Supporting Information

1,5-Diastereoselective Nickel-Catalyzed Conjugate Addition of Dimethylzinc upon Aldimines Across 1,ω-Dienynes

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Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with silica gel (Wakogel-C300) as a slurry in hexane. Flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl under N_2 immediately prior to use. $Ni(acac)_2$ (Aldrich), dimethylzinc (1.0 M solution in hexanes) (Kanto Kagaku Kogyo, Co., Ltd.), *p*-chlorobenzaldehyde, and *p*-anisidine (Tokyo Kasei Kogyo Co., Ltd.) were purchased and used without further

purification. Benzaldehyde, furfral, dihydrocinnamaldehyde, cyclohexanecarboxy-aldehyde, were purchased from Tokyo Kasei Kogyo Co., Ltd., and purified by distillation prior to use. Lactols were prepared according to the literature.[1,2]

Preparation of 5-(3-trimethylsilyl-2-propynyloxy)-(1,3*E*)-pentadiene (**1d**): Into a round-bottom flask was placed NaH (480 mg; a 60% dispersion in oil, 12 mmol). The dispersion was washed with hexane (2 × 5 mL). Into the flask were added THF (30 mL), and was added dropwise a solution of 2-propyn-1-ol (0.67 g, 12 mmol) in 10 mL THF at 0 °C. The resulting mixture was stirred at room temperature for 1 h. This mixture was cooled again to 0 °C, and into this a solution of l-chloro-2,4-pentadiene[3] (1.05 mL, 10 mmol) dissolved in THF (10 mL) was added dropwise. The resulting mixture was allowed to warm to ambient temperature, and stirred for 52 h. The mixture was poured into ice-water and extracted with ether (2 × 30 mL). The organic phase was washed with sat. NH_4C1 and with sat. $NaHCO_3$, and dried ($MgSO_4$). The solvent was removed *in vacuo* to give 5-(2-propynyloxy)-(1,3*E*)-pentadiene. Into a flask containing the crude 5-(2-propynyloxy)-(1,3*E*)-pentadiene was added THF (30 mL), and then *n*-BuLi (6.9 mL. 11 mmol; 1.6 M in hexane) was added dropwise via syringe at - 78 °C. After stirring for 1 h, chlorotrimethylsilane (1.3 g, 12 mmol) was added dropwise at the same temperature, and the reaction mixture was stirred for 1 h. The mixture was poured into water and extracted with ether (2 x 30 mL). The combined organic extracts were washed with sat. NH_4Cl, sat. $NaHCO_3$, and sat. NaCl, and dried ($MgSO_4$). Solvent was removed *in vacuo* and the residue was purified by means of column chromatography over silica gel (hexane/ethyl acetate = 20/1, v/v) to give **1d** in 16% yield. Other 1,ω-dienynes (**1a**-**1c**, **1e**-**1h**) were also prepared under similar way.[3]

5-(3-Trimethylsilyl-2-propynyloxy)-(1,3*E*)-pentadiene (**1d**): IR (neat) 3086 (w), 2963 (m), 1605 (w), 1350 (m), 1250 (s), 1096 (s), 1003 (s), 849 (s), 764 (m) cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 4.10 (d, J = 6.1 Hz, 2 H), 4.14 (s, 2 H), 5.11 (d, J = 10.5 Hz, 1 H), 5.22 (d, J = 16.3 Hz, 1 H), 5.76 (dt, J = 14.6, 6.1 Hz, 1 H), 6.27 (dd, J = 14.6, 10.5 Hz, 1 H), 6.34 (dt, J = 16.3, 10.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 58.3, 70.1, 91.8, 101.8, 118.1, 129.5, 134.3, 136.5; HRMS calcd for $C_{11}H_{18}OSi$: 194.1127. Found *m/z* (relative intensity) 194.1106 (M^+, 29), 193 (63), 179 (100).

General Procedure for the Ni-Catalyzed Coupling of Me_2Zn and Aldimine Across 1,ω-Dienyne (synthesis of **2o**, equation 1): A mixture of *p*-anisidine (246 mg, 2 mmol) and 2-hydroxy-1-oxacyclohexane[1] (103 mg, 1 mmol) in dry THF (2 mL) was stirred at room temperature overnight under N_2. In a flask containing $Ni(acac)_2$ (12.8 mg, 0.05 mmol) was purged with N_2 and into this flask were added successively THF (1 mL), the above-prepared solution (via cannula), dienyne **1a** (125 mg, 0.5 mmol), Me_2Zn (3.6 mL, 1 M hexane). The homogeneous solution was stirred at room temperature for 1 h; R_f(**1a**) = 0.7, R_f(**2o**) = 0.07 (hexane/EtOAc = 2:1 vol/vol). The mixture was partitioned into EtOAc (20 mL)/H_2O (20 mL). The water phase was saturated with NaCl and extracted with EtOAc (2 x 10 mL). The combined organic phase was dried (K_2CO_3) and concentrated in vacuo. The residue was purified by column chromatography over silica gel (hexane/EtOAc gradient; 2:1 to 1:1 v/v) to give **2o** (171.3 mg) in 73% yield as colorless oil.

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2a**): IR (neat) 3395 (w), 2909 (m), 1736 (s), 1512 (s), 1435 (m), 1242 (s), 1042 (m), 818 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3 H), 1.64 (s, 3 H), 2.11 (dd, J = 5.6, 13.2 Hz, 1 H), 2.38 (dt, J = 14.2, 7.6 Hz, 1 H), 2.51

(dt, *J* = 14.2, 5.7 Hz, 1 H), 2.57 (dd, *J* = 9.2, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.2 Hz, 1 H), 2.96 (br d, *J* = 16.2 Hz, 1 H), 3.32 (ddm, *J* = 5.6, 9.2 Hz, 1 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.95 (br s, 1 H), 4.24 (dd, *J* = 5.7, 7.6 Hz, 1 H), 5.28 (dm, *J* = 15.1 Hz, 1 H), 5.41 (dm, *J* = 15.1 Hz, 1 H), 6.43 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 7.18 - 7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 38.7, 41.1, 41.9, 44.1, 52.7, 55.7, 58.2, 59.2, 114.5, 114.7, 125.5, 126.1, 126.2, 126.7, 128.4, 132.6, 136.2, 141.7, 143.8, 151.8, 172.1; HRMS calcd for $C_{29}H_{35}NO_5$: 477.2515. Found *m/z* (relative intensity) 478 (M^++1, 32), 477.2507 (M^+, 100).

(4*S,4'*R**)-3-Isopropylidene-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2b**): IR (neat) 3387 (w), 2909 (m), 2839 (m), 2361 (s), 1620 (w), 1512 (s), 1450 (m), 1242 (s), 1049 (m), 972 (w), 756 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 1.63 (s, 3 H), 2.43 (dt, *J* = 14.2, 7.3 Hz, 1 H), 2.55 (dt, *J* = 14.2, 7.3 Hz, 1 H), 3.29 (ddm, *J* = 2.9, 6.2 Hz, 1 H), 3.64 (s, 3 H), 3.71 (dd, *J* = 2.9, 8.5 Hz, 1 H), 3.86 (dd, *J* = 6.2, 8.5 Hz, 1 H), 4.22 (t, *J* = 7.3 Hz, 1 H), 4.25 (dm, *J* = 12.7 Hz, 1 H), 4.32 (dm, *J* = 12.7 Hz, 1 H), 5.36 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.54 (dd, *J* = 7.3, 15.1 Hz, 1 H), 6.41 (d, *J* = 9.0 Hz, 2 H), 6.66 (d, *J* = 9.0 Hz, 2 H), 7.20 – 7.33 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.0, 21.1, 41.7, 45.6, 55.7, 58.3, 60.3, 70.1, 74.7, 114.5, 114.6, 123.4, 125.8, 126.3, 126.7, 128.3, 133.8, 134.3, 141.4, 143.6, 151.8; HRMS calcd for $C_{24}H_{29}NO_2$: 363.2198. Found *m/z* (relative intensity) 364 (M^++1, 30), 363.2199 (M^+, 100).

(4*S,4'*R**)-3-[(1*Z*)-Phenylethylidene]-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-tetrahydrofuran** (**2c**): IR (neat) 3387 (w), 2909 (w), 1514 (s), 1238 (s), 1036 (s), 820

(m), 762 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (br s, 3 H), 2.56 – 2.64 (m, 2 H), 3.47 (m, 1 H), 3.68 (s, 3 H), 3.71 (dm, *J* = 8.8 Hz, 1 H), 3.97 (dm, *J* = 8.8 Hz, 1 H), 4.12 (br d, *J* = 13.2 Hz, 1 H), 4.31 (m, 1 H), 4.33 (br d, *J* = 13.2 Hz, 1 H), 5.48 (dm, *J* = 15.0 Hz, 1 H), 5.61 (dm, *J* = 15.0 Hz, 1 H), 6.47 (br d, *J* = 8.8 Hz, 2 H), 6.67 (dm, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 7.0 Hz, 2 H), 7.20 - 7.38 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 41.5, 46.2, 55.8, 58.6, 70.6, 74.3, 114.9, 126.6, 126.8, 127.1, 128.3, 128.6, 129.5, 133.7, 137.5, 143.3, 152.3; HRMS calcd for $C_{21}H_{31}NO_2$: 425.2355. Found *m/z* (relative intensity) 426 (M^++1, 30), 425.2342 (M^+, 100).

(4*S,4'*R**)-3-[(1*Z*)-Trimethylsilylethylidene]-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2d**): IR (neat) 3387 (m), 3024 (m), 2955 (m), 2839 (s), 1512 (s), 1450 (m), 1242 (s), 1033 (m), 840 (s), 756 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.56 (br s, 1 H), 1.68 (s, 3 H), 2.46 (br dd, *J* = 13.9, 7.3 Hz, 1 H), 2.55 (br dd, *J* = 13.9, 7.3 Hz, 1 H), 3.42 (m, 1 H), 3.68 (s, 3 H), 3.70 (dm, *J* = 8.8 Hz, 1 H), 3.84 (dm, *J* = 8.8 Hz, 1 H), 4.22 (dm, *J* = 12.9 Hz, 1 H), 4.27 (dm, *J* = 7.3 Hz, 1 H), 4.34 (dm, *J* = 12.9 Hz, 1 H), 5.35 (dt, *J* = 15.2, 7.3 Hz, 1 H), 5.53 (dd, *J* = 15.2, 7.3 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.18 – 7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.8, 18.8, 41.6, 46.5, 55.7, 58.1, 70.8, 73.7, 114.6, 114.7, 126.1, 126.7, 128.3, 133.6, 141.4, 143.5, 149.9, 151.9; HRMS calcd for $C_{26}H_{35}NO_2Si$: 421.2437. Found *m/z* (relative intensity) 422 (M^++1, 35), 421.2434 (M^+, 100), 420 (3), 406 (18).

(4*S,4'*R**)-3-Isopropylidene-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine** (**2e**): IR (neat) 3402 (w), 2916 (w), 1521 (s), 1342 (s), 1242

(s), 1165 (s), 1096 (m), 1042 (m), 817 (m), 664 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 3 H), 1.54 (s, 3 H), 2.39 (br dd, J = 7.3, 13.7 Hz, 1 H), 2.42 (s, 3 H), 2.48 (dt, J = 13.7, 5.7 Hz, 1 H), 3.09 (dm, J = 9.0 Hz, 1 H), 3.25 (dm, J = 7.2 Hz, 1 H), 3.29 (dm, J = 9.0 Hz, 1 H), 3.56 (d, J = 13.4 Hz, 1 H), 3.68 (s, 3 H), 3.88 (d, J = 13.4 Hz, 1 H), 4.24 (dd, J = 5.7, 7.3 Hz, 1 H), 5.29 (dt, J = 15.4, 5.7 Hz, 1 H), 5.41 (dd, J = 7.2, 15.4 Hz, 1 H), 6.43 (br d, J = 8.8 Hz, 2 H), 6.67 (d, J = 8.8 Hz, 2 H), 7.21 – 7.29 (m, 5 H), 7.31 (d, J = 8.2 Hz, 2 H), 7.70 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 21.1, 21.5, 41.5, 44.0, 50.3, 54.3, 55.7, 58.2, 114.7, 126.2, 126.3, 126.8, 127.8, 128.4, 129.5, 129.8, 132.6, 133.5, 143.4, 152.3; HRMS calcd for $C_{31}H_{36}N_2O_3S$: 516.2447. Found *m/z* (relative intensity) 517 (M^++1, 37), 516.2446 (M^+, 100), 515 (4).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-1-isopropylidenecyclohexane (2f)**: IR (neat) 3402 (s), 2947 (s), 1736 (s), 1512 (s), 1450 (s), 1234 (s), 1042 (s), 826 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.62 (dm, J = 14.2 Hz, 1 H), 1.63 (s, 3 H), 2.18 (dm, J = 14.2 Hz, 1 H), 2.28 (m, 1 H), 2.34 – 2.46 (m, 3 H), 2.50 – 2.60 (m, 2 H), 3.46 (br s, 1 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 4.27 (dd, J = 4.8, 7.2 Hz, 1 H), 5.51 (dm, J = 15.4 Hz, 1 H), 5.47 (dm, J = 15.4 Hz, 1 H), 6.53 (d, J = 8.9 Hz, 2 H), 6.65 (d, J = 8.9 Hz, 2 H), 7.18 (m, 1 H), 7.23 – 7.38 (m, 4 H): ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.0, 22.3, 31.5, 36.0, 38.5, 41.9, 52.4, 52.5, 52.6, 55.7, 58.2, 114.6, 114.7, 125.2, 125.4, 126.6, 128.3, 128.4, 135.2, 141.5, 143.6, 151.8, 172.2, 172.5; HRMS calcd for $C_{30}H_{37}NO_5$: 491.2672. Found *m/z* (relative intensity) 492 (M^++1, 33), 491.2665 (M^+, 100), 460 (9).

(2*S,4'*R**)-4-Isopropylidene-3-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydropyran (2g)**:[4] IR (neat) 3364 (m), 2963 (m), 2855 (m), 1512 (s), 1450 (w), 1234 (m), 1096 (m), 1042 (m), 964 (m), 818 (m), 702 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3 H), 1.67 (s, 3 H), 2.25 (m, 1 H), 2.36 (br d, *J* = 12.7 Hz, 1 H), 2.41 (ddm, *J* = 13.9, 7.8 Hz, 1 H), 2.55 (ddm, *J* = 13.9, 5.2 Hz, 1 H), 3.18 (dm, *J* = 6.6 Hz, 1 H), 3.30 (ddm, *J* = 10.7, 12.7 Hz, 1 H), 3.50 (dm, *J* = 11.1 Hz, 1 H), 3.67 (s, 3 H), 3.92 (d, *J* = 11.1 Hz, 1 H), 3.98 (dd, *J* = 5.2, 10.7 Hz, 1 H), 4.25 (dd, *J* = 5.2, 7.8 Hz, 1 H), 5.38 (ddm, *J* = 15.4, 6.6 Hz, 1 H), 5.80 (dd, *J* = 6.6, 15.4 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 7.15 - 7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.8, 27.0, 41.8, 42.2, 55.7, 58.2, 68.7, 72.8, 114.5, 114.6, 124.6, 126.1, 126.2, 126.6, 127.3, 128.3, 135.0, 141.7, 143.9, 151.7; HRMS calcd for $C_{25}H_{31}NO_2$: 377.2355. Found *m/z* (relative intensity) 378 (M^++1, 32), 377.2352 (M^+, 100), 376 (2).

(2*S,4'*R**)-4-Isopropylidene-3-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)piperidine (2h)**: IR (neat) 3395 (w), 2916 (m), 1512 (s), 1458 (m), 1335 (s), 1242 (s), 1165 (s), 1103 (m), 1034 (m), 934 (m), 818 (s), 756 (m), 702 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3 H), 1.60 (s, 3 H), 2.08 – 2.28 (m, 2 H), 2.33 (dm, *J* = 11.2 Hz, 1 H), 2.38 – 2.50 (m, 2 H), 2.40 (s, 3 H), 2.54 (dtm *J* = 6.3 Hz, 1 H), 3.36 (m, 1 H), 3.68 (s, 3 H), 3.74 (br d, *J* = 11.2 Hz, 1 H), 3.78 (m, 1 H), 4.01 (br s, 1 H), 4.27 (dm, *J* = 7.6 Hz, 1 H), 5.40 (dt, *J* = 15.4, 7.6 Hz, 1 H), 5.75 (dd, *J* = 15.4, 6.3 Hz, 1 H), 6.49 (d, *J* = 8.9 Hz, 2 H), 6.67 (d, *J* = 8.9 Hz, 2 H), 7.19 – 7.39 (m, 7 H), 7.62 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.1, 21.5, 25.4, 40.0, 42.0, 47.0, 51.5, 55.7, 58.1, 114.5, 114.6, 125.7, 126.3, 126.6, 126.8, 126.9, 128.3, 129.4,

133.2, 133.8, 141.7, 143.2, 143.9, 151.7; HRMS calcd for $C_{32}H_{38}N_2O_3S$: 530.2603. Found *m/z* (relative intensity) 531 (M^++1, 37), 530.2604 (M^+, 100), 529 (4).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(*p*-anisyl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2i**): IR (neat) 3402 (m), 2947 (m), 1736 (s), 1512 (s), 1443 (m), 1242 (s), 1034 (m), 972 (w), 818 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.64 (s, 3 H), 2.10 (dm, *J* = 13.2 Hz, 1 H), 2.36 (dt, *J* = 14.2, 7.6 Hz, 1 H), 2.47 (ddd, *J* = 5.4, 6.6, 14.2 Hz, 1 H), 2.57 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.3 Hz, 1 H), 2.95 (br d, *J* = 16.3 Hz, 1 H), 3.32 (br dd, *J* = 7.1, 8.5 Hz, 1 H), 3.67 (s, 3 H), 3.69 (s, 6 H), 3.70 (m, 1 H), 3.76 (s, 3 H), 3.92 (br s, 1 H), 4.19 (dd, *J* = 5.4, 7.6 Hz, 1 H), 5.27 (dt, *J* = 15.4, 6.6 Hz, 1 H), 5.40 (dd, *J* = 7.1, 15.4 Hz, 1 H), 6.43 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 38.7, 41.1, 42.0, 44.1, 52.6, 52.7, 55.2, 55.7, 57.6, 59.1, 113.8, 114.5, 114.6, 125.6, 126.1, 127.2, 132.7, 135.8, 136.0, 141.8, 151.7, 158.3, 172.0, 172.1; HRMS calcd for $C_{30}H_{37}NO_6$: 507.2621. Found *m/z* (relative intensity) 508 (M^++1, 33), 507.2618 (M^+, 100), 506 (6).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(*p*-chlorophenyl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2j**): IR (neat) 3398 (w), 2910 (w), 1732 (s), 1514 (s), 1435 (s), 1242 (s), 1204 (s), 1090 (m), 1040 (w), 820 (s), 737 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3 H), 1.64 (s, 3 H), 2.10 (dd, *J* = 5.7, 13.2 Hz, 1 H), 2.35 (dt, *J* = 14.3, 7.7 Hz, 1 H), 2.49 (dt, *J* = 14.3, 5.7 Hz, 1 H), 2.57 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.3 Hz, 1 H), 2.95 (br d, *J* = 16.3 Hz, 1 H), 3.32 (br dd, *J* = 7.0, 8.4 Hz, 1 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 4.22 (dd, *J* = 5.7, 7.7 Hz, 1

H), 5.25 (dt, *J* = 15.4, 7.7 Hz, 1 H), 5.42 (dd, *J* = 7.0, 15.4 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.26 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 38.7, 41.1, 41.8, 44.1, 52.7, 55.7, 59.2, 114.8, 125.1, 126.4, 127.9, 128.7, 132.5, 132.6, 136.8, 141.4, 142.5, 152.3, 172.3, 172.4; HRMS calcd for $C_{29}H_{34}ClNO_5$: 511.2126. Found *m/z* (relative intensity) 511.2098 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(2-furfuryl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2k**): IR (neat) 3398 (w), 2910 (w), 1732 (s), 1514 (s), 1435 (m), 1242 (s), 1204 (m), 1177 (m), 1040 (m), 822 (m), 739 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s), 1.64 (s, 3 H), 2.07 (dd, *J* = 5.8, 13.4 Hz, 1 H), 2.53 – 2.59 (m, 3 H), 2.87 (br d, *J* = 16.5 Hz, 1 H), 2.93 (br d, *J* = 16.5 Hz, 1 H), 3.30 (br dd, *J* = 5.8, 7.0 Hz, 1 H), 3.70 (br s, 6 H), 3.72 (s, 3 H), 4.40 (t, *J* = 6.2 Hz, 1 H), 5.26 (dt, *J* = 15.6, 6.2 Hz, 1 H), 5.39 (dd, *J* = 7.0, 15.6 Hz, 1 H), 6.10 (d, *J* = 3.3 Hz, 1 H), 6.26 (br d, *J* = 3.3 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 7.32 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 37.8, 38.7, 41.1, 44.1, 52.7, 52.9, 55.7, 59.2, 106.2, 110.1, 114.8, 115.3, 124.9, 126.3, 132.9, 136.5, 141.2, 141.4, 152.6, 156.1, 172.3; HRMS calcd for $C_{27}H_{33}NO_6$: 467.2308. Found *m/z* (relative intensity) 468 (M^++1, 32), 467.2306 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-6-phenyl-(1*E*)-hexenyl]-1-isopropylidenecyclopentane** (**2l**): IR (neat) 3395 (m), 2497 (s), 2361 (s), 1736 (s), 1512 (s), 1442 (s), 1242 (s), 1065 (m), 818 (m), 748 (w), 702 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 1.66 (s, 3 H), 1.72 (dm, *J* = 5.7 Hz, 1 H), 1.82 (dm, *J* = 5.7 Hz, 1 H), 2.07 (dm, *J* = 13.2 Hz, 1 H), 2.23 (t, *J* = 5.7 Hz, 2 H), 2.58 (dm, *J* = 13.2

Hz, 1 H), 2.69 – 2.75 (m, 2 H), 2.91 (br s, 2 H), 3.24 – 3.36 (m, 2 H), 3.69 (s, 3 H), 3.72 (s, 3 H), 3.75 (s, 3 H), 5.30 (dm, *J* = 15.2 Hz, 1 H), 5.36 (dm, *J* = 15.2 Hz, 1 H), 6.51 (br d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 7.3 Hz, 2 H), 7.18 (t, *J* = 7.3 Hz, 1 H), 7.27 (t, *J* = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 32.4, 36.0, 38.6, 41.1, 44.2, 52.6, 55.8, 59.1, 60.3, 114.9, 125.1, 125.7, 125.9, 128.2, 128.3, 132.9, 135.8, 141.9, 170.9, 172.1; HRMS calcd for $C_{31}H_{39}NO_5$: 505.2828. Found *m/z* (relative intensity) 506 (M^++1, 33), 505.2827 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-cyclohexyl-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2m**): IR (neat) 3402 (w), 2924 (s), 1736 (s), 1512 (s), 1443 (m), 1242 (s), 1042 (m), 818 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 – 1.28 (m, 5 H), 1.43 (m, 1 H), 1.54 (s, 3 H), 1.64 (s, 3 H), 1.65 – 1.82 (m, 5 H), 2.02 (dd, *J* = 6.6, 13.2 Hz, 1H), 2.11 (dt, *J* = 13.9, 6.2 Hz, 1 H), 2.22 (dt, *J* = 13.9, 6.2 Hz, 1 H), 2.54 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.88 (br s, 2 H), 3.06 (dt, *J* = 8.5, 6.6 Hz, 1 H), 3.22 (m, 1 H), 3.28 (br t, *J* = 6.2 Hz, 1 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 5.26 (dd, *J* = 6.6, 15.4 Hz, 1 H), 5.33 (dt, *J* = 15.4, 6.2 Hz, 1 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 6.73 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.6, 26.5, 26.6, 29.1, 29.7, 34.5, 38.7, 41.2, 41.4, 44.2, 52.5, 52.6, 55.8, 58.9, 59.1, 114.3, 114.8, 125.9, 126.3, 132.9, 135.1, 142.8, 151.4, 172.1; HRMS calcd for $C_{29}H_{41}NO_5$: 483.2985. Found *m/z* (relative intensity) 483.2982 (M^+, 100), 482 (9), 424 (7).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-7-hydroxy-(1*E*)-heptenyl]-1-isopropyl-idenecyclopentane (**2n**): IR (neat) 3383 (w), 2934 (w), 1732 (s), 1512 (s), 1435 (m), 1244 (m), 1040 (m), 822 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (m, 1 H), 1.57

(s, 3 H), 1.65 (s, 3 H), 1.61 – 1.75 (m, 3 H), 2.06 (dd, *J* = 6.0, 13.4 Hz, 1 H), 2.17 – 2.26 (m, 2 H), 2.57 (dd, *J* = 8.5, 13.4 Hz, 1 H), 2.90 (br s, 2 H), 3.24 – 3.34 (m, 2 H), 3.64 (dt, *J* = 5.6, 2.6 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.74 (s, 3 H), 5.28 (dd, *J* = 6.0, 15.2 Hz, 1 H), 5.33 (dt, *J* = 15.2, 5.9 Hz, 1 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 6.76 (d, *J* = 8.9 Hz, 2 H); ^{1}H NMR (400 MHz, THF-d_8) δ 1.40 – 1.62 (m, 4 H), 1.59 (s, 3 H), 1.64 (s, 3 H), 2.01 (dd, *J* = 6.2, 13.1 Hz, 1 H), 2.17 (br dt, *J* = 13.8, 7.3 Hz, 1 H), 2.19 (br dt, *J* = 13.8, 7.3 Hz, 1 H), 2.58 (dm, *J* = 13.1 Hz, 1 H), 2.84 (br d, *J* = 16.3 Hz, 1 H), 2.90 (br d, *J* = 16.3 Hz, 1 H), 3.28 (br t, *J* = 7.3 Hz, 1 H), 3.32 (br d, *J* = 6.2 Hz, 1 H), 3.43 – 3.50 (m, 2 H), 3.63 (s, 3 H), 3.64 (s, 3 H), 3.65 (s, 3 H), 3.97 (m, 1 H), 5.30 (dd, *J* = 7.4, 15.2 Hz, 1 H), 5.43 (dt, *J* = 15.2, 7.3 Hz, 1 H), 6.50 (d, *J* = 9.0 Hz, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 29.6, 30.9, 31.1, 36.7, 38.6, 41.1, 44.2, 52.6, 55.2, 55.3, 59.1, 62.8, 114.9, 116.3, 124.9, 126.0, 132.8, 136.1, 140.2, 152.8, 172.1, 172.2; HRMS calcd for $C_{26}H_{37}NO_6$: 459.2621. Found *m*/*z* (relative intensity) 460 (M^++1, 29), 459.2605 (M^+, 100), 442 (28), 441 (29).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-1-isopropyl-idenecyclopentane (**2o**): IR (neat) 3395 (m), 2932 (w), 1736 (s), 1512 (s), 1443 (s), 1242 (s), 1042 (s), 818 (s), 733 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 – 1.60 (m, 6 H), 1.57 (s, 3 H), 1.65 (s, 3 H), 2.06 (dd, *J* = 5.9, 13.2 Hz, 1 H), 2.18 – 2.22 (m, 2 H), 2.57 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.83 – 2.92 (m, 2 H), 3.28 (ddm, *J* = 5.9, 8.5 Hz, 1 H), 3.30 (m, 1 H), 3.63 (t, *J* = 6.3 Hz, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.31 (dm, *J* = 15.1 Hz, 1 H), 5.36 (dm, *J* = 15.1 Hz, 1 H), 6.55 (br d, *J* = 8.5 Hz, 2 H), 6.75 (d, *J* = 8.5 Hz, 2 H); ^{1}H NMR (400 MHz, THF-d_8) δ 1.32 – 1.56 (m, 6 H), 1.57 (s, 3 H), 1.63 (s, 3 H), 2.00 (dd, *J* = 6.2, 13.1 Hz, 1 H), 2.13 (dt, *J* = 13.7, 6.8 Hz, 1 H), 2.18 (dt,

J = 13.7, 7.6 Hz, 1 H), 2.53 (dd, *J* = 8.4, 13.1 Hz, 1 H), 2.83 (br d, *J* = 16.6 Hz, 1 H), 2.89 (br d, *J* = 16.6 Hz, 1 H), 3.22 (br dd, *J* = 6.2, 7.6 Hz, 1 H), 3.28 (br d, *J* = 8.4 Hz, 1 H), 3.40 – 3.50 (m, 2 H), 3.61 (s, 3 H), 3.62 (s, 3 H), 3.63 (s, 3 H), 3.93 (br s, 1 H), 5.28 (dd, *J* = 7.6, 14.9 Hz, 1 H), 5.41 (dt, *J* = 14.9, 6.8 Hz, 1 H), 6.47 (d, *J* = 9.0 Hz, 2 H), 6.64 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 22.2, 32.7, 33.9, 36.7, 38.7, 41.2, 44.2, 52.6, 54.1, 55.8, 59.1, 62.7, 114.9, 125.2, 125.9, 132.9, 135.8, 152.0, 172.1, 172.2; HRMS calcd for $C_{27}H_{39}NO_6$: 473.2777. Found *m/z* (relative intensity) 474 (M^++1, 32), 473.2770 (M^+, 100), 472 (7), 456 (2), 442 (13).

References and Note

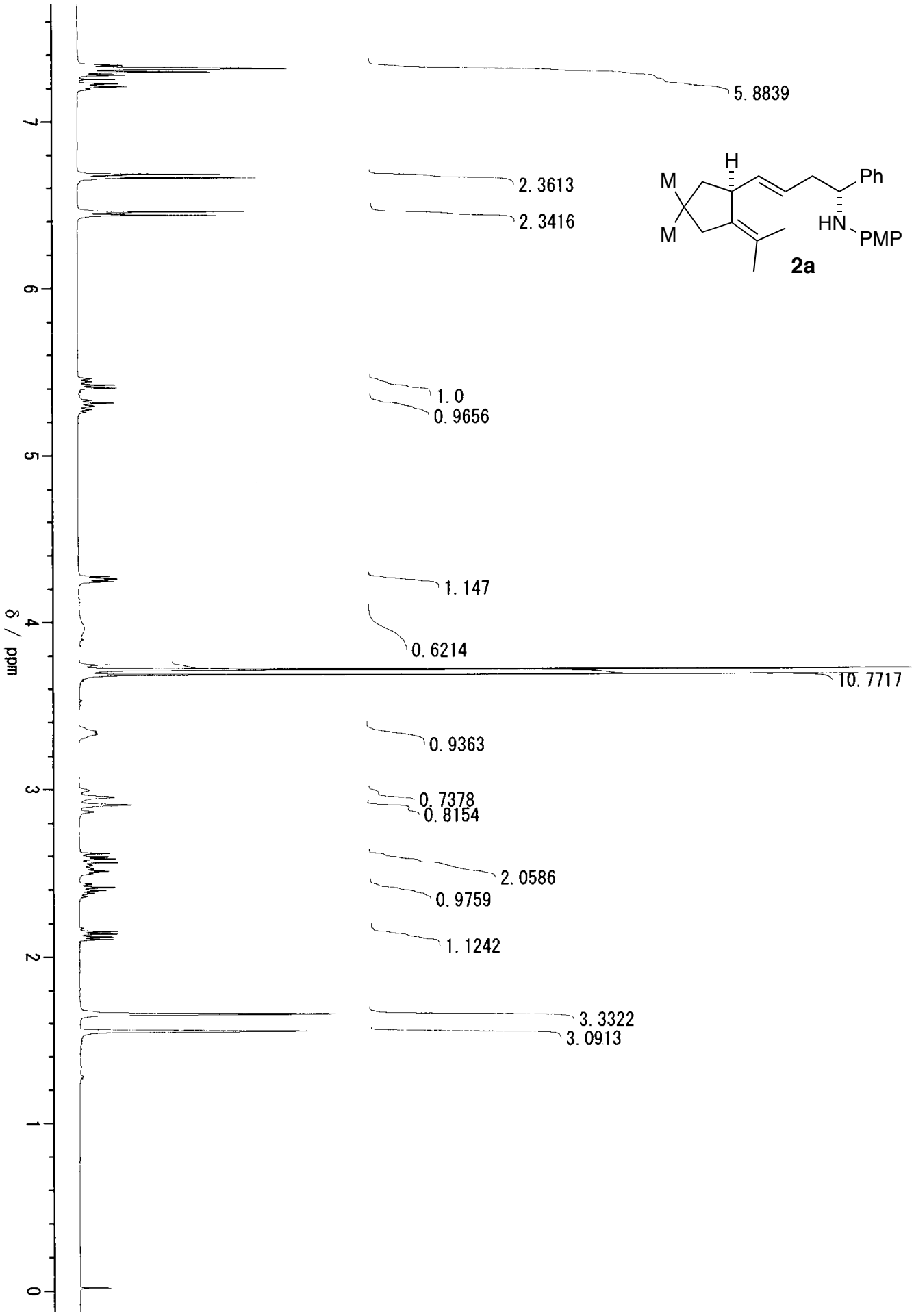
[1] M. Kimura, M. Shimizu, S. Tanaka, Y. Tamaru, *Tetrahedron*, **2005**, *61*, 3709.

[2] S. Kodato, M. Nakagawa, K. Nakayama, T. Hino, *Tetrahedron*, **1989**, *45*, 7247.

[3] M. Kimura, A. Ezoe, M. Mori, Y. Tamaru, *J. Am. Chem. Soc*., **2005**, *127*, 201.

[4] Crystallographic data of **2g** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-209610. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+41)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

^{1}H NMR Spectra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Ph
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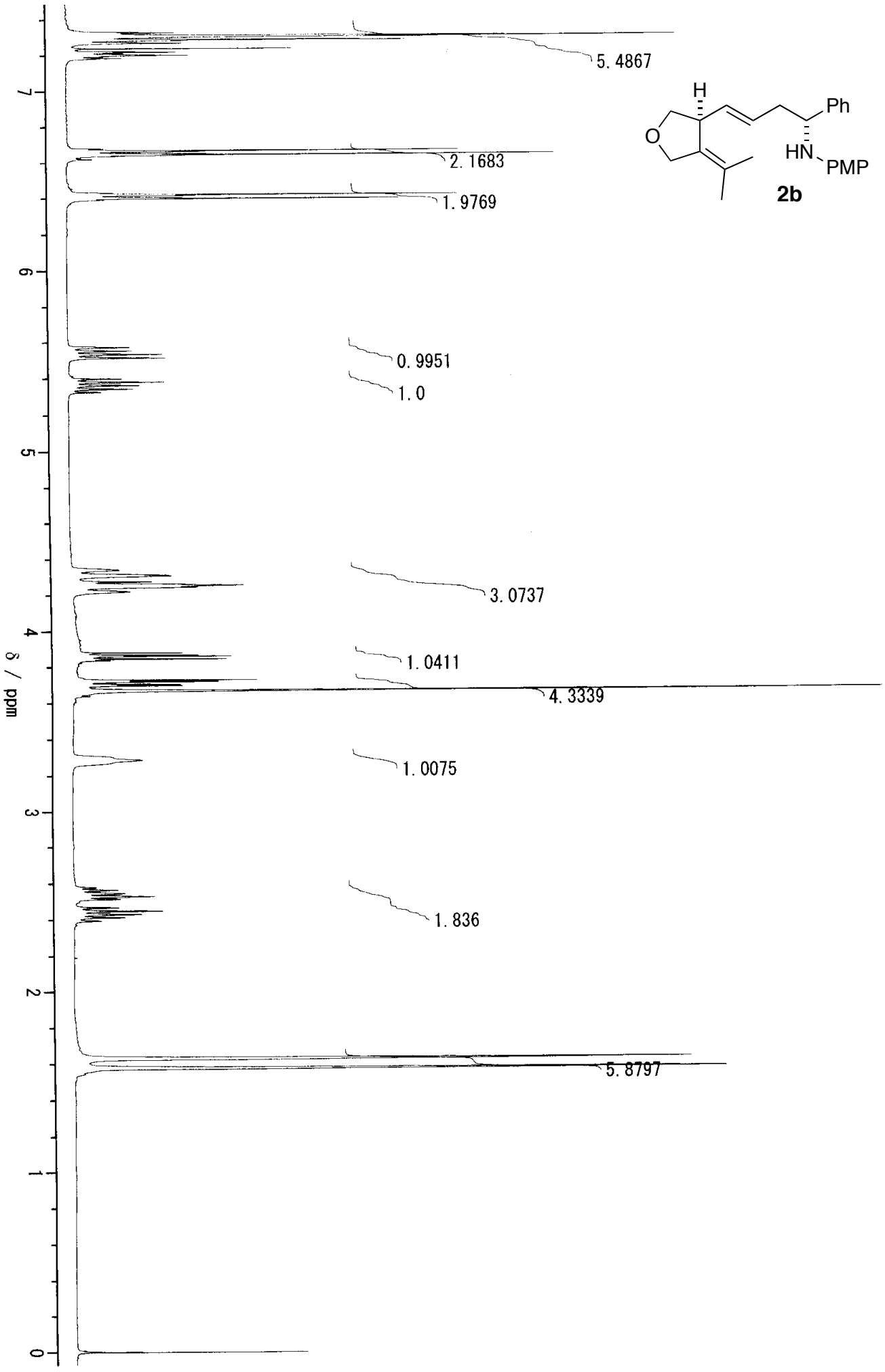
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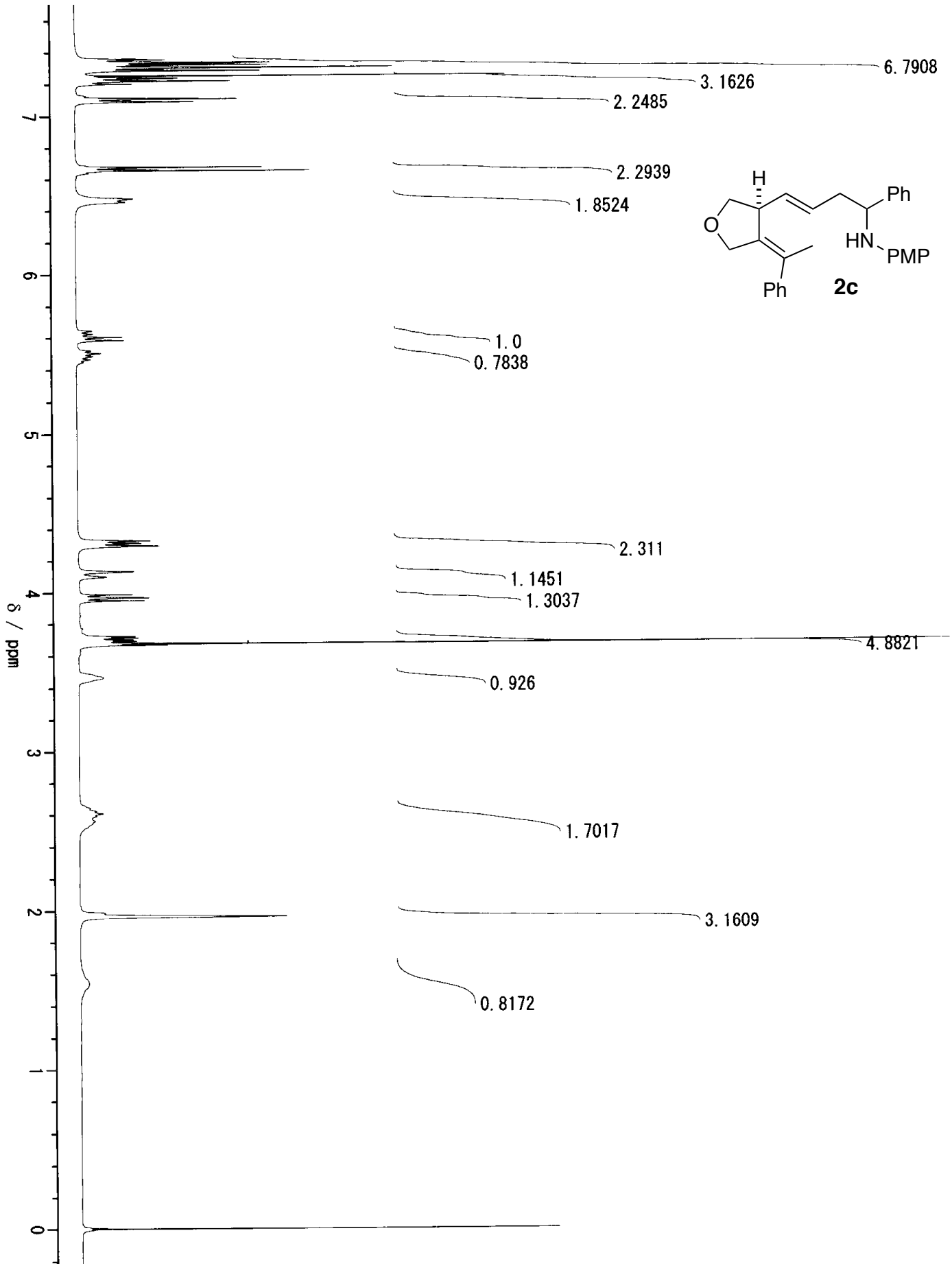
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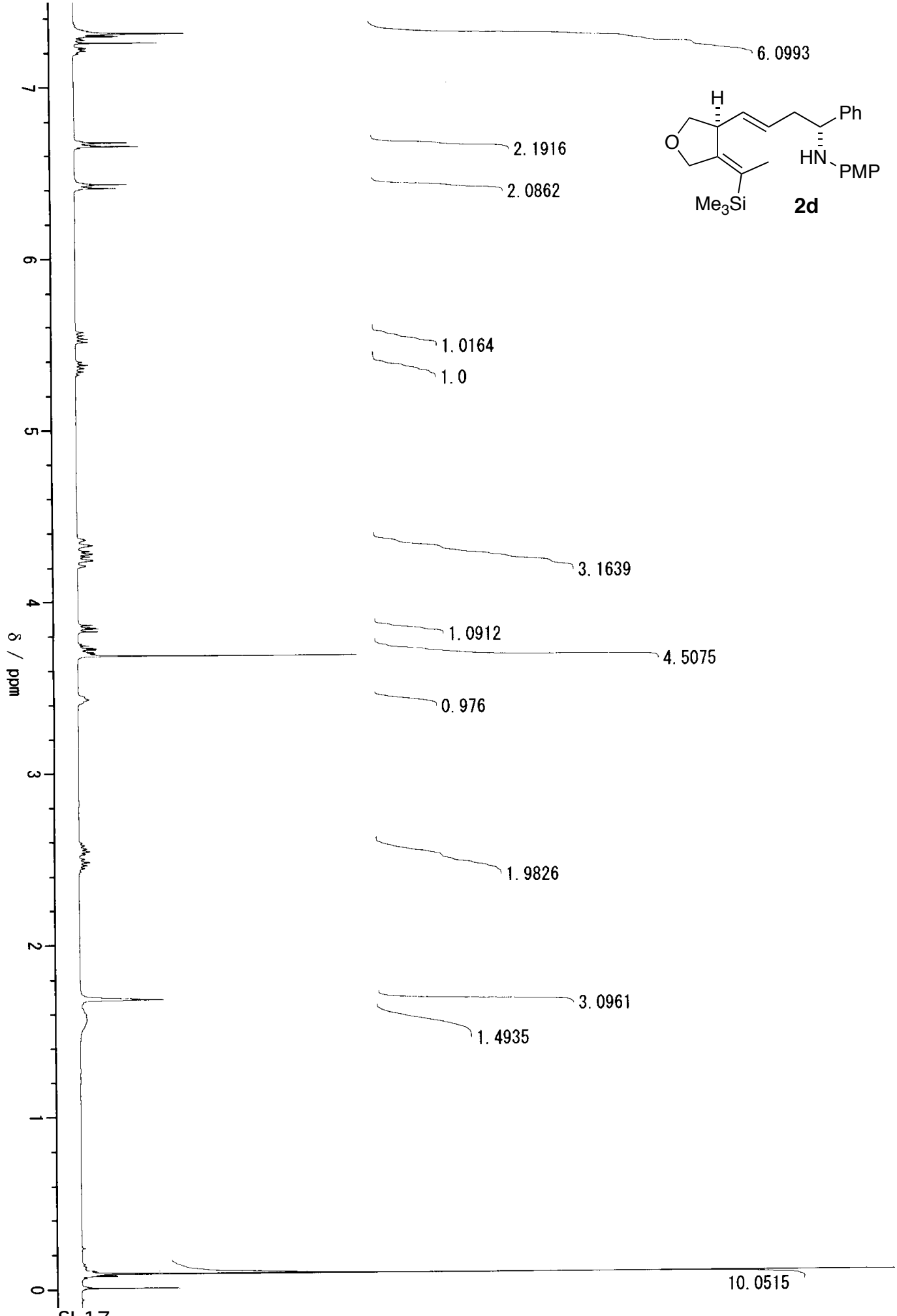
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4
5
6
7
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Ph
O
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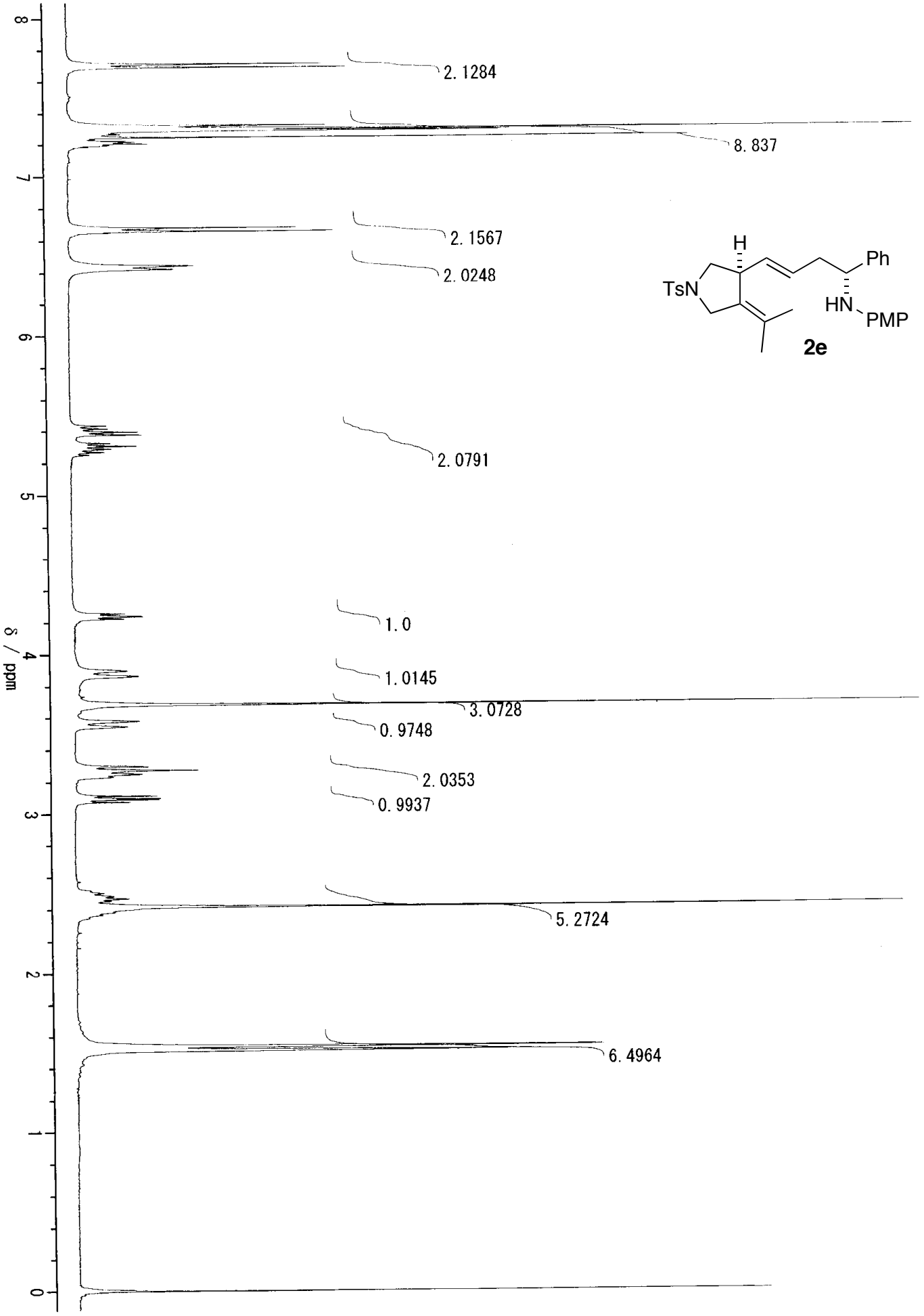
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δ / ppm
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Ph
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HN
PMP
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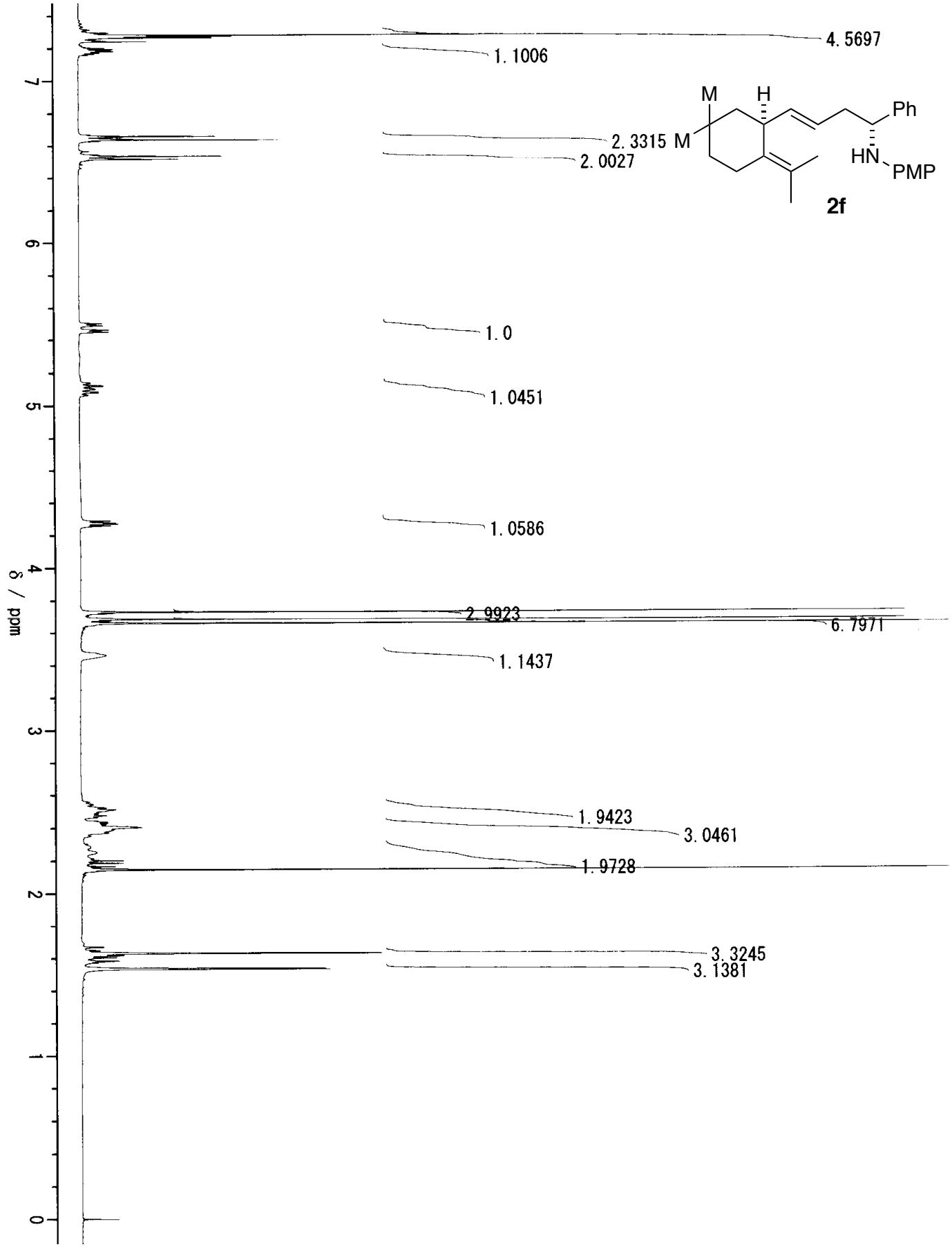
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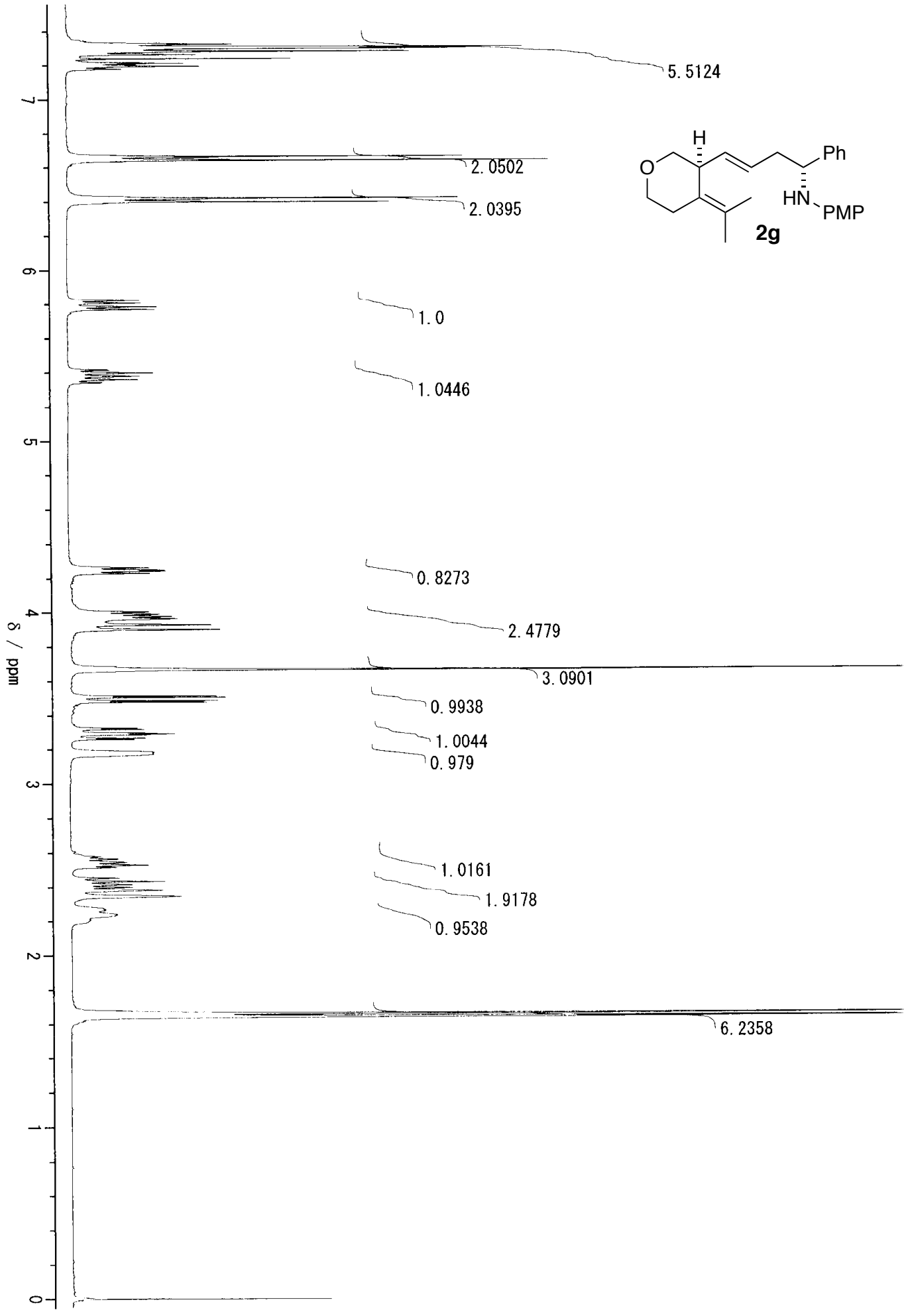
6
7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O
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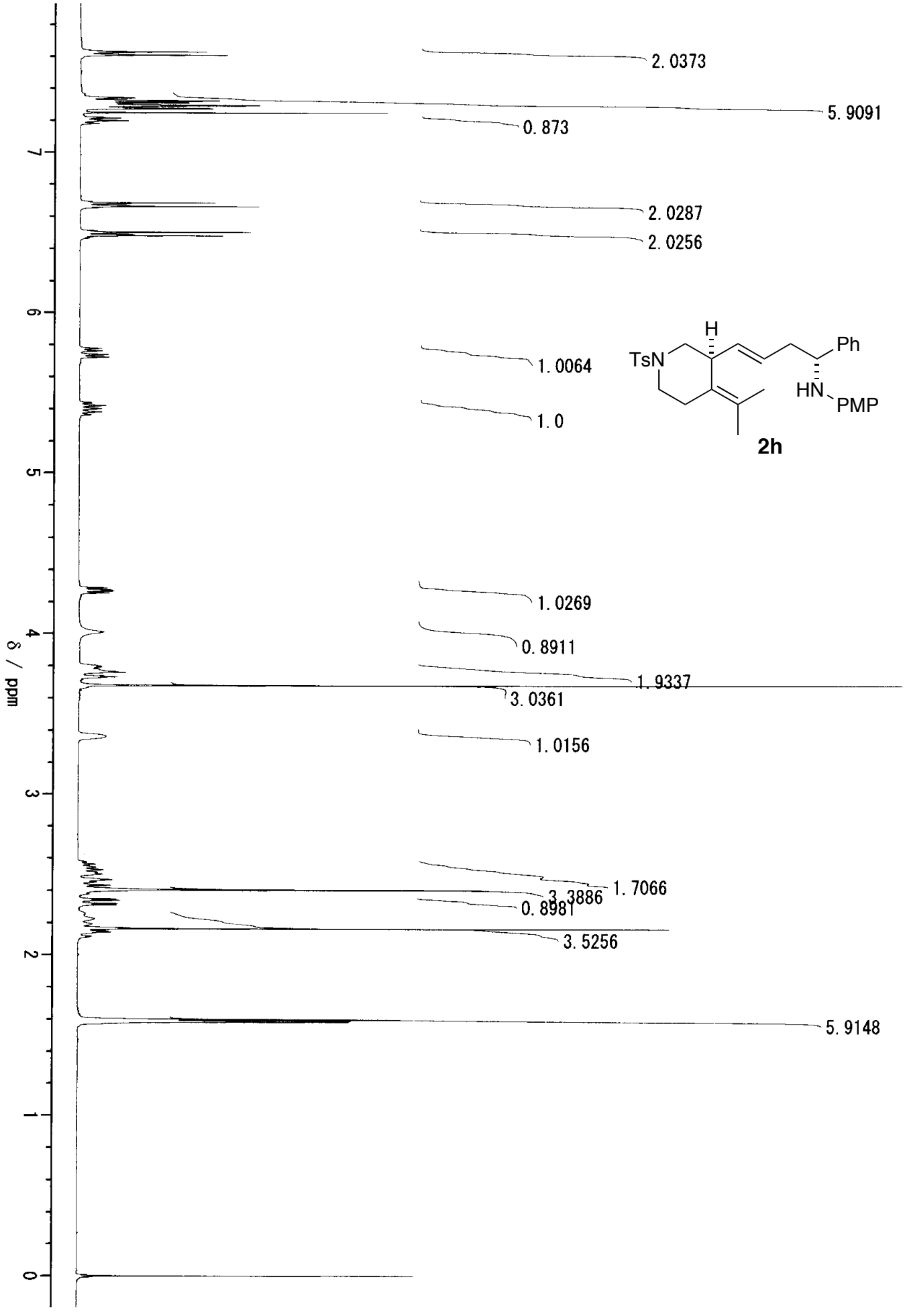
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Ph
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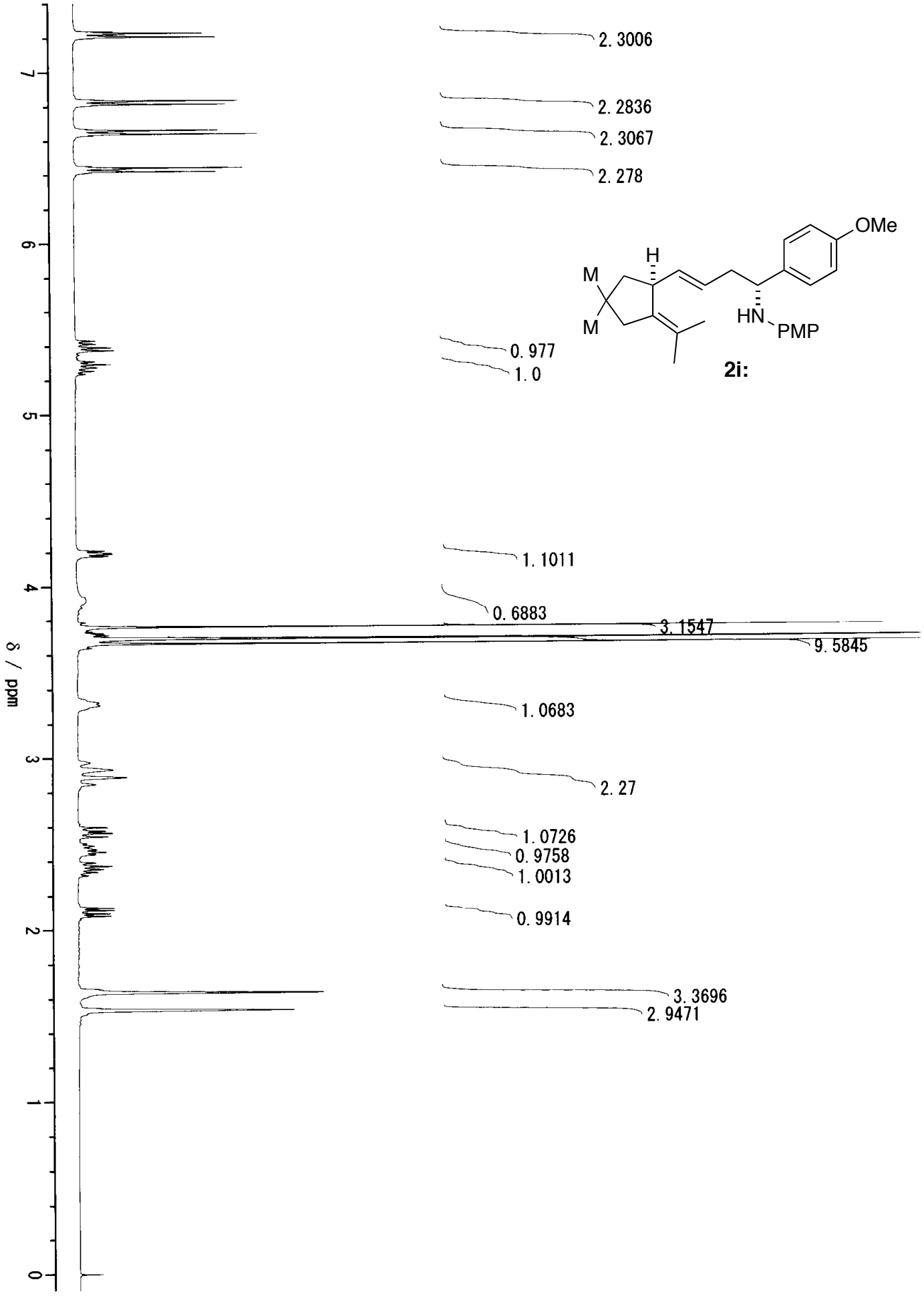
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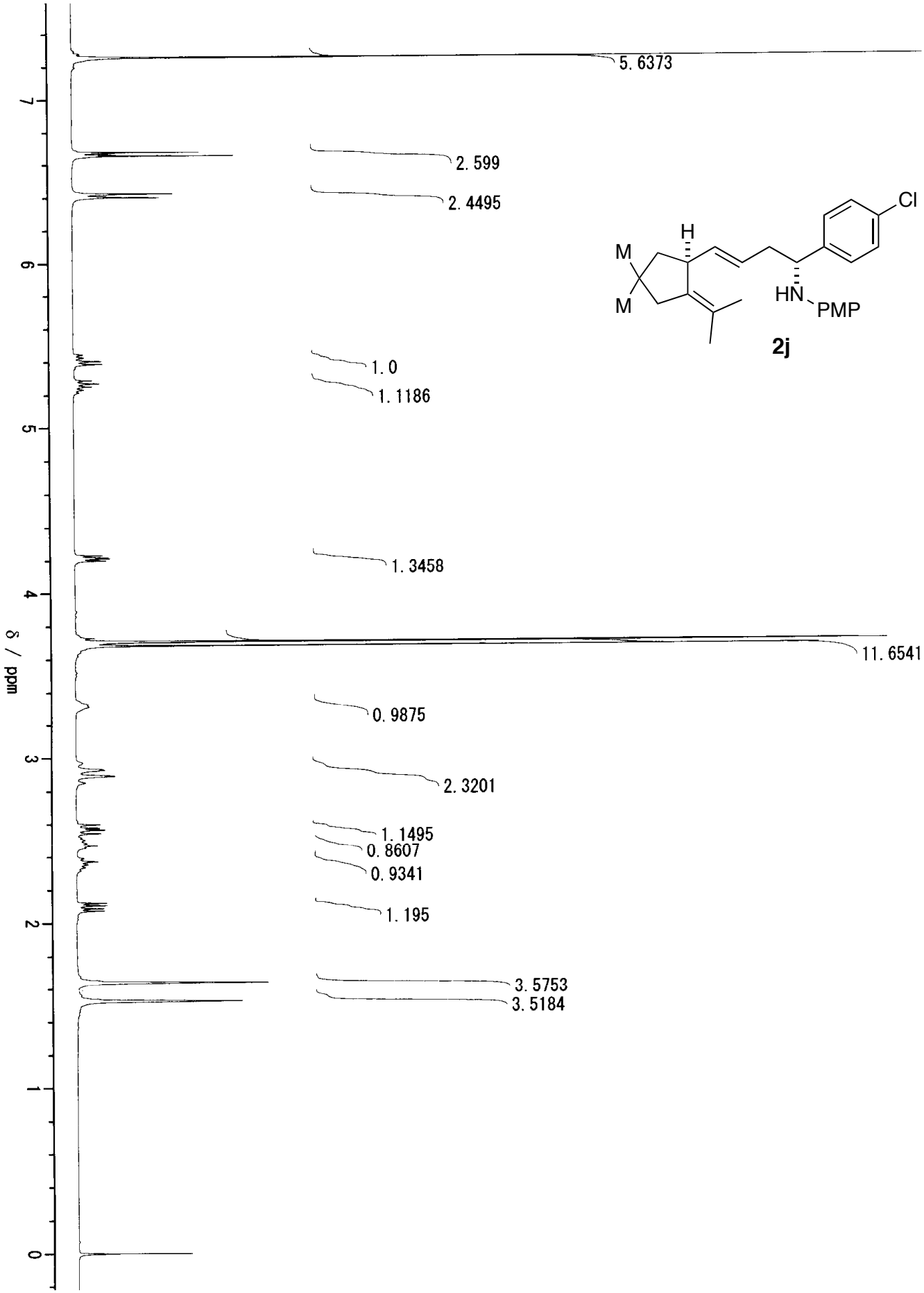
δ / ppm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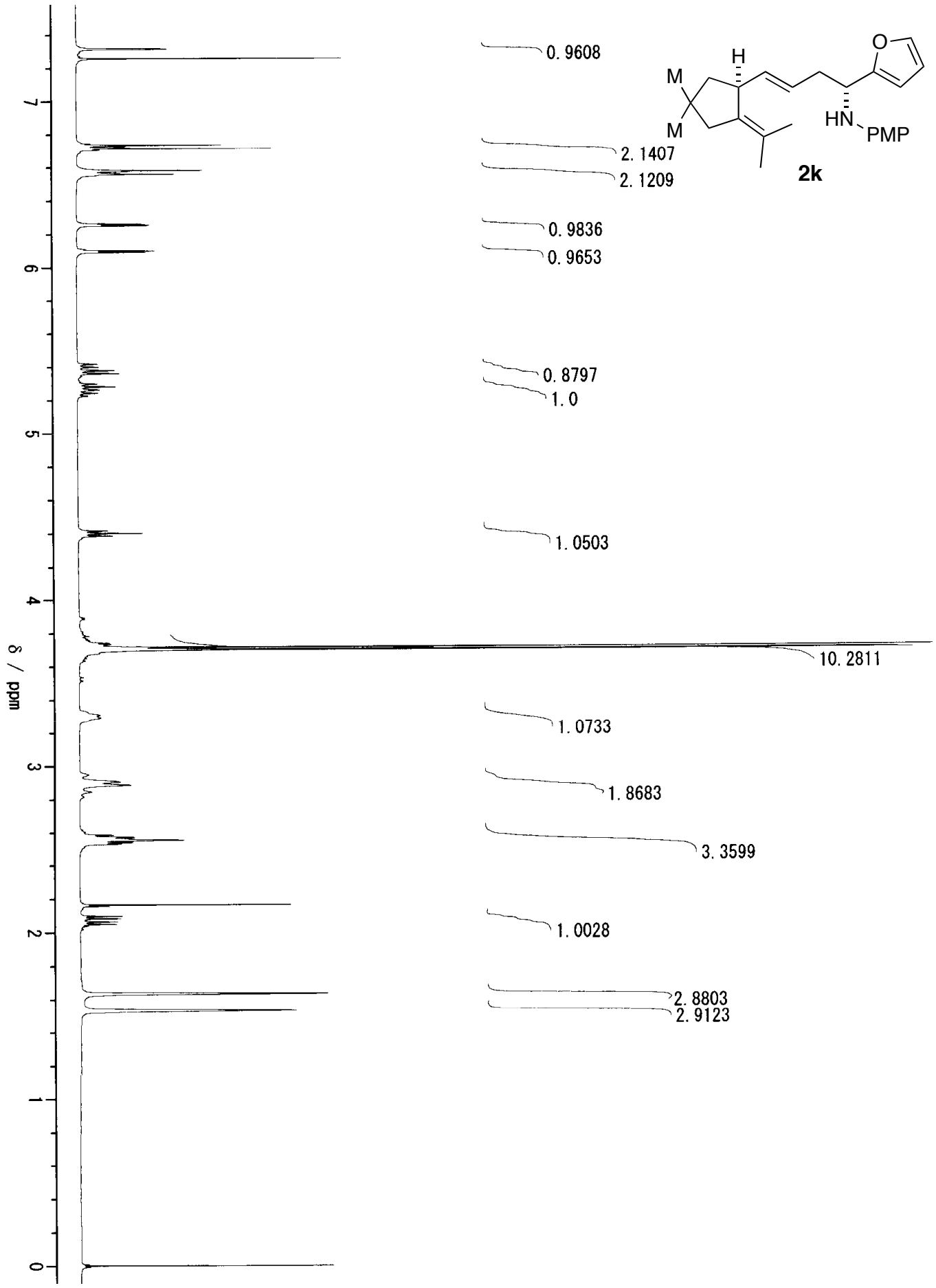
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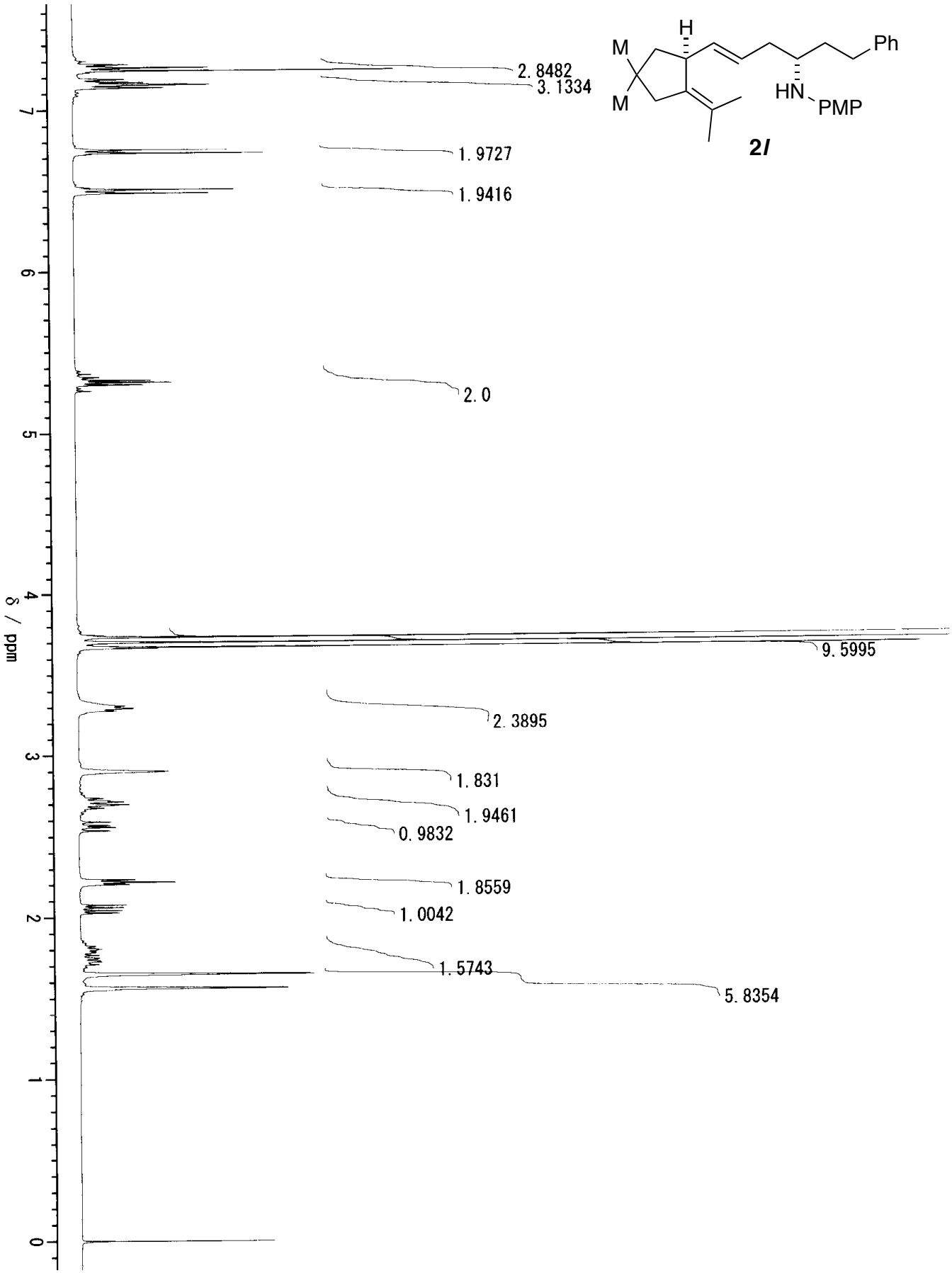
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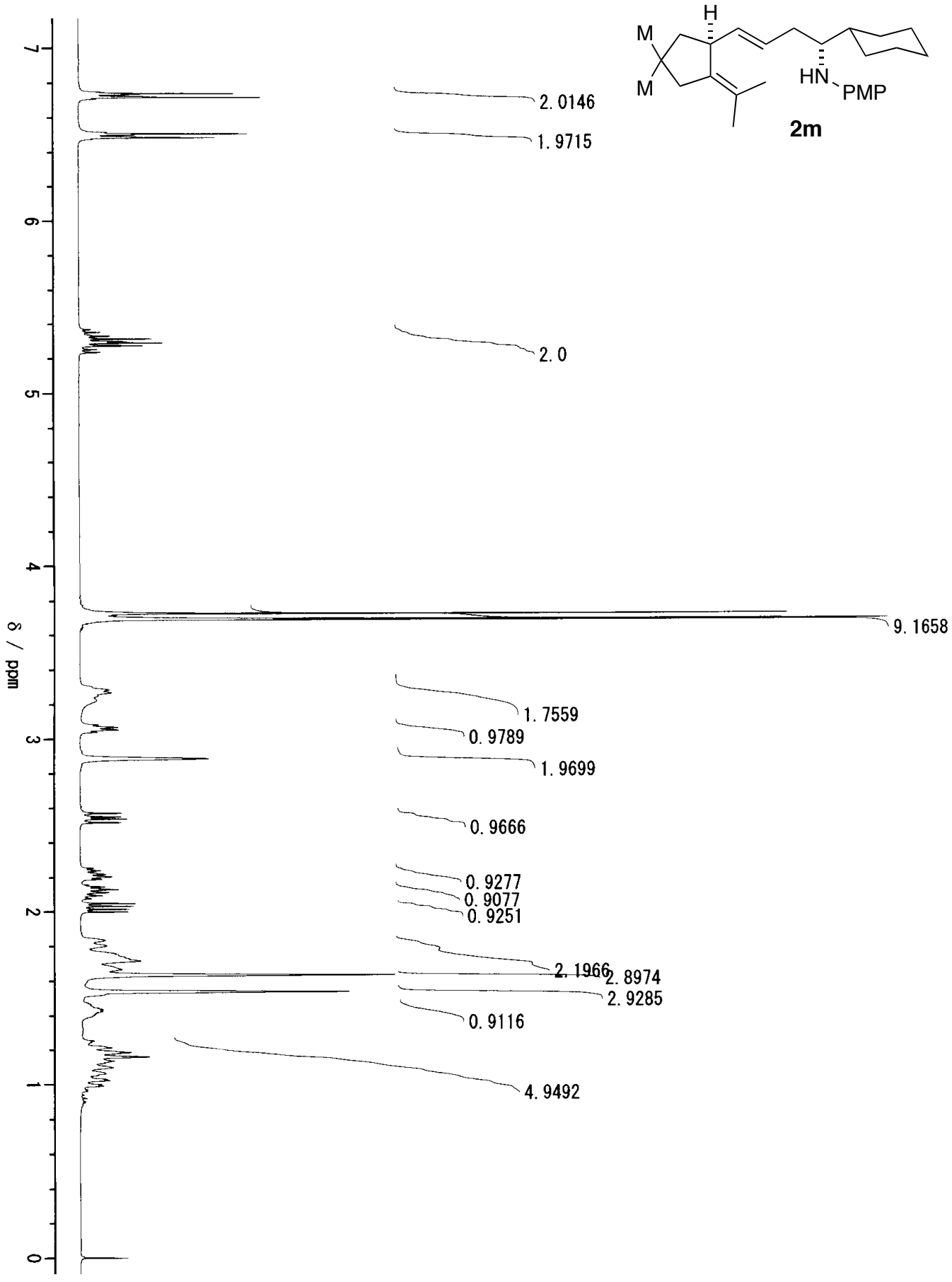
Ph

2*l*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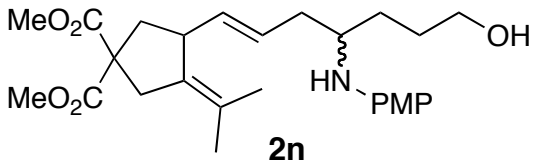
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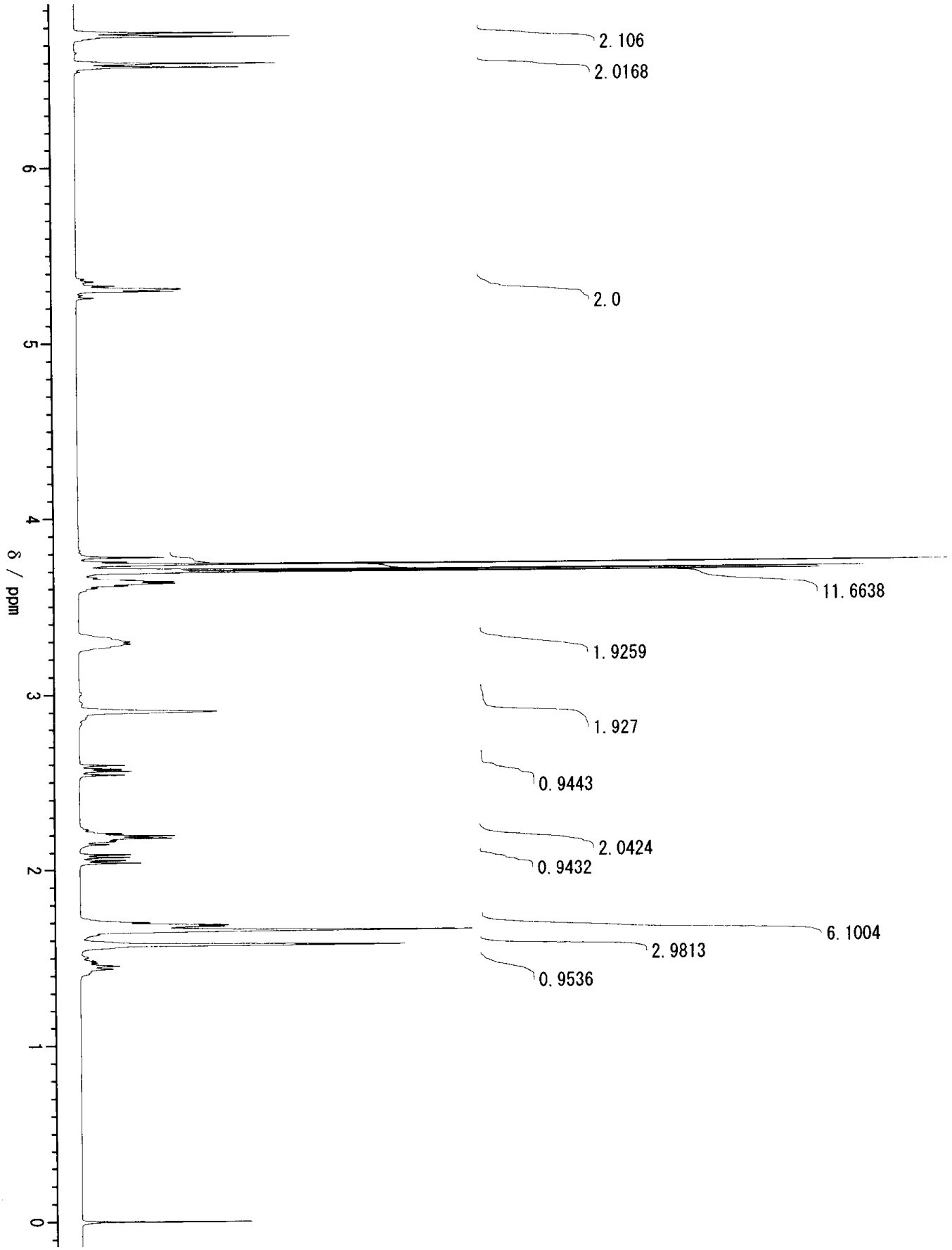
2n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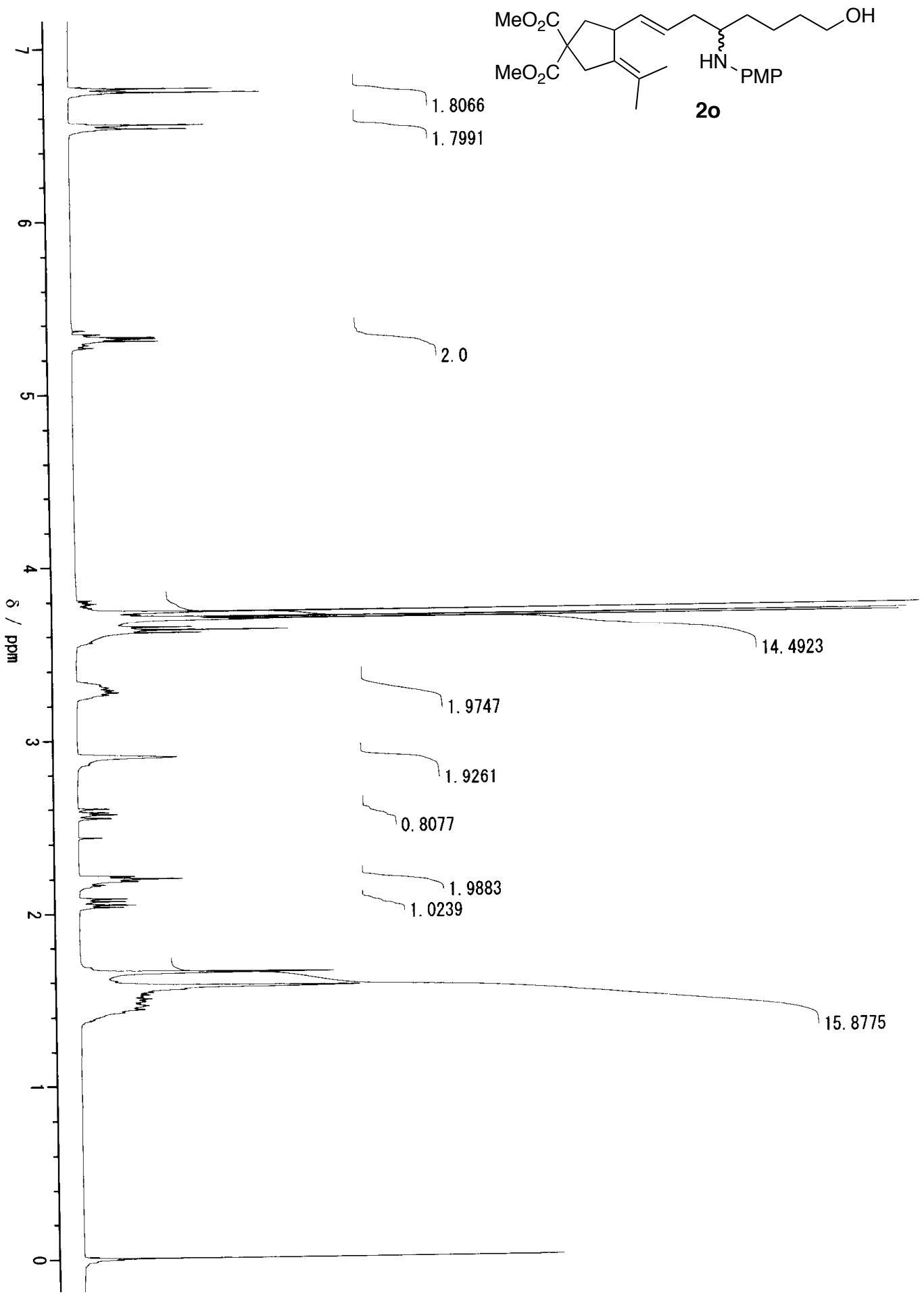
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