endo-Selective Enyne Ring-Closing Metathesis Promoted by Stereogenic-at-Mo Monoalkoxide and Monoaryloxide Complexes. Efficient Synthesis of Cyclic Dienes Not Accessible through Reactions with Ru Carbenes

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SUPPORTING INFORMATION, PART A

General: All reactions were carried out in oven- (135 °C) or flame-dried glassware under an inert atmosphere of dry N_2 unless otherwise stated. All the substrates were dried by azeotropic distillation with C_6H_6 prior to use in reactions with Mo-based reagents. Substrates **1**[1], **8**[1], **9**[1], **10**[2] and **11**[3] bearing diester tether were synthesized according to previously reported procedures. Substrate **12** bearing an acetonide tether was synthesized according to previously reported procedure.[4] Nitrogen-containing susbtrates **16a**[5], **16c**[6], **19**[7], **20**[5], **21**[8], **22**[3], **24**[9] and **27**[9] were synthesized according to previously reported procedures. Oxygen-containing substrates **31**[10] and **34** [11] were synthesized according to previously reported procedures. Dienyne **43** [12] was synthesized according to previously reported procedures. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, υ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the

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internal reference ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.16 ppm, C_6D_6: δ 128.06 ppm). Enantiomer ratios were determined by HPLC (Chiral Technologies Chiralpak AS column (4.6 mm x 250 mm)) in comparison with authentic racemic materials. High resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Boston College Mass Spectrometry Laboratory. Elemental analysis was performed at Midwest Microlab, LLC (Indianapolis, IN). Optical rotation values were recorded on a Rudolph Research Analytical Autopol IV polarimeter. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. X-ray crystallography was performed at the Boston College X-ray Crystallographic Laboratory.

Solvents: Solvents were purged with argon and purified under a positive pressure of dry argon by a modified Innovative Technologies purification system: diethyl ether (Aldrich) and dichloromethane (Doe & Ingalls) were passed through activated alumina columns; benzene (Aldrich), toluene (Doe & Ingalls), and pentane (J T. Baker) were passed successively through activated Cu and alumina columns. Tetrahydrofuran (Aldrich), 2-methyltetrahydrofuran (Aldrich) and 2,5-dimethyltetrahydrofuran (Aldrich) were distilled from sodium benzophenone ketyl. *N,N*-Dimethylformamide and dimethylsulfoxide were distilled from CaH_2 under reduced pressure.

Metal-based Complexes: Mo-based bis(alkoxide) complex **4** was prepared according to a previously reported procedure.[13] Mo-bis(pyrrolide) complex **6** was prepared according to a previously reported procedure.[14] Mo-monoalkoxide-monopyrrolide complexes **5** and **28** were prepared according to previously reported procedures.[1] Mo-monoaryloxide complexes (**44a**, **44b**) bearing chiral aryloxide ligands were generated *in-situ* and used under an inert atmosphere in a dry box according to previously reported procedures.[15] Ru-based complex **7**[16] was obtained from Materia, Inc. and purified by silica gel column chromatography and recrystallization (CH_2Cl_2/ *n*-pentane) prior to use.

Reagents and Ligands:

***o*-Nitrobenzenesulfonyl chloride** was purchased from Aldrich and recrystallized from hexanes and dichloromethane prior to use.

Propargylamine was purchased from Aldrich and distilled over K_2CO_3 prior to use.

1-Phenyl-2-propyn-1-ol was purchased from Aldrich and used as received.

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Chlorodimethylvinylsilane was purchased from Aldrich and used as received.
Triethylamine was purchased from Aldrich and distilled from CaH_2 prior to use.
Chloromethylphenylcinylsilane was purchased from Gelest and used as received.
Sodium hydride was purchased from Aldrich and used as received.
***d*$_6$-Benzene** was purchased from Cambridge Isotope Laboratories and distilled from Na metal into activated 4 Å molecular sieves prior to use.
1-Naphthol, **2-phenylphenol** and **2,6-diphenylphenol** were purchased from Aldrich, recrystallized from hexanes and azeotroped with C_6H_6 prior to use.
Propargyl bromide (80% solution in toluene) was purchased from Aldrich and used as received.
Isopropenylmagnesium bromide (0.5 M solution in tetrahydrofuran) was purchased from Aldrich and used as received.
1,1,1-Trifluoroacetone was purchased from Acros and distilled over K_2CO_3 prior to use.
Na-EDTA (4.0 μM *aqueous* solution) was purchased from Aldrich and used as received.
Oxone® was purchased from Aldrich and used as received.

Preparation of Enyne Substrates

5-(But-3-enyl)-2,2-dimethyl-5-(prop-2-ynyl)-1,3-dioxane (13). This compound was prepared in analogous fashion to **12**[4] starting from **8**[1] (360 mg, 1.43 mmol). Purification by silica gel column chromatography afforded **13** (208 mg, 0.880 mmol, 62% yield over two steps) as a colorless oil. IR (neat): 3305 (br), 3078 (m), 2992 (m), 2862 (m), 1642 (w), 1443 (w), 1196 (s), 1071 (m), 912 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (dddd, *J* = 17.2, 10.0, 6.8, 6.4 Hz, 1H), 5.04 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H), 4.96 (dddd, *J* = 10.0, 2.0, 1.6, 1.2 Hz, 1H), 3.66 (s, 4H), 2.47 (d, *J* = 2.4 Hz, 2H), 2.06-2.01 (m, 2H), 2.00 (t, *J* = 2.8 Hz, 1H), 1.47-1.42 (m, 2H), 1.41 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 114.8, 98.3, 80.9, 70.9, 67.2, 35.2, 32.1, 27.2, 26.8, 21.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found: 209.1537.

5-Allyl-5-(but-2-ynyl)-2,2-dimethyl-1,3-dioxane (14). This compound was prepared in analogous fashion to **12**[4] starting from **9**[1] (558 mg, 2.21mmol). Purification by silica gel column chromatography afforded **14** (280 mg, 1.34 mmol, 63% yield over two steps) as a colorless oil. IR (neat): 3076 (w), 2991 (m), 2920 (br), 2860 (m), 1639 (w), 1439 (m), 1196 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.75 (dddd, *J* = 12.0, 9.6, 8.0, 7.6 Hz, 1H), 5.12 (dddd, *J* = 9.6, 2.0, 1.2, 1.0 Hz, 1H), 5.10-5.08 (m, 1H), 3.64 (s, 4H), 2.29 (dd, *J* = 4.8, 2.4 Hz, 2H), 2.14 (dt, *J* = 7.6, 1.2 Hz, 2H), 1.79 (t, *J* = 2.8 Hz, 3H), 1.41 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.8, 118.8, 98.1, 78.3, 75.2, 66.9, 37.2, 35.7, 25.8, 22.8, 3.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found: 209.1546.

2,2-Dimethyl-5-(2-methylallyl)-5-(prop-2-ynyl)-1,3-dioxane (15). This compound was prepared in analogous fashion to **12**[4] starting from **10**[2] (200 mg, 0.792 mmol). Purification by silica gel column chromatography afforded **15** (104 mg, 0.499 mmol, 63% yield over two steps) as a colorless oil. IR (neat): 3301 (br), 3075 (m), 2940 (br), 2864 (m), 1643 (w), 1452 (m), 1197 (s), 1071 (m), 899 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.92 (d, *J* = 1.6 Hz, 1H), 4.78 (d, *J* =

0.8 Hz, 1H), 3.67 (dd, *J* = 17.2, 11.6 Hz, 4H), 2.45-2.44 (m, 2H), 2.11 (s, 2H), 2.04-2.03 (m, 1H), 1.78 (s, 3H), 1.42(s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 115.7, 98.2, 81.3, 71.4, 67.1, 39.9, 36.0, 26.5, 25.3, 21.4; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found: 209.1538.

***N*-Allyl-2-nitro-*N*-(prop-2-ynyl)benzenesulfonamide (16b).** This compound was prepared in analogous fashion to **16a**[5] starting from *o*-nitrobenzenesulfonyl chloride (560 mg, 2.53 mmol) and propargylamine (0.140 ml, 2.53 mmol). Purification by silica gel column chromatography afforded **16b** (495 mg, 1.77 mmol, 70% yield over two steps) as a white solid. M.p. = 48-51 ºC; IR (neat): 3289 (m), 1543 (s), 1357 (m), 1165 (m), 899 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.74-7.63 (m, 3H), 5.71 (dddd, *J* = 17.2, 10.0, 9.6, 6.8 Hz, 1H), 5.31 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H), 5.26 (ddt, *J* = 10.0, 1.2, 1.2 Hz, 1H), 4.14 (d, *J* = 2.6 Hz, 2H), 4.02 (d, *J* = 6.4 Hz, 2H), 2.15 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 133.9, 132.9, 131.9, 131.5, 131.1, 124.3, 120.6, 76.8, 73.9, 49.5, 36.0; HRMS (ESI): $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O_4S$: 281.0596, found: 281.0584.

Dimethyl(1-phenylprop-2-ynyloxy)(vinyl)silane (39). An oven-dried round-bottom flask with magnetic stir bar was charged with 1-phenyl-2-propyn-1-ol (1.24 mL, 10.0 mmol) and tetrahydrofuran (30.0 mL). At 22 ºC, triethylamine (1.67 mL, 12.0 mmol) was added in one portion followed by the dropwise addition (over 5 min) of chlorodimethylvinylsilane (1.66 mL, 12.0 mmol). The resulting mixture was allowed to stir for 0.5 h, during which time the formation of a white precipitate was observed. The mixture was diluted with diethyl ether (100 mL) and filtered to remove the white precipitates. The filtrate was concentrated and purified by silica gel column chromatography to afford **39** (1.71 g, 7.90 mmol, 79% yield) as a colorless oil. IR (neat): 3300 (m), 2959 (m), 1595 (w), 1407 (w), 1253 (m), 1089 (m), 1065 (s), 842 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.39-7.31 (m, 3H), 6.19 (dd, *J* = 20.4, 15.2 Hz, 1H), 6.06 (dd, *J* = 20.4, 4.0 Hz, 1H), 5.85 (dd, *J* = 20.4, 4.0 Hz, 1H), 5.49 (d, *J* = 2.0 Hz, 1H), 2.59 (d, *J* = 2.0 Hz, 1H), 0.31 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 137.2, 134.0, 128.6, 128.2, 126.5, 84.5, 74.2, 64.8, -1.3, -1.4; HRMS (ESI) $[M]^+$ calcd for $C_{13}H_{16}OSi$: 216.0970, found: 216.0967.

Methyl(phenyl)(1-phenylprop-2-ynyloxy)(vinyl)silane (41). This compound was prepared in analogous fashion to **39** starting from 1-phenyl-2-propyn-1-ol (1.24 mL, 10.0 mmol) and chloromethylphenylvinylsilane (1.67 mL, 12.0 mmol). Purification by silica gel column chromatography afforded **41** (1.43 g, 5.14 mmol, 51% yield) as a colorless oil (1:1 mixture of two diastereomers). IR (neat): 3290 (m), 2949 (m), 1592 (w), 1404 (m), 1254 (m), 1115 (m), 1087 (m), 1062 (s), 847 (s), 696 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 2H), 7.40-7.22 (m, 8H), 6.34-6.18 (m, 1H), 6.14-6.05 (m, 1H), 5.90-5.78 (m, 1H), 5.42 (dd, *J* = 6.4, 2.0 Hz, 1H), 2.49 (dd, *J* = 3.6, 2.0 Hz, 1H), 0.46 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 135.5, 135.2, 134.3, 134.2, 130.0, 128.5, 128.1, 127.9, 126.4, 84.2, 74.4, 65.1, -2.7; HRMS (ESI): $[M]^+$ calcd for $C_{18}H_{18}OSi$: 278.1127, found: 278.1131.

***N*-(2,4-Dimethylpenta-1,4-dien-3-yl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (47).** An oven-dried flask with magnetic stir bar was charged with isopropenylmagnesium bromide (0.5 M solution in tetrahydrofuran, 22.0 mL, 11.0 mmol) under nitrogen. The solution was allowed to cool to 0 ºC and ethyl *N*-tosylformimidate[17] (1.14 g, 5.00 mmol) in 4.00 mL tetrahydrofuran was added dropwise over 5 min; the resulting mixture was allowed to warm to 22 ºC and stir for 12 hr. The mixture was allowed to cool to 0ºC, and the reaction was quenched by the addition of a saturated aqueous solution of ammonium chloride. The resulting mixture was diluted with diethyl ether (50.0 mL), washed with water (10.0 mL x 2) and brine (10.0 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated to afford a pale yellow solid. The crude solid was dissolved in *N,N*-dimethylformamide (5.00 mL) and added dropwise over 5 min to a suspension of NaH (145 mg, 6.00 mmol) in 10.0 ml of *N,N*-dimethylformamide at 0 ºC. Propargyl bromide (80% solution in toluene, 0.67 mL, 6.00 mmol) was added in one portion and the resulting mixture was allowed to warm to 22 ºC and stir for 2 h. The reaction was quenched by the addition of a saturated aqueous solution of ammonium chloride and the mixture was diluted with diethyl ether (80.0 mL), washed with water (15.0 mL x 2) and brine (15 mL), dried over anhydrous magnesium sulfate, filtered and concentrated. The resulting brown oil was purified by silica gel column chromatography to afford **47** (883 mg, 2.91 mmol, 58% yield over two steps) as a white solid. M.p. = 65-70 ºC; IR (neat): 3276 (m), 2920 (m), 1598 (w), 1338 (s), 1160 (s), 908 (m), 661 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 2H), 4.84 (s, 2H), 4.71 (s, 1H), 4.07 (d, *J* = 2.4 Hz, 2H), 2.41 (s, 3H), 2.07 (t, *J* = 2.4 Hz, 1H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.2, 137.8, 129.4, 128.0, 115.7, 79.7, 72.0, 67.7, 34.2, 22.1, 21.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{22}NO_2S$: 304.1371, found: 304.1369.

Ethyl 2-(prop-2-ynyl)pent-4-enoate (50). An oven-dried round-bottom flask with magnetic stir bar was charged with **1**[1] (1.00 g, 4.20 mmol) and dimethylsulfoxide (5.00 mL). Lithium chloride (214 mg, 5.04 mmol) was added followed by the addition of water (0.10 mL). The flask was fitted with a water-jacketed reflux condenser and the mixture was heated to 190 ºC and allowed to stir for 12 h. The mixture was allowed to cool to 22 ºC, washed with diethyl ether (30.0 ml x 2). The organic layer was washed with water (5.00 mL x 2), dried over anhydrous magnesium sulfate, filtered and concentrated. The resulting brown oil was purified by silica gel column chromatography to afford **50** (350 mg, 1.47 mmol, 35% yield) as a colorless oil. IR (neat): 3303 (br), 3080 (m), 1734 (s), 1642 (w), 1178 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.72 (dddd, *J* = 17.2, 10.0, 7.2, 6.8 Hz, 1H), 5.10 (ddd, *J* = 16.8, 3.2, 1.6 Hz, 1H), 5.06 (ddd, *J* = 10.4, 1.6, 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.62 (quin, *J* = 7.2 Hz, 1H), 2.52-2.36 (m, 4H), 1.98 (t, *J* = 2.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 134.5, 117.8, 81.4, 70.1, 60.8, 44.1, 35.2, 20.5, 14.4; HRMS (ESI) $[M + H]^+$ calcd for $C_{10}H_{15}O_2$: 167.1072, found: 167.1070.

Preparation of Mo Complexes

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Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(2,6-diphenylphenoxide) (38a). An oven-dried round-bottom flask with magnetic stir bar was charged with Mo-bispyrrolide complex **6** (200 mg, 0.338 mmol) and 5.00 mL of diethyl ether. To this solution was added 2,6-diphenylphenol (83.2 mg, 0.338 mmol) in 5.00 mL of diethyl ether in one portion at 22 ºC. The resulting mixture was allowed to stir for 1 h at 22 ºC and the volatiles were removed *in vacuo*. The resulting residue was dissolved in pentane (1.00 mL) and this solution was allowed to stand at –55 ºC for 12 h, during which time the formation of orange crystals was observed. The crystals were collected by vacuum filtration to afford **38a** (201 mg, 0.270 mmol, 80% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 11.70 (s, 1H), 7.90-7.88 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.47-7.43 (m, 5H), 7.37-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.23-7.15 (m, 5H), 6.39 (s, 2H), 3.38 (sep, *J* = 6.4 Hz, 2H), 2.52 (br s, 6H), 1.82 (s, 3H), 1.50 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.09 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 290.4, 160.0, 154.1, 148.9, 147.7, 140.0, 133.8, 133.2, 131.1, 129.7, 129.2, 128.4, 127.6, 126.2, 126.0, 123.1, 122.4, 109.4, 55.8, 31.8, 30.4, 28.7, 23.8, 23.4, 17.1; Elemental analysis: C 74.69, H 6.89, N, 3.87 (theory: C 74.38, H 6.78, N 3.77).

Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(2,3,5,6-tetraphenylphenoxide) (38b). This complex was prepared by the exact same procedure for the formation of complex **38a** starting from Mo-bispyrrolide **6** (200 mg, 0.338 mmol) and 2,3,4,6-tetraphenylphenol[18] (135 mg, 0.338 mmol) (Reaction time = 4 h). Crystallization from pentane afforded **38b** as a bright orange solid. (230 mg, 0.257 mmol, 83%): ^{1}H NMR (400 MHz, C_6D_6): δ 11.67 (s, 1H), 7.57-7.53 (m, 5H), 7.42-7.39 (m, 6H), 7.30-7.19 (m, 12H), 7.19-7.05 (m, 6H), 6.30 (s, 2H), 3.43 (sep, *J* = 6.8 Hz, 2H), 2.31 (s, 6H), 1.90 (s, 3H), 1.49 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.11 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 292.4, 160.1, 153.9, 149.0, 147.5, 142.5, 142.3, 137.8, 134.4, 132.1, 130.2, 128.5, 128.3, 127.4, 127.0, 126.6, 126.4, 126.3, 123.4, 55.5, 32.1, 31.1, 28.4, 24.0, 22.7, 17.2; Elemental analysis: C 77.84, H 6.78, N, 3.35 (theory: C 77.83, H 6.53, N 3.13).

***In-situ* generation of Mo-monoaryloxide complex for RCM reaction of 31 (Table 5, entry 1).** A 1 dram vial with magnetic stir bar was charged with **6** (5.92 mg, 10.0 μmol), 1-naphthol (1.44 mg, 10.0 μmol) and C_6D_6 (500 μL) in an N_2-filled glovebox. The mixture was allowed to stir for 1 h at 22 ºC, after which the solution was transferred to a screw-cap NMR tube by syringe. The NMR tube was tightly capped and sealed with Teflon tape. For *in-situ* generated complexes, only the diagnostic signal of the α-proton of the *syn*-alkylidene is reported. ^{1}H NMR (400 MHz, C_6D_6): δ 12.22 (1H, s).

Mo-(2-phenylphenoxide) complex (Table 5, entry 2) was generated from **6** (5.92 mg, 10.0 μmol), 2-phenylphenol (1.70 mg, 10.0 μmol) and C_6D_6 (500 μL) following the same procedure as above (A mixture of **6** (28%), Mo-monoaryloxide (72%) and Mo-bisaryloxide (28%) was obtained). ^{1}H NMR (400 MHz, C_6D_6): δ 11.52 (1H, s).[19]

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(18) Prepared as in Yates, P.; Hyre, J. E. *J. Org. Chem.* **1962**, *27*, 4101–4103.

(19) For the corresponding Mo-bisaryloxide complex, signal of the α-proton of the *syn*-alkylidene (^{1}H NMR, 400 MHz, C_6D_6): δ 10.85 (1H, s).

■ Mo-Catalyzed Enyne Ring-Closing Metathesis Reactions

The procedures for the transformations in Scheme 2 and entries 1, 2 in table 1 and characterizations of the corresponding products have been reported.[1]

Representative procedure for Mo-catalyzed enyne ring-closing metathesis reactions for the synthesis of carbocyclic and *N*-heterocyclic diene (Table 1, entry 3). In an N_2-filled glove box, a 4-mL vial with magnetic stir bar was charged with Mo-monoaryloxide complex **5** (1.36 mg, 2.00 μmol) and 50.0 μL of C_6H_6. A solution of **10** (10.1 mg, 40.0 μmol) in C_6H_6 (200 μL) was added dropwise over five min. The mixture was allowed to stir at 22 ºC for 0.5 h, after which the reaction was quenched by exposure to air. The mixture was concentrated to afford a brown residue, which was purified by silica gel column chromatography to afford the *endo* product (9.28 mg, 36.8 μmol, 92 % yield) as colorless oil. The physical and spectral data were identical to those previously reported.[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (s, 1H), 4.79 (s, 2H), 4.20-4.14 (m, 4H), 2.80 (s, 2H). 2.56 (s, 2H), 1.81 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 139.7, 135.8, 124.5, 111.0, 61.5, 54.5, 35.7, 35.6, 23.5, 14.1.

Diethyl 3,4-dimethyl-5-methylenecyclohex-3-ene-1,1-dicarboxylate (Table 1, entry 4). (The physical and spectral data were identical to those previously reported).[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (s, 1H), 4.79 (s, 1H), 4.16-4.14 (m, 4H), 2.83 (s, 2H). 2.61 (s, 2H), 1.80 (s, 3H), 1.75 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 141.4, 130.5, 126.3, 109.2, 61.5, 54.2, 38.0, 37.6, 20.3, 14.2, 13.9.

3,3-Dimethyl-10-methylene-2,4-dioxaspiro[5.5]undec-8-ene (Table 2, entry 1). (The physical and spectral data were identical to those previously reported).[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (d, *J* = 10.0 Hz, 1H), 5.73-5.67 (m, 1H), 4.89 (s, 1H), 4.86 (s, 1H), 3.57 (s, 4H), 2.26 (t, *J* = 1.2 Hz, 2H), 2.14-2.12 (m, 2H) , 1.43 (s, 3H), 1.41 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.0, 129.2, 127.0, 113.5, 98.3, 68.4, 36.3, 31.8, 24.6, 23.2.

3,3,9-Trimethyl-10-methylene-2,4-dioxaspiro[5.5]undec-8-ene (*endo* product) and 8,8-Dimethyl-2-(prop-1-en-2-yl)-7,9-dioxaspiro[4.5]dec-2-ene (*exo* product) (ratio of *endo* and *exo* product = 66 : 33, Table 2, entry 2). obtained as a colorless oil. IR (neat): 3079 (w), 2991 (m), 2918 (br), 2856 (m), 1598 (w), 1369 (m), 1194 (m), 1073 (s), 893 (m) cm^{-1}; (*endo* product - major) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11 (d, *J* = 17.6 Hz, 1H), 5.79-5.74 (m, 1H), 4.92 (s, 2H), 3.62 (s, 4H), 2.39 (s, 2H), 2.21-2.18 (m, 2H). 1.62-1.57 (m, 2H), 1.43 (s, 3H), 1.41 (s, 3H); (*exo* product - minor) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.72 (s, 1H), 5.11 (d, *J* = 17.6 Hz, 1H), 4.89 (d, *J* = 17.6 Hz, 1H), 3.63 (d, *J* = 11.6 Hz, 2H), 3.56 (d, *J* = 11.6 Hz, 2H), 2.26-2.19 (m, 2H), 2.07 (d, *J* = 2.0 Hz, 2H), 1.62-1.57 (m, 2H), 1.45 (s, 3H), 1.43 (s, 3H); (*endo* and *exo* product) ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 139.9, 133.3, 133.2, 128.6,

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117.2, 113.6, 110.5, 98.4, 98.2, 68.7, 68.6, 68.5, 40.4, 35.3, 34.1, 30.6, 30.2, 27.4, 24.6, 24.2, 23.9, 23.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found: 209.1551.

3,3-Dimethyl-8-methylene-2,4-dioxaspiro[5.6]dodec-9-ene (*endo* product) and 3,3-Dimethyl-8-vinyl-2,4-dioxaspiro[5.5]undec-8-ene (*exo* product) (ratio of *endo* and *exo* product = 75: 25, Table 2, entry 3). obtained as a colorless oil. IR (neat): 2991 (m), 2924 (m), 2855 (m), 1606 (w), 1369 (m), 1196 (s), 1116 (s), 881 (w), 832 (s) cm^{-1}; (*endo* product - major) ^1H NMR (400 MHz, $CDCl_3$): δ 5.53 (s, 1H), 4.99 (s, 1H), 4.86 (s, 1H), 3.55 (dd, *J* = 15.6, 11.2 Hz, 4H), 2.29 (s, 2H), 2.12 (t, *J* = 2.0 Hz, 2H), 1.81-1.80 (m, 3H), 1.42 (s, 3H), 1.41 (s, 3H); (*exo* product - minor) ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (s, 1H), 4.90 (s, 1H), 4.86 (s, 1H), 3.69 (t, *J* = 1.2 Hz, 4H), 2.42 (d, *J* = 1.6 Hz, 2H), 2.38 (s, 2H), 1.91 (s, 3H), 1.45(s, 3H), 1.44 (s, 3H); (*endo* and *exo* product) ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.4, 141.4, 140.0, 132.7, 125.3, 124.9, 123.0, 112.9, 110.9, 98.4, 69.7, 68.5, 66.1, 40.9, 40.2, 38.0, 33.1, 32.8, 24.5, 24.2, 22.7, 20.6, 19.4; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found: 209.1544.

3,3,8-Trimethyl-10-methylene-2,4-dioxaspiro[5.5]undec-8-ene (Table 2, entry 4). obtained as a colorless oil. IR (neat): 3079 (w), 2992 (w), 2923 (br), 2856 (m), 1612 (w), 1381 (m), 1211 (m), 1068 (s), 902 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.92 (s, 1H), 4.79 (s, 1H), 4.76 (s, 1H), 3.56 (d, *J* = 10.8 Hz, 2H), 3.54 (d, *J* = 10.8 Hz, 2H), 2.19 (s, 2H), 2.05 (s, 2H), 1.78 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 135.8, 124.6, 111.0, 98.3, 68.5, 36.8, 36.1, 24.8, 23.8, 23.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}O_2$: 209.1542, found 209.1540.

3-Methylene-1-tosyl-1,2,3,6-tetrahydropyridine (17a). (The physical and spectral data were identical to those previously reported).[11] ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.13 (dt, *J* = 9.2, 1.8 Hz, 1H), 5.72-5.68 (m, 1H), 4.92 (s, 1H), 4.90 (s, 1H), 3.81 (s, 2H), 3.72-3.71 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 137.0, 133.8, 129.8, 128.0, 127.7, 124.9, 113.2, 48.4, 45.0, 21.7.

3-Methylene-1-(2-nitrophenylsulfonyl)-1,2,3,6-tetrahydropyridine (17b). obtained as a colorless viscous oil. IR (neat): 3092 (m), 2903 (m), 2849 (w), 1645 (w), 1543 (s), 1372 (w), 1356 (s), 1166 (s), 1127 (w), 1083 (w), 948 (m), 744 (w), 663 (w), 583 (m), 534 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.70-7.63 (m, 2H), 7.58 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.19 (dt, *J* = 10.0, 0.9 Hz, 1H), 5.81-5.79 (m, 1H), 4.97 (s, 1H), 4.92 (s, 1H), 4.09 (t, J = 1.2 Hz, 2H), 4.00-3.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 133.9, 132.0, 131.7, 130.9, 127.8, 125.2, 124.2, 113.6, 48.3, 44.9; HRMS (ESI): $[M + H]^+$ calcd for $C_{12}H_{13}N_2O_4S$: 281.0596, found: 281.0606.

***tert*-Butyl-5-methylene-5,6-dihydropyridine-1(2*H*)-carboxylate (17c).** obtained as a colorless oil. IR (neat): 3037 (m), 2833 (w), 1695 (s), 1413 (s), 1366 (w), 1260 (w), 1236 (s), 1167 (s), 1106 (m), 1005 (w), 881 (m), 768 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, *J* = 10.0 Hz, 1H), 5.80 (br s, 1H), 4.89 (s, 2H), 4.08 (s, 2H), 3.98 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 155.0, 138.6, 127.5, 123.0, 118.7, 111.7, 80.1, 46.8, 45.5, 43.6, 28.7, 28.2, 22.7; HRMS (ESI): $[M + H]^+$ calcd for $C_{11}H_{18}NO_2$: 196.1338, found: 196.1347.

3-Methylene-1-tosyl-2,3,6,7-tetrahydro-1*H*-azepine (Table 3, entry 1). A solution of **19** (9.45 mg, 40 μmol) in 31.0 mL of C_6H_6 was used. (Concentration of substrate in the reaction mixture = 1.30 μM). IR (neat): 2923 (m), 1597 (w), 1450 (w), 1333 (s), 1153 (s), 1093 (m), 914 (s), 815 (m), 757 (m), 668 (m), 591 (s), 547 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 11.6 Hz, 1H), 5.56 (quin, *J* = 5.6 Hz, 1H), 5.04 (s, 1H), 4.95 (s, 1H), 4.10 (s, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 143.0, 136.9, 131.6, 129.7, 129.0, 127.5, 118.1, 53.1, 48.8, 29.3, 21.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{14}H_{18}NO_2S$: 264.1058, found: 264.1047.

4-Methyl-3-methylene-1-tosyl-1,2,3,6-tetrahydropyridine (*endo* product) and 3-(Prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (*exo* product) (ratio of endo and exo product = 84 : 16, Table 3, entry 2). (The physical and spectral data were identical to those previously reported).[22] (*endo* product, major) ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 4.99 (s, 1H), 4.92 (s, 1H), 3.78 (s, 2H), 3.69 (br s, 2H), 2.40 (s, 3H), 1.72 (s, 3H); (*exo* product - minor) ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.58 (s, 1H), 4.97 (s, 1H), 4.75 (s, 1H), 4.26-4.18 (m, 4H), 2.40 (s, 3H), 1.84 (s, 3H); (*endo* product) ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 133.5, 132.0, 129.9, 129.6, 128.0, 122.2, 110.5, 49.3, 45.7, 21.6, 18.5; (*exo* product) ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 139.4, 136.3, 134.2, 129.5, 127.5, 120.7, 114.7, 55.6, 54.5, 21.6, 20.1.

5-Methyl-3-methylene-1-tosyl-1,2,3,6-tetrahydropyridine (Table 3, entry 3). A solution of **21** (9.45 mg, 40 μmol) in 5.95 ml of C_6H_6 was used. (Concentration of substrate in the reaction mixture = 6.67 μM). (The physical and spectral data were identical to those previously reported).[23] ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 5.85 (s, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 3.75 (s, 2H), 3.60 (s, 2H), 2.40 (s, 3 H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 137.3, 133.7, 129.7, 127.9, 123.6, 113.0, 110.6, 48.5, 48.0, 21.7, 20.7.

4,5-Dimethyl-3-methylene-1-tosyl-1,2,3,6-tetrahydropyridine (Table 3, entry 4). A solution of **22** (9.45 mg, 40.0 μmol) in 20.0 ml of C_6H_6 was used. (Concentration of substrate in the reaction mixture = 2.00 μM). (The physical and spectral data were identical to those previously reported).[3] ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.93 (s, 1H), 4.83 (s, 1H), 3.76 (s, 2H), 3.59 (s, 2H), 2.41 (s, 3H), 1.68 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.7, 139.1, 129.7, 128.5, 128.1, 126.1, 108.8, 50.3, 49.9, 21.7, 17.6, 13.3.

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5-Methylene-1-tosyl-2,5-dihydro-1H-benzo[*b*]azepine (25). obtained as a colorless viscous oil. IR (neat): 3062 (w), 2921 (m), 1649 (w), 1341 (s), 1157 (s), 678 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.43 (m, 3H), 7.37-7.23 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.95 (d, *J* = 12.0 Hz, 1H), 5.53 (dt, *J* = 11.6, 4.0 Hz, 1H), 4.90 (s, 1H), 4.75 (s, 1H), 4.44 (br s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 143.1, 140.7, 137.5, 137.0, 131.4, 129.8, 129.3, 129.2, 129.2, 129.0, 128.3, 126.0, 121.6, 49.4, 21.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S$: 312.1058, found: 312.1052.

3-Methylene-1-tosyl-2,3-dihydro-1*H*-benzo[b]azepine (*endo* product, 29) and 1-Tosyl-3-vinyl-1,2-dihydro-quinoline (*exo* product, 30) (ratio of *endo* and *exo* product = 62 : 38). A solution of **27** (12.5 mg, 40 μmol) in 20.0 ml of C_6H_6 was used. (Concentration of substrate in the reaction mixture = 20.0 μM). IR (neat): 2924 (m), 1598 (w), 1351 (m), 1165 (s), 678 (m) cm^{-1}; (*endo* product - major) ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.36-7.35 (m, 3H), 7.26-7.23 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.07 (d, *J* = 16.4 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.82 (d, *J* = 16.4 Hz, 1H), 4.51 (s, 2H), 2.33 (s, 3H); (*exo* product - minor) ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.38-7.34 (m, 2H), 7.31-7.15 (m, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.16 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.40 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 4.55 (s, 2H), 2.32 (s, 3H); (*endo* and *exo* product) ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 146.8, 143.5, 141.5, 135.8, 135.4, 134.6, 133.5, 130.6, 129.0, 129.0, 128.4, 128.1, 127.6, 127.1, 127.0, 126.9, 126.6, 126.3, 125.6, 124.7, 123.3, 114.9, 45.2, 44.7, 28.9, 21.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S$: 312.1058, found: 312.1050.

Representative procedure for Mo-catalyzed enyne ring-closing metathesis reactions for the synthesis of *O*-heterocyclic dienes (Table 4, entry 2). In an N_2-filled glove box, a 4 mL vial with magnetic stir bar was charged with a solution of **5** (0.02 M solution in C_6H_6, 125 μL, 2.5 μmol), a solution of **31** (8.6 mg, 50 μmol) in 1.13 mL of C_6H_6 was added. The mixture was allowed to stir at 22 ºC for 10 h, after which time the reaction was quenched by exposure to air. The mixture was concentrated to afford a brown residue, which was purified by silica gel column chromatography to afford **32** (4.0 mg, 23 μmol, 46% yield) as colorless oil. IR (neat): 3032 (m), 1604 (w), 1087 (s), 699 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 6.39 (dt, *J* = 10.4, 2.0 Hz, 1H), 5.92 (d, *J* = 9.6 Hz, 1H), 5.19 (s, 1H), 5.00 (s, 1H), 4.53 (s, 1H), 4.31 (dt, *J* = 17.6, 2.4 Hz, 1H), 4.18 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 139.3, 128.6, 128.4, 128.2, 128.1, 127.0, 113.3, 79.0, 64.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{12}H_{13}O$: 173.0966, found: 173.0967.

3-Methylene-6-phenyl-3,6-dihydro-2*H*-pyran (35). obtained as a colorless oil. IR (neat): 2920 (s), 2850 (m), 1736 (w), 1070 (m), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.26 (m, 5H), 6.41 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.96 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.23 (s, 1H), 4.94 (s, 1H), 4.89 (s, 1H), 4.42 (d. *J* =13.6 Hz, 1H), 4.35 (dt, *J* = 13.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 138.9, 131.4, 128.6, 128.2, 127.7, 127.0, 110.3, 76.2, 67.5; HRMS (ESI) $[M + H]^+$ calcd for $C_{12}H_{13}O$: 173.0966, found: 173.0964.

2,2-Dimethyl-5-methylene-6-phenyl-5,6-dihydro-2*H*-1,2-oxasiline (40). obtained as a colorless oil. IR (neat): 2958 (w), 1552 (m), 1453 (w), 1250 (m), 1079 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.26 (m, 5H), 7.16 (d, *J* = 14.4 Hz, 1H), 5.98 (d, *J* = 14.4 Hz, 1H), 5.57 (s, 1H), 5.12 (s, 1H), 4.67 (d, *J* = 1.6 Hz, 1H), 0.27 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 146.7, 142.2, 129.7, 128.3, 128.1, 127.7, 119.3, 76.5, –0.3, –0.4; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{17}OSi$: 217.1049, found: 217.1043.

2-Methyl-5-methylene-2,6-diphenyl-5,6-dihydro-2*H*-1,2-oxasiline (42) (mixture of two diastereomers, dr = 60 : 40). obtained as a colorless oil. IR (neat): 2998 (w), 1550 (m), 1428 (m), 1115 (m), 1079 (m), 696 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 1H), 7.57-7.55 (m, 1H), 7.43-7.26 (m, 8H), 6.14 (d, *J* = 14.0 Hz, 0.6H), 6.08 (d, *J* = 14.4 Hz, 0.4H), 5.70 (s, 0.4H), 5.62 (s, 0.6H), 5.19 (s, 0.6H), 5.17 (s, 0.4H), 4.73 (s, 0.6H), 4.68 (s, 0.4H), 0.58 (s, 1.2 H), 0.41 (s, 1.8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 148.9, 146.9, 146.6, 142.0, 141.8, 136.6, 136.0, 134.2, 134.1, 130.2, 130.1, 129.5, 129.0, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.8, 127.4, 119.9, 119.8, 76.6, 76.6, –1.9, –2.1; HRMS (ESI) $[M]^+$ calcd for $C_{18}H_{18}OSi$: 278.1127, found: 278.1117.

Ethyl 5-methylenecyclohex-3-enecarboxylate (51). In an N_2-filled glove box, a 4-mL vial with magnetic stir bar was charged with a solution of **38a** in C_6H_6 (0.01 M, 500 μL, 5.0 μmol), a solution of **51** (16.2 mg, 100 μmol) in 500 μL C_6H_6 was added. The mixture was allowed to stir at 22 °C for 0.5 h, after which the reaction was quenched by exposure to air. The mixture was concentrated to afford a brown residue, which was purified by silica gel column chromatography to afford **52** (12.2 mg, 75.2 μmol, 75% yield) as a colorless oil. IR (neat): 2976 (br), 1733 (s), 1620 (w), 1170 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, *J* = 9.6 Hz, 1H), 5.81 (quin, *J* = 4.8 Hz, 1H), 4.86 (s, 1H), 4.84 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.68-2.62 (m, 2H), 2.51-2.44 (m, 1H), 2.38-2.34 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 141.4, 129.5, 128.2, 112.4, 60.7, 39.9, 33.2, 28.0, 14.5; HRMS (ESI) $[M + H]^+$ calcd for $C_{10}H_{15}O_2$: 167.1072, found: 167.1072.

Ru-Catalyzed Enyne Ring-Closing Metathesis Reactions

Representative procedure for Ru-catalyzed enyne ring-closing metathesis reactions. Diethyl 3-vinylcyclopent-3-ene-1,1-dicarboxylate (3). A 4-mL vial with magnetic stir bar was charged with **7** (2.51 mg, 4.00 μmol) and 100 μL of C_6H_6. Under nitrogen, a solution of **1** (19.1 mg, 80.0 μmol) in 2.00 mL of C_6H_6 was added dropwise over 5 min and the resulting mixture was allowed to stir at 22 °C for 2 h. The mixture was concentrated and the resulting brown oil was purified by silica gel chromatography to afford **3** (12.4 mg, 52.0 μmol, 65% yield) as colorless oil. The physical and spectral data were identical to those previously reported.[24] ^1H NMR (400 MHz, $CDCl_3$): δ 6.48 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.58-5.57 (m, 1H), 5.12 (d, *J* = 6.0 Hz, 1H), 5.08 (s,

(23) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863-11869.

1H), 4.20 (q, *J* = 7.2 Hz, 4H), 3.12 (d, *J* = 1.2 Hz, 2H), 3.10 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 140.3, 132.7, 127.2, 115.2, 61.9, 59.0, 41.0, 39.4, 14.3.

1-Tosyl-4-vinyl-1,2-dihydroquinoline (26). obtained as colorless viscous oil. IR (neat): 2921 (m), 1642 (w), 1351 (m), 1164 (s), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.28-7.22 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.11 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.56 (td, *J* = 4.8, 1.2 Hz, 1H), 5.11 (d, *J* = 17.6, 1H), 5.00 (d, *J* = 10.2, 1H), 4.39 (d, *J* = 4.8 Hz, 2H), 2.30(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 143.1, 140.7, 137.5, 137.0, 131.4, 129.8, 129.3, 129.2, 129.2, 129.0, 128.3, 126.0, 121.6, 49.4, 21.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S$: 312.1058, found: 312.1053.

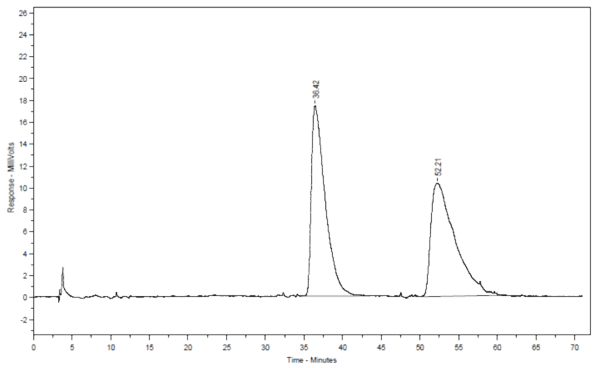
2-Phenyl-3-vinyl-2,5-dihydrofuran (33). obtained as colorless viscous oil. IR (neat): 3030 (w), 2847 (m), 1596 (w), 1082 (s), 698 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 5H), 6.43 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.10 (s, 1H), 5.83 (t, *J* = 2.0 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H), 4.92-4.86 (m, 1H), 4.87 (d, *J* = 17.6 Hz, 1H), 4.76 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.4, 129.0, 128.7, 128.4, 127.7, 126.6, 117.7, 87.5, 75.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{12}H_{13}O$: 173.0966, found: 173.0964.

2-Phenyl-4-vinyl-2,5-dihydrofuran (36). (The physical and spectral data were identical to those previously reported).[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.26 (m, 5H), 6.56 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.85 (br s, 2H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 5.04-4.99 (m, 1H), 4.88 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 138.8, 129.5, 128.7, 128.5, 128.0, 126.6, 117.1, 88.5, 74.6.

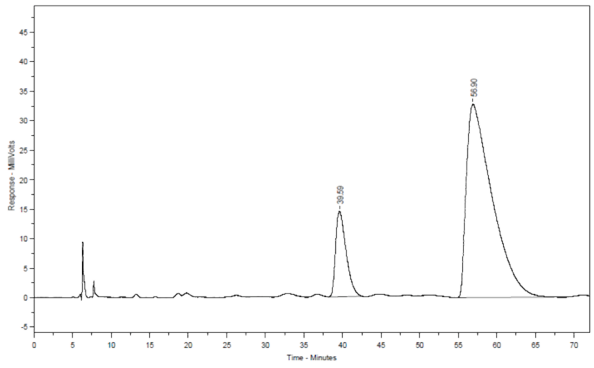
■ Enantioselective Ring-Closing Metathesis Reactions of *N*-Containing Eienynes

Procedure for enantioselective ring-closing metathesis reaction of dienyne 43 (45). In an N_2-filled glove box, a 4-mL vial with magnetic stir bar was charged with a 0.02 M solution of Mo complex **44b** in C_6H_6 (250 μL, 5.00 μmol) generated *in-situ*[15] and 500 μL of C_6H_6. The vial was capped with septa and sealed with electrical tape, then brought out of the glove box and a balloon of ethylene attached. A solution of **43** (12.9 mg, 50.0 μmol) in 500 μL of C_6H_6 was added in one portion and the resulting mixture allowed to stir at 22 ºC under ethylene for 2 h. The reaction was quenched by exposure to air and concentrated *in vacuo* to afford a brown residue, which was purified by silica gel column chromatography to afford desired product **45** (8.11 mg, 31.5 μmol, 63 % yield) as a white solid. M.p. = 96 − 99 ºC; IR (neat): 2922 (m), 1637 (w), 1343 (s), 1161 (s), 668 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.05 (dd, *J* = 10.0, 0.8 Hz, 1H), 5.88-5.80 (m, 1H), 5.61 (dd, *J* = 10.0, 4.8 Hz, 1H), 5.24 (dt, *J* = 10.6, 1.2 Hz, 1H), 5.21 (dt, *J* = 17.6, 1.2 Hz, 1H), 4.87 (s, 1H), 4.86 (s, 1H), 4.79 (s, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 137.1, 136.1, 134.5, 129.3, 128.2, 127.5, 126.7, 118.2, 113.2, 54.9, 44.0, 21.5; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{18}N_1O_2S_1$: 276.1058, found: 276.1048; Optical Rotation: $[\alpha]_D^{20}$ –24.9 (*c* = 0.40, $CHCl_3$) for an enantiomerically enriched sample of 85:15 er (70% ee).

The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic materials (Chiralpak AS, hexane:2-propanol = 99:1.0, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm, retention times; (minor) 39.59 min, (major) 56.90 min, 85:15 er).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %
1	36.42		0.00	N/A	2168516	49.103
2	52.21		0.00	N/A	2247785	50.897

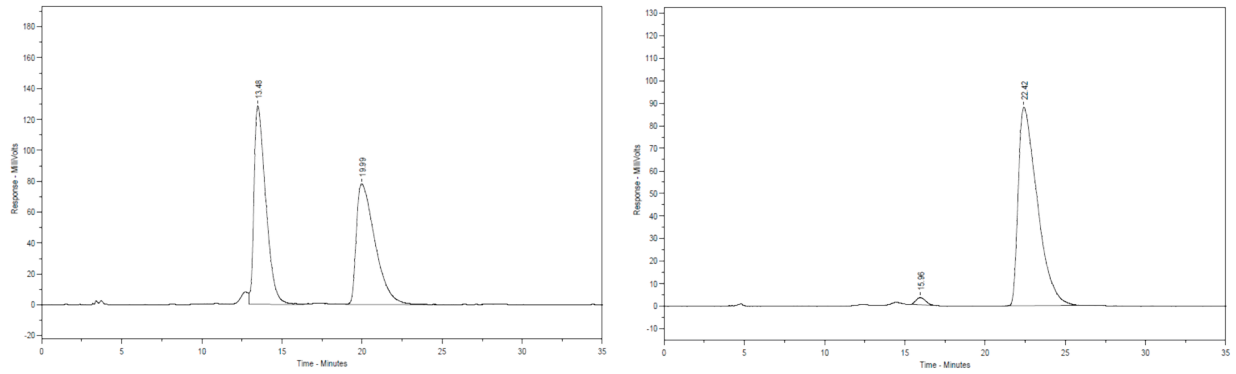


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %
1	39.59		0.00	N/A	1375499	15.287
2	56.90		0.00	N/A	7622566	84.713

***N*-(2,4-Dimethylpenta-1,4-dien-3-yl)-4-methyl-*N*-(2-methylenebut-3-enyl)benzenesulfonamide (48).** This compound was prepared in analogous fashion to **45** starting from **47** (15.2 mg, 50.0 μmol). Purification by silica gel column chrmatography afforded **48** (11.5 mg, 35.0 μmol, 70% yield) as a colorless viscous oil. IR (neat): 2919 (m), 1649 (w), 1340 (s), 1159 (s), 904 (m), 662 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.33 (dd, *J* = 18.0, 11.2 Hz, 1H), 5.32 (s, 1H), 5.16 (s, 1H), 5.09 (d, *J* = 18.0 Hz, 1H), 5.00 (d, *J* = 11.2 Hz, 1H), 4.86 (s, 2H), 4.81 (s, 1H), 4.65 (s, 2H), 4.08 (s, 2H), 2.41 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 140.7, 137.0, 136.7, 134.8, 129.1, 127.6, 125.6, 115.7, 110.4, 61.9, 43.7, 21.6, 21.2; HRMS (ESI) $[M + H]^+$ calcd for $C_{19}H_{26}N_1O_2S_1$: 332.1684, found: 332.1686.

5-Methyl-3-methylene-6-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (49). In an N_2-filled glove box, a 4-mL vial with magnetic stir bar was charged with **48** (9.90 mg, 30.0 μmol). C_6H_6 (680 μL), followed by a solution of **44a** in C_6H_6 (0.02 M, 75.0 μL, 1.50 μmol) was added. The mixture was allowed to stir at 22 °C for 6 h, after which time the reaction was quenched by exposure to air. The mixture was concentrated to afford a brown residue, which was purified by silica gel column chromatography to afford **49** (8.4 mg, 27.7 μmol, 92% yield) as a white solid. M.p. = 94 – 96 °C; IR (neat): 2922 (w), 1648 (w), 1344 (m), 1158 (s), 669 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.67 (s, 1H), 5.05 (t, *J* = 1.6 Hz, 1H), 4.72 (d, *J* = 4.0 Hz, 2H), 4.58 (s, 1H), 4.47 (s, 1H), 4.29 (d, *J* = 16.8 Hz, 1H), 3.80 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H), 1.91 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 140.8, 137.1, 136.8, 134.9, 129.2, 127.6, 125.6, 115.7, 110.5, 62.0, 43.7, 30.0, 21.7, 21.3; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{22}NO_2S$: 304.1371, found: 304.1369; Optical Rotation: $[\alpha]_D^{20}$ +5.0 (*c* = 0.40, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee).

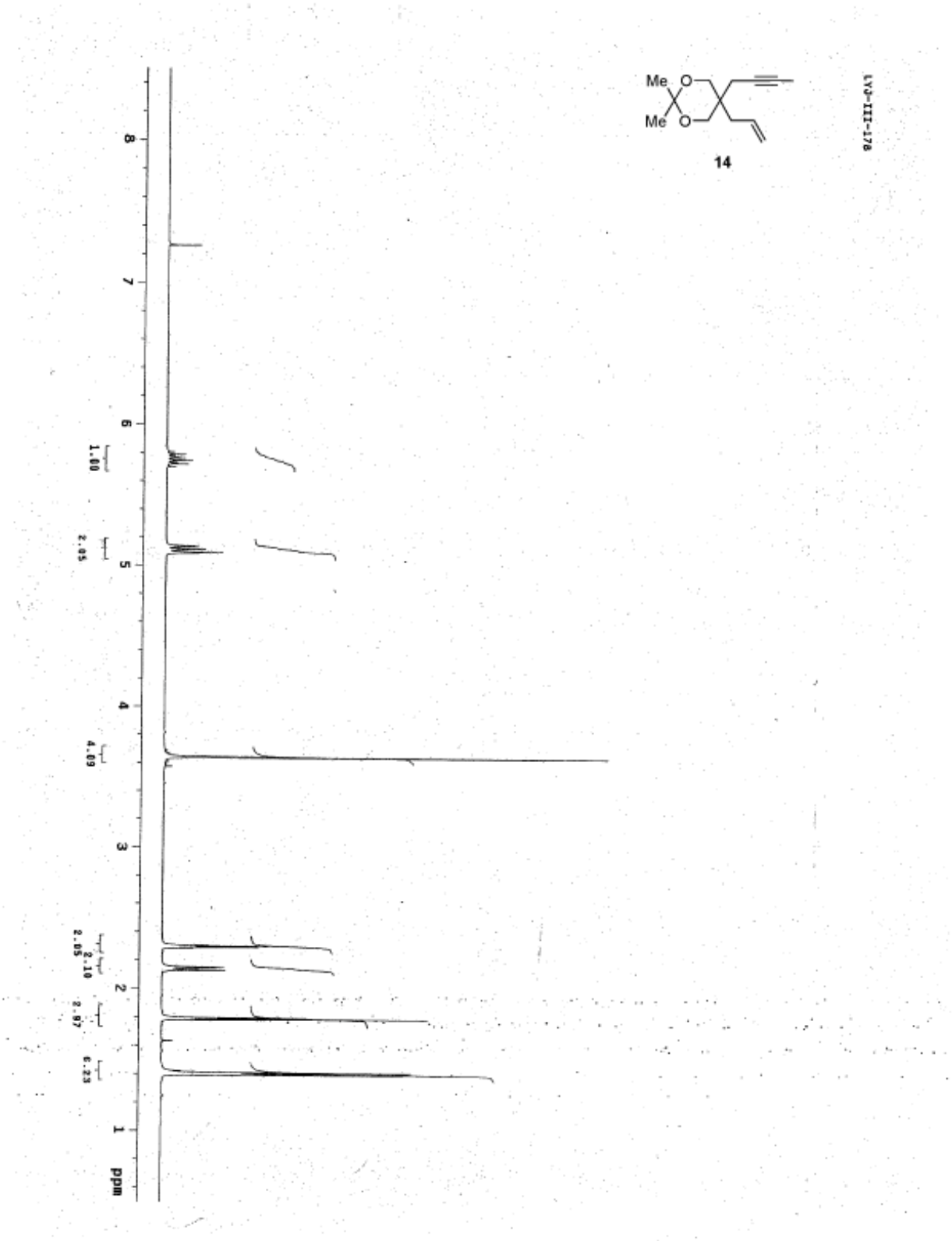
The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic materials (Chiralpak AS, hexane:2-propanol = 99:1.0, flow rate = 1.0 mL/min, 23 ºC, λ = 254 nm, retention times; (minor) 15.96 min, (major) 22.42 min, 98:2 er).

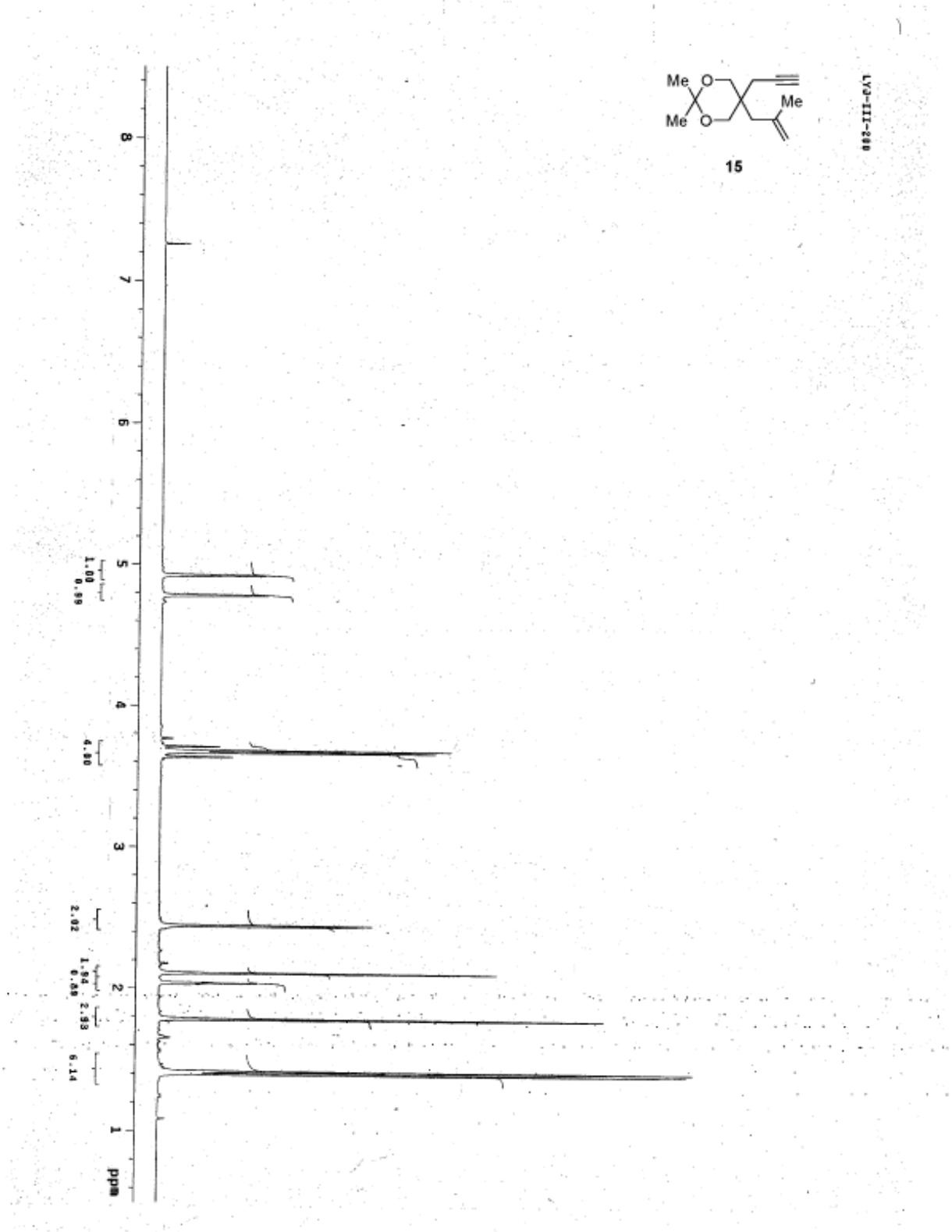


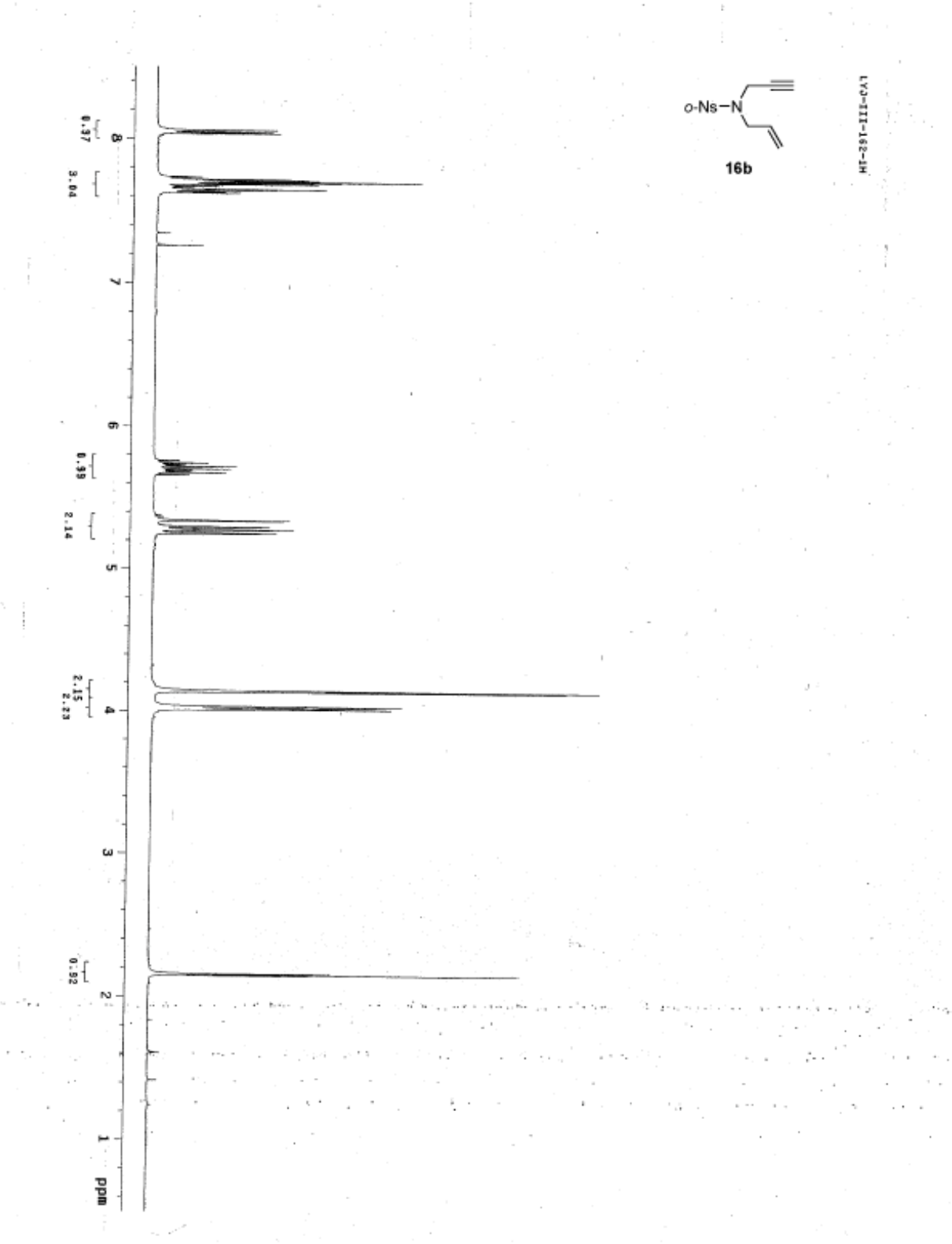
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %
1	13.48		0.00	N/A	6579776	50.956
2	19.99		0.00	N/A	6332816	49.044

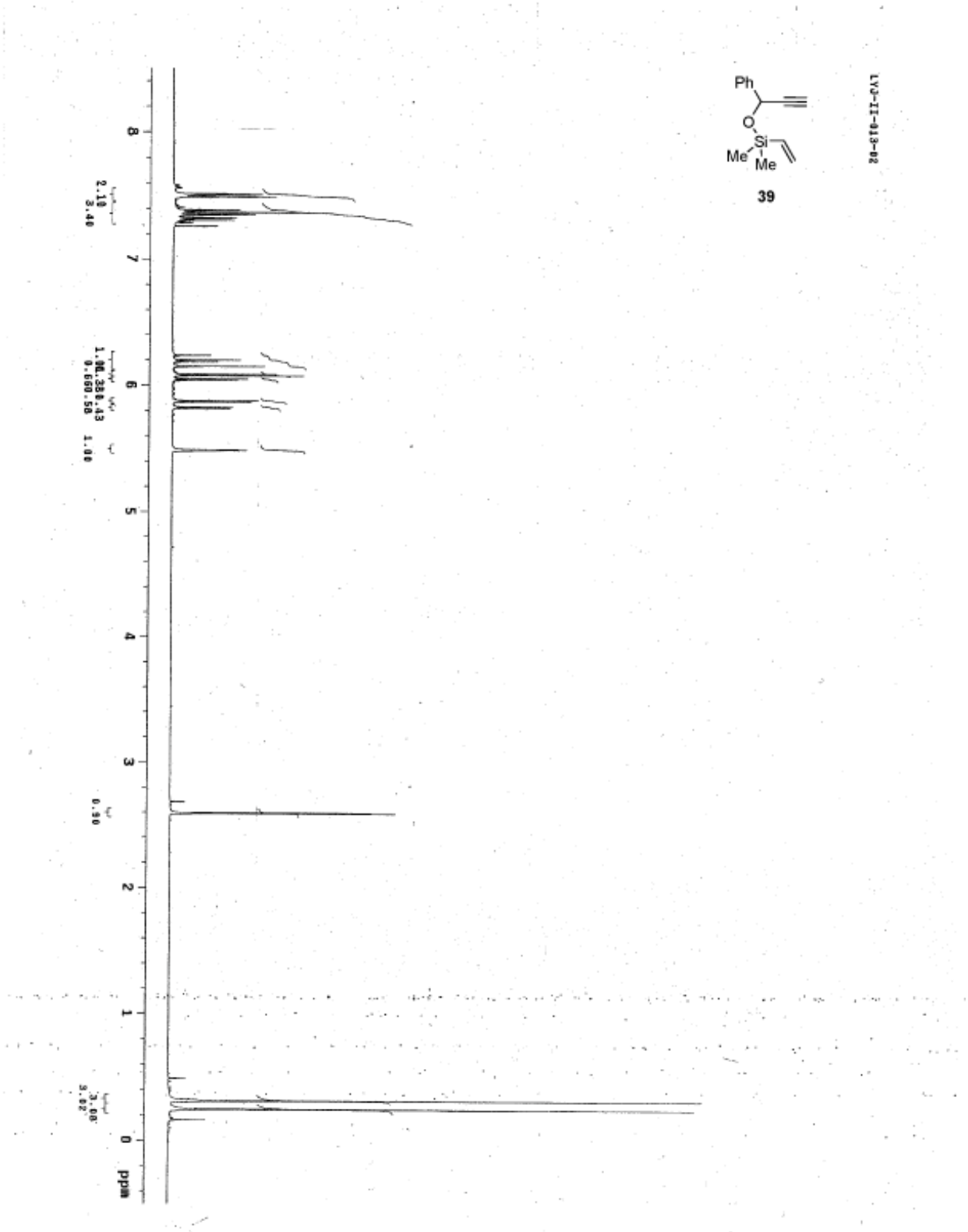
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %
1	15.96		0.00	N/A	132920	1.802
2	22.42		0.00	N/A	7243767	98.198

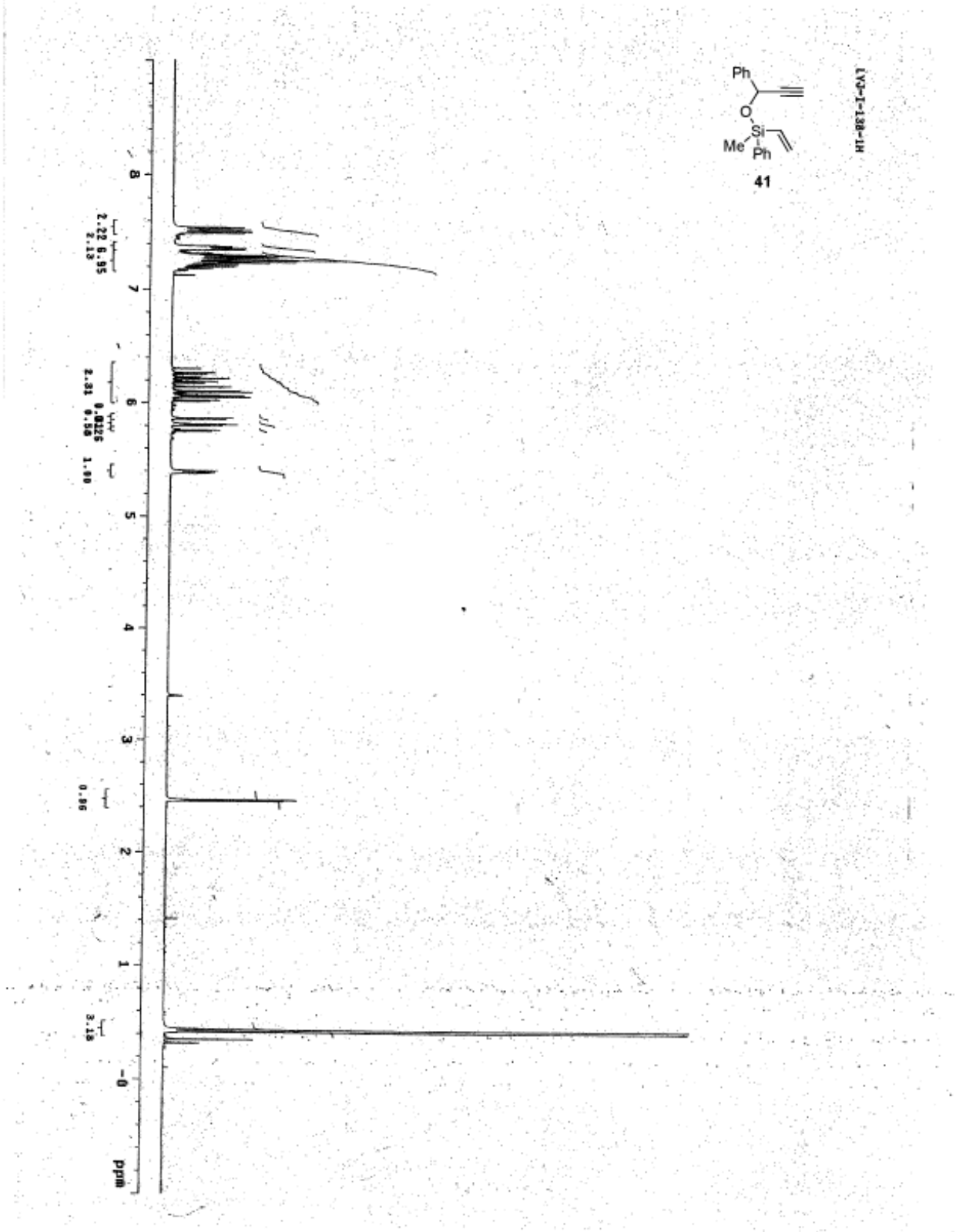
Procedure for site-selective epoxidation of 17a (eq 4). A round bottom flask was charged with **17a** (50.0 mg, 200 μmol) and 0.25 mL of THF. An *aqueous* solution of Na-EDTA (0.4 μM, 1.00 ml) was added followed by trifluoroacetone (0.20ml, 2.23 mmol). The mixture was allowed to cool to 0ºC, then sodium bicarbonate (130 mg, 1.55 mmol) and oxone® (307 mg, 1.00 mmol) was added. The resulting mixture was allowed to stir for 5 min at 0 ºC, and 15 min at 22 ºC. The mixture was diluted with dichloromethane (5.00 mL), washed with water (2.00 ml x 2) and brine (2.00 mL), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography to afford the product (52.0 mg, 196 μmol, 98% yield) as a white solid. M.p. = 110–115 ºC; IR (neat): 1597 (w), 1343 (s), 1164 (s), 670 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.02 (dt, *J* = 10.4, 3.6 Hz, 1H), 5.35 (dt, *J* = 8.0, 2.4 Hz, 1H), 3.80 (dt, *J* = 17.7, 2.4 Hz, 1H), 3.67 (dt, *J* = 17.2, 2.8 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H), 3.22 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 4.4 Hz, 1H), 2.83 (d, *J* = 4.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 133.7, 130.4, 129.9, 127.9, 127.1, 54.3, 53.9, 49.0, 44.6, 21.7; HRMS (ESI) $[M+H]^+$ calcd for $C_{13}H_{16}NO_3S$: 266.0851, found: 266.0853.

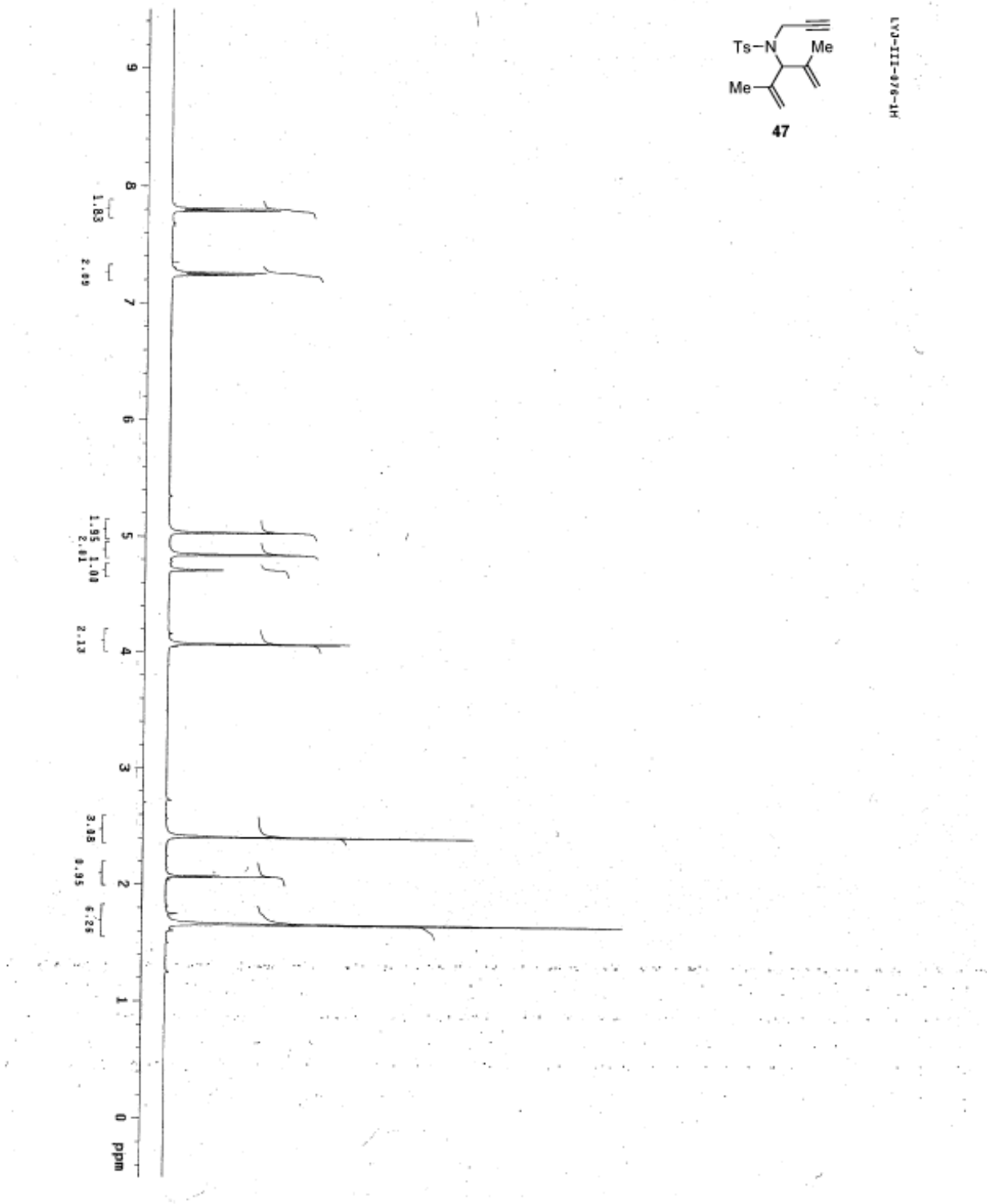

Me
O
Me
O
14
LYD-III-178
8
7
6
5
4
3
2
1
ppm
1.00
2.05
4.69
2.05
2.10
2.07
6.23

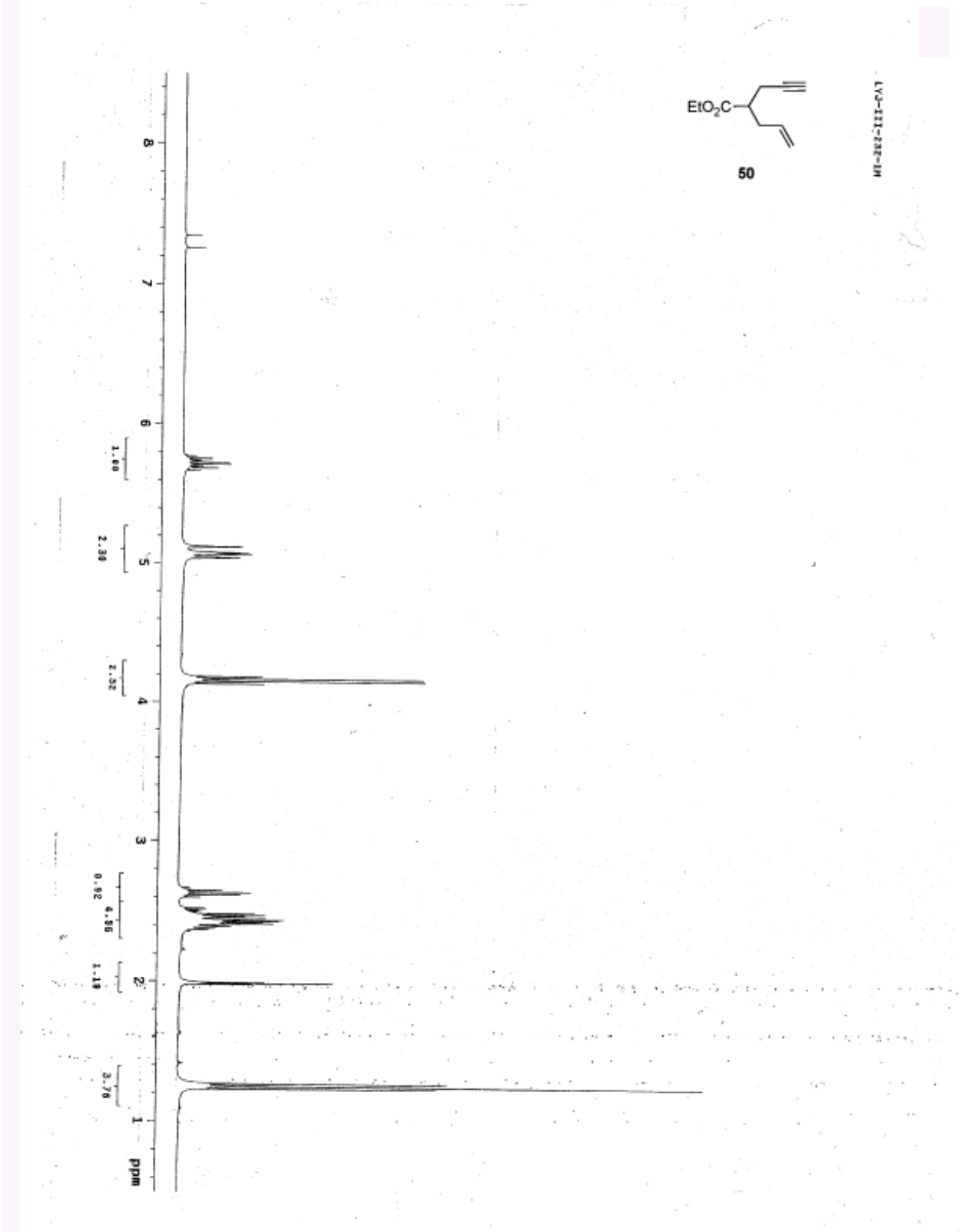

Me
O
Me
O
Me
15
LV3-III-289
8
7
6
5
4
3
2
1
ppm
1.00
0.99
4.86
2.02
1.94
0.88
2.93
6.14

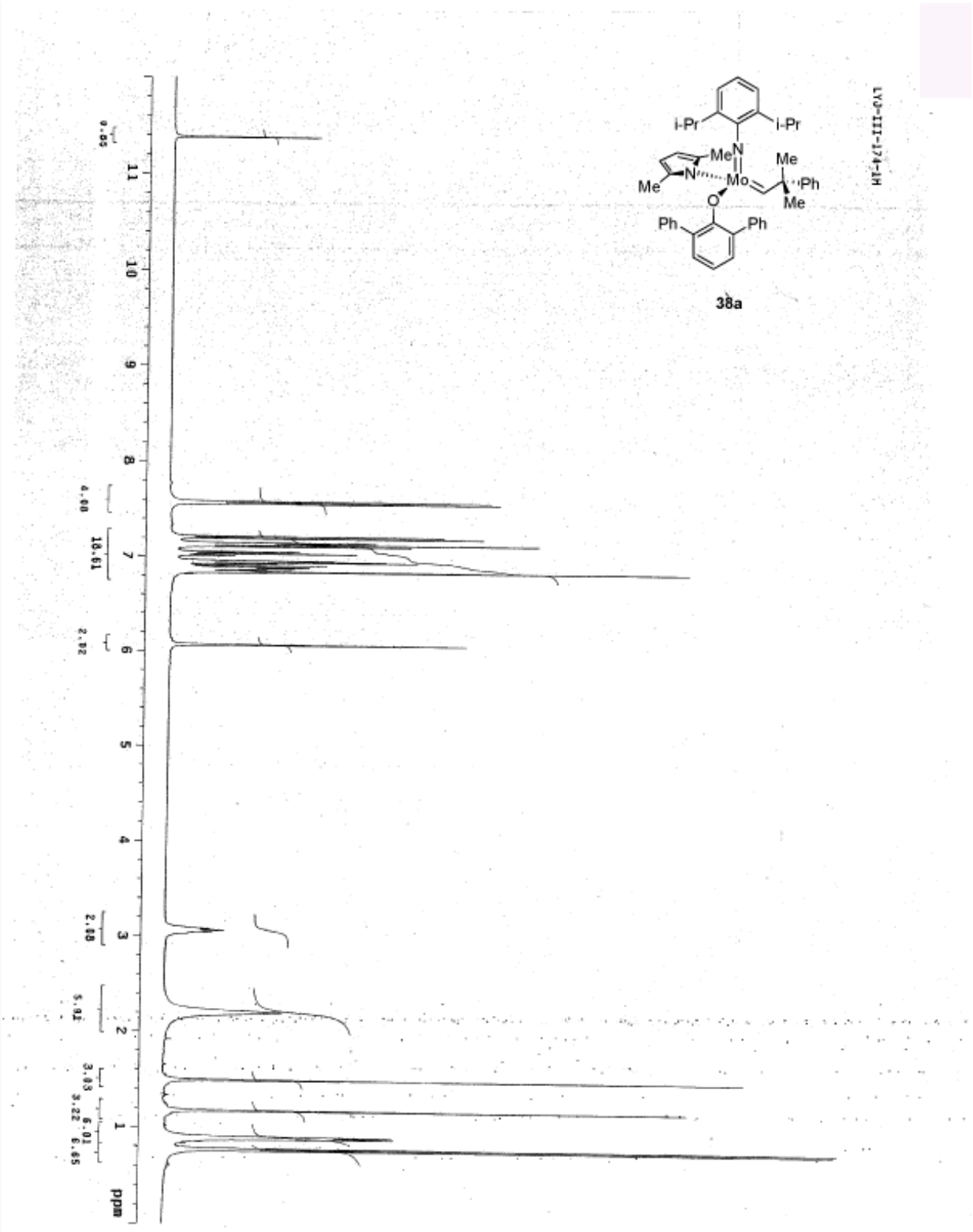

o-Ns–N
16b
HT-291-III-CA1
8.37
8.04
6.56
2.14
2.15
2.23
0.92
8
7
6
5
4
3
2
1
ppm


Ph
O
Si
Me
Me
39
LVJ-II-018-02
8
7
6
5
4
3
2
1
0
ppm


Ph
O
Si
Me
Ph
41
LYJ-I-188-1H
ppm


Ts–N
Me
Me
47
LVC-III-076-1H
1.83
2.69
1.95
1.00
2.81
2.13
3.08
0.95
6.26
9
8
7
6
5
4
3
2
1
0
ppm


EtO2C
50
LYG-III-282-1H
8
7
6
5
4
3
2
1
ppm
1.00
2.38
2.32
0.92
4.85
1.18
2.79


LVJ-III-174-1H
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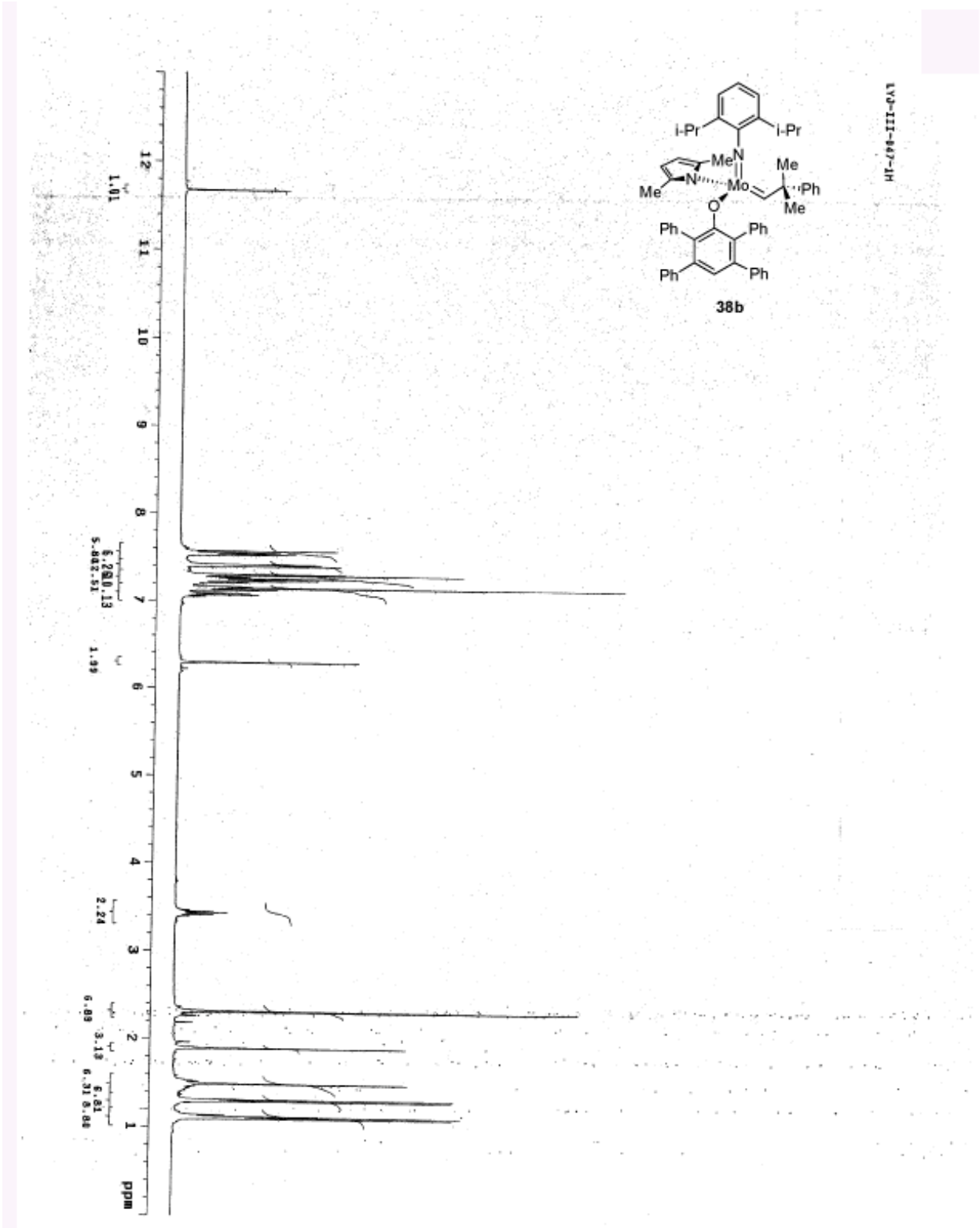
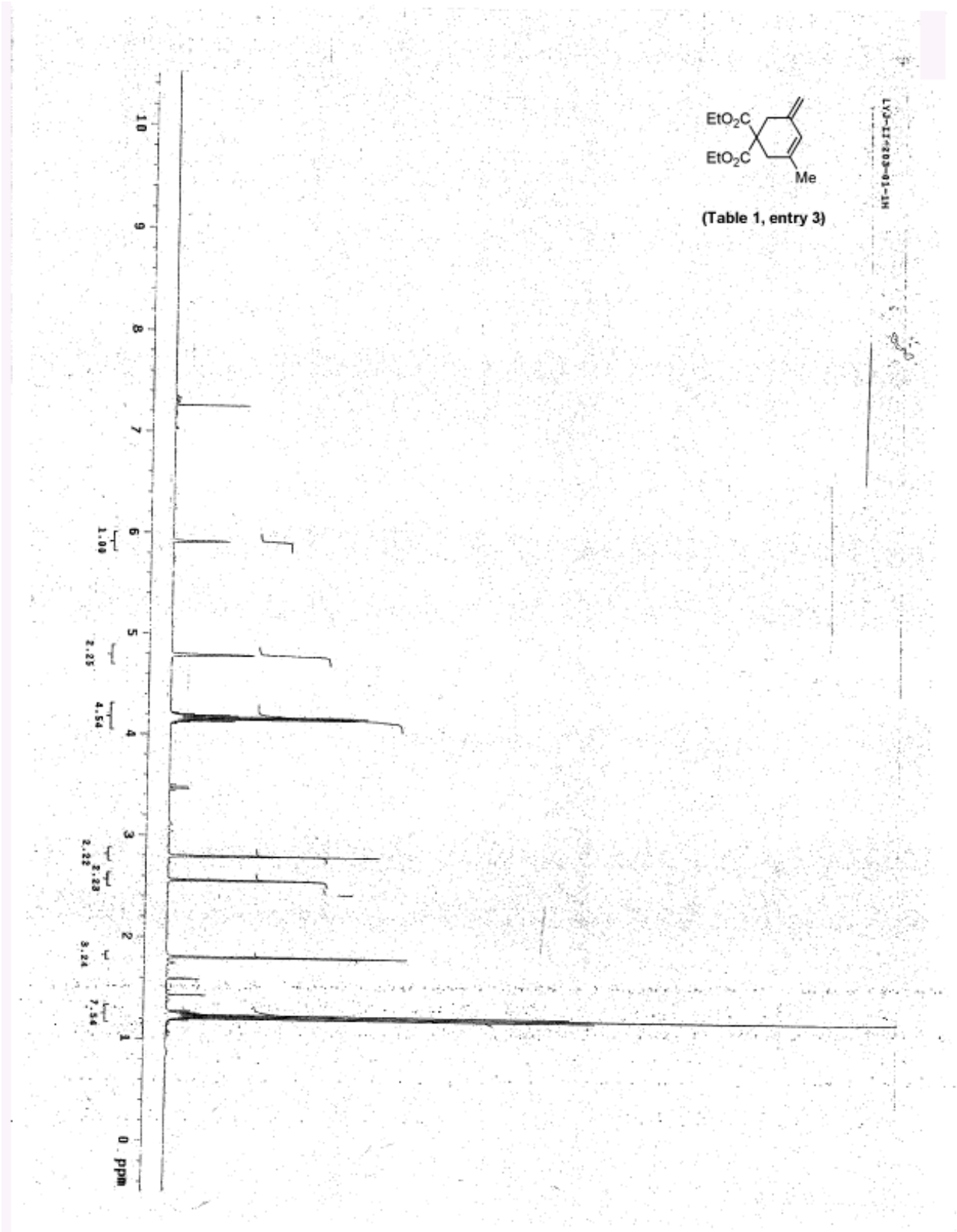
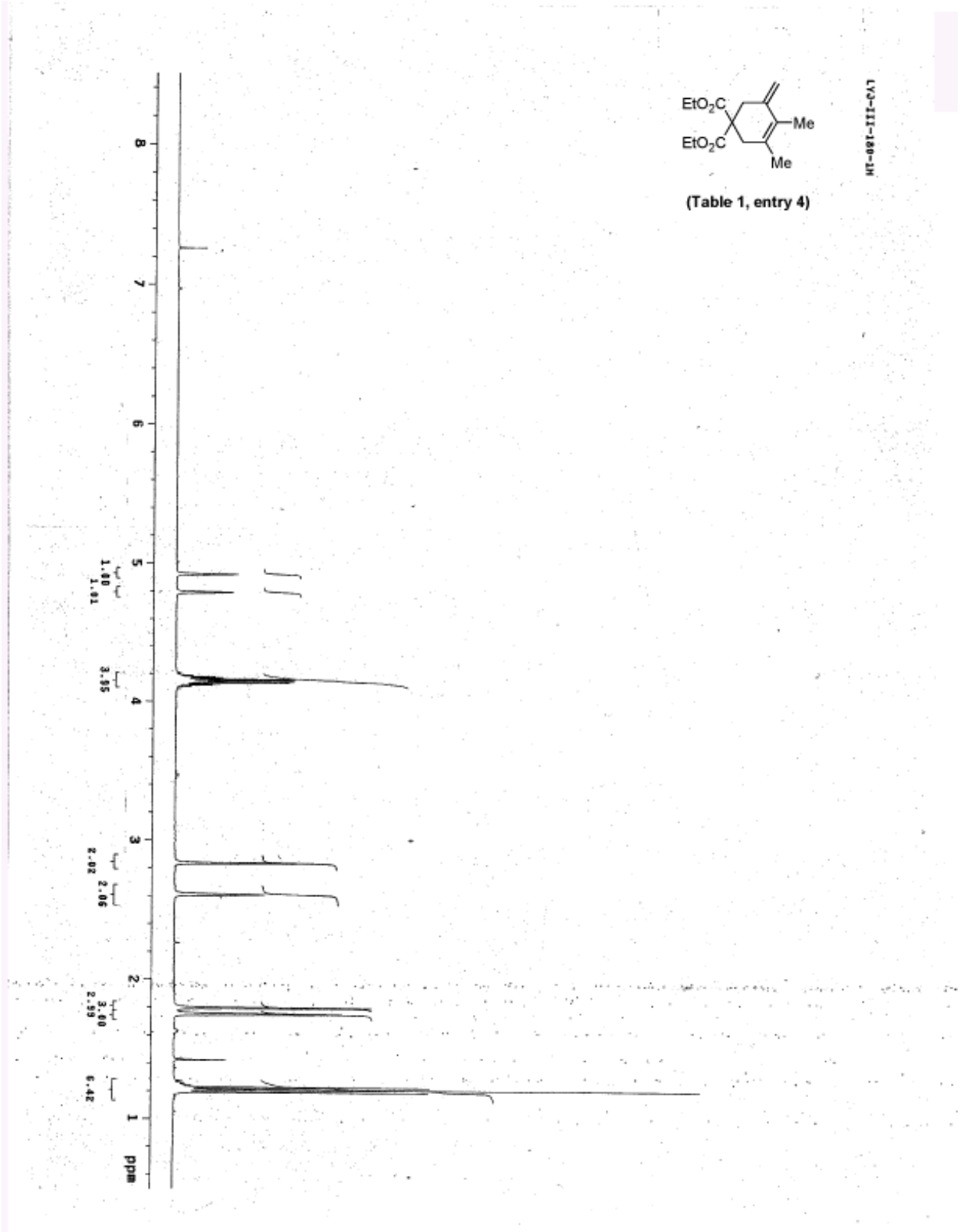
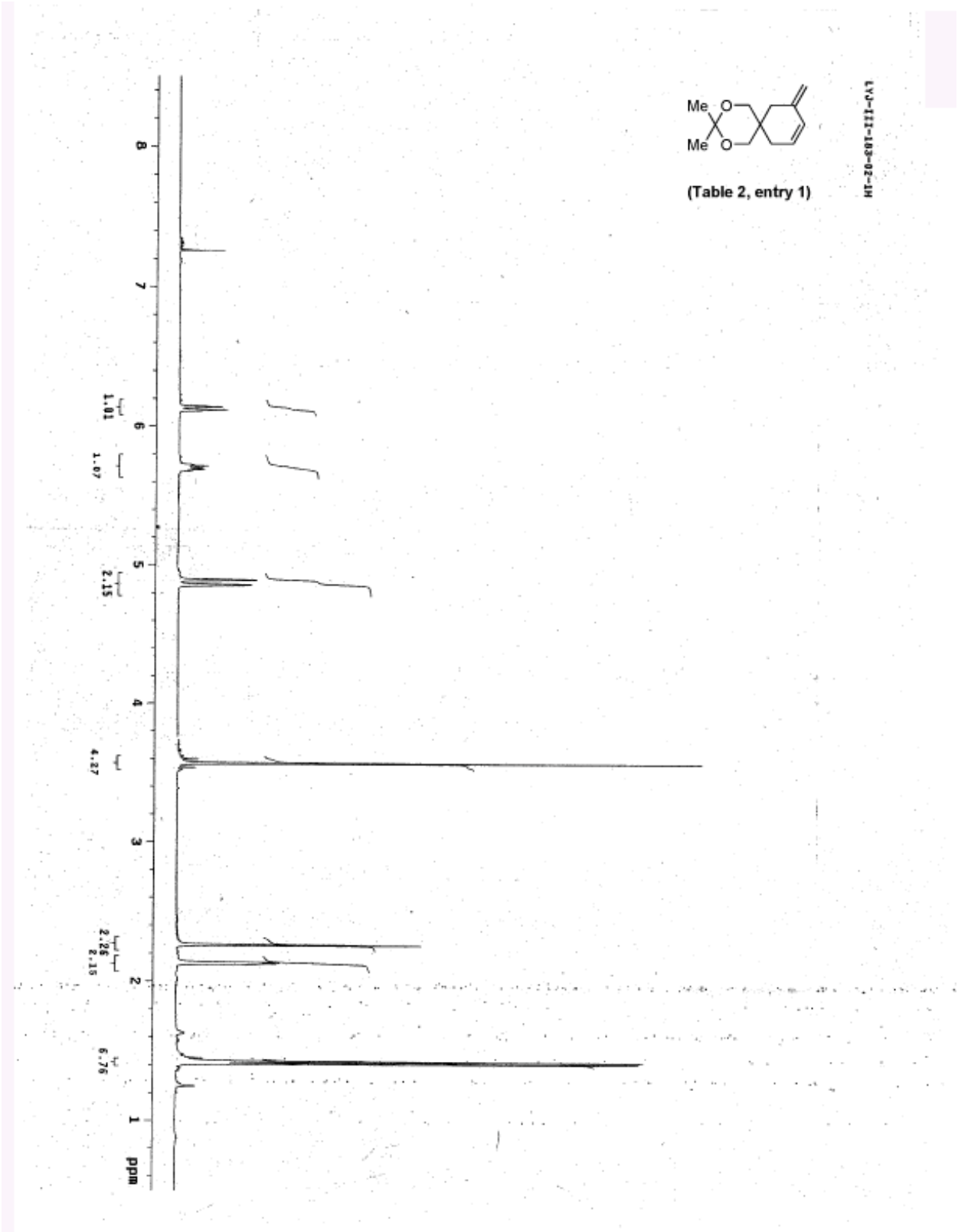
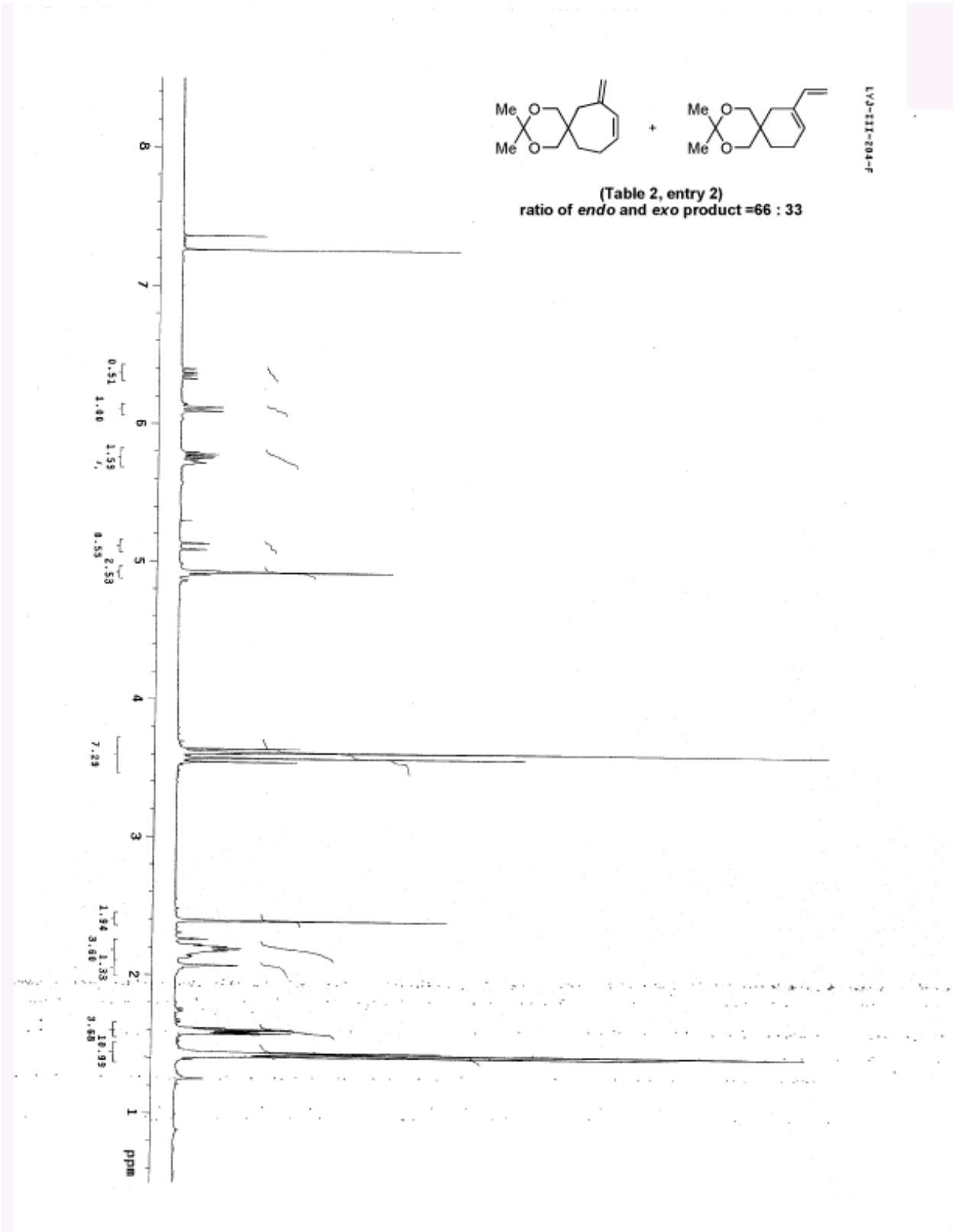
i-Pr
Me
N
Me
N
Mo
Me
Ph
Me
O
Ph
Ph
38a
ppm

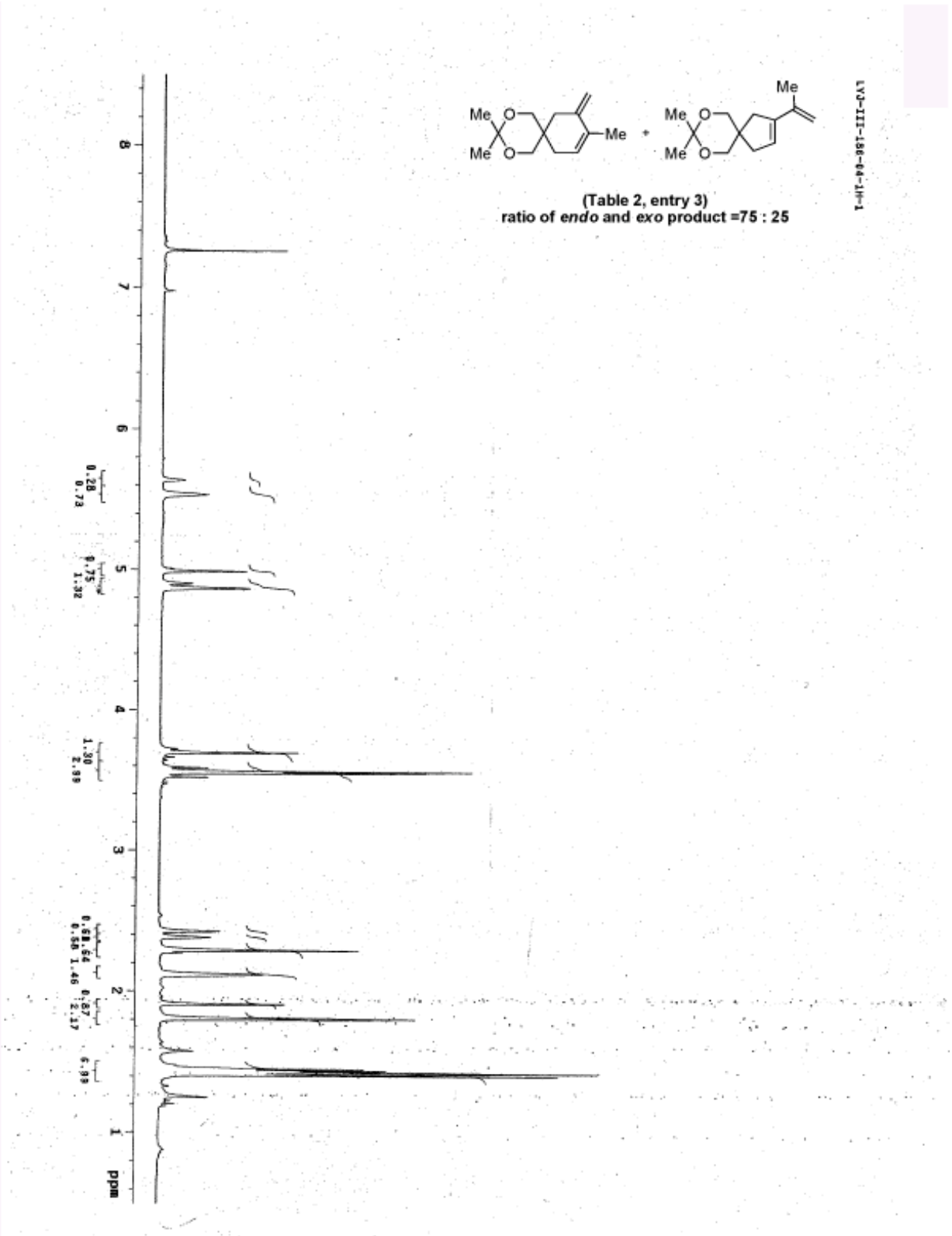

i-Pr
i-Pr
N
Me
N
Me
Mo
Me
Ph
Me
O
Ph
Ph
Ph
Ph
38b
LVP-III-88/7-1H
1.01
6.280.13
5.882.51
1.99
2.24
6.89
3.13
6.81
6.31 6.86
ppm

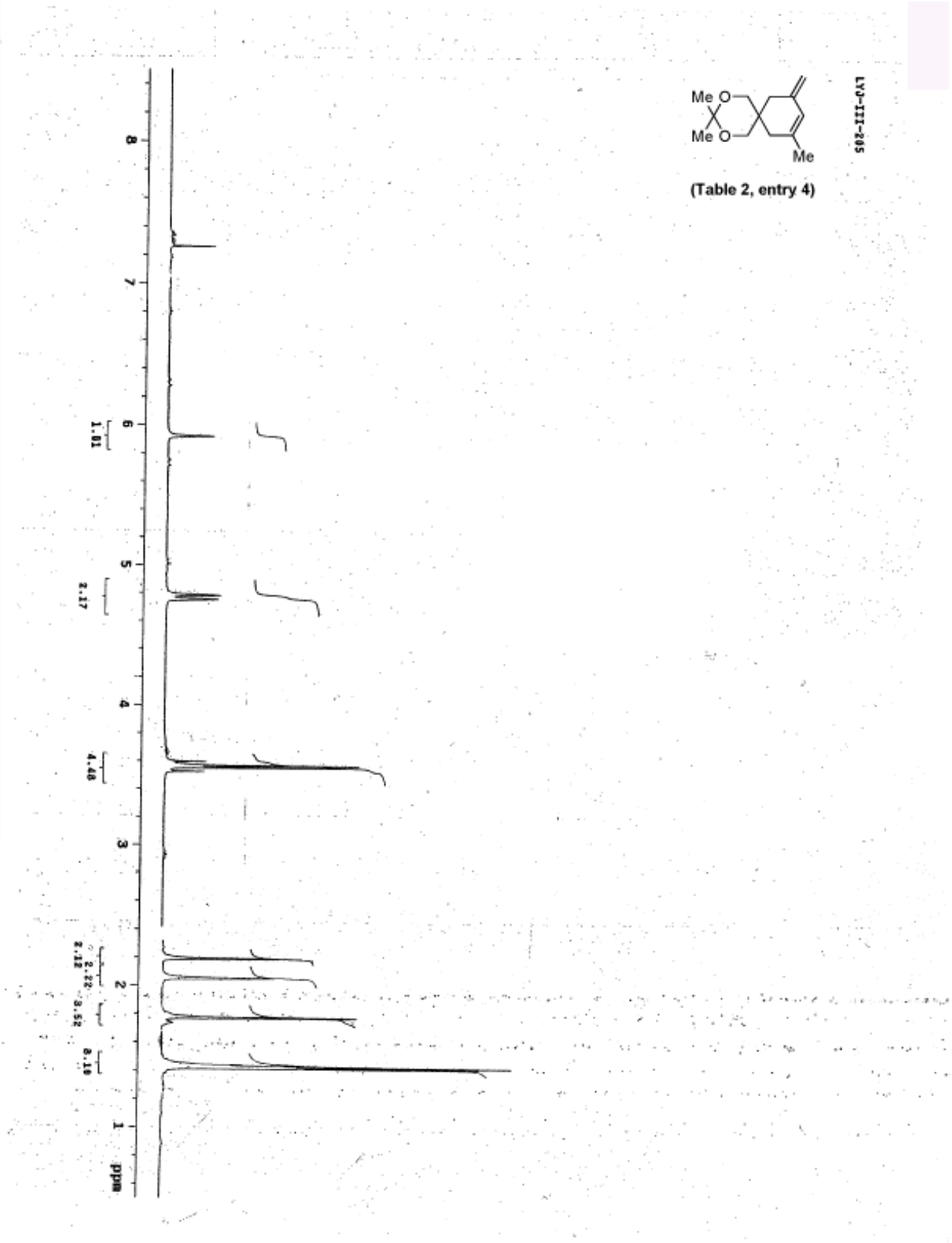

EtO2C
EtO2C
Me
(Table 1, entry 3)
LYJ-F-II-020-B-1H-1H
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.05
4.54
2.22
2.23
3.24
7.56

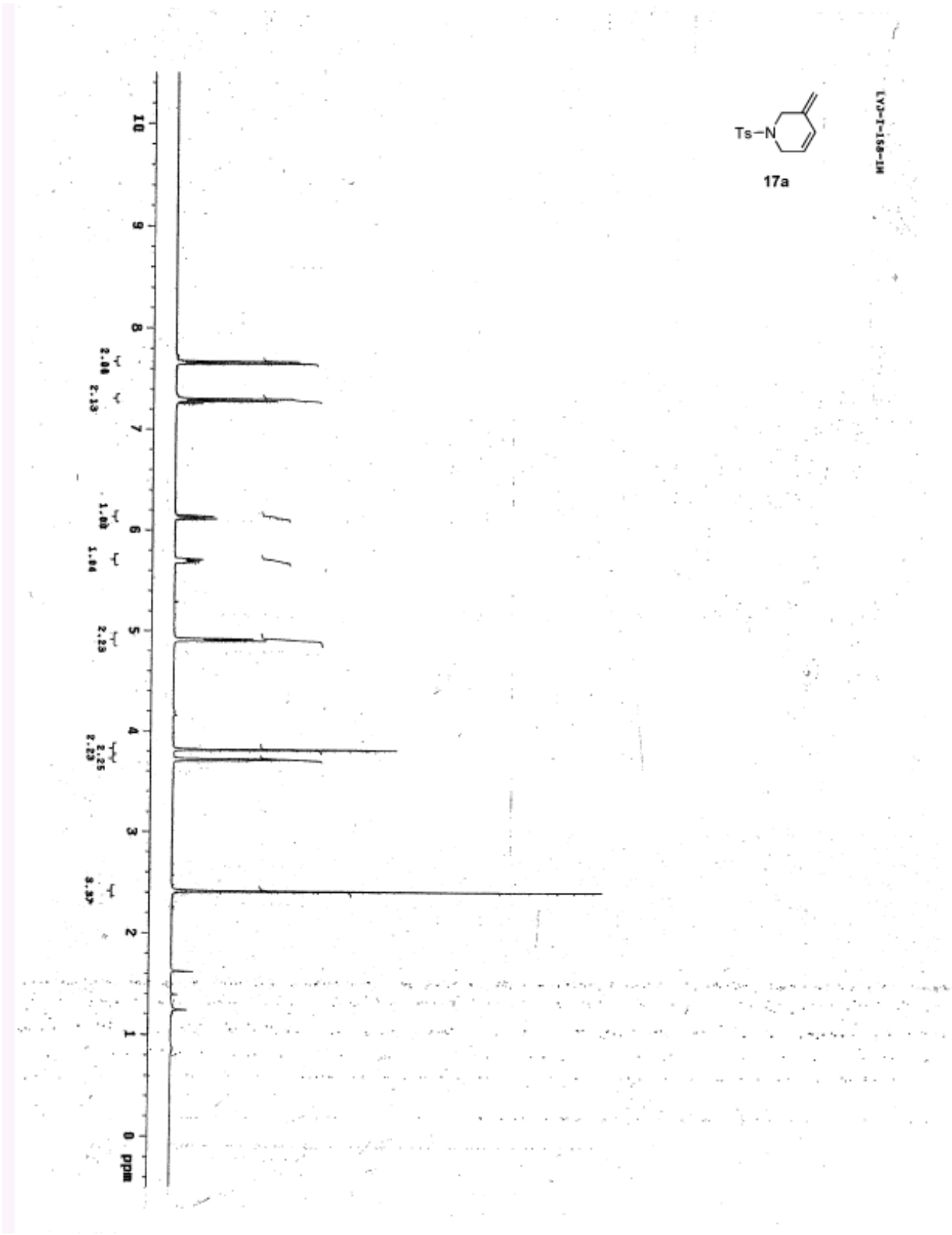

EtO2C
EtO2C
Me
Me
(Table 1, entry 4)
LYS-III-180-1H
8
7
6
5
4
3
2
1
ppm
1.00
1.01
3.85
2.02
2.05
3.00
2.93
6.42

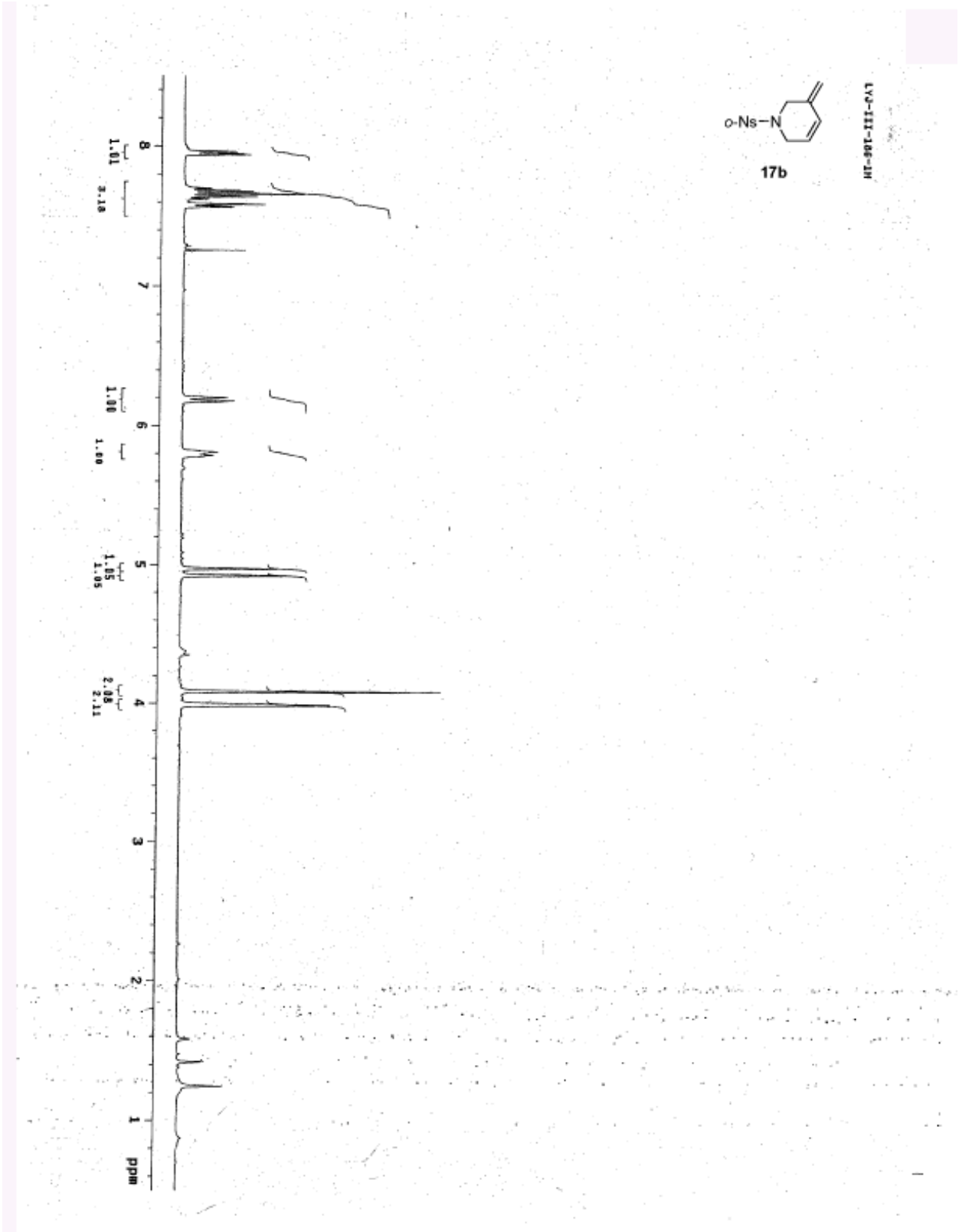

Me
O
Me
O
(Table 2, entry 1)
LYJ-III-189-02-1H
1.01
1.07
2.15
4.27
2.26
2.15
6.76
8
7
6
5
4
3
2
1
ppm

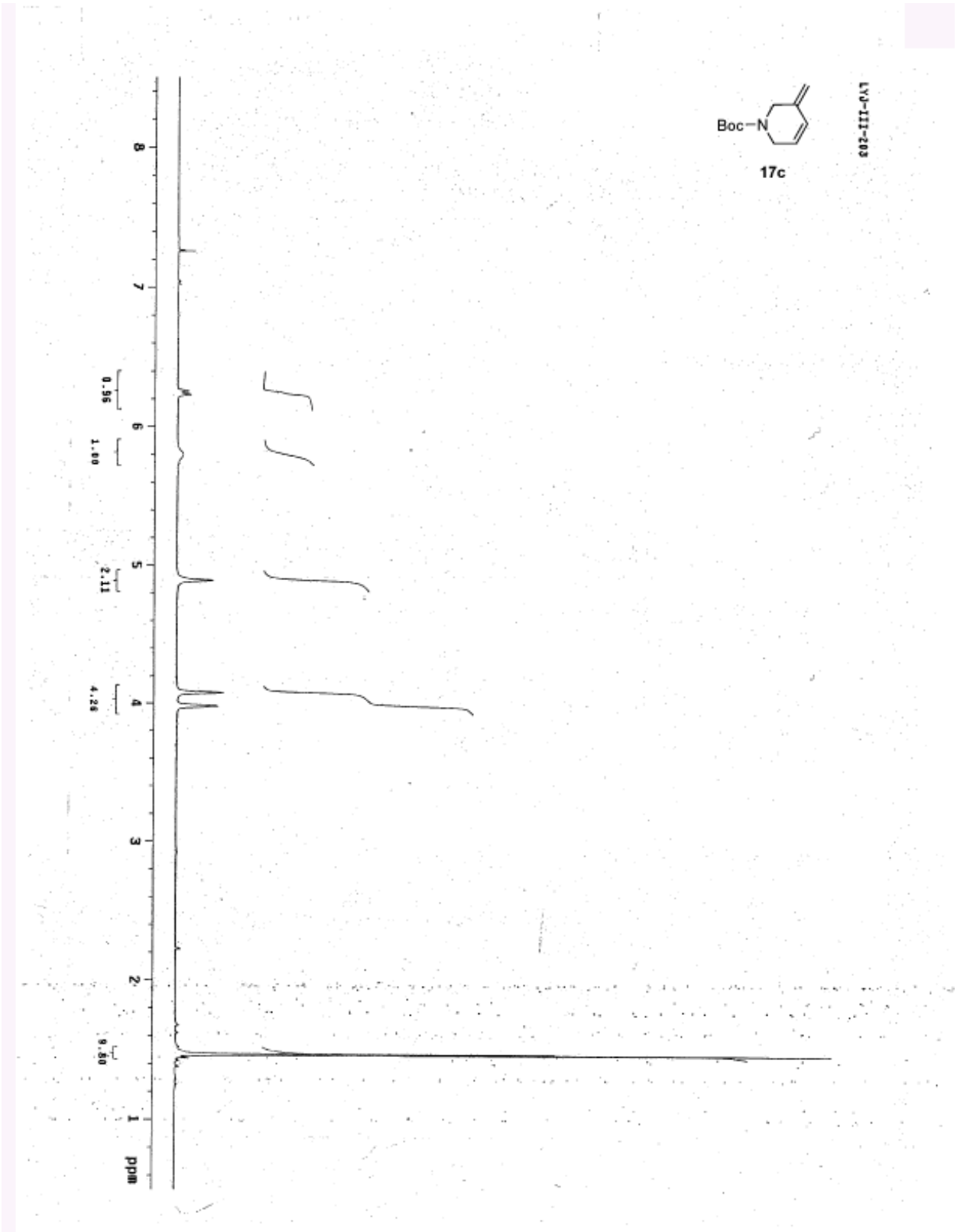

Me
O
Me
O
+
Me
O
Me
O
LYJ-III-204-F
(Table 2, entry 2)
ratio of *endo* and *exo* product =66 : 33
8
7
6
5
4
3
2
1
ppm
0.51
1.00
1.59
0.55
2.53
7.29
1.94
3.66
1.33
10.93
3.68

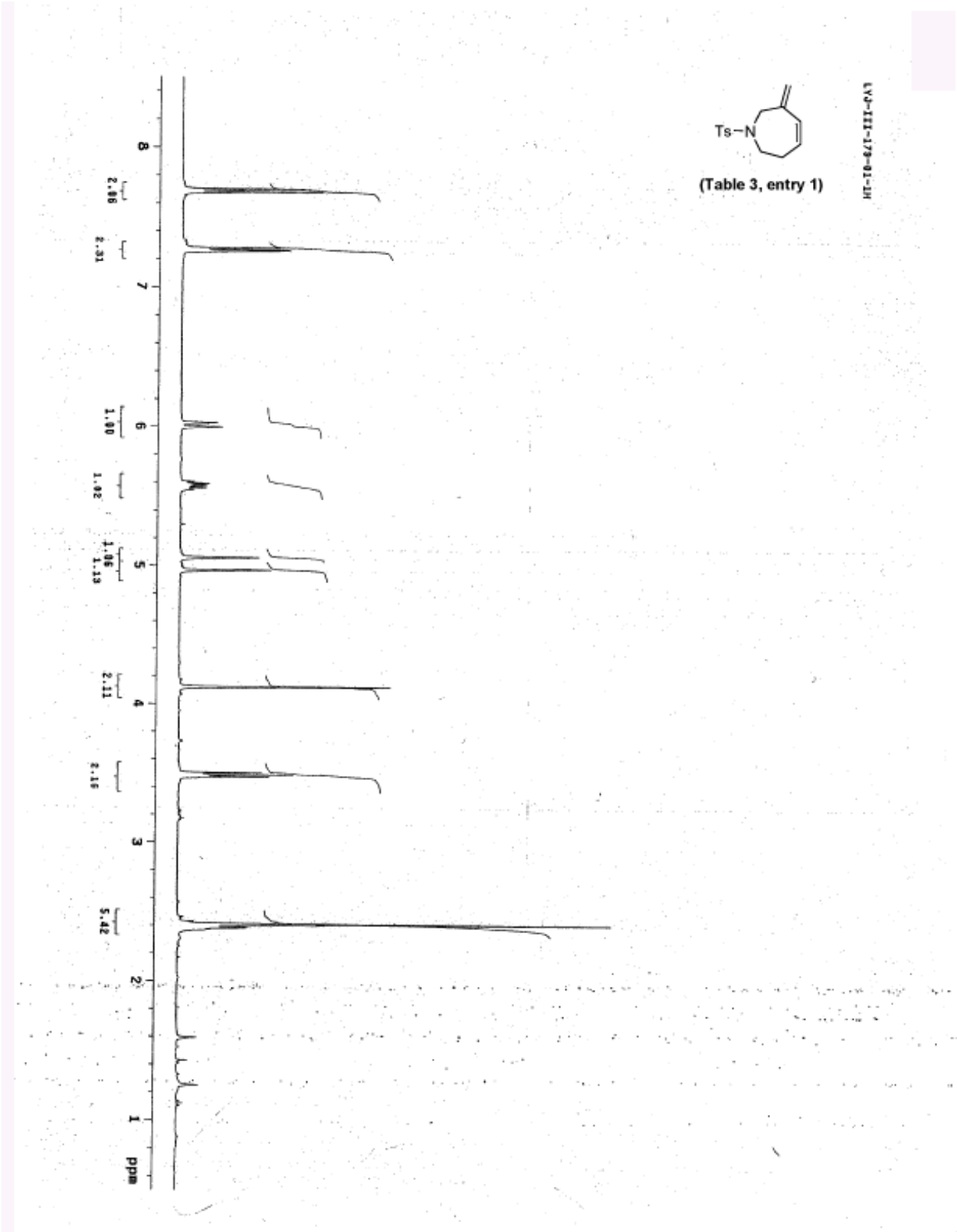

Me
Me
O
O
Me
+
Me
Me
O
O
Me
LAY-JAY-III-158-4-1H-1
(Table 2, entry 3)
ratio of *endo* and exo product =75 : 25
ppm

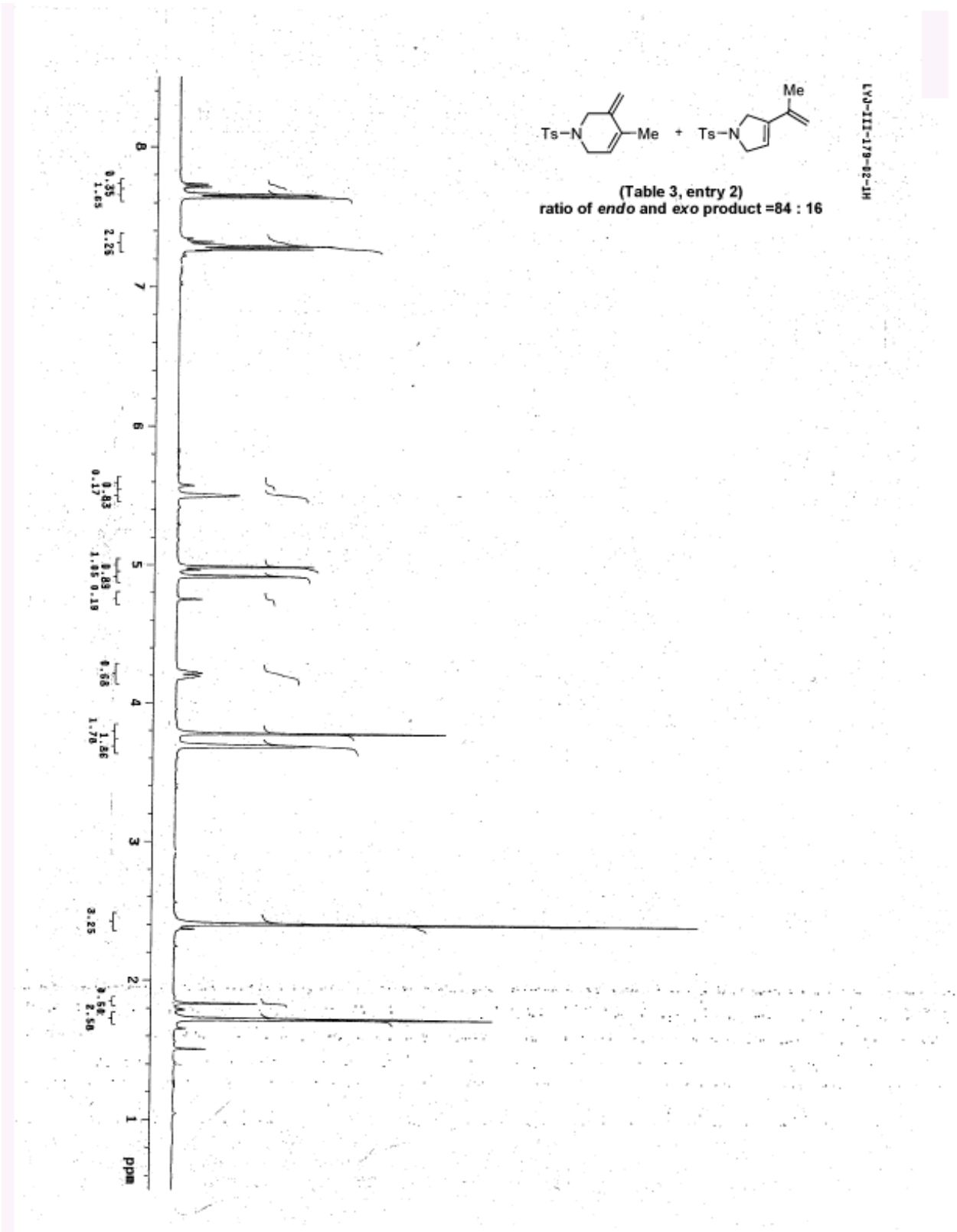

Me O
Me O
Me
(Table 2, entry 4)
LVD-III-205
8
7
6
5
4
3
2
1
ppm
1.01
2.17
4.49
2.22
2.18
8.52
8.18

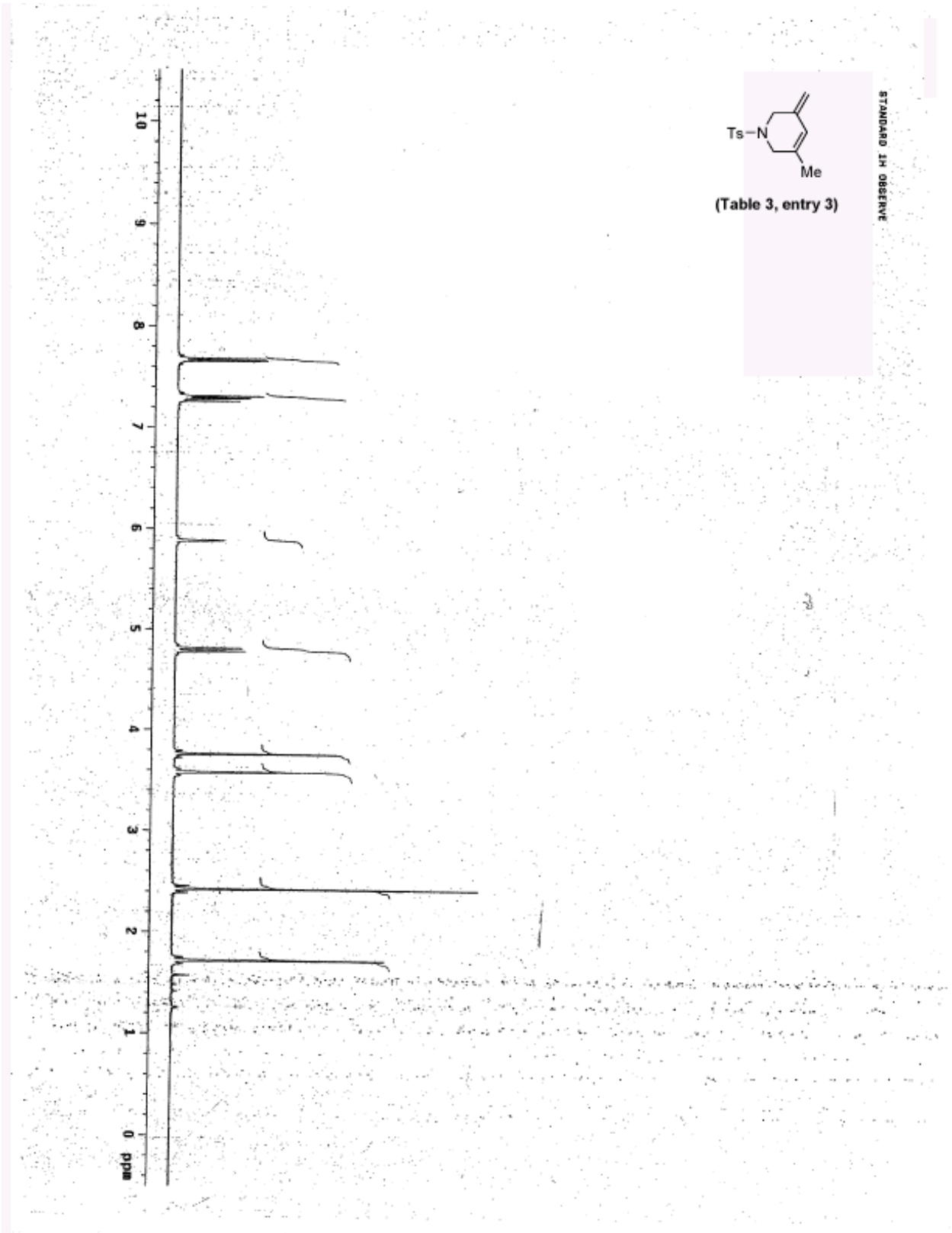

Ts–N
17a
LYJ-I-159-1H
10
9
8
7
6
5
4
3
2
1
0 ppm
2.08
2.13
1.00
1.04
2.23
2.25
2.28
3.37

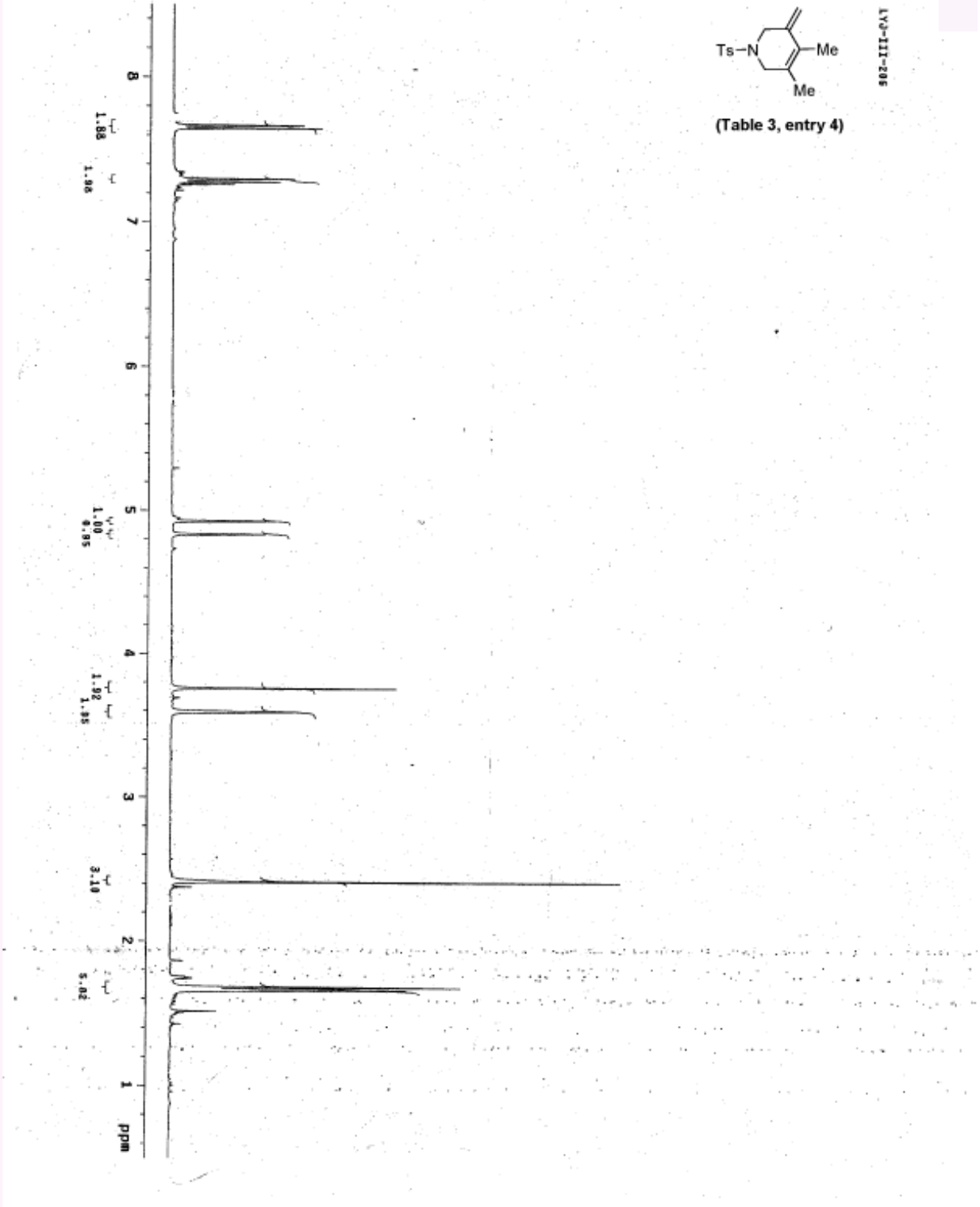

o-Ns–N
17b
LVP-III-186-1H
8
7
6
5
4
3
2
1
ppm
1.01
2.19
1.00
1.00
1.05
1.05
2.08
2.11

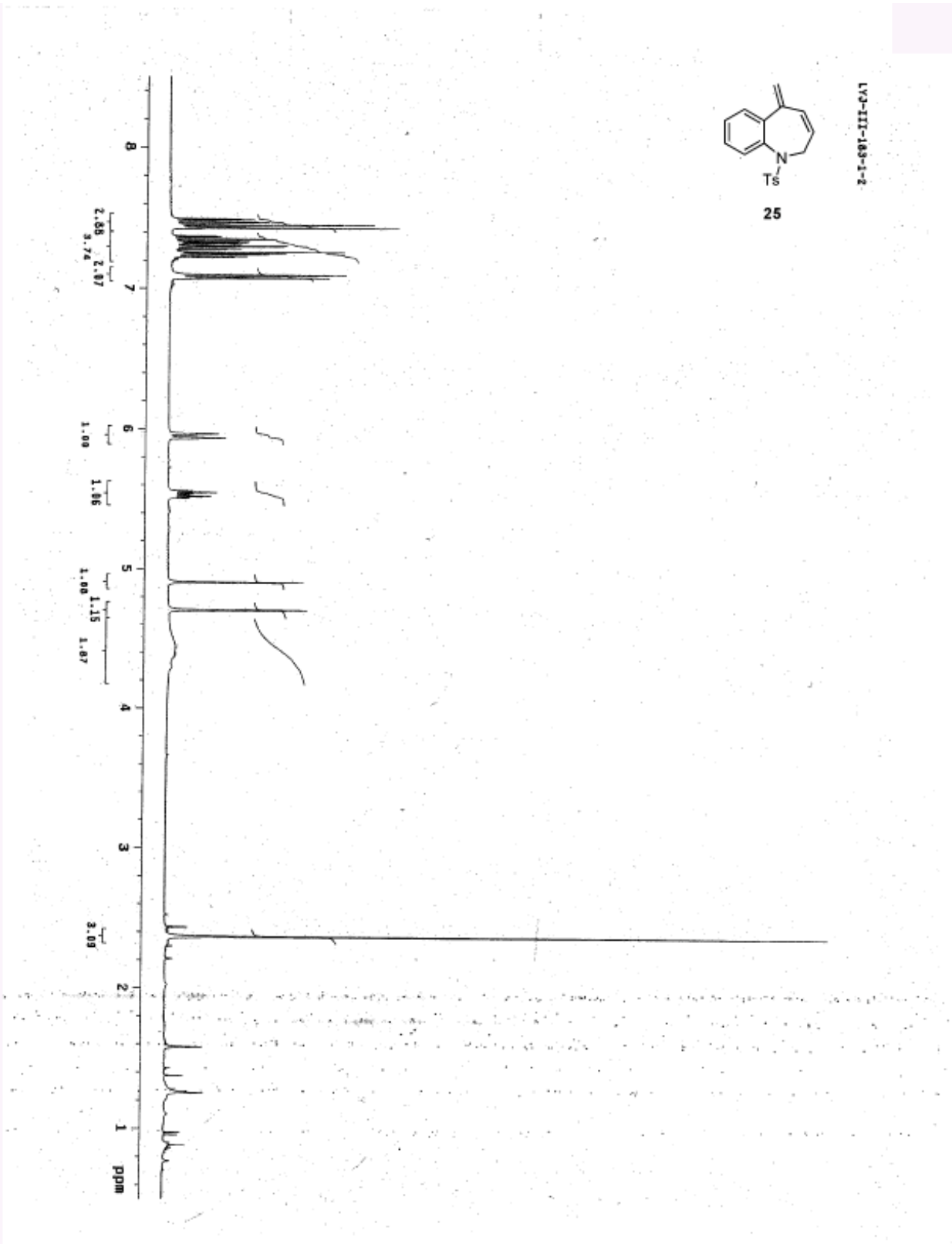

Boc–N
17c
LYG-III-203
8
7
6
5
4
3
2
1
ppm
0.96
1.00
2.11
4.26
9.50

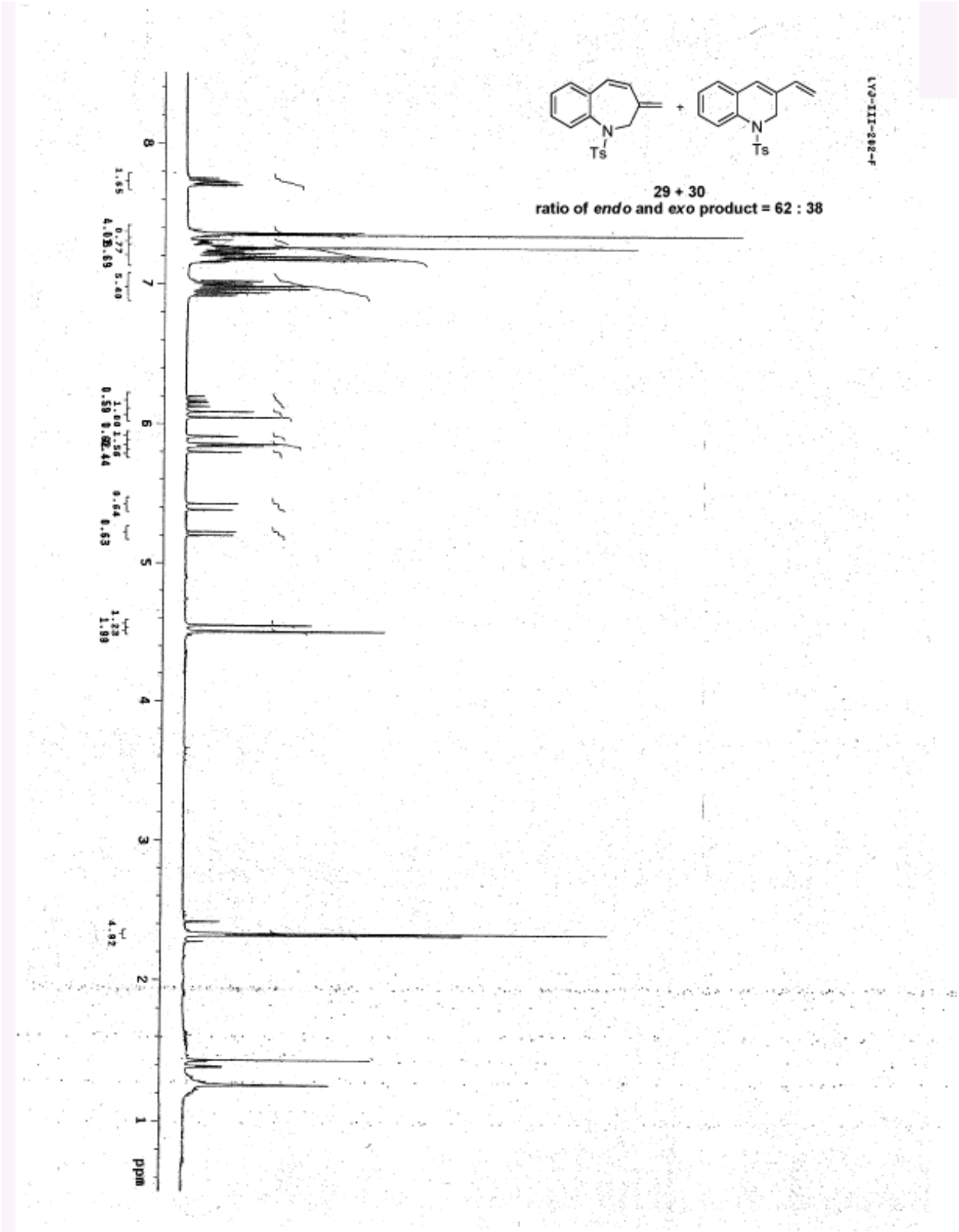

Ts–N
(Table 3, entry 1)
8
7
6
5
4
3
2
1
ppm

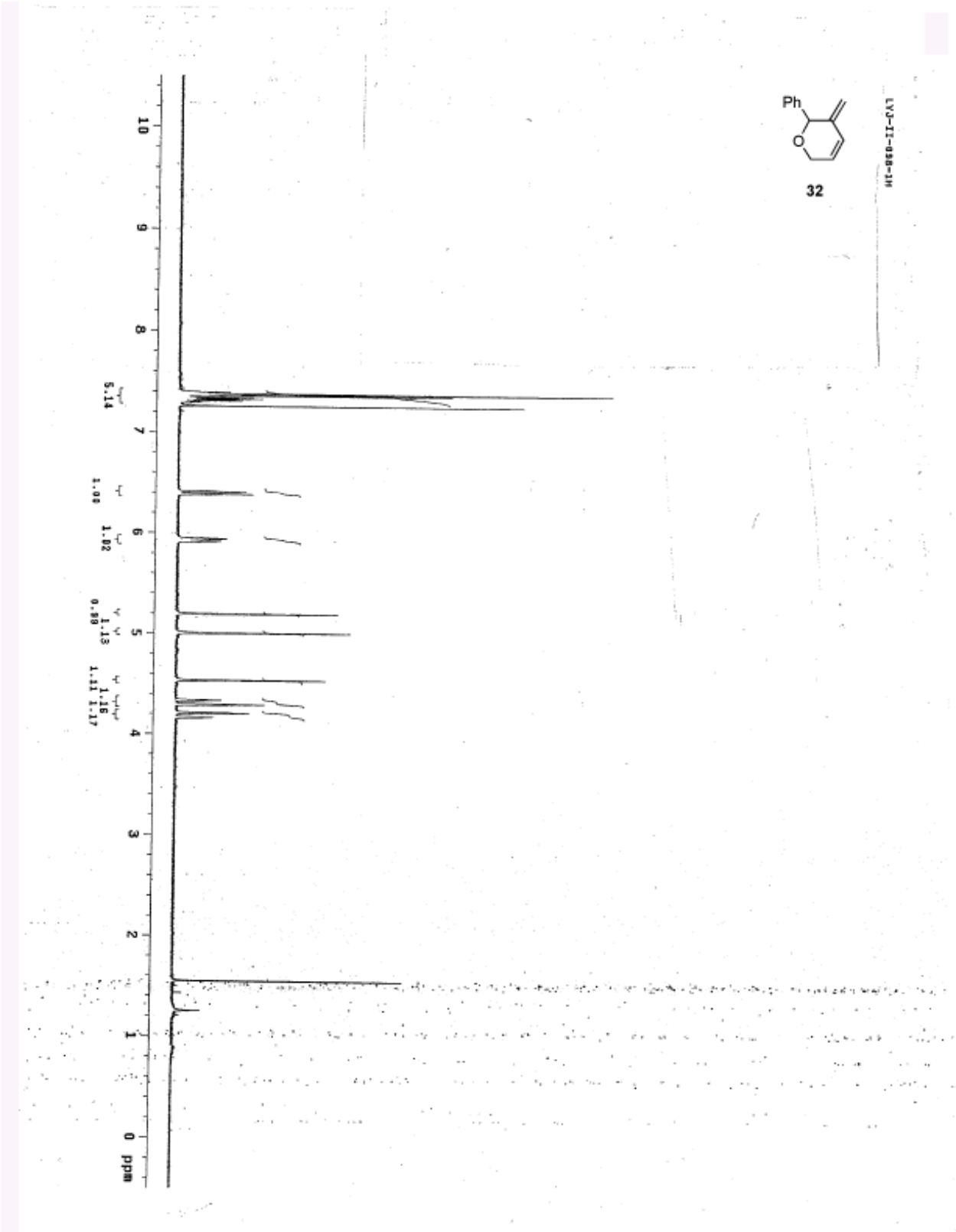

Ts–N
Me
+
Ts–N
Me
(Table 3, entry 2)
ratio of *endo* and *exo* product =84 : 16
ppm

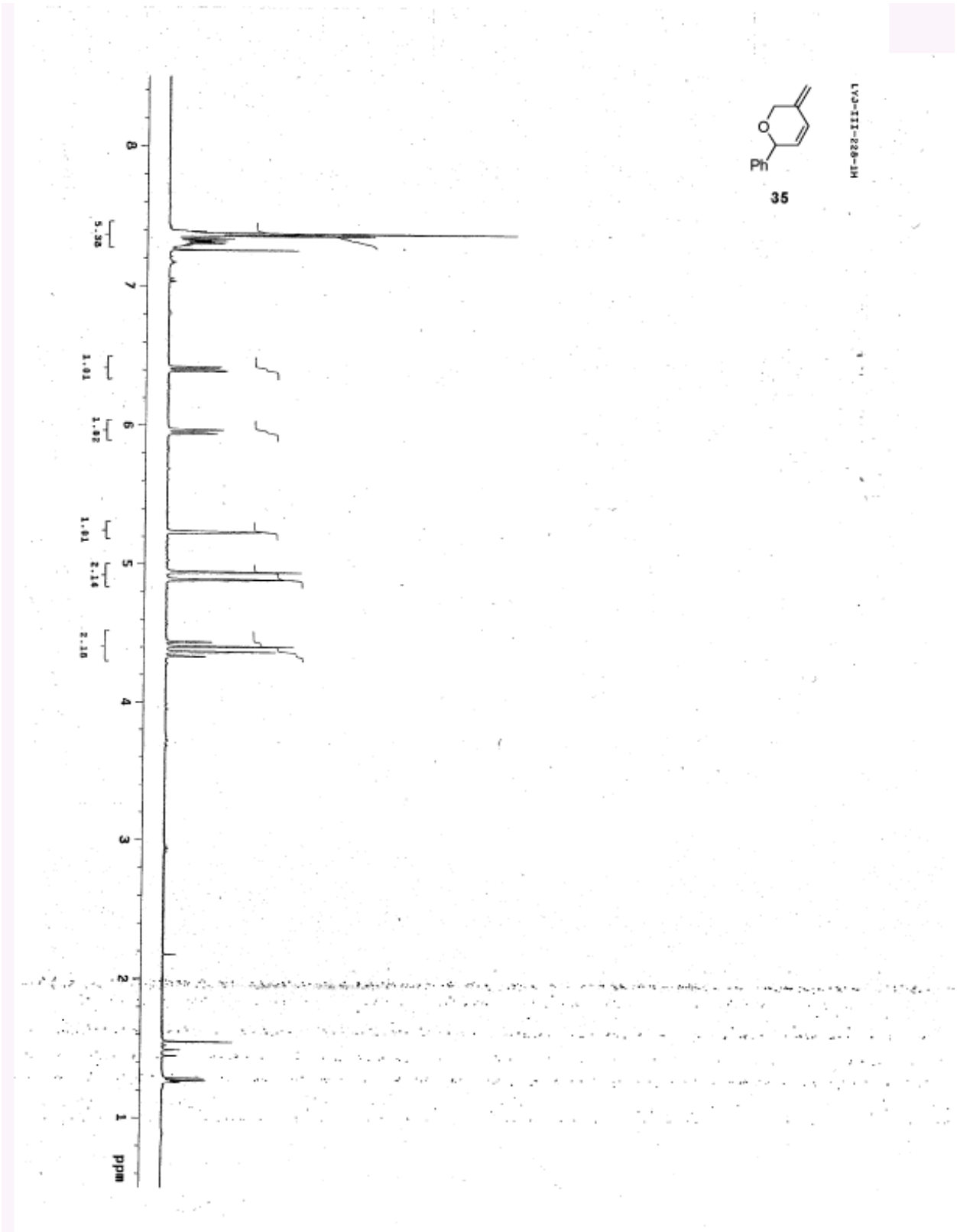

Ts—N
Me
(Table 3, entry 3)
STANDARD 1H OBSERVE
10
9
8
7
6
5
4
3
2
1
0
ppm

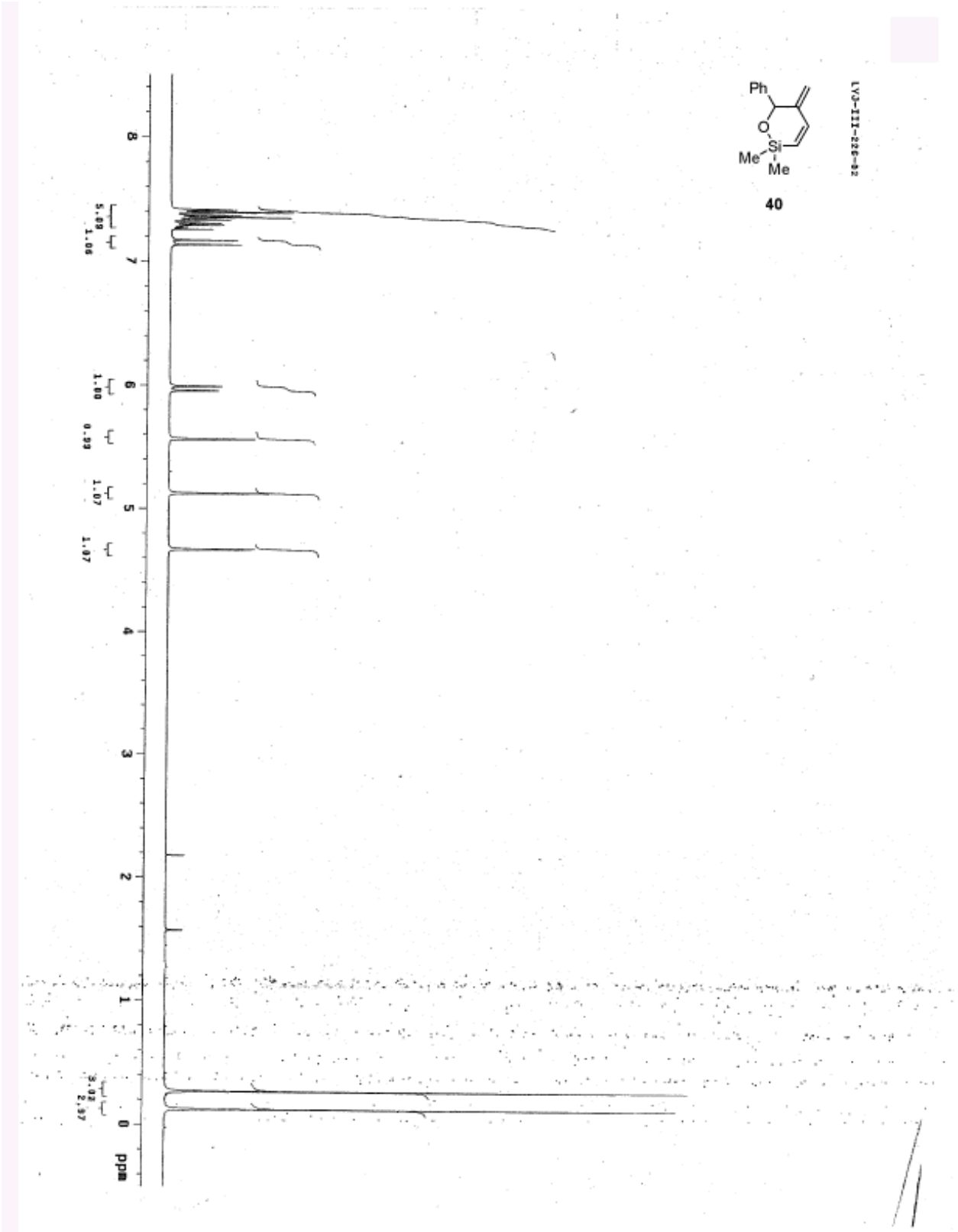

Ts–N
Me
Me
(Table 3, entry 4)
LYG-III-205
1.88
1.98
1.00
0.95
1.92
1.95
3.10
5.02
8
7
6
5
4
3
2
1
ppm

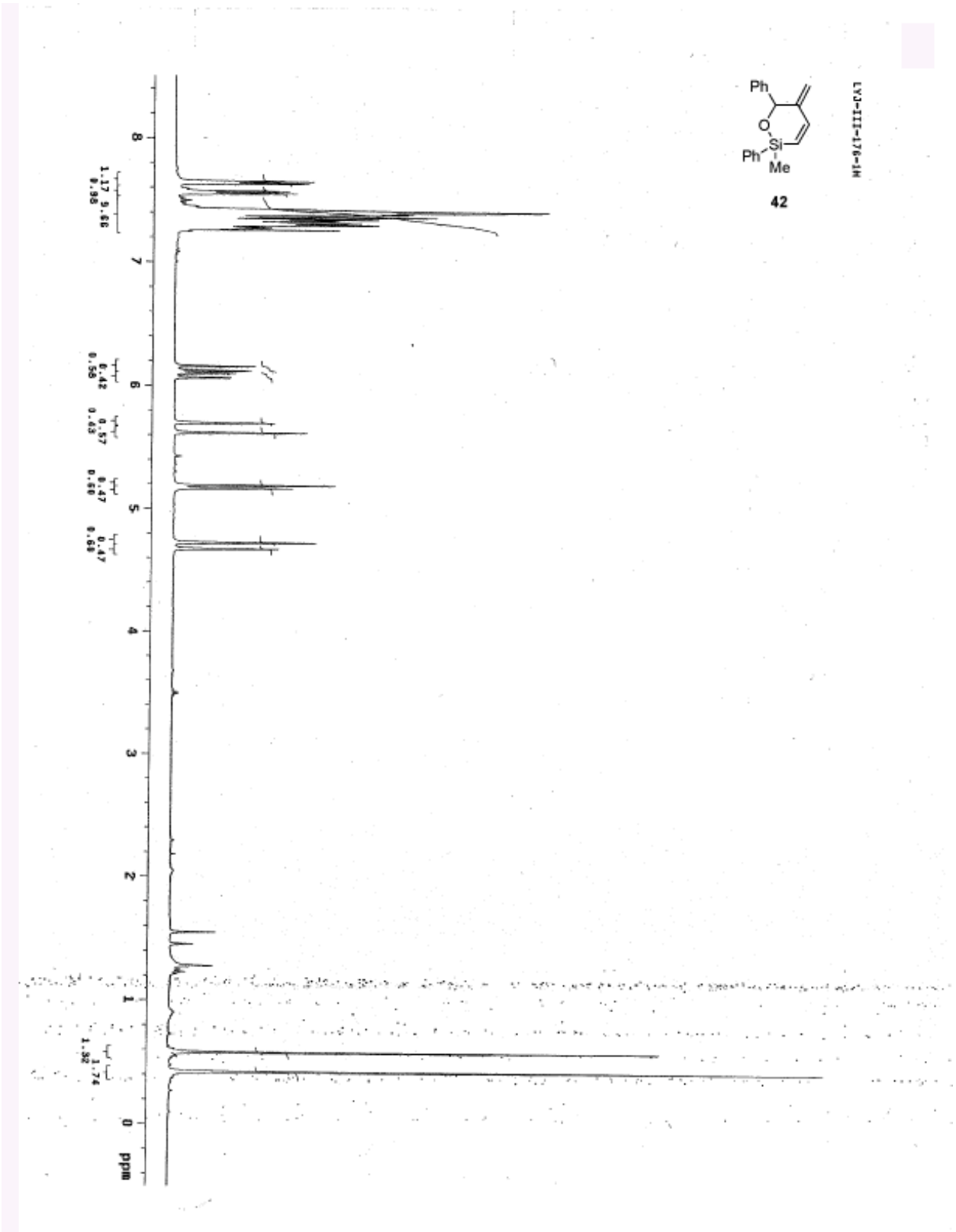

LYJ-III-169-1-2
Ts
25
8
7
6
5
4
3
2
1
ppm
2.69
3.74
2.87
1.00
1.96
1.00
1.15
1.07
3.09

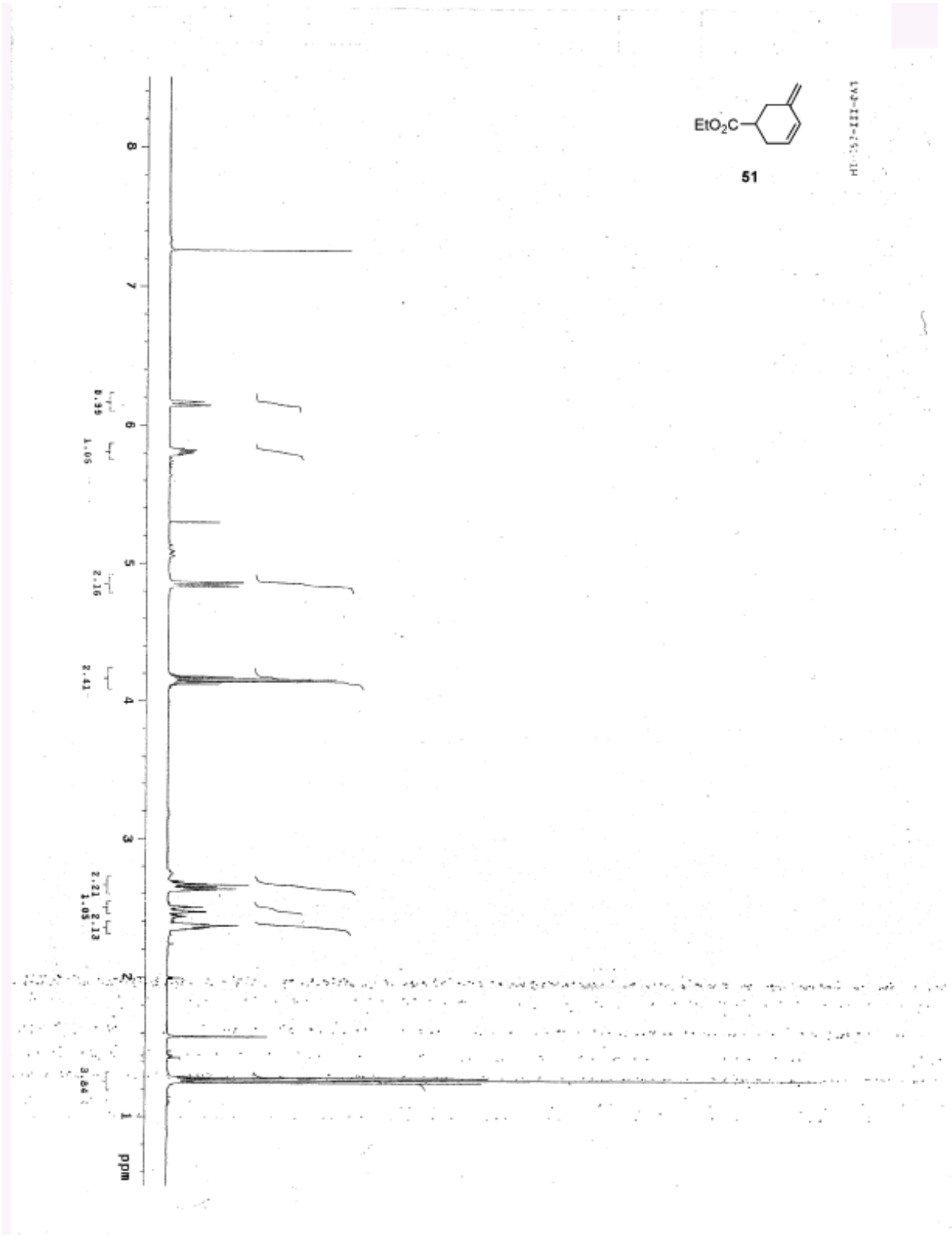

Ts
Ts
29 + 30
ratio of endo and exo product = 62 : 38
ppm

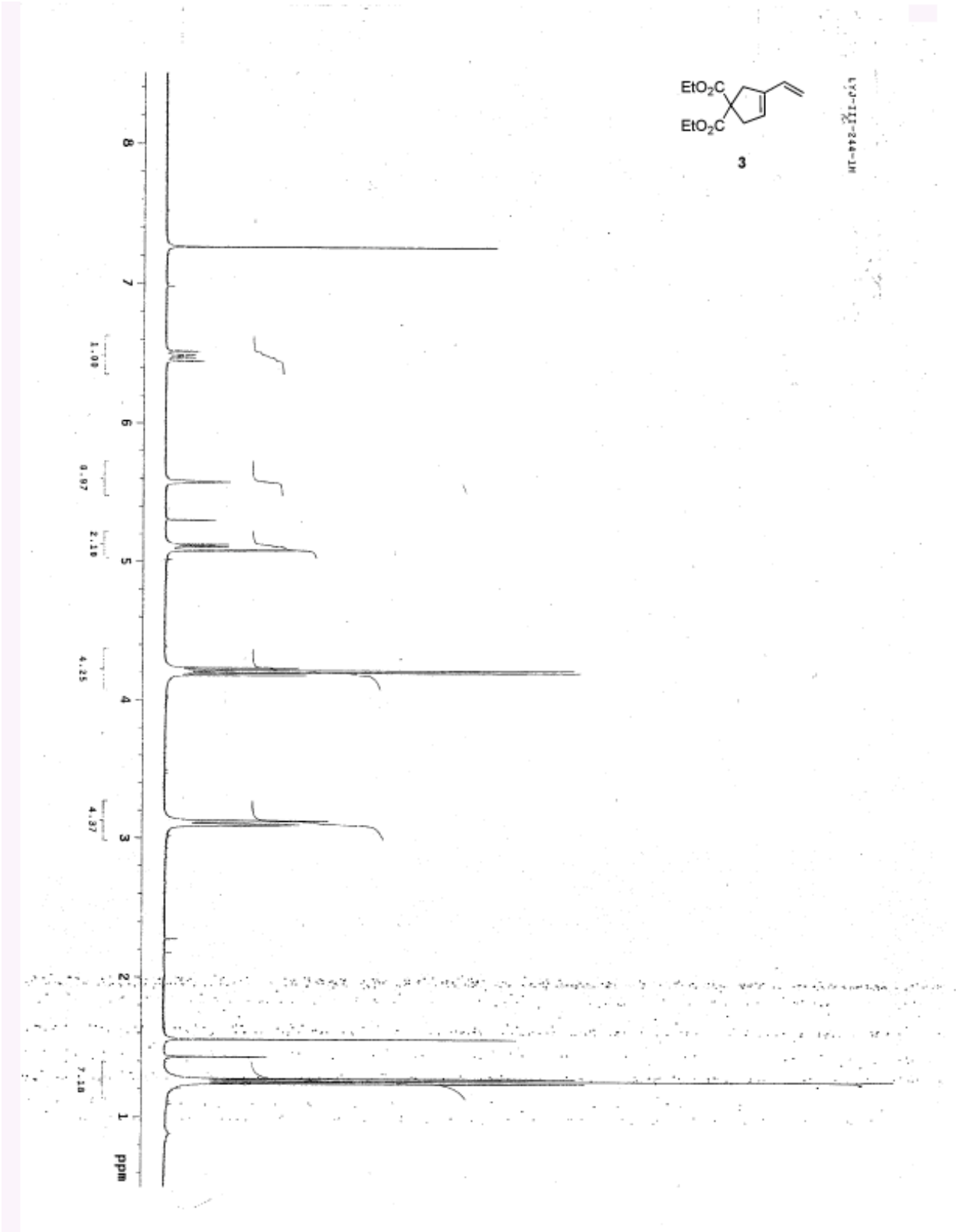

Ph
O
32
LVJ-II-058-1H
10
9
8
7
6
5
4
3
2
1
0 ppm
5.14
2.08
1.02
1.13
0.89
1.16
1.11 1.17

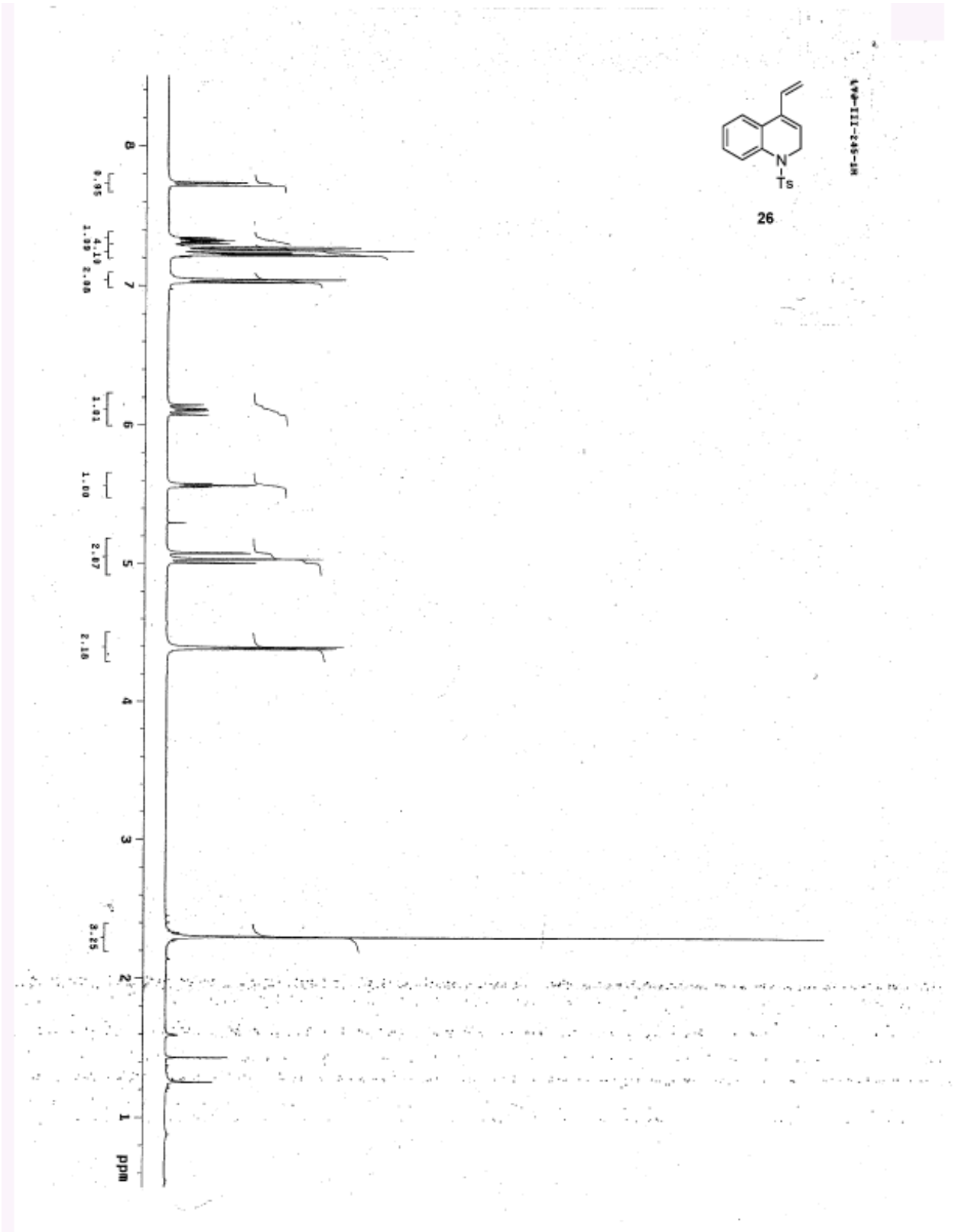

Ph
35
LYJ-III-226-1H
5.36
1.01
1.02
1.01
2.16
2.18
8
7
6
5
4
3
2
1
ppm

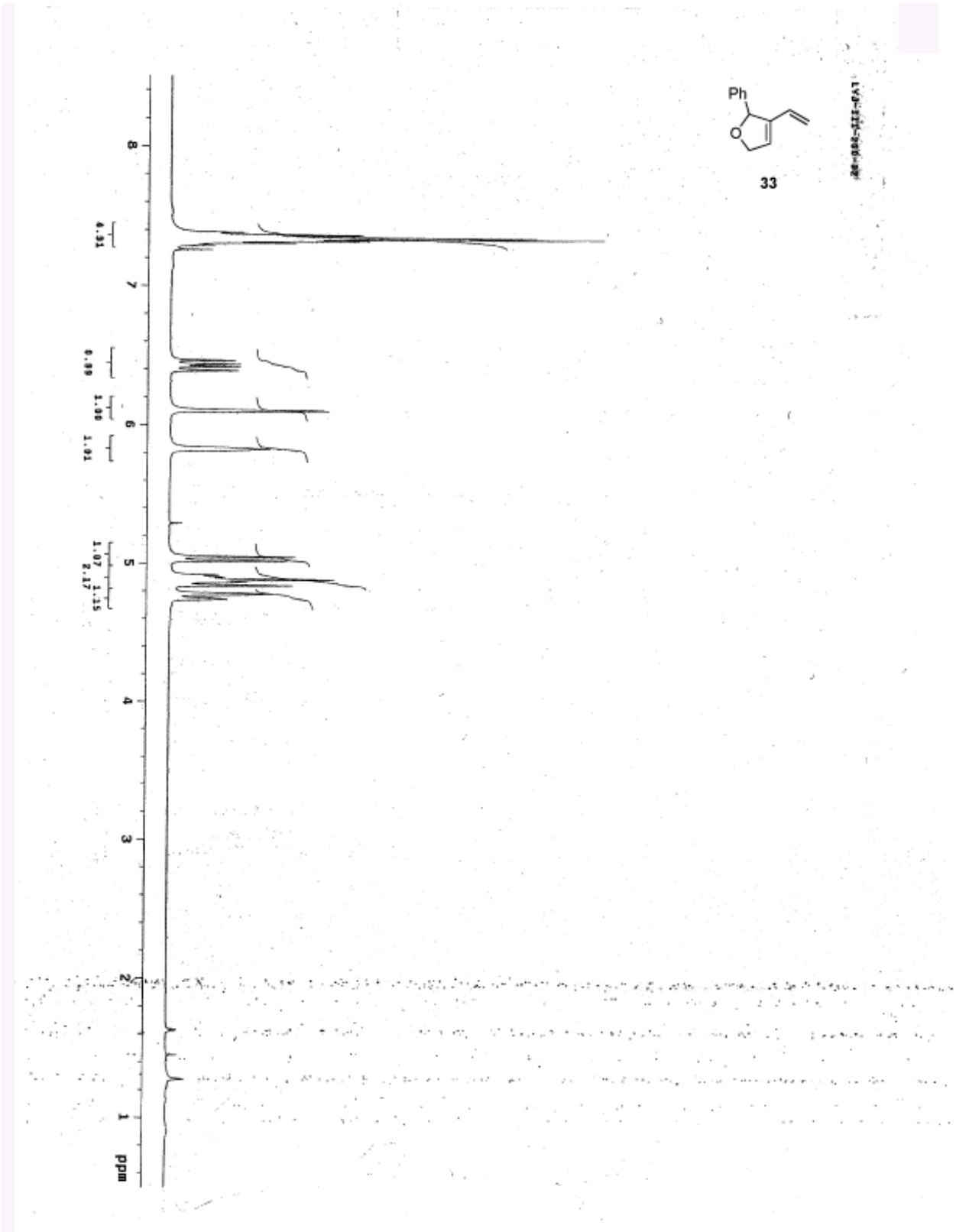

Ph
O
Si
Me
Me
40
LYG-III-226-2
8
7
6
5
4
3
2
1
0
ppm
5.88
1.06
1.00
0.99
1.07
1.07
2.37
3.02

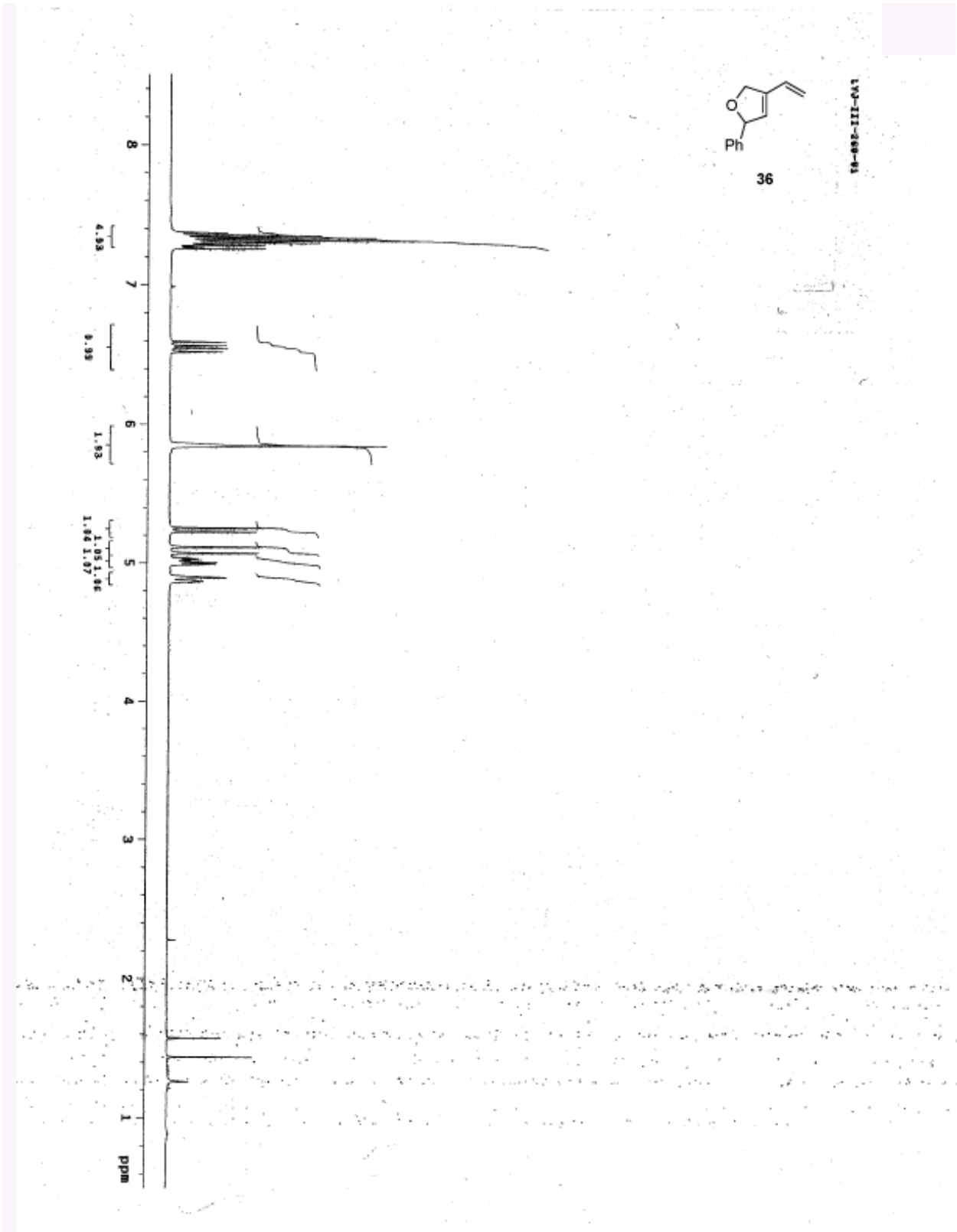

Ph
O
Si
Ph
Me
42
MI-9(1-III-CA1
1.17
5.69
0.98
0.56
0.42
0.43
0.57
0.50
0.47
0.47
0.69
1.36
1.74
8
7
6
5
4
3
2
1
0
ppm

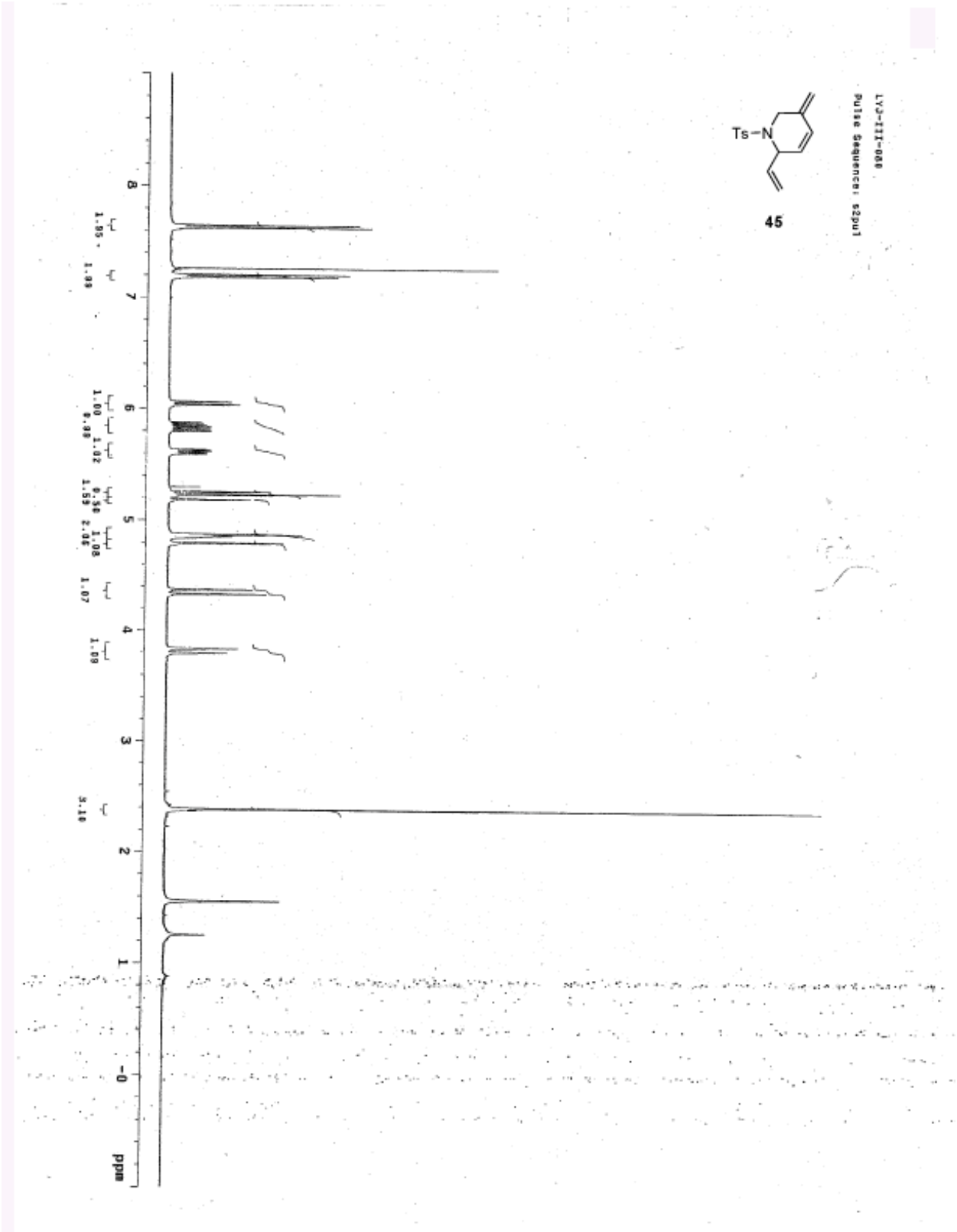

EtO2C
51
ppm

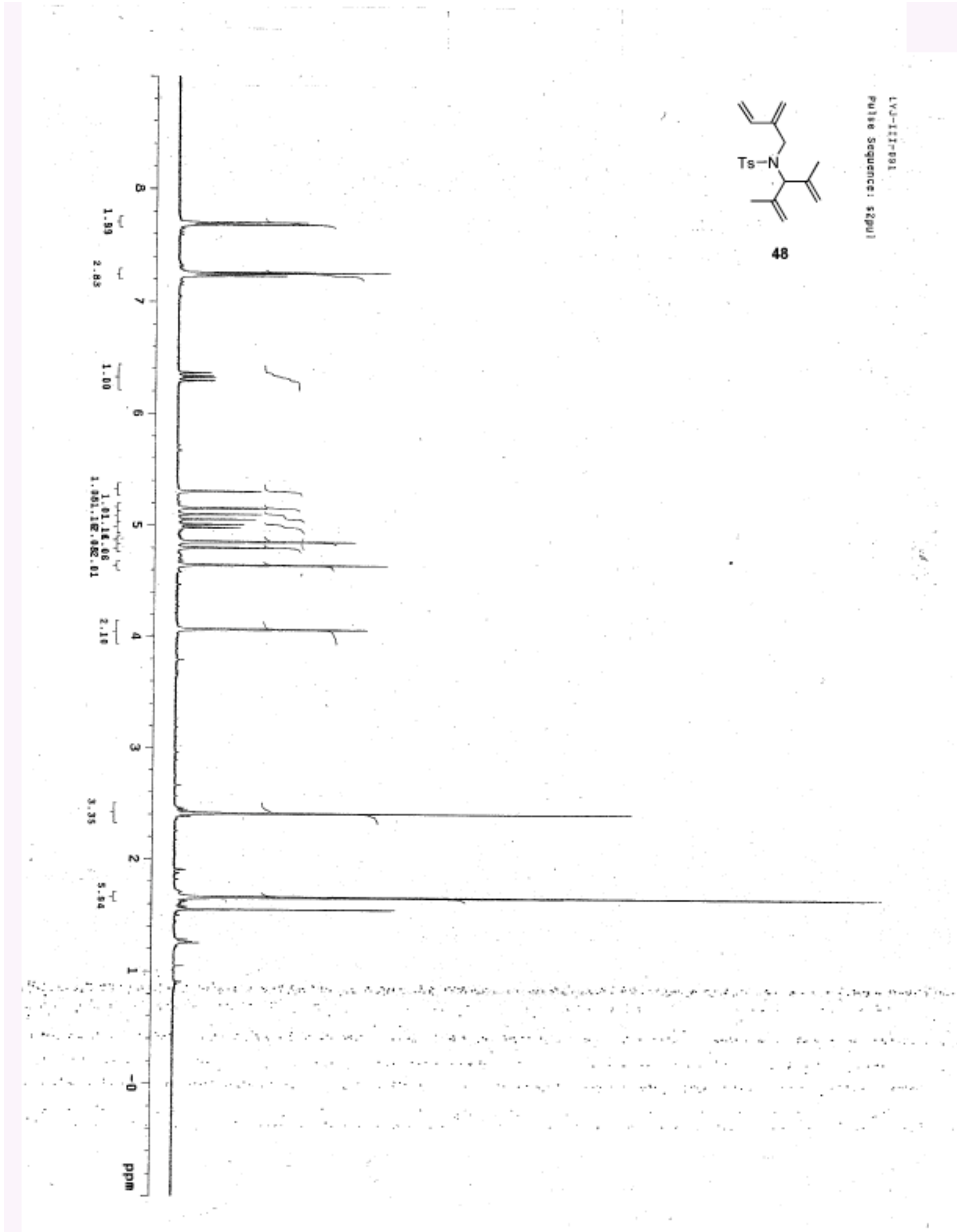

EtO2C
EtO2C
3
1.00
0.97
2.19
4.25
4.37
7.19
ppm

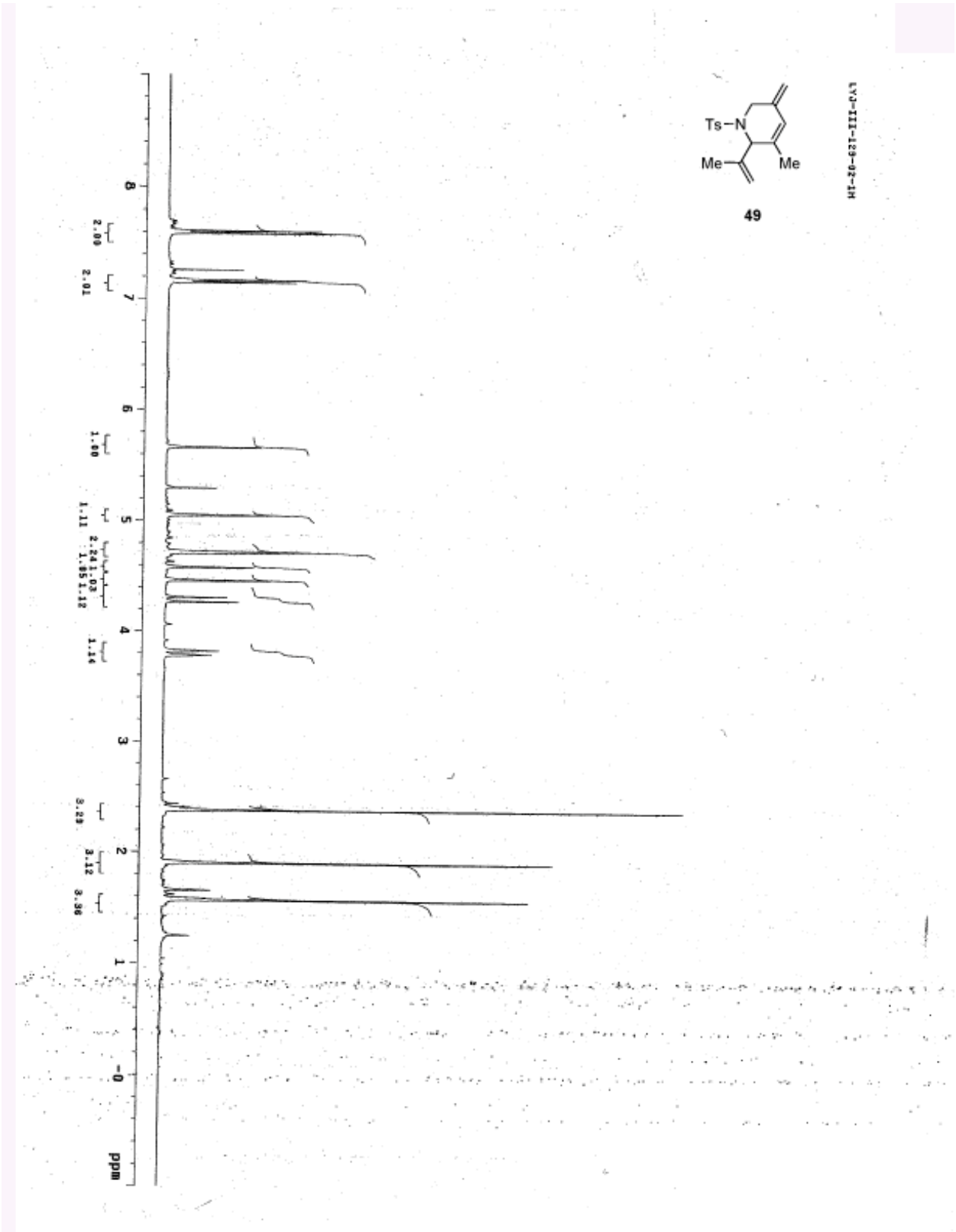

N
Ts
26
8.25
2.10
2.07
1.00
1.01
4.19
2.00
0.95
8
7
6
5
4
3
2
1
ppm

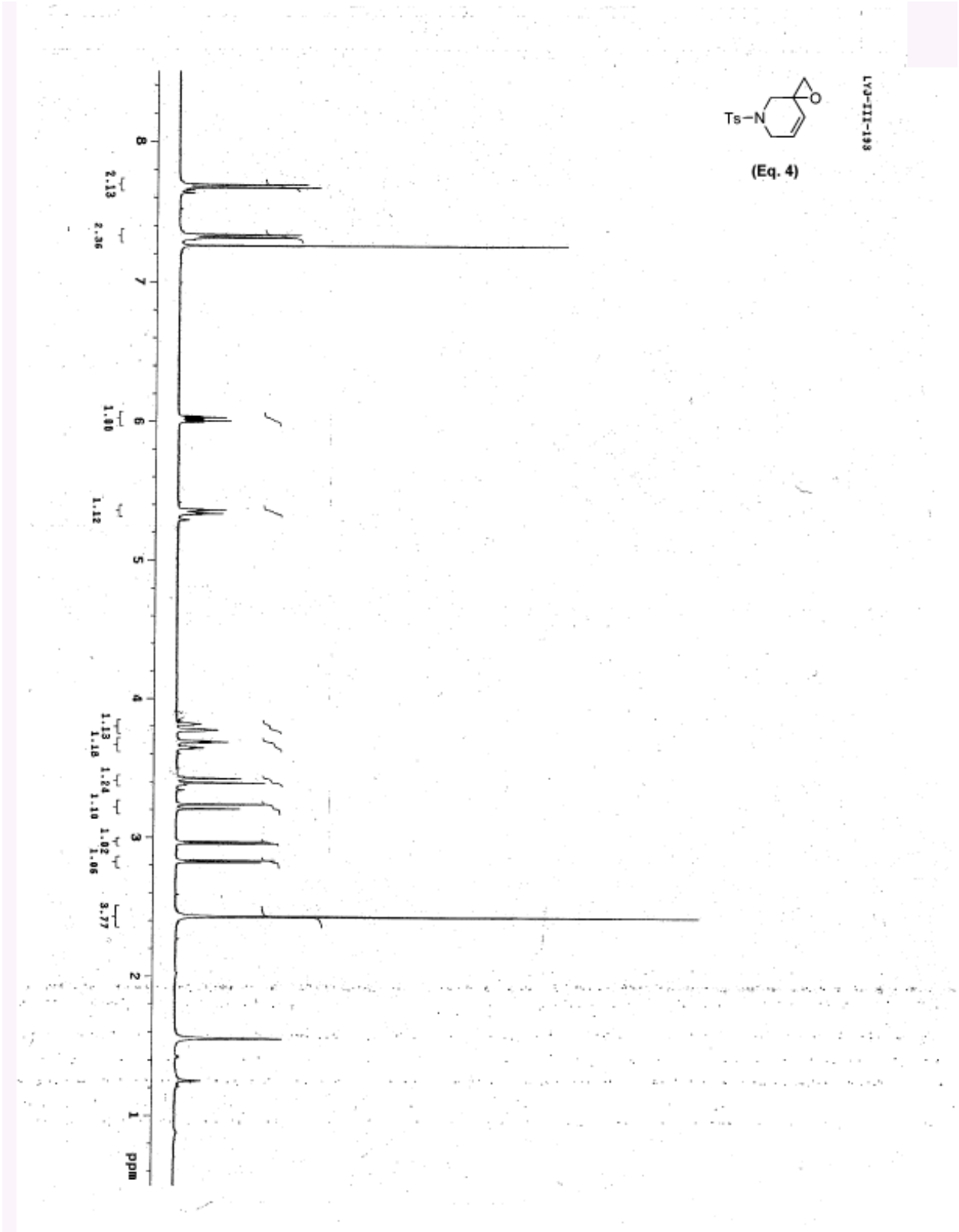

Ph
O
33
4.31
0.99
1.00
1.01
1.07
2.17
1.15
8
7
6
5
4
3
2
1
ppm


Ph
36
ppm


Ts–N
45
LV2-III-060
Pulse Sequence: s2pul
8
7
6
5
4
3
2
1
0
ppm
1.05
1.05
1.00
0.88
1.02
0.56
1.59
2.06
1.08
1.07
1.09
5.10


Pulse Sequence: s2pul
Ts–N
48
ppm


Ts–N
Me
Me
49
ppm


Ts–N
O
(Eq. 4)
LYS-III-185
8
7
6
5
4
3
2
1
ppm
2.13
2.36
1.00
1.12
1.13
1.10
1.24
1.10
1.02
1.06
3.77