Supporting Information

Hydroalkylation of Alkenes Using Alkyl Iodides and Hantzsch Ester under Palladium/light System

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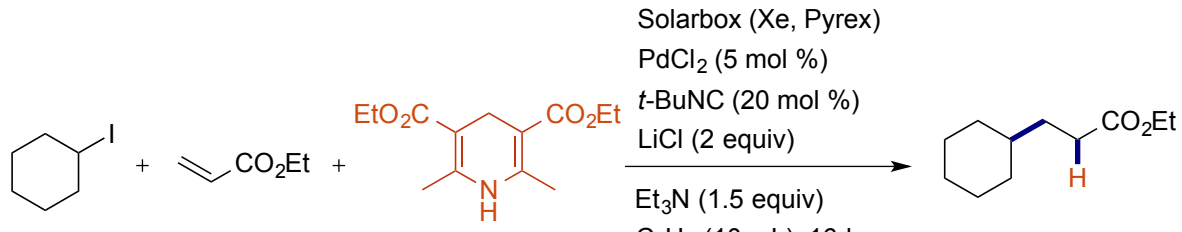
General Information

Photoirradiation was carried out with 1500 W xenon lamp (CO. FO. ME. GRA, Milan, Italy, SolarBox 1500e). Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, Art 5715, 0.25 mm) and were visualized by fluorescence quenching under UV light or by staining with $12MoO_3{\cdot}H_3PO_4$/EtOH or *p*-anisaldeyde/AcOH/H_2SO_4/EtOH. The products were purified by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 mm)) and, if necessary, were further purified by recycling preparative HPLC (Japan Analytical Industry Co. Ltd., LC-918) equipped with GPC columns (JAIGEL-1H + JAIGEL-2H columns) using $CHCl_3$ as eluent. ^{1}H NMR spectra were recorded with a JEOL JMN-ECS400 (400 MHz) spectrometer and referenced to the solvent peak at 7.26 ppm. ^{13}C NMR spectra were recorded with a JEOL JMN-ECS400 (100 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer and are reported as wavenumber (cm^{-1}). High-resolution mass spectra were recorded with a JEOL MS700 spectrometer or Exactive Plus EMR (Thermo Fisher Scientific). Alkyl iodides **1c**, **1d**, **1e**, **1h** were prepared from the corresponding alcohol. **1g** were prepared from the corresponding bromides with sodium iodide in dry acetone. **1i** and **1j** was prepared from corresponding 4-halobenzyl alcohols and 1,6-diiodohexane by the Williamson method using sodium hydride. Hantzsch ester **3** was preparation according to a published procedure.[1]

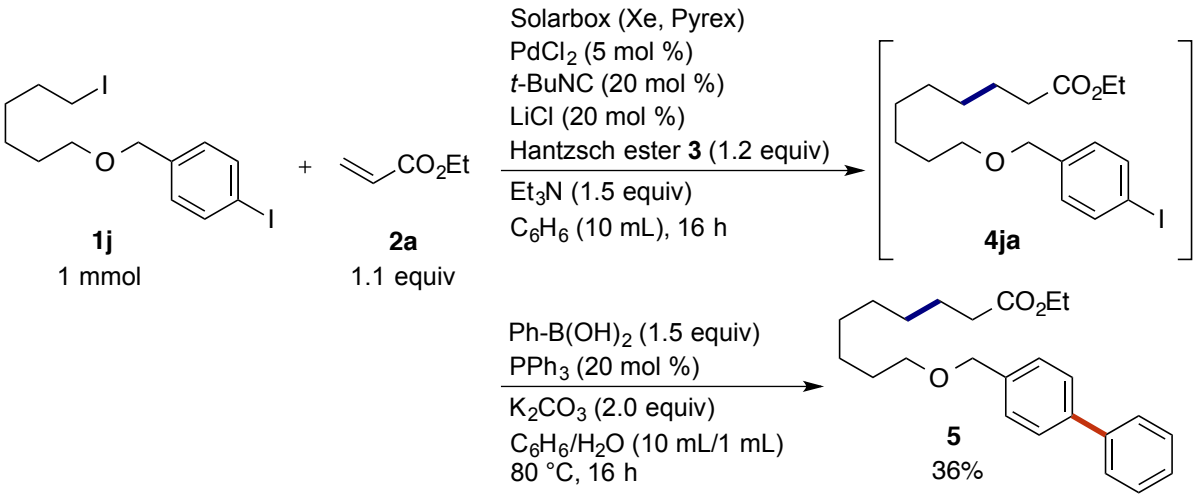
Typical Procedure for the Synthesis of 4aa



1a	**2a**	**3**	**4aa**
1 mmol	1.5 equiv	1.2 equiv	71%

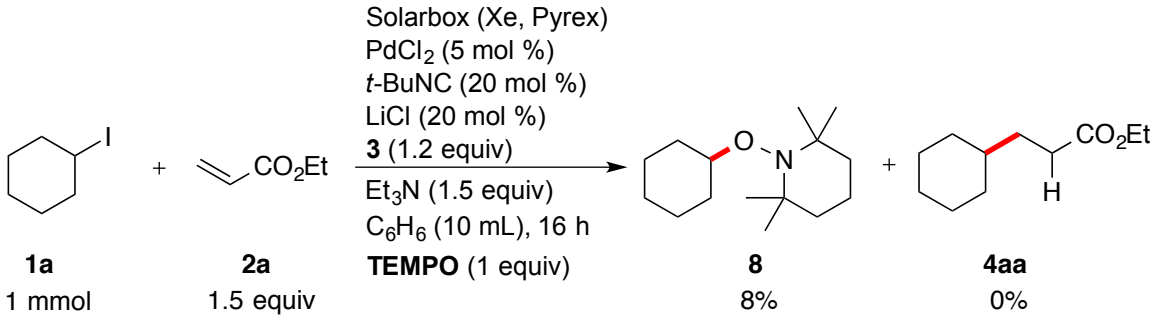
A magnetic stirring bar, **1a** (240.8 mg, 1.0 mmol), **2a** (150.5 mg, 1.5 mmol), **3** (302.1 mg, 1.2 mmol), $PdCl_2$ (9.0 mg, 0.05 mmol), LiCl (8.9 mg, 0.2 mmol), Et_3N (151.0 mg, 1.5 mmol), and C_6H_6 (10 mL) were placed in Pyrex vial under Ar. Then, *t*-BuNC (23 μL, 0.2 mmol) was added. The solution was irradiated with Solarbox (Xe, 1000 W/m^2) with violently stirring for 16 h. The reaction mixture filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 50/1 as eluent affording **4aa** (131.0 mg, 0.71 mmol, 71%).

Typical Procedure for the One-Pot Synthesis of 5 from 1j (Scheme 4)



A magnetic stirring bar, **1j** (444.1 mg, 1.0 mmol), **2a** (91.7mg, 1.5 mmol), **3** (300.1 mg, 1.2 mmol), $PdCl_2$ (8.6 mg, 0.05 mmol), LiCl (7.9 mg, 0.2 mmol), Et_3N (152.5 mg, 1.5 mmol), and C_6H_6 (10 mL) were placed in Pyrex vial under Ar. Then, *t*-BuNC (23 μL, 0.2 mmol) was added. The solution was irradiated with Solarbox (Xe, 1000 W/m^2) with violently stirring for 16 h. After the first reaction, Ph-B(OH)$_2$ (183.2 mg, 1.5 mmol), K_2CO_3 (276.5 mg, 2 mmol), PPh_3 (52.5 mg, 0.2 mmol), and H_2O (1 mL) were added to reaction mixture, then the solution was stirred for 16 h at 80 °C. The reaction mixture was added to water and extracted with ether. The organic layer was washed with brine, and dried over $MgSO_4$, then filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 30/1 as eluent affording **5** (132.8 mg, 0.36 mmol, 36%).

The Reaction of 1a and 2a with TEMPO

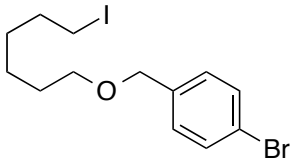


A magnetic stirring bar, **1a** (241.2 mg, 1.0 mmol), **2a** (151.1 mg, 1.5 mmol), **3** (303.8 mg, 1.2 mmol), $PdCl_2$ (8.9 mg, 0.05 mmol), LiCl (8.1 mg, 0.2 mmol), Et_3N (151.9 mg, 1.5 mmol), and C_6H_6 (10 mL) were placed in Pyrex vial under Ar. Then, *t*-BuNC (23 μL, 0.2 mmol) and TEMPO (156.5 mg, 1 mmol) were added. The solution was irradiated with Solarbox (Xe, 1000 W/m^2) with violently stirring for 16 h. The reaction mixture filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography

using hexane/EtOAc = 50/1 as eluent affording **8** (19.2 mg, 0.08 mmol, 8%).

Spectral Data

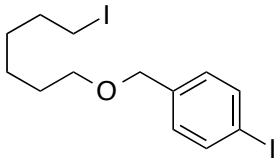
1-bromo-4-(((6-iodohexyl)oxy)methyl)benzene (1i)



1q was prepared from 4-bromobenzyl alcohol and 1,6-diiodohexane by the Williamson method using sodium hydride.

Colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.48-7.46 (m, 2H), 7.22-7.20 (m, 2H), 4.44 (s, 2H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.84-1.80 (m, 2H), 1.65-1.58 (m, 2H), 1.45-1.35 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.60, 131.44, 129.20, 121.31, 72.11, 70.31, 33.39, 30.26, 29.49, 25.14, 7.09; IR (neat) 2933 cm^{-1}, 2856 cm^{-1}, 1467 cm^{-1}, 1104 cm^{-1}, 1070 cm^{-1}, 1011 cm^{-1}, 802 cm^{-1}; MS (relative intensity) m/z 398 ($[M]^+$, 5), 396 ($[M]^+$, 3), 211 (5), 209 (4), 171 (97), 169 (100), 90 (21); HRMS (EI) m/z calcd for $C_{13}H_{18}{}^{79}BrIO$ 395.9586, found 395.9593.

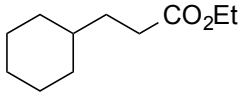
1-iodo-4-(((6-iodohexyl)oxy)methyl)benzene (1j)



1j was prepared from 4-iodobenzyl alcohol and 1,6-diiodohexane by the Williamson method using sodium hydride.

Colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.48-7.66 (m, 2H), 7.09-7.07 (m, 2H), 4.43 (s, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 1.84-1.79 (m, 2H), 1.63-1.57 (m, 2H), 1.45-1.35 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.28, 137.39, 129.44, 92.88, 72.17, 70.30, 33.38, 30.25, 29.48, 25.13, 7.10; IR (neat) 2932 cm^{-1}, 2855 cm^{-1}, 1483 cm^{-1}, 1204 cm^{-1}, 1103 cm^{-1}, 1059 cm^{-1}, 1007 cm^{-1}, 798 cm^{-1}; MS (relative intensity) m/z 444 ($[M]^+$, 6), 217 (100), 90 (13); HRMS (EI) m/z calcd for $C_{13}H_{18}I_2O$ 443.9447, found 443.9454.

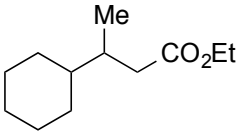
ethyl 3-cyclohexylpropanoate (4aa)[2]



Colorless oil (131.0 mg, 0.71 mmol, 71%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.10 (q, *J* = 7.2 Hz, 2H), 2.30-2.26

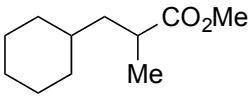
(m, 2H), 1.70-1.58 (m, 5H), 1.53-1.48 (m, 2H), 1.26-1.05 (m, 7H), 0.91-0.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.29, 60.24, 37.31, 33.04, 32.44, 32.04, 26.60, 26.30, 14.32.

ethyl 3-cyclohexylbutanoate (4ab)[3]



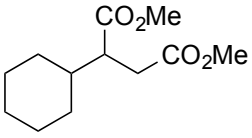
Colorless oil (109.1 mg, 0.55 mmol, 55%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.12 (t, *J* = 7.2 Hz, 2H), 2.36 (dd, *J* = 5.2, 14.8 Hz, 1H), 2.61 (dd, *J* = 9.2, 14.8 Hz, 1H), 1.90-1.80 (m, 1H), 1.77-1.58 (m, 6H), 1.30-0.82 (m, 8H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.88, 60.06, 42.57, 39.28, 35.37, 30.26, 28.88, 26.69, 26.69, 26.63, 26.58, 16.43, 14.26.

methyl 3-cyclohexyl-2-methylpropanoate (4ac)[4]



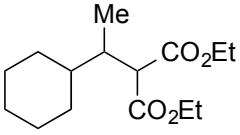
Colorless oil (70.1 mg, 0.38 mmol, 38%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.66 (s, 3H), 2.59-2.50 (m, 1H), 1.75-1.51 (m, 8H), 1.31-1.11 (m, 6H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.91-0.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 177.74, 51.47, 41.51, 36.71, 35.34, 33.26, 33.08, 26.53, 26.23, 26.18, 17.55.

dimethyl 2-cyclohexylsuccinate (4ad)[5]



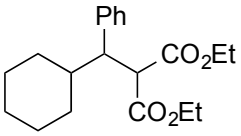
Colorless oil (164.4 mg, 0.72 mmol, 72%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.69 (s, 3H), 3.66 (s, 3H), 2.76-2.68 (m, 2H), 2.49-2.41 (m, 1H), 1.75-1.70 (m, 2H), 1.68-1.55 (m, 4H), 1.28-0.95 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.02, 173.00, 51.76, 51.61, 46.97, 39.90, 33.19, 30.60, 30.10, 26.25, 26.10.

diethyl 2-(1-cyclohexylethyl)malonate (4ae)[6]



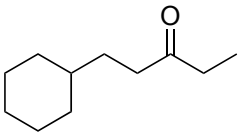
Colorless oil (197.2 mg, 0.73 mmol, 73%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.21-4.15 (m, 4H), 3.38 (d, *J* = 8.8 Hz, 3H), 2.17-2.13 (m, 1H), 1.78-1.70 (m, 2H), 1.69-1.55 (m, 3H), 1.29-1.01 (m, 10H), 0.98-0.88 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 169.29, 169.03, 61.11, 61.04, 55.79, 40.20, 38.53, 31.48, 27.32, 26.69, 26.50, 26.43, 14.10, 12.85.

diethyl 2-(cyclohexyl(phenyl)methyl)malonate (4af)[7]



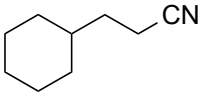
Colorless oil (212.8 mg, 0.64 mmol, 64%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.26-7.12 (m, 5H), 4.27-4.19 (m, 2H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.95-3.89 (m, 2H), 3.37 (dd, *J* = 5.1, 11.5 Hz, 1H), 1.69-1.50 (m, 6H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.25-1.05 (m, 2H), 1.00-0.78 (m, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 168.85, 168.06, 138.94, 129.45, 127.66, 126.63, 61.48, 61.09, 55.30, 51.03, 40.79, 32.02, 28.30, 26.61, 26.42, 26.16, 14.11, 13.62.

1-cyclohexylpentan-3-one (4ag)[2]



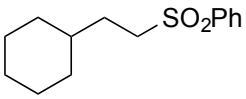
Colorless oil (126.2 mg, 0.75 mmol, 75%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.45-2.38 (m, 4H), 1.73-1.60 (m, 5H), 1.50-1.42 (m, 2H), 1.29-1.10 (m, 4H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.95-0.84 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.15, 39.90, 37.24, 25.73, 33.05, 31.23, 26.47, 26.18, 7.81.

3-cyclohexylpropanenitrile (4ah)[8]



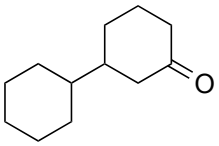
Colorless oil (105.7 mg, 0.77 mmol, 77%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.35 (t, *J* = 7.2 Hz, 2H), 1.72-1.62 (m, 5H), 1.58-1.53 (m, 3H), 1.46-1.33 (m, 1H), 1.31-1.08 (m, 3H), 0.95-0.84 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 120.05, 36.47, 32.48, 32.43, 26.23, 25.87, 14.57.

((2-cyclohexylethyl)sulfonyl)benzene (4ai)[9]



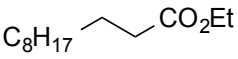
Colorless oil (222.2 mg, 0.88 mmol, 88%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.91-7.90 (m, 2H), 7.68-7.64 (m, 1H), 7.59-7.55 (m, 2H), 3.09 (dt, *J* = 5.2, 6.8 Hz, 2H), 1.68-1.56 (m, 7H), 1.31-1.05 (m, 4H), 0.98-0.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 139.18, 133.57, 129.21, 128.01, 54.35, 36.60, 32.93, 29.58, 26.21, 25.95.

[1,1'-bi(cyclohexan)]-3-one (4aj)[3]



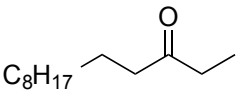
Colorless oil (86.6 mg, 0.48 mmol, 48%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.40-2.30 (m, 2H), 2.28-2.20 (m, 1H), 2.21-2.00 (m, 2H), 1.90-1.82 (m, 1H), 1.78-1.52 (m, 7H), 1.12-1.31 (m, 1H), 1.27-1.04 (m, 4H), 1.02-0.88 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.85, 45.53, 44.63, 42.61, 41.57, 29.90, 29.80, 28.37, 26.54, 26.48, 25.58.

ethyl undecanoate (4ba)[2]



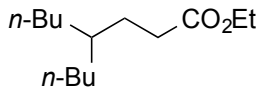
Colorless oil (143.7 mg, 0.67 mmol, 67%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.11 (t, *J* = 7.6 Hz, 2H), 2.29-2.45 (m, 2H), 1.64-1.55 (m, 2H), 1.30-1.22 (m, 17H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.92, 60.12, 34.37, 31.82, 29.44, 29.29, 22.25, 29.12, 24.96, 22.66, 14.23, 14.09.

tridecan-3-one (4bg)[2]



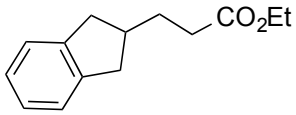
Colorless oil (121.0 mg, 0.61 mmol, 61%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.42-2.35 (m, 4H), 1.56-1.51 (m, 2H), 1.30-1.15 (m, 14H), 1.02 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 211.89, 42.38, 35.78, 31.83, 29.51, 29.43, 29.37, 29.26, 29.24, 23.90, 22.62, 14.04, 7.78.

ethyl 4-butyloctanoate (4ca)[2]



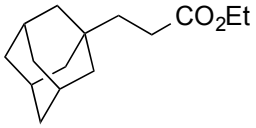
Colorless oil (137.0 mg, 0.60 mmol, 60%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.12 (t, *J* = 7.2 Hz, 2H), 2.29-2.44 (m, 2H), 1.63-1.54 (m, 2H), 1.34-1.17 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.26, 60.17, 36.89, 32.94, 31.81, 28.75, 28.65, 23.05, 14.23, 14.11.

ethyl 3-(2,3-dihydro-1*H*-inden-2-yl)propanoate (4da)



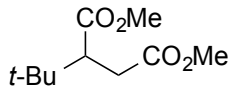
Colorless oil (135.4 mg, 0.62 mmol, 62%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.22-7.16 (m, 2H), 7.15-7.11 (m, 2H), 4.18-4.11 (m, 2H), 3.06 (dd, *J* = 7.6, 15.6 Hz, 2H), 2.61 (dd, *J* = 8.4, 15.6 Hz, 2H), 2.51-2.37 (m, 3H), 1.90-1.83 (m, 2H), 1.30-1.25 (m, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.67, 143.10, 126.13, 124.36, 60.31, 39.63, 38.94, 33.27, 30.71, 14.24; IR (neat) 743 cm^{-1}, 1180 cm^{-1}, 1734 cm^{-1}, 2932 cm^{-1}; MS (relative intensity) m/z 218 (M^+, 47), 172 (100), 129 (72), 116 (60); HRMS (EI) m/z calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1306.

Ethyl 3-(Adamantan-1-yl)propionate (4ea)[2]



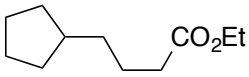
Colorless oil (160.0 mg, 0.68 mmol, 68%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.11 (q, *J* = 7.2 Hz, 2H), 2.29-2.21 (m, 2H), 2.03-1.90 (m, 3H), 1.69-1.57 (m, 6H), 1.46-1.36 (m, 8H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.74, 60.20, 41.98, 38.93, 37.04, 31.87, 28.55, 28.17, 14.21.

dimethyl 2-(*tert*-butyl)succinate (4fd)[10]



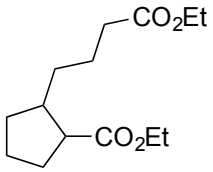
Colorless oil (133.3 mg, 0.66 mmol, 66%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H), 3.64 (s, 3H), 2.81-2.74 (m, 1H), 2.64-2.60 (m, 1H), 2.49-2.44 (m, 1H), 0.94 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.68, 173.12, 51.74, 51.32, 51.11, 32.54, 27.73.

ethyl 4-cyclopentylbutanoate (4ga)[2]



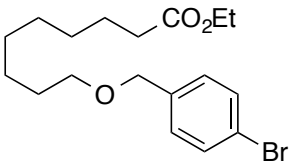
Colorless oil (97.7 mg, 0.53 mmol, 53%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.12 (q, *J* = 7.2 Hz, 2H), 2.30-2.26 (m, 2H), 1.79-1.43 (m, 9H), 1.34-1.27 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13-1.01 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.92, 60.13, 39.82, 35.64, 34.61, 32.58, 25.14, 24.20, 14.25.

ethyl 2-(4-ethoxy-4-oxobutyl)cyclopentane-1-carboxylate (4ha)[2]



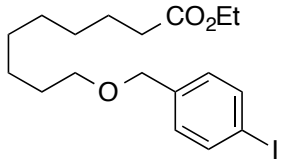
Colorless oil (102.6 mg, 0.40 mmol, 40%). Obtained as a *cis*/*trans* mixture in a 66/34 ratio. *Cis* isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.13-4.06 (m, 4H), 2.84-2.80 (m, 1H), 2.29-2.25 (m, 2H), 2.15-2.00 (m, 1H), 1.95-1.62 (m, 3H), 1.55-1.15 (m, 14H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13-1.01 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.44, 173.62, 60.19, 47.51, 43.43, 34.46, 30.97, 30.61, 2.34, 24.01, 23.79, 14.22. *Trans* isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.13-4.06 (m, 4H), 2.29-2.25 (m, 3H), 2.15-2.00 (m, 1H), 1.95-1.62 (m, 3H), 1.55-1.15 (m, 14H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13-1.01 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.59, 173.62, 59.86, 50.36, 44.01, 34.75, 34.60, 32.46, 30.31, 24.72, 23.63, 14.33.

ethyl 9-((4-bromobenzyl)oxy)nonanoate (4ia)



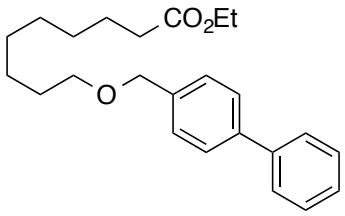
Colorless oil (170.9 mg, 0.46 mmol, 46%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.47-7.44 (m, 2H), 7.22-7.20 (m, 2H), 4.43 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.30-2.26 (m, 2H), 1.63-1.57 (m, 4H), 1.37-1.23 (m, 11H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.84, 137.69, 131.39, 129.17, 121.23, 72.04, 70.12, 34.32, 29.65, 29.21, 29.15, 29.02, 26.07, 24.90, 14.22; IR (neat) 2931 cm^{-1}, 2856 cm^{-1}, 1731 cm^{-1}, 1387 cm^{-1}, 1180 cm^{-1}, 1098 cm^{-1}, 1031 cm^{-1}, 1011 cm^{-1}, 803 cm^{-1}; MS (relative intensity) m/z 291 ([M-Br]$^{+}$, 34), 185 (50), 171 (97), 169 (100), 139 (64), 101 (35); HRMS (ESI) m/z calcd for $C_{18}H_{27}{}^{79}BrO_3Na$ 393.1036, found 393.1302.

ethyl 9-((4-iodobenzyl)oxy)nonanoate (4ja)



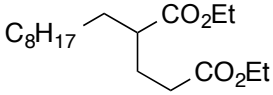
Colorless oil (196.1 mg, 0.47 mmol, 47%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67-7.65 (m, 2H), 7.09-7.07 (m, 2H), 4.43 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.30-2.26 (m, 2H), 1.63-1.57 (m, 4H), 1.35-1.23 (m, 11H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.83, 138.37, 137.36, 129.41, 92.79, 72.09, 70.55, 34.32, 29.65, 29.20, 29.14, 29.02, 26.06, 24.89, 14.22; IR (neat) 2930 cm^{-1}, 2855 cm^{-1}, 1731 cm^{-1}, 1585 cm^{-1}, 1482 cm^{-1}, 1178 cm^{-1}, 1101 cm^{-1}, 1056 cm^{-1}, 1008 cm^{-1}, 800 cm^{-1}; MS (relative intensity) m/z 291 ([M-I]$^+$, 16), 233 (12), 217 (100), 185 (35), 139 (58); HRMS (ESI) m/z calcd for $C_{18}H_{27}IO_3Na$ 441.0897, found 441.0895.

ethyl 9-([1,1'-biphenyl]-4-ylmethoxy)nonanoate (5)



Colorless oil (140.0 mg, 0.38 mmol, 38% (from **1i**)). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.61-7.57 (m, 4H), 7.46-7.41 (m, 4H), 7.36-7.35 (m, 1H), 4.55 (s, 2H), 4.12 (q, *J* = 6.8 Hz, 2H), 3.50 (t, *J* = 6.6 Hz, 2H), 2.31-2.27 (m, 2H), 1.65-1.60 (m, 4H), 1.40-1.30 (m, 8H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 173.87, 140.94, 140.40, 137.71, 128.72, 128.05, 127.19, 127.09, 127.05, 72.56, 70.51, 60.13, 34.34, 29.73, 29.26, 29.19, 29.05, 26.12, 24.92, 14.23; IR (neat) 2931 cm^{-1}, 2855 cm^{-1}, 1730 cm^{-1}, 1600 cm^{-1}, 1488 cm^{-1}, 1463 cm^{-1}, 1371 cm^{-1}, 1180 cm^{-1}, 1099 cm^{-1}, 1008 cm^{-1}, 826 cm^{-1}, 761 cm^{-1}, 698 cm^{-1}; MS (relative intensity) m/z 368 (M$^+$, 9), 183 (85), 167 (100), 153 (8); HRMS (EI) m/z calcd for $C_{24}H_{32}O_3$ 368.2351, found 368.2361.

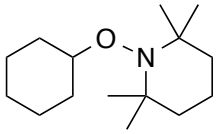
diethyl 2-nonylpentanedioate (7)[11]



Colorless oil (31.5 mg, 0.10 mmol, 10%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.16-4.09 (m, 4H), 2.40-2.23 (m,

3H), 1.91-1.75 (m, 2H), 1.65-1.55 (m, 2H), 1.48-1.35 (m, 1H), 1.25-1.18 (m, 20H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.72, 173.09, 60.36, 60.20, 44.82, 32.29, 32.05, 31.85, 29.50, 29.46, 29.42, 29.27, 27.18, 22.65, 14.29, 14.19, 14.08.

1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (8)[12]



Colorless oil (19.2 mg, 0.08 mmol, 8%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.60-3.56 (m, 1H), 2.08-2.02 (m, 2H), 1.78-1.68 (m, 2H), 1.64-1.03 (m, 24H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 81.73, 59.59, 40.23, 34.44, 32.89, 25.92, 25.08, 20.27, 17.30.

Reference

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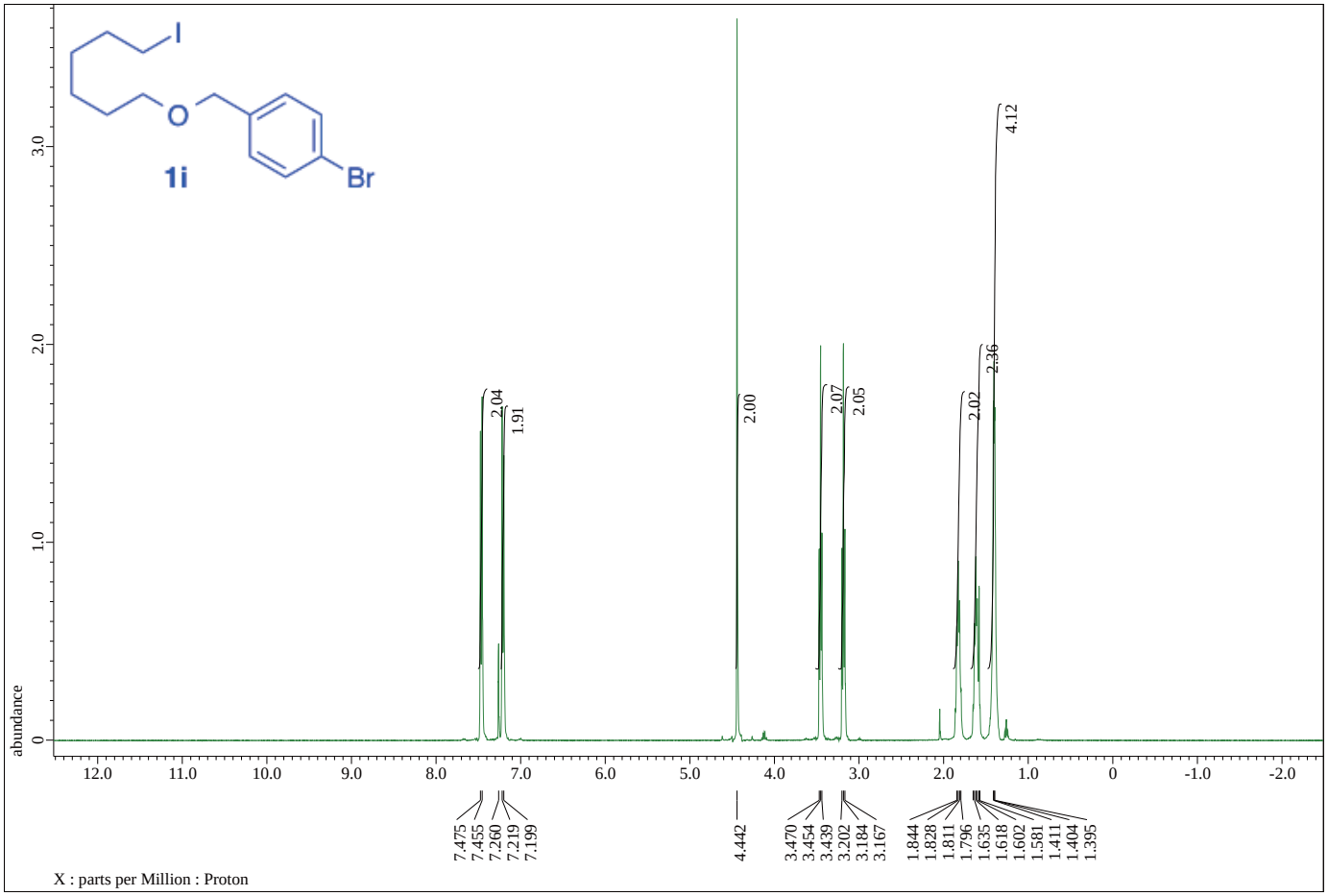
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O
Br
abundance
X : parts per Million : Proton
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2.07
2.05
2.04
2.02
2.00
1.91
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7.455
7.260
7.219
7.199
4.442
3.470
3.454
3.439
3.202
3.184
3.167
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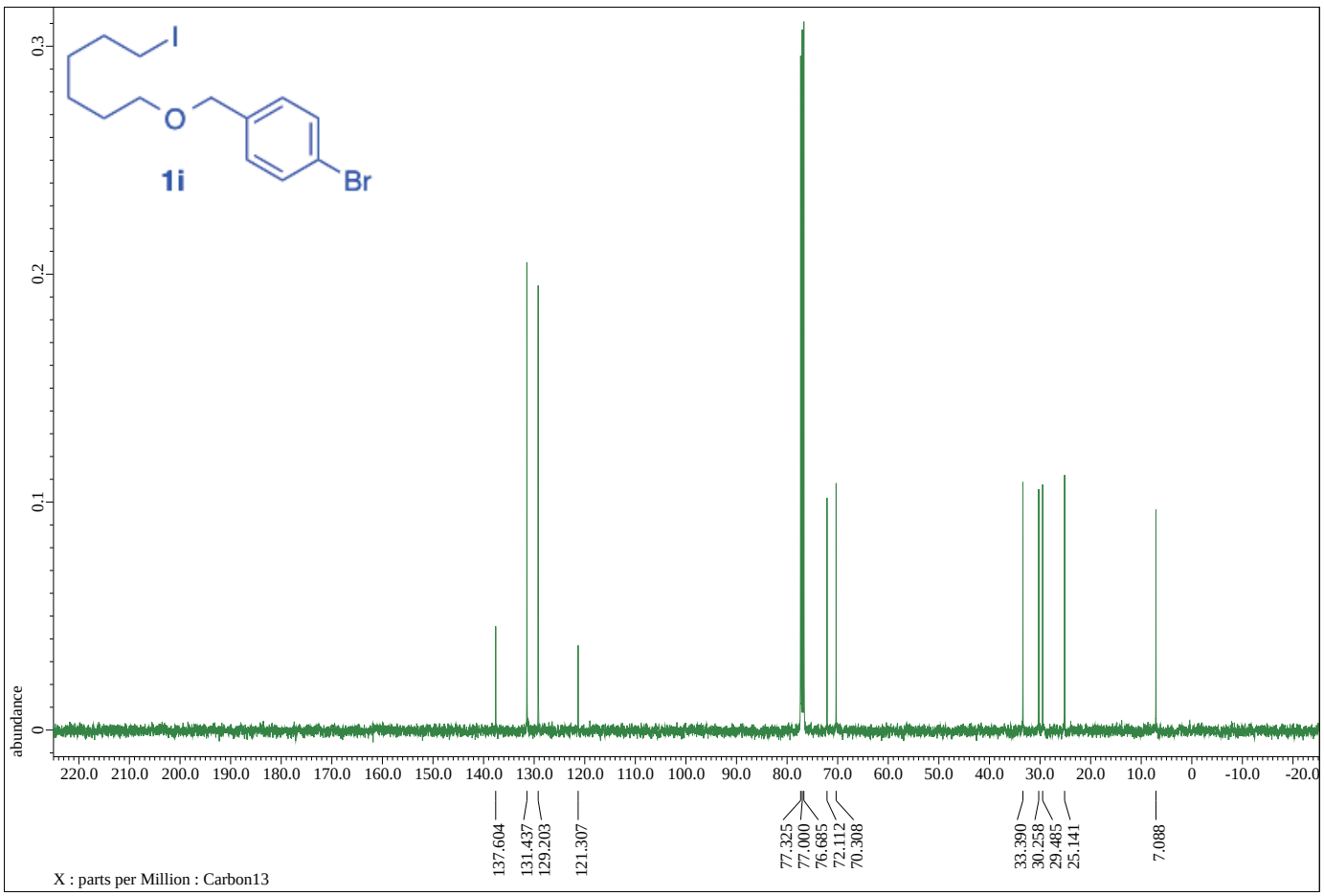
1.602
1.581
1.411
1.404
1.395


1i
I
O
Br
abundance
X : parts per Million : Carbon13
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129.203
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70.308
33.390
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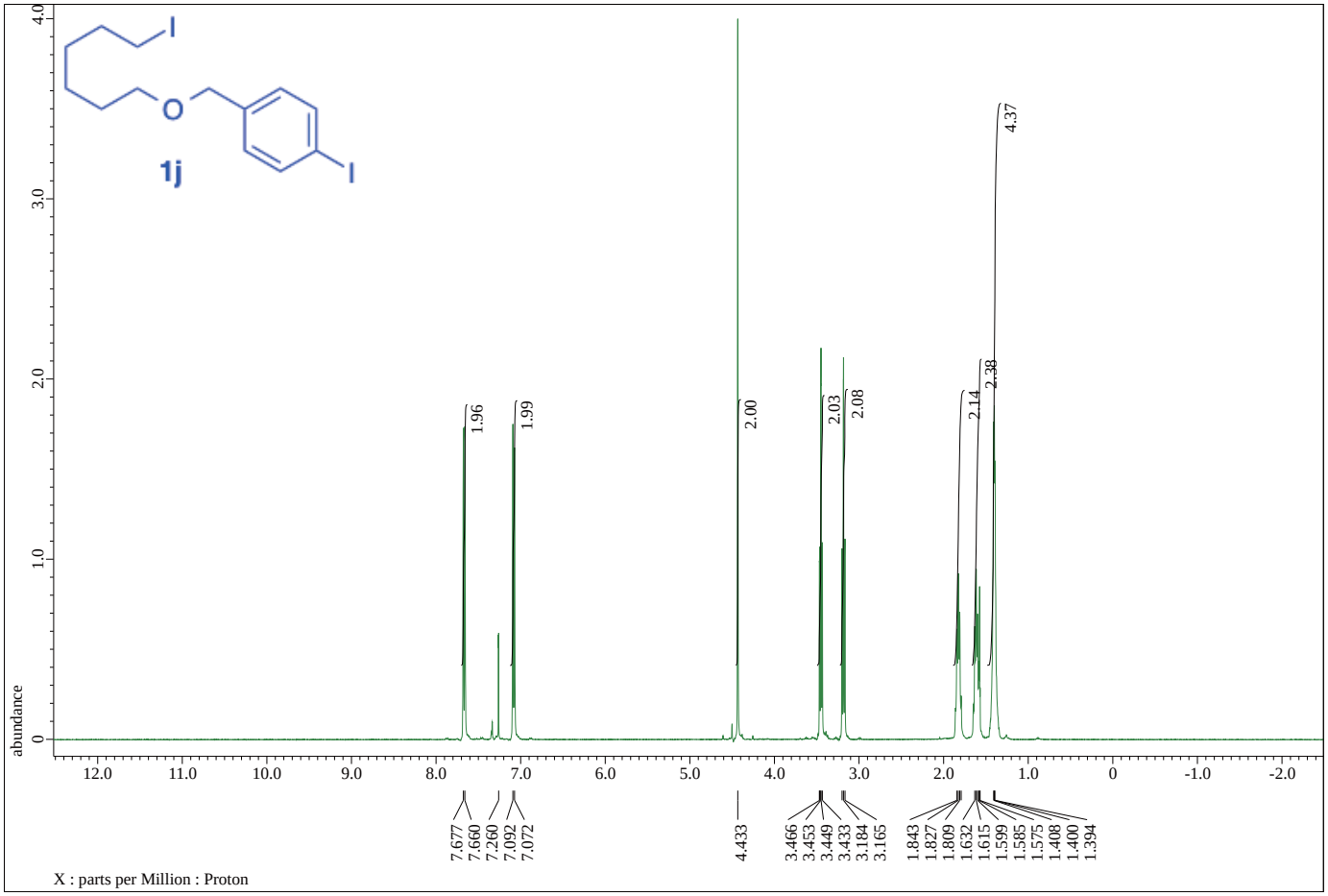
25.141
7.088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2.0
1.0
0
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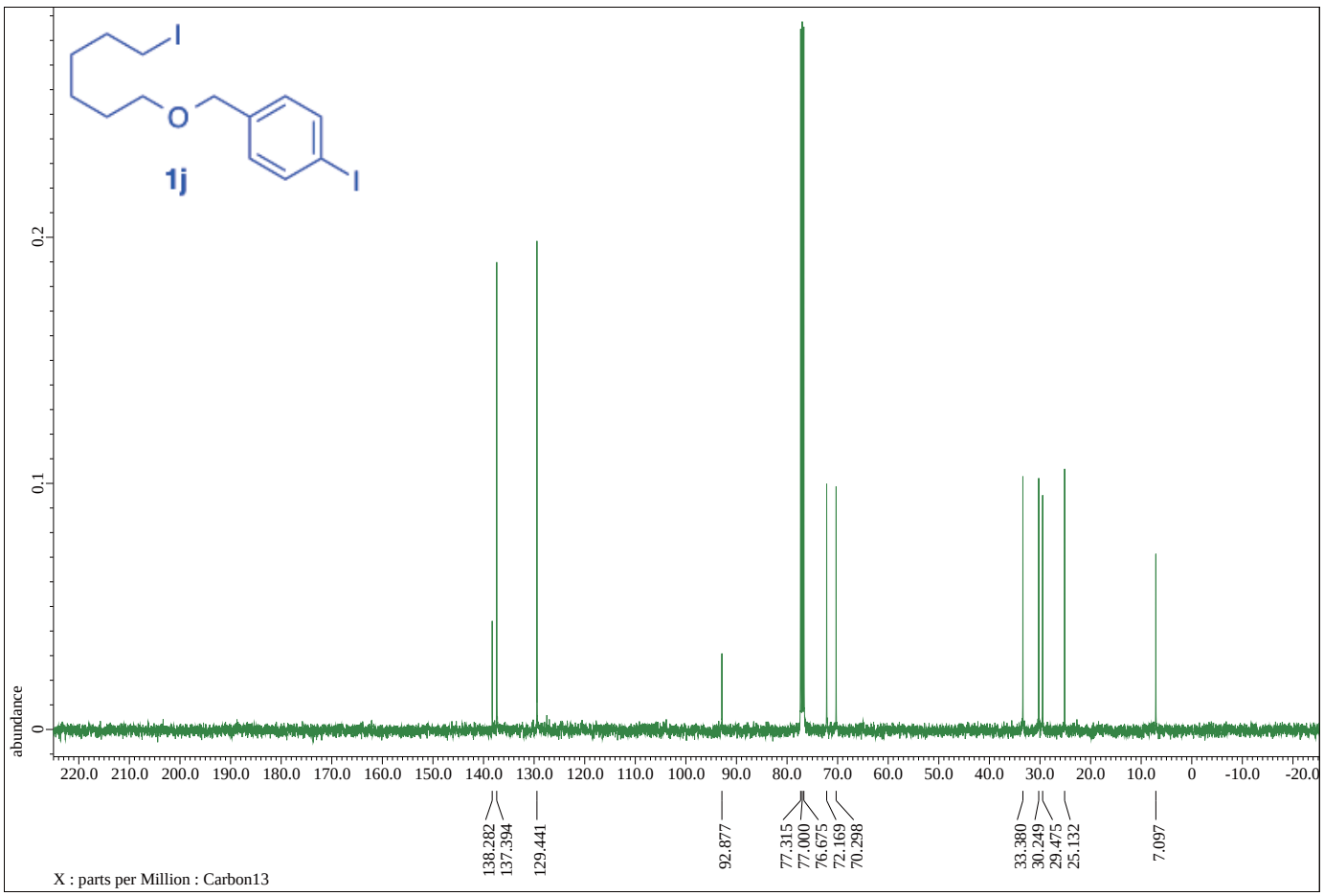
1.96
1.99
2.00
2.03
2.08
2.14
2.38
4.37
7.677 7.660 7.260 7.092 7.072
4.433
3.466 3.453 3.449 3.433 3.184 3.165
1.843 1.827 1.809 1.632 1.615 1.599 1.585 1.575 1.408 1.400 1.394
X : parts per Million : Proton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0.1
0
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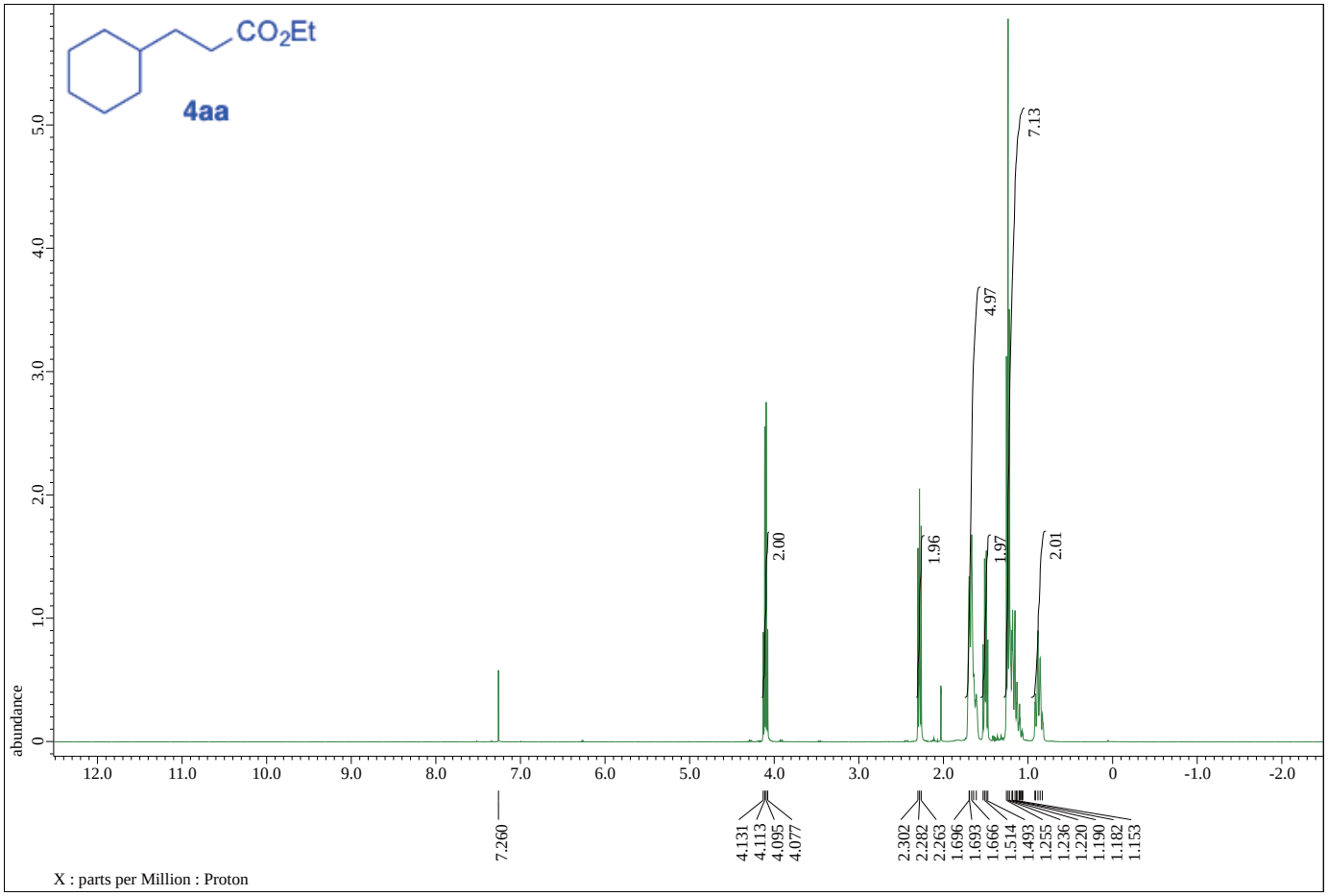
X : parts per Million : Carbon13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3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.13
4.97
2.00
1.96
1.97
2.01
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4.131
4.113
4.095
4.077
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2.282
2.263
1.696
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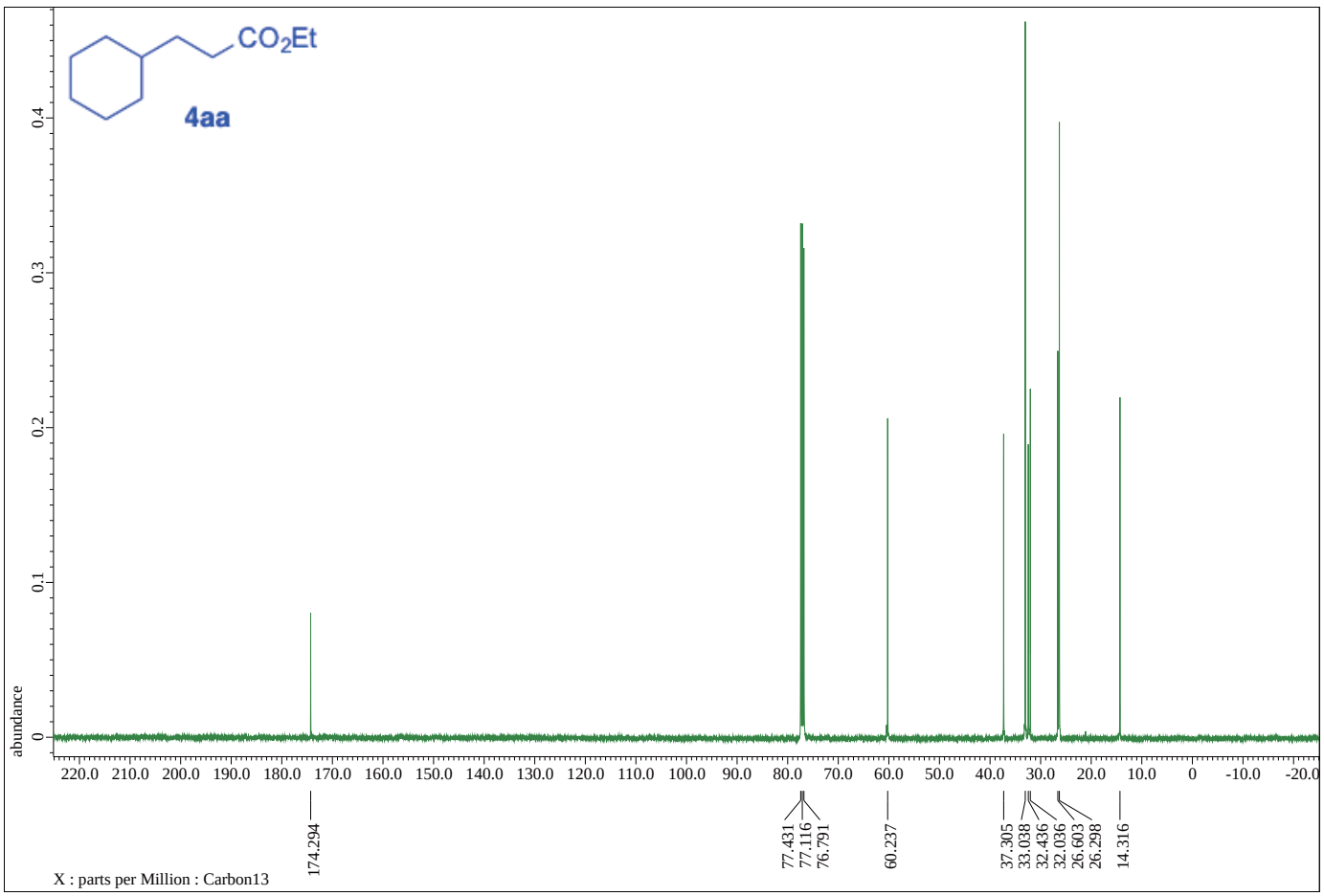
1.190
1.182
1.153
X : parts per Million : Proton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abundance
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0.1
0
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200.0
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180.0
170.0
160.0
150.0
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
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60.237
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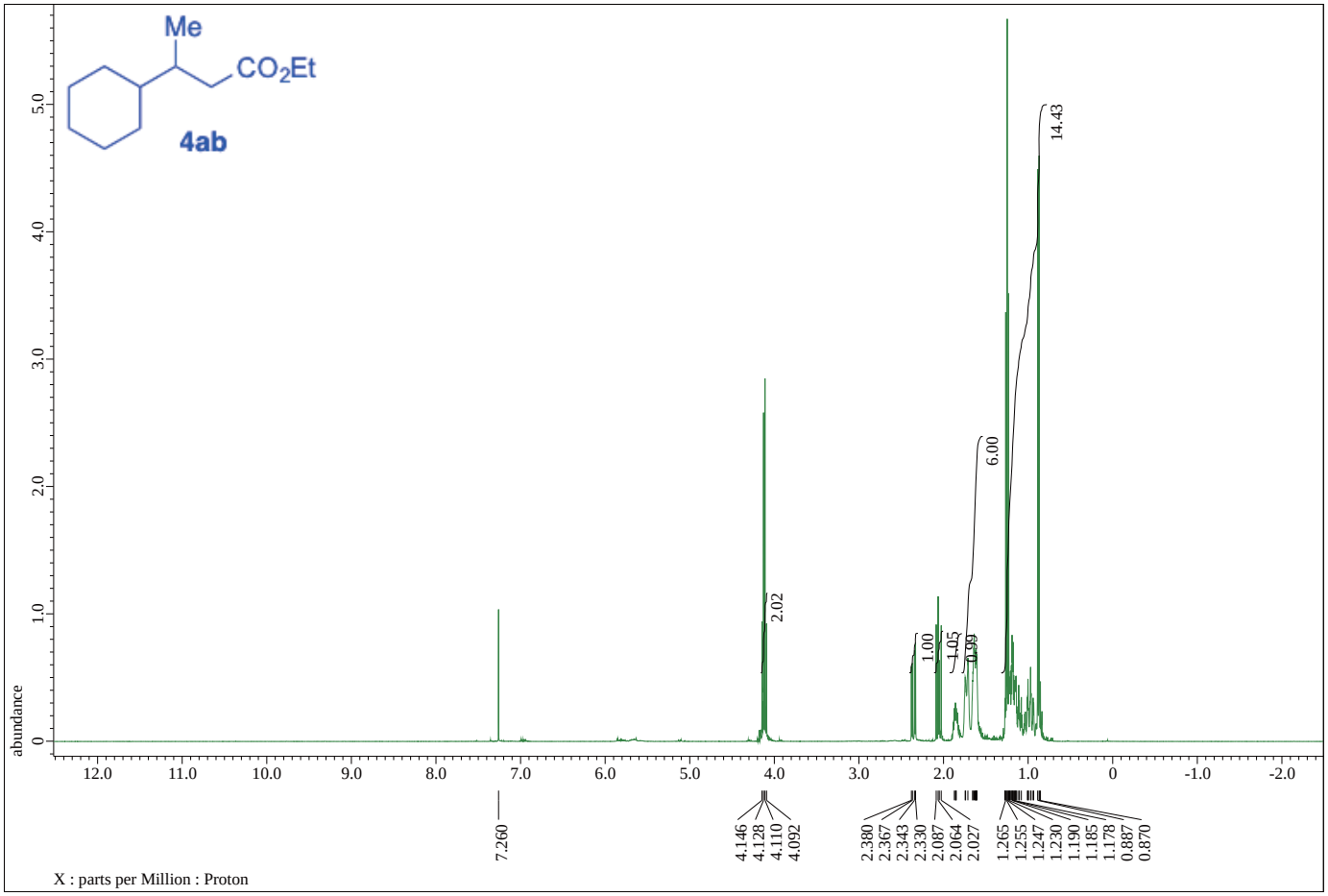
32.436
32.036
26.603
26.298
14.316
X : parts per Million : Carbon13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CO2Et
4ab
abundance
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3.0
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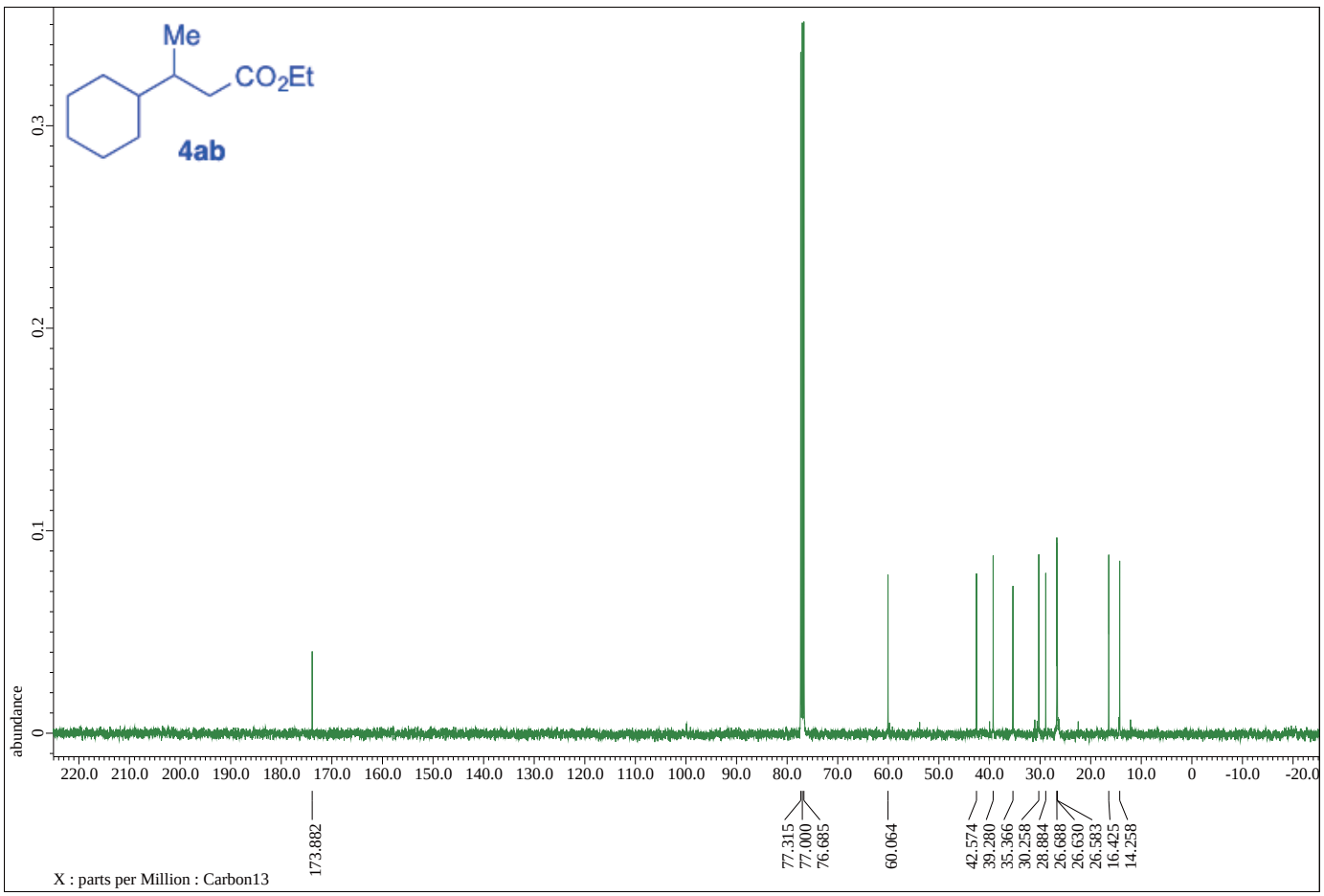
1.0
0
14.43
6.00
2.02
1.00
1.05
0.99
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.260
4.146 4.128 4.110 4.092
2.380 2.367 2.343 2.330 2.087 2.064 2.027
1.265 1.255 1.247 1.230 1.190 1.185 1.178 0.887 0.870
X : parts per Million : Proton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CO2Et
4ab
abundance
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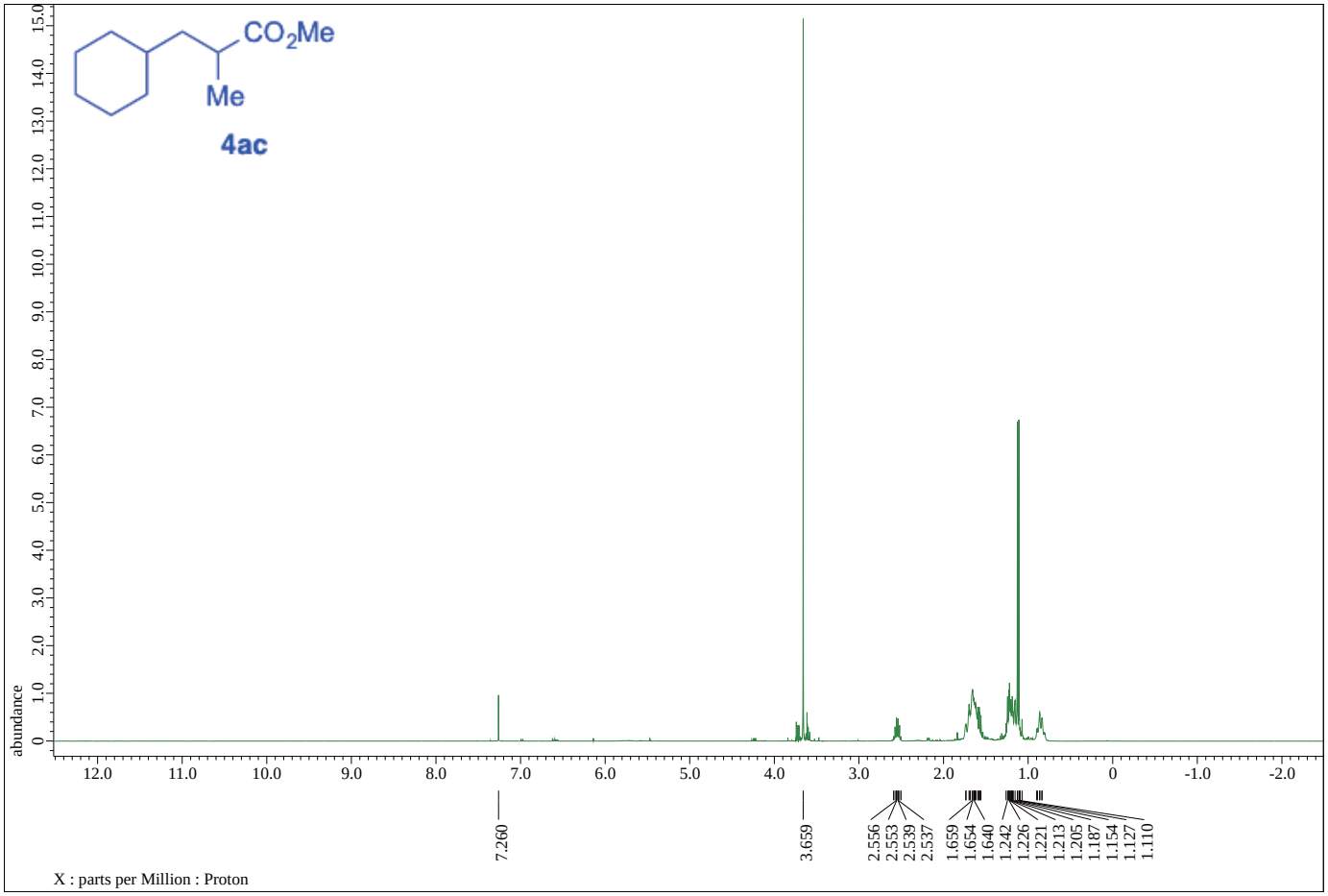
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.882
77.315 77.000 76.685
60.064
42.574 39.280 35.366 30.258 28.884 26.688 26.630 26.583 16.425 14.258
X : parts per Million : Carbon13


CO2Me
Me
4ac
abundance
X : parts per Million : Proton
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2.553
2.539
2.537
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1.213
1.205
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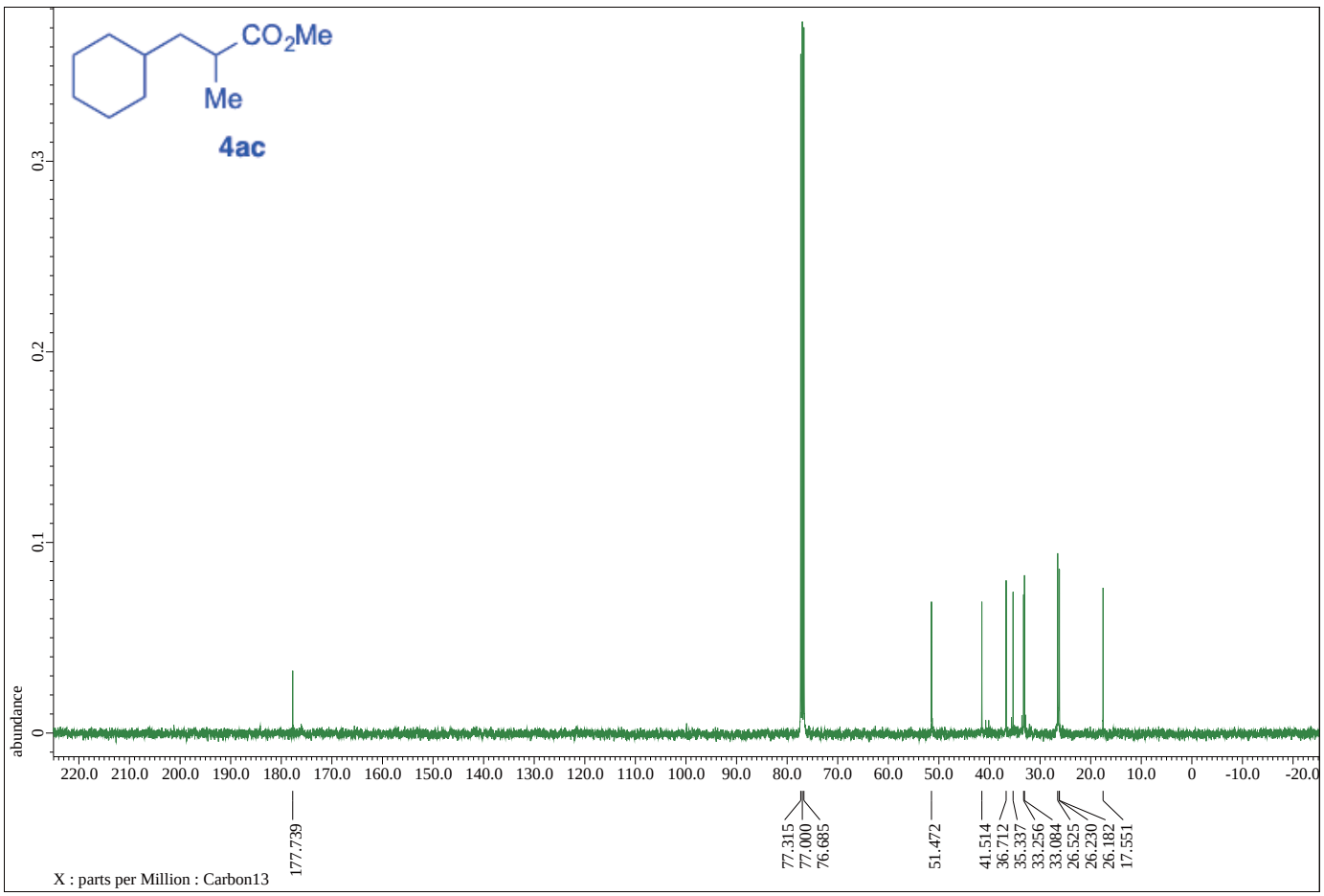
1.154
1.127
1.110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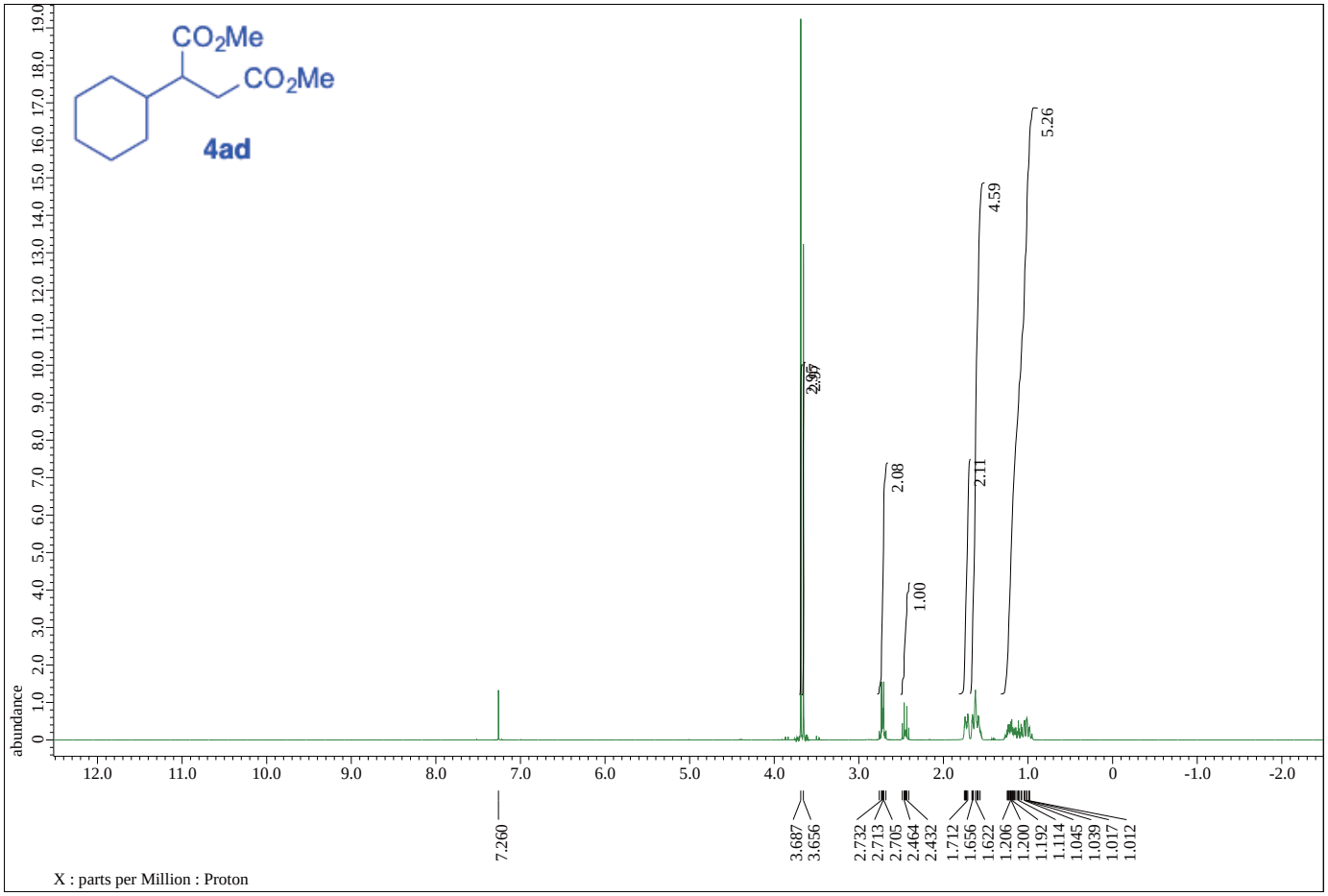
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CO2Me
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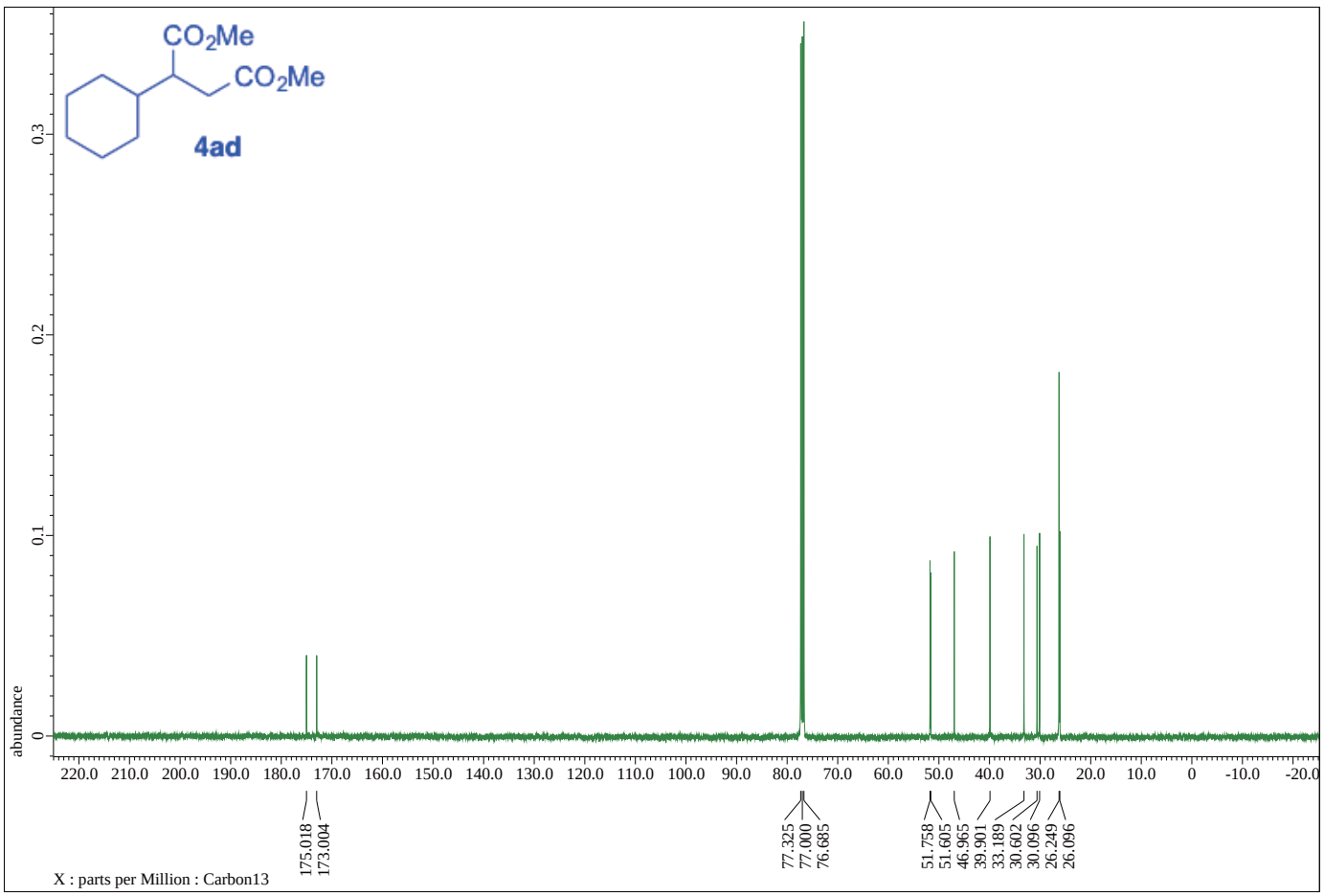
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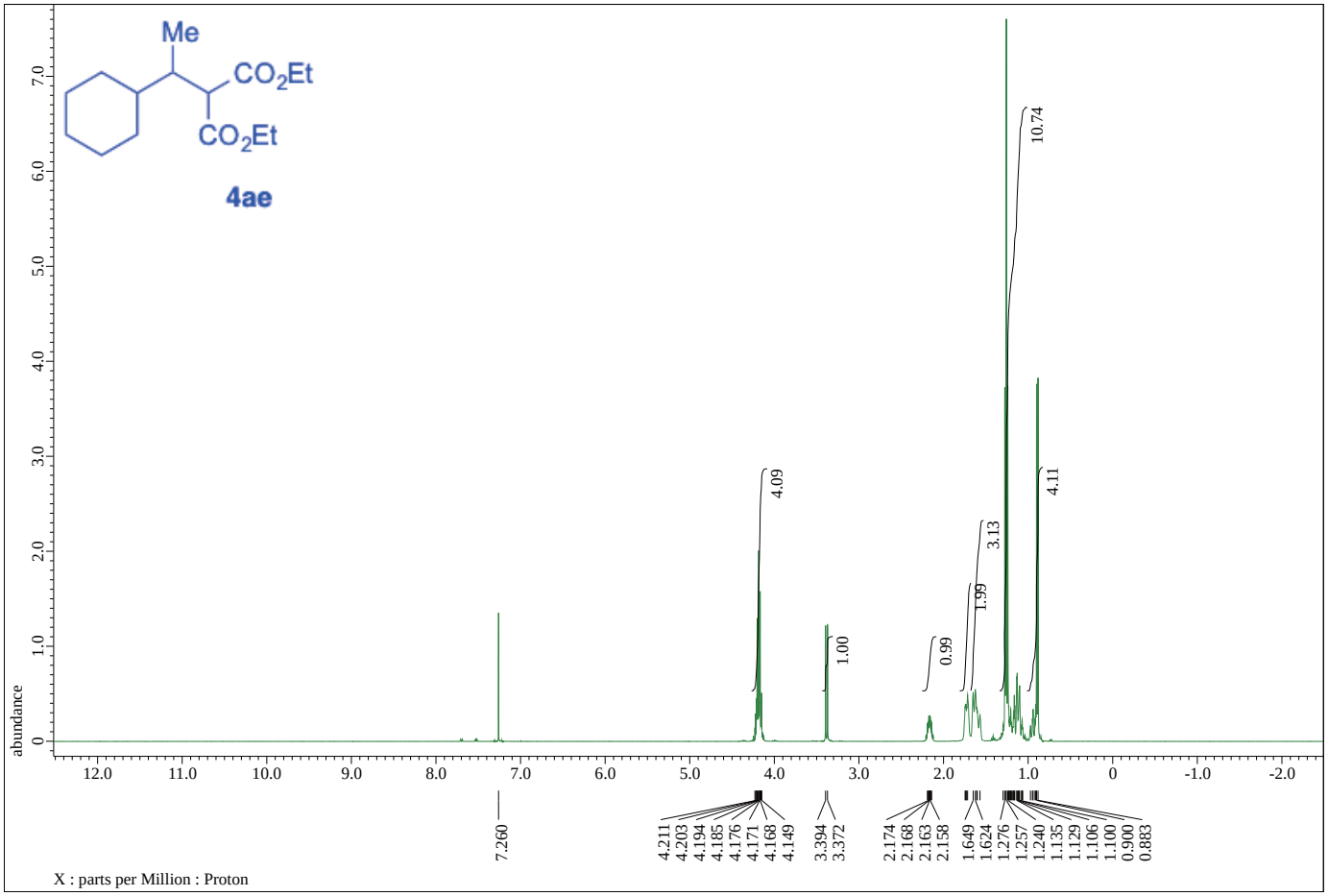
26.096
X : parts per Million : Carbon13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CO2Et
CO2Et
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abundance
X : parts per Million : Proton
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4.11
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4.185
4.176
4.171
4.168
4.149
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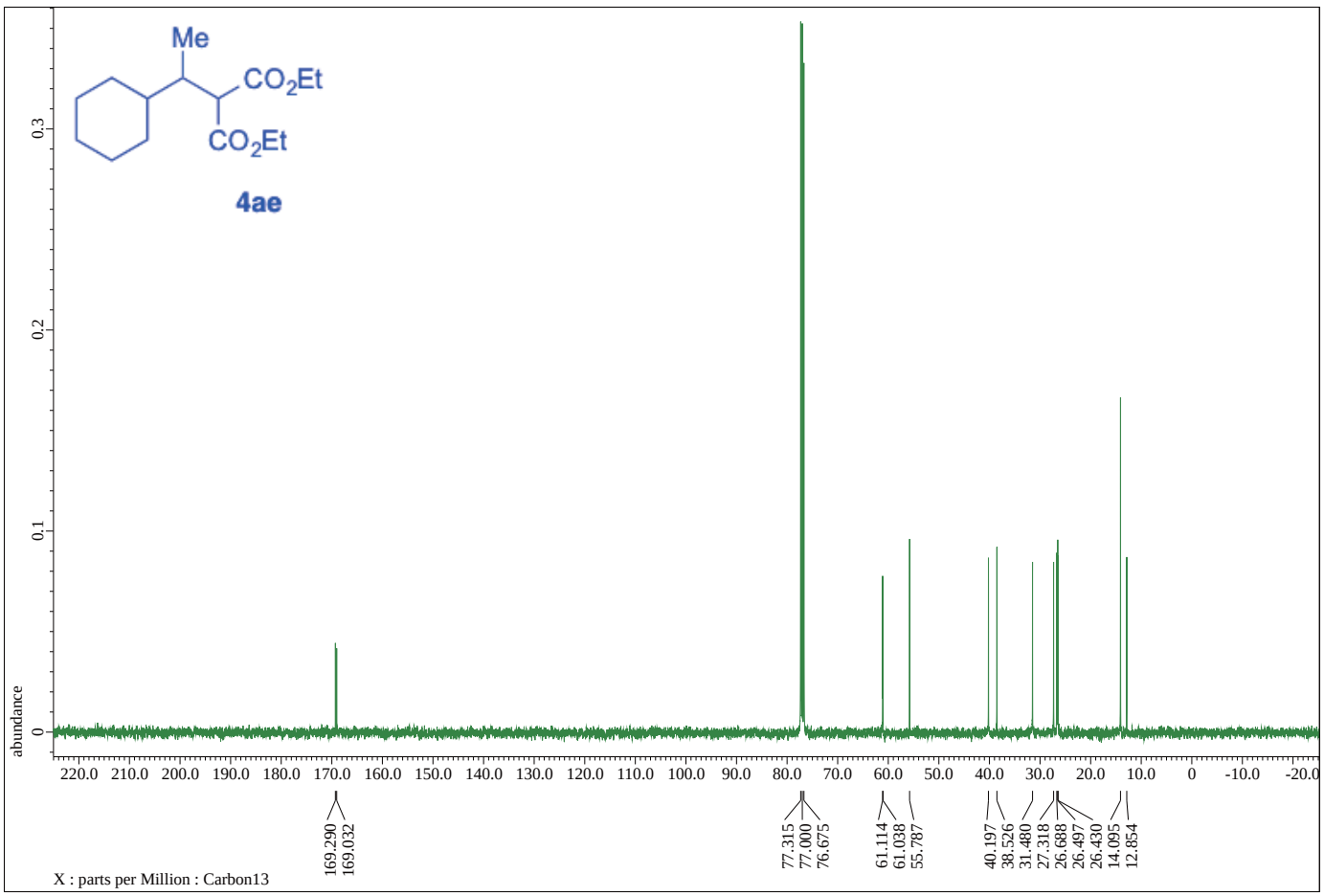
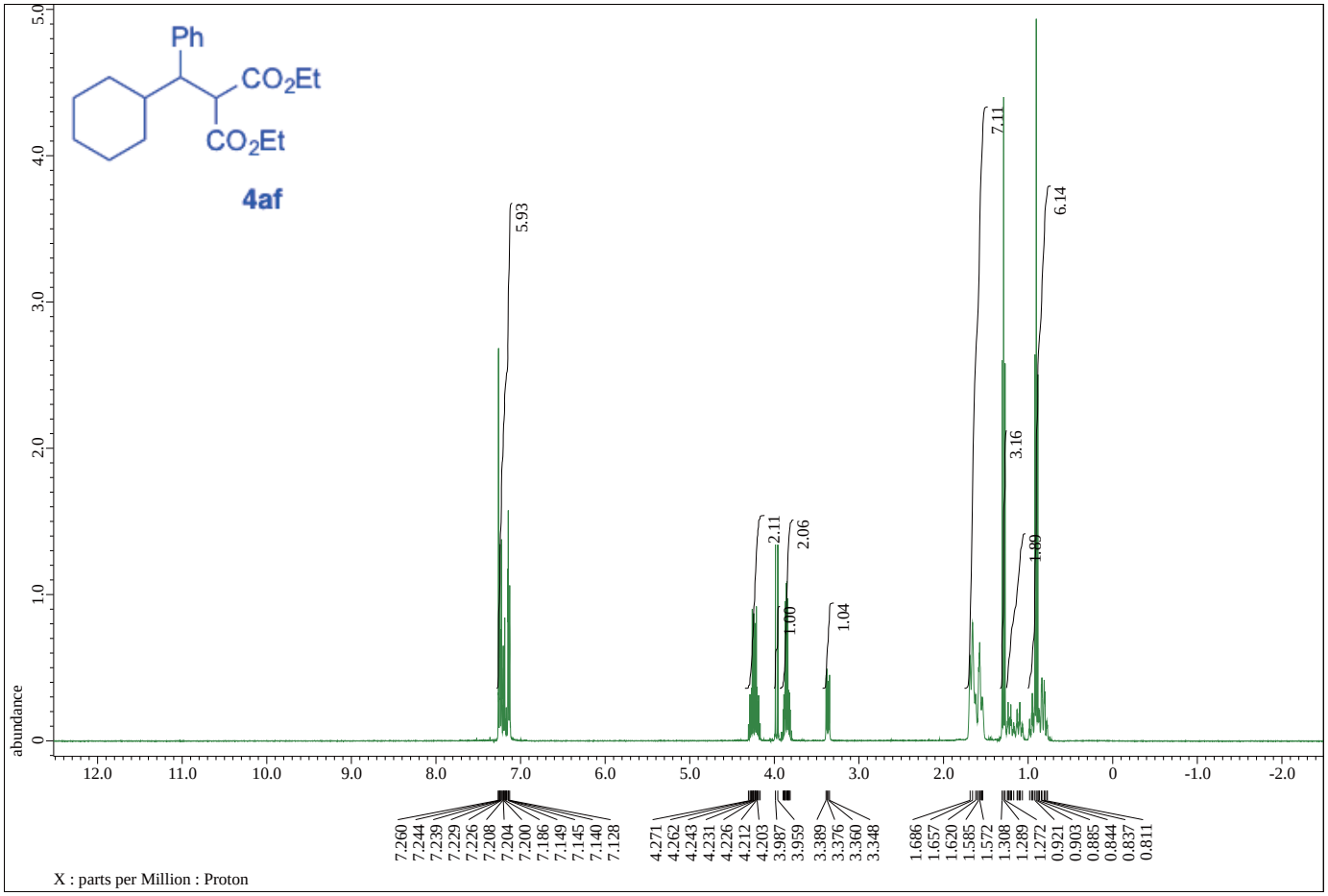
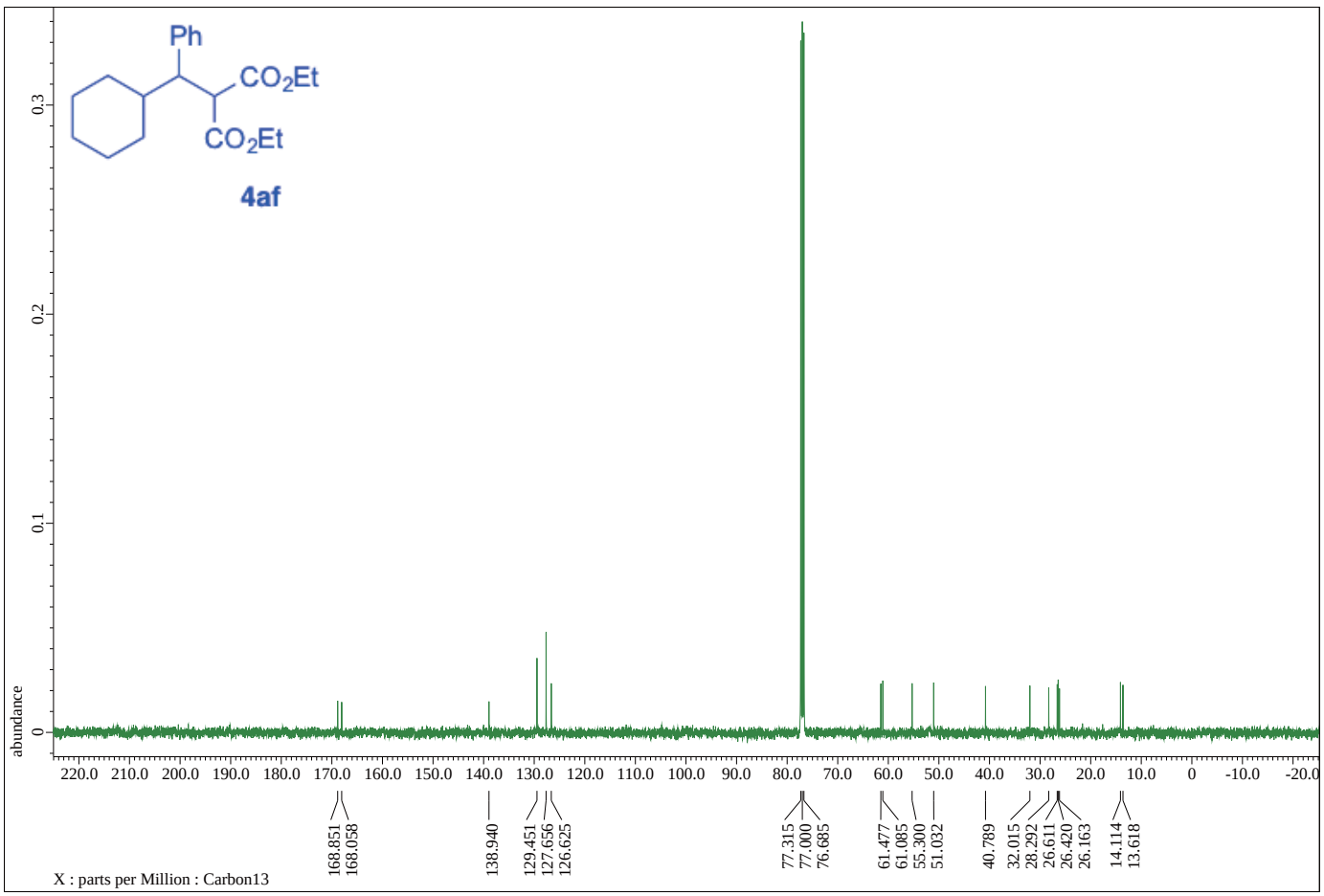
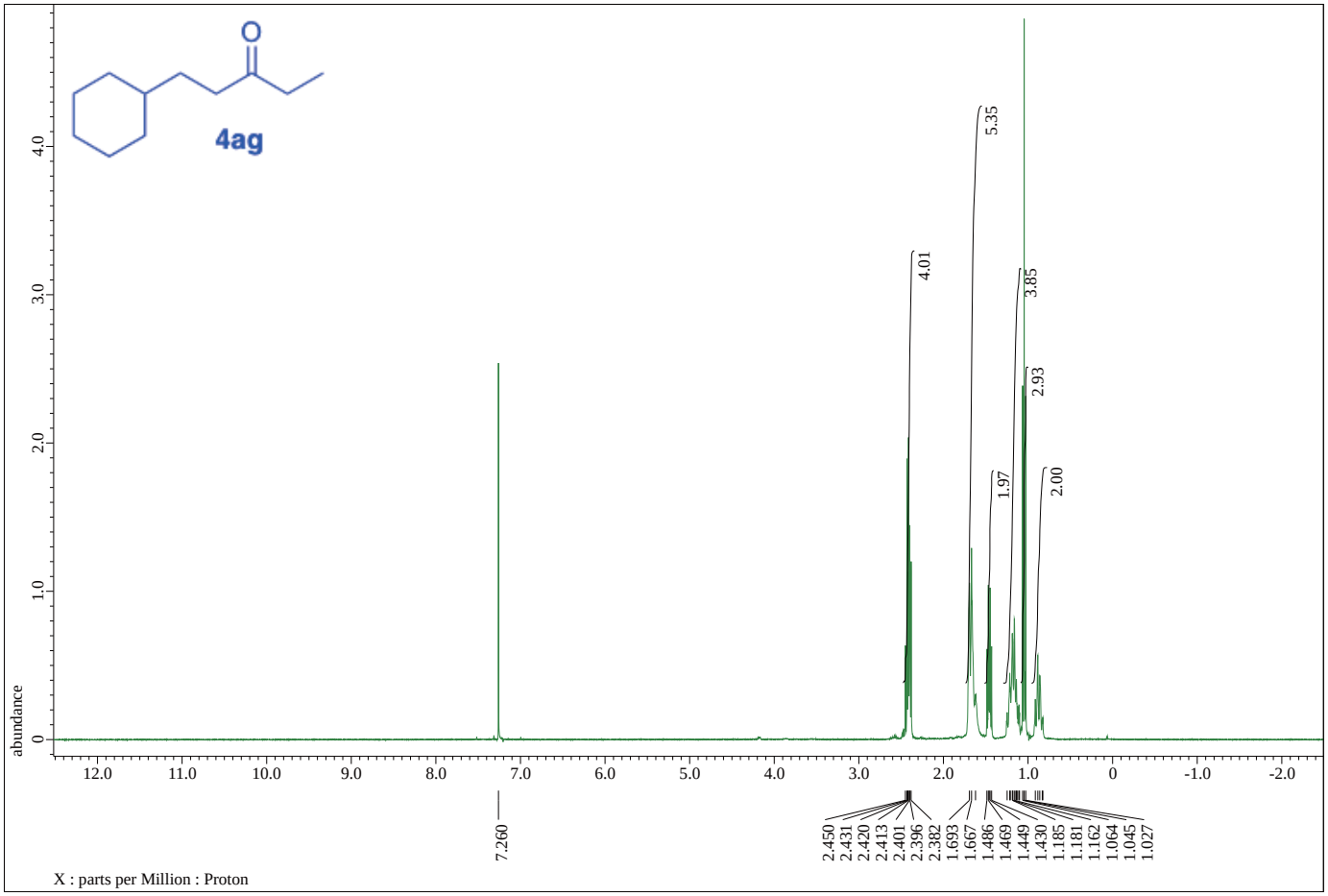
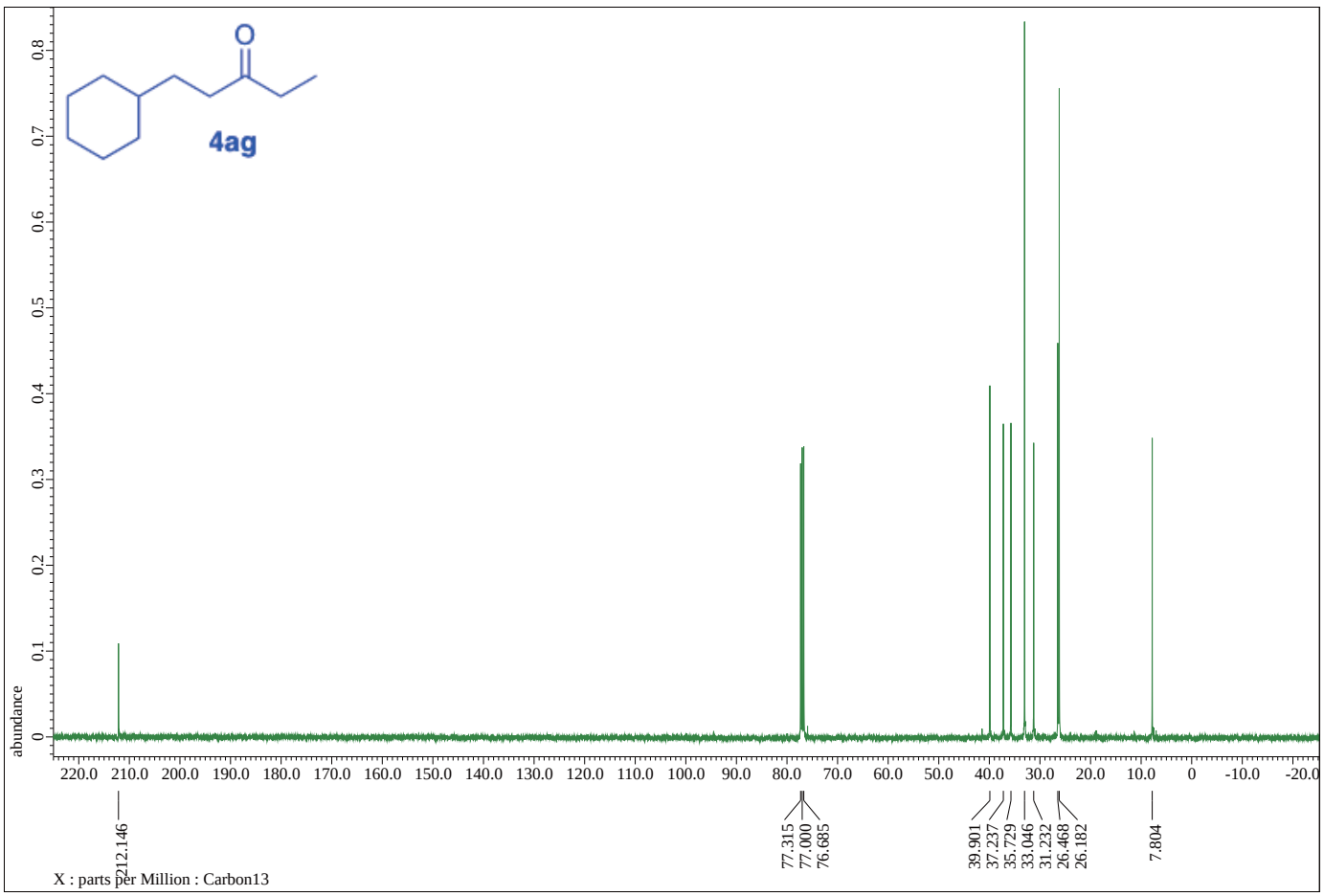
0.900
0.883

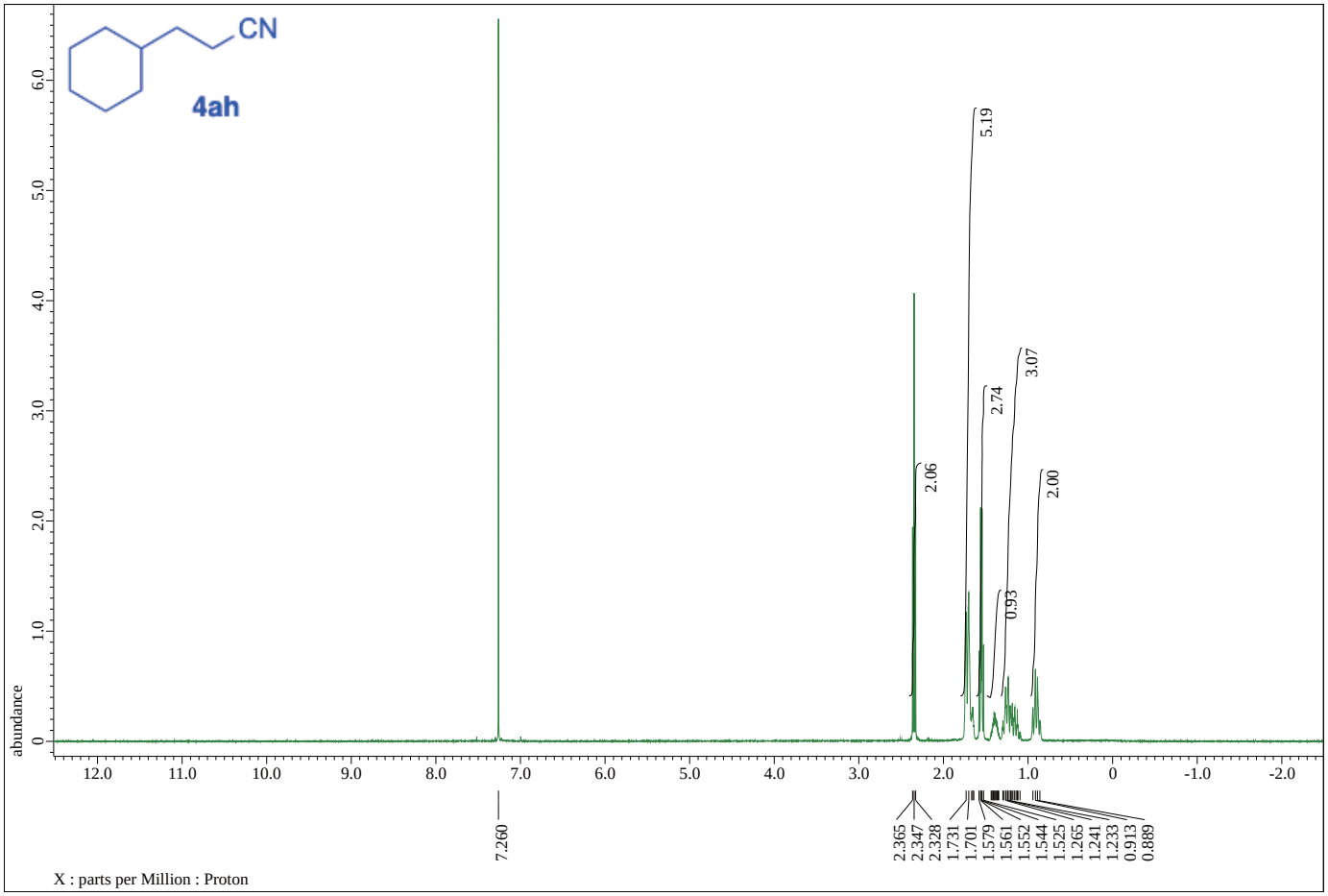

Me
CO2Et
CO2Et
4ae
abundance
X : parts per Million : Carbon13
169.290
169.032
77.315
77.000
76.675
61.114
61.038
55.787
40.197
38.526
31.480
27.318
26.688
26.497
26.430
14.095
12.854

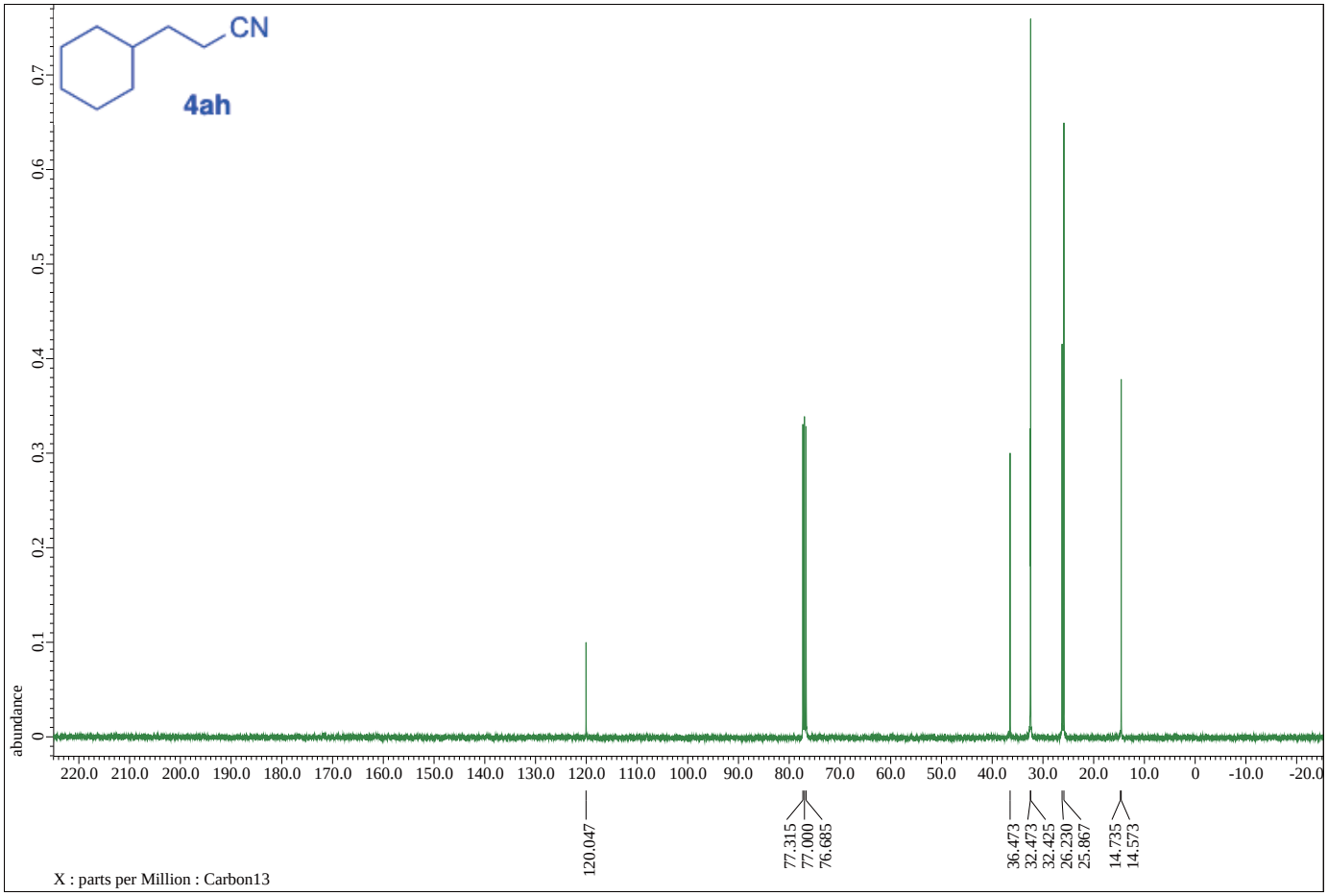

Ph
CO2Et
CO2Et
4af
abundance
X : parts per Million : Proton
5.93
2.11
2.06
1.04
1.00
7.11
6.14
3.16
1.89

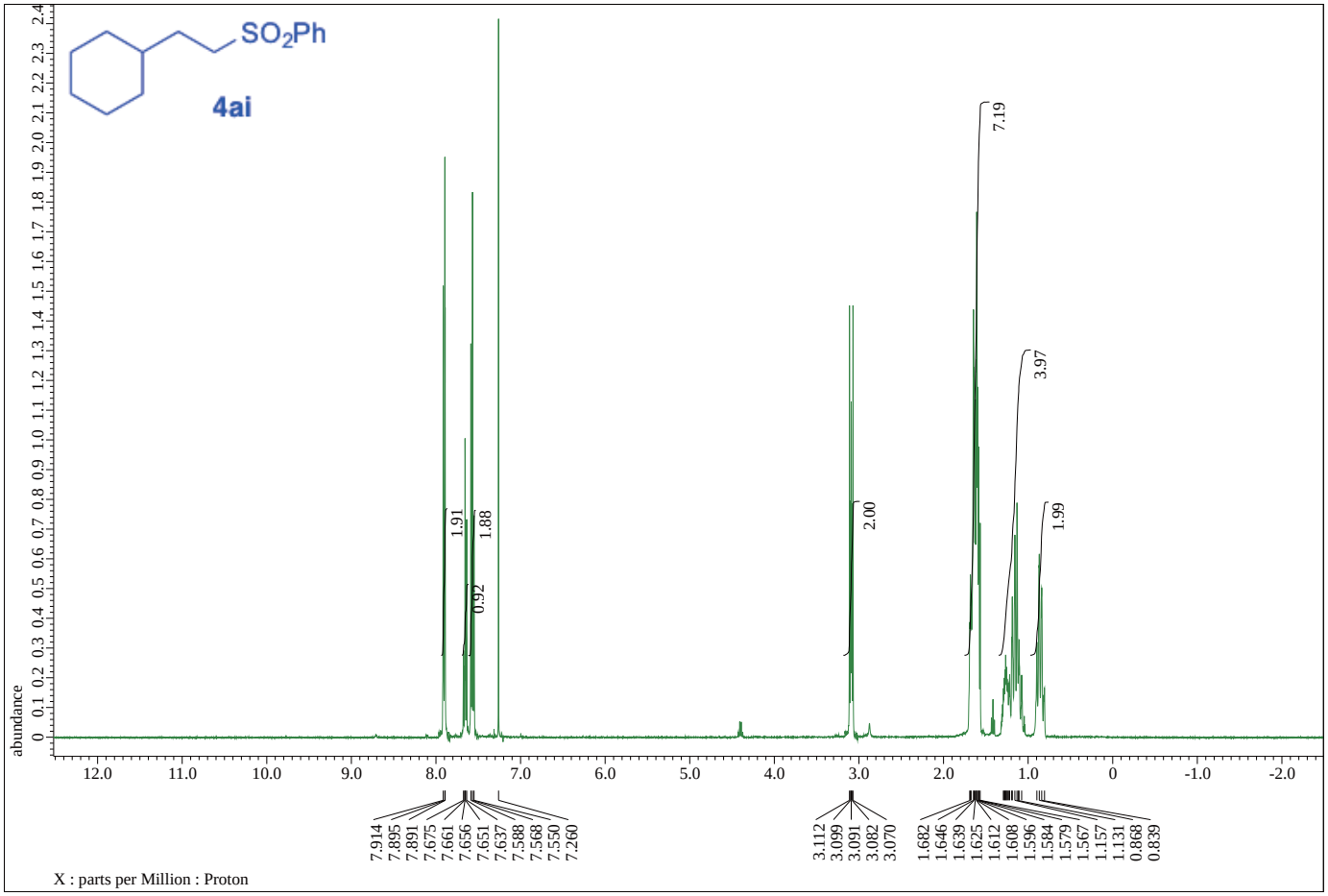

Ph
CO2Et
CO2Et
4af
abundance
X : parts per Million : Carbon13

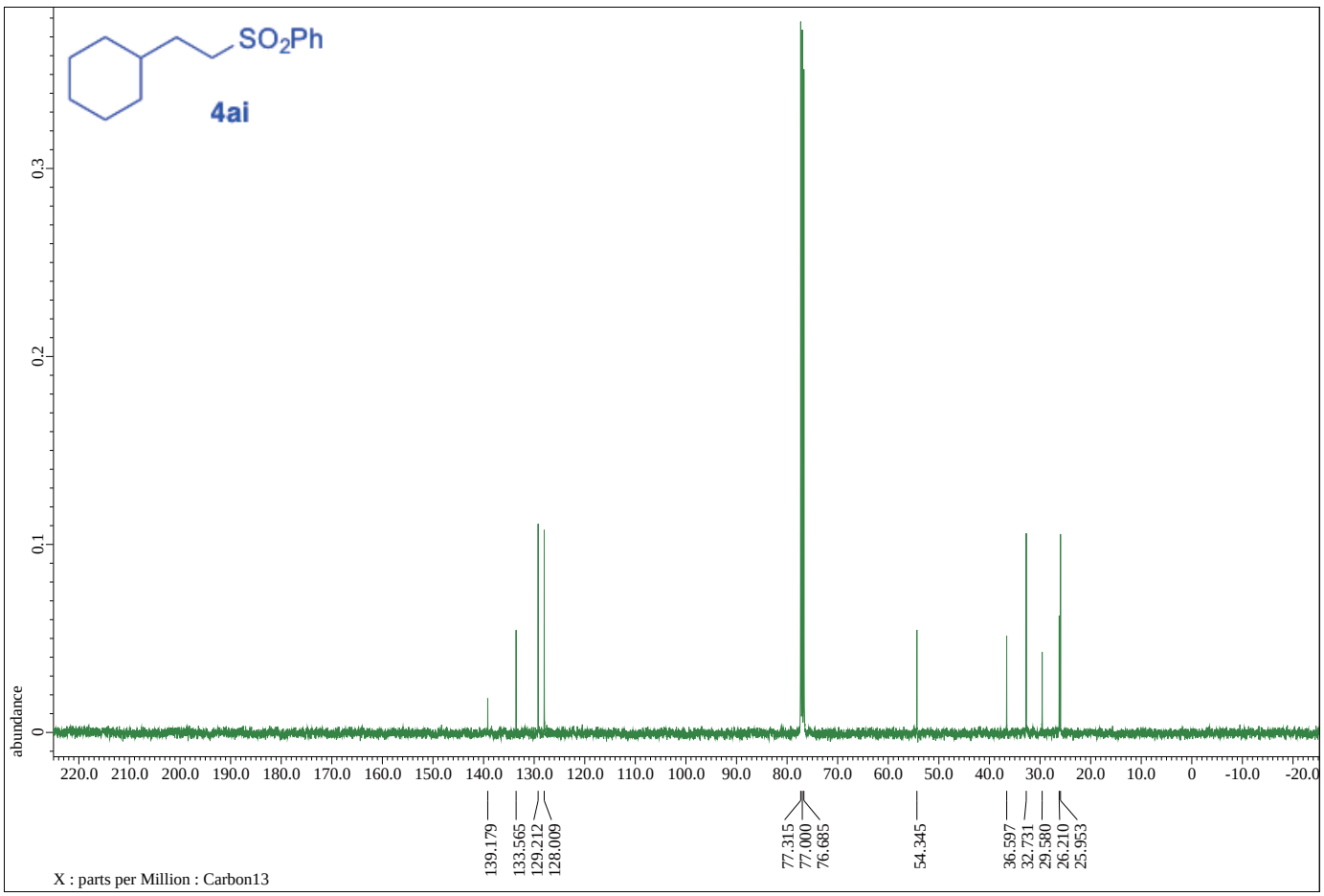

4ag
abundance
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
4.01
5.35
3.85
2.93
1.97
2.00
7.260
2.450
2.431
2.420
2.413
2.401
2.396
2.382
1.693
1.667
1.486
1.469
1.449
1.430
1.185
1.181
1.162
1.064
1.045
1.027
X : parts per Million : Proton

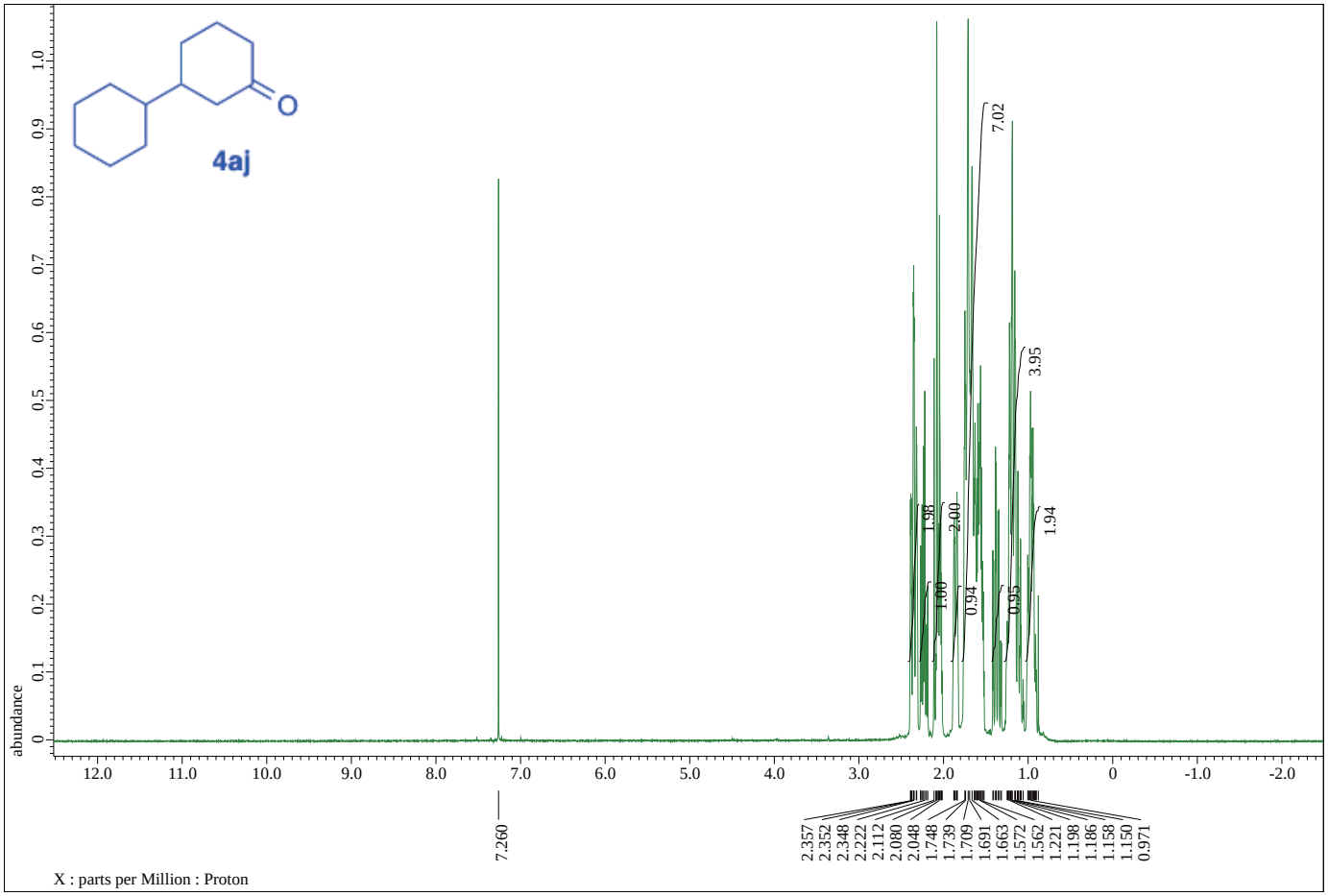

4ag
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
212.146
77.315
77.000
76.685
39.901
37.237
35.729
33.046
31.232
26.468
26.182
7.804
X : parts per Million : Carbon13

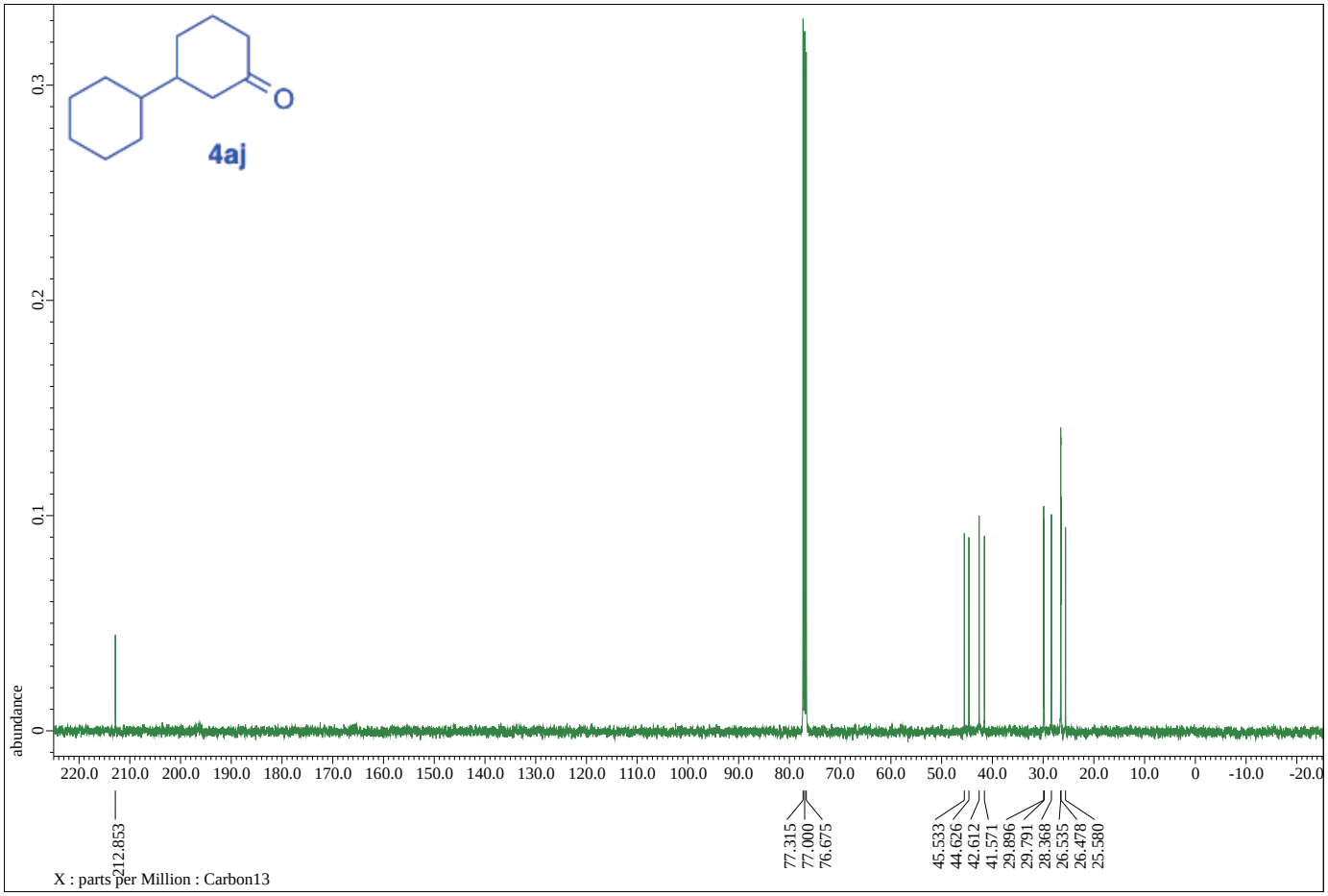

CN
4ah
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
5.19
3.07
2.74
2.06
2.00
0.93
7.260
2.365
2.347
2.328
1.731
1.701
1.579
1.561
1.552
1.544
1.525
1.265
1.241
1.233
0.913
0.889
X : parts per Million : Proton

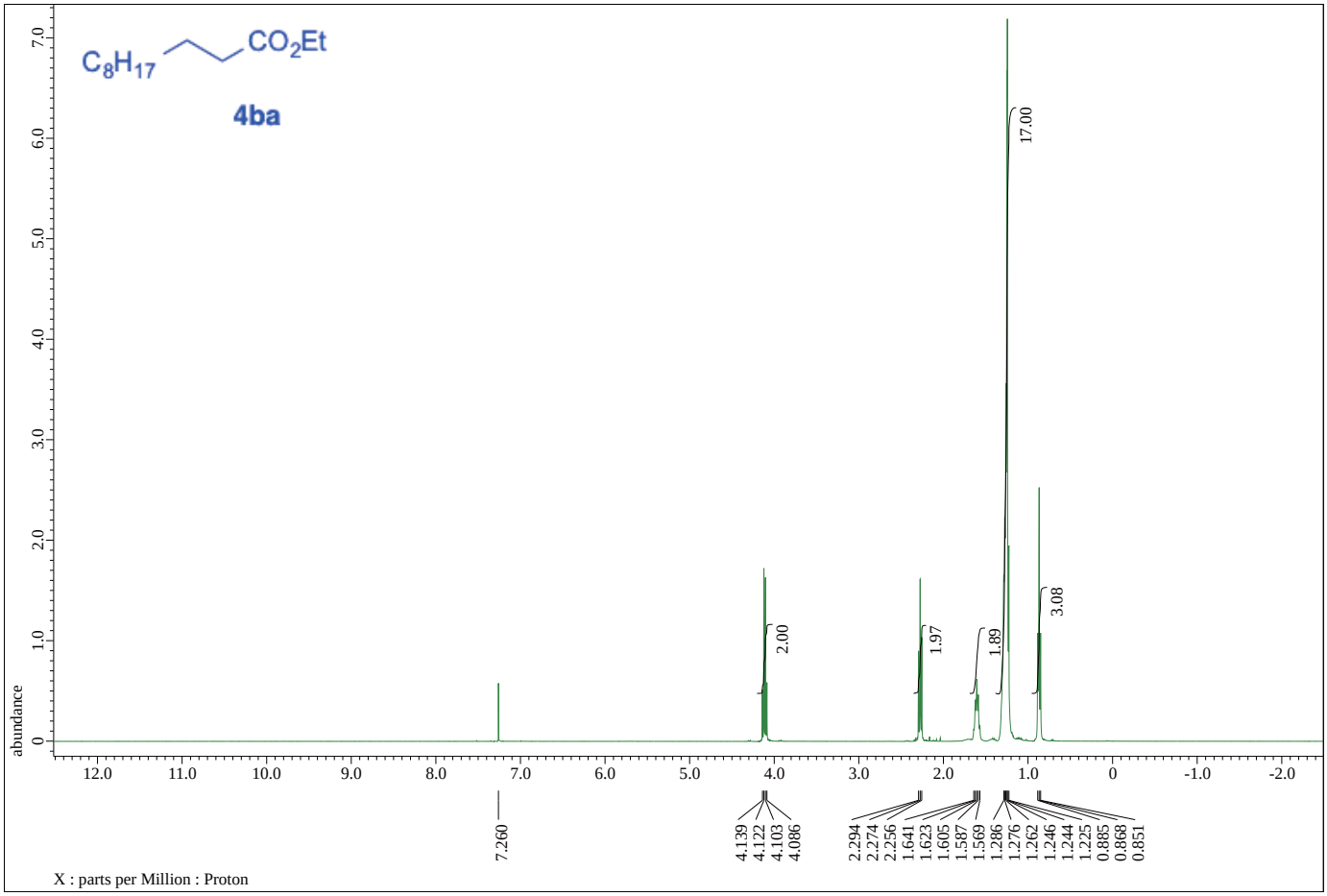

CN
4ah
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
120.047
77.315
77.000
76.685
36.473
32.473
32.425
26.230
25.867
14.735
14.573
X : parts per Million : Carbon13

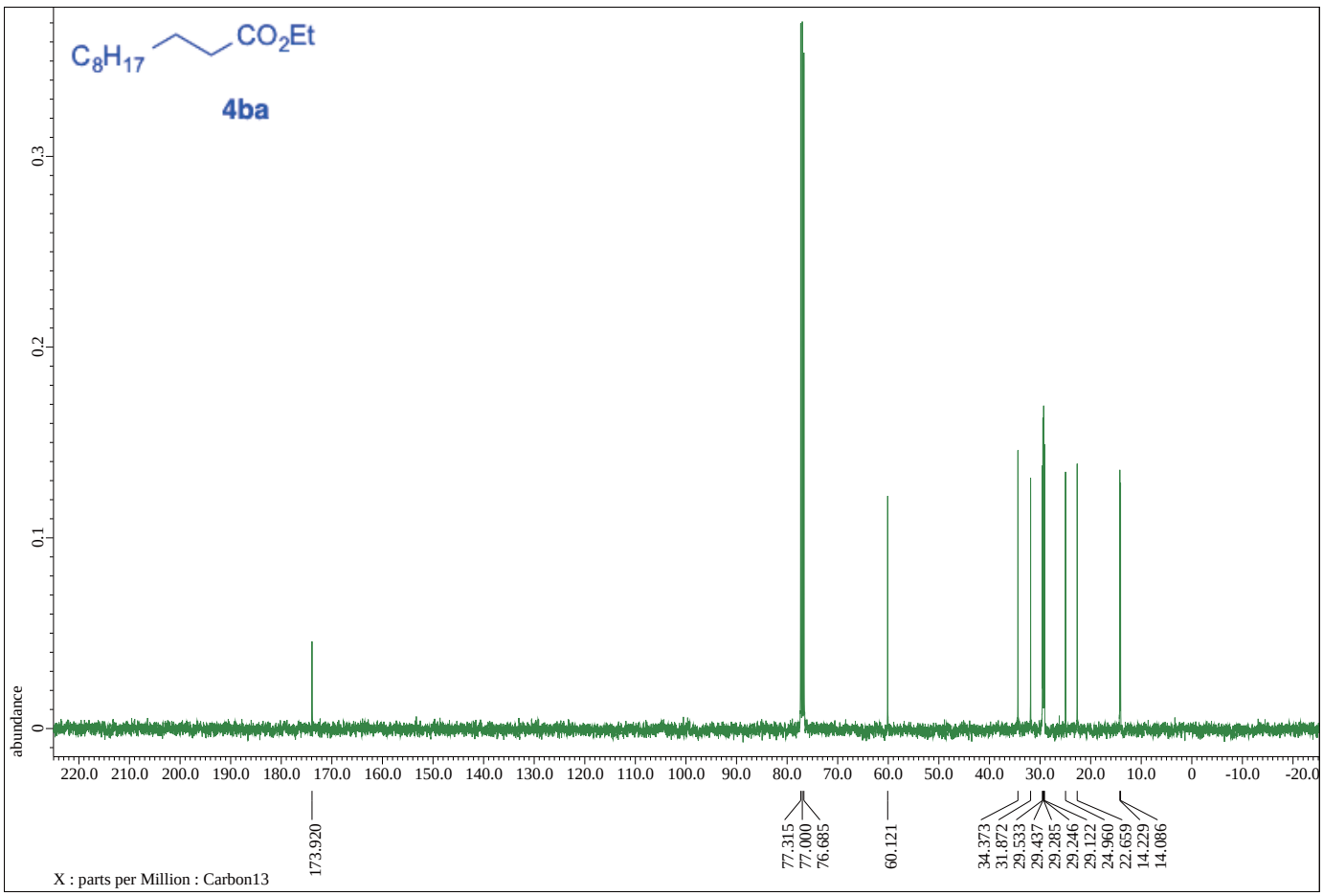

SO2Ph
4ai
abundance
7.19
3.97
1.99
2.00
1.91
1.88
0.92
7.914
7.895
7.891
7.675
7.661
7.656
7.651
7.637
7.588
7.568
7.550
7.260
3.112
3.099
3.091
3.082
3.070
1.682
1.646
1.639
1.625
1.612
1.608
1.596
1.584
1.579
1.567
1.157
1.131
0.868
0.839
X : parts per Million : Proton

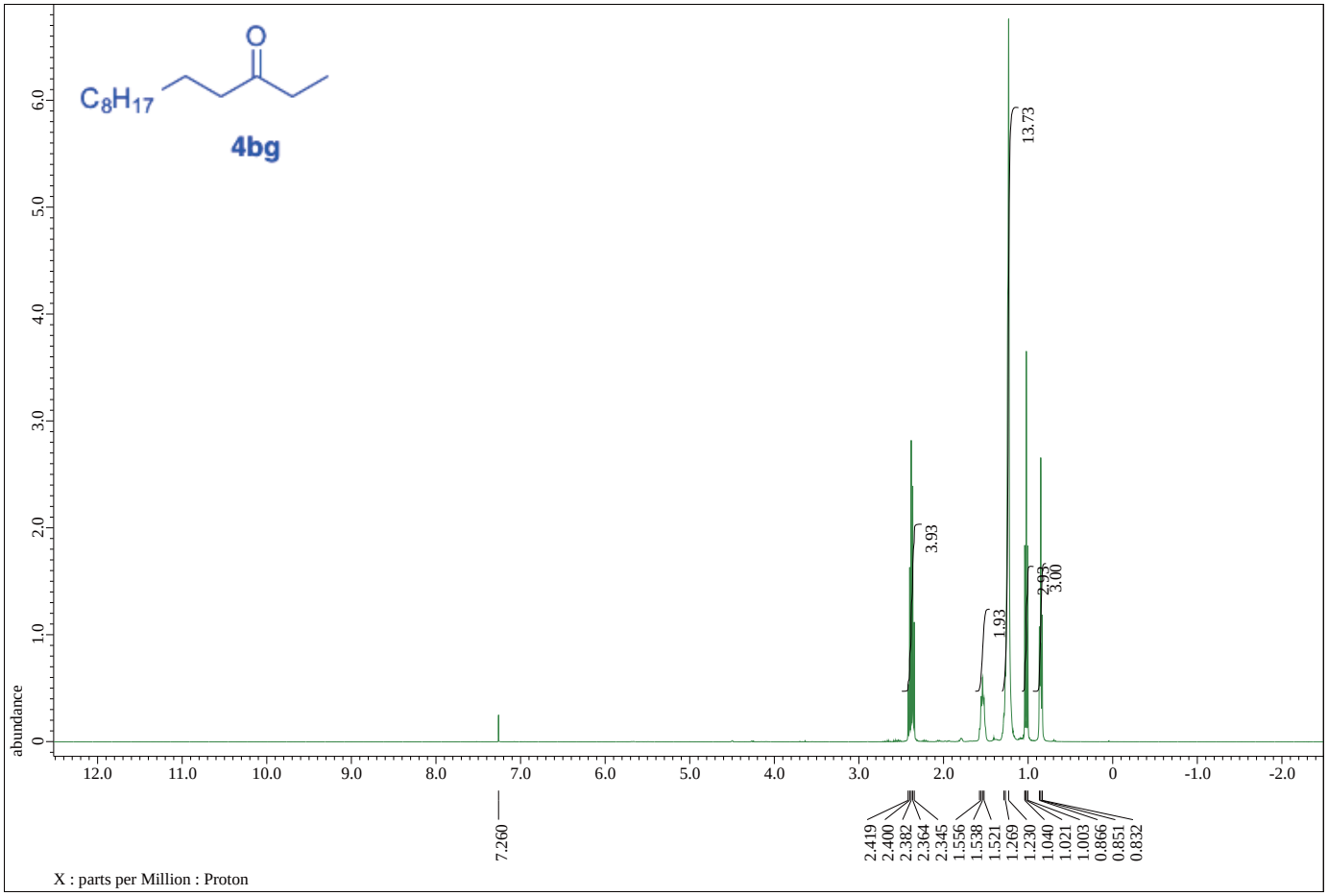

SO2Ph
4ai
abundance
139.179
133.565
129.212
128.009
77.315
77.000
76.685
54.345
36.597
32.731
29.580
26.210
25.953
X : parts per Million : Carbon13

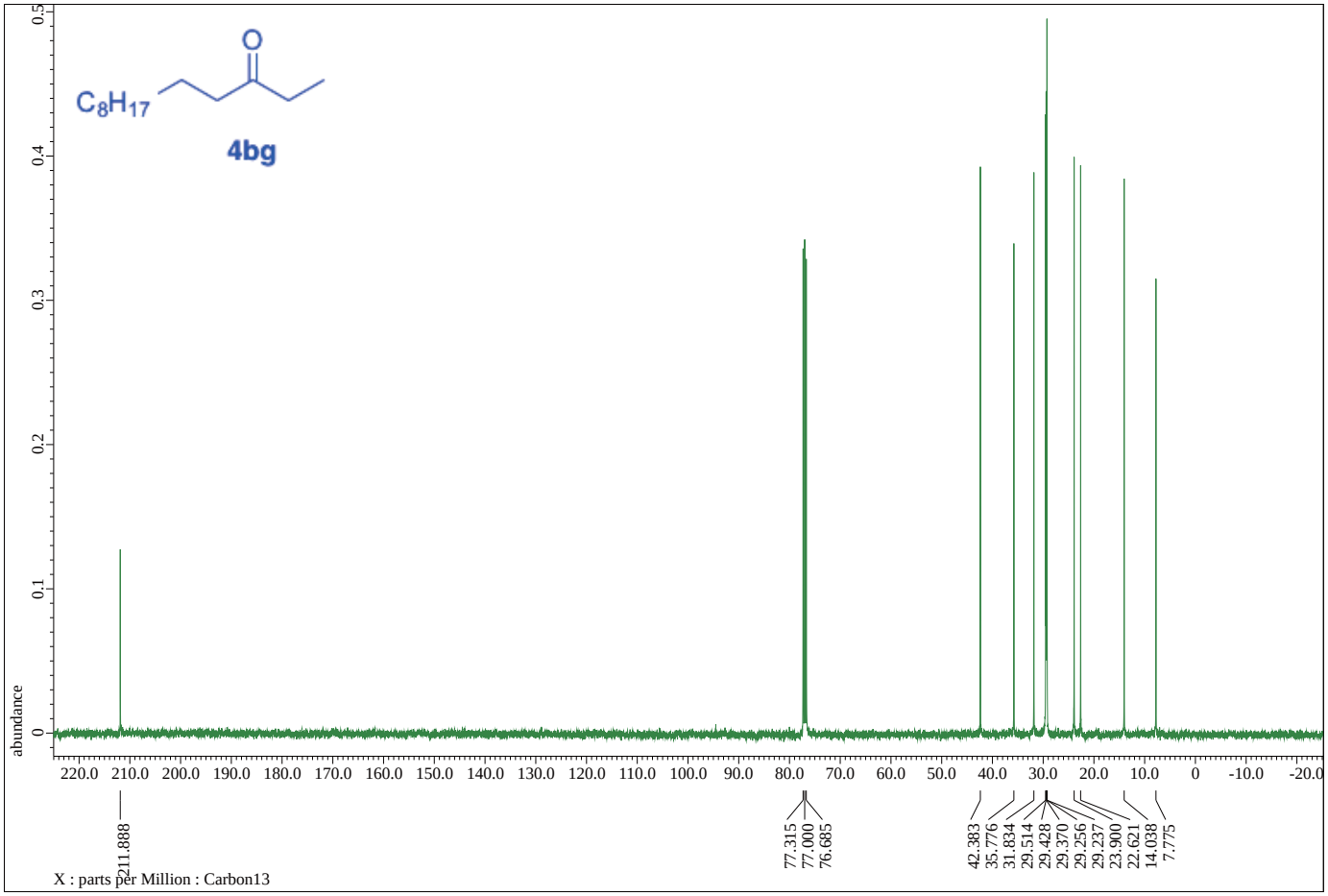

4aj
abundance
7.02
3.95
1.94
2.00
1.98
1.06
0.94
0.95
7.260
2.357
2.352
2.348
2.222
2.112
2.080
2.048
1.748
1.739
1.709
1.691
1.663
1.572
1.562
1.221
1.198
1.186
1.158
1.150
0.971
X : parts per Million : Proton

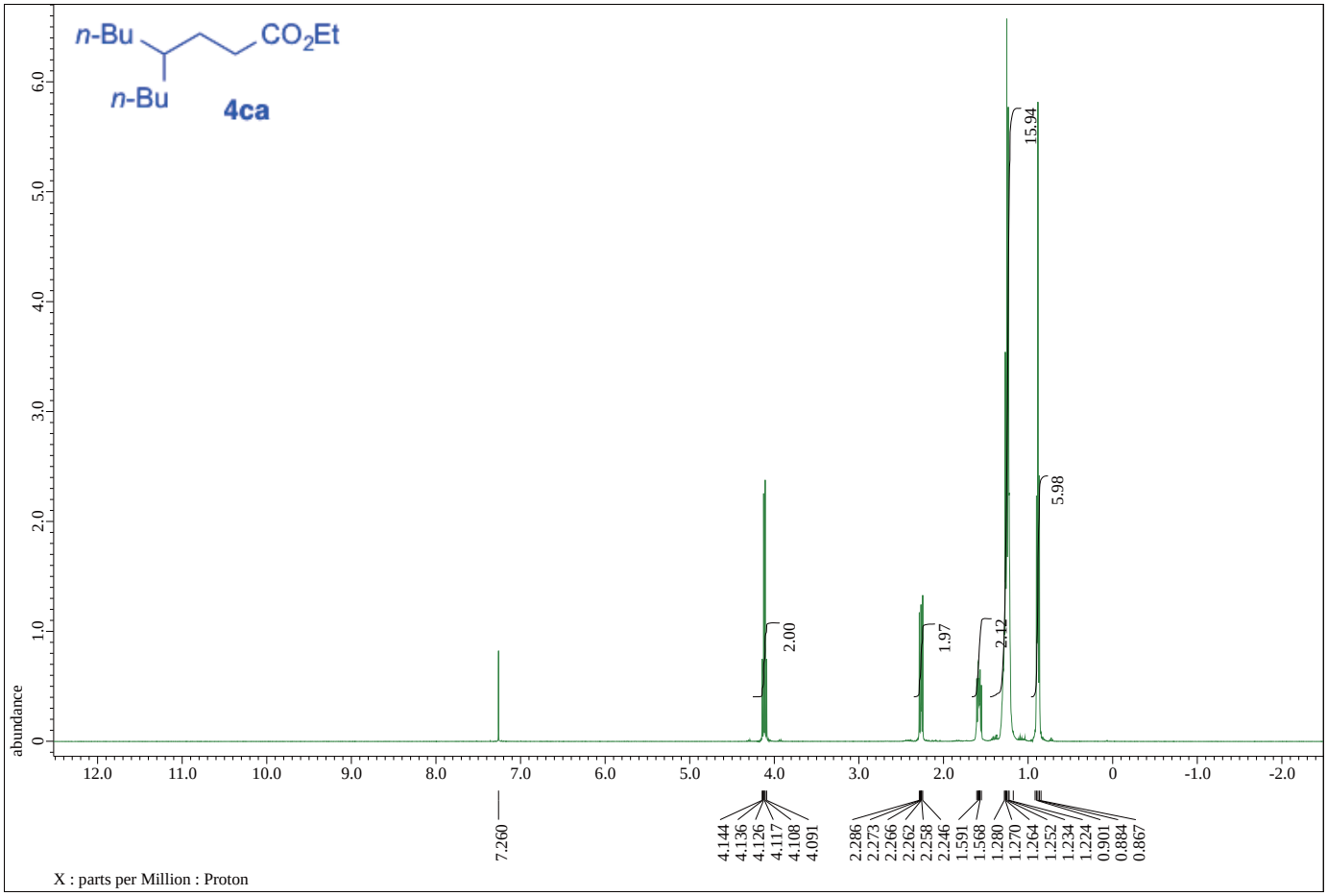

4aj
abundance
212.853
77.315
77.000
76.675
45.533
44.626
42.612
41.571
29.896
29.791
28.368
26.535
26.478
25.580
X : parts per Million : Carbon13

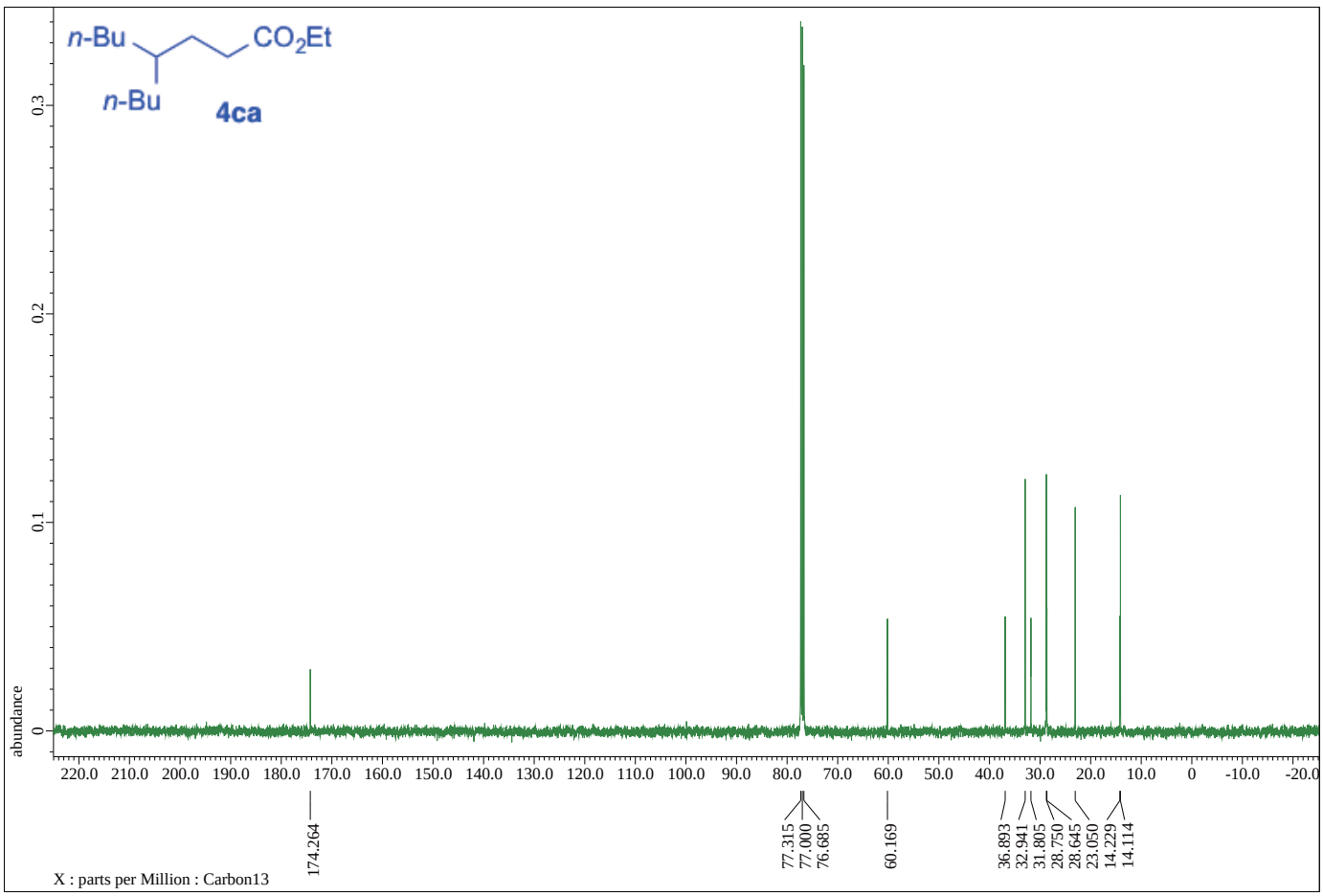

C8H17
CO2Et
4ba
abundance
7.260
4.139
4.122
4.103
4.086
2.294
2.274
2.256
1.641
1.623
1.605
1.587
1.569
1.286
1.276
1.262
1.246
1.244
1.225
0.885
0.868
0.851
2.00
1.97
1.89
17.00
3.08
X : parts per Million : Proton

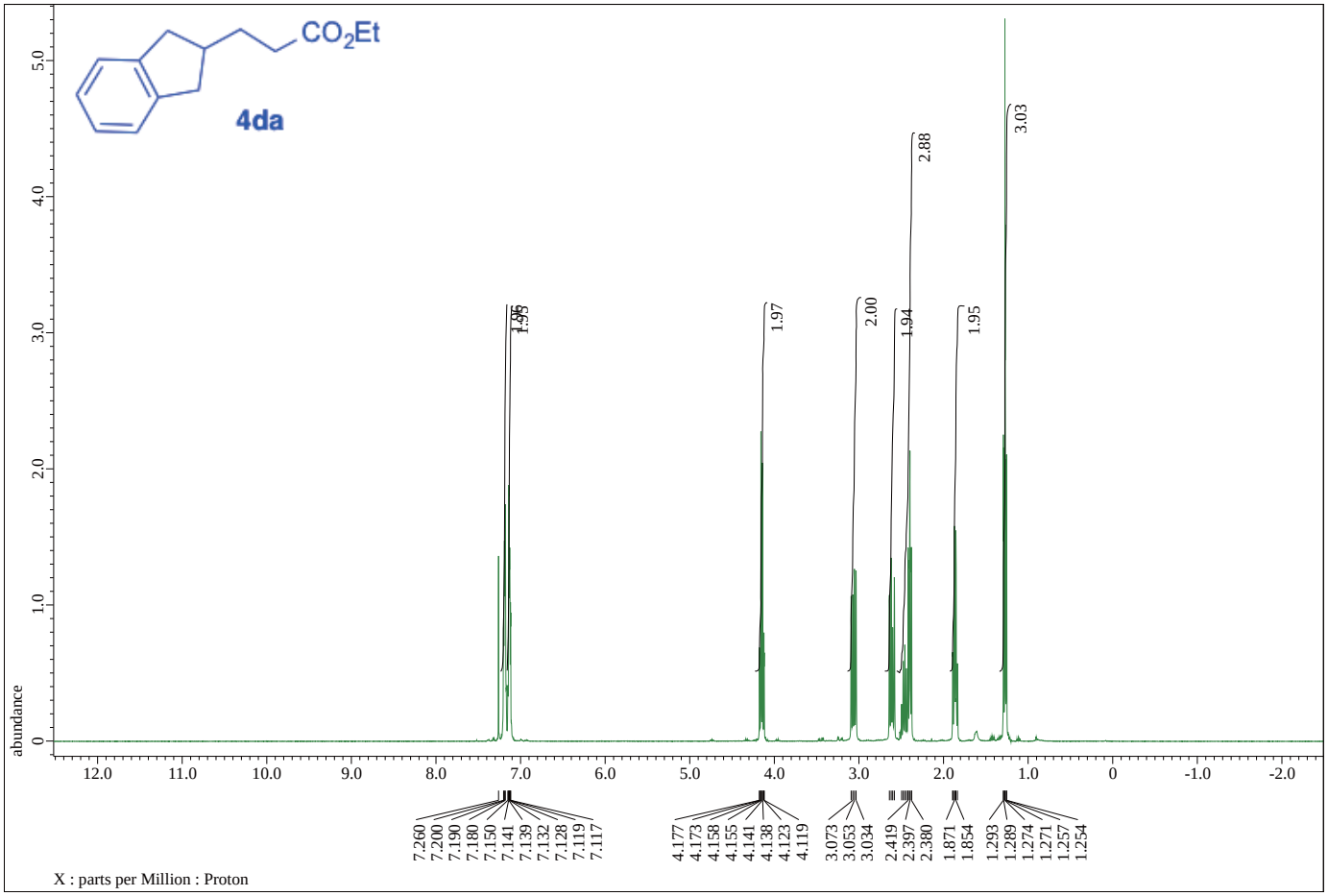

C8H17
CO2Et
4ba
abundance
173.920
77.315
77.000
76.685
60.121
34.373
31.872
29.533
29.437
29.285
29.246
29.122
24.960
22.659
14.229
14.086
X : parts per Million : Carbon13

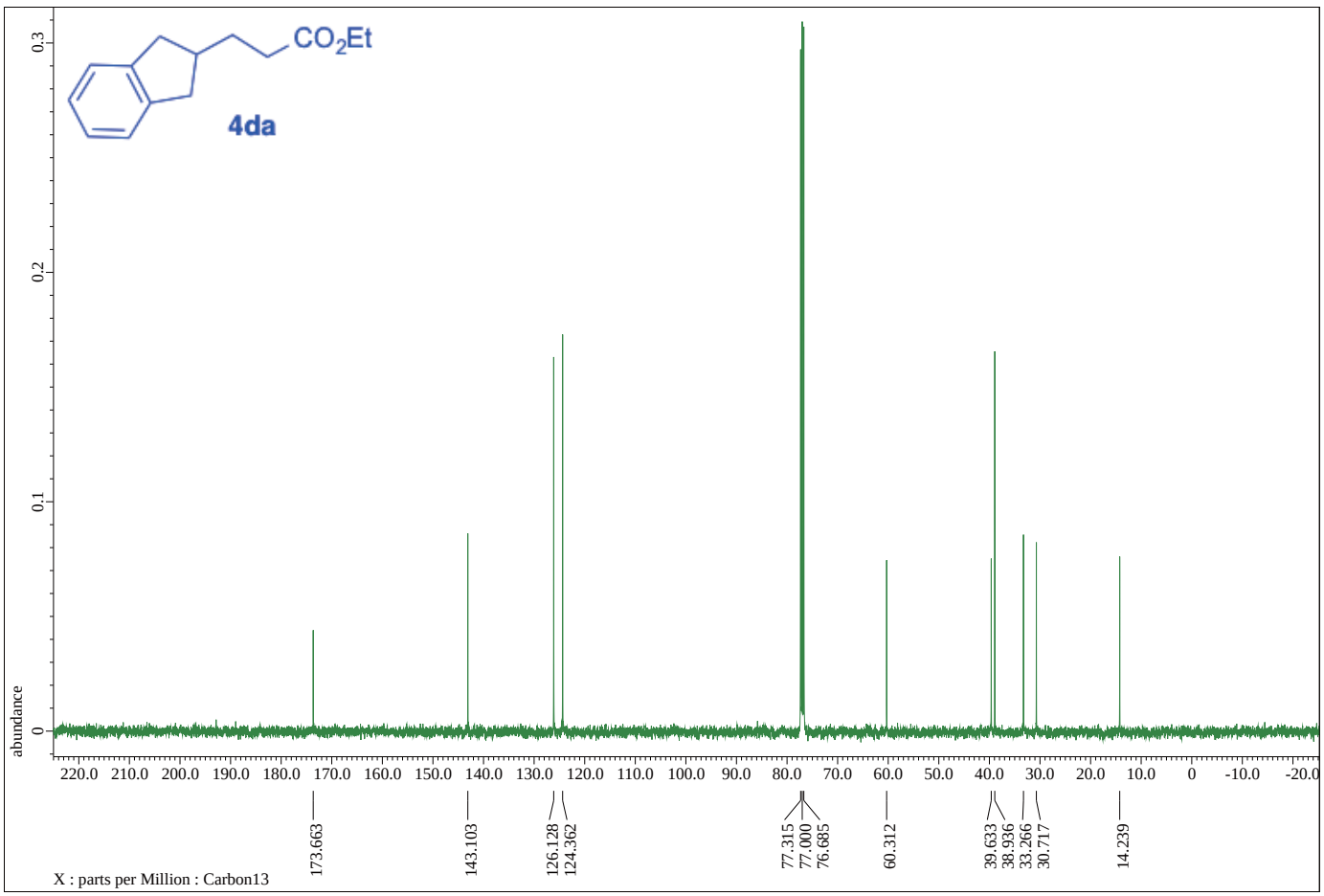

C8H17
O
4bg
abundance
X : parts per Million : Proton
7.260
2.419
2.400
2.382
2.364
2.345
1.556
1.538
1.521
1.269
1.230
1.040
1.021
1.003
0.866
0.851
0.832
3.93
1.93
13.73
2.93
3.00

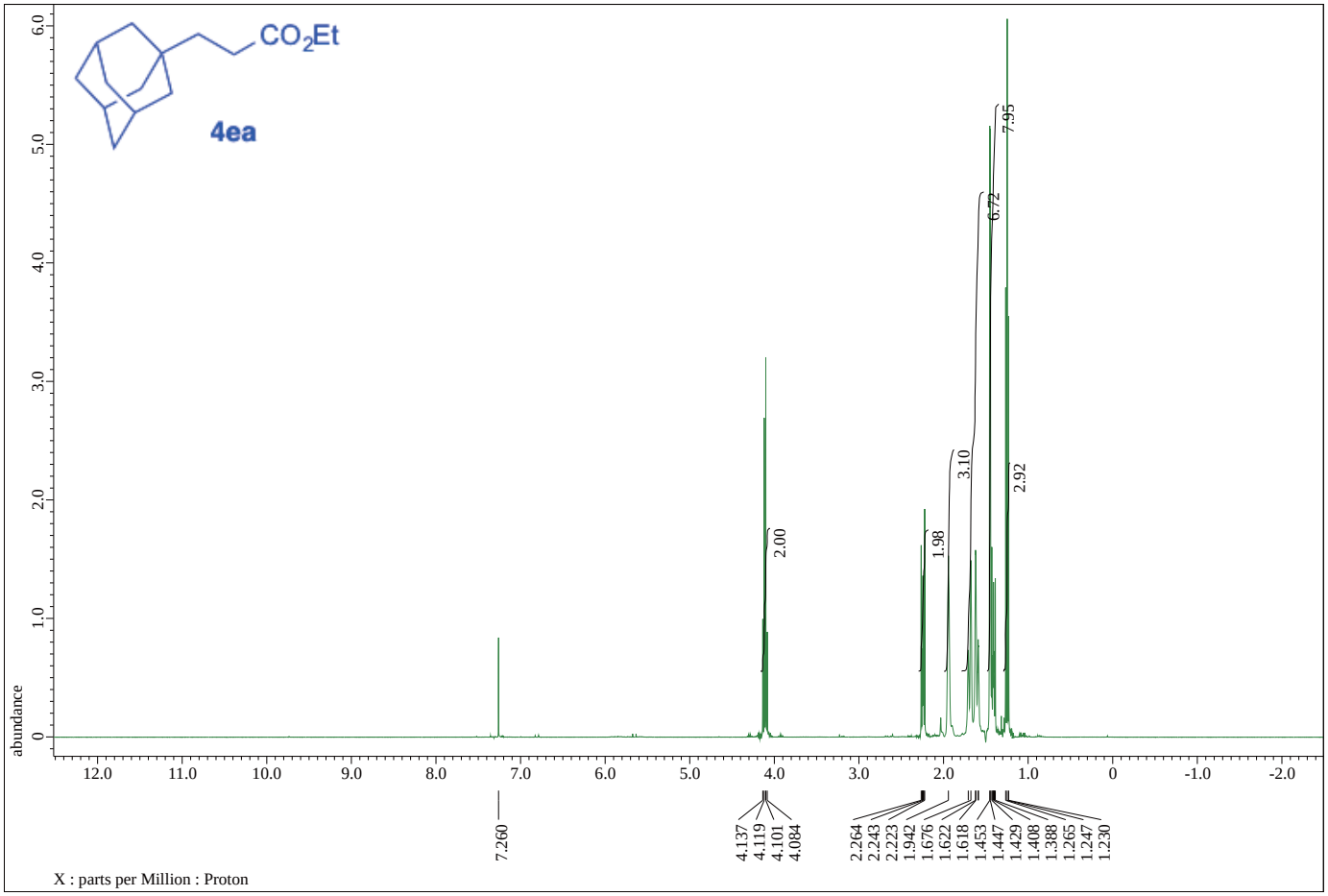

C8H17
O
4bg
abundance
X : parts per Million : Carbon13
211.888
77.315
77.000
76.685
42.383
35.776
31.834
29.514
29.428
29.370
29.256
29.237
23.900
22.621
14.038
7.775

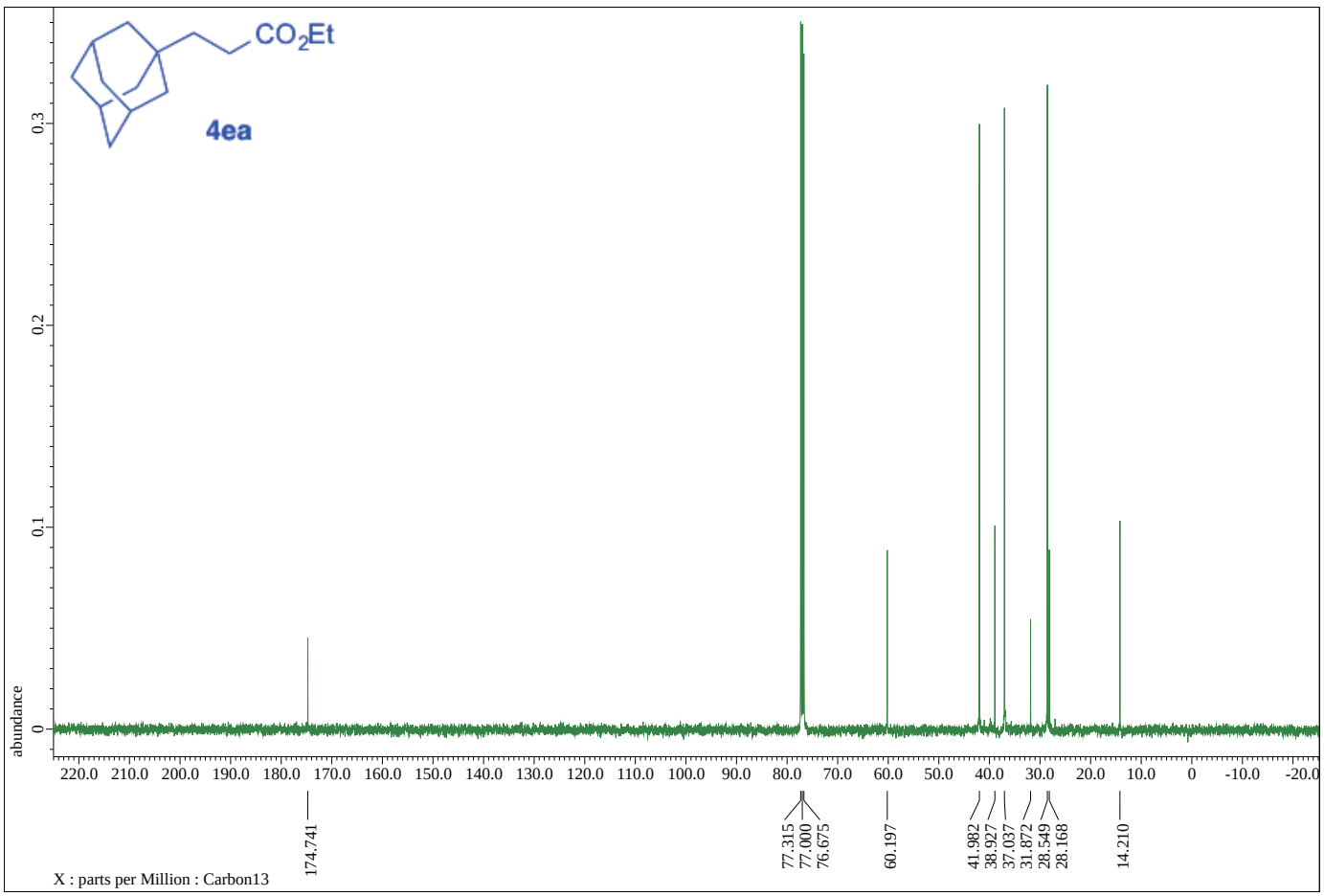

n-Bu
CO2Et
n-Bu
4ca
abundance
X : parts per Million : Proton
7.260
4.144
4.136
4.126
4.117
4.108
4.091
2.286
2.273
2.266
2.262
2.258
2.246
1.591
1.568
1.280
1.270
1.264
1.252
1.234
1.224
0.901
0.884
0.867
2.00
1.97
2.12
15.94
5.98

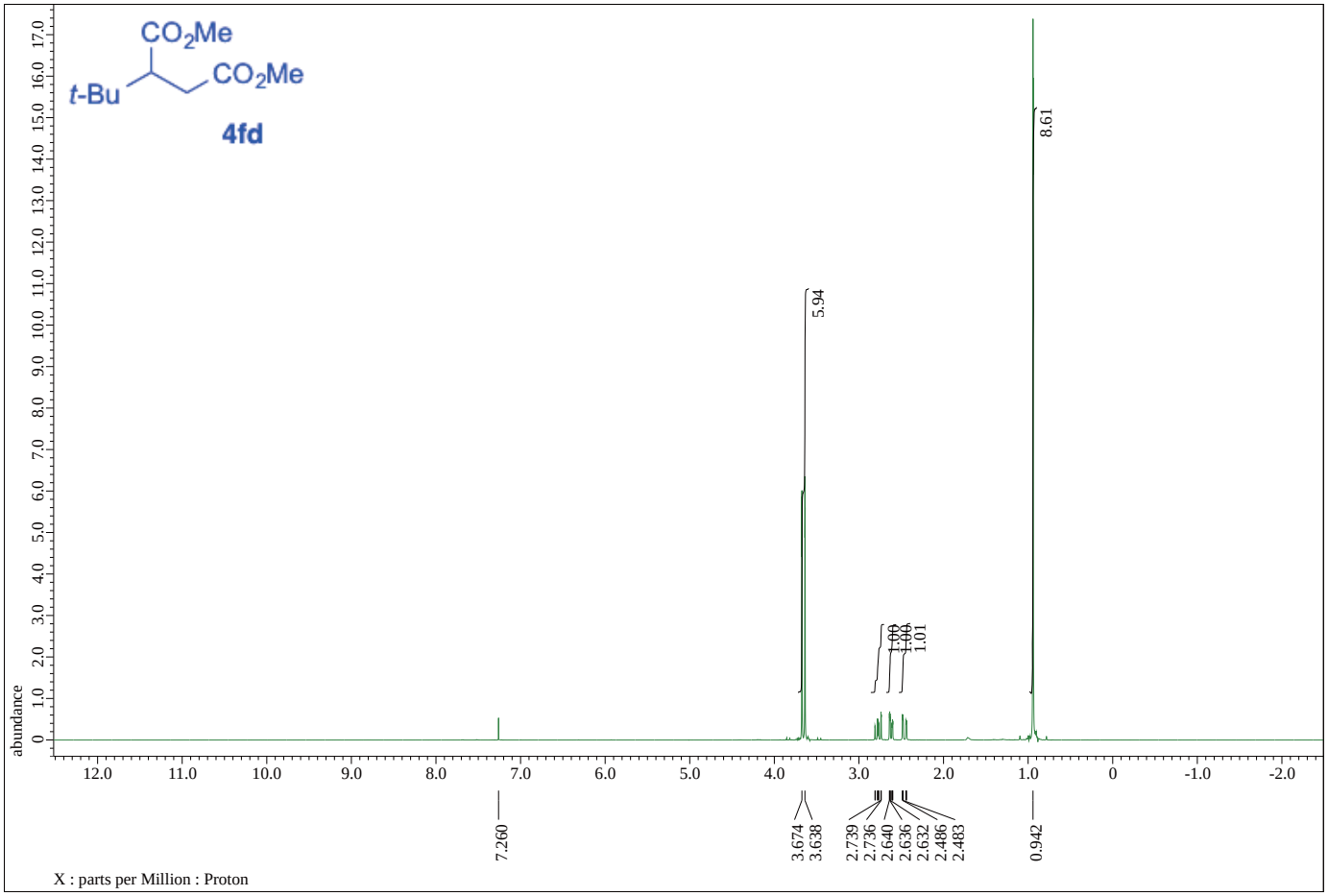

n-Bu
CO2Et
n-Bu
4ca
abundance
X : parts per Million : Carbon13
174.264
77.315
77.000
76.685
60.169
36.893
32.941
31.805
28.750
28.645
23.050
14.229
14.114

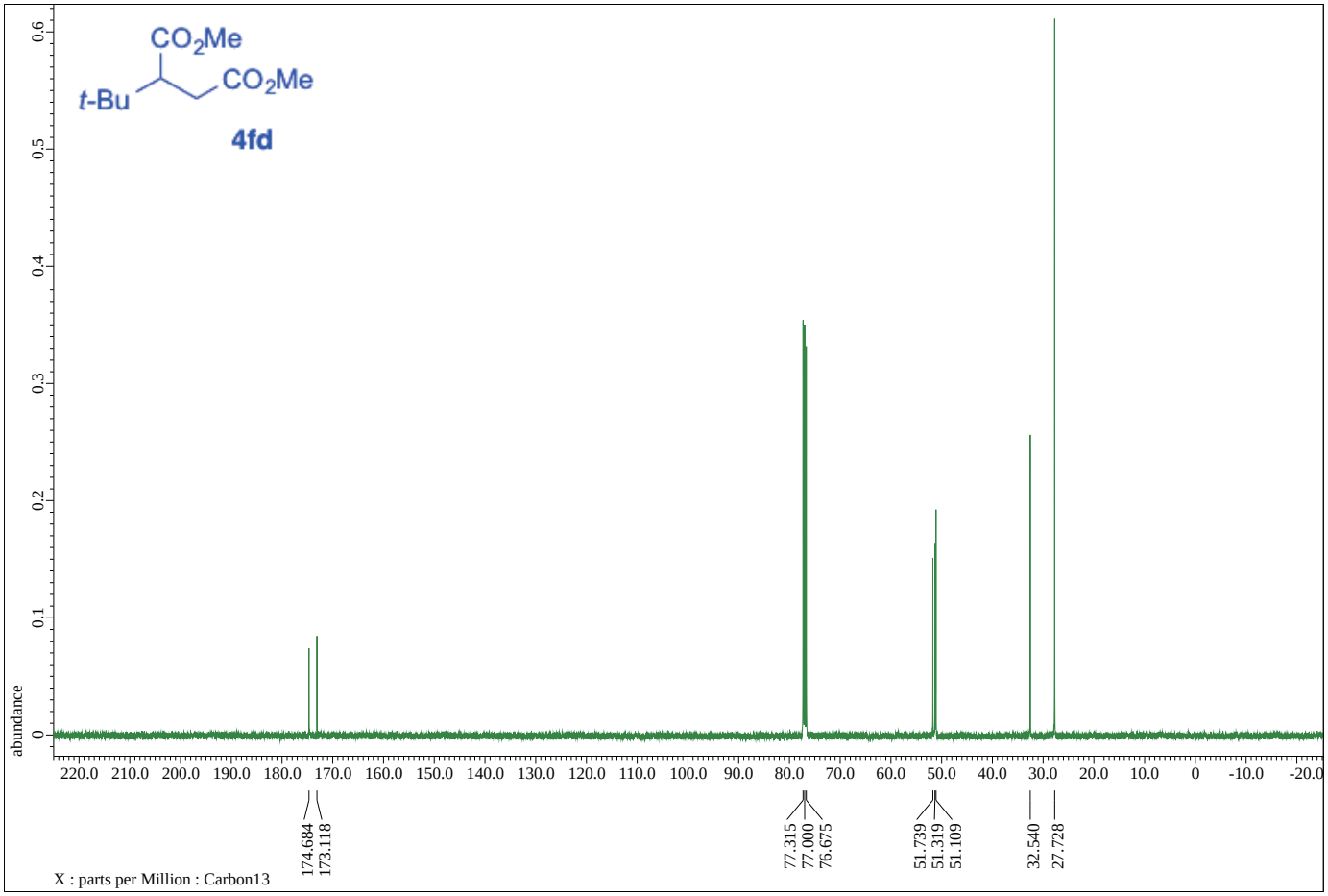

CO2Et
4da
abundance
X : parts per Million : Proton
1.97
2.00
2.88
3.03
1.95
1.94
7.260
7.200
7.190
7.180
7.150
7.141
7.139
7.132
7.128
7.119
7.117
4.177
4.173
4.158
4.155
4.141
4.138
4.123
4.119
3.073
3.053
3.034
2.419
2.397
2.380
1.871
1.854
1.293
1.289
1.274
1.271
1.257
1.254

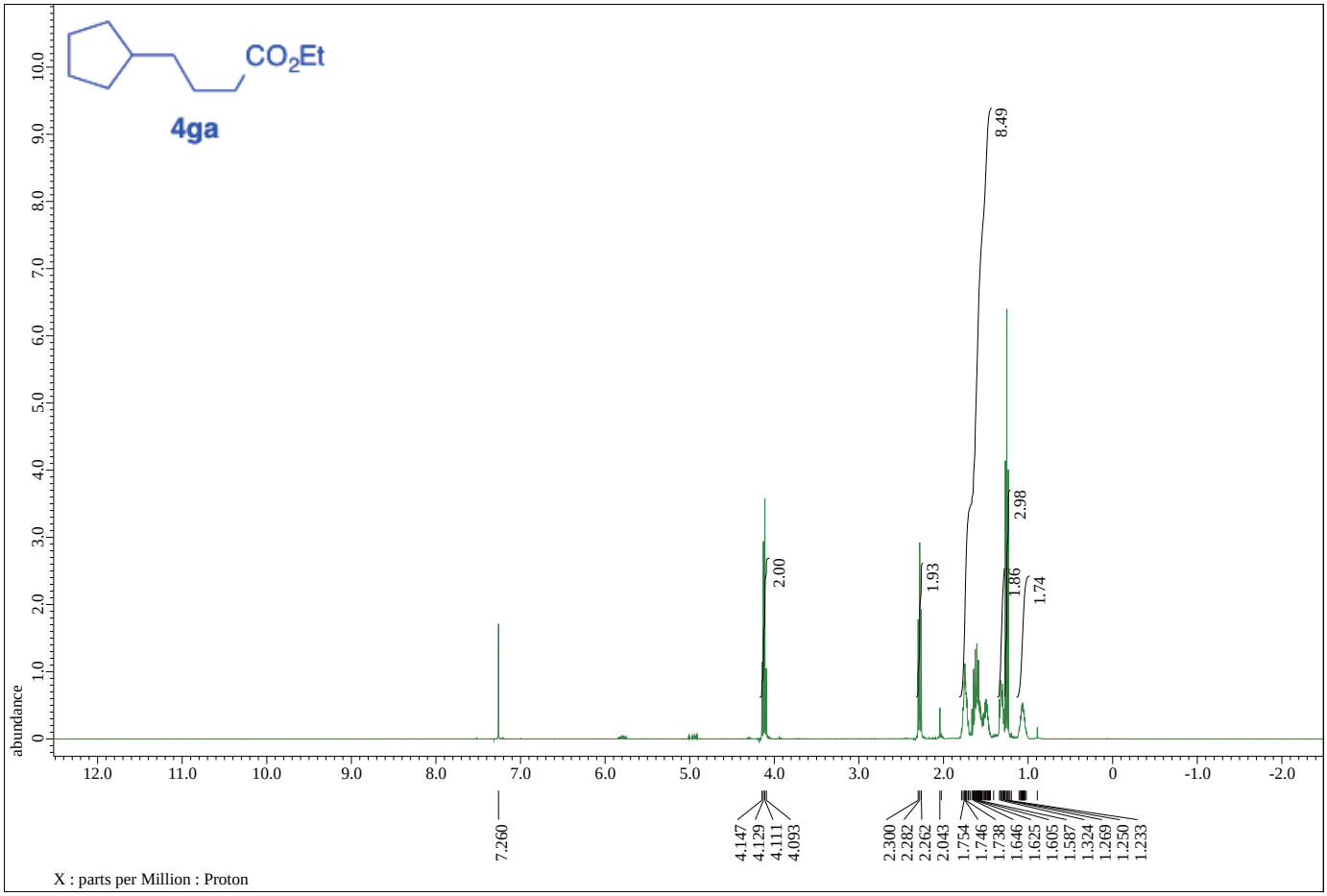

CO2Et
4da
abundance
X : parts per Million : Carbon13
173.663
143.103
126.128
124.362
77.315
77.000
76.685
60.312
39.633
38.936
33.266
30.717
14.239

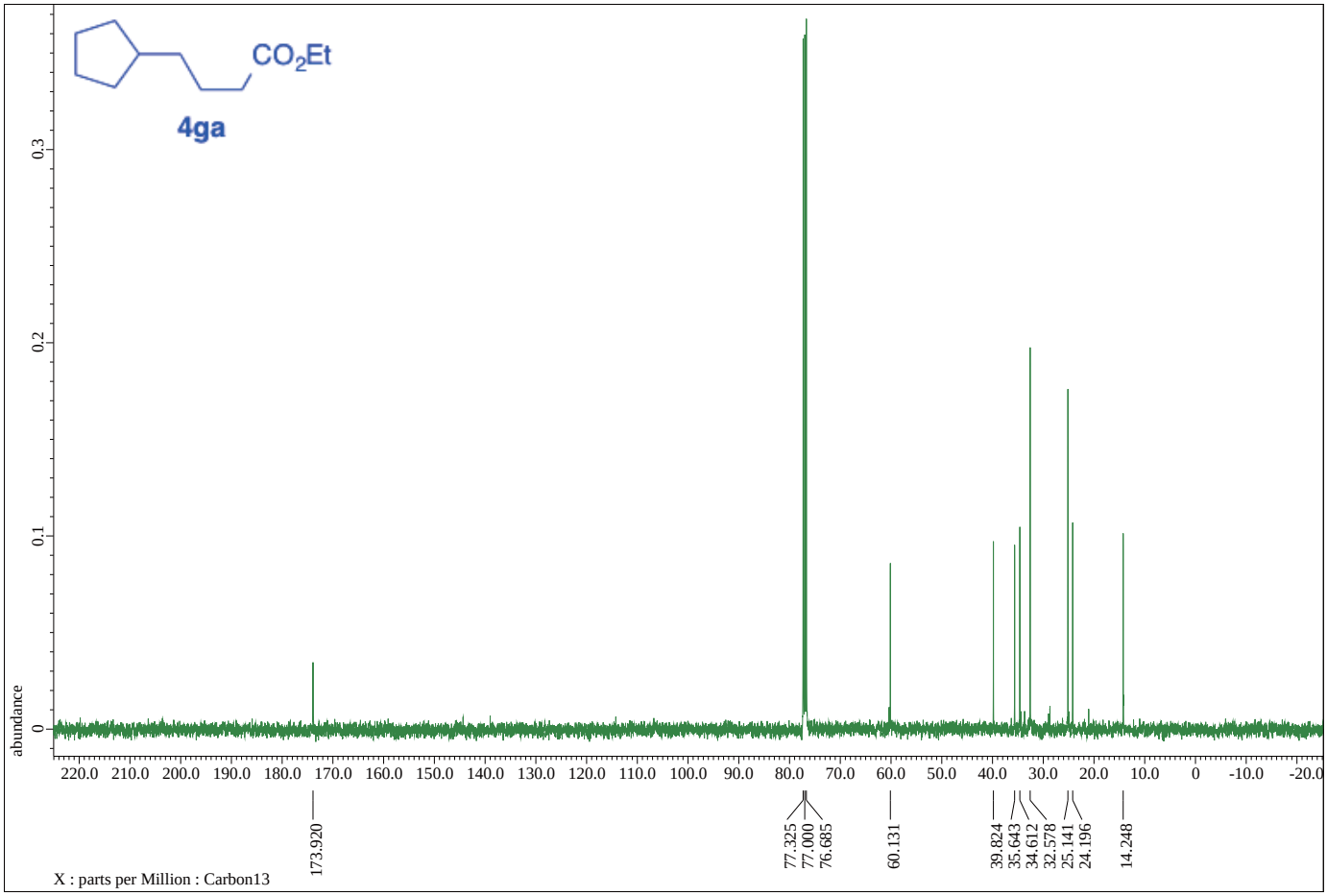

CO2Et
4ea
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.95
6.72
3.10
2.92
2.00
1.98
7.260
4.137 4.119 4.101 4.084
2.264 2.243 2.223 1.942 1.676 1.622 1.618 1.453 1.447 1.429 1.408 1.388 1.265 1.247 1.230
X : parts per Million : Proton

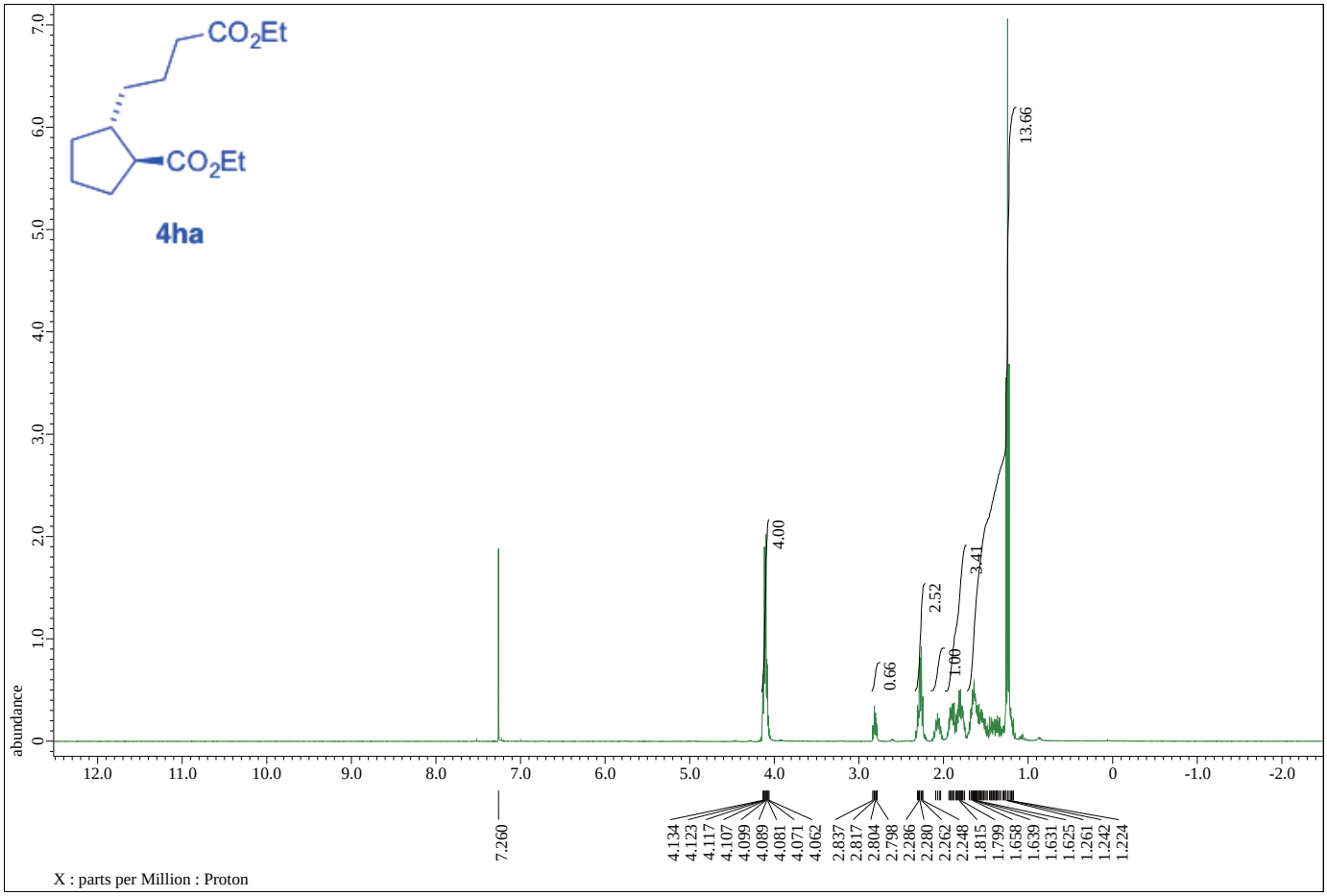

CO2Et
4ea
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.741
77.315 77.000 76.675
60.197
41.982 38.927 37.037 31.872 28.549 28.168
14.210
X : parts per Million : Carbon13

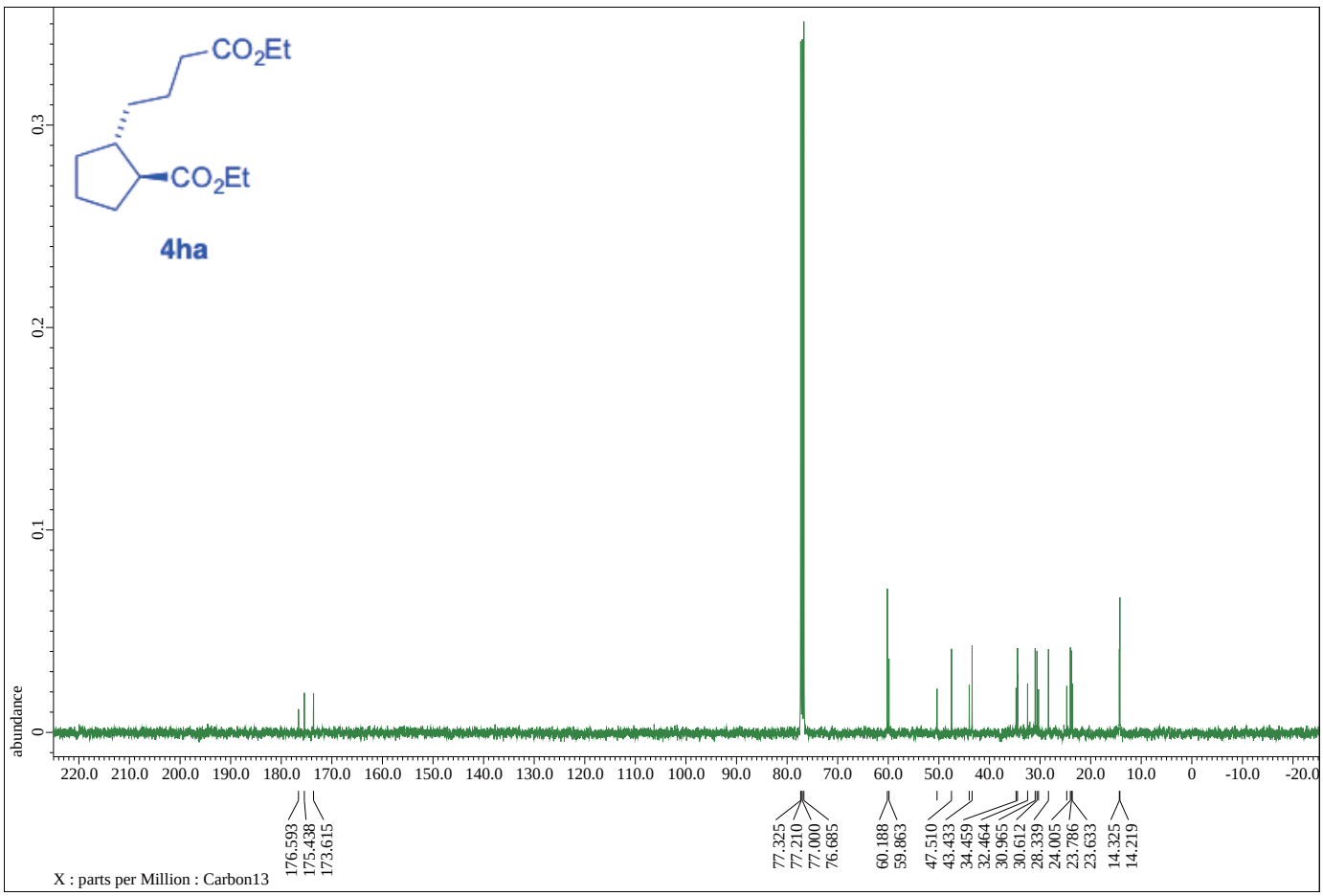

CO2Me
t-Bu
CO2Me
4fd
abundance
5.94
8.61
1.00
1.00
1.00
1.01
7.260
3.674
3.638
2.739
2.736
2.640
2.636
2.632
2.486
2.483
0.942
X : parts per Million : Proton

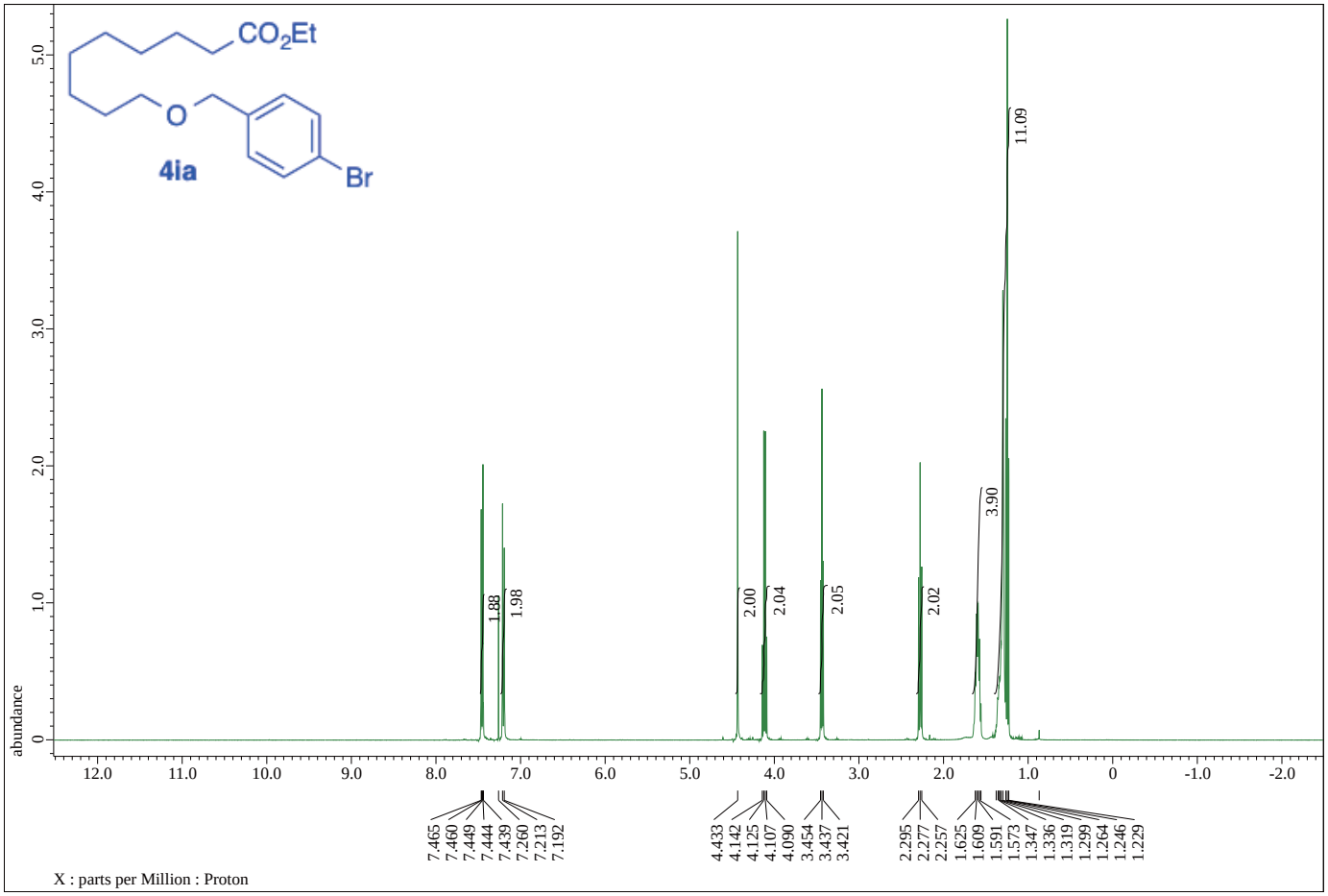

CO2Me
t-Bu
CO2Me
4fd
abundance
174.684
173.118
77.315
77.000
76.675
51.739
51.319
51.109
32.540
27.728
X : parts per Million : Carbon13

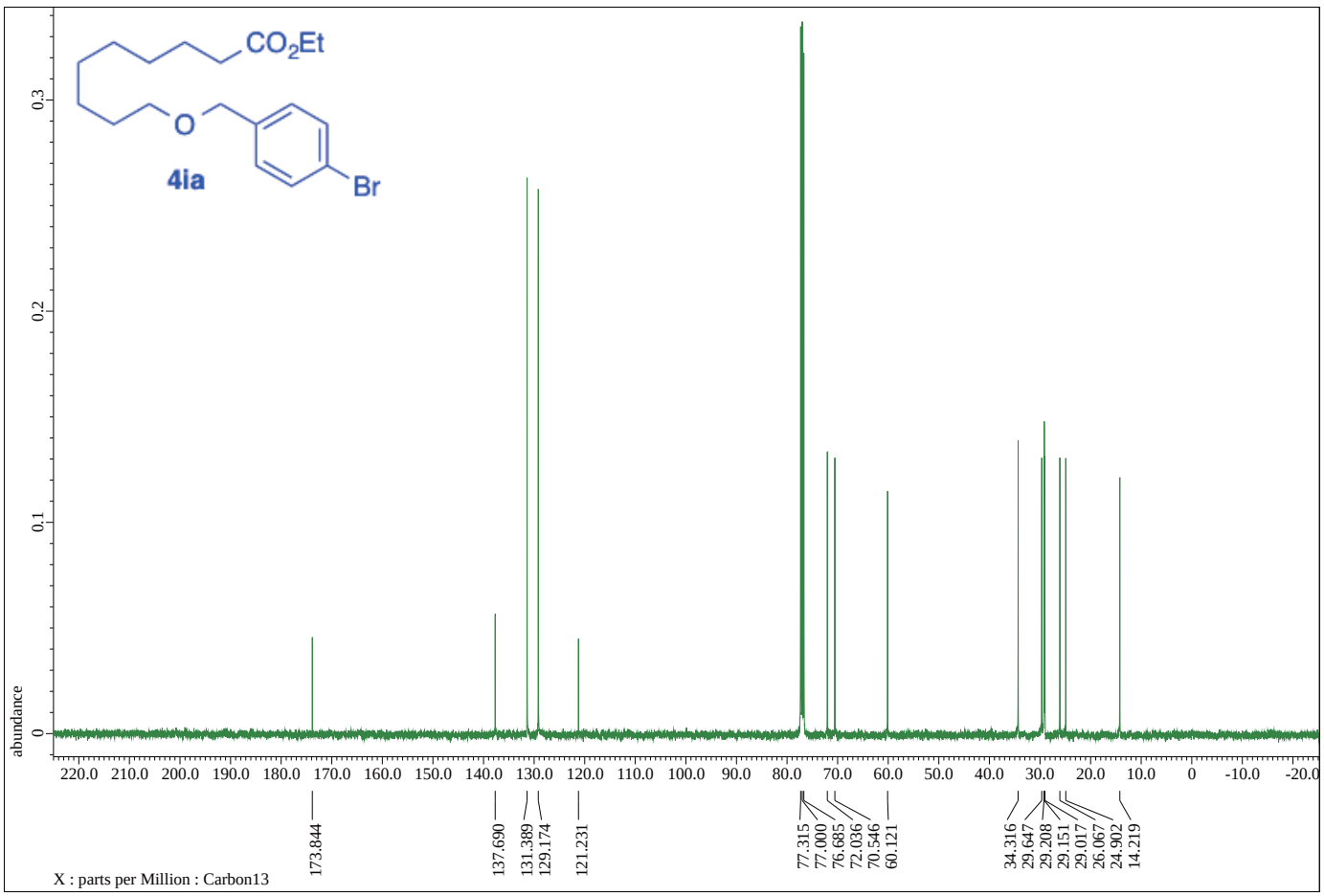

CO2Et
4ga
abundance
8.49
2.98
2.00
1.93
1.86
1.74
7.260
4.147
4.129
4.111
4.093
2.300
2.282
2.262
2.043
1.754
1.746
1.738
1.646
1.625
1.605
1.587
1.324
1.269
1.250
1.233
X : parts per Million : Proton

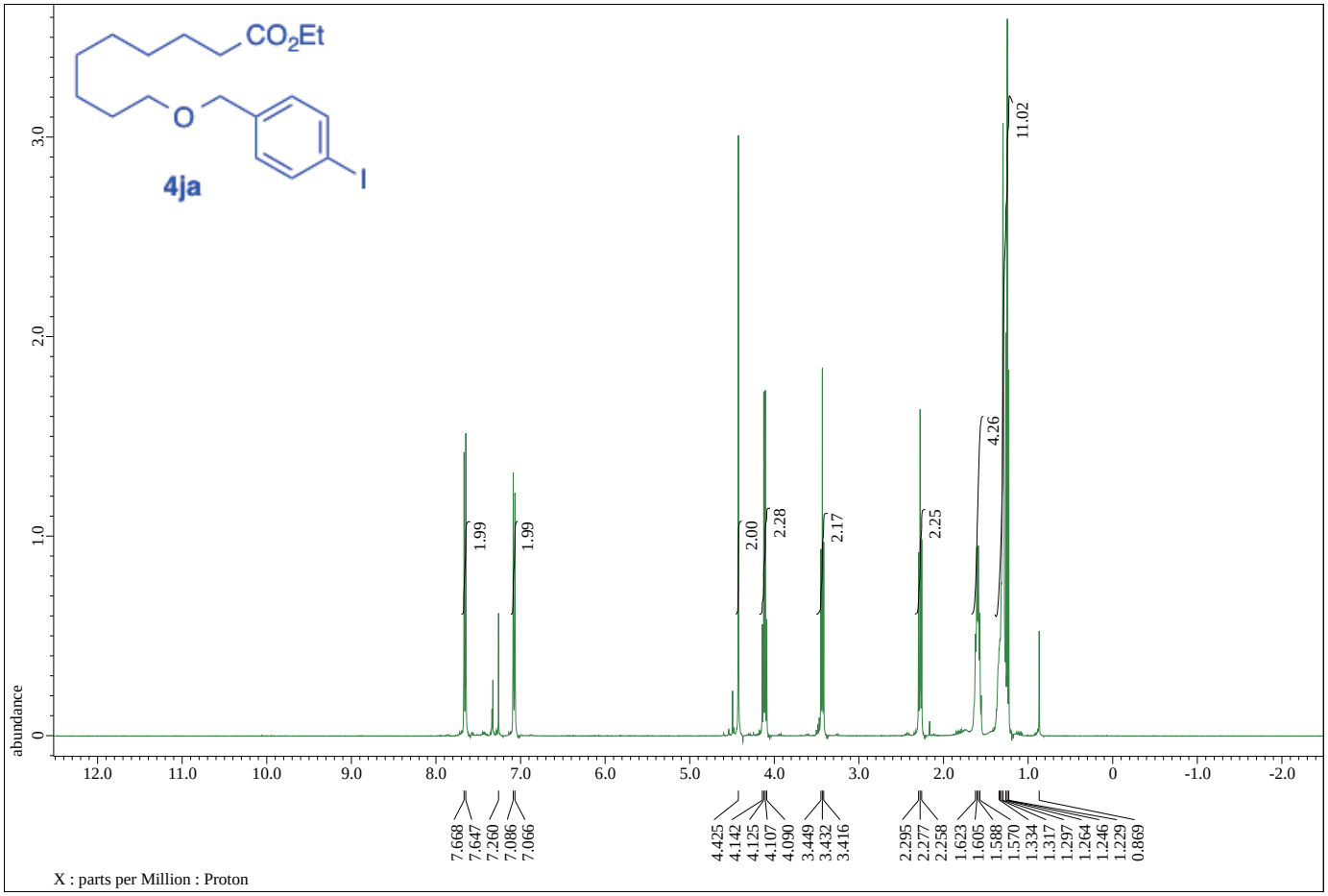

CO2Et
4ga
abundance
173.920
77.325
77.000
76.685
60.131
39.824
35.643
34.612
32.578
25.141
24.196
14.248
X : parts per Million : Carbon13

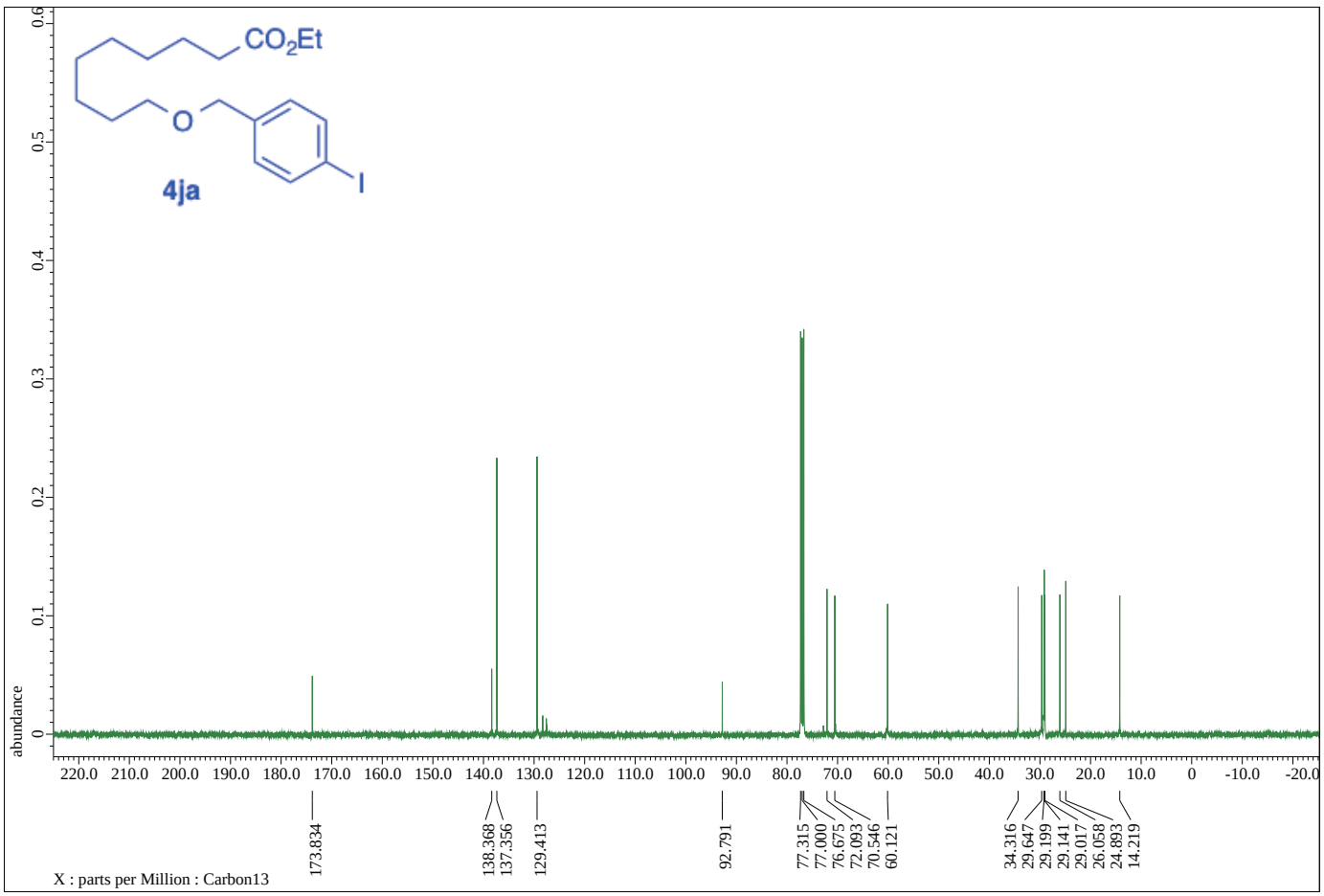

CO2Et
CO2Et
4ha
abundance
X : parts per Million : Proton
7.260
4.134
4.123
4.117
4.107
4.099
4.089
4.081
4.071
4.062
2.837
2.817
2.804
2.798
2.286
2.280
2.262
2.248
1.815
1.799
1.658
1.639
1.631
1.625
1.261
1.242
1.224
4.00
0.66
2.52
1.00
3.41
13.66

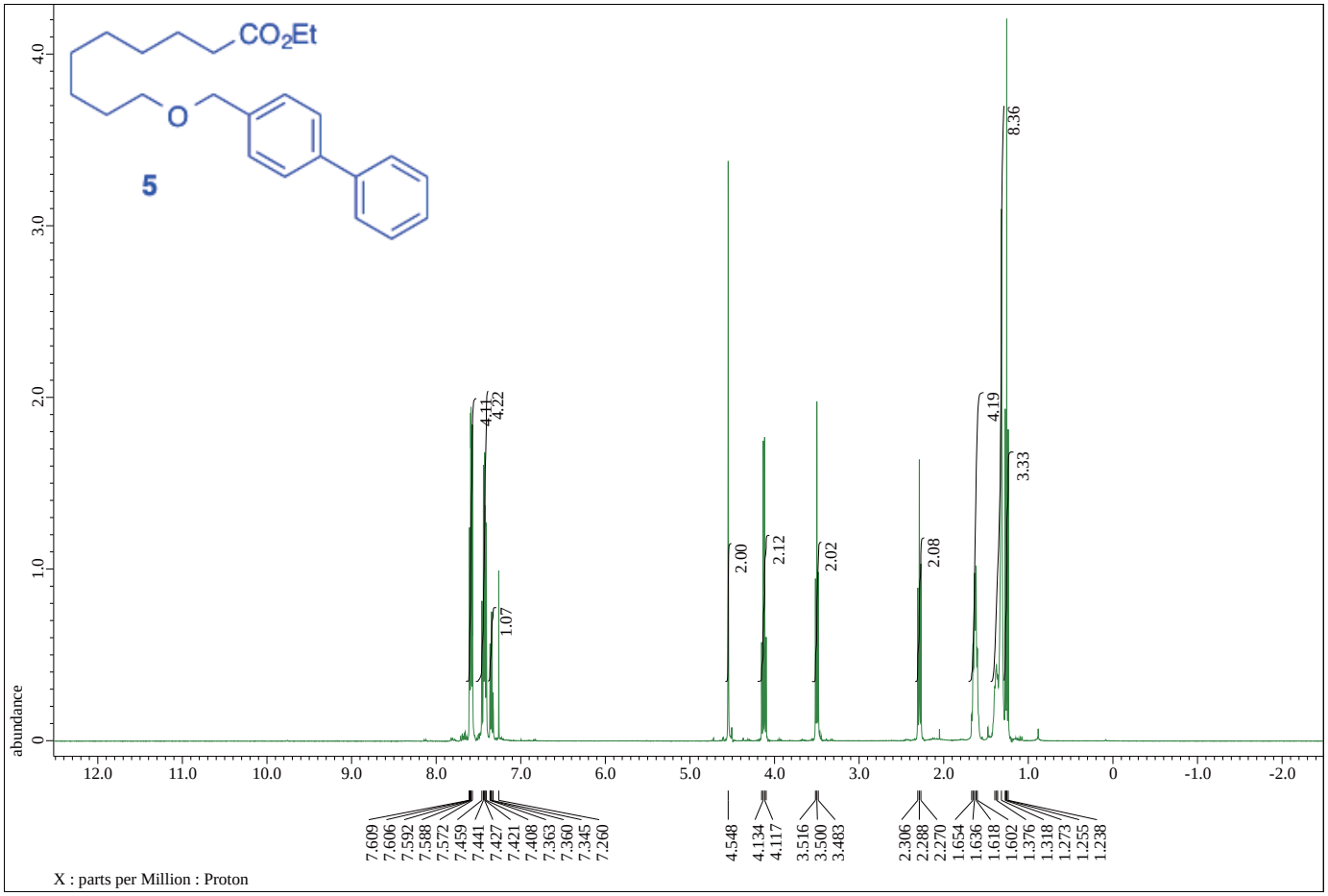

CO2Et
CO2Et
4ha
abundance
X : parts per Million : Carbon13
176.593
175.438
173.615
77.325
77.210
77.000
76.685
60.188
59.863
47.510
43.433
34.459
32.464
30.965
30.612
28.339
24.005
23.786
23.633
14.325
14.219

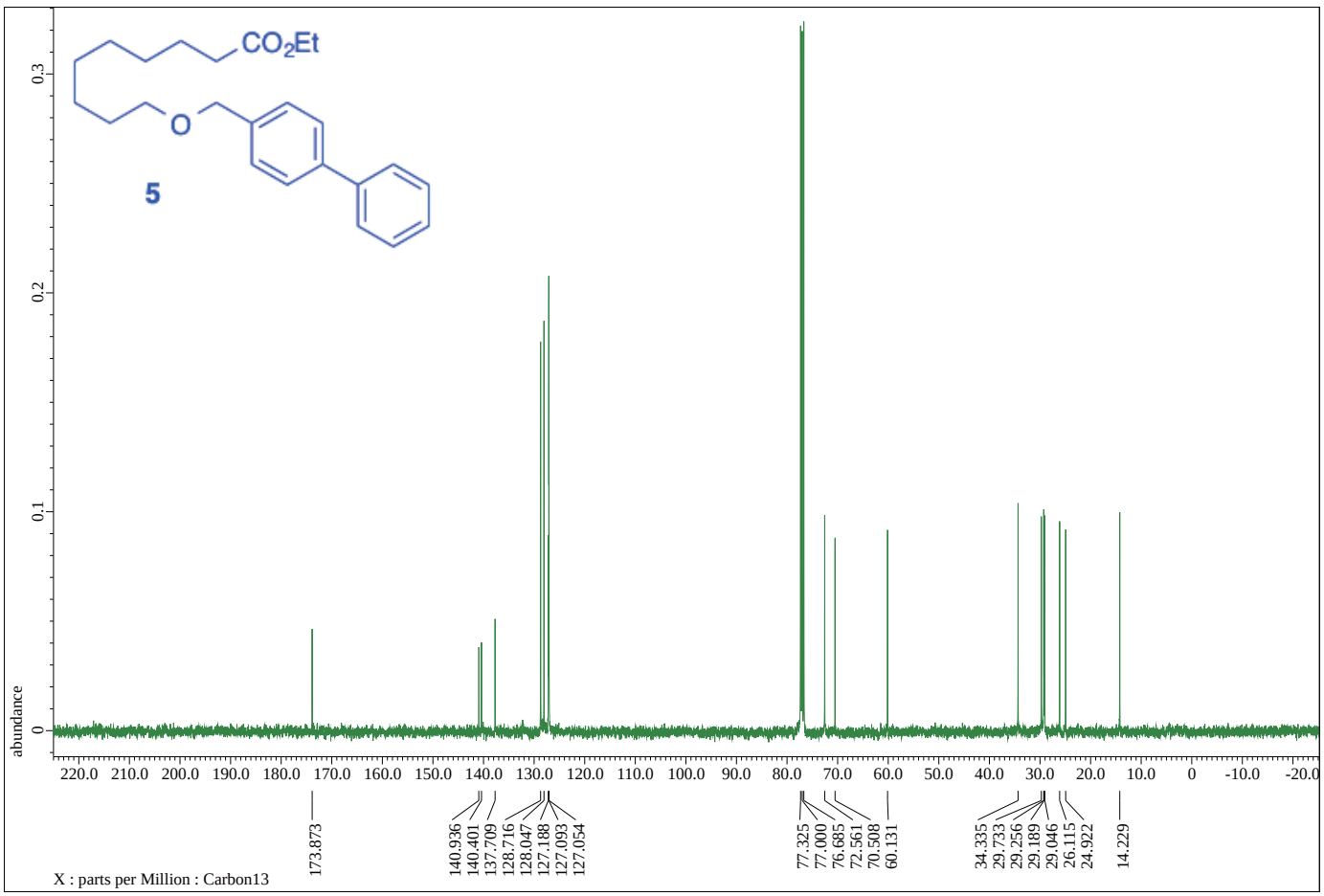

CO2Et
O
4ia
Br
abundance
X : parts per Million : Proton
11.09
3.90
2.05
2.04
2.00
2.02
1.98
1.88
7.465
7.460
7.449
7.444
7.439
7.260
7.213
7.192
4.433
4.142
4.125
4.107
4.090
3.454
3.437
3.421
2.295
2.277
2.257
1.625
1.609
1.591
1.573
1.347
1.336
1.319
1.299
1.264
1.246
1.229

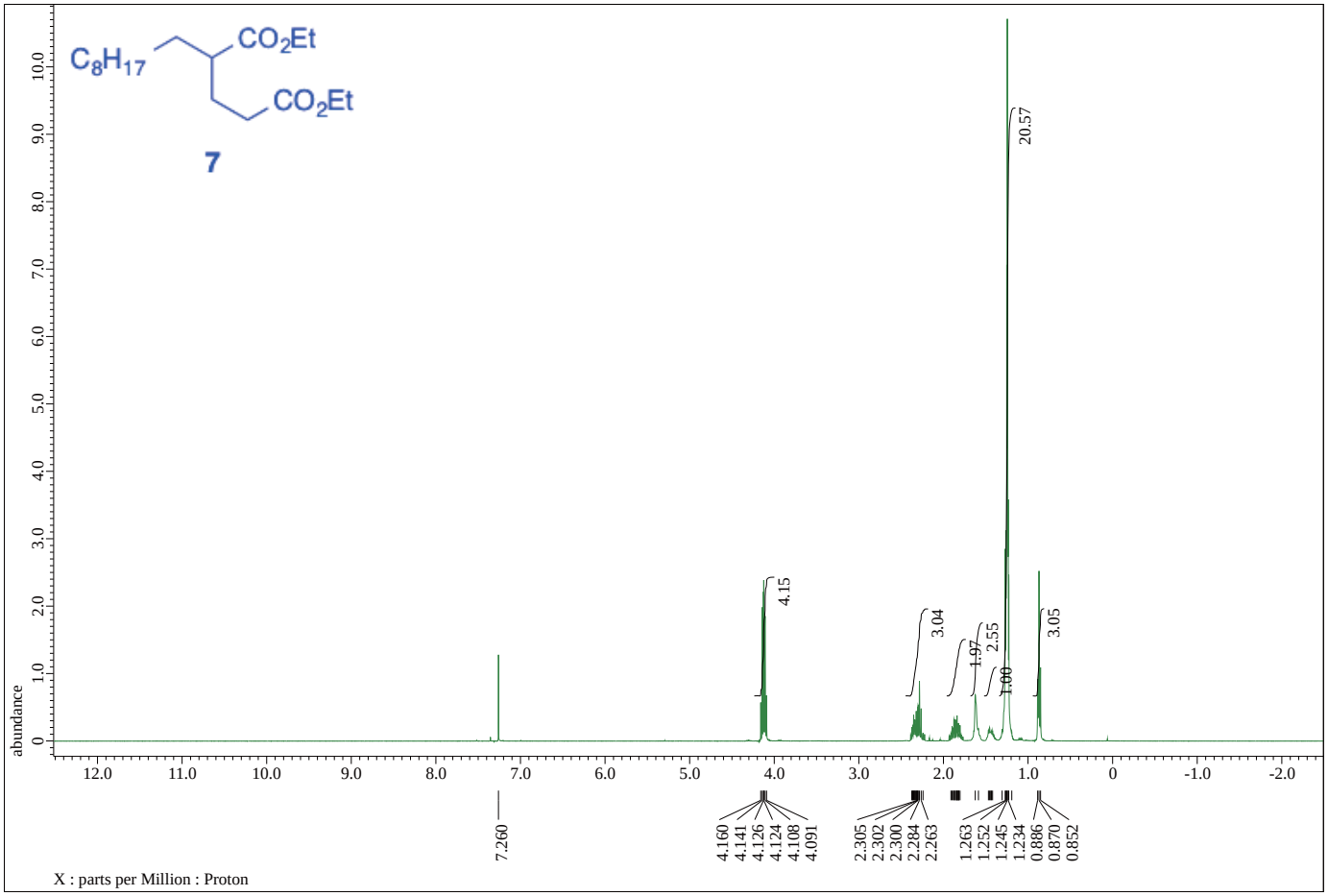

CO2Et
O
4ia
Br
abundance
X : parts per Million : Carbon13
173.844
137.690
131.389
129.174
121.231
77.315
77.000
76.685
72.036
70.546
60.121
34.316
29.647
29.208
29.151
29.017
26.067
24.902
14.219

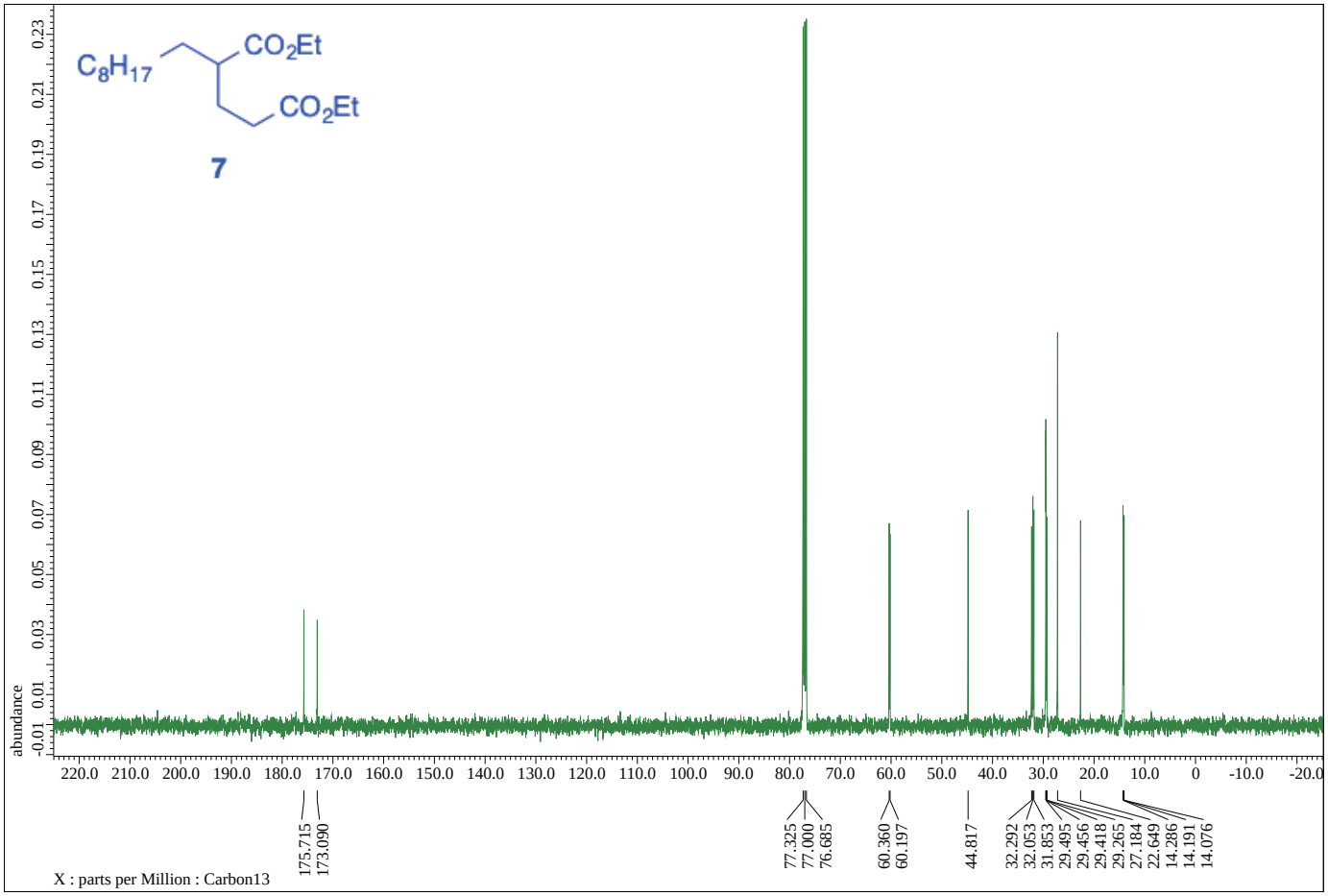

CO2Et
O
I
4ja
abundance
X : parts per Million : Proton
1.99
1.99
2.00
2.28
2.17
2.25
4.26
11.02
7.668
7.647
7.260
7.086
7.066
4.425
4.142
4.125
4.107
4.090
3.449
3.432
3.416
2.295
2.277
2.258
1.623
1.605
1.588
1.570
1.334
1.317
1.297
1.264
1.246
1.229
0.869

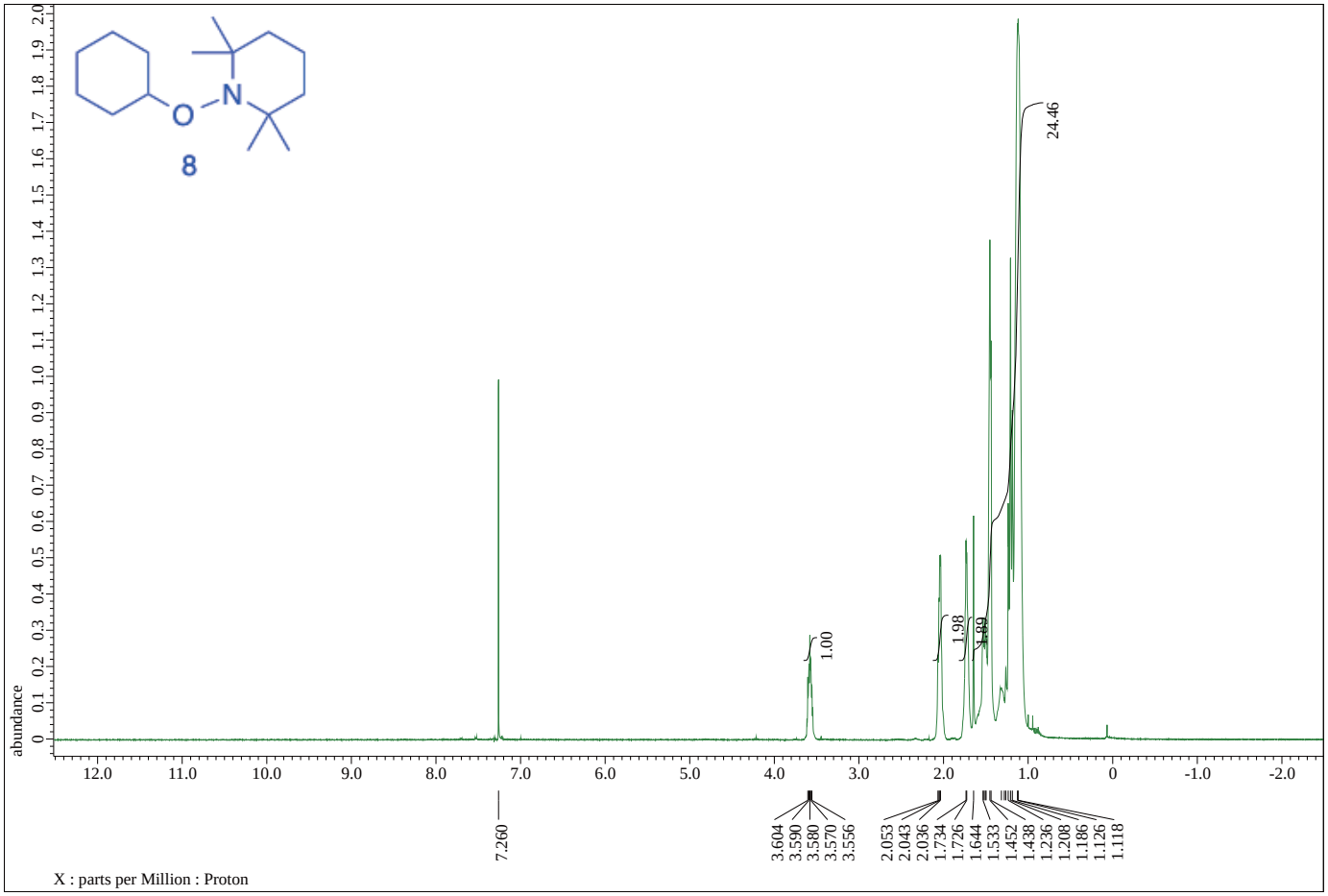

CO2Et
O
I
4ja
abundance
X : parts per Million : Carbon13
173.834
138.368
137.356
129.413
92.791
77.315
77.000
76.675
72.093
70.546
60.121
34.316
29.647
29.199
29.141
29.017
26.058
24.893
14.219

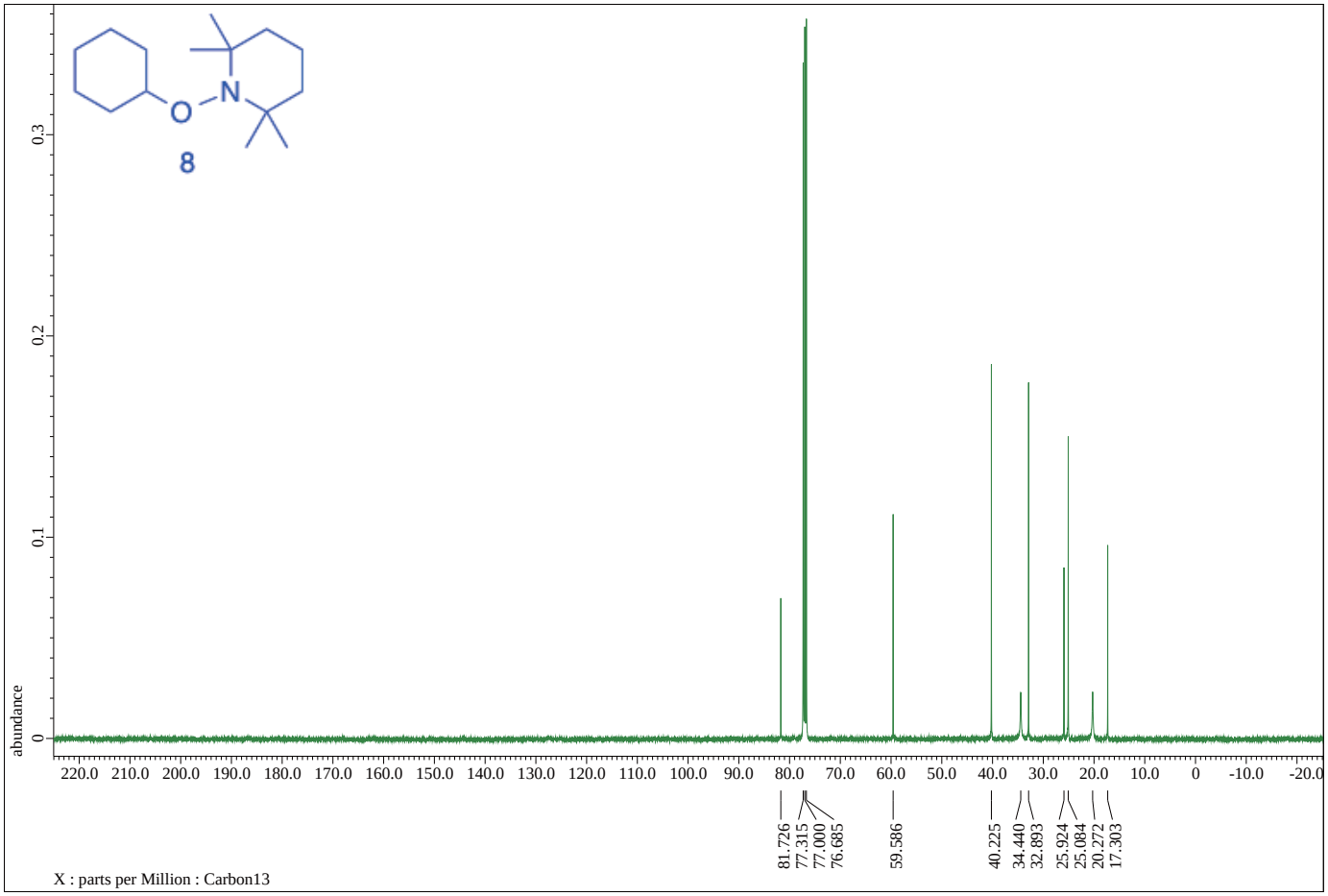

CO2Et
O
5
abundance
X : parts per Million : Proton
8.36
4.19
4.22
4.11
3.33
2.00
2.12
2.02
2.08
1.07
7.609
7.606
7.592
7.588
7.572
7.459
7.441
7.427
7.421
7.408
7.363
7.360
7.345
7.260
4.548
4.134
4.117
3.516
3.500
3.483
2.306
2.288
2.270
1.654
1.636
1.618
1.602
1.376
1.318
1.273
1.255
1.238


CO2Et
O
5
abundance
X : parts per Million : Carbon13
173.873
140.936
140.401
137.709
128.716
128.047
127.188
127.093
127.054
77.325
77.000
76.685
72.561
70.508
60.131
34.335
29.733
29.256
29.189
29.046
26.115
24.922
14.229


C8H17
CO2Et
CO2Et
7
abundance
4.15
3.04
1.97
2.55
1.00
20.57
3.05
7.260
4.160
4.141
4.126
4.124
4.108
4.091
2.305
2.302
2.300
2.284
2.263
1.263
1.252
1.245
1.234
0.886
0.870
0.852
X : parts per Million : Proton


C8H17
CO2Et
CO2Et
7
abundance
175.715
173.090
77.325
77.000
76.685
60.360
60.197
44.817
32.292
32.053
31.853
29.495
29.456
29.418
29.265
27.184
22.649
14.286
14.191
14.076
X : parts per Million : Carbon13


8
abundance
24.46
1.98
1.89
1.00
7.260
3.604
3.590
3.580
3.570
3.556
2.053
2.043
2.036
1.734
1.726
1.644
1.533
1.452
1.438
1.236
1.208
1.186
1.126
1.118
X : parts per Million : Proton


8
abundance
81.726
77.315
77.000
76.685
59.586
40.225
34.440
32.893
25.924
25.084
20.272
17.303
X : parts per Million : Carbon13