Electronic Supplementary Information

Cyclization of 5-Alkynones with Chromium Alkylidene Equivalents Generated *in situ* from *gem*-Dichromiomethanes

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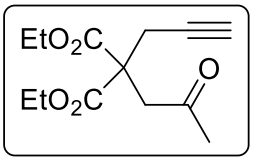
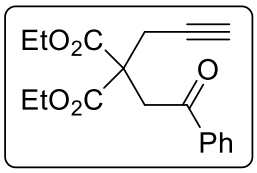
1. General Methods. All operations were performed in a Vac. glove box under a dinitrogen atmosphere or using standard Schlenk techniques under an argon atmosphere. Anhydrous hexane and stabilizer-free THF were purchased from FUJIFILM Wako Pure Chemical. Anhydrous and stabilizer-free DME was purchased from Kanto Chemical. All anhydrous solvents were stored over activated 4 Å molecular sieves and degassed with an argon gas for 20 min before use. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. $CrCl_2$ (anhydrous, powder, 99.99% trace metals basis) was purchased from Sigma-Aldrich. Manganese powder (99.9% trace metals basis) was purchased from Kojundo Chemical Laboratory. (Diiodomethyl)trimethylsilane was prepared according to the reported procedure.[1] ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL ECS-400 spectrometer. Proton chemical shifts were reported in ppm based on the solvent resonance resulting from incomplete deuteration ($CDCl_3$ at 7.26 ppm) as the internal standard. ^{13}C NMR was recorded with complete proton decoupling, and the chemical shifts were reported in ppm relative to $CDCl_3$ at 77.00 ppm as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet. High-resolution mass spectra (HRMS) were measured by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer (JEOL JMS-700 MStation FAB-MS). Melting points were measured on a Yanaco micromelting point apparatus and are uncorrected. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University. Solution state magnetic susceptibility was measured by Evans' method[2] in DME with tetramethylsilane. Corrections were applied for diamagnetism calculated for Pascal constants.[3]

2. Procedure for the Preparation of Diethyl 2-(2-Oxopropyl)-2-(2-propyn-1-yl)-malonate (*pre*-1a). To a mixture of NaH (300 mg, 7.5 mmol) in DMF (65 mL) was treated



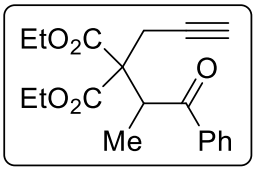
with diethyl 2-(2-propyn-1-yl)malonate (911 mg, 5.0 mmol) at 0 ℃, and stirred at 25 ℃ for 1 h. Bromoacetone (822 mg, 6.0 mmol) was added dropwisely at 0 ℃, and stirred at 25 ℃ for further 24 h. The reaction mixture was quenched with H_2O (30 mL), and extracted with EtOAc (30 mL×3). The combined organic extracts was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent afforded *pre*-**1a** (569 mg, 2.2 mmol, 45% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, J = 6.8 Hz, 6H), 2.01 (t, J = 2.8 Hz, 1H), 2.19 (s, 3H), 3.01 (d, J = 2.8 Hz, 2H), 3.35 (s, 2H), 4.20 (q, J = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 23.1, 30.2, 45.2, 54.3, 62.0, 71.6, 79.3, 169.0, 205.3. HRMS (FAB$^+$): calcd. for $C_{13}H_{19}O_5$ ($[M+H]^+$) 255.1232; found 255.1232.

Diethyl 2-(2-Oxo-2-phenylethyl)-2-(2-propyn-1-yl)malonate (*pre*-1b): Following the



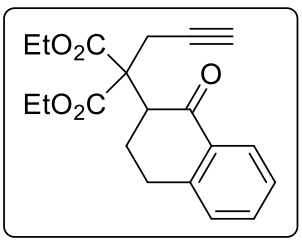
procedure for the synthesis of *pre*-**1a** using diethyl 2-(prop-2-yn-1-yl)malonate (713 mg, 3.6 mmol) provided 900 mg (2.8 mmol, 79% yield) of *pre*-**1b** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 20 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 6H), 1.99 (t, J = 2.8 Hz, 1H), 3.14 (d, J = 2.8 Hz, 2H), 3.91 (s, 2H), 4.23 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.2 Hz, 2H), 7,48 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 23.2, 40.8, 54.6, 62.0, 71.7, 79.4, 128.1, 128.6, 133.5, 136.4, 169.2, 196.8. HRMS (FAB$^+$): calcd. for $C_{18}H_{20}O_5$ ($[M+H]^+$) 317.1389; found 317.1388.

Diethyl 2-(1-Oxo-1-phenylpropan-2-yl)-2-(2-propyn-1-yl)malonate (*pre*-1c): Following the procedure for the synthesis of *pre*-**1c** using diethyl 2-(prop-2-yn-1-yl)malonate (475 mg, 2.4 mmol) provided 396 mg (1.2 mmol, 50% yield) of *pre*-**1c** as a pale yellow oil after



purification by flash chromatography (eluent: hexane / EtOAc = 20 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.44 (d, J = 7.2 Hz, 3H), 2.06 (t, J = 2.8 Hz, 1H), 3.00 (dd, J = 2.8, 17.2 Hz, 1H), 3.07 (dd, J = 2.8, 17.2 Hz, 1H), 4.20-4.28 (m, 4H), 4.46 (q, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 2H), 7.57 (tt, J = 1.6, 7.2 Hz, 1H), 7.99 (dd, J = 1.6, 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.86, 13.89, 14.6, 23.6, 43.8, 58.4, 61.75, 61.8, 71.6, 79.4, 128.5, 128.6, 133.1, 136.1, 169.8, 201.6. HRMS (FAB^+): calcd. for $C_{19}H_{23}O_5$ ($[M+H]^+$) 331.1545; found 331.1548.

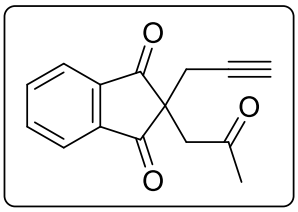
Diethyl 2-(1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-2-(2-propyn-1-yl)malonate (*pre*-1d): Following the procedure for the synthesis of *pre*-**1a** using diethyl 2-(2-propyn-1-yl)malonate (496 mg, 2.5 mmol) provided 315 mg (1.1 mmol, 45% yield) of *pre*-**1d** as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.270 (t, J = 7.2 Hz, 3H), 1.275 (t, J = 7.2 Hz, 3H), 1.70-1.84 (m, 1H), 1.91-2.00 (m, 1H), 2.04 (t, J = 2.8 Hz, 1H), 2.04-2.11 (m, 1H), 2.21-2.38 (m, 3H), 2.85 (dd, J = 2.8, 16.8 Hz, 1H), 2.95 (dd, J = 9.2, 12.4 Hz, 1H), 3.01 (dd, J = 2.8, 16.8 Hz, 1H), 4.19-4.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.92, 13.95, 20.6, 24.2, 26.7, 38.0, 52.3, 57.9, 61.8, 61.9, 71.3, 79.7, 169.0, 169.6, 216.4. HRMS (FAB^+): calcd. for $C_{15}H_{21}O_5$ ($[M+H]^+$) 281.1389; found 281.1393.



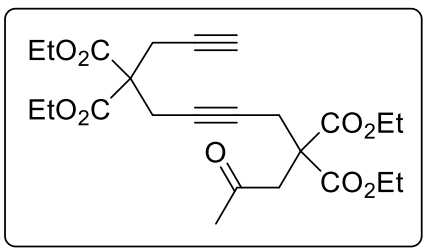
Diethyl 2-(1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-2-(2-propyn-1-yl)malonate (*pre*-1e): Following the procedure for the synthesis of *pre*-**1a** using diethyl 2-(2-propyn-1-yl)malonate (911 mg, 5.0 mmol) provided 703 mg (2.1 mmol, 41% yield) of *pre*-**1e** as a colorless solid after purification by flash chromatography (eluent: hexane / EtOAc =

10 / 1). mp 56.8-57.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 6.8 Hz, 3H), 1.28 (t, J = 6.8 Hz, 3H), 2.00 (t, J = 2.8 Hz, 1H), 2.30 (dd, J = 2.8, 18.0 Hz, 1H), 2.45-2.49 (m, 1H), 2.90 (dd, J = 2.8, 18.0 Hz, 1H), 3.00-3.18 (m, 2H), 3.24 (dd, J = 2.8, 18.0 Hz, 1H), 3.68 (dd, J = 3.6, 13.2 Hz, 1H), 4.22 (q, J = 6.8 Hz, 2H), 4.27 (q, J = 6.8 Hz, 2H), 7.26-7.30 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.8, 26.7, 30.0, 52.9, 57.9, 61.8, 71.3, 80.4, 126.6, 127.5, 128.5, 132.5, 133.4, 143.6, 169.3, 169.4, 196.7. HRMS (FAB$^+$): calcd. for $C_{20}H_{23}O_5$ ([M+H]$^+$) 343.1545; found 343.1540.

2-(2-Oxopropyl)-2-(prop-2-yn-1-yl)-1*H*-indene-1,3-dione (*pre*-1g): Following the procedure for the synthesis of *pre*-**1a** using 2-(prop-2-yn-1-yl)-1*H*-indene-1,3-dione (589 mg, 3.2 mmol) provided 361 mg (1.5 mmol, 47% yield) of *pre*-**1g** as a yellow solid after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). mp 110.9-111.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (t, J = 2.8 Hz, 1H), 2.07 (s, 3H), 2.51 (d, J = 2.8 Hz, 1H), 1.91-2.00 (m, 1H), 2.04 (t, J = 2.8 Hz, 1H), 7.83 (dd, J = 2.8, 6.0 Hz, 2H), 7.97 (dd, J = 2.8, 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 28.6, 48.0, 52.9, 72.9, 77.1, 123.1, 135.4, 141.8, 201.0, 204.7. HRMS (FAB$^+$): calcd. for $C_{15}H_{13}O_3$ ([M+H]$^+$) 241.0865; found 241.0874.



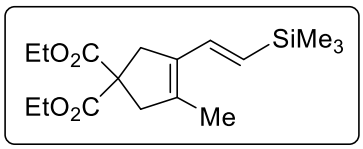
Tetraethyl 11-Oxododeca-1,6-diyne-4,4,9,9-tetracarboxylate (*pre*-2): Following the procedure for the synthesis of *pre*-**1a** using tetraethyl nona-3,8-diyne-1,1,6,6-tetracarboxylate (326 mg, 0.80 mmol) provided 123 mg (0.26 mmol, 33% yield) of *pre*-**2** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 5 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J



= 6.8 Hz, 6H), 1.28 (t, *J* = 6.8 Hz, 6H), 1.58 (s, 3H), 1.99 (d, *J* = 2.4 Hz, 1H), 2.71 (t, *J* = 2.4 Hz, 1H), 2.73 (t, *J* = 2.4 Hz, 1H), 2.91 (d, *J* = 2.4 Hz, 2H), 2.90-2.93 (m, 5H), 3.47 (t, *J* = 8.0 Hz, 1H), 4.17-4.26 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.99, 14.02, 18.7, 22.4, 22.7, 51.2, 56.5, 61.7, 61.9, 71.4, 76.3, 78.7, 79.4, 167.9, 168.7. HRMS (FAB^+): calcd. for $C_{24}H_{33}O_9$ ($[M+H]^+$) 465.2125; found 465.2106.

3. General Procedure for Chromium-Mediated Cyclization of 5-Alkynones. In a nitrogen-filled glovebox, a flame-dried Schlenk flask was charged with $CrCl_2$ (98.3 mg, 0.80 mmol). The flask was removed from the glovebox, and subsequently treated with (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol), manganese (65.9 mg, 1.2 mmol) and DME (2.0 mL) at 25 °C. After stirring for 30 min, 5-alkynones (0.20 mmol) was added to the resulting brown reaction mixture, and further stirred at 70 °C for 20 h. The resulting mixture was quenched with water (10 mL), and extracted with Et_2O for three times (10 mL $\times$3). The combined organic extracts were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel to afford the corresponding ethenylcyclopentenes **1** and **2**.

Diethyl (*E*)-3-Methyl-4-(2-(trimethylsilyl)vinyl)-3-cyclopentene-1,1-dicarboxylate (1a):



Following the general procedure using diethyl 2-(2-oxopropyl)-2-(2-propyn-1-yl) malonate (*pre*-**1a**) (50.8 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 51.9 mg (0.16 mmol, 80% yield) of **1a** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 50 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.79 (s, 3H), 3.07 (s, 2H), 3.15 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 4H), 5.70 (d, *J* = 18.8 Hz), 6.74 (d, *J* = 18.8 Hz). ^{13}C NMR (100

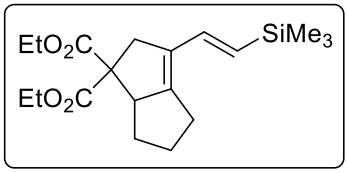
MHz, $CDCl_3$): δ -1.2, 13.5, 14.0, 40.7, 46.6, 56.8, 61.5, 129.6, 132.7, 134.9, 136.8, 172.2. HRMS (FAB^+): calcd. for $C_{17}H_{28}O_4Si$ ($[M+H]^+$) 325.1835; found 325.1821.

Diethyl (*E*)-3-Phethyl-4-(2-(trimethylsilyl)vinyl)-3-cyclopentene-1,1-dicarboxylate (1b): Following the general procedure using diethyl 2-(2-oxo-2-phenylethyl)-2-(2-propyn-1-yl)malonate (*pre*-**1b**) (63.2 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 57.2 mg (0.15 mmol, 74% yield) of **1b** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 50 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.58 (s, 9H), 1.27 (t, *J* = 7.6 Hz, 6H), 3.36 (s, 2H), 3.51 (s, 2H), 4.23 (q, *J* = 7.6 Hz, 4H), 5.91 (d, *J* = 18.8 Hz, 1H), 6.89 (d, *J* = 18.8 Hz, 1H), 7.28-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.3, 14.1, 41.5, 45.3, 56.8, 61.7, 127.4, 128.2, 128.3, 132.7, 134.6, 136.4, 136.9, 137.9, 172.0. HRMS (FAB^+): calcd. for $C_{22}H_{31}O_4Si$ ($[M+H]^+$) 387.1992; found 387.1983.

Diethyl (*E*)-2-Methyl-3-phethyl-4-(2-(trimethylsilyl)vinyl)-3-cyclopentene-1,1-dicarboxylate (1c): Following the general procedure using diethyl 2-(1-oxo-1-phenylpropan-2-yl)-2-(2-propyn-1-yl)-malonate (*pre*-**1c**) (66.1 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 56.9 mg (0.14 mmol, 71% yield) of **1c** as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 9H), 0.91 (d, *J* = 7.2 Hz, 3H), 1.270 (d, *J* = 7.2 Hz, 3H), 1.274 (d, *J* = 7.2 Hz, 3H), 3.00 (d, *J* = 14.0 Hz, 1H), 3.63 (d, *J* = 14.0 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 1H), 4.14-4.31 (m, 4H), 5.86 (d, *J* = 19.2 Hz, 1H), 6.74 (d, *J* = 19.2 Hz, 1H), 7.28-7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.3, 14.0, 14.1, 14.5, 39.2, 49.1, 61.3, 61.5, 62.0, 127.4, 128.2, 129.0, 132.0, 133.1, 135.8, 138.2, 143.7,

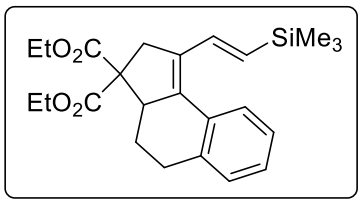
170.3, 172.2. HRMS (FAB$^+$): calcd. for $C_{23}H_{32}O_4Si$ ([M]$^+$) 400.2070; found 400.2070.

Bicycle 1d: Following the general procedure using diethyl 2-(1-oxo-1,2,3,4-tetrahydro-



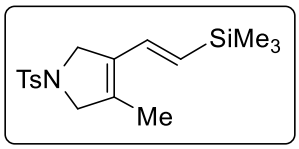
naphthalen-2-yl)-2-(2-propyn-1-yl)malonate (*pre*-**1d**) (56.1 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 52.6 mg (0.15 mmol, 75% yield) of **1d** as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H), 0.99-1.11 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H) 1.25 (t, *J* = 7.2 Hz, 3H), 1.86-2.03 (m, 3H), 2.20-2.31 (m, 2H), 3.00 (d, *J* = 16.4 Hz, 1H), 3.56 (d, *J* = 16.4 Hz, 1H), 3.89-3.92 (m, 1H) 4.11-4.26 (m, 4H), 5.66 (d, *J* = 18.8 Hz, 1H), 6.58 (d, *J* = 18.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.2, 14.1, 14.2, 22.4, 27.6, 28.1, 44.9, 57.8, 60.3, 61.1, 61.3, 128.0, 129.6, 137.6, 148.7, 170.6, 172.1. HRMS (FAB$^+$): calcd. for $C_{19}H_{31}O_4Si$ ([M+H]$^+$) 351.1992; found 351.1986.

Tricycle 1e: Following the general procedure using diethyl 2-(1-oxo-1,2,3,4-tetrahydro-



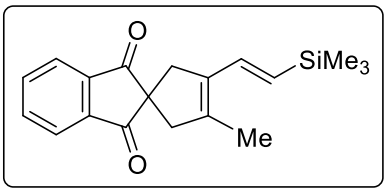
naphthalen-2-yl)-2-(prop-2-yn-1-yl)malonate (*pre*-**1e**) (68.4 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 59.4 mg (0.14 mmol, 72% yield) of **1e** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 20 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.12 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H) 1.28 (t, *J* = 7.2 Hz, 3H), 1.63 (dq, *J* = 5.6, 12.4 Hz, 1H), 2.07-2.14 (m, 1H), 2.89-3.06 (m, 2H), 3.13 (d, *J* = 17.2 Hz, 1H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.86 (dd, *J* = 4.0, 12.4 Hz, 1H) 4.14-4.32 (m, 4H), 5.97 (d, *J* = 18.4 Hz, 1H), 7.13-7.23 (m, 4H), 7.51 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.3, 14.0, 14.1, 26.8, 30.2, 41.8, 51.3, 60.2, 61.3, 61.4, 125.6, 127.4, 128.0, 128.8, 131.8, 132.8, 133.2, 136.0, 137.6, 138.3, 170.5, 172.1. HRMS (FAB$^+$): calcd. for $C_{24}H_{33}O_4Si$ ([M]$^+$) 412.2070; found 412.2080.

Diethyl (*E*)-3-Methyl-4-(2-(trimethylsilyl)vinyl)-3-cyclopentene-1,1-dicarboxylate (1f):



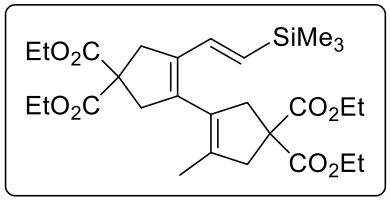
Following the general procedure using 4-methyl-*N*-(2-oxo-propyl)-*N*-(2-propyn-1-yl)benzenesulfonamide (*pre*-**1f**) (53.1 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 42.9 mg (0.13 mmol, 64% yield) of **1f** as a colorless solid after purification by flash chromatography (eluent: hexane / EtOAc = 100 / 1). mp 94.4-95.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 9H), 1.73 (s, 3H), 2.42 (s, 3H), 4.09 (s, 2H), 4.20 (s, 2H), 5.61 (d, *J* = 19.2 Hz, 1H), 6.59 (d, *J* = 19.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.4, 11.4, 21.5, 55.0, 59.6, 127.5, 129.7, 130.8, 131.4, 132.0, 134.0, 134.1, 143.4. HRMS (FAB$^+$): calcd. for $C_{17}H_{25}NO_2SSi$ ([M]$^+$) 335.1375; found 335.1377.

Spiocycle 1g: Following the general procedure using 2-(2-oxopropyl)-2-(prop-2-yn-1-yl)-



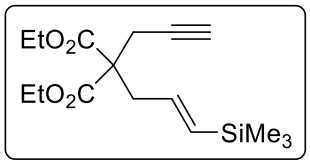
1*H*-indene-1,3-dione (*pre*-**1g**) (48.1 mg, 0.20 mmol) and (diiodomethyl)trimethylsilane (136.0 mg, 0.40 mmol) provided 373.3 mg (0.12 mmol, 60% yield) of **1g** as a yellow solid after purification by flash chromatography (eluent: hexane / EtOAc = 5 / 1). mp 105.5-107.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H), 1.86 (s, 3H), 2.81 (s, 2H), 2.89 (s, 2H), 5.59 (d, *J* = 19.2 Hz, 1H), 6.80 (d, *J* = 19.2 Hz, 1H), 7.84 (dd, *J* = 2.8, 6.0 Hz, 2H), 7.99 (dd, *J* = 2.8, 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.2, 13.6, 41.9, 46.7, 56.1, 123.5, 130.0, 133.2, 135.5, 135.7, 136.8, 141.7, 203.6. HRMS (FAB$^+$): calcd. for $C_{19}H_{22}O_2Si$ ([M]$^+$) 310.1389; found 310.1385.

Conjugated Triene 2: Following the general procedure using tetraethyl 11-oxododeca-1,6-diyne-4,4,9,9-tetracarboxylate (*pre*-**2**) (46.4 mg, 0.10 mmol) and (diiodomethyl)trimethyl-silane (68.0 mg, 0.20 mmol) provided 34.2 mg (0.064 mmol, 64% yield) of **2** as a yellow



oil after purification by flash chromatography (eluent: hexane / EtOAc = 5 / 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (s, 9H), 1.245 (t, *J* = 7.2 Hz, 6H), 1.248 (t, *J* = 7.2 Hz, 6H), 1.56 (s, 3H), 3.02 (m, 2H), 3.06 (m, 2H), 3.13 (m, 2H), 3.20 (m, 2H), 4.14-4.23 (m, 8H), 5.75 (d, *J* = 19.2 Hz, 1H), 6.45 (d, *J* = 19.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.2, 14.0 (two peaks overlapped), 15.3, 40.3, 43.4, 43.8, 45.8, 57.2, 57.8, 61.5, 61.6, 128.2, 130.7, 133.8, 134.2, 135.1, 138.7, 171.96, 172.01. HRMS (FAB$^+$): calcd. for $C_{28}H_{43}O_8Si$ ([M+H]$^+$) 535.2727; found 535.2718.

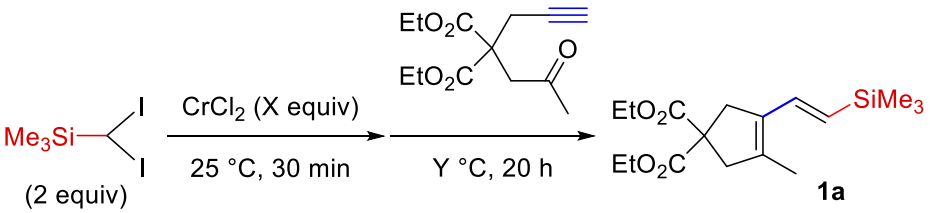
Diethyl (*E*)-2-(prop-2-yn-1-yl)-2-(3-(trimethylsilyl)allyl)- malonate (3): Following the general procedure using diethyl 2-(2-oxoethyl)-2-(prop-2-yn-1-yl)malonate (60.1 mg, 0.25 mmol) provided 58.0 mg (0.16 mmol, 80% yield,) of **3** as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 20 / 1). The stereoselectivity was determined to be *cis* / *trans* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 6H), 2.01 (t, *J* = 2.8 Hz, 1H), 2.78 (d, *J* = 2.8 Hz, 2H), 2.84 (d, *J* = 5.6 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 4H), 5.81-5.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.4, 14.1, 22.7, 39.3, 56.7, 61.6, 71.3, 79.0, 136.6, 139.3, 169.7. HRMS (FAB$^+$): calcd for $C_{16}H_{27}O_4Si$ ([M+H]$^+$) 311.1678; found. 311.1660.



4. Procedure for the Preparation of [CrCl(dme)](μ-CHSiMe$_3$)(μ-Cl)$_2$ (4). To a pale blue suspension of chromium(II) chloride (1.00 g, 8.14 mmol) in THF (20 mL) was added (diiodomethyl)trimethylsilane (600 mg, 1.76 mmol) at 25 °C. After stirring for 6 h at 25 °C, insoluble materials were removed by centrifugation. The brown supernatant was concentrated to *ca.* 5 mL in *vacuo* and stored at –20 °C for 3 h. Brown insoluble materials were removed by centrifugation again, and the supernatant was dried under reduced

pressure. The residue was dissolved in DME (5.0 mL) and stirred for 10 min at 25 °C. Addition of hexane (10 mL) resulted in the precipitation of a brown solid, and the supernatant was removed by a pipette. The precipitate was washed twice by a mixture of DME (2.0 mL) and hexane (3.0 mL), and dried under reduced pressure to give **4** as a yellowish brown powder (611 mg, 1.19 mmol, 68% yield). Yellowish brown crystals of **4** were grown from a DME solution layer with hexane at 25 °C. μ_{eff} (Evans' method, DME, 25 °C): 6.64 μ_B. Anal. Calcd. for $C_{12}H_{30}O_4Cl_4SiCr_2$: C, 28.14; H, 5.90. Found: C, 27.76; H, 5.97.

Table S1. Optimization of reaction conditions



entry	X	solvent	Y	Yield of **1a** [a] / %	Recov.[a] / %
1	8	THF	70	70	0
2	8	THF	50	32	46
3	8	THF	25	0	93
4	8	DME	70	85	0
5	4	DME	70	58	21
6[b]	4	DME	70	82 (80)	0
7[b]	0.4	DME	70	23	58
8[c]	8	DME	70	0	0

[a] Determined by ^{1}H NMR. Isolated yields were in parentheses. [b] Mn (6 equiv) was added. [c] With TMEDA (8 equiv).

5. X-ray Crystallographic Studies of [CrCl(dme)](μ-CHSiMe$_3$)(μ-Cl)$_2$ Complex 4 (CCDC 2006641): A yellowish brown crystal of **4** suitable for X-ray analysis was obtained by recrystallization from a DME solution layer with hexane at 25 °C, and placed on the end of a micro-mount coated with NVH oil. The X-ray intensity data collection was carried out on a Rigaku Varimax with a Saturn 944+ CCD area detector using

graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) at 100(2) K. Details of crystal and data collection parameters are summarized in Table S2. Preliminary indexing was performed from a set of twelve frames. Equivalent reflections were merged, and the collected images were processed by a Rigaku CrystalClear program. The initial structure was determined by the direct method on SHELXS.[4] The further structure determination was performed by Fourier transform method and refined by least squares method on SHELXL.[4] All reflections were used during refinement with the exception of affected reflections by the beam-stopper. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models, except for the methine hydrogen of the $CHSiMe_3$ ligand. One site occupied by hexane was identified in the asymmetric unit. This site was considerably disordered and was treated by SQUEEZE as a diffuse contribution.[5] In the resulting void space, a contribution of 70 e^- per unit cell was found and taken to represent 0.5 hexane in the asymmetric unit for each dinuclear complex. This result was checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups. An ORTEP drawing is shown in Figure 2 in the main text.

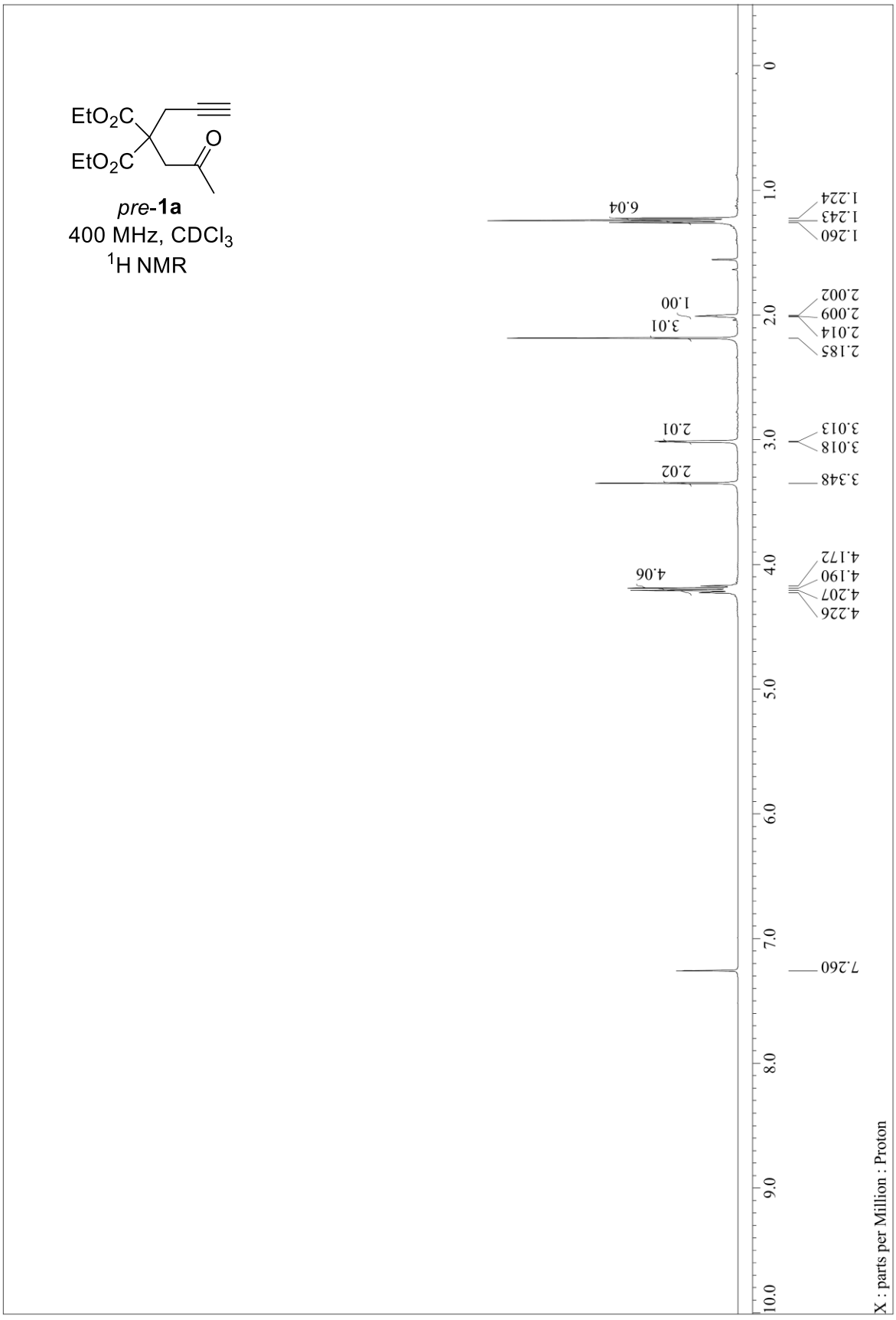
6. References

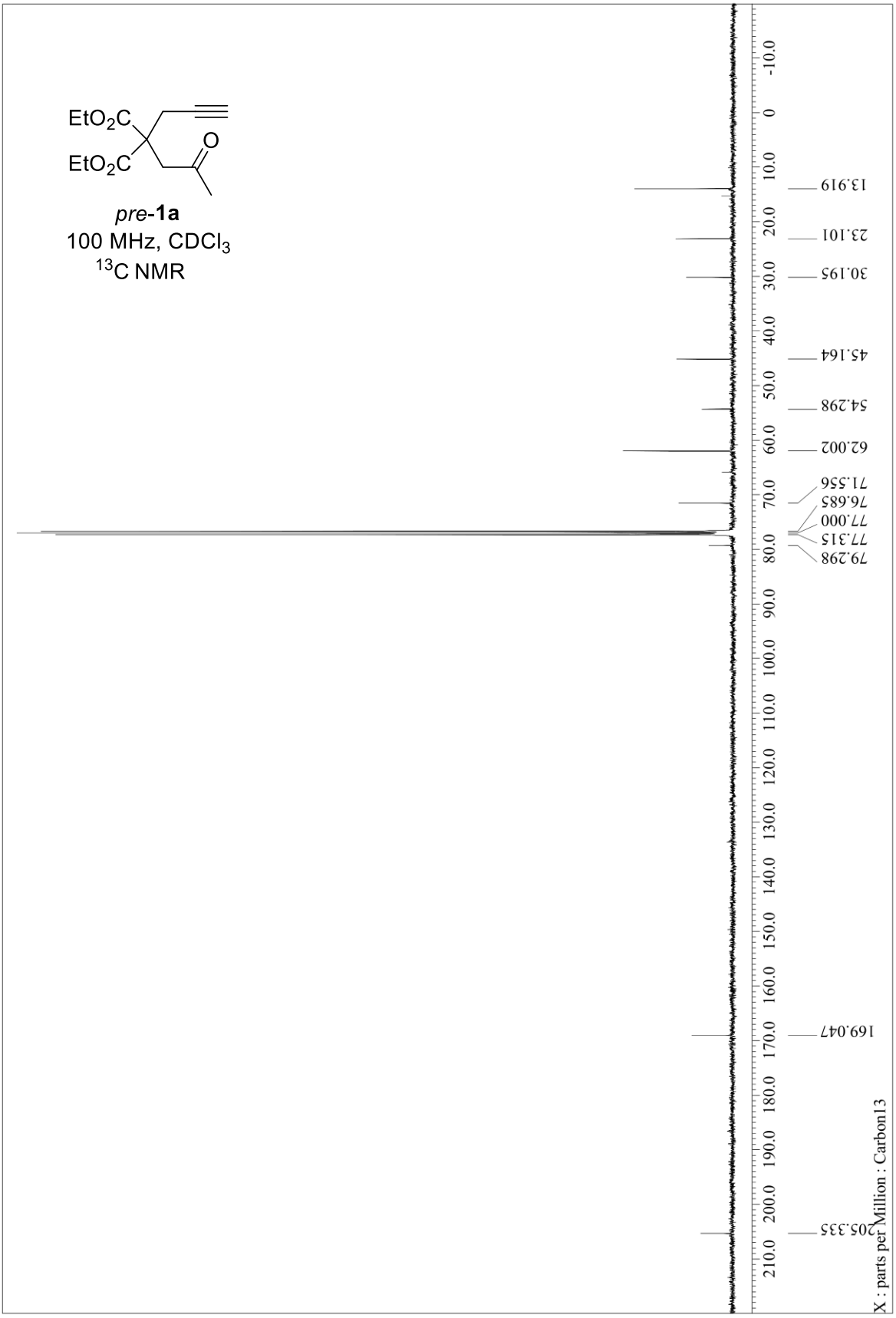
1. (a) K. Takai, Y. Kunisada, Y. Tachibana, N. Yamaji and E. Nakatani, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1581; (b) J. A. Bull and A. B. Charette, *J. Org. Chem.*, 2008, **73**, 8097.
2. (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (b) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.
3. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.
4. (a) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112; (b) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3.
5. (a) P. van der Sluis, A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194; (b) A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148; (c) A. L. Spek, *Acta Crystallogr.*, 2015, **C71**, 9.

Table S2. Summary of Crystallographic Data of [CrCl(dme)](μ-$CHSiMe_3$)(μ-$Cl)_2$ **4**

Empirical formula: $C_{12}H_{30}Cl_4Cr_2O_4Si \cdot 0.5(C_6H_{14})$
Formula weight: 555.33
Crystal system: monoclinic
Space group: $P2_1$ (No. 4)
Crystal color: yellow
Lattice parameters:
a (Å) = 6.5229(16), *b* (Å) = 20.072(5), *c* (Å) = 10.299(3)
β (°) = 104.225(3)
V ($Å^3$) = 1307.1(6), Z = 2
D_{calc} (g cm^{-3}): 1.411
Goodness of fit (GOF) = 1.006
F(000): 578
Temp (°C): -173.0
Completeness to theta = 27.55°: 99.6 %
No. of reflections measured total: 14655
No. of observns ($I > 3.00\sigma(I)$): 5984
Refinement: Full-Matrix Least-Squares on F^2
Residuals (all data): R_1 = 0.0348, wR_2 = 0.0626
Max Shift/Error in Final Cycle: 0.010
Maximum peak in Final Diff Map (e ($Å^{-3}$): 0.322
Minimum peak in Final Diff Map (e ($Å^{-3}$): -0.439

7. ^{1}H NMR and ^{13}C NMR Spectra of New Compounds

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O
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71.556
76.685
77.000
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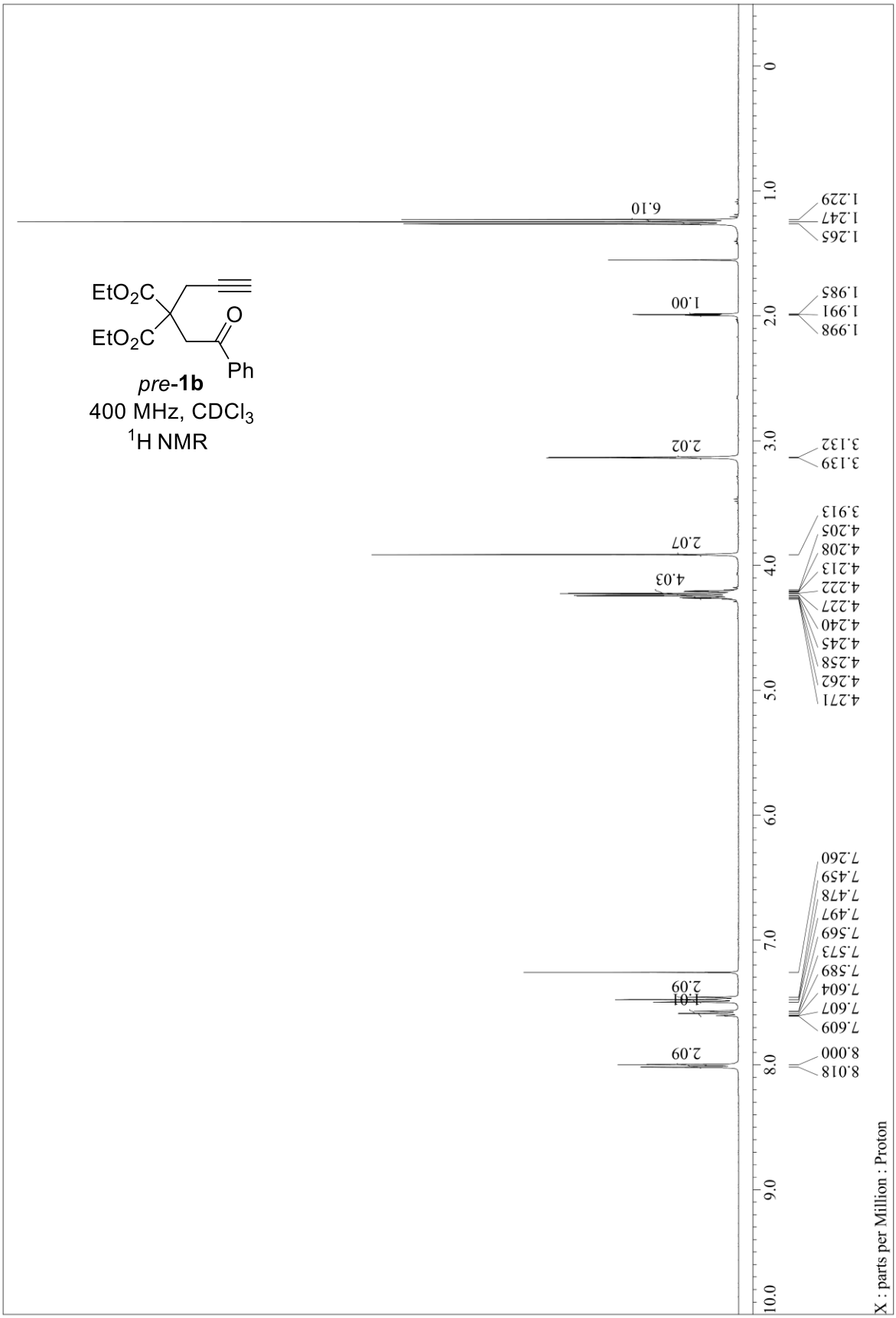
79.298
169.047
205.335
X : parts per Million : Carbon13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EtO2C
O
Ph
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4.03
1.01
2.09
2.09
1.229
1.247
1.265
1.985
1.991
1.998
3.132
3.139
3.913
4.205
4.208
4.213
4.222
4.227
4.240
4.245
4.258
4.262
4.271
7.260
7.459
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7.497
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7.573
7.589
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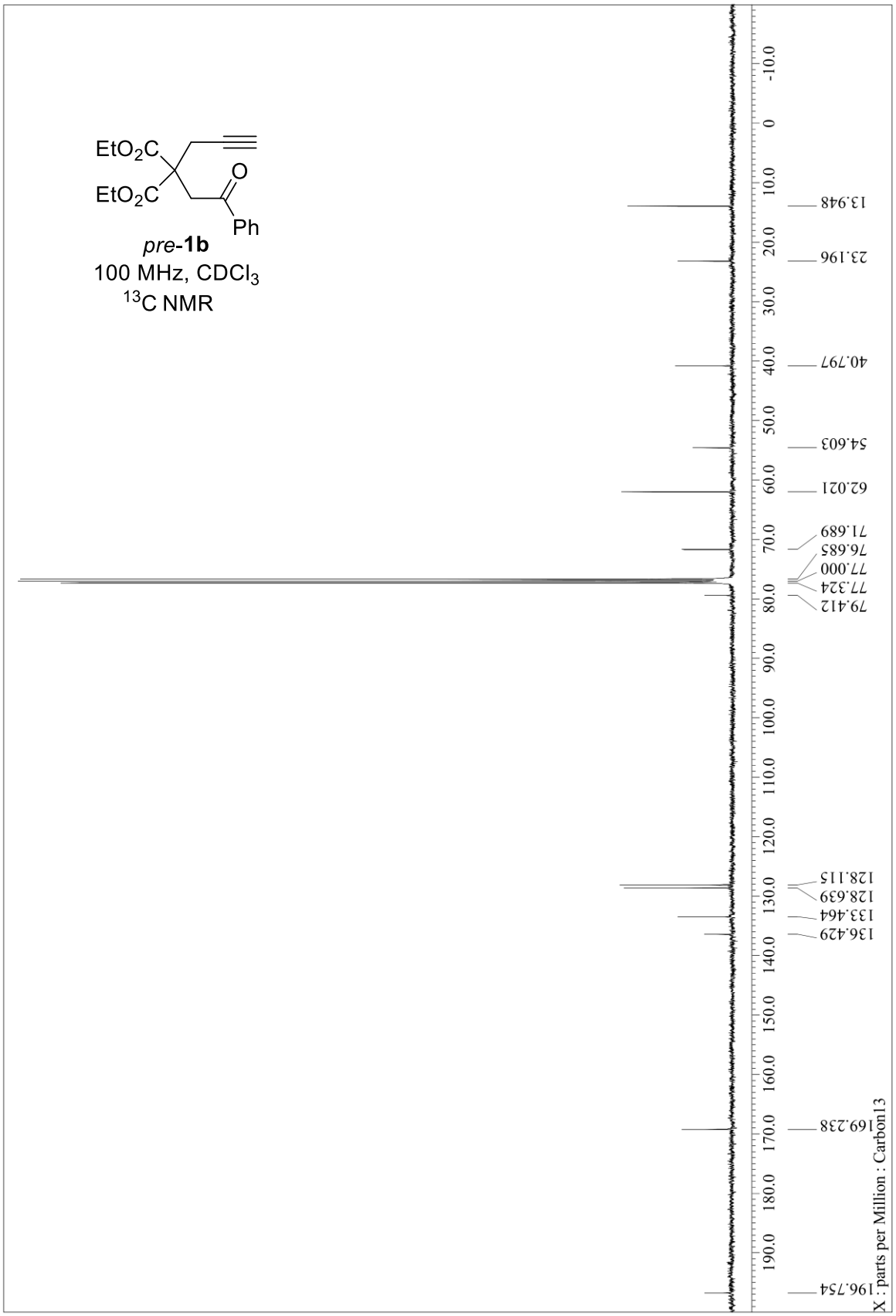
7.607
7.609
8.000
8.018
X : parts per Million : Proton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Ph
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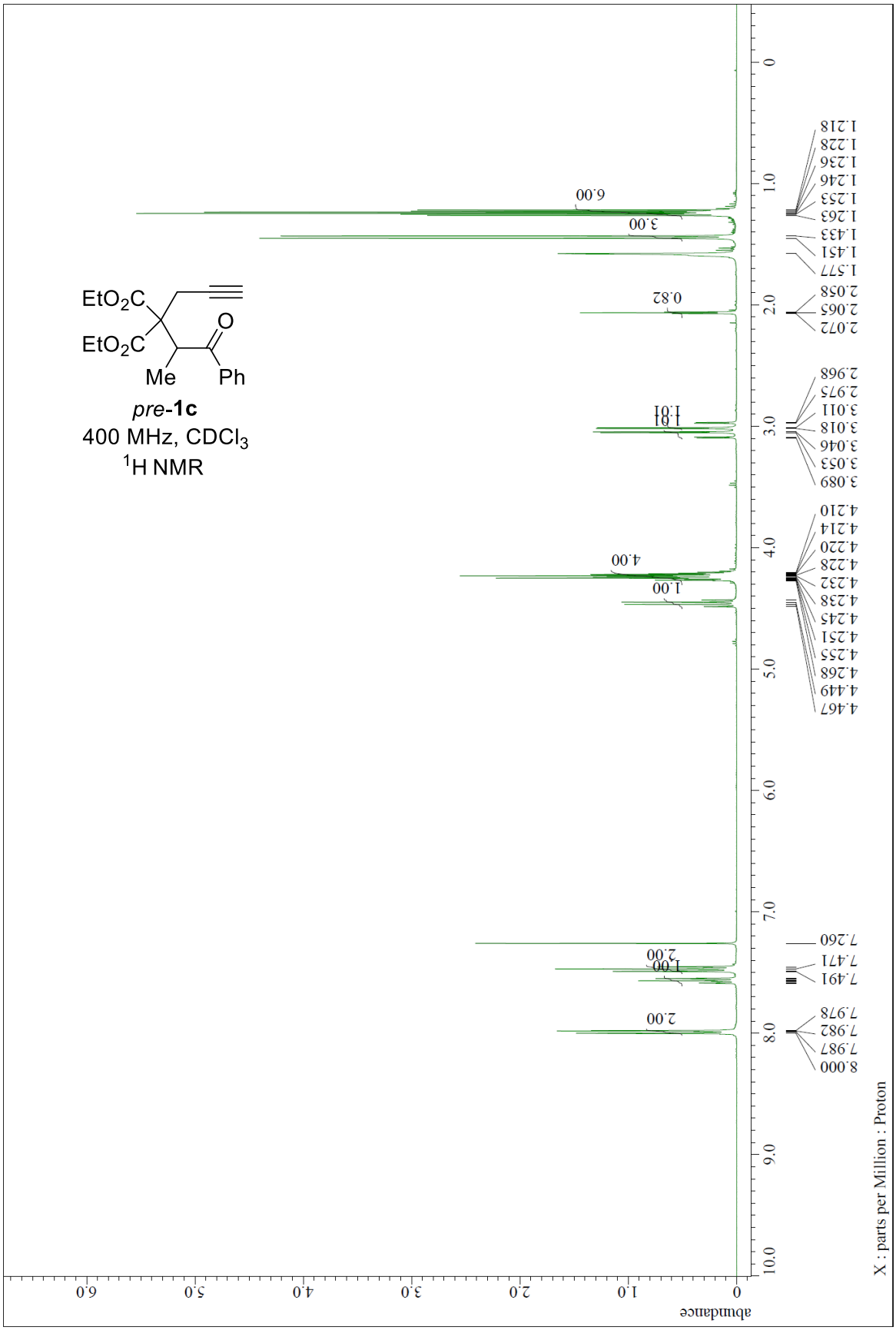
X : parts per Million : Carbon13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EtO2C
O
Me
Ph
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1.01
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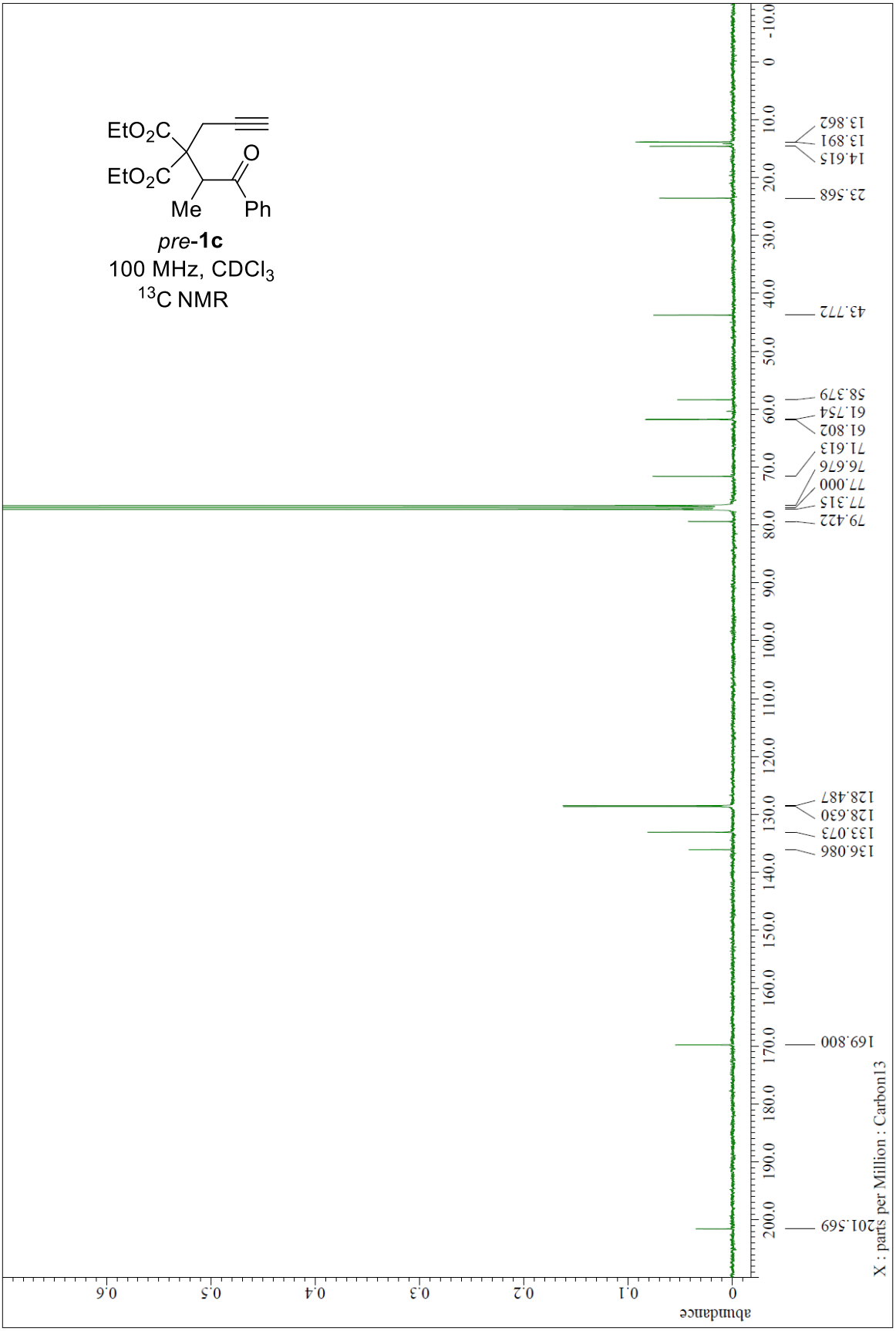
1.00
2.00
1.00
2.00
abundance
X : parts per Million : Proton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Ph
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128.487
79.422
77.315
77.000
76.676
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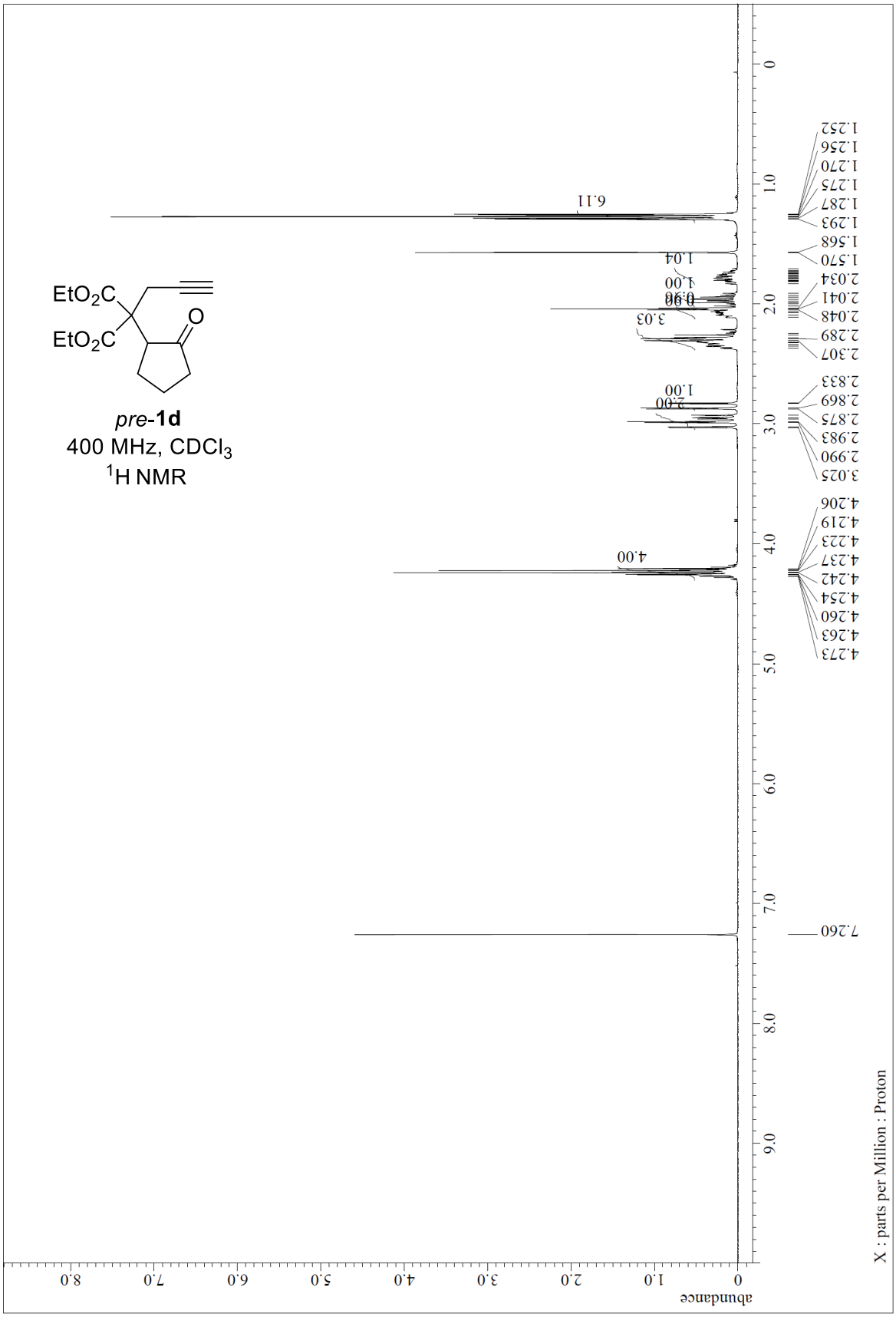
abundance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2.875
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2.990
3.025
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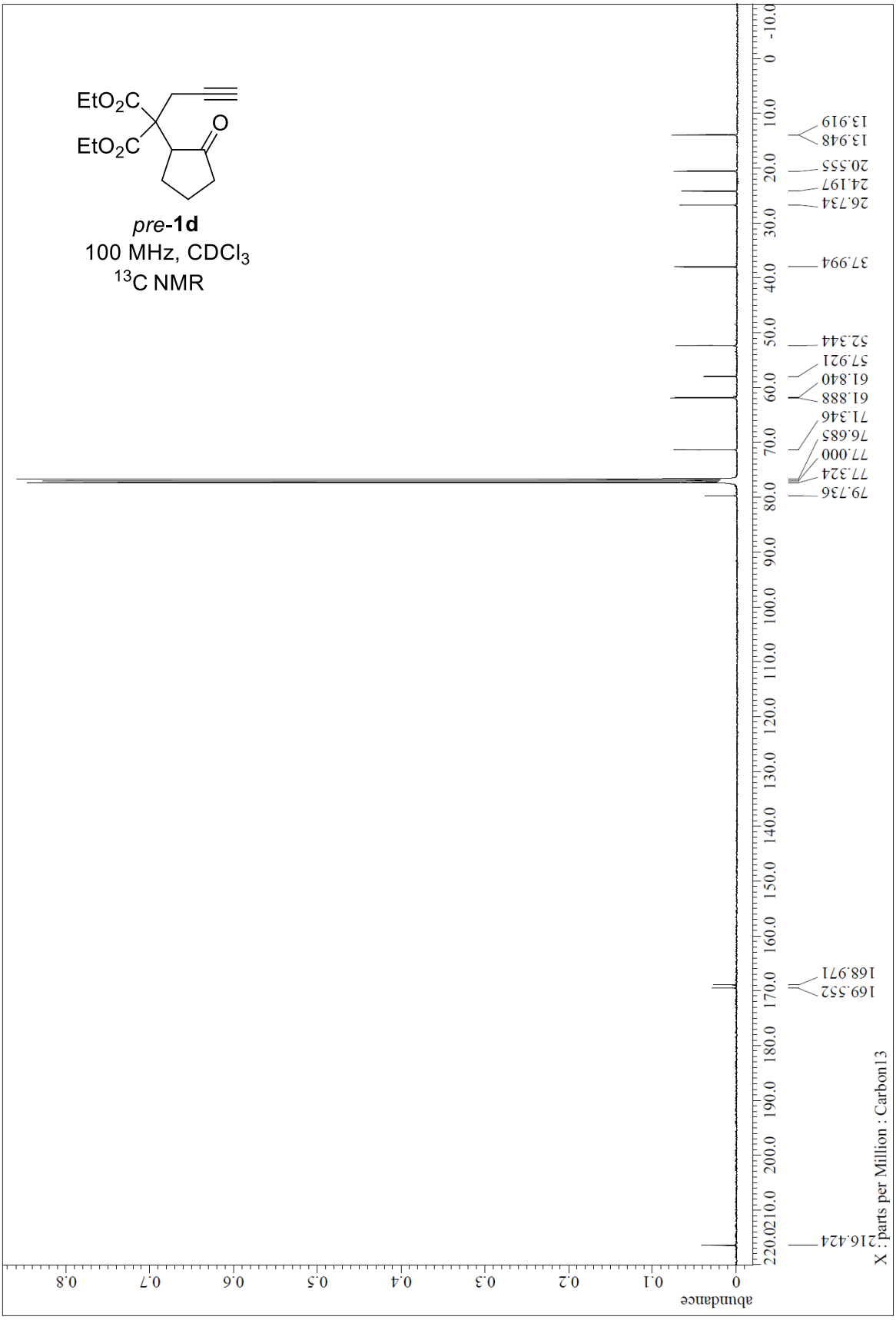
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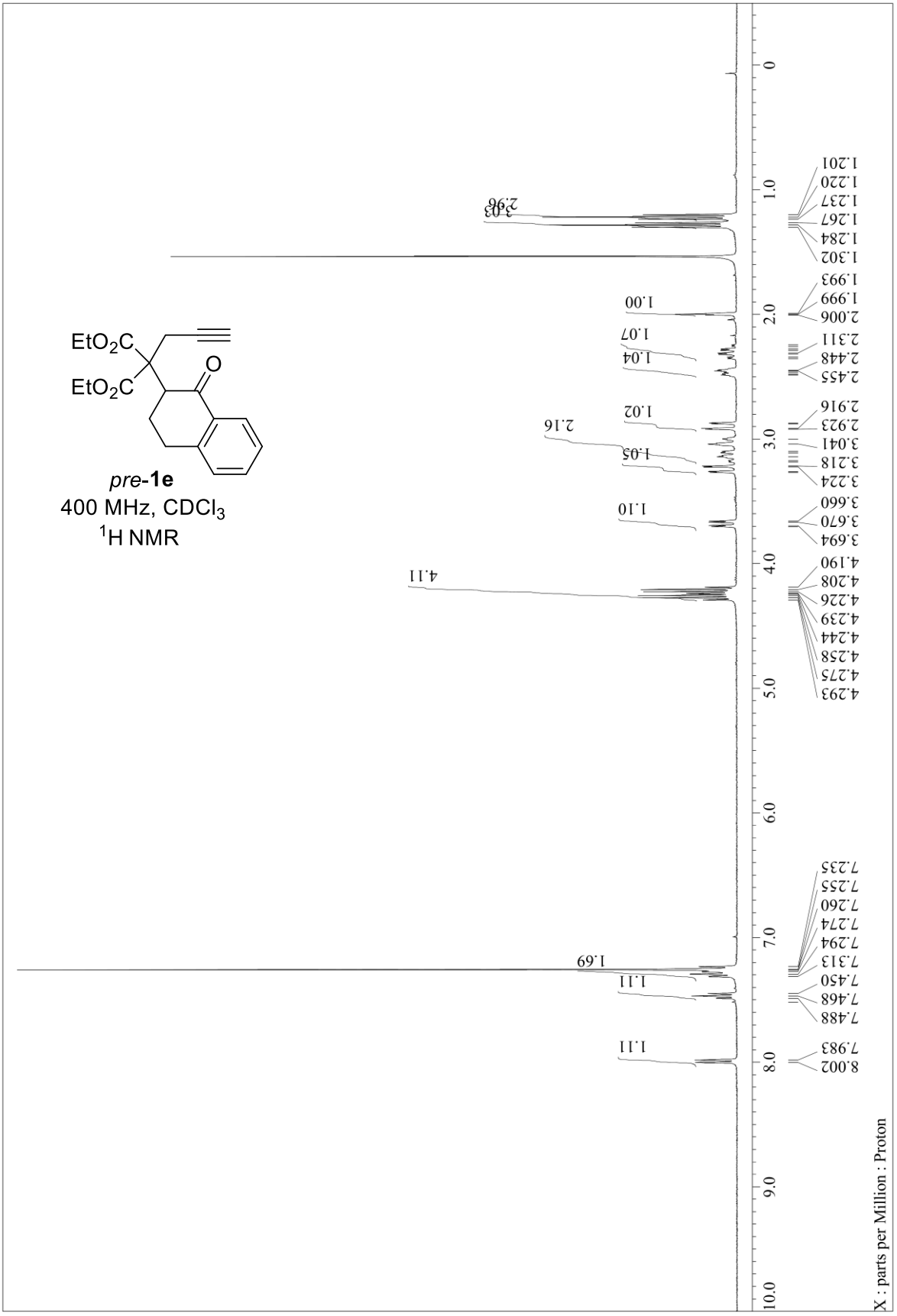
abundance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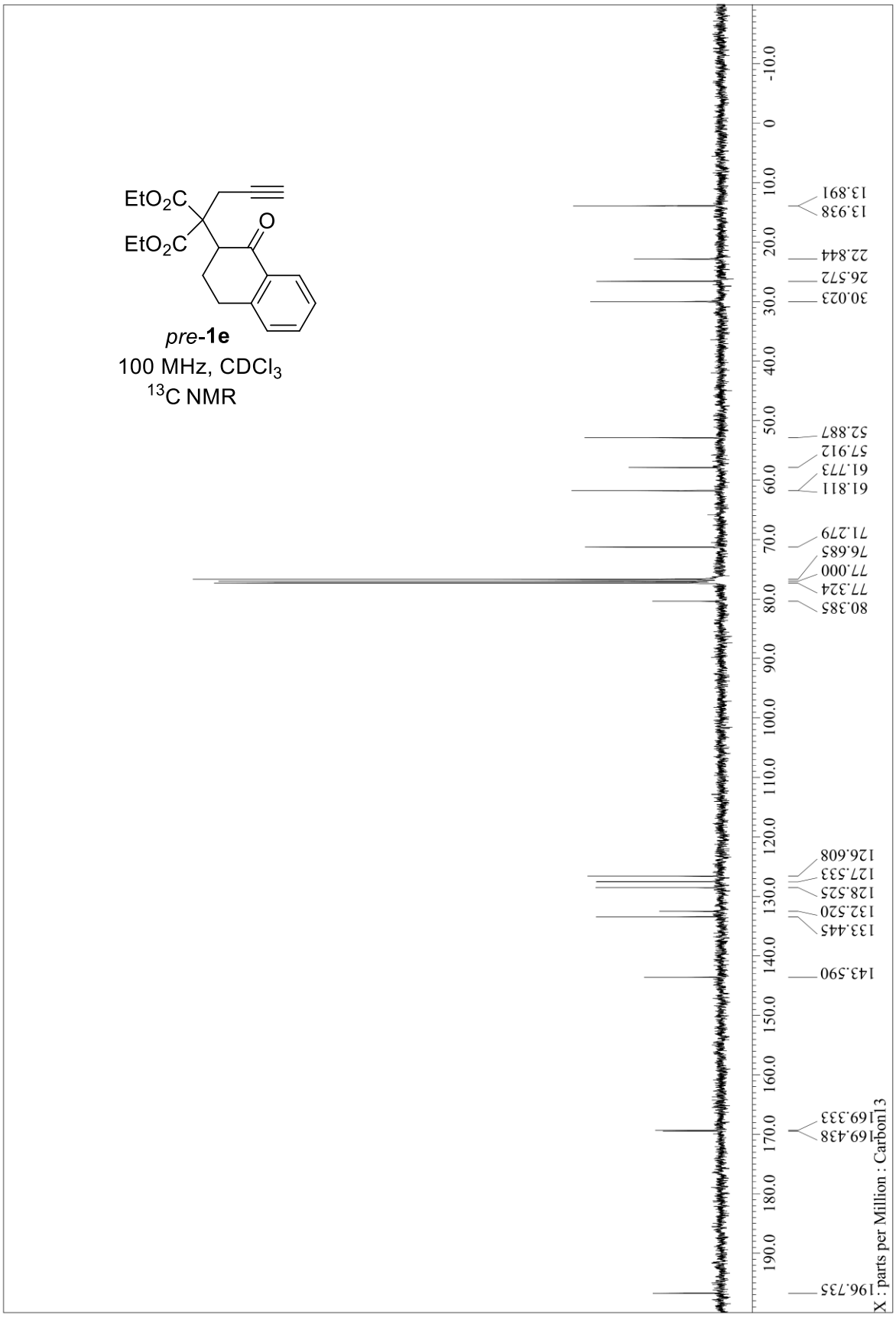
1H NMR
X : parts per Million : Proton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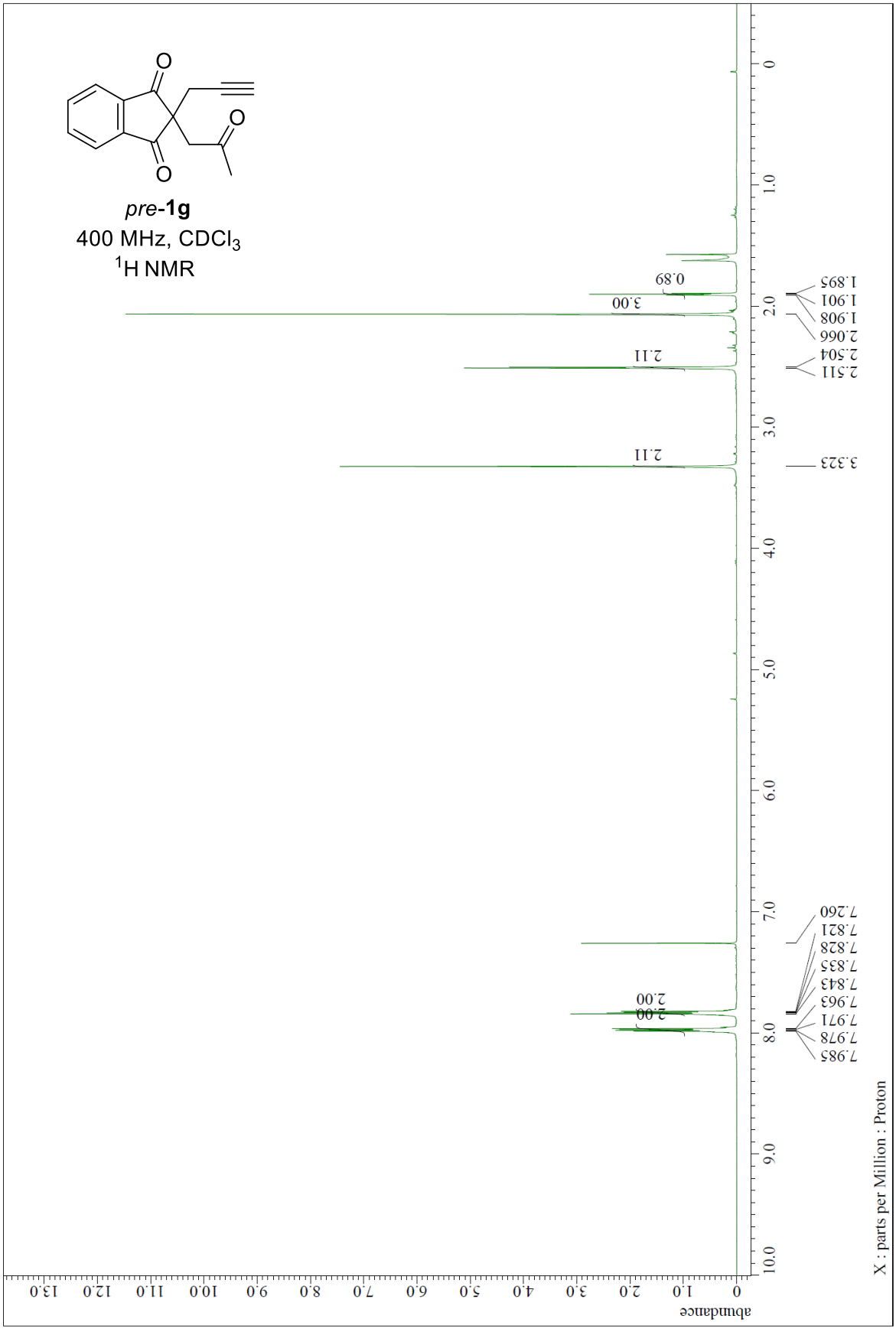
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7.963
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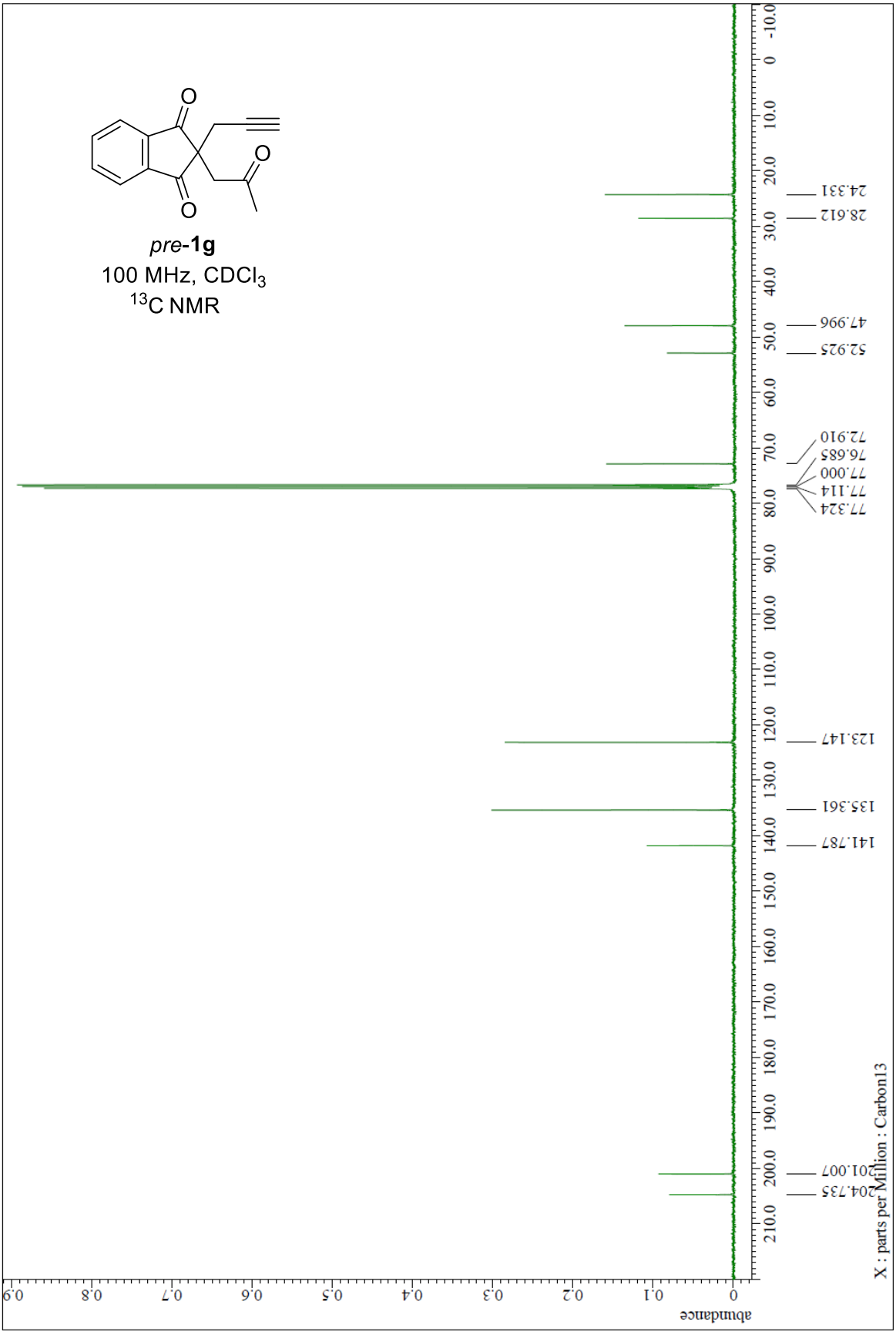
1.895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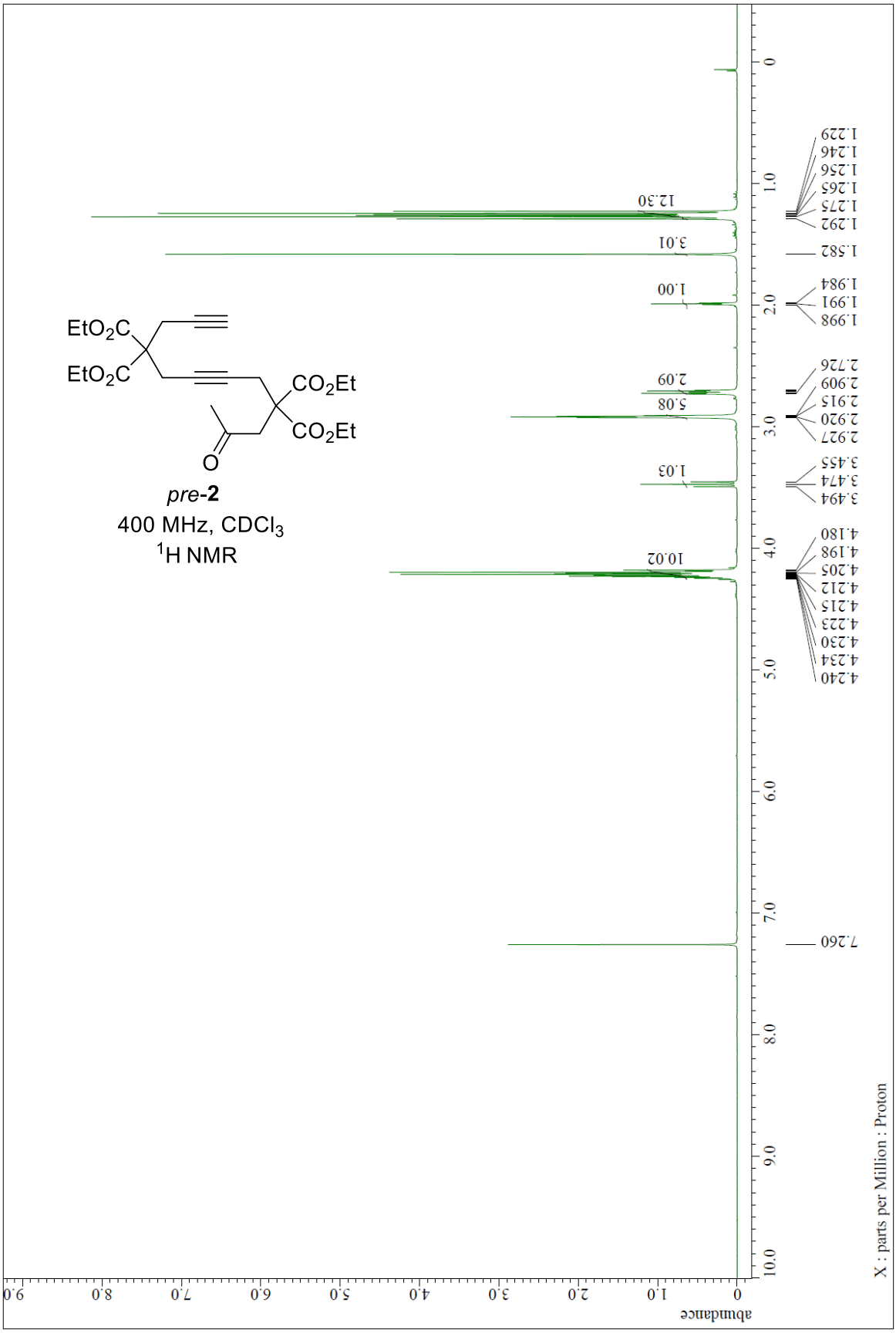
X : parts per Million : Carbon13
abundance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1.03
10.02
7.260
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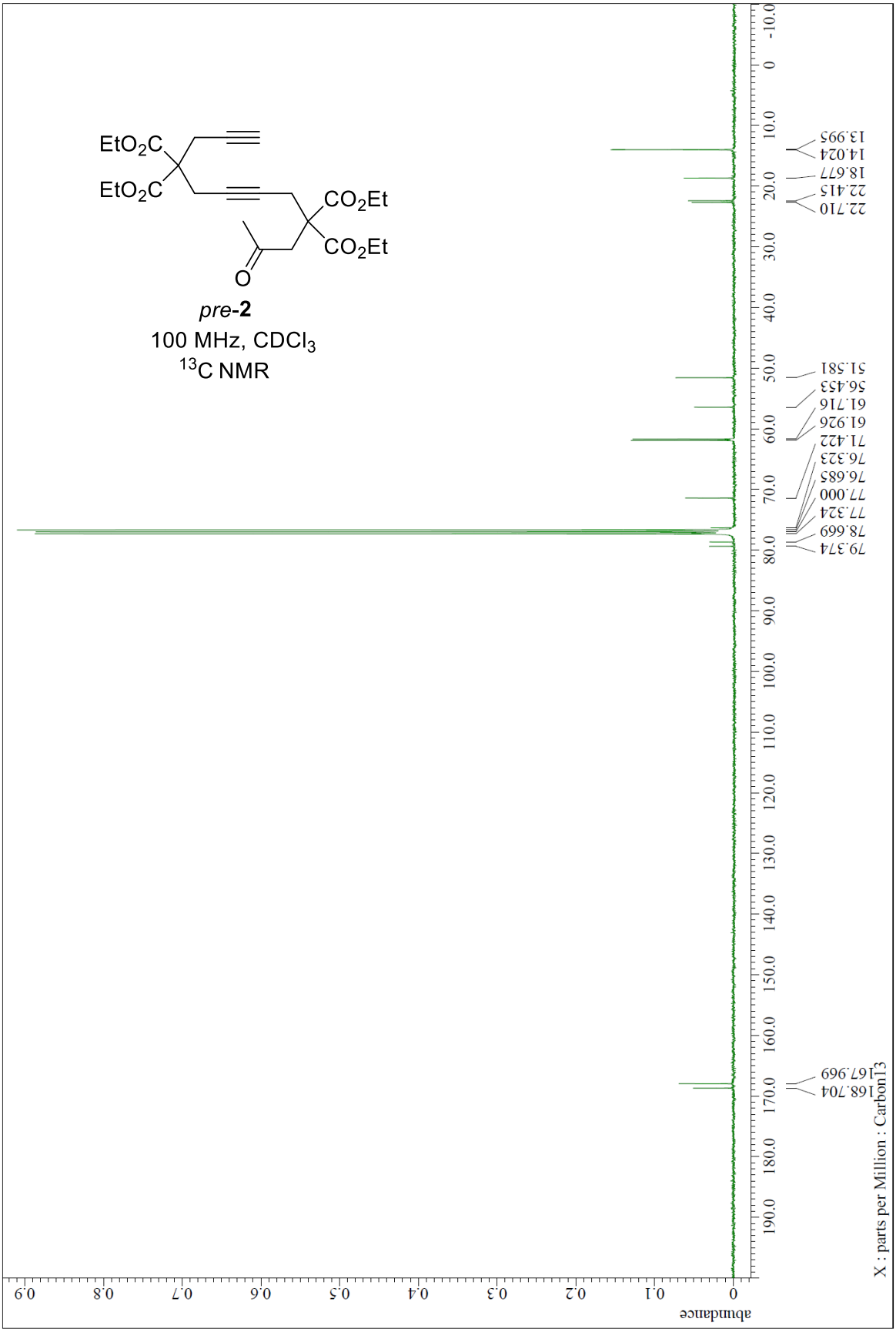
abundance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61.716
61.926
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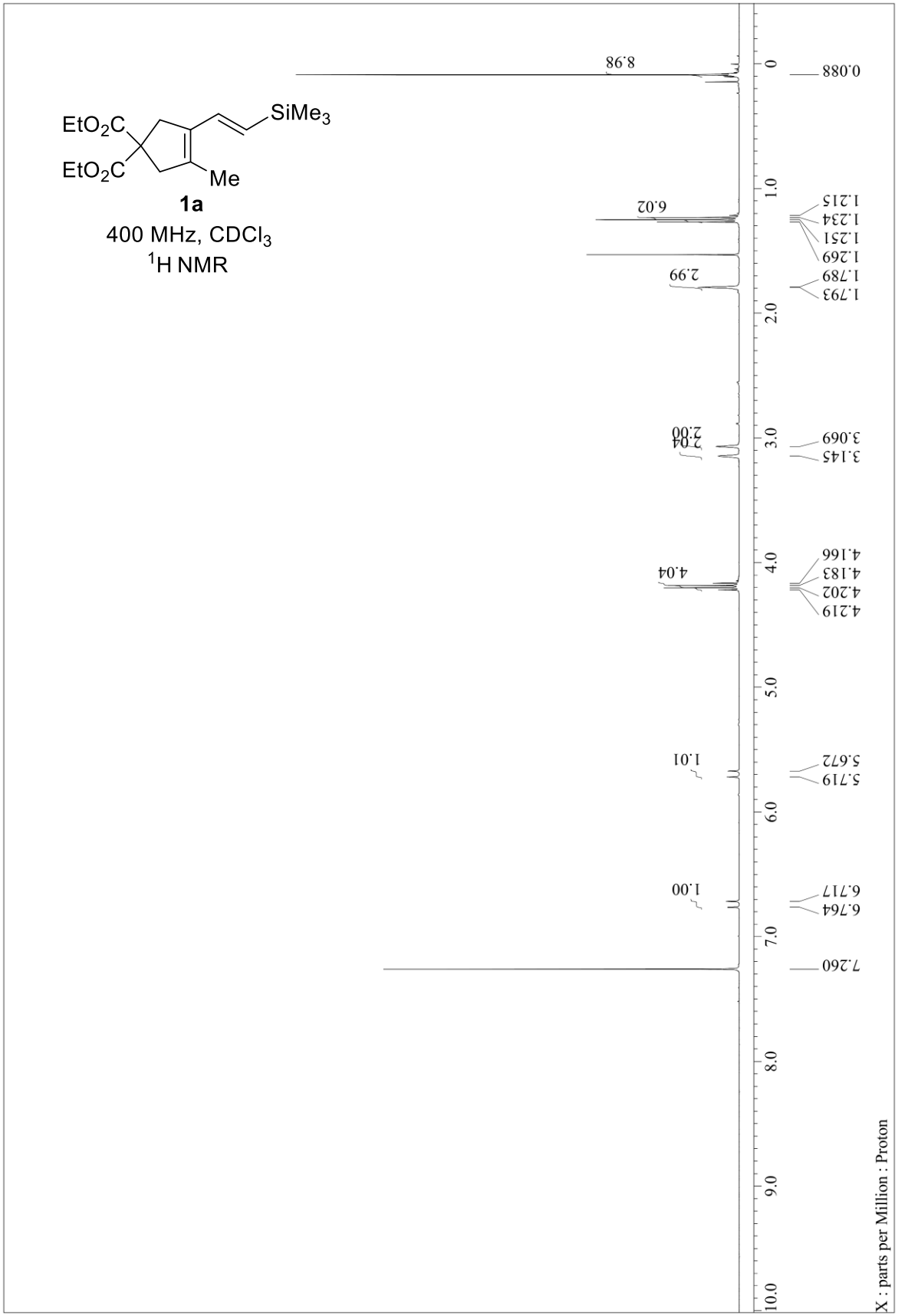
167.969
168.704
abundance
X : parts per Million : Carbon13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1.215
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1.269
1.789
1.793
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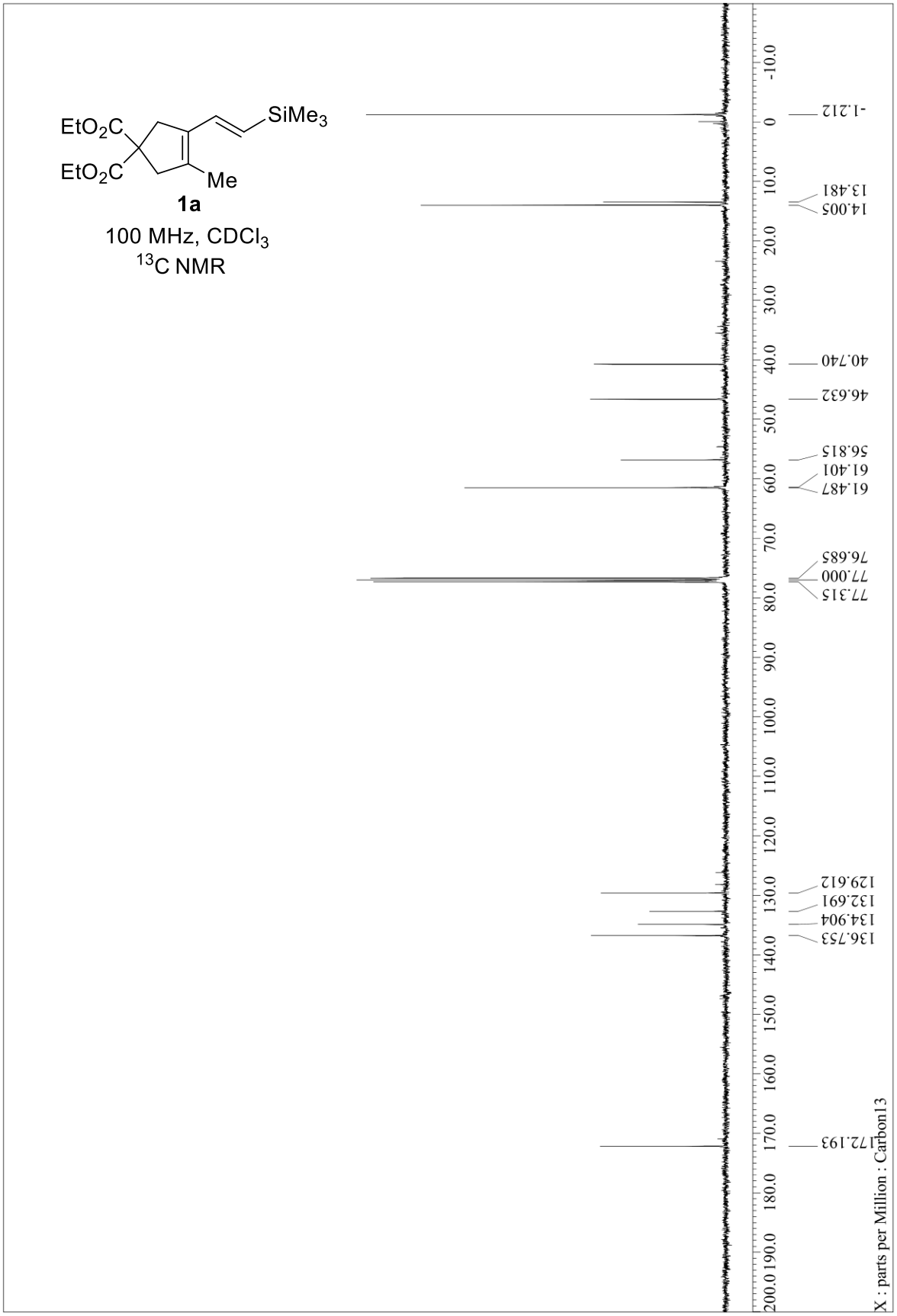
X : parts per Million : Proton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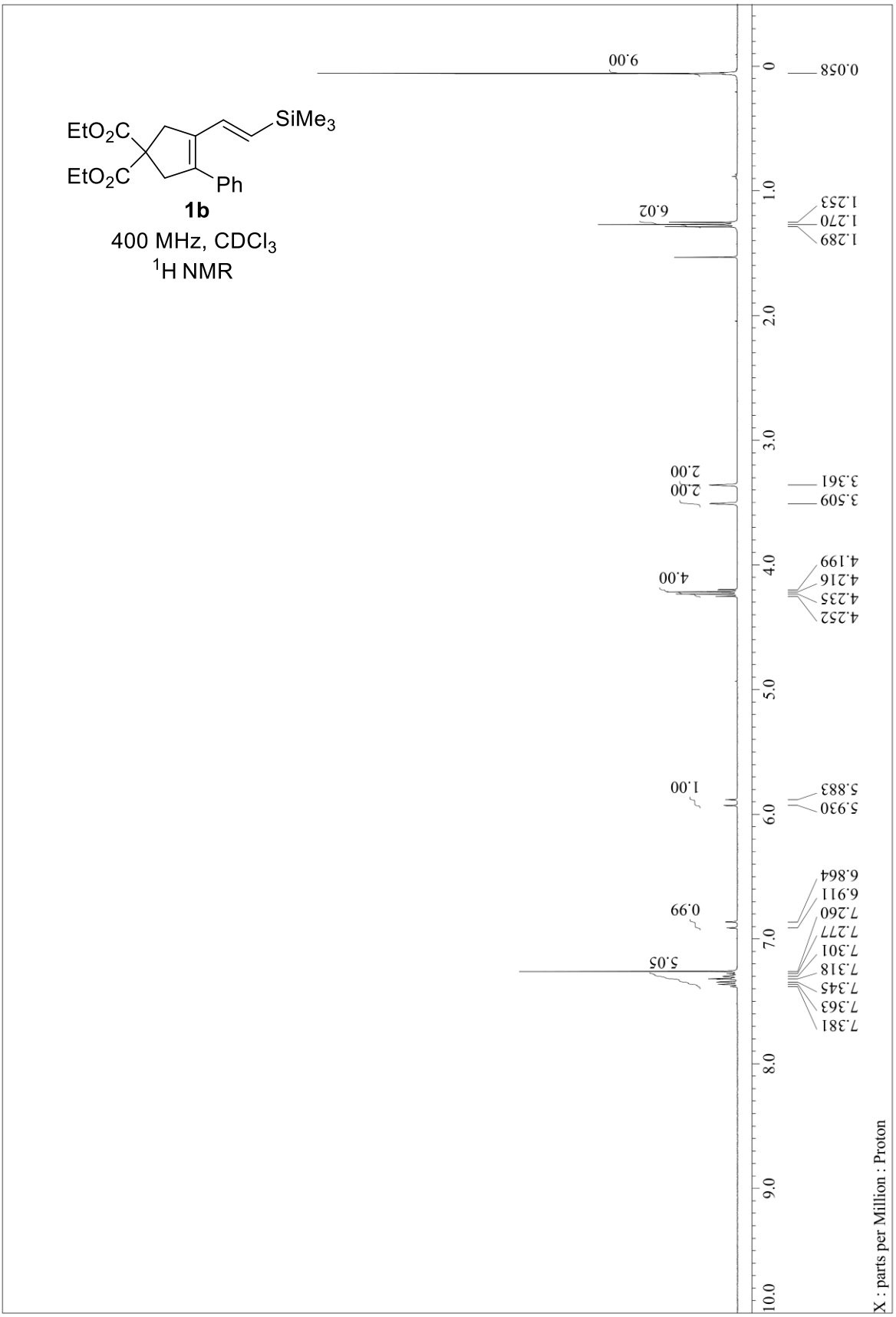
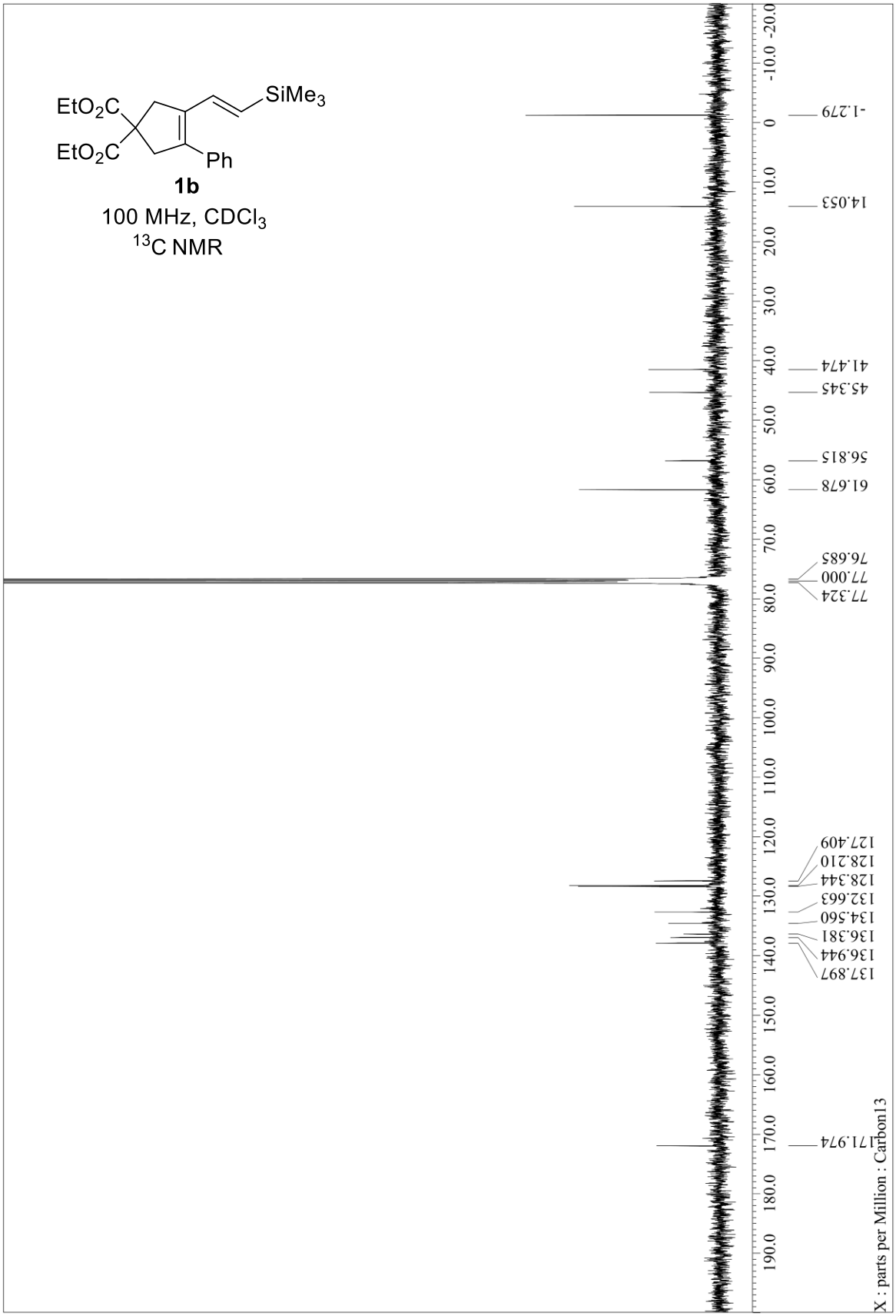
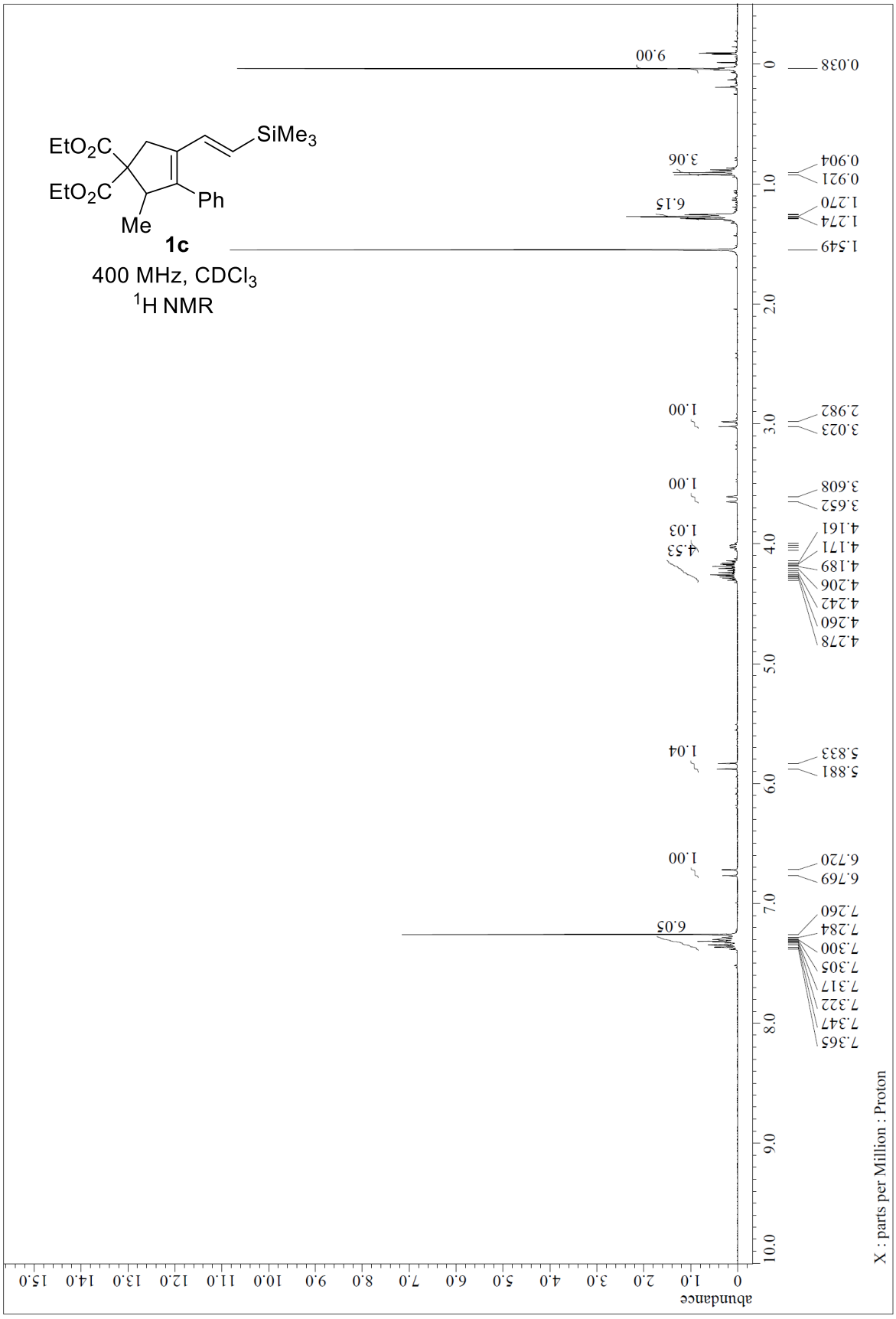
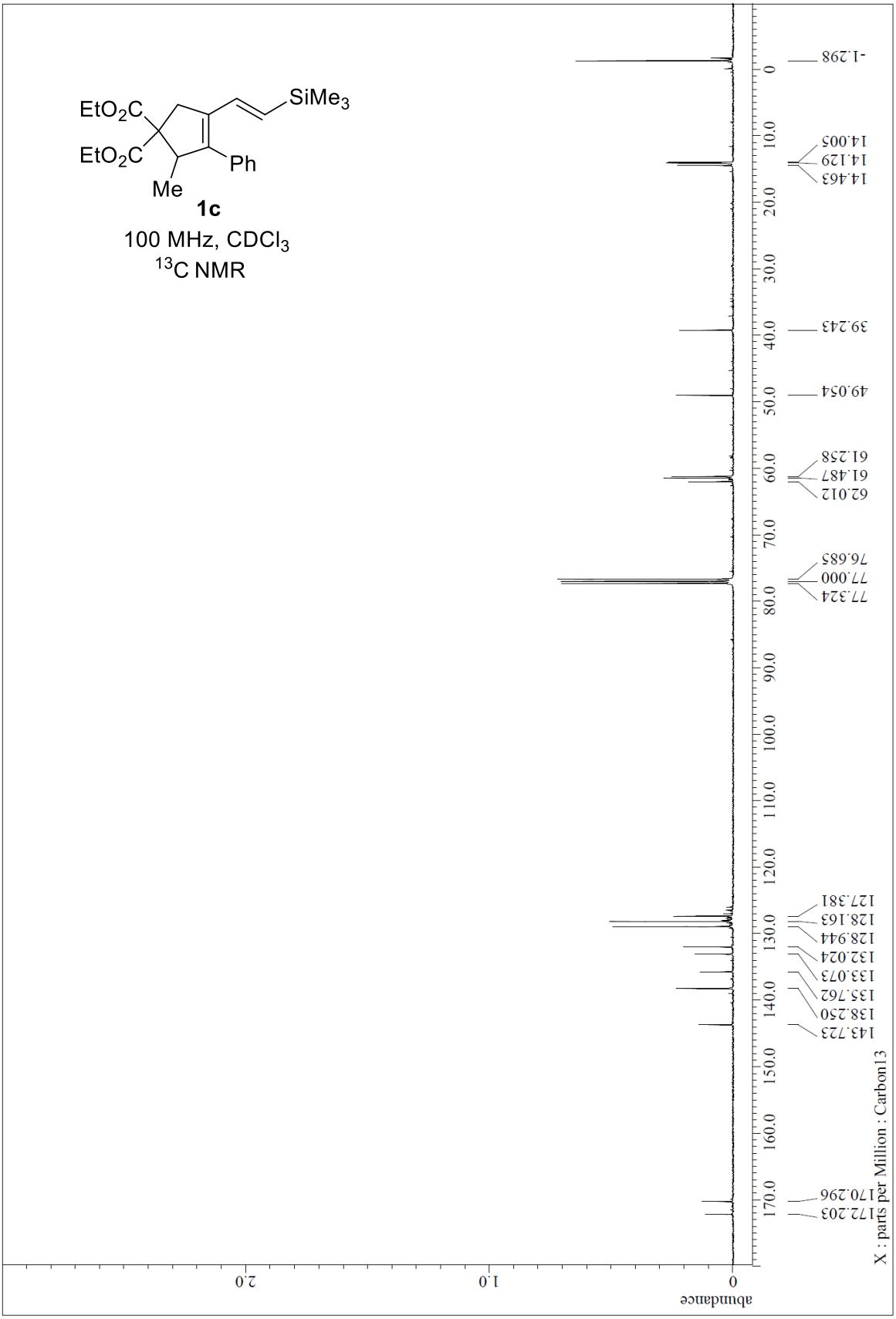
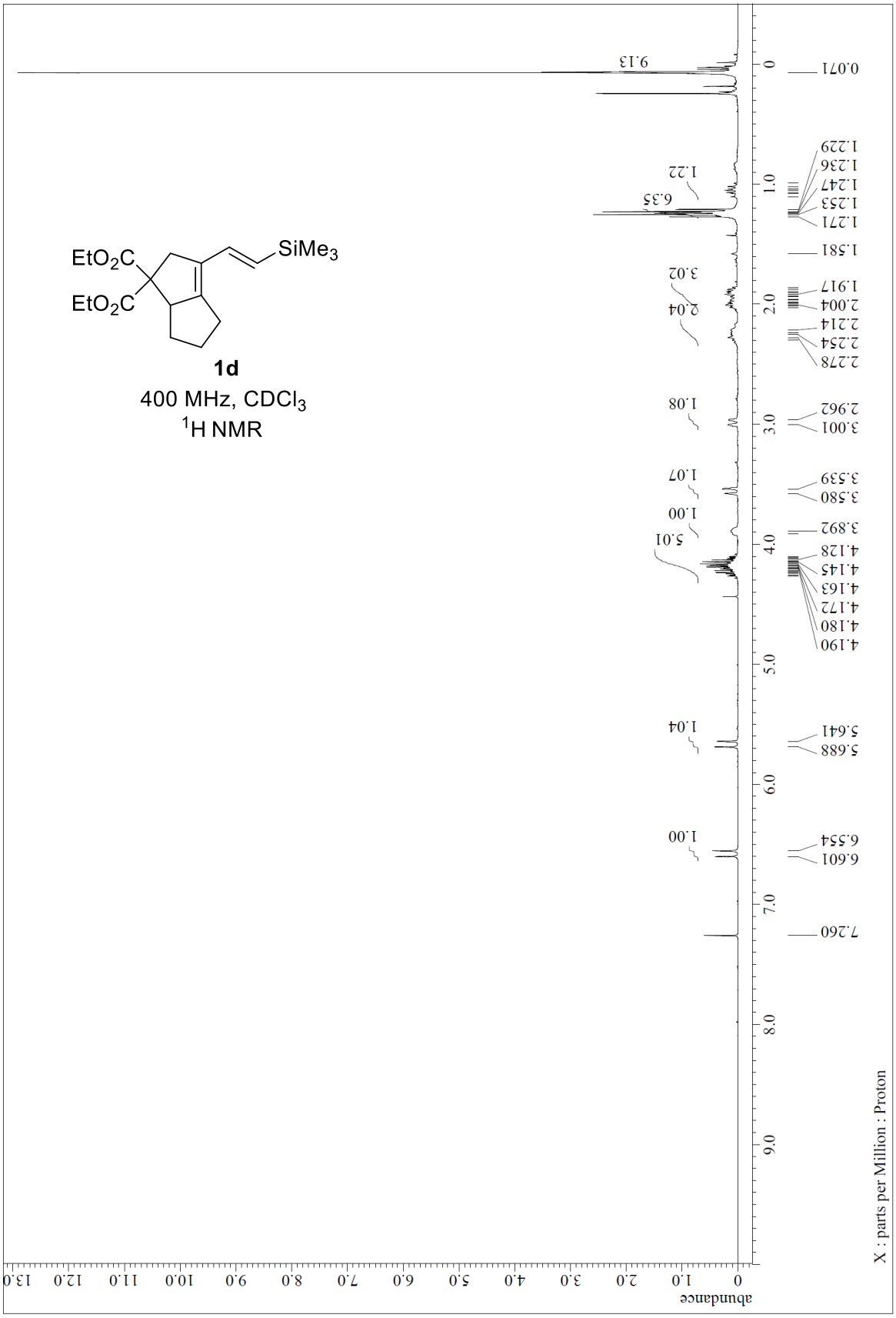
EtO2C
SiMe3
Me
1a
100 MHz, CDCl3
13C NMR
-1.212
13.481
14.005
40.740
46.632
56.815
61.401
61.487
76.685
77.000
77.315
129.612
132.691
134.904
136.753
172.193
X : parts per Million : Carbon13

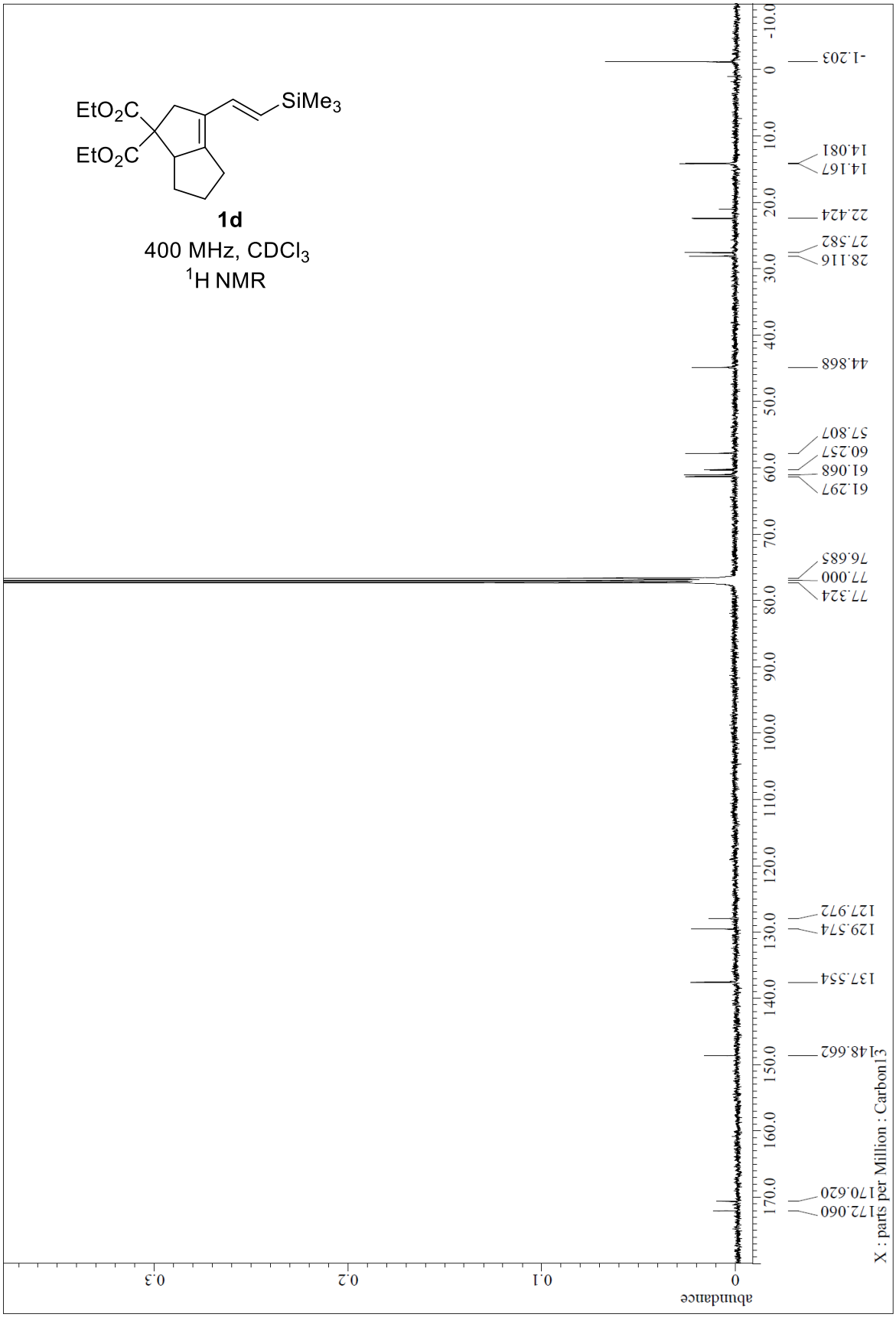

EtO2C
EtO2C
SiMe3
Ph
1b
400 MHz, CDCl3
1H NMR
9.00
6.02
2.00
2.00
4.00
1.00
0.99
5.05
0.058
1.253
1.270
1.289
3.361
3.509
4.199
4.216
4.235
4.252
5.883
5.930
6.864
6.911
7.260
7.277
7.301
7.318
7.345
7.363
7.381
X : parts per Million : Proton

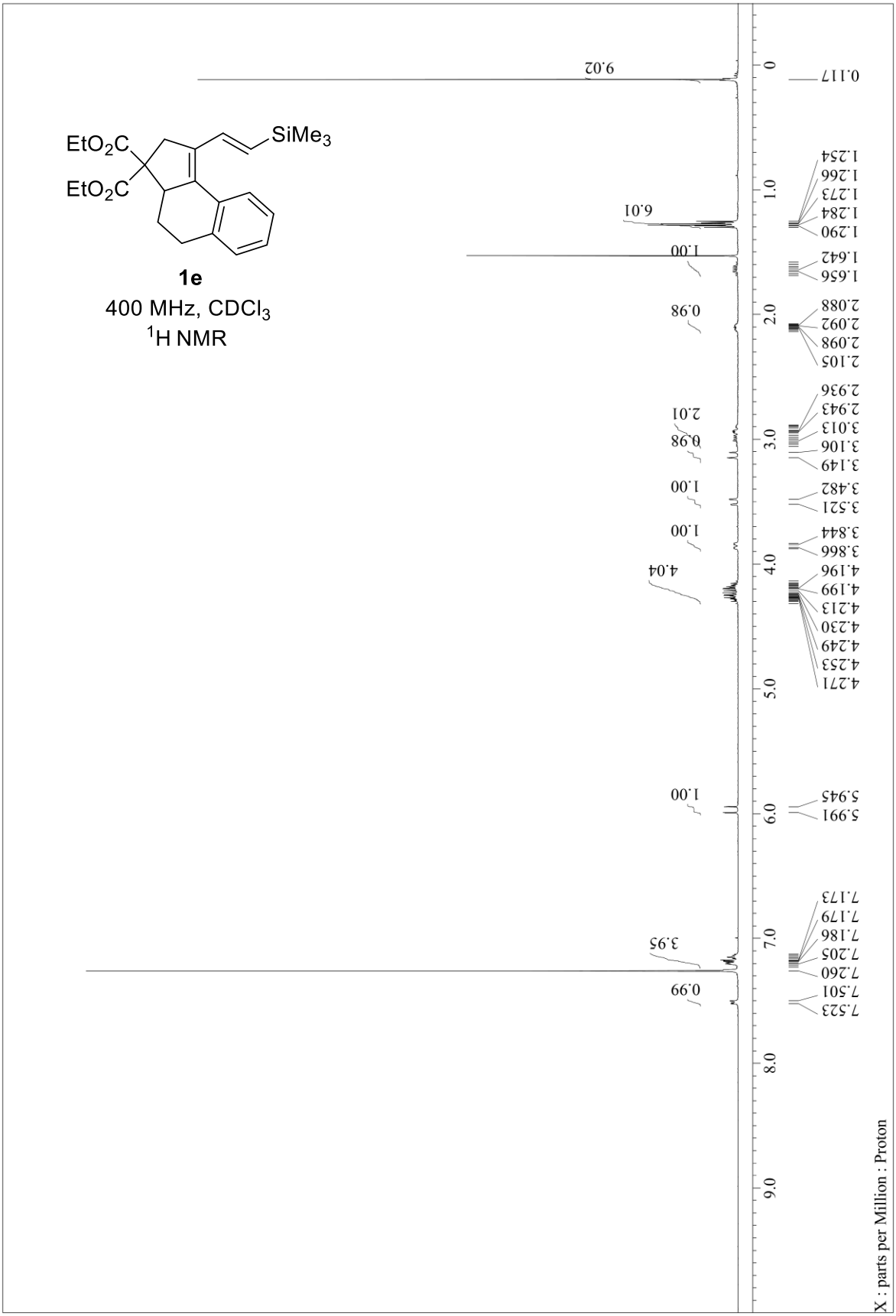

EtO2C
EtO2C
SiMe3
Ph
1b
100 MHz, CDCl3
13C NMR
-1.279
14.053
41.474
45.345
56.815
61.678
76.685
77.000
77.324
127.409
128.210
128.344
132.663
134.560
136.381
136.944
137.897
171.974
X : parts per Million : Carbon13

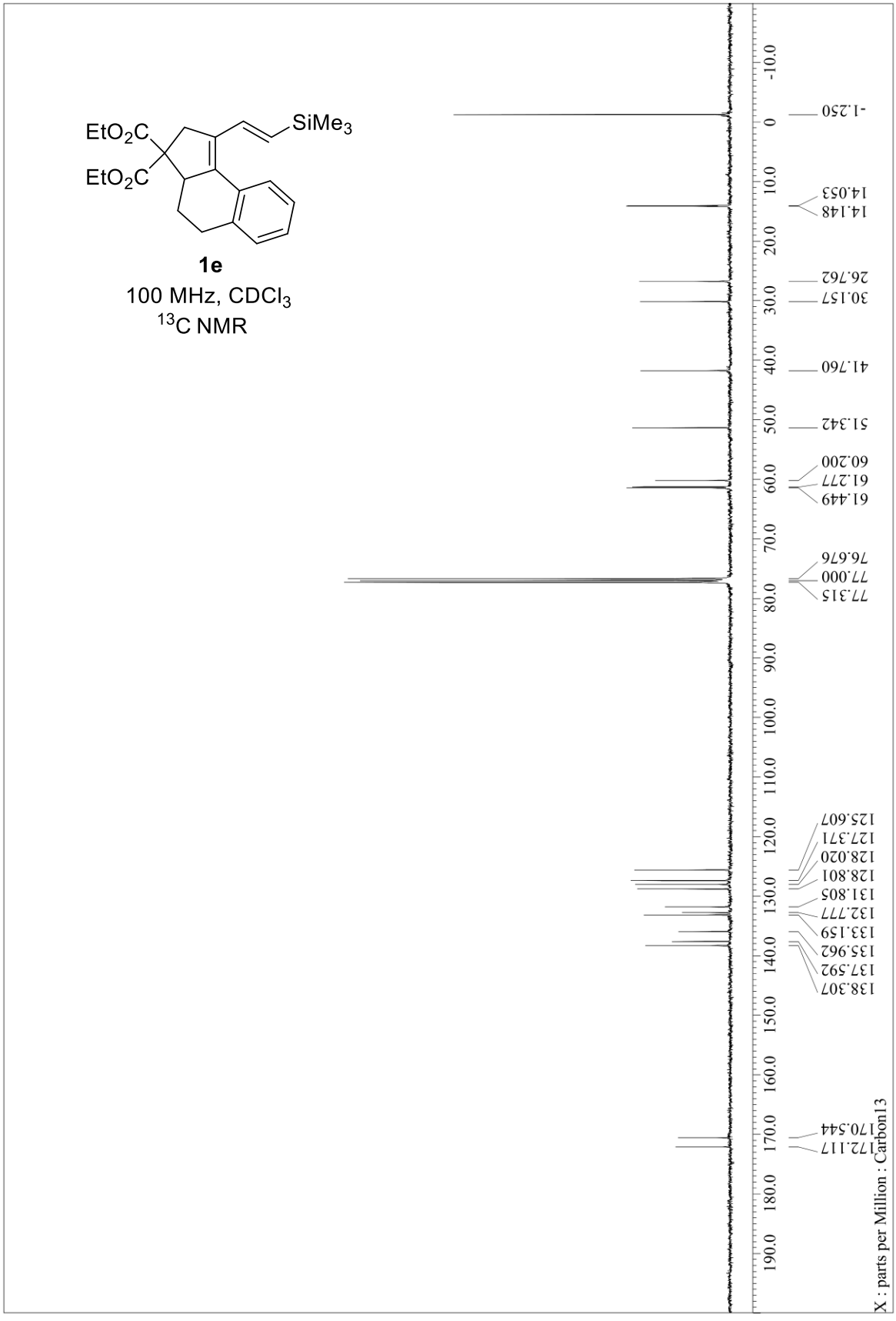

EtO2C
EtO2C
SiMe3
Ph
Me
1c
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton
abundance

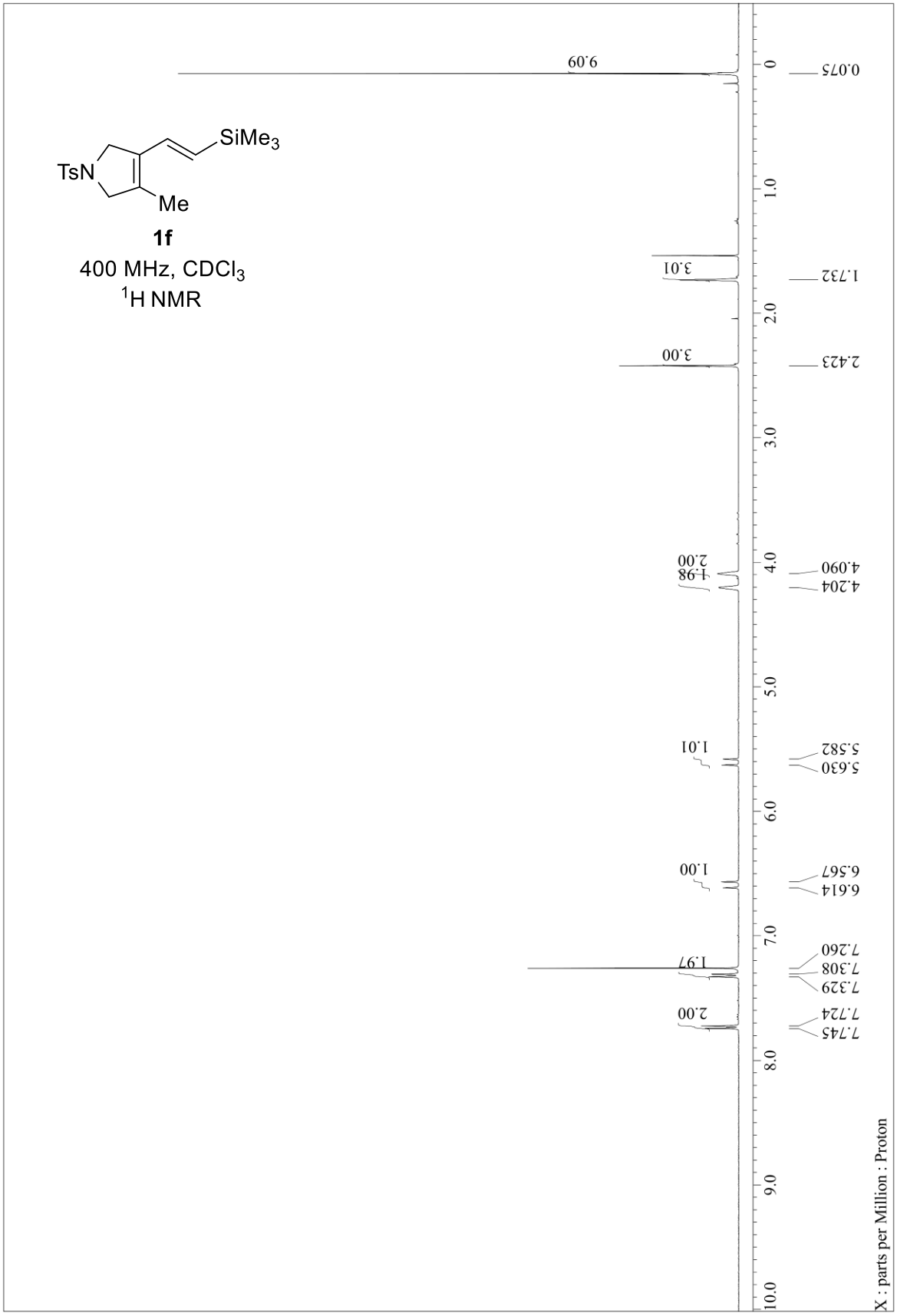

EtO2C
EtO2C
SiMe3
Ph
Me
1c
100 MHz, CDCl3
13C NMR
-1.298
14.005
14.129
14.463
39.243
49.054
61.258
61.487
62.012
76.685
77.000
77.324
127.381
128.163
128.944
132.024
133.073
135.762
138.250
143.723
170.296
172.203
X : parts per Million : Carbon13
abundance
0
1.0
2.0

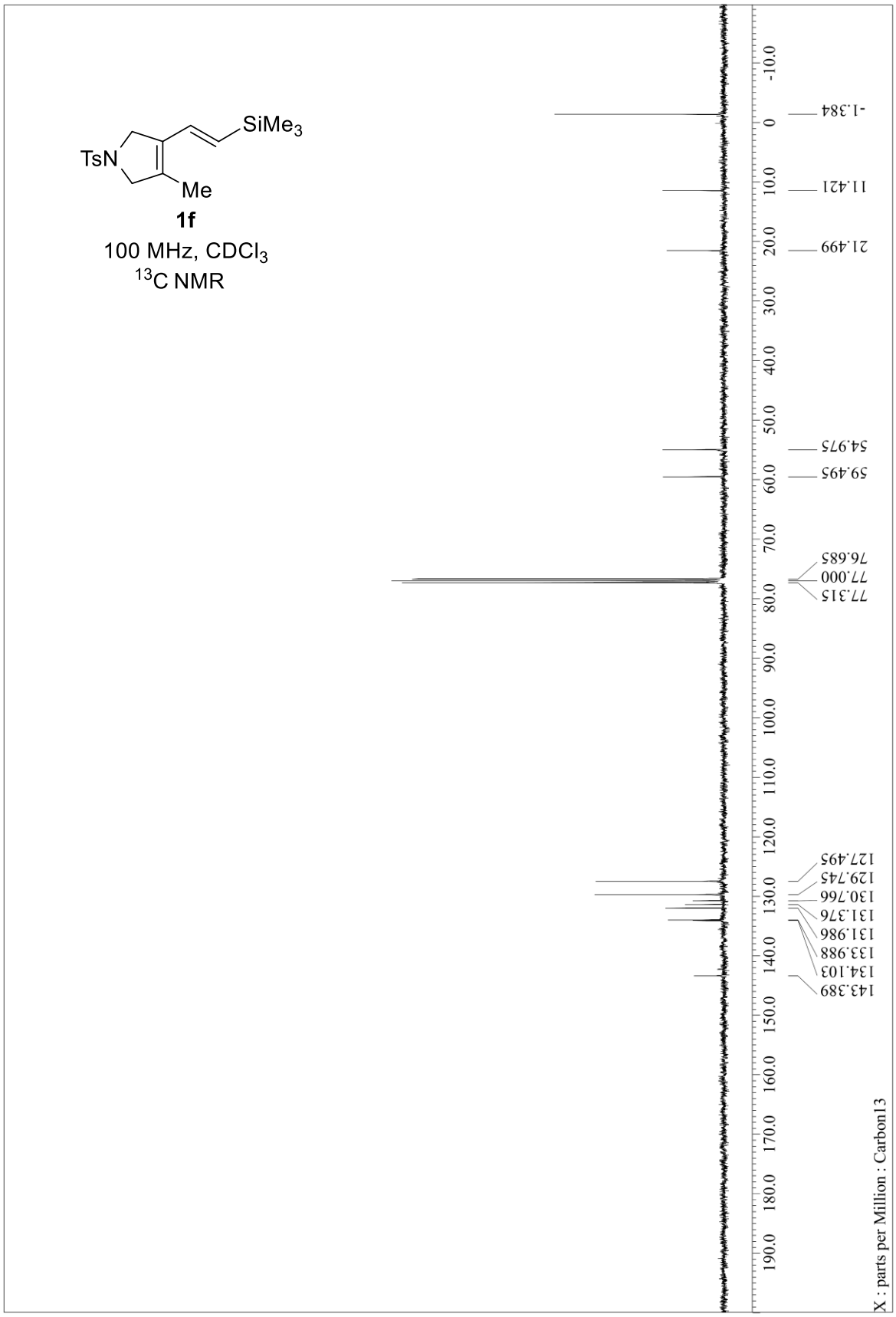

EtO2C
EtO2C
SiMe3
1d
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton
abundance

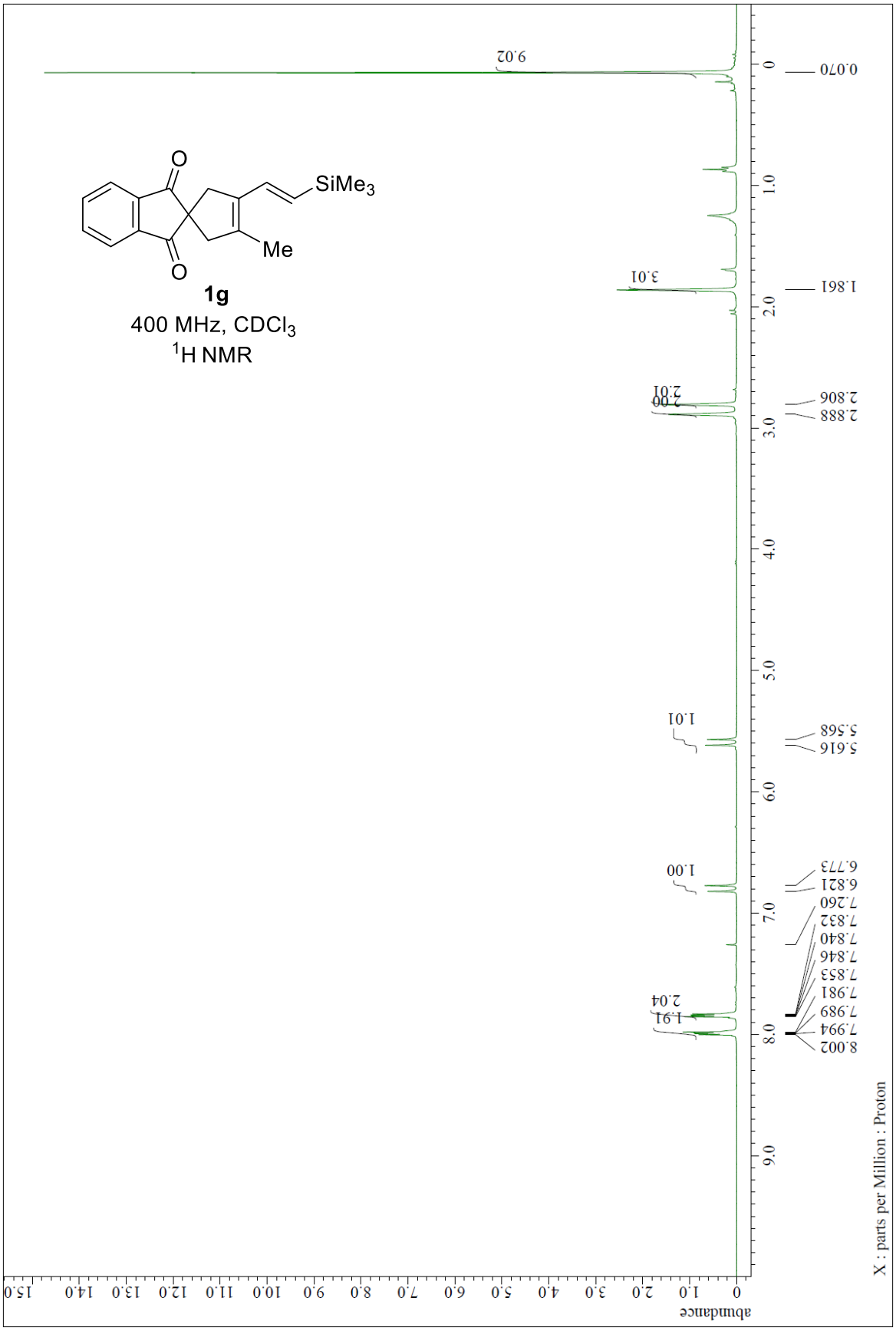

EtO2C
EtO2C
SiMe3
1d
400 MHz, CDCl3
1H NMR
-1.203
14.081
14.167
22.424
27.582
28.116
44.868
57.807
60.257
61.068
61.297
76.685
77.000
77.324
127.972
129.574
137.554
148.662
170.620
172.060
X : parts per Million : Carbon13
abundance

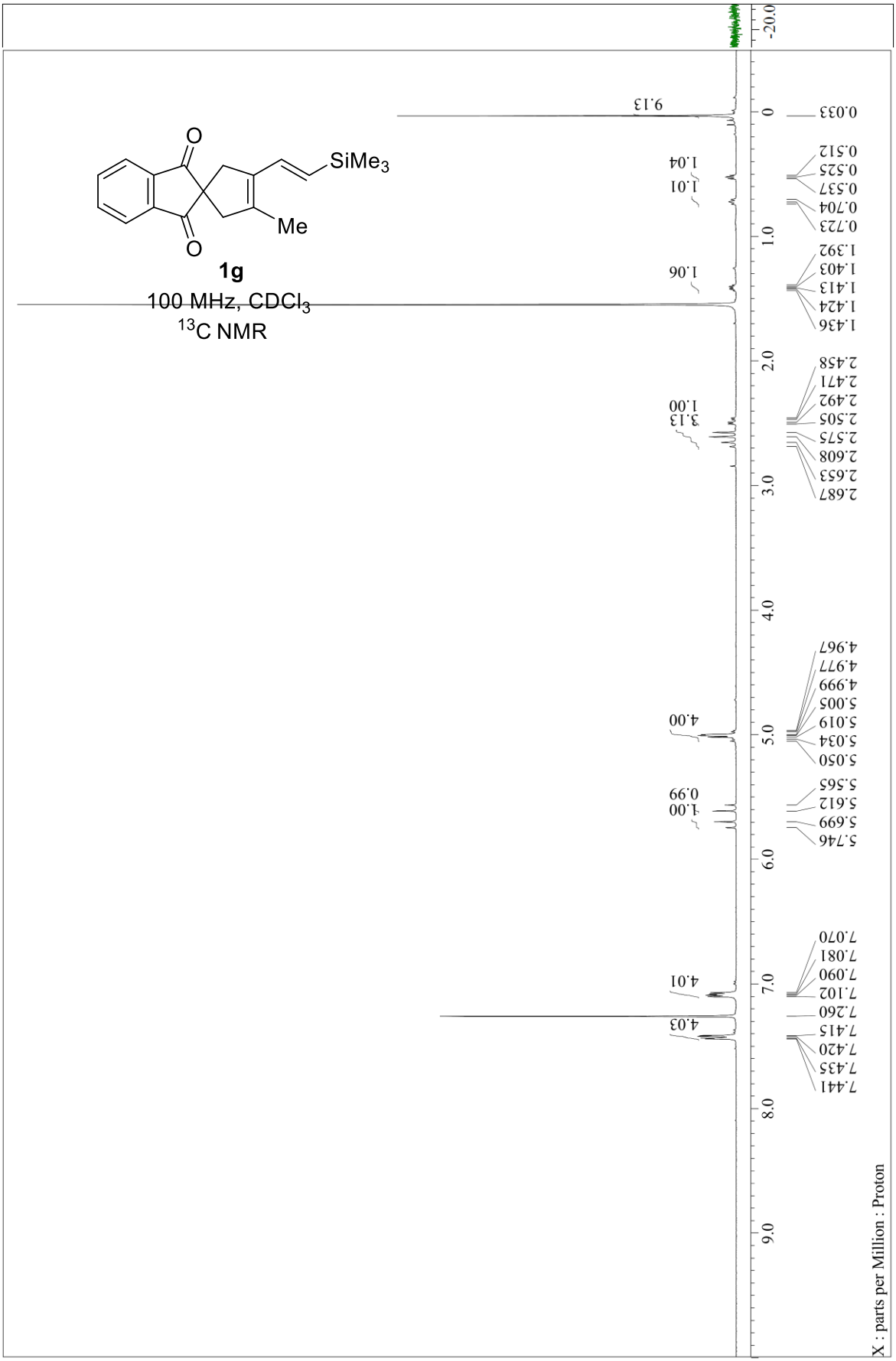

EtO2C
EtO2C
SiMe3
1e
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton

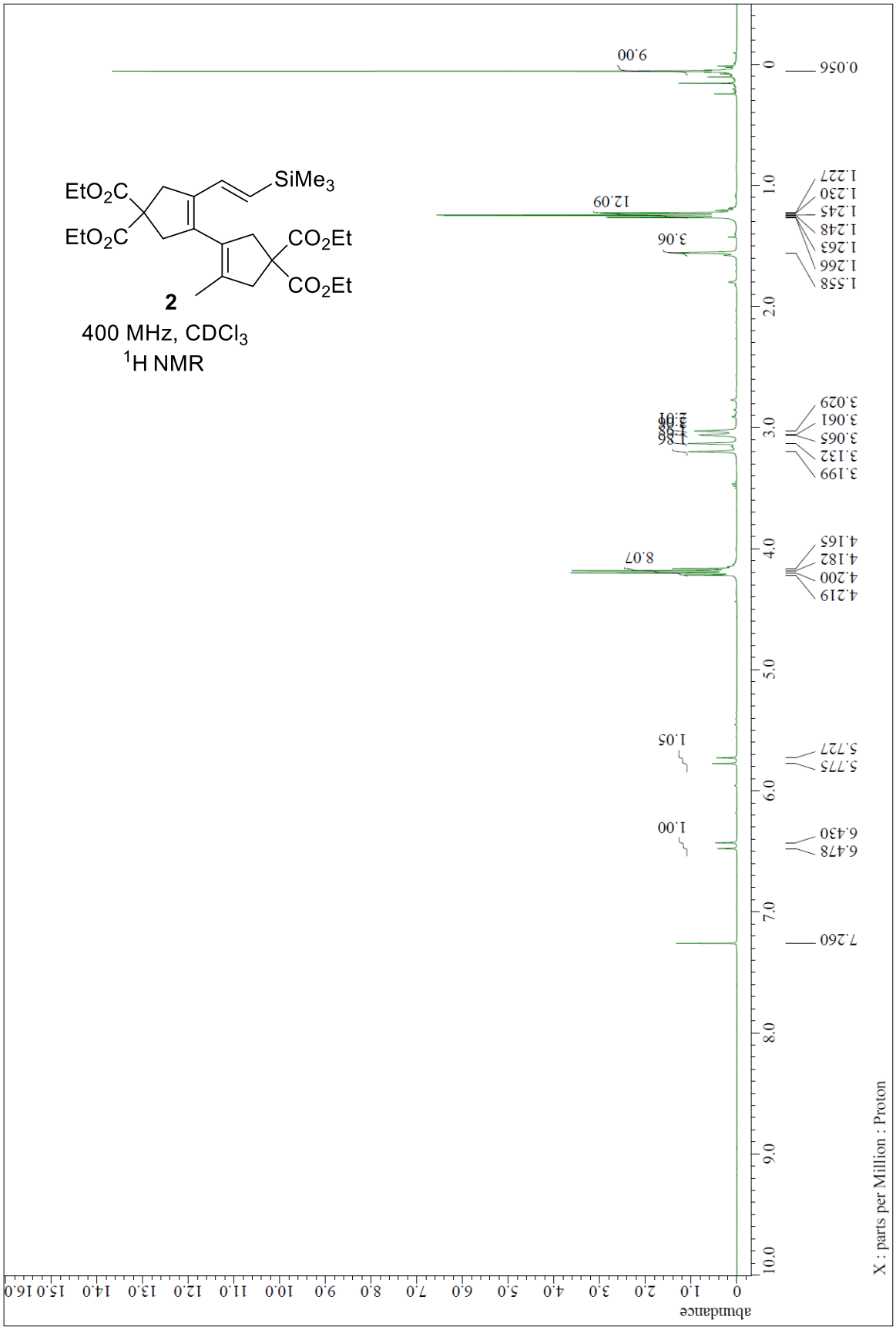

EtO2C
EtO2C
SiMe3
1e
100 MHz, CDCl3
13C NMR
-1.250
14.053
14.148
26.762
30.157
41.760
51.342
60.200
61.277
61.449
76.676
77.000
77.315
125.607
127.371
128.020
128.801
131.805
132.777
133.159
135.962
137.592
138.307
170.544
172.117
X : parts per Million : Carbon13

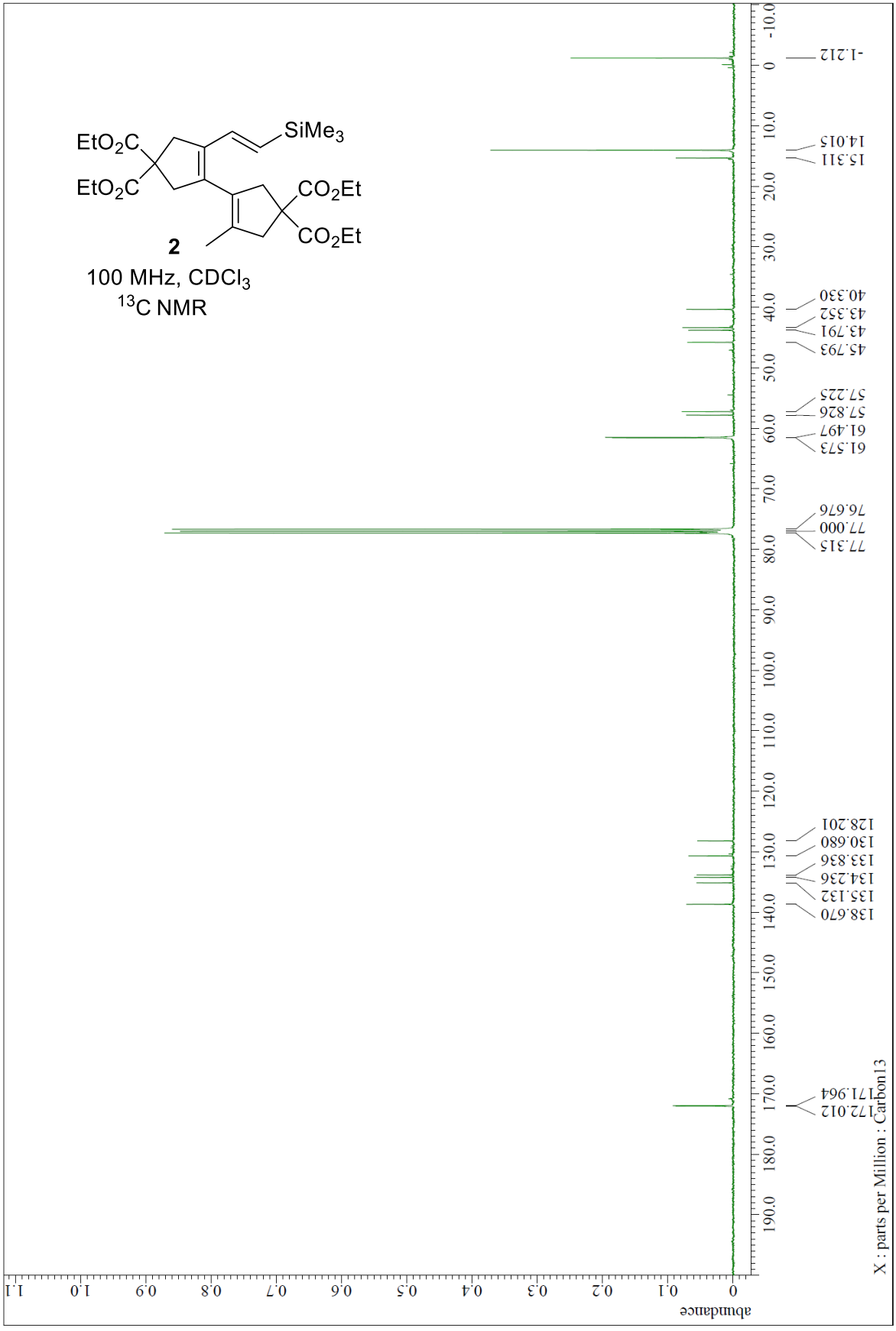

SiMe3
TsN
Me
1f
400 MHz, CDCl3
1H NMR
9.09
3.01
3.00
2.00
1.98
1.01
1.00
1.97
2.00
0.075
1.732
2.423
4.090
4.204
5.582
5.630
6.567
6.614
7.260
7.308
7.329
7.724
7.745
X : parts per Million : Proton


SiMe3
TsN
Me
1f
100 MHz, CDCl3
13C NMR
-1.384
11.421
21.499
54.975
59.495
76.685
77.000
77.315
127.495
129.745
130.766
131.376
131.986
133.988
134.103
143.389
X : parts per Million : Carbon13


O
O
SiMe3
Me
1g
400 MHz, CDCl3
1H NMR
9.02
3.01
2.00
2.01
1.01
1.00
2.04
1.91
0.070
1.861
2.806
2.888
5.568
5.616
6.773
6.821
7.260
7.832
7.840
7.846
7.853
7.981
7.989
7.994
8.002
abundance
X : parts per Million : Proton


O
O
SiMe3
Me
1g
100 MHz, CDCl3
13C NMR
9.13
1.04
1.01
1.06
3.13
1.00
4.00
0.99
1.00
4.01
4.03
0.033
0.512
0.525
0.537
0.704
0.723
1.392
1.403
1.413
1.424
1.436
2.458
2.471
2.492
2.505
2.575
2.608
2.653
2.687
4.967
4.977
4.999
5.005
5.019
5.034
5.050
5.565
5.612
5.699
5.746
7.070
7.081
7.090
7.102
7.260
7.415
7.420
7.435
7.441
-20.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton


EtO2C
EtO2C
SiMe3
CO2Et
CO2Et
2
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton
abundance


EtO2C
EtO2C
SiMe3
CO2Et
CO2Et
2
100 MHz, CDCl3
13C NMR
-1.212
14.015
15.311
40.330
43.352
43.791
45.793
57.225
57.826
61.497
61.573
76.676
77.000
77.315
128.201
130.680
133.836
134.236
135.132
138.670
171.964
172.012
X : parts per Million : Carbon13
abundance