

Allylation of Nitrosobenzene with Pinacol Allylboronates. A Regioselective Complement to Peroxide Oxidation.

Robert E. Kyne, Michael C. Ryan, Laura T. Kliman and James P. Morken*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Supporting Information

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General Information

¹H NMR spectra were recorded on Varian Unity INOVA 500 MHz, Varian Gemini 400 MHz, and Varian VNMRS 500 MHz spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), integration, coupling constants (Hz), and assignment. ¹³C{¹H}NMR spectra were recorded on Varian VNMRS 500 MHz (125 MHz) and Varian Gemini 400 MHz (100 MHz) spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 77.00 ppm). Infrared (IR) spectra were recorded on a Bruker α-P Spectrometer. Frequencies are reported in wavenumbers (cm⁻¹) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (ESI) was performed at Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO₂, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25 μM silica gel glass-backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), potassium permanganate (KMnO₄), and ceric ammonium molybdate (CAM).

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Toluene and tetrahydrofuran were purified using a Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being sparged with argon. Bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) and trichlorohexylphosphine (PCy₃) were purchased from Strem Chemicals, Inc. 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HB(pin)) and nitrosobenzene (PhNO) were purchased from Aldrich and used without further purification. Bis(pinacolato)diboron (B₂(pin))₂ was obtained from AllyChem Co., Ltd., and recrystallized from pentane. All other reagents were purchased from Aldrich or Fisher and used without further purification.

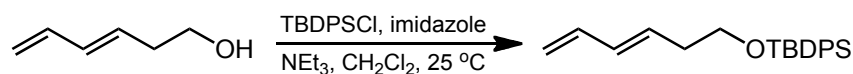
Experimental Procedures

I. Preparation of Starting Materials

A. The following dienes were prepared by Wittig olefination of the commercially available α,β-unsaturated aldehydes with methyltriphenylphosphonium bromide and potassium *tert*-butoxide in tetrahydrofuran: *trans*-1,3-decadiene¹ (Table 2, entry 1) and *trans*-1-phenyl-1,3-butadiene² (Table 2, entry 4).

The following dienes were prepared by the literature procedure: (*E*)-2-methyldeca-1,3-diene³ (Table 2, entry 8), (*E*)-*tert*-butyl(penta-2,4-dienyloxy)diphenylsilane⁴ (Table 2, entry 3), (*E*)-3-methylnona-1,3-diene⁴ (Table 2, entry 9), (*E*)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene⁴ (Table 2, entry 5), and *trans*-1-cyclohexyl-1,3-butadiene⁵ (Table 2, entry 2).

B. **Preparation of (*E*)-*tert*-butyl(hexa-3,5-dien-1-yloxy)diphenylsilane (Table 2, entry 6) (Compound S-1).** The title compound was synthesized as shown below from the known alcohol.⁶



(*E*)-*tert*-butyl(hexa-3,5-dien-1-yloxy)diphenylsilane (Table 2, entry 6) To a flame-dried 50 mL round-bottom flask equipped with a stir bar was added imidazole (1.82 g, 26.7 mmol) and methylene chloride (18 mL, 0.5 M). The flask was then charged with (*E*)-hexa-3,5-dien-1-ol (874 mg, 8.9 mmol) followed by dropwise addition *via* syringe of TBDPSCI (7.34 g, 26.7 mmol). The resulting solution was allowed to stir for five minutes. Triethylamine (3.72 mL, 26.7 mmol) was then added dropwise *via* syringe. The resulting solution was allowed to stir for 15 hours. The reaction mixture was then diluted with CH₂Cl₂ (20 mL) and washed with brine (50 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 100 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. ¹H NMR (500 MHz, CDCl₃): δ 1.03 (s, 9H, C(CH₃)₃), 2.33 (dt, 2H, *J* = 7.4, 6.6 Hz,

¹ Meyers, A. I.; Ford, M. E. *J. Org. Chem.* **1976**, *41*, 1735.

² Yeh, K. L.; Liu, B.; Lo, C. Y.; Huang, H. L.; Liu, R. S. *J. Am. Chem. Soc.* **2002**, *124*, 6510.

³ Burks, H. E.; Kliman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.

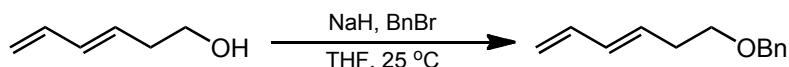
⁴ Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534.

⁵ Habrant, D.; Stengel, B.; Meunier, S.; Mioskowski, C. *Chem. Eur. J.* **2007**, *13*, 5433.

⁶ Miller, C. A.; Batey, R. A. *Org. Lett.* **2004**, *6*, 699.

CH=CHCH₂), 3.69 (t, 2H, *J* = 6.6 Hz, SiOCH₂), 4.95 (dd, 1H, *J* = 10.2, 1.7 Hz, CH=CH_cH), 5.08 (dd, 1H, *J* = 17.1, 1.7 Hz, CH=CH_dH), 5.68 (ddd, 1H, *J* = 15.3, 7.5, 7.1 Hz, SiO(CH₂)₂CH), 6.03-6.08 (m, 1H, CH₂=CHCH), 6.28 (app dt, 1H, *J* = 17.1, 10.2 Hz, CH₂=CH), 7.34-7.42 (m, 4H, Ar-H), 7.63-7.66 (m, 6H, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 19.2, 26.8, 35.9, 63.5, 115.2, 127.6, 129.6, 131.6, 132.8, 133.9, 135.6, 137.2 ppm; IR (neat): 505 (s), 613 (s), 701 (w), 731 (s), 823 (s), 1003 (s), 1109 (s), 1428 (m), 1472 (m), 2858 (m), 2931 (m), 3071 (w); HRMS-(ESI+) for C₂₂H₂₉OSi [M+H]: calculated: 337.1988, found 337.1995. The crude material was purified on silica gel (0.5% Et₂O/pentane) to afford a clear, colorless oil (2.56 g, 86% yield). *R_f* = 0.24 (0.5% Et₂O/pentane, stain in PMA).

C. Preparation of (*E*)-((hexa-3,5-dien-1-yloxy)methyl)benzene (Table 2, entry 7) (Compound S-2). The title compound was synthesized as shown below from the known alcohol.⁵

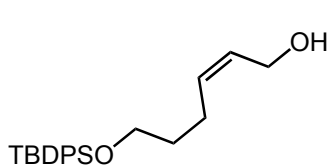


(*E*)-((hexa-3,5-dien-1-yloxy)methyl)benzene (Table 2, entry 7) A flame-dried 50 mL round-bottom flask equipped with a stir bar was brought into the dry-box and charged with sodium hydride (142 mg, 5.91 mmol). The flask was sealed with a rubber septum, removed from the box, and placed under an atmosphere of nitrogen. A separate flame-dried 25 mL round-bottom flask was charged with (*E*)-hexa-3,5-dien-1-ol (527 mg, 5.37 mmol) and THF (18 mL, 0.30 M). The resulting solution was taken up in a syringe and added drop-wise to the reaction flask (containing NaH). The resulting slurry was allowed to stir for 10 minutes. Benzyl bromide (703 μL, 5.91 mmol) was added *via* syringe to the reaction flask. The resulting slurry was allowed to stir for 68 hours at ambient temperature. The reaction was quenched with water (15 mL). The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combined organic layers were dried over sodium sulfate followed by filtration and concentration under reduced pressure. ¹H NMR (500 MHz, CDCl₃): δ 2.40 (dt, 2H, *J* = 6.8, 5.7 Hz, BnOCH₂CH₂), 3.51 (t, 2H, *J* = 6.6 Hz, BnOCH₂), 4.51 (s, 2H, Ar-CH₂), 4.98 (d, 1H, *J* = 10.0 Hz, CH=CH_cH), 5.10 (d, 1H, *J* = 16.6 Hz, CH=CH_dH), 5.71 (ddd, 1H, *J* = 15.4, 7.6, 7.1 Hz, CH₂CH=CH), 6.08-6.14 (m, 1H, CH₂=CHCH), 6.30 (app dt, 1H, *J* = 16.6, 10.2 Hz, CH=CH₂), 7.25-7.29 (m, 1H, Ar-H), 7.31-7.35 (m, 4H, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 33.0, 69.6, 72.9, 115.5, 127.6, 127.7, 128.4, 131.2, 132.7, 137.0, 138.4 ppm; IR (neat): 697 (s), 735 (s), 900 (s), 952 (m), 1004 (s), 1103 (s), 1206 (w), 1361 (m), 1479 (m), 1603 (w), 2789 (s), 3031 (w); HRMS-(ESI+) for C₁₃H₁₇O [M+H]: calculated: 189.1279, found 189.1272. The crude material was purified on silica gel (0-5% EtOAc/hexanes) to afford the product as a clear, yellow oil (841 mg, 83% yield). *R_f* = 0.68 (10% EtOAc/hexanes, stain in PMA).

II. Representative Procedure for Diene Hydroboration/Oxidation.⁴

In the dry-box, an oven-dried 20 mL scintillation vial equipped with a stir bar was charged successively with Ni(cod)₂ (2.5 mg, 0.009 mmol), PCy₃ (2.5 mg, 0.009 mmol), toluene (1.45 mL, 0.25 M), HB(pin) (69.4 mg, 0.54 mmol), and (*E*)-*tert*-butyl(hexa-4,5-dien-1-yloxy)diphenylsilane (121 mg, 0.36 mmol). The vial was sealed with a polypropylene cap, removed from the box, and allowed to stir at ambient temperature for 3 h. The reaction was then cooled to 0 °C (ice/water), diluted with THF (3 mL), and charged with 3 M NaOH (2 mL) and H₂O₂ (1 mL). The resulting mixture was allowed to stir for 12 h while slowly warming to room temperature. The mixture was then cooled to 0 °C (ice/water) and the reaction quenched by drop-wise addition of saturated aqueous sodium thiosulfate (2 mL). The reaction mixture was then diluted with brine (10 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified on silica gel (10% EtOAc/Hexanes) to afford a clear, colorless oil (121 mg, 95% yield). *R_f* = 0.16 (10% EtOAc/hexanes, stain in PMA).

III. Full Characterization of Hydroboration/Oxidation Products.

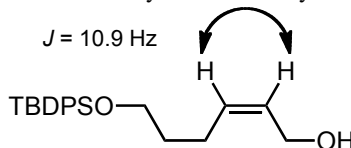


(*Z*)-6-((*tert*-butyldiphenylsilyl)oxy)hex-2-en-1-ol (Table 2, entry 6) (Compound S-3).⁷ ¹H NMR (500 MHz, CDCl₃): δ 1.03 (s, 9H, C(CH₃)₃), 1.57 (tt, 2H, *J* = 7.6, 6.1 Hz, SiOCH₂CH₂), 2.18 (dt, 2H, *J* = 7.5, 6.9 Hz, SiO(CH₂)₂CH₂), 3.65 (t, 2H, *J* = 6.1 Hz, SiOCH₂), 4.16 (app t, 2H, *J* = 5.9 Hz, CH₂OH), 5.49 (dtt, 1H, *J* = 10.9, 7.8, 1.2 Hz, CH=CHCH₂OH), 5.62 (dtt, 1H, *J* = 10.9, 6.8, 1.5 Hz, CH=CHCH₂OH), 7.34-7.43 (m, 6H, Ar-H),

⁷ Narco, K.; Baltas, M.; Gorrichon, L. *Tetrahedron* **1999**, 55, 14013.

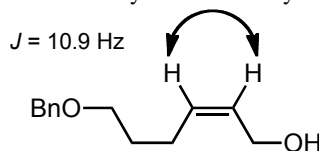
7.63-7.65 (m, 4H, Ar-**H**) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 19.2, 23.6, 26.8, 32.2, 58.4, 63.0, 127.6, 129.0, 129.6, 132.3, 133.8, 135.5 ppm; IR (neat): 505 (s), 613 (m), 702 (s), 739 (m), 823 (m), 1110 (s), 1389 (w), 1428 (m), 1472 (w), 2858 (m), 2931 (m), 3334 (m, b); HRMS-(ESI+) for $\text{C}_{22}\text{H}_{29}\text{OSi}$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 337.1988, found 337.1982.

Proof of Stereochemistry: (Z)-alkene stereochemistry determined by coupling constants as shown below.



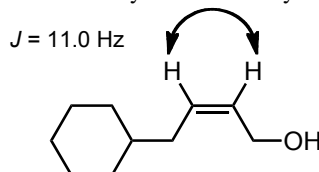
(Z)-6-(benzyloxy)hex-2-en-1-ol (Table 2, entry 7) (Compound S-4).⁸ The reaction was performed with the general procedure. ^1H NMR (500 MHz, CDCl_3): δ 1.68 (tt, 2H, $J = 7.4, 6.3$ Hz, $\text{BnOCH}_2\text{CH}_2$), 2.19 (dt, 2H, $J = 8.4, 6.3$ Hz, $\text{BnO}(\text{CH}_2)_2\text{CH}_2$), 3.47 (t, 2H, $J = 6.3$ Hz, BnOCH_2), 4.15 (d, br, 2H, $J = 6.6$ Hz, CH_2OH), 4.48 (s, 2H, ArCH_2), 5.51 (dtt, 1H, $J = 10.9, 7.6, 1.3$ Hz, $\text{CH}=\text{CHCH}_2\text{OH}$), 5.64 (dtt, 1H, $J = 10.9, 6.9, 1.4$ Hz, $\text{CH}=\text{CHCH}_2\text{OH}$), 7.25-7.28 (m, 2H, Ar-**H**), 7.29-7.35 (m, 3H, Ar-**H**) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 23.8, 29.2, 58.2, 69.1, 72.8, 127.5, 127.6, 128.3, 129.2, 132.0, 138.3 ppm; IR (neat): 698 (s), 736 (s), 1042 (s), 1100 (s), 1206 (w), 1364 (m), 1454 (m), 1496 (w), 2857 (s), 2927 (s), 3064 (w), 3375 (s, br); HRMS-(ESI+) for $\text{C}_{13}\text{H}_{17}\text{O}$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 189.1279, found 189.1279. The crude reaction mixture was purified on silica gel (12.5% EtOAc/hexanes) to afford a clear, colorless oil (69 mg, 93% yield). $R_f = 0.05$ (10% EtOAc/hexanes, stain in PMA).

Proof of Stereochemistry: (Z)-alkene stereochemistry determined by coupling constants as shown below.



(Z)-4-cyclohexylbut-2-en-1-ol (Table 2, entry 2) (Compound S-5).⁹ The reaction was performed with the general procedure. ^1H NMR (500 MHz, CDCl_3): δ 0.83-0.91 (m, 2H, Cy-**H**), 1.07-1.31 (m, 4H, Cy-**H**), 1.55 (s, 1H, OH), 1.60-1.69 (m, 5H, Cy-**H**), 1.95 (app t, 2H, $J = 6.5$ Hz, Cy-CH_2), 4.16 (s, br, 2H, CH_2OH), 5.54 (dtt, 1H, $J = 11.0, 7.5, 1.3$ Hz, $\text{CyCH}_2\text{CH}=\text{CH}$), 5.62 (dtt, 1H, $J = 11.0, 6.8, 1.5$ Hz, $\text{CyCH}_2\text{CH}=\text{CH}$) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 26.3, 26.5, 33.1, 35.1, 38.0, 58.6, 129.0, 131.7 ppm; IR (neat): 669 (w), 1016 (s), 1448 (s), 2851 (s), 2921 (s), 3014 (w), 3317 (s, br); HRMS-(ESI+) for $\text{C}_{10}\text{H}_{17}$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 137.1330, found 137.1328. The crude reaction mixture was purified on silica gel (33% Et₂O/pentane) to afford a clear oil (46 mg, 81% yield). $R_f = 0.15$ (17% Et₂O/pentane, stain in PMA).

Proof of Stereochemistry: (Z)-alkene stereochemistry determined by coupling constants as shown below.



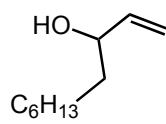
⁸ Schoemaker, J. M.; Luglag, V. R.; Borhan, B. *J. Am. Chem. Soc.* **2004**, *126*, 13600.

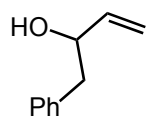
⁹ Krysan, D.; Haight, A.; Menzia, J.; Welch, N. *Tetrahedron* **1994**, *50*(21), 6163.

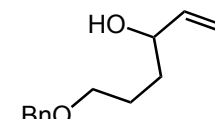
IV. General Procedure for Diene Hydroboration/Allylation.

In the dry-box, and oven-dried 20 mL scintillation vial equipped with a stir bar was charged successively with Ni(cod)₂ (2.5 mg, 0.009 mmol), PCy₃ (2.5 mg, 0.009 mmol), toluene (1.45 mL, 0.25 M), HB(pin) (69.4 mg, 0.54 mmol), and *trans*-1,3-decadiene (50 mg, 0.36 mmol). The vial was sealed with a polypropylene cap, removed from the box, and allowed to stir at room temperature for 3 h. The reaction was then cooled to 0 °C (ice/water) and charged with PhNO (119 mg, 1.11 mmol) and THF (2 mL). The resulting solution was allowed to warm to ambient temperature while stirring for 1 h. The solution was then cooled to 0 °C (ice/water) and charged with 3 M NH₄OH (2 mL). The resulting mixture was allowed to stir for 14 h while warming to room temperature. The reaction mixture was then diluted with brine (10 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified on silica gel (10% Et₂O/pentane) to afford a clear, yellow oil (37 mg, 66% yield). R_f = 0.14 (10% Et₂O/pentane, stain in PMA).

V. Full Characterization of Hydroboration/PhNO Allylation Products.

 **dec-1-en-3-ol (Table 2, entry 1) (Compound S-6).**¹⁰ ¹H NMR (400 MHz, CDCl₃): δ 0.85 (t, 3H, *J* = 6.5 Hz, CH₃), 1.26-1.57 (m, 12H, (CH₂)₆), 4.05-4.08 (m, 1H, CHOH), 5.07 (dd, 1H, *J* = 10.4, 1.2 Hz, CH=CH_cH_c), 5.19 (dd, 1H, *J* = 17.2, 1.4 Hz, CH=CH_cH_c), 5.84 (ddd, 1H, *J* = 17.2, 10.4, 6.3 Hz, CH=CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 22.6, 25.3, 29.2, 29.5, 31.8, 37.0, 73.3, 114.5, 141.3 ppm; IR (neat): 919 (s), 989 (s), 1465 (s), 2855 (s), 2925 (s), 2956 (m), 3354 (s, br); HRMS-(ESI+) for C₁₀H₁₉ [M+H-H₂O]: calculated: 139.1487, found 139.1486.

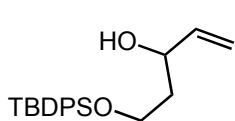
 **1-phenylbut-3-en-2-ol (Table 2, entry 2) (Compound S-7).**¹¹ The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 1.58 (d, 1H, *J* = 3.9 Hz, OH), 2.74 (dd, 1H, *J* = 13.7, 8.0 Hz, ArCH₂), 2.87 (dd, 1H, *J* = 13.5, 5.1 Hz, ArCH₂), 4.33-4.35 (m, 1H, CHOH), 5.12 (app dt, 1H, *J* = 10.9, 0.9 Hz, CH=CH_cH_c), 5.24 (app dt, 1H, *J* = 17.7, 1.2 Hz, CH=CH_cH_c), 5.92 (ddd, 1H, *J* = 17.7, 10.9, 5.8 Hz, CH=CH₂), 7.21-7.24 (m, 3H, Ar-H), 7.29-7.32 (m, 2H, Ar-H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 43.8, 73.6, 114.9, 126.5, 128.4, 129.5, 137.7, 140.1 ppm; IR (neat): 698 (s), 745 (s), 922 (s), 991 (s), 1030 (s), 1077 (m), 1117 (m), 1454 (m), 1496 (m), 2852 (w), 2921 (m, br), 3028 (w), 3375 (s, br); HRMS-(ESI+) for C₁₀H₁₁ [M+H-H₂O]: calculated: 131.0861, found 131.0858. The crude reaction mixture was purified on silica gel (15% Et₂O/pentane) to afford the title compound as a clear oil (36 mg, 64% yield). R_f = 0.08 (10% Et₂O/pentane, stain in CAM).

 **6-(benzyloxy)hex-1-en-3-ol (Table 2, entry 7) (Compound S-8).**¹² The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 1.56-1.74 (m, 4H, C(OH)(CH₂)₂), 2.30 (s, br, 1H, OH), 3.50 (t, 2H, *J* = 5.9 Hz, BnOCH₂), 4.10-4.12 (m, 1H, CHOH), 4.50 (s, 2H, PhCH₂), 5.08 (dt, 1H, *J* = 10.4, 1.5 Hz, CH=CH_cH_c), 5.21 (dt, 1H, *J* = 17.3, 1.4 Hz, CH=CH_cH_c), 5.85 (ddd, 1H, *J* = 17.3, 10.4, 6.1 Hz, CH=CH₂), 7.24-7.36 (m, 5H, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 25.7, 34.2, 70.3, 72.7, 73.0, 114.4, 127.6, 127.7, 128.4, 138.2, 141.1 ppm; IR (neat): 612 (w), 698 (s), 737 (s), 921 (s), 991 (s), 1099 (s), 1204 (w), 1276 (w, b), 1454 (m), 1496 (m), 2855 (s), 2924 (s), 3030 (w), 3065 (w), 3407 (s, br); HRMS-(ESI+) for C₁₃H₁₉O₂ [M+H]: calculated: 207.1385, found 207.1390. The crude reaction mixture was purified on silica gel (25% Et₂O/pentane) to afford a clear oil (47 mg, 63% yield). R_f = 0.12 (25% Et₂O/pentane, stain in PMA).

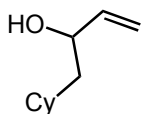
¹⁰ de Frémont, P.; Marion, N.; Nolan, S. P. *J. Orgmet. Chem.* **2009**, *694*, 551.

¹¹ Ruano, J. L. G.; Marcos, V.; Alemán, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 3155.

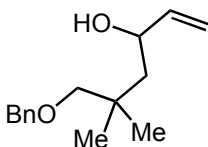
¹² Iyengar, R.; Schildknecht, K.; Morton, M.; Aubé, J. *J. Org. Chem.* **2005**, *70*, 10645.

**5-((tert-butyl-diphenylsilyloxy)pent-1-en-3-ol (Table 2, entry 3) (Compound S-9).**¹³

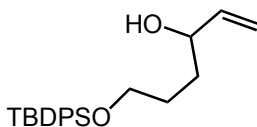
The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 1.04 (s, 9H, C(CH₃)₃), 1.75-1.79 (m, 2H, CH(OH)CH₂), 3.17 (d, 1H, *J* = 2.7 Hz, OH), 3.79-3.89 (m, 2H, CH₂OSi), 4.42 (s, 1H, CH(OH)), 5.11 (dd, 1H, *J* = 10.4, 1.2 Hz, CH=CH_cH_d), 5.29 (dd, 1H, *J* = 17.4, 1.2 Hz, CH=CH_cH_d), 5.87 (ddd, 1H, *J* = 17.4, 10.4, 5.4 Hz, CH=CH₂), 7.37-7.44 (m, 6H, Ar-H), 7.66 (d, 4H, *J* = 7.9 Hz, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 19.0, 26.8, 38.4, 62.6, 72.1, 114.2, 127.7 (2C), 129.8 (2C), 133.0, 133.0, 135.5 (2C), 140.6 ppm; IR (neat): 487 (s), 502 (s), 613 (s), 699 (s), 736 (s), 822 (m), 921 (m), 996 (m), 1078 (s), 1106 (s), 1427 (m), 1472 (w), 2856 (w), 2929 (w), 3071 (w), 3415 (s, br); HRMS-(ESI+) for C₂₁H₂₉O₂Si [M+H]⁺: calculated: 341.1937, found 341.1923. The crude reaction mixture was purified on silica gel (10% Et₂O/pentane) to afford a clear oil (70 mg, 57% yield). R_f = 0.28 (10% Et₂O/pentane, stain in KMnO₄).

**1-cyclohexylbut-3-en-2-ol (Table 2, entry 3) (Compound S-10).**¹⁴

The reaction was performed with the general procedure. ¹H NMR (400 MHz, CDCl₃): δ 0.87-0.96 (m, 4H, Cy-H), 1.12-1.78 (m, 10H, Cy-H, CyCH₂CH(OH)), 4.19 (s, b, 1H, CHOH), 5.07 (dd, 1H, *J* = 10.5, 1.2 Hz, CH=CH_cH_d), 5.20 (dd, 1H, *J* = 17.2, 1.2 Hz, CH=CH_cH_d), 5.85 (ddd, 1H, *J* = 17.2, 10.5, 6.3 Hz, CH=CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 26.2, 26.3, 26.5, 33.1, 33.8, 33.9, 44.9, 70.8, 114.2, 141.8 ppm; IR (neat): 919 (m), 990 (m), 1448 (m), 2851 (s), 2921 (s), 3353 (s, br); HRMS-(ESI+) for C₁₀H₁₇ [M+H-H₂O]⁺: calculated: 137.1330, found 137.1337. The crude reaction mixture was purified on silica gel (10% Et₂O/pentane) to afford a clear oil (34 mg, 62% yield). R_f = 0.09 (10% Et₂O/pentane, stain in PMA).

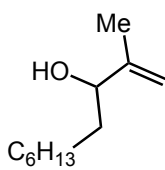
**6-(benzyloxy)-5,5-dimethylhex-1-en-3-ol (Table 2, entry 5) (Compound S-11).**

The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 0.91 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 1.46-1.56 (m, 2H, CH₂COH), 3.24 (d, 1H, *J* = 9.1 Hz, CH_aH_bOBn), 3.27 (d, 1H, *J* = 9.1 Hz, CH_aH_bOBn), 4.05 (d, 1H, *J* = 2.5 Hz, OH), 4.20-4.23 (m, 1H, CHOH), 4.50 (d, 1H, *J* = 11.8 Hz, OCH_aH_bPh), 4.55 (d, 1H, *J* = 11.8 Hz, OCH_aH_bPh), 5.01 (dt, 1H, *J* = 10.5, 1.5 Hz, C(OH)CH=H_cH_d), 5.21 (dt, 1H, *J* = 17.1, 1.6 Hz, C(OH)CH=H_cH_d), 5.83 (ddd, 1H, *J* = 17.1, 10.5, 5.6 Hz, C(OH)CH=CH₂), 7.26-7.35 (m, 5H, Ar-H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 23.9, 28.0, 34.4, 48.9, 69.3, 73.6, 79.5, 113.2, 127.7, 127.8, 128.5, 137.5, 142.1 ppm; IR (neat): 610 (s), 697 (s), 734 (s), 916 (s), 989 (s), 1074 (s), 1092 (s), 1363 (m), 1474 (m), 2867 (m), 2925 (m), 2956 (m), 3413 (s, br); HRMS-(ESI+) for C₁₅H₂₂O₂ [M+H]⁺: calculated: 235.1698, found 235.1694. The crude reaction mixture was purified on silica gel (17% Et₂O/pentane) to afford a clear oil (39 mg, 44% yield). R_f = 0.29 (17% Et₂O/pentane, stain in CAM).

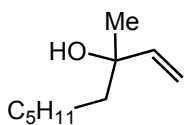
**6-((tert-butyl-diphenylsilyloxy)hex-1-en-3-ol (Table 2, entry 6) (Compound S-12).**

The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 1.03 (s, 9H, SiC(CH₃)₃), 1.59-1.69 (m, 4H, C(OH)(CH₂)₂), 2.13 (d, 1H, *J* = 4.1 Hz, OH), 3.67-3.69 (m, 2H, CH₂OSi), 4.09-4.16 (m, 1H, CHOH), 5.09 (dt, 1H, *J* = 10.3, 1.4 Hz, CH=H_cH_d), 5.21 (dt, 1H, *J* = 17.3, 1.5 Hz, CH=CH_cH_d), 5.85 (ddd, 1H, *J* = 17.3, 10.3, 5.8 Hz, CH=CH₂), 7.35-7.48 (m, 6H, Ar-H), 7.63-7.66 (m, 4H, Ar-H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 19.2, 26.8, 28.4, 33.9, 64.0, 72.8, 114.5, 127.6 (2C), 129.6 (2C), 133.7 (2C), 135.6 (2C), 141.2 ppm; IR (neat): 505 (s), 614 (m), 702 (s), 740 (m), 797 (m), 823 (m), 923 (w), 993 (m), 1109 (s), 1390 (w), 1427 (m), 1472 (w), 2857 (m, br), 2930 (m, br), 3050 (w), 3071 (w), 3380 (s, br); HRMS-(ESI+) for C₂₂H₃₀O₂Si [M+H]⁺: calculated: 355.2093, found 355.2086. The crude reaction mixture was purified on silica gel (17% Et₂O/pentane) to afford a clear oil (74 mg, 58% yield). R_f = 0.11 (17% Et₂O/pentane, stain in PMA).

¹³ Singh, O. V.; Han, H. *Org. Lett.* **2007**, *9*, 4801.¹⁴ Herold, P.; Duthaler, R.; Rihs, G.; Angst, C. *J. Org. Chem.* **1989**, *54*, 1178.

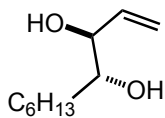


2-methyldec-1-en-2-ol (Table 2, entry 8) (Compound S-13).¹⁵ The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 0.86 (t, 3H, 6.8 Hz, (CH₂)₅CH₃), 1.24-1.30 (m, 10H, CH₃(CH₂)₅), 1.41 (d, 1H, 3.6 Hz, OH), 1.50-1.53 (m, 2H, CH₂CH(OH)), 1.70 (s, 3H, CH₂=C(OH)(CH₃)), 4.02-4.05 (m, 1H, CHOH), 4.81 (dq, 1H, *J* = 1.5, 1.5 Hz, CH₂=C), 4.91-4.92 (m, 1H, CH₂=C) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 17.5, 22.6, 25.6, 29.2, 29.5, 31.8, 35.0, 76.0, 110.9, 147.7 ppm; IR (neat): 561 (w), 897 (s), 991 (m), 1025 (m), 1123 (w), 1376 (m), 1457 (m), 1651 (w), 2855 (s), 2924 (s), 3352 (s, br); HRMS-(ESI+) for C₁₁H₂₁ [M+H-H₂O]: calculated: 153.1643, found 153.1648. The crude reaction mixture was purified on silica gel with no applied pressure (8% EtOAc/hexanes) to afford a clear oil (13 mg, 22% yield). *R_f* = 0.12 (8% EtOAc/hexanes, stain in PMA).



3-methyl-non-1-en-3-ol (Table 2, entry 9) (Compound S-14).¹⁶ The reaction was performed with the general procedure. ¹H NMR (500 MHz, CDCl₃): δ 0.85 (t, 3H, *J* = 6.6 Hz, CH₃(CH₂)₄), 1.24-1.30 (m, 12H, CH₃(CH₂)₄), OH, CH₂=CHC(CH₃)(OH)), 1.40-1.51 (m, 2H, CH₂=CHC(CH₃)(OH)CH₂), 5.02 (dd, 1H, *J* = 10.8, 0.6 Hz, CH=CH₂H), 5.17 (dd, 1H, *J* = 17.4, 0.6 Hz, CH=CH₂H), 5.89 (dd, 1H, *J* = 17.4, 10.8 Hz, CH=CH₂) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 14.0, 22.6, 23.8, 27.6, 29.7, 31.8, 42.4, 73.3, 111.4, 145.3 ppm; IR (neat): 724 (w), 919 (s), 995 (m), 1099 (m), 1306 (m), 1459 (m), 2858 (s), 2930 (s), 2957 (s), 3384 (s, br); HRMS-(ESI+) for C₁₀H₁₉ [M+H-H₂O]: calculated: 139.1487, found 139.1487. The crude reaction mixture was purified on silica gel (8% Et₂O/pentane) to afford a clear oil (33 mg, 58% yield). *R_f* = 0.12 (8% EtOAc/hexanes, stain in PMA).

VI. Diboration/Allylation/Oxidation of *trans*-1,3-decadiene (Scheme 2).



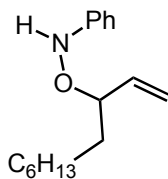
***anti*-dec-1-ene-3,4-diol (Compound 9).**¹⁷ In the dry-box, an oven-dried 20 mL scintillation vial equipped with a stir bar was charged successively with Ni(cod)₂ (9.0 mg, 0.03 mmol), PCy₃ (9.0 mg, 0.03 mmol), toluene (2.4 mL, 0.25 M), B₂(pin)₂ (229 mg, 0.9 mmol), and *trans*-1,3-decadiene (83 mg, 0.6 mmol). The vial was sealed with a polypropylene cap, removed from the box, and allowed to stir at 60 °C for 3 h. The polypropylene cap was exchanged for a rubber septum, the reaction was cooled to -78 °C (CO₂/acetone), and a solution of PhNO (193 mg, 1.80 mmol) in THF (4.86 mL, 0.37 M) was added to the reaction drop-wise over 40 minutes. The resulting solution was allowed to stir for 14 h while slowly warming to room temperature. The solution was then cooled to 0 °C (ice/water) and charged with 3 M NaOH (2.8 mL) and 30%/wt H₂O₂ (1.6 mL). The resulting mixture was allowed to stir for 4 h while warming to room temperature. The mixture was then cooled to 0 °C (ice/water) and quenched by dropwise addition of saturated aqueous sodium thiosulfate (2 mL). The reaction mixture was diluted with brine (10 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified on silica gel (50% EtOAc/hexanes) to afford a clear, colorless oil (49 mg, 47% yield). ¹H NMR (500 MHz, CDCl₃): δ 0.86 (t, 3H, *J* = 6.9 Hz, (CH₂)₅CH₃), 1.23-1.55 (m, 12 H, (CH₂)₅CH₃, (OH)₂), 3.68 (ddd, 1H, *J* = 8.3, 3.9, 3.9 Hz, (CH₂)₅CHOH), 4.08-4.10 (m, 1H, CH₂=CHCHOH), 5.26 (d, 1H, *J* = 10.5 Hz CH=H_cH), 5.32 (dt, 1H *J* = 17.4, 1.5 Hz, CH=CH_cH), 5.91 (ddd, 1H, *J* = 17.4, 10.5, 6.6 Hz, CH=CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 22.6, 25.8, 29.3, 31.7, 32.1, 74.1, 75.9, 117.6, 136.0 ppm; IR (neat): 924 (s), 993 (s), 1031 (m), 1056 (m), 1317 (w), 1428 (w), 1459 (m), 2856 (s), 2926 (s), 2955 (m), 3375 (s, br); HRMS-(ESI+) for C₁₀H₁₉O [M+H-H₂O]: calculated: 155.1435, found 155.1436. The crude reaction mixture was purified on silica gel (50% EtOAc/hexanes) to afford a clear oil (29 mg, 47% yield). *R_f* = 0.21 (50% EtOAc/hexanes, stain in CAM).

¹⁵ Matsuo, J.; Kozai, T.; Nishikawa, O.; Hattori, Y.; Ishibashi, H. *J. Org. Chem.* **2008**, *73*, 6902.

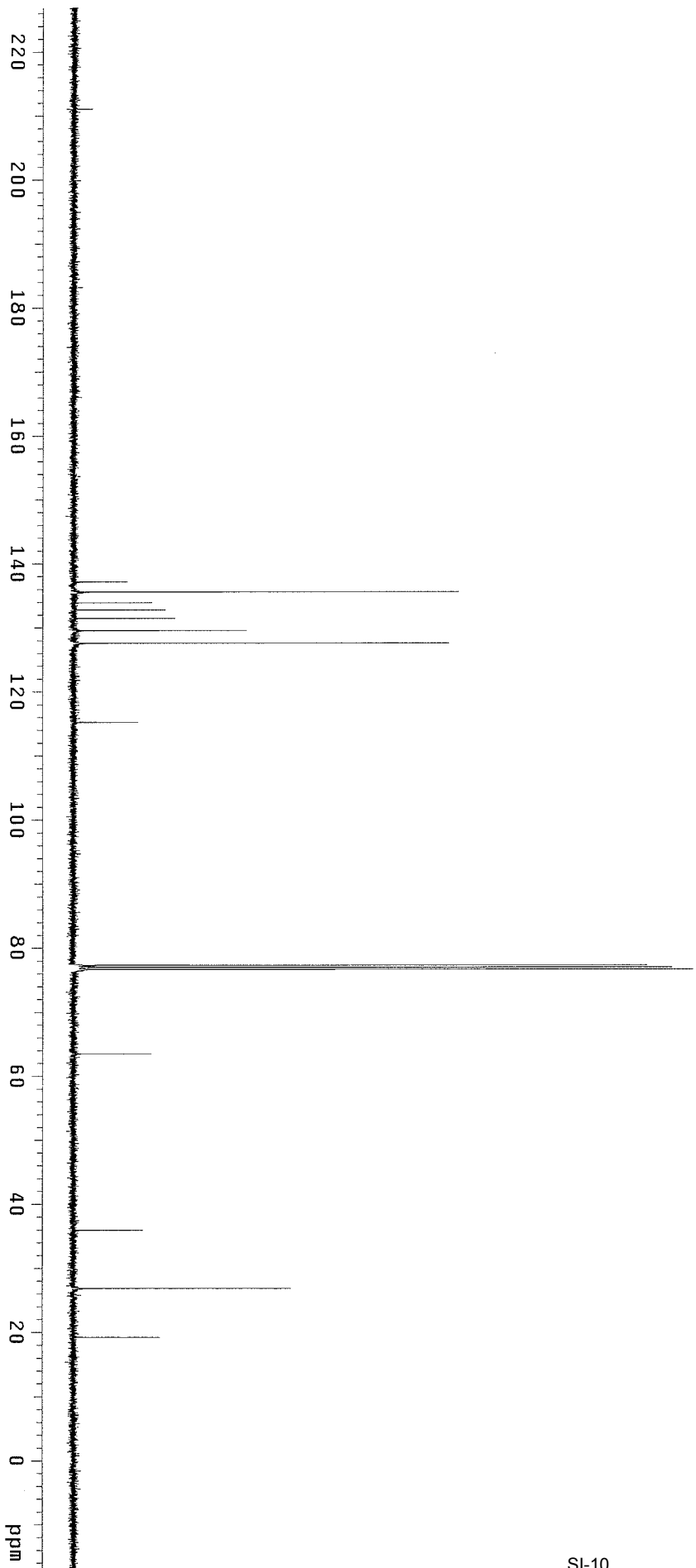
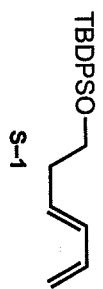
¹⁶ Matsubara, S.; Okazoe, T.; Oshima, K.; Takai, K. *Chem. Bull. Soc. Jpn.* **1985**, *58*, 844.

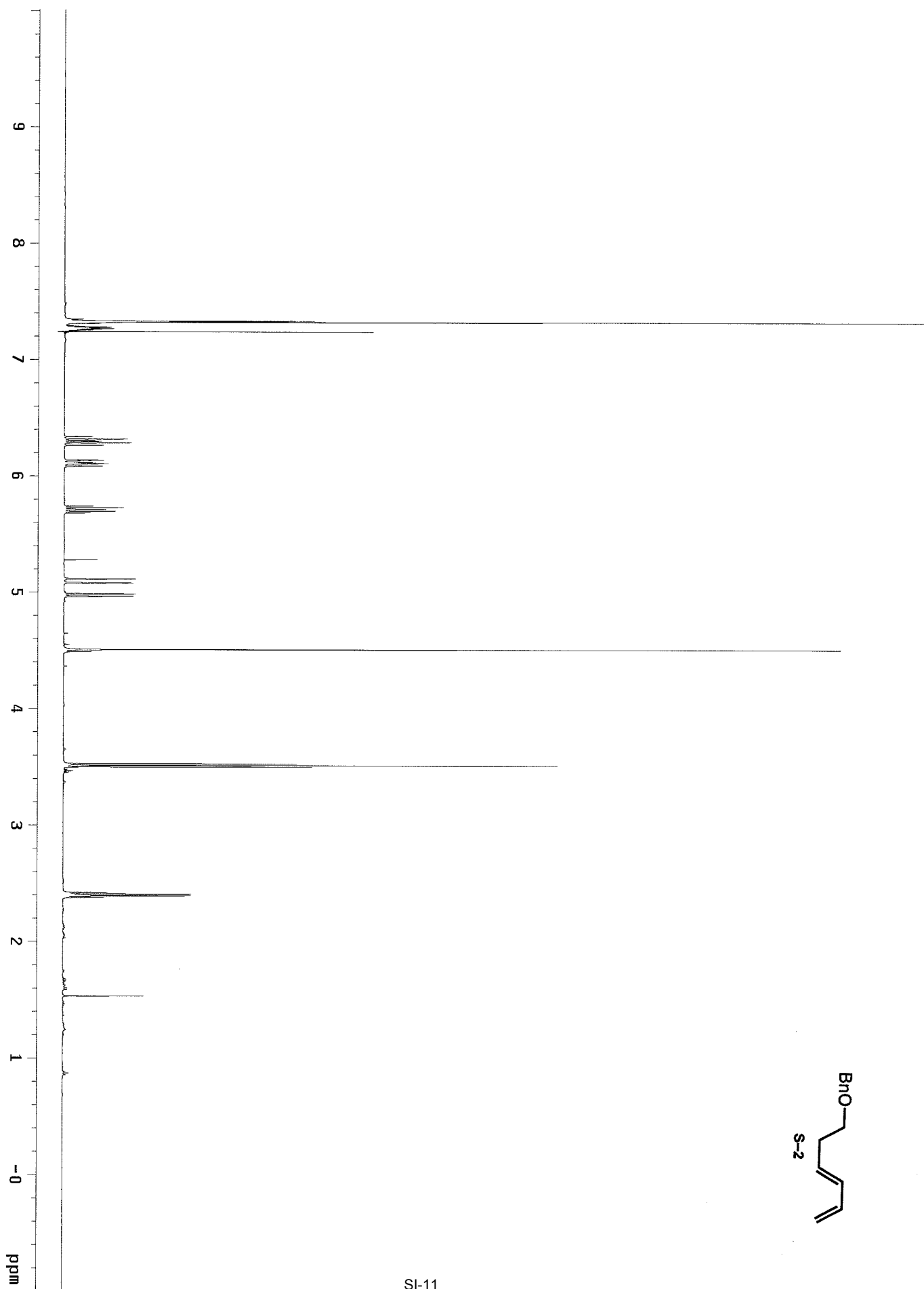
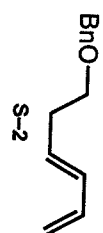
¹⁷ Stereochemical assignment based on comparison to the spectral data of the known *trans*-diol: Lombardo, M.; Morganti, S.; Trombini, C. *J. Org. Chem.* **2003**, *68*, 997.

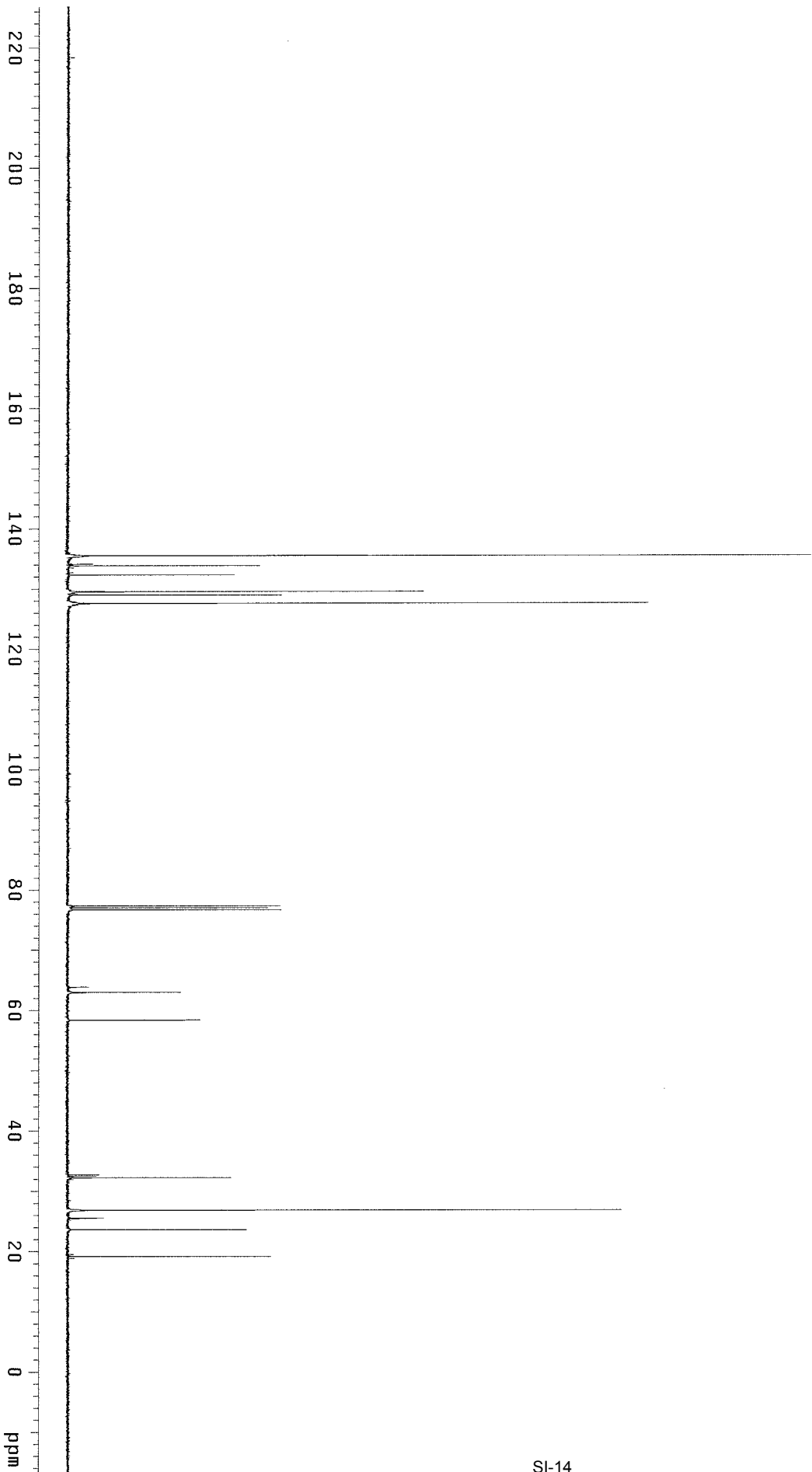
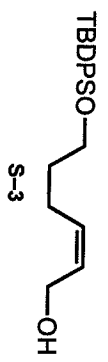
VII. Preparation and Full Characterization of Hydroxylamine (5).

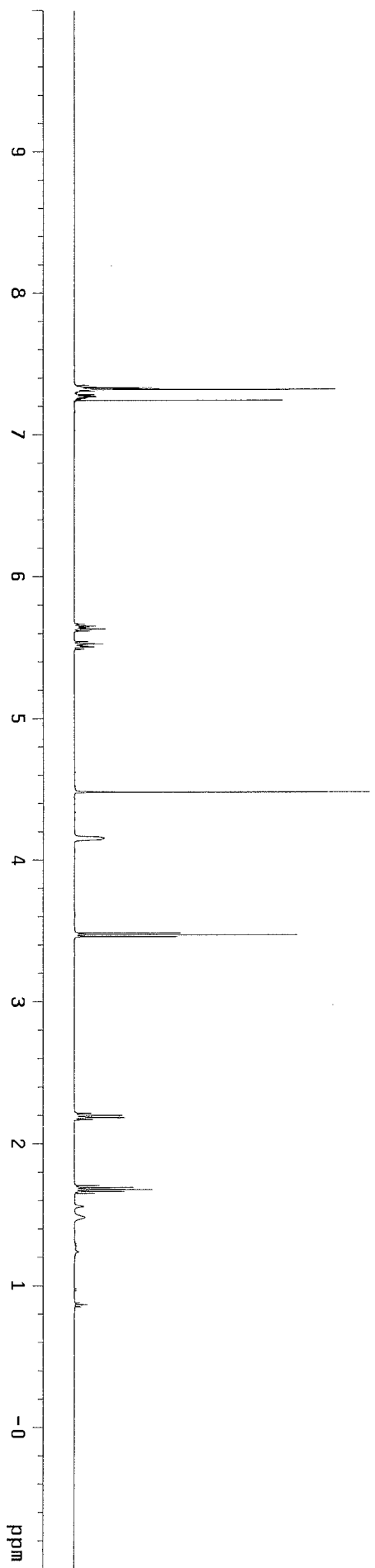
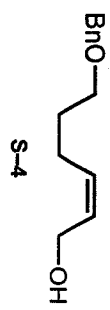


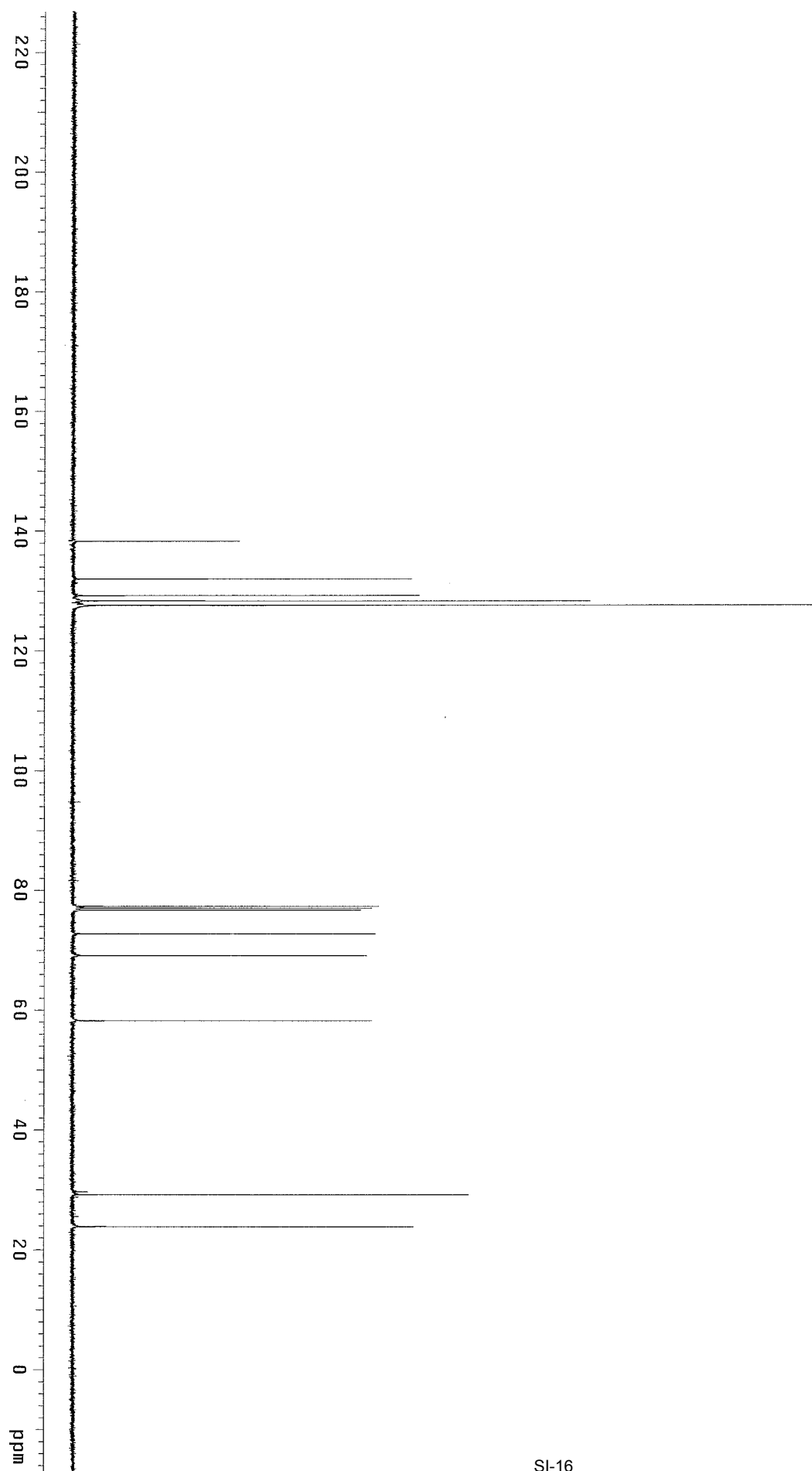
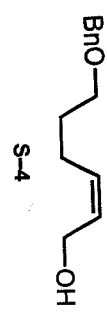
O-(dec-1-en-3-yl)-N-phenylhydroxylamine (Compound 5). In the dry-box, an oven-dried 20 mL scintillation vial equipped with a stir bar was charged with Ni(cod)₂ (2.5 mg, 0.009 mmol), PCy₃ (2.5 mg, 0.009 mmol), HB(pin) (69 mg, 0.539 mmol), toluene (1.45 mL, 0.25 M), and *trans*-1,3-decadiene (50 mg, 0.361 mmol). The vial was sealed with a polypropylene cap, taped, and removed from the box. The reaction was allowed to stir at ambient temperature for 2 h. The polypropylene cap was then exchanged for a rubber septum and the vial was placed under an atmosphere of nitrogen. The vial was cooled to -78 °C in a cryocool. Nitrosobenzene (41 mg, 0.379 mmol) was then dissolved in THF (3 mL), taken up in a syringe, and added dropwise to the reaction mixture at a rate of 0.6 mL/min. The resulting solution was allowed to stir at -78 °C for 13 h. The reaction was diluted with brine (20 mL) and extracted with CH₂Cl₂ (3 x 75 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. ¹H NMR (500 MHz, CDCl₃): δ 0.88 (t, 3H, 6.9 Hz, (CH₂)₅CH₃), 1.22-1.47 (m, 10H, (CH₂)₅CH₃), 1.51-1.58 (m, 1H, CH₃(CH₂)₅CH₂), 1.72-1.79 (m, 1H, CH₃(CH₂)₅CH₂), 4.15 (dt, 1H, $J = 7.8, 6.6$ Hz, CH₂=CHCH(O)), 5.26 (dd, 1H, $J = 18.3, 1.7$ Hz, CH=H_tH_c), 5.27 (dd, 1H, $J = 10.5, 1.7$ Hz, CH=H_cH_v), 5.82 (ddd, 1H, $J = 18.3, 10.5, 8.1$ Hz, CH=CH₂), 6.86 (s, br, 1H, NH), 6.91-6.94 (m, 3H, Ar-H), 7.22-7.26 (m, 2H, Ar-H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 22.6, 25.4, 29.2, 29.6, 31.8, 33.6, 84.8, 114.5, 118.4, 121.8, 128.9, 138.1, 148.5 ppm; IR (neat): 488 (s), 691 (s), 731 (s), 762 (s), 863 (m), 891 (m), 925 (m), 962 (m), 1467 (m), 1494 (s), 1602 (s), 2855 (m), 2952 (s), 3283 (w); HRMS-(ESI+) for C₁₆H₂₆NO [M+H]⁺: calculated: 248.2014, found 248.2009. The crude reaction mixture was purified on silica gel (1% Et₂O/pentane) to afford the product as a clear, yellow oil (39 mg, 43% yield). $R_f = 0.17$ (1% Et₂O/pentane, stain in PMA).

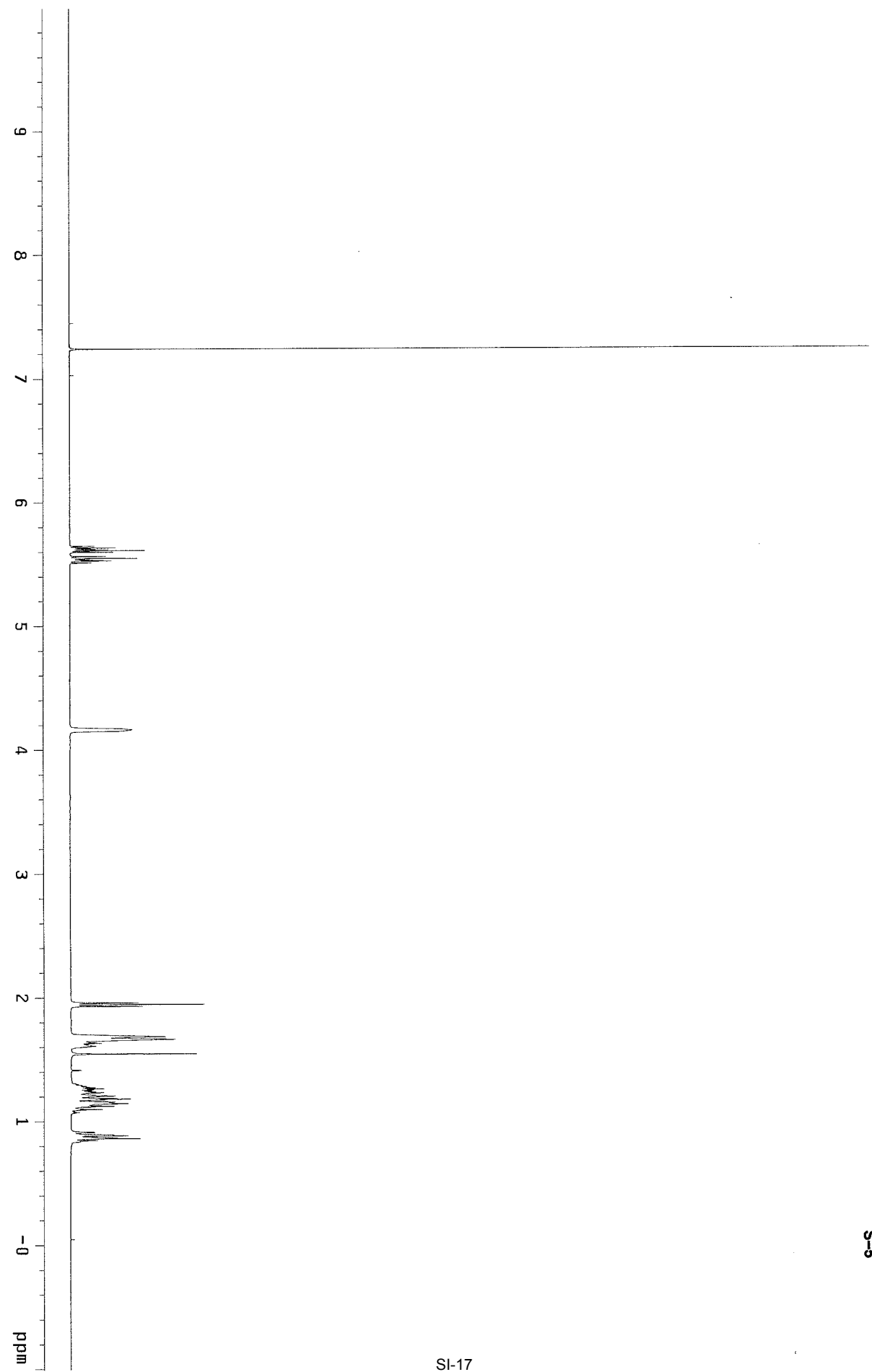
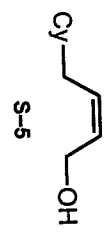


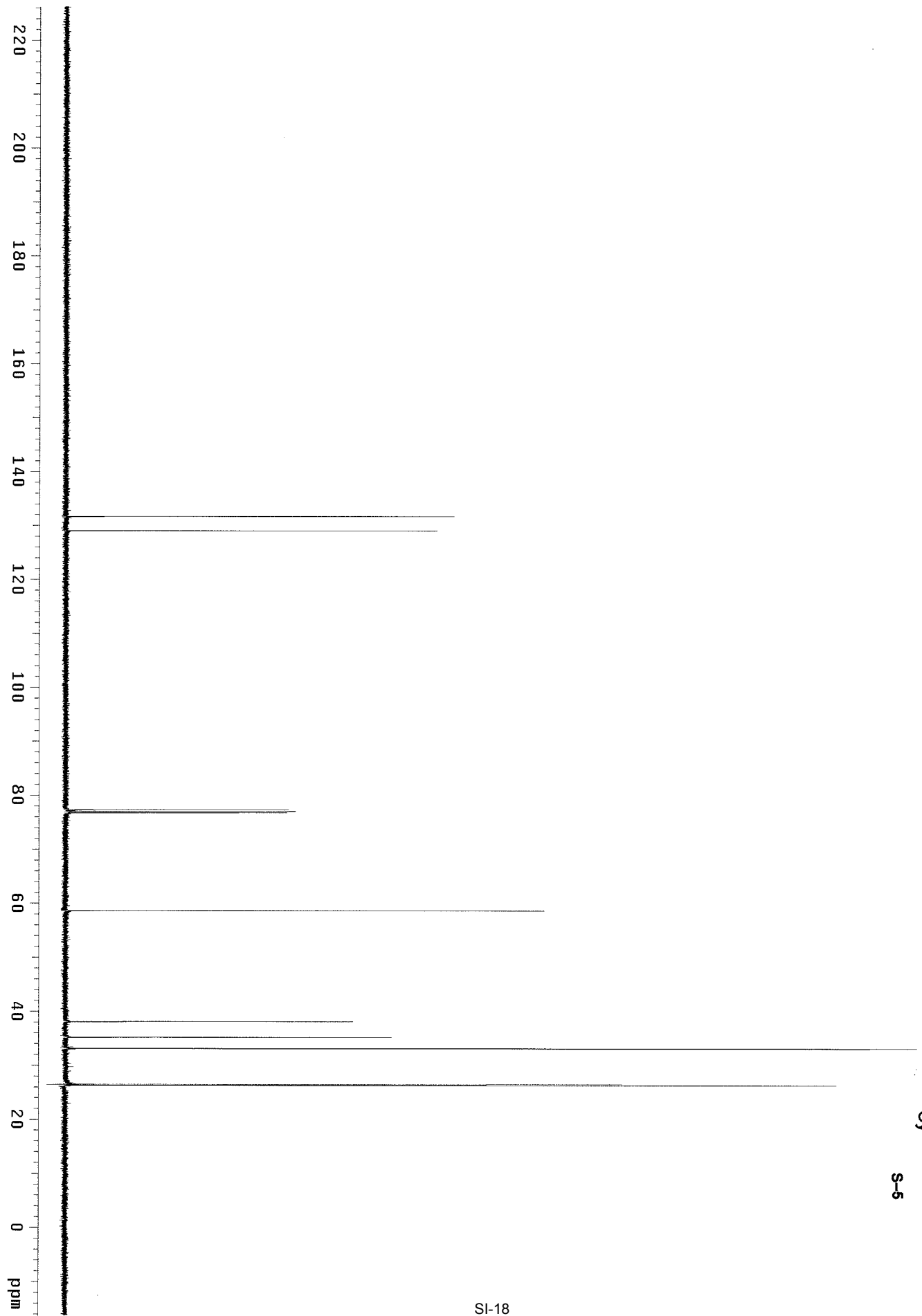


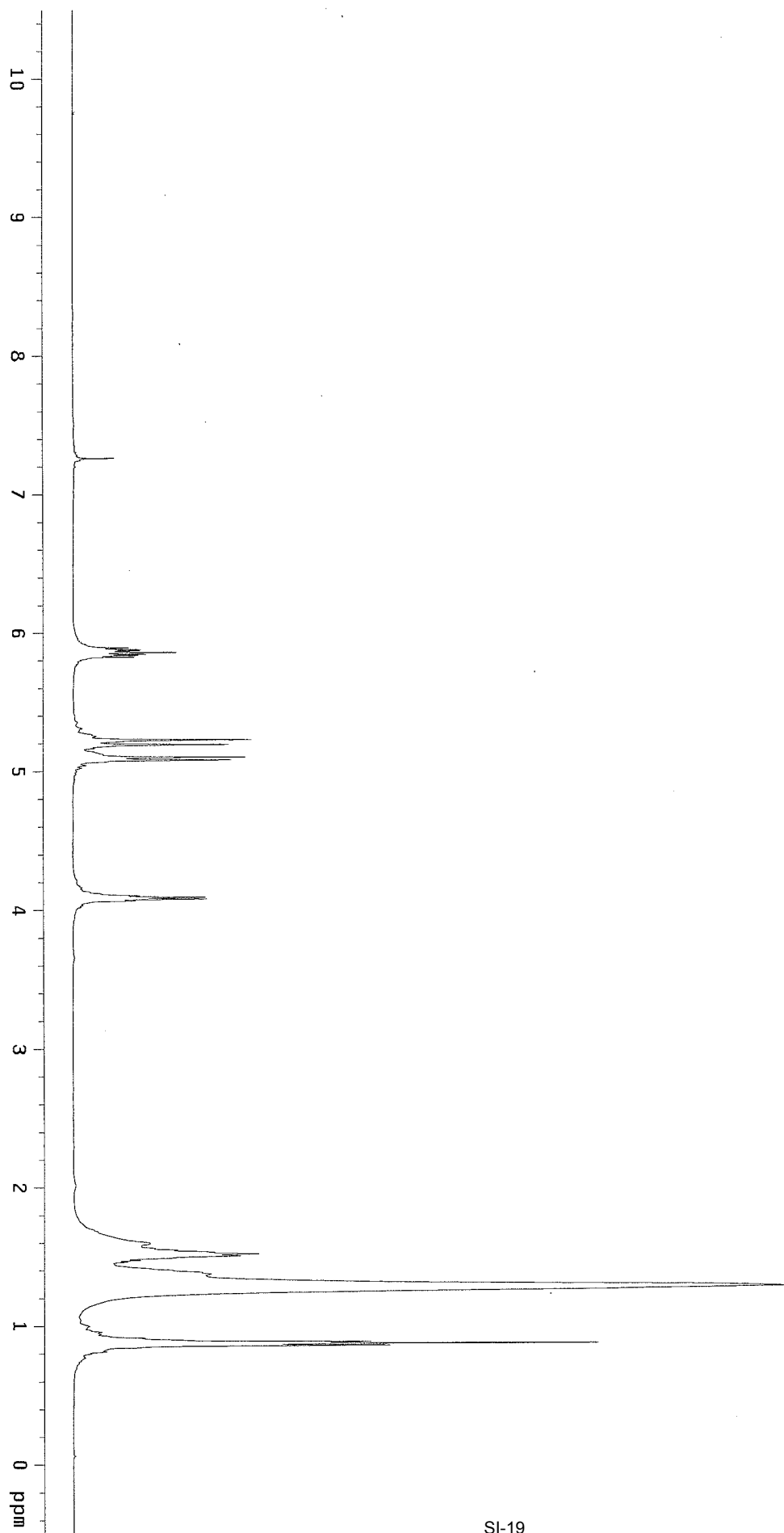
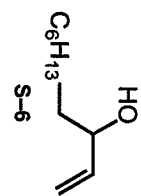


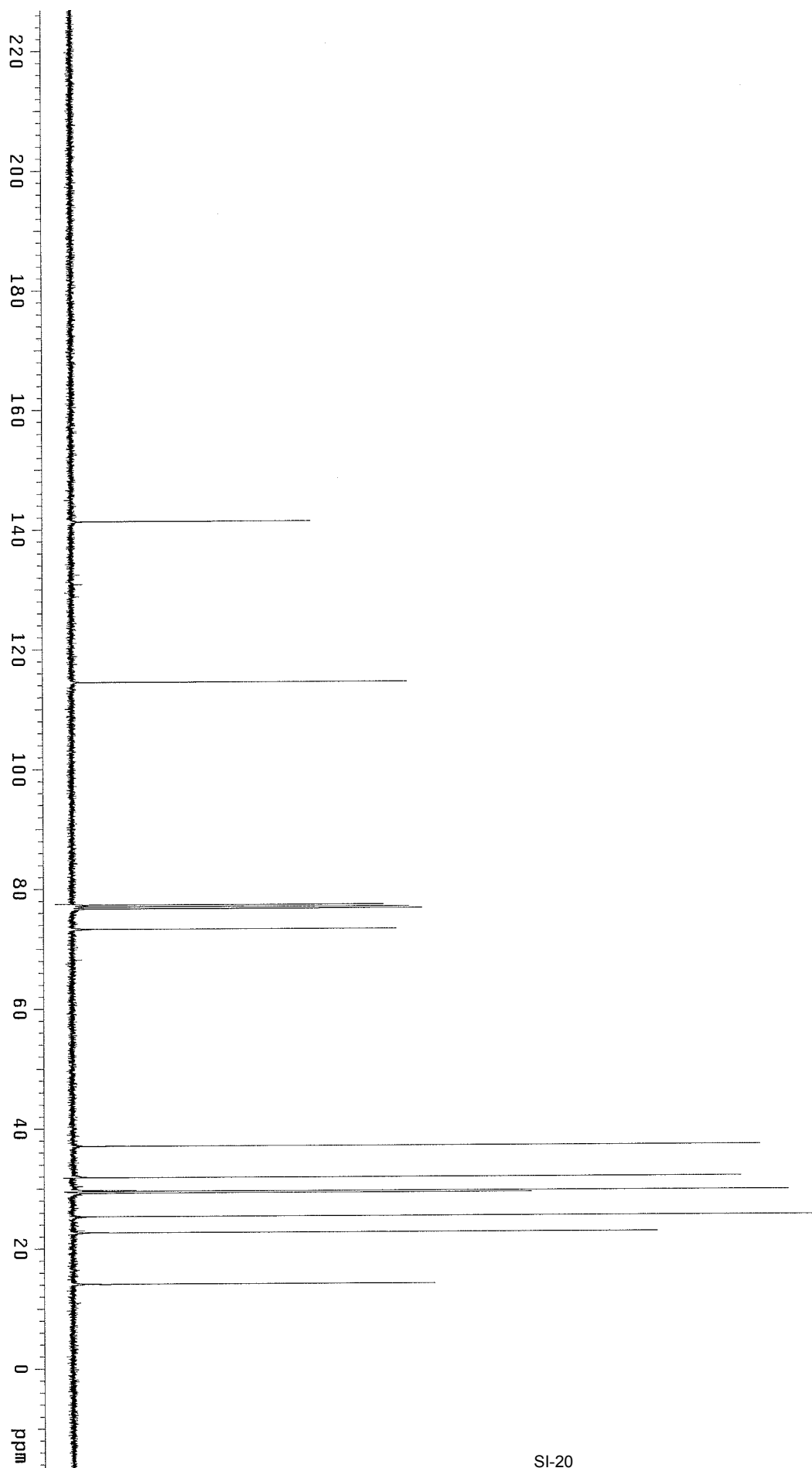
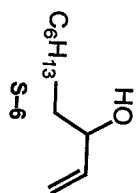


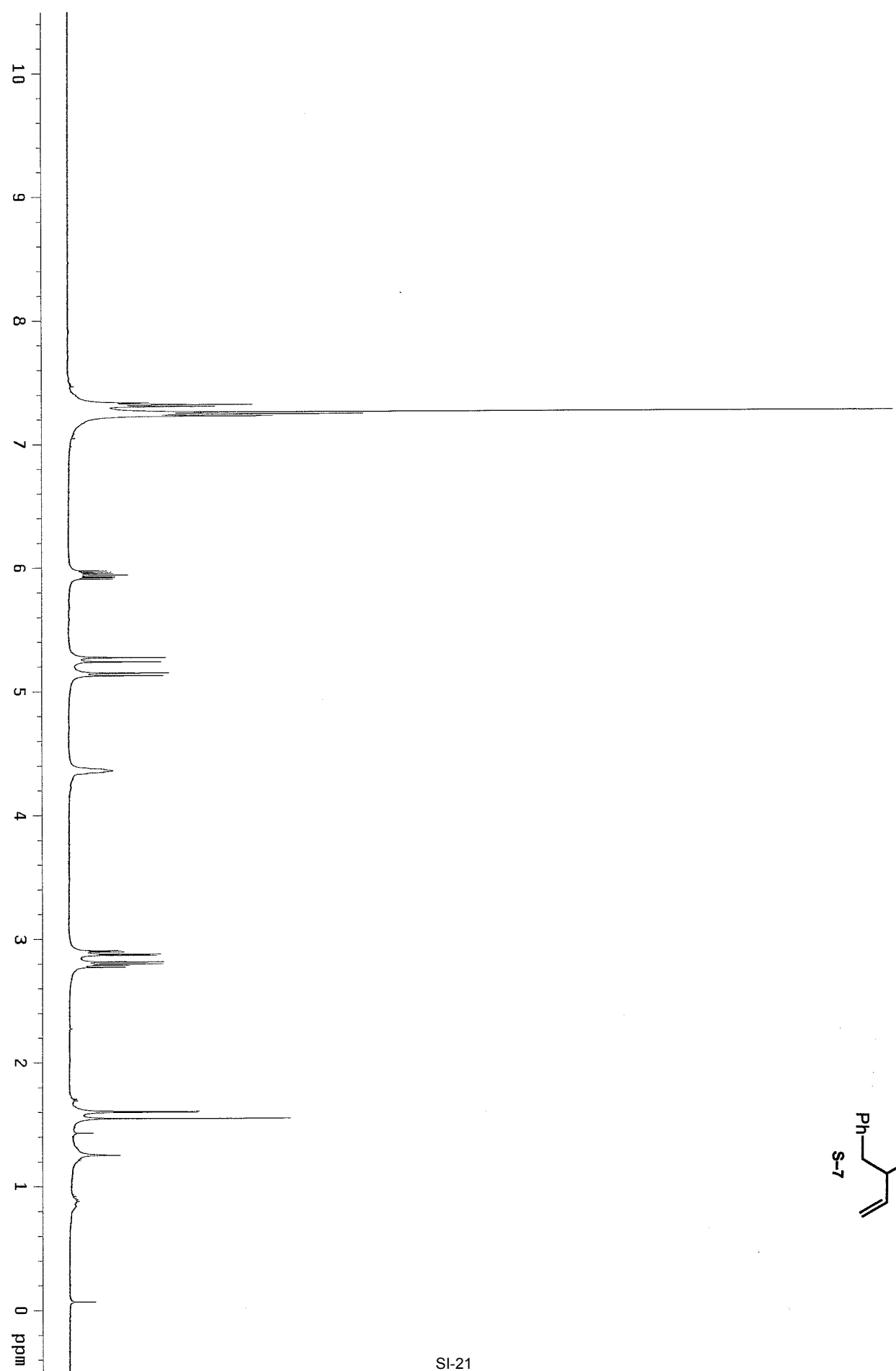
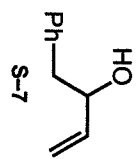


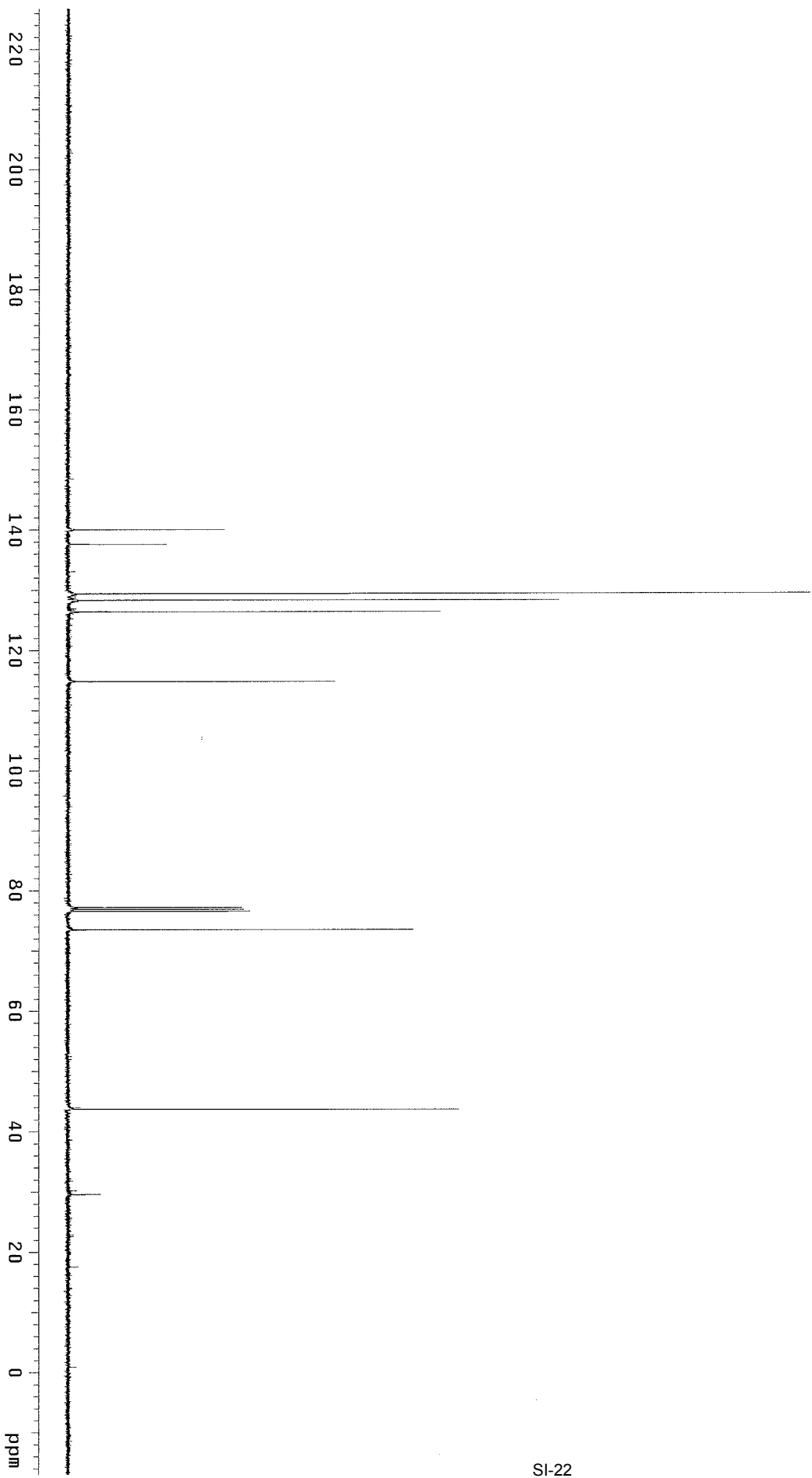
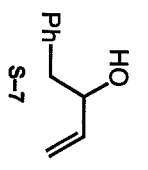


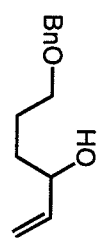




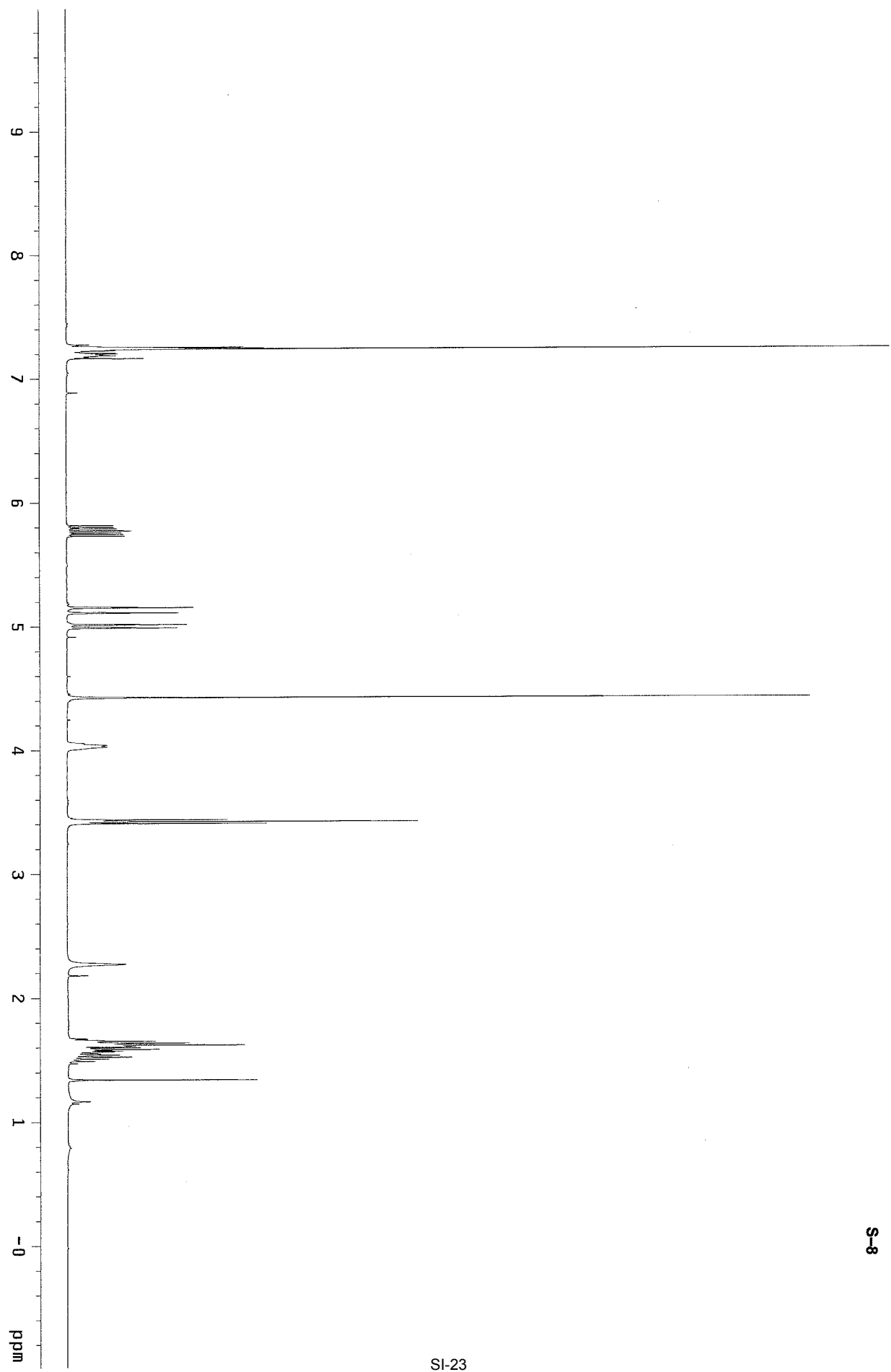


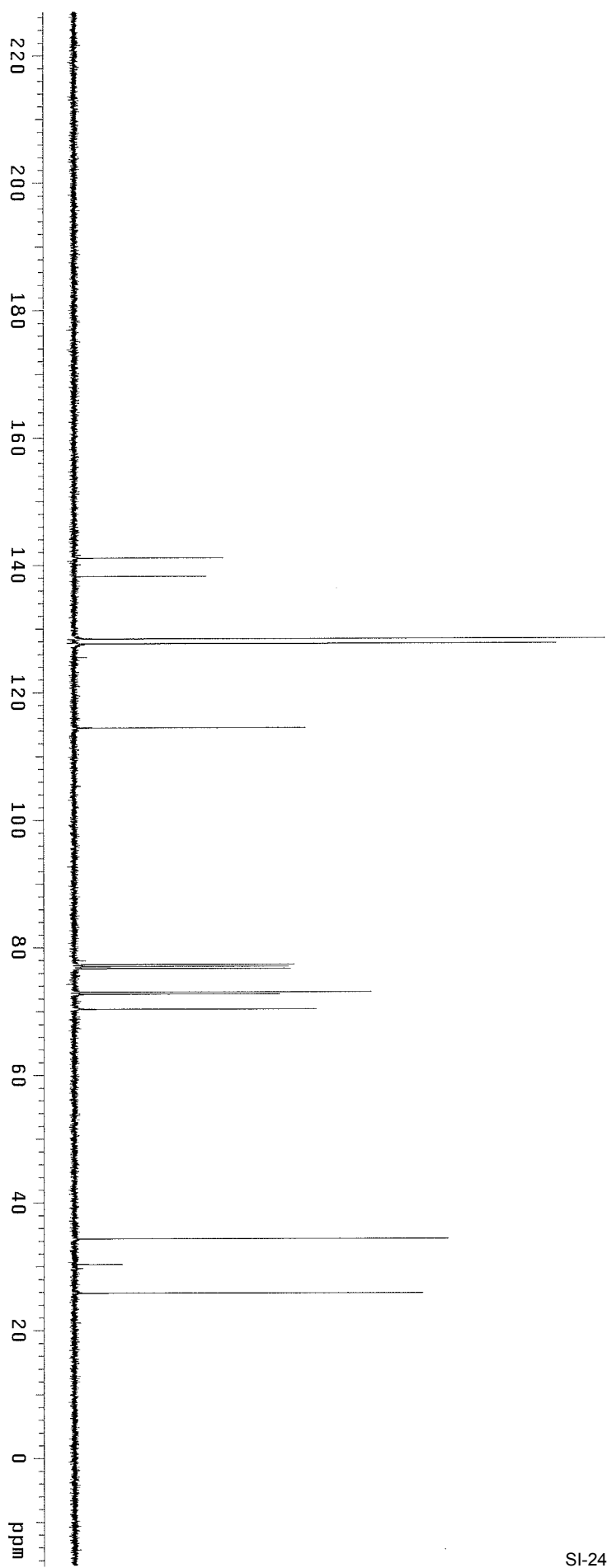
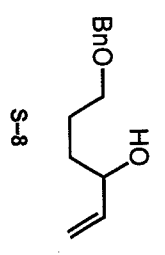


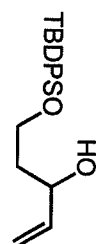
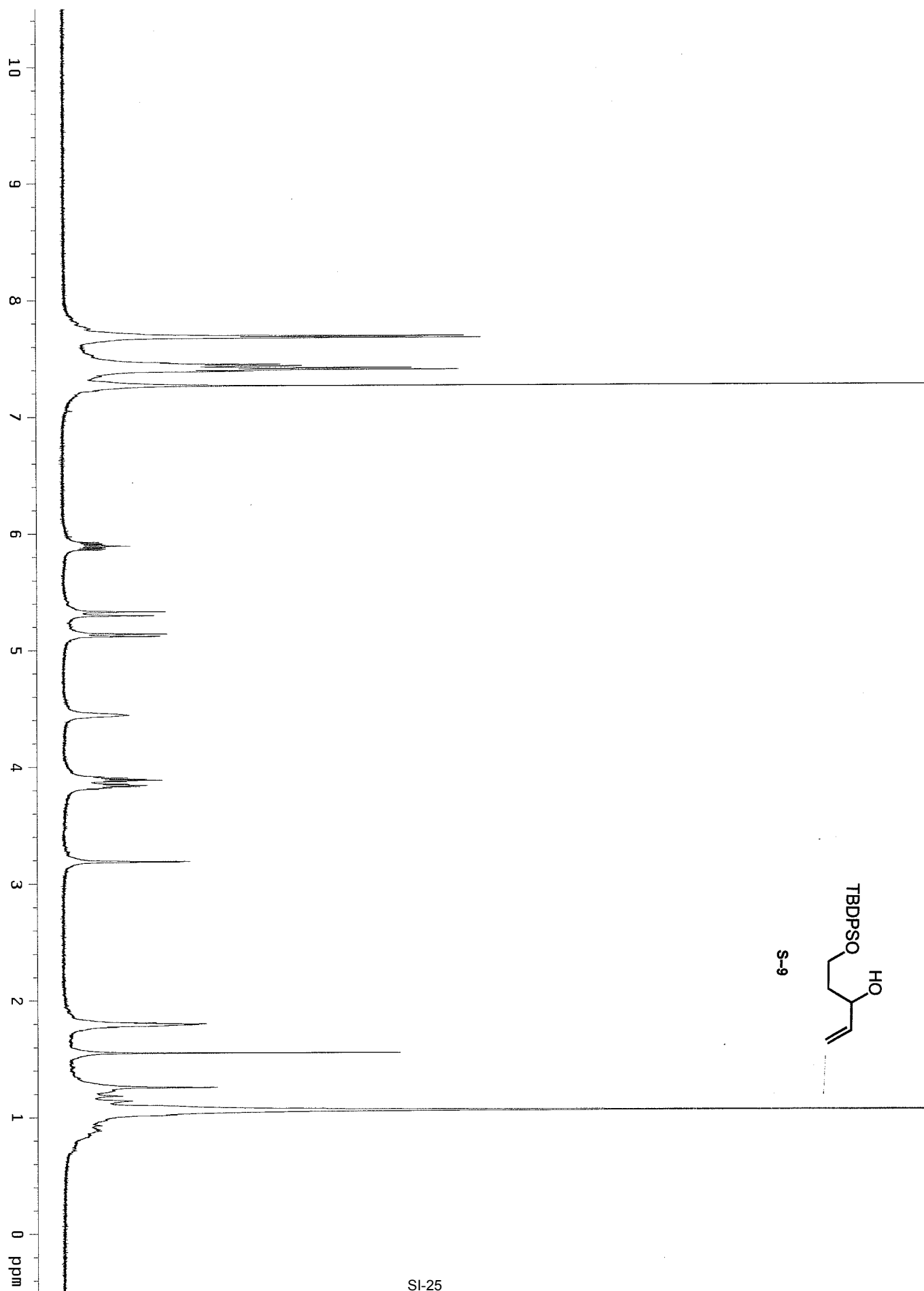




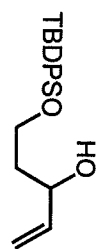
S-8



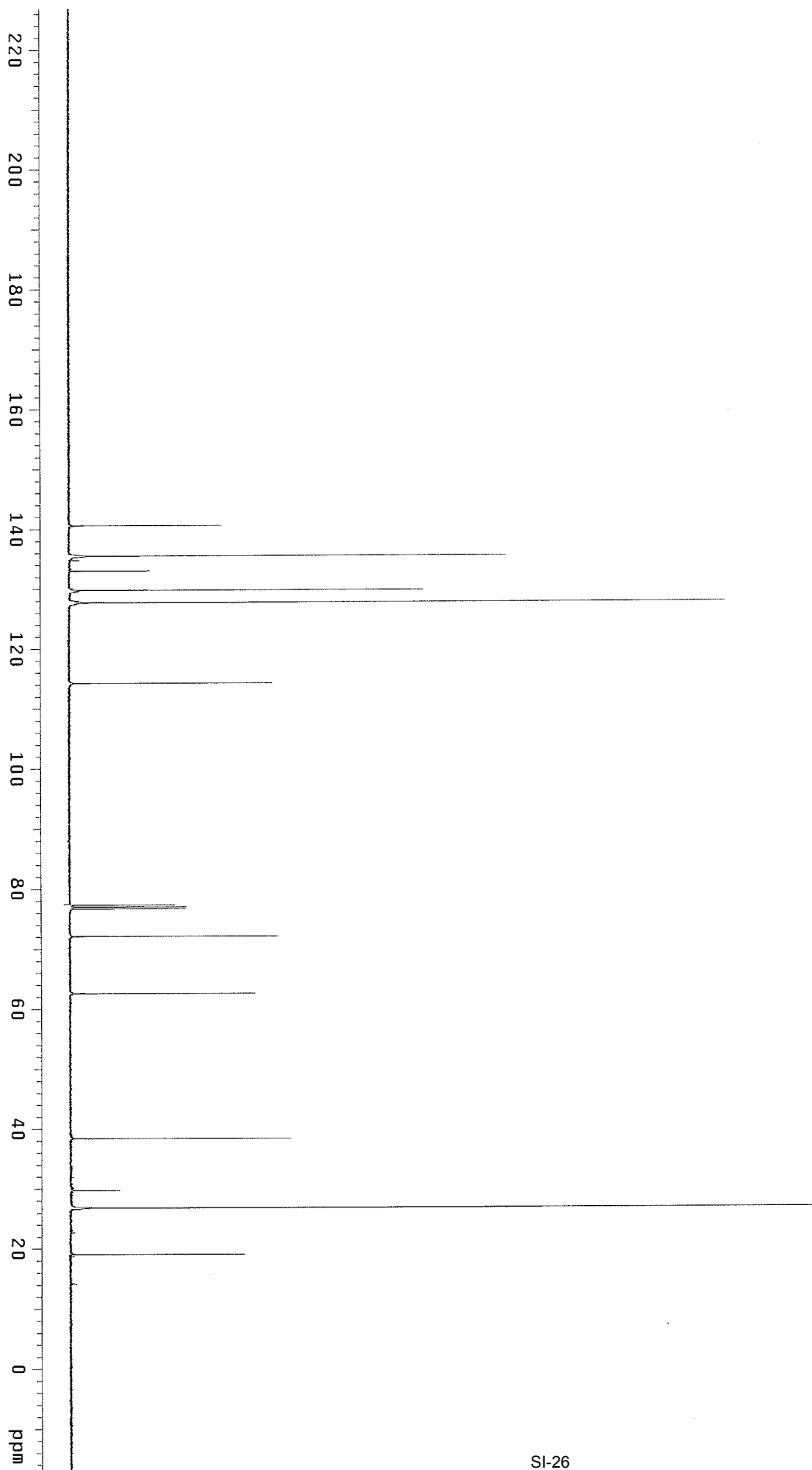


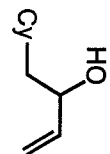


S-9

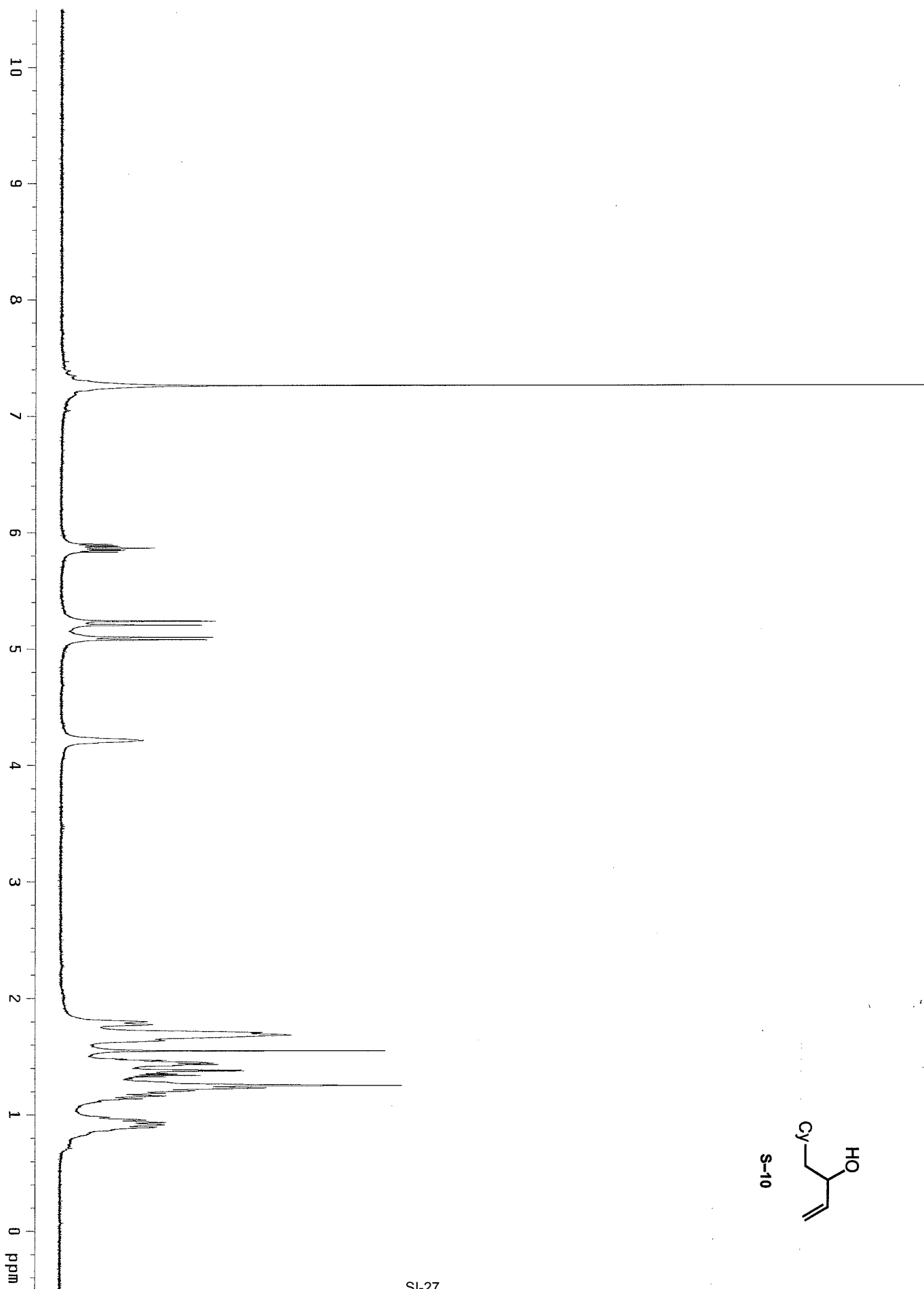


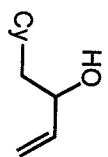
S-9





S-10





S-10

