Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information for

Radical vinylation of dioxolanes and *N*-acylpyrrolidines using vinyl bromides

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General information

^{1}H NMR spectra were recorded with a JEOL ECS-400 (400 MHz) spectrometers in $CDCl_3$ and are referenced at 0.00 ppm for TMS. ^{13}C NMR spectra were recorded with a JEOL ECS-400 (100 MHz) spectrometers in $CDCl_3$ and are referenced at 77.16 ppm for $CDCl_3$. Chemical shifts are reported in parts per million (δ). 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. The products **3a**-**h** and **7a-b** were purified by flash column chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 μm)). The products **3f**, **3h**, and **7a-b** were further purified by preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) with GPC columns using $CHCl_3$ as an eluent. Vinyl bromides **2a-2d** were synthesized according to the literature procedure.[1] Products **3a**-**c**, and **3h** were determined to be *E*-form by referring to ^{1}H NMR of the related compounds.[2] *E*/Z structures of products **3d**-**g** were determined by referring to ^{13}C NMR of the related compounds.[3] *E*/Z structures of products **7a**-**b** were determined by referring to ^{1}H NMR of the related compounds, which showed that vinyl protons *cis* to a methoxycarbonyl group absorbs at lower fields.[2]

[1] X. Li and X. Zeng, *Tetrahedron Lett.,* 2006, **47**, 6839.

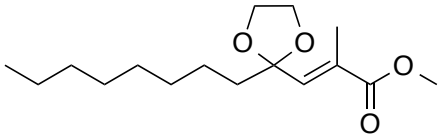
[2] P. F. Schuda, C. B. Ebner and S. J. Potlock, *Synthesis,* **1987**, 1055.

[3] T. Funabiki, H. Hosomi, S. Yoshida and K. Tarama, *J. Am. Chem. Soc.* 1982, **104**, 1560.

Procedure for a large scale reaction.

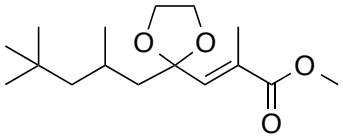
To a 50 mL screw-capped test tube, di-*tert*-butylhyponitrite (DTBHN, 34.8 mg, 0.2 mmol), potassium carbonate (276.4 mg, 2.0 mmol), 2-octyl-1,3-dioxolane (**1a**, 1.863 g, 10.0 mmol), MeCN (2.0 mL), and methyl (*E*)-3-bromo-2-methylacrylate (**2a**, 358.0 mg, 2.0 mmol) were added. The test tube was purged with argon and sealed. Then, the mixture was stirred at 60 °C. After 3 h and 6 h, two portions of an additional solution of DTBHN (34.8 mg, 0.2 mmol) in MeCN (2.0 mL) were added and the reaction was stopped after 12 h of total reaction time. After cooling to room temperature, 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 = 100/1 to 30/1) to give the vinylated product **3a** as a single *E* diatereomer (391.5 mg, 69%).

Methyl (*E*)-2-methyl-3-(2-octyl-1,3-dioxolan-2-yl)acrylate (3a)



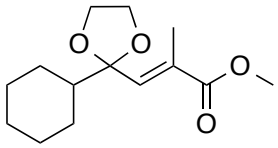
Colorless oil; R_f = 0.60 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.19-1.34 (m, 10H), 1.34-1.44 (m, 2H), 1.72-1.80 (m, 2H), 2.00-2.02 (m, 3H), 3.74 (s, 3H), 3.80-3.88 (m, 2H), 3.90-3.99 (m, 2H), 6.61-6.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.78, 14.24, 22.77, 23.35, 29.35, 29.63, 29.90, 31.97, 38.10, 52.16, 64.52, 109.54, 130.34, 141.66, 168.80; IR (neat): 2951, 2926, 2855, 1721, 1652 cm^{-1}; EIMS *m/z* (relative intensity) 284 (M^+, 2), 253 (M^+-OMe, 7), 185 (25), 172 (29), 171 (100), 127 (13), 111 (22); HRMS (EI) *m/z* calcd for $C_{16}H_{28}O_4$ (M^+): 284.1988, found: 284.1981.

Methyl (*E*)-2-methyl-3-(2-(2,4,4-trimethylpentyl)-1,3-dioxolan-2-yl)acrylate (3b)



Colorless oil; R_f = 0.60 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 9H), 0.99 (d, *J* = 6.4 Hz, 3H), 1.04 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.32 (dd, *J* = 14.4, 4.8 Hz, 1H), 1.62 (dd, *J* = 13.6, 5.2 Hz, 1H), 1.70-1.82 (m, 1H), 1.84 (dd, *J* = 14.4, 4.4 Hz, 1H), 1.99-2.03 (m, 3H), 3.74 (s, 3H), 3.77-3.85 (m, 2H), 3.90-3.99 (m, 2H), 6.62-6.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.70, 24.32, 25.07, 30.12, 31.33, 46.54, 52.13, 52.41, 63.96, 64.31, 109.70, 130.21, 142.36, 168.77; IR (neat): 2953, 2893, 1720, 1650 cm^{-1}; EIMS *m/z* (relative intensity) 284 (M^+, 1), 253 (M^+-OMe, 6), 185 (18), 172 (28), 171 (100), 127 (17), 111 (23), 83 (14); HRMS (EI) *m/z* calcd for $C_{16}H_{28}O_4$ (M^+): 284.1988 , found: 284.1991.

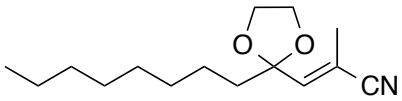
Methyl (*E*)-3-(2-cyclohexyl-1,3-dioxolan-2-yl)-2-methylacrylate (3c)



Colorless oil; R_f = 0.60 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09-1.26 (m, 5H), 1.60-1.86 (m, 6H), 2.01 (d, *J* = 1.2 Hz, 3H) 3.74 (s, 3H), 3.78-3.85 (m, 2H), 3.86-3.93 (m, 2H), 6.56 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.84, 26.26, 26.41, 26.87, 46.27, 52.15, 64.58, 111.26, 130.26, 140.83, 168.84; IR (neat): 2953, 2893, 1720, 1651, 1248 cm^{-1}; EIMS *m/z* (relative

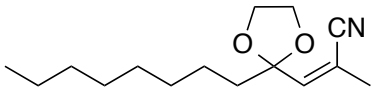
intensity) 223 (M^+-OMe, 3), 171 (100), 111 (16); HRMS (EI) *m/z* calcd for $C_{13}H_{19}O_3$ M^+-OMe: 223.1334, found: 223.1325.

(*E*)-2-Methyl-3-(2-octyl-1,3-dioxolan-2-yl)acrylonitrile (3d(*E*))



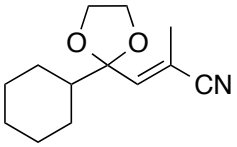
Colorless oil; R_f = 0.55 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.6 Hz, 3H), 1.18-1.34 (m, 10H), 1.34-1.45 (m, 2H), 1.71-1.77 (m, 2H), 2.00 (d, *J* = 1.6 Hz, 3H), 3.93-4.02 (m, 4H), 6.05 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.25, 21.91, 22.78, 23.10, 29.34, 29.62, 29.77, 31.97, 38.18, 65.21, 107.79, 109.79, 117.88, 147.08; IR (neat): 2953, 2926, 2855, 2219, 1648 cm^{-1}; EIMS *m/z* (relative intensity) 251 (M^+, 1), 185 (12), 139 (23), 138 (100), 94 (41); HRMS (EI) *m/z* calcd for $C_{15}H_{25}NO_2$ (M^+): 251.1885 , found: 251.1886.

(*Z*)-2-Methyl-3-(2-octyl-1,3-dioxolan-2-yl)acrylonitrile (3d(*Z*))



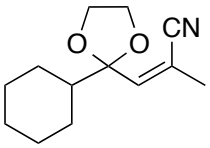
Colorless oil; R_f = 0.60 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.21-1.42 (m, 12H), 1.69-1.76 (m, 2H), 2.05 (d, *J* = 1.6 Hz, 3H), 3.79-3.88 (m, 2H), 3.91-4.00 (m, 2H), 6.23 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.25, 15.65, 22.78, 23.18, 29.33, 29.60, 29.80, 31.97, 38.04, 64.77, 109.09, 112.81, 120.32, 147.95; IR (neat): 2953, 2926, 2855, 2222, 1465 cm^{-1}; EIMS *m/z* (relative intensity) 251 (M^+, 2), 185 (11), 139 (24), 138 (100), 94 (38); HRMS (EI) *m/z* calcd for $C_{15}H_{25}NO_2$ (M^+): 251.1885 , found: 251.1886.

(*E*)-3-(2-Cyclohexyl-1,3-dioxolan-2-yl)-2-methylacrylonitrile (3e(*E*))



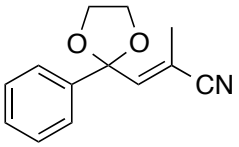
Colorless oil; R_f = 0.35 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04-1.27 (m, 5H), 1.60-1.70 (m, 2H), 1.72-1.85 (m, 4H), 2.02 (d, *J* = 1.2 Hz, 3H), 3.93-3.98 (m, 4H), 6.02 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.02, 26.09, 26.33, 26.64, 45.76, 65.22, 109.33, 110.10, 118.13, 146.33; IR (neat): 2929, 2854, 2219, 1452 cm^{-1}; EIMS *m/z* (relative intensity) 221 (M^+, 3), 139 (33), 138 (100), 94 (48); HRMS (EI) *m/z* calcd for $C_{13}H_{19}NO_2$ (M^+): 221.1416, found: 221.1402.

(*Z*)-3-(2-Cyclohexyl-1,3-dioxolan-2-yl)-2-methylacrylonitrile (3e(*Z*))



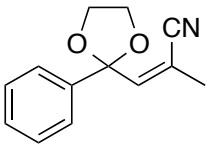
Colorless oil; R_f = 0.40 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01-1.28 (m, 5H), 1.60-1.70 (m, 2H), 1.72-1.82 (m, 4H), 2.05 (d, *J* = 1.6 Hz, 3H), 3.80-3.87 (m, 2H), 3.88-3.96 (m, 2H), 6.17 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.75, 26.09, 26.28, 26.69, 45.15, 64.76, 110.84, 112.78, 120.40, 147.15; IR (neat): 2931, 2855, 2221, 1453 cm^{-1}; EIMS *m/z* (relative intensity) 221 (M^+, 1), 139 (23), 138 (100), 94 (37); HRMS (EI) *m/z* calcd for $C_{13}H_{19}NO_2$ (M^+): 221.1416, found: 221.1430.

(*E*)-2-Methyl-3-(2-phenyl-1,3-dioxolan-2-yl)acrylonitrile (3f(*E*))



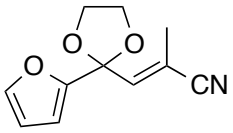
Colorless oil; R_f = 0.30 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (d, *J* = 1.2 Hz, 3H), 3.97-4.06 (m, 2H), 4.11-4.20 (m, 2H), 6.26 (q, *J* = 1.2 Hz, 1H), 7.32-7.41 (m, 3H), 7.54-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.95, 65.23, 106.34, 109.24, 117.61, 125.54, 128.57, 128.88, 140.00, 145.45; IR (neat): 3032, 3001, 2959, 2892, 2219, 1646 cm^{-1}; EIMS *m/z* (relative intensity) 215 (M^+, 72), 200 (100), 156 (10), 149 (50), 143 (20), 140 (13), 138 (53), 115 (11), 105 (35), 94 (30), 77 (25); HRMS (EI) *m/z* calcd for $C_{13}H_{13}NO_2$ (M^+): 215.0946, found: 215.0939.

(*Z*)-2-Methyl-3-(2-phenyl-1,3-dioxolan-2-yl)acrylonitrile (3f(*Z*))



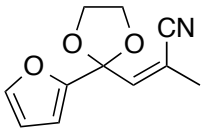
Colorless oil; R_f = 0.35 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (d, *J* = 1.6 Hz, 3H), 3.95-4.09 (m, 4H), 6.56 (q, *J* = 1.2 Hz, 1H), 7.33-7.41 (m, 3H), 7.44-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.09, 64.89, 107.63, 112.74, 120.26, 125.61, 128.71, 129.11, 139.80, 146.42; IR (neat): 3031, 3001, 2959, 2892, 2222, 1646, 1449 cm^{-1}; EIMS *m/z* (relative intensity) 215 (M^+, 42), 200 (M^+-Me, 100), 156 (10), 149 (22), 143 (18), 140 (9), 138 (42), 115 (7), 105 (19), 94 (20), 77 (13); HRMS (EI) *m/z* calcd for $C_{13}H_{13}NO_2$ (M^+): 215.0946, found: 215.0949.

(*E*)-3-(2-(Furan-2-yl)-1,3-dioxolan-2-yl)-2-methylacrylonitrile (3g(*E*))



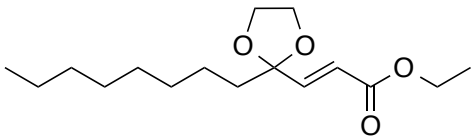
Colorless oil; R_f = 0.23 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (d, *J* = 1.2 Hz, 3H), 4.08-4.19 (m, 4H), 6.35-6.37 (m, 1H), 6.44 (q, *J* = 1.2 Hz, 1H), 6.54-6.58 (m, 1H), 7.42-7.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.04, 65.70, 102.29, 108.81, 110.37, 111.70, 117.06, 142.62, 143.56, 151.18; IR (neat): 3123, 2926, 2896, 2221, 1651 cm^{-1}; EIMS *m/z* (relative intensity) 205 (M^+, 41), 190 (M^+-Me, 100), 177 (9), 146 (17), 145 (9), 139 (30), 138 (16), 133 (91), 117 (10), 116 (10), 104 (13), 95 (45), 94 (26), 90 (10), 89 (9), 86 (6), 63 (23); HRMS (EI) *m/z* calcd for $C_{10}H_8NO_3$ (M^+-Me): 190.0504, found: 190.0510.

(*Z*)-3-(2-(Furan-2-yl)-1,3-dioxolan-2-yl)-2-methylacrylonitrile (3g(*Z*))



Colorless oil; R_f = 0.25 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (d, *J* = 2.0 Hz, 3H), 4.02-4.11 (m, 4H), 6.34-6.36 (m, 1H), 6.54 (q, *J* = 1.6 Hz, 1H), 6.45-6.48 (m, 1H), 7.42-7.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.39, 65.31, 103.39, 108.96, 110.36, 114.93, 120.01, 143.78, 143.86, 151.02; IR (neat): 3121, 2960, 2896, 2224, 1646 cm^{-1}; EIMS *m/z* (relative intensity) 205 (M^+, 55), 190 (M^+-Me, 100), 177 (12), 146 (20), 145 (16), 139 (52), 138 (17), 133 (87), 117 (20), 116 (15), 104 (14), 95 (71), 94 (37), 90 (17), 89 (14), 86 (11), 84 (21), 64 (12), 63 (12); HRMS (EI) *m/z* calcd for $C_{10}H_8NO_3$ (M^+-Me):190.0504, found: 190.0510.

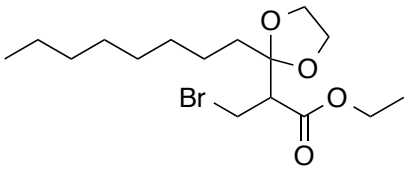
Ethyl (*E*)-3-(2-octyl-1,3-dioxolan-2-yl)acrylate (3h)



Colorless oil; R_f = 0.60 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.19-1.41 (m, 15H), 1.69-1.76 (m, 2H), 3.83-4.01 (m, 4H), 4.20 (q, *J* = 6.8 Hz,2H), 6.06 (d, *J* = 15.6 Hz, 1H), 6.73 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.23, 14.33, 22.77, 23.27, 29.34, 29.60, 29.84, 31.97, 37.96, 60.72, 64.98, 108.49, 121.70, 146.60, 166.42; IR (neat): 2926, 2872, 1724, 1660 cm^{-1}; EIMS *m/z* (relativeintensity) 284 (M^+, 2), 239 (M^+-OEt, 10), 185 (21), 172

(17), 171 (100), 127 (9), 99 (10); HRMS (EI) *m/z* calcd for $C_{14}H_{23}O_3$ (M^+-OEt): 239.1647, found: 239.1645.

Ethyl 3-bromo-2-(2-heptyl-1,3-dioxolan-2-yl)propanoate (3h')

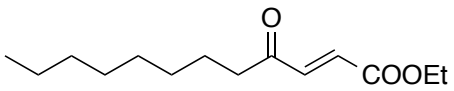


Colorless oil; R_f = 0.63 (hexane : EtOAc = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.18-1.44 (m, 15H), 1.56-1.66 (m, 1H), 1.70-1.81 (m, 1H), 3.19 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.51 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.72 (dd, J = 12.0, 10.0 Hz, 1H), 3.95-4.01 (m, 4H), 4.24 (q, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.22, 14.33, 22.70, 22.76, 29.02, 29.33, 29.65, 29.74, 31.96, 35.66, 57.05, 61.23, 65.63, 65.69, 110.79, 170.49; IR (neat): 2955, 2926, 2855, 1738, 1200 cm^{-1}; EIMS *m/z* (relative intensity) 253 (M^+-C_8H_{17},20), 251 (M^+-C_8H_{17}, 21), 185 (100), 171 (37), 99 (17); HRMS (EI) *m/z* calcd for $C_8H_{12}O_4Br$ (M^+-C_8H_{17}): 250.9919, found: 250.9918.

Procedure for deprotection of vinylated dioxolane 3h

To a 20 mL screw capped test tube, ethyl (*E*)-3-(2-octhyl-1,3-dioxolan-2-yl)acrylate (**3h**, 35.7 mg, 0.126 mmol), and *p*-TsOH · H_2O (28.7 mg, 0.15 mmol), acetone (0.5 mL) were added. This test tube was purged with argon and sealed. The reaction mixture was stirred at room temperature for 20 h. Water was added to the reaction mixture, and the reaction mixture was extracted with diethyl ether and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on SiO_2 (Hexane/EtOAc = 30 : 1) to give ethyl (*E*)-4-oxododec-2-enoate (**5**, 24.8 mg, 82%).

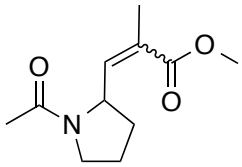
Ethyl (*E*)-4-oxododec-2-enoate (5)



Colorless oil; R_f = 0.25 (hexane : EtOAc = 20 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.27-1.32 (m, 10H), 1.33 (t, *J* = 6.8 Hz, 3H), 1.61-1.65 (m, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 4.24 (q, *J* = 6.8 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.22, 14.26, 22.76, 23.83, 29.23, 29.24, 29.45, 31.93, 41.69, 61.52, 130.80, 139.51, 165.77, 200.12; IR (neat): 2927, 2856, 1728, 1703, 1303 cm^{-1}; EIMS *m/z* (relative intensity) 240

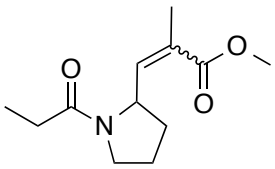
(M^+, 3), 195 (M^+-OEt, 20), 169 (27), 167 (100), 142 (61), 127 (47), 114 (24), 57 (29), 55 (27); HRMS (EI) *m/z* calcd for $C_{12}H_{19}O_2$ (M^+-OEt): 195.1385, found: 195.1385.

Methyl 3-(1-acetylpyrrolidin-2-yl)-2-methylacrylate (7a)



Obtained as an inseparable mixture (*E/Z* = 47/53); yellow oil; R_f = 0.13 (hexane : EtOAc = 1 : 3); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.78 (m, 1H), 1.90-2.10 (m, 2H), 1.97 (d, *J* = 1.4 Hz, 3H), 2.05 (s, 3H), 2.05-2.20 (m, 1H), 3.45-3.70 (m, 2H), 3.71 (s, 3H), 4.77-4.81 (m, 1H), 6.55-6.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.53, 23.08, 24.66, 31.15, 47.65, 51.68, 54.85, 127.65, 141 .99, 167.74, 169.18; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78-1.85 (m,1H), 1.90-2.10 (m, 2H), 1.93 (d, *J* = 1.4 Hz, 3H), 1.95 (s, 3H), 2.20-2.31 (m, 1H), 3.74-3.66 (m, 2H), 3.76 (s, 3H), 4.53-4.58 (m, 1H), 6.65-6.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.41, 22.17, 23.09, 33.15, 46.16, 51.99, 56.33, 127.65, 141.53, 168.36, 169.49; IR(neat): 2952, 2876, 1714, 1650, 1435, 1415, 1257, 748 cm^{-1}; EIMS *m/z* (relative intensity); *Z* isomer: 211 (M^+, 3), 168 (100), 138 (16), 136 (56), 110 (17); HRMS (EI) *m/z* calcd for $C_9H_{14}NO_2$ (M^+-C_2H_3O): 168.1025, found: 168.1033.

Methyl 2-methyl-3-(1-propionylpyrrolidin-2-yl)acrylate (7b)



Obtained as an inseparable mixture (*E/Z* = 40/60); yellow oil; R_f = 0.13 (hexane : EtOAc = 1 : 3); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08-1.15 (m, 3H), 1.70-2.32 (m, 6H), 1.99 (s, 3H), 3.44-3.78 (m, 2H), 3.71 (s, 3H), 4.78-4.80 (m, 1H), 6.54 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.84, 12.67, 24.86, 28.05, 31.13, 46.88, 51.88, 55.11, 127.78, 142.03, 168.64, 172.52; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ1.08-1.15 (m, 3H), 1.70-2.32 (m, 6H), 1.93 (s, 3H), 3.44-3.78 (m, 2H), 3.76 (s, 3H), 4.54-4.59 (m, 1H), 6.64 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.21, 12.61, 23.13, 27.53, 33.41, 46.43, 52.19, 55.74, 127.64, 142.15, 168.00, 172.88; IR(neat): 2975, 2951, 2875, 1714, 1651, 1417, 748 cm^{-1}; EIMS m/z (relative intensity); 225 (M^+, 2), 168 (100), 136 (48), 110 (16); HRMS (EI) m/z calcd for $C_{12}H_{19}O_3N$ (M^+): 225.1365, found: 225.1361.

Data for MO Calculations.

Molecular orbital calculations were carried out using the Gaussian 09 program.[4] Geometry optimizations were performed using standard gradient techniques at the HF level of theory using restricted (RHF) and unrestricted (UHF) methods for closed- and open-shell systems respectively.[5] All ground and transition states were verified by vibrational frequency analysis.

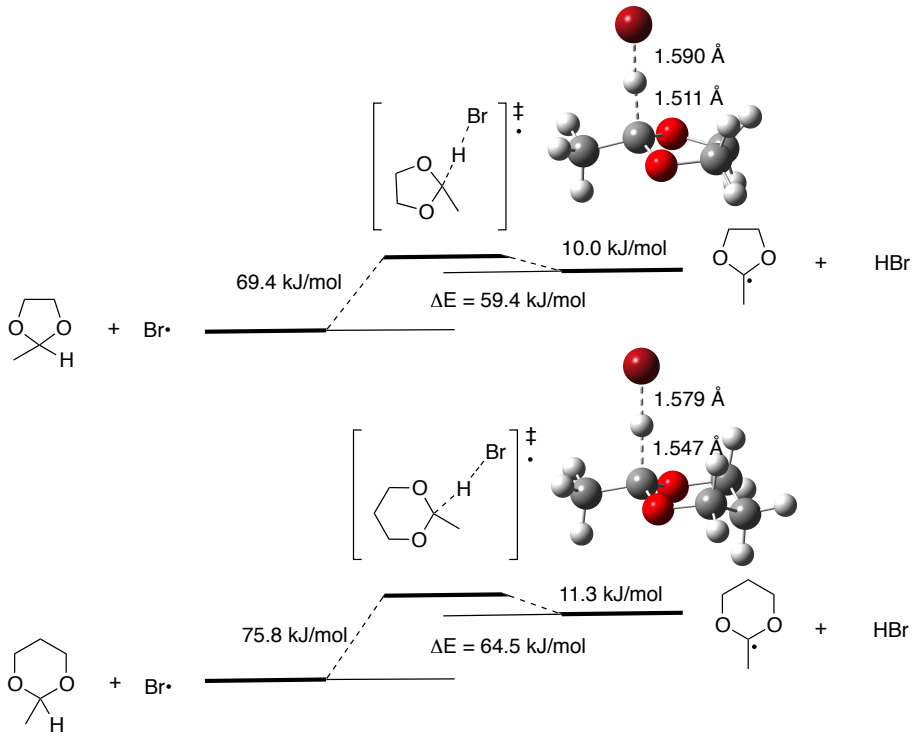


Fig. S1 Reaction profile of abstraction of α-hydrogen in 2-methyl-1,3-dioxolane and 2-methyl-1,3-dioxane with a bromine radical at the HF/6-311G**(C,H,O)+LanL2DZdp(Br) level.

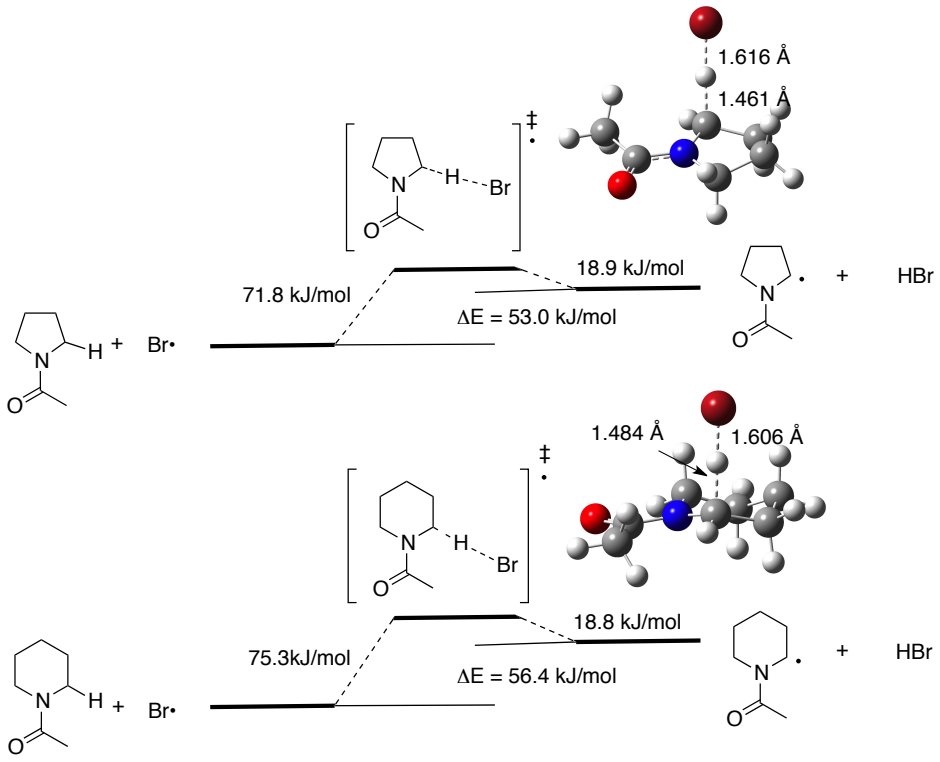


Fig. S2 Reaction profile of abstraction of α-hydrogen in *N*-acetylpyrrolidine and *N*-acetylpiperidine with a bromine radical at the HF/6-311G**(C,H,O)+LanL2DZdp(Br) level.

Gaussian Archives and imaginary frequencies of optimized transition states of α-hydrogen abstraction at the HF/6-311G**(C,H,O,N) + LanL2DZdp (Br) level

2-methyl-1,3-dioxolane

1¥1¥GINC-I7¥FTS¥UHF¥Gen¥C4H8Br1O2(2)¥HIROSHI¥16-Apr-2014¥1¥¥#HF/gen pseudo=read geom=check guess=read OPT=(TS,Z-matrix,NoEigenTest,ReadFC,Maxcycle=150) Nosymm¥¥TS dioxolane¥¥0,2¥C¥C,1,B1¥C,1,B2,2,A1¥H,1,B3,2,A2,3,D1,0¥H,1,B4,2,A3,3,D2,0¥H,2,B5,1,A4,3,D3,0¥H,2,B6,1,A5,3,D4,0¥H,3,B7,1,A6,2,D5,0¥O,3,B8,1,A7,2,D6,0¥O,3,B9,1,A8,9,D7,0¥Br,3,B10,1,A9,9,D8,0¥C,3,B11,1,A10,9,D9,0¥H,12,B12,3,A11,1,D10,0¥H,12,B13,3,A12,1,D11,0¥H,12,B14,3,A13,1,D12,0¥¥B1=1.53066921¥B2=2.22292728¥B3=1.0791913¥B4=1.08307309¥B5=1.08231418¥B6=1.08067038¥B7=1.51072605¥B8=1.34788198¥B9=1.35109563¥B10=3.09943155¥B11=1.49538891¥B12=1.0819875¥B13=1.08194469¥B14=1.08666195¥A1=71.20738143¥A2=113.84468965¥A3=112.23111071¥A4=112.67860308¥A5=113.10827342¥A6=98.42977424¥A7=37.37019019¥A8=76.25420107¥A9=97.07214816¥A10=150.20908567¥A11=109.8768809¥A12=109.79009319¥A13=109.03430193¥D1=133.66414062¥D2=-100.82804652¥D3=-115.05646005¥D4=119.92426128¥D5=-104.99891367¥D6=151.10535321¥D7=-152.76880821¥D8=104.00074442¥D9=-33.65071087¥D10=77.07056897¥D11=-162.38580453¥D12=-42.71799665¥¥Version=EM64L-G09RevC.01¥HF=-318.8136225¥S2=0.777999¥S2-1=0.¥S2A=0.750304¥RMSD=8.927e-09¥RMSF=4.433e-06¥Dipole=-1.128058,-1.430596,0.2905139¥Quadrupole=2.3583151,-3.957663,1.5993479,-7.9787848,-0.0583655,-1.0094782¥PG=C01 [X(C4H8Br1O2)]¥¥@

Imaginary frequency: 692.4552i

2-methyl-1,3-dioxane

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Imaginary frequency: 627.4740i

***N*-acetylpyrrolidine**

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Imaginary frequency: 954.8861i

***N*-acetylpiperidine**

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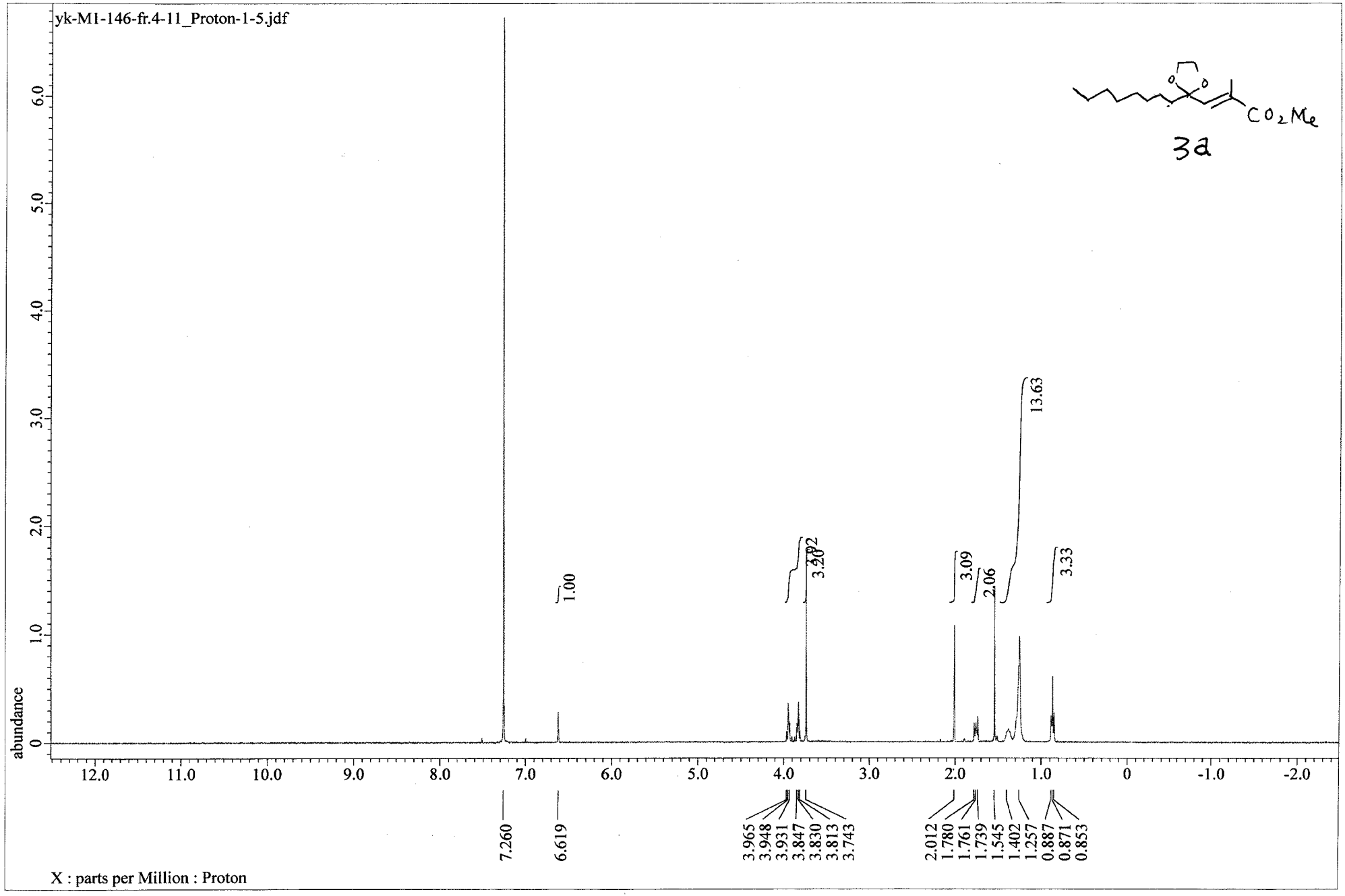
4. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
5. W. J. Hehre, L. Radom, P. v. R. Schleyer, P. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.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3.33
7.260
6.619
3.965
3.948
3.931
3.847
3.830
3.813
3.743
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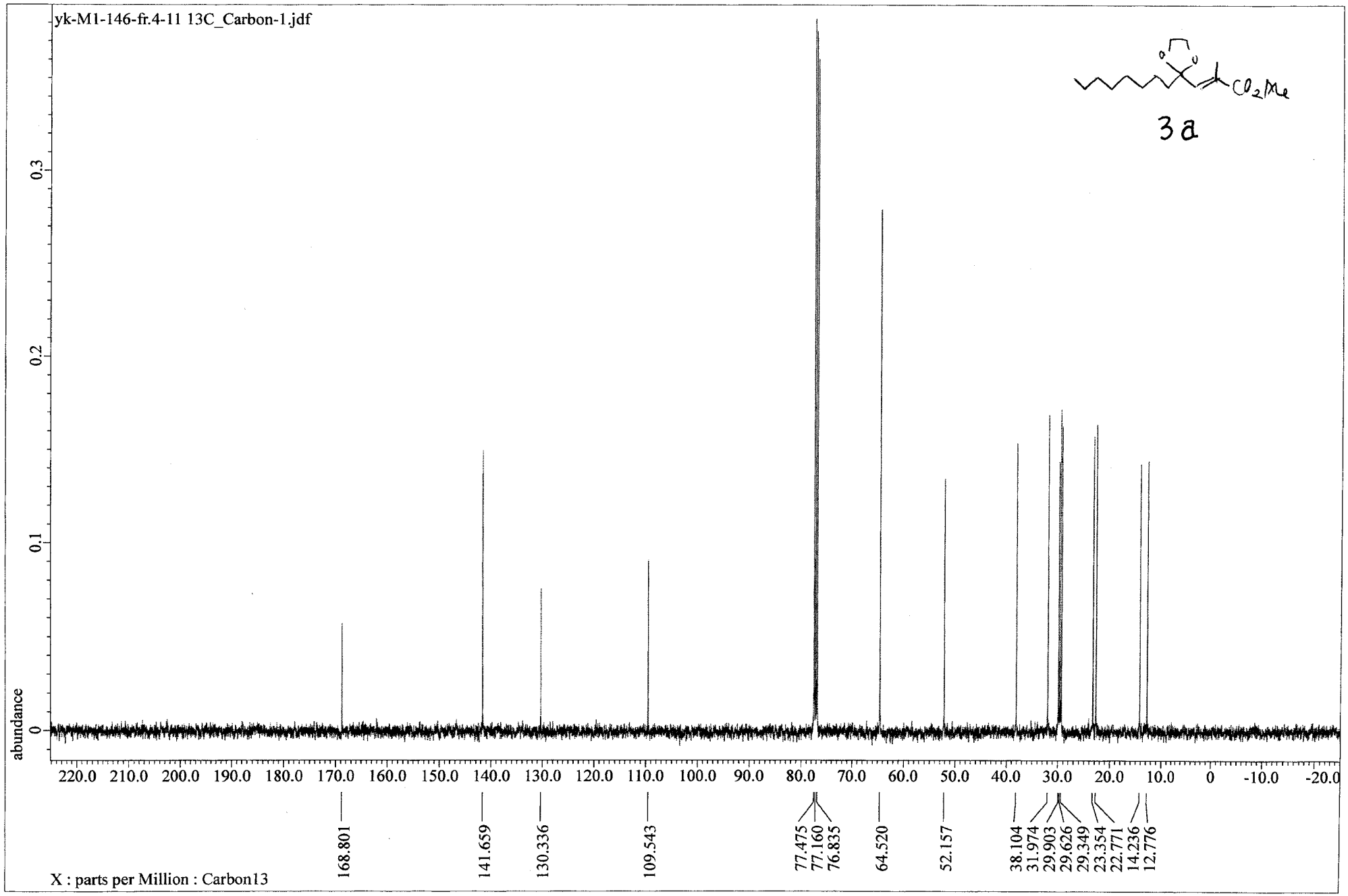
X : parts per Million : Proton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130.336
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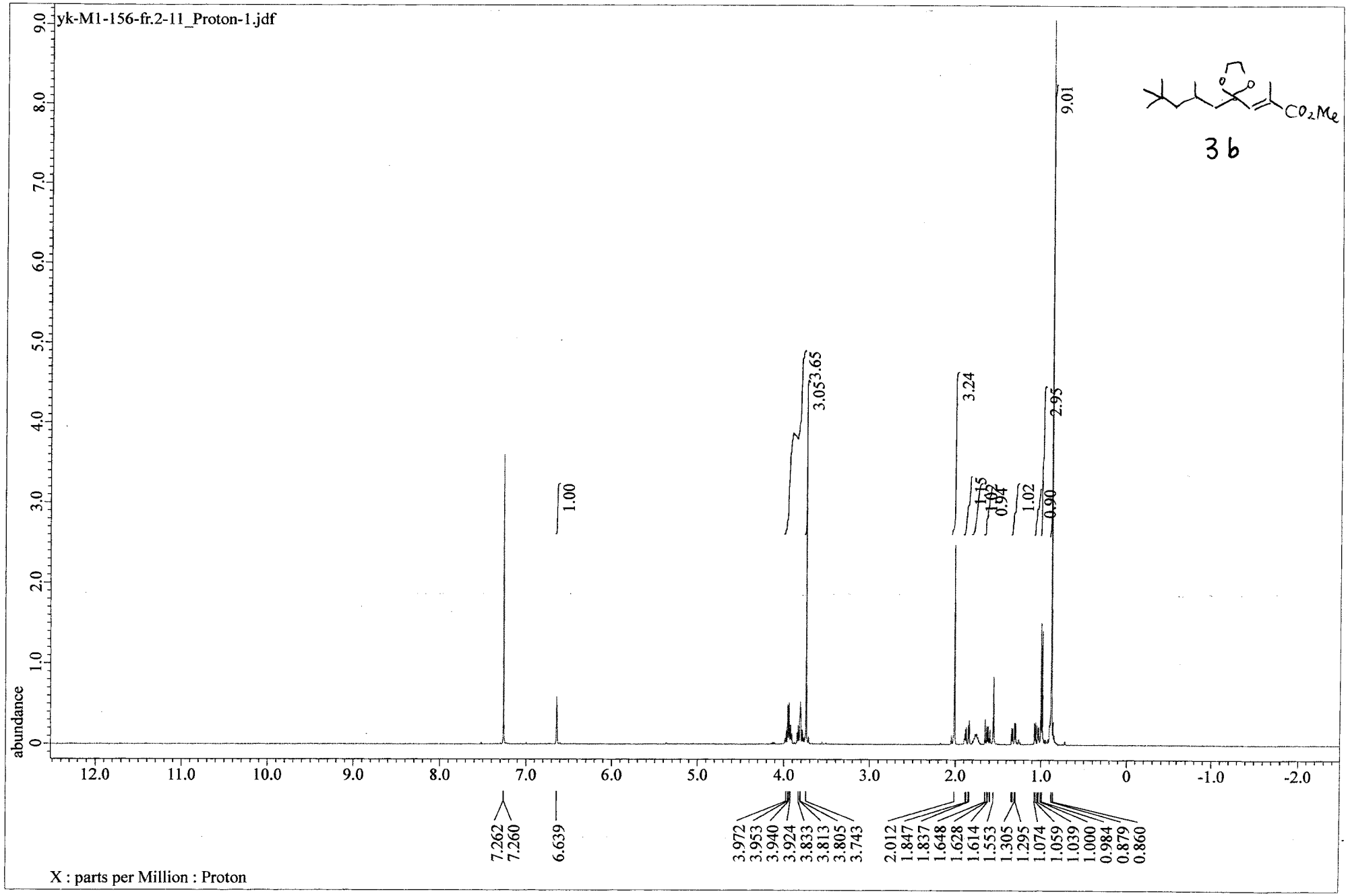
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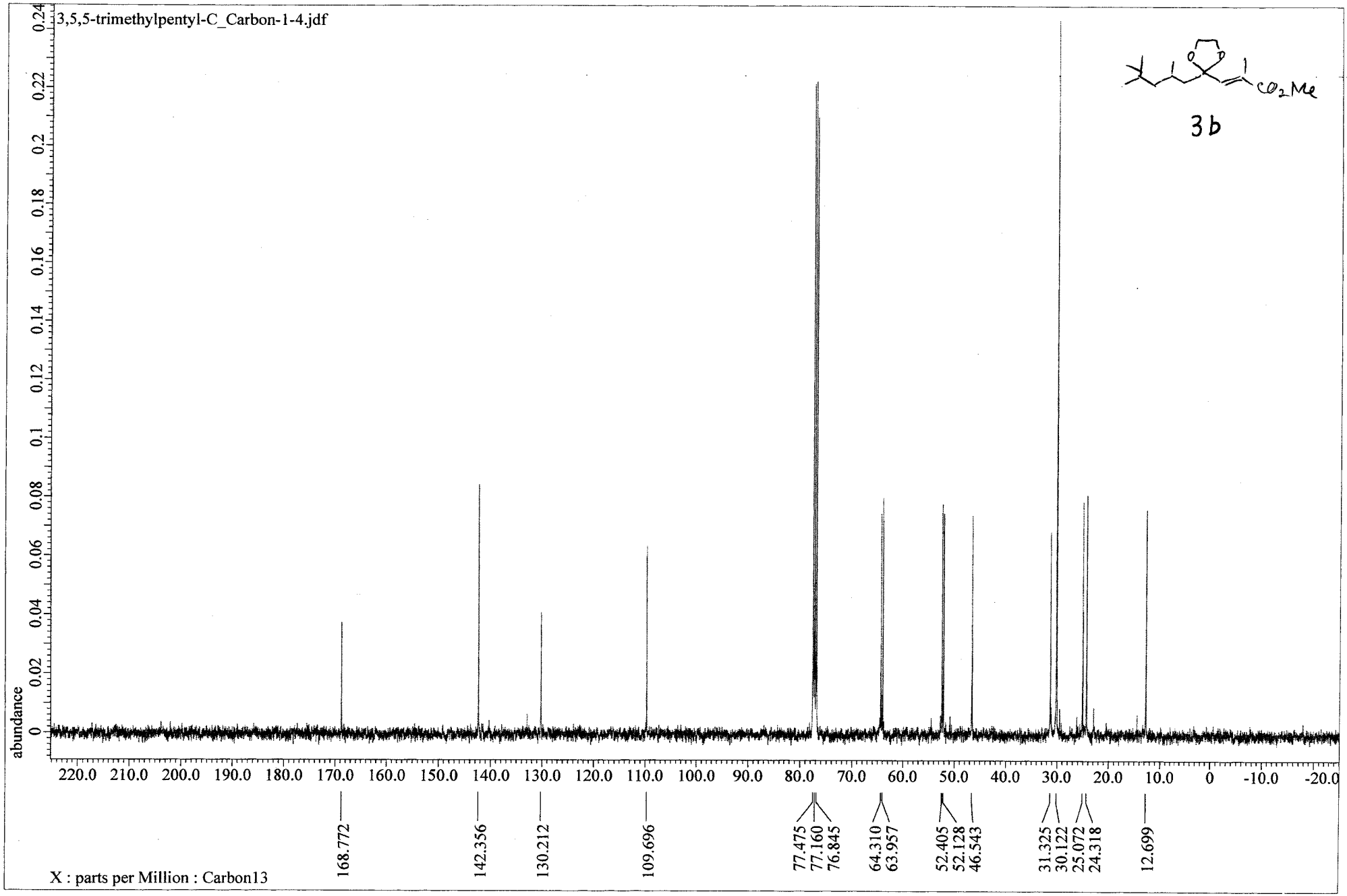
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0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
168.772
142.356
130.212
109.696
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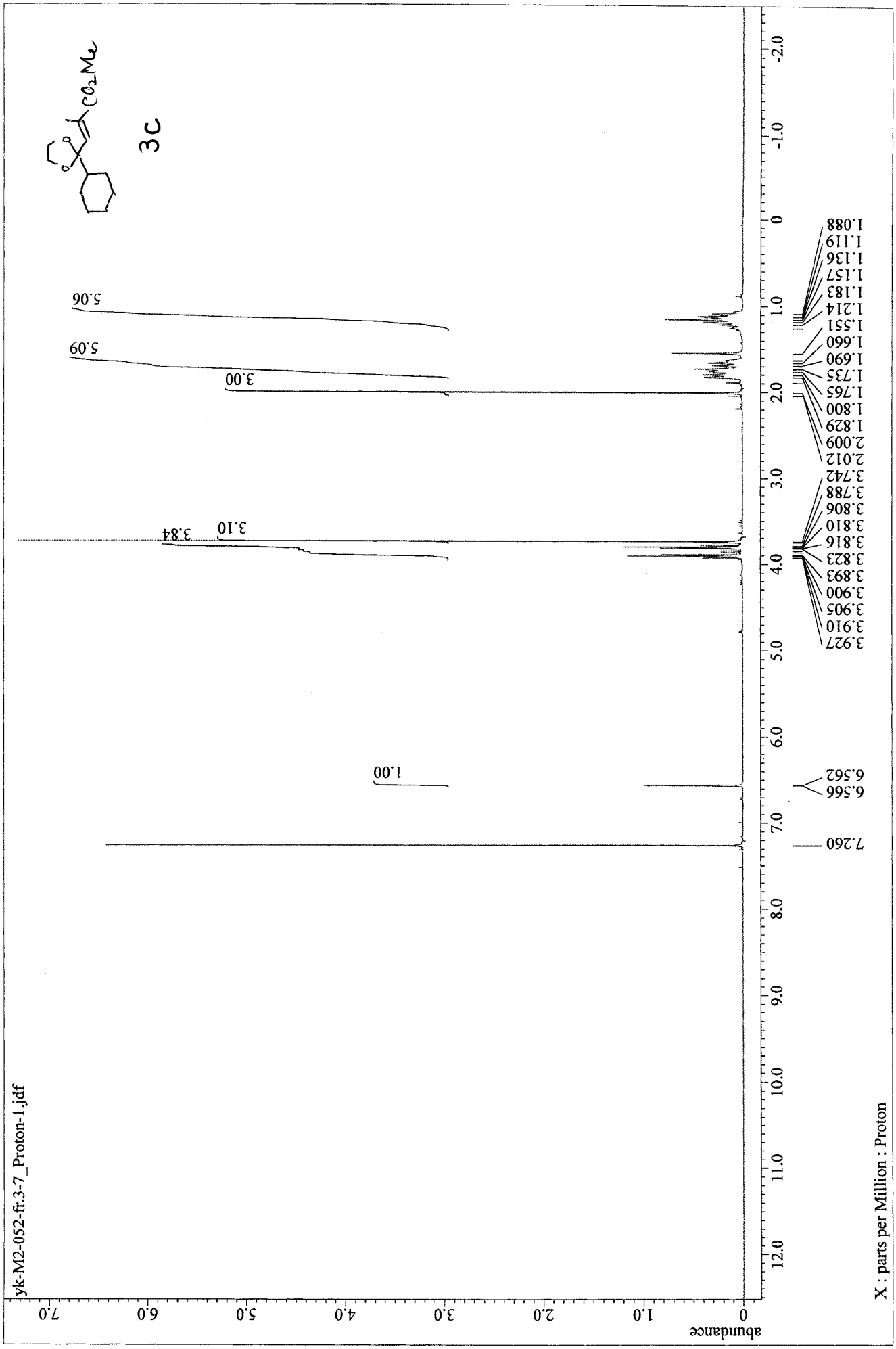
X : parts per Million : Carbon13
CO2Me
3b


yk-M2-052-fr.3-7_Proton-1.jdf
X : parts per Million : Proton
abundance
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CO2Me
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6.566
6.562
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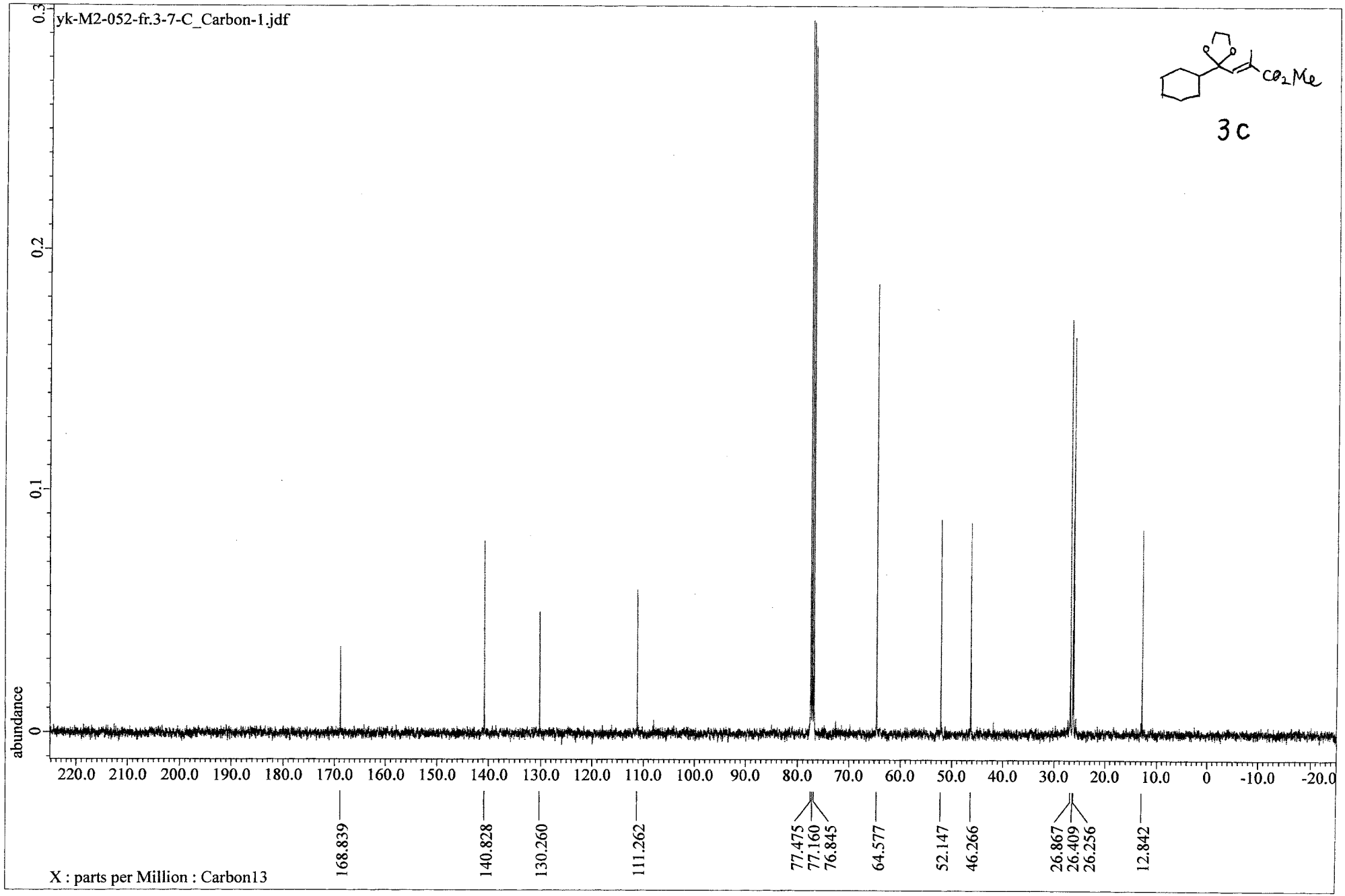
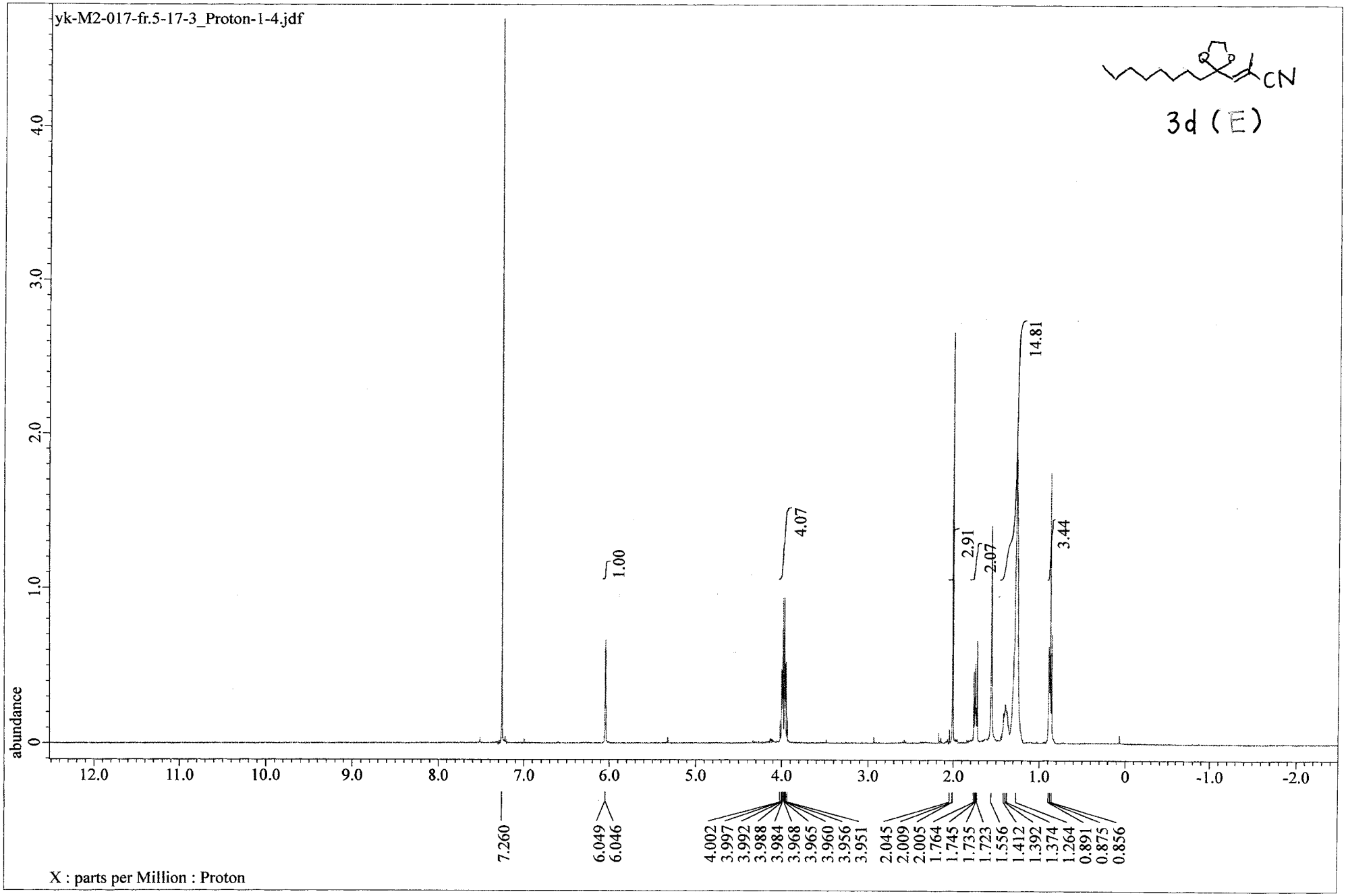
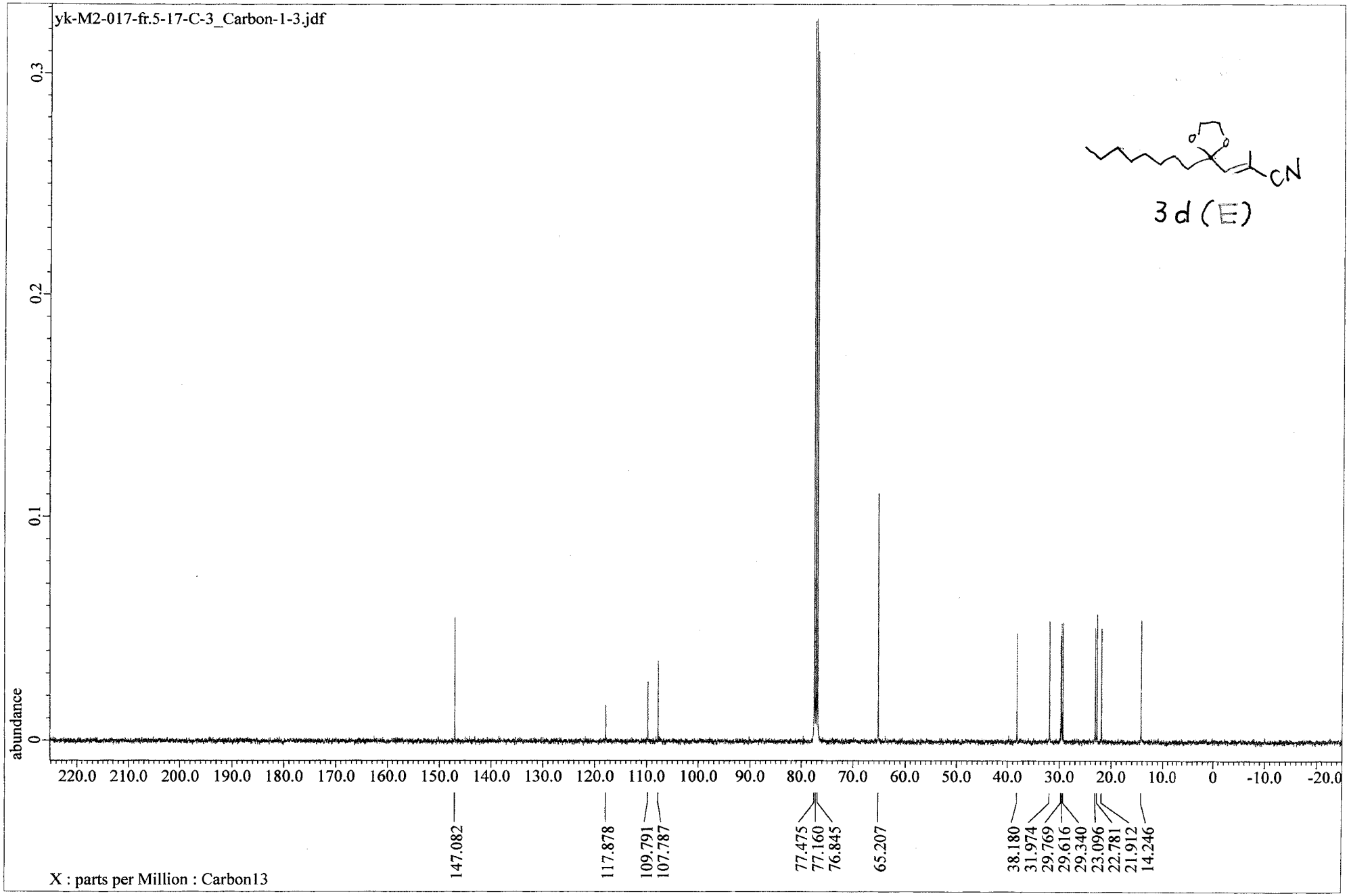
3.900
3.893
3.823
3.816
3.810
3.806
3.788
3.742
2.012
2.009
1.829
1.800
1.765
1.735
1.690
1.660
1.551
1.214
1.183
1.157
1.136
1.119
1.088
5.06
5.09
3.00
3.10
3.84
1.00


yk-M2-052-fr.3-7-C_Carbon-1.jdf
CO2Me
3c
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
168.839
140.828
130.260
111.262
77.475
77.160
76.845
64.577
52.147
46.266
26.867
26.409
26.256
12.842
X : parts per Million : Carbon13

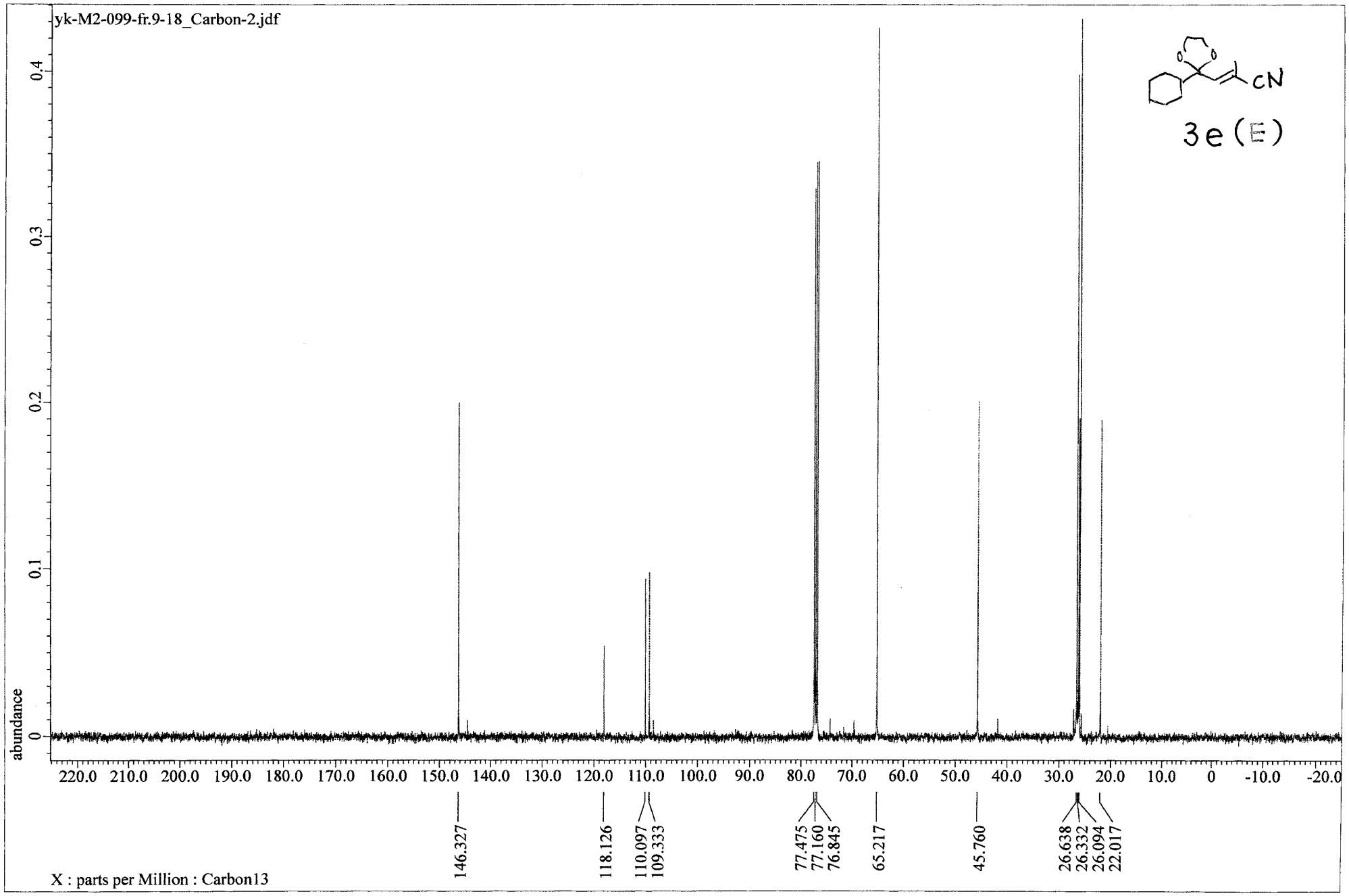

yk-M2-017-fr.5-17-3_Proton-1-4.jdf
3d (E)
CN
abundance
X : parts per Million : Proton
1.00
4.07
2.91
2.07
14.81
3.44
7.260
6.049
6.046
4.002
3.997
3.992
3.988
3.984
3.968
3.965
3.960
3.956
3.951
2.045
2.009
2.005
1.764
1.745
1.735
1.723
1.556
1.412
1.392
1.374
1.264
0.891
0.875
0.856

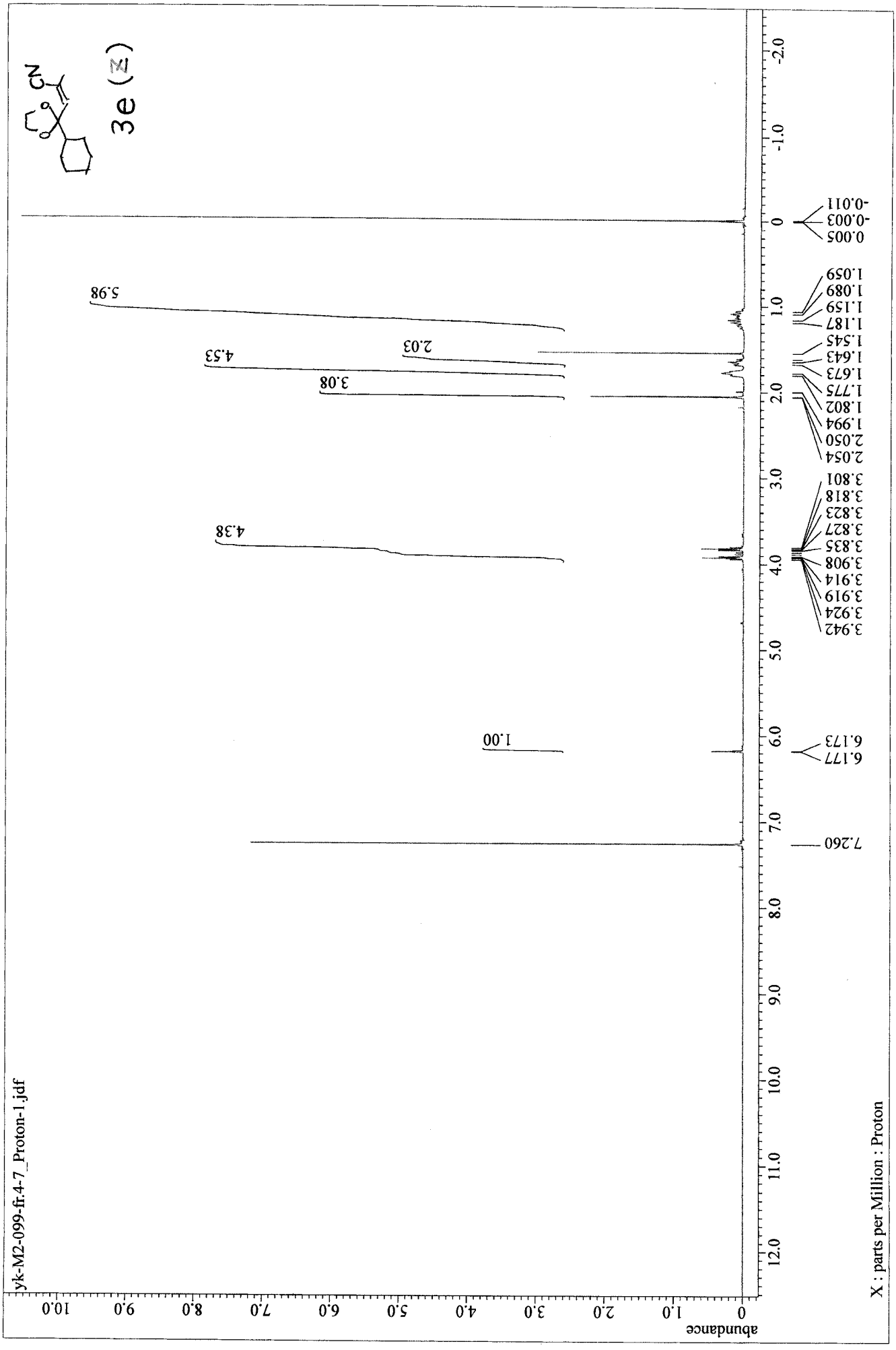

yk-M2-017-fr.5-17-C-3_Carbon-1-3.jdf
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.082
117.878
109.791
107.787
77.475
77.160
76.845
65.207
38.180
31.974
29.769
29.616
29.340
23.096
22.781
21.912
14.246
X : parts per Million : Carbon13
CN
3d (E)

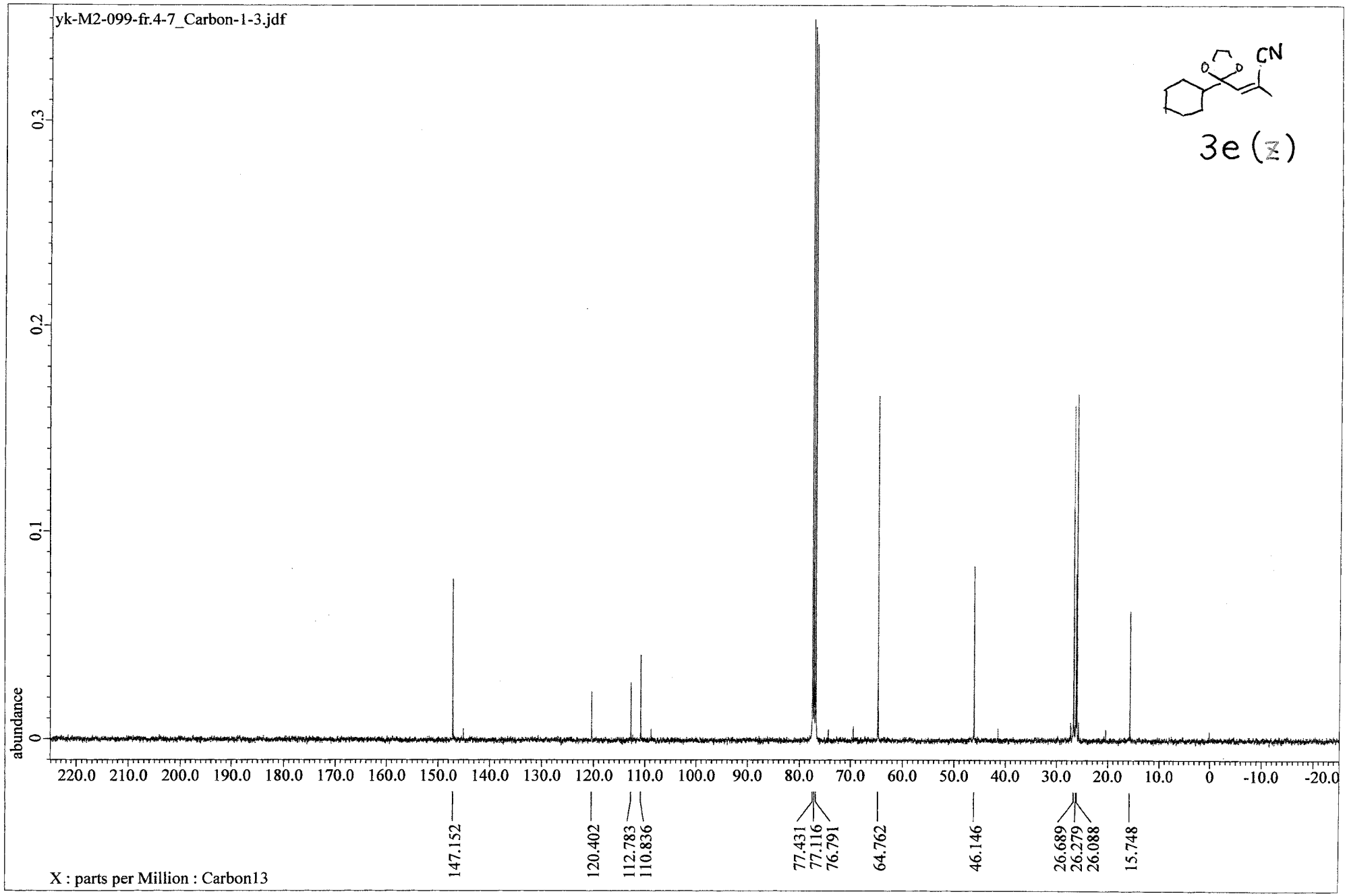
yk-M2-017-fr.1-5-2_Proton-1.jdf
abundance
X : parts per Million : Proton
7.260
6.231
6.228
3.977
3.959
3.956
3.951
3.943
3.878
3.853
3.845
3.840
3.835
3.818
2.057
2.053
1.744
1.726
1.715
1.704
1.554
1.368
1.297
1.265
0.895
0.878
0.861
1.00
2.08
2.12
3.06
2.00
14.06
3.46
3d (Z)

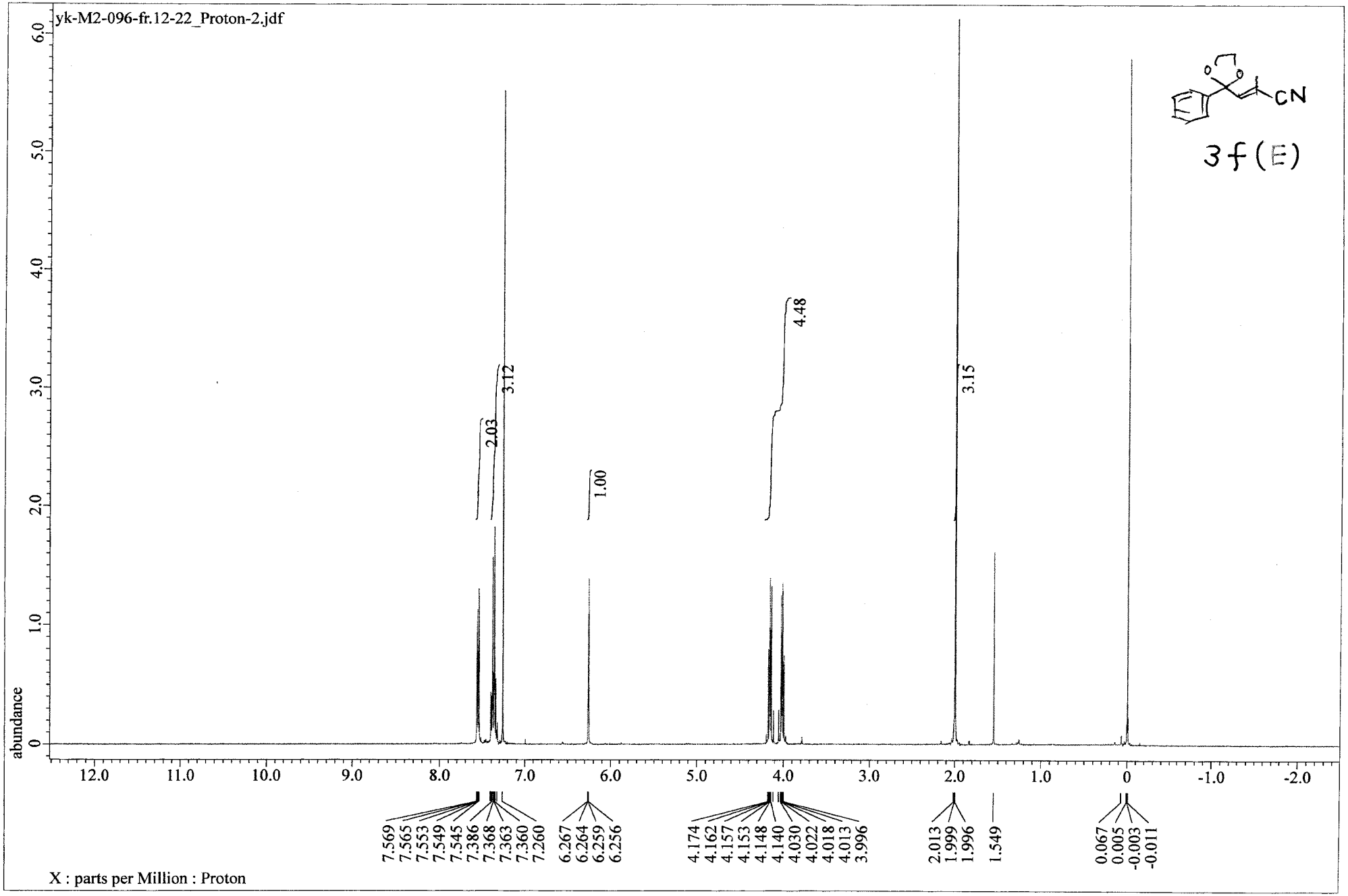
3d (Z)
abundance
0.3
0.2
0.1
0
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.950
120.322
112.808
109.094
77.475
77.160
76.845
64.768
38.037
31.974
29.798
29.597
29.330
23.182
22.781
15.649
14.246

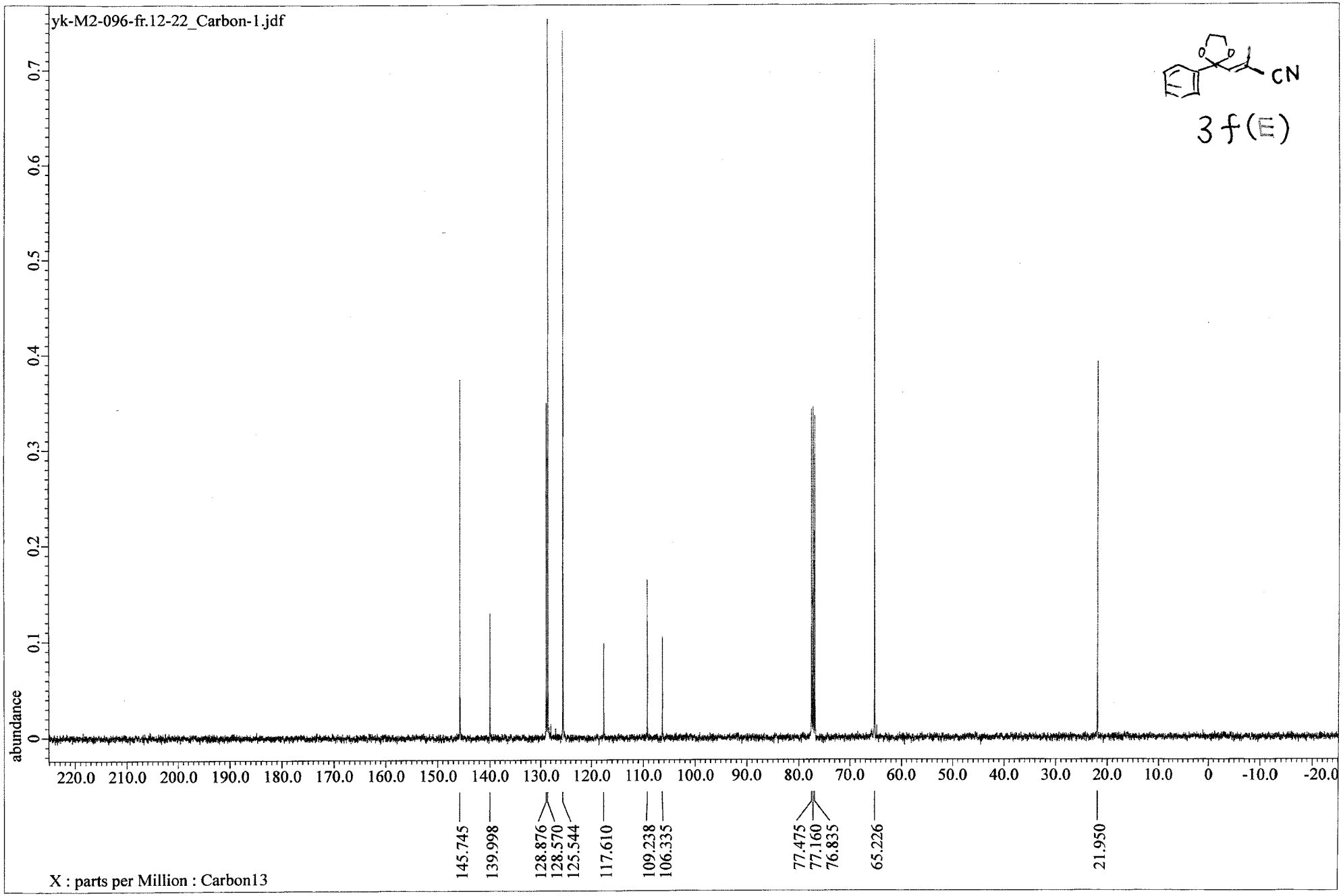
yk-M2-099-fr.9-18_Proton-1.jdf
abundance
X : parts per Million : Proton
3e (E)
CN
7.260
6.030
6.025
6.022
6.018
4.794
4.781
3.955
3.949
3.945
3.520
3.500
2.020
2.017
1.820
1.786
1.751
1.649
1.553
1.189
1.161
1.152
1.119
0.065
0.004
-0.004
-0.012
1.00
4.14
3.18
1.98
4.29
5.71


yk-M2-099-fr.9-18_Carbon-2.jdf
abundance
0
0.1
0.2
0.3
0.4
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
146.327
118.126
110.097
109.333
77.475
77.160
76.845
65.217
45.760
26.638
26.332
26.094
22.017
X : parts per Million : Carbon13
CN
3e(E)

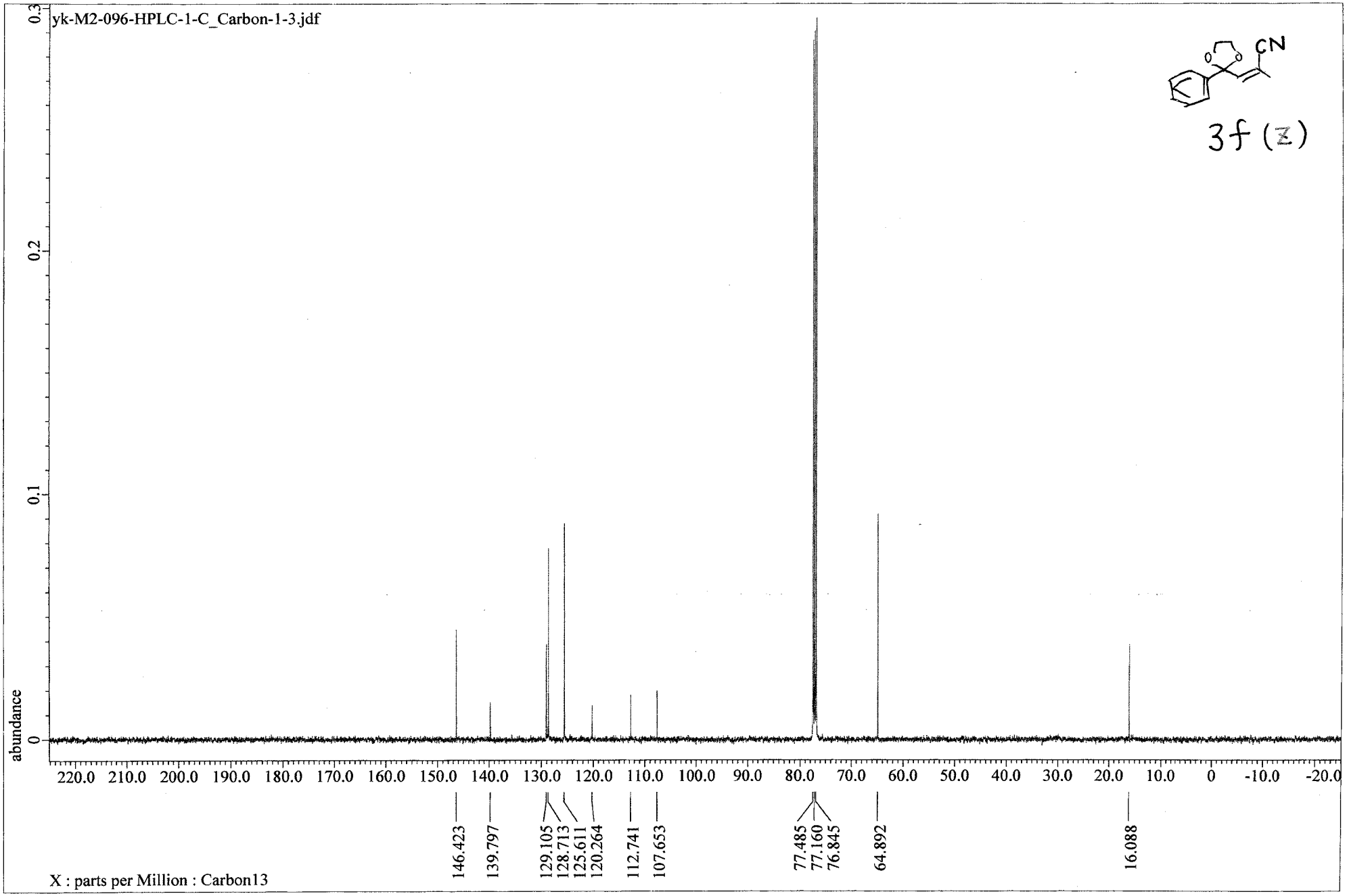

yk-M2-099-fr-4-7_Proton-1.jdf
3e (Z)
CN
X : parts per Million : Proton
abundance
7.260
6.177
6.173
1.00
4.38
3.942
3.924
3.919
3.914
3.908
3.835
3.827
3.823
3.818
3.801
5.98
4.53
3.08
2.03
2.054
2.050
1.994
1.802
1.775
1.673
1.643
1.545
1.187
1.159
1.089
1.059
0.005
-0.003
-0.011

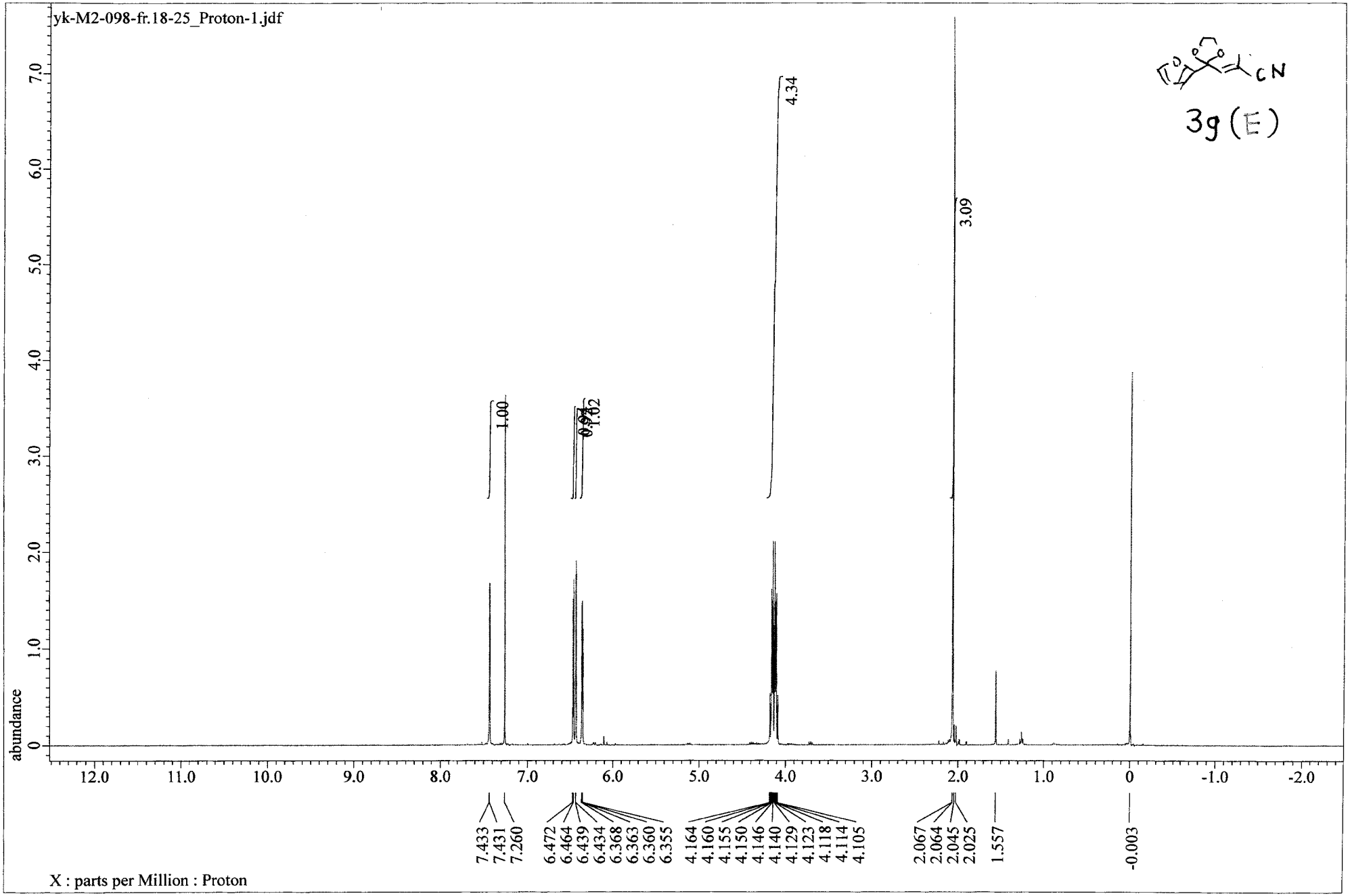

yk-M2-099-fr.4-7_Carbon-1-3.jdf
CN
3e (Z)
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.152
120.402
112.783
110.836
77.431
77.116
76.791
64.762
46.146
26.689
26.279
26.088
15.748
X : parts per Million : Carbon13

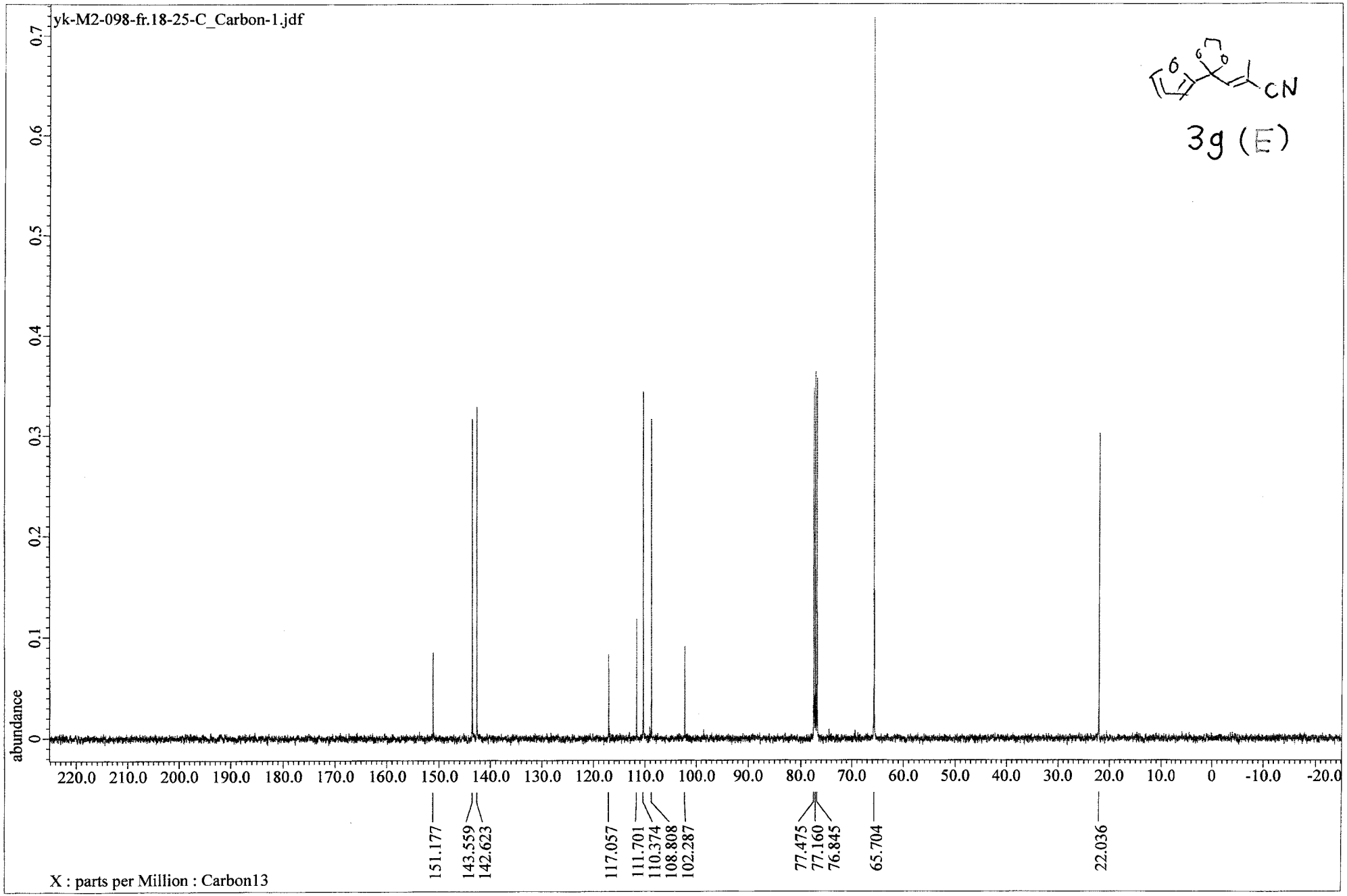

yk-M2-096-fr.12-22_Proton-2.jdf
abundance
X : parts per Million : Proton
2.03
3.12
1.00
4.48
3.15
7.569
7.565
7.553
7.549
7.545
7.386
7.368
7.363
7.360
7.260
6.267
6.264
6.259
6.256
4.174
4.162
4.157
4.153
4.148
4.140
4.030
4.022
4.018
4.013
3.996
2.013
1.999
1.996
1.549
0.067
0.005
-0.003
-0.011
CN
3f(E)

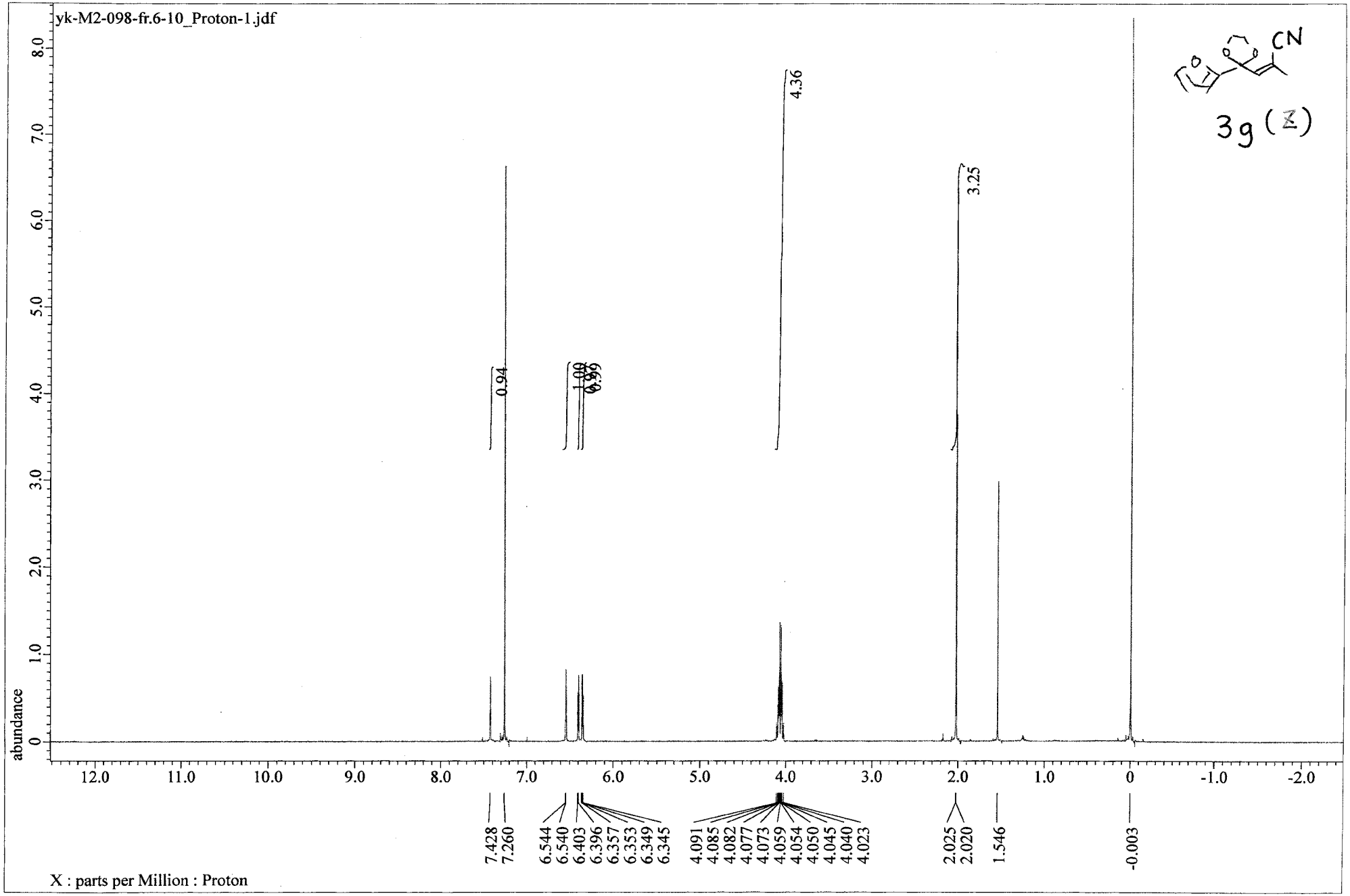

yk-M2-096-fr.12-22_Carbon-1.jdf
CN
3f(E)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
145.745
139.998
128.876
128.570
125.544
117.610
109.238
106.335
77.475
77.160
76.835
65.226
21.950
X : parts per Million : Carbon13

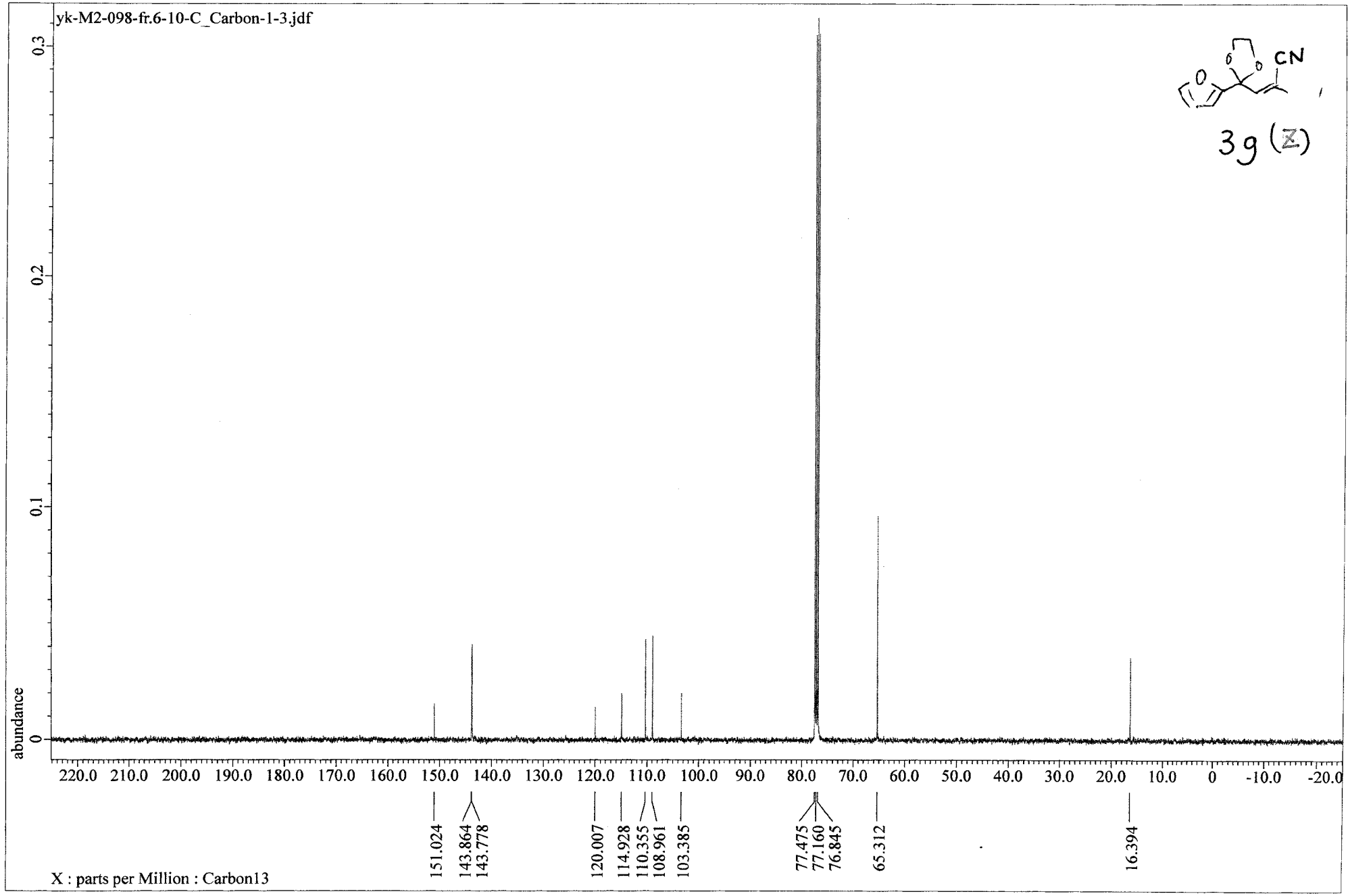
3f (S)
CN
yk-M2-096-HPLC-1_Proton-1-4.jdf
abundance
X : parts per Million : Proton
7.482
7.478
7.462
7.458
7.397
7.384
7.367
7.354
7.260
6.559
6.556
4.059
4.055
4.051
4.046
4.039
4.016
3.999
3.992
3.988
3.983
3.980
2.013
2.009
1.552
-0.001
3.17
2.08
1.00
4.46
3.13

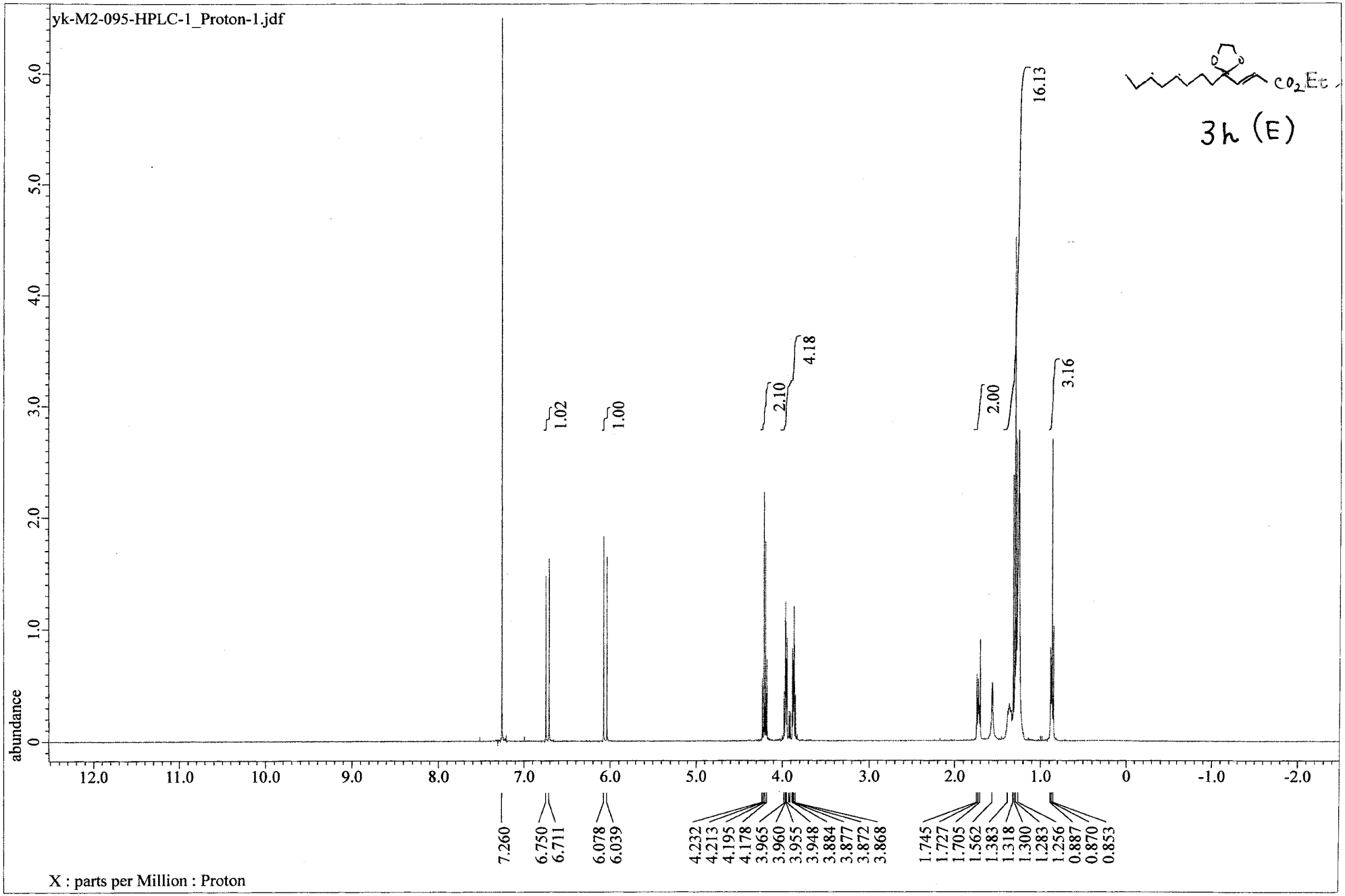

yk-M2-096-HPLC-1-C_Carbon-1-3.jdf
CN
3f (Z)
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
146.423
139.797
129.105
128.713
125.611
120.264
112.741
107.653
77.485
77.160
76.845
64.892
16.088
X : parts per Million : Carbon13

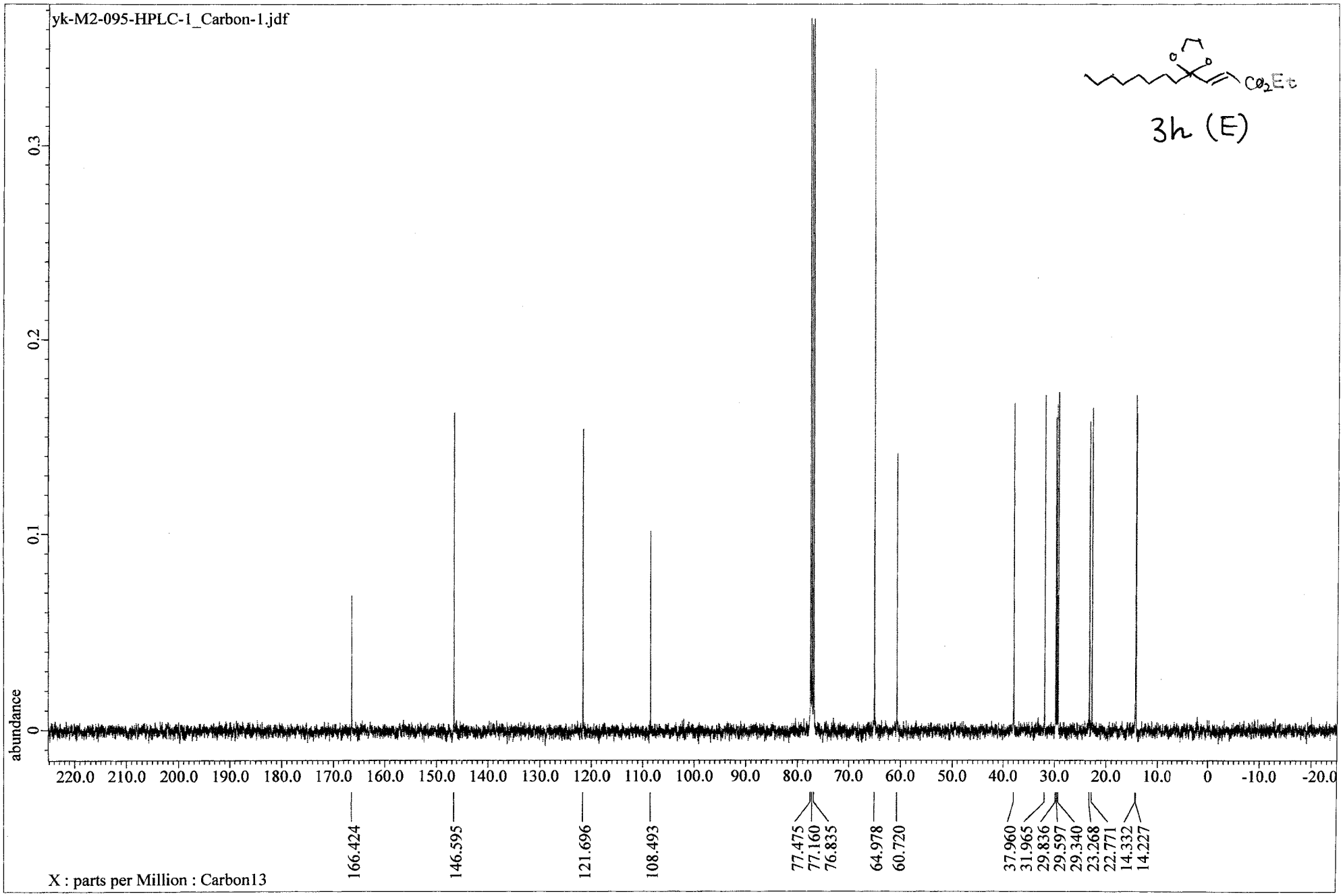

yk-M2-098-fr.18-25_Proton-1.jdf
3g (E)
CN
abundance
X : parts per Million : Proton
1.00
1.02
4.34
3.09
7.433
7.431
7.260
6.472
6.464
6.439
6.434
6.368
6.363
6.360
6.355
4.164
4.160
4.155
4.150
4.146
4.140
4.129
4.123
4.118
4.114
4.105
2.067
2.064
2.045
2.025
1.557
-0.003

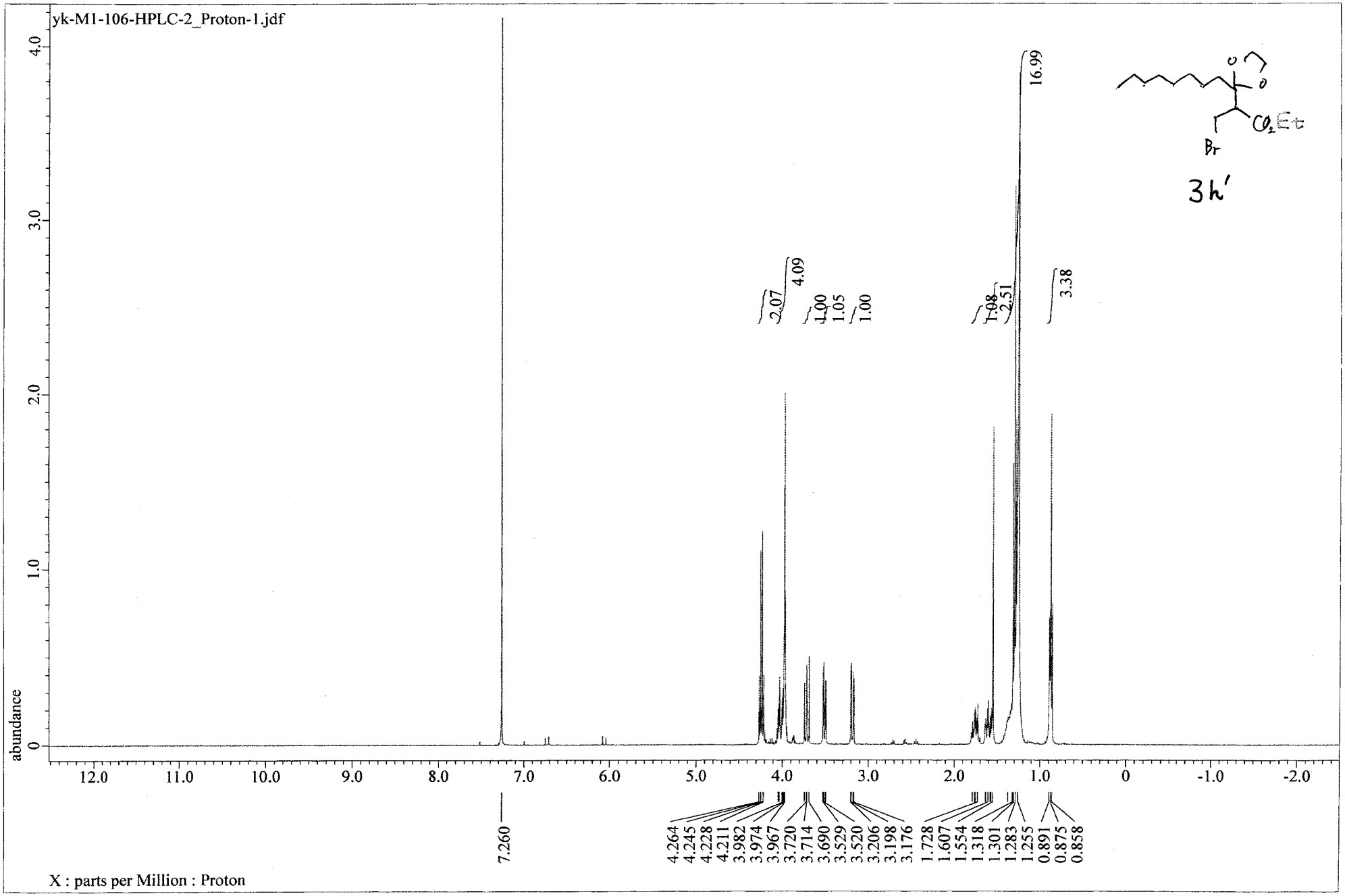

yk-M2-098-fr.18-25-C_Carbon-1.jdf
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
151.177
143.559
142.623
117.057
111.701
110.374
108.808
102.287
77.475
77.160
76.845
65.704
22.036
X : parts per Million : Carbon13
CN
3g (E)

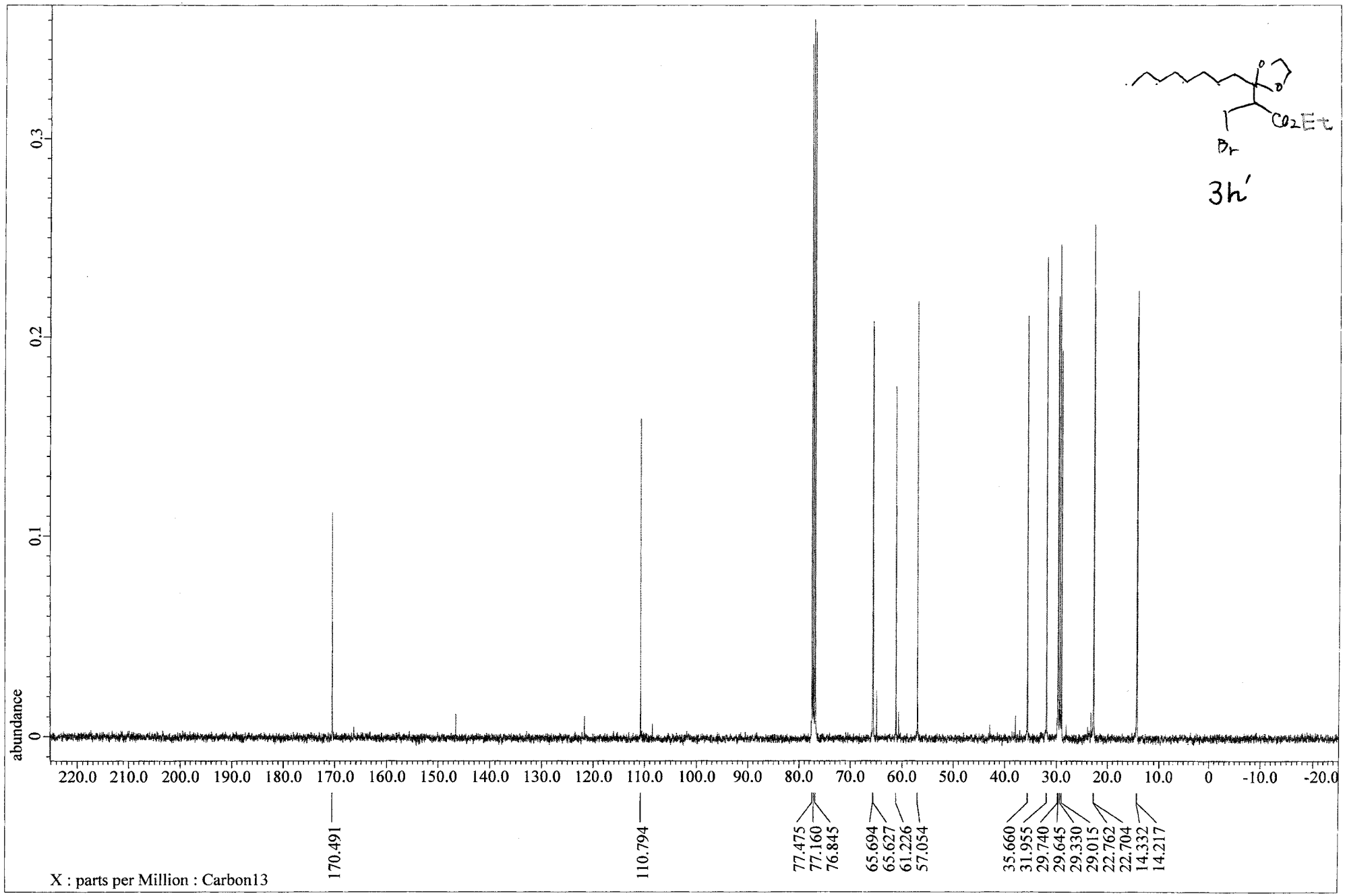

yk-M2-098-fr.6-10_Proton-1.jdf
CN
3g (E)
4.36
3.25
0.94
abundance
X : parts per Million : Proton
7.428
7.260
6.544
6.540
6.403
6.396
6.357
6.353
6.349
6.345
4.091
4.085
4.082
4.077
4.073
4.059
4.054
4.050
4.045
4.040
4.023
2.025
2.020
1.546
-0.003

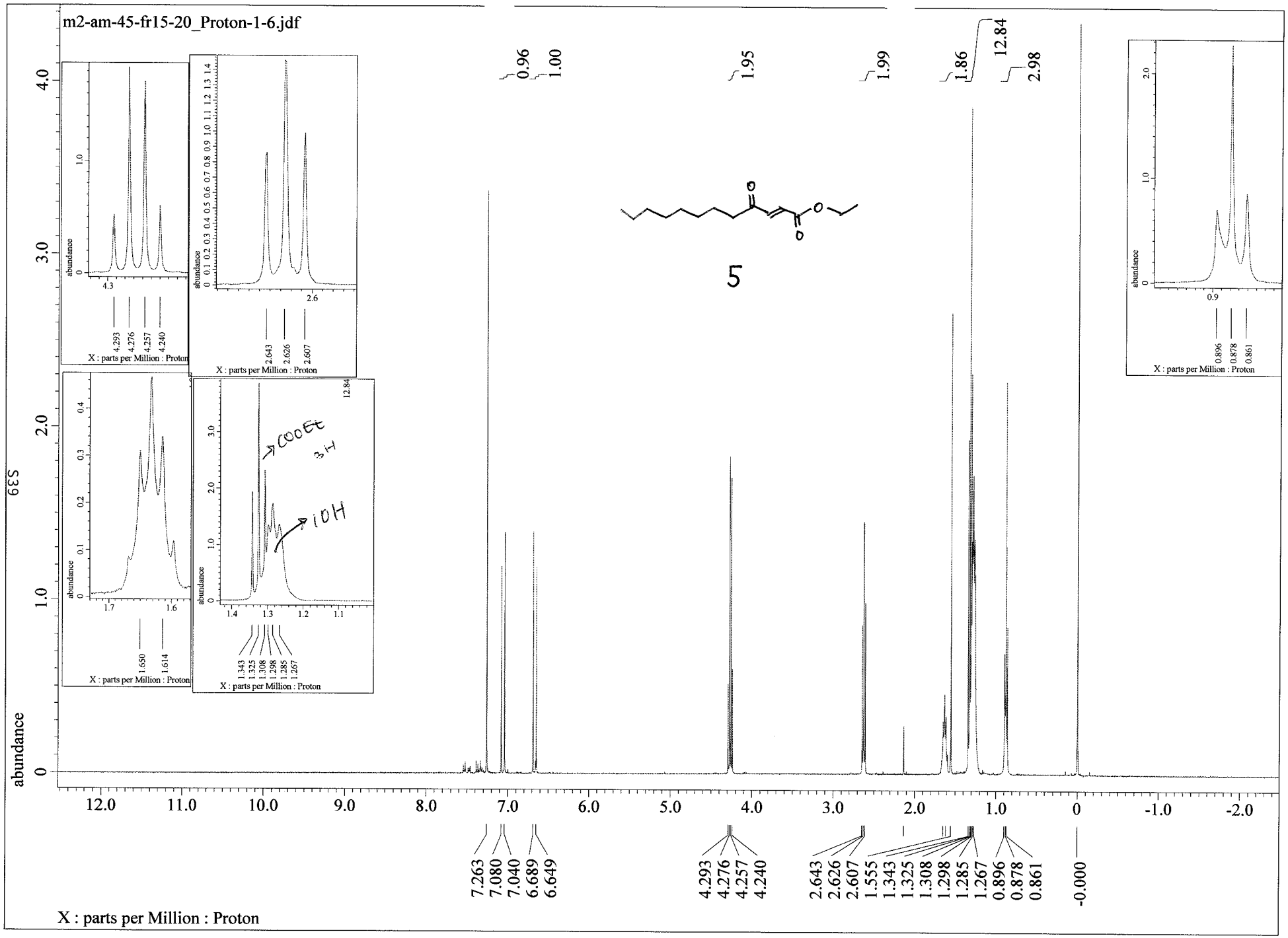

yk-M2-098-fr.6-10-C_Carbon-1-3.jdf
CN
3g (Z)
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
151.024
143.864
143.778
120.007
114.928
110.355
108.961
103.385
77.475
77.160
76.845
65.312
16.394
X : parts per Million : Carbon13

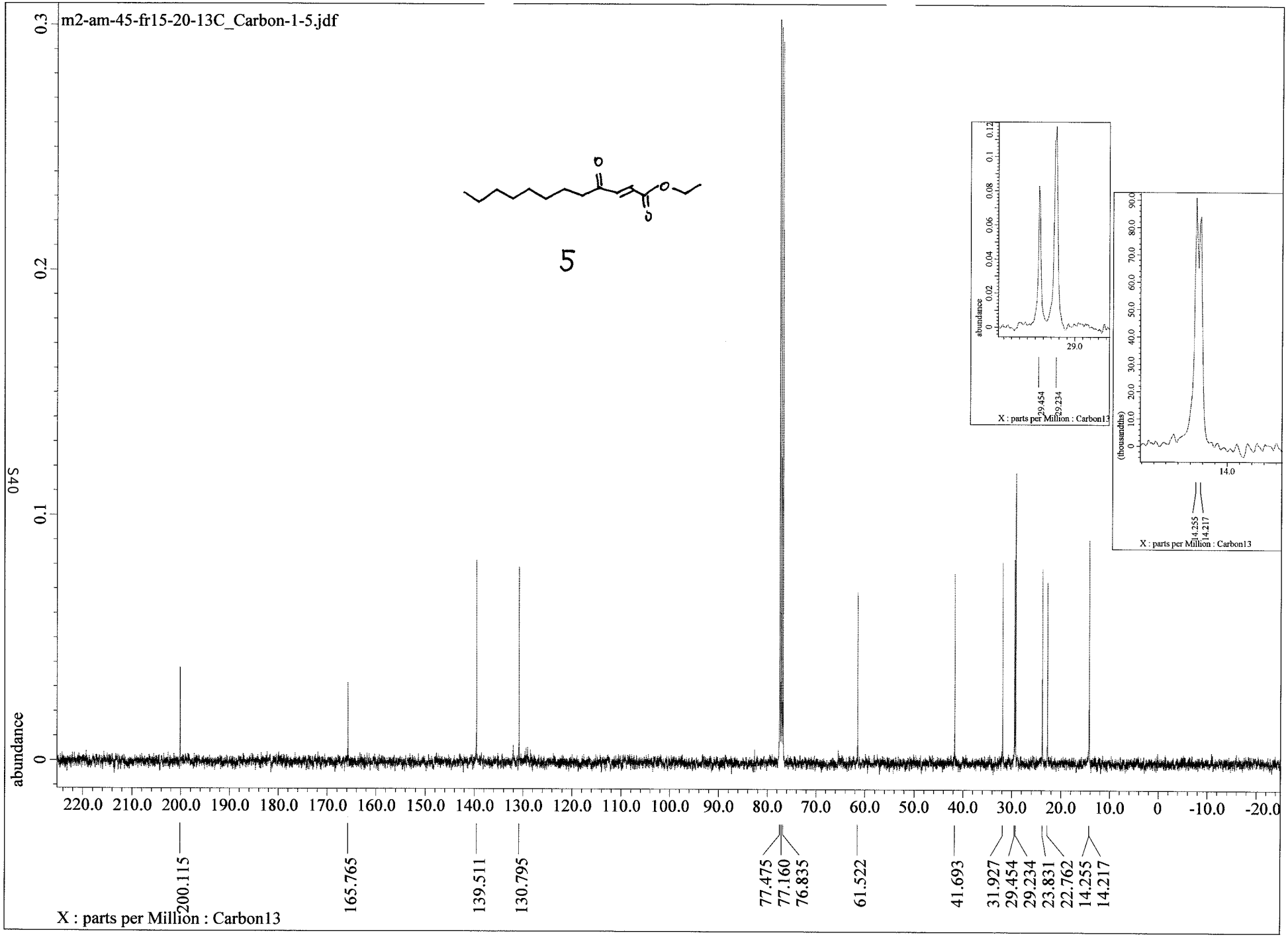

yk-M2-095-HPLC-1_Proton-1.jdf
3h (E)
CO2Et
abundance
X : parts per Million : Proton
1.02
1.00
2.10
4.18
2.00
16.13
3.16
7.260
6.750
6.711
6.078
6.039
4.232
4.213
4.195
4.178
3.965
3.960
3.955
3.948
3.884
3.877
3.872
3.868
1.745
1.727
1.705
1.562
1.383
1.318
1.300
1.283
1.256
0.887
0.870
0.853

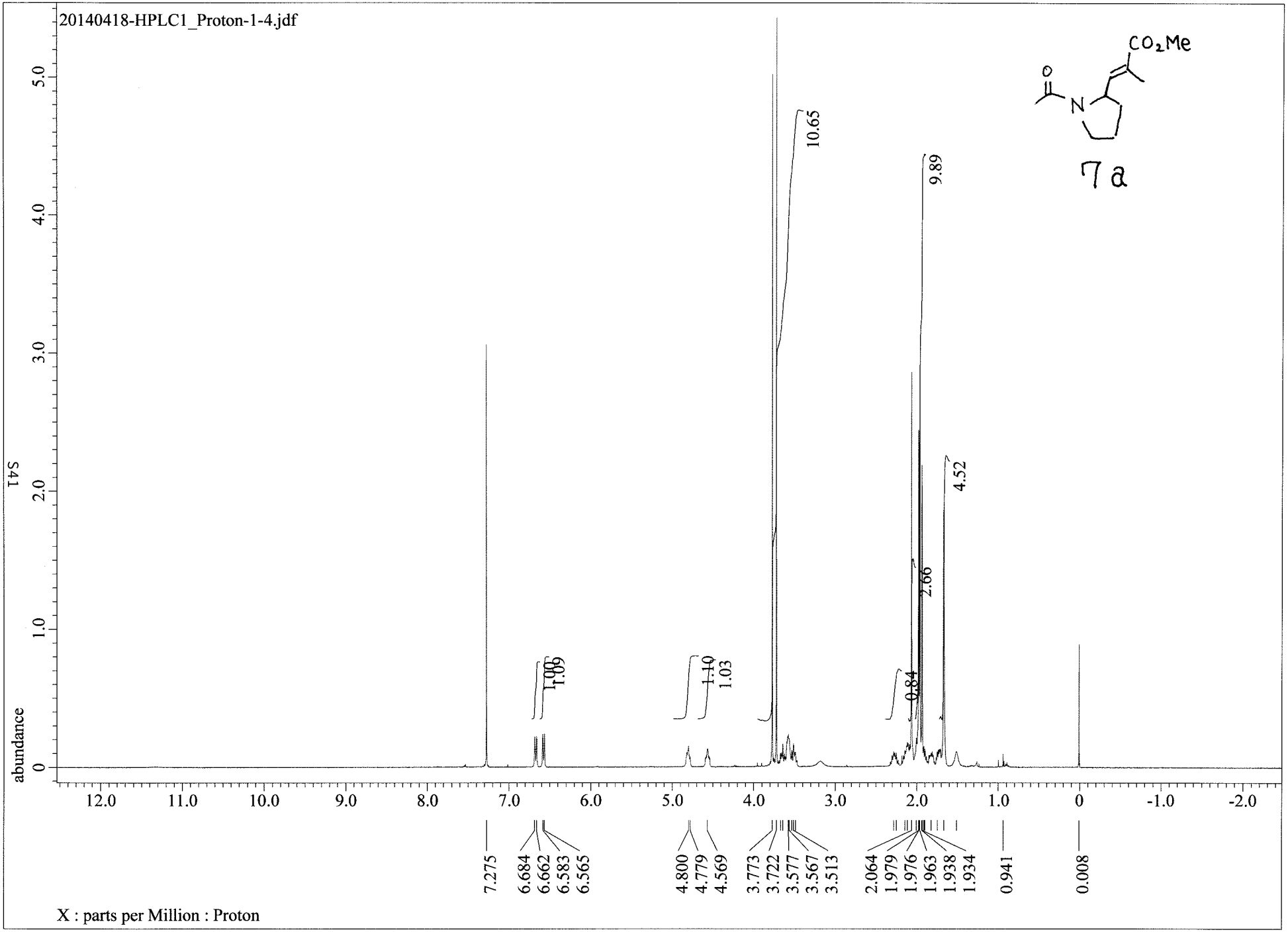

yk-M2-095-HPLC-1_Carbon-1.jdf
3h (E)
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.424
146.595
121.696
108.493
77.475
77.160
76.835
64.978
60.720
37.960
31.965
29.836
29.597
29.340
23.268
22.771
14.332
14.227
X : parts per Million : Carbon13

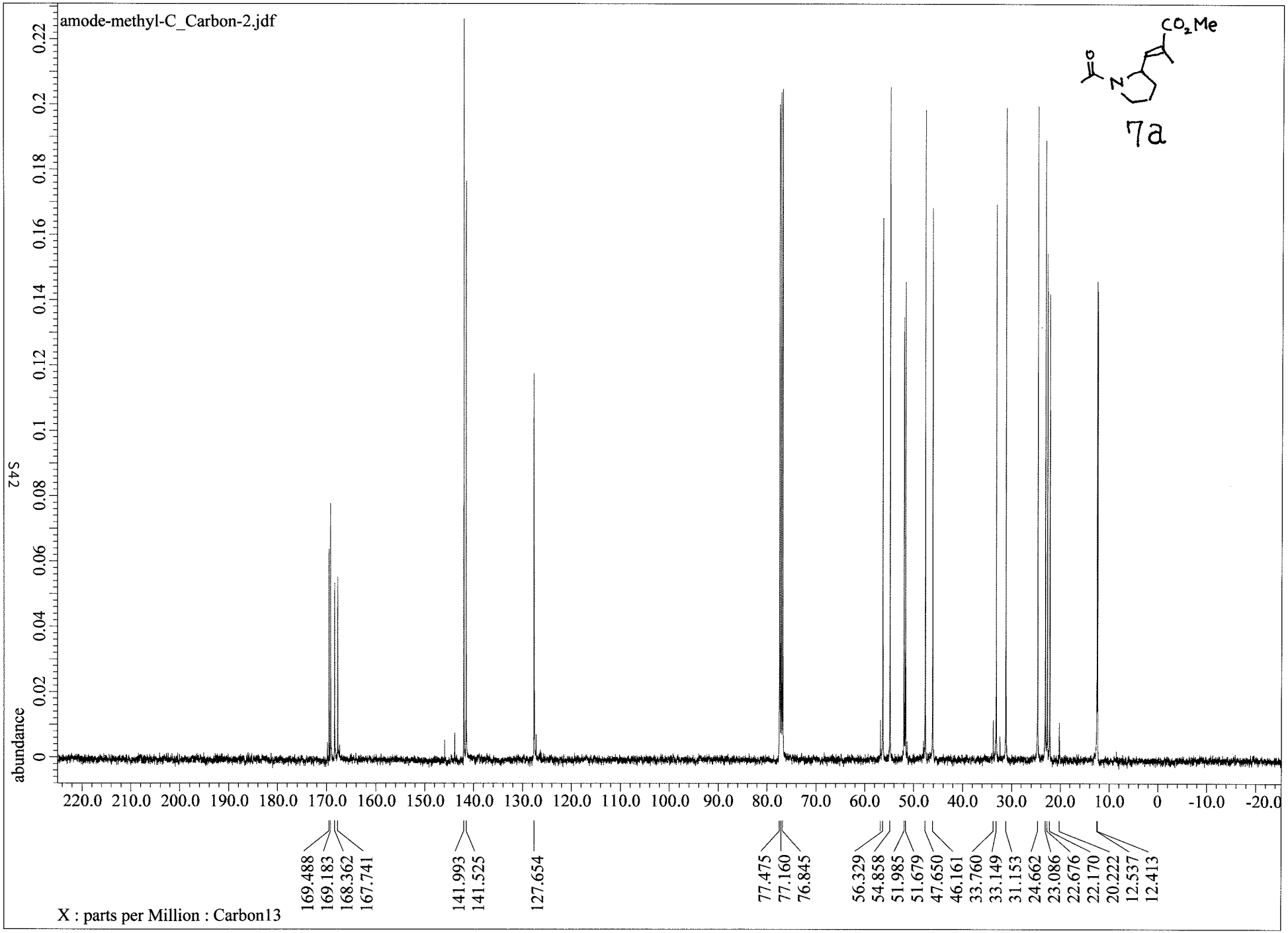

yk-M1-106-HPLC-2_Proton-1.jdf
abundance
X : parts per Million : Proton
7.260
2.07
4.09
1.00
1.05
1.00
1.08
2.51
16.99
3.38
4.264
4.245
4.228
4.211
3.982
3.974
3.967
3.720
3.714
3.690
3.529
3.520
3.206
3.198
3.176
1.728
1.607
1.554
1.318
1.301
1.283
1.255
0.891
0.875
0.858
3h'

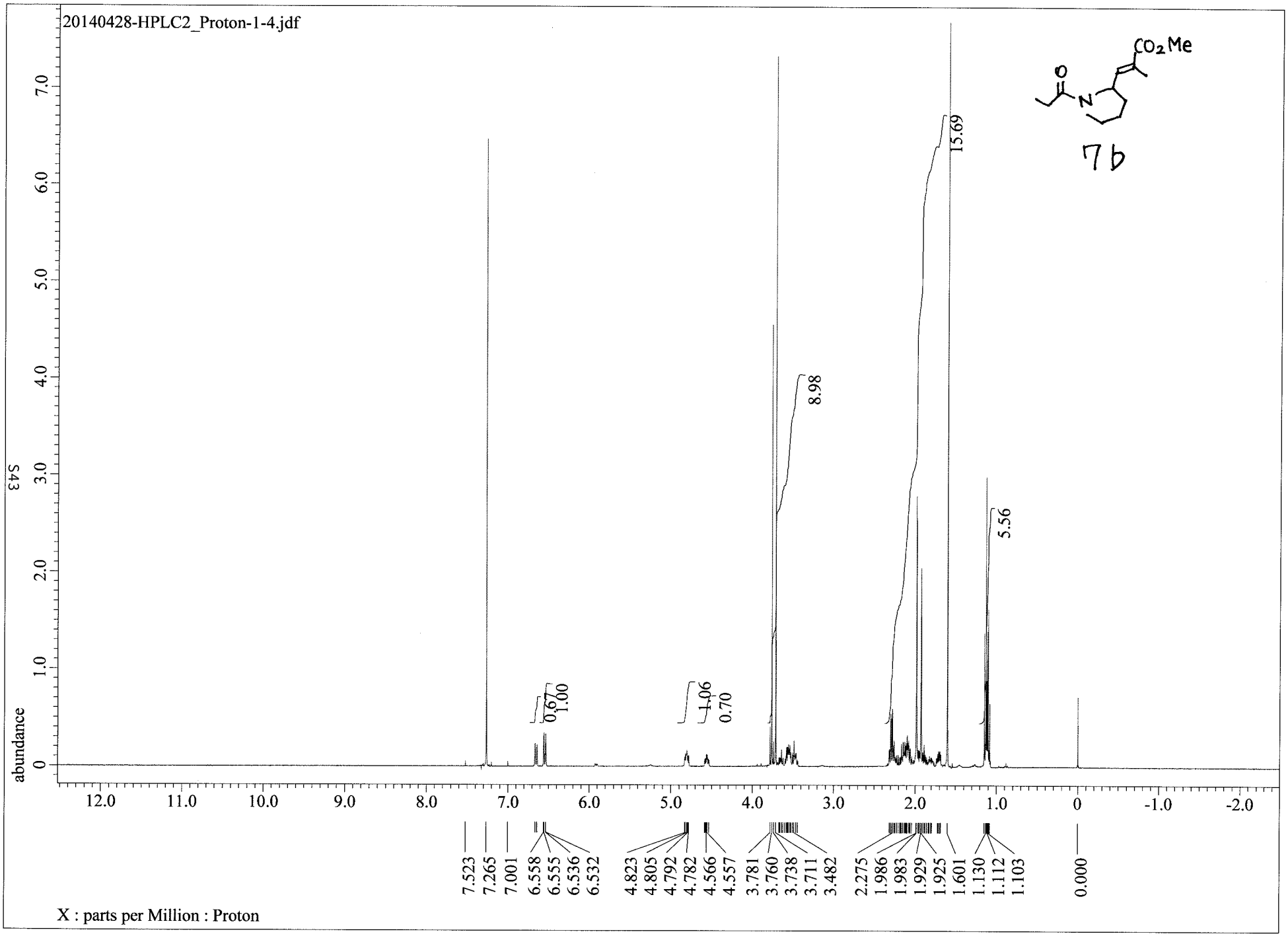

abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.491
110.794
77.475
77.160
76.845
65.694
65.627
61.226
57.054
35.660
31.955
29.740
29.645
29.330
29.015
22.762
22.704
14.332
14.217
X : parts per Million : Carbon13
CO2Et
Br
3h'

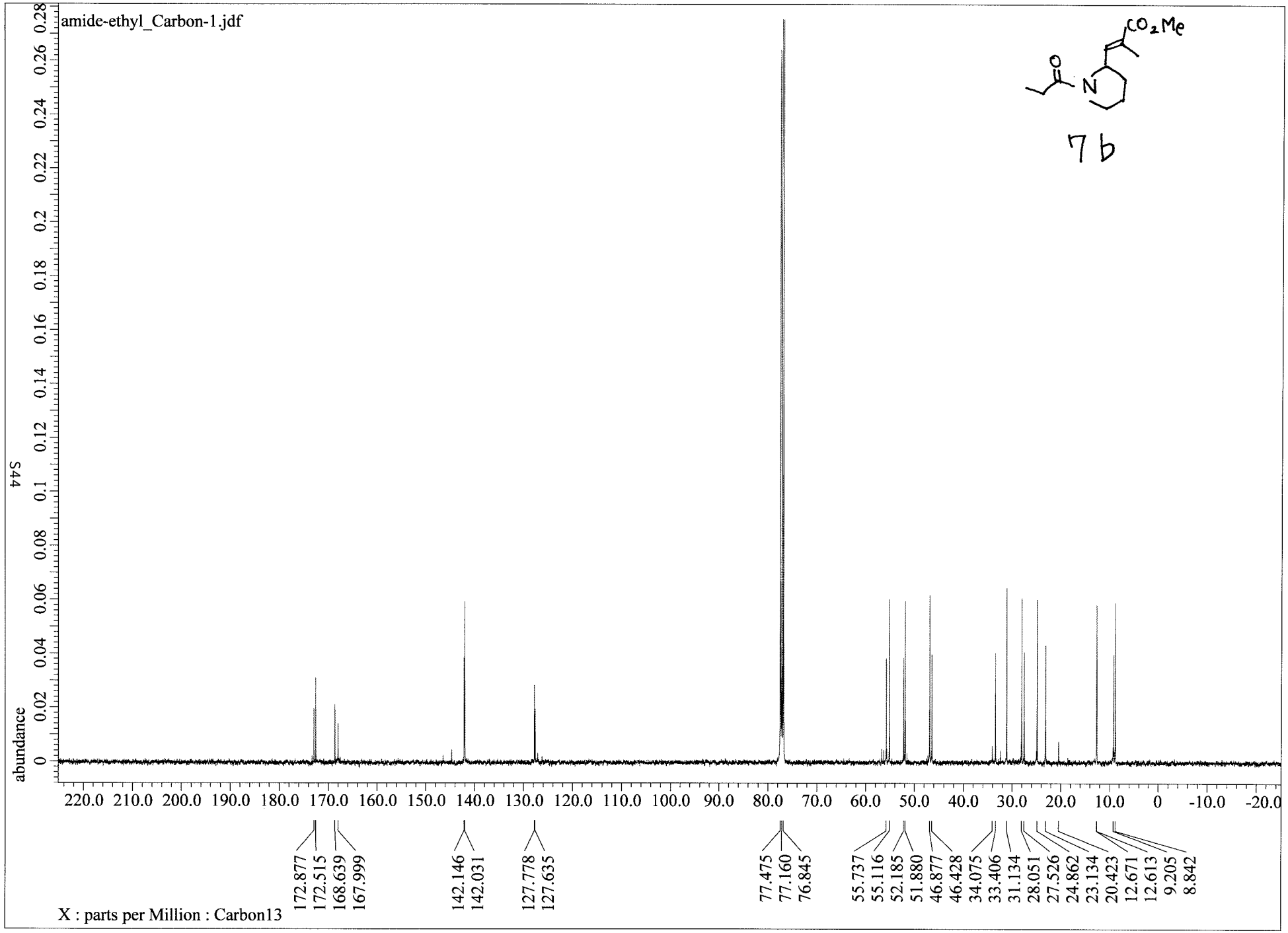

m2-am-45-fr15-20_Proton-1-6.jdf
0.96
1.00
1.95
1.99
1.86
12.84
2.98
5
COOEt
3H
1OH
abundance
X : parts per Million : Proton
7.263
7.080
7.040
6.689
6.649
4.293
4.276
4.257
4.240
2.643
2.626
2.607
1.555
1.343
1.325
1.308
1.298
1.285
1.267
0.896
0.878
0.861
-0.000


m2-am-45-fr15-20-13C_Carbon-1-5.jdf
5
abundance
X : parts per Million : Carbon13
200.115
165.765
139.511
130.795
77.475
77.160
76.835
61.522
41.693
31.927
29.454
29.234
23.831
22.762
14.255
14.217
29.454
29.234
14.255
14.217
S40


20140418-HPLC1_Proton-1-4.jdf
CO2Me
O
N
7a
10.65
9.89
4.52
2.66
1.00
1.09
1.10
1.03
0.84
abundance
S41
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
7.275
6.684
6.662
6.583
6.565
4.800
4.779
4.569
3.773
3.722
3.577
3.567
3.513
2.064
1.979
1.976
1.963
1.938
1.934
0.941
0.008
X : parts per Million : Proton


amode-methyl-C_Carbon-2.jdf
CO2Me
7a
abundance
X : parts per Million : Carbon13
169.488
169.183
168.362
167.741
141.993
141.525
127.654
77.475
77.160
76.845
56.329
54.858
51.985
51.679
47.650
46.161
33.760
33.149
31.153
24.662
23.086
22.676
22.170
20.222
12.537
12.413


20140428-HPLC2_Proton-1-4.jdf
CO2Me
O
N
7b
15.69
8.98
5.56
1.00
0.67
1.06
0.70
abundance
S43
X : parts per Million : Proton
7.523
7.265
7.001
6.558
6.555
6.536
6.532
4.823
4.805
4.792
4.782
4.566
4.557
3.781
3.760
3.738
3.711
3.482
2.275
1.986
1.983
1.929
1.925
1.601
1.130
1.112
1.103
0.000


amide-ethyl_Carbon-1.jdf
abundance
X : parts per Million : Carbon13
172.877
172.515
168.639
167.999
142.146
142.031
127.778
127.635
77.475
77.160
76.845
55.737
55.116
52.185
51.880
46.877
46.428
34.075
33.406
31.134
28.051
27.526
24.862
23.134
20.423
12.671
12.613
9.205
8.842
CO2Me
N
O
7b