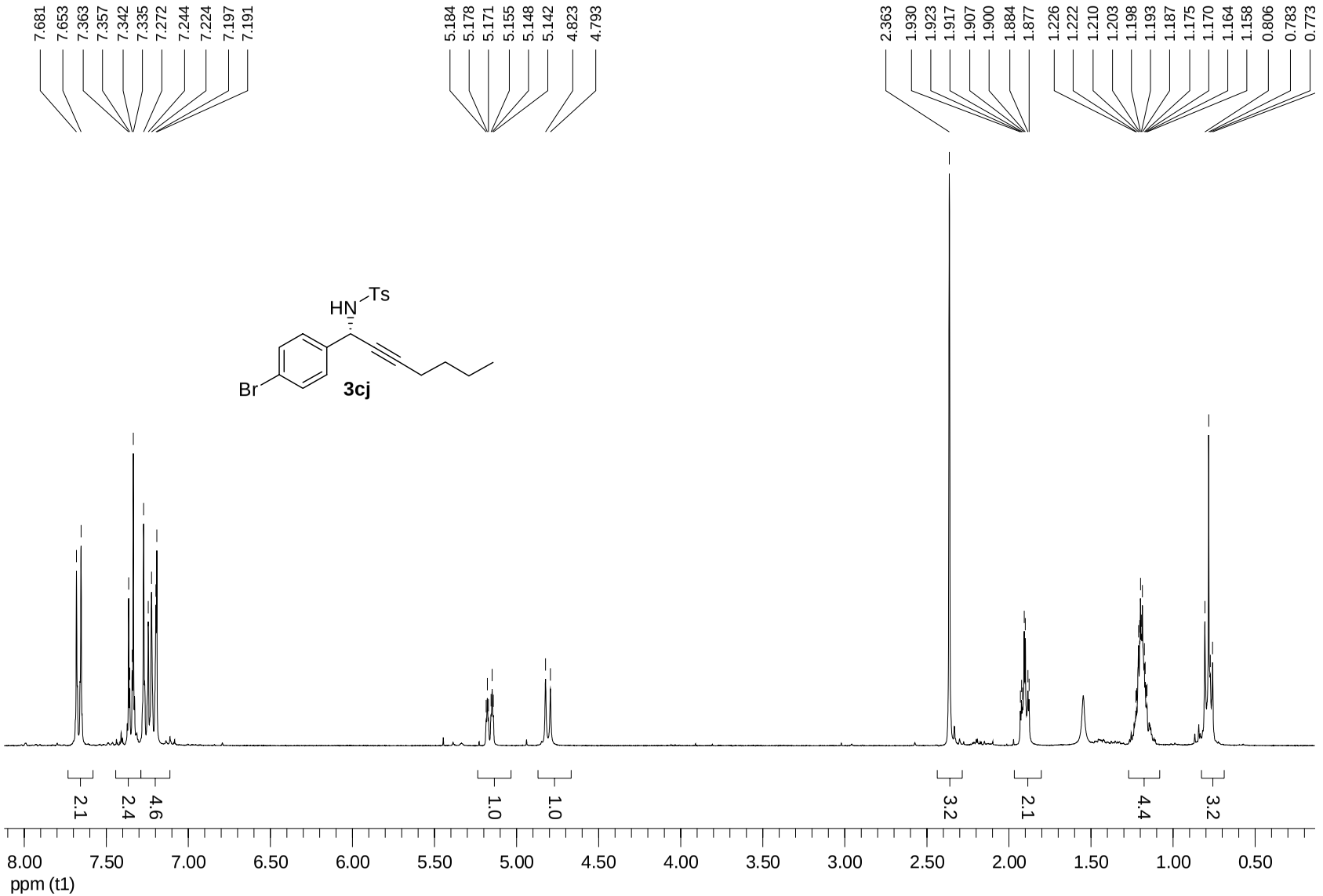
No.	RT	Area	Area %
1	17,73	12631550	50,159
2	20,24	12551715	49,841
		25183265	100,000

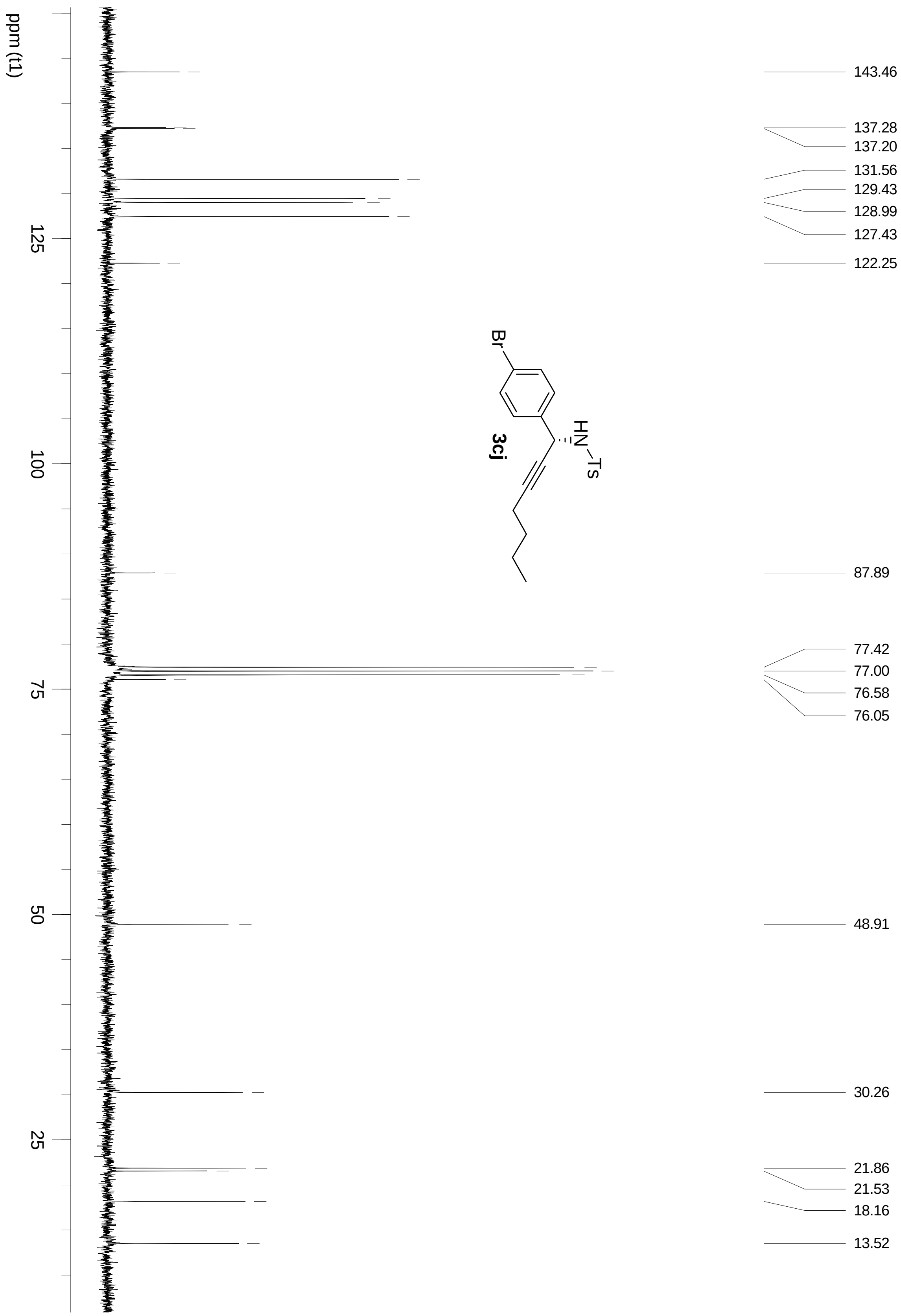


3cf

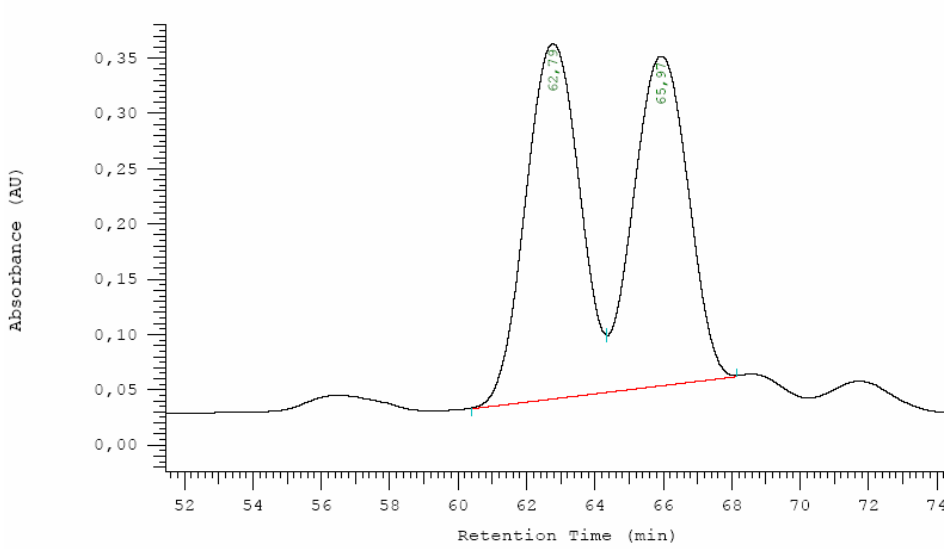


No.	RT	Area	Area %
1	17,73	9340249	94,609
2	20,27	532250	5,391
		9872499	100,000

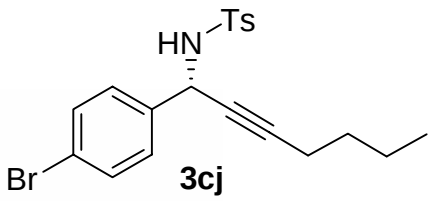

7.681
7.653
7.363
7.357
7.342
7.335
7.272
7.244
7.224
7.197
7.191
5.184
5.178
5.171
5.155
5.148
5.142
4.823
4.793
2.363
1.930
1.923
1.917
1.907
1.900
1.884
1.877
1.226
1.222
1.210
1.203
1.198
1.193
1.187
1.175
1.170
1.164
1.158
0.806
0.783
0.773
HN
Ts
Br
3cj
2.1
2.4
4.6
1.0
1.0
3.2
2.1
4.4
3.2
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)



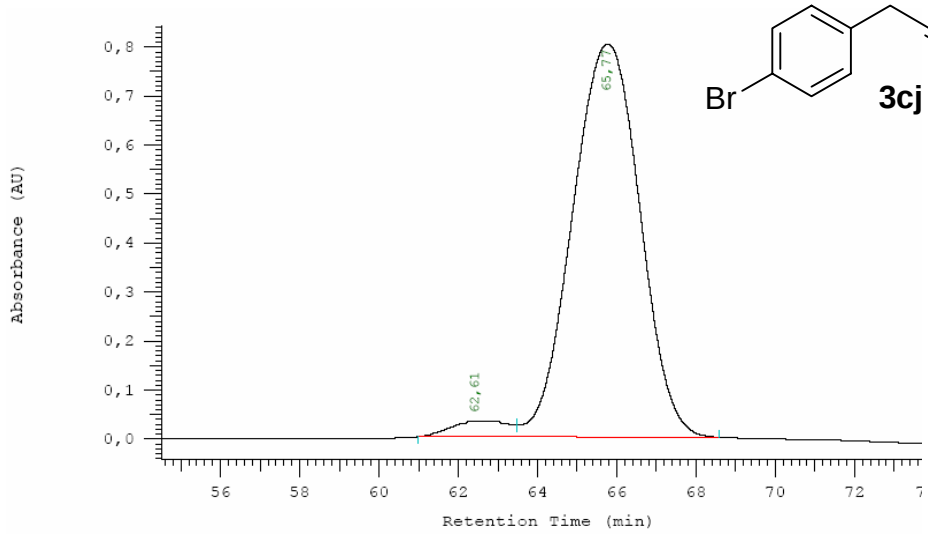
ppm (t1)
125
100
75
50
25
143.46
137.28
137.20
131.56
129.43
128.99
127.43
122.25
87.89
77.42
77.00
76.58
76.05
48.91
30.26
21.86
21.53
18.16
13.52
Br
HN
Ts
3cj



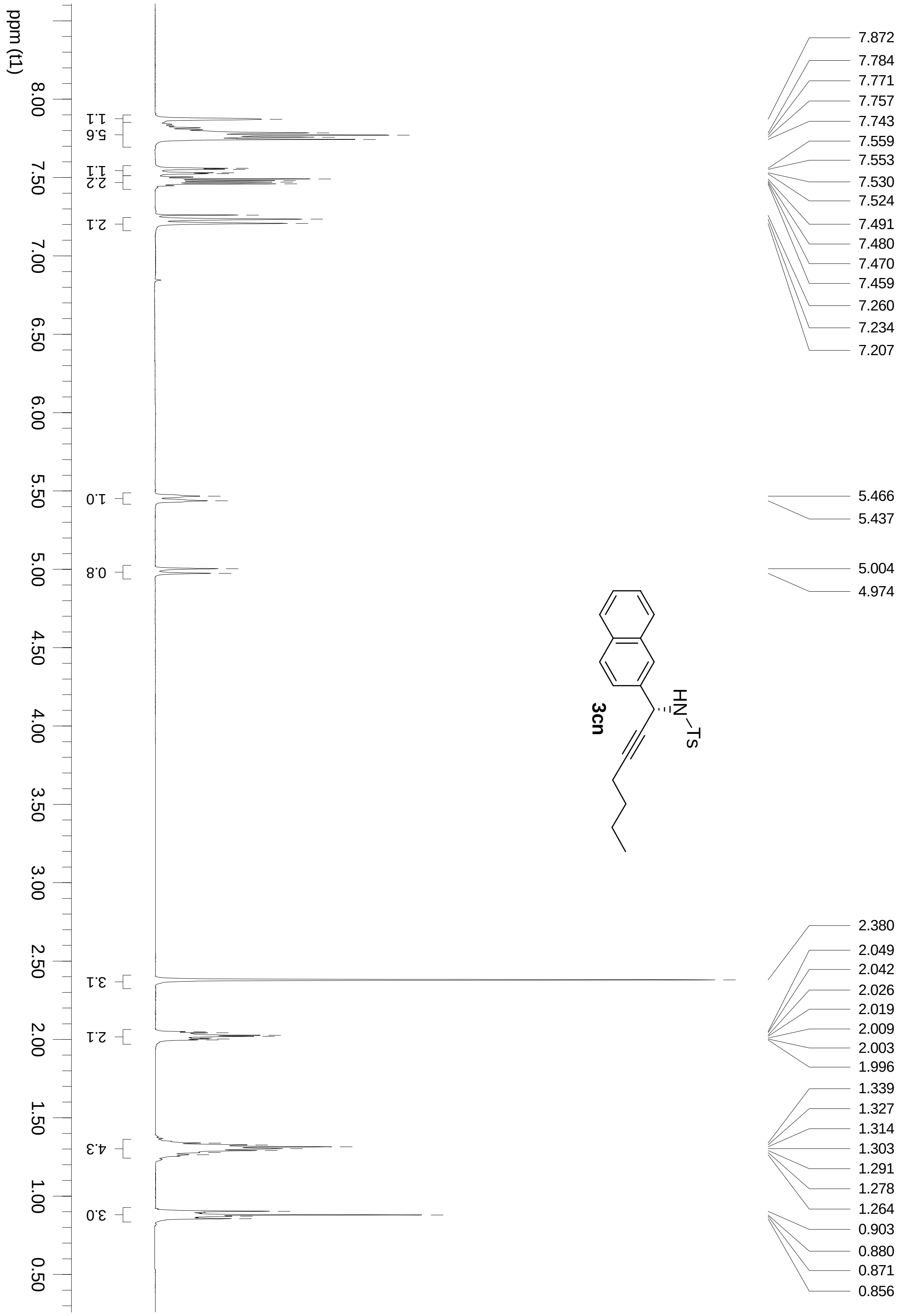
No.	RT	Area	Area %
1	62,79	17305356	51,512
2	65,97	16289172	48,488
		33594528	100,000

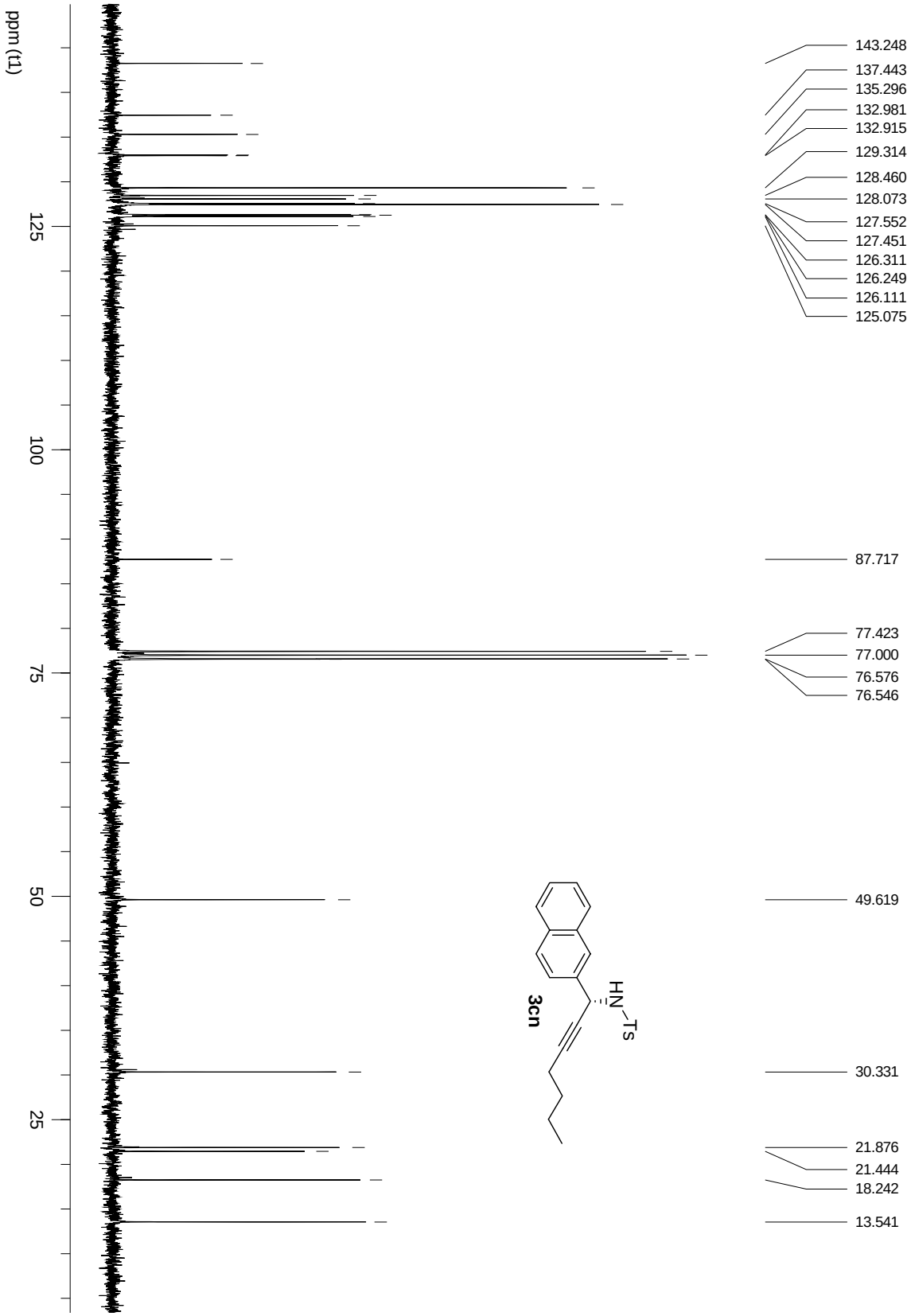


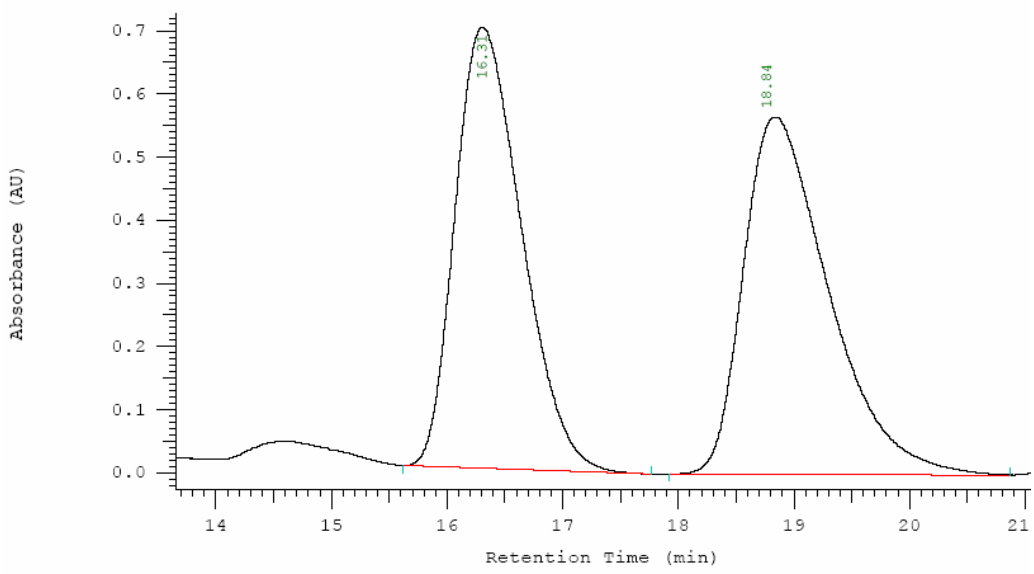
3cj



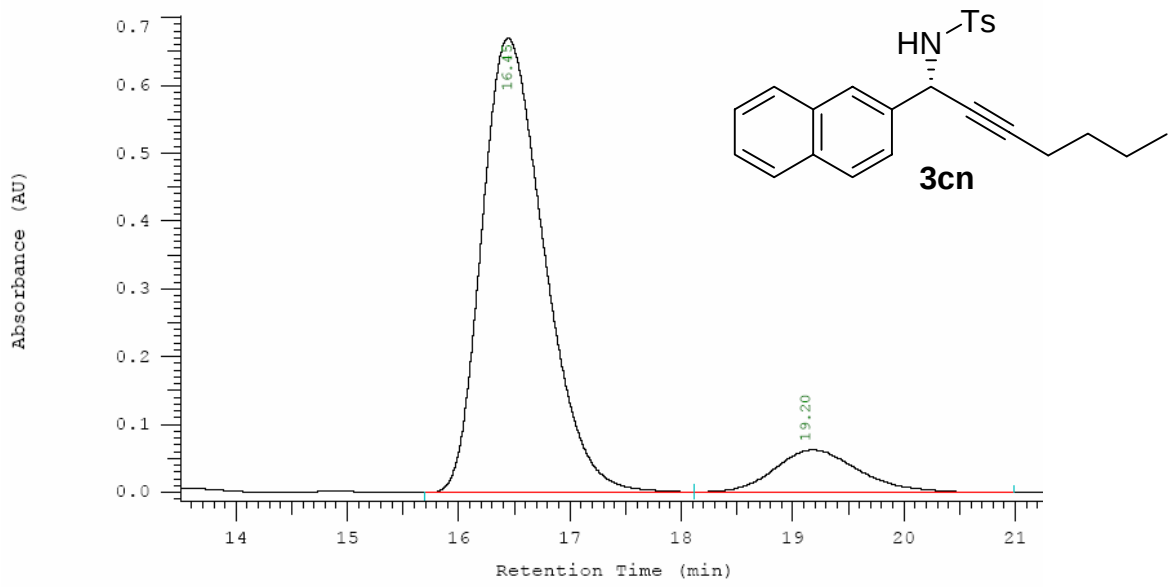
No.	RT	Area	Area %
1	62,61	1591081	3,288
2	65,77	46803072	96,712
		48394153	100,000


ppm (t1)
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
1.1
5.6
1.1
2.2
2.1
1.0
0.8
3.1
2.1
4.3
3.0
7.872
7.784
7.771
7.757
7.743
7.559
7.553
7.530
7.524
7.491
7.480
7.470
7.459
7.260
7.234
7.207
5.466
5.437
5.004
4.974
2.380
2.049
2.042
2.026
2.019
2.009
2.003
1.996
1.339
1.327
1.314
1.303
1.291
1.278
1.264
0.903
0.880
0.871
0.856
HN
Ts
3cn

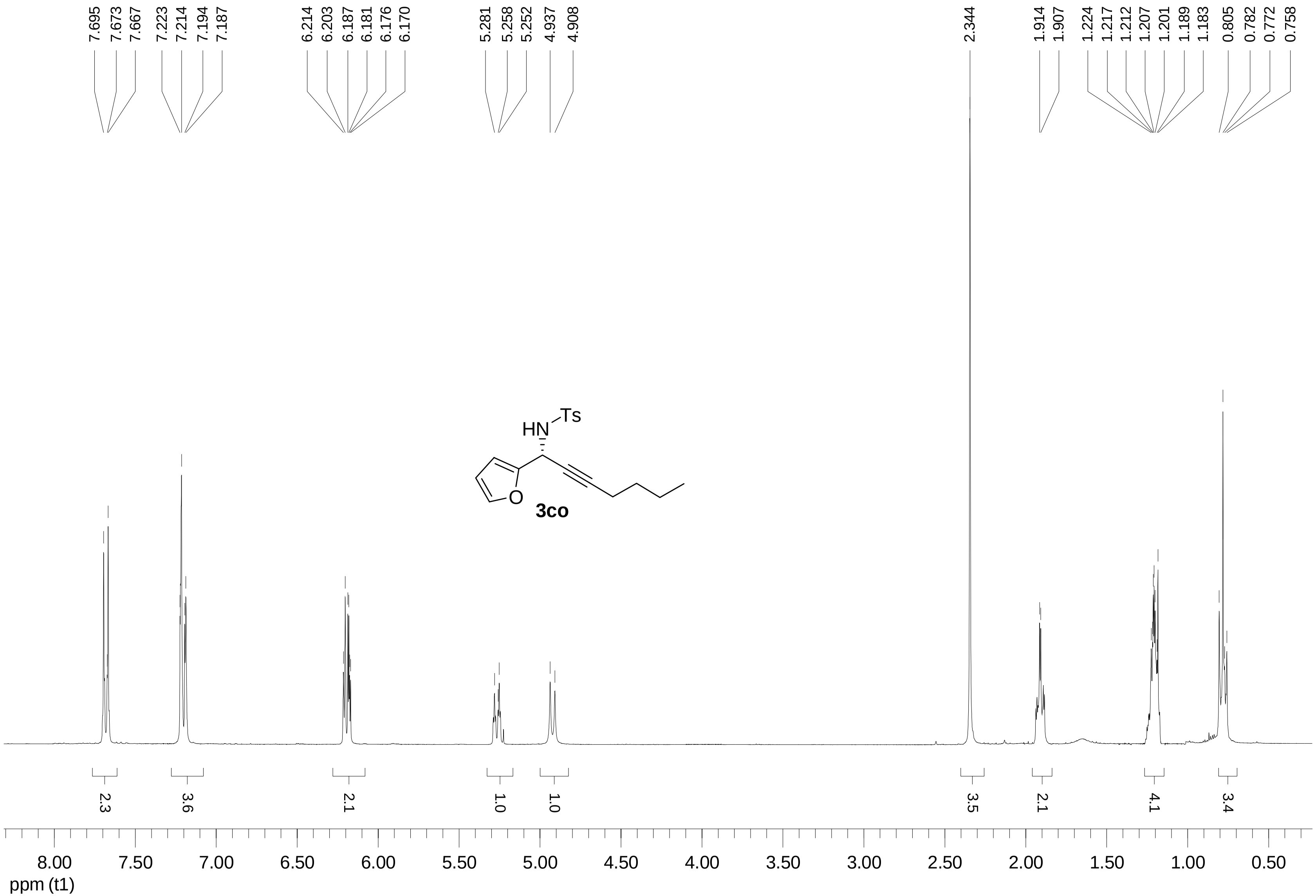

ppm (t1)
125
100
75
50
25
143.248
137.443
135.296
132.981
132.915
129.314
128.460
128.073
127.552
127.451
126.311
126.249
126.111
125.075
87.717
77.423
77.000
76.576
76.546
49.619
30.331
21.876
21.444
18.242
13.541
HN
Ts
3cn

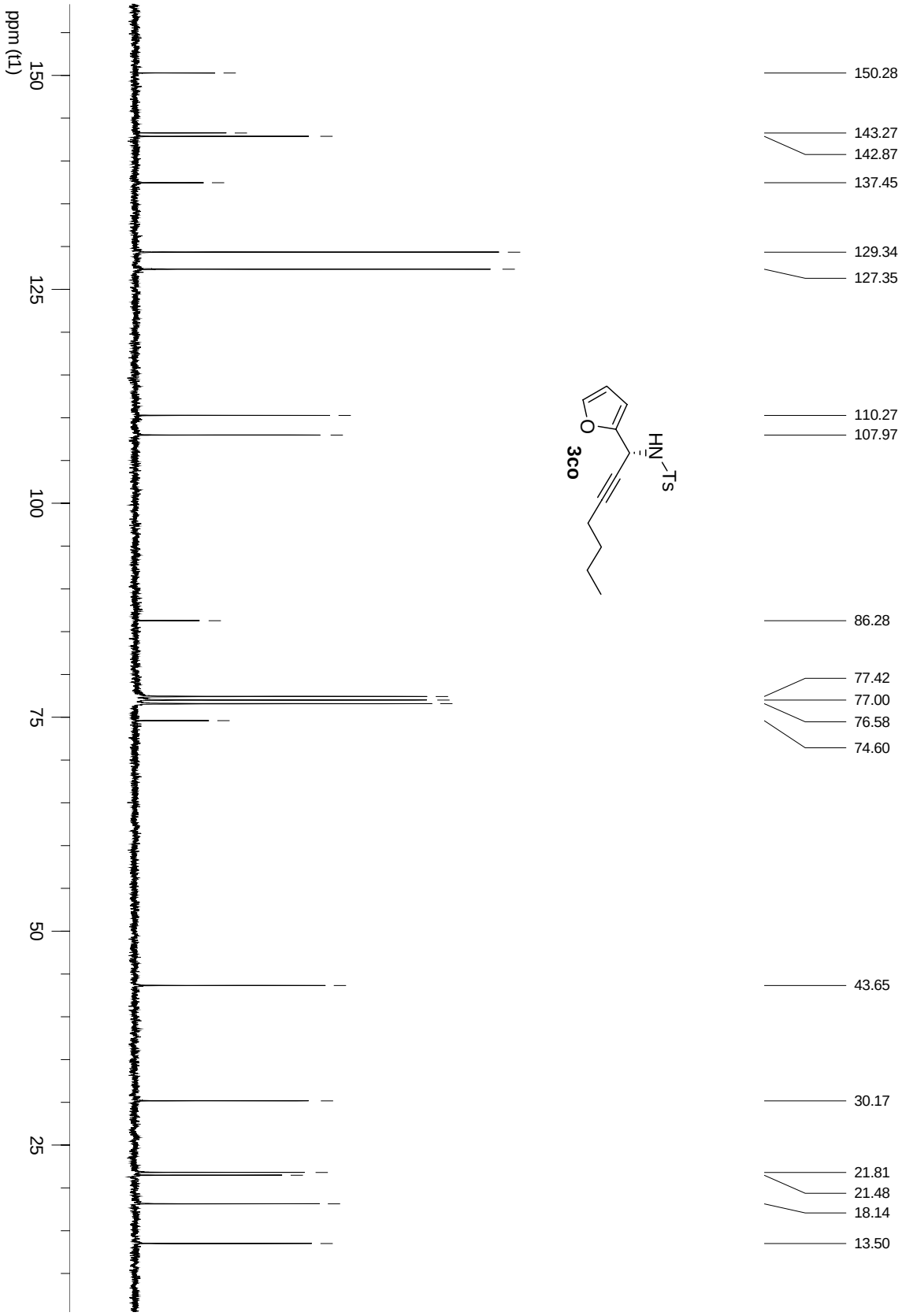


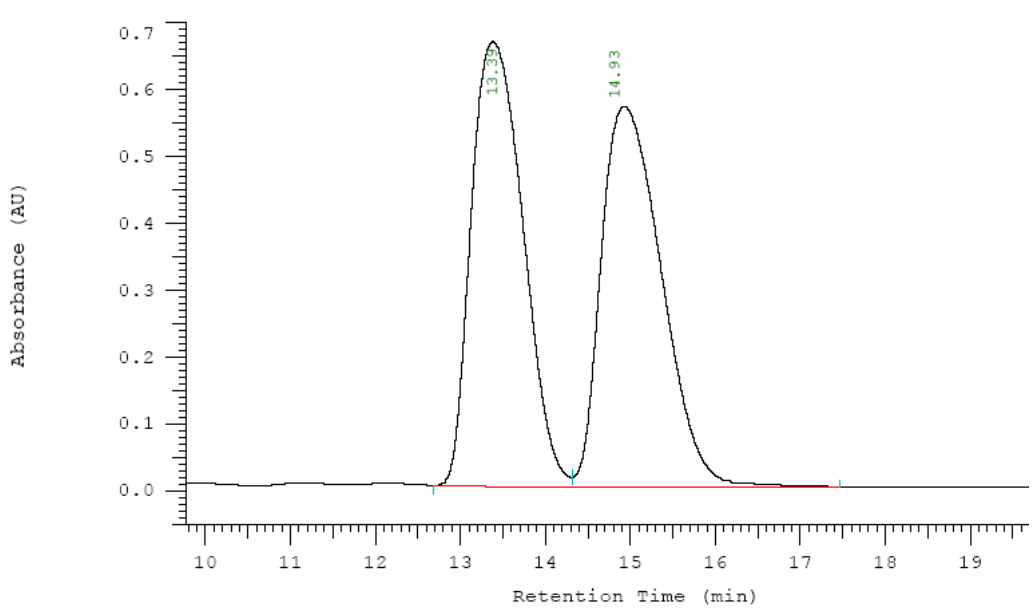
No.	RT	Area	Area %
1	16.31	13880520	49.107
2	18.84	14385360	50.893
		28265880	100.000



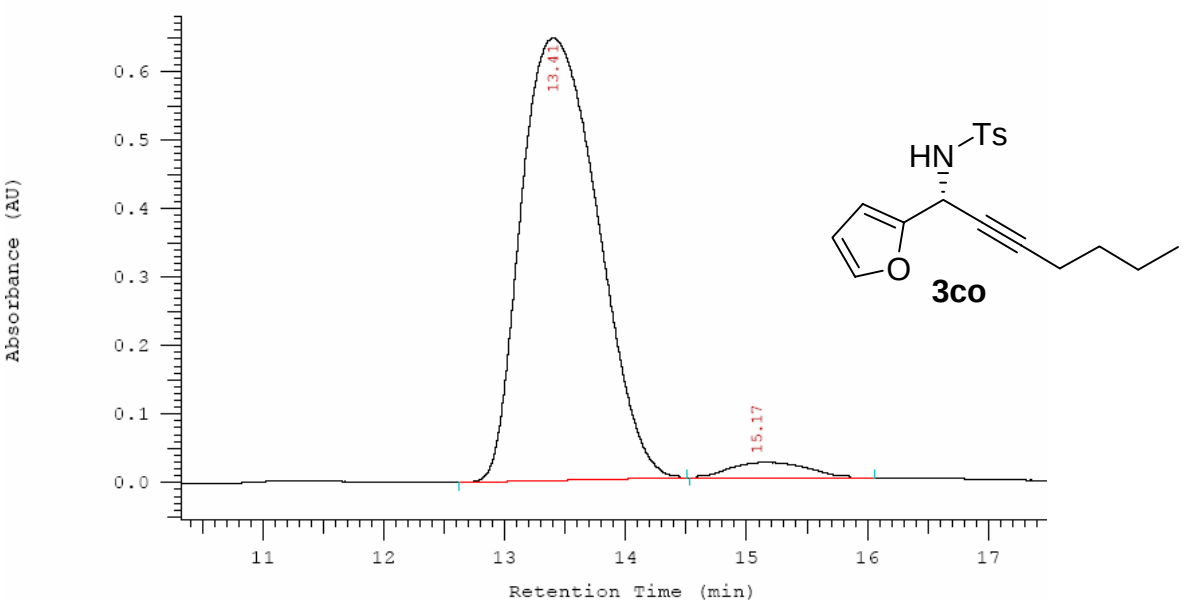
No.	RT	Area	Area %
1	16.45	12999315	88.214
2	19.20	1736805	11.786
		14736120	100.000


7.695
7.673
7.667
7.223
7.214
7.194
7.187
6.214
6.203
6.187
6.181
6.176
6.170
5.281
5.258
5.252
4.937
4.908
2.344
1.914
1.907
1.224
1.217
1.212
1.207
1.201
1.189
1.183
0.805
0.782
0.772
0.758
HN
Ts
O
3co
2.3
3.6
2.1
1.0
1.0
3.5
2.1
4.1
3.4
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)

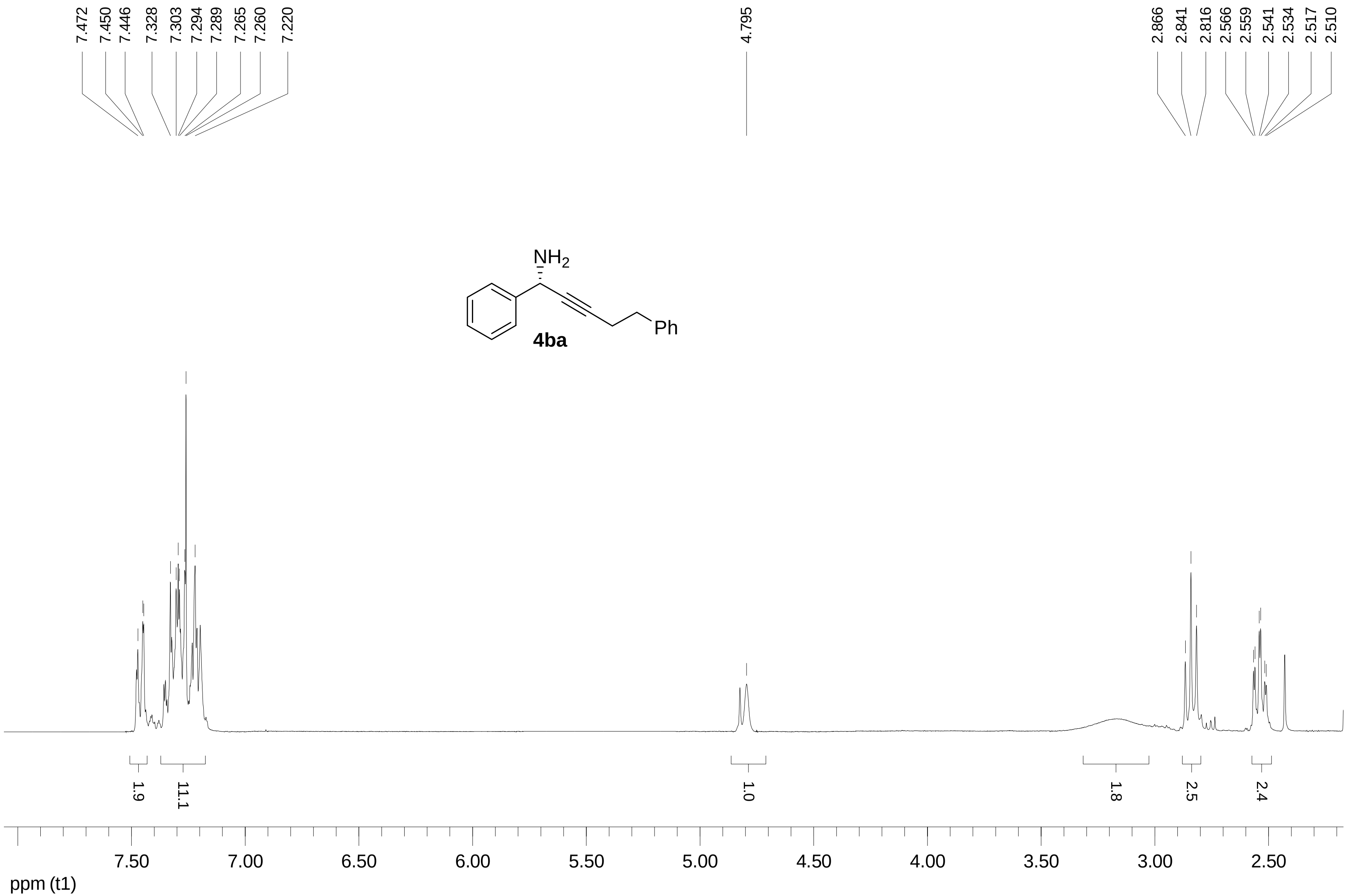

ppm (t1)
150
125
100
75
50
25
O
HN
Ts
3co
150.28
143.27
142.87
137.45
129.34
127.35
110.27
107.97
86.28
77.42
77.00
76.58
74.60
43.65
30.17
21.81
21.48
18.14
13.50

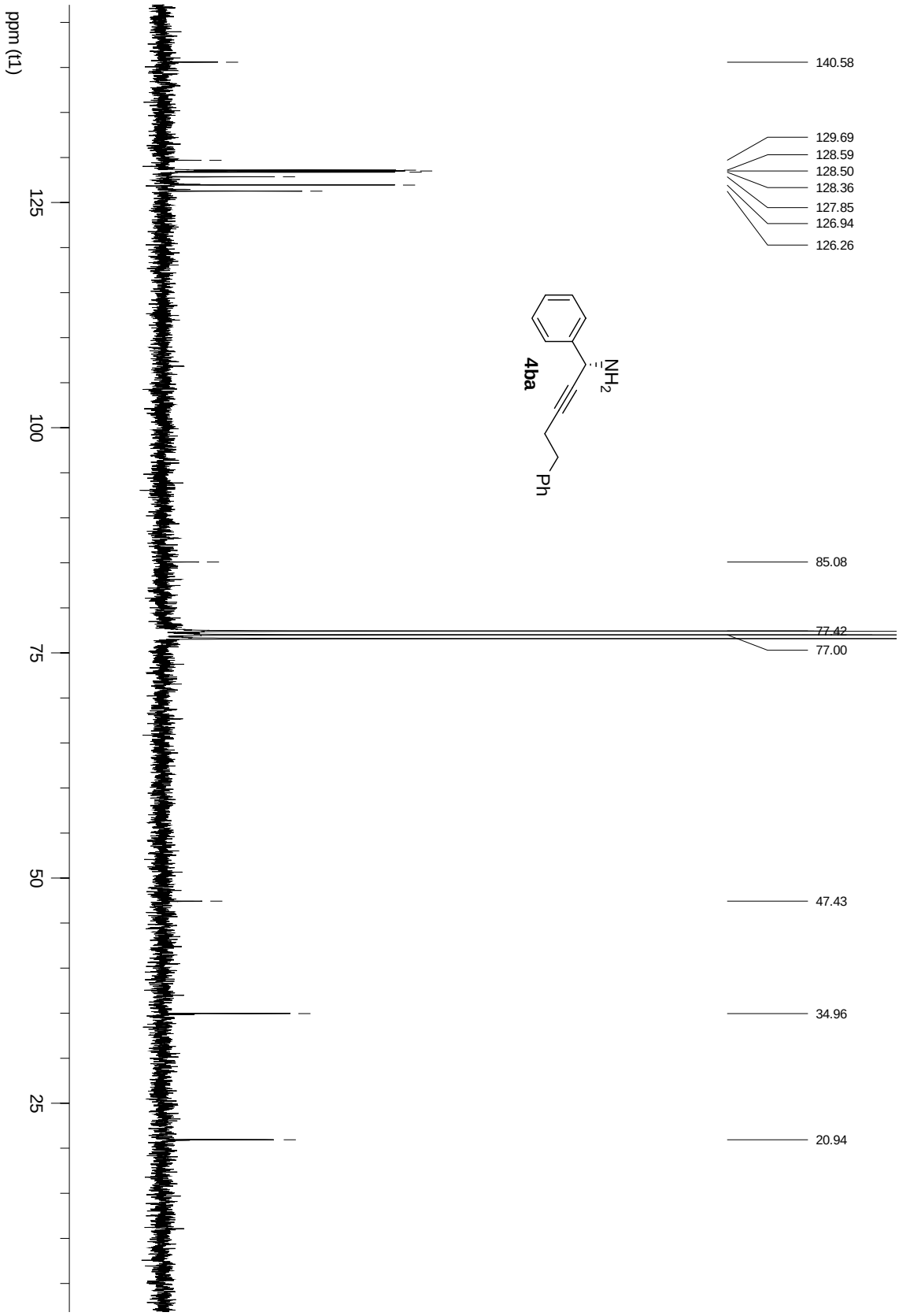


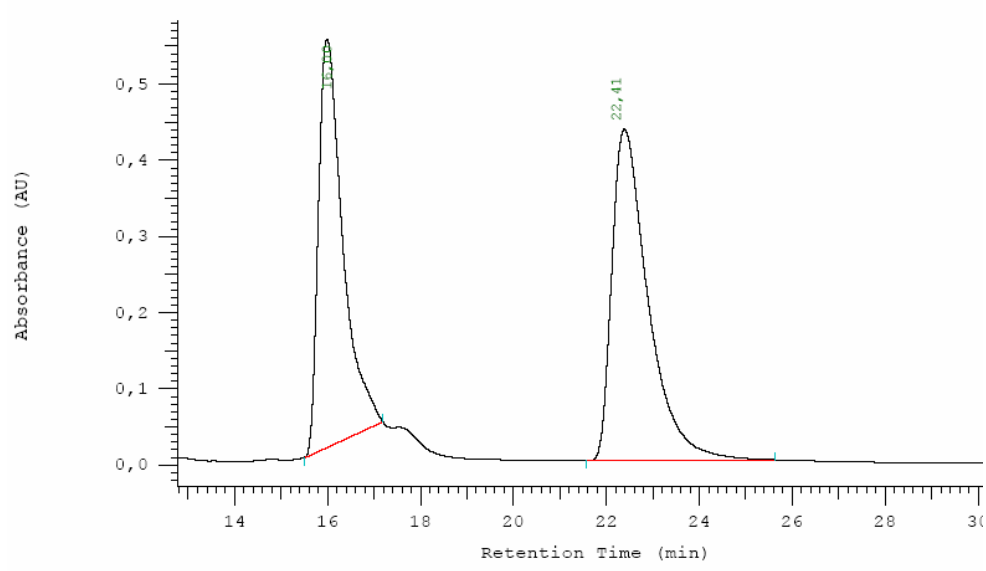
No.	RT	Area	Area %
1	13.39	13883232	50.213
2	14.93	13765217	49.787
		27648449	100.000



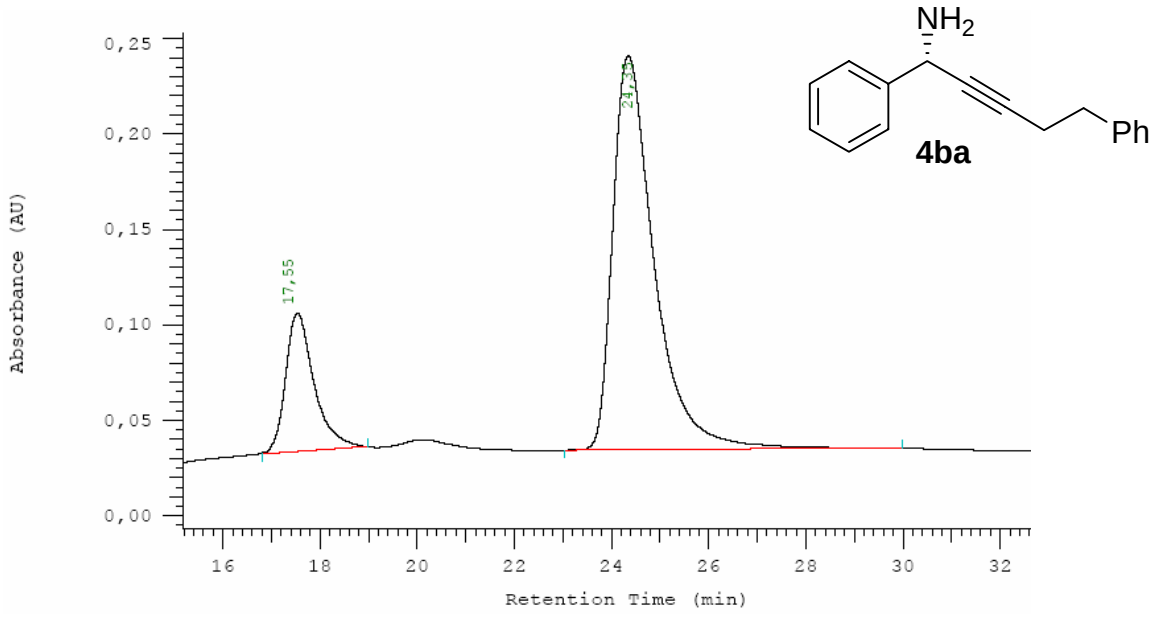
No.	RT	Area	Area %
1	13.41	14181150	96.570
2	15.17	503760	3.430
		14684910	100.000


7.472
7.450
7.446
7.328
7.303
7.294
7.289
7.265
7.260
7.220
4.795
2.866
2.841
2.816
2.566
2.559
2.541
2.534
2.517
2.510
NH2
Ph
4ba
1.9
11.1
1.0
1.8
2.5
2.4
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
ppm (t1)

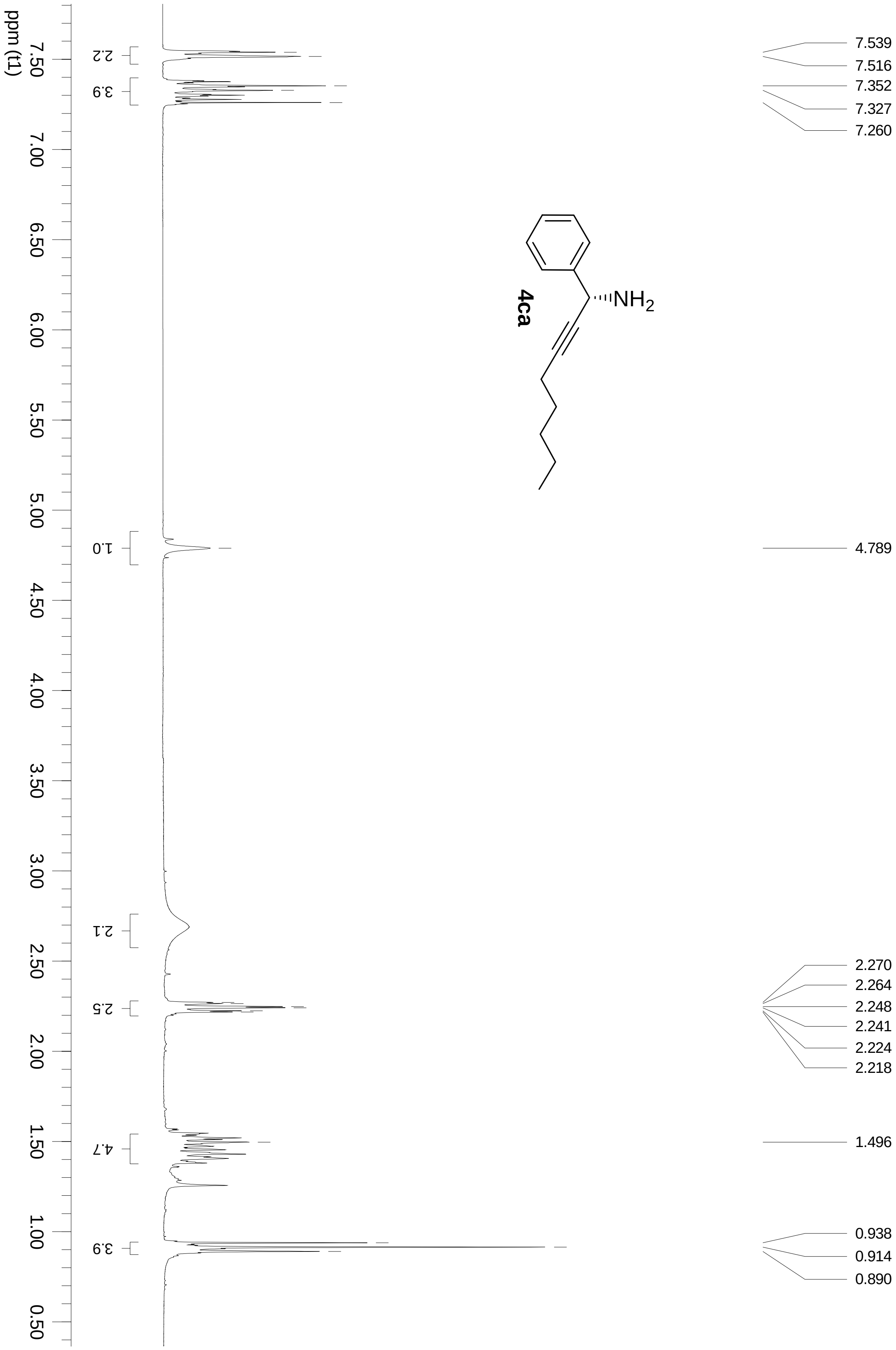

ppm (t1)
125
100
75
50
25
140.58
129.69
128.59
128.50
128.36
127.85
126.94
126.26
85.08
77.42
77.00
47.43
34.96
20.94
NH2
Ph
4ba

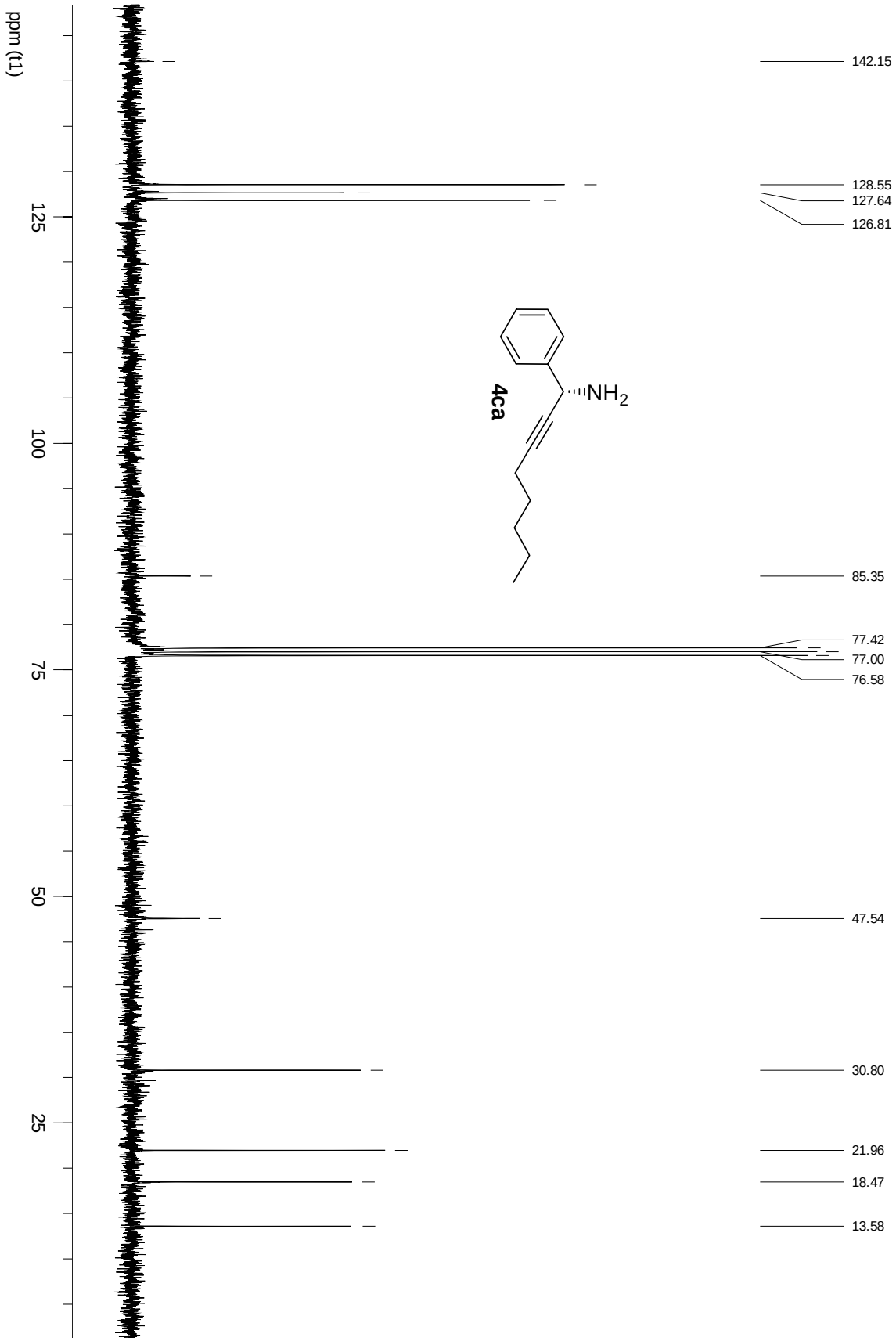


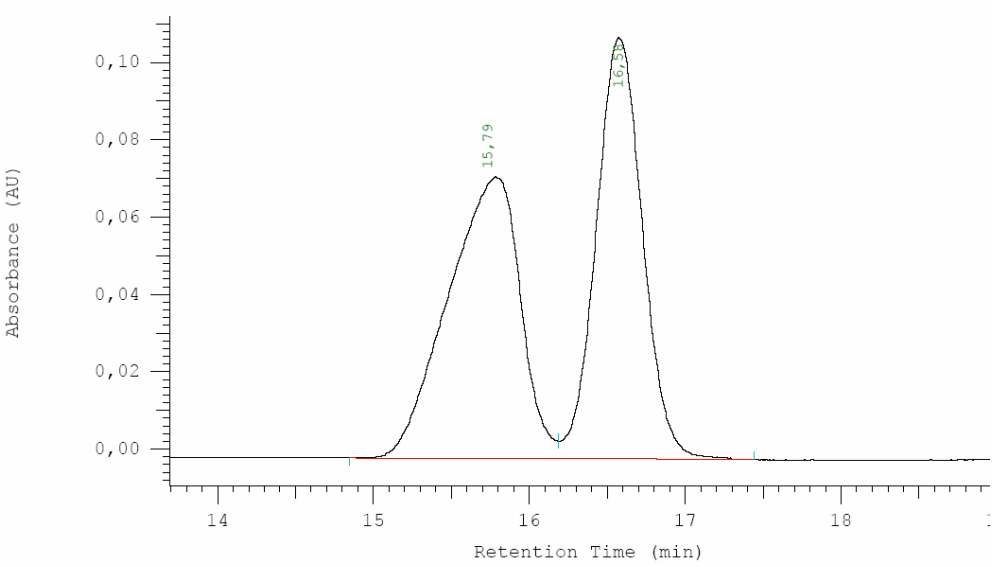
No.	RT	Area	Area %
1	16,00	9473344	45,122
2	22,41	11521735	54,878
		20995079	100,000



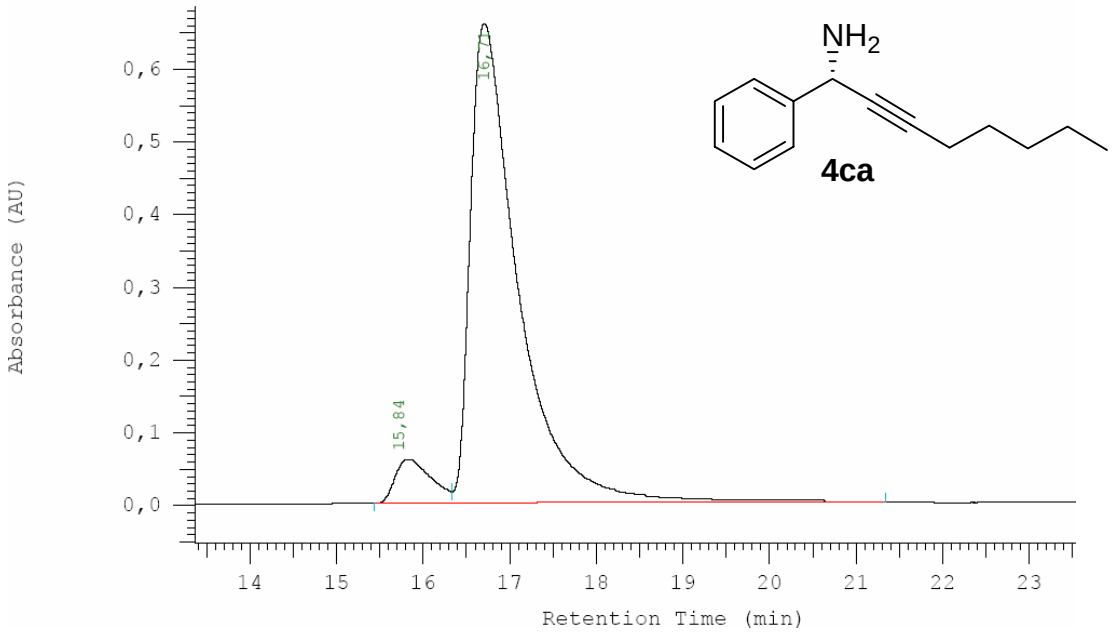
No.	RT	Area	Area %
1	17,55	1379450	19,001
2	24,35	5880610	80,999
		7260060	100,000


ppm (t1)
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
2.2
3.9
1.0
2.1
2.5
4.7
3.9
7.539
7.516
7.352
7.327
7.260
4.789
2.270
2.264
2.248
2.241
2.224
2.218
1.496
0.938
0.914
0.890
NH_2
4ca

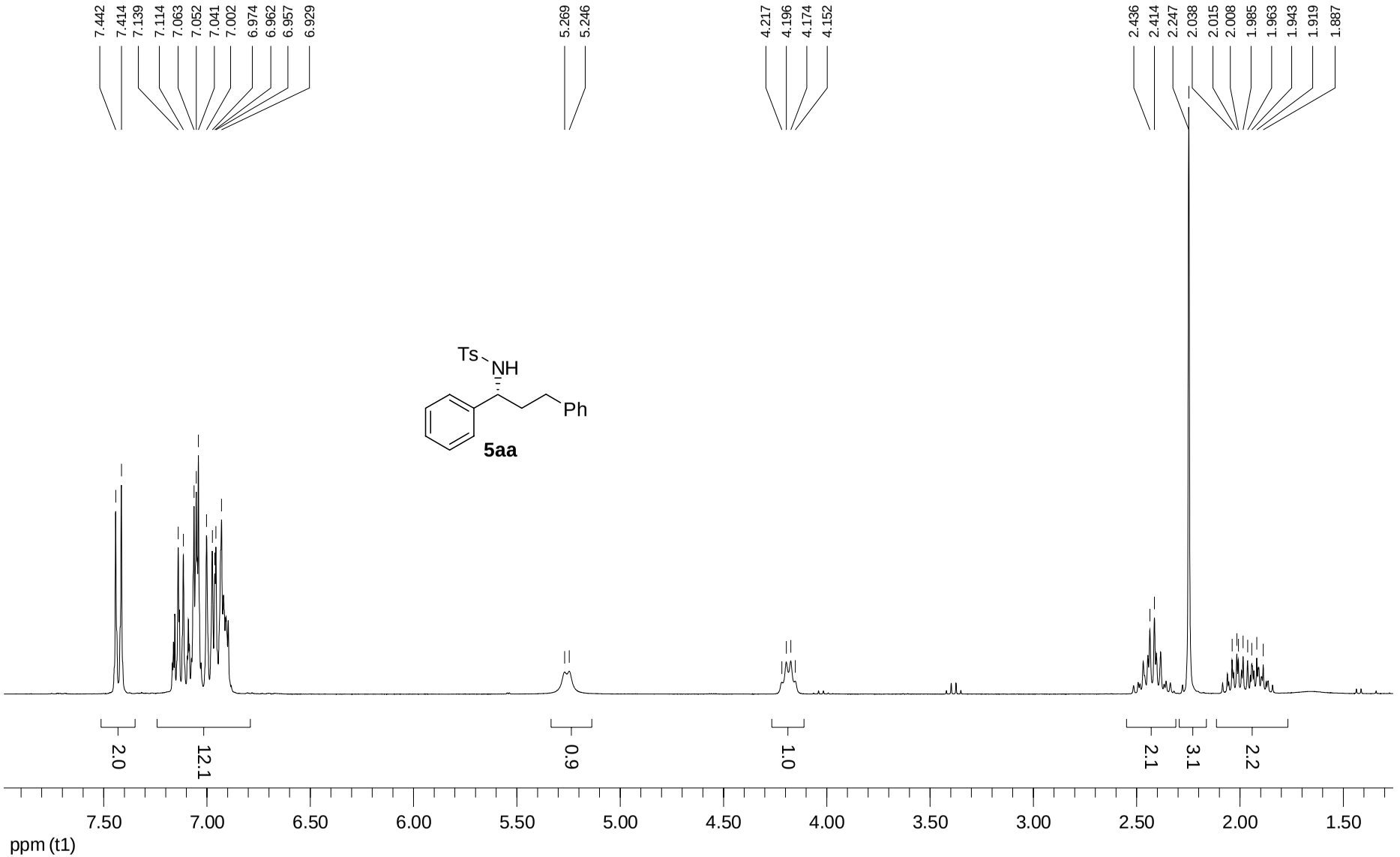

ppm (t1)
125
100
75
50
25
142.15
128.55
127.64
126.81
85.35
77.42
77.00
76.58
47.54
30.80
21.96
18.47
13.58
NH2
4ca

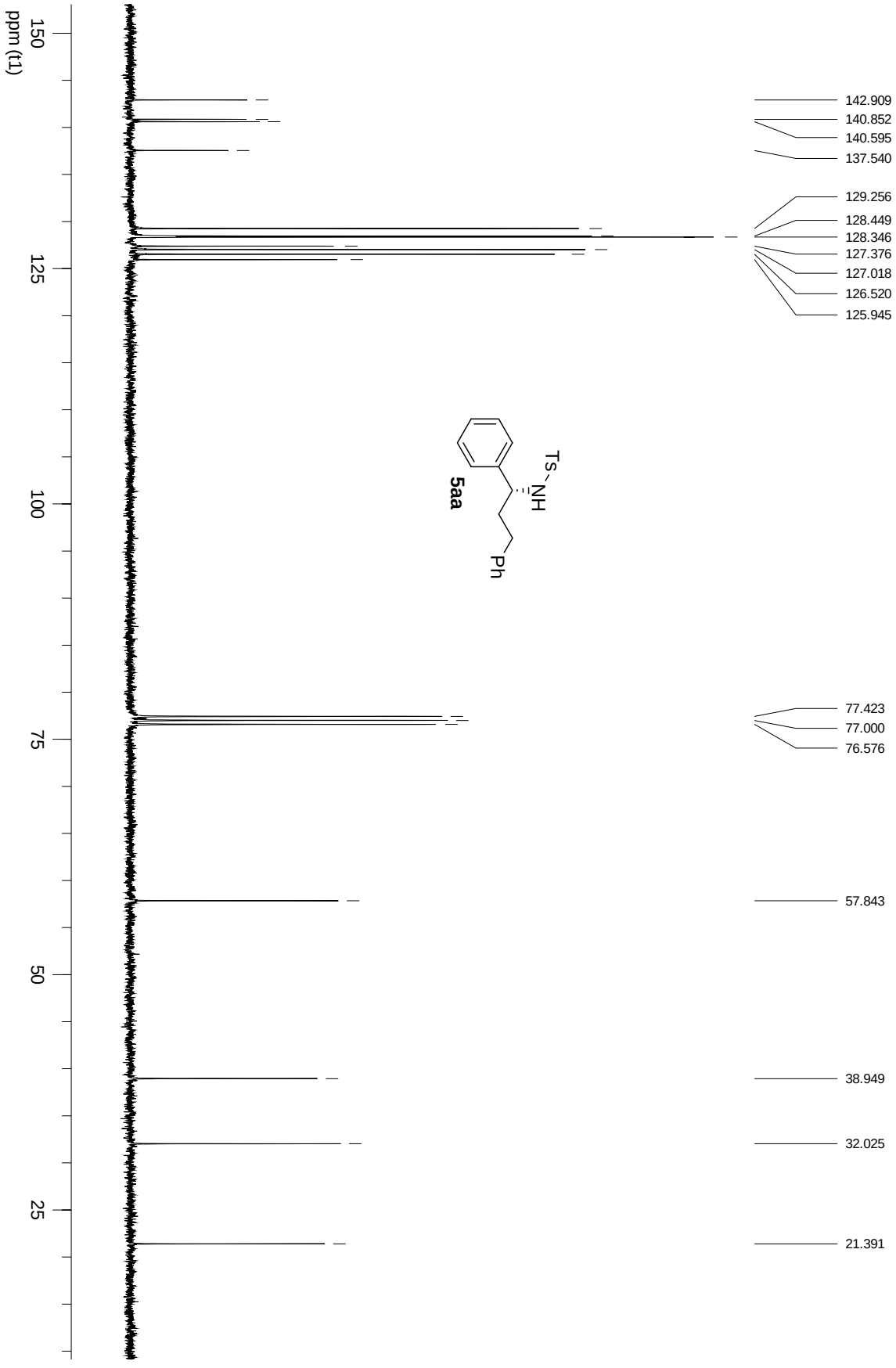


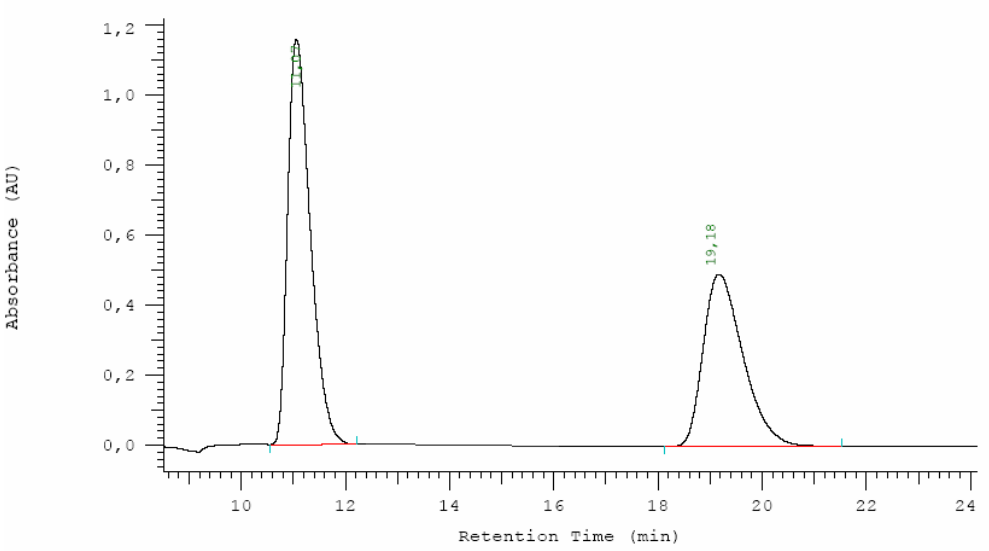
No.	RT	Area	Area %
1	15,79	1174585	51,072
2	16,58	1125274	48,928
		2299859	100,000



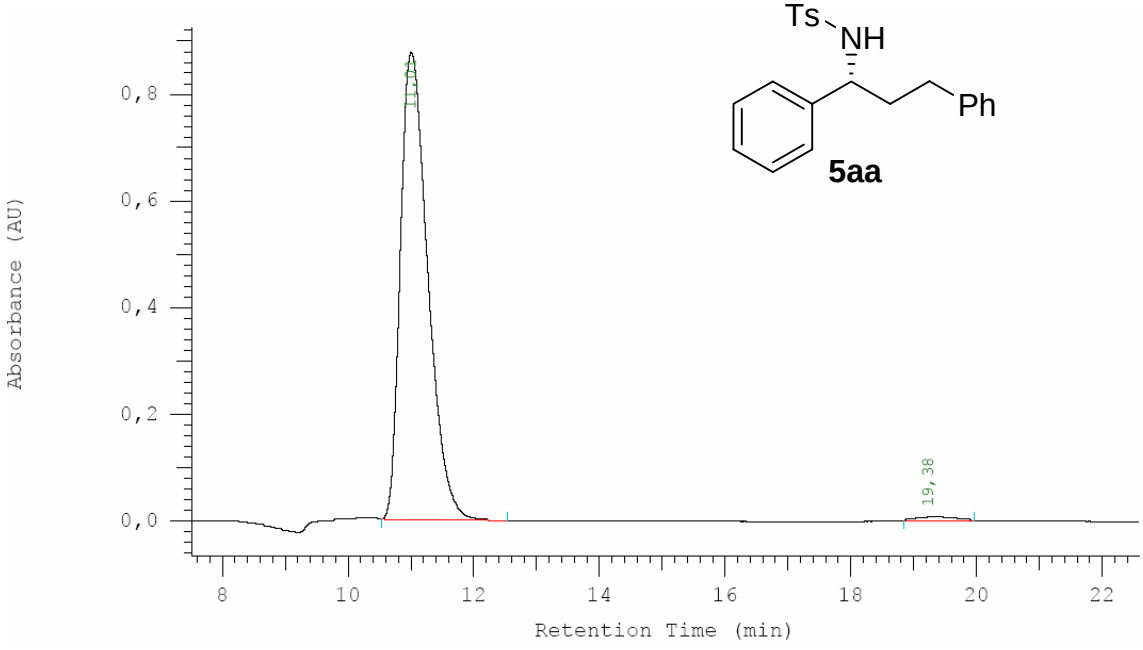
No.	RT	Area	Area %
1	15,84	657090	8,923
2	16,71	6707190	91,077
		7364280	100,000


7.442
7.414
7.139
7.114
7.063
7.052
7.041
7.002
6.974
6.962
6.957
6.929
5.269
5.246
4.217
4.196
4.174
4.152
2.436
2.414
2.247
2.038
2.015
2.008
1.985
1.963
1.943
1.919
1.887
Ts
NH
Ph
5aa
2.0
12.1
0.9
1.0
2.1
3.1
2.2
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)

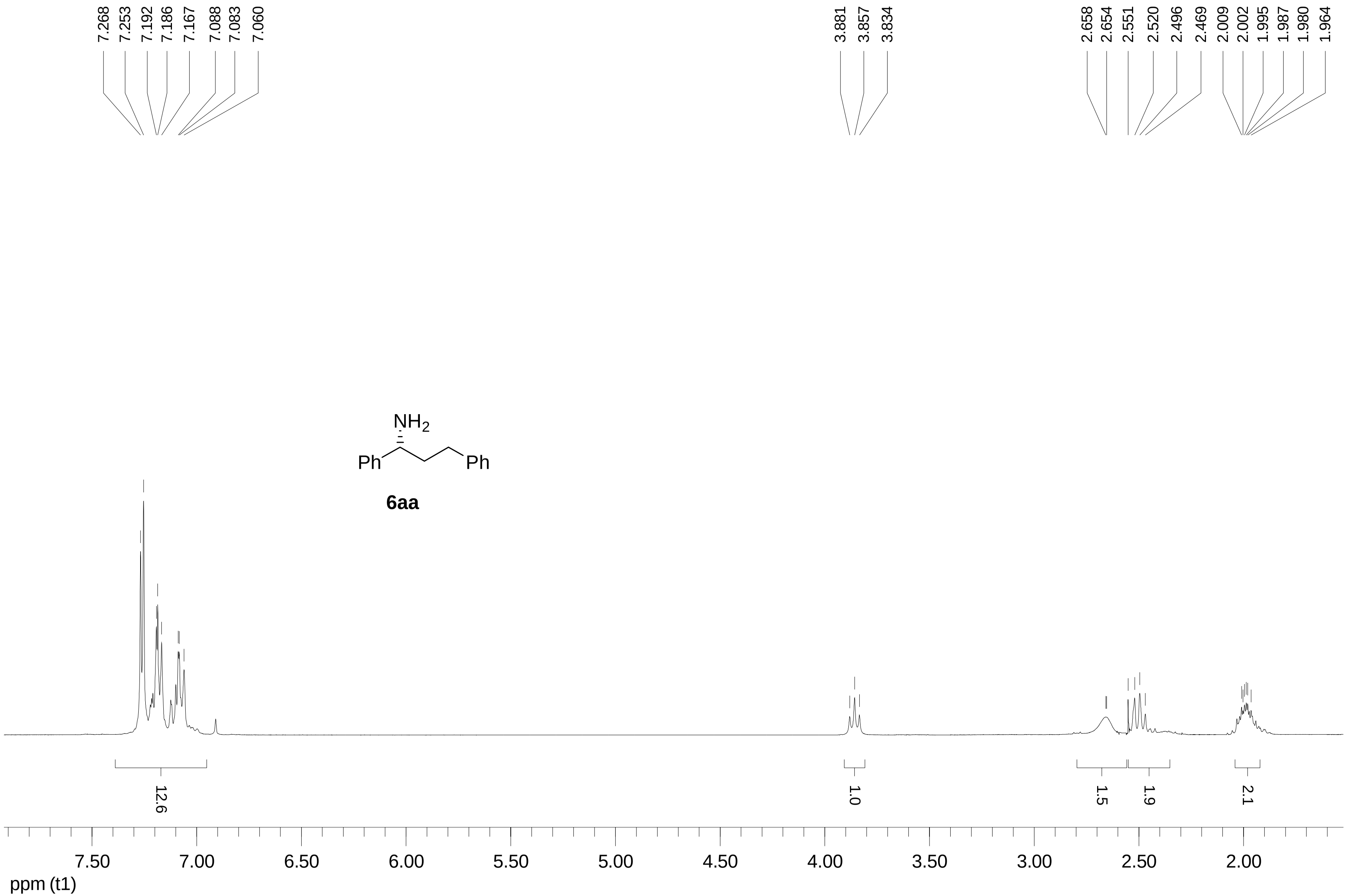

ppm (t1)
150
125
100
75
50
25
142.909
140.852
140.595
137.540
129.256
128.449
128.346
127.376
127.018
126.520
125.945
77.423
77.000
76.576
57.843
38.949
32.025
21.391
Ts
NH
Ph
5aa



No.	RT	Area	Area %
1	11,07	16975150	57,019
2	19,18	12795689	42,981
		29770839	100,000

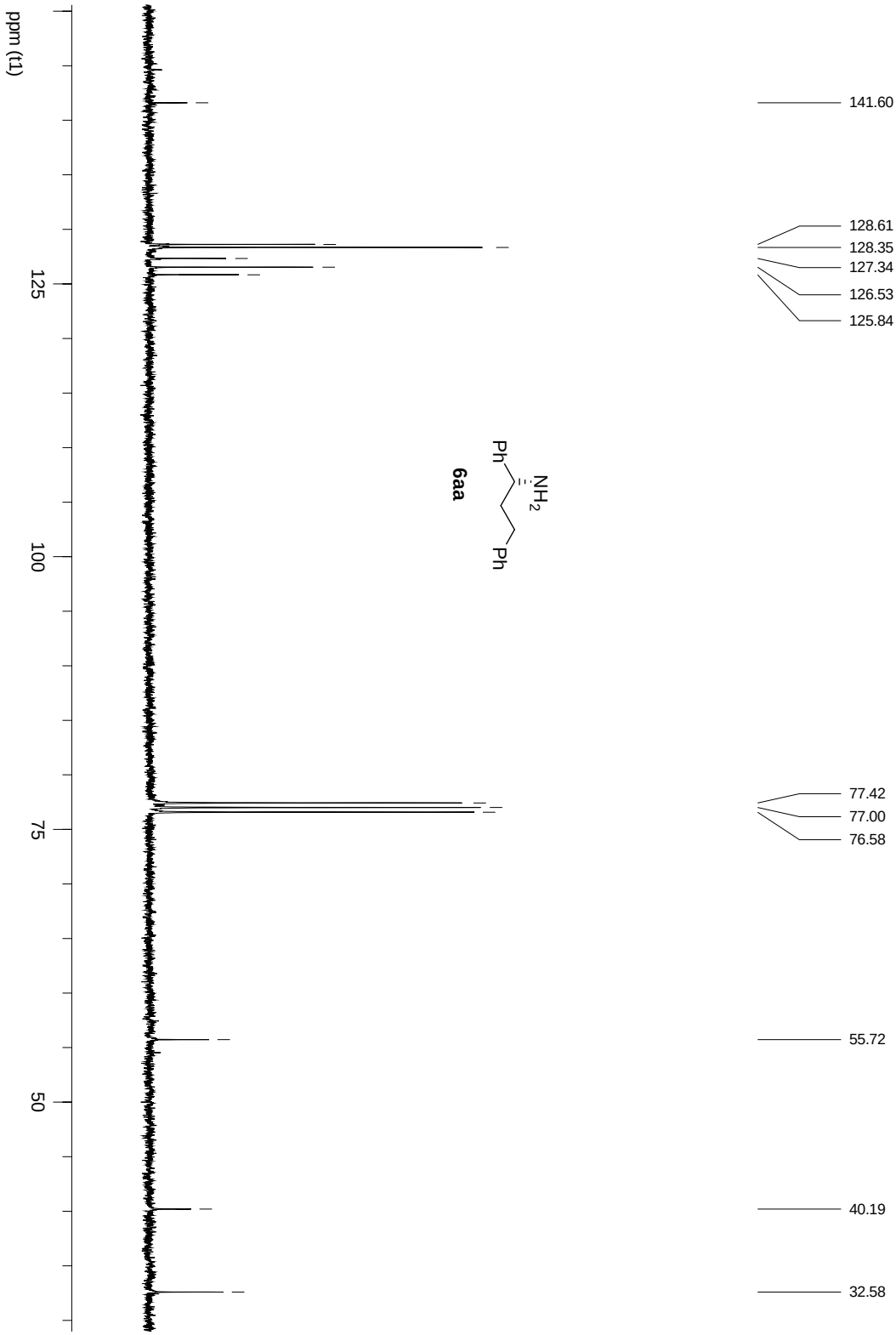


No.	RT	Area	Area %
1	11,02	15629065	98,542
2	19,37	231205	1,458
		15860270	100,000



7.268
7.253
7.192
7.186
7.167
7.088
7.083
7.060
3.881
3.857
3.834
2.658
2.654
2.551
2.520
2.496
2.469
2.009
2.002
1.995
1.987
1.980
1.964
12.6
1.0
1.5
1.9
2.1
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)
NH2
Ph
Ph

6aa


ppm (t1)
125
100
75
50
141.60
128.61
128.35
127.34
126.53
125.84
77.42
77.00
76.58
55.72
40.19
32.58
Ph
NH2
Ph
6aa