Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Iron Nitrate and 4-OH-TEMPO-Cocatalyzed Aerobic Oxidation of Isochromans

Qian Zhang,[a] Jiabin Zhang,[b] Hui Qian,*[a] and Shengming Ma*[a,b,c]

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

[b] Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang Province, China.

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

E-mail: masm@sioc.ac.cn. Homepage: https://masm.fudan.edu.cn

Supporting information

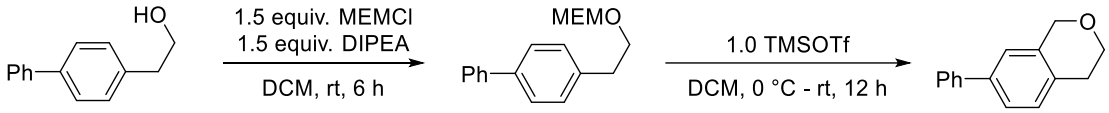
General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR). Flue gas analysis experiments were performed with a Testo 350 flue gas analyzer. All reactions were carried out in 25 mL flasks unless otherwise mentioned. $Fe(NO_3)_3 \cdot 9H_2O$ (98% purity) was purchased from Sinopharm Chemical Reagent Co., Ltd.; 4-OH-TEMPO (98% purity) was purchased from Shanghai Darui Fine Chemical Co., Ltd.; MeCN was purchased from Sinopharm Chemical Reagent Co., Ltd. and used directly without further treatment. Isochroman **1a** was purchased from Shanghai Titan Technology Co., Ltd.; **1g** and **1q** were purchased from Bide Pharmatech Ltd.; **1r** was purchased from Tokyo Chemical Industry Co., Ltd.. NMR yields and recoveries were determined by ^{1}H NMR analysis using dibromomethane as the internal standard. Room temperature is referred to the temperature around 25 °C.

Experimental details and analytical data

1. Preparation of isochromans

Isochromans **1b-1f** and **1h-1o** were prepared following the literature methods.[1-3]

(1) Preparation of 7-phenylisochromane 1p (zhangq-5-026, zhangq-5-028)



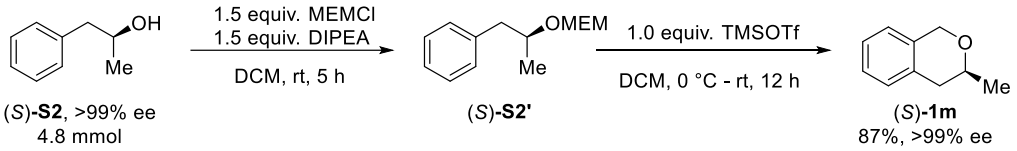
S1, 5 mmol **S1'** **1p**, 95%

Typical Procedure I: To a 100 mL flask was added 2-(4-phenylphenyl)ethan-1-ol **S1** (0.9914 g, 5 mmol). Then the flask was degassed and refilled with argon for three times. After the addition of anhydrous DCM (15 mL), (2-methoxyethoxy)methyl chloride (MEMCl) (0.9 mL, d = 1.091 g/mL, 0.9819 g, 7.6 mmol, 97% purity) and *N*,*N*-diisopropylethylamine (DIPEA) (1.3 mL, d = 0.742 g/mL, 0.9646 g, 7.5 mmol) were added sequentially. The resulting mixture was stirred for 6 h at room temperature until the completion of the reaction as monitored by TLC. The crude reaction mixture was washed with H_2O (30 mL) and dried over Na_2SO_4. After filtration and concentration,

the crude product **S1'** was submitted to the next step without further purification.

The crude product **S1'** was added to a 100 mL flask, which was then degassed and refilled with argon for three times. After the addition of anhydrous DCM (15 mL), the resulting mixture was cooled to 0 °C with an ice-water bath, and trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.9 mL, d = 1.228 g/mL, 1.1052 g, 5 mmol) was added dropwise. The resulting mixture was stirred for 12 h at room temperature, quenched with a saturated aqueous solution of $NaHCO_3$ (aq., 15 mL), and transferred to a separatory funnel. The organic phase was separated, washed with brine, dried with anhydrous Na_2SO_4, filtrated, and concentrated. The residue was purified by Biotage Isorela One purification system on flash silica gel column (Santai Tech. Inc., 120 g) to afford **1p** (0.9957 g, 95%) [eluent: petroleum ether/ethyl acetate = 19/1 (~600 mL); flow rate: 100 mL/min] as a solid: m.p. 62.6-63.1 °C (petroleum ether/dichloromethane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 2 H, ArH), 7.47-7.37 (m, 3 H, ArH), 7.33 (t, *J* = 7.4 Hz, 1 H, ArH), 7.24-7.15 (m, 2 H, ArH), 4.84 (s, 2 H, OCH_2), 4.01 (t, *J* = 5.6 Hz, 2 H, OCH_2), 2.90 (t, *J* = 5.4 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.8, 139.0, 135.2, 132.3, 129.2, 128.7, 127.1, 126.9, 125.1, 122.9, 68.0, 65.3, 28.0; **MS** (FI) *m/z*: 210 (M^+); **Anal. Calcd.** for $C_{15}H_{14}O$: C 85.68, H 6.71; found C 85.77, H 6.81; **IR** (neat): ν = 2852, 2830, 1482, 1451, 1265, 1178, 1132, 1098, 1068, 1041, 1005 cm^{-1}.

(2) Preparation of (*S*)-3-methylisochromane (*S*)-1m (zhangq-5-077)

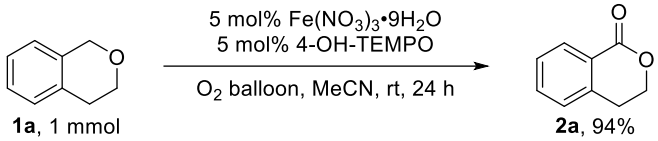


Following **Typical Procedure I**, the reaction of (*S*)-**S2**[4] (0.6486 g, 4.8 mmol), MEMCl (0.9 mL, d = 1.091 g/mL, 0.9819 g, 7.6 mmol, 97% purity), and DIPEA (1.3 mL, d = 0.742 g/mL, 0.9646 g, 7.5 mmol) in anhydrous DCM (14 mL) afforded the crude product (*S*)-**S2'**. The reaction of the crude product (*S*)-**S2'** and TMSOTf (0.9 mL, d = 1.228 g/mL, 1.1052 g, 5 mmol) in anhydrous DCM (14 mL) afforded (*S*)-**1m**[5] (0.6154 g, 87%, ee: >99%) [eluent: petroleum ether/ethyl acetate = 20/1 (~210 mL)] as

an oil: HPLC conditions: OD-H column, hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, λ = 214 nm, t_R(major) = 13.4 min; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21-7.12 (m, 2 H, ArH), 7.12-7.04 (m, 1 H, ArH), 7.04-6.95 (m, 1 H, ArH), 4.88-4.77 (m, 2 H, CH_2), 3.88-3.75 (m, 1 H, CH), 2.71 (d, *J* = 6.8 Hz, 2 H, CH_2), 1.35 (d, *J* = 6.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.6, 133.5, 128.7, 126.3, 125.9, 124.1, 70.9, 68.1, 35.8, 21.6.

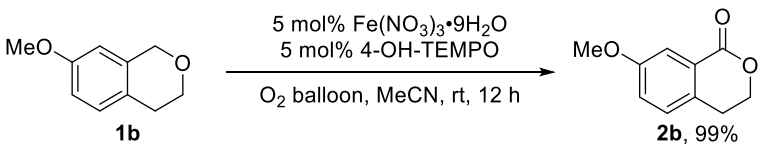
2. Preparation of isochromanones

(1) Preparation of isochroman-1-one 2a (zhangq-3-149, zhangq-5-061)



Typical Procedure II: To a 25 mL flask were added $Fe(NO_3)_3$•$9H_2O$ (20.4 mg, 0.05 mmol), 4-OH-TEMPO (8.7 mg, 0.05 mmol), **1a** (134.3 mg, 1.0 mmol), and MeCN (0.8 mL) sequentially. After the installation of an O_2 balloon, the resulting mixture was stirred at room temperature for 24 h until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1). The crude reaction mixture was filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a**[6] (139.1 mg, 94%) [eluent: petroleum ether/ethyl acetate = 8/1(~225 mL) to 5/1(~180 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.0 Hz, 1 H, ArH), 7.54 (t, *J* = 7.6 Hz, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 1 H, ArH), 7.27 (d, *J* = 7.6 Hz, 1 H, ArH), 4.53 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.06 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.9, 139.4, 133.4, 130.0, 127.4, 127.1, 125.0, 67.1, 27.5; **MS** (70 eV, EI) *m/z* (%): 148 (M^+, 55.3), 118 (100); **IR** (neat): ν = 3002, 2946, 2898, 1716, 1606, 1459, 1392, 1292, 1241, 1119, 1027 cm^{-1}.

(2) Preparation of 7-methoxyisochroman-1-one 2b (zhangq-6-044, zhangq-6-055, zhangq-3-186)

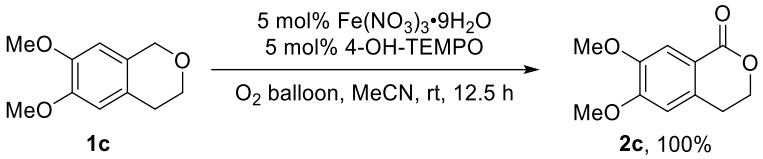


Following **Typical Procedure II**, the reaction of **1b** (163.1 mg, 1.0 mmol),

$Fe(NO_3)_3$•$9H_2O$ (21.0 mg, 0.05 mmol), and 4-OH-TEMPO (8.9 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2b**[6] (175.5 mg, 99%) [eluent: petroleum ether/ethyl acetate = 4/1 (~400mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 2.0 Hz, 1 H, ArH), 7.17 (d, *J* = 8.4 Hz, 1 H, ArH), 7.10 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, ArH), 4.52 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3), 3.00 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.1, 159.0, 131.8, 128.4, 126.1, 121.6, 113.0, 67.6, 55.6, 27.0; **MS** (70 eV, EI) *m/z* (%): 178 (M^+, 83.72), 120 (100); **IR** (neat): ν = 2962, 2898, 2837, 1714, 1613, 1499, 1428, 1320, 1281, 1086, 1027 cm^{-1}.

Second try: following **Typical Procedure II**, the reaction of **1b** (78.0 mg, 0.5 mmol), $Fe(NO_3)_3$•$9H_2O$ (10.3 mg, 0.025 mmol), and 4-OH-TEMPO (4.5 mg, 0.025 mmol) in MeCN (0.4 mL) afforded **2b**[6] (83.8 mg, 99%) [eluent: petroleum ether/ethyl acetate = 5/1 (~280 mL)] as an oil.

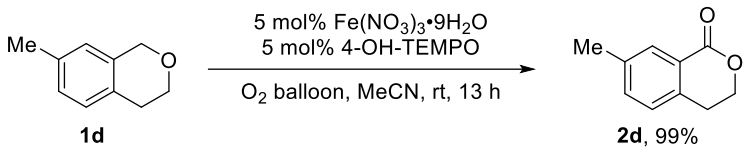
(3) Preparation of 6,7-dimethoxyisochroman-1-one 2c (zhangq-4-058)



1c **2c**, 100%

Following **Typical Procedure II**, the reaction of **1c** (194.8 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.8 mg, 0.05 mmol), and 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2c**[7] (209.4 mg, 100%) [eluent: petroleum ether/ethyl acetate = 4/1 (~600 mL)] as a solid: m.p. 139.9-140.8 °C (petroleum ether/ethyl acetate) (reported:[8] m.p. 140-141 °C (petroleum ether/ethyl acetate)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (s, 1 H, ArH), 6.69 (s, 1 H, ArH), 4.52 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.95 (s, 3 H, CH_3), 3.92 (s, 3 H, CH_3), 2.99 (t, *J* = 6.2 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.2, 153.6, 148.5, 133.9, 117.4, 111.8, 109.1, 67.3, 56.1, 27.5; **MS** (70 eV, EI) *m/z* (%): 208 (M^+, 100); **IR** (neat): ν = 2965, 2922, 1690, 1604, 1510, 1453, 1423, 1391, 1233, 1086, 1031 cm^{-1}.

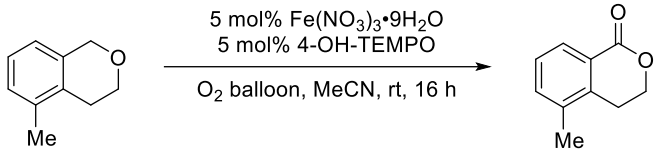
(4) Preparation of 7-methylisochroman-1-one 2d (zhangq-3-171)



1d **2d**, 99%

Following **Typical Procedure II**, the reaction of **1d** (146.9 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (21.0 mg, 0.05 mmol), 4-OH-TEMPO (8.7 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2d**[6] (158.6 mg, 99%) [eluent: petroleum ether/ethyl acetate = 8/1 (~225 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (s, 1 H, ArH), 7.35 (d, *J* = 8.0 Hz, 1 H, ArH), 7.15 (d, *J* = 7.6 Hz, 1 H, ArH), 4.52 (t, *J* = 5.6 Hz, 2 H, CH_2), 3.01 (t, *J* = 5.8 Hz, 2 H, CH_2), 2.39 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.1, 137.1, 136.4, 134.3, 130.1, 126.9, 124.7, 67.2, 27.1, 20.6; **MS** (70 eV, EI) *m/z* (%): 162 (M^+, 90.62), 132 (100); **IR** (neat): ν = 2959, 2907, 1717, 1616, 1500, 1420, 1387, 1285, 1117, 1036 cm^{-1}.

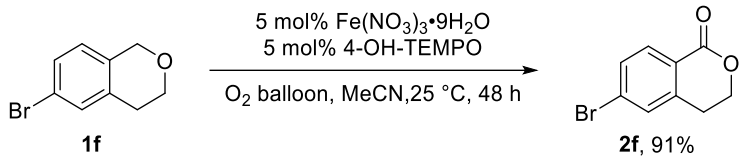
(5) Preparation of 5-methylisochroman-1-one 2e (zhangq-4-044)



1e **2e**, 100%

Following **Typical Procedure II**, the reaction of **1e** (148.2 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.0 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2e**[6] (161.6 mg, 100%) [eluent: petroleum ether/ethyl acetate = 5/1 (~400 mL)] as a solid: m.p. 71.9-72.9 °C (petroleum ether/dichloromethane) (reported:[9] m.p. 68-70 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1 H, ArH), 7.41 (d, *J* = 7.2 Hz, 1 H, ArH), 7.30 (t, *J* = 7.6 Hz, 1 H, ArH), 4.53 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.98 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.33 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 138.1, 134.9, 134.8, 127.9, 126.9, 125.1, 66.5, 24.7, 18.6; **MS** (70 eV, EI) *m/z* (%): 162 (M^+, 68.95), 132 (100); **IR** (neat): ν = 2994, 2965, 2923, 1700, 1596, 1475, 1395, 1300, 1278, 1123, 1042 cm^{-1}.

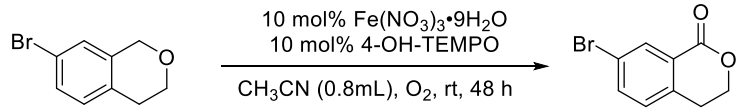
(6) Preparation of 6-bromoisochroman-1-one 2f (zhangq-4-120)



1f **2f**, 91%

Following **Typical Procedure II**, the reaction of **1f** (213.1 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (21.1 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2f**[7] (208.2 mg, 91%, purity: 99%) [eluent: petroleum ether/ethyl acetate = 5/1 (~500 mL)] as a solid: m.p. 123.4-124.1 °C (petroleum ether/dichloromethane) (reported:[10] m.p. 63-65 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1 H, ArH), 7.54 (d, *J* = 8.0 Hz, 1 H, ArH), 7.46 (s, 1 H, ArH), 4.54 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.06 (t, *J* = 5.8 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.2, 141.2, 131.8, 131.0, 130.2, 128.5, 124.0, 67.0, 27.4; **MS** (70 eV, EI) *m/z* (%): 228 (M^+(^{81}Br), 51.66), 226 (M^+(^{79}Br), 51.32), 198 (100); **IR** (neat): ν = 3063, 2921, 1703, 1591, 1568, 1476, 1415, 1339, 1281, 1195, 1131, 1057, 1028 cm^{-1}.

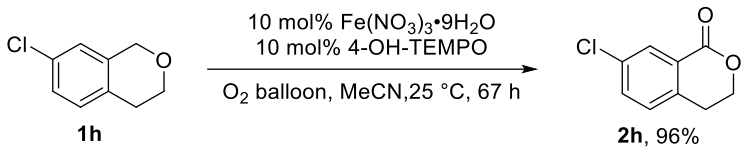
(7) Preparation of 7-bromoisochroman-1-one 2g (zhangq-3-162, zhangq-3-174)



1g **2g**, 100%

Following **Typical Procedure II**, the reaction of **1g** (214.9 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (40.8 mg, 0.1 mmol), 4-OH-TEMPO (17.7 mg, 0.1 mmol) in MeCN (0.8 mL) afforded **2g**[7] (221.3 mg, 100%) [eluent: petroleum ether/ethyl acetate = 8/1 (~225 mL) to 5/1 (~240 mL)] as a solid: m.p. 96.6-97.2 °C (petroleum ether/ethyl ether) (reported:[11] m.p. 79-81.5 °C (ethyl ether)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1 H, ArH), 7.66 (d, *J* = 8.0 Hz, 1 H, ArH), 7.17 (d, *J* = 8.0 Hz, 1 H, ArH), 4.54 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.03 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.7, 138.2, 136.5, 133.1, 128.9, 127.0, 121.3, 67.2, 27.3; **MS** (70 eV, EI) *m/z* (%): 228 (M^+(^{81}Br), 61.84), 226 (M^+(^{79}Br), 61.83), 196 (100); **IR** (neat): ν = 2951, 2925, 1710, 1595, 1478, 1422, 1328, 1293, 1193, 1068 cm^{-1}.

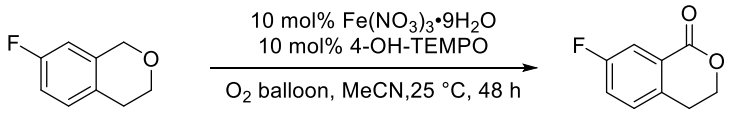
(8) Preparation of 7-chloroisochroman-1-one 2h (zhangq-4-121, zhangq-4-127)



1h **2h**, 96%

Following **Typical Procedure II**, the reaction of **1h** (168.9 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (41.6 mg, 0.1 mmol), 4-OH-TEMPO (17.6 mg, 0.1 mmol) in MeCN (0.8 mL) afforded **2h**[7] (174.7 mg, 96%) [eluent: petroleum ether/ethyl acetate = 10/1 (~220 mL) to 5/1 (~360 mL)] as a solid: m.p. 72.6-73.0 °C (petroleum ether/dichloromethane) (reported:[12] m.p. 73-74 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.4 Hz, 1 H, ArH), 7.51 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1 H, ArH), 7.23 (d, *J* = 8.4 Hz, 1 H, ArH), 4.54 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.05 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.7, 137.7, 133.7, 130.1, 128.7, 126.7, 67.2, 27.2; **MS** (70 eV, EI) *m/z* (%): 184 (M^+(^{37}Cl), 18.87), 182 (M^+(^{35}Cl), 63.48), 152 (100); **IR** (neat): ν = 3077, 2974, 2924, 1711, 1677, 1600, 1478, 1425, 1351, 1296, 1237, 1137, 1083, 1030 cm^{-1}.

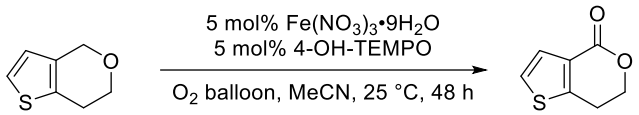
(9) Preparation of 7-fluoroisochroman-1-one 2i (zhangq-4-128, zhangq-4-132)



1i **2i**, 97%

Following **Typical Procedure II**, the reaction of **1i** (151.5 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (41.1 mg, 0.1 mmol), 4-OH-TEMPO (17.6 mg, 0.1 mmol) in MeCN (0.8 mL) afforded **2i**[6] (163.8 mg, 97%, purity: 98%) [eluent: petroleum ether/ethyl acetate = 10/1 (~220 mL) to 5/1 (~240 mL)] as a solid: m.p. 52.4-53.0 °C (petroleum ether/dichloromethane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, ArH), 7.33 - 7.22 (m, 2 H, ArH), 4.55 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.05 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.0 (d, *J* = 2.4 Hz), 161.7 (d, *J* = 245.7 Hz), 135.3 (d, *J* = 3.1 Hz), 129.1 (d, *J* = 7.1 Hz), 126.9 (d, *J* = 7.9 Hz), 121.0 (d, *J* = 22.1 Hz), 116.6 (d, *J* = 22.9 Hz), 67.4, 27.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ –113.64; **MS** (70 eV, EI) *m/z* (%): 166 (M^+, 59.49), 108 (100); **IR** (neat): ν = 3066, 2922, 1713, 1591, 1492, 1434, 1392, 1306, 1260, 1236, 1127, 1083, 1028 cm^{-1}.

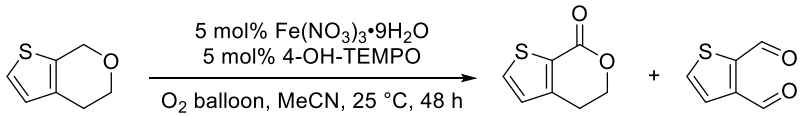
(10) Preparation of 6,7-dihydro-4*H*-thieno[3,2-*c*]pyran-4-one 2j (zhangq-5-019)



1j **2j**, 92%

Following **Typical Procedure II**, the reaction of **1j** (140.9 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.7 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2j**[7] (142.7 mg, 92%) [eluent: petroleum ether/ethyl acetate = 10/1 (~220 mL) to 5/1 (~360 mL)] as a solid: m.p. 86.3-87.9 °C (petroleum ether/dichloromethane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 5.2 Hz, 1 H, ArH), 7.18 (d, *J* = 5.2 Hz, 1 H, ArH), 4.60 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.17 (t, *J* = 6.2 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2, 148.9, 127.9, 126.7, 123.9, 67.6, 24.5; **MS** (70 eV, EI) *m/z* (%): 154 (M^+, 77.8), 124 (100); **IR** (neat): ν = 3106, 3085, 1704, 1534, 1463, 1413, 1334, 1266, 1238, 1110, 1059, 1032 cm^{-1}.

(11) Preparation of 4,5-dihydro-7*H*-thieno[2,3-*c*]pyran-7-one 2k (zhangq-5-033)



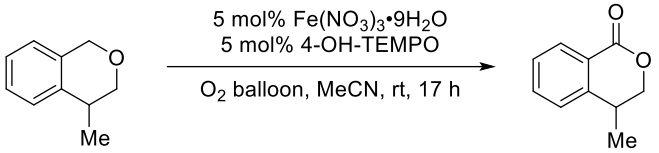
1k **2k**, 71% **3k**, 2%

Following **Typical Procedure II**, the reaction of **1k** (140.6 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.3 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2k**[6] (110.0 mg, 71%) and **3k**[13] (3.4 mg, 2%) [eluent: petroleum ether/ethyl acetate = 10/1 (~400 mL) to 8/1 (~400 mL)] as solids.

2k: m.p. 54.7-55.3 °C (petroleum ether/dichloromethane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 4.8 Hz, 1 H, ArH), 7.03 (d, *J* = 4.8 Hz, 1 H, ArH), 4.60 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.04 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.0, 147.5, 134.2, 126.5, 126.2, 68.2, 24.8; **MS** (70 eV, EI) *m/z* (%): 154 (M^+, 82.42), 124 (100); **IR** (neat): ν = 3091, 3075, 2951, 1691, 1540, 1462, 1423, 1391, 1278, 1207, 1083, 1039 cm^{-1}.

3k: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.49 (s, 1 H, CHO), 10.39 (s, 1 H, CHO), 7.75 (d, *J* = 4.8 Hz, 1 H, ArH), 7.65 (d, *J* = 5.2 Hz, 1 H, ArH).

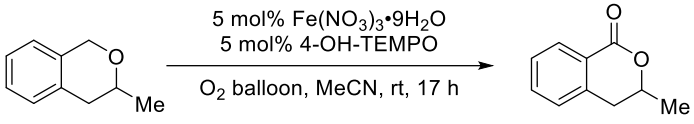
(12) Preparation of 4-methylisochroman-1-one 2l (zhangq-4-046)



1l **2l**, 98%

Following **Typical Procedure II**, the reaction of **1l** (147.0 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.5 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2l**[6] (156.9 mg, 98%) [eluent: petroleum ether/ethyl acetate = 5/1 (~300 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 1 H, ArH), 7.58 (td, J_1 = 7.5 Hz, J_2 = 1.1 Hz, 1 H, ArH), 7.37-7.43 (m, 1 H, ArH), 7.31 (d, *J* = 7.6 Hz, 1 H, ArH), 4.52 (dd, J_1 = 10.8 Hz, J_2 = 4.0 Hz, 1 H, CH), 4.25 (dd, J_1 = 11.2 Hz, J_2 = 6.8 Hz, 1 H, CH), 3.22-3.12 (m, 1 H, CH), 1.38 (d, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.1, 144.5, 133.9, 130.4, 127.5, 125.6, 124.4, 72.4, 31.7, 16.6; **MS** (70 eV, EI) *m/z* (%): 162 (M^+, 47.88), 132 (100); **IR** neat): ν = 2967, 2880, 1714, 1605, 1464, 1396, 1279, 1123, 1086, 1064, 1019 cm^{-1}.

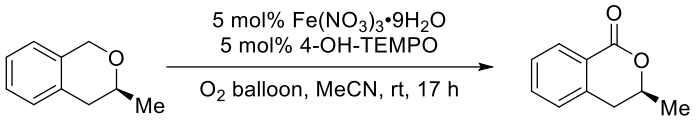
(13) Preparation of 3-methylisochroman-1-one 2m (zhangq-4-047)



1m **2m**, 100%

Following **Typical Procedure II**, the reaction of **1m** (147.8 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.9 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2m**[6] (161.2 mg, 100%) [eluent: petroleum ether/ethyl acetate = 5/1 (~300 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (t, *J* = 7.4 Hz, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 1 H, ArH), 7.24 (d, *J* = 7.6 Hz, 1 H, ArH), 4.75-4.63 (m, 1 H, CH), 3.03-2.88 (m, 2 H, CH_2), 1.53 (d, *J* = 6.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.6, 139.1, 133.7, 130.3, 127.6, 127.3, 125.0, 75.0, 34.9, 20.9; **MS** (70 eV, EI) *m/z* (%): 162 (M^+, 23.22), 118 (100); **IR** (neat): ν = 2980, 2901, 1708, 1607, 1460, 1387, 1351, 1277, 1119, 1084, 1029 cm^{-1}.

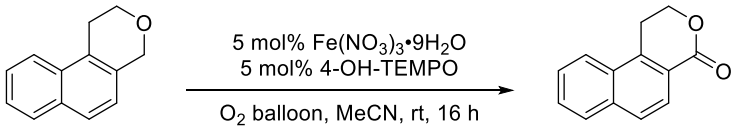
(14) Preparation of (*S*)-3-methylisochroman-1-one (*S*)-**2m (zhangq-5-080)**



(*S*)-**1m** (*S*)-**2m**, 100%

Following **Typical Procedure II**, the reaction of (*S*)-**1m** (148.9 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (21.0 mg, 0.05 mmol), 4-OH-TEMPO (8.9 mg, 0.05 mmol) in MeCN (0.8 mL) afforded (*S*)-**2m**[14] (162.9 mg, 100%, > 99% ee) [eluent: petroleum ether/ethyl acetate = 5/1 (~300 mL)] as an oil: HPLC conditions: AS-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 214 nm, t_R(major) = 8.8 min; $[\alpha]_D^{26}$ = +156.6 (*c* = 1.01, $CHCl_3$) (reported:[14] $[\alpha]_D^{22}$ = +141.0 (*c* = 1.00, $CHCl_3$)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (t, *J* = 7.0 Hz, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 1 H, ArH), 7.24 (d, *J* = 7.6 Hz, 1 H, ArH), 4.75-4.64 (m, 1 H, CH), 3.03-2.88 (m, 2 H, CH_2), 1.53 (d, *J* = 6.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 138.9, 133.4, 129.7, 127.2, 127.1, 124.6, 74.8, 34.4, 20.5; **MS** (70 eV, EI) *m/z* (%): 162 (M^+, 19.58), 118 (100); **IR** (neat): ν = 1707, 1607, 1460, 1386, 1351, 1277, 1238, 1119, 1084, 1030 cm^{-1}.

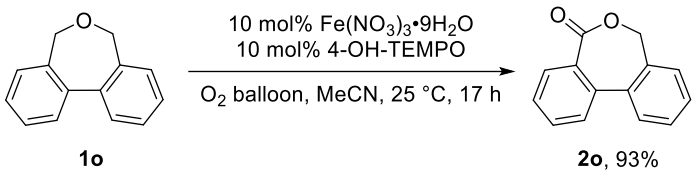
(15) Preparation of 1,2-dihydro-4*H*-benzo[*f*]isochromen-4-one 2n (zhangq-4-045)



1n **2n**, 98%

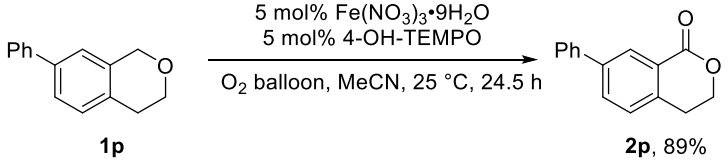
Following Typical Procedure II, the reaction of **1n** (184.2 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.3 mg, 0.05 mmol), 4-OH-TEMPO (8.7 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2n**[7] (195.0 mg, 98%) [eluent: petroleum ether/ethyl acetate = 5/1 (~400 mL)] as a solid: m.p. 106.2-108.4 °C (petroleum ether/dichloromethane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 1 H, ArH), 8.07-8.01 (m, 1 H, ArH), 7.96-7.88 (m, 1 H, ArH), 7.85 (d, *J* = 8.8 Hz, 1 H, ArH), 7.68-7.58 (m, 2 H, ArH), 4.69 (t, *J* = 6.2 Hz, 2 H, CH_2), 3.46 (t, *J* = 6.2 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 138.4, 135.3, 129.6, 128.6, 128.5, 127.5, 127.0, 124.9, 124.2, 122.2, 66.5, 23.9; **MS** (70 eV, EI) *m/z* (%): 198 (M^+, 95.18), 140 (100); **IR** (neat): ν = 2998, 1700, 1621, 1462, 1432, 1323, 1278, 1120, 1079 cm^{-1}.

(16) Preparation of dibenzo[*c*,*e*]oxepin-5(7*H*)-one 2o (zhangq-5-021, zhangq-5-030)



Following **Typical Procedure II**, the reaction of **1o** (194.8 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (41.7 mg, 0.1 mmol), 4-OH-TEMPO (17.5 mg, 0.1 mmol) in MeCN (0.8 mL) afforded **2o**[6] (194.3 mg, 93%) [eluent: petroleum ether/ethyl acetate = 20/1 (~210 mL) to 10/1 (~220 mL)] as a solid: m.p. 133.7-134.2 °C (petroleum ether/dichloromethane) (reported:[15] m.p. 133-135 °C (petroleum ether/dichloromethane)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 6.8 Hz, 1 H, ArH), 7.73-7.58 (m, 3 H, ArH), 7.53 (d, *J* = 6.8 Hz, 2 H, ArH), 7.48-7.38 (m, 2 H, ArH), 5.05 (s, 1 H, one proton of OCH_2), 5.00 (s, 1 H, one proton of OCH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.1, 138.7, 137.0, 134.6, 132.4, 131.7, 130.4, 129.9, 128.52, 128.48, 128.4, 128.2, 69.0; **MS** (70 eV, EI) *m/z* (%): 210 (M^+, 86.47), 165 (100); **IR** (neat): ν = 1701, 1472, 1377, 1295, 1275, 1228, 1110, 1091, 1045, 1009 cm^{-1}.

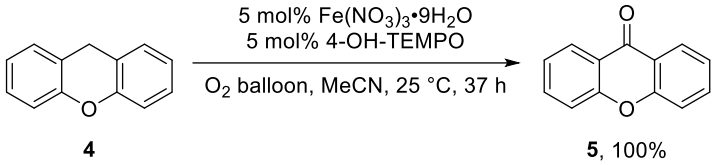
(17) Preparation of 7-phenylisochroman-1-one 2p (zhangq-5-029)



Following **Typical Procedure II**, the reaction of **1p** (210.2 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.0 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2p**[16] (199.0 mg, 89%) [eluent: petroleum ether/ethyl acetate = 10/1 (~300 mL) to 5/1 (~300 mL)] as a solid: m.p. 122.7-123.5 °C (petroleum ether/dichloromethane) (reported:[16] m.p. 119-120 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 1.6 Hz, 1 H, ArH), 7.77 (d, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1 H, ArH), 7.61 (d, *J* = 7.2 Hz, 2 H, ArH), 7.46 (d, *J* = 7.6 Hz, 2 H, ArH), 7.42-7.33 (m, 2 H, ArH), 4.57 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.10 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

164.9, 140.3, 139.1, 138.1, 131.9, 128.7, 128.2, 127.63, 127.58, 126.6, 125.3, 67.1, 27.1; **MS** (FI) *m/z* (%): 224 (M^+); **IR** (neat): ν = 3058, 3015, 1702, 1616, 1482, 1450, 1391, 1280, 1225, 1193, 1145, 1065, 1029 cm^{-1}.

(18) Preparation of 9*H*-xanthen-9-one 5 (zhangq-5-038)

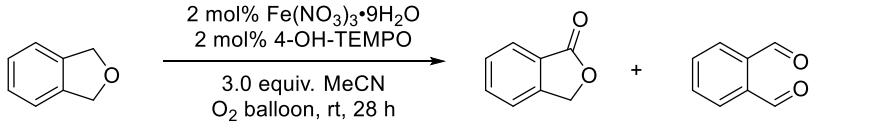


4 **5**, 100%

Following **Typical Procedure II**, the reaction of **4** (182.5 mg, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (21.0 mg, 0.05 mmol), 4-OH-TEMPO (8.7 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **5**[6] (195.8 mg, 100%) [eluent: petroleum ether/ethyl acetate = 5/1 (~220 mL)] as a solid: m.p. 176.1-176.9 °C (petroleum ether/dichloromethane) (reported:[17] m.p. 176-177 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2 H, ArH), 7.75-7.62 (m, 2 H, ArH), 7.45 (d, *J* = 8.4 Hz, 2 H, ArH), 7.35 (t, *J* = 7.4 Hz, 2 H, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.1, 156.0, 134.7, 126.6, 123.8, 121.7, 117.9; **MS** (70 eV, EI) *m/z* (%): 196 (M^+, 100); **IR** (neat): ν = 1654, 1604, 1478, 1455, 1344, 1329, 1239, 1213, 1145 cm^{-1}.

3. Large-Scale Reactions:

(1) Preparation of isobenzofuran-1(3*H*)-one 2q (zhangq-3-150)

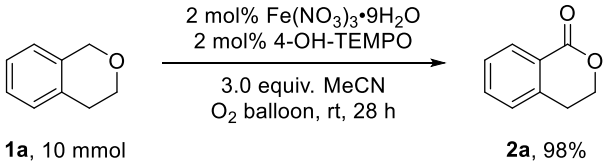


1q, 5 mmol **2q**, 60% **3q**, 12% (NMR yield)

To a 25 mL flask were added $Fe(NO_3)_3$•$9H_2O$ (41.0 mg, 0.1 mmol), 4-OH-TEMPO (17.7 mg, 0.1 mmol), **1q** (618.6 mg, 5 mmol, 97% purity), and MeCN (0.8 mL) sequentially. After the installation of an O_2 balloon, the resulting mixture was stirred at room temperature for 28 h until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1). The crude reaction mixture was filtrated through a short column of silica gel eluted with ethyl acetate (6 x 20 mL) and concentrated. The reaction afforded 66% NMR yield of **2q** and 12% NMR yield of **3q**, which was

determined by ^{1}H NMR analysis of the crude product with CH_2Br_2 (70 μL) as the internal standard. After evaporation, MeCN (10 mL) and a saturated solution of $NaHSO_3$ (aq., 10 mL) were added to the residue. The resulting mixture was stirred vigorously at room temperature for 1 h, extracted with ethyl acetate (3 x 20 mL), dried with anhydrous Na_2SO_4, filtrated, and concentrated. The residue was purified by chromatography on silica gel to afford **2q**[7] (400.5 mg, 60%) [eluent: petroleum ether/ethyl acetate = 10/1 (~220 mL) to 5/1 (~600 mL)] as a solid: m.p. 74.0-74.6 °C (petroleum ether/ethyl ether) (reported:[18] m.p. 74-75 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 1 H, ArH), 7.70 (t, *J* = 7.4 Hz, 1 H, ArH), 7.54 (t, *J* = 7.6 Hz, 2 H, ArH), 5.33 (s, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.9, 146.3, 133.8, 128.7, 125.38, 125.36, 121.9, 69.4; **MS** (70 eV, EI) *m/z* (%): 134 (M^+, 37.76), 105 (100); **IR** (neat): ν = 3062, 3018, 1745, 1615, 1594, 1466, 1364, 1287, 1191, 1108 cm^{-1}.

(2) Gram-scale synthesis of isochroman-1-one 2a (zhangq-5-048)

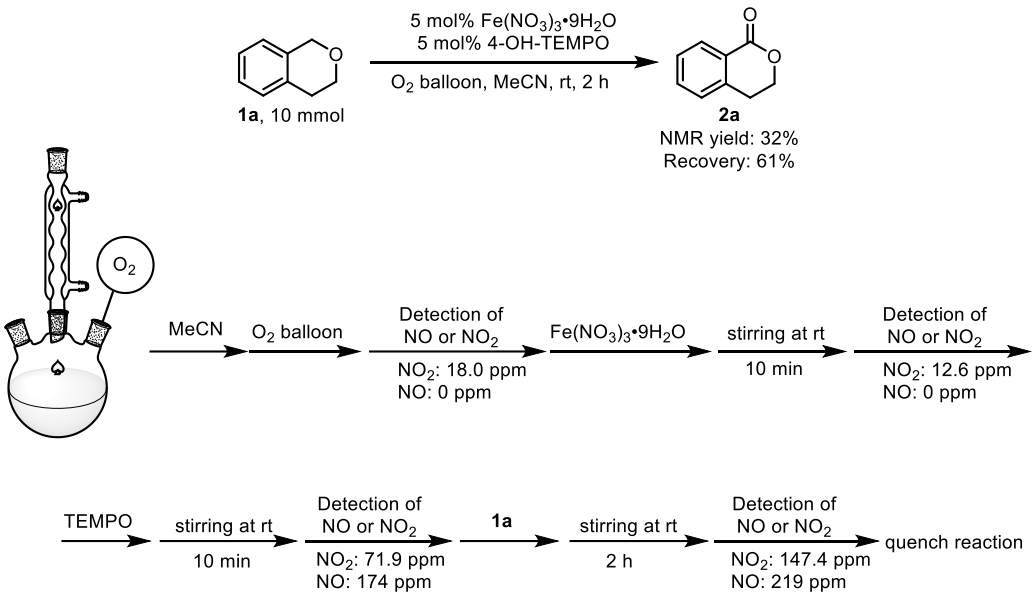


1a, 10 mmol **2a**, 98%

Following **Typical Procedure II**, the reaction of **1a** (1.3389 g, 10 mmol), $Fe(NO_3)_3$•$9H_2O$ (82.3 mg, 0.2 mmol), and 4-OH-TEMPO (35.4 mg, 0.2 mmol) in MeCN (1.6 mL) afforded **2a** (1.4506 g, 98%) [eluent: petroleum ether/ethyl acetate = 10/1 (~600 mL) to 6/1 (~600 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (t, *J* = 7.4 Hz, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 1 H, ArH), 7.27 (d, *J* = 7.6 Hz, 1 H, ArH), 4.54 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.07 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.0, 139.4, 133.5, 130.2, 127.5, 127.1, 125.1, 67.2, 27.6.

Mechanistic studies

(1) Detection of NO_x (zhangq-5-081)



Scheme S1. Detection of NO_x by a flue gas analyzer at the different stages of reaction process.

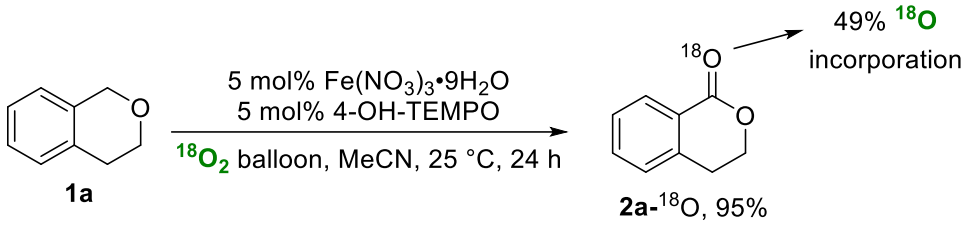
As shown in Scheme S1, MeCN (8 mL) was added to a three-neck flask, which was followed by the installation of an O_2 balloon. Then the flue gas analyzer detecting NO_x was connected. $Fe(NO_3)_3$•$9H_2O$ (208.9 mg, 0.5 mmol) was added to the flask, and the resulting mixture was stirred at rt for 10 min, then NO_x was again detected by the flue gas analyzer. Next, 4-OH-TEMPO (87.5 mg, 0.5 mmol) was added, NO_x was detected after stirring the mixture at rt for 10 min. Finally, **1a** (1.3680 g, 10 mmol) was added and the resulting mixture was stirred at rt for 2 h, then NO_x was once more detected by the flue gas analyzer. The resulting mixture was filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL) and concentrated. The reaction afforded 32% NMR yield of **2a** with 61% recovery of **1a**, which was determined by ^1H NMR analysis of the crude product with CH_2Br_2 (70 μL) as the internal standard.

(2) Study on the effect of H_2O in the aerobic oxidation of isochroman 1a (zhangq-6-045, zhangq-6-050)

$Fe(NO_3)_3$•$9H_2O$ (0.05 mmol), 4-OH-TEMPO (0.05 mmol), **1a** (1.0 mmol), anhydrous MeCN (0.8 mL), and H_2O (X equiv.) were added to a 25 mL flask sequentially, which was followed by the installation of an O_2 balloon. The resulting mixture was stirred at 25 °C for 10 h, diluted with ethyl acetate, and filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL). After evaporation, dibromomethane (35 μL) was added as internal standard for ^{1}H NMR analysis.

$Fe(NO_3)_3$•$9H_2O$ (0.05 mmol), 4-OH-TEMPO (0.05 mmol), 5 Å molecular sieves (X mg), **1a** (1.0 mmol), and anhydrous MeCN (0.8 mL) were added to a 25 mL flask sequentially, which was followed by the installation of an O_2 balloon. The resulting mixture was stirred at 25 °C for 10 h, diluted with ethyl acetate, and filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL). After evaporation, dibromomethane (35 μL) was added as internal standard for ^{1}H NMR analysis.

(3) Isotopic labelling experiment with $^{18}O_2$ (zhangq-5-034)

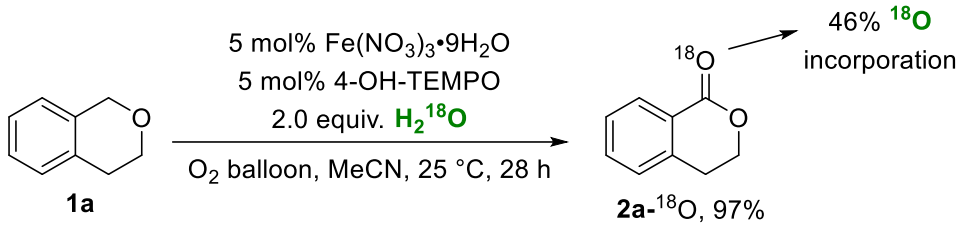


To a 25 mL flask were added $Fe(NO_3)_3$•$9H_2O$ (20.3 mg, 0.05 mmol), 4-OH-TEMPO (8.8 mg, 0.05 mmol), **1a** (134.0 mg, 1.0 mmol), and MeCN (0.8 mL) sequentially. Then the flask was degassed and refilled with $^{18}O_2$ by an $^{18}O_2$ balloon. After the installation of an $^{18}O_2$ balloon, the resulting mixture was stirred at room temperature for 24 h until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1). The crude reaction mixture was filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a**-^{18}O (138.0 mg, 95%, 49% ^{18}O) [eluent: petroleum ether/ethyl acetate = 8/1(~230 mL) to 6/1(~280 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (t, *J* = 7.4 Hz, 1 H, ArH), 7.38 (t, *J* = 7.6 Hz, 1 H, ArH), 7.28 (d, *J* = 7.6 Hz, 1 H, ArH), 4.53 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.06 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$):

δ 164.89, 164.86, 139.4, 133.4, 130.0, 127.4, 127.1, 125.0, 67.1, 27.5; **MS** (70 eV, EI) *m/z* (%): 150 (M($^{16}O^{18}O$)$^+$, 40.17), 148 (M ($^{16}O_2$)$^+$, 41.6), 90 (100); **HRMS** calcd *m/z* for $C_9H_8{}^{16}O^{18}O$ [M^+]: 150.0561, found: 150.0560, $C_9H_8{}^{16}O_2$ [M^+]: 148.0519, found: 148.0520; **IR** (neat): ν = 1719, 1688, 1606, 1459, 1392, 1292, 1241, 1118, 1060, 1027 cm^{-1}.

The ^{18}O% incorporation of **2a**-^{18}O was determined via the analysis of MS spectrum. Due to the known natural abundance of the stable isotopes of C, H, and O, the naturally occurring isotopic ^{18}O will also produce [M (^{18}O)]$^+$ peak: According to the natural abundance of ^{18}O, the ratio of $C_9H_8{}^{16}O_2$:$C_9H_8{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M ($^{16}O^{18}O$)] ($C_9H_8{}^{16}O^{18}O$) peak would be 0.2% of the intensity of the molecular peak [M ($^{16}O_2$)] ($C_9H_8{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-($^{16}O_2$) 148 [M ($^{16}O_2$)] and **2a**-($^{16}O^{18}O$) 150 [M ($^{16}O^{18}O$)] are 41.6 and 40.17, respectively. The ^{18}O% of **2a**-^{18}O can be calculated as follows: ([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2%)/([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2% + [M ($^{16}O_2$)]$^+$) = (40.17 – 41.6 × 0.2%)/(40.17 - 41.6 × 0.2% + 41.6) = 49%.

(4) Isotopic labelling experiment with $H_2{}^{18}O$ (zhangq-5-036)

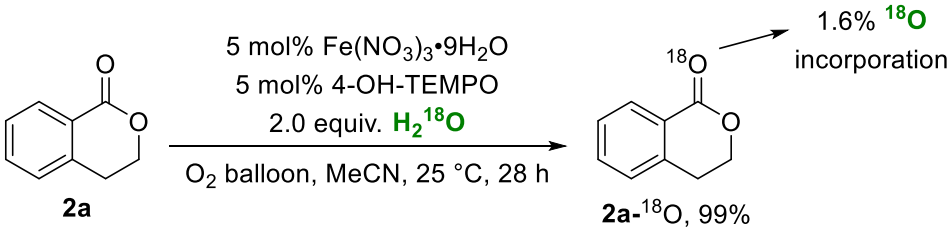


Typical Procedure III: $Fe(NO_3)_3$•$9H_2O$ (20.3 mg, 0.05 mmol), 4-OH-TEMPO (8.7 mg, 0.05 mmol), **1a** (134.7 mg, 1.0 mmol), $H_2{}^{18}O$ (36 μL, d = 1.11 g/mL, 2.0 mmol), and MeCN (0.8 mL) were added to a 25 mL flask sequentially, which was followed by the installation of an O_2 balloon. The resulting mixture was stirred at room temperature for 28 h until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1) and filtrated through a short column of silica gel eluted with ethyl acetate (3 x 20 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a**-^{18}O (142.0 mg, 97%, 46% ^{18}O) [eluent: petroleum ether/ethyl acetate = 8/1(~230 mL) to 6/1(~280 mL)] as an oil: **^{1}H NMR**

(400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 1 H, ArH), 7.54 (t, *J* = 7.6 Hz, 1 H, ArH), 7.38 (t, *J* = 7.6 Hz, 1 H, ArH), 7.28 (d, *J* = 7.6 Hz, 1 H, ArH), 4.52 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.06 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.83, 164.80, 139.3, 133.4, 129.9, 127.3, 127.1, 124.9, 67.0, 27.4; **MS** (70 eV, EI) *m*/*z* (%): 150 (M ($^{16}O^{18}O$)$^+$, 39.94), 148 (M ($^{16}O_2$)$^+$, 46), 90 (100).

The ^{18}O% incorporation of **2a**-^{18}O was determined via the analysis of MS spectrum. Based on the known natural abundance of the stable isotopes of C, H, and O, the naturally occurring isotopic ^{18}O will also produce [M (^{18}O)]$^+$ peak. According to the natural abundance of ^{18}O, the ratio of $C_9H_8{}^{16}O_2$:$C_9H_8{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M ($^{16}O^{18}O$)] ($C_9H_8{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M ($^{16}O_2$)] ($C_9H_8{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-($^{16}O_2$) 148 [M ($^{16}O_2$)] and **2a**-($^{16}O^{18}O$) 150 [M ($^{16}O^{18}O$)] are 46 and 39.94 respectively. The ^{18}O% of **2a**-($^{16}O^{18}O$) can be calculated as follows: ([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2%)/([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2% + [M ($^{16}O_2$)]$^+$) = (39.94 – 46 × 0.2%)/(39.94 - 46 × 0.2% + 46) = 46%.

(5) The reaction of 2a with the addition of $H_2{}^{18}O$ (zhangq-6-040)



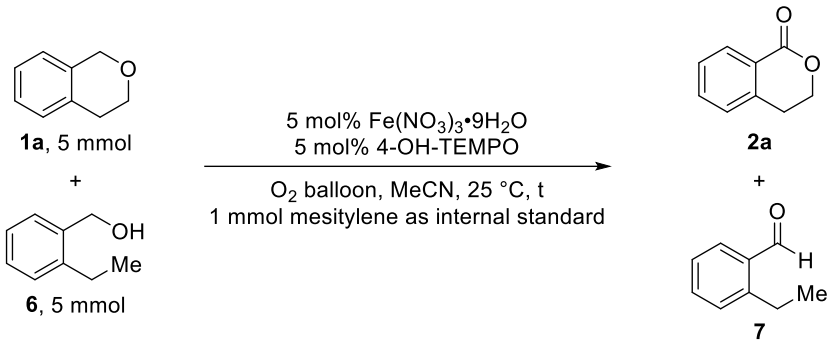
Following **Typical Procedure III**, the reaction of **2a** (0.1482 g, 1.0 mmol), $Fe(NO_3)_3$•$9H_2O$ (20.5 mg, 0.05 mmol), and 4-OH-TEMPO (8.8 mg, 0.05 mmol) in MeCN (0.8 mL) afforded **2a**-^{18}O (147.6 mg, 99%, 99% purity, 1.6% ^{18}O) [eluent: petroleum ether/ethyl acetate = 4/1 (~250 mL)] as an oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (t, *J* = 7.2 Hz, 1 H, ArH), 7.38 (t, *J* = 7.6 Hz, 1 H, ArH), 7.28 (d, *J* = 7.6 Hz, 1 H, ArH), 4.52 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.06 (t, *J* = 6.0 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.8, 139.3, 133.4, 129.9, 127.3, 127.0, 124.9, 67.0, 27.4; **MS** (70 eV, EI) *m*/*z* (%): 150 (M ($^{16}O^{18}O$)$^+$, 1.11), 148 (M ($^{16}O_2$)$^+$, 61.04), 118 (100).

The ^{18}O% incorporation of **2a**-^{18}O was determined via the analysis of MS spectrum. Based on the known natural abundance of the stable isotopes of C, H, and O, the naturally occurring isotopic ^{18}O will also produce [M (^{18}O)]$^+$ peak. According to the natural abundance of ^{18}O, the ratio of $C_9H_8{}^{16}O_2$:$C_9H_8{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M ($^{16}O^{18}O$)] ($C_9H_8{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M ($^{16}O_2$)] ($C_9H_8{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-($^{16}O_2$) 148 [M ($^{16}O_2$)] and **2a**-($^{16}O^{18}O$) 150 [M ($^{16}O^{18}O$)] are 61.04 and 1.11 respectively. The ^{18}O% of **2a**-($^{16}O^{18}O$) can be calculated as follows: ([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2%)/([M ($^{16}O^{18}O$)]$^+$ - [M ($^{16}O_2$)]$^+$ × 0.2% + [M ($^{16}O_2$)]$^+$) = (1.11 – 61.04 × 0.2%)/(1.11 - 61.04 × 0.2% + 61.04) = 1.6%.

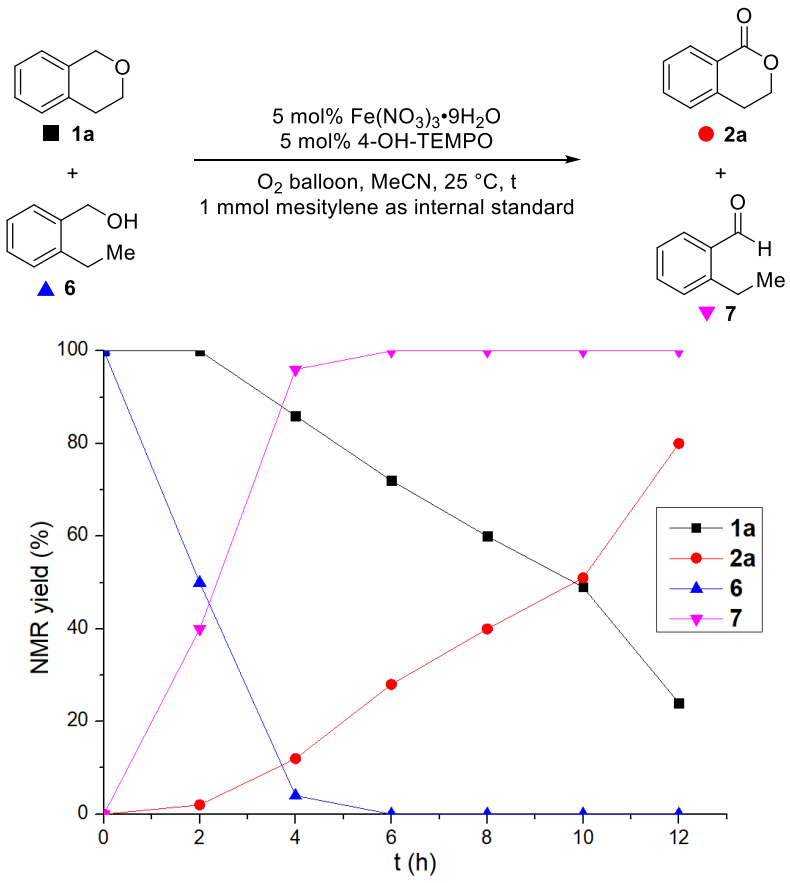
(6) Monitoring the aerobic oxidation of isochroman 1a and *o*-ethylbenzyl alcohol 6 (zhangq-6-053)

$Fe(NO_3)_3$•$9H_2O$ (102.9 mg, 0.25 mmol), 4-OH-TEMPO (43.8 mg, 0.25 mmol), **1a** (0.6830 g, 5.0 mmol), **6** (0.7004 g, 5.0 mmol, 97% purity), MeCN (4 mL), and mesitylene (internal standard, 140 μL, d = 0.861 g/mL, 120.5 mg, 1.0 mmol) were added to a 25 mL flask sequentially, which was followed by the installation of an O_2 balloon. The resulting mixture was stirred at 25 °C. An aliquot (0.1 mL) of the resulting mixture was taken after each indicated time shown in Table S3. The aliquot was filtrated through a short column of silica gel eluted with DCM (4 mL) and diethyl ether (4 mL). After evaporation, the NMR yield and recovery were determined by ^1H NMR analysis.

Table S1. Monitoring the aerobic oxidation of isochroman **1a** and *o*-ethylbenzyl alcohol **6**



Entry	time (h)	Recovery of **1a** (%)	NMR Yield of **2a** (%)	Recovery of **6** (%)	NMR Yield of **7** (%)
1	2	100	2	50	40
2	4	86	12	4	96
3	6	72	28	0	100
4	8	60	40	0	100
5	10	49	51	0	100
6	12	24	80	0	100



References:

1. Xia, Q.; Wang, Q.; Yan, C.; Dong, J.; Song, H.; Li, L.; Liu, Y.; Wang, Q.; Liu, X.; Song, H. Merging Photoredox with Brønsted Acid Catalysis: The Cross-Dehydrogenative C-O Coupling for sp^3 C-H Bond Peroxidation. *Chem. Eur. J.* **2017**, *23*, 10871-10877.

2. Yun, S.; Kim, E.; Kim, H.; Ha, T.; Suh, K.-H.; Lee, G. Method of Preparing Thieno[3,2-C]Pyridine Derivatives and Intermediates Used Therein. WO 2005087779 A1, 2005.

3. Page, P. C. B.; Rassias, G. A.; Barros, D.; Ardakani, A.; Bethell, D.; Merifield, E. New Organocatalysts for the Asymmetric Catalytic Epoxidation of Alkenes Mediated by Chiral Iminium Salts. *Synlett* **2002**, 580-582.

4. (a) For synthetic method of (*S*)-**S2**, see: Xu, D.; Li, Z.; Ma, S. Novozym-435-catalyzed Enzymatic Separation of Racemic Propargylic Alcohols. A Facile Route to Optically Active Terminal Aryl Propargylic Alcohols. *Tetrahedron Lett.* **2003**, *44*, 6343-6346. (b) For report on the analytical data of (*S*)-**S2**, see: Alsafadi, D.; Alsalman, S.; Paradisi, F., Extreme Halophilic Alcohol Dehydrogenase Mediated Highly Efficient Syntheses of Enantiopure Aromatic Alcohols. *Org. Biomol. Chem.* **2017**, *15*, 9169-9175.

5. Kerti, G.; Kurtán, T.; Illyés, T.-Z.; Kövér, K. E.; Sólyom, S.; Pescitelli, G.; Fujioka, N.; Berova, N.; Antus, S. Enantioselective Synthesis of 3-Methylisochromans and Determination of Their Absolute Configurations by Circular Dichroism. *Eur. J. Org. Chem.* **2007**, *2007*, 296-305.

6. Zhang, Z.; Gao, Y.; Liu, Y.; Li, J.; Xie, H.; Li, H.; Wang, W. Organocatalytic Aerobic Oxidation of Benzylic sp^3 C-H Bonds of Ethers and Alkylarenes Promoted by a Recyclable TEMPO Catalyst. *Org. Lett.* **2015**, *17*, 5492-5495.

7. Geng, P.; Tang, Y.; Pan, G.; Wang, W.; Hu, J.; Cai, Y. A g-C_3N_4-based Heterogeneous Photocatalyst for Visible Light Mediated Aerobic Benzylic C-H Oxygenations. *Green Chem.* **2019**, *21*, 6116-6122.

8. Bose, N. K.; Chaudhury, D. N. Dihydroisocoumarins-X: The Preparation and Reduction of Some O-Carboxyphenylacetates. *Tetrahedron* **1964**, *20*, 49-51.

9. Schultz, A. G.; Kirincich, S. J. An Efficient Preparation and Selected Birch-Reduction Alkylations of 3,4-Dihydro-4,5-dialkyl-2-benzopyran-1-ones. *J. Org. Chem.* **1996**, *61*, 5631-5634.

10. Rioz-Martínez, A.; de Gonzalo, G.; Torres Pazmiño, D. E.; Fraaije, M. W.; Gotor, V. Enzymatic Baeyer-Villiger Oxidation of Benzo-Fused Ketones: Formation of Regiocomplementary Lactones. *Eur. J. Org. Chem.* **2009**, *15*, 2526-2532.

11. Yanai, H.; Taguchi, T. Organic Acid Induced Olefination Reaction of Lactones. *Chem. Commun.* **2012,** *48*, 8967-8969.

12. Odasso, G.; Winters, G., [Cyclic Hydrazides. IV. Synthesis of 2-Amino-3,4-Dihydroisoquinolin-1(2H)-One]. *Farmaco Sci* **1978**, *33*, 148-155.

13. Michnowicz, T.; Borca, B.; Pétuya, R.; Schendel, V.; Pristl, M.; Pentegov, I.; Kraft, U.; Klauk, H.; Wahl, P.; Mutombo, P.; Jelínek, P.; Arnau, A.; Schlickum, U.; Kern, K. Controlling Single

Molecule Conductance by a Locally Induced Chemical Reaction on Individual Thiophene Units. *Angew. Chem. Int. Ed.* **2020**, *59*, 6207-6212.

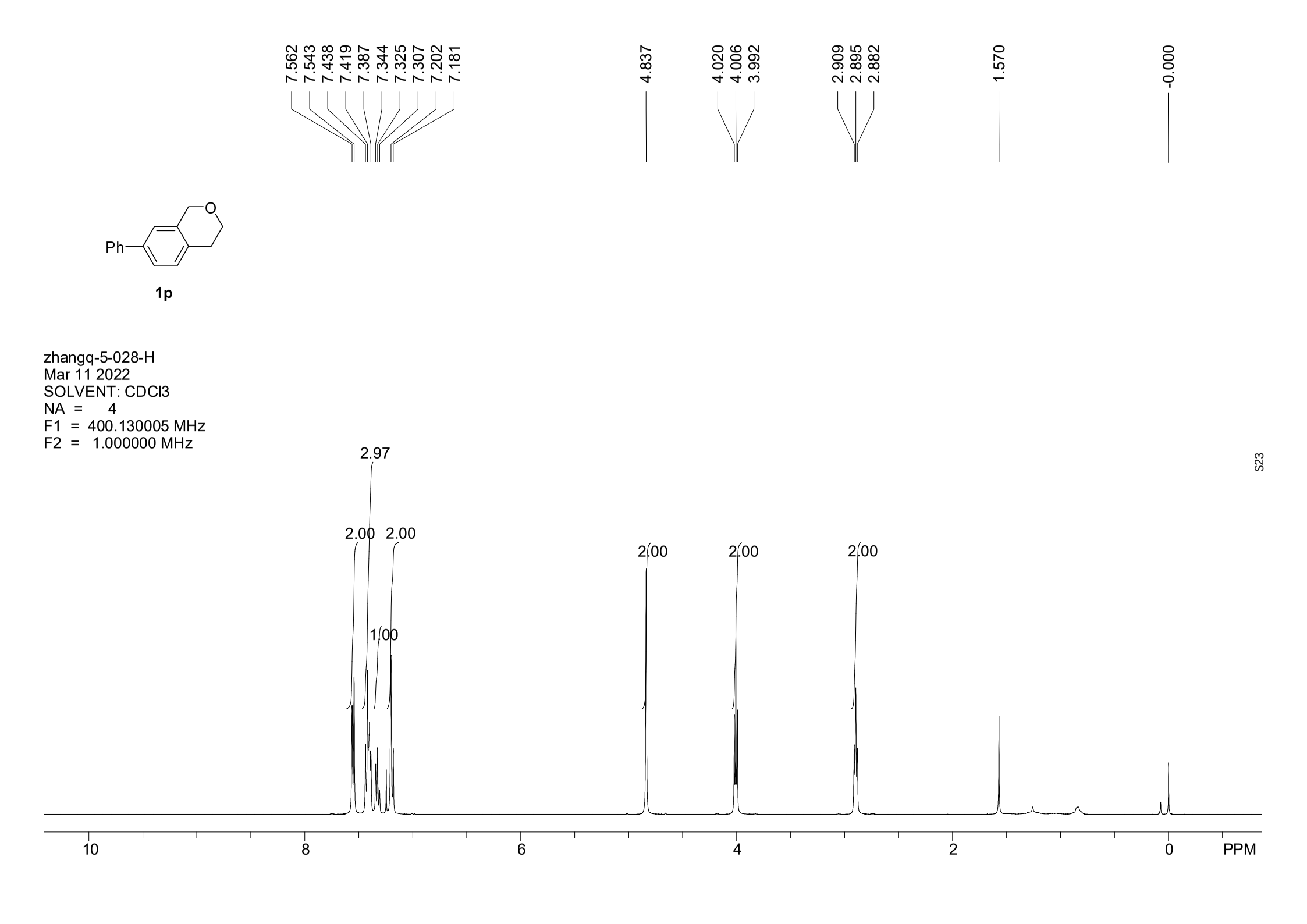
14. Li, W.; Wagener, T.; Hellmann, L.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Neugebauer, J.; Glorius, F. Design of Ru(II)-NHC-Diamine Precatalysts Directed by Ligand Cooperation: Applications and Mechanistic Investigations for Asymmetric Hydrogenation. *J. Am. Chem. Soc.* **2020**, *142*, 7100-7107.

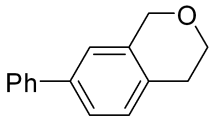
15. Ujjainwalla, F.; Da Mata, M. L. E. N.; Pennell, A. M. K.; Escolano, C.; Motherwell, W. B.; Vázquez, S. Synthesis of Biaryls via Intramolecular Free Radical Ipso-Substitution Reactions. *Tetrahedron* **2015**, *71*, 6701-6719.

16. Hamada, S.; Yano, K.; Kobayashi, Y.; Kawabata, T.; Furuta, T. Oxidaition of Cyclic Benzylic Ethers by an Electronically Tuned Nitroxyl Radical. *Tetrahedron Lett.* **2021**, *83*, 153404.

17. Ju, Z.-Y.; Song, L.-N.; Chong, M.-B.; Cheng, D.-G.; Hou, Y.; Zhang, X.-M.; Zhang, Q.-H.; Ren, L.-H. Selective Aerobic Oxidation of C_{sp3}-H Bonds Catalyzed by Yeast-Derived Nitrogen, Phosphorus, and Oxygen Codoped Carbon Materials. *J. Org. Chem.* **2022**, *87*, 3978-3988.

18. Laudadio, G.; Govaerts, S.; Wang, Y.; Ravelli, D.; Koolman, H. F.; Fagnoni, M.; Djuric, S. W.; Noël, T. Selective C(sp^3)-H Aerobic Oxidation Enabled by Decatungstate Photocatalysis in Flow. *Angew. Chem. Int. Ed.* **2018,** *57*, 4078-4082.


7.562
7.543
7.438
7.419
7.387
7.344
7.325
7.307
7.202
7.181
4.837
4.020
4.006
3.992
2.909
2.895
2.882
1.570
-0.000
O
Ph
1p
zhangq-5-028-H
Mar 11 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S23
2.97
2.00
2.00
1.00
2.00
2.00
2.00
10
8
6
4
2
0
PPM

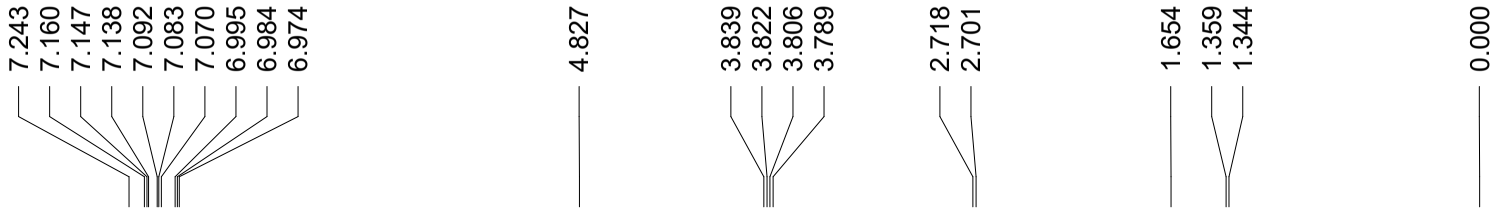


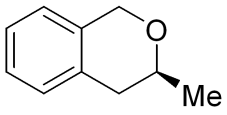
1p

zhangq-5-028-C
Mar 11 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz

140.816
138.975
135.223
132.284
129.243
128.650
127.078
126.865
125.111
122.915
77.316
77.000
76.684
67.970
65.308
27.988

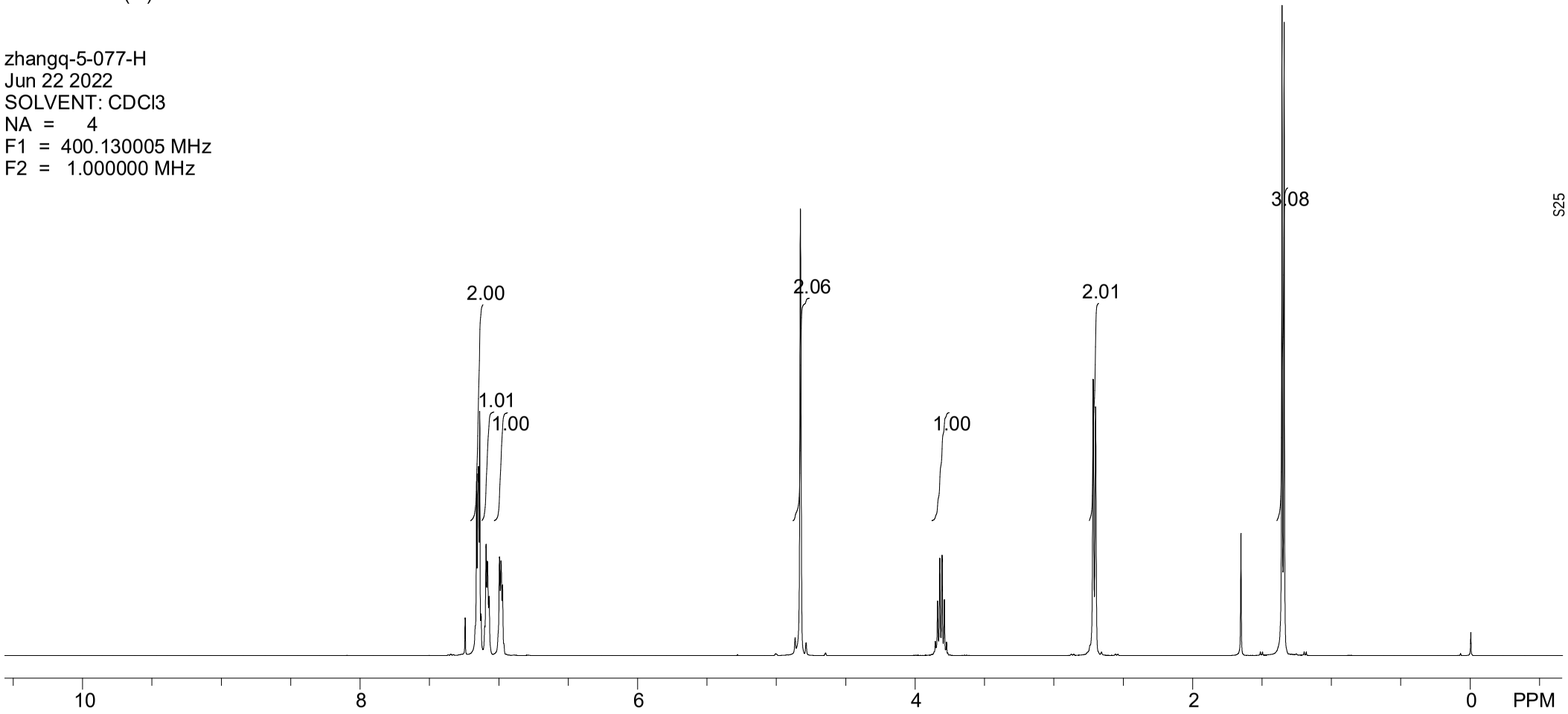
200
150
100
50
PPM

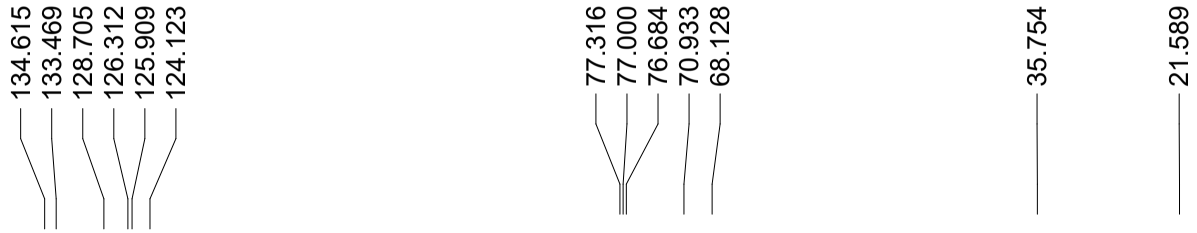


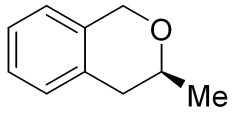


(*S*)-**1m**

zhangq-5-077-H
Jun 22 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz

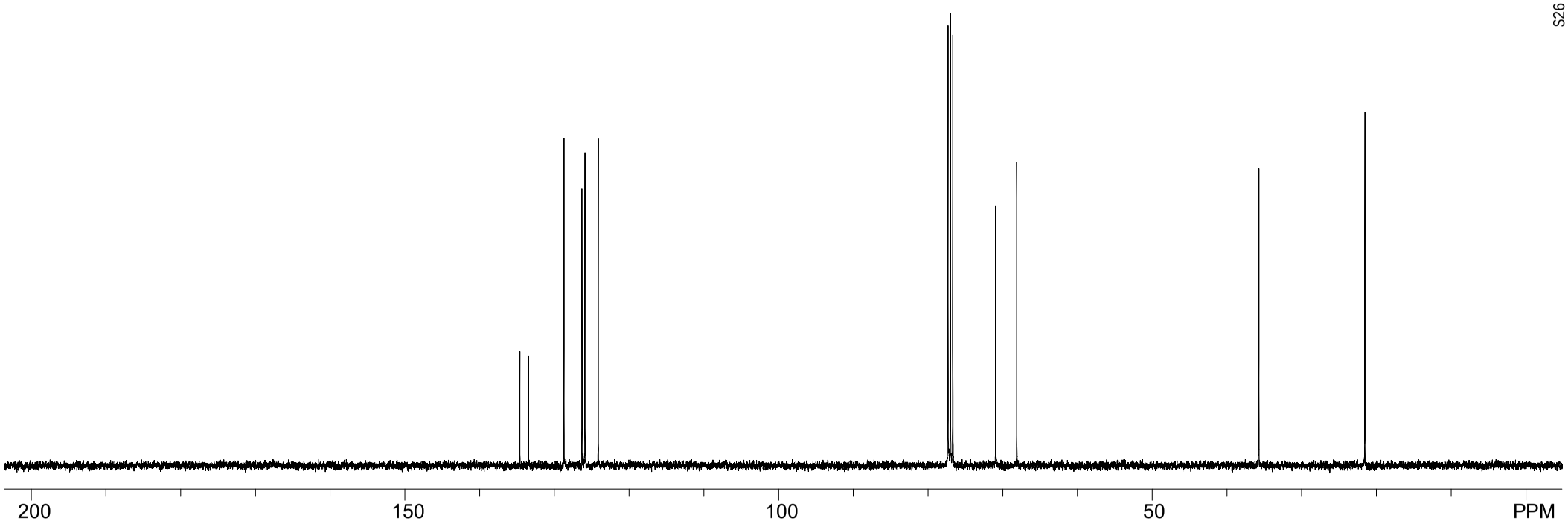






(*S*)-**1m**

zhangq-5-077-C
Jun 22 2022
SOLVENT: CDCl3
NA = 150
F1 = 100.612770 MHz
F2 = 1.000000 MHz

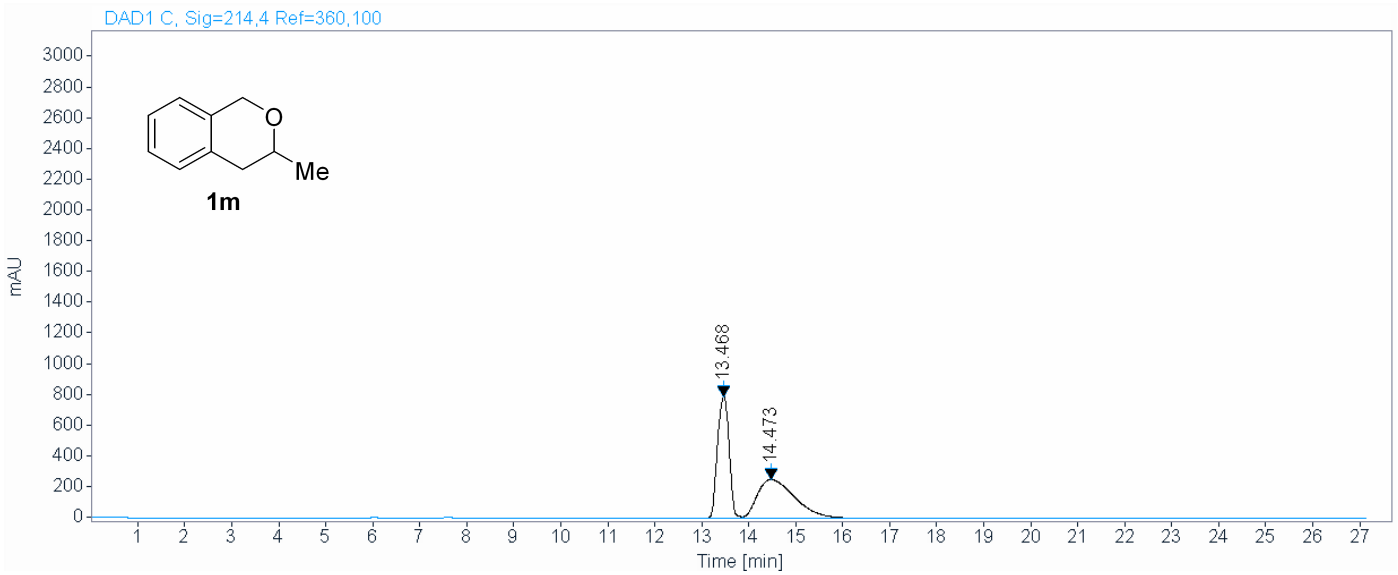


Area Percent Report

sample zhangq-4-043-rac-OD-H-99.5-0.5-0.5-214

Data file: C:\Users\Public\Documents\ChemStation\1\Data\zhangq 2022-06-22 14-13-37\004-P2-D1-zhangq-4-043-rac.D

Acquisition Data:



Signal: DAD1 C, Sig=214,4 Ref=360,100

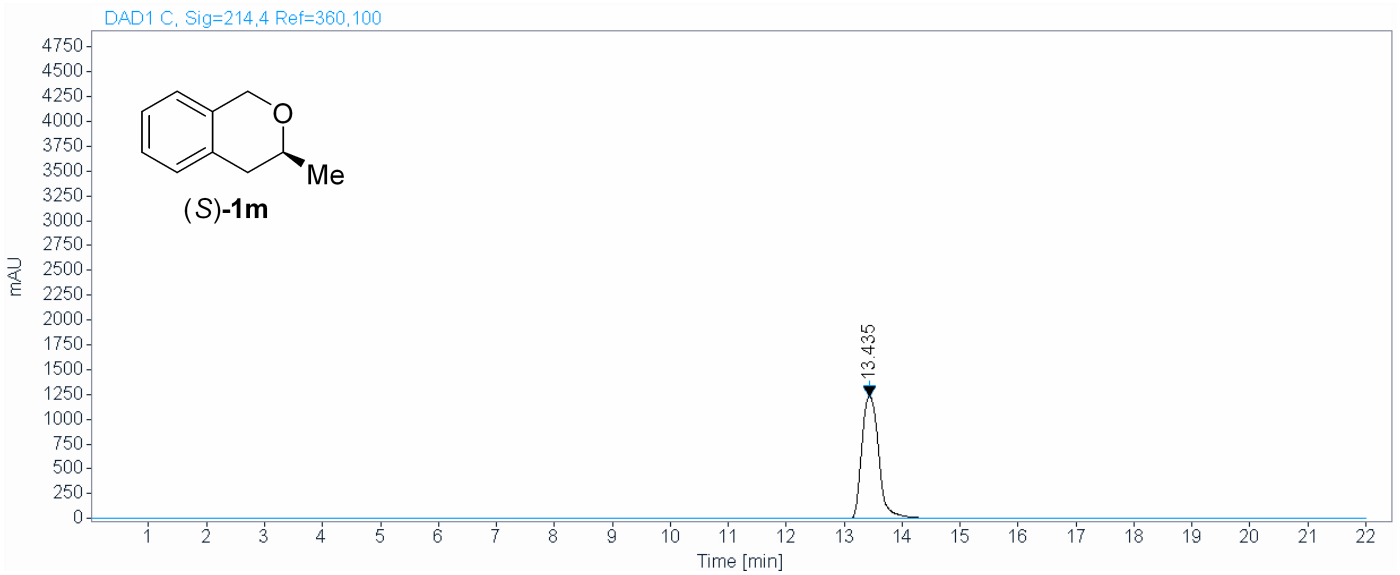
RT [min]	Width [min]	Height	Area	Area%
13.468	0.2918	793.2661	13721.1797	49.1886
14.473	0.8920	252.8439	14173.8564	50.8114
		Sum	27895.0361	100.0000

Area Percent Report

sample zhangq-5-077-OD-H-99.5-0.5-0.5-214

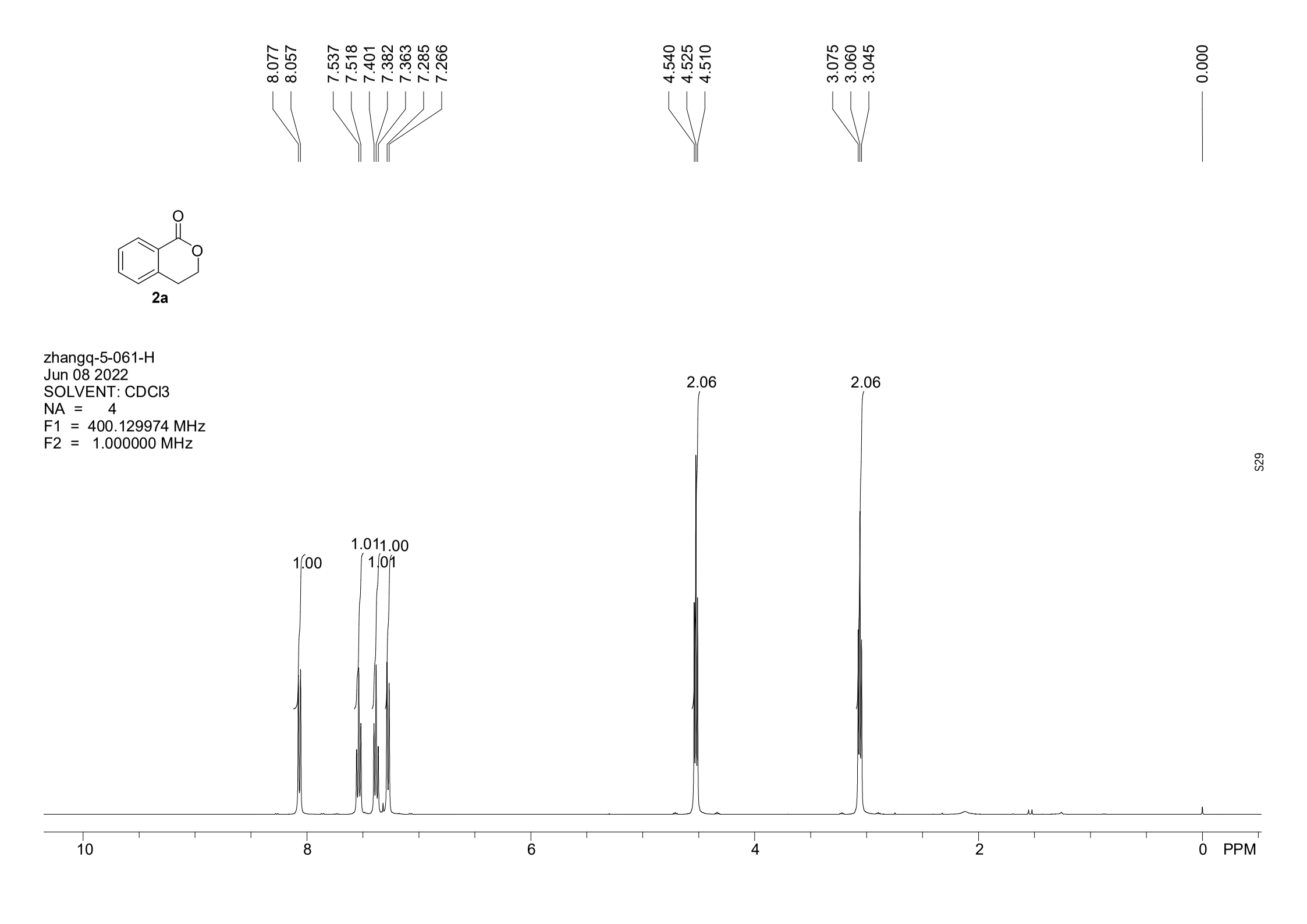
Data file: C:\Users\Public\Documents\ChemStation\1\Data\zhangq 2022-06-22 14-13-37\005-P2-D2-zhangq-5-077.D

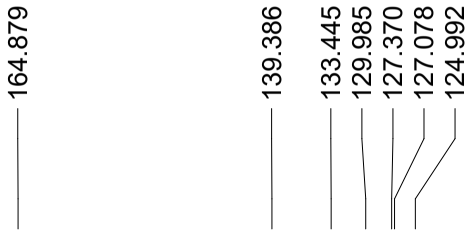
Acquisition Data:

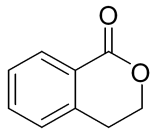


Signal: DAD1 C, Sig=214,4 Ref=360,100

RT [min]	Width [min]	Height	Area	Area%
13.435	0.3312	1229.4689	25211.7051	100.0000
		Sum	25211.7051	100.0000

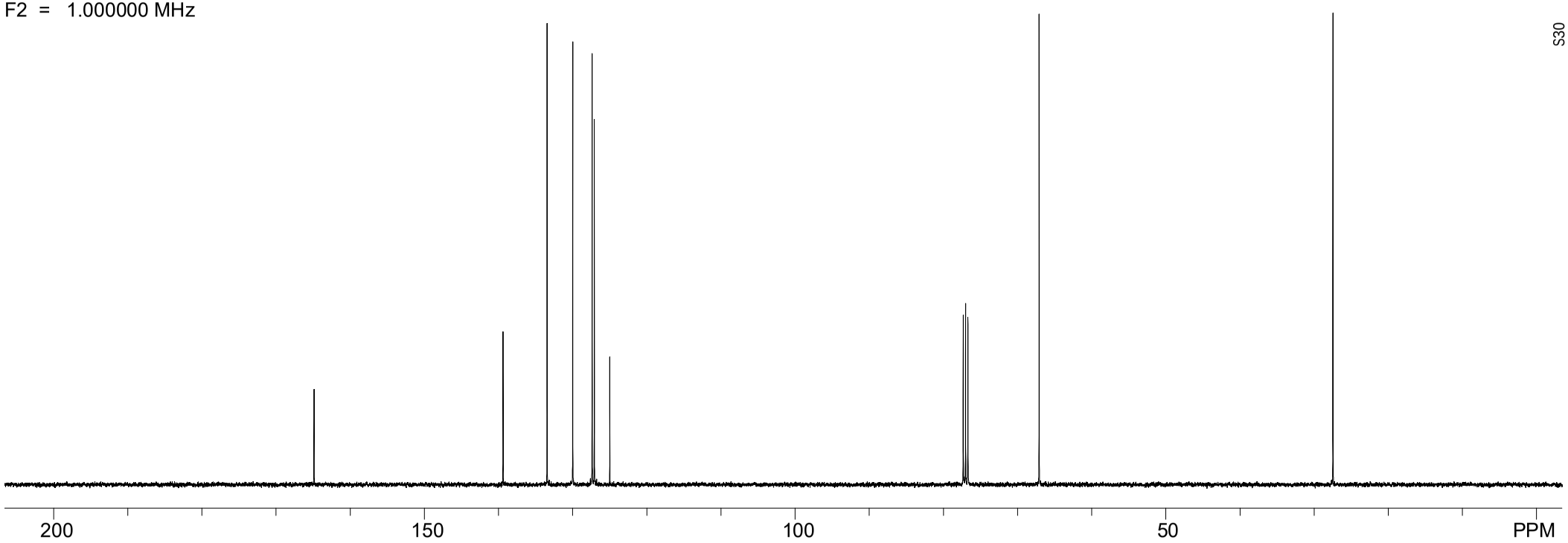

8.077
8.057
7.537
7.518
7.401
7.382
7.363
7.285
7.266
4.540
4.525
4.510
3.075
3.060
3.045
0.000
O
O
2a
zhangq-5-061-H
Jun 08 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.129974 MHz
F2 = 1.000000 MHz
2.06
2.06
1.00
1.01
1.00
1.01
S29
10
8
6
4
2
0
PPM

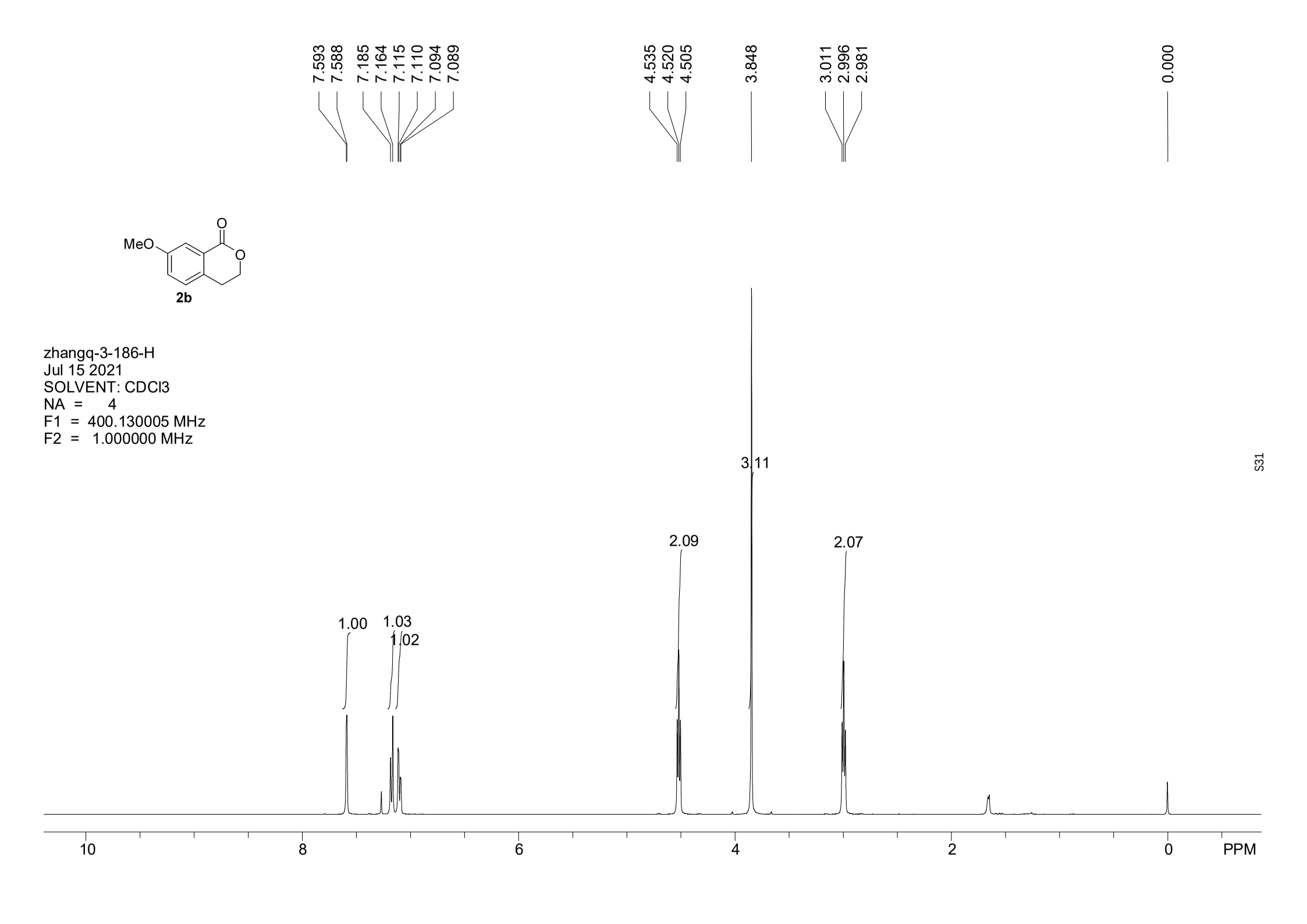


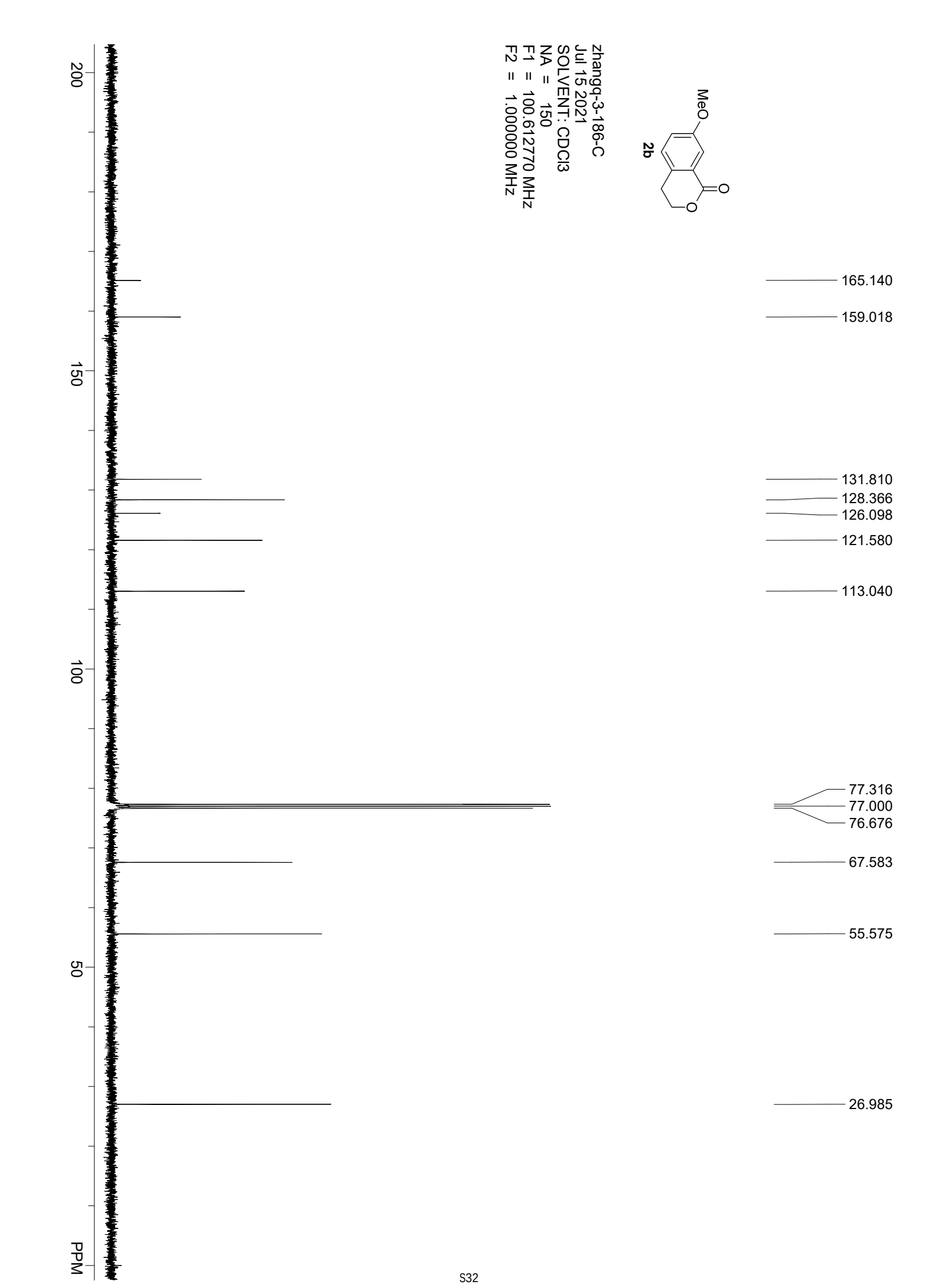


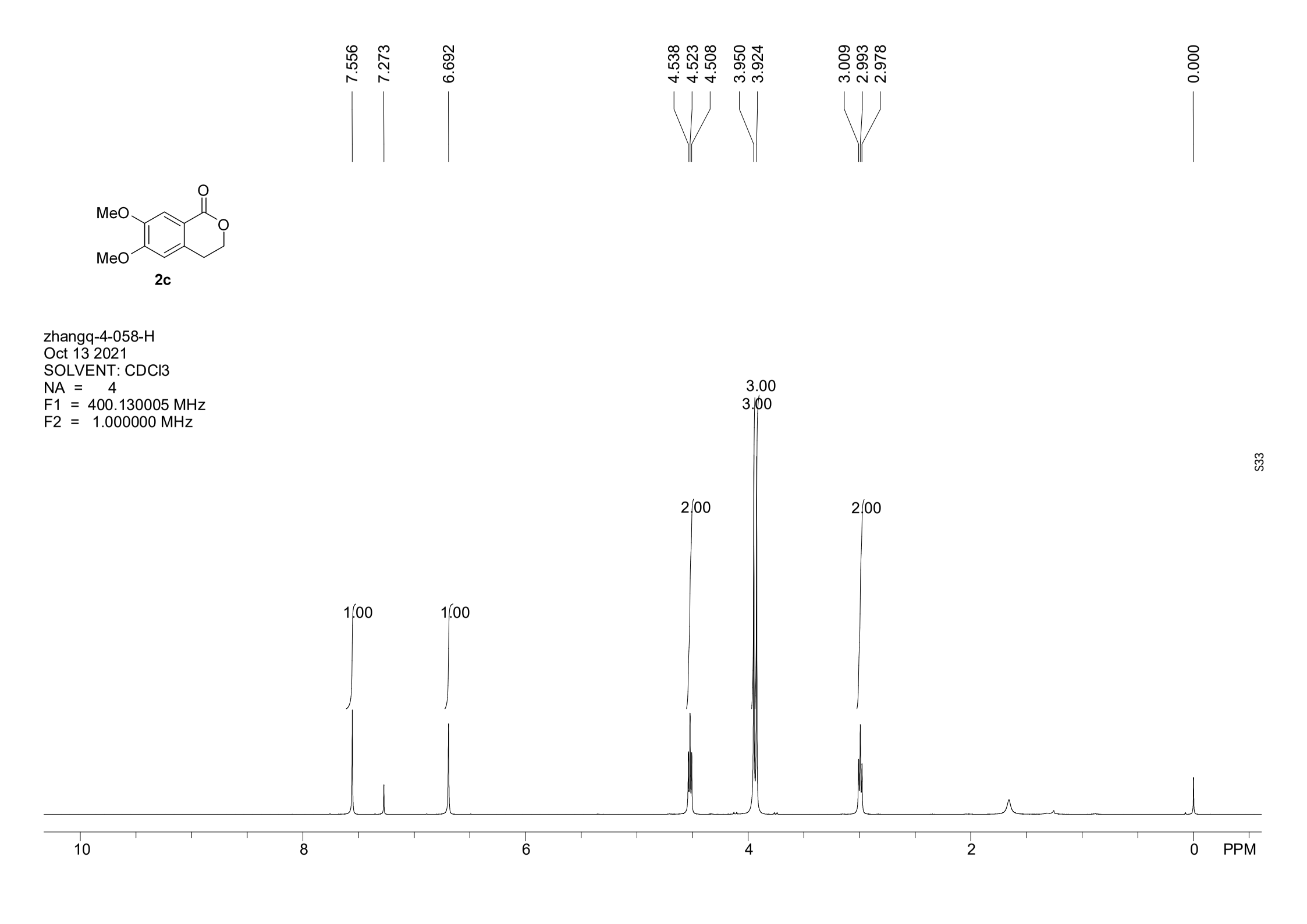
2a

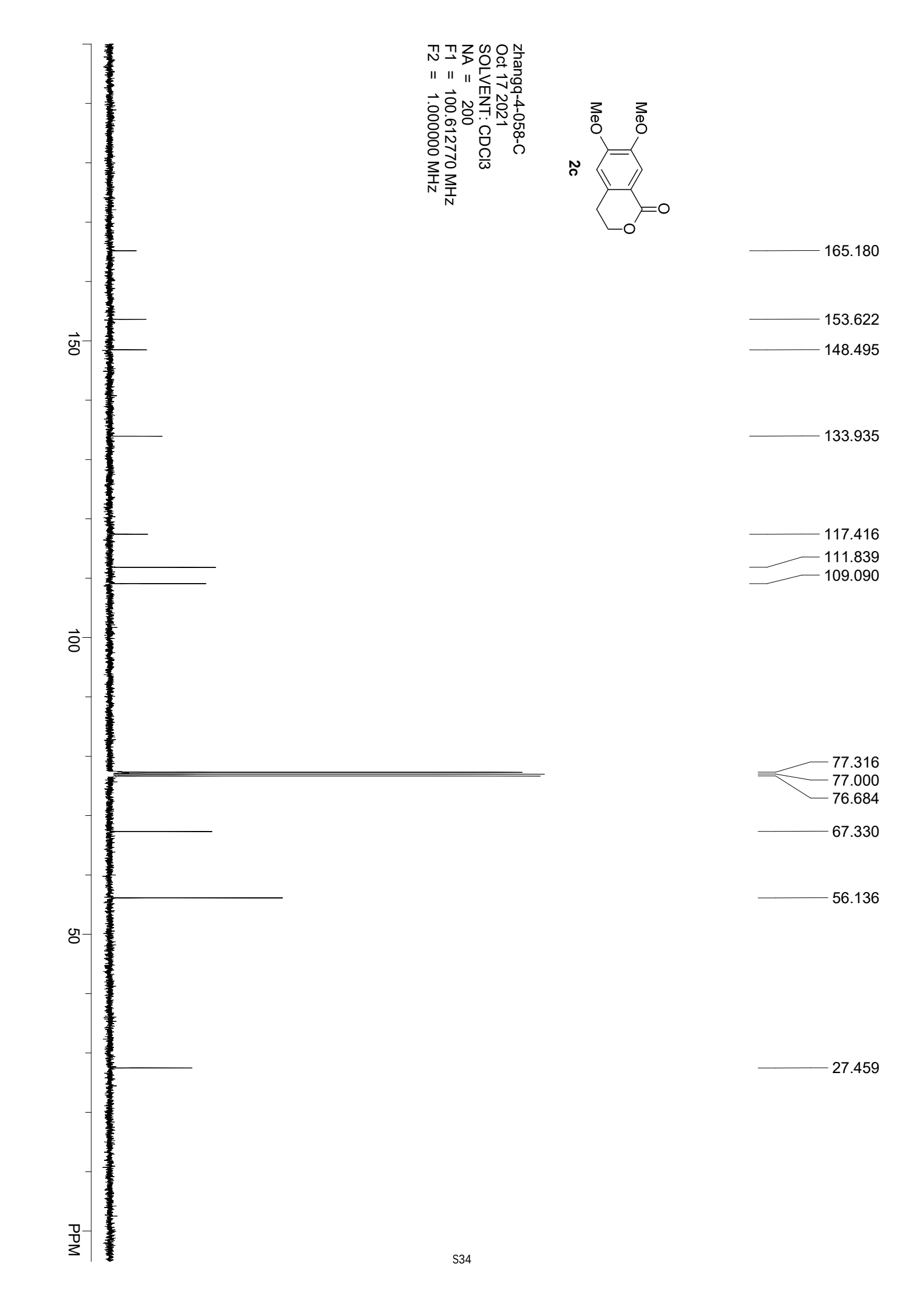
zhangq-5-061-C
Jun 08 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz

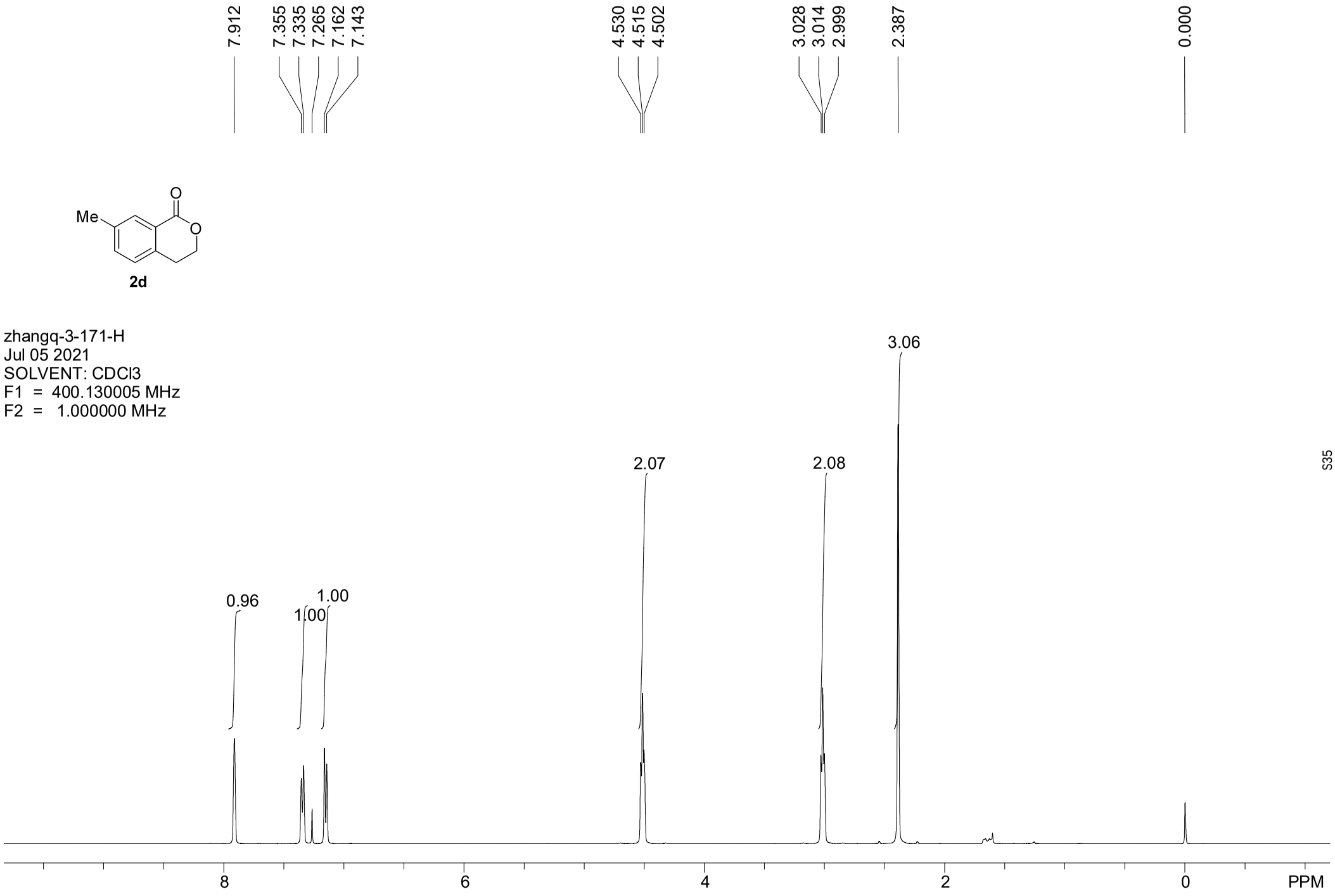


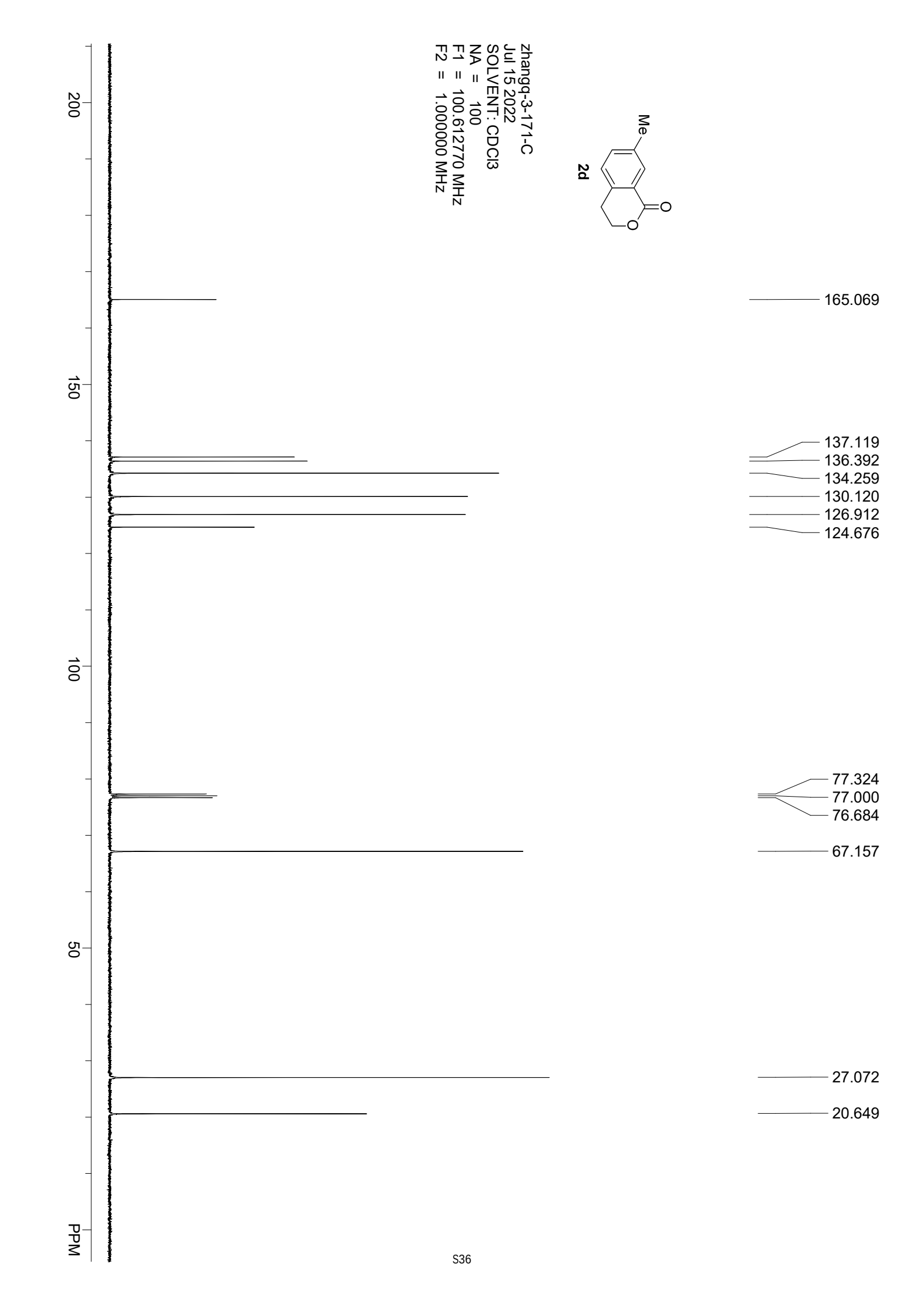

7.593
7.588
7.185
7.164
7.115
7.110
7.094
7.089
4.535
4.520
4.505
3.848
3.011
2.996
2.981
0.000
MeO
O
O
2b
zhangq-3-186-H
Jul 15 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3.11
2.09
2.07
1.00
1.03
1.02
S31
10
8
6
4
2
0
PPM

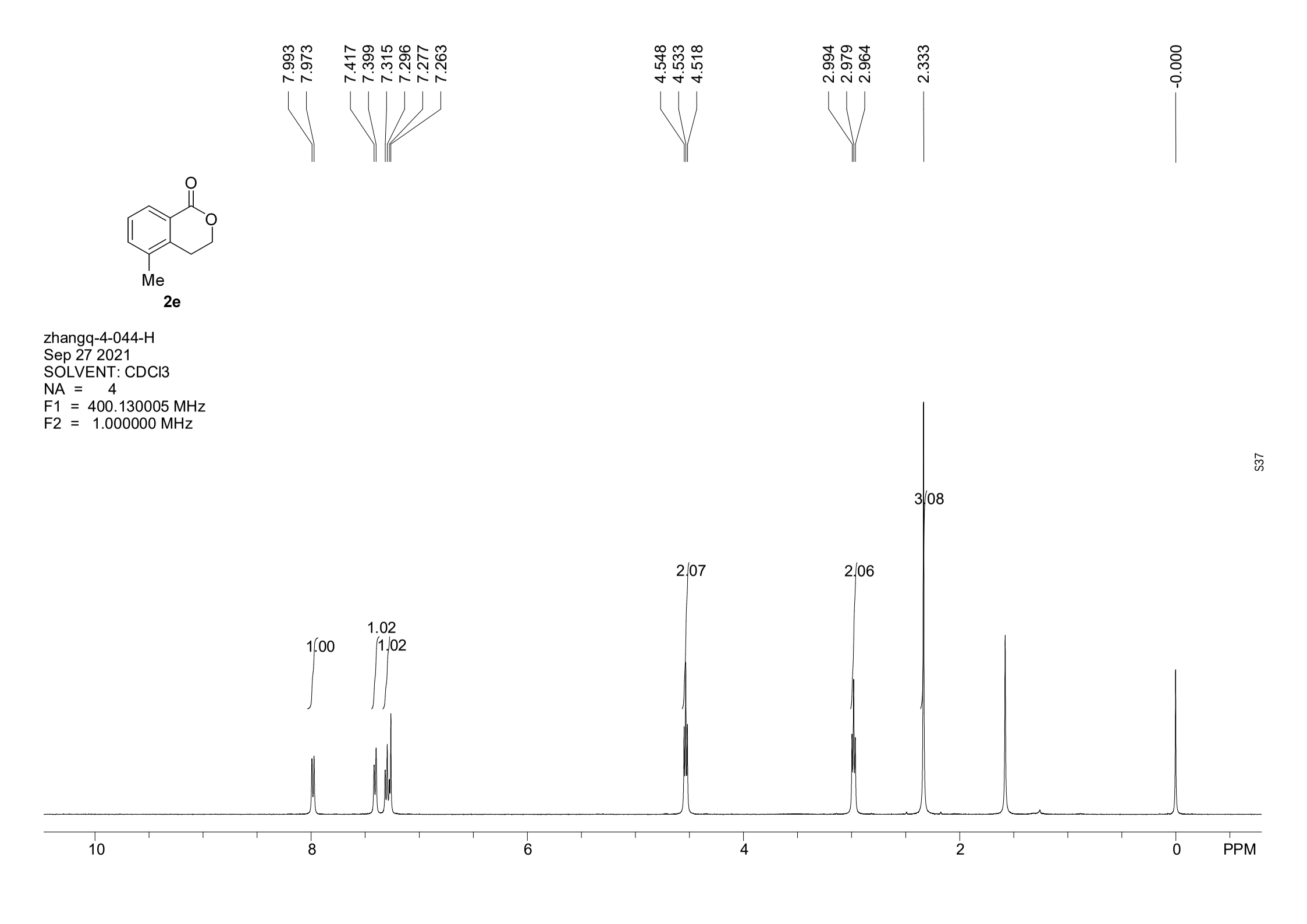

zhangq-3-186-C
Jul 15 2021
SOLVENT: CDCl3
NA = 150
F1 = 100.612770 MHz
F2 = 1.000000 MHz
MeO
O
O
2b
165.140
159.018
131.810
128.366
126.098
121.580
113.040
77.316
77.000
76.676
67.583
55.575
26.985
200
150
100
50
PPM

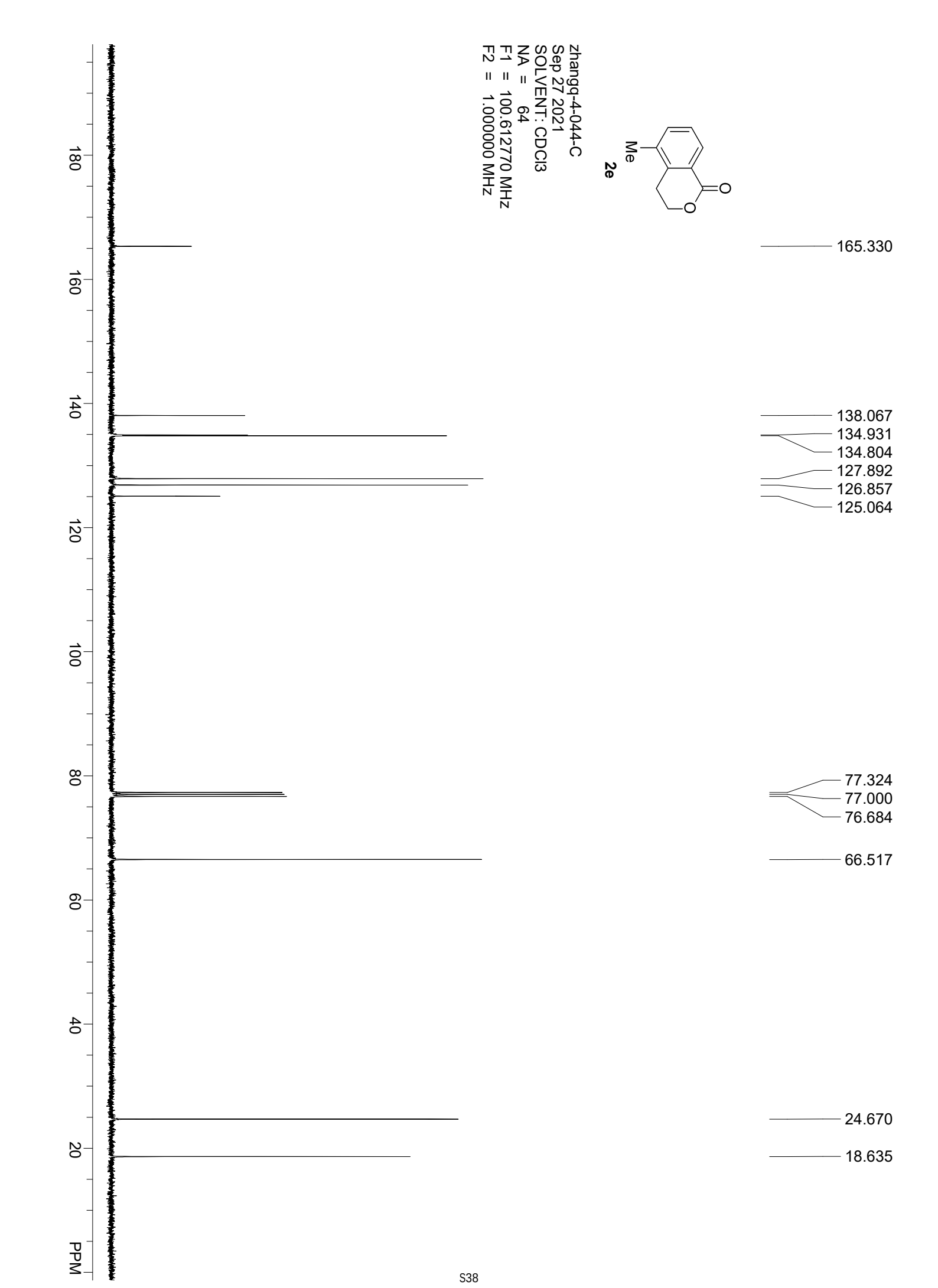

7.556
7.273
6.692
4.538
4.523
4.508
3.950
3.924
3.009
2.993
2.978
0.000
MeO
MeO
O
O
2c
zhangq-4-058-H
Oct 13 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S33
1.00
1.00
2.00
3.00
3.00
2.00
10
8
6
4
2
0
PPM

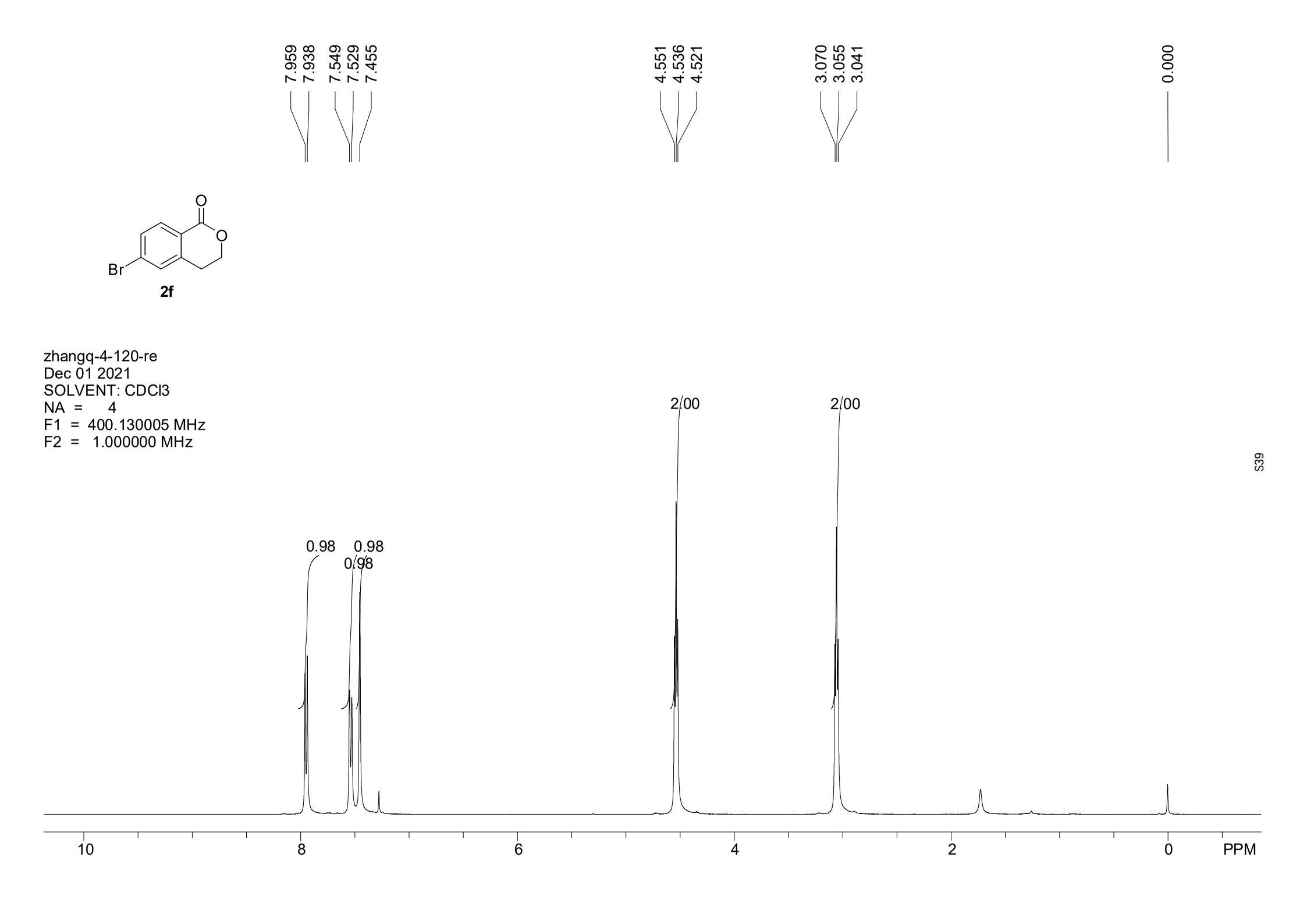

zhangq-4-058-C
Oct 17 2021
SOLVENT: CDCl3
NA = 200
F1 = 100.612770 MHz
F2 = 1.000000 MHz
MeO
MeO
O
O
2c
165.180
153.622
148.495
133.935
117.416
111.839
109.090
77.316
77.000
76.684
67.330
56.136
27.459
150
100
50
PPM

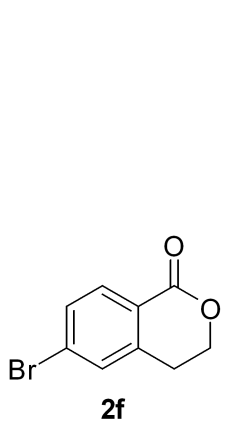

7.912
7.355
7.335
7.265
7.162
7.143
4.530
4.515
4.502
3.028
3.014
2.999
2.387
0.000
O
Me
O
2d
zhangq-3-171-H
Jul 05 2021
SOLVENT: CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3.06
2.07
2.08
S35
0.96
1.00
1.00
8
6
4
2
0
PPM


zhangq-3-171-C
Jul 15 2022
SOLVENT: CDCl3
NA = 100
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Me
O
O
2d
165.069
137.119
136.392
134.259
130.120
126.912
124.676
77.324
77.000
76.684
67.157
27.072
20.649
200
150
100
50
PPM


7.993
7.973
7.417
7.399
7.315
7.296
7.277
7.263
4.548
4.533
4.518
2.994
2.979
2.964
2.333
-0.000
O
O
Me
2e
zhangq-4-044-H
Sep 27 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S37
1.00
1.02
1.02
2.07
2.06
3.08
10
8
6
4
2
0
PPM

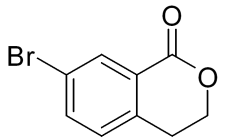

zhangq-4-044-C
Sep 27 2021
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Me
2e
O
O
165.330
138.067
134.931
134.804
127.892
126.857
125.064
77.324
77.000
76.684
66.517
24.670
18.635
180
160
140
120
100
80
60
40
20
PPM


7.959
7.938
7.549
7.529
7.455
4.551
4.536
4.521
3.070
3.055
3.041
0.000
O
O
Br
2f
zhangq-4-120-re
Dec 01 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
2.00
2.00
0.98
0.98
0.98
S39
10
8
6
4
2
0
PPM



2f

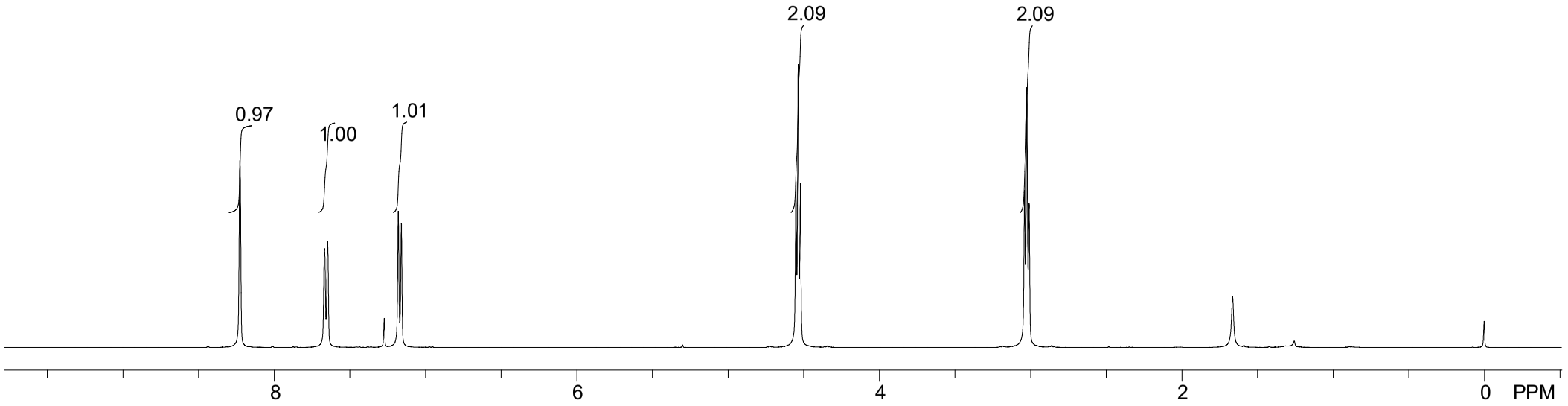
zhangq-4-120-C
Nov 29 2021
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz

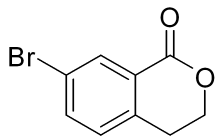


2g

8.227
7.669
7.648
7.273
7.180
7.160
4.552
4.537
4.522
3.041
3.026
3.011
0.000

zhangq-3-174-H
Jul 08 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz



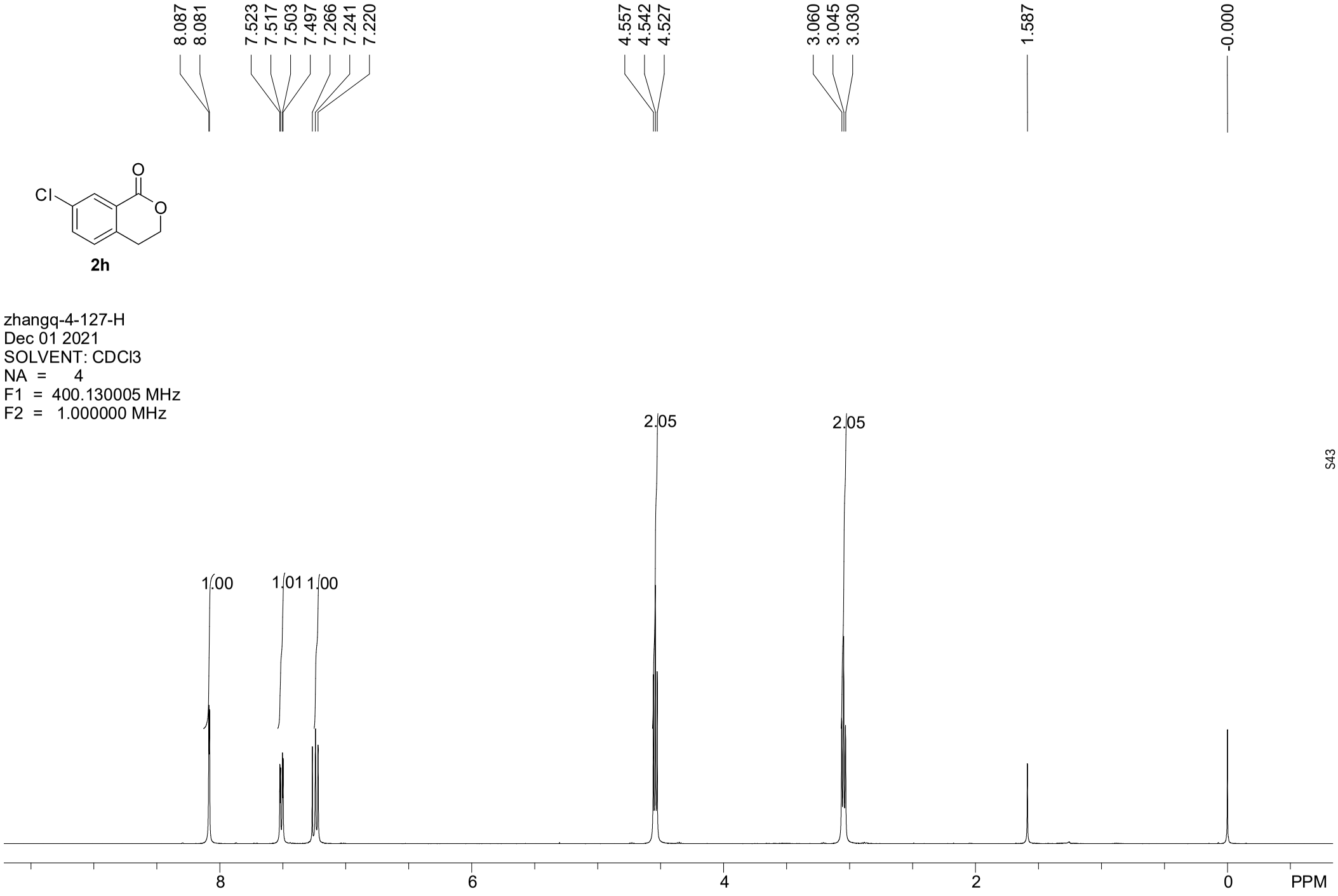


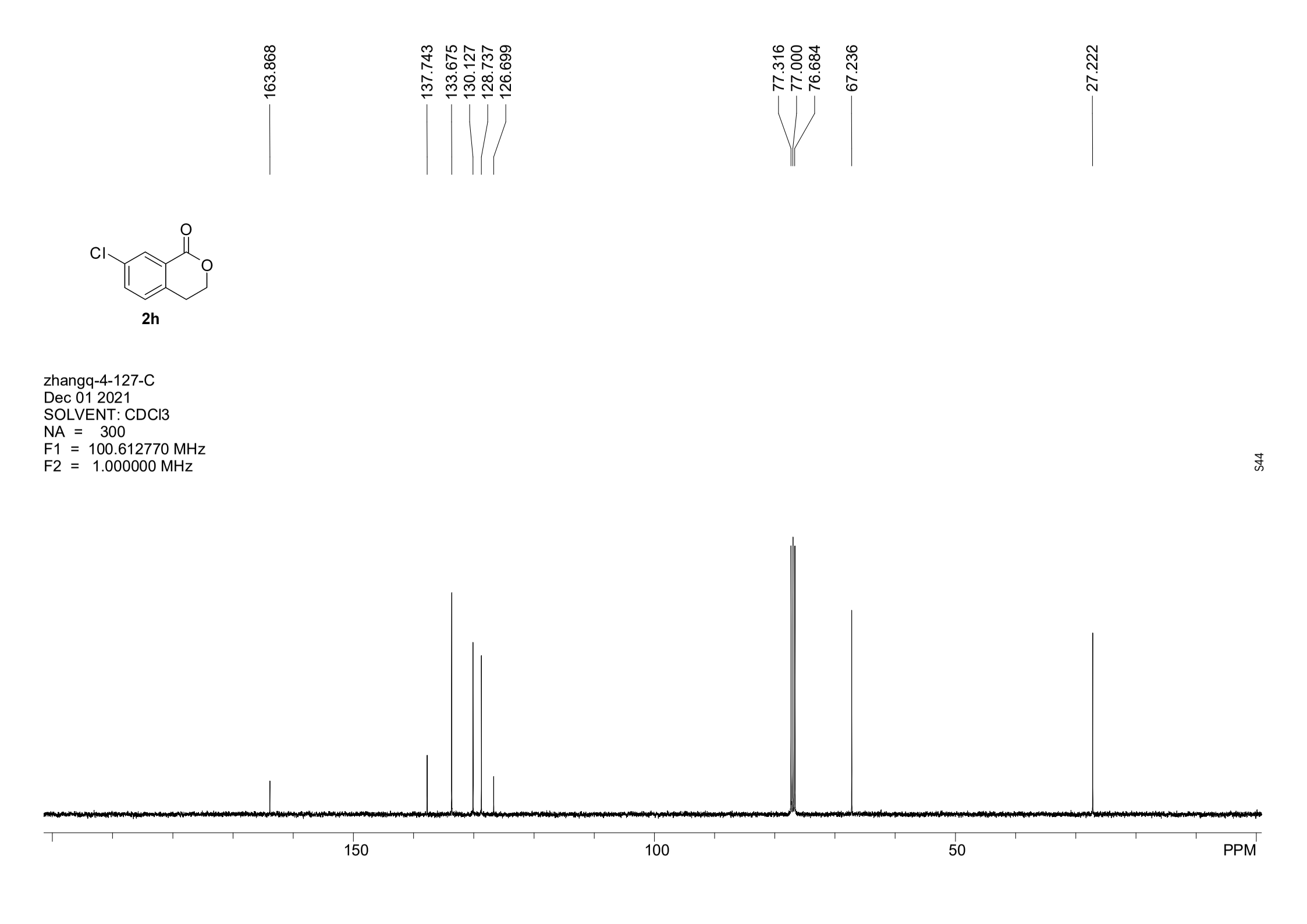
2g

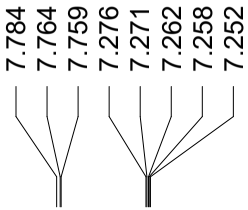
163.679
138.225
136.542
133.114
128.942
126.983
121.327
77.316
77.000
76.684
67.165
27.309

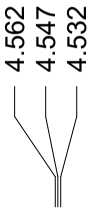
zhangq-3-174-C
Jul 08 2021
SOLVENT: CDCl3
NA = 150
F1 = 100.612770 MHz
F2 = 1.000000 MHz

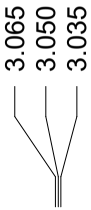
150
100
50
PPM

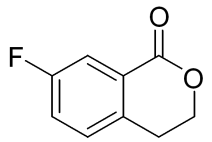

8.087
8.081
7.523
7.517
7.503
7.497
7.266
7.241
7.220
4.557
4.542
4.527
3.060
3.045
3.030
1.587
-0.000
Cl
O
O
2h
zhangq-4-127-H
Dec 01 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
2.05
2.05
1.00
1.01
1.00
S43
8
6
4
2
0
PPM


163.868
137.743
133.675
130.127
128.737
126.699
77.316
77.000
76.684
67.236
27.222
Cl
O
O
2h
zhangq-4-127-C
Dec 01 2021
SOLVENT: CDCl3
NA = 300
F1 = 100.612770 MHz
F2 = 1.000000 MHz
S44
150
100
50
PPM



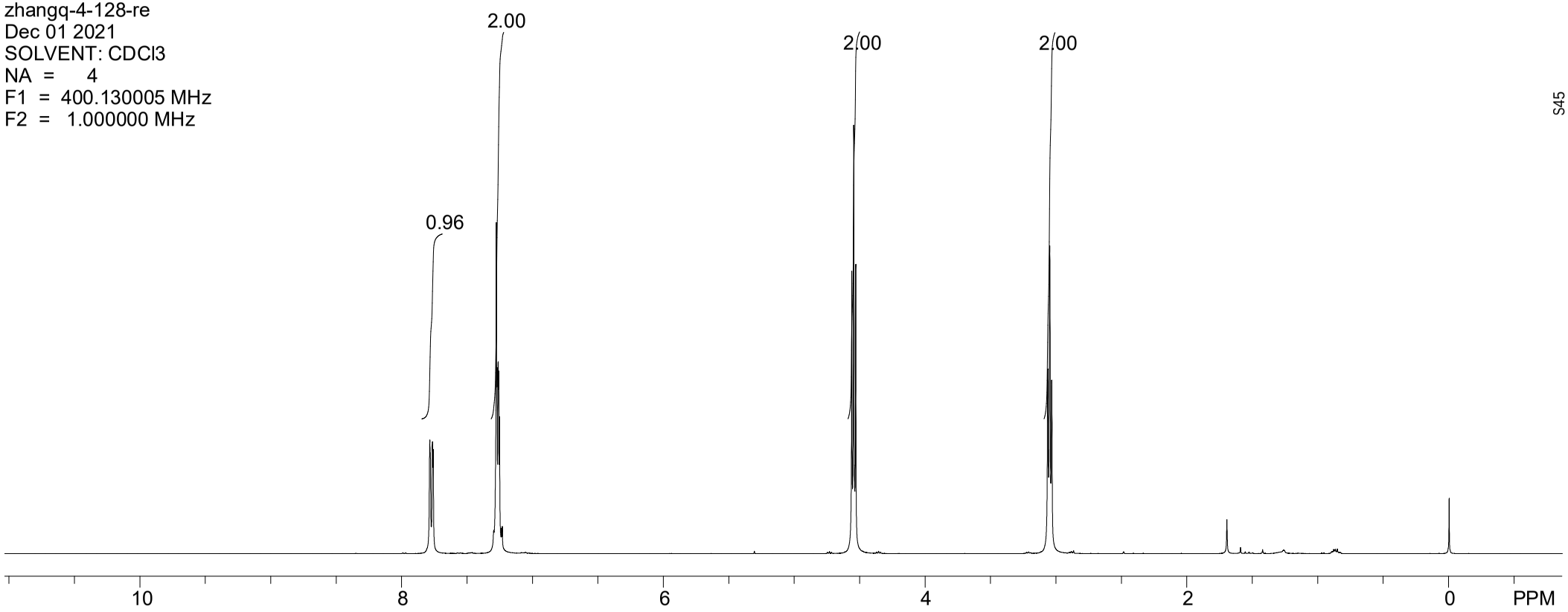




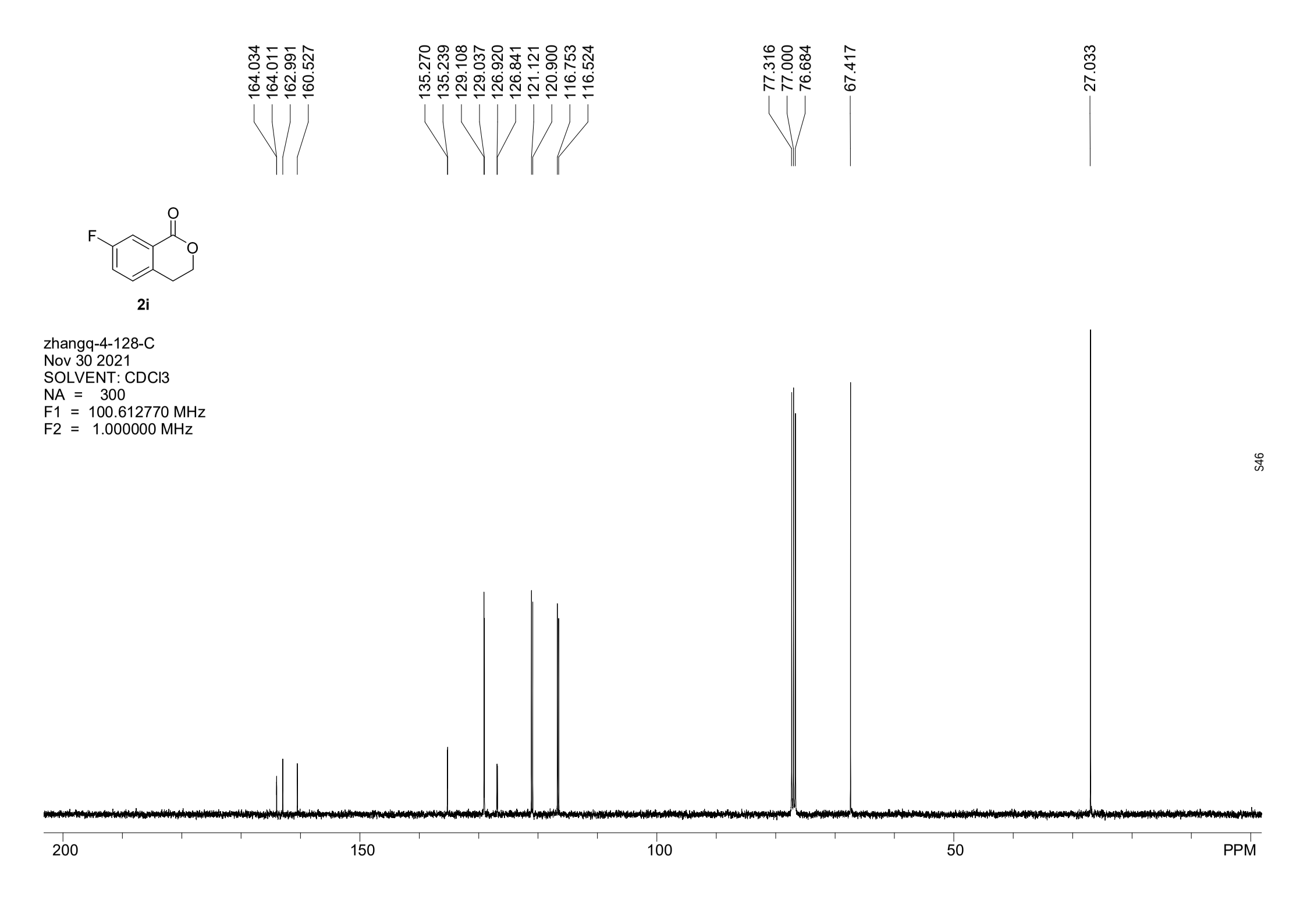


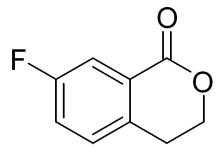
2i

zhangq-4-128-re
Dec 01 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz



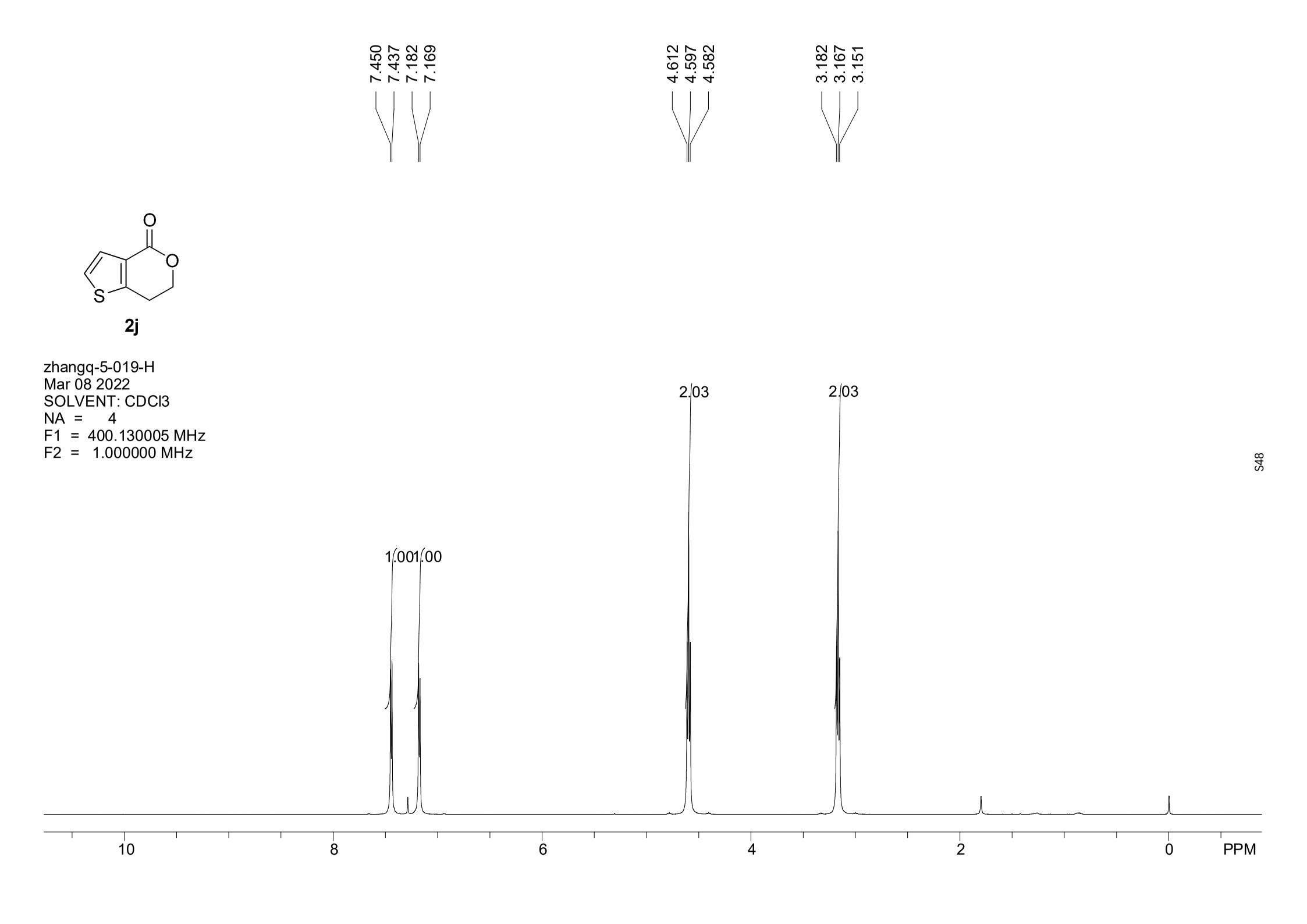
S45

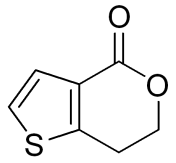

164.034
164.011
162.991
160.527
135.270
135.239
129.108
129.037
126.920
126.841
121.121
120.900
116.753
116.524
77.316
77.000
76.684
67.417
27.033
F
O
O
2i
zhangq-4-128-C
Nov 30 2021
SOLVENT: CDCl3
NA = 300
F1 = 100.612770 MHz
F2 = 1.000000 MHz
S46
200
150
100
50
PPM



2i

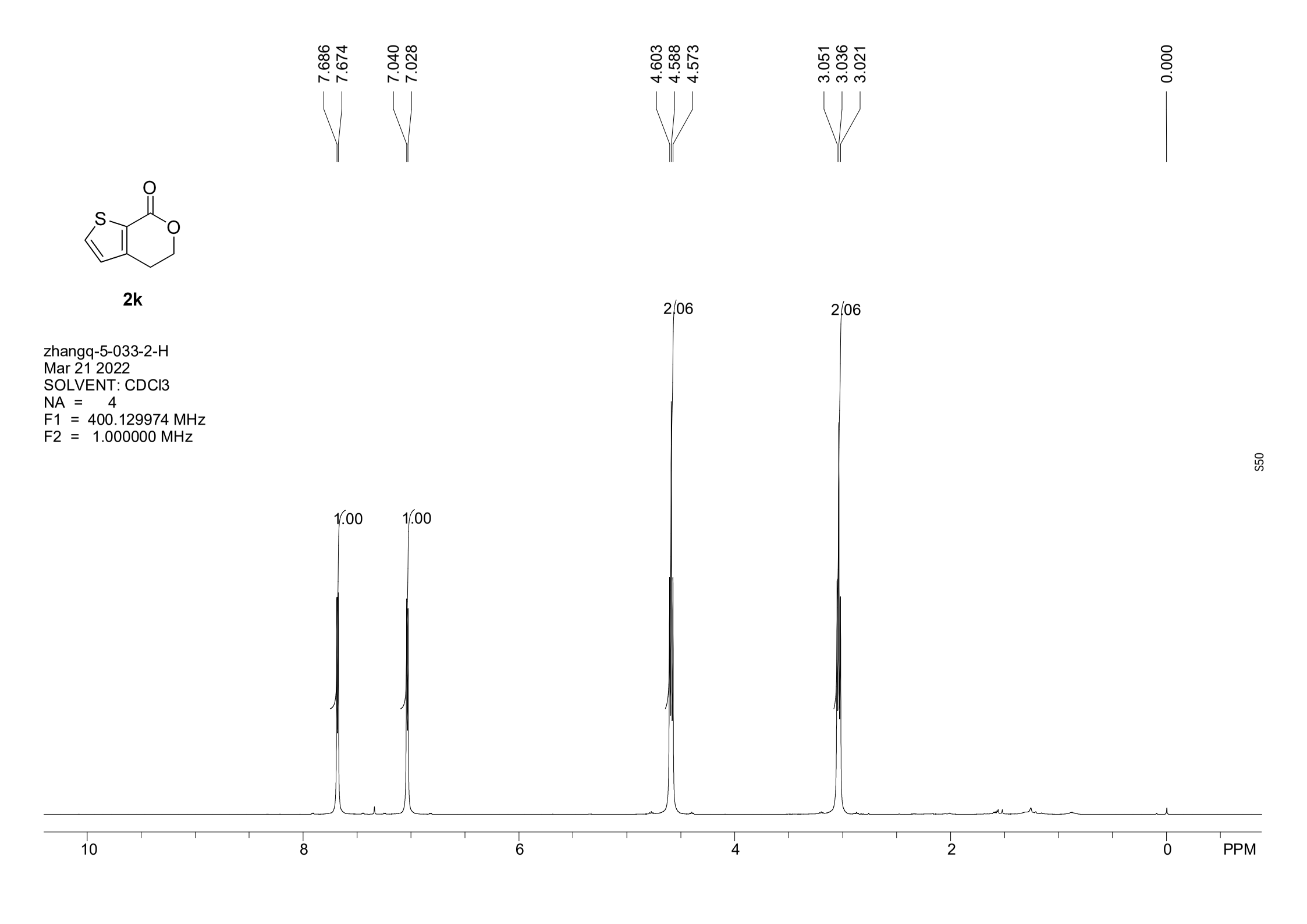
zhangq-4-128-F
Nov 30 2021
SOLVENT: CDCl3
NA = 16
F1 = 376.460724 MHz
F2 = 1.000000 MHz

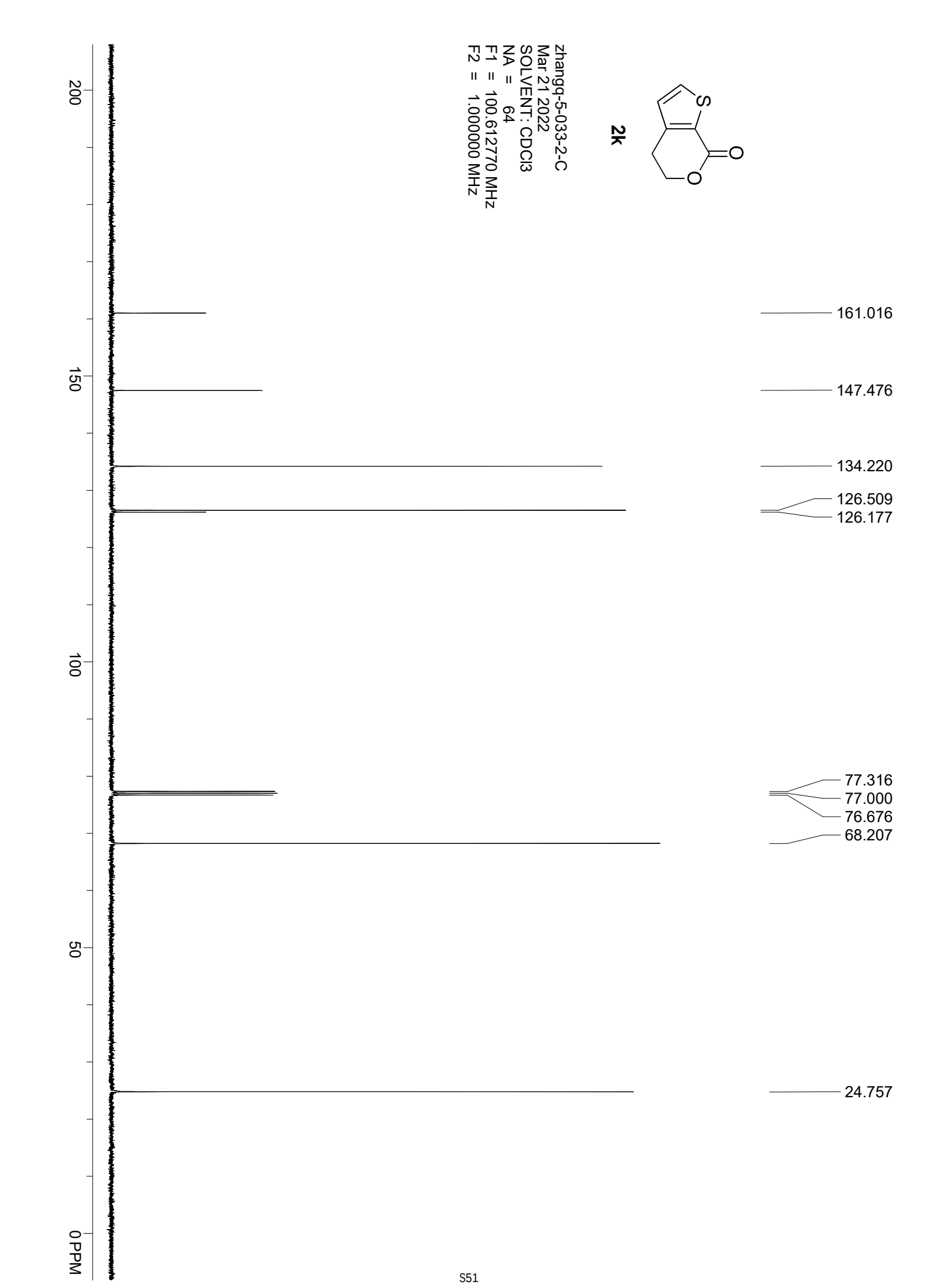

7.450
7.437
7.182
7.169
4.612
4.597
4.582
3.182
3.167
3.151
O
O
S
2j
zhangq-5-019-H
Mar 08 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
2.03
2.03
1.00
1.00
S48
10
8
6
4
2
0
PPM

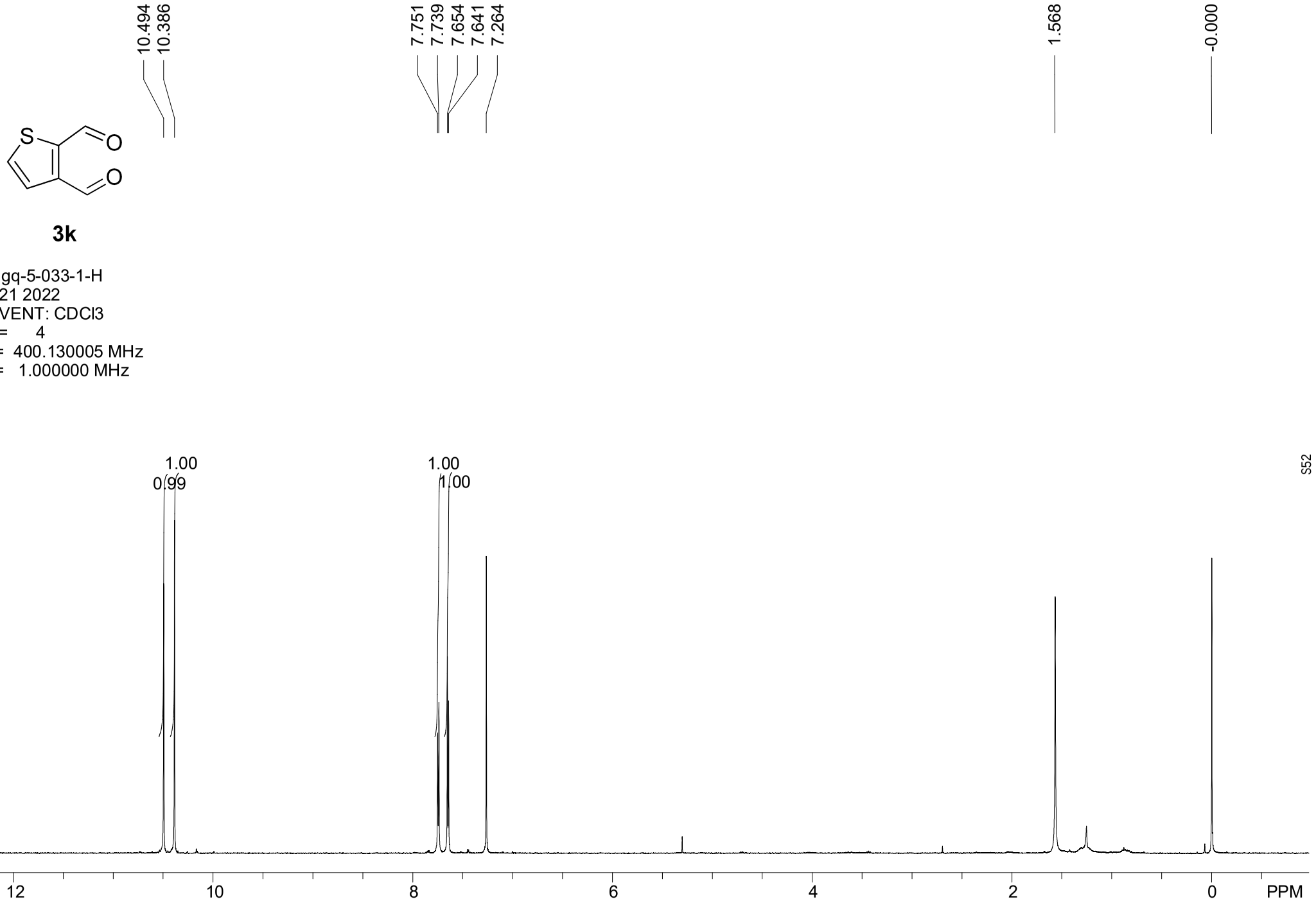


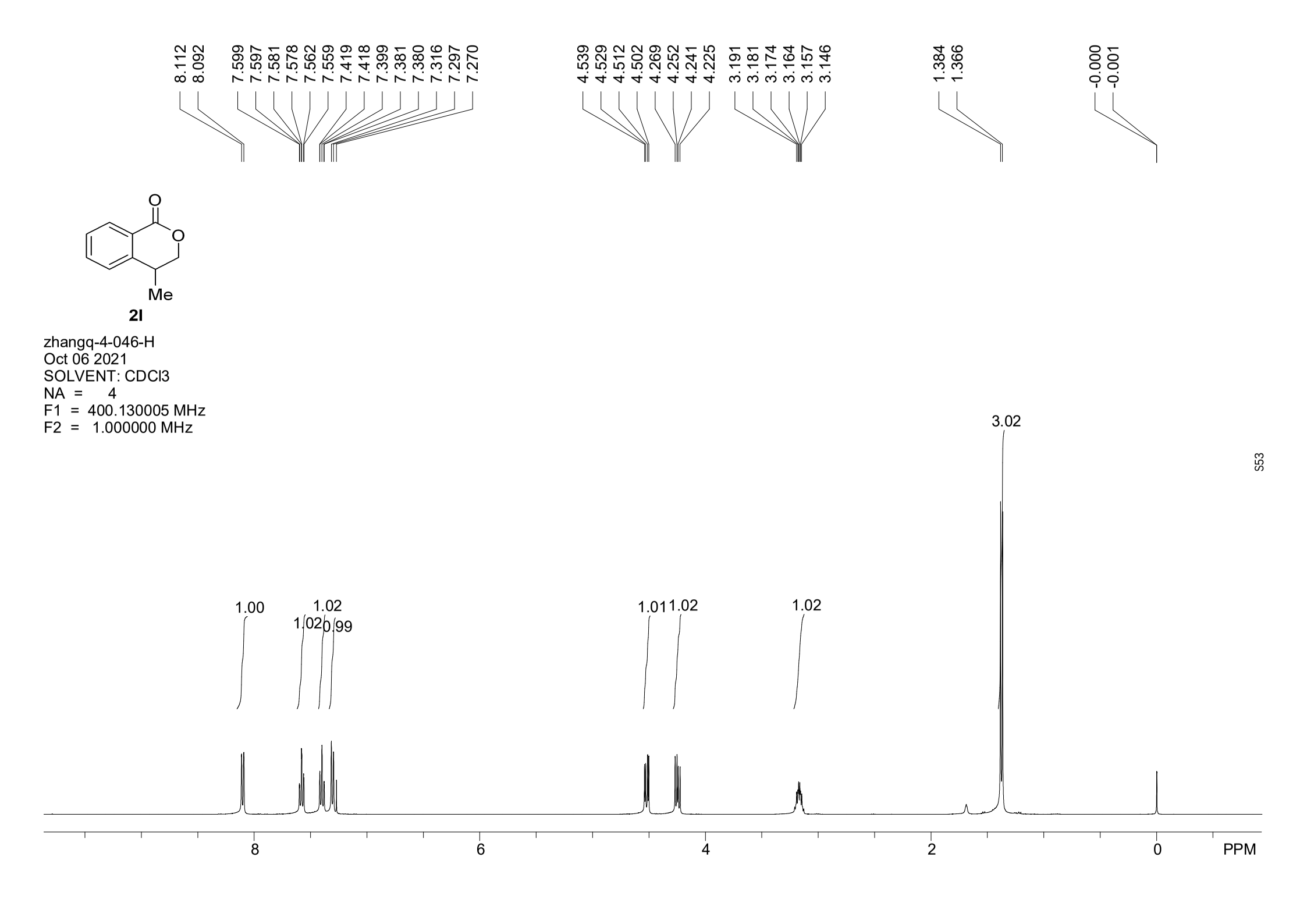
2j

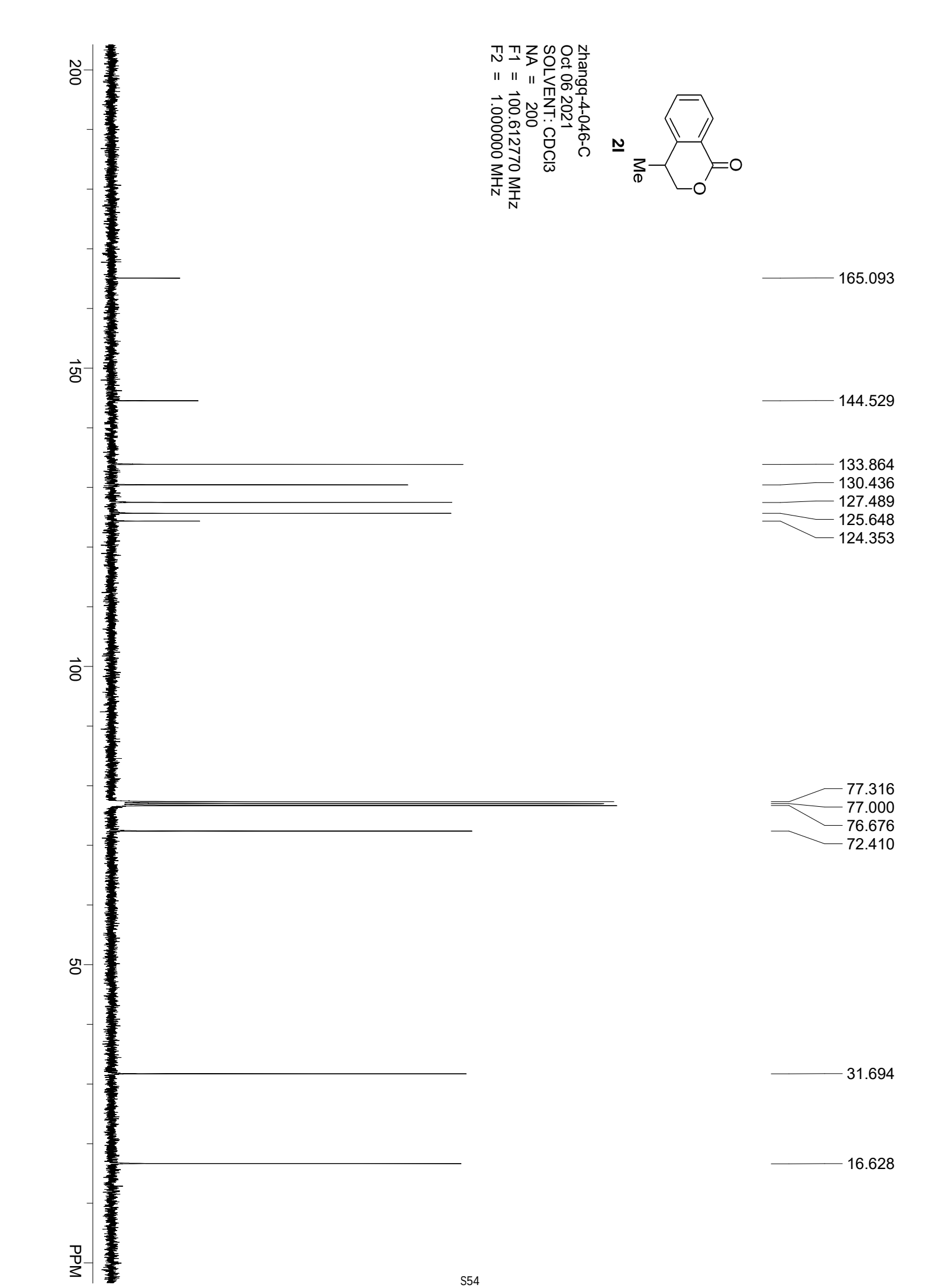
zhangq-5-019-C
Mar 07 2022
SOLVENT: CDCl3
NA = 150
F1 = 100.612770 MHz
F2 = 1.000000 MHz

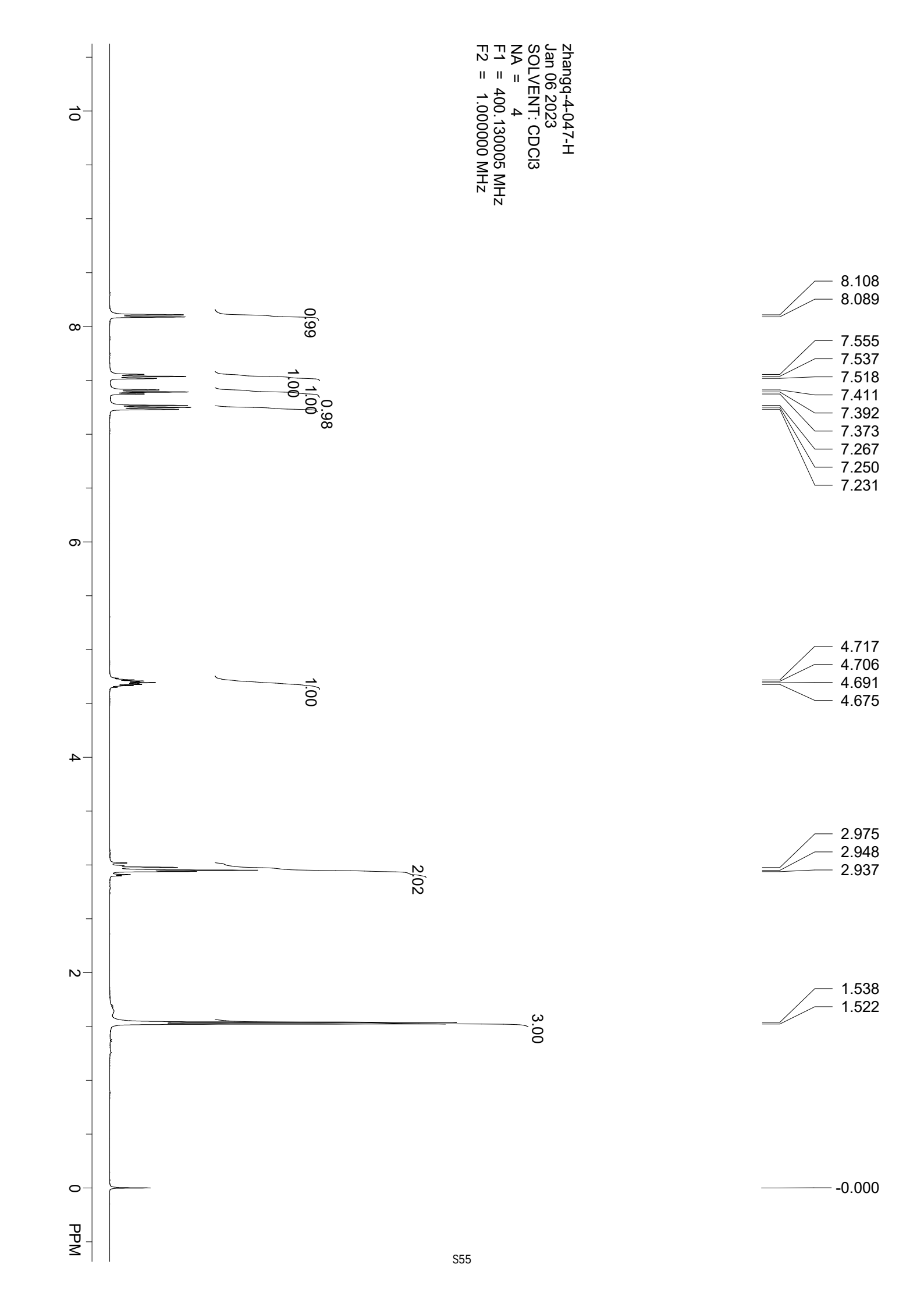

7.686
7.674
7.040
7.028
4.603
4.588
4.573
3.051
3.036
3.021
0.000
O
S
O
2k
zhangq-5-033-2-H
Mar 21 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.129974 MHz
F2 = 1.000000 MHz
1.00
1.00
2.06
2.06
S50
10
8
6
4
2
0
PPM

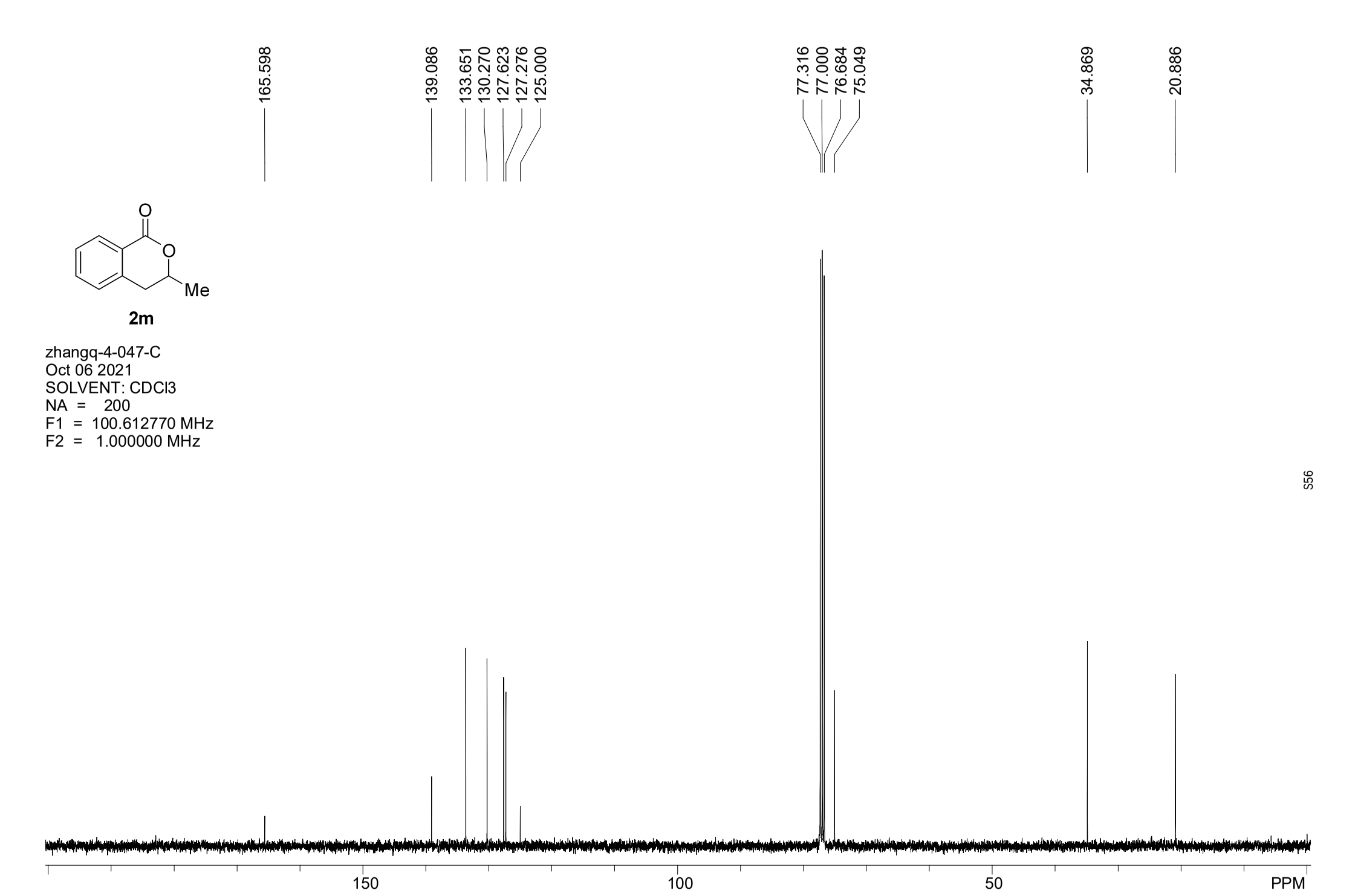

zhangq-5-033-2-C
Mar 21 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz
2k
S
O
O
161.016
147.476
134.220
126.509
126.177
77.316
77.000
76.676
68.207
24.757
200
150
100
50
0 PPM

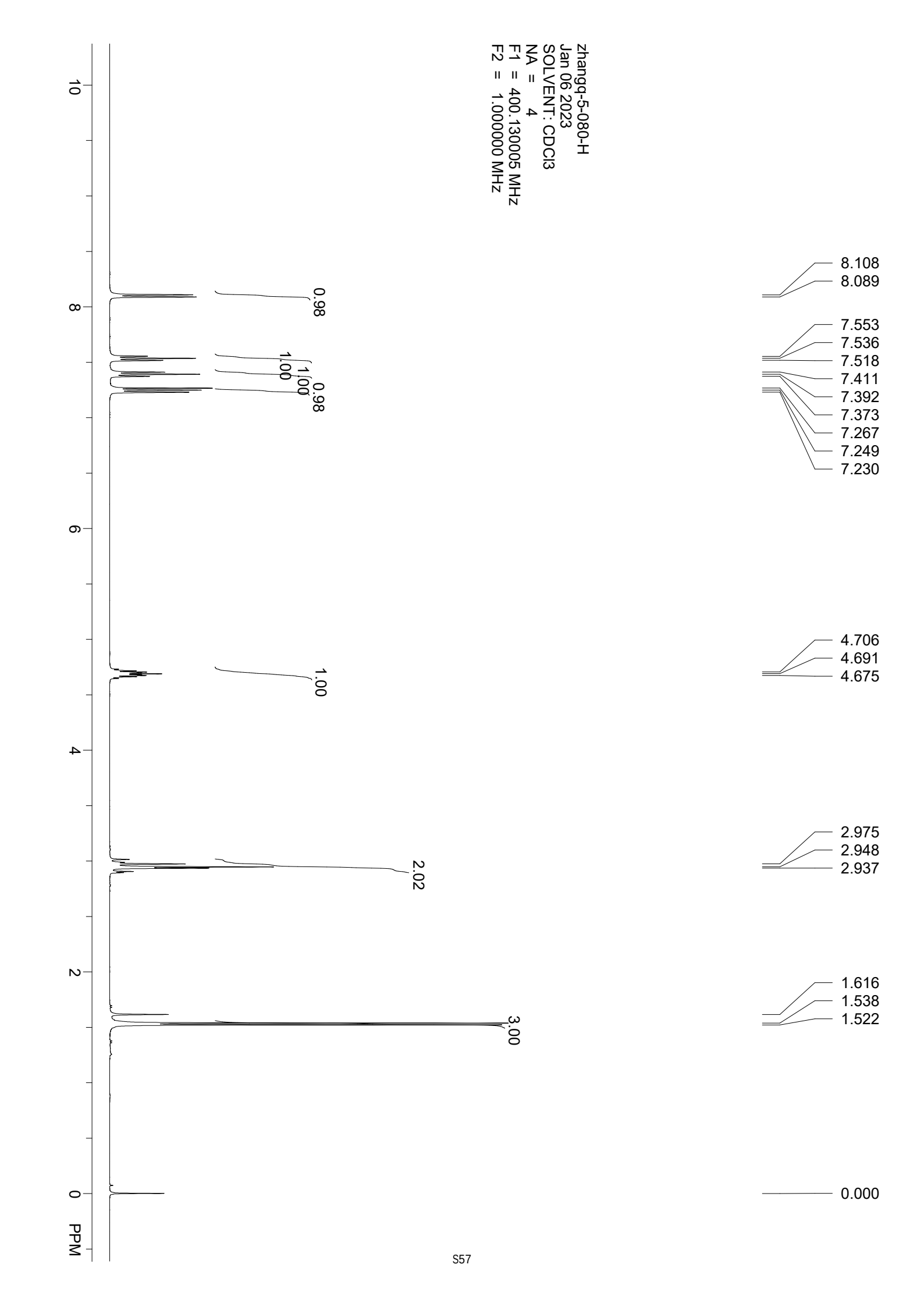

10.494
10.386
7.751
7.739
7.654
7.641
7.264
1.568
-0.000
S
O
O
3k
zhangq-5-033-1-H
Mar 21 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
1.00
0.99
1.00
1.00
S52
12
10
8
6
4
2
0
PPM

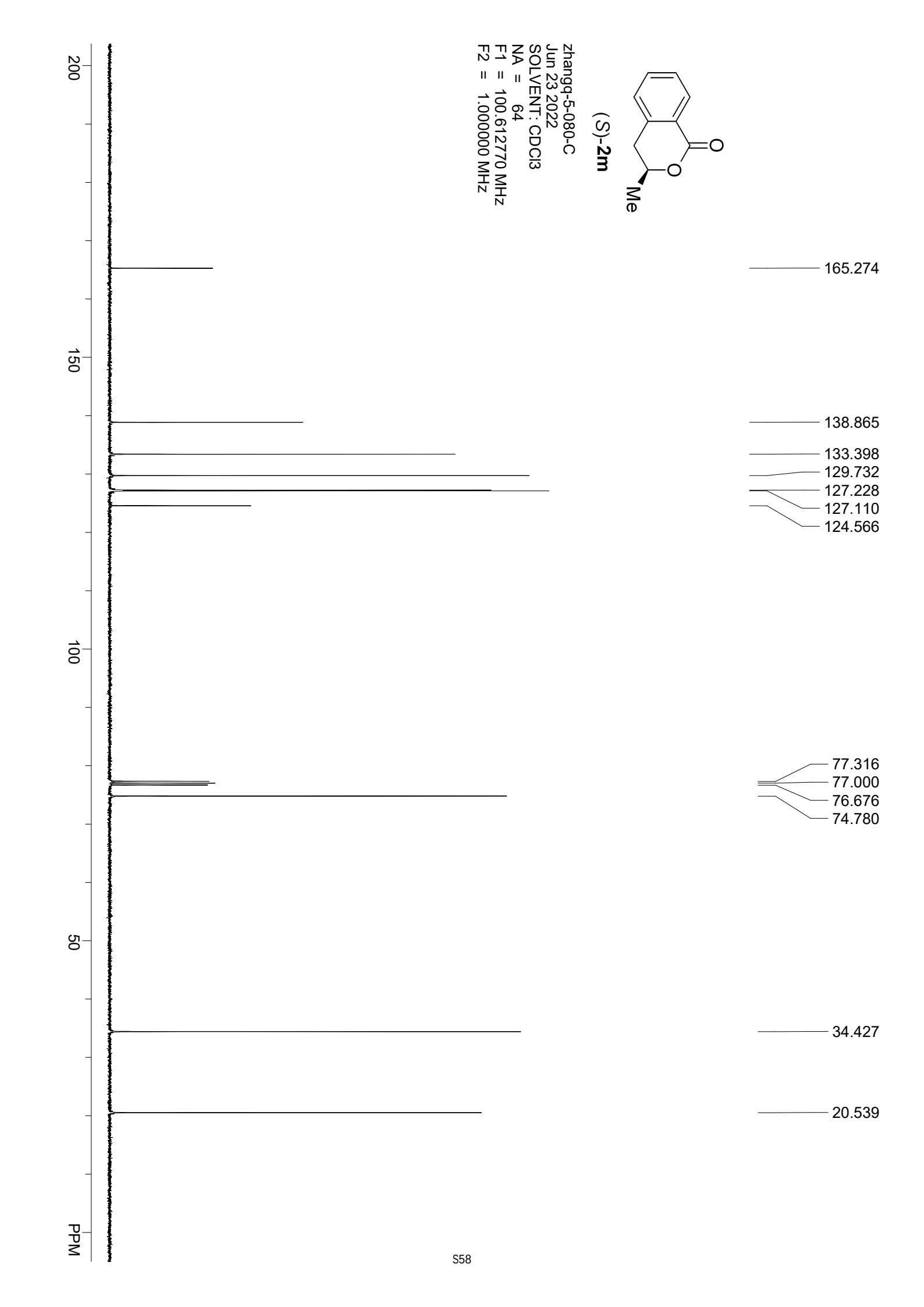

8.112
8.092
7.599
7.597
7.581
7.578
7.562
7.559
7.419
7.418
7.399
7.381
7.380
7.316
7.297
7.270
4.539
4.529
4.512
4.502
4.269
4.252
4.241
4.225
3.191
3.181
3.174
3.164
3.157
3.146
1.384
1.366
-0.000
-0.001
O
O
Me
2l
zhangq-4-046-H
Oct 06 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3.02
1.00
1.02
1.02
0.99
1.01
1.02
1.02
S53
8
6
4
2
0
PPM


zhangq-4-046-C
Oct 06 2021
SOLVENT: CDCl3
NA = 200
F1 = 100.612770 MHz
F2 = 1.000000 MHz
2l
Me
O
O
165.093
144.529
133.864
130.436
127.489
125.648
124.353
77.316
77.000
76.676
72.410
31.694
16.628
200
150
100
50
PPM


zhangq-4-047-H
Jan 06 2023
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
8.108
8.089
7.555
7.537
7.518
7.411
7.392
7.373
7.267
7.250
7.231
4.717
4.706
4.691
4.675
2.975
2.948
2.937
1.538
1.522
-0.000
0.99
1.00
1.00
0.98
1.00
2.02
3.00
10
8
6
4
2
0
PPM


165.598
139.086
133.651
130.270
127.623
127.276
125.000
77.316
77.000
76.684
75.049
34.869
20.886
O
O
Me
2m
zhangq-4-047-C
Oct 06 2021
SOLVENT: CDCl3
NA = 200
F1 = 100.612770 MHz
F2 = 1.000000 MHz
150
100
50
PPM


zhangq-5-080-H
Jan 06 2023
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
8.108
8.089
7.553
7.536
7.518
7.411
7.392
7.373
7.267
7.249
7.230
4.706
4.691
4.675
2.975
2.948
2.937
1.616
1.538
1.522
0.000
0.98
1.00
1.00
0.98
1.00
2.02
3.00
10
8
6
4
2
0
PPM

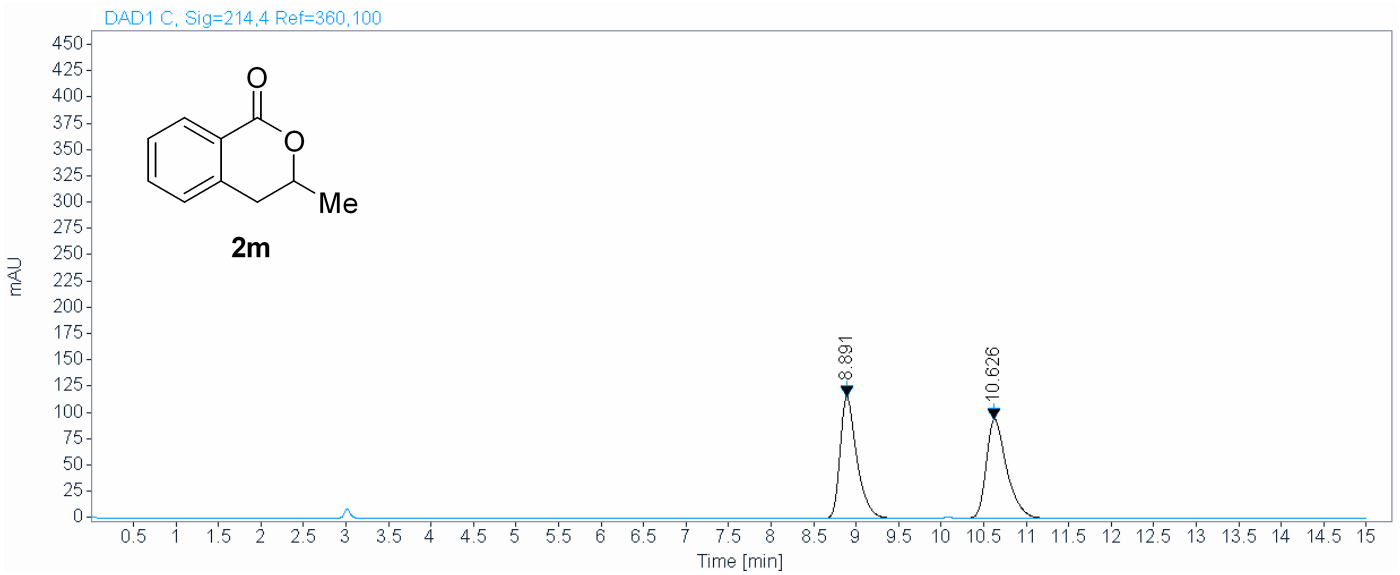

zhangq-5-080-C
Jun 23 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz
(S)-2m
Me
O
O
165.274
138.865
133.398
129.732
127.228
127.110
124.566
77.316
77.000
76.676
74.780
34.427
20.539
200
150
100
50
PPM

Area Percent Report

sample zhangq-4-047-rac-AS-H-80-20-1.0-214

Data file: C:\Users\Public\Documents\ChemStation\1\Data\zhangq 2022-06-23 20-03-33\004-P2-D1-zhangq-4-047-rac.D

Acquisition Data:



Signal: DAD1 C, Sig=214,4 Ref=360,100

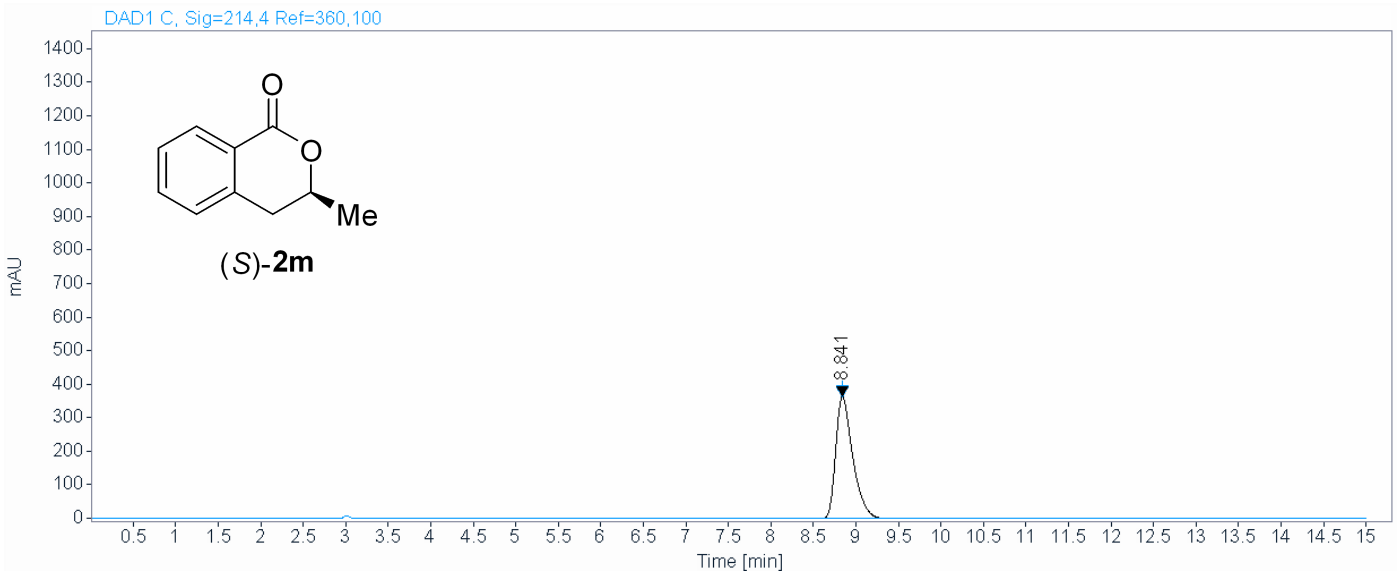
RT [min]	Width [min]	Height	Area	Area%
8.891	0.2058	115.9376	1588.4351	50.3251
10.626	0.2503	94.1655	1567.9149	49.6749
		Sum	3156.3500	100.0000

Area Percent Report

sample zhangq-5-080-AS-H-80-20-1.0-214

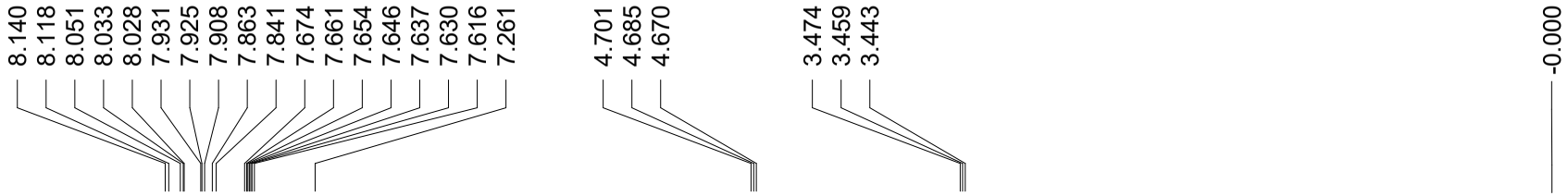
Data file: C:\Users\Public\Documents\ChemStation\1\Data\zhangq 2022-06-23 20-03-33\003-P2-D2-zhangq-5-080.D

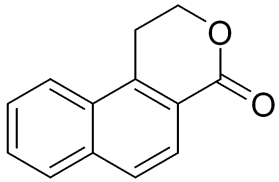
Acquisition Data:



Signal: DAD1 C, Sig=214,4 Ref=360,100

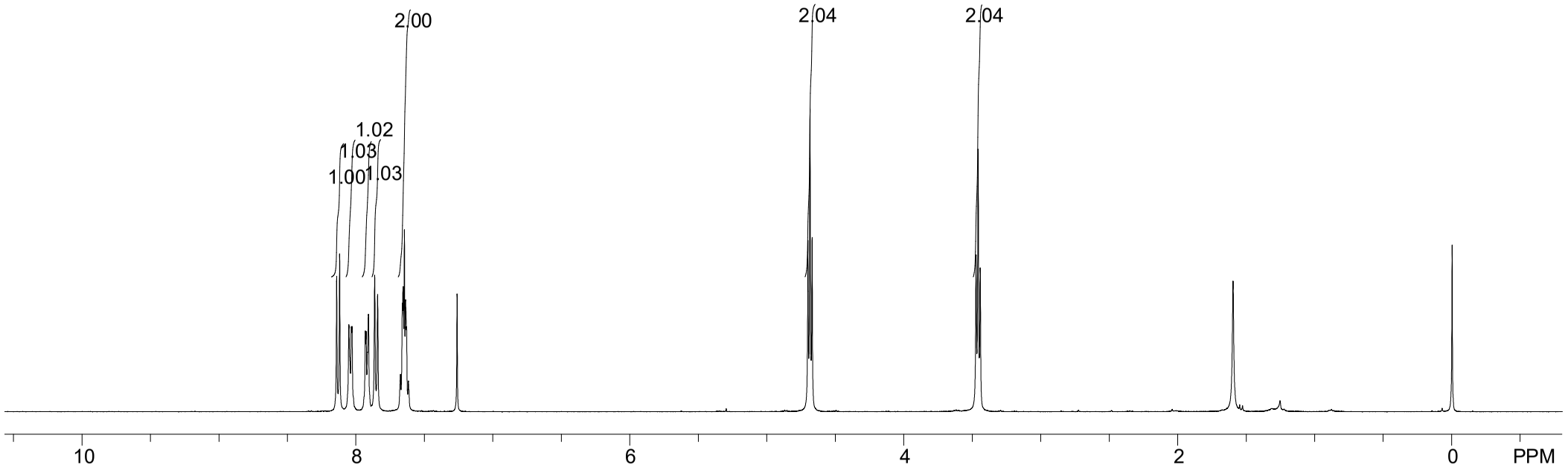
RT [min]	Width [min]	Height	Area	Area%
8.841	0.2113	364.2062	5096.8960	100.0000
		Sum	5096.8960	100.0000

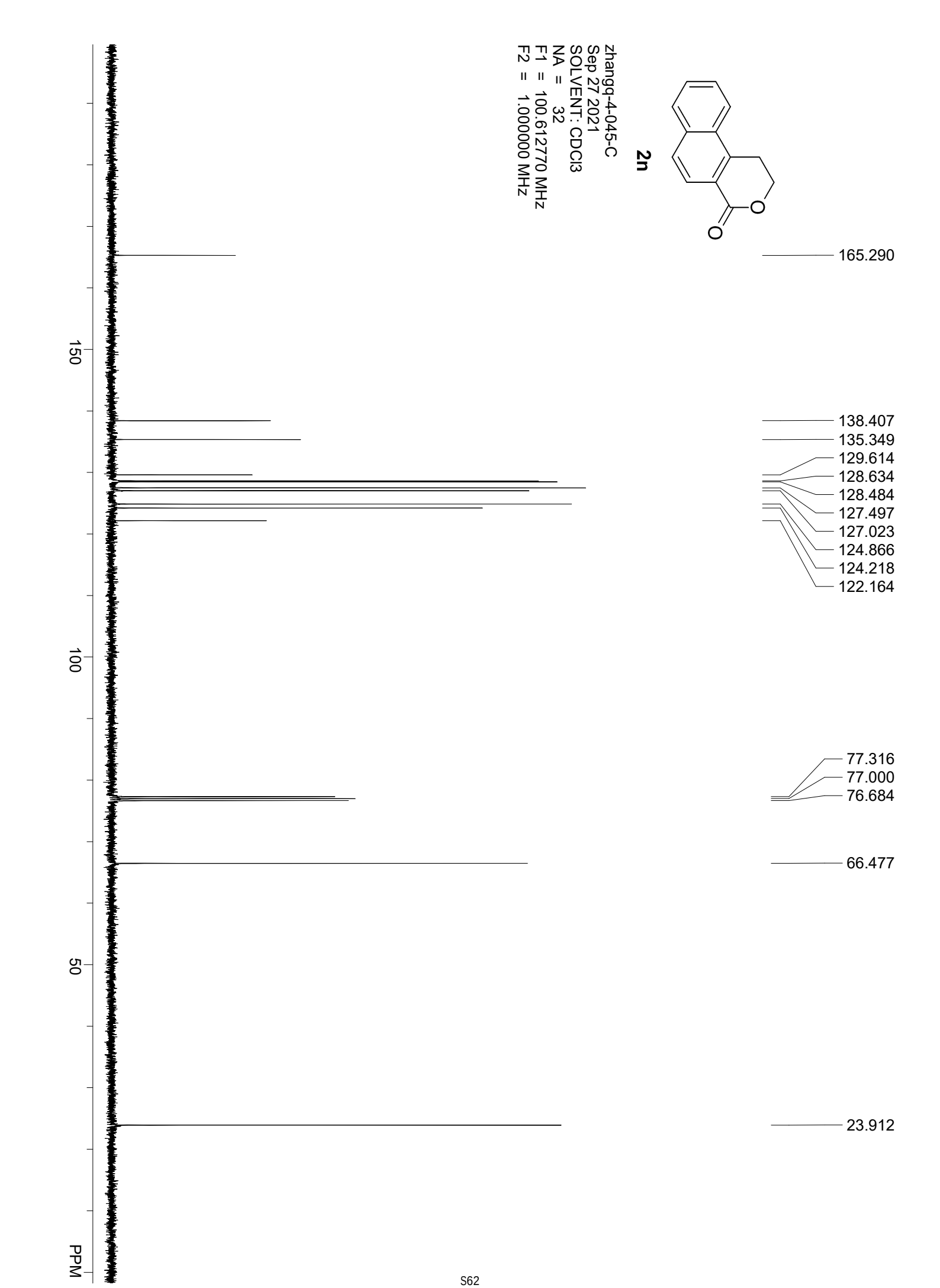


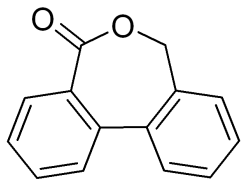


2n

zhangq-4-045-H
Sep 27 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz

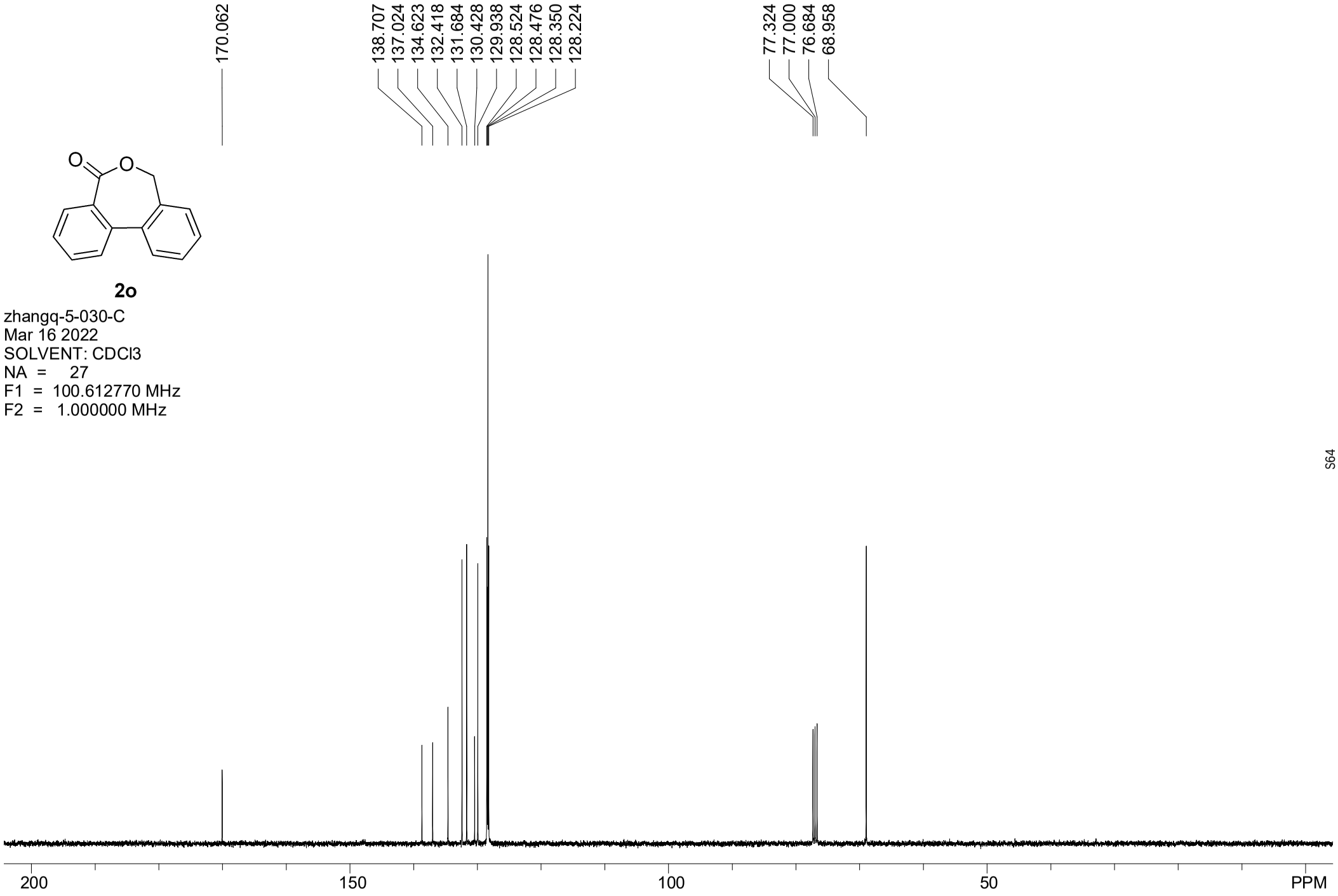


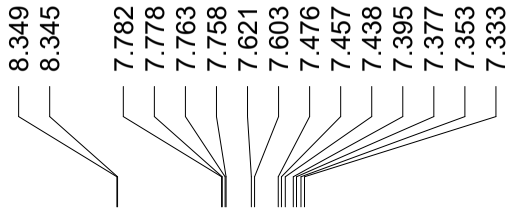

zhangq-4-045-C
Sep 27 2021
SOLVENT: CDCl3
NA = 32
F1 = 100.612770 MHz
F2 = 1.000000 MHz
2n
O
O
165.290
138.407
135.349
129.614
128.634
128.484
127.497
127.023
124.866
124.218
122.164
77.316
77.000
76.684
66.477
23.912
150
100
50
PPM

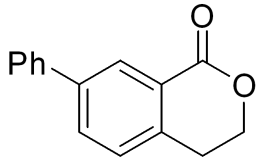


2o

zhangq-5-030-H
Mar 17 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz

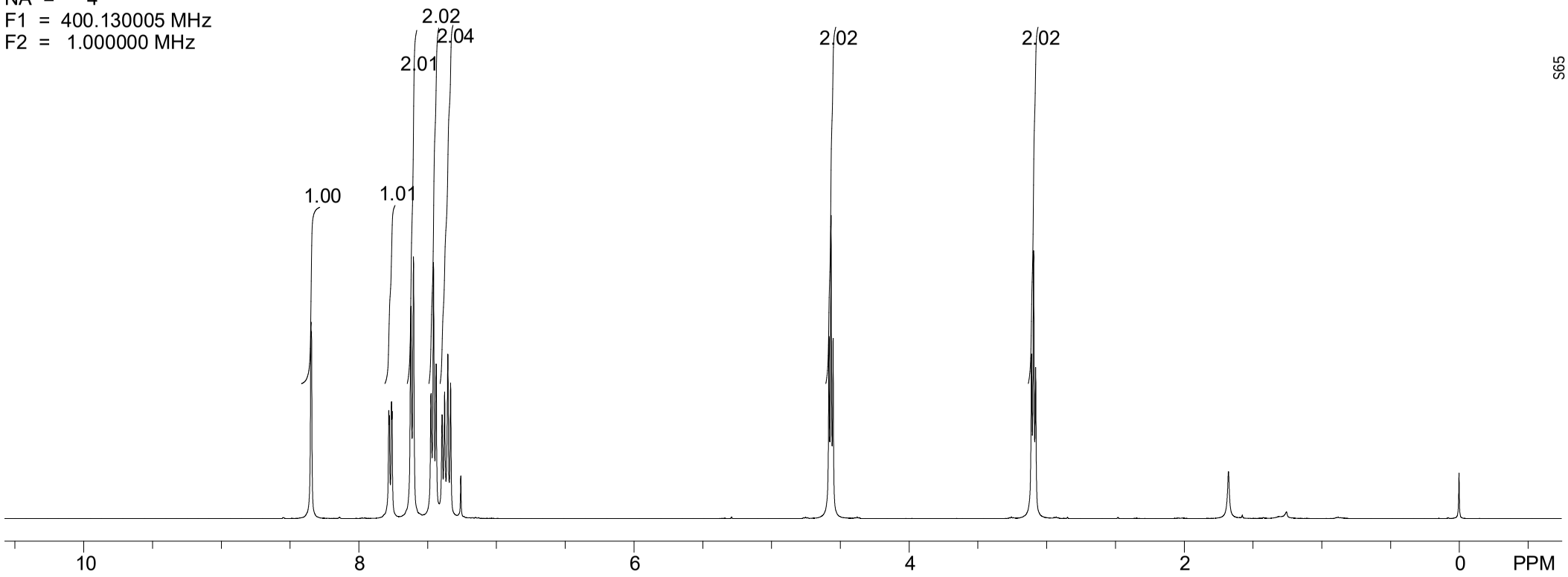

170.062
138.707
137.024
134.623
132.418
131.684
130.428
129.938
128.524
128.476
128.350
128.224
77.324
77.000
76.684
68.958
O
O
2o
zhangq-5-030-C
Mar 16 2022
SOLVENT: CDCl3
NA = 27
F1 = 100.612770 MHz
F2 = 1.000000 MHz
200
150
100
50
PPM

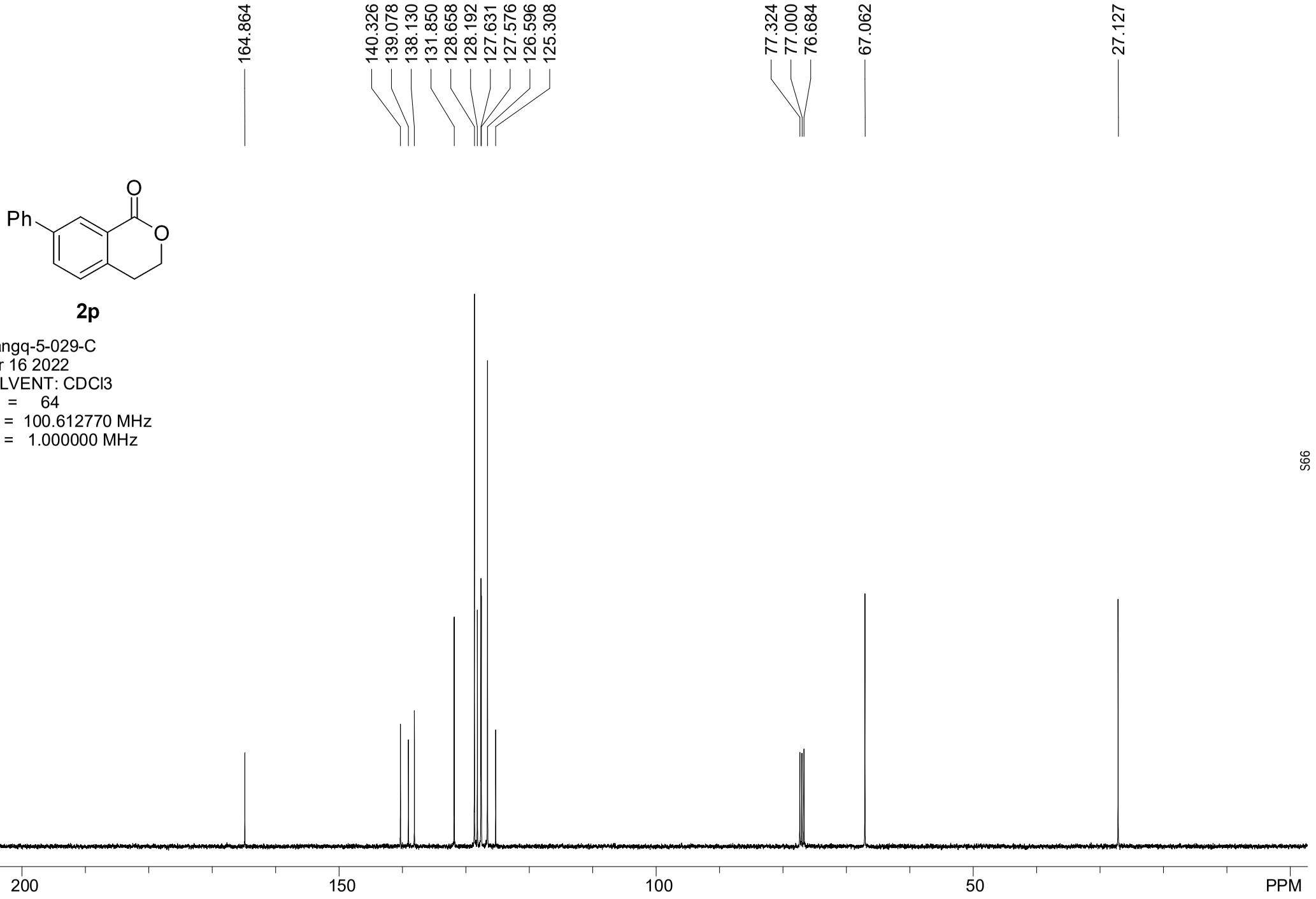


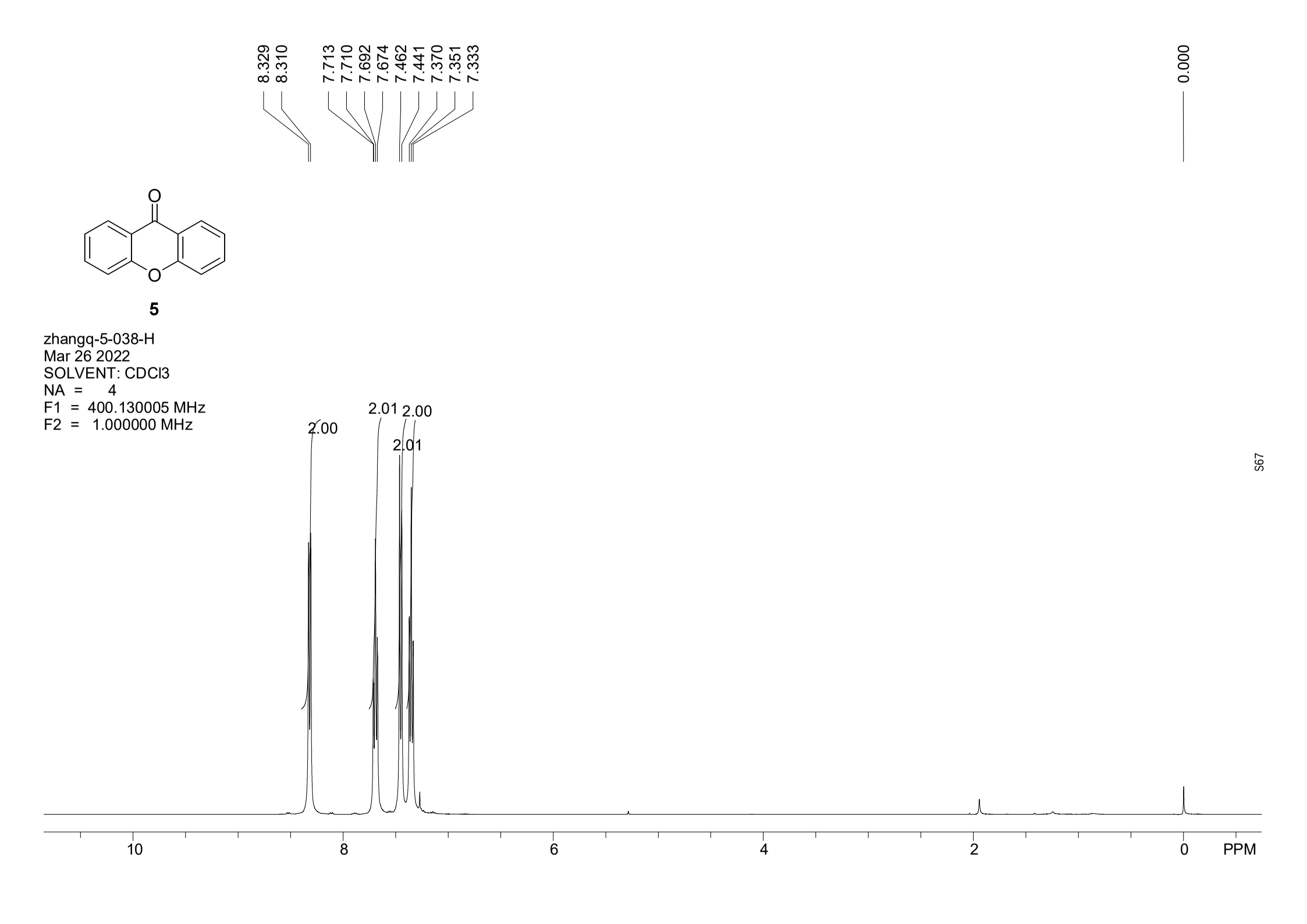


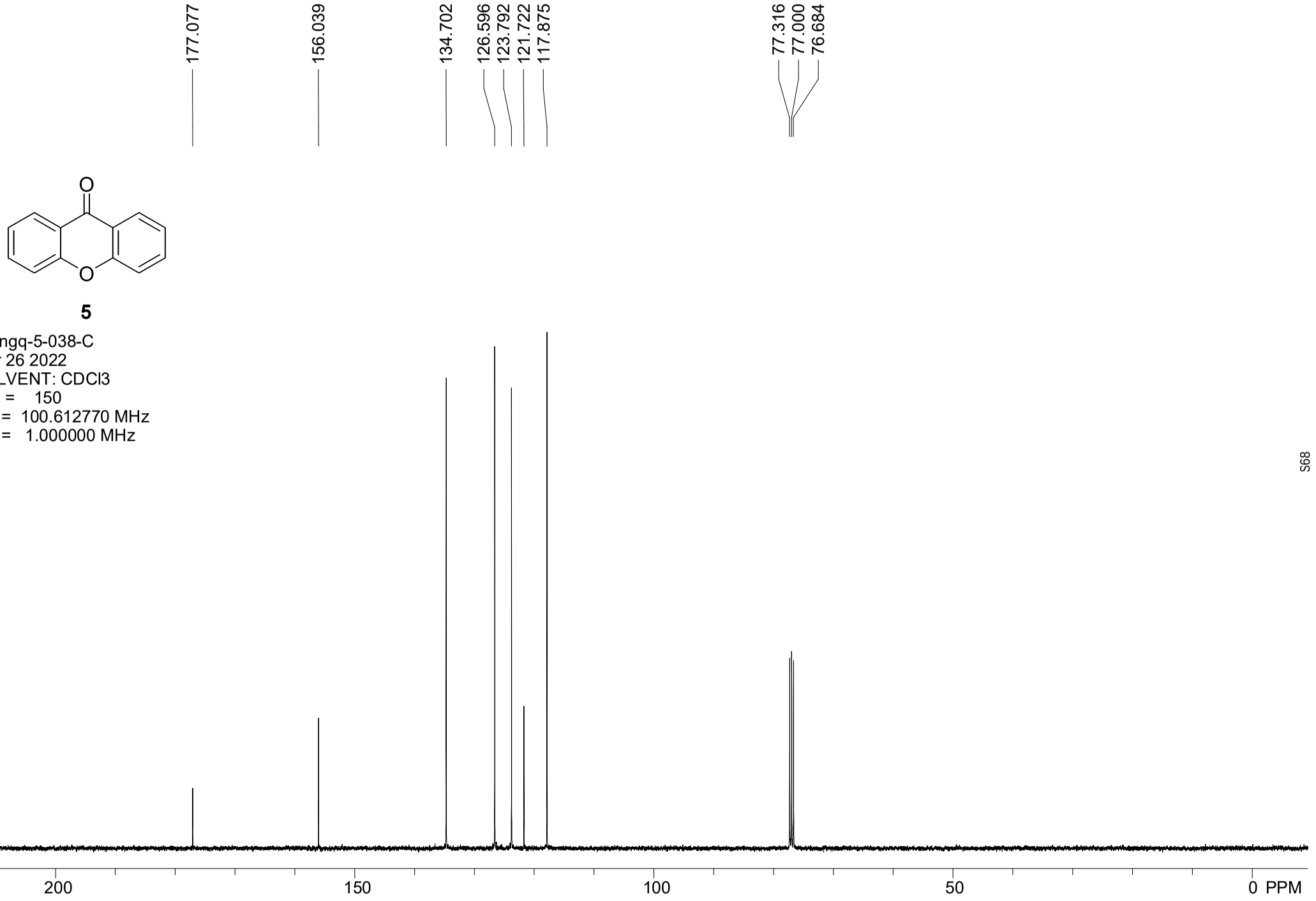
2p

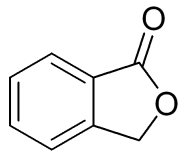
zhangq-5-029-H
Mar 16 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz




164.864
140.326
139.078
138.130
131.850
128.658
128.192
127.631
127.576
126.596
125.308
77.324
77.000
76.684
67.062
27.127
O
Ph
O
2p
zhangq-5-029-C
Mar 16 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz
S66
200
150
100
50
PPM

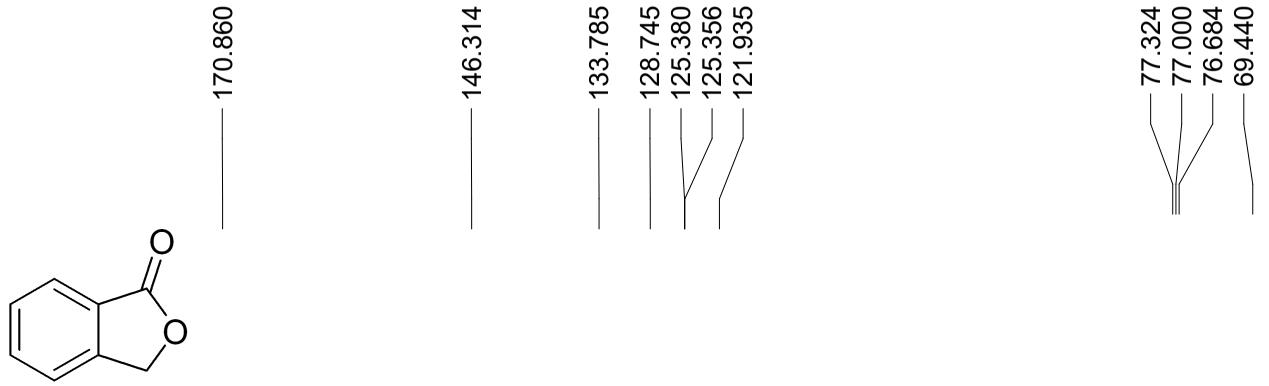

8.329
8.310
7.713
7.710
7.692
7.674
7.462
7.441
7.370
7.351
7.333
0.000
O
O
5
zhangq-5-038-H
Mar 26 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
2.00
2.01
2.01
2.00
10
8
6
4
2
0
PPM


177.077
156.039
134.702
126.596
123.792
121.722
117.875
77.316
77.000
76.684
O
O
5
zhangq-5-038-C
Mar 26 2022
SOLVENT: CDCl3
NA = 150
F1 = 100.612770 MHz
F2 = 1.000000 MHz
200
150
100
50
0 PPM



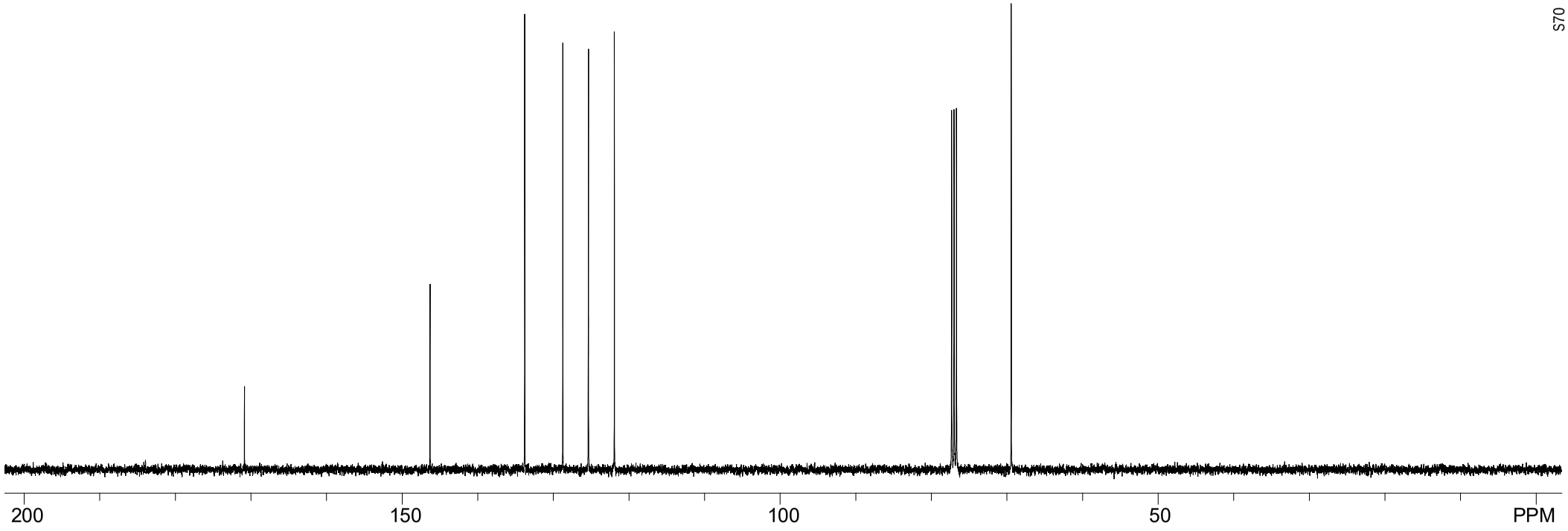
2q

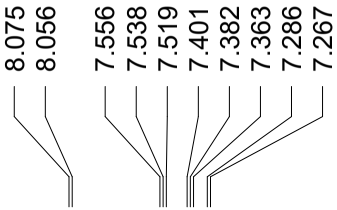
zhangq-3-150-H
Jun 12 2021
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz

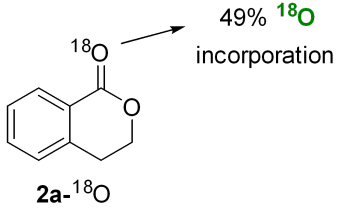


2q

zhangq-3-150-C
Jun 12 021
SOLVENT: CDCl3
NA = 32
F1 = 100.612770 MHz
F2 = 1.000000 MHz

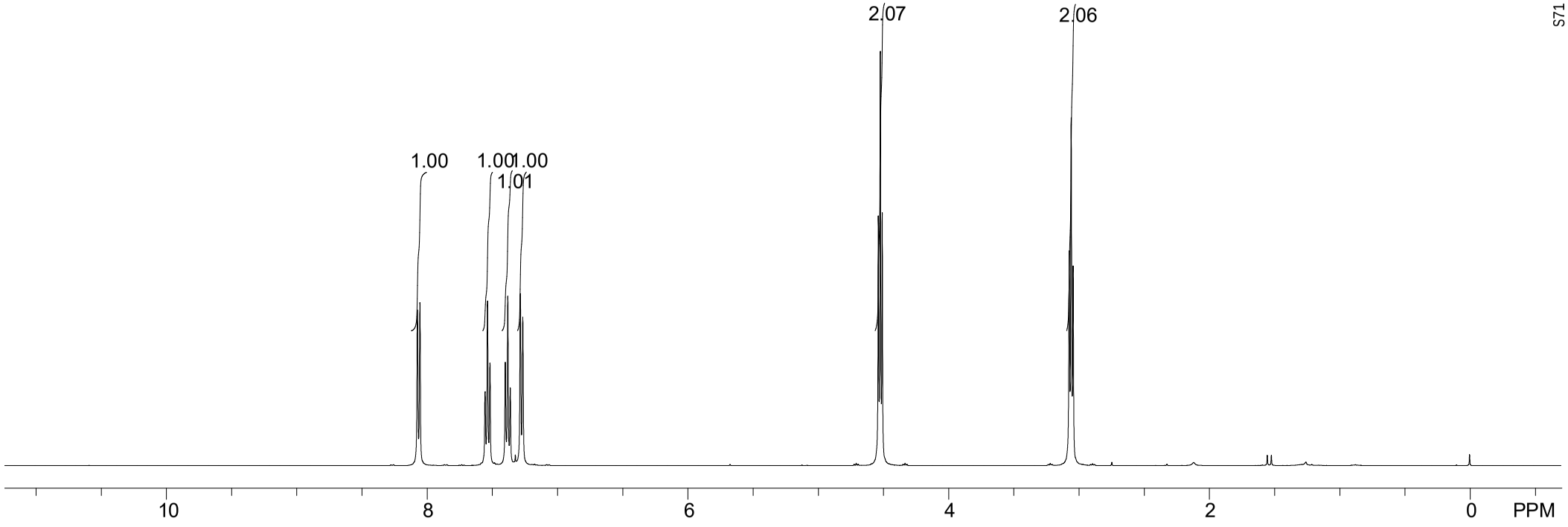


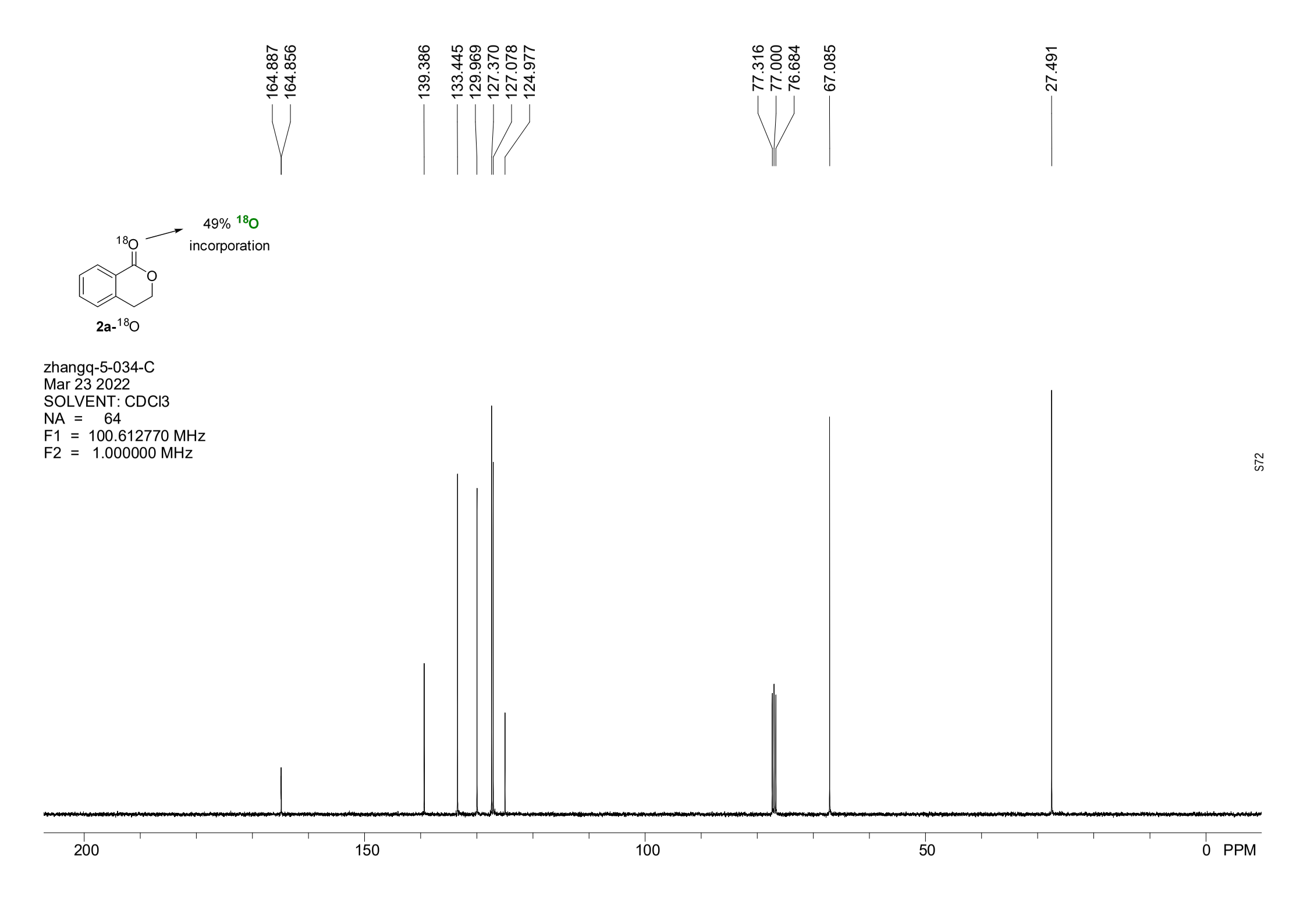




2a-^{18}O

zhangq-5-034-H
Mar 23 2022
SOLVENT: CDCl3
NA = 4
F1 = 400.129974 MHz
F2 = 1.000000 MHz




164.887
164.856
139.386
133.445
129.969
127.370
127.078
124.977
77.316
77.000
76.684
67.085
27.491
49% 18O
incorporation
18O
O
2a-18O
zhangq-5-034-C
Mar 23 2022
SOLVENT: CDCl3
NA = 64
F1 = 100.612770 MHz
F2 = 1.000000 MHz
S72
200
150
100
50
0 PPM