Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Olefin-Directed Palladium-Catalyzed Regio- and Stereoselective Oxidative Arylation of Allenes**

*Can Zhu, Bin Yang, Tuo Jiang, and Jan-E. Bäckvall**

anie_201502924_sm_miscellaneous_information.pdf

Supporting Information

Table of Contents

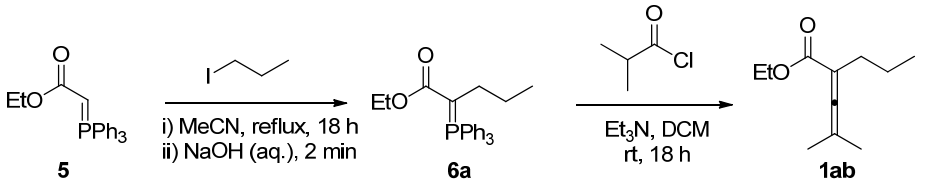
General information

Unless otherwise noted, all reagents were used as received from the commercial suppliers. $Pd(OAc)_2$ was obtained from Pressure Chemicals and used without further purification. Arylboronic acids were commercially available from Sigma Aldrich or Acros. The palladium-catalyzed allene arylation reactions could be performed without any efforts to exclude moisture. THF and toluene were obtained from a VAC Solvent Purifier. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain. Flash chromatography was carried out with 60Å (particle size 35-70 μm) normal flash silica gel. NMR spectra were recorded at 400 MHz (^1H) or 500 MHz (^1H) and at 100 MHz (^{13}C) or 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H = 7.26 and C = 77.0 ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

General procedure for preparation of starting materials

2,3-Dienoates ***1ac****,* ***1ad*** *and* ***1l*** *were prepared as previously described.*[1]

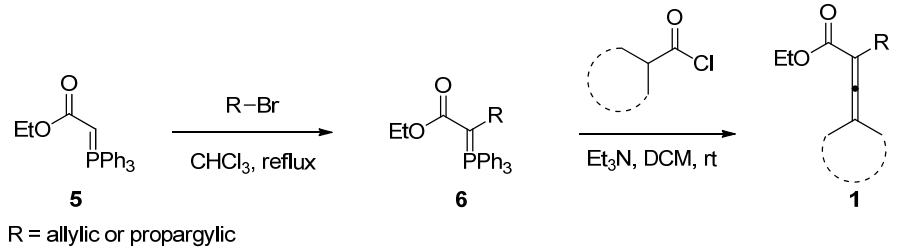
1. Synthesis of 2,3-dienoate 1ab



To a three-necked flask were added ethoxycarbonylmethylene triphenylphosphoran **5**[2] (6.967 g, 20 mmol), MeCN (30 mL), and *n*-propyl iodide (1.95 mL. d = 1.74 g/mL, 20 mmol). The flask was then equipped with a reflux condenser, and the mixture was refluxed for 18 h. The solvent was evaporated, followed by the addition of DCM (50 mL) and NaOH (aq., 2 M, 10 mL). After the mixture was stirred for additional 2 min, the organic layer was separated, and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried over Na_2SO_4. After filtration, evaporation of the solvent afforded the crude product **6a**,[3] which was used as the starting material in the next step without further purification and characterization.

To a one-necked flask were added crude **6a**, DCM (30 mL), and Et_3N (4.2 mL, d = 0.73 g/mL, 30 mmol) sequentially, and then isobutyryl chloride (2.1 mL, d = 1.02 g/mL, 20 mmol) was added at 0 ^oC. The mixture was then stirred for 18 h at room temperature. After evaporation of the solvent, the residue was dissolved in Et_2O (50 mL) and filtered to remove the solid. The mixture was evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether then petroleum ether/ethyl ether = 40/1) to afford the desired product **1ab** (1.392 g, 38% for 2 steps): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 2.17 (t, J = 7.4 Hz, 2H), 1.77 (s, 6H), 1.48-1.36 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 168.2, 99.1, 98.2, 60.5, 30.8, 21.3, 19.6, 14.3, 13.6; HRMS (ESI): calc. for $C_{11}H_{18}NaO_2$ $[M+Na]^+$: 205.1199; found: 205.1190.

2. Synthesis of 2,3-dienoates 1a-e and 1m in a similar manner to 1a.

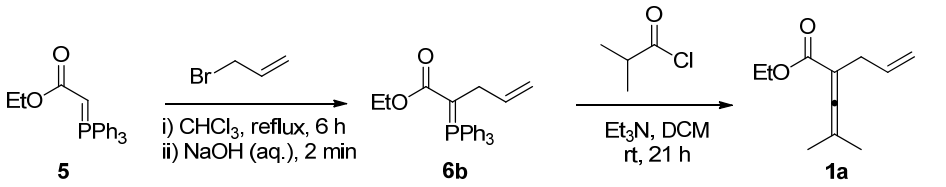


5 **6** **1**

R = allylic or propargylic

*Representative procedure for the synthesis of 2,3-dienoates **1a-e** and **1m**.*

*Ethyl 2-allyl-4-methylpenta-2,3-dienoate (**1a**).*



5 **6b** **1a**

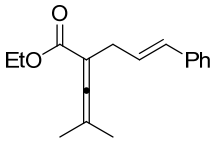
for 2 steps, 45% from **5**

To a three-necked flask were added ethoxycarbonylmethylene triphenylphosphoran **5**[2] (6.967 g, 20 mmol), $CHCl_3$ (30 mL), and allyl bromide (1.90 mL. d = 1.40 g/mL, 22 mmol). The flask was then equipped with a reflux condenser, and the mixture was refluxed for 6 h. The mixture was cooled down to room temperature, followed by the addition of NaOH (aq., 2 M, 10 mL). After the mixture was stirred for additional 2 min, the organic layer was separated, and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried over Na_2SO_4. After filtration, evaporation of the solvent afforded the crude product **6b**,[4] which was used as the starting material in the next step without further purification and characterization.

To a one-necked flask were added crude **6b**, DCM (30 mL), and Et_3N (4.2 mL, d = 0.73 g/mL, 30 mmol) sequentially, and then isobutyryl chloride (2.1 mL, d = 1.02 g/mL, 20 mmol) was added at 0 ^oC. After the addition, the mixture was stirred for 21 h at room temperature. After evaporation of the solvent, the residue was dissolved in Et_2O (50 mL) and filtered to remove the solid. The mixture was evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 40/1) to afford the desired product **1a** (1.620 g, 45% for 2 steps): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.87-5.75 (m, 1H), 5.11-4.97 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.96 (dt, J = 6.6 Hz, 1.4 Hz, 2H), 1.77 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 208.1, 167.7, 135.8, 115.5, 99.8, 96.9, 60.6, 33.4, 19.6, 14.3; HRMS (ESI): calc. for $C_{11}H_{16}NaO_2$ $[M+Na]^+$: 203.1043; found: 203.1063.

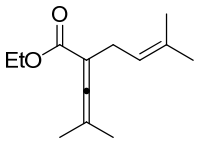
*Ethyl 2-cinnamyl-4-methylpenta-2,3-dienoate (**1b**)*



1b

63% isolated yield for 2 steps, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 4H), 7.23-7.17 (m, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.7 Hz, 6.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 6.8 Hz, 1.3 Hz, 2H), 1.79 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 167.6, 137.7, 130.9, 128.4, 127.7, 127.0, 126.1, 100.0, 97.1, 60.7, 32.8, 19.6, 14.3; HRMS (ESI): calc. for $C_{17}H_{20}NaO_2$ $[M+Na]^+$: 243.1356; found: 243.1346.

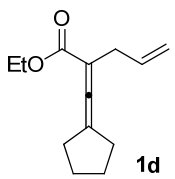
*Ethyl 5-methyl-2-(2-methylprop-1-en-1-ylidene)hex-4-enoate (**1c**)*



1c

49% isolated yield for 2 steps, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.18-5.11 (m, 1H), 4.16 (q, *J* = 7.3 Hz, 2H), 2.88 (d, *J* = 7.2 Hz, 2H), 1.76 (s, 6H), 1.69 (s, 3H), 1.62 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 168.0, 133.0, 121.4, 99.5, 97.8, 60.5, 27.9, 25.7, 19.6, 17.7, 14.3; HRMS (ESI): calc. for $C_{13}H_{20}NaO_2$ $[M+Na]^+$: 231.1356; found: 231.1359.

*Ethyl 2-(cyclopentylidenemethylene)pent-4-enoate (**1d**)*

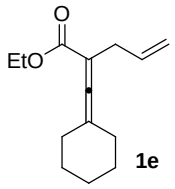


1d

47% isolated yield for 2 steps, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ

5.87-5.75 (m, 1H), 5.11-4.96 (m, 2H), 4.16 (q, J = 7.3 Hz, 2H), 2.97 (dt, J = 6.6 Hz, 1.4 Hz, 2H), 2.57-2.37 (m, 4H), 1.79-1.67 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 167.8, 135.9, 115.5, 108.0, 99.1, 60.6, 33.5, 31.1, 27.2, 14.3; HRMS (ESI): calc. for $C_{13}H_{18}NaO_2$ $[M+Na]^+$: 229.1199; found: 229.1191.

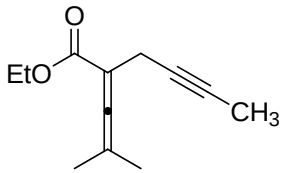
*Ethyl 2-(cyclohexylidenemethylene)pent-4-enoate (**1e**)*



1e

45% isolated yield for 2 steps, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.75 (m, 1H), 5.11-4.98 (m, 2H), 4.16 (q, J = 7.0 Hz, 2H), 2.96 (dt, J = 6.5 Hz, 1.4 Hz, 2H), 2.25-2.11 (m, 4H), 1.72-1.50 (m, 6H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 167.8, 136.0, 115.5, 106.9, 96.7, 60.5, 33.4, 30.6, 27.3, 26.0, 14.2; HRMS (ESI): calc. for $C_{14}H_{20}NaO_2$ $[M+Na]^+$: 243.1356; found: 243.1364.

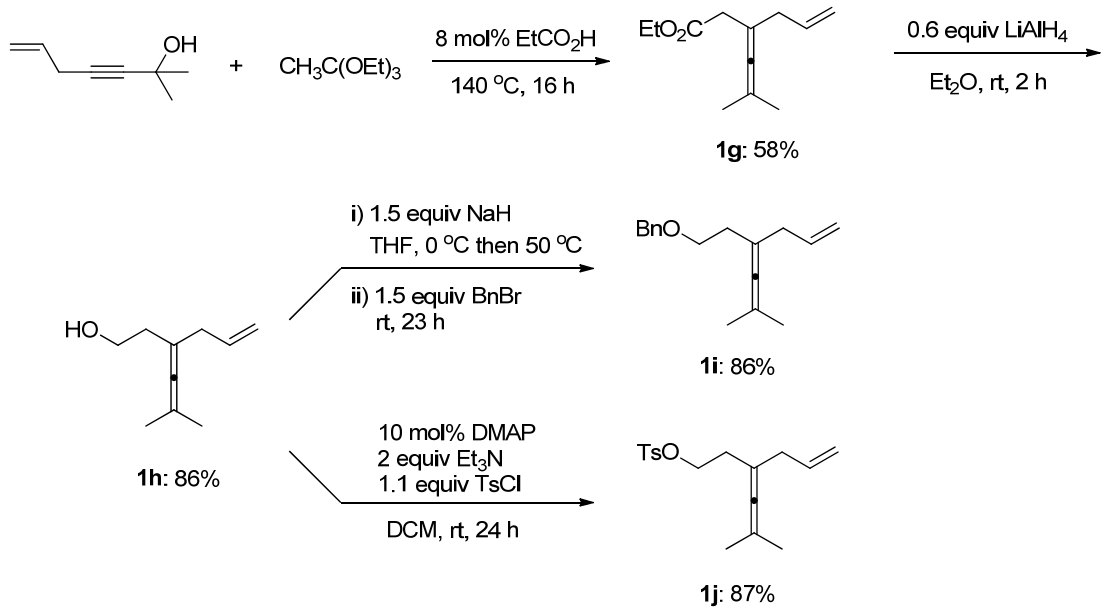
*Ethyl 2-(2-methylprop-1-en-1-ylidene)hex-4-ynoate (**1m**)*



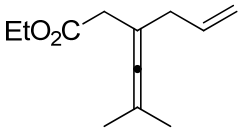
1m

51% isolated yield for 2 steps, slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, J = 7.1 Hz, 2H), 3.06 (q, J = 2.6 Hz, 2H), 1.80 (s, 6H), 1.76 (t, J = 2.5 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 167.1, 101.1, 95.7, 76.9, 75.9, 60.7, 19.9, 19.5, 14.3, 3.4; HRMS (ESI): calc. for $C_{12}H_{16}NaO_2$ $[M+Na]^+$: 215.1043; found: 215.1048.

3. Preparation for allenes 1g-j



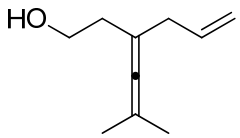
*Ethyl 3-allyl-5-methylhexa-3,4-dienoate (**1g**)*



1g

A dry round-bottomed flask was equipped with a distillation receiver and a condenser. Propargylic alcohol (2.484 g, 20 mmol), triethyl orthoacetate (30 mL), and propanoic acid (118 mg. 1.6 mmol) were added sequentially. After the reaction was refluxed for 16 h, the mixture was cooled down to 0 °C in an ice bath. Et_2O (50 mL) and HCl (aq., 1 M, 20 mL) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 40/1) to afford the desired product **1g** (2.250 g, 58%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.71 (m, 1H), 5.10-4.97 (m, 2H), 4.12 (q, J = 7.2 Hz, 2H), 2.91 (s, 2H), 2.75 (d, J = 6.7 Hz, 2H), 1.67 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 171.7, 135.9, 115.8, 96.6, 94.1, 60.4, 38.8, 37.7, 20.6, 14.2; HRMS (ESI): calc. for $C_{12}H_{18}NaO_2$ $[M+Na]^+$: 217.1199; found: 217.1193.

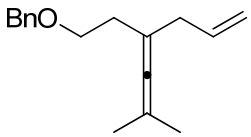
*3-Allyl-5-methylhexa-3,4-dien-1-ol (**1h**)*



1h

A solution of 3,4-dienoate **1g** (971 mg, 5 mmol) in dry Et_2O (5 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (114 mg, 3 mmol) in dry Et_2O (200 mL) at -78 ^oC under Ar atmosphere. The mixture was stirred for 2 h at room temperature, and then carefully quenched with H_2O (2 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, evaporated. The residue was dissolved in Et_2O (20 mL), and quickly filtered via a short column of silica gel (2 cm, eluent: 20 mL of Et_2O). Evaporation of the solvent directly afforded the pure product **1h** (652 mg, 86%): colorless oil. 3,4-dienol **1h** is unstable at room temperature under open-air conditions (see the attached spectra). ^1H NMR (400 MHz, $CDCl_3$) δ 5.85-5.72 (m, 1H), 5.10-4.96 (m, 2H), 3.69 (t, J = 6.1 Hz, 2H), 2.69 (d, J = 6.7 Hz, 2H), 2.17 (t, J = 6.2 Hz, 2H), 1.69 (s, 6H), 1.67 (br.s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 136.2, 115.6, 97.2, 96.9, 61.0, 38.1, 35.5, 20.9; HRMS (ESI): calc. for $C_{10}H_{17}O$ $[M+H]^+$: 153.1274; found: 153.1276.

*(((3-Allyl-5-methylhexa-3,4-dien-1-yl)oxy)methyl)benzene (**1i**)*

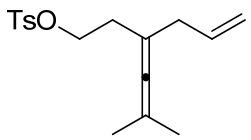


1i

To a stirred suspension of NaH (180 mg, 60% dispersion in mineral oil, 4.5 mmol) in dry THF (15 mL) was added 3,4-dienol **1h** (457 mg, 3 mmol) at 0 ^oC. After the mixture was stirred at 50 ^oC for 30 min, BnBr (0.54 mL, d = 1.43 g/mL, 4.5 mmol) was added at 0 ^oC. The mixture was stirred for another 23 h at room temperature. HCl (aq., 1 M, 10 mL) was carefully added at 0 ^oC to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, evaporated, and purified

via column chromatography on silica gel (eluent: petroleum ether, then petroleum ether/ethyl ether = 40/1) to afford the desired product **1i** (625 mg, 86%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.5 Hz, 4H), 7.32-7.25 (m, 1H), 5.86-5.74 (m, 1H), 5.08-4.96 (m, 2H), 4.51 (s, 2H), 3.56 (t, *J* = 7.1 Hz, 2H), 2.70 (d, *J* = 6.8 Hz, 2H), 2.25 (t, *J* = 7.0 Hz, 2H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 138.6, 136.5, 128.3, 127.6, 127.4, 115.3, 97.0, 96.1, 72.9, 69.3, 38.3, 32.6, 20.9; HRMS (ESI): calc. for $C_{17}H_{22}NaO$ $[M+Na]^+$: 265.1563; found: 265.1560.

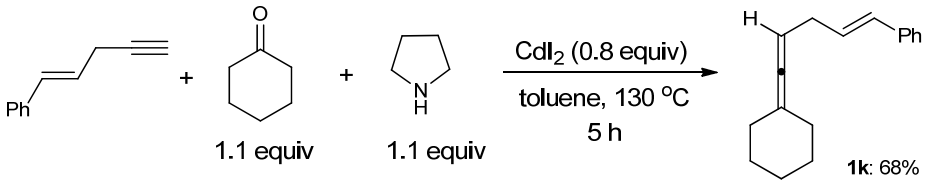
*3-Allyl-5-methylhexa-3,4-dien-1-yl 4-methylbenzenesulfonate (**1j**)*



1j

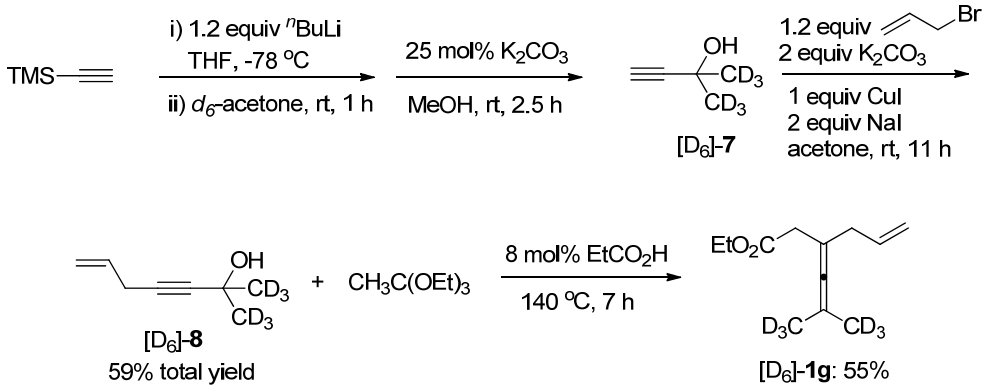
To a one-necked flask were added 3,4-dienol **1h** (685 mg, 4.5 mmol), DCM (20 mL), DMAP (55 mg, 0.45 mmol), Et_3N (1.25 mL, d = 0.73 g/mL, 9 mmol), and TsCl (953 mg, 5 mmol) sequentially. After the mixture was stirred at room temperature for 24 h, HCl (aq., 1 M, 20 mL) was added at 0 ^{o}C to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the desired product **1j** (1.205 g, 87%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.76-5.63 (m, 1H), 5.03-4.92 (m, 2H), 4.07 (t, *J* = 6.9 Hz, 2H), 2.60 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 144.6, 135.9, 133.4, 129.7, 127.8, 115.7, 97.6, 95.2, 68.9, 38.0, 31.5, 21.6, 20.7; HRMS (ESI): calc. for $C_{17}H_{22}NaSO_3$ $[M+Na]^+$: 329.1182; found: 329.1183.

4. Synthesis of allene 1k.[5]

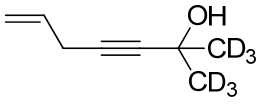


To a dried Schlenk tube was added CdI_2 (1.465 g, 0.8 mmol). The Schlenk tube was then dried under vacuum with a heating gun until the white CdI_2 turned to yellow green. Enyne (711 mg, 5 mmol), toluene (10 mL), cyclohexanone (568 μL, d = 0.95 g/mL, 5.5 mmol), pyrrolidine (459 μL, d = 0.85 g/mL, 5.5 mmol), and toluene (15 mL) were then added sequentially under Ar atmosphere. The Schlenk tube was then equipped with a condenser and placed in a pre-heated oil bath of 130 °C with stirring for 5 h. After cooling to room temperature, the crude reaction mixture was filtrated through a short pad of silica gel eluted with Et_2O (20 mL). After evaporation, the residue was purified via chromatography on silica gel (eluent: *n*-pentane) to afford the desired product **1k** (764 mg, 68%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.38-7.29 (m, 2H), 7.25-7.19 (m, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.8 Hz, 6.6 Hz, 1H), 5.11-5.04 (m, 1H), 2.92 (td, *J* = 6.6 Hz, 1.5 Hz, 2H), 2.22-2.09 (m, 4H), 1.69-1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 137.8, 130.1, 129.2, 128.4, 126.8, 126.0, 103.1, 86.9, 33.2, 31.7, 27.5, 26.1.

5. Synthesis of allene [D_6]-1g.



*[D_6]-2-methylhept-6-en-3-yn-2-ol ([D_6]-**8**)*

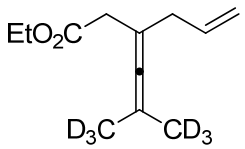


[D_6]-**8**

To a solution of ethynyltrimethylsilane (24 mL, 2.5 M in hexane, 60 mmoL) in dry THF (60 mL) was added ^{n}BuLi (24 mL, 2.5 M in hexane, 60 mmoL) at -78 ^{o}C under Ar atmosphere. After the mixture was stirred at 0 ^{o}C for 30 min, d_6-acetone (4.809 g, 75 mmol) was added at -78 ^{o}C. The reaction was stirred at -78 ^{o}C for 2 h, and then warmed to room temperature for another 1 h. The reaction was carefully quenched with HCl (aq., 1 M, 20 mL) and H_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The residue was dissolved in MeOH (100 mL), and K_2CO_3 (1.728 g, 12.5 mol) was added. The reaction was stirred at room temperature for 2.5 h, then filtered to remove inorganic salts. After evaporation of the solvent under atmospheric conditions (1 atm), H_2O (50 mL) was added, and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered. Evaporation of the solvent under atmospheric conditions (1 atm) afforded the crude product [D_6]-**7**, which could be used as the starting material without further purification and identification.

To a solution of the crude [D_6]-**7** in acetone (150 mL) were added K_2CO_3 (13.821 g, 100 mmol), NaI (14.898 g, 100 mmol), CuI (9.523 g, 50 mmol), and allyl bromide (5.18 mL, d = 1.40 g/mL, 60 mmol) sequentially.[6] The reaction was stirred at room temperature for 11 h, then filtered to remove inorganic salts. After evaporation, Et_2O (100 mL) was added to the residue, and the mixture was filtered again. The mixture was evaporated, and purified via column chromatography on silica gel (eluent: *n*-pentane/ethyl ether = 5/1) to afford the desired product [D_6]-**8** (3.850 g, 59% total yield): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.74 (m, 1H), 5.30 (dq, *J* = 16.9 Hz, 1.8 Hz, 1H), 5.11 (dq, *J* = 10.0 Hz, 1.7 Hz, 1H), 2.97 (dt, *J* = 5.3 Hz, 1.8 Hz, 2H), 1.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 116.0, 87.5, 79.0, 65.0, 22.9; HRMS (ESI): calc. for $C_8H_6D_6NaO$ $[M+Na]^+$: 153.1157; found: 153.1148.

*[D_6]-Ethyl 3-allyl-5-methylhexa-3,4-dienoate ([D_6]-**1g**)*



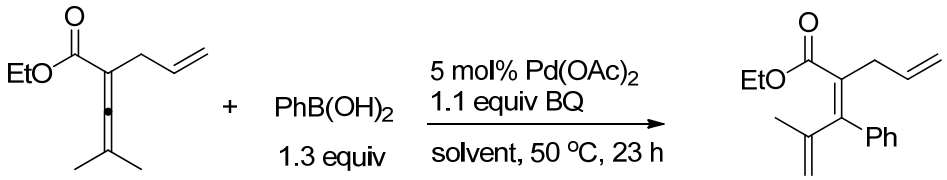
[D_6]-**1g**

A dry round-bottomed flask was equipped with a distillation receiver and a condenser. Propargylic alcohol [D_6]-**8** (2.604 g, 20 mmol), triethyl orthoacetate (30 mL), and propanoic acid (118 mg. 1.6 mmol) were added sequentially. After the reaction was refluxed for 7 h, the mixture was cooled down to 0 ^{o}C in an ice bath. Et_2O (50 mL) and HCl (aq., 1 M, 20 mL) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 40/1) to afford the desired product [D_6]-**1g** (2.215 g, 55%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83-5.71 (m, 1H), 5.10-4.97 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 2H), 2.75 (d, *J* = 6.8 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 171.7, 135.9, 115.8, 96.3, 94.0, 60.4, 38.8, 37.7, 14.2; HRMS (ESI): calc. for $C_{12}H_{12}D_6NaO_2$ $[M+Na]^+$: 223.1576; found: 223.1574.

Optimization of olefin-directed oxidative arylation of allenes

A number of different factors were considered for the optimization of the oxidative arylation of allenes.

Table S1. Investigation of solvent effect.[a]

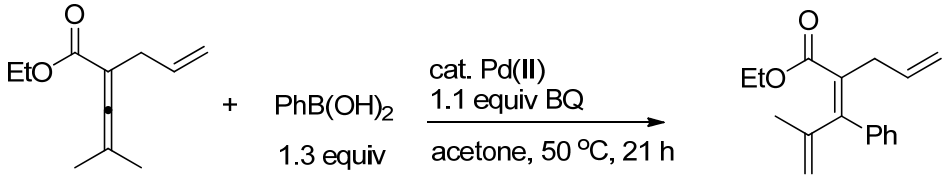


1a **2a** **3aa**

Entry	Solvent	Yield of Product **3aa** [%][b]	Recovery of **1a** [%][b]
1	THF	87(83)	-
2	toluene	83	-
3	**acetone**	**91**	**-**
4	DCE	81	-
5	dioxane	88	-
6	MeCN	25	-

[a] All reactions were carried out with $PhB(OH)_2$ (1.3 equiv.), BQ (1.1 equiv.), $Pd(OAc)_2$ (5 mol%), and **1a** in indicated solvent (0.2 M) at 50 °C for 23 hours. [b] Determined by ^1H NMR analysis of the crude reaction mixture. Value in the parentheses is the isolated yield.

Table S2. Catalyst screening.[a]



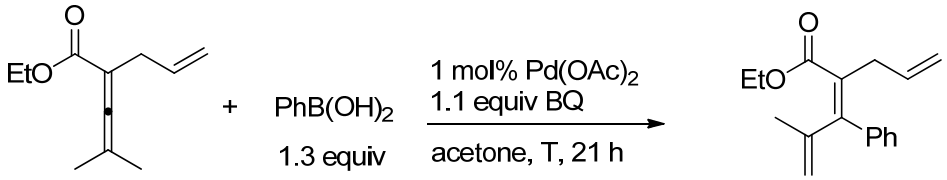
1a **2a** **3aa**

Entry	Cat. (Pd)	Catalyst loading [mol%]	Yield of Product **3aa** [%][b]	Recovery of **1a** [%][b]
1	$Pd(OAc)_2$	5	91	-
2	$Pd(TFA)_2$	5	40	-
3	$Pd(PPh_3)_2Cl_2$	5	-	37
4	$Pd(MeCN)_2Cl_2$	5	-	59
5	$Pd(OAc)_2$	2	91	-
6	**$Pd(OAc)_2$**	**1**	**90(87)**	**-**
7	-	-	-	100

[a] All reactions were carried out with $PhB(OH)_2$ (1.3 equiv.), BQ (1.1 equiv.), and **1a** in acetone (0.2 M) at 50 °C for 21 hours. [b] Determined by ^1H NMR analysis of the crude reaction mixture. Value in the parentheses is the

isolated yield.

Table S3. Influence of reaction temperature.[a]



1a **2a** **3aa**

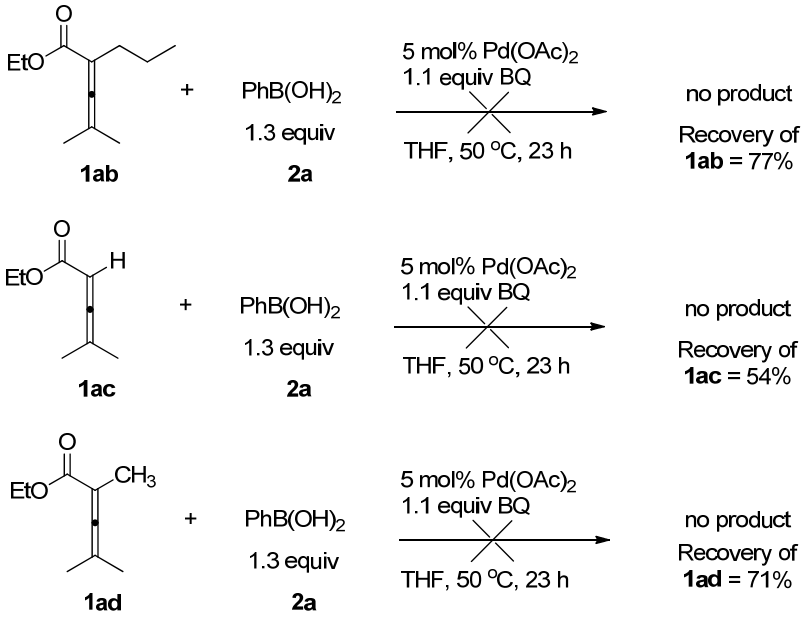
Entry	Temperature [°C]	Yield of Product **3aa** [%][b]	Recovery of **1a** [%][b]
1	60	89	-
2	**50**	**90**	**-**
3	40	89	-
4[c]	50	-	86

[a] All reactions were carried out with $PhB(OH)_2$ (1.3 equiv.), BQ (1.1 equiv.), $Pd(OAc)_2$ (1 mol%) and **1a** in acetone (0.2 M) at indicated temperature for 21 hours.. [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] The reaction was conducted without BQ.

Finnally, $Pd(OAc)_2$ (1 mol%), arylboronic acid (1.3 equiv), and BQ (1.1 equiv) in acetone (1 mL) at 50 °C were defined as the optimal reaction conditions.

Control experiments using allene 1ab, 1ac, or 1ad

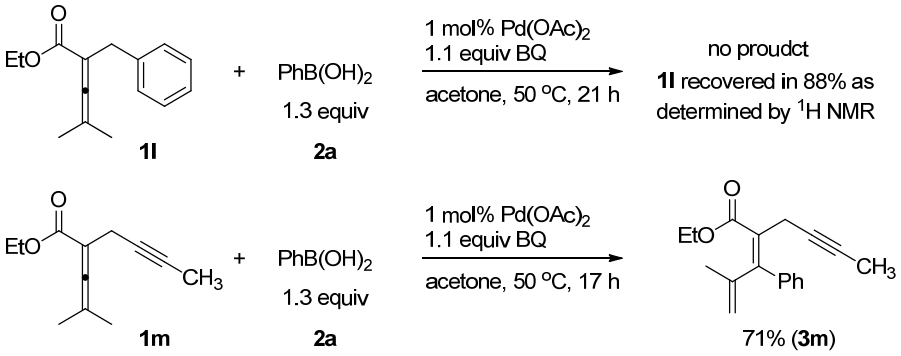
Control experiments using allenes **1ab**, **1ac**, or **1ad** were carried out under conditions (see Scheme 3). No formation of the corresponding triene products was observed, which shows that the olefin moiety in the substrate is crucial for the allene arylation (Scheme S1).



Scheme S1. Control experiments.

Investigation of directing group

Benzyl and propargyl-containing substrates were employed to investigate whether the corresponding substitute could be introduced as directing group for the allene arylation (Scheme S2).

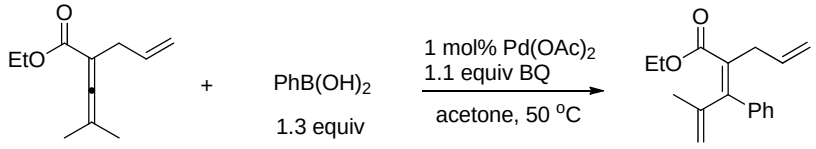


Scheme S2. Investigation of directing group using benzyl and propargyl-substituted allenes respectively.

General procedure for olefin-directed oxidative arylation of allenes for the formation of trienes 3

*Representative procedure A for the synthesis of **3aa-af**, **3b-e**, **3g-k**, and **3m**.*

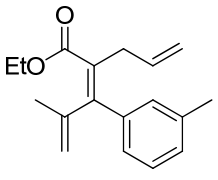
*(E)-Ethyl 2-allyl-4-methyl-3-phenylpenta-2,4-dienoate (**3aa**)*



1a **2a** **3aa**

To a mixture of $Pd(OAc)_2$ (0.4 mg, 0.002 mmol), $PhB(OH)_2$ (31.7 mg, 0.26 mmol), and BQ (23.8 mg, 0.22 mmol) was added a solution of allene **1a** (36.0 mg, 0.2 mmol) in acetone (1 mL). The reaction was stirred at 50 ^oC for 21 h. After full consumption of starting material **1a** as monitored by TLC, the reaction mixture was evaporated and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 30/1) afforded **3aa** (44.5 mg, 87%): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 3H), 7.30-7.25 (m, 2H), 5.93-5.80 (m, 1H), 5.17-5.06 (m, 2H), 4.99-4.96 (m, 1H), 4.96-4.93 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.02 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.75 (t, *J* = 1.1 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 149.3, 146.9, 137.8, 135.4, 129.0, 128.3, 128.1, 127.9, 116.1, 114.0, 60.4, 35.3, 21.7, 13.8; HRMS (ESI): calc. for $C_{17}H_{20}NaO_2$ $[M+Na]^+$: 279.1356; found: 279.1348.

*(E)-Ethyl 2-allyl-4-methyl-3-(m-tolyl)penta-2,4-dienoate (**3ab**)*

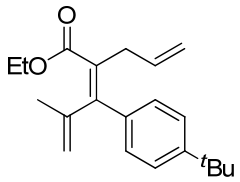


3ab

94% isolated yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 1H), 7.15-7.09 (m, 1H), 7.08-7.04 (m, 2H), 5.90-5.78 (m, 1H), 5.15-5.03 (m, 2H), 4.96-4.89 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.99 (dt, *J* = 6.0 Hz, 1.6 Hz, 2H), 2.35 (s, 3H), 1.74 (t, *J* = 1.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

170.5, 149.4, 147.0, 137.7, 135.5, 128.9, 128.8, 128.6, 128.0, 125.4, 116.0, 113.9, 60.4, 35.3, 21.7, 21.4, 13.8; HRMS (ESI): calc. for $C_{18}H_{22}NaO_2$ $[M+Na]^+$: 293.1512; found: 293.1508.

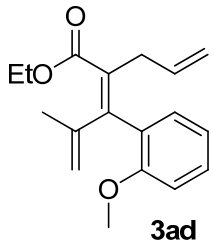
*(E)-Ethyl 2-allyl-3-(4-(tert-butyl)phenyl)-4-methylpenta-2,4-dienoate (**3ac**)*



3ac

64% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 5.92-5.79 (m, 1H), 5.16-5.04 (m, 2H), 4.95-4.89 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.02 (dt, *J* = 6.0 Hz, 1.7 Hz, 2H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.32 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 150.9, 149.4, 147.2, 135.6, 134.6, 128.6, 128.1, 125.0, 116.1, 113.8, 60.4, 35.3, 34.6, 31.3, 21.8, 13.8; HRMS (ESI): calc. for $C_{21}H_{28}NaO_2$ $[M+Na]^+$: 335.1982; found: 335.1991.

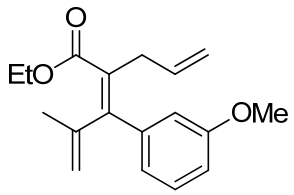
*(E)-Ethyl 2-allyl-3-(2-methoxyphenyl)-4-methylpenta-2,4-dienoate (**3ad**)*



3ad

76% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 1H), 7.09 (dd, *J* = 7.3 Hz, 1.7 Hz, 1H), 6.98-6.89 (m, 2H), 5.82-5.70 (m, 1H), 5.03-4.95 (m, 2H), 4.95-4.92 (m, 1H), 4.89-4.84 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.83 (d, *J* = 6.2 Hz, 2H), 1.80 (t, *J* = 1.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 156.4, 146.4, 145.3, 135.0, 130.1, 129.6, 128.9, 127.5, 120.2, 116.0, 113.5, 110.9, 60.3, 55.3, 35.8, 21.5, 13.9; HRMS (ESI): calc. for $C_{18}H_{22}NaO_3$ $[M+Na]^+$: 309.1461; found: 309.1457.

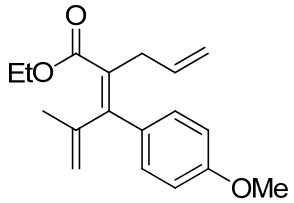
*(E)-Ethyl 2-allyl-3-(3-methoxyphenyl)-4-methylpenta-2,4-dienoate (**3ae**)*



3ae

77% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 1H), 6.88-6.81 (m, 2H), 6.81-6.78 (m, 2H), 5.90-5.77 (m, 1H), 5.16-5.03 (m, 2H), 4.96-4.89 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.01 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.4, 149.1, 146.8, 139.2, 135.5, 129.2, 129.0, 120.8, 116.1, 114.1, 113.8, 113.6, 60.5, 55.2, 35.3, 21.7, 13.8; HRMS (ESI): calc. for $C_{18}H_{22}NaO_3$ $[M+Na]^+$: 309.1461; found: 309.1458.

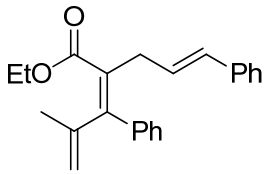
*(E)-Ethyl 2-allyl-3-(4-methoxyphenyl)-4-methylpenta-2,4-dienoate (**3af**)*



3af

80% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.92-5.79 (m, 1H), 5.17-5.03 (m, 2H), 4.94-4.88 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.03 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.72 (t, *J* = 1.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.4, 149.2, 147.2, 135.6, 129.9, 129.7, 128.3, 116.0, 113.9, 113.5, 60.4, 55.2, 35.4, 21.8, 13.8; HRMS (ESI): calc. for $C_{18}H_{22}NaO_3$ $[M+Na]^+$: 309.1461; found: 309.1461.

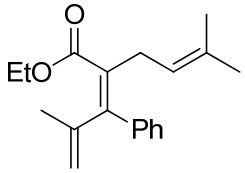
*(E)-Ethyl 2-cinnamyl-4-methyl-3-phenylpenta-2,4-dienoate (**3b**)*



3b

78% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 9H), 7.25-7.20 (m, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9 Hz, 6.3 Hz, 1H), 5.02-4.93 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.17 (dd, *J* = 6.2 Hz, 1.4 Hz, 2H), 1.80-1.75 (m, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 149.4, 146.9, 137.8, 137.5, 131.3, 129.1, 128.42, 128.41, 128.2, 128.0, 127.2, 127.1, 126.1, 114.1, 60.5, 34.5, 21.7, 13.8; HRMS (ESI): calc. for $C_{23}H_{24}NaO_2$ $[M+Na]^+$: 355.1669; found: 355.1660.

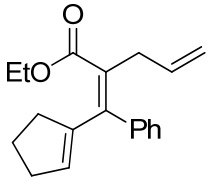
*(E)-Ethyl 5-methyl-2-(2-methyl-1-phenylallylidene)hex-4-enoate (**3c**)*



3c

75% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 3H), 7.25-7.20 (m, 2H), 5.15-5.07 (m, 1H), 4.97-4.87 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.93 (d, *J* = 7.1 Hz, 2H), 1.73-1.67 (m, 6H), 1.52-1.48 (m, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 147.4, 146.9, 138.0, 133.1, 130.6, 128.6, 128.2, 127.7, 120.7, 114.1, 60.4, 30.3, 25.8, 21.7, 17.8, 13.8; HRMS (ESI): calc. for $C_{19}H_{25}O_2$ $[M+H]^+$: 285.1849; found: 285.1842.

*(E)-Ethyl 2-(cyclopent-1-en-1-yl(phenyl)methylene)pent-4-enoate (**3d**)*

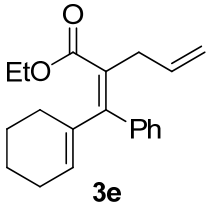


3d

81% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 3H),

7.22-7.16 (m, 2H), 5.85-5.72 (m, 1H), 5.58-5.52 (m, 1H), 5.10-4.99 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.94 (dt, *J* = 6.2 Hz, 1.5 Hz, 2H), 2.40-2.26 (m, 4H), 1.93-1.81 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 144.6, 142.8, 139.1, 135.3, 131.6, 129.0, 128.5, 128.0, 127.5, 116.1, 60.5, 36.0, 34.4, 32.8, 24.0, 14.1; HRMS (ESI): calc. for $C_{19}H_{22}NaO_2$ $[M+Na]^+$: 305.1512; found: 305.1507.

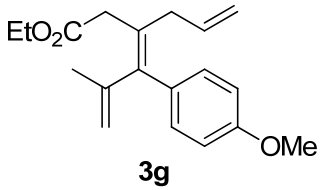
*(E)-Ethyl 2-(cyclohex-1-en-1-yl(phenyl)methylene)pent-4-enoate (**3e**)*



3e

91% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 3H), 7.27-7.22 (m, 2H), 5.93-5.80 (m, 1H), 5.74-5.68 (m, 1H), 5.17-5.04 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.01 (dt, *J* = 5.9 Hz, 1.5 Hz, 2H), 2.16-2.05 (m, 2H), 1.97-1.85 (m, 2H), 1.64-1.52 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 149.7, 140.2, 138.5, 135.6, 128.5, 128.4, 128.0, 127.7, 125.5, 115.9, 60.3, 35.5, 27.5, 25.4, 22.6, 21.9, 14.3; HRMS (ESI): calc. for $C_{20}H_{24}NaO_2$ $[M+Na]^+$: 319.1669; found: 319.1665.

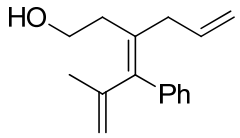
*(E)-Ethyl 3-allyl-4-(4-methoxyphenyl)-5-methylhexa-3,5-dienoate (**3g**)*



3g

81% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.81-5.69 (m, 1H), 5.07-4.95 (m, 4H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.30 (s, 2H), 2.83 (dt, *J* = 6.5 Hz, 1.4 Hz, 2H), 1.64 (t, *J* = 1.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 158.5, 145.8, 144.2, 136.3, 132.1, 129.8, 126.5, 116.2, 114.1, 113.3, 60.4, 55.1, 37.7, 37.2, 22.3, 14.2; HRMS (ESI): calc. for $C_{19}H_{24}NaO_3$ $[M+Na]^+$: 323.1618; found: 323.1609.

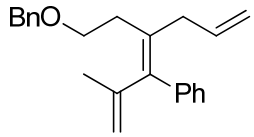
*(E)-3-Allyl-5-methyl-4-phenylhexa-3,5-dien-1-ol (**3h**)*



3h

50% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (m, 5H), 5.83-5.70 (m, 1H), 5.09-4.93 (m, 4H), 3.78 (d, *J* = 7.2 Hz, 2H), 2.76 (dt, *J* = 6.5 Hz, 1.5 Hz, 2H), 2.60 (d, *J* = 7.1 Hz, 2H), 1.75-1.70 (m, 3H), 1.47 (br.s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.0, 140.6, 136.8, 129.9, 128.7, 128.0, 126.7, 115.9, 113.6, 61.8, 36.4, 35.4, 22.8; HRMS (ESI): calc. for $C_{16}H_{20}NaO$ $[M+Na]^+$: 251.1406; found: 251.1415.

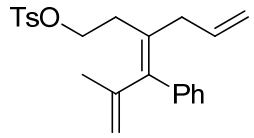
*(E)-(((3-Allyl-5-methyl-4-phenylhexa-3,5-dien-1-yl)oxy)methyl)benzene (**3i**)*



3i

93% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.20 (m, 10H), 5.86-5.72 (m, 1H), 5.10-4.99 (m, 3H), 4.98-4.93 (m, 1H), 4.59 (s, 2H), 3.65 (d, *J* = 7.3 Hz, 2H), 2.77 (dt, *J* = 6.5 Hz, 1.5 Hz, 2H), 2.68 (d, *J* = 7.4 Hz, 2H), 1.75-1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 143.2, 140.7, 138.6, 136.8, 130.5, 128.7, 128.3, 127.9, 127.5, 127.4, 126.6, 115.7, 113.5, 72.7, 69.7, 36.7, 32.2, 22.7; HRMS (ESI): calc. for $C_{23}H_{26}NaO$ $[M+Na]^+$: 341.1876; found: 341.1868.

*(E)-3-Allyl-5-methyl-4-phenylhexa-3,5-dien-1-yl 4-methylbenzenesulfonate (**3j**)*

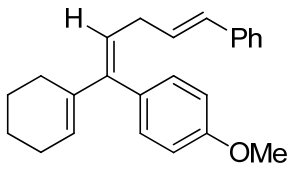


3j

80% isolated yield, slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.34-7.22 (m, 3H), 7.17-7.11 (m, 2H), 5.71-5.59

(m, 1H), 5.03-4.90 (m, 3H), 4.85-4.81 (m, 1H), 4.14 (t, J = 7.3 Hz, 2H), 2.68-2.61 (m, 4H), 2.48 (s, 3H), 1.64 (t, J = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 145.0, 144.6, 240.0, 136.2, 133.2, 129.8, 128.5, 127.94, 127.87, 126.8, 116.3, 113.7, 69.2, 36.3, 31.2, 22.5, 21.6; HRMS (ESI): calc. for $C_{23}H_{26}NaSO_3$ $[M+Na]^+$: 405.1495; found: 405.1488.

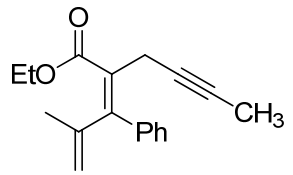
*1-((1Z,4E)-1-(Cyclohex-1-en-1-yl)-5-phenylpenta-1,4-dien-1-yl)-4-methoxybenzene (**3k**)*



3k

54% isolated yield, slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 4H), 7.25-7.19 (m, 1H), 7.07 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.35 (d, J = 15.9 Hz, 1H), 6.18 (dt, J = 15.9 Hz, 6.4 Hz, 1H), 5.76 (t, J = 7.4 Hz, 1H), 5.40-5.32 (m, 1H), 3.86 (s, 3H), 2.82 (t, J = 6.9 Hz, 2H), 2.37-2.27 (m, 2H), 2.14-2.02 (m, 2H), 1.80-1.70 (m, 2H), 1.66-1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 144.2, 138.1, 137.8, 132.0, 130.7, 129.8, 129.5, 128.4, 128.1, 126.8, 125.9, 122.1, 113.3, 55.2, 33.0, 26.1, 26.0, 23.0, 22.4; HRMS (ESI): calc. for $C_{24}H_{26}NaO$ $[M+Na]^+$: 353.1876; found: 353.1867.

*(E)-Ethyl 2-(2-methyl-1-phenylallylidene)hex-4-ynoate (**3m**)*



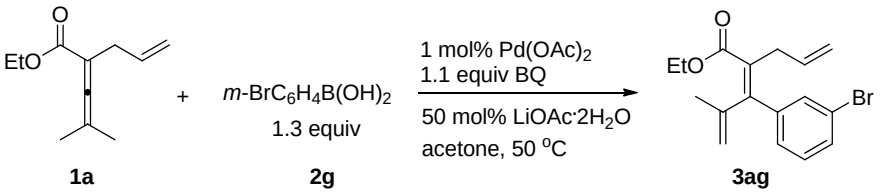
3m

71% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 4.99-4.87 (m, 2H), 4.23 (q, J = 7.2 Hz, 2H), 3.08 (q, J = 2.5 Hz, 2H), 1.80 (t, J = 2.5 Hz, 3H), 1.75-1.70 (m, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 149.1, 146.6, 137.3, 128.6, 128.3, 128.1, 127.0, 114.4, 76.9, 75.5, 60.7, 21.53,

21.49, 13.8, 3.7; HRMS (ESI): calc. for $C_{18}H_{20}NaO_2$ $[M+Na]^+$: 291.1356; found: 291.1366.

*Representative procedure B for the synthesis of **3ag-am** and **3f**.*

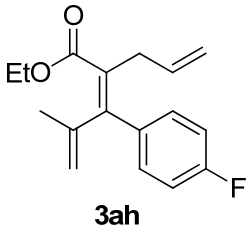
*(E)-Ethyl 2-allyl-3-(3-bromophenyl)-4-methylpenta-2,4-dienoate (**3ag**)*



1a **2g** **3ag**

To a mixture of $Pd(OAc)_2$ (0.4 mg, 0.002 mmol), *m*-$BrC_6H_4B(OH)_2$ (52.2 mg, 0.26 mmol), BQ (23.8 mg, 0.22 mmol), and $LiOAc{\cdot}2H_2O$ (10.2 mg, 0.1 mmol) were added a solution of allene **1a** (36.0 mg, 0.2 mmol) in acetone (1 mL). The reaction was stirred at 50 ^oC for 14 h. After full consumption of starting material **1a** as monitored by TLC, the reaction mixture was evaporated and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 30/1) afforded **3ag** (55.2 mg, 82%): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.38 (m, 2H), 7.25-7.15 (m, 2H), 5.88-5.75 (m, 1H), 5.15-5.04 (m, 2H), 4.97-4.90 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.97 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.72 (t, *J* = 1.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 147.6, 146.2, 139.9, 135.0, 131.3, 131.0, 130.0, 129.7, 127.0, 122.3, 116.4, 114.7, 60.6, 35.3, 21.6, 13.8; HRMS (ESI): calc. for $C_{17}H_{19}NaBrO_2$ $[M+Na]^+$: 357.0461; found: 357.0453.

*(E)-Ethyl 2-allyl-3-(4-fluorophenyl)-4-methylpenta-2,4-dienoate (**3ah**)*

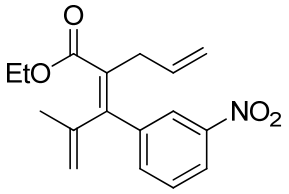


3ah

90% isolated yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.08-7.02 (m, 2H), 5.91-5.79 (m, 1H), 5.17-5.06 (m, 2H), 4.98-4.92 (m, 2H), 4.19 (q,

J = 7.1 Hz, 2H), 3.01 (dt, *J* = 5.8 Hz, 1.6 Hz, 2H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 162.5 (*J* = 246 Hz), 148.2, 146.8, 135.3, 133.6 (*J* = 3 Hz), 130.1 (*J* = 9 Hz), 129.3, 116.2, 115.1 (*J* = 21 Hz), 114.3, 60.5, 35.3, 21.6, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9; HRMS (ESI): calc. for $C_{17}H_{19}NaFO_2$ $[M+Na]^+$: 297.1261; found: 297.1262.

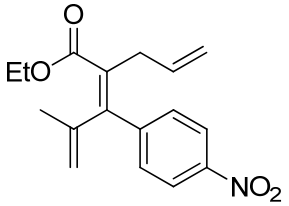
*(E)-Ethyl 2-allyl-4-methyl-3-(3-nitrophenyl)penta-2,4-dienoate (**3ai**)*



3ai

91% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.11 (m, 2H), 7.61-7.50 (m, 2H), 5.90-5.77 (m, 1H), 5.17-5.08 (m, 2H), 5.05-4.99 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.97 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 148.2, 146.5, 145.7, 139.6, 134.5, 131.0, 129.3, 123.4, 123.0, 116.8, 115.7, 60.8, 35.3, 21.6, 13.8; HRMS (ESI): calc. for $C_{17}H_{19}NaNO_4$ $[M+Na]^+$: 324.1206; found: 324.1204.

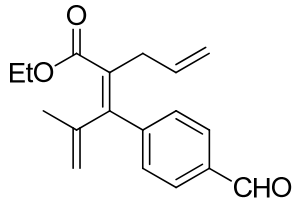
*(E)-Ethyl 2-allyl-4-methyl-3-(4-nitrophenyl)penta-2,4-dienoate (**3aj**)*



3aj

80% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.0 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 5.87-5.74 (m, 1H), 5.14-5.06 (m, 2H), 5.02-4.97 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.94 (dt, *J* = 5.8 Hz, 1.6 Hz, 2H), 1.71 (t, *J* = 1.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 147.4, 146.8, 145.6, 144.6, 134.5, 130.9, 129.3, 123.5, 116.7, 115.6, 60.8, 35.2, 21.6, 13.8; HRMS (ESI): calc. for $C_{17}H_{19}NaNO_4$ $[M+Na]^+$: 324.1206; found: 324.1200.

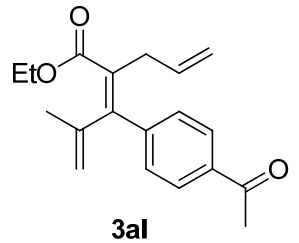
*(E)-Ethyl 2-allyl-3-(4-formylphenyl)-4-methylpenta-2,4-dienoate (**3ak**)*



3ak

70% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.88-5.75 (m, 1H), 5.15-5.04 (m, 2H), 5.01-4.94 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.96 (dt, *J* = 5.9 Hz, 1.5 Hz, 2H), 1.74-1.69 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 169.9, 147.8, 146.0, 144.3, 135.8, 134.8, 130.4, 129.6, 129.1, 116.5, 115.1, 60.7, 35.3, 21.7, 13.8; HRMS (ESI): calc. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485; found: 285.1478.

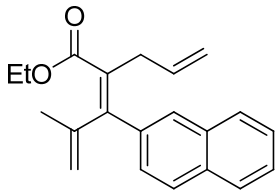
*(E)-Ethyl 3-(4-acetylphenyl)-2-allyl-4-methylpenta-2,4-dienoate (**3al**)*



3al

85% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.87-5.75 (m, 1H), 5.13-5.03 (m, 2H), 4.99-4.92 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.95 (dt, *J* = 5.9 Hz, 1.5 Hz, 2H), 2.60 (s, 3H), 1.72-1.67 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 170.0, 148.0, 146.1, 142.8, 136.5, 134.9, 130.1, 128.6, 128.2, 116.4, 114.8, 60.6, 35.2, 26.6, 21.6, 13.8; HRMS (ESI): calc. for $C_{19}H_{22}NaO_3$ $[M+Na]^+$: 321.1461; found: 321.1468.

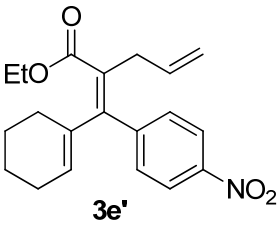
*(E)-Ethyl 2-allyl-4-methyl-3-(naphthalen-2-yl)penta-2,4-dienoate (**3am**)*



3am

71% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 3H), 7.78-7.75 (m, 1H), 7.54-7.46 (m, 2H), 7.39 (dd, *J* = 8.5 Hz, 1.7 Hz, 1H), 5.97-5.84 (m, 1H), 5.22-5.09 (m, 2H), 5.08-5.03 (m, 1H), 5.03-4.97 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.06 (dt, *J* = 5.9 Hz, 1.6 Hz, 2H), 1.79-1.75 (m, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 149.2, 146.8, 135.4, 135.3, 133.0, 132.9, 129.4, 128.1, 127.8, 127.6, 127.5, 126.4, 126.24, 126.21, 116.2, 114.4, 60.5, 35.5, 21.8, 13.8; HRMS (ESI): calc. for $C_{21}H_{22}NaO_2$ $[M+Na]^+$: 329.1512; found: 329.1514.

*(E)-Ethyl 2-(cyclohex-1-en-1-yl(4-nitrophenyl)methylene)pent-4-enoate (**3e'**)*



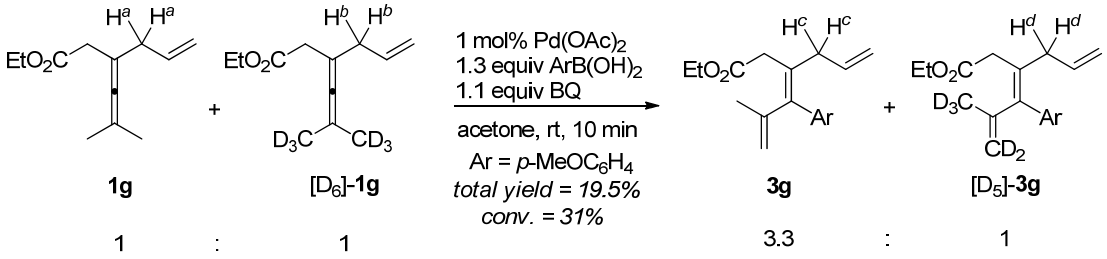
3e'

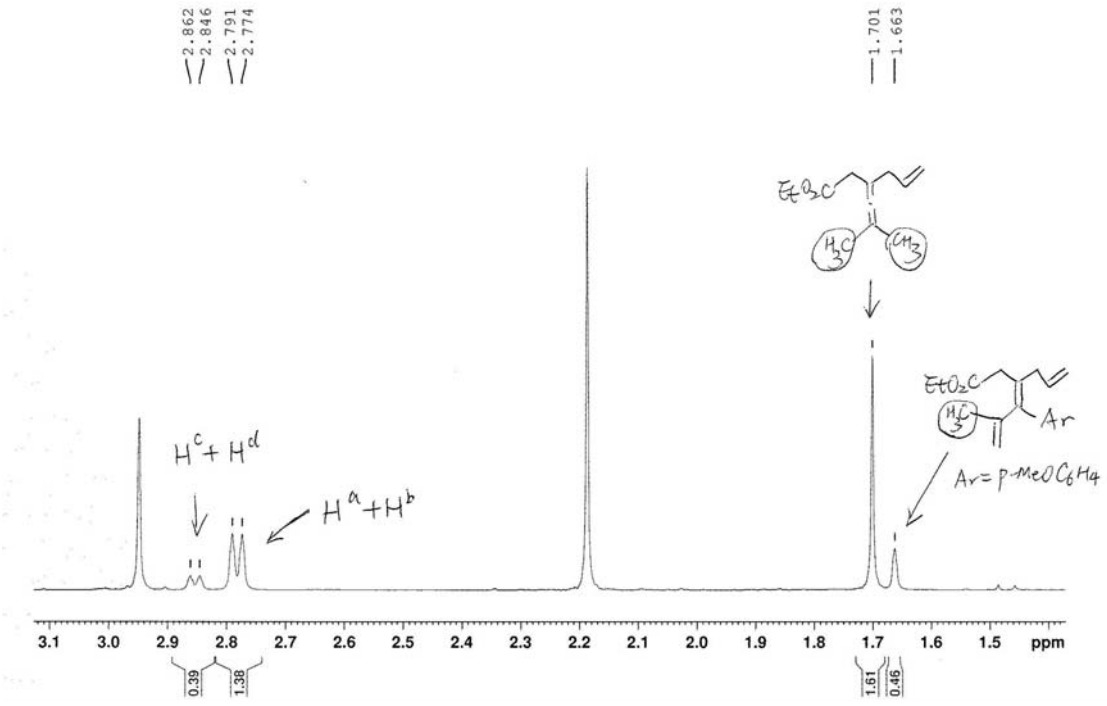
85% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 5.87-5.75 (m, 1H), 5.75-5.70 (m, 1H), 5.10 (dd, *J* = 8.5 Hz, 1.6 Hz, 1H), 5.08-5.05 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.93 (dt, *J* = 5.8 Hz, 1.6 Hz, 2H), 2.14-2.02 (m, 2H), 1.89-1.78 (m, 2H), 1.59-1.51 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 147.34, 147.26, 145.5, 139.1, 134.8, 130.5, 129.4, 127.1, 123.4, 116.5, 60.6, 35.4, 27.5, 25.4, 22.4, 21.7, 14.2; HRMS (ESI): calc. for $C_{20}H_{23}NaNO_4$ $[M+Na]^+$: 364.1519; found: 364.1516.

Kinetic Isotope Effect (KIE) Experiments

1. Determination of Intermolecular Competition KIE

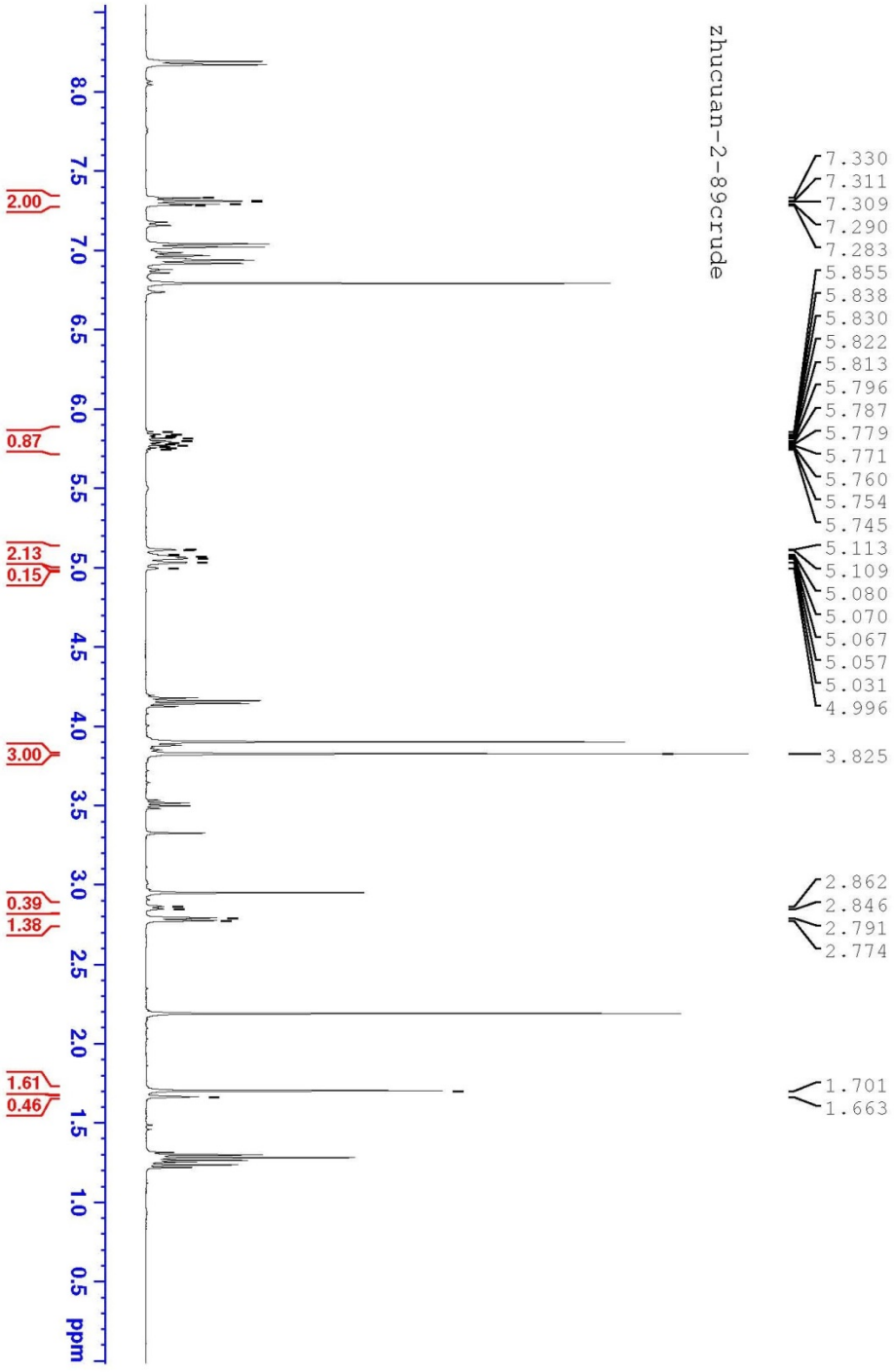
To a solution of mixture of $Pd(OAc)_2$ (0.4 mg, 0.002 mmol), *p*-$MeOC_6H_4B(OH)_2$ (39.5 mg, 0.26 mmol), and BQ (23.8 mg, 0.22 mmol) in acetone (0.5 mL) was added a mixture of allenes **1g** (19.4 mg, 0.1 mmol) and [D_6]-**1g** (20.0 mg, 0.1 mmol) in acetone (0.5 mL). The reaction was stirred at room temperature for 10 min, then quickly evaporated. The yields and the ratio of **3g** and [D_5]-**3g** were determined by ^1H NMR measurement using anisole as the internal standard (22 μL, 0.2 mmol).





As shown in the attached spectra, the combined yield of **3g** and [D_5]-**3g** was 19.5% [(Integration of H^c+H^d)/2], and the yield of **3g** was 0.46/3 ≈ 15% [0.46 was the integration at δ 1.66 (s, 3H for **3g**)], thus the yield of [D_5]-**3g** was 4.5%. Therefore, the ratio of **3g** and [D_5]-**3g** was determined as 3.3:1. Furthermore, the combined

recovery of **1g** and [D_6]-**1g** was 69% [(Integration of H^a+H^b)/2], so the reaction conversion was 31%. Additionally, recovery of **1g** was 1.61/6 ≈ 27% [1.61 was the integration at δ 1.70 (s, 6H for **1g**)], thus the yield of [D_6]-**1g** was 42%, thus the ratio of recovered **1g** and [D_6]-**1g** was determined as 1:1.6. Finally, the isotope effect value calculated from the product ratio and the change of the starting material ratio is 4.1 according to Sih's equation.[7]



2. Intermolecular KIE Experiments (Separate experiments)

To an NMR tube with a solution of allene **1g** (19.4 mg, 0.1 mmol) [or [D_6]-**1g** (20.0 mg, 0.1 mmol)], *p*-$MeOC_6H_4B(OH)_2$ (19.8 mg, 0.13 mmol), and anisole (22 μL, 0.2 mmol, internal standard) in d_6-acetone (0.2 mL) was added a solution of $Pd(OAc)_2$ (0.2 mg, 0.001 mmol) and BQ (23.8 mg, 0.22 mmol) in d_6-acetone (0.3 mL). The reactions were running at room temperature in the NMR machine, and the online detections were recorded at different time (see **Table S4** and **S5** respectively). The yields were determined by ^{1}H NMR measurement using anisole as the internal standard.

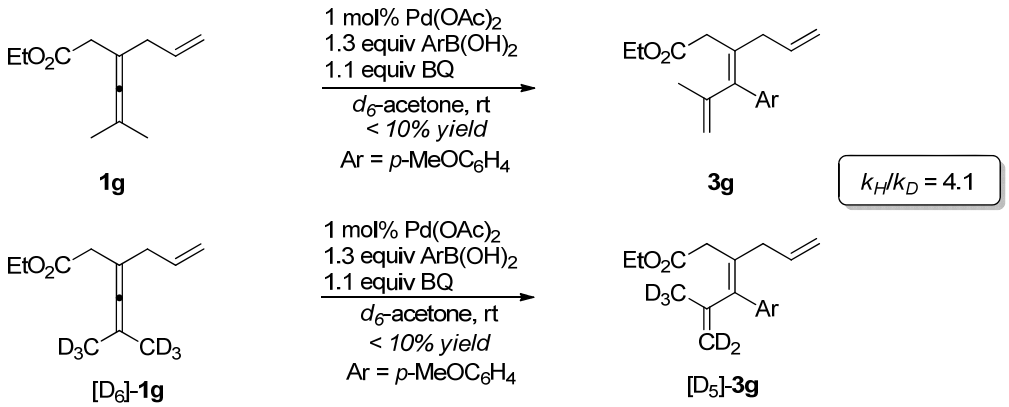


Table S4. For **1g**:

Time/min	0	5.8	8.3	11.2	12.9	18.5
Yield of **3g**/%	0	1	2	3.5	5	10.5

Due to the nature of the experiment, plots to determine the KIE were taken for **1g** (Figures S1 and S2).

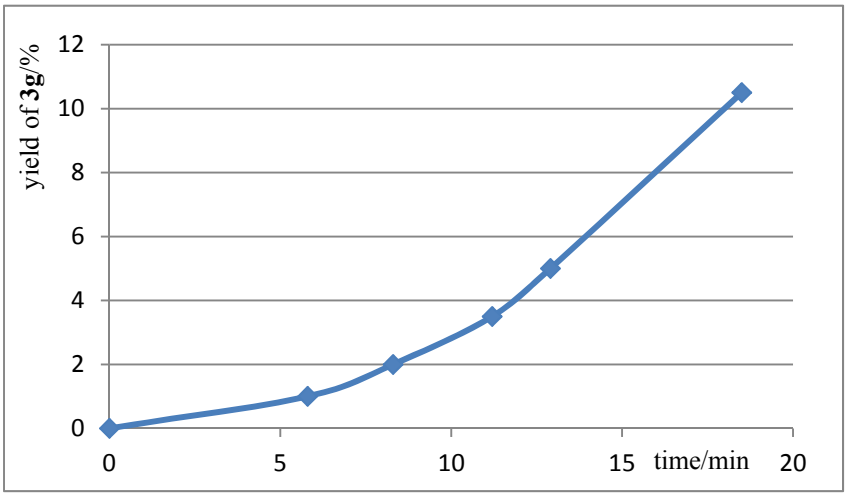


Figure S1. Progress of the reaction of **1g** in the early stage.

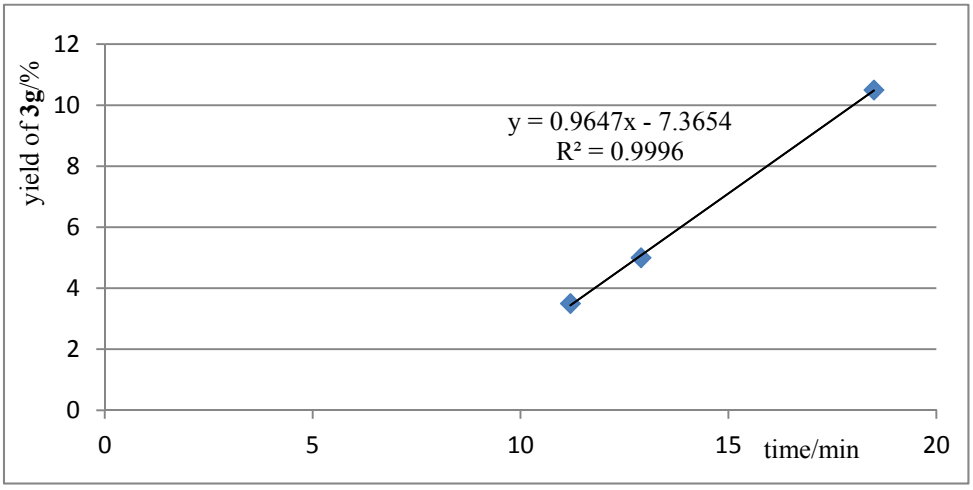


Figure S2. Linear function fit for reaction rate of **1g**.

Table S5. For [D_6]-**1g**:

Time/min	0	9.1	17.4	30.7
Yield of [D_5]-**3g**/%	0	0.5	2	5.5

Due to the nature of the experiment, plots to determine the KIE were taken for [D_6]-**1g** (Figures S3 and S4).

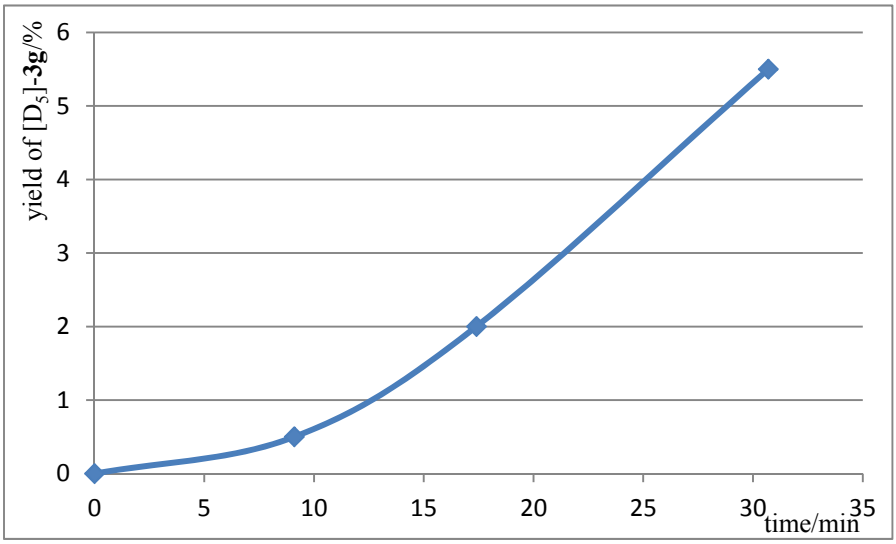


Figure S3. Progress of the reaction of [D_6]-**1g** in the early stage.

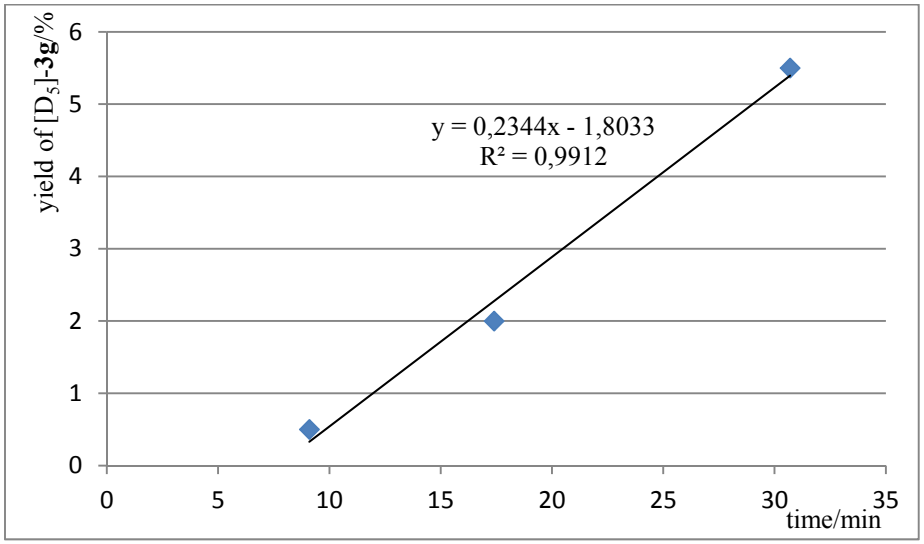
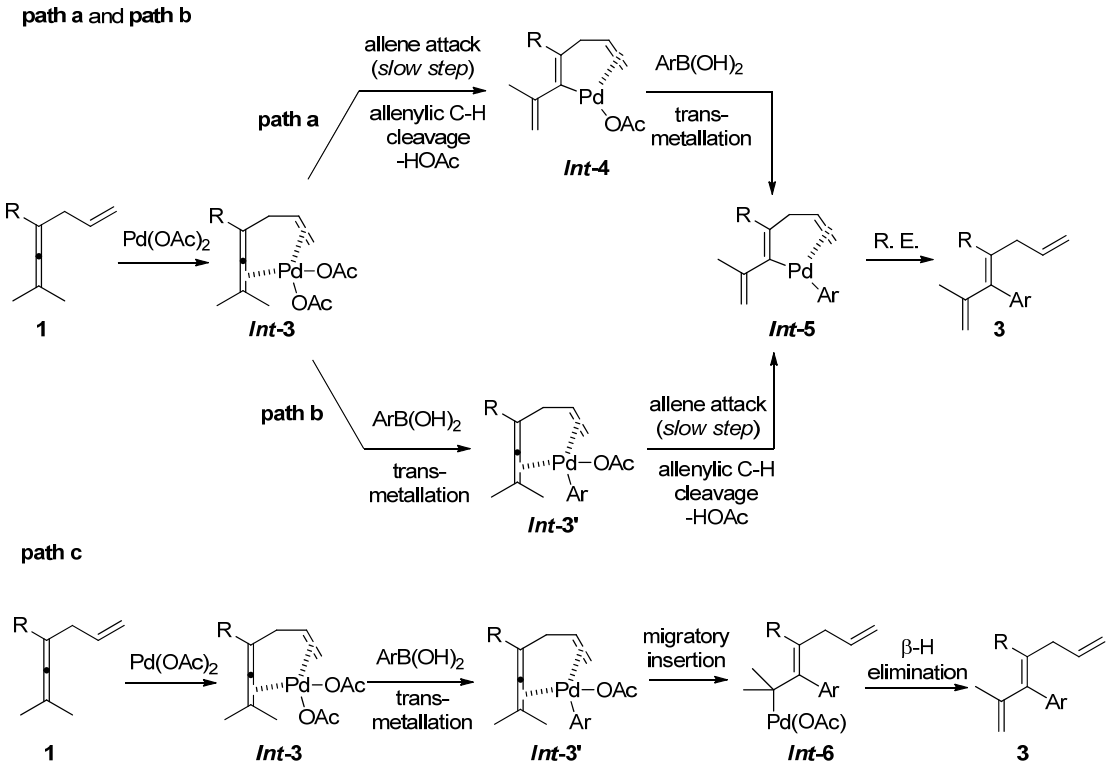


Figure S4. Linear function fit for reaction rate of [D_6]-**1g**.

Finally, the intermolecular isotope effect value is determined as 4.1.

$$k_H/k_D = (0.9647)/(0.2344) = 4.1$$

Proposed Mechanism



Path a (proposed mechanism): Based on the observation and mechanistic studies, we proposed a possible mechanism for the allene arylation. As shown in the above scheme, simultaneous coordination of the allyl C=C bond and the allenic C=C bond of substrate **1** to the Pd(II) center would generate chelate ***Int*-3**, followed by allene attack to afford vinylpalladium intermediate ***Int*-4** involving allenylic C-H bond cleavage. Further, transmetallation of ***Int*-4** with $ArB(OH)_2$ would produce ***Int*-5**, which on subsequent reductive elimination would lead to 1,3,6-triene **3**.

Path b (less likely): Differ from **path a**, transmetallation of the Pd(II) species with $ArB(OH)_2$ via ***Int*-3'** would occur before allene attack in **path b**. However, this pathway seems less likely than that via ***Int*-4** (path a), considering the fact that ***Int*-3** provides a more electron-deficient Pd(II) for the nucleophilic attack by the allene unit.

Path c (ruled out): In this pathway, the reaction would proceed via migratory insertion and sequential rate-determining β-H elimination. However, the possibility of **path c** can be ruled out based on the following points: A KIE value k_H/k_D = 4.1 in both

competitive and parallel experiments. The competition experiment requires that the cleavage of the C-H bond has to occur before any irreversible steps. In this pathway, there would be an irreversible allene insertion (arylpalladation, ***Int*-3' → *Int*-6)**. (It is highly unlikely that arylpalladation would be reversible in this case). This irreversible step would occur before the cleavage of the C-H bond (β-hydride elimination) and as a consequence one would not have observed any isotope effect from the competition experiment.

In addition, migratory insertion of the allene into the aryl palladium bond to form ***Int*-6** would require olefin disassociation from Pd(II), considering the planar Pd(II) complex in ***Int*-3'**. In this case, allenes **1ab**, **1ac**, **1ad** would have been expected to work in this transformation, which is inconsistent with our observation in Scheme 3. Moreover, palladium-catalyzed β-hydride elimination was commonly considered as a fast and low-energy step,[8] which is also inconsistent with our observed KIE value of $k_H/k_D = 4.1$.

Finally, in a pathway via migratory insertion (***Int*-3' → *Int*-6)**, one would expect 3,4-dienoate (e.g. **1g**) to mainly give 2(*E*),4-dienoate instead of the observed 3,5-dienoate (e.g. **3g**) as previously reported.[9]

References:

[1] a) G. E. Keck, R. L. Giles, V. J. Cee, C. A. Wager, T. Yu, M. B. Kraft, *J. Org. Chem*. **2008**, *73*, 9675; b) B. M. Trost , A. B. Pinkerton, M. Seidel, *J. Am. Chem. Soc.* **2001**, *123*, 12466; c) Y. Liu, J. Zhu, J. Qian, Z. Xu, *J. Org. Chem.* **2012**, *77*, 5411.

[2] a) I. P. Andrews, O. Kwon, *Organic Syntheses*, **2012**, *88*, 138; b) M. Hanack, C. J. Collins, H. Stutz, B. M. Benjamin, *J. Am. Chem. Soc*. **1981**, *103*, 2356.

[3] Y. J. Yoo, D. H. Nam, S. Y. Jung, J. W. Jang, H. J. Kim, C. Jin, A. N. Pae, Y. S. Lee, *Bioorg. Med. Chem. Lett*. **2011**, *21*, 2850.

[4] D. Scholz, S. Weber-roth, E. Macoratti, E. Francotte, *Synth. Commun.* **1999**, *29*, 1143.

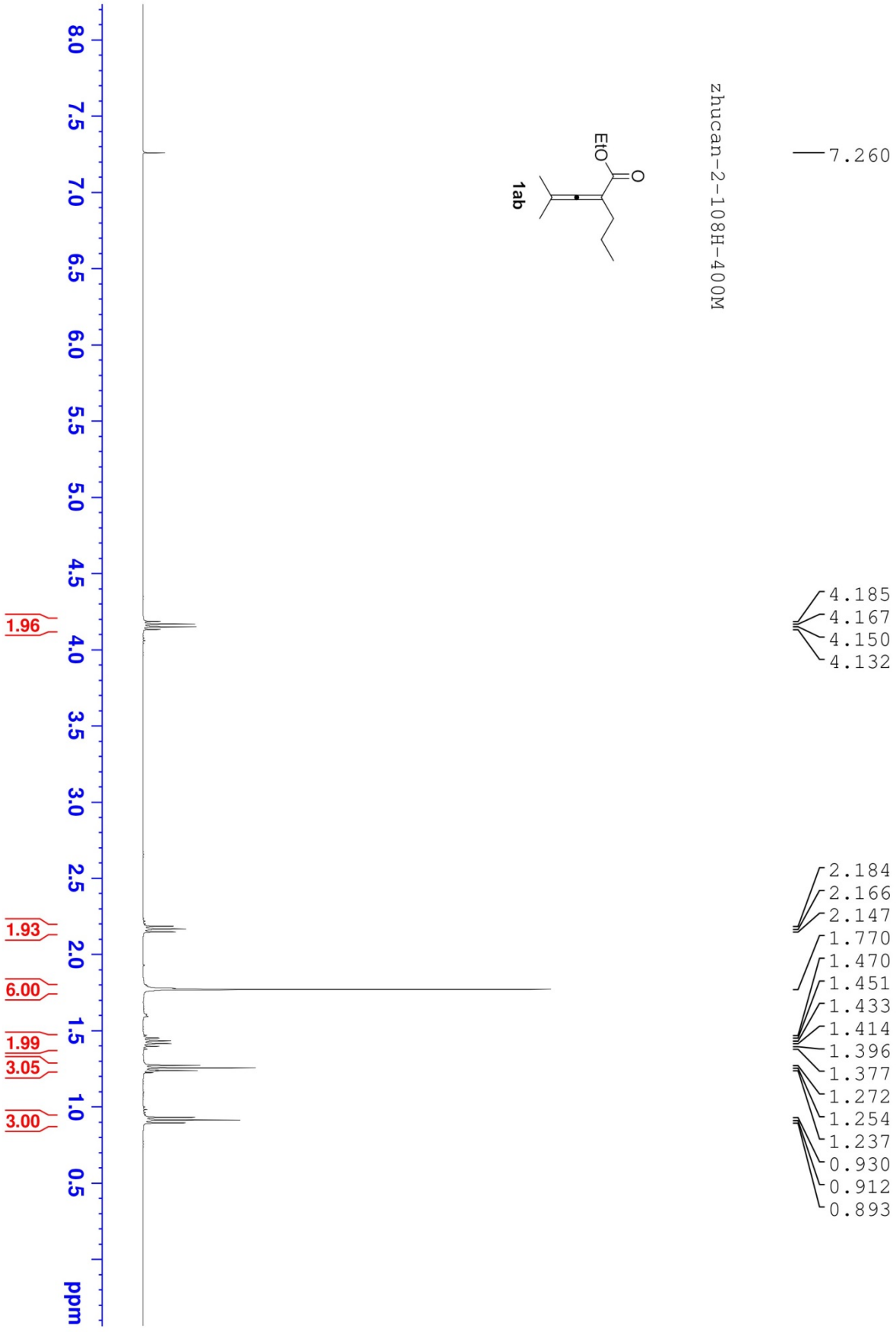
[5] X. Tang, C. Zhu, T. Cao, J. Kuang, W. Lin, S. Ni, J. Zhang, S. Ma, *Nature Commun.* **2013**, 4:2450 doi: 10.1038/ncomms3450.

[6] N. P. Villalva-Servín, A. Laurent, A. G. Fallis, *Can. J. Chem*. **2004**, *82*, 227.

[7] C.-S. Chen, Y. Fujimoto, G. Girdaukas, C. J. Sih, *J. Am. Chem. Soc*. **1982**, *104*, 7294.

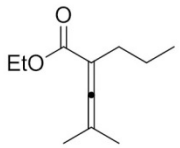
[8] a) C. Ryan, A. K. de K. Lewis, S. Caddick, N. Kaltsoyannis, *Theor. Chem. Acc.* **2011**, *129*, 303; b) P. van de Weghe, *Lett. Org. Chem*. **2005**, *2*, 113.

[9] C. Fu, S. Ma, *Org. Lett*. **2005**, *7*, 1707

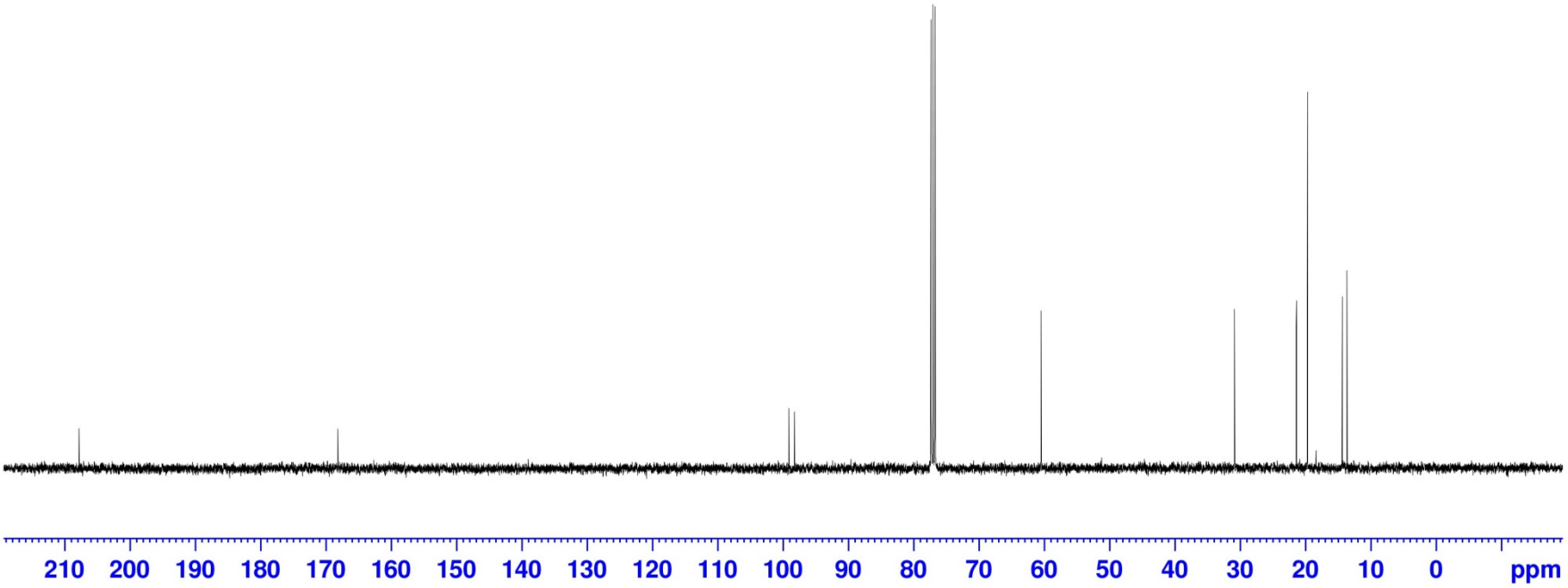

zhucan-2-108H-400M
1ab
EtO
O
7.260
4.185
4.167
4.150
4.132
2.184
2.166
2.147
1.770
1.470
1.451
1.433
1.414
1.396
1.377
1.272
1.254
1.237
0.930
0.912
0.893
1.96
1.93
6.00
1.99
3.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

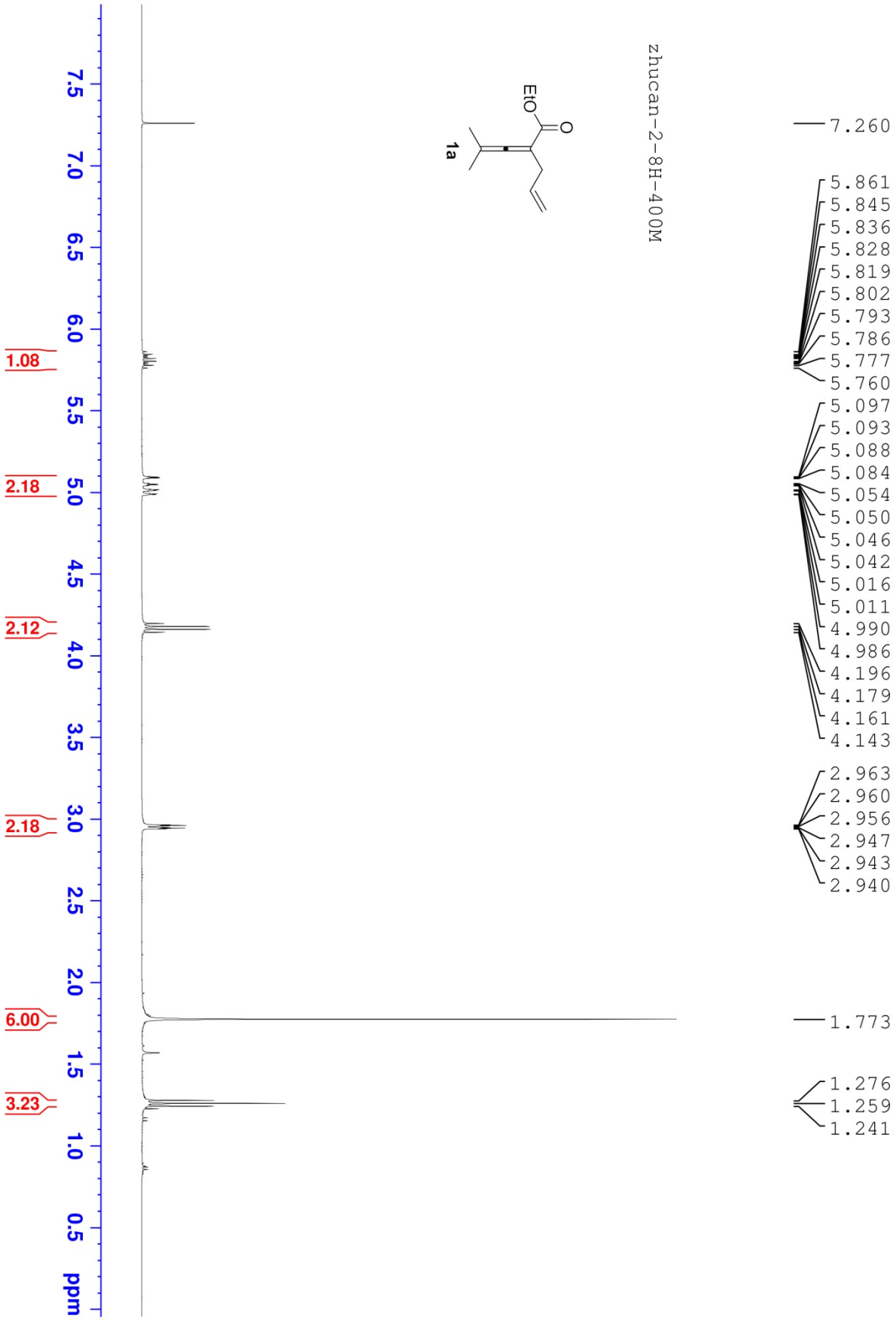
207.80
168.19
99.07
98.22
77.31
77.00
76.68
60.45
30.82
21.33
19.63
14.30
13.57

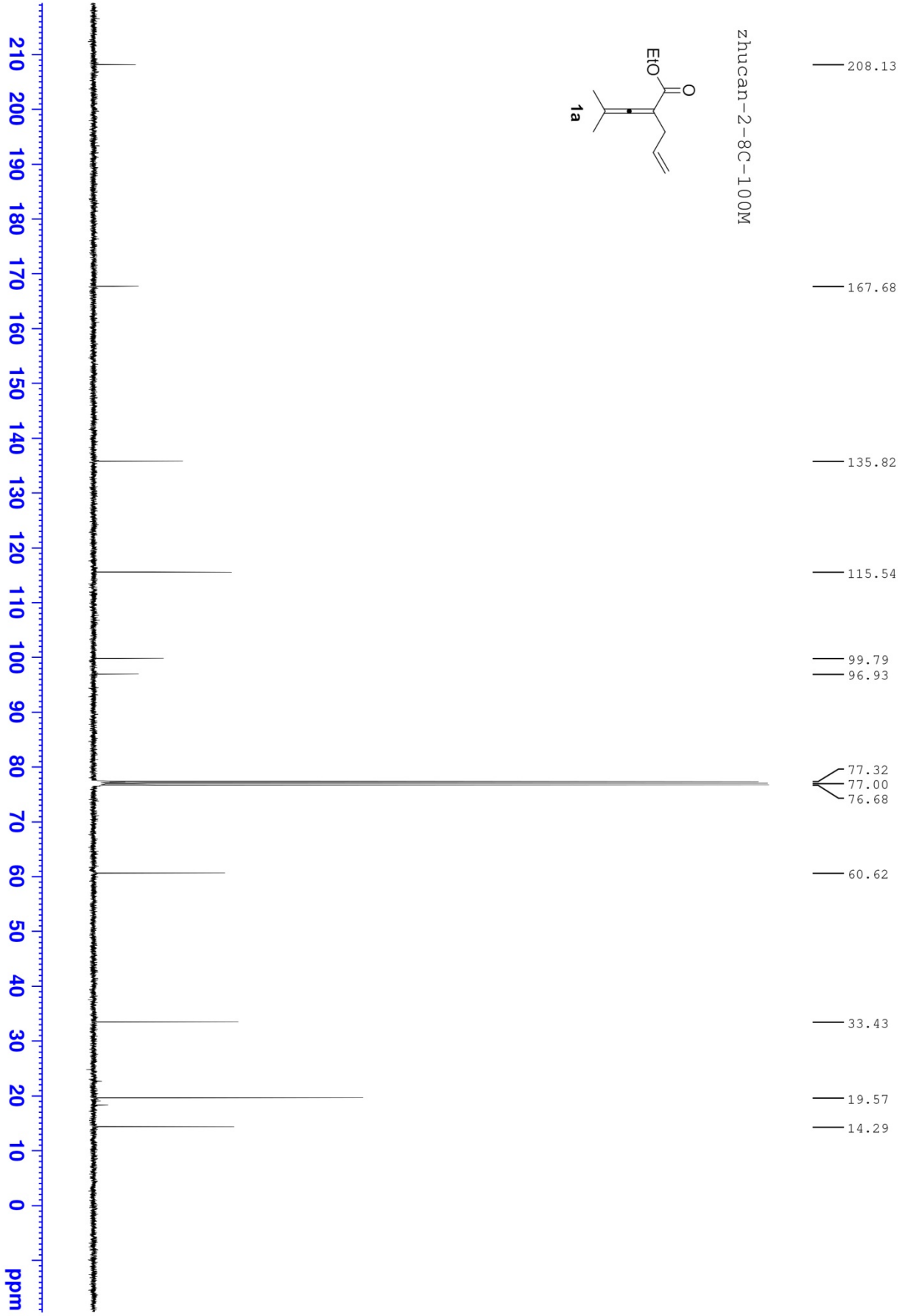
zhucan-2-108C-100M

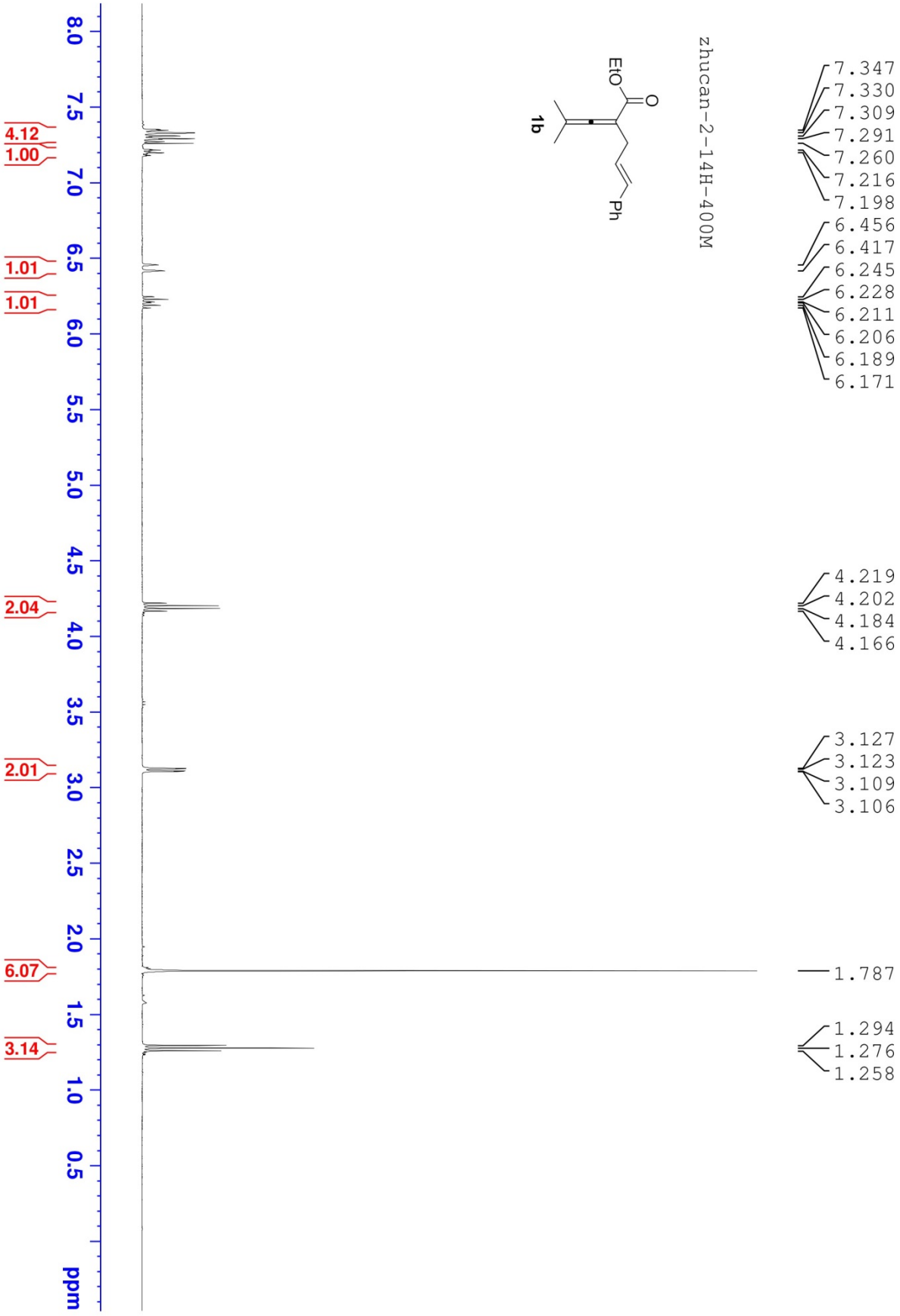


1ab



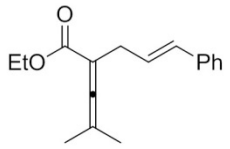

zhucan-2-8H-400M
EtO
O
1a
7.260
5.861
5.845
5.836
5.828
5.819
5.802
5.793
5.786
5.777
5.760
5.097
5.093
5.088
5.084
5.054
5.050
5.046
5.042
5.016
5.011
4.990
4.986
4.196
4.179
4.161
4.143
2.963
2.960
2.956
2.947
2.943
2.940
1.773
1.276
1.259
1.241
1.08
2.18
2.12
2.18
6.00
3.23
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


zhucan-2-8C-100M
EtO
O
1a
208.13
167.68
135.82
115.54
99.79
96.93
77.32
77.00
76.68
60.62
33.43
19.57
14.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

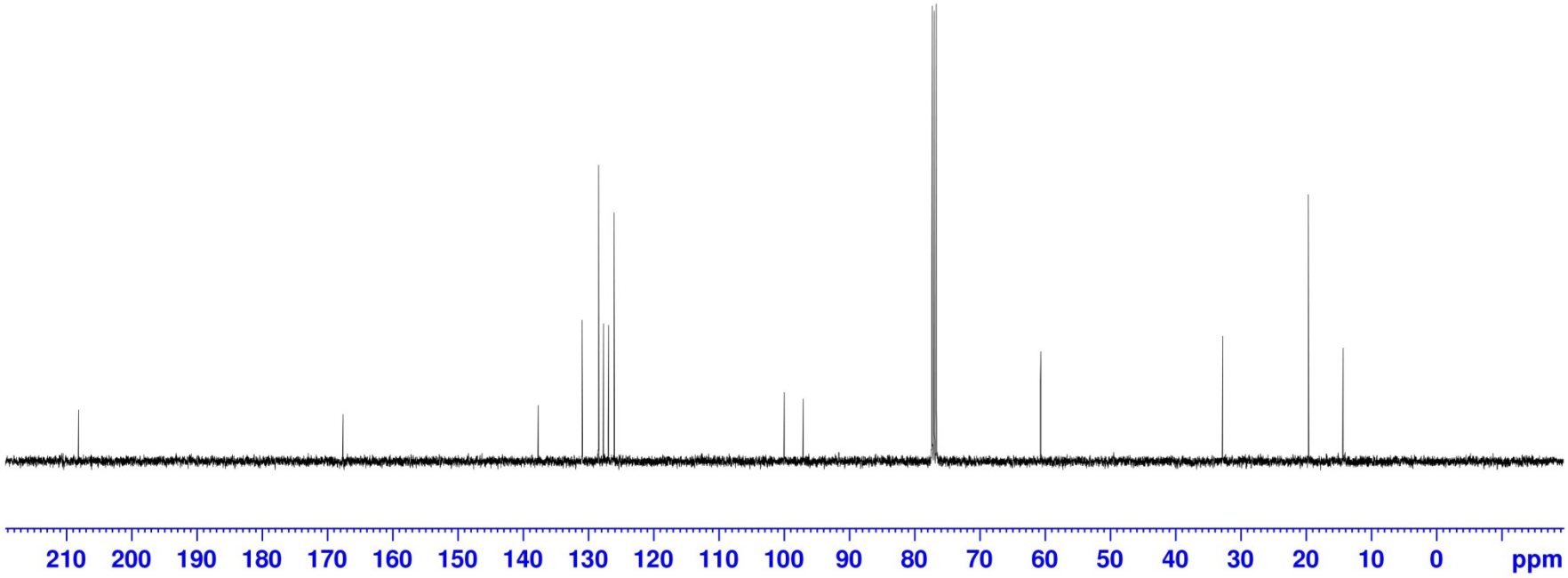

zhucan-2-14H-400M
EtO
O
Ph
1b
7.347
7.330
7.309
7.291
7.260
7.216
7.198
6.456
6.417
6.245
6.228
6.211
6.206
6.189
6.171
4.219
4.202
4.184
4.166
3.127
3.123
3.109
3.106
1.787
1.294
1.276
1.258
4.12
1.00
1.01
1.01
2.04
2.01
6.07
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

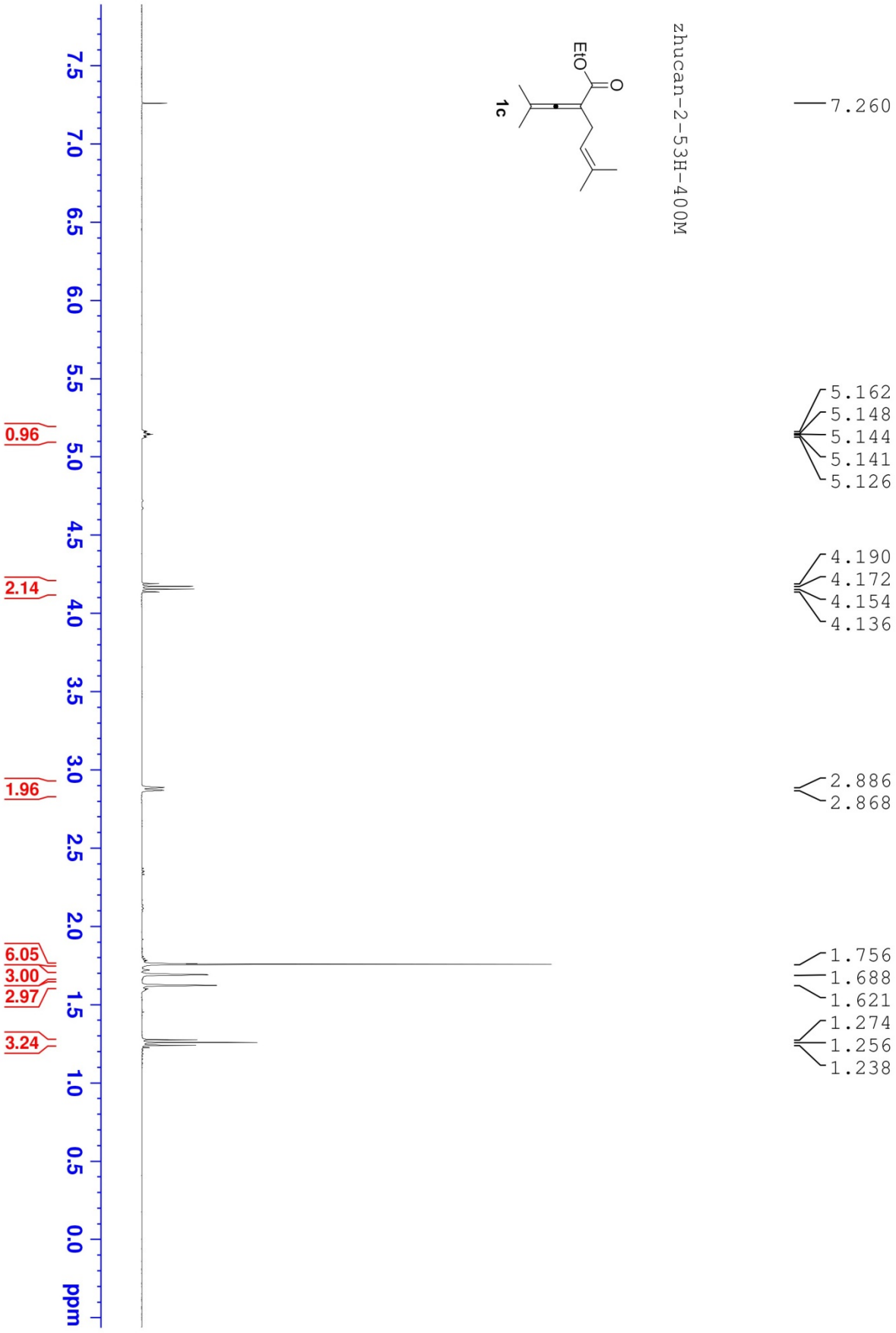
208.17
167.63
137.71
130.94
128.44
127.71
126.95
126.05
99.98
97.08
77.32
77.00
76.68
60.68
32.78
19.63
14.32

zhucan-2-14C-100M



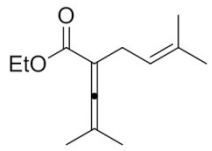
1b



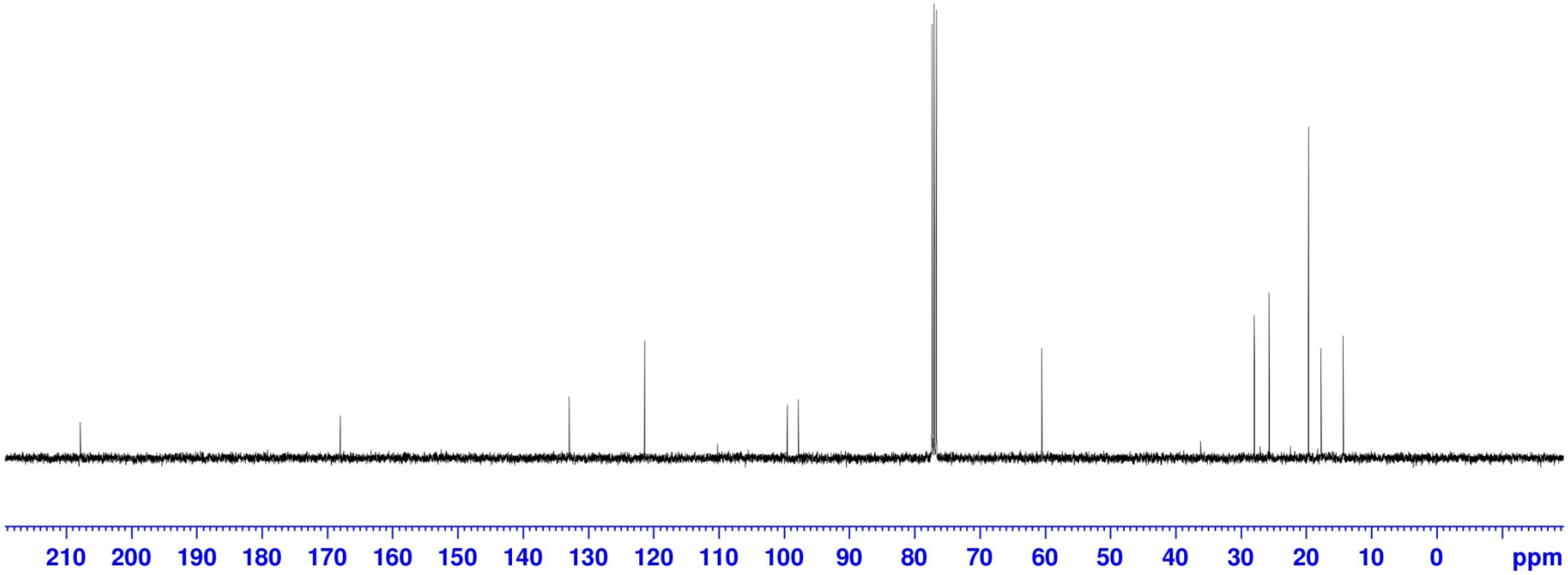

zhucan-2-53H-400M
EtO
O
1c
7.260
5.162
5.148
5.144
5.141
5.126
4.190
4.172
4.154
4.136
2.886
2.868
1.756
1.688
1.621
1.274
1.256
1.238
0.96
2.14
1.96
6.05
3.00
2.97
3.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

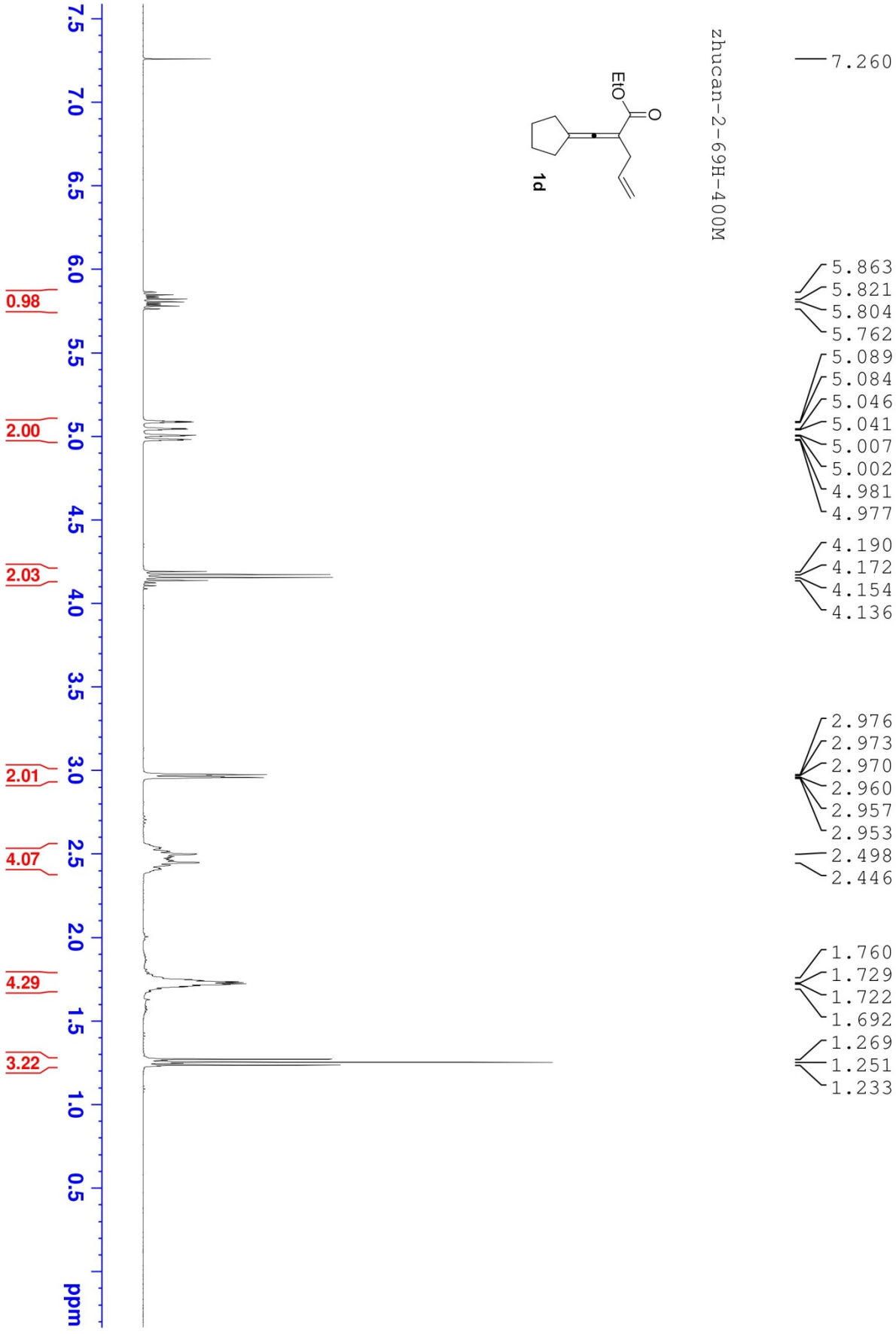
207.84
168.01
132.95
121.36
99.52
97.81
77.32
77.00
76.68
60.53
27.93
25.67
19.63
17.71
14.31

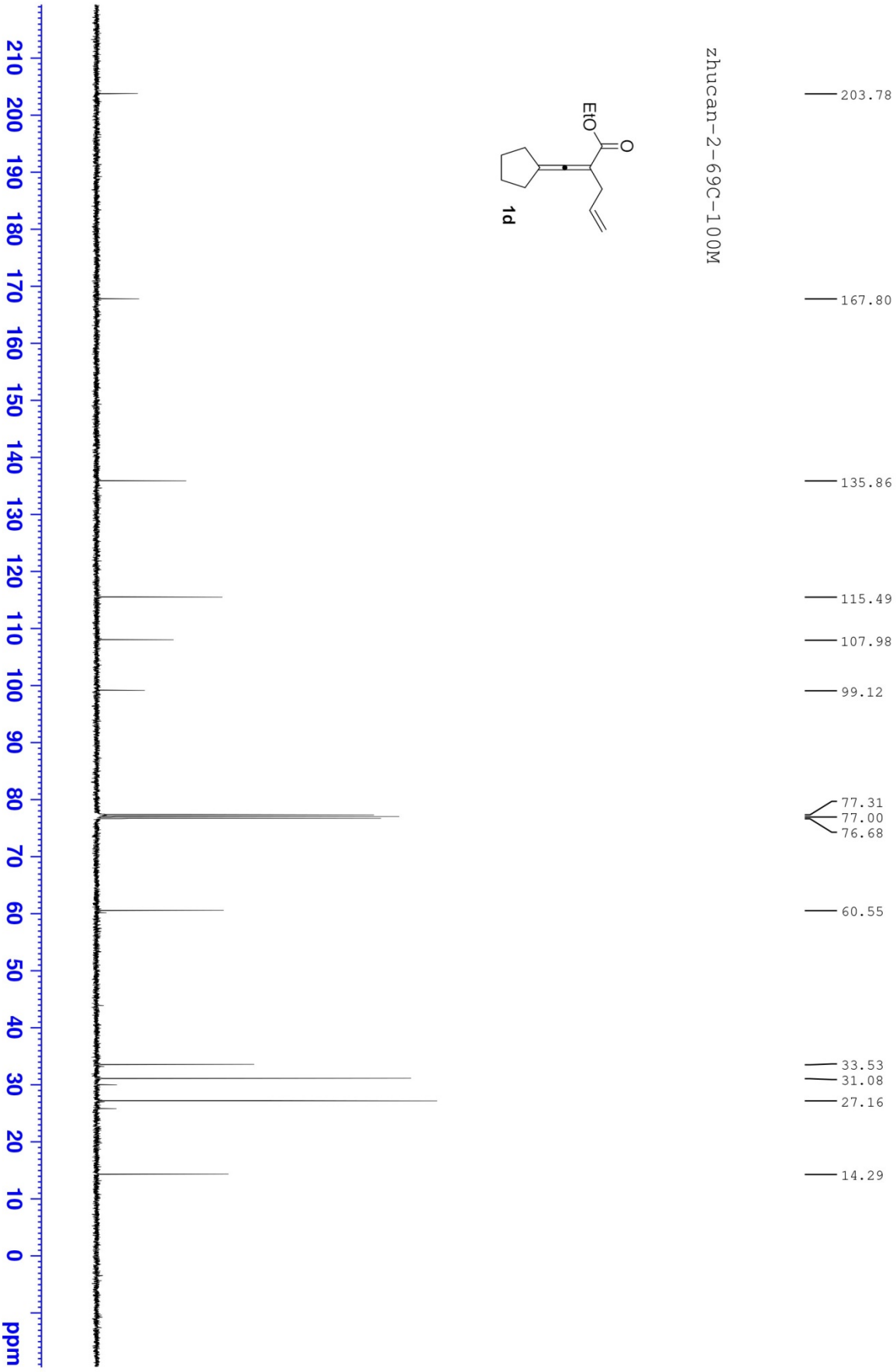
zhucan-2-53C-100M

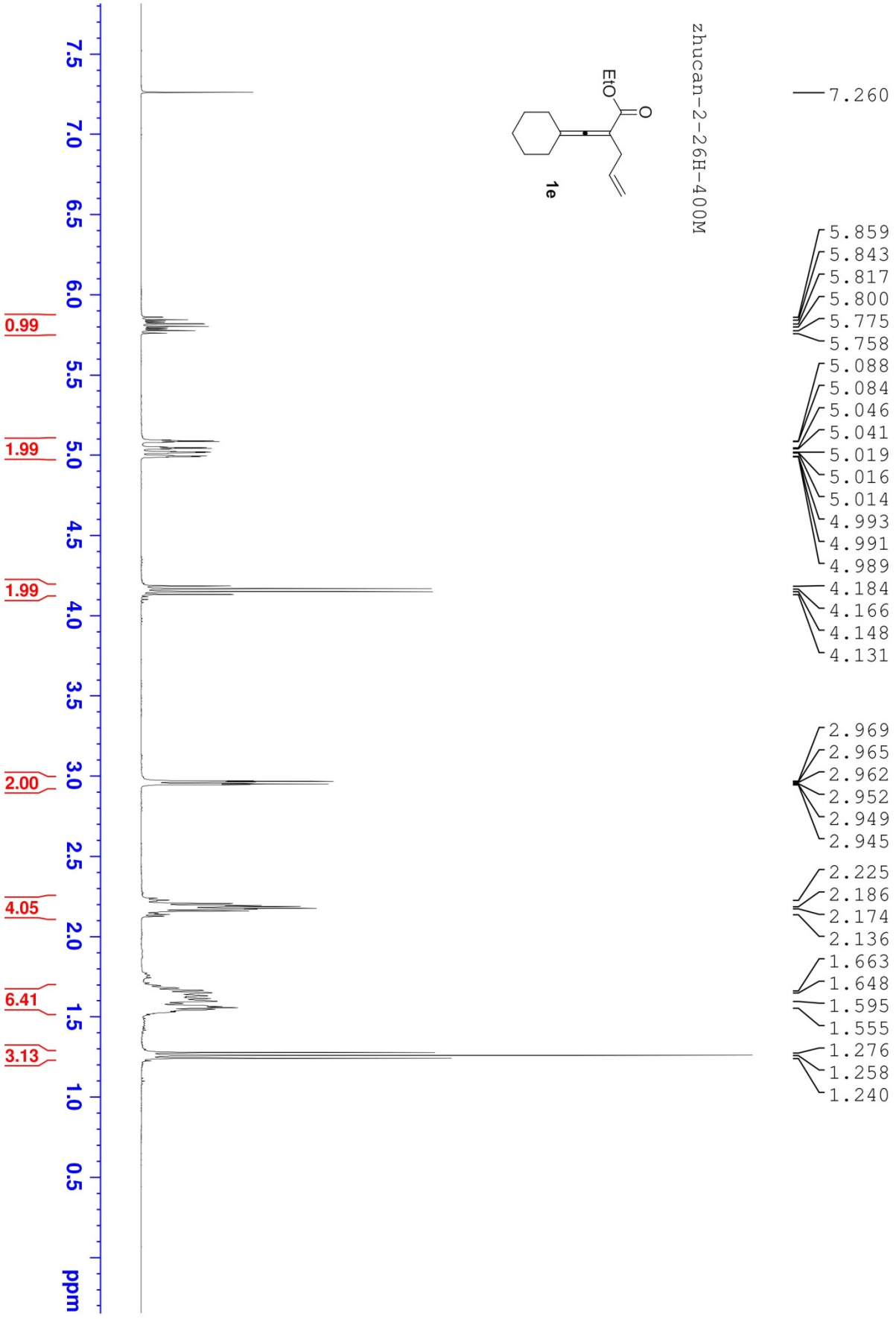


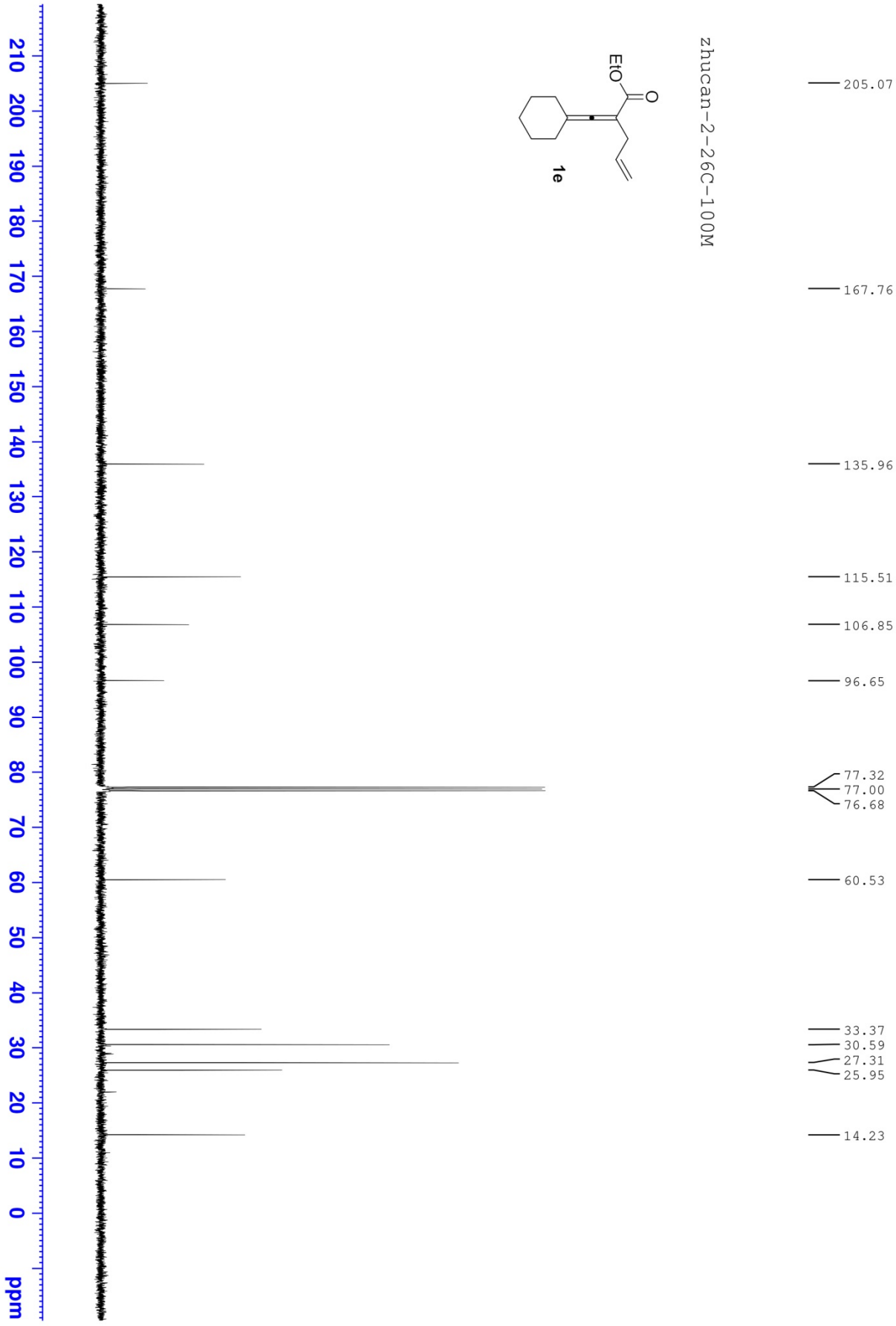
1c

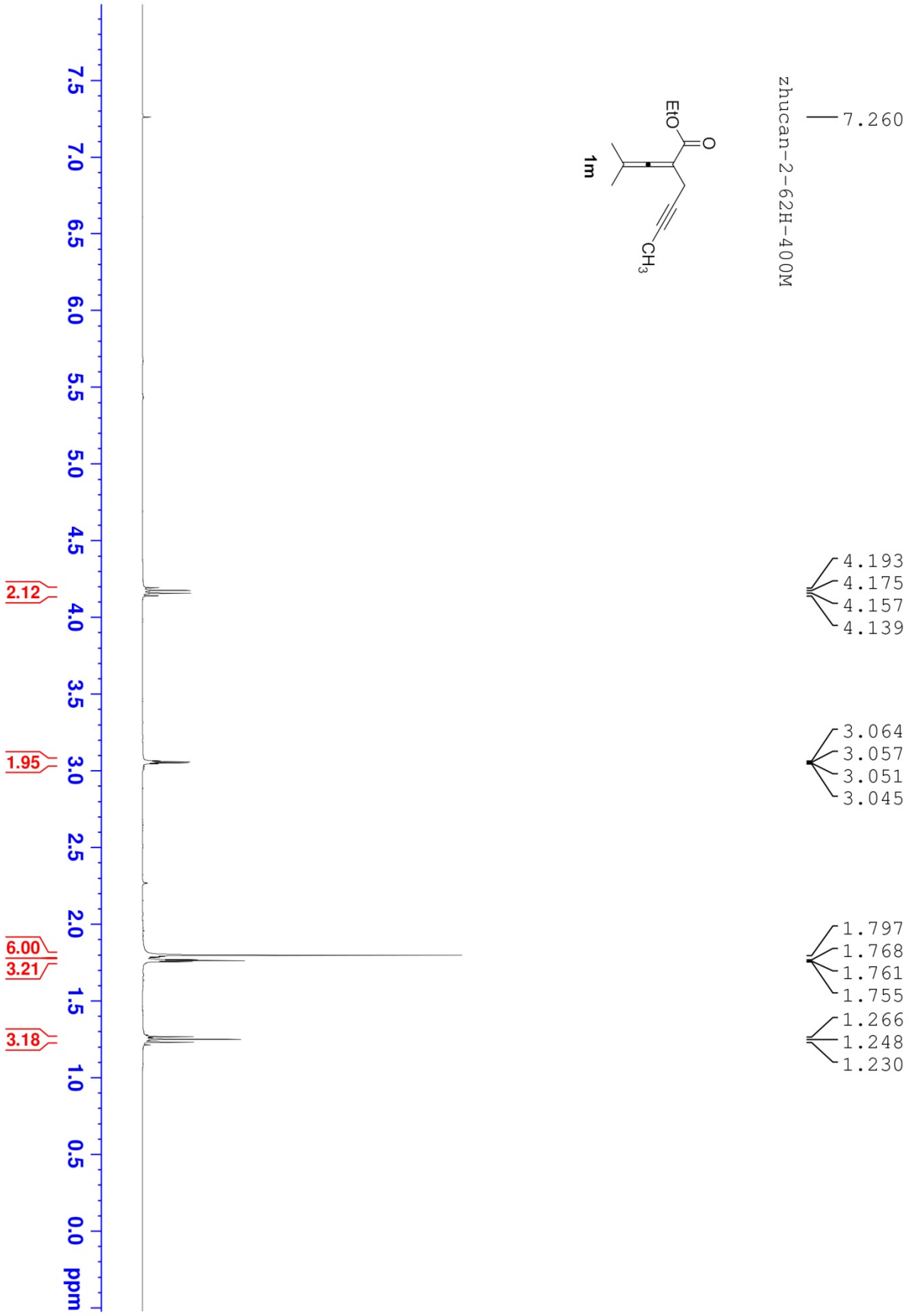


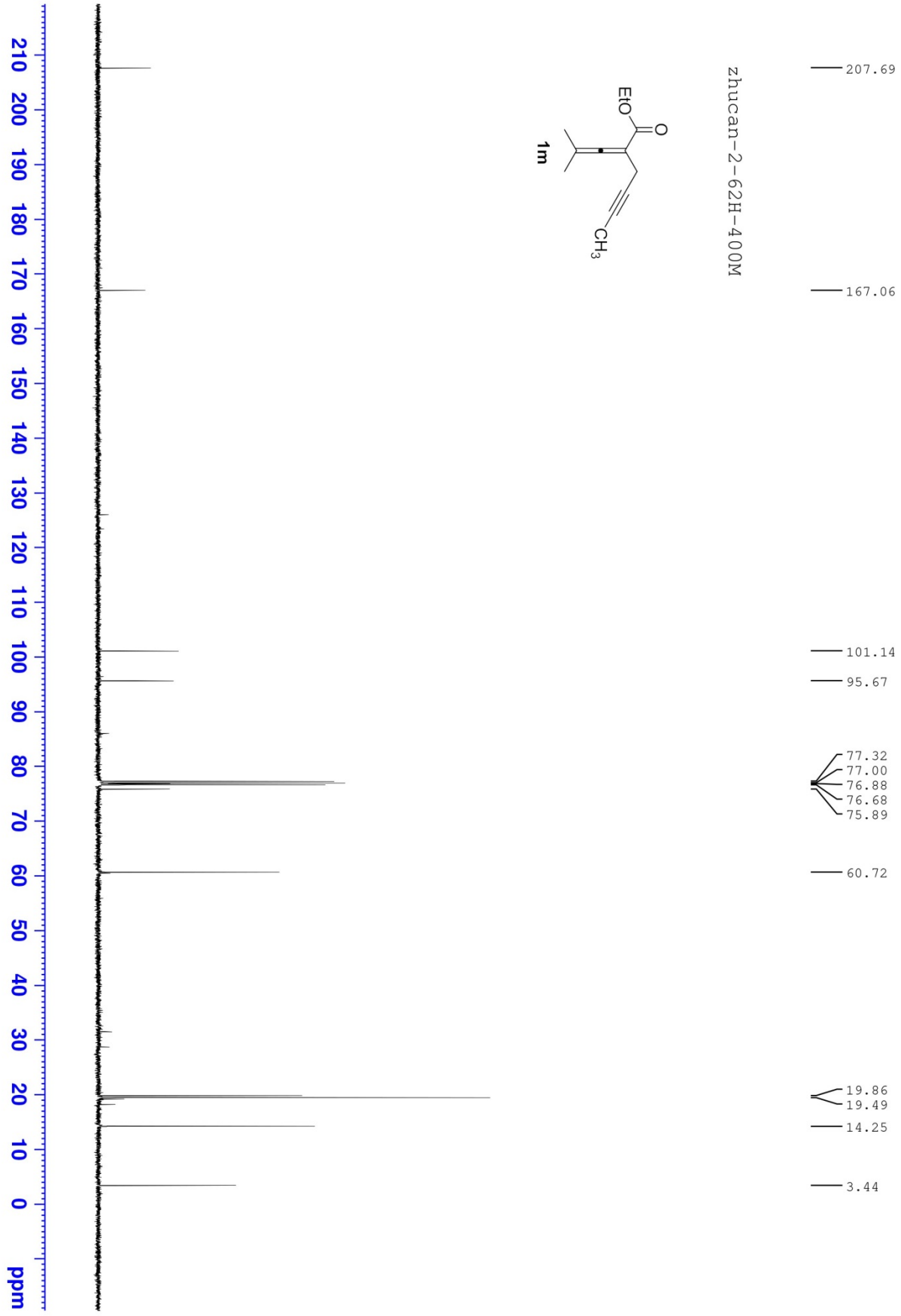

zhucan-2-69H-400M
1d
EtO
O
7.260
5.863
5.821
5.804
5.762
5.089
5.084
5.046
5.041
5.007
5.002
4.981
4.977
4.190
4.172
4.154
4.136
2.976
2.973
2.970
2.960
2.957
2.953
2.498
2.446
1.760
1.729
1.722
1.692
1.269
1.251
1.233
0.98
2.00
2.03
2.01
4.07
4.29
3.22
ppm

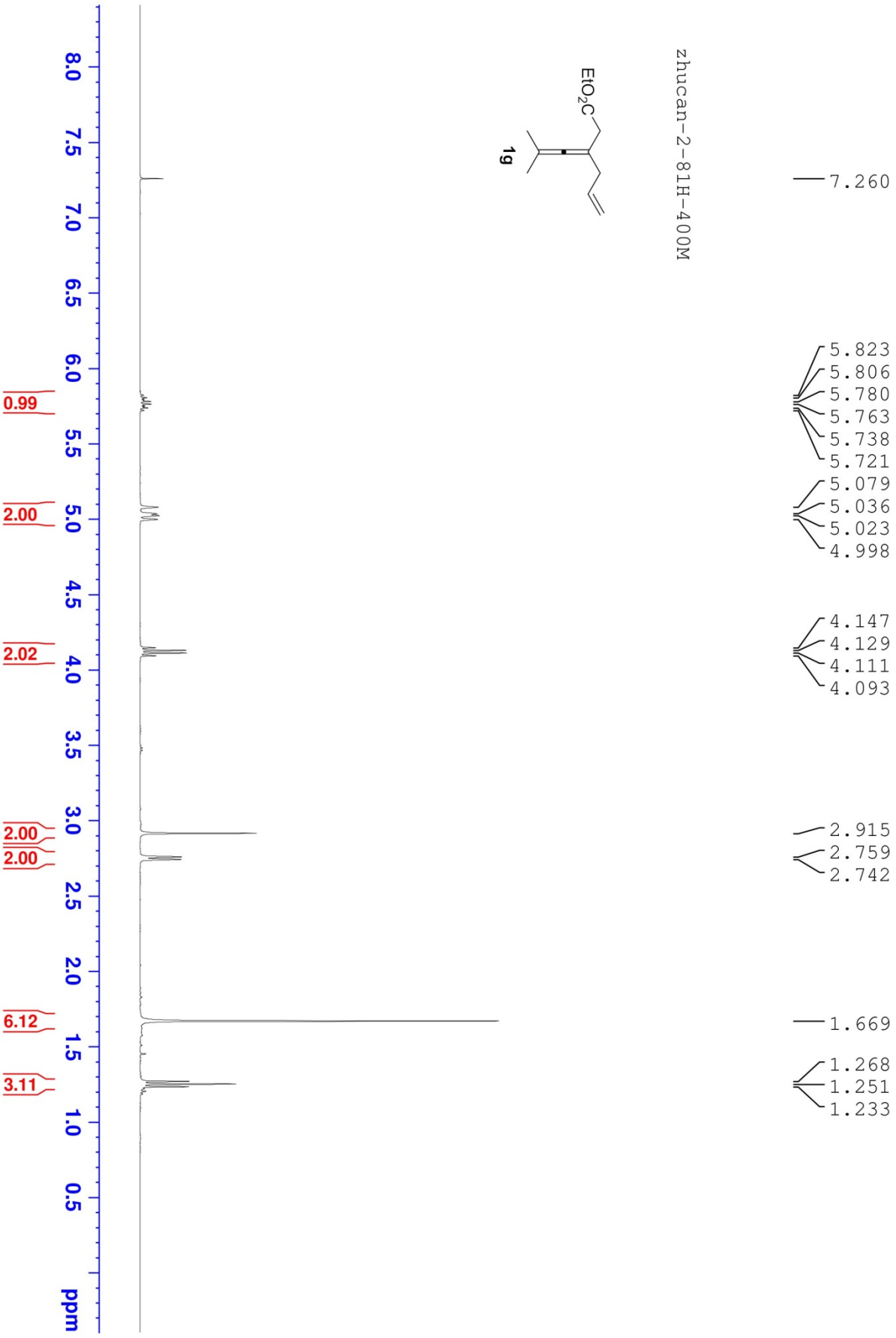

zhucan-2-69C-100M
EtO
O
1d
203.78
167.80
135.86
115.49
107.98
99.12
77.31
77.00
76.68
60.55
33.53
31.08
27.16
14.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

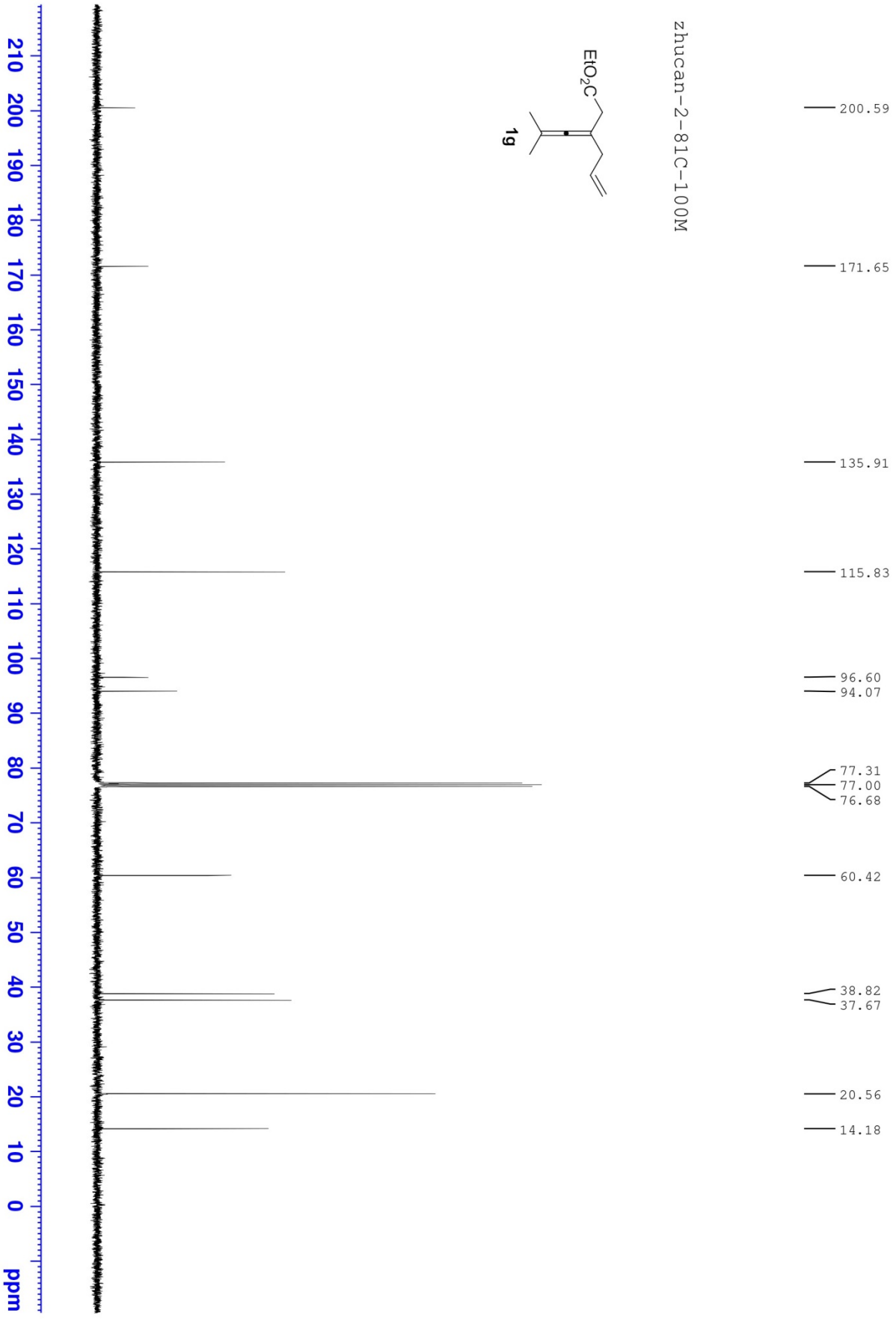

zhucan-2-26H-400M
EtO
O
1e
7.260
5.859
5.843
5.817
5.800
5.775
5.758
5.088
5.084
5.046
5.041
5.019
5.016
5.014
4.993
4.991
4.989
4.184
4.166
4.148
4.131
2.969
2.965
2.962
2.952
2.949
2.945
2.225
2.186
2.174
2.136
1.663
1.648
1.595
1.555
1.276
1.258
1.240
0.99
1.99
1.99
2.00
4.05
6.41
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

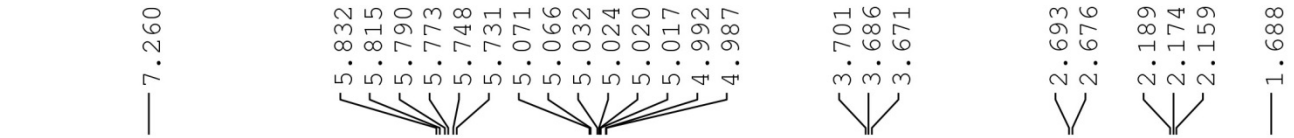

zhucan-2-26C-100M
EtO
O
1e
205.07
167.76
135.96
115.51
106.85
96.65
77.32
77.00
76.68
60.53
33.37
30.59
27.31
25.95
14.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


zhucan-2-62H-400M
7.260
4.193
4.175
4.157
4.139
3.064
3.057
3.051
3.045
1.797
1.768
1.761
1.755
1.266
1.248
1.230
1m
EtO
O
CH3
2.12
1.95
6.00
3.21
3.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

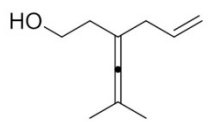

zhucan-2-62H-400M
1m
EtO
O
CH3
207.69
167.06
101.14
95.67
77.32
77.00
76.88
76.68
75.89
60.72
19.86
19.49
14.25
3.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


zhucan-2-81H-400M
EtO2C
1g
7.260
5.823
5.806
5.780
5.763
5.738
5.721
5.079
5.036
5.023
4.998
4.147
4.129
4.111
4.093
2.915
2.759
2.742
1.669
1.268
1.251
1.233
0.99
2.00
2.02
2.00
2.00
6.12
3.11
ppm


zhucan-2-81C-100M
EtO2C
1g
200.59
171.65
135.91
115.83
96.60
94.07
77.31
77.00
76.68
60.42
38.82
37.67
20.56
14.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



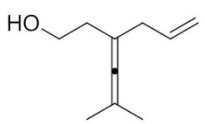
zhucan-2-87H-400M



1h

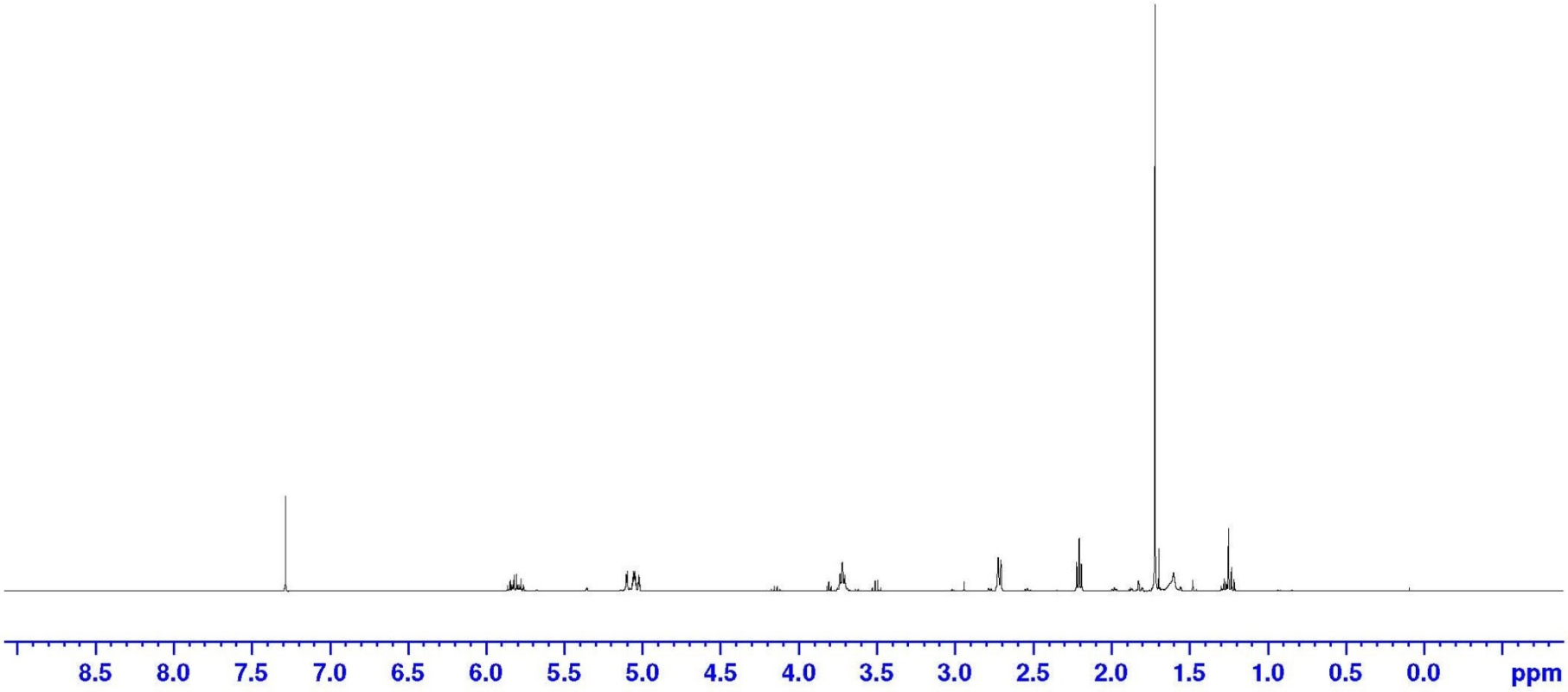
198.92
136.19
115.58
97.20
96.88
77.32
77.00
76.68
61.01
38.09
35.48
20.88

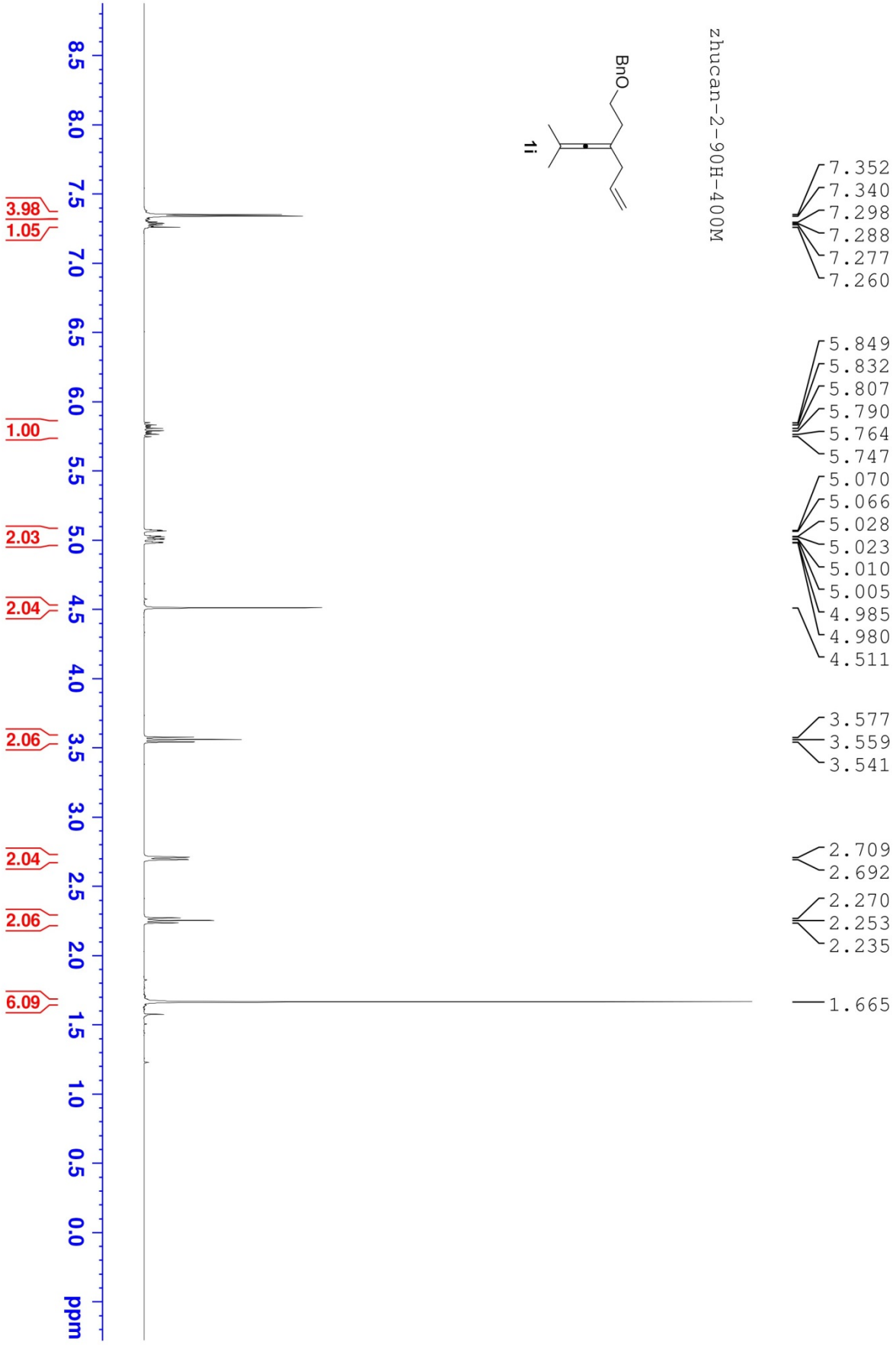
zhucan-2-87C-100M



1h

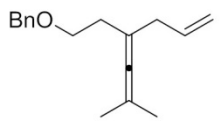
impure sample (after 10 h under romm temperature and open-air conditions)



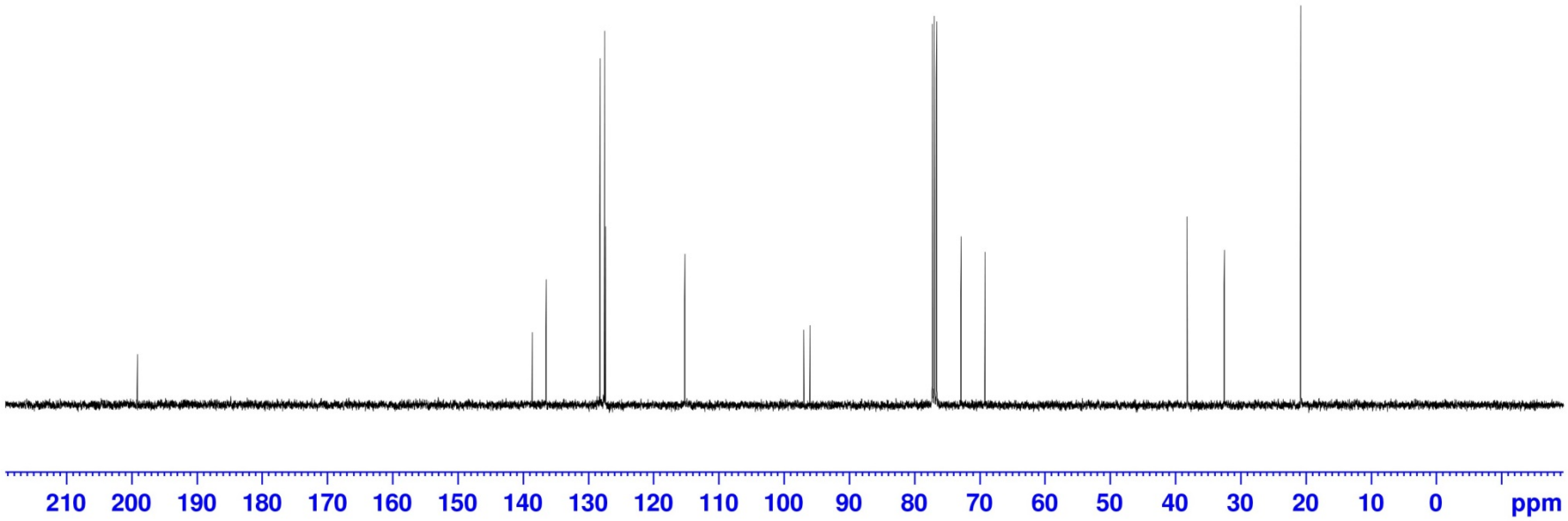

zhucan-2-90H-400M
BnO
1i
7.352
7.340
7.298
7.288
7.277
7.260
5.849
5.832
5.807
5.790
5.764
5.747
5.070
5.066
5.028
5.023
5.010
5.005
4.985
4.980
4.511
3.577
3.559
3.541
2.709
2.692
2.270
2.253
2.235
1.665
3.98
1.05
1.00
2.03
2.04
2.06
2.04
2.06
6.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

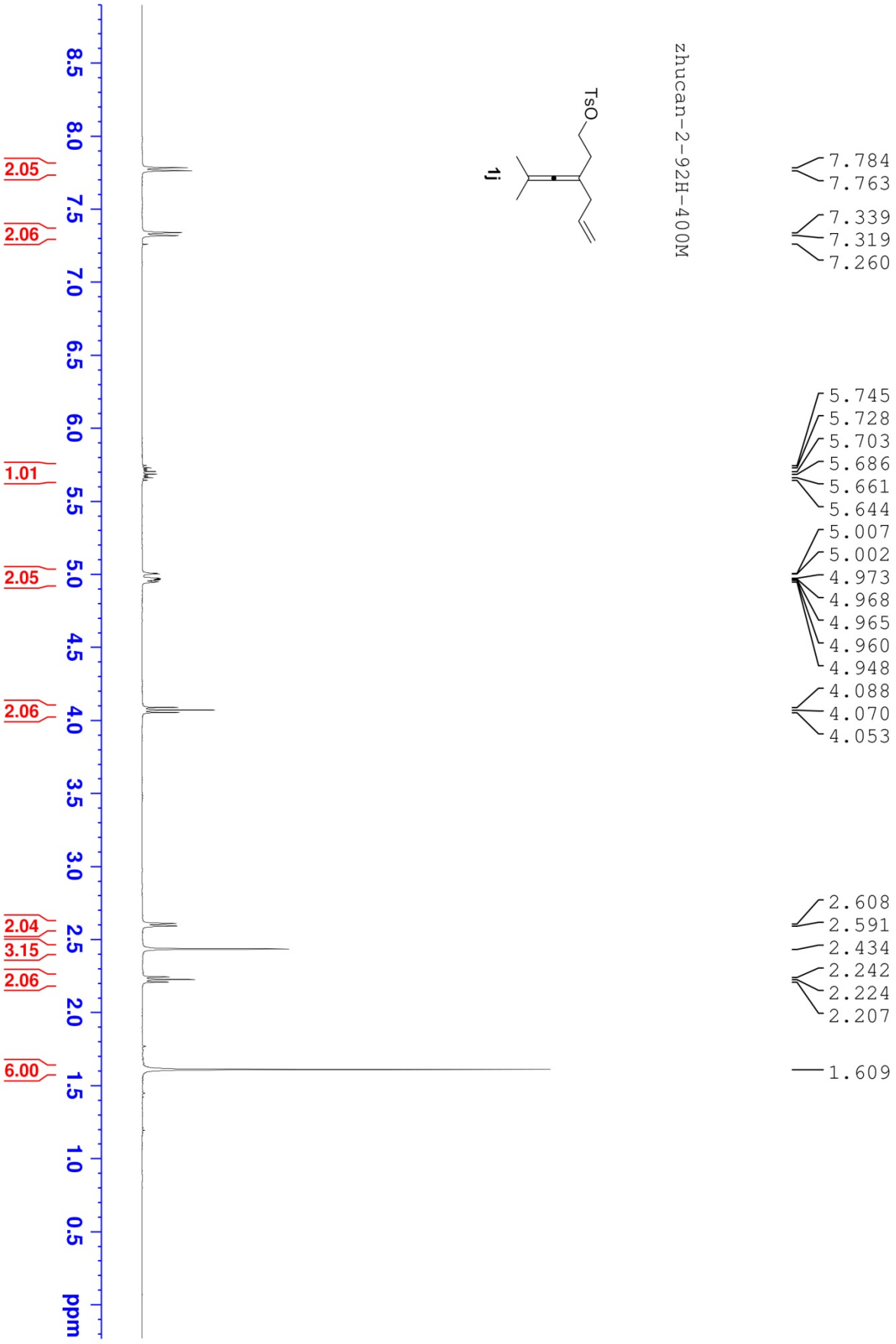
199.23
138.64
136.54
128.29
127.59
127.42
115.29
97.03
96.09
77.32
77.00
76.68
72.93
69.25
38.27
32.57
20.86

zhucan-2-90C-100M



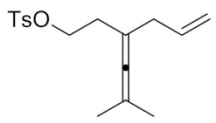
1i



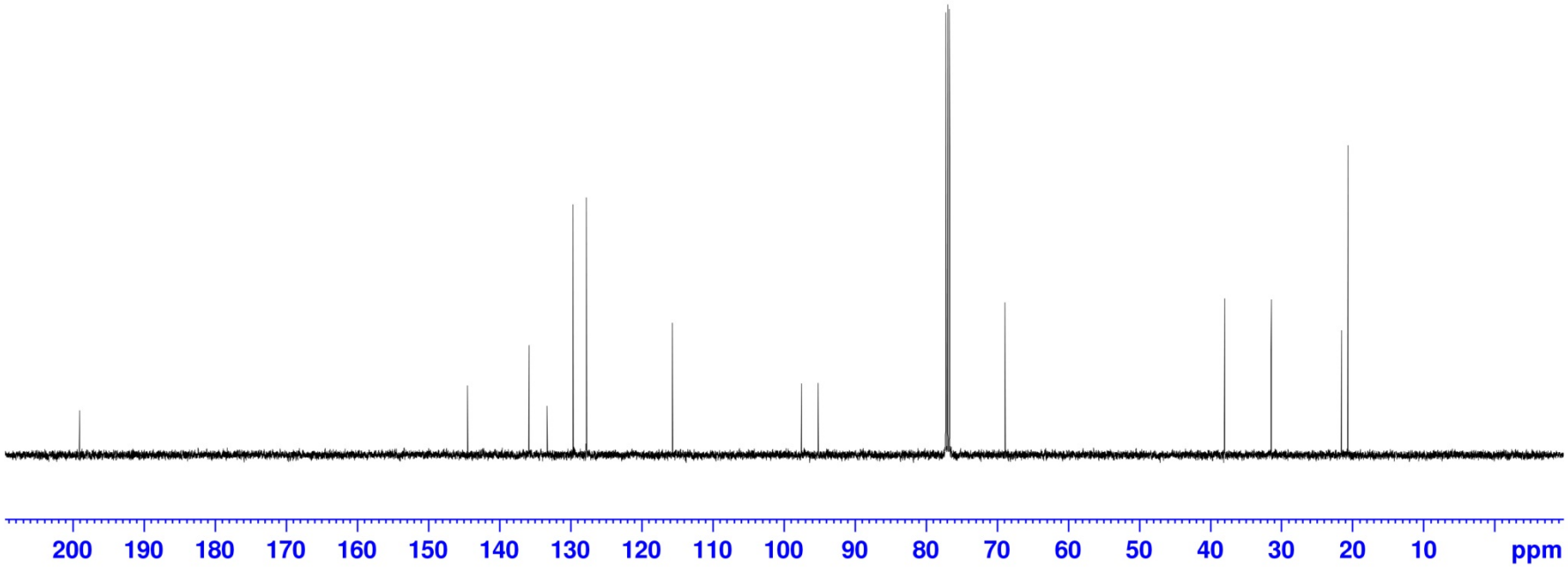

zhucan-2-92H-400M
TsO
1j
7.784
7.763
7.339
7.319
7.260
5.745
5.728
5.703
5.686
5.661
5.644
5.007
5.002
4.973
4.968
4.965
4.960
4.948
4.088
4.070
4.053
2.608
2.591
2.434
2.242
2.224
2.207
1.609
2.05
2.06
1.01
2.05
2.06
2.04
3.15
2.06
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

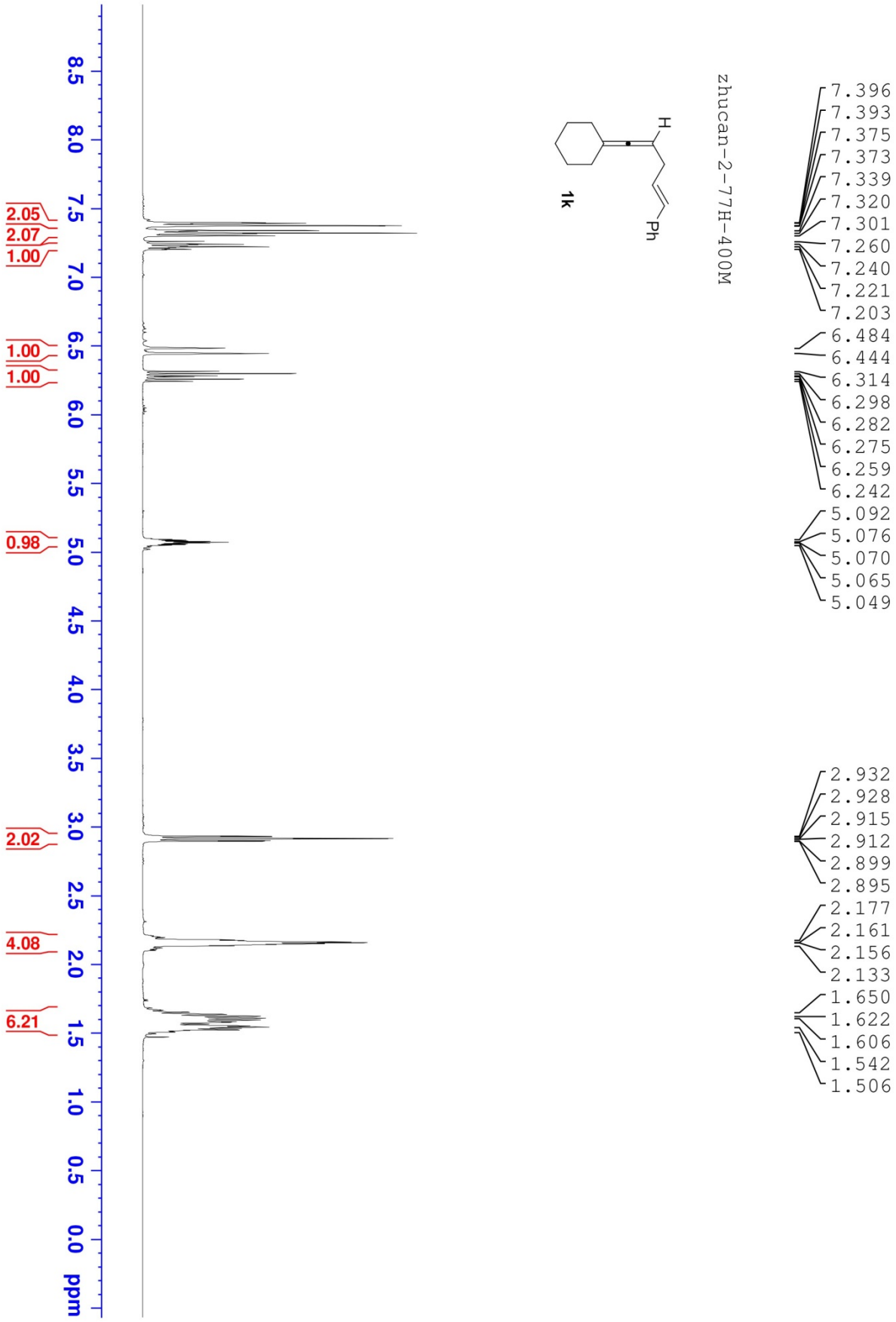
199.14
144.56
135.90
133.35
129.72
127.84
115.73
97.55
95.23
77.25
77.00
76.74
68.93
38.04
31.47
21.59
20.68

zhucan-2-92C-100M



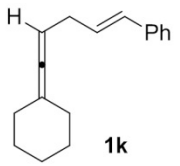
1j



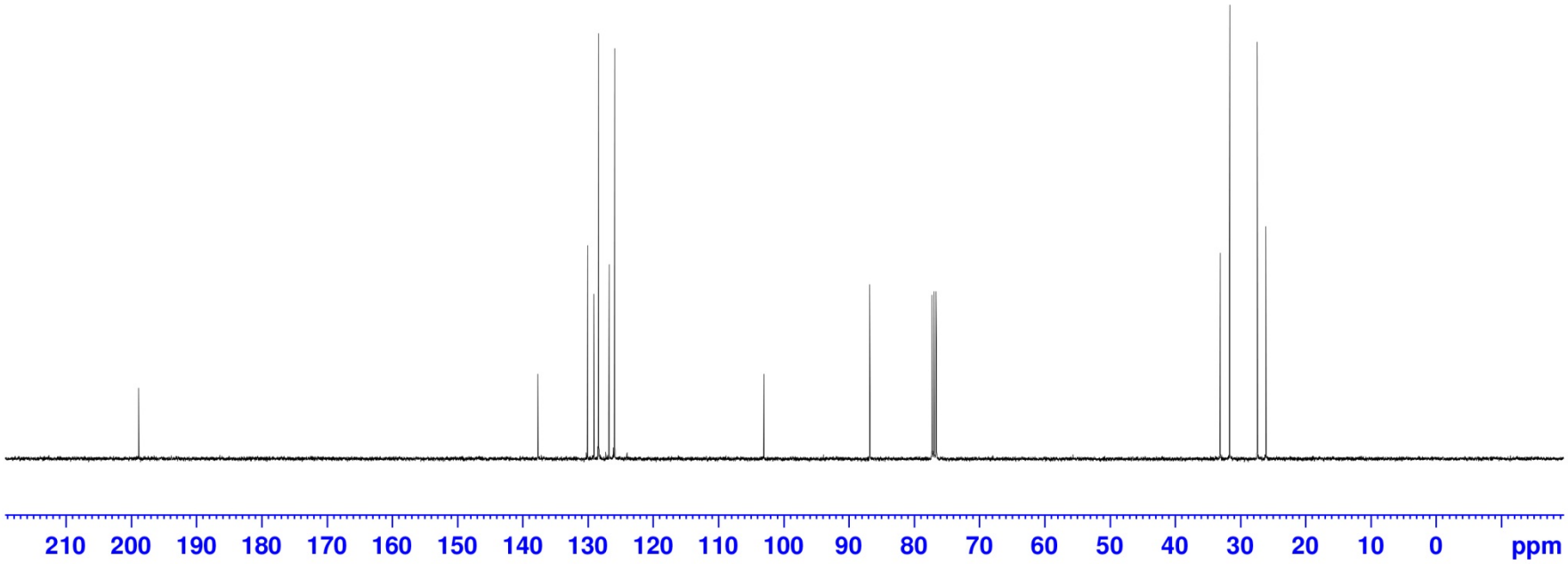

zhucan-2-77H-400M
1k
H
Ph
7.396
7.393
7.375
7.373
7.339
7.320
7.301
7.260
7.240
7.221
7.203
6.484
6.444
6.314
6.298
6.282
6.275
6.259
6.242
5.092
5.076
5.070
5.065
5.049
2.932
2.928
2.915
2.912
2.899
2.895
2.177
2.161
2.156
2.133
1.650
1.622
1.606
1.542
1.506
2.05
2.07
1.00
1.00
1.00
0.98
2.02
4.08
6.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

198.96
137.76
130.12
129.17
128.42
126.84
125.98
103.08
86.87
77.31
77.00
76.68
33.15
31.70
27.45
26.14

zhucan-2-77C-100M

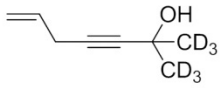


1k

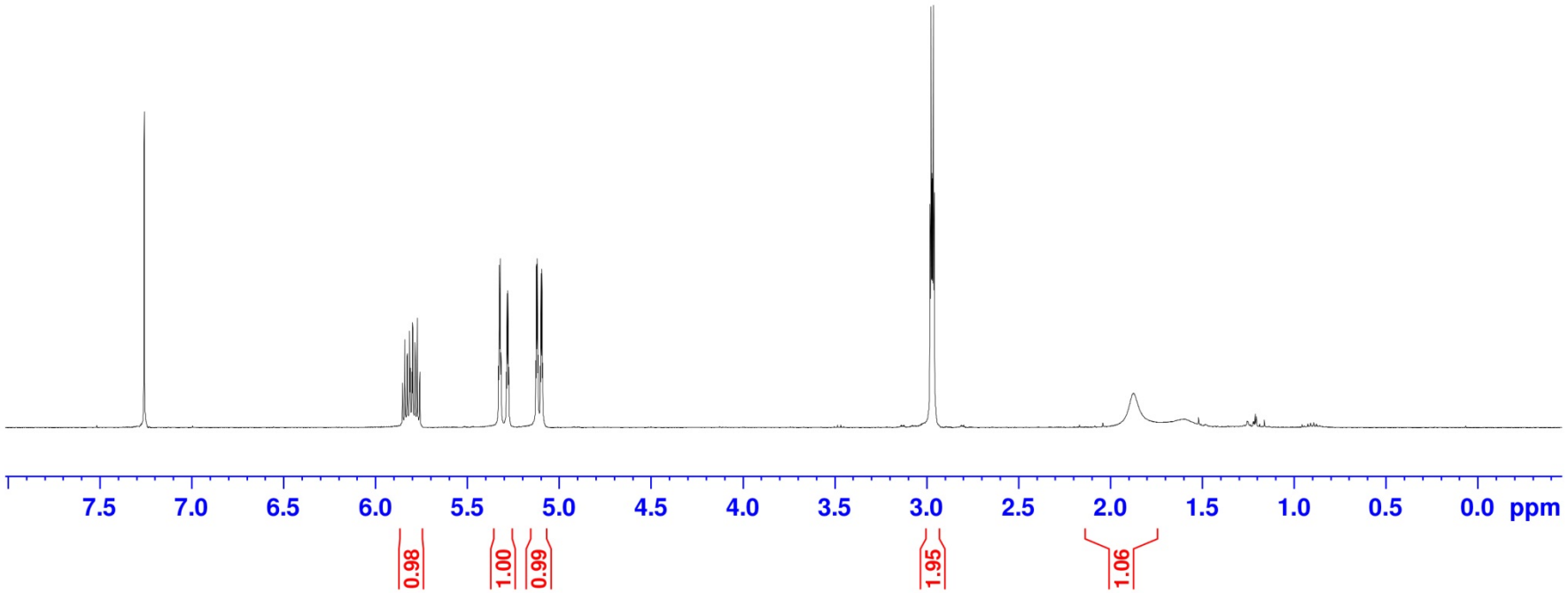


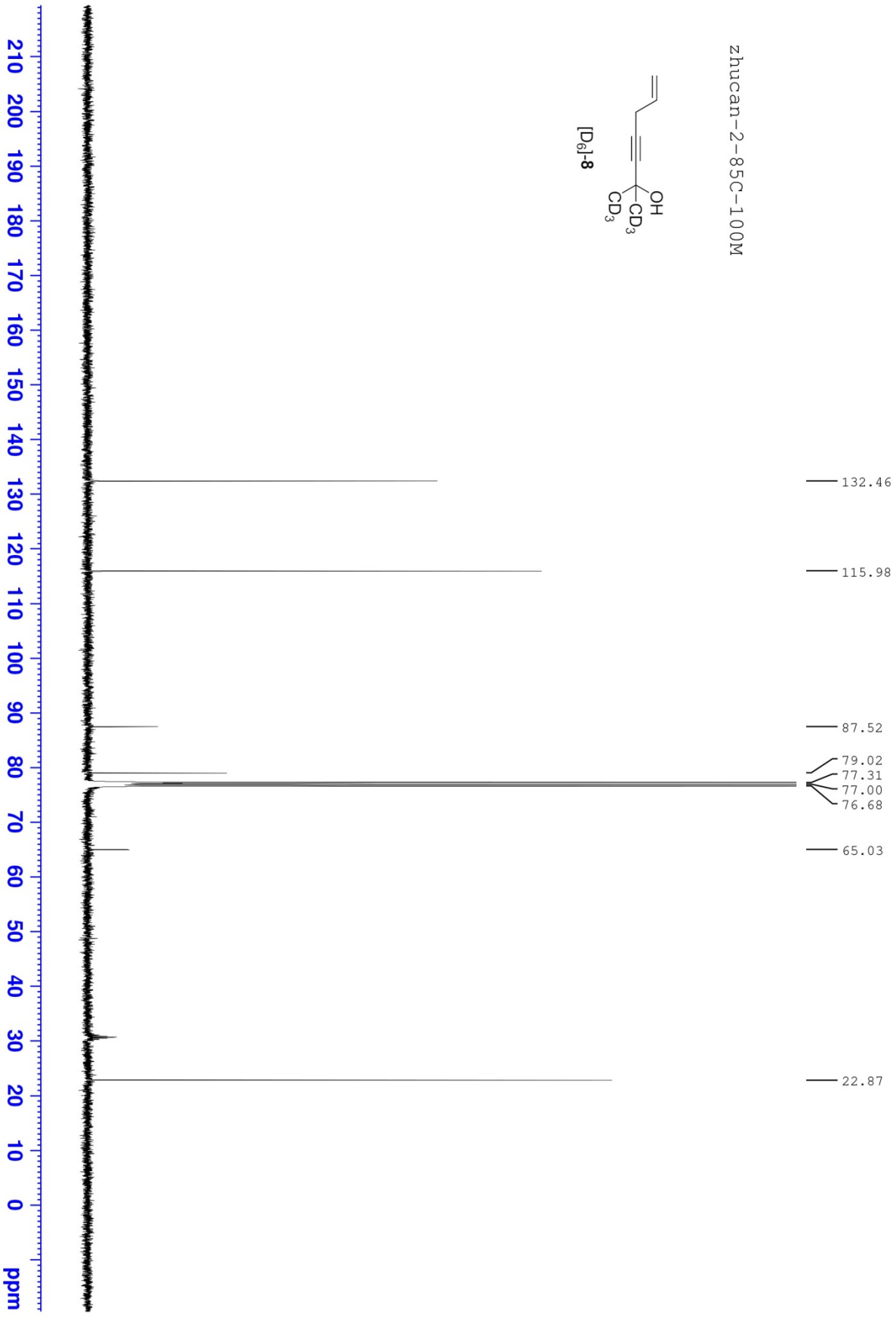
7.260
5.854
5.840
5.828
5.816
5.798
5.786
5.773
5.760
5.331
5.327
5.322
5.318
5.289
5.284
5.280
5.275
5.129
5.124
5.120
5.116
5.104
5.099
5.095
5.091
2.982
2.977
2.973
2.969
2.964
2.959
1.875

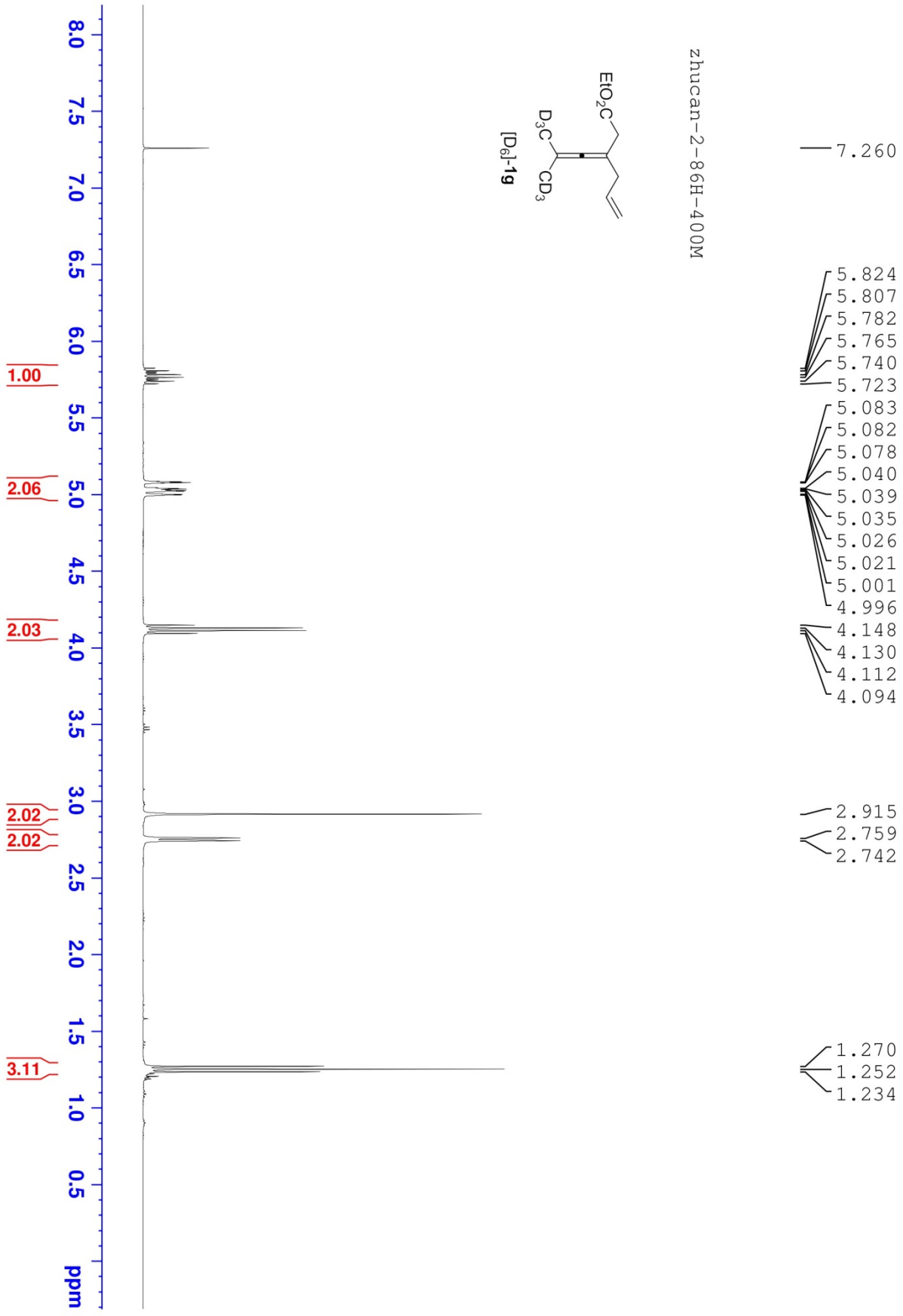
zhucan-2-85H-400M

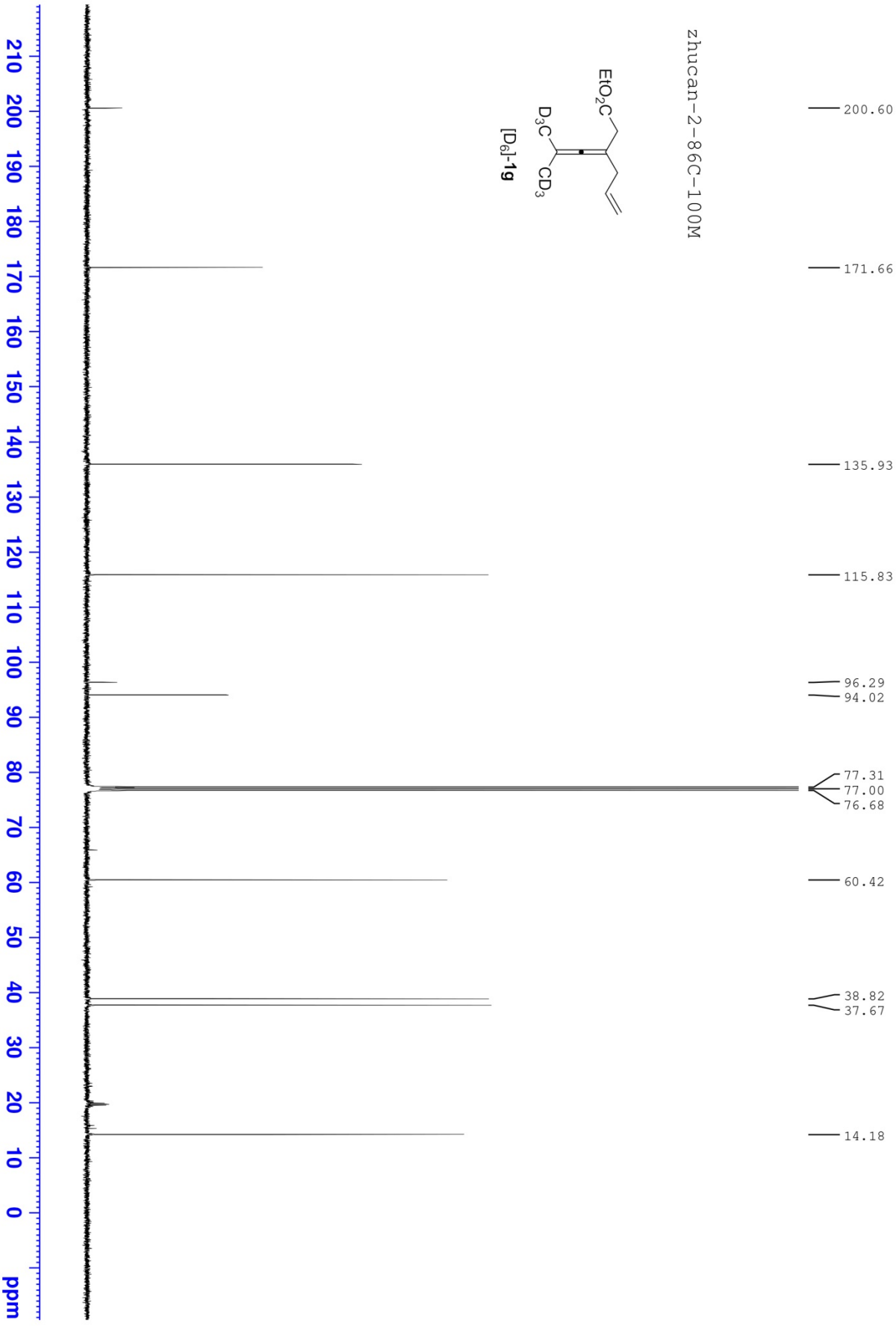


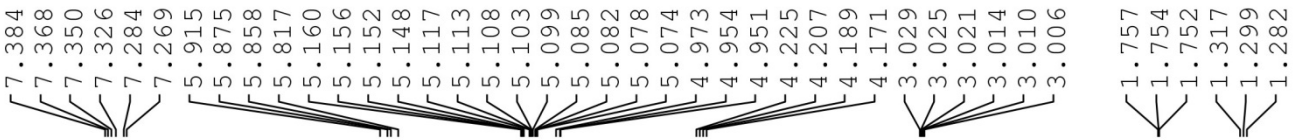
[D_6]-**8**



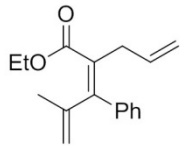

zhucan-2-85C-100M
[D6]-8
OH
CD3
CD3
132.46
115.98
87.52
79.02
77.31
77.00
76.68
65.03
22.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


zhucan-2-86H-400M
[D6]-1g
EtO2C
D3C
CD3
7.260
5.824
5.807
5.782
5.765
5.740
5.723
5.083
5.082
5.078
5.040
5.039
5.035
5.026
5.021
5.001
4.996
4.148
4.130
4.112
4.094
2.915
2.759
2.742
1.270
1.252
1.234
1.00
2.06
2.03
2.02
2.02
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

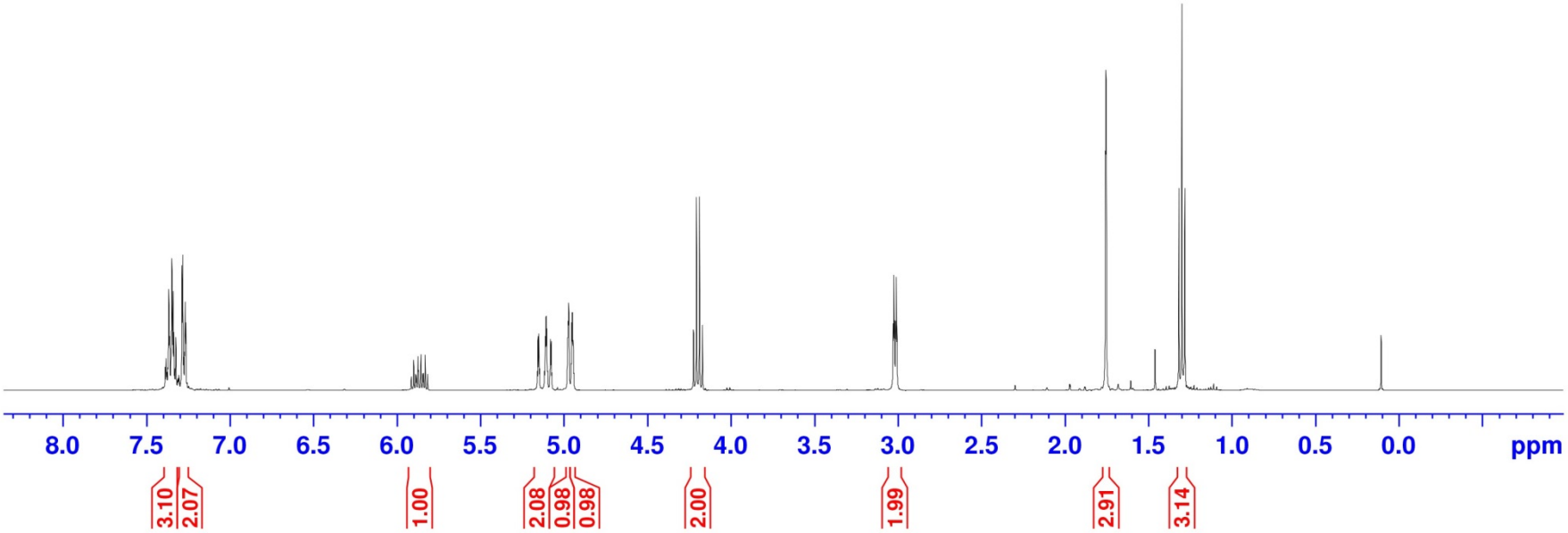

zhucan-2-86C-100M
EtO2C
D3C
CD3
[D6]-1g
200.60
171.66
135.93
115.83
96.29
94.02
77.31
77.00
76.68
60.42
38.82
37.67
14.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

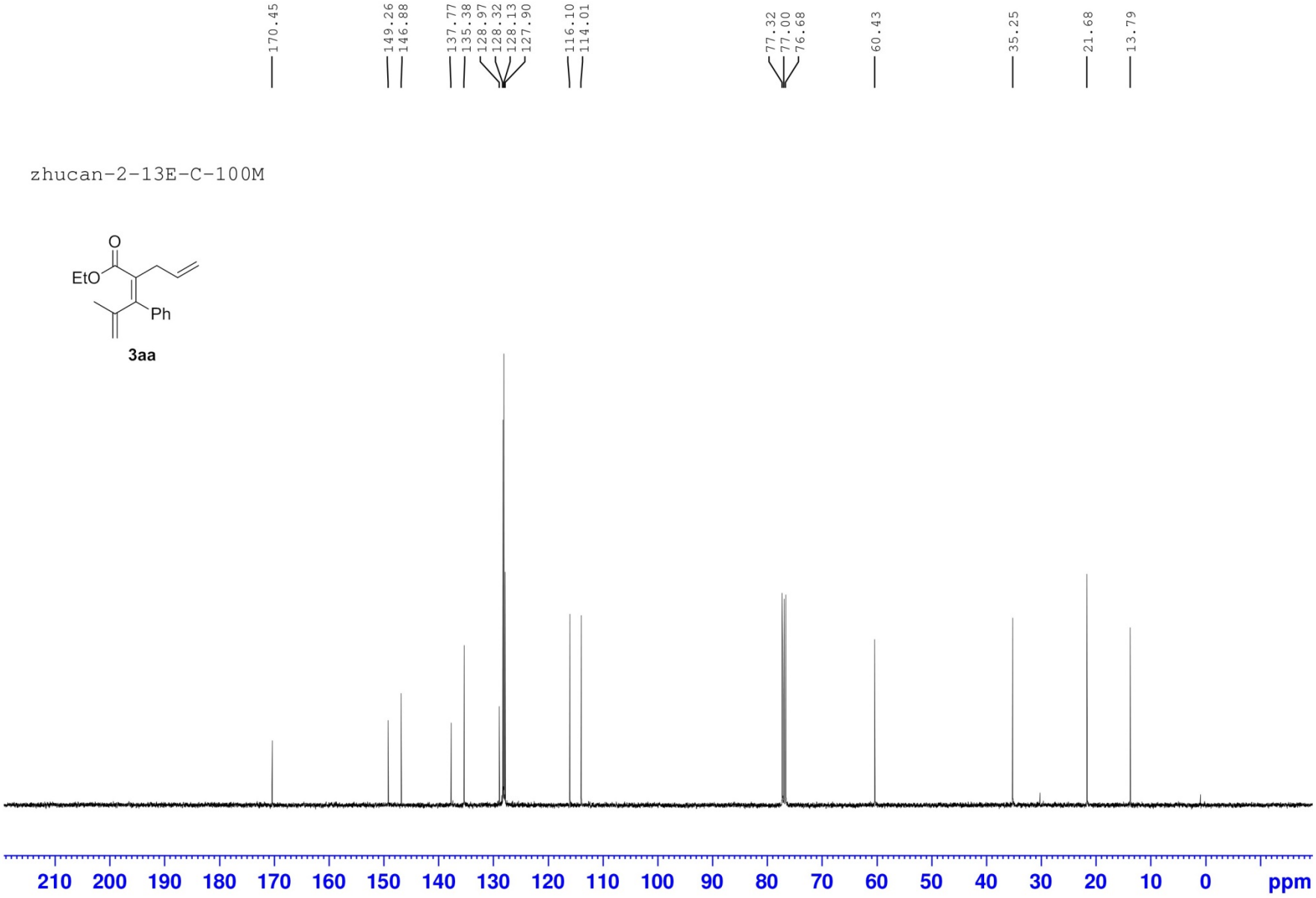


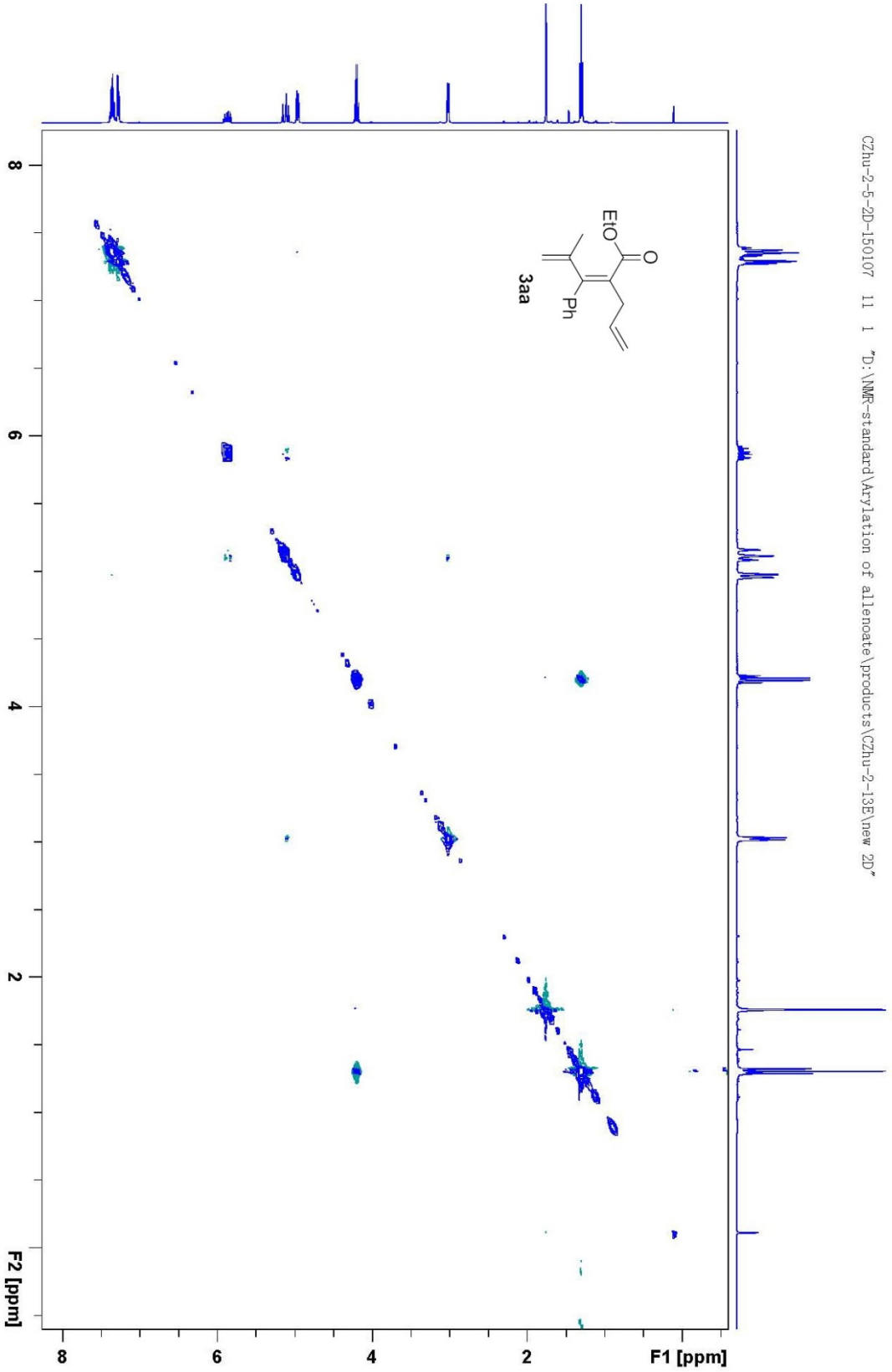
zhucan-2-13E-H-400M

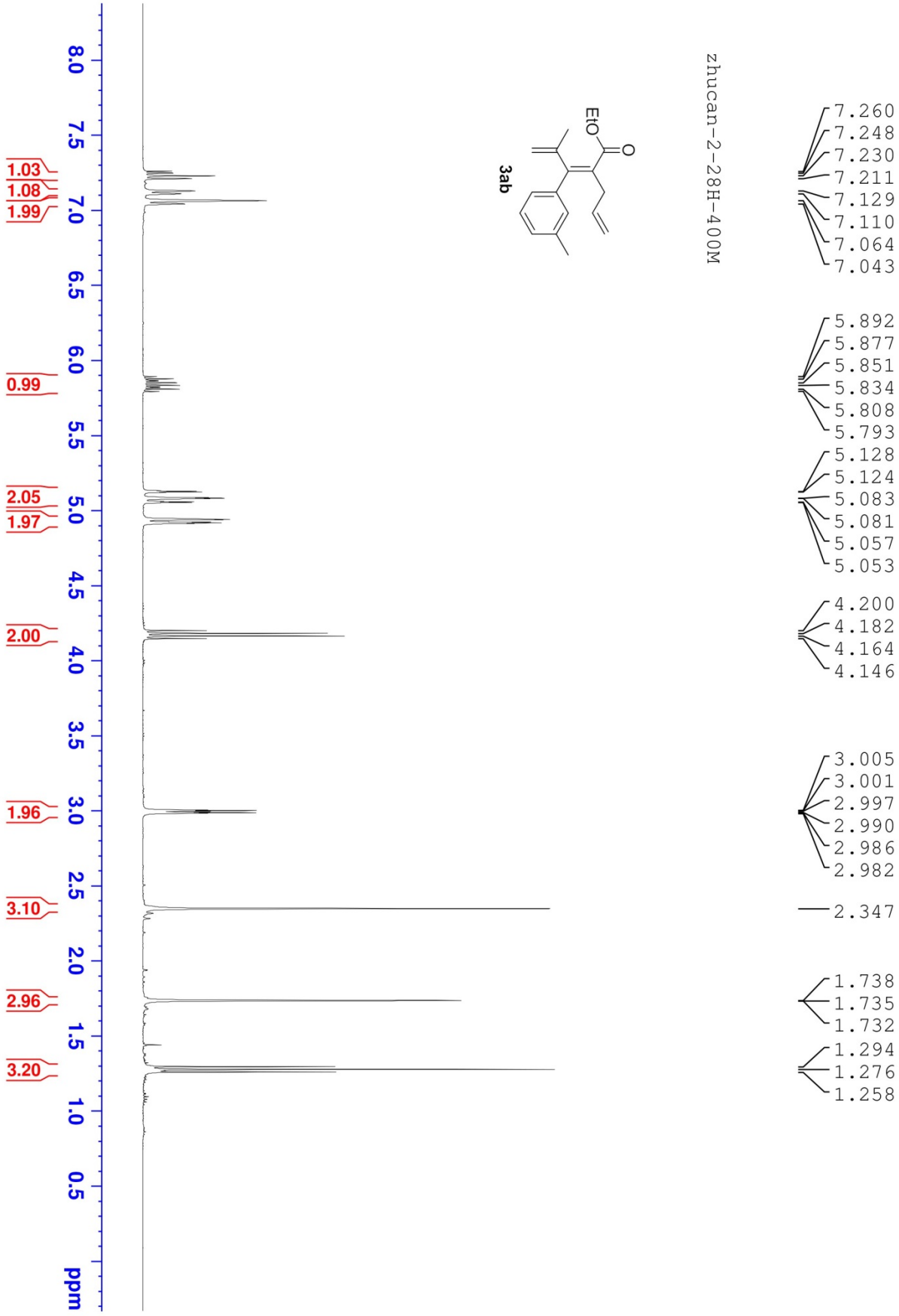


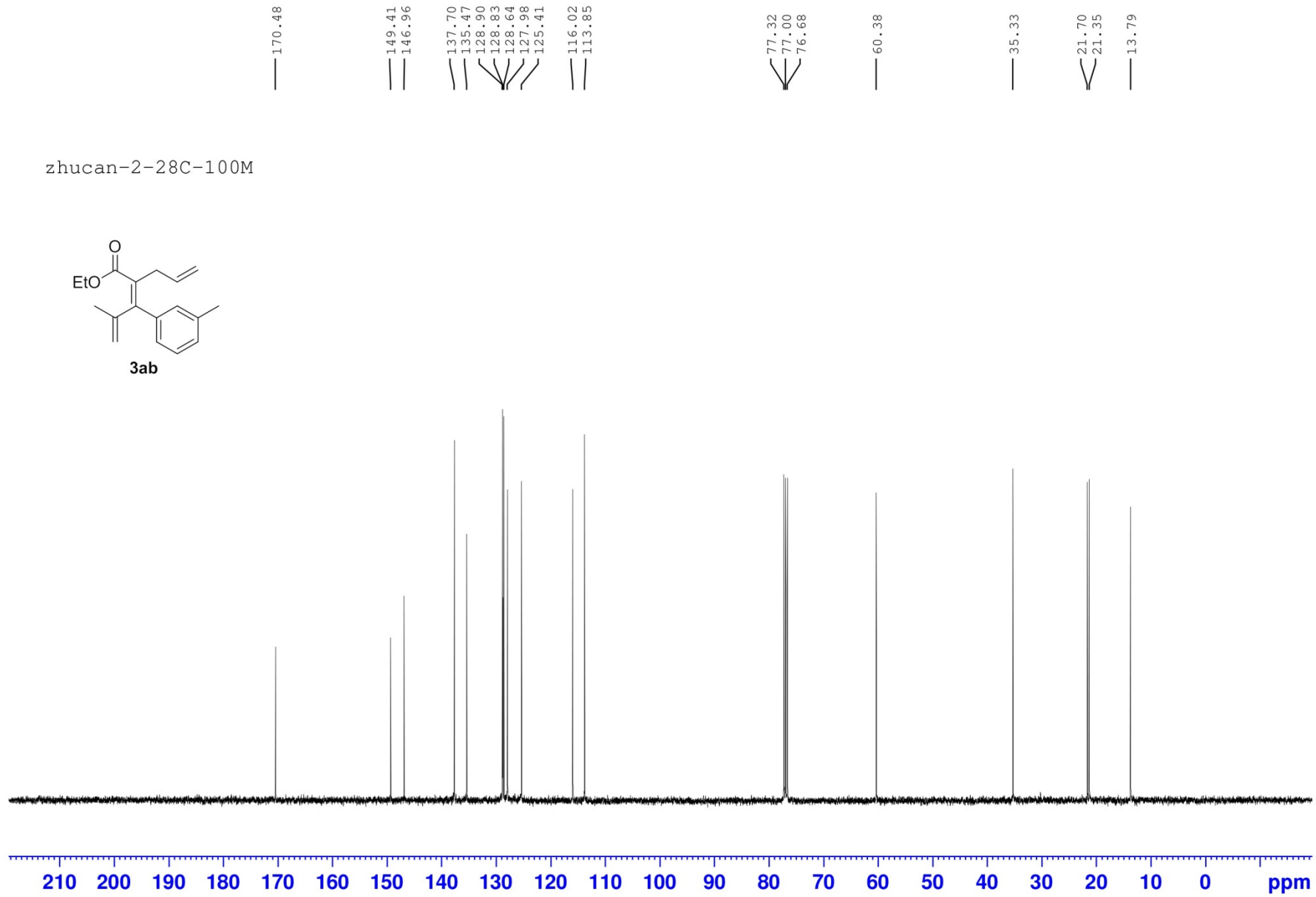
3aa

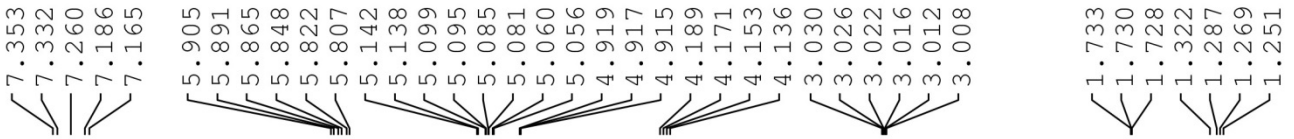



170.45
149.26
146.88
137.77
135.38
128.97
128.32
128.13
127.90
116.10
114.01
77.32
77.00
76.68
60.43
35.25
21.68
13.79
zhucan-2-13E-C-100M
O
EtO
Ph
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

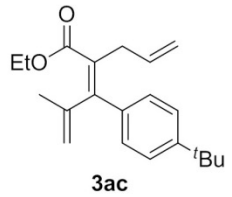

CZhu-2-5-2D-150107 11 1 "D:\NMR-standard\Arylation of allenoate\products\CZhu-2-13E\new 2D"
EtO
O
Ph
3aa
F2 [ppm]
F1 [ppm]
8
6
4
2


zhucan-2-28H-400M
3ab
EtO
O
7.260
7.248
7.230
7.211
7.129
7.110
7.064
7.043
5.892
5.877
5.851
5.834
5.808
5.793
5.128
5.124
5.083
5.081
5.057
5.053
4.200
4.182
4.164
4.146
3.005
3.001
2.997
2.990
2.986
2.982
2.347
1.738
1.735
1.732
1.294
1.276
1.258
1.03
1.08
1.99
0.99
2.05
1.97
2.00
1.96
3.10
2.96
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

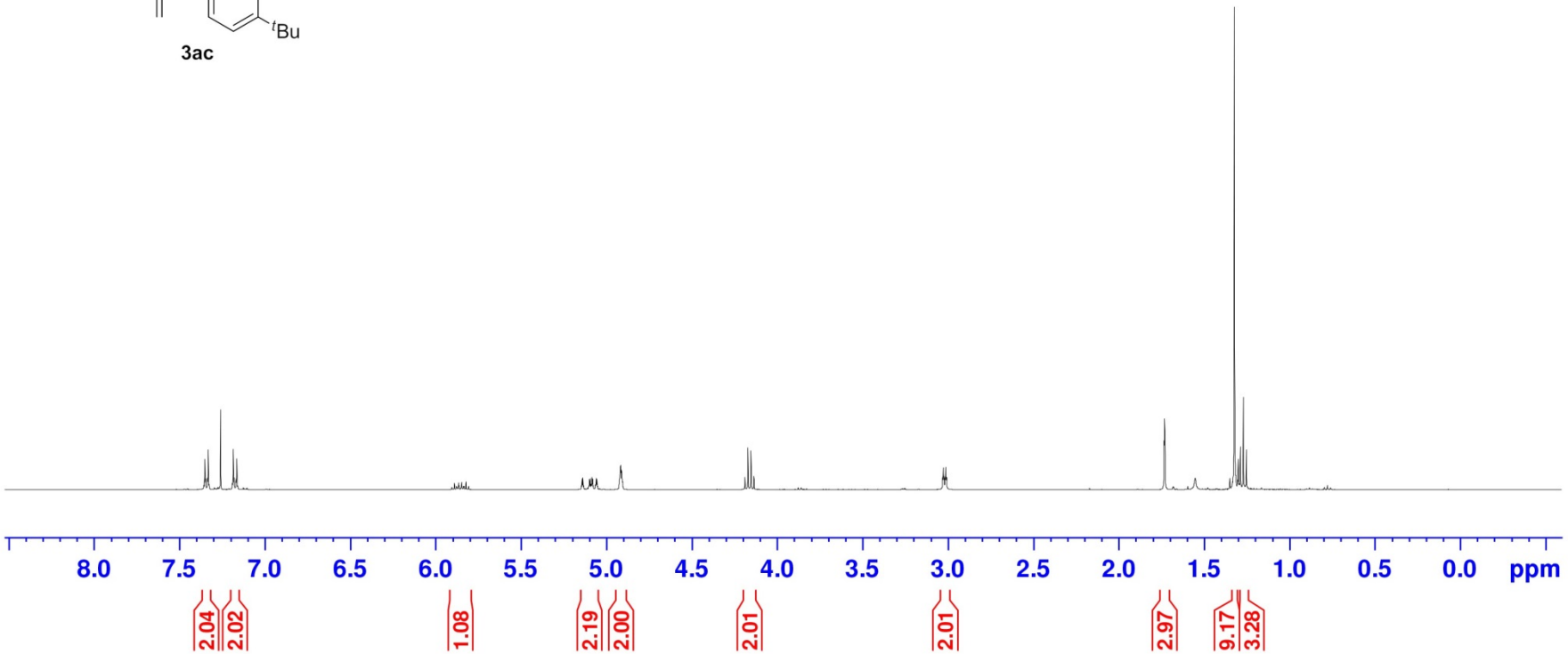

170.48
149.41
146.96
137.70
135.47
128.90
128.83
128.64
127.98
125.41
116.02
113.85
77.32
77.00
76.68
60.38
35.33
21.70
21.35
13.79
zhucan-2-28C-100M
O
EtO
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

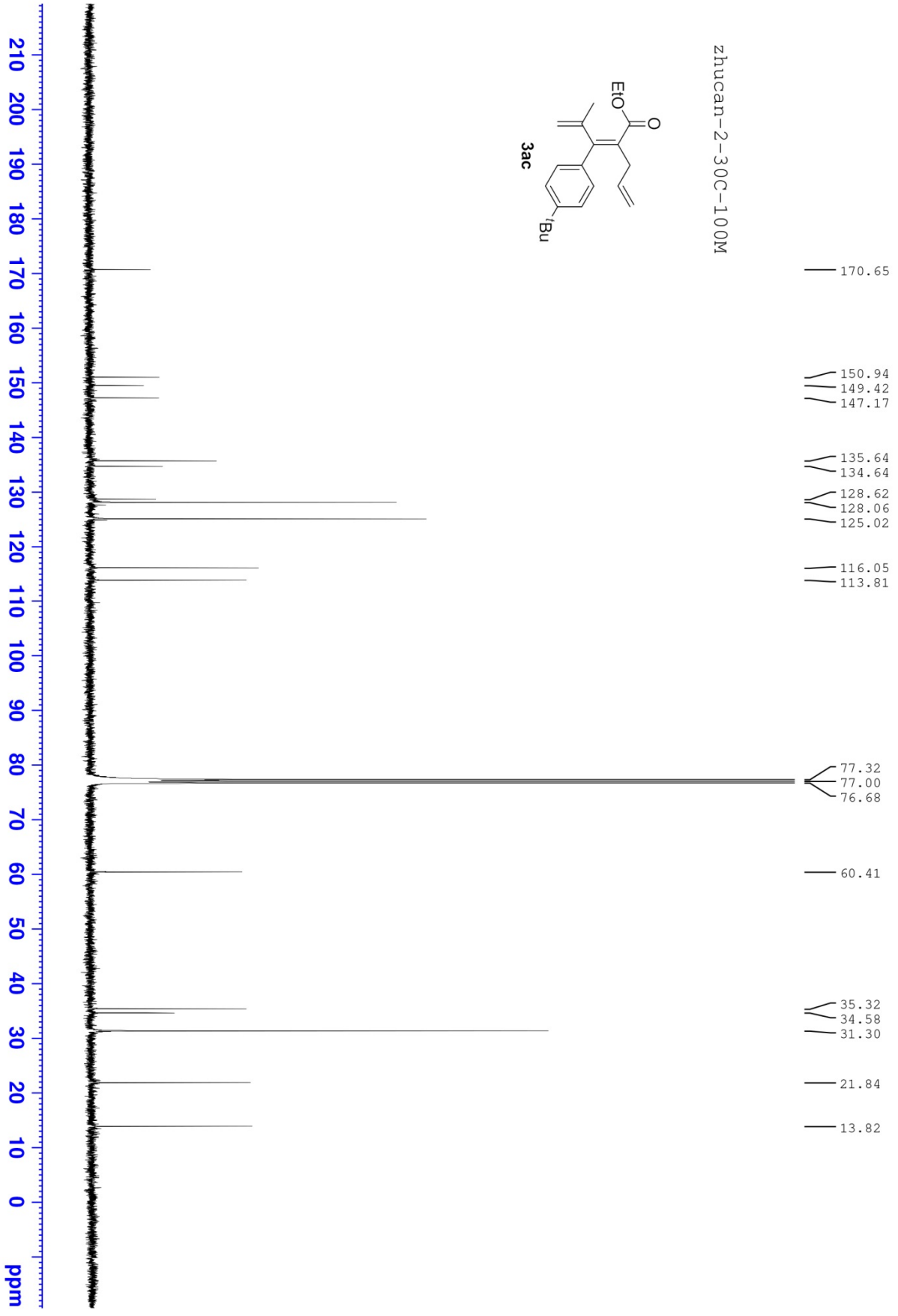


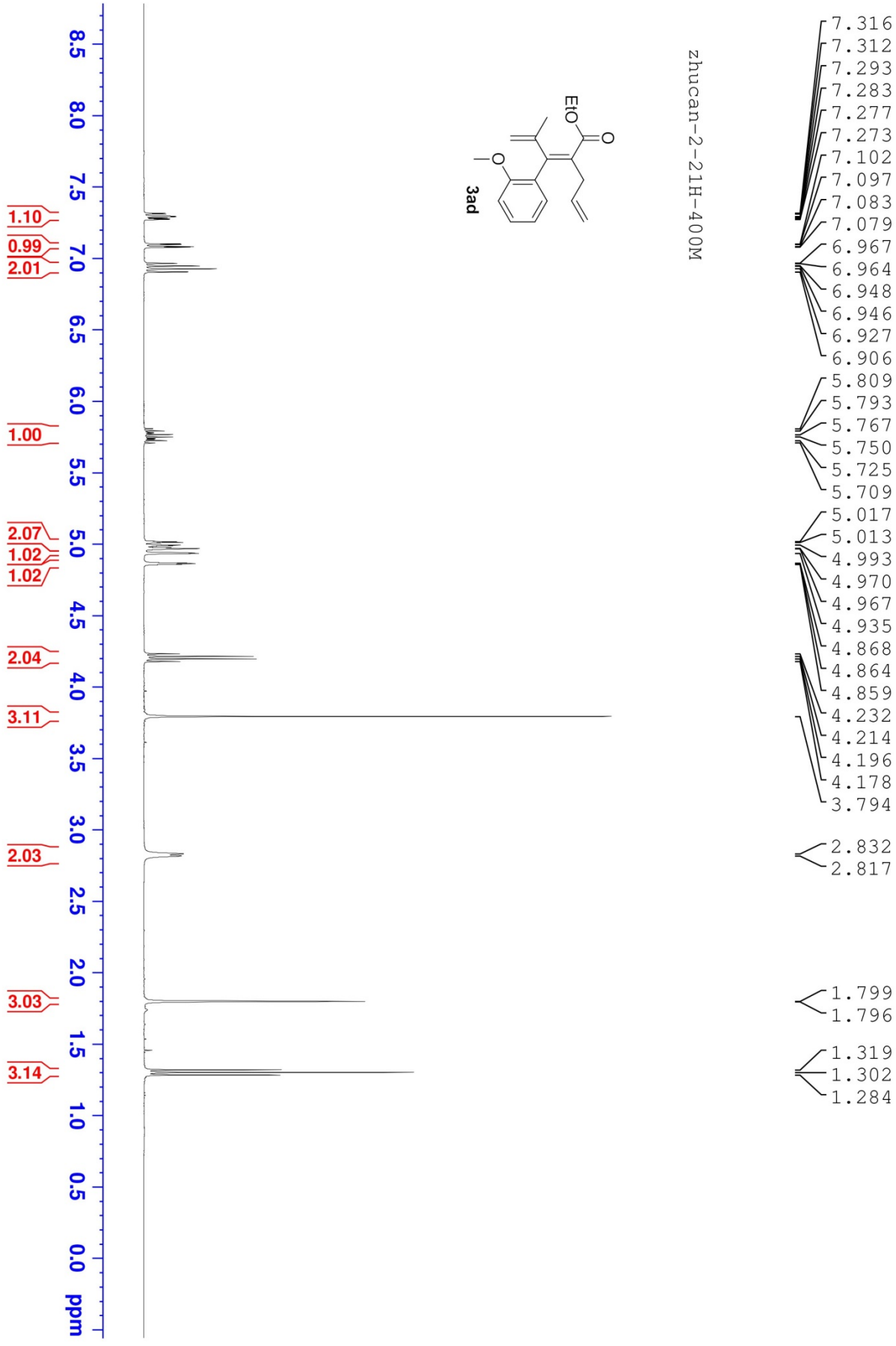
zhucan-2-30H-400M

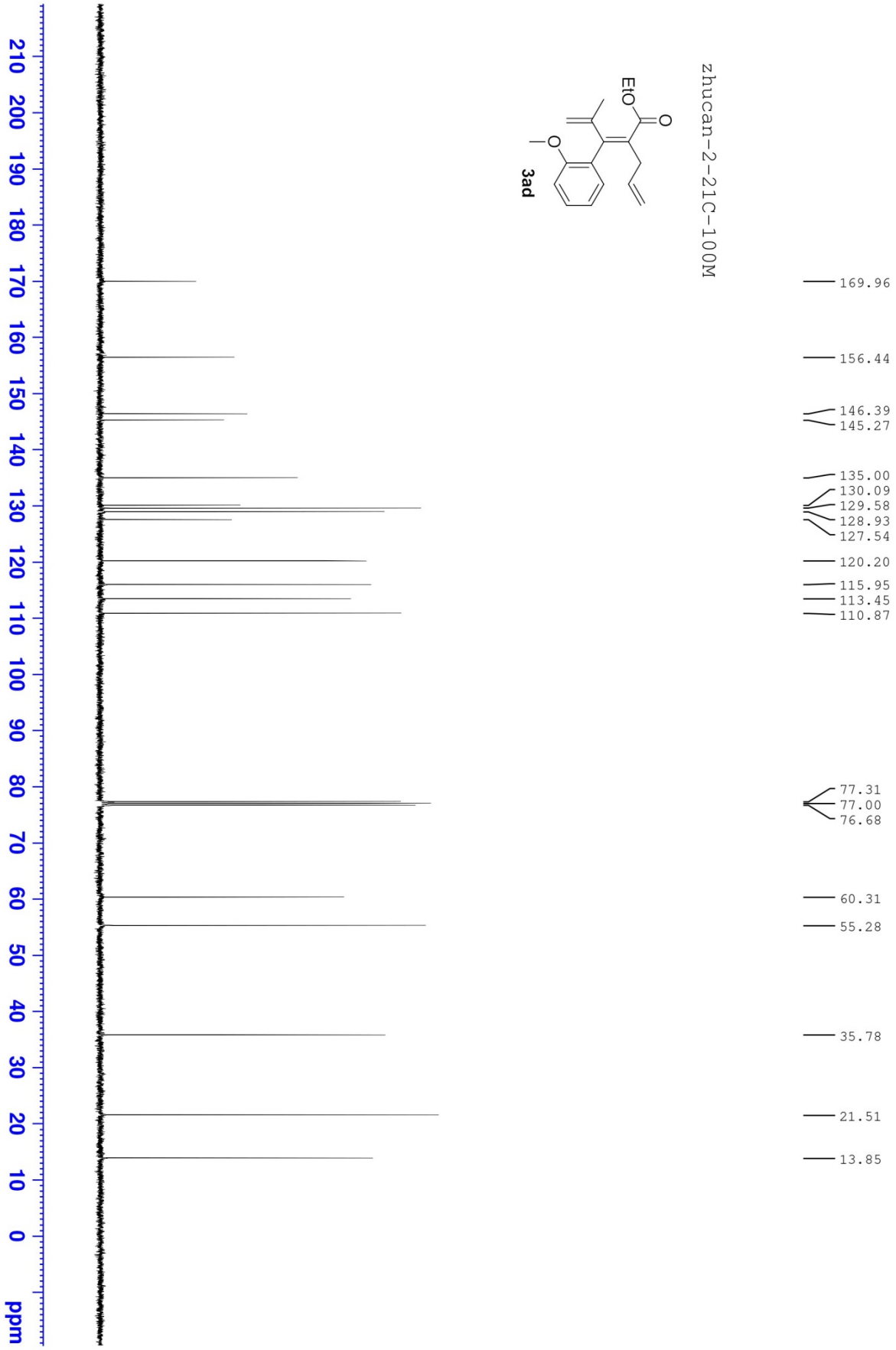


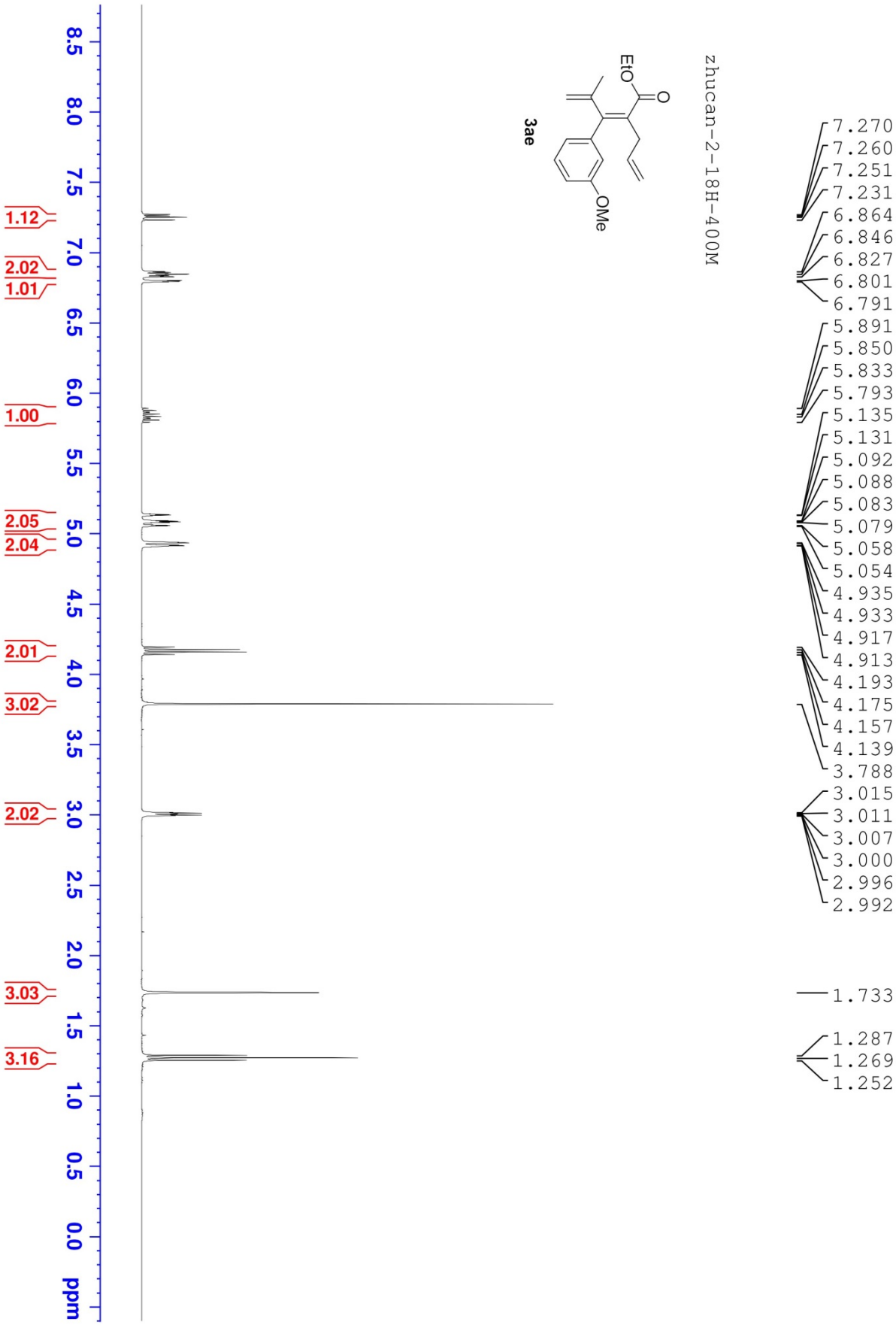
3ac

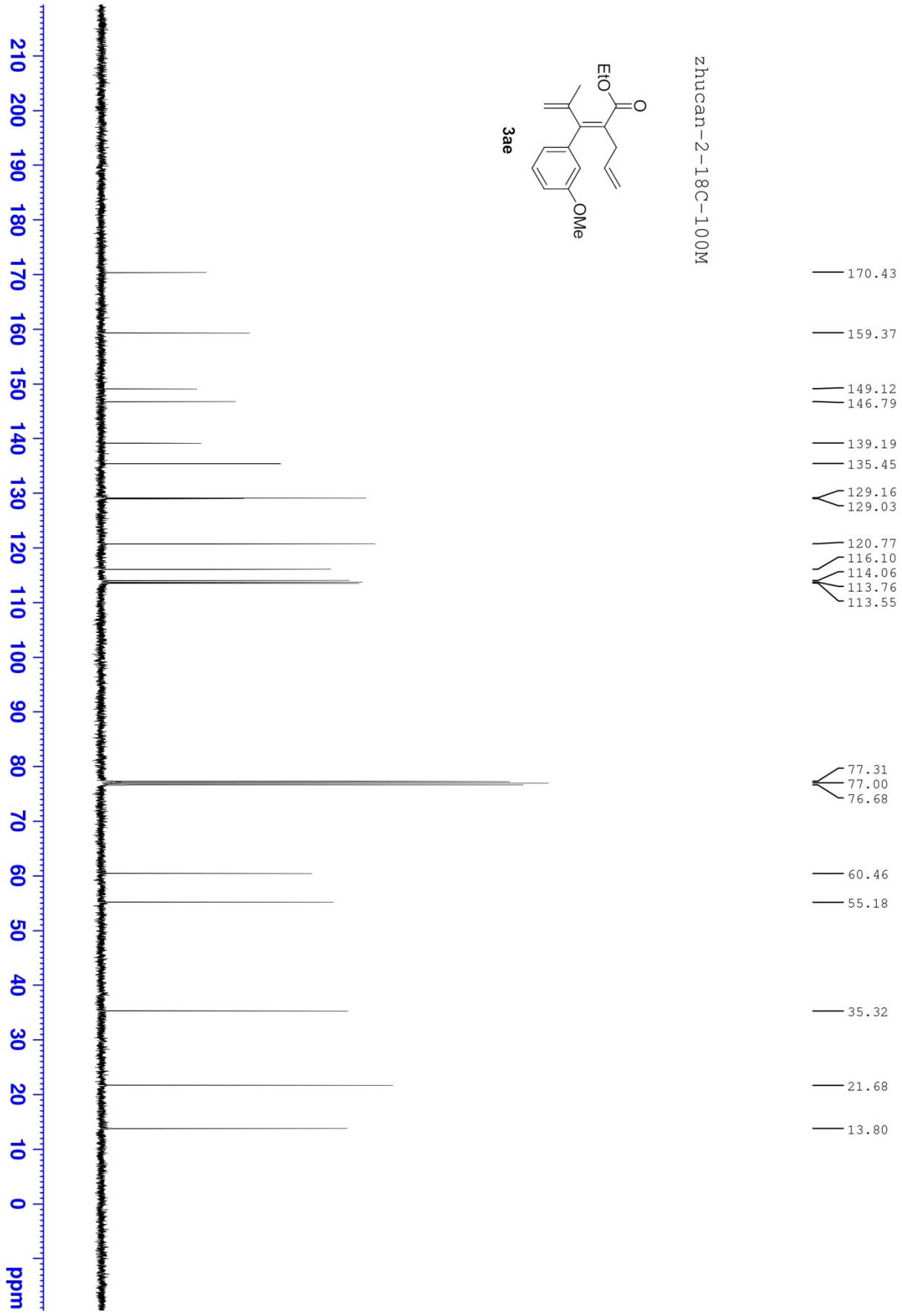


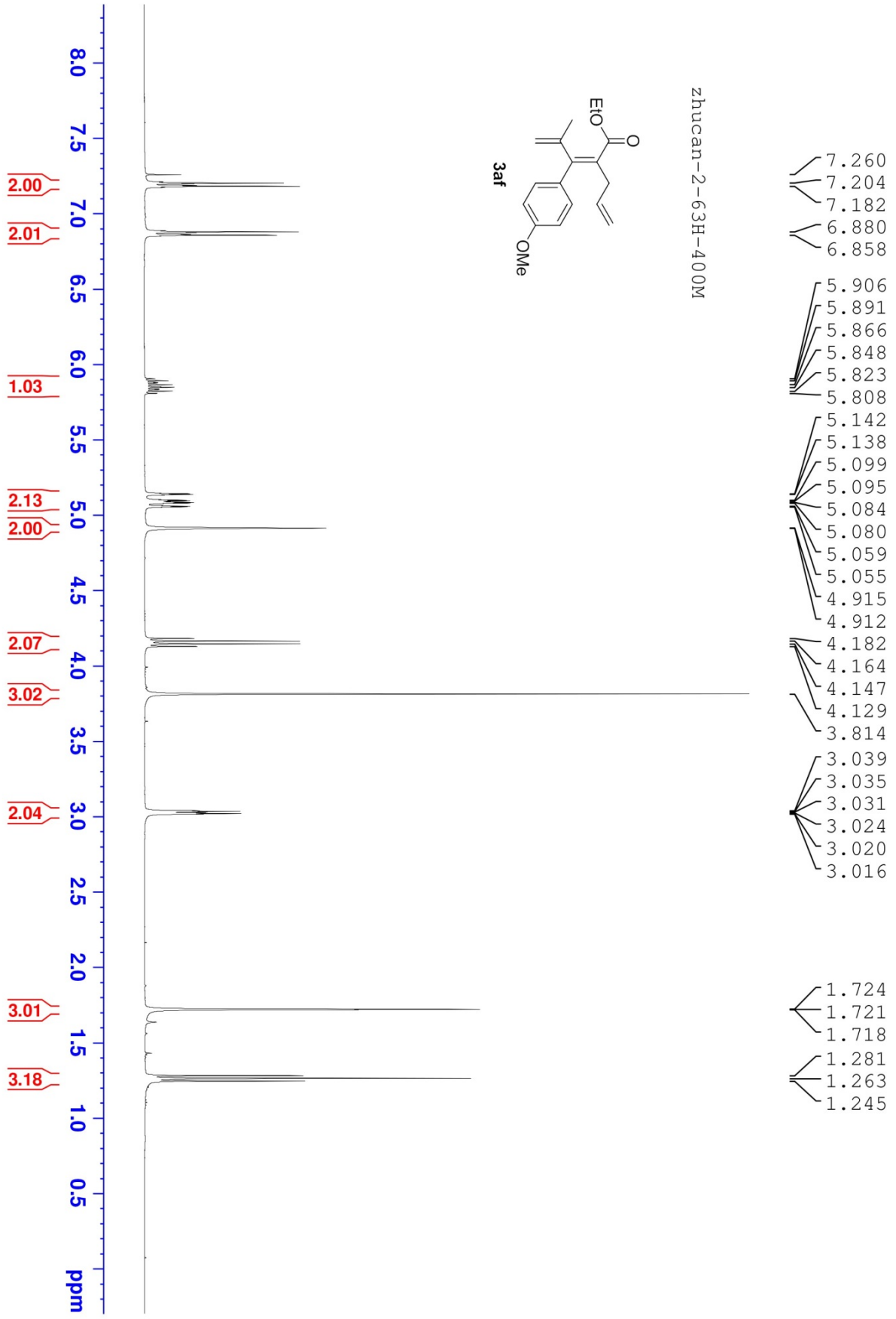

zhucan-2-30C-100M
EtO
O
3ac
tBu
170.65
150.94
149.42
147.17
135.64
134.64
128.62
128.06
125.02
116.05
113.81
77.32
77.00
76.68
60.41
35.32
34.58
31.30
21.84
13.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

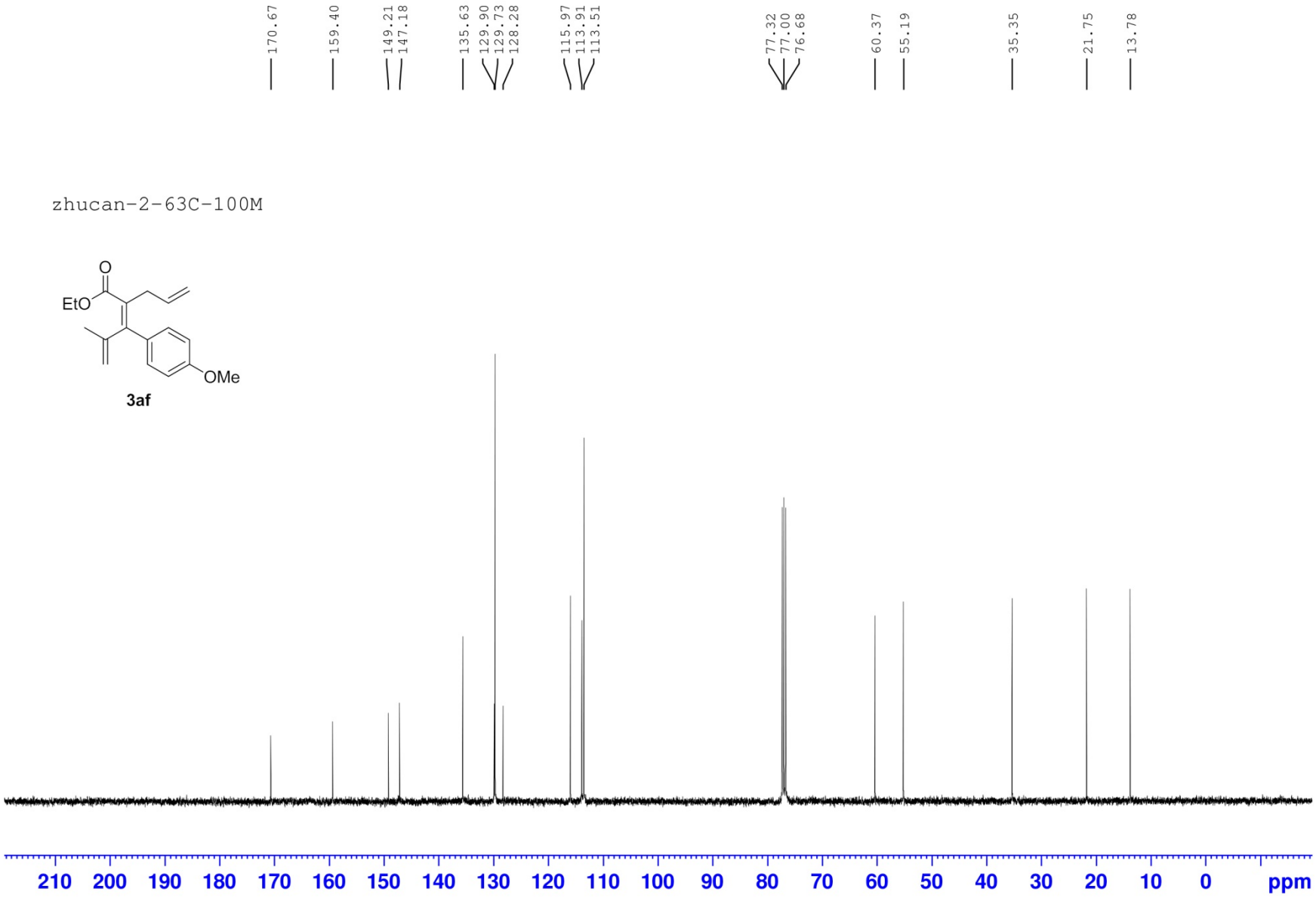

zhucan-2-21H-400M
3ad
EtO
O
O
7.316
7.312
7.293
7.283
7.277
7.273
7.102
7.097
7.083
7.079
6.967
6.964
6.948
6.946
6.927
6.906
5.809
5.793
5.767
5.750
5.725
5.709
5.017
5.013
4.993
4.970
4.967
4.935
4.868
4.864
4.859
4.232
4.214
4.196
4.178
3.794
2.832
2.817
1.799
1.796
1.319
1.302
1.284
1.10
0.99
2.01
1.00
2.07
1.02
1.02
2.04
3.11
2.03
3.03
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

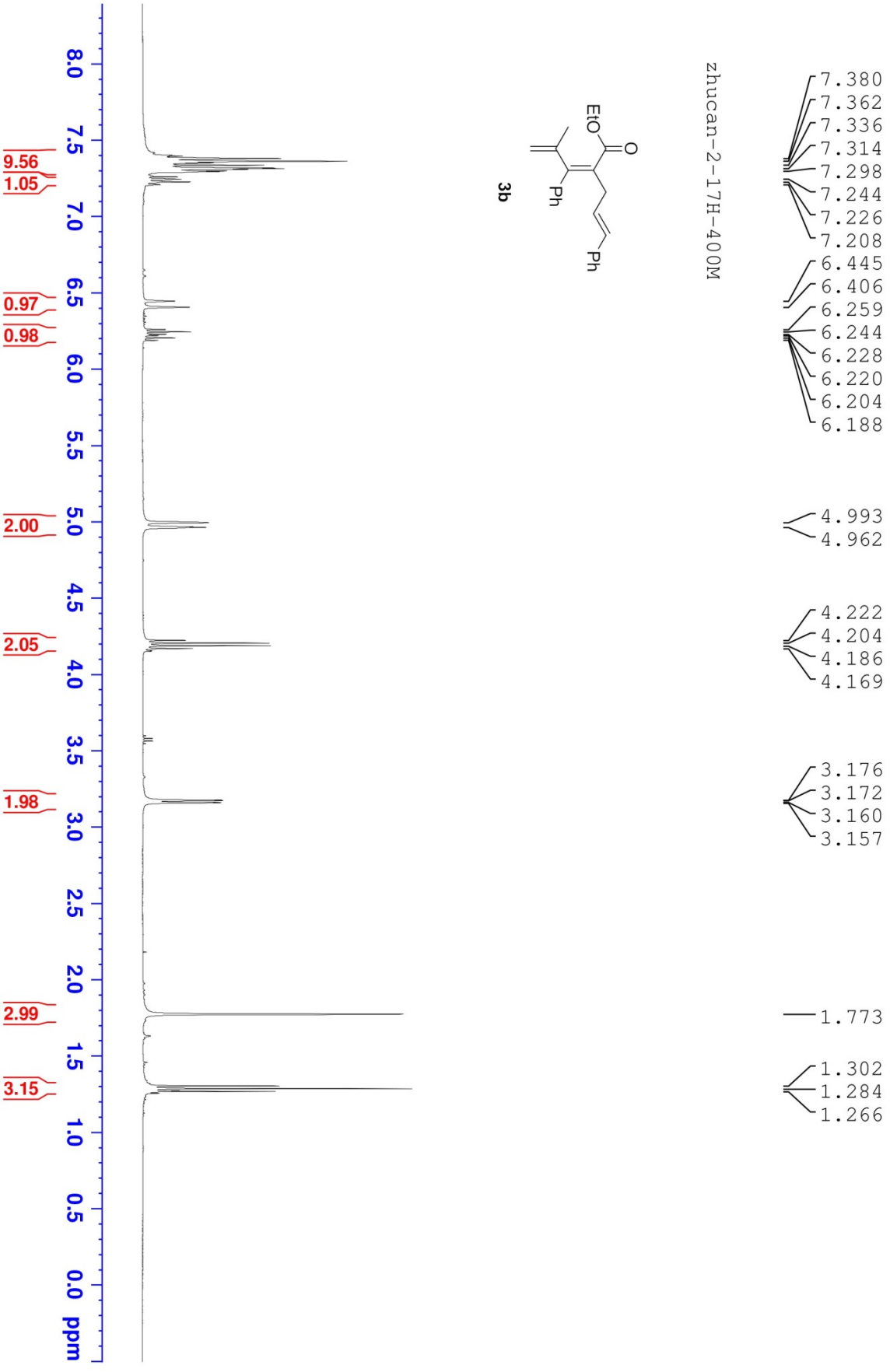

zhucan-2-21C-100M
EtO
O
O
3ad
169.96
156.44
146.39
145.27
135.00
130.09
129.58
128.93
127.54
120.20
115.95
113.45
110.87
77.31
77.00
76.68
60.31
55.28
35.78
21.51
13.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

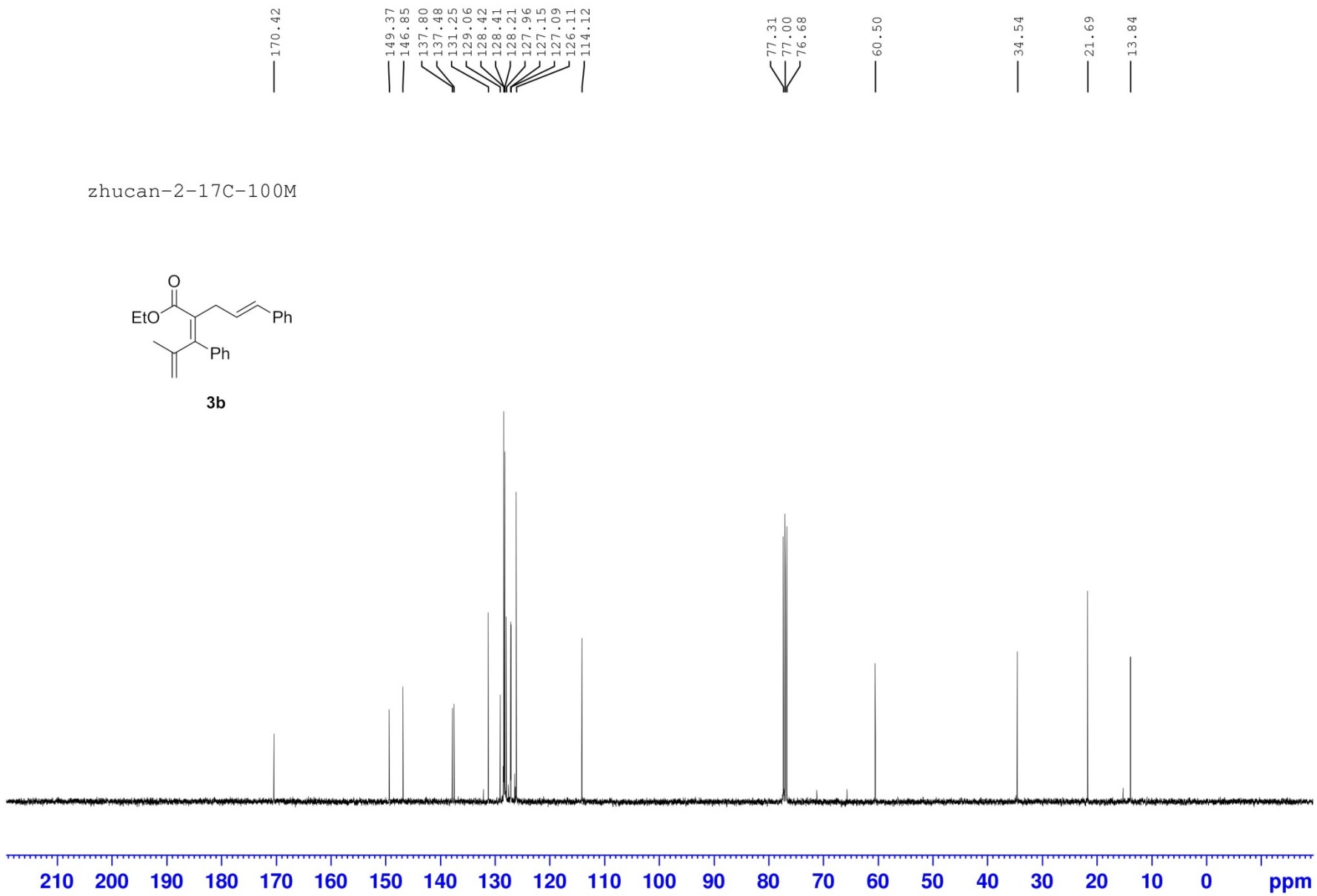

zhucan-2-18H-400M
3ae
EtO
O
OMe
7.270
7.260
7.251
7.231
6.864
6.846
6.827
6.801
6.791
5.891
5.850
5.833
5.793
5.135
5.131
5.092
5.088
5.083
5.079
5.058
5.054
4.935
4.933
4.917
4.913
4.193
4.175
4.157
4.139
3.788
3.015
3.011
3.007
3.000
2.996
2.992
1.733
1.287
1.269
1.252
1.12
2.02
1.01
1.00
2.05
2.04
2.01
3.02
2.02
3.03
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


zhucan-2-18C-100M
3ae
EtO
O
OMe
170.43
159.37
149.12
146.79
139.19
135.45
129.16
129.03
120.77
116.10
114.06
113.76
113.55
77.31
77.00
76.68
60.46
55.18
35.32
21.68
13.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


zhucan-2-63H-400M
3af
EtO
O
OMe
7.260
7.204
7.182
6.880
6.858
5.906
5.891
5.866
5.848
5.823
5.808
5.142
5.138
5.099
5.095
5.084
5.080
5.059
5.055
4.915
4.912
4.182
4.164
4.147
4.129
3.814
3.039
3.035
3.031
3.024
3.020
3.016
1.724
1.721
1.718
1.281
1.263
1.245
2.00
2.01
1.03
2.13
2.00
2.07
3.02
2.04
3.01
3.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


170.67
159.40
149.21
147.18
135.63
129.90
129.73
128.28
115.97
113.91
113.51
77.32
77.00
76.68
60.37
55.19
35.35
21.75
13.78
zhucan-2-63C-100M
O
EtO
OMe
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


zhucan-2-17H-400M
3b
EtO
O
Ph
Ph
7.380
7.362
7.336
7.314
7.298
7.244
7.226
7.208
6.445
6.406
6.259
6.244
6.228
6.220
6.204
6.188
4.993
4.962
4.222
4.204
4.186
4.169
3.176
3.172
3.160
3.157
1.773
1.302
1.284
1.266
9.56
1.05
0.97
0.98
2.00
2.05
1.98
2.99
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


170.42
149.37
146.85
137.80
137.48
131.25
129.06
128.42
128.41
128.21
127.96
127.15
127.09
126.11
114.12
77.31
77.00
76.68
60.50
34.54
21.69
13.84
zhucan-2-17C-100M
O
EtO
Ph
Ph
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

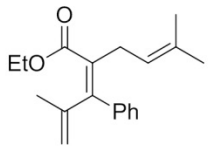
7.357
7.340
7.322
7.305
7.288
7.260
7.236
7.232
7.215

5.127
5.113
5.109
5.106
5.092
4.942
4.940
4.909
4.905
4.196
4.178
4.160
4.142

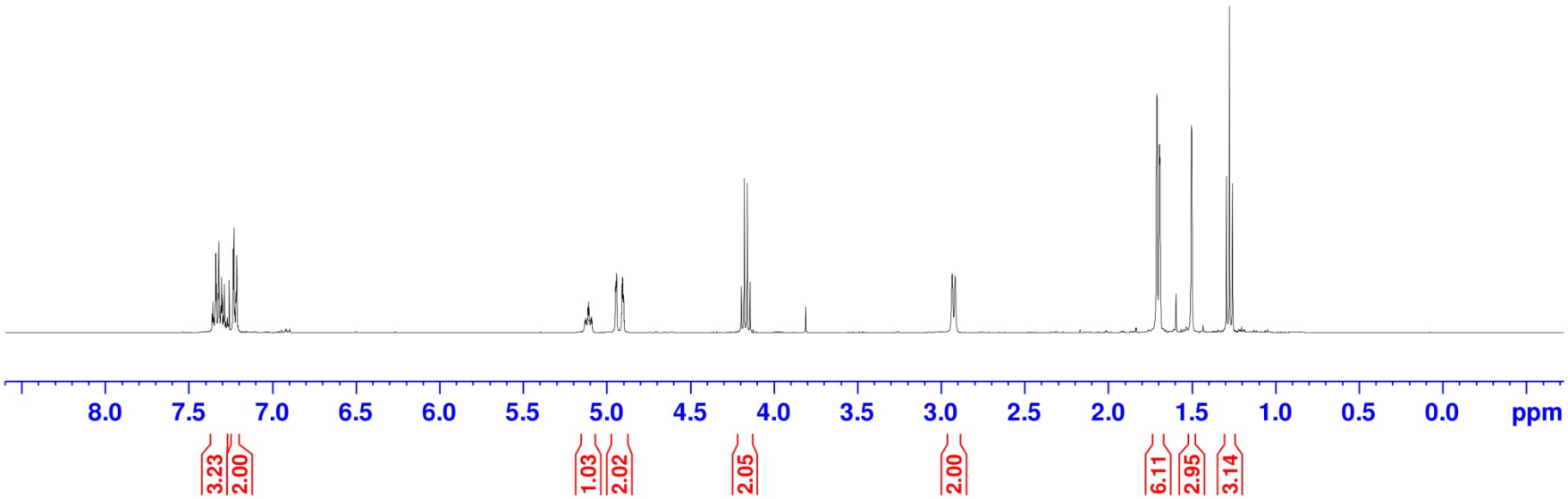
2.934
2.916

1.711
1.709
1.706
1.694
1.691
1.502
1.292
1.274
1.256

zhucan-2-55H-400M

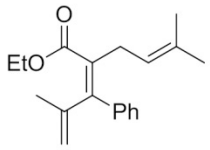


3c

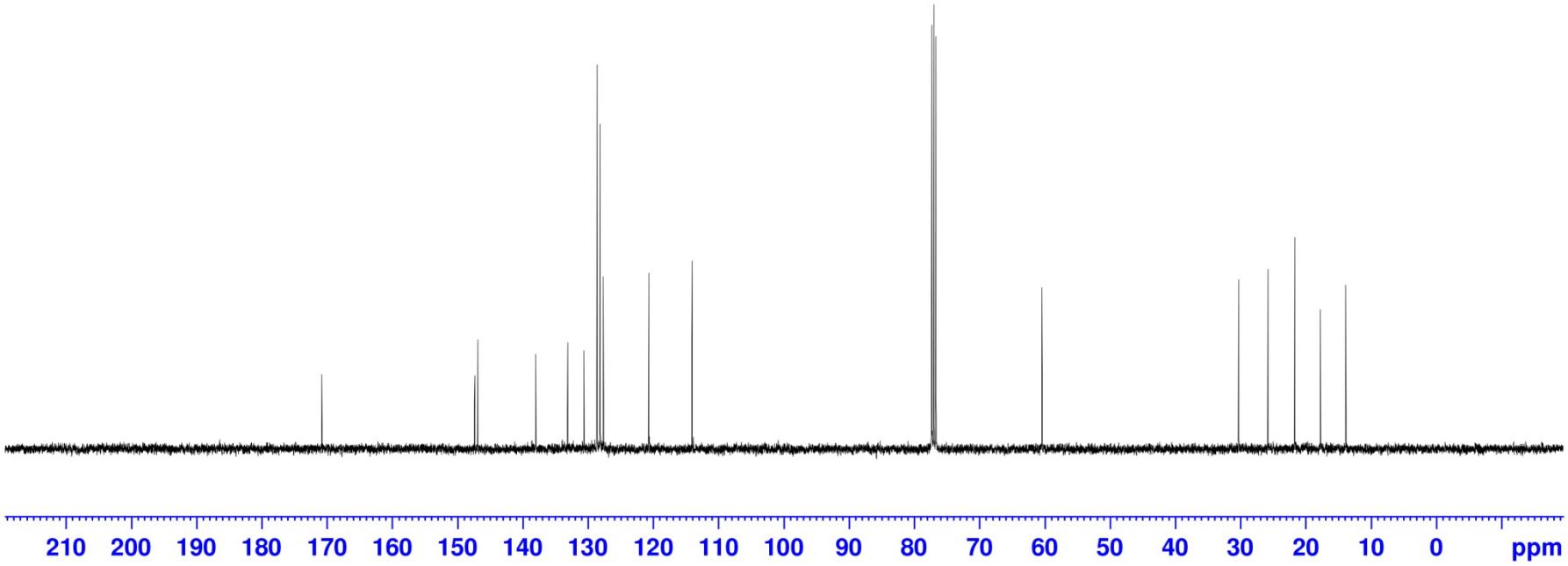


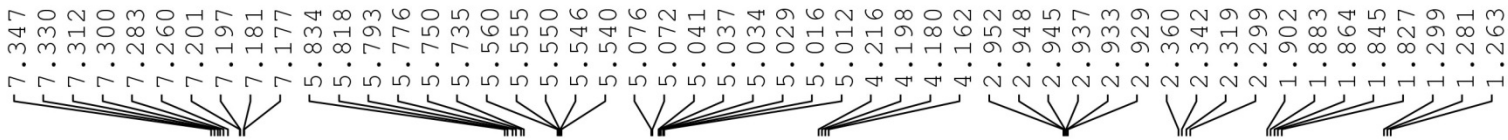
170.79
147.38
146.89
138.02
133.12
130.63
128.62
128.15
127.65
120.67
114.07
77.32
77.00
76.68
60.41
30.26
25.77
21.65
17.75
13.83

zhucan-2-55C-100M

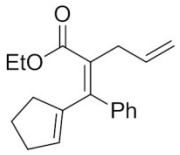


3c

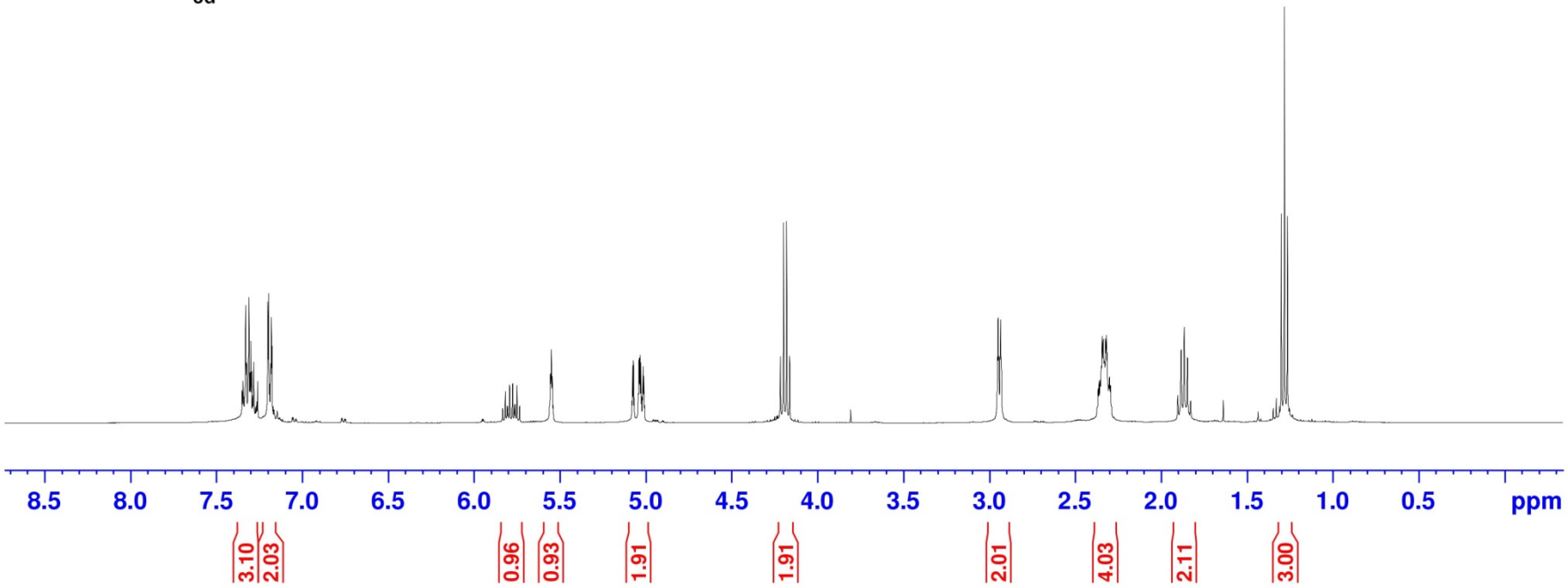




zhucan-2-71H-400M

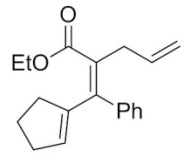


3d

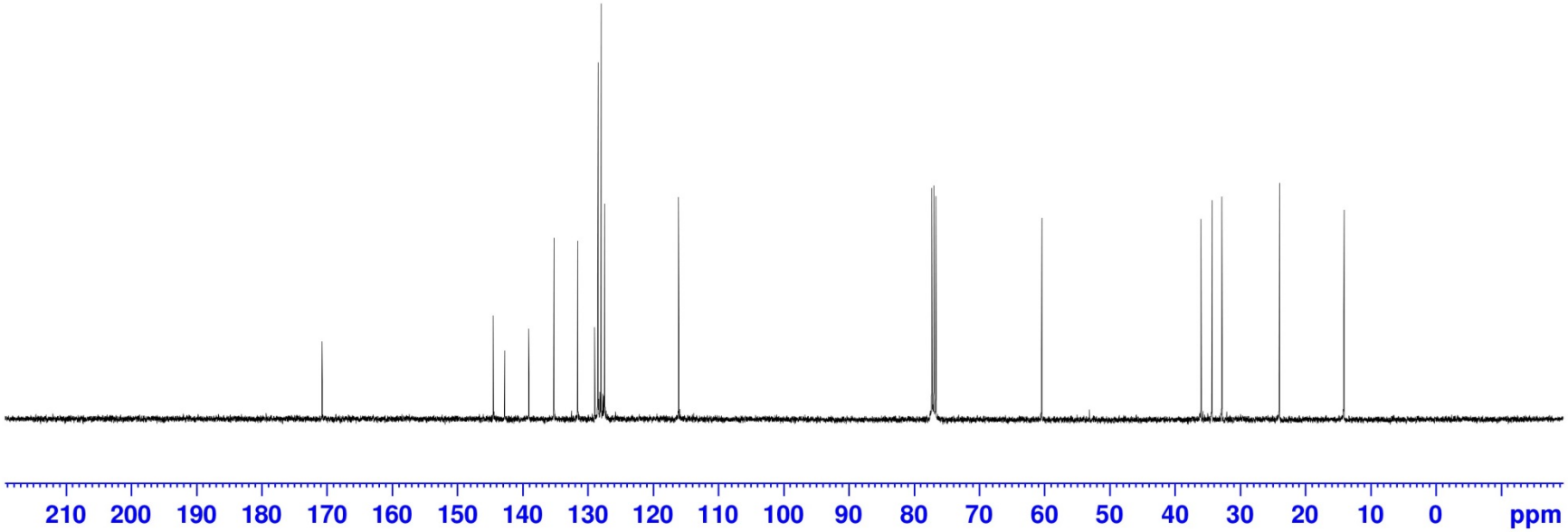


170.79
144.59
142.81
139.10
135.25
131.60
128.99
128.51
128.02
127.46
116.14
77.32
77.00
76.68
60.46
36.04
34.35
32.83
24.01
14.14

zhucan-2-71C-100M

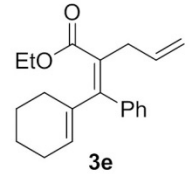


3d

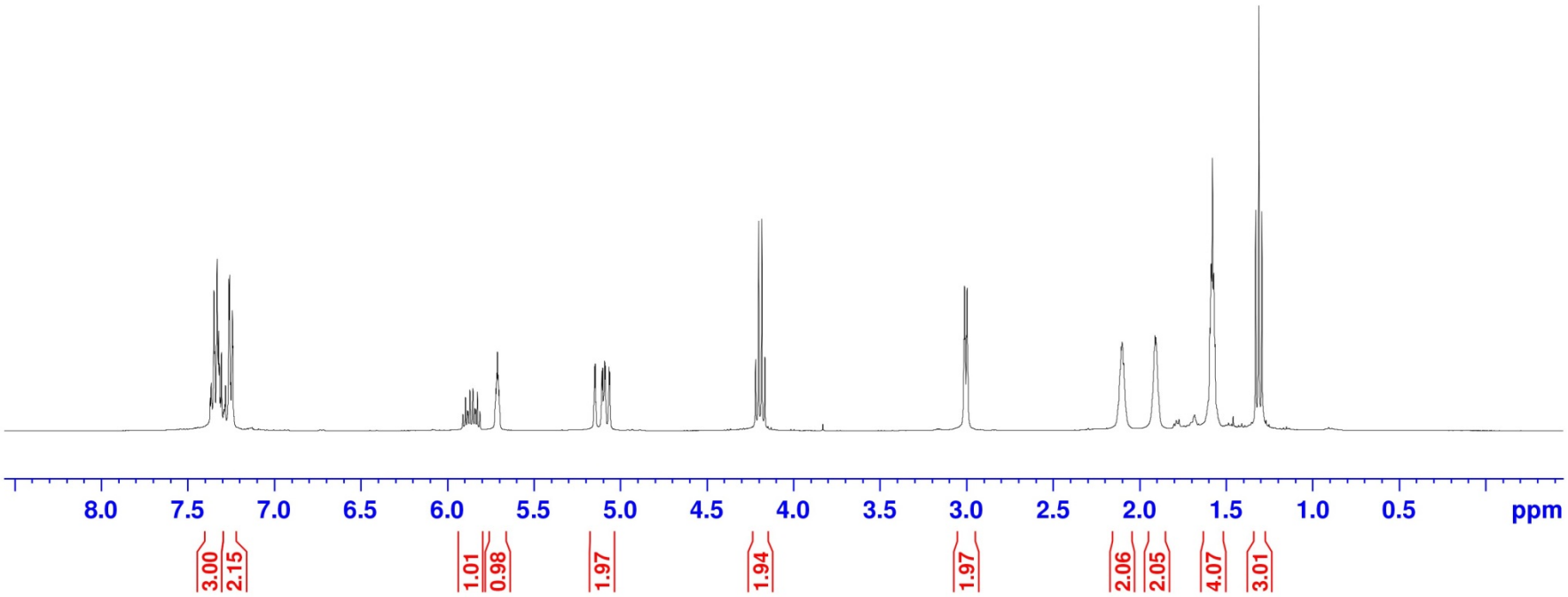


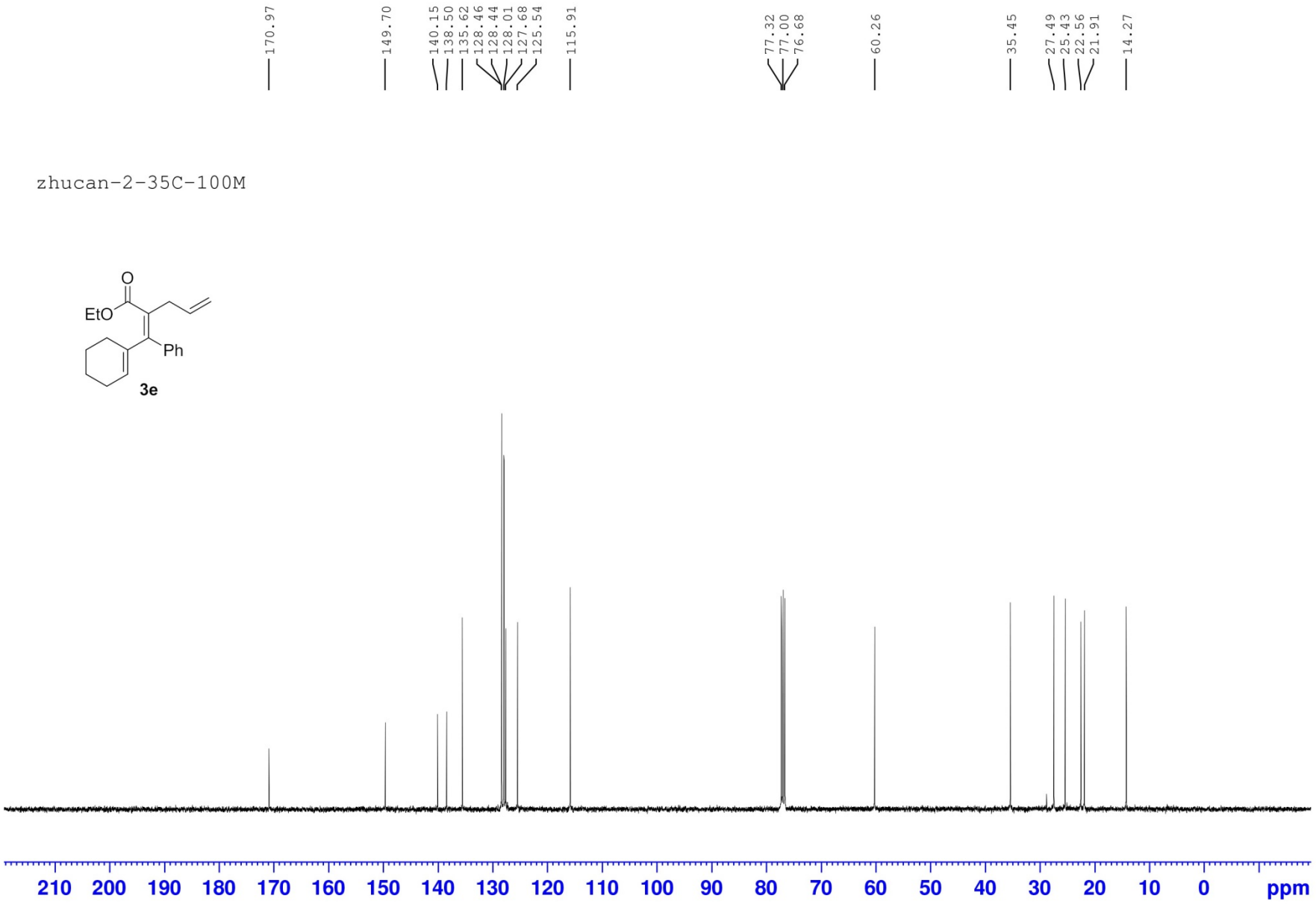
7.366
7.350
7.331
7.306
7.264
7.259
7.244
5.910
5.896
5.870
5.853
5.827
5.813
5.720
5.715
5.711
5.707
5.702
5.149
5.145
5.106
5.102
5.091
5.087
5.066
5.062
4.219
4.201
4.183
4.165
3.014
3.011
3.007
3.000
2.996
2.993
2.106
2.101
1.910
1.904
1.585
1.578
1.571
1.328
1.310
1.292

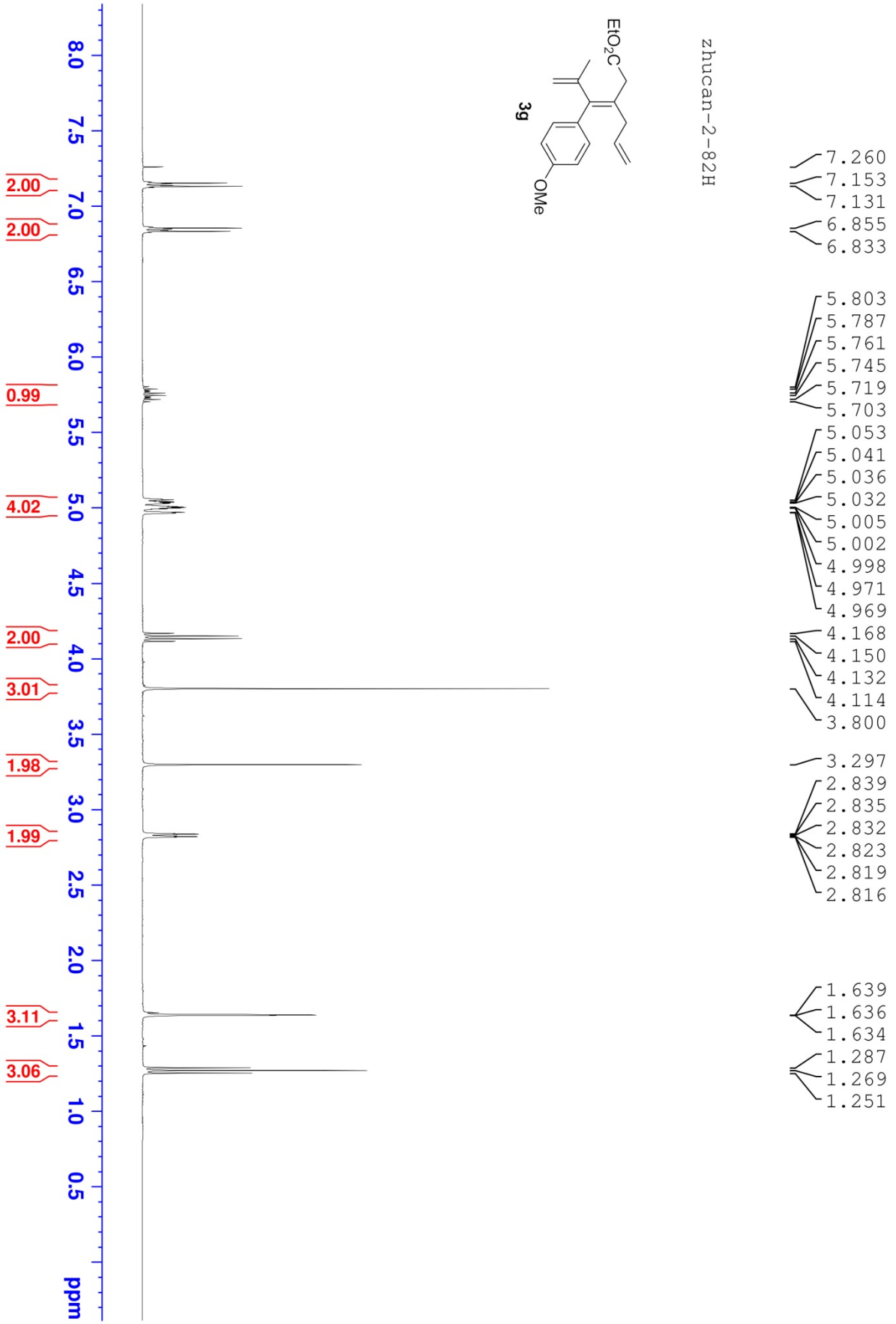
zhucan-2-35H-400M

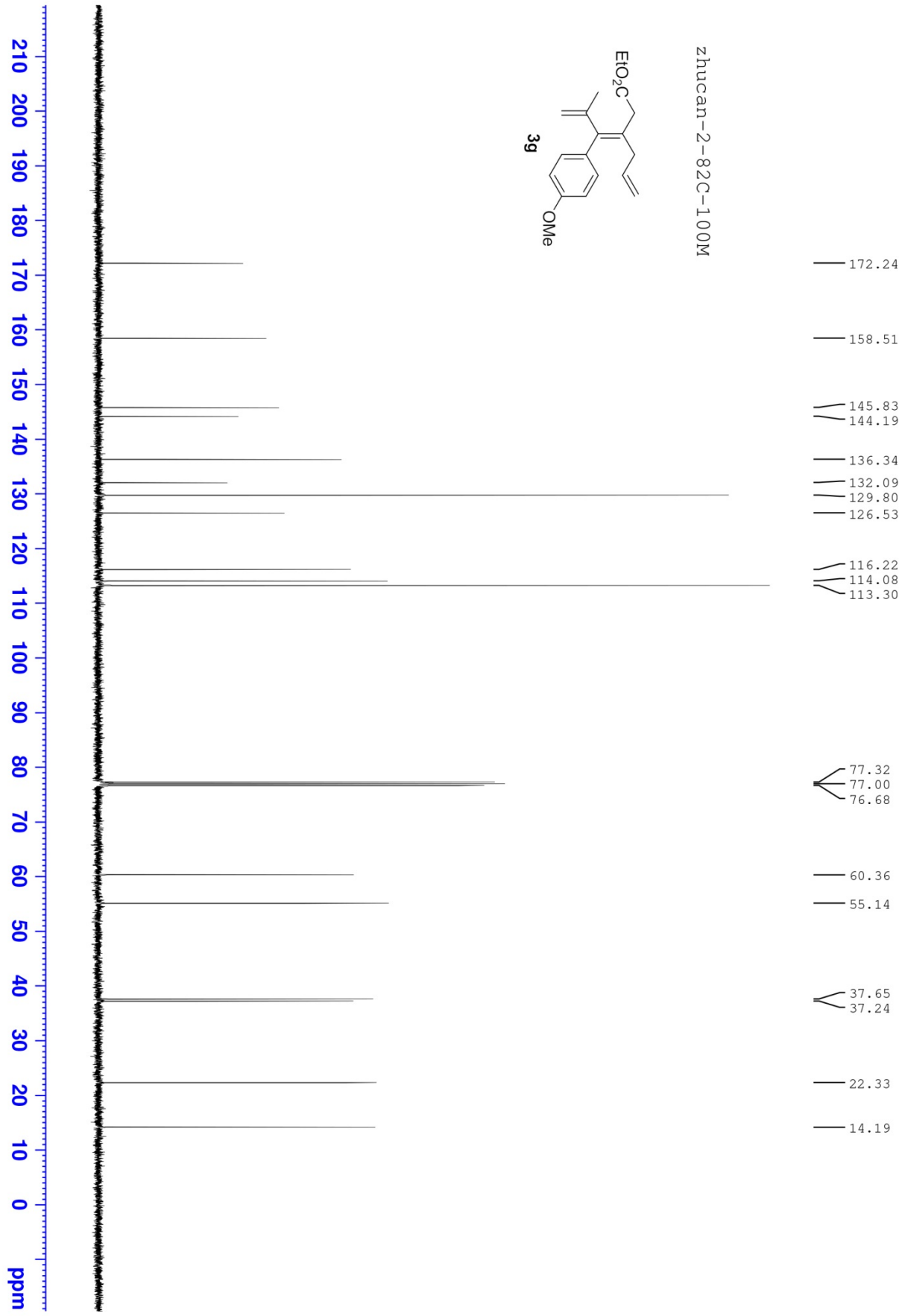


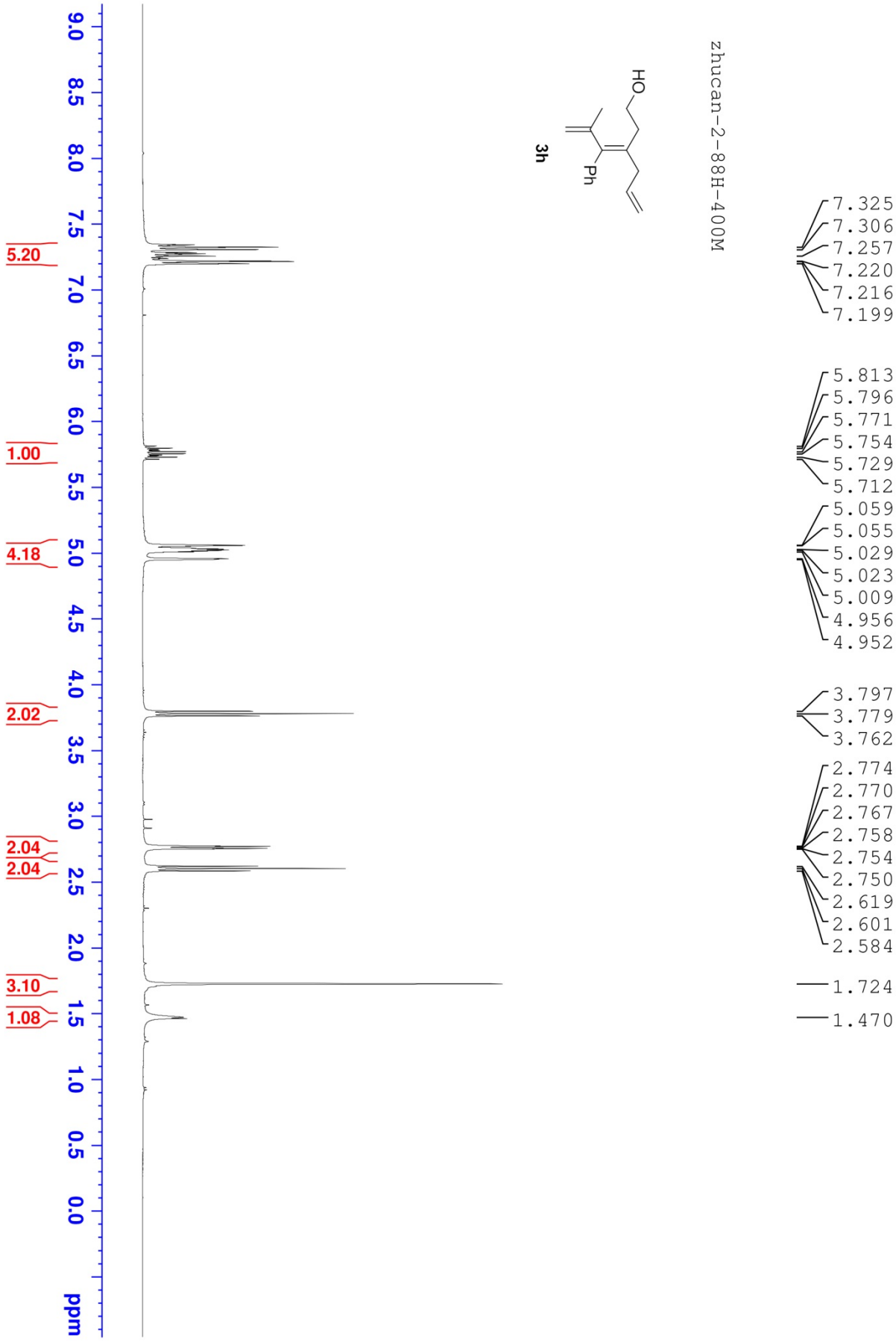
3e




170.97
149.70
140.15
138.50
135.62
128.46
128.44
128.01
127.68
125.54
115.91
77.32
77.00
76.68
60.26
35.45
27.49
25.43
22.56
21.91
14.27
zhucan-2-35C-100M
O
EtO
Ph
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

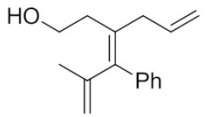

zhucan-2-82H
3g
EtO2C
OMe
7.260
7.153
7.131
6.855
6.833
5.803
5.787
5.761
5.745
5.719
5.703
5.053
5.041
5.036
5.032
5.005
5.002
4.998
4.971
4.969
4.168
4.150
4.132
4.114
3.800
3.297
2.839
2.835
2.832
2.823
2.819
2.816
1.639
1.636
1.634
1.287
1.269
1.251
2.00
2.00
0.99
4.02
2.00
3.01
1.98
1.99
3.11
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


zhucan-2-82C-100M
3g
EtO2C
OMe
172.24
158.51
145.83
144.19
136.34
132.09
129.80
126.53
116.22
114.08
113.30
77.32
77.00
76.68
60.36
55.14
37.65
37.24
22.33
14.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

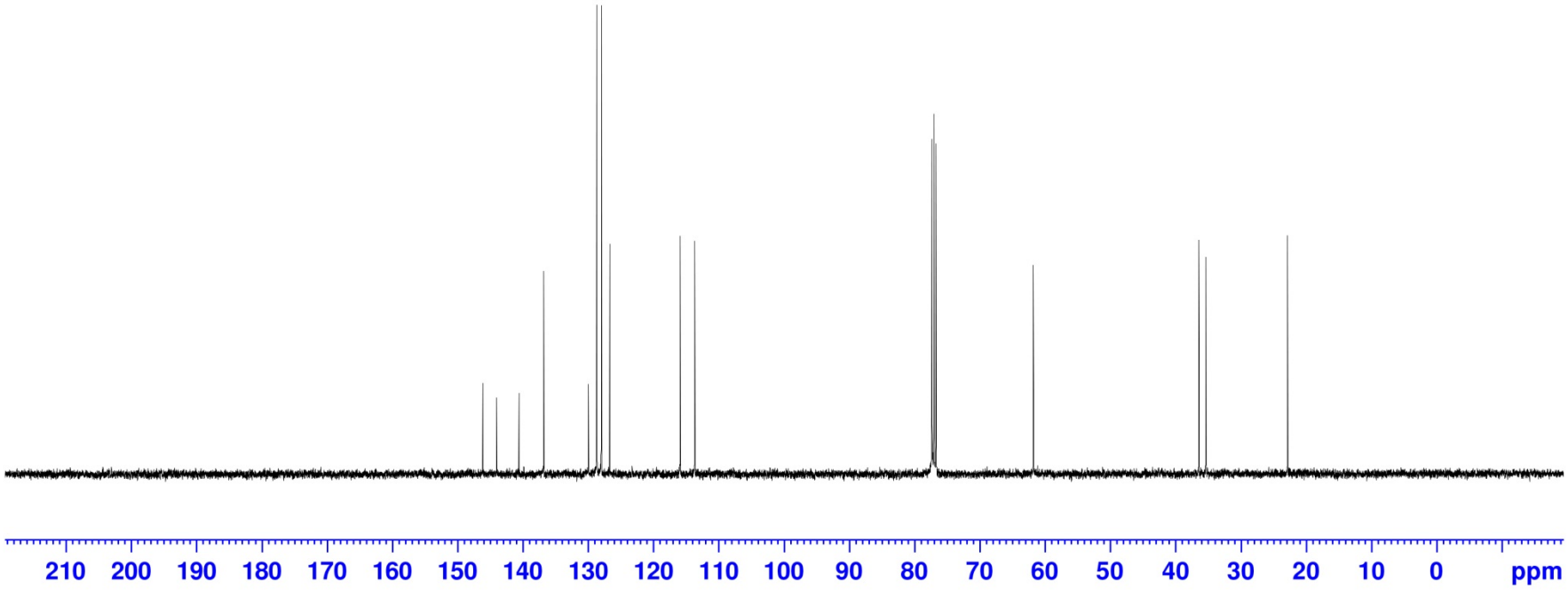

zhucan-2-88H-400M
3h
HO
Ph
7.325
7.306
7.257
7.220
7.216
7.199
5.813
5.796
5.771
5.754
5.729
5.712
5.059
5.055
5.029
5.023
5.009
4.956
4.952
3.797
3.779
3.762
2.774
2.770
2.767
2.758
2.754
2.750
2.619
2.601
2.584
1.724
1.470
5.20
1.00
4.18
2.02
2.04
2.04
3.10
1.08
ppm

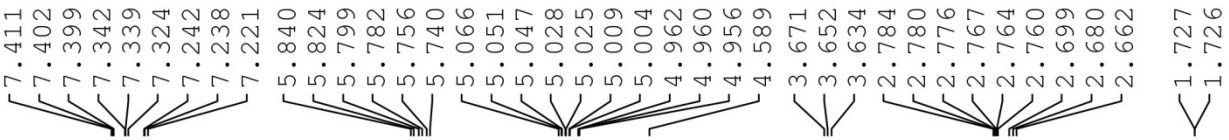
146.11
144.01
140.57
136.78
129.94
128.66
127.95
126.67
115.88
113.64
77.31
77.00
76.68
61.76
36.39
35.35
22.81

zhucan-2-88C-100M

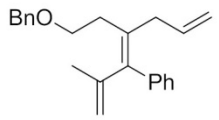


3h

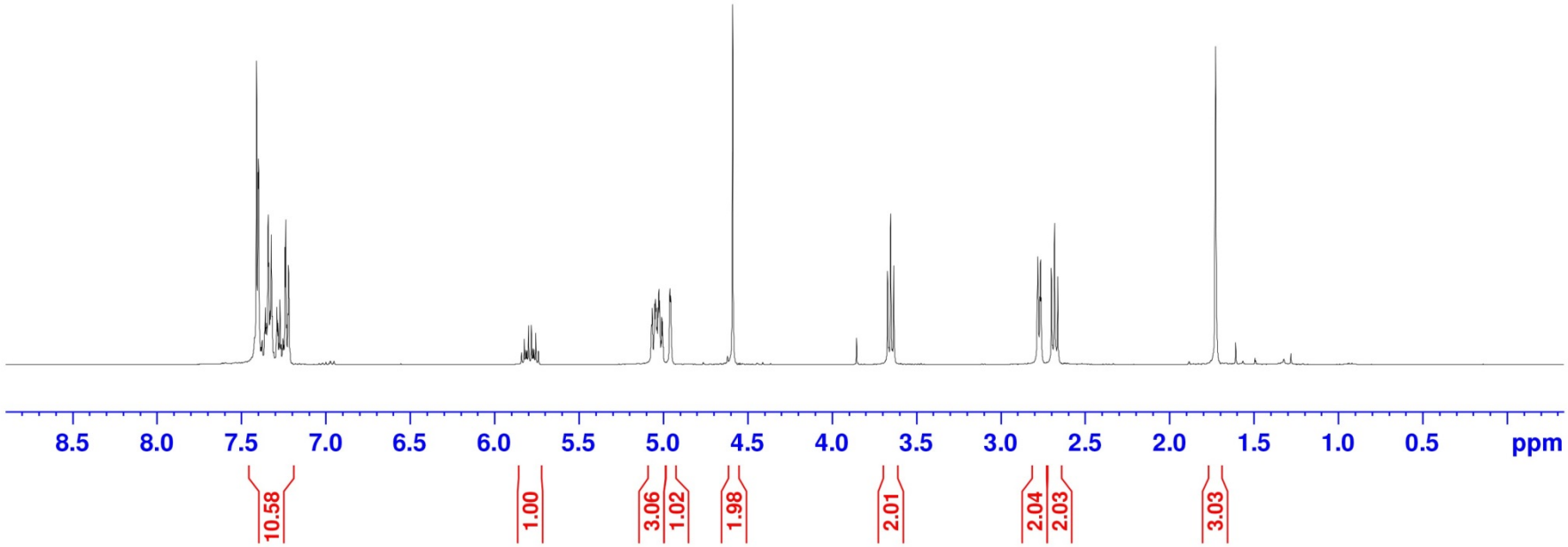




zhucan-2-93H-400M



3i



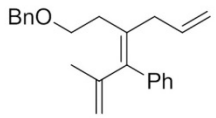
146.00
143.15
140.69
138.62
136.82
130.48
128.70
128.30
127.88
127.49
127.43
126.55
115.74
113.48

77.31
77.00
76.68
72.67
69.66

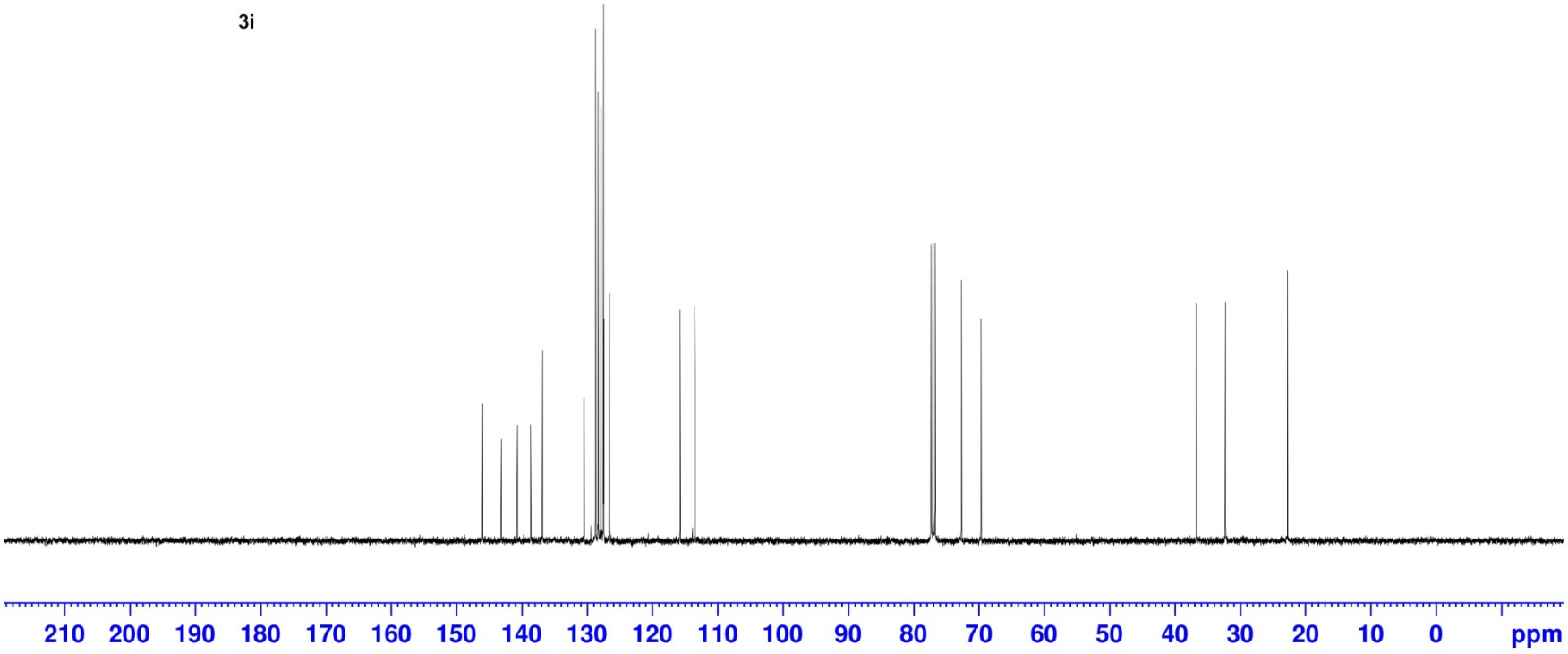
36.66
32.22

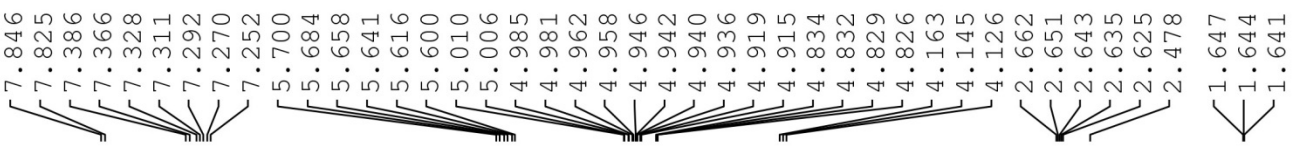
22.71

zhucan-2-93C-100M

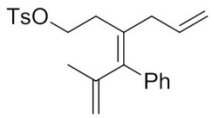


3i

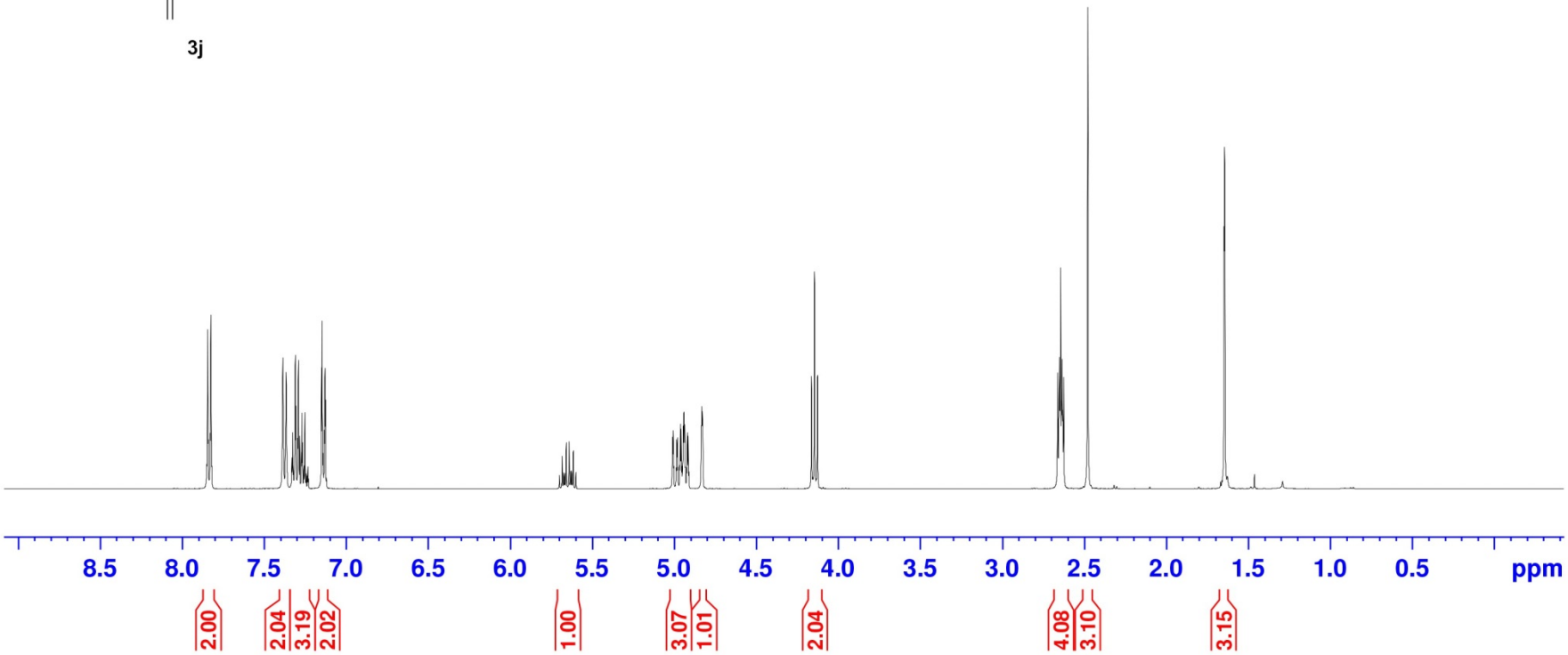




zhucan-2-94H-400M

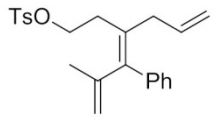


3j

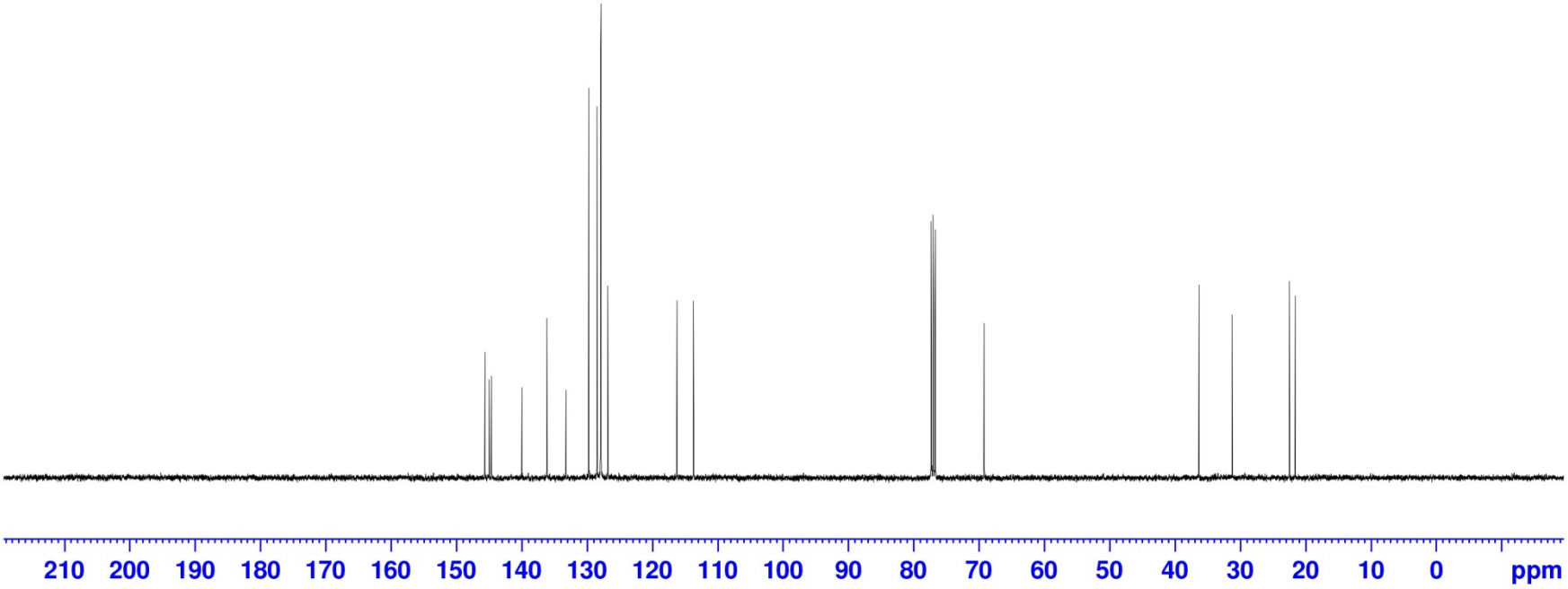


145.63
144.99
144.62
139.98
136.15
133.22
129.75
128.47
127.94
127.87
126.82
116.25
113.71
77.32
77.00
76.68
69.20
36.32
31.23
22.45
21.58

zhucan-2-94C-100M



3j

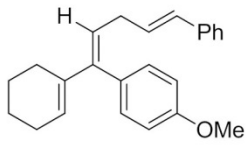


7.368
7.351
7.315
7.235
7.218
7.082
7.061
6.940
6.918
6.366
6.326
6.220
6.204
6.188
6.181
6.165
6.149
5.777
5.758
5.740
5.361

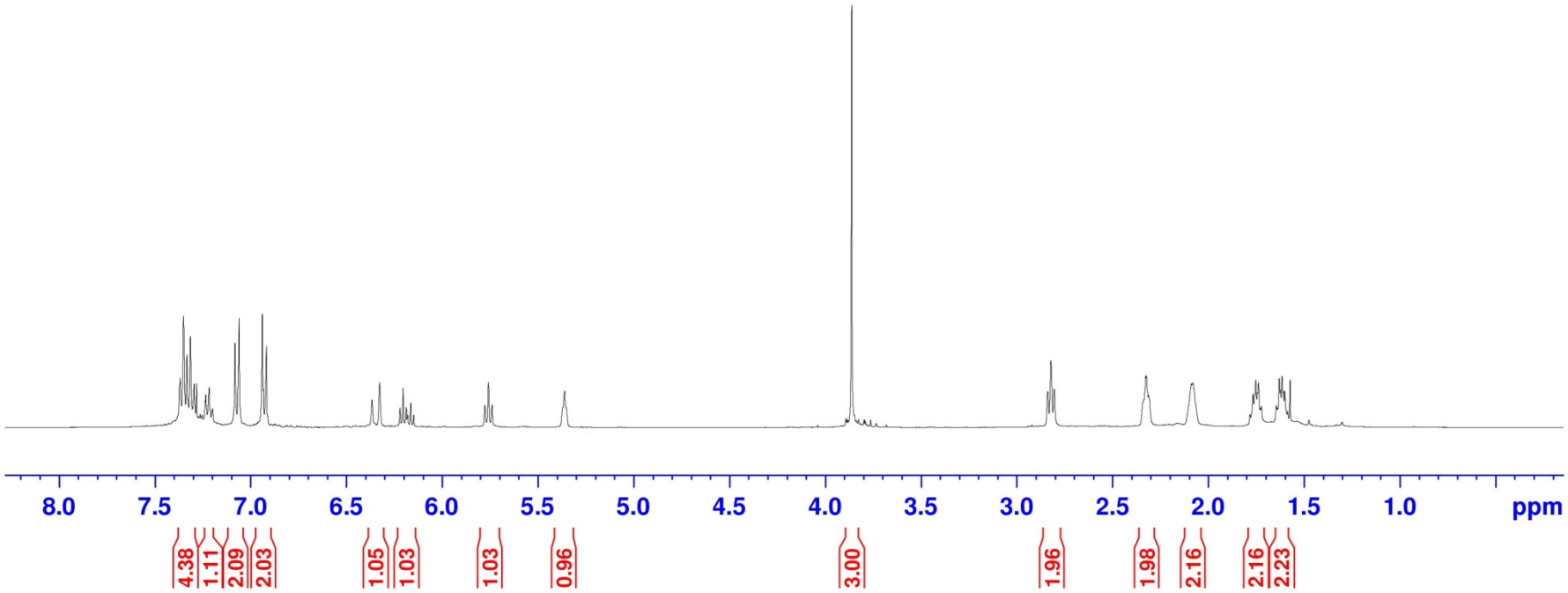
3.862

2.839
2.821
2.804
2.341
2.337
2.326
2.323
2.311
2.088
2.080
1.766
1.752
1.737
1.629
1.614
1.600

zhucan-2-78H-400M

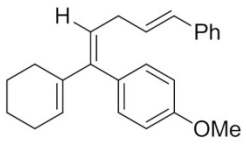


3k

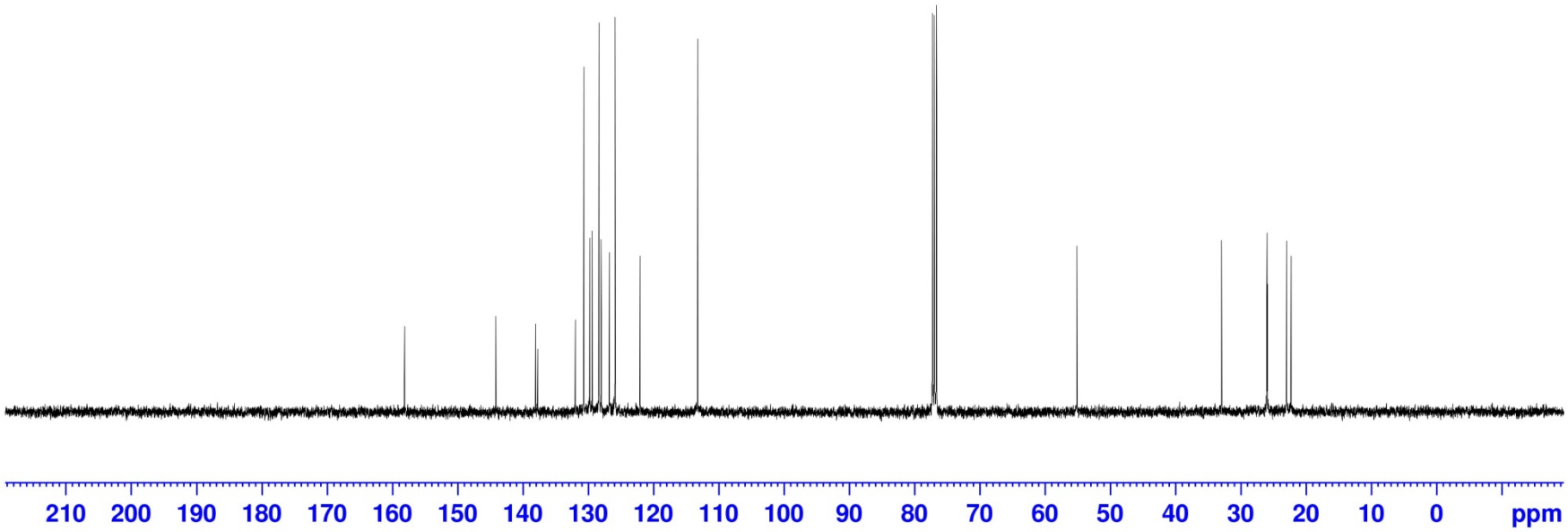


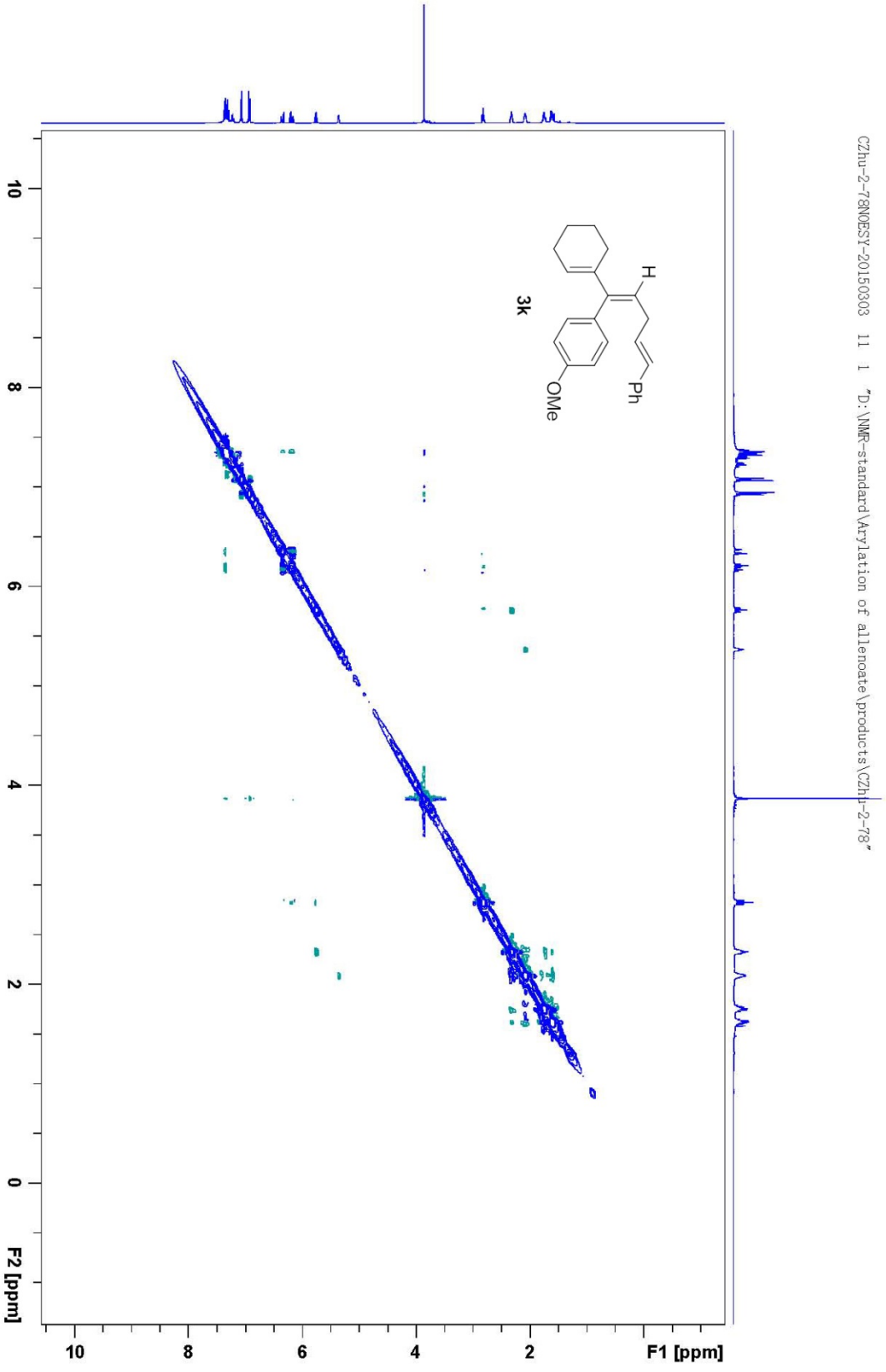
158.21
144.22
138.12
137.82
132.04
130.74
129.80
129.47
128.42
128.06
126.81
125.94
122.10
113.28
77.31
77.00
76.68
55.16
33.01
26.05
25.98
23.02
22.35

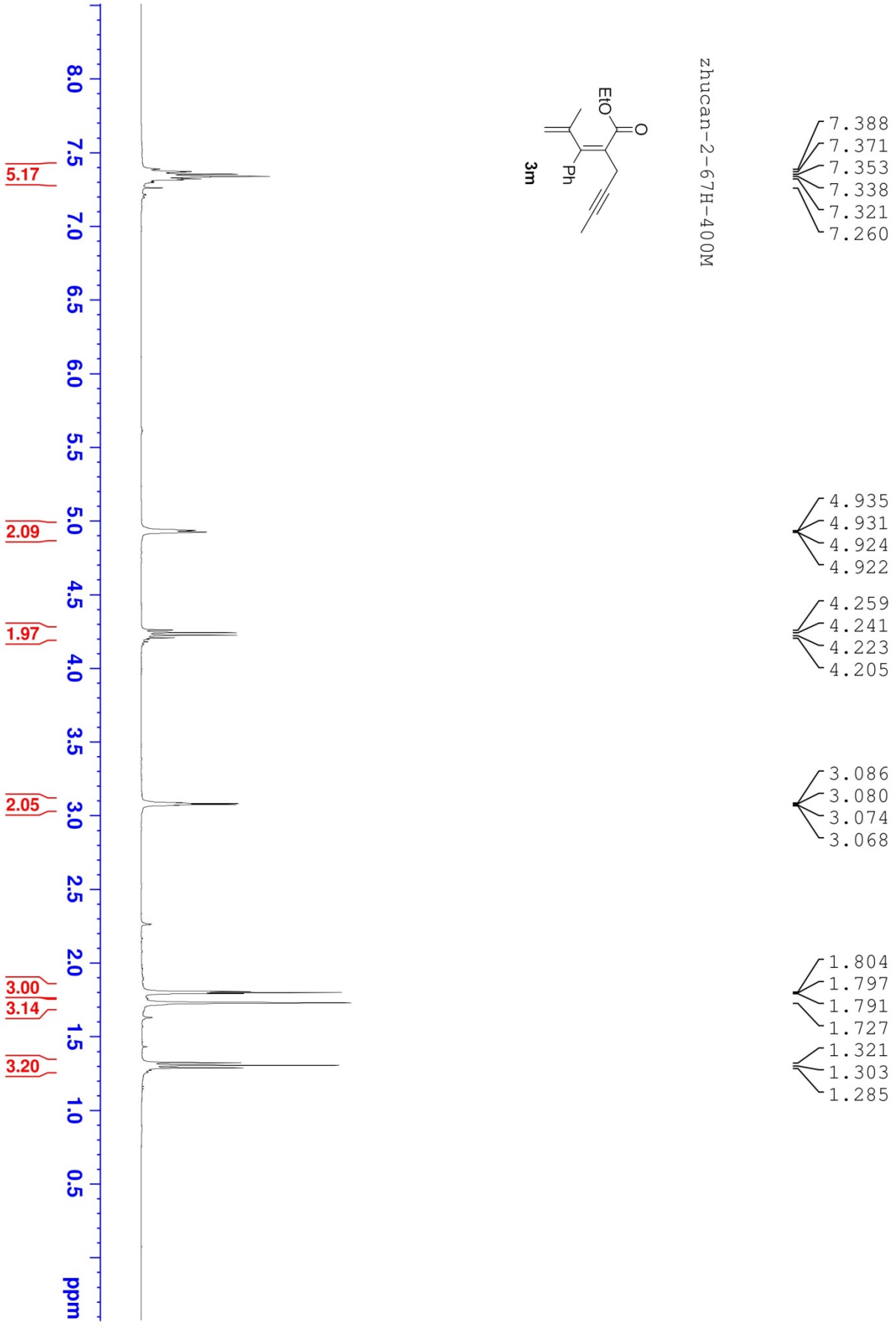
zhucan-2-78C-100M

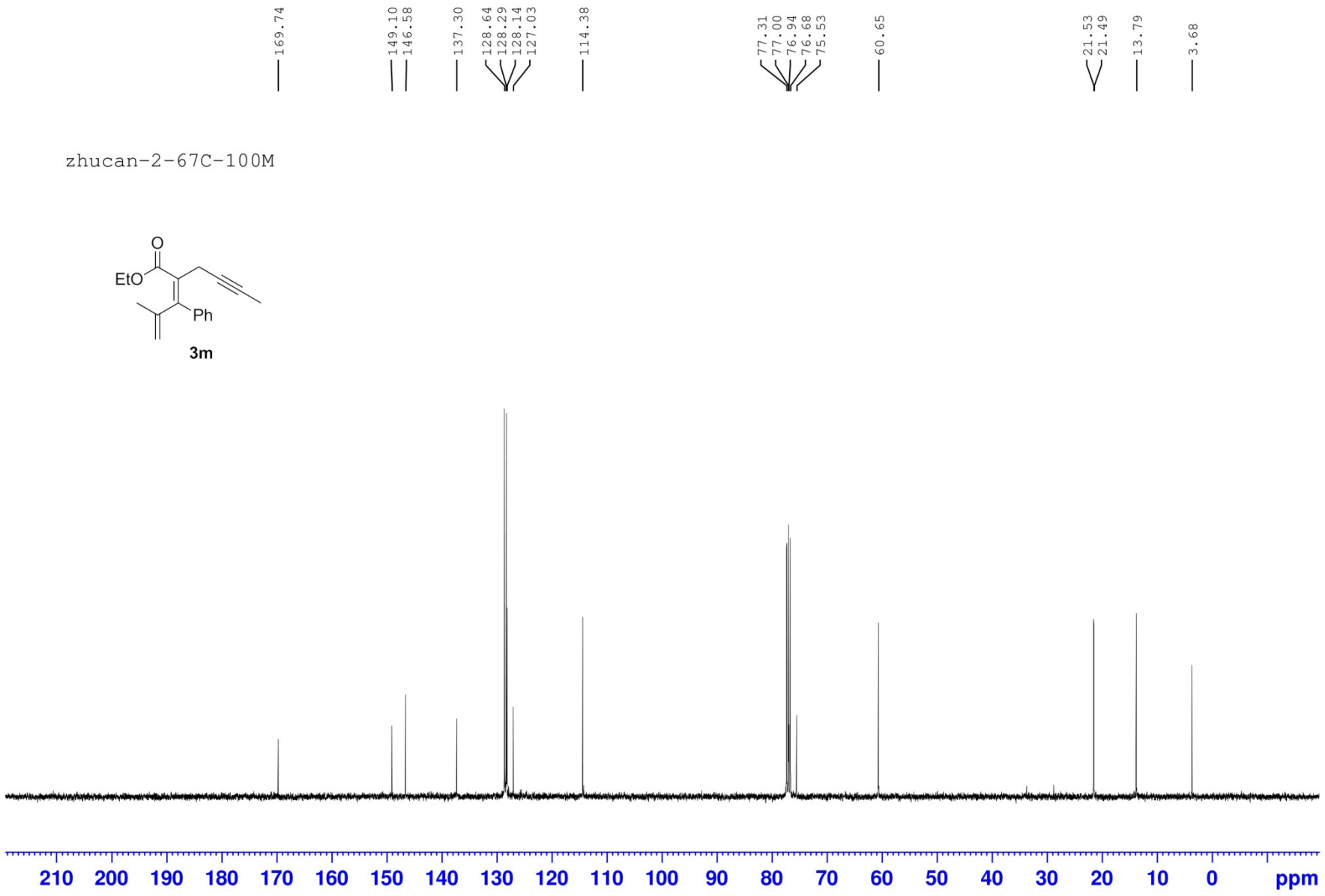


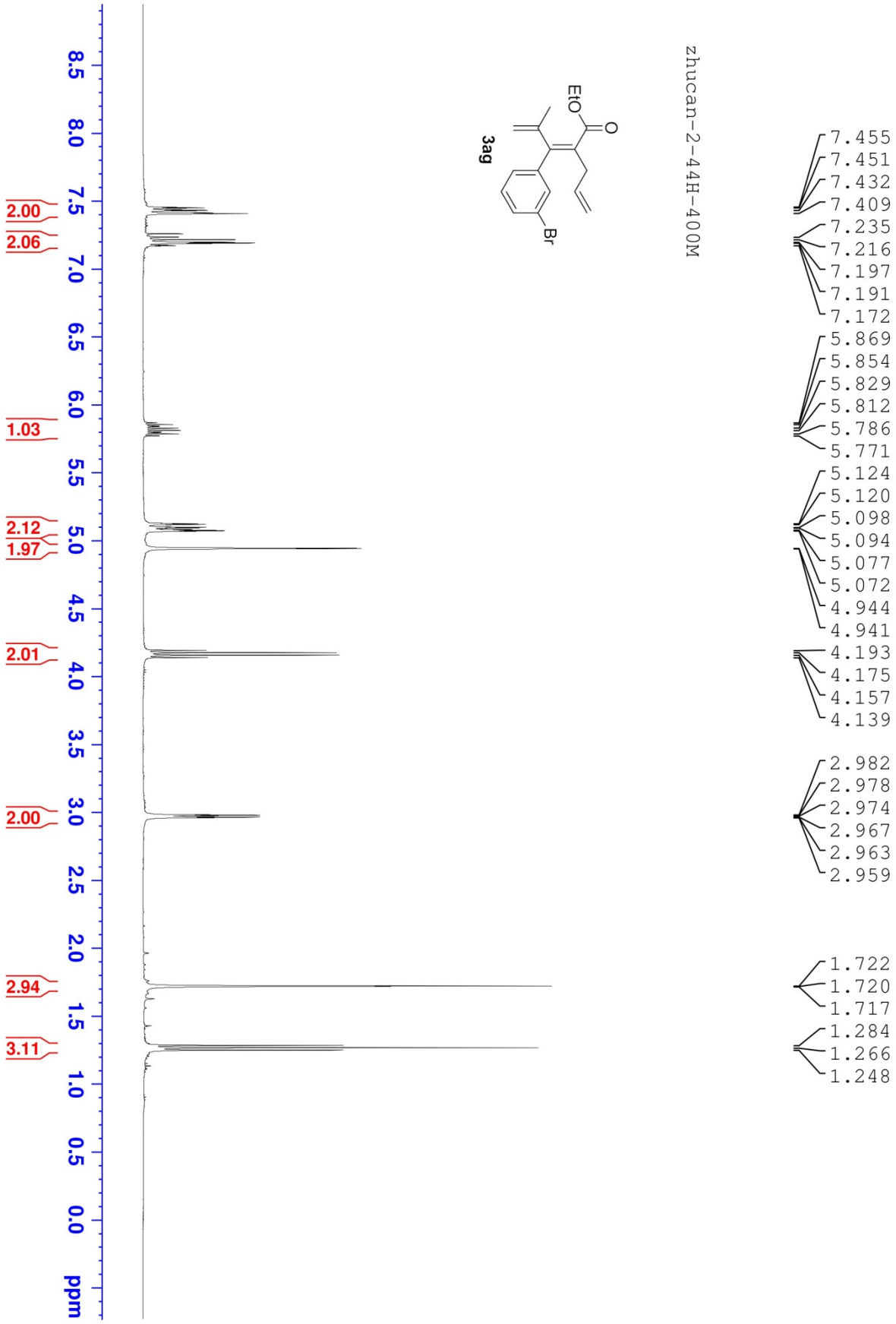
3k




CZhu-2-78NOESY-20150303 11 1 "D:\NMR-standard\Arylation of allenoate\products\CZhu-2-78"
3k
OMe
Ph
H
F2 [ppm]
F1 [ppm]
10
8
6
4
2
0

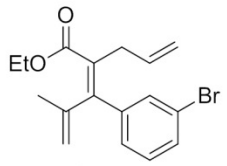

zhucan-2-67H-400M
3m
EtO
O
Ph
7.388
7.371
7.353
7.338
7.321
7.260
4.935
4.931
4.924
4.922
4.259
4.241
4.223
4.205
3.086
3.080
3.074
3.068
1.804
1.797
1.791
1.727
1.321
1.303
1.285
5.17
2.09
1.97
2.05
3.00
3.14
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


169.74
149.10
146.58
137.30
128.64
128.29
128.14
127.03
114.38
77.31
77.00
76.94
76.68
75.53
60.65
21.53
21.49
13.79
3.68
zhucan-2-67C-100M
O
EtO
Ph
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

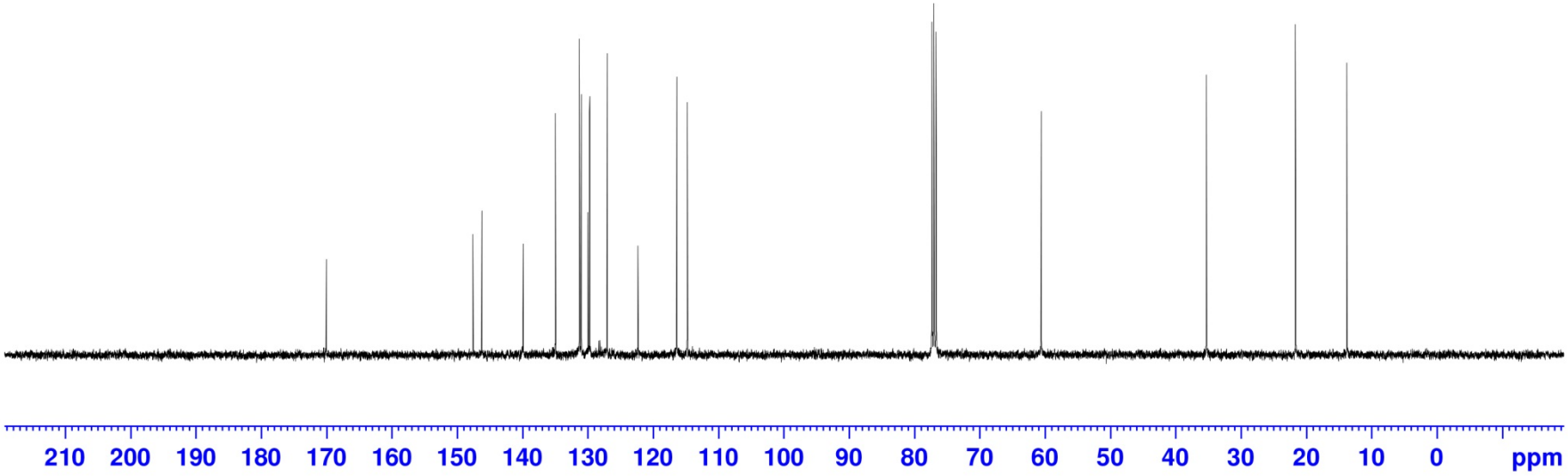

zhucan-2-44H-400M
3ag
EtO
O
Br
7.455
7.451
7.432
7.409
7.235
7.216
7.197
7.191
7.172
5.869
5.854
5.829
5.812
5.786
5.771
5.124
5.120
5.098
5.094
5.077
5.072
4.944
4.941
4.193
4.175
4.157
4.139
2.982
2.978
2.974
2.967
2.963
2.959
1.722
1.720
1.717
1.284
1.266
1.248
2.00
2.06
1.03
2.12
1.97
2.01
2.00
2.94
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

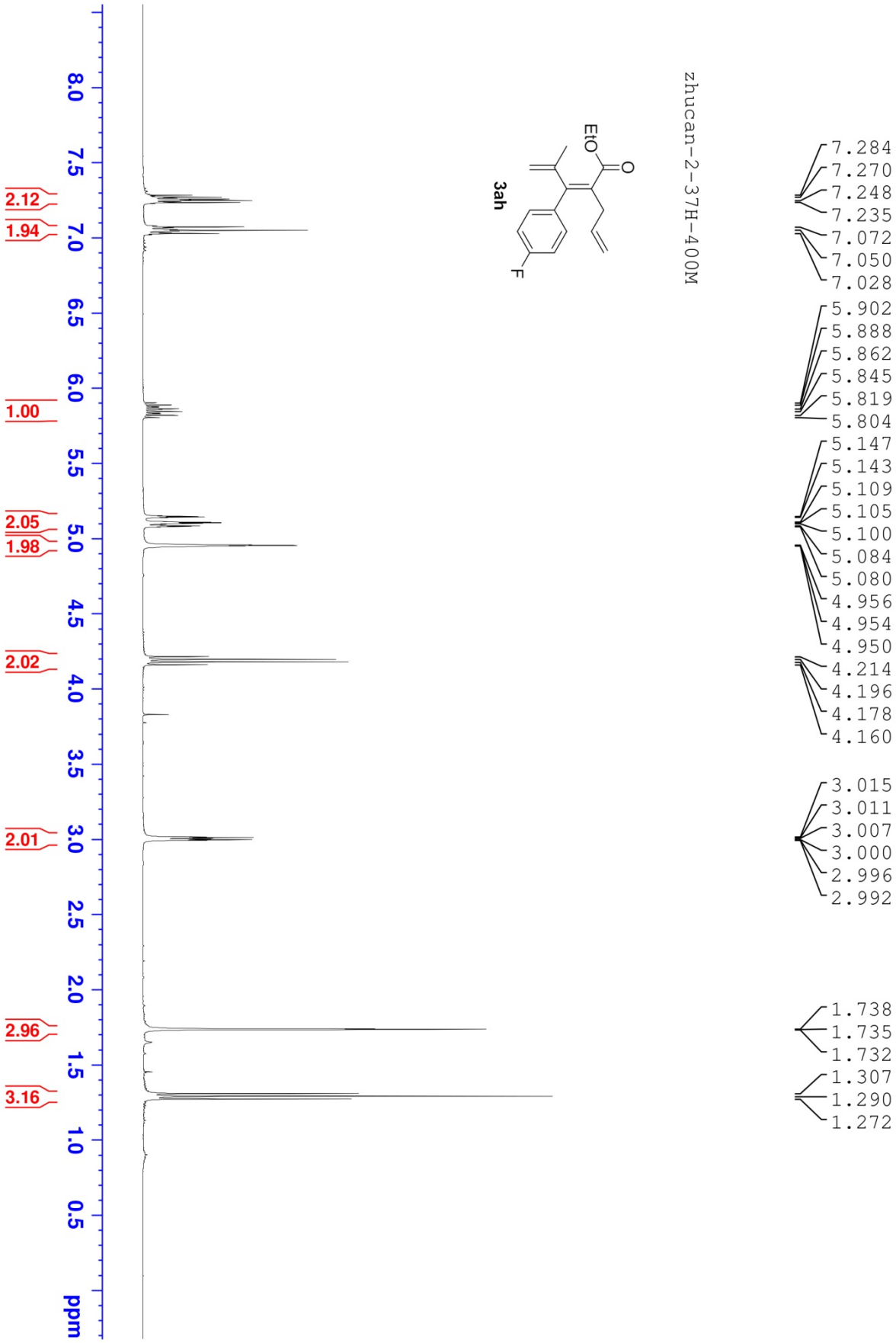
170.04
147.58
146.24
139.90
134.95
131.27
131.00
129.97
129.72
127.04
122.31
116.39
114.74
77.31
77.00
76.68
60.58
35.29
21.63
13.78

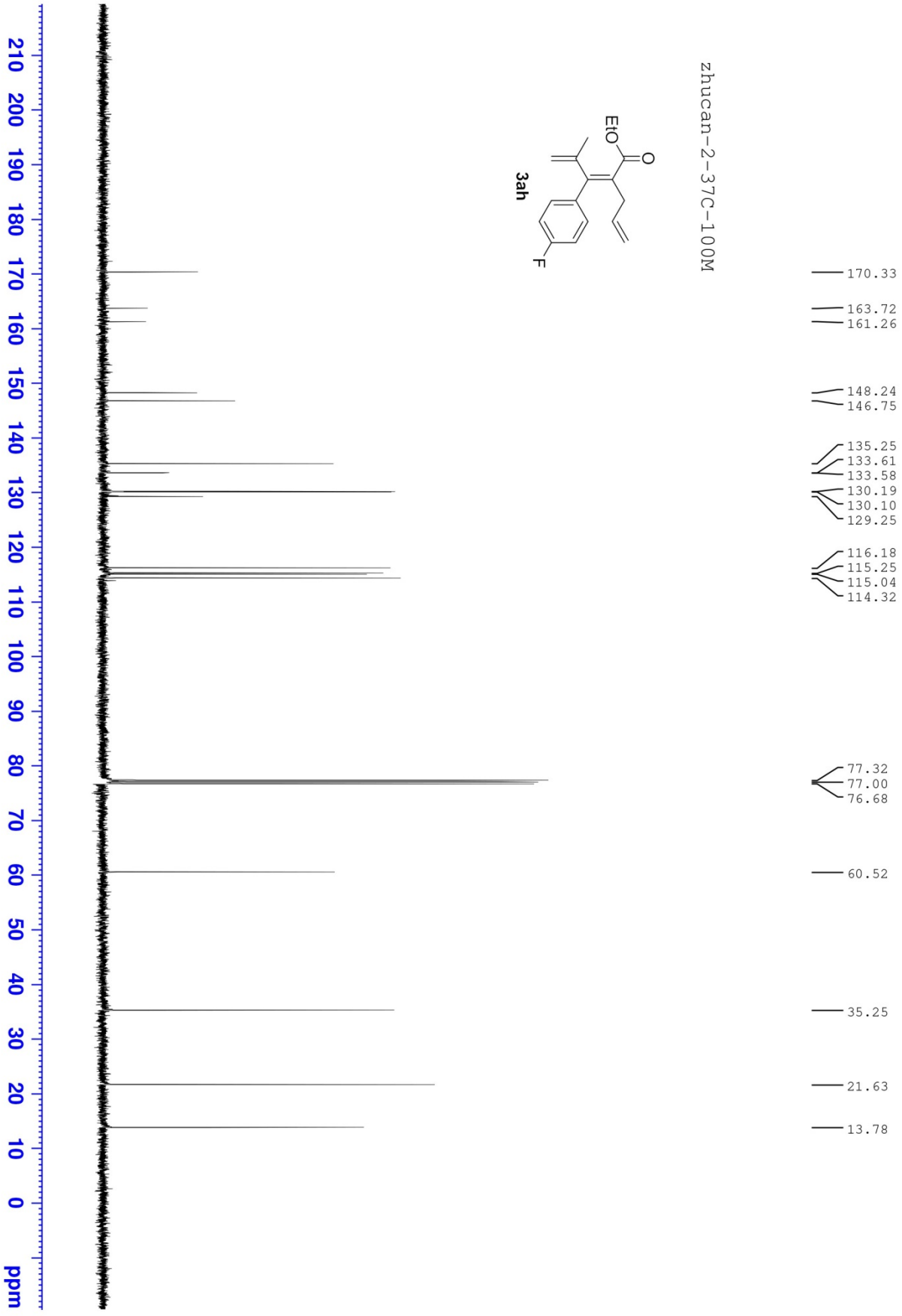
zhucan-2-44C-100M



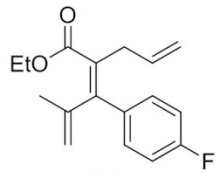
3ag




zhucan-2-37H-400M
3ah
EtO
O
F
7.284
7.270
7.248
7.235
7.072
7.050
7.028
5.902
5.888
5.862
5.845
5.819
5.804
5.147
5.143
5.109
5.105
5.100
5.084
5.080
4.956
4.954
4.950
4.214
4.196
4.178
4.160
3.015
3.011
3.007
3.000
2.996
2.992
1.738
1.735
1.732
1.307
1.290
1.272
2.12
1.94
1.00
2.05
1.98
2.02
2.01
2.96
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


zhucan-2-37C-100M
3ah
EtO
O
F
170.33
163.72
161.26
148.24
146.75
135.25
133.61
133.58
130.19
130.10
129.25
116.18
115.25
115.04
114.32
77.32
77.00
76.68
60.52
35.25
21.63
13.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

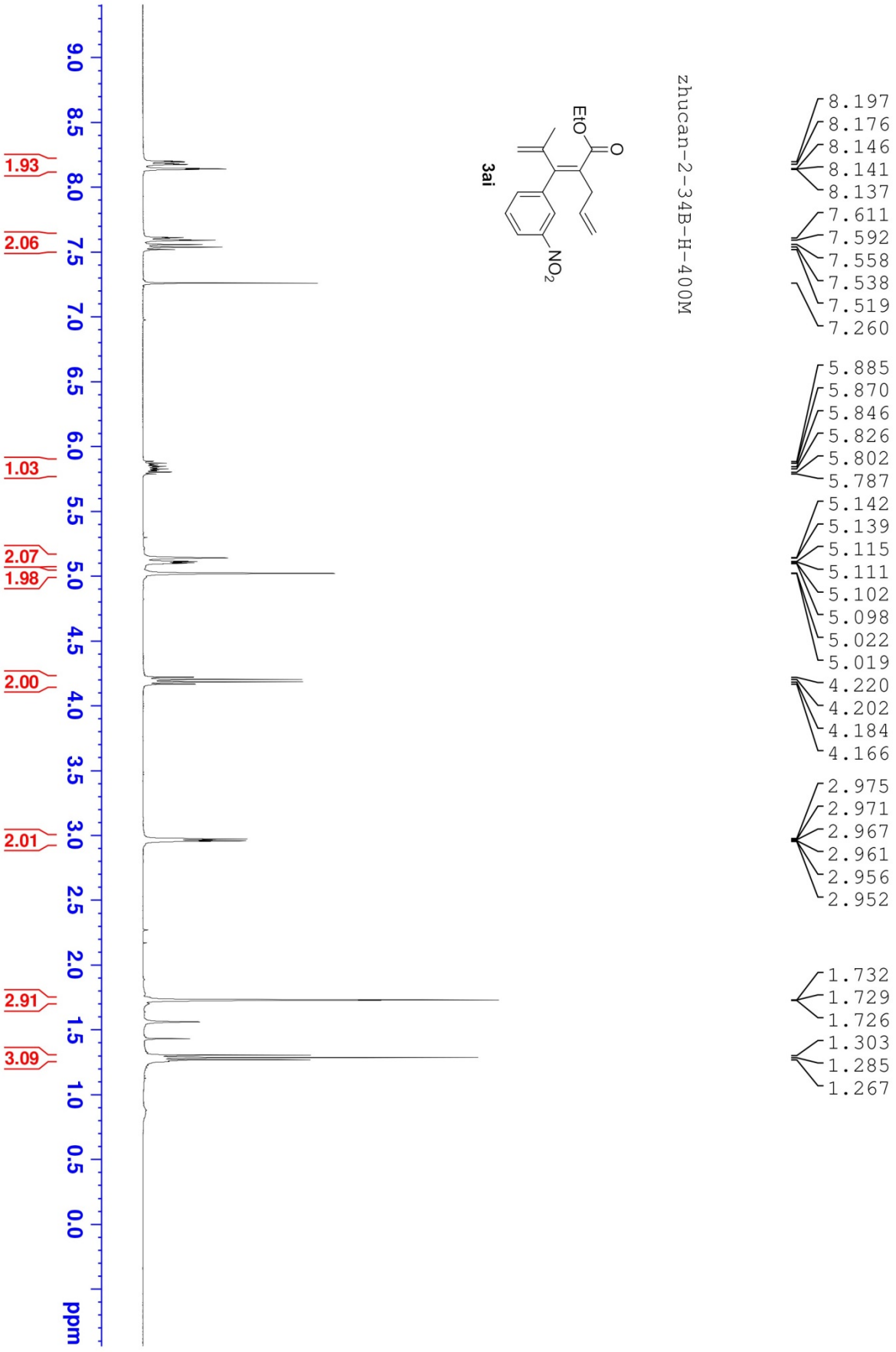
zhucan-2-37F-376M

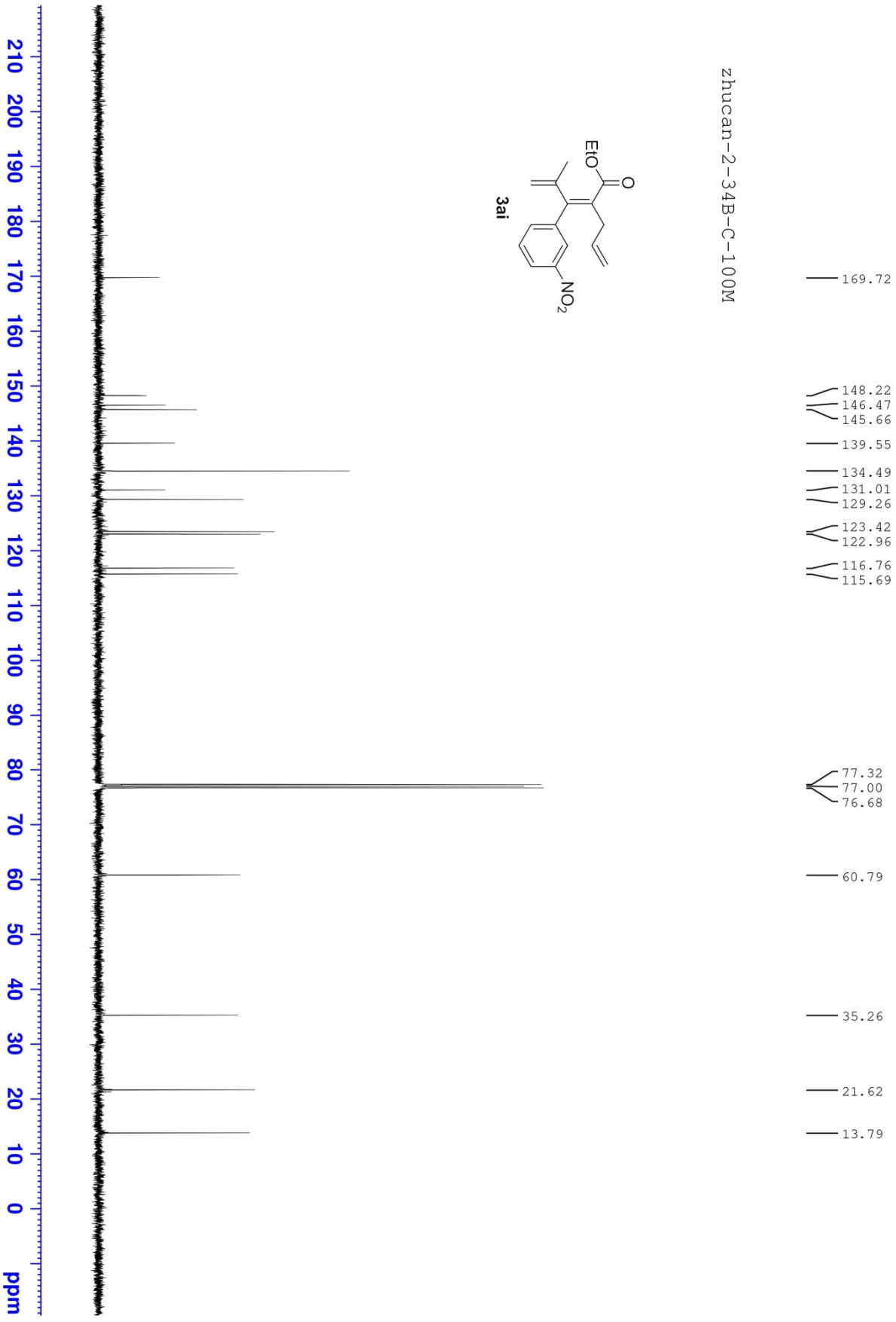


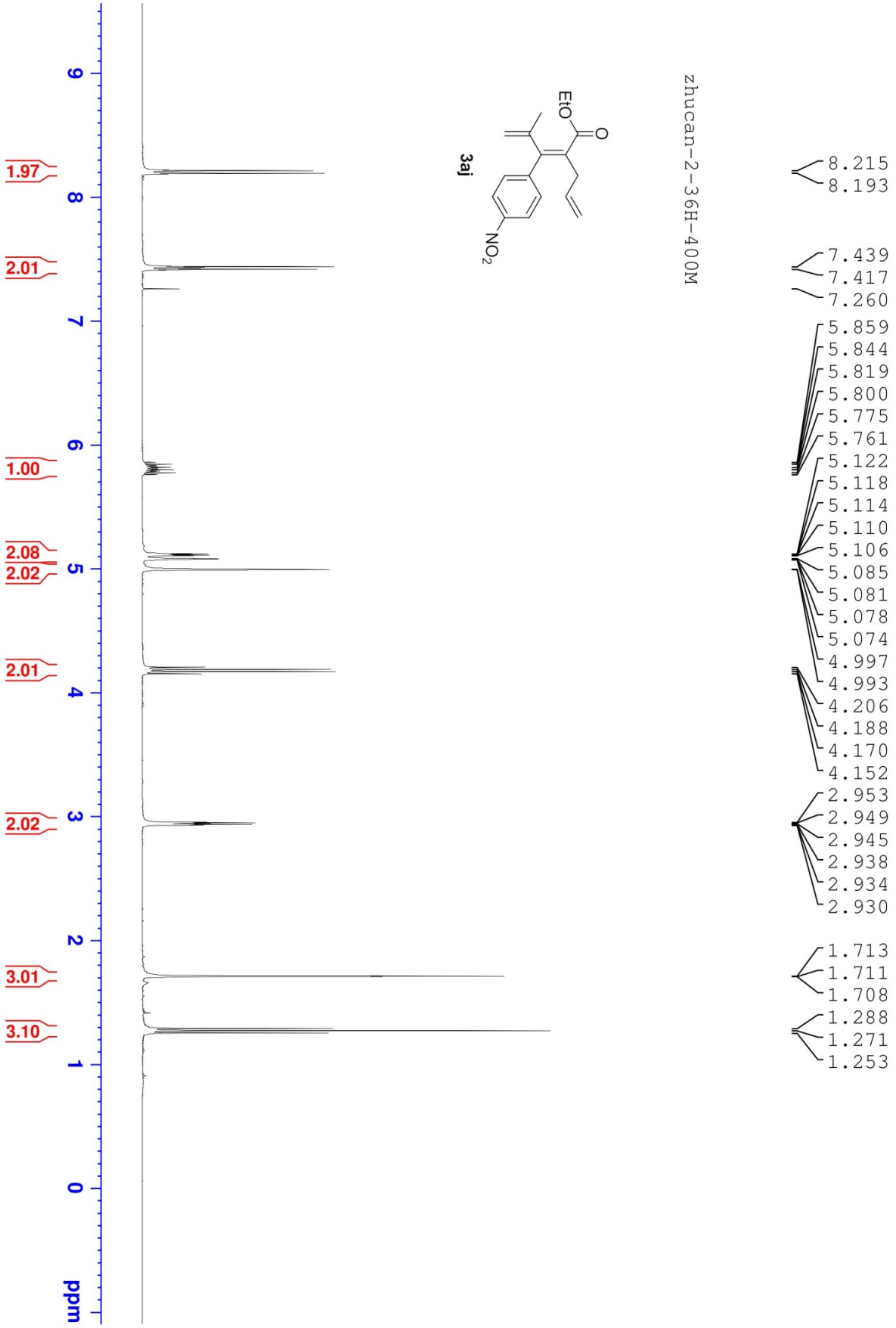
3ah

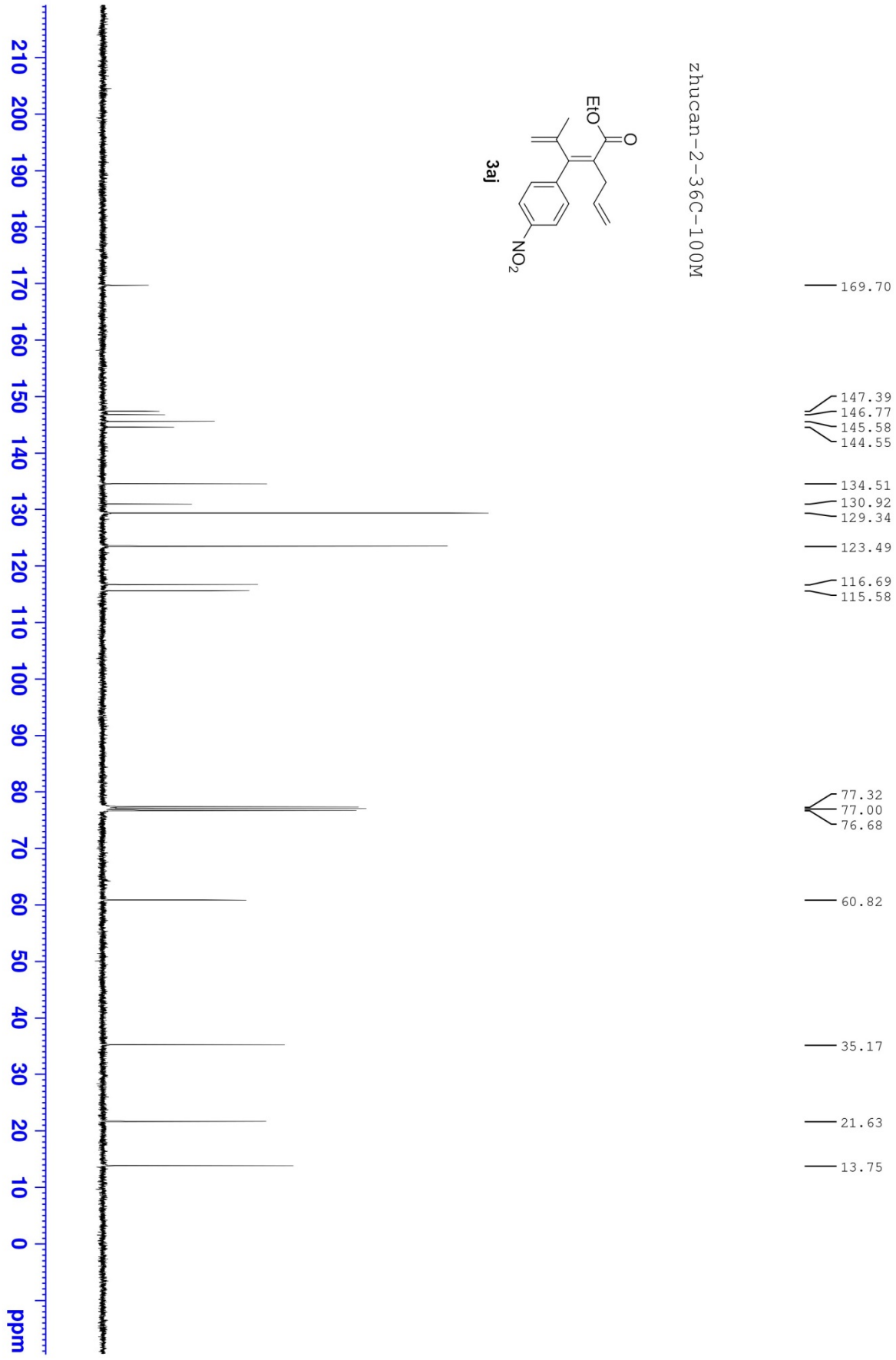
-113.85

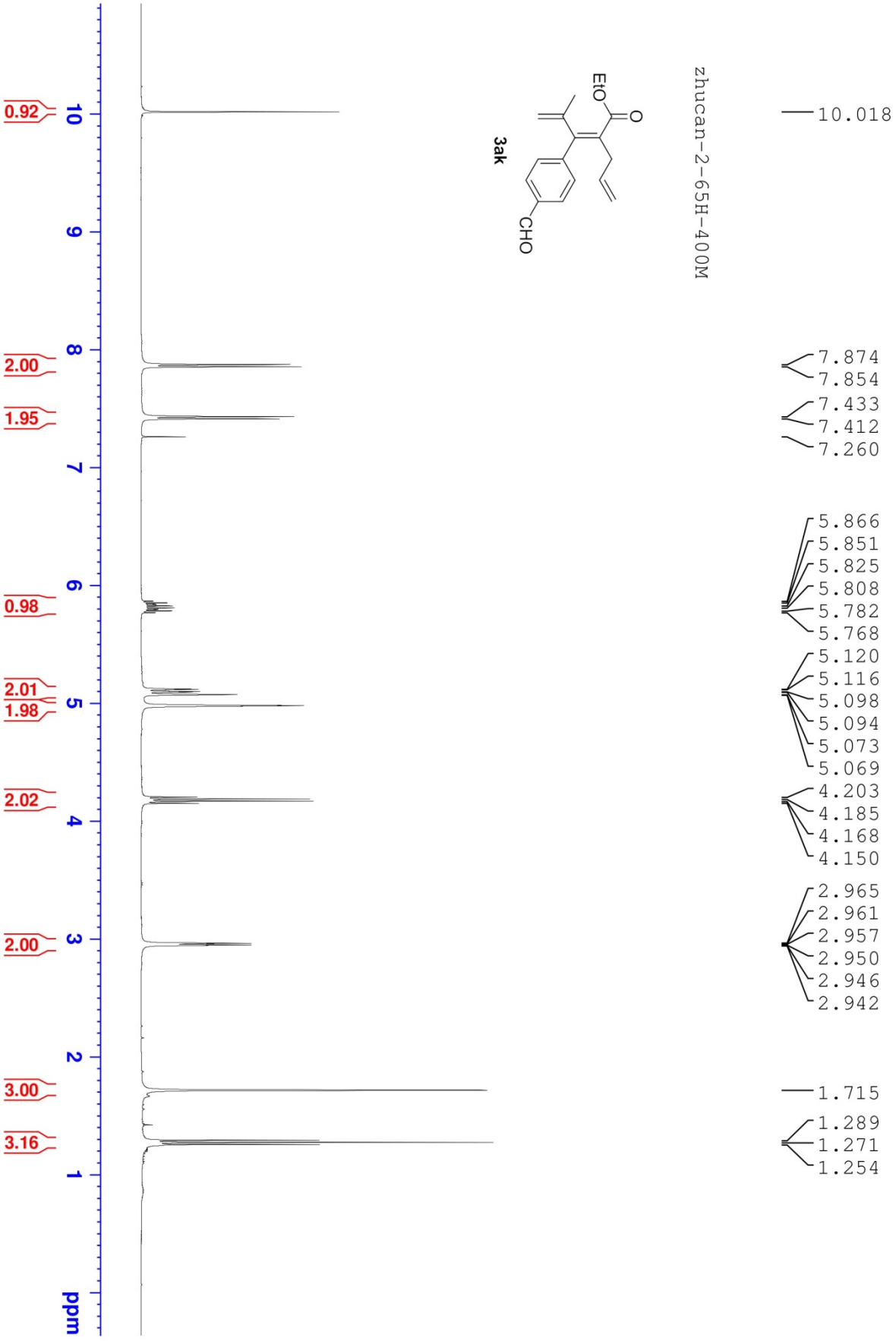
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

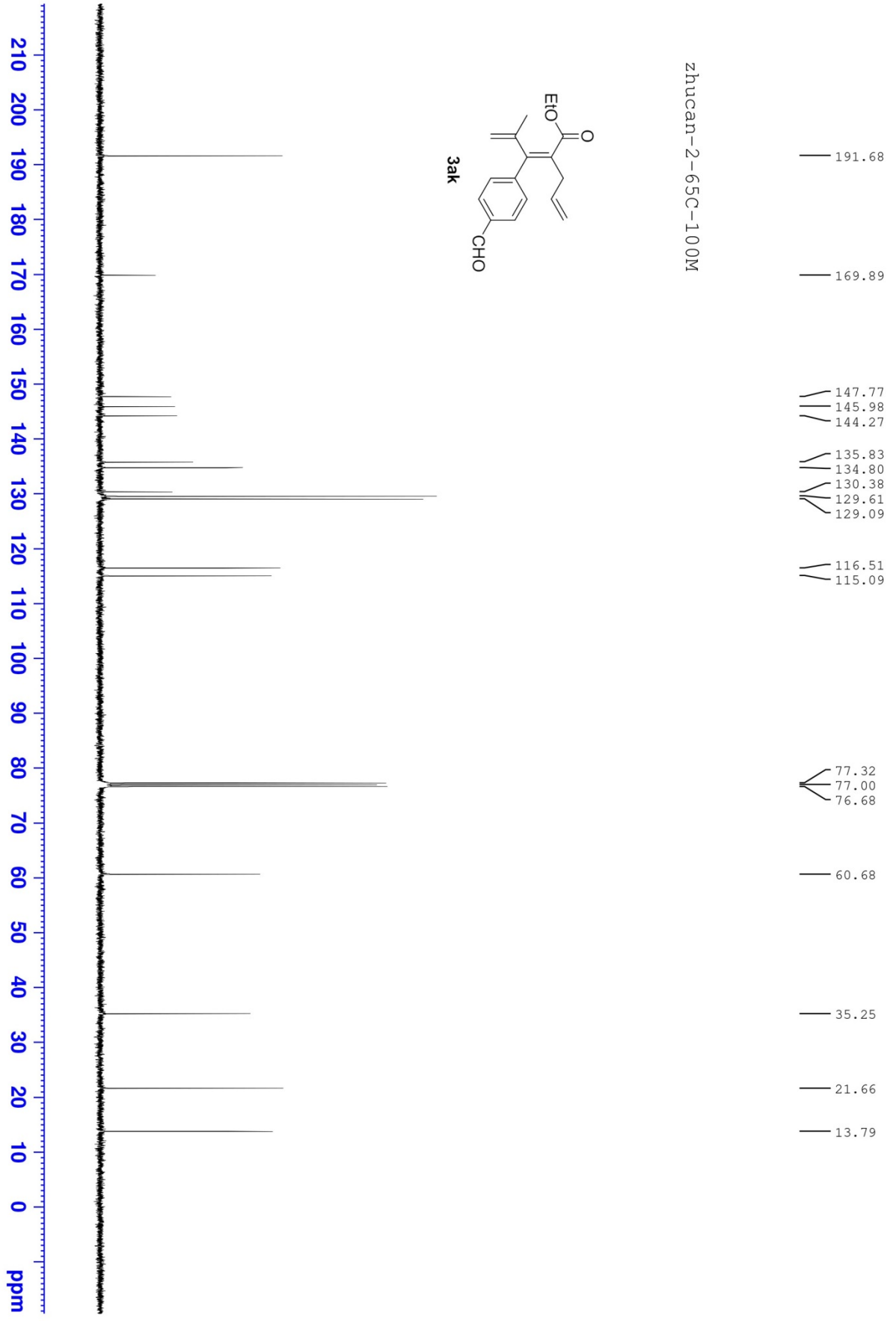

zhucan-2-34B-H-400M
3ai
EtO
O
NO2
8.197
8.176
8.146
8.141
8.137
7.611
7.592
7.558
7.538
7.519
7.260
5.885
5.870
5.846
5.826
5.802
5.787
5.142
5.139
5.115
5.111
5.102
5.098
5.022
5.019
4.220
4.202
4.184
4.166
2.975
2.971
2.967
2.961
2.956
2.952
1.732
1.729
1.726
1.303
1.285
1.267
1.93
2.06
1.03
2.07
1.98
2.00
2.01
2.91
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

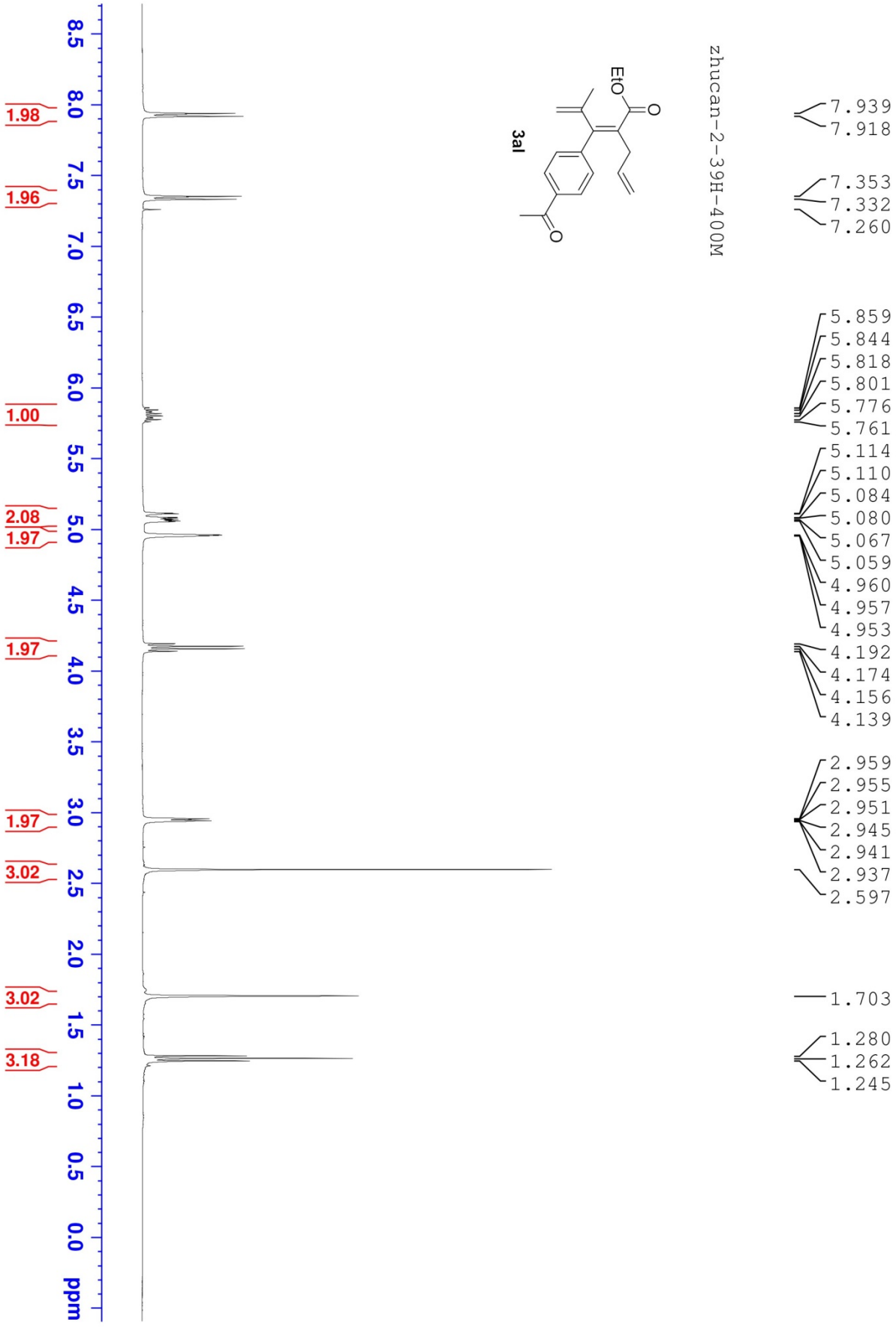

zhucan-2-34B-C-100M
3ai
EtO
O
NO2
169.72
148.22
146.47
145.66
139.55
134.49
131.01
129.26
123.42
122.96
116.76
115.69
77.32
77.00
76.68
60.79
35.26
21.62
13.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

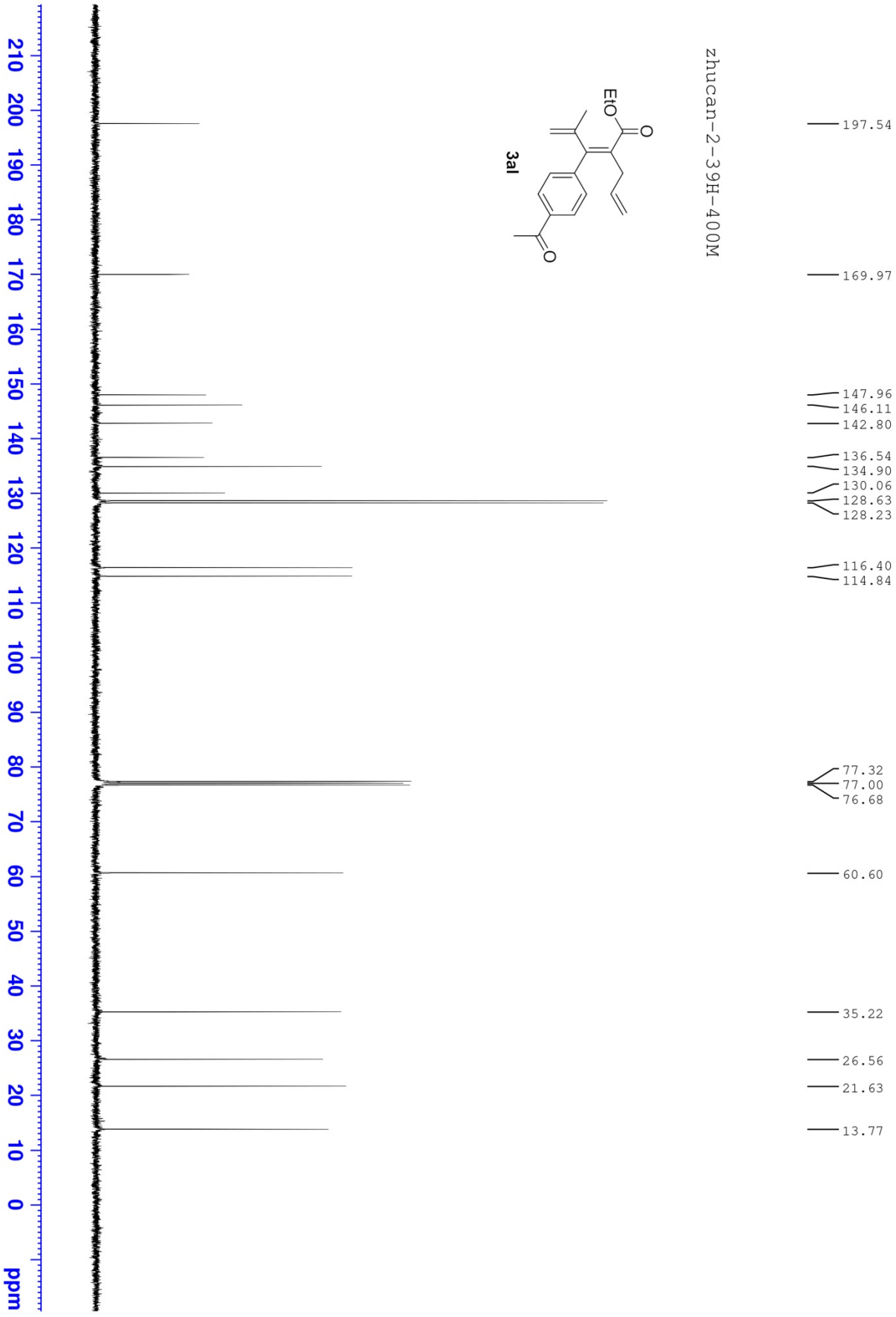

zhucan-2-36H-400M
3aj
EtO
O
NO2
8.215
8.193
7.439
7.417
7.260
5.859
5.844
5.819
5.800
5.775
5.761
5.122
5.118
5.114
5.110
5.106
5.085
5.081
5.078
5.074
4.997
4.993
4.206
4.188
4.170
4.152
2.953
2.949
2.945
2.938
2.934
2.930
1.713
1.711
1.708
1.288
1.271
1.253
1.97
2.01
1.00
2.08
2.02
2.01
2.02
3.01
3.10
ppm

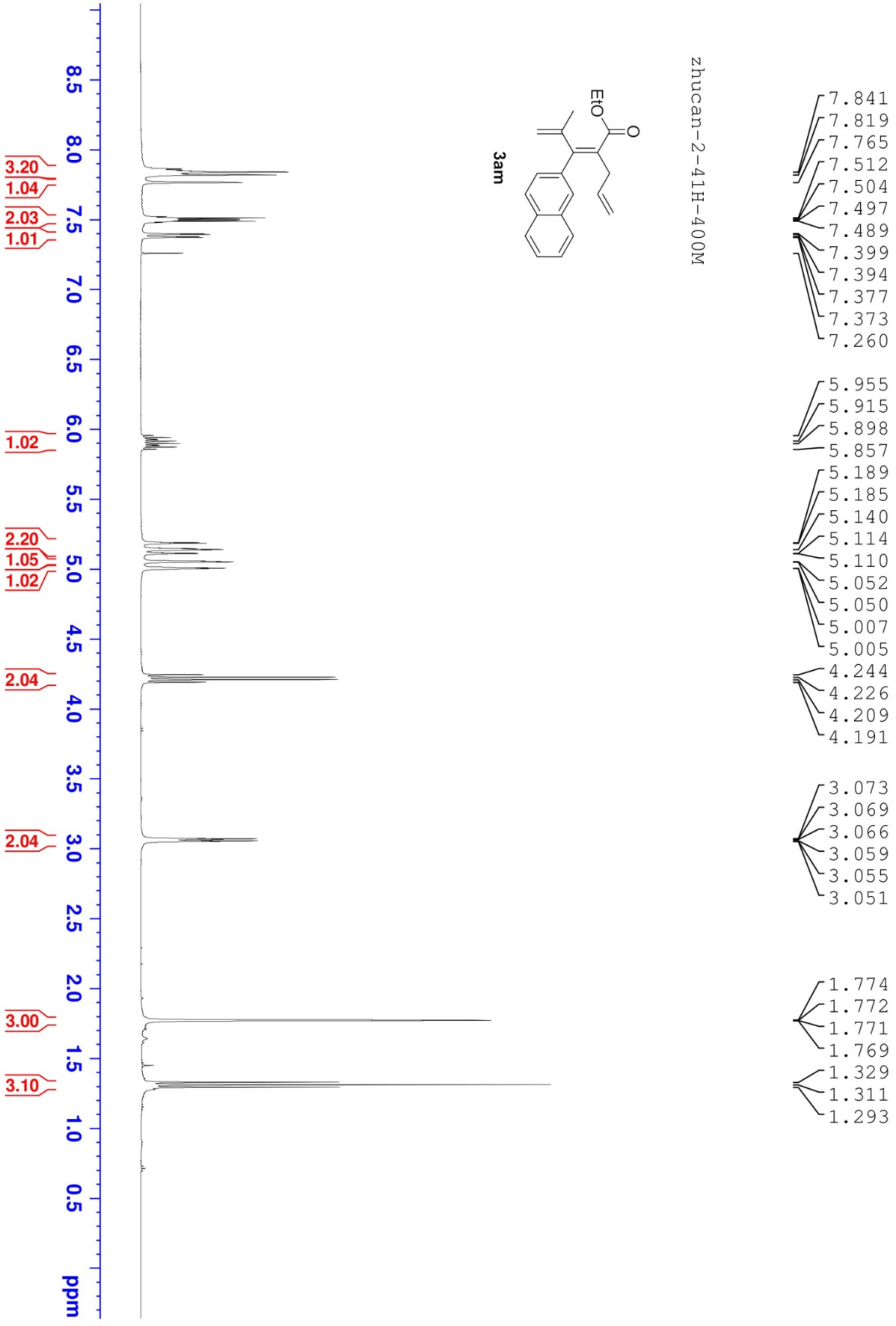

zhucan-2-36C-100M
3aj
EtO
O
NO2
169.70
147.39
146.77
145.58
144.55
134.51
130.92
129.34
123.49
116.69
115.58
77.32
77.00
76.68
60.82
35.17
21.63
13.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

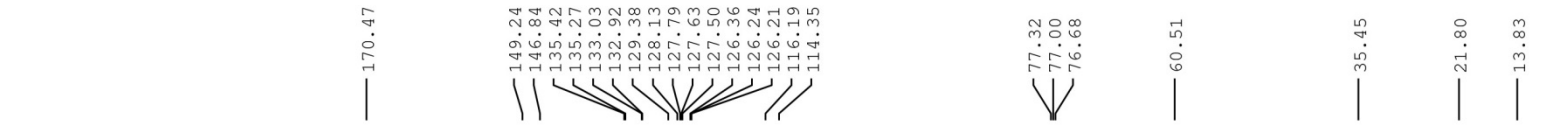

zhucan-2-65H-400M
3ak
EtO
O
CHO
10.018
7.874
7.854
7.433
7.412
7.260
5.866
5.851
5.825
5.808
5.782
5.768
5.120
5.116
5.098
5.094
5.073
5.069
4.203
4.185
4.168
4.150
2.965
2.961
2.957
2.950
2.946
2.942
1.715
1.289
1.271
1.254
0.92
2.00
1.95
0.98
2.01
1.98
2.02
2.00
3.00
3.16
ppm


zhucan-2-65C-100M
3ak
EtO
O
CHO
191.68
169.89
147.77
145.98
144.27
135.83
134.80
130.38
129.61
129.09
116.51
115.09
77.32
77.00
76.68
60.68
35.25
21.66
13.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

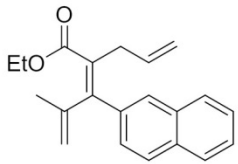

zhucan-2-39H-400M
3al
EtO
O
O
7.939
7.918
7.353
7.332
7.260
5.859
5.844
5.818
5.801
5.776
5.761
5.114
5.110
5.084
5.080
5.067
5.059
4.960
4.957
4.953
4.192
4.174
4.156
4.139
2.959
2.955
2.951
2.945
2.941
2.937
2.597
1.703
1.280
1.262
1.245
1.98
1.96
1.00
2.08
1.97
1.97
1.97
3.02
3.02
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


zhucan-2-39H-400M
3al
EtO
O
O
197.54
169.97
147.96
146.11
142.80
136.54
134.90
130.06
128.63
128.23
116.40
114.84
77.32
77.00
76.68
60.60
35.22
26.56
21.63
13.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

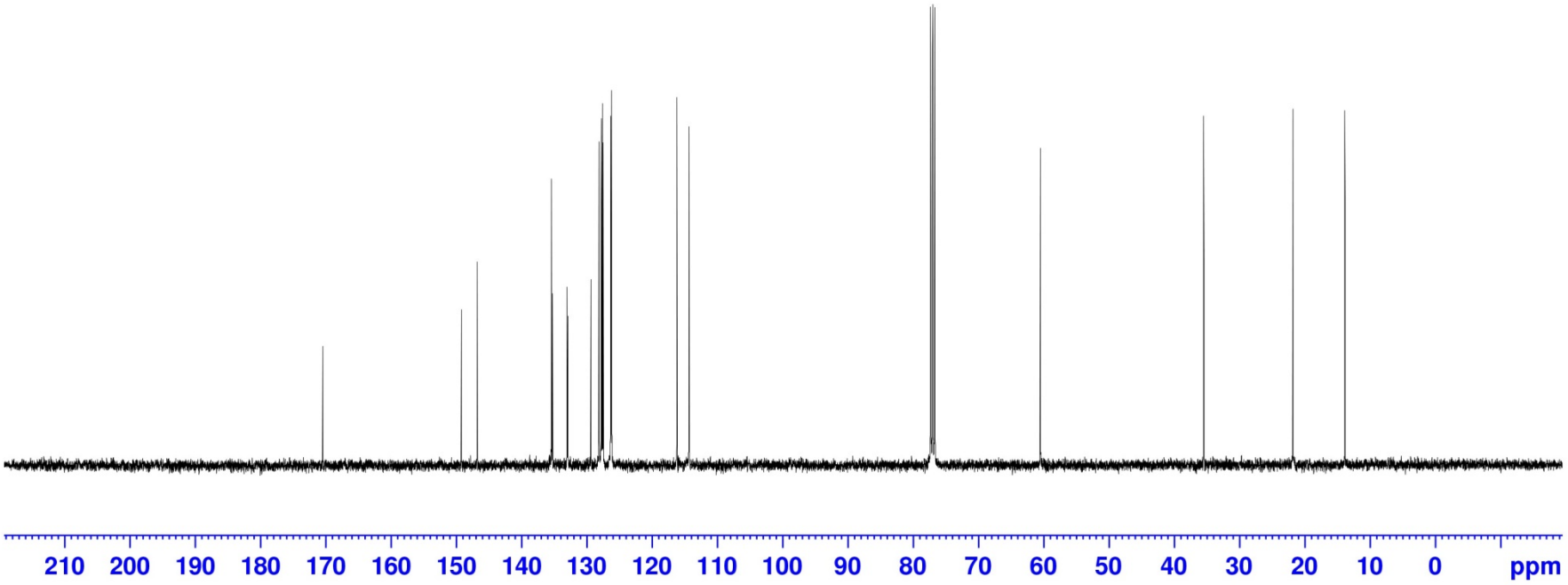

zhucan-2-41H-400M
3am
EtO
O
7.841
7.819
7.765
7.512
7.504
7.497
7.489
7.399
7.394
7.377
7.373
7.260
5.955
5.915
5.898
5.857
5.189
5.185
5.140
5.114
5.110
5.052
5.050
5.007
5.005
4.244
4.226
4.209
4.191
3.073
3.069
3.066
3.059
3.055
3.051
1.774
1.772
1.771
1.769
1.329
1.311
1.293
3.20
1.04
2.03
1.01
1.02
2.20
1.05
1.02
2.04
2.04
3.00
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

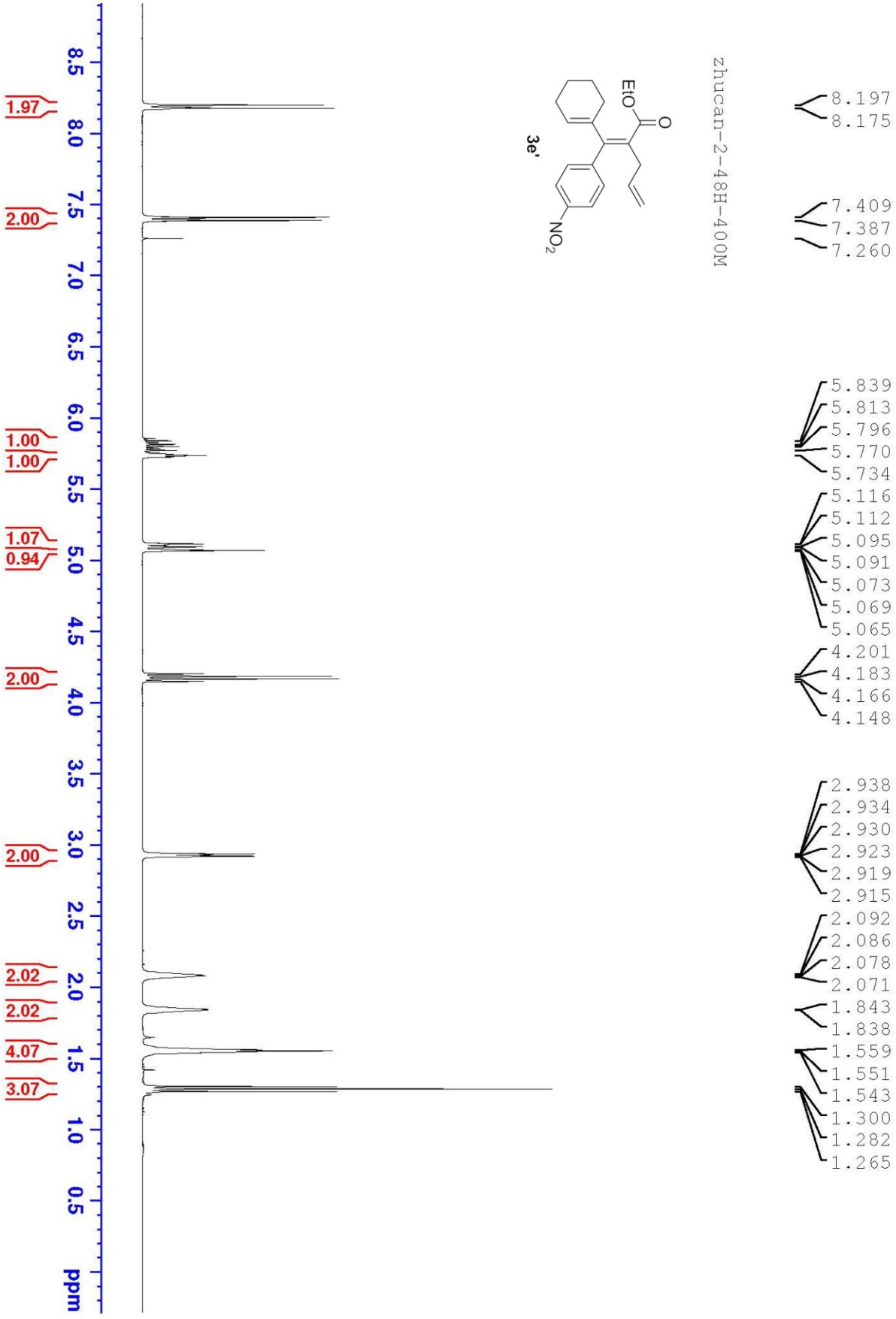


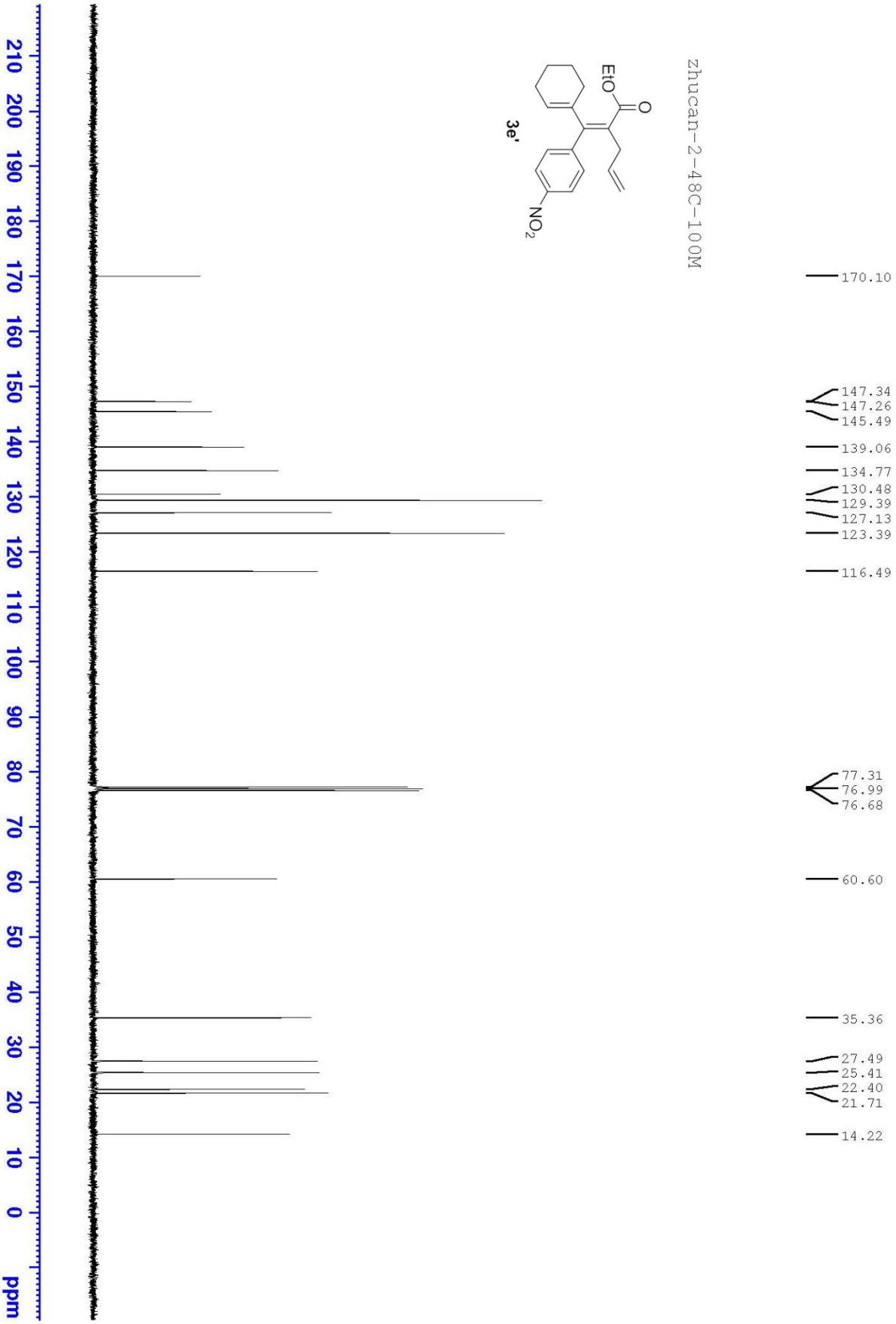
zhucan-2-41C-100M



3am




zhucan-2-48H-400M
3e'
EtO
O
NO2
8.197
8.175
7.409
7.387
7.260
5.839
5.813
5.796
5.770
5.734
5.116
5.112
5.095
5.091
5.073
5.069
5.065
4.201
4.183
4.166
4.148
2.938
2.934
2.930
2.923
2.919
2.915
2.092
2.086
2.078
2.071
1.843
1.838
1.559
1.551
1.543
1.300
1.282
1.265
1.97
2.00
1.00
1.00
1.07
0.94
2.00
2.00
2.02
2.02
4.07
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


zhucan-2-48C-100M
3e'
EtO
O
NO2
170.10
147.34
147.26
145.49
139.06
134.77
130.48
129.39
127.13
123.39
116.49
77.31
76.99
76.68
60.60
35.36
27.49
25.41
22.40
21.71
14.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm