Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

2,3-Allenoic acids *via* palladium-catalyzed carboxylation of propargylic alcohols

Wei-Feng Zheng,[a] Wanli Zhang,[c] Jianhao Huang,[d] Yibo Yu,[d] Hui Qian,*[a] Shengming Ma*[a,b]

[a]Research Center for Molecular Recognition and Synthesis, Department of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P. R. China

[b]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

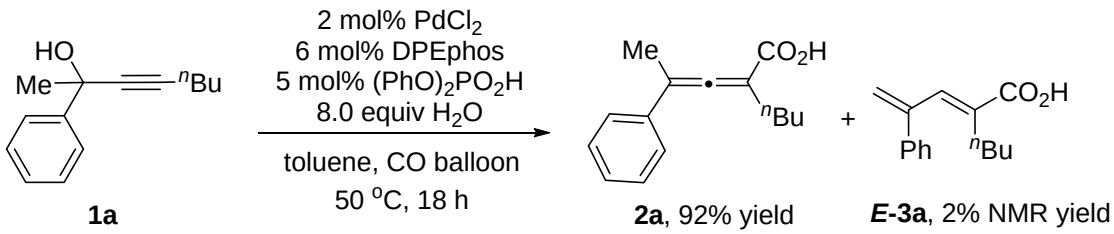
[c]Shanghai Key Laboratory of Green Chemistry and Chemical Process, College of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Lu, Shanghai, 200062, P. R. China

[d]College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China.

General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR) in $CDCl_3$ or d_6-DMSO. All ^{1}H NMR experiments were measured with tetramethylsilane (0 ppm) in $CDCl_3$ or the signal of residual DMSO (2.50 ppm) in d_6-DMSO as the internal reference; ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.0 ppm) or the signal of d_6-DMSO (39.52 ppm); ^{19}F NMR experiments were measured in relative to the signal of $CFCl_3$ (0 ppm) in $CDCl_3$. All reactions were carried out in Schlenk tubes. $PdCl_2$ was purchased from J&K Chemicals; DPEphos was purchased from Energy Chemical; $(PhO)_2POOH$ was purchased from Energy Chemical, acidified with 1 N HCl under stirring, and extracted with dichloromethane, and the solvent was removed under vacuum; ^{n}BuLi (2.5 M in Hexane) was purchased from Energy Chemical. Petroleum ether (b.p. 60-90 ^{o}C) was purchased from Shanghai Titan Scientific Co., Ltd. Toluene was used as received without further purification. Anhydrous toluene was obtained via drying over sodium wire with benzophenone as the indicator and distillation freshly before use. The reaction should be conducted in a hood working efficiently due to the toxicity of CO gas. All the temperatures are referred to the oil baths used. Recovery of substrates were determined by ^{1}H NMR analysis using dibromomethane or 1,3,5-trimethylbenzene as the internal standard. The propargylic alcohols were prepared according to the literature methods.[1-3]

1. Synthesis of 2,3-allenoic acids

(1) Preparation of 2-butyl-4-phenyl-2,3-pentadienoic acid (2a) (zwf-2-119)

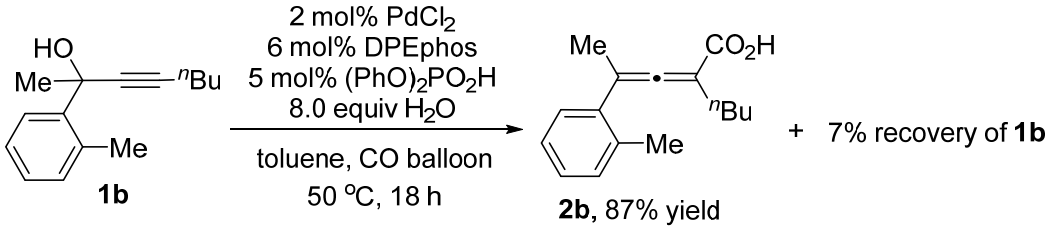


1a **2a**, 92% yield ***E*-3a**, 2% NMR yield

Typical Procedure I: To a Schlenk flask (25 mL) were added $PdCl_2$ (3.8 mg, 0.02 mmol), DPEphos (33.1 mg, 0.06 mmol), and $(PhO)_2PO_2H$ (12.7 mg, 0.05 mmol). After addition of each chemical, the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then **1a** (203.6 mg, 1.0 mmol), toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) were added sequentially. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO (about 1 L) for three times. Then the liquid nitrogen bath was removed and the mixture was warmed up to room temperature. Then the resulting mixture was vigorously stirred at 50 ^oC with a balloon of CO for 18 h. After that, the resulting mixture was diluted with 5 mL of ethyl acetate, filtered through a short column silica gel (3 cm) eluted with ethyl acetate (20 mL), and concentrated. The reaction afforded a mixture of **2a** (97% NMR yield), and ***E*-3a** (2% NMR yield), which was determined by ^1H NMR analysis of the crude product. The mixture was purified by chromatography on silica gel to afford the pure product **2a** (213.4 mg, 92%) [eluent: petroleum ether/ ethyl acetate = 30/1 (310 mL), 5/1 (120 mL)]: white solid; m.p. 118.2-119.6 ^oC (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42-7.30 (m, 4 H, Ar-H), 7.29-7.22 (m, 1 H, Ar-H), 2.32 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.19 (s, 3 H, CH_3), 1.52-1.40 (m, 2 H, CH_2), 1.40-1.29 (m, 2 H, CH_2), 0.88 (t, *J* = 7.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.6, 173.0, 135.0, 128.5, 127.6, 126.1, 105.2, 101.8, 30.2, 28.3, 22.3, 16.3, 13.8; **IR** (neat): v = 3200-2410, 1935, 1673, 1419, 1279, 1248, 1122, 1066 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 230 (M^+, 4.81), 143 (100);

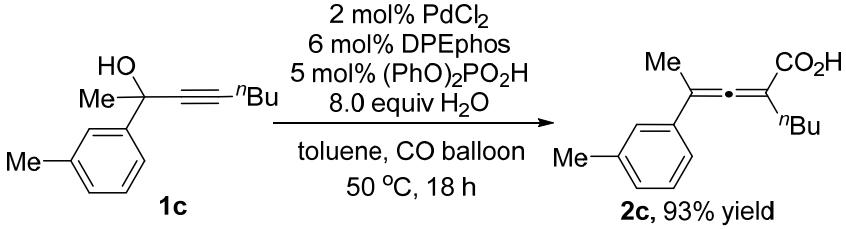
Anal. Calcd. for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found: C 78.22, H 7.98.

(2) Preparation of 2-butyl-(2-methylphenyl)-2,3-pentadienoic acid (2b) (zwf-1-125)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.7 mg, 0.05 mmol), **1b** (220.5 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2b** (216.9 mg, 87%) (7% of **1b** remained based ^{1}H NMR analysis of the crude product) [eluent: petroleum ether/ ethyl acetate = 20/1 (315 mL), 10/1 (660 mL)]: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31-7.24 (m, 1 H, Ar-H), 7.24-7.11 (m, 3 H, Ar-H), 2.40 (s, 3 H, CH_3), 2.35-2.15 (m, 2 H, CH_2), 2.13 (s, 3 H, CH_3), 1.52-1.40 (m, 2 H, CH_2), 1.40-1.27 (m, 2 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 210.2, 173.8, 136.2, 136.0, 130.6, 127.9, 127.6, 125.9, 104.5, 98.9, 30.1, 28.1, 22.2, 20.4, 19.9, 13.9; **IR** (neat): *v* = 3240-2460, 1950, 1675, 1458, 1414, 1379, 1275, 1121, 1077, 1042 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 245 (M^++1, 2.19), 244 (M^+, 11.87), 201 (100); **HRMS** calcd for $C_{16}H_{20}O_2$ [M^+]: 244.1463, found: 244.1460.

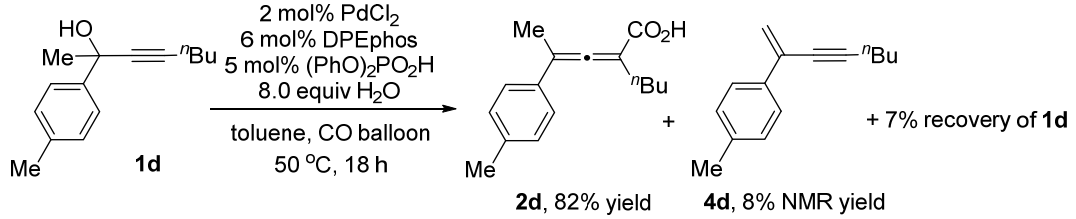
(3) Preparation of 2-butyl-(3-methylphenyl)-2,3-pentadienoic acid (2c) (zwf-1-124)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol),

DPEphos (32.5 mg, 0.06 mmol), $(PhO)_2PO_2H$ (13.0 mg, 0.05 mmol), **1c** (228.0 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2c** (238.9 mg, 93%) [eluent: petroleum ether/ ethyl acetate = 20/1 (315 mL), 10/1 (330 mL)]: white solid; m.p. 116.9-119.0 ^oC (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.12 (m, 3 H, Ar-H), 7.06 (d, *J* = 7.6 Hz, 1 H, Ar-H), 2.43-2.25 (m, 5 H, CH_2 and CH_3), 2.18 (s, 3 H, CH_3), 1.53-1.41 (m, 2 H, CH_2), 1.41-1.28 (m, 2 H, CH_2), 0.88 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.6, 173.2, 138.1, 134.9, 128.41, 128.36, 126.7, 123.2, 105.2, 101.6, 30.2, 28.3, 22.2, 21.4, 16.4, 13.8; **IR** (neat): *v* = 3230-2450, 1933, 1673, 1491, 1421, 1278, 1246, 1125, 1070, 1052, 1015 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 245 (M^++1, 1.97), 244 (M^+, 10.80), 157 (100); Anal. Calcd. for $C_{16}H_{20}O_2$: C 78.65, H 8.25; found C 78.46, H 8.31.

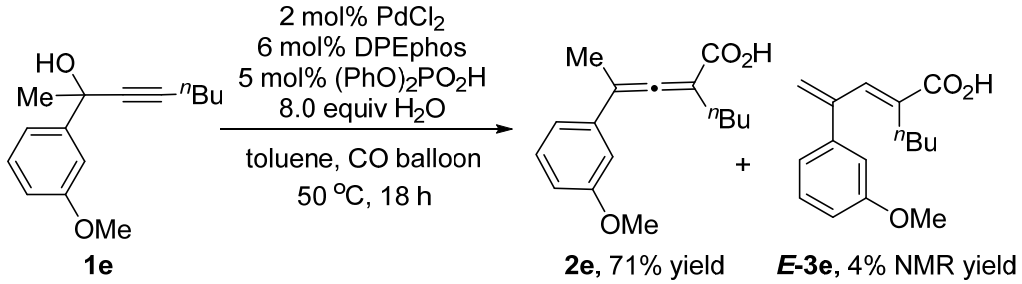
(4) Preparation of 2-butyl-(4-methylphenyl)-2,3-pentadienoic acid (2d) (zwf-1-082)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.5 mg, 0.05 mmol), **1d** (216.6 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/cm^3, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded a mixture of **2d** (87% NMR yield), **4d** (8% NMR yield), and 7% recovery of **1d**, which was determined by ^{1}H NMR analysis of the crude product. The mixture was purified by chromatography on silica gel to afford the pure product **2d** (200.4 mg, 82%) [eluent: petroleum ether (b.p. 60-90 ^oC)/ ethyl acetate = 15/1 (960 mL)]: white solid; m.p. 125.7-127.6 ^oC (petroleum ether/ $CDCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.14 (d, *J* = 7.6 Hz, 2 H, Ar-H), 2.40-2.25 (m, 5 H, CH_2 and CH_3), 2.17 (s, 3 H, CH_3), 1.52-1.41 (m, 2 H, CH_2),

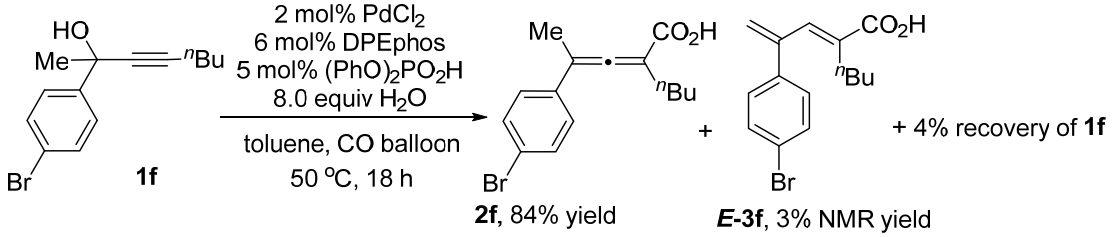
1.41-1.28 (m, 2 H, CH_2), 0.87 (t, J = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.5, 173.1, 137.4, 132.0, 129.2, 125.9, 105.0, 101.7, 30.2, 28.3, 22.2, 21.1, 16.3, 13.8; **IR** (neat): ν = 3230-2410, 1937, 1671, 1509, 1418, 1283, 1251, 1121, 1061, 1009 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 244 (M^+, 6.15), 157 (100); **HRMS** calcd for $C_{16}H_{20}O_2$ [M^+]: 244.1463, found: 244.1465.

(5) Preparation of 2-butyl-(3-methoxyphenyl)-2,3-pentadienoic acid (2e) (hjh-1-030)



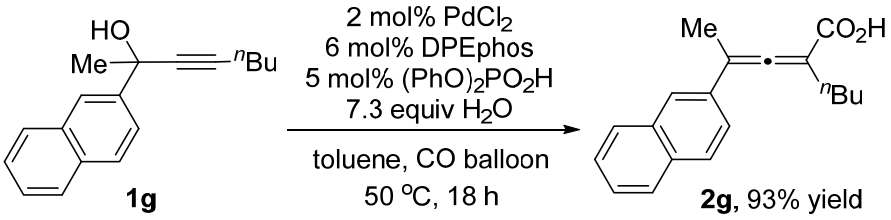
Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.3 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.6 mg, 0.05 mmol), **1e** (232.5 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded a mixture of **2e** (77% NMR yield), and ***E*-3e** (4% NMR yield), which was determined by ^{1}H NMR analysis of the crude product. The mixture was purified by chromatography on silica gel to afford the pure product **2e** (188.0 mg, 71%, purity: 97%) [eluent: petroleum ether/ ethyl acetate = 8/1 (200 mL), 4/1 (200mL)]: white solid; m.p. 96.3-98.1 °C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.8 Hz, 1 H, Ar-H), 7.06-6.87 (m, 2 H, Ar-H), 6.80 (dd, J_1 = 8.2 Hz, J_2= 1.8 Hz, 1 H, Ar-H), 3.80 (s, 3 H, OCH_3), 2.32 (t, J = 7.4 Hz, 2 H, CH_2), 2.18 (s, 3H, CH_3), 1.58-1.24 (m, 4 H, 2 x CH_2), 0.88 (t, J = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.6, 172.9, 159.7, 136.5, 129.5, 118.6, 112.8, 112.0, 105.1, 101.8, 55.2, 30.2, 28.3, 22.2, 16.3, 13.8; **IR** (neat): ν = 3245-2440, 1939, 1676, 1602, 1576, 1488, 1417, 1272, 1170, 1047 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 261 (M^++1, 1.94), 260 (M^+, 10.95), 173 (100); Anal. Calcd. for $C_{16}H_{20}O_3$: C 73.82, H 7.74; found C 73.60, H 7.49.

(6) Preparation of 2-butyl-(4-bromophenyl)-2,3-pentadienoic acid (2f) (zwf-1-092)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.7 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.8 mg, 0.05 mmol), **1f** (281.1 mg, 1.1 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded a mixture of **2f** (87% NMR yield), ***E*-3f** (3% NMR yield), and 4% recovery of **1f**, which was determined by ^{1}H NMR analysis of the crude product. The mixture was purified by chromatography on silica gel to afford the pure product **2f** (260.1 mg, 84%) [eluent: petroleum ether/ ethyl acetate = 15/1 (320 mL), 5/1 (360 mL)]: white solid; m.p. 117.4-118.6 °C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.25 (d, *J* = 8.4 Hz, 2 H, Ar-H), 2.32 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.17 (s, 3 H, CH_3), 1.52-1.28 (m, 4 H, 2 x CH_2), 0.88 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.4, 172.6, 134.0, 131.7, 127.6, 121.5, 104.5, 102.2, 30.2, 28.2, 22.2, 16.3, 13.8; **IR** (neat): *v* = 3150-2400, 1939, 1672, 1483, 1416, 1278, 1250, 1120, 1076,1008 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 310 (M^+(^{81}Br), 2.61), 308 (M^+(^{79}Br), 2.58); Anal. Calcd. for $C_{15}H_{17}BrO_2$: C 58.27, H 5.54; found C 58.05, H 5.25.

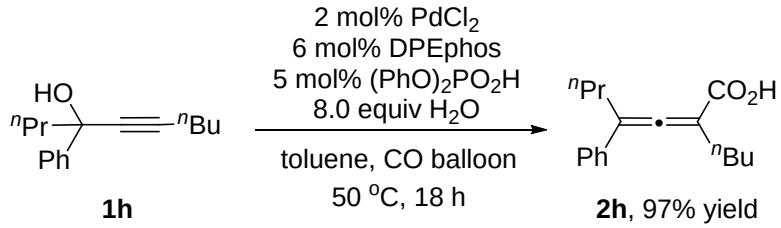
(7) Preparation of 2-butyl-4-(2-naphthyl)-2,3-pentadienoic acid (2g) (zwf-1-140)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.7 mg, 0.02 mmol), DPEphos (32.8 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.8 mg, 0.05 mmol), **1g** (277.9 mg,

1.1 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2g** (287.3 mg, 93%) [eluent: petroleum ether/ ethyl acetate = 20/1 (210 mL), 5/1 (240 mL)]: white solid; m.p. 158.9-160.0 ^oC (petroleum ether/DCM); **^{1}H NMR** (400 MHz, d_6-DMSO): δ = 12.52 (s, 1 H, COOH), 8.03-7.82 (m, 4 H, Ar-H), 7.59-7.43 (m, 3 H, Ar-H), 2.33 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.27 (s, 3 H, CH_3), 1.54-1.39 (m, 2 H, CH_2), 1.38-1.25 (m, 2 H, CH_2), 0.85 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, d_6-DMSO): δ = 211.2, 167.9, 133.3, 132.6, 132.3, 128.1, 128.0, 127.5, 126.5, 126.2, 124.6, 123.8, 103.9, 102.3, 29.9, 28.3, 21.8, 16.3, 13.8; **IR** (neat): *v* = 3145-2430, 1939, 1672, 1407, 1275, 1246, 1116, 1081 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 280 (M^+, 6.42), 143 (100); Anal. Calcd. for $C_{19}H_{20}O_2$: C 81.40, H 7.19; found C 81.05, H 7.19.

(8) Preparation of 2-butyl-4-phenyl-2,3-heptadienoic acid (2h) (zwf-2-141)

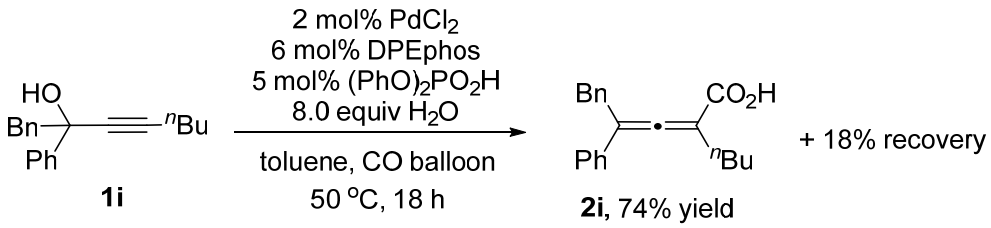


1h **2h**, 97% yield

Following Typical Procedure I, the reaction of $PdCl_2$ (3.8 mg, 0.02 mmol), DPEphos (32.8 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.8 mg, 0.05 mmol), **1h** (235.3 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2h** (255.1 mg, 97%) [eluent: petroleum ether/ ethyl acetate = 20/1 (210 mL), 5/1 (240 mL)]: white solid; m.p. 74.5-76.7 ^oC (petroleum ether /DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.46-7.28 (m, 4 H, Ar-H), 7.28-7.19 (m, 1 H, Ar-H), 2.51 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.32 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.68-1.52 (m, 2 H, CH_2), 1.52-1.42 (m, 2 H, CH_2), 1.40-1.28 (m, 2 H, CH_2), 1.01 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.4, 173.2, 134.9, 128.5, 127.5, 126.4, 110.3, 102.9, 32.2, 30.4, 28.4, 22.4, 21.0, 13.9, 13.8; **IR** (neat): *v* = 3150-2430, 1930, 1673, 1494, 1454, 1418, 1274, 1121 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 259 (M^++1, 1.27), 258 (M^+, 6.49), 129 (100); Anal. Calcd. for $C_{17}H_{22}O_2$: C 79.03, H

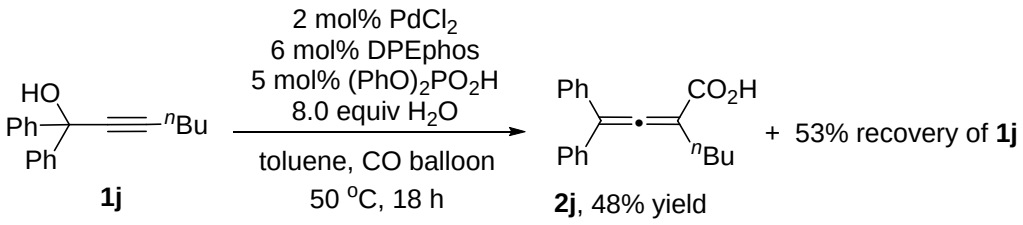
8.58; found C 79.01, H 8.45.

(9) Preparation of 2-butyl-4,5-diphenyl-2,3-pentadienoic acid (2i) (zwf-1-172)



Following Typical Procedure I, the reaction of $PdCl_2$ (4.0 mg, 0.02 mmol), DPEphos (34.2 mg, 0.06 mmol), $(PhO)_2PO_2H$ (13.1 mg, 0.05 mmol), **1i** (284.2 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2i** (232.1 mg, 74%) (18% of **1i** remained based ^{1}H NMR analysis of the crude product) [eluent: petroleum ether/ethyl acetate = 10/1 (220 mL), 5/1 (180 mL)]: white solid; m.p. 118.7-121.0 ^{o}C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.47-7.09 (m, 10 H, Ar-H), 3.90 (d, *J* = 15.6 Hz, 1 H, one proton of CH_2), 3.85 (d, *J* = 15.6 Hz, 1 H, one proton of CH_2), 2.23-2.10 (m, 2 H, CH_2), 1.48-1.15 (m, 4 H, 2 x CH_2), 0.84 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 213.5, 172.9, 138.0, 134.2, 128.9, 128.6, 128.3, 127.6,126.54, 126.47, 109.7, 103.3, 36.9, 30.2, 28.2, 22.3, 13.8; **IR** (neat): *v* = 3140-2430, 1942, 1686, 1598, 1494, 1455, 1419, 1283, 1250, 1186, 1121, 1075, 1005 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 307 (M^++1, 2.85), 306 (M^+, 12.61), 91 (100); Anal. Calcd. for $C_{21}H_{22}O_2$: C 82.32, H 7.24; found C 82.34, H 7.48.

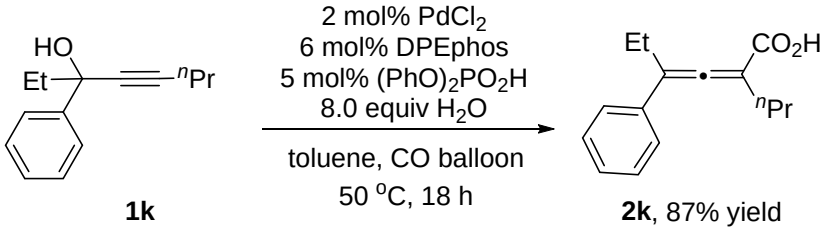
(10) Preparation of 2-butyl-4,4-diphenyl-2,3-butadienoic acid (2j) (hcf-2-144)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.7 mg, 0.02 mmol), DPEphos (32.3 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.5 mg, 0.05 mmol), **1j** (264.7 mg,

1.0 mmol)/toluene (3 mL), H_2O (146.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2j** (141.6 mg, 48%) (53% of **1j** remained based ^{1}H NMR analysis of the crude product) [eluent: petroleum ether/ethyl acetate = 15/1 (320 mL), 10/1 (330 mL)]: white solid; m.p. 99.5-100.4 ^{o}C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.74 (br, 1 H, COOH), 7.43-7.28 (m, 10 H, Ar-H), 2.40 (t, *J* = 7.8 Hz, 2 H, CH_2), 1.60-1.48 (m, 2 H, CH_2), 1.40-1.28 (m, 2 H, CH_2), 0.86 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 213.3, 172.5, 135.0, 128.63, 128.58, 128.0, 113.9, 102.8, 30.2, 28.5, 22.3, 13.8; **IR** (neat): *v* = 3150-2430, 1924, 1677, 1492, 1454, 1408, 1277, 1246, 1121, 1028 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 293 (M^++1, 2.10), 292 (M^+, 9.11), 205 (100); Anal. Calcd. for $C_{20}H_{20}O_2$: C 82.16, H 6.90; found C 81.95, H 6.98.

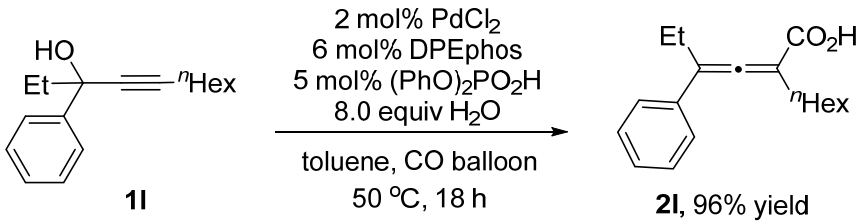
(11) Preparation of 2-propyl-4-phenyl-2,3-hexadienoic acid (2k) (hjh-1-025)



1k **2k**, 87% yield

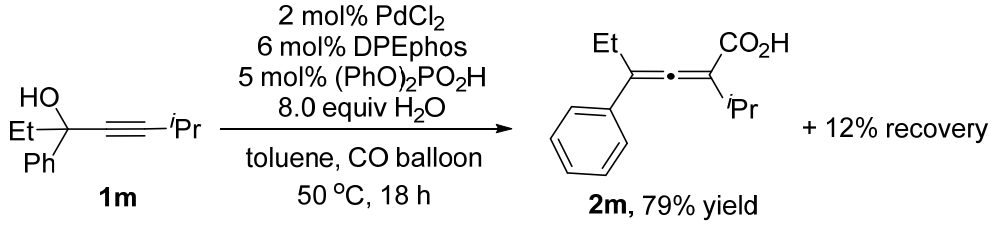
Following Typical Procedure I, the reaction of $PdCl_2$ (3.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.7 mg, 0.05 mmol), **1k** (202.8 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2k** (201.8 mg, 87%) [eluent: petroleum ether/ ethyl acetate = 5/1 (250 mL)]: white solid; m.p. 70.2-70.9 ^{o}C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42-7.28 (m, 4 H, Ar-H), 7.28-7.19 (m, 1 H, Ar-H), 2.56 (q, *J* = 7.3 Hz, 2 H, CH_2), 2.36-2.25 (m, 2 H, CH_2), 1.58-1.45 (m, 2 H, CH_2), 1.17 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.93 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.3, 173.5, 134.8, 128.5, 127.5, 126.3, 112.1, 103.6, 30.7, 23.2, 21.6, 13.8, 12.2; **IR** (neat): *v* = 3120-2400, 1937, 1673, 1493, 1455, 1418, 1293, 1269, 1121, 1062 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 231 (M^++1, 5.89), 230 (M^+, 34.18), 129 (100); Anal. Calcd. for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found C 78.00, H 7.96.

(12) Preparation of 2-hexyl-4-phenyl-2,3-hexadienoic acid (2l) (zwf-1-099)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.6 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.4 mg, 0.05 mmol), **1l** (244.0 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2l** (261.5 mg, 96%) [eluent: petroleum ether/ethyl acetate = 15/1 (320 mL), 5/1 (360 mL)]; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.28 (m, 4 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 2.56 (q, *J* = 7.2 Hz, 2 H, CH_2), 2.32 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.55-1.41 (m, 2 H, CH_2), 1.37-1.20 (m, 6 H, 3 x CH_2), 1.17 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.84 (t, *J* = 6.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.3, 173.4, 134.9, 128.5, 127.5, 126.3, 112.1, 103.7, 31.6, 29.0, 28.7, 28.2, 23.2, 22.6, 14.0, 12.3; **IR** (neat): *ν* = 3210-2430, 1938, 1677, 1494, 1454, 1413, 1275, 1091 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 273 (M^++1, 1.53), 272 (M^+, 8.54), 129 (100); **HRMS** calcd for $C_{18}H_{24}O_2$ [M^+]: 272.1776, found: 272.1779.

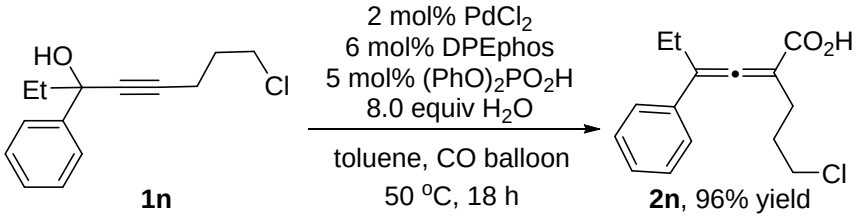
(13) Preparation of 2-isopropyl-4-phenyl-2,3-hexadienoic acid (2m) (zwf-1-171)



Following Typical Procedure I, the reaction of $PdCl_2$ (4.0 mg, 0.02 mmol), DPEphos (32.9 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.7 mg, 0.05 mmol), **1m** (217.9 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2m** (196.9 mg, 79%) (12% of **1m** remained based ^{1}H NMR analysis of the crude product) [eluent: petroleum ether/ ethyl acetate = 10/1 (220 mL), 5/1 (180 mL)]: white solid; m.p. 73.5-75.2 °C (petroleum ether/DCM); **^{1}H NMR** (400

MHz, $CDCl_3$): δ = 7.45-7.36 (m, 2 H, Ar-H), 7.36-7.27 (m, 2 H, Ar-H), 7.27-7.18 (m, 1 H, Ar-H), 2.81 (hept, *J* = 6.8 Hz, 1 H, CH), 2.56 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.17 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.14-1.05 (m, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.1, 173.0, 134.8, 128.6, 127.5, 126.1, 113.5, 110.5, 28.1, 23.1, 22.20, 22.16, 12.3; **IR** (neat): *v* = 3180-2410, 1936, 1672, 1494, 1452, 1417, 1275, 1042 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 231 (M^++1, 13.62), 230 (M^+, 79.61), 215 (100); Anal. Calcd. for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found C 78.25, H 7.95.

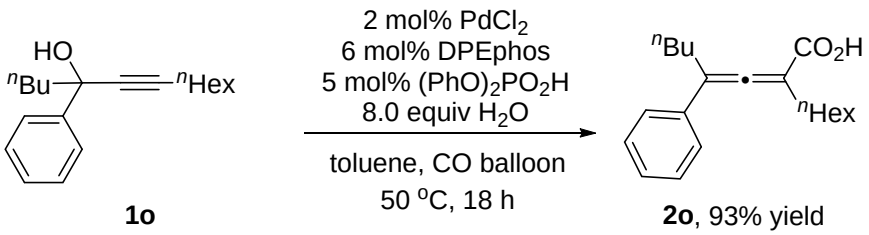
(14) Preparation of 2-(3-chloropropyl)-4-phenyl-2,3-hexadienoic acid 2-(3-chloropropyl)-4-phenylhexa-2,3-dienoic acid (2n) (zwf-1-122)



1n **2n**, 96% yield

Following Typical Procedure I, the reaction of $PdCl_2$ (3.8 mg, 0.02 mmol), DPEphos (32.2 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.9 mg, 0.05 mmol), **1n** (251.3 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/cm^3, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2n** (269.1 mg, 96%) [eluent: petroleum ether/ ethyl acetate = 15/1 (320 mL), 10/1 (660 mL)]: white solid; m.p. 88.5-88.8 °C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.41-7.31 (m, 4 H, Ar-H), 7.30-7.22 (m, 1 H, Ar-H), 3.54 (t, *J* = 6.6 Hz, 2 H, CH_2), 2.58 (qd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2 H, CH_2), 2.54-2.45 (m, 2 H, CH_2), 2.02-1.92 (m, 2 H, CH_2), 1.17 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.2, 173.0, 134.4, 128.6, 127.8, 126.3, 112.9, 102.2, 44.2, 31.0, 26.1, 23.3, 12.2; **IR** (neat): *v* = 3120-2420, 1939, 1670, 1493, 1457, 1416, 1287, 1096, 1037 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 266 (M^+(^{37}Cl) 2.86), 264 (M^+(^{35}Cl) 8.71), 129 (100); Anal. Calcd. for $C_{15}H_{17}ClO_2$: C 68.05, H 6.47; found C 68.08, H 6.55.

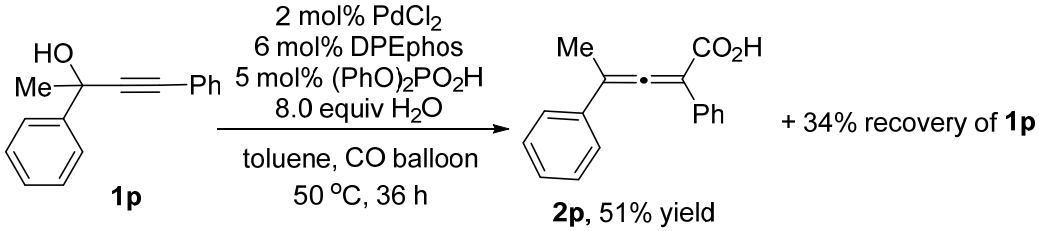
(15) Preparation of 2-hexyl-4-phenyl-2,3-octadienoic acid (2o) (hjh-1-023)



1o **2o**, 93% yield

Following Typical Procedure I, the reaction of $PdCl_2$ (3.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.6 mg, 0.05 mmol), **1o** (272.0 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded **2o** (295.6 mg, 93%, 94% purity) [eluent: petroleum ether/ethyl acetate = 5/1 (120 mL), 2/1 (60 mL)]: white solid; m.p. 70.0-70.6 ^oC (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45-7.28 (m, 4 H, Ar-H), 7.28-7.17 (m, 1 H, Ar-H), 2.53 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.32 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.62-1.37 (m, 6 H, 3 x CH_2), 1.37-1.18 (m, 6 H, 3 x CH_2), 0.93 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.89-0.77 (m, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.4, 173.3, 134.9, 128.5, 127.4, 126.4, 110.3, 102.9, 31.6, 29.83, 29.80, 29.0, 28.7, 28.2, 22.6, 22.4, 14.0, 13.9; **IR** (neat): *v* = 3120-2440, 1934, 1672, 1494, 1454, 1413, 1376, 1270, 1219 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 301 (M^++1, 1.84), 300 (M^+, 8.03), 129 (100); Anal. Calcd. for $C_{20}H_{28}O_2$: C 79.96, H 9.39; found C 79.93, H 9.32.

(16) Preparation of 2-phenyl-4-phenyl-2,3-pentadienoic acid (2p) (zwf-1-165)

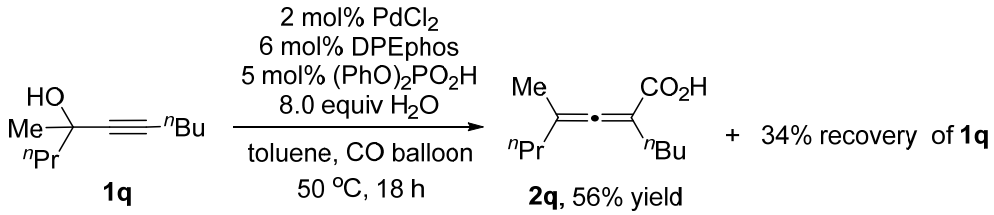


1p **2p**, 51% yield

Following Typical Procedure I, the reaction of $PdCl_2$ (4.0 mg, 0.02 mmol), DPEphos (33.1 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.3 mg, 0.05 mmol), **1p** (226.1 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/cm^3, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded product **2p** (129.6 mg, 51%) (34% of **1p** remained based ^{1}H NMR analysis of the crude product) [eluent: petroleum ether (b.p. 60-90 ^oC)/ ethyl acetate = 10/1 (220 mL), 5/1 (240 mL)]: white solid; m.p. 156.3-159.4 ^oC (petroleum

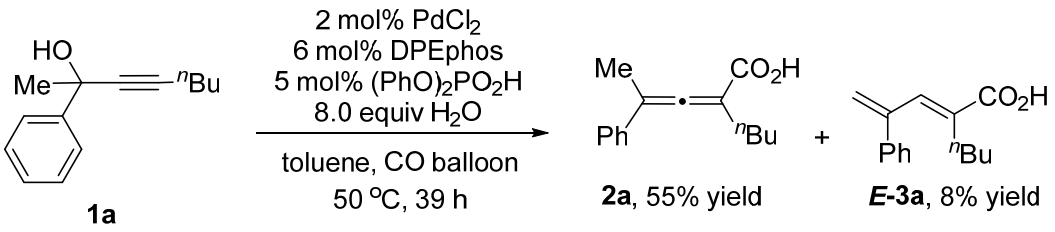
ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59-7.51 (m, 2 H, Ar-H), 7.48-7.42 (m, 2 H, Ar-H), 7.38-7.22 (m, 6 H, Ar-H), 2.29 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 215.3, 171.9, 134.0, 132.4, 128.7, 128.5, 128.3, 128.0, 127.8, 126.2, 106.5, 104.0, 16.2; **IR** (neat): *v* = 3160-2460, 1929, 1677, 1491, 1459, 1444, 1290, 1202, 1023 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 250 (M^+, 72.42), 207 (100); **HRMS** calcd for $C_{17}H_{14}O_2$ [M^+]: 250.0994, found: 250.0993.

(17) Preparation of 2-butyl-4-propyl-2,3-pentadienoic acid (2q) (zwf-1-173)



Following Typical Procedure I, the reaction of $PdCl_2$ (3.9 mg, 0.02 mmol), DPEphos (34.0 mg, 0.06 mmol), $(PhO)_2PO_2H$ (12.4 mg, 0.05 mmol), **1q** (178.1 mg, 1.0 mmol)/toluene (3 mL), H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0 mmol), and toluene (2 mL) afforded a mixture of **2q** (52% NMR yield), and 34% recovery of **1q**, which were determined by ^{1}H NMR analysis of the crude product, which was purified by chromatography on silica gel to afford the pure product **2q** (117.4 mg, 56%) [eluent: petroleum ether/diethyl ether/DCM = 30/1/1 (960 mL)]: white solid; m.p. 43.2-44.5 °C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.25-2.10 (m, 2 H, CH_2), 2.04 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.77 (s, 3 H, CH_3), 1.54-1.27 (m, 6 H, 3 x CH_2), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.90 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.9, 174.1, 104.0, 99.1, 35.5, 30.4, 28.2, 22.2, 20.5, 17.9, 13.9, 13.7; **IR** (neat): *v* = 3230-2460, 1956, 1675, 1416, 1274, 1107 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 196 (M^+, 5.60), 69 (100); Anal. Calcd. for $C_{12}H_{20}O_2$: C 73.43, H 10.27; found C 73.29, H 10.22.

2. (1) Preparation of 2-butyl-4-phenyl-2,3-pentadienoic acid (2a) and (*E*)-2-butyl-4-phenyl-2,4-pentadienoic acid (*E*-3a) (qh-2-068-1)

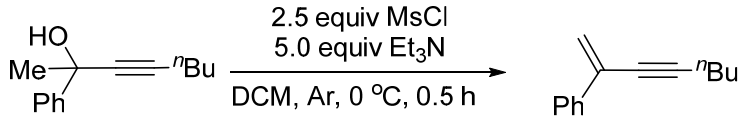


*The purpose of this large scale reaction is to isolate the byproduct **E-3a** and confirm its structure. So the reaction was conducted at a very low stirring rate via a longer reaction time.*

To a Schlenk flask (100 mL) were added $PdCl_2$ (36.6 mg, 0.2 mmol), DPEphos (323.1 mg, 0.6 mmol), and $(PhO)_2PO_2H$ (126.4 mg, 0.5 mmol). After the addition of each chemical, the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then **1a** (2.0277 g, 10.0 mmol)/toluene (30 mL), H_2O (1.5 mL, d = 1.0 g/mL, 1.5 g, 80.0 mmol), and toluene (20 mL) were added sequentially. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO (about 1 L) for three times. Then the liquid nitrogen bath was removed and the mixture was warmed up to room temperature and the resulting mixture was vigorously stirred at 50 ^oC with a balloon of CO for 39 h. After that, the resulting mixture was diluted with 20 mL of ethyl acetate and then filtered through a short column silica gel (3 cm), eluted with ethyl acetate (80 mL), and concentrated. The residue was purified by chromatography on silica gel to afford **2a** (1.2675 g, 55%) and **3a** (190.4 mg, 8%) [eluent: petroleum ether/diethyl ether/ DCM = 5/1/1 (420 mL), 3.75/1/1 (460 mL), 2.5/1/1 (360 mL)]: **2a**: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.83 (br, 1 H, COOH), 7.42-7.28 (m, 4 H, Ar-H), 7.27-7.22 (m, 1 H, Ar-H), 2.32 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.19 (s, 3 H, CH_3), 1.54-1.41 (m, 2 H, CH_2), 1.40-1.28 (m, 2 H, CH_2), 0.88 (t, *J* = 7.6 Hz, 3 H, CH_3); ***E*-3a**: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.36 (br, 1 H, COOH), 7.55 (s, 1 H, =CH), 7.45-7.23 (m, 5 H, Ar-H), 5.70 (s, 1 H, =CH), 5.34 (s, 1 H, =CH), 2.33 (t, *J* = 7.8 Hz, 2 H, CH_2), 1.50-1.35 (m, 2 H, CH_2), 1.30-1.20 (m, 2 H, CH_2), 0.83 (t, *J* = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 174.1, 143.9, 141.1, 139.3, 134.8, 128.4, 128.0, 126.5, 117.5, 31.6, 27.2, 22.8,

13.8; **IR** (neat): v = 3260-2745, 1680, 1621, 1494, 1414, 1262, 1212, 1145, 1062, 1027 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 231 (M^+, 1.97), 230 (M^+, 11.38), 143 (100); **HRMS** calcd for $C_{15}H_{18}O_2$ [M^+]: 230.1307, found: 230.1308.

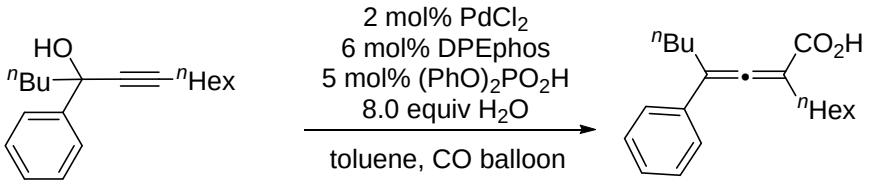
(2) Preparation of 2-phenyl-3-yn-1-octene (4a)[1] (zwf-2-076)



1a, 2 mmol — **4a**, 84% yield

To a Schlenk flask (25 mL) were added **1a** (403.2 mg, 0.2 mmol) and DCM (2 mL) at 0 °C under argon. Then methanesulfonyl chloride (386 uL, d = 1.48 g/mL, 572.8 mg, 5 mmol) and triethylamine (1.39 mL, d = 0.728 g/mL, 1012 mg, 10 mmol) were added at 0 °C sequentially. After stirring for 0.5 h at 0 °C, the reaction was quenched with a saturated aqueous solution of NH_4Cl (2 mL). After extraction with ethyl ether (2 mL x 3), the organic layer was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. The residue was then purified by column chromatography on aluminum oxide to afford **4a**[1] (319.8 mg, 84%, 97% purity) [eluent: petroleum ether]: oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60-7.52 (m, 2 H, Ar-H), 7.45-7.18 (m, 3 H, Ar-H), 5.84 (s, 1 H, one proton of $=CH_2$), 5.58 (s, 1 H, one proton of $=CH_2$), 2.41 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.67-1.53 (m, 2 H, CH_2), 1.53-1.40 (m, 2 H, CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 137.8, 130.9, 128.2, 128.1, 126.0, 119.3, 92.0, 79.6, 30.8, 22.0, 19.1, 13.6.

3. Gram scale synthesis of 2-hexyl-4-phenyl-2,3-octadienoic acid (2o) (zwf-1-164)



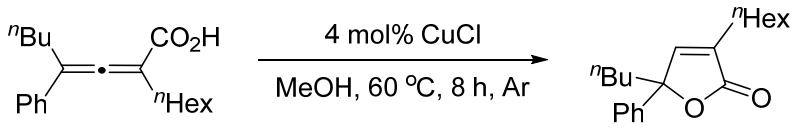
1o — **2o**, 92% yield

To a Schlenk flask (100 mL) were added $PdCl_2$ (18.2 mg, 0.1 mmol), DPEphos (162.9 mg, 0.3 mmol), and $(PhO)_2PO_2H$ (63.2 mg, 0.25 mmol). After the addition of

each chemical, the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Compound **1o** (1.3680 g, 5.0 mmol)/toluene (15 mL), H_2O (720 uL, d = 1.0 g/mL, 720.0 mg, 40.0 mmol), and toluene (10 mL) were added sequentially. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO (about 1 L) for three times. Then the liquid nitrogen bath was removed and the mixture was warmed up to room temperature and the resulting mixture was vigorously stirred at 50 ^oC with a balloon of CO for 24 h. After that, the resulting mixture was diluted with 20 mL of ethyl acetate and then filtered through a short column silica gel (3 cm), eluted with ethyl acetate (80 mL), and concentrated. The residue was purified by chromatography on silica gel to afford **2o** (1.4371 g, 92%, purity: 96%) [eluent: petroleum ether/ethyl acetate = 10/1 (220 mL), 5/1 (480 mL)]: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.28 (m, 4 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 2.53 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.32 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.65-1.37 (m, 6 H, 3 x CH_2), 1.37-1.16 (m, 6 H, 3 x CH_2), 0.93 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.84 (t, *J* = 6.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.4, 173.3, 134.9, 128.5, 127.4, 126.4, 110.3, 102.9, 31.6, 29.83, 29.80, 29.0, 28.7, 28.2, 22.6, 22.4, 14.0, 13.9.

4. Synthetic applications:

(1) Preparation of 5-butyl-3-hexyl-5-phenyl-furan-2(5*H*)-one (5) (zwf-1-186)[4]

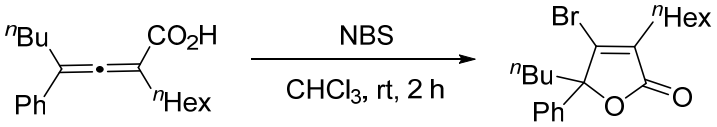


2o **5**, 93% yield

To an oven-dried Schlenk flask (25 mL) were added **2o** (150.9 mg, 0.5 mmol) and CuCl (2.0 mg, 0.02 mmol), and MeOH (5 mL, injected by syringe) under Argon. The resulting mixture was vigorously stirred at 60 ^oC for 8 h as monitored by TLC. After evaporation, the residue was diluted with 5 mL of ethyl acetate, filtered through a short column silica gel (3 cm), eluted with ethyl acetate (15 mL), and concentrated. The residue was purified by chromatography on silica gel to afford **5** (142.8 mg, 93%,

purity: 98%) [eluent: petroleum ether/ethyl acetate = 20/1 (220 mL)]: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.24 (m, 5 H, Ar-H), 7.21 (s, 1 H, =CH), 2.36-2.18 (m, 2 H, CH_2), 2.18-2.03 (m, 1 H, one proton of CH_2), 1.98-1.84 (m, 1 H, one proton of CH_2), 1.63-1.45 (m, 2 H, CH_2), 1.41-1.08 (m, 10 H, 5 x CH_2), 0.95-0.76 (m, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 173.2, 151.2, 139.9, 132.8, 128.5, 127.7, 124.8, 89.1, 39.7, 31.3, 28.7, 27.2, 25.7, 25.0, 22.49, 22.38, 13.9, 13.7; **IR** (neat): ν = 2956, 2928, 2859, 1749, 1448, 1217, 1121, 1073, 1026 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 300 (M^+, 2.46), 243 (100); **HRMS** calcd for $C_{20}H_{28}O_2$ [M^+]: 300.2089, found: 300.2093.

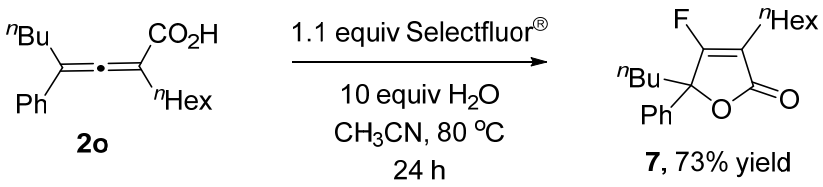
(2) Preparation of 4-bromo-5-butyl-3-hexyl-5-phenyl-furan-2(5*H*)-one (6) (zwf-1-187)



2o **6**, 90% yield

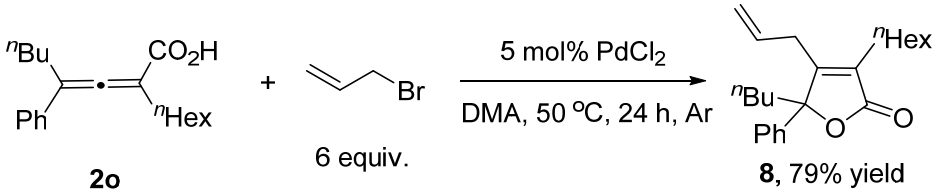
To a Schlenk flask (25 mL) were added **2o** (151.6 mg, 0.5 mmol), NBS (109.7 mg, 0.6 mmol), and $CHCl_3$ (5 mL) sequentially. The resulting mixture was vigorously stirred at room temperature for 2 h as monitored by TLC. After evaporation, the residue was purified by chromatography on silica gel to afford **6** (176.6 mg, 90%, purity: 97%) [eluent: petroleum ether/ethyl acetate = 20/1 (220 mL)]: white solid; m.p. 56.5-57.7 ^{o}C (petroleum ether/DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48-7.27 (m, 5 H, Ar-H), 2.42-2.24 (m, 3 H, CH_2 and one proton of CH_2), 2.22-2.08 (m, 1 H, one proton of CH_2), 1.65-1.48 (m, 2 H, CH_2), 1.44-1.13 (m, 10 H, CH_2), 0.99-0.78 (m, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.7, 149.4, 137.2, 131.7, 128.5, 125.4, 90.3, 35.6, 31.3, 28.7, 26.8, 25.1, 24.8, 22.42, 22.40, 13.9, 13.8; **IR** (neat): ν = 2928, 2859, 1759, 1650, 1448, 1267, 1111, 1071, 1038 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 380 (M^+(^{81}Br), 3.09), 378 (M^+(^{79}Br), 2.98), 321 (100); Anal. Calcd. for $C_{20}H_{27}BrO_2$: C 63.33, H 7.17; found C 63.31, H 7.20.

(3) Preparation of 5-butyl-4-fluoro-3-hexyl-5-phenyl-furan-2(5*H*)-one (7) (zwf-2-009)[5]



To a Schlenk flask (25 mL) were added **2o** (150.2 mg, 0.5 mmol), CH_3CN (5 mL), H_2O (90 uL, d = 1.0 g/mL, 90 mg, 5.0 mmol), and Selectfluor (195.0 mg, 0.55 mmol) sequentially. The resulting mixture was vigorously stirred at 80 °C for 24 h as monitored by TLC. The resulting mixture was quenched with 5 mL of H_2O and extracted with 5 x 3 mL of Et_2O. The combined organic layer was washed with an aqueous saturated solution of NaCl, dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by chromatography on silica gel to afford **7** (118.3 mg, 73%, purity: 99%) [eluent: petroleum ether/diethyl ether/DCM = 50/1/1 (208 mL)]: pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55-7.42 (m, 2 H, Ar-H), 7.42-7.28 (m, 3 H, Ar-H), 2.32-2.17 (m, 3 H, CH_2 and one proton of CH_2), 2.16-1.97 (m, 1 H, one proton of CH_2), 1.64-1.48 (m, 2 H, CH_2), 1.42-1.17 (m, 10 H, CH_2), 0.96-0.76 (m, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 176.6 (d, *J* = 298.3 Hz), 170.7 (d, *J* = 23.6 Hz), 137.3 (d, *J* = 3.0 Hz), 128.7, 128.5, 124.7 (d, *J* = 1.5 Hz), 108.0 (d, *J* = 6.8 Hz), 84.6 (d, *J* = 20.5 Hz), 36.8 (d, *J* = 2.3 Hz), 31.2, 28.7, 26.8 (d, *J* = 2.3 Hz), 25.3, 22.39, 22.34, 21.3 (d, *J* = 2.3 Hz), 13.9, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -110.9; **IR** (neat): *v* = 2929, 2860, 1772, 1715, 1495, 1449, 1353, 1273, 1140, 1104, 1054 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 318 (M^+, 2.30), 261 (100); **HRMS** calcd for $C_{20}H_{27}FO_2$ [M^+]: 318.1995, found: 318.1992.

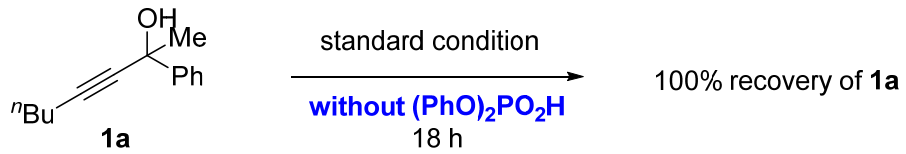
(4) Preparation of 4-allyl-5-butyl-3-hexyl-5-phenyl-furan-2(5*H*)-one (8) (zwf-1-191)[6]



To an oven-dried Schlenk flask (25 mL) were added **2o** (150.6 mg, 0.5 mmol) and $PdCl_2$ (4.8 mg, 0.025 mmol). Then the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air. DMA (3 mL) and allyl bromide (260 uL, d = 1.398 g/mL, 363.5 mg, 3.0 mmol) were added by syringe under a flow of argon. The resulting mixture was vigorously stirred at 50 ^oC for 24 h as monitored by TLC. The resulting mixture was quenched with 5 mL of H_2O and extracted with 5 x 3 mL of Et_2O. The combined organic layer was washed with aqueous saturated NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford **8** (139.0 mg, 79%, purity: 97%) [eluent: petroleum ether/diethyl ether/DCM = 50/1/1 (318 mL)]: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42-7.26 (m, 5 H, Ar-H), 5.52-5.36 (m, 1 H, =CH), 5.08-4.91 (m, 2 H, $=CH_2$), 3.03-2.84 (m, 2 H, CH_2), 2.39-2.22 (m, 3 H, CH_2 and one proton of CH_2), 2.12-1.96 (m, 1 H, one proton of CH_2), 1.62-1.44 (m, 2 H, CH_2), 1.42-1.12 (m, 10 H, CH_2), 0.97-0.76 (m, 6 H, 2 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 174.1, 163.2, 138.2, 132.2, 128.5, 128.0, 127.8, 125.3, 117.6, 90.2, 34.9, 31.4, 30.6, 29.1, 27.9, 25.1, 23.7, 22.6, 22.4, 13.9, 13.8; **IR** (neat): *v* = 2928, 2859, 1748, 1667, 1495, 1447, 1184, 1092, 1050 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 341 (M^++1, 1.31), 340 (M^+, 5.36), 283 (100); **HRMS** calcd for $C_{23}H_{32}O_2$ [M^+]: 340.2402, found: 340.2405.

5. Mechanistic studies:

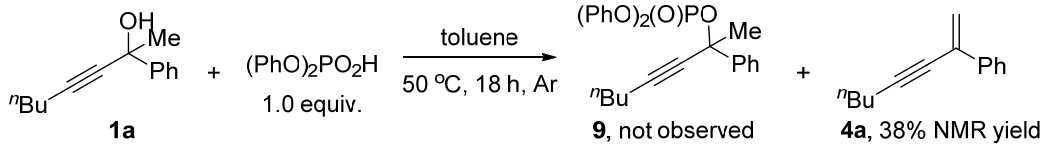
(1) The reaction without $(PhO)_2PO_2H$ (hjh-1-037)



To a Schlenk flask (25 mL) were added $PdCl_2$ (1.8 mg, 0.01 mmol), and DPEphos (16.3 mg, 0.03 mmol). After addition of each chemical, the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then **1a** (101.3 mg, 0.5 mmol)/toluene (1.5 mL), H_2O (72 uL, d = 1.0 g/mL, 72.0 mg, 4.0 mmol), and toluene (1 mL) were added sequentially. The resulting mixture was then frozen with a

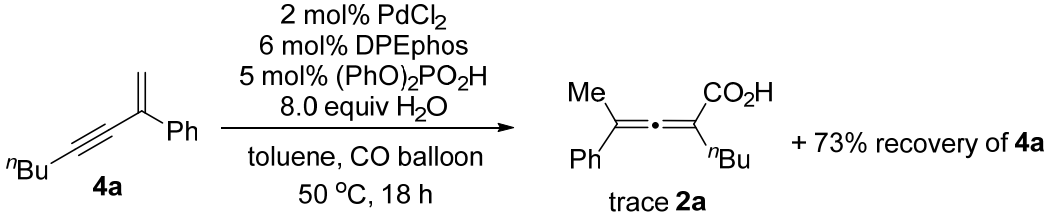
liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO (about 1 L) for three times. Then the liquid nitrogen bath was removed and the mixture was warmed up to room temperature. Then the resulting mixture was vigorously stirred at 50 °C with a balloon of CO for 18 h. After that, the resulting mixture was diluted with 5 mL of ethyl acetate, filtered through a short column silica gel (3 cm) eluted with ethyl acetate (20 mL), and concentrated. The crude product was analyzed by ^{1}H NMR with CH_2Br_2 (17.5 μL) as the internal standard. 100% of **1a** was recovered and no desired product **2a** was obtained.

(2) Preparation of diphenyl (2-phenyloct-3-yn-2-yl) phosphate 9. (zwf-2-168)



To a Schlenk flask (25 mL) were added **1a** (101.1 mg, 0.5 mmol), $(PhO)_2POOH$ (127.2 mg, 0.5 mmol) and toluene (2.5 mL). The resulting mixture was vigorously stirred under argon at 50 °C for 18 h as monitored by TLC. After that, the resulting mixture was diluted with 3 mL of ethyl acetate and then filtered through a short column silica gel (2 cm), eluted with EA (15 mL), and concentrated. The ^{1}H NMR and TLC analysis of the crude product showed no phosphate **9** was formed, instead, 38% of **4a** was formed.

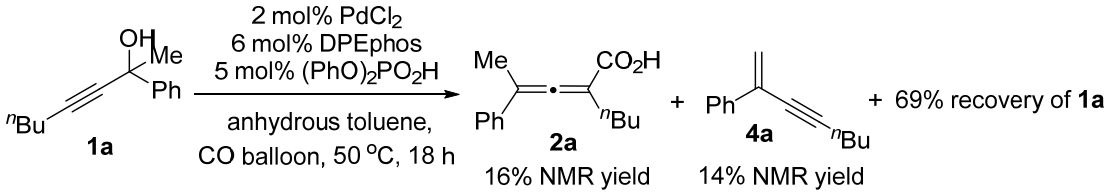
(3) Preparation of 2-butyl-4-phenyl-2,3-pentadienoic acid (2a) from 2-phenyl-3-yn-1-octene (4a) (zwf-2-171)



Following Typical Procedure III, the reaction of $PdCl_2$ (3.9 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol) and $(PhO)_2PO_2H$ (12.5 mg, 0.05 mmol), **4a** (182.1 mg, 1.0 mmol)/toluene (3 mL) and H_2O (144 uL, d = 1.0 g/mL, 144.0 mg, 8.0

mmol)/toluene (2 mL) afforded trace **2a** (If any, less than 3% NMR yield.) and 73% recovery of **4a**.

(4) Preparation of 2-butyl-4-phenyl-2,3-pentadienoic acid 2a in anhydrous toluene. (hjh-1-015B)



Following Typical Procedure III, the reaction of $PdCl_2$ (2.0 mg, 0.01 mmol), DPEphos (16.5 mg, 0.03 mmol) and $(PhO)_2PO_2H$ (6.4 mg, 0.025mmol), **1a** (101.0 mg, 0.5 mmol)/anhydrous toluene (2.5 mL) afforded **2a** in 16% NMR yield, **4a** in 14% NMR yield and 69% recovery of **1a**.

References:

1. Zhang, W.; Huang, C.; Yuan, Y.; Ma, S. *Chem. Commun.* **2017**, *53*, 12430.

2. Zhang, H.; Tanimoto, H.; Morimoto, T.; Nishiyama, Y.; Kakiuchi K. *Org. Lett.* **2013**, *15*, 5222.

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4. Ma, S.; Yu, Z.; Wu, S. *Tetrahedron* **2001**, *57,* 1585.

5. Zhou, C.; Ma, Z.; Gu, Z.; Fu, C.; Ma, S. *J. Org. Chem.* **2008**, *73,* 772.

6. Ma, S.; Yu, Z. *J. Org. Chem.* **2003**, *68,* 6149.

zwf-2-119-H
Jan 18 2018
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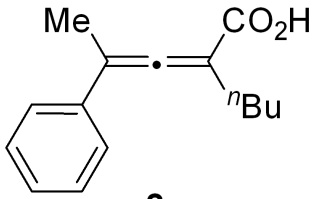
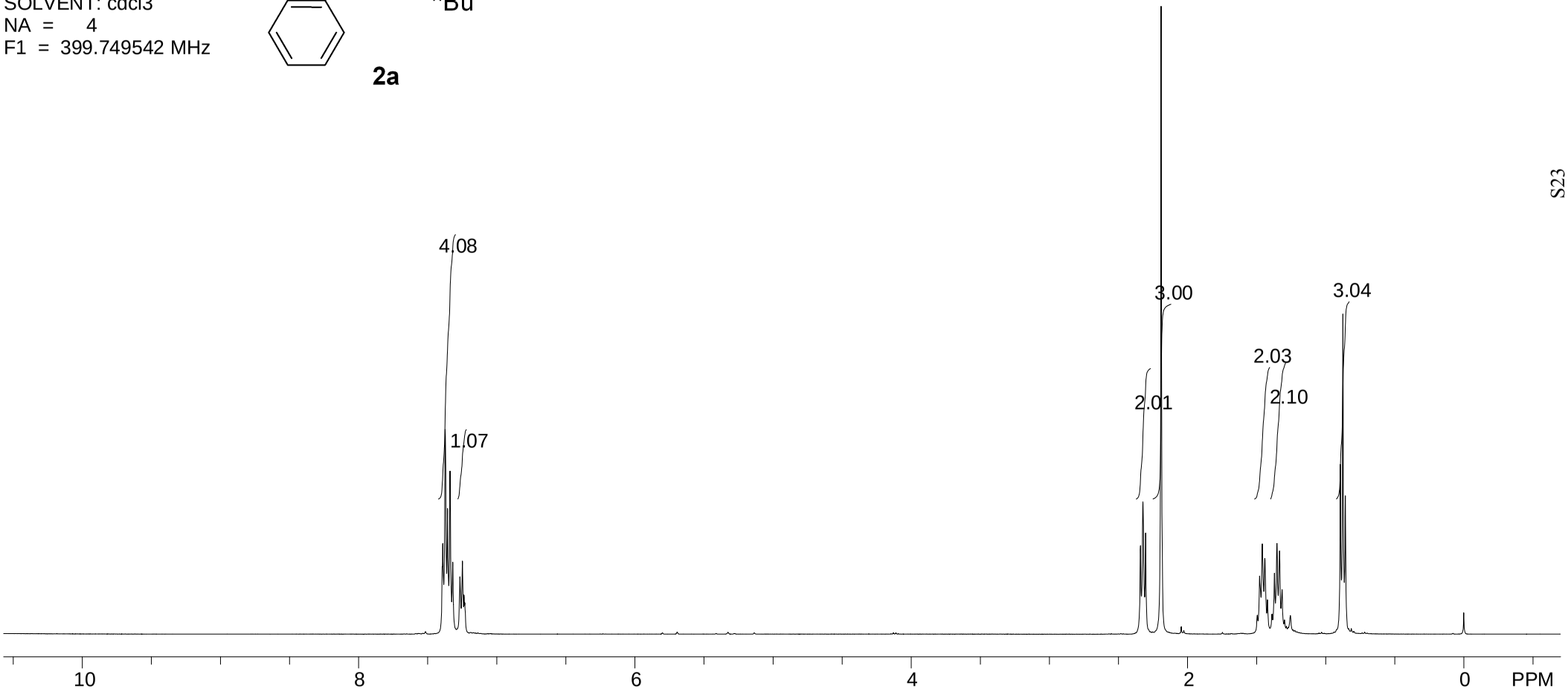
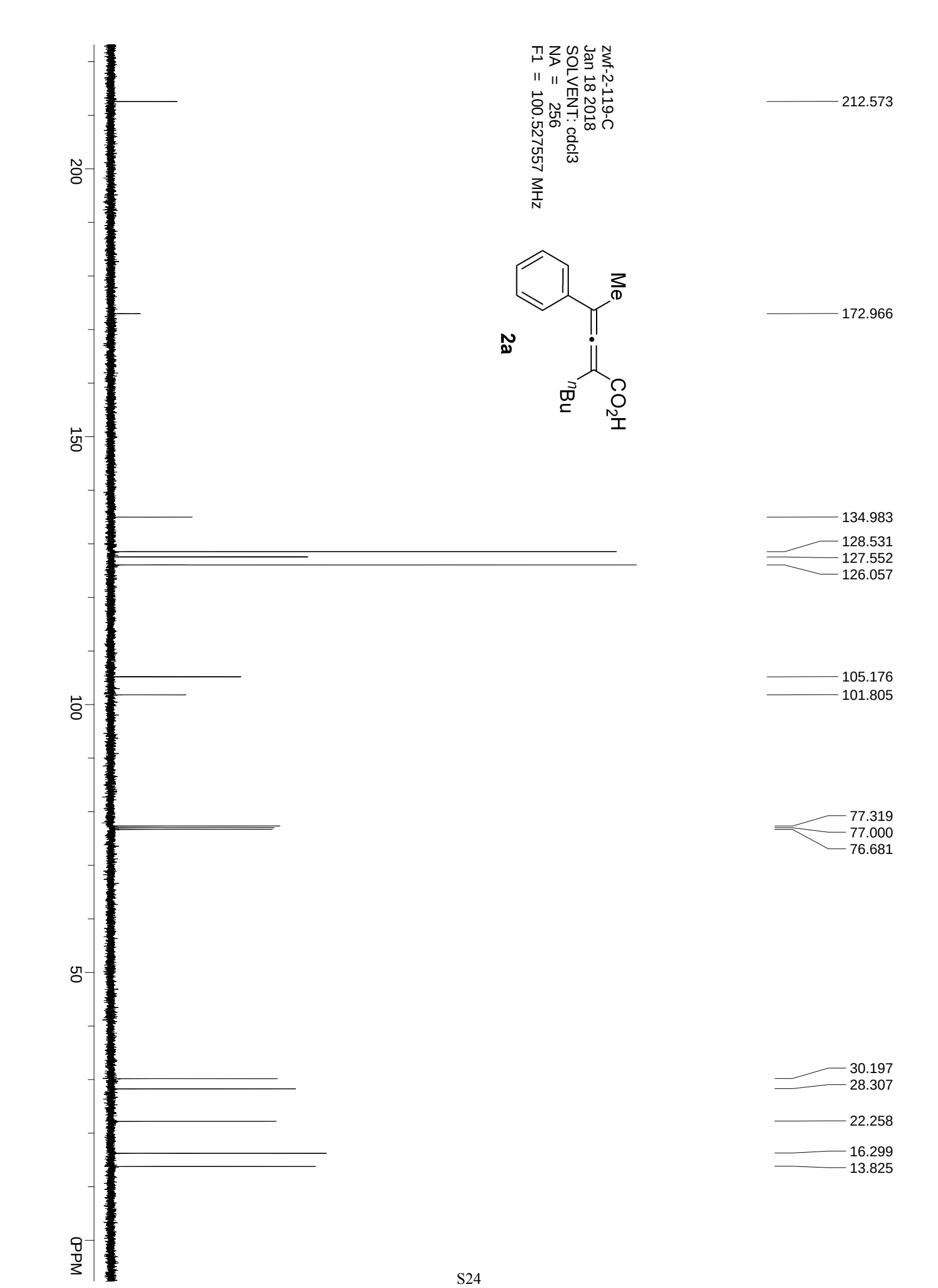
NA = 4
F1 = 399.749542 MHz



2a




zwf-2-119-C
Jan 18 2018
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
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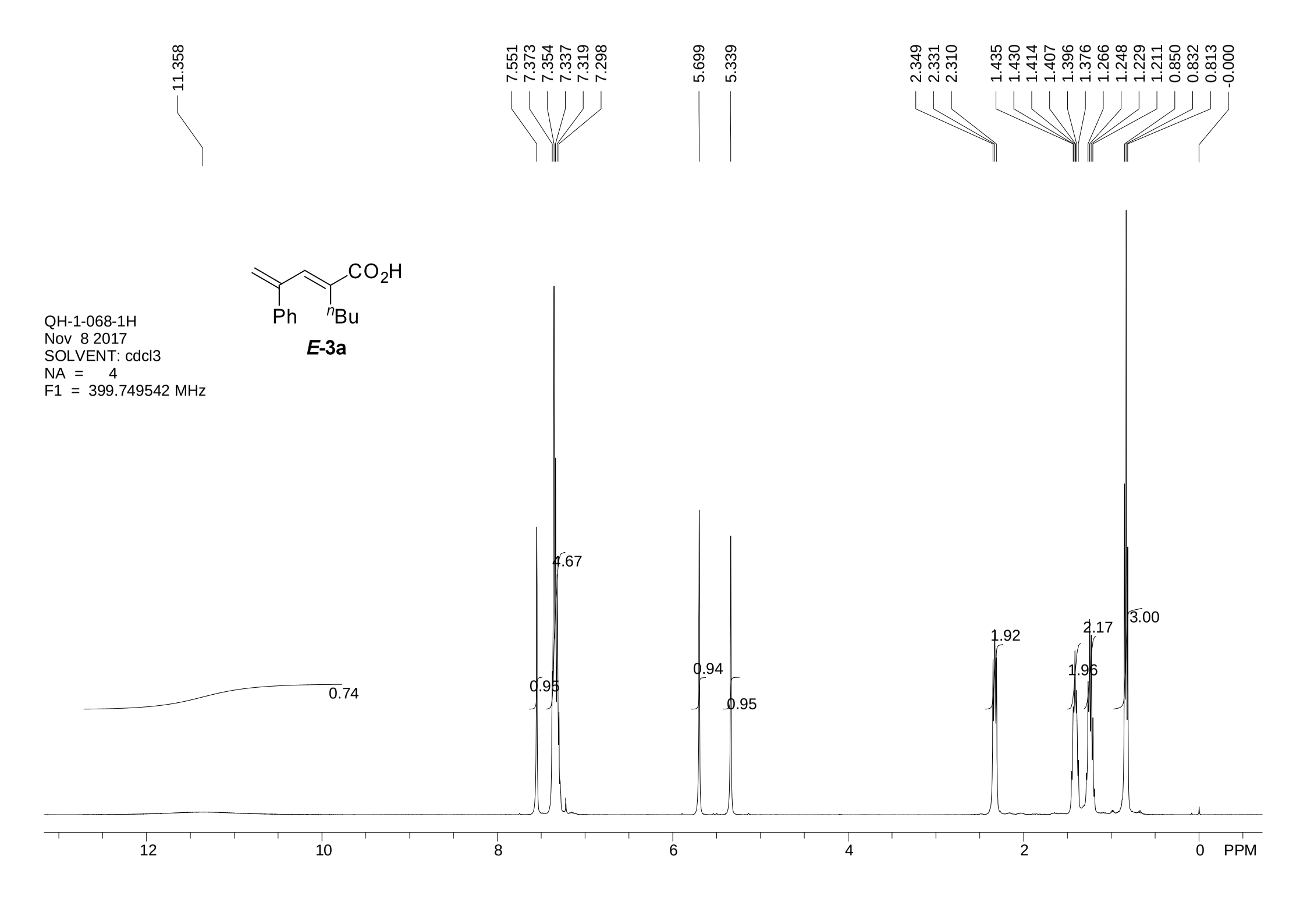
^{n}Bu
CO_2H
2a
212.573
172.966
134.983
128.531
127.552
126.057
105.176
101.805
77.319
77.000
76.681
30.197
28.307
22.258
16.299
13.825
200
150
100
50
0PPM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7.551
7.373
7.354
7.337
7.319
7.298
5.699
5.339
2.349
2.331
2.310
1.435
1.430
1.414
1.407
1.396
1.376
1.266
1.248
1.229
1.211
0.850
0.832
0.813
-0.000
CO2H
Ph
nBu
E-3a
QH-1-068-1H
Nov 8 2017
SOLVENT: cdcl3
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F1 = 399.749542 MHz
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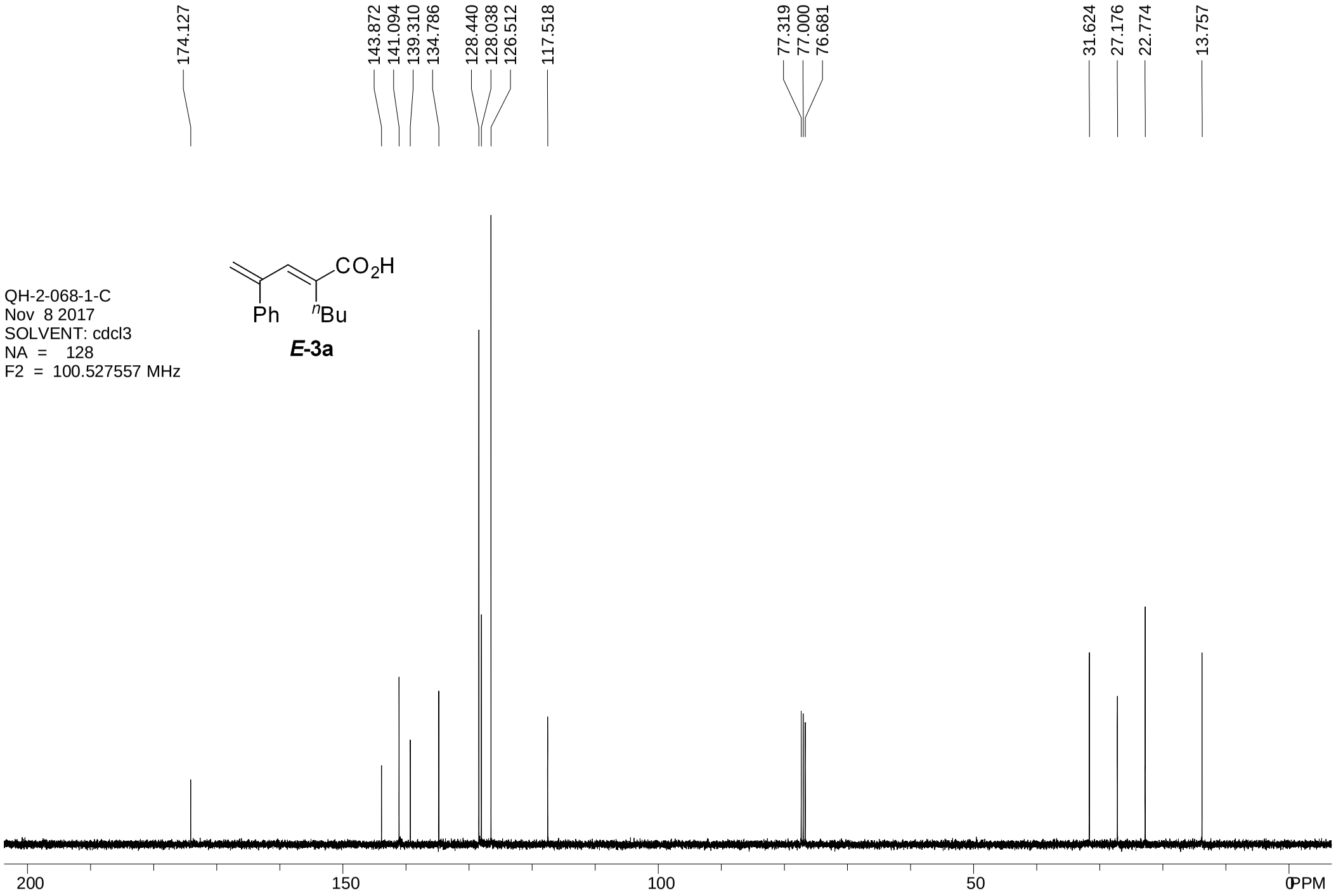
0.95
4.67
0.94
0.95
1.92
1.96
2.17
3.00
12
10
8
6
4
2
0
PPM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139.310
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128.038
126.512
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77.000
76.681
31.624
27.176
22.774
13.757
CO2H
Ph
nBu
E-3a
QH-2-068-1-C
Nov 8 2017
SOLVENT: cdcl3
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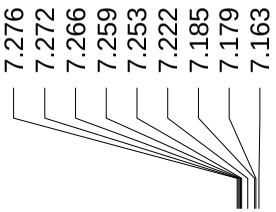
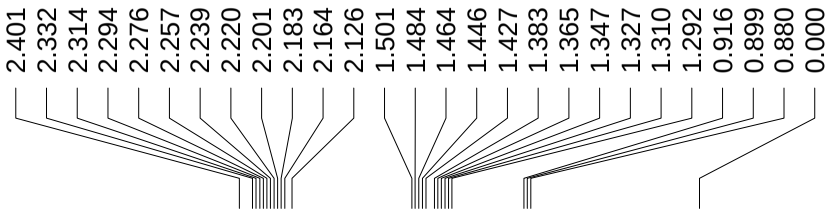
F2 = 100.527557 MHz
200
150
100
50
0
PPM





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Oct 3 2017
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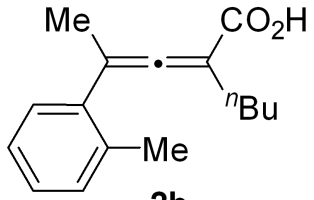
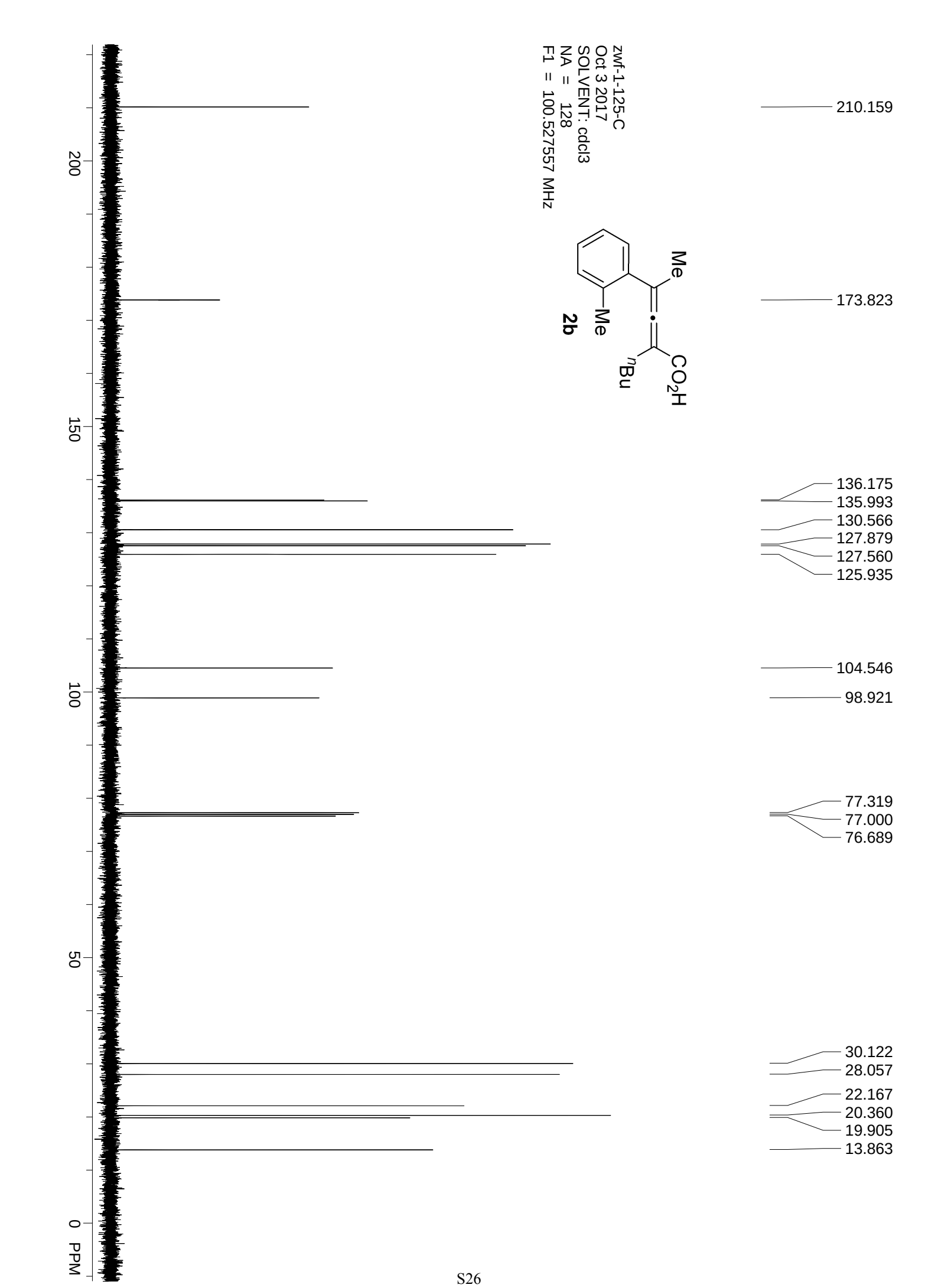
F1 = 399.749542 MHz



2b


zwf-1-125-C
Oct 3 2017
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
Me
Me
2b
nBu
CO2H
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173.823
136.175
135.993
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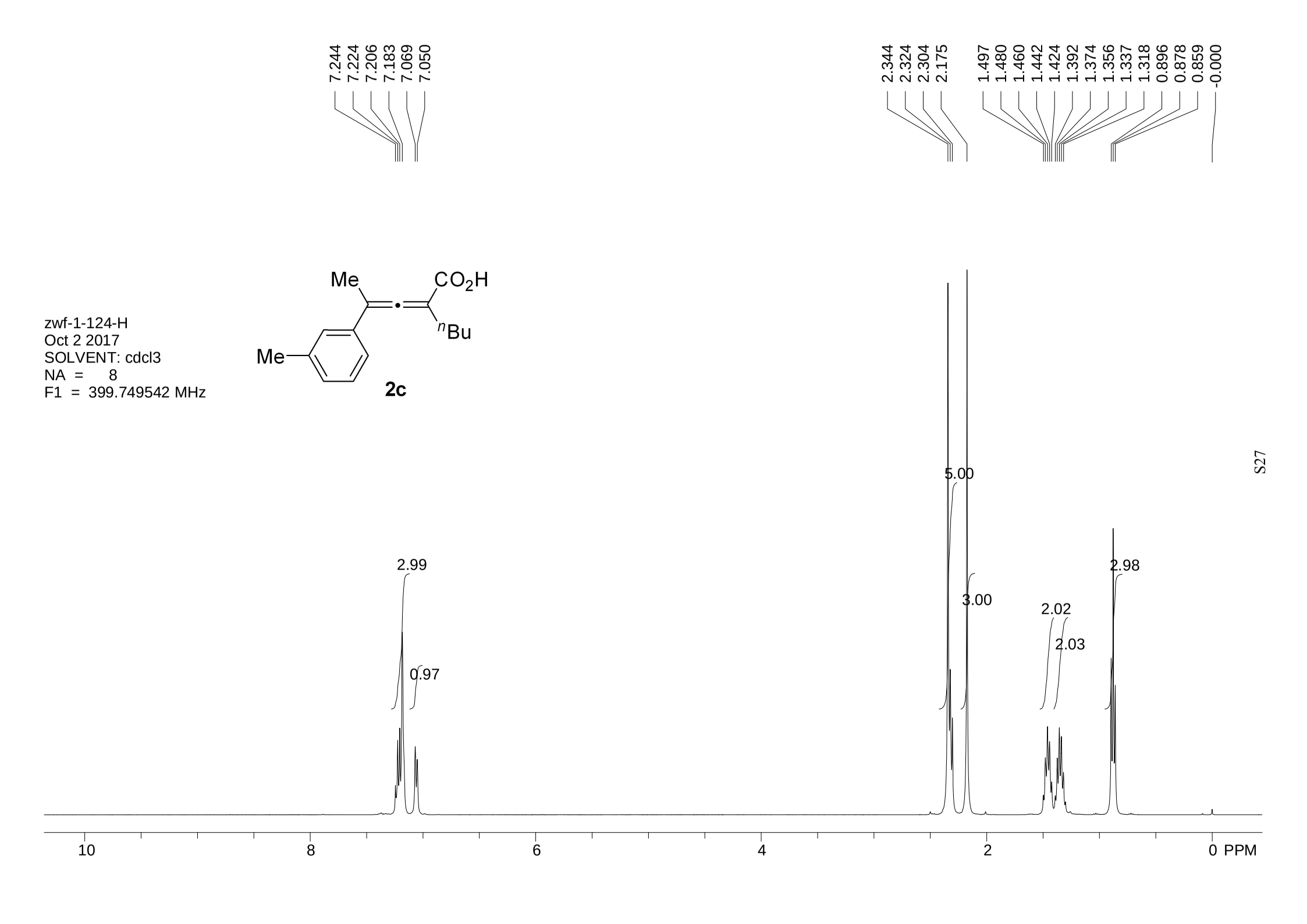
127.560
125.935
104.546
98.921
77.319
77.000
76.689
30.122
28.057
22.167
20.360
19.905
13.863
200
150
100
50
0
PPM


7.244
7.224
7.206
7.183
7.069
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2.324
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1.392
1.374
1.356
1.337
1.318
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-0.000
zwf-1-124-H
Oct 2 2017
SOLVENT: cdcl3
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F1 = 399.749542 MHz
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CO2H
nBu
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3.00
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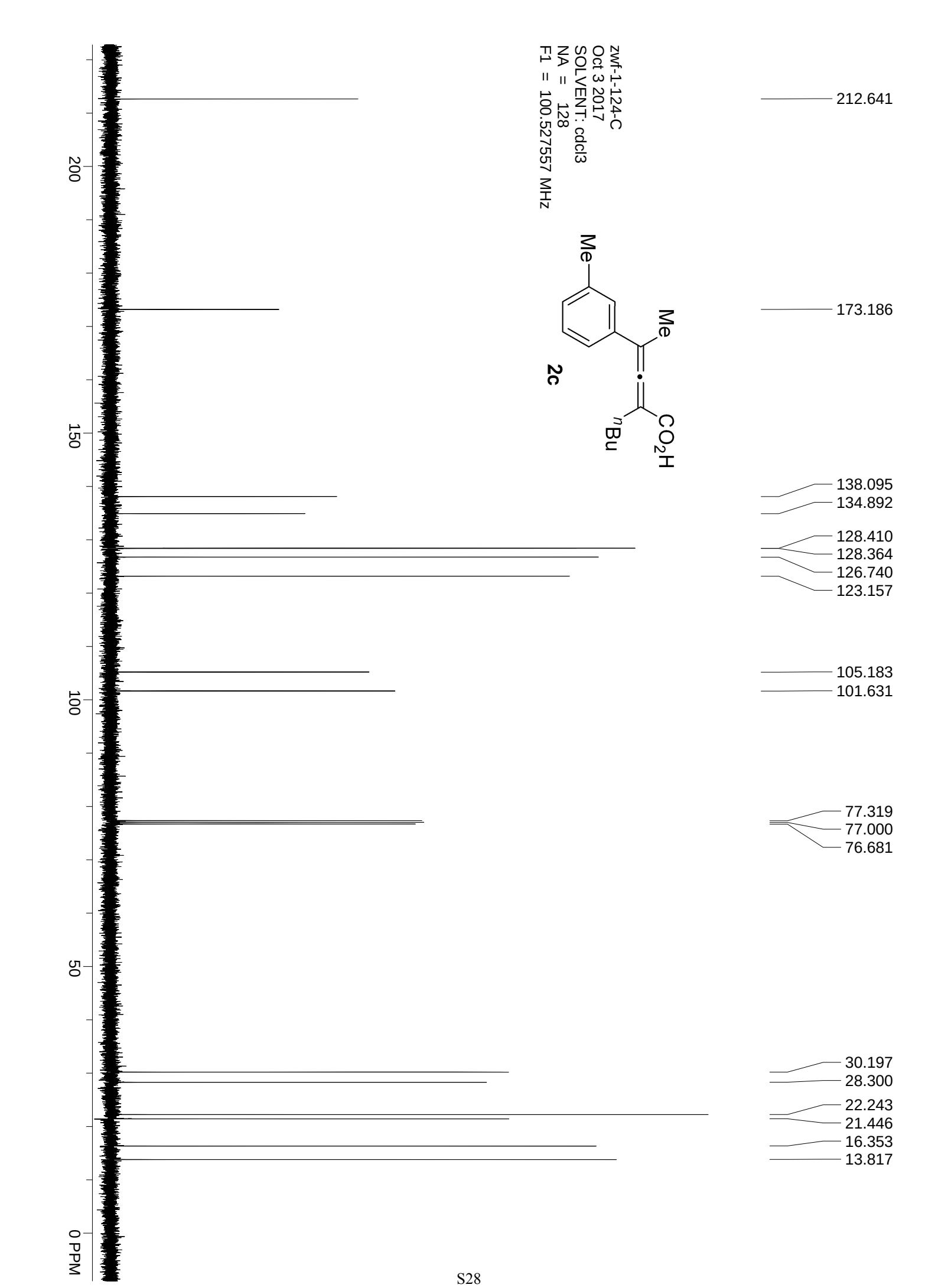
2.03
2.98
0.97
10
8
6
4
2
0 PPM


zwf-1-124-C
Oct 3 2017
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^{n}Bu
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134.892
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128.364
126.740
123.157
105.183
101.631
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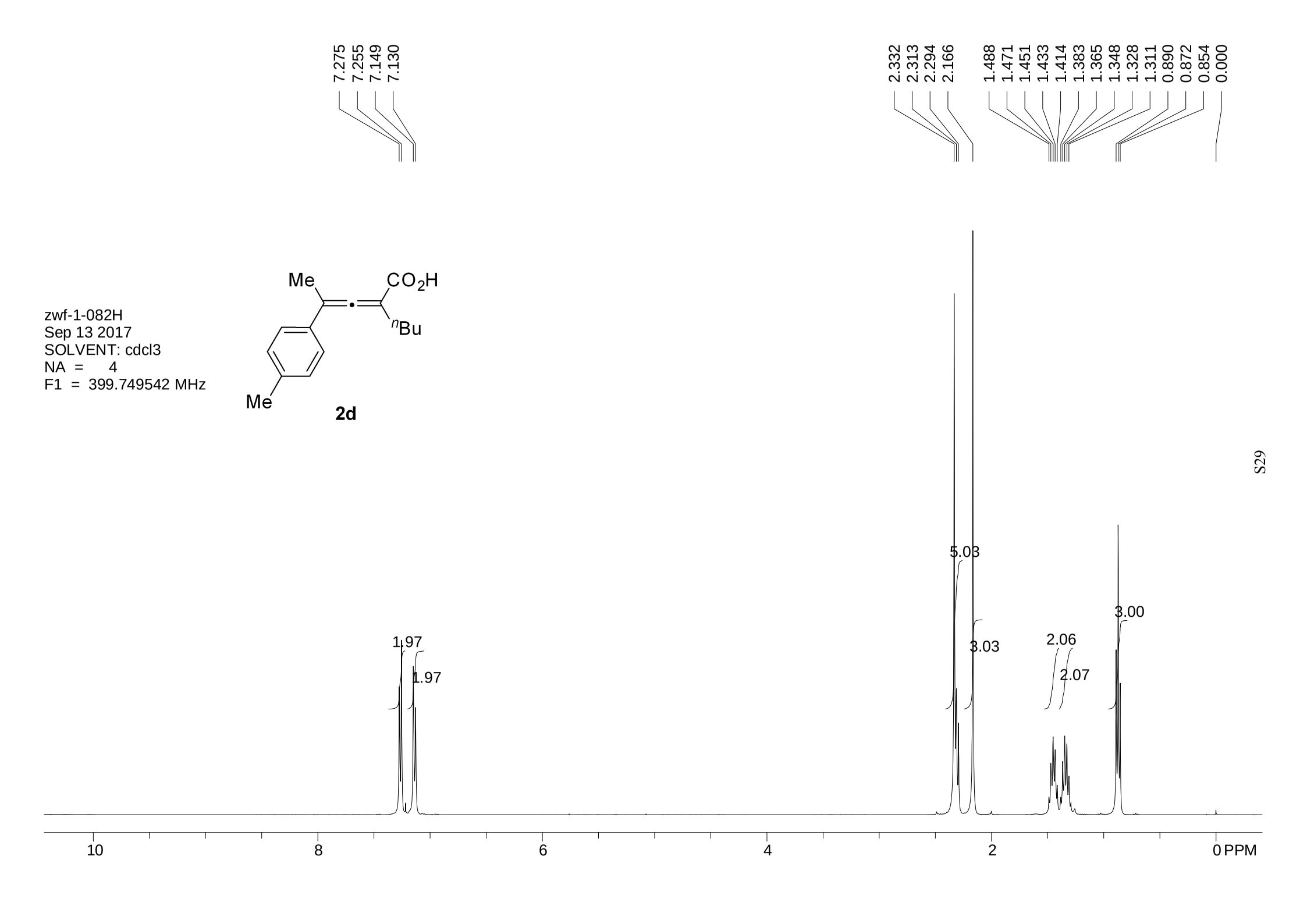
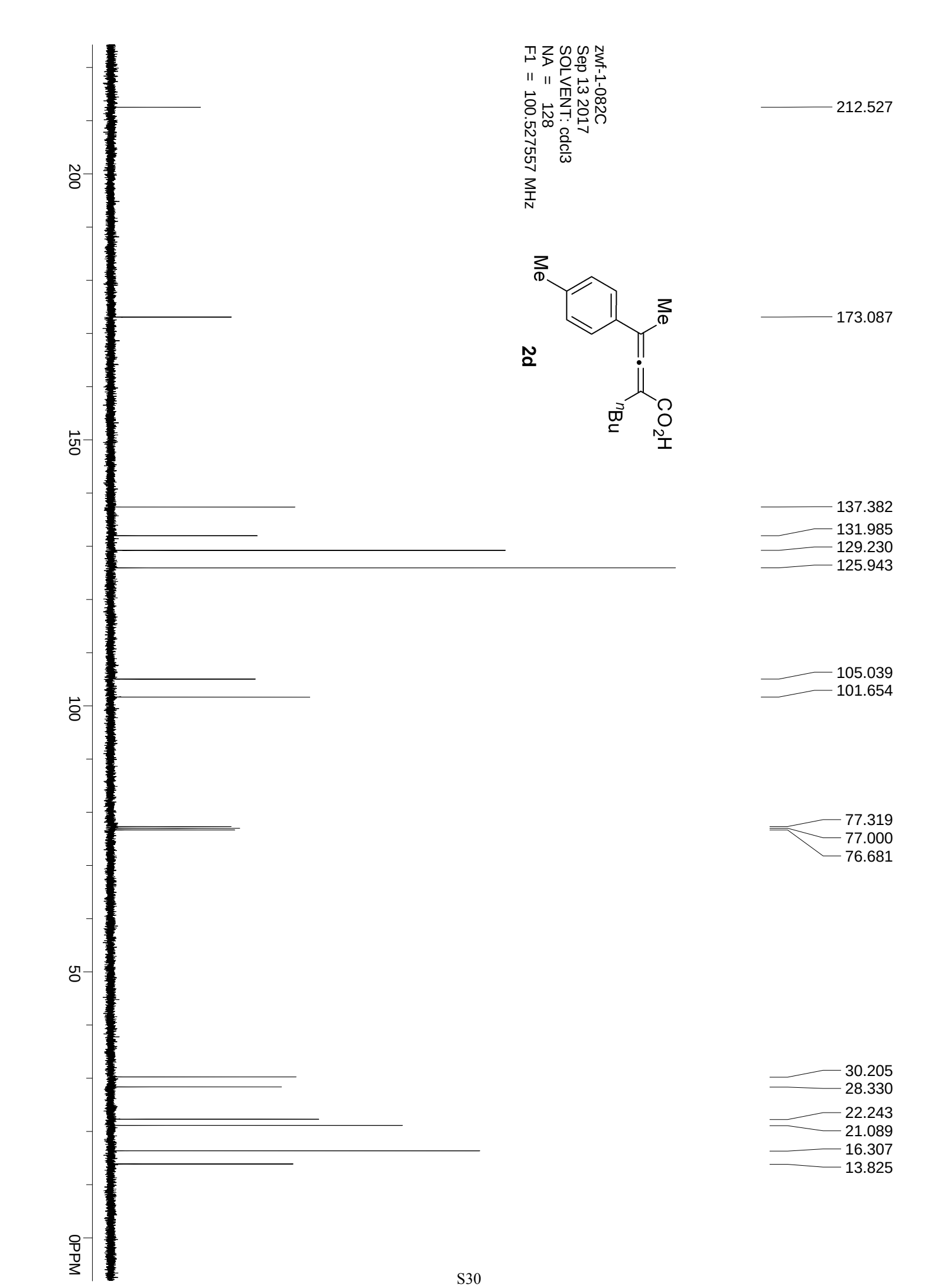
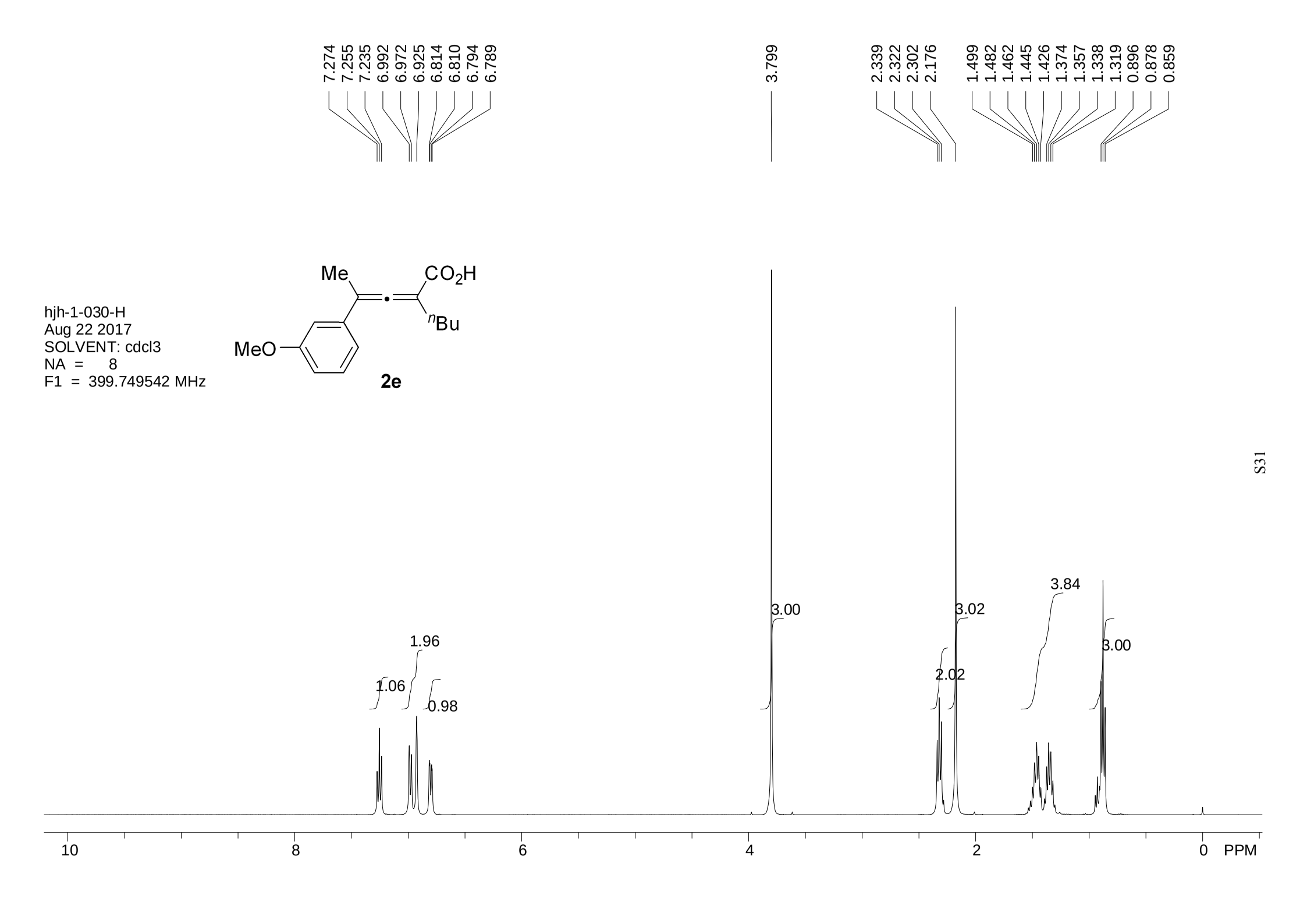
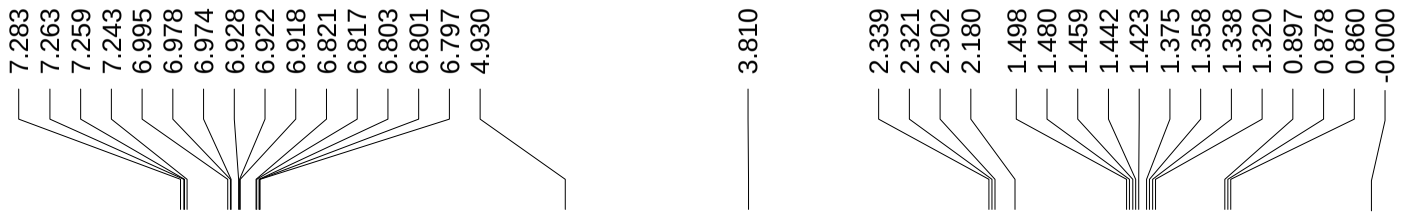
21.446
16.353
13.817
200
150
100
50
0 PPM

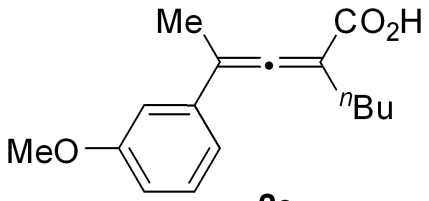

7.275
7.255
7.149
7.130
2.332
2.313
2.294
2.166
1.488
1.471
1.451
1.433
1.414
1.383
1.365
1.348
1.328
1.311
0.890
0.872
0.854
0.000
zwf-1-082H
Sep 13 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
Me
CO2H
nBu
Me
2d
1.97
1.97
5.03
3.03
2.06
2.07
3.00
10
8
6
4
2
0 PPM


zwf-1-082C
Sep 13 2017
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
Me
Me
^{n}Bu
CO_2H
2d
212.527
173.087
137.382
131.985
129.230
125.943
105.039
101.654
77.319
77.000
76.681
30.205
28.330
22.243
21.089
16.307
13.825
200
150
100
50
0PPM


7.274
7.255
7.235
6.992
6.972
6.925
6.814
6.810
6.794
6.789
3.799
2.339
2.322
2.302
2.176
1.499
1.482
1.462
1.445
1.426
1.374
1.357
1.338
1.319
0.896
0.878
0.859
hjh-1-030-H
Aug 22 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
Me
CO2H
nBu
MeO
2e
1.06
1.96
0.98
3.00
2.02
3.02
3.84
3.00
10
8
6
4
2
0
PPM
S31

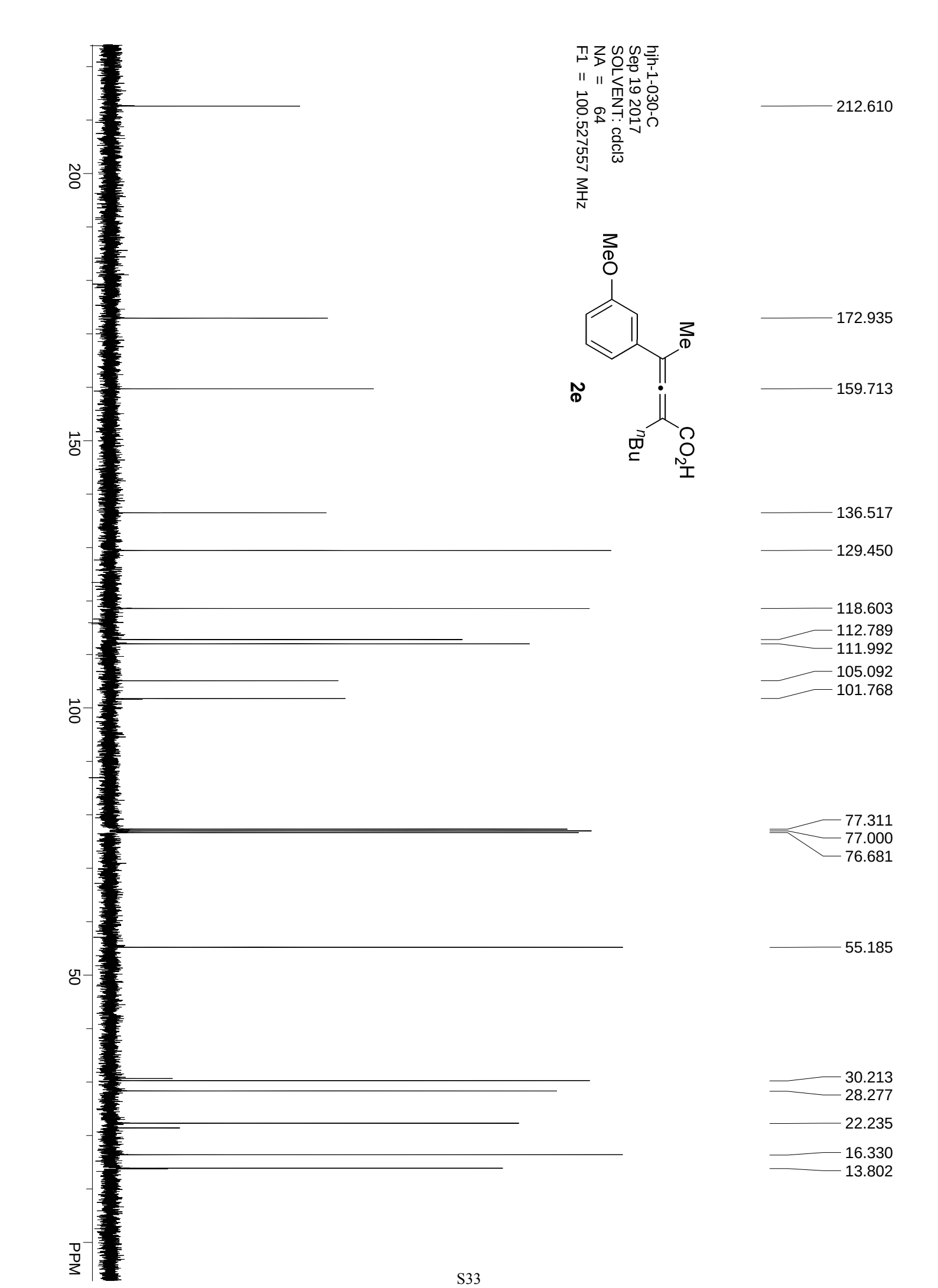


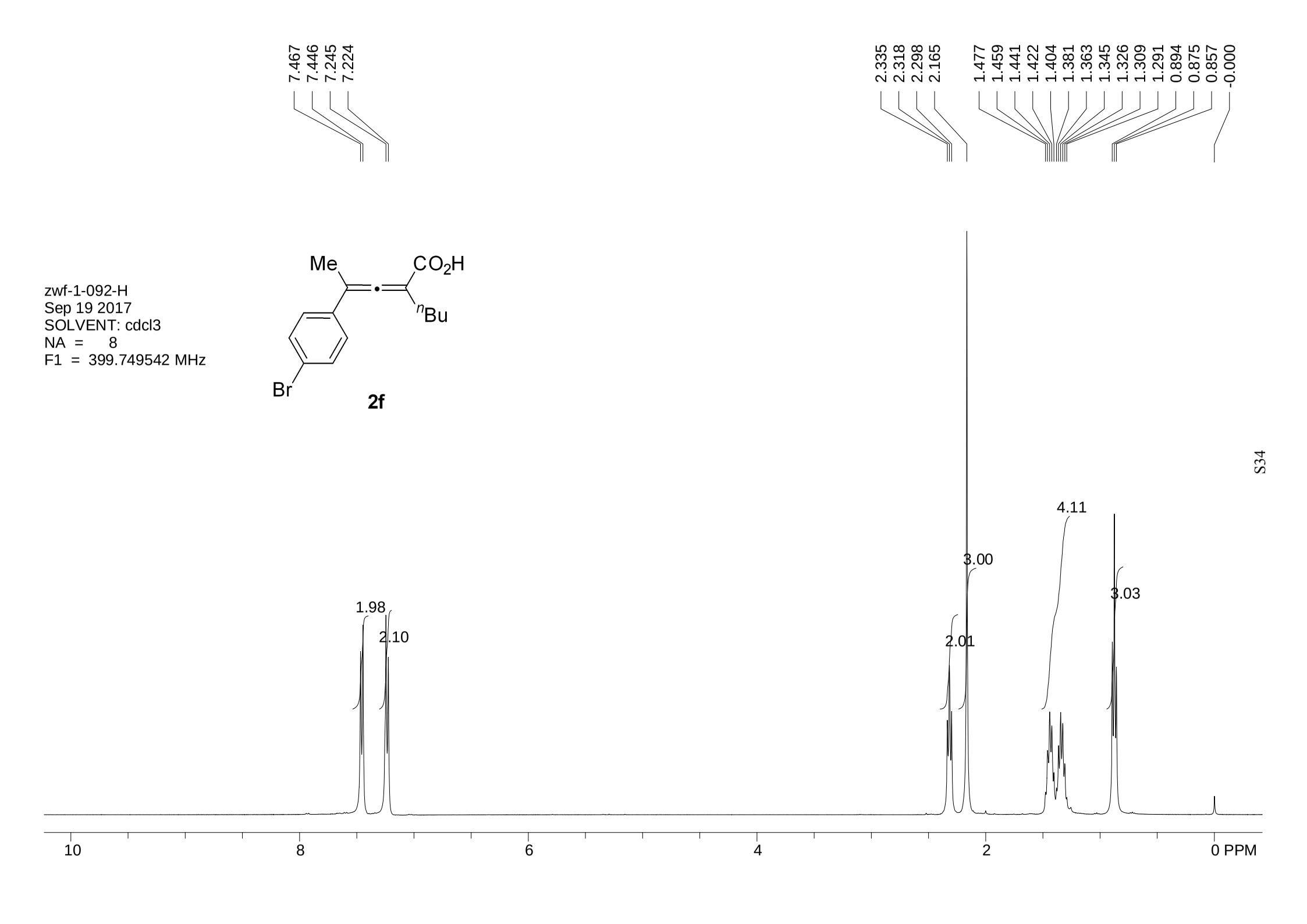
hjh-1-030-cd
Aug 23 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

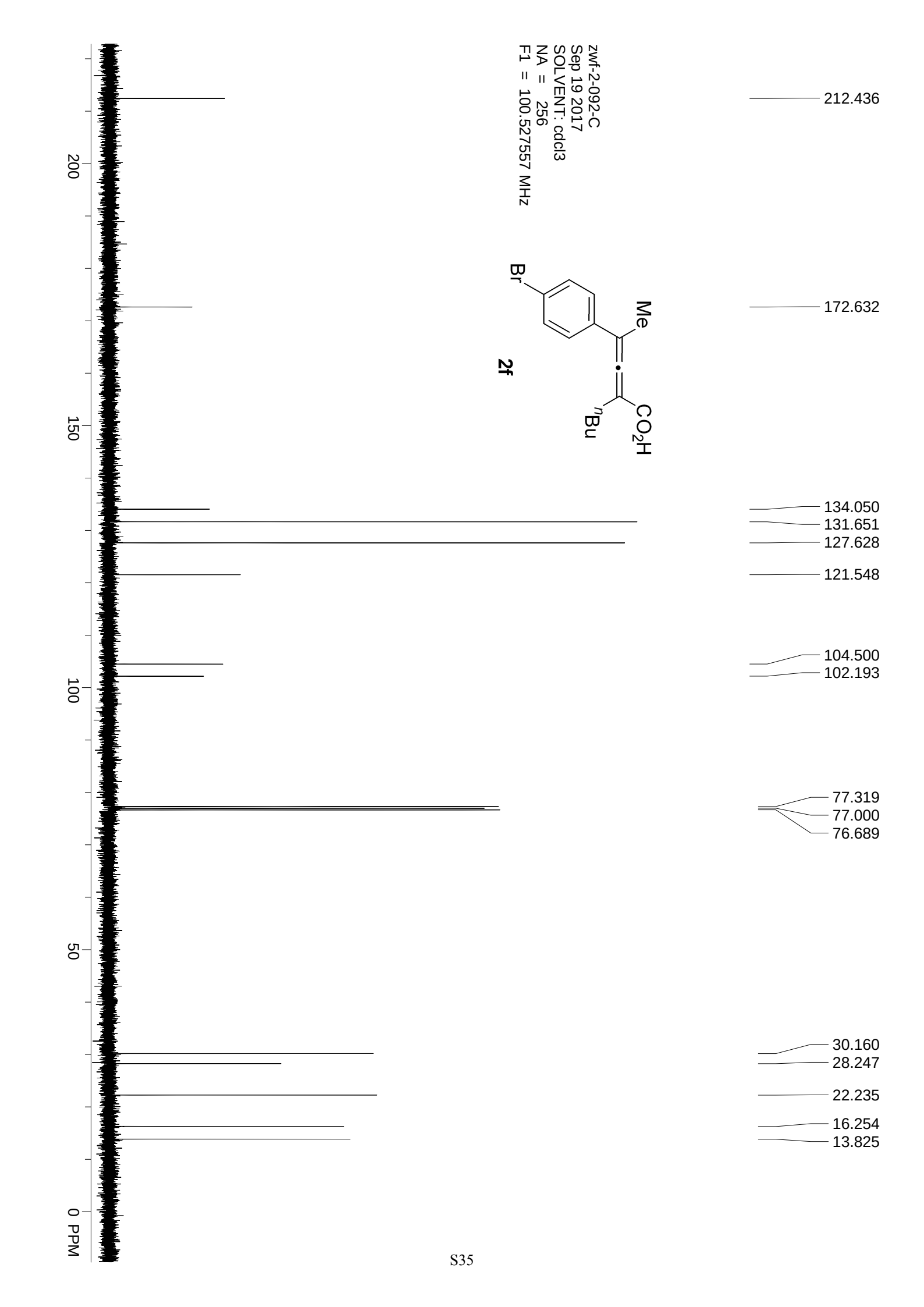


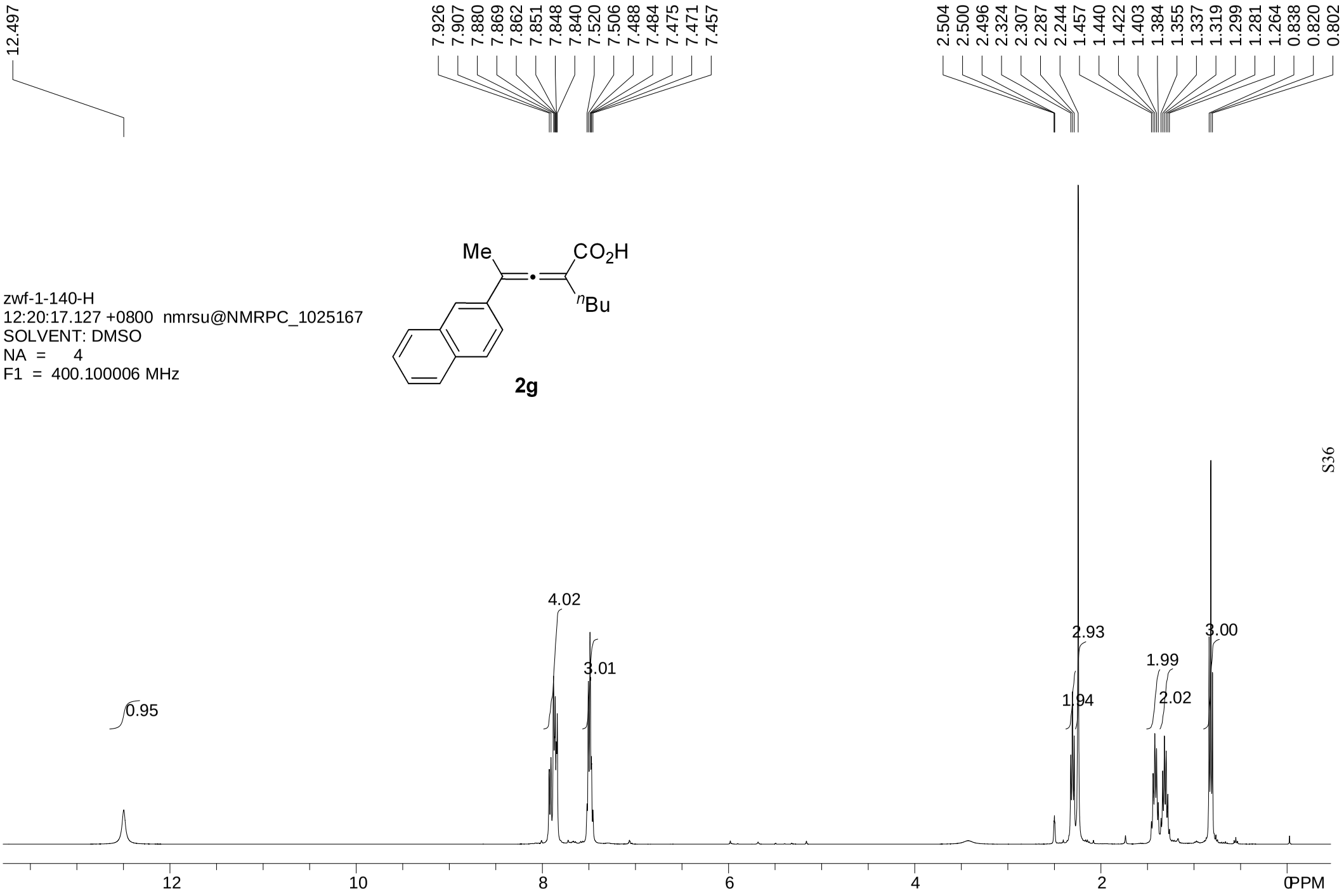
2e

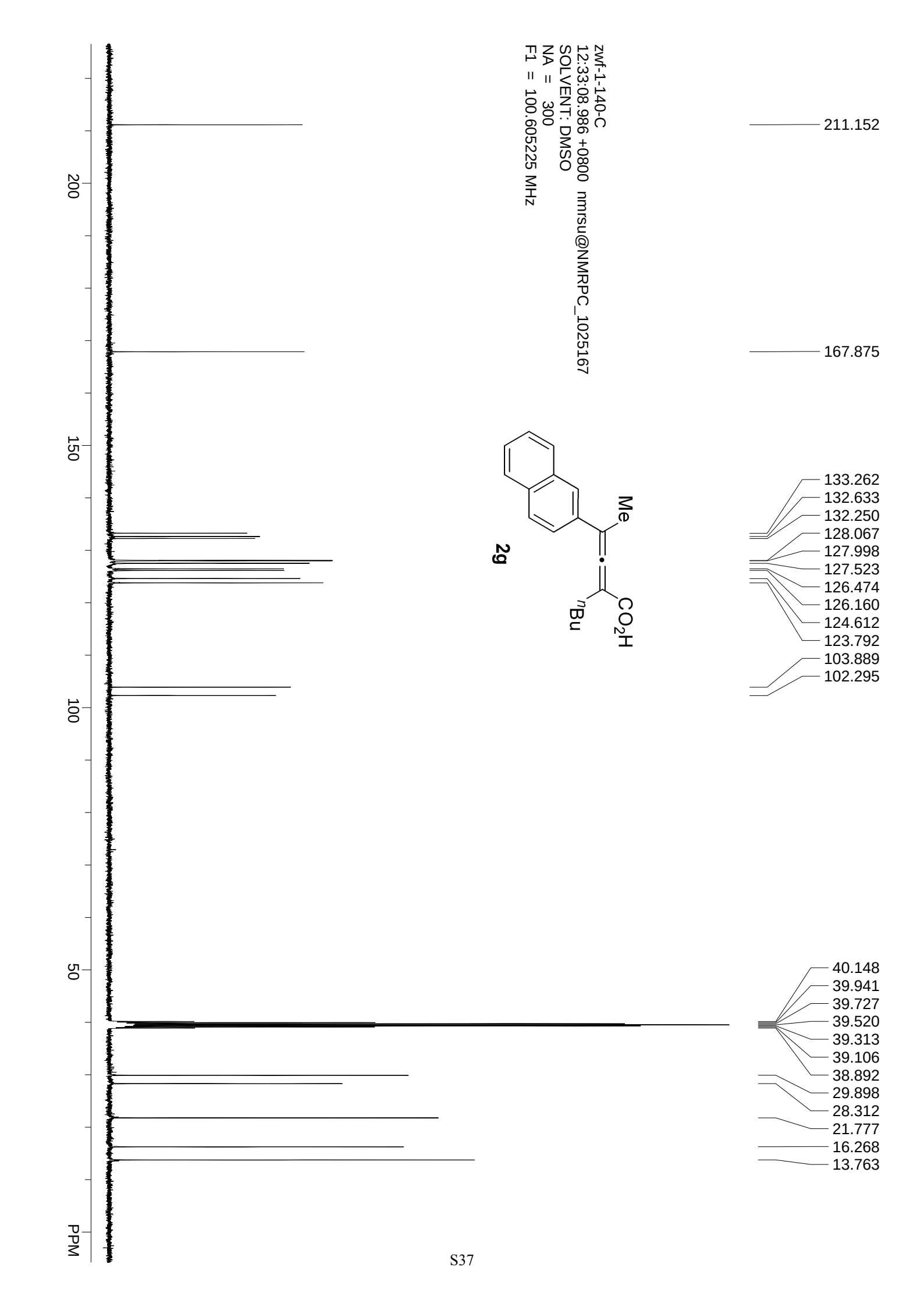
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 52.0 mg product

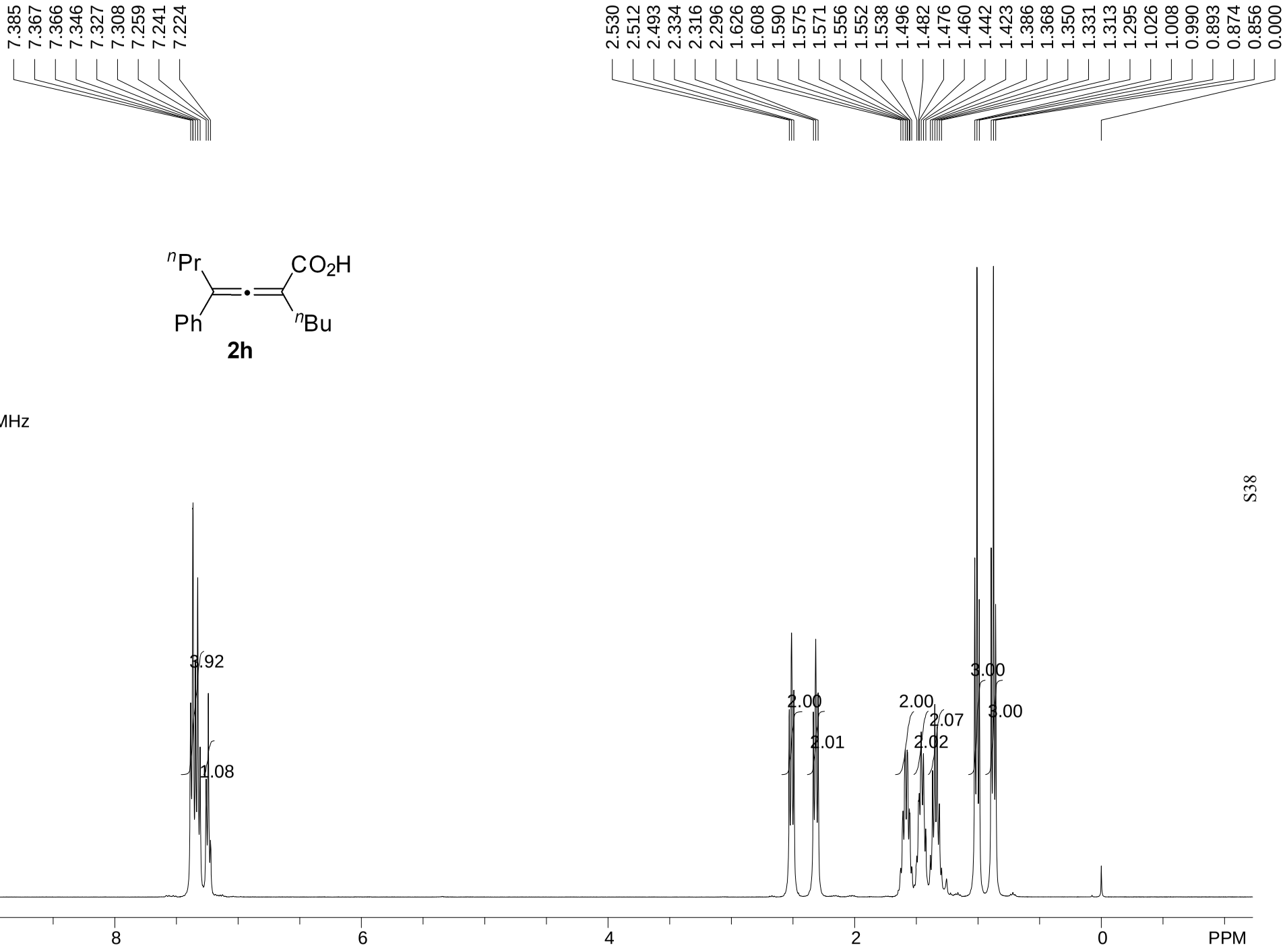

hjh-1-030-C
Sep 19 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.527557 MHz
MeO
Me
nBu
CO2H
2e
212.610
172.935
159.713
136.517
129.450
118.603
112.789
111.992
105.092
101.768
77.311
77.000
76.681
55.185
30.213
28.277
22.235
16.330
13.802
200
150
100
50
PPM

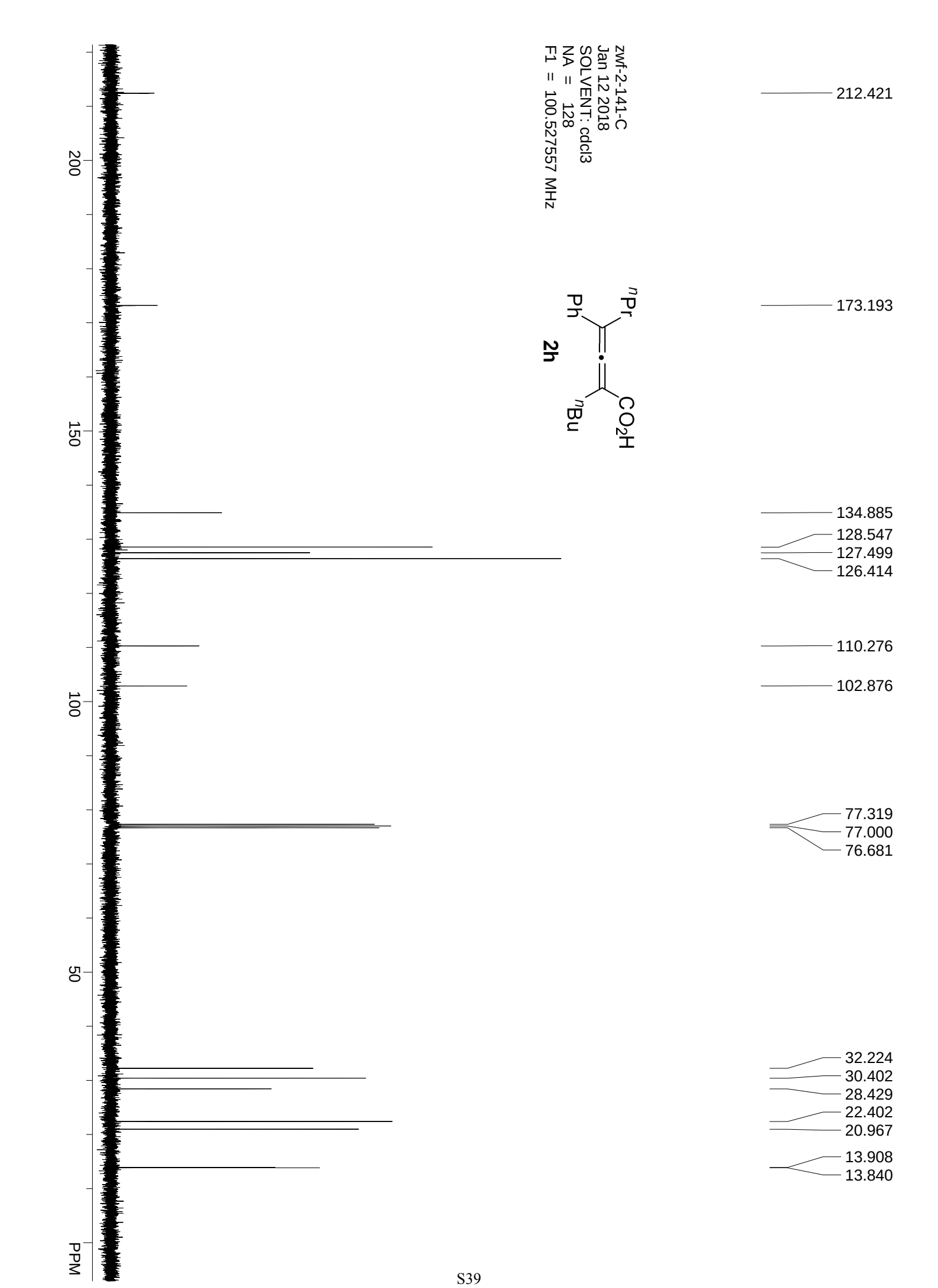

7.467
7.446
7.245
7.224
2.335
2.318
2.298
2.165
1.477
1.459
1.441
1.422
1.404
1.381
1.363
1.345
1.326
1.309
1.291
0.894
0.875
0.857
-0.000
zwf-1-092-H
Sep 19 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
Me
CO2H
nBu
Br
2f
S34
1.98
2.10
2.01
3.00
4.11
3.03
10
8
6
4
2
0 PPM

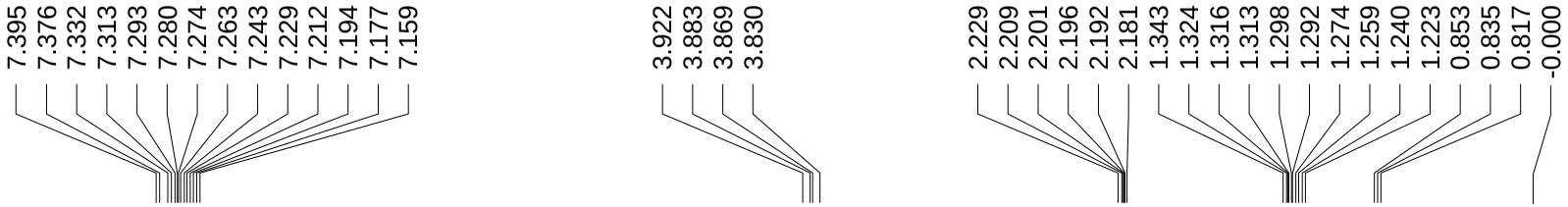

zwf-2-092-C
Sep 19 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
Br
Me
^{n}Bu
CO$_2$H
2f
212.436
172.632
134.050
131.651
127.628
121.548
104.500
102.193
77.319
77.000
76.689
30.160
28.247
22.235
16.254
13.825
200
150
100
50
0 PPM

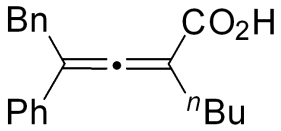

12.497
7.926
7.907
7.880
7.869
7.862
7.851
7.848
7.840
7.520
7.506
7.488
7.484
7.475
7.471
7.457
2.504
2.500
2.496
2.324
2.307
2.287
2.244
1.457
1.440
1.422
1.403
1.384
1.355
1.337
1.319
1.299
1.281
1.264
0.838
0.820
0.802
zwf-1-140-H
12:20:17.127 +0800 nmrsu@NMRPC_1025167
SOLVENT: DMSO
NA = 4
F1 = 400.100006 MHz
Me
CO2H
nBu
2g
S36
0.95
4.02
3.01
1.94
2.93
1.99
2.02
3.00
12
10
8
6
4
2
0
PPM


zwf-1-140-C
12:33:08.986 +0800 nmrsu@NMRPC_1025167
SOLVENT: DMSO
NA = 300
F1 = 100.605225 MHz
Me
^{n}Bu
CO_2H
2g
211.152
167.875
133.262
132.633
132.250
128.067
127.998
127.523
126.474
126.160
124.612
123.792
103.889
102.295
40.148
39.941
39.727
39.520
39.313
39.106
38.892
29.898
28.312
21.777
16.268
13.763
200
150
100
50
PPM


7.385
7.367
7.366
7.346
7.327
7.308
7.259
7.241
7.224
2.530
2.512
2.493
2.334
2.316
2.296
1.626
1.608
1.590
1.575
1.571
1.556
1.552
1.538
1.496
1.482
1.476
1.460
1.442
1.423
1.386
1.368
1.350
1.331
1.313
1.295
1.026
1.008
0.990
0.893
0.874
0.856
0.000
nPr
CO2H
Ph
nBu
2h
zwf-2-141-H
Sep 8 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
3.92
1.08
2.00
2.01
2.00
2.07
2.02
3.00
3.00
10
8
6
4
2
0
PPM

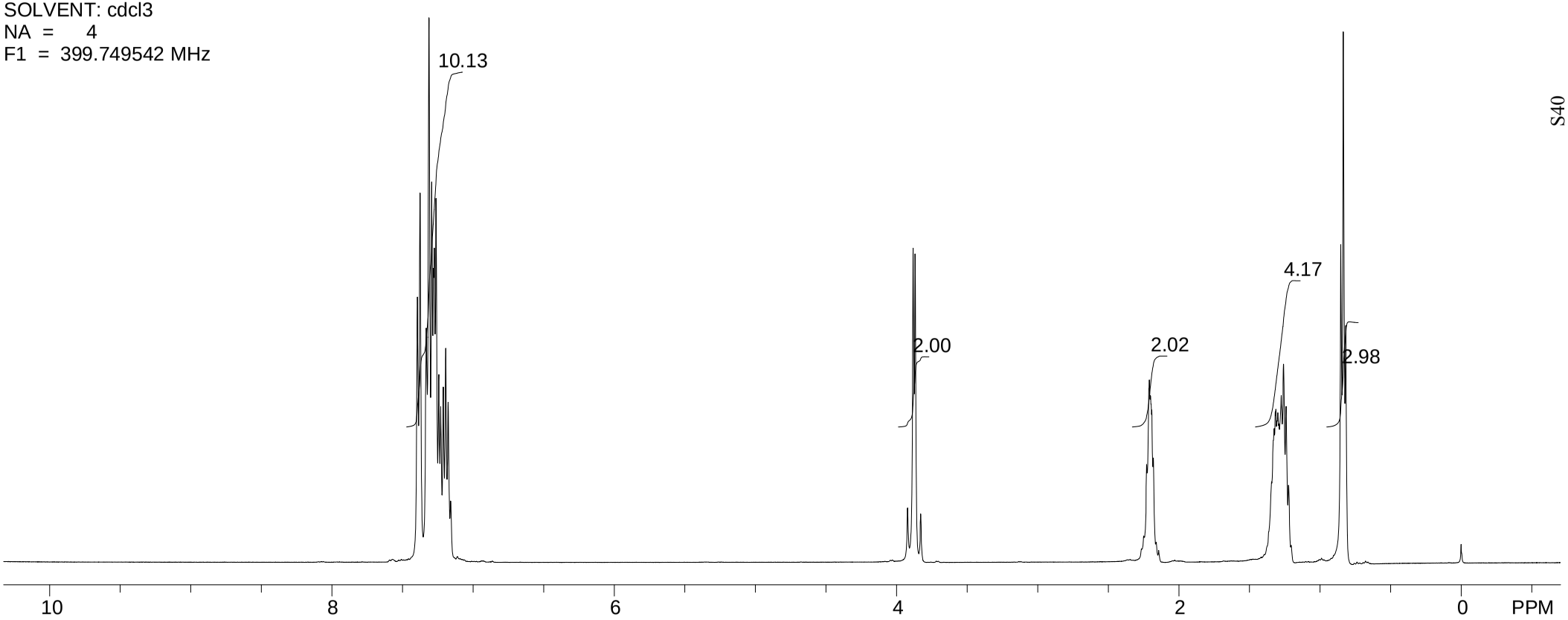

zwf-2-141-C
Jan 12 2018
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
2h
nPr
Ph
nBu
CO2H
212.421
173.193
134.885
128.547
127.499
126.414
110.276
102.876
77.319
77.000
76.681
32.224
30.402
28.429
22.402
20.967
13.908
13.840
200
150
100
50
PPM

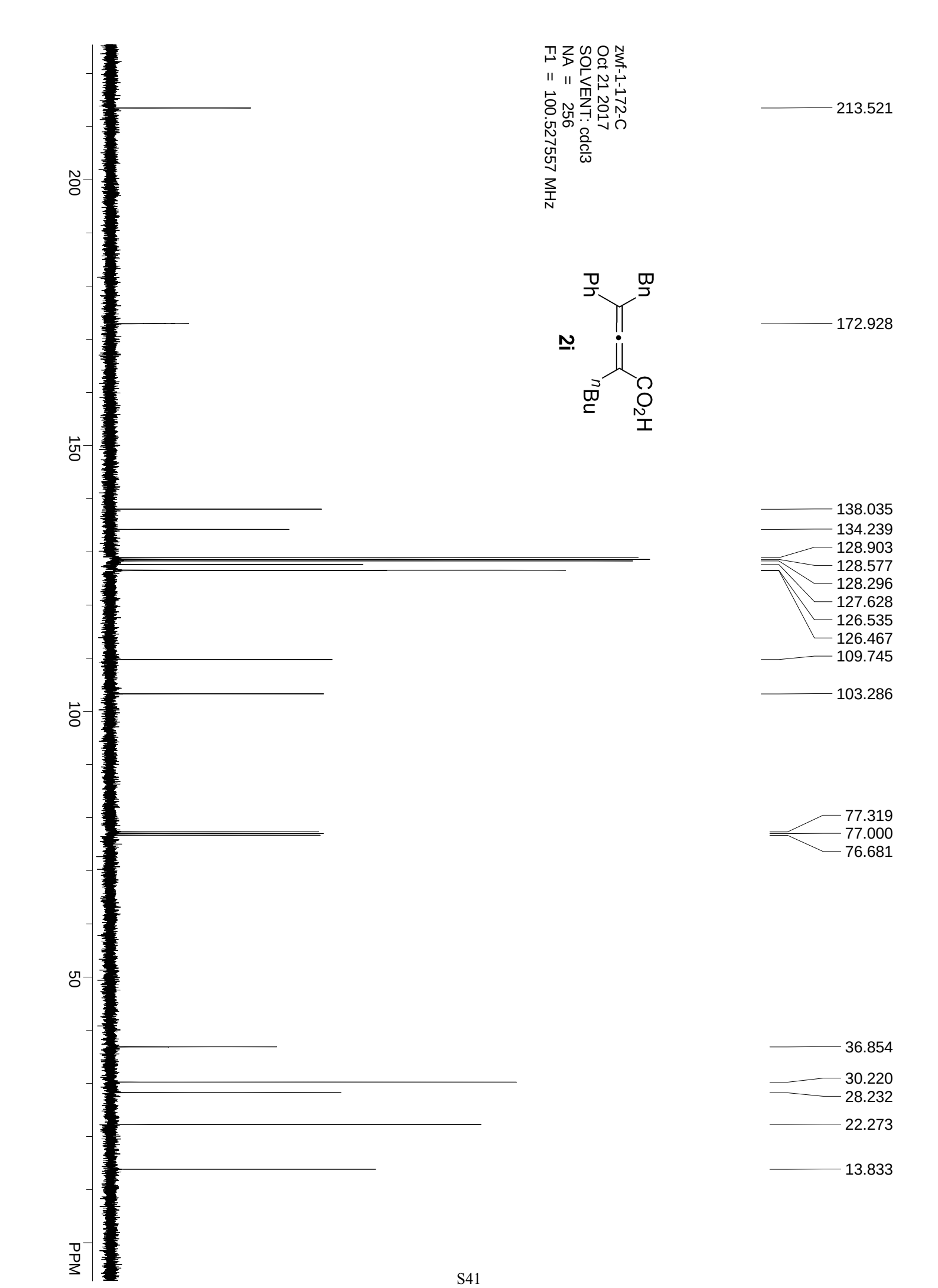


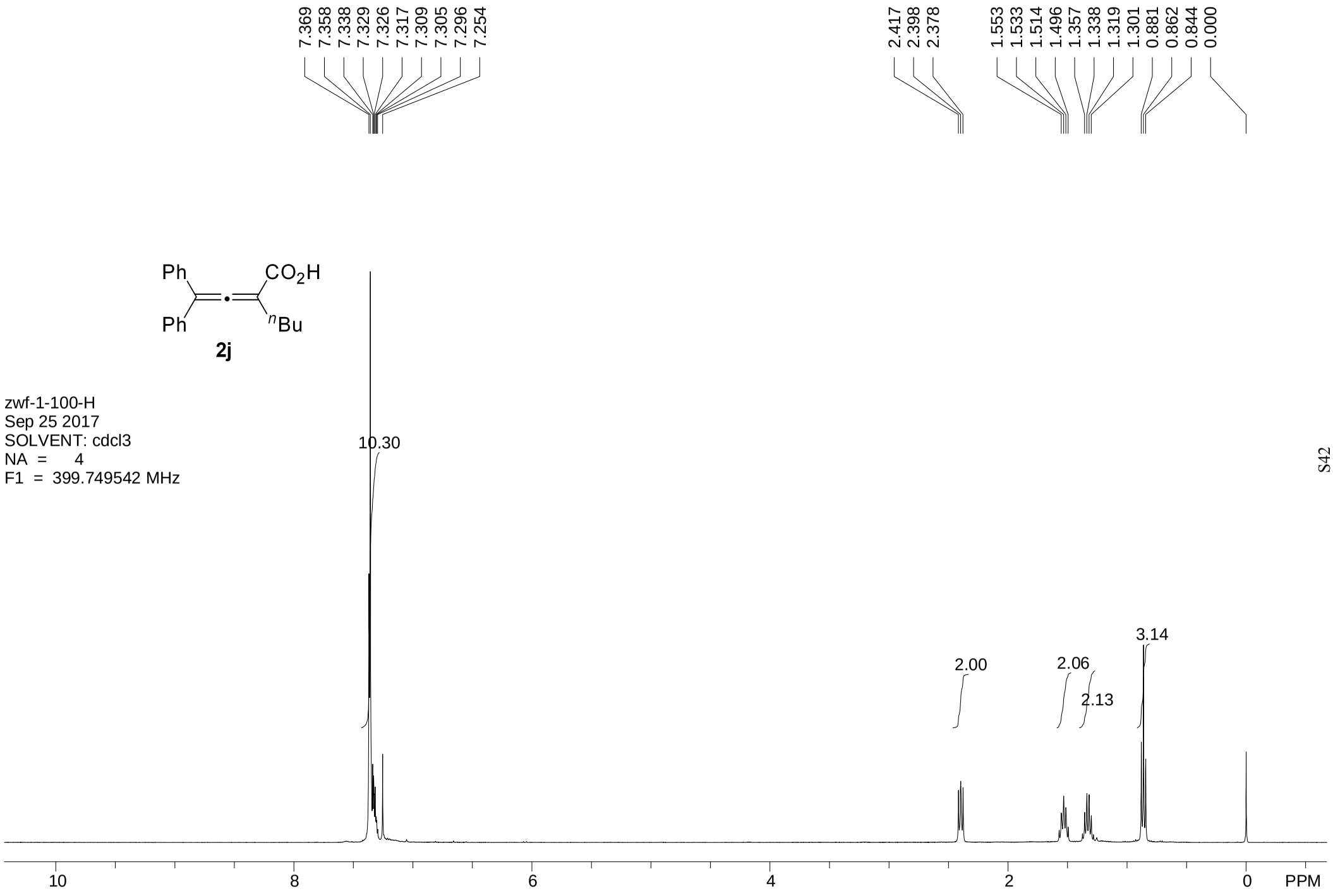


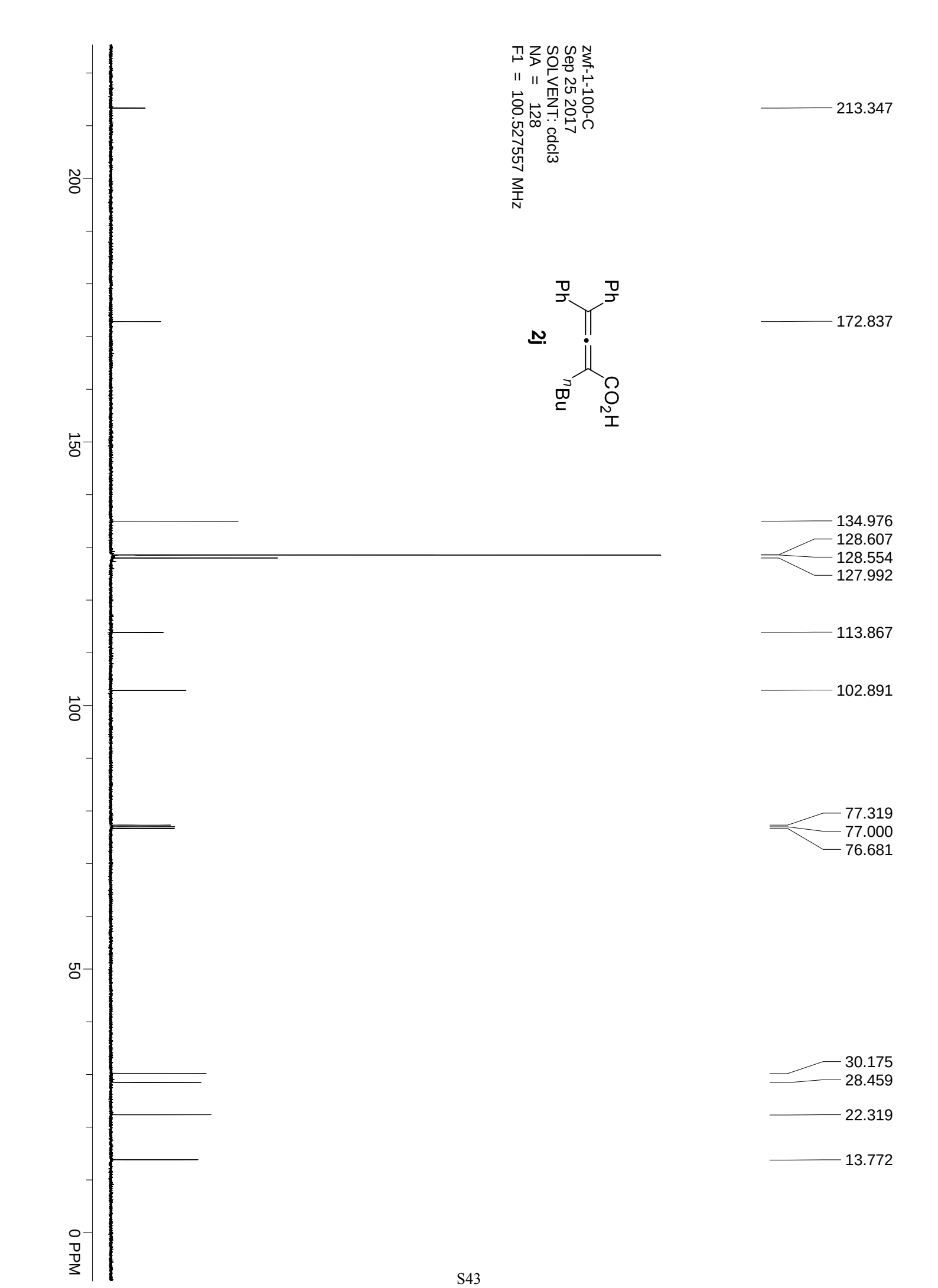
2i

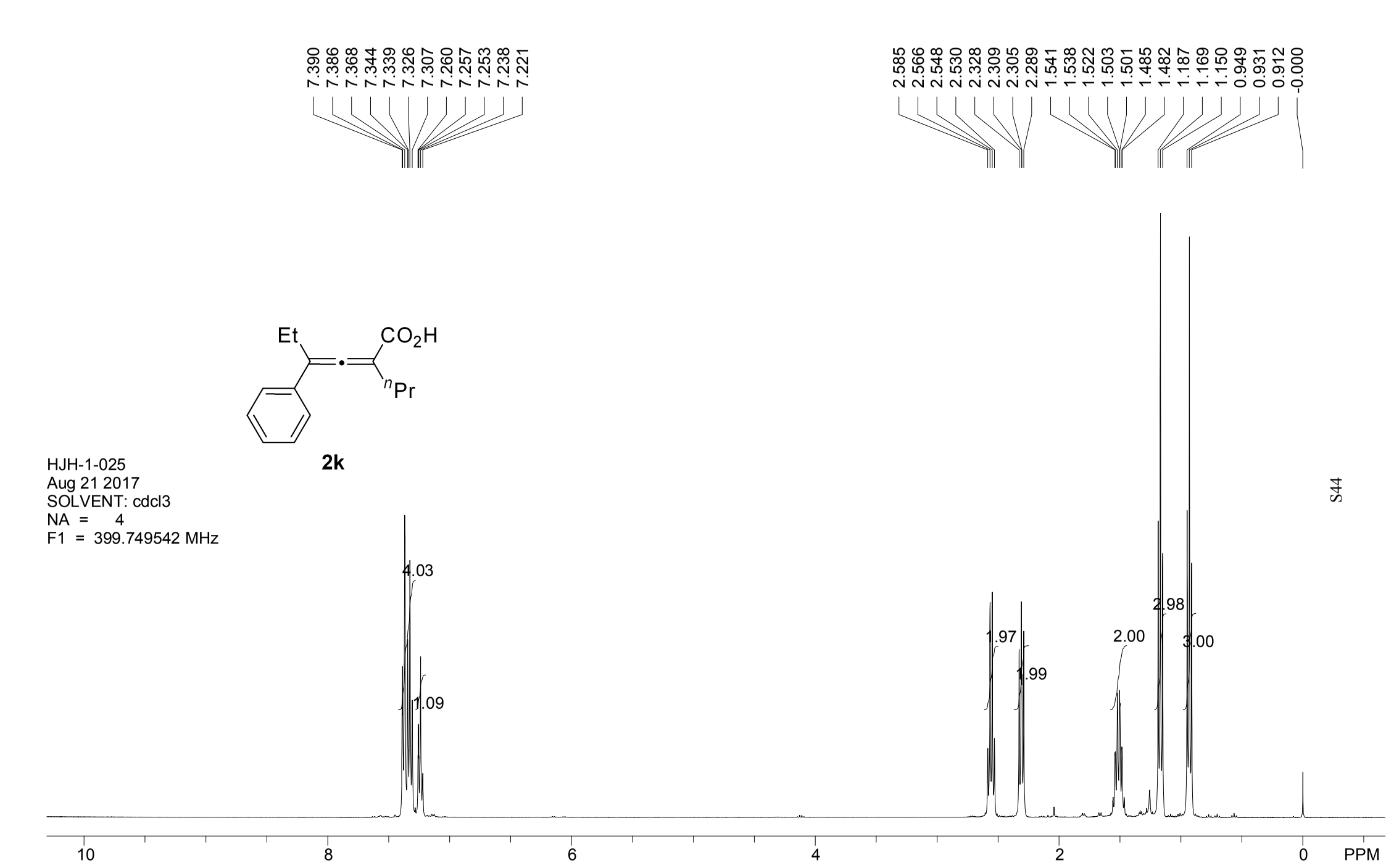
zwf-1-172-H
Oct 21 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

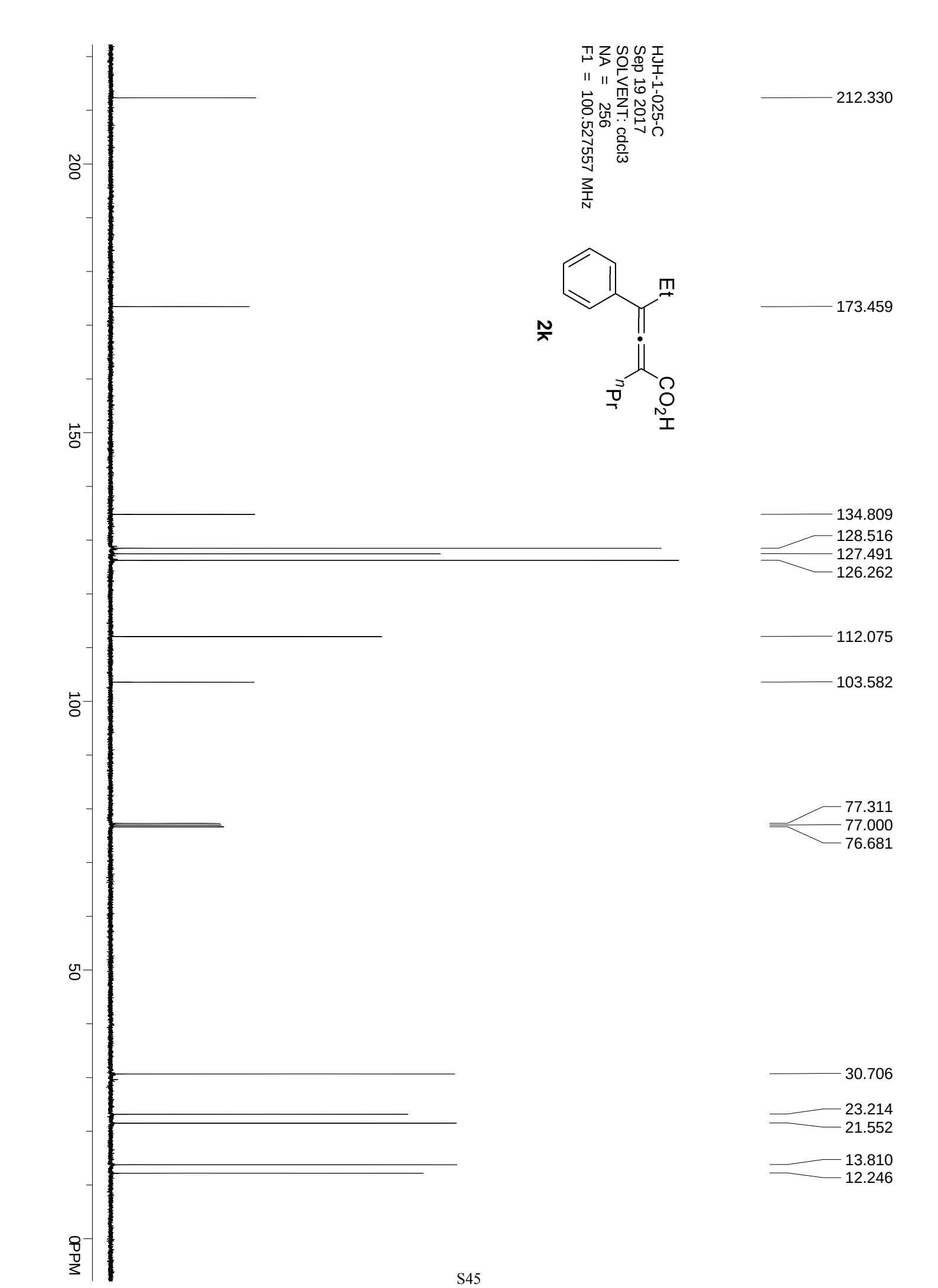


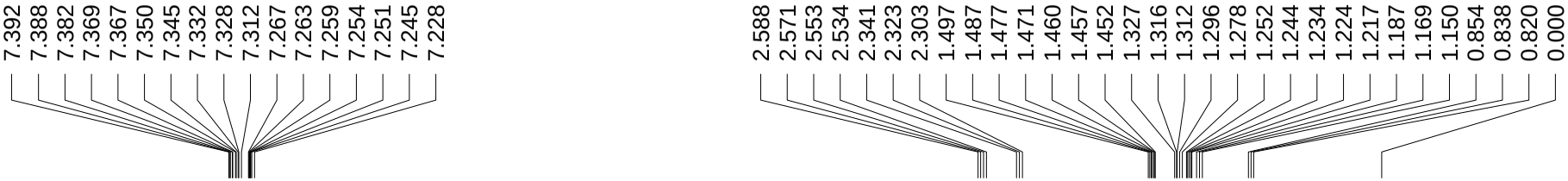

zwf-1-172-C
Oct 21 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
Ph
Bn
^{n}Bu
CO_2H
2i
213.521
172.928
138.035
134.239
128.903
128.577
128.296
127.628
126.535
126.467
109.745
103.286
77.319
77.000
76.681
36.854
30.220
28.232
22.273
13.833
200
150
100
50
PPM


7.369
7.358
7.338
7.329
7.326
7.317
7.309
7.305
7.296
7.254
2.417
2.398
2.378
1.553
1.533
1.514
1.496
1.357
1.338
1.319
1.301
0.881
0.862
0.844
0.000
Ph
CO2H
Ph
nBu
2j
zwf-1-100-H
Sep 25 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
10.30
2.00
2.06
2.13
3.14
10
8
6
4
2
0
PPM

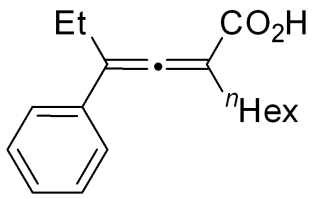

zwf-1-100-C
Sep 25 2017
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
Ph
Ph
^{n}Bu
CO_2H
2j
213.347
172.837
134.976
128.607
128.554
127.992
113.867
102.891
77.319
77.000
76.681
30.175
28.459
22.319
13.772
200
150
100
50
0 PPM


7.390
7.386
7.368
7.344
7.339
7.326
7.307
7.260
7.257
7.253
7.238
7.221
2.585
2.566
2.548
2.530
2.328
2.309
2.305
2.289
1.541
1.538
1.522
1.503
1.501
1.485
1.482
1.187
1.169
1.150
0.949
0.931
0.912
-0.000
Et
CO2H
nPr
2k
HJH-1-025
Aug 21 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
4.03
1.09
1.97
1.99
2.00
2.98
3.00
S44
10
8
6
4
2
0
PPM

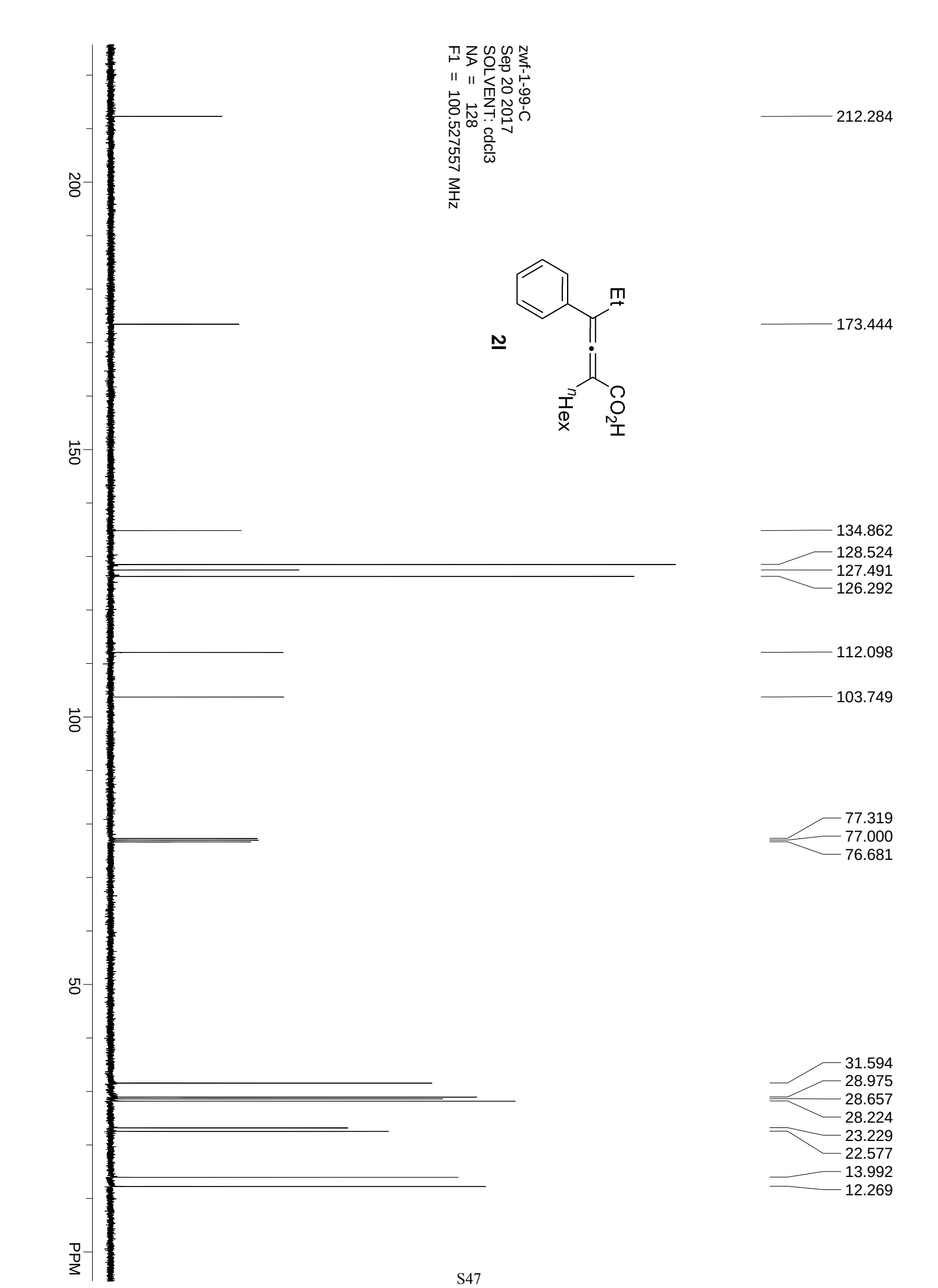

HJH-1-025-C
Sep 19 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
Et
^{n}Pr
CO_2H
2k
212.330
173.459
134.809
128.516
127.491
126.262
112.075
103.582
77.311
77.000
76.681
30.706
23.214
21.552
13.810
12.246
200
150
100
50
0PPM

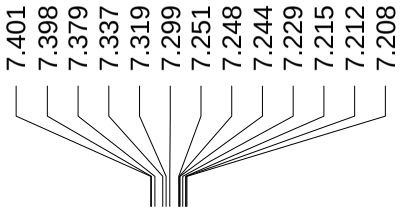


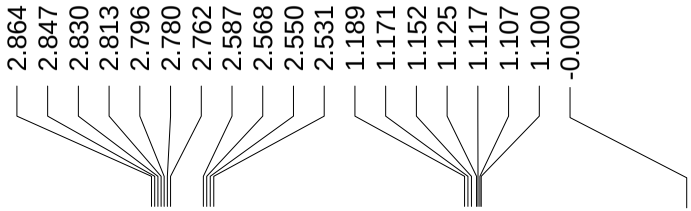
zwf-1-099-H
Sep 20 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

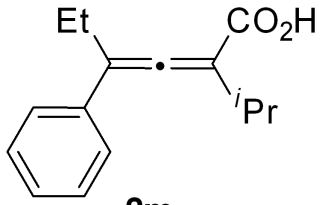


2l


zwf-1-99-C
Sep 20 2017
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
2l
Et
^{n}Hex
CO_2H
212.284
173.444
134.862
128.524
127.491
126.292
112.098
103.749
77.319
77.000
76.681
31.594
28.975
28.657
28.224
23.229
22.577
13.992
12.269
200
150
100
50
PPM

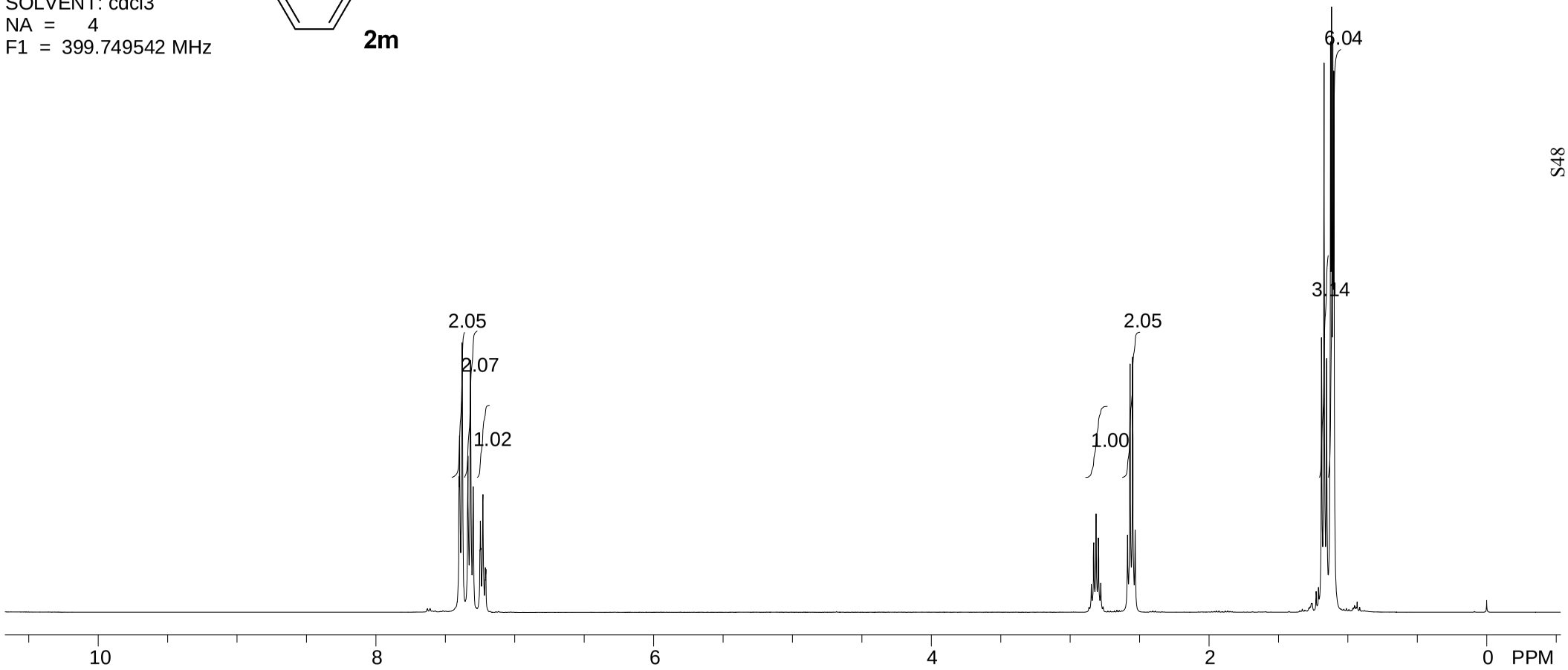


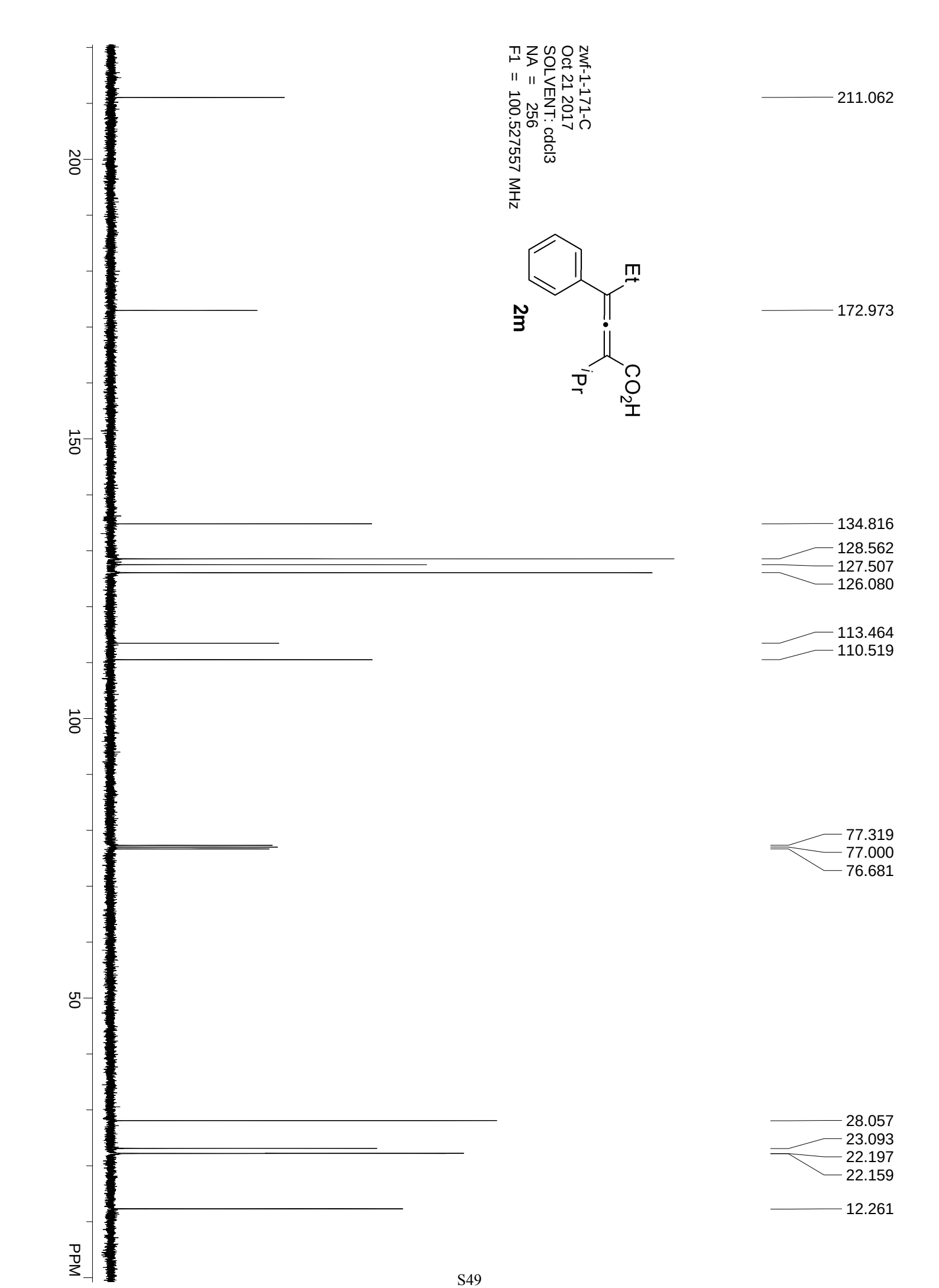


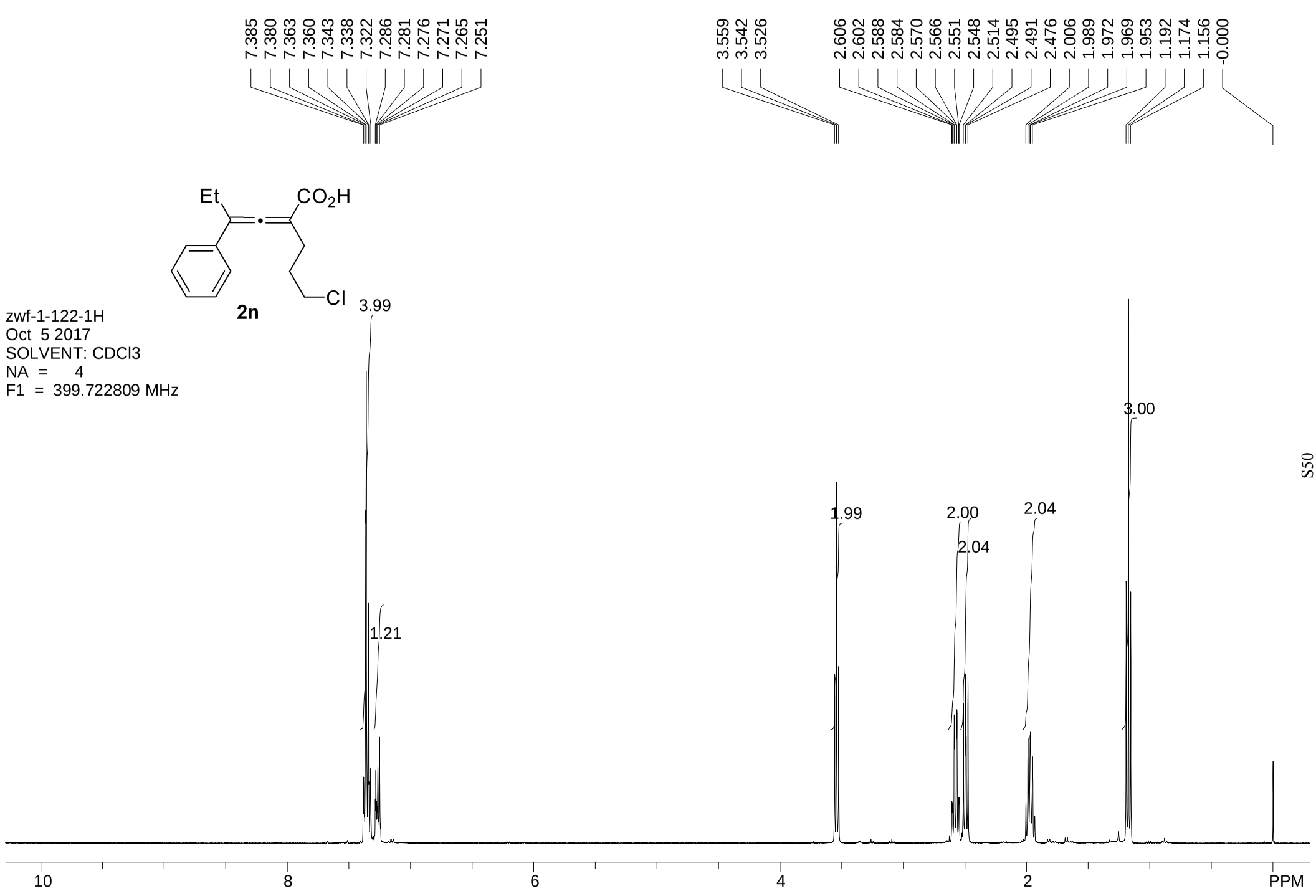


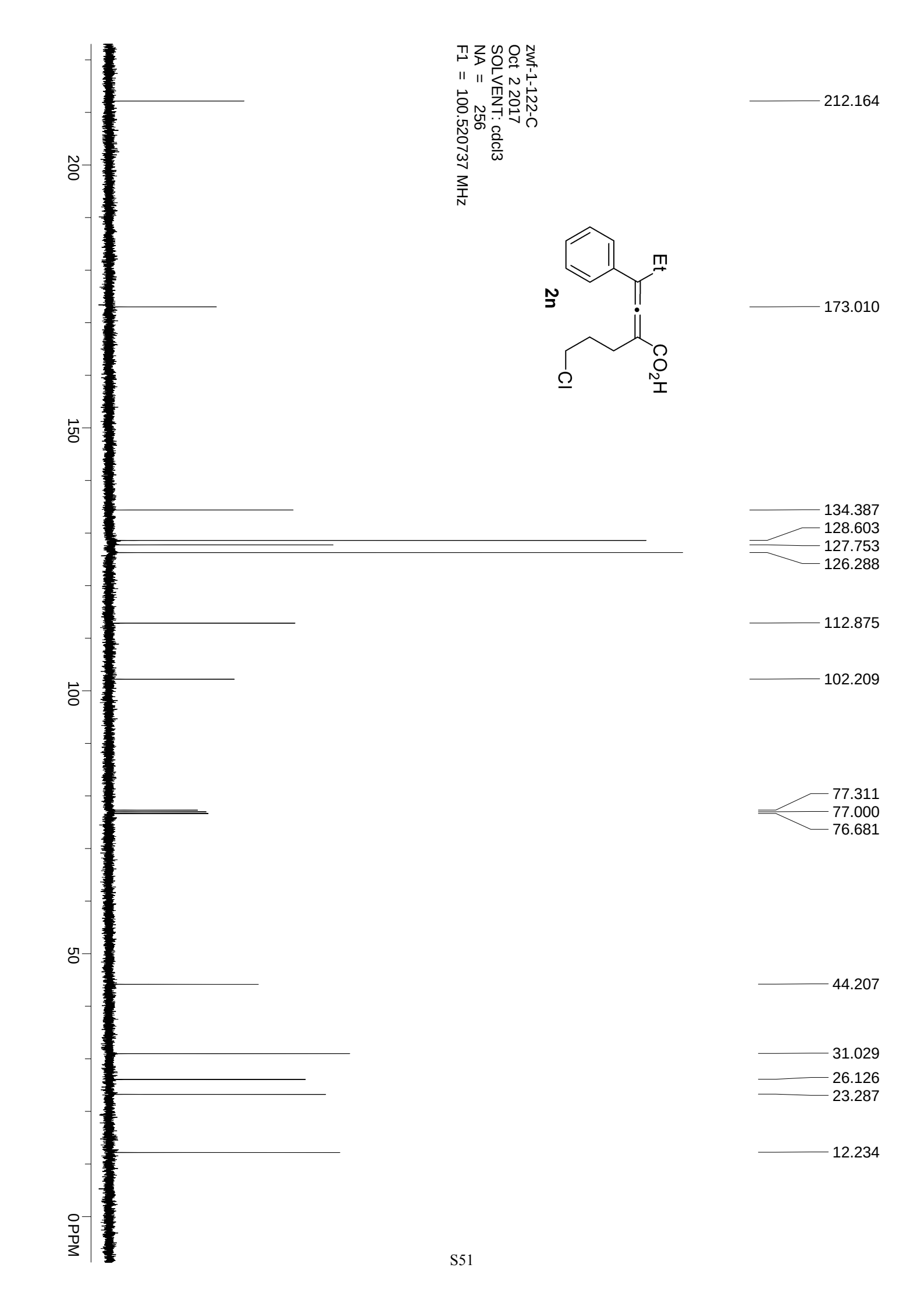
2m

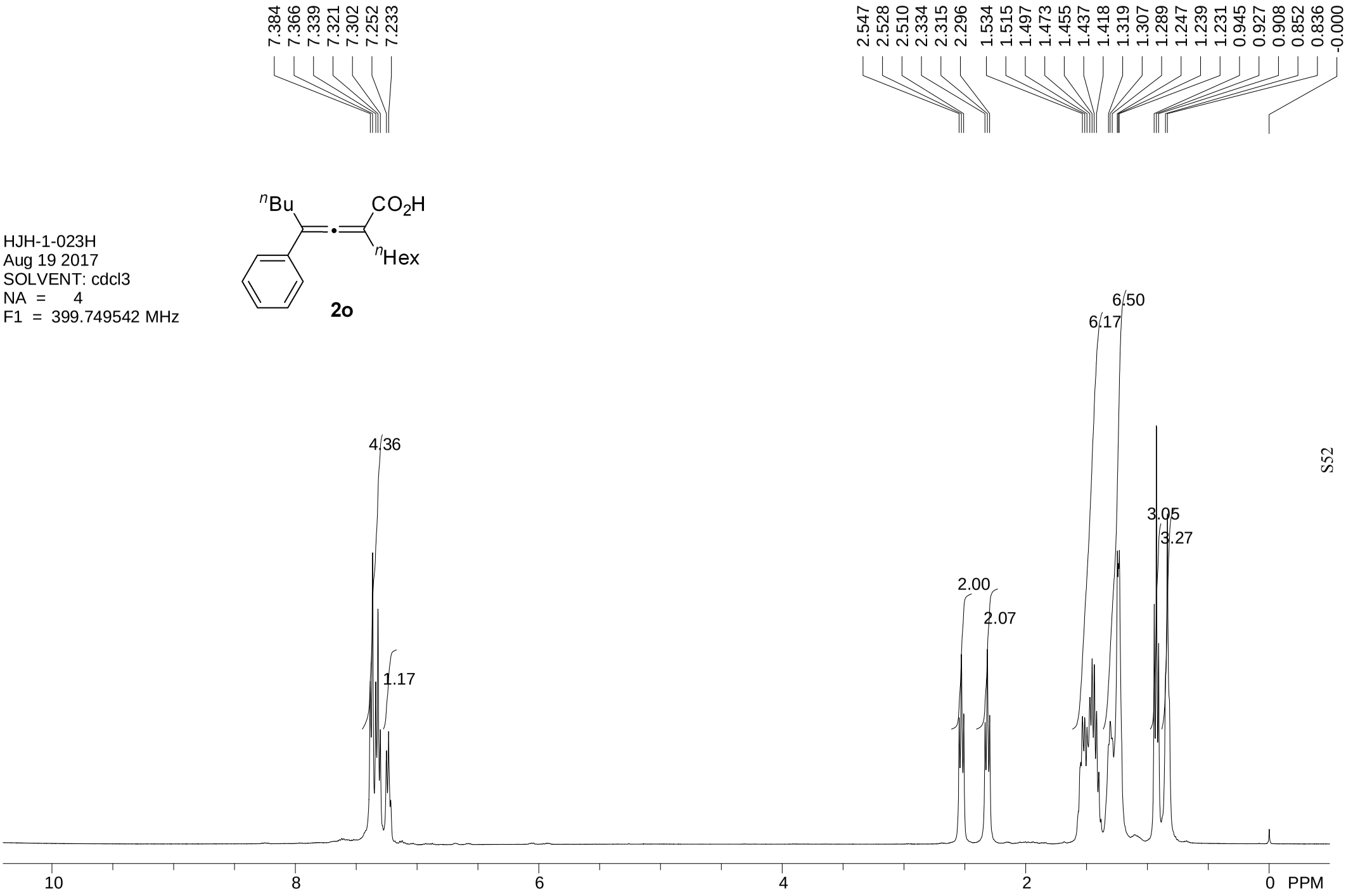
zwf-1-171-H
Oct 21 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

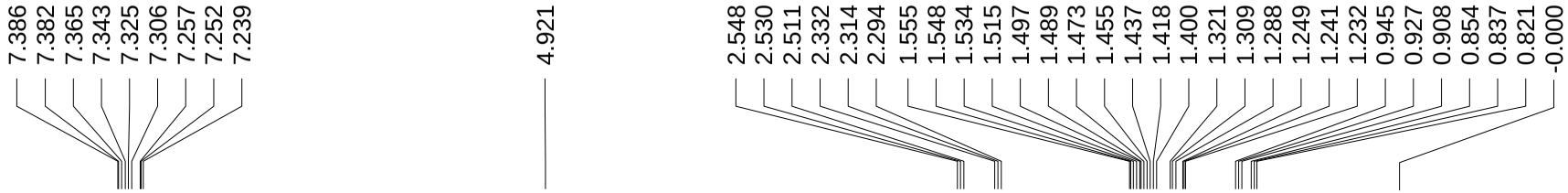



zwf-1-171-C
Oct 21 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
2m
Et
iPr
CO2H
211.062
172.973
134.816
128.562
127.507
126.080
113.464
110.519
77.319
77.000
76.681
28.057
23.093
22.197
22.159
12.261
200
150
100
50
PPM

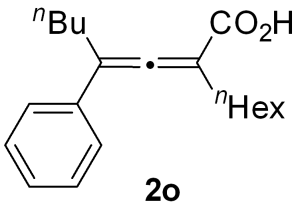

7.385
7.380
7.363
7.360
7.343
7.338
7.322
7.286
7.281
7.276
7.271
7.265
7.251
3.559
3.542
3.526
2.606
2.602
2.588
2.584
2.570
2.566
2.551
2.548
2.514
2.495
2.491
2.476
2.006
1.989
1.972
1.969
1.953
1.192
1.174
1.156
-0.000
Et
CO2H
Cl
2n
zwf-1-122-1H
Oct 5 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
3.99
1.21
1.99
2.00
2.04
2.04
3.00
S50
10
8
6
4
2
PPM


zwf-1-122-C
Oct 2 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.520737 MHz
2n
Et
Cl
CO2H
212.164
173.010
134.387
128.603
127.753
126.288
112.875
102.209
77.311
77.000
76.681
44.207
31.029
26.126
23.287
12.234
200
150
100
50
0 PPM


7.384
7.366
7.339
7.321
7.302
7.252
7.233
2.547
2.528
2.510
2.334
2.315
2.296
1.534
1.515
1.497
1.473
1.455
1.437
1.418
1.319
1.307
1.289
1.247
1.239
1.231
0.945
0.927
0.908
0.852
0.836
-0.000
HJH-1-023H
Aug 19 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
nBu
CO2H
nHex
2o
6.50
6.17
4.36
3.05
3.27
2.00
2.07
1.17
10
8
6
4
2
0
PPM

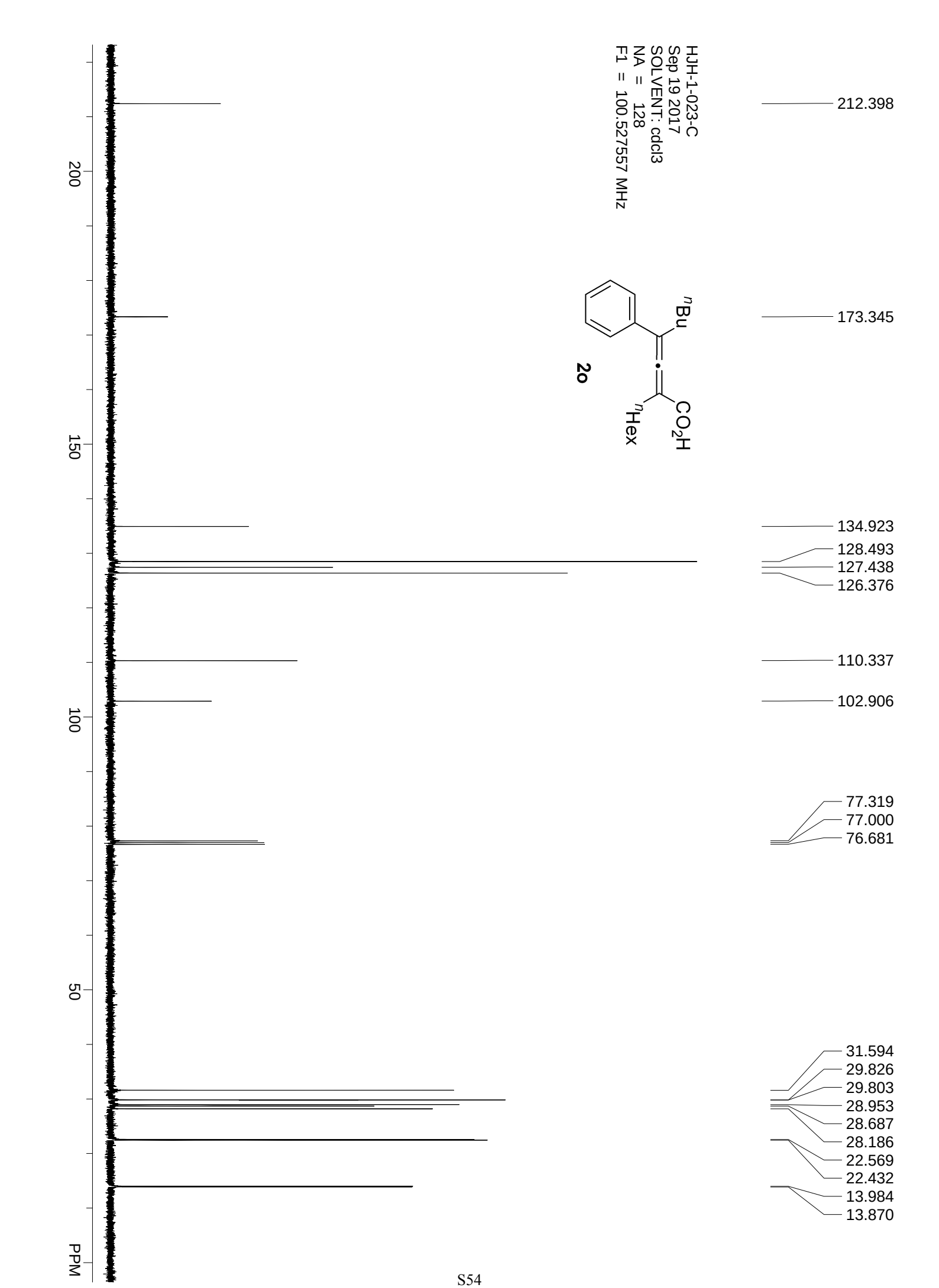


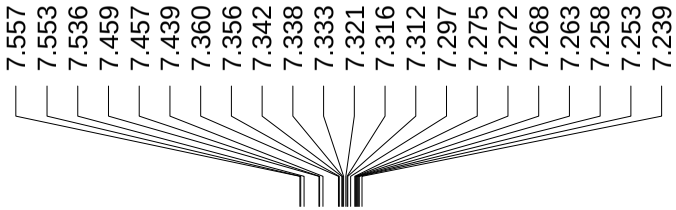
hjh-1-023-cd
Aug 22 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

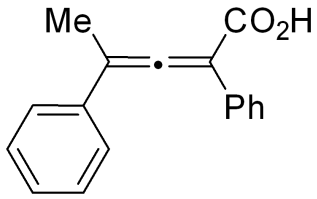


2o

Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 60.2 mg product

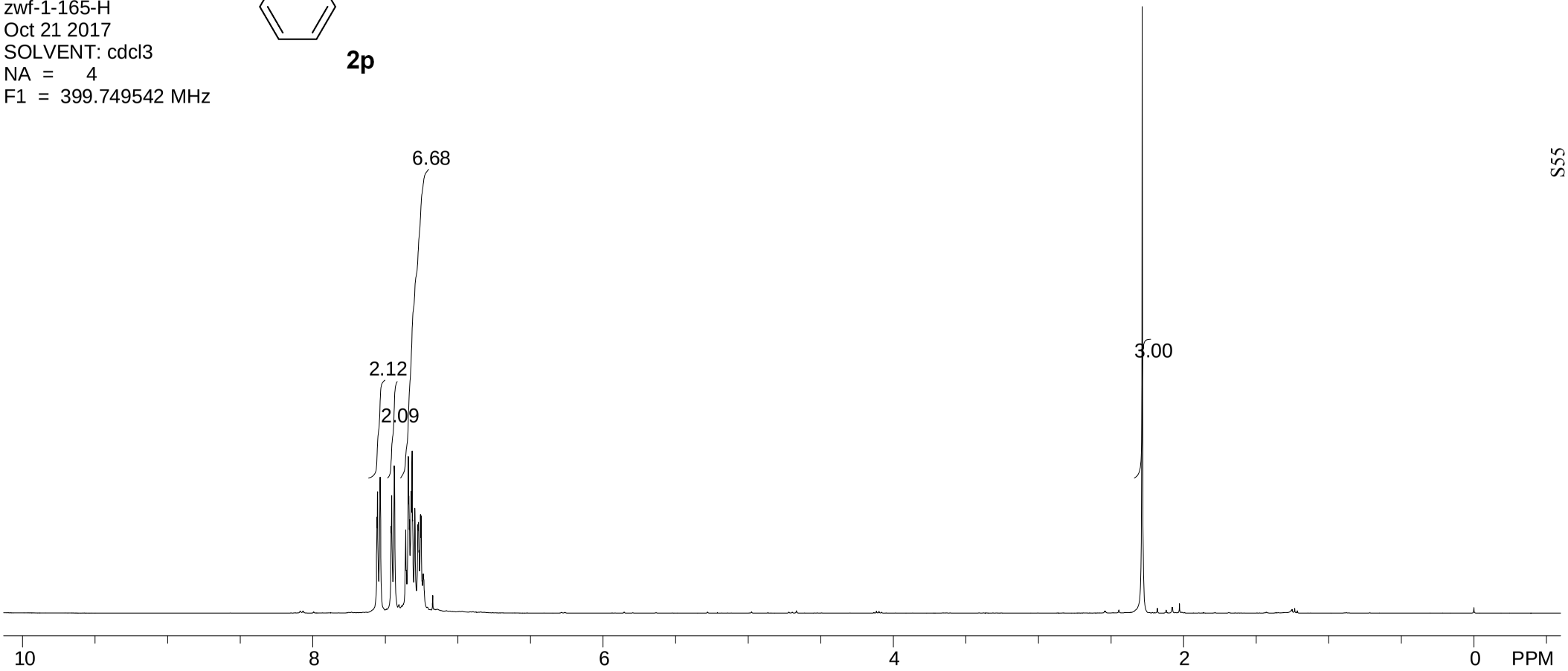

HJH-1-023-C
Sep 19 2017
SOLVENT: cdcl3
NA = 128
F1 = 100.527557 MHz
2o
^{n}Bu
^{n}Hex
CO_2H
212.398
173.345
134.923
128.493
127.438
126.376
110.337
102.906
77.319
77.000
76.681
31.594
29.826
29.803
28.953
28.687
28.186
22.569
22.432
13.984
13.870
200
150
100
50
PPM

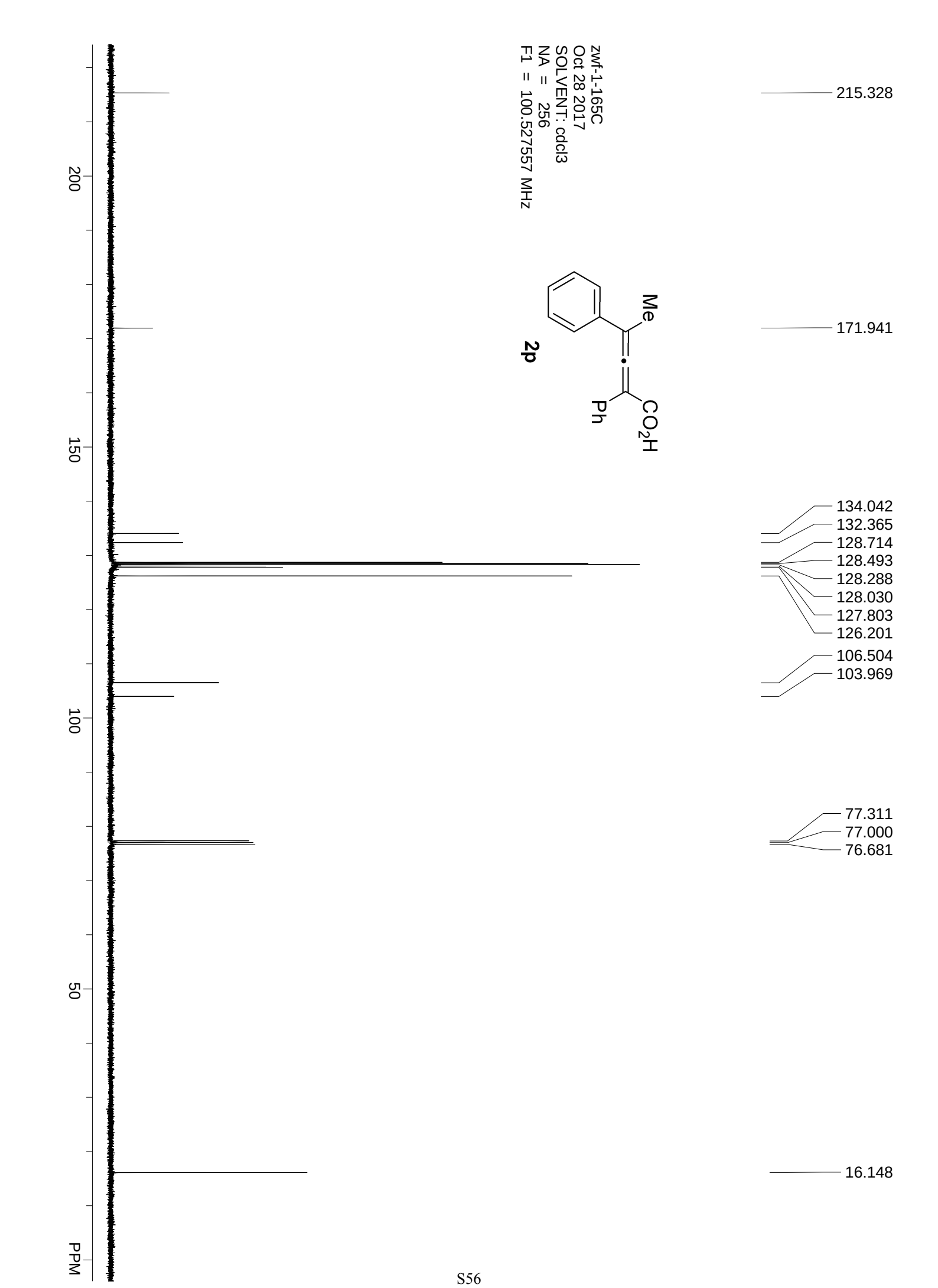


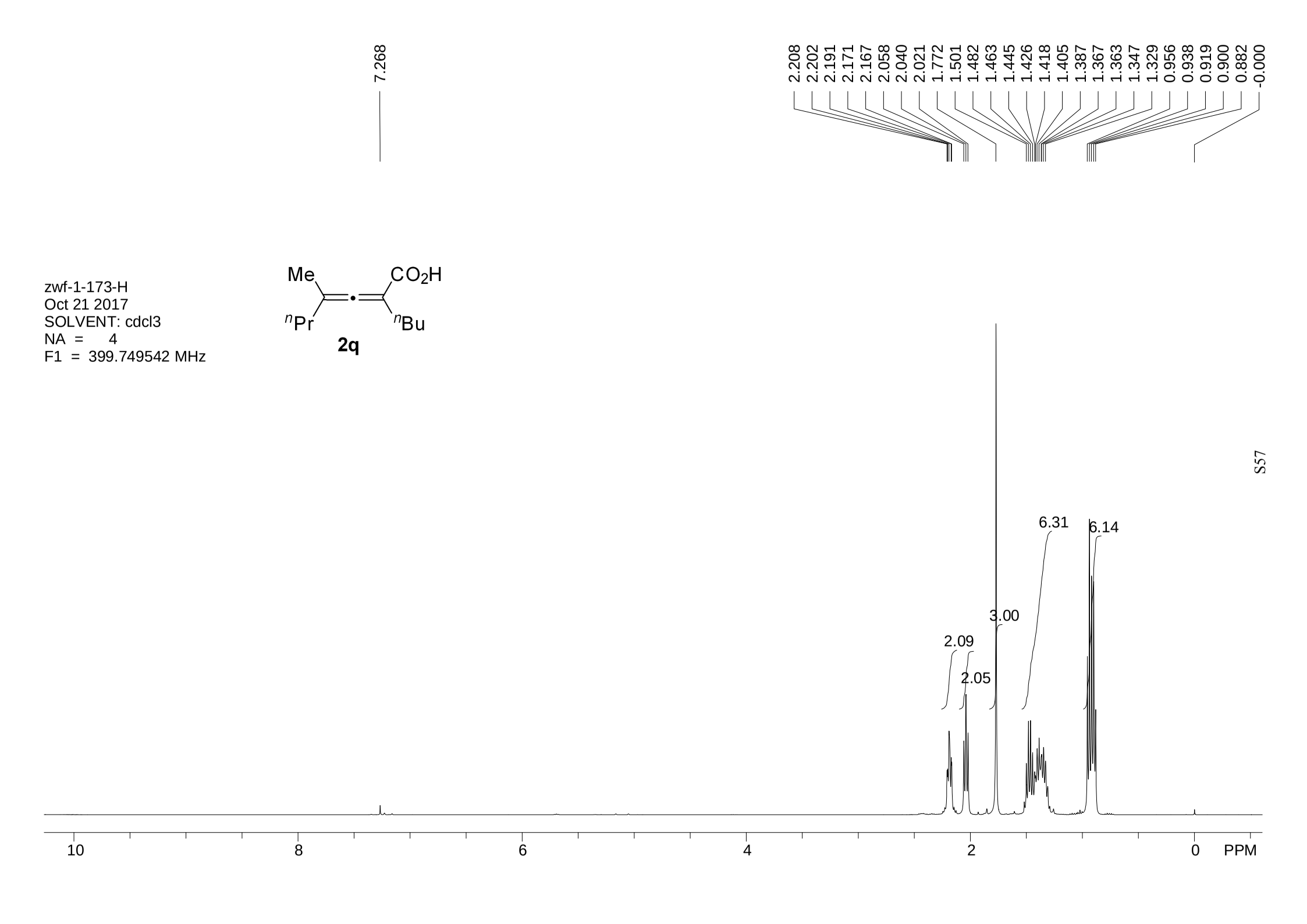


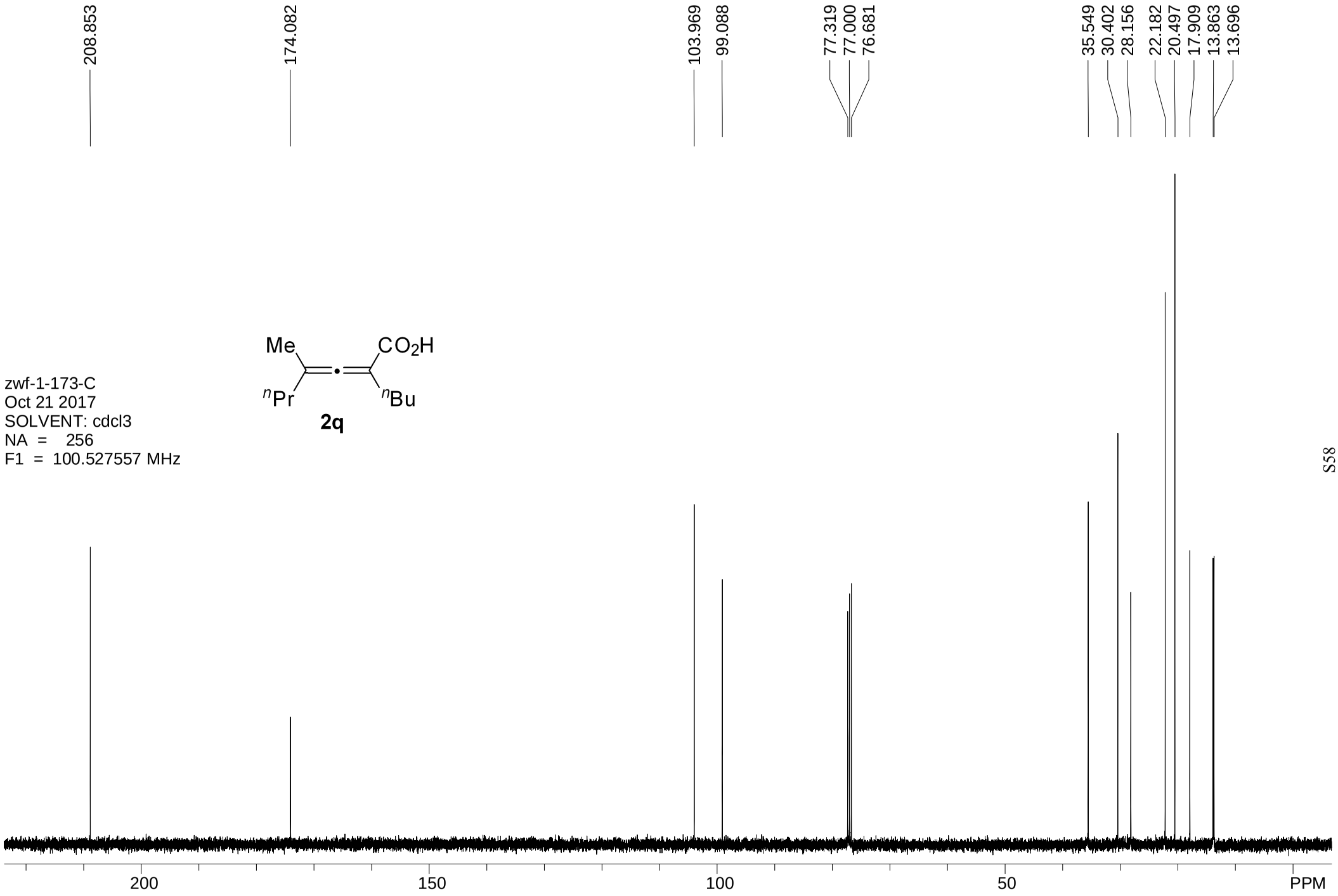
2p

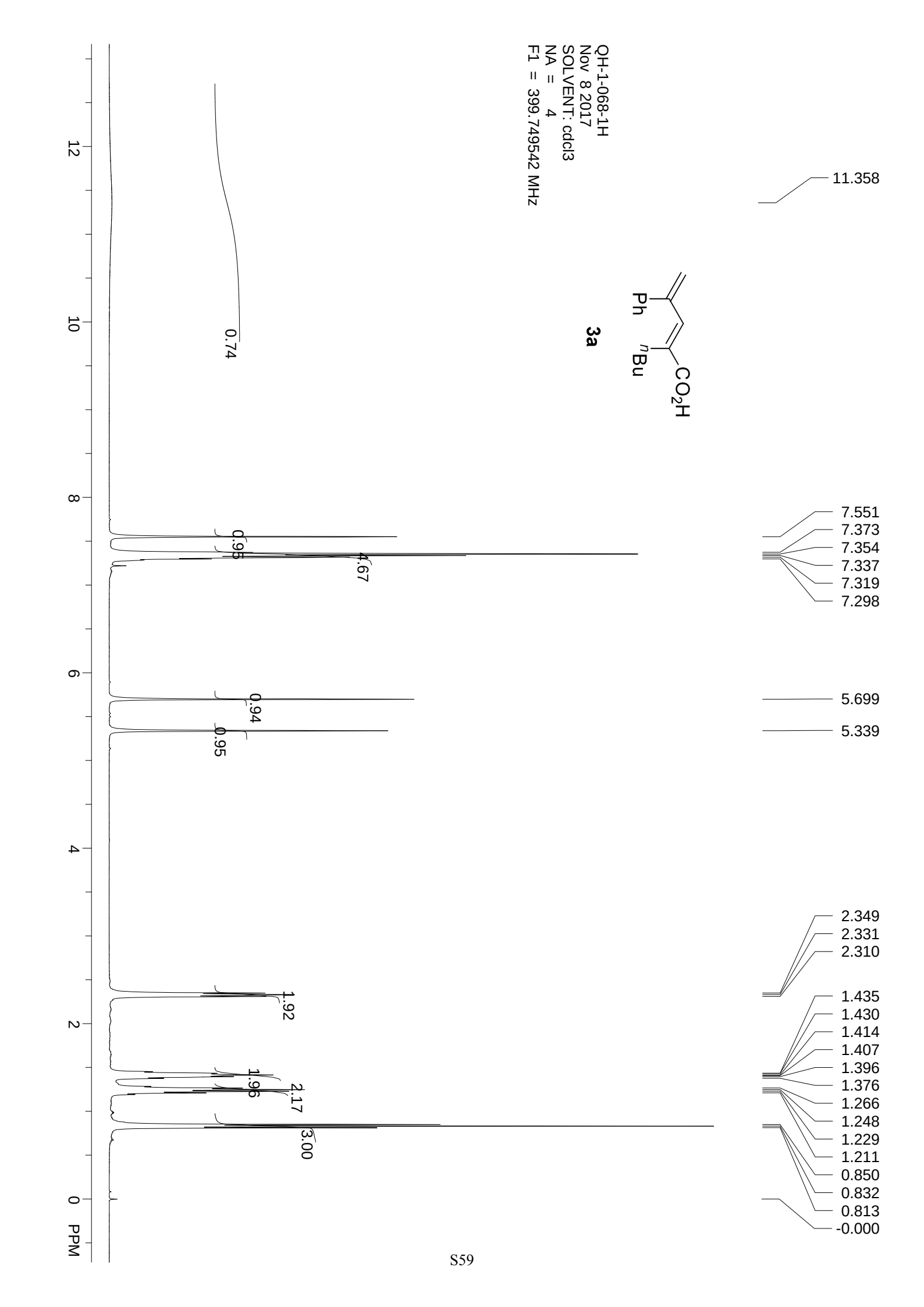
zwf-1-165-H
Oct 21 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

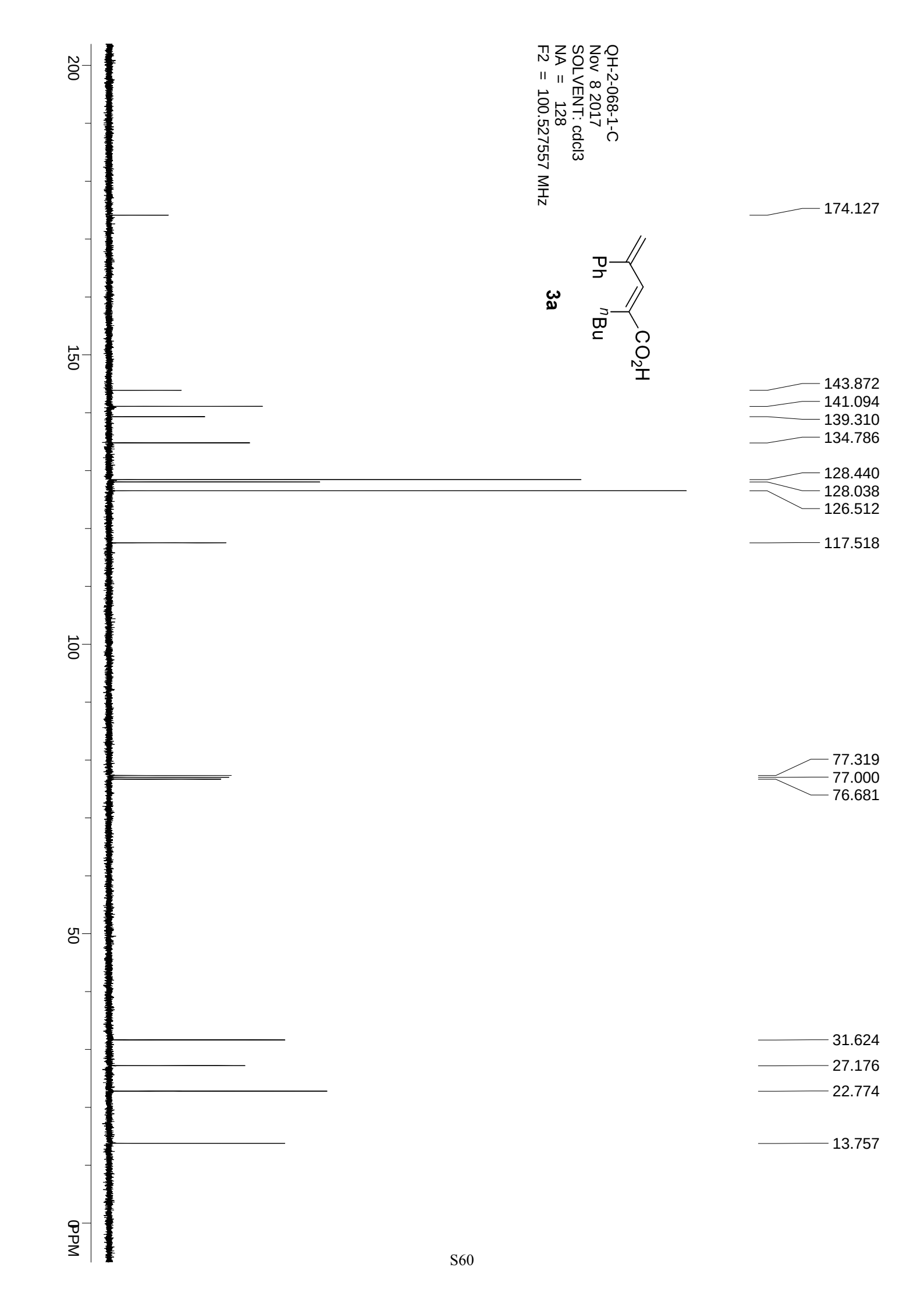


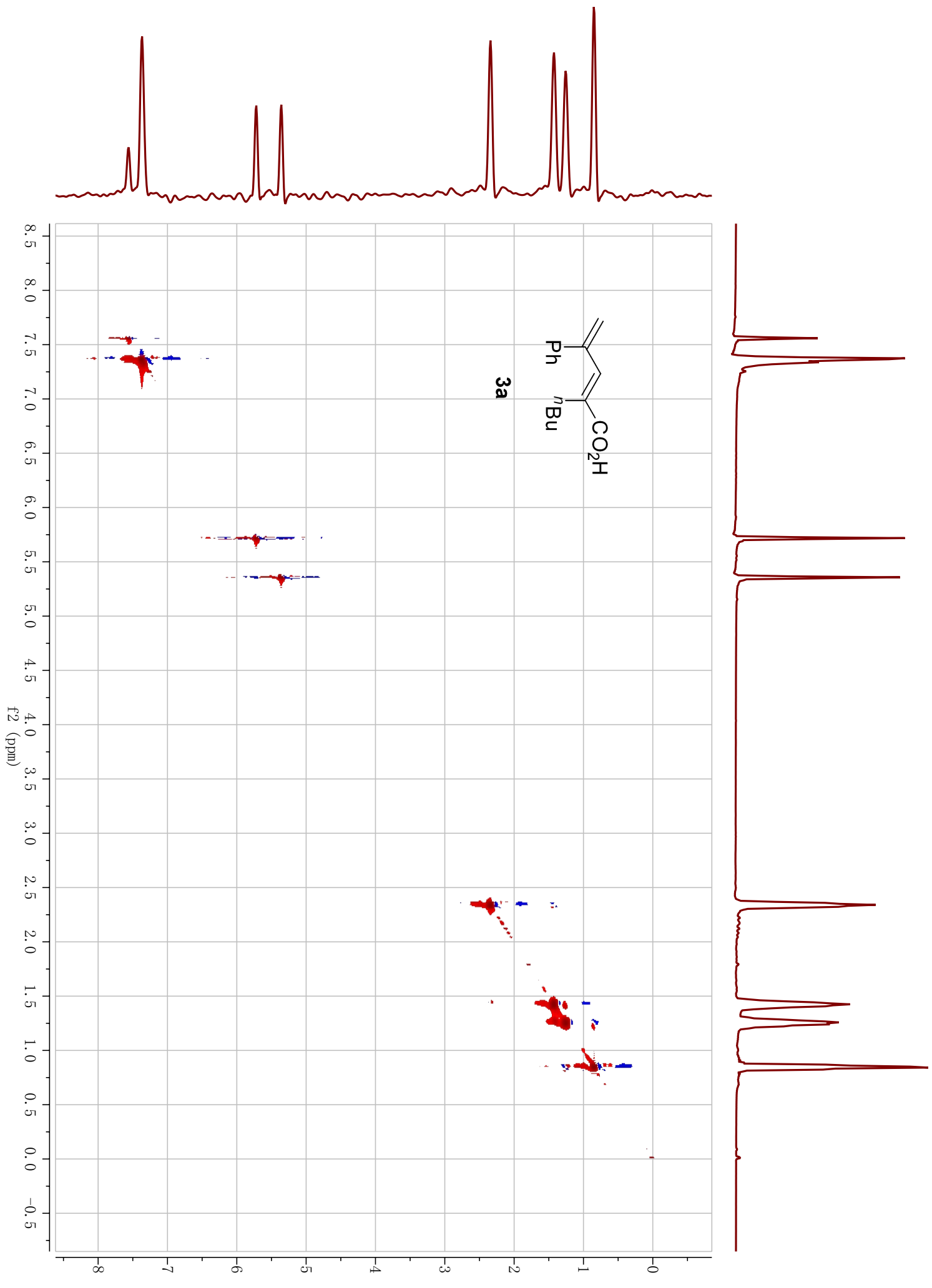

zwf-1-165C
Oct 28 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
2p
Me
Ph
CO2H
215.328
171.941
134.042
132.365
128.714
128.493
128.288
128.030
127.803
126.201
106.504
103.969
77.311
77.000
76.681
16.148
200
150
100
50
PPM

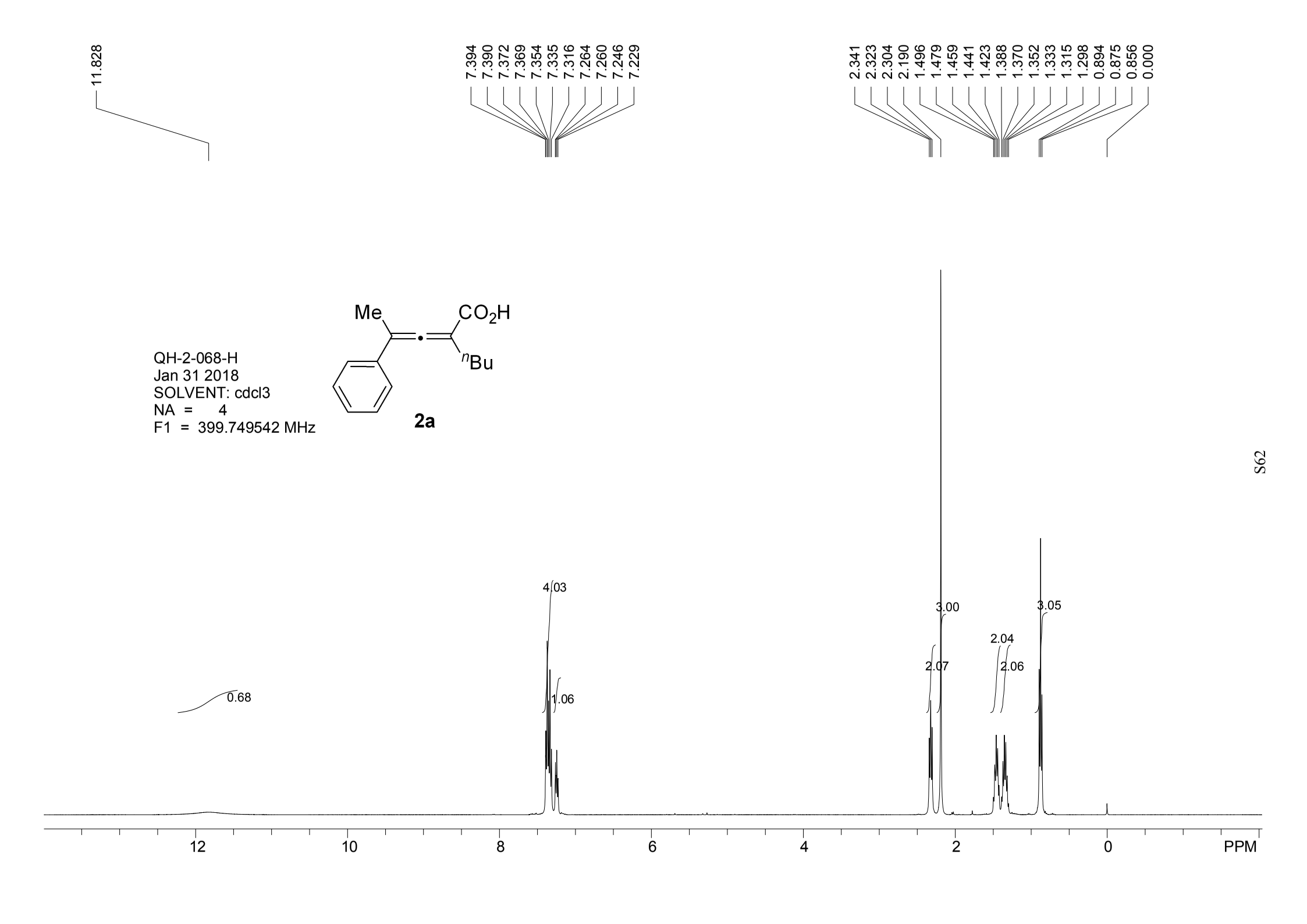

7.268
2.208
2.202
2.191
2.171
2.167
2.058
2.040
2.021
1.772
1.501
1.482
1.463
1.445
1.426
1.418
1.405
1.387
1.367
1.363
1.347
1.329
0.956
0.938
0.919
0.900
0.882
-0.000
zwf-1-173-H
Oct 21 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
Me
CO2H
nPr
nBu
2q
S57
6.31
6.14
3.00
2.09
2.05
10
8
6
4
2
0
PPM

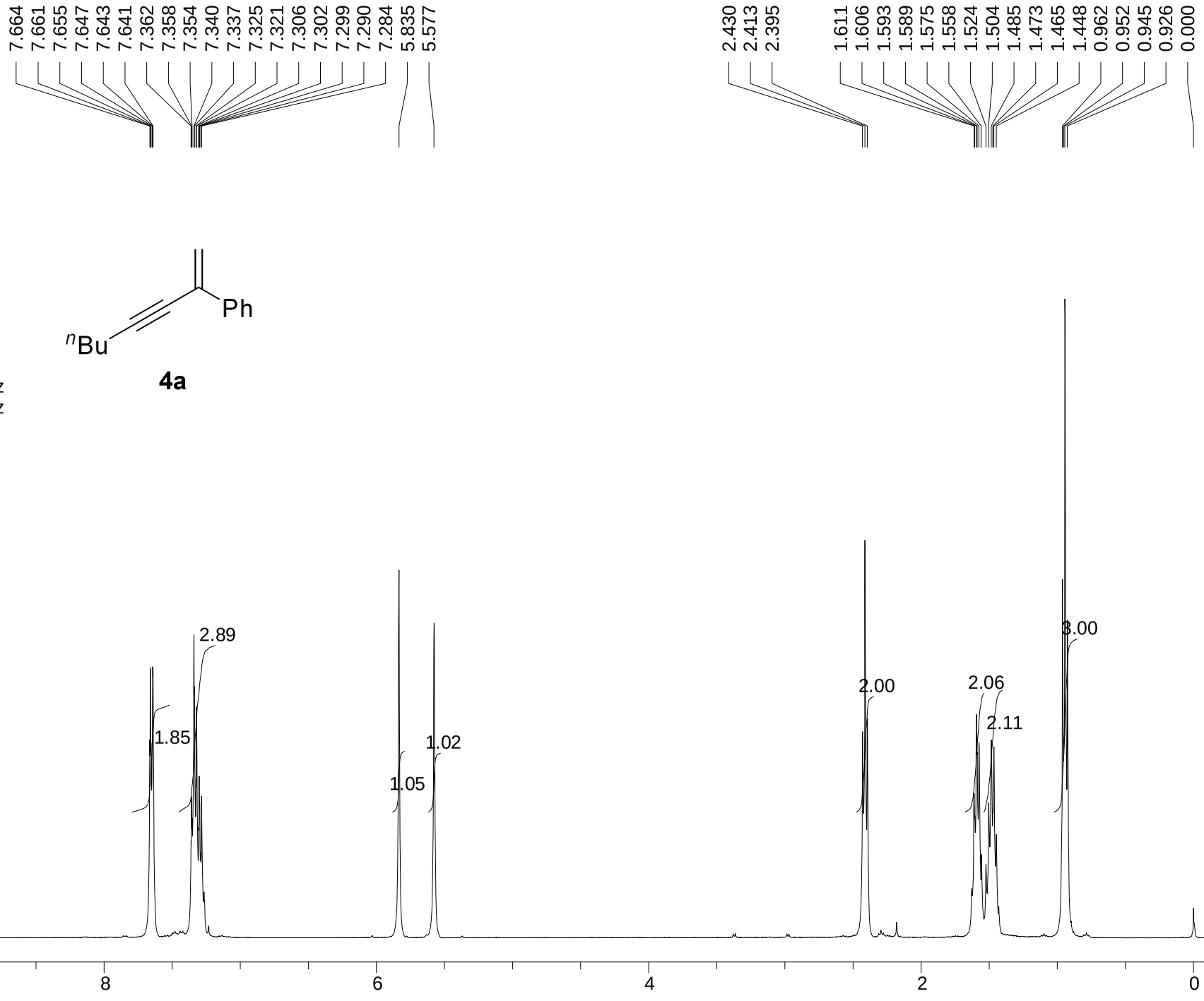

208.853
174.082
103.969
99.088
77.319
77.000
76.681
35.549
30.402
28.156
22.182
20.497
17.909
13.863
13.696
Me
CO2H
nPr
nBu
2q
zwf-1-173-C
Oct 21 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
200
150
100
50
PPM


QH-1-068-1H
Nov 8 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
3a
Ph
nBu
CO2H
11.358
7.551
7.373
7.354
7.337
7.319
7.298
5.699
5.339
2.349
2.331
2.310
1.435
1.430
1.414
1.407
1.396
1.376
1.266
1.248
1.229
1.211
0.850
0.832
0.813
-0.000
0.74
0.95
4.67
0.94
0.95
1.92
1.96
2.17
3.00
12
10
8
6
4
2
0
PPM

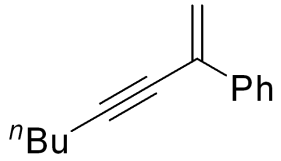

QH-2-068-1-C
Nov 8 2017
SOLVENT: cdcl3
NA = 128
F2 = 100.527557 MHz
3a
Ph
nBu
CO2H
174.127
143.872
141.094
139.310
134.786
128.440
128.038
126.512
117.518
77.319
77.000
76.681
31.624
27.176
22.774
13.757
200
150
100
50
0
PPM


3a
Ph
nBu
CO2H
f2 (ppm)
f1 (ppm)


11.828
7.394
7.390
7.372
7.369
7.354
7.335
7.316
7.264
7.260
7.246
7.229
2.341
2.323
2.304
2.190
1.496
1.479
1.459
1.441
1.423
1.388
1.370
1.352
1.333
1.315
1.298
0.894
0.875
0.856
0.000
QH-2-068-H
Jan 31 2018
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
Me
CO2H
nBu
2a
0.68
4.03
1.06
2.07
3.00
2.04
2.06
3.05
12
10
8
6
4
2
0
PPM

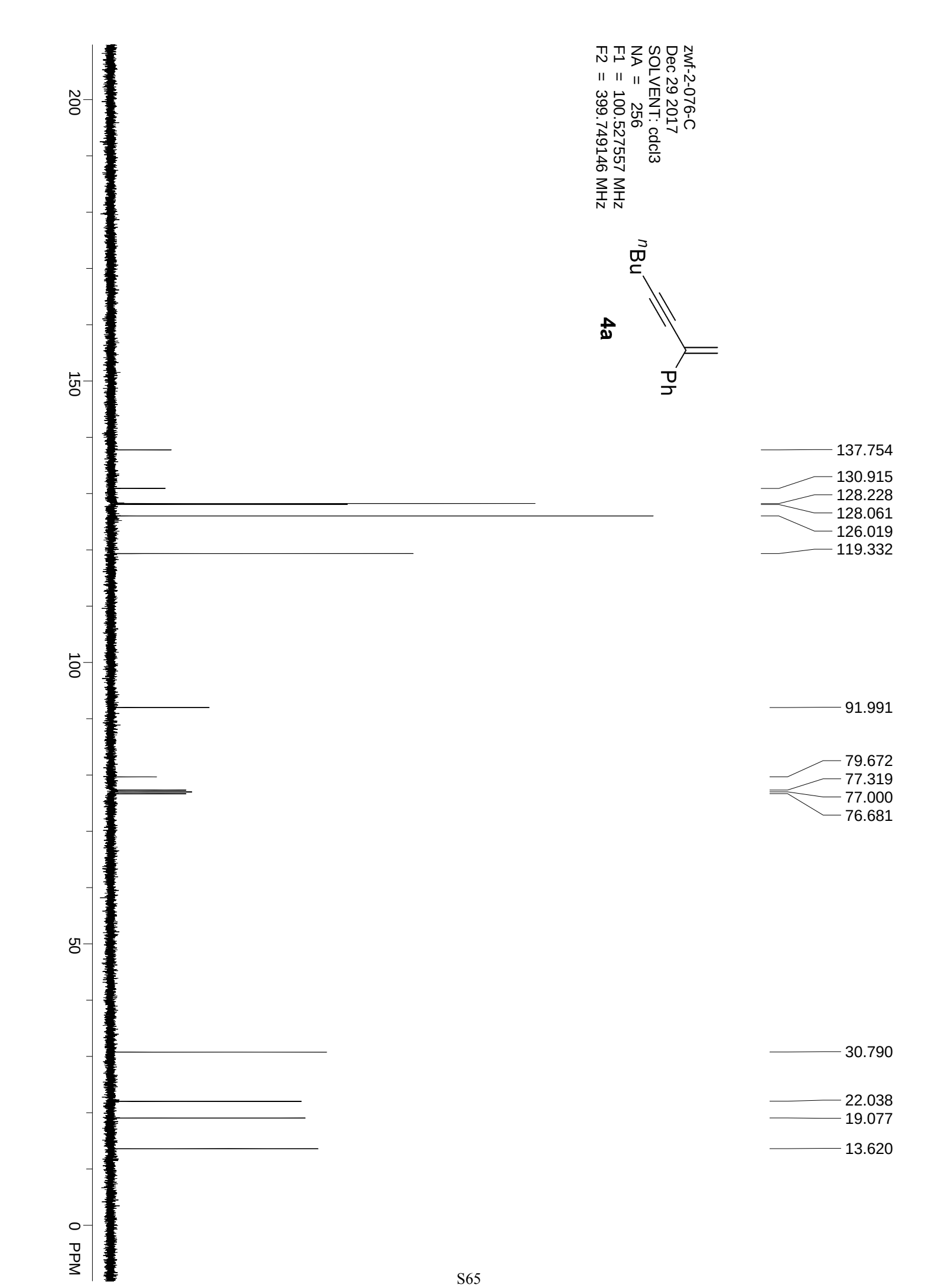

7.664
7.661
7.655
7.647
7.643
7.641
7.362
7.358
7.354
7.340
7.337
7.325
7.321
7.306
7.302
7.299
7.290
7.284
5.835
5.577
2.430
2.413
2.395
1.611
1.606
1.593
1.589
1.575
1.558
1.524
1.504
1.485
1.473
1.465
1.448
0.962
0.952
0.945
0.926
0.000
zwf-2-076-2
Dec 29 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
nBu
4a
2.89
1.85
1.05
1.02
2.00
2.06
2.11
3.00
10
8
6
4
2
0
PPM

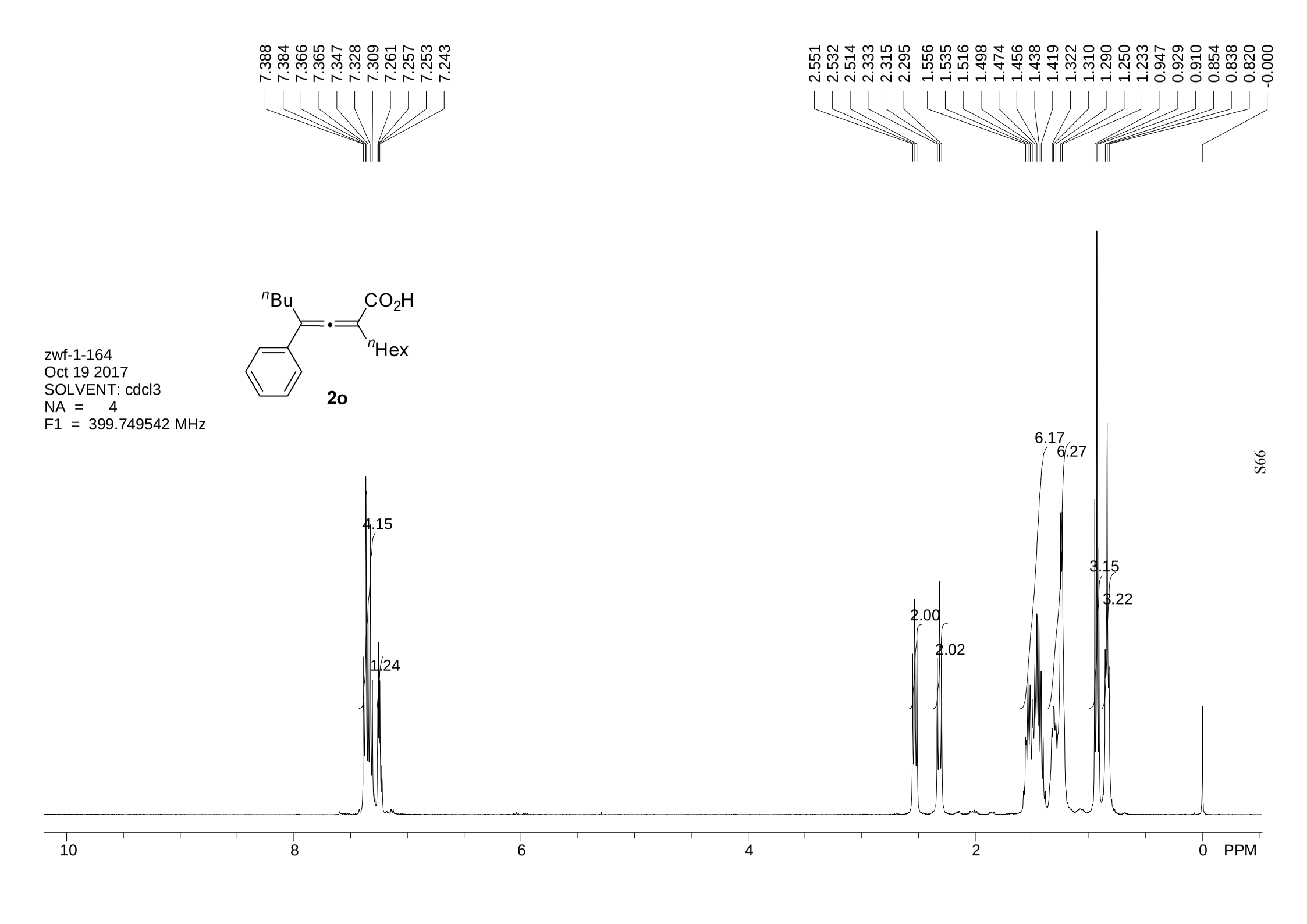
zwf-2-076-2-cd
Dec 29 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz

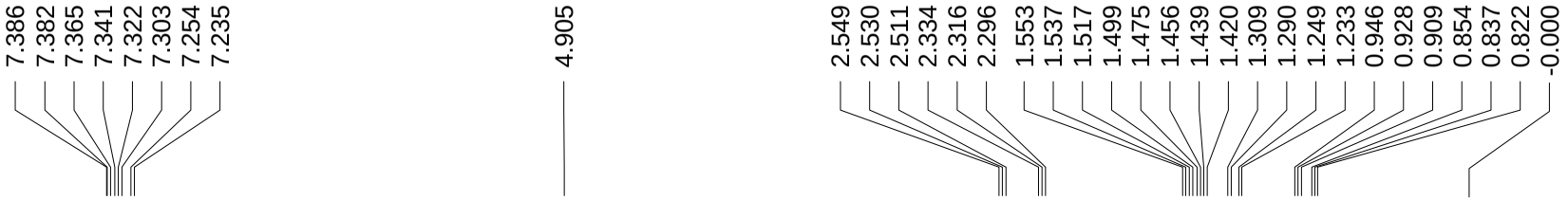


4a

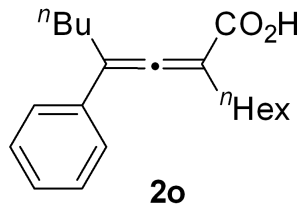
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 36.9 mg product


zwf-2-076-C
Dec 29 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
nBu
Ph
4a
137.754
130.915
128.228
128.061
126.019
119.332
91.991
79.672
77.319
77.000
76.681
30.790
22.038
19.077
13.620
200
150
100
50
0 PPM


7.388
7.384
7.366
7.365
7.347
7.328
7.309
7.261
7.257
7.253
7.243
2.551
2.532
2.514
2.333
2.315
2.295
1.556
1.535
1.516
1.498
1.474
1.456
1.438
1.419
1.322
1.310
1.290
1.250
1.233
0.947
0.929
0.910
0.854
0.838
0.820
-0.000
nBu
CO2H
nHex
2o
zwf-1-164
Oct 19 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
S66
4.15
1.24
2.00
2.02
6.17
6.27
3.15
3.22
10
8
6
4
2
0
PPM

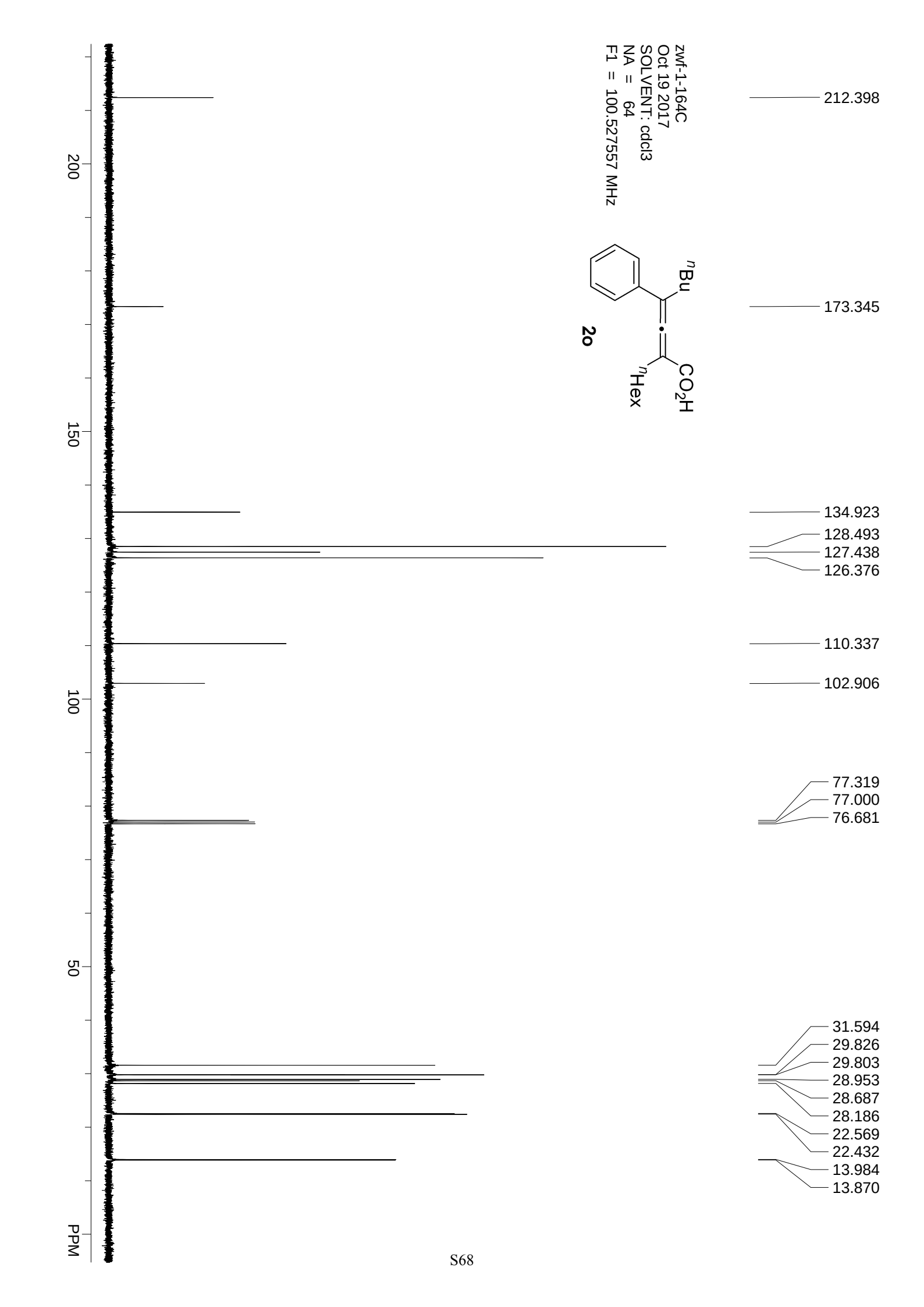


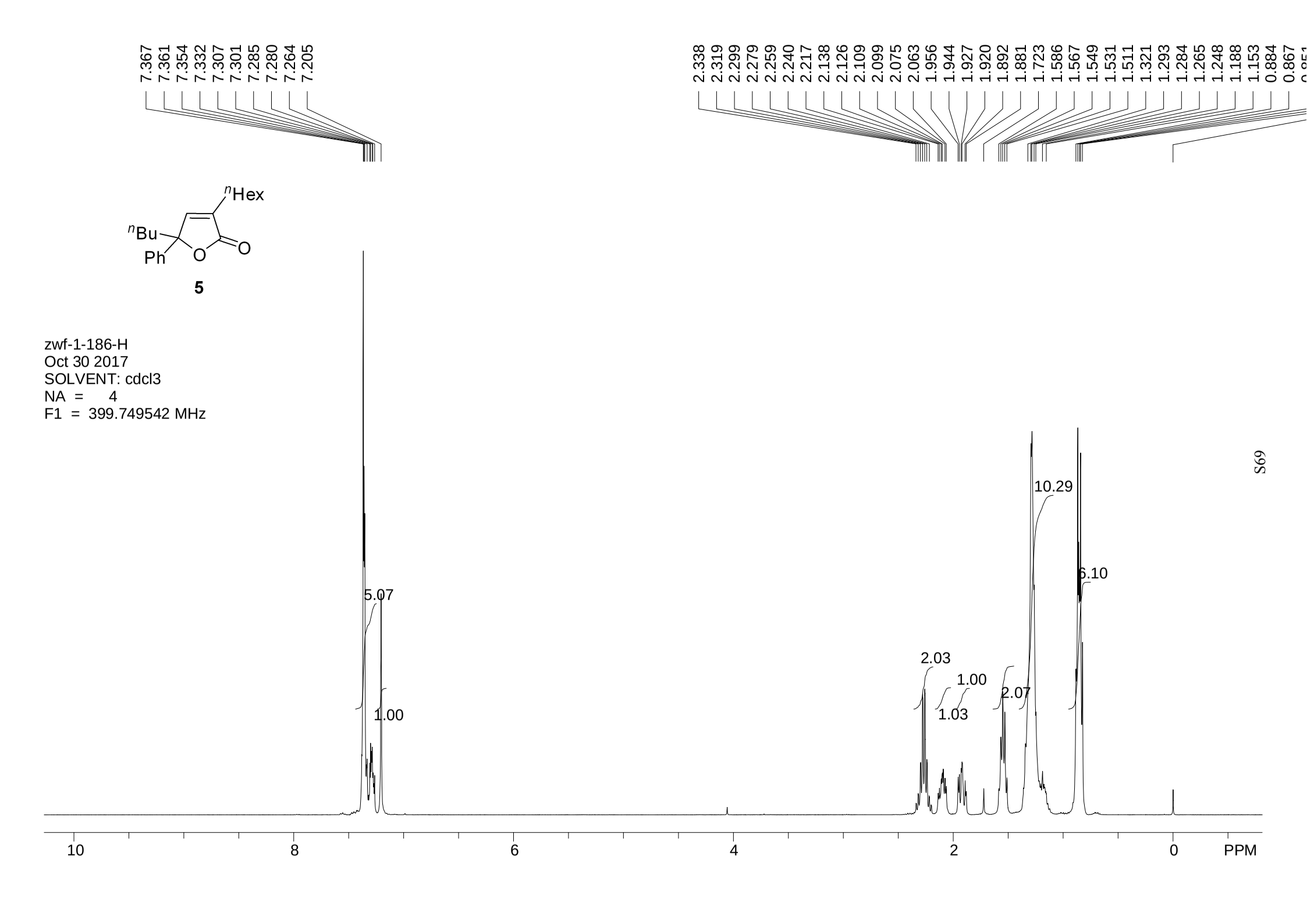
zwf-1-164-cd
Oct 19 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

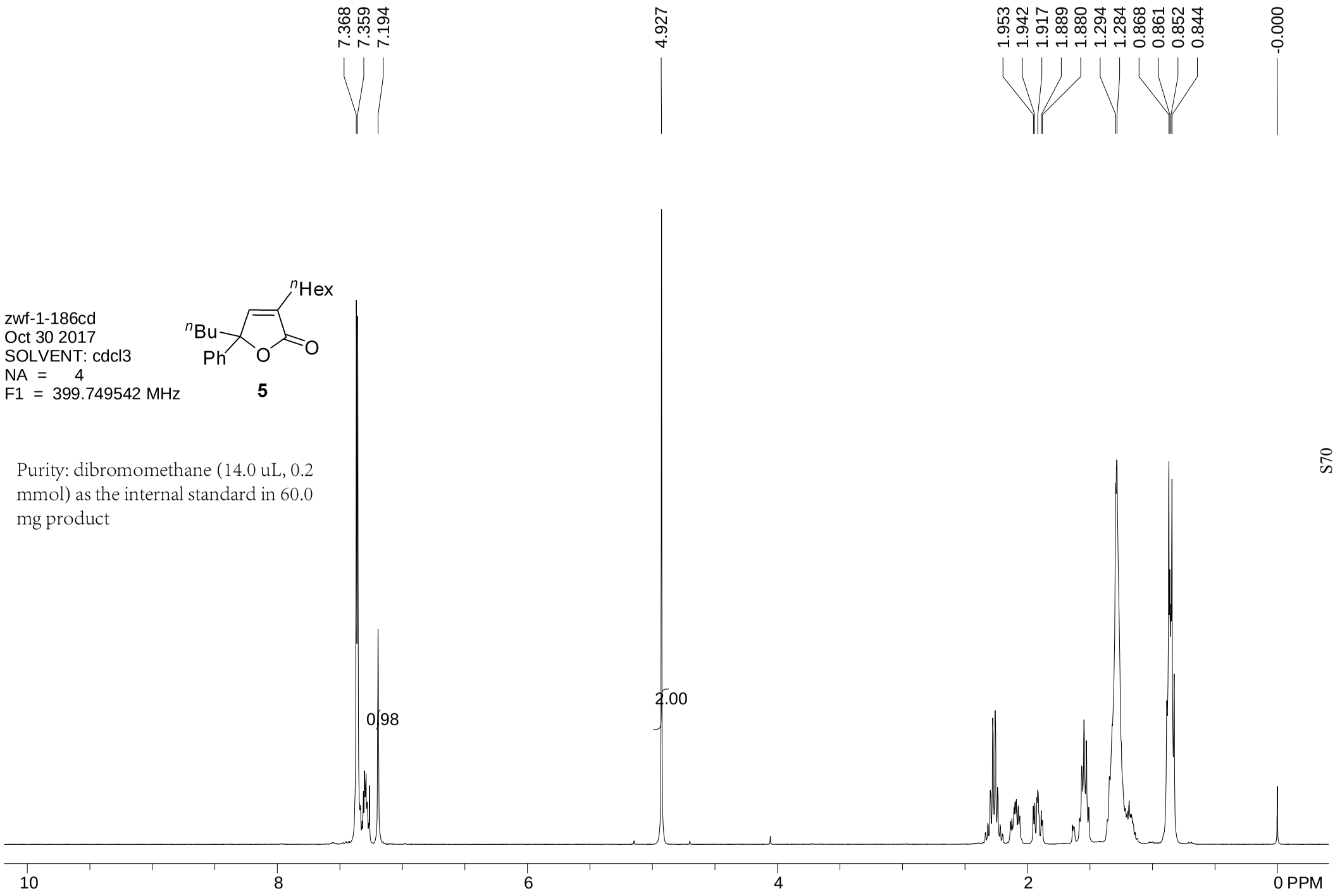


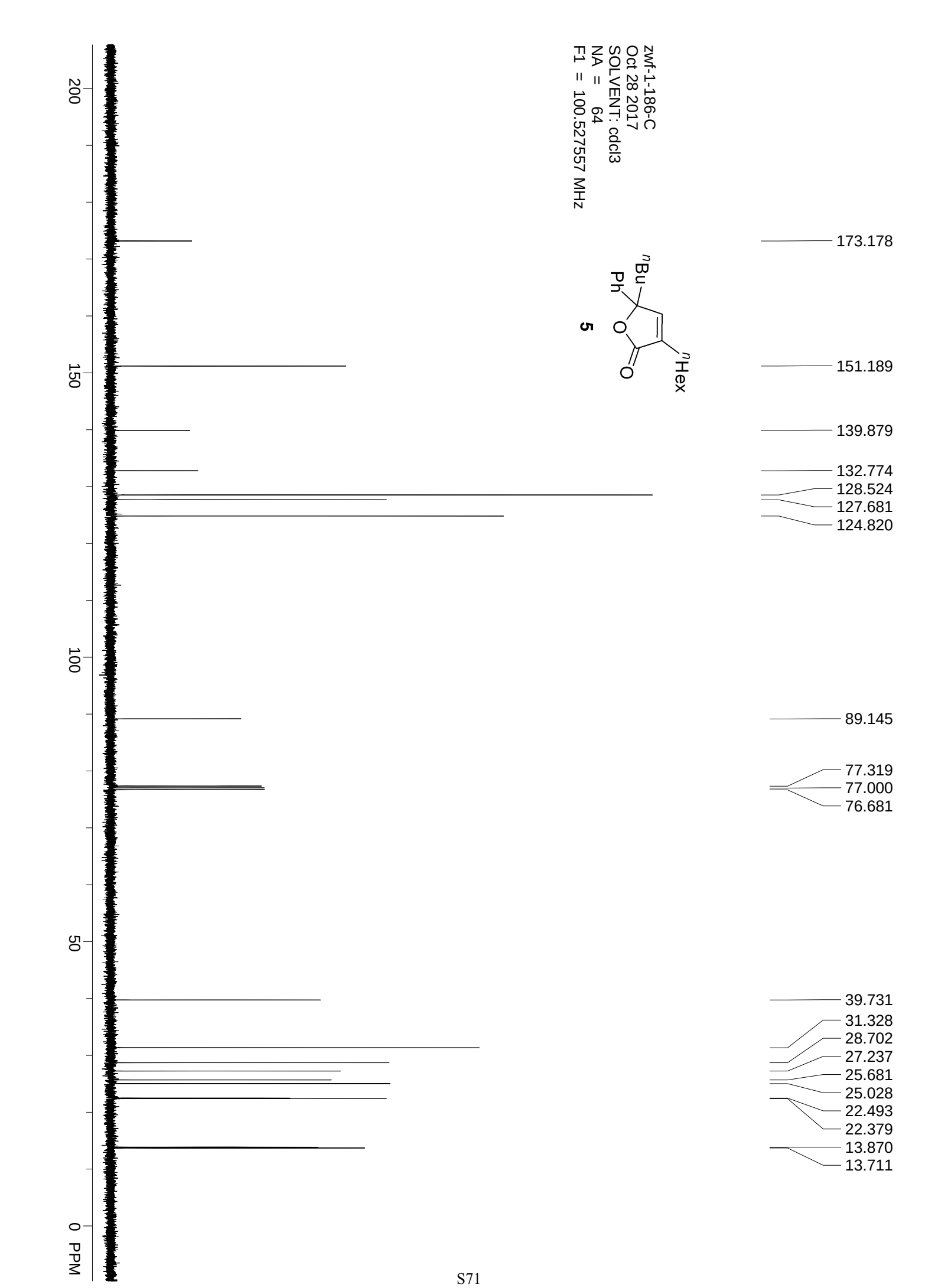
2o

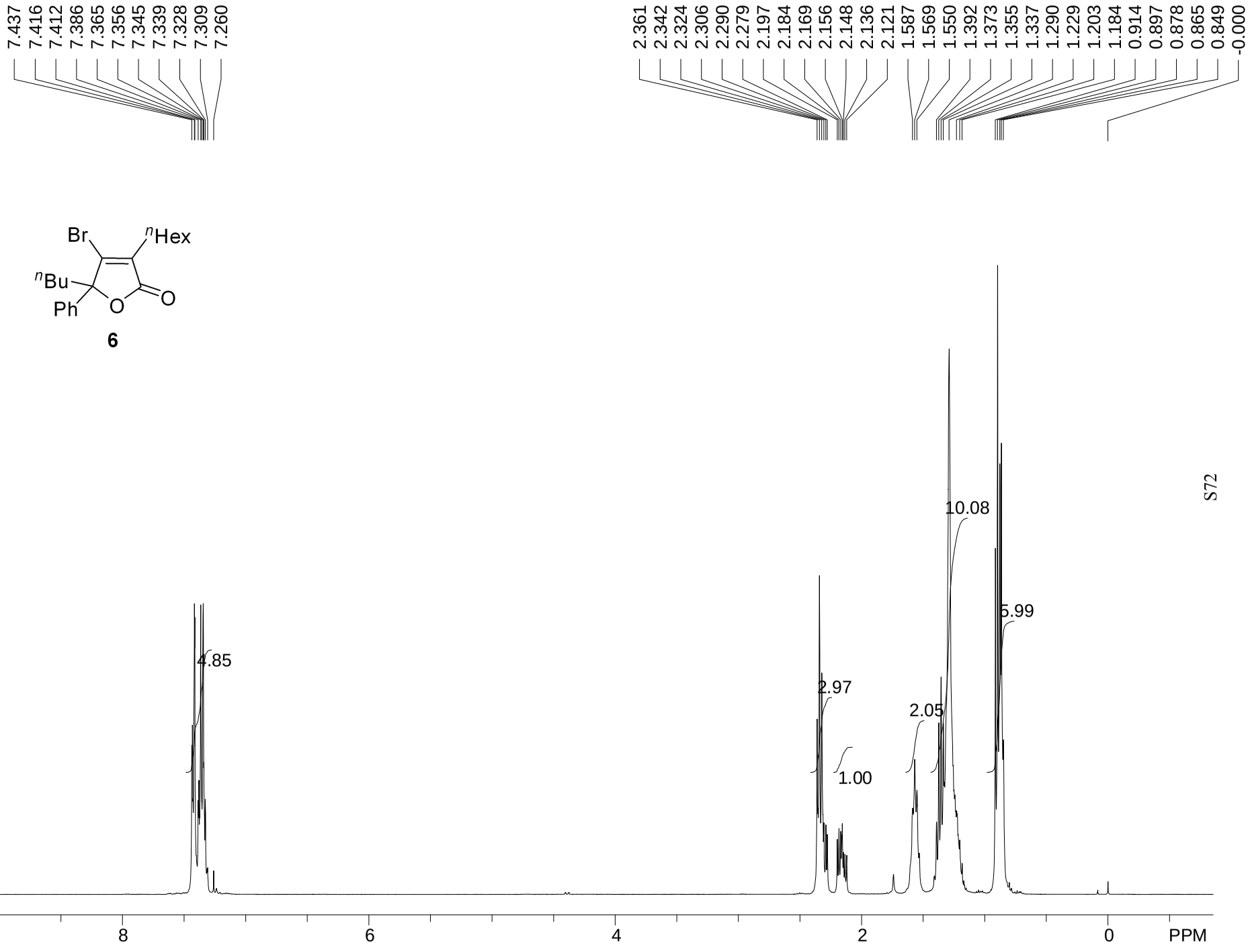
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 60.8 mg product

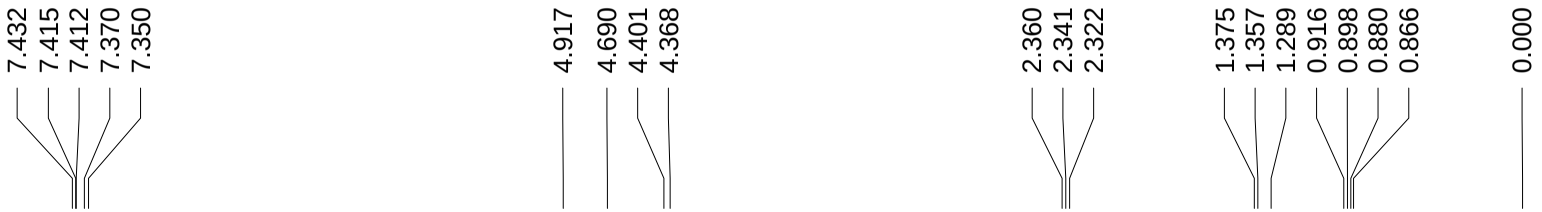

zwf-1-164C
Oct 19 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.527557 MHz
2o
nBu
nHex
CO2H
212.398
173.345
134.923
128.493
127.438
126.376
110.337
102.906
77.319
77.000
76.681
31.594
29.826
29.803
28.953
28.687
28.186
22.569
22.432
13.984
13.870
200
150
100
50
PPM


7.367
7.361
7.354
7.332
7.307
7.301
7.285
7.280
7.264
7.205
2.338
2.319
2.299
2.279
2.259
2.240
2.217
2.138
2.126
2.109
2.099
2.075
2.063
1.956
1.944
1.927
1.920
1.892
1.881
1.723
1.586
1.567
1.549
1.531
1.511
1.321
1.293
1.284
1.265
1.248
1.188
1.153
0.884
0.867
nHex
nBu
Ph
O
O
5
zwf-1-186-H
Oct 30 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
5.07
1.00
2.03
1.00
1.03
2.07
10.29
6.10
10
8
6
4
2
0
PPM

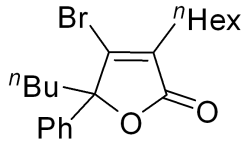

7.368
7.359
7.194
4.927
1.953
1.942
1.917
1.889
1.880
1.294
1.284
0.868
0.861
0.852
0.844
-0.000
zwf-1-186cd
Oct 30 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
nHex
nBu
Ph
O
O
5
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 60.0 mg product
0.98
2.00
10
8
6
4
2
0 PPM


zwf-1-186-C
Oct 28 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.527557 MHz
nBu
Ph
O
O
nHex
5
173.178
151.189
139.879
132.774
128.524
127.681
124.820
89.145
77.319
77.000
76.681
39.731
31.328
28.702
27.237
25.681
25.028
22.493
22.379
13.870
13.711
200
150
100
50
0 PPM


7.437
7.416
7.412
7.386
7.365
7.356
7.345
7.339
7.328
7.309
7.260
2.361
2.342
2.324
2.306
2.290
2.279
2.197
2.184
2.169
2.156
2.148
2.136
2.121
1.587
1.569
1.550
1.392
1.373
1.355
1.337
1.290
1.229
1.203
1.184
0.914
0.897
0.878
0.865
0.849
-0.000
Br
nHex
nBu
Ph
O
O
6
zwf-1-187-H
Oct 28 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
S72
4.85
2.97
1.00
2.05
10.08
5.99
10
8
6
4
2
0
PPM

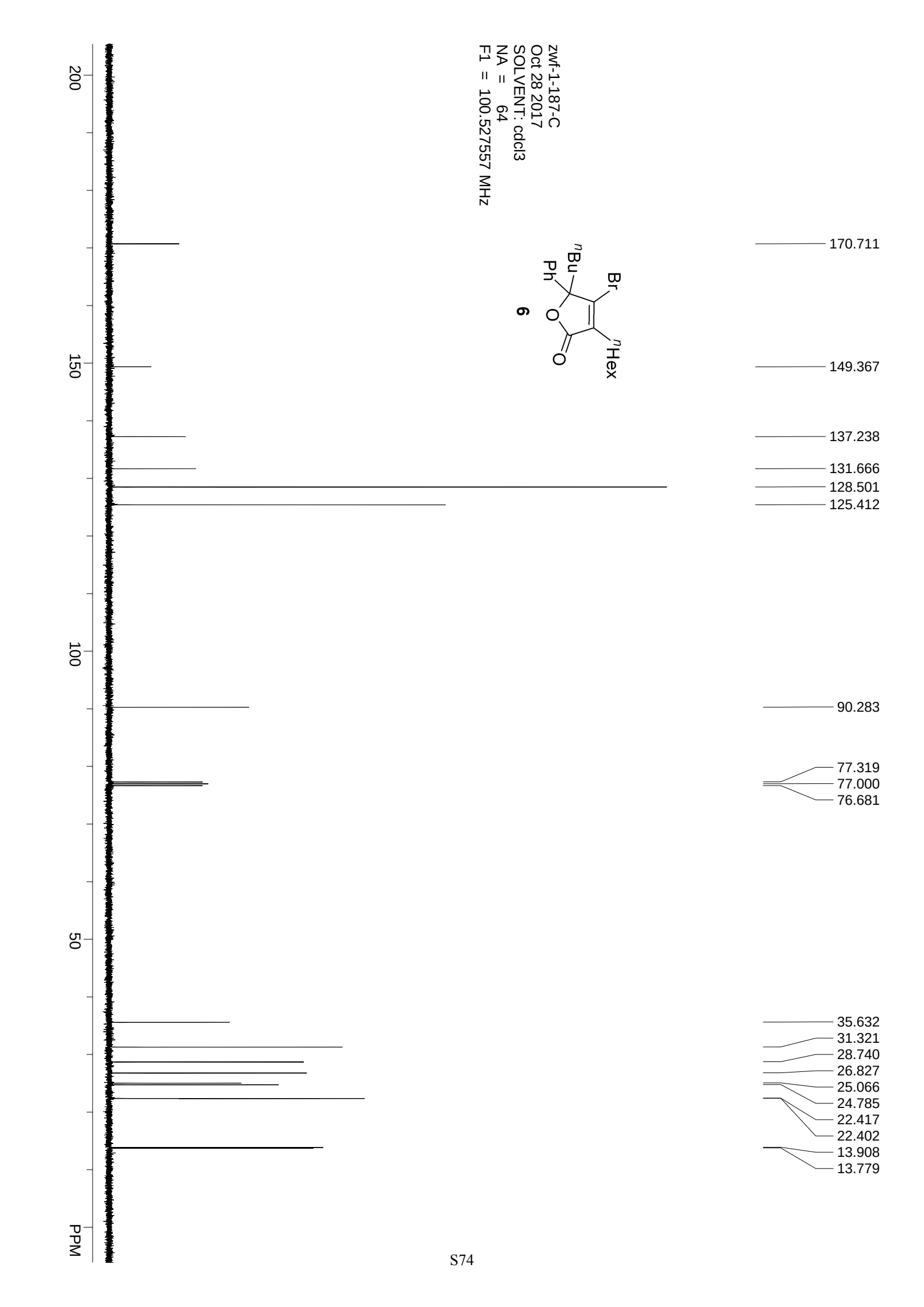


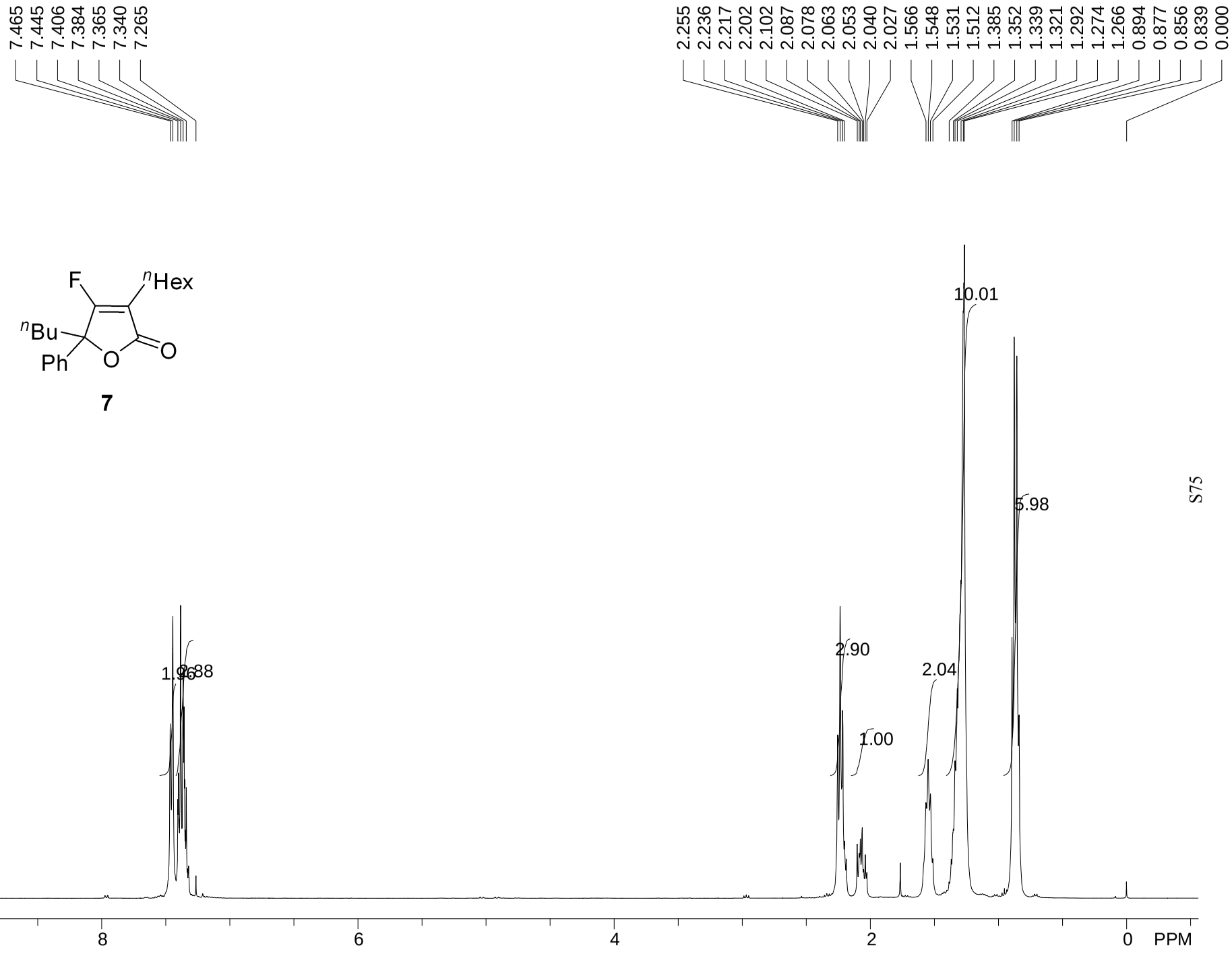
zwf-1-187-cd
Oct 30 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz

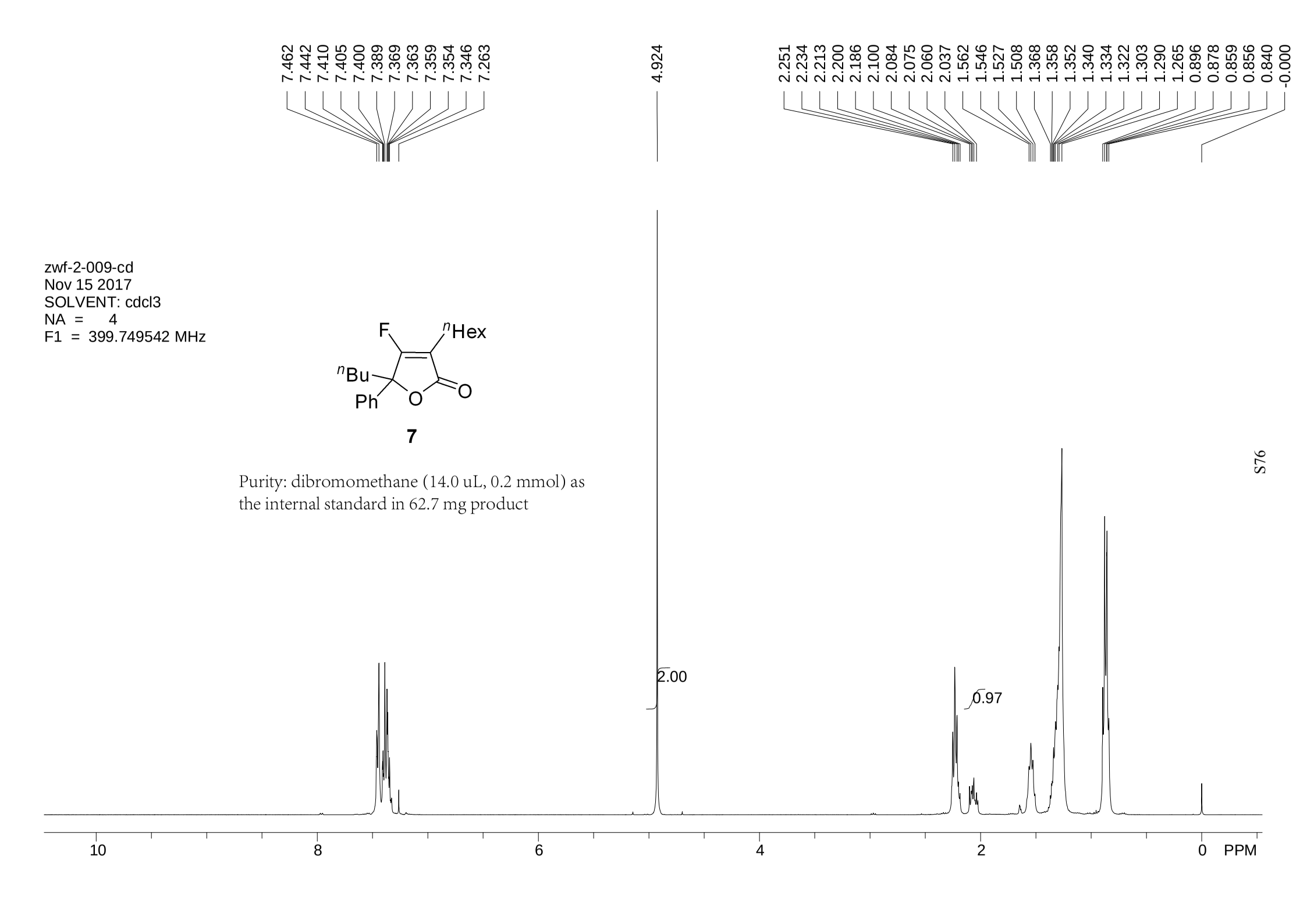


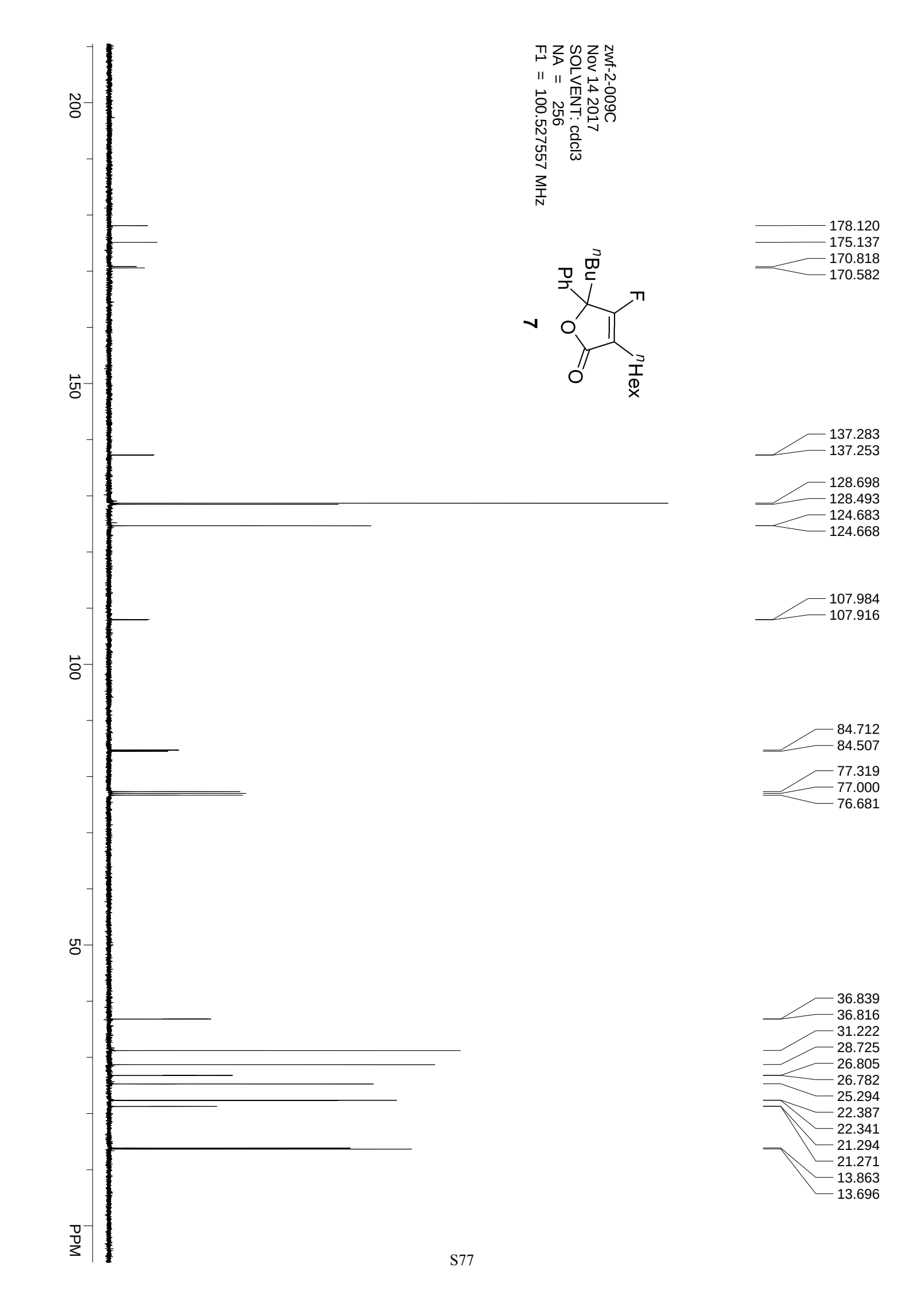
6

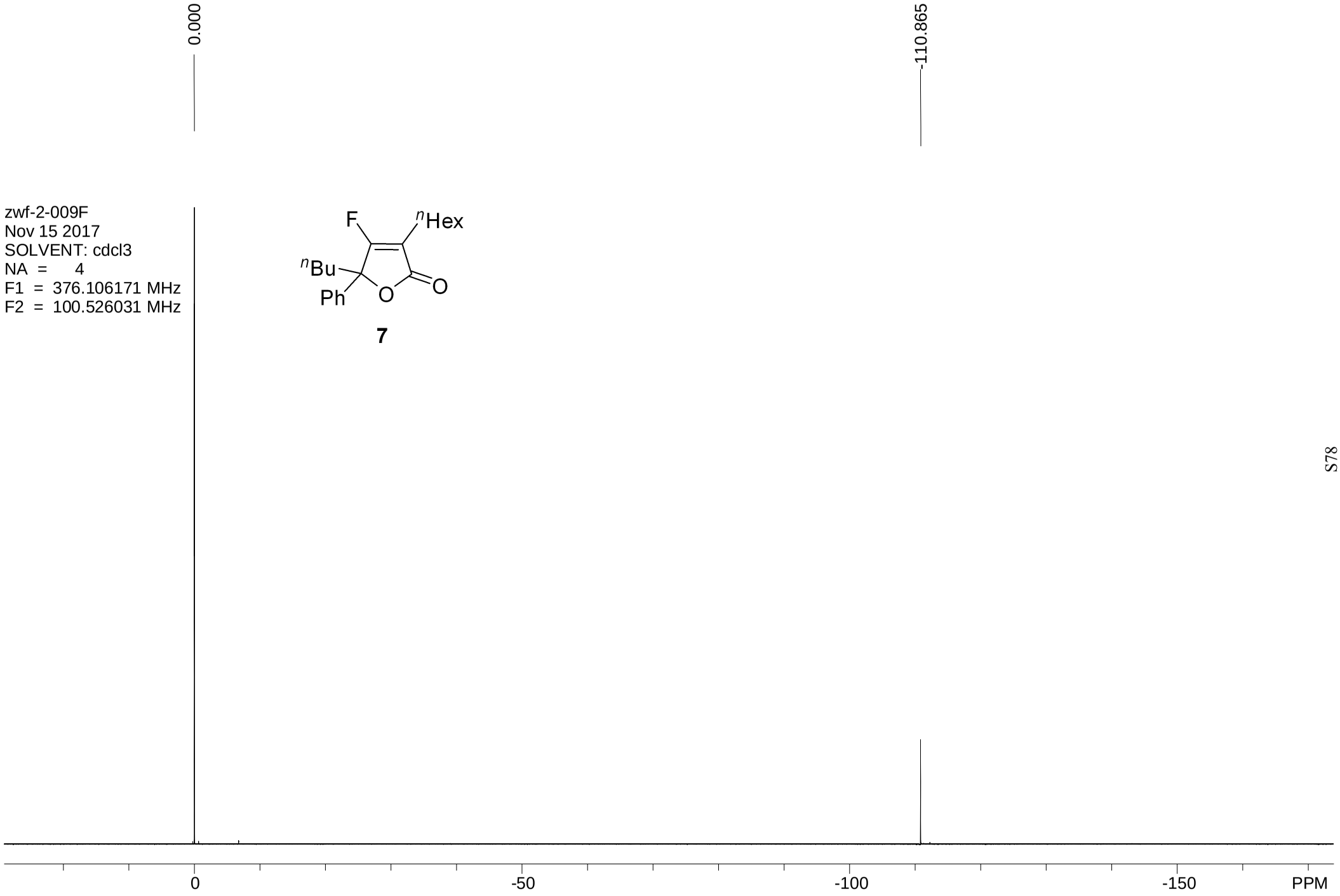
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 75.8 mg product

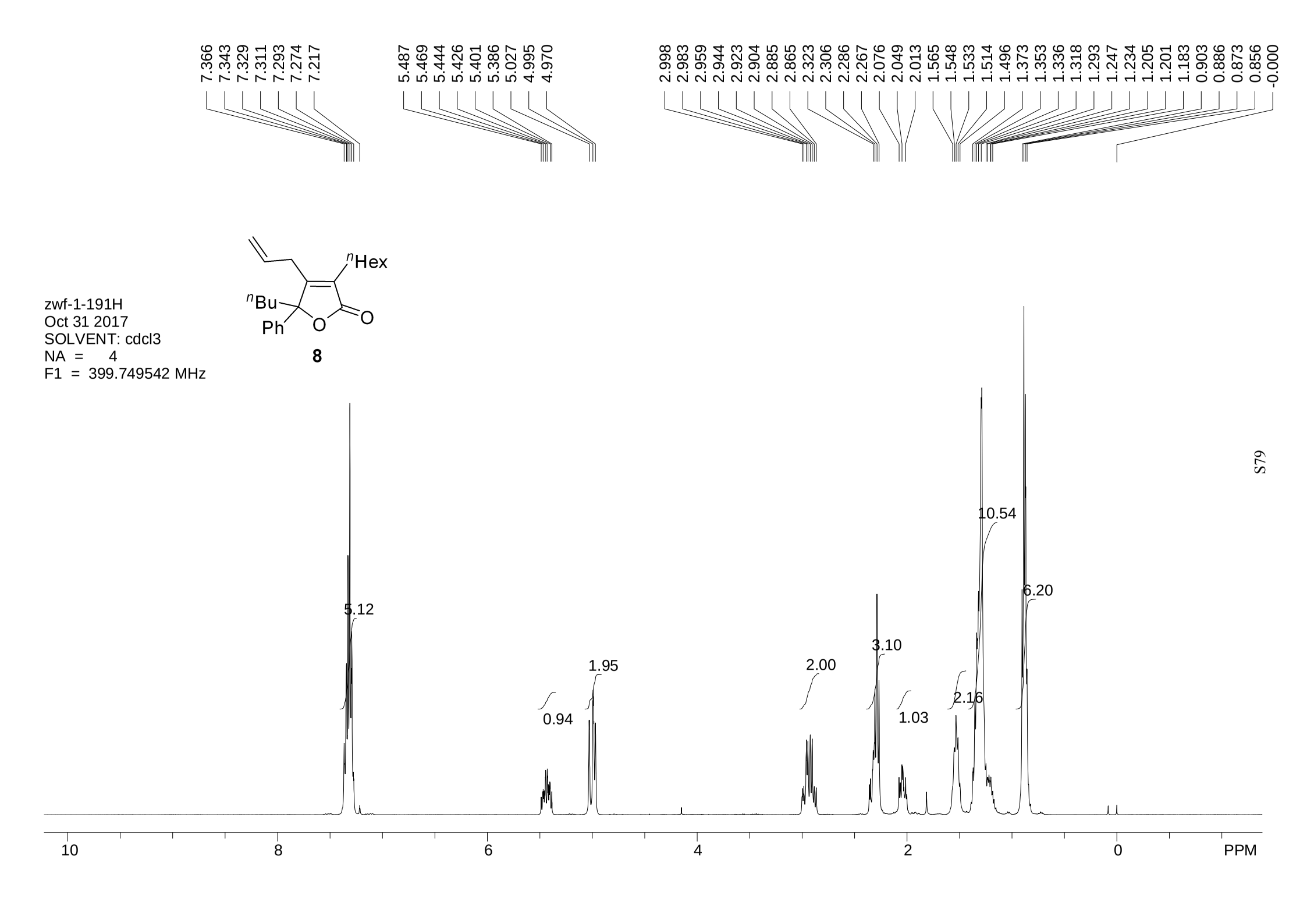

zwf-1-187-C
Oct 28 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.527557 MHz
6
nBu
Ph
Br
nHex
O
O
200
150
100
50
PPM
170.711
149.367
137.238
131.666
128.501
125.412
90.283
77.319
77.000
76.681
35.632
31.321
28.740
26.827
25.066
24.785
22.417
22.402
13.908
13.779

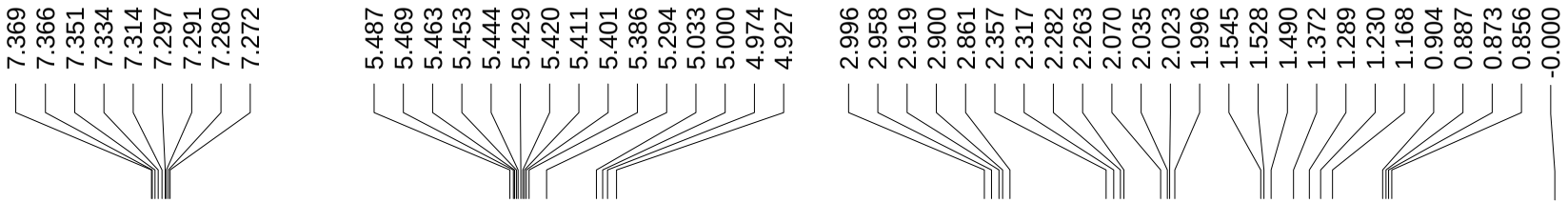

7.465
7.445
7.406
7.384
7.365
7.340
7.265
2.255
2.236
2.217
2.202
2.102
2.087
2.078
2.063
2.053
2.040
2.027
1.566
1.548
1.531
1.512
1.385
1.352
1.339
1.321
1.292
1.274
1.266
0.894
0.877
0.856
0.839
0.000
F
nHex
nBu
Ph
O
O
7
zwf-2-009H
Nov 14 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
10.01
5.98
2.90
2.04
1.00
1.96
2.88
S75
10
8
6
4
2
0
PPM


7.462
7.442
7.410
7.405
7.400
7.389
7.369
7.363
7.359
7.354
7.346
7.263
4.924
2.251
2.234
2.213
2.200
2.186
2.100
2.084
2.075
2.060
2.037
1.562
1.546
1.527
1.508
1.368
1.358
1.352
1.340
1.334
1.322
1.303
1.290
1.265
0.896
0.878
0.859
0.856
0.840
-0.000
zwf-2-009-cd
Nov 15 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F
nHex
nBu
Ph
O
O
7
Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 62.7 mg product
S76
2.00
0.97
10
8
6
4
2
0
PPM

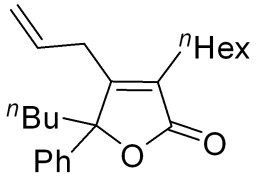

zwf-2-009C
Nov 14 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
7
nBu
Ph
O
O
F
nHex
178.120
175.137
170.818
170.582
137.283
137.253
128.698
128.493
124.683
124.668
107.984
107.916
84.712
84.507
77.319
77.000
76.681
36.839
36.816
31.222
28.725
26.805
26.782
25.294
22.387
22.341
21.294
21.271
13.863
13.696
200
150
100
50
PPM


0.000
-110.865
zwf-2-009F
Nov 15 2017
SOLVENT: cdcl3
NA = 4
F1 = 376.106171 MHz
F2 = 100.526031 MHz
F
nHex
nBu
Ph
O
O
7
0
-50
-100
-150
PPM


7.366
7.343
7.329
7.311
7.293
7.274
7.217
5.487
5.469
5.444
5.426
5.401
5.386
5.027
4.995
4.970
2.998
2.983
2.959
2.944
2.923
2.904
2.885
2.865
2.323
2.306
2.286
2.267
2.076
2.049
2.013
1.565
1.548
1.533
1.514
1.496
1.373
1.353
1.336
1.318
1.293
1.247
1.234
1.205
1.201
1.183
0.903
0.886
0.873
0.856
-0.000
nHex
nBu
Ph
O
O
8
zwf-1-191H
Oct 31 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
S79
5.12
0.94
1.95
2.00
3.10
1.03
2.16
10.54
6.20
10
8
6
4
2
0
PPM

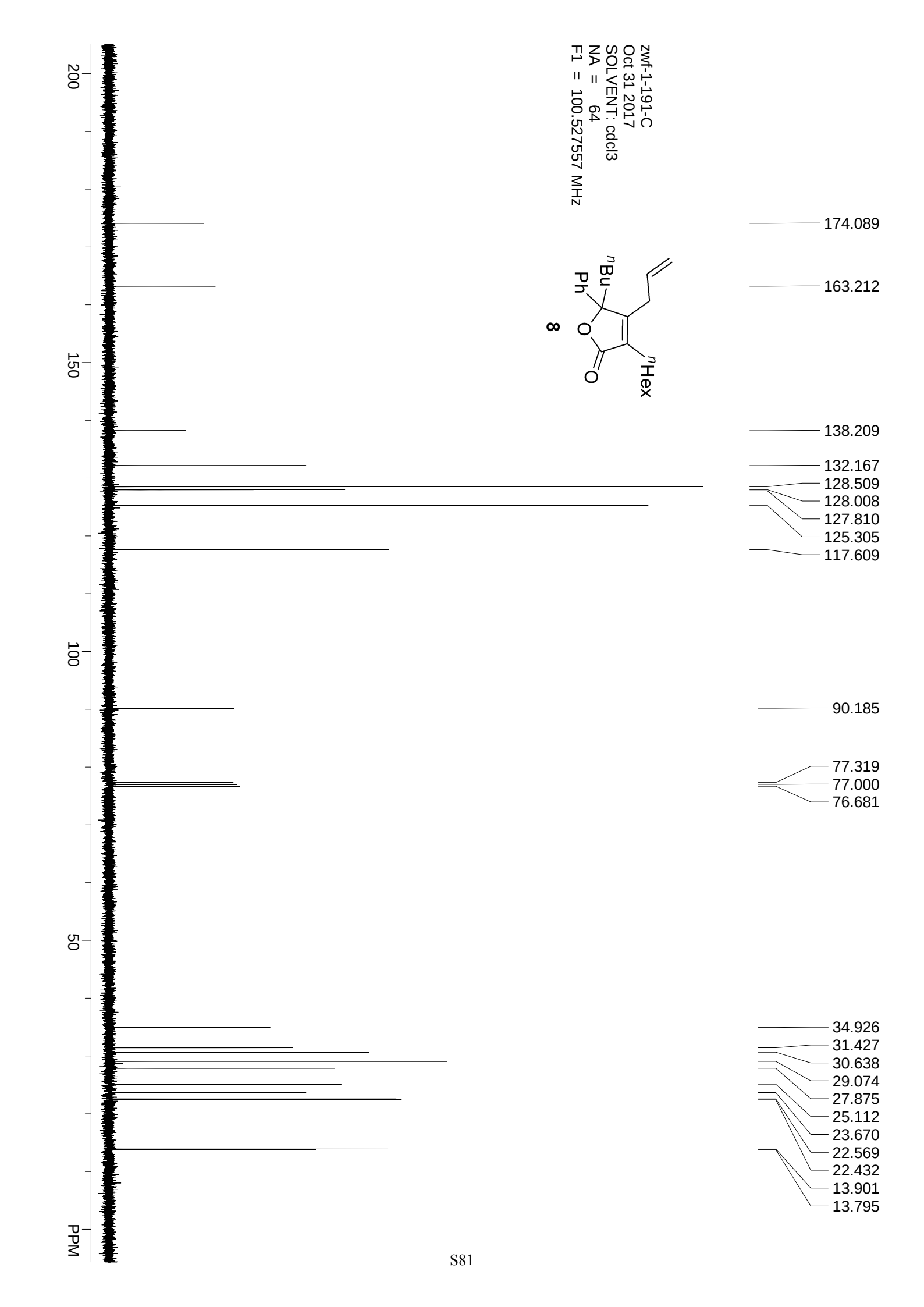


zwf-1-1-191cd
Nov 4 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz



8

Purity: dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 70.1 mg product


zwf-1-191-C
Oct 31 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.527557 MHz
8
nBu
Ph
O
O
nHex
174.089
163.212
138.209
132.167
128.509
128.008
127.810
125.305
117.609
90.185
77.319
77.000
76.681
34.926
31.427
30.638
29.074
27.875
25.112
23.670
22.569
22.432
13.901
13.795
200
150
100
50
PPM