Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Bromine-Radical Mediated Three-Component Reaction Comprising Allenes, Electron-Deficient Alkenes and Allyl Bromides: Facile Synthesis of 2-Bromo-1,7-Dienes

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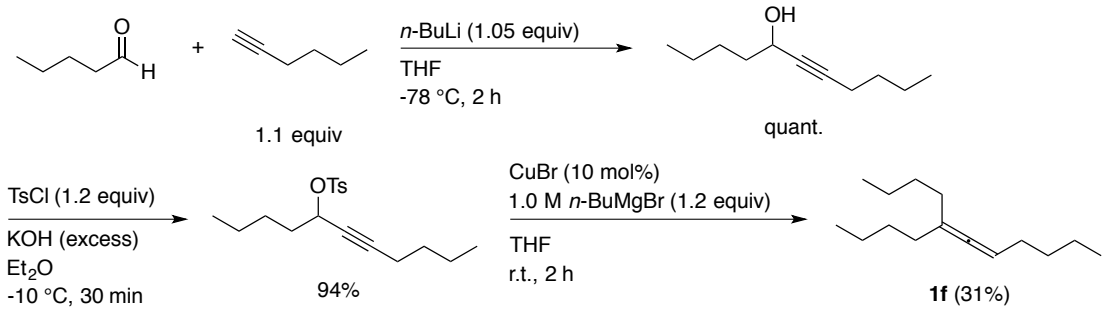
General Information. ^{1}H NMR spectra were recorded with JEOL ECP-500 (500 MHz) and JEOL ECS-400 (400 MHz) spectrometers in $CDCl_3$ and are referenced at 7.26 ppm for $CHCl_3$. ^{13}C NMR spectra were recorded with JEOL ECP-500 (125 MHz) and JEOL ECS-400 (100 MHz) spectrometers in $CDCl_3$ and are referenced at 77.00 ppm for $CHCl_3$. Chemical shifts are reported in parts per million (δ). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sex, sextet; sep, septet; m, multiplet. Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Both conventional and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer. Melting point was measured by BÜCHI Melting Point B-540. The products were purified by flash column chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 mm)) and/or preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) with GPC columns using distilled $CHCl_3$ as an eluent. Benzene was degassed by argon bubbling before use for 30 min. The starting materials **1a**,[1] **1c**,[1] **1e,**[1] **2d**,[2] and **3b**[3] are previously known compounds and are prepared according to literature procedures. Allene **1f** and alkylidenecyclopropane **6** are new compounds and were prepared by the following procedures. Electron-deficient alkenes **2a-c**, **2e** were distilled to remove a trace amount of radical inhibitor before use. Other reagents were commercially available and used without further purification.

Experimental Procedure and Spectral Data for 5-Butyl-5,6-Undecadiene (1f)



Preparation of 6-Undecyn-5-ol

To a solution of 1-hexyne (88 mmol) in distilled THF (40 mL) at -78 °C under argon atmosphere, 1.6 M *n*-BuLi in *n*-hexane (52.5 mL, 84 mmol) was dropwise added. After the mixture was stirred for 1 h at -78 °C, 1-pentanal (80 mmol) was added with stirring for additional 30 min at -78 °C. Then, the reaction mixture was warmed up to room temperature in 30 min. The mixture was quenched by water and extracted with diethyl

[1] Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, *13*, 3864.
[2] Nanteuil, F.; Waser, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 9009.
[3] Ohmura, T.; Masuda, K.; Takase, I.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 16624.

ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure. 6-undecyn-5-ol was obtained in quantitative yield, which was used without further purification.

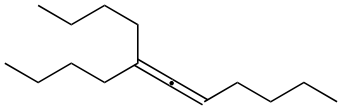
_p_-Toluenesulfonyl Protection of 6-Undecyn-5-ol

To a stirred solution of 6-undecyn-5-ol (80 mmol) in Et_2O (160 mL) was added *p*-toluenesulfonyl chloride (18.3 g, 96 mmol), the reaction mixture was cooled to 0 °C. Then, crushed KOH (30 g) was added in small portions and stirred for 30 min at 0 °C. The reaction mixture was poured into ice water, which was transferred to a separatory funnel. After the extraction with diethyl ether, the combined organic phase was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. 6-undecynyl tosylate was obtained in 94% yield, which was used without further purification.

Prepararion of 5-Butyl-5,6-undecadiene (1f)

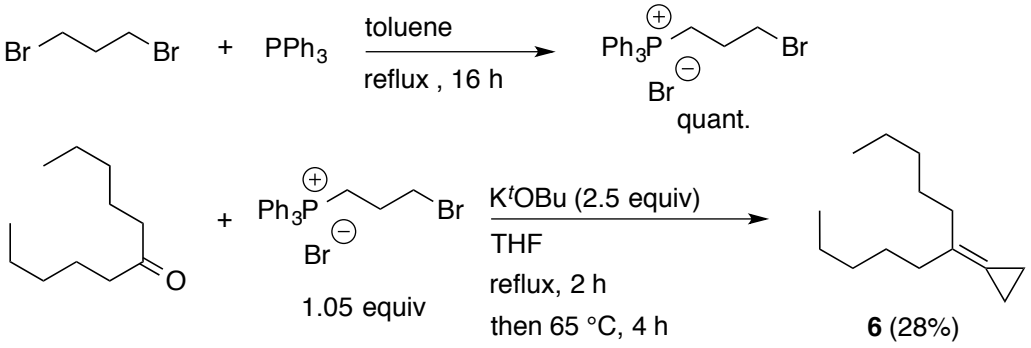
CuBr (1.1 g, 7.5 mmol), 6-undecynyl tosylate (75 mmol) and distilled THF (150 mL) were added to flame dried 300 mL two-neck round bottom flask under argon atmosphere. Then, 1.0 M *n*-BuMgBr in THF (90 mL, 90 mmol) was slowly added. The reaction mixture was stirred for 2 h at room temperature, was quenched by a saturated NH_4Cl aqueous solution (30 mL). After the extraction with diethyl ether, the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the crude reaction mixture was purified by flash column chromatography on SiO_2 (hexane) to afford 5-butyl-5,6-undecadiene (**1f**) in 31% yield as a colorless liquid.

5-Butyl-5,6-undecadiene (1f)



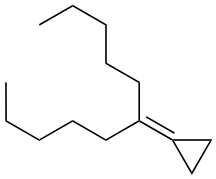
Colorless oil; R_f = 0.95 (Hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86-0.92 (m, 9H), 1.25-1.42 (m, 12H), 1.88-2.00 (m, 6H), 5.04 (sep, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.97, 14.01, 22.26, 22.47, 29.29, 29.95, 31.69, 32.49, 91.58, 104.00, 200.67; IR (neat): 2957, 2927, 2872, 2859, 1961, 1465 cm^{-1}; EIMS *m*/*z* (relative intensity) 208 ($[M]^+$, 5), 166 (68), 124 (98), 109 (100), 95 (92), 81 (78), 67 (62); HRMS (EI) *m*/*z* calcd for $C_{15}H_{28}$ $[M]^+$: 208.2191, found: 208.2196.

Experimental Procedure and Spectral Data for 6-Undecanylidenecyclopropane (6)



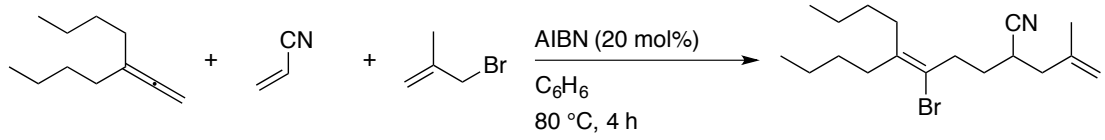
To a 500 mL round bottom flask, 1,3-dibromopropane (41.6 g, 200 mmol), triphenylphosphine (52.5 g, 200 mmol) and toluene (100 mL) were added. The mixture was heated at 110 °C and maintained with stirring for 16 h. The white precipitate was filtered and washed with additional 50 ml of toluene and dried overnight in a vacuum stove, yielding 3-bromopropyltriphenylphosphonium bromide quantitatively. Then, K^{t}OBu (14.0 g, 125 mmol) was added at room temperature in three portions (41.7 mmol each) to a stirred suspension of 3-bromopropyltriphenylphosphonium bromide (24.4 g, 50 mmol) in dry THF (300 mL). After the solution was stirred at room temperature for 30 min, The orange solution was then refluxed for 2 h before the addition of 6-undecanone (8.5 g, 50 mmol) and stirring was continued at 65 °C for 4 h. The reaction mixture was quenched by water (200 mL) at room temperature, the aqueous layer was extracted with hexane (3 × 50 mL). The combined organic layers were washed with brine (4 × 100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on SiO_2 (hexane) to afford 6-undecanylidenecyclopropane (**6**) in 28% yield as a colorless liquid.

6-Undecanylidenecyclopropane (6)



Colorless oil; R_f = 0.95 (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 6H), 0.96-1.00 (m, 4H), 1.20-1.38 (m, 8H), 1.47 (quint, *J* = 7.6 Hz, 4H), 2.13 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.88, 14.11, 22.62, 27.46, 31.82, 34.84, 114.40, 128.41; IR (neat): 3044, 2957, 2928, 2871, 2857, 1466 cm^{-1}; EIMS *m/z* (relative intensity) 194 ([M]$^+$, 1), (1), 179 (1), 165 (2), 151 (5), 137 (8), 123 (14), 109 (32), 95 (69), 81 (100), 67 (75), 55 (50); HRMS (EI) *m/z* calcd for $C_{14}H_{26}$ [M]$^+$: 194.2035, found: 194.2035.

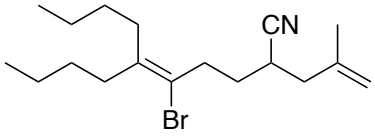
General Procedure of the Bromine Radical Mediated Three-Component Reaction for 4



1a (1.0 M) **2a** (1.8 equiv) **3a** (1.8 equiv) **4a** 79%

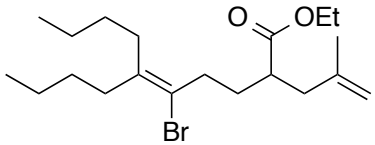
To a 20 mL screw capped test tube, 3-butyl 1,2-heptadiene (**1a**, 152.3 mg, 1.00 mmol), acrylonitrile (**2a**, 95.5 mg, 1.8 mmol), β-methallyl bromide (**3a**, 243.0 mg, 1.8 mmol), 2,2'-azobisisobutylonitrile (AIBN, 32.8 mg, 0.2 mmol) and degassed benzene (1 mL) were added. Then, this test tube was purged with argon and sealed. The mixture was stirred at 80 °C for 4 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on SiO_2 (Hexane/EtOAc = 1 : 0 to 100 : 1) and preparative HPLC (chloroform) to give 5-bromo-6-butyl-2-(2-methallyl)-5-decenenitrile (**4a**, 268.1 mg, 79%).

5-Bromo-6-butyl-2-(2-methylallyl)-5-decenenitrile (4a)



Colorless oil; R_f = 0.50 (Hexane : EtOAc = 5 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90-0.94 (m, 6H), 1.29-1.43 (m, 8H), 1.73-1.81 (m, 4H), 1.95 (dtd, *J* = 13.0, 8.0, 4.0 Hz, 1H), 2.06-2.31 (m, 5H), 2.40 (dd, *J* = 14.0, 9.0 Hz, 1H), 2.64-2.75 (m, 3H), 4.86 (s, 1H), 4.93 (t, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.89, 13.91, 21.87, 22.61, 22.68, 28.67, 28.83, 29.52, 29.70, 30.86, 31.02, 32.27, 32.46, 34.40, 36.38, 40.35, 114.16, 120.37, 121.68, 140.31, 141.13; IR (neat): 3078, 2957, 2931, 2871, 2861, 2238, 1652, 1456, 1379, 898 cm^{-1}; EIMS *m/z* (relative intensity) 341 ([M]$^+$, 9), 339 ([M]$^+$, 9), 260 ([M-Br]$^+$, 100), 204 (76), 55 (22); HRMS (EI) *m/z* calcd for $C_{18}H_{30}N^{79}Br$ [M]$^+$: 339.1562, found: 339.1555.

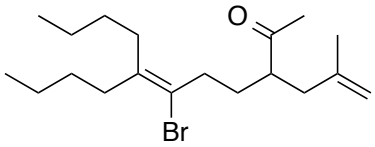
Ethyl 5-bromo-6-butyl-2-(2-methallyl)-5-decenoate (4b)



Colorless oil; R_f = 0.27 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.94 (m, 6H), 1.23-1.41 (m, 11H), 1.72 (s, 3H), 1.74-1.85 (m, 2H), 1.99-2.10 (m, 2H), 2.11-2.24 (m, 3H), 2.38 (dd, *J* = 14.5, 8.5 Hz, 1H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.52-2.59 (m, 1H) 4.08-4.18 (m, 2H), 4.71 (s, 1H), 4.77 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.93, 13.98, 14.31, 22.09, 22.73, 29.78, 30.86, 30.97, 32.14, 35.18, 36.37, 40.72, 42.89, 60.24, 112.34, 122.09, 139.57, 142.70, 175.44; IR (neat): 3076, 29.57, 29.31, 2871, 2861, 1734, 1456, 1159 cm^{-1}; EIMS *m/z* (relative intensity) 343 ([M-OEt]$^+$, 4), 341 ([M-OEt]$^+$, 4), 307 ([M-Br]$^+$,

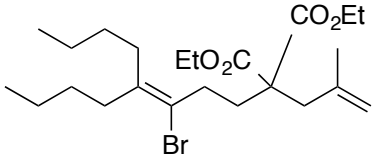
100), 261 (14), 233 (19), 167 (14), 142 (18), 93 (18); HRMS (EI) *m/z* calcd for $C_{18}H_{30}O^{79}Br$ $[M\text{-}OEt]^+$: 341.1480, found: 341.1486.

6-Bromo-7-butyl-3-(2-methallyl) -6-undecen-2-one (4c)



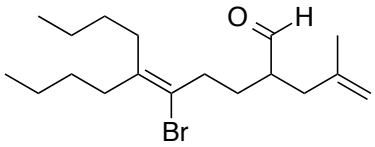
Colorless oil; R_f = 0.24 (Hexane : EtOAc = 30 : 1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.89-0.93 (m, 6H), 1.26-1.41 (m, 8H), 1.66-1.74 (m, 4H), 1.82 (dtd, *J* = 14.5, 8.5, 6.0 Hz, 1H), 2.20-2.22 (m, 8H), 2.34 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.37-2.47 (m, 2H), 2.64-2.71 (m, 1H), 4.69 (s, 1H), 4.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.91, 22.19, 22.70, 22.73, 28.57, 29.76, 30.01, 30.88, 32.18, 34.87, 36.35, 39.77, 49.94, 112.54, 122.03, 139.71, 142.62 ,211.44; IR (neat): 3076, 2957, 2931, 2861, 1714, 1456, 893 cm^{-1}; EIMS *m/z* (relative intensity) 358 ($[M]^+$, 1). 356 ($[M]^+$, 1), 277 ($[M\text{-}Br]^+$, 100), 246 (17), 244 (18), 165 (11), 109 (27), 107 (82), 95 (31), 67 (29), 55 (28); HRMS (EI) *m/z* calcd for $C_{19}H_{33}O^{79}Br$ $[M]^+$: 356.1715, found: 356.1709.

Diethyl 2-(3-bromo-4-butyl-3-octen-1-yl)-2-(2-methylallyl)malonate (4d)



Colorless oil; R_f = 0.21 (Hexane : EtOAc = 30 : 1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.88-0.94 (m, 6H), 1.24-1.40 (m, 14H), 1.69 (s, 3H), 2.01-2.06 (m, 2H), 2.10-2.19 (m, 4H), 2.35-2.40 (m, 2H), 2.72 (s, 2H), 4.15-4.24 (m, 4H), 4.80 (s, 1H), 4.88 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.92, 14.01, 22.71, 22.75, 23.03, 29.69, 30.85, 31.38, 32.03, 32.90, 36.26, 40.37, 56.49, 61.26, 115.64, 121.30, 139.61, 140.51, 171.31; IR (neat): 3076, 2958, 2935, 2871, 2860, 1733, 1463, 1457, 1447, 1198 cm^{-1}; EIMS *m/z* (relative intensity) 460 ($[M]^+$, 1), 458 ($[M]^+$, 1), 415 ($[M\text{-}OEt]^+$, 2), 413 ($[M\text{-}OEt]^+$, 2), 379 ($[M\text{-}Br]^+$, 50), 214 (100), 168 (19), 122 (32); HRMS (EI) *m/z* calcd for $C_{21}H_{34}O_3{}^{79}Br$ $[M\text{-}OEt]^+$: 413.1691, found: 413.1690.

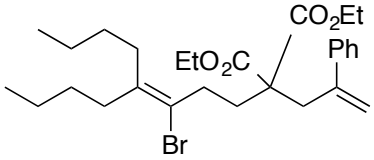
5-Bromo-6-butyl-2-(2-methylallyl)-5-decenal (4e)



Colorless oil; R_f = 0.28 (Hexane : EtOAc = 30 : 1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.88-0.94 (m, 6H), 1.27-1.40 (m, 8H), 1.70-1.79 (m, 4H), 1.80-1.89 (m, 1H), 2.03-2.08 (m, 2H), 2.11-2.23 (m, 3H), 2.40 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.44-2.51 (m, 3H), 4.74 (s, 1H), 4.83 (s,

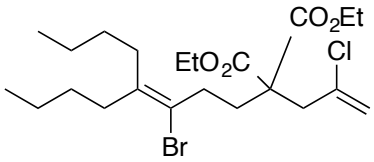
1H), 9.61 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.93, 13.96, 22.28, 22.70, 22.75, 27.66, 29.72, 30.87, 32.22, 34.74, 36.38, 37.40, 48.59, 112.98, 121.83, 139.99, 141.94, 204.28; IR (neat): 2957, 2930, 2860, 1728, 1650, 1456, 895 cm^{-1}; EIMS *m*/*z* (relative intensity) 344 ([M]$^+$, 3). 342 ([M]$^+$, 3), 263 ([M-Br]$^+$, 100), 246 (40), 244 (40), 165 (12), 109 (30), 93 (35), 67 (23), 55 (24); HRMS (EI) *m*/*z* calcd for $C_{18}H_{31}O^{79}Br$ [M]$^+$: 342.1558, found: 342.1554.

Diethyl 2-(3-bromo-4-butyl-3-octen-1-yl)-2-(2-phenylallyl)malonate (4f)



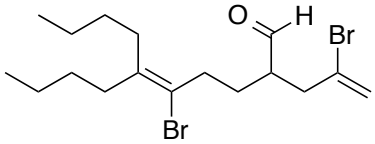
Colorless oil; R_f = 0.18 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.93 (m, 6H), 1.14 (t, *J* = 7.5 Hz, 6H), 1.24-1.40 (m, 8H), 1.95-2.01 (m, 2H), 2.04-2.10 (m, 2H), 2.11-2.18 (m, 2H), 2.30-2.36 (m, 2H), 3.17 (s, 2H), 3.81 (dq, *J* = 11.0, 7.5 Hz, 2H), 3.91 (dq, *J* = 11.0, 7.5 Hz, 2H), 5.22 (s, 1H), 5.26 (d, *J* = 1.5 Hz, 1H), 7.20-7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.83, 13.95, 22.70, 29.68, 30.65, 30.78, 31.94, 32.73, 36.18, 37.48, 56.56, 61.05, 118.58, 121.23, 126.89, 127.41, 127.92, 139.50, 141.53, 144.33, 170.77; IR (neat): 2957, 2932, 2871, 2861, 1732, 1199 cm^{-1}; EIMS *m*/*z* (relative intensity) 523 ([M]$^+$, 1), 521 ([M]$^+$, 1), 477 ([M-OEt]$^+$, 3), 475 ([M-OEt]$^+$, 3), 441 ([M-Br]$^+$, 97), 395 (21), 276 (100), 230 (47), 202 (95), 184 (58), 173 (28), 84 (24); HRMS (EI) *m*/*z* calcd for $C_{26}H_{36}O_3{}^{79}Br$ [M-OEt]$^+$: 475.1848, found: 475.1861.

Diethyl 2-(3-bromo-4-butyl-3-octen-1-yl)-2-(2-chloroallyl)malonate (4g)



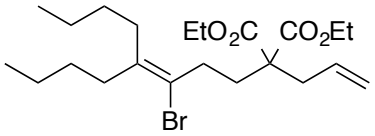
Colorless oil; R_f = 0.21 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.93 (m, 6H), 1.23-1.40 (m, 14H), 2.01-2.07 (m, 2H), 2.14-2.19 (m, 2H), 2.19-2.25 (m, 2H), 2.35-2.41 (m, 2H), 3.06 (s, 2H), 4.16-4.26 (m, 4H), 5.28 (s, 1H), 5.34 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.97, 14.01, 22.75, 22.82, 29.72, 30.61, 30.88, 32.10, 32.87, 36.29, 41.32, 56.31, 61.65, 117.19, 120.89, 137.13, 139.96, 170.39; IR (neat): 2958, 2860, 1734, 1632, 1464 cm^{-1}; EIMS *m*/*z* (relative intensity) 437 ([M-OEt]$^+$, 1), 435 ([M-OEt]$^+$, 2), 433 ([M-OEt]$^+$, 1), 401 ([M-Br]$^+$, 36), 399 ([M-Br]$^+$, 100), 236 (33), 234 (96), 199 (66), 153 (41), 109 (24), 95 (37). 79 (37), 67 (39), 55 (36); HRMS (EI) *m*/*z* calcd for $C_{20}H_{31}O_3{}^{35}Cl^{79}Br$ [M-OEt]$^+$: 433.1145, found: 433.1144.

5-Bromo-2-(2-bromoallyl)-6-butyl-5-undecenal (4h)



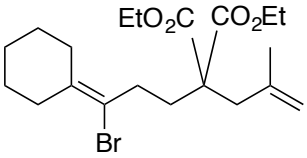
Colorless oil; R_f = 0.27 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-0.94 (m, 6H), 1.26-1.43 (m, 8H), 1.74-1.83 (m, 1H), 1.88-1.96 (m, 1H), 2.05-2.10 (m, 2H), 2.16-2.22 (m, 2H), 2.45-2.56 (m, 3H), 2.70-2.77 (m, 1H), 2.86 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 5.67-5.70 (m, 1H), 9.71 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.95, 22.73, 22.76, 27.00, 29.71, 30.89, 32.29, 34.54, 36.40, 40.48, 48.79, 119.42, 121.44, 130.71, 140.29, 202.69; IR (neat): 2956, 2929, 2860, 1728, 1631, 1457, 892 cm^{-1}; EIMS *m*/*z* (relative intensity) 410 ([M]$^+$, 1), 408 ([M]$^+$, 2), 406 ([M]$^+$, 1), 329 ([M-Br]$^+$, 99), 327 ([M-Br]$^+$, 100), 246 (71), 244 (74), 189 (36), 165 (21), 123 (29), 109 (55), 95 (52), 79 (50), 67 (65), 55 (55); HRMS (EI) *m*/*z* calcd for $C_{17}H_{28}O^{79}Br^{81}Br$ [M]$^+$: 408.0486, found: 408.0492.

Diethyl 2-allyl-2-(3-bromo-4-butyl-3-octen-1-yl)malonate (4i)



Colorless oil; R_f = 0.20 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86-0.95 (m, 6H), 1.23-1.40 (m, 14H), 2.01-2.07 (m, 2H), 2.07-2.13 (m, 2H), 2.13-2.20 (m, 2H), 2.35-2.41 (m, 2H), 2.66 (d, *J* = 7.5 Hz, 2H), 4.20 (q, *J* = 7.5 Hz, 4H), 5.09-5.18 (m, 2H), 5.70 (ddt, *J* = 17.5, 10.0, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.92, 13.95, 14.11, 22.73, 22.76, 29.71, 30.85, 31.30, 32.03, 32.65, 36.29, 37.03, 56.86, 61.27, 119.09, 121.26, 132.23, 139.67, 170.91; IR (neat): 2958, 2932, 2861, 1732, 1207, 1192 cm^{-1}; EIMS *m*/*z* (relative intensity) 446 ([M]$^+$, 1), 444 ([M]$^+$, 1), 401 ([M-OEt]$^+$, 2), 399 ([M-OEt]$^+$, 2), 365 ([M-Br]$^+$, 72), 319 (12), 250 (10), 200 (100). 154 (24), 108 (23), 67 (17); HRMS (EI) *m*/*z* calcd for $C_{20}H_{32}O_3{}^{79}Br$ [M-OEt]$^+$: 399.1535, found: 399.1529.

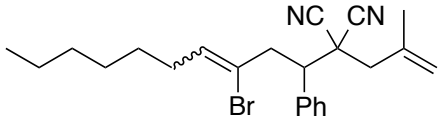
Diethyl 2-(3-bromo-3-cyclohexylidenepropyl)-2-(2-methallyl)malonate (4j)



Colorless oil; R_f = 0.50 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.5 Hz, 6H), 1.47-1.55 (m, 6H), 1.68 (s, 3H), 2.08-2.13 (m, 2H), 2.15-2.20 (m, 2H), 2.32-2.38 (m, 2H), 2.41-2.46 (m, 2H), 2.72 (s, 2H), 4.14-4.25 (m, 4H), 4.80 (s, 1H), 4.88 (t, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.97, 23.03, 26.24, 27.06, 27.71, 30.86, 31.31, 32.64, 35.24, 40.40, 56.43, 61.20, 115.67, 117.41, 138.37, 140.43, 171.24; IR

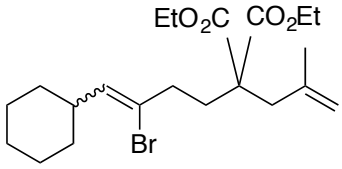
(neat): 2979, 2928, 2854, 1731, 1447 cm^{-1}; EIMS *m*/*z* (relative intensity) 371 ($[M\text{-}OEt]^+$, 4), 369 ($[M\text{-}OEt]^+$, 4), 335 ($[M\text{-}Br]^+$, 100), 214 (78), 122 (50), 79 (56); HRMS (EI) *m*/*z* calcd for $C_{18}H_{26}O_3{}^{79}Br$ $[M\text{-}OEt]^+$: 369.1065, found: 369.1069.

2-(3-bromo-1-phenyl-3-decen-1-yl)-2-(2-methallyl)malononitrile (4k)



Obtained as an inseparable mixture (*E*/*Z* = 14/86); Colorless oil; R_f = 0.29 (Hexane : EtOAc = 10 : 1); *Z* isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.0 Hz, 3H), 0.90-1.25 (m, 8H), 1.88-1.96 (m, 5H), 2.30 (d, *J* = 13.5 Hz, 1H), 2.52 (d, *J* = 14.5 Hz, 1H), 2.94-2.99 (m, 1H), 3.15-3.25 (m ,1H), 3.43-3.55 (m, 1H), 5.04 (s, 1H), 5.12-5.15 (m, 1H), 5.75 (t, *J* = 7.0 Hz, 1H), 7.31-7.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.98, 22.38, 22.99, 27.76, 28.19, 30.91, 31.45, 41.44, 43.91, 44.27, 50.85, 114.75, 115.32, 118.39, 121.87, 128.85, 133.68, 134.43, 137.25; *E* isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 3H), 0.90-1.25 (m, 8H), 1.88-1.96 (m, 5H), 2.29 (d, *J* = 17.0 Hz, 1H), 2.52 (d, *J* = 14.5 Hz, 1H), 3.15-3.27 (m, 2H), 3.52 (dd, *J* = 11.0, 4.0 Hz, 1H), 5.04 (s, 1H), 5.12-5.15 (m, 1H), 5.48 (t, *J* = 6.5 Hz, 1H), 7.31-7.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.98, 22.38, 22.99, 28.63, 29.79, 38.12, 41.44, 43.91, 44.27, 50.97, 114.75, 115.32, 118.39, 119.27, 128.85, 134.65, 136.34 (Some carbon signals superposed that of Z isomers); IR (neat): 2954, 2927, 2856, 2247, 1649, 1455, 1437, 910, 721, 700 cm^{-1}; EIMS *m*/*z* (relative intensity) 414 ($[M]^+$, 3), 416 ($[M]^+$, 3), 334 (43), 333 ($[M\text{-}Br]^+$, 100), 277 (19), 229 (12), 213 (15), 183 (14), 143 (18), 129 (28), 128 (19), 123 (38), 91 (63), 55 (28); HRMS (EI) *m*/*z* calcd for $C_{23}H_{29}N_2{}^{79}Br$ $[M]^+$: 412.1514, found: 412.1506.

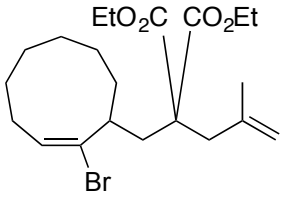
Diethyl 2-(3-bromo-4-cyclohexyl-3-buten-1-yl)-2-(2-methaallyl)malonate (4l)



Obtained as an inseparable mixture (*E*/*Z* = 28/72); Colorless oil; R_f = 0.65 (Hexane : EtOAc = 10 : 1); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.36 (m, 11H), 1.56-1.73 (m, 8H), 2.03-2.17 (m, 2H), 2.27-2.40 (m, 3H), 2.70 (s, 2H), 4.12-4.26 (m, 4H), 4.76 (s, 1H), 4.88 (t, *J* = 1.2 Hz, 1H), 5.45 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 23.16, 25.62, 25.90, 31.48, 31.77, 36.62, 40.30, 40.38, 56.36, 61.27, 115.75, 124.59, 134.52, 140.38, 171.21, 171.25; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.36 (m, 11H), 1.56-1.73 (m, 8H), 2.03-2.17 (m, 3H), 2.27-2.40 (m, 2H), 2.73 (s, 2H), 4.12-4.26 (m, 4H), 4.80 (s, 1H), 4.90 (t, *J* = 1.2 Hz, 1H), 5.70 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 22.96, 25.69, 31.14, 31.21, 32.82, 36.62, 39.14, 40.18, 56.36, 61.34, 115.75, 122.95, 138.66, 140.43, 171.21, 171.25; IR (neat): 2926, 2851, 1733, 1447, 1196

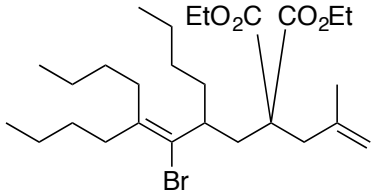
cm^{-1}; EIMS *m*/*z* (relative intensity) 430 ($[M]^+$, 1), 428 ($[M]^+$, 1), 385 ($[M\text{-}OEt]^+$, 3), 383 ($[M\text{-}OEt]^+$, 3), 349 ($[M\text{-}Br]^+$, 86), 214 (100), 122 (46); HRMS (EI) *m*/*z* calcd for $C_{19}H_{28}O_3{}^{79}Br$ $[M\text{-}OEt]^+$: 383.1222, found: 383.1222.

(*E*)-Diethyl 2-(2-(2-bromocyclo-1-nonen-1-yl)ethyl)-2-(2-methallyl)malonate (4m)



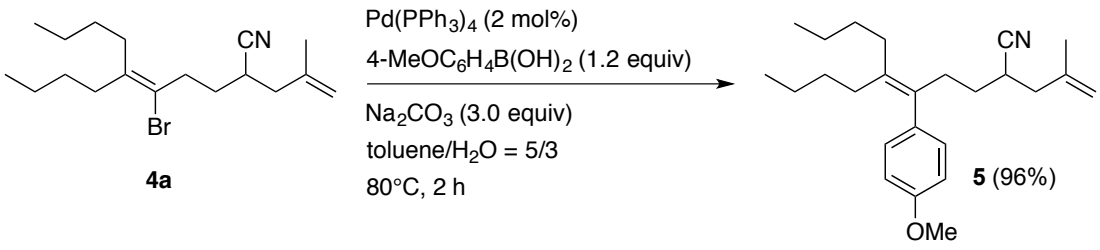
Colorless oil; R_f = 0.28 (Hexane : EtOAc = 30 : 1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.16-1.60 (m, 16H), 1.66 (s, 1H), 1.72-1.83 (m, 3H), 2.06-2.14 (m, 2H), 2.42 (dd, *J* = 15.0, 8.5 Hz, 1H), 2.72-2.82 (m, 2H), 2.91-2.99 (m, 1H), 4.04 (dq, *J* = 11.0, 7.5 Hz, 1H), 4.09-4.22 (m, 3H), 4.76 (s, 1H), 4.88 (s, 1H), 6.09 (t, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.82, 13.93, 22.45, 23.15, 26.25, 27.54, 28.67, 29.94, 34.04, 36.80, 41.31, 55.97, 61.01, 61.08, 115.59, 132.24, 134.11, 140.84, 171.11, 171.75; IR (neat): 2979, 2929, 2868, 1732, 1447, 1214, 1182 cm^{-1}; EIMS *m*/*z* (relative intensity) 430 ($[M]^+$, 1), 428 ($[M]^+$, 1), 385 ($[M\text{-}OEt]^+$, 2), 383 ($[M\text{-}OEt]^+$, 2), 349 ($[M\text{-}Br]^+$, 100), 275 (19), 229 (21), 214 (57), 122 (44); HRMS (EI) *m*/*z* calcd for $C_{19}H_{28}O_3{}^{79}Br$ $[M\text{-}OEt]^+$: 383.1222, found: 383.1214.

Diethyl 2-(3-bromo-2,4-dibutyl-3-octen-1-yl)-2-(2-methylallyl)malonate (4n)



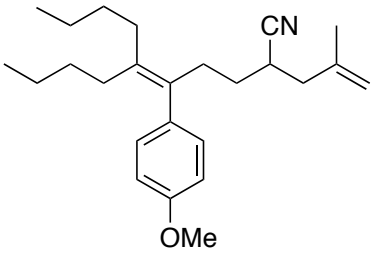
Colorless oil; R_f = 0.25 (Hexane : EtOAc = 30 : 1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.5 Hz, 3H), 0.89-0.95 (m, 6H), 1.00-1.53 (m, 20H), 1.67 (s, 3H), 1.93 (dd, *J* = 15.5, 4.56 Hz, 1H), 1.97-2.06 (m, 1H), 2.13-2.25 (m, 3H), 2.39 (dd, *J* = 15.0, 8.0 Hz, 1H), 2.62-2.71 (m, 2H), 2.75 (d, *J* = 14.5 Hz, 1H), 4.03 (dq, *J* = 10.5, 7.0 Hz, 1H), 4.09-4.22 (m, 3H), 4.73 (s, 1H), 4.84 (t, *J* = 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.88, 13.95, 22.72, 22.97, 23.18, 23.36, 29.28, 29.56, 30.41, 33.58, 35.64, 36.86, 37.04, 38.71, 40.87, 56.22, 60.97, 61.10, 115.14, 129.59, 139.93, 141.10, 171.05, 171.83; IR (neat): 3075, 2957, 2932, 2871, 2860, 1732, 1644, 1464, cm^{-1}; EIMS *m*/*z* (relative intensity) 516 ($[M]^+$, 1), 514 ($[M]^+$, 1), 471 ($[M\text{-}OEt]^+$, 2), 469 ($[M\text{-}OEt]^+$, 2), 435 ($[M\text{-}Br]^+$, 100), 380 (21), 306 (64), 221 (51), 214 (39), 177 (31), 149 (33); HRMS (EI) *m*/*z* calcd for $C_{25}H_{42}O_3{}^{79}Br$ $[M\text{-}OEt]^+$: 469.2317, found: 469.2326.

Experimental Procedure for Suzuki-Miyaura Coupling Reaction of 4a and Spectral Data of 5



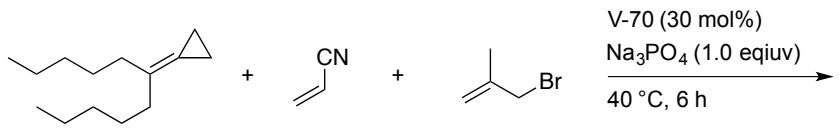
5-Bromo-6-butyl-2-(2-methallyl)-5-decenenitrile **4a** (170.2 mg, 0.50 mmol), 4-methoxyphenylboronic acid (92.1 mg, 0.6 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), 2.0 M Na_2CO_3 aqueous solution (1.5 mL, 3.0 mmol), toluene (2.5 mL) were placed in a 20 mL two-neck round bottom flask under argon atmosphere. The reaction mixture was stirred at 80 °C for 2 h, which was quenched by a saturated NH_4Cl aqueous solution (5 mL). After the extraction with diethyl ether (3 × 20 mL), the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on SiO_2 (hexane : EtOAc = 100 : 1) to give 6-butyl-5-(4-methoxyphenyl) -2-(2-methallyl)-5-decenenitrile **5** (176.7 mg, 96%).

6-Butyl-5-(4-methoxyphenyl)-2-(2-methallyl)-5-decenenitrile (5)

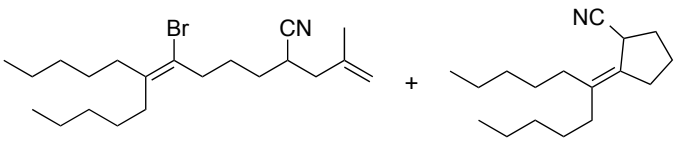


Colorless oil; R_f = 0.14 (Hexane : EtOAc = 30 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 6.8 Hz, 3H), 1.12 (sex, *J* = 7.2 Hz, 2H), 1.22-1.31 (m, 1H), 1.32-1.60 (m, 6H), 1.70 (s, 3H), 1.80-1.85 (m, 2H), 2.09-2.31 (m, 4H), 2.40-2.64 (m, 3H), 3.81 (s, 3H), 4.78 (s, 1H), 4.86 (t, *J* = 1.2 Hz, 1H), 6.81-6.87 (m, 2H), 6.92-6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.93, 14.12, 21.99, 22.73, 23.01, 29.77, 30.71, 30.84, 31.15, 31.35, 31.51, 32.50, 40.33, 55.15, 113.38, 113.91, 121.94, 129.79, 133.15, 135.26, 138.32, 140.59, 157.80; IR (neat): 2955, 2929, 2859, 1607, 1509, 1457, 1284, 1244, 1175, 1034, 834, 617, 445, 436, 423, 402 cm^{-1}; EIMS *m/z* (relative intensity) 367 ($[M]^+$, 100), 324 (30), 310 (13), 245 (13), 173 (12), 159 (17), 147 (11), 121 (22), 55 (14); HRMS (EI) *m/z* calcd for $C_{25}H_{37}ON$ $[M]^+$: 367.2875, found: 367.2876.

Experimental Procedure of the Bromine Radical Mediated Three-Component Reaction of 6, 2a, and 3a and Spectral Data of 7 and 8



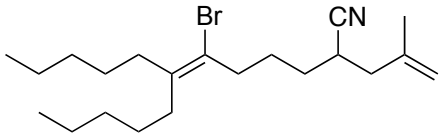
6 **2a** (2.0 equiv) **3a** (5.0 eqiuv)



7 44% **8** 19%

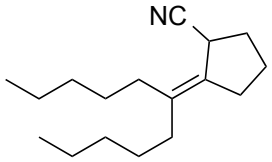
To a 20 mL screw capped test tube, 6-undecanylidenecyclopropane (**6**, 97.2 mg, 0.5 mmol), acrylonitrile (**2a**, 53.1 mg, 1.0 mmol), β-methallyl bromide (**3a**, 338 mg, 2.5 mmol), V-70 (2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), 24.6 mg, 0.3 mmol), and anhydrous Na_3PO_4 (82.0 mg, 0.5 mmol) were added. Then, this test tube was purged with argon and sealed. The mixture was stirred at 40 °C for 6 h. The reaction mixture was filtered through a short plug of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on SiO_2 (Hexane/EtOAc = 1 : 0 to 100 : 1) and preparative HPLC (chloroform) to give 6-bromo-2-(2-methallyl)-7-pentyl-6-dodecenenitrile (**7**, 84.2 mg, 44%) and 2-(6-undecanylidene)cyclopentane-1-carbonitrile (**8**, 23.5 mg, 19%) respectively.

6-Bromo-2-(2-methallyl)-7-pentyl-6-dodecenenitrile (7)

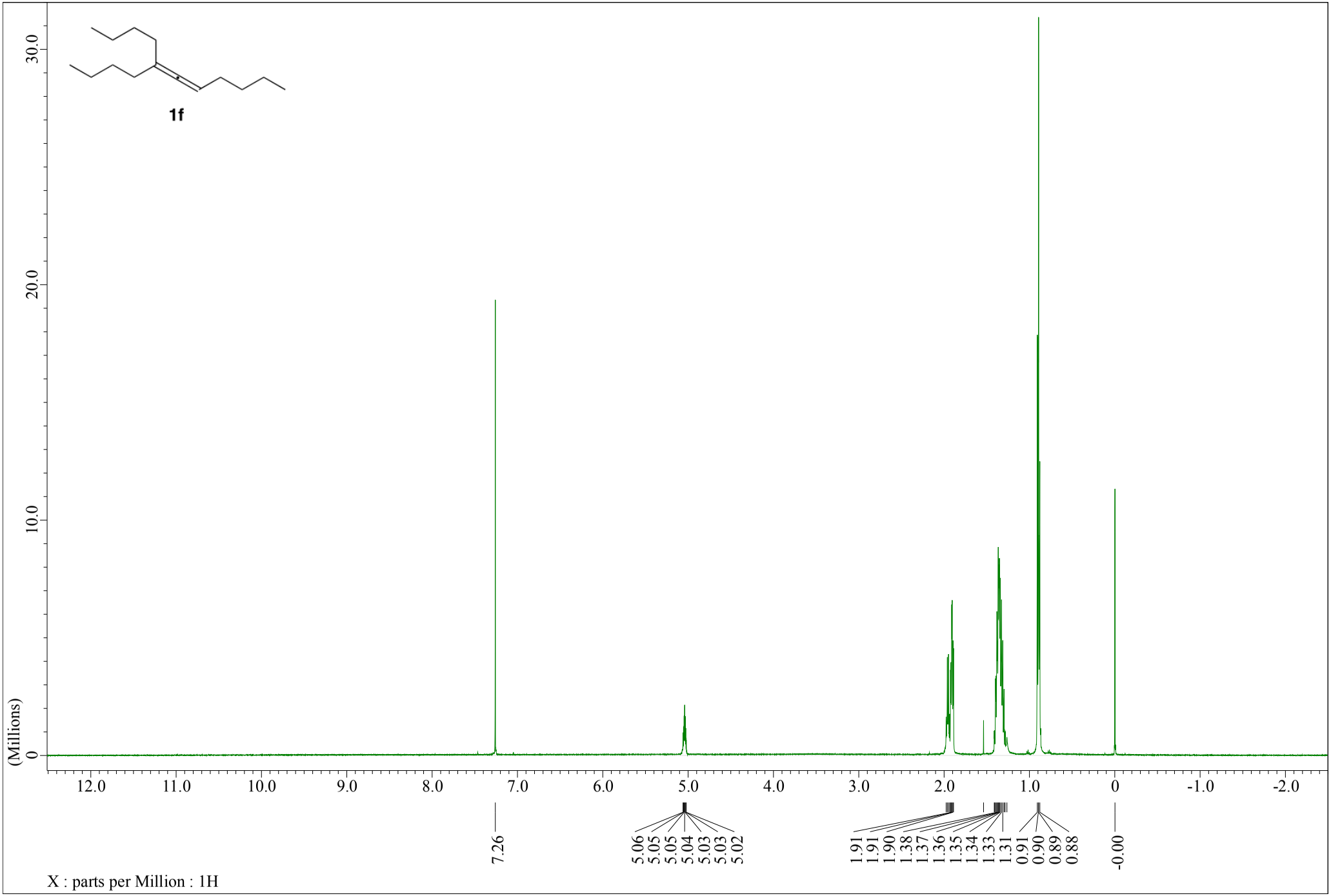


Colorless oil; R_f = 0.25 (Hexane : EtOAc = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88-0.93 (m, 6H), 1.22-1.44 (m, 12H), 1.54-1.62 (m, 2H), 1.65-1.89 (m, 5H), 2.04-2.12 (m, 2H), 2.15-2.24 (m, 2H), 2.26 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.37 (dd, *J* = 14.4, 8.8 Hz, 1H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.70 (quint, *J* = 8.0 Hz, 1H), 4.85 (s, 1H), 4.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.00, 14.05, 22.03, 22.51, 26.11, 27.24, 28.36, 29.99, 30.75, 31.79, 31.82, 32.48, 36.44, 36.60, 40.31, 114.16, 121.80, 139.92, 140.49; IR (neat): 2955, 2929, 2860, 2239, 1652, 1457, 1378, 898 cm^{-1}; EIMS *m*/*z* (relative intensity) 383 ([M]$^+$, 9), 381 ([M]$^+$, 9), 303 (23), 302 ([M-Br]$^+$, 100), 246 (29), 77 (17), 55 (23); HRMS (EI) *m*/*z* calcd for $C_{21}H_{36}N^{79}Br$ [M]$^+$: 381.2031, found: 381.2032.

2-(6-Undecanylidene)cyclopentane-1-carbonitrile (8)



Colorless oil; R_f = 0.25 (Hexane : EtOAc = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85-0.93 (m, 6H), 1.20-1.44 (m, 11H), 1.44-1.55 (m, 1H), 1.73-2.40 (m, 5H), 2.40-2.16 (m, 3H), 2.19-2.30 (m, 1H), 2.34-2.44 (m, 1H), 3.44-3.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.05, 22.57, 25.16, 27.32, 27.35, 29.55, 31.19, 31.94, 32.08, 32.35, 32.82, 33.20, 122.00, 130.49, 137.83; IR (neat): 2956, 2931, 2859, 2234, 1466, 1378 cm^{-1}; EIMS *m*/*z* (relative intensity) 247 ([M]$^+$, 100), 205 (75), 192 (51), 176 (81), 149 (60), 148 (82), 136 (93), 135 (67), 108 (59), 107 (54), 93 (47), 79 (39), 55 (35); HRMS (EI) *m*/*z* calcd for $C_{17}H_{29}N$ [M]$^+$: 247.2300, found: 247.2301.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10.0
0
(Millions)
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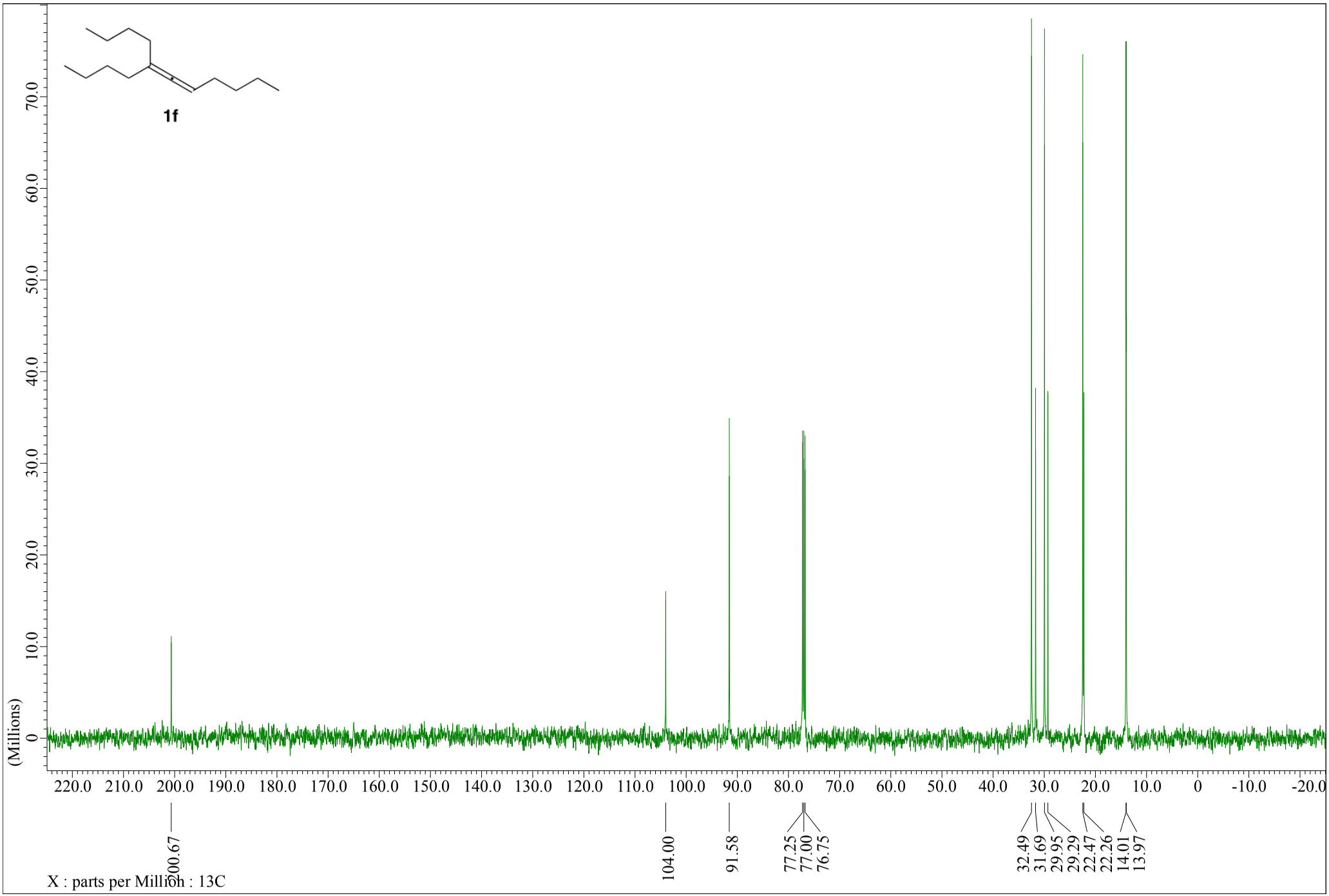
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
5.06
5.05
5.05
5.04
5.03
5.03
5.02
1.91
1.91
1.90
1.38
1.37
1.36
1.35
1.34
1.33
1.31
0.91
0.90
0.89
0.88
-0.00
X : parts per Million : 1H


1f
(Millions)
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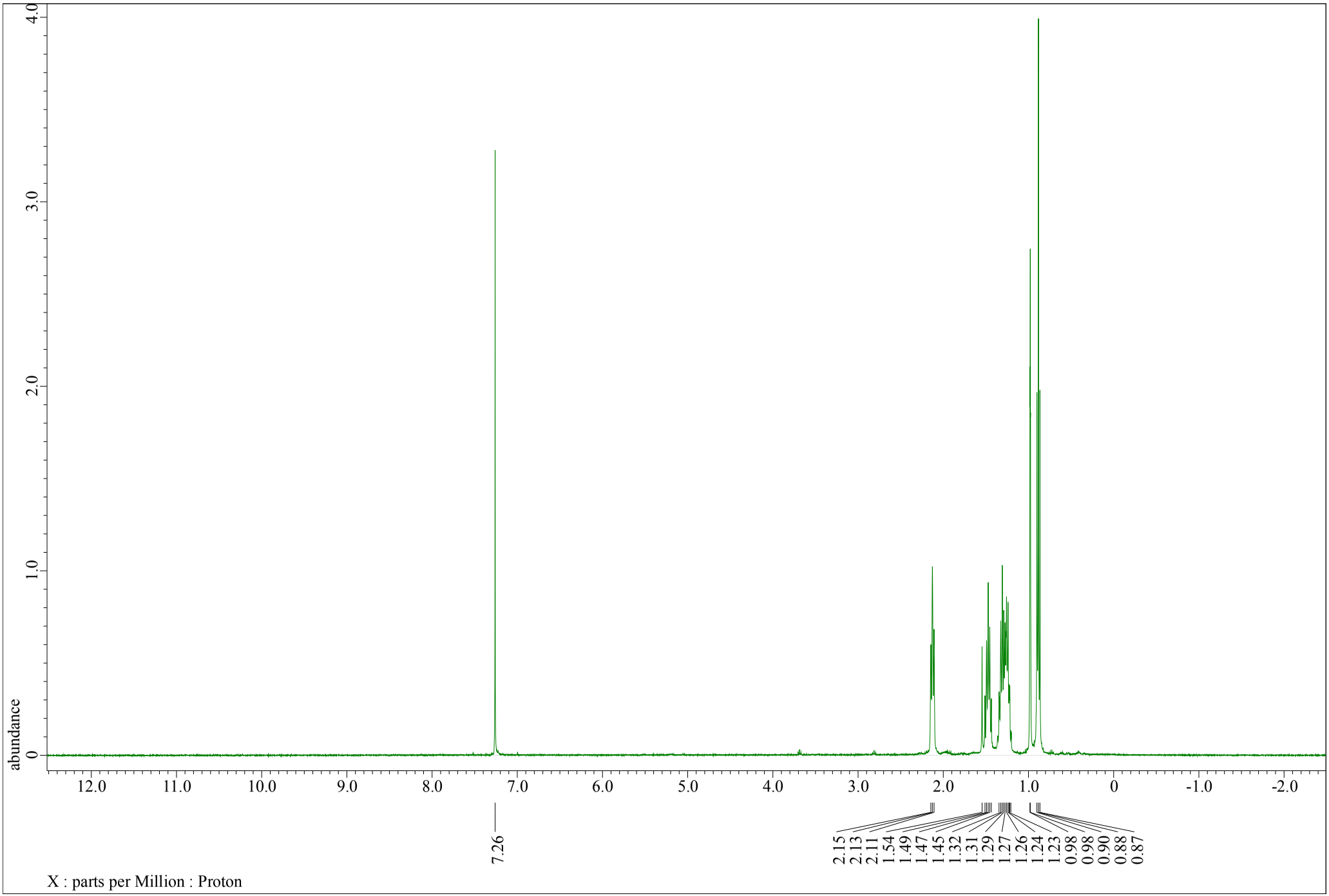
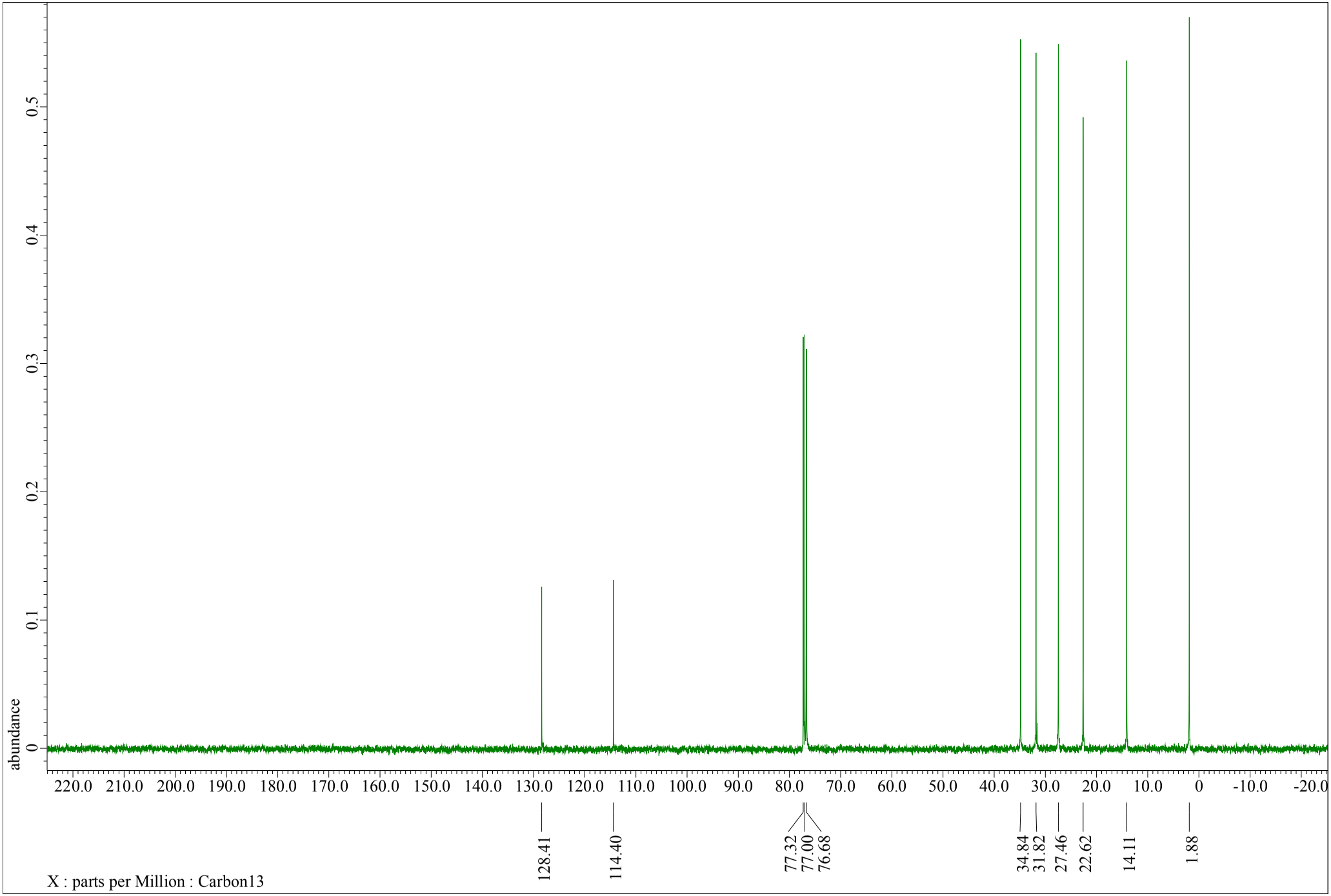
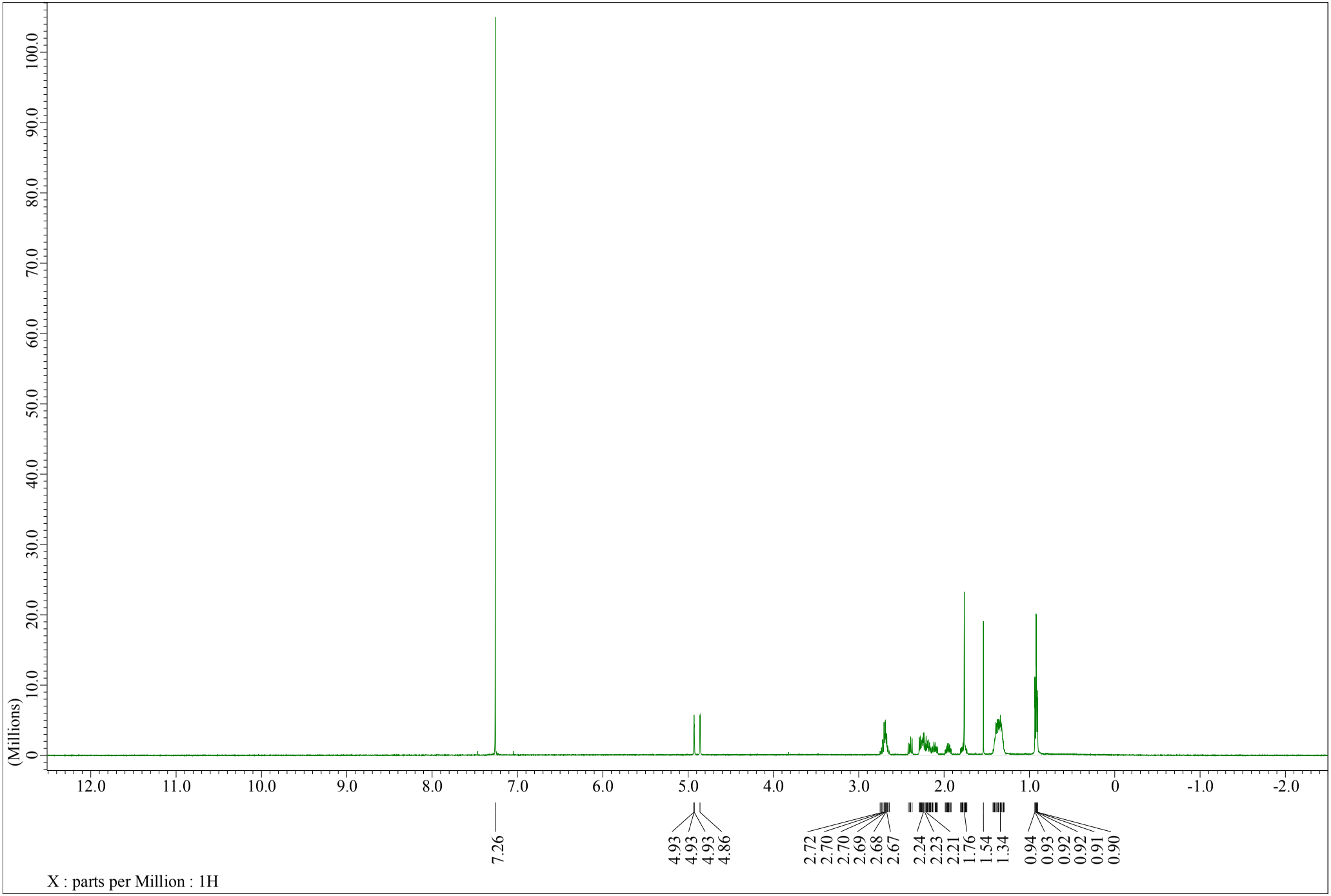
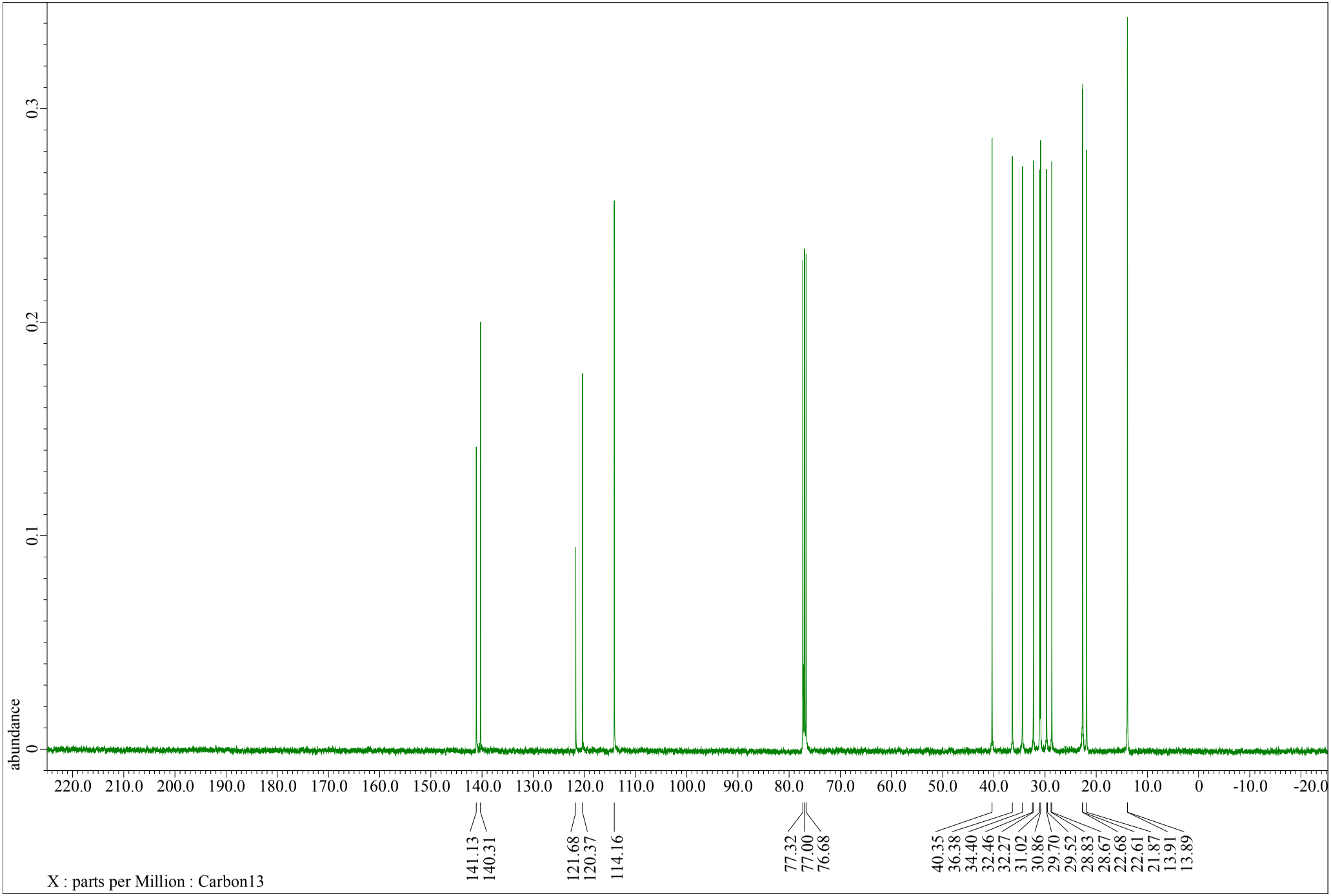
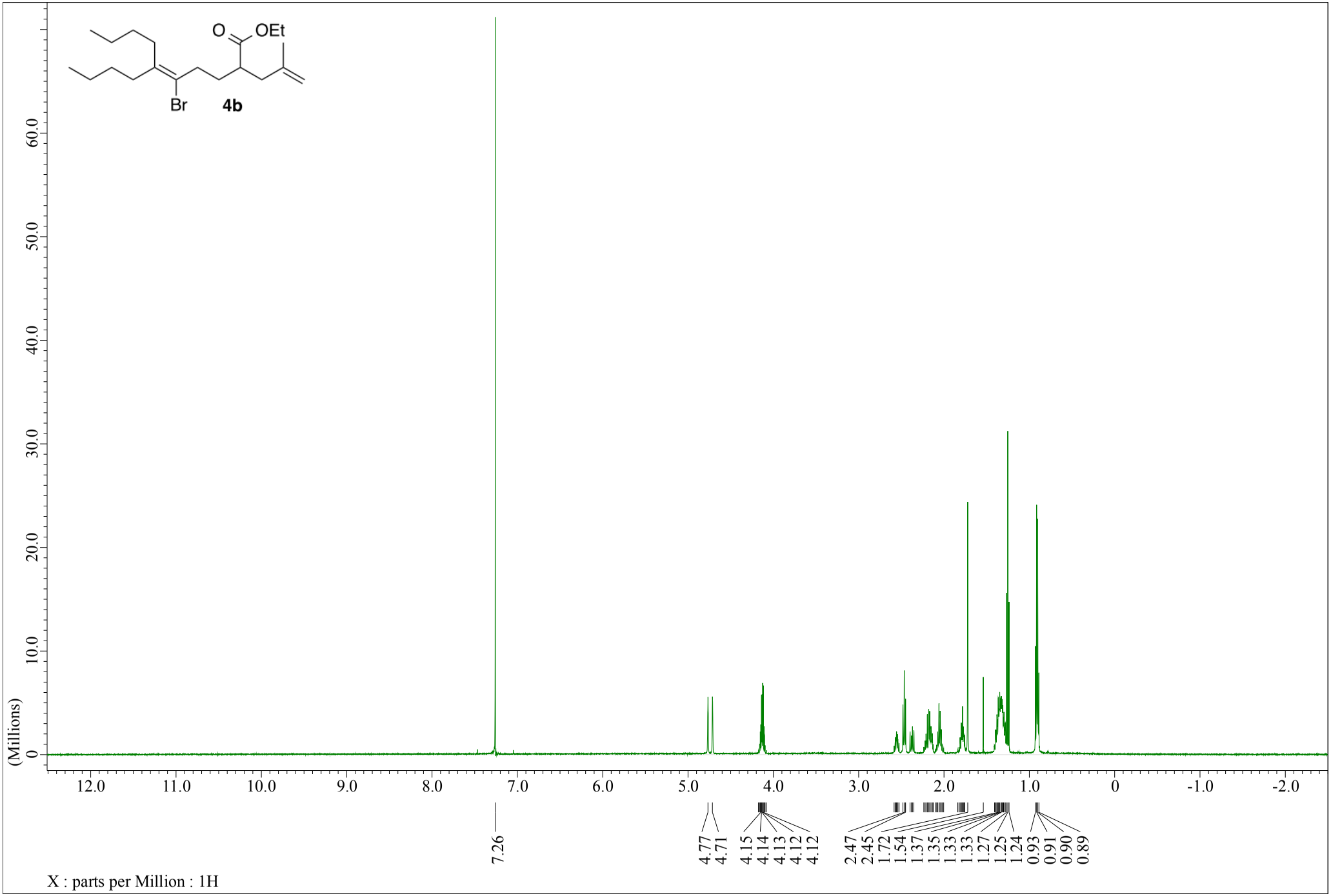
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
200.67
104.00
91.58
77.25
77.00
76.75
32.49
31.69
29.95
29.29
22.47
22.26
14.01
13.97
X : parts per Million : 13C

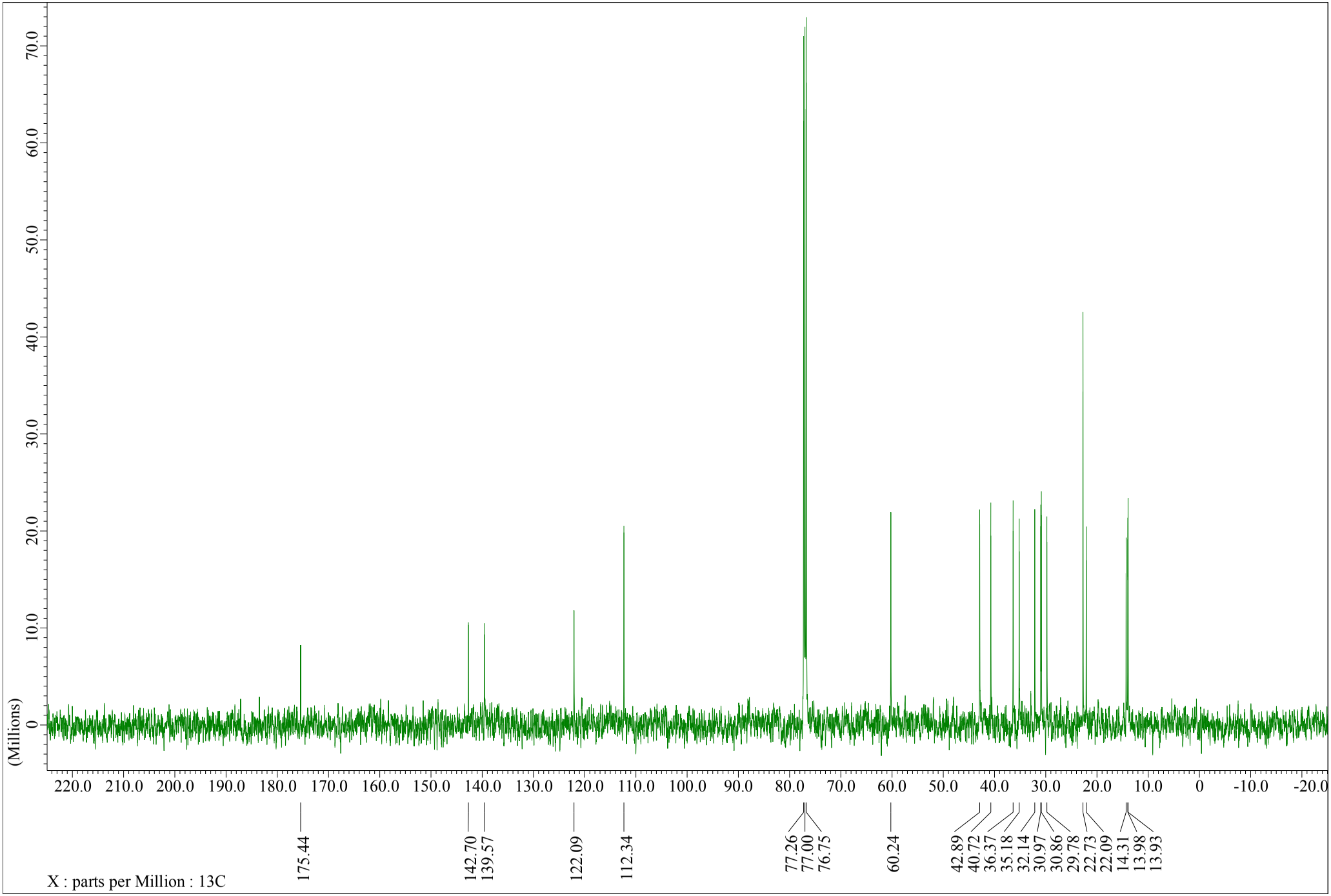

abundance
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
2.15
2.13
2.11
1.54
1.49
1.47
1.45
1.32
1.31
1.29
1.27
1.26
1.24
1.23
0.98
0.98
0.90
0.88
0.87
X : parts per Million : Proton

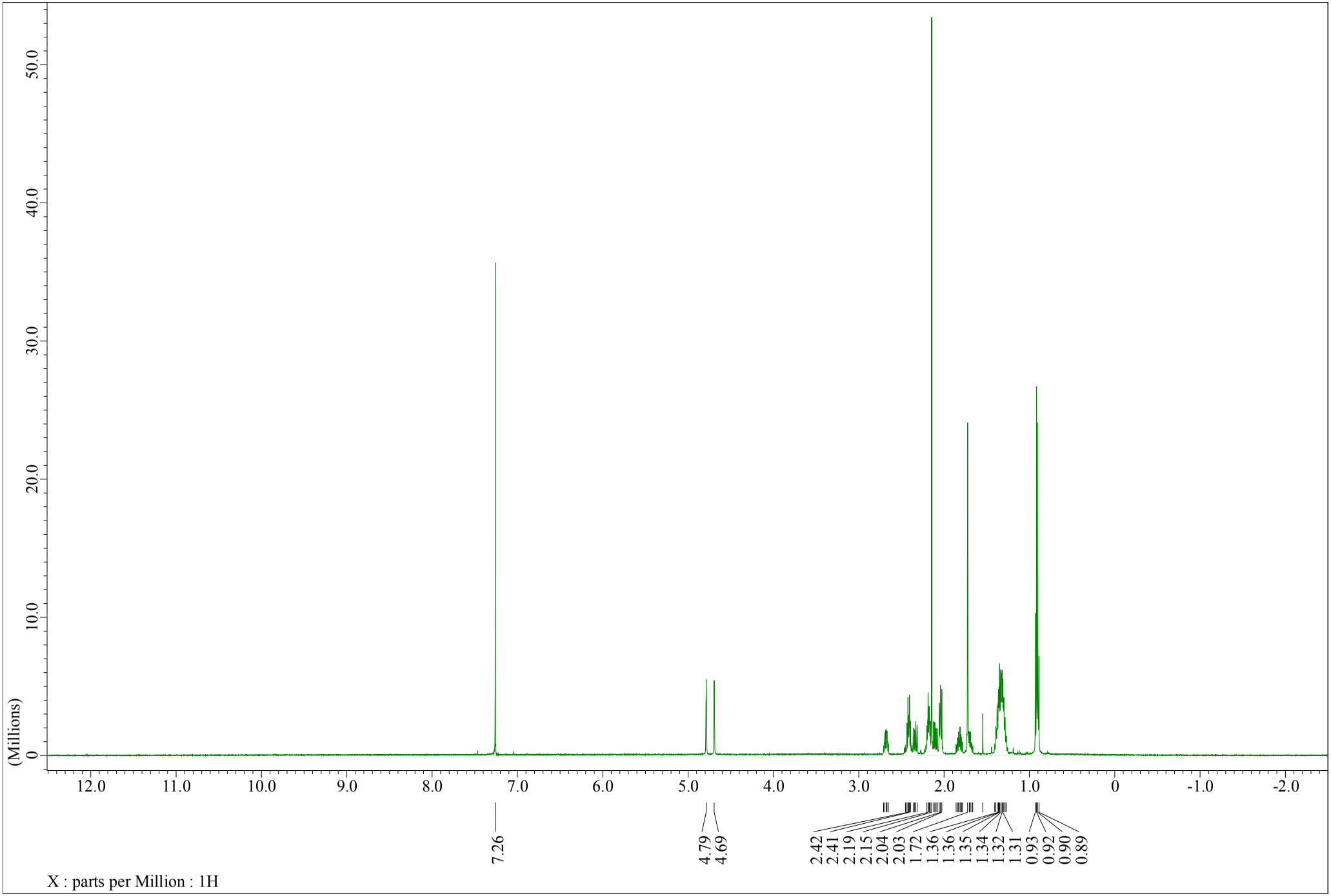

abundance
0
0.1
0.2
0.3
0.4
0.5
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
128.41
114.40
77.32
77.00
76.68
34.84
31.82
27.46
22.62
14.11
1.88
X : parts per Million : Carbon13

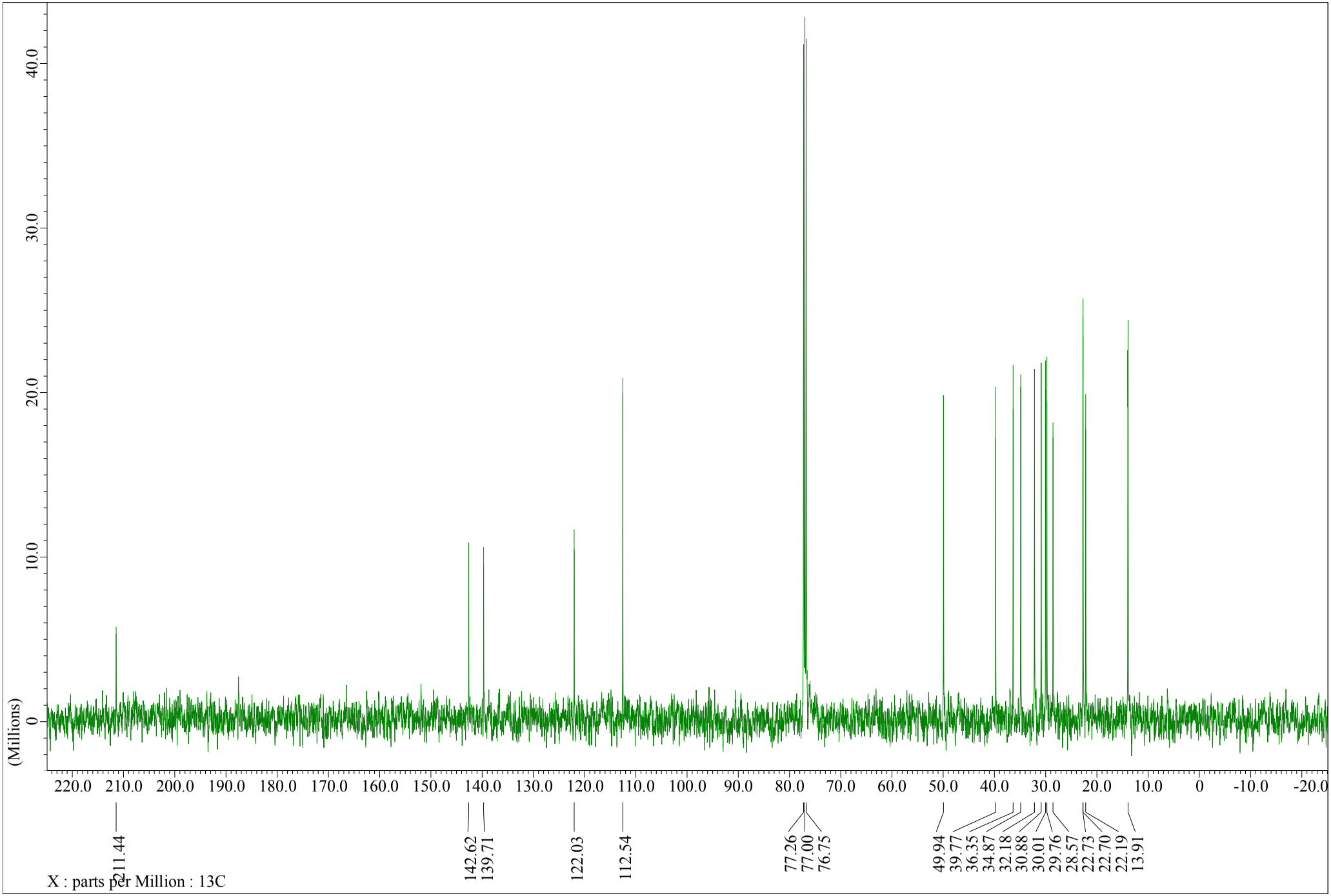

(Millions)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.93
4.93
4.93
4.86
2.72
2.70
2.70
2.69
2.68
2.67
2.24
2.23
2.21
1.76
1.54
1.34
0.94
0.93
0.92
0.92
0.91
0.90
X : parts per Million : 1H

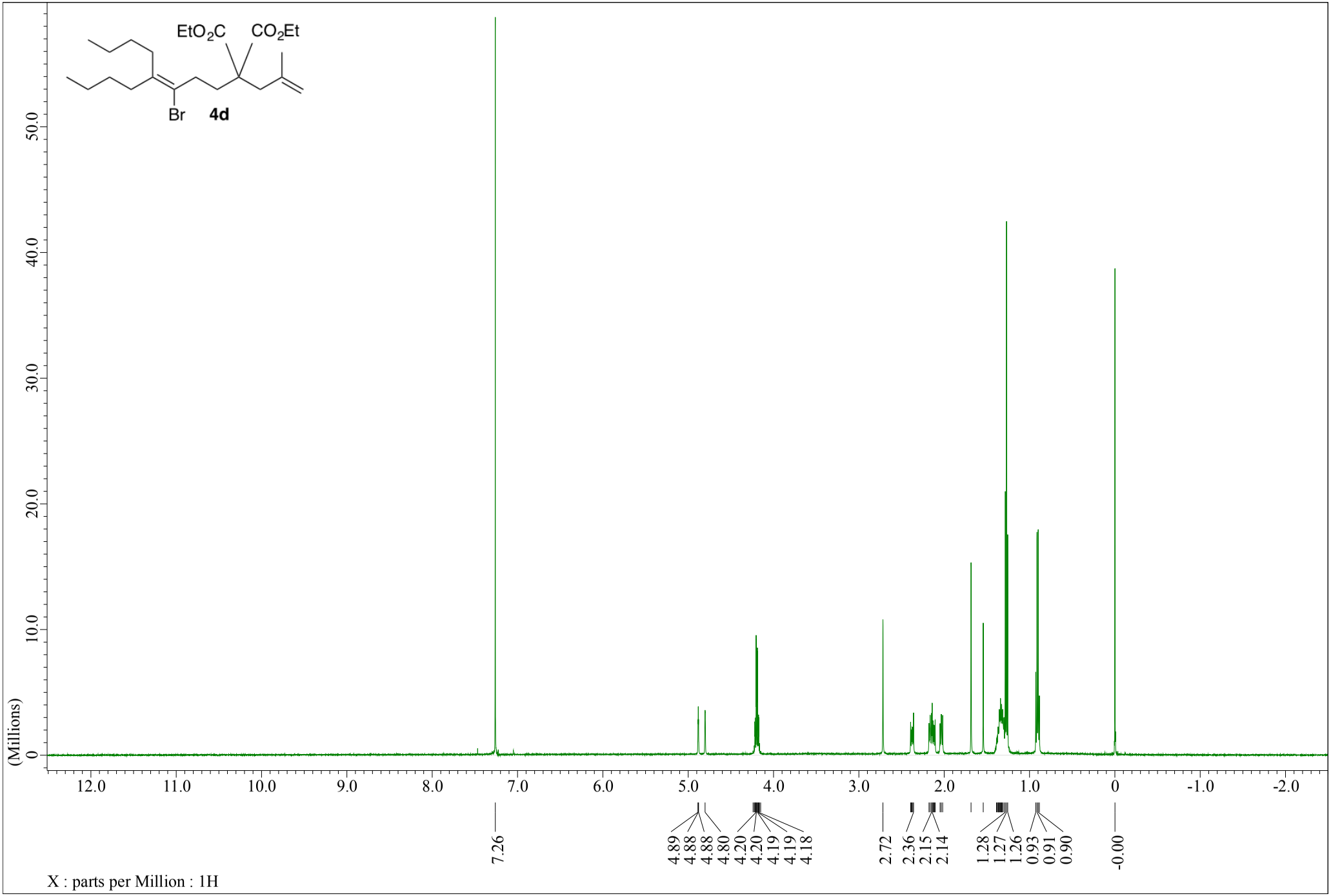

abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
141.13
140.31
121.68
120.37
114.16
77.32
77.00
76.68
40.35
36.38
34.40
32.46
32.27
31.02
30.86
29.70
29.52
28.83
28.67
22.68
22.61
21.87
13.91
13.89
X : parts per Million : Carbon13

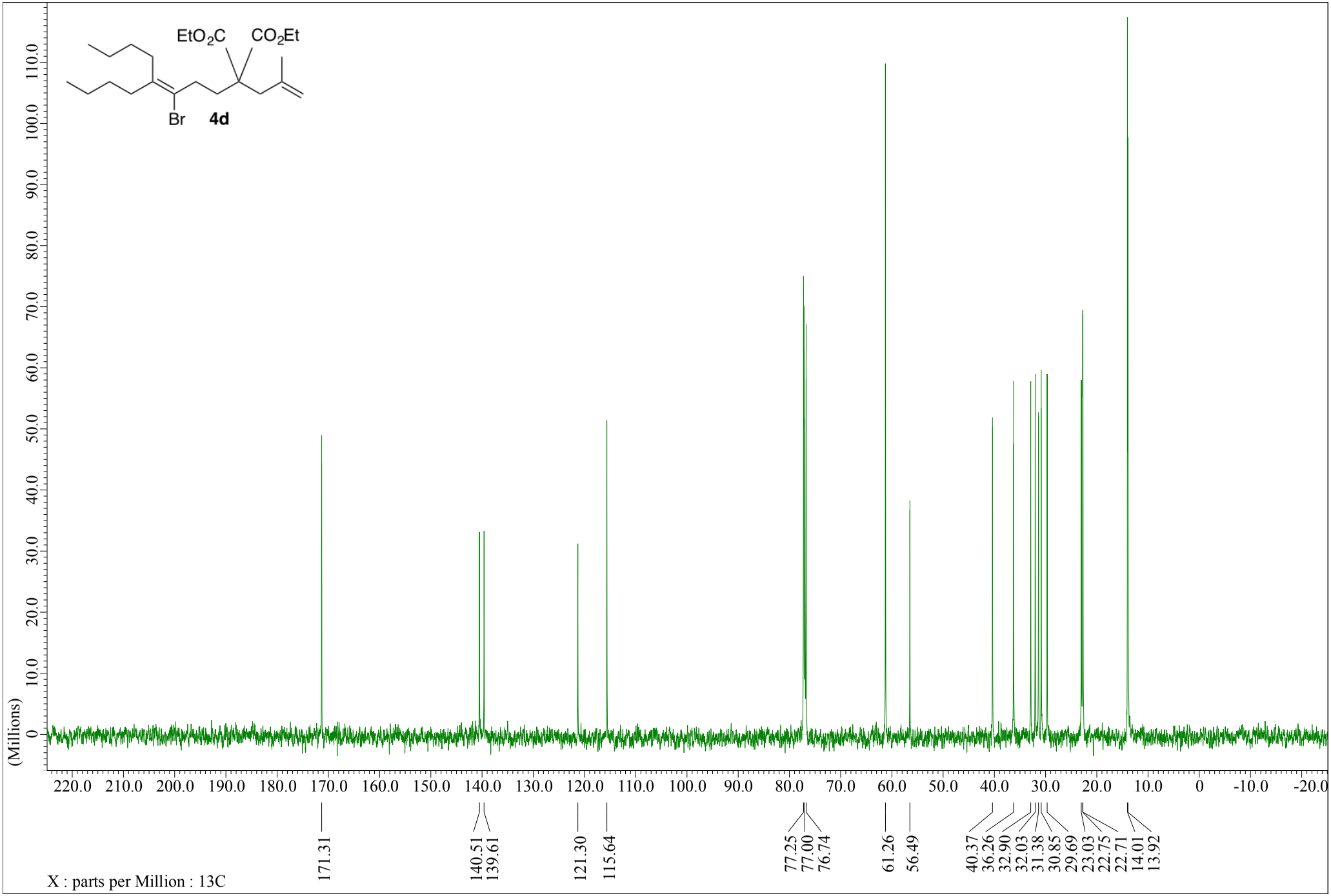

O
OEt
Br
4b
(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.77
4.71
4.15
4.14
4.13
4.12
4.12
2.47
2.45
1.72
1.54
1.37
1.35
1.33
1.33
1.27
1.25
1.24
0.93
0.91
0.90
0.89
X : parts per Million : 1H

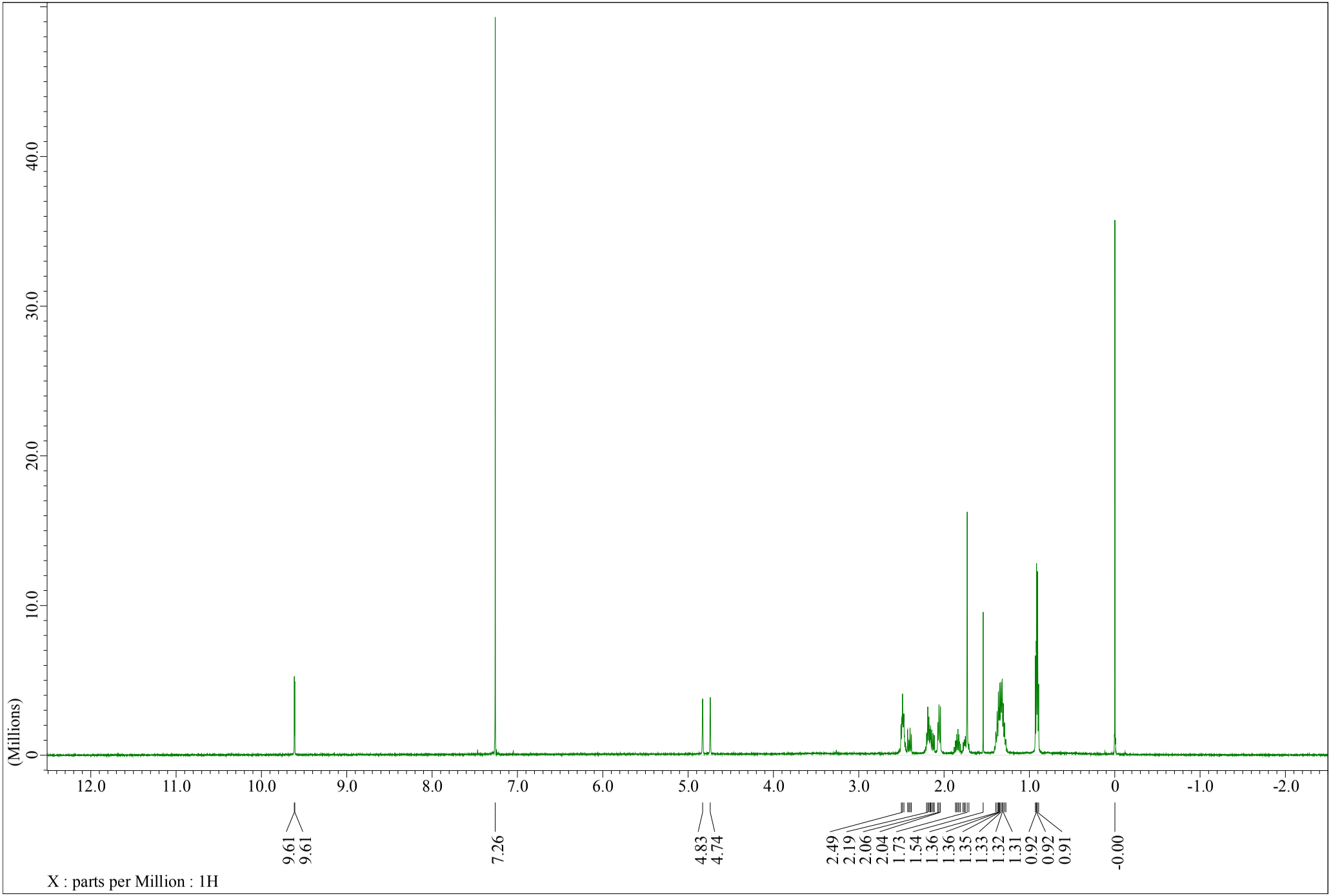

(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
175.44
142.70
139.57
122.09
112.34
77.26
77.00
76.75
60.24
42.89
40.72
36.37
35.18
32.14
30.97
30.86
29.78
22.73
22.09
14.31
13.98
13.93
X : parts per Million : 13C

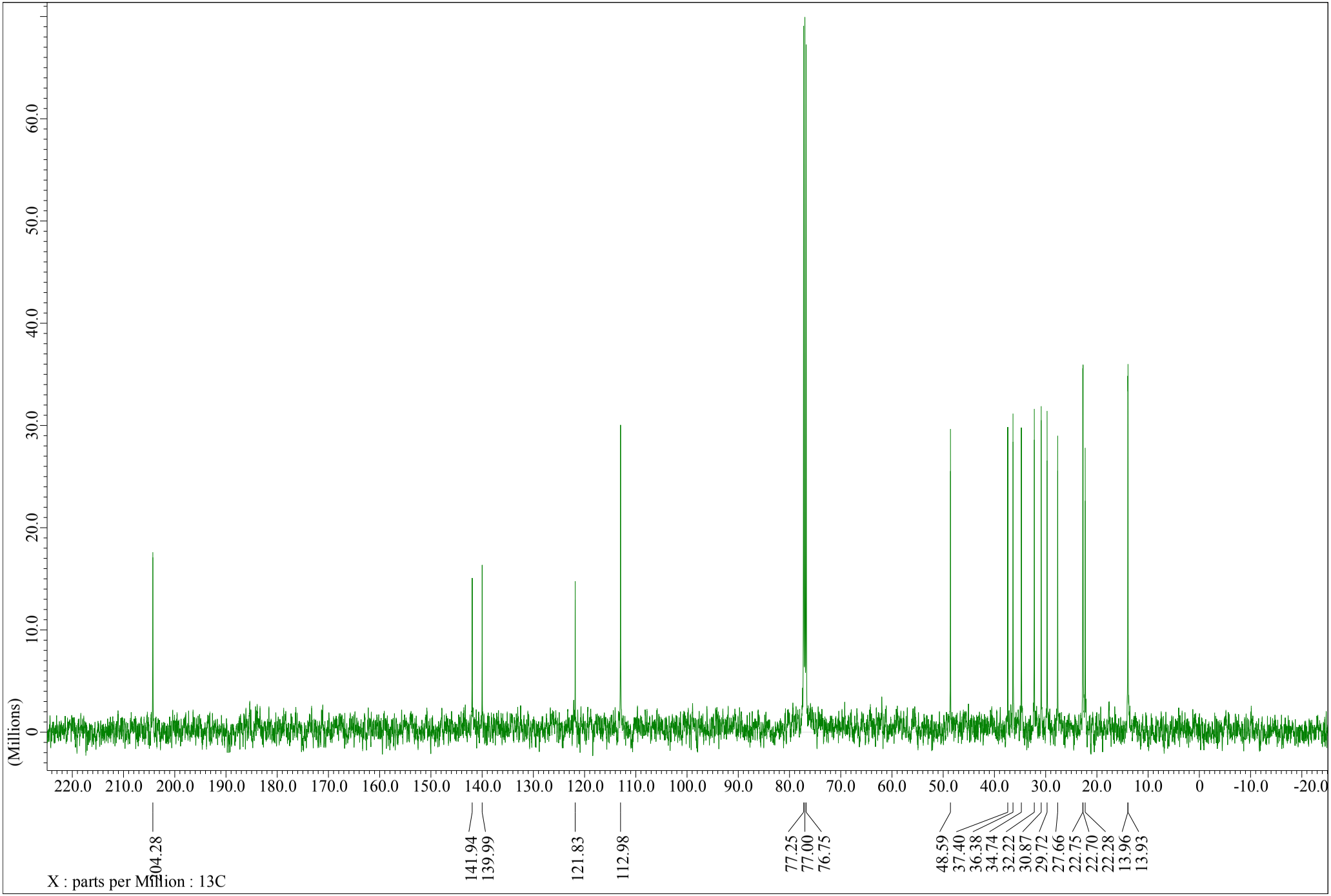

(Millions)
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.79
4.69
2.42
2.41
2.19
2.15
2.04
2.03
1.72
1.36
1.36
1.35
1.34
1.32
1.31
0.93
0.92
0.90
0.89
X : parts per Million : 1H

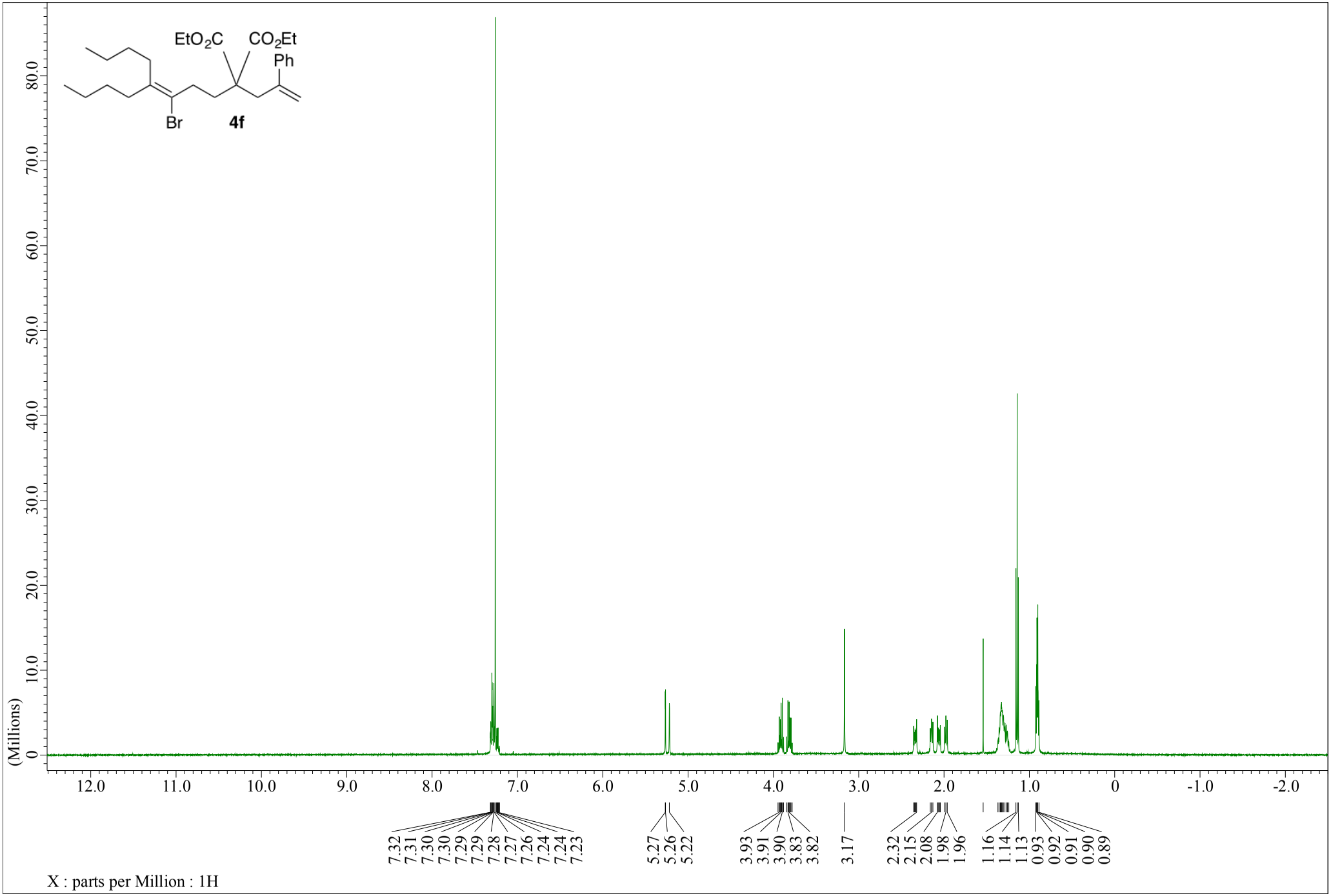

(Millions)
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
211.44
142.62
139.71
122.03
112.54
77.26
77.00
76.75
49.94
39.77
36.35
34.87
32.18
30.88
30.01
29.76
28.57
22.73
22.70
22.19
13.91
X : parts per Million : 13C

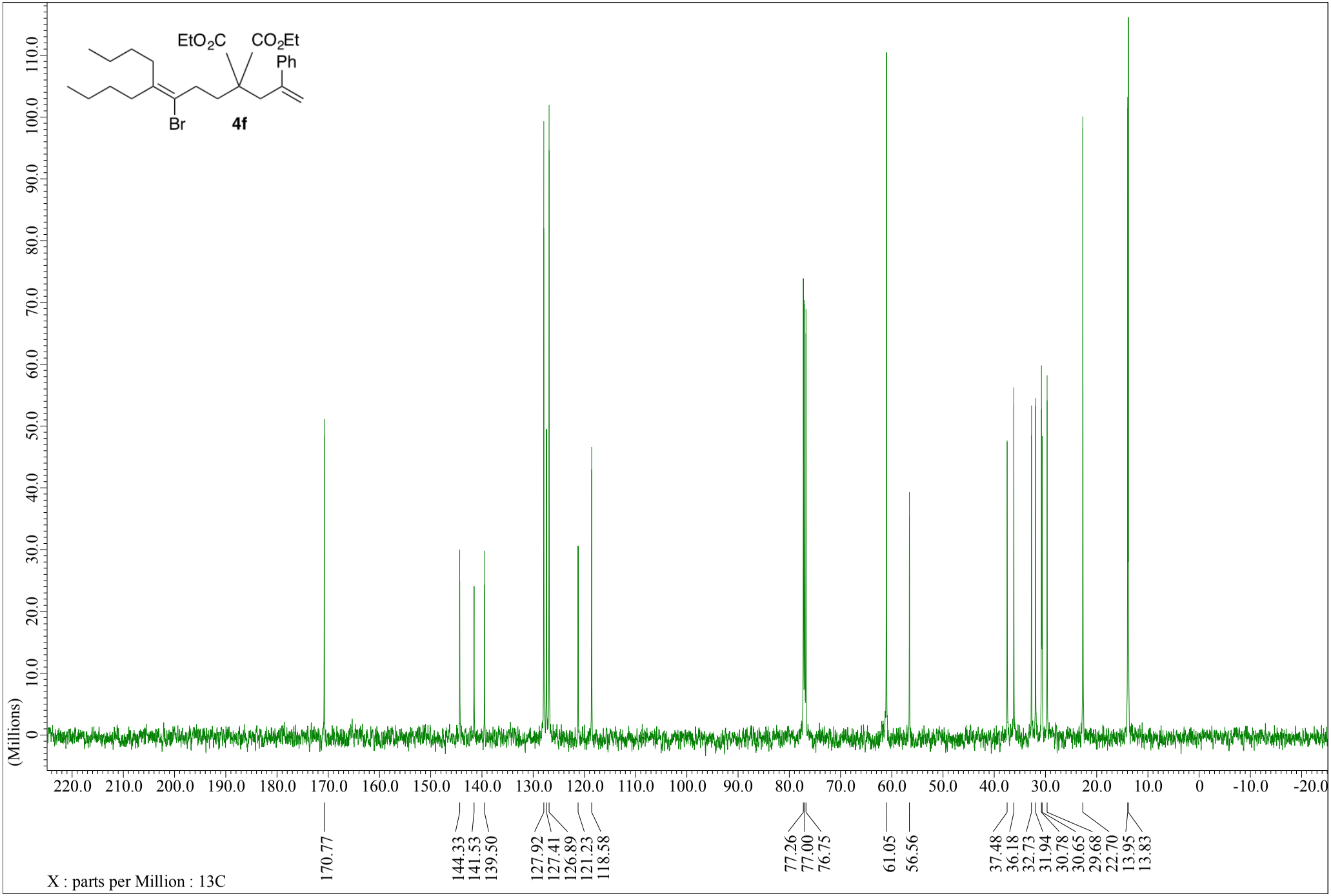

EtO2C
CO2Et
Br
4d
(Millions)
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.89
4.88
4.88
4.80
4.20
4.20
4.19
4.19
4.18
2.72
2.36
2.15
2.14
1.28
1.27
1.26
0.93
0.91
0.90
-0.00
X : parts per Million : 1H

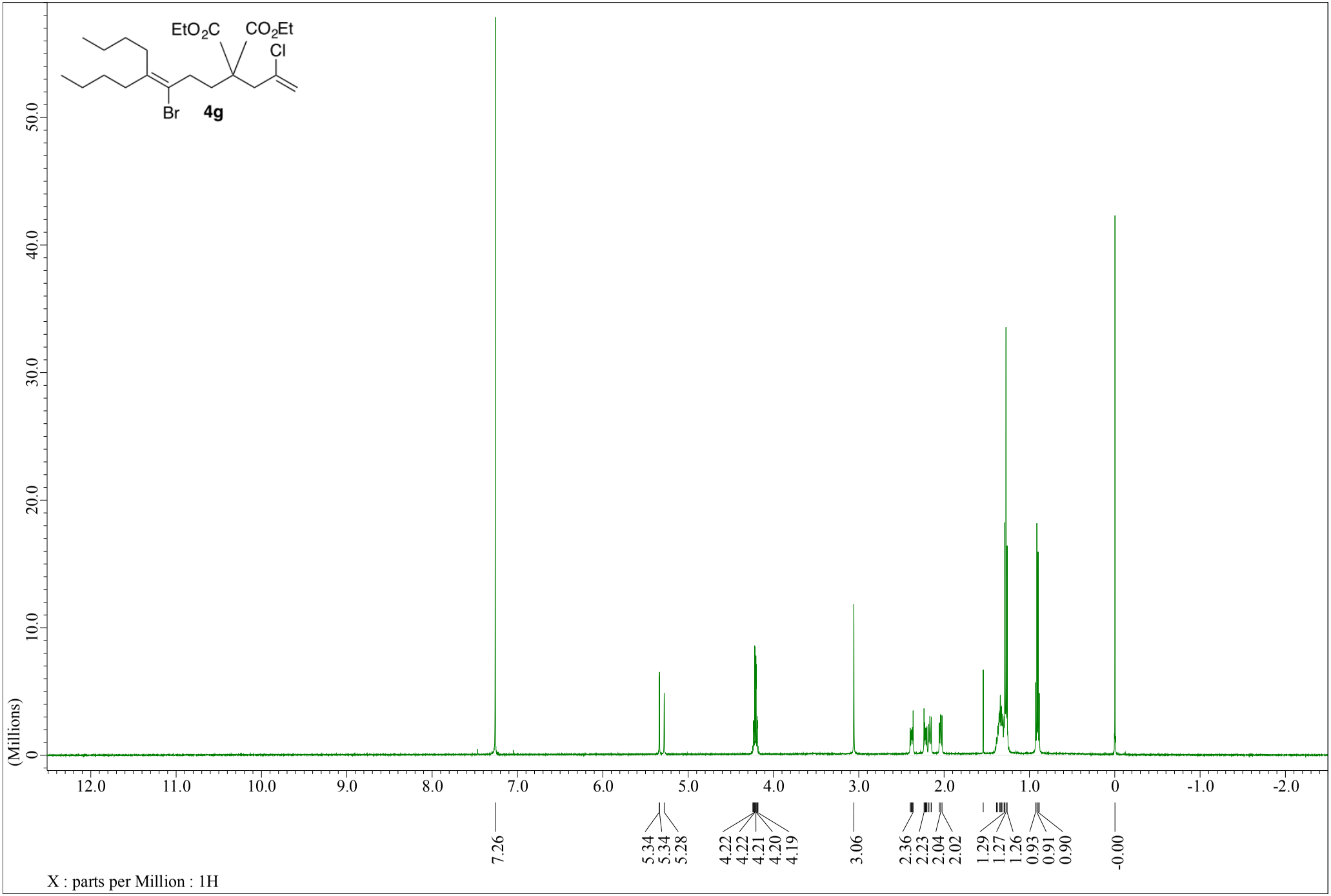

EtO2C
CO2Et
Br
4d
(Millions)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.31
140.51
139.61
121.30
115.64
77.25
77.00
76.74
61.26
56.49
40.37
36.26
32.90
32.03
31.38
30.85
29.69
23.03
22.75
22.71
14.01
13.92
X : parts per Million : 13C

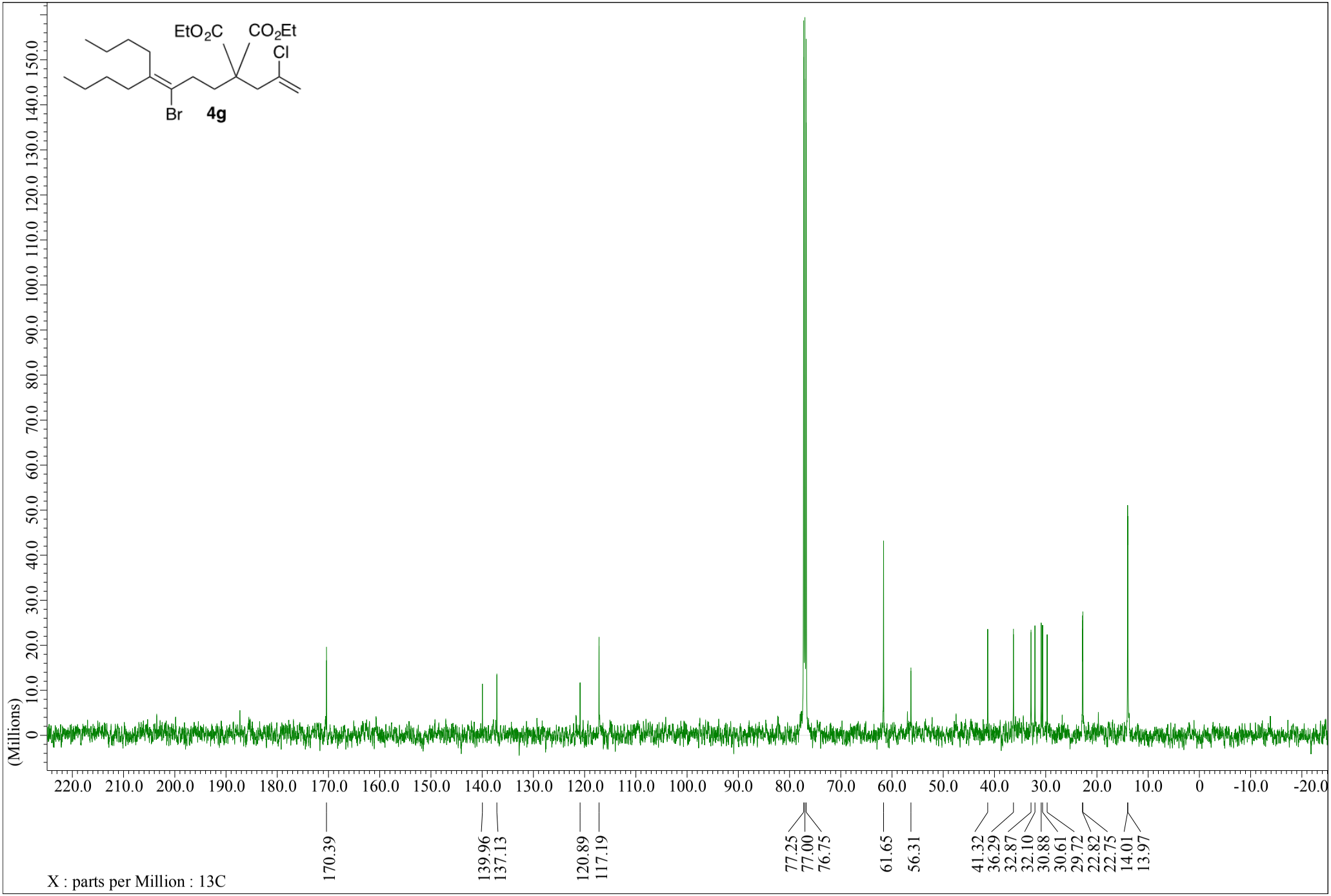

(Millions)
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
9.61
9.61
7.26
4.83
4.74
2.49
2.19
2.06
2.04
1.73
1.54
1.36
1.36
1.35
1.33
1.32
1.31
0.92
0.92
0.91
-0.00
X : parts per Million : 1H

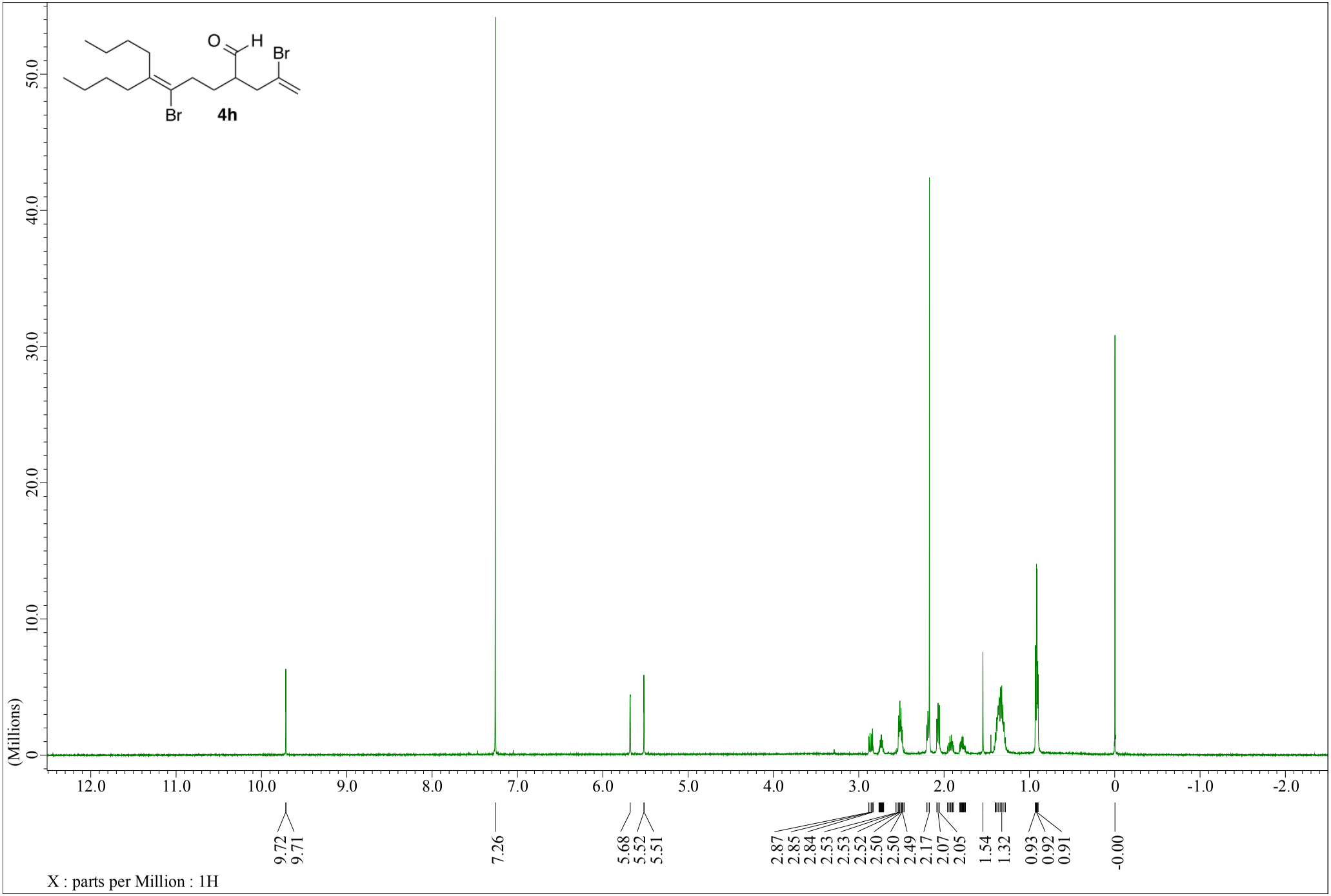

(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
204.28
141.94
139.99
121.83
112.98
77.25
77.00
76.75
48.59
37.40
36.38
34.74
32.22
30.87
29.72
27.66
22.75
22.70
22.28
13.96
13.93
X : parts per Million : 13C

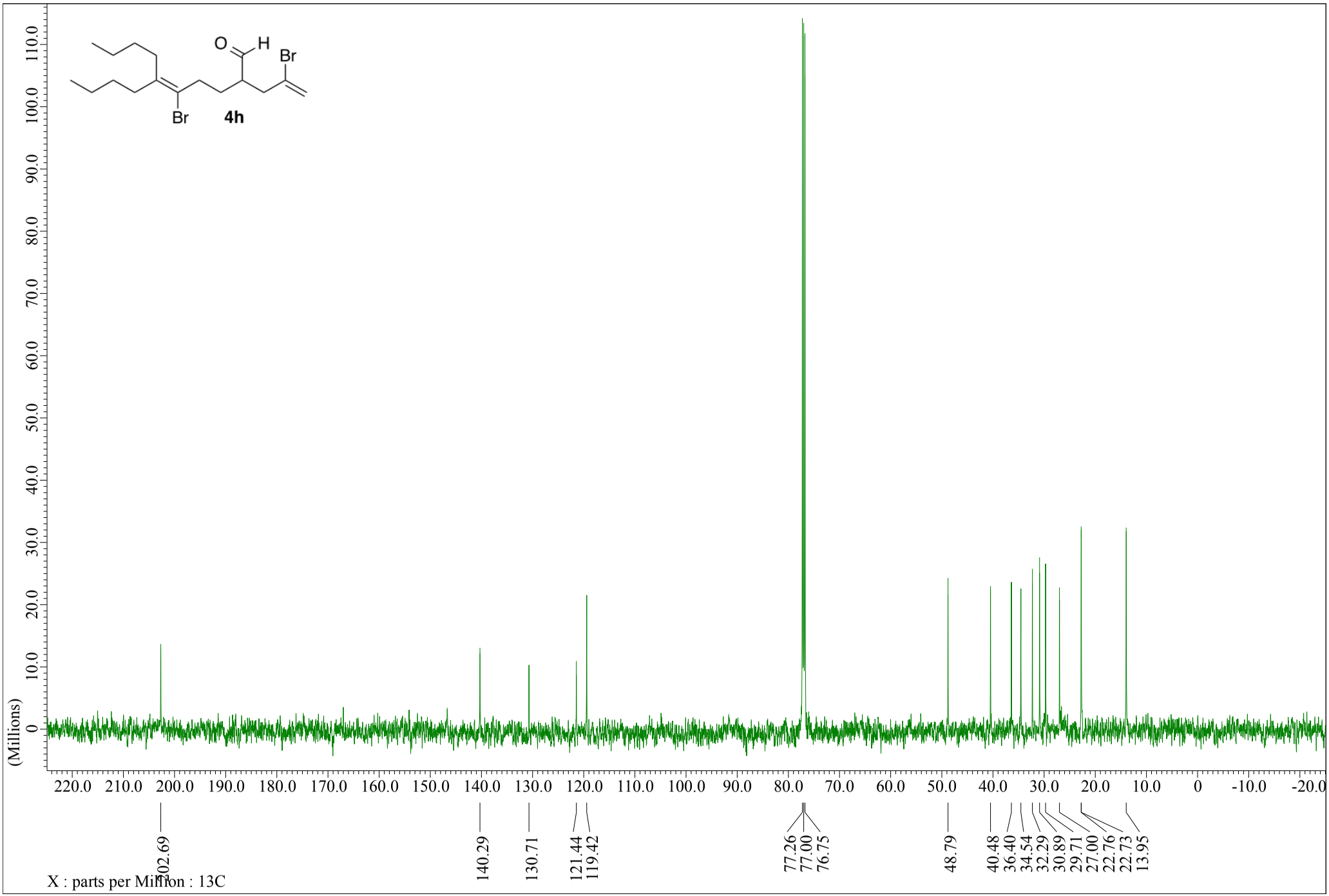

EtO2C
CO2Et
Ph
Br
4f
(Millions)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.24
7.24
7.23
5.27
5.26
5.22
3.93
3.91
3.90
3.83
3.82
3.17
2.32
2.15
2.08
1.98
1.96
1.16
1.14
1.13
0.93
0.92
0.91
0.90
0.89
X : parts per Million : 1H

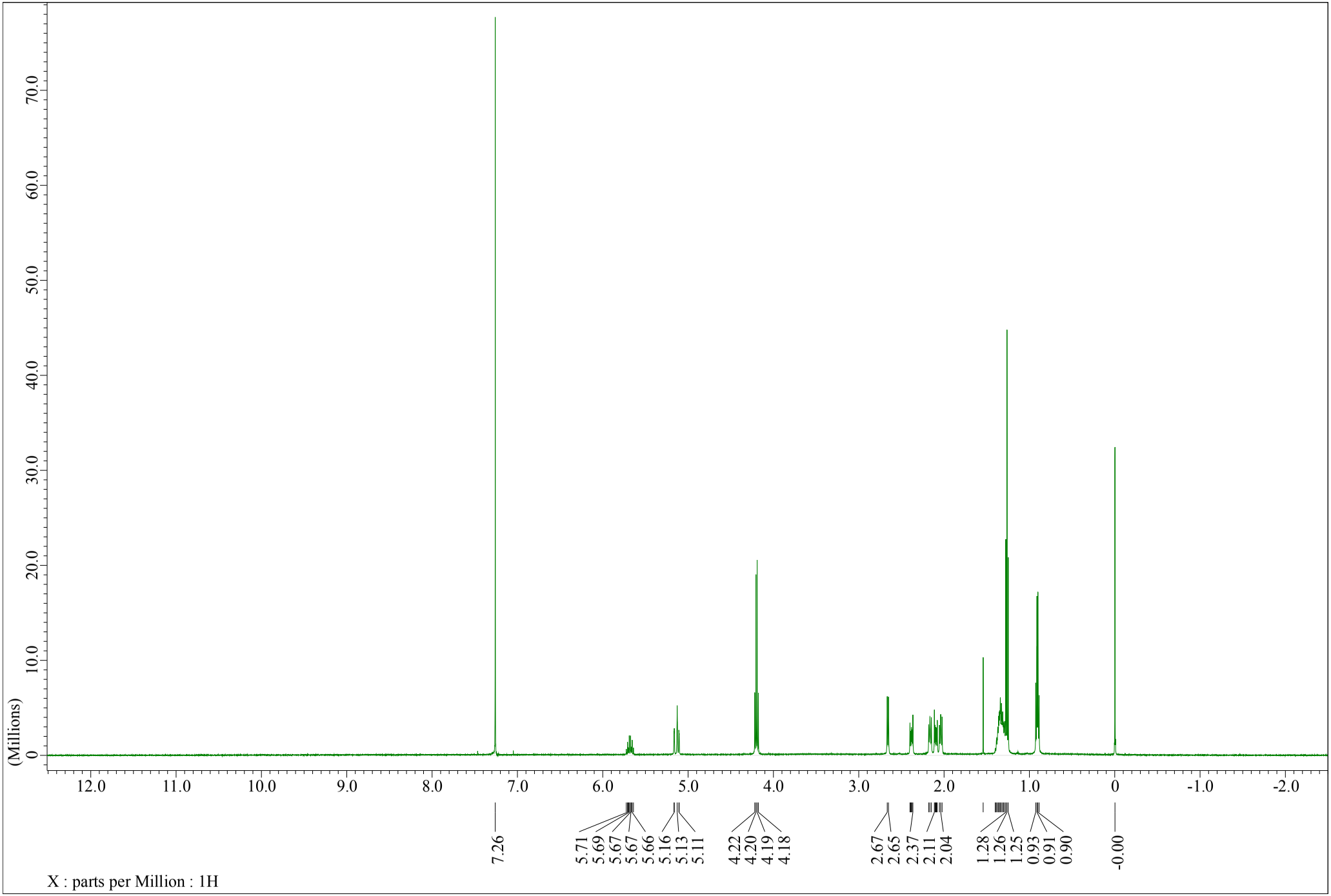

EtO2C
CO2Et
Ph
Br
4f
(Millions)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.77
144.33
141.53
139.50
127.92
127.41
126.89
121.23
118.58
77.26
77.00
76.75
61.05
56.56
37.48
36.18
32.73
31.94
30.78
30.65
29.68
22.70
13.95
13.83
X : parts per Million : 13C

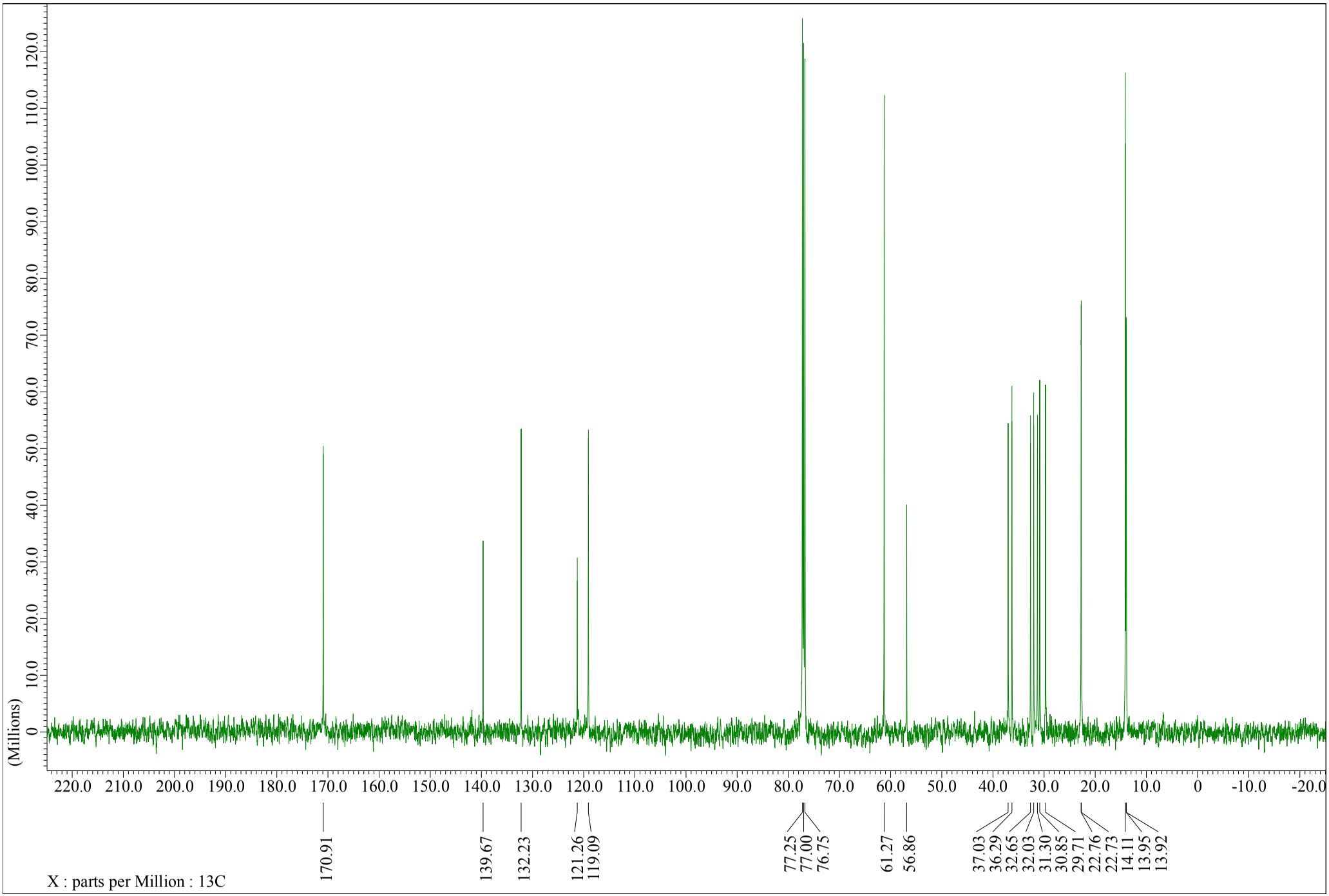

EtO2C
CO2Et
Cl
Br
4g
(Millions)
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
5.34
5.34
5.28
4.22
4.22
4.21
4.20
4.19
3.06
2.36
2.23
2.04
2.02
1.29
1.27
1.26
0.93
0.91
0.90
-0.00
X : parts per Million : 1H

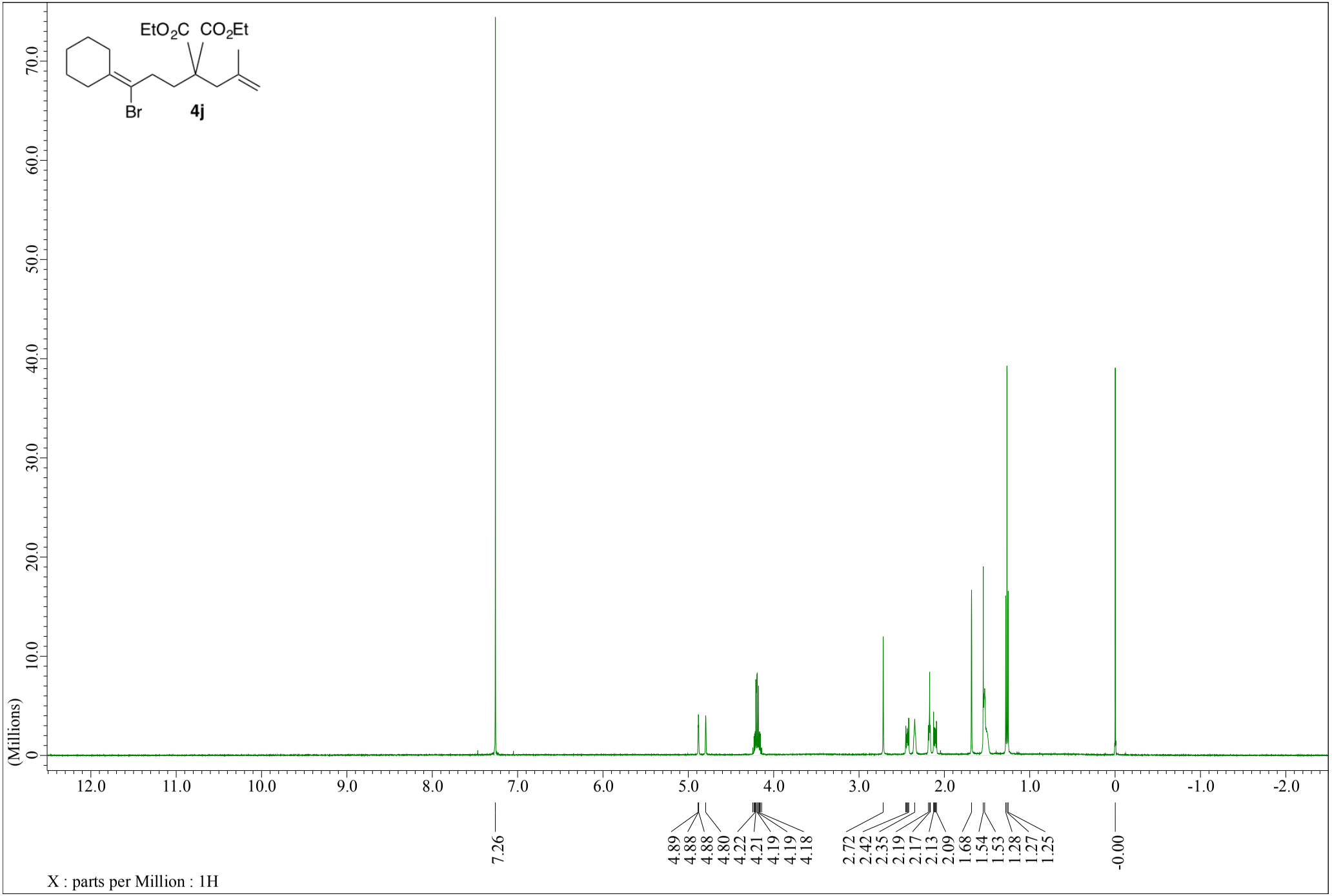

EtO2C
CO2Et
Cl
Br
4g
(Millions)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.39
139.96
137.13
120.89
117.19
77.25
77.00
76.75
61.65
56.31
41.32
36.29
32.87
32.10
30.88
30.61
29.72
22.82
22.75
14.01
13.97
X : parts per Million : 13C

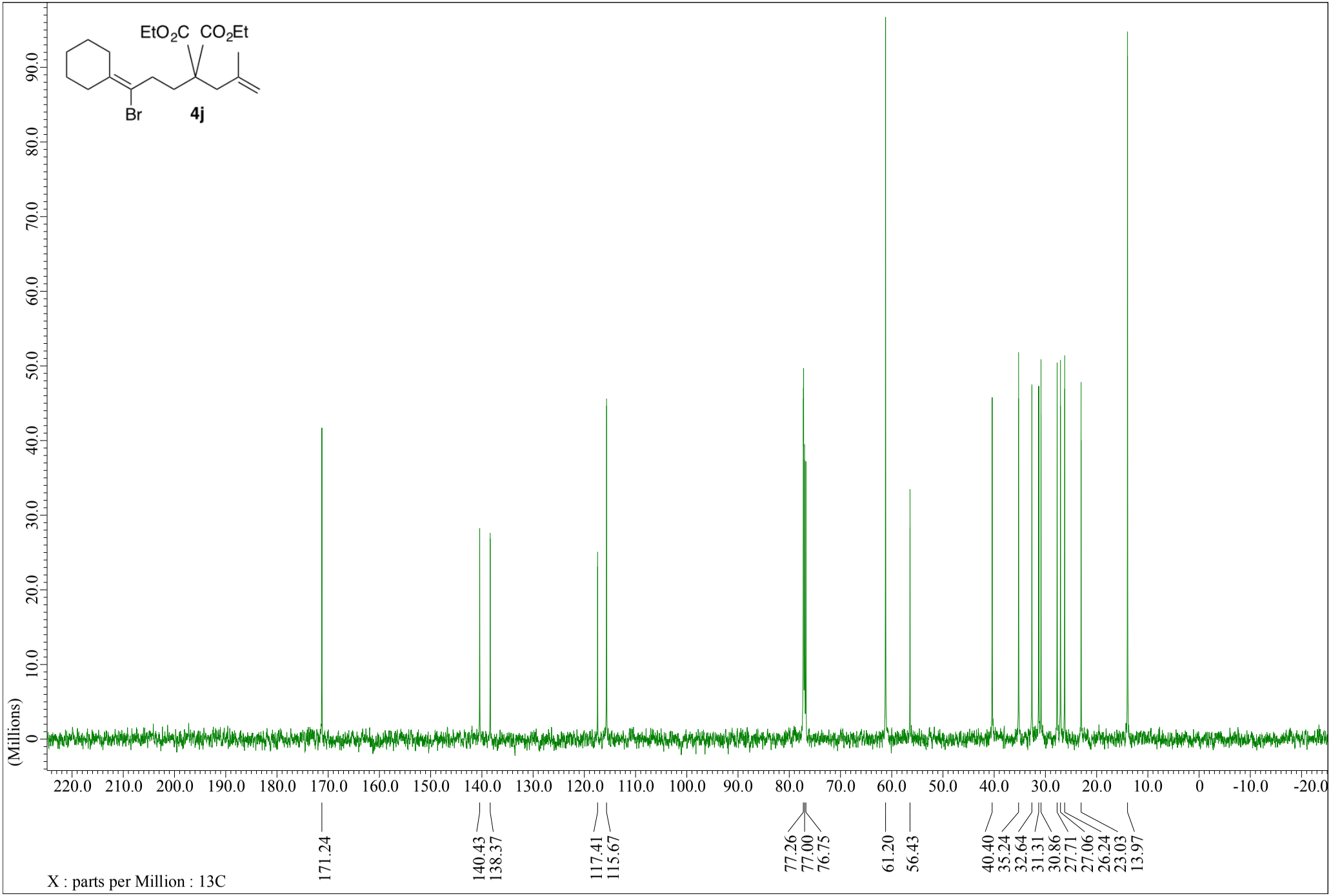

O
H
Br
Br
4h
(Millions)
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
9.72
9.71
7.26
5.68
5.52
5.51
2.87
2.85
2.84
2.53
2.53
2.52
2.50
2.50
2.49
2.17
2.07
2.05
1.54
1.32
0.93
0.92
0.91
-0.00
X : parts per Million : 1H

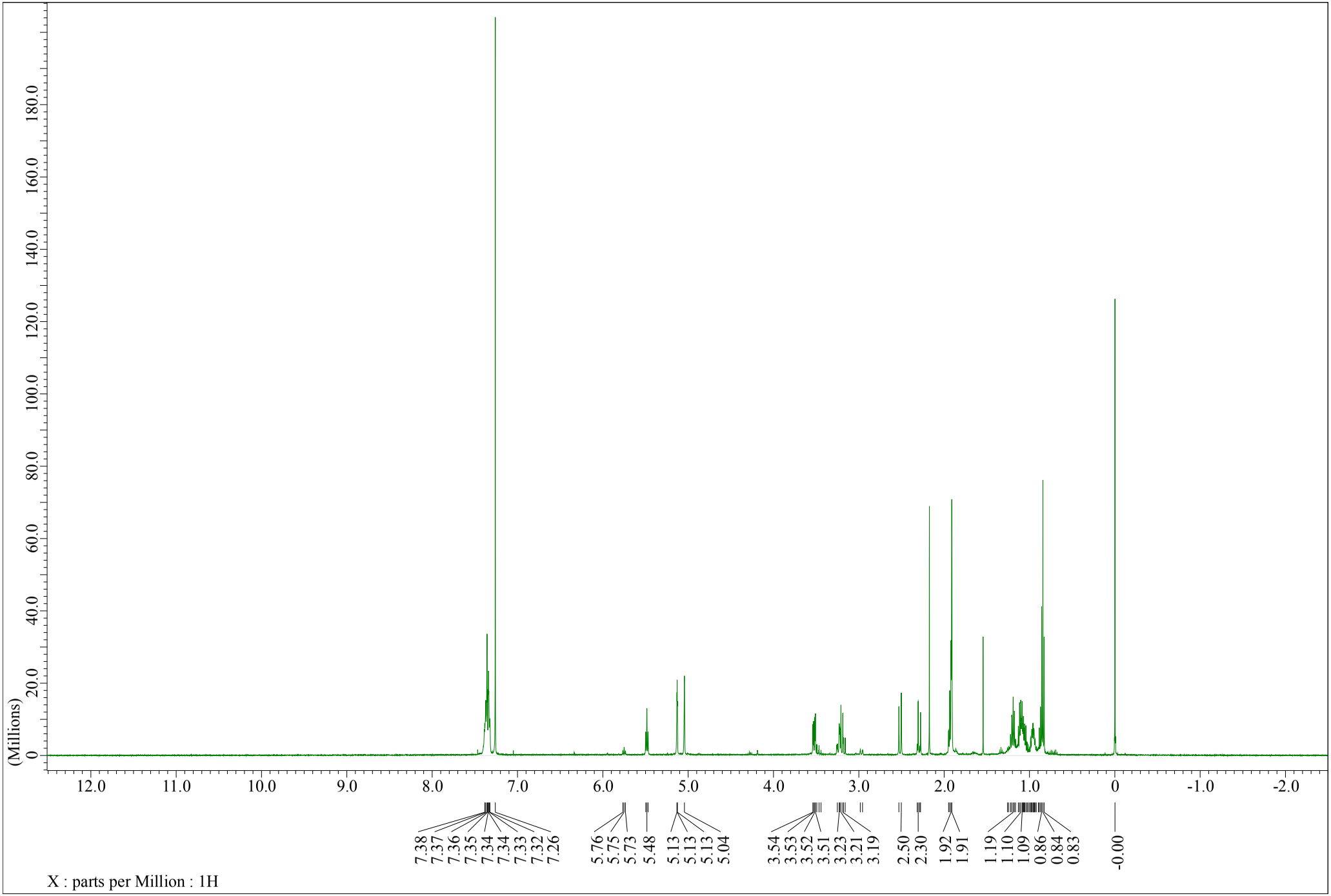

O
H
Br
Br
4h
(Millions)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
202.69
140.29
130.71
121.44
119.42
77.26
77.00
76.75
48.79
40.48
36.40
34.54
32.29
30.89
29.71
27.00
22.76
22.73
13.95
X : parts per Million : 13C

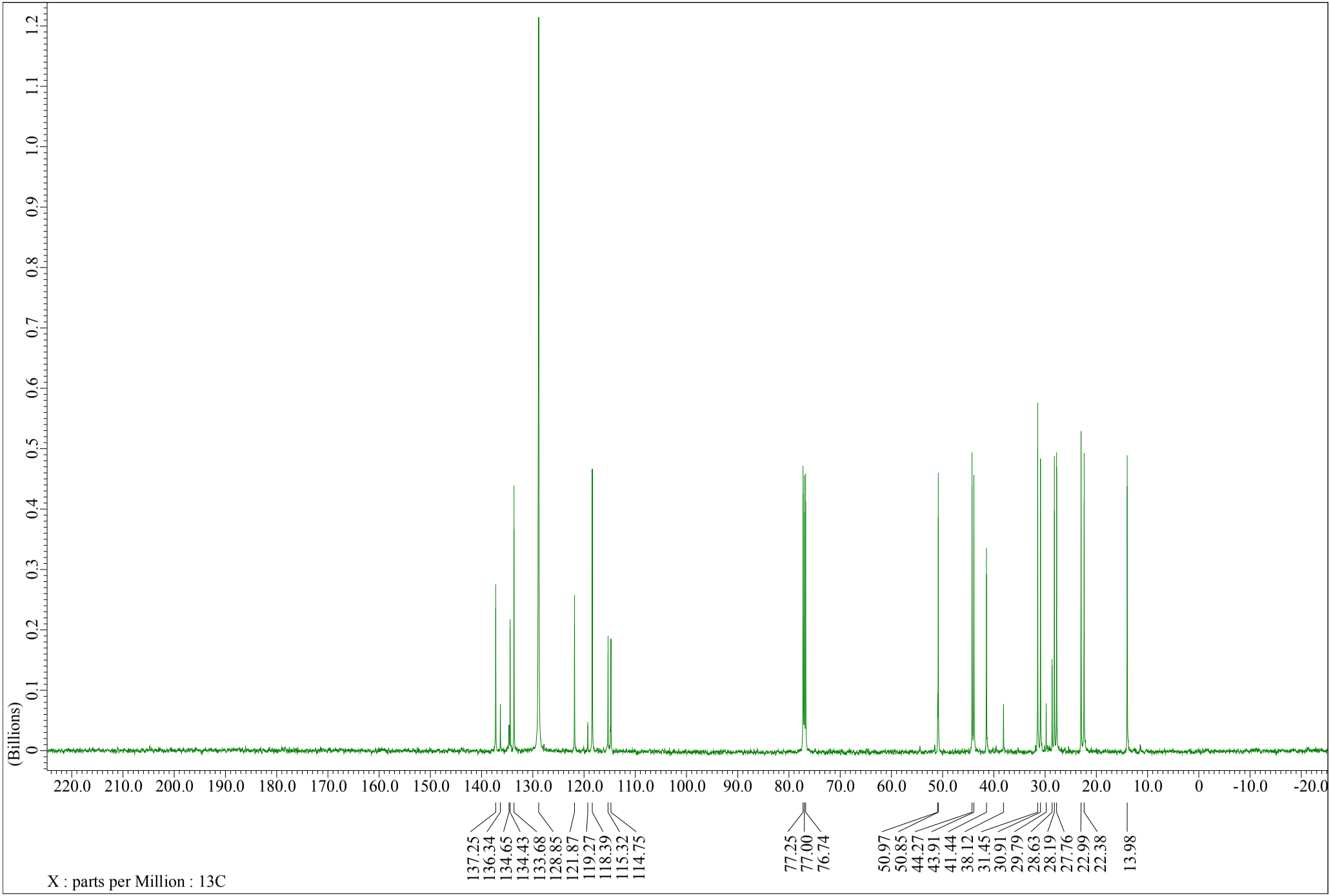

(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
5.71
5.69
5.67
5.67
5.66
5.16
5.13
5.11
4.22
4.20
4.19
4.18
2.67
2.65
2.37
2.11
2.04
1.28
1.26
1.25
0.93
0.91
0.90
-0.00
X : parts per Million : 1H

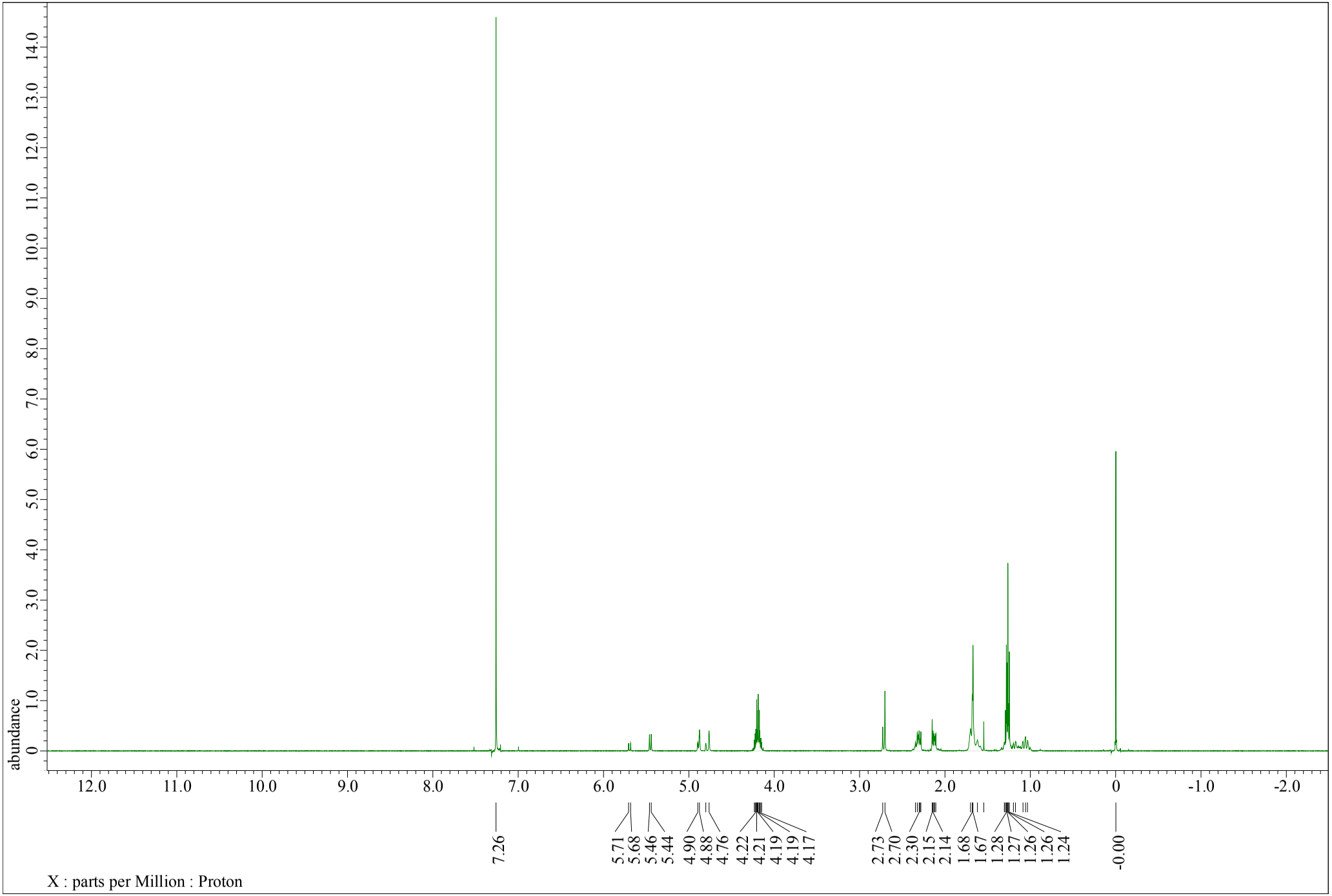

(Millions)
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.91
139.67
132.23
121.26
119.09
77.25
77.00
76.75
61.27
56.86
37.03
36.29
32.65
32.03
31.30
30.85
29.71
22.76
22.73
14.11
13.95
13.92
X : parts per Million : 13C

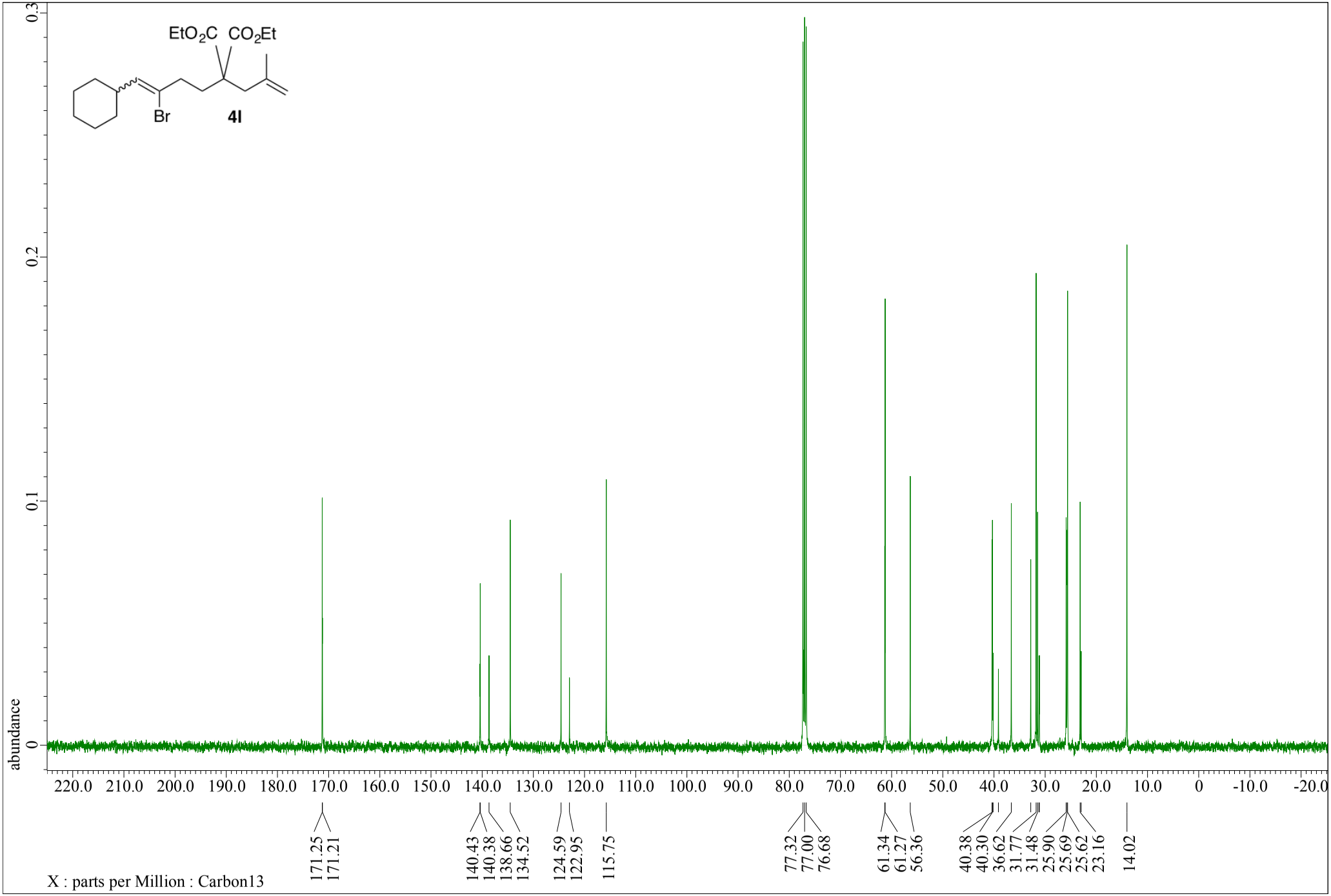

EtO2C CO2Et
Br
4j
(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.89
4.88
4.88
4.80
4.22
4.21
4.19
4.19
4.18
2.72
2.42
2.35
2.19
2.17
2.13
2.09
1.68
1.54
1.53
1.28
1.27
1.25
-0.00
X : parts per Million : 1H

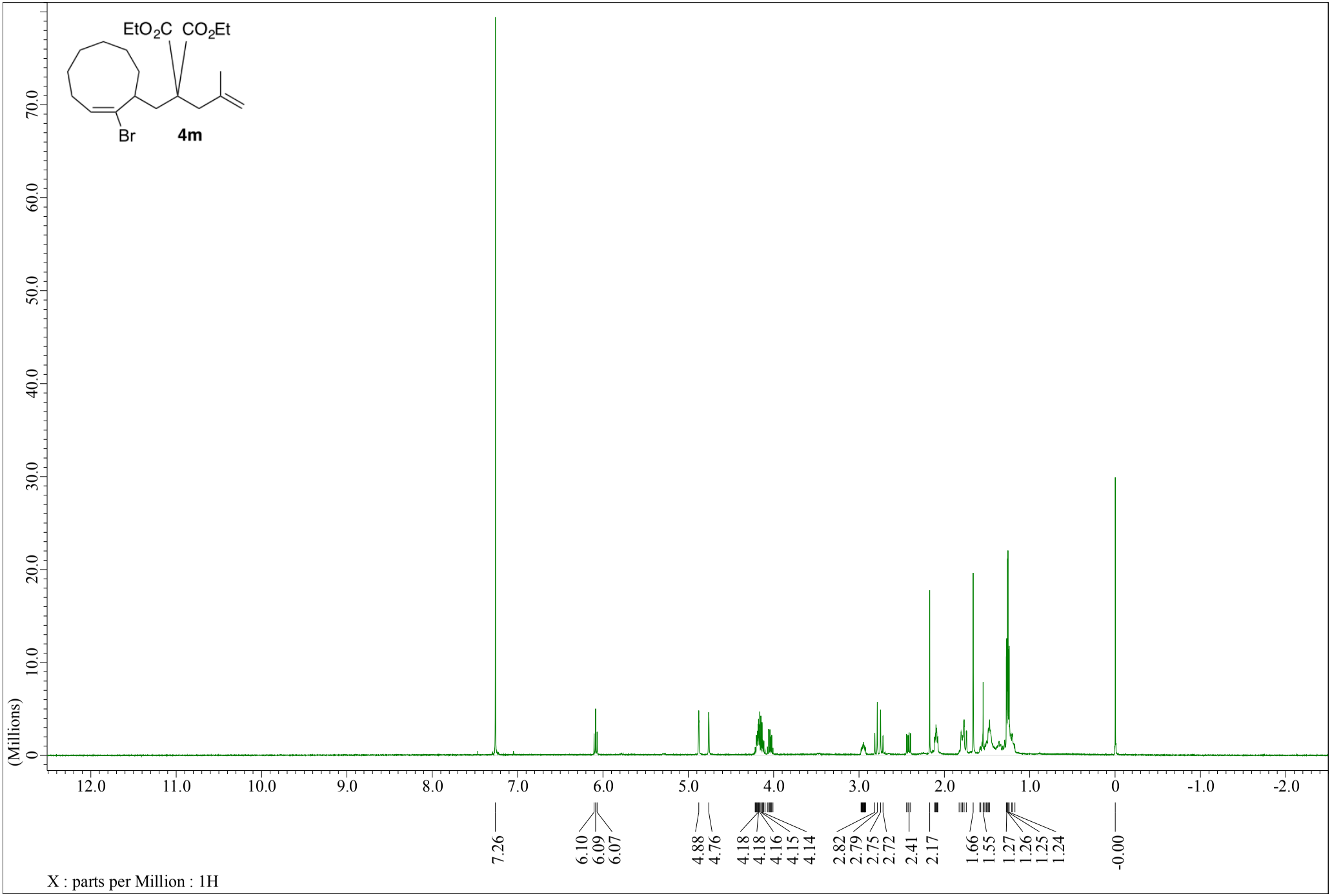

EtO2C CO2Et
Br
4j
(Millions)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.24
140.43
138.37
117.41
115.67
77.26
77.00
76.75
61.20
56.43
40.40
35.24
32.64
31.31
30.86
27.71
27.06
26.24
23.03
13.97
X : parts per Million : 13C

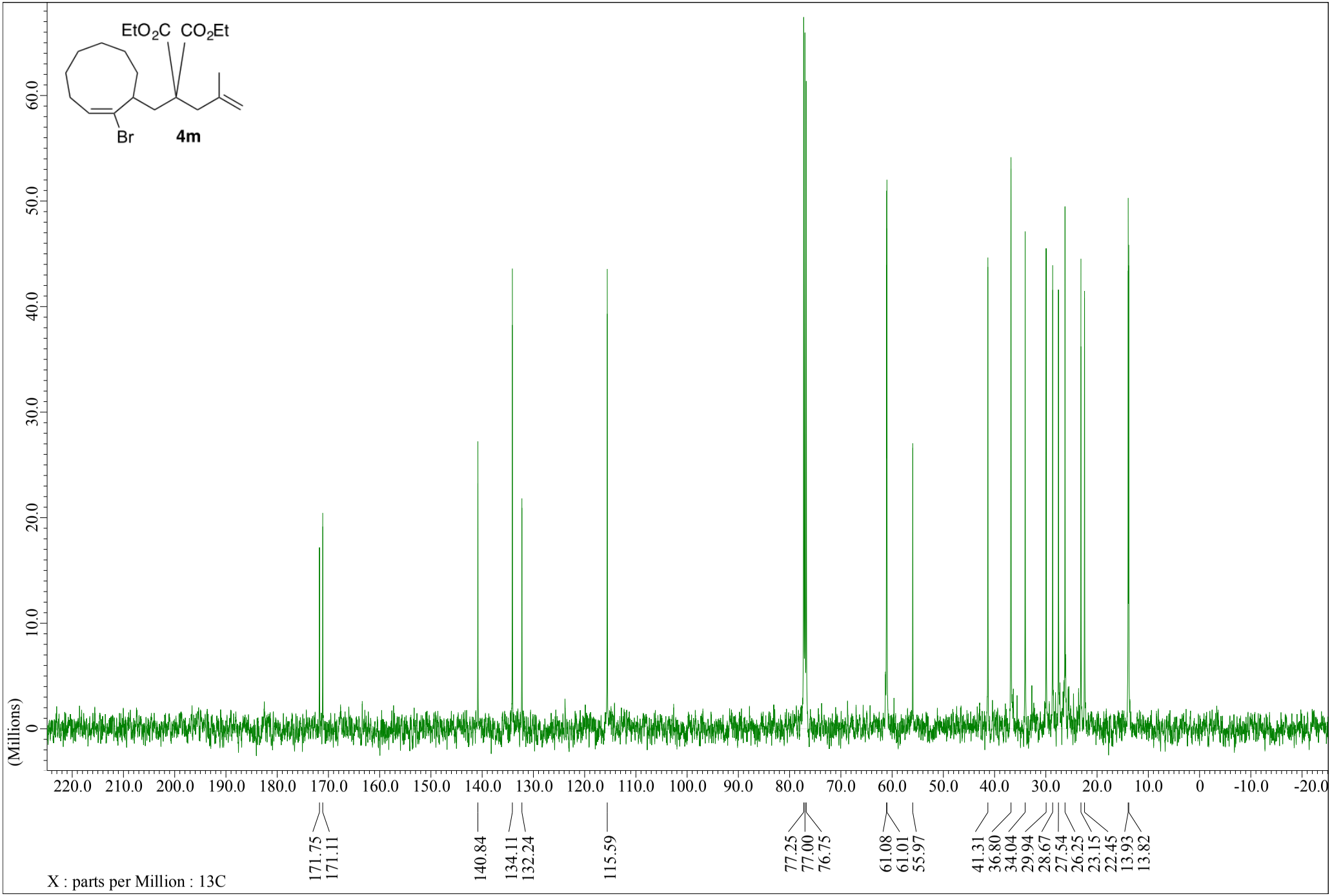

(Millions)
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.26
5.76
5.75
5.73
5.48
5.13
5.13
5.13
5.04
3.54
3.53
3.52
3.51
3.23
3.21
3.19
2.50
2.30
1.92
1.91
1.19
1.10
1.09
0.86
0.84
0.83
-0.00
X : parts per Million : 1H

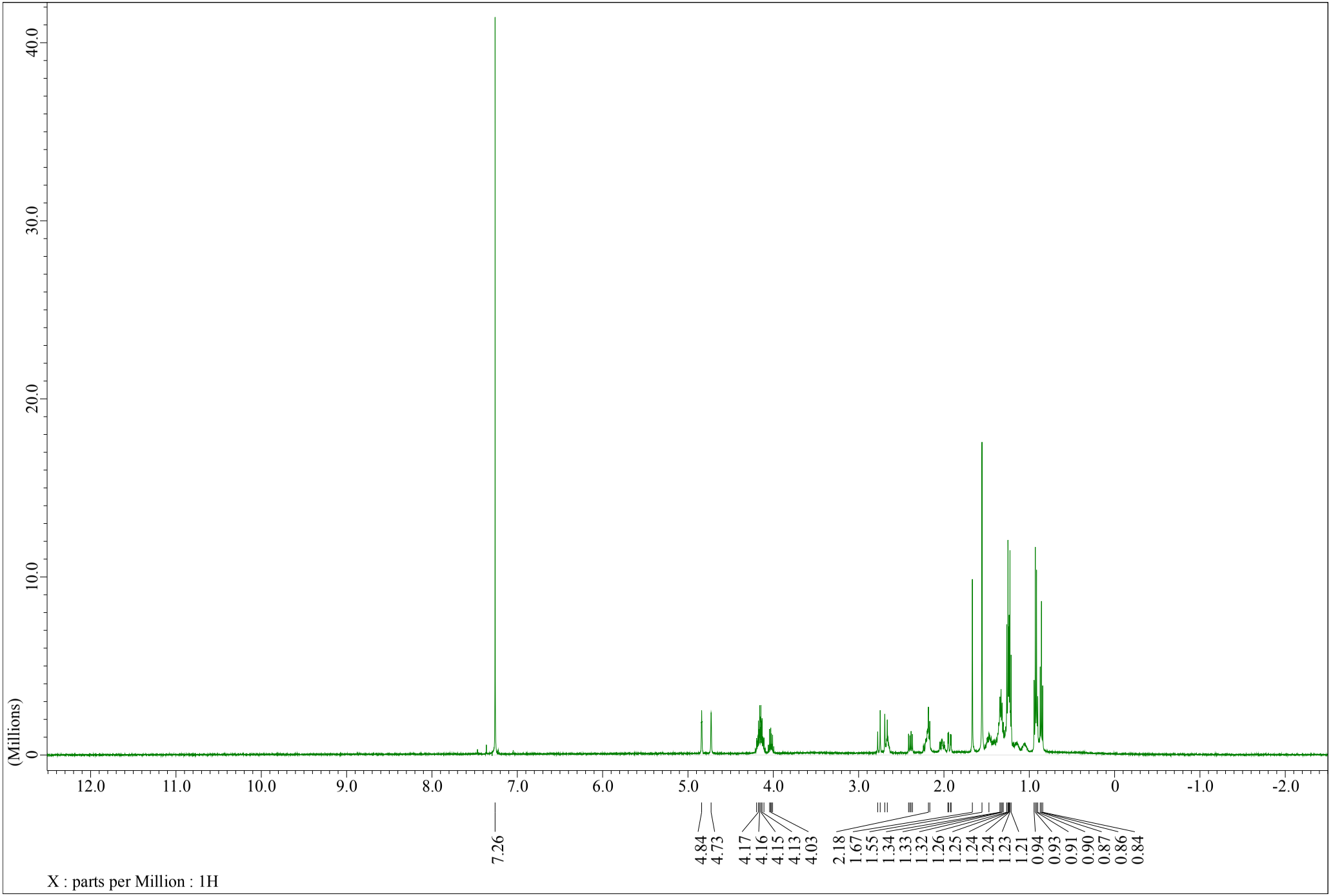

(Billions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
137.25
136.34
134.65
134.43
133.68
128.85
121.87
119.27
118.39
115.32
114.75
77.25
77.00
76.74
50.97
50.85
44.27
43.91
41.44
38.12
31.45
30.91
29.79
28.63
28.19
27.76
22.99
22.38
13.98
X : parts per Million : 13C

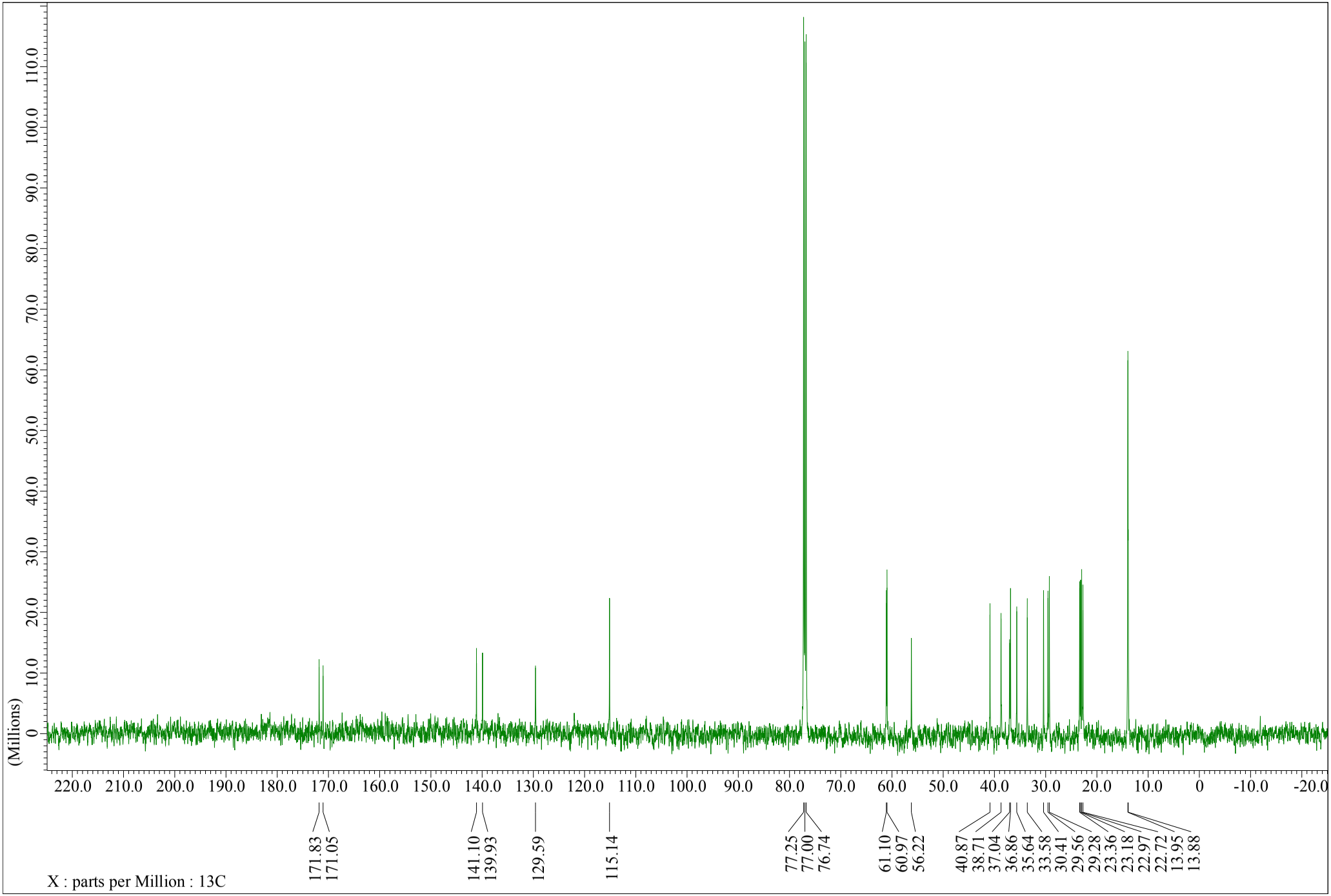

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
5.71
5.68
5.46
5.44
4.90
4.88
4.76
4.22
4.21
4.19
4.19
4.17
2.73
2.70
2.30
2.15
2.14
1.68
1.67
1.28
1.27
1.26
1.26
1.24
-0.00
X : parts per Million : Proton

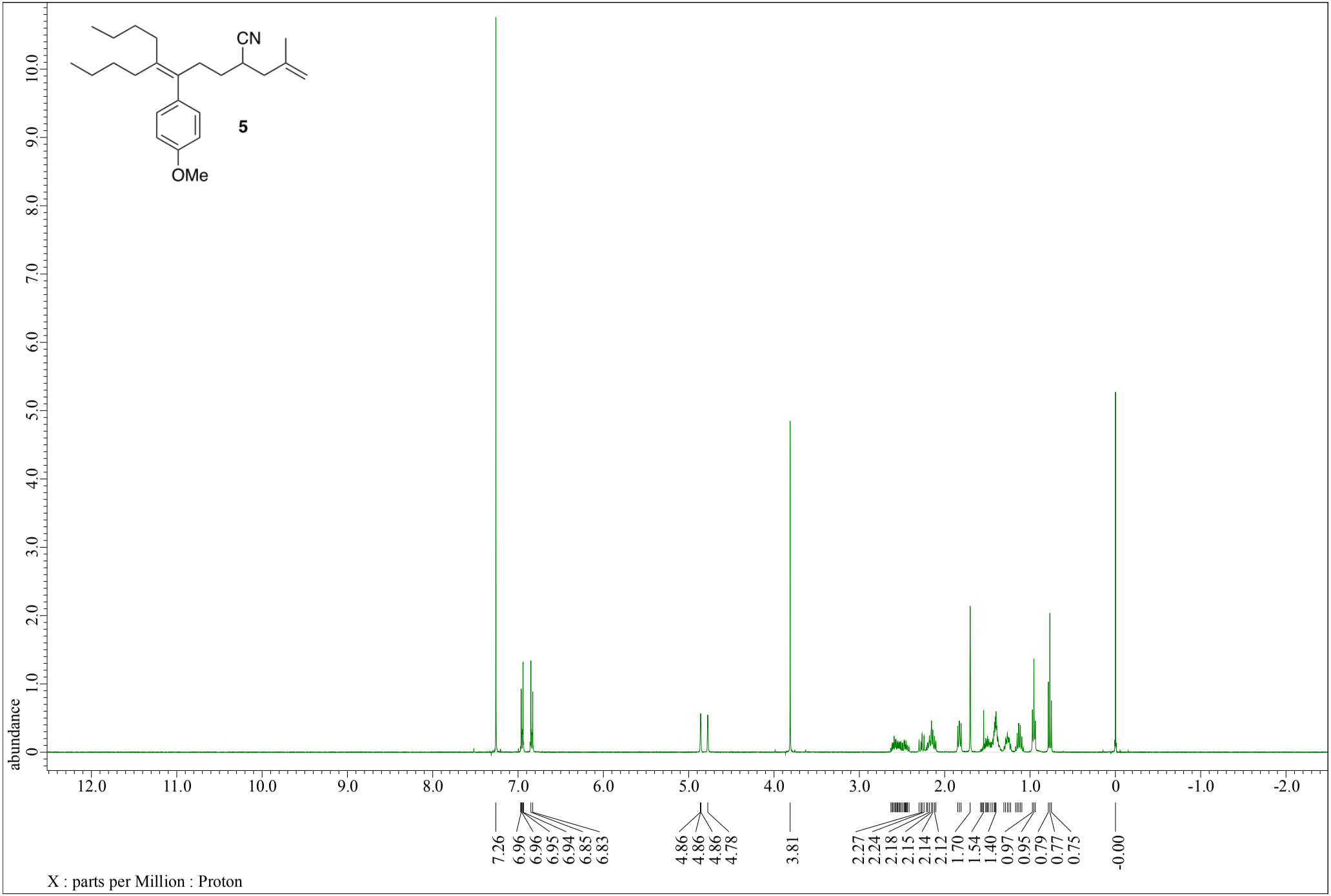

EtO2C CO2Et
Br
4l
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.25
171.21
140.43
140.38
138.66
134.52
124.59
122.95
115.75
77.32
77.00
76.68
61.34
61.27
56.36
40.38
40.30
36.62
31.77
31.48
25.90
25.69
25.62
23.16
14.02
X : parts per Million : Carbon13

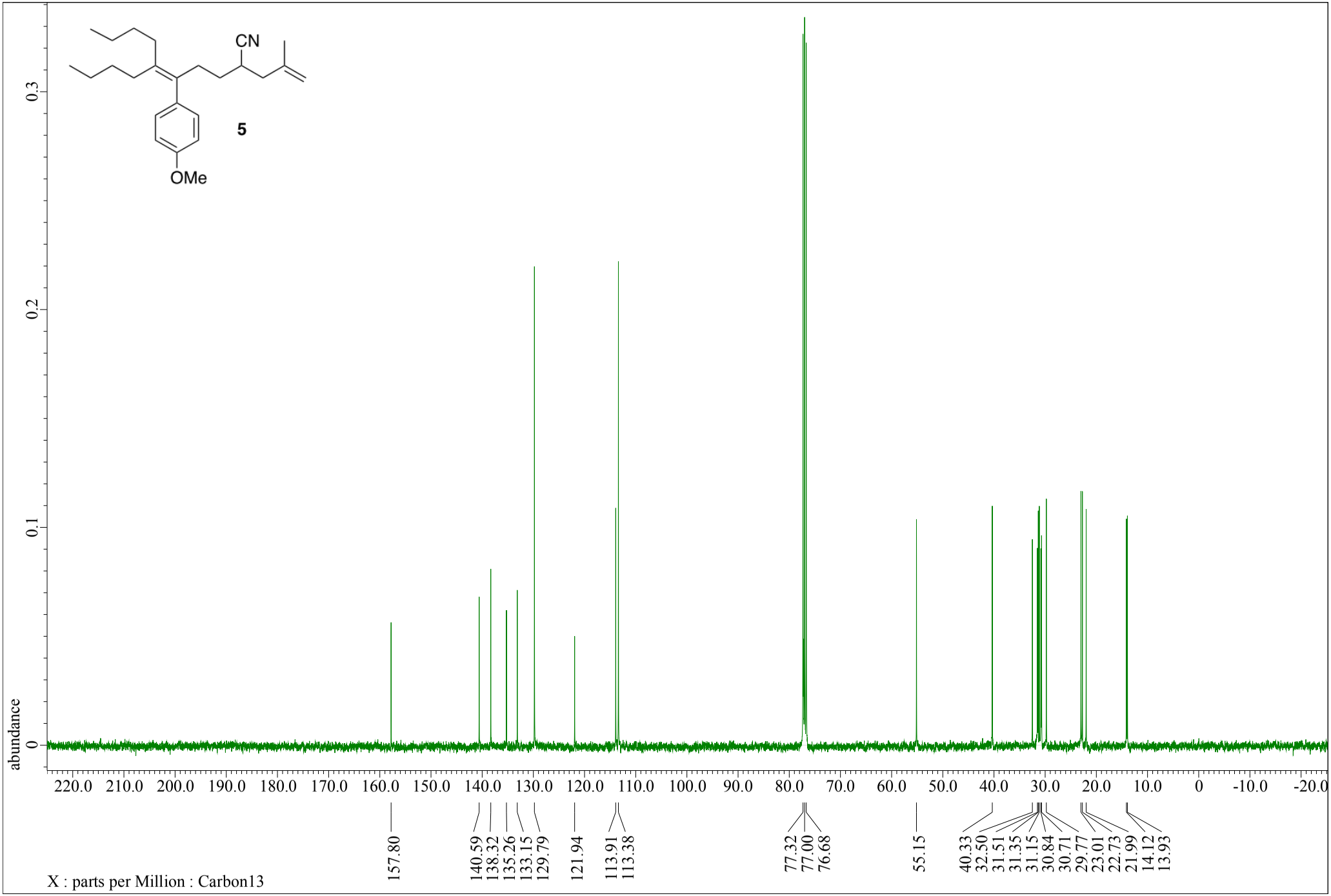

EtO2C CO2Et
Br
4m
(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
6.10
6.09
6.07
4.88
4.76
4.18
4.18
4.16
4.15
4.14
2.82
2.79
2.75
2.72
2.41
2.17
1.66
1.55
1.27
1.26
1.25
1.24
-0.00
X : parts per Million : 1H

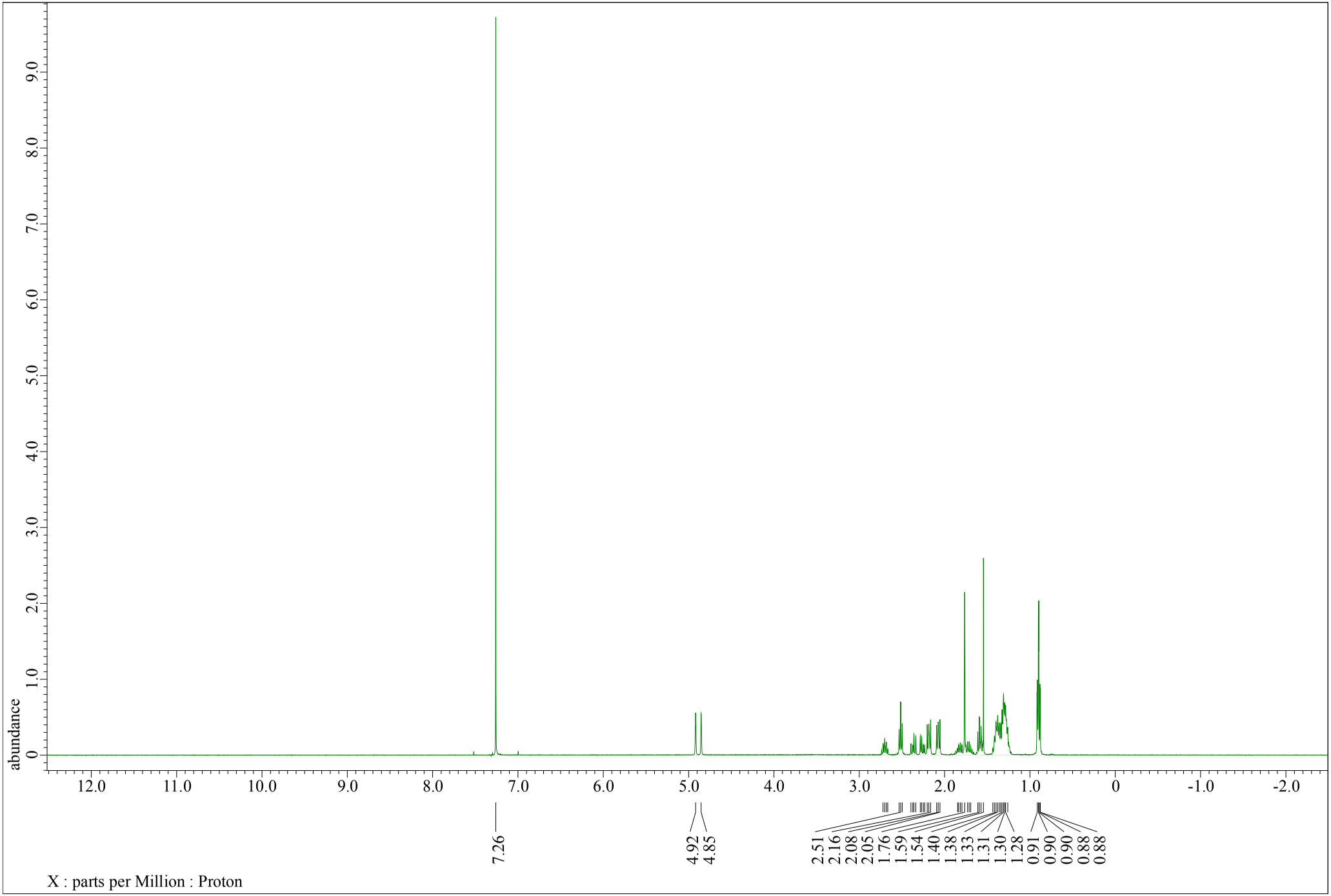

EtO2C CO2Et
Br
4m
(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.75
171.11
140.84
134.11
132.24
115.59
77.25
77.00
76.75
61.08
61.01
55.97
41.31
36.80
34.04
29.94
28.67
27.54
26.25
23.15
22.45
13.93
13.82
X : parts per Million : 13C

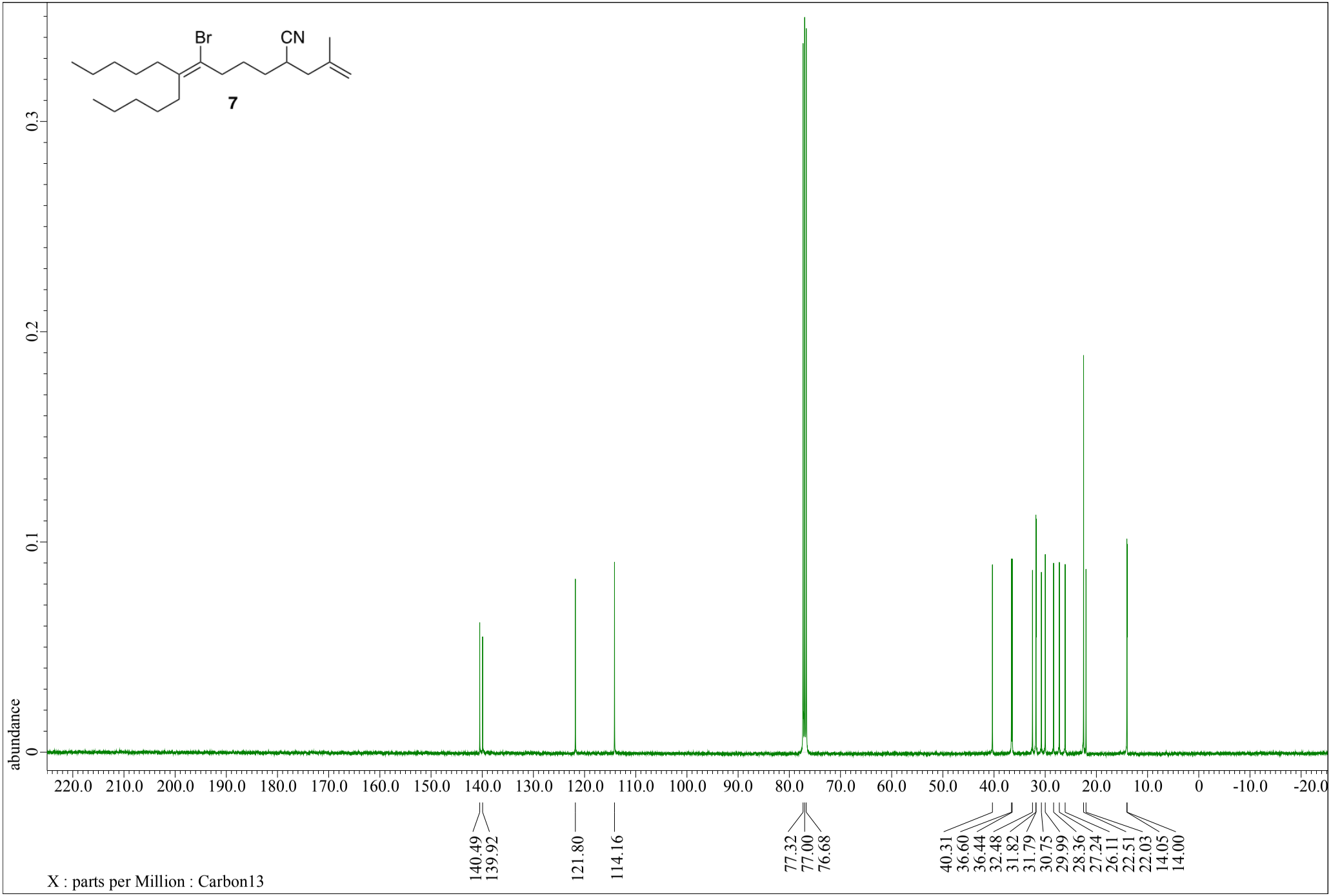

(Millions)
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.84
4.73
4.17
4.16
4.15
4.13
4.03
2.18
1.67
1.55
1.34
1.33
1.32
1.26
1.25
1.24
1.24
1.23
1.21
0.94
0.93
0.91
0.90
0.87
0.86
0.84
X : parts per Million : 1H

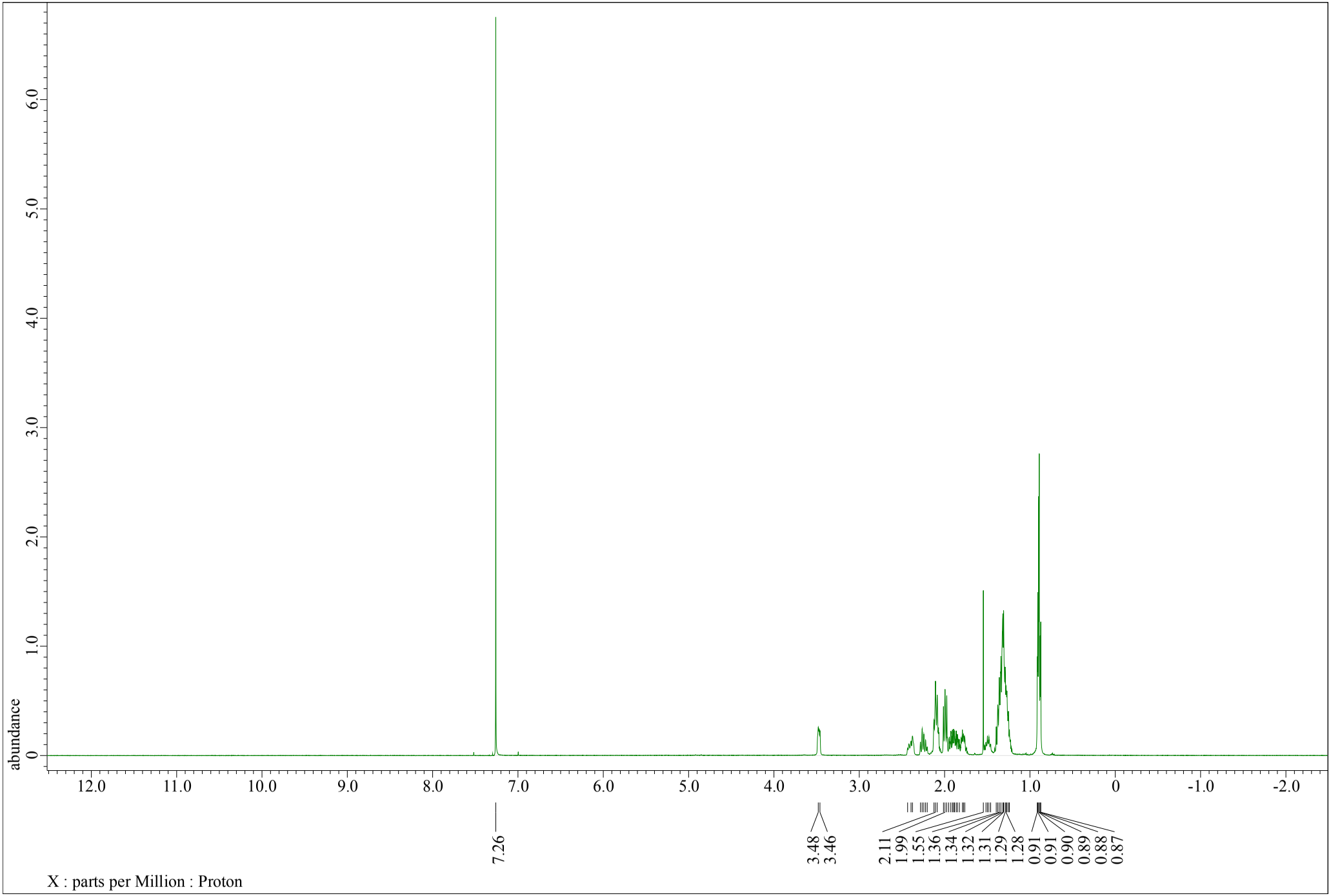

(Millions)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.83
171.05
141.10
139.93
129.59
115.14
77.25
77.00
76.74
61.10
60.97
56.22
40.87
38.71
37.04
36.86
35.64
33.58
30.41
29.56
29.28
23.36
23.18
22.97
22.72
13.95
13.88
X : parts per Million : 13C

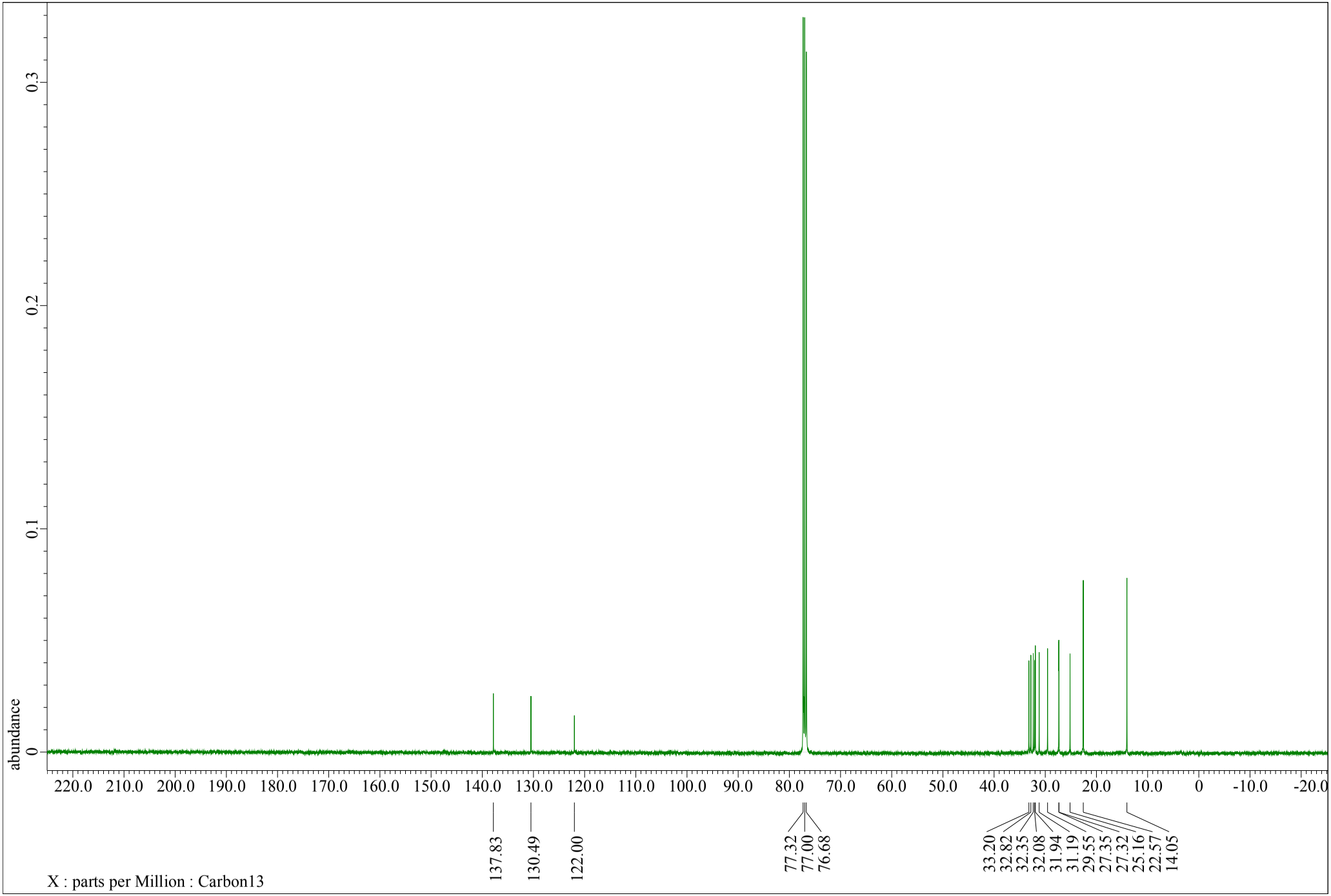

CN
OMe
5
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
6.96
6.96
6.95
6.94
6.85
6.83
4.86
4.86
4.86
4.78
3.81
2.27
2.24
2.18
2.15
2.14
2.12
1.70
1.54
1.40
0.97
0.95
0.79
0.77
0.75
-0.00
X : parts per Million : Proton


CN
OMe
5
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
157.80
140.59
138.32
135.26
133.15
129.79
121.94
113.91
113.38
77.32
77.00
76.68
55.15
40.33
32.50
31.51
31.35
31.15
30.84
30.71
29.77
23.01
22.73
21.99
14.12
13.93
X : parts per Million : Carbon13


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
4.92
4.85
2.51
2.16
2.08
2.05
1.76
1.59
1.54
1.40
1.38
1.33
1.31
1.30
1.28
0.91
0.90
0.90
0.88
0.88
X : parts per Million : Proton


Br
CN
7
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
140.49
139.92
121.80
114.16
77.32
77.00
76.68
40.31
36.60
36.44
32.48
31.82
31.79
30.75
29.99
28.36
27.24
26.11
22.51
22.03
14.05
14.00
X : parts per Million : Carbon13


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.26
3.48
3.46
2.11
1.99
1.55
1.36
1.34
1.32
1.31
1.29
1.28
0.91
0.91
0.90
0.89
0.88
0.87
X : parts per Million : Proton


abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.83
130.49
122.00
77.32
77.00
76.68
33.20
32.82
32.35
32.08
31.94
31.19
29.55
27.35
27.32
25.16
22.57
14.05
X : parts per Million : Carbon13