Carbon-Sulfur Bond Formation via Iridium-Catalyzed Asymmetric Allylation of Aliphatic Thiols

Ning Gao, Shengcai Zheng, Weikang Yang, and Xiaoming Zhao*

Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092 P.R. China and Key Laboratory of Fluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032 P.R. China

xmzhao08@mail.tongji.edu.cn

Supporting Information

Table of Contents

General Experimental Details:

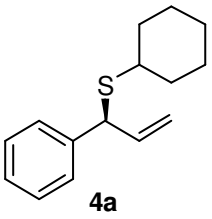
All air-sensitive manipulations were conducted under an argon atmosphere by standard Schlenk techniques. All glassware was dried by oven or flame immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. All reagents were purchased from commercial sources and used without further purification. Sodium cyclohexanethiolate and sodium allylthiolate were prepared by reaction of cyclohexyl mercaptan or allyl mercaptan with NaH (80 % in liquid paraffin) in THF at room temperature. After stirring overnight at 0 °C to room temperature, the solvent was evaporated and the residual was washed with petroleum ether 3 times to afford sodium cyclohexanethiolate as a white powder or sodium allylthiolate as a light brown powder.[1] The phosphoramidite ligands[2] and substituted allylic carbonates[3] were prepared according to known procedures.

^{1}H NMR spectra were obtained at 300 MHz or 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 75 MHz or 100 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

HPLC analyses were carried out on a Waters chromatography system or Agilent 1100 HPLC system or SHIMADZU LC-15 system. IR analyses were obtained on Nicolet FT-IR spectrometers. Flash column chromatography was performed on silica gel. Products were visualized on TLC plates by UV or by staining with $KMnO_4$ or iodine vapor.

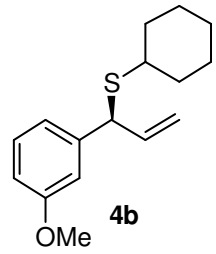
General Procedure for the Synthesis of Allylic Sulfane 4 and 6, 7:

$[Ir(COD)Cl]_2$ (0.0020 mmol, 1.0 mol %), phosphoramidite ligand **L3** [*O,O'*-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-[phenylethylphosphoramidite] (0.0040 mmol, 2.0 mol %) were dissolved in THF (0.5 mL) and propylamine (0.2 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **2** (0.40 mmol, 200 mol %), sodium cyclohexanethiolate or sodium allylthiolate **3** (0.20 mmol), cesium fluoride (0.60 mmol, 300 mol %) or without the cesium fluoride, and dichloromethylene (2.0 mL) were added. The reaction mixture was stirred at room temperature overnight. Then the crude reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography to give the desired products. The ratio of regionisomers (branched to linear) was determined by ^{1}H NMR or GC-MS of the crude reaction mixture.



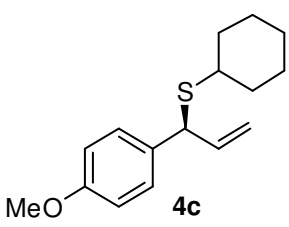
4a

(*S*)-cyclohexyl(1-phenylallyl)sulfane (4a): ^{1}H NMR spectroscopy showed a 91:9 branched:linear ratio. The mixture was purified by flash column chromatography (100 % petroleum ether) to give **4a** as a colorless liquid in 72% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 17.80 min (major); 32.10 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 96%. $[\alpha]_D^{20}$ = -66.0° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.29 (m, 4H), 7.23 (dddd, *J* = 7.2, 7.2, 1.6, 1.2 Hz, 1H), 6.05 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.12 (d, *J* = 16.8 Hz, 1H), 5.10 (ddd, *J* = 10.0, 0.8, 0.4 Hz, 1H), 4.52 (d, *J* = 8.4 Hz, 1H), 2.56 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.94-1.91 (m, 2H), 1.75-1.72 (m, 2H), 1.60-1.59 (m, 1H), 1.41-1.33 (m, 2H), 1.29-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.9, 138.6, 128.5, 127.7, 127.1, 115.2, 51.1, 43.0, 33.5, 33.3, 26.0, 25.83, 25.80. MS (EI, *m/z*, rel. intensity) 117 (100), 232 (M+); HRMS (EI) calcd for $C_{15}H_{20}S$ (M^+): 232.1286, Found: 232.1291. IR (KBr): ν_{max} (cm^{-1}) = 3081, 3061, 3028, 2927, 2851, 1633, 1600, 1490, 1448, 1414, 1262, 1072, 1028, 998, 915, 887, 804, 739, 697, 664.



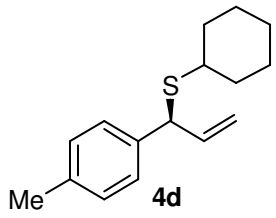
4b

(*S*)-cyclohexyl(1-(3-methoxyphenyl)allyl)sulfane (4b): ^{1}H NMR spectroscopy showed a 84:16 (91:9 in the presence of CsF) branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/DCM = 20:1) to give **4b** as a colorless liquid in 78% yield. The enantiomeric excess of the product was determined by HPLC analysis (254 nm, 25 °C) t_R = 9.65 min (major); 16.52 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 100/10, 0.7 mL/min] to be 96%. $[\alpha]_D^{20}$ = -65.2° (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 2.4, 2.0 Hz, 1H), 6.78 (ddd, *J* = 8.0, 2.4, 1.2 Hz, 1H), 6.02 (ddd, *J* = 16.8, 9.6, 8.4 Hz, 1H), 5.13 (ddd, *J* = 16.8, 1.2, 1.2 Hz, 1H), 5.13 (ddd, *J* = 10.0, 1.2, 0.8 Hz, 1H),4.48 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.56 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.94-1.91 (m, 2H), 1.75-1.70 (m, 2H), 1.59-1.54 (m, 1H), 1.40-1.32 (m, 2H), 1.29-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 142.5, 138.5, 129.5, 120.1, 115.2, 113.3, 112.6, 55.2, 51.1, 43.0, 33.5, 33.3, 26.0, 25.82, 25.78. MS (EI, *m/z*, rel. intensity) 147 (100), 262 (M^+); HRMS (EI) calcd for $C_{16}H_{22}OS$ (M^+): 262.1391, Found: 262.1393. IR (KBr): ν_{max} (cm^{-1}) = 2928, 2851, 1599, 1585, 1490, 1449, 1436, 1316, 1263, 1149, 1048, 998, 916, 886, 771, 695.



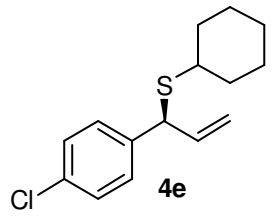
4c

(*S*)-cyclohexyl(1-(4-methoxyphenyl)allyl)sulfane (4c): ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/DCM = 7/1) to give **4c** as a colorless liquid in 71% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 20.48 min (major); 28.82 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 100/10, 0.7 mL/min] to be 98%. $[\alpha]_D^{20}$ = -51.6° (c 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (ddd, *J* = 8.8, 2.8, 2.0 Hz, 2H), 6.85 (ddd, *J* = 8.8, 2.8, 2.0 Hz, 2H), 6.02 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.10 (d, *J* = 16.8Hz, 1H), 5.08 (ddd, *J* = 9.2, 0.8, 0.4 Hz, 1H),4.49 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 2.54 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.93-1.90 (m, 2H), 1.74-1.71 (m, 2H) 1.59-1.56 (m, 1H), 1.37-1.31 (m, 2H), 1.29-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 138.8, 132.9, 128.7, 114.9, 113.9, 55.2, 50.4, 42.9, 33.5, 33.3, 26.0, 25.83, 25.80. MS (EI, *m/z*, rel. intensity) 147 (100), 262 (M^+); HRMS (EI) calcd for $C_{16}H_{22}OS$ (M^+): 262.1391, Found: 262.1387. IR (KBr): ν_{max} (cm^{-1}) = 3000, 2928, 2851, 1632, 1609, 1510, 1448, 1303, 1247, 1177, 1036, 998, 915, 830, 781, 762, 740, 643, 535.



4d

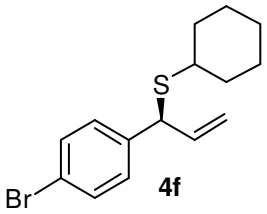
(*S*)-cyclohexyl(1-p-tolylallyl)sulfane (4d): ^{1}H NMR spectroscopy showed a 93:7 branched:linear ratio. The mixture was purified by flash column chromatography (100% petroleum ether) to give **4d** as a colorless liquid in 74% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25°C) t_R = 15.17 min (major); 20.84 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 100/10, 0.7 mL/min] to be 97%. $[\alpha]_D^{20}$ = -56° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.03 (ddd, *J* = 16.8, 10.0, 8.8 Hz, 1H), 5.11 (ddd, *J* = 16.8, 1.2, 0.8 Hz, 1H), 5.08 (ddd, *J* = 16.8, 1.2, 1.2 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 2.55 (tt, *J* = 10.4, 3.6 Hz, 1H), 2.32 (s, 3H), 1.94-1.90 (m, 2H), 1.76-1.71 (m, 2H), 1.59-1.54 (m, 1H), 1.38-1.31 (m, 2H), 1.29-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 137.9, 136.8, 129.2, 127.6, 115.0, 50.8, 43.0, 33.5, 33.3, 26.0, 25.9, 25.8, 21.0. MS (EI, *m/z*, rel. intensity) 131 (100), 246 (M^+); HRMS (EI) calcd for $C_{16}H_{22}S$ (M^+): 246.1442, Found: 246.1445. IR (KBr): ν_{max} (cm^{-1}) = 2927, 2851, 2361, 1635, 1541, 1509, 1448, 1262, 998, 913, 818, 779.



4e

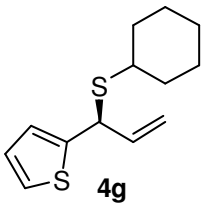
(*S*)-(1-(4-chlorophenyl)allyl)(cyclohexyl)sulfane (4e): ^{1}H NMR spectroscopy showed a 88:12 (92:8 in the presence of CsF) branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 40/1) to give **4e** as a colorless liquid in 71% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 7.25 min (major); 7.92 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 95%. $[\alpha]_D^{20}$ = -70.3° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (m, 4H), 5.99 (dt, *J* = 17.6, 8.8 Hz 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 5.11 (d, *J* = 16.8 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 2H), 2.54 (t, *J* = 10.0 Hz, 1H), 1.92-1.89 (m, 2H), 1.78-1.68 (m, 2H), 1.61-1.52 (m, 1H), 1.37-1.32 (m, 1H), 1.29-1.19 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.5, 138.1, 132.8, 129.2, 128.6, 115.7, 50.3, 43.1, 33.4, 33.2, 26.0, 25.8. MS (EI, *m/z*, rel. intensity) 151 (100), 266 (M^+); HRMS (EI) calcd for $C_{15}H_{19}ClS$ (M^+): 266.0896, Found: 266.0902. IR (KBr): ν_{max} (cm^{-1}) = 2928, 2852, 1633,

1489, 1448, 1403, 1262, 1092, 1014, 998, 917, 819, 763, 742, 609, 520.



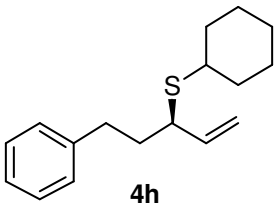
4f

(*S*)-(1-(4-bromophenyl)allyl)(cyclohexyl)sulfane (4f): ^{1}H NMR spectroscopy showed a 86:14 (90:10 in the presence of CsF) branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 40/1) to give **4f** as a colorless liquid in 80% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 4.96 min (minor); 5.16 min (major) [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol, 100/10, 0.7 mL/min] to be 98%. $[\alpha]_D^{20}$ = -54.8° (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (ddd, *J* = 8.8, 2.4, 2.0 Hz, 2H), 7.24(ddd, *J* = 8.4, 2.4, 2.0 Hz, 2H), 5.98 (ddddd, *J* = 16.8, 9.6, 8.4, 1.6, 0.8 Hz, 1H), 5.12 (ddd, *J* = 10.0, 1.2, 0.8 Hz, 1H), 5.11 (ddd, *J* = 17.2, 1.2, 0.8 Hz, 1H), 4.47 (d, *J* = 10.4, 3.6 Hz, 1H), 2.53 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.92-1.88 (m, 2H), 1.75-1.69 (m, 2H), 1.60-1.54 (m, 1H), 1.40-1.30 (m, 2H), 1.29-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.0, 138.0, 131.6, 129.5, 120.9, 115.7, 50.4, 43.1, 33.4, 33.2, 25.9, 25.8. MS (EI, *m/z*, rel. intensity) 116 (100), 310 (M^+); HRMS (EI) calcd for $C_{15}H_{19}BrS$ (M^+): 310.0391, Found: 310.0394. IR (KBr): ν_{max} (cm^{-1}) = 2928, 2851, 1634, 1486, 1448, 1399, 1263, 1073, 1010, 998, 918, 817, 759, 593, 517.



4g

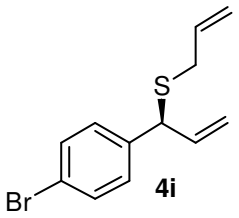
(*S*)-2-(1-(cyclohexylthio)allyl)thiophene (4g): ^{1}H NMR spectroscopy showed a 86:14 branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether) to give **4g** as a colorless liquid in 74% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 9.12 min (major); 15.19 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 98%. $[\alpha]_D^{20}$ = -128.2° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.97 (d, *J* = 3.6Hz, 1H), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.01 (ddd, *J* = 16.8, 10.0, 8.8 Hz, 1H), 5.16 (d, *J* = 16.8 Hz, 1H), 5.14 (d, *J* = 9.6 Hz, 1H), 4.78 (d, *J* = 8.4 Hz, 1H), 2.64 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.97-1.91 (m, 2H), 1.76-1.73 (m, 2H), 1.60-1.55 (m, 1H), 1.43-1.33 (m, 2H), 1.30-1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8, 138.4, 126.6, 124.8, 124.6, 115.5, 46.2, 43.4, 33.5, 33.2, 26.0, 25.8. MS (EI, *m/z*, rel. intensity) 123 (100), 238 (M^+); HRMS (EI) calcd for $C_{13}H_{18}S_2$ (M^+): 238.0850, Found: 238.0856. IR (KBr): ν_{max} (cm^{-1}) = 2928, 2854, 1635, 1447, 1413, 1262, 1232, 988, 914, 850, 804, 696.



4h

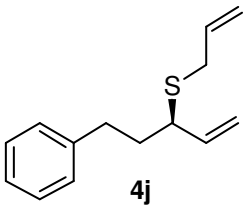
(*R*)-cyclohexyl(5-phenylpent-1-en-3-yl)sulfane (4h): GC-MS showed a 71:29 branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/DCM = 35/1) to give **4h** as a colorless liquid in 56% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 11.56 min (minor); 12.12 min (major) [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol, 98/2, 0.3 mL/min] to be 95%. $[\alpha]_D^{20}$ = -8.6° (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.17 (m, 5H), 5.65(ddd, *J* = 18.4, 9.6, 8.0 Hz, 1H) , 5.06 (d, *J* = 9.6 Hz, 1H), 4.99 (d, *J* = 16.8 Hz, 1H), 3.29-3.23 (m, 1H), 2.78-2.64 (m, 2H), 2.62-2.52 (m, 1H), 1.94-1.80 (m, 4H), 1.77-1.68 (m, 2H), 1.6-1.55 (m, 1H), 1.38-1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.6, 140.0, 128.4, 128.3, 125.8, 114.8, 46.4, 42.0, 36.0, 34.1, 33.4, 33.3, 26.2, 25.85, 25.81. MS (EI, *m/z*, rel.

intensity) 129 (100), 260 (M^+); HRMS (EI) calcd for $C_{17}H_{24}S$ (M^+): 260.1599, Found: 260.1587. IR (KBr): ν_{max} (cm^{-1}) = 3026, 2928, 2852, 1630, 1604, 1496, 1448, 1384, 1263, 997, 911, 747, 698.



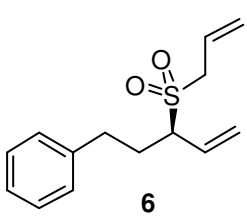
4i

(*S*)-allyl(1-(4-bromophenyl)allyl)sulfane (4i): ^{1}H NMR spectroscopy showed a 94:6 branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether) to give **4i** as a colorless liquid in 60% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 7.30 min (major); 7.92 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 94%. $[\alpha]_D^{20}$ = -24.5° (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 5.96 (ddd, *J* = 16.8, 8.4, 8.4 Hz, 1H), 5.80 (ddt, *J* = 14.8, 7.6, 7.2Hz, 1H), 5.19-5.05 (m, 4H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.13-2.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.4, 137.2, 134.1, 131.7, 129.7, 121.1, 117.4, 116.6, 50.6, 34.4. MS (EI, *m/z*, rel. intensity) 116 (100), 268 and 270 (M^+); HRMS (EI) calcd for $C_{12}H_{13}BrS$ (M^+): 267.9921, Found: 267.9929. IR (KBr): ν_{max} (cm^{-1}) = 3853, 3080, 2978, 2912, 2360, 2341, 1634, 1486, 1399, 1423, 1073, 1010, 987, 917, 843, 816, 756, 740, 599, 515.



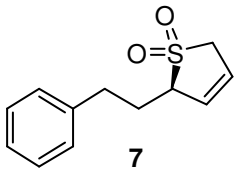
4j

(*R*)-allyl(5-phenylpent-1-en-3-yl)sulfane (4j): GC-MS showed a 77:23 branched:linear ratio. The mixture was purified by flash column chromatography (petroleum ether/DCM = 35/1) to give **4j** as a colorless liquid in 34% yield. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 7.98 min (major); 8.49 min (minor) [Diacel CHIRALPAK OJ-H (0.46 cm x 25 cm); hexane/2-propanol, 98/2, 0.7 mL/min] to be 95%. $[\alpha]_D^{20}$ = -35.0° (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.23 (m, 2H), 7.21-7.14 (m, 3H), 5.77 (ddd, *J* = 16.4, 7.6, 7.2 Hz, 1H), 5.62(ddt, *J* = 17.6, 9.6, 8.4 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 18.4 Hz, 1H), 5.04 (d, *J* = 8.4 Hz, 1H), 4.99(d, *J* = 17.2 Hz, 1H), 3.20-3.13 (m, 1H), 3.08 (d, *J* = 6.0 Hz, 2H), 2.77-2.65 (m, 2H), 1.95-1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.5, 139.0, 134.7, 128.4, 128.3, 125.9, 116.8, 115.7, 46.9, 35.7, 33.35, 33.32.



6

(*R*)-(3-(allylsulfonyl)pent-4-enyl)benzene (6): **4j**[4] (22.3 mg, 0.10 mmol) was oxidized with *m*-CPBA (75%) (85.6 mg, 0.35 mmol) in DCM (4 mL) and the reaction mixture was purified by flash column chromatography (DCM) to give **6** as a thick yellow oil in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.21 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.90-5.80 (m, 2H), 5.58 (d, 10.4 Hz, 1H), 5.44 (d, *J* = 16.8 Hz, 1H), 5.40 (d, *J* = 23.2 Hz, 1H), 5.35 (d, *J* = 16.0 Hz, 1H), 3.77 (dd, *J* = 14.0, 8.0 Hz, 1H), 3,63 (dd, *J* = 14.0, 6.4 Hz, 1H), 3.55 (dt, *J* = 10.4, 2.8 Hz, 1H), 2.82 (ddd, *J* = 13.9, 9.2, 4.8 Hz, 1H), 2.56 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 2.48-2.39 (m, 1H), 2.09-1.99 (m, 1H).

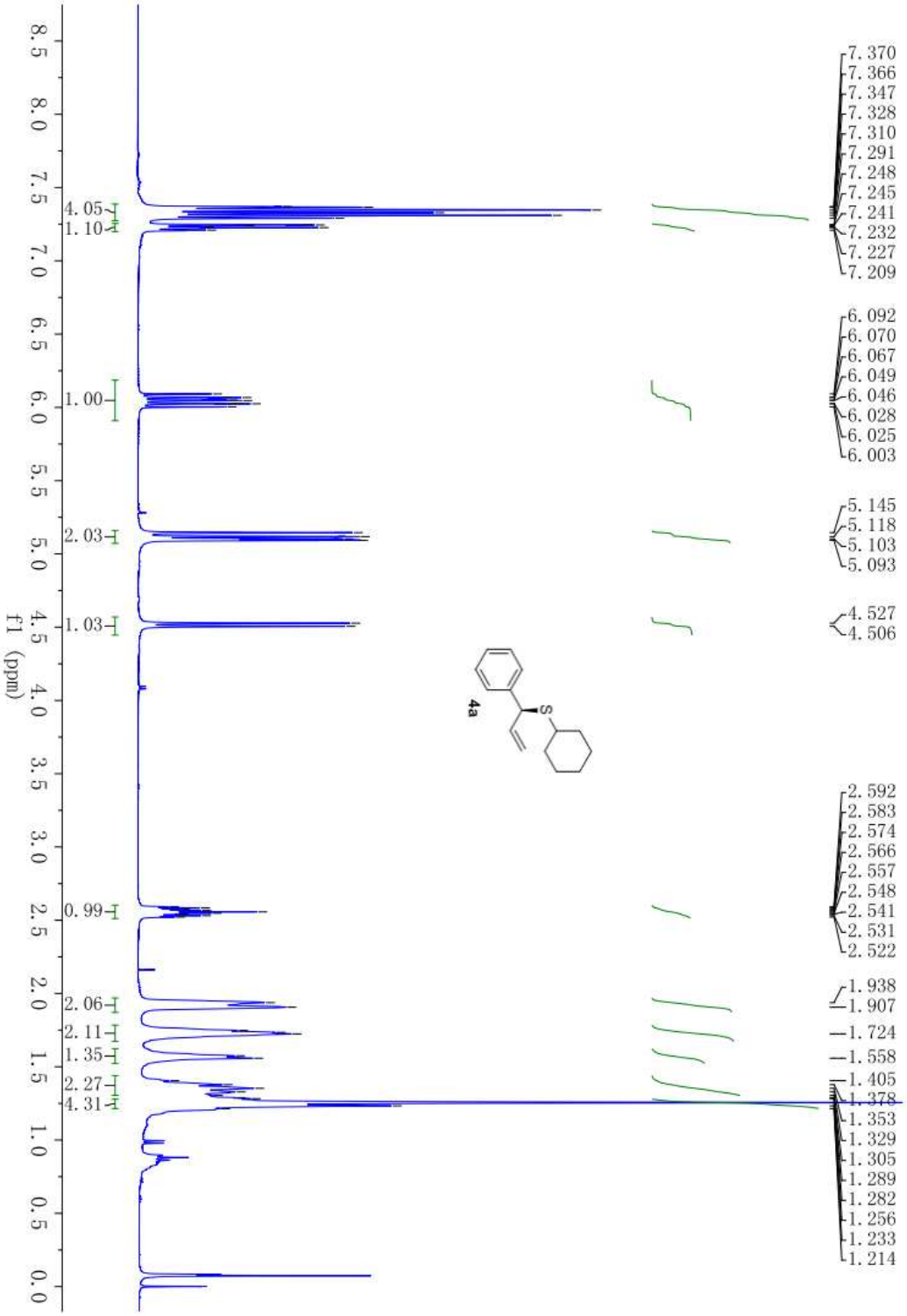


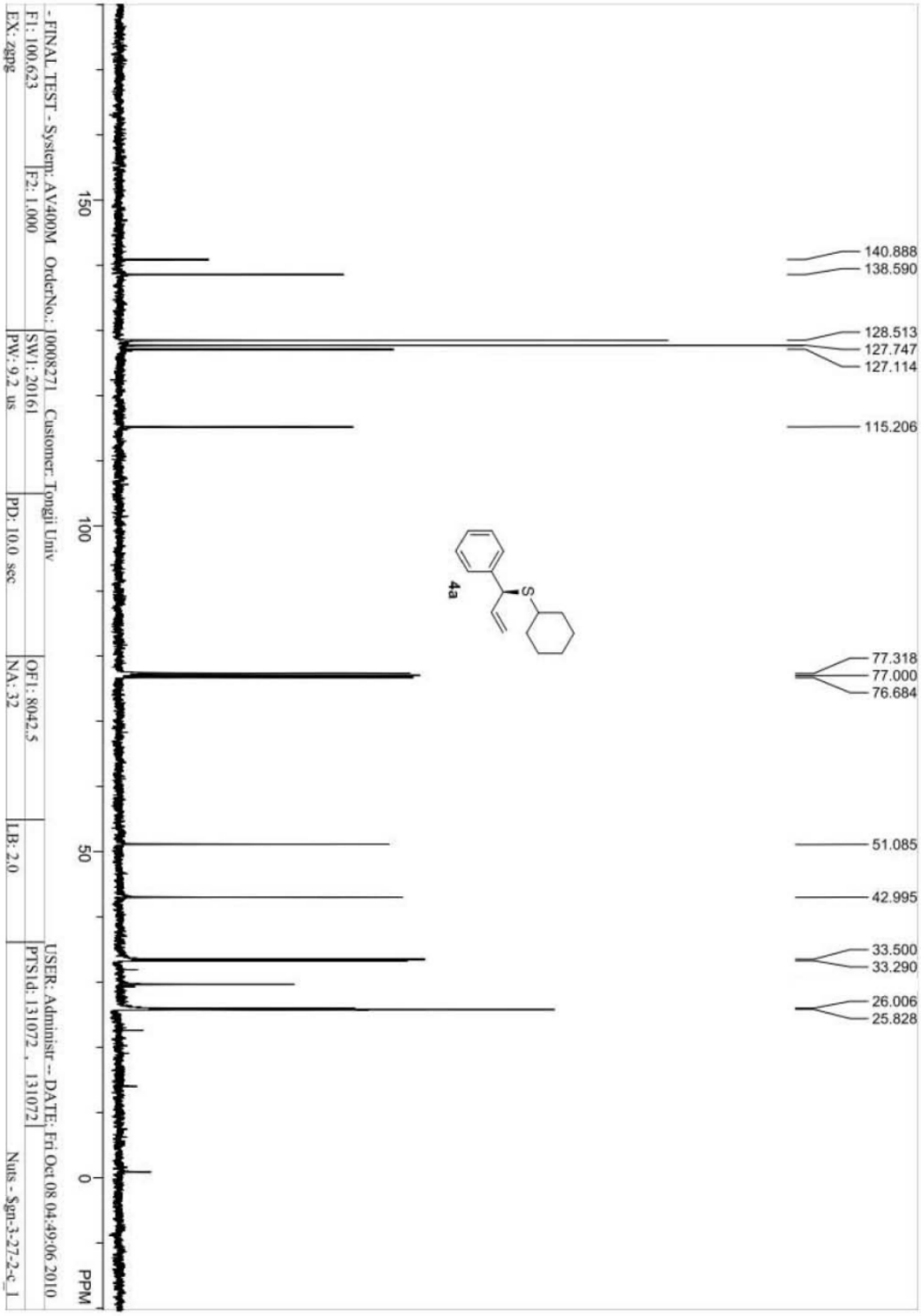
7

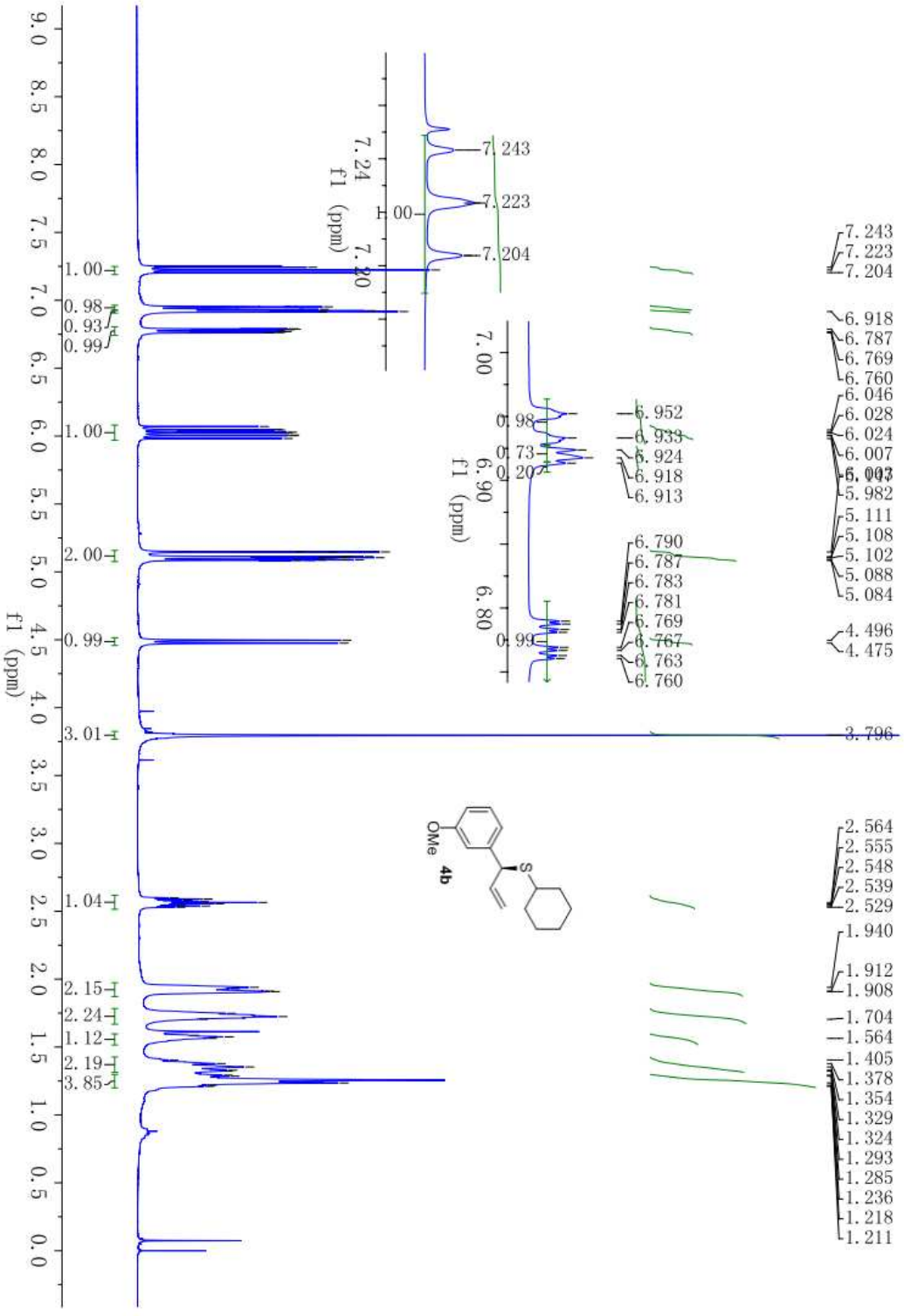
(*R*)-Cyclic Sulfone (7)[4]: To a solution of **6** (23.2 mg, 0.093 mmol) in CH_2Cl_2 (4 mL, 0.02 M) was added Grubbs catalyst I (1.5 mg, 2.0 mol %) and the reaction mixture was heated to reflux under an argon atmosphere

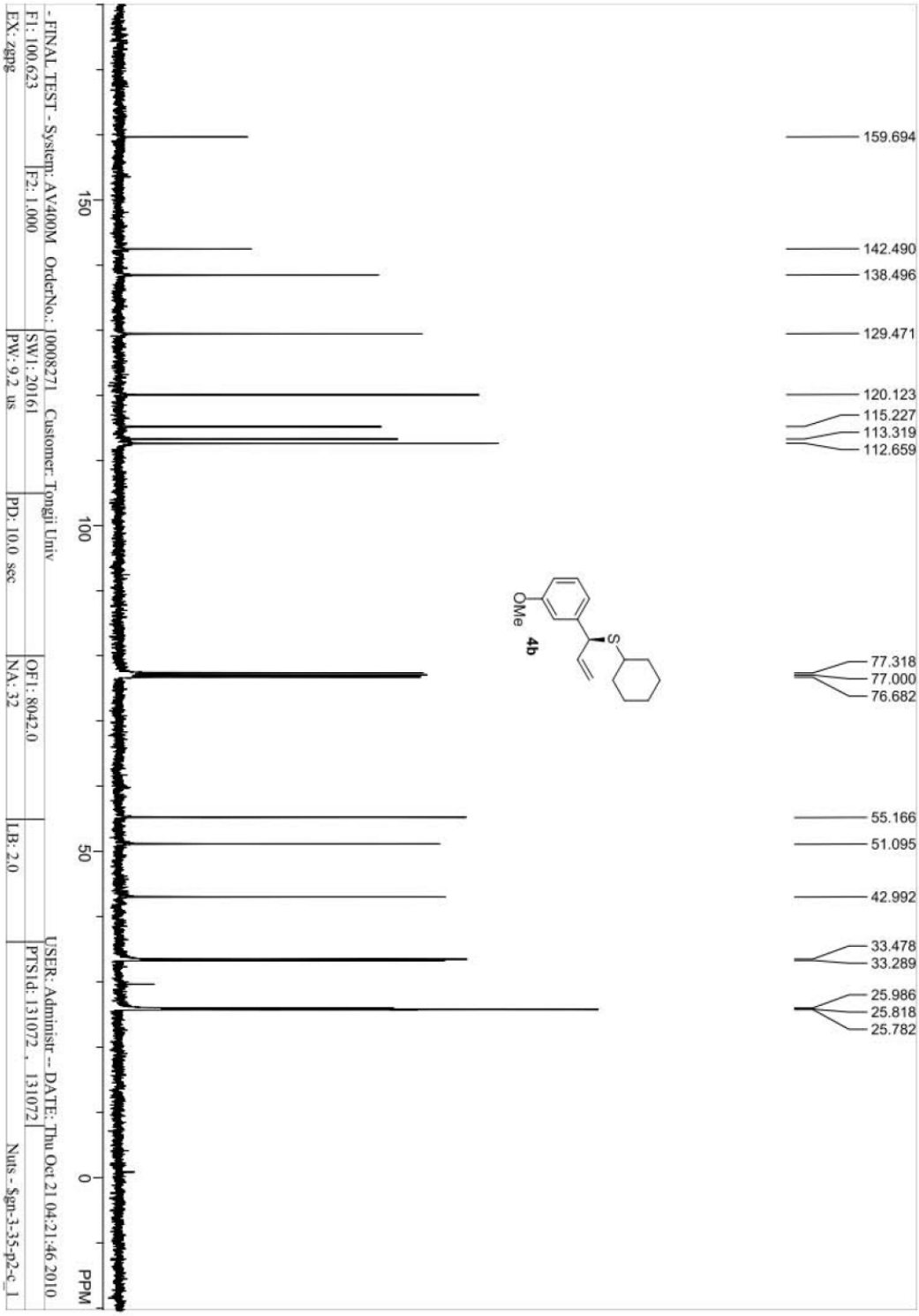
overnight. The reaction was cooled to rt and concentrated to dryness under vacuum. Flash chromatography on silica gel (CH_2Cl_2) gave **7** (17.0 mg, 83% yield) as a colorless thick oil. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R = 16.83 min (major); 17.60 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 6.05-6.01 (m, 1H), 5.98-5.94 (m, 1H), 3.81-3.72 (m, 2H), 3.70-3.65 (m, 1H), 2.93-2.78 (m, 2H), 2.35-2.26 (m, 1H), 1.99-1.90 (m, 1H).

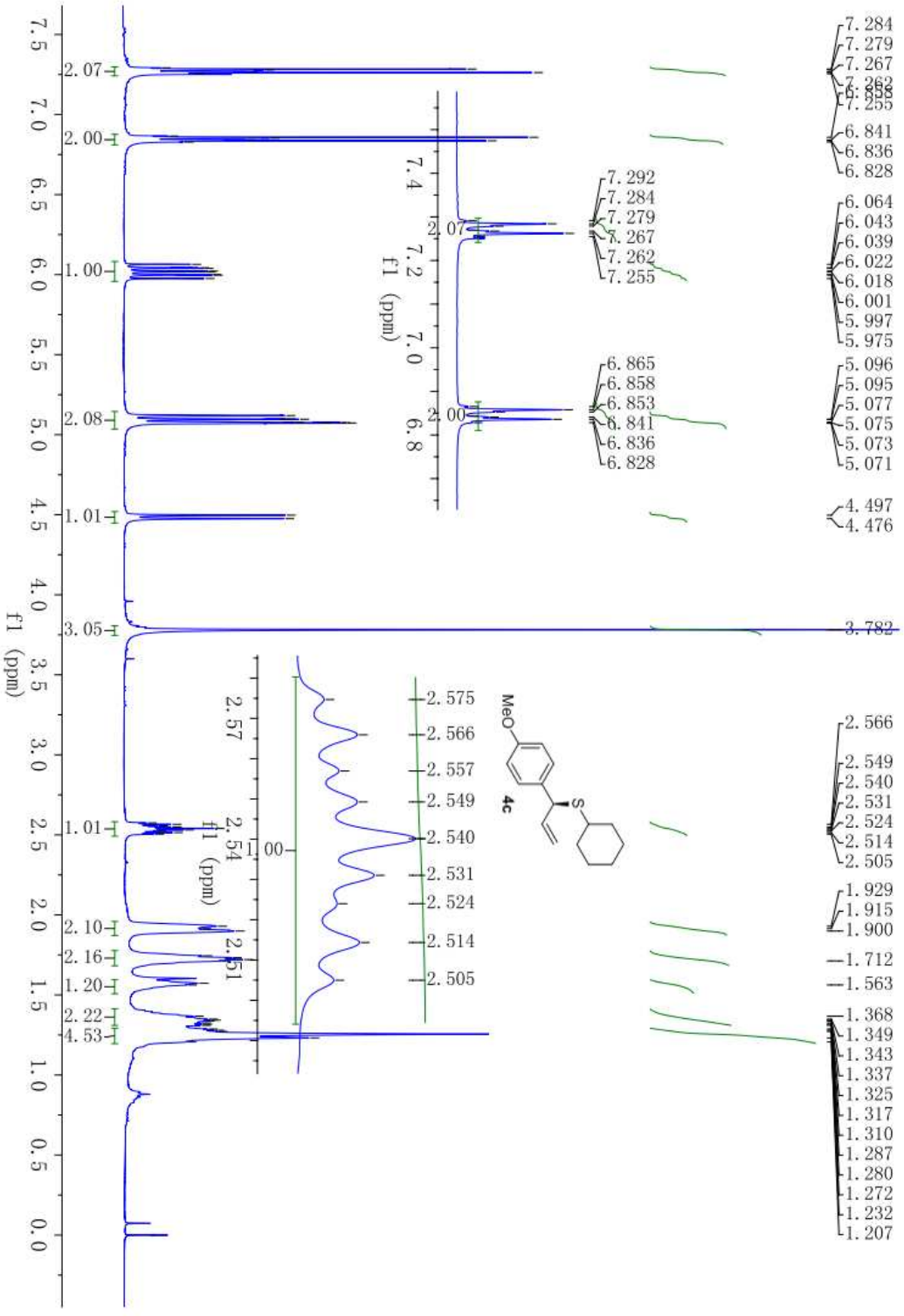
NMR Spectra of the compounds 4 and 6, 7:

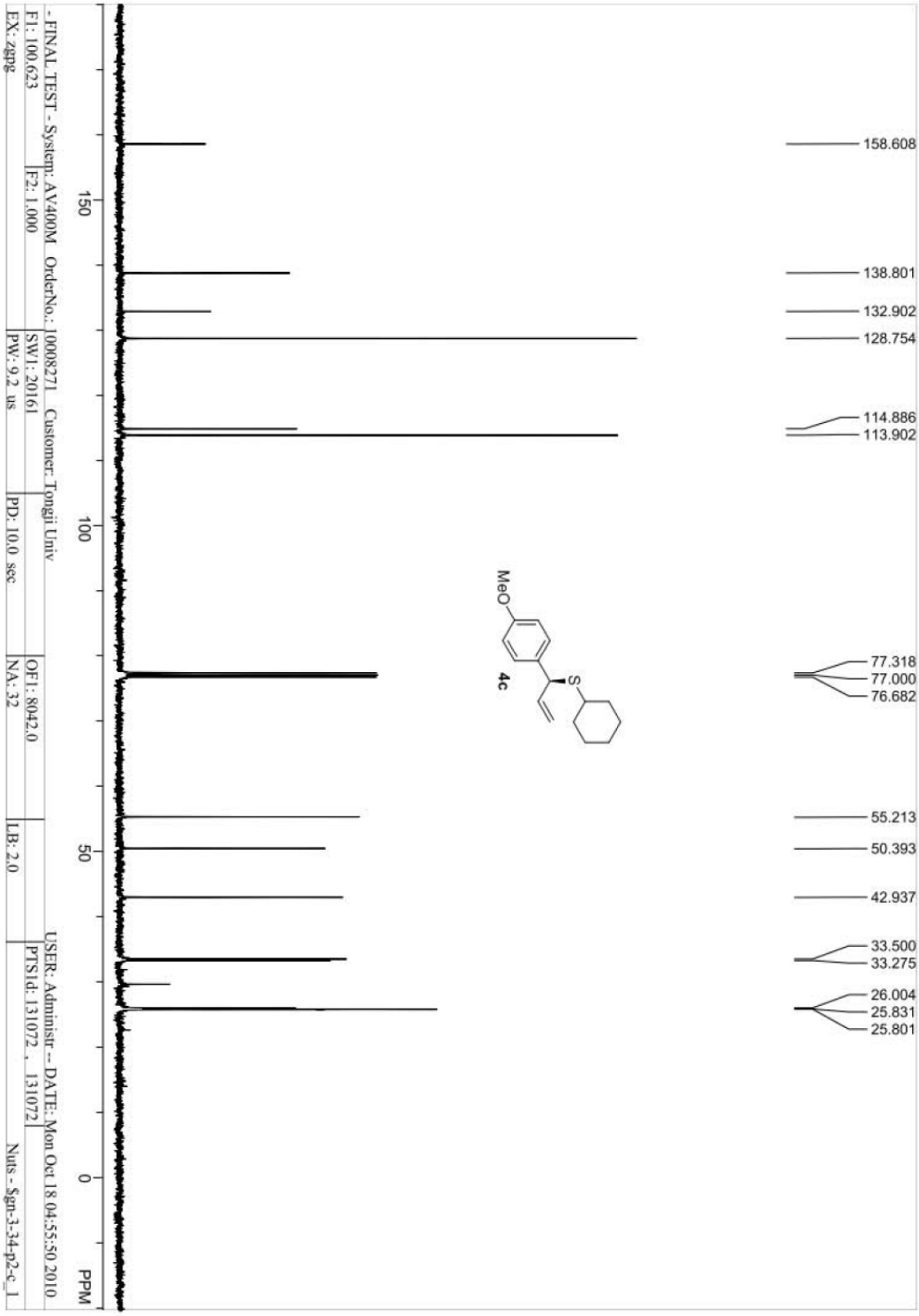


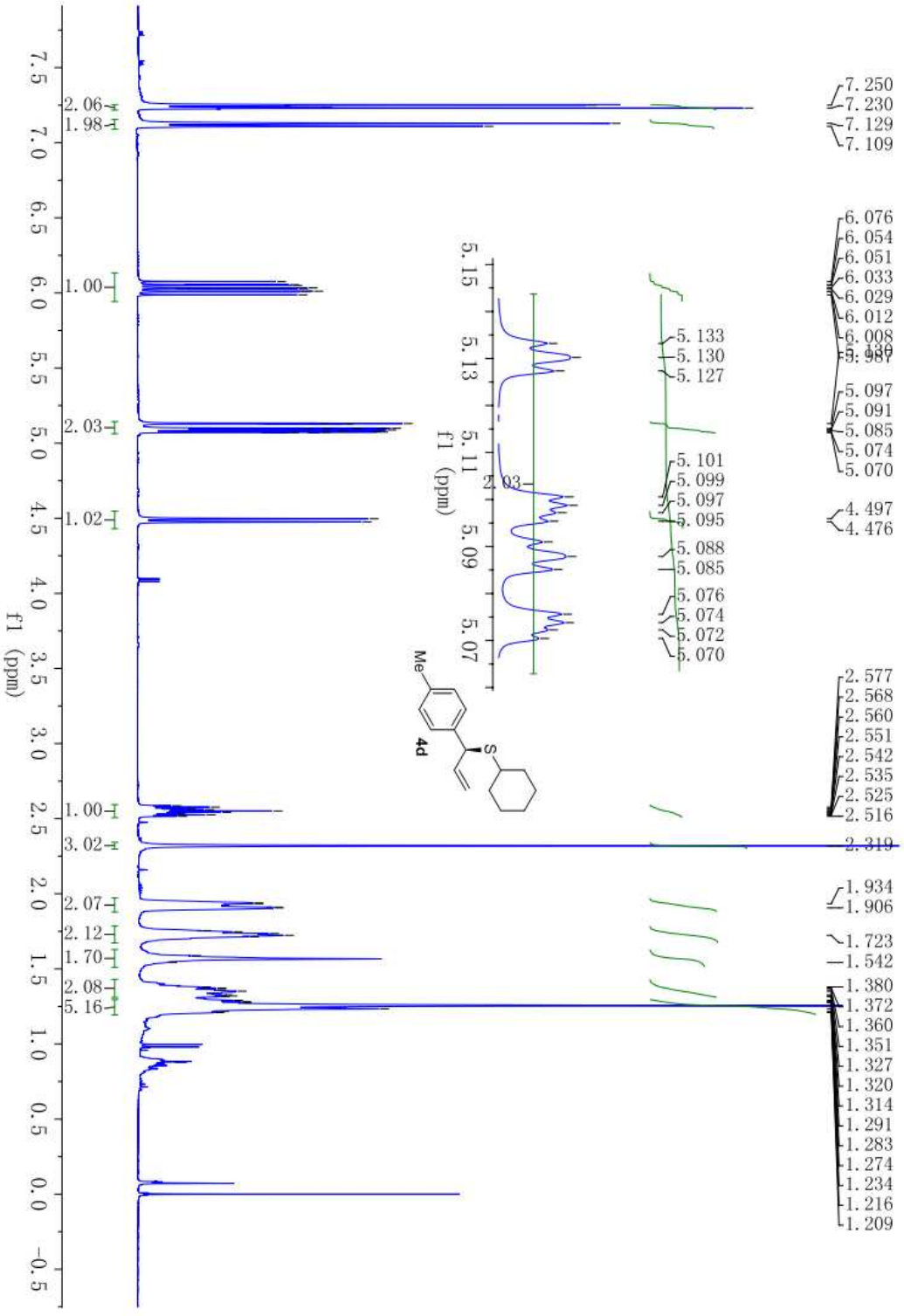

- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623
F2: 1.000
SW1: 20161
PW: 9.2 us
PD: 10.0 sec
OF1: 8042.5
NA: 32
LB: 2.0
USER: Administr -- DATE: Fri Oct 08 04:49:06 2010
PTS1d: 131072 , 131072
EX: zgpg
Nuts - Sgn-3-27-2-c_1
PPM
150
100
50
0
4a
S
140.888
138.590
128.513
127.747
127.114
115.206
77.318
77.000
76.684
51.085
42.995
33.500
33.290
26.006
25.828

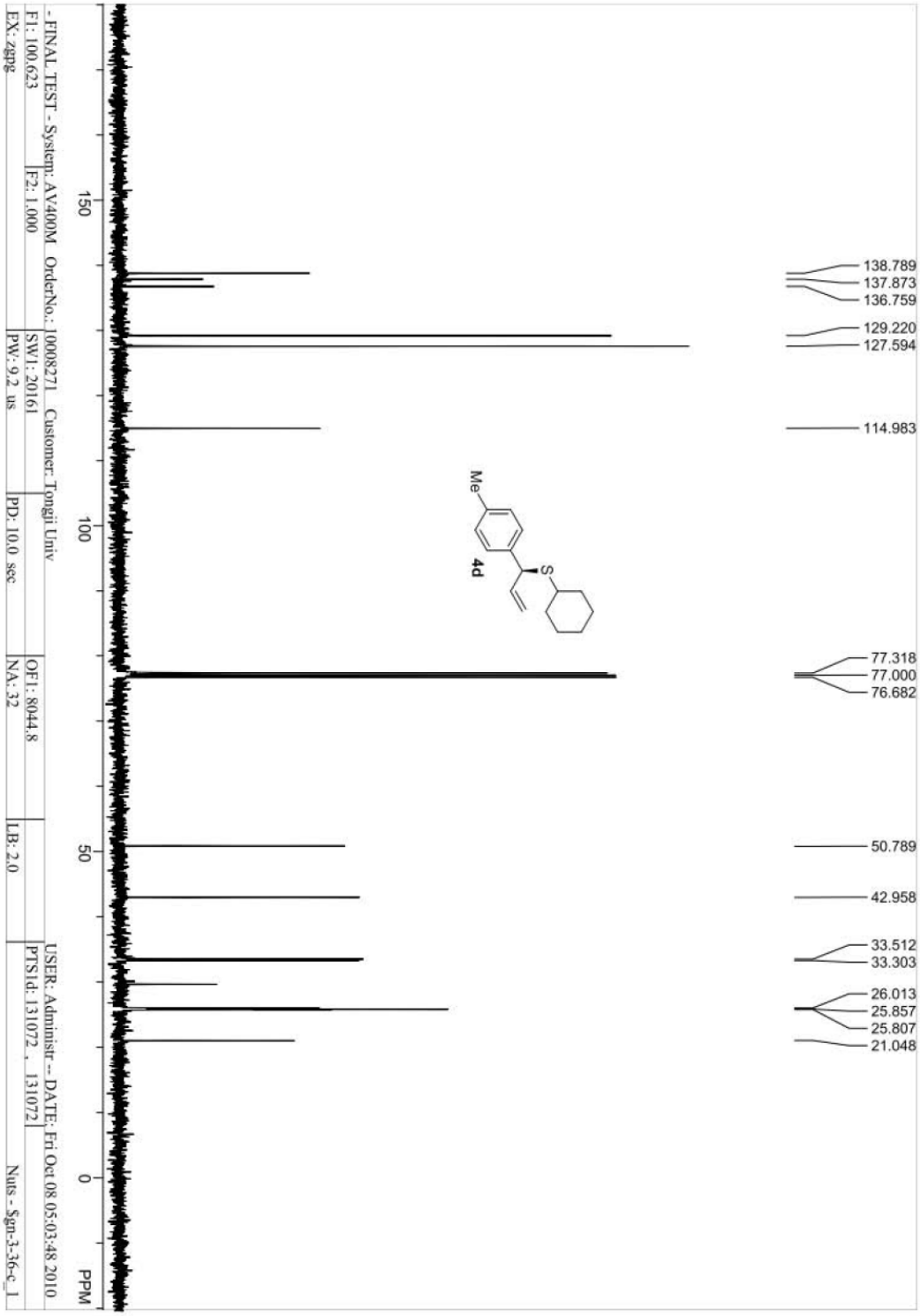

f1 (ppm)
1.00
0.98
0.93
0.99
1.00
2.00
0.99
3.01
1.04
2.15
2.24
1.12
2.19
3.85
7.24
7.20
7.243
7.223
7.204
7.00
6.90
6.80
0.98
0.73
0.20
0.99
6.952
6.933
6.924
6.918
6.913
6.790
6.787
6.783
6.781
6.769
6.767
6.763
6.760
7.243
7.223
7.204
6.918
6.787
6.769
6.760
6.046
6.028
6.024
6.007
5.982
5.111
5.108
5.102
5.088
5.084
4.496
4.475
3.796
2.564
2.555
2.548
2.539
2.529
1.940
1.912
1.908
1.704
1.564
1.405
1.378
1.354
1.329
1.324
1.293
1.285
1.236
1.218
1.211
OMe
4b
S

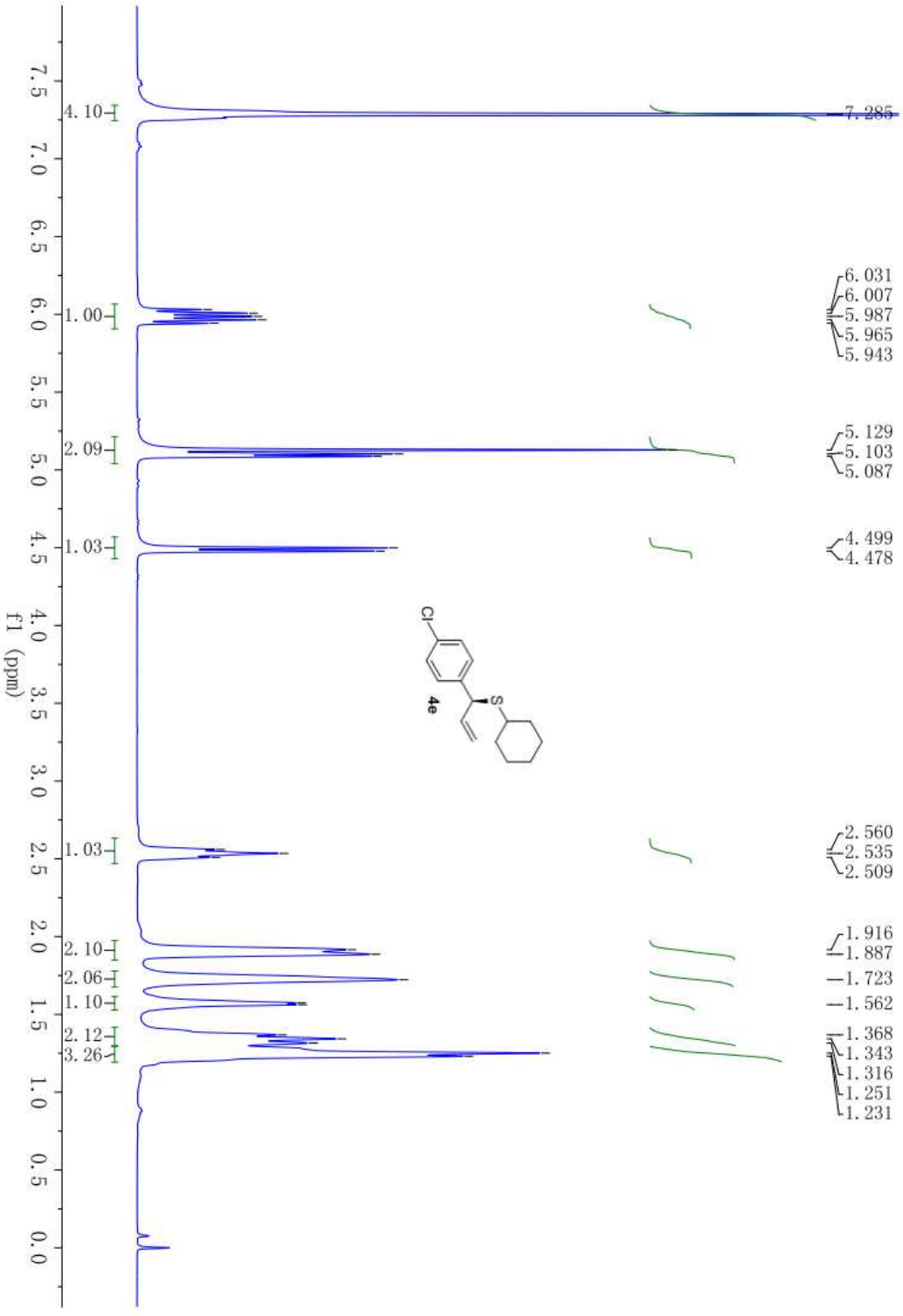

159.694
142.490
138.496
129.471
120.123
115.227
113.319
112.659
77.318
77.000
76.682
55.166
51.095
42.992
33.478
33.289
25.986
25.818
25.782
OMe
4b
S
150
100
50
0
PPM
- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623
F2: 1.000
SW1: 20161
PW: 9.2 us
PD: 10.0 sec
OF1: 8042.0
NA: 32
LB: 2.0
USER: Administr -- DATE: Thu Oct 21 04:21:46 2010
PTS1d: 131072 , 131072
EX: zgpg
Nuts - $gn-3-35-p2-c_1

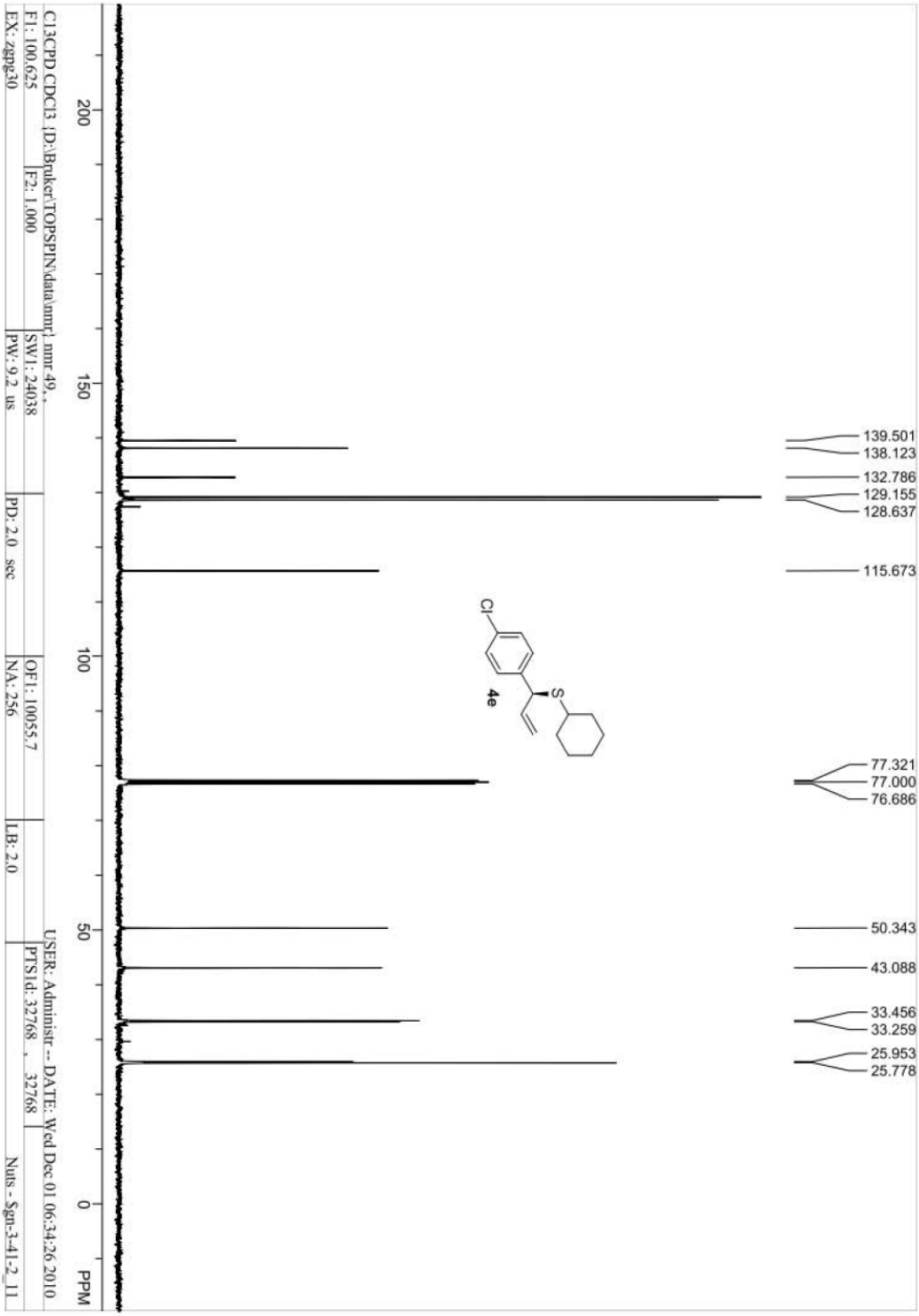

f1 (ppm)
7.284
7.279
7.267
7.262
7.255
6.841
6.836
6.828
6.064
6.043
6.039
6.022
6.018
6.001
5.997
5.975
5.096
5.095
5.077
5.075
5.073
5.071
4.497
4.476
3.782
2.566
2.549
2.540
2.531
2.524
2.514
2.505
1.929
1.915
1.900
1.712
1.563
1.368
1.349
1.343
1.337
1.325
1.317
1.310
1.287
1.280
1.272
1.232
1.207
MeO
S
4c

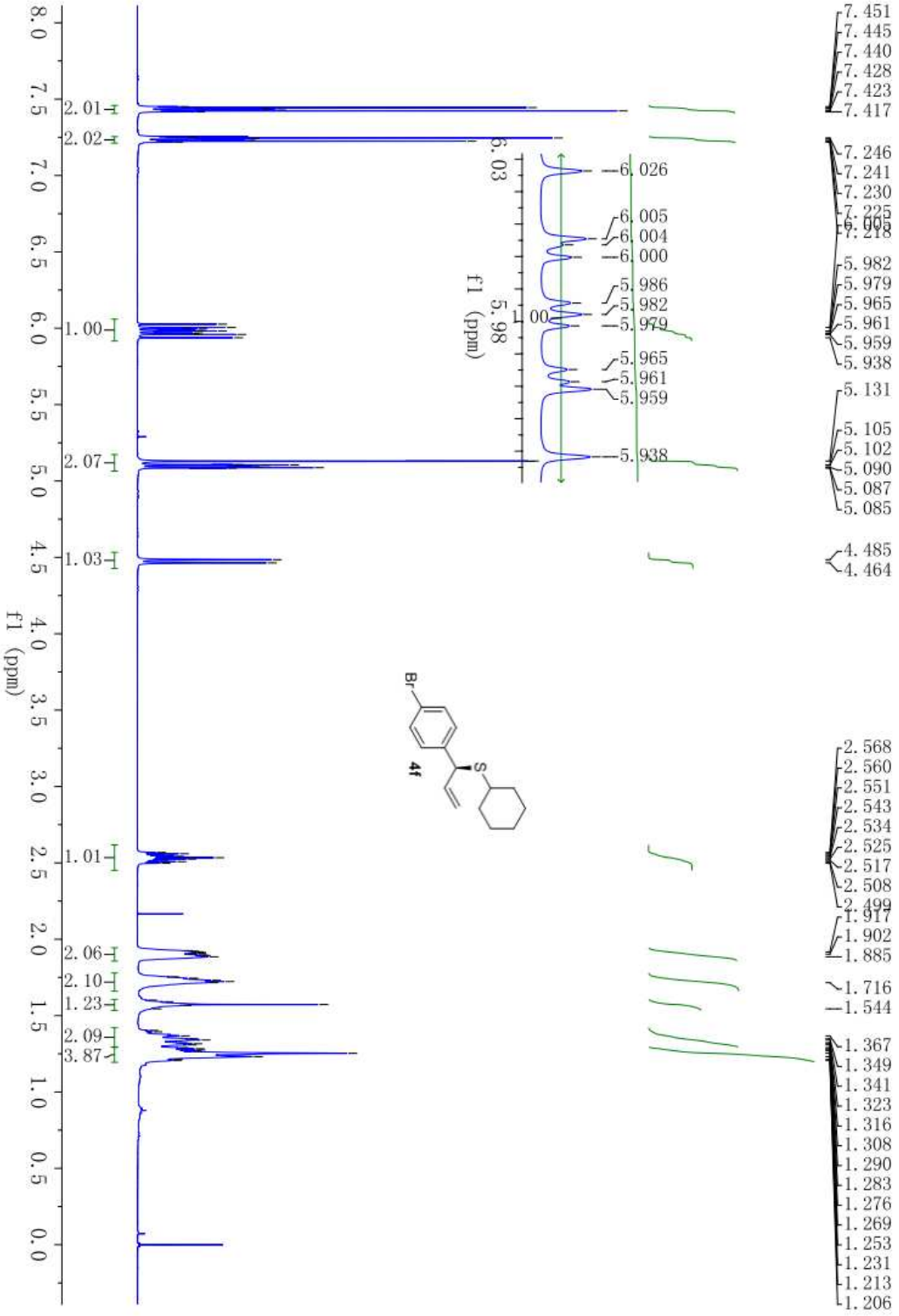

158.608
138.801
132.902
128.754
114.886
113.902
77.318
77.000
76.682
55.213
50.393
42.937
33.500
33.275
26.004
25.831
25.801
MeO
S
4c
150
100
50
0
PPM
- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623
F2: 1.000
SW1: 20161
PW: 9.2 us
PD: 10.0 scc
OF1: 8042.0
NA: 32
LB: 2.0
USER: Administr -- DATE: Mon Oct 18 04:55:50 2010
PTS1d: 131072 , 131072
EX: zgpg
Nuts - Sgn-3-34-p2-c_1

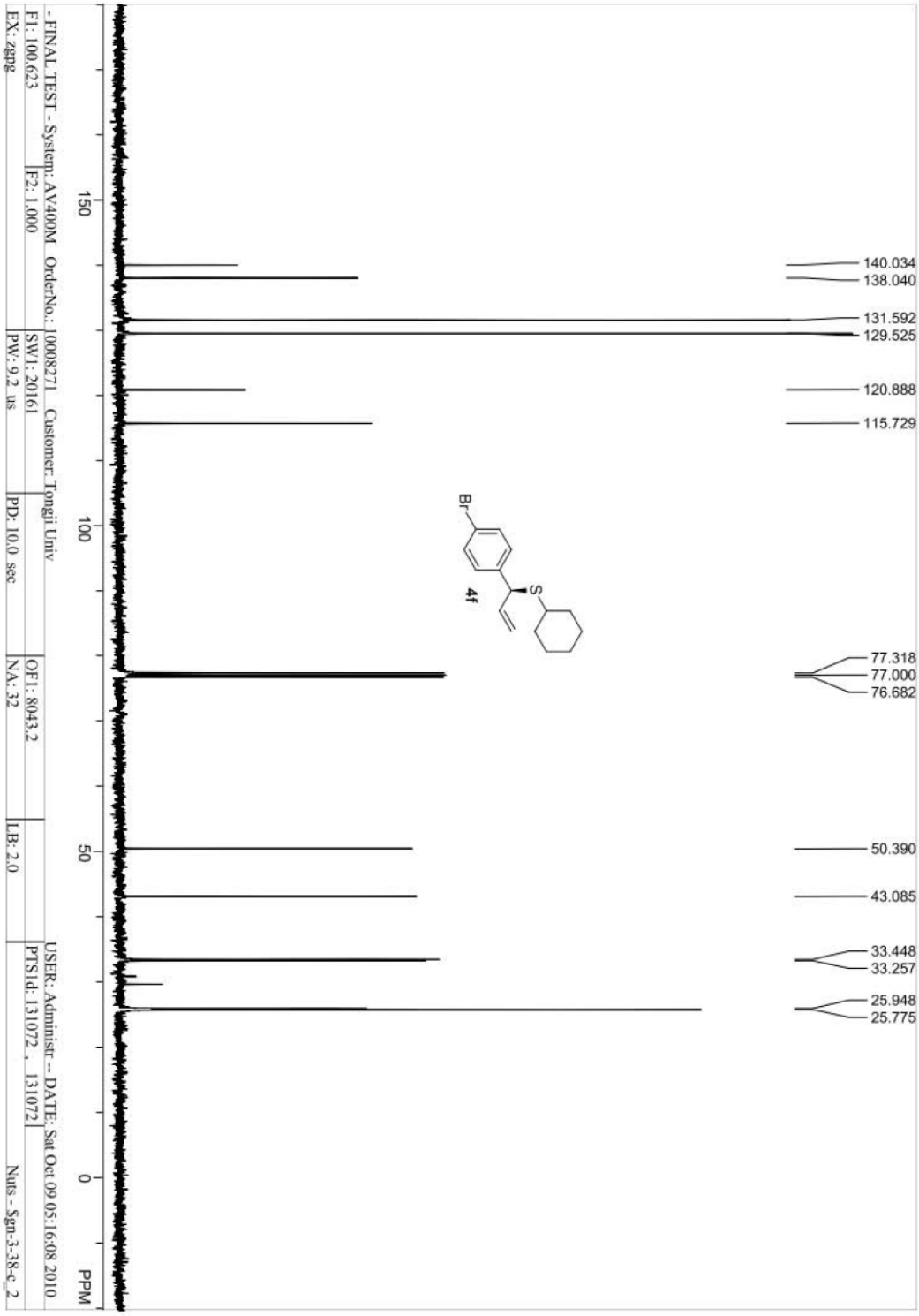

f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
2.06
1.98
1.00
2.03
1.02
1.00
3.02
2.07
2.12
1.70
2.08
5.16
7.250
7.230
7.129
7.109
6.076
6.054
6.051
6.033
6.029
6.012
6.008
5.987
5.133
5.130
5.127
5.097
5.091
5.085
5.074
5.070
5.101
5.099
5.097
5.095
5.088
5.085
5.076
5.074
5.072
5.070
4.497
4.476
2.577
2.568
2.560
2.551
2.542
2.535
2.525
2.516
2.319
1.934
1.906
1.723
1.542
1.380
1.372
1.360
1.351
1.327
1.320
1.314
1.291
1.283
1.274
1.234
1.216
1.209
5.15
5.13
5.11
5.09
5.07
f1 (ppm)
2.03
Me
S
4d

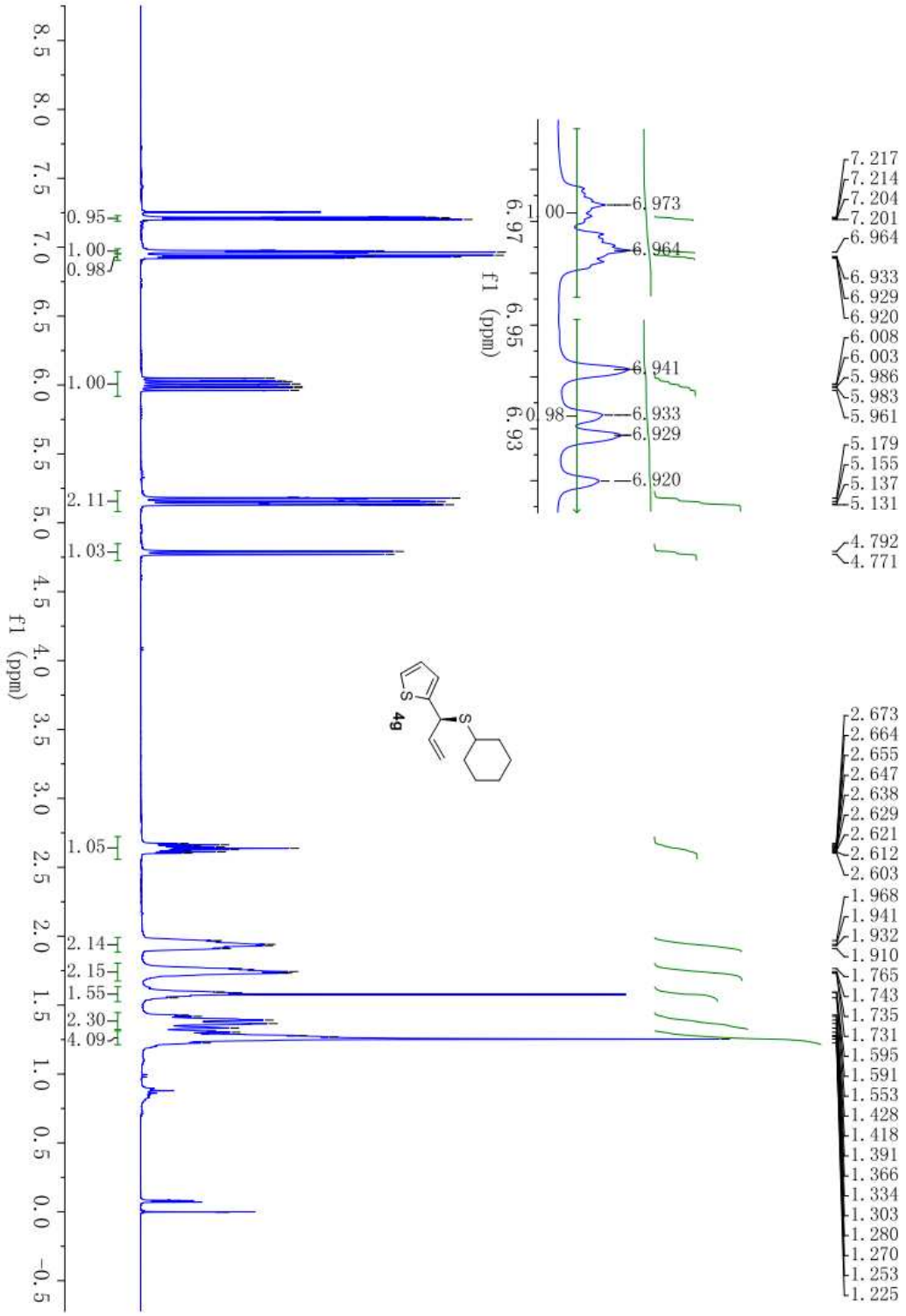

- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623
F2: 1.000
SW1: 20161
PW: 9.2 us
PD: 10.0 scc
OF1: 8044.8
NA: 32
LB: 2.0
USER: Administr -- DATE: Fri Oct 08 05:03:48 2010
PTS1d: 131072 , 131072
EX: zgpg
Nuts - Sgn-3-36-c_1
PPM
150
100
50
0
Me
S
4d
138.789
137.873
136.759
129.220
127.594
114.983
77.318
77.000
76.682
50.789
42.958
33.512
33.303
26.013
25.857
25.807
21.048

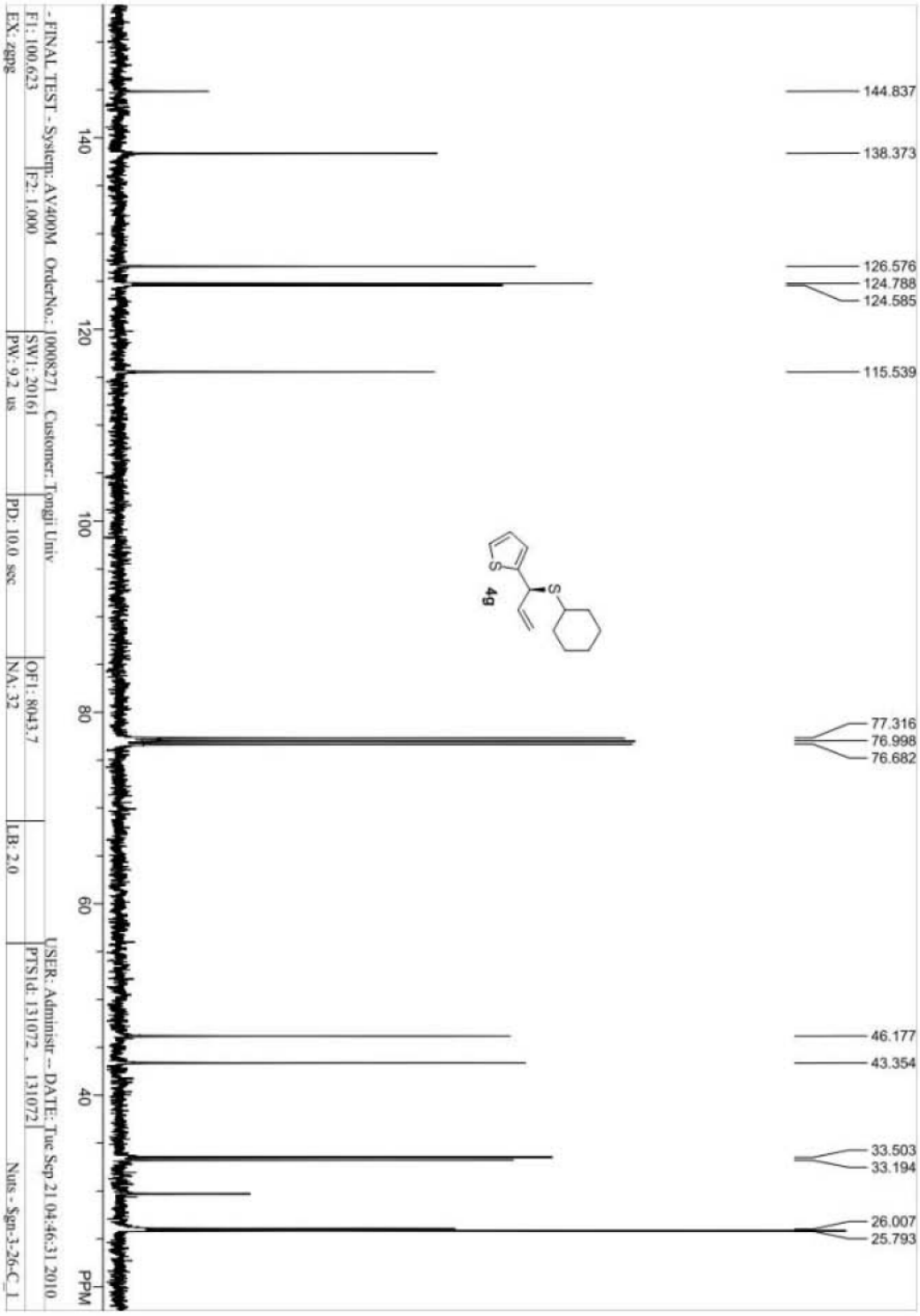

7.285
6.031
6.007
5.987
5.965
5.943
5.129
5.103
5.087
4.499
4.478
2.560
2.535
2.509
1.916
1.887
1.723
1.562
1.368
1.343
1.316
1.251
1.231
4.10
1.00
2.09
1.03
1.03
2.10
2.06
1.10
2.12
3.26
Cl
S
4e
f1 (ppm)

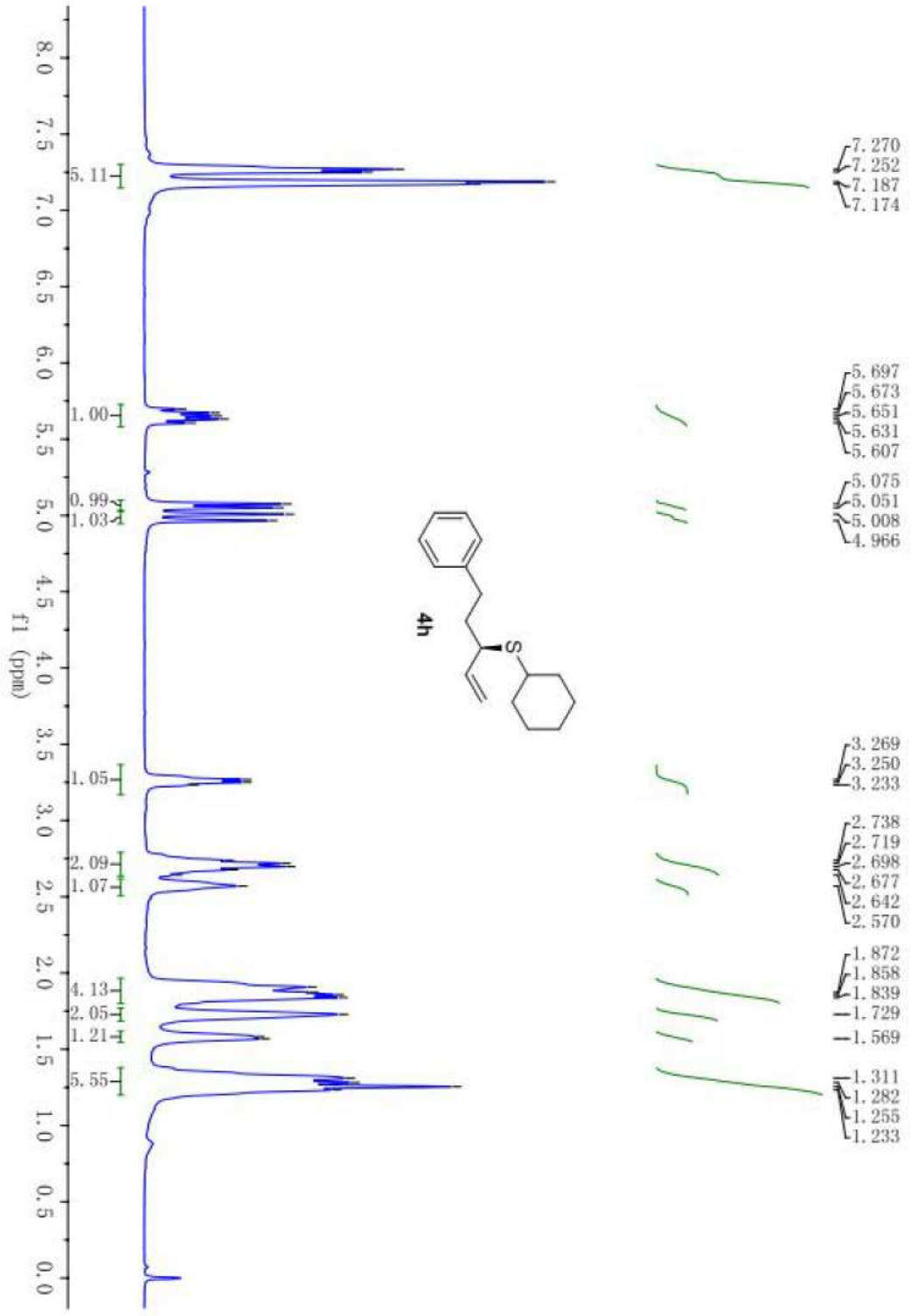

C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\nmr} nmr 49 , ,
F1: 100.625
F2: 1.000
SW1: 24038
PW: 9.2 us
PD: 2.0 scc
OF1: 10055.7
NA: 256
LB: 2.0
EX: zgpg30
USER: Administr -- DATE: Wed Dec 01 06:34:26 2010
PTS1d: 32768 , 32768
Nuts - Sgn-3-41-2_11
200
150
100
50
0
PPM
139.501
138.123
132.786
129.155
128.637
115.673
77.321
77.000
76.686
50.343
43.088
33.456
33.259
25.953
25.778
Cl
S
4e

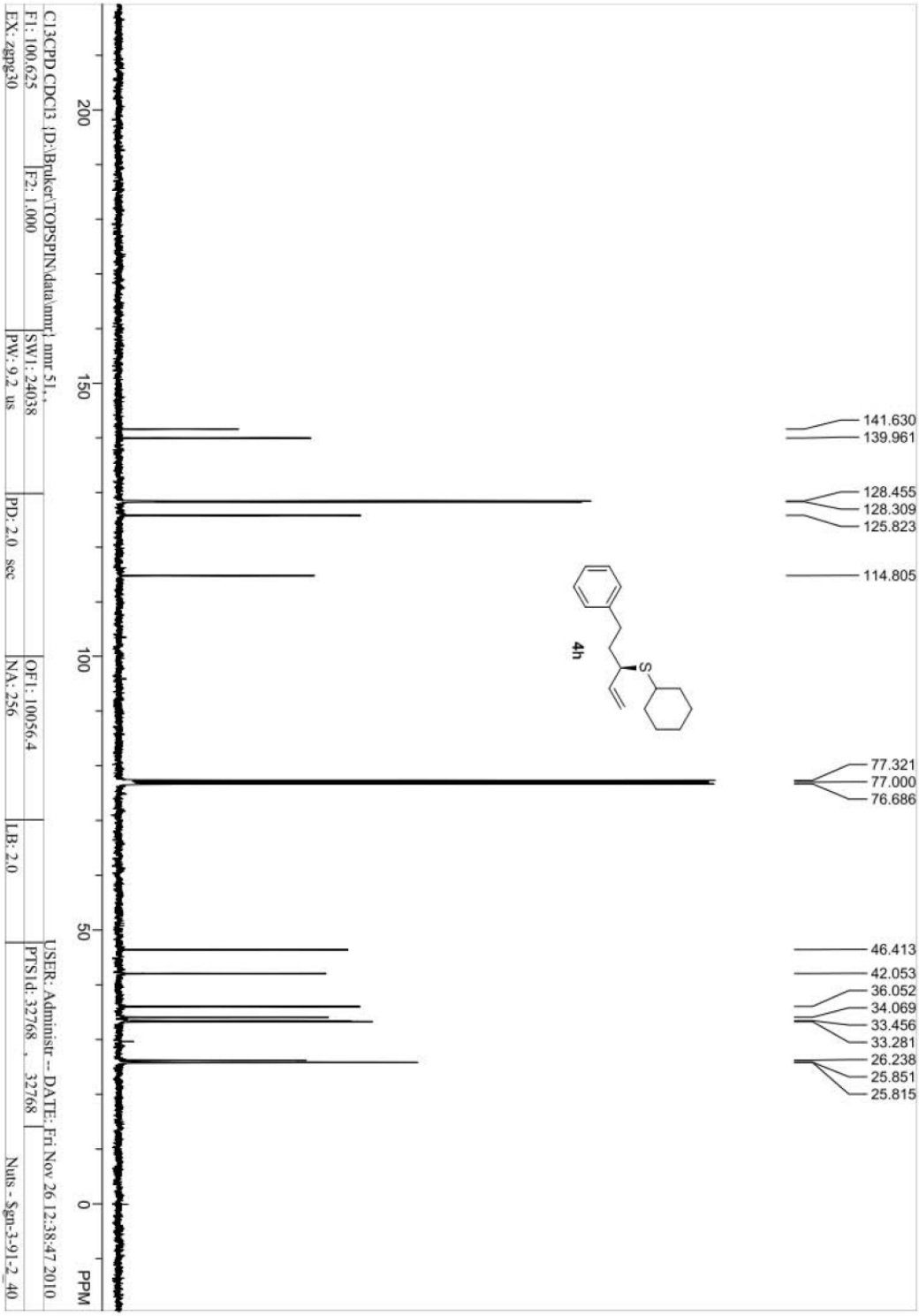

f1 (ppm)
2.01
2.02
1.00
2.07
1.03
1.01
2.06
2.10
1.23
2.09
3.87
6.03
5.98
1.00
6.026
6.005
6.004
6.000
5.986
5.982
5.979
5.965
5.961
5.959
5.938
Br
S
4f
7.451
7.445
7.440
7.428
7.423
7.417
7.246
7.241
7.230
7.225
7.218
5.982
5.979
5.965
5.961
5.959
5.938
5.131
5.105
5.102
5.090
5.087
5.085
4.485
4.464
2.568
2.560
2.551
2.543
2.534
2.525
2.517
2.508
2.499
1.917
1.902
1.885
1.716
1.544
1.367
1.349
1.341
1.323
1.316
1.308
1.290
1.283
1.276
1.269
1.253
1.231
1.213
1.206

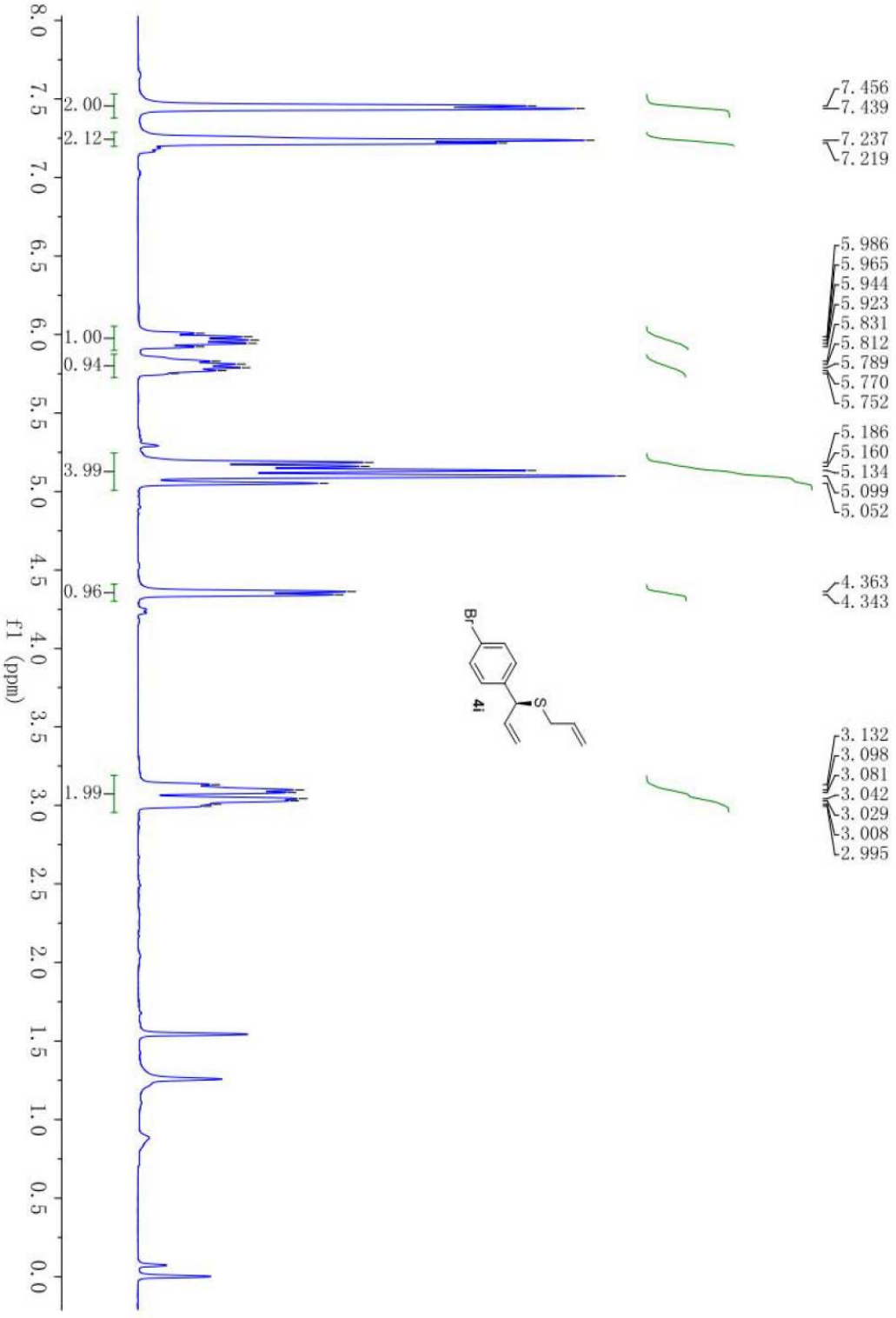

- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623 F2: 1.000 SW1: 20161 PW: 9.2 us PD: 10.0 sec OF1: 8043.2 NA: 32 LB: 2.0
EX: zgpg
USER: Administr -- DATE: Sat Oct 09 05:16:08 2010
PTS1d: 131072 , 131072
Nuts - Sgn-3-38-c_2
PPM
150
100
50
0
Br
S
4f
140.034
138.040
131.592
129.525
120.888
115.729
77.318
77.000
76.682
50.390
43.085
33.448
33.257
25.948
25.775

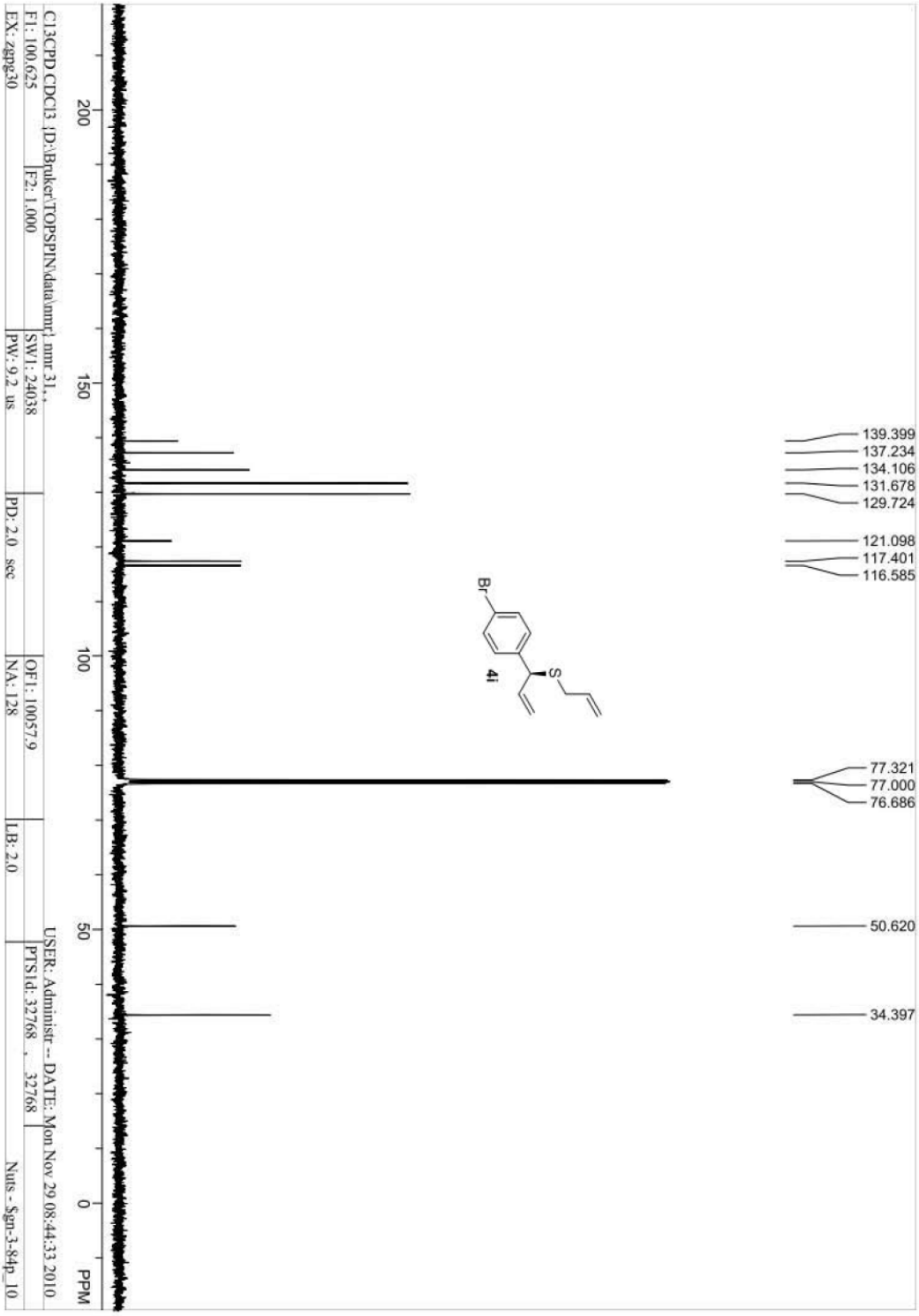

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
0.95
1.00
0.98
1.00
2.11
1.03
1.05
2.14
2.15
1.55
2.30
4.09
6.97 6.95 6.93
f1 (ppm)
1.00
6.973
6.964
6.941
0.98
6.933
6.929
6.920
7.217
7.214
7.204
7.201
6.964
6.933
6.929
6.920
6.008
6.003
5.986
5.983
5.961
5.179
5.155
5.137
5.131
4.792
4.771
2.673
2.664
2.655
2.647
2.638
2.629
2.621
2.612
2.603
1.968
1.941
1.932
1.910
1.765
1.743
1.735
1.731
1.595
1.591
1.553
1.428
1.418
1.391
1.366
1.334
1.303
1.280
1.270
1.253
1.225
S
S
4g

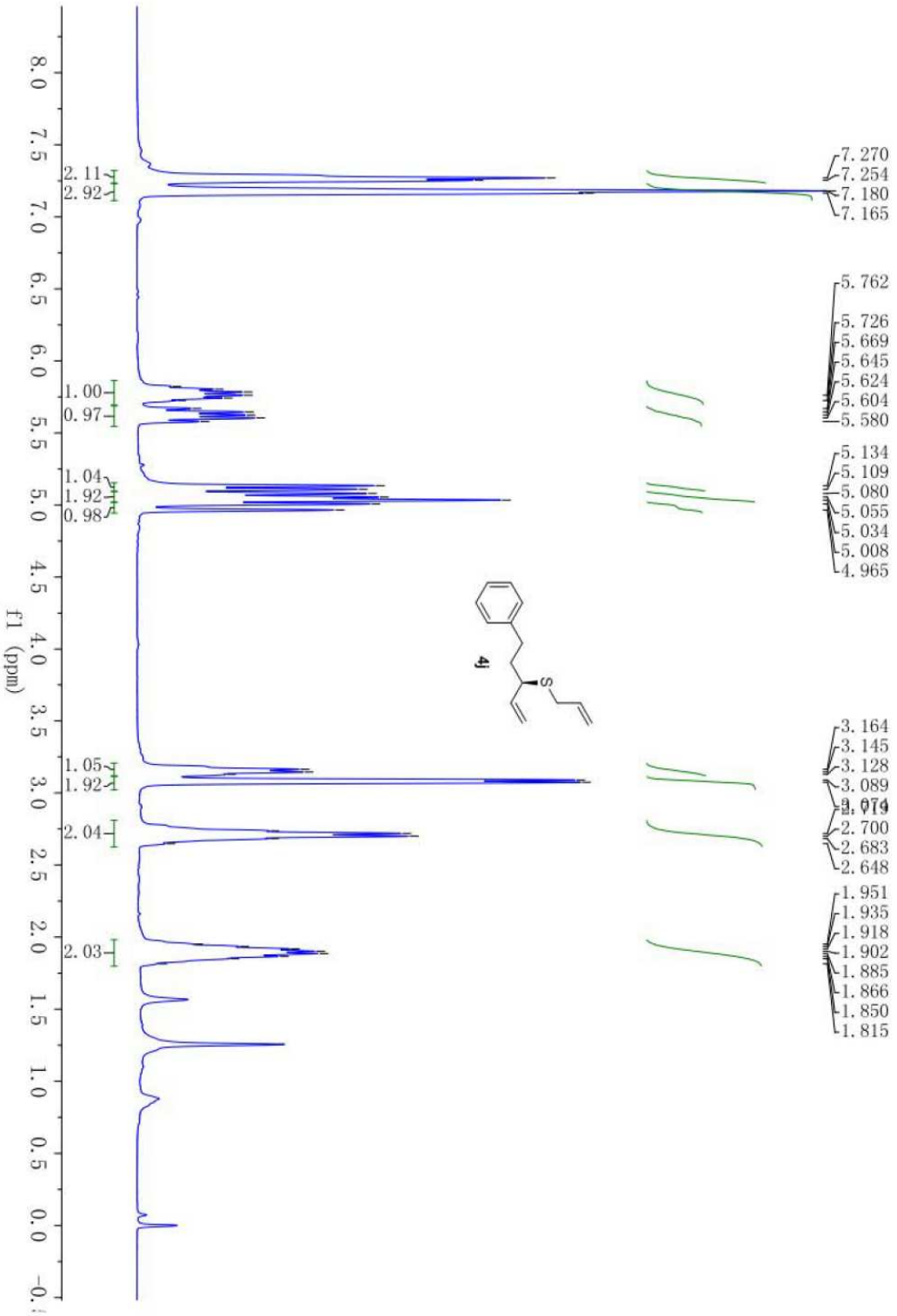

- FINAL_TEST - System: AV400M OrderNo.: 10008271 Customer: Tongji Univ
F1: 100.623 F2: 1.000 SW1: 20161 PW: 9.2 us PD: 10.0 sec OF1: 8043.7 NA: 32 LB: 2.0 PTSId: 131072 , 131072
EX: zgpg
USER: Administr -- DATE: Tue Sep 21 04:46:31 2010
Nuts - Sgm-3-26-C_1
4g
144.837
138.373
126.576
124.788
124.585
115.539
77.316
76.998
76.682
46.177
43.354
33.503
33.194
26.007
25.793
140
120
100
80
60
40
PPM

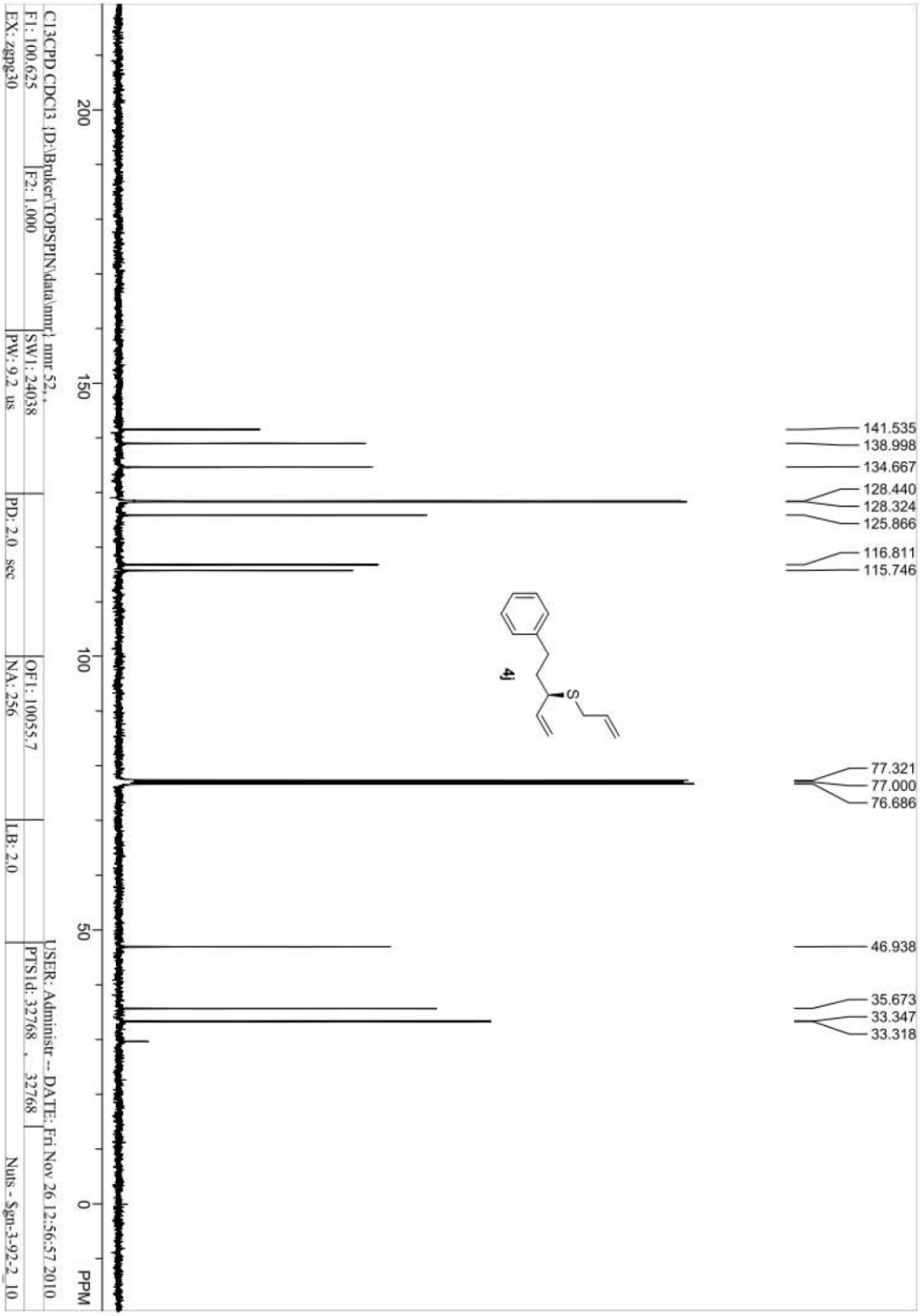

f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5.11
1.00
0.99
1.03
1.05
2.09
1.07
4.13
2.05
1.21
5.55
4h
S
7.270
7.252
7.187
7.174
5.697
5.673
5.651
5.631
5.607
5.075
5.051
5.008
4.966
3.269
3.250
3.233
2.738
2.719
2.698
2.677
2.642
2.570
1.872
1.858
1.839
1.729
1.569
1.311
1.282
1.255
1.233

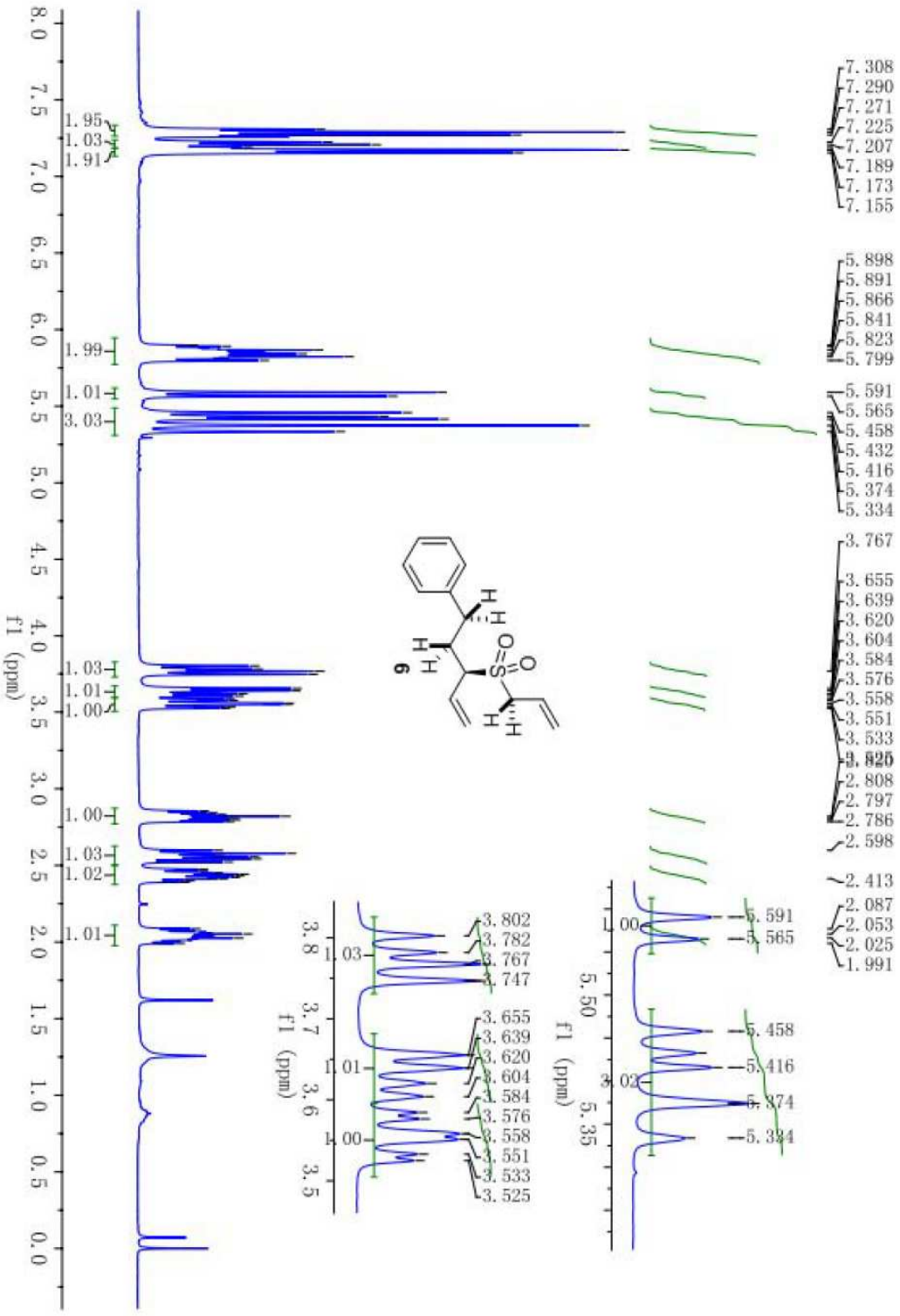

C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\nmr} nmr 5l 1
F1: 100.625
F2: 1.000
EX: zgpg30
SW1: 24038
PW: 9.2 us
PD: 2.0 scc
OF1: 10056.4
NA: 256
LB: 2.0
USER: Administr -- DATE: Fri Nov 26 12:38:47 2010
PTS1d: 32768 , 32768
Nuts - Sgn-3-91-2_40
4h
141.630
139.961
128.455
128.309
125.823
114.805
77.321
77.000
76.686
46.413
42.053
36.052
34.069
33.456
33.281
26.238
25.851
25.815
200
150
100
50
0
PPM

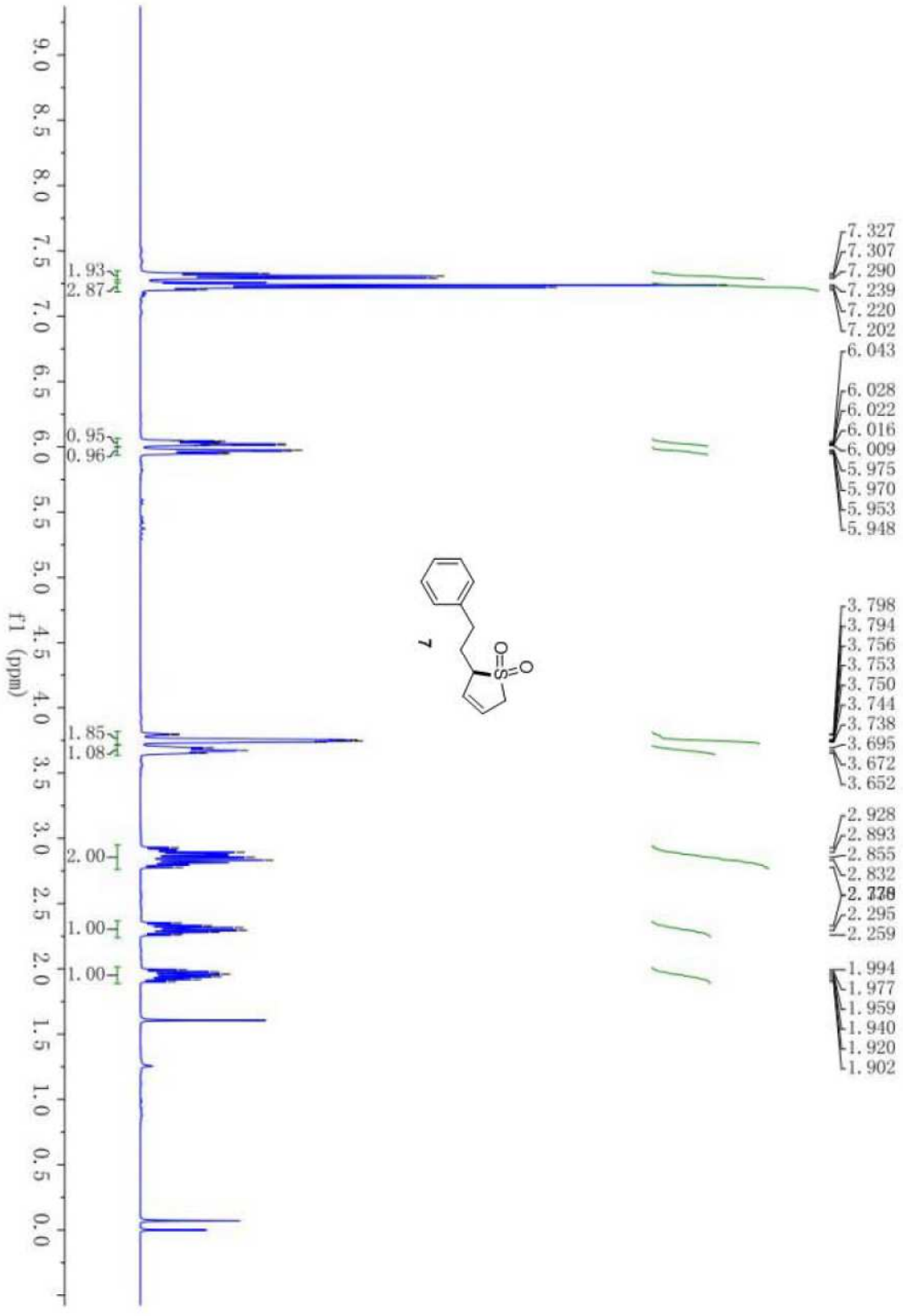

7.456
7.439
7.237
7.219
5.986
5.965
5.944
5.923
5.831
5.812
5.789
5.770
5.752
5.186
5.160
5.134
5.099
5.052
4.363
4.343
3.132
3.098
3.081
3.042
3.029
3.008
2.995
2.00
2.12
1.00
0.94
3.99
0.96
1.99
Br
S
4i
f1 (ppm)


139.399
137.234
134.106
131.678
129.724
121.098
117.401
116.585
77.321
77.000
76.686
50.620
34.397
Br
S
4i
200
150
100
50
0
PPM
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\nmr} nmr 31 1
F1: 100.625
F2: 1.000
EX: zgpg30
SW1: 24038
PW: 9.2 us
PD: 2.0 scc
OF1: 10057.9
NA: 128
LB: 2.0
USER: Administr -- DATE: Mon Nov 29 08:44:33 2010
PTS1d: 32768 , 32768
Nuts - Sgn-3-84p_10

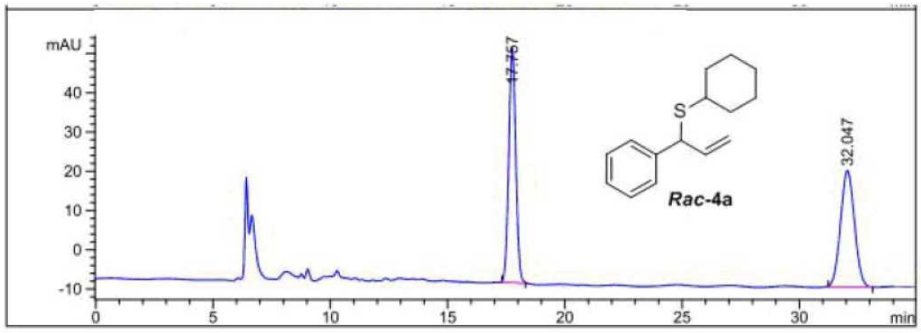

7.270
7.254
7.180
7.165
5.762
5.726
5.669
5.645
5.624
5.604
5.580
5.134
5.109
5.080
5.055
5.034
5.008
4.965
3.164
3.145
3.128
3.089
2.700
2.683
2.648
1.951
1.935
1.918
1.902
1.885
1.866
1.850
1.815
2.11
2.92
1.00
0.97
1.04
1.92
0.98
1.05
1.92
2.04
2.03
4j
f1 (ppm)


C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\nmr} nmr 52 1
F1: 100.625
F2: 1.000
EX: zgpg30
SW1: 24038
PW: 9.2 us
PD: 2.0 scc
OF1: 10055.7
NA: 256
LB: 2.0
USER: Administr -- DATE: Fri Nov 26 12:56:57 2010
PTS1d: 32768 , 32768
Nuts - Sgn-3-92-2_10
PPM
200
150
100
50
0
141.535
138.998
134.667
128.440
128.324
125.866
116.811
115.746
77.321
77.000
76.686
46.938
35.673
33.347
33.318
4j
S

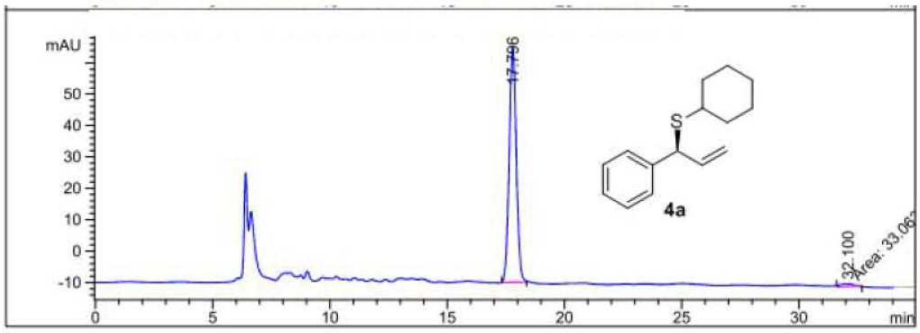

f1 (ppm)
1.95
1.03
1.91
1.99
1.01
3.03
1.03
1.01
1.00
1.00
1.03
1.02
1.01
7.308
7.290
7.271
7.225
7.207
7.189
7.173
7.155
5.898
5.891
5.866
5.841
5.823
5.799
5.591
5.565
5.458
5.432
5.416
5.374
5.334
3.767
3.655
3.639
3.620
3.604
3.584
3.576
3.558
3.551
3.533
2.808
2.797
2.786
2.598
2.413
2.087
2.053
2.025
1.991
6
3.802
3.782
3.767
3.747
3.655
3.639
3.620
3.604
3.584
3.576
3.558
3.551
3.533
3.525
1.03
1.01
1.00
5.591
5.565
5.458
5.416
5.374
5.334
1.00
3.02


f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.93
2.87
0.95
0.96
1.85
1.08
2.00
1.00
1.00
7.327
7.307
7.290
7.239
7.220
7.202
6.043
6.028
6.022
6.016
6.009
5.975
5.970
5.953
5.948
3.798
3.794
3.756
3.753
3.750
3.744
3.738
3.695
3.672
3.652
2.928
2.893
2.855
2.832
2.295
2.259
1.994
1.977
1.959
1.940
1.920
1.902
7

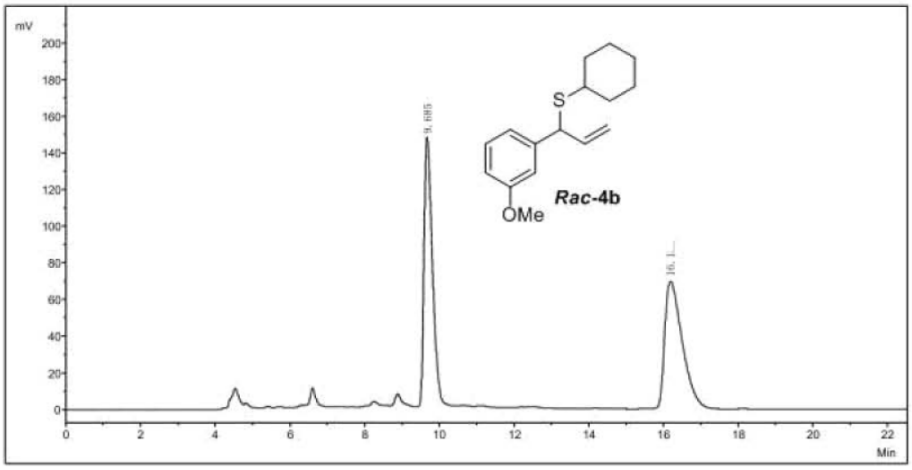
HPLC Chromatograms of the Chiral Compounds:



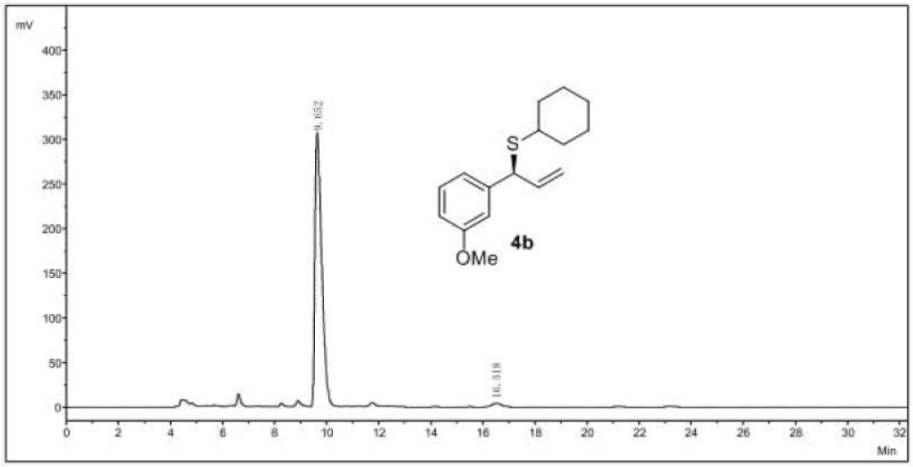
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.757	BB	0.3270	1246.62988	59.85107	50.5448
2	32.047	BP	0.6362	1219.75464	29.63425	49.4552



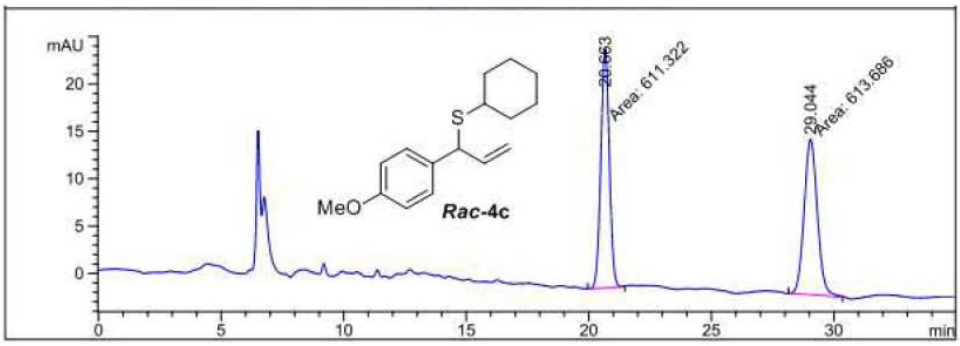
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.796	BB	0.3284	1576.23145	74.62935	97.9455
2	32.100	MM	0.6490	33.06375	8.49095e-1	2.0545



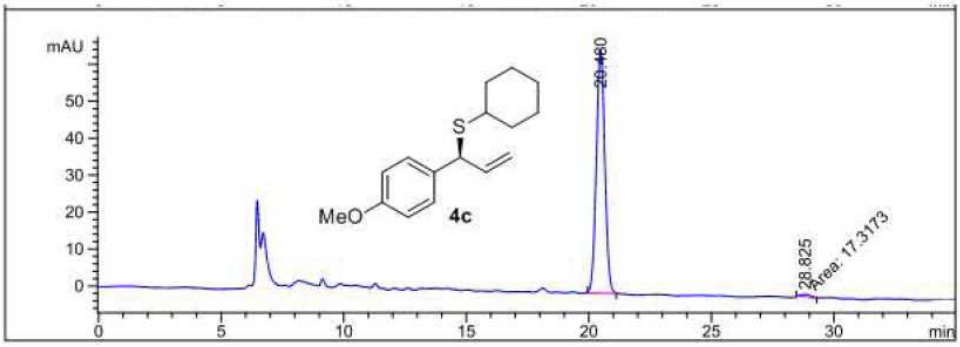
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.685	146106.9	2294107.6	50.3093
2	2		16.185	69413.2	2265899.1	49.6907



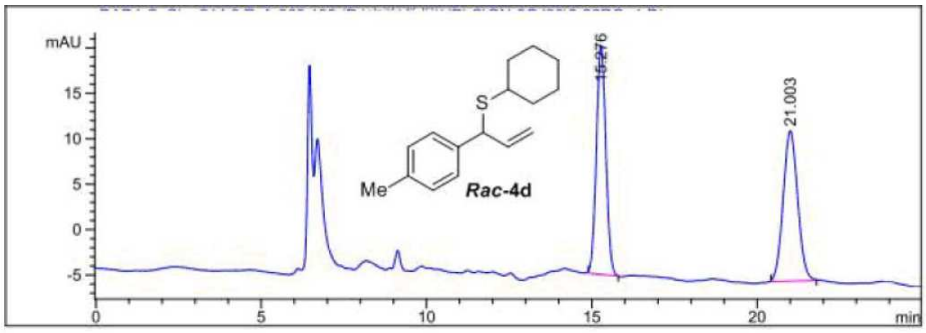
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.652	302958.3	5569541.4	97.9739
2	2		16.518	4118.1	115176.7	2.0261



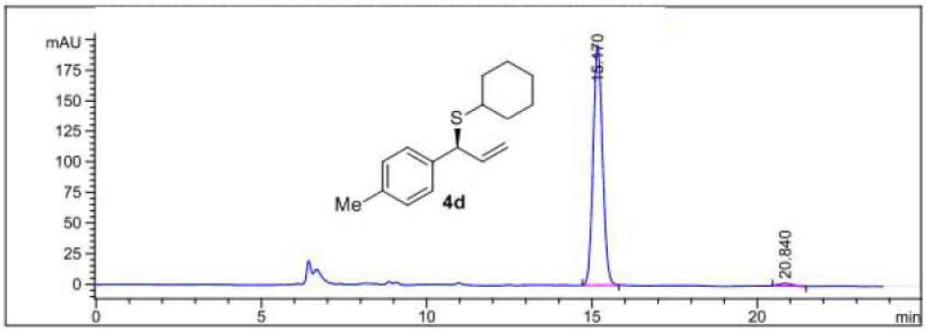
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.663	MM	0.4037	611.32166	25.23993	49.9035
2	29.044	MM	0.6237	613.68591	16.39943	50.0965



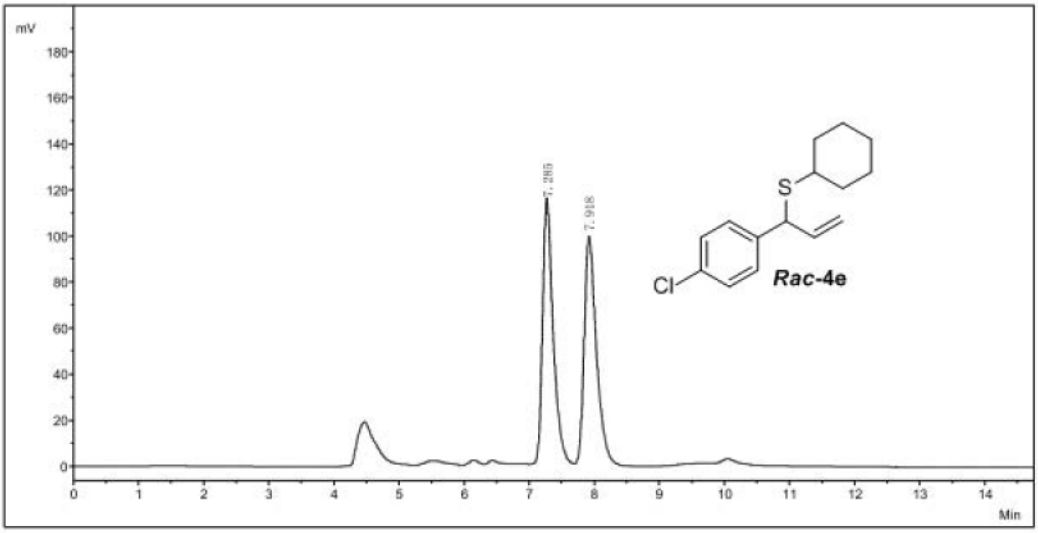
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.480	BB	0.3741	1583.99280	65.96557	98.9186
2	28.825	MM	0.4408	17.31732	6.54775e-1	1.0814



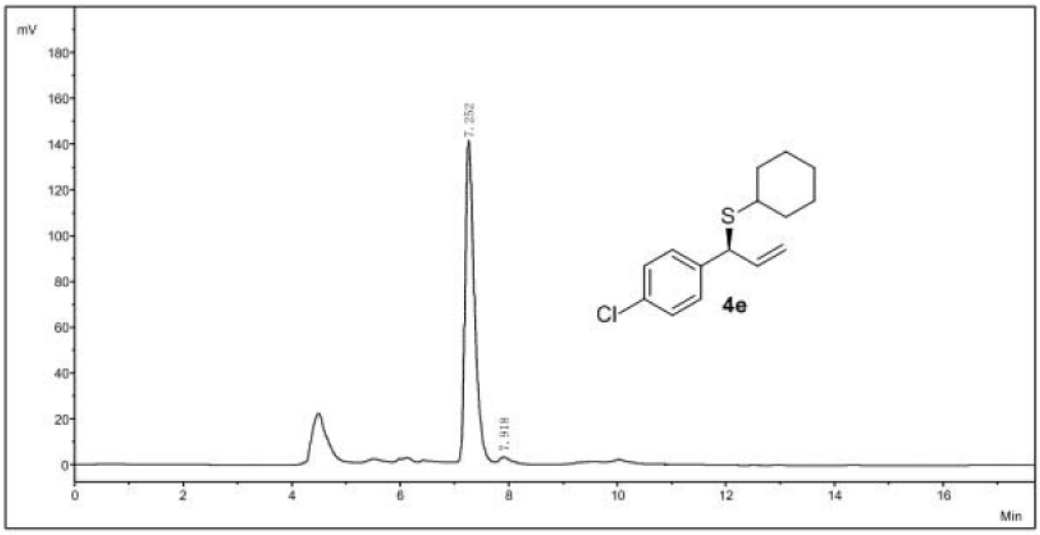
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.276	BB	0.3096	500.84778	25.22774	49.7472
2	21.003	BB	0.4666	505.93835	16.55463	50.2528



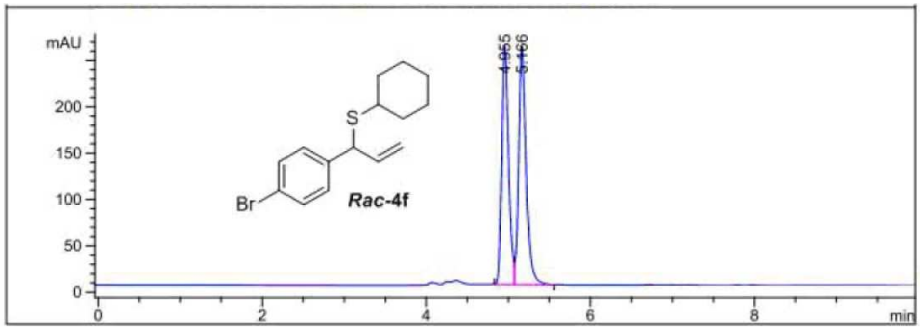
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.170	BB	0.3067	3871.83179	195.81642	98.5424
2	20.840	BP	0.3349	57.26894	2.06915	1.4576



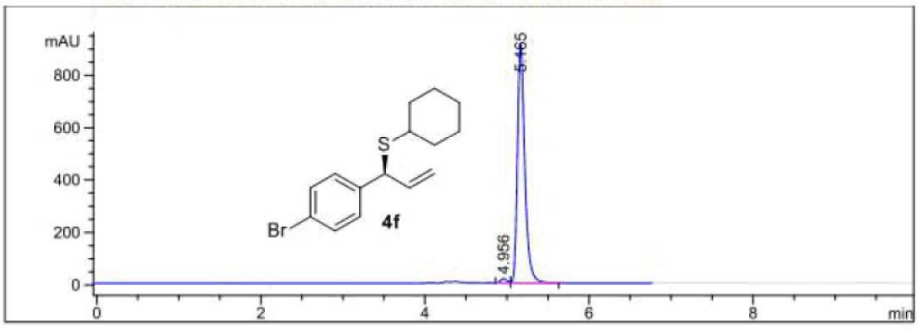
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.285	113454.5	1308841.2	50.2532
2	2		7.918	99300.5	1295649.5	49.7468



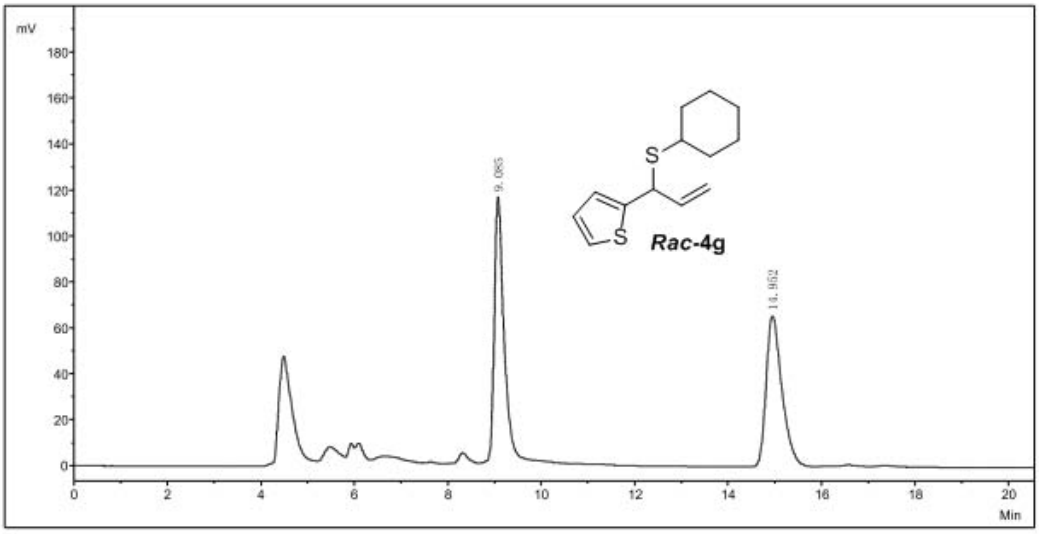
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.252	139760.0	1684332.7	97.4390
2	2		7.918	2956.3	44269.7	2.5610



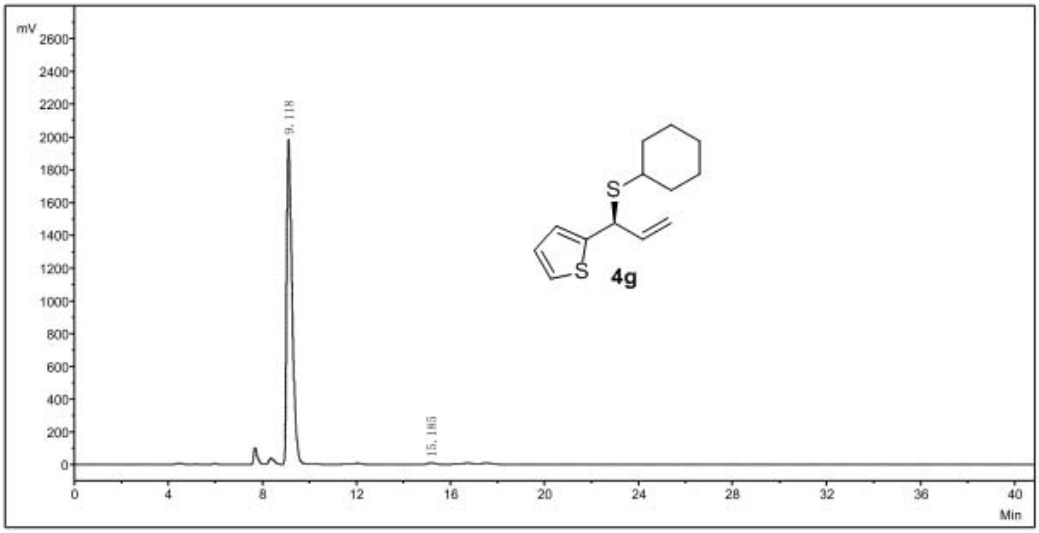
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.955	BV	0.0865	1470.88281	257.90927	47.7945
2	5.166	VB	0.0950	1606.63098	256.79333	52.2055



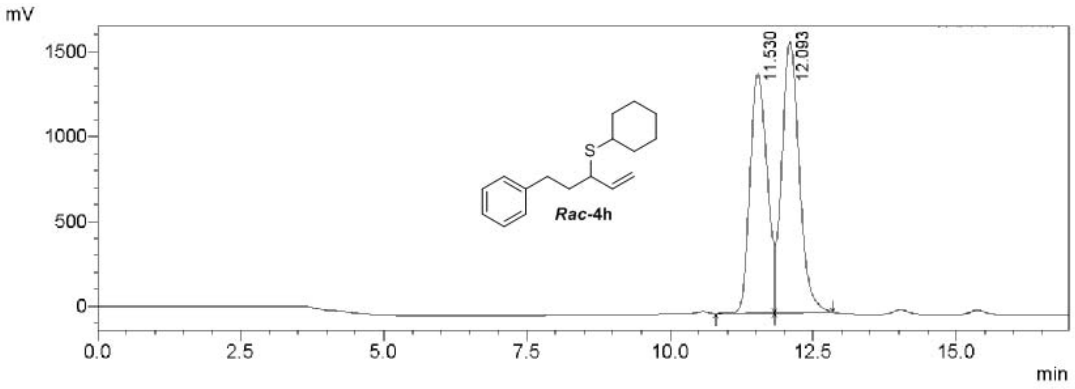
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.956	BV	0.0836	91.40450	16.76164	1.5985
2	5.165	VB	0.0941	5626.82861	910.15894	98.4015



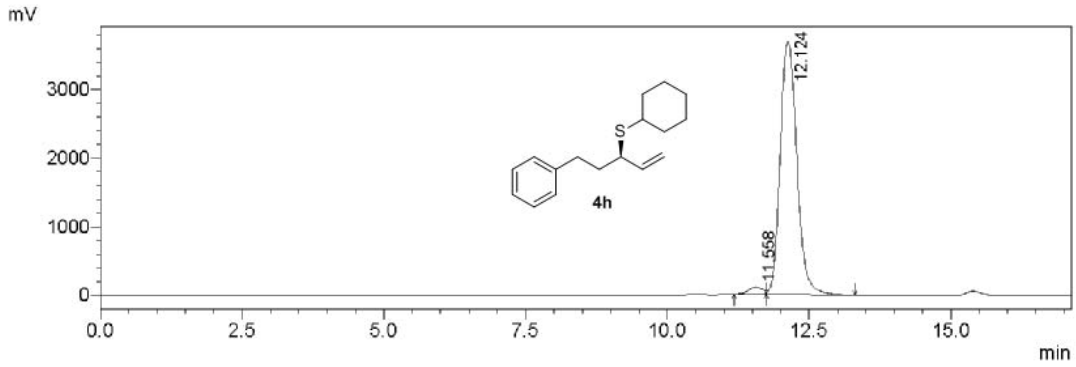
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.085	114961.5	1635119.7	51.5851
2	2		14.952	65635.7	1534633.9	48.4149



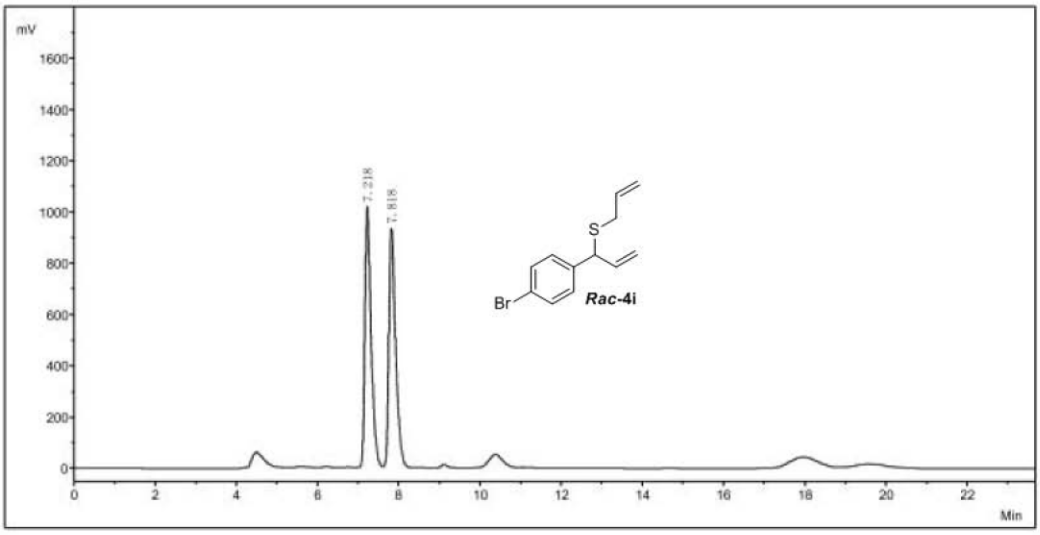
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.118	1980425.0	31781197.2	99.0905
2	2		15.185	12471.8	291703.3	0.9095



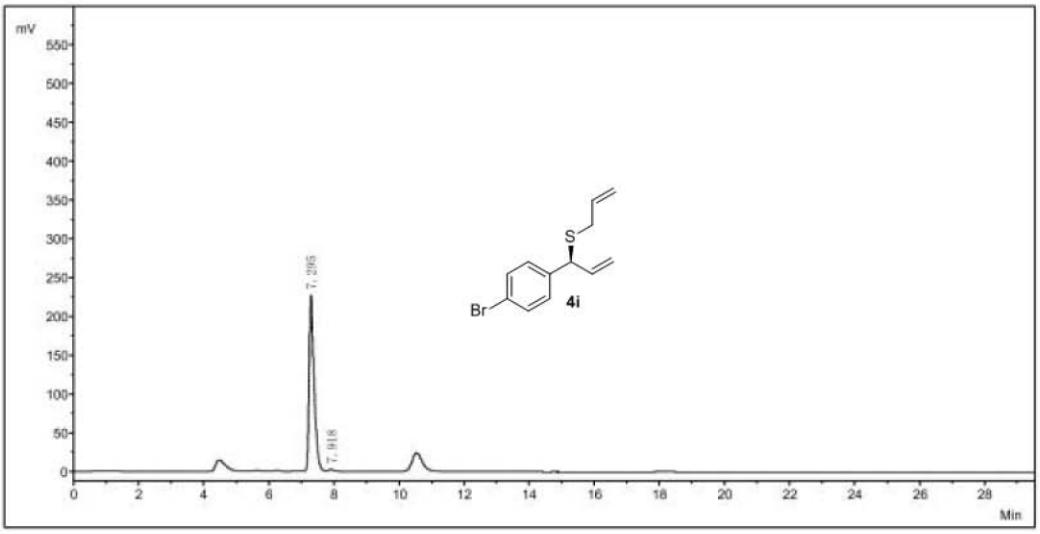
PeakNo	R. Time	PeakArea	PeakHeight	PerCent
1	11.530	29693621	1411720	46.738
2	12.093	33838967	1597282	53.262



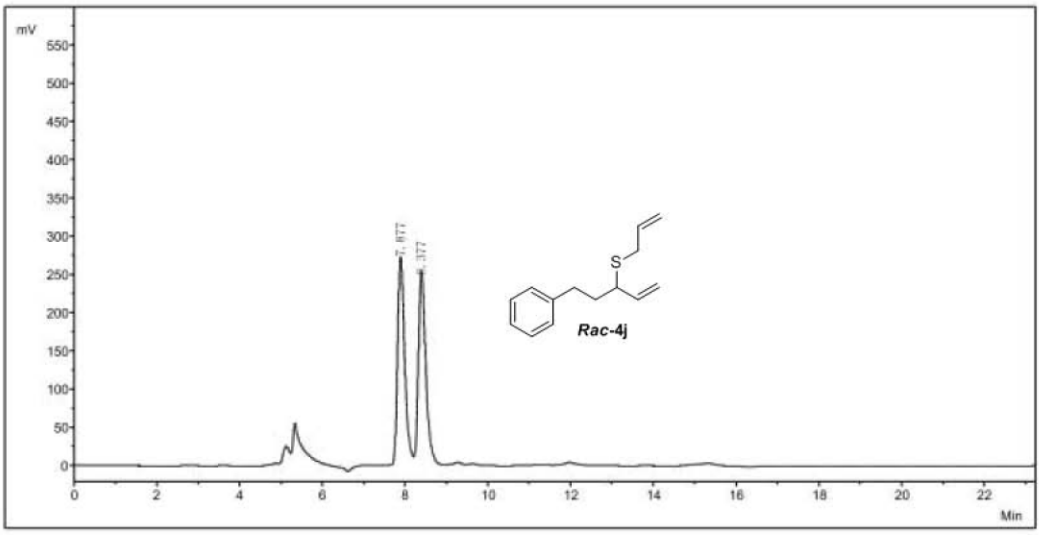
PeakNo	R. Time	PeakArea	PeakHeight	PerCent
1	11.558	1830747	101548	2.370
2	12.124	75429987	3695596	97.630



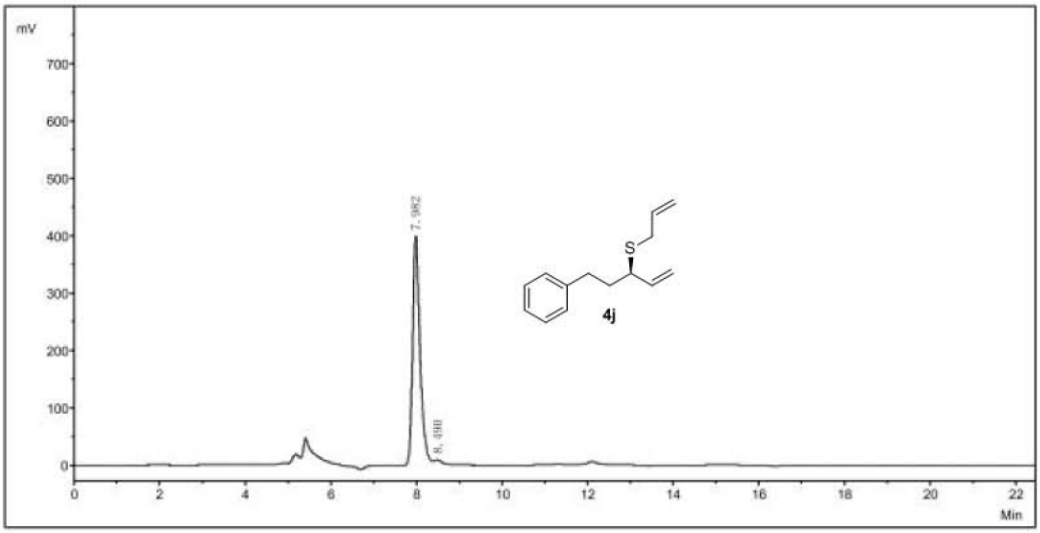
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.218	1010925.3	10779489.0	50.2139
2	2		7.818	931415.3	10687643.6	49.7861



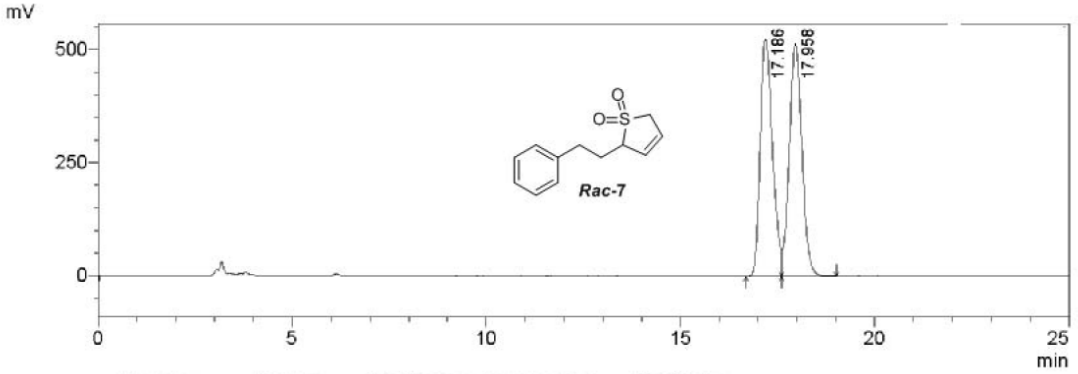
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.295	226205.4	2410964.3	99.2247
2	2		7.918	1904.0	18838.8	0.7753



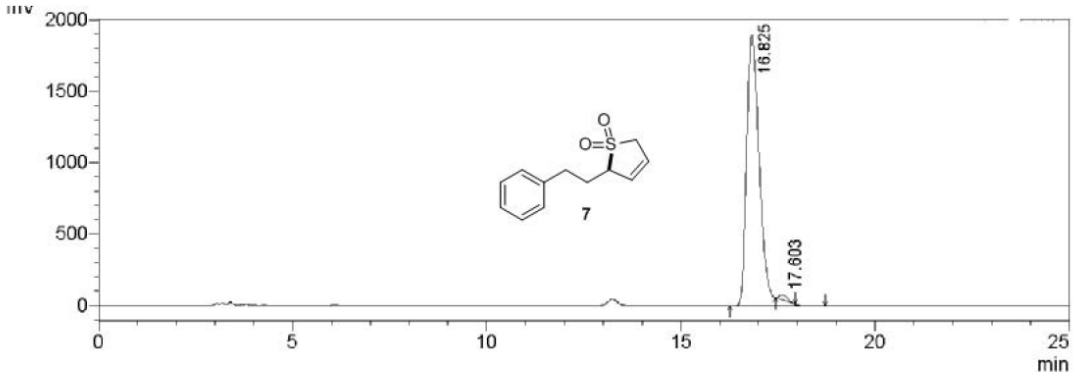
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.877	265974.7	3231881.8	50.3784
2	2		8.377	242060.2	3183326.8	49.6216



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		7.982	398441.9	4789883.9	97.5541
2	2		8.490	9270.7	120094.3	2.4459



PeakNo	R.Time	PeakArea	PeakHeight	PerCent
1	17.186	11553513	525192	49.925
2	17.958	11588380	514861	50.075



PeakNo	R.Time	PeakArea	PeakHeight	PerCent
1	16.825	43709804	1897828	98.756
2	17.603	550672	36214	1.244

Reference:

1. L. C. Liang, P. S. Chien, P. Y. Lee, J. M. Lin and Y. L. Huang. *Dalton Trans* **2008**, 3320.

2. a) A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim. *Synlett* **2001**, *9*, 1375; b) R. Naasz, L. A. Arnold, A. J. Minnaard, B. L. Feringa. *Angew. Chem. Int. Ed.* **2001**, *40*, 927; c) D. Polet, A. Alexakis. *Synthesis* **2004**, *15*, 2586.

3. P. G. M. Wuts, S. W. Ashford, A. M. Anderson, J. R. Atkins. *Org. Lett.* **2003**, *5*, 1483.

4. Qingwei Yao. *Org. Lett.* **2002**, *3*, 427.