Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Mechanistic studies on $Cu(NO_3)_2$/TEMPO-catalyzed aerobic oxidation of alcohols to carboxylic acids

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Supplementary Information

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General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Flue gas analysis experiments were performed with a Testo 350 flue gas analyzer. All reactions were carried out in 25 mL Schlenk tubes unless otherwise mentioned. $Cu(NO_3)_2 \cdot 3H_2O$ and $KHSO_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd; TEMPO (98%) was purchased from Shanghai Darui Fine Chemical Co., Ltd.; $H_2{}^{18}O$ (97% ^{18}O) was purchased from Meryer Co., Ltd.; DCE and Et_2O were used directly without further treatment unless otherwise noted. Anhydrous DCM and MeCN were used. Recovery of substrates was determined by ^{1}H NMR analysis using dibromomethane as the internal standard.

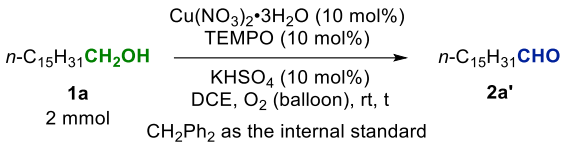
SAESI-MS spectra were recorded on a Thermo TSQ Quantum Access triple-quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) equipped with a home-made SAESI ion source in positive mode. The basic SAESI conditions were: vacuum, 2.6×10^{-6} torr; spray voltage, 3000 V; capillary temperature, 275 ^{o}C; sheath gas pressure of two sprayers, 3 arb. units; the collision energy of CID, 20 eV. Data acquisition and analysis were done with the Xcalibur (version 2.0, Thermo Fisher Scientific) software package. In this solvent-assisted electrospray ionization mass spectrometric experiment, the angle (a) between the two sprayers is 50^{o} and the distance (b) between the tip of sprayers and the inlet to the mass is 5 mm. The chemical solutions were injected by a 500-μL air-tight syringe with a speed at 20 μL/min to SAESI-MS. The assisted solvent of acetonitrile was injected by another 500-μL air-tight syringe with a speed at 5 μL/min.

Mechanistic studies

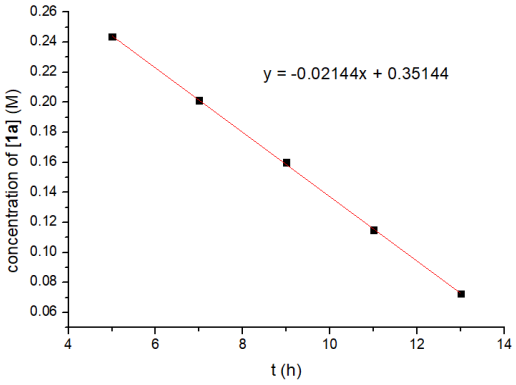
(1) Determination of the order for alcohol 1a (yyb-6-010).

A Schlenk tube was degassed to remove the air inside completely and refilled with O_2 with an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (48.0 mg, 0.2 mmol), TEMPO (31.8 mg, 0.2 mmol), $KHSO_4$ (27.1 mg, 0.2 mmol), **1a** (484.3 mg, 2.0 mmol), CH_2Ph_2 (internal standard, 168.0 μL, d = 1.066 g/mL, 1.0 mmol), and DCE (8.0 mL) were added sequentially. An aliquot of the resulting mixture (about 0.1 mL) was taken after each indicated time shown in Table S1 and filtrated through a short column of silica gel eluted with DCM (2 x 5 mL). After evaporation, the NMR yield and recovery were determined by ^{1}H NMR analysis.

Table S1. Determination of the order for alcohol **1a**



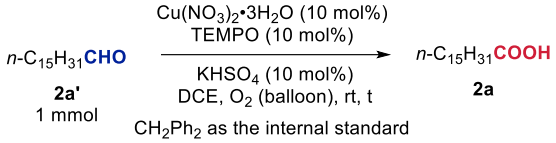
Entry	time (h)	Recovery of **1a** (%)	[**1a**]
1	5	97.5	0.24375
2	7	80.5	0.20125
3	9	64	0.16
4	11	46	0.115
5	13	29	0.0725



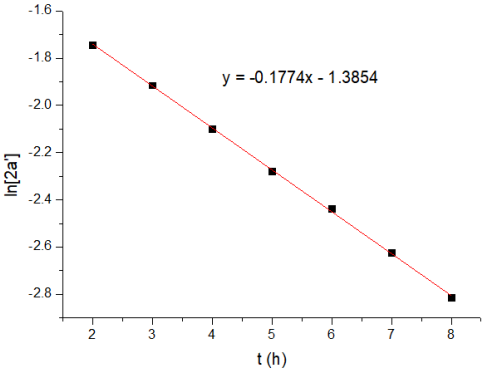
(2) Determination of the order for aldehyde 2a' (yyb-6-049).

A Schlenk tube was degassed to remove the air inside completely and refilled with O_2 with an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (24.8 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), $KHSO_4$ (13.7 mg, 0.1 mmol), **2a'** (240.4 mg, 1.0 mmol), CH_2Ph_2 (internal standard, 84.0 μL, d = 1.066 g/mL, 0.5 mmol), H_2O (0.1 mL), and DCE (4.0 mL) were added sequentially. An aliquot of the resulting mixture (about 0.1 mL) was taken after each indicated time shown in Table S2 and filtrated through a short column of silica gel eluted with DCM (2 x 5 mL). After evaporation, the NMR yield and recovery were determined by ^{1}H NMR analysis.

Table S2. Determination of the order for aldehyde **2a'**

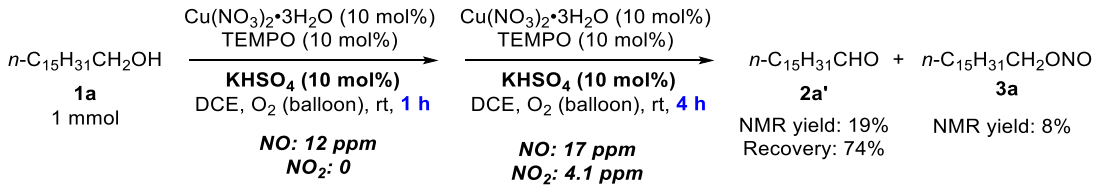


Entry	time (h)	Recovery of **2a'** (%)	[**2a'**] (M)	ln[**2a'**]
1	2	70	0.175	-1.74297
2	3	59	0.1475	-1.91393
3	4	49	0.1225	-2.09964
4	5	41	0.1025	-2.27789
5	6	35	0.0875	-2.43612
6	7	29	0.0725	-2.62417
7	8	24	0.06	-2.81341



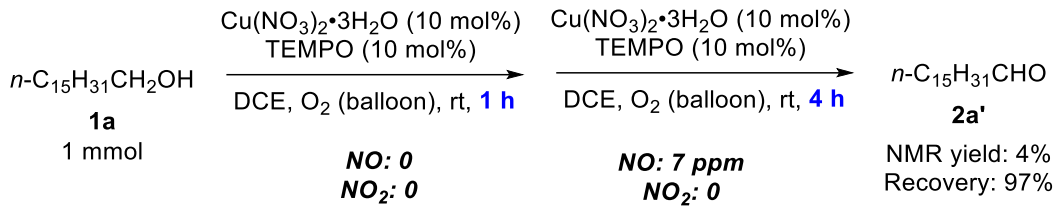
(3) Detection of NO_x

1) Detection of NO_x under standard conditions (yyb-6-130A)



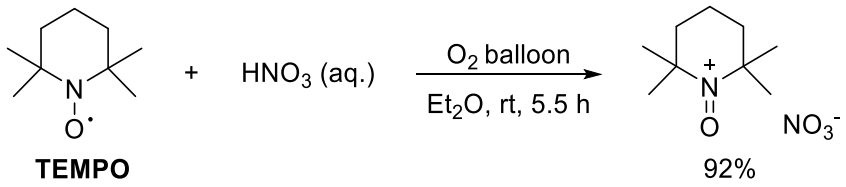
A Schlenk tube was degassed to remove the air inside and refilled with O_2 with an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (24.3 mg, 0.1 mmol), TEMPO (16.2 mg, 0.1 mmol), $KHSO_4$ (13.8 mg, 0.1 mmol), **1a** (242.8 mg, 1.0 mmol), and DCE (4.0 mL) were added sequentially. The Schlenk tube was then stirred at rt. After 1 h and 4 h, NO_x was detected by the flue gas analyzer, respectively. The resulting mixture was filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL) after 4 h. After evaporation, 35.0 μL of dibromomethane was added as the internal standard for ^{1}H NMR analysis: 19% of aldehyde **2a'** and 8% of nitrite **3a** were detected with 74% of alcohol **1a** recovered.

2) Detection of NO_x under standard conditions without addition of $KHSO_4$ (yyb-6-130B)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 with an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (24.1 mg, 0.1 mmol), TEMPO (16.3 mg, 0.1 mmol), **1a** (242.5 mg, 1.0 mmol), and DCE (4.0 mL) were added sequentially. The Schlenk tube was then stirred at rt. After 1 h and 4 h, NO_x was detected by the flue gas analyzer, respectively. The resulting mixture was filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL) after 4 h. After evaporation, 35.0 μL of dibromomethane was added as the internal standard for ^{1}H NMR analysis: 4% of aldehyde **2a'** was detected with 97% of alcohol **1a** recovered.

(4) Preparation of $TEMPO^+NO_3^-$ (yyb-4-106)



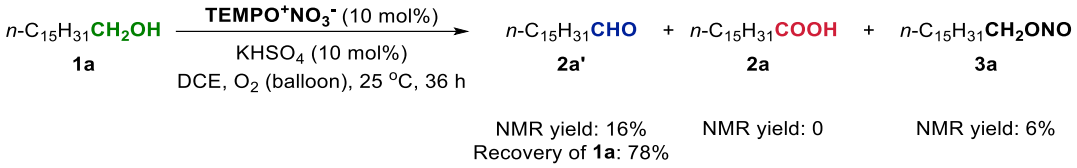
To a flask was added **TEMPO** (637.4 mg, 4.0 mmol) and the flask was degassed and refilled with argon for three times. After the addition of Et_2O (60 mL) and conc. HNO_3 (67% aqueous solution, 564.0 mg, 6 mmol), the solution was stirred for 5.5 h under O_2 atmosphere until completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1) and turned colorless. The yellow precipitate was filtered, washed with Et_2O (100 mL), and dried in vacuo to afford **$TEMPO^+NO_3^-$** (801.1 mg, 92%) as bright yellow solid.[1]

$TEMPO^+NO_3^-$: m.p. 118.6-120.3 °C (decomposition, diethyl ether/dichloromethane) (reported:[1b] m.p. 110-120 °C (decomposition)); **IR** (neat, cm^{-1}): 1621, 1471, 1396, 1379, 1320; **MS** (ESI) *m/z*: 156 $(M\text{-}NO_3^-)^+$; **HRMS** calcd *m/z* for $C_9H_{18}NO$ $[M\text{-}NO_3^-]^+$:

156.1383, found 156.1381. **Anal. Calcd.** For $C_9H_{18}N_2O_4$: C 49.53, H 8.31; found C 48.96, H 8.63.

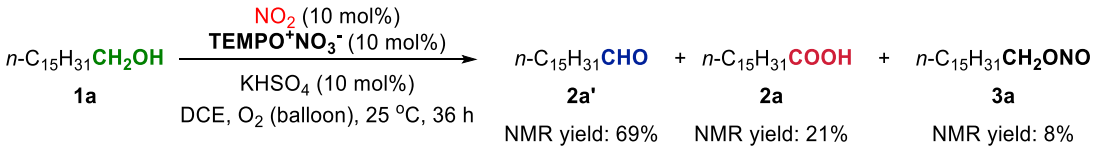
(5) Aerobic oxidation of alcohol 1a with $TEMPO^+NO_3^-$ as catalyst

1) $TEMPO^+NO_3^-$ as catalyst without the assistance of NO_2 (yyb-8-053B)



A Schlenk tube was degassed to remove the air inside completely and refilled with O_2 with an O_2 balloon for three times. Then **$TEMPO^+NO_3^-$** (21.8 mg, 0.1 mmol), $KHSO_4$ (13.5 mg, 0.1 mmol), **1a** (242.8 mg, 1.0 mmol), and DCE (4.0 mL) were added sequentially. The resulting mixture was then stirred at 25 ℃ for 36 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, 35.0 μL of dibromomethane was added as the internal standard for ^1H NMR analysis: 16% of aldehyde **2a'** and 6% of nitrite **3a** were detected with 78% of alcohol **1a** recovered.

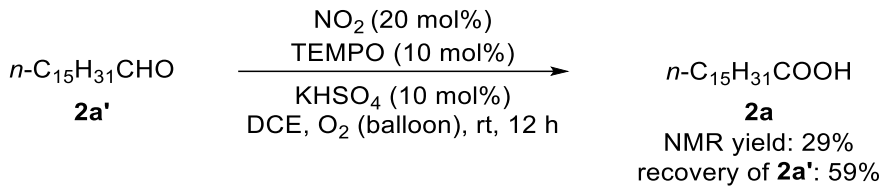
2) $TEMPO^+NO_3^-$ as catalyst with the assistance of NO_2 (yyb-8-055B)



To an oven-dried Schlenk tube were added **$TEMPO^+NO_3^-$** (21.9 mg, 0.1 mmol), $KHSO_4$ (13.9 mg, 0.1 mmol), and **1a** (242.3 mg, 1.0 mmol). Then the tube was degassed to remove the air inside followed by the injection of NO_2 (2.4 mL, 0.1 mmol) with a syringe and refilled O_2 using an O_2 balloon followed by the addition of DCE (4.0 mL). The resulting mixture was then stirred at 25 ℃ for 36 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, 35.0 μL of dibromomethane was added as the standard for ^1H NMR analysis: 69% of aldehyde **2a'**, 21% of carboxylic acid **2a** and 8% of nitrite **3a** were detected.

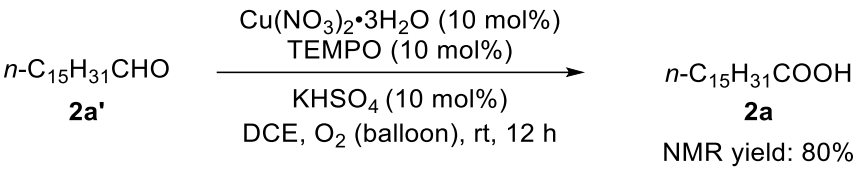
(6) Aerobic oxidation of aldehyde 2a' to carboxylic acid 2a

1) Aerobic oxidation of aldehyde 2a' via TEMPO/NO_2 system (yyb-8-057B)



To an oven-dried Schlenk tube were added TEMPO (8.0 mg, 0.05 mmol), $KHSO_4$ (6.7 mg, 0.05 mmol), and **2a'** (120.6 mg, 0.5 mmol). Then the tube was degassed to remove the air inside followed by the injection of NO_2 (2.4 mL, 0.1 mmol) with a syringe and refilled O_2 using an O_2 balloon. DCE (2.0 mL) was added. The resulting mixture was stirred at rt for 12 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, 35.0 μL of dibromomethane was added as the internal standard for ^{1}H NMR analysis: 29% of carboxylic acid **2a** was detected with 59% of aldehyde **2a'** recovered.

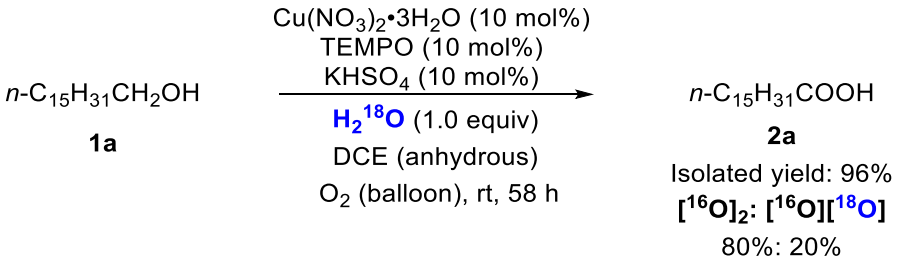
2) Aerobic oxidation of aldehyde 2a' under standard conditions (yyb-6-051A)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 with an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (12.0 mg, 0.05 mmol), TEMPO (7.9 mg, 0.05 mmol), $KHSO_4$ (6.9 mg, 0.05 mmol), **2a'** (119.8 mg, 0.5 mmol), and DCE (2.0 mL) were added sequentially. The resulting mixture was stirred at rt for 12 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, 35.0 μL of dibromomethane was added as the internal standard for ^{1}H NMR analysis: 80% of carboxylic acid **2a** was detected.

(7) ^{18}O labelling experiments of alcohol 1a

1) ^{18}O labelling experiment with 1 equiv of $H_2{}^{18}O$ (yyb-5-162)

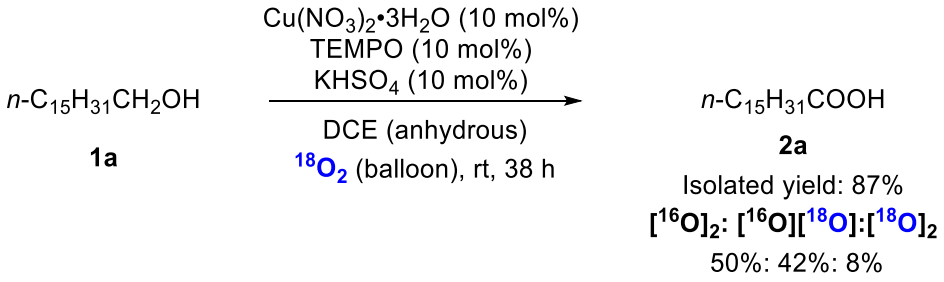


Typical Procedure I: A Schlenk tube was degassed to remove the air inside, and refilled with O_2 using an O_2 balloon for three times. Then $Cu(NO_3)_2$•$3H_2O$ (24.7 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), $KHSO_4$ (13.9 mg, 0.1 mmol), **1a** (241.7 mg, 1.0 mmol), $H_2{}^{18}O$ (18.0 μL, 20.0 mg, d = 1.11 g/mL, 1.0 mmol), and anhydrous DCE (4.0 mL) were added sequentially. The resulting mixture was stirred at room temperature until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1) (36 h) and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a** (245.9 mg, 96%) [eluent: petroleum ether/ethyl acetate = 20/1 (~210 mL) to 5/1 (~240 mL)] as white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.34 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.70-1.57 (m, 2 H, CH_2), 1.42-1.17 (m, 24 H, 12 x CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 180.4, 34.1, 31.9, 29.68, 29.66, 29.58, 29.43, 29.36, 29.2, 29.1, 24.7, 22.7, 14.1; **MS** (70 eV, EI) *m*/*z* (%): 258 (M (^{16}O) (^{18}O)$^+$, 19.24), 256 (M (^{16}O)$_2^+$, 76.7), 73 (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 $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O)$_2$] ($C_{16}H_{32}{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O)$_2$ 256 [M (^{16}O)$_2$] and **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] are 76.7 and 19.24, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample

according to the MS spectrum of **2a**, the ^{18}O incorporation of **2a** 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)$_2$]$^+$) = (19.24 – 76.7 ×0.2%)/(19.24 - 76.7 ×0.2% + 76.7) = 20%.

2) ^{18}O labelling experiment with $^{18}O_2$ (yyb-5-178)



Following **Typical Procedure I**, the reaction of **1a** (121.9 mg, 0.5 mmol), $Cu(NO_3)_2$•$3H_2O$ (12.5 mg, 0.05 mmol), TEMPO (8.2 mg, 0.05 mmol), and $KHSO_4$ (7.0 mg, 0.05 mmol) in anhydrous DCE (2.0 mL) afforded **2a** (113.2 mg, 87%) [eluent: petroleum ether/ethyl acetate = 15/1 (~320 mL) to 5/1 (~240 mL)] as white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.35 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.63 (quintet, *J* = 7.2 Hz, 2 H, CH_2), 1.37-1.14 (m, 24 H, 12 x CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 179.9, 34.0, 31.9, 29.7, 29.64, 29.62, 29.58, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 14.1; **MS** (70 eV, EI) *m*/*z* (%): 260 (M (^{18}O)$_2^+$, 17.3), 258 (M (^{16}O) (^{18}O)$^+$, 85.23), 256 (M (^{16}O)$_2^+$, 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 $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O)$_2$] ($C_{16}H_{32}{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O)$_2$ 256 [M (^{16}O)$_2$] and **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] are 100 and 85.23, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{16}O) (^{18}O) in **2a**-(^{16}O) (^{18}O) and **2a**-(^{16}O)$_2$ can be calculated as follows: ([M (^{16}O) (^{18}O)]$^+$ - [M (^{16}O)$_2$]$^+$ ×0.2%)/([M (^{16}O)

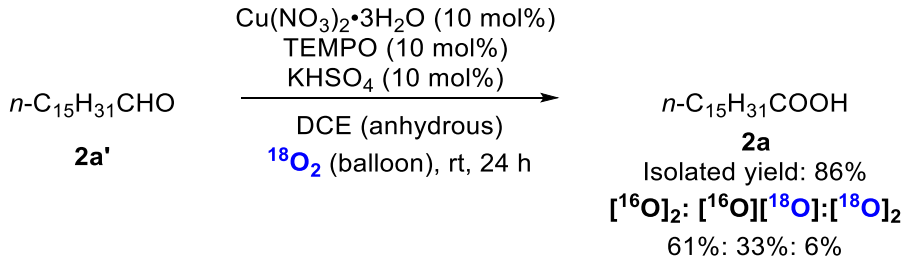
(^{18}O)]$^+$ - [M (^{16}O)$_2$]$^+$ ×0.2% + [M (^{16}O)$_2$]$^+$) = (85.23 – 100 ×0.2%)/(85.23 - 100 ×0.2% + 100) = 46%.

Besides, the ratio of $C_{16}H_{32}{}^{16}O{}^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is also 99.76:0.2. Thus, the intensity of [M (^{18}O)$_2$] ($C_{16}H_{32}{}^{18}O_2$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O{}^{18}O$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] and **2a**-(^{18}O)$_2$ 260 [M (^{18}O)$_2$] are 85.23 and 17.3, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{18}O)$_2$ in **2a**-(^{16}O) (^{18}O) and **2a**-(^{18}O)$_2$can be calculated as follows: ([M (^{18}O)$_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ ×0.2%)/([M (^{18}O)$_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ × 0.2% + [M (^{16}O) (^{18}O)]$^+$) = (17.3 – 85.23 × 0.2%)/(17.3 – 85.23 × 0.2% + 85.23) = 17%. Based on these results, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O{}^{18}O$ is 54%:46%, and the ratio of $C_{16}H_{32}{}^{16}O{}^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 83%:17%.

To sum up, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O{}^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 54%:46%:(17×46/83)% = 50%:42%:8% (based on 100%).

(8) ^{18}O labelling experiments of aldehyde 2a'

1) ^{18}O labelling experiment with $^{18}O_2$ (yyb-8-047)



Following **Typical Procedure I**, the reaction of **2a'** (120.3 mg, 0.5 mmol), $Cu(NO_3)_2$•$3H_2O$ (12.5 mg, 0.05 mmol), TEMPO (8.1 mg, 0.05 mmol), and $KHSO_4$ (6.6 mg, 0.05 mmol) in anhydrous DCE (2.0 mL) afforded **2a** (110.6 mg, 86%) [eluent: petroleum ether/ethyl acetate = 15/1 (~160 mL) to 5/1 (~180 mL)] as white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.35 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.63 (quintet, *J* = 7.3 Hz, 2 H, CH_2), 1.38-1.19 (m, 24 H, 12 x CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 180.2, 34.0, 31.9, 29.67, 29.66, 29.64, 29.62, 29.58, 29.4, 29.3,

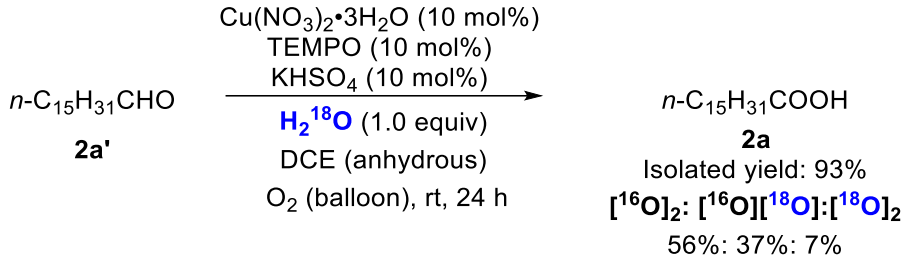
29.2, 29.0, 24.7, 22.7, 14.1; **MS** (70 eV, EI) *m*/*z* (%): 260 (M $(^{18}O)_2^+$, 7.58), 258 (M (^{16}O) $(^{18}O)^+$, 39.13), 256 (M $(^{16}O)_2^+$, 71.1).

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 $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M $(^{16}O)_2$] ($C_{16}H_{32}{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-$(^{16}O)_2$ 256 [M $(^{16}O)_2$] and **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] are 71.1 and 39.13, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{16}O) (^{18}O) in **2a**-(^{16}O) (^{18}O) and **2a**-$(^{16}O)_2$ 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 $(^{16}O)_2]^+$) = (39.13 – 71.1 × 0.2%)/(39.13 – 71.1 × 0.2% + 71.1) = 35%.

Besides, the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is also 99.76:0.2. Thus, the intensity of [M $(^{18}O)_2$] ($C_{16}H_{32}{}^{18}O_2$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] and **2a**-$(^{18}O)_2$ 260 [M $(^{18}O)_2$] are 39.13 and 7.58, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-$(^{18}O)_2$ in **2a**-(^{16}O) (^{18}O) and **2a**-$(^{18}O)_2$can be calculated as follows: ([M $(^{18}O)_2]^+$ - [M (^{16}O) $(^{18}O)]^+$ × 0.2%)/([M $(^{18}O)_2]^+$ - [M (^{16}O) $(^{18}O)]^+$ × 0.2% + [M (^{16}O) $(^{18}O)]^+$) = (7.58 – 39.13 × 0.2%)/(7.58 – 39.13 × 0.2% + 39.13) = 16%. Based on these results, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 65%:35%, and the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 84%:16%.

To sum up, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 65%:35%:(16×35/84)% = 61%:33%:6% (based on 100%).

2) ^{18}O labelling experiment with 1 equiv of $H_2{}^{18}O$ (yyb-8-046)



Following **Typical Procedure I**, the reaction of **2a'** (120.2 mg, 0.5 mmol), $Cu(NO_3)_2$•$3H_2O$ (12.2 mg, 0.05 mmol), TEMPO (8.3 mg, 0.05 mmol), $KHSO_4$ (6.9 mg, 0.05 mmol), and $H_2{}^{18}O$ (9.0 μL, 10.0 mg, d = 1.11 g/mL, 0.5 mmol) in anhydrous DCE (2.0 mL) afforded **2a** (119.6 mg, 93%) [eluent: petroleum ether/ethyl acetate = 15/1 (~160 mL) to 5/1 (~180 mL)] as white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.34 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.70-1.56 (m, 2 H, CH_2), 1.38-1.17 (m, 24 H, 12 x CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 180.4, 34.1, 31.9, 29.67, 29.66, 29.6, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 14.1; **MS** (70 eV, EI) *m*/*z* (%): 260 (M $(^{18}O)_2^+$, 9.26), 258 (M (^{16}O) $(^{18}O)^+$, 48.24), 256 (M $(^{16}O)_2^+$, 70.81).

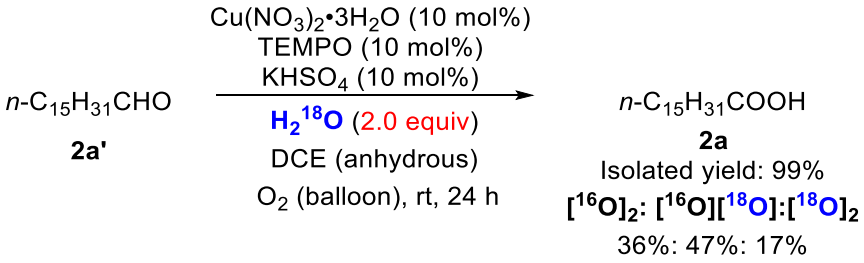
The ^{18}O% incorporation of **2a**-^{18}O was determined via the analysis of MS spectrum. Based on the known natural abundance of the stable isotopes of C, H, and O, the naturally occurring isotopic ^{18}O will also produce [M $(^{18}O)]^+$ peak. According to the natural abundance of ^{18}O, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M $(^{16}O)_2$] ($C_{16}H_{32}{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-$(^{16}O)_2$ 256 [M $(^{16}O)_2$] and **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] are 70.81 and 48.24, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{16}O) (^{18}O) in **2a**-(^{16}O) (^{18}O) and **2a**-$(^{16}O)_2$ 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 $(^{16}O)_2]^+$) = (48.24 –70.81 × 0.2%)/(48.24 –70.81 × 0.2% + 70.81) = 40%.

Besides, the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is also 99.76:0.2. Thus, the intensity of [M $(^{18}O)_2$] ($C_{16}H_{32}{}^{18}O_2$) peak will be 0.2% of the intensity of the molecular peak [M

(^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] and **2a**-($^{18}O)_2$ 260 [M ($^{18}O)_2$] are 48.24 and 9.26, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-($^{18}O)_2$ in **2a**-(^{16}O) (^{18}O) and **2a**-($^{18}O)_2$can be calculated as follows: ([M ($^{18}O)_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ ×0.2%)/([M ($^{18}O)_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ × 0.2% + [M (^{16}O) (^{18}O)]$^+$) = (9.26 – 48.24 × 0.2%)/(9.26 – 48.24 × 0.2% + 48.24) = 16%. Based on these results, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 60%:40%, and the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 84%:16%.

To sum up, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 60%:40%:(16×40/84)% = 56%:37%:7% (based on 100%).

3) ^{18}O labelling experiment with 2 equiv of $H_2{}^{18}O$ (yyb-8-063)



Following **Typical Procedure I**, the reaction of **2a'** (120.3 mg, 0.5 mmol), $Cu(NO_3)_2$•$3H_2O$ (12.1 mg, 0.05 mmol), TEMPO (8.0 mg, 0.05 mmol), $KHSO_4$ (7.0 mg, 0.05 mmol), and $H_2{}^{18}O$ (18.0 μL, 20.0 mg, d = 1.11 g/mL, 1.0 mmol) in anhydrous DCE (2.0 mL) afforded **2a** (127.9 mg, 99%) [eluent: petroleum ether/ethyl acetate = 15/1 (~160 mL) to 5/1 (~180 mL)] as white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.34 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.63 (quintet, *J* = 7.3 Hz, 2 H, CH_2), 1.38-1.19 (m, 24 H, 12 x CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 180.32, 180.30, 34.1, 31.9, 29.67, 29.66, 29.64, 29.62, 29.58, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 14.1; **MS** (70 eV, EI) *m/z* (%): 260 (M ($^{18}O)_2^+$, 24.03), 258 (M (^{16}O) (^{18}O)$^+$, 69.37), 256 (M ($^{16}O)_2^+$, 51.26).

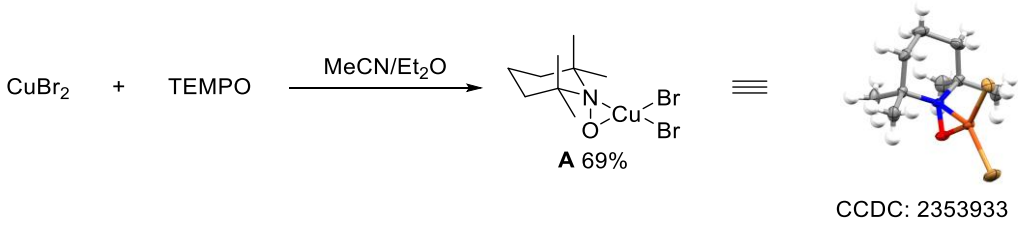
The ^{18}O% incorporation of **2a**-^{18}O was determined via the analysis of MS spectrum. Based on the known natural abundance of the stable isotopes of C, H, and O,

the naturally occurring isotopic ^{18}O will also produce [M (^{18}O)]$^+$ peak. According to the natural abundance of ^{18}O, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 99.76:0.2. Thus, the intensity of [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O)$_2$] ($C_{16}H_{32}{}^{16}O_2$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O)$_2$ 256 [M (^{16}O)$_2$] and **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] are 51.26 and 69.37, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{16}O) (^{18}O) in **2a**-(^{16}O) (^{18}O) and **2a**-(^{16}O)$_2$ 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)$_2$]$^+$) = (69.37 – 51.26 × 0.2%)/(69.37 – 51.26 × 0.2% + 51.26) = 57%.

Besides, the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is also 99.76:0.2. Thus, the intensity of [M (^{18}O)$_2$] ($C_{16}H_{32}{}^{18}O_2$) peak will be 0.2% of the intensity of the molecular peak [M (^{16}O) (^{18}O)] ($C_{16}H_{32}{}^{16}O^{18}O$). According to the MS spectrum of **2a**-^{18}O, the relative abundance of **2a**-(^{16}O) (^{18}O) 258 [M (^{16}O) (^{18}O)] and **2a**-(^{18}O)$_2$ 260 [M (^{18}O)$_2$] are 69.37 and 24.03, respectively. Since there was no detected contributions to the isotope peak intensities from background peaks or from impurities in the sample according to the MS spectrum of **2a**, the incorporation of **2a**-(^{18}O)$_2$ in **2a**-(^{16}O) (^{18}O) and **2a**-(^{18}O)$_2$can be calculated as follows: ([M (^{18}O)$_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ ×0.2%)/([M (^{18}O)$_2$]$^+$ - [M (^{16}O) (^{18}O)]$^+$ × 0.2% + [M (^{16}O) (^{18}O)]$^+$) = (24.03 – 69.37 × 0.2%)/(24.03 – 69.37 × 0.2% + 69.37) = 26%. Based on these results, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$ is 43%:57%, and the ratio of $C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 74%:26%.

To sum up, the ratio of $C_{16}H_{32}{}^{16}O_2$:$C_{16}H_{32}{}^{16}O^{18}O$:$C_{16}H_{32}{}^{18}O_2$ is 43%:57%:(26×57/74)% = 36%:47%:17% (based on 100%).

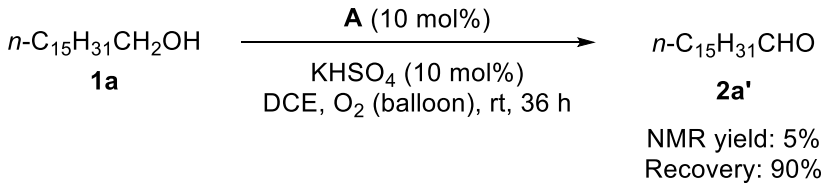
(9) Preparation of $CuBr_2$•TEMPO (A)[2] (yyb-8-067)



To a 4 mL glass vial were added $CuBr_2$ (223.7 mg, 1.0 mmol) and 2.0 mL of anhydrous MeCN. The resulting mixture was stirred at rt for 2 h before transferring to a solution of TEMPO (160.4 mg, 1.0 mmol) in 2.0 mL of anhydrous Et_2O. The resulting mixture was stirred for an additional 2 h and concentrated to about 2 mL. Et_2O (2.0 mL) was added to the mixture and the liquid was decanted from the precipitated solid. The solid was then dissolved in DCM (2 mL) and filtered through cotton. An additional 2.0 mL of Et_2O were added and the recrystallization afforded dark crystals (264.1 mg, 69%).

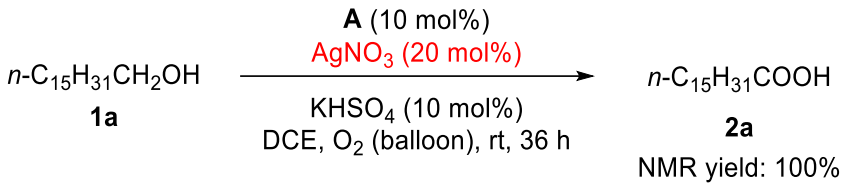
(10) Aerobic oxidation of alcohol 1a with $CuBr_2$•TEMPO (A) as catalyst

1) $CuBr_2$•TEMPO (A) as catalyst (yyb-8-093B)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 using an O_2 balloon for three times. Then **A** (19.4 mg, 0.05 mmol), $KHSO_4$ (7.0 mg, 0.05 mmol), **1a** (122.0 mg, 0.5 mmol), and DCE (2.0 mL) were added sequentially. The resulting mixture was stirred at rt for 36 h and filtrated through a short column of silica gel eluted with ethyl acetate (3 x 25 mL). After evaporation, dibromomethane (35.0 μL) was added as the internal standard for ^1H NMR analysis: 5% of aldehyde **2a'** was detected with 90% of alcohol **1a** recovered.

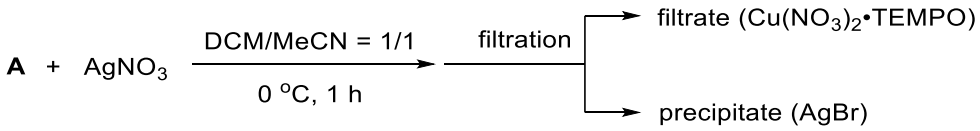
2) $CuBr_2$•TEMPO (A) as catalyst with the addition of $AgNO_3$ (yyb-8-093A)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 using an O_2 balloon for three times. Then $AgNO_3$ (16.8 mg, 0.1 mmol), **A** (18.9 mg, 0.05 mmol), $KHSO_4$ (6.7 mg, 0.05 mmol), **1a** (121.8 mg, 0.5 mmol), and DCE (2.0 mL) were added sequentially. The resulting mixture was stirred at rt for 36 h before filtrating through a short column of silica gel eluted with ethyl acetate (3 x 25 mL). After evaporation, dibromomethane (35.0 μL) was added as the internal standard for ^{1}H NMR analysis: 100% of carboxylic acid **2a** was detected.

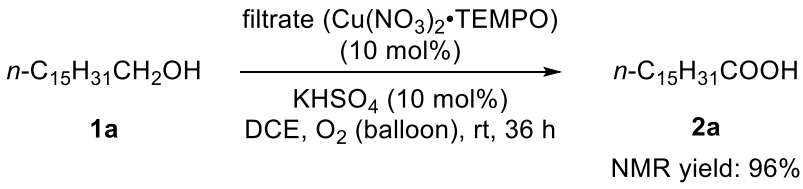
(11) Aerobic oxidation of alcohol 1a with $Cu(NO_3)_2$•TEMPO or AgBr as catalyst

1) Preparation of filtrate ($Cu(NO_3)_2$•TEMPO) and precipitate (AgBr) from $CuBr_2$•TEMPO (A) and $AgNO_3$ (yyb-9-013)



To a 20 mL glass vial were added **A** (378.2 mg, 1.0 mmol) and anhydrous DCM (5.0 mL). Then a solution of $AgNO_3$ (338.6 mg, 2.0 mmol) in 5.0 mL of anhydrous MeCN was added. The resulting mixture was stirred at 0 °C for 1 h and filtrated through a filter paper to afford the filtrate and the precipitate, respectively. The precipitate was identified as AgBr.

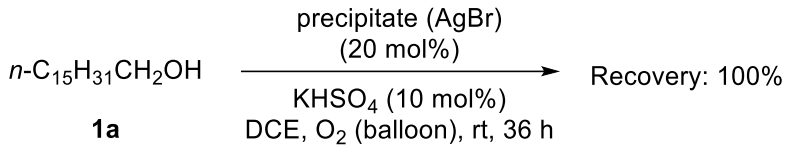
2) Aerobic oxidation of alcohol 1a with filtrate ($Cu(NO_3)_2$•TEMPO) as catalyst (yyb-9-014A)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 using

an O_2 balloon for three times. Then the evaporated filtrate (0.5 mL), $KHSO_4$ (6.5 mg, 0.05 mmol), **1a** (120.7 mg, 0.5 mmol), and DCE (2.0 mL) were added sequentially. The resulting mixture was stirred at rt for 36 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 25 mL). After evaporation, dibromomethane (35.0 μL) was added as the internal standard for ^{1}H NMR analysis: 96% of carboxylic acid **2a** was detected.

3) Aerobic oxidation of alcohol 1a with precipitate (AgBr) as catalyst (yyb-8-197)



A Schlenk tube was degassed to remove the air inside and refilled with O_2 using an O_2 balloon for three times. Then the precipitate (7.2 mg, 0.04 mmol), $KHSO_4$ (2.7 mg, 0.02 mmol), **1a** (48.9 mg, 0.2 mmol), and DCE (0.8 mL) were added sequentially. The resulting mixture was stirred at rt for 36 h and filtrated through a short column of silica gel eluted with diethyl ether (3 x 15 mL). After evaporation, dibromomethane (35.0 μL) was added as the internal standard for ^{1}H NMR analysis: 100% recovery of alcohol **1a** was detected.

(12) SAESI-MS studies for identification of $Cu(NO_3)_2$-TEMPO adduct (yyb-11-169)

To a 10 mL glass vial were added **A** (38.0 mg, 0.1 mmol) and DCM (4.0 mL). Then a solution of $AgNO_3$ (34.0 mg, 0.2 mmol) in 4.0 mL of MeCN was added. The resulting mixture was stirred at 0 ^{o}C for 1 h and then the supernatant was detected by solvent-assisted electrospray ionization mass spectrometry (SAESI-MS).[3]

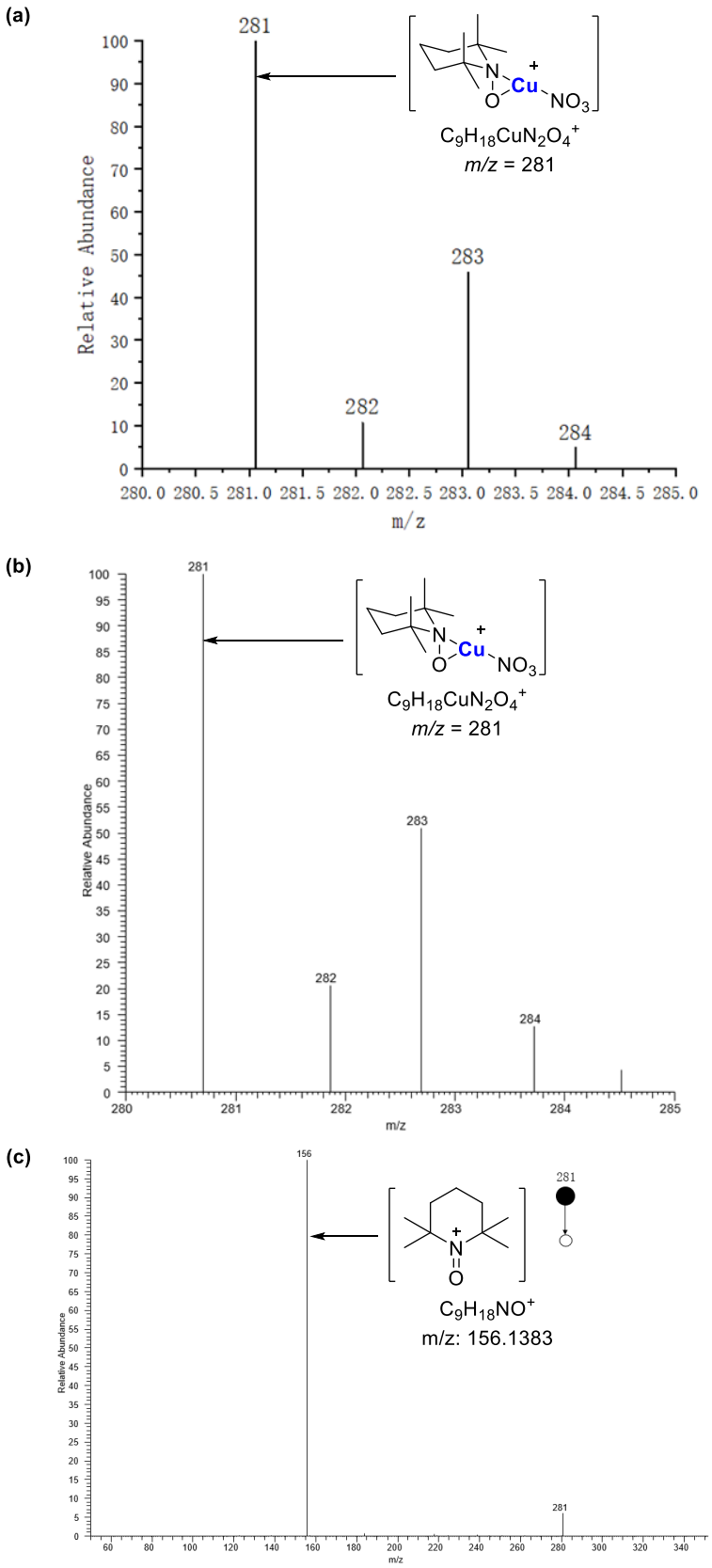


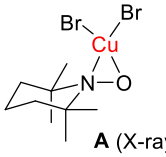
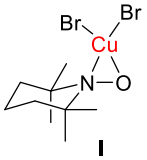
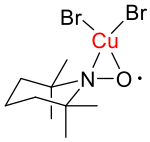
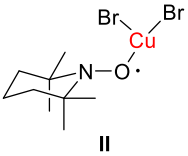
Fig. S1. SAESI-MS studies. (a) Theoretical isotopic distribution of $[TEMPO•Cu(NO_3)]^+$. (b) Expanded SAESI-MS spectrum, showing the major signal from m/z 280 to 285. (c) SAESI-MS/MS spectrum of $[TEMPO•Cu(NO_3)]^+$ at m/z 281.

Computational Method.

All the DFT calculations were performed with Gaussian 16 package.[4] The DFT method was employed using the (U)M06 functional.[5] The standard 6-31G(d)[6] basis sets were used for C, H, O and N atoms and LANL2DZ basis set[7] with effective core potential (ECP) for copper. Frequency analyses (at 298.15 K and 1 atm) were carried out to confirm each structure being a minimum (no imaginary frequency) or a transition state (only one imaginary frequency). Intrinsic reaction coordinate (IRC)[8] calculations were carried out to confirm the connection of the transition structures with their corresponding reactants and products. Single-point energies and solvent effects in DCE (ε = 10.125) were computed with (U)M06/SDD[9]-6-311+G(d,p) basis sets by using SMD[10] solvation model. The reported relative energies are the Gibbs free energies (ΔG_{sol}) in DCE.

The calculations on the X-ray structure of $CuBr_2$•TEMPO (A)

Single point energy calculations on the X-ray structure of $CuBr_2$•TEMPO (**A**) shows that the closed-shell singlet structure of **A** is lower in electronic energy than its triplet state by 28.3 kcal/mol (Scheme S1a). Further optimization of **A** with closed-shell singlet state produces a similar η^2–TEMPO structure **I**. However, the optimization of **A** with triplet state converges to a η^1–TEMPO adduct **II**, which is less stable by 6.9 kcal/mol than I (Scheme S1b). Therefore, we considered that **A** is more inclined to be a Cu(III) species.

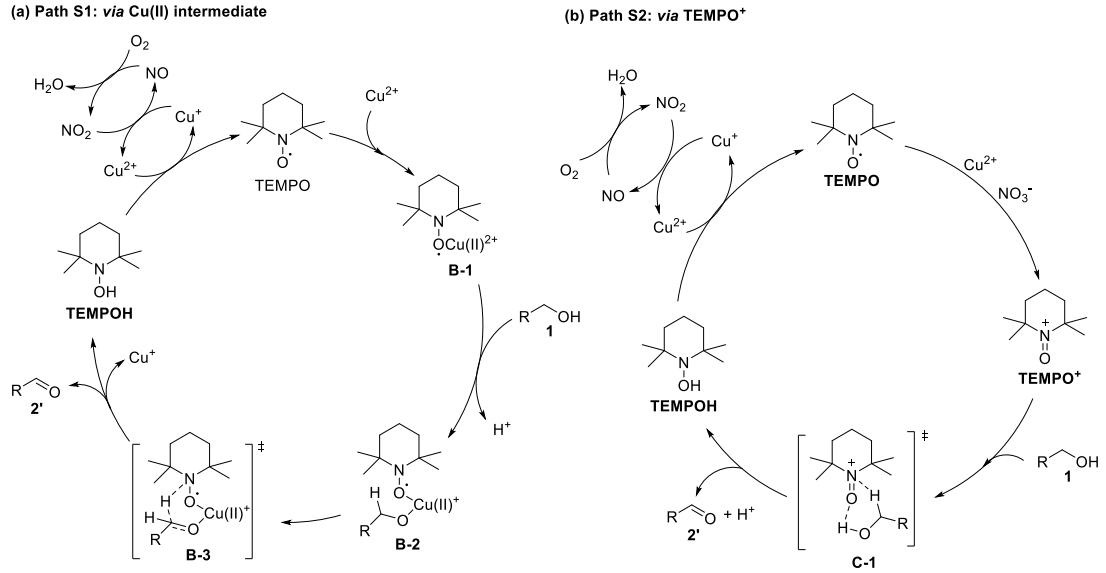
	single point energy [a]		optimization [b]	
singlet	 **A** (X-ray)	**0.0**	 **I**	**0.0**
triplet	 **A** (X-ray)	**28.3**	 **II**	**6.9**

Scheme S1. a) The electronic energies (kcal/mol) calculated at (U)M06/SDD-6-311+G(d,p) level of theory with respect to the singlet state. b) The electronic energies (kcal/mol) calculated at (U)M06/SDD,6-311+G(d,p)//(U)M06/LANL2DZ,6-31G(d)

level of theory with respect to **I**.

Two alternative possible aerobic oxidation mechanisms.

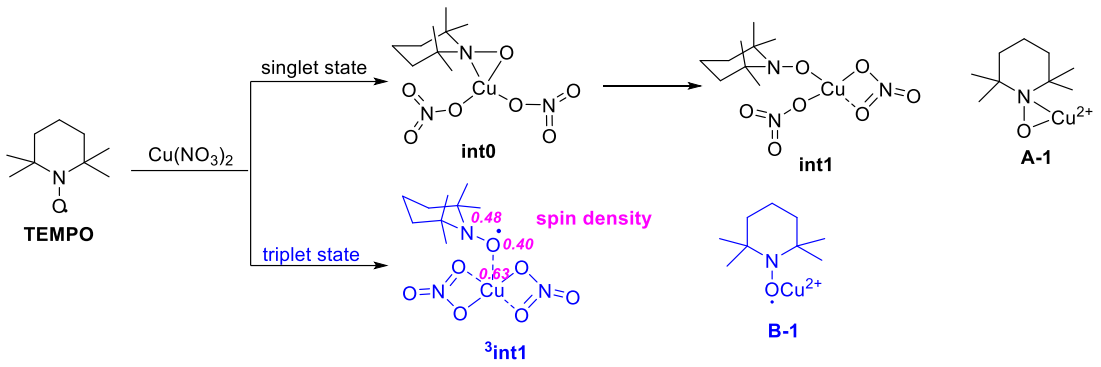
Other than the mechanism proposed in Scheme 4 of the main text, two possible pathways for this copper-catalyzed aerobic oxidation reaction have also been proposed. As shown in Scheme S2, in **Path S1**, TEMPO merely coordiates to Cu^{2+} to generate **B-1**, in which the oxidation state of copper has not been changed.[11] Subsequently **B-1** would react with the alcohol **1** to produce **B-2** upon releasing a proton. Then aldehyde **2'** is formed via a six-membered cyclic transition state **B-3** with the formation of Cu^{+} and TEMPOH. For **Path S2**, $TEMPO^{+}$ would be formed from TEMPO in the presence of Cu^{2+} and NO_3^-.[12] As reported,[13] the alcohol could also be oxidized to aldehyde **2'** by $TEMPO^{+}$ with the formation of TEMPOH, which could be oxidized back to TEMPO by Cu^{2+} (Scheme S2).



Scheme S2. The other two possible mechanisms.

For the pathway showed in Scheme 4 of the main text, TEMPO couples with Cu(II) to generate the **A-1** type Cu species **int0**, which is with a closed-shell singlet electronic structure. As to **Path S1** in Scheme S2, the interaction of TEMPO to Cu(II) merely results in the formation of the coordination complex **B-1** type triplet Cu species ^{3}**int1**. We conducted Mulliken atomic spin density analysis (Scheme S3), which shows that ^{3}**int1** has one electron distributes on TEMPO and the other electron distributes on Cu

moiety, indicating that only coordination takes place between TEMPO and Cu(II). It is noteworthy that such adduct of M-TEMPO has been isolated when M is Fe or Al.[14]



Scheme S3. Mulliken atomic spin density analysis.

DFT calculations were performed to evaluate these reaction pathways. The free energy profile of **Path S1** are presented in Fig. S2a with blue line. Initial coupling of TEMPO with $Cu(NO_3)_2$ provides **A-1** type η^2–TEMPO adduct species **int0** with closed-shell singlet electronic structure, or **B-1** type triplet Cu-TEMPO intermediate ^{3}**int1**.[11] Mulliken atomic spin density analysis shows that ^{3}**int1** has one electron distributes on TEMPO and the other electron distributes on Cu moiety, indicating that only coordination takes place between TEMPO and Cu(II). The isomerization of **int0** yields a more stable η^1–TEMPO adduct **int1**, which is more stable by 1.7 kcal/mol than ^{3}**int1**. For the singlet profile from **int1** (black line in Fig. S2a, the pathway showed in the main text), subsequent coordination with alcohol yields intermediate **int2**. Then displacement of one of the nitrate ion by alkoxide ligand occurs uphill energetically (+21.3 kcal/mol, **int4** with respective to **int1**) to produce the **A-2** type Cu-alkoxide species **int4**, accompany with the release of nitric acid. Subsequently, a six-member-ring transition structure **TS1** is located for the migration of hydrogen from the alkoxide to the nitrogen atom of TEMPO, resulting in the formation of aldehyde, TEMPOH and $CuNO_3$. Notably, the activation barrier for hydrogen shift is very low (almost no barrier) from **int4**, while the overall free energy of this singlet profile for oxidation of alcohol to aldehyde is 21.3 kcal/mol (**int4** with respective to **int1**, black line in Fig. S2a). On the other hand, the triplet profile (blue line in Fig. S2a) proceeds in a similar pathway. The triplet intermediates ^{3}**int2**-^{3}**int4** feature lower free energies by about 2 kcal/mol than their corresponding singlet structures, respectively. It is noteworthy that **TS1** is

more stable by 18.6 kcal/mol than its corresponding **^{3}TS1**, indicating the preference of the singlet pathway (black line in Fig. S2a, the pathway showed in the main text).

Furthermore, the possibility of the TEMPO$^+$ participated oxidation mechanism (**Path S2**, Scheme S2b) was also evaluated by DFT calculations (Fig. S2b). The oxidation of alcohol to aldehyde with TEMPO$^+$ proceeds via a **C-1** type six-membered cyclic transition structure **TS4** or **TS4'**, which involves the migrations of two hydrogens from alcohol to TEMPO$^+$. **TS4** and **TS4'** feature similar free energy barriers at 27.4 and 27.6 kcal/mol, respectively. The subsequent reaction of aldehyde with water with the aid of HNO_3 provides aldehyde hydrate **int7**, which would be further oxidized to acetic acid by TEMPO$^+$ via six-membered cyclic transition structure **TS5** or **TS5'**, with a similar activation free energy of 24.7 and 26.0 kcal/mol, respectively. Due to the higher free energy barrier of **TS4** (27.4 kcal/mol) than **TS1** (17.8 kcal/mol), the TEMPO$^+$ participated pathway is less favorable.

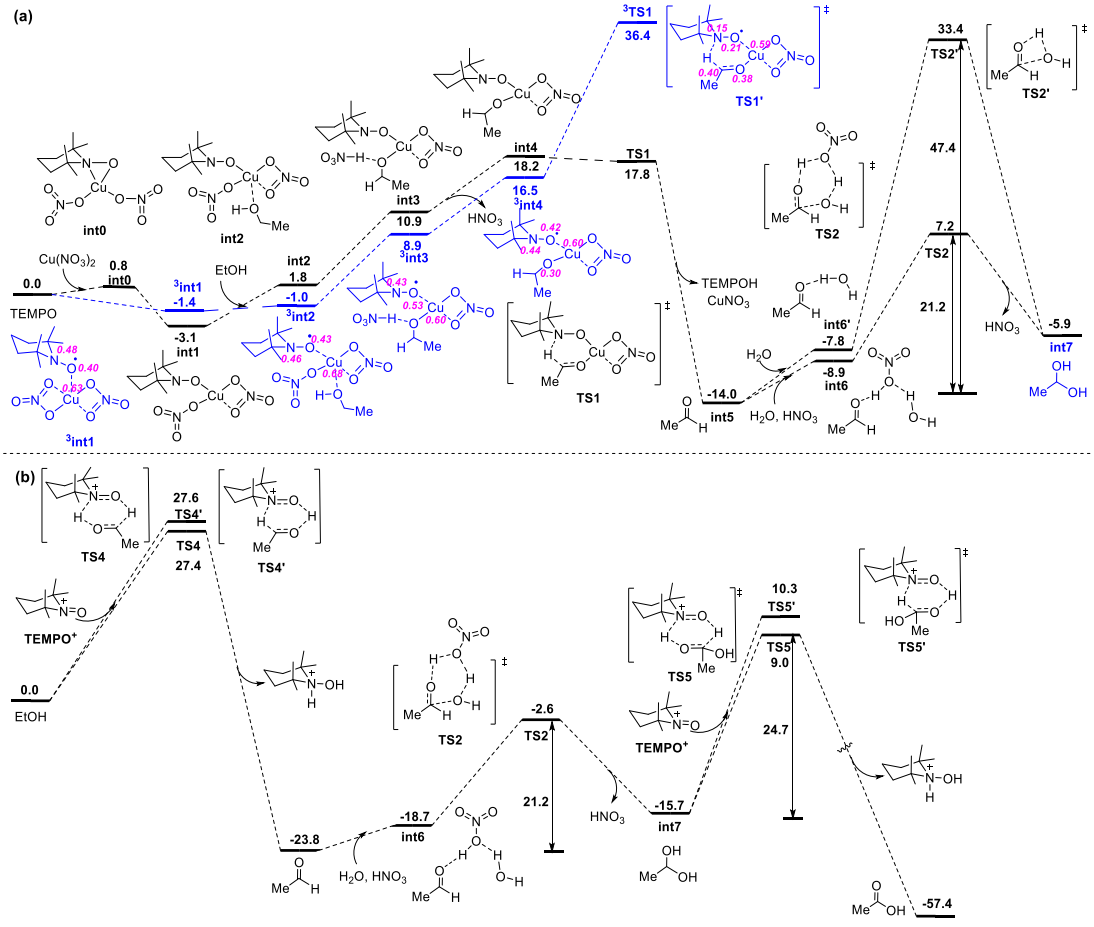


Fig. S2. (a) Free energy profiles (ΔG_{sol} in kcal/mol) for the copper-catalyzed oxidation

of alcohol to aldehyde. (The pink numbers are spin densities for the structures in the triplet profile.) (b) Free energy profiles (ΔG_{sol} in kcal/mol) for the $TEMPO^+$-catalyzed oxidation of alcohol to acetic acid.

Energies of intermediates and transition states

Table S3. Electronic energies (E_{elec}), Gibbs free energies (G_{298}), thermal correction to Gibbs free energy ($cor\ G_{gas}$), solvation energies (E_{sol}), solvation free energies (G_{sol}) in THF (ε = 7.43) for all stationary points of the process.

species	E_{elec} (a.u.)	G_{298} (a.u.)	$cor\ G_{gas}$ (a.u.)	E_{sol} (a.u.)	G_{sol} (a.u.)
Cu(NO3)2	-756.5464367	-756.547944	-0.001507	-757.9176976	-757.9192046
TEMPO	-483.370202	-483.145174	0.225028	-483.5077736	-483.2827456
int0	-1239.923176	-1239.67495	0.248224	-1241.44894	-1241.2007
int1	-1239.932756	-1239.686498	0.246258	-1241.453228	-1241.20697
EtOH	-154.9300104	-154.875403	0.054607	-154.9907838	-154.9361768
int2	-1394.88472	-1394.564345	0.320375	-1396.455699	-1396.135324
int3	-1394.868188	-1394.547629	0.32056	-1396.441255	-1396.120695
HNO_3	-280.7564902	-280.754986	0.001504	-280.8474382	-280.84593
int4	-1114.078685	-1113.777648	0.301038	-1115.564195	-1115.263157
TS1	-1114.0761	-1113.777489	0.29861	-1115.562498	-1115.263888
^{3}int1	-1239.937964	-1239.69326	0.244705	-1241.448959	-1241.2043
^{3}int2	-1394.889387	-1394.56991	0.319475	-1396.459202	-1396.1397
^{3}int3	-1394.868496	-1394.54956	0.318935	-1396.442871	-1396.1239
^{3}int4	-1114.082229	-1113.78701	0.295223	-1115.561201	-1115.266
^{3}TS1	-1114.043243	-1113.74813	0.295114	-1115.529377	-1115.2343
CuNO3	-476.356381	-476.369391	-0.01301	-477.667158	-477.68017
TEMPOH	-483.9763747	-483.73879	0.237585	-484.1210405	-483.88346
int5	-153.7288757	-153.69801	0.030866	-153.7818048	-153.75094
$H_2O\_HNO_3$	-357.15589	-357.133152	0.022738	-357.286185	-357.26345
int6	-510.893664	-510.826584	0.067079	-511.073384	-511.00631
TS2	-510.866689	-510.79157	0.075118	-511.055704	-510.98059
int6'	-230.1188955	-230.067587	0.051309	-230.2144776	-230.16317
TS2'	-230.0556745	-230.004181	0.051494	-230.1490077	-230.09751
int7	-230.1256546	-230.068052	0.057603	-230.2177603	-230.16016
int8	-1470.088555	-1469.76297	0.325587	-1471.688785	-1471.3632
int9	-1470.074645	-1469.74967	0.324977	-1471.686394	-1471.3614
int10	-1189.285106	-1188.98137	0.303739	-1190.79789	-1190.4942
TS3	-1189.276304	-1188.97634	0.299963	-1190.794511	-1190.4945

CH_3COOH	-228.959398	-228.924098	0.035299	-229.03962	-229.00432
TEMPO+	-483.1191696	-482.891584	0.227586	-483.3190082	-483.09142
TS4	-638.029972	-637.730103	0.299869	-638.283848	-637.98398
TS4'	-638.0347535	-637.732484	0.30227	-638.2859606	-637.98369
TS5	-713.238016	-712.935551	0.302464	-713.514604	-713.21214
TS5'	-713.239157	-712.933738	0.305419	-713.515583	-713.21016

Cartesian coordinates for the optimized structures

$Cu(NO_3)_2$

Cu	0.00000000	0.00006900	0.00001700
N	2.37607400	0.00000900	0.00019700
O	1.65940000	1.06669900	-0.00004900
O	1.65871600	-1.06637700	-0.00005000
O	-1.65884500	1.06638600	0.00002300
N	-2.37607500	-0.00007100	-0.00013500
O	3.56460700	-0.00044300	-0.00012200
O	-3.56460600	0.00022700	0.00006200
O	-1.65927300	-1.06668700	0.00002200

TEMPO

H	0.00000000	2.18831600	1.09462900
C	0.00000000	2.11345800	-0.00346900
C	1.23718000	1.38218800	-0.49626900
C	-1.23718100	1.38218700	-0.49626900
H	-0.00000100	3.14651300	-0.37654600
H	2.15898300	1.89347100	-0.18023200
H	1.23450300	1.39250000	-1.59898700
H	-2.15898300	1.89347000	-0.18023200
H	-1.23450300	1.39249900	-1.59898700
N	0.00000000	-0.74227800	-0.22275900
O	0.00000100	-2.01000600	-0.09490900
C	-1.31740700	-0.07050500	-0.02456500
C	1.31740700	-0.07050500	-0.02456500
C	2.33988600	-0.82228000	-0.86748000
H	2.44938600	-1.85493900	-0.52297600
H	2.03224000	-0.84291600	-1.92084400
H	3.31253900	-0.31698200	-0.79869900
C	1.71551600	-0.16505200	1.44982200
H	1.61224200	-1.20186100	1.79241200
H	2.76336100	0.14029400	1.57444000
H	1.10238300	0.47454400	2.09649500
C	-1.71551600	-0.16505200	1.44982200
H	-1.10238300	0.47454400	2.09649500
H	-2.76336100	0.14029300	1.57444000
H	-1.61224200	-1.20186200	1.79241200
C	-2.33988700	-0.82228000	-0.86748000
H	-2.03224000	-0.84291700	-1.92084400
H	-2.44938600	-1.85494000	-0.52297500
H	-3.31253900	-0.31698200	-0.79870000

Int0

Cu	-0.75390000	-0.18977500	-0.31235100
O	0.37942600	-1.74474500	-0.01693500
N	1.11846700	-0.69667800	0.03523200
C	1.57557800	-0.26785600	1.44167600
C	1.97113000	-0.43303300	-1.22491200
C	2.17016500	1.13358300	1.33129600
C	2.54911100	0.97699500	-1.12710500
H	2.61108000	1.37131000	2.31023000
H	3.27528500	1.08238700	-1.94645600
H	1.34757500	1.84826900	1.17368600
H	1.74180600	1.69886600	-1.31868600
C	3.19083400	1.29069400	0.21544600
H	3.56237200	2.32295400	0.20584900
H	4.07193700	0.65592700	0.39386400
C	0.36648600	-0.26728200	2.36434500
C	1.07603400	-0.56341300	-2.45168200
H	-0.41681300	0.43210700	2.03910600
H	0.28111100	0.19448400	-2.48084200
H	1.70002800	-0.39115000	-3.33748600
H	-0.07393300	-1.26348200	2.47413500
H	0.63504900	-1.56261900	-2.53903500
C	2.57929400	-1.30710200	1.94467100
C	3.04638300	-1.51938600	-1.28781500
H	2.18567400	-2.32201100	1.81129400
H	2.60129200	-2.51596400	-1.18025500
H	3.52029000	-1.46450500	-2.27591900
H	3.56096800	-1.23547600	1.46778800
H	3.83505700	-1.39902700	-0.53995300
H	0.70584700	0.07221200	3.35113100
H	2.72281400	-1.13979500	3.01930600
O	-0.64578400	1.65806200	-0.77773300
O	-2.46688300	-0.69087000	-0.96210200
N	-1.43904700	2.37908600	-0.00132300
O	-1.55890800	3.54688000	-0.28585400
O	-1.96540700	1.80204300	0.94575300
N	-3.08424500	-1.28293400	0.03534900
O	-4.20976400	-1.67462700	-0.15232900
O	-2.44776200	-1.38881100	1.08796100

int1

Cu	-1.53799300	0.11528300	0.01360300
O	-0.59077500	1.37385800	1.11457000
H	4.34038300	-0.56234100	0.86728200

C	4.06292700	-1.08029100	-0.06220300
C	2.99866400	-2.13267600	0.20023100
C	3.57874200	-0.09082000	-1.10970900
H	4.97897000	-1.57130900	-0.41580000
H	3.31264300	-2.83223200	0.98865700
H	2.85094800	-2.73022700	-0.71386200
H	4.33714400	0.67844400	-1.31500800
H	3.39493900	-0.62023900	-2.05875300
N	1.30663600	-0.43727500	-0.32926800
O	0.19326800	-0.44919200	-0.87086200
C	2.28845100	0.64651600	-0.70512100
C	1.63144500	-1.56473100	0.61624300
C	0.56384500	-2.63750300	0.47060400
H	-0.40953500	-2.31611500	0.85956700
H	0.42483000	-2.94321000	-0.57252500
H	0.88675600	-3.51077500	1.05115500
C	1.62616400	-1.03440600	2.05444400
H	0.73732900	-0.41922900	2.24512900
H	1.60329700	-1.89737800	2.73221000
H	2.51233100	-0.44138300	2.29851400
C	2.55845600	1.61119000	0.45540400
H	3.18582300	1.17589100	1.23856700
H	3.10238200	2.47024000	0.04229900
H	1.63630700	1.98029400	0.91366400
C	1.71395800	1.40826200	-1.88695100
H	1.47404500	0.74026100	-2.72254800
H	0.80658300	1.96571100	-1.62414200
H	2.47055900	2.12675300	-2.22475200
O	-3.59690800	-0.21076000	0.55425300
N	-3.61188400	-1.15651900	-0.28080400
O	-4.57027100	-1.84356100	-0.50967900
O	-2.48619300	-1.34468300	-0.88840800
N	-0.76140300	2.51769400	0.50054300
O	-1.44378000	2.49139900	-0.53244400
O	-0.21950200	3.50082500	0.95568700

EtOH

C	1.21120600	-0.21978500	-0.00000600
H	1.27249600	-0.86158400	-0.88680900
H	1.27251100	-0.86160000	0.88678500
H	2.07080800	0.46075600	-0.00000500
C	-0.08837000	0.54604100	0.00000600
H	-0.13855200	1.20243500	0.88771200
H	-0.13856400	1.20245100	-0.88768800

O	-1.13750100	-0.39758900	0.00001200
H	-1.97571200	0.08071700	-0.00008900

int2

Cu	-1.13219800	0.37837200	-0.39659000
O	-0.35456400	1.24257300	1.14559800
H	4.45142800	-1.13061800	1.10515800
C	4.34925400	-1.28081900	0.02068100
C	3.22061200	-2.24951500	-0.28868600
C	4.11427200	0.04177900	-0.68990200
H	5.30161400	-1.71349400	-0.31276400
H	3.35048600	-3.20078300	0.24777100
H	3.23573800	-2.48821700	-1.36459400
H	4.92158200	0.75862500	-0.48119900
H	4.10727600	-0.12321700	-1.77967200
N	1.71777700	-0.31899100	-0.47851800
O	0.72806500	-0.03329100	-1.15679500
C	2.79431100	0.72629300	-0.29203500
C	1.81668100	-1.72678000	0.05664600
C	0.76044400	-2.57917800	-0.62892400
H	-0.25032700	-2.33548400	-0.28166600
H	0.79600800	-2.48031100	-1.71999300
H	0.96238400	-3.62596300	-0.36762100
C	1.54583100	-1.70559700	1.56484900
H	0.64138200	-1.12500200	1.78529500
H	1.37317800	-2.74046700	1.88723900
H	2.37796900	-1.30281900	2.14999800
C	2.85449200	1.22742600	1.15540400
H	3.31056600	0.50565100	1.83925500
H	3.48303400	2.12711100	1.16121000
H	1.86647200	1.49954800	1.53858200
C	2.49023700	1.88202300	-1.22983100
H	2.39352200	1.54559200	-2.26890400
H	1.57127900	2.41507600	-0.95880800
H	3.32573300	2.59018600	-1.17155700
O	-3.43664500	0.14194400	-0.68687000
N	-3.12004500	-0.26799300	-1.83874800
O	-3.91944800	-0.57626700	-2.68469000
O	-1.85347200	-0.35218700	-2.06113900
N	-0.33488700	2.51912200	0.86005300
O	-0.83545900	2.85617900	-0.21879700
O	0.19487600	3.27359300	1.64996800
O	-1.93813600	-1.37923800	1.10740100
H	-2.70368400	-1.31850000	0.50677700

C	-2.38061100	-0.81497000	2.34427300
H	-2.56522400	0.26377300	2.22058200
H	-1.53856500	-0.91933300	3.03997200
C	-3.61417800	-1.51955300	2.85654800
H	-3.92809000	-1.10802100	3.82369700
H	-4.45001600	-1.39007500	2.15419500
H	-3.42972400	-2.59412100	2.97712600

int3

Cu	-1.42451900	-0.58021000	-0.16669200
O	-0.85504800	2.59153000	-0.56785100
H	4.59979100	-0.38198000	0.42135500
C	4.26829900	-1.08926100	-0.35280100
C	3.37314000	-2.16240900	0.24526600
C	3.54912800	-0.36277000	-1.47794100
H	5.18325200	-1.55338900	-0.74406900
H	3.86944700	-2.67846000	1.08037400
H	3.15756800	-2.92541200	-0.52046500
H	4.17481900	0.43611200	-1.90228800
H	3.33809100	-1.07257600	-2.29434000
N	1.44385700	-0.80249200	-0.34574500
O	0.36510500	-1.17079000	-0.83617300
C	2.21638100	0.28503900	-1.05165000
C	2.02878800	-1.62572400	0.77346900
C	1.08475900	-2.78021200	1.06319100
H	0.13452500	-2.42906300	1.48494300
H	0.86909700	-3.37475800	0.16875500
H	1.56419200	-3.43070700	1.80525700
C	2.20727500	-0.78695400	2.04096400
H	1.29373600	-0.21716800	2.24390500
H	2.39888600	-1.47343600	2.87595100
H	3.04986900	-0.09170300	1.98804900
C	2.44581300	1.49516400	-0.14094900
H	3.28243500	1.36195300	0.55192300
H	2.68578000	2.35740200	-0.77679200
H	1.54942100	1.73368400	0.44033300
C	1.42850000	0.70931900	-2.27878500
H	1.18585300	-0.13949300	-2.92734900
H	0.49931300	1.22616300	-2.00913200
H	2.04881000	1.41349000	-2.84704400
O	-3.55357700	-0.60659700	0.00891100
N	-3.57195000	-1.47461300	-0.91455900
O	-4.57570000	-1.97202000	-1.34597000
O	-2.40587000	-1.79364900	-1.36394900

N	-0.35448100	3.74522400	-0.06439100
O	-0.46646600	4.70706000	-0.77598100
O	0.15507000	3.68593000	1.03919300
O	-0.55070200	0.59122300	0.99042400
H	-0.66611800	1.85060500	0.13342800
C	-1.29349600	0.94628900	2.13847300
H	-2.20346300	1.50763500	1.85062200
H	-0.67246800	1.64266600	2.72826100
C	-1.67754400	-0.25671700	2.97358700
H	-2.22415600	0.04770600	3.87516600
H	-2.33153300	-0.93381100	2.40399100
H	-0.78683400	-0.81827800	3.29033500

HNO_3

N	-0.14298100	0.04133900	-0.00011900
O	1.09059200	-0.59748800	-0.00004500
O	-1.07457600	-0.70560100	0.00007000
O	-0.10647100	1.24864500	0.00001400
H	1.72450400	0.14617700	0.00051700

int4

Cu	-1.60433600	0.24786900	-0.34508100
O	-1.10754800	1.99037000	-0.53731100
H	4.34387700	-1.10327000	0.27299600
C	3.53724200	-1.74451800	-0.11358800
C	2.45534800	-1.94627300	0.93958600
C	2.95158100	-1.16424900	-1.39481100
H	4.01062800	-2.71027000	-0.33596300
H	2.87851000	-2.35085600	1.87137600
H	1.72040800	-2.68040000	0.57245700
H	3.73357100	-1.00230700	-2.15205500
H	2.23392600	-1.88348500	-1.82062900
N	1.22539300	-0.09736100	-0.05389900
O	0.13465300	-0.61762500	-0.45430400
C	-0.13212800	2.47707700	0.25482500
H	0.42483200	3.28516100	-0.26626900
C	2.20729400	0.16767900	-1.18505400
C	1.68982500	-0.65561000	1.28275600
C	0.45328700	-0.96929300	2.11342300
H	-0.10366600	-0.04955400	2.34590300
H	-0.22558100	-1.66883900	1.61648400
H	0.77806400	-1.41044400	3.06408200
C	2.55469300	0.32599100	2.06584700
H	2.07700700	1.31130400	2.14150400

H	2.66852600	-0.06384200	3.08537500
H	3.56214600	0.45758700	1.66371300
C	3.17021300	1.31013400	-0.87686600
H	3.92238600	1.07039700	-0.12172700
H	3.71320600	1.55197100	-1.79923800
H	2.63584600	2.21468500	-0.56293600
C	1.40265300	0.53360300	-2.42548900
H	0.75550600	-0.28650000	-2.74958600
H	0.77143200	1.41366000	-2.24679000
H	2.10455100	0.76191700	-3.23719500
C	-0.60222200	2.92955600	1.62747000
H	0.22607500	3.31194000	2.24003600
H	-1.07909300	2.09596600	2.16361600
H	-1.35299600	3.72229600	1.52275500
O	-3.79283300	0.17201700	-0.26518000
N	-3.68602000	-1.07257000	-0.09522200
O	-4.62018100	-1.81803700	0.04954100
O	-2.47072600	-1.50763600	-0.08550500
H	0.67734200	1.67690400	0.39674400

TS1

Cu	-1.63475100	0.21230700	-0.27088600
O	-1.04208500	1.94811800	-0.56538200
H	4.28073900	-1.29200800	0.14941200
C	3.38825800	-1.89667000	-0.07305800
C	2.40706000	-1.85835300	1.09217000
C	2.72583200	-1.43086600	-1.36345300
H	3.75543800	-2.92319900	-0.20397000
H	2.89760500	-2.16297900	2.02889200
H	1.59229200	-2.57461400	0.90655700
H	3.44446100	-1.42872900	-2.19681300
H	1.92223100	-2.13345100	-1.63195500
N	1.19172800	-0.05597600	-0.03852100
O	0.09984500	-0.69414300	-0.28874500
C	0.05481500	2.38005800	-0.00160100
H	0.79978300	1.36390600	0.12801100
H	0.70890200	2.96497700	-0.68477600
C	2.10983700	-0.02847900	-1.27113300
C	1.77306100	-0.47945100	1.31907800
C	0.61514800	-0.58696300	2.30221800
H	0.15635900	0.39458100	2.48656700
H	-0.15922300	-1.28029200	1.96175800
H	1.01007800	-0.94965900	3.25987900
C	2.77504200	0.53347200	1.86185800

H	2.40387600	1.56264100	1.77260700
H	2.91663000	0.33214500	2.93111800
H	3.76274800	0.48019500	1.39685000
C	3.17790300	1.05719200	-1.18316100
H	4.01022500	0.81438200	-0.51792600
H	3.60431000	1.19186600	-2.18508400
H	2.76170400	2.02466600	-0.87717500
C	1.23814800	0.24647500	-2.49060900
H	0.46864500	-0.51859900	-2.62308500
H	0.74151900	1.22303800	-2.42855100
H	1.88251500	0.24667800	-3.37893900
C	-0.08817100	3.00940900	1.37088100
H	0.88335300	3.21826700	1.83854800
H	-0.67677400	2.36108200	2.03334700
H	-0.63243400	3.95878000	1.27756000
O	-3.79253200	0.26062400	-0.42204400
N	-3.81623800	-0.92878500	0.00742300
O	-4.83245100	-1.55249500	0.18774800
O	-2.65993200	-1.43862900	0.24484700

^{3}int1

Cu	-1.80816500	0.27462000	0.00567600
O	-1.25747700	1.67860800	1.31666100
H	4.10308200	-0.25985400	1.32443900
C	4.13663300	-0.65226200	0.29663700
C	3.22402800	-1.85735500	0.14853900
C	3.72889700	0.41574800	-0.70445400
H	5.17868400	-0.95086200	0.12152700
H	3.49471100	-2.65420200	0.85699300
H	3.35365500	-2.27740700	-0.86286100
H	4.38029000	1.29956200	-0.63530100
H	3.84729900	0.01350600	-1.72436300
N	1.39648200	-0.30962600	-0.41928800
O	0.17522200	-0.15007600	-0.74645300
C	2.28358500	0.88806000	-0.53362800
C	1.73874200	-1.54309000	0.34833000
C	0.90564200	-2.69558600	-0.19979600
H	-0.14812400	-2.60684500	0.08289800
H	0.97745000	-2.75075700	-1.29290300
H	1.28973200	-3.63406200	0.22112800
C	1.39055000	-1.32364500	1.82244400
H	0.36425800	-0.94487100	1.92090000
H	1.44767100	-2.28221900	2.35523600
H	2.06732400	-0.61960600	2.32022200

C	2.12867000	1.76479500	0.71293100
H	2.64021100	1.35136700	1.58993200
H	2.55926900	2.75497700	0.51314900
H	1.07151800	1.89649900	0.97364800
C	1.84867700	1.67474100	-1.76318500
H	1.81860200	1.03187700	-2.65161500
H	0.85804100	2.12418200	-1.63337100
H	2.57466800	2.47907900	-1.93924200
O	-2.22306000	-1.49066500	0.85704100
N	-2.77271900	-1.90517900	-0.22606700
O	-3.20139800	-3.01136000	-0.36166800
O	-2.80266400	-1.01494300	-1.14307400
N	-1.40304200	2.59945600	0.43324200
O	-1.86176500	2.16357100	-0.67567200
O	-1.11624800	3.74294700	0.62976900

^{3}int2

Cu	-1.25764900	0.41743600	-0.13474800
O	-0.65965800	1.37123700	1.48655200
H	4.32935600	-1.32570700	1.16328300
C	4.39962000	-1.34848900	0.06503300
C	3.27524200	-2.17735800	-0.53236800
C	4.34830200	0.05743400	-0.50833400
H	5.36776600	-1.81205300	-0.16631300
H	3.29177000	-3.20948000	-0.15170600
H	3.42080500	-2.24084500	-1.62354200
H	5.15777800	0.68430600	-0.10605600
H	4.50323200	0.00235300	-1.59870200
N	1.89408900	-0.14534300	-0.56435700
O	0.78050200	0.42356300	-0.81101400
C	3.02528600	0.77796900	-0.24414400
C	1.87945200	-1.60714200	-0.26612300
C	0.87625300	-2.27243800	-1.20207300
H	-0.16065900	-2.04228000	-0.93629700
H	1.04138100	-1.96340500	-2.24138800
H	1.00783100	-3.36063500	-1.13563100
C	1.45128200	-1.82797700	1.18760900
H	0.56157100	-1.22977100	1.41944700
H	1.19270900	-2.88591800	1.33273800
H	2.23768700	-1.56941600	1.90623200
C	2.90075700	1.22808700	1.21406700
H	3.13380800	0.42919400	1.92823500
H	3.59973500	2.05499300	1.39745400
H	1.88399700	1.58682900	1.42091100

C	2.91015800	1.99365500	-1.15486000
H	2.84772000	1.69213100	-2.20779700
H	2.02681600	2.59596800	-0.91752100
H	3.80431500	2.61674600	-1.02246900
O	-3.79841800	-0.25500900	-0.72826400
N	-3.22643400	-0.28446800	-1.83876000
O	-3.78930700	-0.45872400	-2.88884100
O	-1.93468900	-0.12481600	-1.84304500
N	-0.73358800	2.54281100	0.94243200
O	-1.23985400	2.53718900	-0.21263600
O	-0.33512000	3.52291200	1.50715100
O	-1.90276500	-1.28080400	0.88162700
H	-2.74875300	-1.32953400	0.38230200
C	-2.23920600	-1.11160200	2.27168300
H	-2.96932200	-0.29366500	2.36952100
H	-1.31712400	-0.78925000	2.76790700
C	-2.75654500	-2.40738900	2.84336900
H	-2.97596100	-2.29455200	3.91189200
H	-3.68063000	-2.72221100	2.34147900
H	-2.01159800	-3.20333900	2.72312800

^{3}int3

Cu	-1.56732400	-0.10952100	-0.27620800
O	0.33964400	2.62931200	-0.92007600
H	3.82703800	-1.83618100	1.51179300
C	3.57855300	-2.43299100	0.62139400
C	2.18750800	-3.03023300	0.74793800
C	3.66541900	-1.58719000	-0.63819300
H	4.32328400	-3.23868300	0.58217200
H	2.09965100	-3.64183000	1.65797700
H	2.00641600	-3.70351400	-0.10658300
H	4.65872600	-1.12611800	-0.74015700
H	3.52384000	-2.23490000	-1.51915600
N	1.28678500	-1.04439400	-0.35035800
O	0.29983900	-0.41120500	-0.86605500
C	2.62789600	-0.46574200	-0.69285300
C	1.06070100	-1.99035500	0.78469600
C	-0.26839700	-2.70978500	0.58130600
H	-1.13333500	-2.10157200	0.88725600
H	-0.41315100	-3.03202700	-0.45670800
H	-0.28182000	-3.59716200	1.22704500
C	1.01991200	-1.22517900	2.11098400
H	0.36981200	-0.34349900	2.02342900
H	0.61388100	-1.88729200	2.88817900

H	2.01011200	-0.89222200	2.43973700
C	2.94078200	0.66094100	0.30053800
H	3.35917200	0.29673400	1.24548200
H	3.67330900	1.34502800	-0.14776700
H	2.03370800	1.23221600	0.53139700
C	2.55503000	0.11427400	-2.09964200
H	2.14943500	-0.61521300	-2.81143300
H	1.94118600	1.02145700	-2.13295500
H	3.57477600	0.37459400	-2.41186400
O	-3.57005600	-0.00502500	-0.20371800
N	-3.69039400	-0.96143200	-1.05314500
O	-4.74864900	-1.37126800	-1.42805400
O	-2.56825400	-1.42642300	-1.44775800
N	1.23031700	3.46403200	-0.33823000
O	2.03964700	3.94806400	-1.08710200
O	1.13117600	3.62325900	0.86233400
O	-0.94744100	1.25292200	0.83570000
H	-0.18108100	2.18334800	-0.15208500
C	-1.88016500	1.89584400	1.66716000
H	-2.76664400	2.22190000	1.09298600
H	-1.39351200	2.81375300	2.04056200
C	-2.30297500	1.01419700	2.82269600
H	-3.03360800	1.52152400	3.46537700
H	-2.77180500	0.09033700	2.45090900
H	-1.43679000	0.73824000	3.43825900

^{3}int4

Cu	-1.52628000	0.37257900	-0.53803700
O	-0.97629100	2.03855100	-0.10754500
H	3.75015300	0.55668300	1.65239300
C	3.95080400	-0.34848900	1.05901100
C	2.92460200	-1.42770800	1.35208900
C	3.92825100	-0.03952900	-0.42735700
H	4.95046700	-0.69190400	1.35680000
H	2.92645600	-1.70813100	2.41569000
H	3.19648700	-2.33517100	0.78756800
H	4.67615000	0.72261200	-0.69196200
H	4.19735900	-0.95337900	-0.98311700
N	1.48873500	-0.42694100	-0.38333600
O	0.39040100	-0.43316900	-1.03560800
C	-1.48031700	2.83188100	0.90947500
H	-1.49560400	3.87196100	0.53032500
C	2.56903400	0.45388300	-0.92634400
C	1.49010300	-1.04171700	0.97795900

C	0.63502300	-2.30294500	0.93376800
H	-0.43091100	-2.07820200	0.82639300
H	0.94427700	-2.95535900	0.10785600
H	0.77122700	-2.84953100	1.87639500
C	0.89782200	-0.05645600	1.98921300
H	-0.10502800	0.26754700	1.67946900
H	0.80149500	-0.55548900	2.96281500
H	1.51740700	0.83872200	2.12312500
C	2.30116900	1.89752300	-0.49165200
H	2.50575700	2.05977900	0.57436000
H	2.95680100	2.57020100	-1.06159400
H	1.25523700	2.17031000	-0.68139400
C	2.52283900	0.36760800	-2.44636300
H	2.57220200	-0.67555400	-2.78294500
H	1.60972400	0.81694600	-2.84814200
H	3.38839100	0.90610200	-2.85426300
C	-2.86090800	2.43464500	1.39038700
H	-3.22822100	3.12637800	2.15936600
H	-2.85238300	1.42340700	1.82057500
H	-3.57491500	2.44127300	0.55466300
O	-2.54505600	-0.98466100	0.73105000
N	-3.00723300	-1.55743000	-0.31015000
O	-3.73629400	-2.51008000	-0.26804900
O	-2.62630200	-1.02819800	-1.41286100
H	-0.76312500	2.84488100	1.75607100

^{3}TS1

Cu	-1.63642800	0.03300100	-0.26645600
O	-0.99175200	1.46904600	-1.31656700
H	4.37960700	-1.06202000	0.22473600
C	3.50763900	-1.71335000	0.39262700
C	2.67860600	-1.21749500	1.56630300
C	2.64148800	-1.79012600	-0.85353900
H	3.91705300	-2.70629000	0.62220600
H	3.29276200	-1.12671700	2.47527700
H	1.88688900	-1.95002400	1.78508400
H	3.22539900	-2.12741900	-1.72347400
H	1.84630000	-2.53385100	-0.69320600
N	1.22599300	0.06902800	0.00343800
O	0.09912000	-0.66851300	0.20680200
C	-0.12680300	2.25691300	-0.68341700
H	0.79069600	1.31622100	-0.29273000
H	0.38679400	2.95807200	-1.36821600
C	1.97368200	-0.46356600	-1.22691700

C	2.01089300	0.13817300	1.31740100
C	1.03378900	0.42343200	2.45200700
H	0.60120000	1.42795700	2.37033300
H	0.22622800	-0.31174800	2.48696800
H	1.58865500	0.38230700	3.39856900
C	3.02829500	1.27904200	1.28897800
H	2.59996500	2.19298700	0.85460700
H	3.31409100	1.51174500	2.32282900
H	3.95101400	1.04459100	0.75196100
C	2.98049500	0.56417500	-1.74039200
H	3.88666200	0.65041500	-1.13582600
H	3.29758100	0.26108900	-2.74628400
H	2.52674800	1.56019500	-1.83017500
C	0.96671700	-0.71636500	-2.34483000
H	0.22226300	-1.46259100	-2.05160300
H	0.44481800	0.19982200	-2.64334100
H	1.51538800	-1.10502900	-3.21277300
C	-0.61250900	2.93178500	0.58186900
H	0.19871600	3.45146400	1.10838700
H	-1.07339800	2.20987000	1.27249700
H	-1.38577900	3.67165800	0.32668400
O	-3.62338800	0.28444100	-0.19138700
N	-3.79302500	-0.87566900	0.32937100
O	-4.87022900	-1.30967800	0.61939200
O	-2.70222000	-1.51516400	0.50607500

$CuNO_3$

Cu	-1.22761300	-0.00003200	-0.00004400
O	0.50668200	-1.08394400	0.00013700
N	1.19168300	-0.00001600	0.00005700
O	2.39361800	-0.00032700	-0.00016400
O	0.50707300	1.08440100	0.00013700

TEMPOH

H	-0.00000300	2.19600400	1.16098100
C	-0.00000400	2.14238600	0.06121200
C	1.23864300	1.42151700	-0.44481000
C	-1.23864900	1.42151300	-0.44480900
H	-0.00000600	3.18361600	-0.28950500
H	2.16005100	1.90876600	-0.09171100
H	1.25074700	1.47367400	-1.54551100
H	-2.16005800	1.90876000	-0.09170900
H	-1.25075300	1.47367000	-1.54551000
N	0.00000200	-0.66387300	-0.43706300

O	0.00000600	-2.04302200	-0.15735600
C	-1.28949300	-0.05615500	-0.04301600
C	1.28949300	-0.05615000	-0.04301600
C	2.37519500	-0.74570200	-0.86671500
H	2.49592900	-1.79343500	-0.57033500
H	2.10893800	-0.72359100	-1.93042400
H	3.33696900	-0.23195600	-0.73069700
C	1.65595500	-0.19812400	1.44203500
H	1.61200400	-1.24497200	1.77348300
H	2.69364300	0.12874700	1.59208000
H	1.02658700	0.39947300	2.11041500
C	-1.65595400	-0.19812900	1.44203500
H	-1.02658800	0.39947000	2.11041500
H	-2.69364200	0.12874100	1.59208100
H	-1.61200200	-1.24497600	1.77348400
C	-2.37519400	-0.74570700	-0.86671600
H	-2.10893700	-0.72359600	-1.93042400
H	-2.49592700	-1.79344000	-0.57033500
H	-3.33696900	-0.23196300	-0.73069800
H	0.00000800	-2.13439000	0.81501200

int5

C	-0.23704400	0.41124400	0.00001000
O	-1.22078600	-0.28590800	-0.00000300
H	-0.32933100	1.52397600	-0.00002000
C	1.16430900	-0.13514100	-0.00000300
H	1.30465900	-0.77378300	-0.88072300
H	1.92262000	0.65403300	-0.00012400
H	1.30474700	-0.77358400	0.88084800

H_2O_HNO_3

H	-1.94617000	-0.84364100	-0.11254500
O	-2.35987300	0.03456800	-0.07474500
H	-2.83770300	0.05634500	0.76483800
O	0.11777300	1.08253900	-0.02308400
H	-0.84786200	0.80219700	-0.04710500
N	0.83081600	-0.07455300	0.00053200
O	0.19949700	-1.11871300	-0.01154400
O	2.01960600	0.06497800	0.03326000

int6

C	2.13569400	-0.22541800	0.00165700
H	1.88219200	0.83628400	-0.20835000
C	3.54060200	-0.65470700	-0.23583500

H	3.67140000	-1.71147200	0.01390600
H	3.80568900	-0.47924100	-1.28721100
H	4.22443400	-0.03591000	0.36052500
O	1.27567700	-0.98747500	0.41434600
H	-0.27131200	2.08201300	-0.13443400
O	0.56654900	2.56599500	-0.20306600
H	0.54422500	3.18147000	0.53918200
O	-1.04310800	0.32563000	0.50043500
H	-0.24455200	-0.29150300	0.51016400
N	-2.07926400	-0.40339600	-0.03862200
O	-1.84257200	-1.55790500	-0.29877900
O	-3.09592200	0.21911500	-0.17773200

TS2

C	-1.83908100	-0.24931200	-0.33942800
H	-1.60592100	0.01413600	-1.37865500
C	-3.24407100	-0.17492300	0.12217700
H	-3.26950400	-0.18631700	1.21579500
H	-3.75000400	0.71656500	-0.25888800
H	-3.77459000	-1.06146700	-0.24848500
O	-1.08493900	-1.11607200	0.23186600
H	-0.16487600	1.17403200	0.07496500
O	-1.13646400	1.37977600	0.30676800
H	-1.38311100	2.14175500	-0.24220300
O	0.87596600	0.13646500	-0.59684400
H	-0.12503600	-0.96229500	-0.13497200
N	2.06018100	-0.05061300	-0.04299400
O	2.37787700	-1.20479300	0.20089200
O	2.73639500	0.93753500	0.17943100

int6’

C	0.60702300	0.12771100	0.00108600
H	2.37079000	0.94595600	-0.87773800
H	2.38513300	0.90408700	0.88058300
O	0.07789100	-0.96382600	-0.00088300
H	-0.02354900	1.04437300	0.01388300
C	2.08473000	0.33605900	-0.01030500
H	-1.78665900	-0.37469000	0.13599500
O	-2.43669000	0.34827000	0.09079600
H	-2.83532300	0.24552900	-0.78065600
H	2.60948100	-0.62342500	-0.03604500

TS2’

C	-0.14297600	0.20126300	0.41854800

H	-0.03890600	0.07784500	1.51933100
C	-1.42553000	-0.34600800	-0.12787100
H	-1.35360600	-0.41094100	-1.21893200
H	-1.67098900	-1.32722600	0.29235200
H	-2.22987000	0.35782000	0.12153500
O	0.41001700	1.23163500	-0.14952300
H	1.22095900	0.26153600	-0.48547400
O	1.06449100	-0.85986100	-0.16612200
H	1.68738200	-1.06476500	0.55228600

int7

C	-0.04326900	-0.00642500	0.34699900
H	-0.10706000	0.04755400	1.45537200
C	1.39809200	0.02168300	-0.09638900
H	1.42824400	-0.00445400	-1.19150600
H	1.89453200	0.93541800	0.25283000
H	1.94185300	-0.84462400	0.29680500
O	-0.60519900	-1.18386000	-0.12330700
H	-1.56100000	-1.10740700	0.00956600
O	-0.78881000	1.06087400	-0.20328200
H	-0.57343500	1.86585900	0.28598700

int8

Cu	-1.04320400	0.49792900	-0.49066800
O	-0.44570500	1.12655200	1.25251500
H	4.38641500	-1.42881900	1.07323100
C	4.37949500	-1.36021400	-0.02430900
C	3.26456500	-2.20720900	-0.61384900
C	4.23488000	0.08330700	-0.47625800
H	5.34991300	-1.75310600	-0.35457200
H	3.32895000	-3.25014900	-0.27080200
H	3.36632800	-2.22787100	-1.71100800
H	5.03175200	0.71604900	-0.05935400
H	4.32875800	0.13423500	-1.57317000
N	1.81773500	-0.22434600	-0.53478000
O	0.87016300	0.22430200	-1.18436500
C	2.89690700	0.72771100	-0.07384900
C	1.84971200	-1.71132500	-0.28003000
C	0.82857500	-2.37806200	-1.18808600
H	-0.20141200	-2.17244900	-0.87314900
H	0.94543100	-2.07029300	-2.23362500
H	0.99039200	-3.46180700	-1.12397700
C	1.46902900	-1.96058400	1.18367000
H	0.59924600	-1.35277100	1.46250100

H	1.19123500	-3.01758700	1.28594900
H	2.28306900	-1.75319800	1.88486900
C	2.82585800	0.95189500	1.44133500
H	3.20480800	0.10304500	2.01845900
H	3.45853900	1.81790000	1.67386300
H	1.80850400	1.17561700	1.77718900
C	2.70225000	2.04541900	-0.80408800
H	2.68273600	1.90461600	-1.89138100
H	1.77849400	2.55825100	-0.51189000
H	3.54980500	2.69537100	-0.55447400
O	-3.25900400	0.45530000	-1.00201200
N	-2.88338700	0.13324300	-2.16470100
O	-3.63418400	-0.06001700	-3.08492400
O	-1.60872500	0.01242400	-2.30659400
N	-0.28230300	2.43148200	1.14157100
O	-0.55650500	2.92997000	0.04916100
O	0.15147100	3.02954500	2.10193400
O	-1.98126400	-1.46291000	0.62678300
H	-2.80838900	-1.17369200	0.19189100
C	-2.24095500	-1.41176100	2.03251200
C	-3.29685100	-2.41763800	2.41412400
H	-3.44537300	-2.42356800	3.49938700
H	-4.24900000	-2.13794800	1.94357200
H	-3.01380800	-3.42117500	2.07948900
O	-2.67844000	-0.16198800	2.42182600
H	-1.95497800	0.47093100	2.25533800
H	-1.26603100	-1.66882500	2.48478800

int9

Cu	-1.70797800	0.04671200	-0.33865500
O	0.56680300	2.62815500	-1.20820300
H	3.86159000	-2.23180100	0.92123700
C	3.31116300	-2.80630800	0.16270500
C	1.97308400	-3.27690500	0.70848800
C	3.11627800	-1.98724400	-1.10264600
H	3.93792200	-3.67923800	-0.06220000
H	2.09522600	-3.83663200	1.64735700
H	1.50091900	-3.96185000	-0.01446700
H	4.07407300	-1.61066900	-1.48967800
H	2.67930100	-2.62192500	-1.89042200
N	0.95171600	-1.30068400	-0.26757800
O	-0.11263200	-1.21389800	-0.86729900
C	2.20592500	-0.75284100	-0.92140300
C	0.98066600	-2.13228100	0.99692900

C	-0.41229200	-2.68952700	1.23360000
H	-1.12438600	-1.90244500	1.51592500
H	-0.81241000	-3.21540700	0.35970300
H	-0.35202000	-3.39658800	2.06993300
C	1.40958800	-1.28456300	2.19798700
H	0.88859600	-0.31927100	2.23478100
H	1.15212200	-1.84996900	3.10282600
H	2.48494800	-1.09096000	2.22786900
C	2.86564200	0.31448100	-0.04181400
H	3.52653900	-0.10484300	0.72238800
H	3.46953200	0.96070100	-0.69099800
H	2.12697700	0.95358500	0.45142400
C	1.82595700	-0.16690600	-2.26719400
H	1.29401200	-0.88969800	-2.89629100
H	1.22175000	0.74432900	-2.16099200
H	2.75531100	0.11981600	-2.77429600
O	-3.85669500	0.47308000	-0.24852000
N	-4.02108400	-0.61241100	-0.87118100
O	-5.09153900	-1.05472500	-1.18844300
O	-2.92435500	-1.24014800	-1.15131600
N	1.68497400	3.10928900	-0.79563700
O	2.58671000	3.28604600	-1.59704700
O	1.81500200	3.35647500	0.42076800
O	-0.47079200	1.18292200	0.55118500
H	-0.03556300	1.82221600	-0.14666000
C	-0.78095200	1.98996200	1.71718000
H	-1.12589900	2.96395900	1.32821200
C	-1.84103800	1.30227600	2.53100700
H	-2.05811700	1.89549900	3.42541200
H	-2.76925900	1.17400500	1.96104100
H	-1.47291700	0.32005400	2.86064900
O	0.36222600	2.12070400	2.46881300
H	0.98193600	2.65934900	1.93045900

int10

Cu	-1.61586500	0.13849400	0.37049700
O	-1.06333000	1.89478300	0.46998900
H	4.32137900	-1.26520700	-0.29893000
C	3.53281600	-1.91773800	0.10575200
C	2.96433100	-1.34057300	1.39610000
C	2.43354300	-2.13552800	-0.92594700
H	4.02336200	-2.87630400	0.32172800
H	3.75658000	-1.17023900	2.14067700
H	2.25538300	-2.06055800	1.83558300

H	2.84387900	-2.53534200	-1.86527700
H	1.71833000	-2.88120000	-0.54262400
N	1.20588900	-0.30325900	0.08679600
O	0.10994100	-0.77535800	0.51064500
C	-0.12986400	2.22663300	-0.41472800
C	1.63486900	-0.86227100	-1.26350700
C	2.21282900	-0.01247300	1.18902600
C	1.43497900	0.37569700	2.43904000
H	0.80644500	1.25804800	2.25610200
H	0.78974000	-0.43400400	2.79180400
H	2.15315400	0.61557400	3.23278500
C	3.17280300	1.12165800	0.84232000
H	2.64186800	2.01397100	0.48917900
H	3.70836300	1.39864900	1.75908700
H	3.93169800	0.85477600	0.10293200
C	2.44880200	0.13681700	-2.07854200
H	3.44938600	0.33263600	-1.68547800
H	2.57817500	-0.28176800	-3.08477500
H	1.91216700	1.08849400	-2.18804200
C	0.38174900	-1.20938600	-2.05533000
H	-0.26293600	-1.92376300	-1.53392400
H	-0.19384300	-0.30126700	-2.28071400
H	0.69593300	-1.65699300	-3.00680200
C	0.43604100	3.61799100	-0.15217800
H	1.22825800	3.84955500	-0.87471200
H	0.83380500	3.68573600	0.86775400
H	-0.36750200	4.35786800	-0.25708300
O	-3.79157400	0.16153400	0.17455500
N	-3.74584500	-1.09907500	0.13703300
O	-4.71316500	-1.80547500	0.01680700
O	-2.55866300	-1.59352900	0.23787900
H	0.74251800	1.49503700	-0.36282700
O	-0.55566300	2.09913000	-1.76551400
H	-1.48410500	2.38263900	-1.77458100

TS3

Cu	-1.66665900	0.17057900	0.21520500
O	-0.98715300	1.90272800	0.37978900
H	4.21225600	-1.53313500	-0.06133200
C	3.31615600	-2.12587600	0.17869200
C	2.64571800	-1.60507400	1.44323800
C	2.33968200	-2.12489000	-0.98949400
H	3.67590000	-3.14889900	0.35121900
H	3.35054900	-1.58935200	2.28831900

H	1.82168200	-2.27913200	1.72267700
H	2.82626600	-2.47707000	-1.91153500
H	1.51716700	-2.82405300	-0.77416200
N	1.15407100	-0.24433100	0.05267400
O	0.03684600	-0.81525000	0.32848000
C	0.05176100	2.21222700	-0.31742500
H	0.82927600	1.21896400	-0.19346500
C	1.71526200	-0.75401400	-1.28552900
C	2.06851200	-0.19182100	1.28714000
C	1.19523600	0.16705300	2.48218500
H	0.69193700	1.13246100	2.33885300
H	0.42714300	-0.58829300	2.66765100
H	1.83431900	0.23848500	3.37116800
C	3.17619200	0.84826500	1.15974500
H	2.79654300	1.81954100	0.82224900
H	3.61196000	0.99964300	2.15536400
H	3.99544300	0.54921500	0.50122900
C	2.71721900	0.22160700	-1.89025300
H	3.68690200	0.24696300	-1.38696600
H	2.90321400	-0.08156600	-2.92827000
H	2.30981700	1.24064000	-1.91871800
C	0.54834700	-0.91128800	-2.25273800
H	-0.20624000	-1.60944000	-1.87872200
H	0.06653100	0.05366700	-2.45422400
H	0.94308500	-1.30342600	-3.19916100
C	0.83534900	3.41705900	0.18700900
H	1.78359200	3.55041500	-0.35227800
H	1.04462900	3.31613800	1.25667200
H	0.21654600	4.31208300	0.04176900
O	-3.84742800	0.26203900	0.44086900
N	-3.88097700	-0.95075600	0.09568900
O	-4.89846300	-1.59107500	-0.00801000
O	-2.73036300	-1.47733700	-0.14486000
O	-0.20694800	2.27825500	-1.69825700
H	0.49439600	2.78060500	-2.13733100

CH3COOH

C	-1.38738500	-0.09756600	-0.00000100
H	-1.90471900	0.86369600	0.00014100
H	-1.67878600	-0.67990300	-0.88141500
H	-1.67879000	-0.68014600	0.88125300
C	0.09275500	0.12519000	0.00000600
O	0.65527800	1.19132800	-0.00000200
O	0.76031500	-1.04811200	0.00000000

H	1.70532500	-0.81511300	0.00000000

TEMPO+

H	0.00000000	2.29693100	0.91400700
C	0.00000000	2.10015600	-0.16724600
C	1.24270700	1.33896900	-0.59290400
C	-1.24270600	1.33896800	-0.59290500
H	0.00000000	3.08633500	-0.64598300
H	2.15937800	1.87172100	-0.30458100
H	1.26652600	1.25540800	-1.69040100
H	-2.15937800	1.87172000	-0.30458500
H	-1.26652200	1.25540500	-1.69040200
N	0.00000000	-0.77135500	-0.12573400
O	0.00000200	-1.94867100	-0.28507500
C	-1.35873700	-0.06651800	0.00161600
C	1.35873700	-0.06651700	0.00161600
C	2.38207700	-0.91165500	-0.73491800
H	2.55184700	-1.88056000	-0.25576800
H	2.09795200	-1.07647700	-1.78106900
H	3.32781800	-0.35704600	-0.72684800
C	1.66946800	-0.05426600	1.50681100
H	1.57565800	-1.05654400	1.94241400
H	2.71653900	0.25782700	1.60476900
H	1.05547400	0.64880600	2.07596100
C	-1.66946900	-0.05426500	1.50681000
H	-1.05547300	0.64880300	2.07596100
H	-2.71653900	0.25783100	1.60476700
H	-1.57566300	-1.05654400	1.94241300
C	-2.38207900	-0.91165400	-0.73491800
H	-2.09795400	-1.07647600	-1.78106900
H	-2.55185000	-1.88055900	-0.25576700
H	-3.32781900	-0.35704400	-0.72684700

TS4

H	3.22185300	0.54518900	0.52221200
C	2.80967900	0.49886200	-0.49646500
C	2.25285800	-0.88711200	-0.79202200
C	1.75175800	1.57457200	-0.69977900
H	3.65846600	0.69545000	-1.16342300
H	3.00973100	-1.66458200	-0.61244600
H	1.97250400	-0.95111900	-1.85563300
H	2.15005300	2.56981200	-0.45526200
H	1.45461500	1.60011300	-1.76059400
N	0.04175500	-0.07399200	-0.12360300

O	-0.65767300	-0.18476600	-1.23379900
H	-1.58540100	-1.21542700	1.32211100
C	0.48027900	1.35270800	0.13979800
C	1.00783400	-1.23072200	0.04462300
C	0.35458600	-2.50171800	-0.48406400
H	-0.52296500	-2.79828600	0.11450000
H	0.05902000	-2.42652100	-1.53386000
H	1.07570700	-3.32235600	-0.39602900
C	1.36018800	-1.45790600	1.51401700
H	0.47575300	-1.44222000	2.16693100
H	1.81741600	-2.44973900	1.61059400
H	2.07803900	-0.74050400	1.91619400
C	0.71583800	1.59104000	1.62833000
H	1.63731400	1.15085700	2.01497500
H	0.79274600	2.67240300	1.79305000
H	-0.12912900	1.22696300	2.22625500
C	-0.62057400	2.30124300	-0.31150900
H	-0.88326800	2.18162000	-1.36685400
H	-1.51942000	2.18248900	0.31004300
H	-0.26471400	3.32850200	-0.17137400
H	-1.69102400	-0.35754500	-1.00291700
C	-2.82254800	-0.69848800	-0.04871800
O	-2.14323700	-0.46236500	1.05190800
H	-2.89586100	-1.74260700	-0.37923900
C	-3.85426900	0.29393400	-0.41229300
H	-3.50952000	1.31616900	-0.21764800
H	-4.15099400	0.19311300	-1.46026600
H	-4.74969500	0.12474700	0.20753100

TS4'

O	2.65612800	-0.22976300	-1.11452400
H	-2.84044700	0.49532400	1.29067200
C	-2.78925600	0.42528200	0.19465500
C	-1.89830900	1.51291500	-0.38308800
C	-2.31826200	-0.95055900	-0.24816700
H	-3.81737200	0.57816500	-0.15542300
H	-2.23548000	2.51108100	-0.06871000
H	-1.95317700	1.49088000	-1.48180900
H	-2.95591300	-1.74048800	0.17444000
H	-2.39850300	-1.03096400	-1.34289500
N	-0.01223200	-0.07686100	-0.38968400
O	0.25955400	-0.17026800	-1.62007700
C	2.43867400	-0.60337300	0.12327400
H	1.06679000	-0.22884500	0.25434000

H	2.23046500	-1.67278100	0.28700100
C	-0.87660000	-1.29367200	0.14675900
C	-0.42653300	1.39645500	0.02184000
C	0.43690100	2.33637100	-0.79888200
H	1.50408900	2.23047900	-0.56668600
H	0.30133100	2.18969500	-1.87280800
H	0.14443100	3.36363000	-0.55050400
C	-0.19726000	1.65050400	1.50179200
H	0.83203600	1.42262800	1.80852400
H	-0.34412800	2.72311100	1.67773800
H	-0.88405100	1.12516400	2.16772700
C	-0.70349500	-1.48910900	1.64482300
H	-1.28148500	-0.79292600	2.25645400
H	-1.05709700	-2.49666800	1.89482300
H	0.34736900	-1.43892900	1.96388300
C	-0.41841700	-2.53669500	-0.59492400
H	-0.47264700	-2.41878900	-1.67942100
H	0.59705300	-2.84927900	-0.31687400
H	-1.08632500	-3.35834100	-0.30957900
C	3.20858200	0.12217800	1.16547900
H	2.79920600	-0.05434800	2.16533600
H	3.25547700	1.19600600	0.95666700
H	4.23958200	-0.26272400	1.15607200
H	2.03281800	-0.66458500	-1.74571400

TS5

H	3.28120700	-0.02838500	1.05738700
C	3.15629800	-0.02935400	-0.03552100
C	2.40164700	-1.26183200	-0.49989100
C	2.43941600	1.22349800	-0.50856300
H	4.17211500	-0.04944700	-0.44958000
H	2.90030800	-2.18640300	-0.17604200
H	2.38788200	-1.27721800	-1.60129800
H	2.97631100	2.13285100	-0.20292700
H	2.40164500	1.22808000	-1.60982600
N	0.31490200	0.01991600	-0.29731200
O	-0.54696000	0.04274100	-1.25036500
H	-1.60175600	-0.41667600	1.62991100
C	0.99947500	1.33800000	0.02326700
C	0.93967900	-1.33098500	-0.01721000
C	0.20796200	-2.40349600	-0.80744300
H	-0.84229600	-2.49733900	-0.50287700
H	0.24677400	-2.22350500	-1.88641000
H	0.69857100	-3.36302000	-0.60442900

C	0.84558600	-1.67632100	1.46763500
H	-0.20147100	-1.82147000	1.77600300
H	1.34459900	-2.63825300	1.63786400
H	1.31038800	-0.94524800	2.13283300
C	0.99943900	1.63877900	1.52155800
H	1.64548200	0.97881000	2.10684300
H	1.38631400	2.65587200	1.66058300
H	-0.01246400	1.61274900	1.93922800
C	0.26756100	2.45685900	-0.69804700
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C	-2.64882700	-0.02086600	0.08423100
O	-1.92681400	0.36055800	1.13559300
C	-3.62486500	0.99067800	-0.42880900
H	-3.14731400	1.97200900	-0.50346000
H	-4.00594700	0.70771000	-1.41534100
H	-4.46596800	1.06471800	0.27496700
O	-2.98003400	-1.32315300	0.14377200
H	-3.60145400	-1.56936100	-0.56173000

TS5'

O	2.43972300	0.44192000	-1.18090200
H	-3.03525900	0.11221800	1.35719200
C	-3.00496000	0.06151100	0.25947300
C	-2.30358700	1.27486800	-0.32798700
C	-2.34341900	-1.22110500	-0.21368900
H	-4.05411400	0.05978300	-0.06073000
H	-2.77422500	2.20901800	0.01062000
H	-2.38378900	1.25759700	-1.42544300
H	-2.83391000	-2.10350000	0.22223800
H	-2.45313000	-1.30569900	-1.30546300
N	-0.20465300	-0.01126100	-0.42477800
O	0.05156500	-0.04358700	-1.64501400
C	2.35763800	-0.03460900	0.04703900
H	1.00140200	0.02267500	0.22540200
C	-0.84693900	-1.35431800	0.11325100
C	-0.81863500	1.37289300	0.04239800
C	-0.13535900	2.46108200	-0.76362800
H	0.92514700	2.56867100	-0.50476000
H	-0.21245300	2.28897600	-1.83952100
H	-0.63153800	3.41063000	-0.52975700
C	-0.61571900	1.62209000	1.52749000

H	0.42471100	1.47738400	1.84310800
H	-0.85834200	2.67424900	1.72026800
H	-1.26035200	1.02602700	2.17646200
C	-0.57706800	-1.55056800	1.59551600
H	-1.18735600	-0.92840200	2.25357900
H	-0.80339400	-2.59453600	1.84400300
H	0.47907000	-1.38727300	1.84972600
C	-0.26547400	-2.50651000	-0.68758500
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H	2.62174900	1.89744600	0.94896000
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H	2.01999300	-0.16398700	-1.83219300
O	2.63322800	-1.35565000	0.12468900
H	2.80118300	-1.62810000	1.04192100

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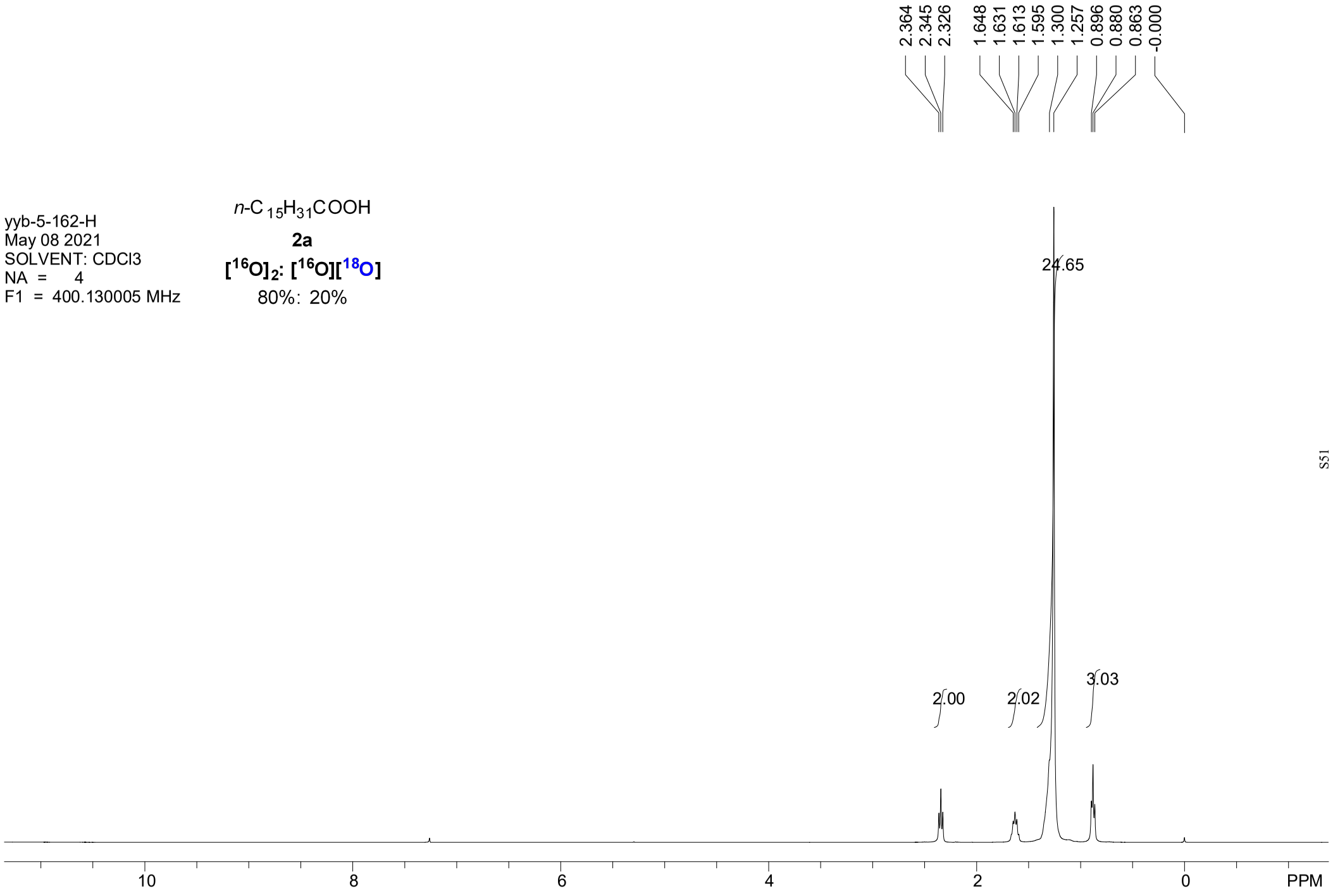
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1.648
1.631
1.613
1.595
1.300
1.257
0.896
0.880
0.863
-0.000
yyb-5-162-H
May 08 2021
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NA = 4
F1 = 400.130005 MHz
n-C15H31COOH
2a
[16O]2: [16O][18O]
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3.03
S51
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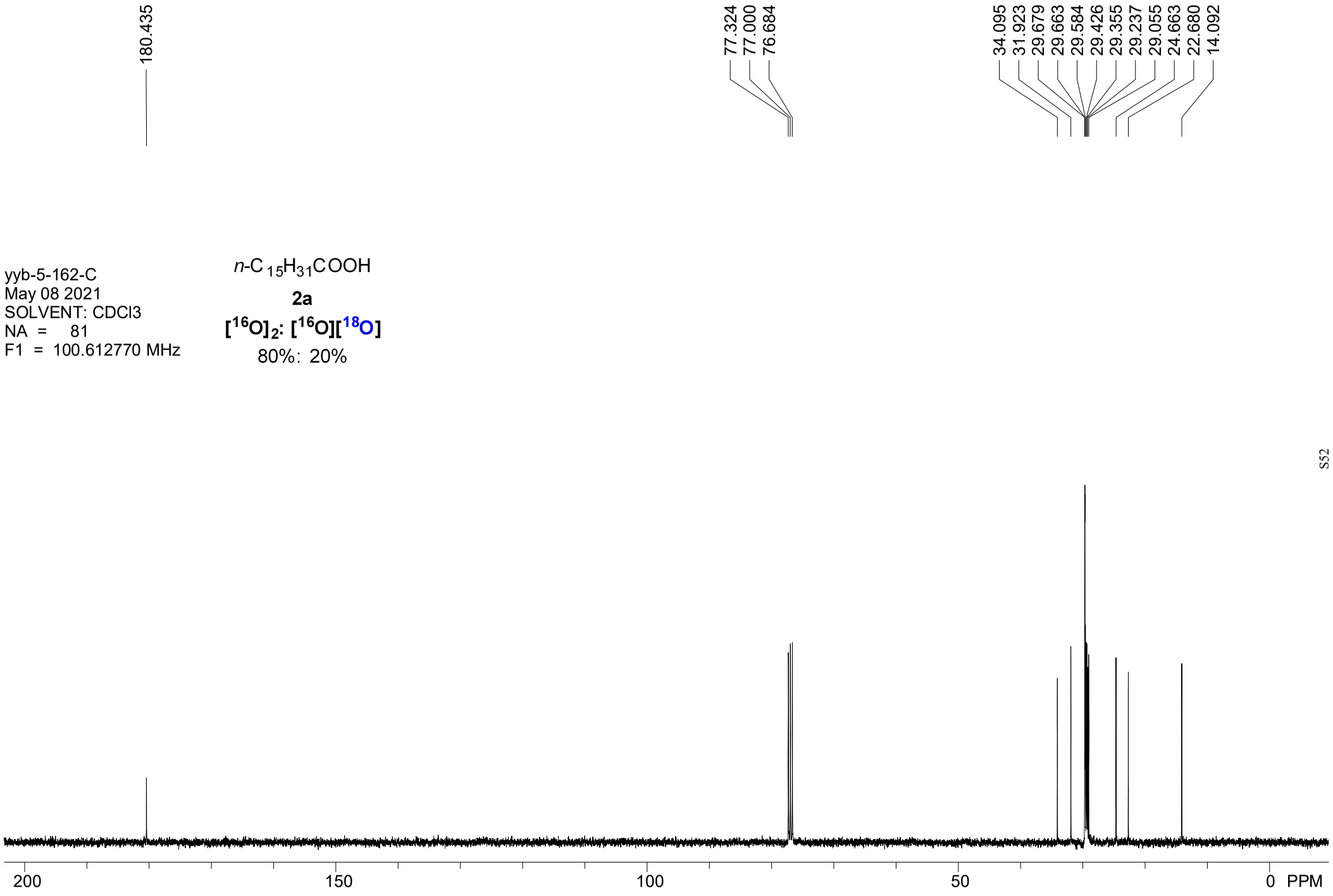
8
6
4
2
0
PPM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29.055
24.663
22.680
14.092
yyb-5-162-C
May 08 2021
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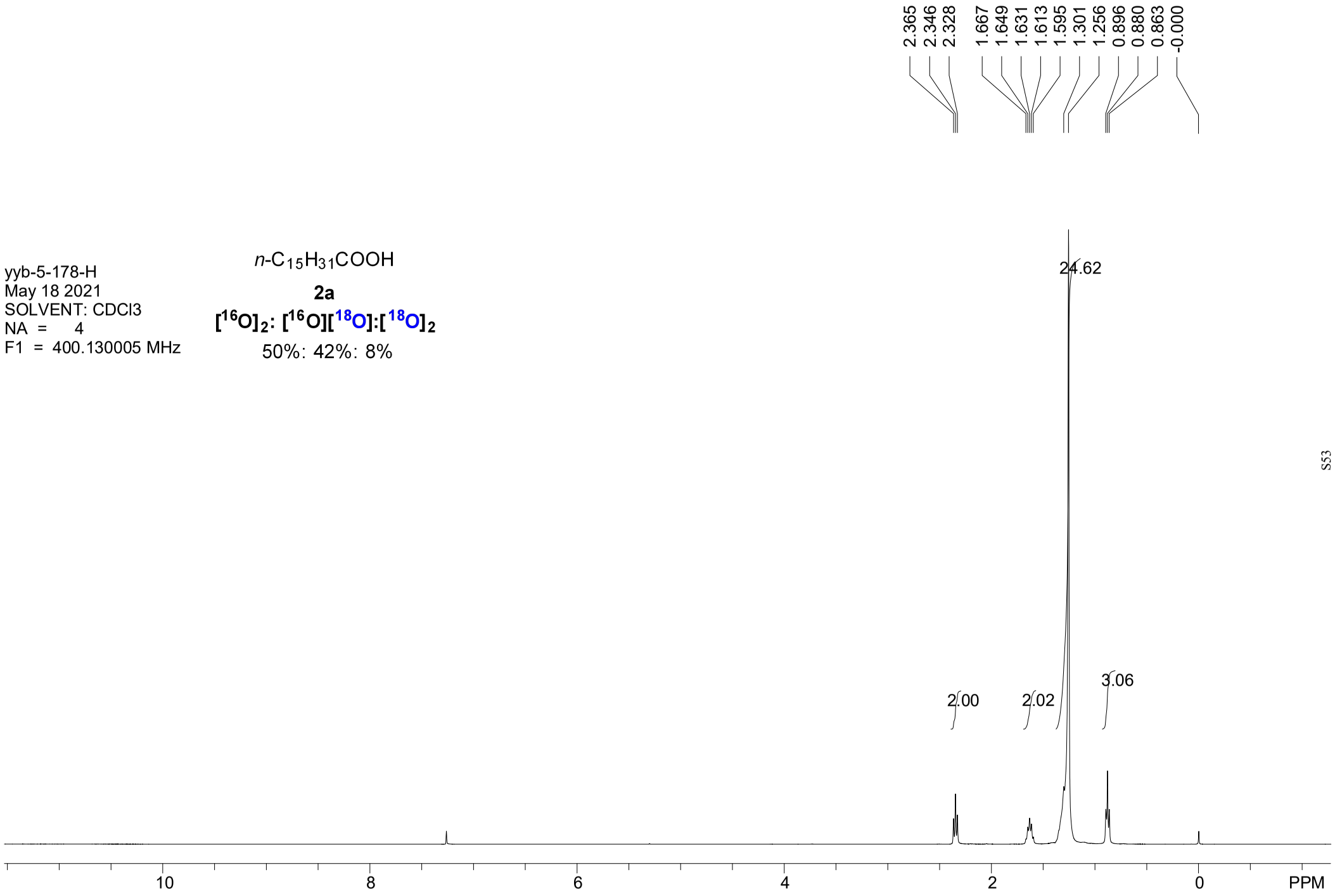
50
0
PPM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0.863
-0.000
yyb-5-178-H
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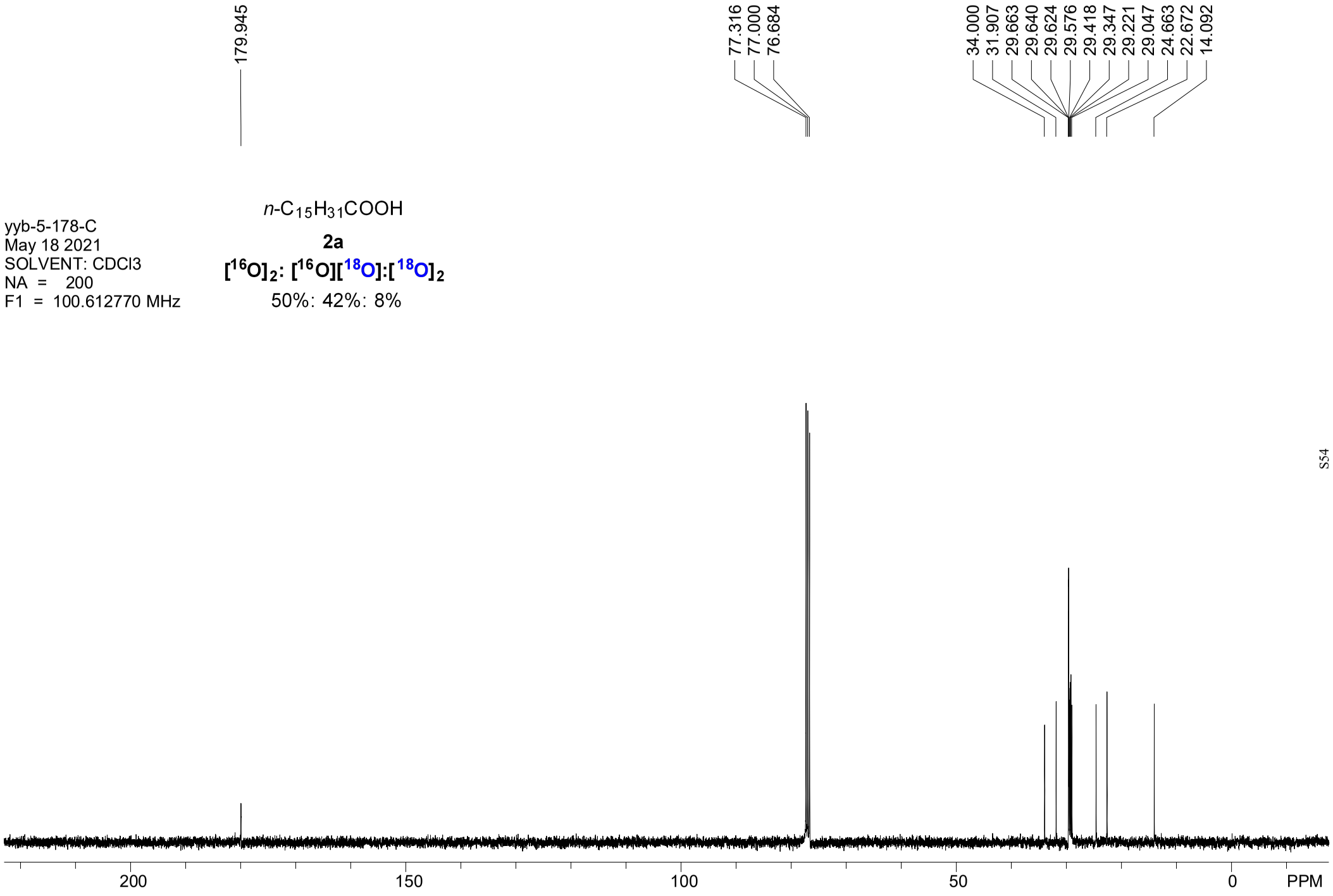
6
4
2
0
PPM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29.221
29.047
24.663
22.672
14.092
yyb-5-178-C
May 18 2021
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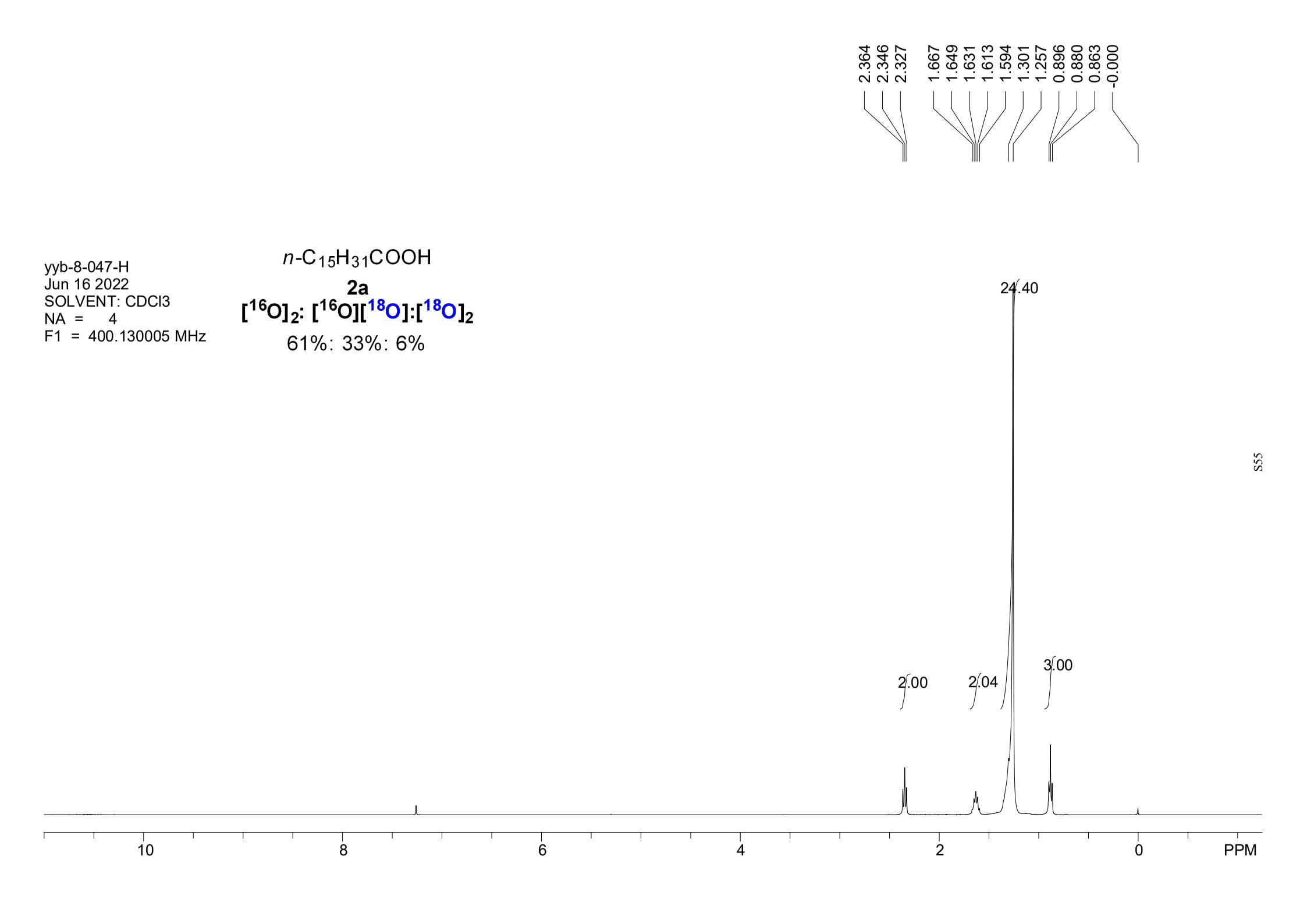
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0.863
-0.000
yyb-8-047-H
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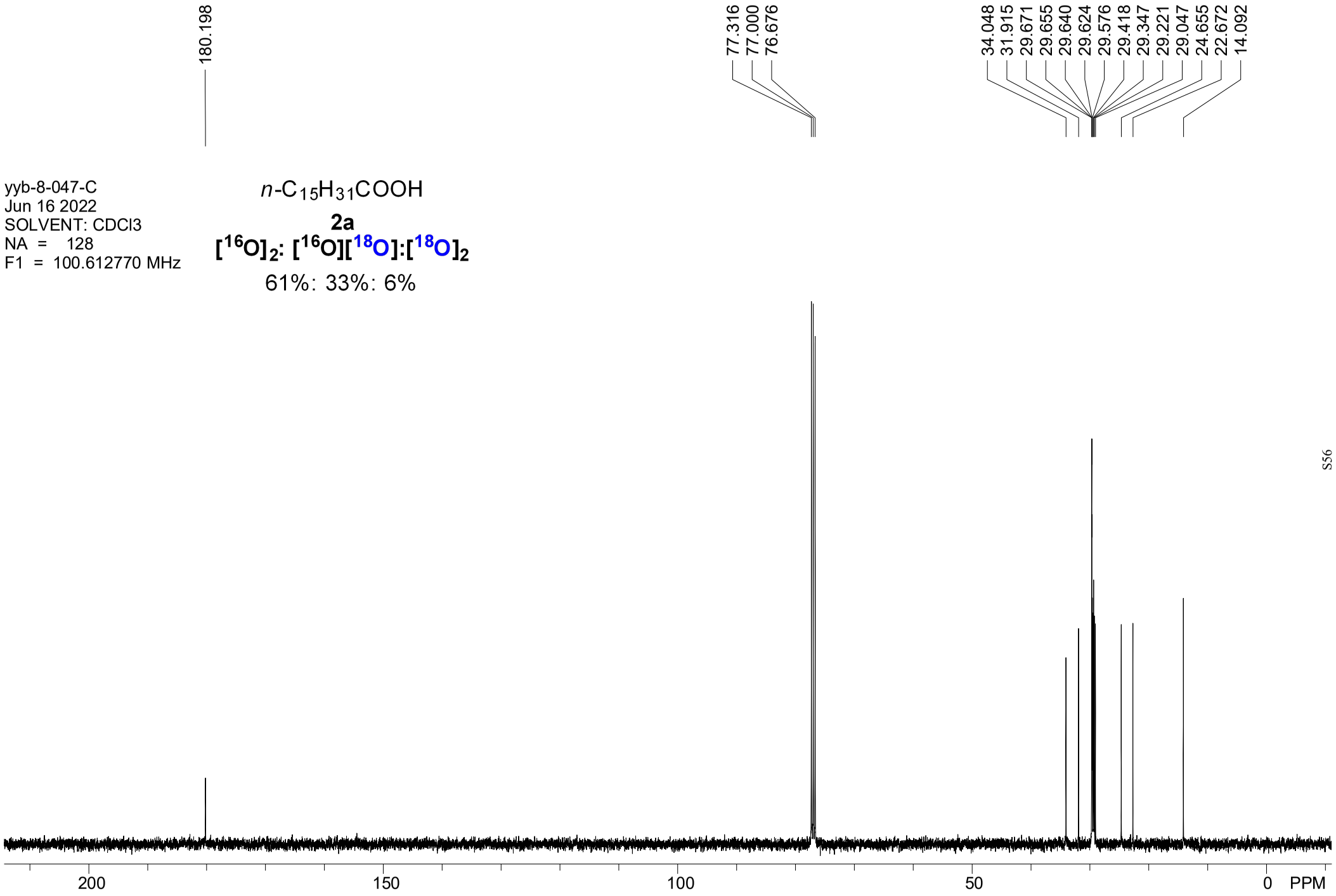
PPM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29.047
24.655
22.672
14.092
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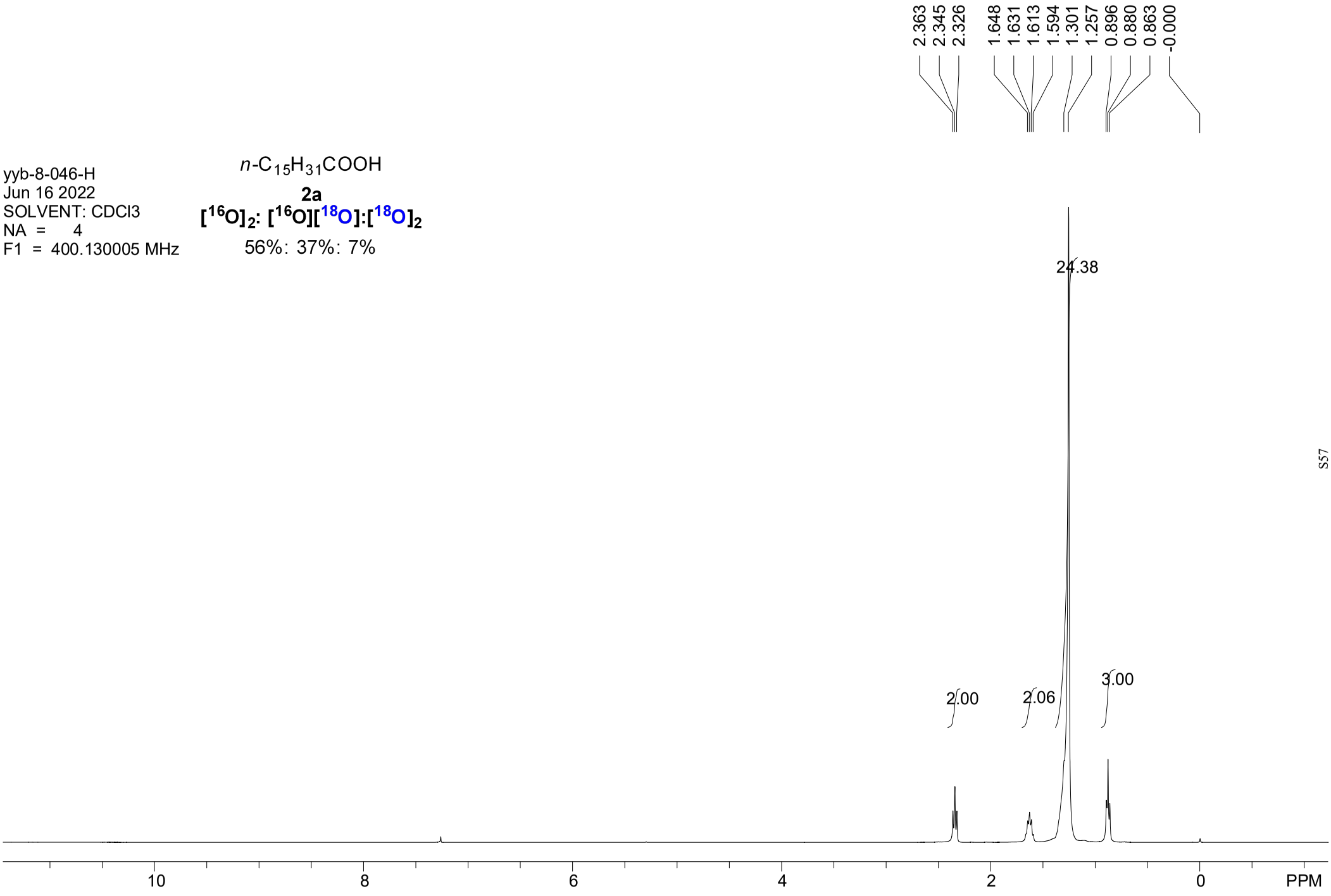
PPM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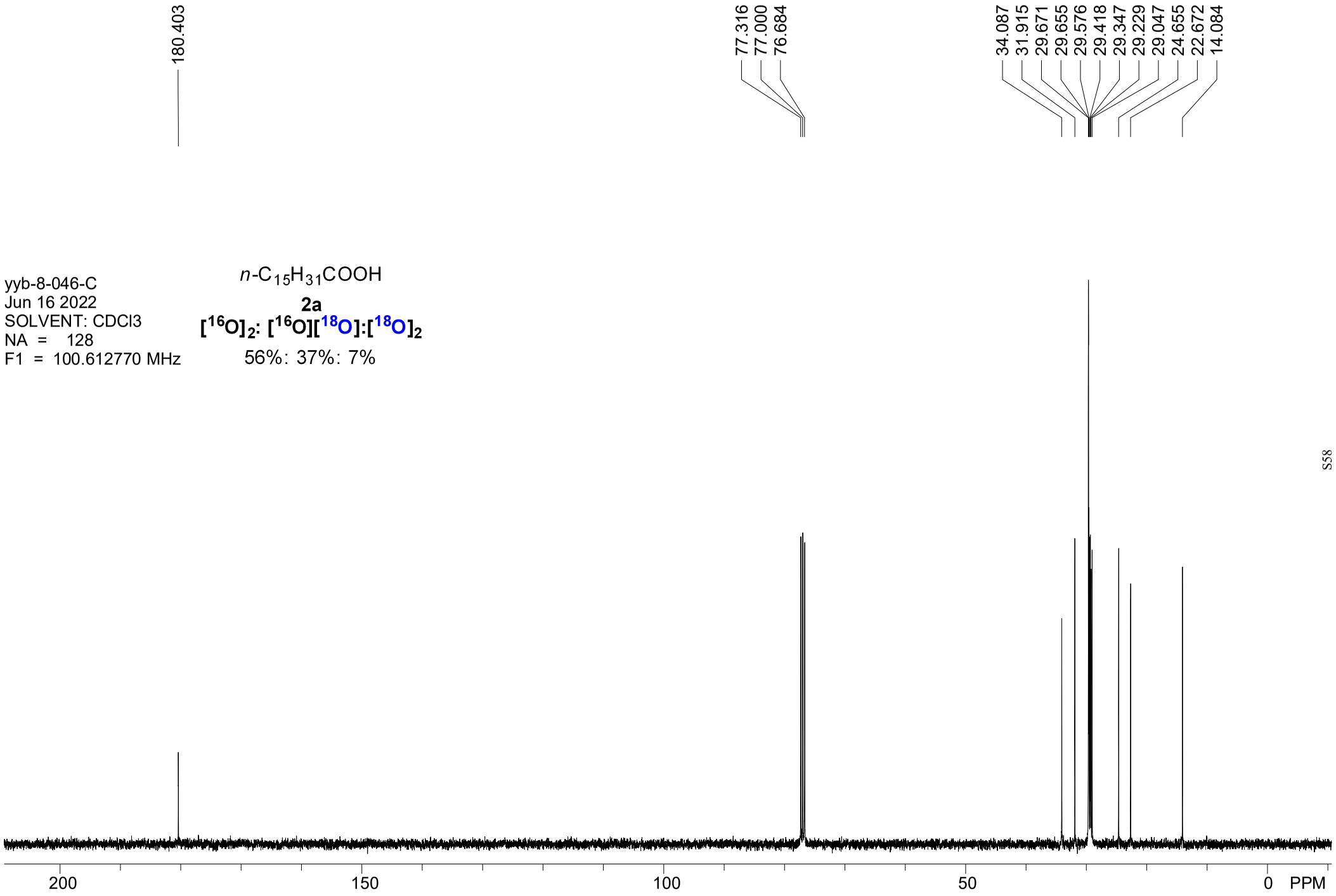
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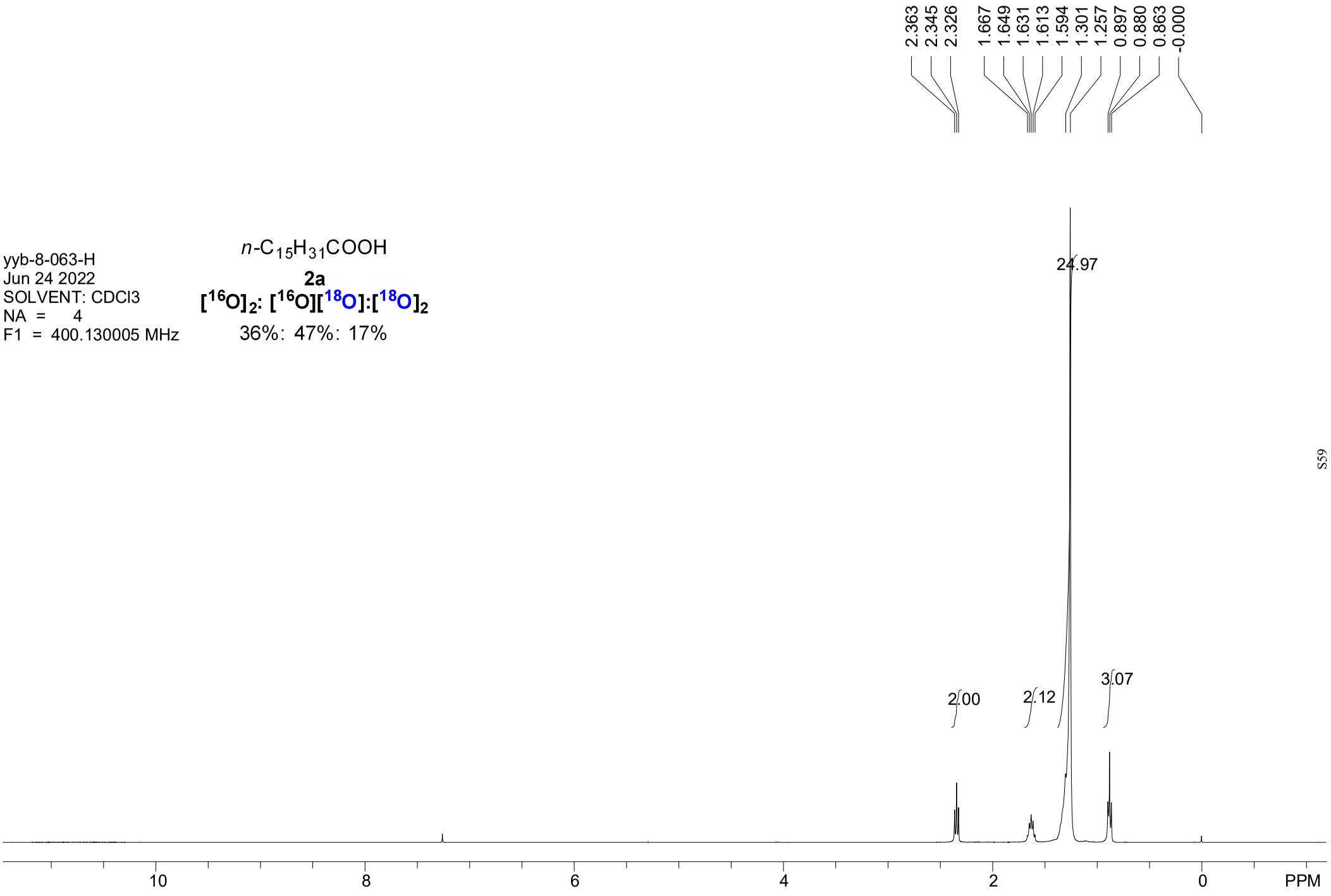
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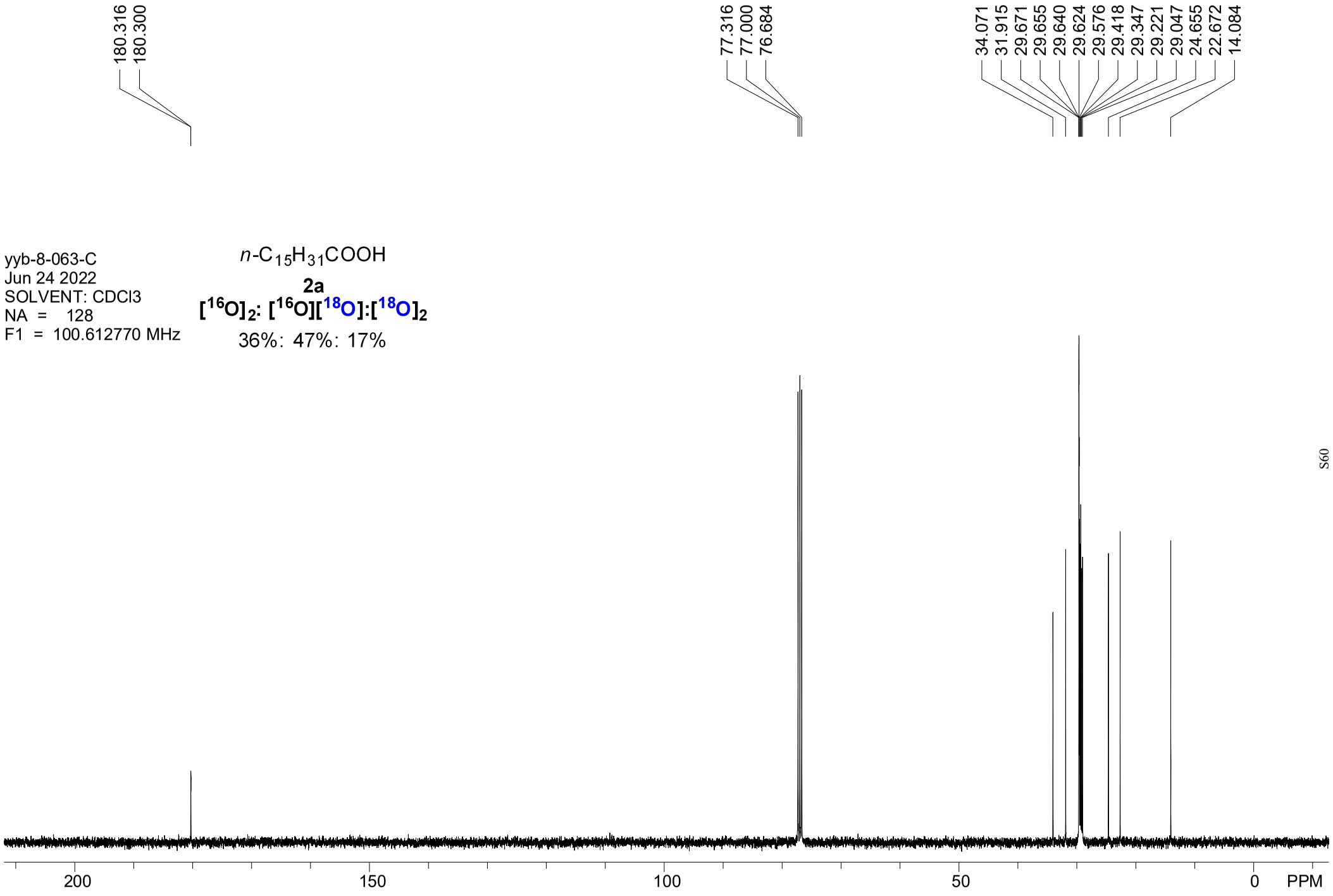
180.316
180.300
77.316
77.000
76.684
34.071
31.915
29.671
29.655
29.640
29.624
29.576
29.418
29.347
29.221
29.047
24.655
22.672
14.084
yyb-8-063-C
Jun 24 2022
SOLVENT: CDCl3
NA = 128
F1 = 100.612770 MHz
n-C15H31COOH
2a
[16O]2: [16O][18O]:[18O]2
36%: 47%: 17%
S60
200
150
100
50
0
PPM