

Chiral Carbon-Sulfur Center Formation via Pd-Catalyzed Asymmetric Allylic Thioetherification: Synthesis of Allylic Thioethers

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General Experimental Details:

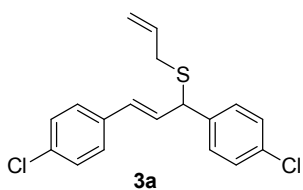
All air-sensitive manipulations were conducted under an argon atmosphere by standard Schlenk techniques. All glassware was dried by oven or flame immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. All reagents were purchased 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 diphenylphosphino ligands and substituted allylic carbonates² were prepared according to known procedures.

¹H NMR spectra were obtained at 300 MHz or 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. ¹³C NMR spectra were obtained at 75 MHz or 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl₃, 77.0 ppm). Data for ¹H 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 ¹³C NMR are reported in terms of chemical shift (δ, ppm).

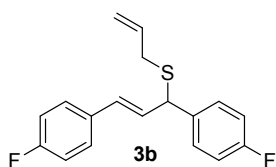
HPLC analyses were carried out on a Waters chromatography system or Agilent 1100 HPLC

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 KMnO₄ or iodine vapor.

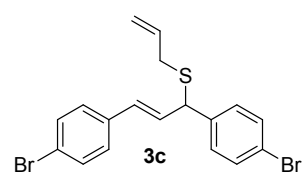
General procedure for Pd-catalyzed allylic thioetherification reaction: To the solution of allylic acetate **1** (0.2 mmol, 1 equiv.) and DCM (2.0 mL) were sequentially added the catalyst made from both [Pd(C₃H₅)Cl]₂ (2.5 mol%) and **L1** (5 mol%), KOAc (0.2 mmol)/BSA (0.20 mol), and sodium thiolate **2** (0.24 mmol, 1.2 equiv.) at 0 °C under argon. After that, the reaction mixture was vigorously stirred at -10 °C for the stated time and it was stirring until the allylic acetate **1** was completely consumed. The crude residue was purified by flash column chromatography (hexane/ethyl acetate = 10/1) to provide the desired products **3**.



(E)-Allyl(1,3-bis(4-chlorophenyl)allyl)sulfane (3a): Colorless oil; 81% yield; 95% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 8.099 (minor), 9.871 (major) min]; [α]_D²⁰ = -5.18 (c 1.0, CHCl₃). IR (film, cm⁻¹): 3153, 3080, 2968, 2872, 2360, 2341, 1634, 1486, 1399, 1423, 1073, 1010, 987, 917, 860, 816, 776, 730, 599, 515. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.27 (m, 7H), 7.25 (d, *J* = 3.0 Hz, 1H), 6.41 – 6.33 (m, 1H), 6.29 (dd, *J* = 15.6, 8.3 Hz, 1H), 5.82 (tt, *J* = 10.0, 7.1 Hz, 1H), 5.11 (dd, *J* = 25.1, 13.5 Hz, 2H), 4.54 (d, *J* = 8.2 Hz, 1H), 3.07 (ddd, *J* = 20.3, 13.8, 6.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.81 (s), 134.92 (s), 134.20 (s), 133.51 (s), 133.23 (s), 130.41 (s), 129.64 (s), 129.42 (s), 128.87 (d, *J* = 10.4 Hz), 127.71 (s), 117.59 (s), 50.19 (s), 34.63 (s). HRMS (ESI) calcd for C₁₈H₁₅Cl₂S (M⁻): 333.0277, Found: 333.0301.

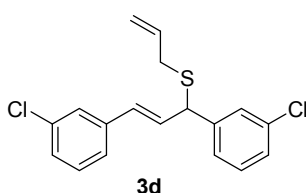


(E)-Allyl(1,3-bis(4-fluorophenyl)allyl)sulfane (3b): Colorless oil; 67% yield; 94% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 10.193 (minor), 14.623 (major) min]; [α]_D²⁰ = -10.01 (c 1.0, CHCl₃). IR (film, cm⁻¹): 3128, 2912, 1733, 1619, 1448, 1403, 1282, 1072, 1035, 994, 911, 819, 763, 742, 639, 528. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (ddd, *J* = 13.9, 8.6, 5.4 Hz, 4H), 7.08 – 6.96 (m, 4H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.25 (dd, *J* = 15.7, 8.5 Hz, 1H), 5.83 (ddt, *J* = 14.2, 9.9, 7.1 Hz, 1H), 5.12 (dd, *J* = 19.1, 13.5 Hz, 2H), 4.55 (d, *J* = 8.5 Hz, 1H), 3.08 (ddd, *J* = 20.5, 13.9, 6.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 163.45 (d, *J* = 43.9 Hz), 162.66 – 159.61 (m), 136.16 (s), 134.28 (s), 132.61 (s), 130.24 (s), 129.57 (d, *J* = 8.1 Hz), 129.04 (s), 128.00 (d, *J* = 8.0 Hz), 117.42 (s), 115.57 (dd, *J* = 21.6, 2.7 Hz), 50.13 (s), 34.61 (s). HRMS (ESI) calcd for C₁₈H₁₅F₂S (M⁻): 301.0868, Found: 301.0888.



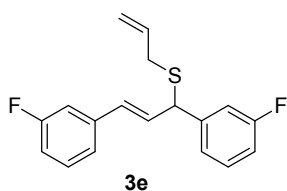
(E)-Allyl(1,3-bis(4-bromophenyl)allyl)sulfane (3c): Colorless oil; 78% yield; 95% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =

11.765 (minor), 13.617 (major) min]; $[\alpha]_{\text{D}}^{20} = -13.06$ (c 1.0, CHCl_3). IR (film, cm^{-1}): 3098, 2912, 1653, 1509, 1418, 1413, 1252, 1072, 1035, 998, 919, 866, 743, 752, 649, 520. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, $J = 17.9, 8.3$ Hz, 2H), 7.37 – 7.25 (m, 2H), 6.42 (d, $J = 15.7$ Hz, 1H), 6.37 (d, $J = 7.8$ Hz, 1H), 6.10 – 5.59 (m, 1H), 5.16 (dd, $J = 29.8, 13.5$ Hz, 1H), 4.57 (d, $J = 7.8$ Hz, 1H), 3.13 (dd, $J = 25.0, 7.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.24 (d, $J = 11.4$ Hz), 161.80 (d, $J = 12.3$ Hz), 142.71 (d, $J = 7.0$ Hz), 138.68 (d, $J = 7.7$ Hz), 134.14 (s), 130.56 (d, $J = 2.5$ Hz), 130.16 (s), 123.71 (d, $J = 2.8$ Hz), 122.42 (d, $J = 2.7$ Hz), 117.72 (s), 115.65 – 114.37 (m), 112.98 (d, $J = 21.8$ Hz), 50.19 (s), 34.61 (s). HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{Br}_2\text{S}$ (M^-): 420.9267, Found: 420.9266.



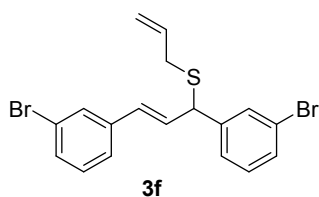
(E)-Allyl(1,3-bis(3-chlorophenyl)allyl)sulfane (3d): Colorless oil; 72% yield; 92% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 7.122$ (minor), 7.834 (major) min]; $[\alpha]_{\text{D}}^{20} = -13.373$ (c

1.0, CHCl_3). IR (film, cm^{-1}): 3240, 2929, 2862, 1623, 1499, 1448, 1413, 1222, 1092, 1014, 996, 927, 809, 762, 742, 619, 525. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (ddd, $J = 27.2, 16.8, 8.6$ Hz, 1H), 6.40 (d, $J = 15.7$ Hz, 1H), 6.33 (dd, $J = 15.7, 7.9$ Hz, 1H), 5.99 – 5.63 (m, 1H), 5.13 (dd, $J = 26.7, 13.4$ Hz, 1H), 4.53 (d, $J = 7.9$ Hz, 1H), 3.25 – 2.93 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.64 (s), 163.21 (s), 161.19 (s), 160.77 (s), 136.09 (d, $J = 3.2$ Hz), 134.28 (s), 132.57 (d, $J = 3.3$ Hz), 130.23 (s), 129.58 (d, $J = 8.1$ Hz), 128.95 (s), 128.02 (d, $J = 8.0$ Hz), 117.53 (s), 115.61 (dd, $J = 21.5, 4.0$ Hz), 50.05 (s), 50.05 (s), 34.63 (s), 34.63 (s), 1.11 (s). HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{S}$ (M^-): 333.0277, Found: 333.0306.



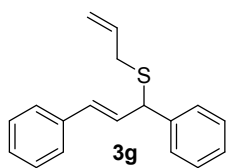
(E)-Allyl(1,3-bis(3-fluorophenyl)allyl)sulfane (3e): Colorless oil; 61% yield; 94% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 6.715$ (minor), 7.254 (major) min]; $[\alpha]_{\text{D}}^{20} = -44.56$ (c

1.0, CHCl_3). IR (film, cm^{-1}): 3018, 2892, 1734, 1599, 1438, 1413, 1292, 1372, 1015, 984, 901, 809, 753, 742, 629, 518. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 6.79 (m, 1H), 6.43 (d, $J = 15.7$ Hz, 1H), 6.34 (dd, $J = 15.7, 8.3$ Hz, 1H), 5.83 (ddt, $J = 17.0, 9.9, 7.1$ Hz, 1H), 5.13 (dd, $J = 23.7, 13.4$ Hz, 1H), 4.56 (d, $J = 8.3$ Hz, 1H), 3.11 (dd, $J = 20.6, 7.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.26 (d, $J = 11.6$ Hz), 161.81 (d, $J = 12.5$ Hz), 142.75 (d, $J = 7.0$ Hz), 138.72 (d, $J = 7.7$ Hz), 134.14 (s), 130.57 (d, $J = 2.5$ Hz), 130.18 (dd, $J = 14.1, 8.4$ Hz), 123.70 (d, $J = 2.8$ Hz), 122.41 (d, $J = 2.7$ Hz), 117.66 (s), 115.11 (s), 115.03 – 114.32 (m), 113.09 (s), 112.87 (s), 50.25 (s), 50.25 (s), 34.60 (s), 34.60 (s). HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{F}_2\text{S}$ (M^-): 301.0865, Found: 308.0868.



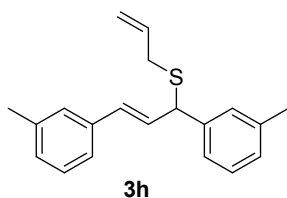
(E)-Allyl(1,3-bis(3-bromophenyl)allyl)sulfane(3f): Colorless oil; 81% yield; 94% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 8.734 (minor), 9.424 (major) min]; $[\alpha]^{20}_D = -14.26$ (c 1.0, CHCl_3).

IR (film, cm^{-1}): 3099, 2922, 1663, 1519, 1408, 1400, 1292, 1172, 1135, 993, 909, 856, 733, 702, 649, 530. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (dd, $J = 17.9, 8.3$ Hz, 2H), 7.37 – 7.25 (m, 2H), 6.42 (d, $J = 15.7$ Hz, 1H), 6.37 (d, $J = 7.8$ Hz, 1H), 6.10 – 5.59 (m, 1H), 5.16 (dd, $J = 29.8, 13.5$ Hz, 1H), 4.57 (d, $J = 7.8$ Hz, 1H), 3.13 (dd, $J = 25.0, 7.1$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.24 (d, $J = 11.4$ Hz), 161.80 (d, $J = 12.3$ Hz), 142.71 (d, $J = 7.0$ Hz), 138.68 (d, $J = 7.7$ Hz), 134.14 (s), 130.56 (d, $J = 2.5$ Hz), 130.16 (s), 123.71 (d, $J = 2.8$ Hz), 122.42 (d, $J = 2.7$ Hz), 117.72 (s), 115.65 – 114.37 (m), 112.98 (d, $J = 21.8$ Hz), 50.19 (s), 34.61 (s). HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{F}_2\text{S}$ (M^-): 420.9267, Found: 420.9228.



(E)-Allyl(1,3-bis(phenyl)allyl)sulfane (3g): Colorless oil; 50% yield; 77% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 10.753 (minor), 14.658 (major) min]; $[\alpha]^{20}_D = -6.21$ (c 1.0, CHCl_3). IR (film, cm^{-1}): 3120, 2930, 2802, 1665, 1639,

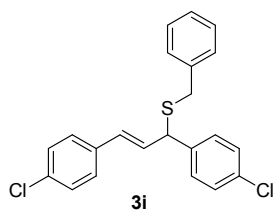
1318, 1213, 1152, 1072, 1035, 990, 929, 876, 703, 702, 650, 524. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 – 6.90 (m, 5H), 6.47 (d, $J = 15.7$ Hz, 1H), 6.38 (dd, $J = 15.6, 8.4$ Hz, 1H), 5.84 (dq, $J = 9.6, 7.1$ Hz, 1H), 5.12 (t, $J = 12.4$ Hz, 1H), 4.58 (d, $J = 8.4$ Hz, 1H), 3.11 (dd, $J = 24.5, 7.0$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.49 (s), 136.6 (s), 134.49 (s), 131.30 (s), 129.53 (s), 128.77 (s), 128.65 (s), 128.05 (s), 127.76 (s), 127.48 (s), 126.53 (s), 117.37 (s), 51.08 (s), 34.64 (s). HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{S}$ (M^-): 265.1025, Found: 265.1030.



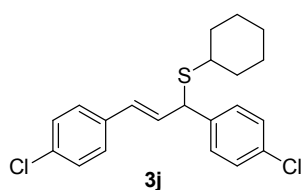
(E)-Allyl(1,3-di-m-tolylallyl)sulfane (3h): Colorless oil; 45% yield; 63% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 9.292 (minor), 11.337 (major) min]; $[\alpha]^{20}_D = -9.23$ (c 1.0, CHCl_3). IR (film,

cm^{-1}): 3012, 2889, 2622, 1673, 1509, 1438, 1405, 1282, 1162, 1125, 995, 889, 856, 733, 712, 639, 520. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 6.87 (m, 1H), 6.44 (d, $J = 15.7$ Hz, 1H), 6.40 – 6.31 (m, 1H), 5.85 (dq, $J = 10.0, 7.2$ Hz, 1H), 5.13 (dd, $J = 13.3, 8.2$ Hz, 1H), 4.68 – 4.30 (m, 1H), 3.36 – 2.88 (m, 1H), 2.56 – 2.17 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.41 (s), 138.41 (s), 138.18 (s), 136.62 (s), 134.53 (s), 131.22 (s), 129.39 (s), 128.47 (dd, $J = 20.6, 19.0$ Hz), 128.23 (s),

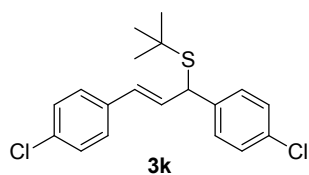
127.18 (s), 125.04 (s), 123.73 (s), 117.30 (s), 51.10 (s), 34.64 (s), 21.49 (d, $J = 7.6$ Hz). HRMS(ESI) calcd for $C_{20}H_{21}S$ (M⁻): 293.1369, Found: 293.1389.



(E)-Benzyl(1,3-bis(4-chlorophenyl)allyl)sulfane (3i): Colorless oil; 71% yield; 95% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_R = 28.874$ (minor), 34.451 (major) min]; $[\alpha]_D^{20} = -26.36$ (c 1.0, $CHCl_3$). IR (film, cm^{-1}): 2978, 2802, 1663, 1489, 1478, 1403, 1212, 1132, 1005, 996, 917, 826, 761, 745, 629, 531. 1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.16 (m, 5H), 6.33 (d, $J = 9.4$ Hz, 1H), 4.42 (d, $J = 7.0$ Hz, 1H), 3.66 (d, $J = 12.4$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.66 (s), 137.82 (s), 134.87 (s), 133.52 (s), 133.26 (s), 130.51 (s), 129.46 (d, $J = 10.7$ Hz), 128.85 (dd, $J = 24.7, 14.8$ Hz), 127.73 (s), 127.19 (s), 50.72 (s), 36.14 (s). HRMS(ESI) calcd for $C_{19}H_{20}Cl_2S$ (M⁻): 383.0443, Found: 383.0434.

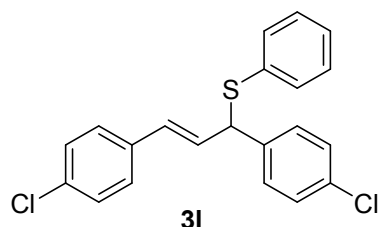


(E)-(1,3-Bis(4-chlorophenyl)allyl)(cyclohexyl)sulfane (3j): Colorless oil; 70% yield; 93% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_R = 6.957$ (minor), 8.693 (major) min]; $[\alpha]_D^{20} = -21.29$ (c 1.0, $CHCl_3$). IR (film, cm^{-1}): 3026, 2928, 2852, 1630, 1604, 1496, 1448, 1384, 1263, 997, 911, 747, 698. 1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.17 (m, 1H), 6.37 (ddd, $J = 21.5, 14.5, 6.6$ Hz, 1H), 4.68 (d, $J = 7.9$ Hz, 1H), 2.08 – 1.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.45 (s), 135.07 (s), 133.40 (s), 133.05 (s), 130.51 (s), 129.57 (s), 129.24 (s), 128.87 (s), 128.79 (s), 127.70 (s), 49.90 (s), 43.35 (s), 33.48 (d, $J = 10.7$ Hz), 25.82 (s). HRMS(ESI) calcd for $C_{19}H_{20}Cl_2S$ (M⁻): 375.0749, Found: 375.0747.



(E)-Allyl(1,3-di-m-tolylallyl)sulfane (3k): Colorless oil; 88% yield; 91% ee. The ee of the product was determined by HPLC [Daicel CHIRALPAK OJ-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_R = 7.632$ (minor), 9.073 (major) min]; $[\alpha]_D^{20} = -10.12$ (c 1.0, $CHCl_3$). IR (film, cm^{-1}): 3029, 2872, 1653, 1499, 1458, 1413, 1380, 1372, 1215, 990, 927, 820, 760, 741, 619, 522.

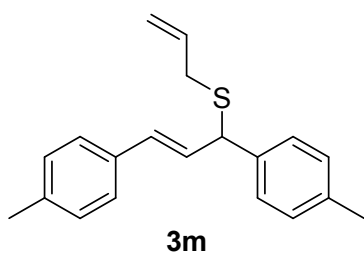
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.23 (m, 8H), 6.46 – 6.22 (m, 2H), 4.71 (d, $J = 7.1$ Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.75 (s), 135.21 (s), 133.29 (s), 132.87 (s), 132.16 (s), 129.43 (s), 128.79 (d, $J = 5.9$ Hz), 127.63 (s), 49.48 (s), 44.93 (s), 31.50 (s). HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{S}$ (M^-): 349.0590, Found: 349.0597.



(E)-(1,3-Bis(4-chlorophenyl)allyl)(phenyl)sulfane (3I):

Colorless oil; 72% yield; 53% ee. The ee of the product was determined by HPLC [Lux Cellulose-1 (0.46*25 cm, 5 μ m) CO_2 :methanol 97:3 (V/V %) UV 214 nm 1.5 mL/min Back pressure 2000 psi Column Temperature 40 $^\circ\text{C}$]; $[\alpha]_{\text{D}}^{20} = -$

16.12 (c 1.0, CHCl_3). IR (film, cm^{-1}): 3823, 3081, 2976, 2911, 2360, 2341, 1634, 1486, 1399, 1423, 1073, 1010, 987, 917, 843, 816, 736, 740, 593, 515. ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.17 (m, 1H), 6.37 (ddd, $J = 21.5, 14.5, 6.6$ Hz, 1H), 4.68 (d, $J = 7.9$ Hz, 1H), 2.08 – 1.11 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.45 (s), 135.07 (s), 133.40 (s), 133.05 (s), 130.51 (s), 129.57 (s), 129.24 (s), 128.87 (s), 128.79 (s), 127.70 (s), 49.90 (s), 43.35 (s), 33.48 (d, $J = 10.7$ Hz), 25.82 (s). HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{S}$ (M^-): 369.0278, Found: 369.0312.



(E)-Allyl(1,3-di-p-tolylallyl)sulfane (3m): Colorless oil; 43% yield; 3% ee. The ee of the product **3I** was determined by HPLC [Daicel CHIRALPAK AD-H (0.46 cm*25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 6.835$ (minor), 7.334 (major) min]. IR (film, cm^{-1}): 3015, 2883, 2626, 1669, 1513, 1434, 1411, 1276, 1168,

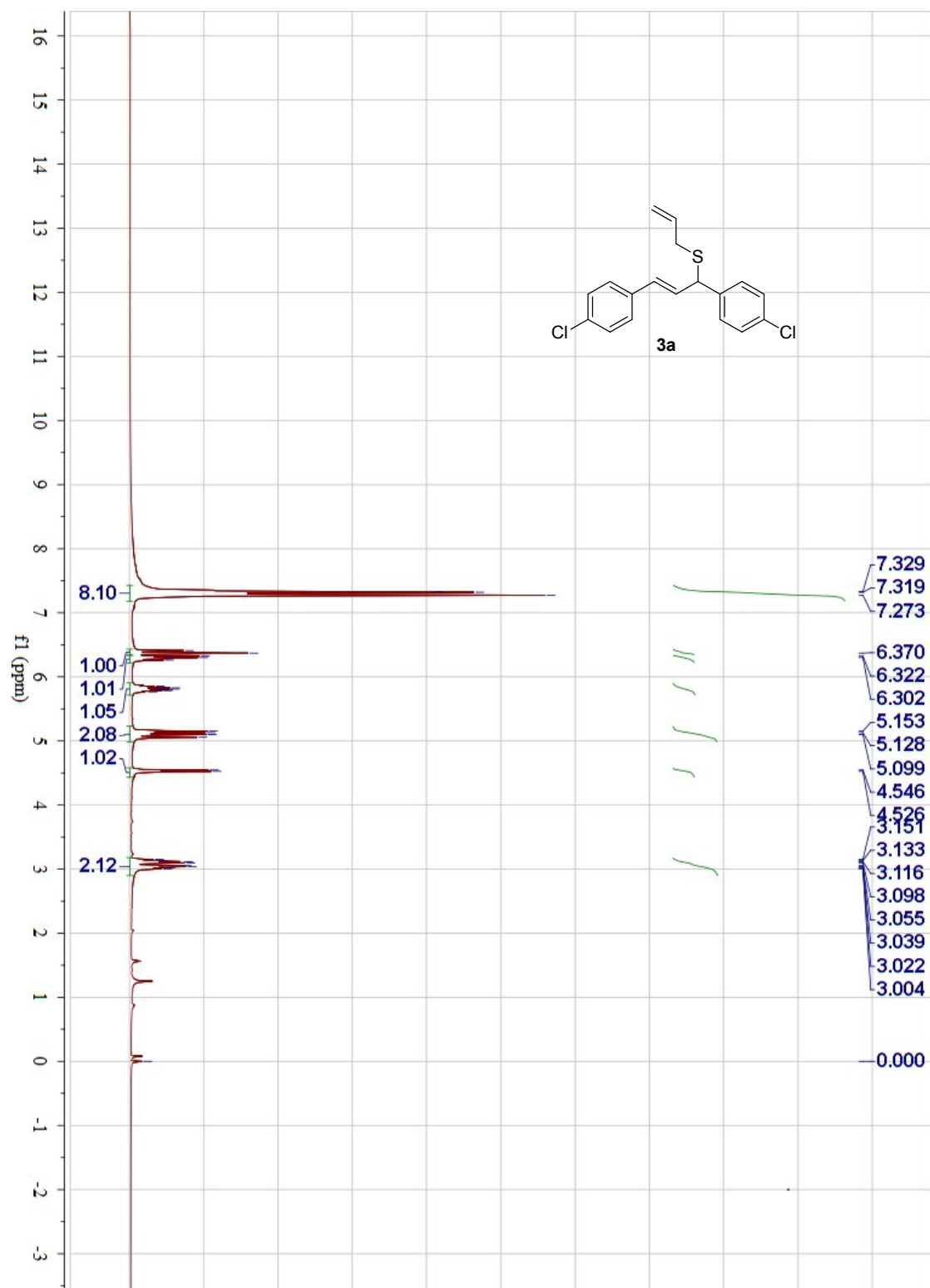
1131, 991, 893, 859, 740, 718, 633, 526. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (dd, $J = 11.9, 7.6$ Hz, 4H), 7.11 (dd, $J = 15.2, 7.6$ Hz, 4H), 6.42 (d, $J = 15.6$ Hz, 1H), 6.31 (dd, $J = 15.5, 8.6$ Hz, 1H), 5.82 (dq, $J = 10.6, 6.9$ Hz, 1H), 5.13 – 5.06 (m, 2H), 4.53 (d, $J = 8.3$ Hz, 1H), 3.08 (ddd, $J = 20.2, 13.8, 7.1$ Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.64, 137.55, 137.11, 134.65, 134.00, 131.07, 129.46, 129.37, 128.72, 127.95, 126.48, 117.25, 50.94, 34.67, 21.31, 21.22. HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{S}$ (M^-): 293.1358, Found: 293.1356.

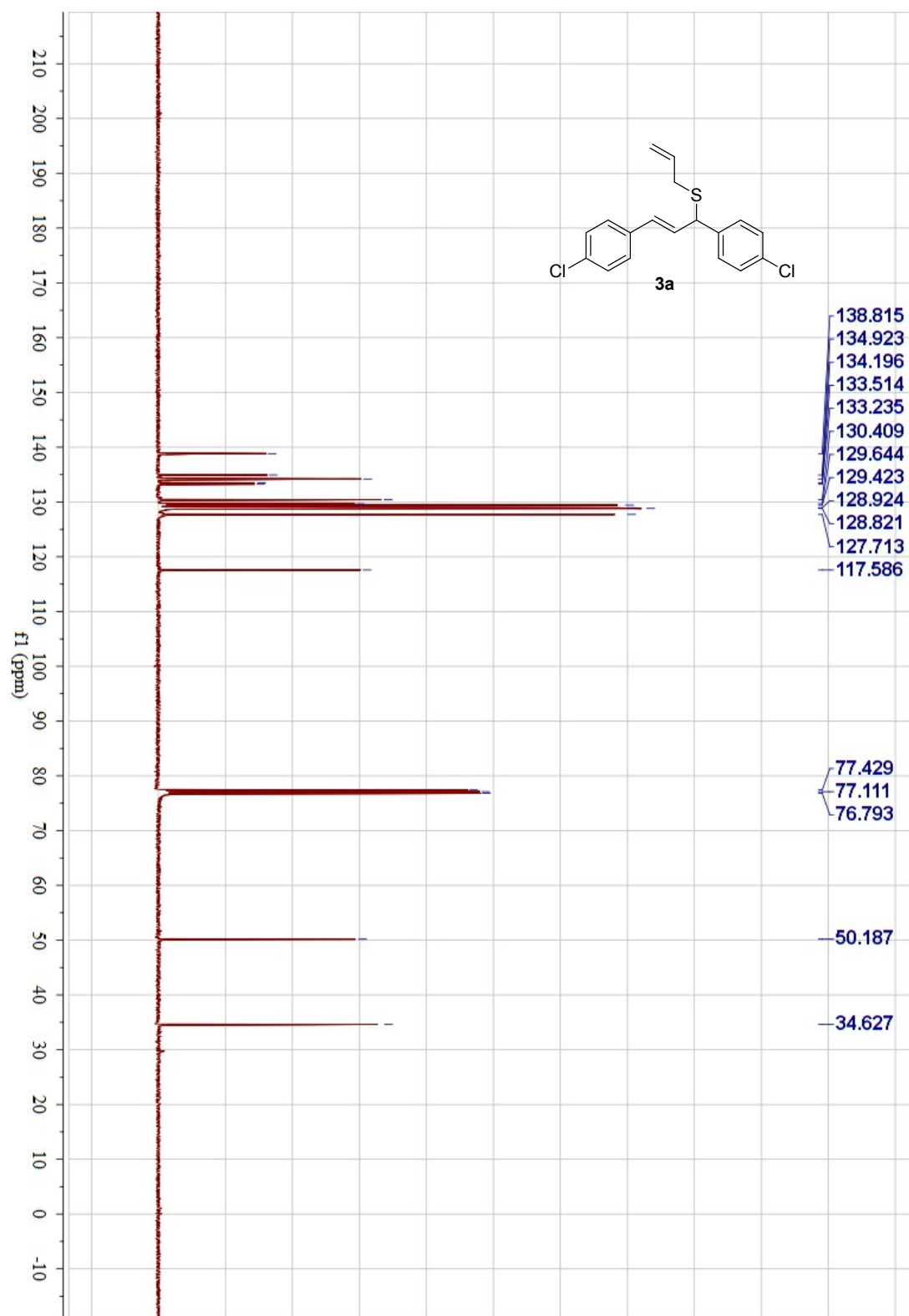
References:

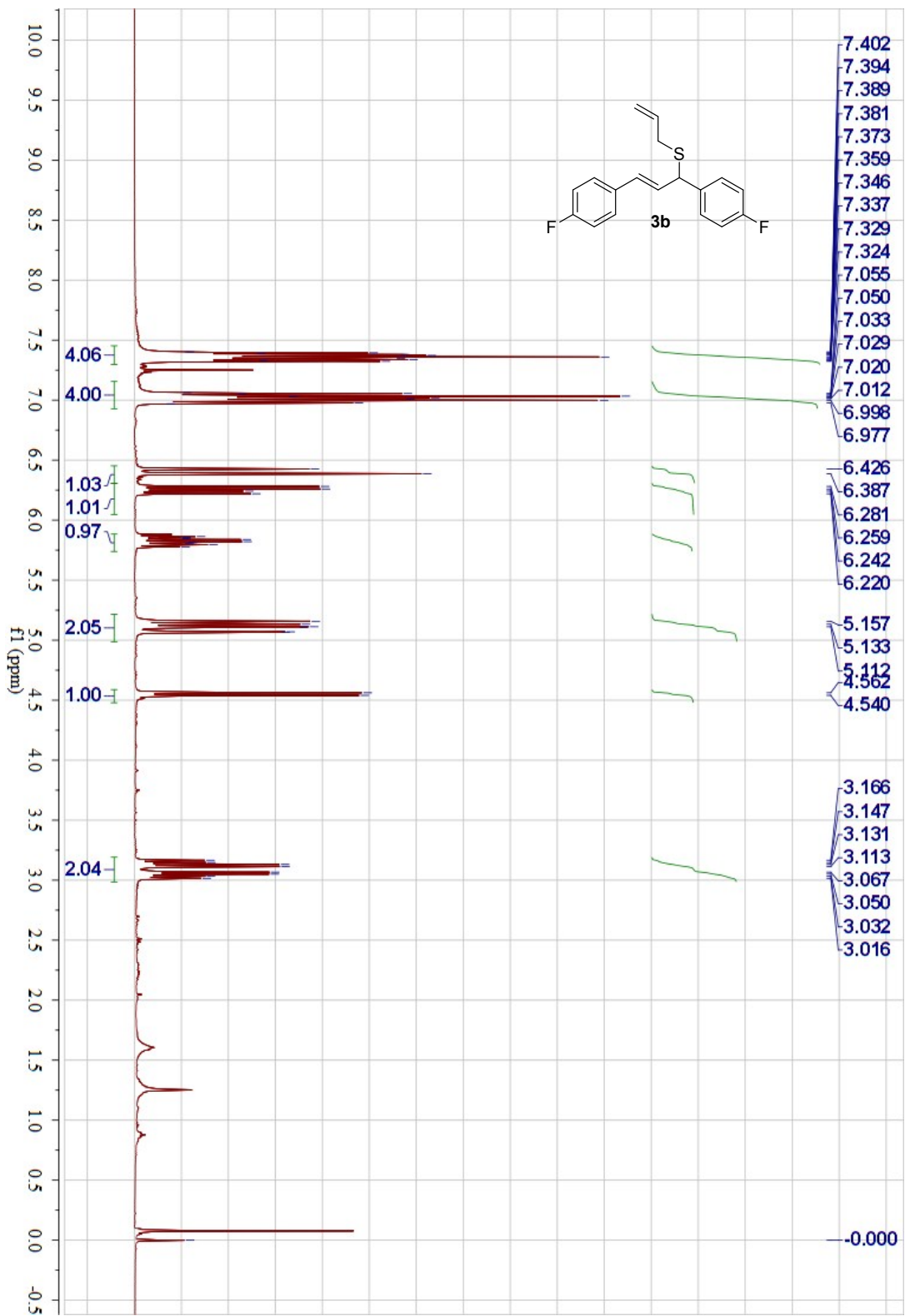
1. L. C. Liang, P. S. Chien, P. Y. Lee, J. M. Lin and Y. L. Huang. *Dalton Trans* **2008**, 3320.
2. a) A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim. *Synlett* **2001**, 9, 1375; b) R. Naasz, L. A. Arnold, A. J. Minnaard, B. L. Feringa. *Angew. Chem. Int. Ed.*

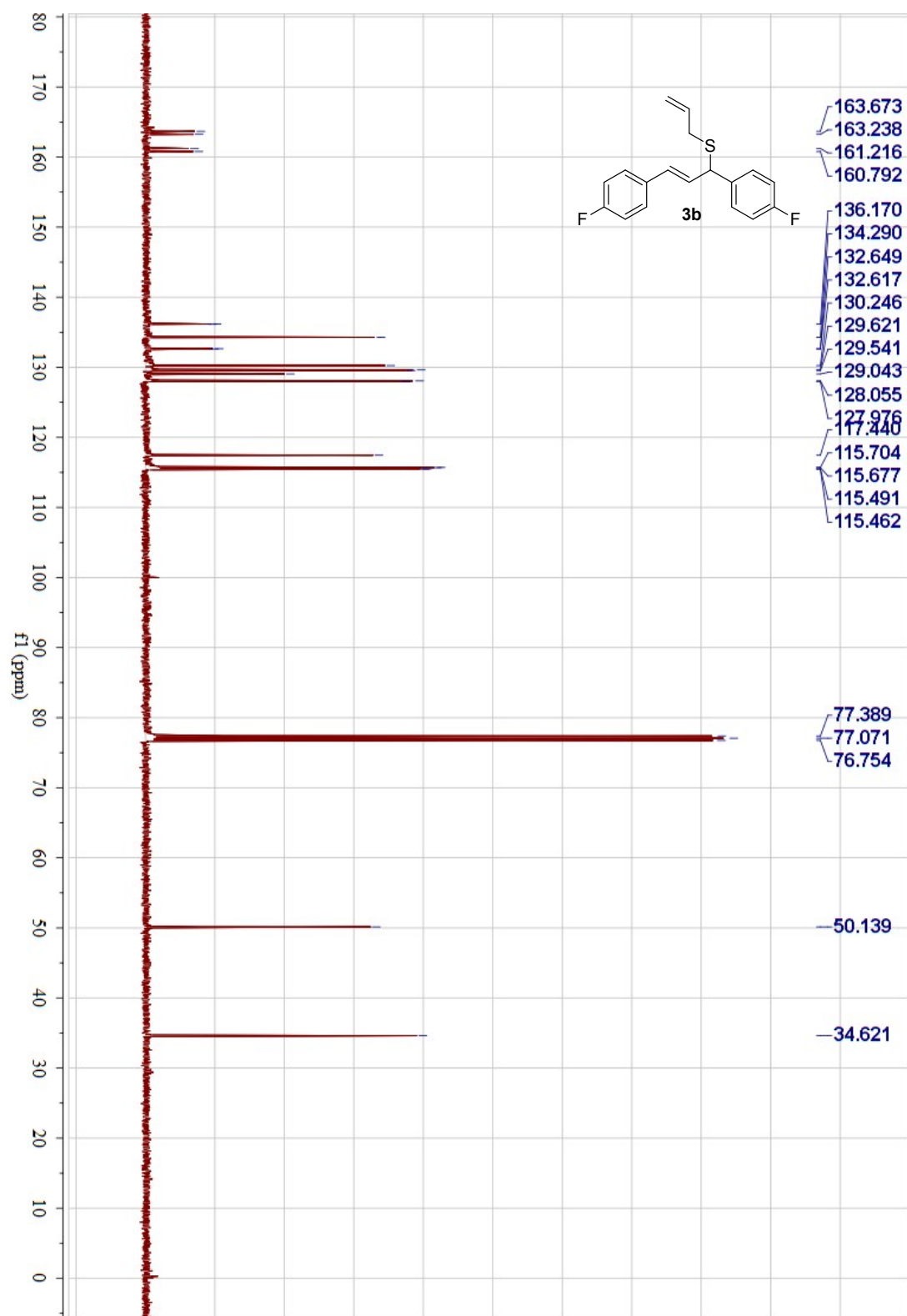
2001, 40, 927; c) D. Polet, A. Alexakis. *Synthesis* 2004, 15, 2586.

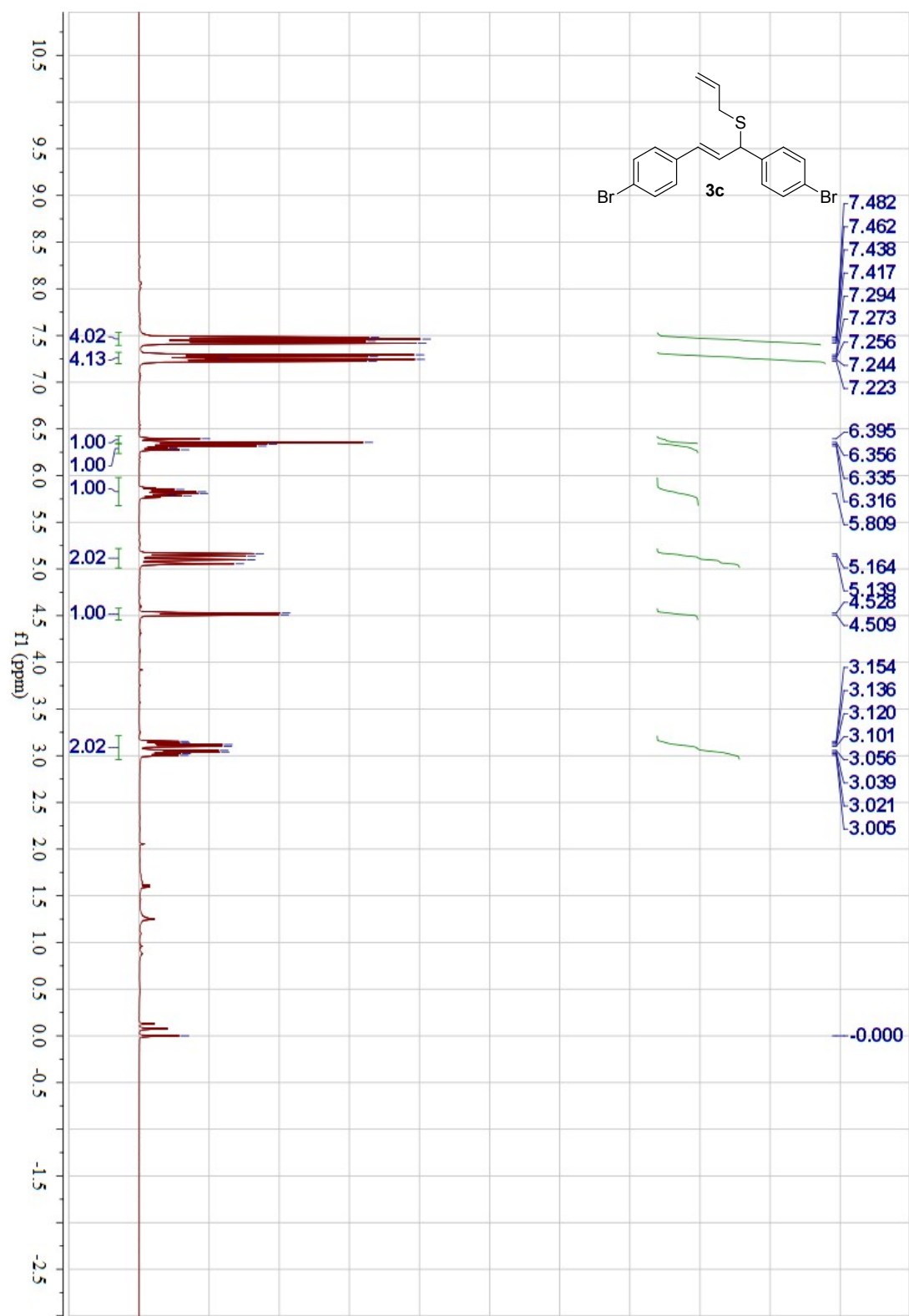
NMR Spectra of the compounds 3

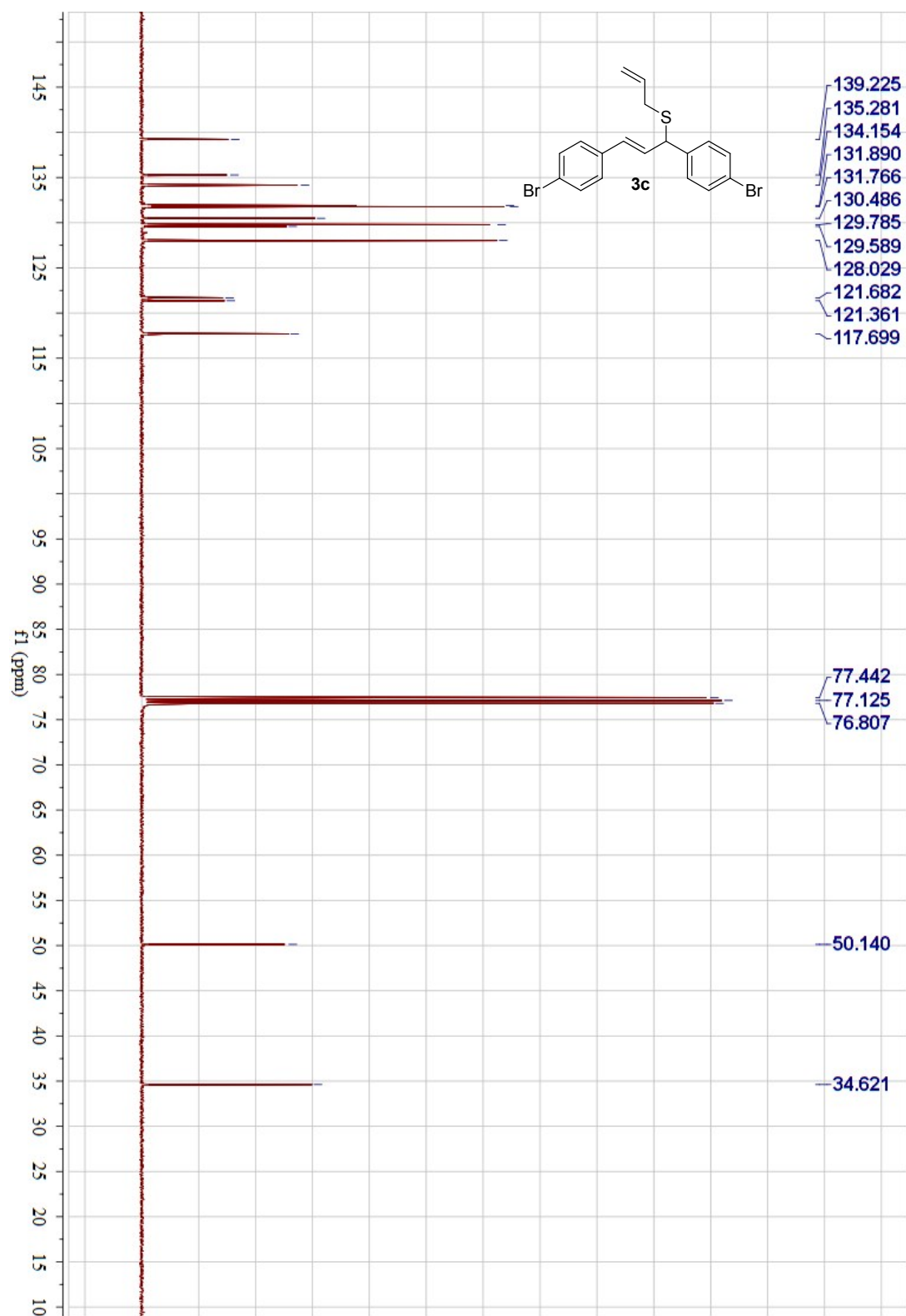


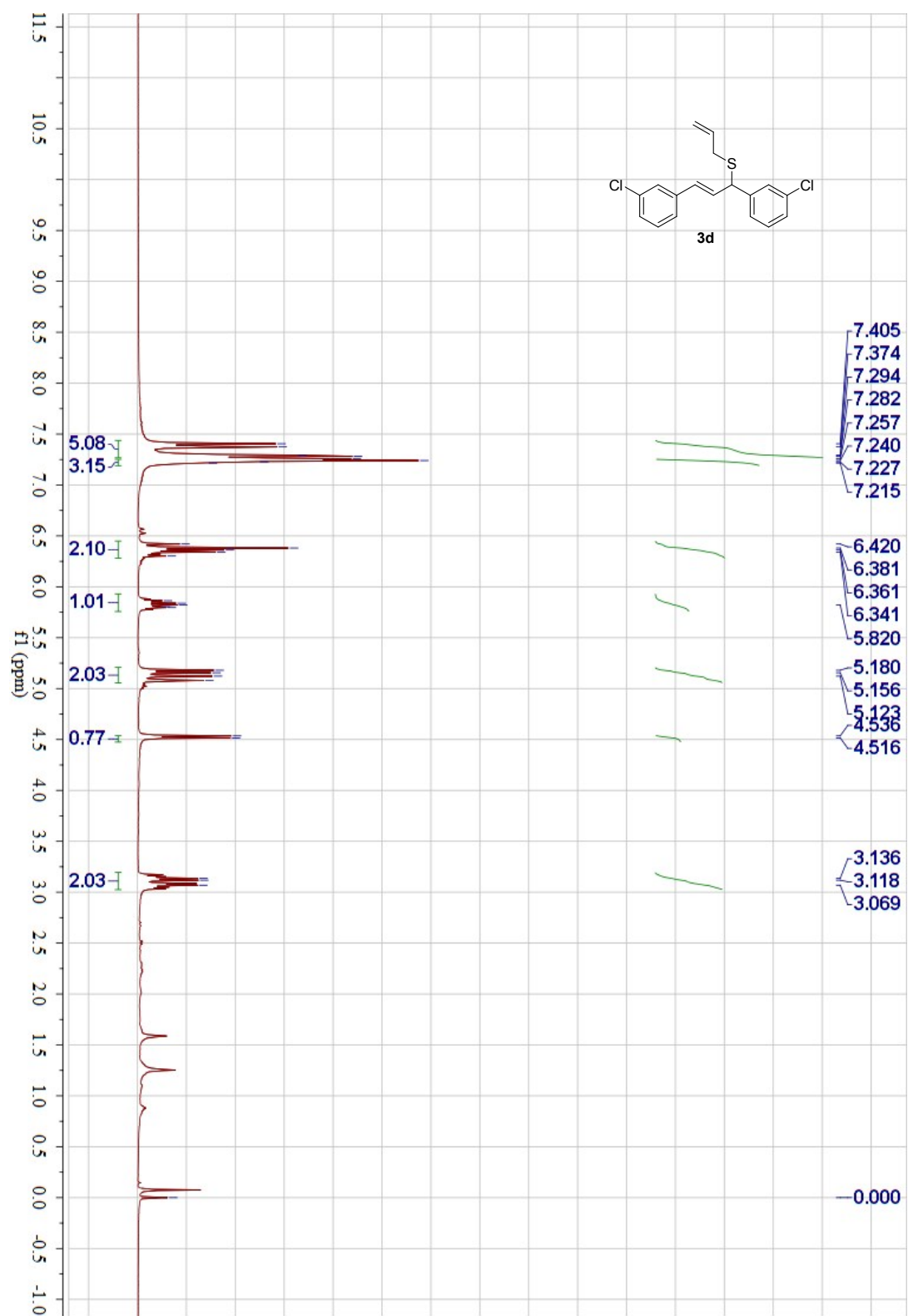


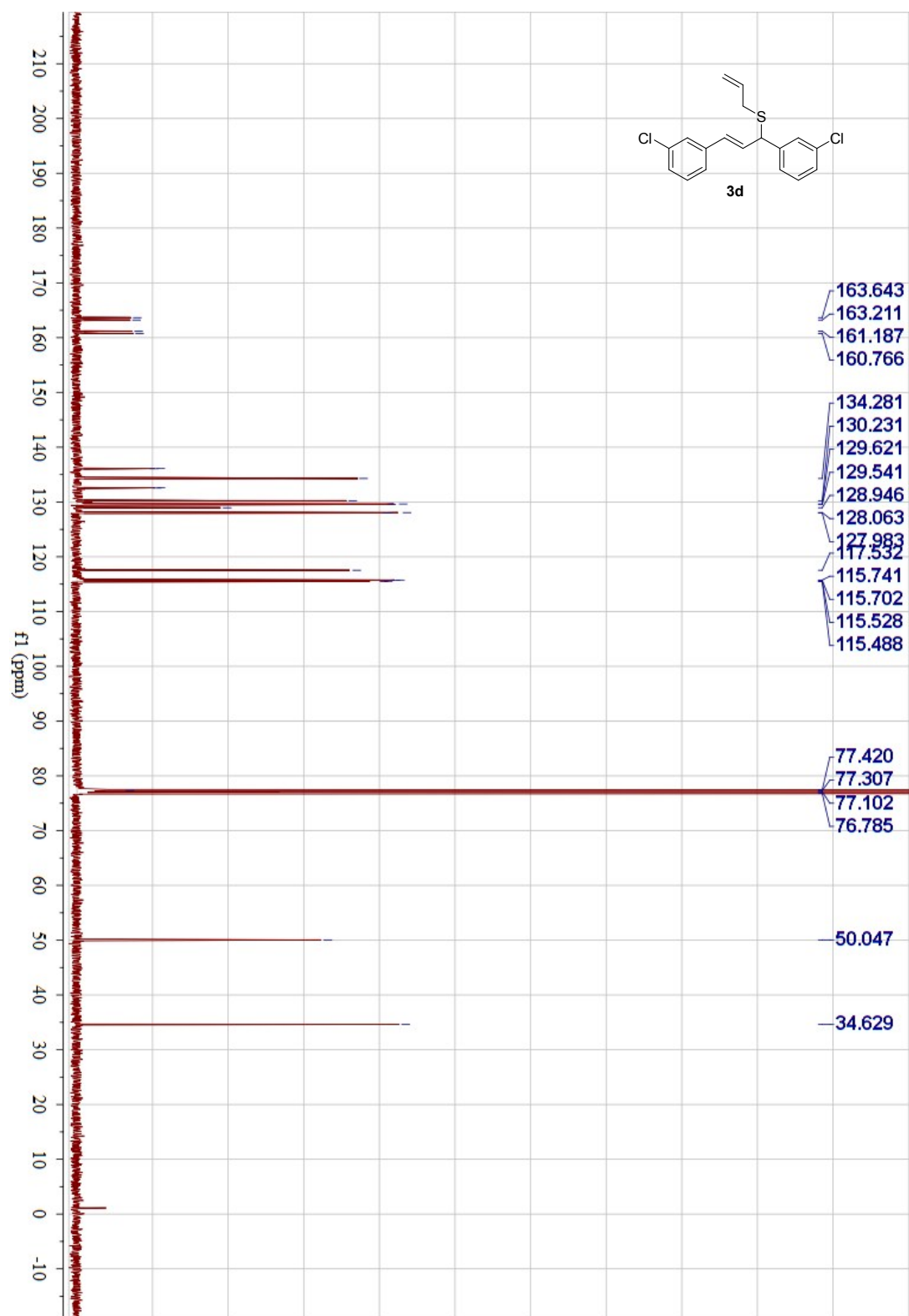


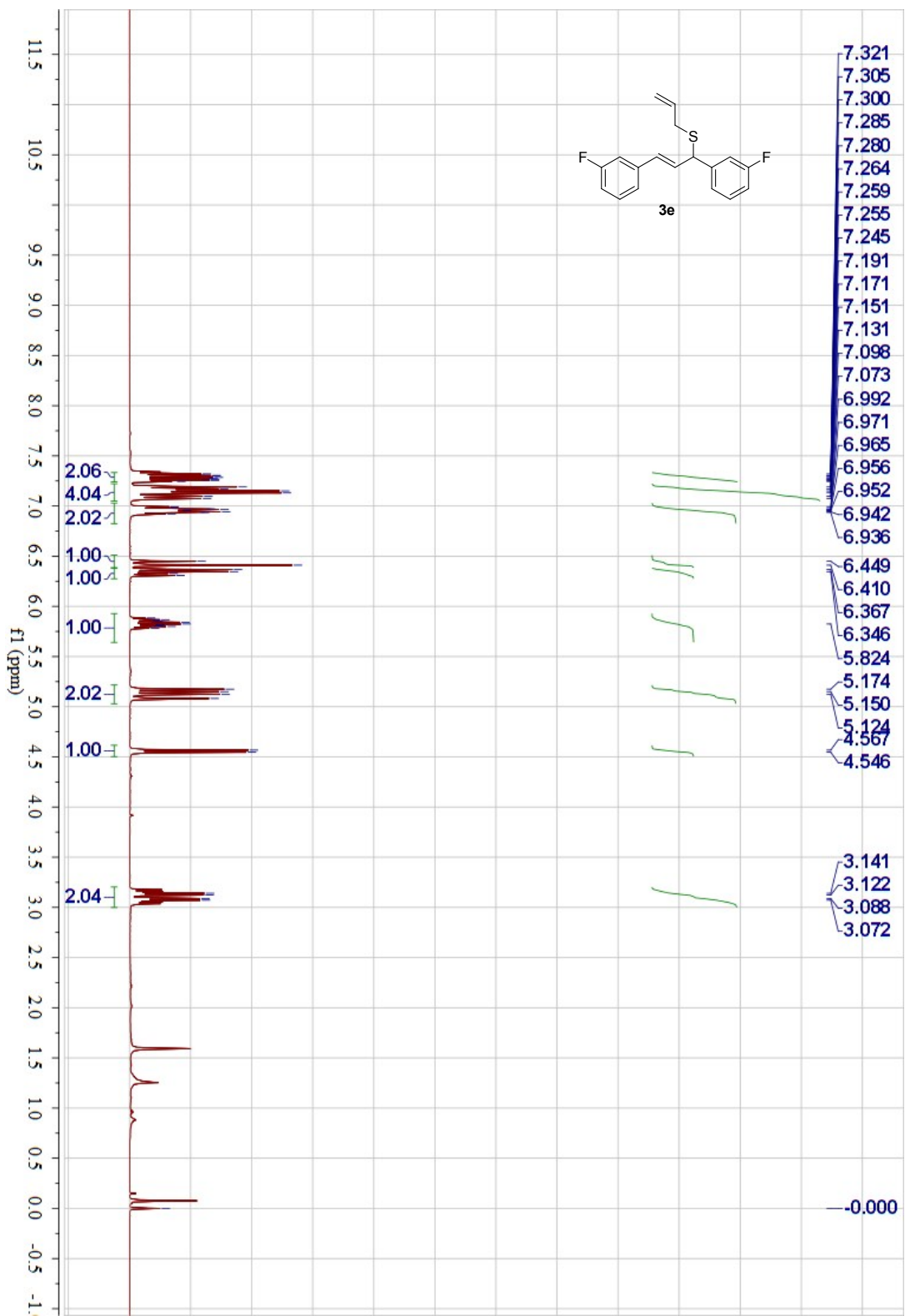


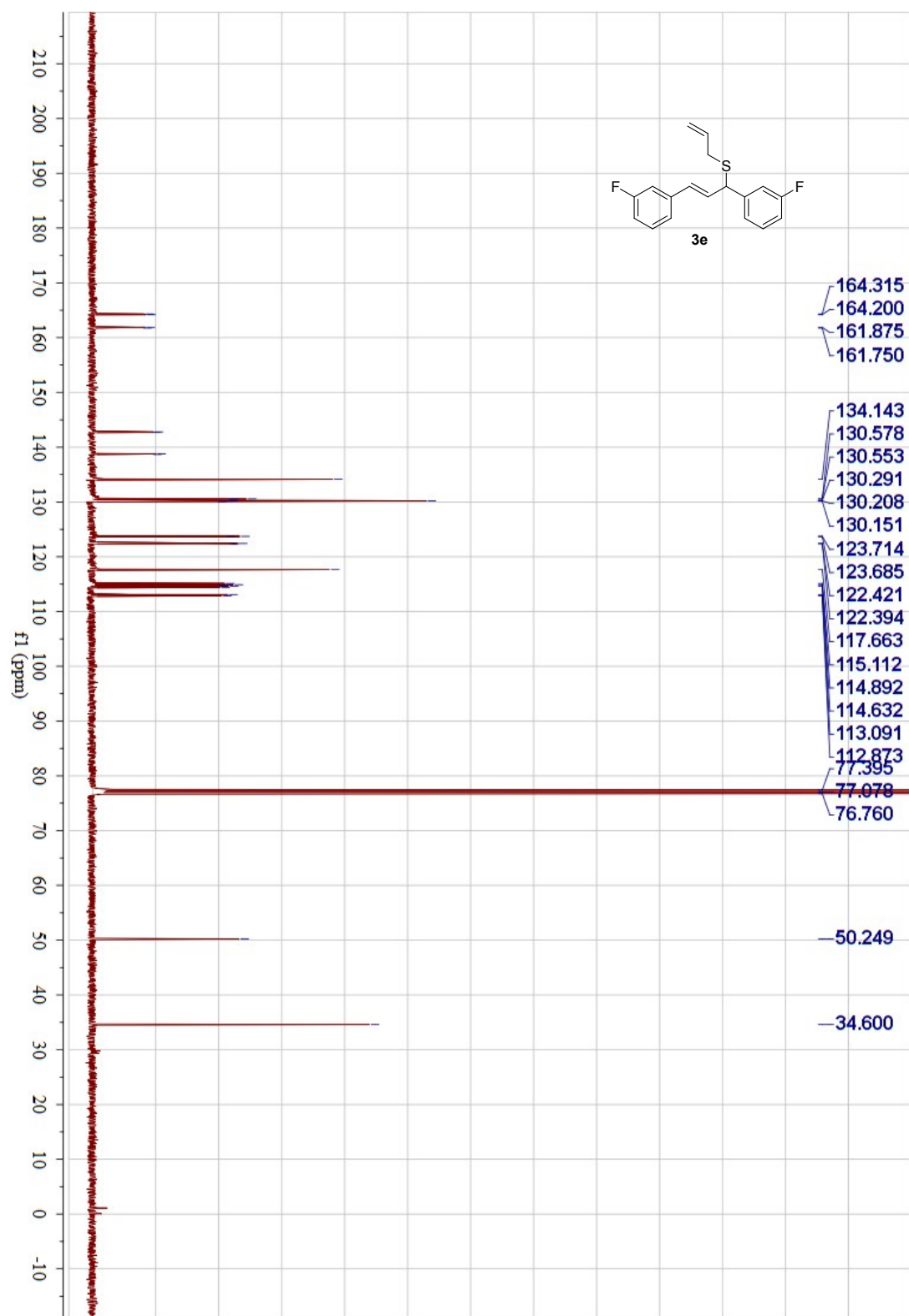


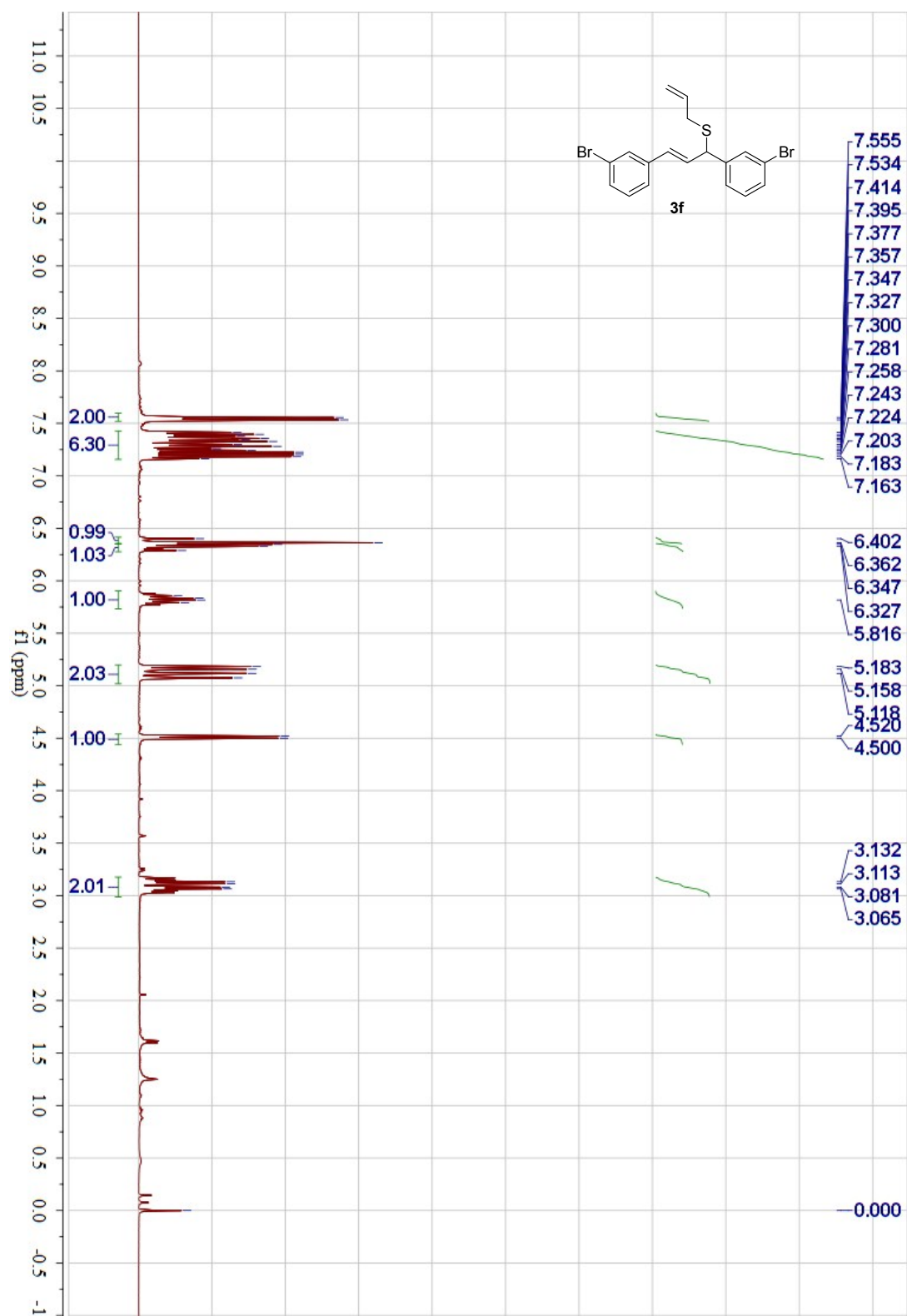


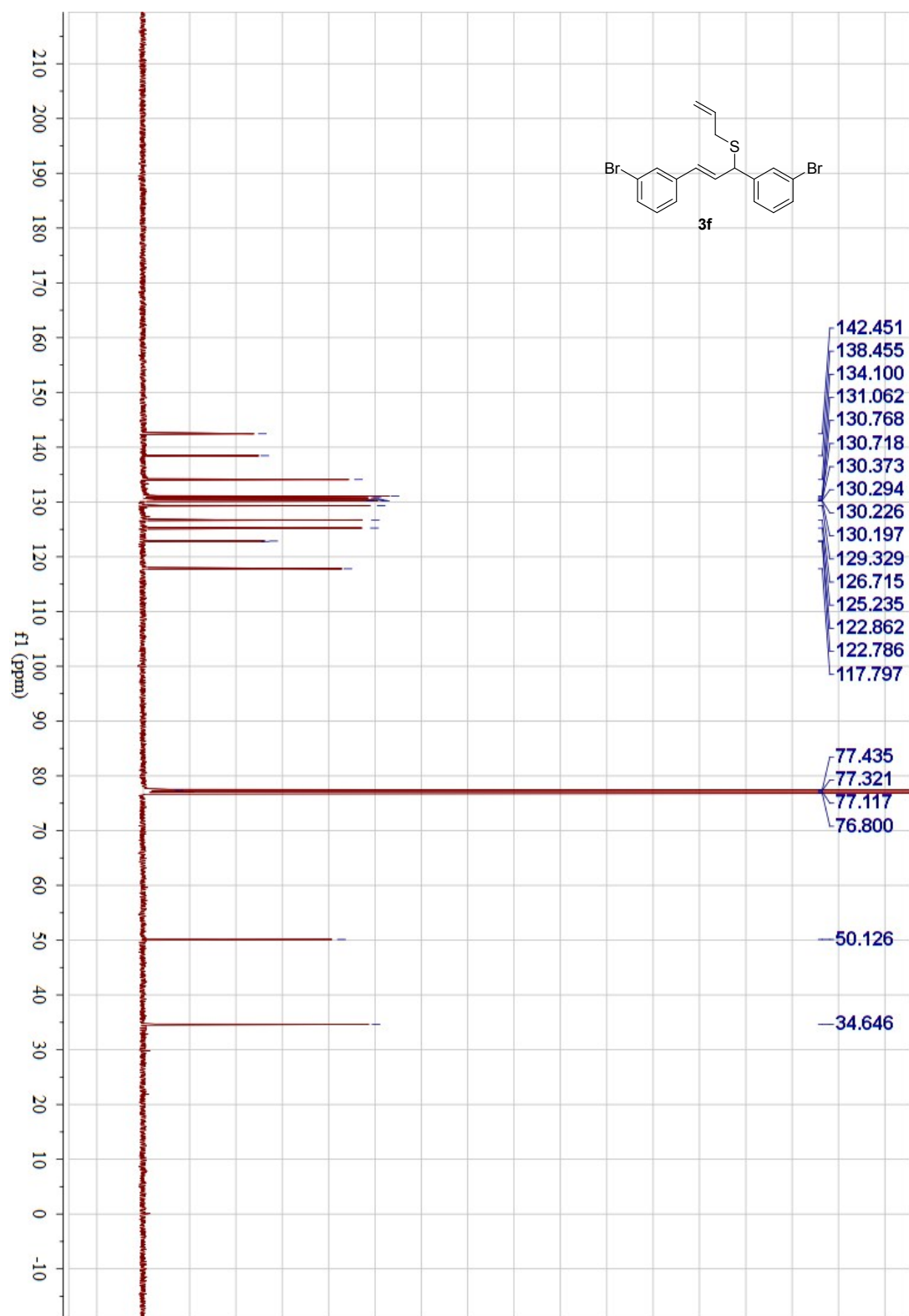


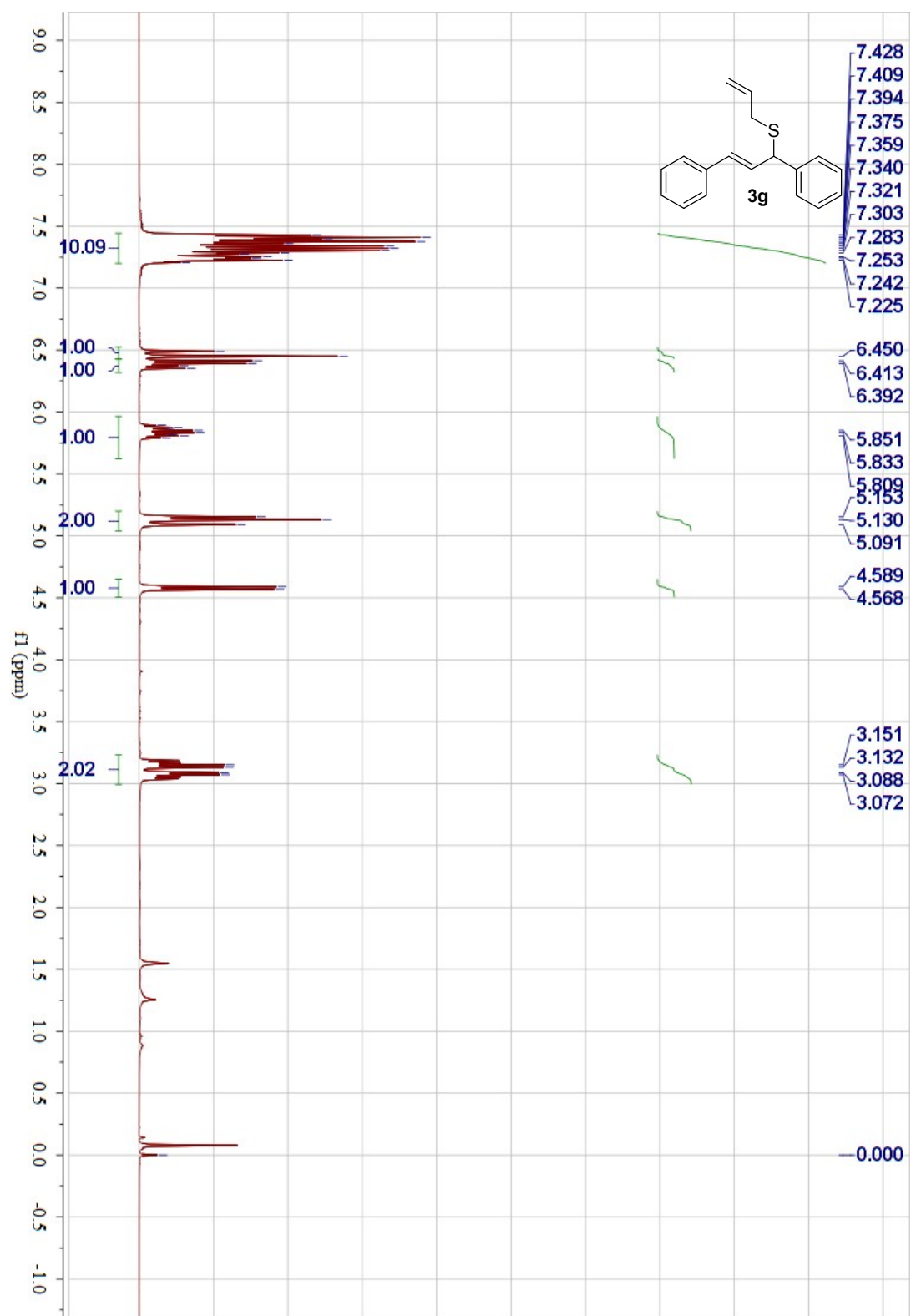


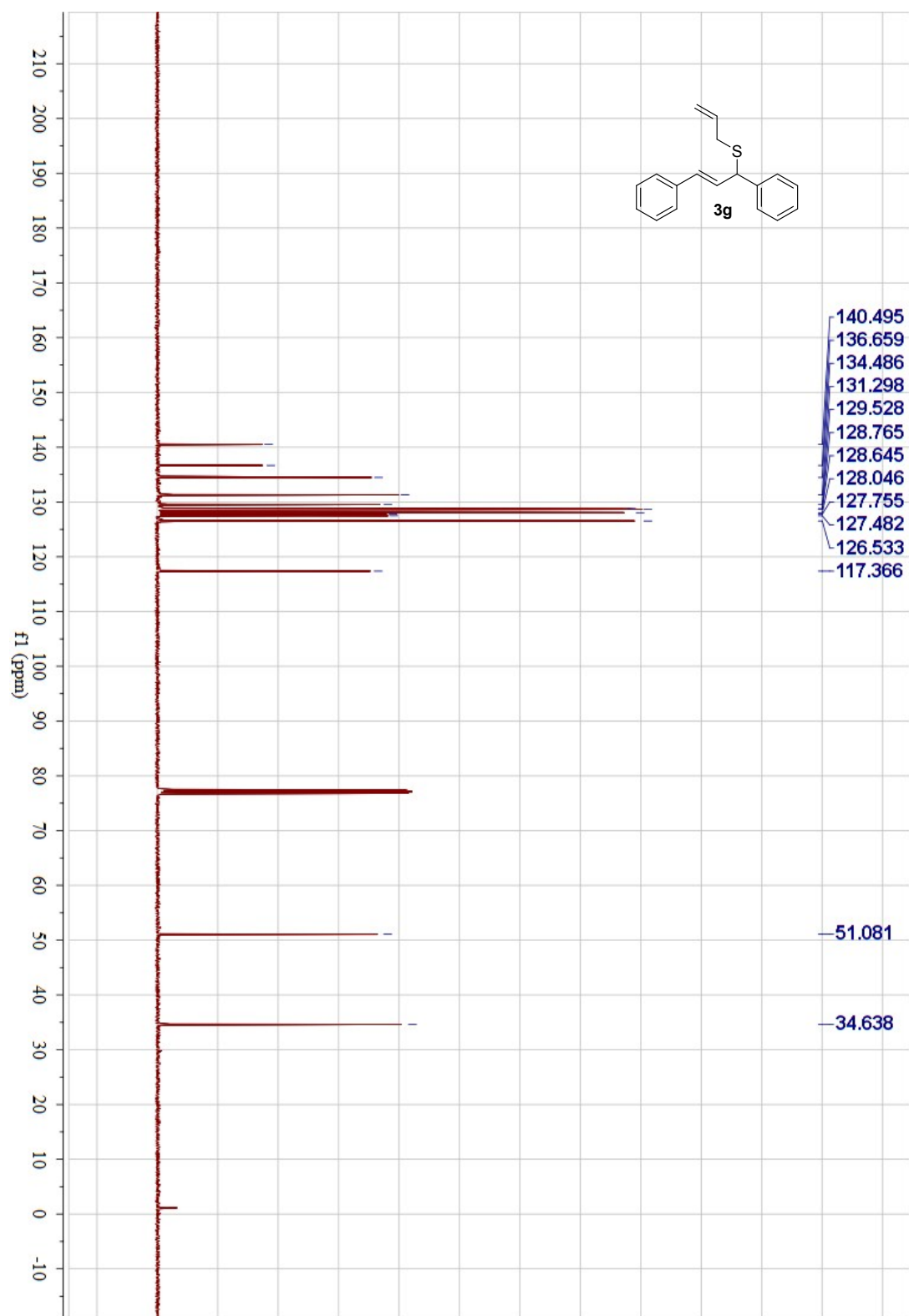


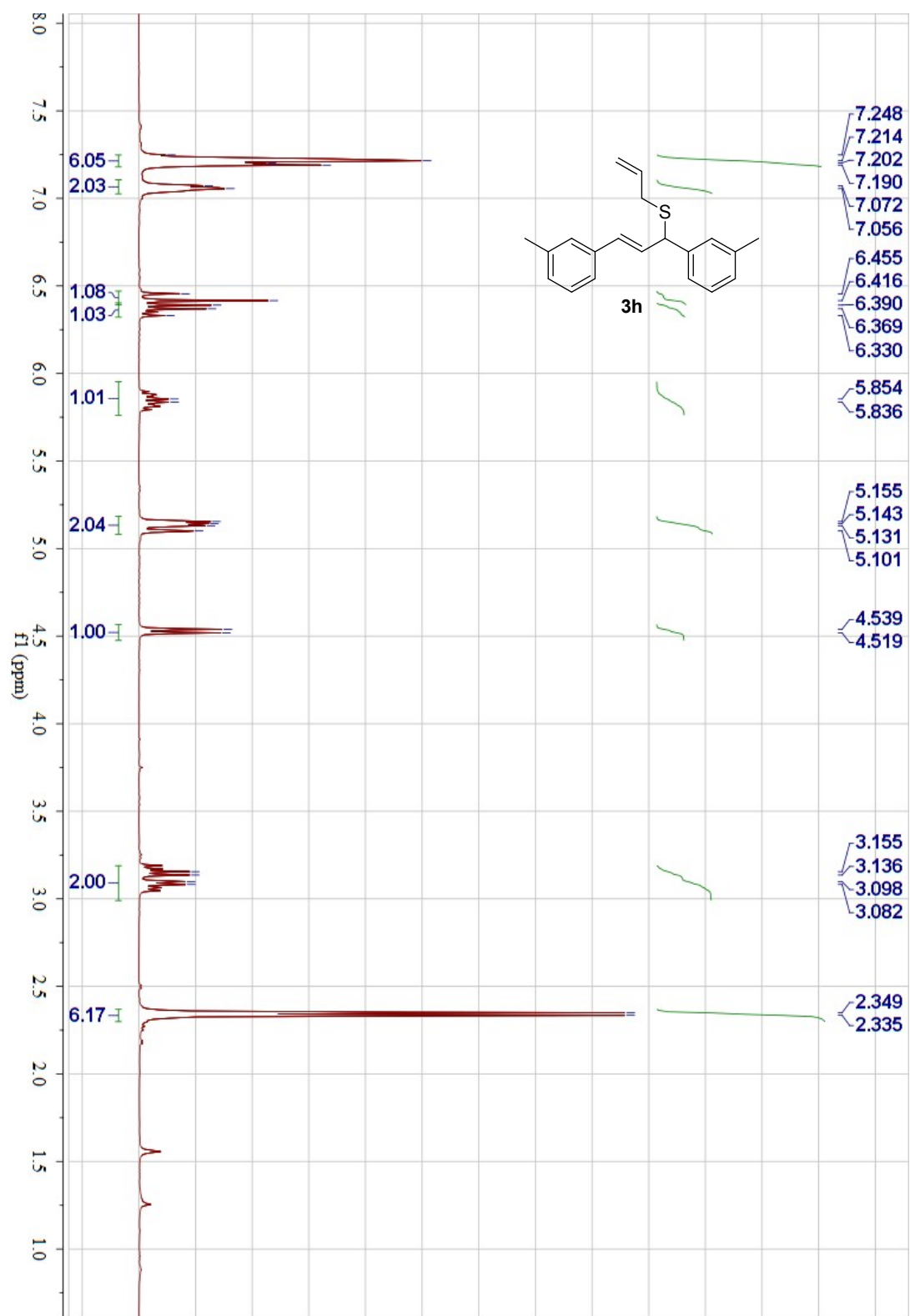


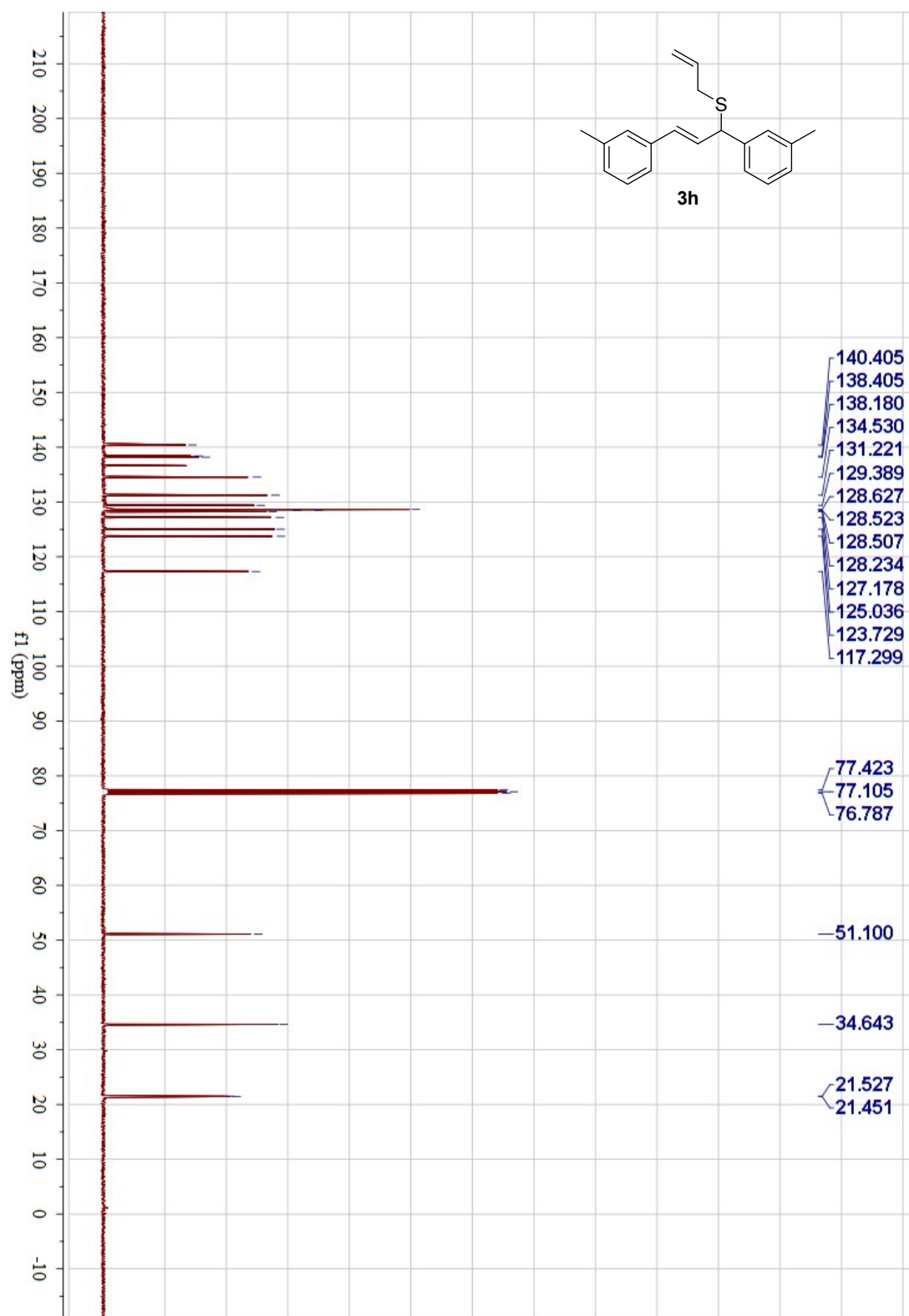


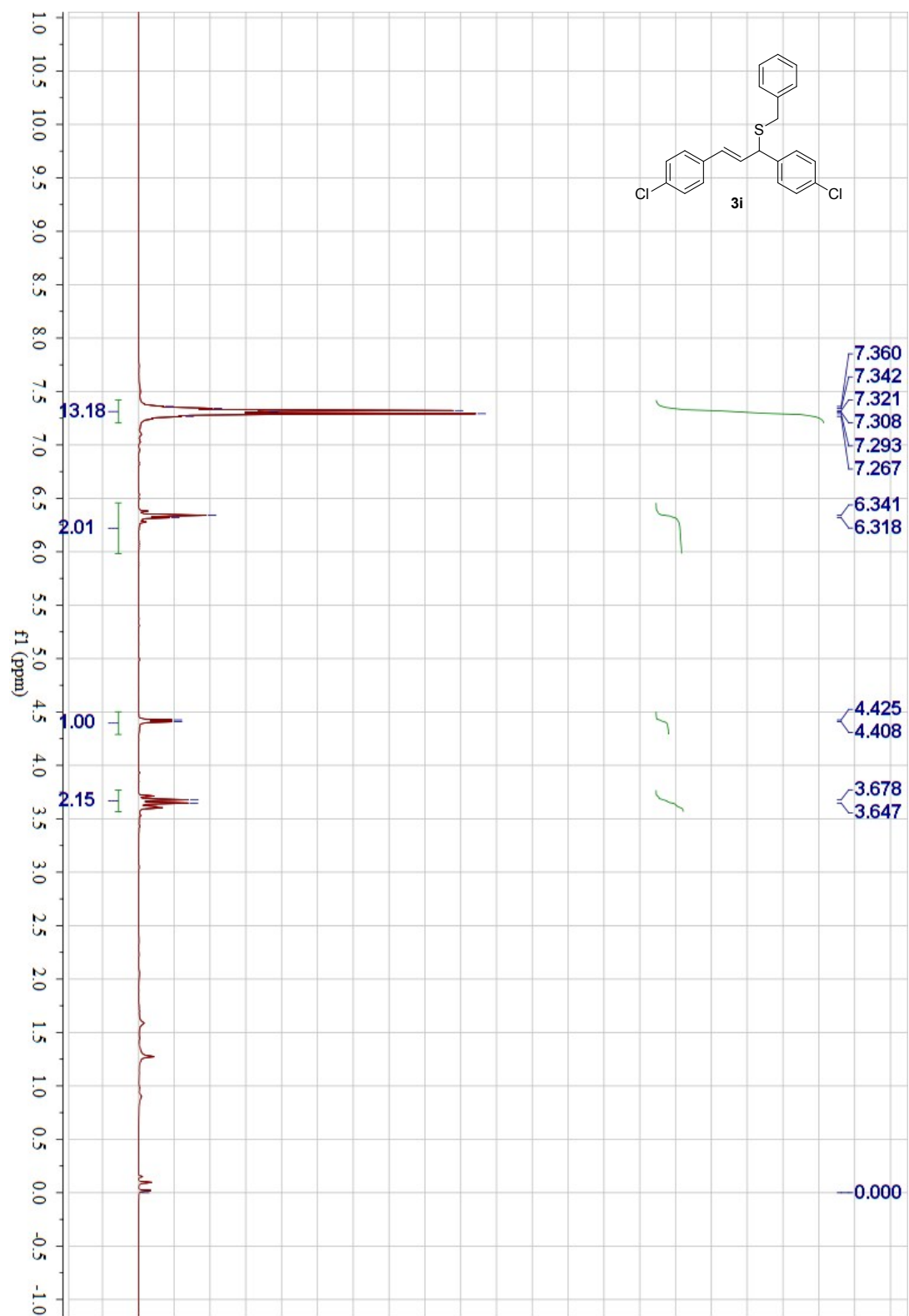


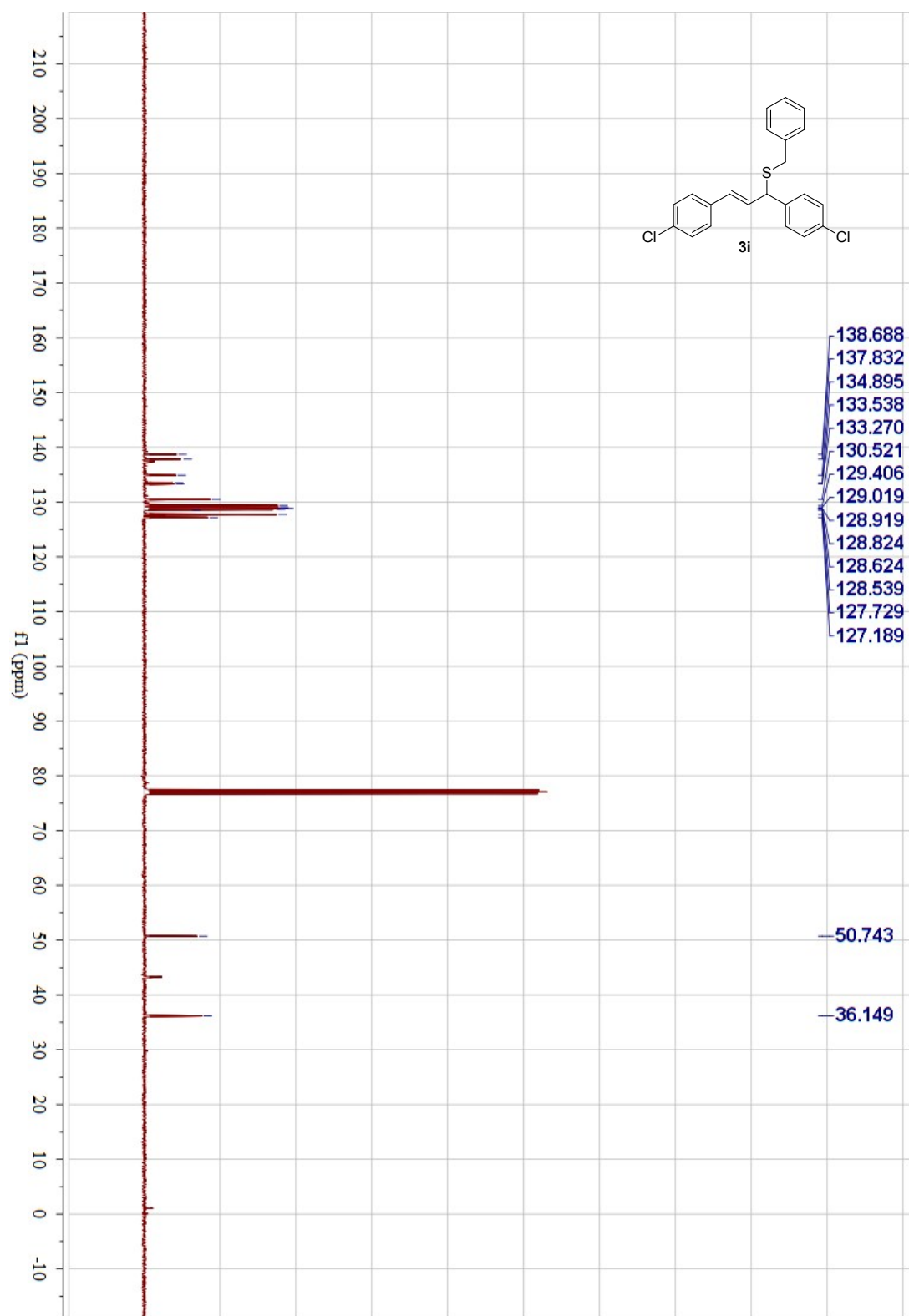


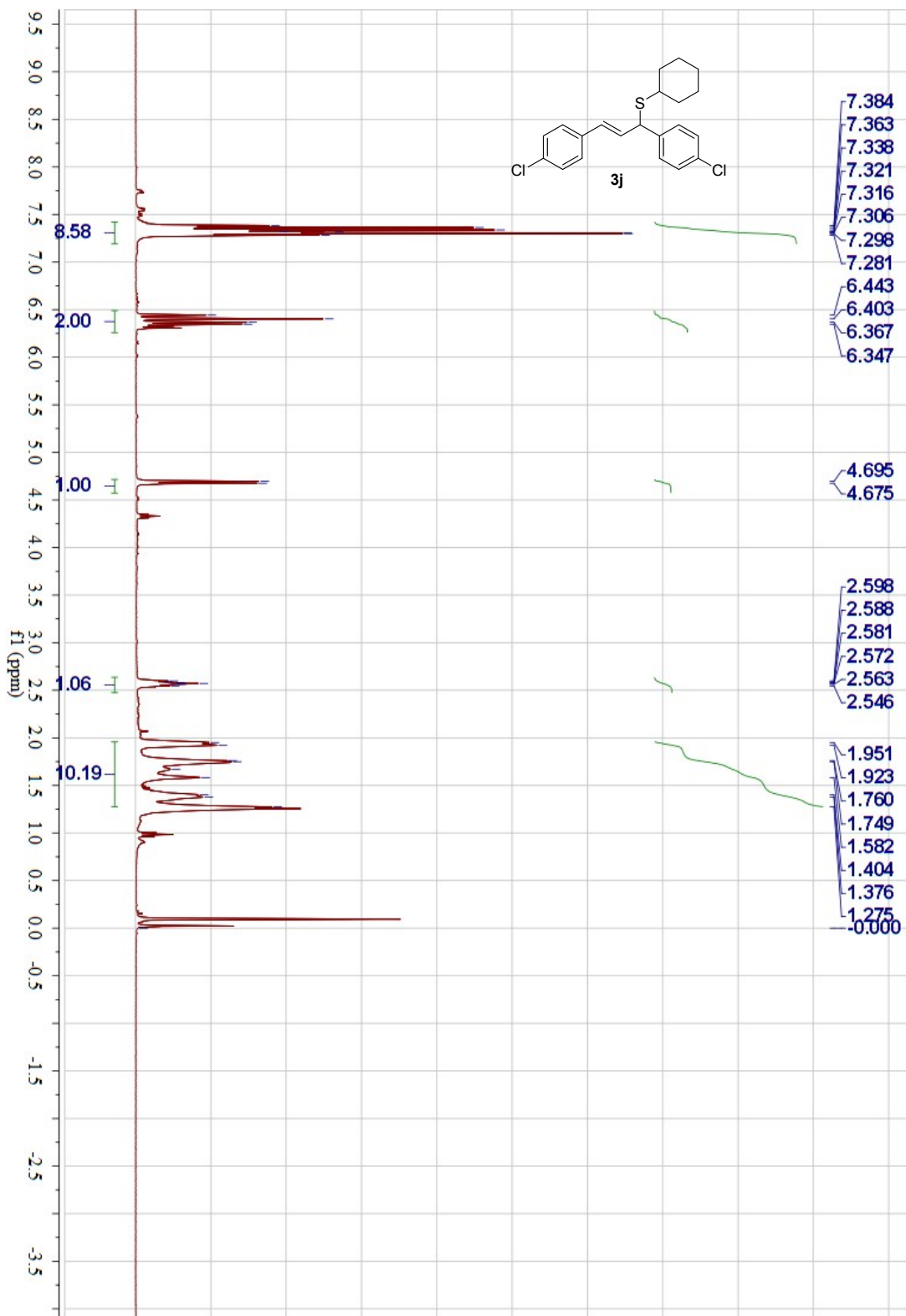


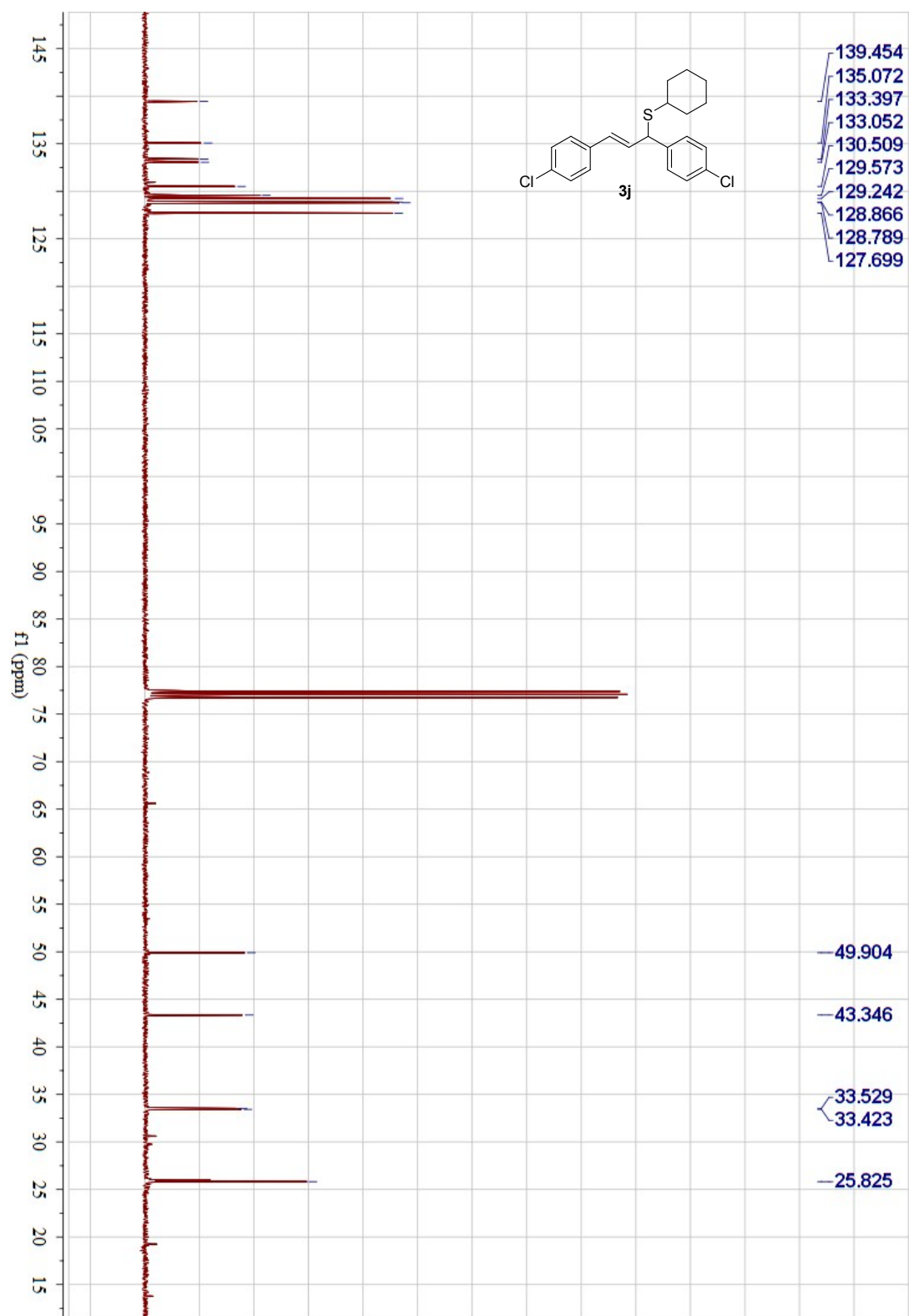


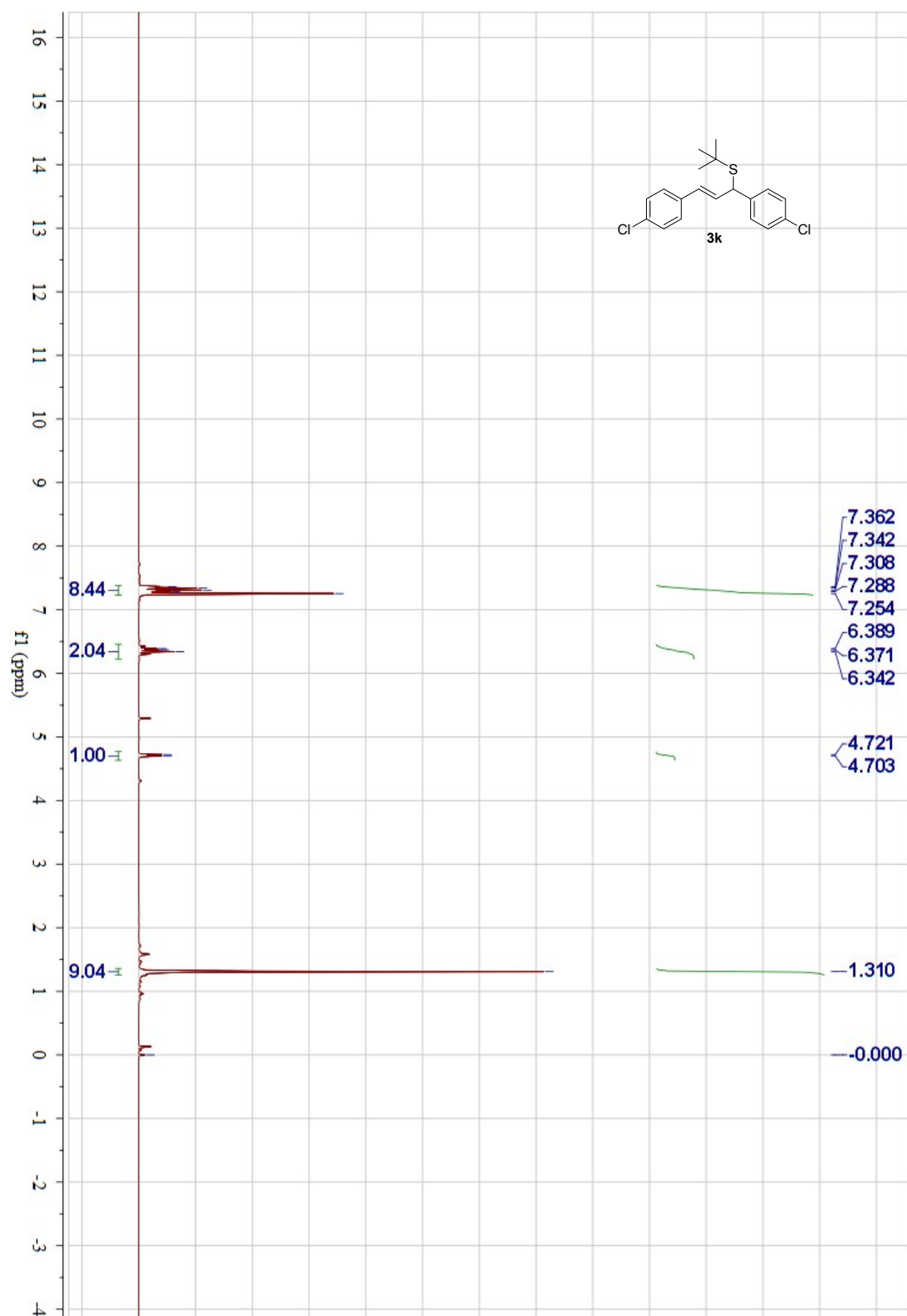


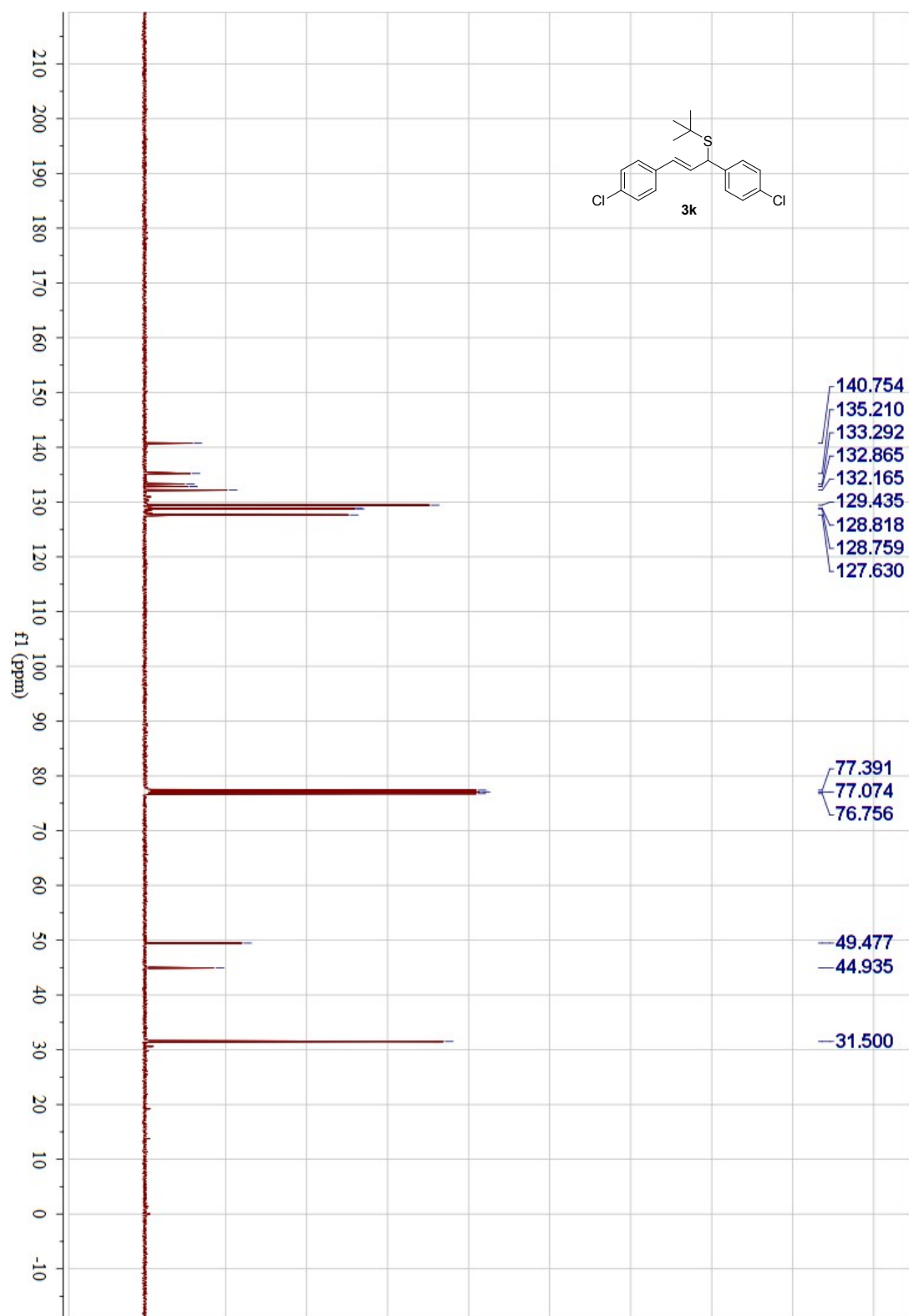


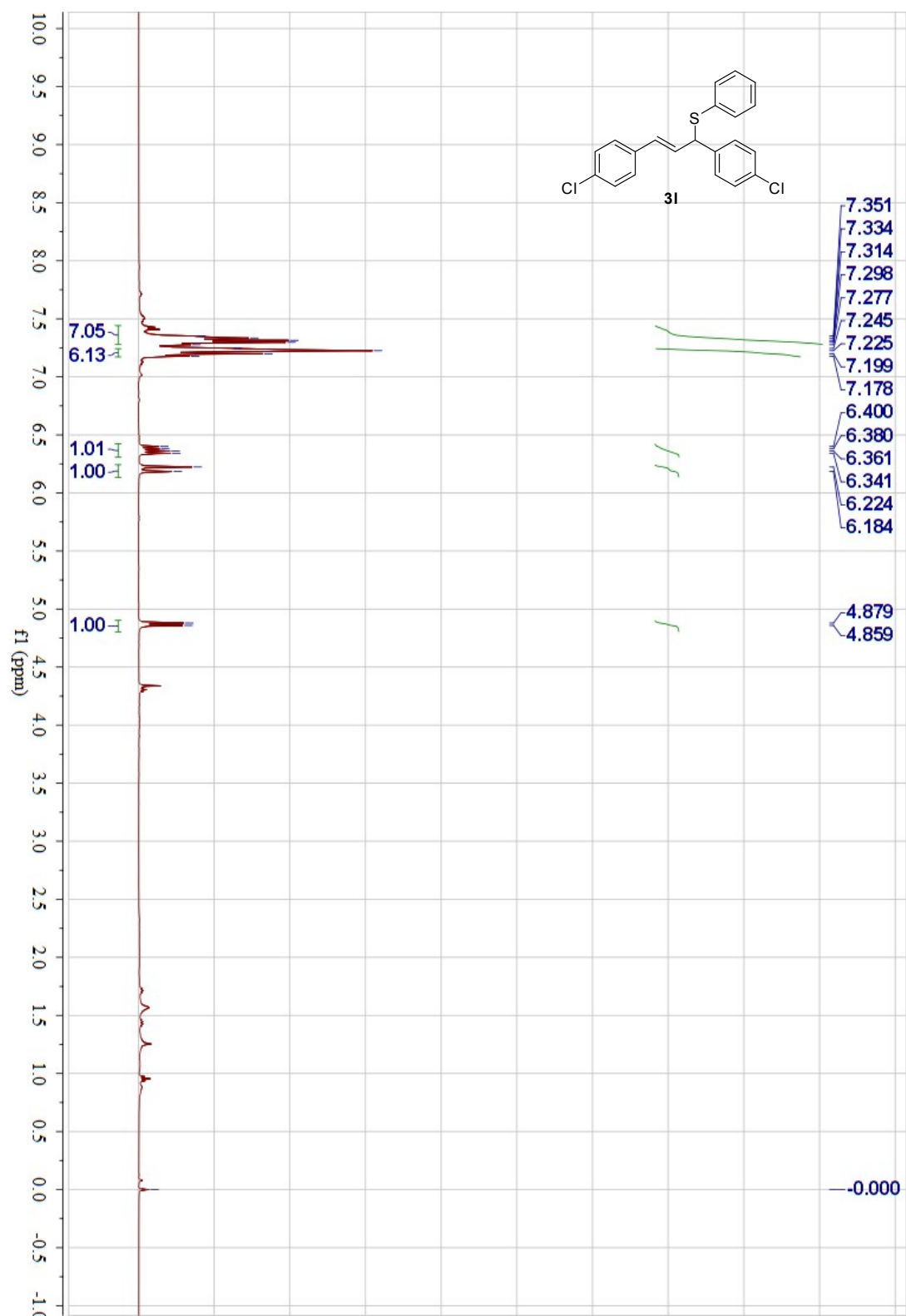


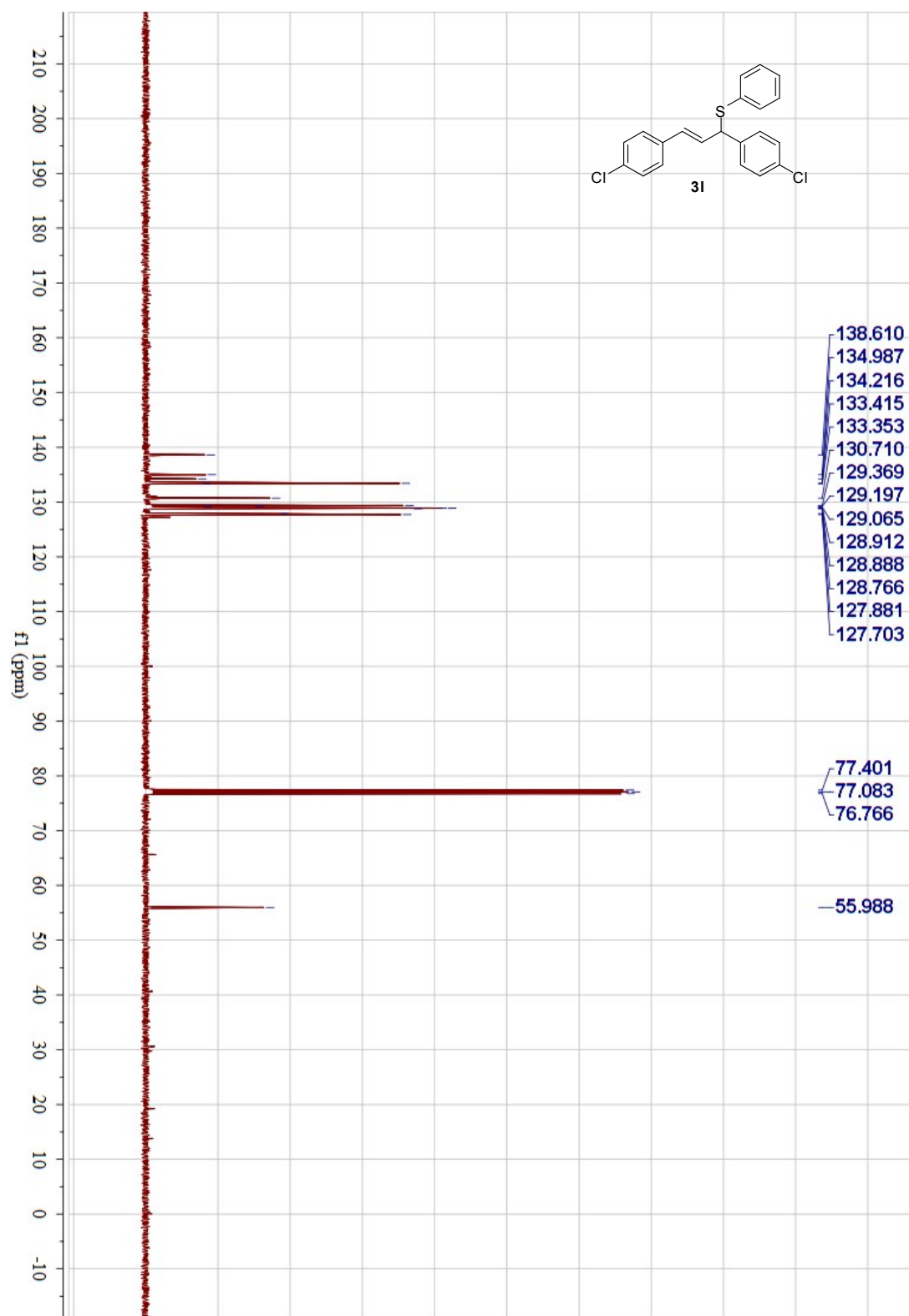


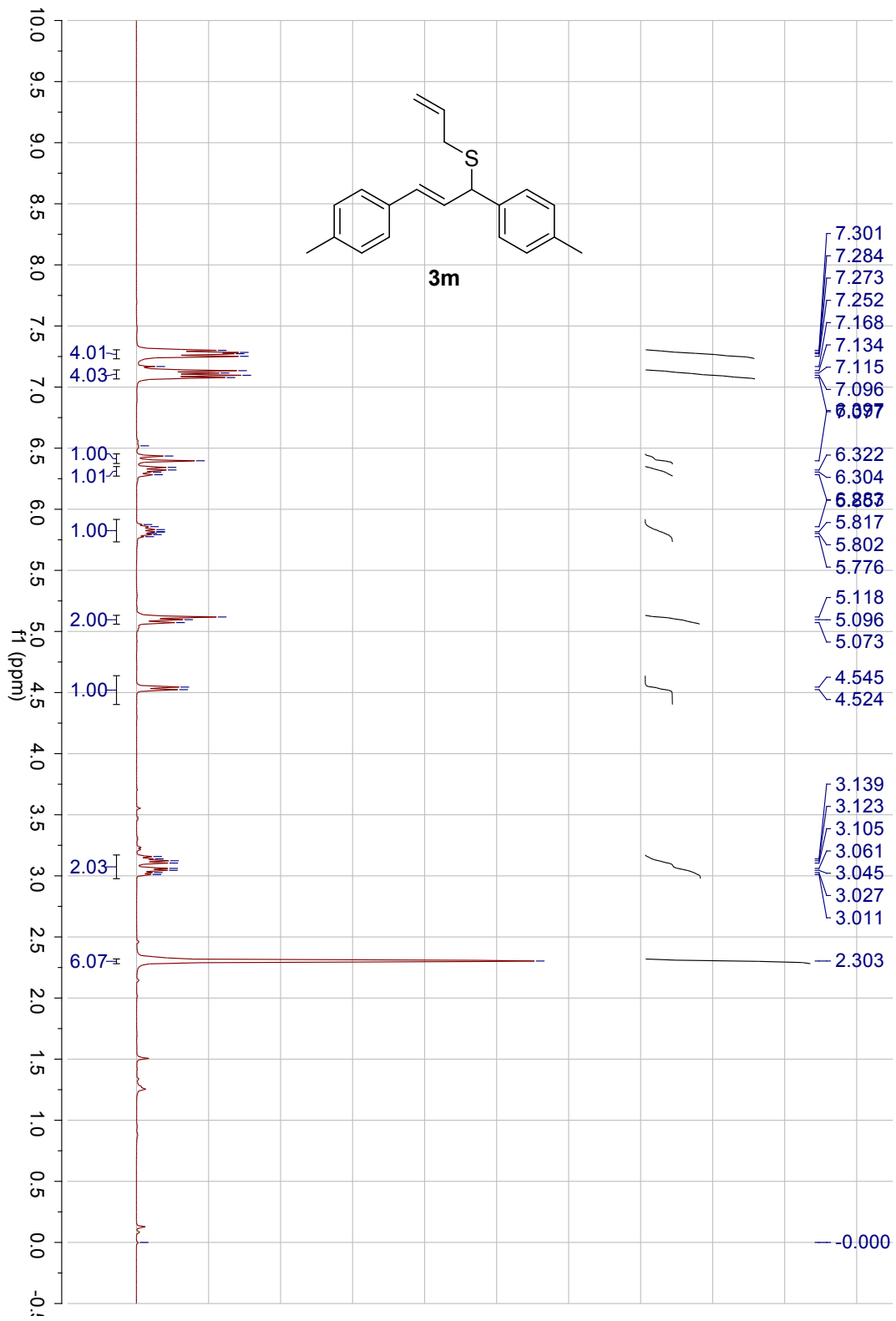


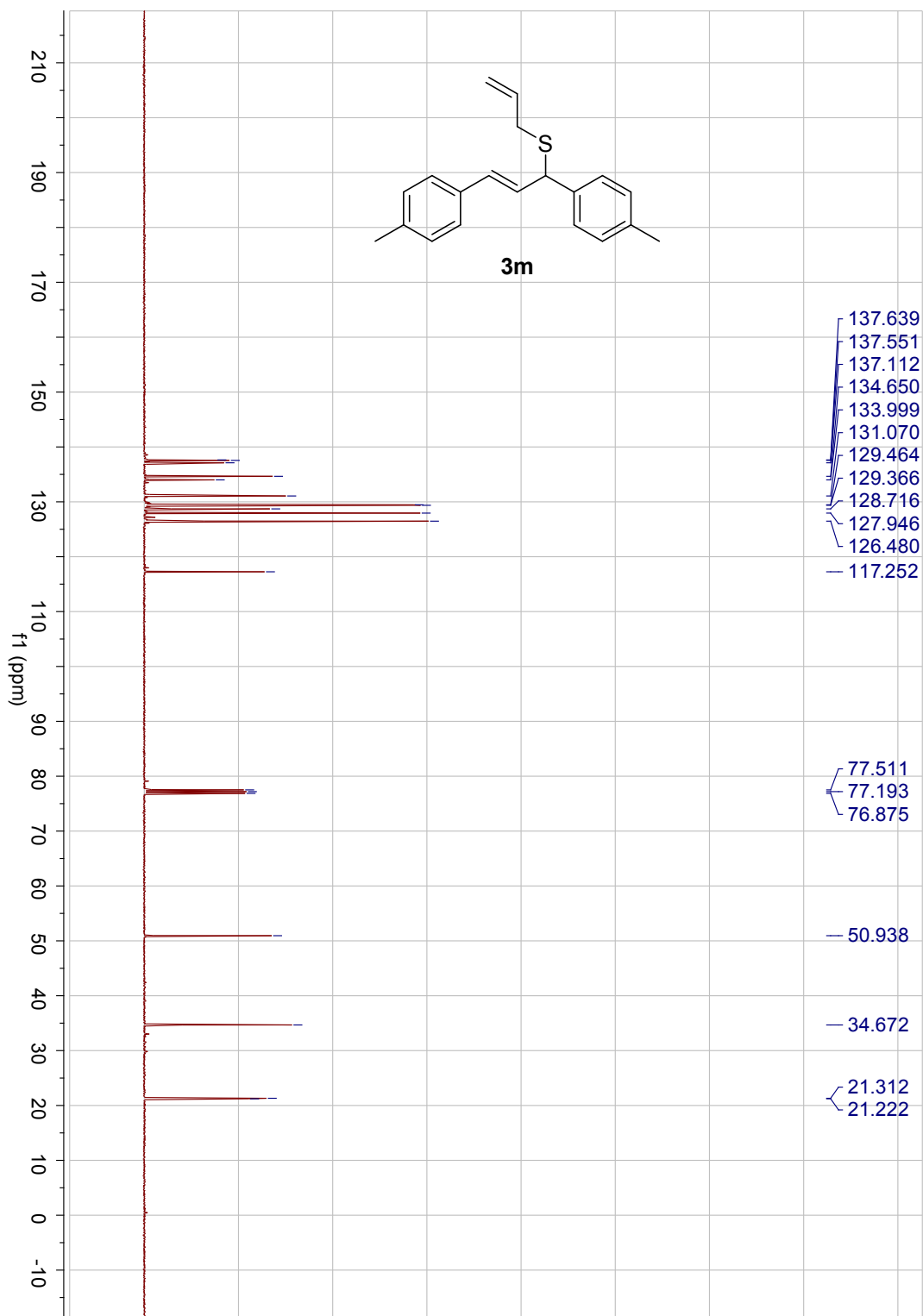






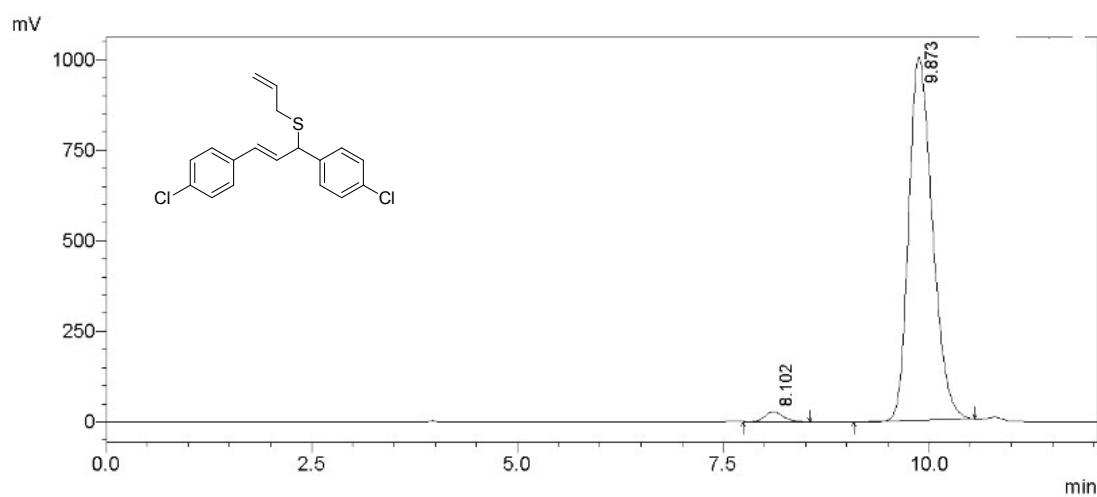






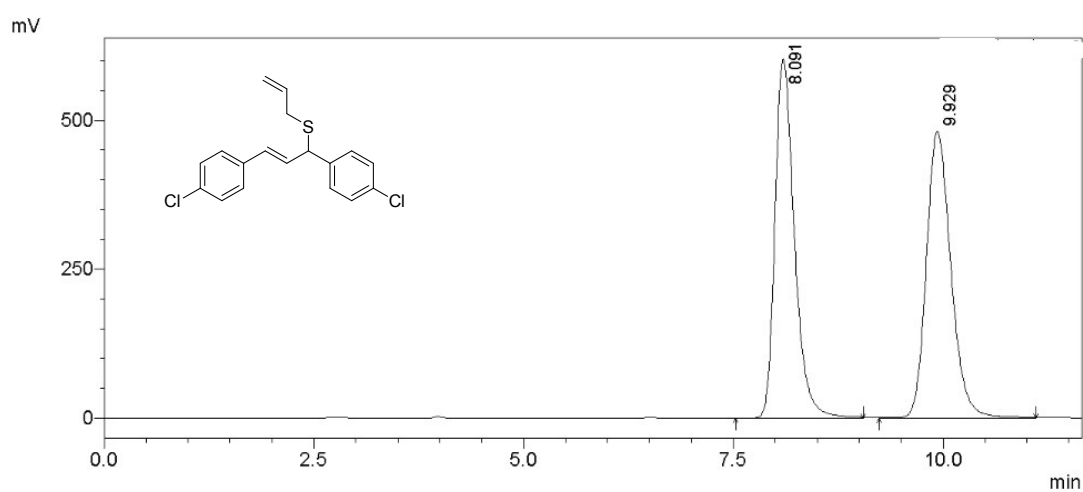
HPLC Chromatograms of the Chiral Compounds 3:

Chiral-3a



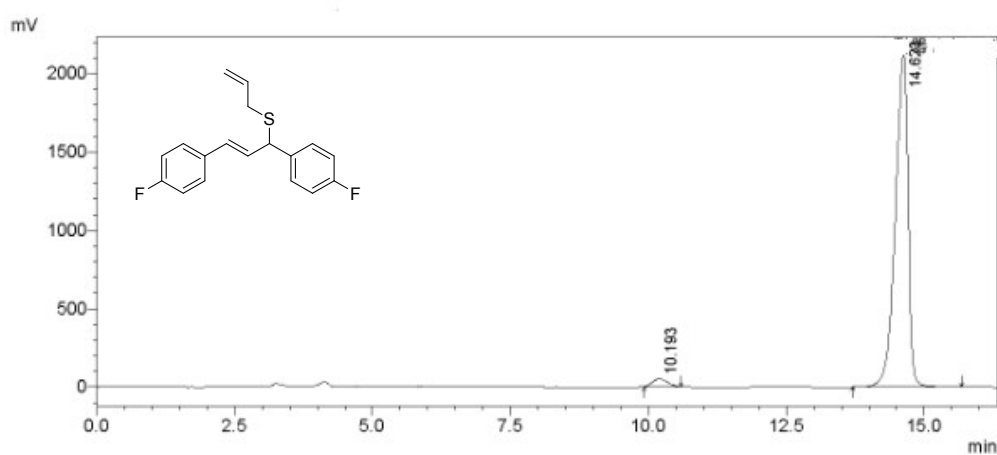
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	8.099	490030	31942	2.078
2	9.871	23092573	1141784	97.922
Total		23582603	1173726	100.000

Rac-3a



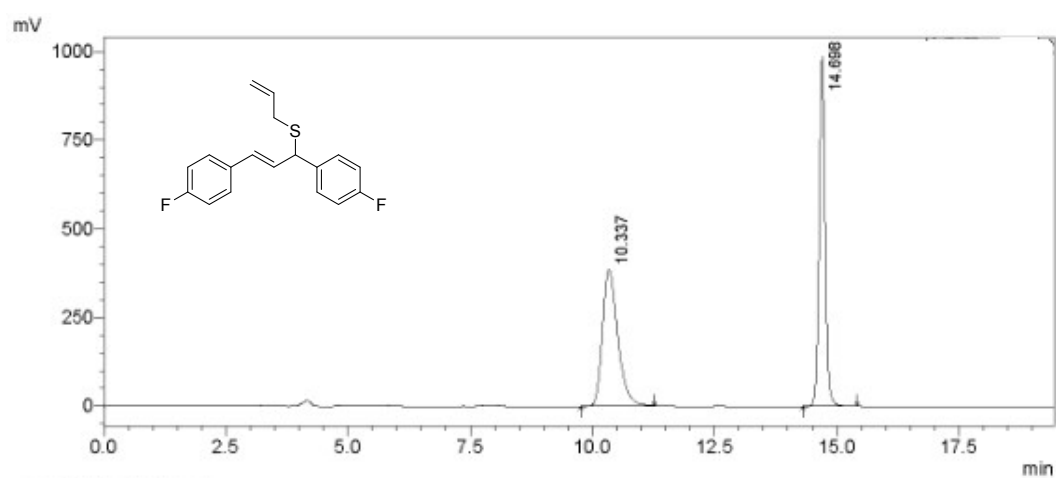
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	8.090	10956316	687914	49.683
2	9.927	11096313	548026	50.317
Total		22052630	1235940	100.000

Chiral-3b



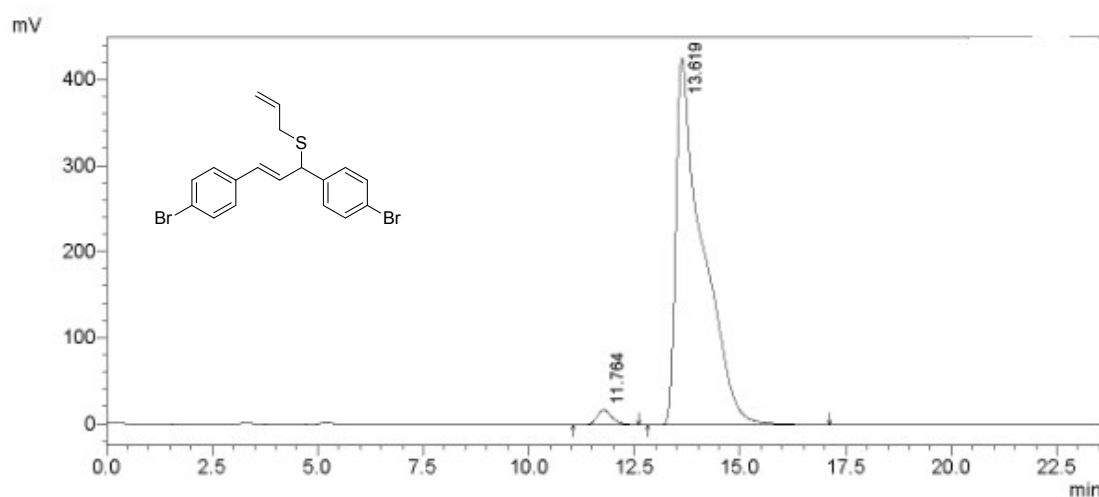
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	10.193	990948	51704	2.816
2	14.623	34203130	2115594	97.184
Total		35194078	2167298	100.000

Rac-3b



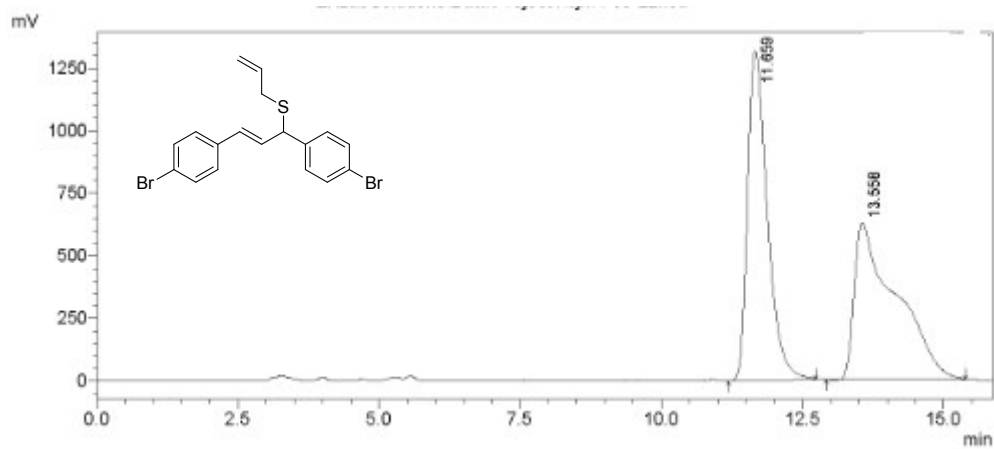
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	10.336	9005813	405227	50.713
2	14.696	8752411	1007688	49.287
Total		17758223	1412915	100.000

Chiral-3c



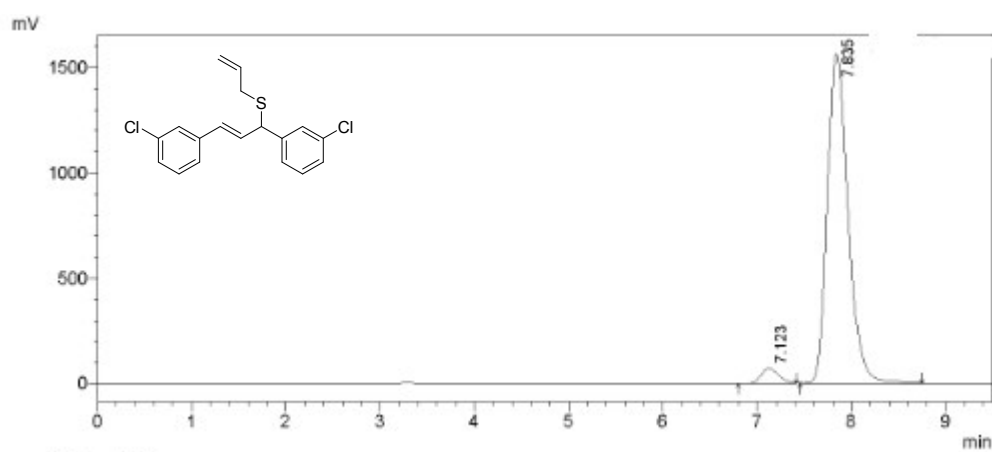
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	11.764	516469	21179	2.217
2	13.619	22776307	519244	97.783
Total		23292777	540423	100.000

Rac-3c



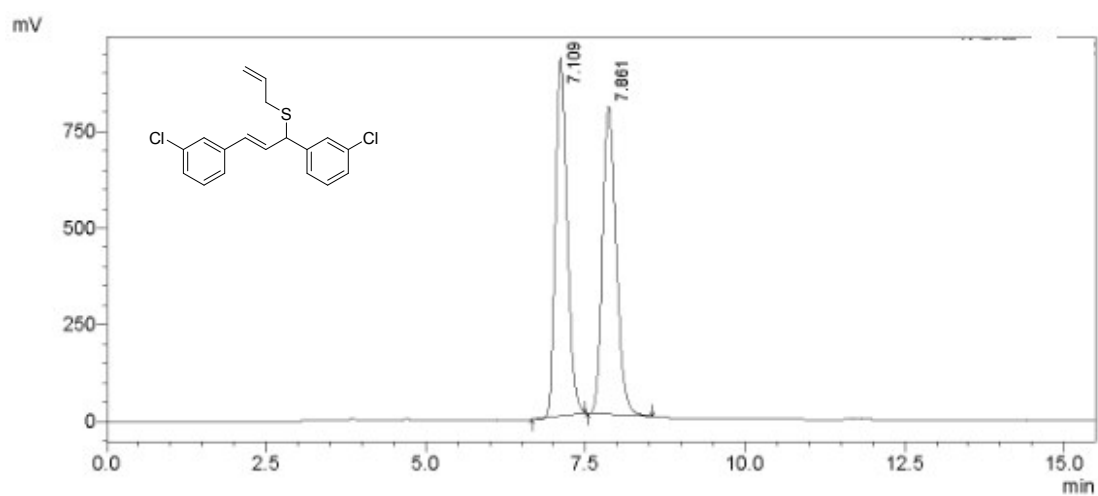
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	11.659	32027070	1314412	50.127
2	13.558	31864259	625720	49.873
Total		63891329	1940132	100.000

Chiral-3d



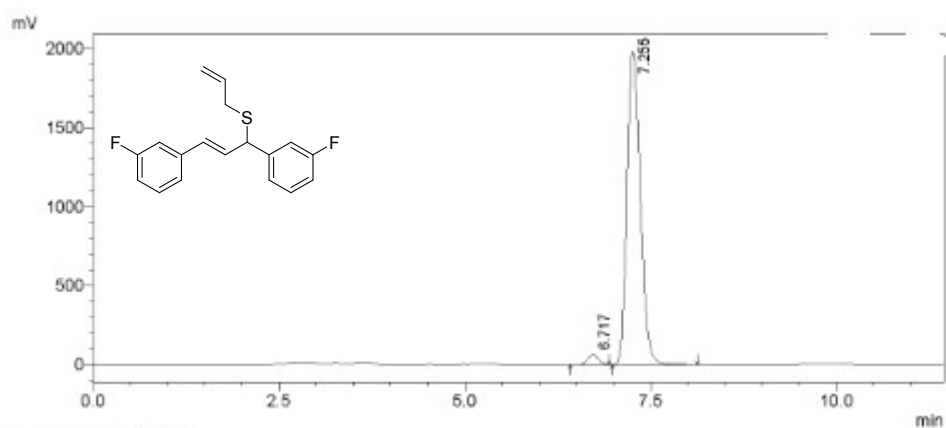
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	7.123	920864	72895	3.698
2	7.835	23978207	1563799	96.302
Total		24899071	1636693	100.000

Rac-3d



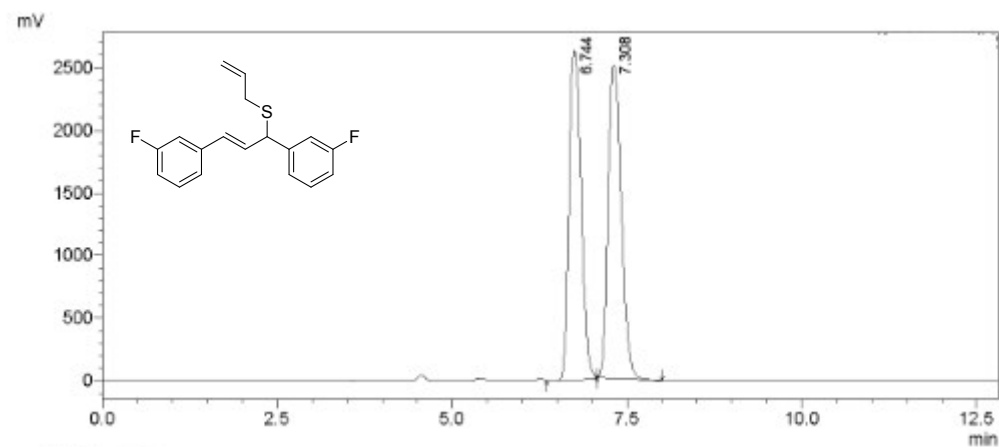
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	7.109	11727470	926642	49.447
2	7.861	11989790	796792	50.553
Total		2371726	1723434	100.000

Chiral-3e



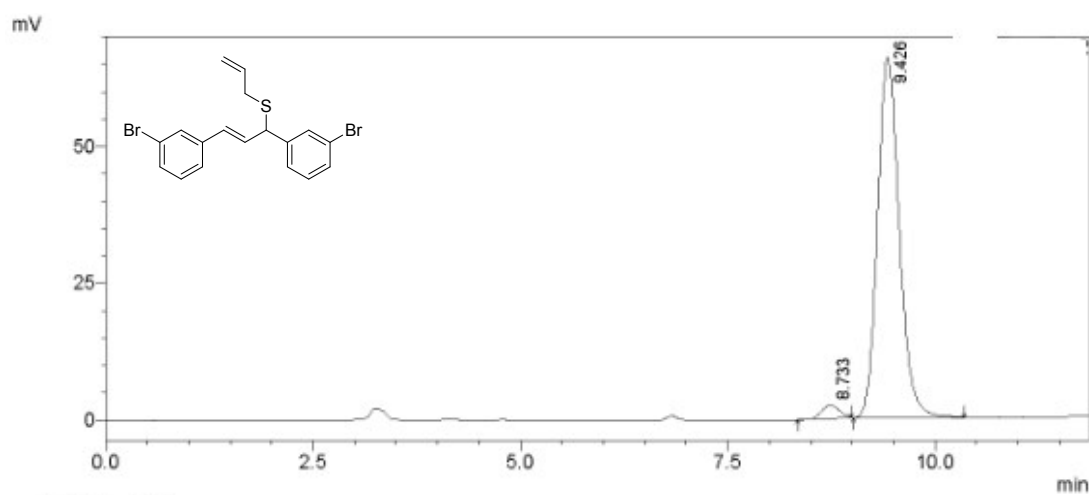
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.717	680435	63018	2.674
2	7.255	24769493	1982542	97.326
Total		25449928	2045560	100.000

Rac-3e



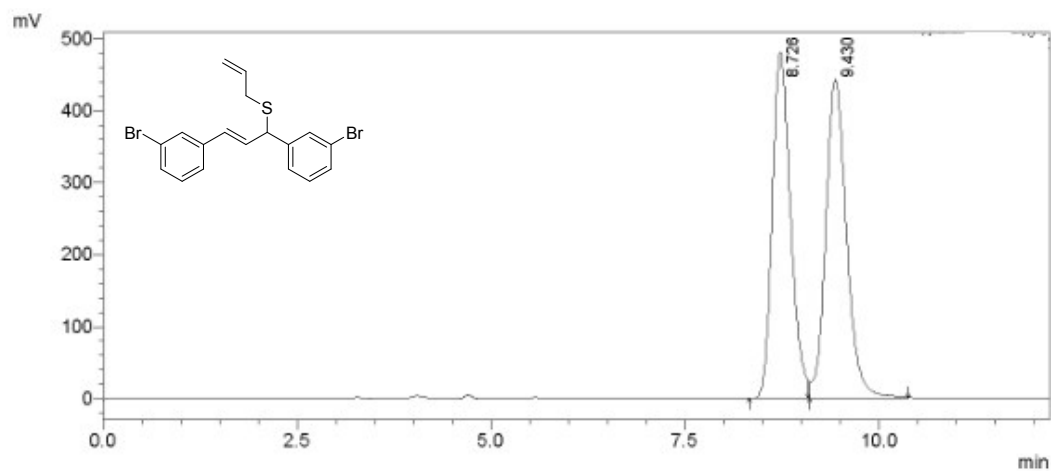
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.744	31791852	2628060	48.990
2	7.308	33103172	2493495	51.010
Total		64895024	5121555	100.000

Chiral-3f



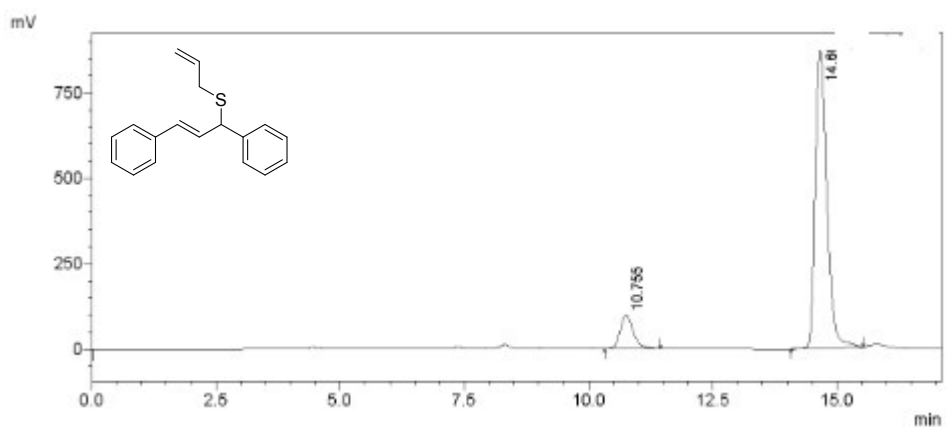
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	8.733	34503	2405	2.778
2	9.426	1207649	65924	97.222
Total		1242151	68329	100.000

Rac-3f



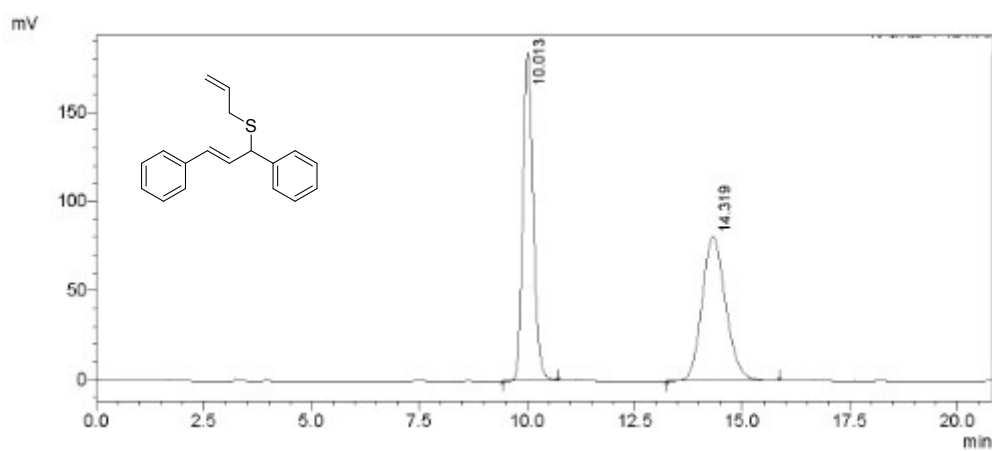
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	8.726	7854168	480216	48.735
2	9.430	8261777	442154	51.265
Total		16115946	922370	100.000

Chiral-3g



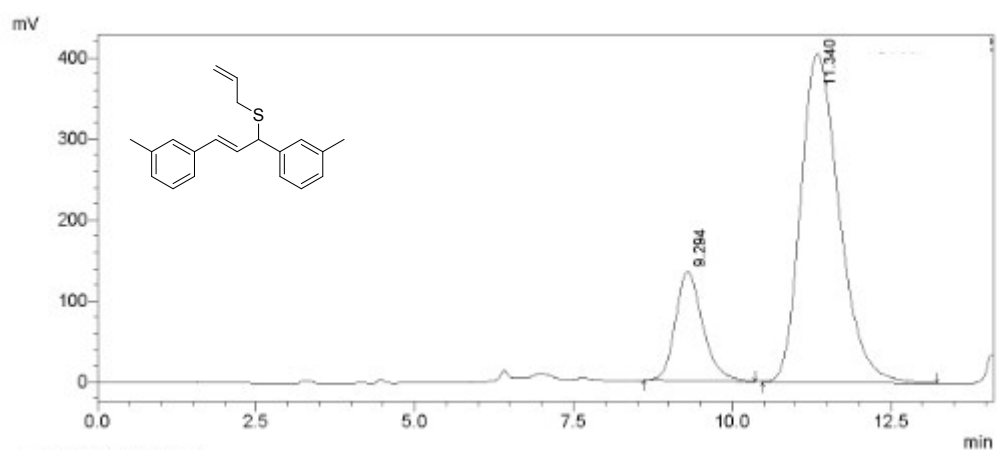
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	10.755	1819034	98154	11.340
2	14.660	14222168	870426	88.660
Total		16041202	968580	100.000

Rac-3g



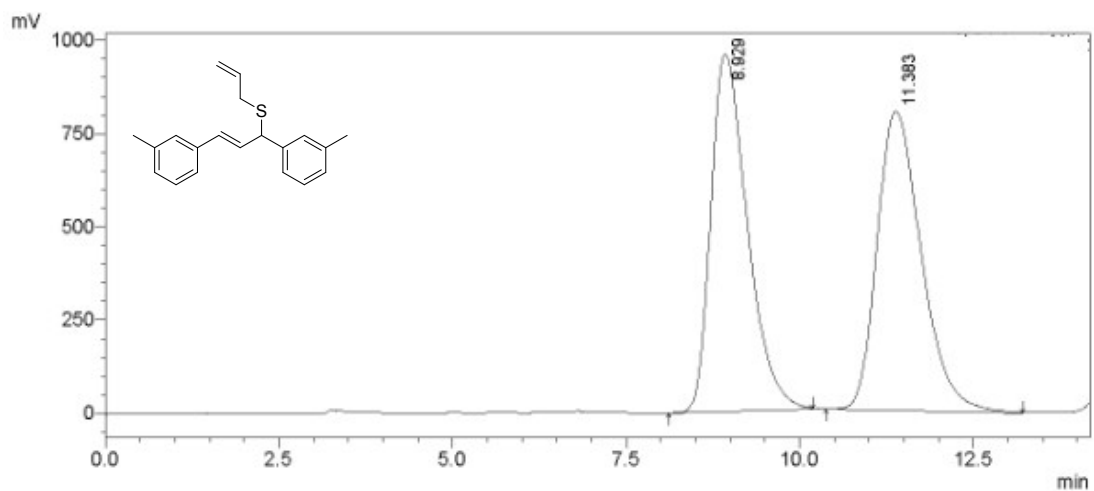
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	10.013	3096722	183904	50.026
2	14.319	3093525	80822	49.974
Total		6190247	264726	100.000

Chiral-3h



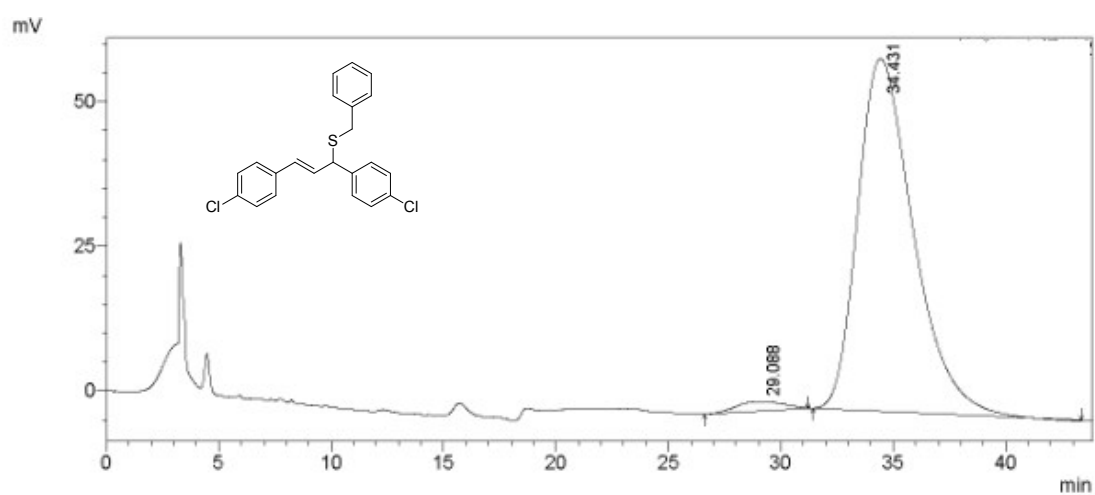
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	9.294	4054181	134110	19.130
2	11.340	17138655	405193	80.870
Total		21192837	539303	100.000

Rac-3h



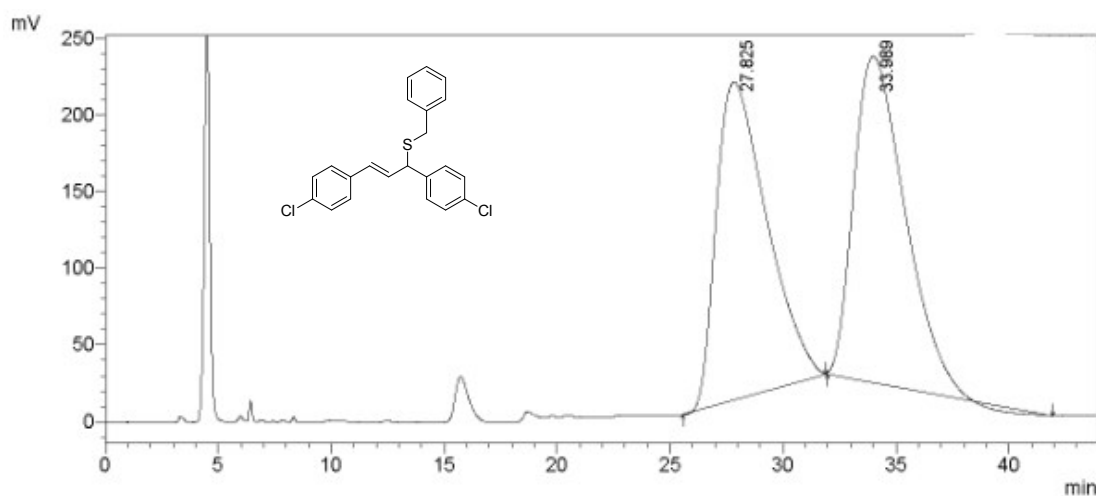
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	8.929	35124929	958356	49.694
2	11.383	35557137	801813	50.306
Total		70682065	1760169	100.000

Chiral-3i



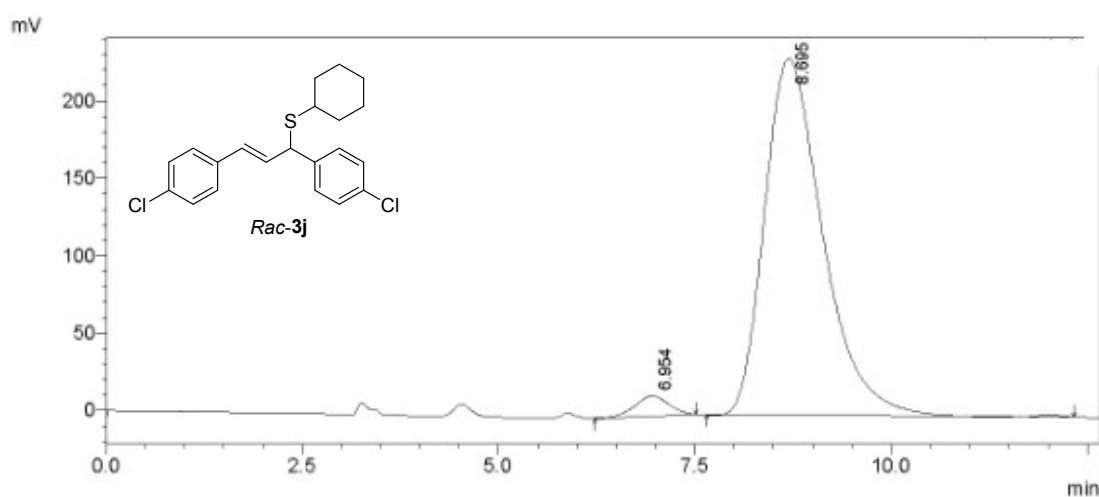
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	29.088	229586	1629	2.143
2	34.431	10484714	60982	97.857
Total		10714300	62611	100.000

Rac-3i



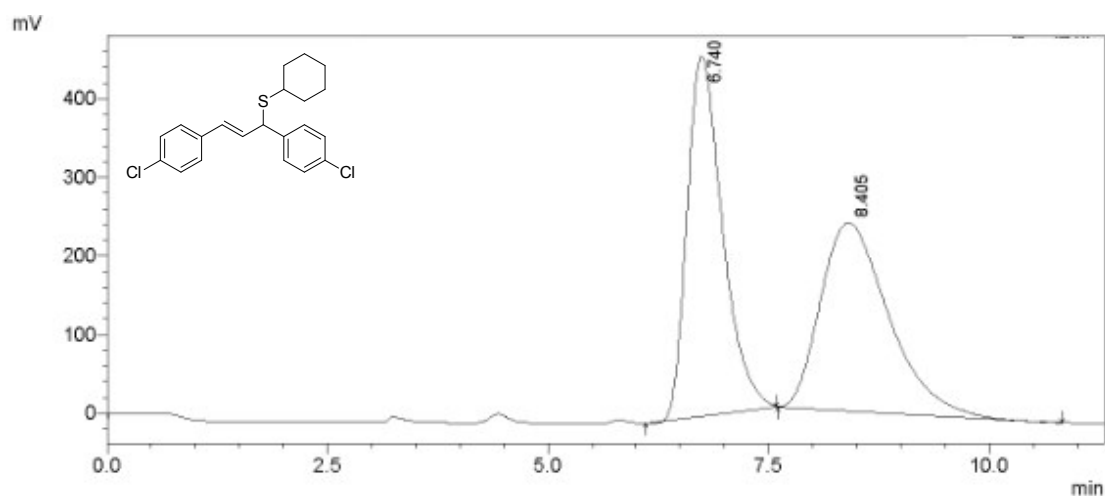
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	27.825	32263413	207484	49.003
2	33.989	33575798	212946	50.997
Total		65839212	420430	100.000

Chiral-3j



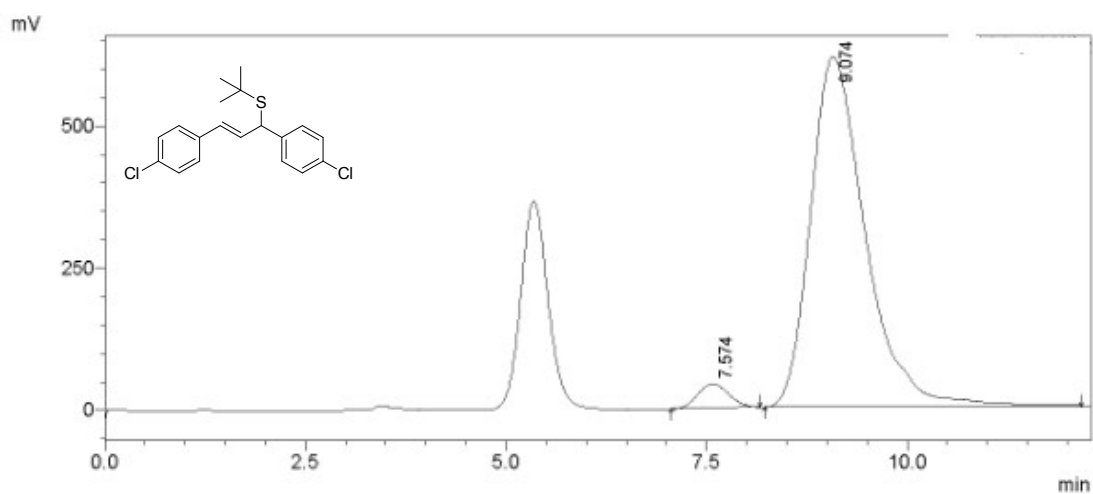
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.954	407354	13213	3.322
2	8.695	11855430	230350	96.678
Total		12262784	243563	100.000

Rac-3j



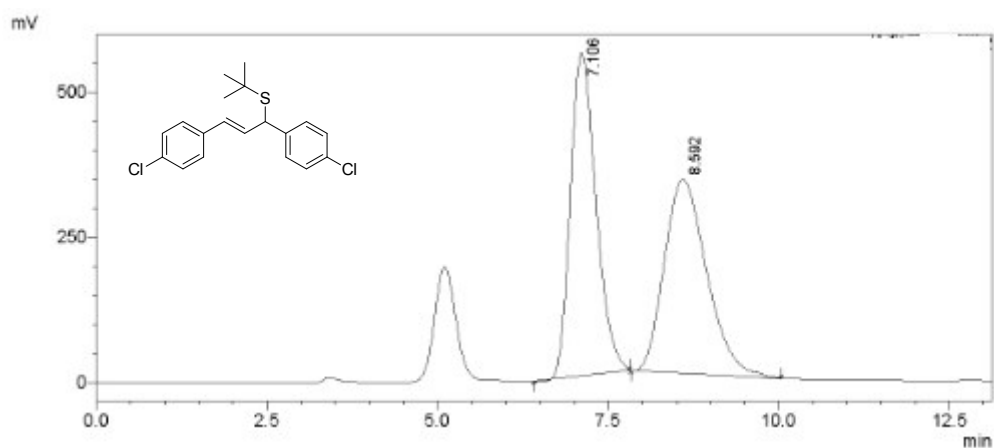
Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.740	12785243	457468	49.868
2	8.405	12853048	238985	50.123
Total		25638291	696453	100.000

Chiral-3k

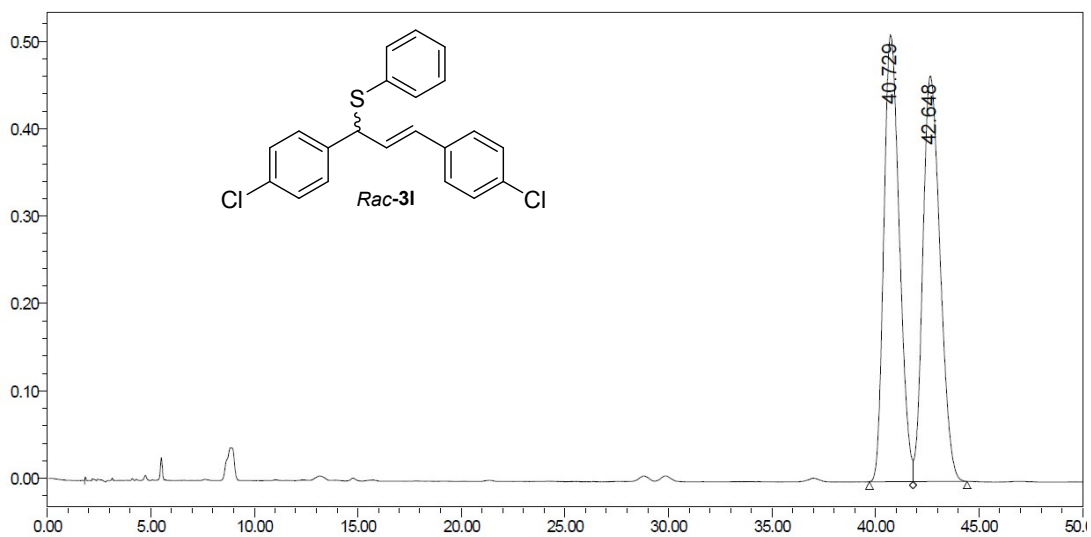


Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	7.574	1097011	41872	3.608
2	9.074	29309043	614939	96.392
Total		30406054	656811	100.000

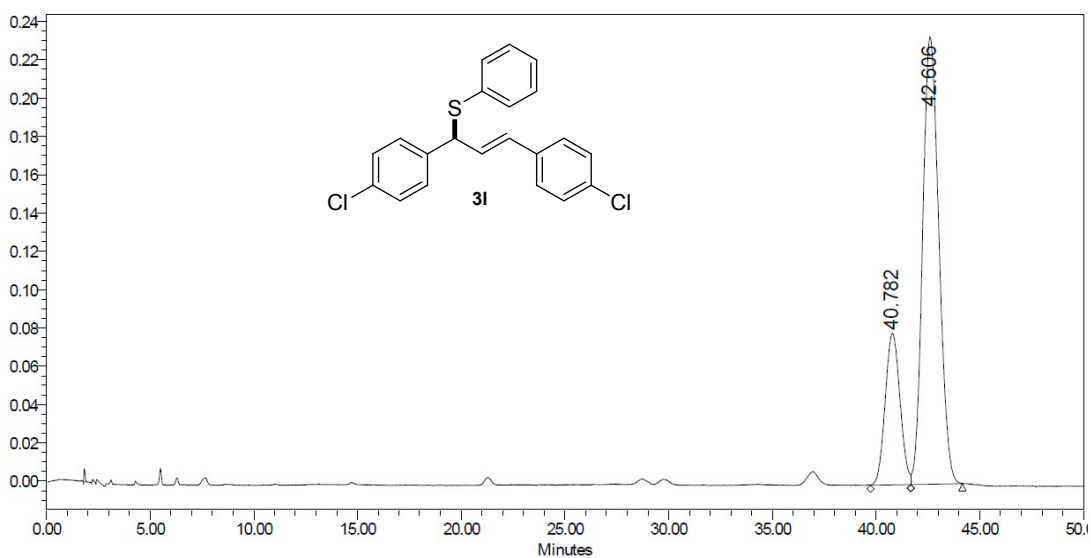
Rac-3k



Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	7.106	14501510	557144	50.144
2	8.592	14418489	333449	49.856
Total		28919999	890593	100.000

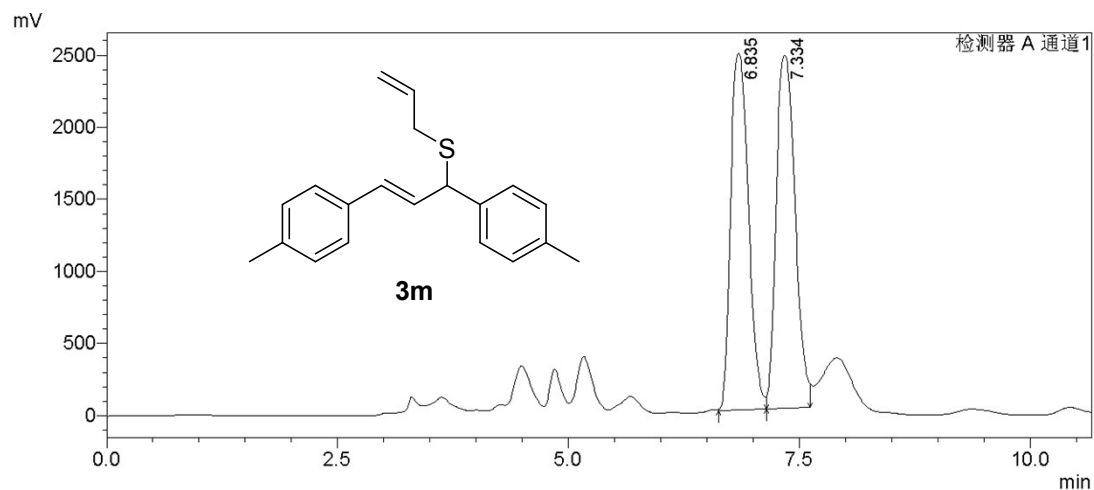


	RT	Area	Height	% Area
1	40.729	26614262	511103	49.77
2	42.648	26863719	464307	50.23



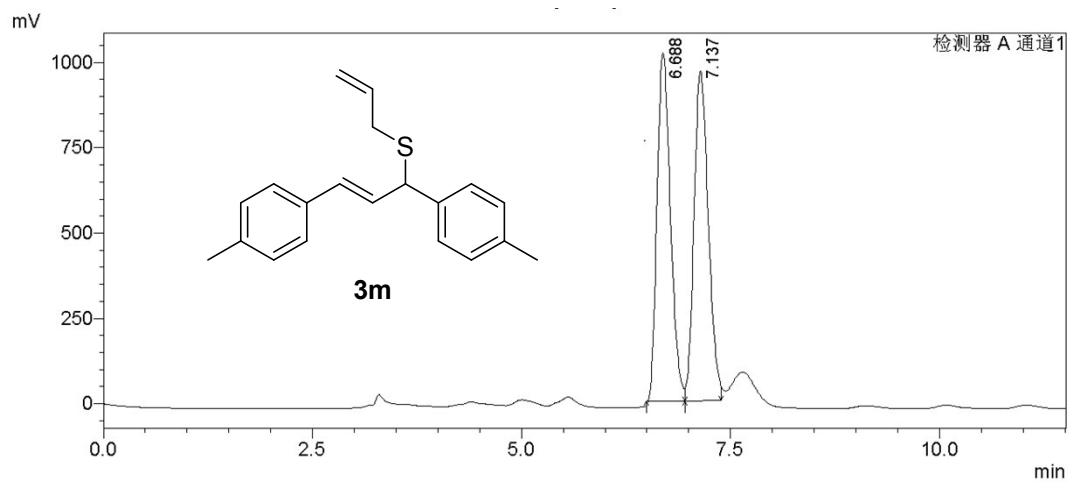
	RT	Area	Height	% Area
1	40.782	3929710	79154	23.66
2	42.606	12680548	233268	76.34

Chiral-3m



Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.835	33169402	2471080	48.746
2	7.334	34876332	2447695	51.254
Total		68045734	4918775	100.000

Rac-3m



Peak No.	R. Time	Peak Area	Peak Hight	Area Percent
1	6.688	11375875	1018782	49.767
2	7.137	11482232	965018	50.233
Total		22858107	1983799	100.000

Figure 1. Single crystal data 3c

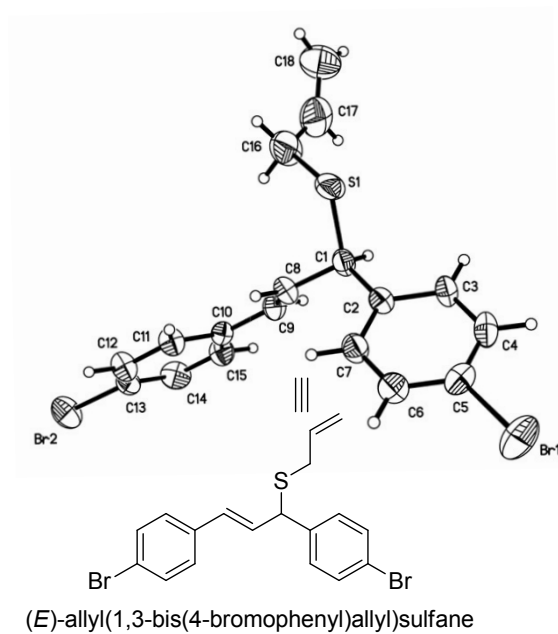


Table 1. Crystal data and structure refinement for mo_160425b.

Identification code	mo_160425b	
Empirical formula	C ₁₈ H ₁₆ Br ₂ S	
Formula weight	424.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 7.604(8) Å	α = 90°.
	b = 9.541(10) Å	β = 90°.
	c = 24.58(3) Å	γ = 90°.
Volume	1783(3) Å ³	
Z	4	
Density (calculated)	1.580 Mg/m ³	
Absorption coefficient	4.654 mm ⁻¹	
F(000)	840	
Crystal size	0.410 x 0.380 x 0.100 mm ³	
Theta range for data collection	2.804 to 27.099°.	
Index ranges	-6 ≤ h ≤ 9, -12 ≤ k ≤ 9, -31 ≤ l ≤ 31	
Reflections collected	21002	
Independent reflections	3893 [R(int) = 0.0662]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3893 / 18 / 190	
Goodness-of-fit on F ²	1.015	
Final R indices [I > 2σ(I)]	R1 = 0.0528, wR2 = 0.0964	
R indices (all data)	R1 = 0.1302, wR2 = 0.1194	
Absolute structure parameter	-0.012(8)	
Largest diff. peak and hole	0.371 and -0.404 e.Å ⁻³	

Table 2. Bond lengths [\AA] and angles [$^\circ$] for mo_160425b.

Br(1)-C(5)	1.887(8)
S(1)-C(16)	1.809(11)
S(1)-C(1)	1.846(8)
C(1)-C(2)	1.491(10)
C(1)-C(8)	1.500(9)
C(1)-H(1)	0.9800
C(2)-C(7)	1.391(10)
C(2)-C(3)	1.406(10)
Br(2)-C(13)	1.907(7)
C(3)-C(4)	1.386(11)
C(3)-H(3)	0.9300
C(5)-C(6)	1.358(12)
C(5)-C(4)	1.383(11)
C(4)-H(4)	0.9300
C(6)-C(7)	1.379(10)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(9)	1.308(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.463(9)
C(9)-H(9)	0.9300
C(10)-C(15)	1.384(10)
C(10)-C(11)	1.386(9)
C(11)-C(12)	1.380(10)
C(11)-H(11)	0.9300
C(12)-C(13)	1.351(10)
C(12)-H(12)	0.9300
C(13)-C(14)	1.364(11)
C(14)-C(15)	1.391(12)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.341(16)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18)	1.291(15)
C(17)-H(17)	0.9300

C(18)-H(18A)	0.9300
C(18)-H(18B)	0.9300
C(16)-S(1)-C(1)	104.1(5)
C(2)-C(1)-C(8)	114.5(6)
C(2)-C(1)-S(1)	106.8(5)
C(8)-C(1)-S(1)	110.4(5)
C(2)-C(1)-H(1)	108.3
C(8)-C(1)-H(1)	108.3
S(1)-C(1)-H(1)	108.3
C(7)-C(2)-C(3)	117.4(7)
C(7)-C(2)-C(1)	122.6(6)
C(3)-C(2)-C(1)	120.0(6)
C(4)-C(3)-C(2)	120.1(7)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(6)-C(5)-C(4)	119.6(7)
C(6)-C(5)-Br(1)	120.9(7)
C(4)-C(5)-Br(1)	119.5(6)
C(5)-C(4)-C(3)	120.7(7)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(5)-C(6)-C(7)	120.6(8)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(6)-C(7)-C(2)	121.6(7)
C(6)-C(7)-H(7)	119.2
C(2)-C(7)-H(7)	119.2
C(9)-C(8)-C(1)	126.1(7)
C(9)-C(8)-H(8)	116.9
C(1)-C(8)-H(8)	116.9
C(8)-C(9)-C(10)	127.5(7)
C(8)-C(9)-H(9)	116.2
C(10)-C(9)-H(9)	116.2
C(15)-C(10)-C(11)	116.9(6)
C(15)-C(10)-C(9)	120.0(7)
C(11)-C(10)-C(9)	123.1(6)
C(12)-C(11)-C(10)	121.8(6)

C(12)-C(11)-H(11)	119.1
C(10)-C(11)-H(11)	119.1
C(13)-C(12)-C(11)	119.8(7)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	120.9(6)
C(12)-C(13)-Br(2)	120.9(6)
C(14)-C(13)-Br(2)	118.2(6)
C(13)-C(14)-C(15)	119.3(7)
C(13)-C(14)-H(14)	120.3
C(15)-C(14)-H(14)	120.3
C(10)-C(15)-C(14)	121.4(7)
C(10)-C(15)-H(15)	119.3
C(14)-C(15)-H(15)	119.3
C(17)-C(16)-S(1)	117.1(8)
C(17)-C(16)-H(16A)	108.0
S(1)-C(16)-H(16A)	108.0
C(17)-C(16)-H(16B)	108.0
S(1)-C(16)-H(16B)	108.0
H(16A)-C(16)-H(16B)	107.3
C(18)-C(17)-C(16)	134.0(14)
C(18)-C(17)-H(17)	113.0
C(16)-C(17)-H(17)	113.0
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0

Symmetry transformations used to generate equivalent atoms: