Drastic effect of bidentate phosphine ligands on Pd-catalyzed hydroarylation of ethyl propiolate: a simple route to arylbutadienes

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General

All the reactions were carried out in dry Pyrex tubes capped with rubber septa and stirred with magnetic stirring bars. Thin layer chromatography (TLC) analyses were carried out using TLC aluminum sheet (Silica gel 60 F_{254}, Merck). Silica gel column chromatography was carried out using Silica Gel 60 (spherical, 63-210 m) from Kanto Chemical Co., Inc. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR using tetramethylsilane (TMS) as an internal standard. Melting points were measured with a YANACO micro melting apparatus and are not corrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000. GC analyses were performed on a Shimadzu GC-14B equipped with a flame ionization detector using capillary column (DB-1, 15 m x 0.53 mm i.d. x 1.5 mm film thickness, J&W Scientific). GC yields were determined using *n*-heptadecane or *n*-pentadecane as an internal standard. Mass spectra were measured on a Shimadzu GC/MS 5020A. Elemental analyses were performed by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Materials

All of arenes (**1**), ethyl propiolate (**2**) and solvent used in the reaction were commercially available and used as received without further purification. $Pd(OAc)_2$ (Aldrich), AgOAc (Kanto Chemical Co., Inc.), bis(diphenylphosphino)methane (dppm) (Aldrich), 1,2-bis(diphenylphosphino)ethane (dppe) (Wako Pure Chemical Industries, Ltd.), 1,2-bis(diphenylphosphino)propane (dppp) (Wako Pure Chemical Industries, Ltd.) and triphenylphosphine (Wako Pure Chemical Industries, Ltd.) were purchased and used as received. $Pd(dppe)(OAc)_2$,[1] $Pd(dppp)(OAc)_2$,[2] $Pd(PPh_3)_2(OAc)_2$[3] and $Pd(dppe)_2(OAc)_2$[4] were prepared from $Pd(OAc)_2$ and the corresponding phosphine according to the literature. $PdCl_2(PhCN)_2$ was prepared from $PdCl_2$ and benzonitrile according to the literature[5]. $Pd(dppm)Cl_2$ was prepared from $PdCl_2(PhCN)_2$ and dppm according to the reported method[6].

Optimization of reaction conditions of the $Pd(dppe)(OAc)_2$-catalyzed reaction of mesitylene (1a) with ethyl propiolate (2)

After a mixture of $Pd(dppe)(OAc)_2$ (0.005 mmol), mesitylene (**1a**), trifluoroacetic acid (TFA) and CH_2Cl_2 was stirred on an ice/water bath for 10 min, ethyl propiolate (**2**) was added to the cold mixture (the amounts of starting materials and solvents were described in Table 1). Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After 5 h, *n*-heptadecane (ca. 0.15g) as an internal standard was added to the reaction mixture. Then, the mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with Et_2O (20 mL + 10 mL x 2). The ethereal layer was analyzed by GC to determine the yields of the products and conversion of **1a**.

Effect of a phosphine ligand of a Pd catalyst in the reaction of mesitylene (1a) with ethyl propiolate (2)

After a mixture of a Pd catalyst (0.005 mmol), mesitylene (**1a**) (2 mmol), TFA (0.25 mL) and CH_2Cl_2 (0.75 mL) was stirred on an ice/water bath for 10 min, ethyl propiolate (**2**) (2 mmol) was added to the cold mixture. Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After 5 h, *n*-heptadecane (ca. 0.15g) as an internal standard was added to the reaction mixture. After the mixture became homogeneous by addition of CH_2Cl_2 (ca. 0.5 mL), a portion of the mixture was poured into water (ca. 1 mL), neutralized by $NaHCO_3$, and extracted with Et_2O (1 mL). The ethereal layer was analyzed by GC to determine the yields of the products and conversion of **1a**.

In the case of Pd(dppm)$(OAc)_2$, the catalyst was prepared *in situ* from Pd(dppm)Cl_2 and AgOAc. The procedure is as follows: a mixture of Pd(dppm)Cl_2 (0.005 mmol) and AgOAc (0.02 mmol) in TFA and CH_2Cl_2 was stirred at room temperature for 30 min (the amounts of solvents were described in Table 2). After mesitylene (2 mmol) was added to the mixture, the mixture was stirred on an ice/water bath for 10 min. After addition of ethyl propiolate (2 mmol), the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C.

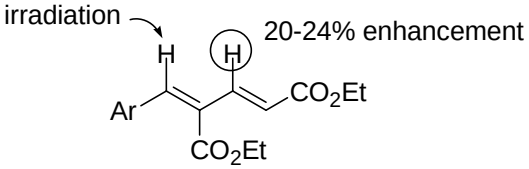
Genaral procedure for Pd(dppe)$(OAc)_2$-catalyzed reaction of an arene with ethyl propiolate (2)

After a mixture of Pd(dppe)$(OAc)_2$ (0.005 mmol), an arene (2 mmol), TFA and CH_2Cl_2 was stirred on an ice/water bath for 10 min, ethyl propiolate (**2**) (2 mmol) was added to the cold mixture (the amounts of solvents were described in Table 3). Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After the reaction, the mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with CH_2Cl_2 (20 mL + 10 mL x 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent, affording arylbutadiene **4** along with cinnamate **3**.

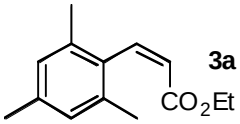
Genaral procedure for Pd(dppm)$(OAc)_2$-catalyzed reaction of an arene with ethyl propiolate (2)

A mixture of Pd(dppm)Cl_2 (0.005 mmol) and AgOAc (0.02 mmol) in TFA and CH_2Cl_2 was stirred at room temperature for 30 min (the amounts of solvents were described in Table 3). After an arene (2 mmol) was added to the mixture, the mixture was stirred on an ice/water bath for 10 min. After addition of ethyl propiolate (2 mmol), the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After the reaction, the mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with CH_2Cl_2 (20 mL + 10 mL x 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent, affording arylbutadiene **4** along with cinnamate **3**.

All products were characterized by ^1H and ^{13}C NMR. In addition, new compounds were characterized by elemental analyses, IR and Mass spectra. The stereochemistry of arylbutadiene **4** was determined by coupling constant in ^1H NMR spectra and differential NOE experiments showing 20-24% enhancement in intensity (see, an example at page S32).

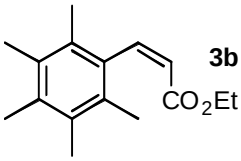


Ethyl (2*Z*)-3-(2,4,6-trimethylphenyl)prop-2-enoate (**3a**)[7]



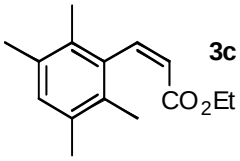
Colorless liquid. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.1 Hz, 3H, CH_3), 2.16 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 4.03 (q, *J* = 7.1 Hz, 2H, CH_2), 6.11 (d, *J* = 12.0 Hz, 1H, vinyl), 6.84 (s, 2H, aryl), 7.02 (d, *J* = 12.0 Hz, 1H, vinyl). ^{13}C NMR (75MHz, $CDCl_3$): δ 13.94, 20.11, 21.01, 59.92, 122.77, 127.78, 132.77, 134.44, 136.65, 144.13, 165.47.

Ethyl (2*Z*)-3-(pentamethylphenyl)prop-2-enoate (**3b**)[7]



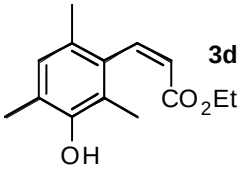
Colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.1 Hz, 3H, CH_3), 2.14 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 4.02 (q, *J* = 7.1 Hz, 2H, CH_2), 6.13 (d, *J* = 11.9 Hz, 1H, vinyl), 7.13 (d, *J* = 11.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.95, 16.35, 16.74, 17.59, 59.76, 122.09, 129.73, 131.87, 133.20, 133.93, 146.48, 165.39.

Ethyl (2*Z*)-3-(2,3,5,6-tetramethylphenyl)prop-2-enoate (**3c**)[7]



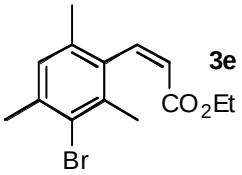
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (t, *J* = 7.1 Hz, 3H, CH_3), 2.08 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 4.00 (q, *J* = 7.1 Hz, 2H, CH_2), 6.14 (d, *J* = 11.9 Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.09 (d, *J* = 11.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.86, 16.47, 19.93, 59.80, 122.44, 130.21, 130.51, 133.02, 135.69, 145.59, 165.43.

Ethyl (2*Z*)-3-(3-hydroxy-2,4,6-trimethylphenyl)prop-2-enoate (**3d**)[7]



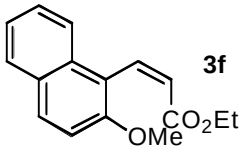
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.1 Hz, 3H, CH_3), 2.09 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 4.04 (q, *J* = 7.1 Hz, 2H, CH_2), 4.65 (brs, 1H, OH), 6.13 (d, *J* = 11.9 Hz, 1H, vinyl), 6.79 (s, 1H, aryl), 7.00 (d, *J* = 11.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.95, 13.93, 15.84, 19.51, 59.99, 120.23, 121.93, 122.72, 126.03, 129.09, 134.20, 144.07, 149.77, 165.42.

Ethyl (2*Z*)-3-(3-bromo-2,4,6-trimethylphenyl)prop-2-enoate (**3e**)[7]



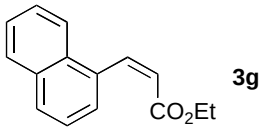
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.1 Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.02 (q, *J* = 7.1 Hz, 2H, CH_2), 6.13 (d, *J* = 11.9 Hz, 1H, vinyl), 6.93 (s, 1H, aryl), 7.02 (d, *J* = 11.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.88, 19.91, 21.24, 23.91, 60.07, 123.24, 125.02, 129.27, 133.18, 134.34, 134.58, 136.92, 143.59, 165.17.

Ethyl (2*Z*)-3-(2-methoxynaphthalen-1-yl)prop-2-enoate (**3f**)



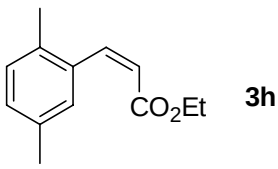
Light yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.1 Hz, 3H, CH_3), 3.90 (q, *J* = 7.1 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 6.32 (d, *J* = 11.9 Hz, 1H, vinyl), 7.26 (d, *J* = 9.0 Hz, 1H, naphthyl), 7.26 (d, *J* = 11.9 Hz, 1H, vinyl), 7.32 (dd, *J* = 6.9, 8.1 Hz, 1H, naphthyl), 7.42 (dd, *J* = 6.9, 8.4 Hz, 1H, naphthyl), 7.77 (d, *J* = 8.1 Hz, 1H, naphthyl), 7.77 (d, *J* = 8.4 Hz, 1H, naphthyl), 7.81 (d, *J* = 9.0 Hz, 1H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.62, 56.27, 59.84, 112.77, 119.19, 123.51, 123.94, 124.28, 126.53, 128.16, 128.63, 129.68, 131.91, 137.44, 153.52, 165.94. MS (EI, m/z): 256 (M^+, 40), 225 (15), 211 (15), 197 (33), 183 (100), 168 (38), 153 (29), 139 (44). IR (neat, cm^{-1}): 3058 (w), 2980 (m), 2840 (w), 1725 (ν (C=O), s), 1623 (m), 1592 (m), 1510 (m), 1466 (m), 1268 (s), 1184 (s), 1086 (m), 1025 (m), 808 (m), 749 (m). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.00; H, 6.30.

Ethyl (2*Z*)-3-naphthalen-1-ylprop-2-enoate (**3g**)[7]



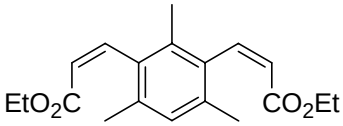
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.1 Hz, 3H, CH_3), 4.00 (q, *J* = 7.1 Hz, 2H, CH_2), 6.23 (d, *J* = 12.1 Hz, 1H, vinyl), 7.41-7.50 (m, 4H, naphthyl), 7.54 (d, *J* = 12.1 Hz, 1H, vinyl), 7.80-7.90 (m, 3H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.77, 60.09, 122.77, 124.36, 124.95, 125.79, 126.19, 126.48, 128.49, 128.66, 131.04, 133.00, 133.22, 141.80, 165.88.

Ethyl (2*Z*)-3-(2,5-dimethylphenyl)prop-2-enoate (**3i**)[7]



Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, *J* = 7.1 Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.09 (q, *J* = 7.1 Hz, 2H, CH_2), 6.00 (d, *J* = 12.1 Hz, 1H, vinyl), 7.00-7.07 (m, 2H, aryl), 7.08 (d, *J* = 12.1 Hz, 1H, vinyl), 7.12 (s, 1H, aryl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.92, 19.29, 20.85, 60.02, 120.99, 129.06, 129.24, 129.52, 132.59, 134.44, 134.86, 142.81, 166.07.

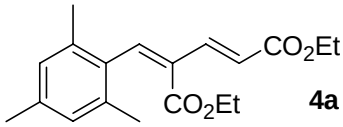
Diethyl (2*Z*,2'*Z*)-3,3'-(2,4,6-trimethylbenzene-1,3-diyl)bisprop-2-enoate (5a)[7]



5a

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.1 Hz, 6H, CH_3), 2.05 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.03 (q, *J* = 7.1 Hz, 4H, CH_2), 6.12 (d, *J* = 11.9 Hz, 2H, vinyl), 6.88 (s, 1H, aryl), 7.03 (d, *J* = 11.9 Hz, 2H, vinyl). ^{13}C NMR (75MHz, $CDCl_3$): δ 13.98, 17.66, 20.17, 59.90, 122.68, 128.36, 130.97, 132.98, 133.46, 144.40, 165.38.

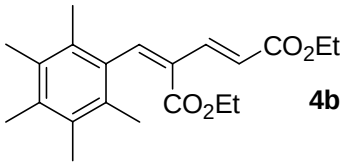
Diethyl (2*E*,4*Z*)-4-(2,4,6-trimethylbenzylidene)pent-2-enedioate (4a)[7]



4a

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.15 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 3.99 (q, *J* = 7.1 Hz, 2H, CH_2), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2), 6.22 (d, *J* = 15.9 Hz, 1H, vinyl), 6.83 (s, 2H, aryl), 7.15 (s, 1H, vinyl), 7.46 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.44, 14.24, 20.08, 20.94, 60.49, 60.70, 120.72, 127.81, 132.05, 134.40, 135.15, 137.29, 141.36, 143.06, 166.03, 166.80. MS (EI, m/z (relative intensity)): 316 (M^+, 8), 271 (27), 243 (59), 225 (40), 213 (28), 197 (77), 183 (36), 169 (100), 157 (76), 141 (34), 128 (46), 115 (29). IR (neat, cm^{-1}): 2981 (m), 1720 (ν(C=O), s), 1628 (m), 1447 (m), 1377 (m), 1311 (m), 1218 (m), 1179 (s), 1033 (m), 981 (m), 856 (m).

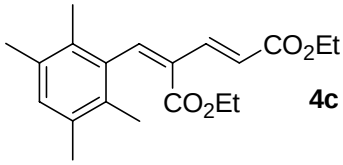
Diethyl (2*E*,4*Z*)-4-(pentamethylbenzylidene)pent-2-enedioate (4b)[7]



4b

Colorless crystals. Mp. 79-81°C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.12 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 3.97 (q, *J* = 7.1 Hz, 2H, CH_2), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2), 6.20 (d, *J* = 15.8 Hz, 1H, vinyl), 7.26 (s, 1H, vinyl), 7.49 (d, *J* = 15.8 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.40, 14.26, 16.19, 16.66, 17.78, 60.47, 60.52, 120.41, 130.36, 132.04, 132.44, 133.98, 134.44, 141.47, 145.25, 166.01, 166.83. MS (EI, m/z (relative intensity)): 344 (M^+, 22), 299 (25), 271 (100), 256 (52), 225 (45), 198 (72), 185 (57), 141 (22), 128 (17), 115 (14). IR (KBr, cm^{-1}): 2989 (m), 2907 (m), 1713 (ν(C=O), s), 1623 (m), 1454 (m), 1407 (m), 1384 (m), 1362 (m), 1309 (s), 1233 (s), 1164 (s), 1023 (m), 989 (m), 861 (m).

Diethyl (2*E*,4*Z*)-4-(2,3,5,6-tetramethylbenzylidene)pent-2-enedioate (4c)[7]

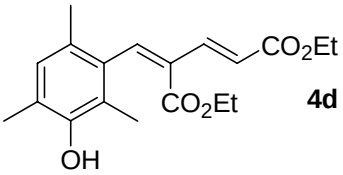


4c

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz,

3H, CH_3), 2.06 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 3.95 (q, *J* = 7.1 Hz, 2H, CH_2), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2), 6.22 (d, *J* = 15.9 Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.22 (s, 1H, vinyl), 7.49 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.34, 14.26, 16.63, 19.78, 60.51, 60.54, 120.62, 130.86, 130.92, 133.27, 134.18, 134.93, 141.34, 144.42, 165.99, 166.83. MS (EI, m/z (relative intensity)): 330 (M^+, 30), 285 (36), 257 (100), 242 (53), 211 (75), 197 (46), 185 (89), 183 (89), 171 (87), 153 (43), 141 (41), 128 (36), 115 (29). IR (neat, cm^{-1}): 2981 (m), 2938 (m), 1719 (ν(C=O), s), 1628 (m), 1467 (m), 1378 (m), 1313 (m), 1284 (m), 1224 (m), 1180 (s), 1033 (m), 981 (m), 866 (m). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.65; H, 7.90.

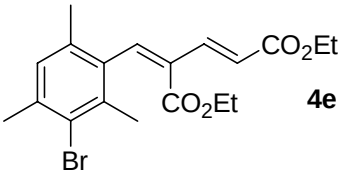
Diethyl (2*E*,4*Z*)-4-(3-hydroxy-2,4,6-trimethylbenzylidene)pent-2-enedioate (**4d**)



4d

Yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.08 (s, 6H, CH_3), 2.20 (s, 3H, CH_3), 4.00 (q, *J* = 7.1 Hz, 2H, CH_2), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2), 4.77 (br s, 1H, OH), 6.23 (d, *J* = 15.9 Hz, 1H, vinyl), 6.79 (s, 1H, aryl), 7.12 (s, 1H, vinyl), 7.47 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.16, 13.47, 14.23, 15.84, 19.45, 60.58, 60.76, 120.72, 120.79, 122.53, 126.78, 129.20, 133.49, 134.44, 141.37, 142.88, 149.89, 165.99, 166.87. MS (EI, m/z (relative intensity)): 332 (M^+, 75), 287 (43), 271 (57), 259 (57), 244 (59), 229 (35), 213 (93), 199 (56), 185 (100), 173 (68), 157 (36), 141 (40), 128 (47), 115 (46). IR (neat, cm^{-1}): 3494 ((O-H), s), 2982 (m), 2937 (m), 1713 (ν(C=O), s), 1626 (m), 1476 (m), 1377 (m), 1312 (s), 1181 (s), 1101 (m), 1030 (m), 981 (m), 865 (m). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.39; H, 7.29.

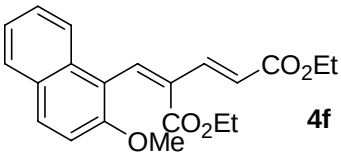
Diethyl (2*E*,4*Z*)-4-(3-bromo-2,4,6-trimethylbenzylidene)pent-2-enedioate (**4e**)



4e

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.99 (q, *J* = 7.1 Hz, 2H, CH_2), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2), 6.25 (d, *J* = 15.9 Hz, 1H, vinyl), 6.92 (s, 1H, aryl), 7.13 (s, 1H, vinyl), 7.46 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.46, 14.26, 19.89, 21.50, 23.88, 60.61, 60.85, 121.44, 125.03, 129.33, 133.84, 133.93, 134.77, 135.06, 137.58, 140.89, 142.10, 165.64, 166.67. MS (EI, m/z): 396 (M^++2, 9), 394 (M^+, 9), 351 (15), 349 (15), 242 (82), 224 (37), 213 (33), 196 (100), 156 (47), 153 (55), 141 (38),128 (32) 115 (31). IR (neat, cm^{-1}): 2981 (m), 1720 (ν(C=O), s), 1629 (m), 1451 (m), 1378 (m), 1312 (m), 1223 (m), 1181 (s), 1033 (m), 980 (m), 863 (m). Anal. Calcd for $C_{19}H_{23}BrO_4$: C, 57.73; H, 5.86. Found: C, 57.72; H, 5.86.

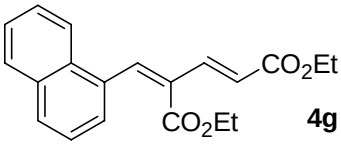
Diethyl (2*E*,4*Z*)-4-[(2-methoxynaphthalen-1-yl)methylidene]pent-2-enedioate (**4f**)



4f

Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75 (t, *J* = 7.1 Hz, 3H, CH_3), 1.33 (t, *J* = 7.1 Hz, 3H, CH_3), 3.90 (s, 3H, OCH_3), 3.91 (q, *J* = 7.1 Hz, 2H, CH_2), 4.26 (d, *J* = 7.1 Hz, 2H, CH_2), 6.39 (d, *J* = 15.8 Hz, 1H, vinyl), 7.24 (d, *J* = 9.2 Hz, 1H, aryl), 7.35 (dd, *J* = 6.9, 8.1 Hz, 1H, aryl), 7.47 (dd, *J* = 6.9, 8.4 Hz, 1H, aryl), 7.50 (s, 1H, vinyl), 7.59 (d, *J* = 15.8 Hz, 1H, vinyl), 7.78 (d, *J* = 8.1 Hz, 1H, aryl), 7.79 (d, *J* = 8.4 Hz, 1H, aryl), 7.84 (d, *J* = 9.2 Hz, 1H, aryl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.28, 14.23, 56.00, 60.35, 60.41, 112.50, 118.20, 120.29, 123.59, 123.80, 127.04, 128.28, 128.59, 130.73, 132.09, 133.86, 137.64, 142.51, 154.22, 166.18, 166.98. MS (EI, m/z (relative intensity)): 354 (M^+, 32), 280 (100), 235 (67), 208 (51), 165 (37), 139 (26). IR (KBr, cm^{-1}): 2981 (m), 2936 (m), 2839 (m), 1713 (ν(C=O), s), 1619 (m), 1589 (m), 1510 (m), 1468 (m), 1407 (m), 1367 (m), 1256 (s), 1176 (s), 1048 (m), 1022 (m), 978 (m), 858 (m), 811 (m), 759 (m). Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.13; H, 6.26.

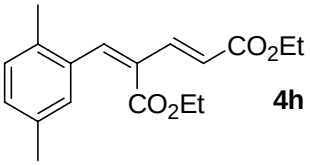
Diethyl (2*E*,4*Z*)-4-(naphthalen-1-ylmethylidene)pent-2-enedioate (**4 g**)



4g

Yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.1 Hz, 3H, CH_3), 1.33 (t, *J* = 7.1 Hz, 3H, CH_3), 4.05 (q, *J* = 7.1 Hz, 2H, CH_2), 4.26 (q, *J* = 7.1 Hz, 2H, CH_2), 6.18 (d, *J* = 15.8 Hz, 1H, vinyl), 7.38-7.58 (m, 5H, naphthyl and vinyl), 7.65 (s, 1H, vinyl), 7.82-7.96 (m, 3H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.56, 14.27, 60.59, 61.14, 120.96, 124.09, 125.07, 126.08, 126.23, 126.69, 128.58, 129.57, 131.20, 132.45, 133.32, 134.25, 138.97, 141.90, 166.67, 167.02. MS (EI, m/z (relative intensity)): 324 (M^+, 13), 251 (38), 250 (28), 223 (18), 205 (55), 179 (100), 165 (24), 152 (16). IR (neat, cm^{-1}): 3059 (m), 2982 (m), 1714 (ν(C=O), s), 1622 (m), 1464 (m), 1368 (m), 1312 (m), 1269 (m), 1219 (m), 1180 (s), 1033 (m), 978 (m), 859 (m), 800 (m), 777 (m). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 73.96; H, 6.20.

Diethyl (2*E*,4*Z*)-4-(2,5-dimethylbenzylidene)pent-2-enedioate (**4h**)

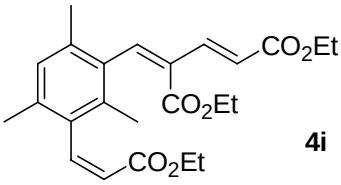


4h

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.17 (q, *J* = 7.1 Hz, 2H, CH_2), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2), 6.08 (d, *J* = 15.9 Hz, 1H, vinyl), 7.02-7.09 (m, 3H, aryl), 7.14 (s, 1H, vinyl), 7.42 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.70, 14.25, 19.34, 20.79, 60.52, 61.17, 120.23, 128.28, 129.94, 130.08, 132.51, 133.74, 133.93, 135.09, 139.90, 142.32, 166.73, 167.29. MS (EI, m/z (relative intensity)): 302 (M^+, 9), 257 (31), 229 (87), 211 (39), 201 (44), 183 (97), 157 (100), 141 (51), 128 (55), 115 (47). IR (neat, cm^{-1}): 2981 (m), 1719 (ν(C=O), s), 1622 (m), 1463 (m), 1380 (m), 1313 (m), 1229 (m), 1179 (s), 1036 (m), 978 (m), 861 (m), 813 (m). Anal. Calcd for

$C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.48; H, 7.40.

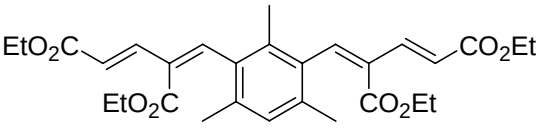
Diethyl
(2*E*,4*Z*)-4-{3-[(*Z*)-2-(ethoxycarbonyl)ethenyl]-2,4,6-trimethylbenzylidene}pent-2-enedioate (**4i**)



4i

Colorless viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.1 Hz, 3H, CH_3), 1.14 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.01 (q, *J* = 7.1 Hz, 2H, CH_2), 4.03 (q, *J* = 7.1 Hz, 2H, CH_2), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2), 6.13 (d, *J* = 11.9 Hz, 1H, vinyl), 6.22 (d, *J* = 15.9 Hz, 1H, vinyl), 6.87 (s, 1H, aryl), 6.99 (d, *J* = 11.9 Hz, 1H, vinyl), 7.15 (s, 1H, vinyl), 7.46 (d, *J* = 15.9 Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.54, 13.99, 14.24, 17.77, 20.10, 59.86, 60.49, 60.76, 120.71, 122.89, 128.40, 131.71, 132.27, 133.18, 134.16, 134.18, 134.44, 141.38, 143.11, 143.78, 165.10, 165.96, 166.78. MS (EI, m/z (relative intensity)): 414 (M^+, 5), 369 (35), 295 (100), 281 (47), 267 (41), 249 (67), 221 (54), 209 (49), 193 (40), 179 (48), 165 (61). IR (neat, cm^{-1}): 2981 (m), 1716 (ν(C=O), s), 1628 (m), 1447 (m), 1378 (m), 1311 (m), 1205 (m), 1173 (s), 1029 (m), 981 (m), 864 (m). Anal. Calcd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30. Found: C, 69.49; H, 7.26.

Tetraethyl
(2*E*,4*Z*,2'*E*,4'*Z*)-4,4'-[2,4,6-trimethylbenzene-1,3-diyldi(*Z*)methylylidene]bispent-2-enedioate (**4j**)



4j

Light yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.1 Hz, 6H, CH_3), 1.32 (t, *J* = 7.1 Hz, 6H, CH_3), 2.04 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.03 (q, *J* = 7.1 Hz, 4H, CH_2), 4.25 (q, *J* = 7.1 Hz, 4H, CH_2), 6.21 (d, *J* = 15.9 Hz, 2H, vinyl), 6.86 (s, 1H, aryl), 7.11 (s, 2H, vinyl), 7.46 (d, *J* = 15.9 Hz, 2H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.64, 14.25, 17.92, 20.12, 60.56, 60.79, 120.93, 128.53, 132.45, 132.48, 134.62, 134.89, 141.27, 142.47, 165.75, 166.73. MS (EI, m/z (relative intensity)): 512 (M^+, 6), 467 (29), 451 (16), 393 (100), 379 (57), 365 (23), 347 (32), 333 (29), 319 (28), 305 (21), 291 (23), 261 (19), 178 (22), 95 (26). IR (neat, cm^{-1}): 2982 (m), 1713 (ν(C=O), s), 1628 (m), 1448 (m), 1376 (m), 1311 (s), 1222 (s), 1178 (s), 1031 (m), 981 (m), 863 (m). Anal. Calcd for $C_{29}H_{36}O_8$: C, 67.95; H, 7.08. Found: C, 67.83; H, 7.06.

References

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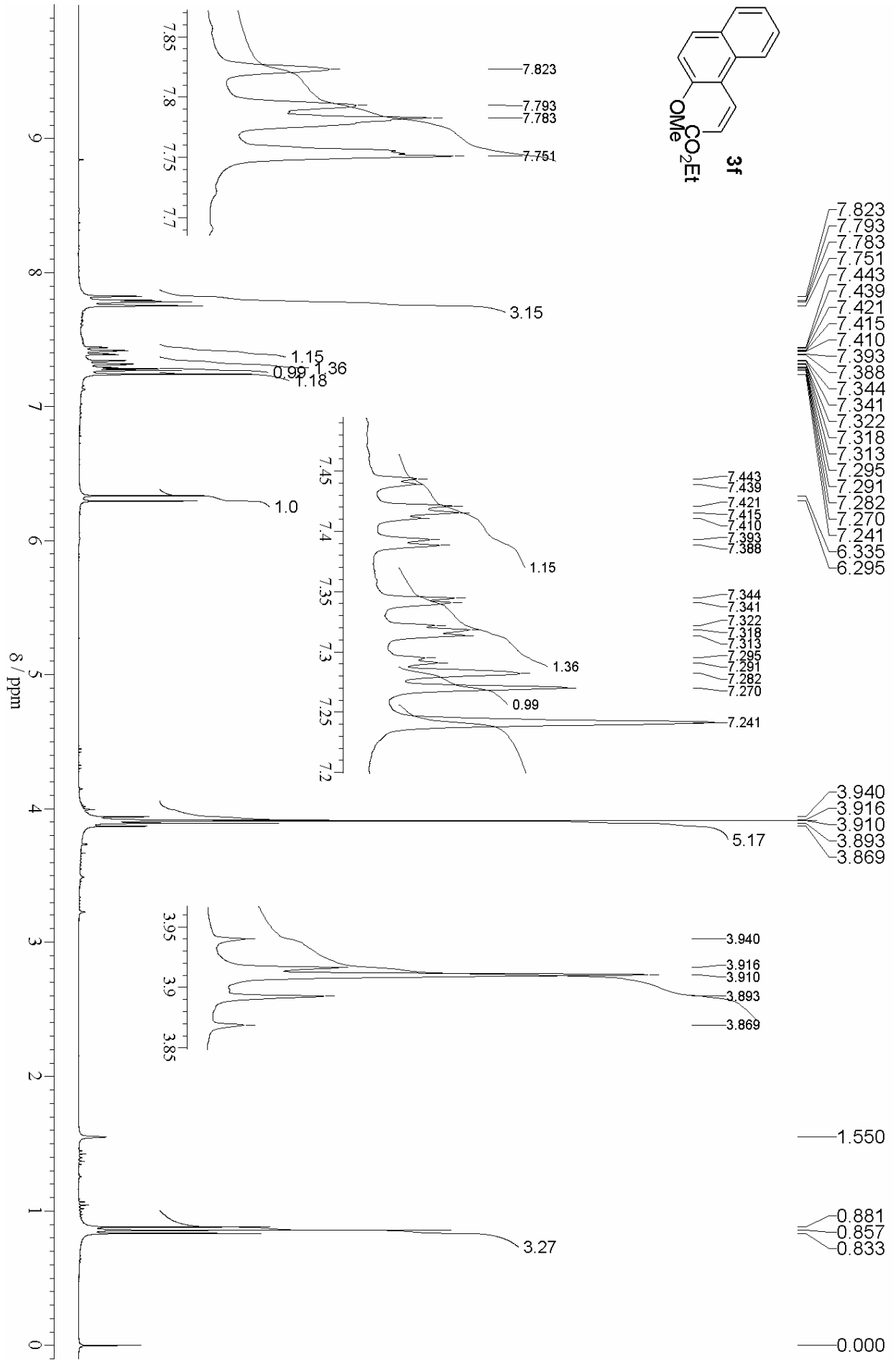
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7.783
7.751
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1.36
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1.18
1.0
7.443
7.439
7.421
7.415
7.410
7.393
7.388
7.344
7.341
7.322
7.318
7.313
7.295
7.291
7.282
7.270
7.241
6.335
6.295
3.940
3.916
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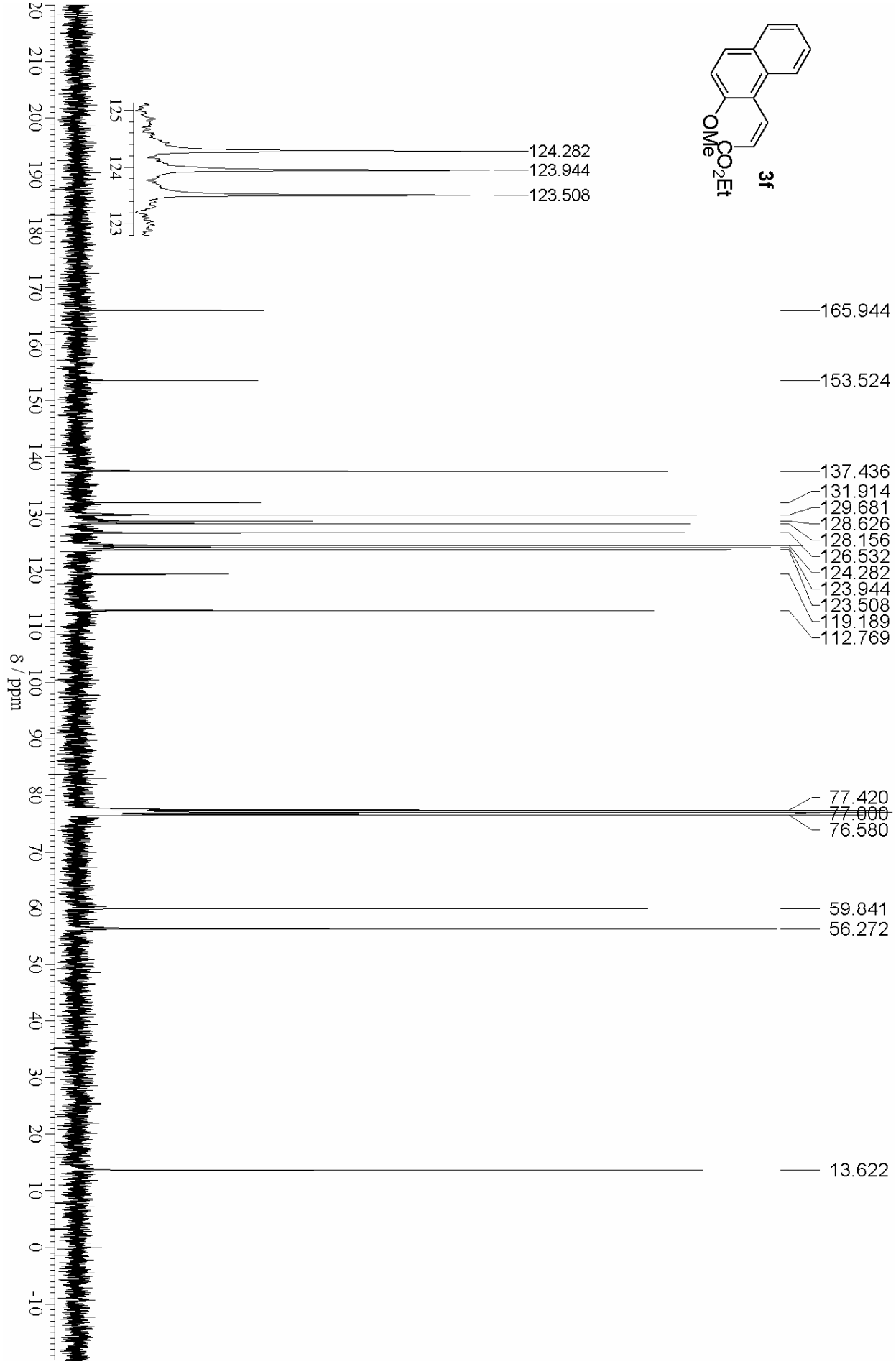
3.893
3.869
5.17
1.550
0.881
0.857
0.833
3.27
0.000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123.508
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CO2Et
3f
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153.524
137.436
131.914
129.681
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128.156
126.532
124.282
123.944
123.508
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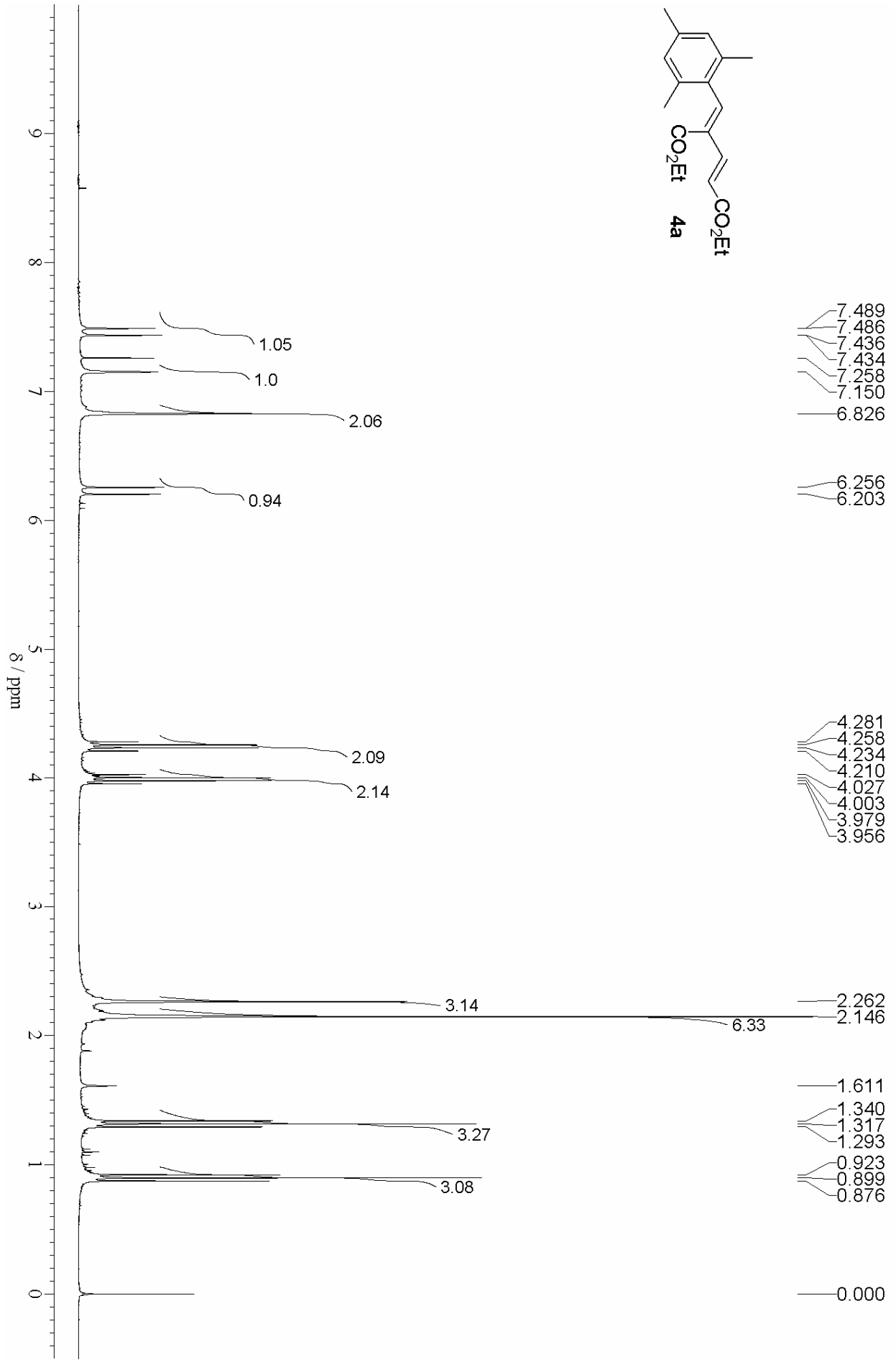
77.000
76.580
59.841
56.272
13.622
δ / ppm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CO2Et
4a
δ / ppm
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2.09
2.14
3.14
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3.27
3.08
7.489
7.486
7.436
7.434
7.258
7.150
6.826
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4.210
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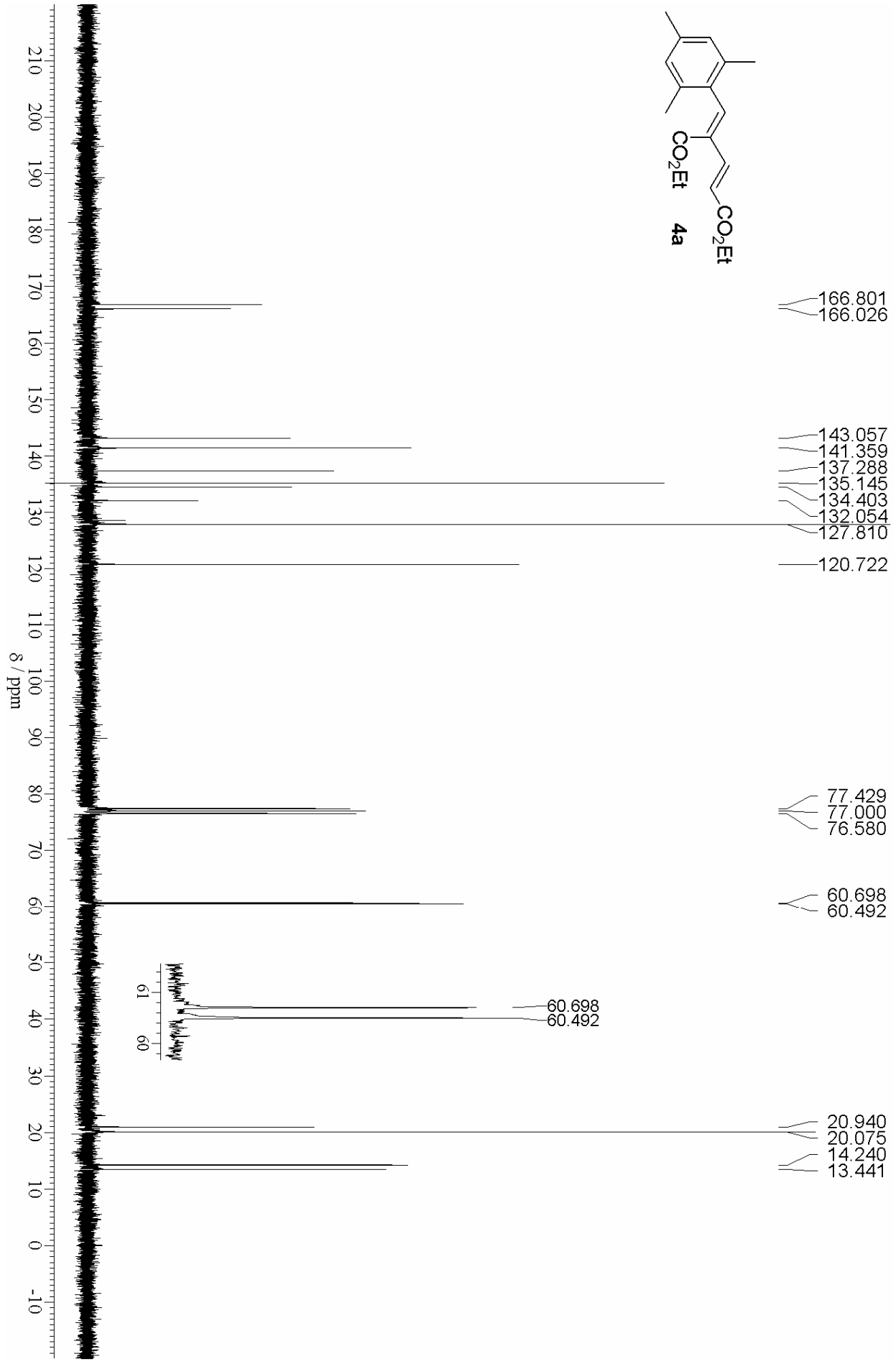
0.000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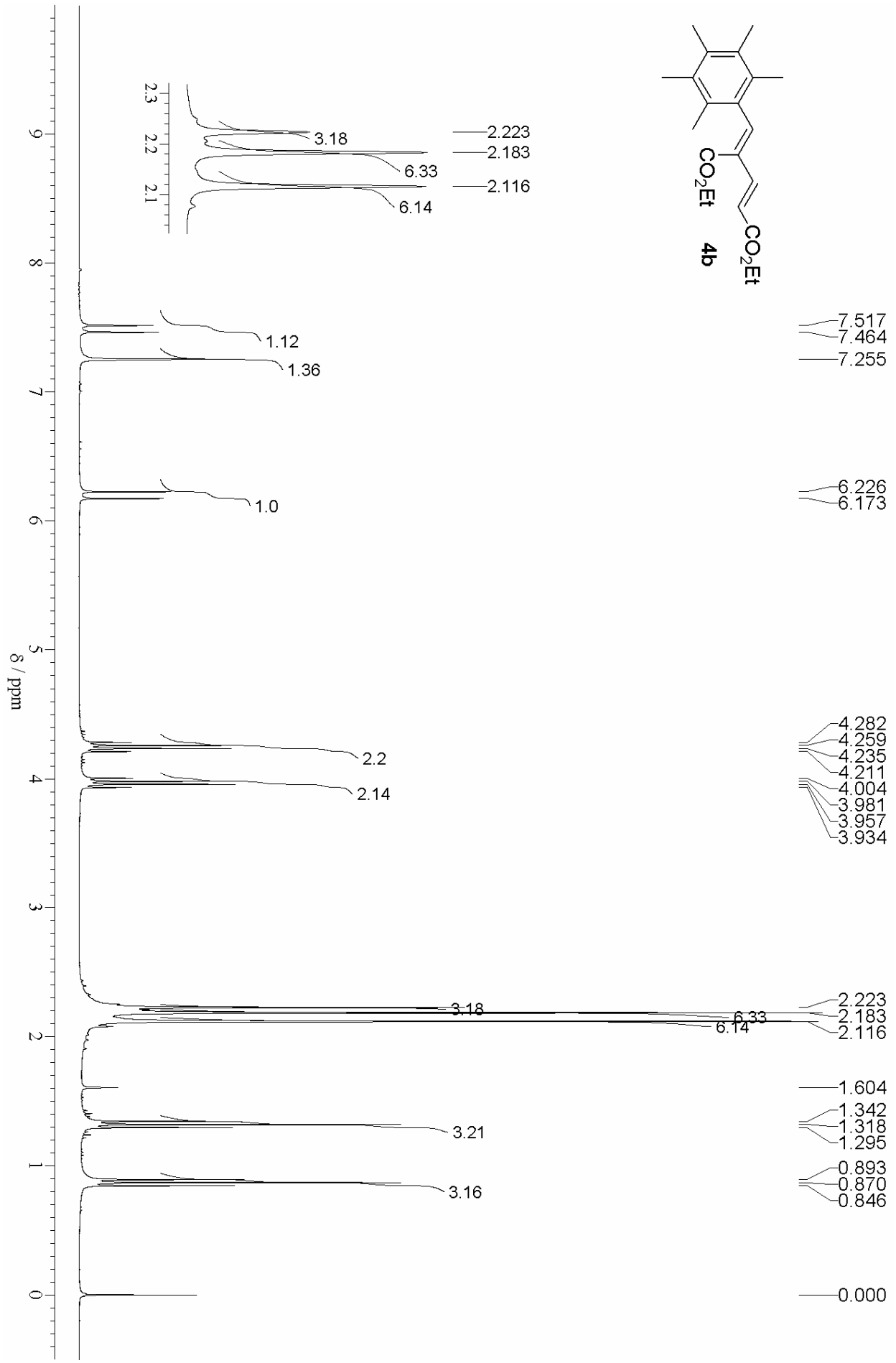
14.240
13.441
δ / ppm


δ / ppm
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CO2Et
4b
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6.33
6.14
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2.116
1.12
1.36
1.0
2.2
2.14
3.21
3.16
7.517
7.464
7.255
6.226
6.173
4.282
4.259
4.235
4.211
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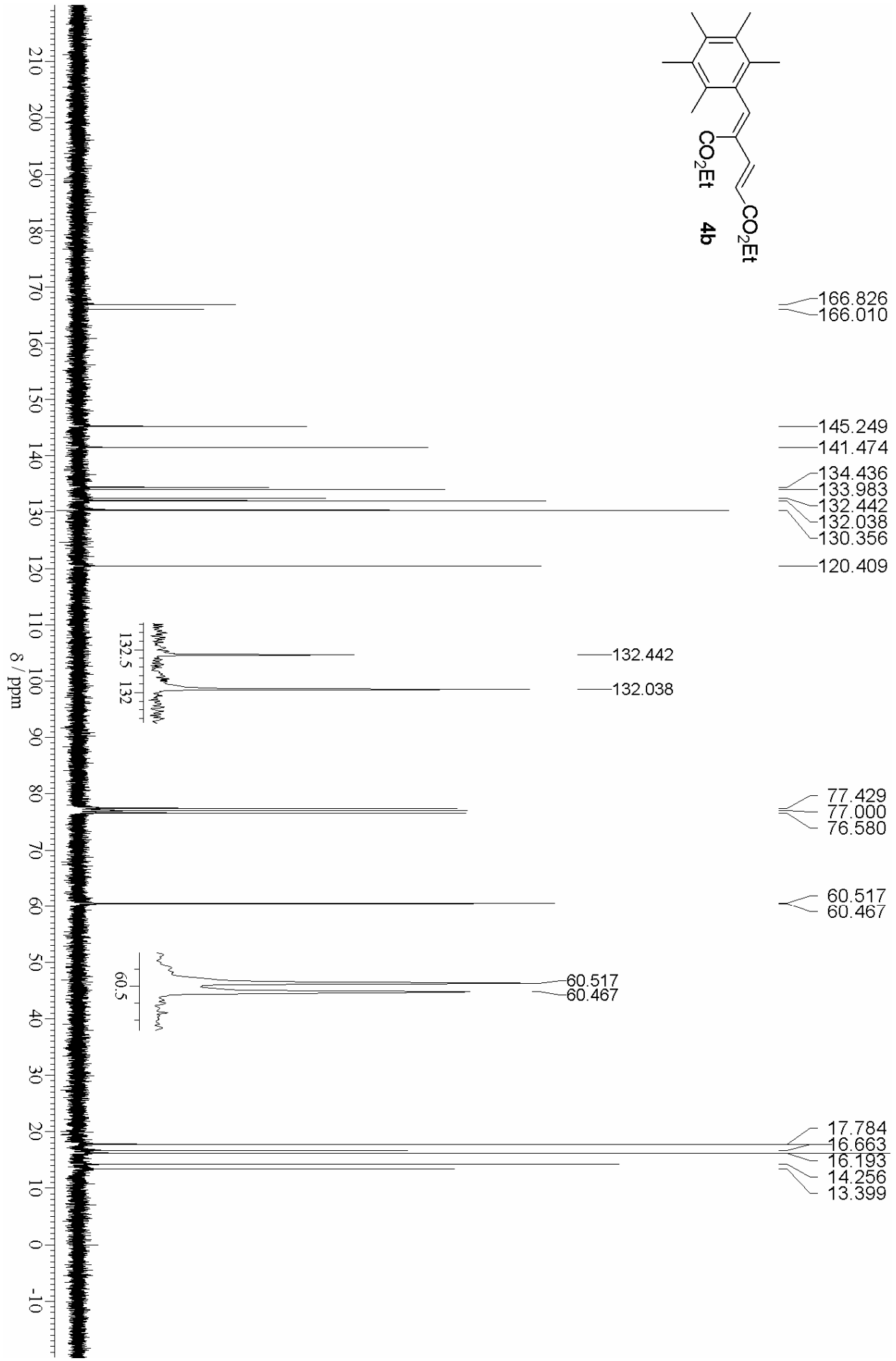
0.000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120.409
132.442
132.038
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77.000
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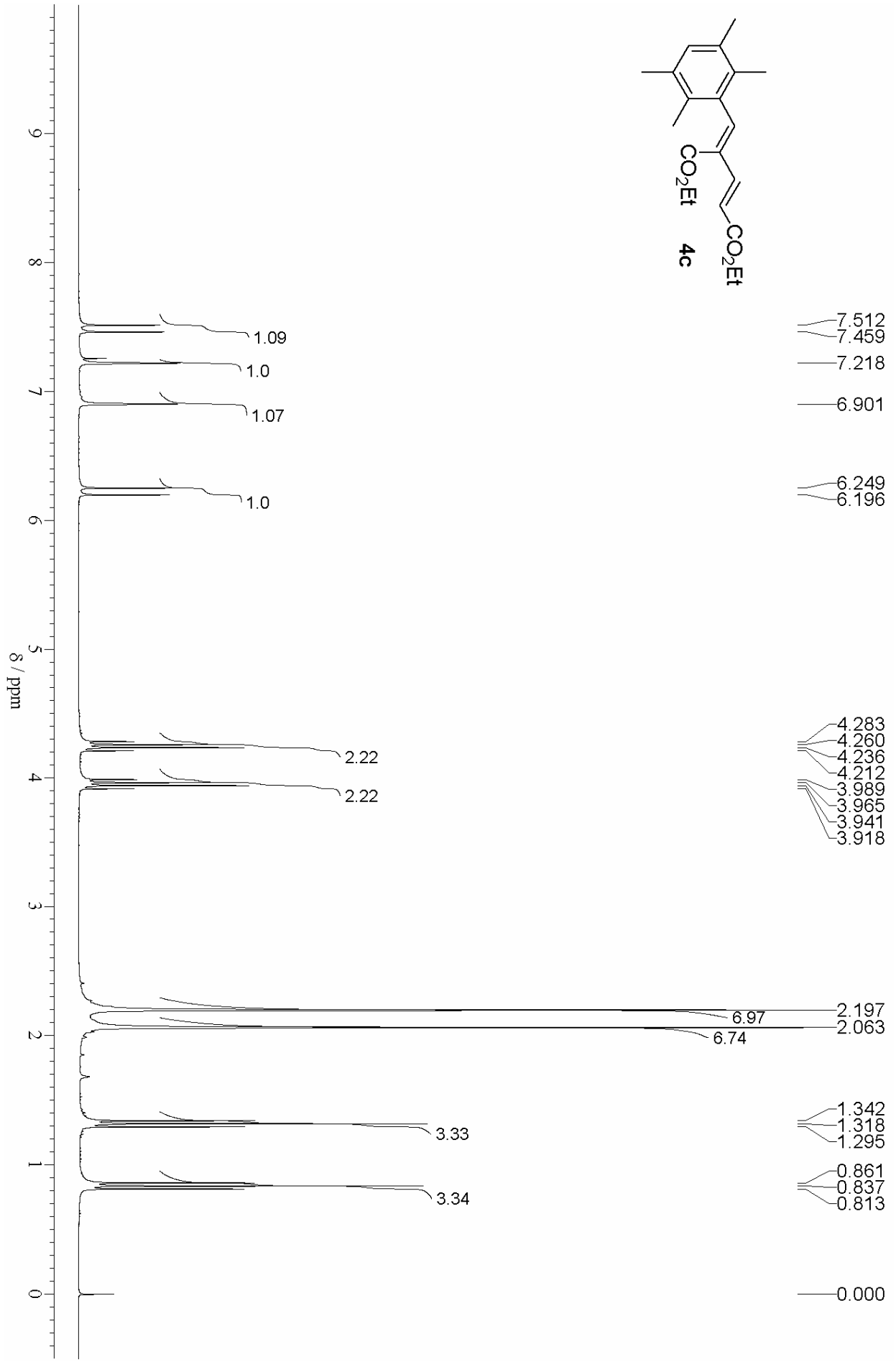
60.467
60.517
60.467
17.784
16.663
16.193
14.256
13.399
δ / ppm


CO2Et
4c
CO2Et
δ / ppm
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8
7
6
5
4
3
2
1
0
1.09
1.0
1.07
1.0
2.22
2.22
6.97
6.74
3.33
3.34
7.512
7.459
7.218
6.901
6.249
6.196
4.283
4.260
4.236
4.212
3.989
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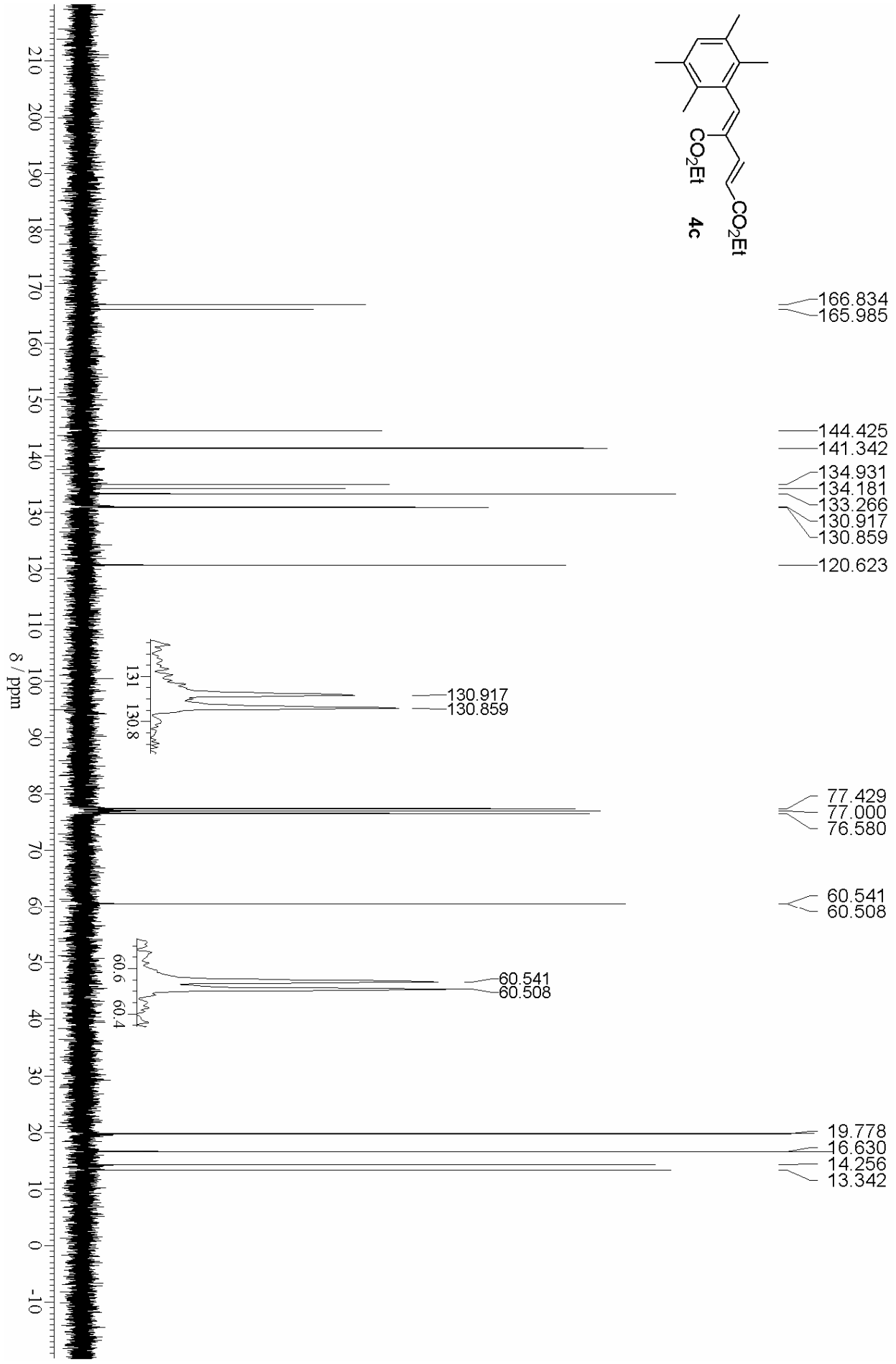
0.000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CO2Et
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131
130.8
130.917
130.859
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77.000
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60.6
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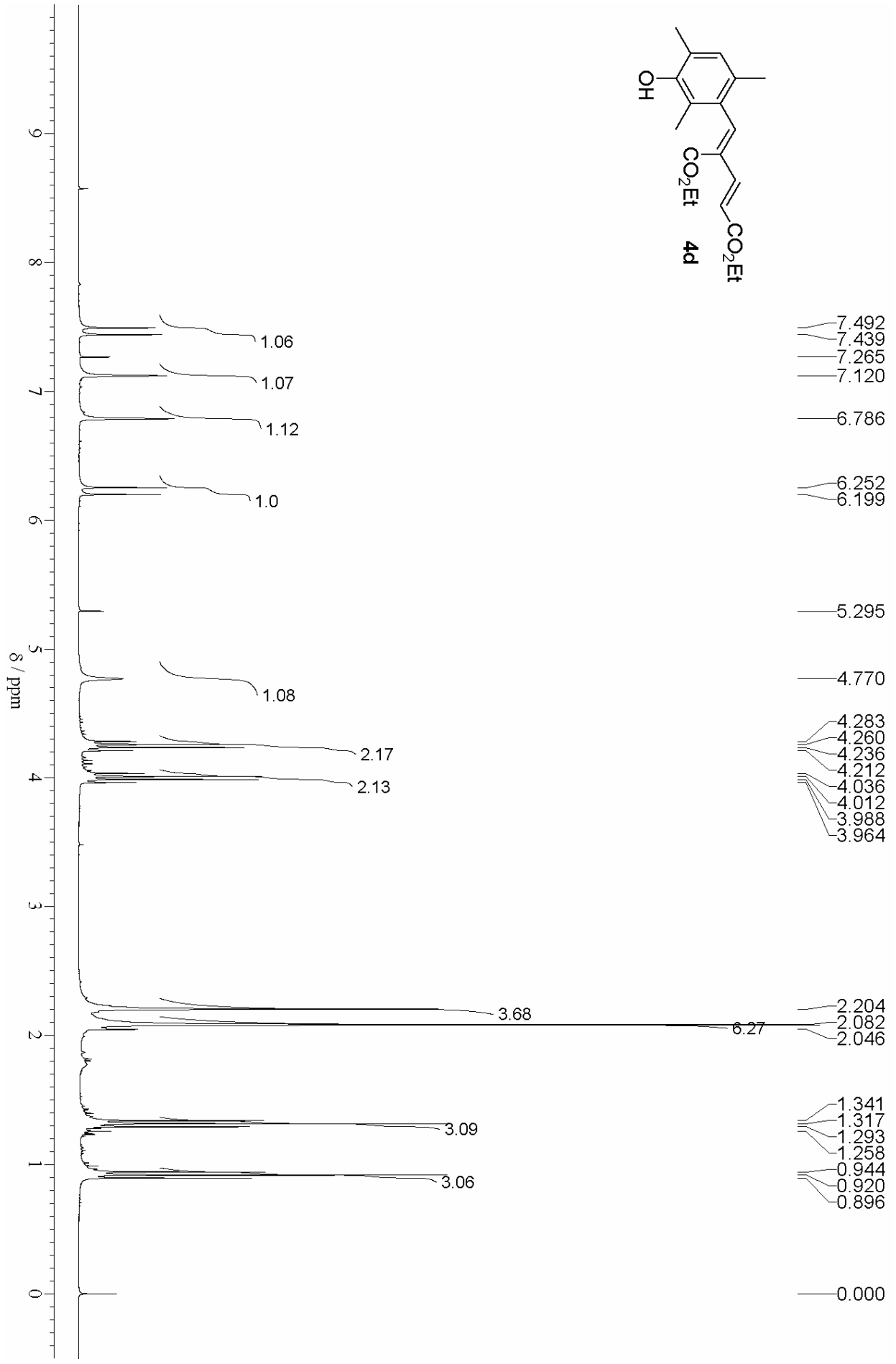
60.541
60.508
19.778
16.630
14.256
13.342
δ / ppm


OH
CO2Et
CO2Et
4d
δ / ppm
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2
3
4
5
6
7
8
9
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1.12
1.0
1.08
2.17
2.13
3.68
6.27
3.09
3.06
7.492
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7.265
7.120
6.786
6.252
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4.036
4.012
3.988
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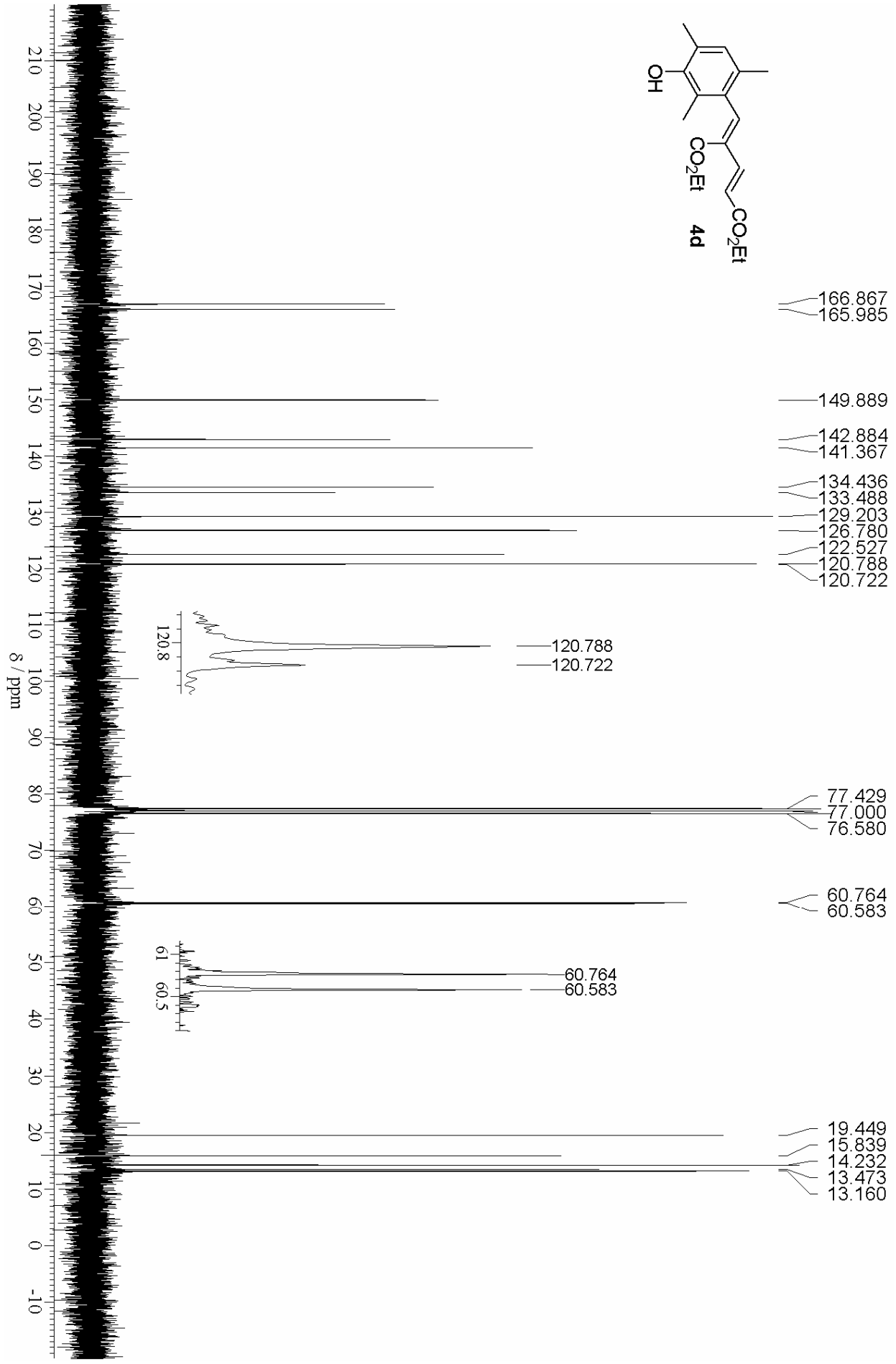
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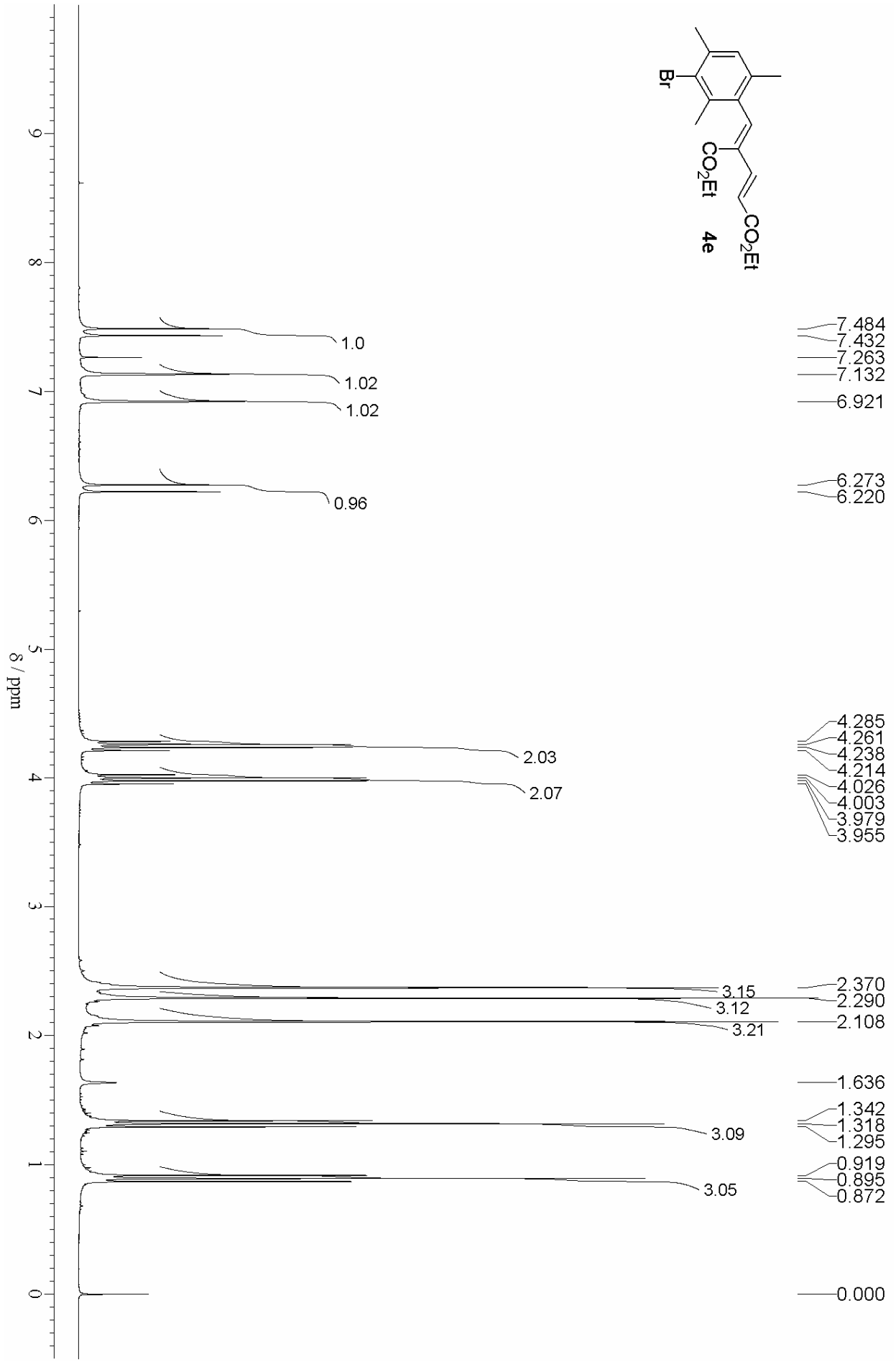
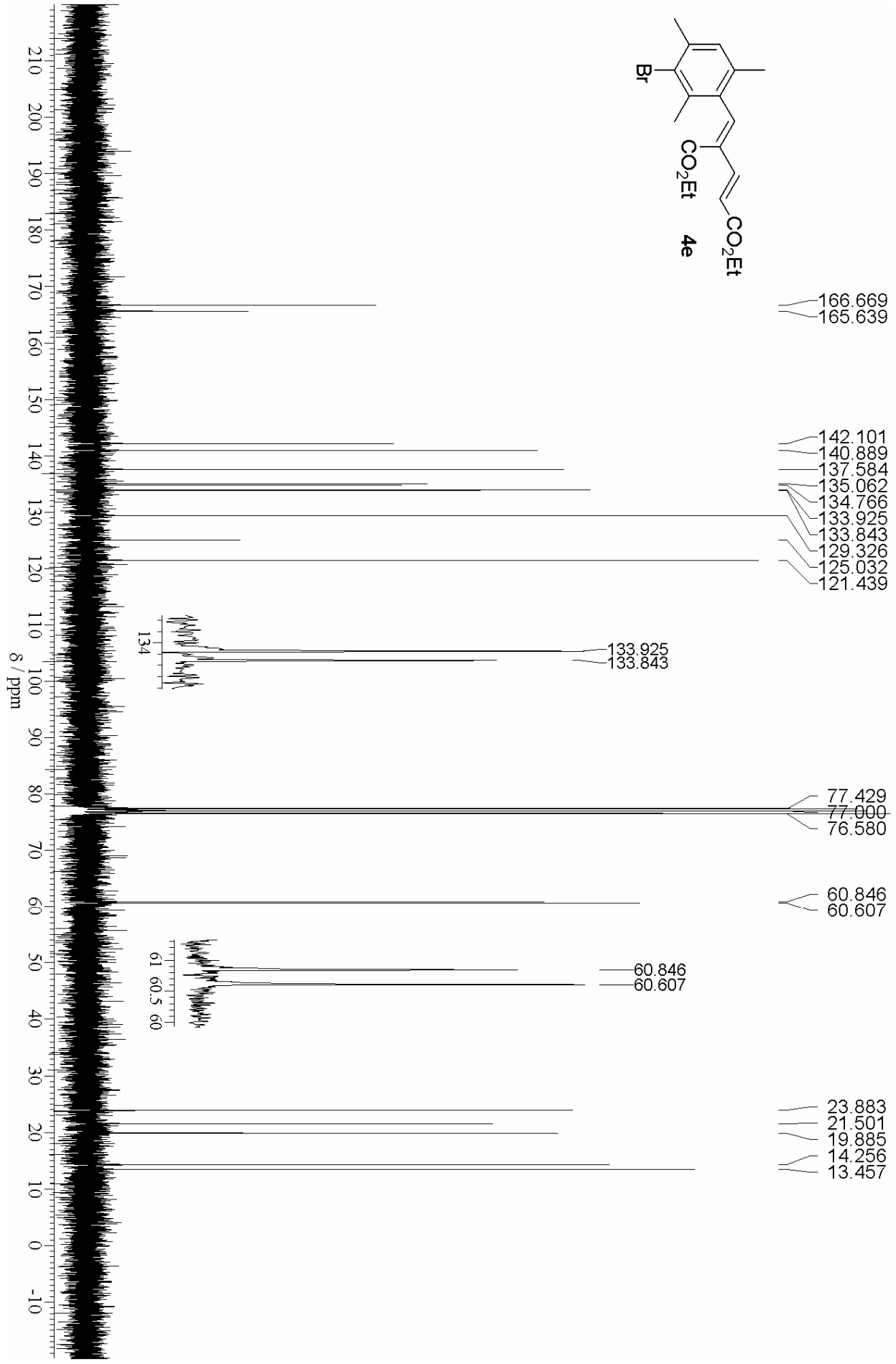
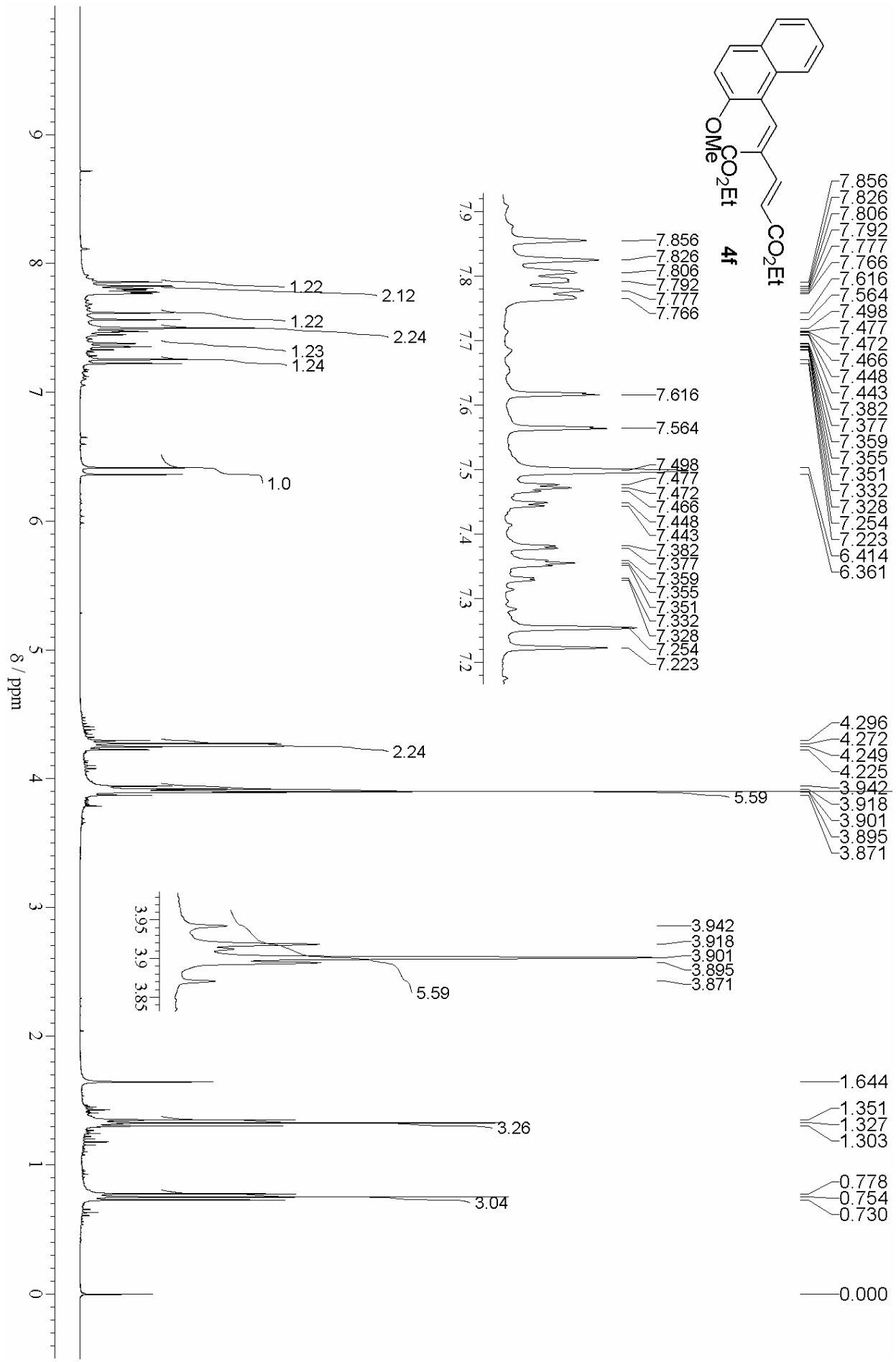
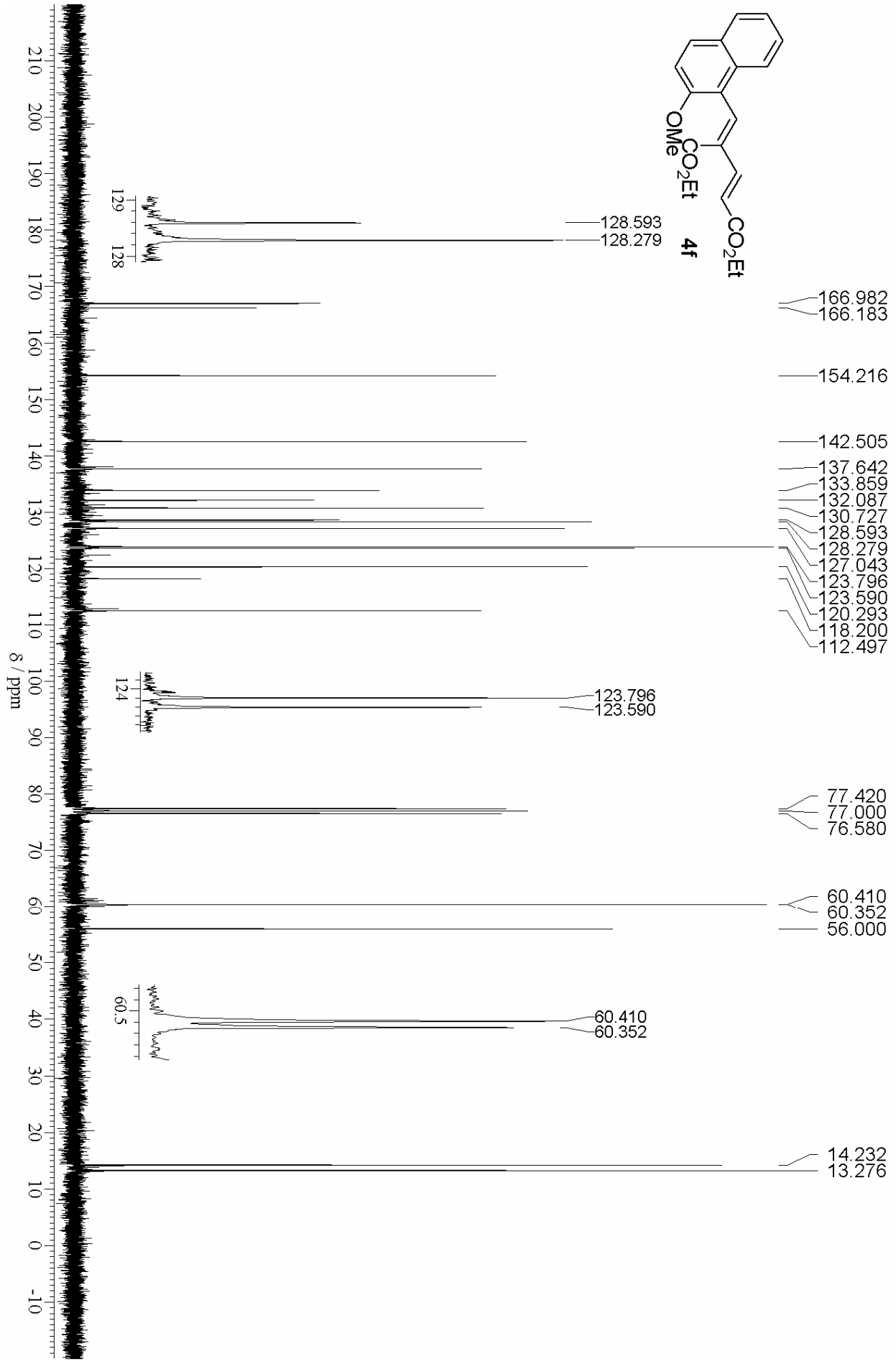
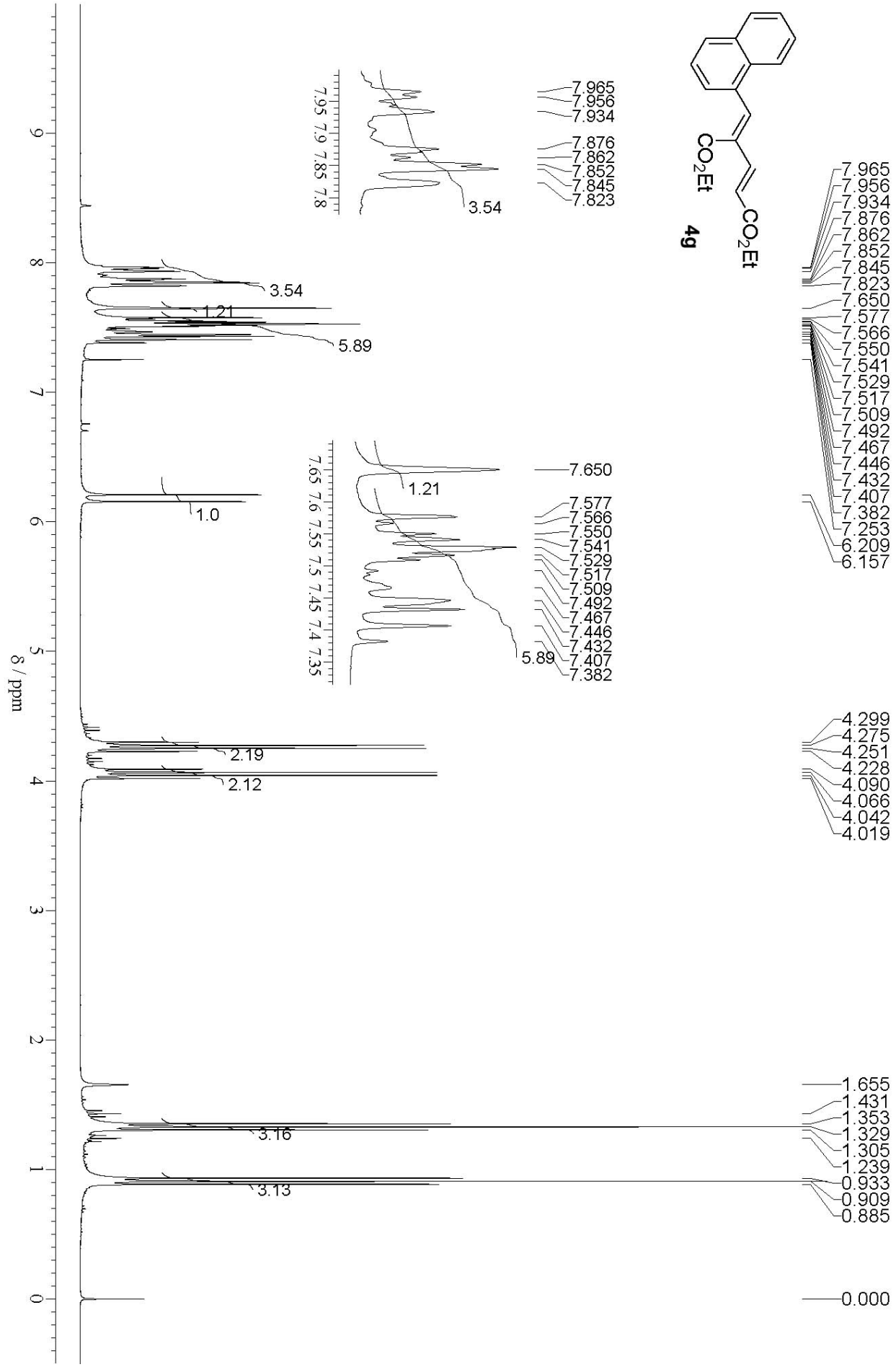
76.580
60.764
60.583
61
60.5
60.764
60.583
19.449
15.839
14.232
13.473
13.160
δ / ppm

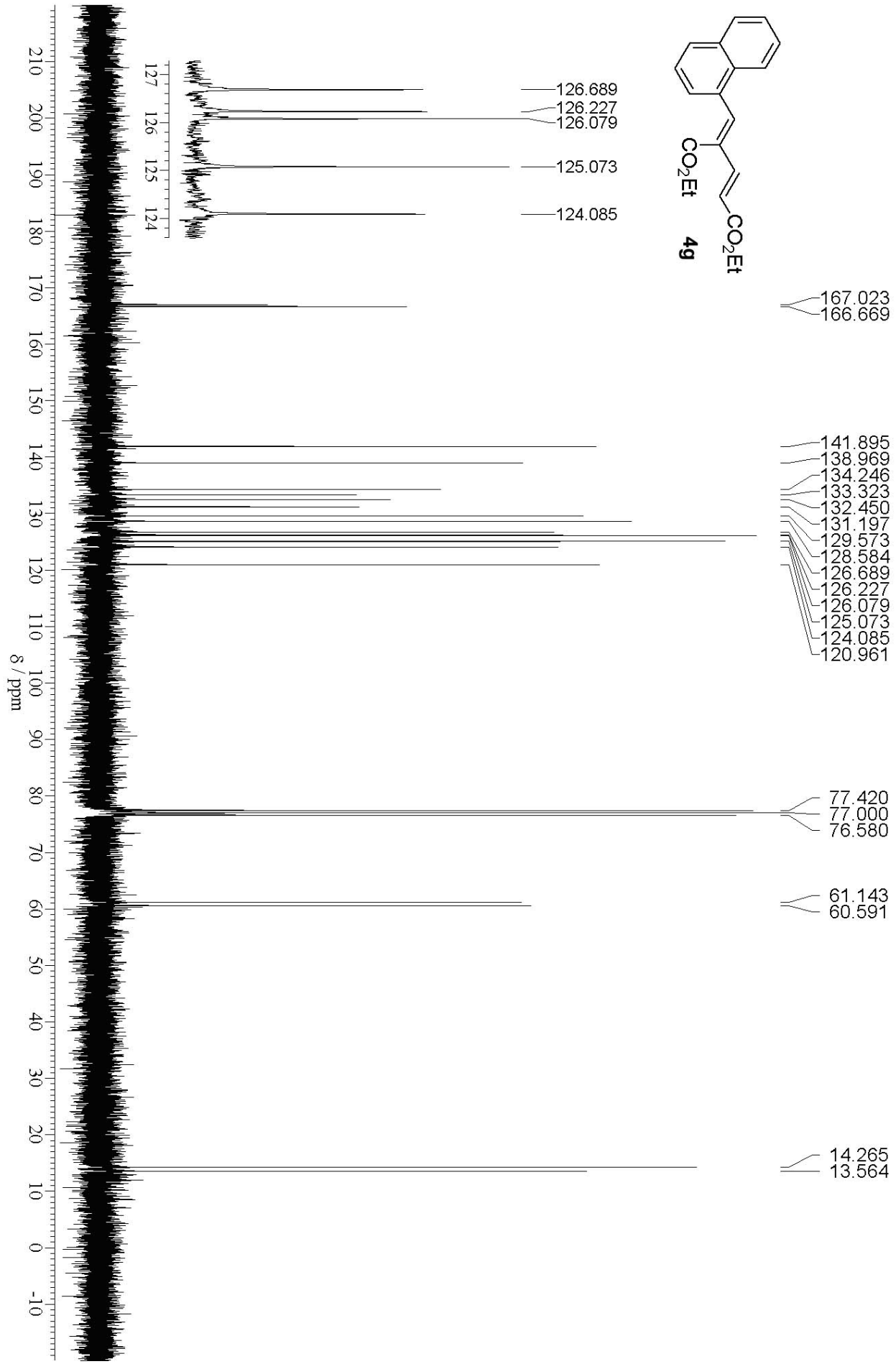

Br
CO2Et
CO2Et
4e
δ / ppm
0
1
2
3
4
5
6
7
8
9
1.0
1.02
1.02
0.96
2.03
2.07
3.15
3.12
3.21
3.09
3.05
7.484
7.432
7.263
7.132
6.921
6.273
6.220
4.285
4.261
4.238
4.214
4.026
4.003
3.979
3.955
2.370
2.290
2.108
1.636
1.342
1.318
1.295
0.919
0.895
0.872
0.000

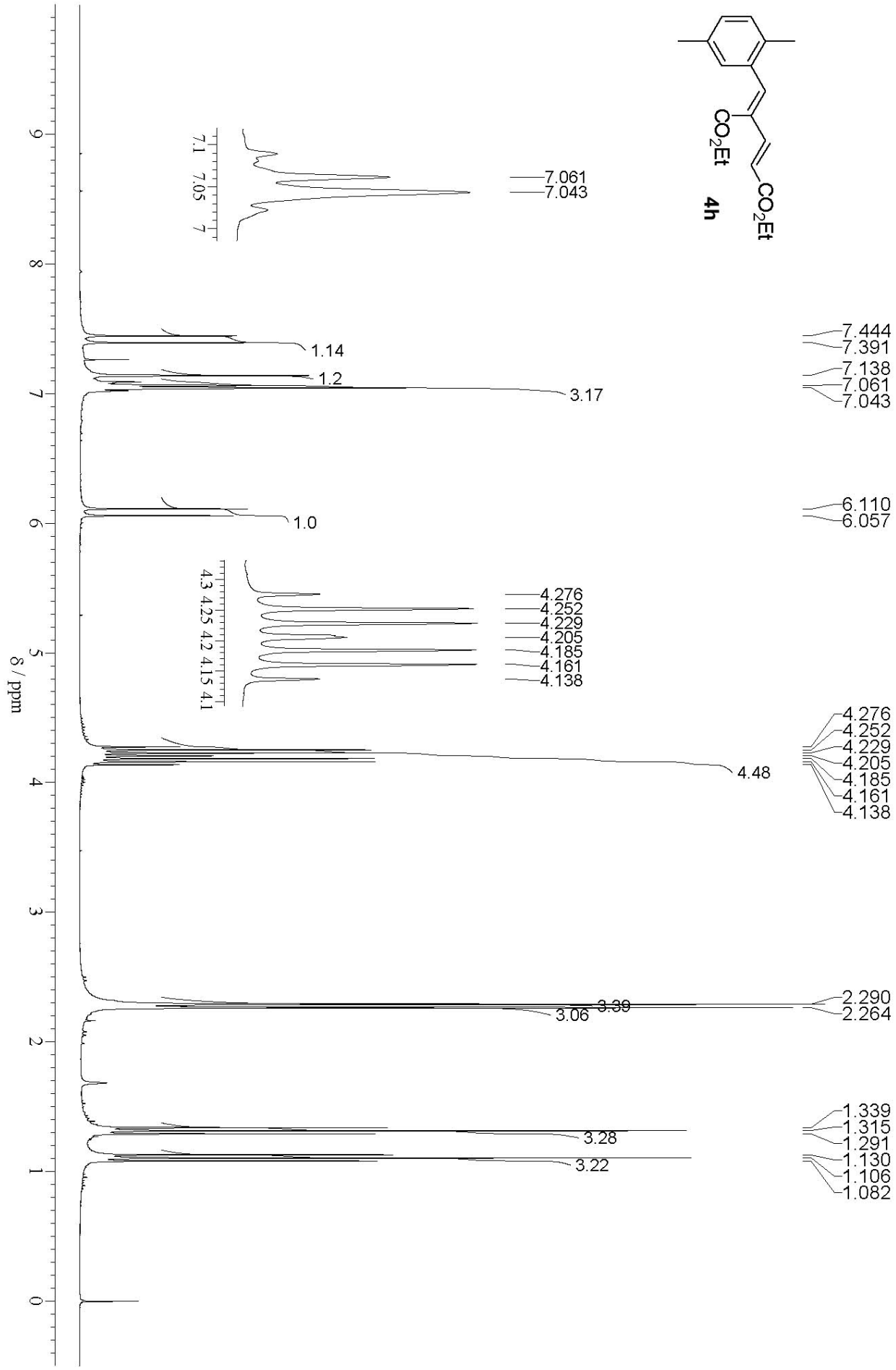

Br
CO2Et
CO2Et
4e
166.669
165.639
142.101
140.889
137.584
135.062
134.766
133.925
133.843
129.326
125.032
121.439
134
133.925
133.843
77.429
77.000
76.580
60.846
60.607
61
60.5
60
60.846
60.607
23.883
21.501
19.885
14.256
13.457
δ / ppm

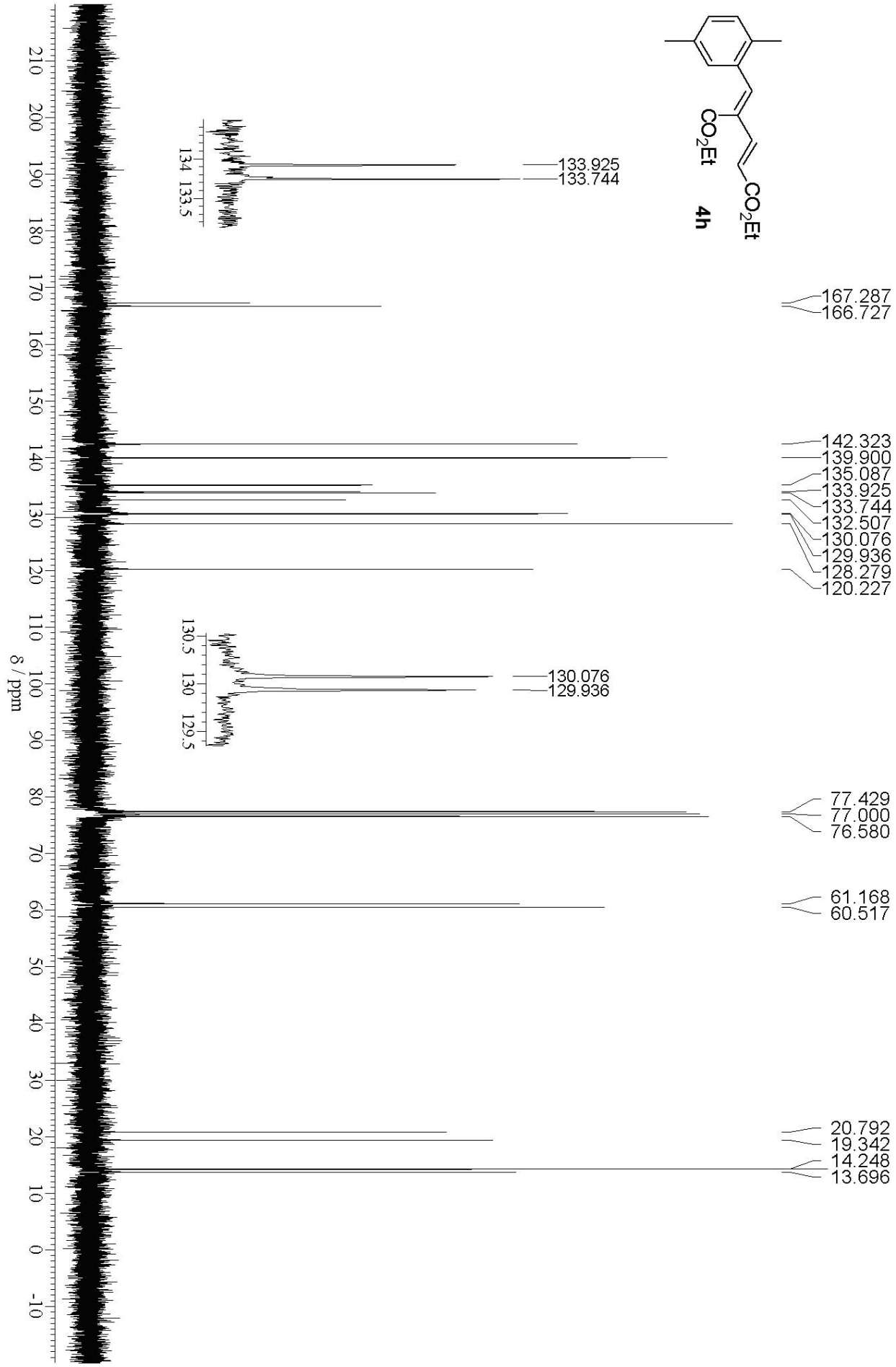

OMe
CO2Et
CO2Et
4f
δ / ppm
1.22
2.12
1.22
2.24
1.23
1.24
1.0
2.24
5.59
3.26
3.04
7.856
7.826
7.806
7.792
7.777
7.766
7.616
7.564
7.498
7.477
7.472
7.466
7.448
7.443
7.382
7.377
7.359
7.355
7.351
7.332
7.328
7.254
7.223
6.414
6.361
4.296
4.272
4.249
4.225
3.942
3.918
3.901
3.895
3.871
1.644
1.351
1.327
1.303
0.778
0.754
0.730
0.000

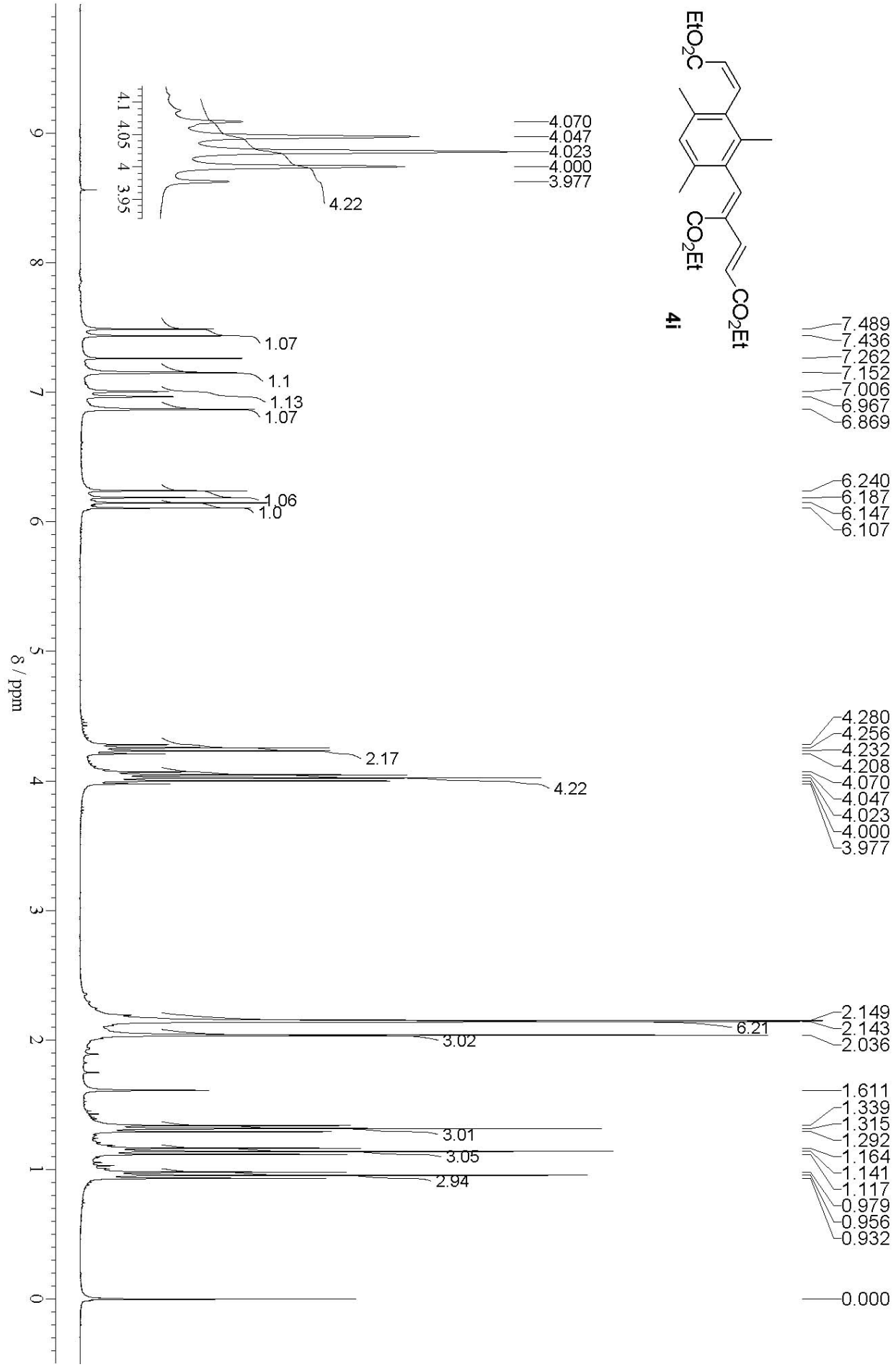

OMe
CO2Et
CO2Et
4f
δ / ppm
166.982
166.183
154.216
142.505
137.642
133.859
132.087
130.727
128.593
128.279
127.043
123.796
123.590
120.293
118.200
112.497
77.420
77.000
76.580
60.410
60.352
56.000
14.232
13.276

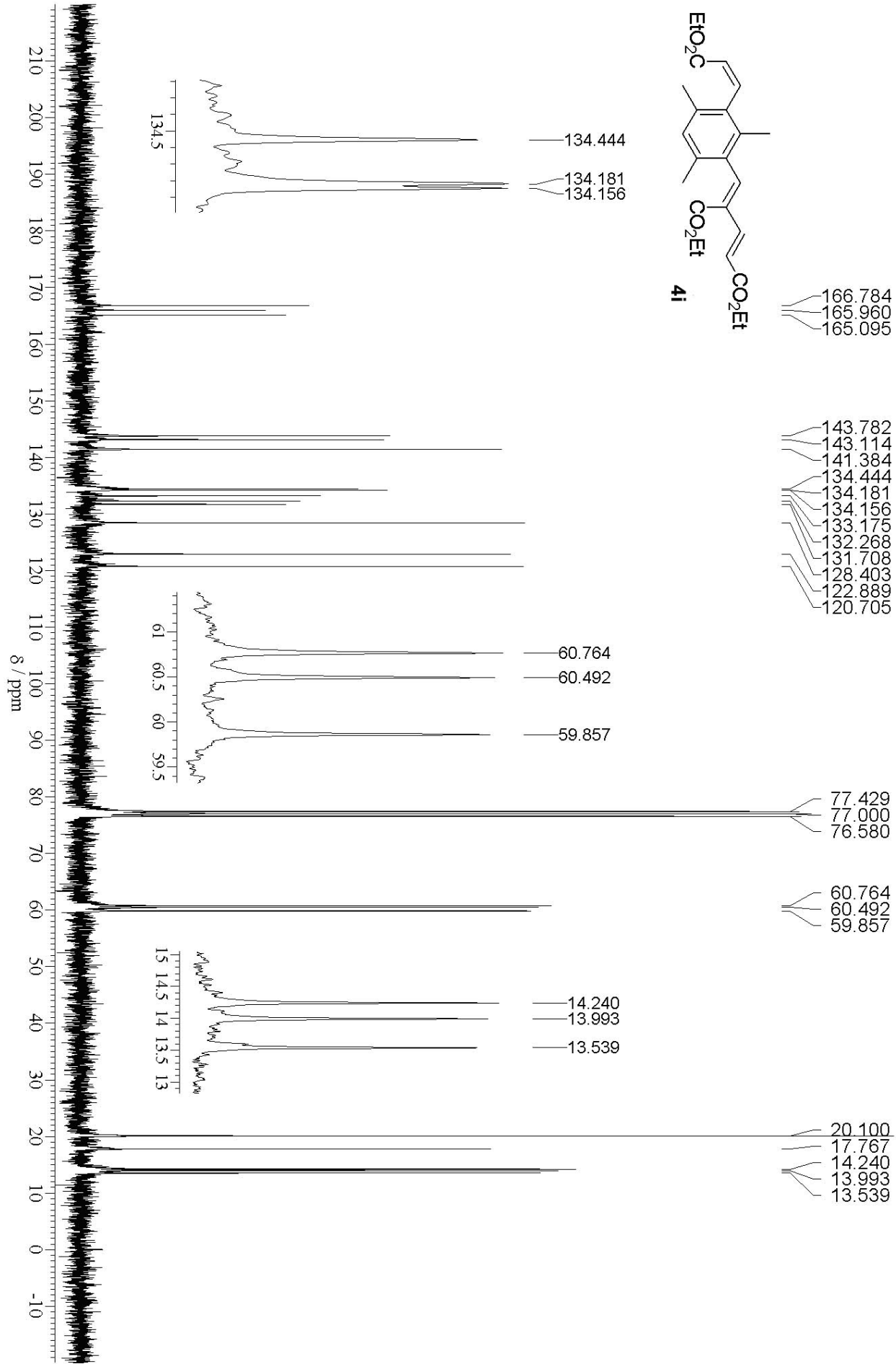

4g
CO2Et
CO2Et
δ / ppm
7.965
7.956
7.934
7.876
7.862
7.852
7.845
7.823
7.650
7.577
7.566
7.550
7.541
7.529
7.517
7.509
7.492
7.467
7.446
7.432
7.407
7.382
7.253
6.209
6.157
4.299
4.275
4.251
4.228
4.090
4.066
4.042
4.019
1.655
1.431
1.353
1.329
1.305
1.239
0.933
0.909
0.885
0.000
3.54
1.21
5.89
1.0
2.19
2.12
3.16
3.13

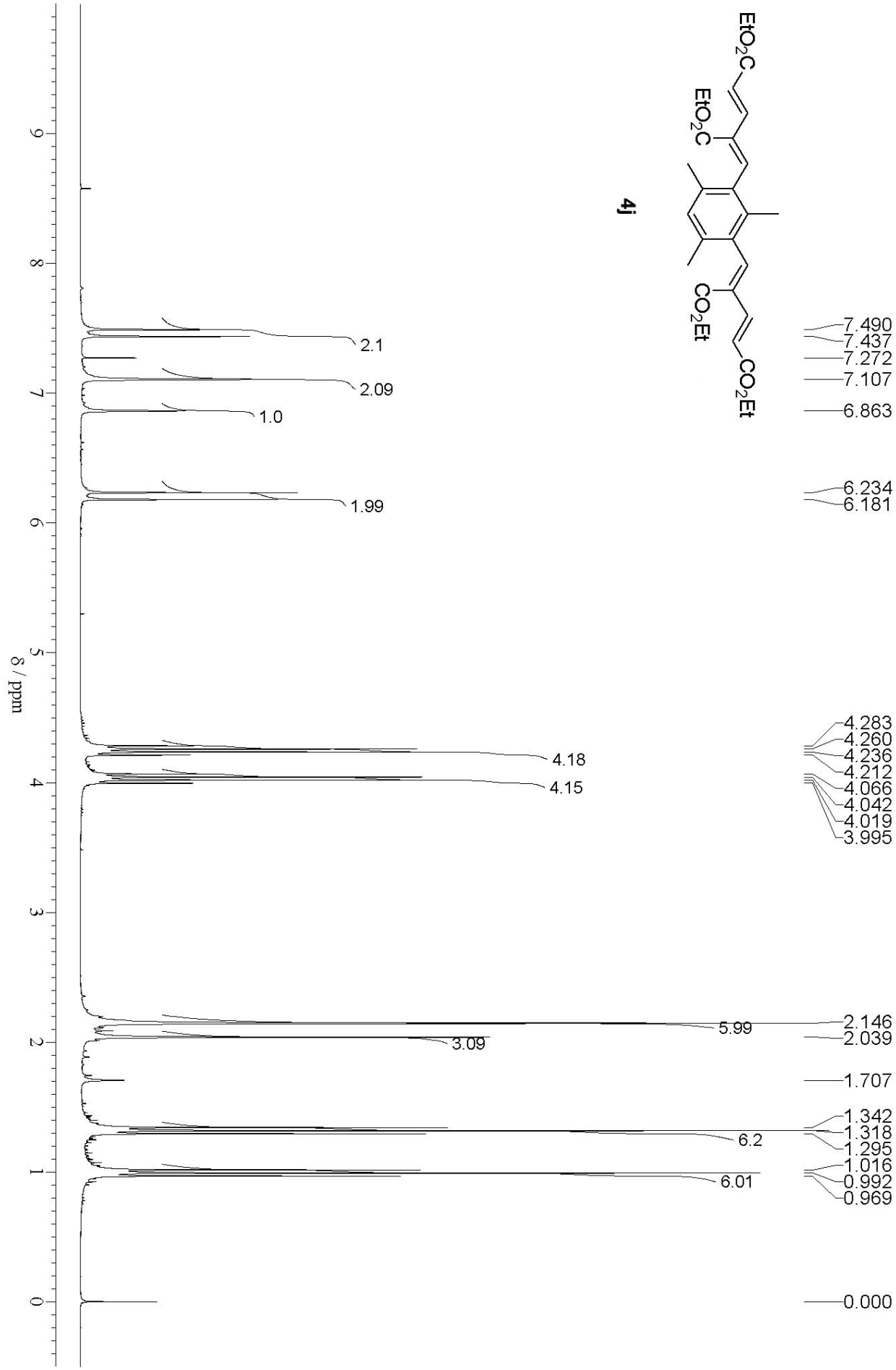

126.689
126.227
126.079
125.073
124.085
167.023
166.669
141.895
138.969
134.246
133.323
132.450
131.197
129.573
128.584
126.689
126.227
126.079
125.073
124.085
120.961
77.420
77.000
76.580
61.143
60.591
14.265
13.564
δ / ppm
CO2Et
CO2Et
4g

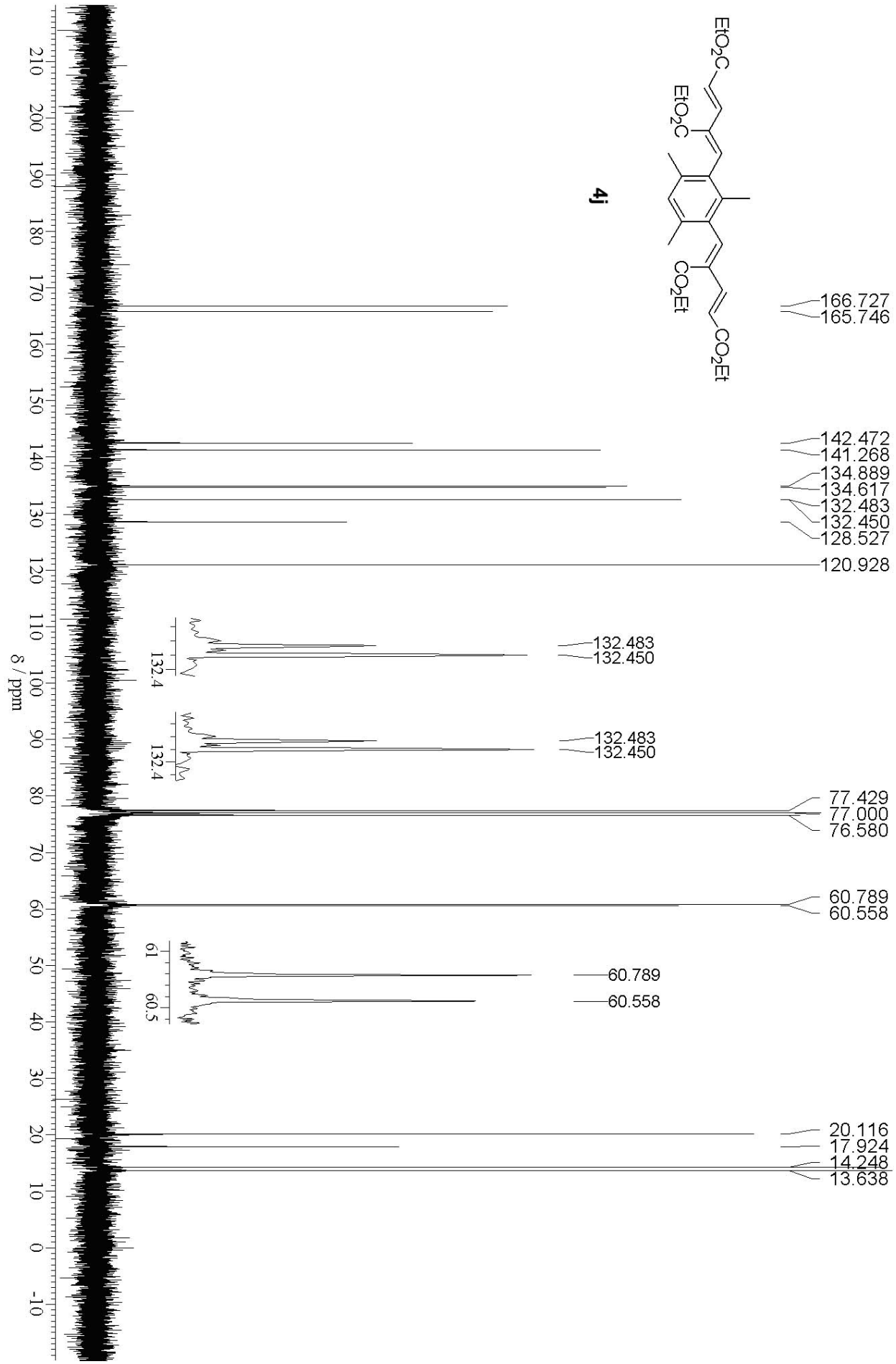

CO2Et
CO2Et
4h
7.061
7.043
1.14
1.2
3.17
1.0
4.276
4.252
4.229
4.205
4.185
4.161
4.138
4.48
3.39
3.06
3.28
3.22
7.444
7.391
7.138
7.061
7.043
6.110
6.057
4.276
4.252
4.229
4.205
4.185
4.161
4.138
2.290
2.264
1.339
1.315
1.291
1.130
1.106
1.082
δ / ppm

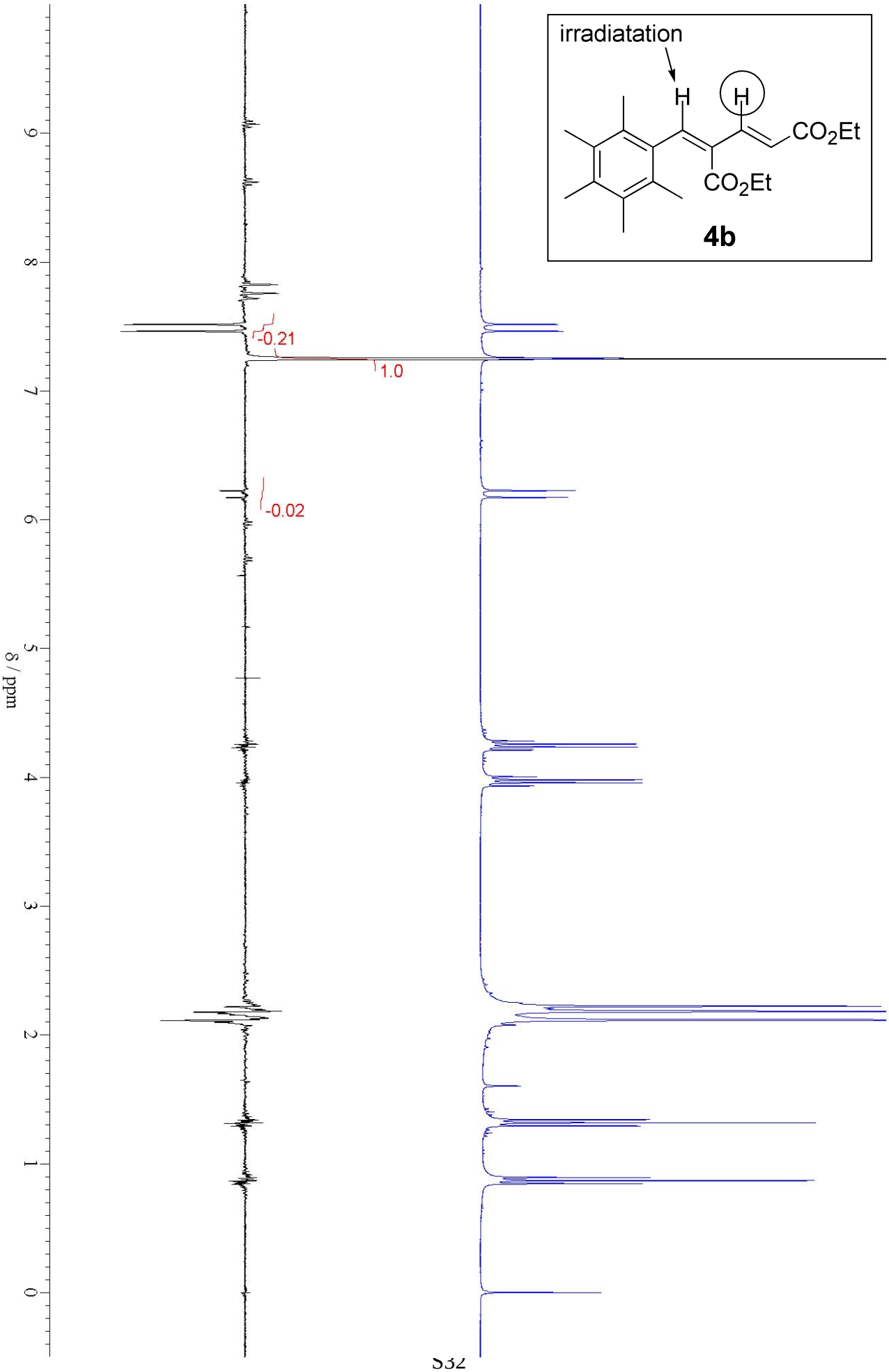

δ / ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
134
133.5
133.925
133.744
130.5
130
129.5
130.076
129.936
167.287
166.727
142.323
139.900
135.087
133.925
133.744
132.507
130.076
129.936
128.279
120.227
77.429
77.000
76.580
61.168
60.517
20.792
19.342
14.248
13.696
CO2Et
CO2Et
4h


EtO2C
CO2Et
CO2Et
4i
δ / ppm
4.1 4.05 4 3.95
4.070
4.047
4.023
4.000
3.977
4.22
1.07
1.1
1.13
1.07
1.06
1.0
2.17
4.22
6.21
3.02
3.01
3.05
2.94
7.489
7.436
7.262
7.152
7.006
6.967
6.869
6.240
6.187
6.147
6.107
4.280
4.256
4.232
4.208
4.070
4.047
4.023
4.000
3.977
2.149
2.143
2.036
1.611
1.339
1.315
1.292
1.164
1.141
1.117
0.979
0.956
0.932
0.000


EtO2C
CO2Et
CO2Et
4i
δ / ppm
166.784
165.960
165.095
143.782
143.114
141.384
134.444
134.181
134.156
133.175
132.268
131.708
128.403
122.889
120.705
77.429
77.000
76.580
60.764
60.492
59.857
20.100
17.767
14.240
13.993
13.539


4j
EtO2C
EtO2C
CO2Et
CO2Et
δ / ppm
0
1
2
3
4
5
6
7
8
9
2.1
2.09
1.0
1.99
4.18
4.15
5.99
3.09
6.2
6.01
7.490
7.437
7.272
7.107
6.863
6.234
6.181
4.283
4.260
4.236
4.212
4.066
4.042
4.019
3.995
2.146
2.039
1.707
1.342
1.318
1.295
1.016
0.992
0.969
0.000


4j
EtO2C
EtO2C
CO2Et
CO2Et
166.727
165.746
142.472
141.268
134.889
134.617
132.483
132.450
128.527
120.928
132.483
132.450
132.4
132.483
132.450
132.4
77.429
77.000
76.580
60.789
60.558
61
60.5
60.789
60.558
20.116
17.924
14.248
13.638
δ / ppm


irradiatation
H
H
CO2Et
CO2Et
4b
-0.21
1.0
-0.02
δ / ppm
9
8
7
6
5
4
3
2
1
0