Supporting Information

Highly Diastereoselective Preparation of *anti*-1,2-Diols by Catalytic Addition of Alkynylsilanes to α-Silyloxyaldehydes

Kanicha Sa-ei and John Montgomery*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

jmontg@umich.edu

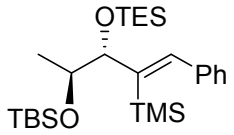
Unless otherwise noted, all reactions were conducted in flame-dried glassware under a nitrogen atmosphere. Tetrahydrofuran was purified with an Innovative Technologies SPS-400 solvent system under nitrogen. $Ni(COD)_2$ (Strem Chemicals Inc., used as received), 1,3-dimesitylimidazolium chloride[1] (**1**) and *tert*-butoxide (Acros, Fisher Scientific International Inc., used as received) were stored and weighed in an argon or nitrogen inert atmosphere glovebox. All alkynes (Sigma-Aldrich) were distilled and stored under nitrogen gas. All aldehydes were freshly prepared or re-purified with column chromatography (SiO_2) and flushed with nitrogen gas before using. ^1H and ^{13}C spectra were obtained in $CDCl_3$ at rt, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.21 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the

University of Michigan Mass Spectrometry Laboratory. Where the diastereomers are separable, data for the pure major diastereomer is provided; where the diastereomers are not separable, ^{1}H NMR assignments for the minor isomer are tentative in overlapping regions. A complete list of all resolved peaks in the ^{13}C NMR is provided.

General Procedure for Ni-catalyzed Diastereoselective Coupling Reaction:

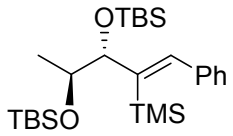
Tetrahydrofuran (4.0 mL) was added to a solid mixture of imidazolium chloride salt **1** (17.0 mg, 0.050 mmol), potassium *t*-butoxide (6 mg, 0.05 mmol) and $Ni(COD)_2$ (14 mg, 0.05 mmol) at rt. The resulting solution was stirred for 5 min until the color turned dark blue. The silane (200 mol %) was added, followed by addition of a tetrahydrofuran solution (1.0 mL) of the aldehyde (0.50 mmol) and alkyne (0.60 mmol). The reaction mixture was stirred 1 h at rt or until the aldehyde was consumed. The reaction mixture was quenched with 50% sodium bicarbonate solution and was extracted with diethyl ether three times. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash chromatography (SiO_2) to afford the desired product. The diastereoselectivities were determined by crude NMR and/or GC-MS.

Table 1 Optimization of Diastereoselectivity



(3*S*,4*S*,*Z*)-4-(*tert*-Butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (Entry 1)

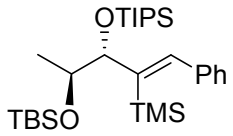
Following the general procedure, (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal[2] (94 mg, 0.50 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (104 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triethylsilane (116 mg, 1.0 mmol) gave, after column chromatography (hexanes), 86 mg of (3*S*,4*S*,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (36%, dr 89:11) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.52 (s, 1H), 7.12-7.27 (m, 5H), 4.40 (dd, *J* = 1.6, 2.8 Hz, 1H), 3.81 (dq, *J* = 2.8, 6.4 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.88 (s, 9H), 0.62 (q, *J* = 8.0 Hz, 6H), 0.052 (s, 6H), -0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major diastereomer 143.6, 142.2, 140.8, 128.3, 127.7, 126.7, 80.0, 71.5, 26.0, 18.1, 16.0, 7.0, 5.1, 0.85, 4.3, 4.1; IR (film) 3058, 2954, 1593 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{26}H_{50}O_2Si_3$, 501.3016; found 501.3026.



(3*S*,4*S*,*Z*)-3,4-(Bis-*tert*-butyldimethylsiloxy)-1-phenyl-2-(trimethylsilyl)pent-1-ene (Entry 2)

Following the general procedure, (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal[2] (94 mg, 0.50 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (104 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and *t*-butyldimethylsilane (116 mg, 1.0 mmol) gave, after column chromatography (hexanes), 116 mg of (3*S*,4*S*,*Z*)-3,4-(bis-*tert*-butyldimethylsiloxy)-1-phenyl-2-(trimethylsilyl)pent-1-ene (48%, dr 88:12) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer

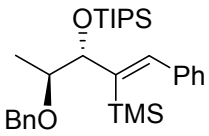
7.51 (s, 1H), 7.16-7.26 (m, 3H), 7.10-7.12 (m, 2H), 4.39 (dd, *J* = 2.0, 2.8 Hz, 1H), 3.79 (dq, *J* = 2.8, 6.4 Hz, 1H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.04 (s, 9H), -0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 143.4, 142.5, 140.8, 128.3, 127.7, 126.7, 79.9, 71.4, 26.0, 25.98, 18.4, 18.1, 15.7, 0.8, -4.18, -4.24, -4.4, -4.6; IR (film) 3058, 3023, 2955, 2857, 1593 cm^{-1}; HRMS ES$^+$ (*m/z*): $[M+Na]^+$ calc for $C_{26}H_{50}O_2Si_3$ 501.3016; found 501.3021.



(3*S*,4*S*,*Z*)-4-(*tert*-Butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (Entry 3)

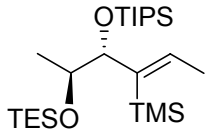
Following the general procedure, (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal[2] (94 mg, 0.50 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (104 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17.0 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 196 mg of (3*S*,4*S*,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (75%, dr 89:11) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 7.61 (s, 1H), 7.18-7.27 (m, 3H), 7.12-7.14 (m, 2H), 4.70-4.71 (m, 1H), 3.81 (dq, *J* = 1.6, 6.0 Hz, 1H), 1.03-1.19 (m, 24H), 0.88 (s, 9H), 0.05 (s, 6H), -0.08 (s, 9H), minor diastereomer: 7.63 (s, 1H), 7.18-7.27 (m, 3H), 7.12-7.14 (m, 2H), 4.69 (dd, *J* = 1.2, 4.0 Hz, 1H), 3.96-3.48 (m, 1H), 1.03-1.19 (m, 24H), 0.89 (s, 9H), 0.08 (s, 6H), -0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers 143.6, 142.0, 140.8, 128.5, 128.3, 127.8, 127.7, 126.7, 79.4, 71.9, 26.2, 26.0, 18.4, 18.3, 18.2, 18.1,

14.6, 12.9, 12.4, 1.2, 0.60, -4.2, -4.3, IR (film) 3057, 3023, 2944, 2805, 1593 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{29}H_{56}O_2Si_3$, 543.3486; found 543.3492.



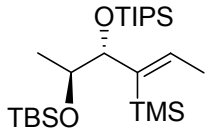
(3*S*,4*S*,*Z*)-4-Benzyloxy-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (Entry 4)

Following the general procedure, (*S*)-2-(benzyloxy)propanal[3] (164 mg, 1.0 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (209 mg, 1.2 mmol), $Ni(COD)_2$ (28 mg, 0.05 mmol), imidazolium salt **1** (34.0 mg, 0.1 mmol), *t*-BuOK (11 mg, 0.1 mmol) and triisopropylsilane (316 mg, 2.0 mmol) gave, after column chromatography (3% diethyl ether in hexanes), 401 mg of (3*S*,4*S*,*Z*)-4-benzyloxy-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (81%, dr 78:22) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 7.62 (s, 1H), 7.12-7.35 (m, 5H), 4.80 (m, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.45 (dq, *J* = 2.0, 6.0 Hz, 1H), 1.03-1.14 (m, 24H), -0.16 (s, 9H), minor diastereomer: 7.59 (s, 1H), 7.12-7.35 (m, 5H), 4.76 (d, *J* = 4.4 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.68 (dq, *J* = 1.6, 6.0 Hz, 1H), 1.03-1.14 (m, 24H), -0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.4, 142.9, 142.0, 140.9, 140.7, 139.0, 138.7, 128.5, 128.3, 128.2, 128.1, 127.8, 127.4, 127.2, 126.8, 78.6, 77.6, 70.9, 70.4, 18.3, 18.2, 18.1, 12,7, 12.4, 11.3, 1.2, 0.5; IR (flim) 3061, 3026, 2942, 2864, 1592 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{30}H_{48}O_2Si_2$, 519.3091; found 519.3090.



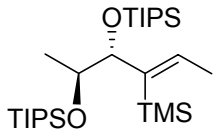
(4*S*,5*S*,*Z*)-5-(Triethylsiloxy)-4-(triisopropylsiloxy)-3-(trimethylsilyl)hex-2-ene (Entry 5)

Following the general procedure, (*S*)-2-(triethylsilyloxy)propanal[4] (94 mg, 0.50 mmol), 1-(trimethylsilyl)-1-propyne (67 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 172 mg of (4*S*,5*S*,*Z*)-5-(triethylsiloxy)-4-(triisopropylsiloxy)-3-(trimethylsilyl)hex-2-ene (75%, dr 81:19) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer; 6.43 (dq, *J* = 1.2, 7.2 Hz, 1H), 4.39 (m, 1H), 3.59 (dq, *J* = 2.2, 6.4 Hz, 1H), 1.75 (dd, *J* = 1.2, 7.2 Hz, 3H), 0.96-1.04 (m, 24H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.54 (q, *J* = 8 Hz, 6H), 0.11 (s, 9H); minor diastereomer: 6.38 (q, *J* = 7.2 Hz, 1H), 4.46 (m, 1H), 3.84 (dq, *J* = 4.6, 6.0 Hz, 1H), 1.79 (d, *J* = 7.2 Hz, 3H), 0.96-1.04 (m, 24H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers: 139.9, 139.0, 137.4, 79.1, 72.6, 72.0, 18.2, 18.1, 17.6, 17.5, 12.8, 12.6, 6.9, 5.1, 4.9, 0.6, 0.04; IR (film) 2953, 2867, 1617 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{24}H_{54}O_2Si_3$, 481.3329; found 481.3330.



(4*S*,5*S*,*Z*)-5-(*tert*-Butyldimethylsiloxy)-4-(triisopropylsiloxy)-2-(trimethylsilyl)hex-2-ene (Entry 6)

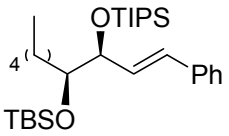
Following the general procedure, (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal[2] (94 mg, 0.50 mmol), 1-(trimethylsilyl)-1-propyne (67 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 185 mg of (4*S*,5*S*,*Z*)-5-(*tert*-butyldimethylsiloxy)-4-(triisopropylsiloxy)-2-(trimethylsilyl)hex-2-ene (81%, dr 89:11) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 6.40 (dq, *J* = 0.8, 6.8 Hz, 1H), 4.34(m, 1H), 3.53 (dq, *J* = 2.0, 6.4 Hz, 1H), 1.69 (dd, *J* = 1.2, 7.2 Hz, 3H), 0.93-0.98 (m, 21H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.78 (s, 9H), 0.05 (s, 9H), -0.057 (s, 3H), -0.06(s, 3H), minor diastereomer: 6.30-6.36 (m, 1H), 4.29 (d, *J* = 4.0 Hz, 1H), 3.76 (dq, *J* = 4.4, 6.0 Hz, 1H), 1.73 (dd, *J* = 0.8, 7.2 Hz, 3H), 0.93-0.98 (m, 21H), 0.86 (d, *J* = 6.0 Hz, 3H), 0.78 (s, 9H), 0.06 (s, 9H), -0.057 (s, 3H), -0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers: 140.0, 137.5, 79.2, 72.4, 26.2, 26.0, 18.28, 18.23, 18.15, 18.08, 17.5, 12.7, 12.4, 0.6, 0.1, -4.1, -4.4; IR (film) 2944, 1617 cm^{-1}; HRMS ES$^+$ (*m/z*): $[M+Na]^+$ calc for $C_{24}H_{54}O_2Si_3$, 481.3329; found 481.3333.



(4*S*,5*S*,*Z*)-4,5-(Bistriisopropylsiloxy)-2-(trimethylsilyl)hex-2-ene (Entry 7)

Following the general procedure, (*S*)-2-(triisopropylsilyloxy)propanal[2] (116 mg, 0.50 mmol), 1-(trimethylsilyl)-1-propyne (67 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 182 mg of (4*S*,5*S*,*Z*)-4,5-(bistriisopropylsiloxy)-2-(trimethylsilyl)hex-2-ene (73%, dr 88:12)

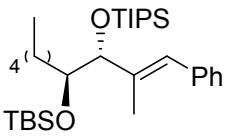
as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 6.42 (dq, *J* = 1.2, 7.2 Hz, 1H), 4.45 (m, 1H), 3.78 (dq, *J* = 2.0, 6.4 Hz, 1H), 1.74 (dd, *J* = 0.8, 7.2 Hz, 3H), 0.89-1.01 (m, 45H), 0.10 (s, 9H), minor isomer: 6.39 (dq, *J* = 0.8, 7.2 Hz, 1H), 4.38 (d, *J* = 3.6 Hz, 1H), 3.89-3.95 (m, 1H), 1.78, (dd, *J* = 0.8, 7.2 Hz, 3H), 0.89-1.01 (m, 45H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers: 140.2, 139.2, 137.5, 128.0, 127.9, 127.6, 127.2, 127.1, 78.9, 78.8, 71.2, 70.5, 18.18, 18.14, 18.13, 18.10, 17.6, 17.5, 12.6, 12.4, 0.69, 0.04; IR (flim) 2943, 2865, 1617 cm^{-1}; HRMS ES^{+} (*m/z*): $[M+Na]^{+}$ calc for $C_{27}H_{60}O_2Si_3$, 523.3799; found 523.3809.



(3*S,4*S**,*E*)-4-(*tert*-Butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)non-1-ene (Entry 8)**

Tetrahydrofuran (3.0 mL) was added to a solid mixture of imidazolium chloride salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and $Ni(COD)_2$ (14 mg, 0.05 mmol) at rt. The resulting solution was stirred for 5 min until the color turned to dark blue. Triisopropylsilane (158 mg, 1.0 mmol) was added, followed by addition of a tetrahydrofuran solution (1.0 mL) of 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol). The solution of phenyl acetylene (61 mg, 0.60 mmol) in tetrahydrofuran (1.0 mL) was added by syringe drive over 2 h. The reaction mixture was stirred for 0.5 h after the addition was completed. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with diethyl ether three times. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated *in*

vacuo. The residue was purified via flash chromatography (SiO_2) (2 % diethylether in hexanes) to afford 90 mg of (3*S**,4*S**,*E*)-4-(*tert*-butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)non-1-ene, (19%, dr 59:41) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer:7.26-7.35 (m, 3H), 7.16-7.23 (m, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 16.0, 5.0 Hz, 1H), 4.41 (dt, *J* = 1.2, 4.8 Hz, 1H), 3.65-3.72 (m, 1H), 1.62-1.67 (m, 1H), 1.34-1.49 (m, 2H), 1.14-1.30 (m, 5H), 0.96-1.10 (m, 21H), 0.88 (s, 9H), 0.81-0.87 (m, 3H), 0.07 (s, 3H), 0.04 (s, 3H); minor diastereomer: 7.26-7.35 (m, 3H), 7.16-7.23 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.18 (dd, *J* = 4.0, 8.0 Hz, 1H), 3.65-3.72 (m, 1H), 1.34-1.49 (m, 2H), 1.14-1.30 (m, 6H), 0.96-1.10 (m, 21H), 0.83 (s, 9H), 0.81-0.87 (m, 3H), 0.01 (s, 2H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers: 137.5, 137.2, 131.05, 131.01, 130.00, 129.6, 128.5, 128.4, 127.2, 127.0, 126.4, 126.3, 77.8, 76.9, 75.9, 75.6, 33.9, 32.1, 31.9, 30.6, 29.7, 26.0, 25.9, 25.0, 22.63, 22.61, 18.22, 18.18, 18.15, 18.11, 18.09, 14.1, 14.0, 12.5, 12.4, -4.0, -4.1, -4.5, -4.6; IR (film) 3027, 2955, 2865 cm^{-1}; HRMS ES$^+$ (*m/z*): $[M+Na]^+$ calc for $C_{24}H_{54}O_2Si_3$, 527.3717; found 527.3711.

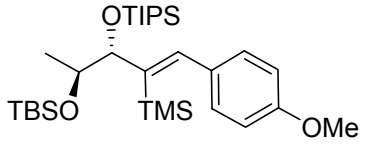


((3*R,4*S**,*E*)-4-(*tert*-Butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-methylnon-1-ene (Entry 9)**

Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol), phenylpropyne (70 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg,

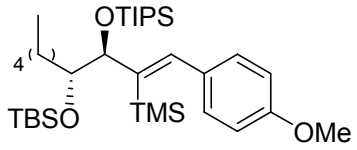
1.0 mmol) gave, after column chromatography (2 % diethyl ether in hexanes), 217 mg of ((3*R**,4*S**,*E*)-4-(*tert*-butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-methylnon-1-ene (82%, dr 73:27) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 7.31-7.14 (m, 5H), 6.38 (s, 1H), 4.14 (d, *J* = 4.0 Hz, 1H), 3.73(q, *J* = 5.6 Hz, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.17-1.54 (m, 8H), 1.02-1.07 (m, 21H), 0.84 (s, 9H), 0.80-0.87 (m, 3H), 0.02 (s, 3H), 0.01 (s, 3H); minor diastereomer: 7.31-7.14 (m, 5H), 6.56 (s, 1H), 4.27 (d, *J* = 4.0 Hz, 1H), 3.76 (q, *J* = 4.0 Hz, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.17-1.54 (m, 8H), 1.02-1.07 (m, 21H), 0.87 (s, 9H), 0.80-0.87 (m, 3H), 0.08 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomer: 139.2, 138.4, 138.2, 138.0, 129.1, 129.0, 127.99, 127.96, 127.2, 126.1, 126.0, 125.9, 81.7, 79.4, 76.0, 33.5, 32.2, 32.1, 31.5, 26.0, 25.97, 25.2, 22.7, 18.23, 18.19, 18.14, 18.10, 17.3, 15.3, 14.1, 12.7, 12.4, -3.6, -4.1, -4.5, -4.8; IR (film) 3022, 2928, 2864 cm^{-1}; HRMS ES^{+} (*m/z*): $[M+Na]^{+}$ calc for $C_{31}H_{68}O_2Si_2$, 541.3873, found 541.3884.

Table 2 Examination of Reaction Scope



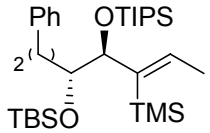
((3*S*,4*S*,*Z*)-4-(*tert*-Butyldimethylsiloxy)-1-(4-methoxyphenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (Entry 3)

Following the general procedure, (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal[2] (94 mg, 0.50 mmol), (4-ethoxyphenylethynyl) trimethylsilane (122 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (2 % diethyl ether in hexanes), 222 mg of ((3*S*,4*S*,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-(4-methoxyphenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (81%, dr 89:11) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 7.55 (s, 1H), 7.07-7.10 (m, 2H), 6.79-6.84 (m, 2H), 4.70-4.71 (m, 1H), 3.78-3.83 (m, 1H), 3.79 (s, 3H), 1.01-1.18 (m, 24H), 0.89 (s, 9H), 0.06 (s, 6H), -0.04 (s, 9H), minor diastereomer: 7.57 (s, 1H), 7.13-7.15 (m, 2H), 6.79-6.84 (m, 2H), 4.67 (dd, J = 1.6, 4.0 Hz, 1H), 3.78-3.83 (m, 1H), 3.79 (s, 3H), 1.01-1.18 (m, 24H), 0.91 (s, 9H), 0.09 (s, 6H), -0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2 diastereomers: 158.6, 142.4, 141.6, 133.2, 129.7, 129.5, 113.1, 79.4, 72.0, 55.2, 26.2, 26.0, 18.4, 18.3, 18.2, 18.1, 14.7, 12.8, 12.4, 1.3, 0.66, -4.2, -4.3; IR (film) 2964, 2864, 1610, 1507 cm^{-1}; HRMS ES$^+$ (*m/z*): $[M+Na]^+$ calc for $C_{30}H_{58}O_3Si_3$, 573.3592; found 573.3566.



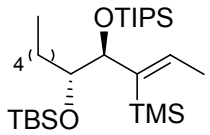
((3*R,4*R**,*Z*)-4-(*tert*-Butyldimethylsiloxy)-1-(4-methoxyphenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)non-1-ene (Entry 4)**

Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol), (4-ethoxyphenylethynyl) trimethylsilane (122 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (2 % diethyl ether in hexanes), 242 mg of ((3*R**,4*R**,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-(4-methoxyphenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)non-1-nene (81%, dr 98:2) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.08-7.06(m, 2H), 6.80-6.84 (m, 2H), 4.69-4.70 (m, 1H), 3.79 (s, 3H), 3.61-3.64 (m, 1H), 1.62-1.69(m, 1H), 1.36-1.50 (m, 2H), 1.04-1.31 (m, 26H), 0.89 (s, 9H), 0.84 (t, J = 6.8 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), -0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 142.3, 142.1, 133.3, 129.4, 113.1, 79.6, 76.2, 55.2, 32.3, 29.5, 26.4, 26.2, 22.6, 18.41, 18.37, 14.1, 12.9, 0.94, -3.2, -4.4; IR (film) 2952, 2864, 1610, 1507 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{34}H_{66}O_3Si_3$, 629.4218; found 629.4231.



((4*R,5*R**,*Z*)-5-(*tert*-Butyldimethoxysiloxy)-7-(phenyl)-4-(triisopropylsiloxy)-3-(trimethysilyl)hept-2-ene (Entry 5)**

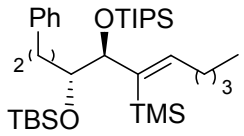
Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)-4-phenylbutanal[6] (139 mg, 0.50 mmol), 1-(trimethylsilyl)-1-propyne (67 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 182 mg of ((3*R**,4*R**,*Z*)-5-(*tert*-butyldimethoxysiloxy)-7-(phenyl)-4-(triisopropylsiloxy)-3-(trimethysilyl)hept-2-ene (85%, dr 98:2) as a colorless oil. ^{1P}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.25 (m, 2H), 7.09-7.15 (m, 3H), 6.53 (q, *J* = 7.2 Hz, 1H), 4.5 (m, 1H), 3.50-3.53 (m, 1H), 2.80 (dt, *J* = 4.8, 12.8 Hz, 1H), 2.47 (dt, *J* = 8.6, 12.8 Hz, 1H), 1.85-1.94 (m, 1H), 1.78 (dd, *J* = 1.2, 7.2 Hz, 3H), 1.66-1.76 (m, 1H), 1.00-1.06 (m, 21H), 0.90 (s, 9H), 0.12 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 139.6, 138.3, 128.29, 128.26, 125.5, 79.2, 76.0, 32.9, 31.4, 26.2, 18.4, 18.33, 18.31, 17.6, 12.8, 0.23, -3.3, -4.4; IR (flim) 3025, 2945, 2864, 1615 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{31}H_{60}O_2Si_3$, 571.3799; found 571.3819.



((4*R,5*R**,*Z*)-5-(*tert*-Butyldimethylsiloxy)-4-(triisopropylsiloxy)-3-(trimethylsilyl)dec-2-ene (Entry 6)**

Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol), 1-(trimethylsilyl)-1-propyne (67 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 218 mg of ((4*R**,5*R**,*Z*)-5-(*tert*-butyldimethylsiloxy)-4-(triisopropylsiloxy)-3-

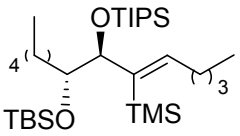
(trimethylsilyl)dec-2-ene (85%, dr 98:2) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (dq, *J* = 1.6, 7.2 Hz, 1H), 4.44 (m, 1H), 3.46 (ddd, *J* = 2.4, 3.6, 6 Hz, 1H), 1.77 (dd, *J* = 1.2, 7.2 Hz, 3H), 1.53- 1.62 (m, 1H), 1.12-1.44 (m, 7H), 1.02-1.05 (m, 21H), 0.86 (s, 9H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.14 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.4, 79.5, 76.8, 32.3, 30.0, 26.3, 26.2, 22.6, 18.4, 18.3, 17.5, 14.0, 12.9, 0.39, -3.3, -4.3; IR (flim) 2929, 2864, 1651 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{28}H_{62}O_2Si_3$, 537.3955; found 537.3973.



((7*R,8*R**,*Z*)-8-(*tert*-Butyldimethylsiloxy)-10-(phenyl)-7-(triisopropylsiloxy)-6-(trimethysilyl)dec-5-ene (Entry 7)**

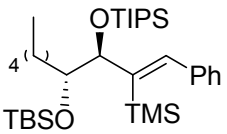
Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)-4-phenylbutanal[6] (139 mg, 0.50 mmol), 1-(trimethylsilyl)-1-hexyne (92 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 249 mg of ((7*R**,8*R**,*Z*)-8-(*tert*-butyldimethylsiloxy)-10-(phenyl)-7-(triisopropylsiloxy)-6-(trimethysilyl)dec-5-ene (85%, dr 98:2) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.17 (m, 2H), 7.01-7.07 (m, 3H), 6.40 (t, *J* = 7.2 Hz, 1H), 4.44 (m, 1H), 3.42-3.45 (m, 1H), 2.74 (ddd, *J* = 4.8, 12.0, 13.2 Hz, 1H), 2.39 (ddd, *J* = 5.6, 12.0, 13.2 Hz, 1H), 2.00-2.11 (m, 2H), 1.78-1.87 (m, 1H), 1.58-1.68 (m, 1H), 1.21-1.28 (m, 4H), 0.94-0.98 (m, 21H), 0.83 (s, 9H), 0.79 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.3, 138.2, 128.3, 128.2, 125.5, 79.0, 76.0, 33.0, 32.0,

31.8, 26.2, 22.6, 18.41, 18.38, 18.36, 14.0, 12.8, 0.48, -3.2, -4.4; IR (film) 3026, 2955, 2864, 1610 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{34}H_{66}O_2Si_3$, 613.4268; found 613.4255.



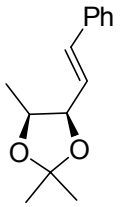
((7*R,8*R**,*Z*)-8-(*tert*-Butyldimethylsiloxy)-7-(triisopropylsiloxy)-6-(trimethysilyl))tridec-5-ene (Entry 8)**

Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol), 1-(trimethylsilyl)-1-hexyne (92 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 216 mg of ((7*R**,8*R**,*Z*)-8-(*tert*-butyldimethylsiloxy)-7-(triisopropylsiloxy)-6-(trimethysilyl)) tridec-5-ene (78%, dr 98:2) as a colorless oil.^{1}H NMR (500 MHz, C_6D_6) δ 6.65-6.74 (m, 1H), 4.71(m, 1H), 3.66-3.73 (m, 1H), 2.23 (septet, *J* = 7.3Hz, 2H), 1.86-1.92 (m, 1H), 1.62-1.71 (m, 2H), 1.27-1.46 (m, 9H), 1.21-1.25 (m, 21H), 1.06 (s, 9H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.28 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 144.7, 128.3, 79.8, 77.0, 32.6, 32.4, 32.2, 27.0, 26.5, 23.0, 22.9, 18.70, 18.69, 14.3, 14.2, 13.3, 0.76, -3.0, -4.1; IR (film) 2955, 1612 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{31}H_{68}O_2Si_3$, 579.4425; found 579.4414.



((3*R,4*R**,*Z*)-4-(*tert*-Butyldimethylsiloxy)-1-(phenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)non-2-ene (Entry 9)**

Following the general procedure, 2-(*tert*-butyldimethylsilyloxy)heptanal[5] (122 mg, 0.50 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (104 mg, 0.60 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17.0 mg, 0.05 mmol), *t*-BuOK (6 mg, 0.05 mmol) and triisopropylsilane (158 mg, 1.0 mmol) gave, after column chromatography (hexanes), 238 mg of ((3*R**,4*R**,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-(phenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)non-2-ene (83%, dr 98:2) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.18-7.7.28 (m, 3H), 7.11-7.13 (m, 2H), 4.70(t, *J* = 1.6 Hz, 1H), 3.61-3.64(m, 1H), 1.61-1.68 (m, 1H), 1.36-1.48 (m, 2H), 1.05-1.29 (m, 26H), 0.87 (s, 9H), 0.82 (t, *J* = 7 Hz, 3H), 0.78 (s, 3H), 0.68 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.5, 140.9, 128.3, 127.8, 126.8, 79.7, 76.1, 32.3, 29.4, 26.5, 26.2, 22.6, 19.4, 18.41, 18.38, 14.1, 12.9, 10.2, 0.87, -3.2, -4.4; IR (flim) 3058, 3023, 2954, 2865, 1593 cm^{-1}; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{33}H_{64}O_2Si_3$, 599.4112; found 599.4101.

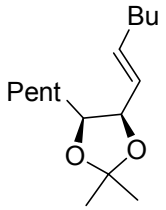


Compound 3a

(4*S*,5*R*)-2,2,4-Trimethyl-5-styryl-1,3-dioxolane

n-Bu_4NF (1.2 mL of a 1.0 M THF solution) was added to dissolve (3*S*,4*S*,*Z*)-4-(*tert*-butyldimethylsiloxy)-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-enyl)benzene (**2a**) (104 mg, 0.20 mmol) at rt The reaction solution was stirred for 3 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with ethyl acetate (10 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash column chromatography (50 % ethyl acetate in hexanes) to afford 174 mg of (2*S*, 3*R*, *E*)-5-phenylpent-4-ene-2, 3-diol (98%) as a white solid. The spectral data were identical to the previous report.[7] $TsOH{\cdot}H_2O$ (2 mg, 0.01 mmol) was added to the solution of (2*S*,3*R*,*E*)-5-phenylpent-4-ene-2, 3-diol (20 mg, 0.12 mmol) in dichloromethane at rt, followed with dimethoxypropane (64 mg, 0.020 mmol). The reaction mixture was stirred for 3 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and was extracted with diethyl ether three times. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash chromatography (2 % diethyl ether in hexanes) to afford 23 mg of (4*S*,5*R*)-2,2,4-trimethyl-5-styryl-1,3-dioxolane (**2b**) (89%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.37 (m, 2H), 7.27-7.31 (m, 2H), 7.20-7.24 (m, 1H), 6.58 (d, *J*

= 16.0 Hz, 1H), 6.13 (dd, *J* = 8.0, 16.0 Hz, 1H), 4.64 (dd, *J* = 8.0, 7.2 Hz, 1H), 4.37 quint, *J* = 6.3 Hz, 1H), 1.52 (s, 3H), 1.38 (s, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 133.2, 128.5, 127.8, 126.6, 125.7, 108.1, 79.8, 74.4, 28.3, 25.6, 16.2; IR (film) 3025, 2983, 1948, 1733, 1653, 1599 cm^{-1}; HRMS EI (*m/z*): $[M]^+$ calc for $C_{14}H_{18}O_2$, 218.1307; found 218.1304.



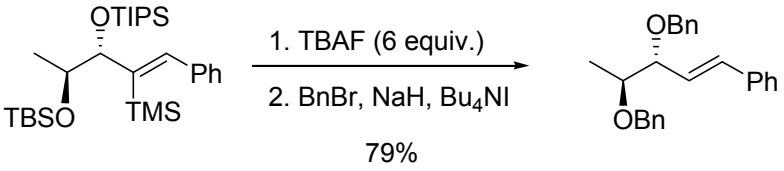
Compound 3b

(4*R,5*S**)-4-((E)-hex-1-enyl)-2,2-dimethyl-5-pentyl-1, 3-dioxolane**

n-Bu_4NF (1.8 mL of a 1.0 M THF solution)) was added to dissolve compound **2b** (100 mg, 0.18 mmol) at 45 ^oC. The reaction solution was stirred for 3 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with ethyl acetate (10 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo* to obtain yellow oil. The residue was dissolved in dichloromethane (1 mL), followed with addition of $TsOH{\cdot}H_2O$ (2 mg, 0.01 mmol) and dimethoxypropane (94 mg, 0.90 mmol) at rt to give a brown resulting solution after stirring for 2 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and was extracted with diethyl ether (10 mL) three times. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash chromatography (2 % diethyl ether in hexanes) to afford 29 mg of (4*R**,5*S**)-4-((*E*)-hex-1-enyl)-2,2-dimethyl-5-

pentyl-1,3-dioxolane (**3b**) (89%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (td, *J* = 6.8, 15.2 Hz, 1H), 5.39 (tdd, *J* = 1.6, 8.4, 15.2 Hz, 1H), 4.39 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.00-4.06 (m, 1H), 1.97-2.05 (m, 2H), 1.42 (s, 3H), 1.30 (s, 3H), 1.20-1.52 (m, 12H), 0.82-0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 126.0, 107.6, 79.8, 78.4, 32.0, 31.9, 31.1, 30.4, 28.4, 25.8, 25.7, 22.5, 22.2, 14.0, 13.9; IR (film) 2930, 2859, 1669 cm^{-1}; HRMS EI (*m/z*): $[M\text{-}Me]^+$ calc for $C_{15}H_{27}O_2$, 239.2011; found 239.2010.

Stereochemical Characterization of Table 1 Entry 3

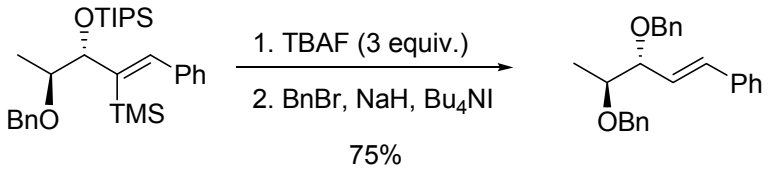


(3*R*,4*S*,*E*)-3,4-Dibenzyloxy-1-phenylpent-1-ene

n-Bu_4NF (1.2 mL of a 1.0 M THF solution) was added to dissolve compound (3*S*,4*S*,*Z*)-4-(*tert*-butyldimethylsiloxy)-1-phenyl-3-(triisopropylsiloxy)-2-(trimethylsilyl)pent-1-ene (**2a**) (104 mg, 0.20 mmol) at rt. The reaction solution was stirred for 3 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with ethyl acetate (10 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo* to afford a brown oil. The residue was dissolved in THF (1.0 mL) and added to the reaction flask which contained NaH (15 mg, 0.62 mmol) and Bu_4NI (7 mg, 0.02 mmol) in THF (2 mL) at rt, followed by addition of benzylbromide (102 mg, 0.60 mmol). The resulting yellow solution was stirred at rt for 4 h. The reaction mixture was quenched with 50% sodium bicarbonate and extracted with diethyl ether (5 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash column chromatography (5 % diethyl ether in hexanes) to afford (3*R*,4*S*,*E*)-3,4-dibenzyloxy-1-phenylpent-1-ene 56 mg (79%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.40 (m, 15H), 6.57 (d, J =16.0 Hz, 1H), 6.20 (ddd, J = 0.8, 8.0, 16.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12.4 Hz, 1H), , 4.58 (d, J = 12.4 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 3.91 (dd, J = 4.8, 8.0 Hz, 1H), 3.67 (quint, J = 6.0 Hz, 1H), 1.23 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 138.8, 138.6, 136.6, 133.9, 128.6, 128.3, 128.2, 127.73, 127.70, 127.66, 127.41, 127.38, 126.6, 83.1, 77.3, 71.4, 70.4, 16.4; IR (film) 3027, 2971, 1949, 1877, 1806, 1717, 1651, 1599 cm^{-1}; ; HRMS ES^+ (*m/z*): $[M+Na]^+$ calc for $C_{25}H_{26}O_2$, 381.1830; found 381.1824.

Stereochemical Characterization from Table 1 Entry 4

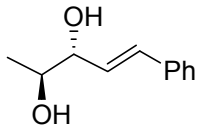


(3*R*,4*S*,*E*)-3,4-Dibenzyloxy-1-phenylpent-1-ene

n-Bu_4NF (0.6 mL of a 1.0 M THF solution) was added to dissolve ((3*S*,4*S*,*Z*)-4-(benzyloxy)-1-(phenyl)-3-(triisopropylsiloxy)-2-(trimethylsilyl)non-2-ene (**table 1 entry 4**) (99 mg, 0.20 mmol) at rt. The reaction solution was stirred for 3 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with ethyl acetate (10 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo* to afford a yellow oil. The residue was dissolved in THF (1.0 mL) and added to the reaction flask which contained NaH (15 mg, 0.62 mmol) and Bu_4NI (7 mg, 0.02 mmol) in THF (2 mL) at rt, followed with addition of benzylbromide (102 mg, 0.60 mmol). The resulting yellow solution was stirred at rt for 4 h. The reaction mixture was quenched with 50% sodium bicarbonate solution and extracted with diethyl ether (5 mL) three times. The combined organic layer was washed with brine and dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified via flash column chromatography (5 %

diethyl ether in hexanes) to afford (3*R*,4*S*,*E*)-3,4-dibenzyloxy-1-phenylpent-1-ene 53 mg (75%) as a light yellow oil.

The major product was identical to that obtained from **Table 1**, **entry 3**.



(*S*, *R*)

Compound 5

(2*S*, 3*R*, *E*)-5-phenylpent-4-ene-2, 3-diol

Beginning from compound **4** (>98 % ee) derived from (*S*)-ethyl lactate, compound **5** was prepared by the procedure given previously in the experimental for compound **3a**. Chiral HPLC analysis (Agilent 1100 series, Chiralcel OD-H, 20% isopropanol in hexane, 1 mL/min) comparing this product to the racemate indicated >98% ee product was obtained.

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3. (*S*)-2-(benzyloxy)propanal; Wuts, G. M. P.; Bigelow, S. S. *J. Org. Chem.* **1983**, *48*, 3489.

4. (*S*)-2-(triethylsilyloxy)propanal; (*S*)-2-(triisopropylsilyloxy)propanal: Cainelli, G.; Panunzio, M.; Bandini, E.; Marteli, G.; Spunta, G. *Tetrahedron* **1996**, *52*, 1685.

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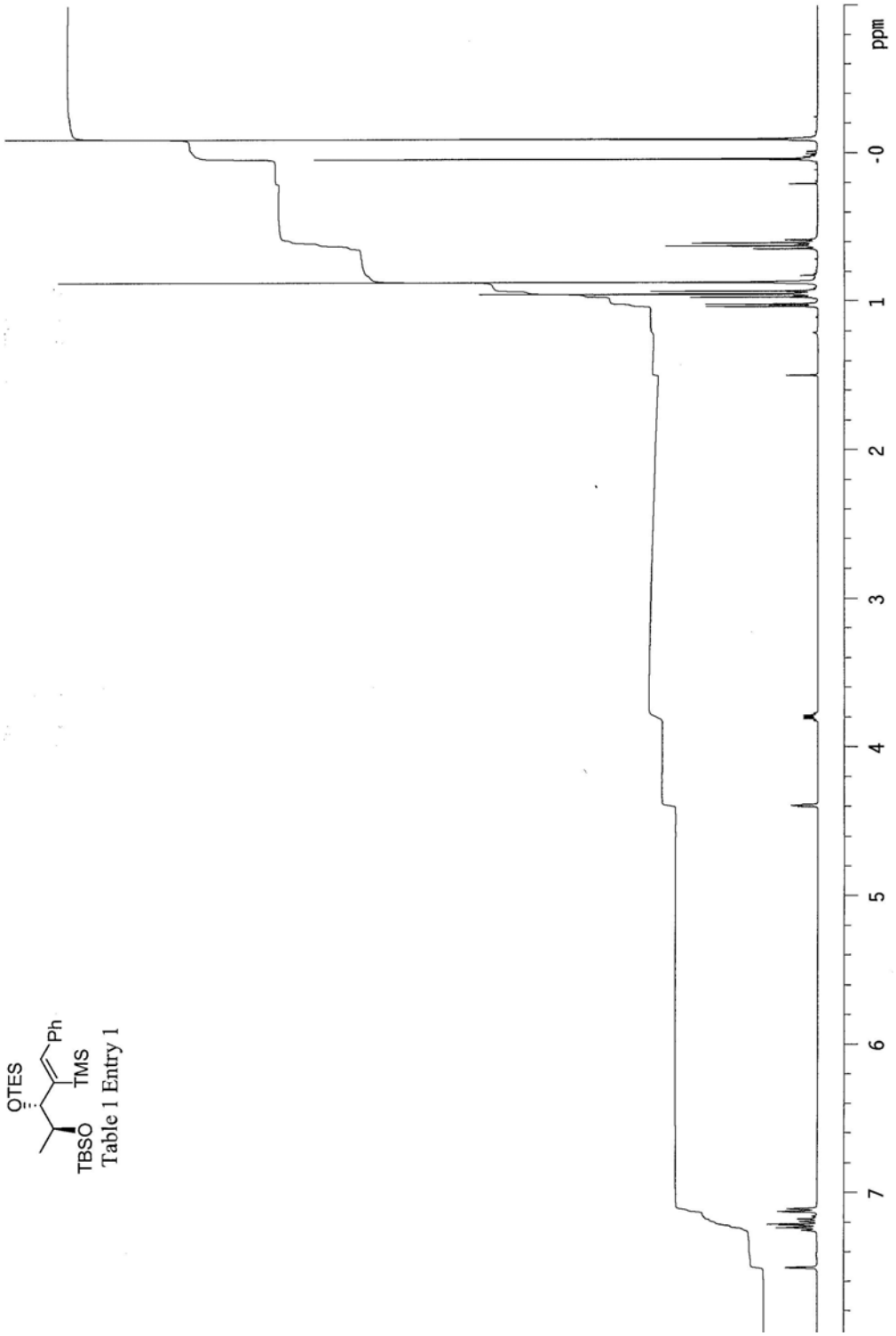

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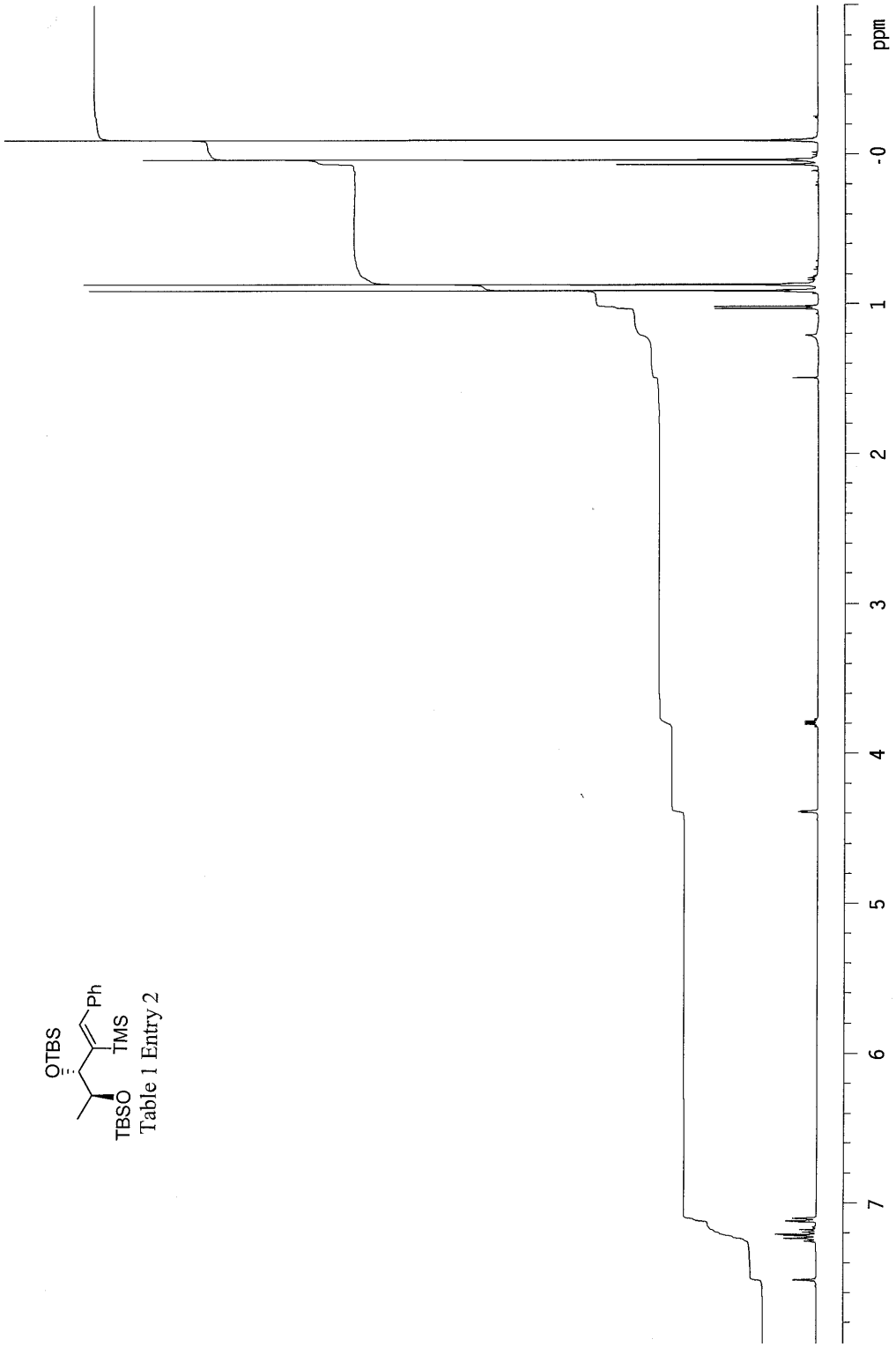

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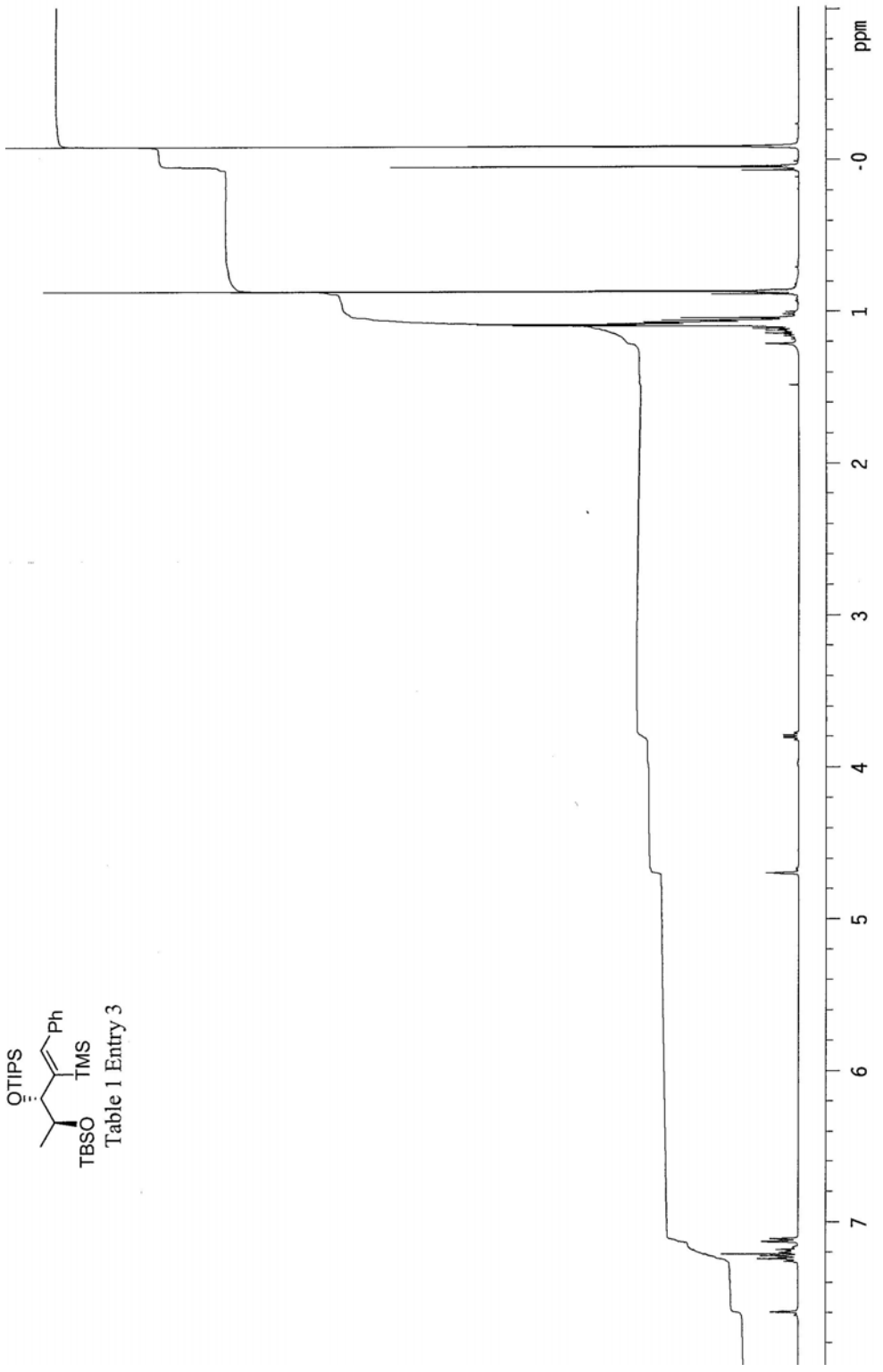

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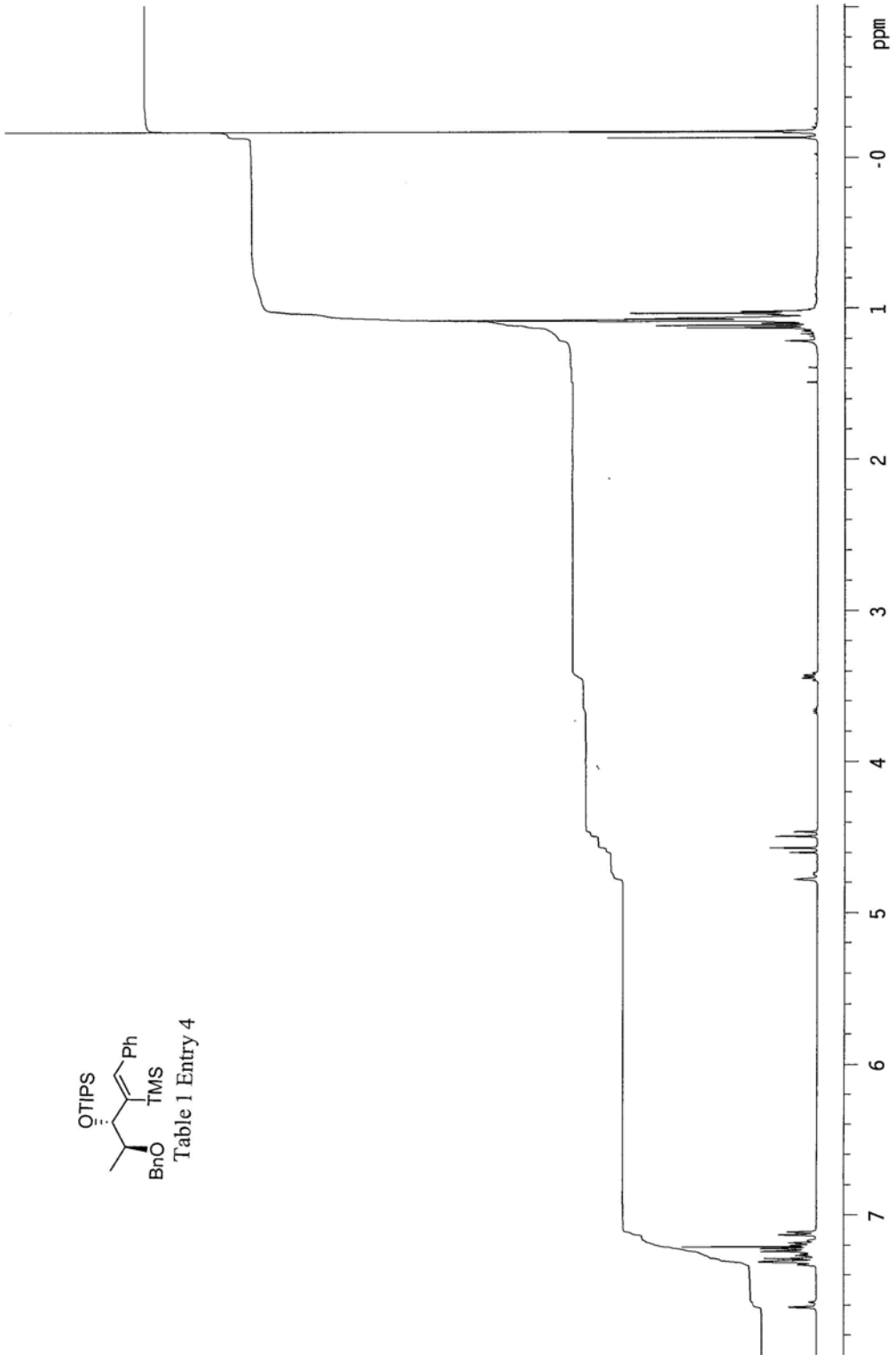

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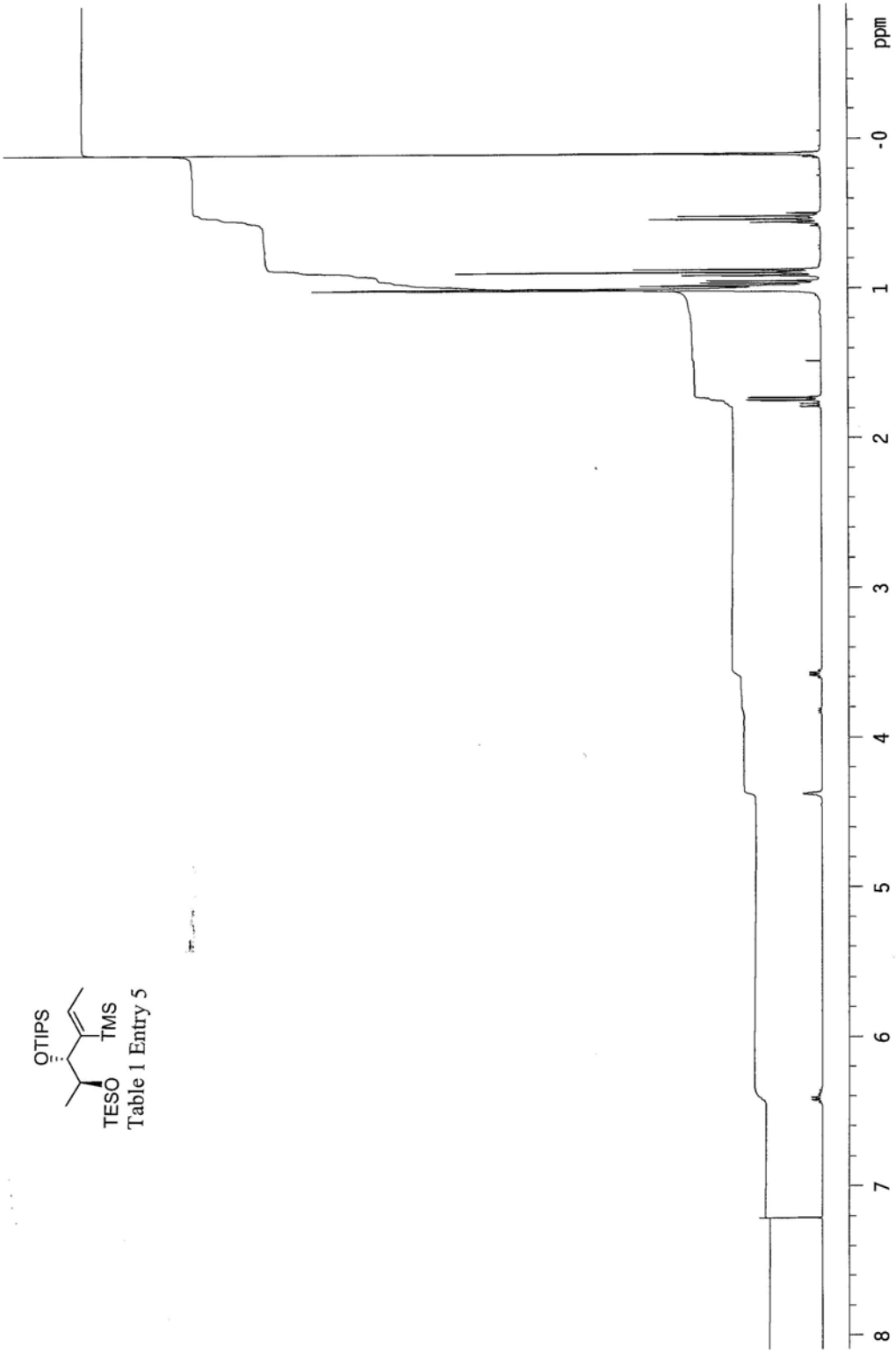

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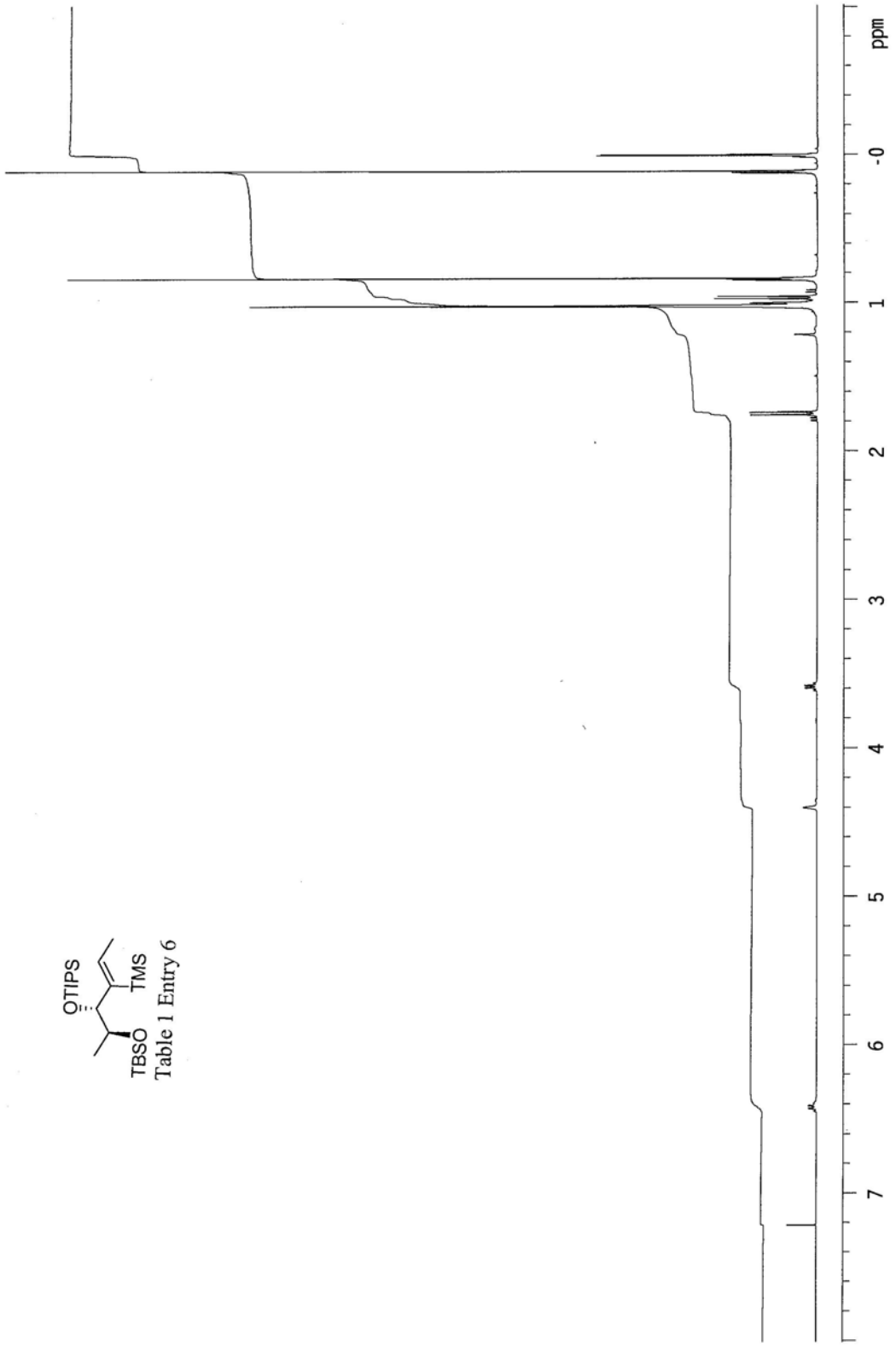

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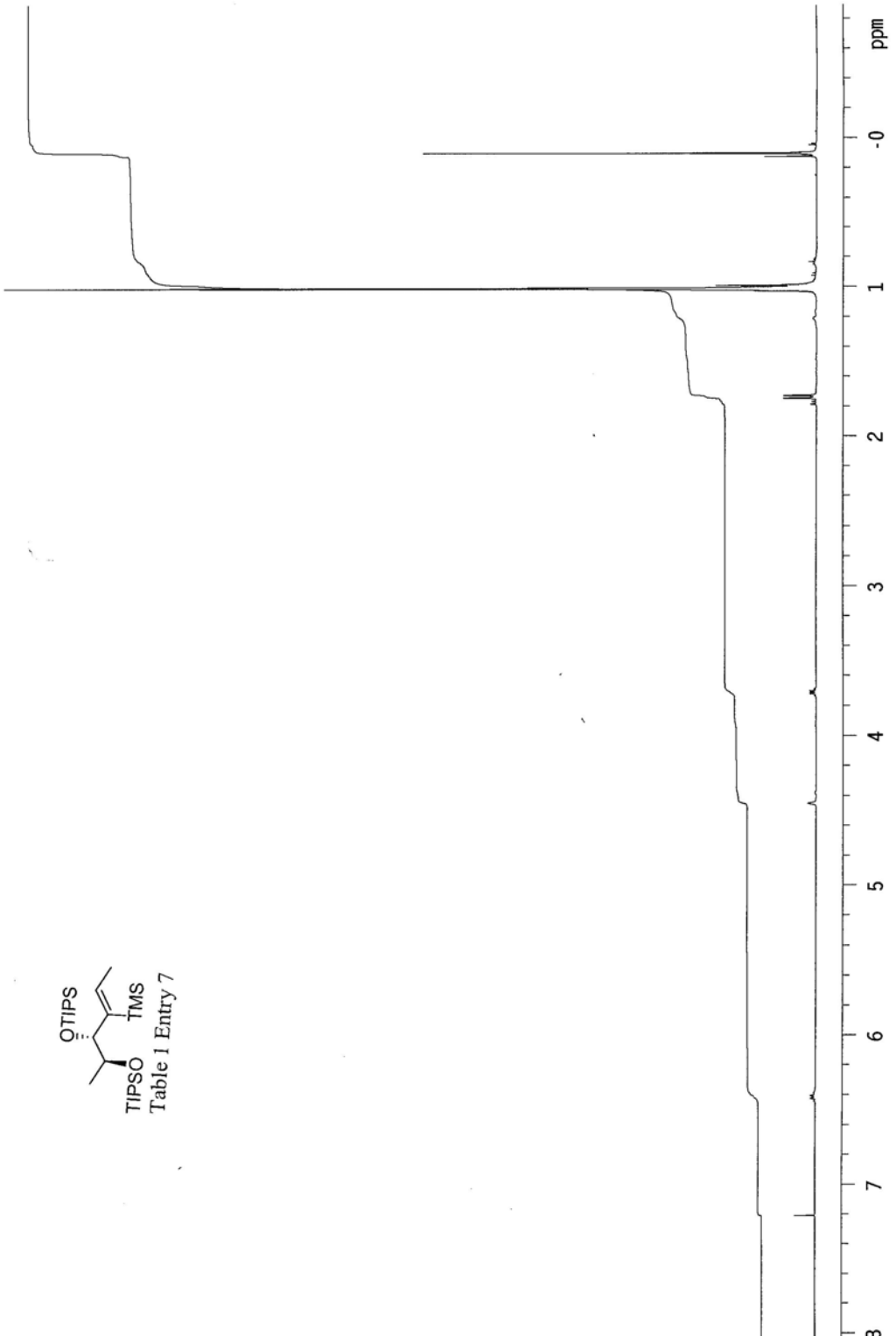

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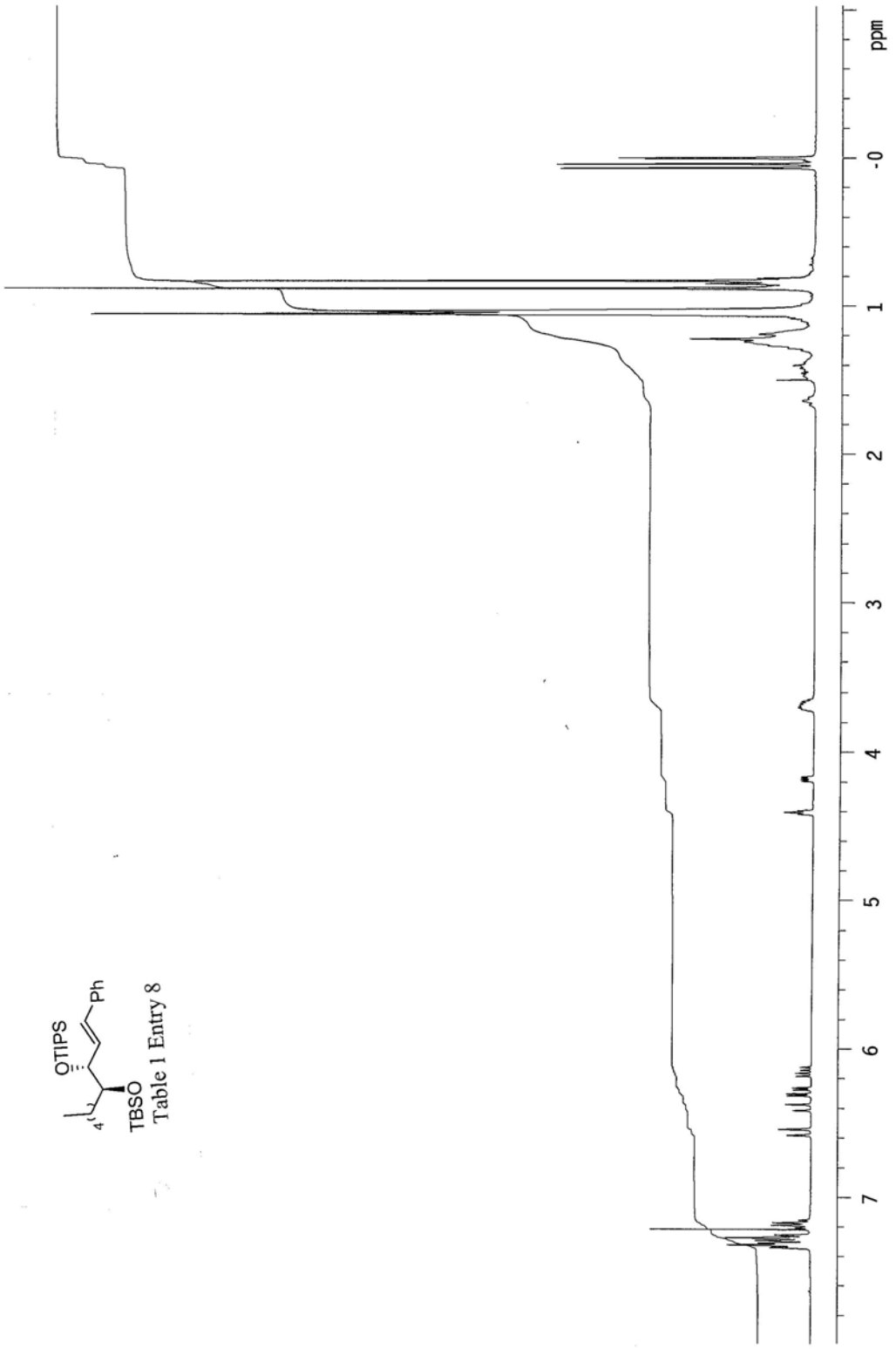

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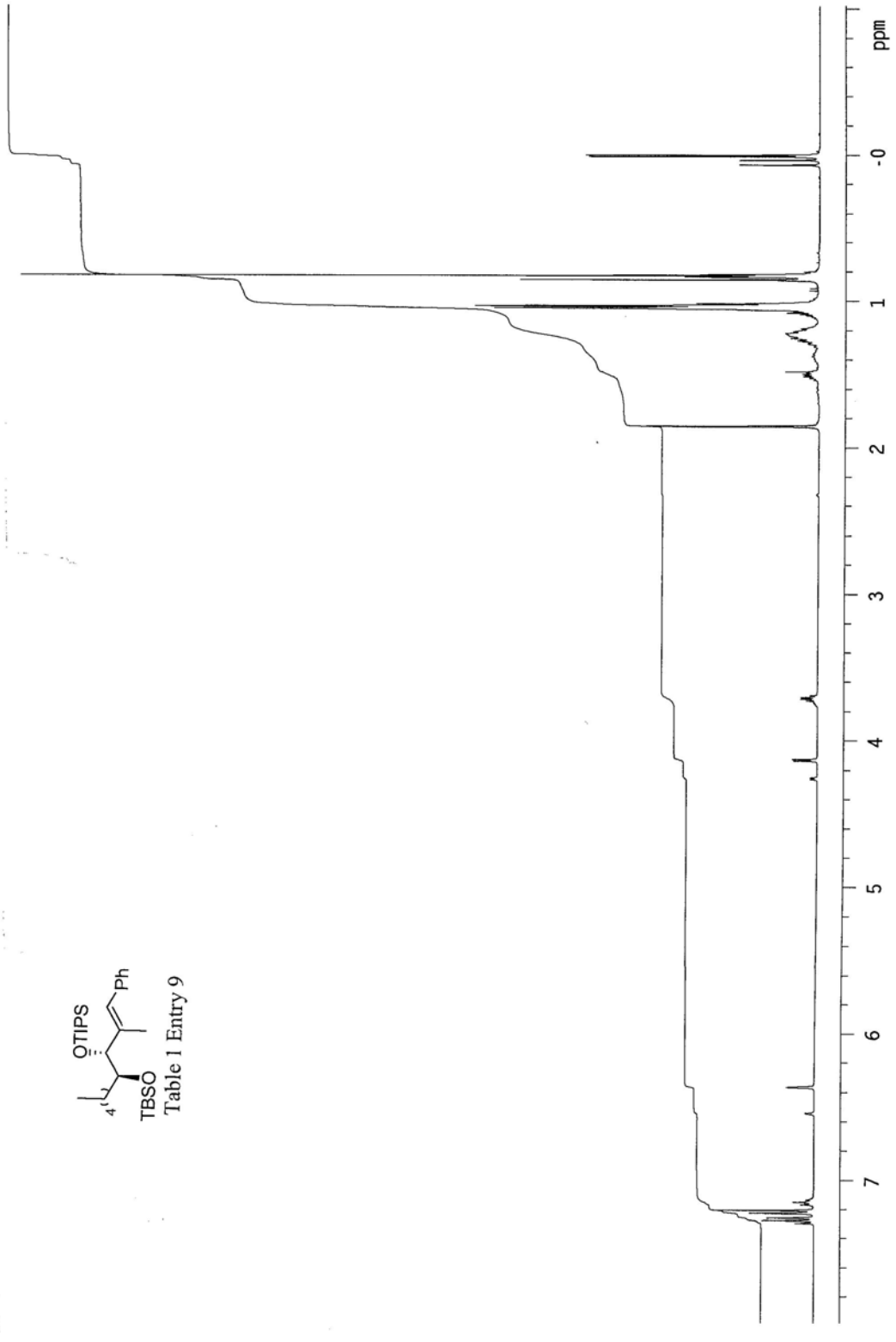

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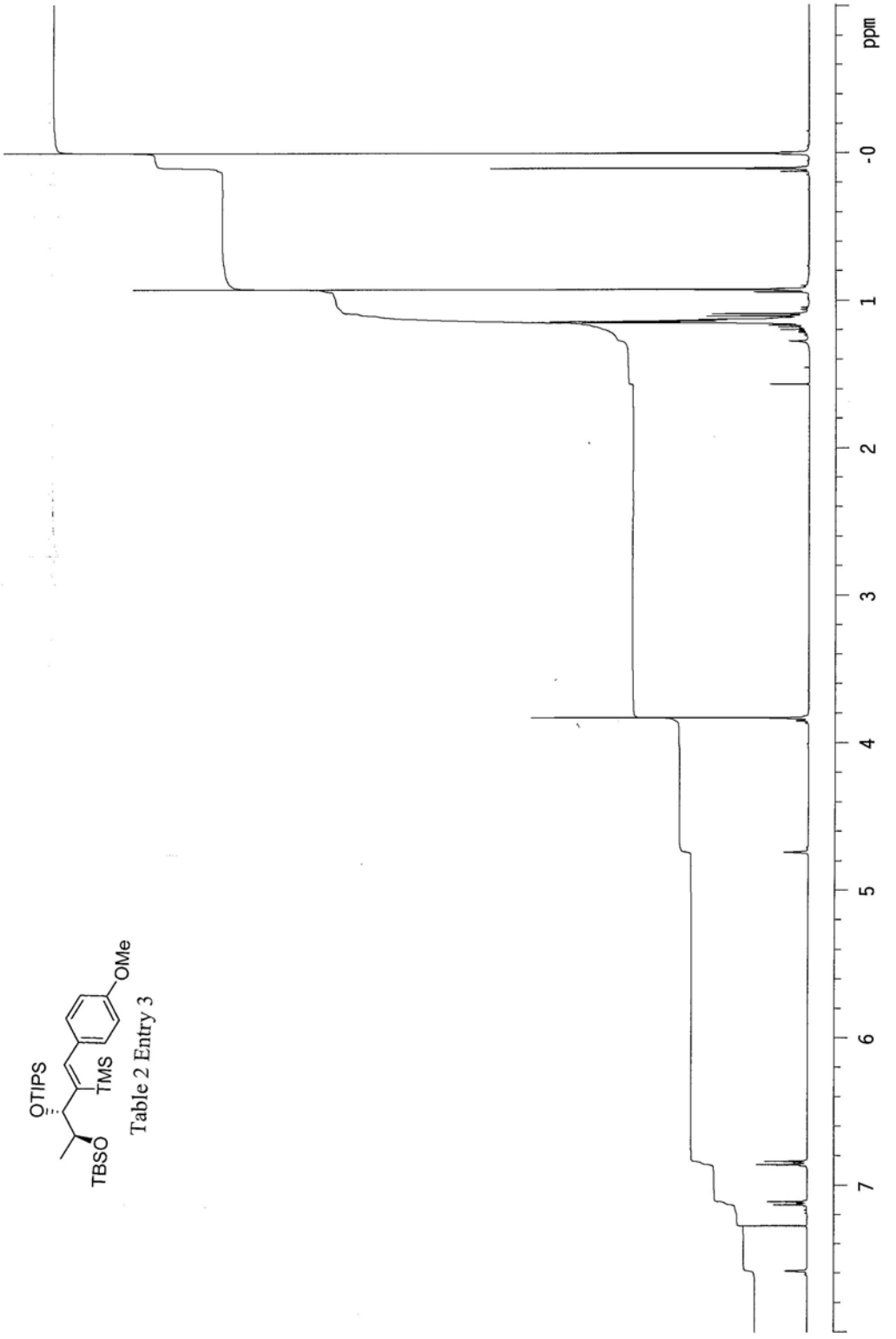

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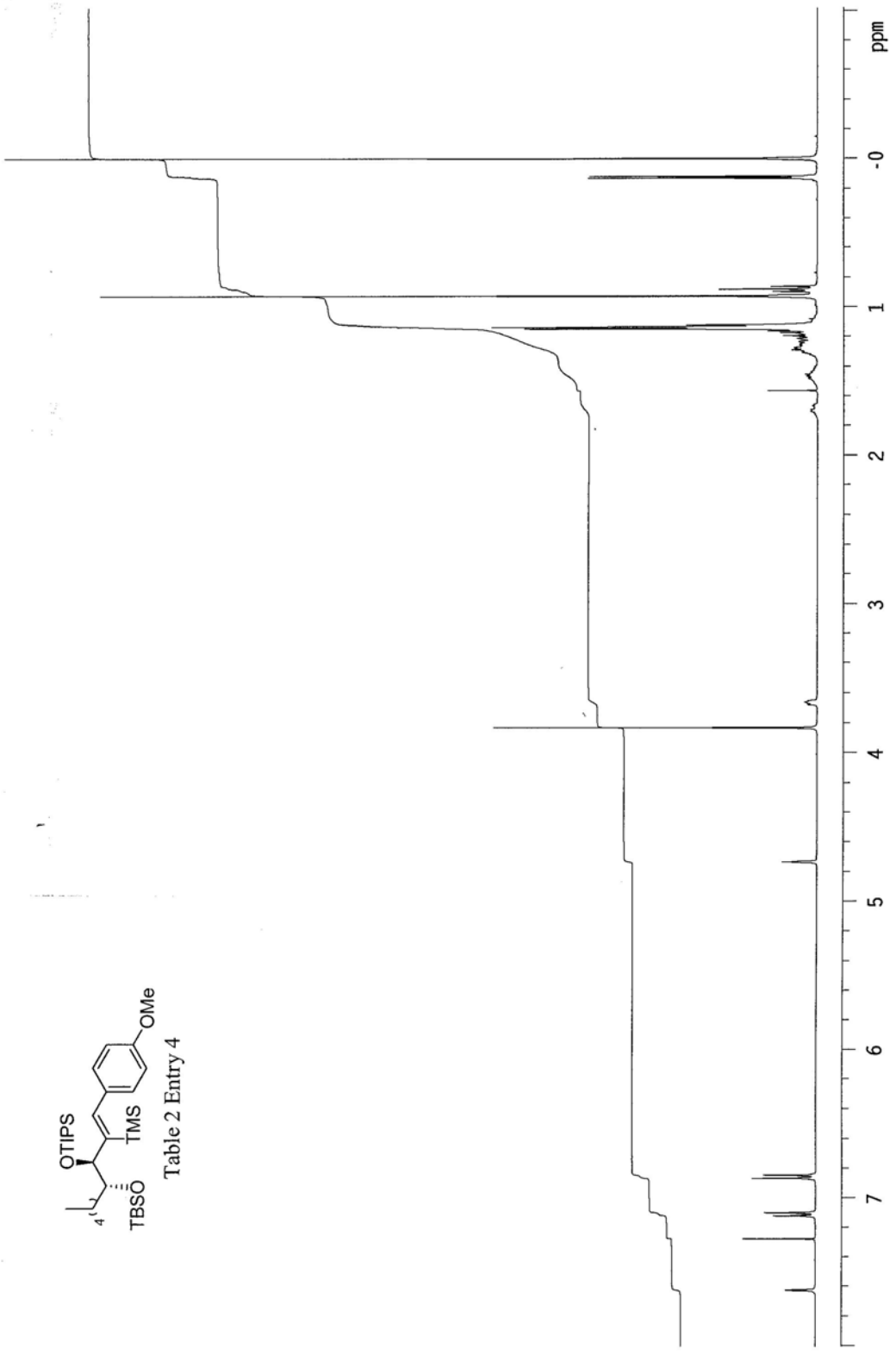

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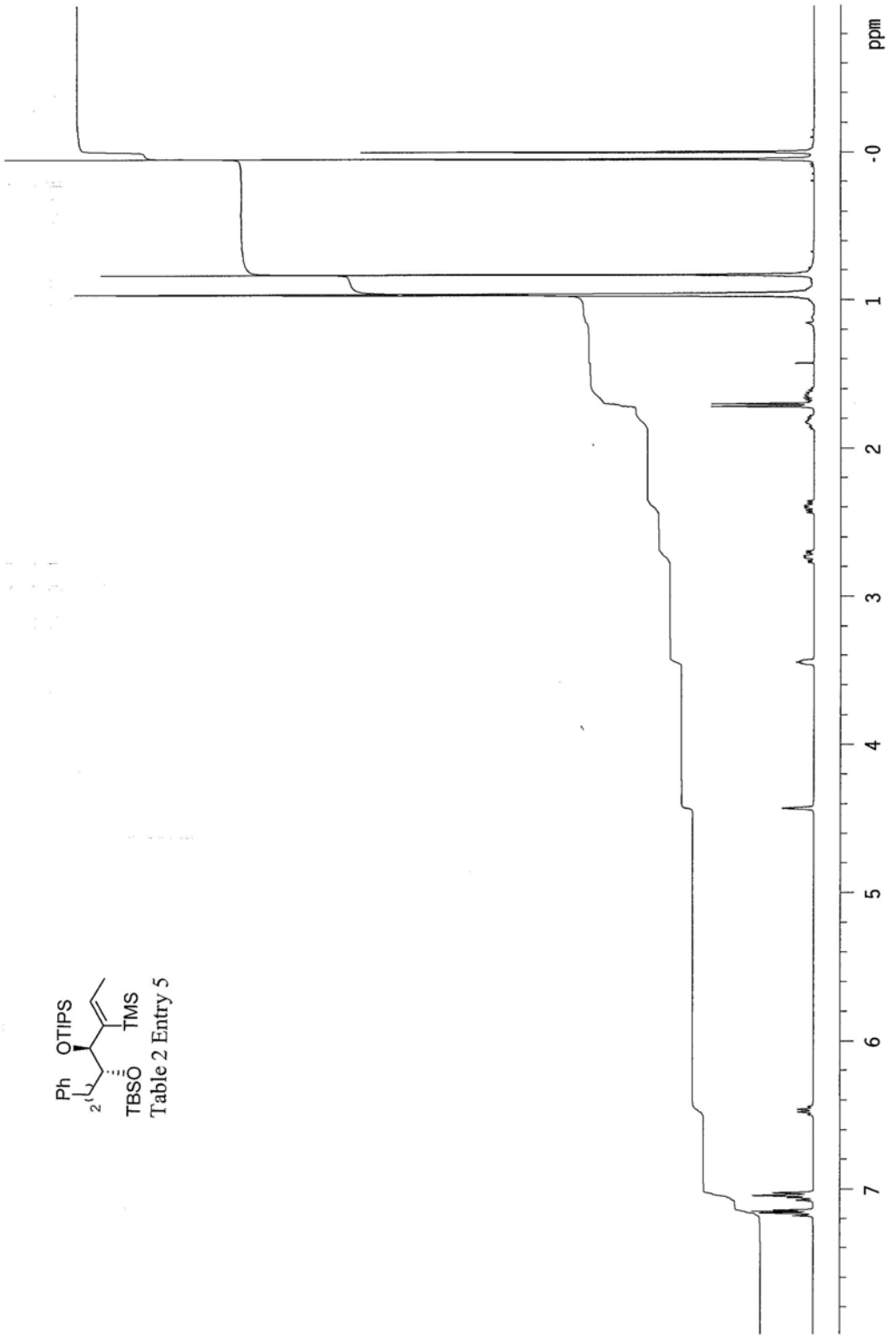

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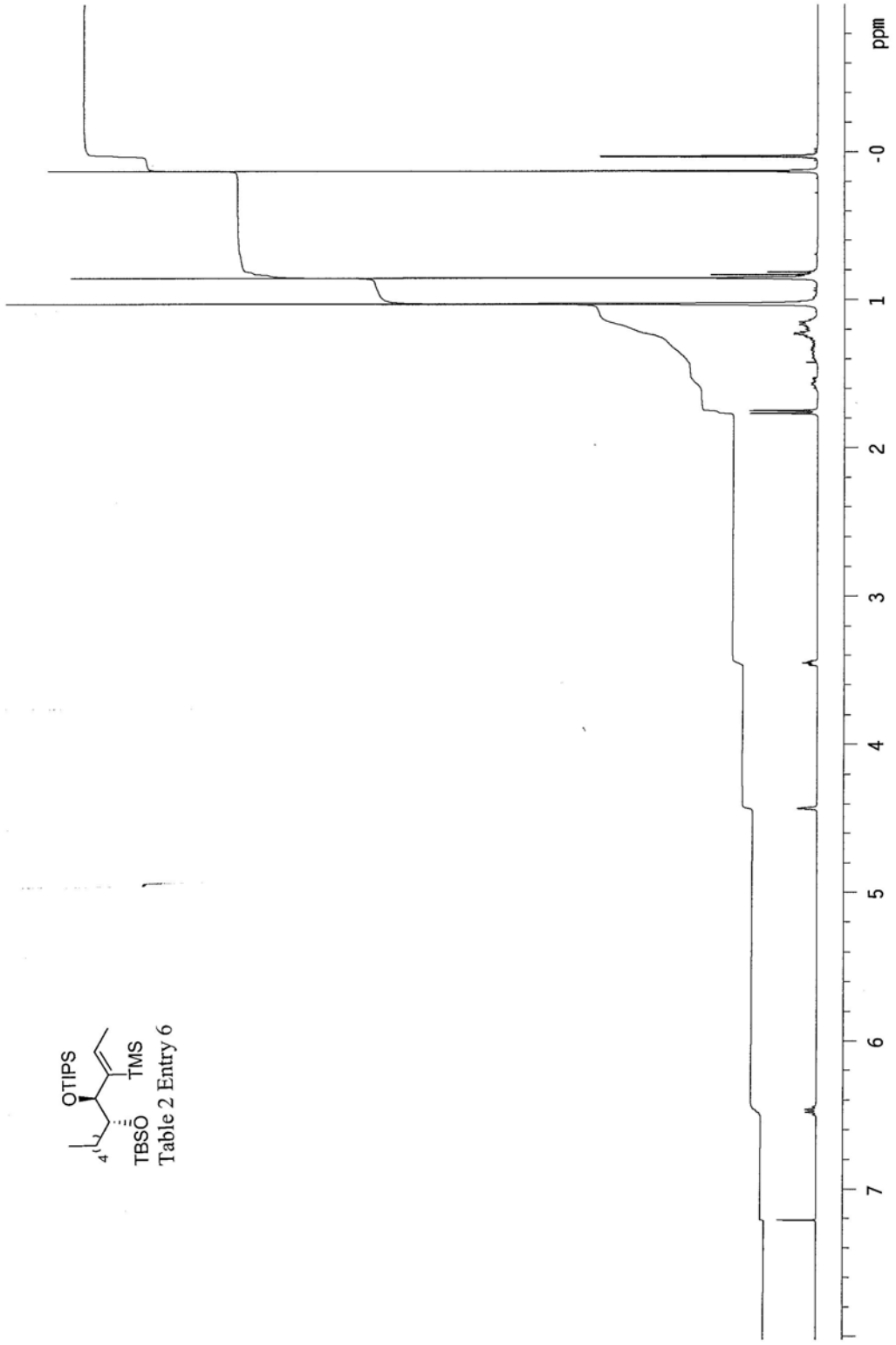

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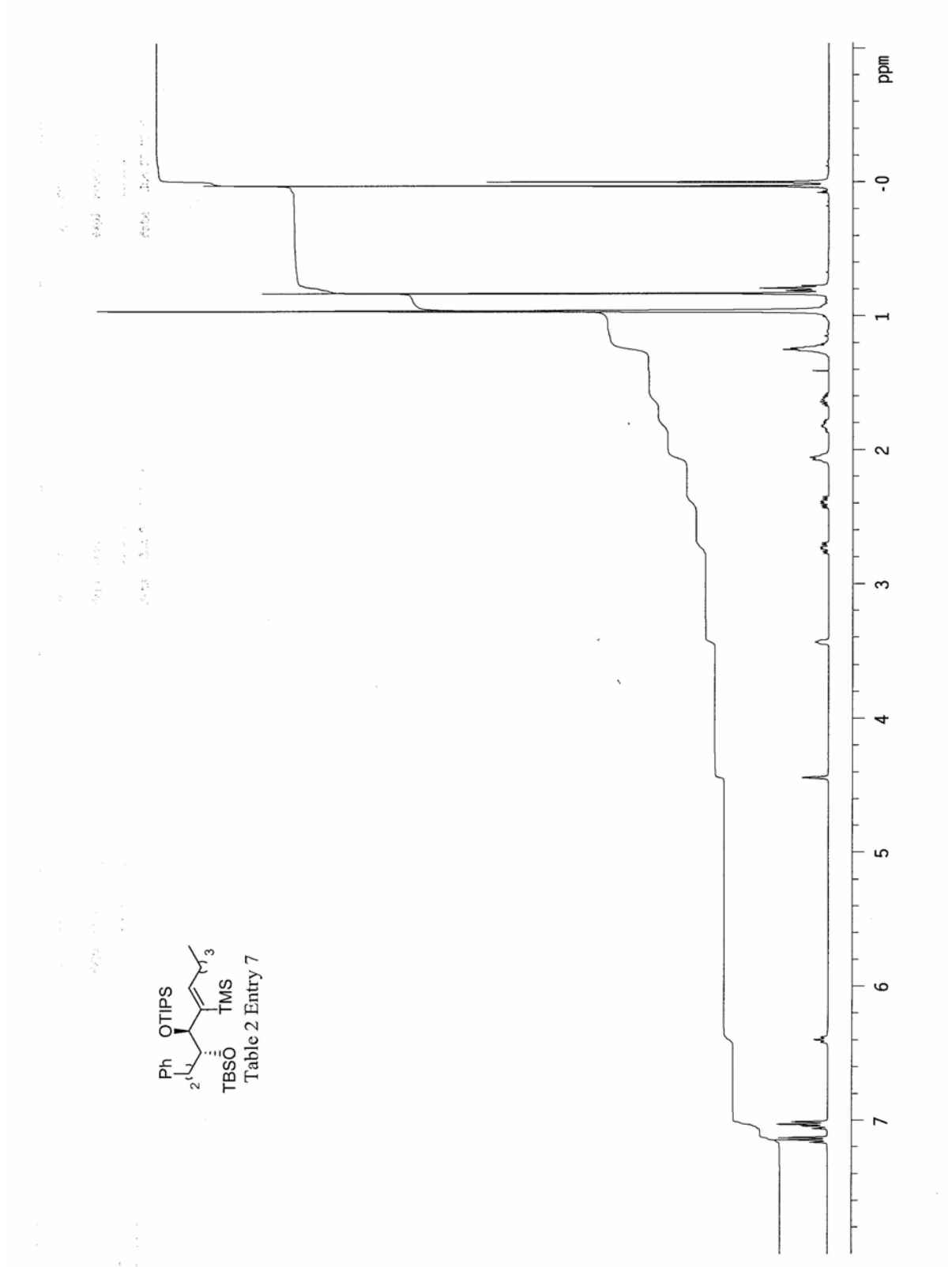
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TMS
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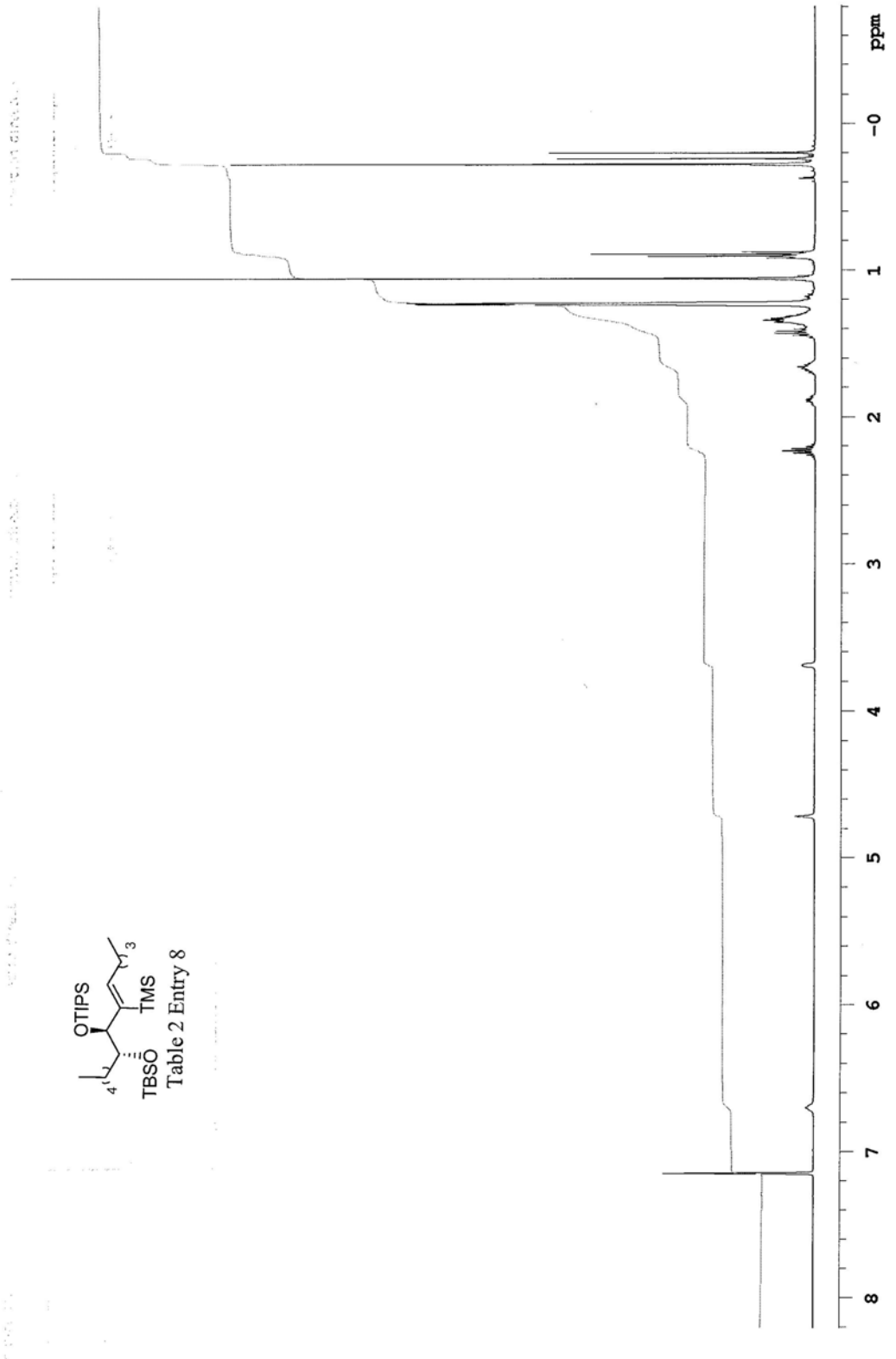
3
4
5
6
7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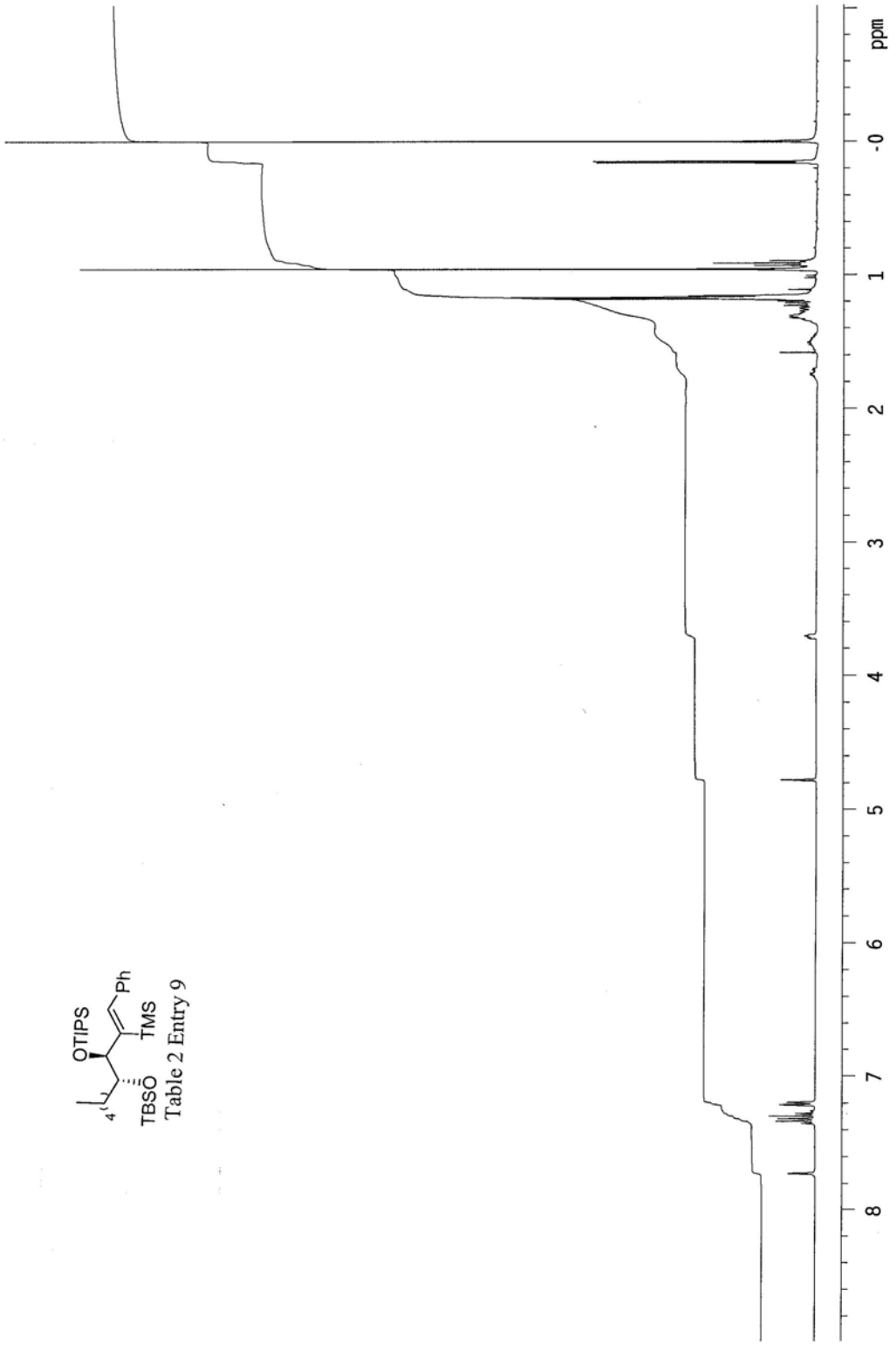

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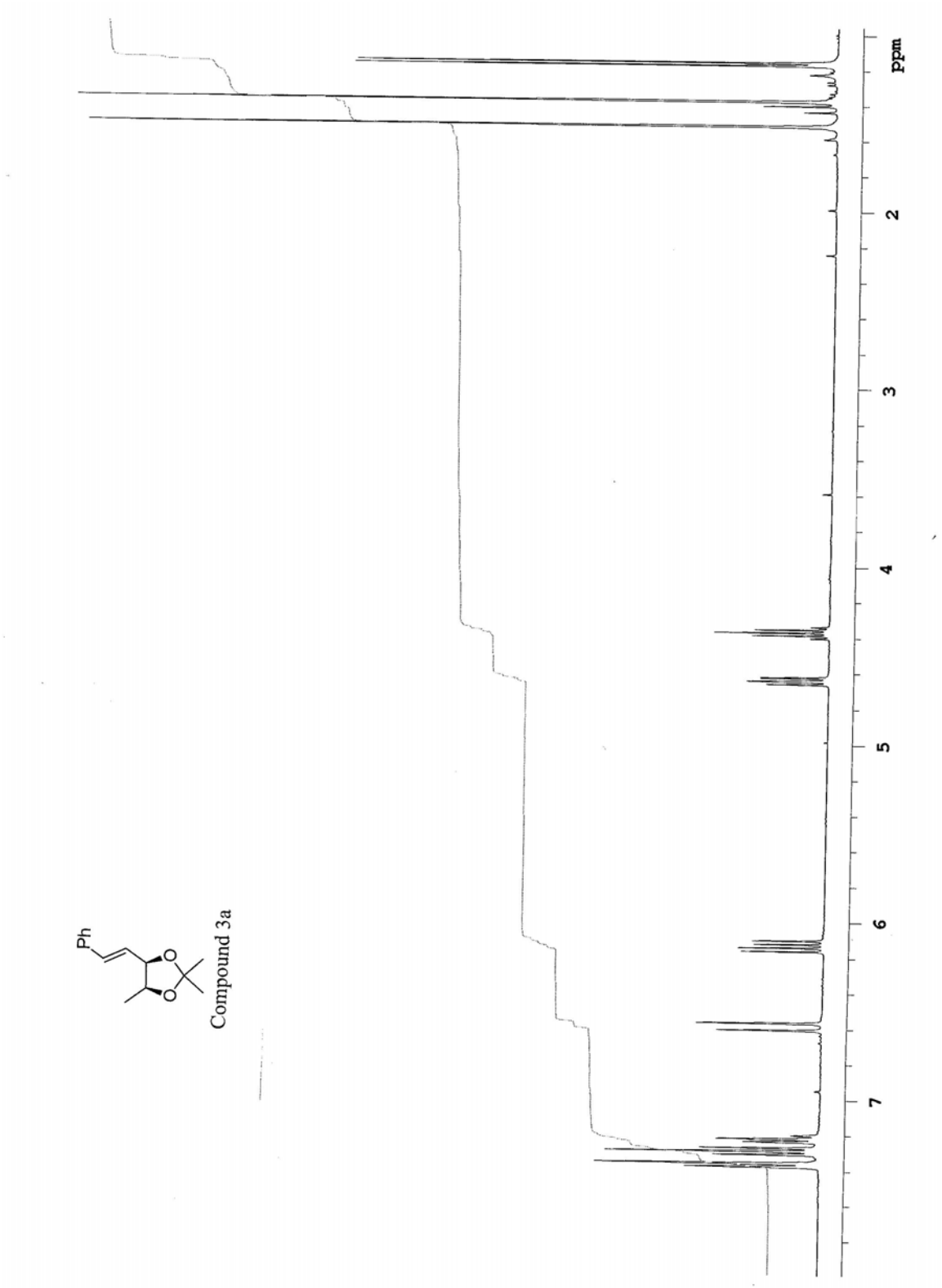
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5
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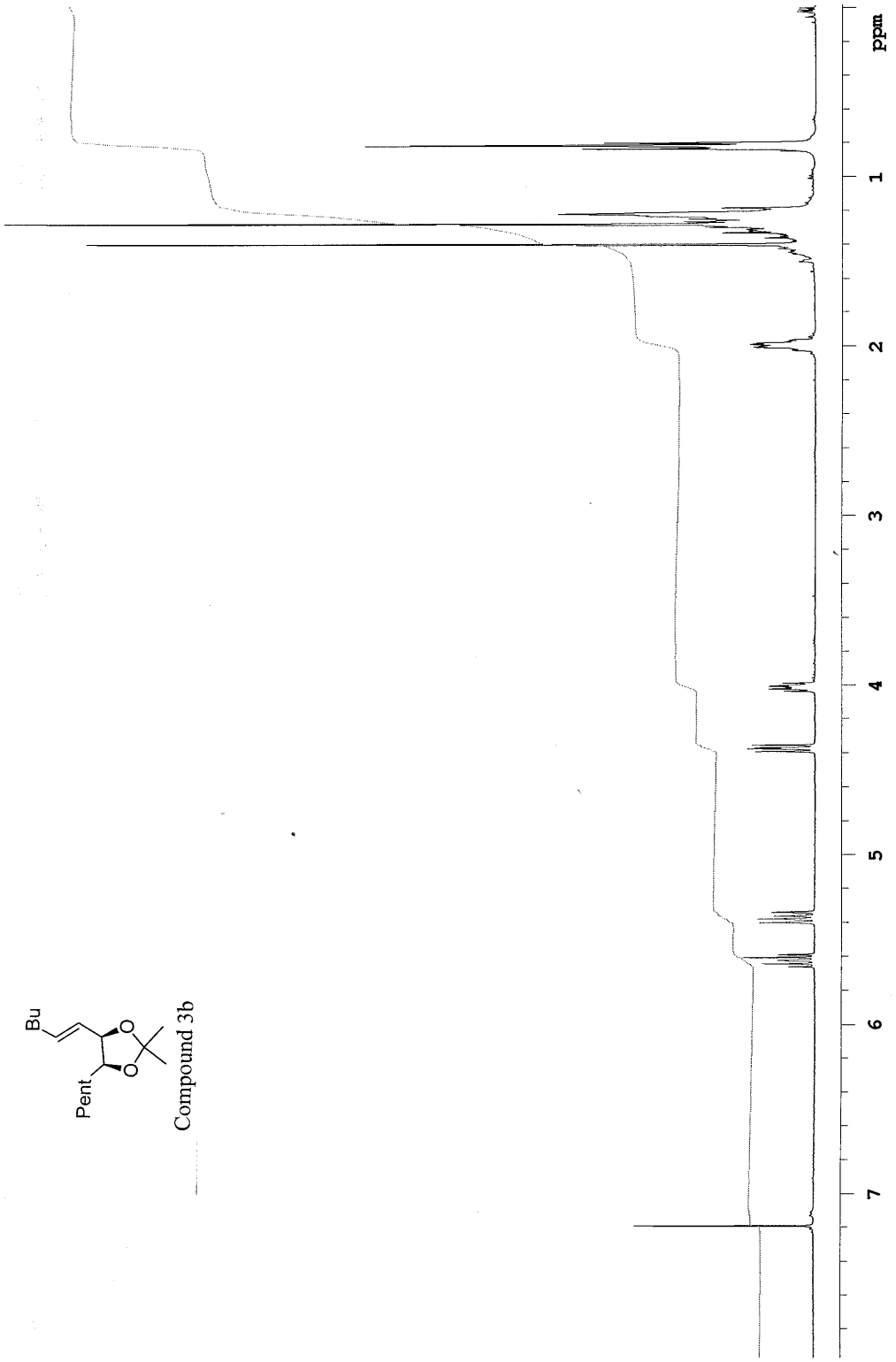
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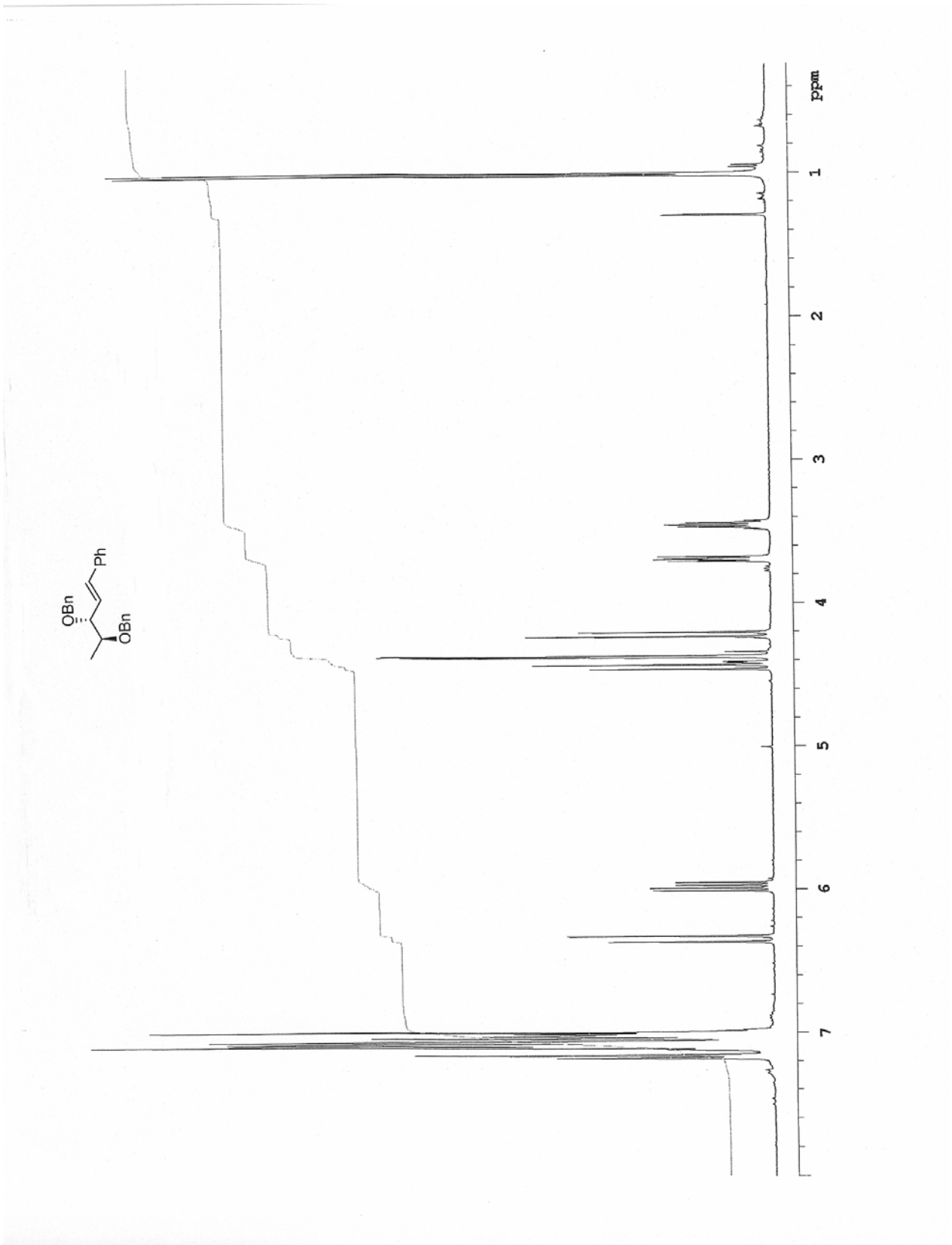
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OBn
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7

Compound 5 (Scheme 1)