Molybdenum-Catalyzed Ring-Closing Metathesis of Allenynes

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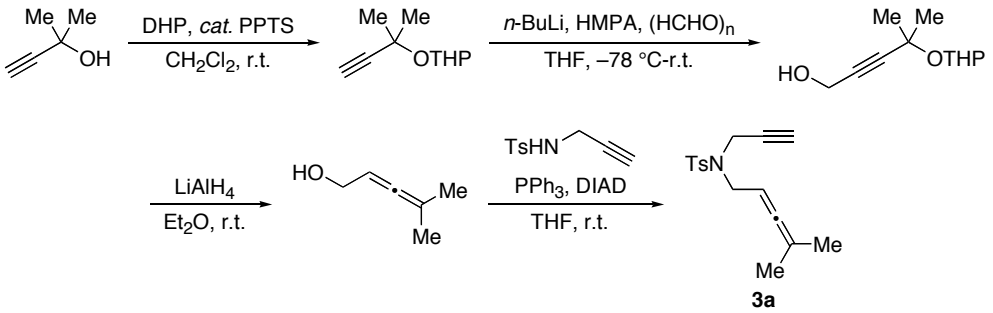
Supporting Information

General. All manipulations were carried out in a nitrogen-filled gloved box and with standard Schlenk techniques under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.77 MHz and ^{13}C NMR at 75.46 MHz) or a Varian Mercury 400 (^1H at 400.44 MHz). All NMR data were obtained in $CDCl_3$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.00 ppm. High resolution mass spectra were recorded on a JEOL JMS-SX102A. IR spectra was recorded on a Shimadzu FTIR-8100 spectrometer.

Materials. 2,6-Diisopropylphenylimidoneophilidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide) (Schrock catalyst, **1**) was purchased from Strem. Toluene was distilled from sodium–benzophenone ketyl before using for catalytic reactions. All other commercially available chemical resources were used without further purifications.

Typical Procedure for the Preparation of Tosylamine-bridged Allenynes[1,2]



3a

To a solution of pyridinium *p*-toluenesulfonate (PPTS) (1.78 g, 7.10 mmol, 5 mol %) in CH_2Cl_2 (60 mL) were added 2-methylbut-3-yne-2-ol (12.0 g, 143 mmol) and 3,4-dihydropyran (DHP) (50.0 g, 594 mmol). After being stirred at room temperature for 16 h, the volatile materials were removed under reduced pressure. The residue was taken up in ether, washed with water, dried over $MgSO_4$, and concentrated. Distillation under reduced pressure (35 °C/1.8 mmHg) gave pure 1,1-dimethylprop-2-ynyl tetrahydropyran-2-yl ether

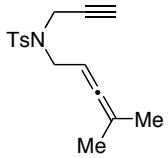
(1) Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 3807.
(2) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348.

(22.0 g, 90%).

To a solution of 1,1-dimethylprop-2-ynyl tetrahydropyran-2-yl ether (4.00 g, 23.8 mmol) in THF (70.0 mL) at –78 °C was slowly added *n*-butyllithium (1.59 M hexane solution; 20 mL) over 30 min. HMPA (5.0 mL) was added to the mixture at 0 °C, and then paraformaldehyde (1.43 g, 47.6 mmol) was added. After being stirred at room temperature for 2h, the reaction was quenched by a phosphate buffer solution (pH 6.9), and the mixture was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. Distillation under reduced pressure (100 °C/1.8 mmHg) gave pure 4-methyl-4-(tetrahydropyran-2-yloxy)pent-2-yn-1-ol (3.40 g, 72%).

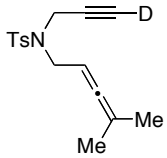
To an ether suspension (50 mL) of lithium aluminum hydride (1.57 g, 41.5 mmol) was added dropwise ether solution (15 mL) of 4-methyl-4-(tetrahydropyran-2-yloxy)pent-2-yn-1-ol (3.29 g, 16.6 mmol) over 30 min. After being stirred at room temperature for 3 h, the reaction was quenched by addition of a mixture of Celite® and sodium sulfate decahydrate (v/v = 1/1), and the mixture was filtrated. The solvent was removed under reduced pressure, and the residue was distilled under reduced pressure (35 °C/1.8 mmHg) to give pure 4-methylpenta-2,3-dien-1-ol (1.03 g, 63%).

To a stirred solution of *N*-(prop-2-ynyl)tosylamine (584 mg, 2.79 mmol) in THF (7.0 mL) were added successively triphenylphosphine (1.39 g, 5.30 mmol), 4-methylpenta-2,3-dien-1-ol (903 mg, 9.20 mmol), and diisopropylcarbodiimide (DIAD) (903 mg, 4.46 mmol) at 0 °C. The reaction was warmed to room temperature over 30 min and was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:AcOEt = 14:1) to give pure *N*-(4-methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (**3a**, 419 mg, 52%).

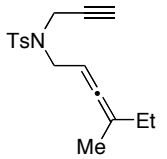


***N*-(4-Methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3a).** White solid; mp: 56-57 °C; ^{1}H NMR δ 1.67 (d, J = 3.0 Hz, 6H), 1.99 (t, J = 2.5 Hz, 1H), 2.42 (s, 3H), 3.79 (d, J = 6.9 Hz, 2H), 4.16 (d, J = 2.5 Hz, 2H), 4.81-4.87 (m, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 20.3, 21.5, 35.5, 46.6, 73.3, 76.5, 83.6, 97.0, 127.6, 129.4, 136.1, 143.4, 203.8; HRMS (EI) calcd for $C_{16}H_{19}NO_2S$ (M^+) 289.1136, found 289.1136.

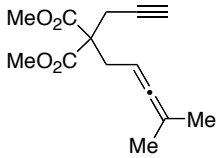
Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.26; H, 6.61; N, 4.80.



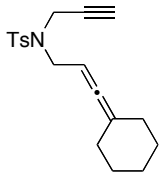
***N*-(4-Methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl-3-*d*)tosylamine (3a-*d*).** White solid; mp: 52-53 °C; ^{1}H NMR δ 1.66 (d, J = 2.7 Hz, 6H), 2.42 (s, 3H), 3.79 (d, J = 7.2 Hz, 2H), 4.15 (s, 2H), 4.83-4.84 (m, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 20.3, 21.6, 35.5, 46.6, 73.6 (t, J = 17.7 Hz), 76.0, 83.6, 97.1, 127.7, 129.4, 136.1, 143.4, 203.9; HRMS (CI) calcd for $C_{16}H_{19}DNO_2S$ (M^+ + H) 291.1276, found 291.1273.



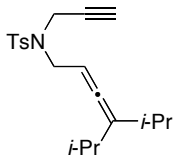
***N*-(4-Methylhexa-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3b).** Pale yellow solid; mp: 42-43 °C; ^{1}H NMR δ 0.97 (t, J = 7.4 Hz, 3H) 1.67 (d, J = 3.0 Hz, 3H), 1.92 (dq, J = 3.0, 7.4 Hz 1H), 1.98 (t, J = 2.4 Hz, 1H), 2.41 (s, 3H), 3.77 (dd, J = 13.8, 6.9 Hz, 1H), 3.83 (dd, J = 13.8, 6.9 Hz, 1H), 4.13 (dd, J = 18.0, 2.4 Hz, 1H), 4.20 (dd, J = 18.0, 2.4 Hz, 1H), 4.90-4.97 (m, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 12.0, 18.8, 21.5, 26.8, 35.5, 46.6, 73.4, 76.5, 85.6, 103.3, 127.6, 129.4, 136.1, 143.4, 202.9; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1293.



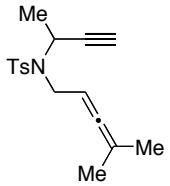
Dimethyl 8-methylnona-6,7-dien-1-yne-4,4-dicarboxylate (3c). Yellow oil; ^{1}H NMR δ 1.64 (d, J = 3.0 Hz, 6H), 1.98 (t, J = 2.7 Hz, 1H), 2.70 (d, J = 7.5 Hz, 2H), 2.85 (d, J = 2.7 Hz, 2H), 3.72 (s, 6H), 4.71-4.80 (m, 1H); ^{13}C NMR δ 20.4, 22.5, 32.5, 52.7, 57.1, 71.2, 78.8, 82.1, 95.4, 170.1, 203.8; HRMS (EI) calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, found 250.1212.



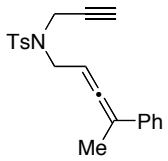
***N*-(3-Cyclohexylideneprop-2-enyl)-*N*-(prop-2-ynyl)tosylamine (3e).** White solid; mp: 79-80 °C; ^{1}H NMR δ 1.42-1.62 (m, 6H), 1.98 (t, J = 2.4 Hz, 1H), 2.06-2.10 (m, 4H), 2.42 (s, 3H), 3.80 (d, J = 6.9 Hz, 2H), 4.16 (d, J = 2.4 Hz, 2H), 4.81-4.86 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 25.8, 27.1, 31.2, 35.4, 46.7, 73.3, 76.4, 83.2, 104.1, 127.5, 129.3, 136.0, 143.3, 200.6; HRMS (EI) calcd for $C_{19}H_{23}NO_2S$ (M^+) 329.1449, found 329.1451.



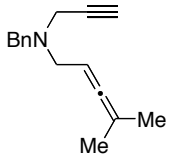
***N*-(4-Isopropyl-5-methylhexa-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3f).** White solid; mp: 55-56 °C; ^{1}H NMR δ 0.99 (d, J = 7.1 Hz, 12H), 1.97 (t, J = 2.4 Hz, 1H), 2.15 (dsep, J = 2.4, 7.1 Hz, 2H), 2.42 (s, 3H), 3.81 (d, J = 6.9 Hz, 2H), 4.20 (d, J = 2.4 Hz, 2H), 5.10 (tt, J = 7.0, 2.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.5, 22.1, 22.4, 29.5, 35.6, 46.8, 73.7, 89.7, 120.1, 127.7, 129.4, 136.2, 143.4, 200.9; HRMS (CI) calcd for $C_{20}H_{28}NO_2S$ (M^+ + H) 346.1841, found 346.1837.



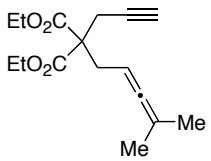
***N*-(4-Methylpenta-2,3-dienyl)-*N*-(1-methylprop-2-ynyl)tosylamine (3g).** White solid; mp: 58-59 °C; ^{1}H NMR δ 1.49 (d, J = 7.0 Hz, 3H), 1.67 (d, J = 2.7 Hz, 6H), 2.12 (d, J = 2.2 Hz, 1H), 2.41 (s, 3H), 3.68 (dd, J = 15.6, 8.0 Hz, 1H), 3.90 (dd, J = 15.6, 5.3 Hz, 1H), 4.88 (dq, J = 7.0, 2.2 Hz, 1H), 5.03-5.11 (m, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 19.8, 20.2, 21.5, 22.6, 44.8, 45.9, 73.0, 81.5, 87.8, 97.0, 127.5, 129.4, 136.5, 143.2, 202.0; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1306.



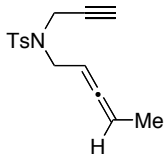
***N*-(4-Phenylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3h).** Pale yellow oil; ^{1}H NMR δ 1.99 (t, J = 2.6 Hz, 1H) 2.89 (d, J = 2.7 Hz, 3H), 2.41 (s, 3H), 3.90 (dd, J = 14.4, 7.2 Hz, 1H), 4.01 (dd, J = 14.4, 6.6 Hz, 1H), 4.16 (dd, J = 18.0, 2.6 Hz, 1H), 4.25 (dd, J = 15.9, 2.6 Hz, 1H), 5.33-5.40 (m, 1H), 7.19-7.39 (m, 7H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 17.0, 21.5, 36.0, 46.0, 73.8, 76.4, 88.1, 102.6, 125.8, 127.0, 127.6, 128.3, 129.5, 136.0, 136.1, 143.5, 205.8; HRMS (EI) calcd for $C_{21}H_{21}NO_2S$ (M^+) 351.1293, found 351.1297.



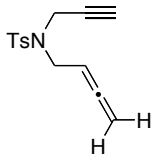
***N*-(4-Methylpenta-2,3-dienyl)-*N*-(but-3-ynyl)benzylamine (3i).** Yellow oil; ^{1}H NMR δ 1.65 (d, J = 2.7 Hz, 6H), 2.17 (t, J = 2.6 Hz, 1H), 3.09 (d, J = 6.9 Hz, 2H), 3.30 (d, J = 2.6 Hz, 2H), 3.63 (s, 2H), 4.12-4.98 (m, 1H), 7.19-7.33 (m, 5H); ^{13}C NMR δ 20.5, 41.3, 53.6, 56.7, 73.0, 78.7, 85.9, 95.3, 127.0, 128.2, 129.1, 138.5, 203.3; HRMS (EI) calcd for $C_{16}H_{19}N$ (M^+) 225.1517, found 225.1517.



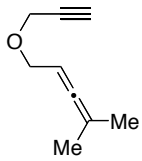
Diethyl 8-methylnona-6,7-dien-1-yne-4,4-dicarboxylate (3j). Yellow oil; ^{1}H NMR δ 1.25 (t, J = 7.1 Hz, 6H), 1.65 (d, J = 3.0 Hz, 6H), 1.98 (t, J = 2.7 Hz, 1H), 2.71 (d, J = 7.8 Hz, 2H), 2.85 (d, J = 2.7 Hz, 2H), 4.12-4.25 (m, 4H), 4.72-4.81 (m, 1H); ^{13}C NMR δ 14.0, 20.4, 22.3, 32.3, 57.0, 61.5, 71.1, 78.9, 82.2, 95.2, 169.6, 203.9; HRMS (EI) calcd for $C_{16}H_{22}O_4$ (M^+) 278.1518, found 278.1516.



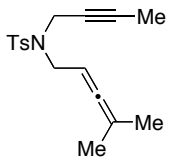
***N*-(Penta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3k).** White solid; mp: 45-46 °C; ^{1}H NMR δ 1.63 (dd, J = 7.1, 3.0 Hz, 3H), 2.00 (t, J = 2.7 Hz, 1H), 2.40 (s, 3H), 3.78 (ddd, J = 21.2, 7.2, 2.2 Hz, 1H), 3.86 (ddd, J = 21.2, 7.2, 2.2 Hz, 1H), 4.11 (dd, J = 18.3, 2.5 Hz, 1H), 4.18 (dd, J = 18.3, 2.5 Hz, 1H), 4.90-4.98 (m, 1H), 5.10-5.18 (m, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 14.0, 21.5, 35.7, 46.2, 73.5, 76.4, 85.2, 87.4, 127.6, 129.4, 136.0, 143.5, 206.5; HRMS (EI) calcd for $C_{15}H_{17}NO_2S$ (M^+) 275.0980, found 275.0974.



***N*-(Buta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3l).** White solid; mp: 55-56 °C; ^{1}H NMR δ 2.03 (t, J = 2.4 Hz, 1H), 2.42 (s, 3H), 3.88 (dt, J = 6.8, 2.5 Hz, 2H), 4.15 (d, J = 2.4 Hz, 2H), 4.78 (dt, J = 6.8, 2.5 Hz, 2H), 5.04 (quint, J = 6.8 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 21.5, 35.8, 45.6, 73.7, 76.4, 85.3, 127.6, 129.5, 136.0, 143.6, 209.7; HRMS (EI) calcd for $C_{14}H_{15}NO_2S$ (M^+) 261.0823, found 261.0825.

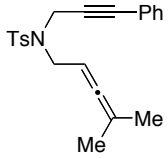


4-Methylpent-2,3-dienyl prop-2-ynyl ether (3m). Yellow oil; ^{1}H NMR δ 1.71 (d, J = 3.0 Hz, 6H), 2.41 (t, J = 2.5 Hz, 1H), 4.04 (d, J = 6.9 Hz, 2H), 4.17 (d, J = 2.5 Hz, 2H), 5.01-5.07 (m, 1H); ^{13}C NMR δ 20.3, 56.3, 68.5, 74.1, 79.7, 85.4, 96.1, 203.4; HRMS (EI) calcd for $C_9H_{12}O$ (M^+) 136.0888, found 136.0886.

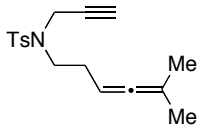


***N*-(4-Methylpent-2,3-dienyl)-*N*-(but-2-ynyl)tosylamine (3n).** White solid; mp: 42-43 °C; ^{1}H NMR δ 1.54 (t, J = 2.4 Hz, 3H), 1.66 (d, J = 2.7 Hz, 6H) 2.40 (s, 3H), 3.75 (d, J = 6.6

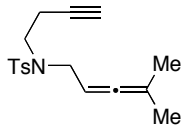
Hz, 2H), 4.07 (q, *J* = 2.4 Hz, 2H), 4.82-4.84 (m, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR δ 3.2, 20.4, 21.5, 36.1, 46.5, 71.6, 81.1, 83.9, 96.8, 127.7, 129.2, 136.2, 143.0, 203.6; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1290.



***N*-(4-Methylpent-2,3-dienyl)-*N*-(3-phenylprop-2-ynyl)tosylamine (3o).** White solid; mp: 58-59 °C; ^{1}H NMR δ 1.70 (d, *J* = 2.7 Hz, 6H), 2.36 (s, 3H), 3.88 (d, *J* = 6.9 Hz, 2H), 4.41 (s, 2H), 4.91-4.97 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 7.23-7.33 (m, 5H), 7.71 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR δ 20.3, 21.4 ,36.5, 46.8, 81.7, 83.7, 85.3, 97.0, 122.3, 127.7, 128.0, 128.2, 129.4, 131.4, 135.9, 143.3, 203.9; HRMS (EI) calcd for $C_{22}H_{23}NO_2S$ (M^+) 365.1449, found 365.1457.



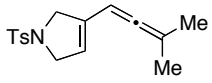
***N*-(5-Methylhex-3,4-dienyl)-*N*-(prop-2-ynyl)tosylamine (3p).** Pale yellow oil; ^{1}H NMR δ 1.67 (d, *J* = 3.0 Hz, 6H), 2.02 (t, *J* = 2.4 Hz, 1H), 2.22 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.42 (s, 2H), 3.25 (t, *J* = 7.5 Hz, 2H), 4.15 (d, *J* = 2.4 Hz, 2H), 4.85-4.94 (m, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR δ 20.6, 21.6, 27.8, 36.3, 46.0, 73.6, 76.6, 85.0, 95.9, 127.6, 129.4, 136.0, 143.4, 202.4; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1299.



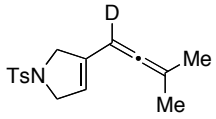
***N*-(4-Methylpent-2,3-dienyl)-*N*-(but-3-ynyl)tosylamine (3q).** Pale yellow solid; mp: 62-63 °C; ^{1}H NMR δ 1.65 (d, *J* = 2.7 Hz, 6H), 1.96 (t, *J* = 2.7 Hz, 1H), 2.41 (s, 3H), 2.41-2.50 (m, 2H), 3.03-3.35 (m, 2H), 3.78 (d, *J* = 7.2 Hz, 2H), 4.71-4.80 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 19.0, 20.3, 21.5, 45.6, 48.3, 70.0, 80.9, 84.2, 97.1, 127.1, 129.7, 136.9, 143.2, 203.5; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293 found,

303.1296.

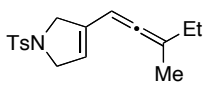
General Procedure for RCM of Allenynes. To a solution of Schrock complex (27.7 mg, 0.036 mmol) in dry toluene (4.0 mL) was added a solution of diethyl 8-methyl nona-2,3-diene-1-yne-4,4-dicarboxylate (**3j**, 67.1 mg, 0.241 mmol) in dry toluene (4.8 mL). After being stirred under argon atmosphere for 3 h at room temperature, the volatile material was removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:AcOEt = 5:1) to give pure diethyl 3-(3-methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (**4j**, 63.9 mg, 95%).



3-(3-Methylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (**4a**)**.** Pale yellow solid; mp: 114-115 °C; ^{1}H NMR δ 1.70 (d, J = 2.7 Hz, 6H), 2.42 (s, 3H), 4.05-4.07 (m, 2H), 4.13-4.16 (m, 2H), 5.42 (t, J = 1.8 Hz, 1H), 5.69 (t, J = 2.9 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 20.4, 21.5, 54.8, 55.5, 86.1, 98.6, 119.2, 127.4, 129.7, 134.3, 135.1, 143.3, 204.2; HRMS (EI) calcd for $C_{16}H_{19}NO_2S$ (M^+) 289.1136, found 289.1138. Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.50; H, 6.64; N, 4.80.

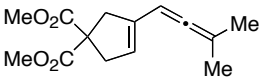


3-(3-Methylbuta-1,2-dienyl-1-*d*)-1-tosyl-3-pyrroline (**4a-*d***)**.** Pale yellow solid; mp: 112-113 °C; ^{1}H NMR δ 1.71 (s, 6H), 2.43 (s, 3H), 4.04-4.07 (m, 2H), 4.14-4.17 (m, 2H), 5.42 (t, J = 1.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 20.4, 21.5, 54.8, 55.5, 86.1, 98.6, 119.1, 127.4, 129.7, 134.2, 135.1, 143.3, 204.1; HRMS (EI) calcd for $C_{16}H_{18}DNO_2S$ (M^+) 290.1198, found 290.1199.

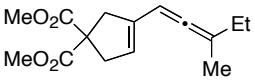


3-(3-Methylpenta-1,2-dienyl)-1-tosyl-3-pyrroline (**4b**)**.** Yellow solid; mp: 88-89 °C; ^{1}H NMR δ 0.95 (t, J = 7.5 Hz, 3H), 1.71 (d, J = 2.7 Hz, 3H), 1.98 (dq, J = 3.3, 7.5 Hz, 2H),

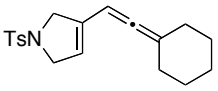
2.42 (s, 3H), 4.03-4.06 (m, 2H), 4.13-4.17 (m, 2H), 5.42 (t, J = 2.0 Hz, 1H), 5.79 (q, J = 3.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 12.2, 19.0, 21.5, 26.9, 54.9, 55.5, 88.1, 104.9, 119.0, 127.4, 129.7, 134.1, 135.1, 143.4, 203.5; HRMS (EI) calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1290.



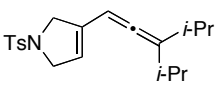
Dimethyl 3-(3-Methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (4c). Pale yellow solid; mp: 62-63 °C; ^{1}H NMR δ 1.72 (d, J = 3.0 Hz, 6H), 2.96-3.02 (m, 2H), 3.09 (q, J = 2.0 Hz, 2H), 3.74 (s, 6H), 5.42 (t, J = 2.1 Hz, 1H), 5.79 (t, J = 2.9 Hz, 1H); ^{13}C NMR δ 20.5, 41.0, 41.2, 52.8, 58.6, 88.4, 97.5, 122.6, 137.1, 172.6, 204.1; HRMS (EI) calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, found 250.1212.



Dimethyl 3-(3-Methylpenta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (4d). ^{1}H NMR δ 0.99 (t, J = 7.5 Hz, 3H), 1.72 (d, J = 2.7 Hz, 3H), 1.99 (dq, J = 3.3, 7.2 Hz, 2H), 2.991-2.996 (m, 2H), 3.087-3.094 (m, 2H), 3.74 (s, 6H), 5.38-5.42 (m, 1H), 5.86-5.92 (m, 1H).

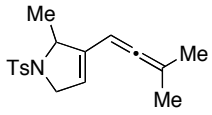


3-(2-Cyclohexylidenevinyl)-1-tosyl-3-pyrroline (4e). Yellow solid; mp: 101-102 °C; ^{1}H NMR δ 1.40-1.60 (m, 6H), 2.09-2.11 (m, 4H), 2.42 (s, 3H), 4.05-4.07 (m, 2H), 4.14-4.17 (m, 2H), 5.41 (t, J = 1.8 Hz, 1H), 5.70 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.5, 25.9, 27.3, 31.3, 54.8, 55.6, 85.9, 105.7, 118.9, 127.4, 129.7, 134.2, 135.1, 143.3, 200.9; HRMS (CI) calcd for $C_{19}H_{24}NO_2S$ (M^+ + H) 330.1528, found 330.1524.

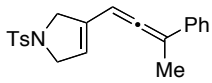


3-(3-Isopropyl-4-methylpenta-1,2-dienyl)-1-tosyl-3-pyrroline (4f). Yellow solid; mp: 75-76 °C; ^{1}H NMR δ 0.98 (d, J = 6.6 Hz, 6H), 1.00 (d, J = 6.6 Hz, 6H), 2.19 (dsep, J = 2.1, 6.6

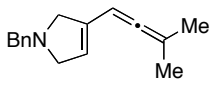
Hz, 2H), 2.42 (s, 3H), 4.01-4.04 (m, 2H), 4.15-4.18 (m, 2H), 5.41 (t, J = 2.0 Hz, 1H), 5.93 (s, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 21.5, 22.2, 22.4, 29.9, 54.7, 55.7, 91.5, 118.8, 121.3, 127.4, 129.7, 134.0, 135.0, 143.4, 201.9; HRMS (CI) calcd for $C_{20}H_{28}NO_2S$ (M^+ + H) 346.1841, found 346.1840.



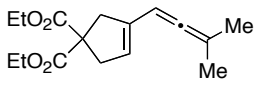
2-Methyl-3-(3-methylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (**4g**)**.** Yellow solid; mp: 89-90 °C; ^{1}H NMR δ 1.42 (d, J = 6.3 Hz, 3H), 1.72 (dd, J = 8.3, 2.9 Hz, 6H), 2.41 (s, 3H), 4.07 (dt, J = 15.6, 2.1 Hz, 1H), 4.18 (dq, J = 15.6, 2.1 Hz, 1H), 4.51 (t, J = 6.3 Hz, 1H), 5.35 (s, 1H), 5.63 (t, J = 3.0 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 20.0, 20.3, 21.5, 22.1, 54.4, 63.1, 85.9, 98.2, 118.9, 127.2, 129.6, 135.3, 139.8, 143.2, 204.2; HRMS (CI) calcd for $C_{17}H_{22}NO_2S$ (M^+ + H) 304.1371, found 304.1290.



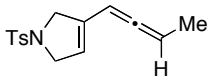
3-(3-Phenylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (**4h**)**.** Yellow solid; mp: 144-145 °C; ^{1}H NMR δ 2.13 (d, J = 2.7 Hz, 3H), 2.43 (s, 3H), 4.08-4.11 (m, 2H), 4.18-4.22 (m, 2H), 5.58 (t, J = 2.1 Hz, 1H), 5.79 (d, J = 2.7 Hz, 1H), 7.22-7.34 (m, 7H), 7.70 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 17.3, 21.8, 54.9, 55.8, 90.3, 104.2, 121.0, 126.1, 127.5, 127.6, 128.6, 130.0, 134.3, 134.4, 136.0, 143.6, 207.6; HRMS (EI) calcd for $C_{21}H_{21}NO_2S$ (M^+) 351.1293, found 351.1295.



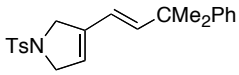
1-Benzyl-3-(3-methylbuta-1,2-dienyl)-3-pyrroline (**4i**). Yellow oil; ^{1}H NMR δ 1.68 (d, J = 2.7 Hz, 6H), 3.47-3.48 (m, 2H), 3.52-3.56 (m, 2H), 3.82 (s, 2H), 5.60 (t, J = 1.8 Hz, 1H), 5.81 (t, J = 2.7 Hz, 1H), 7.23-7.39 (m, 5H); ^{13}C NMR δ 20.5, 59.9, 60.5, 60.6, 87.1, 97.4, 122.5, 126.9, 128.3, 128.6, 137.1, 139.5, 204.0; HRMS (EI) calcd for $C_{16}H_{19}N$ (M^+) 225.1517, found 225.1521.



Diethyl 3-(3-Methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (**4j**)**.** Yellow oil; ^{1}H NMR δ 1.24 (t, J = 7.2 Hz, 6H), 1.72 (d, J = 2.7 Hz, 6H), 2.97-2.98 (m, 2H), 3.06-3.07 (m, 2H), 4.19 (q, J = 7.2 Hz, 4H), 4.13 (t, J = 8.1 Hz, 1H), 5.41 (J = 2.1 Hz, 1H), 5.79 (t, J = 2.7 Hz, 1H); ^{13}C NMR δ 14.0, 20.6, 40.9, 41.1, 58.7, 61.5, 88.4, 97.5, 122.7, 137.0, 172.1, 204.1; HRMS (EI) calcd for $C_{16}H_{22}O_4$ (M^+) 278.1518, found 278.1517.



3-(Buta-1,2-dienyl)-1-tosyl-3-pyrroline (4k). Yelow solid; mp: 121-122 °C; ^{1}H NMR δ 1.69 (dd, J = 7.1, 3.1 Hz, 3H), 2.43 (s, 3H), 4.07-4.08 (m, 2H), 4.15-4.27 (m, 2H), 5.37 (quint, J = 6.6 Hz, 1H), 5.46 (d, J = 1.2 Hz, 1H), 5.80 (sext, J = 3.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 14.2, 21.5, 54.7, 55.5, 87.6, 89.1, 119.9, 127.4, 129.7, 134.1, 134.6, 143.4, 207.1; HRMS (EI) calcd for $C_{15}H_{17}NO_2S$ (M^+) 275.0980, found 275.0981.

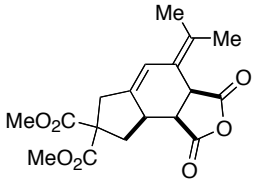


3-(3-Methyl-3-phenylbut-1-enyl)-1-tosyl-3-pyrroline (5). Yellow oil; ^{1}H NMR δ 1.40 (s, 6H), 2.42 (s, 3H), 4.17 (s, 4H), 5.51 (s, 1H), 5.68 (d, J = 16.2 Hz, 1H), 6.06 (d, J = 16.2 Hz, 1H), 7.28-7.33 (m, 7H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 28.5, 40.7, 53.8, 55.0, 77.2, 119.8, 121.4, 126.0, 127.4, 128.2, 129.8, 134.2, 137.1, 143.3, 143.4, 147.9 [one sp^2 carbon signal is missing due to overlapping]; HRMS (EI) calcd for $C_{22}H_{25}NO_2S$ (M^+) 367.5054, found 367.1604.

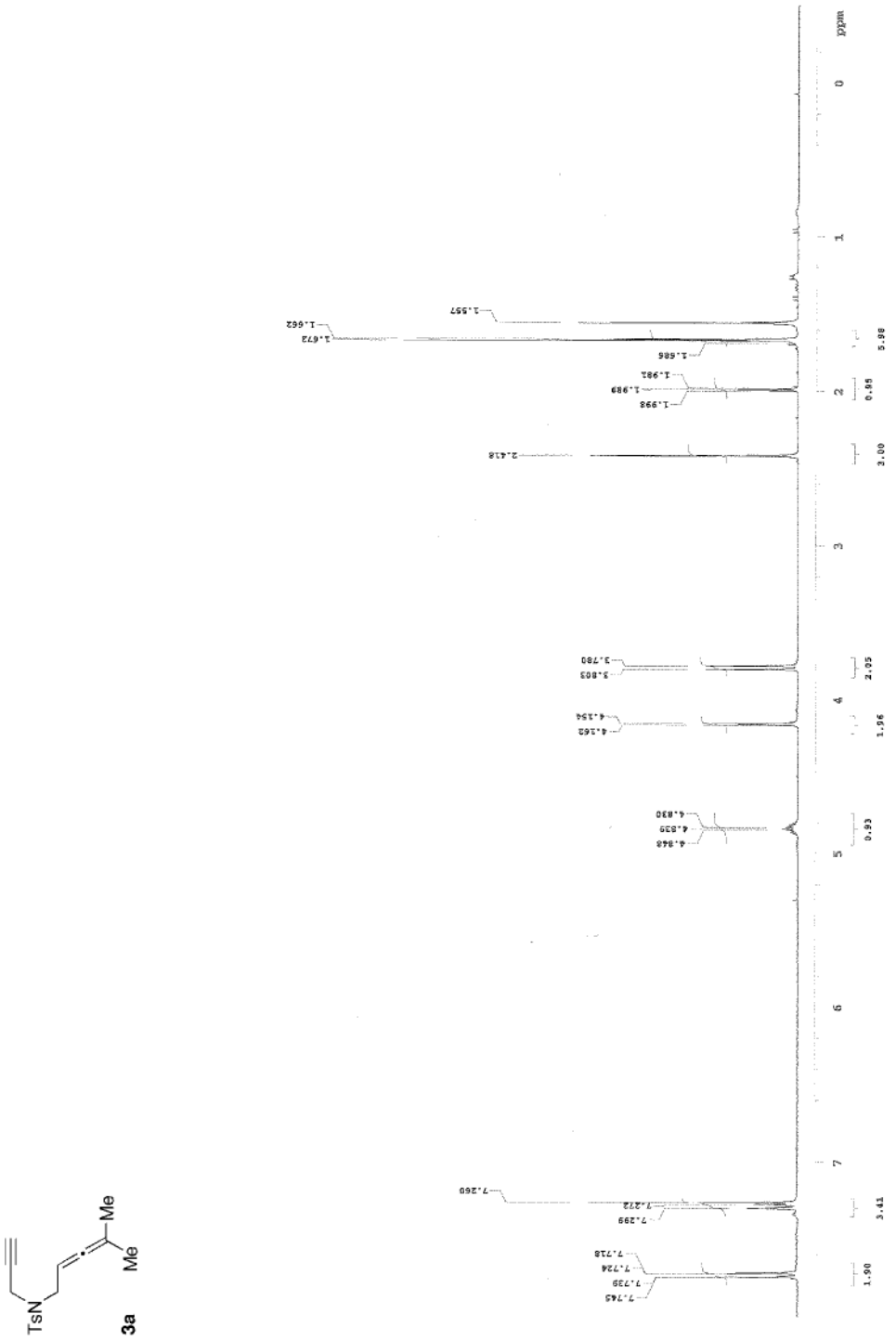
Diels–Alder Reaction of Vinylallene 4c and Maleic Anhydride[3]

To a stirred solution of vinylallene **4c** (23.5 mg, 0.093 mmol) in dry toluene (0.30 mL) at room temperature was added maleic anhydride (18.2 mg, 0.186 mmol). After 4 days, the solvent was removed, and the residue was purified by preparative thin-layer chromatography (hexane:AcOEt = 1:1) to give the Diels–Alder adduct **6** (22.5 mg, 70%).

(3) (a) Regás, D.; Afonso, M. M.; Rodríguez, M. L; Palenzuela, J. A. *J. Org. Chem.* **2003**, *68*, 7845. (b) Bentz, D.; Laschat, S. *Synthesis*, **2000**, 1766.



Dimethyl 4-isopropylidene-1,3-dioxo-1,3,3a,4,6,8,8a,8b-octahydroindeno[4,5-*c*]furan-7,7-dicarboxylate (6). White solid; 145-146 °C; ^{1}H NMR δ 1.81 (s, 3H), 1.99 (s, 3H), 2.69 (dd, J = 11.0, 7.5 Hz, 1H), 2.76 (m, 1H), 2.89 (dd, J = 11.0, 10.5 Hz, 1H), 3.05 (s, 2H), 3.62 (dd, J = 9.2, 5.8 Hz, 1H), 4.22 (d, J = 5.8 Hz, 1H), 6.32 (s, 1H); ^{13}C NMR δ 21.6, 21.9, 34.9, 37.3, 38.8, 44.2, 44.6, 52.93, 52.95, 59.7, 119.3, 119.8, 134.9, 141.4, 170.5, 170.9, 171.4, 171.9; HRMS (EI) calcd for $C_{18}H_{20}O_7$ (M^+) 348.1209, found 348.1208.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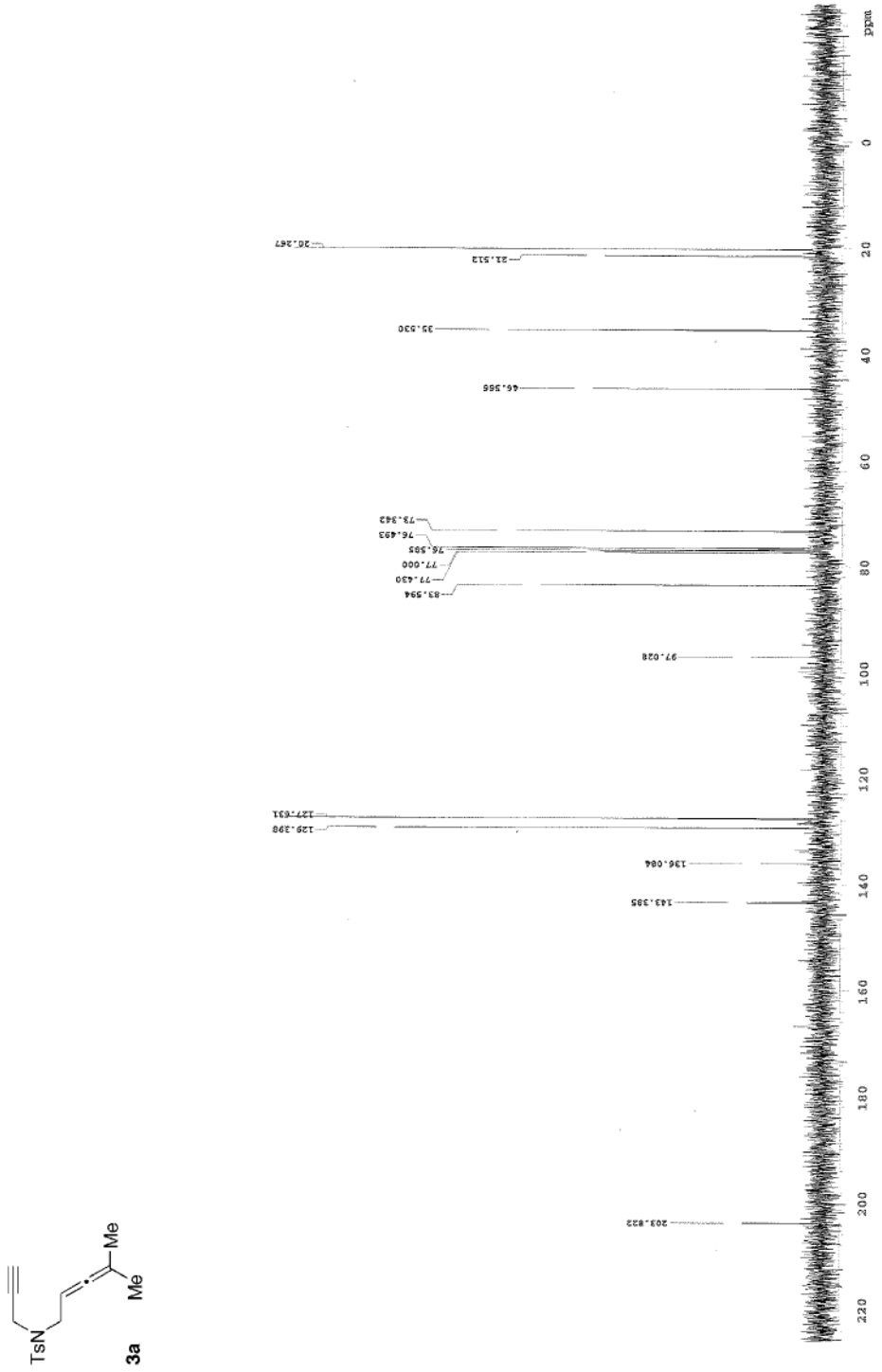
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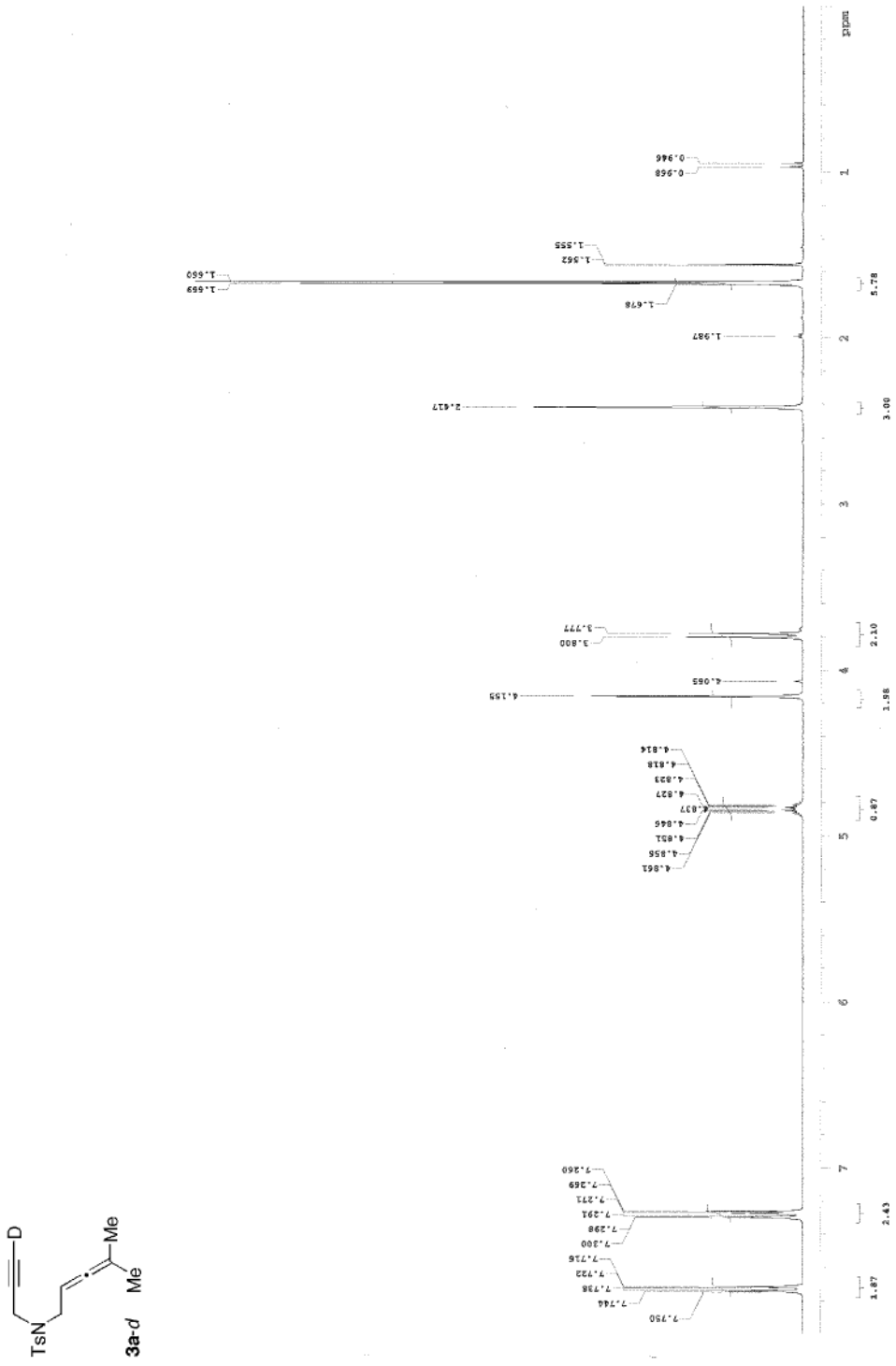
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7.298
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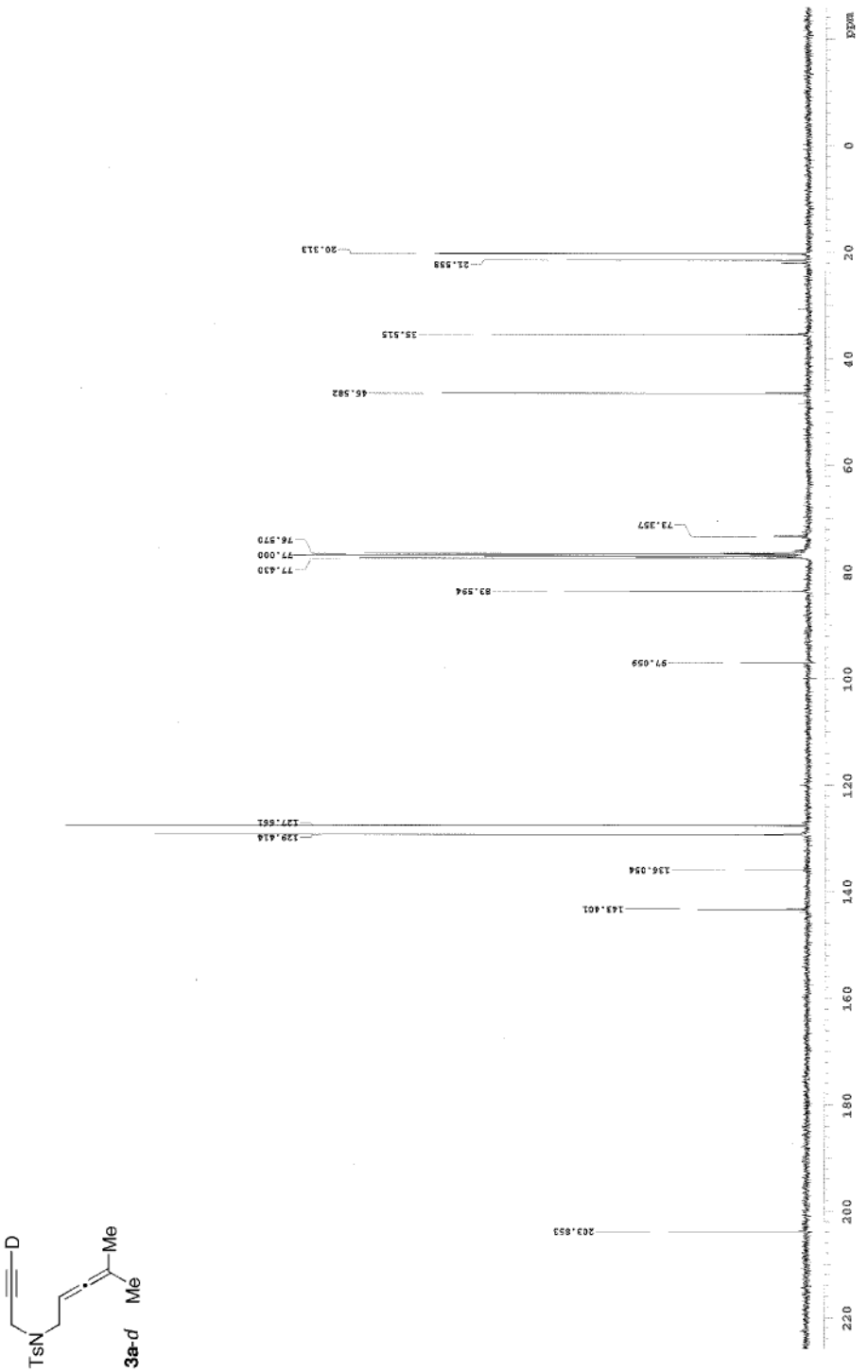
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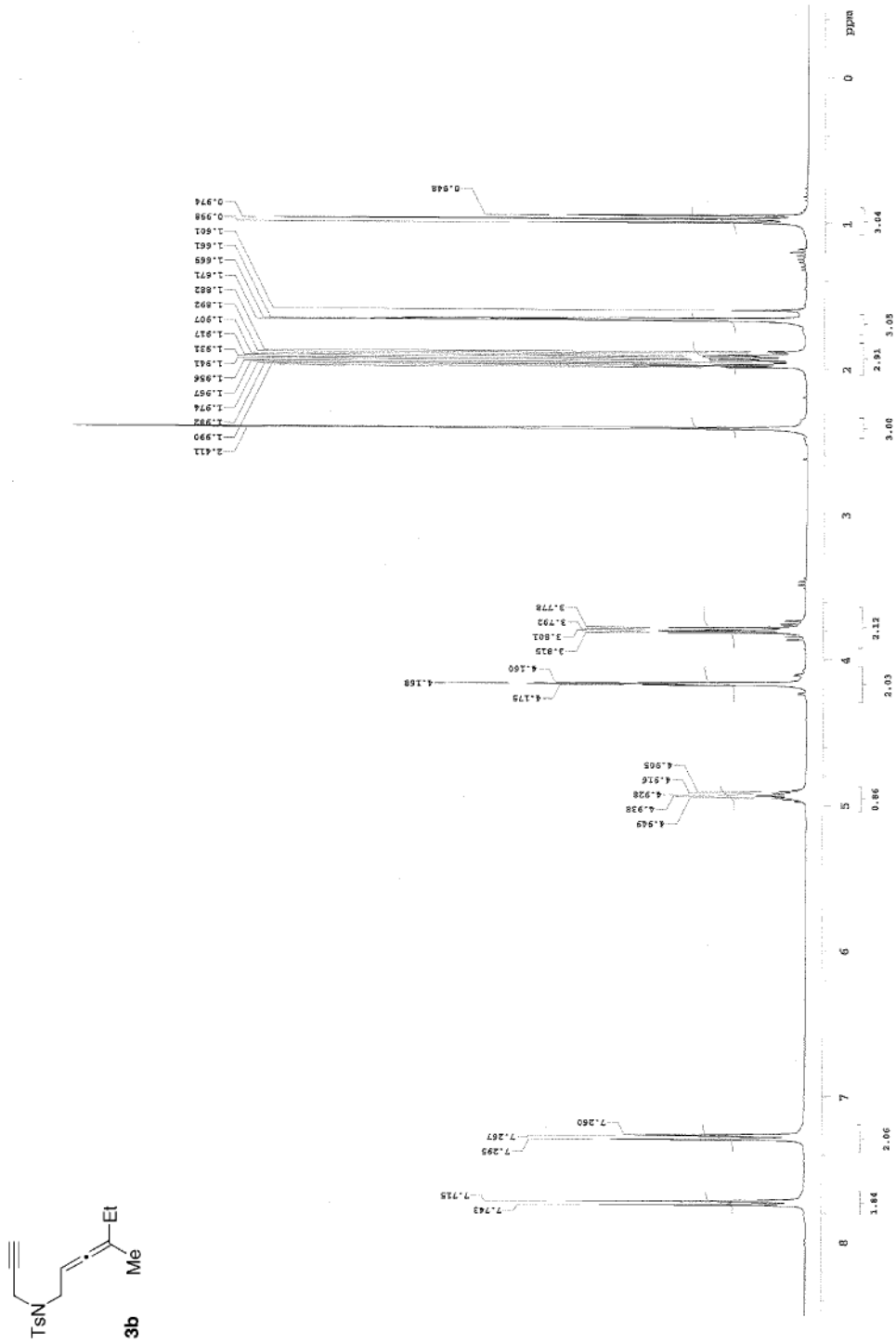
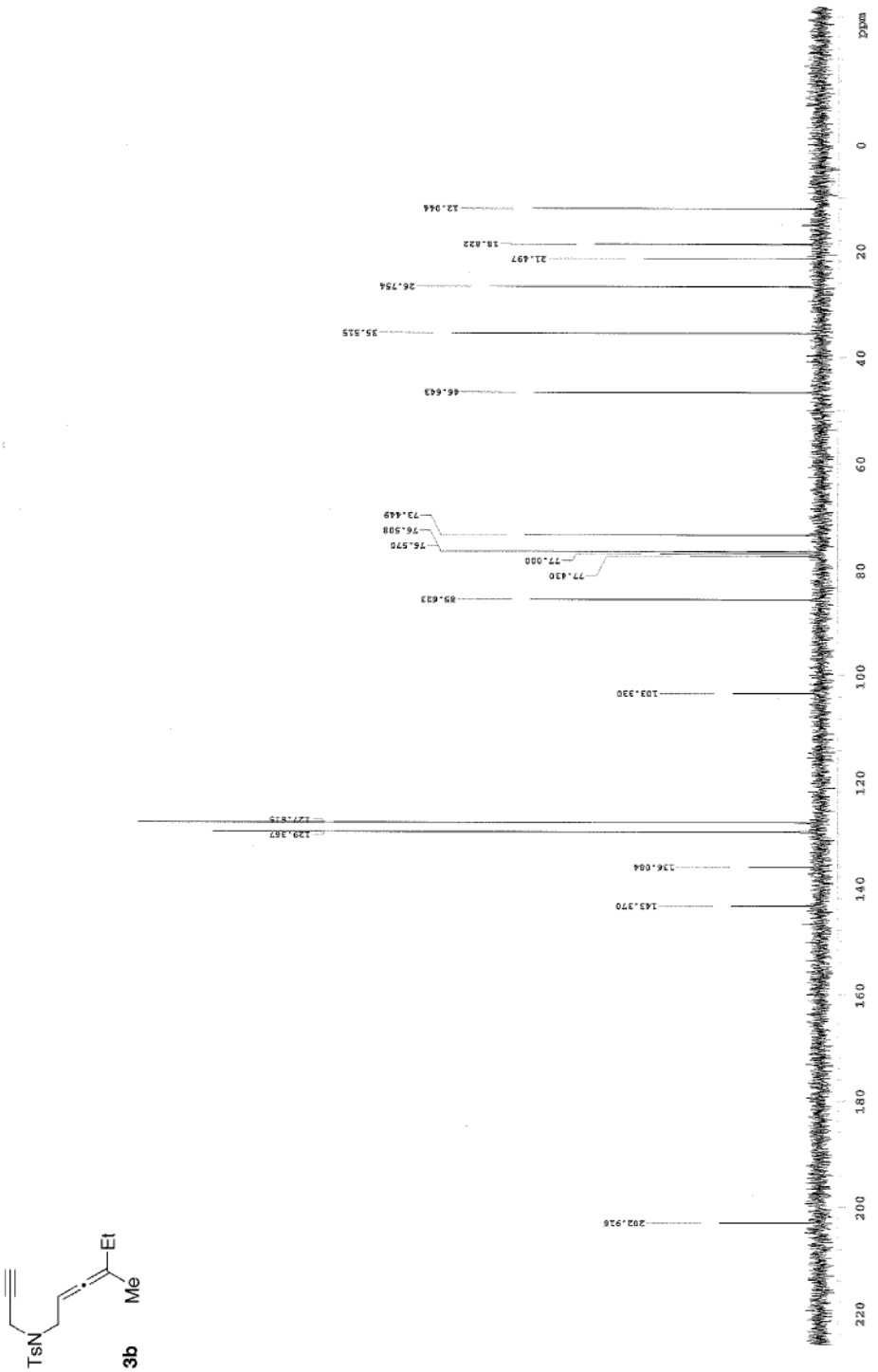

TsN
Et
Me
3b


ppm
0
20
40
60
80
100
120
140
160
180
200
220
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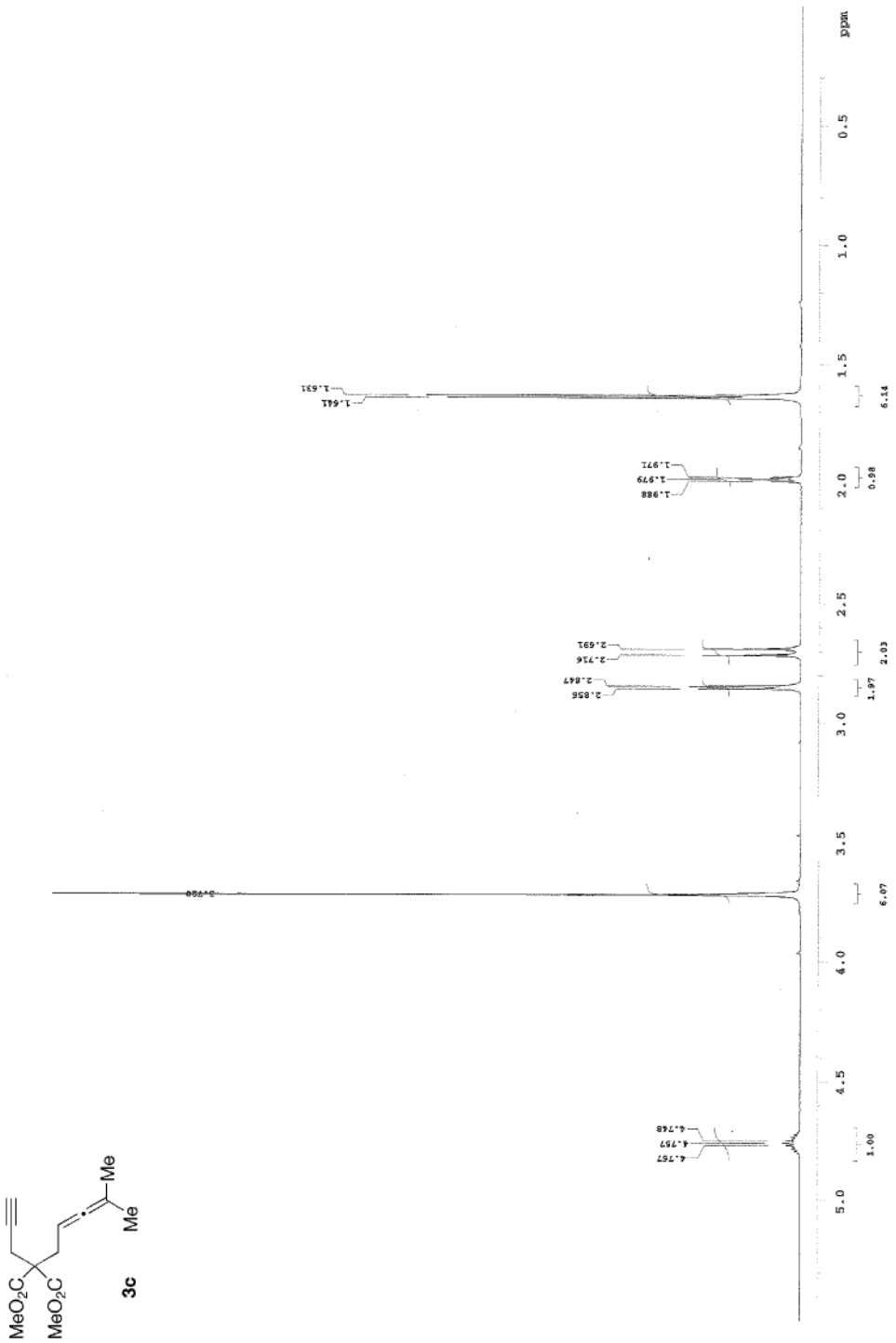
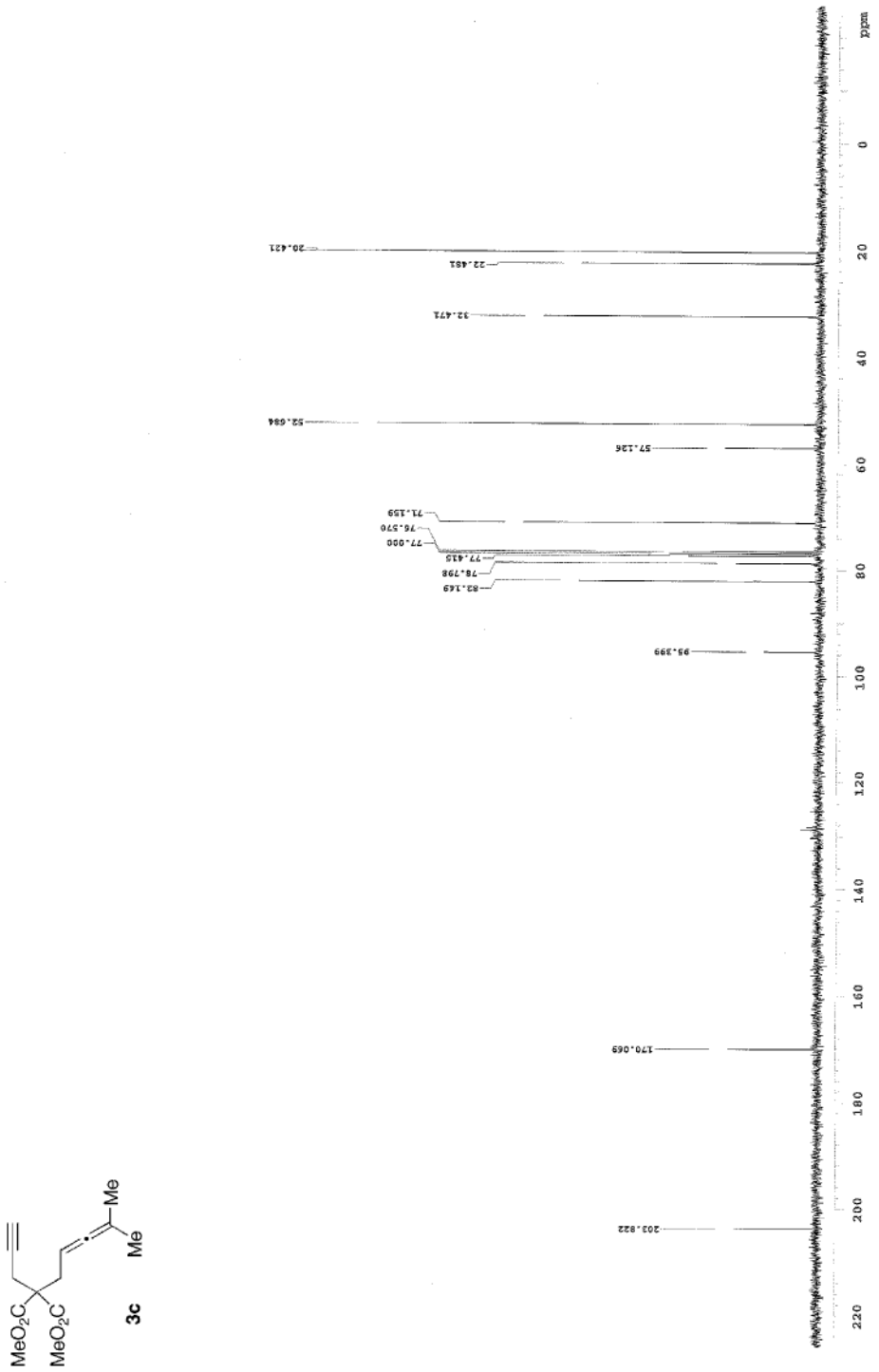
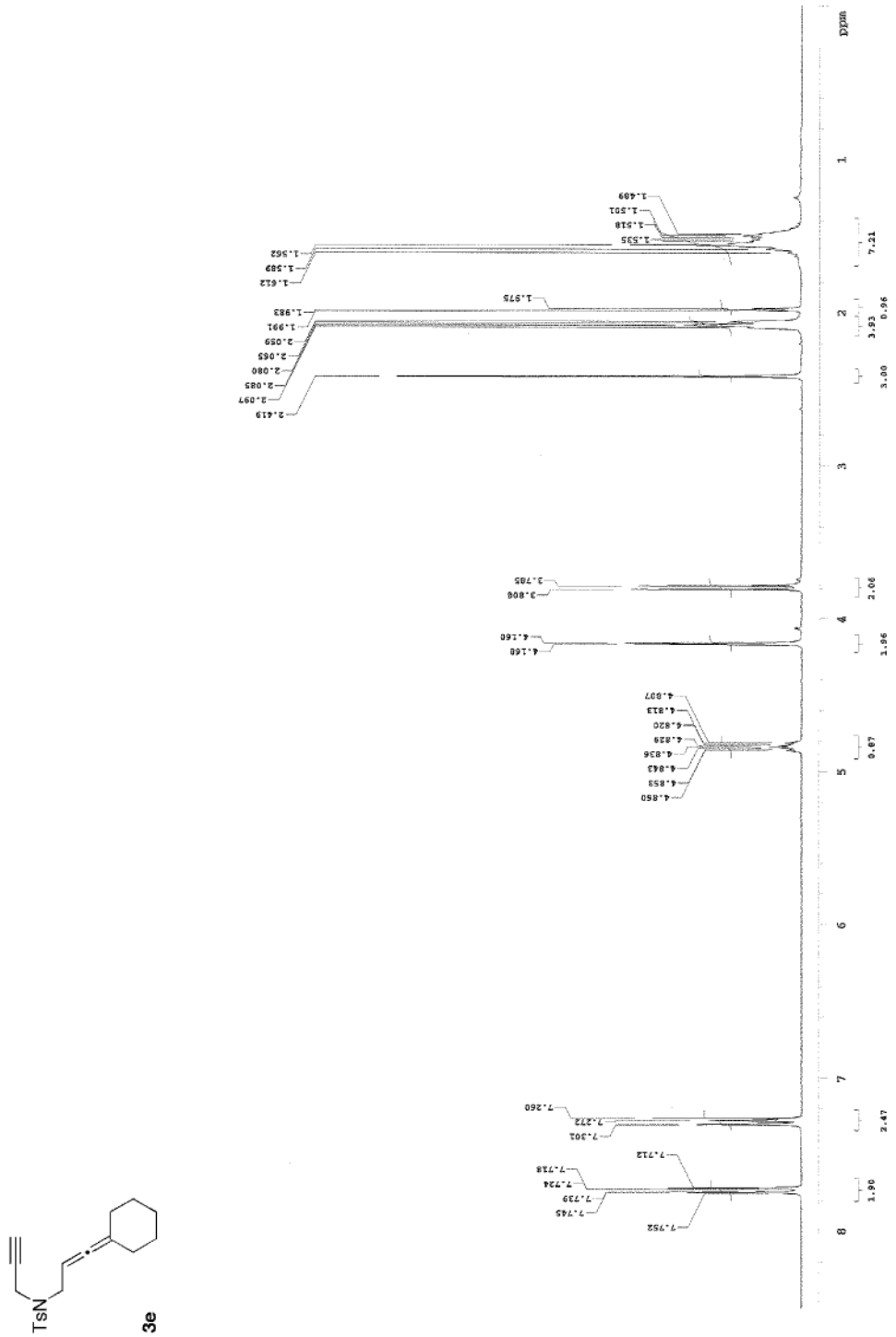
18.822
21.497
26.754
35.515
46.643
73.449
76.508
76.570
77.000
77.430
85.633
103.330
127.815
129.387
136.084
143.370
202.926
TsN
Et
Me
3b


MeO2C
MeO2C
Me
Me
3c
ppm


MeO2C
MeO2C
Me
Me
3c
203.822
170.069
95.399
82.149
78.798
77.415
77.000
76.570
71.159
57.136
52.684
32.474
22.482
20.421
ppm


TsN
3e
ppm
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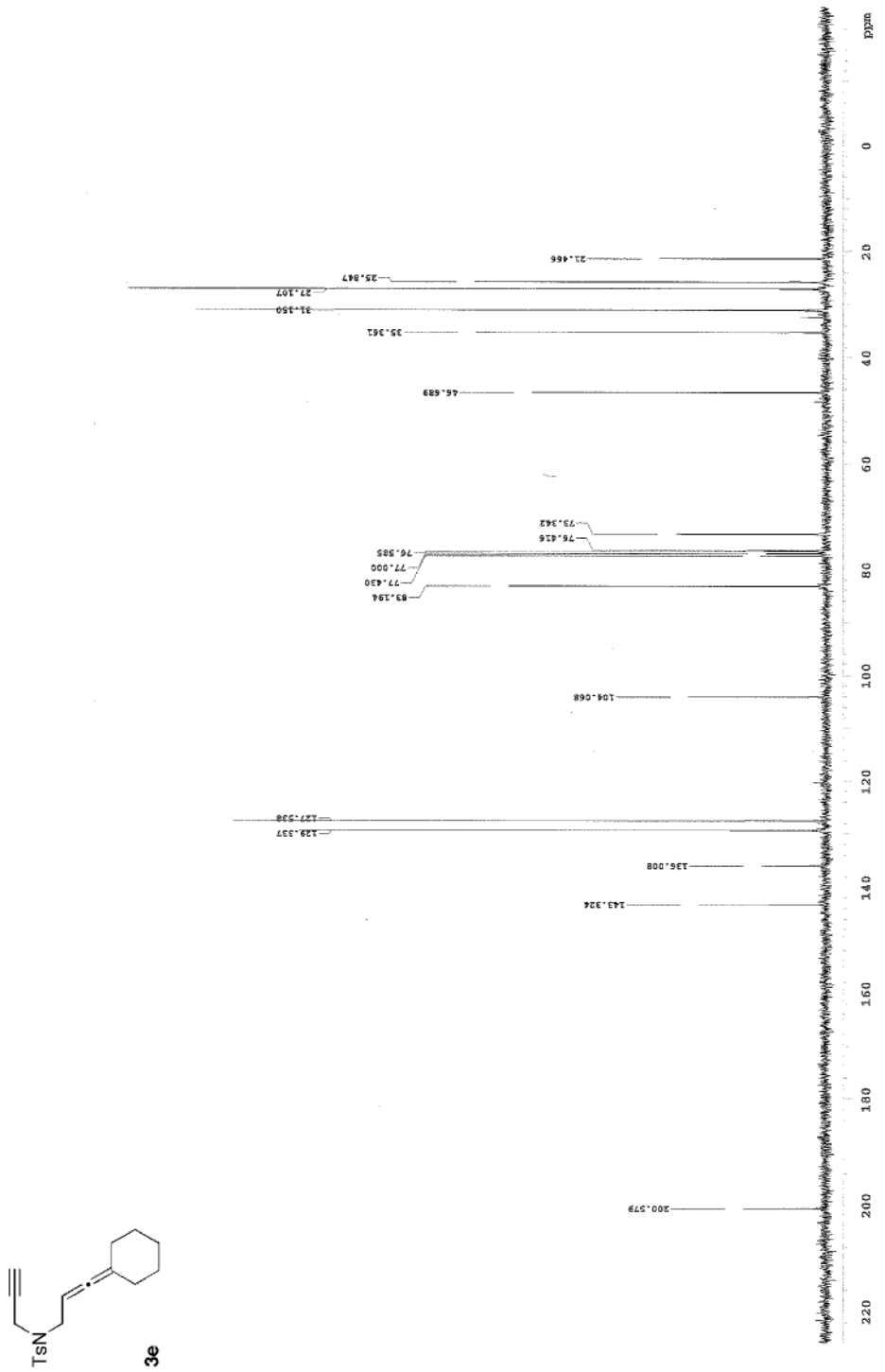
1.518
1.535
1.562
1.589
1.612
1.975
1.983
1.991
2.059
2.065
2.080
2.083
2.097
2.419
3.705
3.808
4.160
4.168
4.807
4.813
4.820
4.829
4.836
4.843
4.850
7.260
7.272
7.301
7.712
7.738
7.734
7.739
7.745
7.752
7.21
3.93
0.96
3.00
2.06
1.96
0.67
2.47
1.90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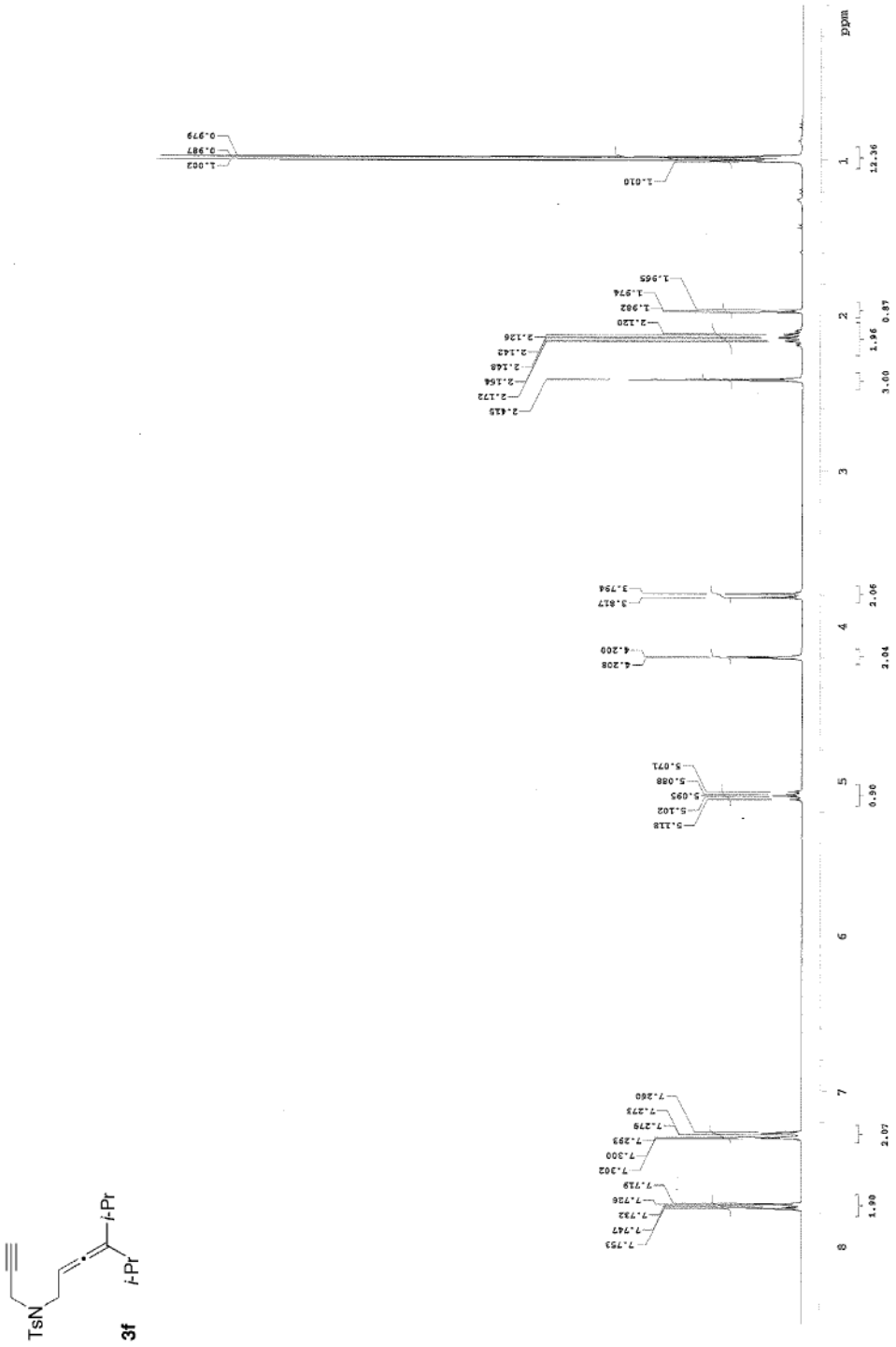
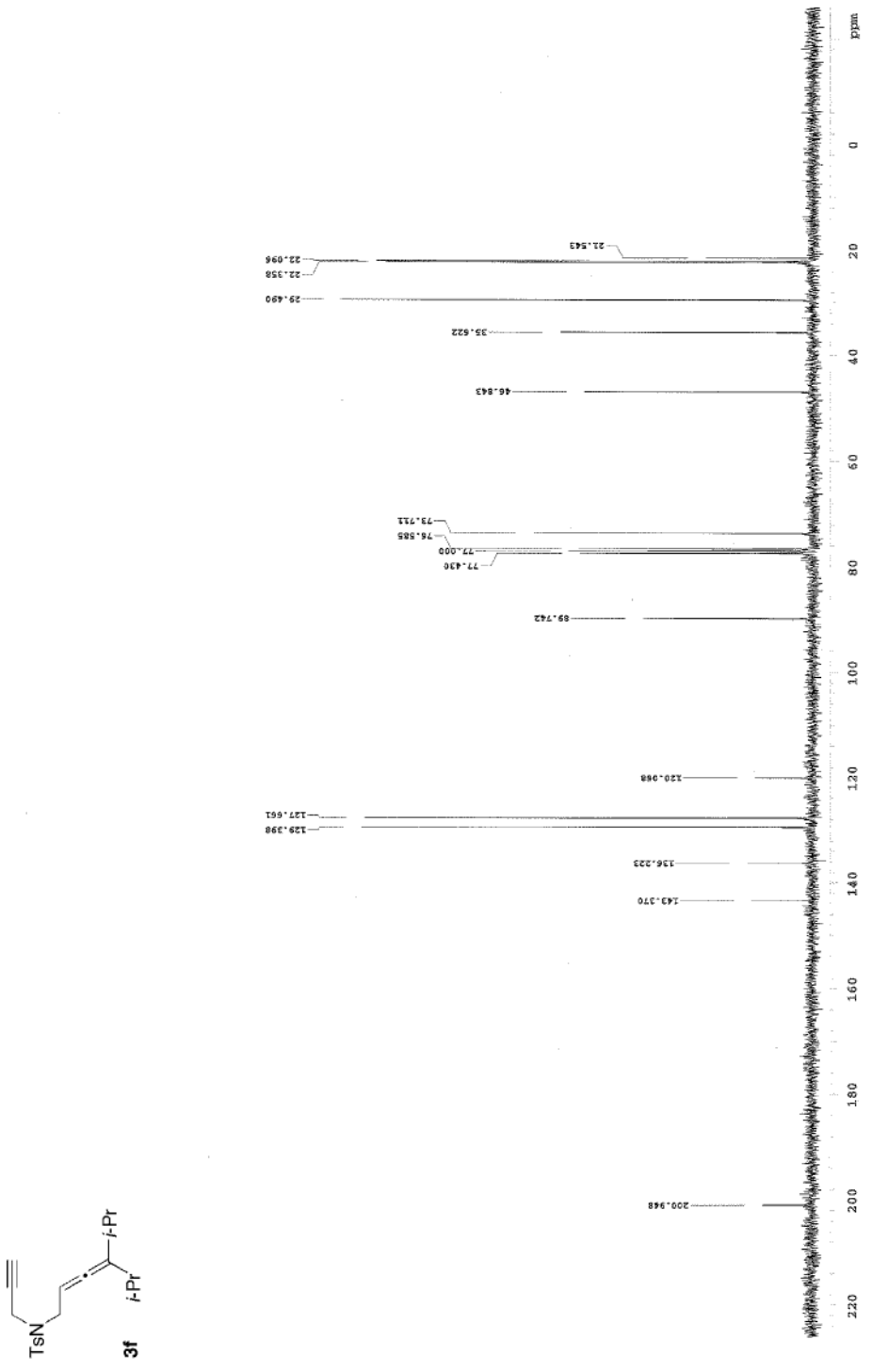
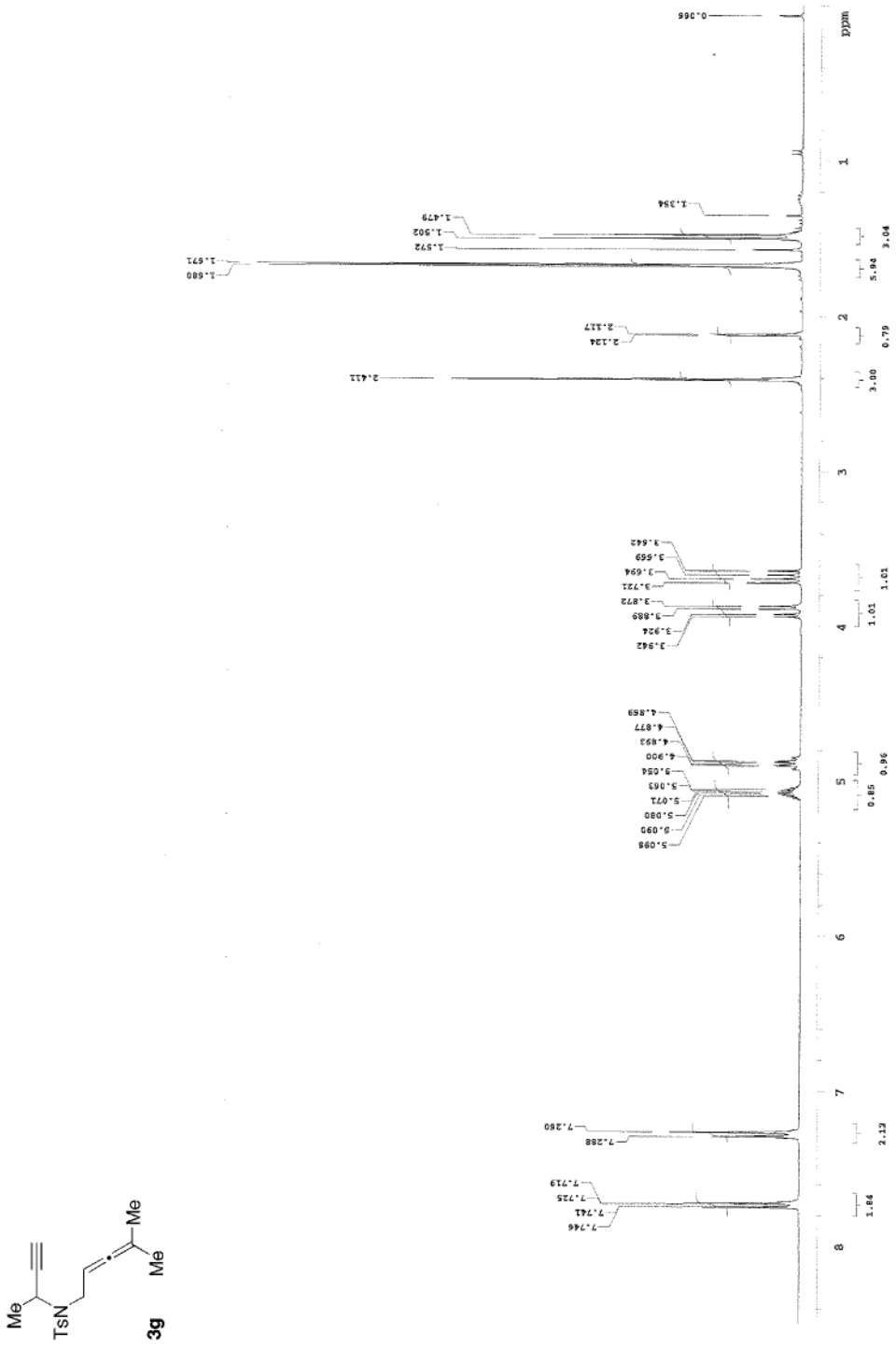
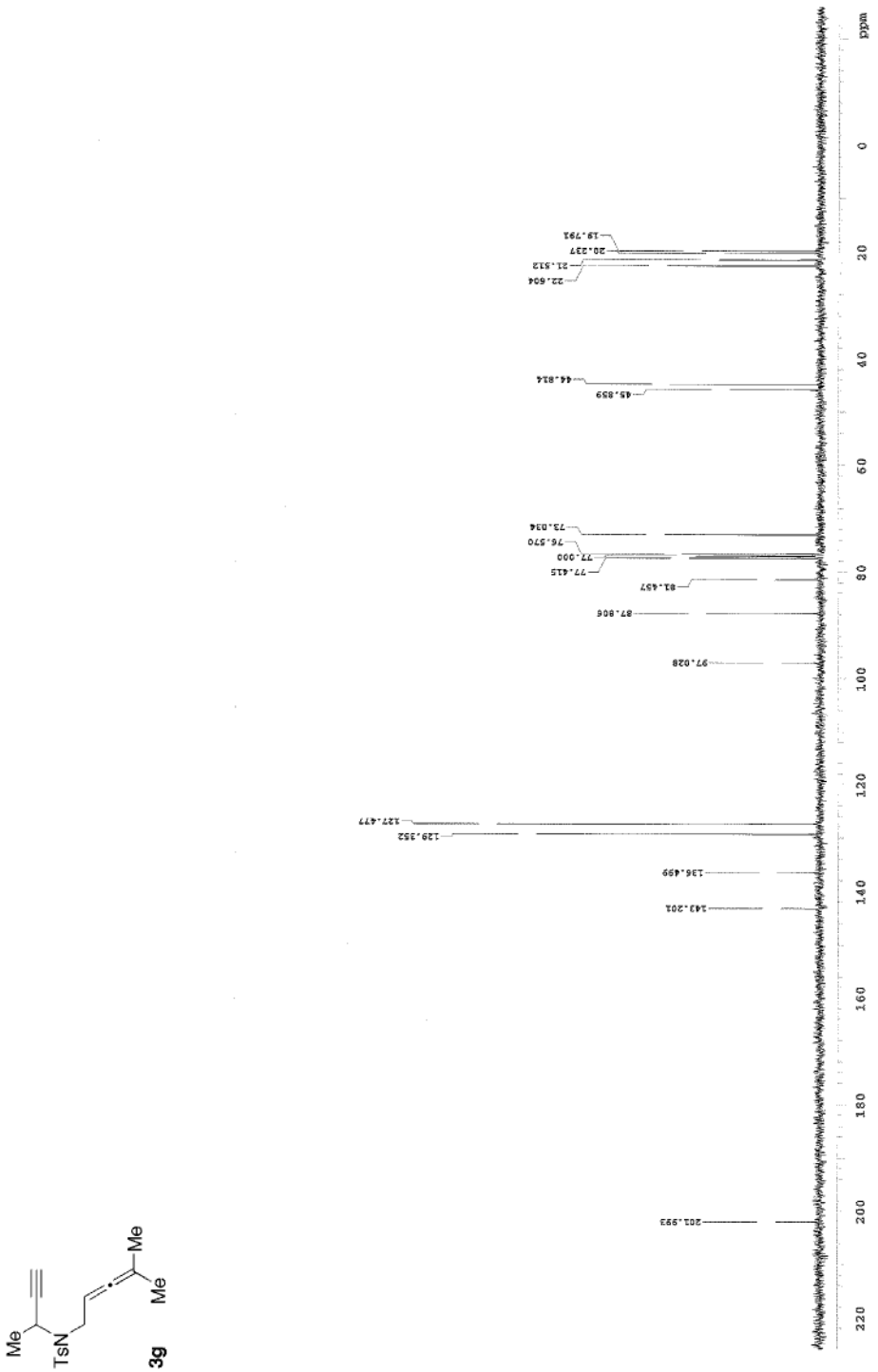
27.107
31.150
35.361
46.689
73.342
76.416
76.585
77.000
77.430
83.194
104.068
127.538
129.337
136.008
143.324
200.579
ppm
0
20
40
60
80
100
120
140
160
180
200
220
TsN
3e


TsN
i-Pr
i-Pr
3f
ppm


TsN
i-Pr
i-Pr
3f
ppm
0
20
40
60
80
100
120
140
160
180
200
220
21.543
22.358
23.096
29.490
35.622
46.843
73.721
76.585
77.000
77.436
89.742
120.068
127.651
129.398
136.223
143.370
200.948


Me
TsN
Me
Me
3g


Me
TsN
Me
Me
3g
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143.201
136.499
139.352
127.477
97.028
87.806
81.457
77.415
77.000
76.570
73.034
45.859
44.814
22.604
21.512
20.237
19.791
ppm
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40
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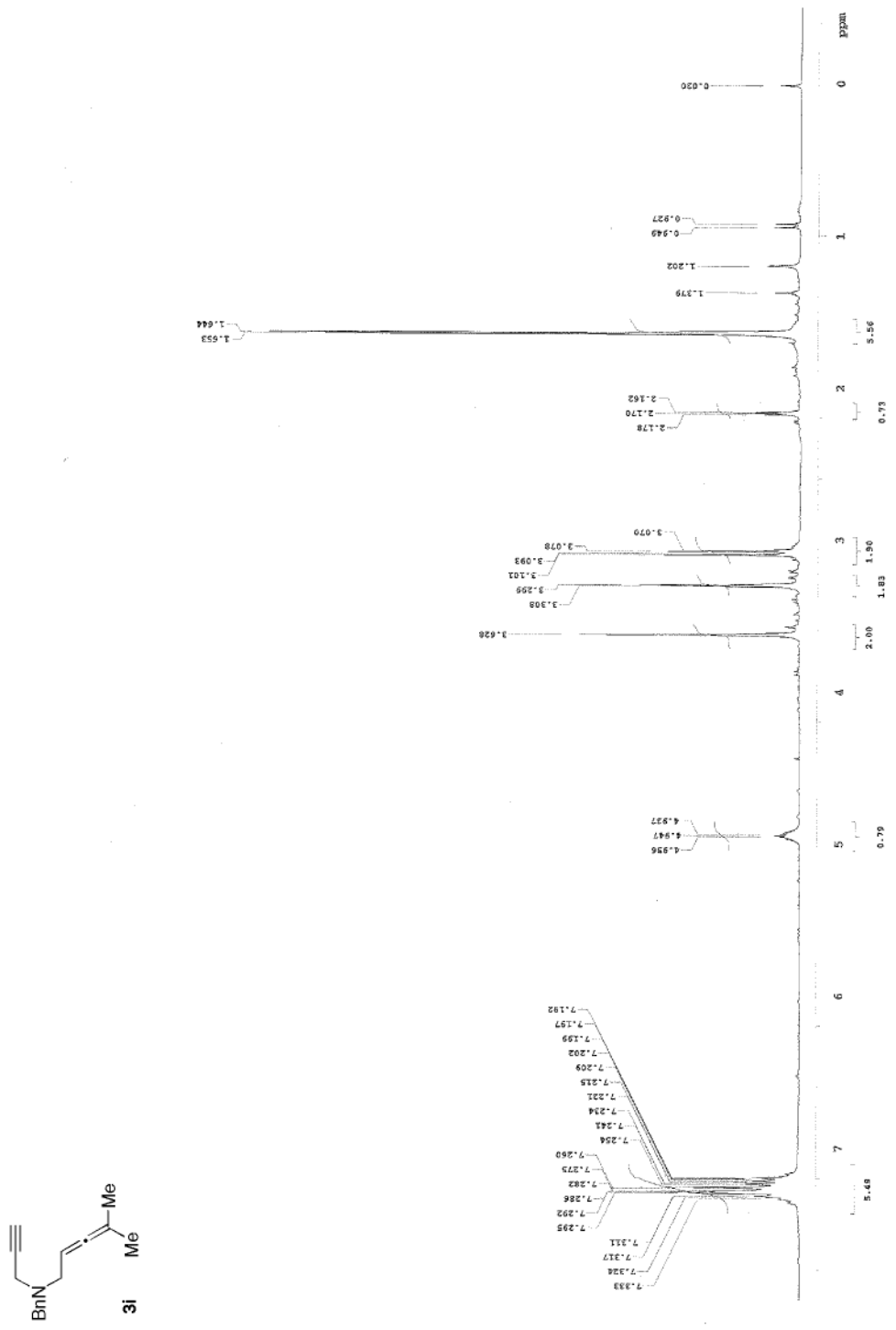
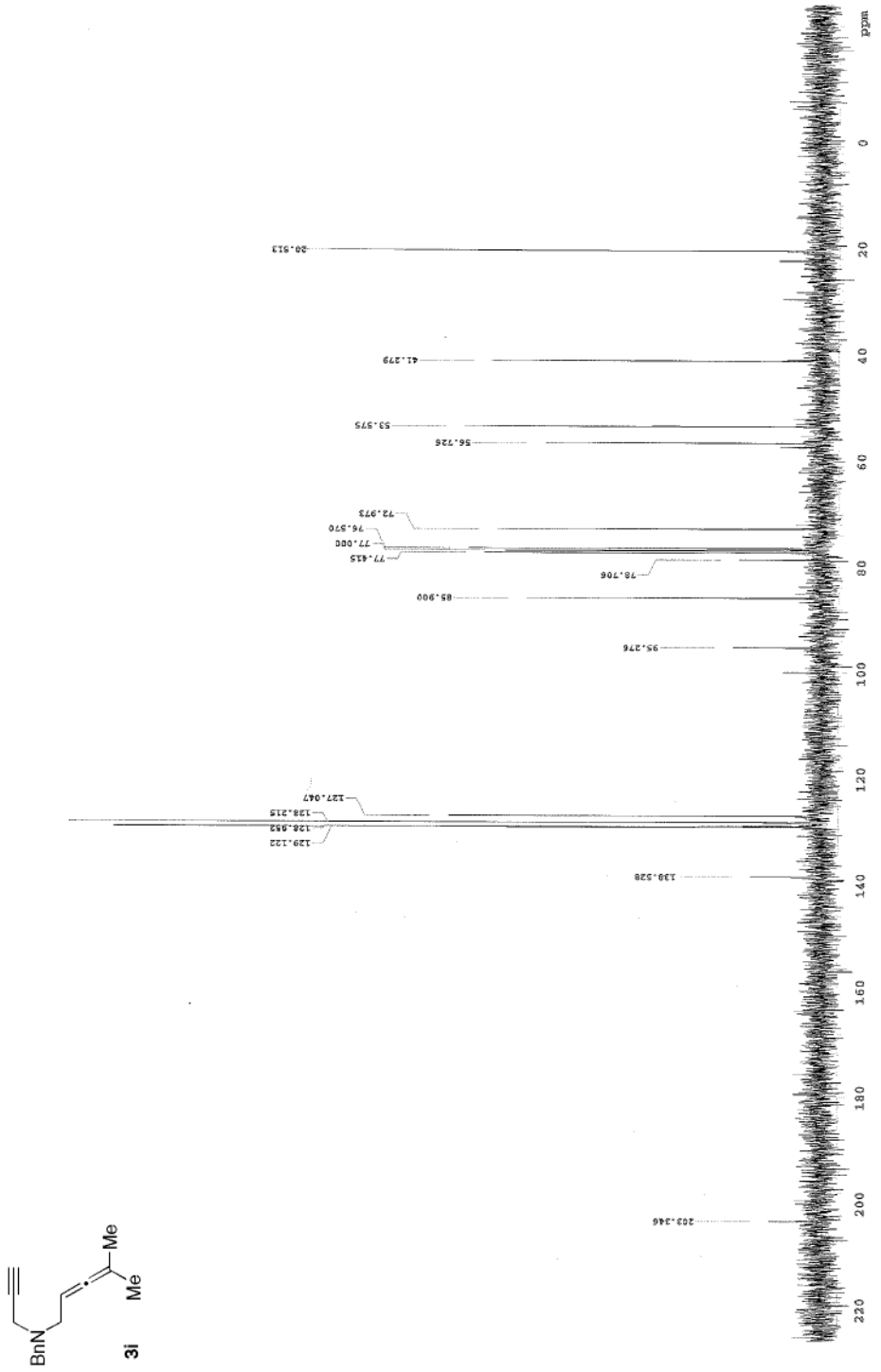
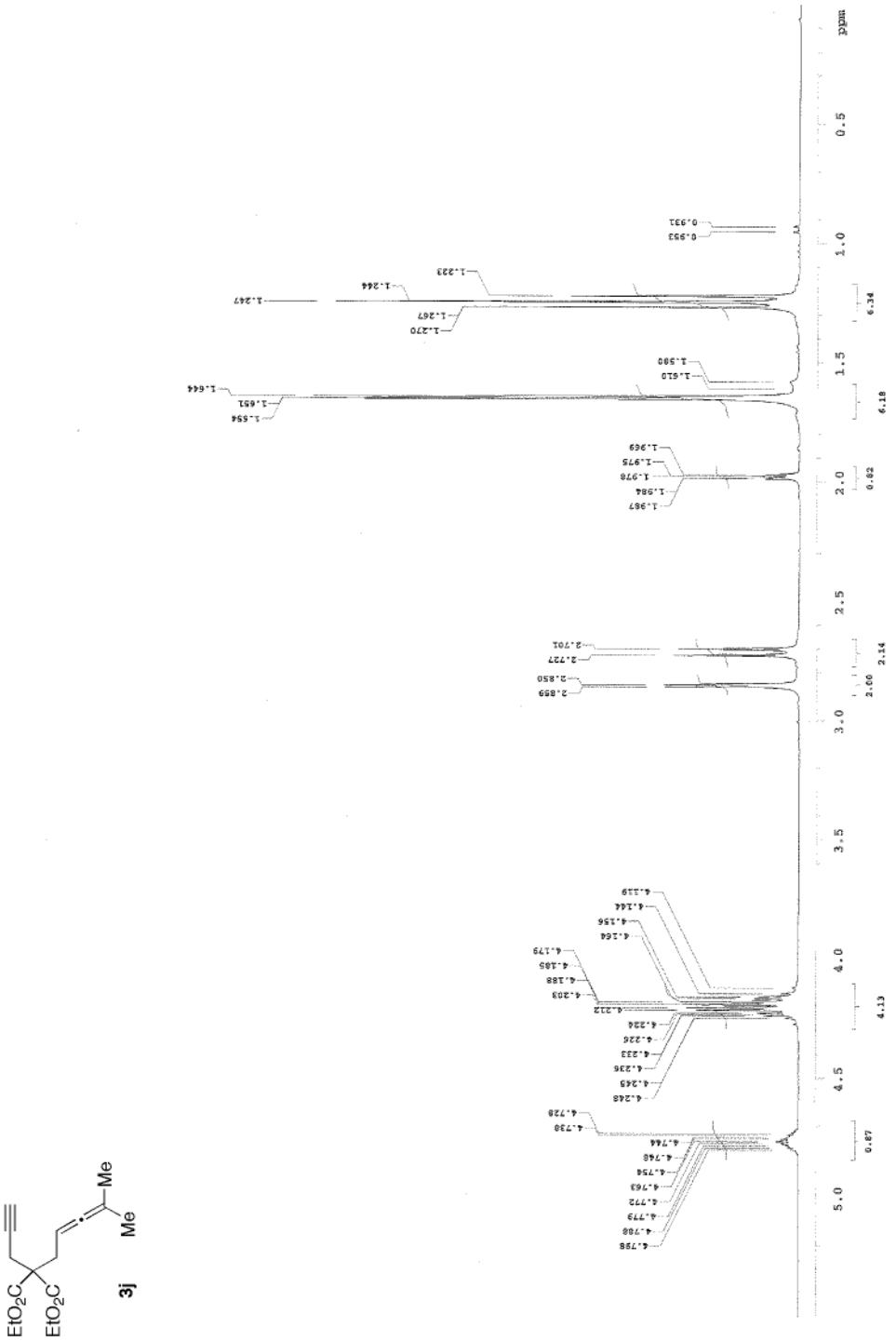
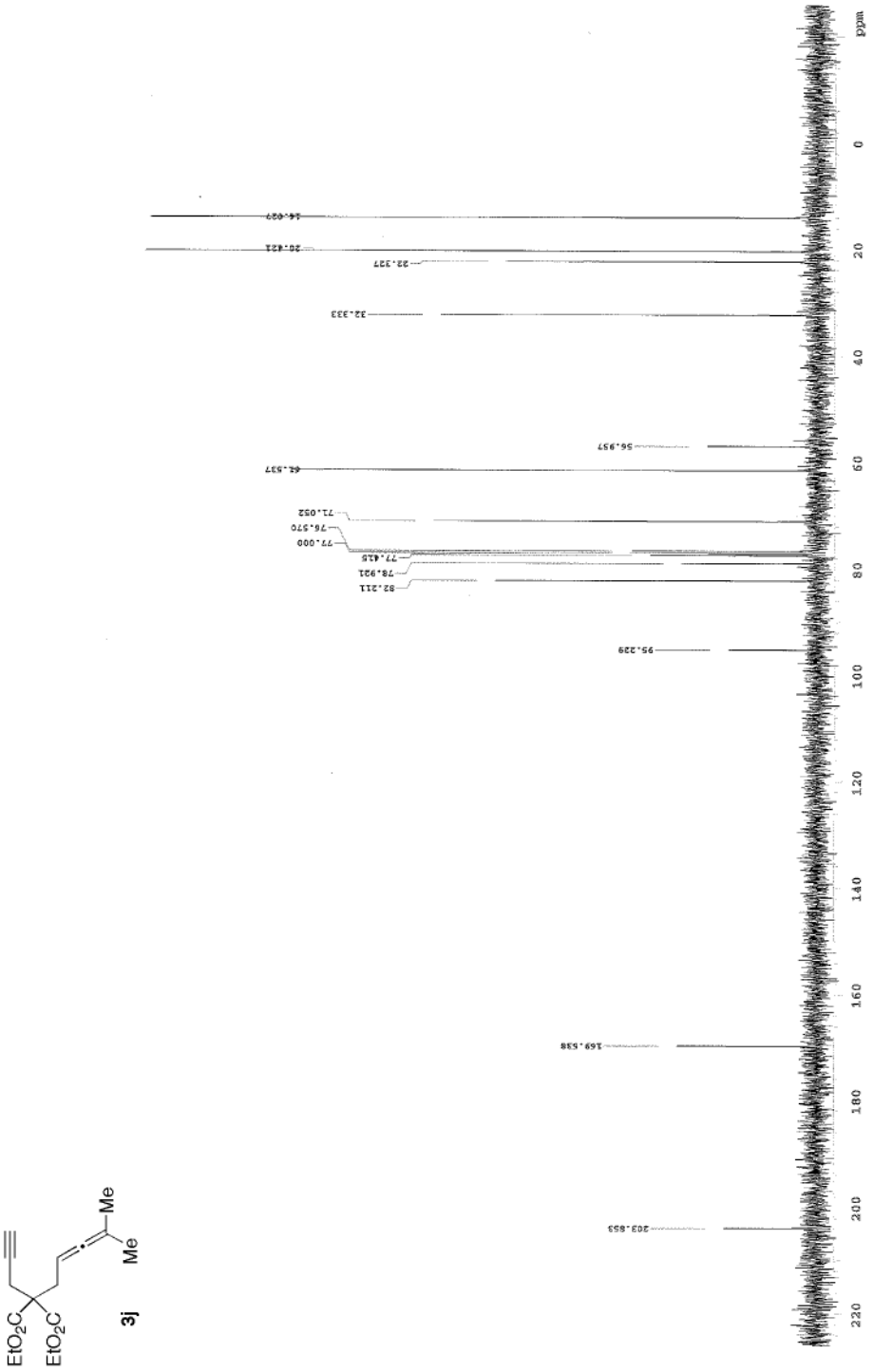
80
100
120
140
160
180
200
220


BnN
Me
Me
3i
ppm


BnN
Me
Me
3i
ppm
0
20
40
60
80
100
120
140
160
180
200
220
20.513
41.279
53.575
56.726
72.973
76.570
77.000
77.415
78.706
85.900
95.376
127.047
128.215
128.952
129.122
138.528
203.346


EtO2C
EtO2C
Me
Me
3j
ppm


EtO2C
EtO2C
Me
Me
3j
ppm
0
20
40
60
80
100
120
140
160
180
200
220
14.027
20.821
23.327
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71.052
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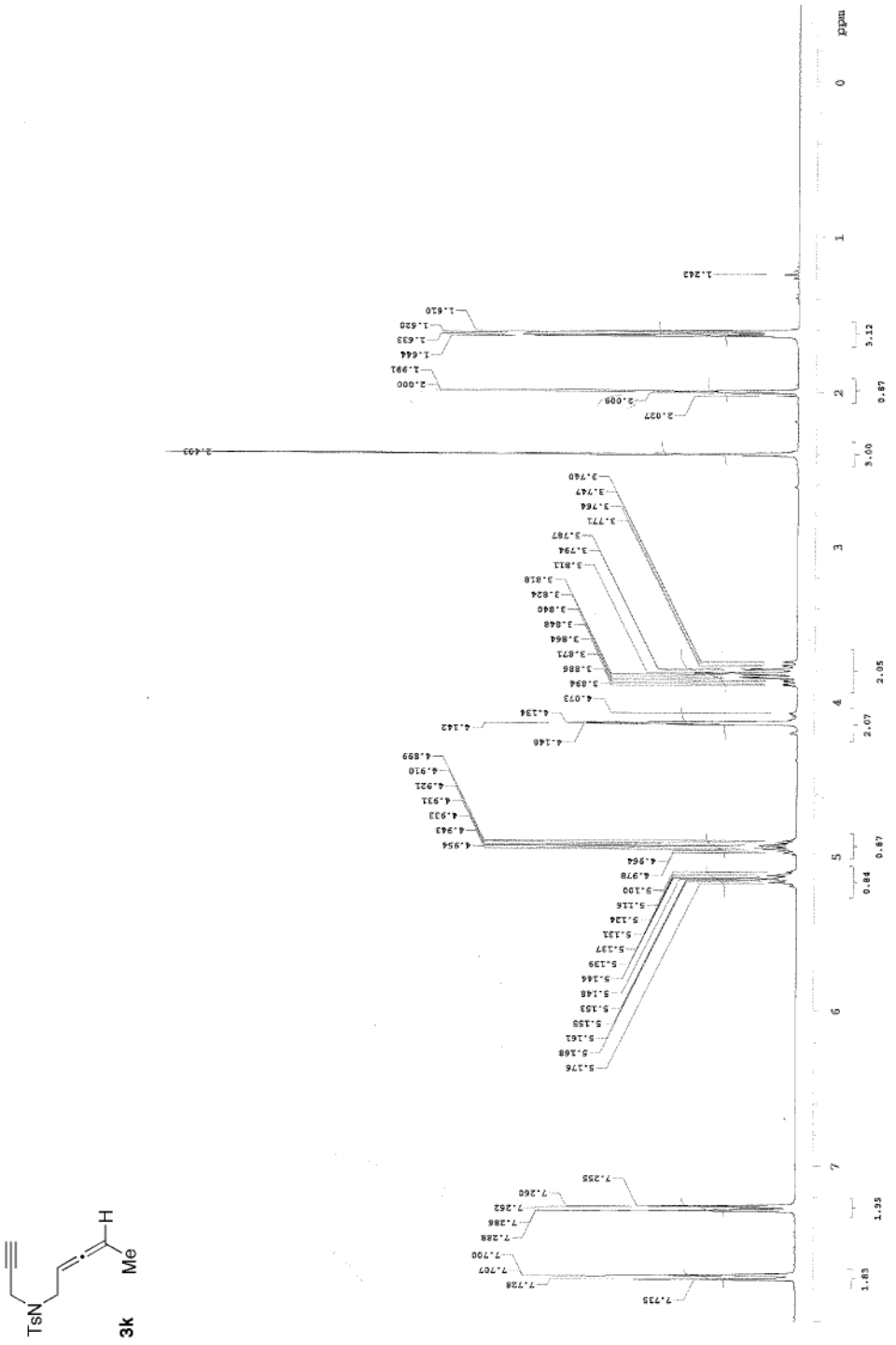
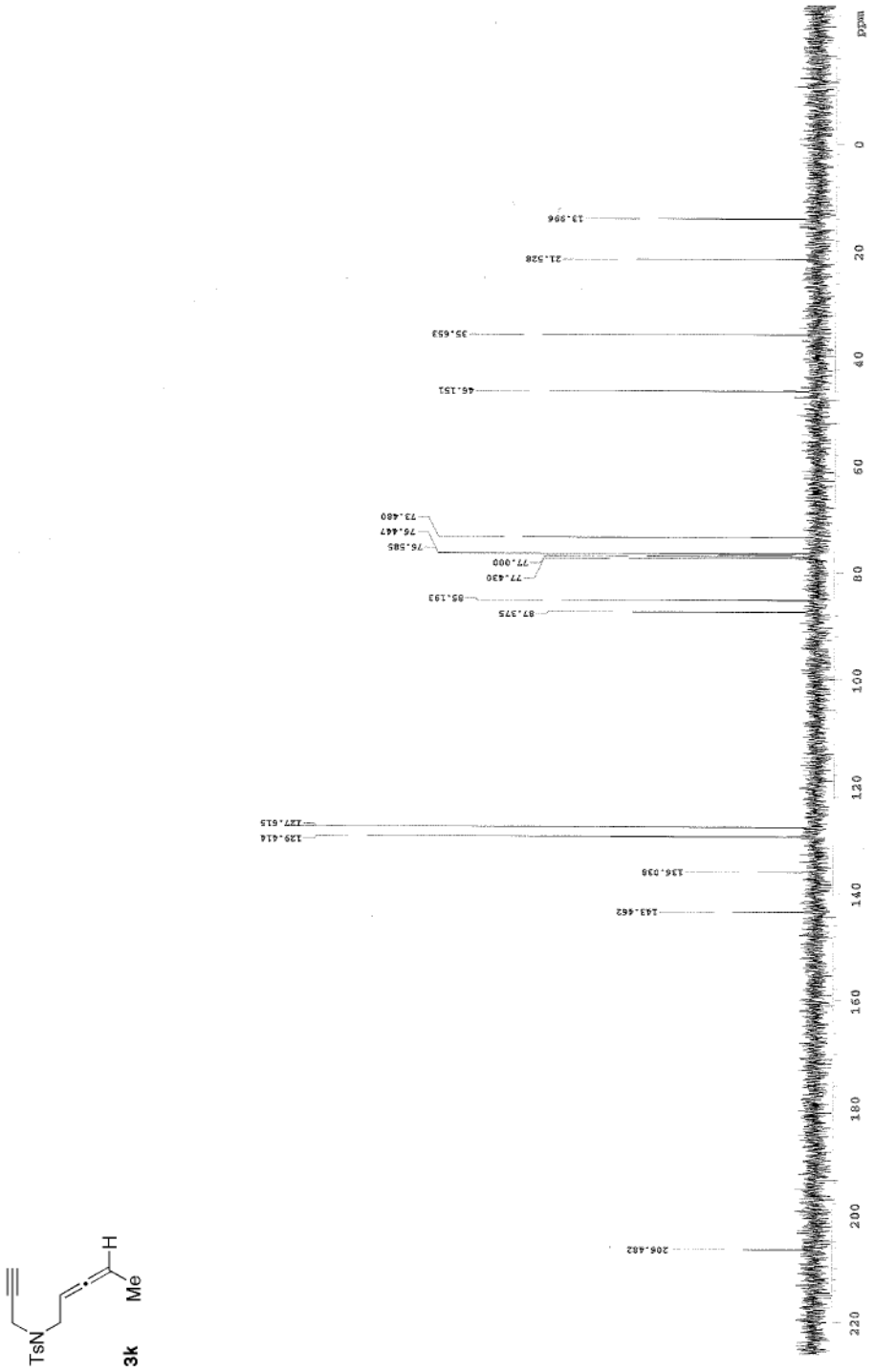
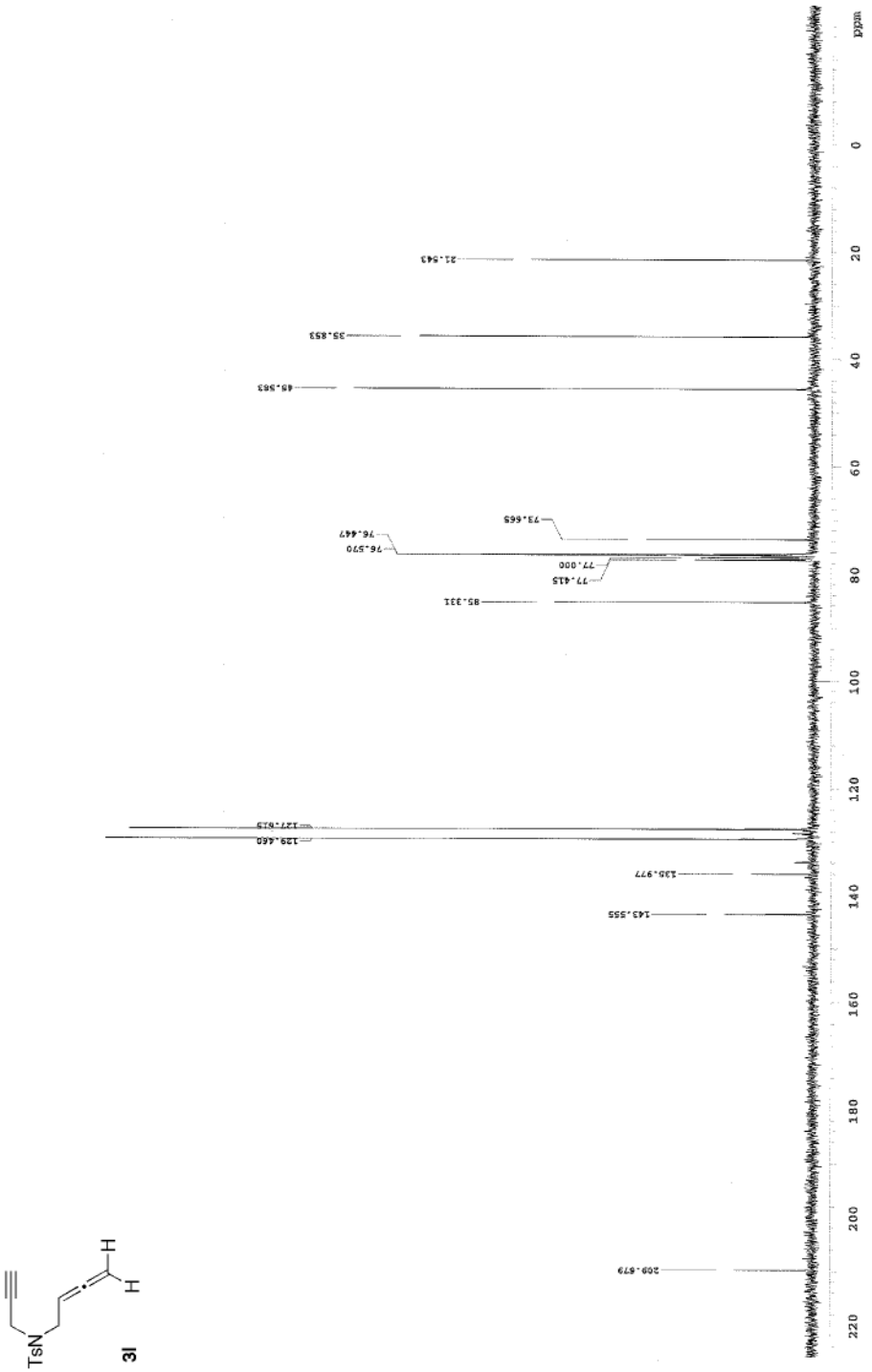
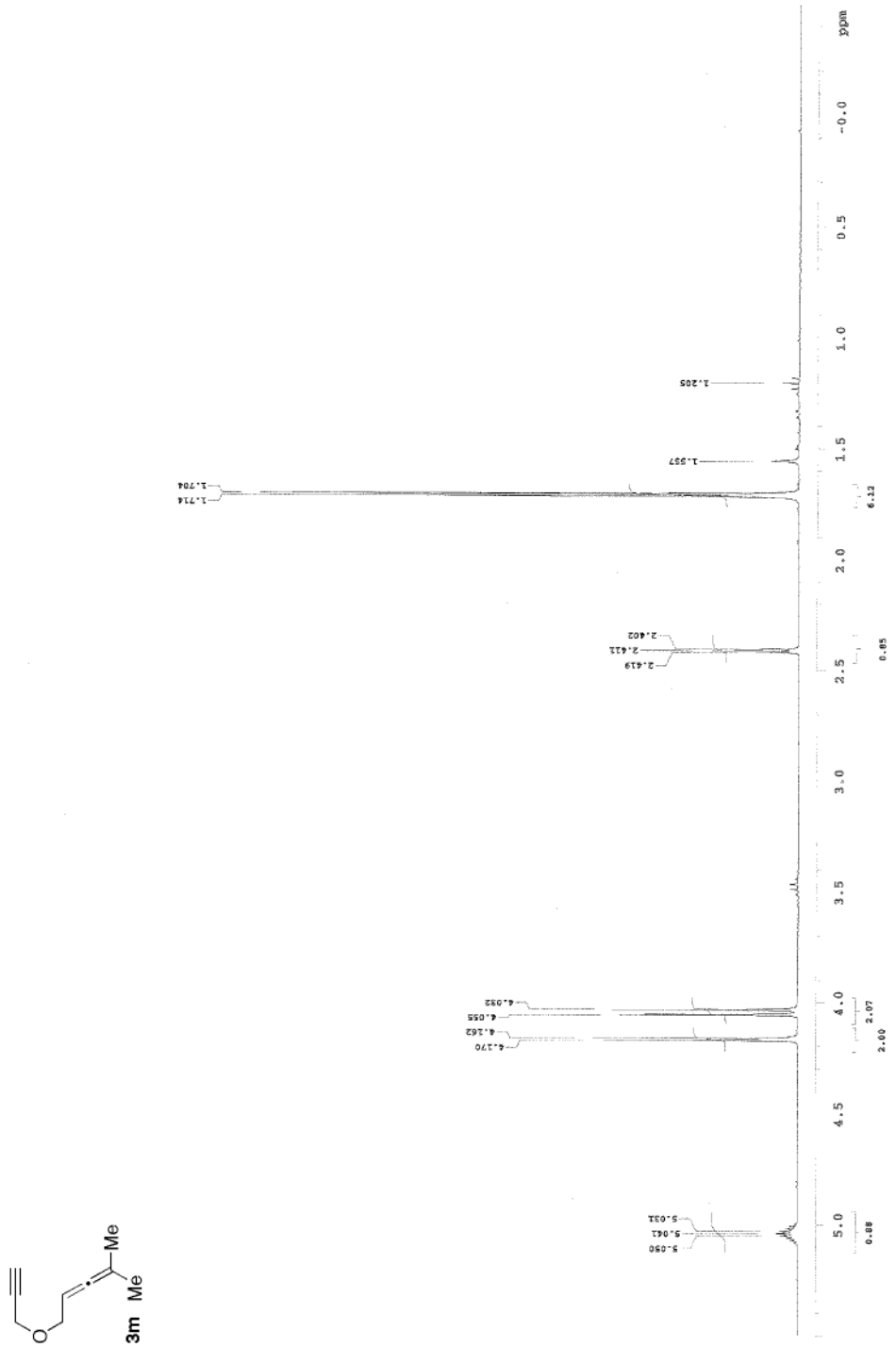
77.000
77.425
78.921
82.211
95.229
169.538
203.853

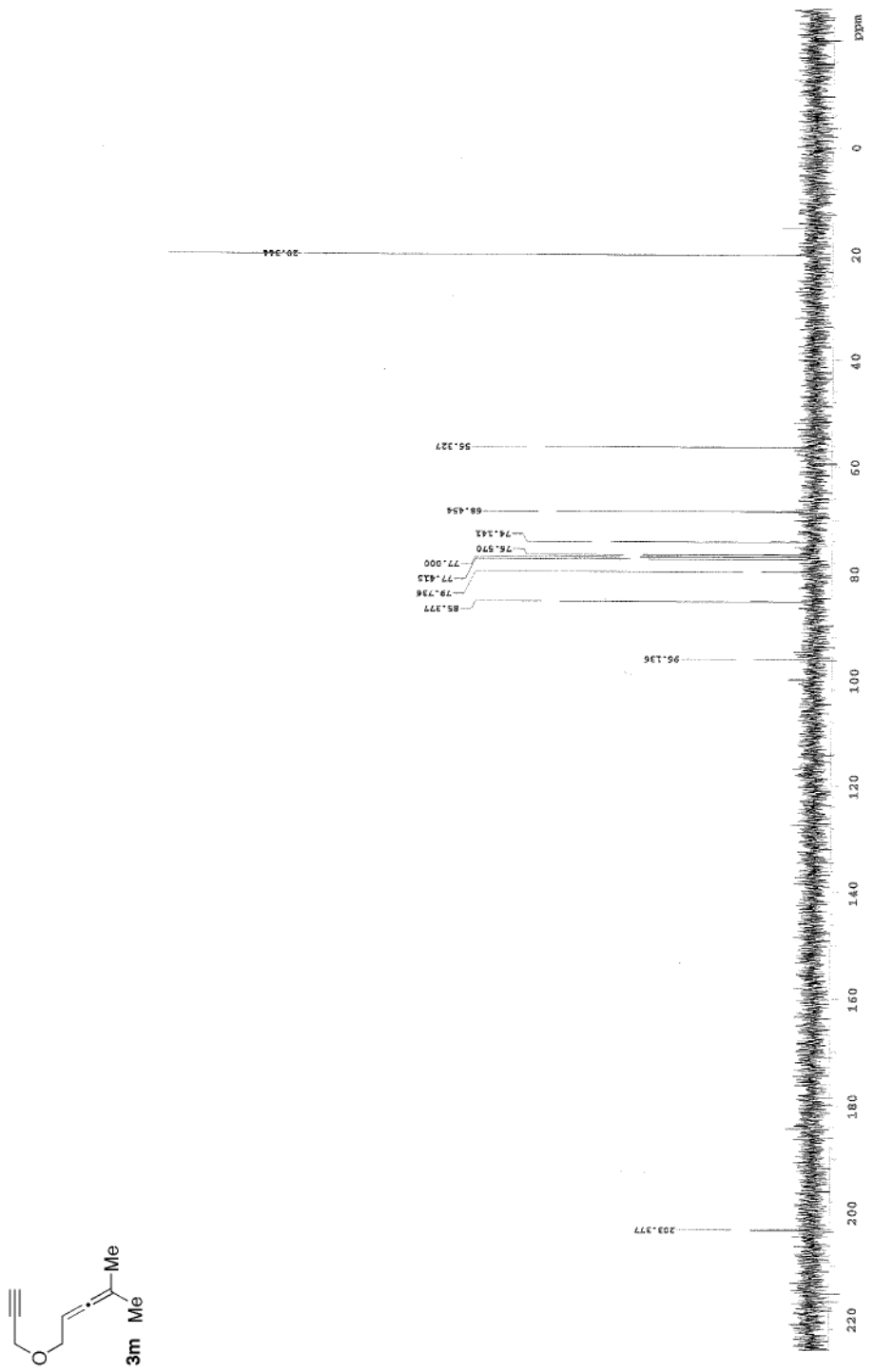

TsN
Me
H
3k

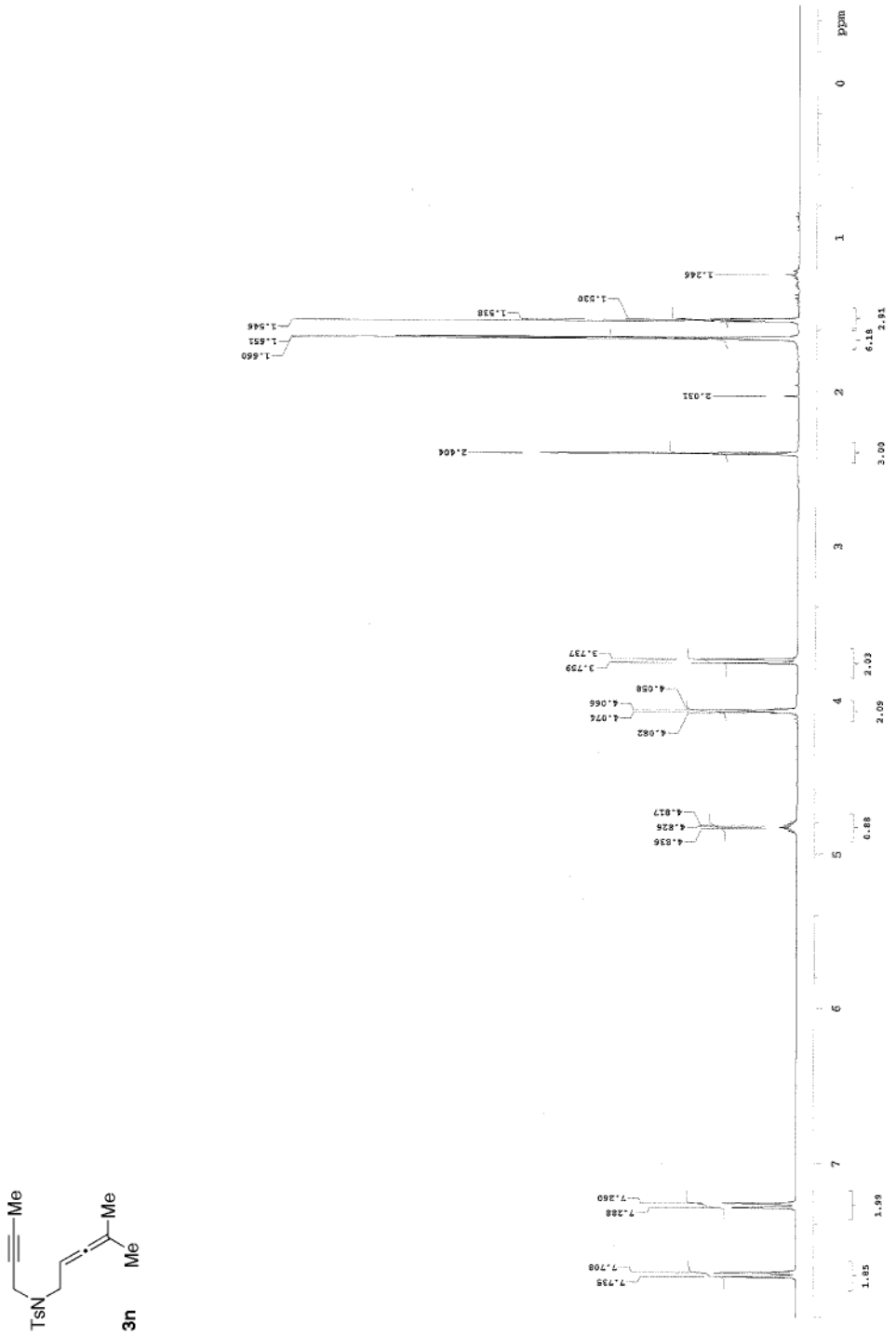

TsN
Me
H
3k
ppm
0
20
40
60
80
100
120
140
160
180
200
220
13.996
21.528
35.653
45.151
73.480
76.447
76.585
77.000
77.430
85.193
87.375
127.615
129.414
136.038
143.462
206.482

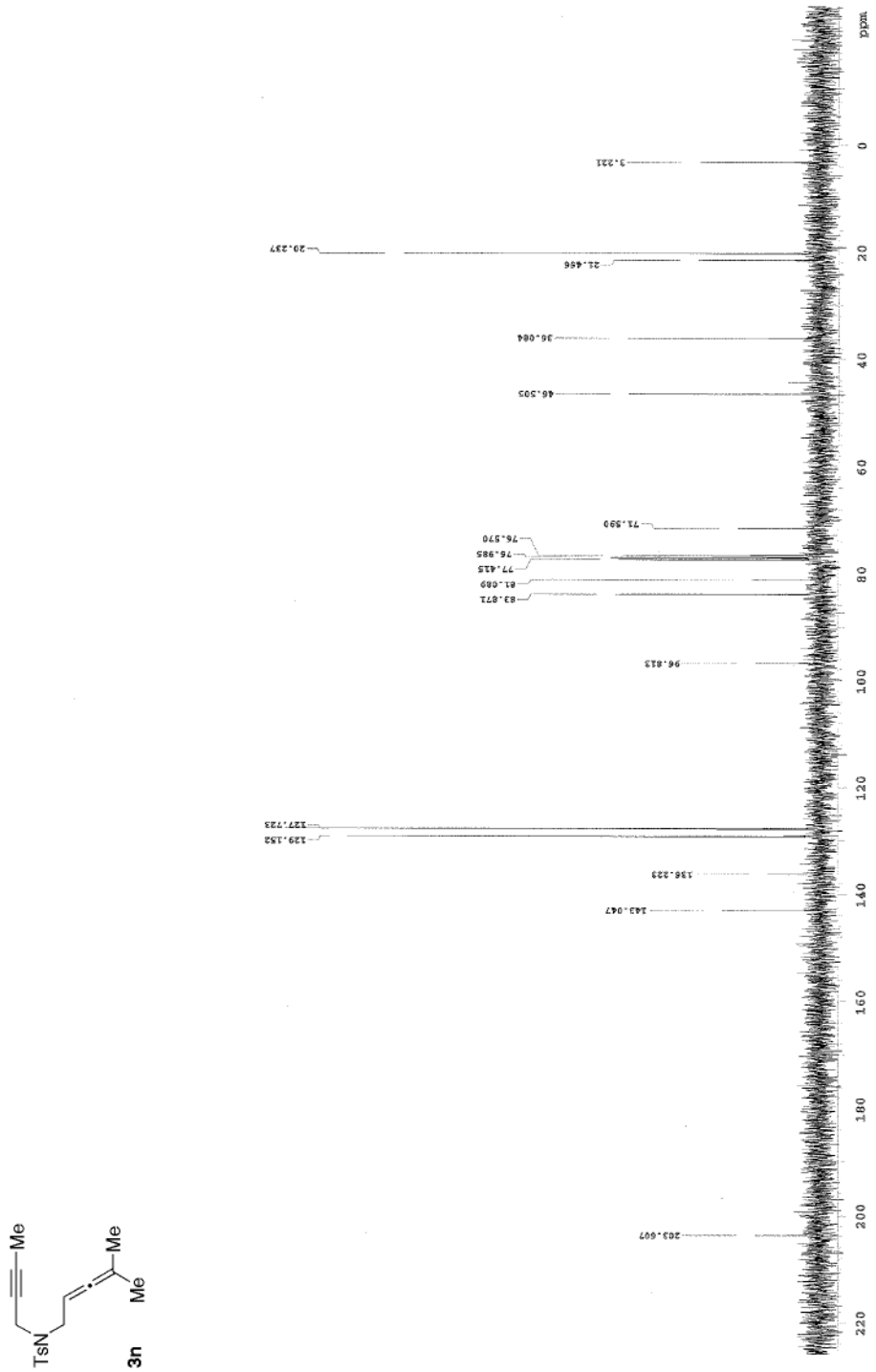

TsN
H
H
3l
ppm
1
2
3
4
5
6
7
8
1.589
2.014
2.022
2.030
2.434
3.854
3.862
3.870
3.878
3.886
3.894
4.150
4.158
4.762
4.770
4.778
4.783
4.792
4.801
4.955
5.018
5.040
5.062
7.260
7.266
7.279
7.306
7.716
7.722
7.738
7.743
7.750
0.80
3.00
2.01
1.97
1.89
0.85
2.45
1.81


TsN
H
H
3l
209.679
143.555
136.977
129.460
127.619
85.331
77.415
77.000
76.590
76.447
73.665
49.583
35.853
21.543
ppm
0
20
40
60
80
100
120
140
160
180
200
220


Me
Me
O
3m
5.050
5.041
5.034
4.170
4.162
4.055
4.032
2.619
2.611
2.602
1.714
1.704
1.537
1.305
ppm


Me
Me
3m
ppm
0
20
40
60
80
100
120
140
160
180
200
220
30.344
55.327
68.454
74.343
76.570
77.000
77.415
79.736
85.377
96.136
203.377


Me
Me
Me
TsN
3n
7.735
7.708
7.288
7.260
4.836
4.825
4.817
4.082
4.074
4.066
4.058
3.759
3.737
2.464
2.031
1.660
1.651
1.546
1.538
1.530
1.246
ppm
0
1
2
3
4
5
6
7
1.85
1.99
0.88
2.09
2.03
3.00
6.18
2.91


Me
Me
Me
TsN
3n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
203.607
143.047
136.223
129.152
127.723
96.813
83.871
81.089
77.435
76.985
76.570
73.589
46.505
36.084
21.456
20.237
3.321


Ph
Me
Me
TsN
3o
ppm
1.660
1.705
1.696
2.358
3.870
3.893
4.607
4.932
4.941
4.950
7.079
7.084
7.091
7.103
7.105
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7.233
7.261
7.347
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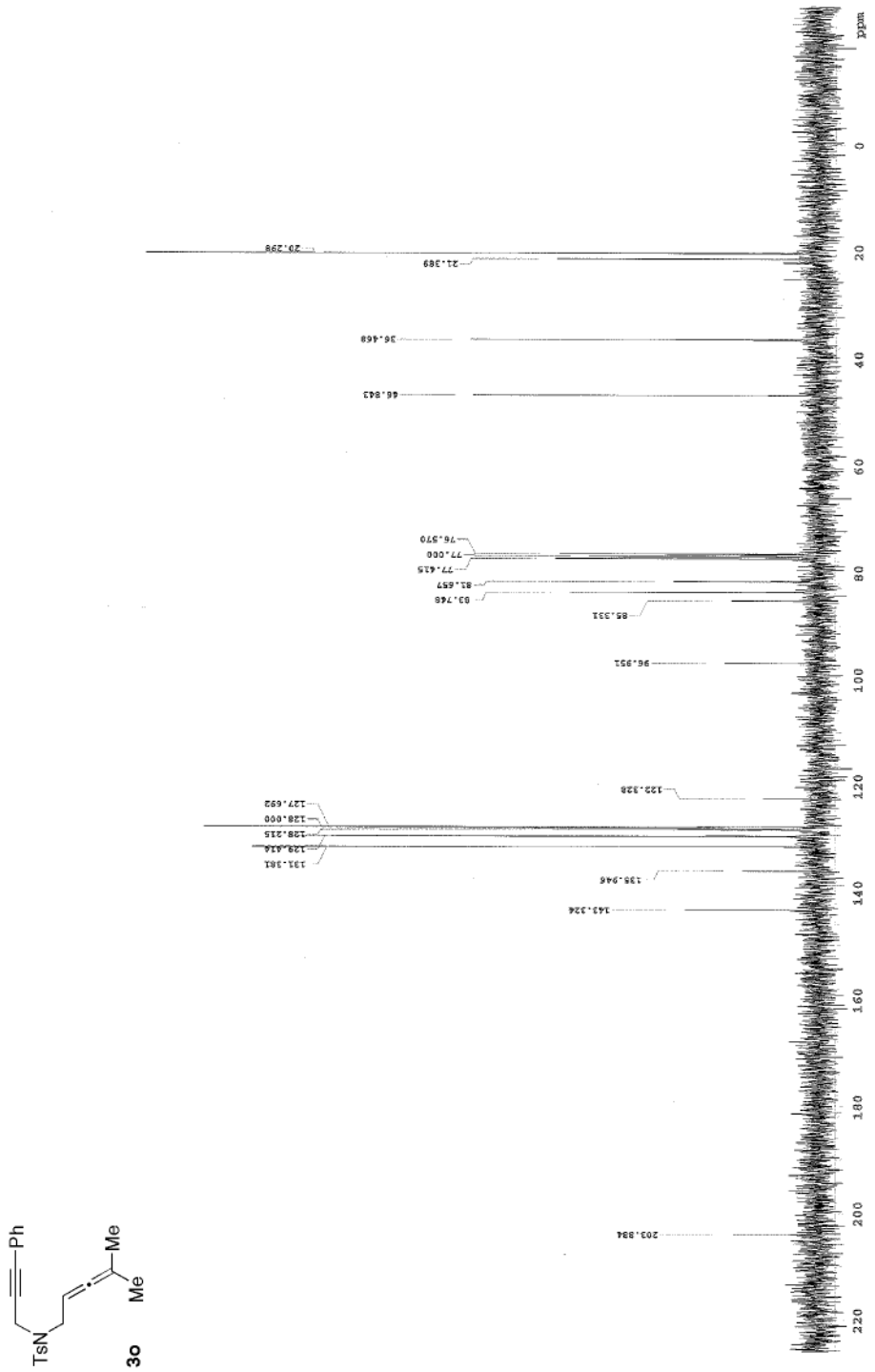
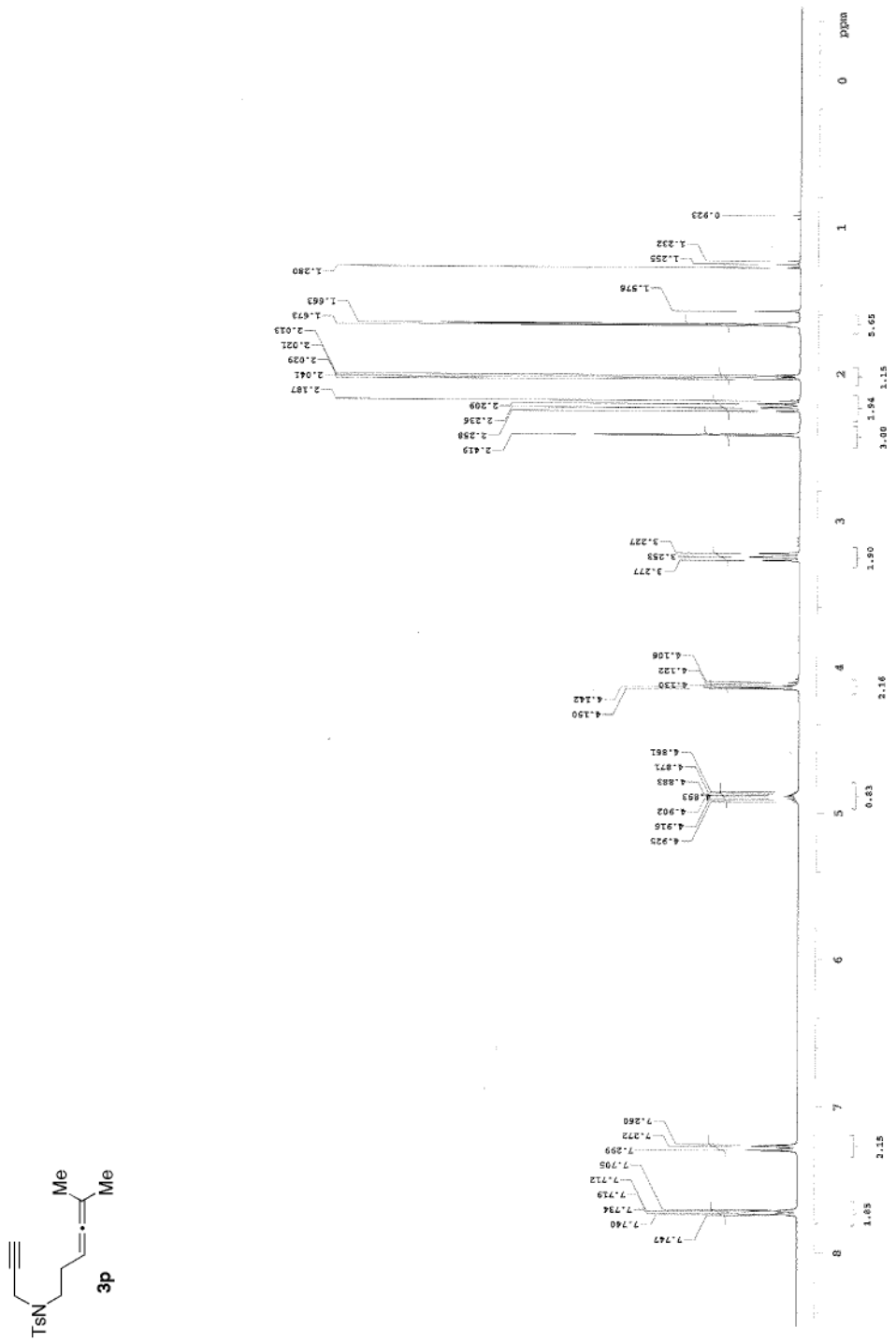
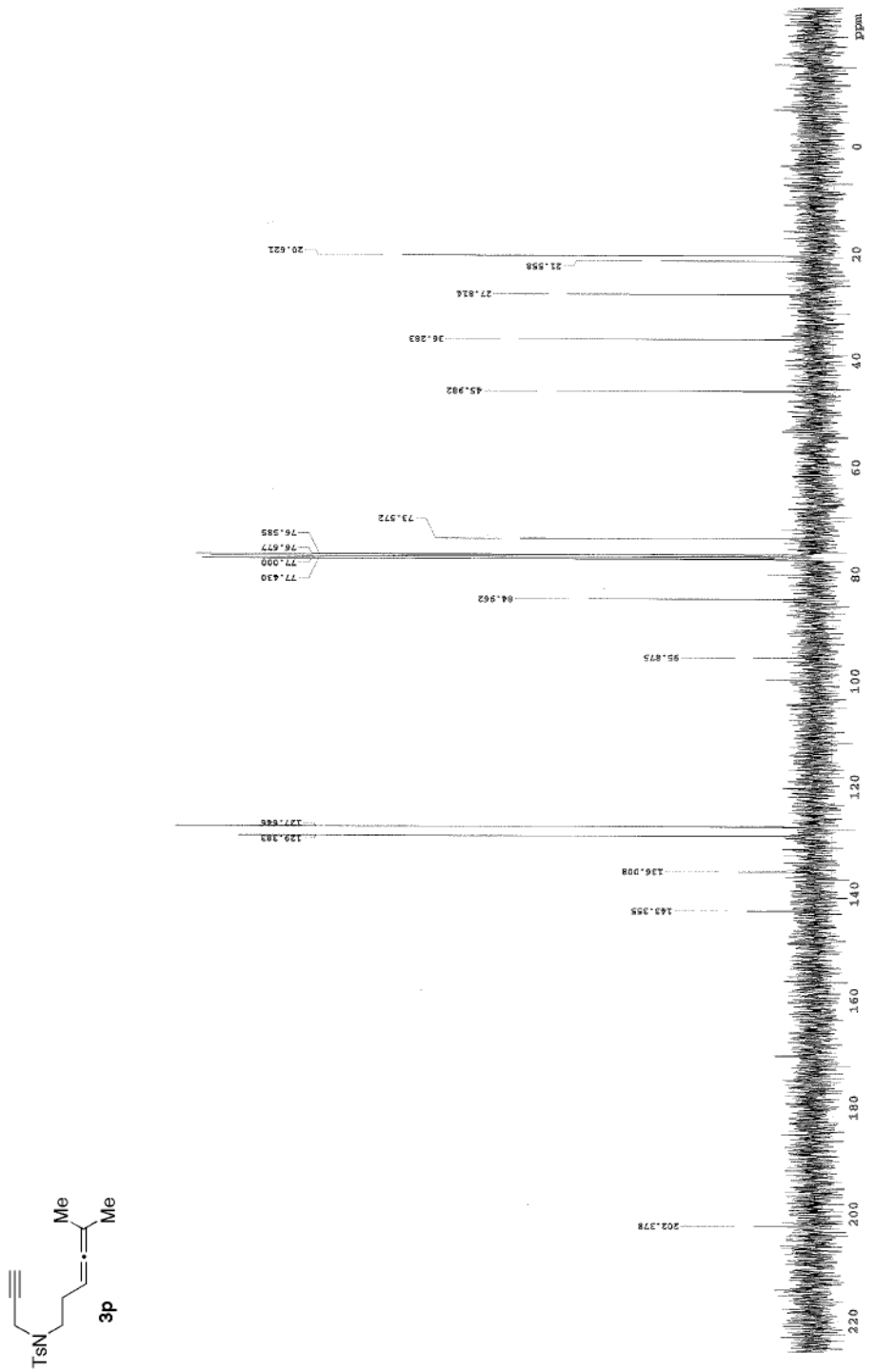
7.308
7.311
7.766
7.813


Ph
Me
Me
TsN
3o
203.884
143.324
139.946
133.328
131.361
129.414
128.315
128.000
127.692
96.951
85.331
83.748
81.657
77.425
77.000
76.570
66.843
36.468
21.389
20.298
ppm


Me
Me
TsN
3p


Me
Me
TsN
3p
202.378
143.355
136.008
129.383
127.686
95.875
64.962
77.430
77.000
76.677
76.385
73.572
45.982
36.283
27.834
21.558
20.621
ppm
0
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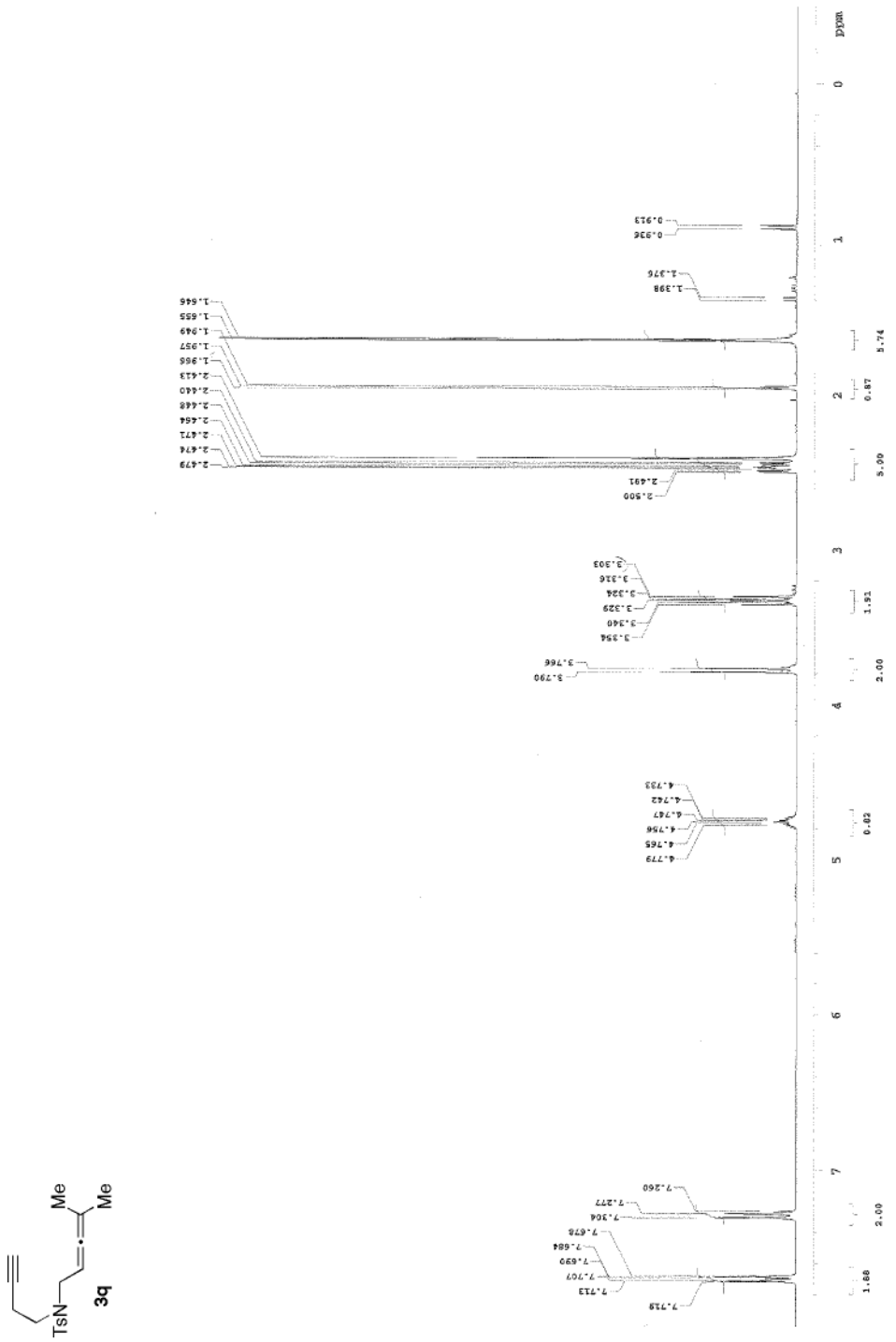
40
60
80
100
120
140
160
180
200
220


Me
Me
TsN
3q
7.739
7.713
7.707
7.690
7.684
7.678
7.304
7.277
7.260
4.779
4.765
4.756
4.747
4.742
4.733
3.790
3.766
3.354
3.340
3.329
3.324
3.316
3.303
2.500
2.491
2.479
2.474
2.471
2.464
2.448
2.440
2.413
1.966
1.957
1.949
1.655
1.646
1.398
1.376
0.936
0.919
ppm
0
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3
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5
6
7
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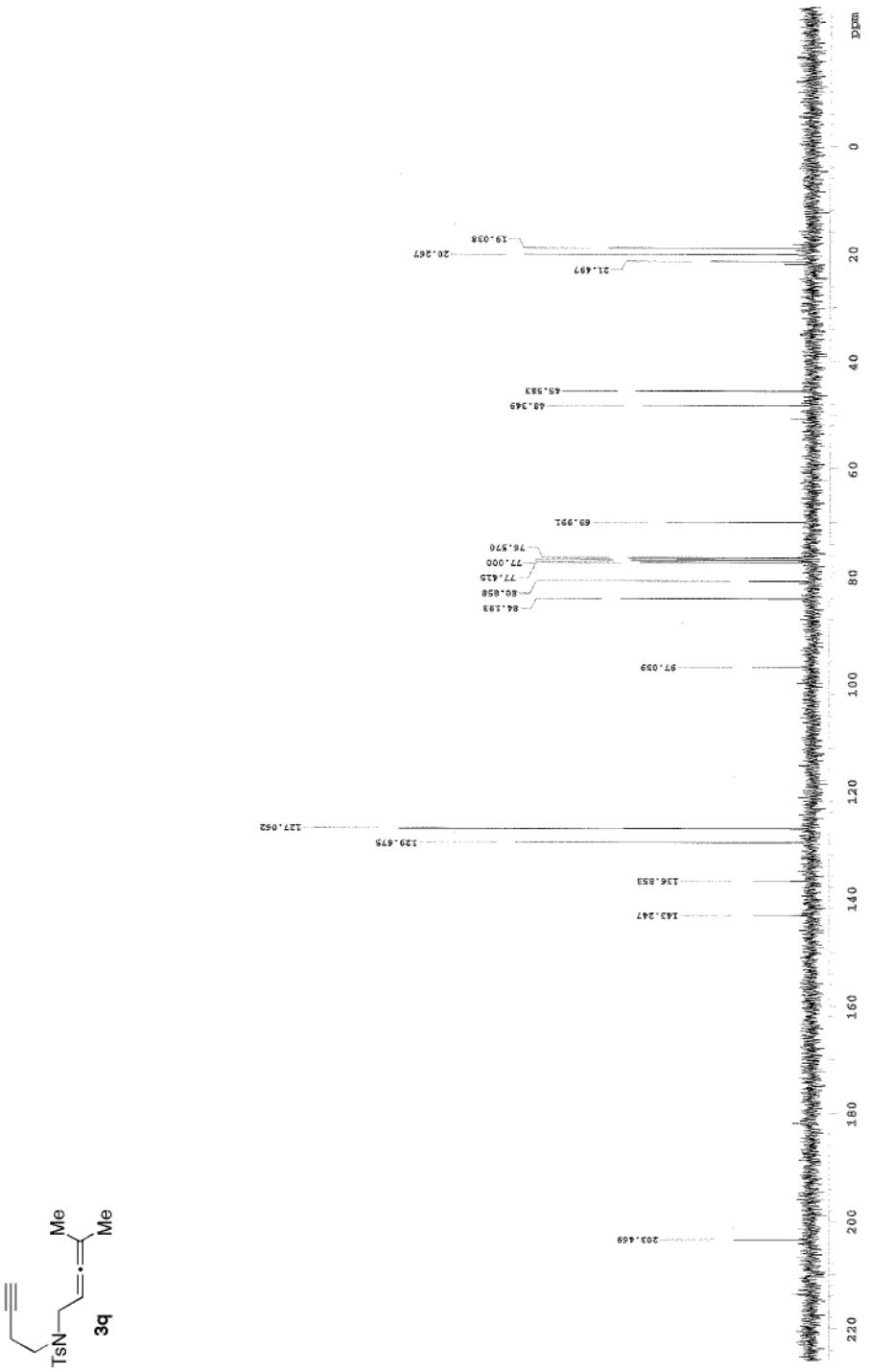
2.00
0.02
2.00
1.91
3.00
0.87
5.74


Me
Me
TsN
3q
203.459
143.247
136.853
129.675
127.062
97.059
84.193
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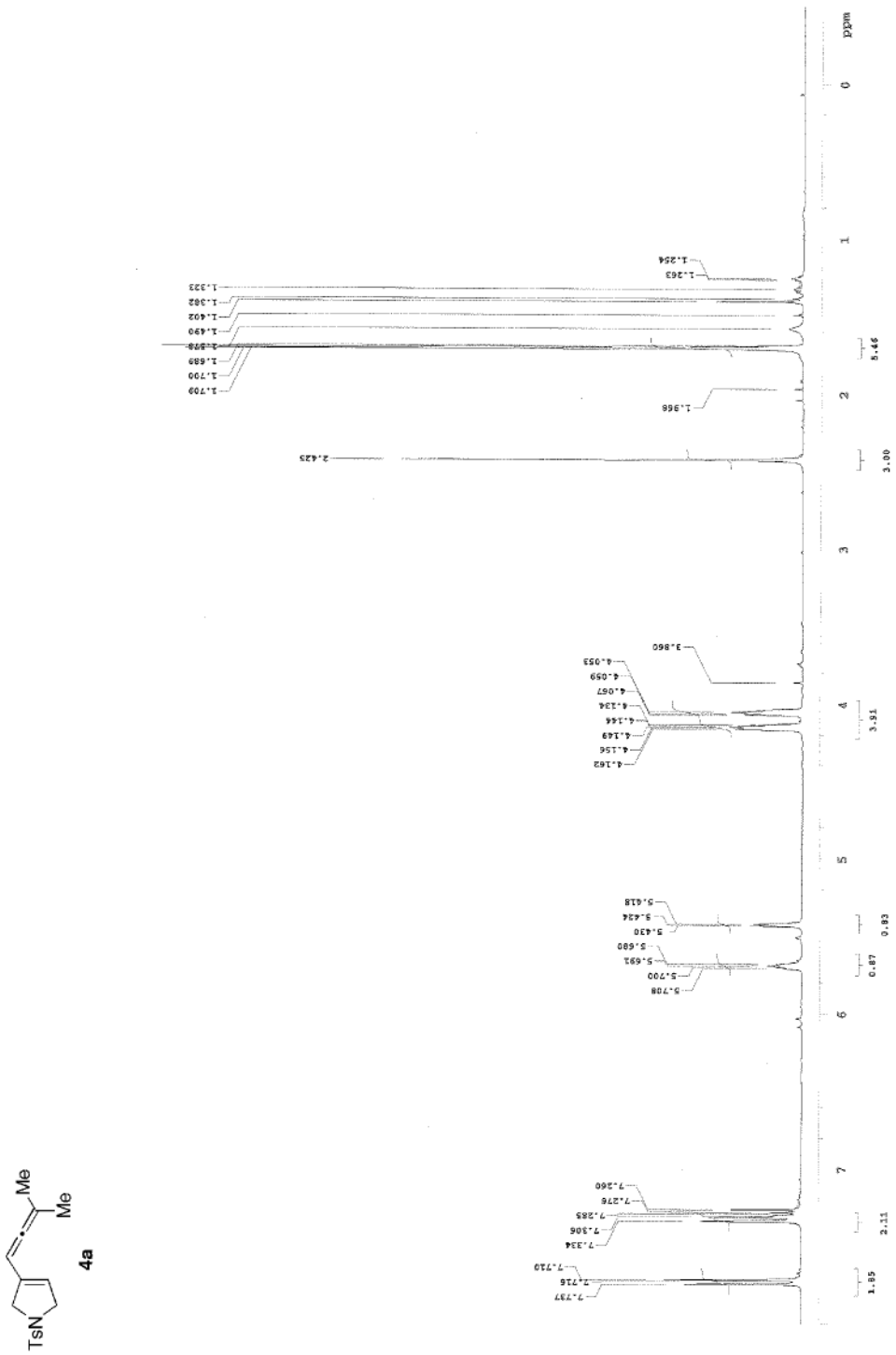
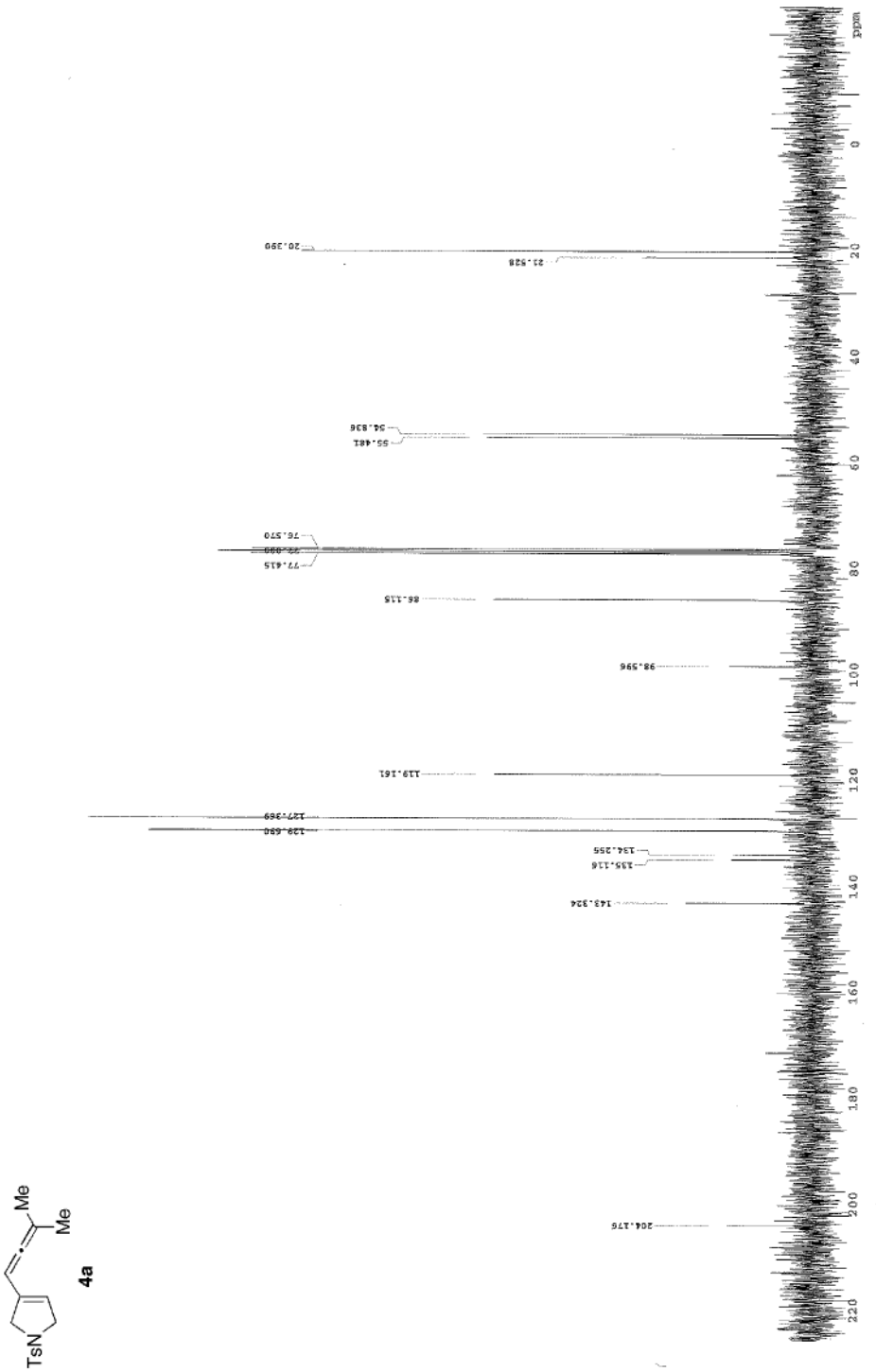
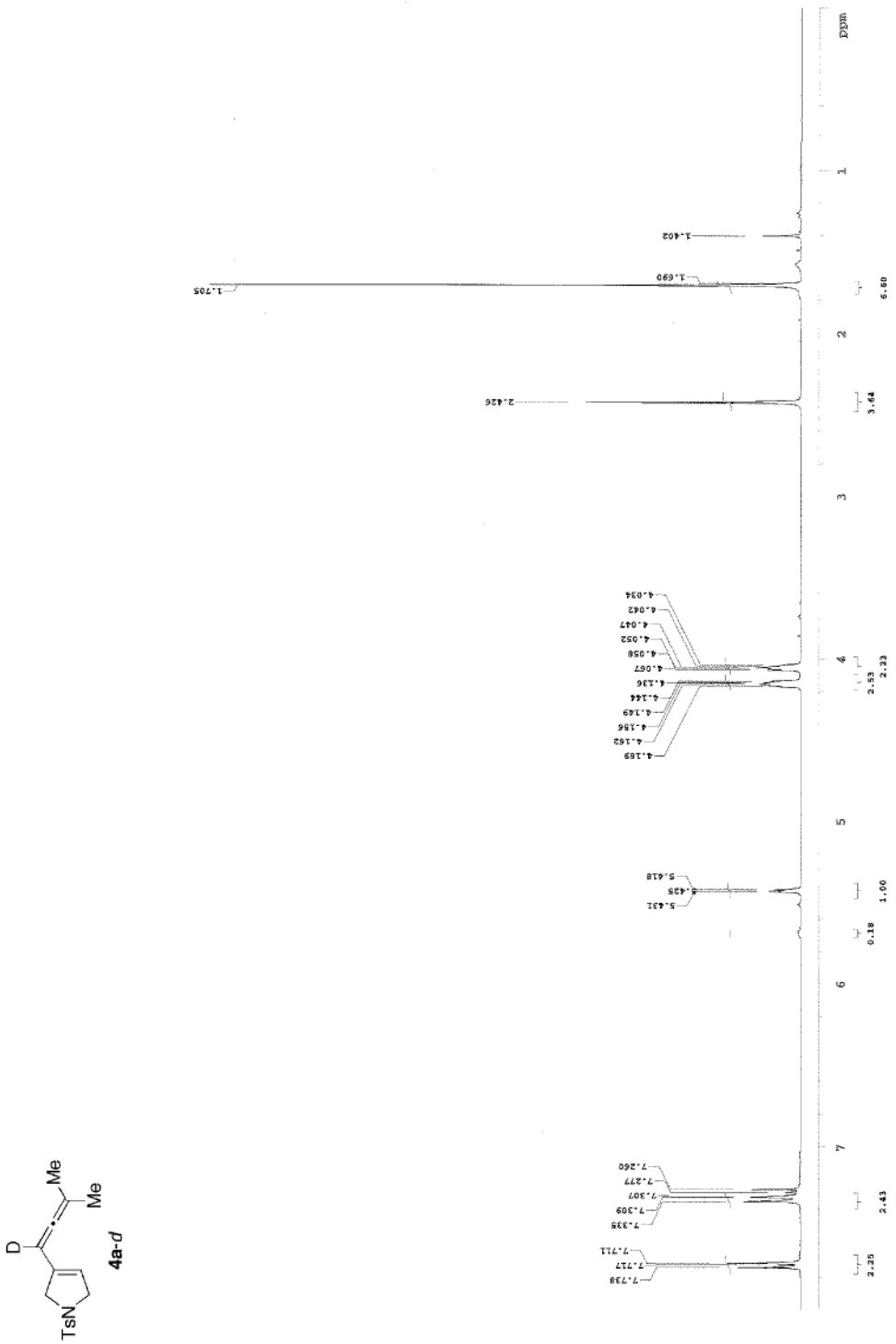
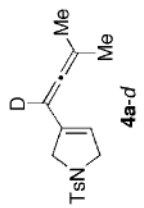
77.425
77.000
76.570
69.991
48.349
45.583
21.497
20.267
19.038
ppm

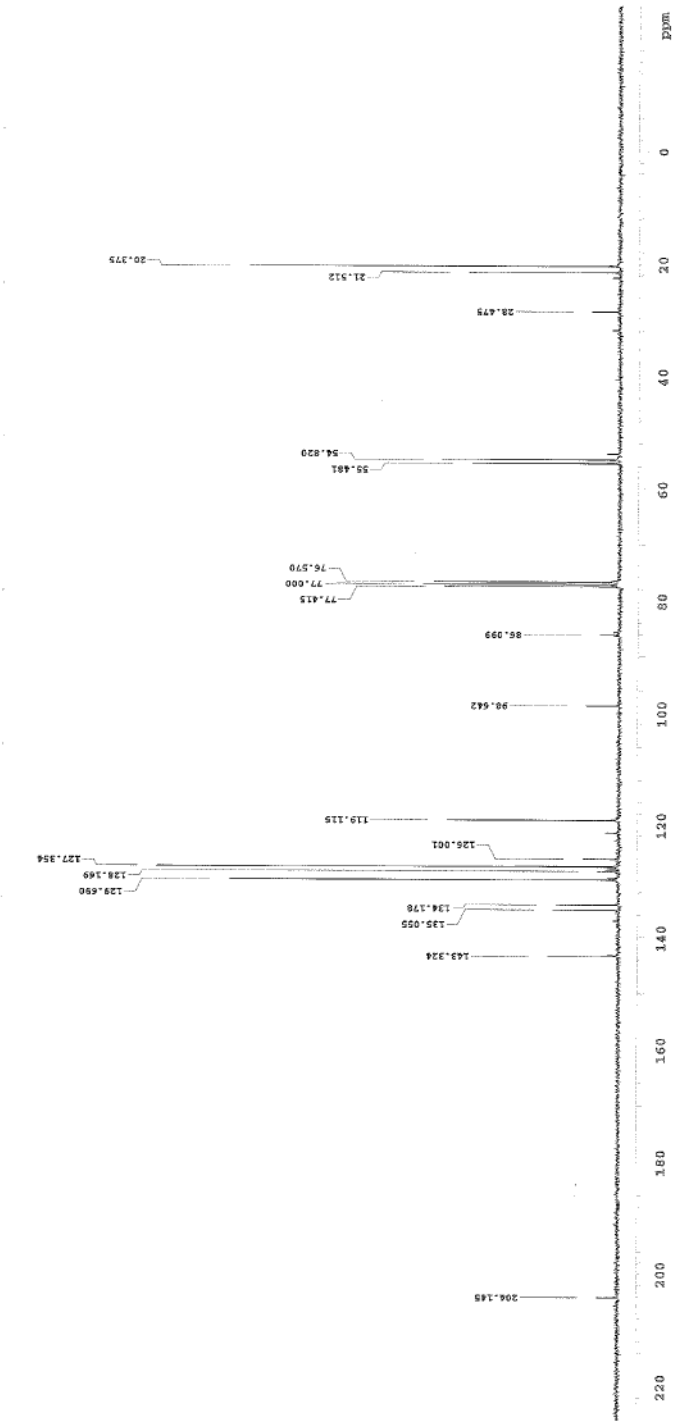

Me
Me
TsN
4a
7.737
7.716
7.719
7.334
7.306
7.285
7.276
7.260
5.708
5.700
5.693
5.680
5.438
5.434
5.430
4.162
4.156
4.149
4.144
4.134
4.067
4.059
4.053
3.860
2.425
1.966
1.709
1.700
1.689
1.490
1.402
1.382
1.323
1.263
1.254
ppm
1.85
2.11
0.87
0.83
3.91
3.00
5.46

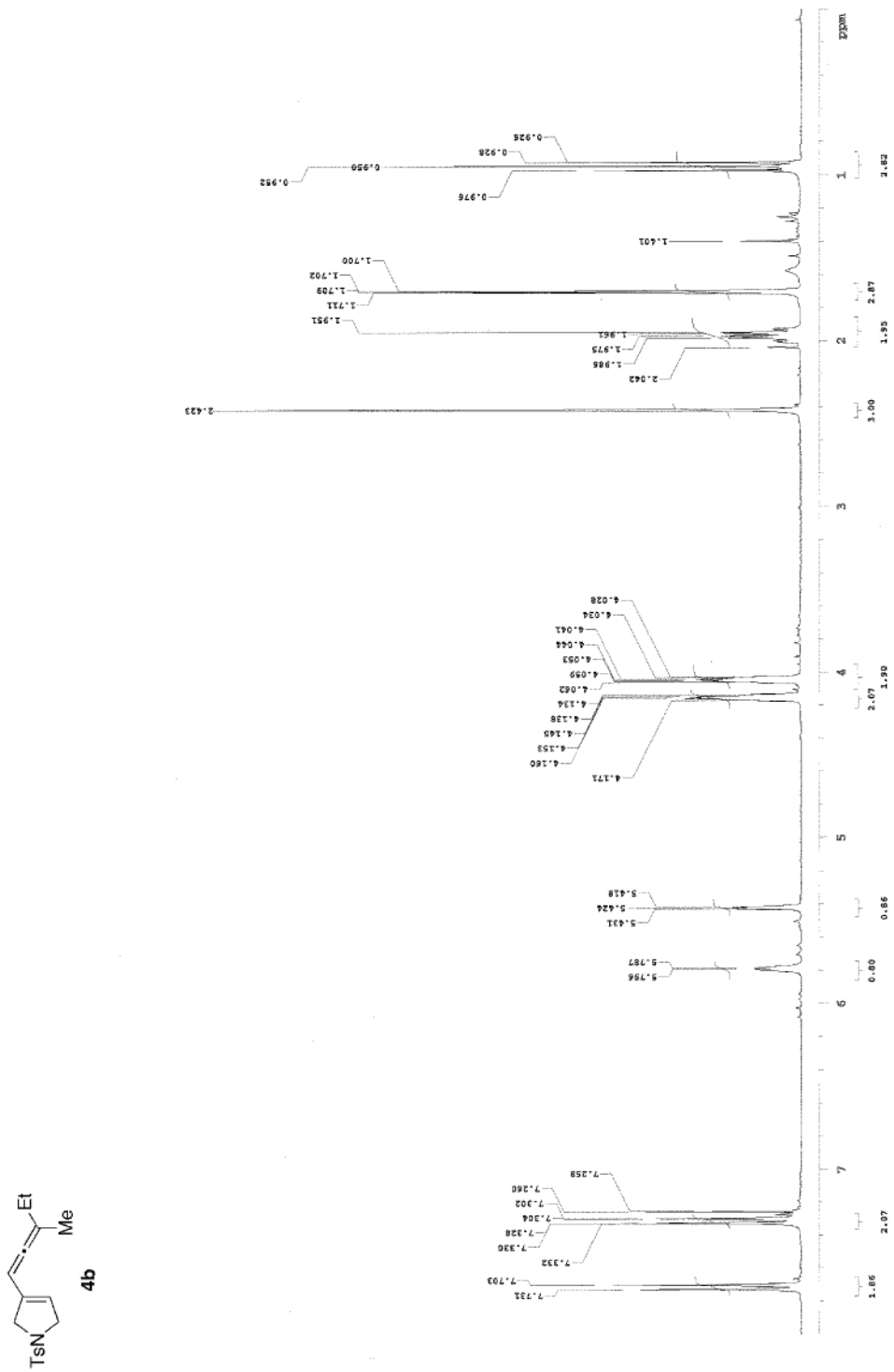

Me
Me
TsN
4a
204.176
143.324
135.116
134.255
129.690
127.369
119.161
98.596
86.115
77.415
76.570
55.461
54.836
21.528
20.350
ppm

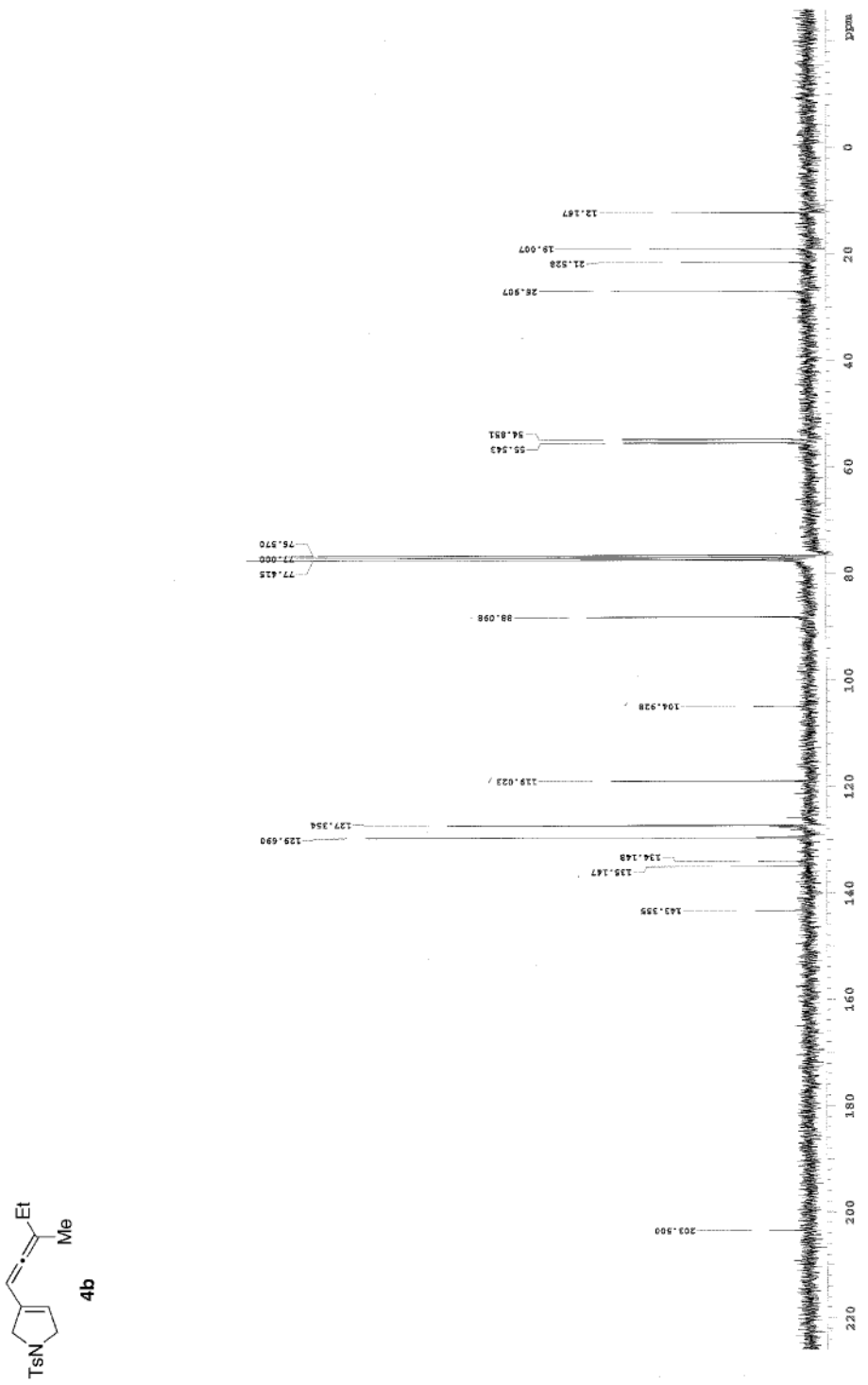

Me
Me
D
TsN
4a-d
ppm
1.402
1.690
1.705
2.436
4.034
4.042
4.047
4.052
4.058
4.067
4.136
4.144
4.149
4.156
4.162
4.169
5.418
5.425
5.431
7.260
7.277
7.307
7.309
7.335
7.711
7.717
7.738
6.60
3.64
2.53
2.23
1.00
0.18
2.35
2.43

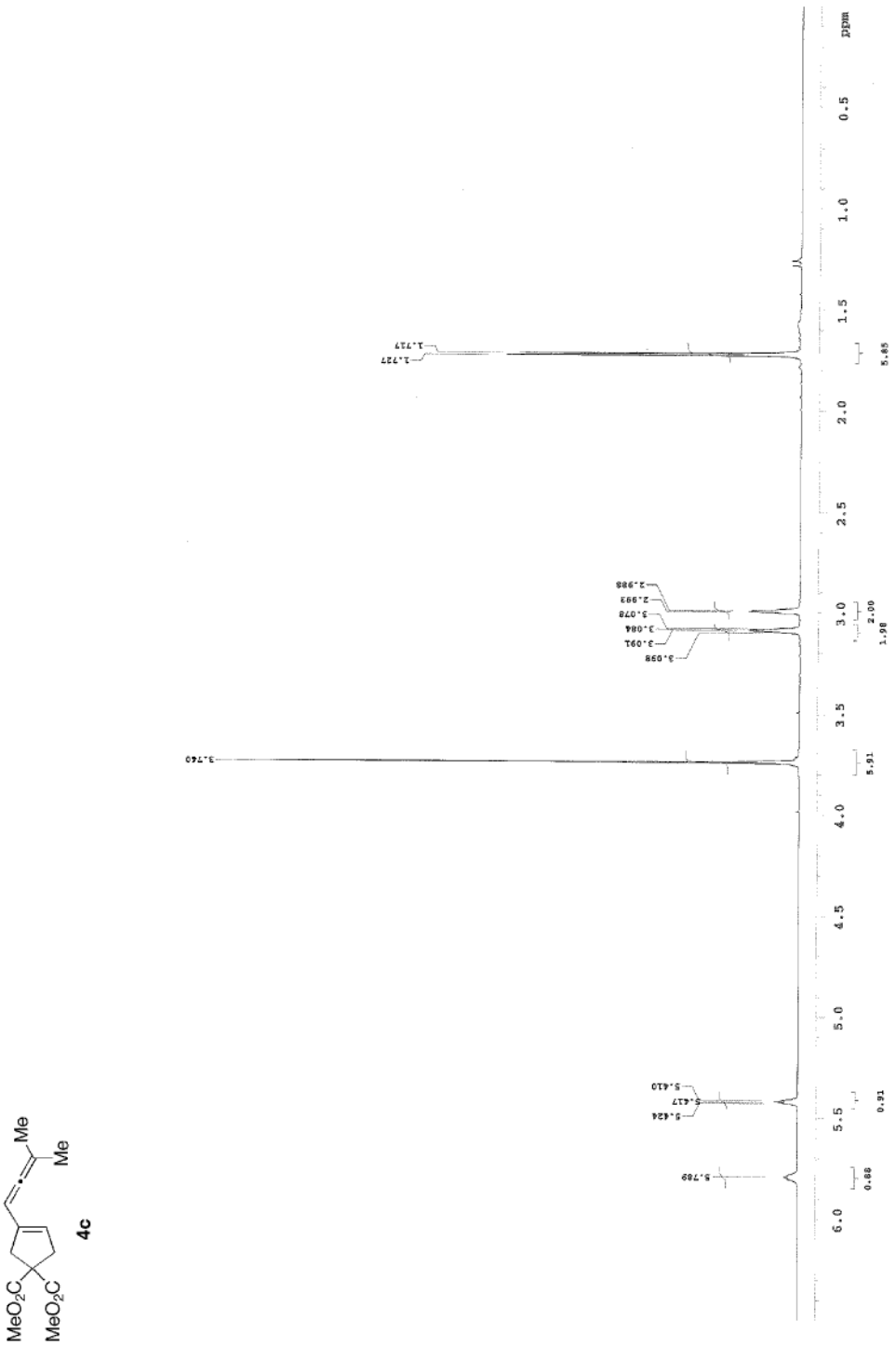

Me
Me
D
TsN

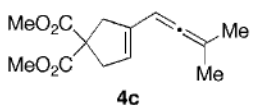
4a-*d*


206.145
143.324
135.055
134.178
129.690
128.169
127.354
126.001
119.115
98.642
86.099
77.415
77.000
76.570
55.481
54.820
28.479
21.512
20.375
ppm

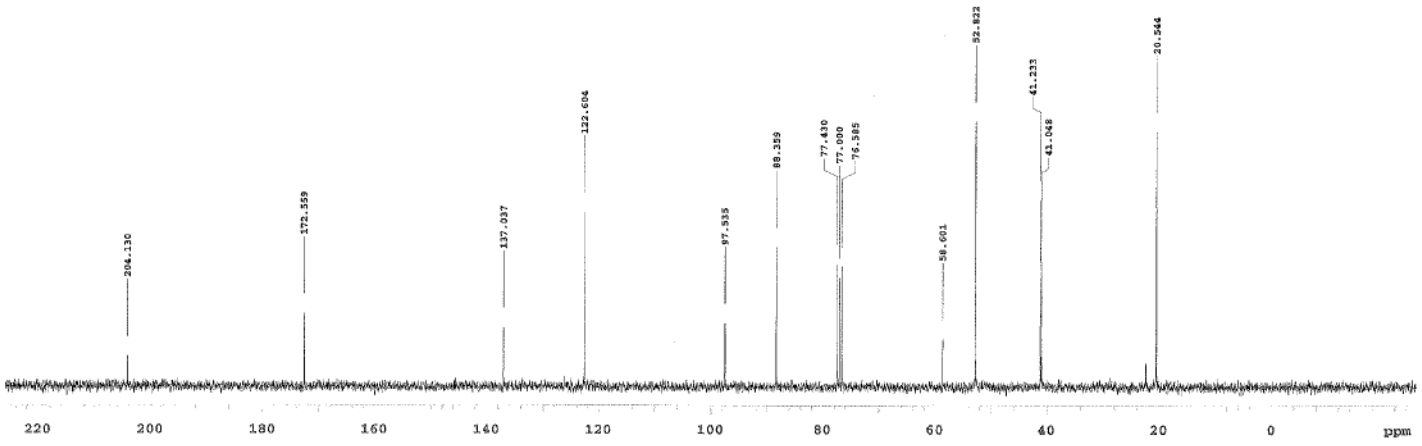

Et
Me
TsN
4b

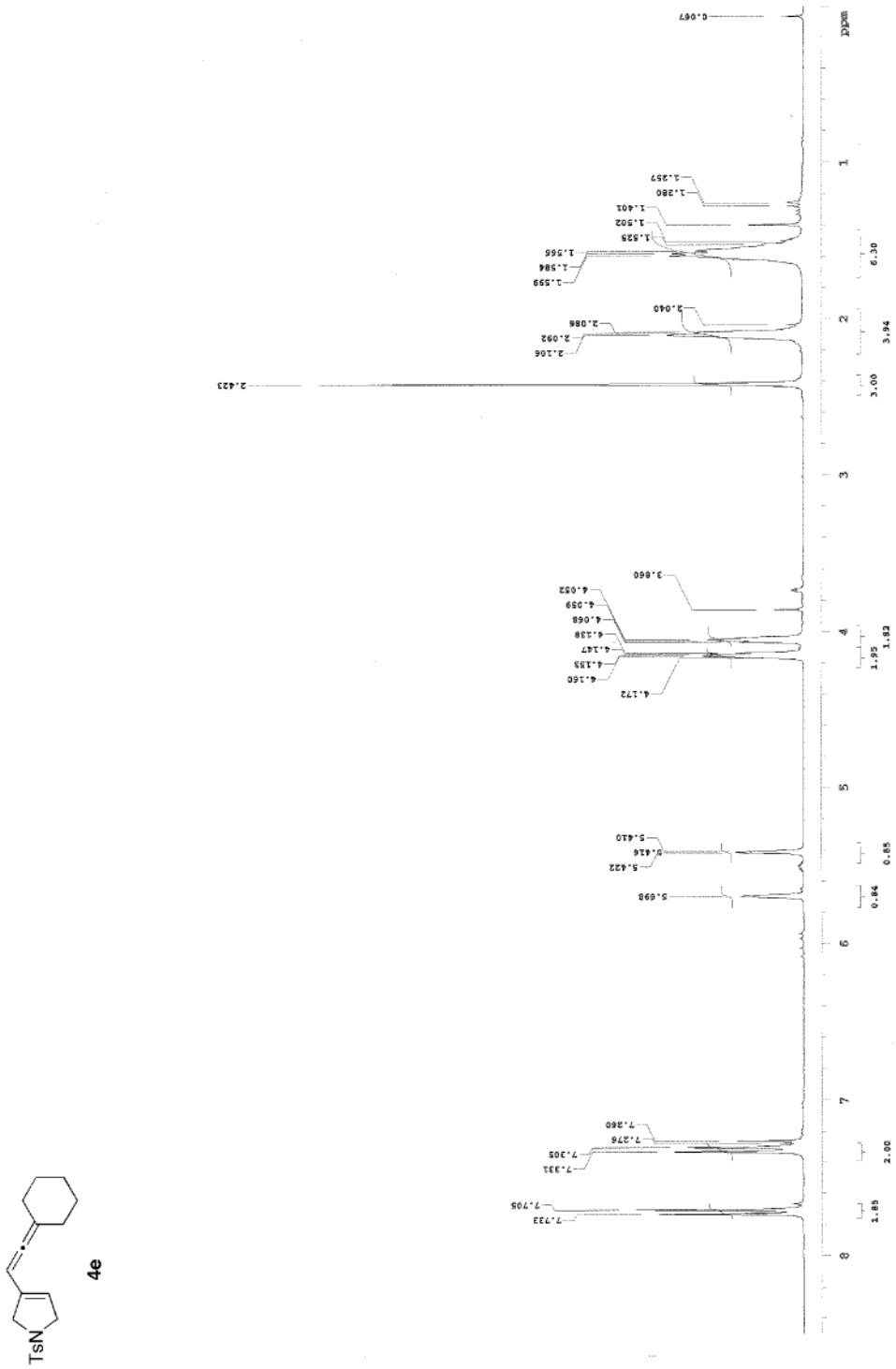

Et
Me
TsN
4b
12.167
19.007
21.528
26.907
54.851
55.543
76.570
77.000
77.425
88.098
104.928
139.023
137.354
135.690
134.148
133.147
143.355
203.900
ppm

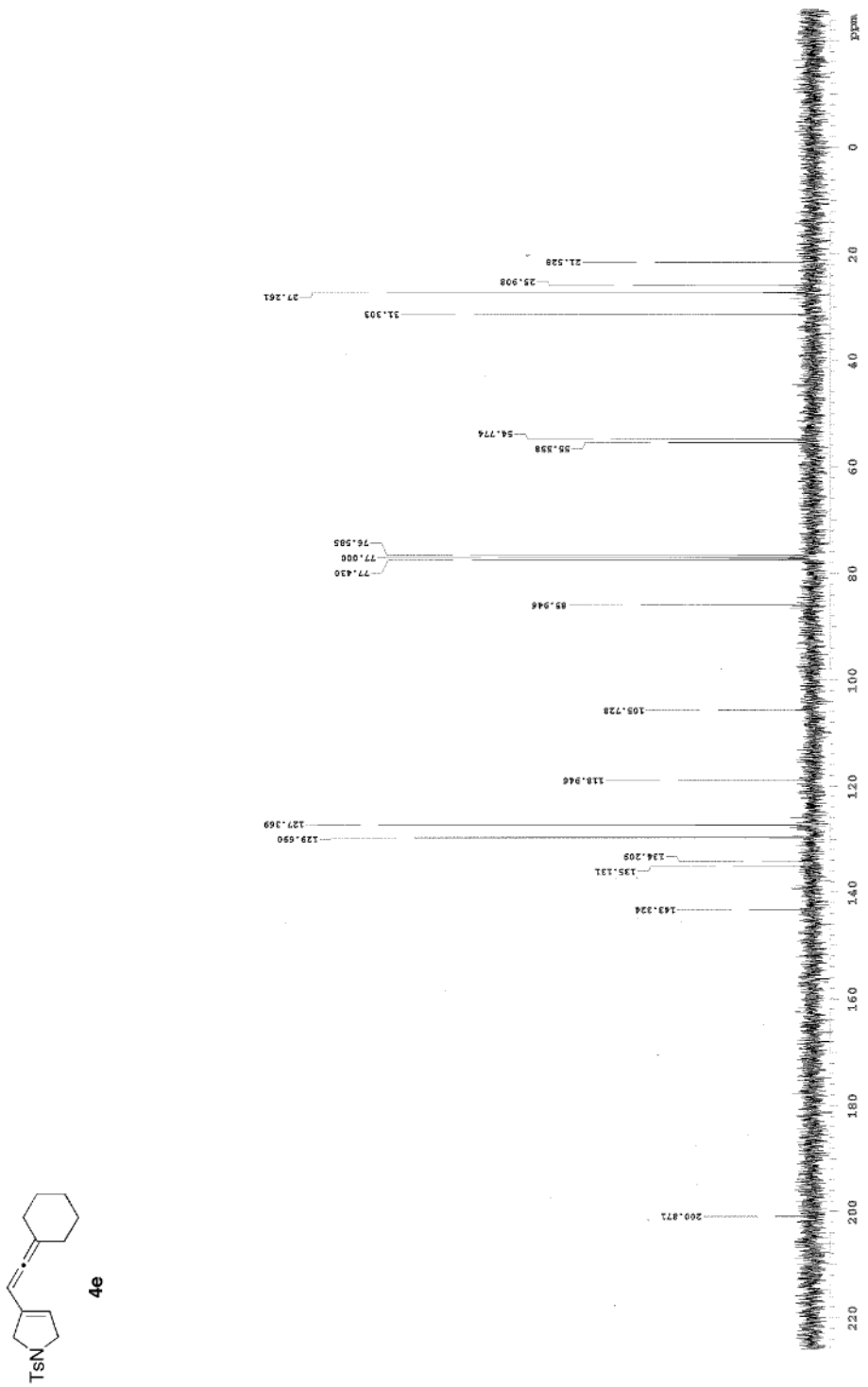

MeO2C
MeO2C
Me
Me
4c
5.789
5.434
5.417
5.410
3.740
3.098
3.091
3.084
3.078
2.993
2.986
1.737
1.727
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.88
0.91
5.91
2.00
1.98
5.85

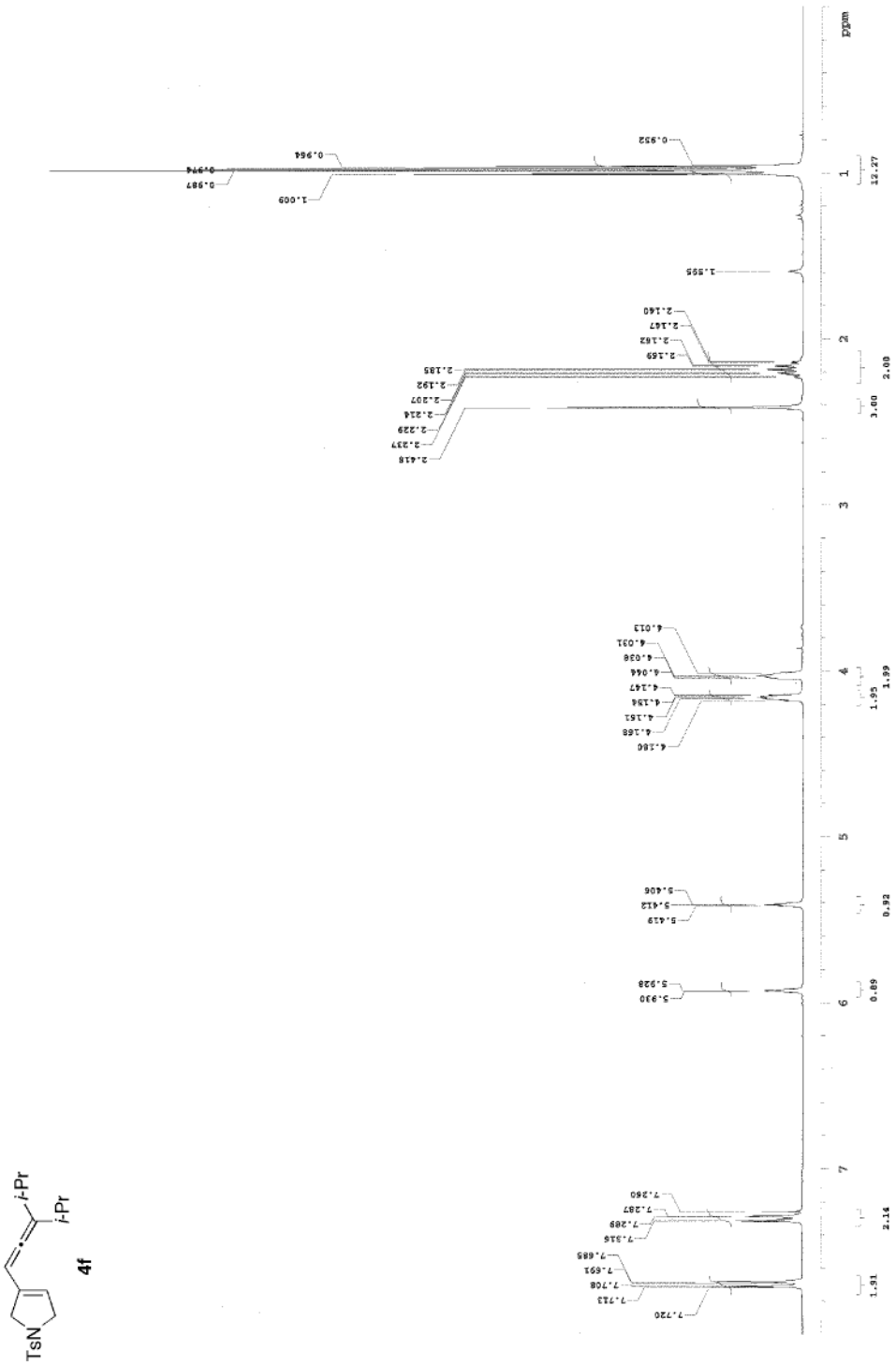

MeO2C
MeO2C
Me
Me

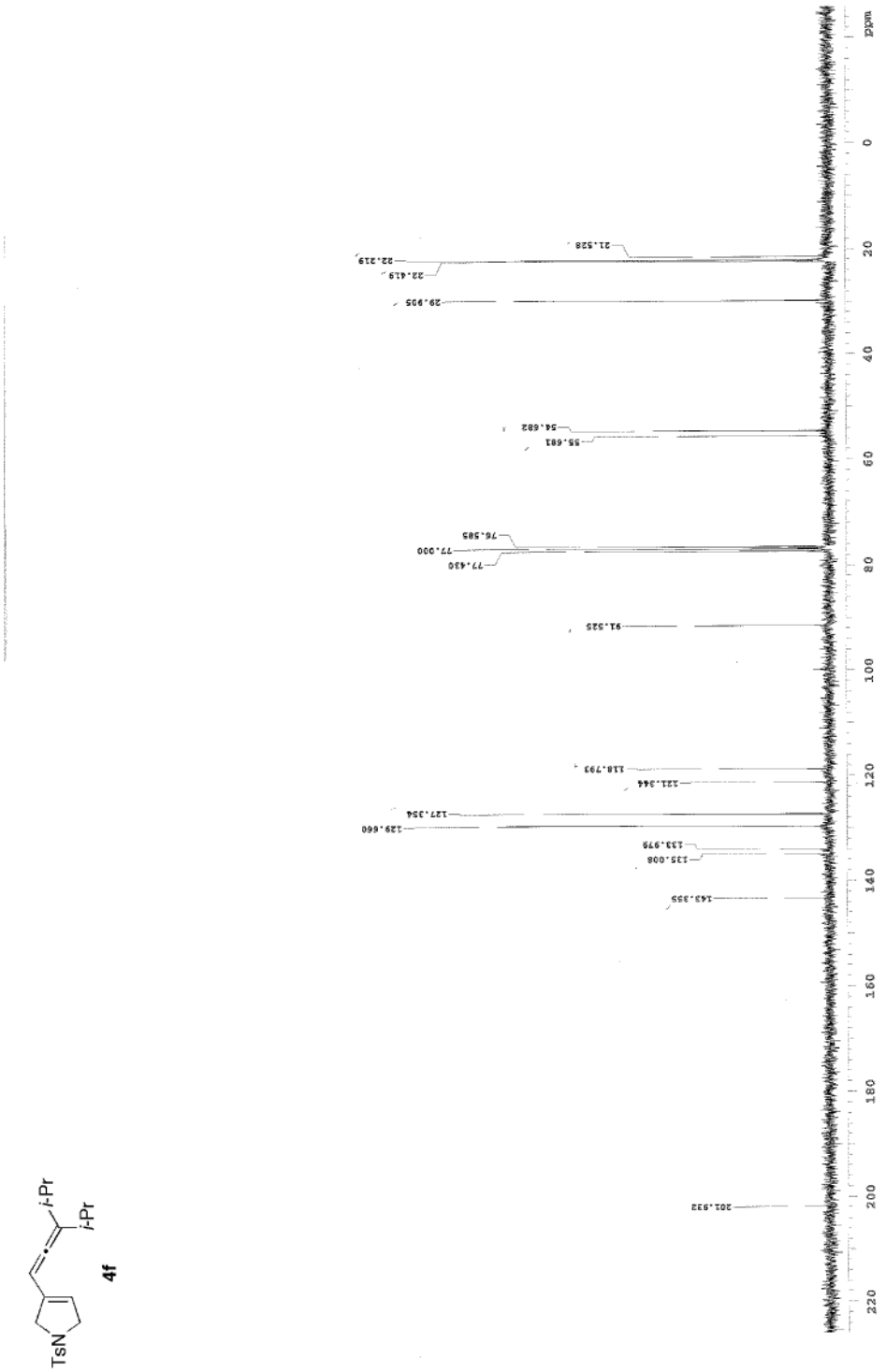
4c

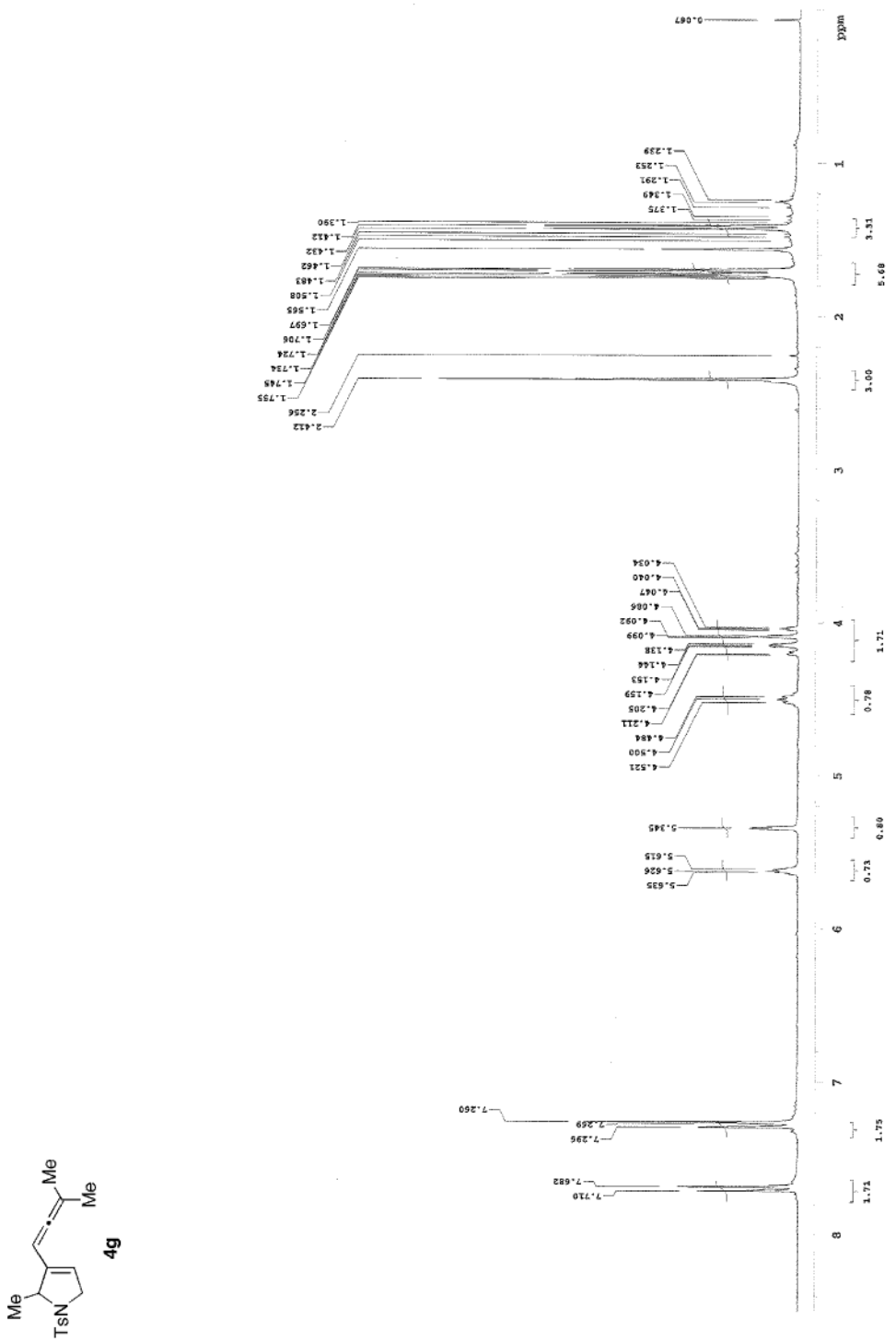

204.130
172.559
137.037
122.604
97.535
88.359
77.430
77.000
76.585
58.601
52.822
41.233
41.048
20.544
220
200
180
160
140
120
100
80
60
40
20
0
ppm

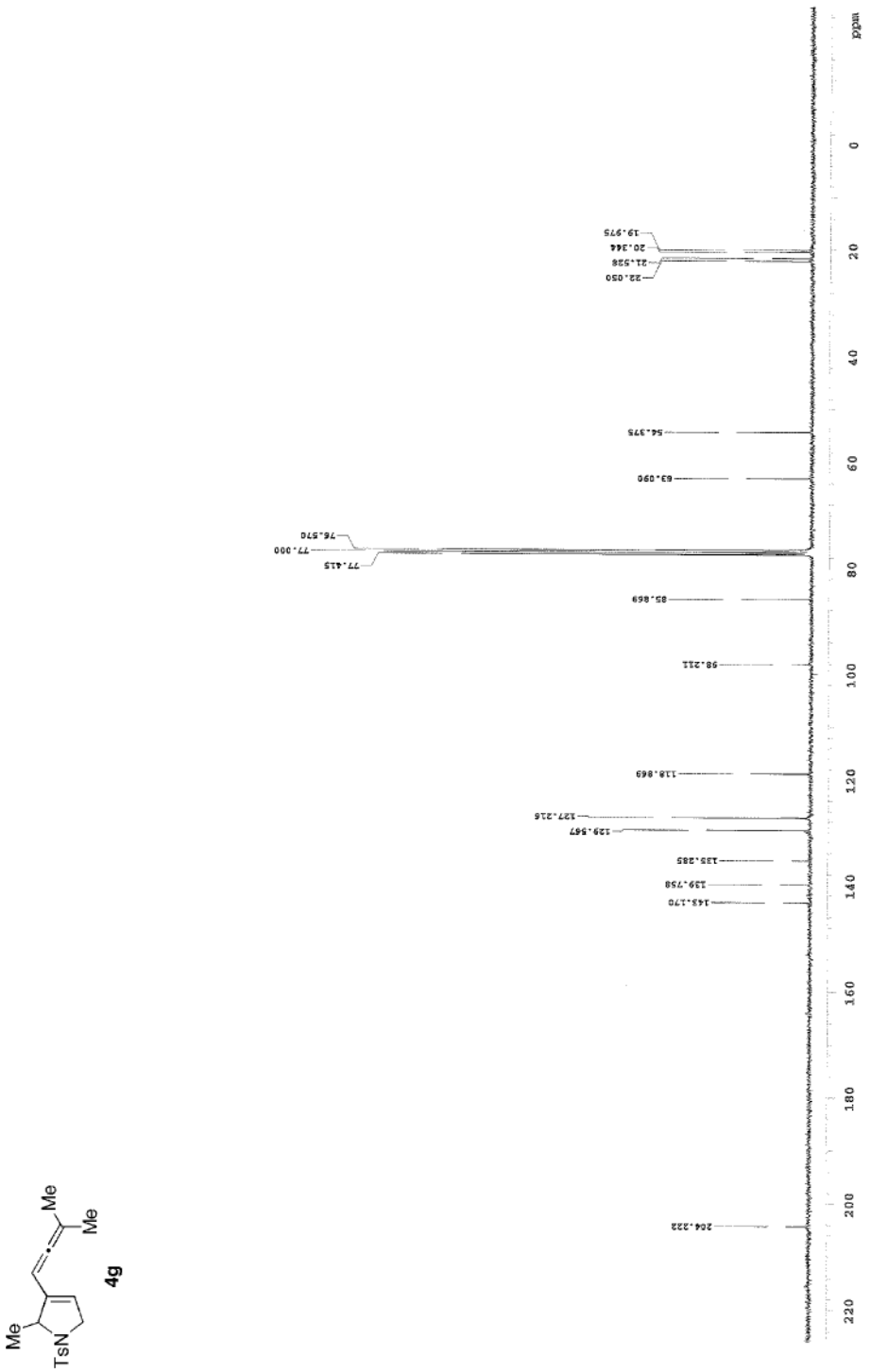

TsN
4e
ppm

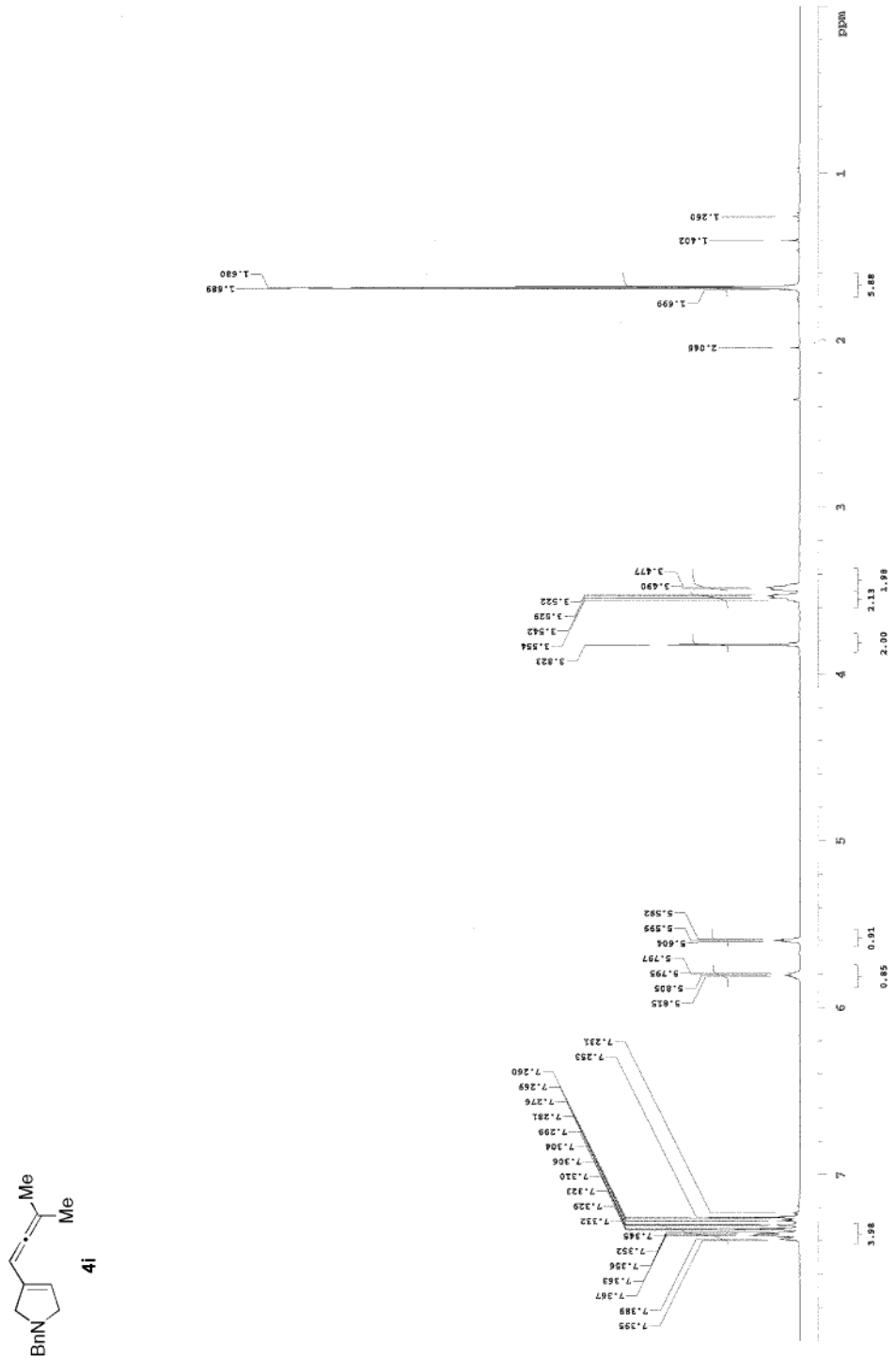

TsN
4e
ppm
0
20
40
60
80
100
120
140
160
180
200
220
21.528
25.908
31.303
37.261
54.774
55.358
76.585
77.000
77.430
85.946
105.728
118.946
127.369
129.690
134.205
135.131
143.334
200.871

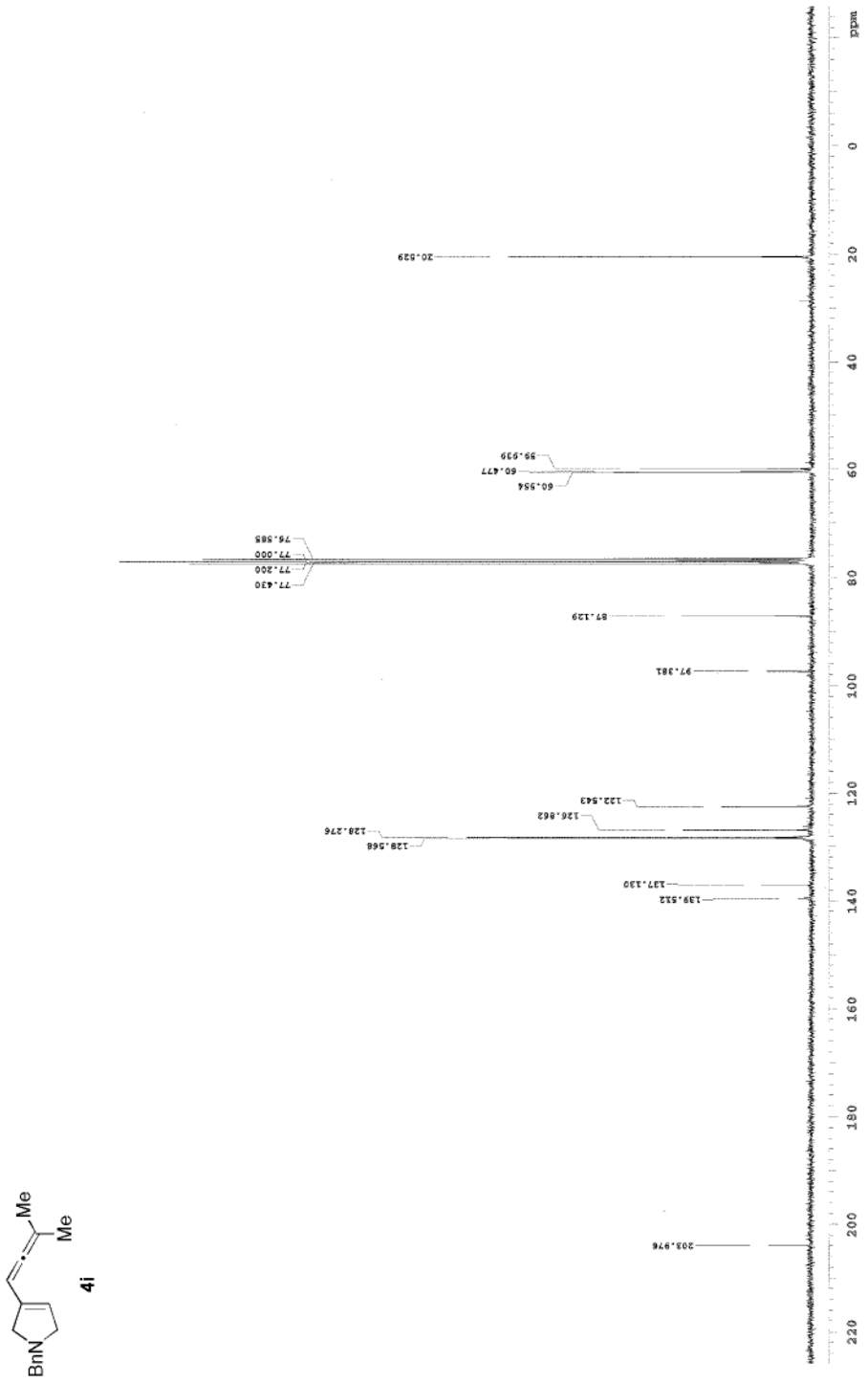

i-Pr
i-Pr
TsN
4f

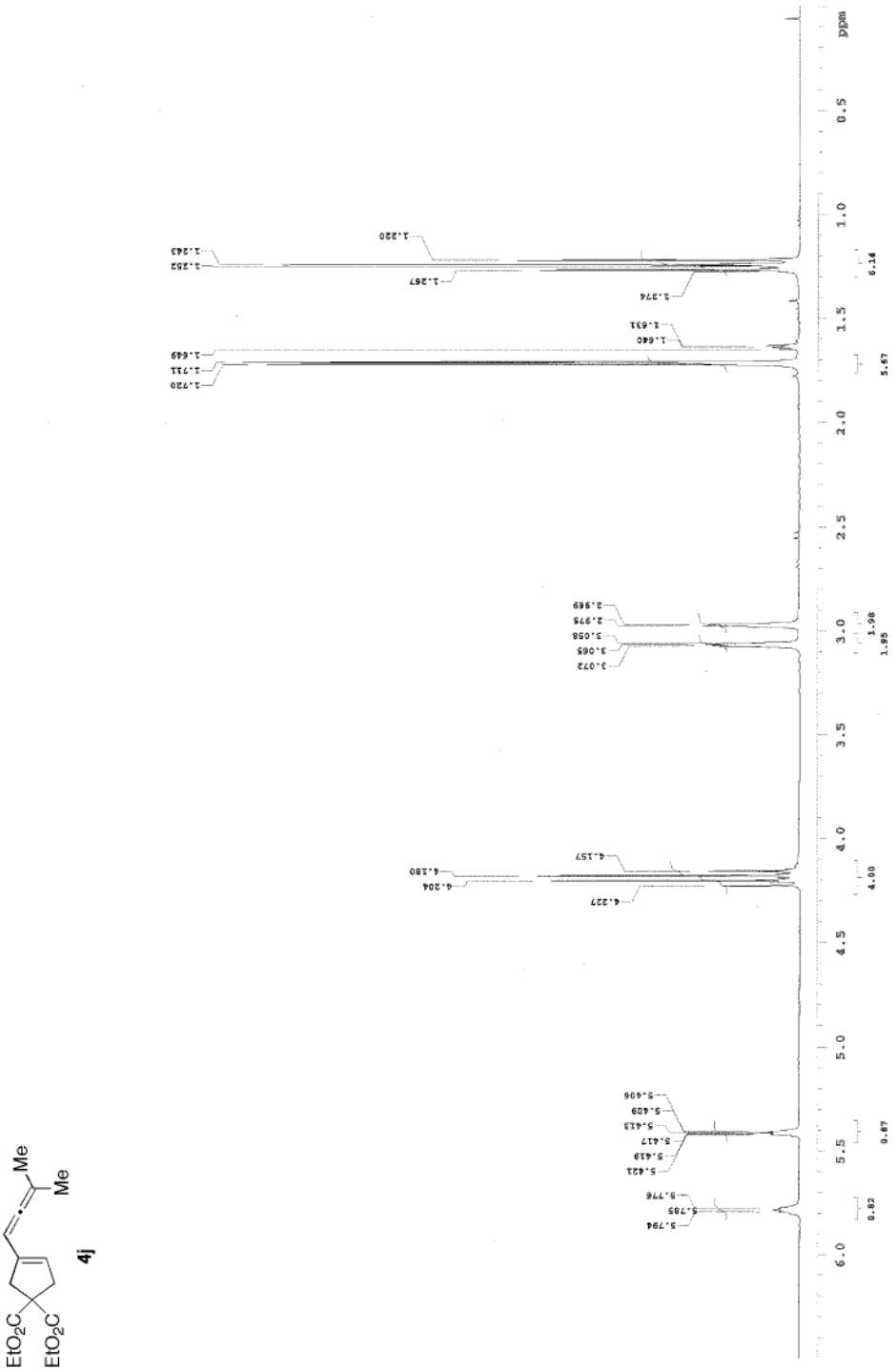

i-Pr
i-Pr
TsN
4f
201.932
143.355
135.008
133.979
129.660
127.354
121.344
118.793
91.525
77.430
77.000
76.585
55.681
54.682
29.905
22.419
22.319
21.528
ppm

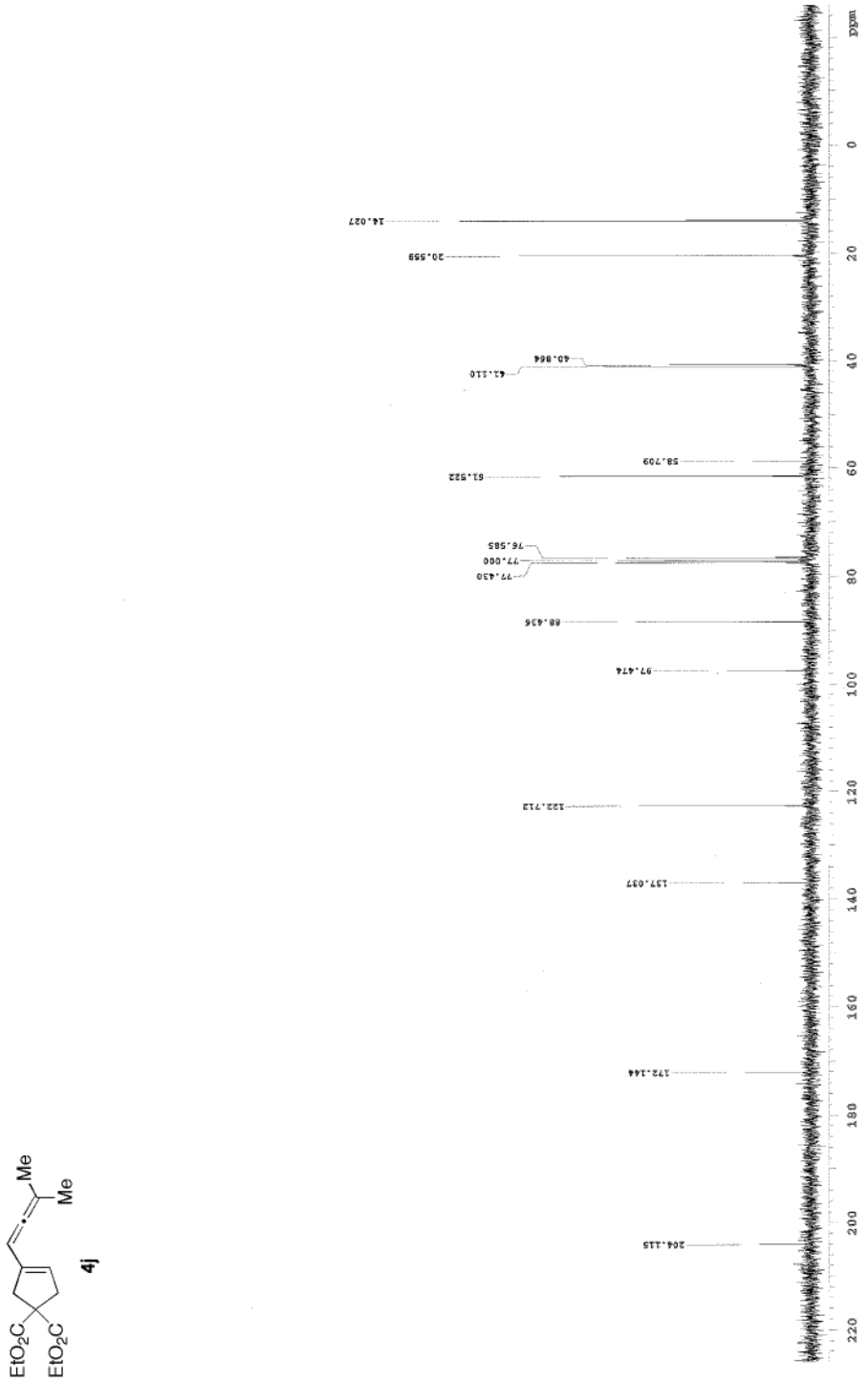

Me
Me
Me
TsN
4g

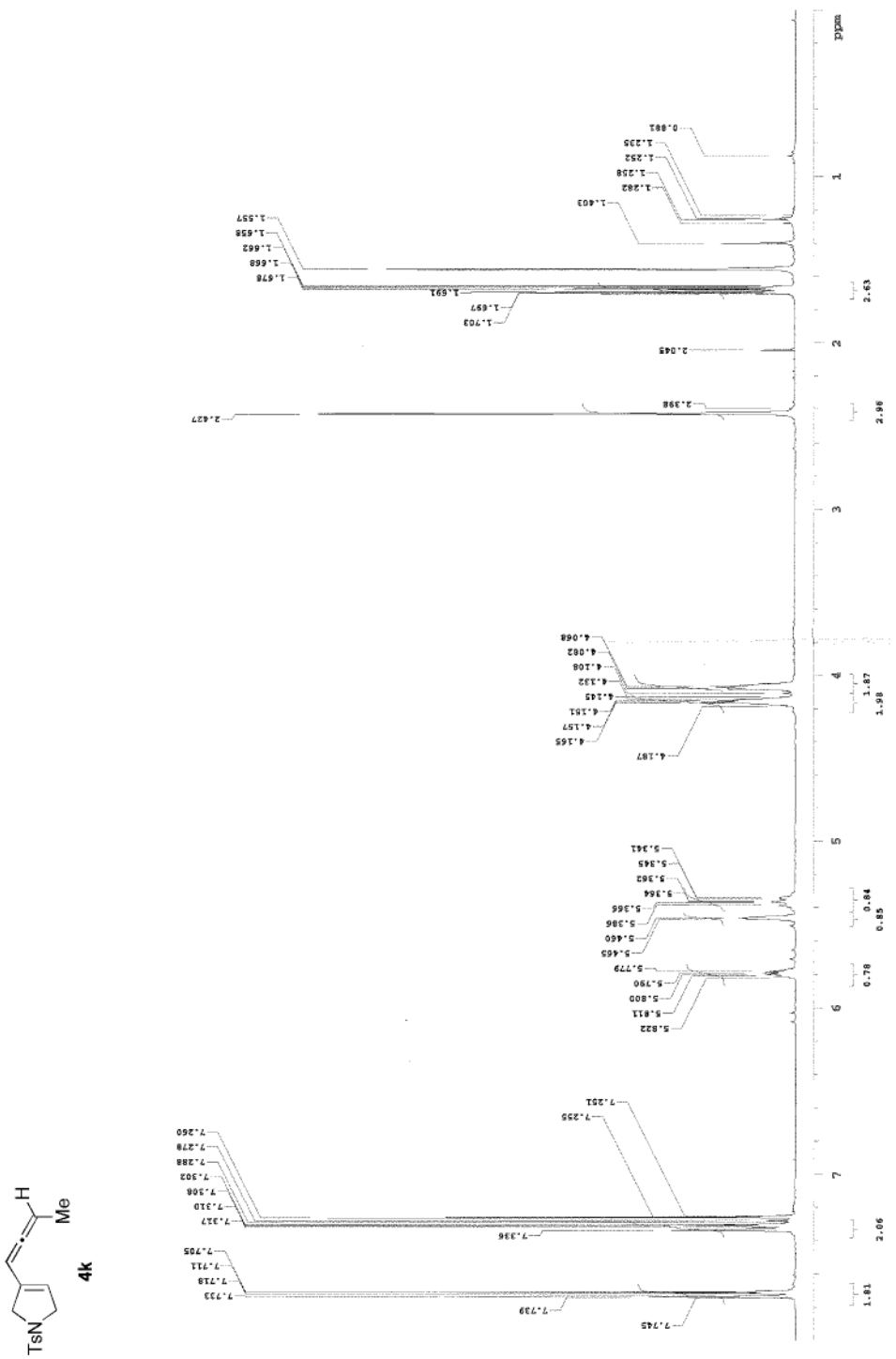

Me
Me
Me
TsN
4g
204.223
143.170
139.758
135.285
129.567
127.316
118.869
98.211
85.869
77.415
77.000
76.570
63.090
54.375
32.050
21.538
20.344
19.975
ppm
0
20
40
60
80
100
120
140
160
180
200
220

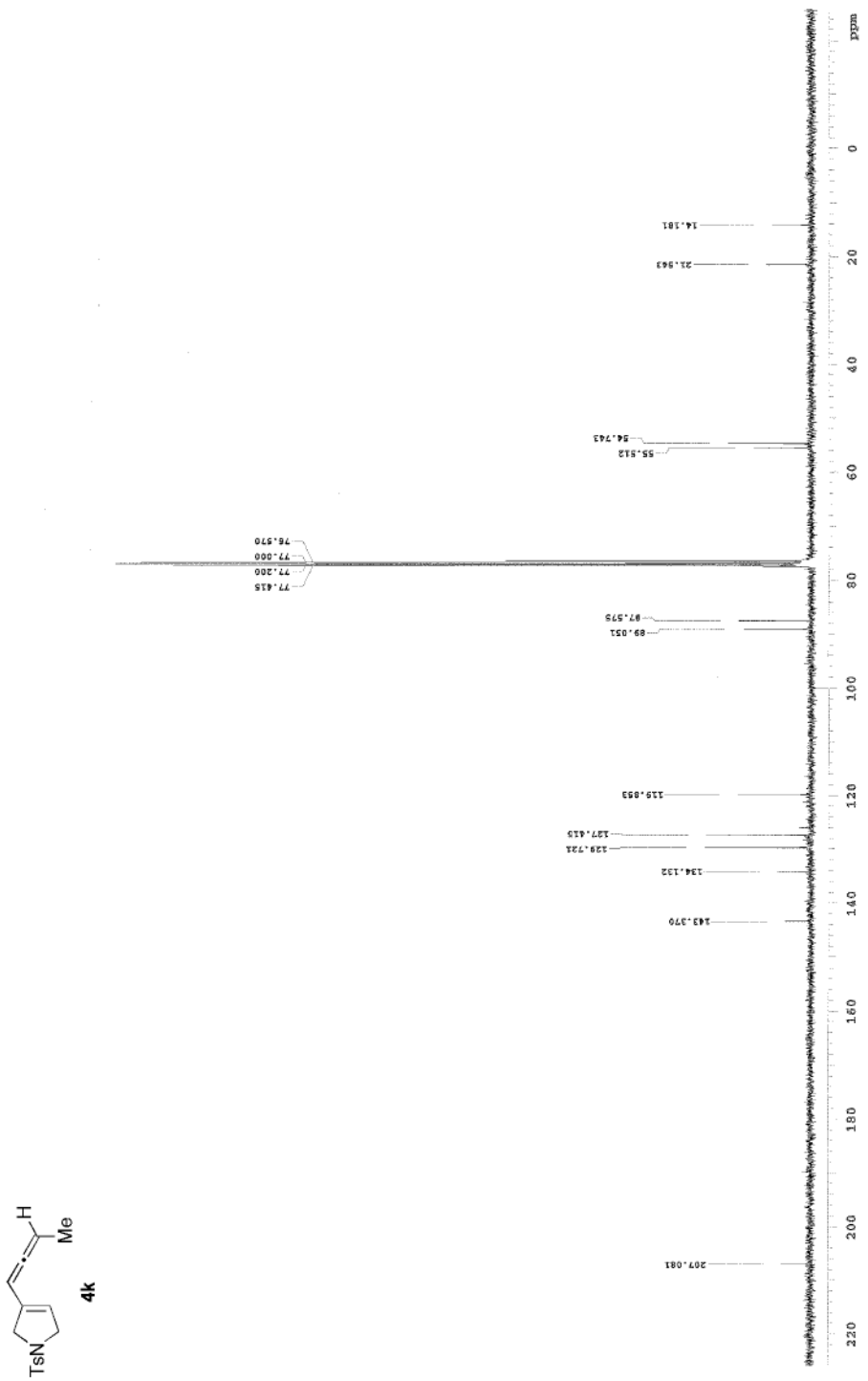

Me
Me
BnN
4i
ppm
1
2
3
4
5
6
7
1.260
1.402
1.680
1.689
1.699
2.048
3.477
3.490
3.522
3.529
3.542
3.554
3.823
5.582
5.599
5.604
5.787
5.795
5.805
5.815
7.231
7.253
7.260
7.269
7.376
7.381
7.299
7.304
7.306
7.310
7.323
7.329
7.332
7.345
7.352
7.356
7.363
7.367
7.389
7.395
5.88
1.98
2.13
2.00
0.91
0.85
3.98

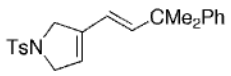

Me
Me
BnN
4i
203.976
139.512
137.130
128.568
128.276
126.862
122.543
97.381
87.129
77.430
77.200
77.000
76.585
60.554
60.477
59.939
20.529
ppm
0
20
40
60
80
100
120
140
160
180
200
220


EtO2C
EtO2C
Me
Me
4j
5.794
5.785
8.776
5.421
5.419
5.417
5.413
5.408
5.406
4.237
4.204
4.180
4.157
3.072
3.065
3.058
2.975
2.969
1.720
1.711
1.649
1.640
1.631
1.374
1.267
1.252
1.243
1.220
ppm

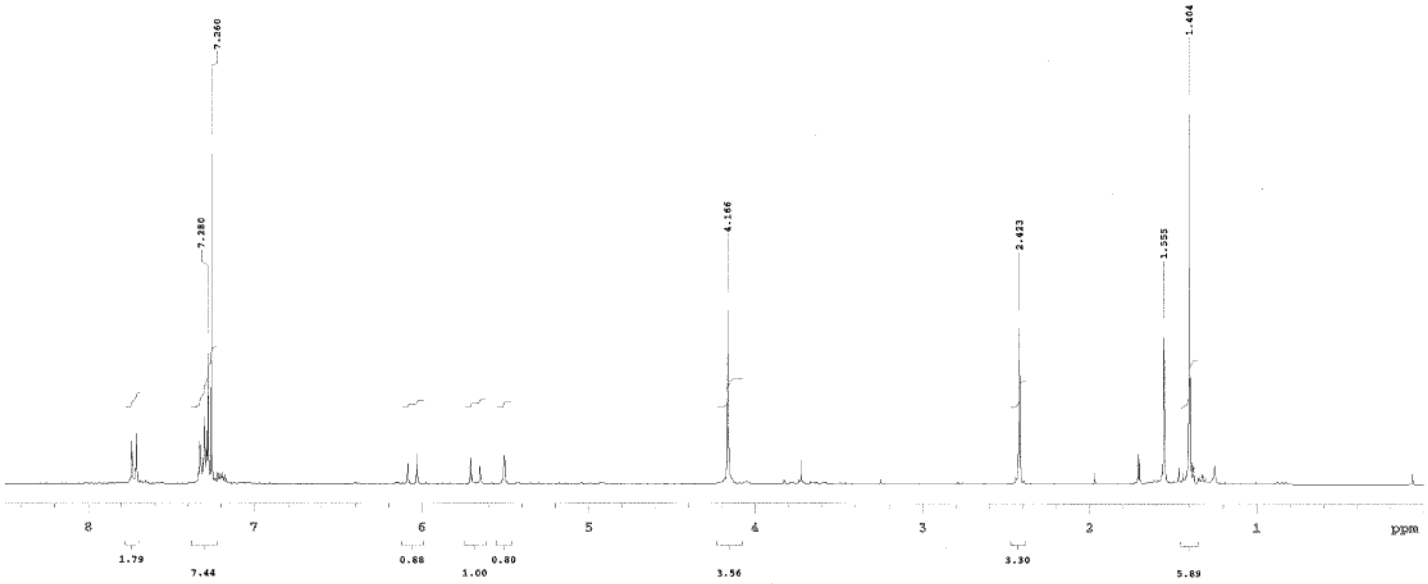

Me
Me
EtO2C
EtO2C
4j
14.027
20.559
40.864
43.110
58.709
61.522
76.585
77.000
77.430
88.436
97.474
122.713
137.037
172.144
204.115
ppm

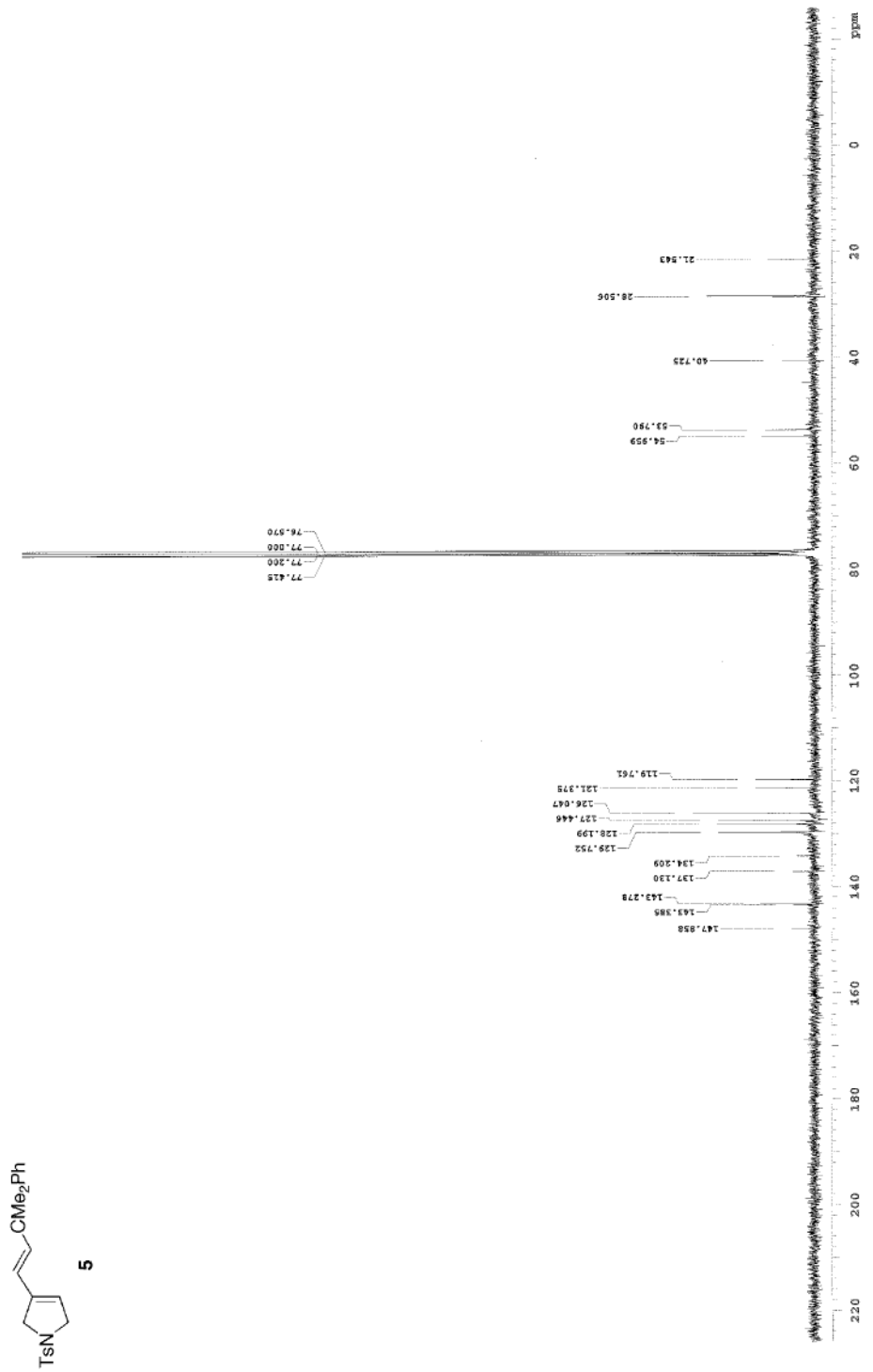

H
Me
TsN
4k

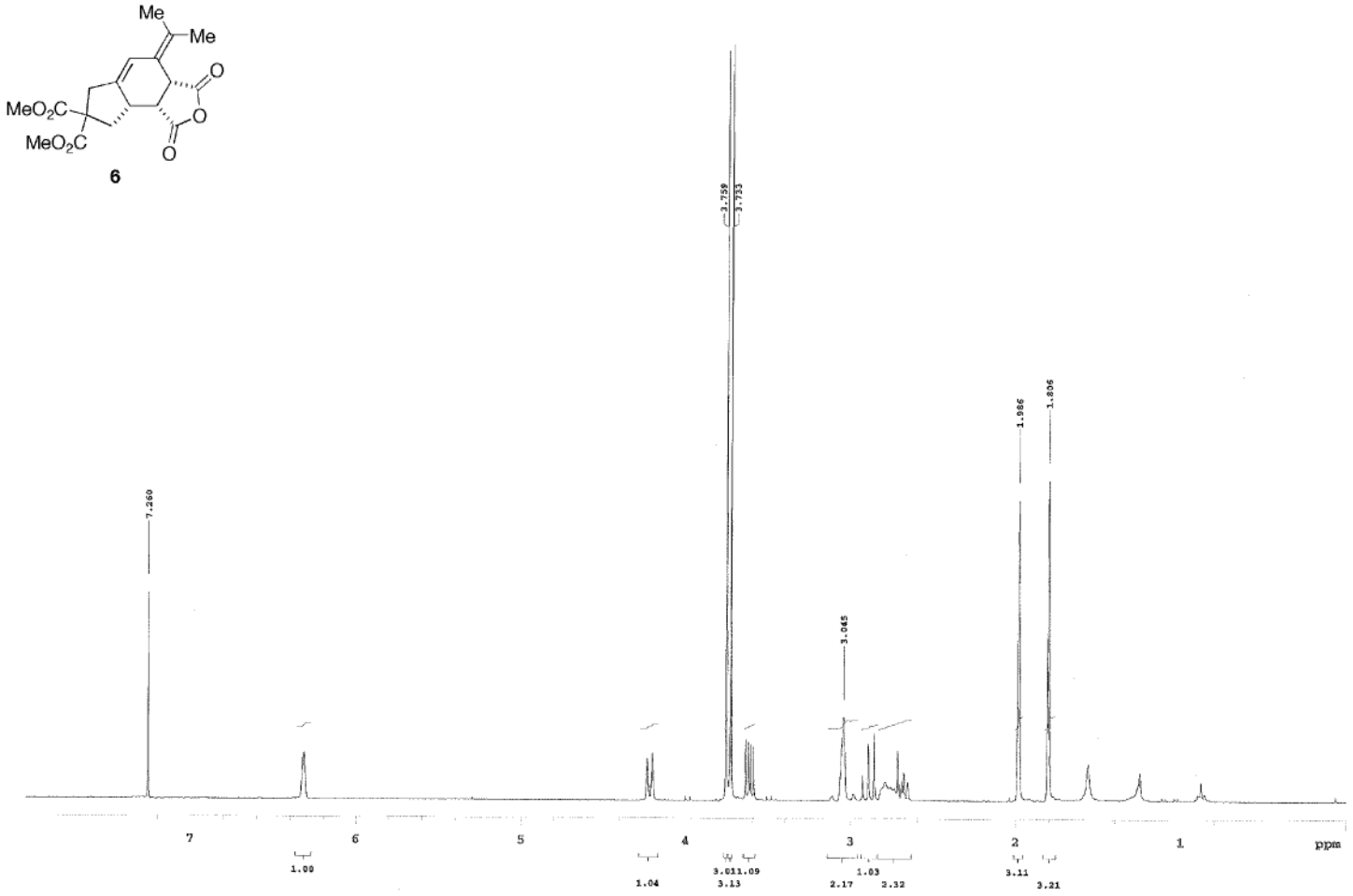

TsN
Me
H
4k
207.081
143.370
134.132
139.724
137.415
119.853
89.051
87.575
77.415
77.200
77.000
76.570
55.512
54.743
21.543
14.181
ppm

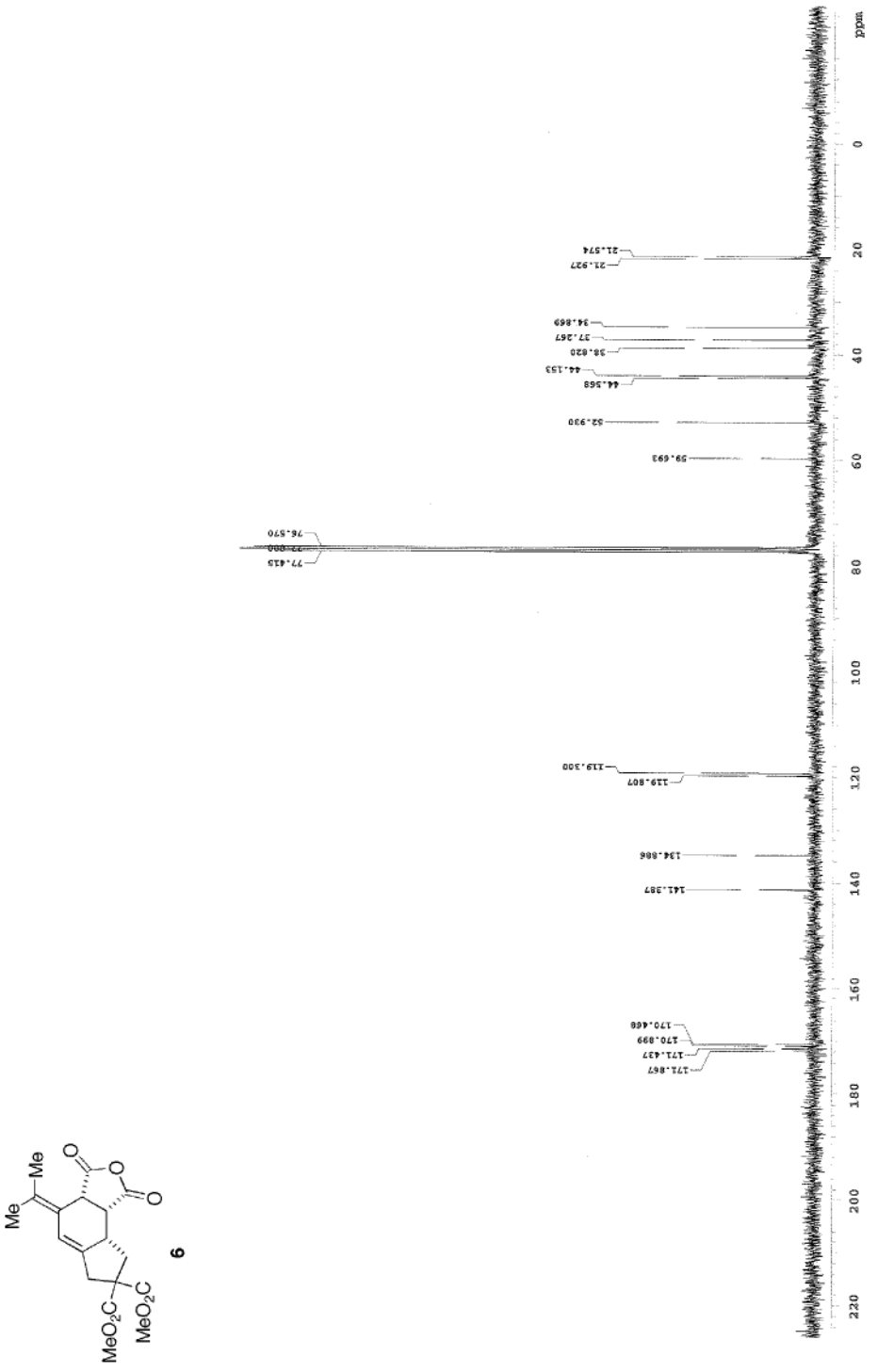

TsN
CMe2Ph

5


7.260
7.280
4.166
2.423
1.555
1.404
8
7
6
5
4
3
2
1
ppm
1.79
7.44
0.88
1.00
0.80
3.56
3.30
5.89


CMe2Ph
TsN
5
147.858
143.385
143.278
137.130
134.309
129.752
128.199
127.446
126.047
121.379
119.761
77.415
77.200
77.000
76.870
54.959
53.780
40.725
28.506
21.543
ppm
220
200
180
160
140
120
100
80
60
40
20
0


Me
Me
MeO2C
MeO2C
O
O
O
6
7.260
3.759
3.733
3.045
1.986
1.806
7
6
5
4
3
2
1
ppm
1.00
1.04
3.011.09
3.13
1.03
2.17
2.32
3.11
3.21


Me
Me
O
O
O
O
MeO2C
MeO2C
6
ppm
0
20
40
60
80
100
120
140
160
180
200
220
21.574
21.927
34.869
37.267
38.820
44.153
44.568
52.930
59.693
76.570
77.000
77.435
119.300
119.807
134.886
141.387
170.468
170.899
171.437
171.867