Supporting Information

Intramolecular Participation in Alkoxycarbenium Ion Pools

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Experimental Procedures and Characterization Data

General Remarks. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 2000, Varian MERCURYplus-400 or JEOL ECA-600 spectrometer with Me_4Si as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL JMS SX-102A mass spectrometer. IR spectra were measured with a SHIMADZU FTIR 8100 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm). Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluant. All reactions were carried out under Ar atmosphere unless otherwise noted.

Materials. Tetrabutylammonium tetrafluoroborate was purchased from TCI and dried at 50 ^{o}C/1 mmHg overnight before use. Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. α-Silyl ethers **4a-4d** were prepared according to the method that we reported previously.[1]

Generation of Alkoxycarbenium Ions. Typical Procedure. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 ^{o}C/1 mmHg for 1 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of α-silyl ether (0.4 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL) and trifluoromethanesulfonic acid (150.1 mg, 1.0 mmol). The constant current electrolysis

(8 mA) was carried out at -78 ^{o}C with magnetic stirring until 2.5 F/mol of electricity was consumed.

3-(2-Methoxyethoxymethyl)cyclohexene. Prepared from **4a** (59.4 mg, 0.366 mmol) and 3-(trimethylsilyl)cyclohexene (146.6 mg, 0.950 mmol). After stilled for 60 min, the reaction mixture was added triethylamine (219.7 mg, 2.171 mg) at -78 ^{o}C. Purified with flash chromatography (pentane/Et_2O 15:1 to 7:1) (39.8 mg, 64%): TLC R_f 0.56 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.40 (m, 1H), 1.49-1.59 (m, 1H), 1.67-1.84 (m, 2H), 1.96-2.03 (m, 2H), 2.38-2.49 (m, 1H), 3.33-3.37 (m, 2H), 3.40 (s, 3H), 3.54-3.62 (m, 4H), 3.50 (t, 2H, J = 6.5 Hz), 5.59-5.64 (m, 1H), 5.72-5.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 25.3, 25.9, 35.6, 59.0, 70.2, 71.9, 75.7, 128.2, 128.5; IR (neat) 2936, 2863, 1123 cm^{-1}; LRMS (EI) m/e 170 (M^+), 95 (M^+-$C_3H_7O_2$); HRMS (EI) calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1303.

3-(2-Methoxyethoxy)-1-phenylpropan-1-one. Prepared from **4a** (65.7 mg, 0.405 mmol) and 1-phenyl-1-trimethylsilyloxyethylene (161.3 mg, 0.839 mmol) (reaction time, 15 min), followed by the aqueous work up, and purified with flash chromatography (hexane/EtOAc 7:1 to 3:1) (22.4 mg, 27%): TLC R_f 0.16 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (t, 2H, J = 6.6 Hz), 3.38 (s, 3H), 3.53-3.55 (m, 2H), 3.64-3.67 (m, 2H), 3.92 (t, 2H, J = 6.8 Hz), 7.43-7.47 (m, 2H), 7.53-7.57 (m, 1H), 7.94-7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.8, 59.0, 66.4, 70.4, 71.7, 127.9, 128.4, 132.9, 136.7, 197.9; IR (neat) 2872, 1684, 1122 cm^{-1}; LRMS (FAB) m/e 209 (MH^+), 105 (M^+-$C_5H_{11}O_2$); HRMS (FAB) calcd for $C_{12}H_{17}O_3$ 209.1178, found 209.1177.

3-(3-Methoxypropoxymethyl)cyclohexene. Prepared from **4b** (70.7 mg, 0.401 mmol) and 3-(trimethylsilyl)cyclohexene (133.5 mg, 0.865 mmol). After stilled for 60 min, the reaction mixture was added triethylamine (210.5 mg, 2.080 mg) at -78 ^{o}C. Purified with flash chromatography (hexane/EtOAc 20:1 to 10:1) (56.6 mg, 77%): TLC R_f 0.50 (hexane/EtOAc 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.38 (m, 2H), 1.48-1.83 (m, 2H), 1.84 (t, 2H, J = 6.4 Hz), 1.95-2.03 (m, 2H), 2.32-2.46 (m, 1H), 3.28 (d, 2H, J = 6.9 Hz), 3.33 (s, 3H), 3.46 (t, 2H, J = 6.3 Hz), 3.50 (t, 2H, J = 6.5 Hz), 5.54-5.64 (m, 1H), 5.72-5.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 25.3, 26.0, 30.0, 35.8, 58.6, 67.8, 69.8, 75.2, 128.4, 128.5; IR (neat) 2936, 2861, 1119 cm^{-1}; LRMS (FAB) m/e 185 (M-H^+), 95 (M^+-$C_4H_9O_2$).

3-(3-Methoxypropoxy)-1-phenylpropan-1-one. Prepared from **4b** (71.2 mg, 0.404 mmol) and 1-phenyl-1-trimethylsilyloxyethylene (159.5 mg, 0.829 mmol) (reaction time, 15 min) followed by the aqueous work up, and purified with flash chromatography (hexane/EtOAc 7:1 to 3:1) (53.8 mg, 60%): TLC R_f 0.37

(hexane/EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83 (tt, 2H, *J* = 6.5 Hz, *J* = 6.5 Hz), 3.25 (t, 2H, *J* = 6.5 Hz), 3.31 (s, 3H), 3.42 (t, 2H, *J* = 6.3 Hz), 3.55 (t, 2H, *J* = 6.5 Hz), 3.86 (t, 2H, *J* = 6.6 Hz), 7.44-7.49 (m, 2H), 7.55-7.62 (m, 1H), 7.95-7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.9, 38.8, 58.6, 66.1, 68.0, 69.6, 127.9, 128.4, 132.9, 126.8, 198.1; IR (neat) 2872, 1683, 1115 cm^{-1}; LRMS (FAB) m/e 223 (MH^+), 105 (M^+-$C_6H_{13}O_2$); HRMS (FAB) calcd for $C_{13}H_{19}O_3$ 223.1334, found 223.1333.

Methyl 3-(3-Methoxypropoxy)-2,2-dimethylpropionate. Prepared from **4b** (71.2 mg, 0.404 mmol) and dimethylketene methyl trimethylsilyl acetal (135.7 mg, 0.778 mmol) (reaction time, 15 min) followed by the aqueous work up, and purified with flash chromatography (hexane/EtOAc 15:1 to 7:1) (46.0 mg, 56%): TLC R_f 0.52 (hexane/EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 6H), 1.80 (tt, 2H, *J* = 6.3 Hz), 3.32 (s, 3H), 3.41 (s, 2H), 3.42 (t, 2H, *J* = 6.5 Hz), 3.48 (t, 2H, *J* = 6.5 Hz), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 26.2, 26.4, 43.7, 51.8, 58.5, 71.2, 72.5, 176.9; IR (neat) 1874, 1733, 1119 cm^{-1}; LRMS (FAB) m/e 205 (MH^+); HRMS (FAB) calcd for $C_{10}H_{21}O_4$ 205.1440, found 205.1444.

3-(4-Methoxybutoxymethyl)cyclohexene. Prepared from **4c** (60.6 mg, 0.318 mmol) and 3-(trimethylsilyl)cyclohexene (100.7 mg, 0.653 mmol) (reaction time, 15 min). Purified with flash chromatography (hexane/EtOAc 10:1) (45.3 mg, 72%): TLC R_f 0.23 (hexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.38 (m, 2H), 1.46-1.83 (m, 6H), 1.94-2.02 (m, 2H), 2.30-2.44 (m, 1H), 3.27 (d, 2H, *J* = 6.6 Hz), 3.33 (s, 3H), 3.36-3.49 (m, 4H), 5.56-5.64 (m, 1H), 5.70-5.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 25.5, 26.1, 26.4, 26.5, 35.9, 58.5, 70.7, 72.6, 75.1, 76.7, 128.3, 128.3; IR (neat) 2926, 2859, 1119 cm^{-1}; LRMS (FAB) m/e 199 (MH^+), 95 (M^+-$C_5H_{11}O_2$); HRMS (FAB) calcd for $C_{12}H_{23}O_2$ 199.1698, found 199.1699.

3-(4-Methoxybutoxy)-1-phenylpropan-1-one. Prepared from **4c** (79.0 mg, 0.415 mmol) and 1-phenyl-1-trimethylsilyloxyethylene (173.4 mg, 0.902 mmol) (reaction time, 15 min) followed by the aqueous work up, and purified with flash chromatography (hexane/EtOAc 7:1 to 3:1) (37.3 mg, 38%): TLC R_f 0.22 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.68 (m, 4H), 3.25 (t, 2H, *J* = 6.6 Hz), 3.31 (s, 3H), 3.35-3.41 (m, 2H), 3.47-3.50 (m, 2H), 3.86 (t, 2H, *J* = 6.6 Hz), 7.43-7.49 (m, 2H), 7.54-7.59 (m, 1H), 7.95-7.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.4, 39.0, 58.5, 66.1, 71.0, 72.5, 128.0, 128.4, 132.9, 136.9, 198.2; IR (neat) 2870, 1685, 1115 cm^{-1}; LRMS (FAB) m/e 237 (MH^+), 105 (M^+-$C_7H_{15}O_2$); HRMS (FAB) calcd for $C_{14}H_{21}O_3$ 237.1491, found 237.1490.

Methyl 3-(4-Methoxybutoxy)-2,2-dimethylpropionate. Prepared from **4c** (75.7 mg, 0.398 mmol) and dimethylketene methyl trimethylsilyl acetal (154.5 mg,

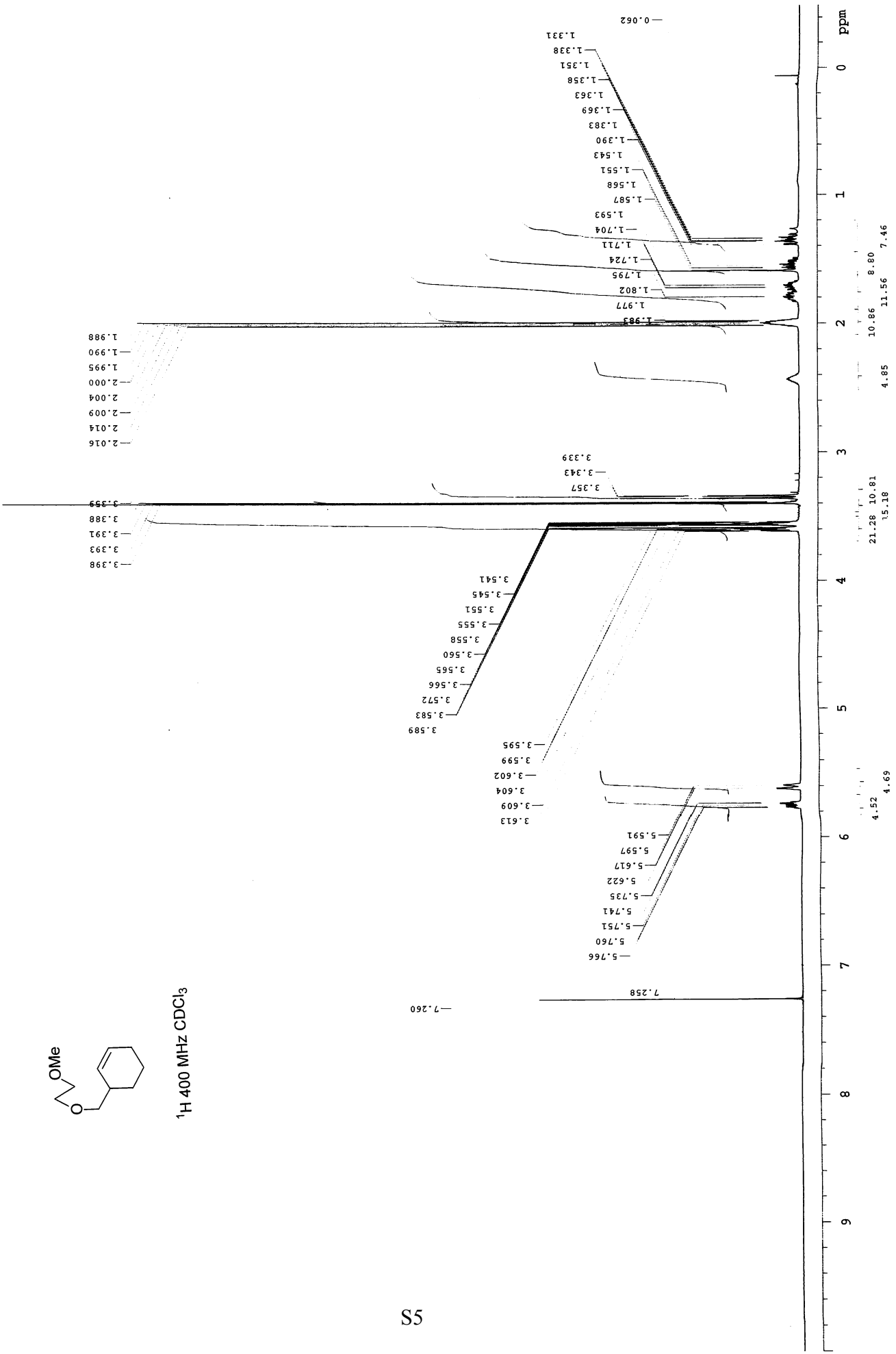
0.886 mmol) (reaction time, 15 min) followed by the aqueous work up, and purified with flash chromatography (hexane/EtOAc 15:1 to 7:1) (26.3 mg, 32%): TLC R_f 0.36 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 6H), 1.57-1.64 (m, 4H), 3.33 (s, 3H), 3.35-3.45 (m, 4H), 3.40 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 26.2, 26.4, 43.7, 51.8, 58.5, 71.2, 72.5, 77.5, 176.9; IR (neat) 1870, 1737, 1117 cm^{-1}; LRMS (FAB) m/e 219 (MH^+), 145 (M^+-C_4H_9O); HRMS (CI) calcd for $C_{10}H_{19}O_3$ (M^+-OCH_3) 187.1334, found 187.1333.

3-(5-Methoxypentoxymethyl)cyclohexene. Prepared from **4d** (80.5 mg, 0.394 mmol) and 3-(trimethylsilyl)cyclohexene (128.7 mg, 0.834 mmol) (reaction time, 15 min). Purified with flash chromatography (hexane/EtOAc 30:1 to 10:1) (34.4 mg, 41%): TLC R_f 0.56 (hexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.47 (m, 3H), 1.49-1.83 (m, 7H), 1.95-2.02 (m, 2H), 2.31-2.43 (m, 1H), 3.27 (d, 2H, J = 6.9 Hz), 3.33 (s, 3H), 3.37 (t, 2H, J = 6.5 Hz), 3.42 (t, 2H, J = 6.5 Hz), 5.56-5.63 (m, 1H), 5.71-5.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 22.9, 25.5, 26.1, 29.5, 29.6, 35.9, 58.5, 71.0, 72.8, 75.2, 128.3, 128.3; IR (neat) 2932, 2858, 1121 cm^{-1}; LRMS (FAB) m/e 213 (M^+), 95 (M^+-$C_6H_{13}O_2$); HRMS (FAB) calcd for $C_{10}H_{17}NO_4$ 213.1855, found 213.1860.

Reference for Supporting information

1. Suga, S.; Miyamoto, K.; Watanabe, M.; Yoshida J. *Appl. Organometal. Chem.* **1999**, *13*, 469.

^{1}H and ^{13}C NMR spectra of the above-described compounds are listed as follows: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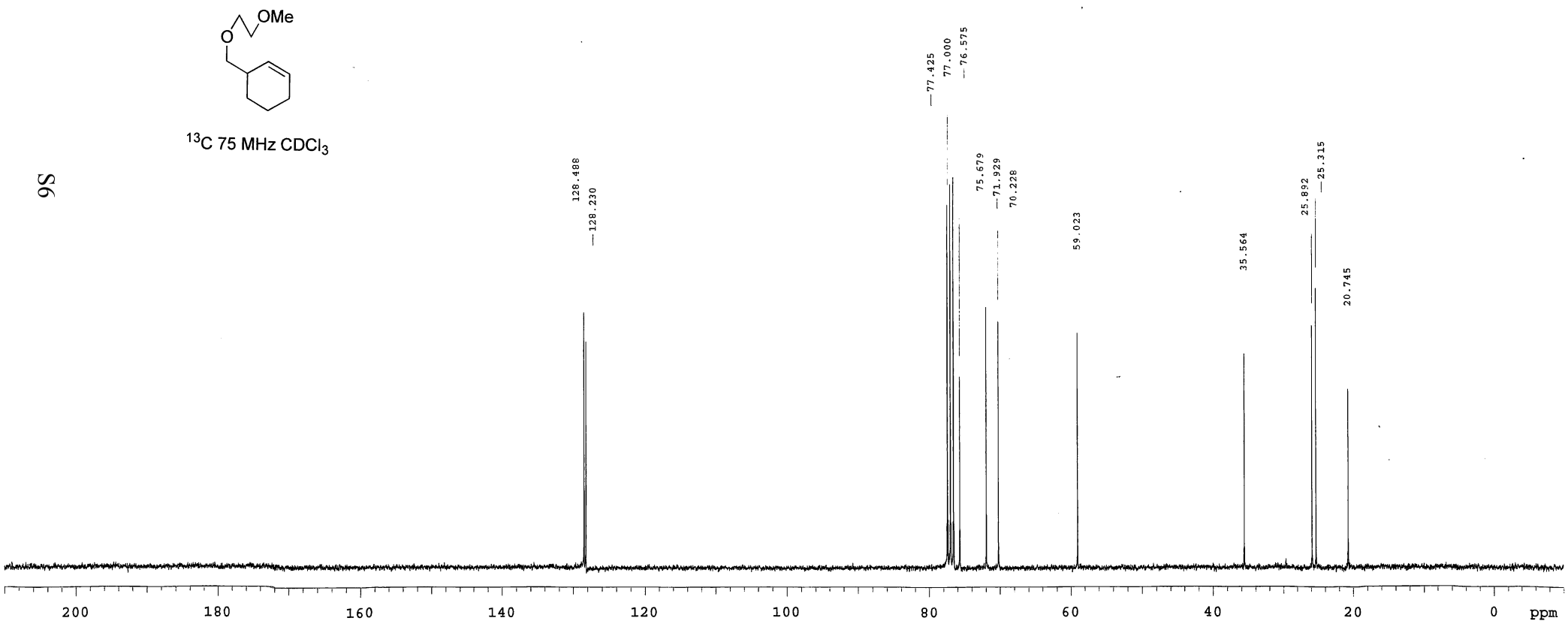
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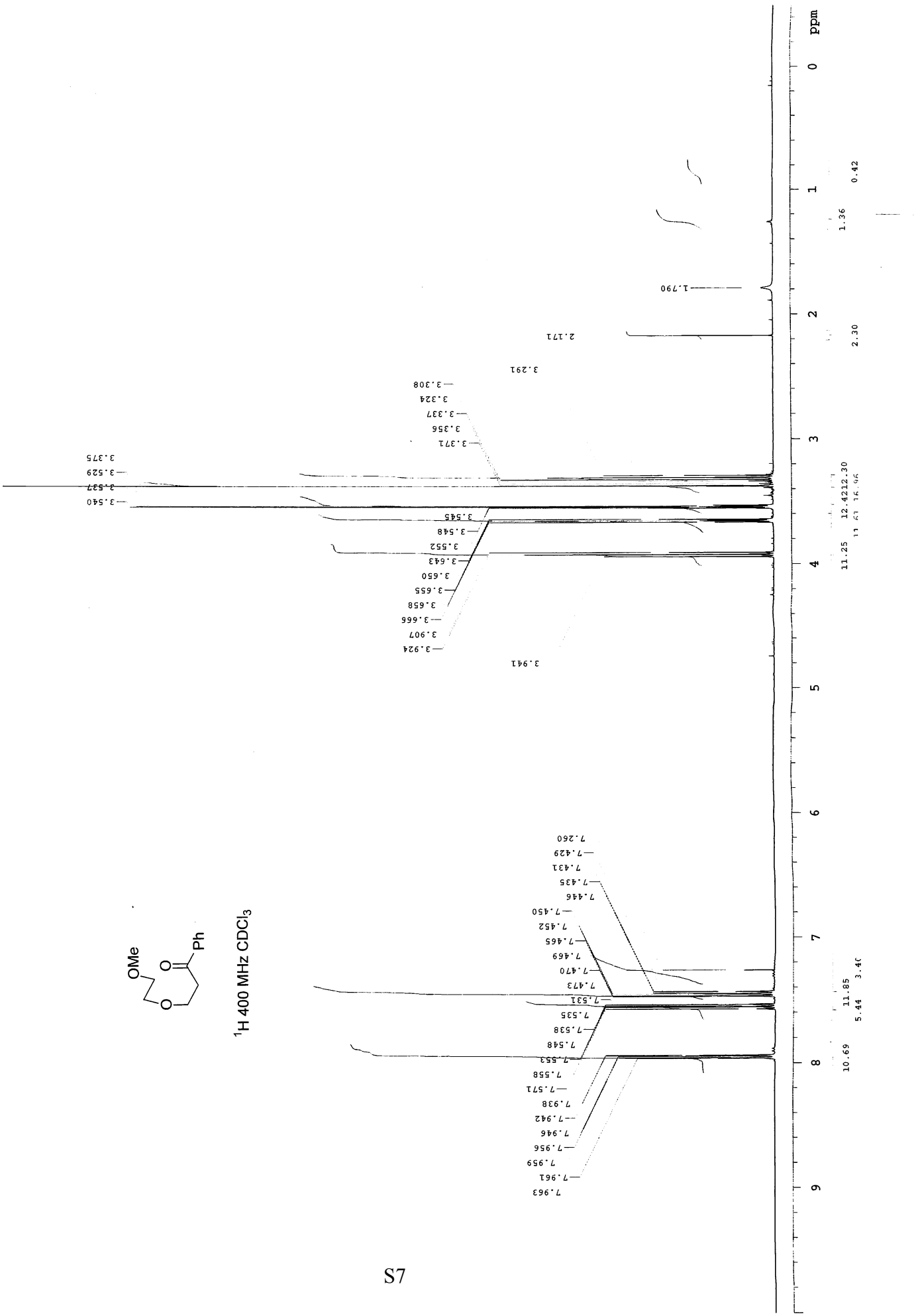
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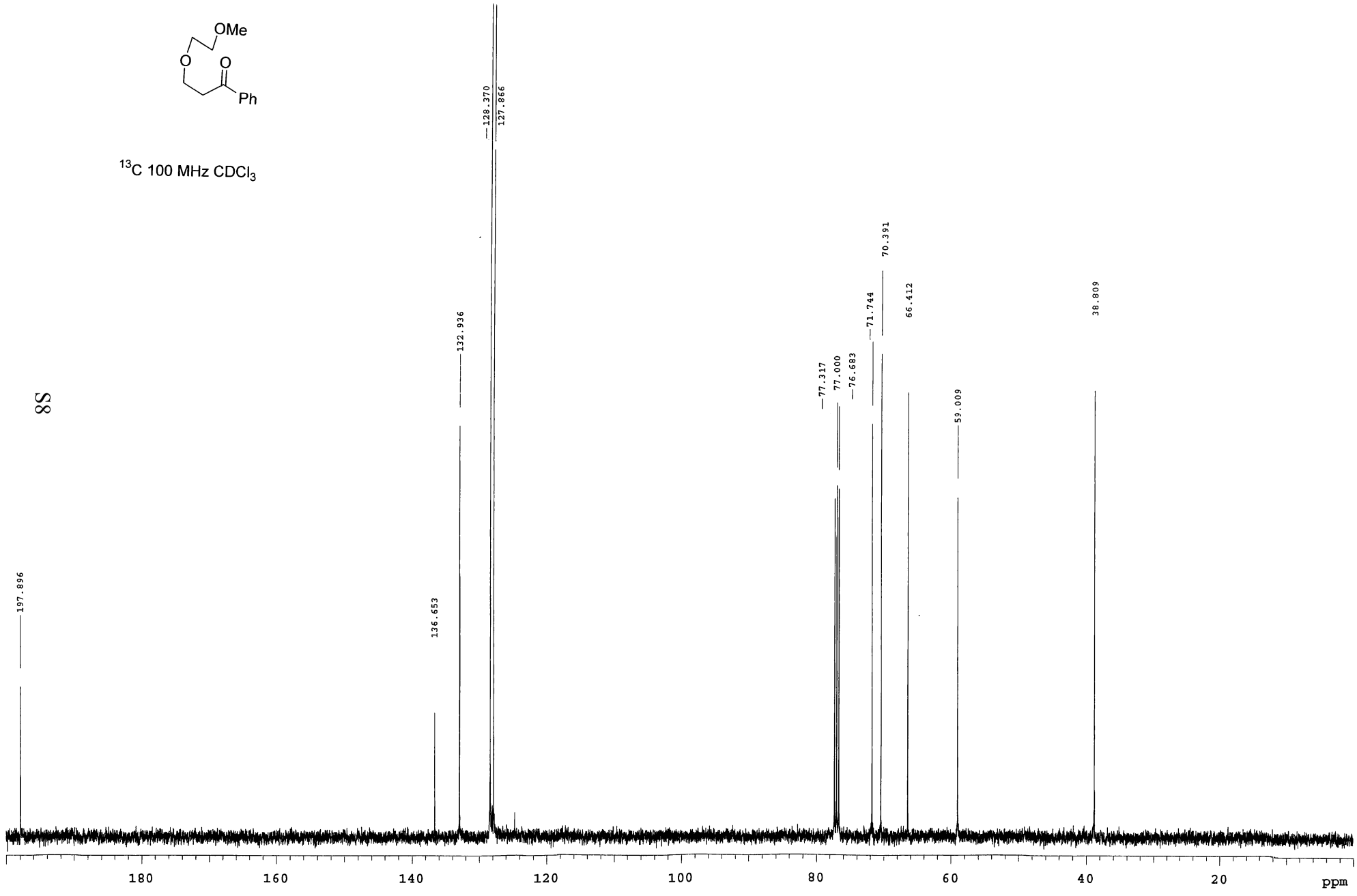
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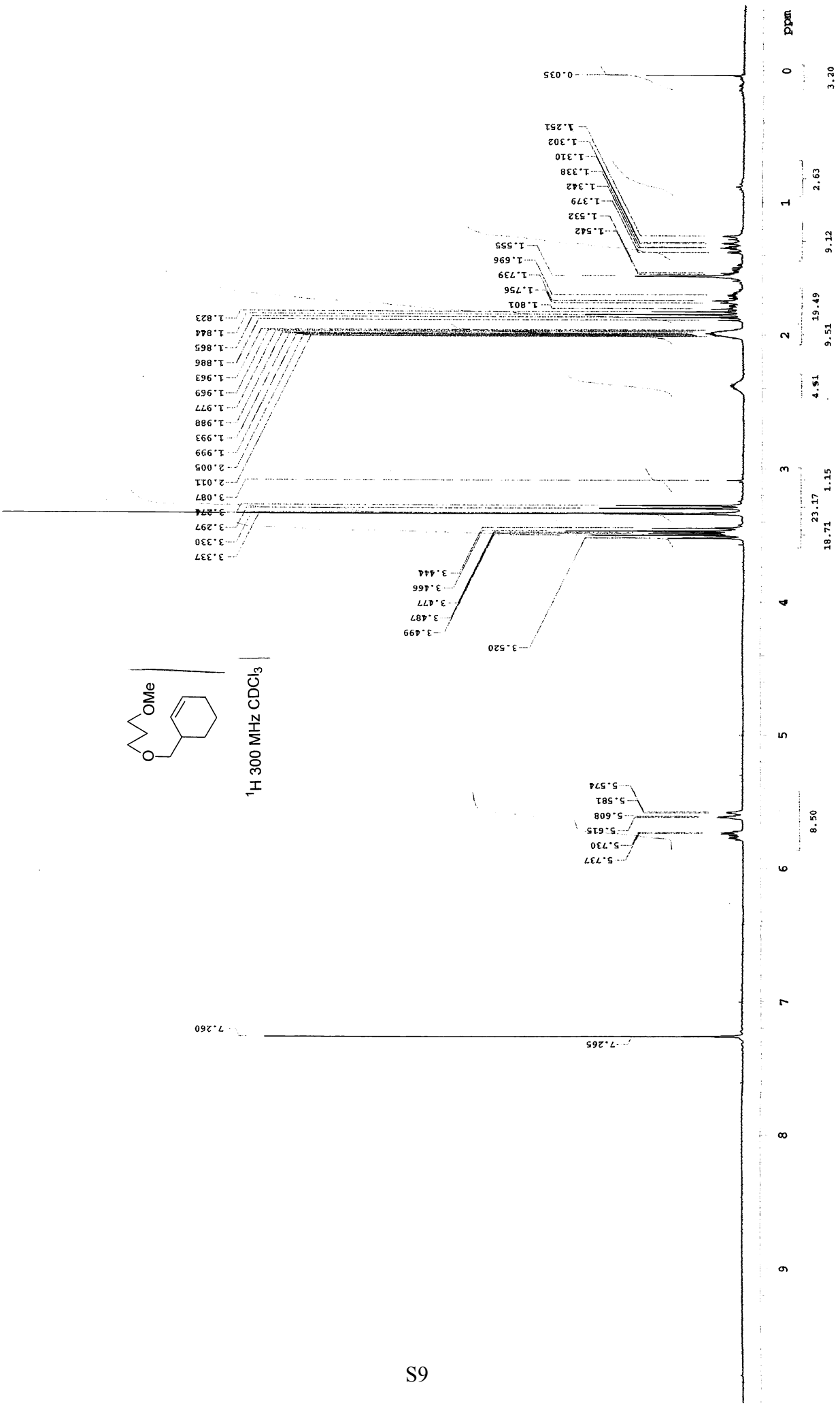
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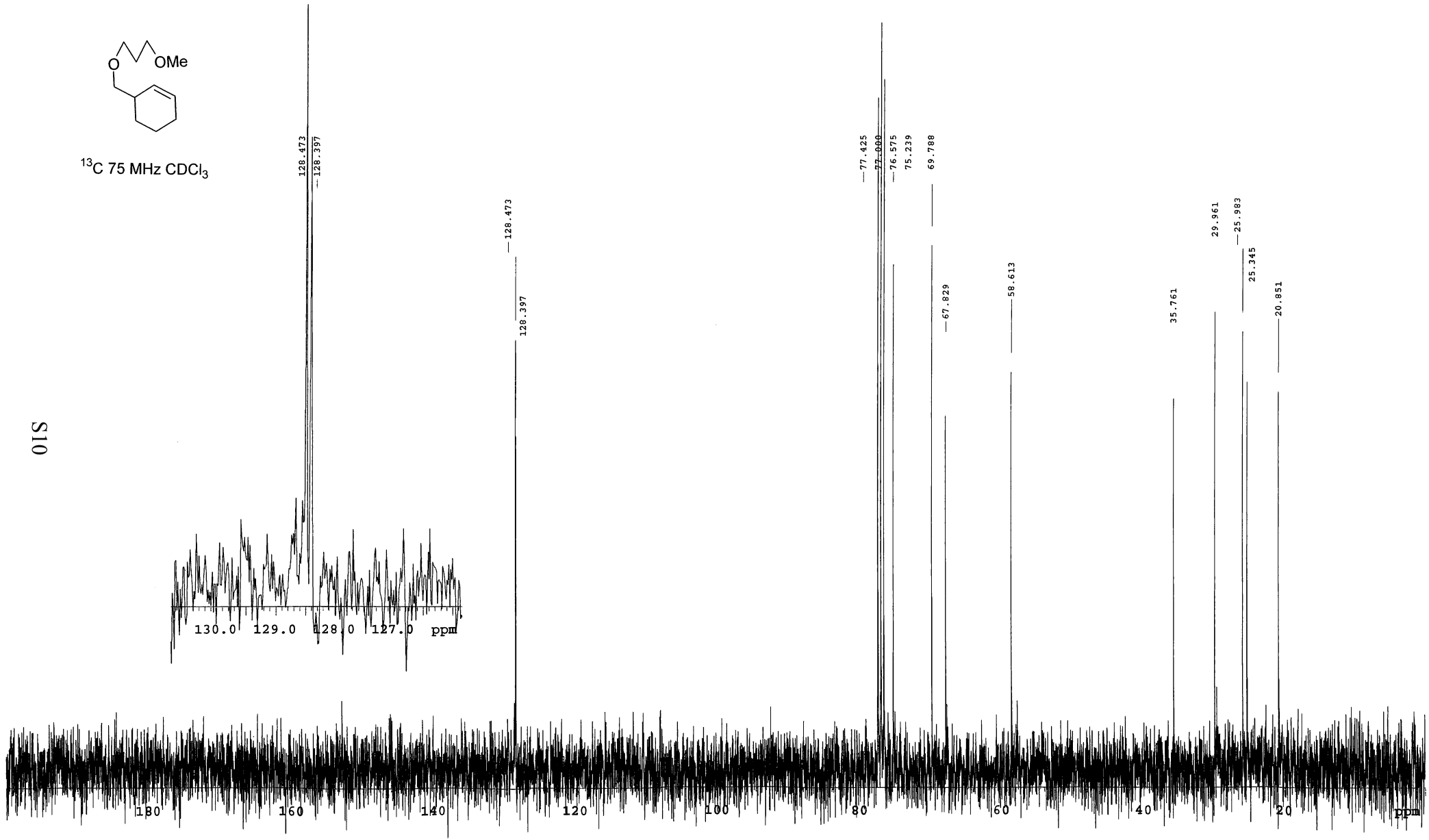
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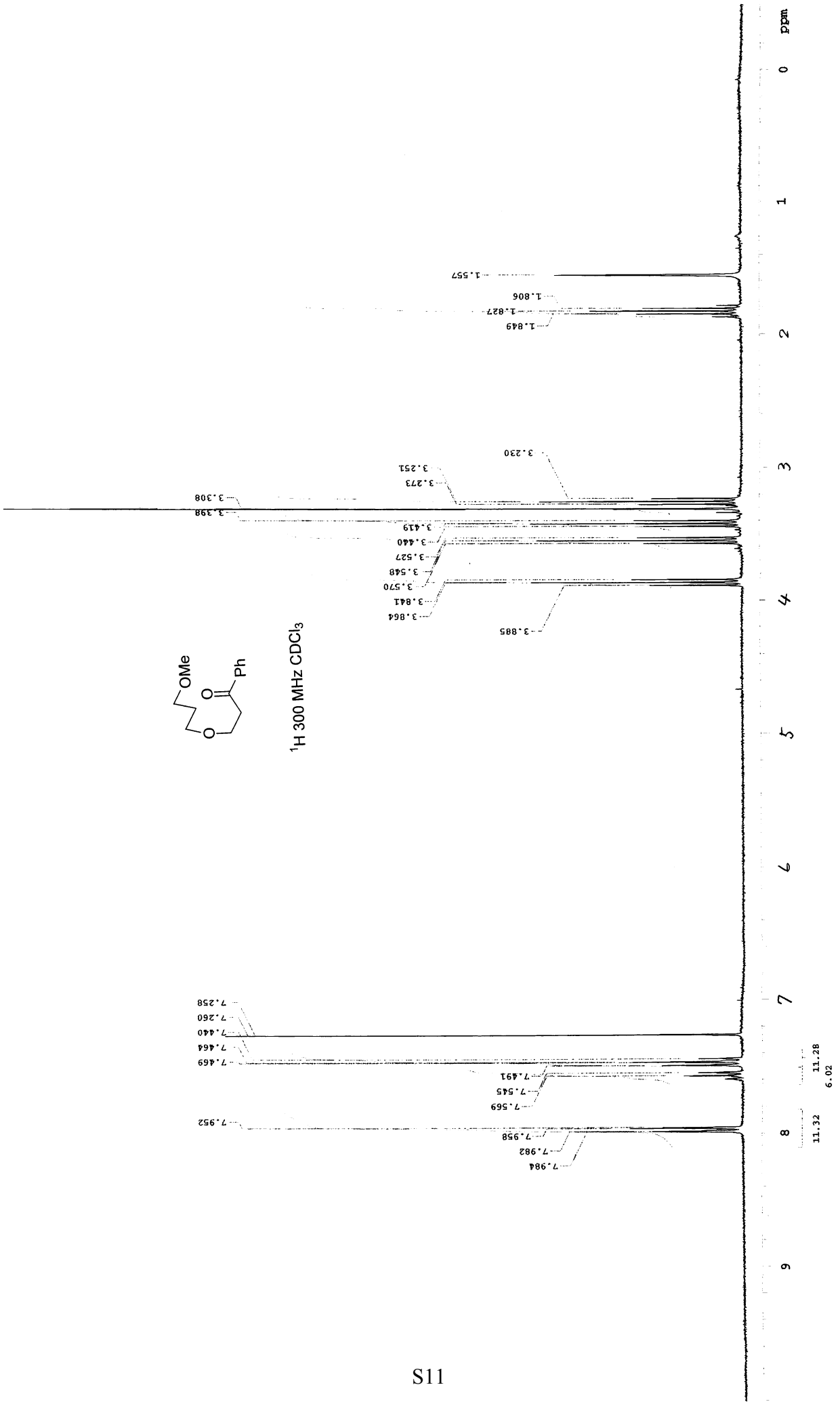
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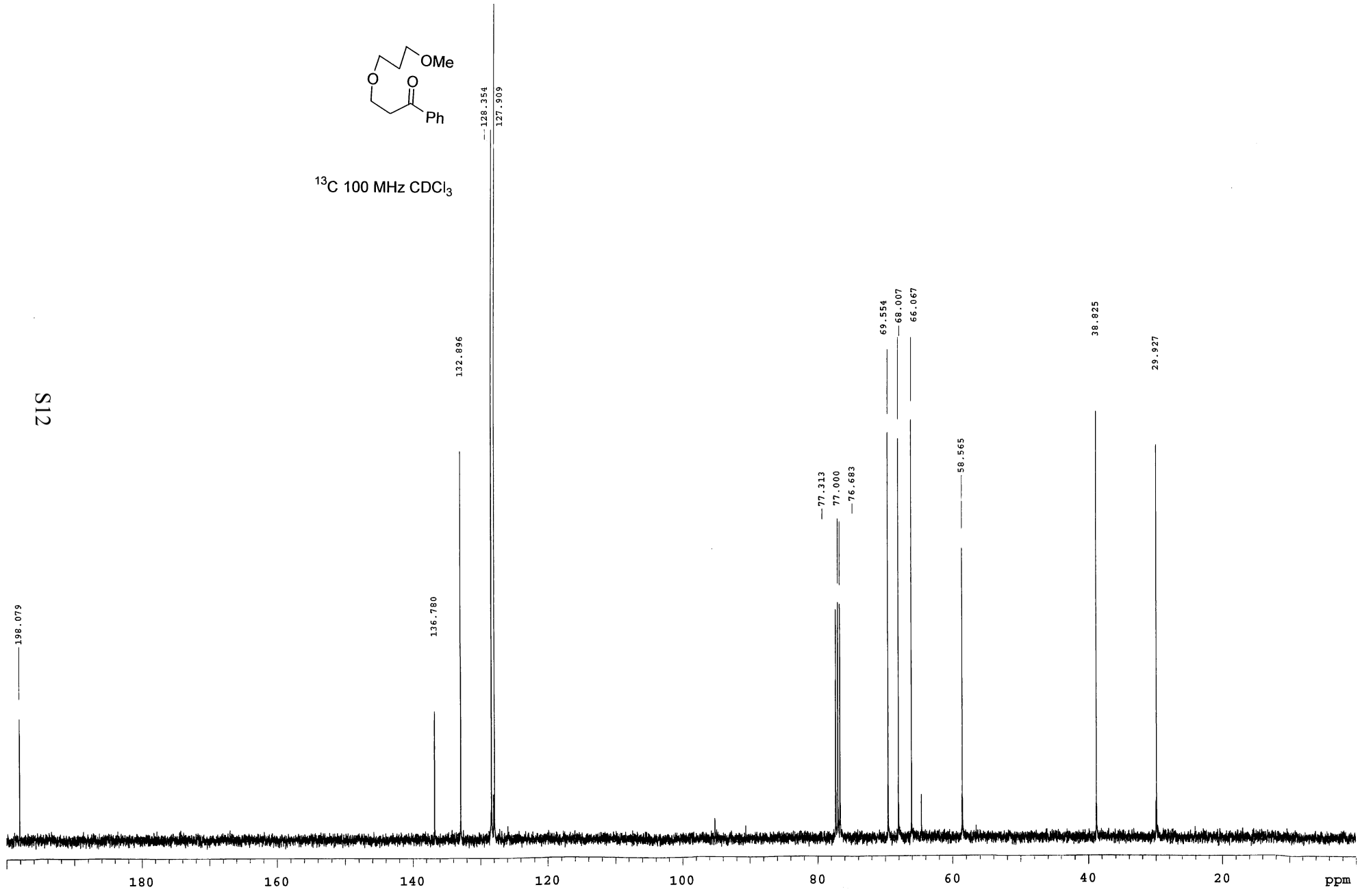
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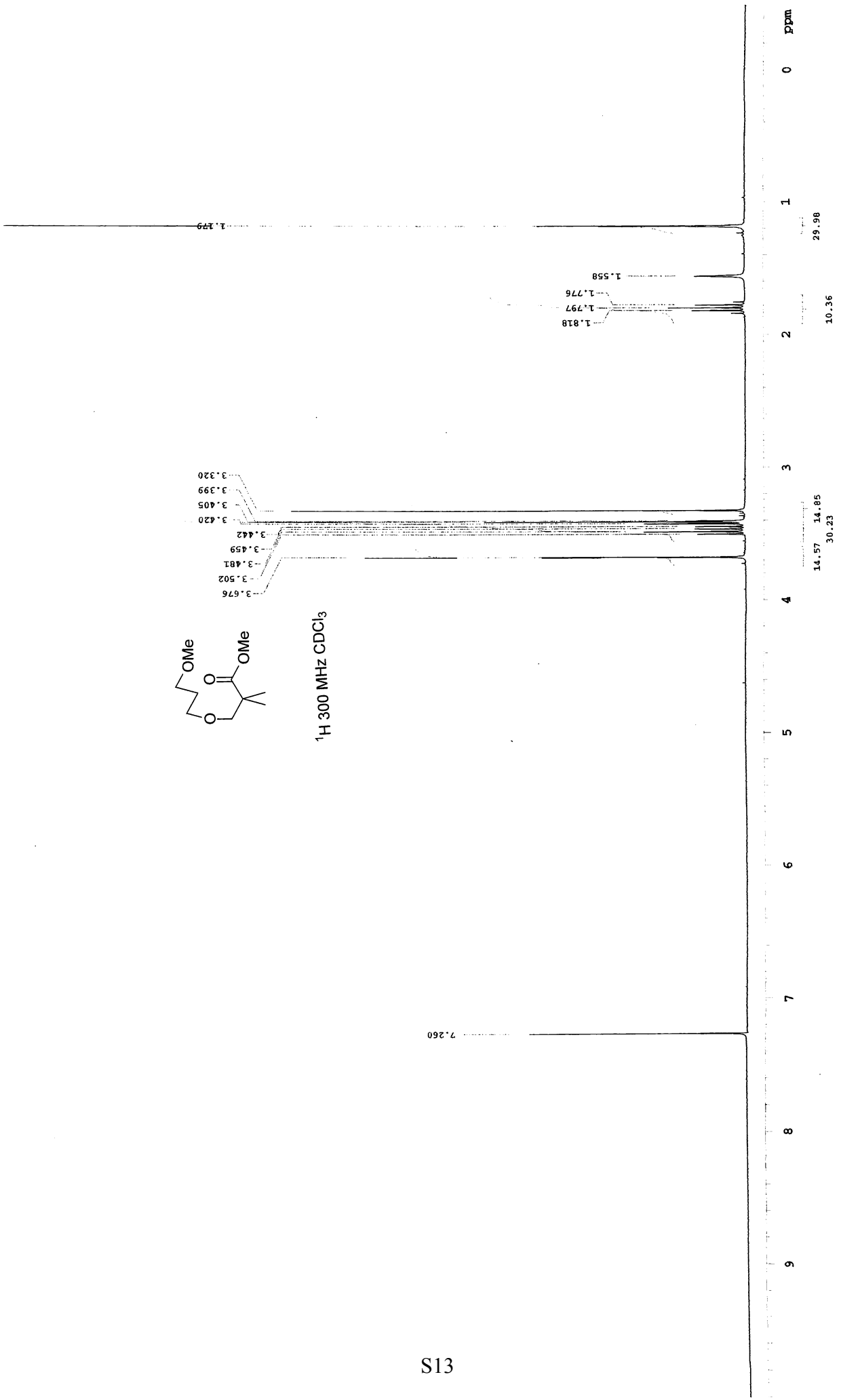
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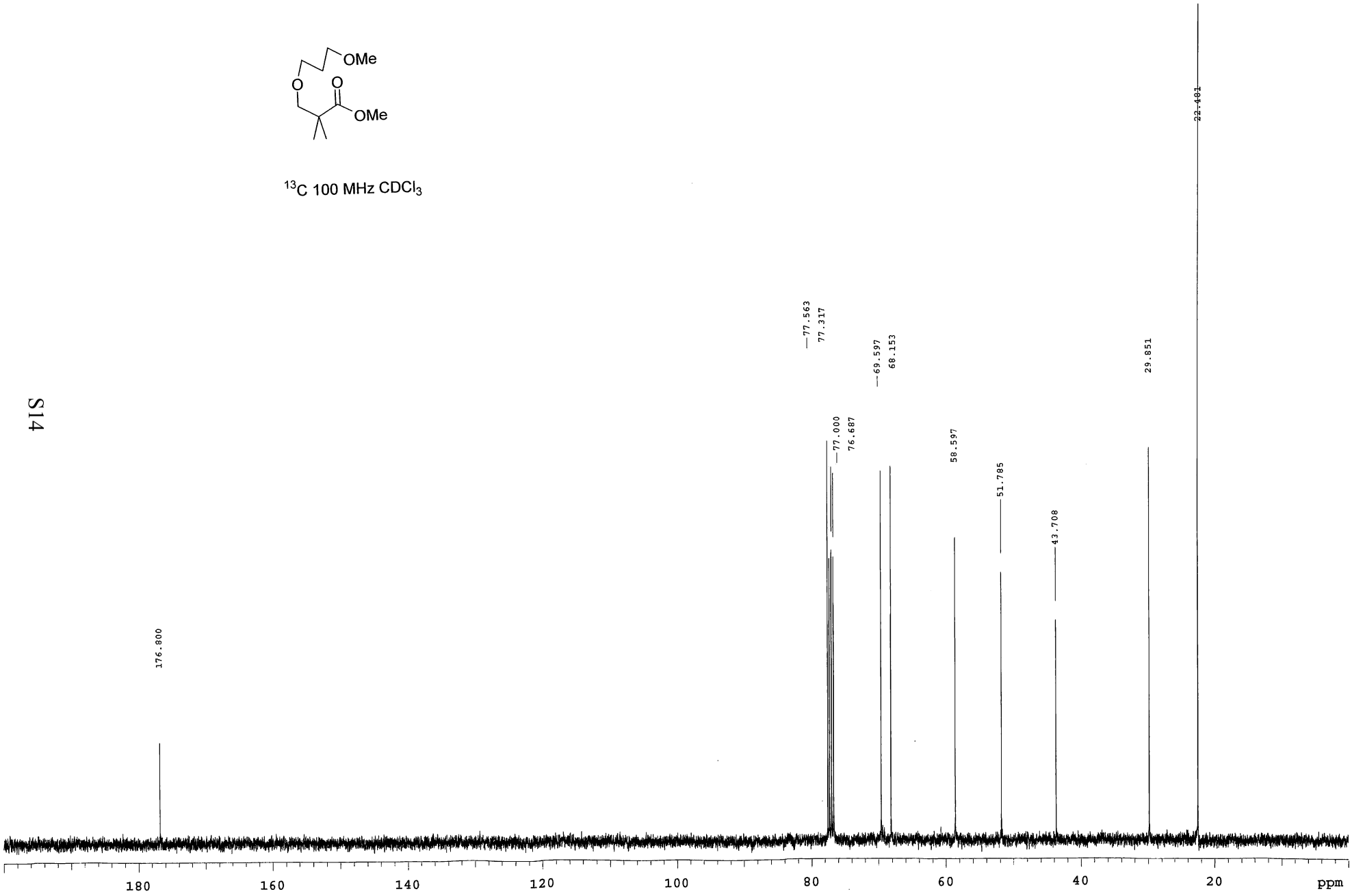
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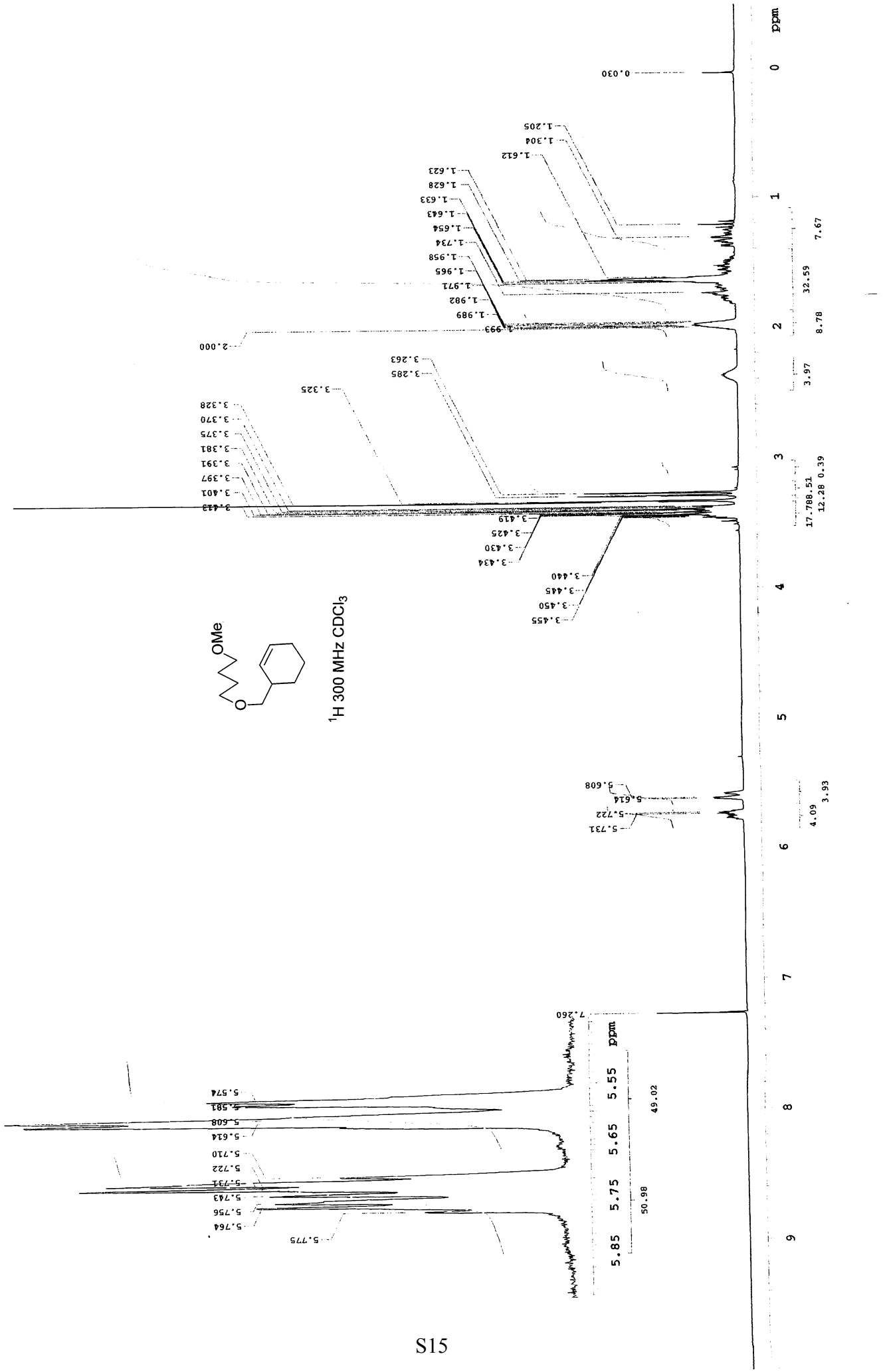
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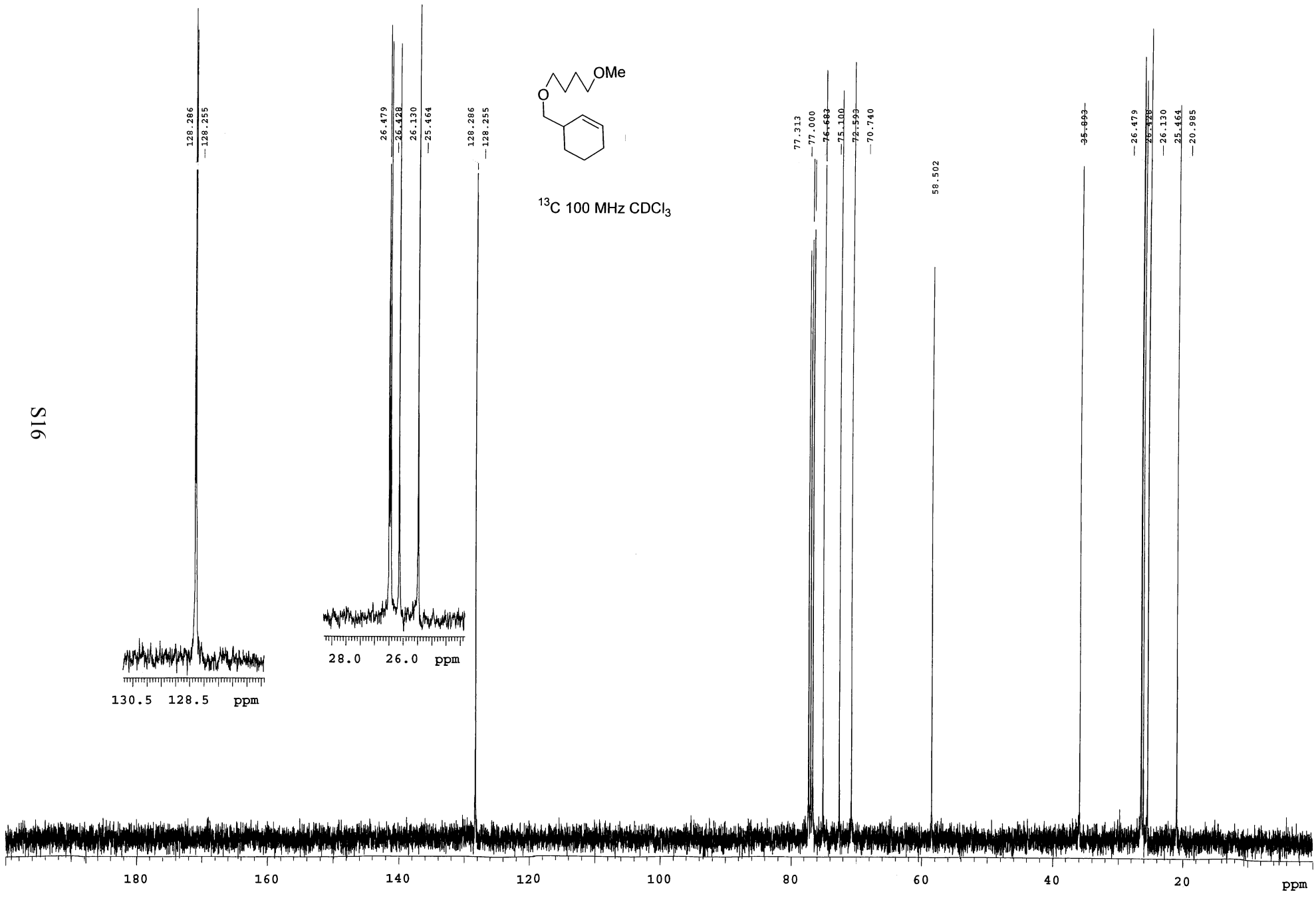
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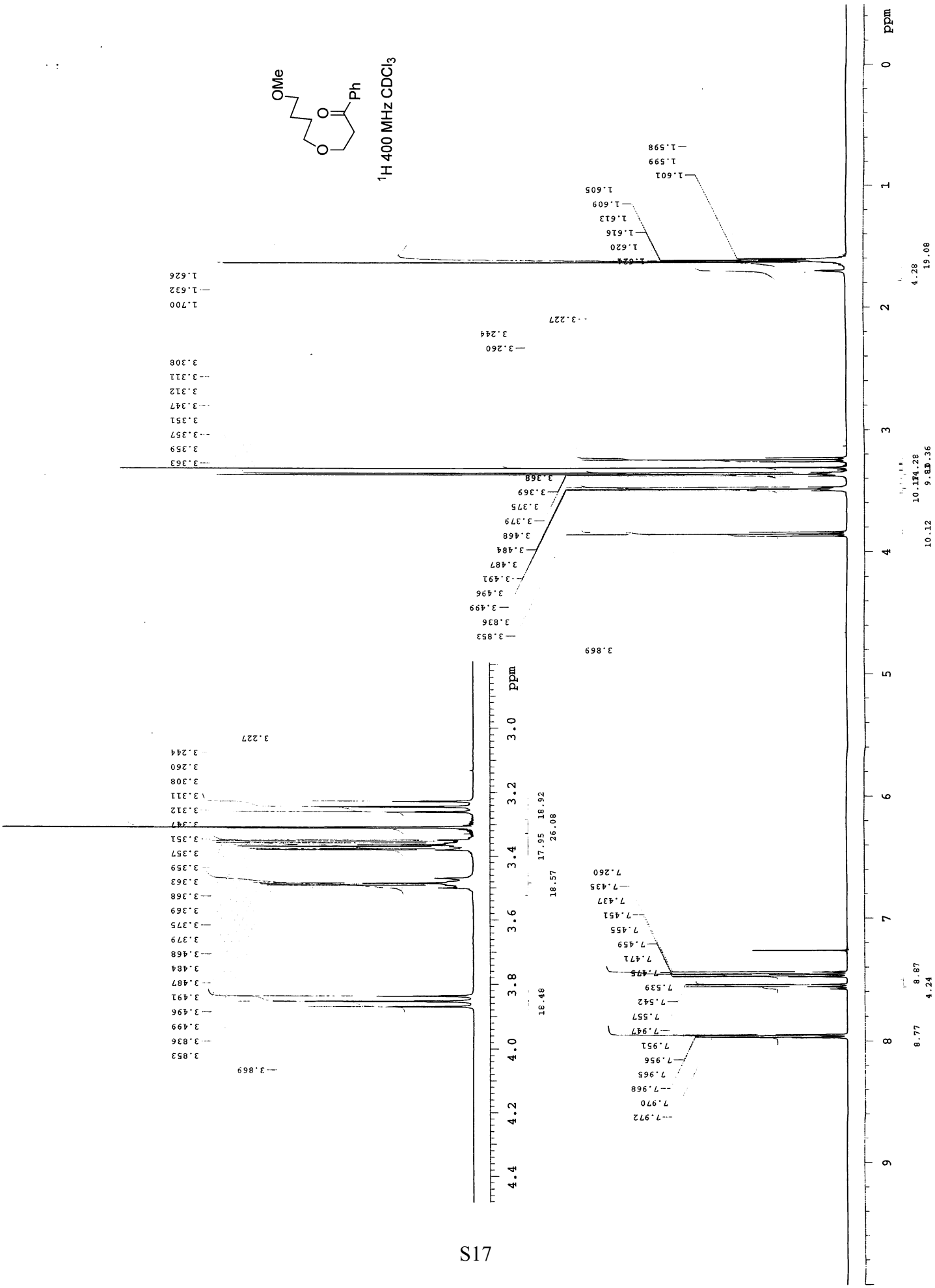
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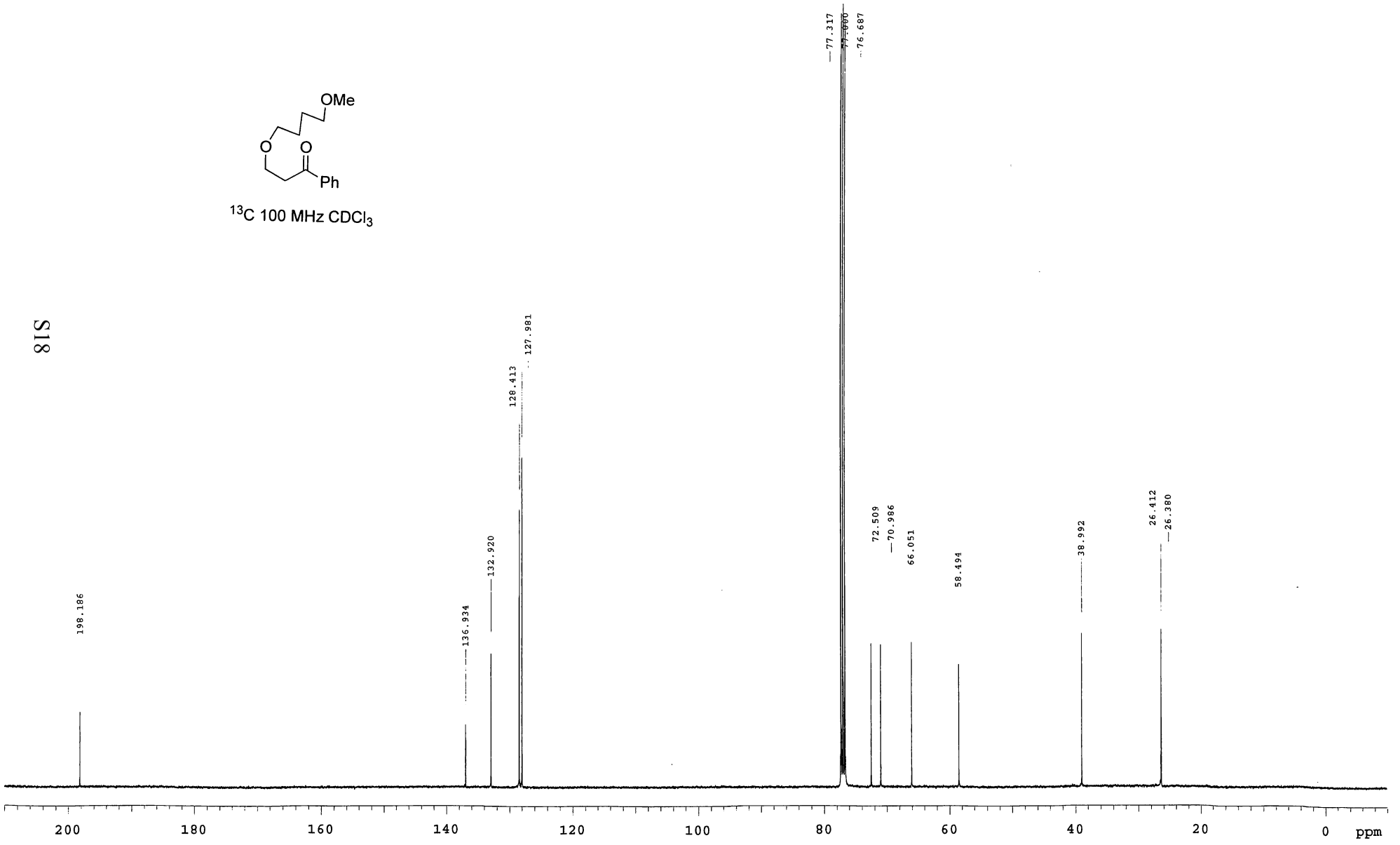
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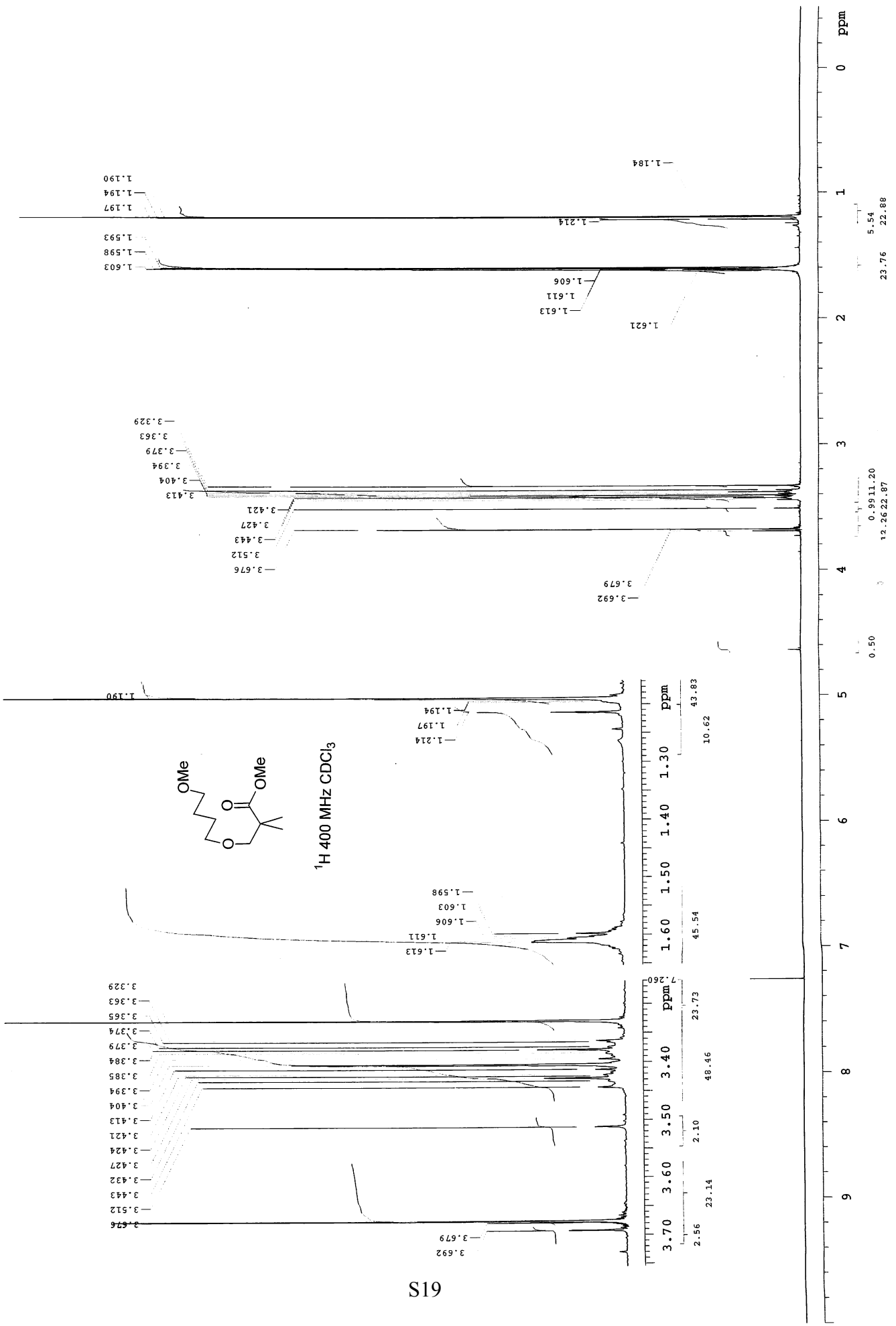
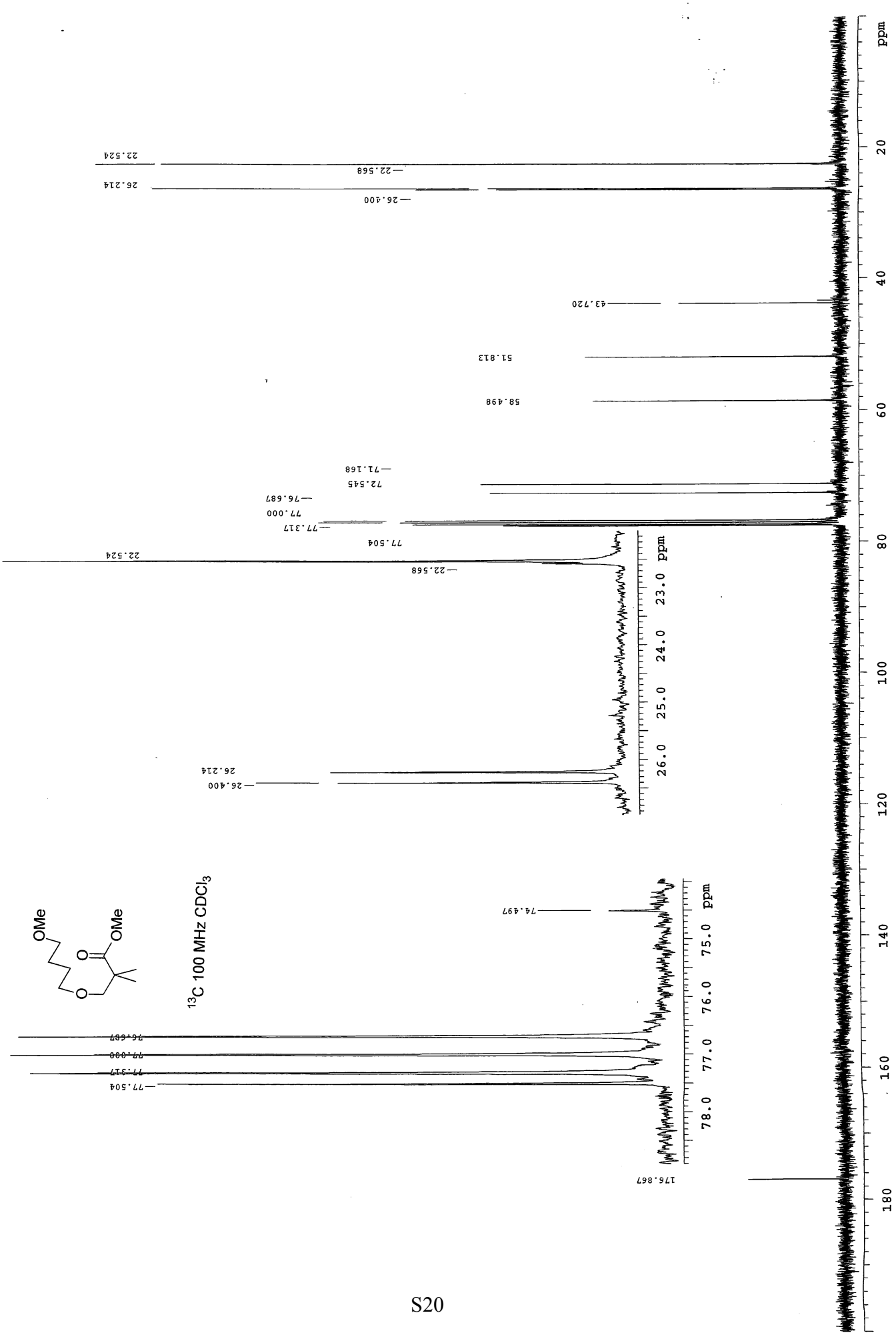
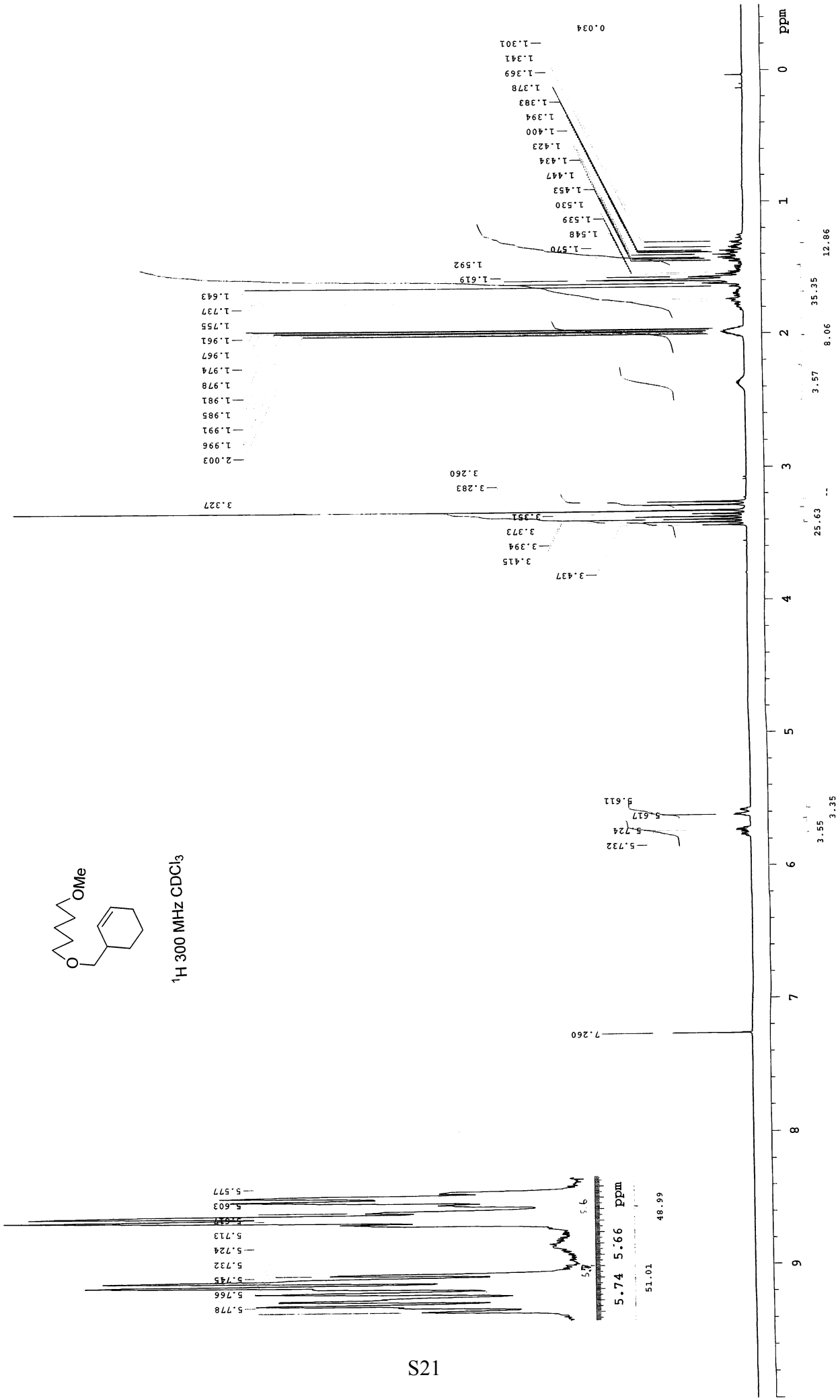
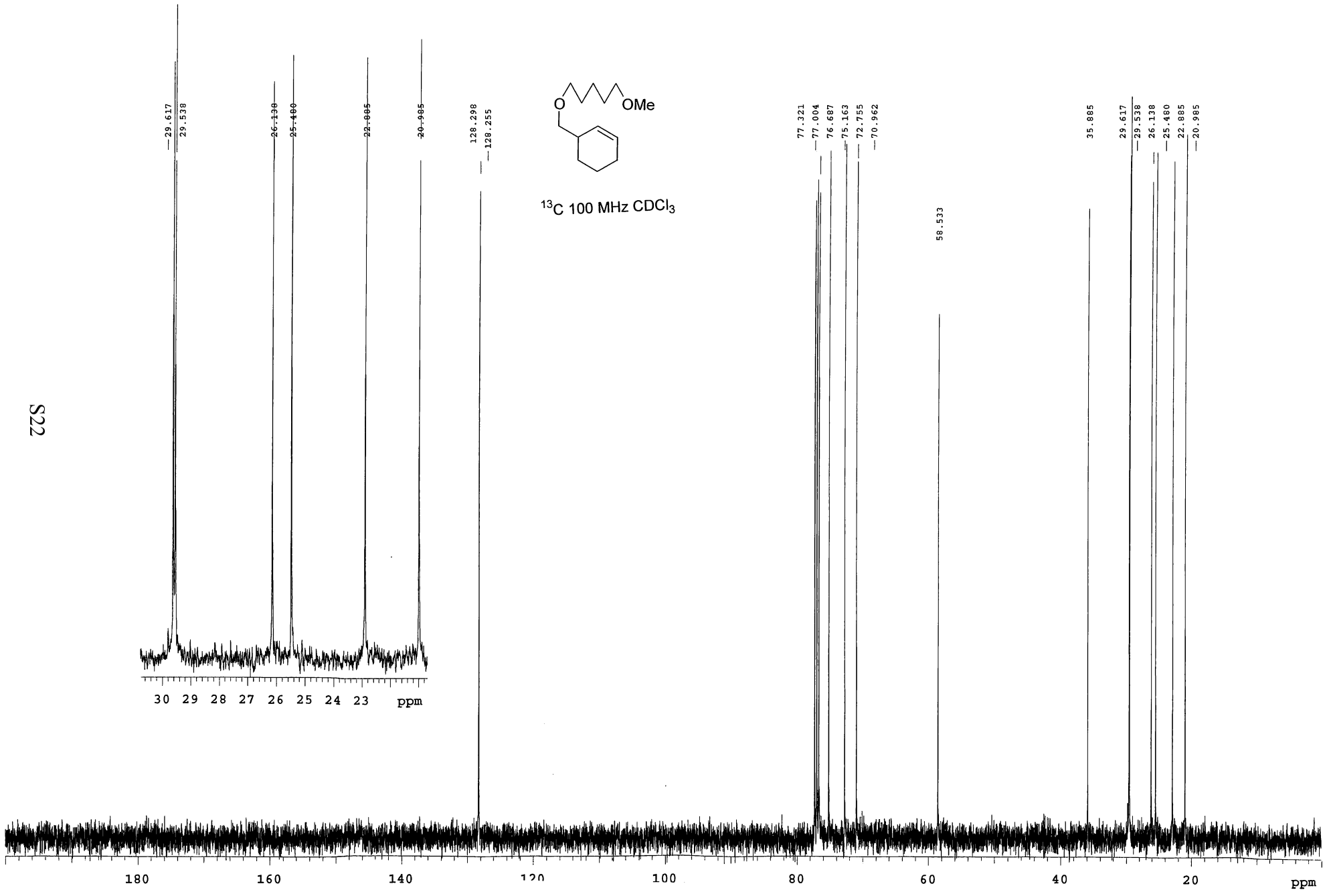
0
ppm


OMe
OMe
O
O
^{1}H 400 MHz CDCl$_3$
ppm


OMe
OMe
O
O
^{13}C 100 MHz $CDCl_3$
176.867
74.497
77.504
77.317
77.000
76.687
72.545
71.168
58.498
51.813
43.720
26.400
26.214
22.568
22.524
ppm


OMe
O
^{1}H 300 MHz $CDCl_3$
ppm


29.617
29.538
26.138
25.480
22.885
20.985
128.298
128.255
77.321
77.004
76.687
75.163
72.755
70.962
58.533
35.885
29.617
29.538
26.138
25.480
22.885
20.985
O
OMe
^{13}C 100 MHz $CDCl_3$
30 29 28 27 26 25 24 23 ppm
180 160 140 120 100 80 60 40 20 ppm