

# Atypical Dearomative Spirocyclization of $\beta$ -Naphthols with Diazoacetamides using a Silver Catalyst

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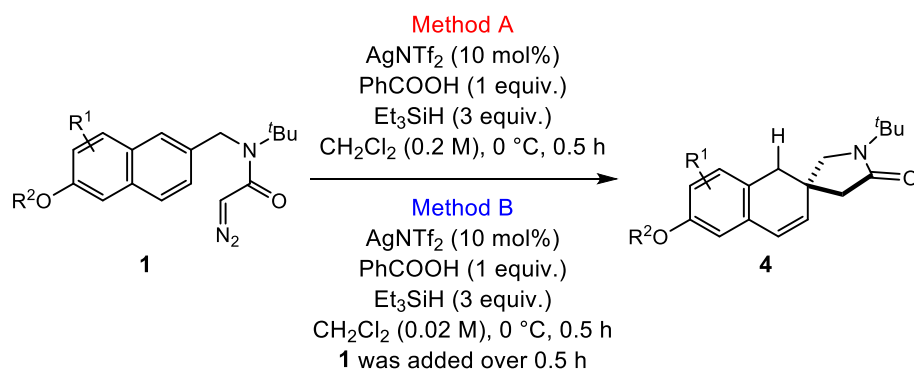
## Supporting Information

### 1. [General Information](#)

NMR spectra were recorded at 400 MHz or 600 MHz for  $^1\text{H}$  NMR, 100 MHz or 150 MHz for  $^{13}\text{C}$  NMR, and 564 MHz for  $^{19}\text{F}$  NMR. Chemical shifts in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$ , or  $\text{DMSO-d}_6$ , were reported downfield from TMS (= 0 ppm) or solvent signals [ $\text{CH}_3\text{OH}$  (3.31 ppm),  $\text{DMSO}$  (2.50 ppm)] for  $^1\text{H}$  NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, and br = broad), integration and coupling constants in Hz. For  $^{13}\text{C}$  NMR, chemical shifts were reported in the scale relative to the solvent signal [ $\text{CHCl}_3$  (77.16 ppm),  $\text{CH}_3\text{OH}$  (49.00 ppm),  $\text{DMSO}$  (39.52 ppm)] as an internal reference. ESI mass spectra were measured on JEOL AccuTOF LC-plus JMS-T100LP. Optical rotations were measured on a JASCO P-1020 polarimeter. Melting points were measured with a SIBATA NEL-270 melting point apparatus. The UV-Vis spectrometer was a JASCO V-730 spectrometer. Analytical thin layer chromatography was performed on Kieselgel 60F254, 0.25 mm-thick plates. Column chromatography was performed with silica gel 60 N (spherical, neutral 63-210 mesh). Reactions were conducted in dry solvent. Other reagents were purified by the usual methods.

2. [Characterization of Dearomatized Cyclic Products 4a–4i, 5a, 6a, 7c, 8c, 9a–9l, 10a](#)

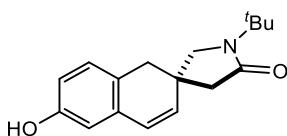
**General Procedure A for Reductive Dearomatization**



**Method A:** A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with AgNTf<sub>2</sub> (3.9 mg, 0.01 mmol, 10 mol%), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and triethylsilane (47.9 μL, 0.3 mmol, 3 equiv.), which were subsequently dissolved partially in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under an argon gas atmosphere. Diazo compound **1** (0.1 mmol) was added to the suspension at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water and 1 M TBAF in THF (0.1 mL), and stirred for 15 min at room temperature. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> × 2. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 3/1 → 1/1) to afford spirocyclic compound **4**.

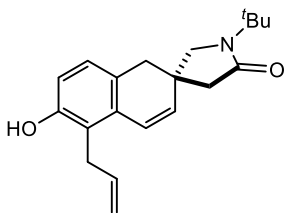
**Method B:** A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with AgNTf<sub>2</sub> (3.9 mg, 0.01 mmol, 10 mol%), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and triethylsilane (47.9 μL, 0.3 mmol, 3 equiv.), which were subsequently dissolved partially in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) under an argon gas atmosphere. Diazo compound **1** (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added slowly over 0.5 h *via* a syringe pump to the suspension at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water and 1 M TBAF in THF (0.1

mL), and stirred for 15 min at room temperature. The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2 \times 2$ . The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 3/1  $\rightarrow$  1/1) to afford spirocyclic compound **4**.



**1'-(*tert*-Butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4a)**

Prepared according to the general procedure A (Method A) using **1a** (29.7 mg), and isolated as white solid (21.6 mg, 80% yield).: m.p. 220–221 °C;  $R_f$  = 0.4 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (d,  $J$  = 9.6 Hz, 1H), 6.63 (d,  $J$  = 9.6 Hz, 1H), 6.58 (s, 1H), 6.39 (d,  $J$  = 9.6 Hz, 1H), 5.86 (d,  $J$  = 9.6 Hz, 1H), 5.67 (br s, 1H), 3.37 (d,  $J$  = 10.8 Hz, 1H), 3.30 (d,  $J$  = 10.8 Hz, 1H), 2.81 (d,  $J$  = 15.6 Hz, 1H), 2.77 (d,  $J$  = 15.6 Hz, 1H), 2.38 (d,  $J$  = 18.6 Hz, 1H), 2.35 (d,  $J$  = 18.6 Hz, 1H), 1.39 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 155.1, 134.9, 134.3, 129.4, 128.5, 124.9, 114.2, 113.5, 55.8, 54.2, 45.5, 38.6, 36.8, 27.9 (3C); IR (ATR) 3113, 2970, 2928, 1730, 1650, 1601, 1445, 1421, 1365, 1284, 1218  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{21}\text{NNaO}_2^+$   $m/z$  294.1465, found  $m/z$  294.1465.

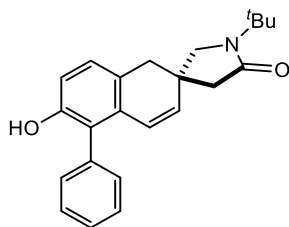


**5-Allyl-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4b)**

Prepared according to the general procedure A (Method B) using **1b** (33.7 mg), and isolated as yellow solid (24.3 mg, 78% yield).: m.p. 69–71 °C;  $R_f$  = 0.5 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.84 (d,  $J$  = 7.8 Hz, 1H),

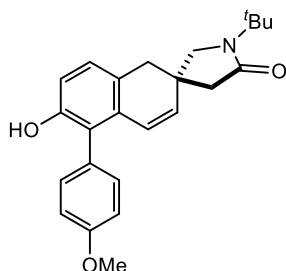
## Supporting Information

6.66 (d,  $J = 9.6$  Hz, 1H), 6.65 (d,  $J = 7.8$  Hz, 1H), 5.95 (ddt,  $J = 16.8, 9.6, 6.0$  Hz, 1H), 5.88 (d,  $J = 9.6$  Hz, 1H), 5.01 (dd,  $J = 9.6, 1.8$  Hz, 1H), 4.92 (dd,  $J = 16.8, 1.8$  Hz, 1H), 3.47 (d,  $J = 6.0$  Hz, 2H), 3.37 (d,  $J = 10.2$  Hz, 1H), 3.31 (d,  $J = 10.2$  Hz, 1H), 2.79 (d,  $J = 15.6$  Hz, 1H), 2.75 (d,  $J = 15.6$  Hz, 1H), 2.36 (d,  $J = 16.8$  Hz, 1H), 2.33 (d,  $J = 16.8$  Hz, 1H), 1.39 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 153.6, 136.4, 134.8, 132.3, 127.3, 125.6, 125.0, 122.0, 115.3, 114.2, 55.9, 54.3, 44.9, 39.6, 36.1, 29.6, 27.9 (3C); IR (ATR) 3275, 2971, 2926, 2876, 1739, 1649, 1365, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{25}\text{NNaO}_2^+$   $m/z$  334.1778, found  $m/z$  334.1770.



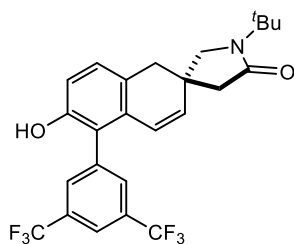
### 1'-(*tert*-Butyl)-6-hydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4c)

Prepared according to the general procedure A (Method B) using **1c** (37.3 mg), and isolated as yellow solid (25.4 mg, 73% yield).: m.p. 225–227 °C;  $R_f = 0.4$  (*n*-hexane/EtOAc, 2/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J = 8.4, 8.4$  Hz, 2H), 7.43 (dd,  $J = 8.4, 8.4$  Hz, 1H), 7.29 (d,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 9.6$  Hz, 1H), 6.83 (d,  $J = 9.6$  Hz, 1H), 6.16 (d,  $J = 10.8$  Hz, 1H), 5.76 (d,  $J = 10.8$  Hz, 1H), 5.26 (br s, 1H), 3.41 (d,  $J = 10.8$  Hz, 1H), 3.28 (d,  $J = 10.8$  Hz, 1H), 2.87 (d,  $J = 15.6$  Hz, 1H), 2.84 (d,  $J = 15.6$  Hz, 1H), 2.39 (s, 2H), 1.39 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 152.1, 135.0, 134.3, 131.7, 130.9, 130.8, 129.4, 129.3, 128.8, 128.4, 126.3, 125.6, 125.1, 114.0, 55.5, 54.1, 45.6, 39.3, 36.1, 27.9 (3C); IR (ATR) 3030, 2970, 2934, 2710, 1745, 1644, 1568, 1432, 1364, 1279, 1215  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{25}\text{NNaO}_2^+$   $m/z$  370.1778, found  $m/z$  370.1778.



**1'-(*tert*-Butyl)-6-hydroxy-5-(4-methoxyphenyl)-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4d)**

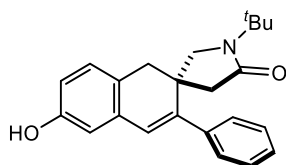
Prepared according to the general procedure A (Method B) using **1d** (40.3 mg), and isolated as yellow solid (28.5 mg, 76% yield).: m.p. 199–201 °C;  $R_f$  = 0.4 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J$  = 9.0 Hz, 2H), 7.04 (d,  $J$  = 9.0 Hz, 2H), 7.01 (d,  $J$  = 7.8 Hz, 1H), 6.81 (d,  $J$  = 7.8 Hz, 1H), 6.18 (d,  $J$  = 9.6 Hz, 1H), 5.77 (d,  $J$  = 9.6 Hz, 1H), 5.04 (br s, 1H), 3.87 (s, 3H), 3.40 (d,  $J$  = 10.8 Hz, 1H), 3.27 (d,  $J$  = 10.8 Hz, 1H), 2.86 (d,  $J$  = 15.6 Hz, 1H), 2.83 (d,  $J$  = 15.6 Hz, 1H), 2.37 (s, 2H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 159.7, 152.3, 135.0, 135.0, 132.1, 132.0, 128.6, 126.4, 125.9, 125.2, 125.1, 114.9, 114.8, 113.8, 55.5, 55.5, 54.1, 45.7, 39.4, 36.1, 27.9 (3C); IR (ATR) 2956, 2829, 1749, 1648, 1601, 1514, 1444, 1430, 1364, 1281, 1243, 1218  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{28}\text{NO}_3^+$   $m/z$  378.2064, found  $m/z$  378.2065



**5-(3,5-Bis(trifluoromethyl)phenyl)-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4e)**

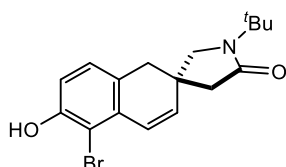
Prepared according to the general procedure A (Method B) using **1e** (30.0 mg), and isolated as colorless oil (13.4 mg, 47% yield, 0.059 mmol scale).:  $R_f$  = 0.5 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1H), 7.77 (s, 1H), 7.74 (s, 1H), 7.05 (d,  $J$  = 8.4 Hz, 1H), 6.78 (d,  $J$  = 8.4 Hz, 1H), 6.32 (br s, 1H), 6.08 (d,  $J$  = 9.6 Hz, 1H), 5.84 (d,  $J$  = 9.6 Hz, 1H), 3.41 (d,  $J$  = 10.2 Hz, 1H), 3.35 (d,  $J$  = 10.2 Hz, 1H), 2.88 (d,  $J$  = 15.0 Hz, 1H), 2.82 (d,  $J$  = 15.0 Hz, 1H), 2.38

(d,  $J = 17.4$  Hz, 1H), 2.35 (d,  $J = 17.4$  Hz, 1H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 152.4, 137.9, 136.0, 131.9, 131.8 ( $J = 27.3$  Hz, 2C), 131.3, 129.8, 125.5, 125.3, 123.5 ( $J = 270.0$  Hz, 2C), 123.2, 121.5 ( $J = 3.0$  Hz, 2C), 114.5, 55.9, 54.4, 44.7, 39.3, 36.2, 27.9 (3C);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6; IR (ATR) 3331, 1659, 1577, 1456, 1424, 1369, 1279, 1218, 1176  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{F}_6\text{NNaO}_2^+$   $m/z$  506.1525, found  $m/z$  506.1536



**1'-(*tert*-Butyl)-6-hydroxy-3-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4f)**

Prepared according to the general procedure A (Method B) using **1f** (37.3 mg),  $\text{CH}_2\text{Cl}_2$  (0.01 M), and MS  $3\text{\AA}$  (100 mg) and isolated as white solid (22.5 mg, 65% yield).: m.p. 230–232  $^\circ\text{C}$ ;  $R_f = 0.3$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (dd,  $J = 8.4, 7.2$  Hz, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.22 (d,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 8.4$  Hz, 1H), 6.66 (d,  $J = 8.4$  Hz, 1H), 6.62 (s, 1H), 6.42 (s, 1H), 5.00 (br s, 1H), 3.51 (d,  $J = 9.0$  Hz, 1H), 3.38 (d,  $J = 9.0$  Hz, 1H), 2.97 (d,  $J = 15.0$  Hz, 1H), 2.90 (d,  $J = 15.0$  Hz, 1H), 2.74 (d,  $J = 15.6$  Hz, 1H), 2.32 (d,  $J = 15.6$  Hz, 1H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  172.4, 156.4, 145.4, 140.1, 134.3, 128.9, 128.4 (2C), 127.9, 127.8 (2C), 127.5, 123.2, 114.3, 113.5, 53.3, 53.0, 43.8, 40.6, 38.1, 27.2 (3C); IR (ATR) 2956, 2829, 1749, 1648, 1601, 1514, 1444, 1430, 1364, 1281, 1243, 1218  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{25}\text{NNaO}_2^+$   $m/z$  370.1778, found  $m/z$  370.1762

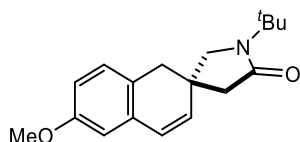


**5-Bromo-1'-(*tert*-butyl)-6-hydroxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4g)**

Prepared according to the general procedure A (Method B) using **1g** (37.6 mg)

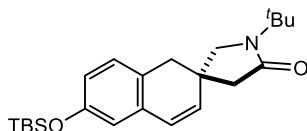
## Supporting Information

and MS 3Å (100 mg) and isolated as white solid (16.7 mg, 48% yield).: m.p. 205–207 °C;  $R_f$  = 0.5 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.96 (d,  $J$  = 8.4 Hz, 1H), 6.91 (d,  $J$  = 9.6 Hz, 1H), 6.73 (d,  $J$  = 8.4 Hz, 1H), 6.06 (d,  $J$  = 9.6 Hz, 1H), 3.45 (d,  $J$  = 10.2 Hz, 1H), 3.41 (d,  $J$  = 10.2 Hz, 1H), 2.85 (d,  $J$  = 16.2 Hz, 1H), 2.78 (d,  $J$  = 16.2 Hz, 1H), 2.37 (d,  $J$  = 16.2 Hz, 1H), 2.31 (d,  $J$  = 16.2 Hz, 1H), 1.39 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  176.0, 154.5, 137.4, 134.1, 129.0, 128.2, 127.0, 115.5, 111.1, 56.4, 55.4, 45.9, 39.7, 37.4, 27.9 (3C); IR (ATR) 3373, 2973, 2925, 2485, 2077, 1651, 1471, 1418, 1295, 1217, 1117  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{20}\text{BrNNaO}_2^+$   $m/z$  372.0570, found  $m/z$  372.0572



### 1'-(*tert*-Butyl)-6-methoxy-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4h)

Prepared according to the general procedure A (Method B) using **1h** (31.1 mg) and MS 3Å (100 mg), and isolated as colorless oil (21.6 mg, 76% yield).:  $R_f$  = 0.6 (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (d,  $J$  = 8.4 Hz, 1H), 6.65 (d,  $J$  = 2.4 Hz, 1H), 6.44 (d,  $J$  = 9.6 Hz, 1H), 5.88 (d,  $J$  = 9.6 Hz, 1H), 5.71 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 3.80 (s, 3H), 3.37 (d,  $J$  = 8.4 Hz, 1H), 3.27 (d,  $J$  = 8.4 Hz, 1H), 2.83 (d,  $J$  = 16.2 Hz, 1H), 2.81 (d,  $J$  = 16.2 Hz, 1H), 2.41 (d,  $J$  = 16.8 Hz, 1H), 2.35 (d,  $J$  = 16.8 Hz, 1H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 158.9, 135.1, 134.1, 129.2, 128.5, 125.2, 112.6, 112.2, 55.5, 55.5, 54.1, 45.8, 38.6, 36.7, 27.9 (3C); IR (ATR) 3352, 2971, 2871, 1682, 1604, 1573, 1494, 1404, 1364, 1300, 1261, 1222  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{23}\text{NNaO}_2^+$   $m/z$  308.1621, found  $m/z$  308.1635



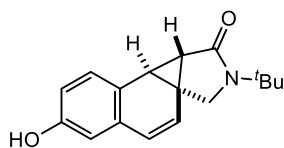
### 1'-(*tert*-Butyl)-6-((*tert*-butyldimethylsilyloxy)-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (4i)

Prepared according to the general procedure A using **1i** (41.2 mg) and MS 3Å

## Supporting Information

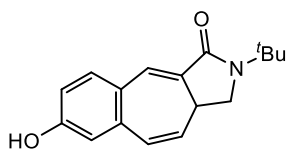
(100 mg), and isolated as colorless oil (37.2 mg, 96% yield).;  $R_f = 0.8$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (d,  $J = 8.4$  Hz, 1H), 6.63 (dd,  $J = 8.4, 3.0$  Hz, 1H), 6.56 (d,  $J = 3.0$  Hz, 1H), 6.39 (d,  $J = 9.6$  Hz, 1H), 5.84 (d,  $J = 9.6$  Hz, 1H), 3.36 (d,  $J = 9.6$  Hz, 1H), 3.27 (d,  $J = 9.6$  Hz, 1H), 2.81 (d,  $J = 15.6$  Hz, 1H), 2.78 (d,  $J = 15.6$  Hz, 1H), 2.39 (d,  $J = 16.2$  Hz, 1H), 2.34 (d,  $J = 16.2$  Hz, 1H), 1.38 (s, 9H), 0.98 (s, 9H), 0.20 (s, 6H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 154.8, 134.7, 134.1, 129.2, 128.5, 125.8, 118.8, 118.1, 55.6, 54.1, 45.8, 38.7, 36.7, 27.9 (3C), 25.8 (3C), 18.3, -4.3 (2C); IR (ATR) 2957, 2929, 2858, 1747, 1688, 1604, 1568, 1492, 1401, 1363, 1277  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{35}\text{NNaO}_2\text{Si}^+$   $m/z$  408.2329, found  $m/z$  408.2343

### Characterization of 5a and 6a



#### 2-(*tert*-Butyl)-7-hydroxy-2,3,9b,9c-tetrahydro-1H-naphtho[2',1':1,3]cyclopropa[1,2-*c*]pyrrol-1-one (5a)

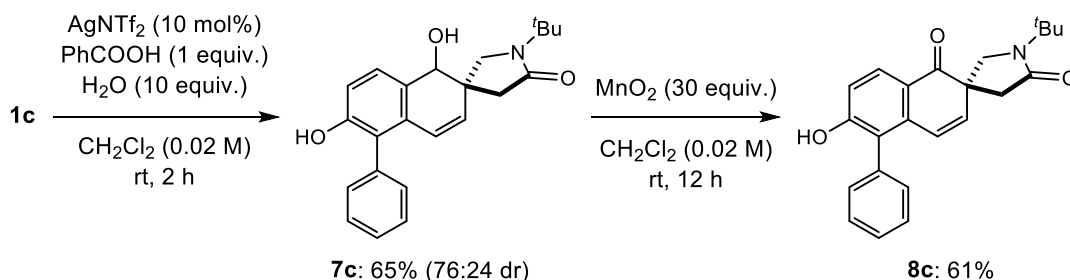
Prepared according to general procedure A using  $\text{Rh}_2(\text{OAc})_4$  (4.4 mg) instead of  $\text{AgNTf}_2$ , and isolated yellow solid (23.7 mg, 88% yield) (preparative thin layer chromatography condition: toluene/EtOAc 2/1).: m.p. 206–208 °C;  $R_f = 0.4$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.4$  Hz, 1H), 6.77 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.62 (d,  $J = 2.4$  Hz, 1H), 6.29 (d,  $J = 9.6$  Hz, 1H), 6.08 (br s, 1H), 6.08 (d,  $J = 9.6$  Hz, 1H), 3.76 (d,  $J = 10.8$  Hz, 1H), 3.59 (d,  $J = 10.8$  Hz, 1H), 2.56 (d,  $J = 1.8$  Hz, 1H), 1.41 (s, 9H), 0.72 (d,  $J = 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 154.9, 132.4, 130.0, 126.1, 125.4, 124.1, 115.5, 114.7, 54.0, 52.1, 33.4, 28.0, 27.8 (3C), 26.3; IR (ATR) 3250, 2967, 2927, 1708, 1636, 1562, 1486, 1417, 1365, 1277, 1216  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{19}\text{NNaO}_2^+$   $m/z$  292.1308, found  $m/z$  292.1310.



**2-(*tert*-Butyl)-7-hydroxy-1,10a-dihydrobenzo[4,5]cyclohepta[1,2-*c*]pyrrol-3(2*H*)-one (6a)**

Prepared according to general procedure A using  $\text{Rh}_2(\text{OAc})_4$  (4.4 mg) instead of  $\text{AgNTf}_2$ , and isolated yellow solid (2.4 mg, 9% yield) (preparative thin layer chromatography condition: toluene/EtOAc 2/1): m.p. 216–218 °C;  $R_f = 0.4$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 7.6$  Hz, 1H), 7.71 (br s, 1H), 7.70 (d,  $J = 7.6$  Hz, 1H), 7.48 (d,  $J = 8.8$  Hz, 1H), 7.16 (s, 1H), 7.13 (d,  $J = 8.8$  Hz, 1H), 5.21 (s, 1H), 4.70 (dd,  $J = 5.2, 2.4$  Hz, 1H), 3.28 (dd,  $J = 14.8, 5.2$  Hz, 1H), 2.74 (dd,  $J = 14.8, 2.4$  Hz, 1H), 1.26 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 154.0, 136.2, 134.6, 129.8, 128.8, 127.5, 126.0, 124.3, 118.5, 109.7, 54.9, 53.5, 45.9, 28.3 (3C); IR (ATR) 3287, 2973, 2929, 1711, 1635, 1607, 1446, 1366, 1287, 1226  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{19}\text{NNaO}_2^+$   $m/z$  292.1308, found  $m/z$  292.1315.

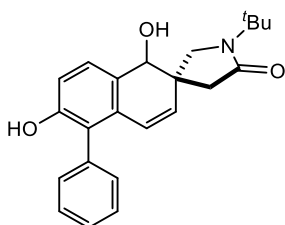
**Procedure for Dearomatizative Spirocyclization with Water and Oxidation**



A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with  $\text{AgNTf}_2$  (5.8 mg, 0.015 mmol, 10 mol%), benzoic acid (18.3 mg, 0.15 mmol, 1 equiv.), and  $\text{H}_2\text{O}$  (27  $\mu\text{L}$ , 1.5 mmol, 10 equiv.), which were subsequently dissolved partially in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) under an argon gas atmosphere. Diazo compound **1c** (56.0 mg, 0.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL) was added slowly over 0.5 h *via* a syringe pump to the suspension at room temperature, and the reaction mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with the addition of water. The

aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2 \times 2$ . The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; gradient elution: *n*-hexane/EtOAc, 1/1  $\rightarrow$  1/3) to afford spirocyclic compound **7c** as colorless oil (35.5 mg, 65% yield, 76:24 dr).

A pre-dried 30 mL eggplant-shaped flask were equipped with a magnetic stir bar was charged with **7c** (35.3 mg, 0.098 mmol), which was subsequently dissolved in  $\text{CH}_2\text{Cl}_2$  (4.9 mL) under an argon gas atmosphere. To a stirred solution was added  $\text{MnO}_2$  (252.1 mg, 2.9 mmol, 30 equiv.), and the reaction mixture was stirred for 12 h at room temperature. The reaction was diluted with  $\text{CH}_2\text{Cl}_2$ , filtrated through Celite<sup>®</sup>. The filtrate was concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/EtOAc, 1/2) to afford spirocyclic compound **8c** as pale yellow solid (21.8 mg, 61% yield).

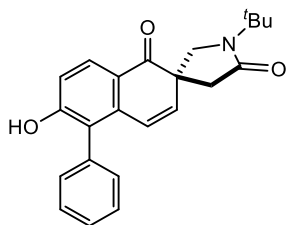


**1'-(*tert*-Butyl)-1,6-dihydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidin]-5'-one (**7c**)**

$R_f = 0.2$  (*n*-hexane/EtOAc, 1/2);  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.40 (br s, 1H), 7.40 (dd,  $J = 7.8, 7.8$  Hz, 2H), 7.33 (d,  $J = 7.8$  Hz, 1H), 7.26 (t,  $J = 7.8$  Hz, 1H), 7.22 (d,  $J = 9.6$  Hz, 1H), 7.26-7.19 (m, 1H), 7.16 (d,  $J = 9.6$  Hz, 1H), 6.80 (d,  $J = 7.8$  Hz, 1H), 6.19 (d,  $J = 9.6$  Hz, 1H), 5.81 (d,  $J = 9.6$  Hz, 1H), 4.44 (s, 1H), 3.97 (d,  $J = 10.2$  Hz, 1H), 3.39 (d,  $J = 10.2$  Hz, 1H), 2.51 (d,  $J = 16.2$  Hz, 1H), 2.12 (d,  $J = 16.2$  Hz, 1H), 1.41 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  176.1, 155.9, 137.5, 134.8, 132.6, 132.0, 131.9, 131.8, 129.4, 129.3, 129.0, 128.1, 128.0, 126.6, 115.2, 74.7, 55.5, 53.1, 44.1, 42.3, 27.9 (3C) (NMR data of major diastereomer of **7c** were shown.); IR (ATR) 2970, 2950, 1746, 1714, 1666, 1646,

## Supporting Information

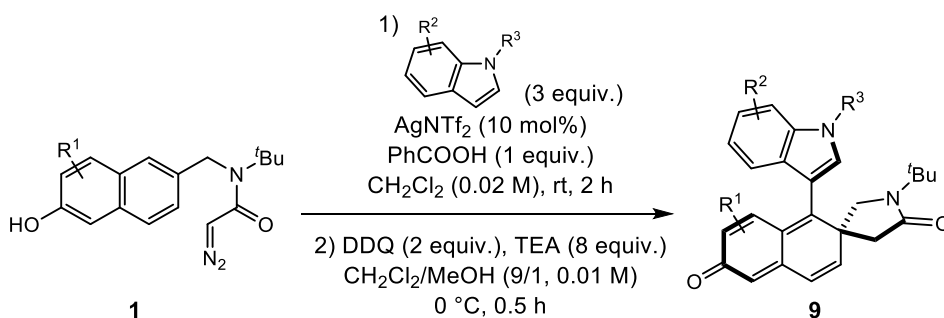
1369, 1316, 1284  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{25}\text{NNaO}_3^+$   $m/z$  386.1727, found  $m/z$  386.1727.



### 1'-(*tert*-Butyl)-6-hydroxy-5-phenyl-1*H*-spiro[naphthalene-2,3'-pyrrolidine]-1,5'-dione (**8c**)

m.p. 235–237 °C;  $R_f$  = 0.4 (*n*-hexane/EtOAc, 1/2);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J$  = 7.8 Hz, 1H), 7.55 (d,  $J$  = 6.0 Hz, 1H), 7.53 (d,  $J$  = 6.0 Hz, 1H), 7.48 (t,  $J$  = 7.2 Hz, 1H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.30 (d,  $J$  = 7.2 Hz, 1H), 7.03 (d,  $J$  = 7.8 Hz, 1H), 6.69 (br s, 1H), 6.32 (d,  $J$  = 10.2 Hz, 1H), 6.18 (d,  $J$  = 10.2 Hz, 1H), 3.86 (d,  $J$  = 9.6 Hz, 1H), 3.33 (d,  $J$  = 9.6 Hz, 1H), 2.94 (d,  $J$  = 16.2 Hz, 1H), 2.30 (d,  $J$  = 16.2 Hz, 1H), 1.42 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 172.4, 159.6, 137.6, 136.8, 133.2, 131.0, 130.8, 129.6, 129.5 (2C), 128.9, 125.8, 122.4, 122.2, 115.7, 55.3, 54.7, 47.0, 44.4, 27.8 (3C); IR (ATR) 2971, 2751, 2702, 2665, 1745, 1656, 1565, 1434, 1409, 1304, 1262, 1207, 1088  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{NNaO}_3^+$   $m/z$  384.1570, found  $m/z$  384.1572.

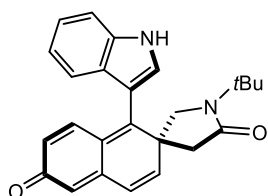
### General Procedure B for One-pot Double Dearomative Spirocyclization



## Supporting Information

A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with AgNTf<sub>2</sub> (3.9 mg, 0.01 mmol, 10 mol%), an indole derivative (0.3 mmol, 3 equiv.), benzoic acid (12.2 mg, 0.1 mmol, 1 equiv.), and **1** (0.1 mmol), which were subsequently dissolved partially in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) under an argon gas atmosphere. The reaction mixture was stirred for 2 h at room temperature, and then cooled to 0 °C in an ice bath. TEA (111.5 μL, 0.8 mmol, 8 equiv.), MeOH (1 mL), and DDQ (45.4 mg, 0.2 mmol, 2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added dropwise to the reaction mixture, and stirring was continued for 0.5 h at the same temperature. The reaction was quenched with the addition of 1 N aqueous NaOH. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>×3, and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition; diol SiO<sub>2</sub>, gradient elution: *n*-hexane/EtOAc, 2/1 → 1/4) to afford **9**.

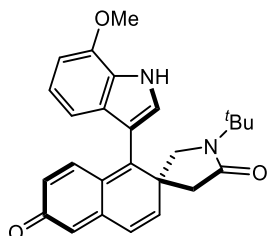
NMR data of major diastereomers of **9a-i**, **k**, **l** and **10a** were shown.



### 1'-(*tert*-Butyl)-1-(1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (**9a**)

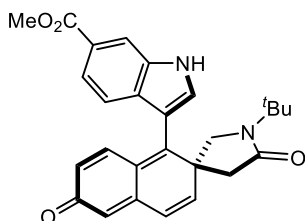
Prepared according to the general procedure B using **1a** and indole, and isolated as orange solid (37.4 mg, 97% yield): m.p. 159–161 °C; *R*<sub>f</sub> = 0.2 (*n*-hexane/EtOAc, 1/3); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.32 (br s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.27 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.16 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.01 (d, *J* = 9.6 Hz, 1H), 6.66 (d, *J* = 9.6 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 6.24 (d, *J* = 9.6, 1.8 Hz, 1H), 3.51 (d, *J* = 10.8 Hz, 1H), 3.45 (d, *J* = 10.8 Hz, 1H), 2.91 (d, *J* = 18.0 Hz, 1H), 2.80 (d, *J* = 18.0 Hz, 1H), 0.84 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 187.9, 172.3, 153.8, 140.2, 139.6, 137.4, 135.6, 129.5, 128.7, 128.1, 126.1, 124.0, 123.4, 123.3, 121.3, 118.9, 111.9, 110.5, 54.8, 54.2, 44.5, 43.1,

27.0 (3C); IR (ATR) 3134, 2971, 2923, 1748, 1672, 1621, 1549, 1509, 1453, 1410, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_2^+$   $m/z$  407.1730, found  $m/z$  407.1739.



**1'-(*tert*-Butyl)-1-(7-methoxy-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (9b)**

Prepared according to the general procedure B using **1a** and 7-methoxyindole, and isolated as orange solid (39.6 mg, 95% yield).: m.p. 155–156 °C;  $R_f$  = 0.2 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (br s, 1H), 7.29 (d,  $J$  = 1.8 Hz, 1H), 7.08 (dd,  $J$  = 7.8, 7.2 Hz, 1H), 7.00 (d,  $J$  = 10.2 Hz, 1H), 6.87 (d,  $J$  = 7.8 Hz, 1H), 6.71 (d,  $J$  = 7.2 Hz, 1H), 6.64 (d,  $J$  = 9.0 Hz, 1H), 6.35 (d,  $J$  = 9.0 Hz, 1H), 6.28 (d,  $J$  = 1.8 Hz, 1H), 6.23 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 3.99 (s, 3H), 3.47 (d,  $J$  = 10.2 Hz, 1H), 3.44 (d,  $J$  = 10.2 Hz, 1H), 2.91 (d,  $J$  = 17.4 Hz, 1H), 2.73 (d,  $J$  = 17.4 Hz, 1H), 0.88 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.1, 153.5, 146.5, 140.5, 139.6, 137.4, 129.9, 129.4, 128.2, 126.2, 125.9, 124.0, 122.8, 121.1, 111.5, 111.1, 102.9, 55.7, 54.7, 54.2, 44.5, 43.0, 27.1 (3C); IR (ATR) 3204, 2925, 2853, 1746, 1668, 1620, 1544, 1420, 1366, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_3^+$   $m/z$  437.1836, found  $m/z$  437.1843.

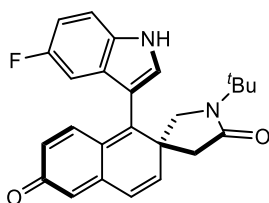


**Methyl 3-(1'-(*tert*-butyl)-5',6-dioxo-6*H*-spiro[naphthalene-2,3'-pyrrolidin]-1-yl)-1*H*-indole-6-carboxylate (9c)**

Prepared according to the general procedure B using **1a** and methyl indole-6-

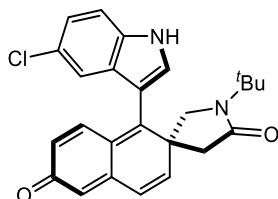
## Supporting Information

carboxylate, and isolated as orange solid (36.1 mg, 82% yield).: m.p. 155–156 °C;  $R_f$  = 0.1 (*n*-hexane/EtOAc, 1/2);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (br s, 1H), 8.28 (d,  $J$  = 1.8 Hz, 1H), 7.86 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 7.50 (d,  $J$  = 3.0 Hz, 1H), 7.34 (d,  $J$  = 10.2 Hz, 1H), 6.93 (d,  $J$  = 10.2 Hz, 1H), 6.67 (d,  $J$  = 9.6 Hz, 1H), 6.35 (d,  $J$  = 9.6 Hz, 1H), 6.30 (d,  $J$  = 1.8 Hz, 1H), 6.24 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 3.97 (s, 3H), 3.55 (d,  $J$  = 11.4 Hz, 1H), 3.43 (d,  $J$  = 11.4 Hz, 1H), 2.90 (d,  $J$  = 17.4 Hz, 1H), 2.85 (d,  $J$  = 17.4 Hz, 1H), 0.82 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.4, 168.0, 152.6, 140.0, 139.5, 137.0, 135.1, 132.0, 129.7, 128.3, 126.8, 126.3, 124.9, 124.2, 122.2, 118.5, 114.6, 110.6, 54.8, 54.3, 52.4, 44.4, 43.2, 27.0 (3C); IR (ATR) 3208, 2972, 2918, 1709, 1661, 1618, 1544, 1434, 1311, 1274, 1214  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}_4^+$   $m/z$  465.1785, found  $m/z$  465.1774.



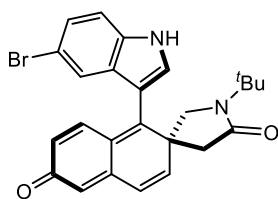
### 1'-(*tert*-Butyl)-1-(5-fluoro-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidinel]-5',6-dione (9d)

Prepared according to the general procedure B using **1a** and 5-fluoroindole, and isolated as pale orange solid (34.9 mg, 87% yield).: m.p. 206–208 °C;  $R_f$  = 0.2 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.56 (br s, 1H), 7.42 (dd,  $J$  = 9.0, 5.4 Hz, 1H), 7.37 (d,  $J$  = 2.4 Hz, 1H), 7.02 (ddd,  $J$  = 9.0, 9.0, 1.8 Hz, 1H), 6.98 (d,  $J$  = 10.2 Hz, 1H), 6.95 (dd,  $J$  = 9.0, 1.8 Hz, 1H), 6.66 (d,  $J$  = 9.6 Hz, 1H), 6.34 (d,  $J$  = 9.6 Hz, 1H), 6.29 (d,  $J$  = 1.8 Hz, 1H), 6.26 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 3.53 (d,  $J$  = 10.8 Hz, 1H), 3.41 (d,  $J$  = 10.8 Hz, 1H), 2.89 (d,  $J$  = 17.4 Hz, 1H), 2.82 (d,  $J$  = 17.4 Hz, 1H), 0.86 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.4, 158.1, 152.9, 140.0, 139.5, 137.1, 132.1, 129.7, 129.0 (dd,  $J$  = 10.1 Hz), 128.1, 126.2, 125.2, 124.2, 112.9 (d,  $J$  = 10.1 Hz), 111.9 (d,  $J$  = 25.8 Hz), 110.5 (d,  $J$  = 4.4 Hz), 103.7 (d,  $J$  = 24.5 Hz), 54.8, 54.3, 44.4, 43.2, 27.1;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.9; IR (ATR) 3167, 3111, 2971, 2926, 1739, 1669, 1615, 1542, 1417, 1231  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{FN}_2\text{NaO}_2^+$   $m/z$  425.1636, found  $m/z$  425.1632.



**1'-(*tert*-Butyl)-1-(5-chloro-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidinel]-5',6-dione (9e)**

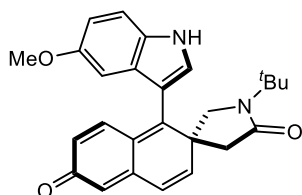
Prepared according to the general procedure B using **1a** and 5-chloroindole, and isolated as pale orange solid (34.6 mg, 83% yield).: m.p. 235–237 °C;  $R_f$  = 0.1 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.79 (br s, 1H), 7.42 (d,  $J$  = 9.0 Hz, 1H), 7.34 (d,  $J$  = 2.4 Hz, 1H), 7.27 (s, 1H), 7.22 (d,  $J$  = 9.0 Hz, 1H), 6.95 (d,  $J$  = 10.2 Hz, 1H), 6.67 (d,  $J$  = 9.6 Hz, 1H), 6.34 (d,  $J$  = 9.6 Hz, 1H), 6.30 (s, 1H), 6.27 (d,  $J$  = 10.2 Hz, 1H), 3.55 (d,  $J$  = 10.2 Hz, 1H), 3.43 (d,  $J$  = 10.2 Hz, 1H), 2.87 (d,  $J$  = 17.4 Hz, 1H), 2.83 (d,  $J$  = 17.4 Hz, 1H), 0.86 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.4, 152.6, 140.0, 139.5, 137.0, 134.0, 129.8, 129.6, 128.3, 127.1, 126.3, 124.8, 124.2, 123.7, 118.1, 113.2, 110.0, 54.9, 54.3, 44.3, 43.3, 27.0 (3C); IR (ATR) 3104, 2971, 2924, 2877, 1739, 1668, 1612, 1541, 1508, 1416, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{ClN}_2\text{NaO}_2^+$   $m/z$  441.1340, found  $m/z$  441.1336.



**1-(5-Bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidinel]-5',6-dione (9f)**

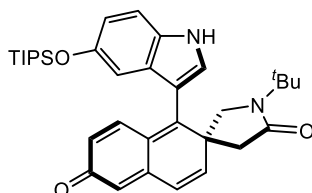
Prepared according to the general procedure B using **1a** and 5-bromoindole, and isolated as pale orange solid (36.6 mg, 79% yield).: m.p. 238–240 °C;  $R_f$  = 0.2 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.54 (br s, 1H), 7.43 (s, 1H), 7.36 (d,  $J$  = 2.4 Hz, 1H), 7.38–7.35 (m, 1H), 7.32 (d,  $J$  = 2.4 Hz, 1H), 6.94 (d,  $J$  = 10.2 Hz, 1H), 6.66 (d,  $J$  = 9.6 Hz, 1H), 6.33 (d,  $J$  = 9.6 Hz, 1H), 6.30 (d,  $J$  = 1.8 Hz, 1H), 6.27 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 3.54 (d,  $J$  = 10.2 Hz, 1H), 3.43 (d,  $J$  = 10.2 Hz, 1H), 2.86 (d,  $J$  = 17.4 Hz, 1H), 2.81 (d,  $J$  = 17.4 Hz, 1H),

0.85 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.3, 152.4, 140.0, 139.4, 136.9, 134.3, 130.2, 129.9, 128.4, 126.3, 126.3, 124.7, 124.3, 121.2, 114.5, 113.5, 110.0, 54.9, 54.3, 44.3, 43.3, 27.0 (3C); IR (ATR) 3213, 2971, 2924, 1746, 1673, 1610, 1541, 1507, 1413, 1218  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{NaO}_2^+$   $m/z$  485.0835, found  $m/z$  485.0842.



**1'-(*tert*-Butyl)-1-(5-methoxy-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (9g)**

Prepared according to the general procedure B using **1a**, 5-methoxyindole, and 3 equiv. of DDQ and isolated as orange solid (34.2 mg, 82% yield): m.p. 173–175 °C;  $R_f$  = 0.2 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.06 (br s, 1H), 7.36 (d,  $J$  = 8.4 Hz, 1H), 7.28 (s, 1H), 7.04 (d,  $J$  = 10.2 Hz, 1H), 6.93 (d,  $J$  = 8.4 Hz, 1H), 6.65 (s, 1H), 6.65 (d,  $J$  = 9.6 Hz, 1H), 6.35 (d,  $J$  = 9.6 Hz, 1H), 6.29 (s, 1H), 6.26 (d,  $J$  = 10.2 Hz, 1H), 3.76 (s, 3H), 3.50 (d,  $J$  = 10.8 Hz, 1H), 3.42 (d,  $J$  = 10.8 Hz, 1H), 2.90 (d,  $J$  = 16.8 Hz, 1H), 2.78 (d,  $J$  = 16.8 Hz, 1H), 0.88 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 172.3, 157.0, 155.5, 140.3, 139.7, 137.5, 130.7, 129.4, 129.1, 127.8, 126.1, 124.1, 124.0, 113.5, 112.7, 110.3, 100.4, 56.1, 54.9, 54.3, 44.5, 43.1, 27.1 (3C); IR (ATR) 3647, 3469, 3229, 2939, 1739, 1658, 1616, 1544, 1486, 1422, 1288, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_3^+$   $m/z$  437.1836, found  $m/z$  437.1849.

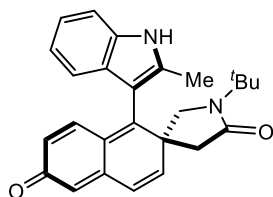


**1'-(*tert*-Butyl)-1-(5-((triisopropylsilyl)oxy)-1*H*-indol-3-yl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (9h)**

Prepared according to the general procedure B using **1a** and 5-((triisopropylsilyl)oxy)-indole, and isolated as orange solid (47.1 mg, 83%

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yield): m.p. 156–158 °C;  $R_f$  = 0.3 (*n*-hexane/EtOAc, 1/2);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.98 (br s, 1H), 7.30 (d,  $J$  = 1.2 Hz, 1H), 7.30 (d,  $J$  = 9.0 Hz, 1H), 7.03 (d,  $J$  = 9.6 Hz, 1H), 6.88 (dd,  $J$  = 9.0, 1.8 Hz, 1H), 6.68 (d,  $J$  = 1.8 Hz, 1H), 6.65 (d,  $J$  = 9.6 Hz, 1H), 6.35 (d,  $J$  = 9.6 Hz, 1H), 6.29 (d,  $J$  = 1.8 Hz, 1H), 6.23 (dd,  $J$  = 9.6, 1.8 Hz, 1H), 3.48 (d,  $J$  = 10.2 Hz, 1H), 3.35 (d,  $J$  = 10.2 Hz, 1H), 2.93 (d,  $J$  = 18.0 Hz, 1H), 2.78 (d,  $J$  = 18.0 Hz, 1H), 1.20 (sep,  $J$  = 7.8 Hz, 3H), 1.05 (d,  $J$  = 7.8 Hz, 18H), 0.91 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.3, 153.7, 151.3, 140.2, 139.6, 137.6, 130.7, 129.6, 129.4, 127.7, 126.0, 124.2, 123.9, 117.5, 112.2, 110.2, 107.7, 54.8, 54.3, 44.4, 43.0, 27.1 (3C), 18.1 (6C), 12.7 (3C); IR (ATR) 2942, 2865, 1746, 1672, 1621, 1543, 1469, 1419, 1365, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{34}\text{H}_{44}\text{N}_2\text{NaO}_3\text{Si}^+$   $m/z$  579.3013, found  $m/z$  579.3002.



### 1-(1-Benzyl-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidinel]-5',6-dione (9i)

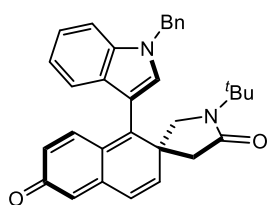
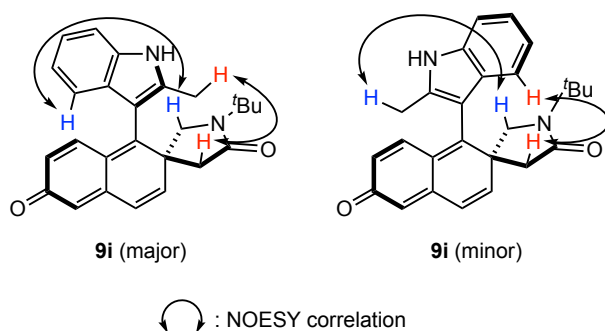
Prepared according to the general procedure B using **1a** and 2-methylindole. Major atropisomer: Orange solid (22.6 mg, 58% yield): m.p. 174–176 °C;  $R_f$  = 0.2 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (br s, 1H), 7.37 (d,  $J$  = 7.8 Hz, 1H), 7.20 (dd,  $J$  = 7.8, 7.2 Hz, 1H), 7.15 (d,  $J$  = 7.2 Hz, 1H), 7.10 (dd,  $J$  = 7.2, 7.2 Hz, 1H), 6.82 (d,  $J$  = 9.6 Hz, 1H), 6.67 (d,  $J$  = 10.8 Hz, 1H), 6.50 (d,  $J$  = 9.6 Hz, 1H), 6.29 (d,  $J$  = 2.4 Hz, 1H), 6.22 (dd,  $J$  = 10.8, 2.4 Hz, 1H), 3.87 (d,  $J$  = 9.6 Hz, 1H), 3.42 (d,  $J$  = 9.6 Hz, 1H), 2.83 (d,  $J$  = 16.8 Hz, 1H), 2.45 (d,  $J$  = 16.8 Hz, 1H), 2.33 (s, 3H), 1.05 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 172.0, 153.5, 140.0, 139.7, 136.6, 135.6, 133.5, 131.3, 129.9, 129.5, 125.8, 124.0, 122.4, 120.8, 118.5, 111.1, 108.0, 54.3, 54.2, 47.4, 43.4, 27.3 (3C), 13.4; IR (ATR) 3272, 2973, 2925, 1747, 1670, 1621, 1524, 1456, 1228  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_2^+$   $m/z$  421.1886, found  $m/z$  421.1893.

Minor atropisomer: Orange solid (16.7 mg, 42% yield): m.p. 183–184 °C;  $R_f$  =

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0.3 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (br s, 1H), 7.38 (d,  $J = 7.8$  Hz, 1H), 7.21 (dd,  $J = 7.8, 7.8$  Hz, 1H), 7.16 (d,  $J = 7.8$  Hz, 1H), 7.10 (dd,  $J = 7.8, 7.8$  Hz, 1H), 6.78 (d,  $J = 9.6$  Hz, 1H), 6.67 (d,  $J = 10.8$  Hz, 1H), 6.61 (d,  $J = 10.2$  Hz, 1H), 6.30 (s, 1H), 6.23 (d,  $J = 9.6$  Hz, 1H), 3.70 (d,  $J = 9.0$  Hz, 1H), 3.29 (d,  $J = 9.0$  Hz, 1H), 3.14 (d,  $J = 15.6$  Hz, 1H), 2.33 (d,  $J = 15.6$  Hz, 1H), 2.26 (s, 3H), 1.31 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 171.9, 153.1, 139.8, 139.6, 136.6, 135.5, 132.9, 132.4, 130.0, 129.4, 125.4, 123.9, 122.7, 121.2, 119.4, 110.9, 108.4, 54.5, 53.7, 48.0, 43.7, 27.8 (3C), 13.0; IR (ATR) 3272, 2972, 2924, 1746, 1671, 1621, 1523, 1456, 1228  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_2^+$   $m/z$  421.1886, found  $m/z$  421.1882.

The relative configurations of **9i** were determined by NOESY experiments.

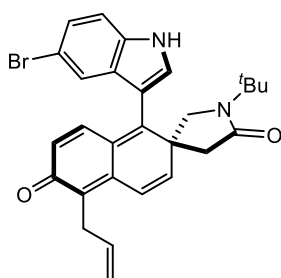


### 1-(1-Benzyl-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (**9j**)

Prepared according to the general procedure B using **1a** and *N*-benzylindole, and isolated as pale orange solid (37.4 mg, 79% yield): m.p. 90–91 °C;  $R_f = 0.2$  (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.34 (m, 3H), 7.30 (dd,  $J = 7.2, 7.2$  Hz, 2H), 7.29 (s, 1H), 7.24 (d,  $J = 7.2$  Hz, 2H), 7.16 (d,  $J = 6.6$  Hz, 1H), 7.16 (t,  $J = 7.2$  Hz, 1H), 7.03 (d,  $J = 9.6$  Hz, 1H), 6.63 (d,  $J = 9.6$  Hz, 1H), 6.35 (d,  $J = 9.6$  Hz, 1H), 6.27 (d,  $J = 2.4$  Hz, 1H), 6.25 (dd,  $J = 9.6, 2.4$  Hz, 1H), 5.39 (d,  $J = 15.0$  Hz, 1H), 5.32 (d,  $J = 15.0$  Hz, 1H), 3.47 (d,  $J = 10.4$

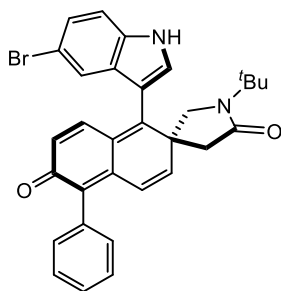
## Supporting Information

Hz, 1H), 3.43 (d,  $J$  = 10.4 Hz, 1H), 2.91 (d,  $J$  = 17.4 Hz, 1H), 2.72 (d,  $J$  = 17.4 Hz, 1H), 0.86 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8, 172.0, 153.5, 140.2, 139.6, 137.4, 136.4, 135.9, 129.4, 129.4, 129.1 (2C), 128.2, 128.1, 127.4, 127.3 (2C), 125.8, 123.9, 123.1, 121.2, 119.3, 110.5, 109.8, 54.7, 54.1, 50.7, 44.4, 42.9, 27.0 (3C); IR (ATR) 3029, 2970, 2927, 1746, 1680, 1625, 1550, 1455, 1415, 1218  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{32}\text{H}_{30}\text{N}_2\text{NaO}_2^+$   $m/z$  497.2199, found  $m/z$  497.2210.



### 5-Allyl-1-(5-bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-6*H*-spiro[naphthalene-2,3'-pyrrolidinel]-5',6-dione (**9k**)

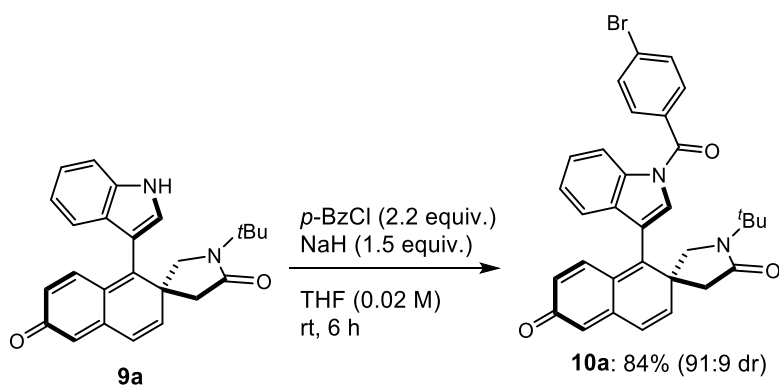
Prepared according to the general procedure B using 5-bromoindole and **1b** which was added slowly over 0.5 h *via* a syringe pump at room temperature, and isolated as yellow solid (42.2 mg, 84% yield).: m.p. 187–189 °C;  $R_f$  = 0.4 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (br s, 1H), 7.43 (s, 1H), 7.35 (d,  $J$  = 4.0 Hz, 1H), 7.35 (d,  $J$  = 2.8 Hz, 1H), 7.29 (d,  $J$  = 2.8 Hz, 1H), 6.98 (d,  $J$  = 10.4 Hz, 1H), 6.93 (d,  $J$  = 10.0 Hz, 1H), 6.34 (d,  $J$  = 10.0 Hz, 1H), 6.28 (d,  $J$  = 10.4 Hz, 1H), 5.90 (ddt,  $J$  = 17.2, 10.0, 6.4 Hz, 1H), 5.09 (dd,  $J$  = 17.2, 2.4 Hz, 1H), 5.05 (dd,  $J$  = 10.0, 2.4 Hz, 1H), 3.53 (d,  $J$  = 10.8 Hz, 1H), 3.46 (d,  $J$  = 6.4 Hz, 2H), 3.44 (d,  $J$  = 10.8 Hz, 1H), 2.84 (d,  $J$  = 18.4 Hz, 1H), 2.80 (d,  $J$  = 18.4 Hz, 1H), 0.84 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.4, 172.5, 151.1, 139.4, 136.5, 135.7, 134.8, 134.4, 131.7, 130.4, 129.0, 128.7, 126.1, 124.6, 123.3, 121.3, 115.6, 114.3, 113.5, 110.3, 55.0, 54.2, 43.6, 28.8, 27.8, 27.0 (3C); IR (ATR) 3214, 2979, 2922, 1667, 1617, 1548, 1419, 1361, 1210  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{27}\text{BrN}_2\text{NaO}_2^+$   $m/z$  525.1148, found  $m/z$  525.1172.



**1-(5-Bromo-1*H*-indol-3-yl)-1'-(*tert*-butyl)-5-phenyl-6*H*-spiro[naphthalene-2,3'-pyrrolidine]-5',6-dione (9l)**

Prepared according to the general procedure B using 5-bromoindole and **1c** which was added slowly over 0.5 h *via* a syringe pump at room temperature, and isolated as pale orange solid (40.2 mg, 74% yield): m.p. 185–186 °C;  $R_f$  = 0.4 (*n*-hexane/EtOAc, 1/3);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.07 (br s, 1H), 7.49 (s, 1H), 7.46 (dd,  $J$  = 6.0, 7.2 Hz, 2H), 7.40–7.32 (m, 4H), 7.26 (s, 2H), 0.85 (s, 9H), 7.03 (d,  $J$  = 9.6 Hz, 1H), 6.65 (d,  $J$  = 9.6 Hz, 1H), 6.37 (d,  $J$  = 9.6 Hz, 1H), 6.22 (d,  $J$  = 9.6 Hz, 1H), 3.51 (d,  $J$  = 10.8 Hz, 1H), 3.46 (d,  $J$  = 10.8 Hz, 1H), 2.89 (d,  $J$  = 17.4 Hz, 1H), 2.88 (d,  $J$  = 17.4 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  186.3, 172.4, 152.8, 139.5, 136.8, 135.0, 135.0, 134.5, 134.4, 130.7, 130.6, 130.3, 129.4, 128.6, 128.4, 128.3, 128.0, 126.0, 124.8, 124.6, 121.2, 114.3, 113.7, 110.0, 55.0, 54.3, 43.9, 43.4, 27.0 (3C); IR (ATR) 3238, 2972, 2923, 2864, 1745, 1669, 1622, 1541, 1456, 1415, 1362, 1215  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{31}\text{H}_{27}\text{BrN}_2\text{NaO}_2^+$   $m/z$  561.1148, found  $m/z$  561.1135.

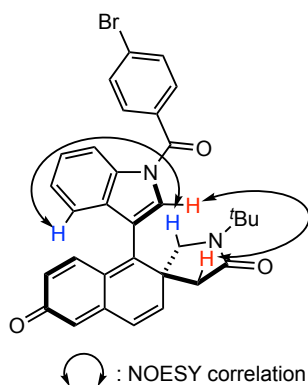
**Preparation of 10a**



A pre-dried 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **9a** (19.2 mg, 0.05 mmol), which was subsequently

## Supporting Information

dissolved in THF (2.5 mL) under an argon gas atmosphere. NaH (5 mg, 0.125 mmol, 1.5 equiv.) was added to the solution at 0 °C in an ice bath, and the reaction mixture was stirred for 0.5 h at room temperature. The resulting solution was cooled to 0 °C in an ice bath, *para*-bromo-benzoyl chloride (24.2 mg, 0.11 mmol, 2.2 equiv.) was then added, and stirring was continued for 6 h at room temperature. The reaction was quenched with the addition of water. The aqueous solution was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (column condition: diol SiO<sub>2</sub>, gradient elution: *n*-hexane/EtOAc = 3/1 → 2/1) to give **10a** as yellow solid (23.8 mg, 84% yield).



### 1-(1-(4-Bromobenzoyl)-1*H*indol-3-yl)-1'-(*tert*-butyl)-6*H*spiro[naphthalene-2,3'-pyrrolidine]-5',6'-dione (**10a**)

m.p. 157–159 °C; *R<sub>f</sub>* = 0.4 (*n*-hexane/EtOAc, 1/3); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.54 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.51 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.39 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.35 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.30 (d, *J* = 9.6 Hz, 1H), 6.27 (d, *J* = 1.2 Hz, 1H), 6.23 (dd, *J* = 9.6, 1.2 Hz, 1H), 3.56 (d, *J* = 10.4 Hz, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 2.80 (d, *J* = 17.4 Hz, 1H), 2.64 (d, *J* = 17.4 Hz, 1H), 0.84 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 187.5, 172.0, 167.9, 149.6, 139.6, 138.9, 136.0, 135.7, 132.4 (2C), 132.4, 131.5, 131.3 (2C), 130.2, 128.7, 127.7, 126.6, 126.5, 125.5, 125.4, 124.5, 119.2, 117.3, 116.5, 54.5, 54.1, 44.3, 43.3, 27.0 (3C); IR (ATR) 2976, 1690, 1670, 1626, 1585, 1450, 1362, 1332, 1261, 1224 cm<sup>-1</sup>; HRMS (ESI-TOF) [M + Na]<sup>+</sup> calcd for

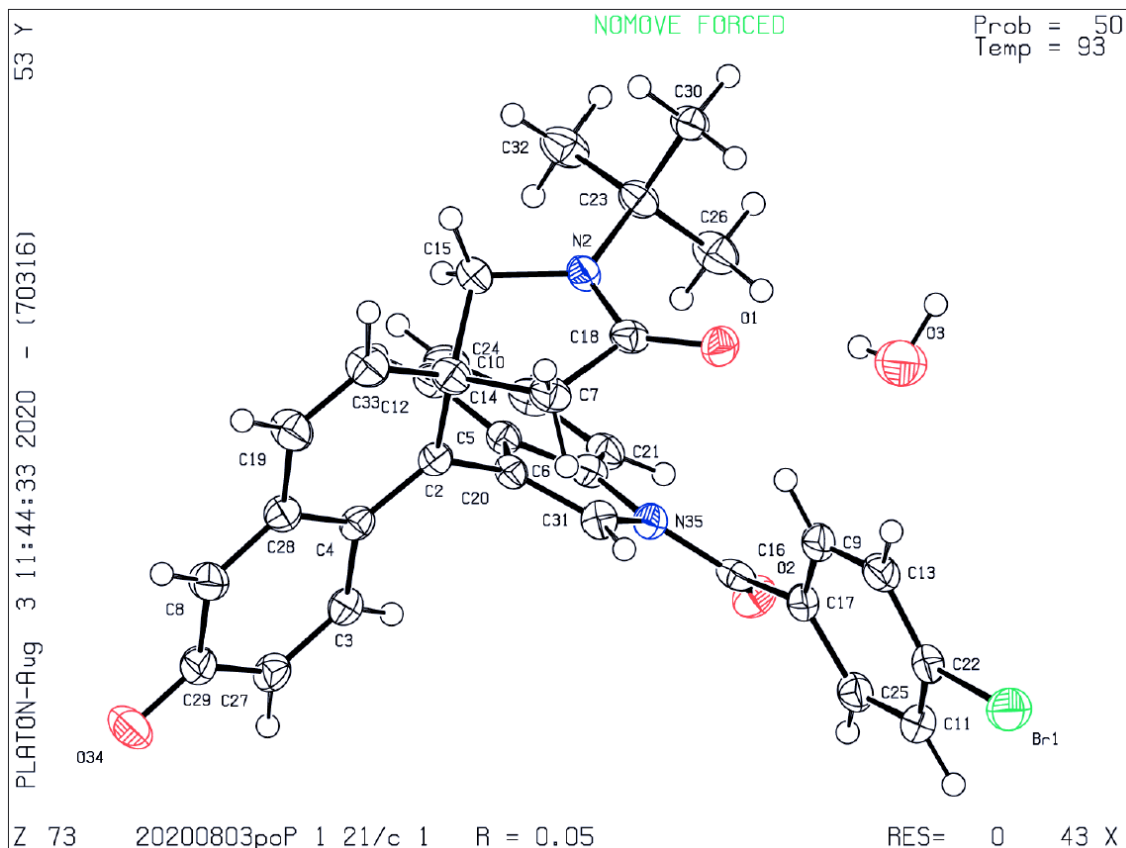
## Supporting Information

$\text{C}_{32}\text{H}_{27}\text{BrN}_2\text{NaO}_3^+$   $m/z$  589.1097, found  $m/z$  589.1105.

## Supporting Information

### 3. [X-ray Crystallographic Data](#)

#### ORTEP of 10a, CCDC No. 2031608



The ellipsoid contour probability level in the ORTEP is 50%. Experimental

#### Data Collection

A colorless block crystal of C<sub>32</sub>H<sub>29</sub>BrN<sub>2</sub>O<sub>4</sub> having approximate dimensions of 0.200 x 0.200 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID diffractometer using multi-layer mirror monochromated Cu-K $\alpha$  radiation.

The crystal-to-detector distance was 127.40 mm.

## Supporting Information

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned} a &= 7.77343(14) \text{ \AA} \\ b &= 13.7756(3) \text{ \AA} & \beta &= 90.465(6)^\circ \\ c &= 24.8433(5) \text{ \AA} \\ V &= 2660.22(8) \text{ \AA}^3 \end{aligned}$$

For  $Z = 4$  and F.W. = 585.50, the calculated density is  $1.462 \text{ g/cm}^3$ . The reflection conditions of:

$$\begin{aligned} h0l: & l = 2n \\ 0k0: & k = 2n \end{aligned}$$

uniquely determine the space group to be:

$$P2_1/c \text{ (\#14)}$$

The data were collected at a temperature of  $-180 \pm 1^\circ\text{C}$  to a maximum  $2\theta$  value of  $136.4^\circ$ . A total of 45 oscillation images were collected. A sweep of data was done using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $6.0 \text{ [sec./}^\circ]$ . A second sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 90.0^\circ$ . The exposure rate was  $6.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 180.0^\circ$ . The exposure rate was  $6.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 270.0^\circ$ . The exposure rate was  $6.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=0.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $6.0 \text{ [sec./}^\circ]$ . The crystal-to-detector distance was  $127.40 \text{ mm}$ . Readout was performed in the  $0.100 \text{ mm}$  pixel mode.

*EXPERIMENTAL DETAILS*

The sample for X-ray crystal structure analysis was prepared by condensation method. A pre-dried 1 mL sample tube was charged with **10a**, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The sample tube was left to stand in a 5 mL sample tube charged with argon gas until a single crystal forms.

## A. Crystal Data

Empirical Formula	C <sub>32</sub> H <sub>29</sub> BrN <sub>2</sub> O <sub>4</sub>
Formula Weight	585.50
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.77343(14) Å b = 13.7756(3) Å c = 24.8433(5) Å β = 90.465(6) ° V = 2660.22(8) Å <sup>3</sup>
Space Group	P2 <sub>1</sub> /c (#14)

## Supporting Information

Z value	4
D <sub>calc</sub>	1.462 g/cm <sup>3</sup>
F <sub>000</sub>	1208.00
μ(CuKα)	24.469 cm <sup>-1</sup>

### B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å)
monochromated	multi-layer mirror
Voltage, Current	40kV, 30mA
Temperature	-180.0°C
Detector Aperture	460.0 x 256.0 mm
Data Images	45 exposures
ω oscillation Range (χ=54.0, φ=0.0)	80.0 - 260.0°
Exposure Rate	6.0 sec./°
ω oscillation Range (χ=54.0, φ=90.0)	80.0 - 260.0°

## Supporting Information

Exposure Rate	6.0 sec./ $^{\circ}$
$\omega$ oscillation Range ( $\chi=54.0$ , $\phi=180.0$ )	80.0 - 260.0 $^{\circ}$
Exposure Rate	6.0 sec./ $^{\circ}$
$\omega$ oscillation Range ( $\chi=54.0$ , $\phi=270.0$ )	80.0 - 260.0 $^{\circ}$
Exposure Rate	6.0 sec./ $^{\circ}$
$\omega$ oscillation Range ( $\chi=0.0$ , $\phi=0.0$ )	80.0 - 260.0 $^{\circ}$
Exposure Rate	6.0 sec./ $^{\circ}$
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\max}$	136.4 $^{\circ}$
No. of Reflections Measured	Total: 29736 Unique: 4860 ( $R_{\text{int}} = 0.0614$ )
Corrections	Lorentz-polarization Absorption (trans. factors: 0.582 - 0.783)

### C. Structure Solution and Refinement

## Supporting Information

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F <sup>2</sup>
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [ \sigma^2(F_o^2) + (0.0461 \cdot P)^2 + 2.4256 \cdot P ]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	136.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4860
No. Variables	360
Reflection/Parameter Ratio	13.50
Residuals: R1 (I>2.00σ(I))	0.0501
Residuals: R (All reflections)	0.0801
Residuals: wR2 (All reflections)	0.1172
Goodness of Fit Indicator	1.047
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.82 e <sup>-</sup> /Å <sup>3</sup>

## Supporting Information

Minimum peak in Final Diff. Map       $-0.57 \text{ e}^-/\text{\AA}^3$

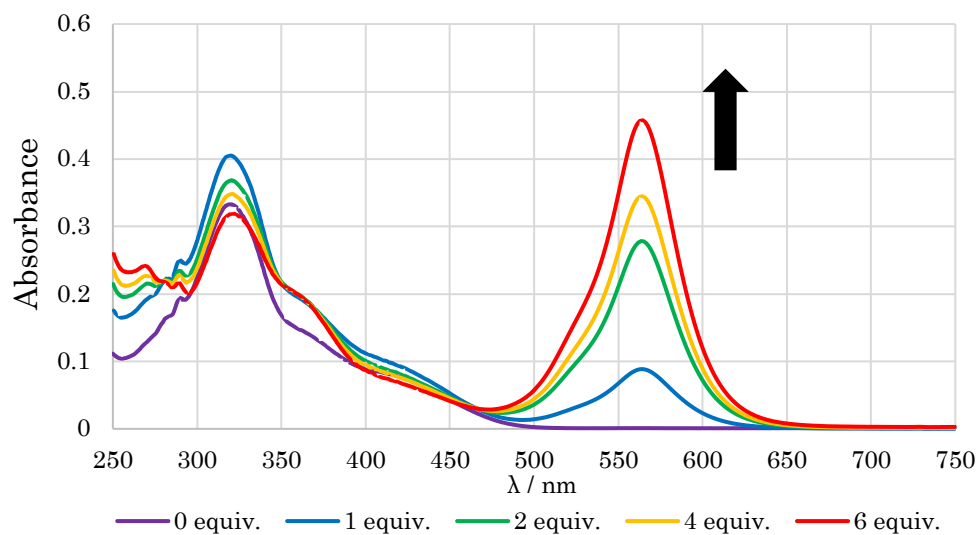
4. [Additional Studies on F<sup>-</sup> Anion Sensor](#)**Figure S1. Additional Colorimetric Experiments**

free (9a only) F<sup>-</sup> (1 eq.) F<sup>-</sup> (10 eq.)

conditions: 9a (0.19 mg, 0.5 μmol), TBAF (1 M in THF) (0.5 μL, 0.5 μmol, 1 equiv. or 5 μL, 5 μmol, 10 equiv.), MeCN (10 mL, 0.05 mM)

**Figure S2. Additional UV/vis Spectra Experiments**

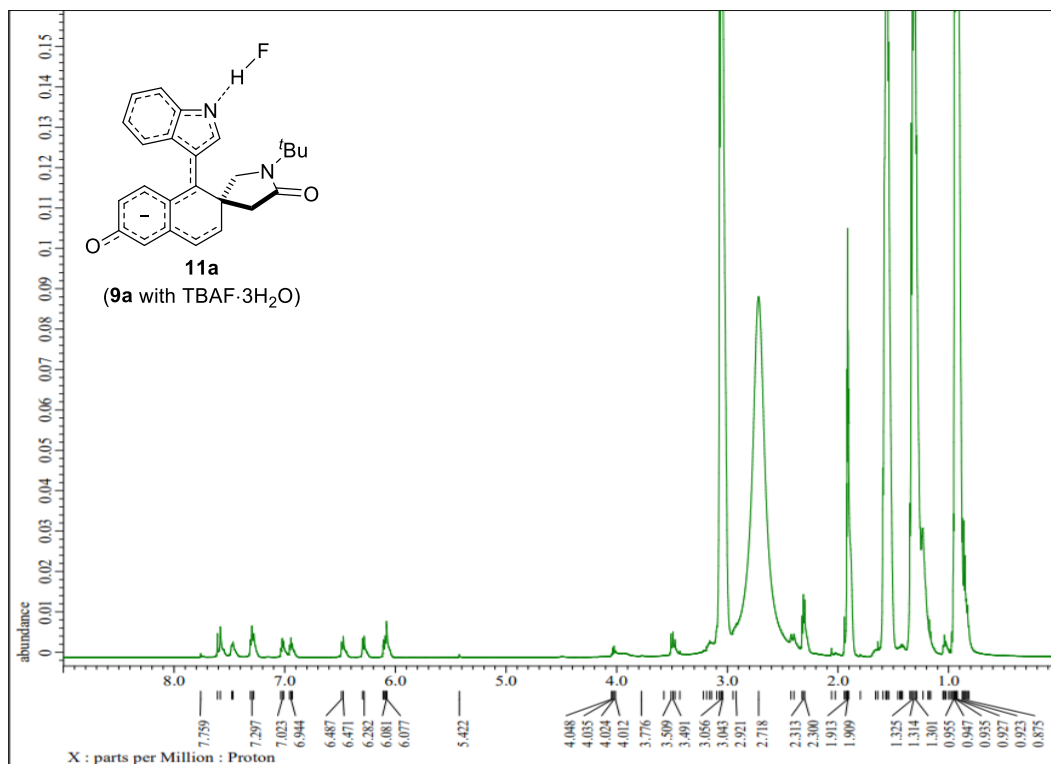
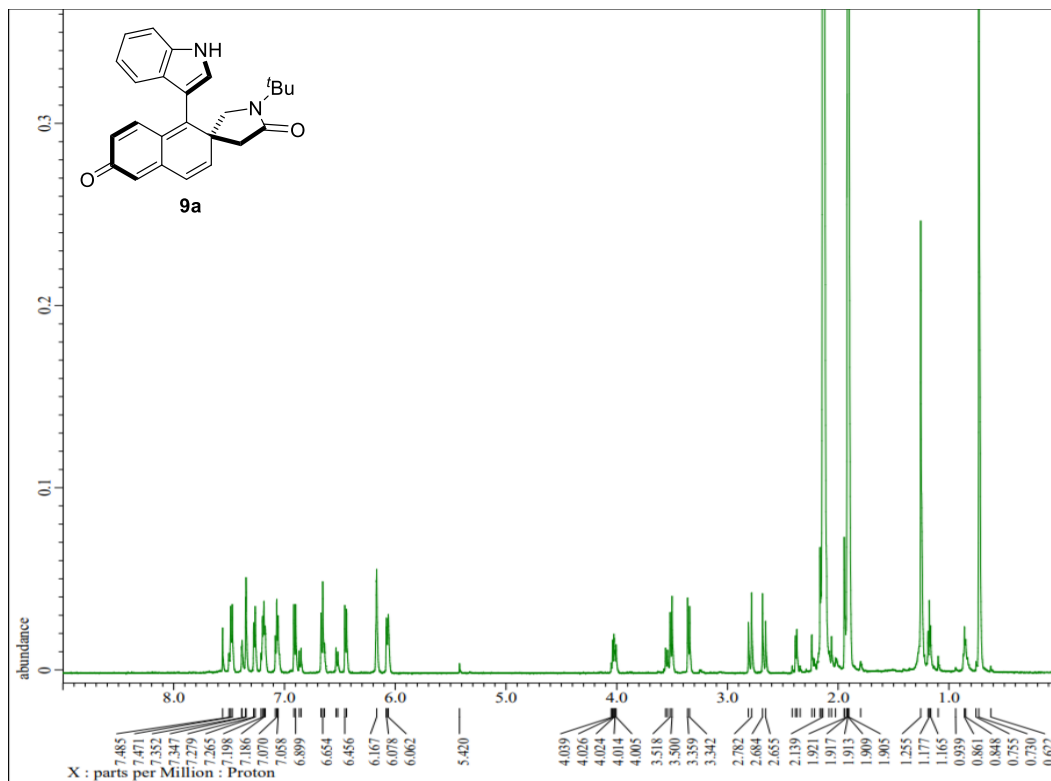
UV/vis spectra of 9a recorded in MeCN (0.017 mM) after addition of TBAF (1 M in THF, 0–6 equiv.).



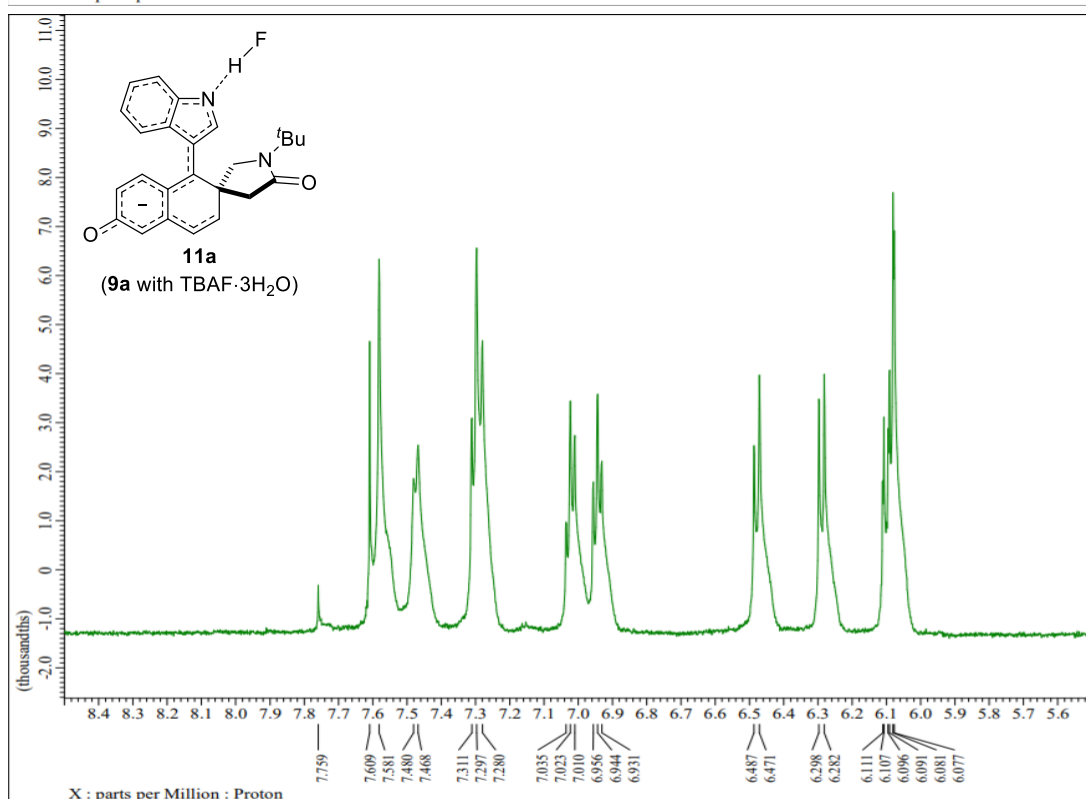
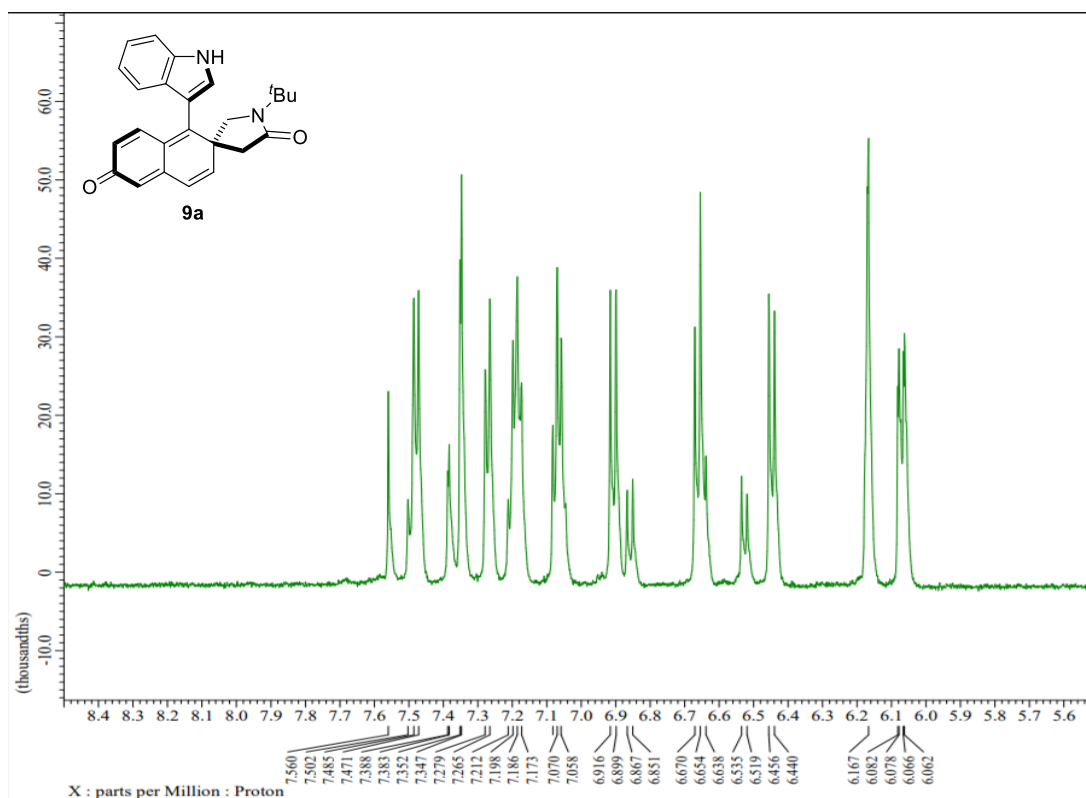
## Supporting Information

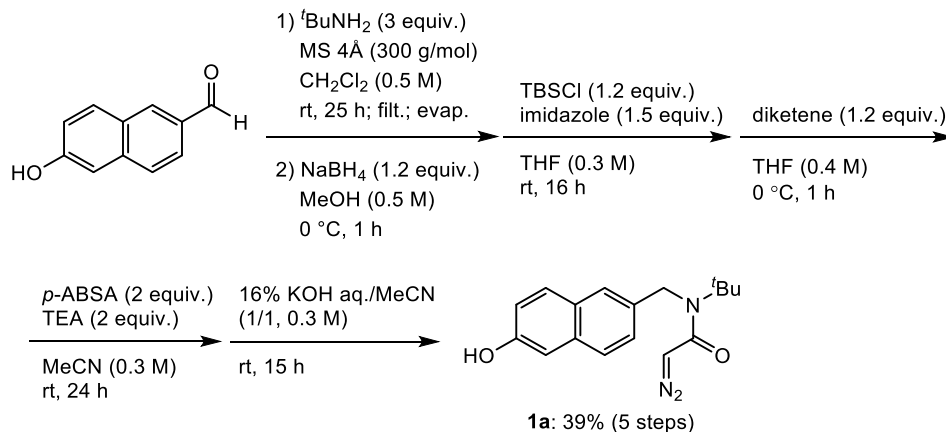
### Figure S3. $^1\text{H}$ NMR Experiments

Samples (1.9 mg, 0.005 mmol) were dissolved in acetonitrile- $d_6$  (1 mL, 5 mM). TBAF $\cdot$ 3H $_2$ O (15.8 mg, 10 equiv.) was used as F $^-$  anion.



# Supporting Information



5. [Synthesis and Characterization of Substrates](#)

To a stirred suspension of 6-hydroxy-2-naphthaldehyde (860.9 mg, 5 mmol) and activated MS 4Å (1500 mg, 300 g/mol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added  $^t\text{BuNH}_2$  (1.6 mL, 15 mmol, 3 equiv.), and the reaction mixture was stirred for 25 h at room temperature. The mixture was then filtered through Celite® and concentrated under reduced pressure to remove  $\text{CH}_2\text{Cl}_2$ . MeOH (10 mL) was added to the residue. The resulting solution was cooled to 0 °C in an ice bath,  $\text{NaBH}_4$  (227 mg, 6 mmol, 1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with  $\text{EtOAc} \times 3$ , and the combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford crude secondary amine (750.4 mg), which was used for the next step without further purification.

To a stirred solution of crude secondary amine and imidazole (333.6 mg, 4.9 mmol, 1.5 equiv.) in THF (11 mL) was added TBSCl (587.8 mg, 3.9 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 16 h at room temperature, saturated aqueous  $\text{NH}_4\text{Cl}$  was added. The reaction mixture was extracted with  $\text{EtOAc} \times 3$ , washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford the crude mixture, which was used for the next step without further purification.

To a stirred solution of the crude residue obtained above in THF (8.3 mL) was added diketene (0.31 mL, 4.0 mmol, 1.2 equiv.) at 0 °C in an ice bath, and

## Supporting Information

the reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched with the addition of 1 N aqueous KHSO<sub>4</sub> and the aqueous layer was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove polar compounds (*n*-hexane/EtOAc = 3/1). The filtrate was concentrated to give crude mixture, which was used for the next step without further purification.

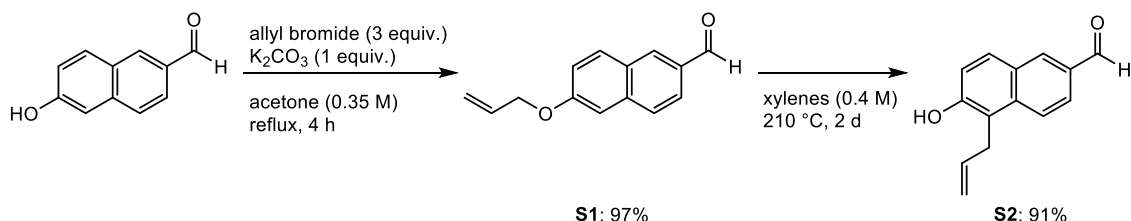
The crude residue obtained above was dissolved in MeCN (11 mL), and *para*-acetamidobenzenesulfonyl azide (1585.6 mg, 6.6 mmol, 2 equiv.) and Et<sub>3</sub>N (0.92 mL, 6.6 mmol, 2 equiv.) were added at 0 °C in an ice bath. After being stirred for 24 h at room temperature, the reaction mixture was quenched with the addition of saturated aqueous NH<sub>4</sub>Cl and the aqueous layer was extracted with EtOAc×2. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove polar compounds (*n*-hexane/EtOAc = 2/1) and concentrated to give crude mixture (987.0 mg), which was used for the next step without further purification.

A solution of the crude residue obtained above in 16% aqueous KOH/CH<sub>3</sub>CN (1/1, 7.4 mL) was stirred for 15 h at room temperature. The reaction was quenched with the addition of saturated aqueous NH<sub>4</sub>Cl and diluted with EtOAc. The aqueous layer was extracted with EtOAc×3, and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and purified by recrystallization (*n*-hexane/ CH<sub>2</sub>Cl<sub>2</sub>) to afford diazocarbonyl compound **1a** as yellow solid (585.8 mg, 39% yield (5 steps)).

***N*-(*tert*-Butyl)-2-diazo-*N*-((6-hydroxynaphthalen-2-yl)methyl)acetamide (1a)**  
m.p. 147–149 °C; R<sub>f</sub> = 0.4 (*n*-hexane/EtOAc, 1/3); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.71 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.55 (s, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.10 (s, 1H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.62 (s, 1H), 4.54 (s, 2H), 1.39 (s, 9H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 167.0, 155.2, 134.0, 133.7, 129.2, 127.7, 126.5, 124.6, 123.9, 118.9, 108.6, 57.7, 48.4, 48.2, 28.6 (3C); IR (ATR) 3157, 3095, 2960, 2098, 1632, 1575, 1415, 1393, 1365,

## Supporting Information

1220, 1189, 1172  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{NaO}_2^+$   $m/z$  320.1369, found  $m/z$  320.1363.



A pre-dried 100 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with 6-hydroxy-2-naphthaldehyde (1721.8 mg, 10 mmol) and  $\text{K}_2\text{CO}_3$  (1382.1 mg, 10 mmol, 1 equiv.), which were subsequently dissolved partially in acetone (28.6 mL) under an argon gas atmosphere. To the stirred suspension was added allyl bromide (2.6 mL, 30 mmol, 3 equiv.) at room temperature. The reaction mixture was refluxed for 4 h in an oil bath. The reaction mixture was then cooled to room temperature, diluted with  $\text{Et}_2\text{O}$ , and quenched with the addition of water. The aqueous layer was extracted with  $\text{Et}_2\text{O} \times 2$  and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (*n*-hexane/ $\text{EtOAc}$  = 6/1) to afford **S1** as beige solid (2.1 g, 97% yield).

A pre-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with **S1** (2.1 g, 9.7 mmol), which was subsequently dissolved in xylenes (24.3 mL) under an argon gas atmosphere. After being stirred for 2 days at 210 °C, the reaction mixture was then cooled to room temperature, and concentrated under reduced pressure. The aqueous layer was extracted with  $\text{Et}_2\text{O} \times 2$  and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (*n*-hexane/ $\text{EtOAc}$  = 3/1) to afford **S2** as green solid (1.9 g, 91% yield).

### 6-(Allyloxy)-2-naphthaldehyde (**S1**)

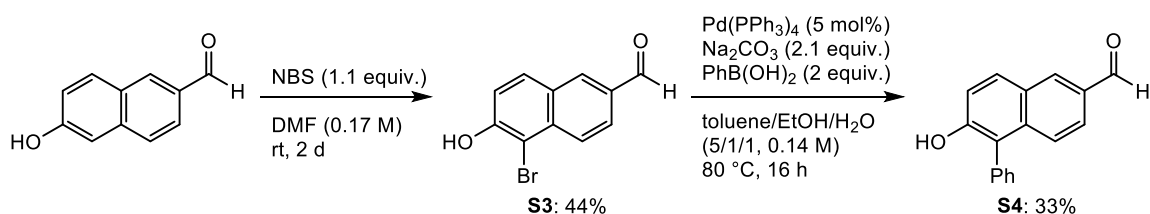
m.p. 56–58 °C;  $R_f$  = 0.6 (*n*-hexane/ $\text{EtOAc}$ , 3/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$

## Supporting Information

10.09 (s, 1H), 8.24 (d,  $J = 1.6$  Hz, 1H), 7.91 (dd,  $J = 8.8, 1.6$  Hz, 1H), 7.89 (d,  $J = 8.8$  Hz, 1H), 7.78 (d,  $J = 8.8$  Hz, 1H), 7.26 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.18 (d,  $J = 2.4$  Hz, 1H), 6.12 (ddt,  $J = 17.2, 10.4, 5.6$  Hz, 1H), 5.49 (dd,  $J = 17.2, 1.6$  Hz, 1H), 5.36 (dd,  $J = 10.4, 1.6$  Hz, 1H), 4.69 (d,  $J = 5.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 159.3, 138.3, 134.4, 132.7, 132.5, 131.3, 128.1, 127.9, 123.7, 120.3, 118.4, 107.3, 69.1; IR (ATR) 2915, 2831, 2725, 2119, 1907, 1678, 1620, 1474, 1420, 1383, 1360, 1333, 1264, 1240, 1178, 1150  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{14}\text{H}_{12}\text{NaO}_2^+$   $m/z$  235.0730, found  $m/z$  235.0735.

### 5-Allyl-6-hydroxy-2-naphthaldehyde (S2)

m.p. 122–124 °C;  $R_f = 0.3$  (*n*-hexane/EtOAc, 3/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.28 (d,  $J = 1.6$  Hz, 1H), 7.99 (d,  $J = 9.2$  Hz, 1H), 7.95 (dd,  $J = 9.2, 1.6$  Hz, 1H), 7.85 (d,  $J = 9.2$  Hz, 1H), 7.22 (d,  $J = 9.2$  Hz, 1H), 6.07 (ddt,  $J = 17.2, 10.0, 4.0$  Hz, 1H), 5.60 (s, 1H), 5.14 (dd,  $J = 10.0, 1.6$  Hz, 1H), 5.06 (dd,  $J = 17.2, 1.6$  Hz, 1H), 3.85 (dd,  $J = 4.0, 1.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.4, 154.4, 137.0, 135.4, 135.3, 131.9, 130.4, 128.6, 124.3, 123.7, 119.2, 117.8, 116.5, 29.4; IR (ATR) 2970, 1747, 1670, 1488, 1426, 1365, 1285, 1230  $\text{cm}^{-1}$ ;  $[\text{M} + \text{Na} + 2\text{H}_2\text{O}]^+$  calcd for  $\text{C}_{14}\text{H}_{16}\text{NaO}_4^+$   $m/z$  271.0941, found  $m/z$  271.0946.

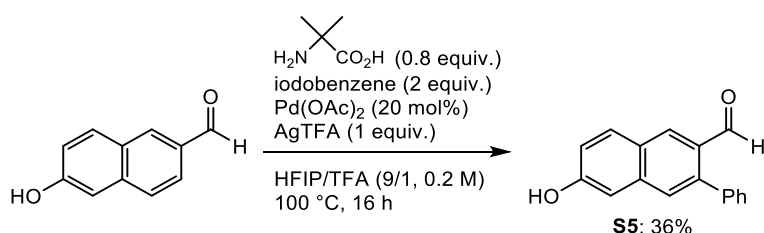


**S3** was synthesized with reported procedure.<sup>[1]</sup>

A pre-dried 50 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with toluene/EtOH/H<sub>2</sub>O (5/1/1, 14.3 mL) and the solvents were degassed by bubbling with argon gas over 0.5 h. To the stirred solution were added Pd(PPh<sub>3</sub>)<sub>4</sub> (115.6 mg, 0.1 mmol, 5 mol%), Na<sub>2</sub>CO<sub>3</sub> (22.3 mg, 0.21 mmol, 2.1 equiv.), **S3** (502.2 mg, 2 mmol), and PhB(OH)<sub>2</sub> (607.8 mg, 4 mmol, 2 equiv.) at room temperature. After being stirred for 16 h at 80 °C, the reaction

## Supporting Information

mixture was then cooled and diluted with water. The aqueous layer was extracted with EtOAc×3 and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through a plug of cotton, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (gradient elution: toluene/ EtOAc = 15/1 → 5/1) and recrystallization (*n*-hexane/EtOAc) to afford as white solid **S4** (162.3 mg, 33% yield). <sup>1</sup>H and <sup>13</sup>C NMR, and other data are identical to those reported.<sup>[2]</sup>

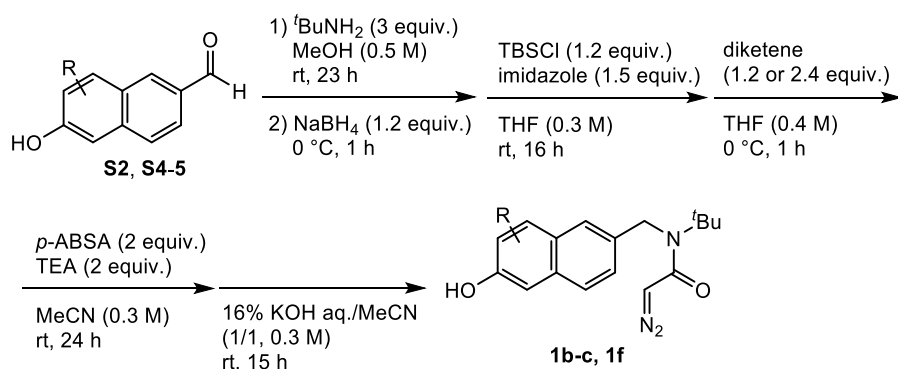


A 100mL Schlenk tube equipped with a magnetic stir bar was charged with 6-hydroxy-2-naphthaldehyde (516.5 mg, 3 mmol), iodobenzene (0.67 mL, 6 mmol, 2 equiv.), Pd(OAc)<sub>2</sub> (134.7 mg, 0.6 mmol, 20 mol%), 2-aminoisobutyric acid (247.5 mg, 2.4 mmol, 0.8 equiv.), and AgTFA (662.6 mg, 3 mmol, 1 equiv.), which were subsequently dissolved in HFIP/TFA (9/1, 15 mL) under an argon gas atmosphere. After being stirred for 16 h at 100 °C, the reaction mixture was then cooled, diluted with EtOAc, filtrated through Celite®, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (*n*-hexane/EtOAc = 6/1) to afford **S5** as white solid (270.6 mg, 36% yield).

### 6-Hydroxy-3-phenyl-2-naphthaldehyde (**S5**)

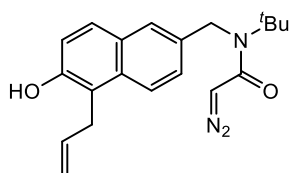
m.p. 147–149 °C; R<sub>f</sub> = 0.1 (*n*-hexane/EtOAc, 5/1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 10.06 (s, 1H), 8.51 (s, 1H), 7.95 (d, *J* = 9.6 Hz, 1H), 7.68 (s, 1H), 7.51-7.48 (m, 1H), 7.49 (d, *J* = 6.0 Hz, 1H), 7.46 (s, 1H), 7.45-7.46 (m, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.20-7.18 (m, 2H), 5.51 (br s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.7, 156.7, 141.8, 138.5, 137.5, 132.2, 130.2 (2C), 130.2, 130.0, 128.6 (2C), 128.2, 128.0, 127.4, 119.5, 109.6; IR (ATR) 2970, 1746, 1661, 1610, 1430, 1396, 1366, 1282, 1229, 1145 cm<sup>-1</sup>; HRMS (ESI-TOF) [M + Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>NaO<sub>2</sub><sup>+</sup> *m/z* 271.0730, found *m/z* 271.0735.

## Supporting Information



To a stirred solution of **S2** or **S4-5** in MeOH was added  $t\text{BuNH}_2$  (3 equiv.), and the reaction mixture was stirred for 23 h at room temperature. The reaction mixture was cooled to 0 °C in an ice bath,  $\text{NaBH}_4$  (1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with  $\text{EtOAc} \times 3$ , and the combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford crude secondary amine, which was used for the next step without further purification.

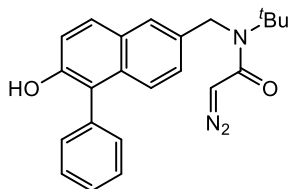
**1b-c** and **1f** were synthesized from secondary amine under the same conditions as synthesis of **1a**.



### *N*-((5-Allyl-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (**1b**)

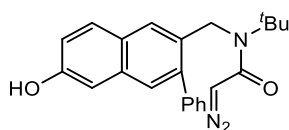
5 mmol of **S2** and 2.4 equiv. of diketene were used and **1b** was afforded as pale yellow solid (197.2 mg, 12% yield (5 steps)).: m.p. 133–135 °C;  $R_f = 0.6$  (*n*-hexane/ $\text{EtOAc}$ , 1/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.8$  Hz, 1H), 7.65 (d,  $J = 8.8$  Hz, 1H), 7.60 (s, 1H), 7.31 (d,  $J = 8.8$  Hz, 1H), 7.15 (d,  $J = 8.8$  Hz, 1H), 6.07 (ddt,  $J = 17.2, 10.4, 5.6$  Hz, 1H), 5.37–5.51 (m, 1H), 5.11 (d,  $J = 10.4$  Hz, 1H), 5.08 (d,  $J = 17.2$  Hz, 1H), 4.81 (s, 1H), 4.57 (s, 2H), 3.83 (d,  $J = 5.6$  Hz, 2H), 1.53 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 151.7, 135.9, 133.3, 132.7, 129.5, 128.1, 125.1, 124.4, 124.1, 118.8, 117.3, 116.0, 58.6, 49.2,

49.0, 29.5, 29.2 (3C); IR (ATR) 3155, 2971, 2926, 2098, 1745, 1574, 1413, 1379, 1218, 1193  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{23}\text{N}_3\text{NaO}_2^+$   $m/z$  360.1682, found  $m/z$  360.1686.



***N*-(*tert*-Butyl)-2-diazo-*N'*((6-hydroxy-5-phenylnaphthalen-2-yl)methyl)acetamide (1c)**

1.8 mmol of **S4** was used and **1c** was afforded as pale yellow solid (146.6 mg, 33% yield (5 steps)).: m.p. 225–227 °C;  $R_f = 0.5$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 7.2$  Hz, 1H), 7.63 (d,  $J = 7.2$  Hz, 1H), 7.60 (dd,  $J = 6.8, 6.0$  Hz, 1H), 7.59 (d,  $J = 8.0$  Hz, 1H), 7.53 (ddd,  $J = 7.6, 7.6, 1.6$  Hz, 1H), 7.43 (s, 1H), 7.42 (d,  $J = 6.8$  Hz, 1H), 7.40 (d,  $J = 6.0$  Hz, 1H), 7.29 (d,  $J = 9.2$  Hz, 1H), 7.18 (dd,  $J = 9.2, 1.6$  Hz, 1H), 5.15 (a, 1H), 4.79 (s, 1H), 4.55 (s, 2H), 1.56 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 150.4, 134.0, 133.8, 132.6, 131.2 (2C), 129.9 (2C), 129.4, 129.0, 128.8, 125.7, 124.6, 124.5, 121.2, 118.2, 58.5, 49.0, 48.9, 29.1 (3C); IR (ATR) 3372, 3113, 2955, 2112, 1739, 1613, 1598, 1405, 1380, 1217, 1191, 1159, 1138  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_3\text{NaO}_2^+$   $m/z$  396.1682, found  $m/z$  396.1686.

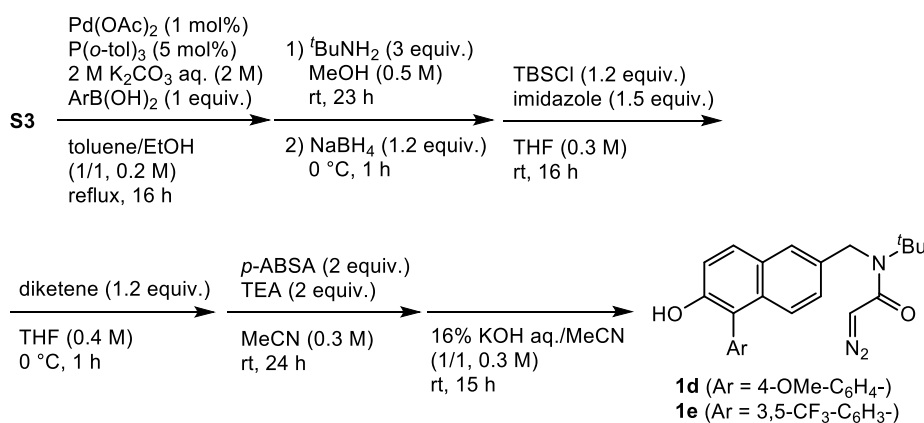


***N*-(*tert*-Butyl)-2-diazo-*N'*((6-hydroxy-3-phenylnaphthalen-2-yl)methyl)acetamide (1f)**

1.1 mmol of **S5** was used and **1f** was afforded as pale pink solid (60.1 mg, 15% yield (5 steps)).: m.p. 161–163 °C;  $R_f = 0.3$  (*n*-hexane/EtOAc, 3/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 9.0$  Hz, 1H), 7.71 (s, 1H), 7.54 (s, 1H), 7.49 (t,  $J = 7.8$  Hz, 1H), 7.47 (d,  $J = 7.8$  Hz, 1H), 7.43 (dd,  $J = 7.8, 9.0$  Hz, 1H), 7.32 (d,  $J = 7.8$  Hz, 2H), 7.18 (s, 1H), 7.17 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.03 (br s, 1H), 4.80 (s, 1H), 4.31 (s, 2H), 1.46 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4,

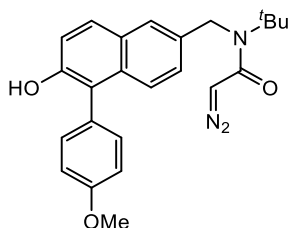
## Supporting Information

154.5, 140.4, 139.2, 133.7, 131.6, 129.7, 128.9 (2C), 128.8 (2C), 128.2, 127.9, 127.8, 125.1, 118.7, 109.4, 58.5, 49.1, 48.4, 29.0 (3C); IR (ATR) 3220, 3099, 2956, 2925, 2109, 1746, 1588, 1415, 1372, 1212  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_3\text{NaO}_2^+$   $m/z$  396.1682, found  $m/z$  396.1684.



A 50 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **S3** (749.9 mg, 3 mmol),  $\text{ArB}(\text{OH})_2$  (3 mmol, 1 equiv.),  $\text{P}(o\text{-tol})_3$  (45.7 mg, 0.15 mmol, 5 mol%), and 2 M aqueous  $\text{K}_2\text{CO}_3$  (1.5 mL), which were subsequently dissolved partially in toluene/EtOH (1/1, 15 mL) under an argon gas atmosphere. After being refluxed for 16 h, the reaction mixture was then cooled, diluted with EtOAc and water. The aqueous layer was extracted with EtOAc $\times$ 3 and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered through a plug of cotton, concentrated under reduced pressure, and passed through a short pad of silica to remove borane reagents (*n*-hexane/EtOAc) to give the crude mixture.

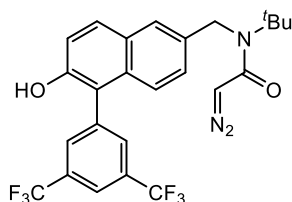
**1d** and **1e** were synthesized from the crude aldehyde with the same conditions as synthesis of **1c**.



***N*-(*tert* Butyl)-2-diazo-*N*-((6-hydroxy-5-(4-methoxyphenyl)naphthalen-2-yl)methyl)acetamide (1d)**

## Supporting Information

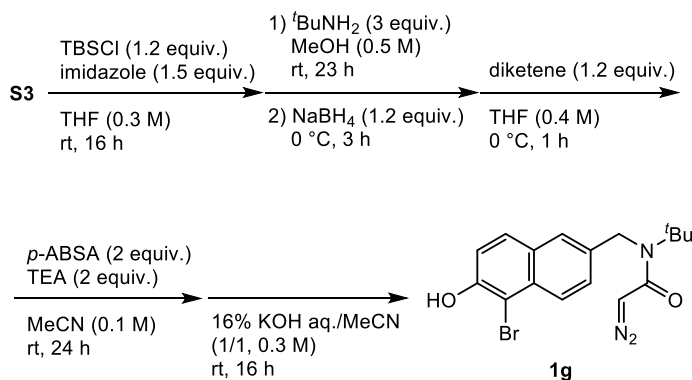
3 mmol of **S3** was used and **1d** was afforded as pale yellow solid (77.3 mg, 6% yield (6 steps)).: m.p. 199–201 °C;  $R_f = 0.6$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.8$  Hz, 1H), 7.63 (s, 1H), 7.42 (d,  $J = 8.8$  Hz, 1H), 7.34 (d,  $J = 8.8$  Hz, 2H), 7.28 (d,  $J = 8.8$  Hz, 1H), 7.17 (d,  $J = 8.8$  Hz, 1H), 7.13 (d,  $J = 8.8$  Hz, 2H), 5.21 (br s, 1H), 4.79 (s, 1H), 4.55 (s, 2H), 3.92 (s, 3H), 1.51 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 160.0, 150.7, 133.7, 133.0, 132.4 (2C), 129.2, 129.1, 125.7 (2C), 124.6, 124.4, 120.9, 118.1, 115.3 (2C), 58.5, 55.6, 49.0, 49.0, 29.1 (3C); IR (ATR) 3296, 2970, 2107, 1739, 1596, 1515, 1406, 1379, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{25}\text{N}_3\text{NaO}_3^+$   $m/z$  426.1788, found  $m/z$  426.1798.



### *N*-((5-(3,5-Bis(trifluoromethyl)phenyl)-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (**1e**)

3 mmol of **S3** was used and **1e** was afforded as pale yellow solid (79.0 mg, 6% yield (6 steps)).: m.p. 136–138 °C;  $R_f = 0.6$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 2H), 7.81 (d,  $J = 9.0$  Hz, 1H), 7.80 (s 1H), 7.66 (s, 1H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.30 (d,  $J = 9.0$  Hz, 1H), 7.23 (d,  $J = 7.2$  Hz, 1H), 6.10 (br s, 1H), 4.80 (s, 1H), 4.57 (s, 2H), 1.53 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 151.0, 137.8, 134.1, 132.4 ( $J = 34.5$  Hz, 2C), 132.3, 131.7 (2C), 130.5, 129.1, 127.8, 125.3, 124.9, 124.4, 122.6, 122.0, 118.8, 118.6, 58.7, 49.3, 49.0, 29.2 (3C);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6; IR (ATR) 3296, 2970, 2107, 1739, 1596, 1515, 1406, 1379, 1217  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{21}\text{F}_6\text{N}_3\text{NaO}_2^+$   $m/z$  532.1430, found  $m/z$  532.1437.

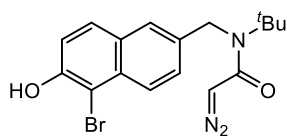
## Supporting Information



To a stirred solution of **S3** (2510.8 mg, 10 mmol) and imidazole (1021.2 mg, 15 mmol, 1.5 equiv.) in THF (33.3 mL) was added TBSCl (1808.6 mg, 12 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 16 h at room temperature, saturated aqueous  $\text{NH}_4\text{Cl}$  was added. The reaction mixture was extracted with  $\text{EtOAc} \times 3$ , washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The resulting residue was passed through a short pad of silica to remove excessive imidazole (*n*-hexane/ $\text{EtOAc}$  = 5/1) and azeotropically distilled with toluene to remove *tert*-butyldimethylsilanol and give crude silylated product (913.4 mg), which was used for the next step without further purification.

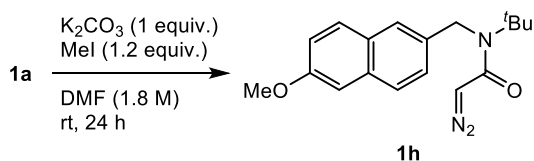
To a stirred solution of the silylated product in MeOH was added  $^t\text{BuNH}_2$  (0.79 mL, 7.5 mmol, 3 equiv.), and the reaction mixture was stirred for 23 h at room temperature. The reaction mixture was cooled to 0 °C in an ice bath,  $\text{NaBH}_4$  (113.5 mg, 3 mmol, 1.2 equiv.) was then added, and stirring was continued for 1 h at 0 °C. The reaction was quenched with the addition of water and concentrated under reduced pressure to remove most of the MeOH. The aqueous solution was extracted with  $\text{EtOAc} \times 3$ , and the combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford crude secondary amine, which was used for the next step without further purification.

**1g** was synthesized from silylated product under the same conditions as synthesis of **1a**.



***N*-((5-Bromo-6-hydroxynaphthalen-2-yl)methyl)-*N*-(*tert*-butyl)-2-diazoacetamide (**1g**)**

**1g** was afforded as beige solid (69.8 mg, 3% yield (5 steps)).: m.p. 112–114 °C;  $R_f = 0.7$  (*n*-hexane/EtOAc, 1/1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.4$  Hz, 1H), 7.72 (d,  $J = 8.4$  Hz, 1H), 7.61 (s, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 7.29 (d,  $J = 8.4$  Hz, 1H), 4.78 (s, 1H), 4.59 (s, 2H), 1.51 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 150.8, 134.8, 131.7, 129.8, 129.2, 127.8, 126.4, 125.8, 118.0, 106.1, 58.5, 49.0, 48.8, 29.1 (3C); IR (ATR) 3095, 2969, 2925, 2105, 1714, 1584, 1416, 1362, 1329, 1296  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{18}\text{BrN}_3\text{NaO}_2^+$   $m/z$  398.0475, found  $m/z$  398.0495.

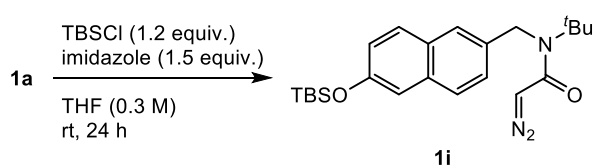


A 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **1a** (61.5 mg, 0.21 mmol) and  $\text{K}_2\text{CO}_3$  (34.6 mg, 0.25 mmol, 1.2 equiv.), which were subsequently dissolved in DMF (0.12 mL) under an argon gas atmosphere. To the stirred solution was added dropwise MeI (15.6  $\mu\text{L}$ , 0.25 mmol, 1.2 equiv.) at room temperature. After being stirred for 24 h, the reaction mixture was quenched with the addition of water. The aqueous layer was extracted with  $\text{Et}_2\text{O} \times 3$  and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered through a plug of cotton, concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/EtOAc = 6/1) to afford **1h** as yellow oil (64.7 mg, 99% yield).

***N*-(*tert*-Butyl)-2-diazo-*N*-((6-methoxynaphthalen-2-yl)methyl)acetamide (**1h**)**

$R_f = 0.6$  (*n*-hexane/EtOAc, 3/1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.4$  Hz, 1H), 7.71 (d,  $J = 9.2$  Hz, 1H), 7.59 (s, 1H), 7.28 (d,  $J = 9.2$  Hz, 1H), 7.18

(dd,  $J = 8.4, 2.4$  Hz, 1H), 7.14 (d,  $J = 2.4$  Hz, 1H), 4.81 (s, 1H), 4.56 (s, 2H), 3.93 (s, 3H), 1.52 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 157.9, 134.1, 133.9, 129.3, 129.1, 127.7, 124.4, 124.3, 119.4, 105.9, 58.5, 55.5, 49.0, 49.0, 29.1 (3C); IR (ATR) 2963, 2101, 1739, 1607, 1484, 1400, 1360, 1264, 1210, 1194, 1171  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_3\text{NaO}_2^+$   $m/z$  334.1526, found  $m/z$  334.1541.



A 30 mL eggplant-shaped flask equipped with a magnetic stir bar was charged with **1a** (89.2 mg, 0.3 mmol) and imidazole (30.6 mg, 0.45 mmol, 1.5 equiv.), which were subsequently dissolved in THF (1 mL) under an argon gas atmosphere. To the stirred solution was added TBSCl (54.3 mg, 0.36 mmol, 1.2 equiv.) at 0 °C in an ice bath. After being stirred for 24 h at room temperature, the reaction mixture was quenched with the addition of water. The aqueous layer was extracted with  $\text{Et}_2\text{O} \times 3$  and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered through a plug of cotton, concentrated under reduced pressure, and purified by flash column chromatography (*n*-hexane/ $\text{EtOAc} = 8/1$ ) to afford **1g** as yellow oil (99.4 mg, 80% yield).

***N*-(*tert*-Butyl)-*N*-(6-((*tert*-butyldimethylsilyloxy)naphthalen-2-yl)methyl)-2-diazoacetamide (**1i**)**

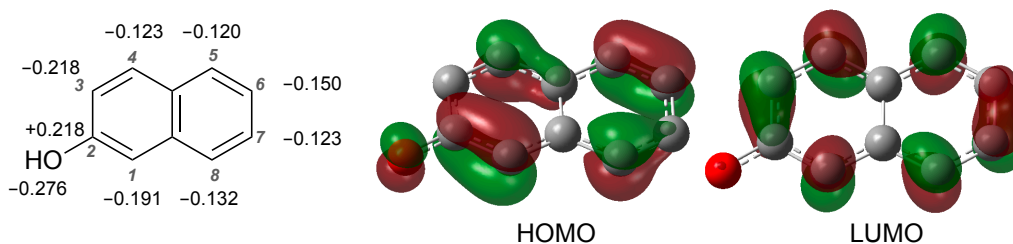
$R_f = 0.7$  (*n*-hexane/ $\text{EtOAc}$ , 2/1);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 9.0$  Hz, 1H), 7.69 (d,  $J = 9.0$  Hz, 1H), 7.59 (s, 1H), 7.25 (dd,  $J = 9.0, 2.4$  Hz, 1H), 7.19 (d,  $J = 3.0$  Hz, 1H), 7.10 (dd,  $J = 9.0, 3.0$  Hz, 1H), 4.81 (s, 1H), 4.55 (s, 2H), 1.52 (s, 9H), 1.02 (s, 9H), 0.25 (s, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 153.8, 134.3, 133.9, 129.4, 129.2, 127.6, 124.2, 124.1, 122.9, 115.0, 58.5, 49.1, 49.0, 29.2 (3C), 25.9 (3C), 18.4,  $-4.2$  (2C); IR (ATR) 2952, 2929, 2858, 2098, 1602, 1482, 1399, 1380, 1264, 1232, 1216  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{33}\text{N}_3\text{NaO}_2\text{Si}^+$   $m/z$  434.2234, found  $m/z$  434.2241.

6. [Computational Details](#)

All the calculations were performed with Gaussian 16 program.<sup>[3]</sup>

**Mulliken Charge Distribution and Frontier Molecular Orbital of  $\beta$ -Naphthol**

The molecular structure optimizations were carried out using the hybrid density functional method based on  $\omega$ B97XD functional and the cc-pVTZ basis set for H, C, and O. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency), and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K.



Energy (RwB97XD): -461.107554 A.U.

Zero-point correction=	0.153124
(Hartree/Particle)	
Thermal correction to Energy=	0.161079
Thermal correction to Enthalpy=	0.162023
Thermal correction to Gibbs Free Energy=	0.120520
Sum of electronic and zero-point Energies=	-460.954430
Sum of electronic and thermal Energies=	-460.946475
Sum of electronic and thermal Enthalpies=	-460.945531
Sum of electronic and thermal Free Energies=	-460.987033

## Cartesian Coordinates

Atom	X	Y	Z
-----			
C	1.852093	1.260232	-0.000084
C	2.678805	-0.99614	0.000102

## Supporting Information

C	0.522034	0.779055	0.000090
H	2.018765	2.330236	0.000089
C	1.407348	-1.490583	0.000109
H	3.521431	-1.674438	0.000723
C	0.290043	-0.619732	-0.000080
C	-0.592807	1.646779	0.000130
H	1.234947	-2.559283	0.000307
C	-1.034759	-1.105582	-0.000168
C	-1.865408	1.157536	0.000025
H	-0.425732	2.716379	0.000182
C	-2.090174	-0.236866	-0.000051
H	-1.223861	-2.170492	-0.000166
H	-2.711026	1.835595	-0.000075
O	-3.349814	-0.745755	-0.000137
H	-3.984483	-0.028991	0.001163
C	2.907404	0.396008	-0.000154
H	3.921000	0.772798	-0.000639

### Mechanistic Studies on Dearomative Spirocyclization of $\beta$ -Naphthols

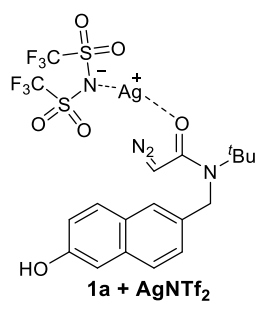
The molecular structure optimizations were carried out using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-YangParr nonlocal correlation functional (B3LYP)<sup>[4]</sup> and the LANL2DZ basis set for Ag, and the 6-31G\* basis set for H, C, N, O, F and S. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.<sup>[5]</sup> Single point energies were calculated at the RB3PW91 level using SDD basis set<sup>[6]</sup> for Ag and 6-311++G\*\* basis set for H, C, N, O, F and S in CH<sub>2</sub>Cl<sub>2</sub> solvent using CPCM model.

## Supporting Information

	E(RB3LYP/6-31G*) (A.U.)	Thermal Correction to Free Energy (A.U.)	Sum of Electronic and Thermal Free Energies (A.U.)
<b>1a+AgNTf<sub>2</sub></b>	-2946.817203	0.310667	-1848962.316
<b>TS1</b>	-2946.802981	0.311878	-1848952.632
<b>CP1</b>	-2946.809715	0.311874	-1848956.86
<b>TS2A</b>	-2946.780869	0.309385	-1848940.321
<b>TS2B</b>	-2946.779106	0.309294	-1848939.272
<b>TS2C</b>	-2946.764332	0.312167	-1848928.198
<b>INT1</b>	-2946.829151	0.303944	-1848974.033
<b>CP2</b>	-2946.874147	0.304287	-1849002.053

	E(RB3PW91/6-311++G**) (A.U.)	Thermal Correction to Free Energy (A.U.)	Sum of Electronic and Thermal Free Energies (A.U.)
<b>1a+AgNTf<sub>2</sub></b>	-2947.926064	0.310667	-1849658.138
<b>TS1</b>	-2947.91443	0.311878	-1849650.077
<b>CP1</b>	-2947.925639	0.311874	-1849657.114
<b>TS2A</b>	-2947.890114	0.309385	-1849636.383
<b>TS2B</b>	-2947.888362	0.309294	-1849635.341
<b>TS2C</b>	-2947.872962	0.312167	-1849623.874
<b>INT1</b>	-2947.944093	0.303944	-1849673.67
<b>CP2</b>	-2947.985516	0.304287	-1849699.448

## Supporting Information



Zero-point correction=	0.390951 (Hartree/Particle)
Thermal correction to Energy=	0.430293
Thermal correction to Enthalpy=	0.431237
Thermal correction to Gibbs Free Energy=	0.310667
Sum of electronic and zero-point Energies=	-2946.426252
Sum of electronic and thermal Energies=	-2946.386910
Sum of electronic and thermal Enthalpies=	-2946.385966
Sum of electronic and thermal Free Energies=	-2946.506536

### Cartesian Coordinates

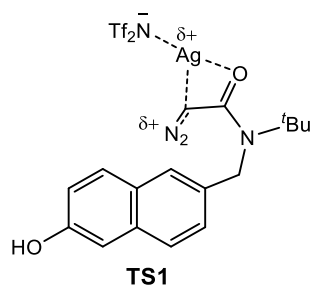
Atom	X	Y	Z
-----			
Ag	1.49104	-1.46036	-0.18948
C	-1.48621	-2.16885	-2.06415
H	-2.33682	-1.61238	-2.42909
C	-1.26056	-2.6282	-0.69343
O	-0.09204	-2.97063	-0.33981
N	-2.32359	-2.68468	0.14594
C	-2.13828	-3.03901	1.61876
C	-3.67166	-2.47467	-0.40926
H	-3.69404	-2.92182	-1.40985
H	-4.37478	-3.06816	0.17487
N	0.39987	-2.39546	-3.60577
N	-0.47955	-2.28128	-2.89649
C	-4.15307	-1.03097	-0.46931
C	-3.33363	0.0547	-0.2389
C	-5.51744	-0.80367	-0.80928

## Supporting Information

C	-3.8237	1.38561	-0.33546
H	-2.28855	-0.08141	0.02419
C	-6.02221	0.4704	-0.90934
H	-6.16995	-1.65614	-0.98923
C	-5.19708	1.60786	-0.67761
H	-7.06731	0.62447	-1.16651
C	-5.68771	2.93164	-0.77477
H	-6.72633	3.11632	-1.03223
C	-4.84692	4.00329	-0.54403
C	-2.98598	2.50936	-0.10578
C	-3.48503	3.78744	-0.20804
H	-2.8342	4.64231	-0.03228
H	-1.94142	2.34832	0.14771
O	-5.36378	5.26252	-0.65018
H	-4.66519	5.90968	-0.46622
N	2.56893	0.3732	0.18311
S	4.20053	0.40551	-0.12816
S	1.6897	1.62512	0.80429
O	4.93914	1.37145	0.67531
O	4.60206	-1.0008	-0.2126
O	2.22896	2.94953	0.5228
O	0.28339	1.30252	0.51386
C	1.84451	1.35738	2.65017
C	4.24268	1.02203	-1.89452
F	3.69579	2.23183	-1.98486
F	5.51046	1.07095	-2.30411
F	3.5609	0.17222	-2.67592
F	1.3543	0.14716	2.96501
F	3.11404	1.4268	3.0348
F	1.13049	2.29092	3.28244
C	-3.46846	-2.86325	2.37811
H	-4.21872	-3.61105	2.10256
H	-3.26469	-3.00005	3.44396

## Supporting Information

H	-3.89315	-1.86377	2.24484
C	-1.10849	-2.09664	2.27511
H	-0.09872	-2.27029	1.9041
H	-1.36803	-1.04563	2.1153
H	-1.09693	-2.2799	3.35455
C	-1.69324	-4.50975	1.72707
H	-1.59412	-4.78681	2.78265
H	-2.43756	-5.17402	1.27297
H	-0.73259	-4.66933	1.23442



(Figure 2)

Zero-point correction=	0.390225 (Hartree/Particle)
Thermal correction to Energy=	0.428914
Thermal correction to Enthalpy=	0.429858
Thermal correction to Gibbs Free Energy=	0.311878
Sum of electronic and zero-point Energies=	-2946.412756
Sum of electronic and thermal Energies=	-2946.374067
Sum of electronic and thermal Enthalpies=	-2946.373122
Sum of electronic and thermal Free Energies=	-2946.491102

### Cartesian Coordinates

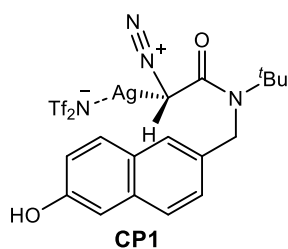
Atom	X	Y	Z
Ag	0.87109	-1.1831	-0.96533
C	-1.3719	-1.63938	-2.09569
H	-1.92279	-0.71592	-2.23308
C	-1.49866	-2.55054	-0.89968

## Supporting Information

O	-0.55046	-3.32707	-0.67078
N	-2.59754	-2.40805	-0.1201
C	-2.6568	-3.10594	1.23695
C	-3.7849	-1.72816	-0.6695
H	-3.83984	-1.95574	-1.74008
H	-4.66813	-2.20123	-0.23682
N	-0.57946	-2.70138	-4.16749
N	-0.95573	-2.20993	-3.21921
C	-3.86151	-0.22142	-0.46693
C	-2.88764	0.5151	0.17476
C	-5.00432	0.45133	-0.98764
C	-3.00613	1.92482	0.32608
H	-2.00607	0.03142	0.58653
C	-5.14828	1.81126	-0.85782
H	-5.77614	-0.12534	-1.49434
C	-4.15821	2.59539	-0.19909
H	-6.02796	2.30774	-1.26005
C	-4.27904	3.99744	-0.05226
H	-5.14637	4.51935	-0.44526
C	-3.2918	4.71647	0.59383
C	-2.01053	2.69347	0.98569
C	-2.14964	4.05623	1.11629
H	-1.37999	4.63595	1.62304
H	-1.13497	2.19107	1.38747
O	-3.45067	6.06713	0.7113
H	-2.68623	6.43799	1.17911
N	2.27953	0.14215	0.05343
S	3.6623	0.46808	-0.7984
S	1.9849	0.57253	1.61704
O	4.85565	0.64095	0.02035
O	3.63009	-0.46826	-1.92913
O	2.70544	1.75742	2.06677
O	0.52833	0.46073	1.79183

## Supporting Information

C	2.66923	-0.88117	2.57708
C	3.2766	2.136	-1.55409
F	3.05256	3.04251	-0.60603
F	4.30988	2.51829	-2.30505
F	2.18699	2.03041	-2.32776
F	2.04535	-2.00377	2.18377
F	3.97465	-1.01147	2.36592
F	2.43953	-0.68968	3.87679
C	-3.87908	-2.60913	2.03322
H	-4.83017	-2.96789	1.62698
H	-3.80062	-3.00635	3.04941
H	-3.91066	-1.51785	2.10279
C	-1.39565	-2.76851	2.05811
H	-0.48862	-3.15385	1.59477
H	-1.28712	-1.68837	2.19981
H	-1.49106	-3.22783	3.04771
C	-2.77976	-4.6237	1.00832
H	-2.86699	-5.13622	1.97292
H	-3.67598	-4.8581	0.42151
H	-1.90372	-5.01362	0.48639



(Figure 2)

Zero-point correction=	0.390225 (Hartree/Particle)
Thermal correction to Energy=	0.428914
Thermal correction to Enthalpy=	0.429858
Thermal correction to Gibbs Free Energy=	0.311878
Sum of electronic and zero-point Energies=	-2946.412756
Sum of electronic and thermal Energies=	-2946.374067

## Supporting Information

Sum of electronic and thermal Enthalpies= -2946.373122

Sum of electronic and thermal Free Energies= -2946.491102

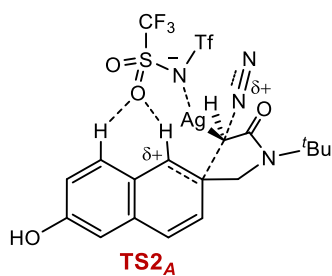
## Cartesian Coordinates

Atom	X	Y	Z
Ag	-0.90295	-0.21523	1.07009
C	1.05377	-0.94454	1.85897
H	1.72566	-0.16636	1.48874
C	1.27523	-2.40101	1.40964
O	1.04409	-3.29049	2.22285
N	1.71601	-2.57576	0.12843
C	1.88021	-4.00523	-0.37949
C	1.79594	-1.41841	-0.78752
H	1.88527	-1.81098	-1.7975
H	0.84508	-0.87296	-0.78936
N	0.96341	-0.91219	4.33792
N	1.02077	-0.90234	3.21843
C	2.93593	-0.44208	-0.53737
C	2.74282	0.90229	-0.80565
C	4.21257	-0.8796	-0.09398
C	3.793	1.84415	-0.65685
H	1.77113	1.25116	-1.15263
C	5.24998	0.0121	0.06395
H	4.36584	-1.931	0.13217
C	5.07901	1.39601	-0.21189
H	6.22109	-0.33885	0.40525
C	6.12839	2.33858	-0.05719
H	7.1049	1.99547	0.28124
C	5.91476	3.6738	-0.33467
C	3.61226	3.22901	-0.9311
C	4.64174	4.12368	-0.77656
H	4.5136	5.1808	-0.98597

## Supporting Information

H	2.63918	3.57302	-1.27222
O	6.87664	4.6327	-0.20977
H	7.70218	4.21947	0.08923
N	-2.5336	0.53423	-0.13531
S	-2.24376	0.73353	-1.74853
S	-4.01698	0.64243	0.60239
O	-3.21091	1.57575	-2.43869
O	-0.79859	0.97118	-1.86596
O	-5.14698	0.3573	-0.27248
O	-3.84292	-0.04068	1.88906
C	-4.10436	2.46211	1.03044
C	-2.46617	-1.00437	-2.41056
F	-3.69565	-1.45011	-2.18254
F	-2.21803	-1.01034	-3.71997
F	-1.58406	-1.82453	-1.80039
F	-3.08431	2.77439	1.84114
F	-4.03342	3.20663	-0.06948
F	-5.25411	2.70005	1.66167
C	2.43562	-4.01813	-1.81533
H	3.37088	-3.45537	-1.90912
H	2.65248	-5.05834	-2.07686
H	1.71924	-3.6483	-2.55613
C	0.50442	-4.70101	-0.37967
H	0.10032	-4.78008	0.63078
H	-0.20548	-4.14591	-1.00379
H	0.6007	-5.71113	-0.79345
C	2.89004	-4.75929	0.51102
H	2.99906	-5.78428	0.1401
H	3.87637	-4.28248	0.46768
H	2.56123	-4.80034	1.54828

## Supporting Information



(Figure 2)

Zero-point correction=	0.388381 (Hartree/Particle)
Thermal correction to Energy=	0.427673
Thermal correction to Enthalpy=	0.428618
Thermal correction to Gibbs Free Energy=	0.309385
Sum of electronic and zero-point Energies=	-2946.392488
Sum of electronic and thermal Energies=	-2946.353195
Sum of electronic and thermal Enthalpies=	-2946.352251
Sum of electronic and thermal Free Energies=	-2946.471484

### Cartesian Coordinates

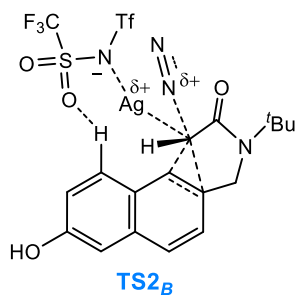
Atom	X	Y	Z
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Ag	-0.30376	-0.42018	0.72663
C	1.69885	-0.59646	1.4147
H	2.24657	0.31133	1.6559
C	2.53344	-1.85482	1.2085
O	2.64728	-2.65166	2.14204
N	3.06145	-2.0547	-0.04105
C	3.70056	-3.40497	-0.34215
C	2.71984	-1.11631	-1.12892
H	3.3826	-1.3315	-1.96454
H	1.69438	-1.28662	-1.48612
N	0.91598	-0.9946	4.31753
N	1.36259	-0.89019	3.31116
C	2.89047	0.34139	-0.75415
C	1.9051	1.26398	-1.0763
C	4.10832	0.80771	-0.17683

## Supporting Information

C	2.07015	2.64588	-0.81178
H	0.98233	0.93964	-1.55095
C	4.29588	2.14279	0.0904
H	4.88808	0.09002	0.0648
C	3.28816	3.10496	-0.21317
H	5.22818	2.48347	0.53454
C	3.45012	4.48575	0.05273
H	4.37567	4.83734	0.50586
C	2.44251	5.37954	-0.26293
C	1.05292	3.59349	-1.1199
C	1.23194	4.9283	-0.85298
H	0.46588	5.66203	-1.08162
H	0.12818	3.23866	-1.56686
O	2.53308	6.71866	-0.03651
H	3.39405	6.92009	0.36372
N	-2.28691	-0.1821	-0.11768
S	-2.46474	0.18891	-1.71641
S	-3.52679	-0.64453	0.88653
O	-3.8024	0.62717	-2.0905
O	-1.27858	0.97023	-2.09111
O	-4.65901	-1.26211	0.20807
O	-2.86601	-1.2928	2.02535
C	-4.12086	1.00083	1.55188
C	-2.18656	-1.46906	-2.53933
F	-3.08561	-2.35869	-2.13259
F	-2.26365	-1.3215	-3.86178
F	-0.95494	-1.92032	-2.22573
F	-3.11757	1.60176	2.20539
F	-4.53194	1.78863	0.56172
F	-5.1268	0.78293	2.39967
C	4.21376	-3.45825	-1.79256
H	4.97361	-2.69606	-1.99896
H	4.68825	-4.43356	-1.9387

## Supporting Information

H	3.41233	-3.37635	-2.53394
C	2.65314	-4.52275	-0.16241
H	2.28674	-4.56327	0.86381
H	1.80326	-4.36744	-0.83746
H	3.10295	-5.49144	-0.40726
C	4.91493	-3.6152	0.58584
H	5.39863	-4.56694	0.33907
H	5.6511	-2.81603	0.43887
H	4.62041	-3.6359	1.634



(Figure 2)

Zero-point correction=	0.388891 (Hartree/Particle)
Thermal correction to Energy=	0.427726
Thermal correction to Enthalpy=	0.428670
Thermal correction to Gibbs Free Energy=	0.312167
Sum of electronic and zero-point Energies=	-2946.375441
Sum of electronic and thermal Energies=	-2946.336606
Sum of electronic and thermal Enthalpies=	-2946.335662
Sum of electronic and thermal Free Energies=	-2946.452165

### Cartesian Coordinates

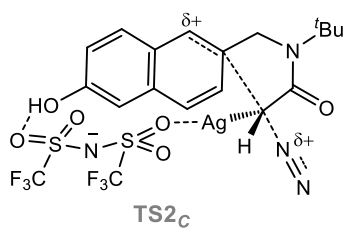
Atom	X	Y	Z
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Ag	0.24449	-0.64637	0.85368
C	2.22494	-0.27896	1.50736
H	2.43947	0.56977	2.15521
C	3.36904	-0.9192	0.74828

## Supporting Information

O	3.50577	-2.14003	0.8119
N	4.10735	-0.07925	-0.04679
C	5.05085	-0.67532	-1.07717
C	4.15527	1.34697	0.32136
H	4.50345	1.44982	1.35943
H	4.92086	1.82277	-0.28935
N	2.06093	-2.20953	3.86389
N	2.29882	-1.48157	3.06604
C	2.84421	2.09582	0.15734
C	1.89699	1.74154	-0.79058
C	2.61431	3.24956	0.96079
C	0.70505	2.49479	-0.96237
H	2.05709	0.87222	-1.42285
C	1.47419	4.00166	0.81314
H	3.35735	3.53636	1.70231
C	0.47828	3.65053	-0.14435
H	1.31266	4.87578	1.43895
C	-0.7182	4.38701	-0.29256
H	-0.91022	5.25723	0.32757
C	-1.67148	3.98755	-1.21187
C	-0.28553	2.12602	-1.91089
C	-1.4466	2.85219	-2.03248
H	-2.20935	2.54226	-2.74361
H	-0.13711	1.23789	-2.51655
O	-2.82016	4.71241	-1.30065
H	-3.42219	4.28414	-1.92966
N	-1.77156	-0.98033	0.14748
S	-3.00273	-0.71111	1.22479
S	-1.9788	-1.41356	-1.43533
O	-4.24868	-1.38973	0.89045
O	-2.39386	-0.82543	2.55282
O	-3.2189	-0.93202	-2.03568
O	-0.68277	-1.16721	-2.0829

## Supporting Information

C	-2.10054	-3.28006	-1.3464
C	-3.32444	1.12223	1.02188
F	-3.70791	1.40619	-0.22437
F	-4.28423	1.48773	1.87298
F	-2.20698	1.8071	1.302
F	-0.98374	-3.76845	-0.79347
F	-3.14981	-3.65309	-0.62042
F	-2.22074	-3.75766	-2.58693
C	5.59687	0.42572	-2.00509
H	6.31816	1.08601	-1.51186
H	6.12723	-0.05983	-2.82981
H	4.79577	1.03316	-2.44091
C	4.27439	-1.67624	-1.95863
H	3.8703	-2.50415	-1.37755
H	3.45073	-1.17547	-2.48016
H	4.9526	-2.08469	-2.71535
C	6.22755	-1.36434	-0.35915
H	6.92965	-1.76827	-1.0975
H	6.77395	-0.64799	0.2662
H	5.87261	-2.18297	0.26914



(Figure 2)

Zero-point correction=	0.387681 (Hartree/Particle)
Thermal correction to Energy=	0.427160
Thermal correction to Enthalpy=	0.428104
Thermal correction to Gibbs Free Energy=	0.309294
Sum of electronic and zero-point Energies=	-2946.391425
Sum of electronic and thermal Energies=	-2946.351946

## Supporting Information

Sum of electronic and thermal Enthalpies= -2946.351002

Sum of electronic and thermal Free Energies= -2946.469812

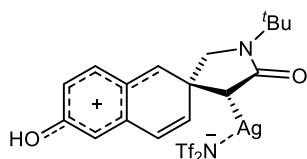
## Cartesian Coordinates

Atom	X	Y	Z
Ag	0.86997	-0.8617	-0.21971
C	2.77702	-0.41864	0.65883
H	2.76124	0.30644	1.46751
C	4.12937	-0.77904	0.05433
O	4.43708	-1.97446	0.07229
N	4.94333	0.19849	-0.45818
C	6.26284	-0.24551	-1.08787
C	4.47416	1.5659	-0.8011
H	5.28893	2.25447	-0.57273
H	4.3094	1.61049	-1.88563
N	2.52431	-2.65175	2.60972
N	2.77308	-1.8331	1.90734
C	3.23384	2.05513	-0.10153
C	2.01723	2.07473	-0.76923
C	3.29582	2.59858	1.21826
C	0.82779	2.51511	-0.1432
H	1.96498	1.72978	-1.80092
C	2.15677	3.02595	1.85776
H	4.25678	2.64616	1.72574
C	0.87814	2.95865	1.22249
H	2.21389	3.41469	2.87145
C	-0.32311	3.26349	1.8958
H	-0.30994	3.55945	2.94045
C	-1.54615	3.10821	1.25547
C	-0.43046	2.46703	-0.79998
C	-1.5875	2.75649	-0.12384
H	-2.54733	2.6795	-0.61944

## Supporting Information

H	-0.47373	2.16288	-1.84293
O	-2.67863	3.30271	1.95721
H	-3.41533	2.82188	1.52041
N	-2.91194	-0.18493	-0.13607
S	-4.4849	0.20919	0.07929
S	-2.41336	-1.67083	-0.45426
O	-5.35447	-0.86133	0.5575
O	-4.50144	1.51665	0.75834
O	-3.30875	-2.59387	-1.14073
O	-1.03441	-1.54312	-1.03857
C	-2.07462	-2.43545	1.2234
C	-5.05023	0.61968	-1.65662
F	-4.88532	-0.42697	-2.4633
F	-6.33926	0.95941	-1.62343
F	-4.3397	1.65324	-2.13361
F	-1.13456	-1.71484	1.87397
F	-3.17898	-2.4603	1.95695
F	-1.61042	-3.67607	1.05801
C	7.09038	0.97658	-1.5377
H	7.3485	1.63581	-0.70173
H	8.02952	0.60095	-1.95491
H	6.6054	1.56702	-2.32015
C	5.97275	-1.11982	-2.32393
H	5.42989	-2.02484	-2.04895
H	5.38503	-0.56348	-3.06441
H	6.91571	-1.41158	-2.79964
C	7.11528	-0.99788	-0.04445
H	8.09511	-1.22264	-0.48006
H	7.27723	-0.36886	0.83861
H	6.65027	-1.93083	0.26699

## Supporting Information



**INT1** + N<sub>2</sub> (Figure 2)

Zero-point correction=	0.388117 (Hartree/Particle)
Thermal correction to Energy=	0.428748
Thermal correction to Enthalpy=	0.429692
Thermal correction to Gibbs Free Energy=	0.303944
Sum of electronic and zero-point Energies=	-2946.441034
Sum of electronic and thermal Energies=	-2946.400403
Sum of electronic and thermal Enthalpies=	-2946.399459
Sum of electronic and thermal Free Energies=	-2946.525207

### Cartesian Coordinates

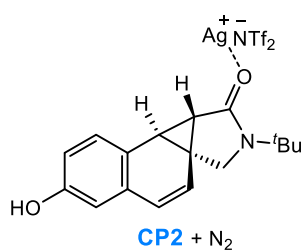
Atom	X	Y	Z
-----			
Ag	-0.18357	-0.36575	0.66453
C	1.95797	-0.52876	1.04082
H	2.12329	-0.00011	1.97841
C	2.2978	-1.98607	1.08987
O	2.02349	-2.72908	2.02572
N	2.98456	-2.34597	-0.06365
C	3.1343	-3.77465	-0.48418
C	2.97436	-1.25001	-1.01885
H	3.87284	-1.24055	-1.63941
H	2.09613	-1.28083	-1.68307
N	-0.77907	-2.30992	4.25465
N	-0.51511	-1.30219	3.88681
C	2.89704	0.02371	-0.12849
C	2.06585	1.10541	-0.6535
C	4.20479	0.46631	0.42556
C	2.33366	2.45291	-0.40014
H	1.19239	0.85124	-1.24731

## Supporting Information

C	4.50221	1.76847	0.6197
H	4.89488	-0.31504	0.73274
C	3.57134	2.81459	0.24189
H	5.44408	2.06237	1.07536
C	3.84429	4.16336	0.45757
H	4.775	4.45833	0.93826
C	2.92591	5.14424	0.05582
C	1.42291	3.47385	-0.80659
C	1.70993	4.79792	-0.58235
H	1.0308	5.59133	-0.87411
H	0.49191	3.17629	-1.28133
O	3.14634	6.45714	0.24747
H	3.99654	6.59546	0.69776
N	-2.16104	0.05774	-0.22385
S	-2.18692	0.65972	-1.75182
S	-3.50632	-0.48208	0.58756
O	-3.45674	1.23594	-2.17429
O	-0.93521	1.41959	-1.92582
O	-4.61475	-0.87635	-0.27401
O	-2.99659	-1.36848	1.63593
C	-4.04649	1.0688	1.48351
C	-1.90944	-0.86677	-2.80039
F	-2.84826	-1.77824	-2.57122
F	-1.92093	-0.52221	-4.08914
F	-0.70496	-1.39787	-2.50803
F	-3.07155	1.47182	2.30837
F	-4.31285	2.04383	0.61493
F	-5.1396	0.79728	2.19822
C	3.9093	-3.83837	-1.81147
H	4.89863	-3.37425	-1.72449
H	4.05879	-4.88847	-2.08164
H	3.36847	-3.36245	-2.6369
C	1.73746	-4.40208	-0.66627

## Supporting Information

H	1.1815	-4.38337	0.2747
H	1.15898	-3.8612	-1.42525
H	1.82814	-5.44442	-0.99222
C	3.93814	-4.53347	0.58869
H	4.06374	-5.57852	0.28311
H	4.93341	-4.08905	0.70598
H	3.42759	-4.50413	1.55162



(Figure 2)

Zero-point correction=	0.389350 (Hartree/Particle)
Thermal correction to Energy=	0.429881
Thermal correction to Enthalpy=	0.430825
Thermal correction to Gibbs Free Energy=	0.304287
Sum of electronic and zero-point Energies=	-2946.484797
Sum of electronic and thermal Energies=	-2946.444267
Sum of electronic and thermal Enthalpies=	-2946.443323
Sum of electronic and thermal Free Energies=	-2946.569861

### Cartesian Coordinates

Atom	X	Y	Z
-----			
Ag	-0.44564	-1.24761	0.62415
C	2.66284	0.13886	0.69992
H	2.1638	0.59769	1.54676
C	2.56962	-1.3293	0.52109
O	1.58968	-2.03996	0.85927
N	3.69578	-1.80488	-0.05978
C	3.91375	-3.24889	-0.41276

## Supporting Information

C	4.74559	-0.77336	-0.16033
H	5.5674	-0.99514	0.53463
H	5.15976	-0.73675	-1.17183
N	-1.04643	-1.73659	4.62437
N	-0.63866	-1.29289	3.69863
C	4.05896	0.53409	0.22208
C	2.84534	0.92966	-0.59889
C	4.83764	1.61438	0.85837
C	2.47337	2.36841	-0.6308
H	2.63514	0.3702	-1.50957
C	4.42718	2.89569	0.81955
H	5.7594	1.34114	1.36717
C	3.22962	3.31893	0.09763
H	5.01052	3.66643	1.31742
C	2.85153	4.66783	0.07705
H	3.41866	5.40973	0.63159
C	1.74156	5.08118	-0.66112
C	1.37545	2.8007	-1.38022
C	1.00449	4.14381	-1.3963
H	0.13575	4.45864	-1.97094
H	0.78191	2.07689	-1.93199
O	1.42648	6.40915	-0.63225
H	0.63182	6.55808	-1.16848
N	-2.29338	-0.40421	-0.13247
S	-3.59178	-0.27187	0.89108
S	-2.26209	0.14128	-1.69324
O	-4.87628	-0.15341	0.21262
O	-3.36524	-1.26227	1.94633
O	-3.16091	1.25642	-1.96767
O	-0.83949	0.21084	-2.0602
C	-2.91159	-1.33042	-2.64964
C	-3.26395	1.37512	1.71659
F	-3.23974	2.3595	0.82113

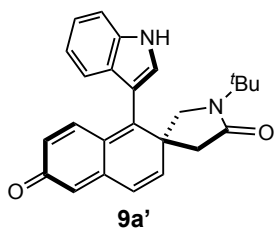
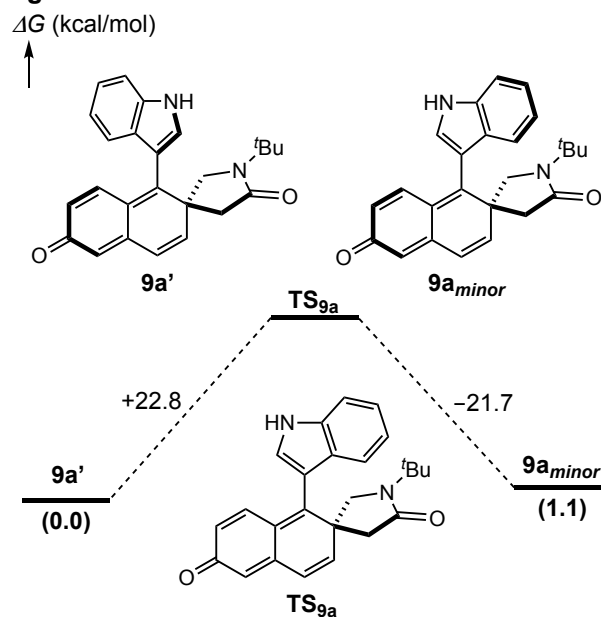
## Supporting Information

F	-4.22203	1.60998	2.61418
F	-2.07842	1.32825	2.34641
F	-2.10728	-2.3825	-2.44331
F	-4.14473	-1.63907	-2.26082
F	-2.91249	-1.03118	-3.95035
C	5.2506	-3.39919	-1.15917
H	6.10524	-3.0733	-0.55748
H	5.39863	-4.45821	-1.39107
H	5.25605	-2.85054	-2.10687
C	2.77887	-3.72988	-1.33728
H	1.80987	-3.68751	-0.83817
H	2.73364	-3.11807	-2.24516
H	2.96838	-4.76664	-1.63553
C	3.95653	-4.07535	0.88755
H	4.12195	-5.13234	0.65192
H	4.77528	-3.74081	1.53514
H	3.01653	-3.98679	1.43684

### Calculation of Axial Rotation of 9a and 11a

The molecular structure optimizations were carried out using the hybrid density functional method based on  $\omega$ B97XD functional and the 6-311+G\* basis set for H, C, N, O, and F. The vibrational frequencies were computed at the same level to check whether each optimized structure is at an energy minimum on the potential energy surfaces (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.<sup>[5]</sup>

Figure S3



(Figure S4)

Zero-point correction=	0.440038 (Hartree/Particle)
Thermal correction to Energy=	0.464539
Thermal correction to Enthalpy=	0.465484
Thermal correction to Gibbs Free Energy=	0.385051
Sum of electronic and zero-point Energies=	-1226.506488
Sum of electronic and thermal Energies=	-1226.481987
Sum of electronic and thermal Enthalpies=	-1226.481043
Sum of electronic and thermal Free Energies=	-1226.561476

## Cartesian Coordinates

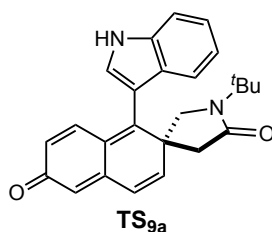
Atom	X	Y	Z
O	-3.59463	-1.59654	1.96351
O	5.84025	-2.33083	-0.69463

## Supporting Information

N	-2.69622	-1.00913	-0.09089
C	3.31718	-0.00991	0.31161
H	3.1976	1.01846	0.63646
C	0.68505	2.19813	-0.02922
C	0.51451	3.37165	0.73533
C	3.51483	-2.70467	-0.5257
H	3.65165	-3.73134	-0.85403
C	-1.41023	-0.52138	-0.57153
H	-1.36018	0.57408	-0.53062
H	-1.21538	-0.83706	-1.5986
C	2.11184	-0.83088	0.20951
C	0.69852	3.54058	-2.01377
H	0.77464	3.63363	-3.0926
C	0.78236	2.29228	-1.42523
H	0.93073	1.39793	-2.02426
C	-1.20385	-1.22526	1.70439
H	-0.93817	-2.05913	2.35691
H	-1.11463	-0.29623	2.27628
C	0.52138	4.70044	-1.23395
H	0.46021	5.66646	-1.72558
C	1.09271	-3.04962	-0.34748
H	1.22228	-4.07641	-0.6789
C	-4.86923	-1.97583	-0.72302
H	-5.79758	-1.78996	-1.27379
H	-5.11262	-2.21449	0.31256
H	-4.36763	-2.83837	-1.17499
C	-0.37778	-1.16785	0.39948
C	0.42862	4.6359	0.14521
H	0.2962	5.53231	0.74361
C	0.72479	1.08868	0.89242
C	-2.65147	-1.32199	1.24242
C	-4.65236	0.48025	-0.16341
H	-4.00313	1.36163	-0.22131

## Supporting Information

H	-4.88304	0.27917	0.88543
H	-5.58585	0.71012	-0.68809
C	4.53441	-0.49171	0.01688
H	5.42679	0.1215	0.09304
C	-3.96761	-0.73638	-0.80389
C	-3.67444	-0.44159	-2.27936
H	-3.0613	0.45617	-2.41015
H	-4.62299	-0.27182	-2.79745
H	-3.17424	-1.28561	-2.76629
C	4.73131	-1.88656	-0.42653
C	2.28683	-2.22317	-0.23197
C	0.59254	1.62671	2.14423
H	0.60304	1.13681	3.10784
C	-0.11986	-2.57415	-0.06422
H	-0.99819	-3.20783	-0.16566
C	0.88453	-0.33414	0.51033
N	0.46488	2.99297	2.05705
H	0.35883	3.61492	2.84081



(Figure S4)

Zero-point correction=	0.441555 (Hartree/Particle)
Thermal correction to Energy=	0.464633
Thermal correction to Enthalpy=	0.465578
Thermal correction to Gibbs Free Energy=	0.390535
Sum of electronic and zero-point Energies=	-1226.474182
Sum of electronic and thermal Energies=	-1226.451104
Sum of electronic and thermal Enthalpies=	-1226.450160
Sum of electronic and thermal Free Energies=	-1226.525202

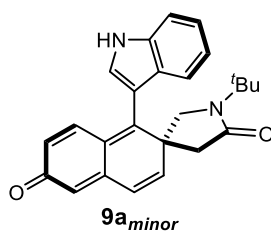
## Supporting Information

## Cartesian Coordinates

Atom	X	Y	Z
O	-3.00083	-1.5689	2.02116
O	6.36581	-1.05285	-1.02103
N	-1.90419	-1.65804	-0.01521
C	3.65185	0.98479	0.11
H	3.52199	2.0094	0.40055
C	-0.79755	2.17487	0.01831
C	-0.76382	3.58474	-0.10382
C	4.26112	-1.71817	-0.16399
H	4.55817	-2.763	-0.18599
C	-0.69206	-1.12085	-0.61832
H	-0.88984	-0.23438	-1.23183
H	-0.20004	-1.85826	-1.2551
C	2.54671	0.03449	0.25925
C	-3.20762	2.40791	-0.24899
H	-4.17981	1.92703	-0.29825
C	-2.08989	1.61385	-0.06563
H	-2.26798	0.55744	0.0133
C	-0.79368	-0.57249	1.75988
H	-0.43668	-0.97159	2.71193
H	-1.05092	0.47512	1.92474
C	-3.11457	3.80192	-0.36249
H	-4.00833	4.40076	-0.50426
C	2.12092	-2.41418	0.70411
H	2.52827	-3.40792	0.86519
C	-3.40901	-3.60415	-0.13754
H	-4.18277	-4.09245	-0.73963
H	-3.79681	-3.43364	0.86711
H	-2.54755	-4.27796	-0.07397
C	0.2161	-0.80847	0.6143

## Supporting Information

C	-1.877	4.40553	-0.29018
H	-1.76008	5.48203	-0.37453
C	0.60715	1.71196	0.19259
C	-2.03953	-1.32829	1.31233
C	-4.1886	-1.31292	-0.86911
H	-3.9093	-0.39707	-1.40278
H	-4.52721	-1.05289	0.13688
H	-5.0217	-1.77714	-1.40745
C	4.89169	0.64814	-0.28428
H	5.67513	1.39542	-0.36635
C	-2.99807	-2.28199	-0.80095
C	-2.50771	-2.58	-2.22223
H	-2.18914	-1.67485	-2.74938
H	-3.33313	-3.01957	-2.79006
H	-1.68257	-3.29967	-2.22483
C	5.27138	-0.74456	-0.56435
C	3.01785	-1.3708	0.24803
C	1.33388	2.89353	0.14895
H	2.38416	3.08398	0.21626
C	0.84316	-2.14209	0.9203
H	0.1566	-2.91503	1.25676
C	1.19859	0.34439	0.35739
N	0.54362	3.97915	-0.01285
H	0.87603	4.92738	-0.07429



(Figure S4)

Zero-point correction=

0.440237 (Hartree/Particle)

Thermal correction to Energy=

0.464653

## Supporting Information

Thermal correction to Enthalpy=	0.465597
Thermal correction to Gibbs Free Energy=	0.385441
Sum of electronic and zero-point Energies=	-1226.504993
Sum of electronic and thermal Energies=	-1226.480577
Sum of electronic and thermal Enthalpies=	-1226.479632
Sum of electronic and thermal Free Energies=	-1226.559789

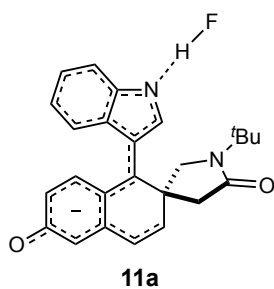
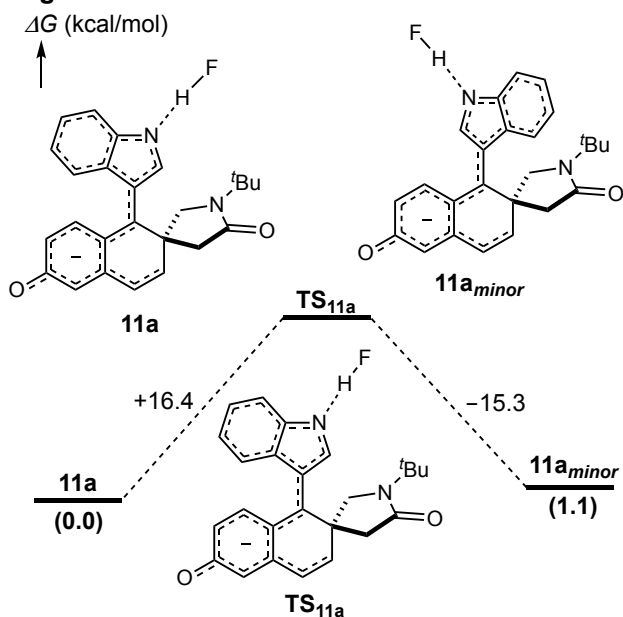
### Cartesian Coordinates

Atom	X	Y	Z
-----			
O	3.48166	0.41467	-2.10443
O	-5.18087	-3.56154	0.20367
N	2.96022	-0.59571	-0.08542
C	-3.11062	-0.69634	0.72386
H	-3.15345	0.31587	1.11215
C	-1.30509	2.13002	-0.06628
C	-1.22745	3.27504	0.75396
C	-2.89135	-3.31627	-0.31975
H	-2.86811	-4.32909	-0.71249
C	1.75951	-0.76766	0.72097
H	1.61484	0.08498	1.39657
H	1.79783	-1.68191	1.31655
C	-1.82617	-1.17033	0.21091
C	-2.22113	3.49128	-1.81156
H	-2.61923	3.6013	-2.81531
C	-1.81509	2.2467	-1.36765
H	-1.89219	1.37046	-2.00521
C	1.16556	0.08095	-1.43511
H	0.84799	-0.20057	-2.44105
H	0.87602	1.12388	-1.26697
C	-2.12972	4.62471	-0.9797
H	-2.45674	5.58833	-1.35792
C	-0.51446	-3.02225	-0.84828

## Supporting Information

H	-0.48441	-4.035	-1.24116
C	5.28085	-1.32233	-0.46427
H	6.28295	-1.35931	-0.02358
H	5.3329	-0.80395	-1.42181
H	4.94278	-2.34971	-0.63765
C	0.61364	-0.84978	-0.32822
C	-1.63549	4.536	0.30954
H	-1.56959	5.41078	0.94954
C	-0.80496	1.01681	0.70381
C	2.67754	-0.00465	-1.29129
C	4.77799	0.84191	0.7407
H	4.08982	1.35179	1.4252
H	4.81122	1.39447	-0.2011
H	5.77705	0.856	1.18935
C	-4.20756	-1.46923	0.72242
H	-5.15903	-1.11332	1.10475
C	4.32322	-0.6049	0.49732
C	4.3082	-1.36865	1.82632
H	3.67151	-0.88703	2.57601
H	5.32599	-1.3954	2.22672
H	3.97445	-2.40312	1.69197
C	-4.18389	-2.85084	0.20145
C	-1.78447	-2.54109	-0.32155
C	-0.46556	1.52211	1.92994
H	-0.08381	1.01131	2.80291
C	0.57712	-2.25752	-0.85425
H	1.51625	-2.63943	-1.24859
C	-0.71967	-0.38312	0.22403
N	-0.7136	2.87412	1.96592
H	-0.55328	3.47119	2.75965

Figure S4



(Figure S4)

Zero-point correction=	0.438313 (Hartree/Particle)
Thermal correction to Energy=	0.464260
Thermal correction to Enthalpy=	0.465204
Thermal correction to Gibbs Free Energy=	0.381072
Sum of electronic and zero-point Energies=	-1326.457501
Sum of electronic and thermal Energies=	-1326.431554
Sum of electronic and thermal Enthalpies=	-1326.430609
Sum of electronic and thermal Free Energies=	-1326.514741

## Cartesian Coordinates

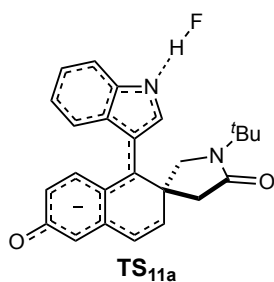
Atom	X	Y	Z
O	3.13664	-2.53287	-1.70496

## Supporting Information

O	-6.24052	-1.86716	-0.13849
N	2.57182	-1.22476	0.12246
C	-3.23497	-0.01827	-0.81756
H	-2.90314	0.87037	-1.34509
C	-1.04406	2.14813	-0.00512
C	-0.0668	3.1395	-0.29036
C	-4.00699	-2.39863	0.43451
H	-4.34037	-3.32426	0.89841
C	1.39593	-0.99548	0.95066
H	1.28053	0.06139	1.18901
H	1.48711	-1.54488	1.89802
C	-2.22797	-0.82523	-0.1742
C	-2.42122	3.86931	0.96331
H	-3.33846	4.16717	1.4653
C	-2.22262	2.53229	0.65287
H	-2.97758	1.79847	0.91708
C	0.81577	-2.02425	-1.19615
H	0.48844	-3.03005	-1.46757
H	0.57686	-1.36533	-2.03672
C	-1.46146	4.84454	0.64147
H	-1.64805	5.88574	0.89288
C	-1.688	-2.96916	0.9839
H	-2.03971	-3.86885	1.4834
C	4.59236	-2.10507	1.18402
H	5.59949	-1.86872	1.54603
H	4.66592	-2.89408	0.43012
H	4.00452	-2.47961	2.03114
C	0.17399	-1.52432	0.1344
C	-0.27618	4.48585	0.02025
H	0.49012	5.22014	-0.21297
C	-0.44022	0.88487	-0.4005
C	2.31803	-1.98939	-0.97744
C	4.75516	-0.31698	-0.60494

## Supporting Information

H	4.31092	0.61469	-0.96932
H	4.82306	-1.0463	-1.412
H	5.76632	-0.08524	-0.25012
C	-4.54697	-0.35274	-0.82511
H	-5.28018	0.25691	-1.34535
C	3.93401	-0.85881	0.57556
C	3.84111	0.27071	1.61032
H	3.42036	1.17339	1.15523
H	4.85551	0.5141	1.94332
H	3.26104	-0.01057	2.4956
C	-5.04312	-1.5614	-0.16525
C	-2.68593	-2.06931	0.41504
C	0.838	1.26792	-0.87873
H	1.61588	0.61468	-1.25618
C	-0.38589	-2.72855	0.84699
H	0.3526	-3.44202	1.21063
C	-0.88663	-0.45126	-0.15437
N	1.06726	2.57406	-0.84137
H	2.58759	2.85762	-0.80407
F	3.57186	2.79499	-0.69091



(Figure S4)

Zero-point correction=	0.439236 (Hartree/Particle)
Thermal correction to Energy=	0.464418
Thermal correction to Enthalpy=	0.465363
Thermal correction to Gibbs Free Energy=	0.383143
Sum of electronic and zero-point Energies=	-1326.432471
Sum of electronic and thermal Energies=	-1326.407289

## Supporting Information

Sum of electronic and thermal Enthalpies= -1326.406344

Sum of electronic and thermal Free Energies= -1326.488564

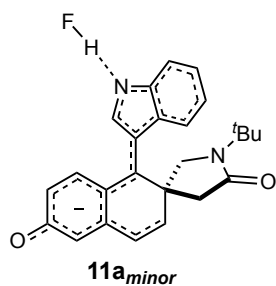
## Cartesian Coordinates

Atom	X	Y	Z
O	-3.37508	-1.69624	2.12647
O	6.0245	-2.72506	-0.505
N	-2.65725	-1.11467	-0.00956
C	3.45104	-0.2402	-0.01812
H	3.36755	0.81744	0.09422
C	1.32258	2.36101	0.15493
C	0.26054	3.33201	0.11907
C	3.67275	-2.98368	-0.282
H	3.77448	-4.06265	-0.38233
C	-1.40215	-1.10994	-0.76589
H	-1.2569	-0.17505	-1.30749
H	-1.39897	-1.92071	-1.50632
C	2.2308	-0.99191	0.03329
C	2.82482	4.29632	0.00117
H	3.84764	4.66582	-0.0243
C	2.62118	2.92058	0.11604
H	3.52579	2.33815	0.19853
C	-1.01368	-1.2746	1.66844
H	-0.71447	-2.0693	2.35653
H	-0.84923	-0.32154	2.17888
C	1.75704	5.19899	-0.07147
H	1.94274	6.26658	-0.16456
C	1.28105	-3.31626	-0.04707
H	1.45043	-4.38579	-0.15287
C	-4.55749	-2.42	-0.88051
H	-5.53603	-2.37509	-1.37403
H	-4.6776	-2.91833	0.08604

## Supporting Information

H	-3.89085	-3.0261	-1.50697
C	-0.26198	-1.36164	0.30158
C	0.46037	4.7091	-0.00328
H	-0.40578	5.36528	-0.03105
C	0.6365	1.03383	0.26606
C	-2.49363	-1.40646	1.32453
C	-4.94222	-0.14168	0.17911
H	-4.53292	0.86793	0.28551
H	-5.10405	-0.58208	1.1626
H	-5.90611	-0.06464	-0.33955
C	4.69114	-0.77507	-0.18895
H	5.5729	-0.13865	-0.21366
C	-3.98984	-1.00223	-0.67747
C	-3.81986	-0.2763	-2.02552
H	-3.45554	0.7436	-1.86297
H	-4.80112	-0.20787	-2.50847
H	-3.15166	-0.80573	-2.71351
C	4.90156	-2.20926	-0.34265
C	2.42757	-2.43289	-0.10443
C	-0.74057	1.4405	0.34676
H	-1.60549	0.81366	0.46937
C	0.0582	-2.82675	0.1438
H	-0.80598	-3.48767	0.20525
C	0.9593	-0.38432	0.194
N	-0.97703	2.73533	0.24209
H	-2.47176	2.93291	-0.15071
F	-3.40918	2.76898	-0.44958

## Supporting Information



(Figure S4)

Zero-point correction=	0.438603 (Hartree/Particle)
Thermal correction to Energy=	0.464628
Thermal correction to Enthalpy=	0.465573
Thermal correction to Gibbs Free Energy=	0.381001
Sum of electronic and zero-point Energies=	-1326.455404
Sum of electronic and thermal Energies=	-1326.429378
Sum of electronic and thermal Enthalpies=	-1326.428434
Sum of electronic and thermal Free Energies=	-1326.513006

## Cartesian Coordinates

Atom	X	Y	Z
O	-3.53885	-0.65644	2.20213
O	5.7776	-2.64158	-0.89876
N	-2.69315	-1.06244	0.08858
C	3.03259	-0.3229	-0.91247
H	2.76728	0.64958	-1.31253
C	1.34491	2.09346	0.22187
C	0.51631	3.22096	-0.032
C	3.60318	-2.90554	-0.00358
H	3.84705	-3.9195	0.30567
C	-1.44528	-1.51491	-0.50213
H	-1.17594	-0.92959	-1.38384
H	-1.51867	-2.56435	-0.817
C	2.02796	-1.02967	-0.15385
C	3.10289	3.60131	0.87915
H	4.11289	3.76459	1.24704

## Supporting Information

C	2.64498	2.3041	0.70687
H	3.29265	1.46412	0.94017
C	-1.14075	-0.78015	1.81883
H	-0.97816	-1.33161	2.74808
H	-0.8748	0.26507	1.99898
C	2.2864	4.70796	0.58578
H	2.67535	5.71377	0.72469
C	1.33514	-3.20464	0.86295
H	1.60253	-4.21356	1.16849
C	-4.81724	-2.24129	-0.24292
H	-5.7713	-2.24564	-0.78264
H	-5.01947	-2.20316	0.83044
H	-4.28944	-3.17541	-0.47096
C	-0.3534	-1.36991	0.62319
C	0.98879	4.52594	0.13586
H	0.33448	5.36837	-0.07137
C	0.50255	0.93189	-0.00654
C	-2.60573	-0.8287	1.43288
C	-4.71444	0.28561	-0.36087
H	-4.11548	1.15844	-0.64474
H	-4.96473	0.3595	0.69773
H	-5.64311	0.30665	-0.94361
C	4.25598	-0.84029	-1.17152
H	4.98199	-0.29472	-1.76757
C	-3.97221	-1.02786	-0.65732
C	-3.68713	-1.07783	-2.16368
H	-3.10109	-0.21058	-2.48498
H	-4.64151	-1.04914	-2.69882
H	-3.16512	-1.99304	-2.46283
C	4.65446	-2.16661	-0.69757
C	2.36693	-2.38733	0.23532
C	-0.75092	1.50198	-0.34773
H	-1.66709	0.97951	-0.58857

## Supporting Information

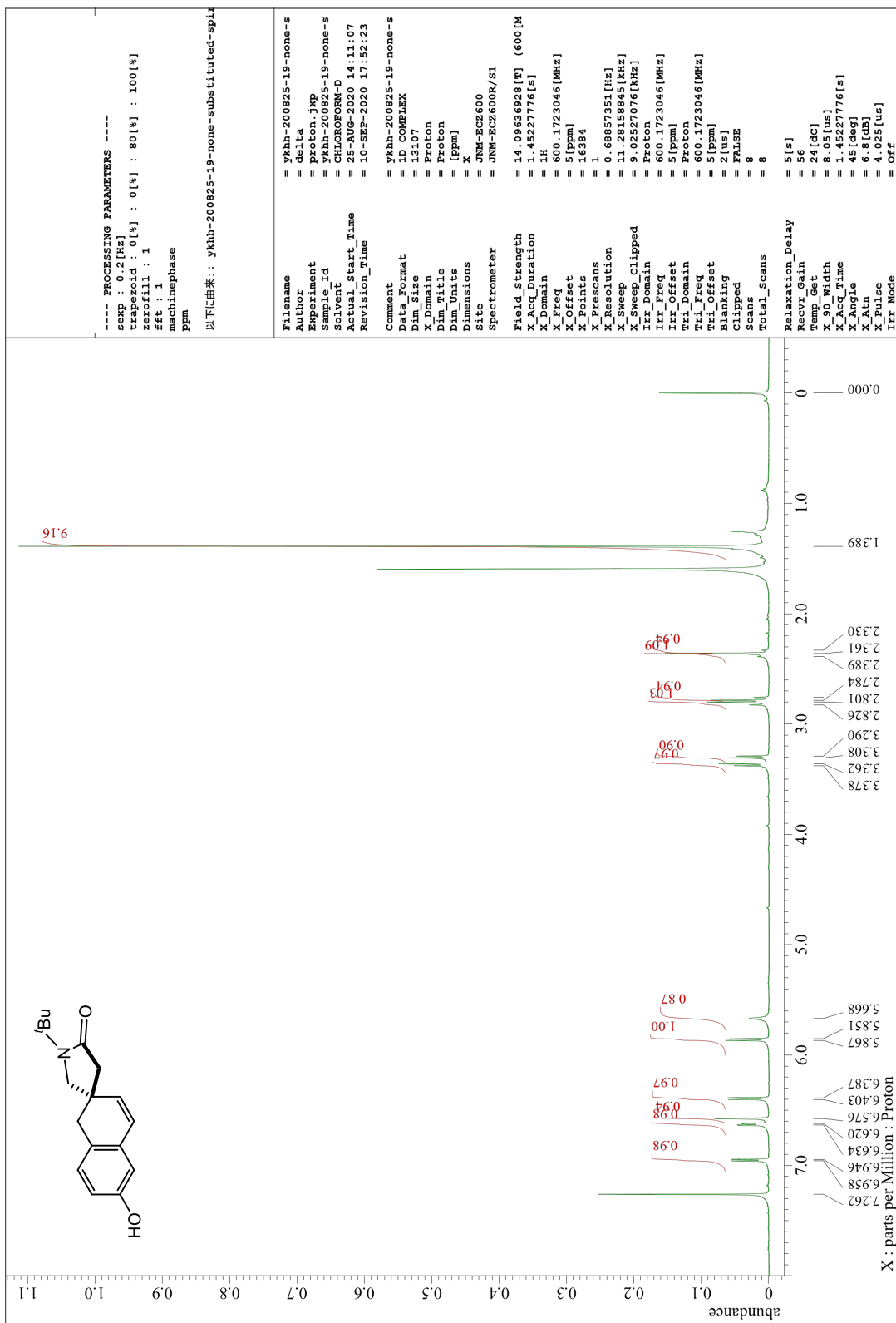
C	0.09118	-2.7546	1.00719
H	-0.68768	-3.39299	1.42332
C	0.78926	-0.46477	0.13735
N	-0.754	2.82678	-0.40108
H	-2.18247	3.24683	-0.91535
F	-3.10405	3.19371	-1.26108

# Supporting Information

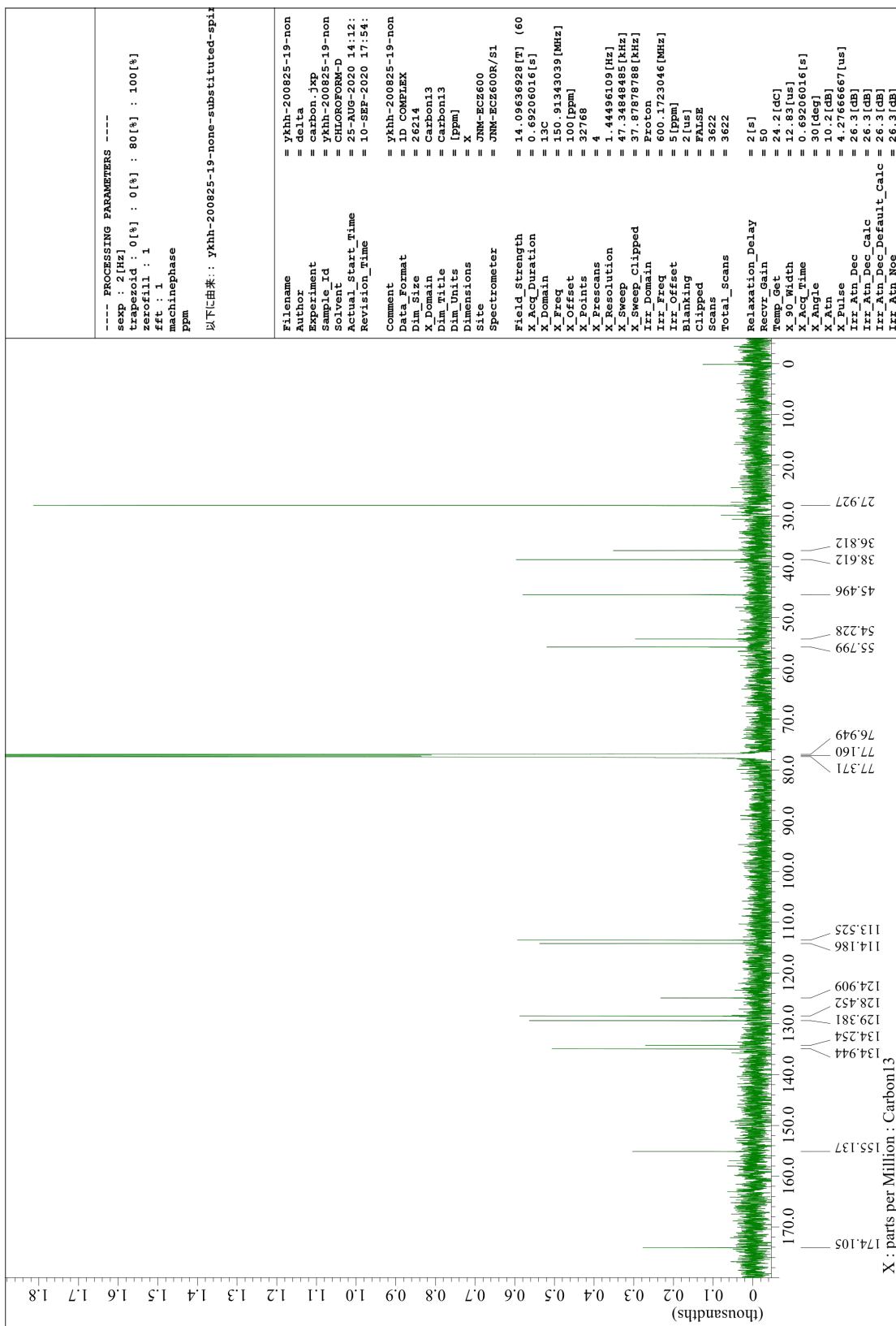
## 7. Charts of <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra

The dr values were determined by the signals inside the red frames.

4a

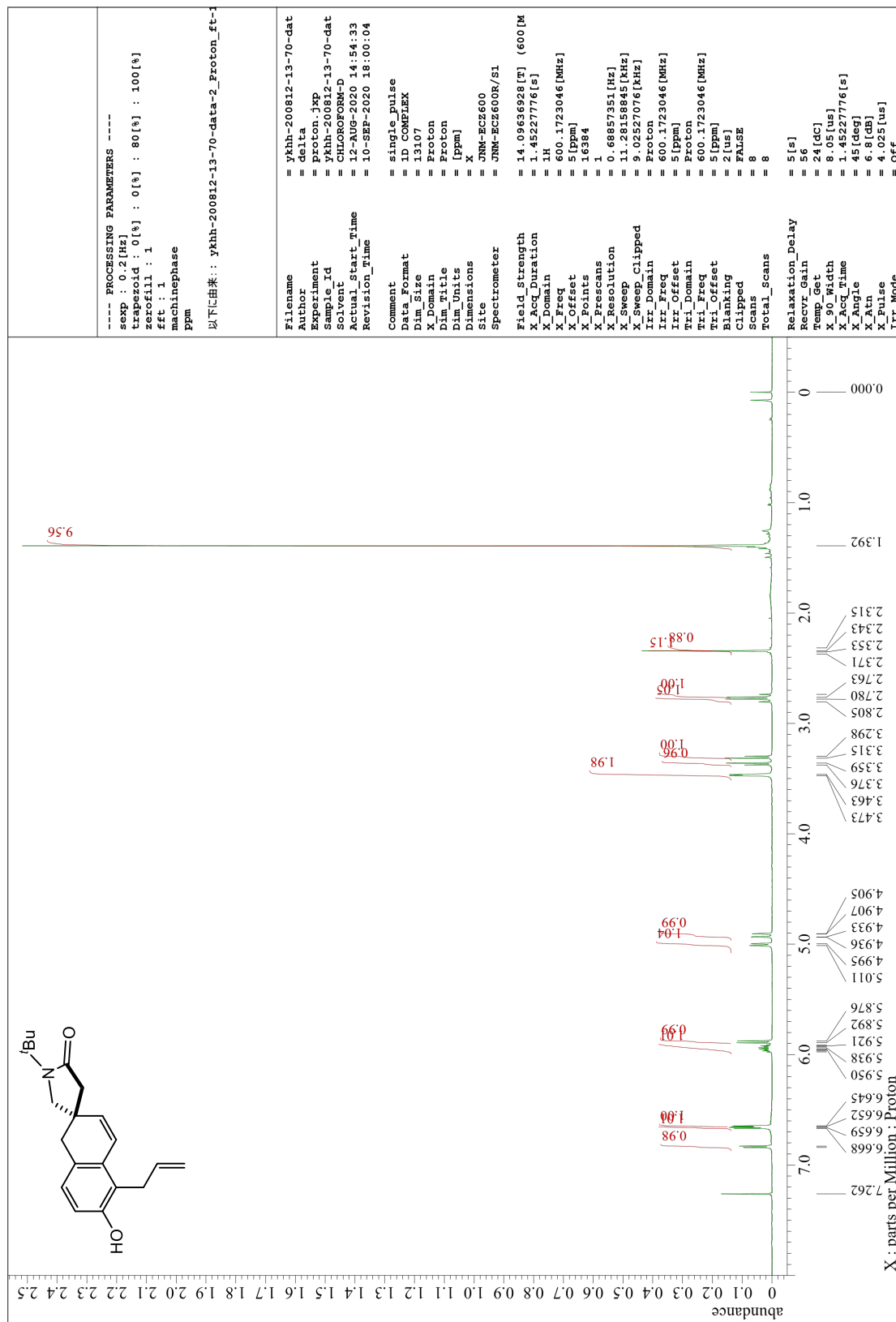


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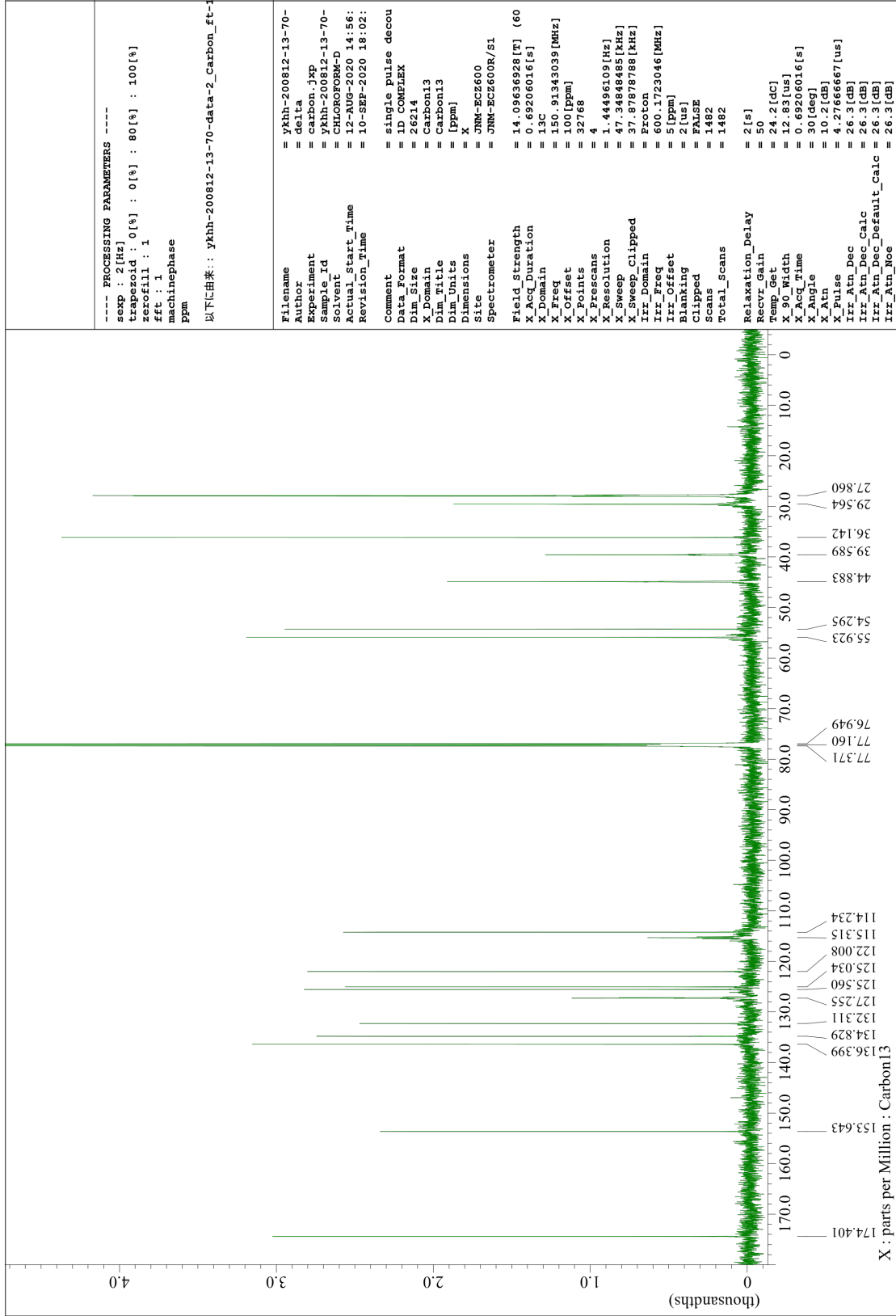


# Supporting Information

4b

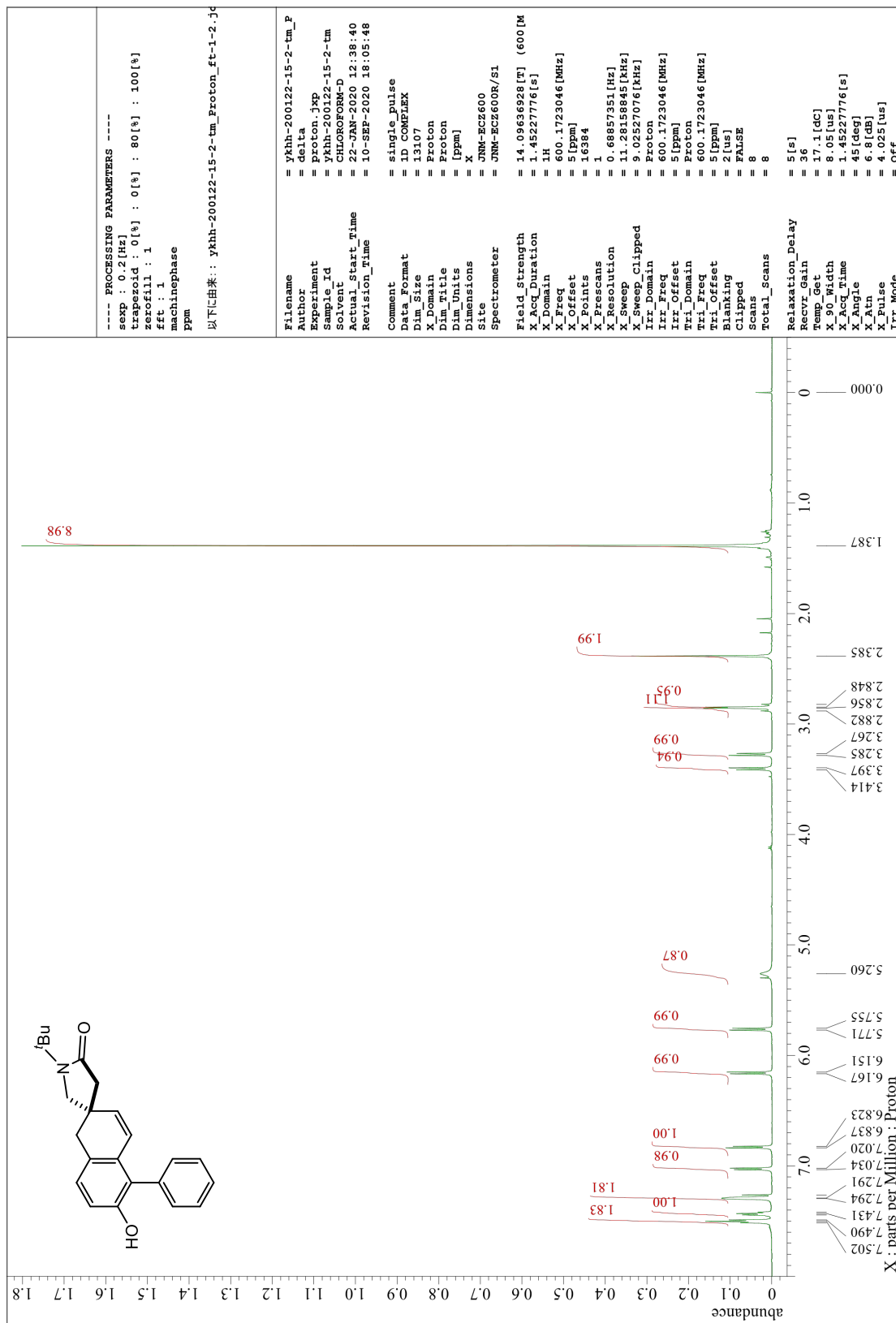


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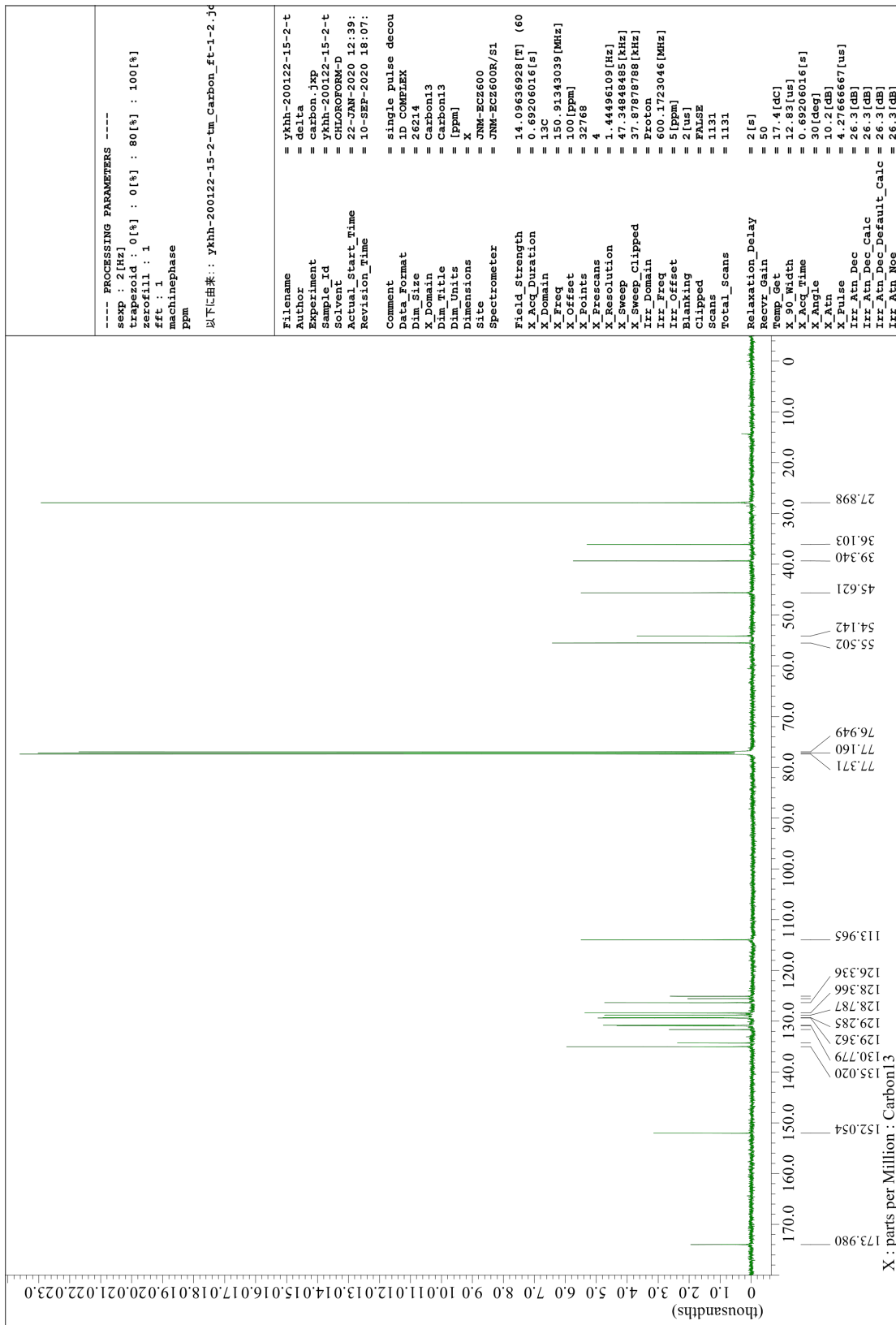


# Supporting Information

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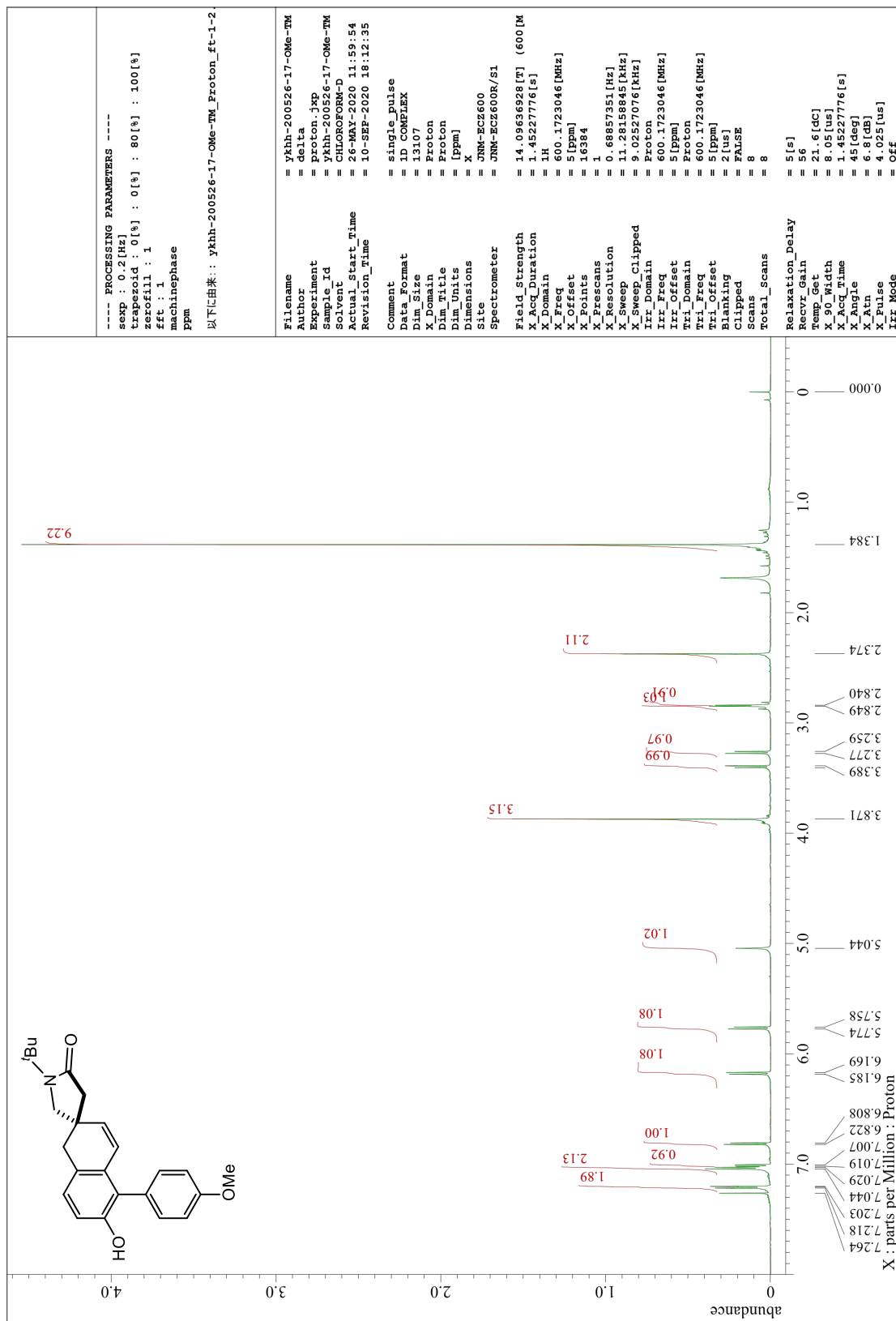


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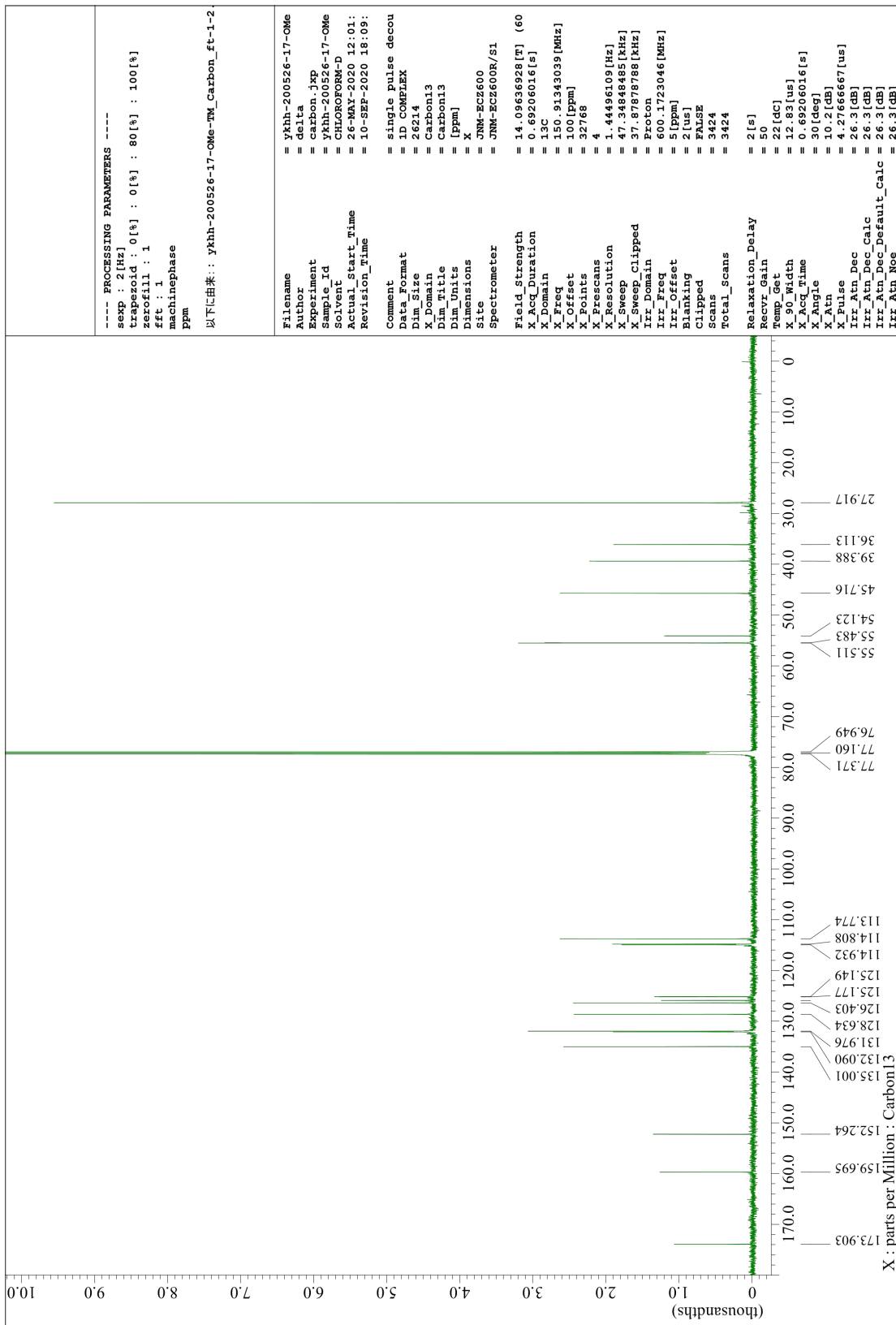


# Supporting Information

4d

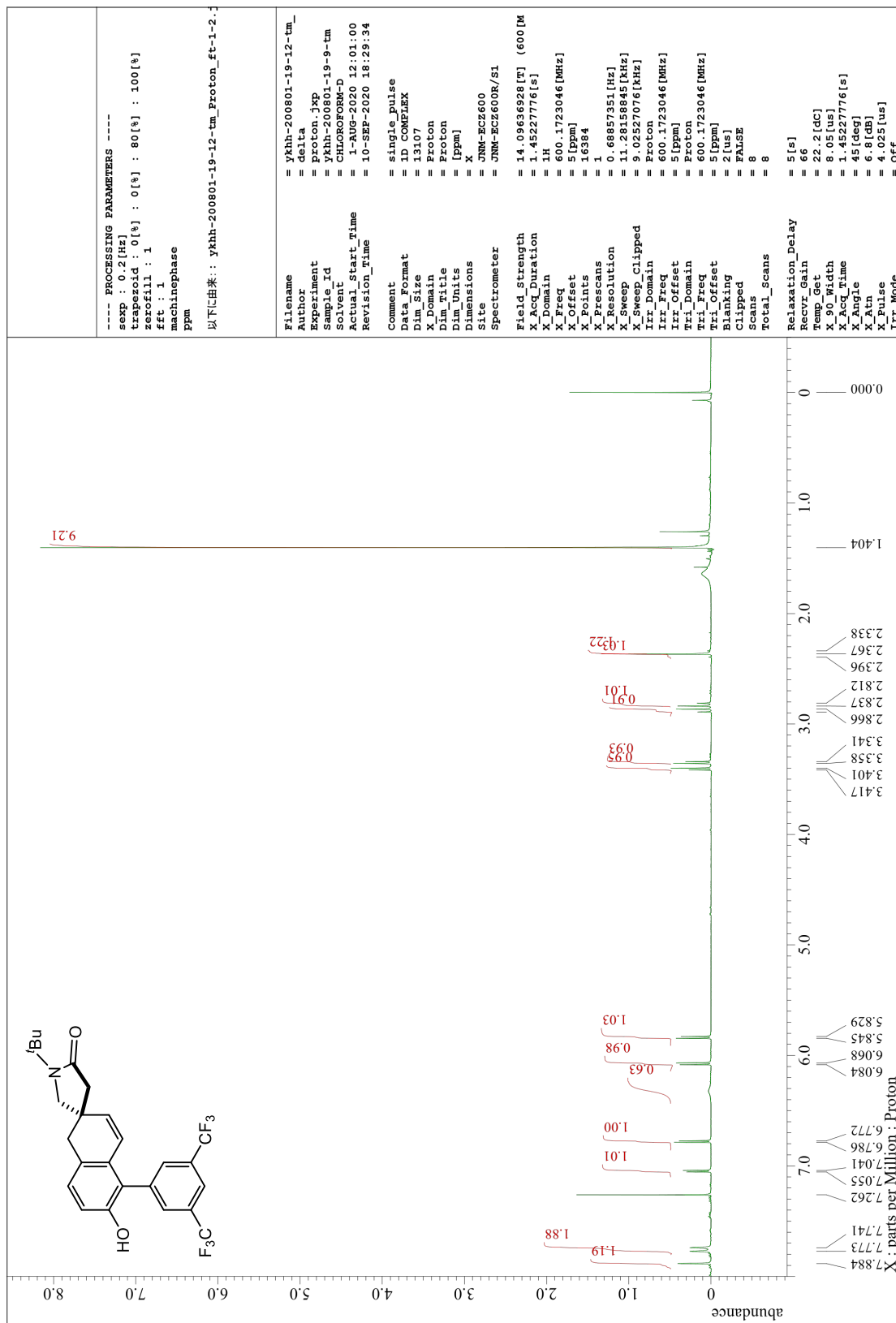


# Supporting Information

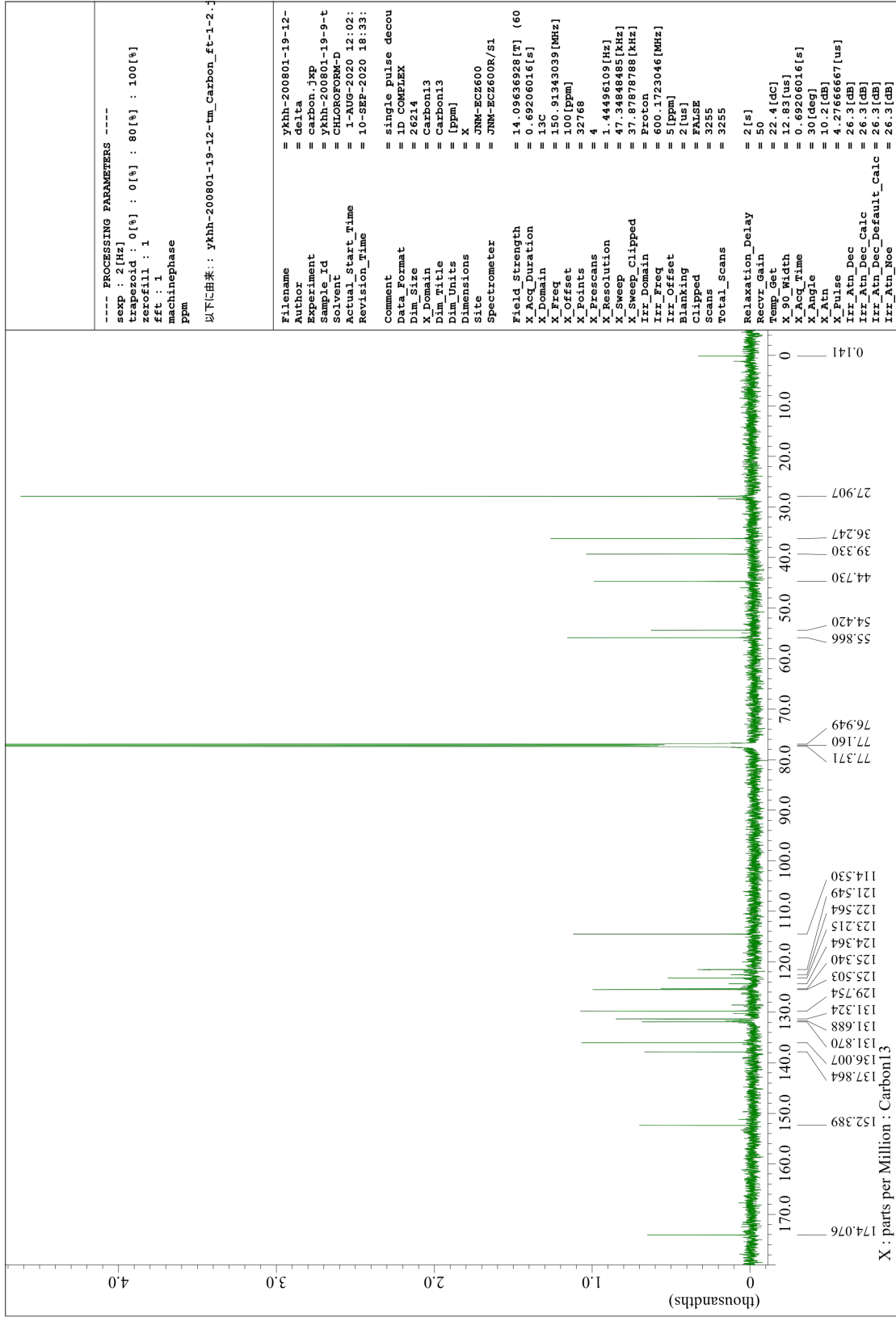


# Supporting Information

4e



# Supporting Information



---- PROCESSING PARAMETERS ----

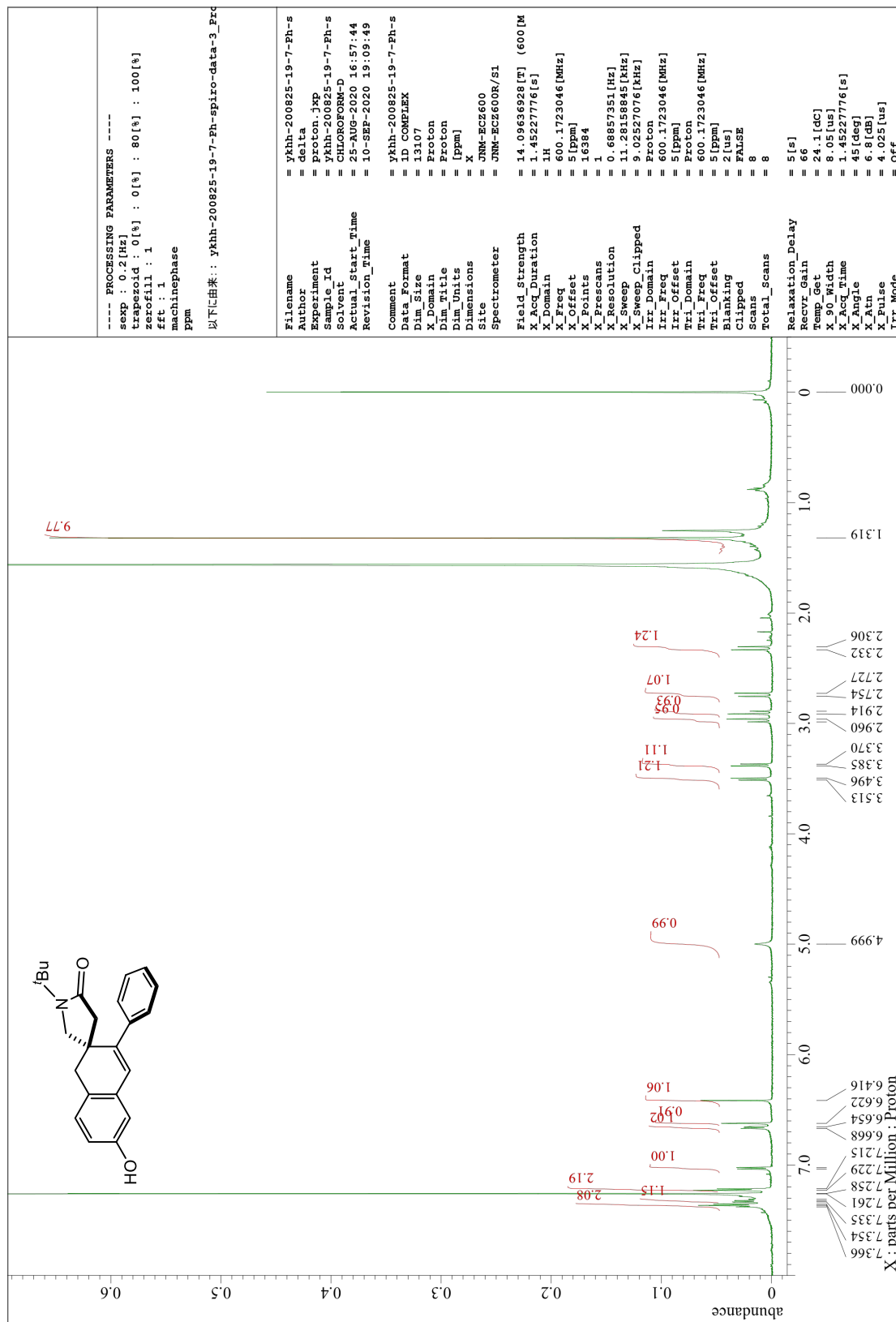
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 Ppm  
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 Author = delta  
 Experiment = carbon\_13p  
 Sample\_ID = ykhh200801-19-9-t  
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 Actual\_Start\_Time = 1-10-2008 12:02:  
 Revision\_Time = 10-SEP-2020 18:33:  
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 Num\_Size = 26214  
 Num1 = Carbon13  
 Num2 = Carbon13  
 Num3 = [ppm]  
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 Spectrometer = JNM-ECZ600R/S1  
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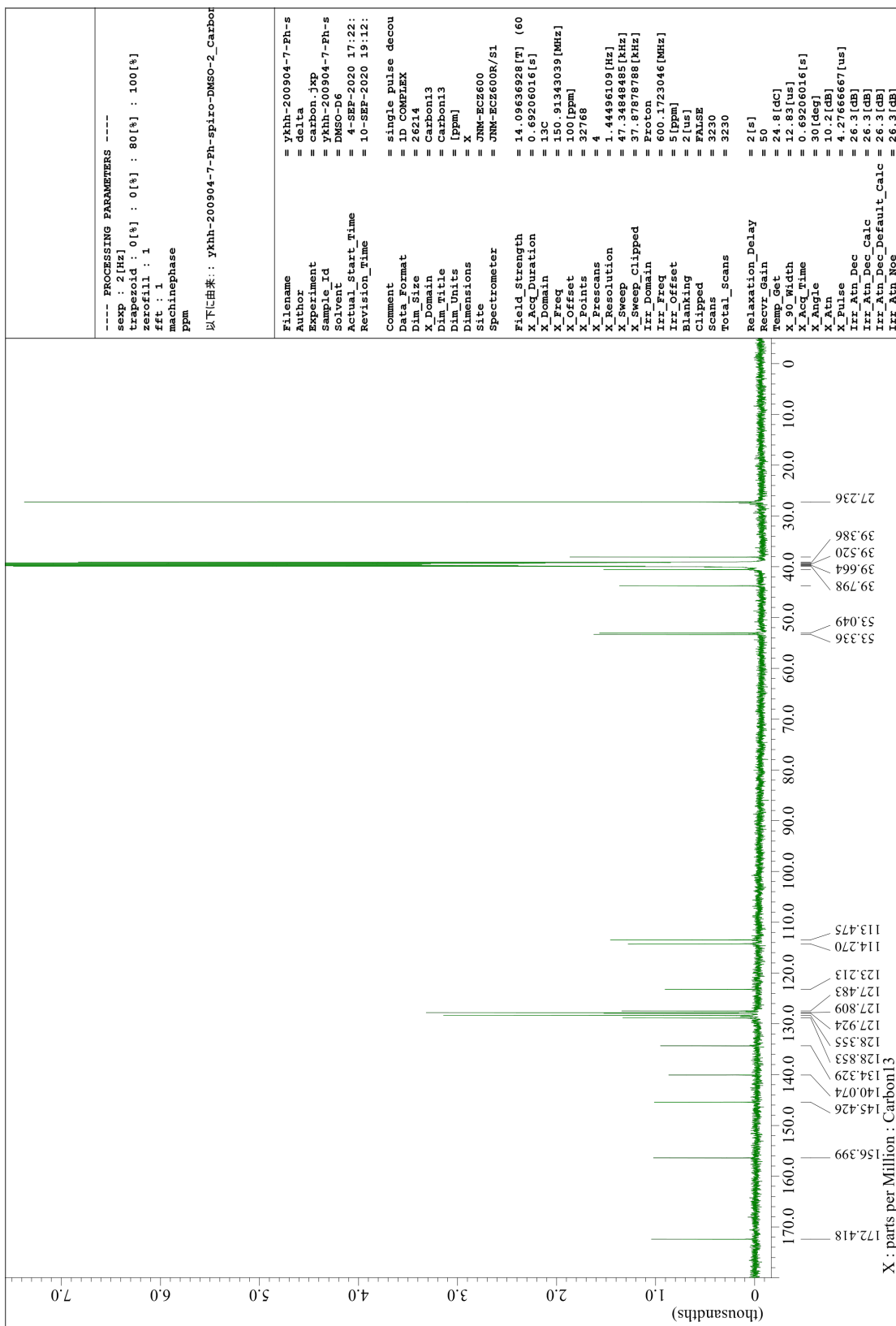
# Supporting Information



4f

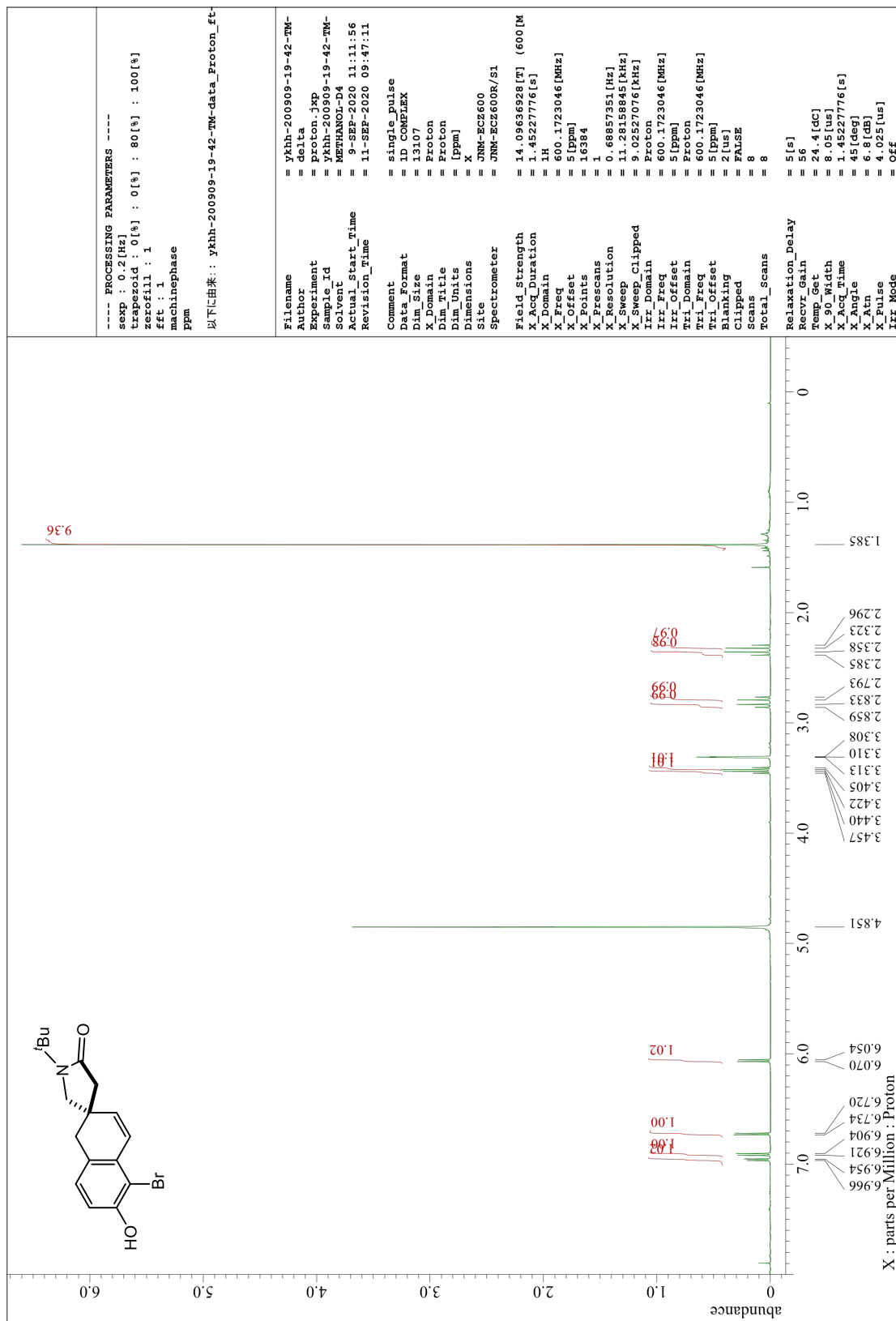


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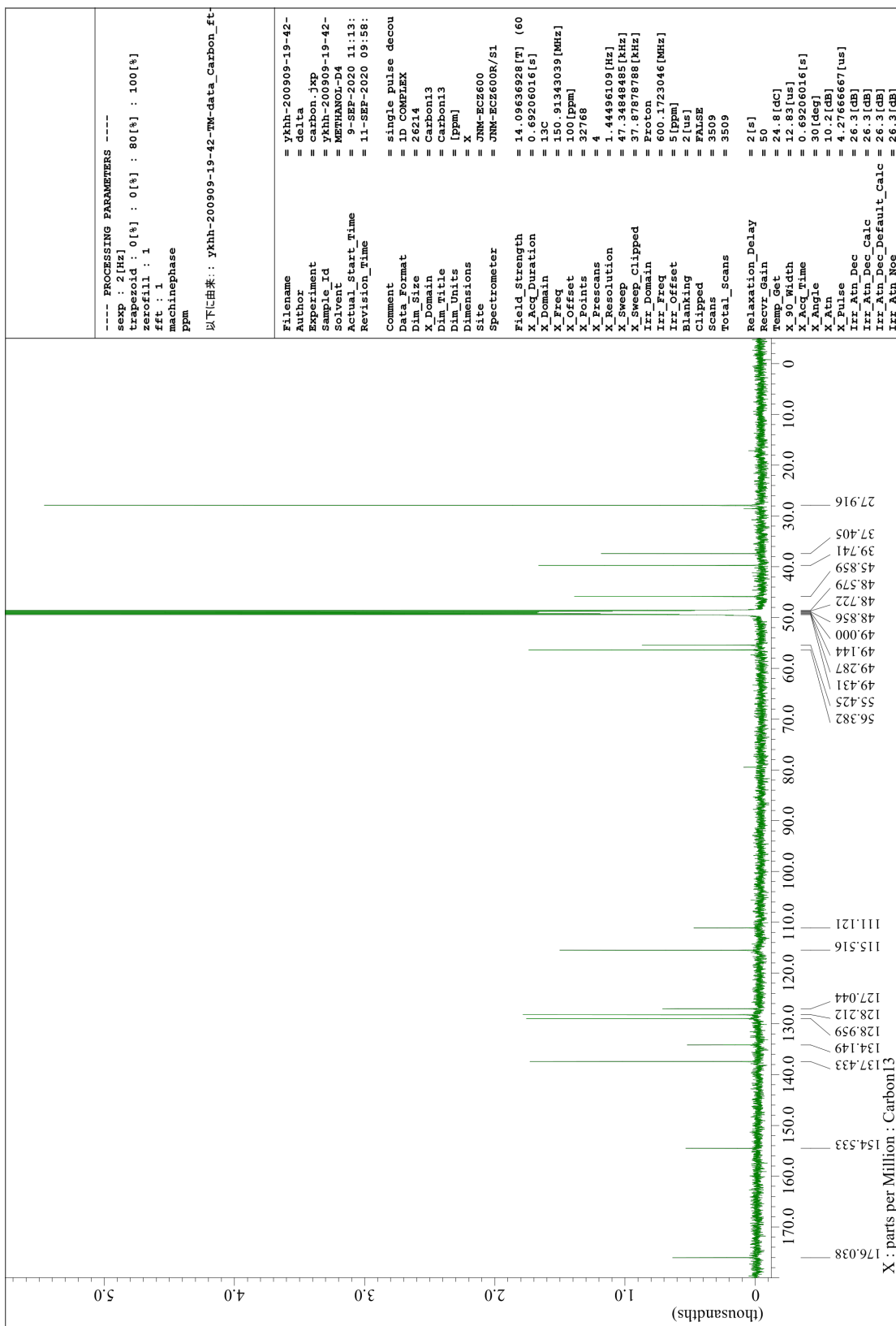


# Supporting Information

4g

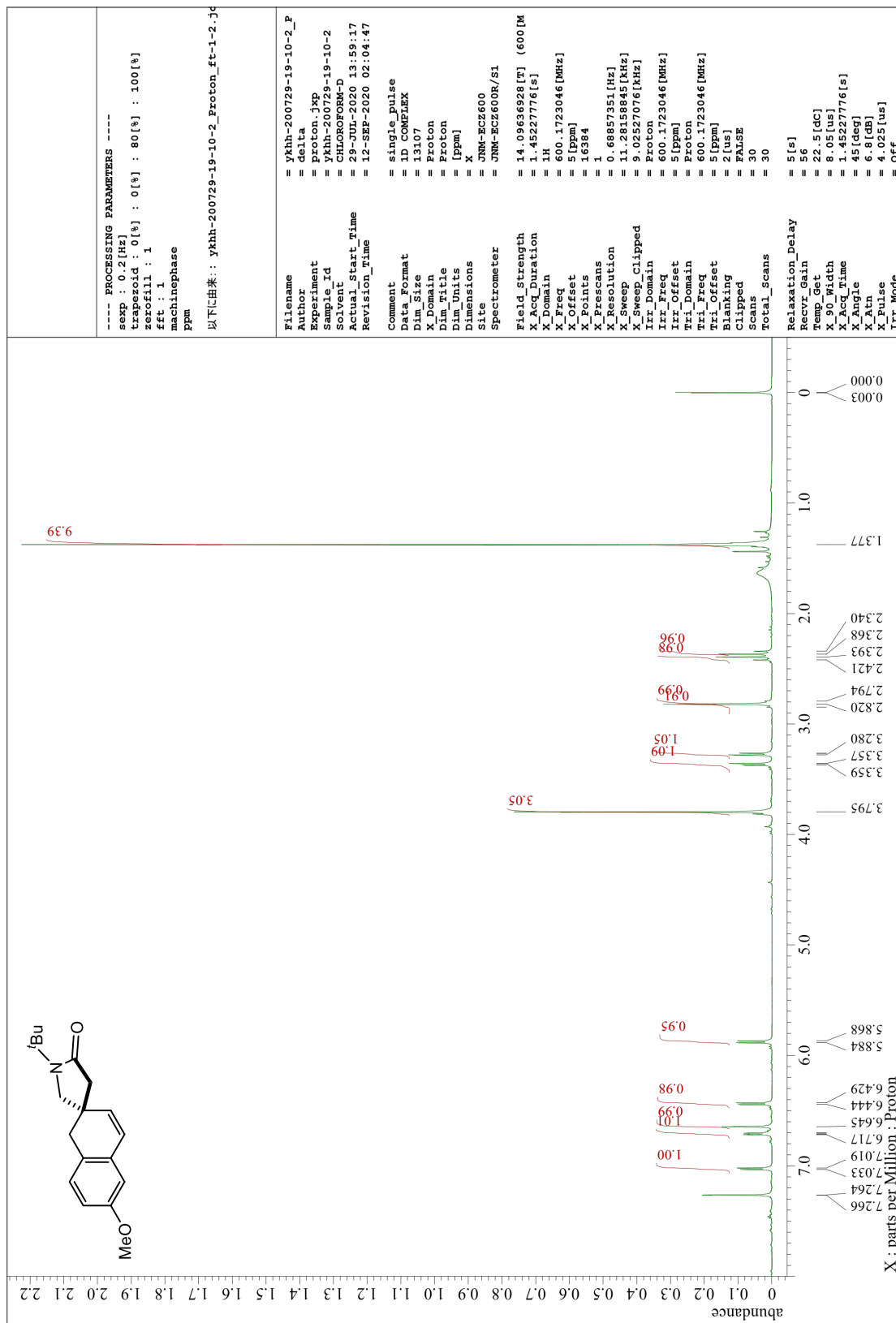


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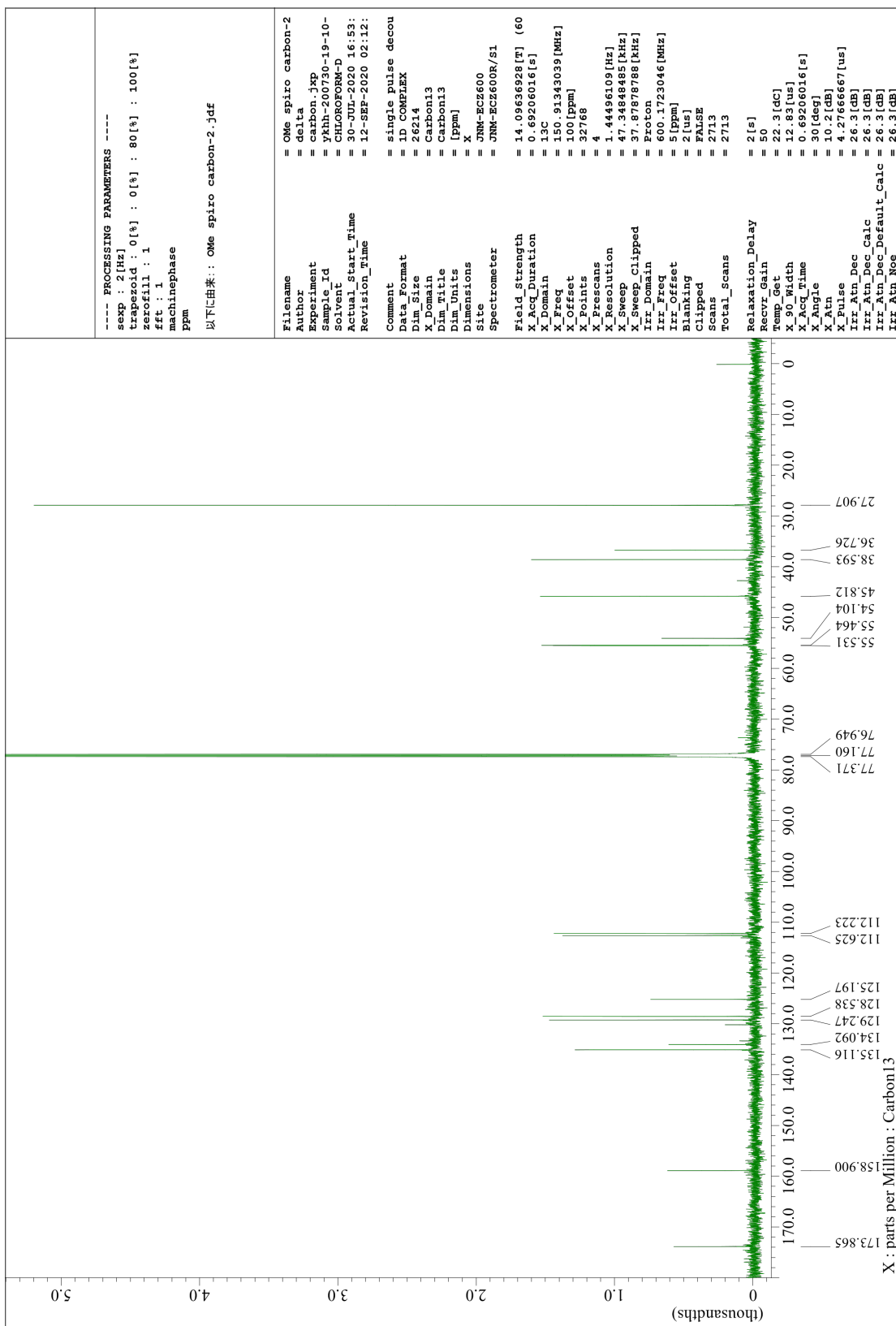


# Supporting Information

## 4h

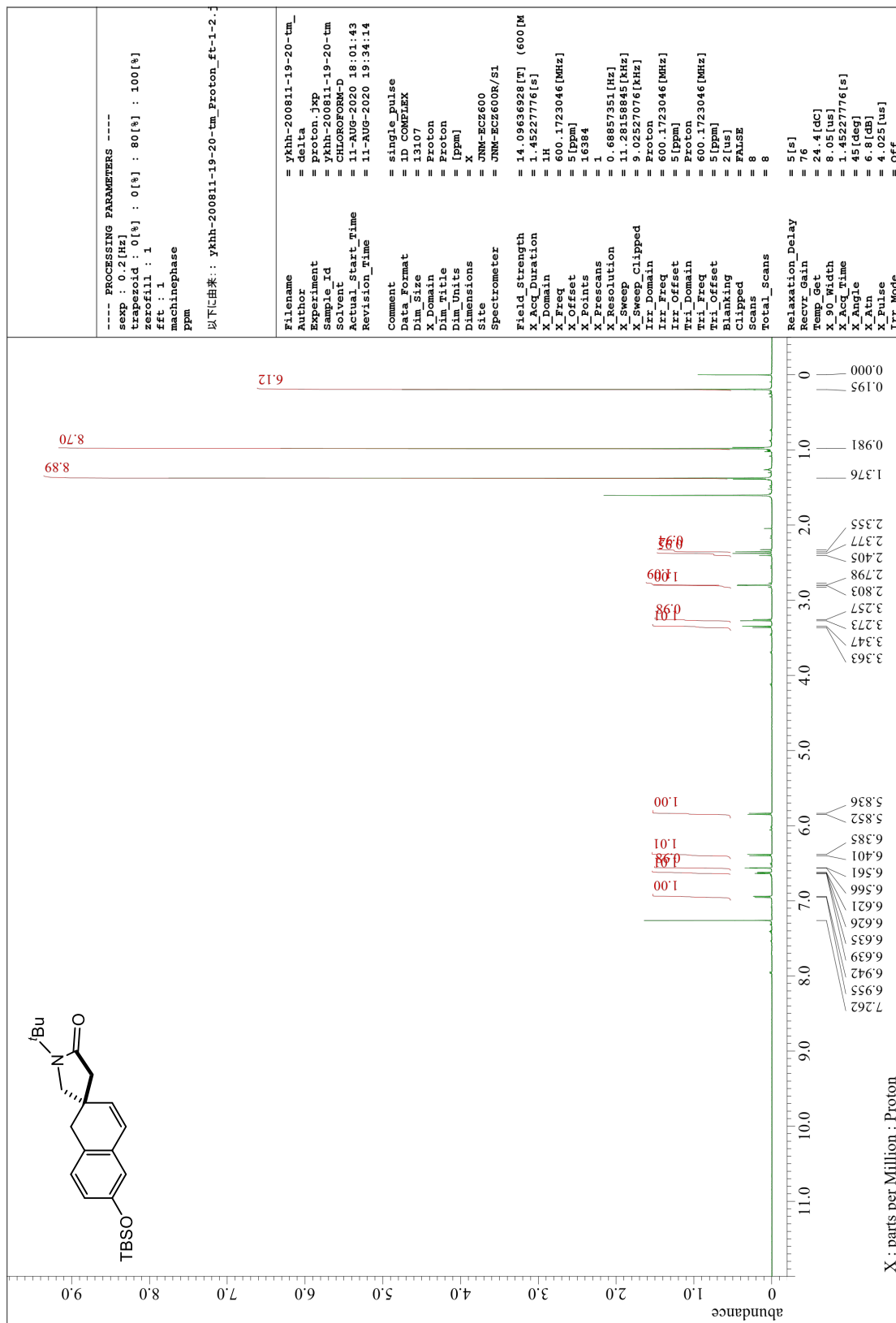


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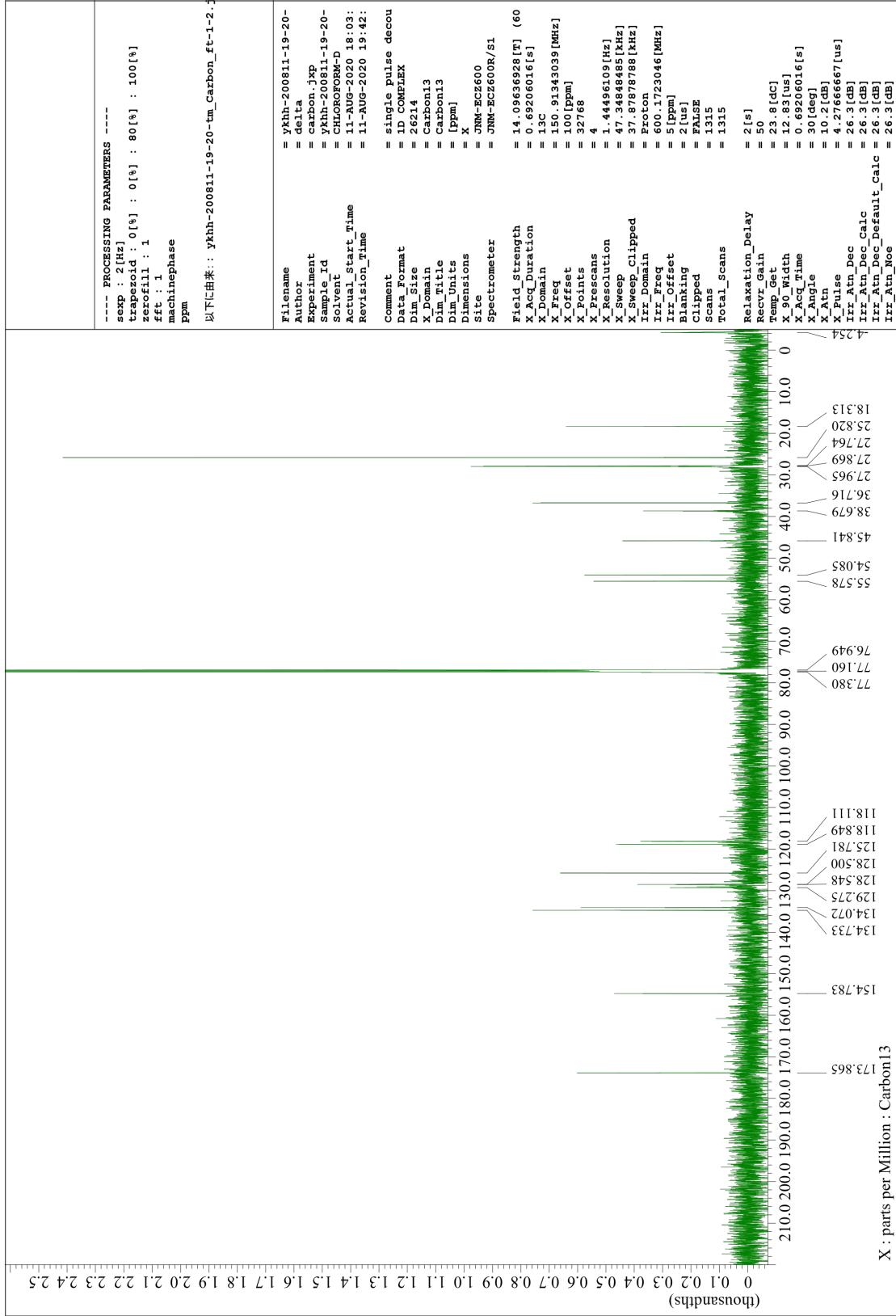


# Supporting Information

4i

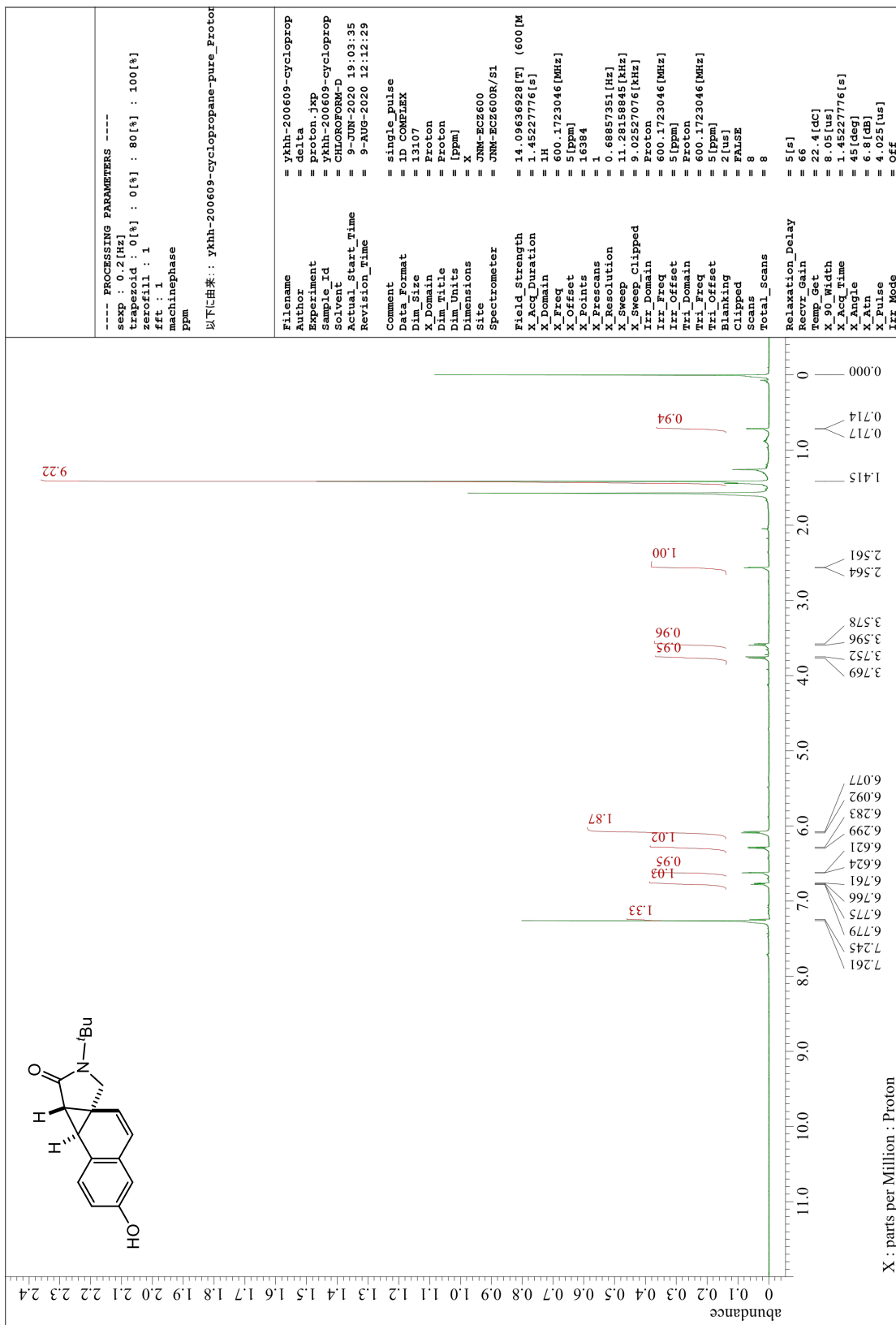


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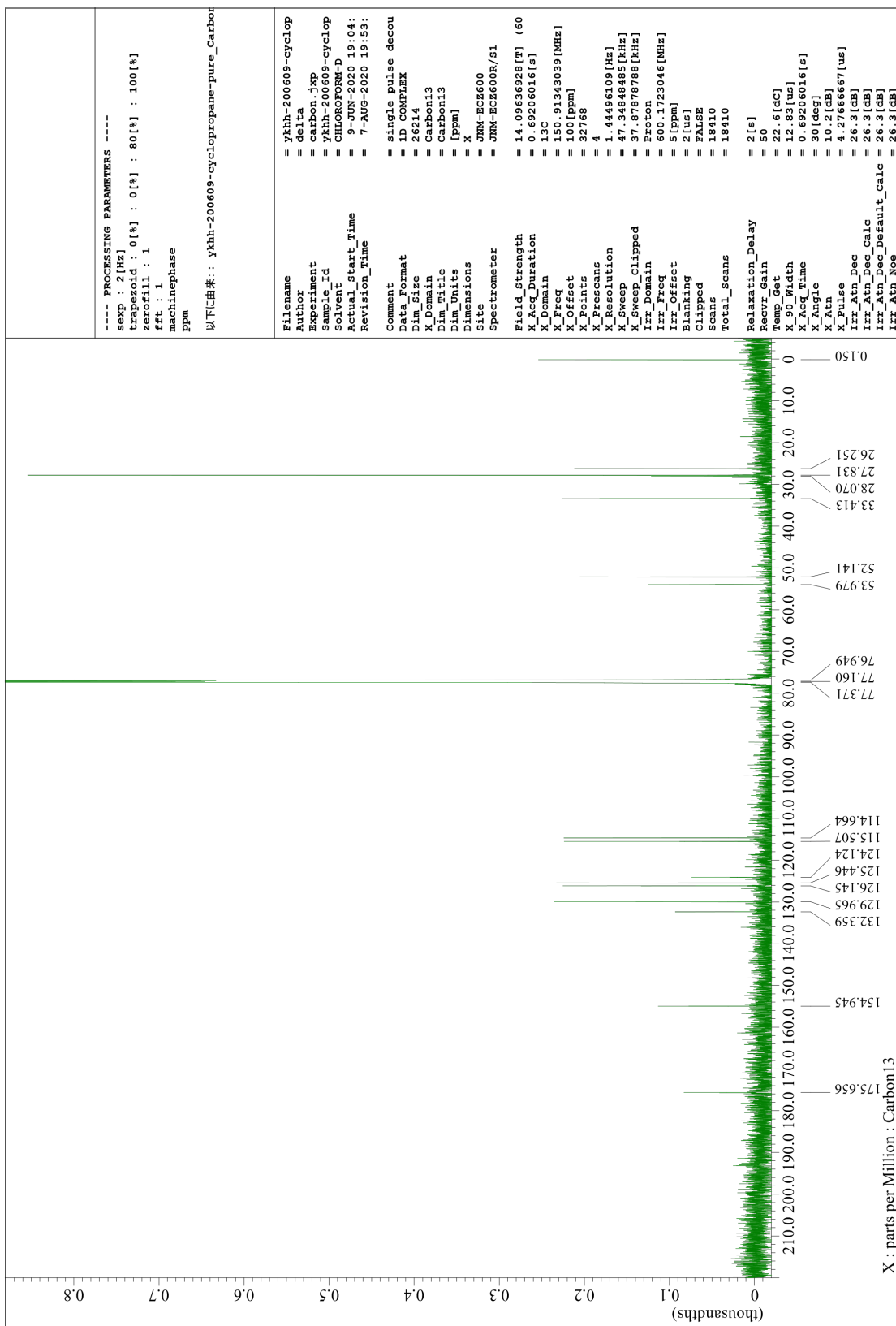


Supporting Information

5a

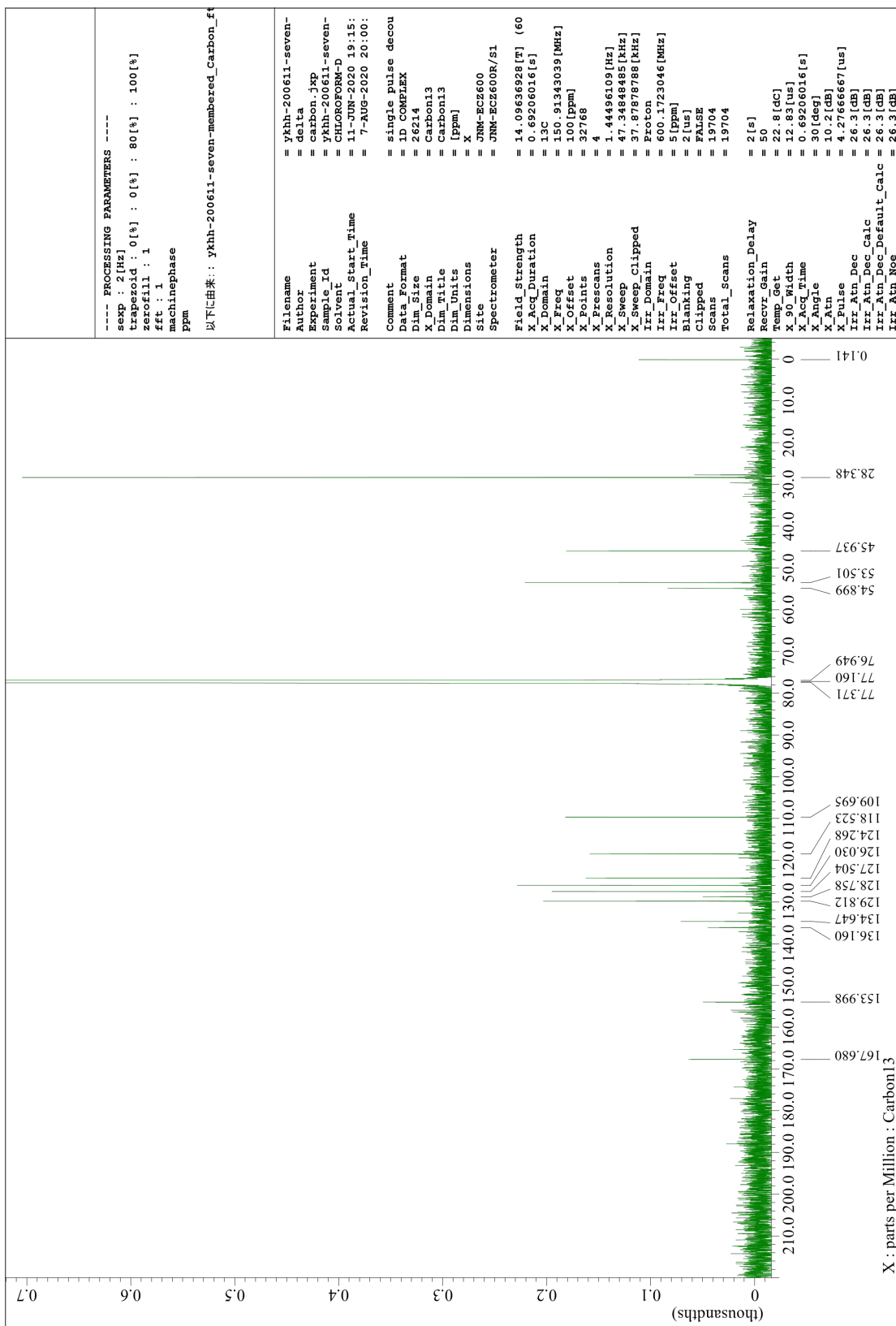


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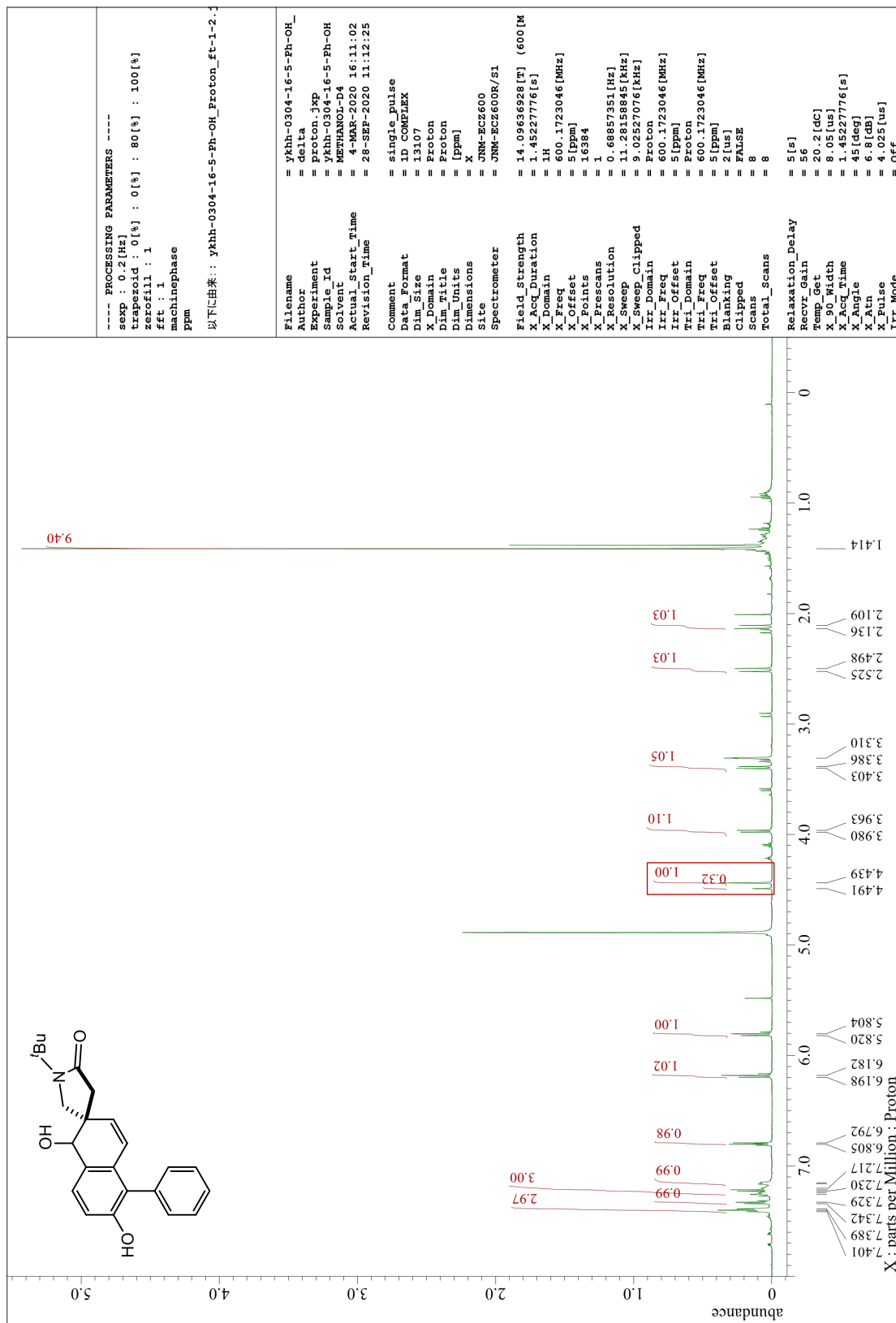


# Supporting Information



# Supporting Information

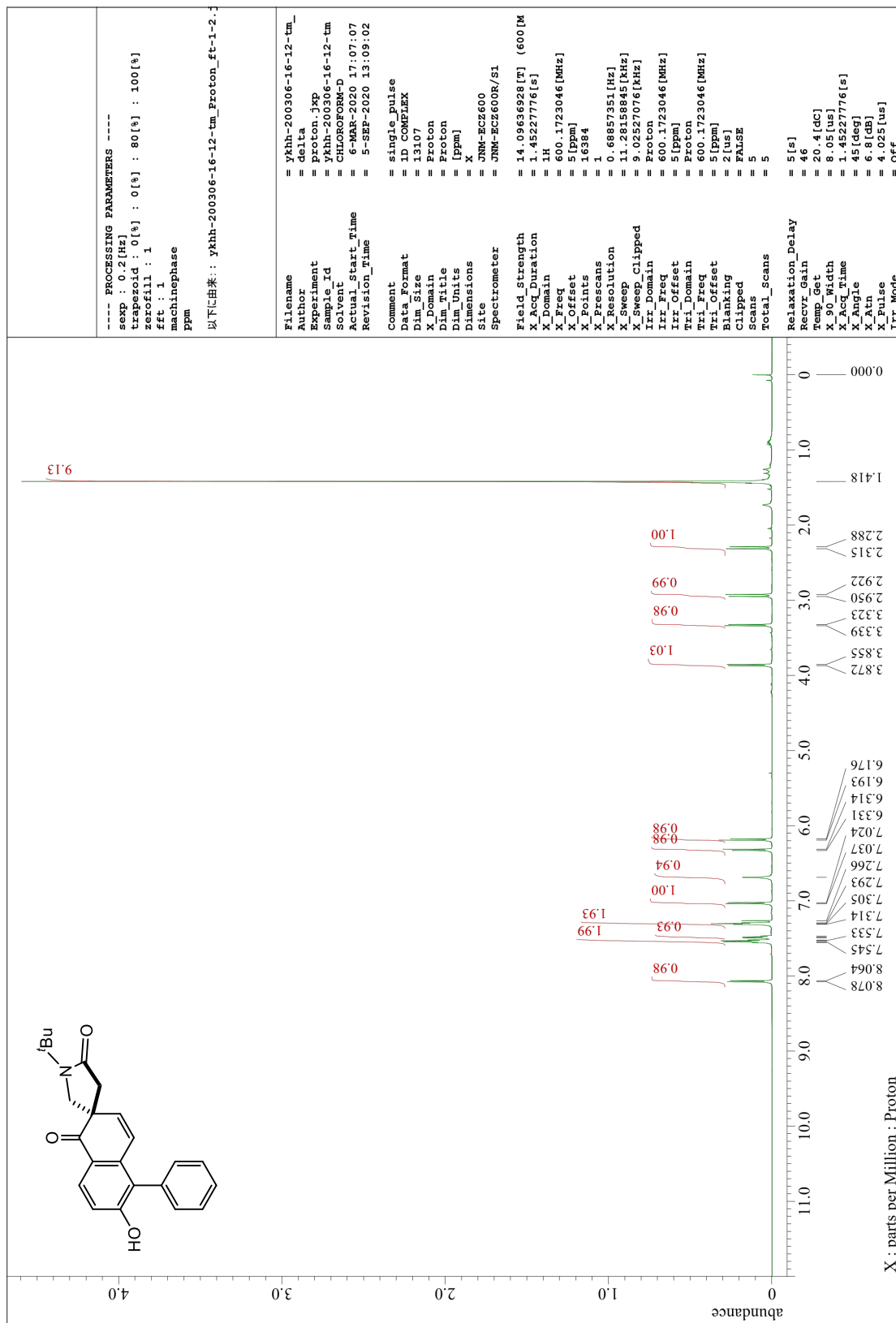
7c



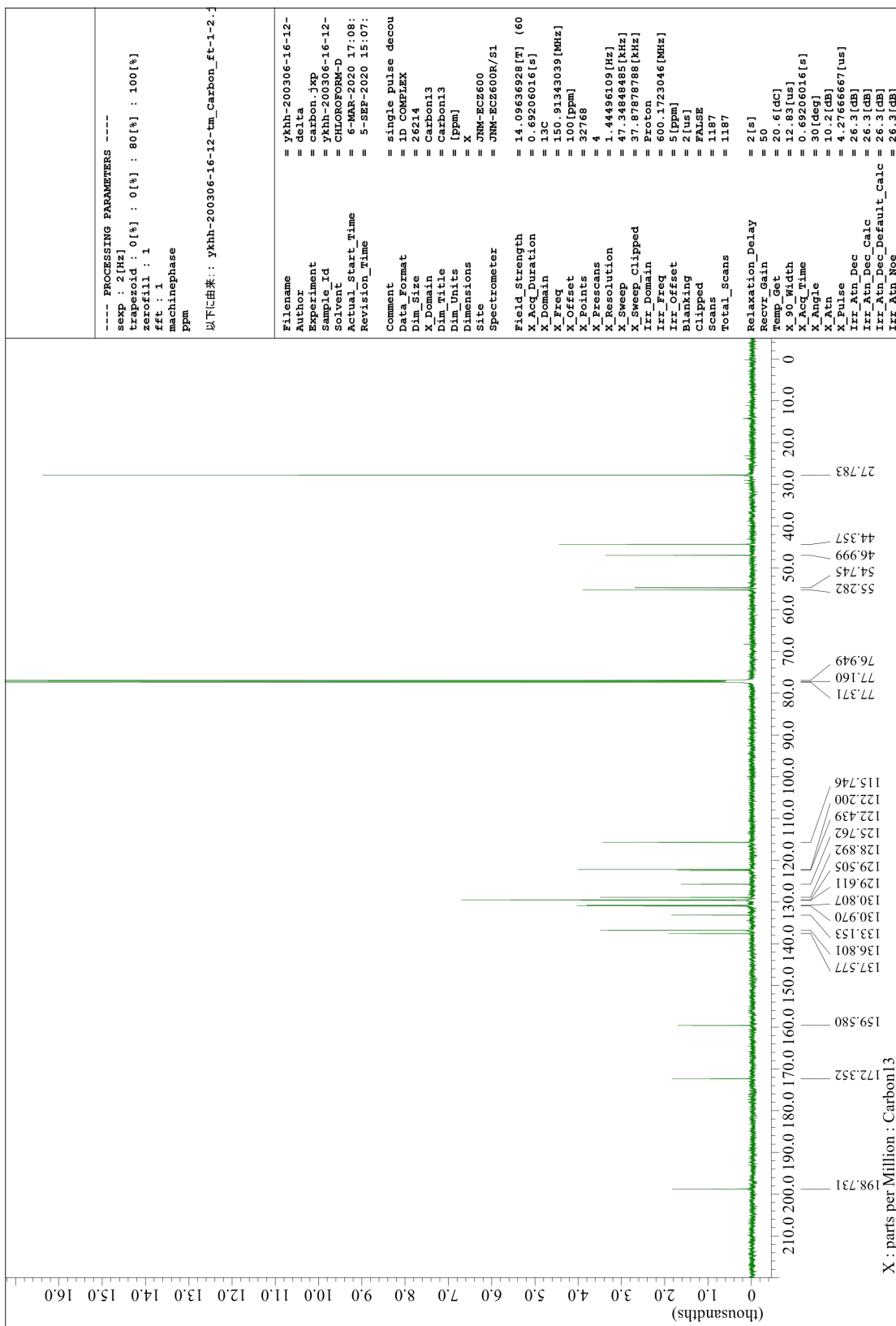


# Supporting Information

8c

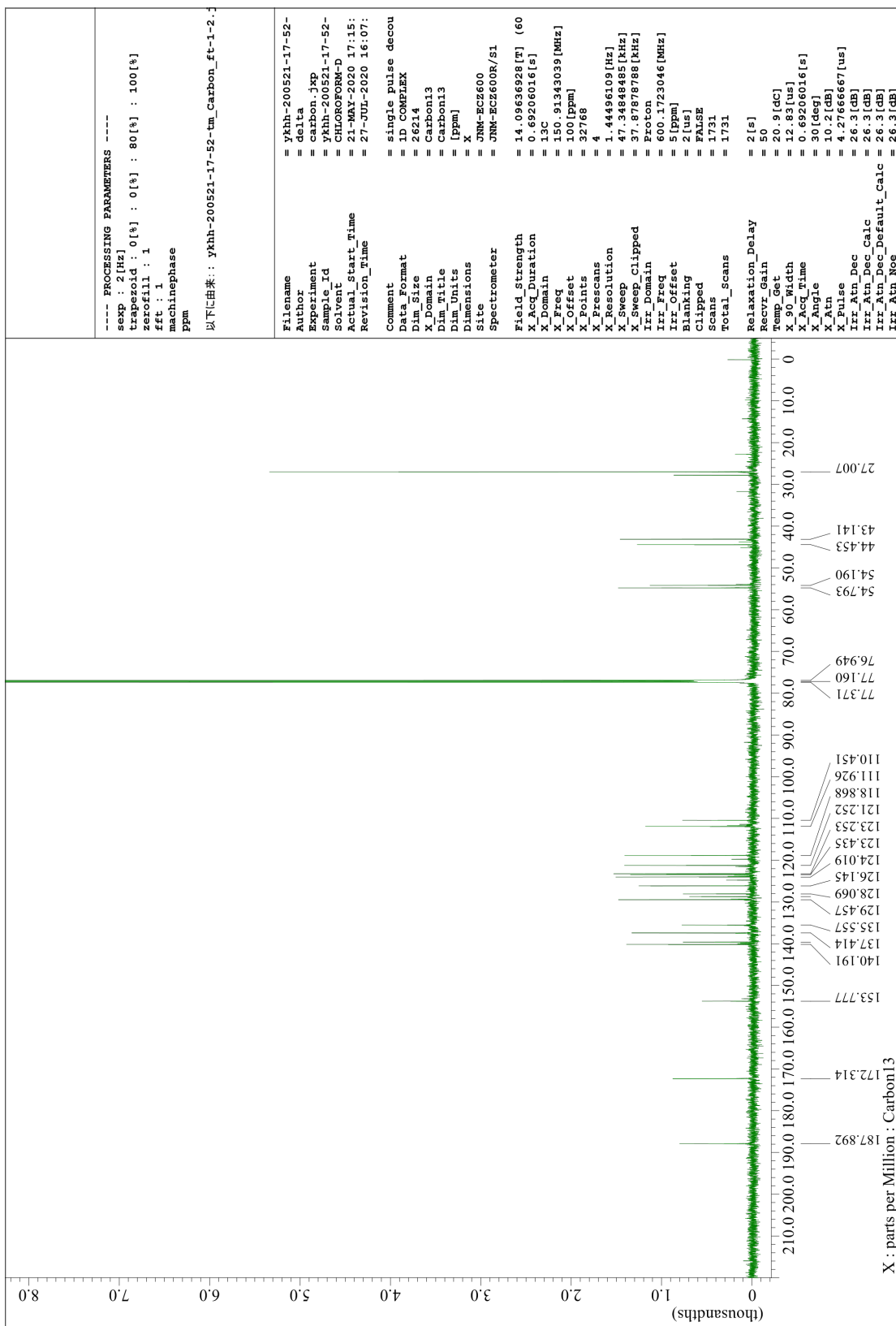


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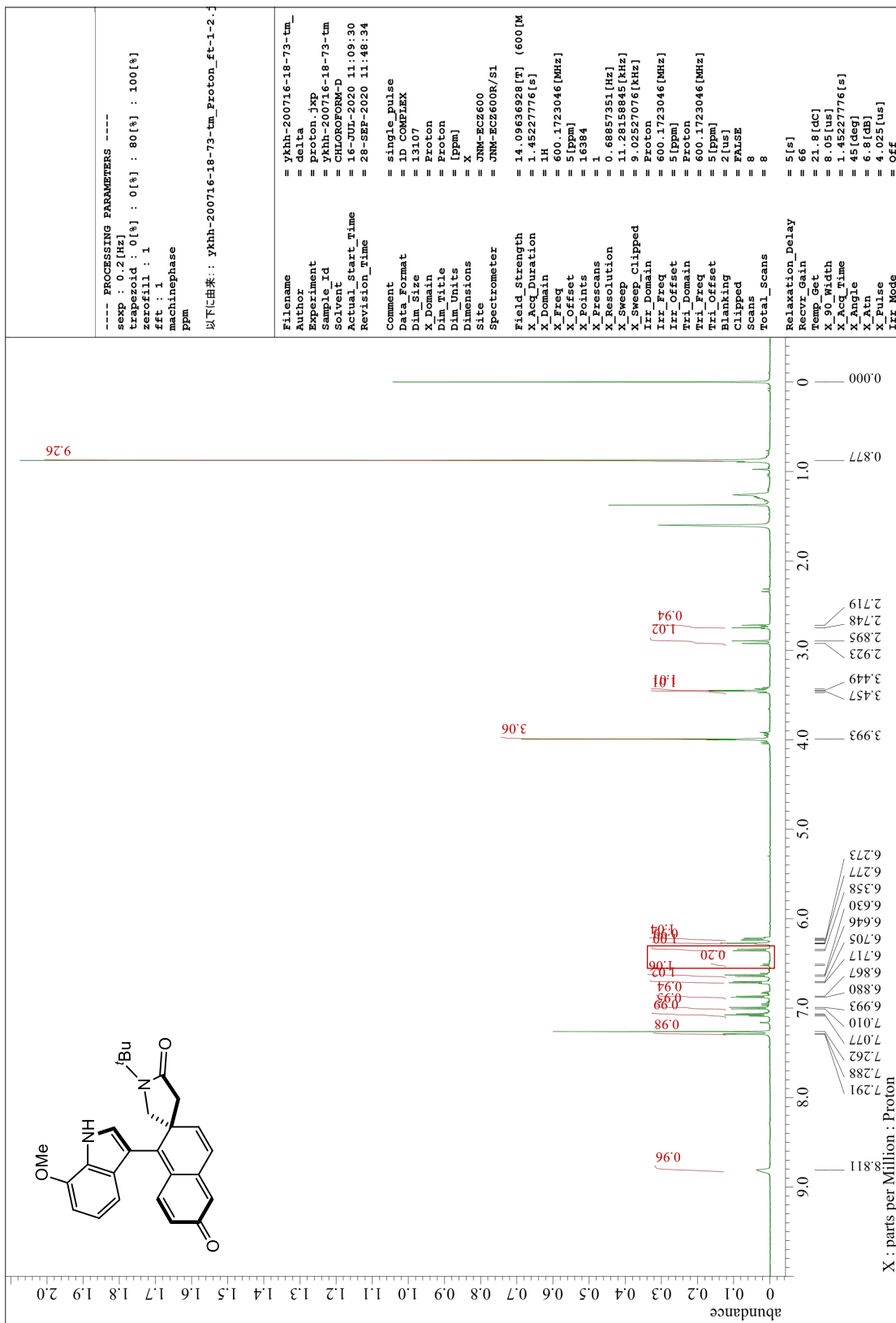


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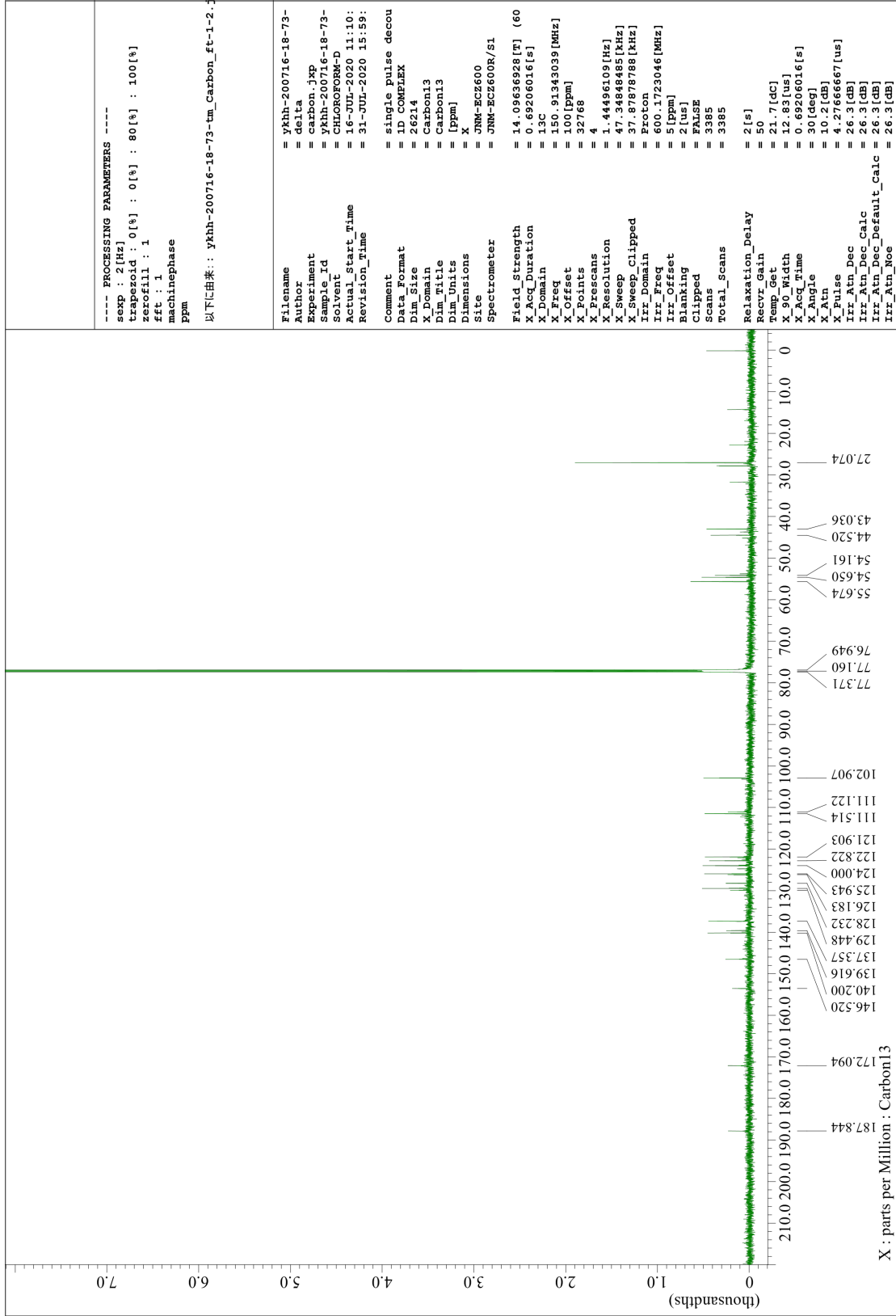


Supporting Information

9b

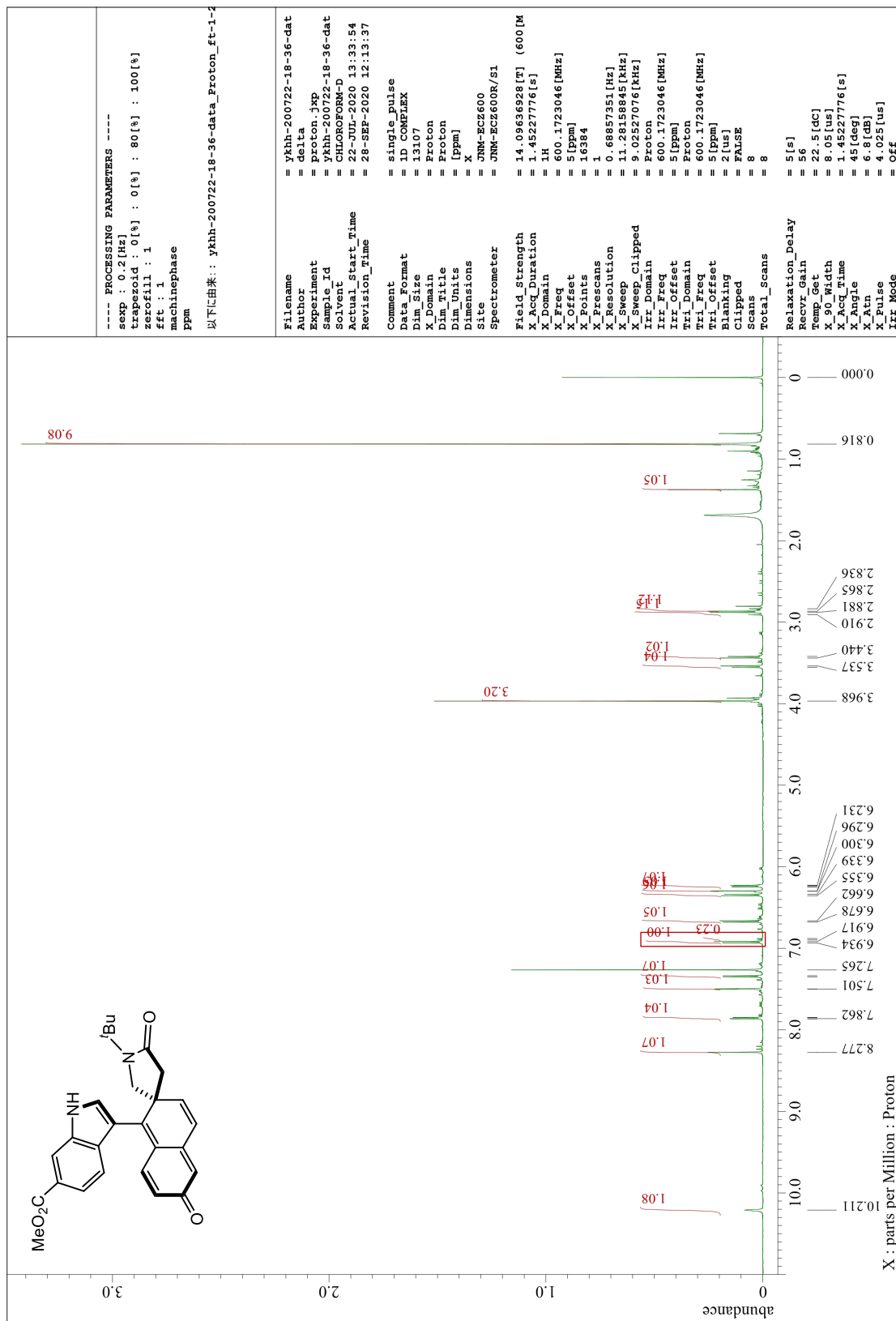


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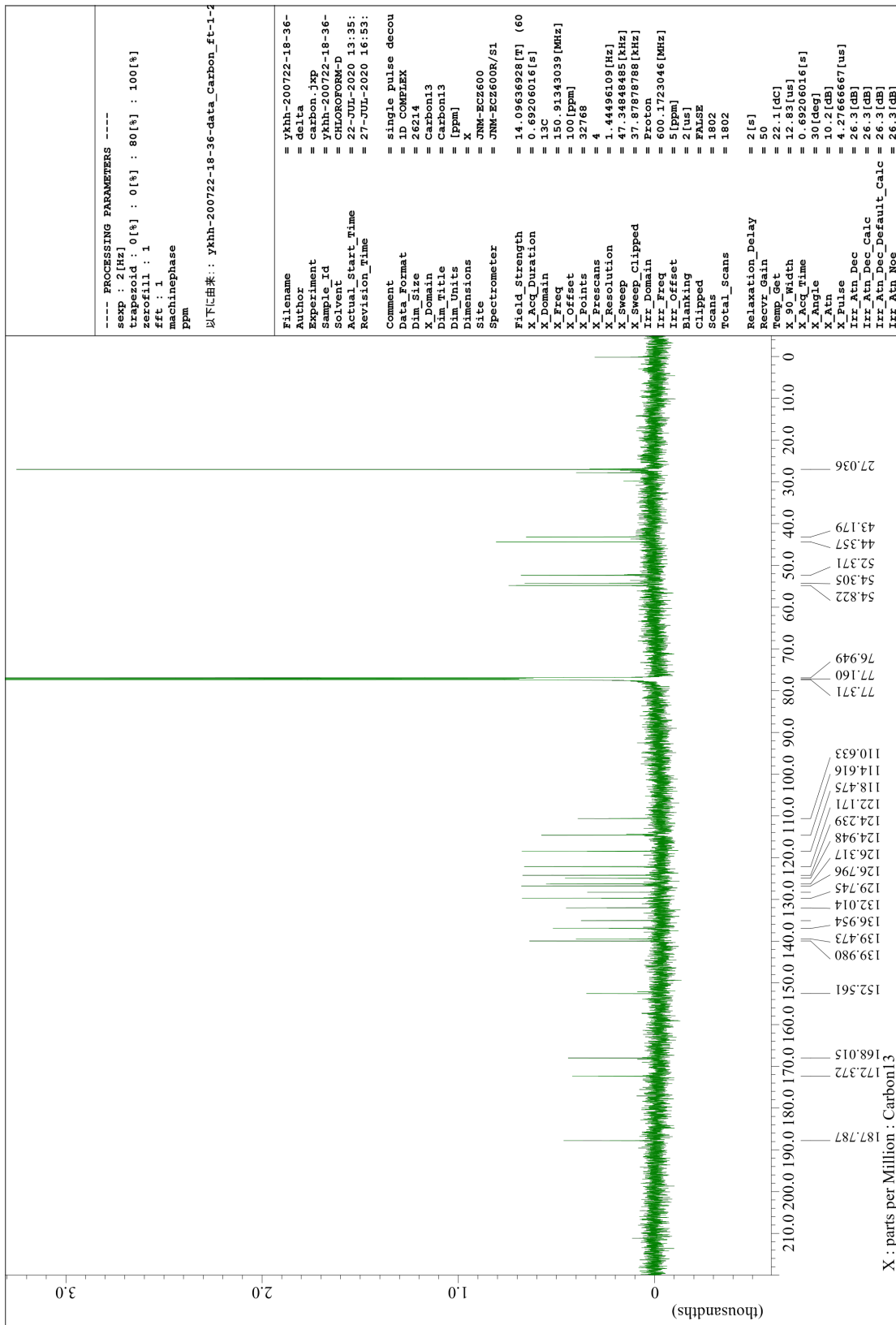


# Supporting Information

9c

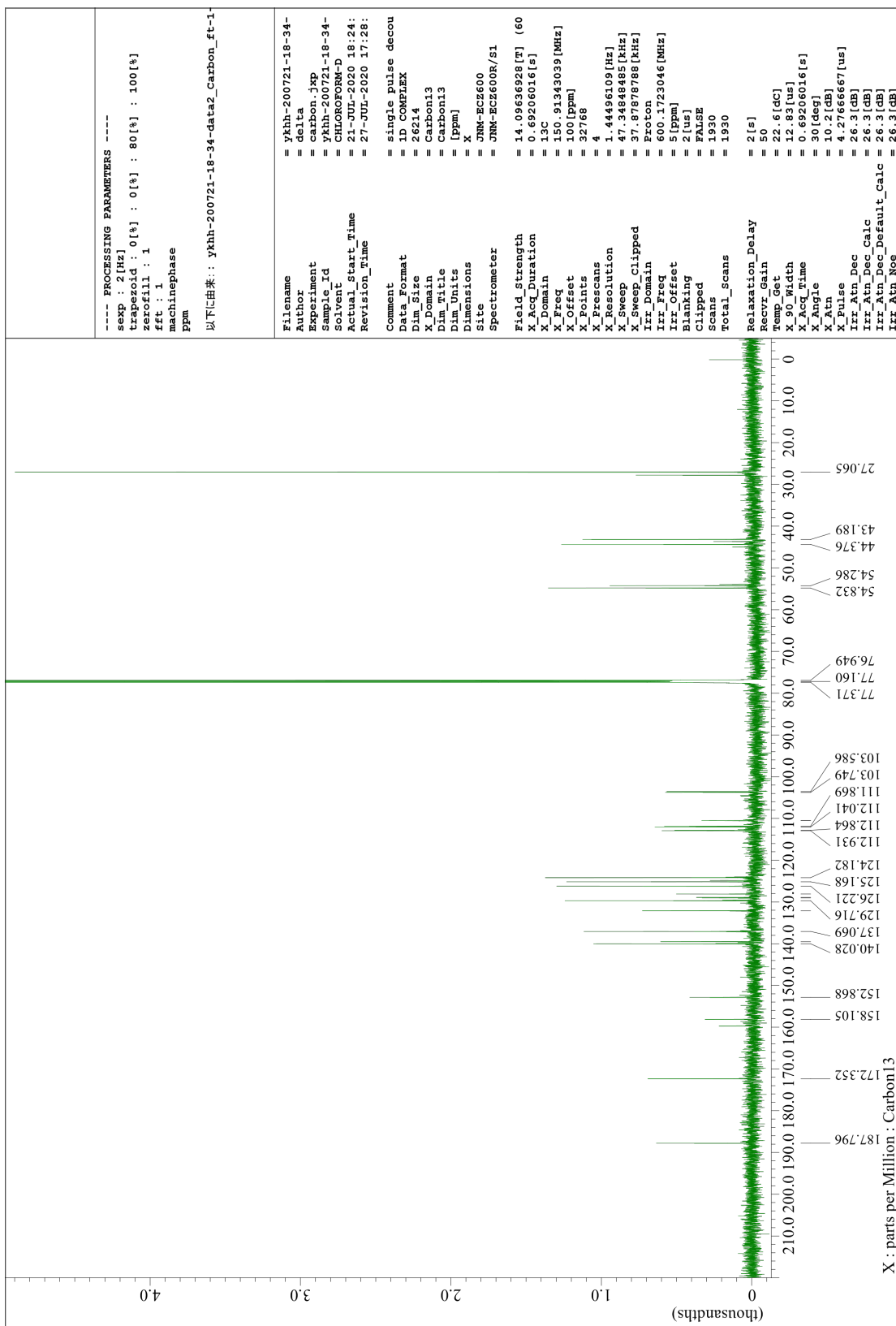


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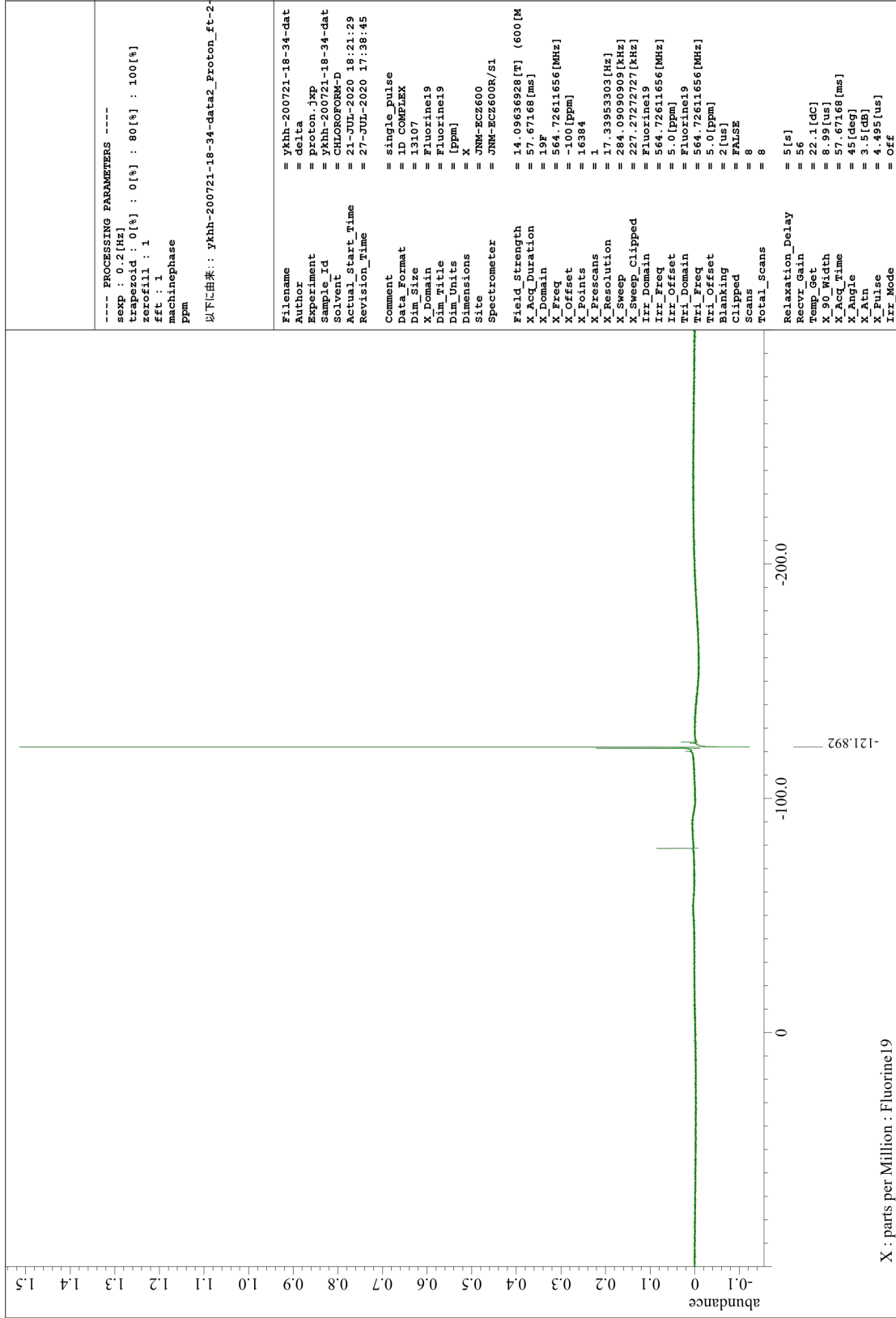




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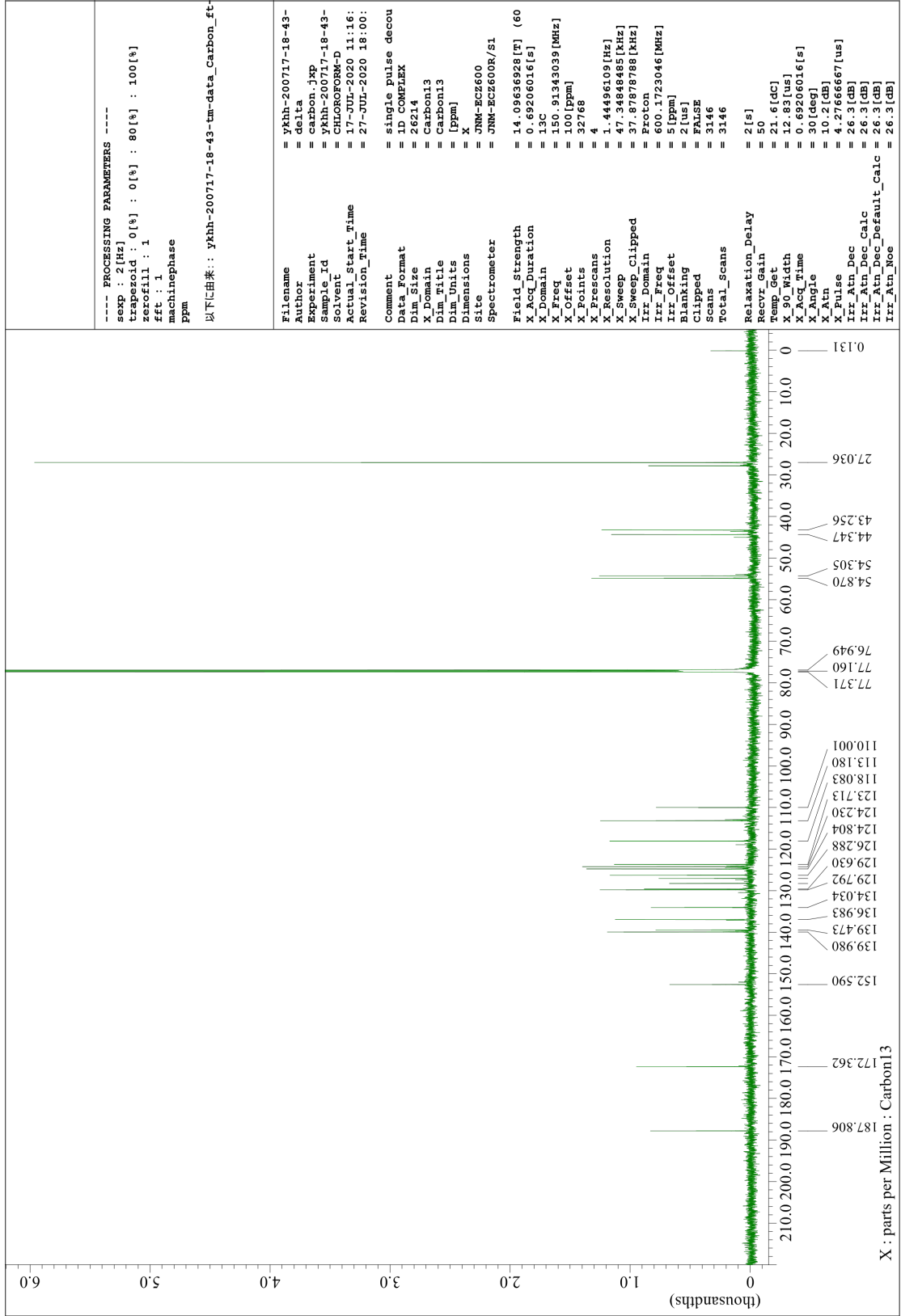


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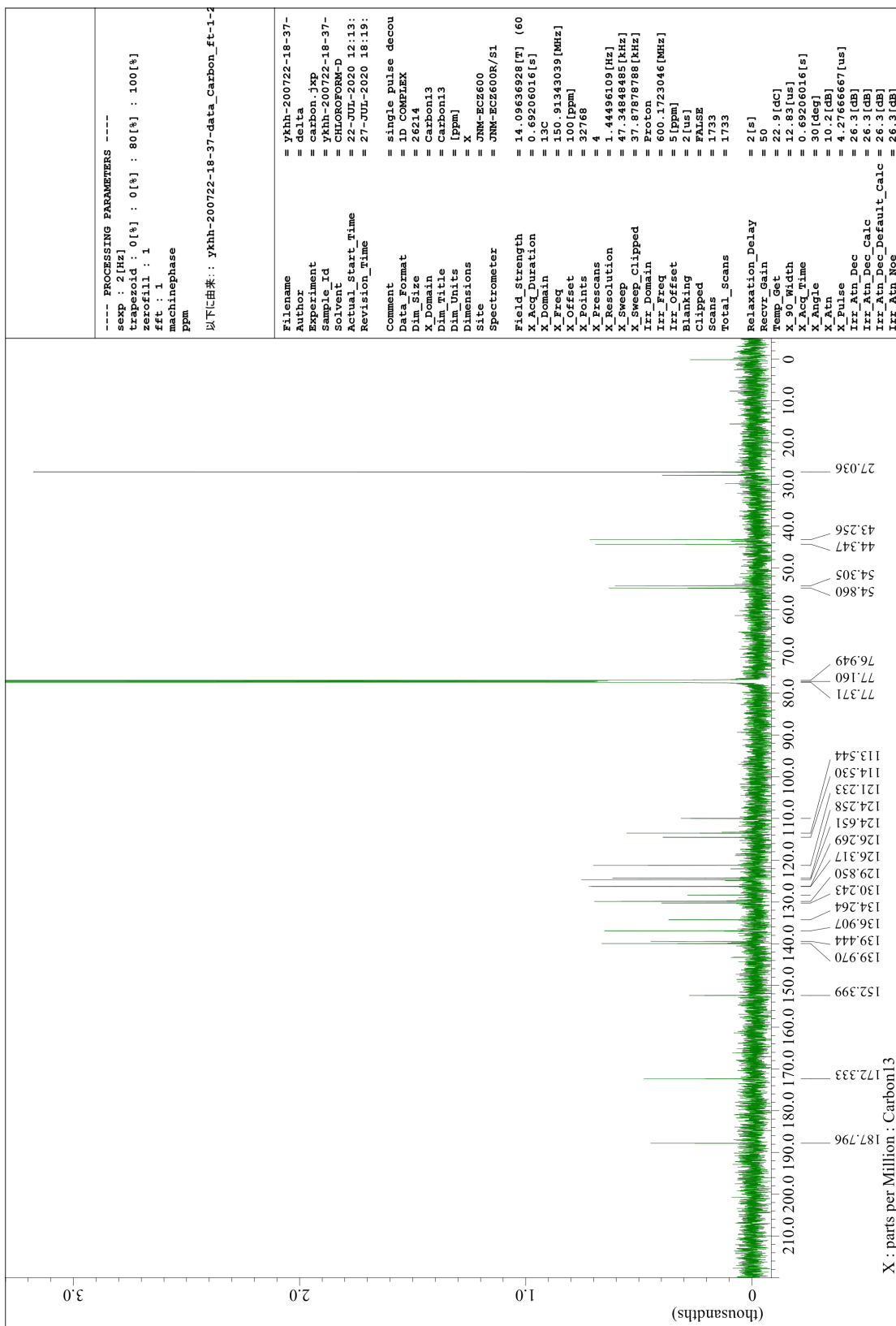


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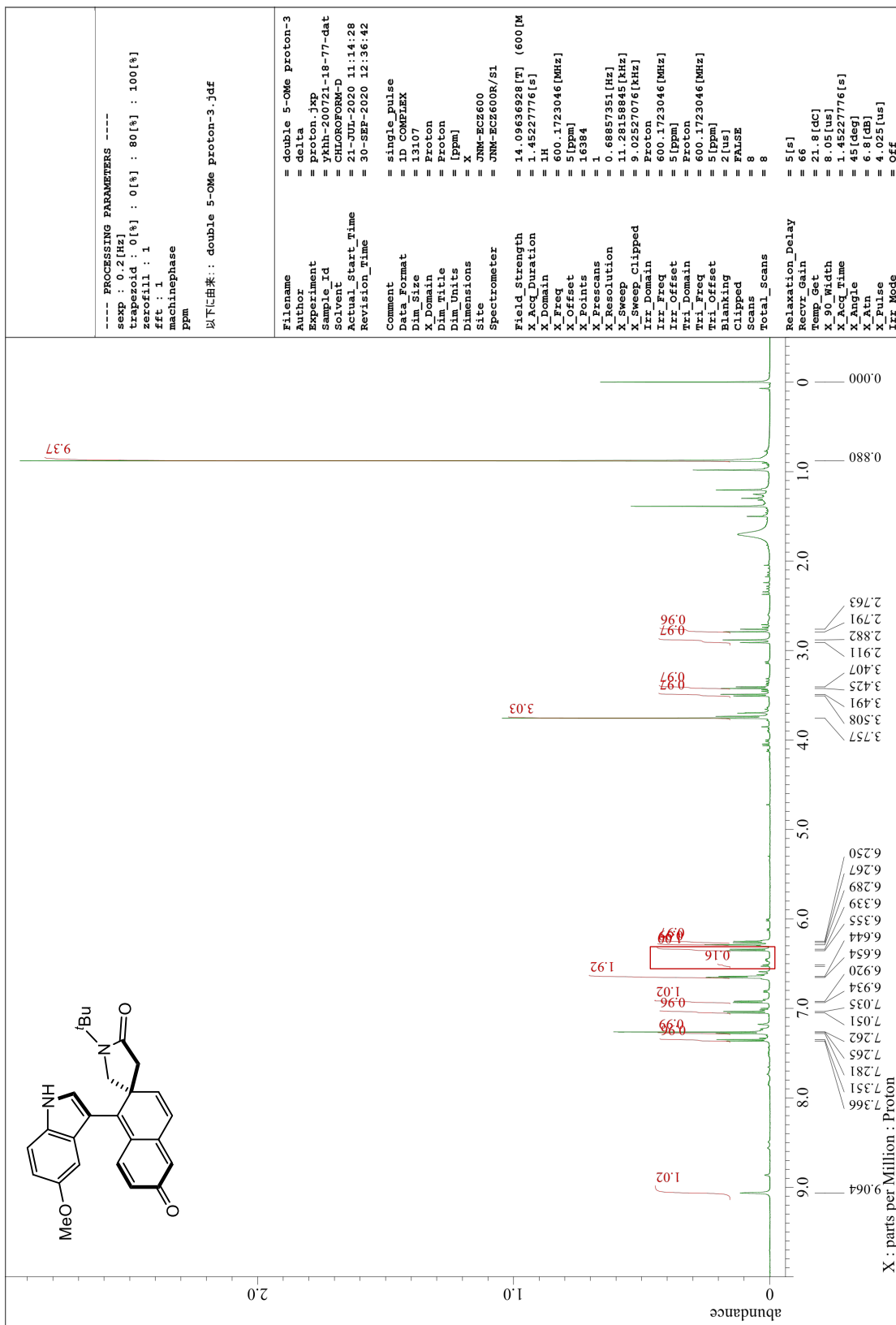


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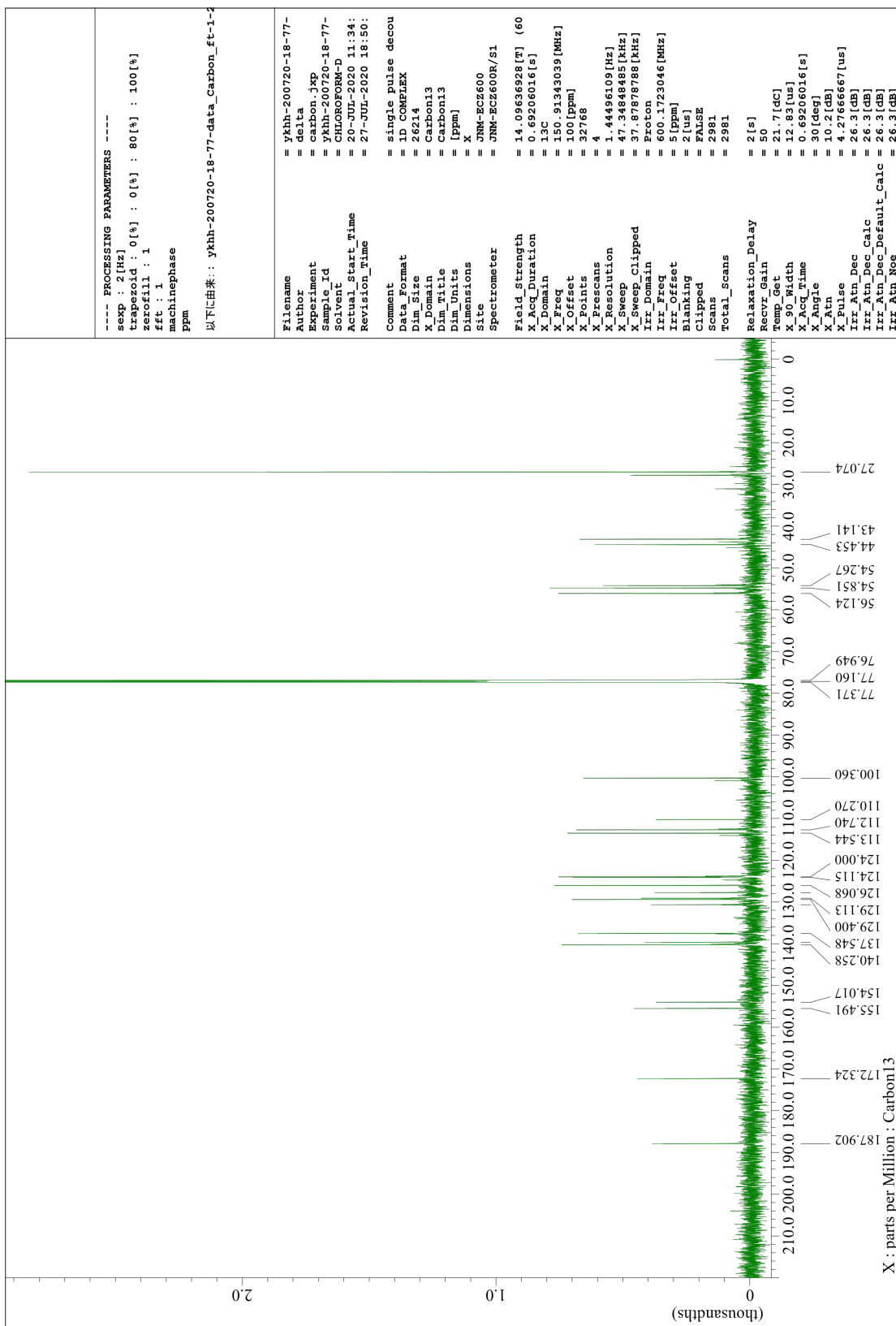


# Supporting Information

9g

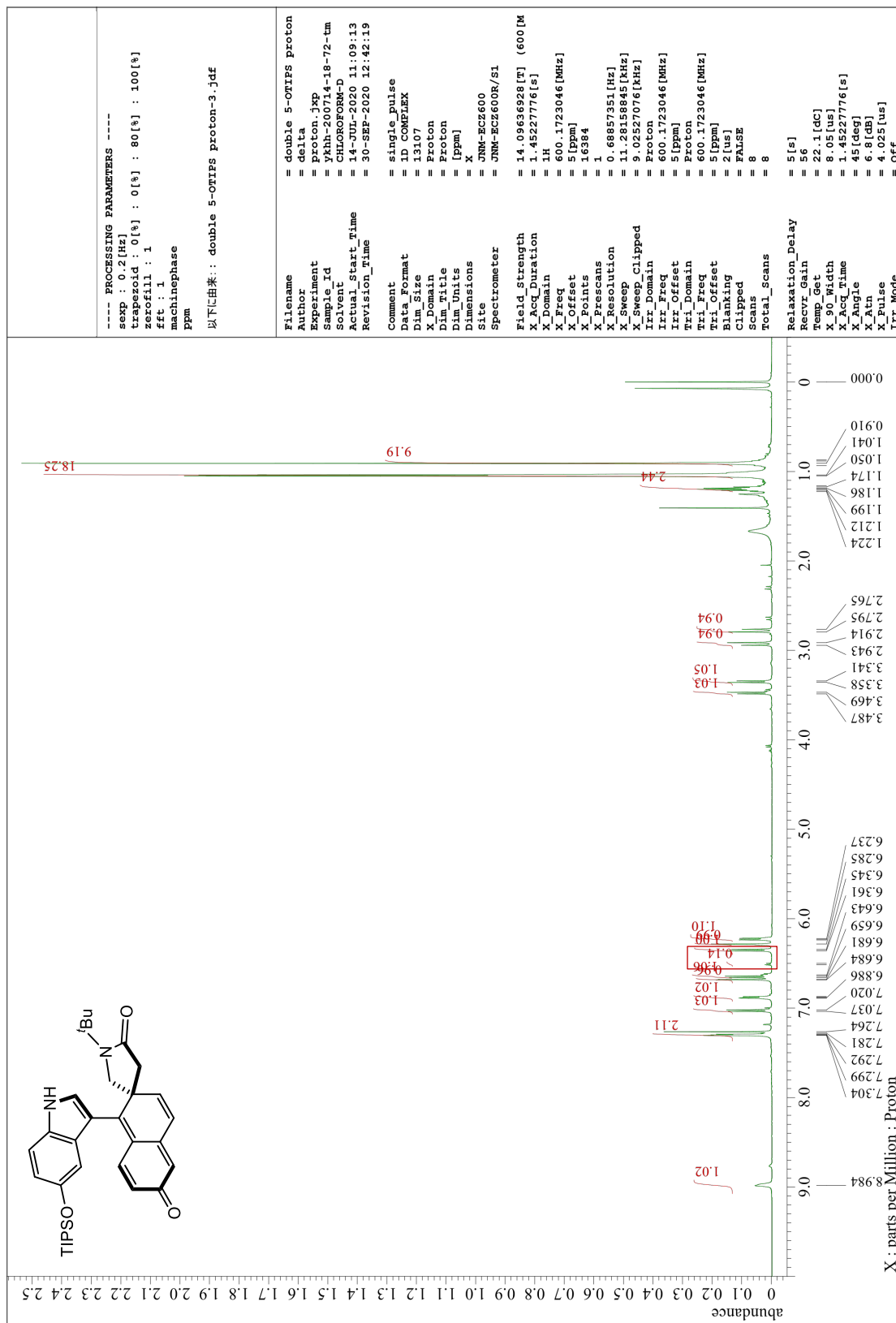


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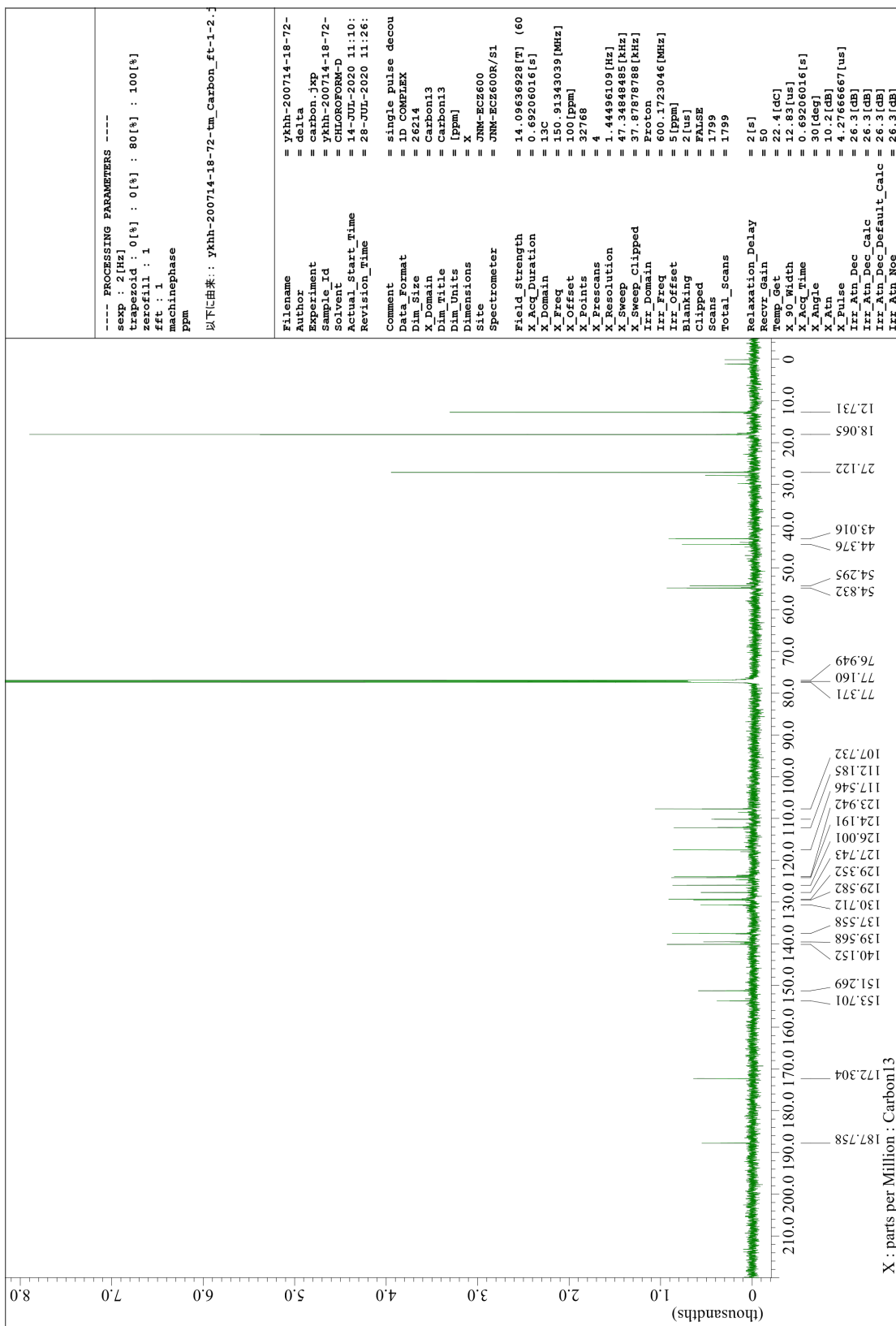


# Supporting Information

9h

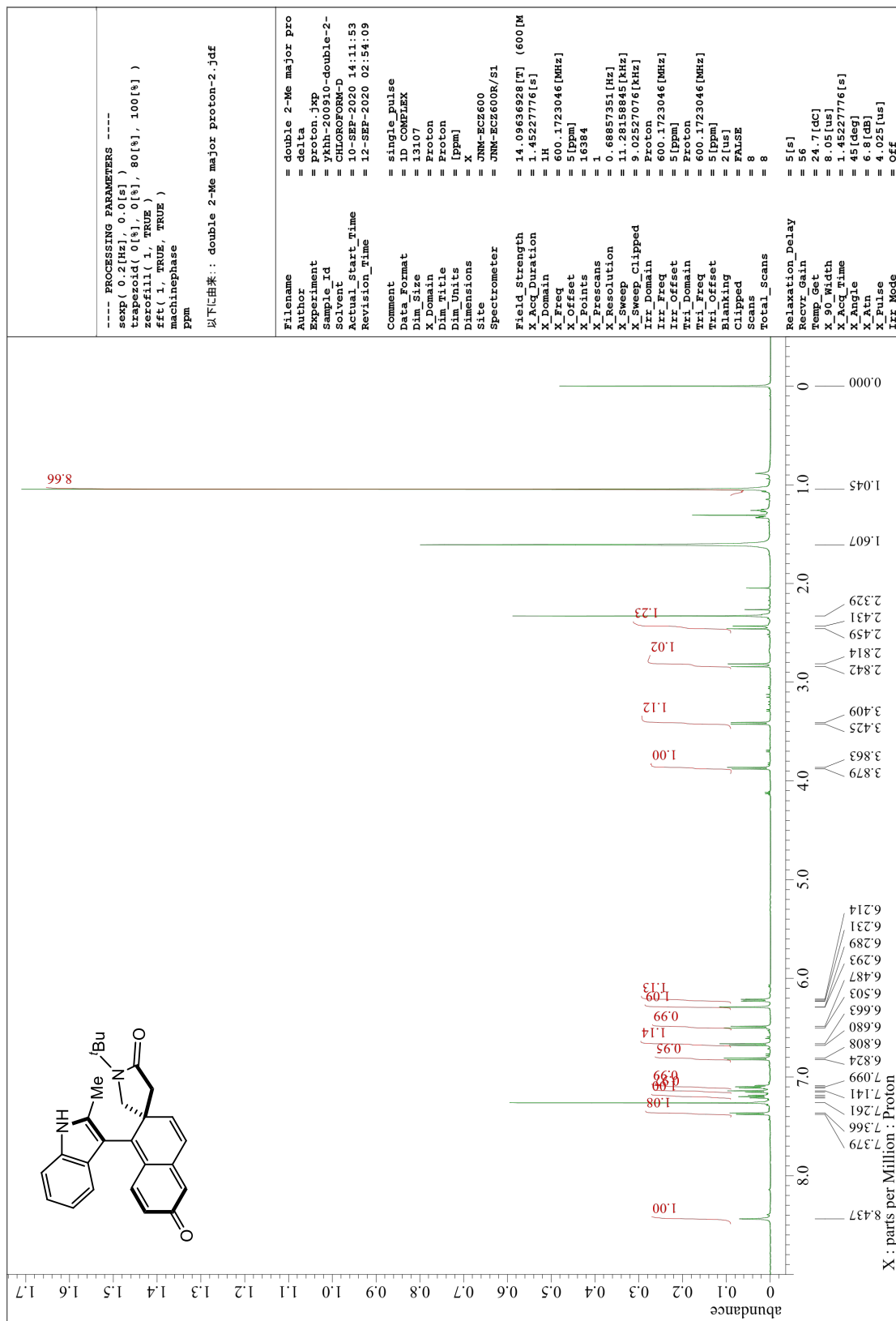


# Supporting Information

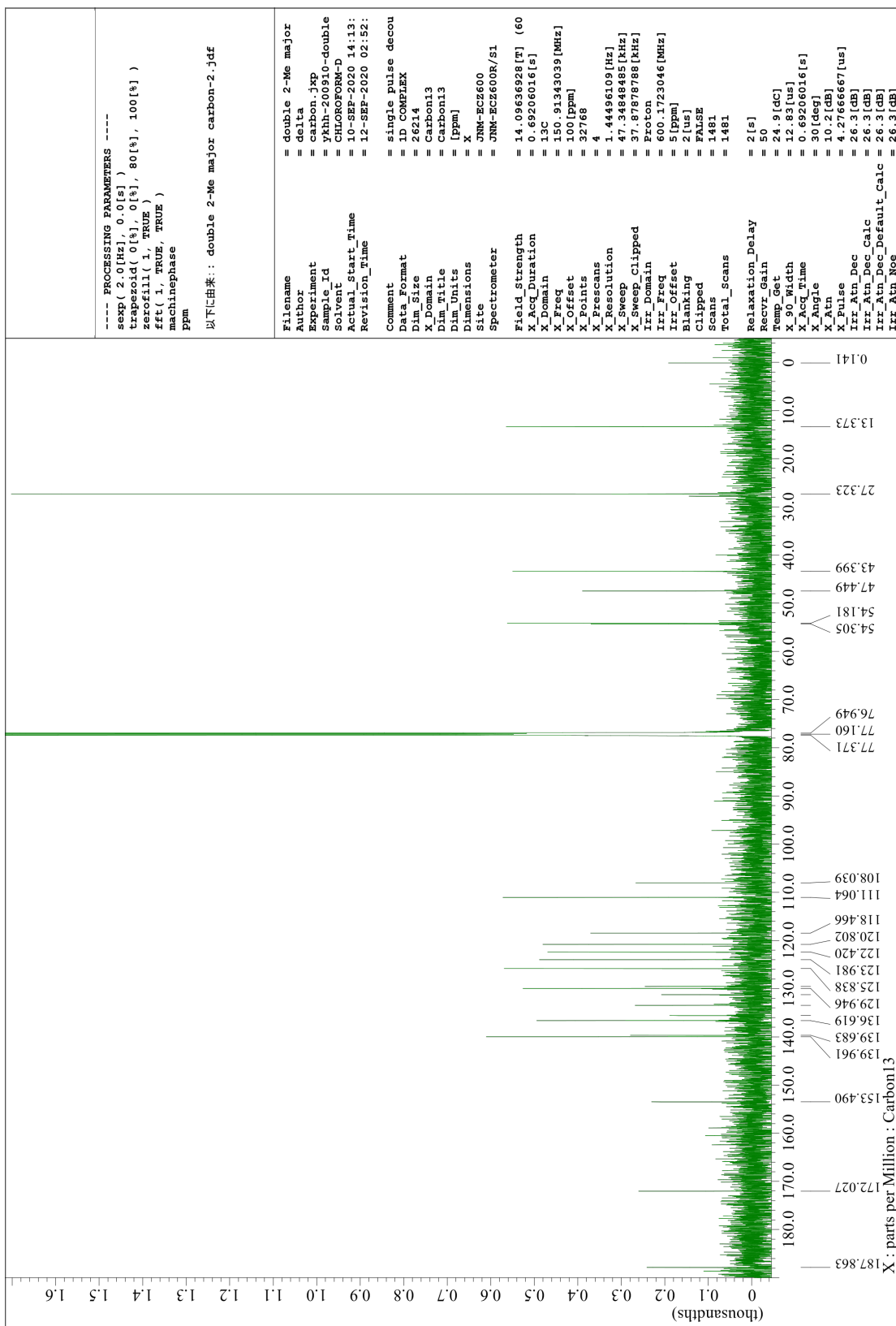


# Supporting Information

## 9i (major diastereomer)

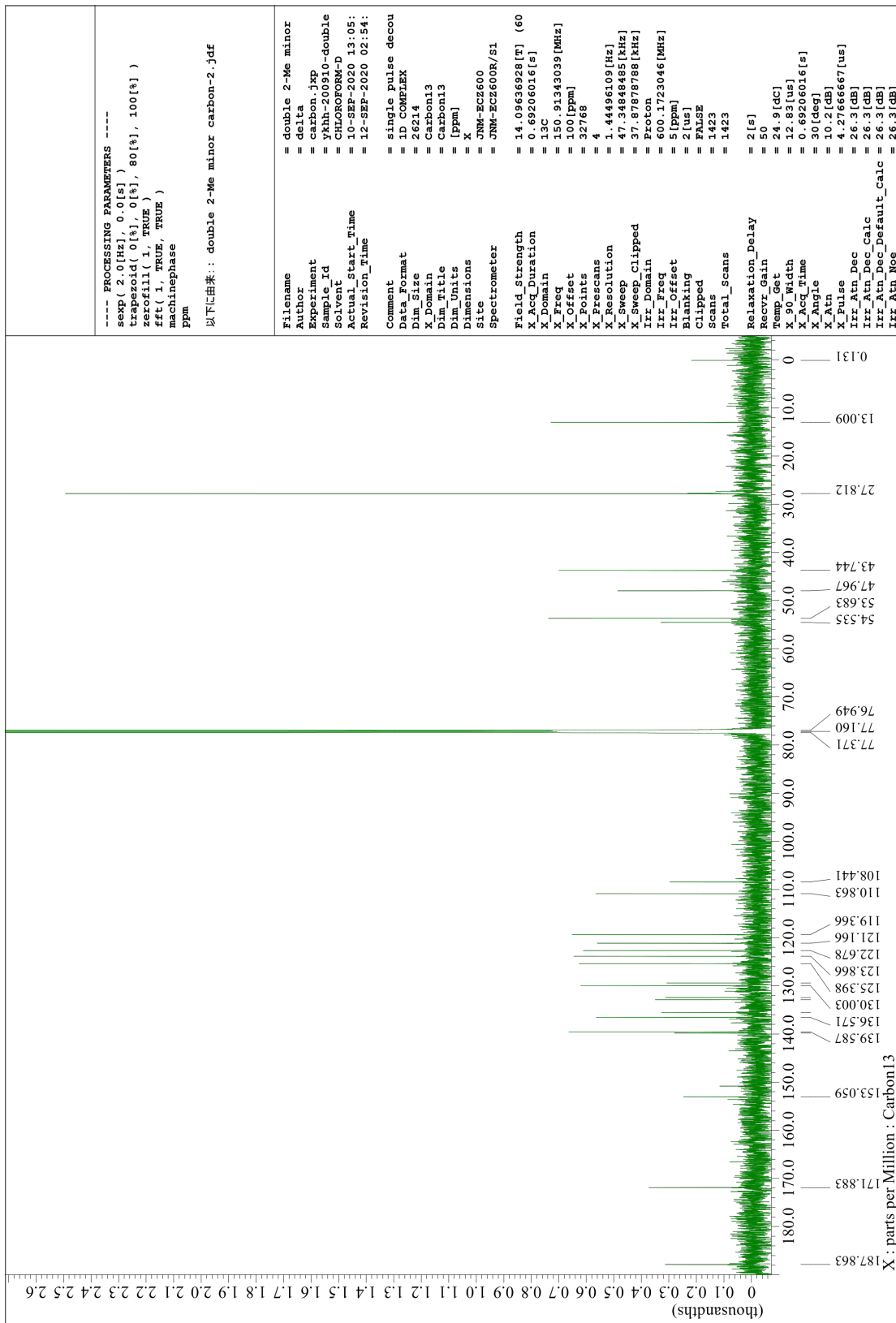


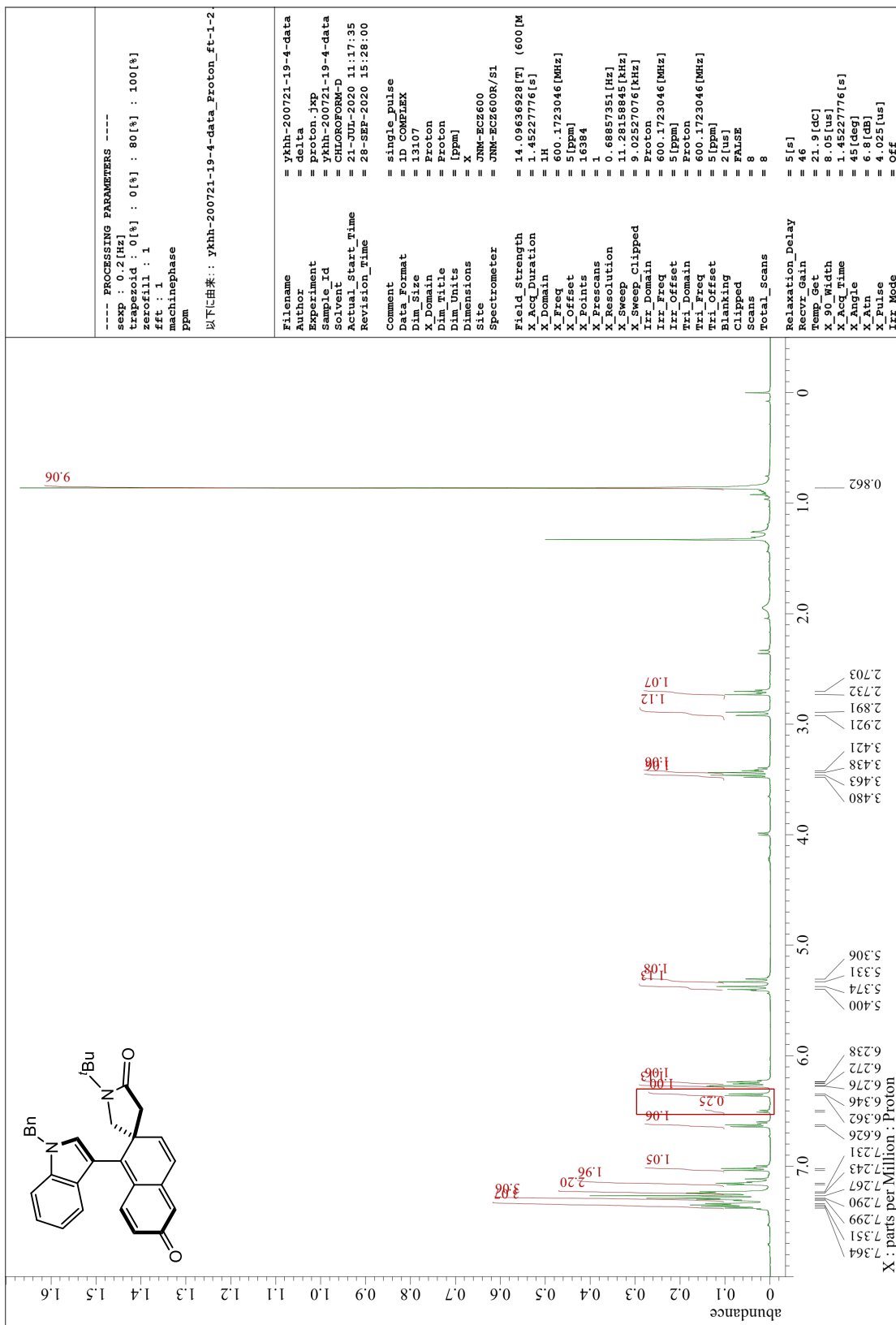
# Supporting Information



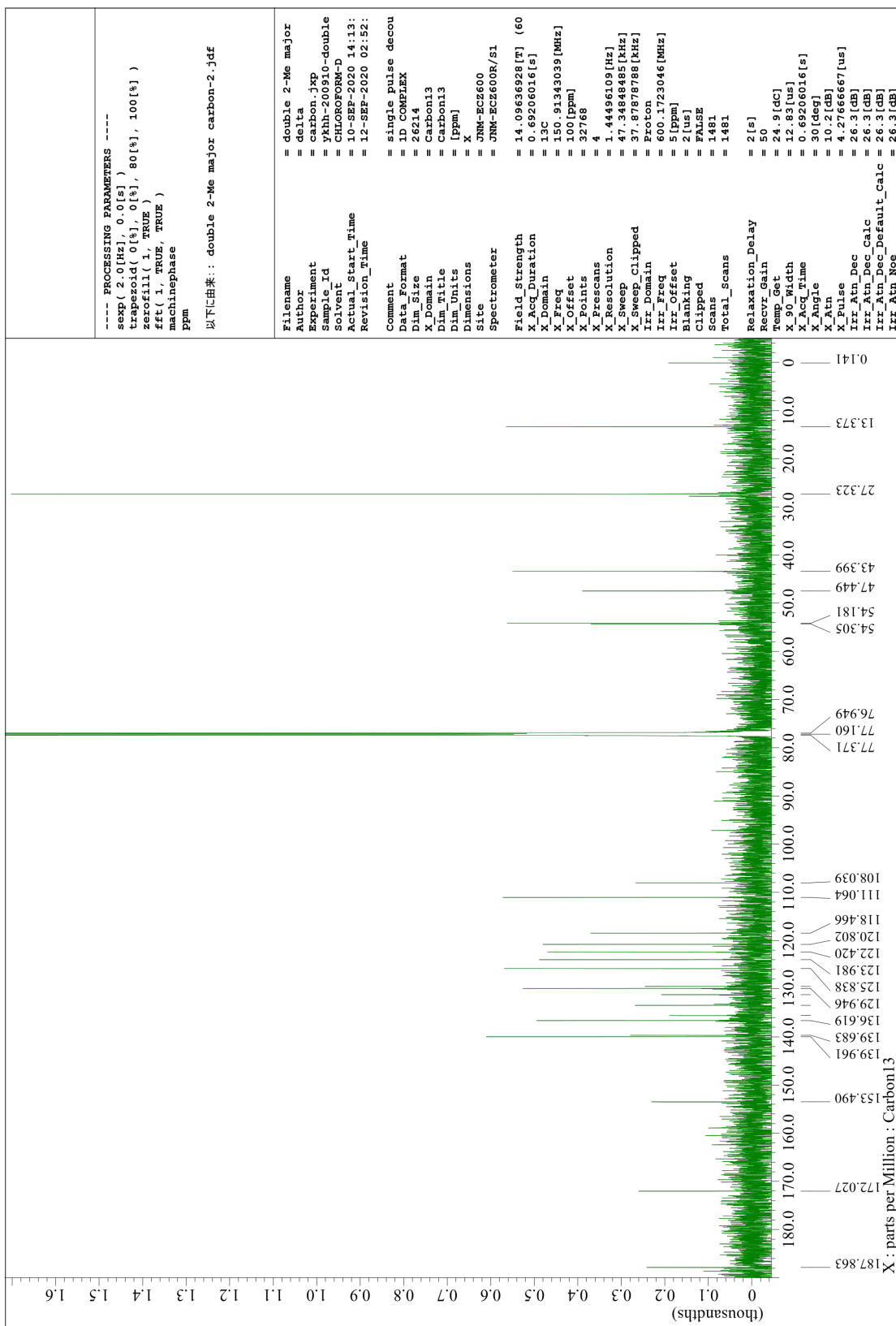


# Supporting Information



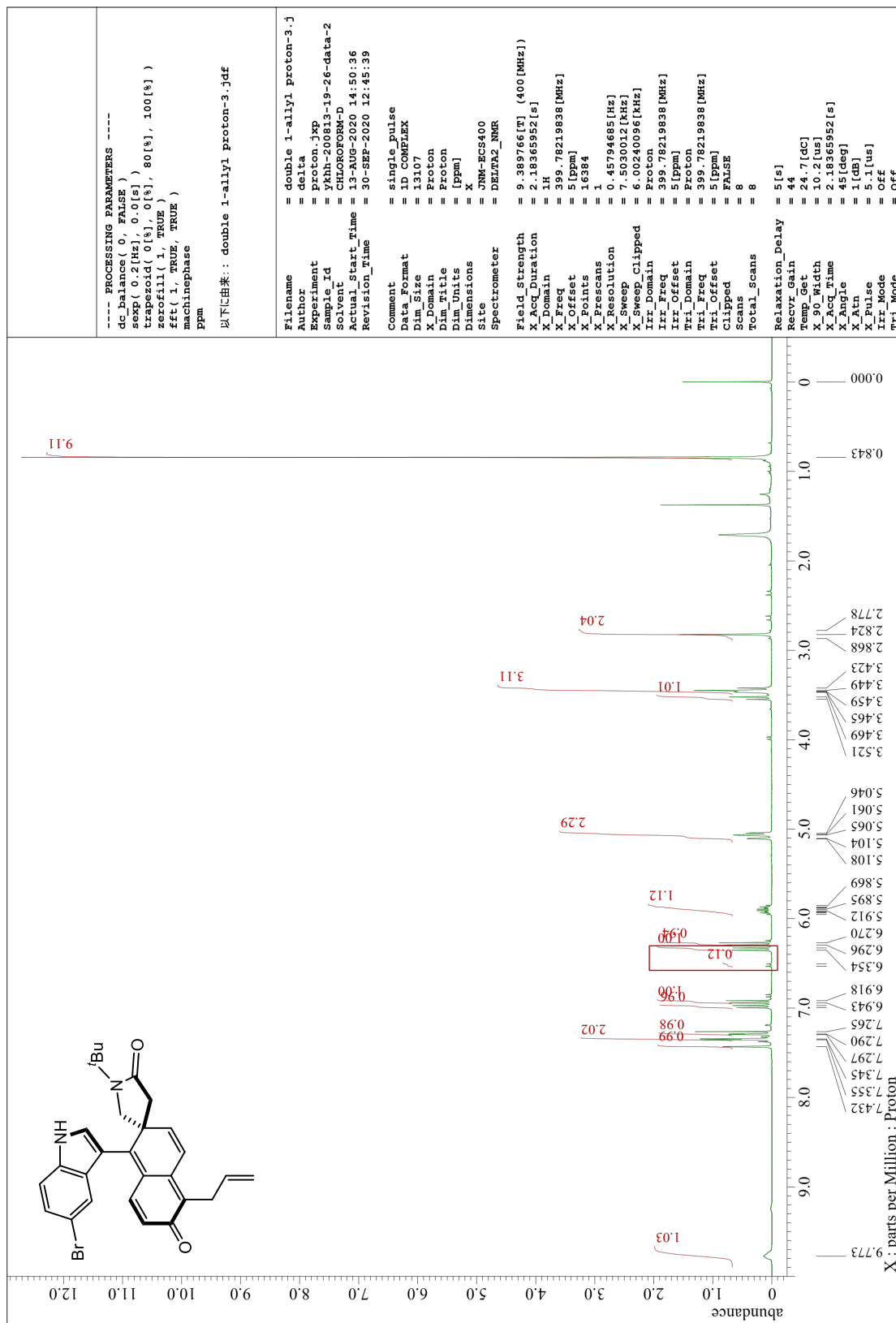


# Supporting Information



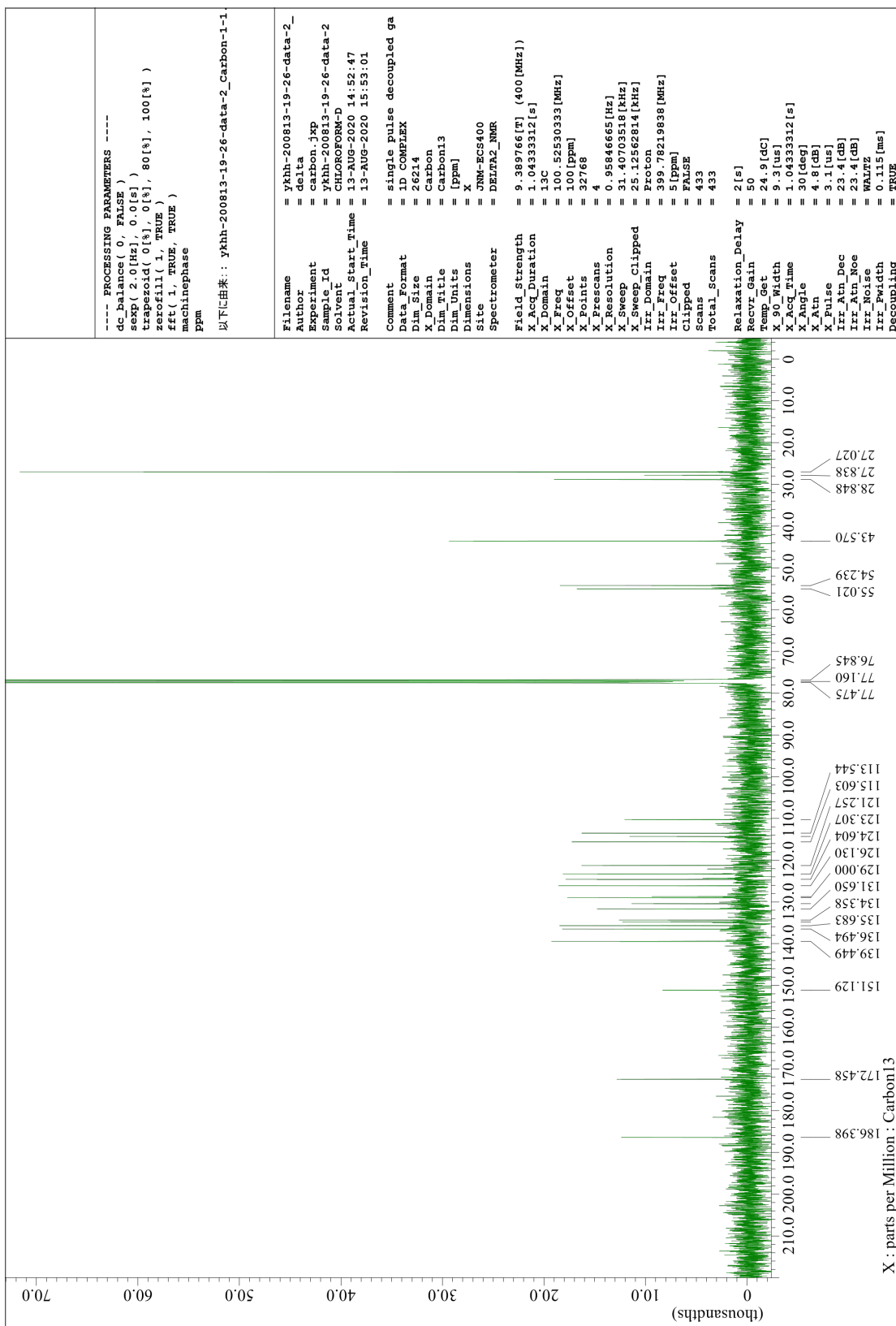
# Supporting Information

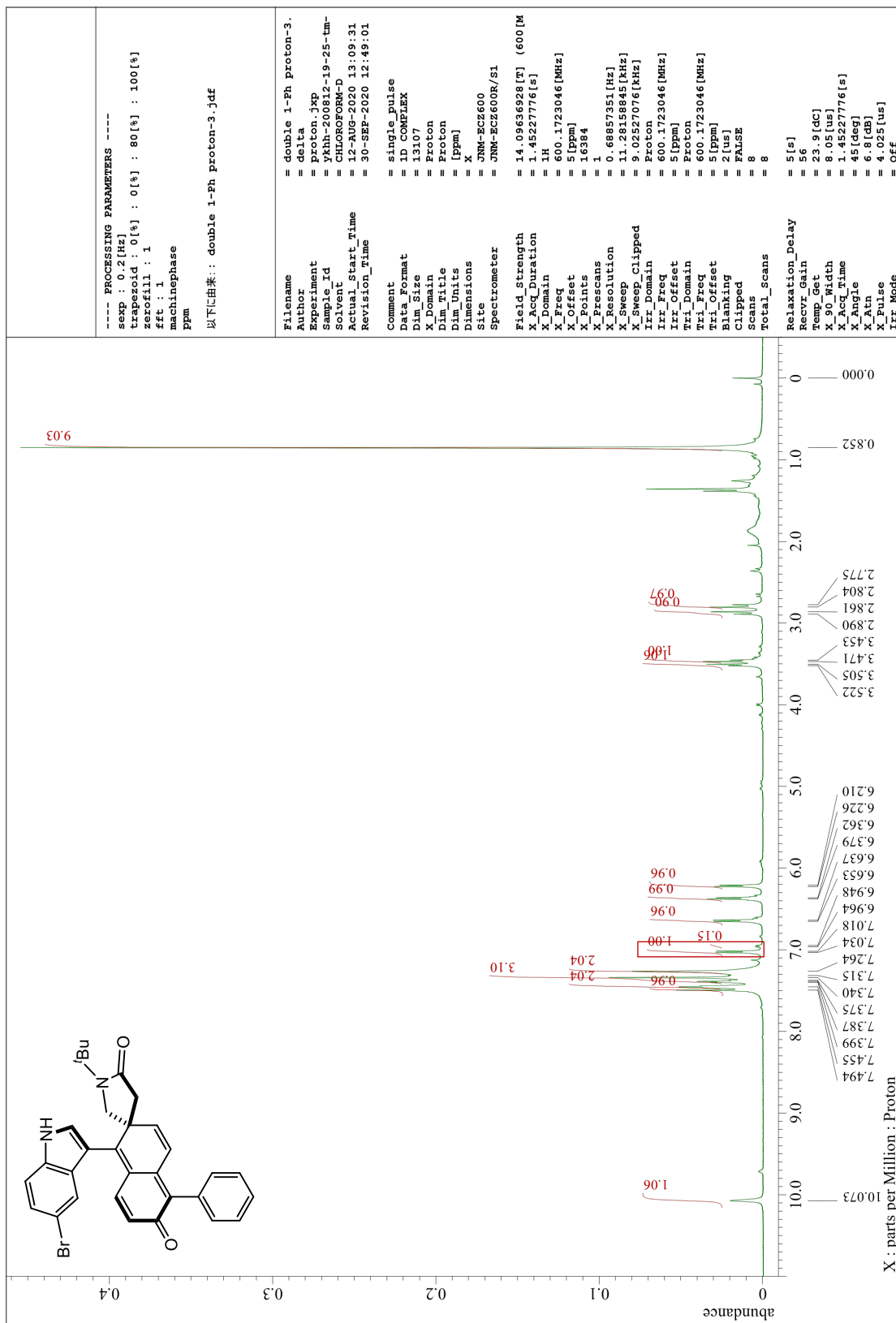
9k



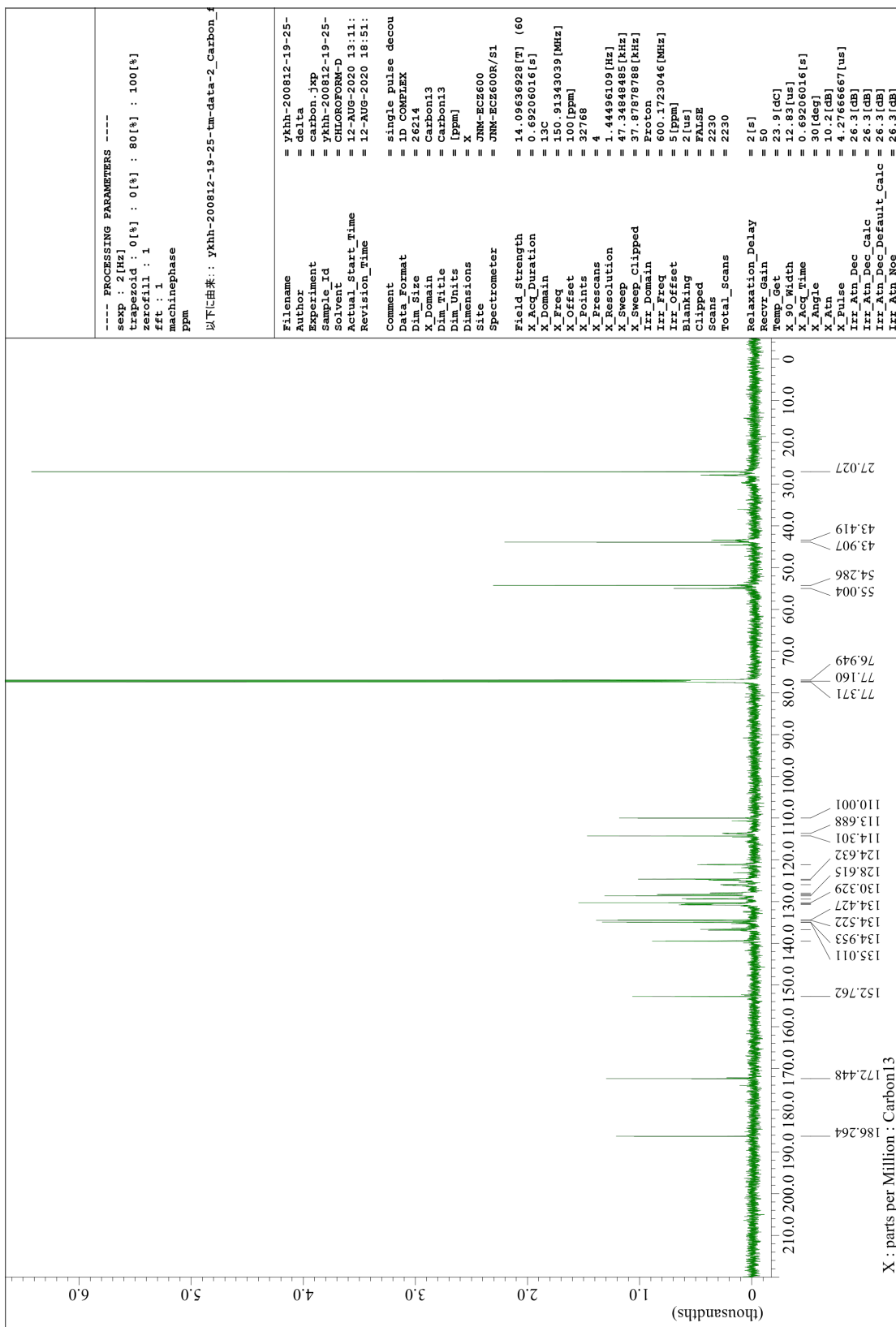
S133

# Supporting Information



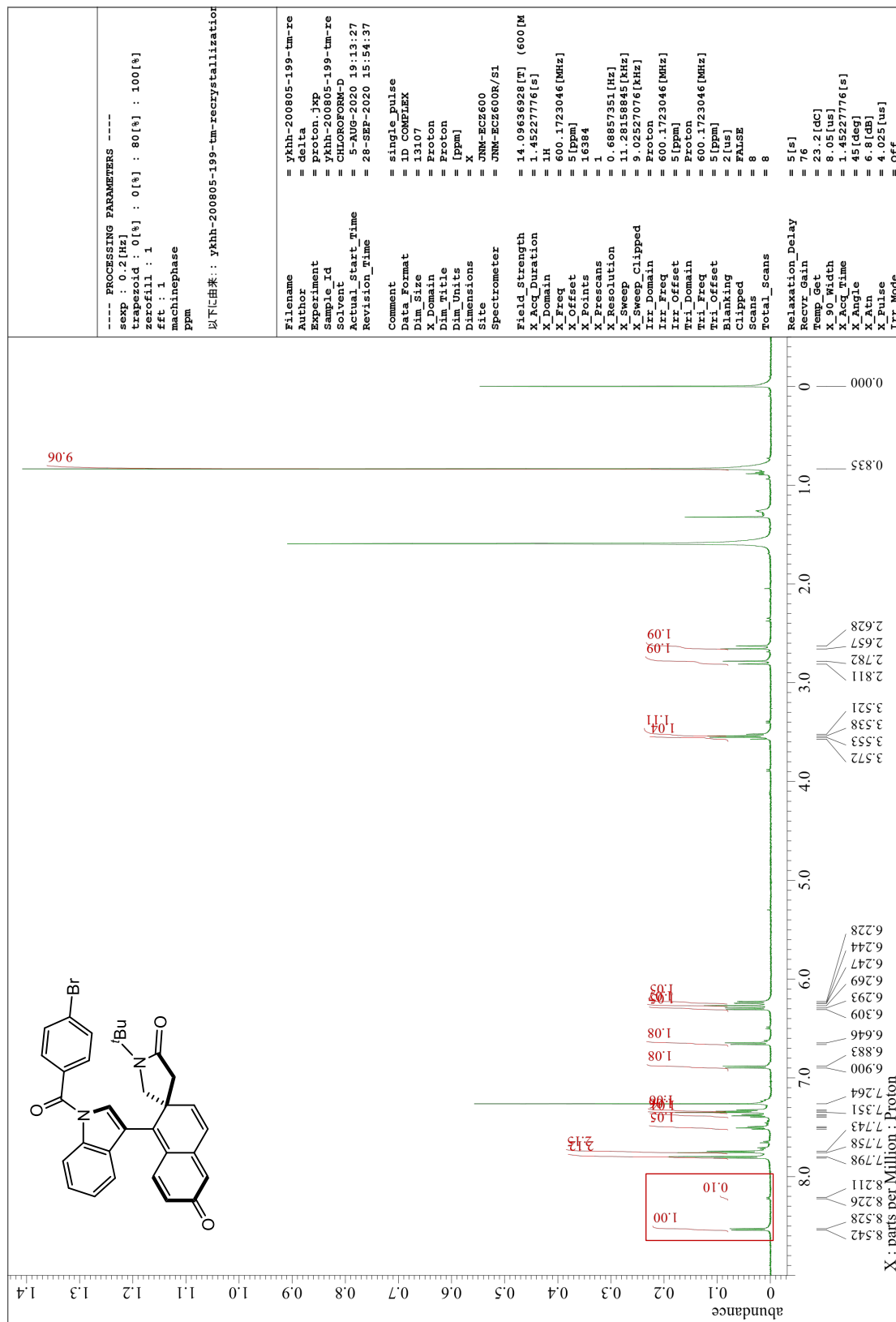


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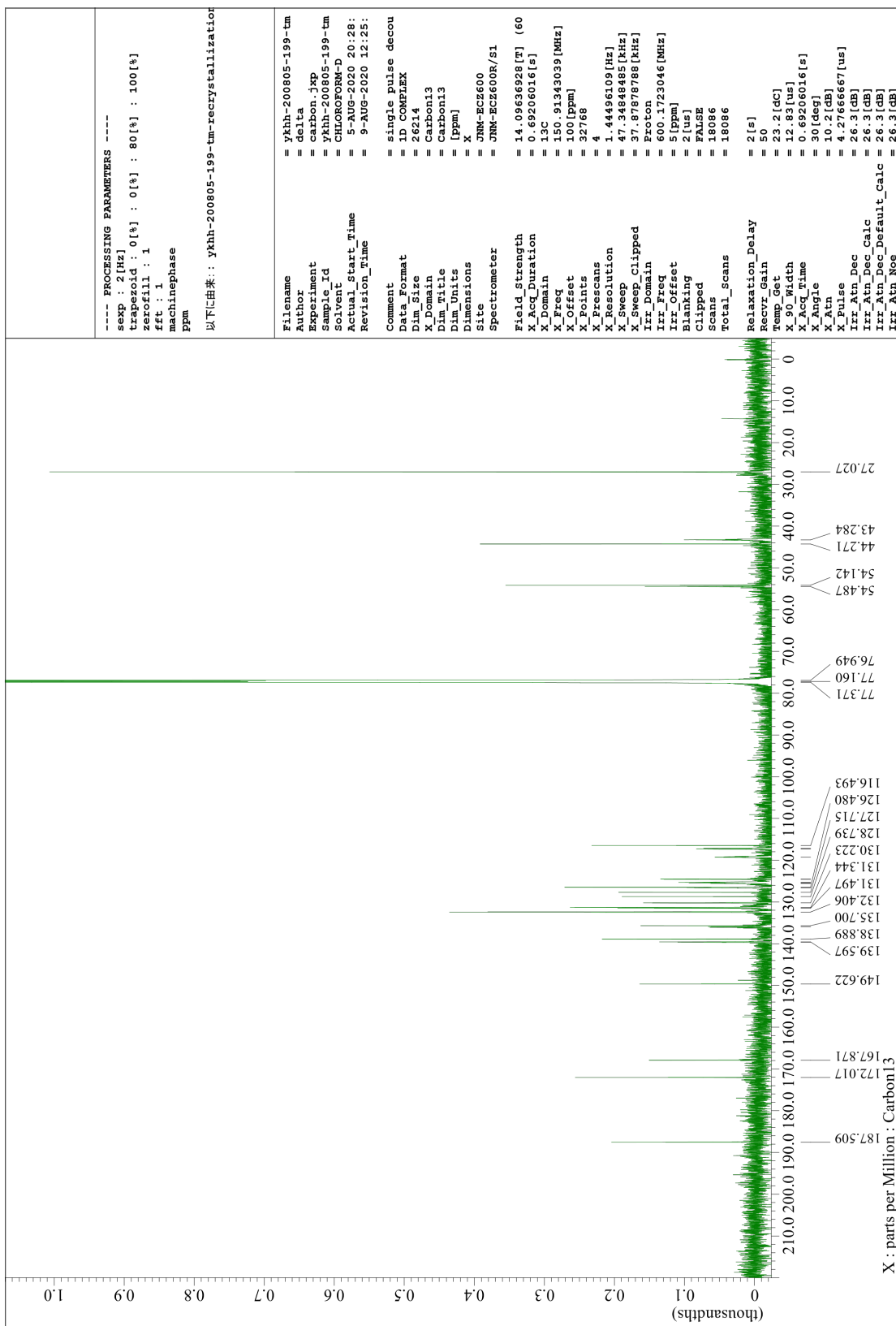


# Supporting Information

10a

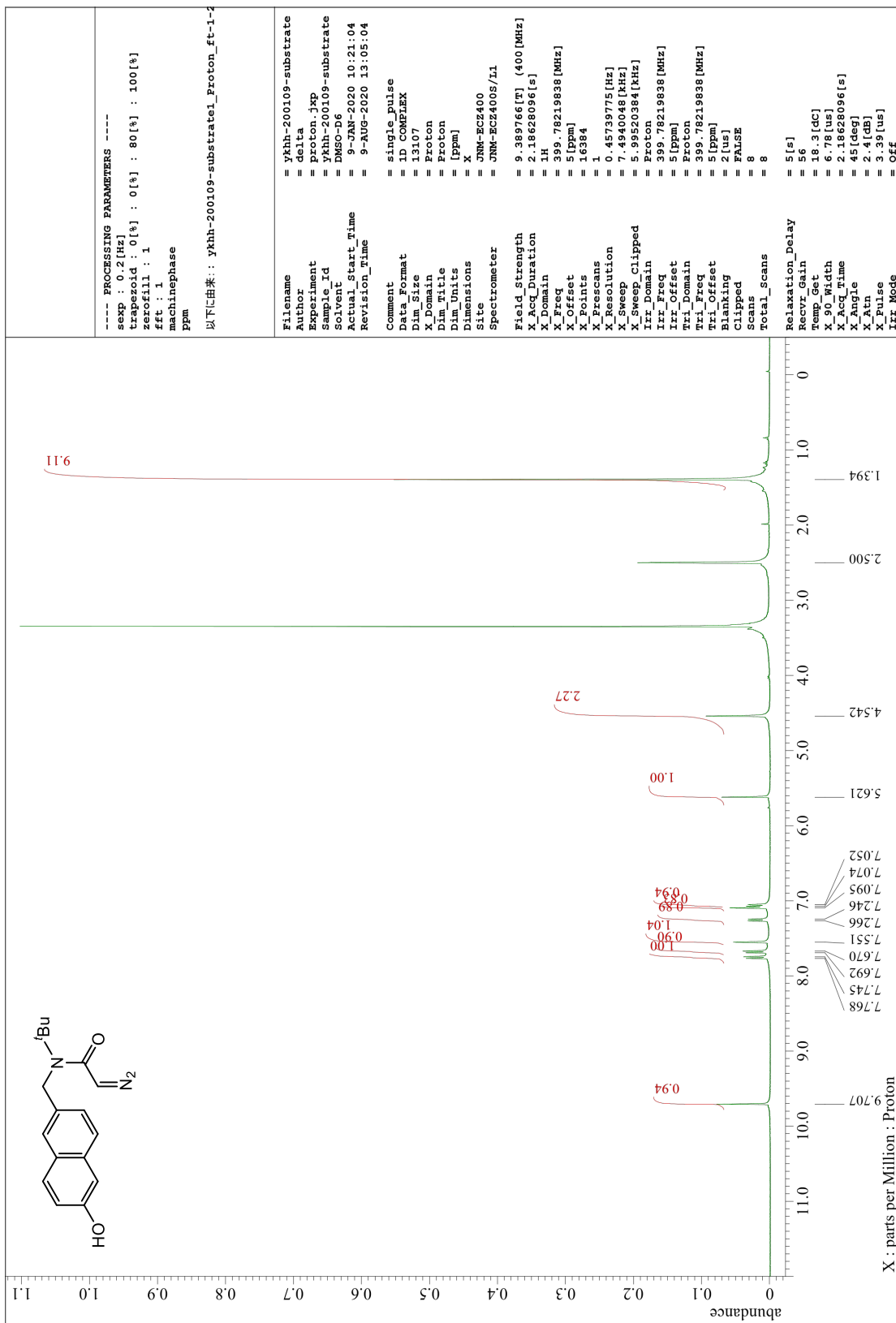


# Supporting Information

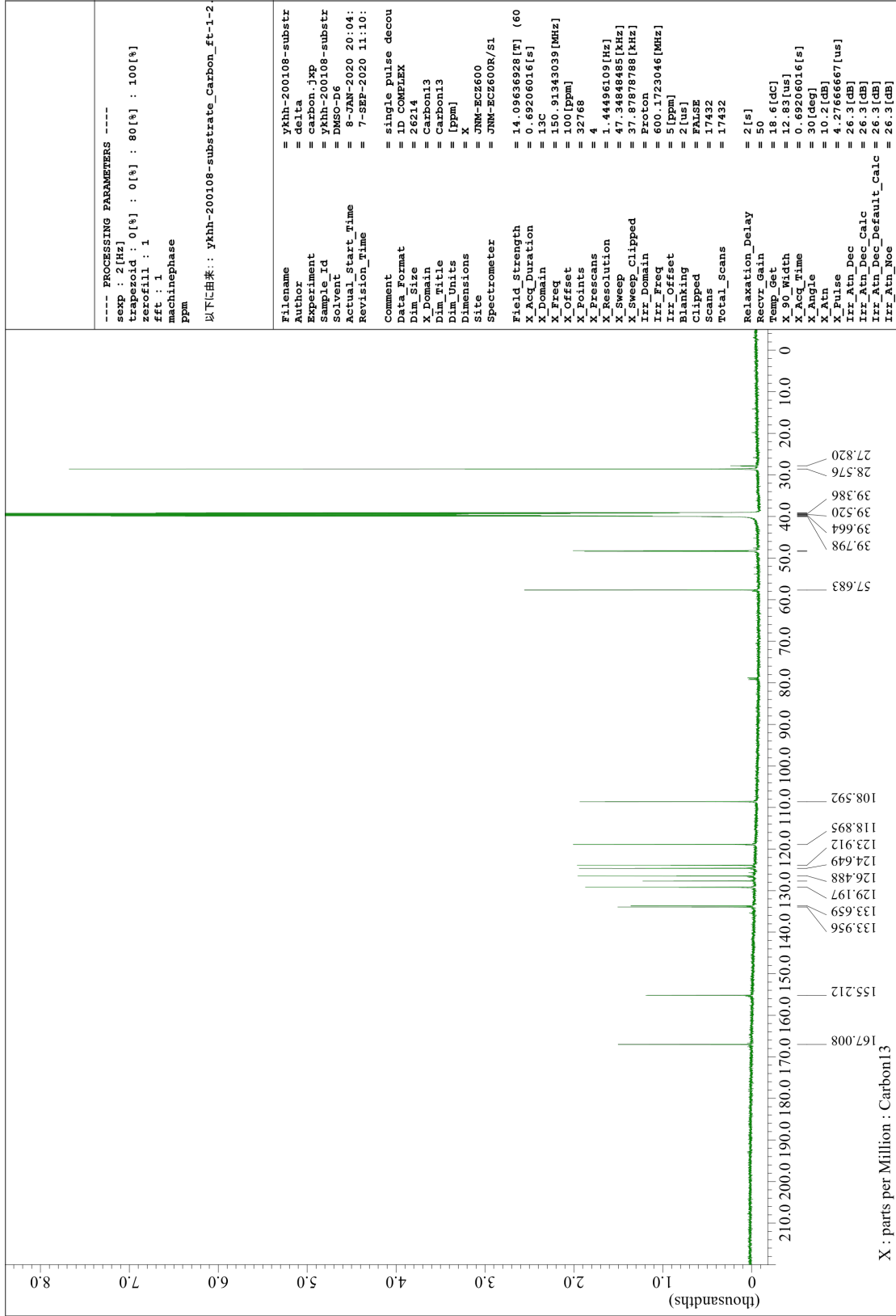


# Supporting Information

1a

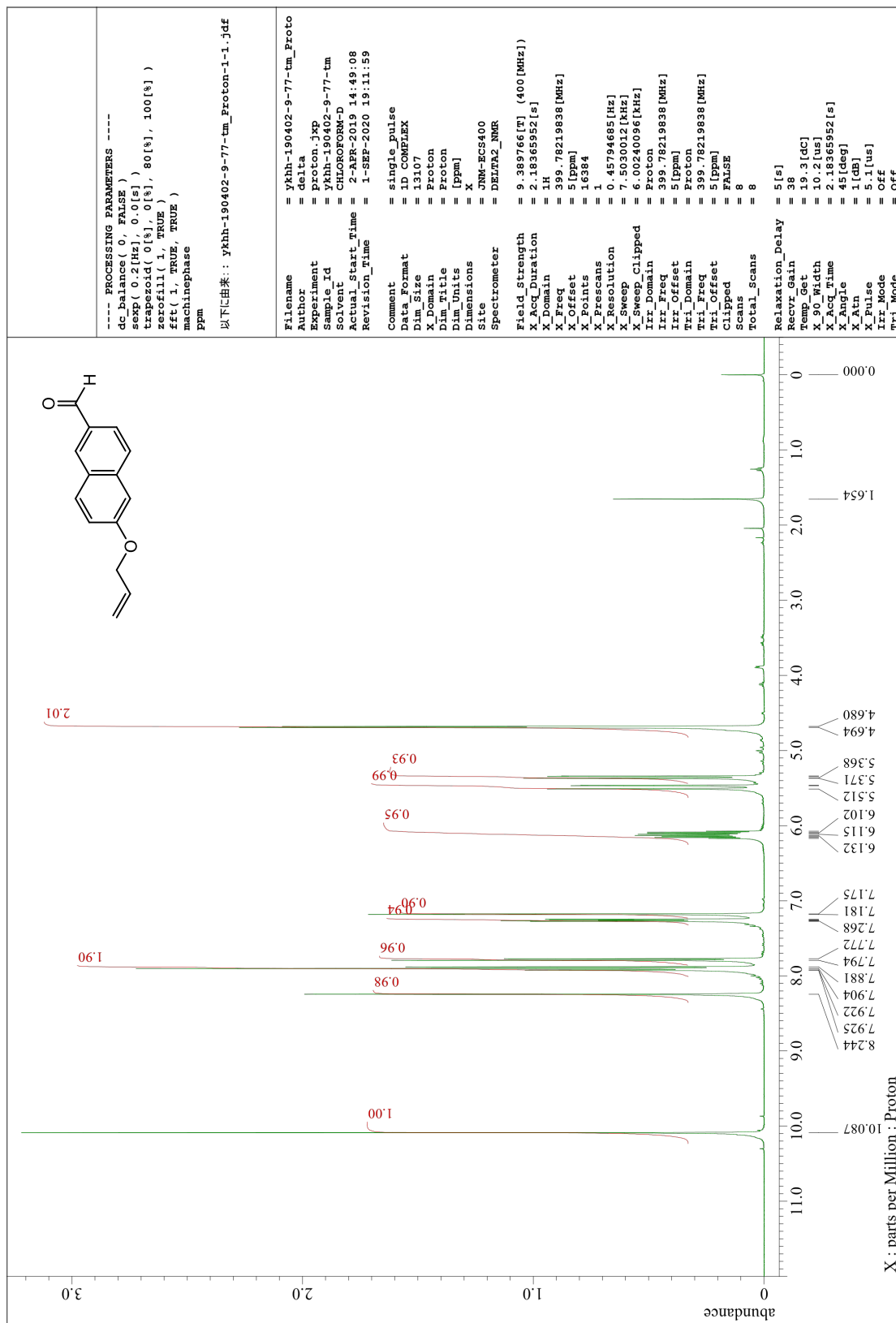


# Supporting Information



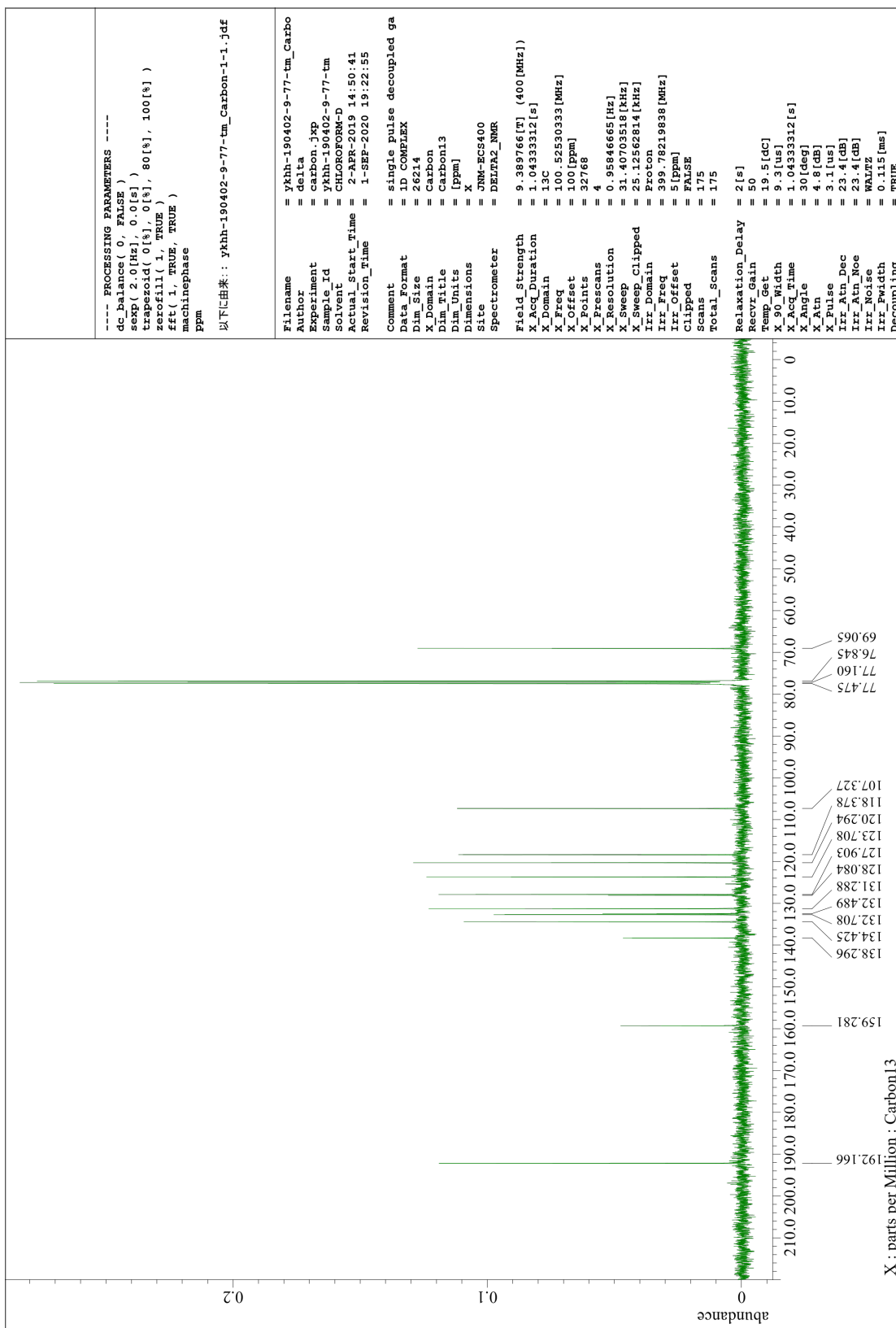
# Supporting Information

S1



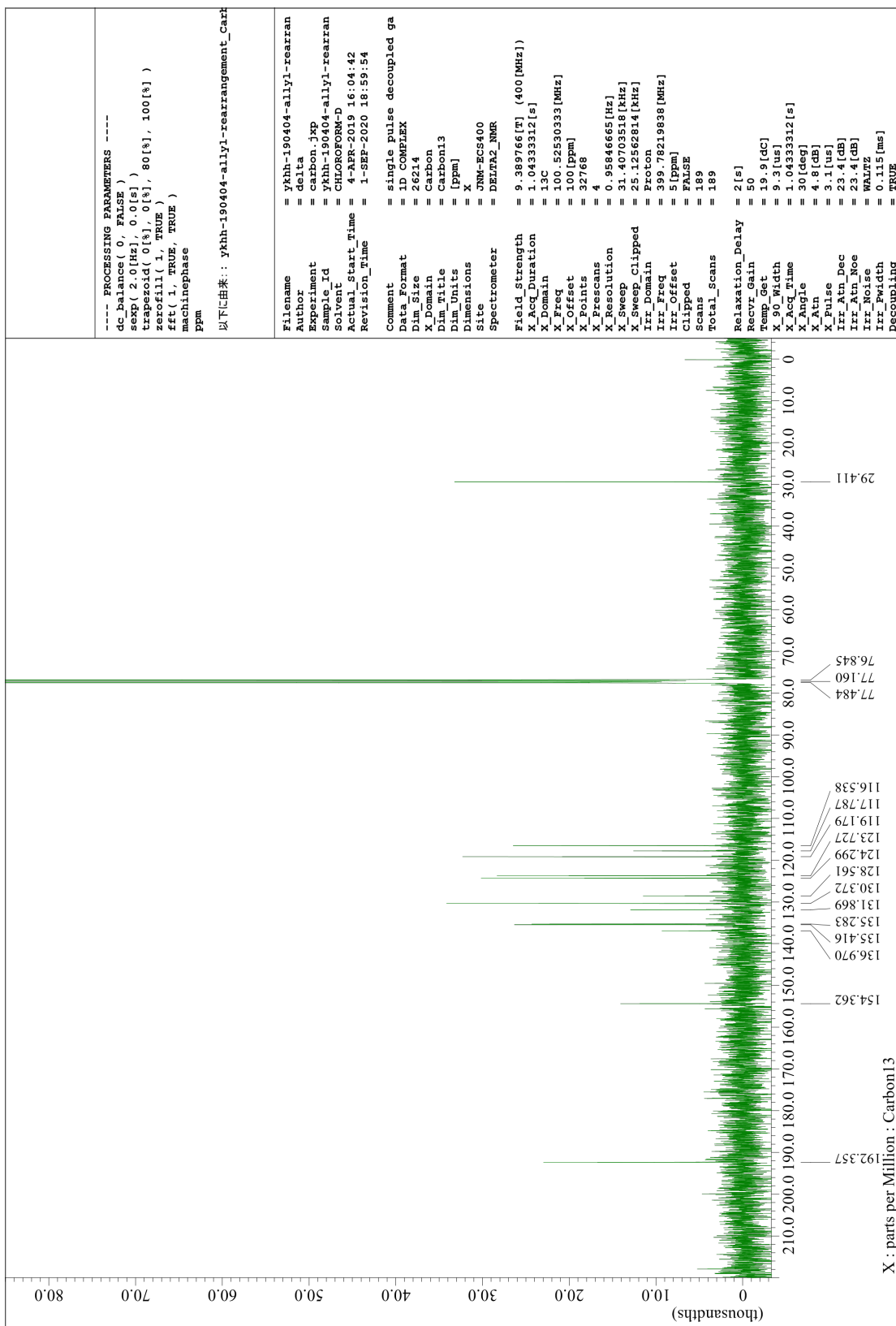
S141

# Supporting Information



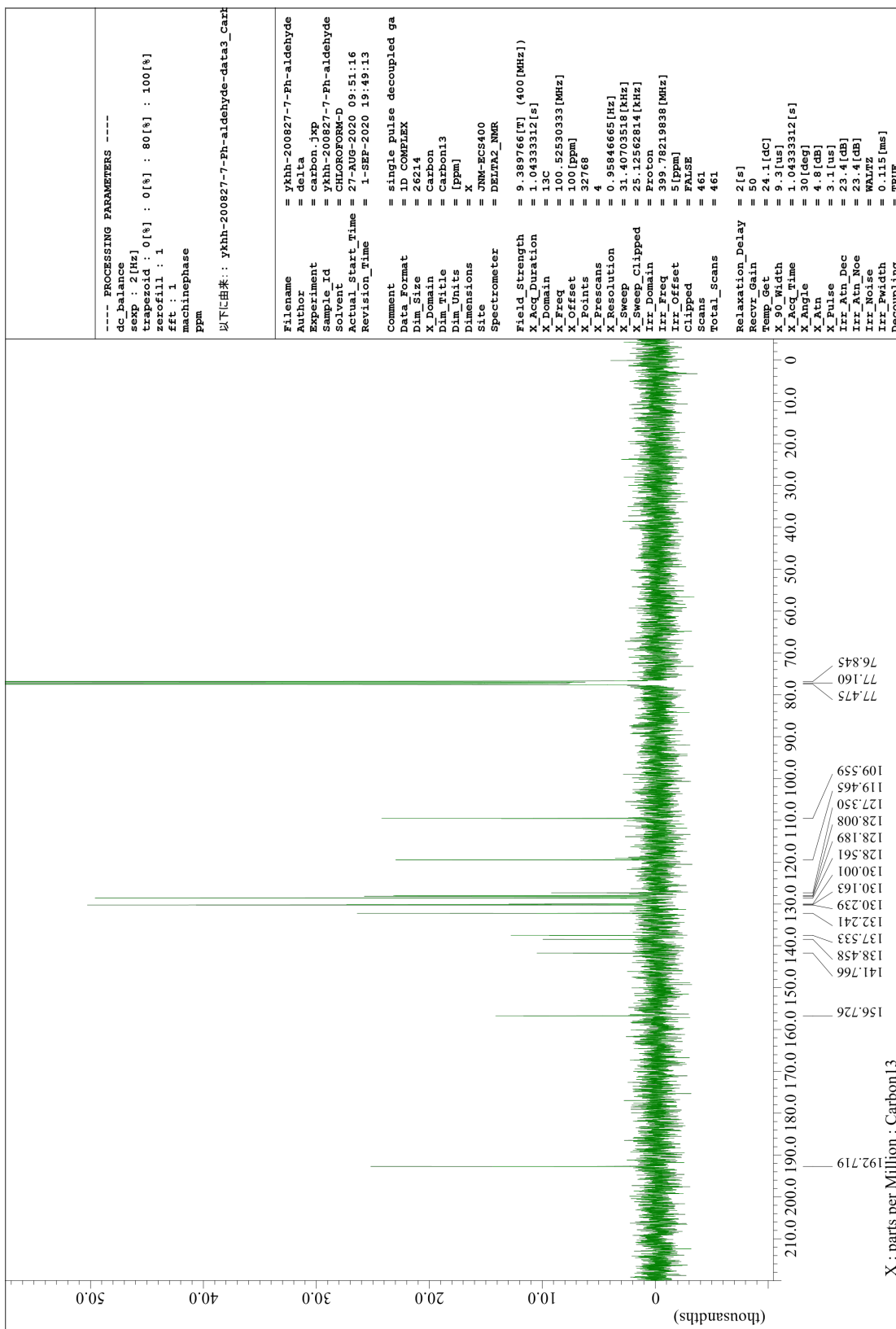


# Supporting Information



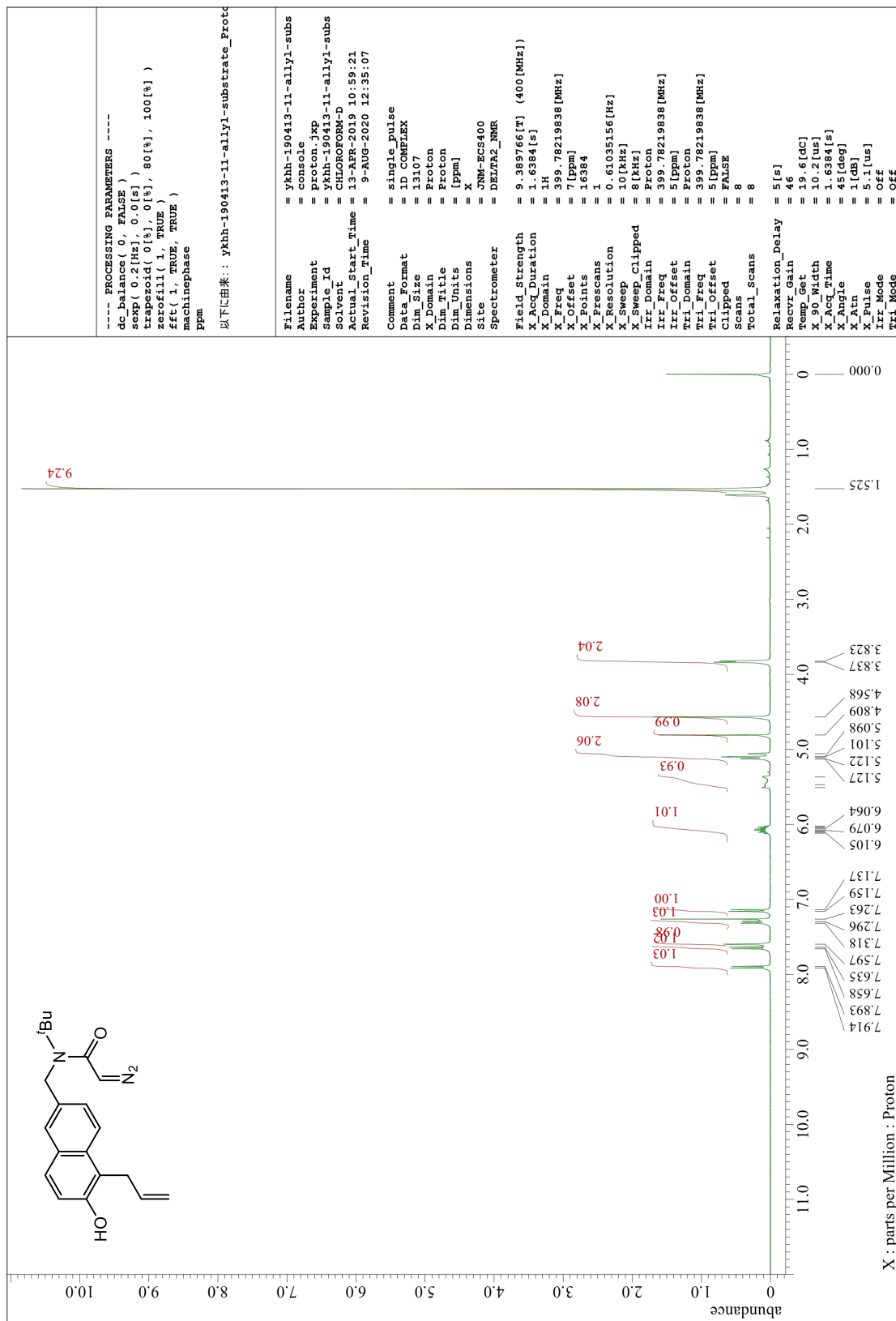


# Supporting Information

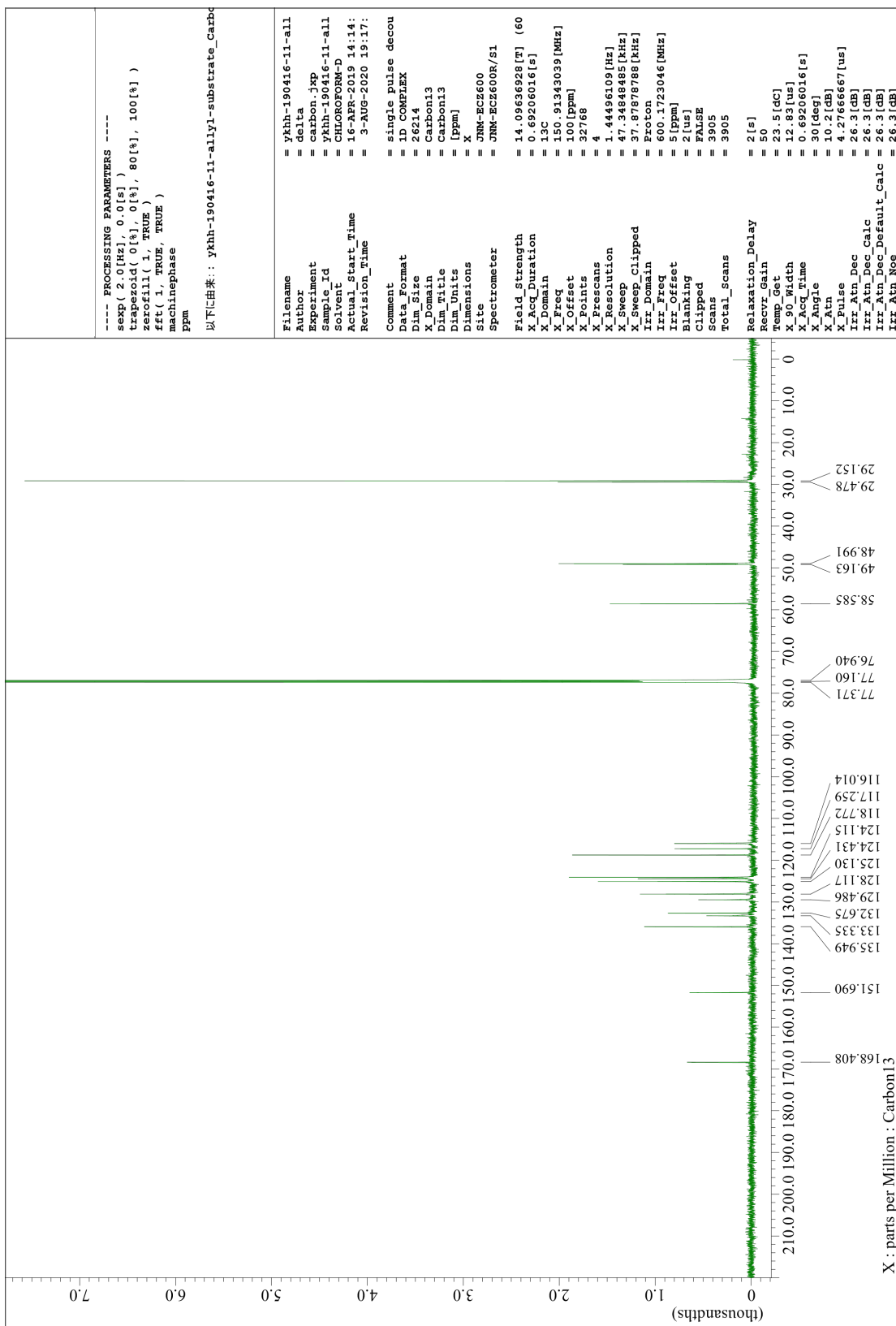


## Supporting Information

1b

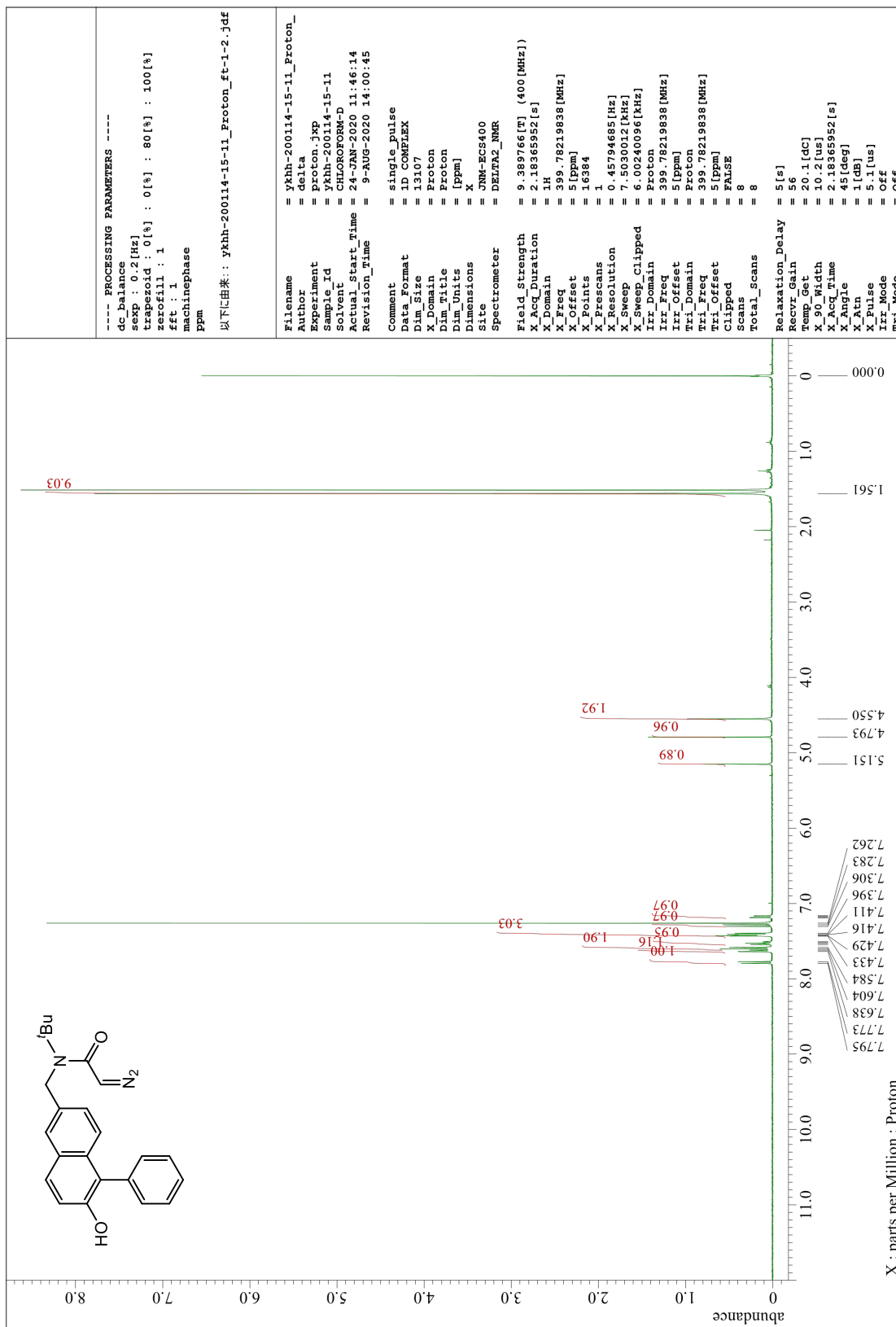


# Supporting Information

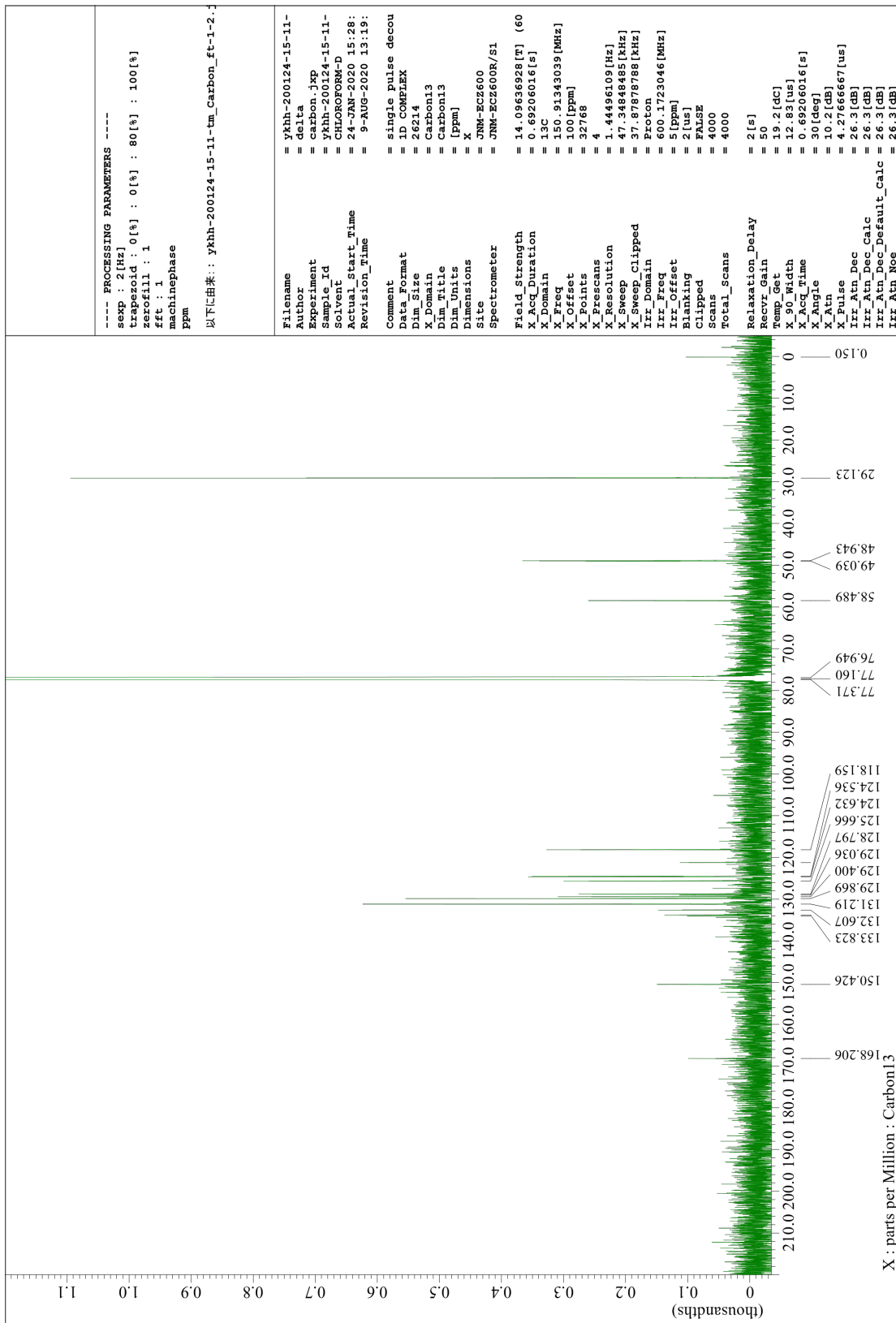


# Supporting Information

1c



# Supporting Information



```

---- PROCESSING PARAMETERS ----
sexp : 2 [Hz]
trapezoid : 0 [%] : 0 [%] : 80 [%] : 100 [%]
zerofill : 1
fft : 1
machinephase
Ppm
以下に由来: ykhh-200124-15-11-tm_Carbon_ft-1-2.
    
```

```

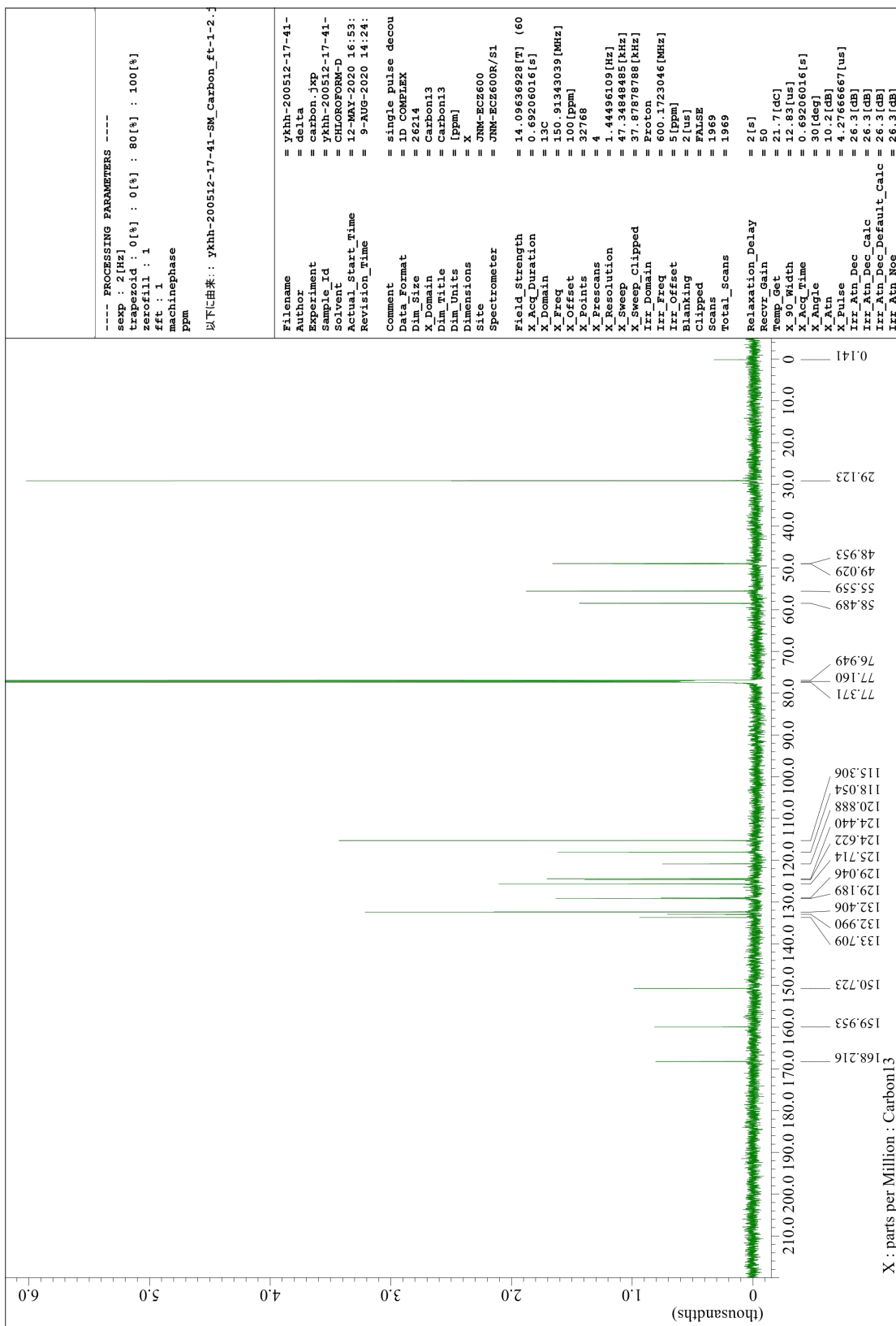
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Author = delta
Experiment = carbon_13p
Sample_Id = Ykhh200124-15-11-
Solvent = MUCROFOSM-D
Actual_Start_Time = 24-JAN-2020 15:28:
Revision_Time = 9-AUG-2020 13:13:
Comment = single pulse decou
Data_Format = 1D COMPLEX
Dim_Size = 26224
X_Domain = Carbon13
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECZ600
Spectrometer = JNM-ECZ600/S1
Field_Strength = 14.09636928 [T] (60
X_Acq_Duration = 1.69206016 [s]
X_F0 = 150.91343039 [MHz]
X_Offset = 100 [ppm]
X_Points = 32768
X_Frescans = 1
X_Resolution = 1.44486108 [Hz]
X_Sweep = 37.3464685 [MHz]
X_Sweep_Clippped = 37.87878788 [MHz]
Procop = 600.1723046 [MHz]
Irr_Domain = 5 [ppm]
Irr_Freq = 2 [us]
Irr_Offset = 4000
Blanking = FALSE
Clipped = 4000
Total_Scans = 2 [s]
Relaxation_Delay = 90
recvr_gain = 13.2 [dc]
Temp_Get = 12.83 [us]
X_F0_Width = 0.69206016 [s]
X_Acq_Time = 30 [deg]
X_Angle = 10.7 [db]
X_Atn = 4.2766667 [us]
Irr_Atn_Dec = 26.3 [db]
Irr_Atn_Dec_Calc = 26.3 [db]
Irr_Atn_Dec_Default_Calc = 26.3 [db]
Irr_Atn_Noise = 26.3 [db]
    
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# Supporting Information

1d

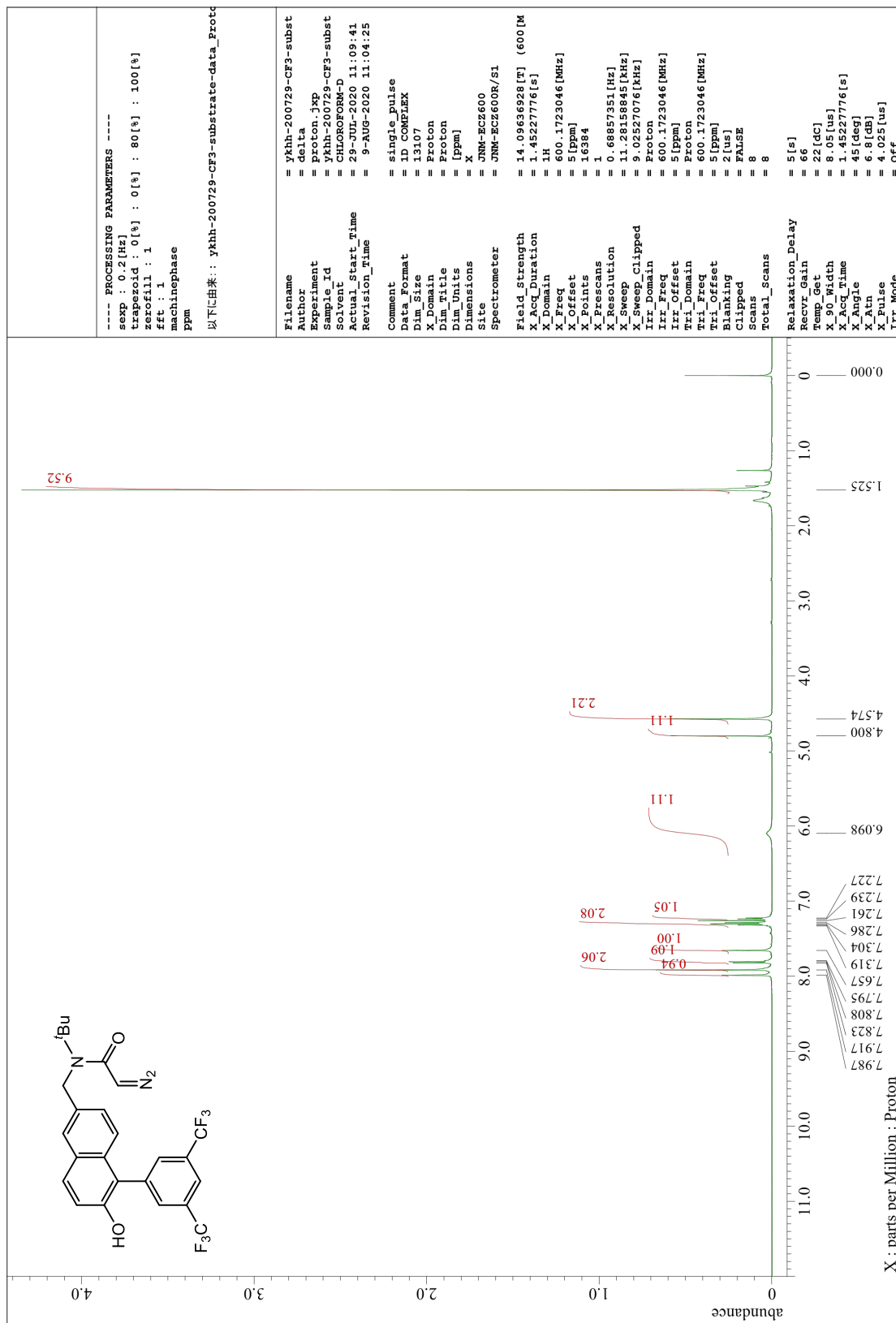


# Supporting Information

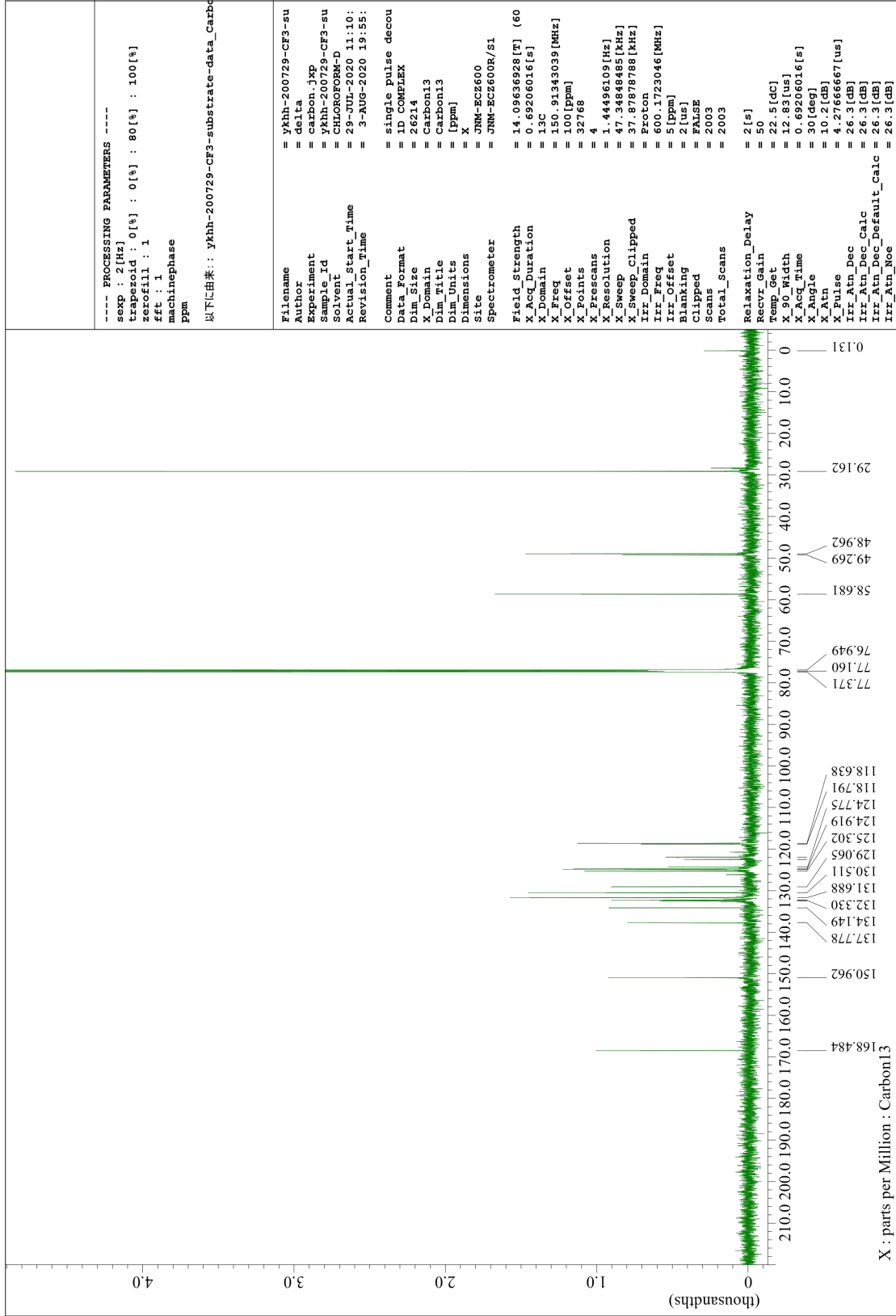


# Supporting Information

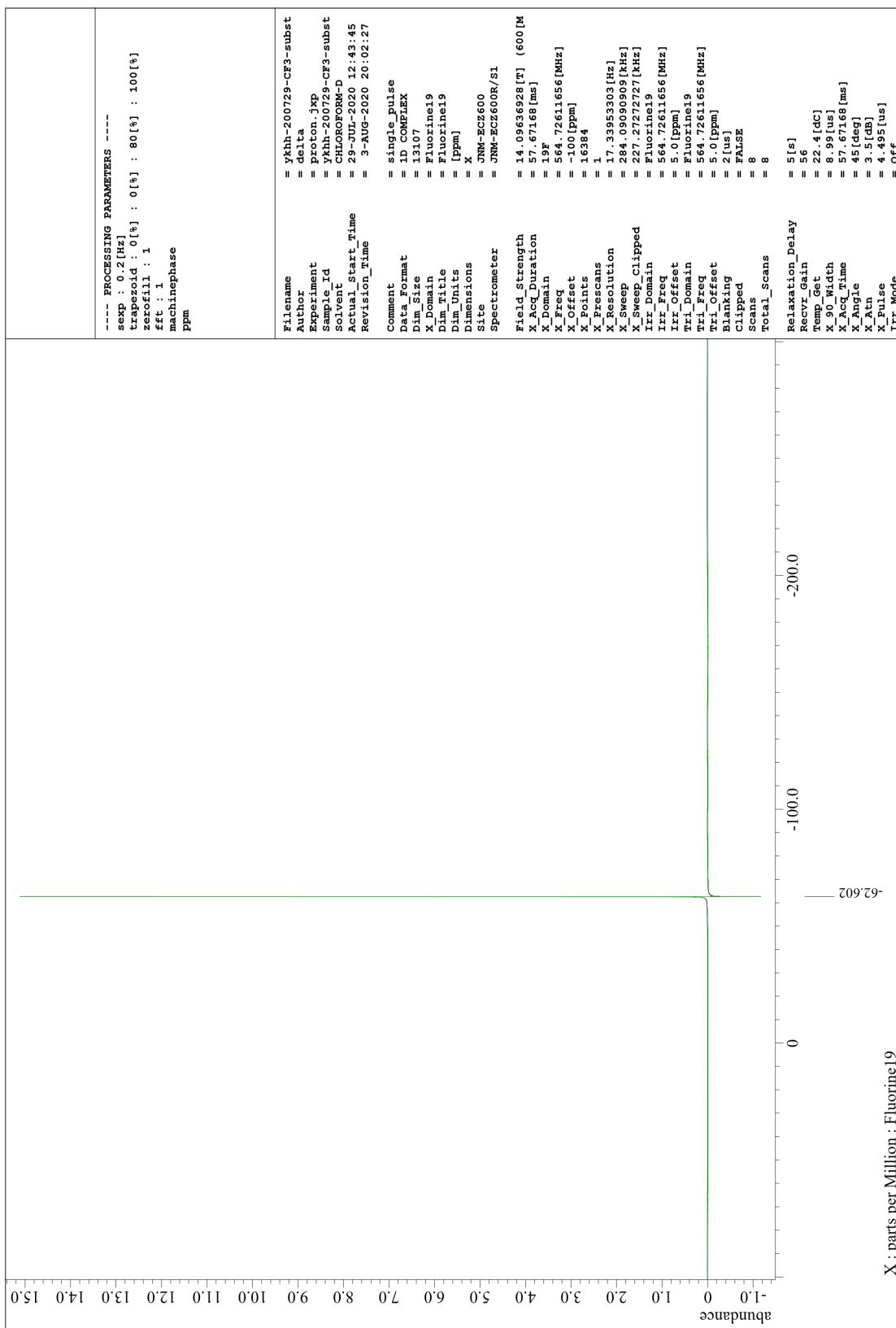
1e



# Supporting Information

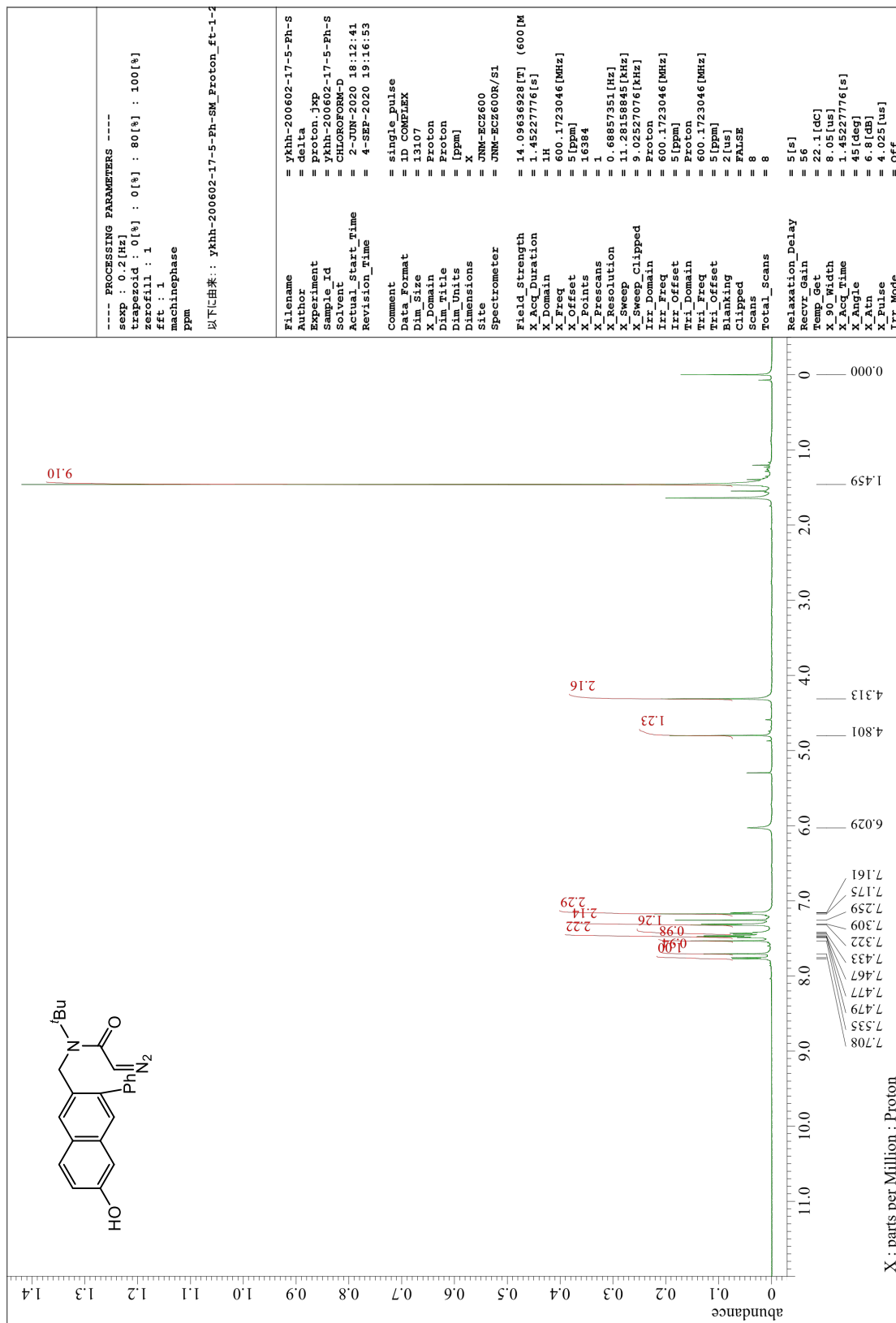


# Supporting Information

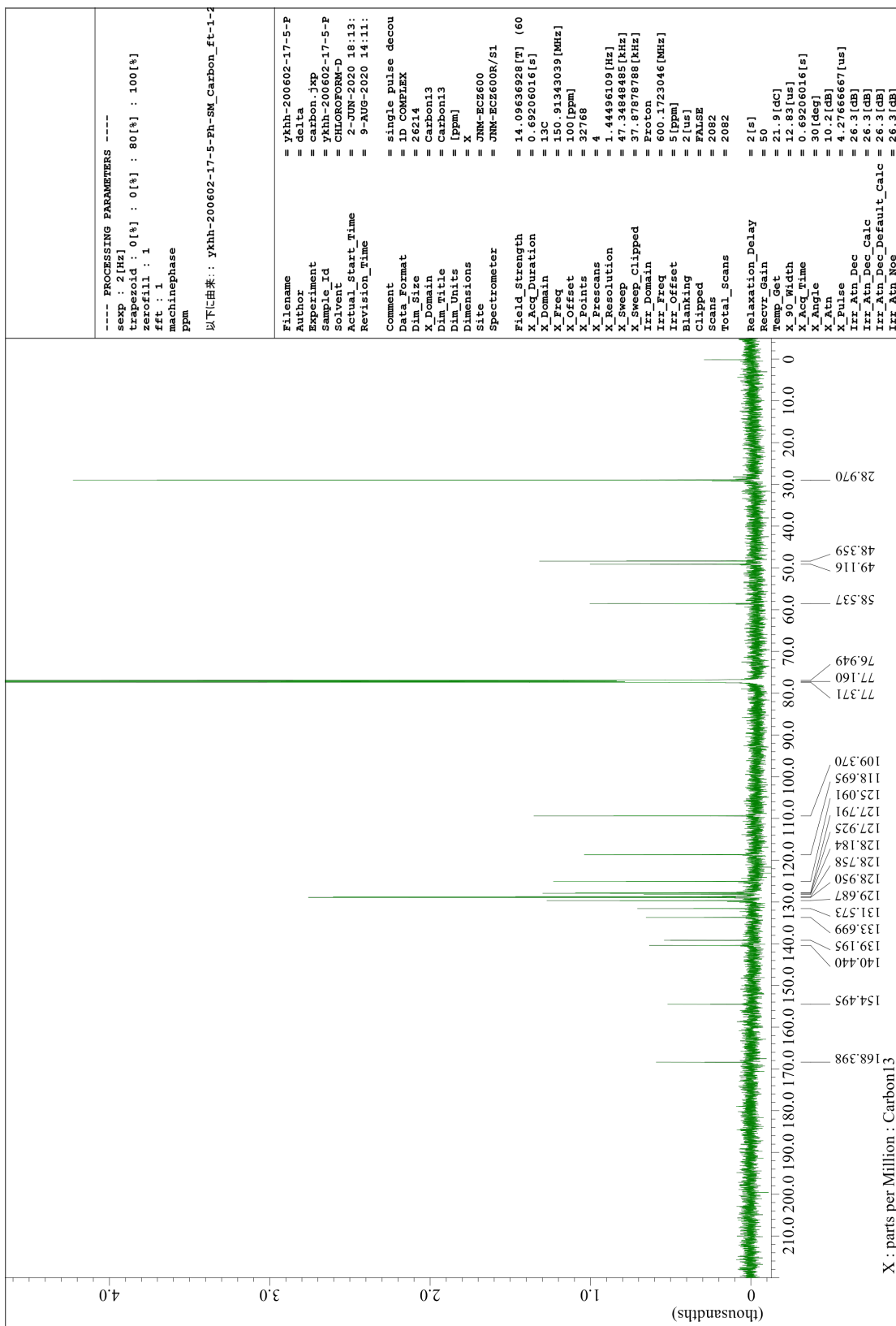


# Supporting Information

1f

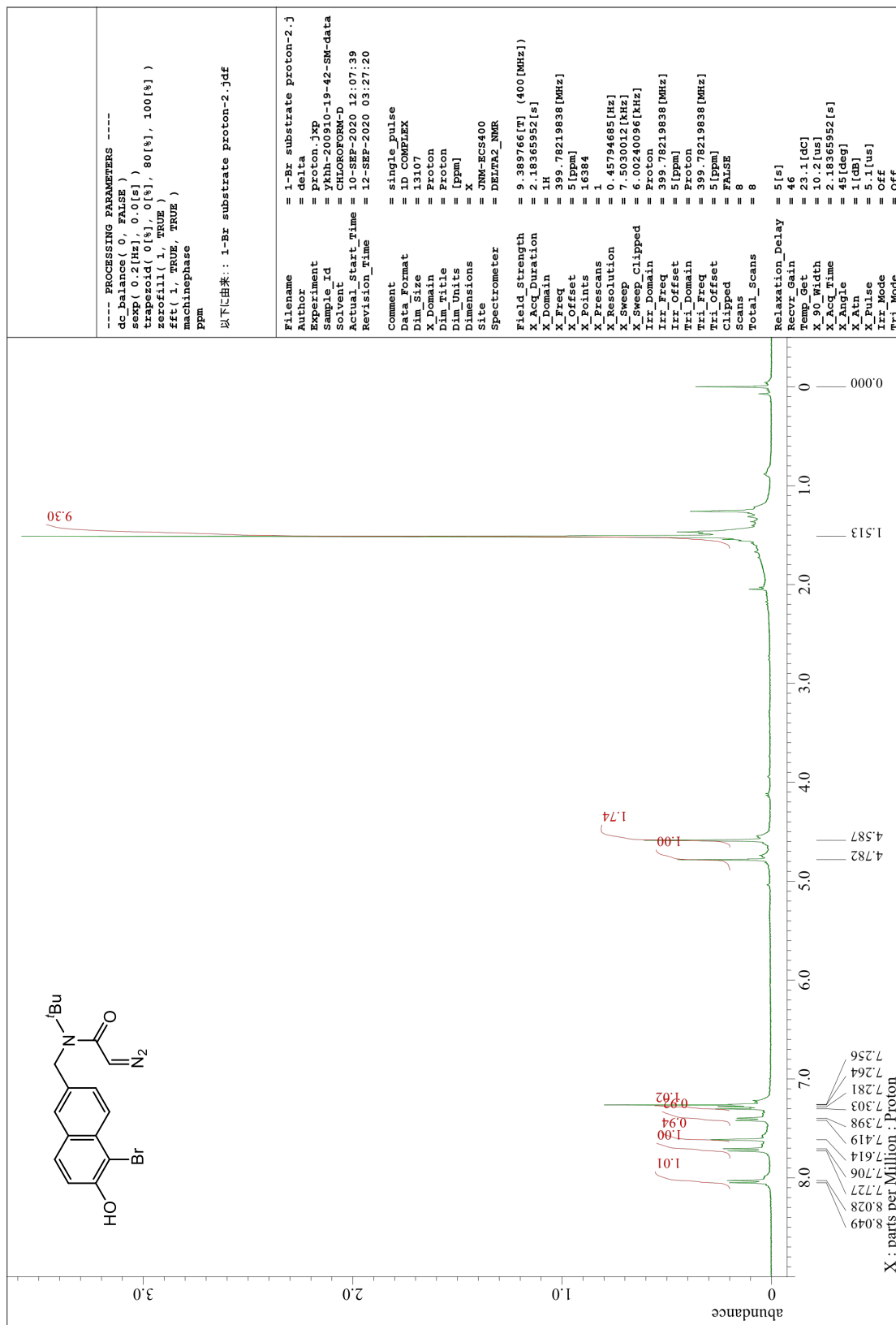


# Supporting Information

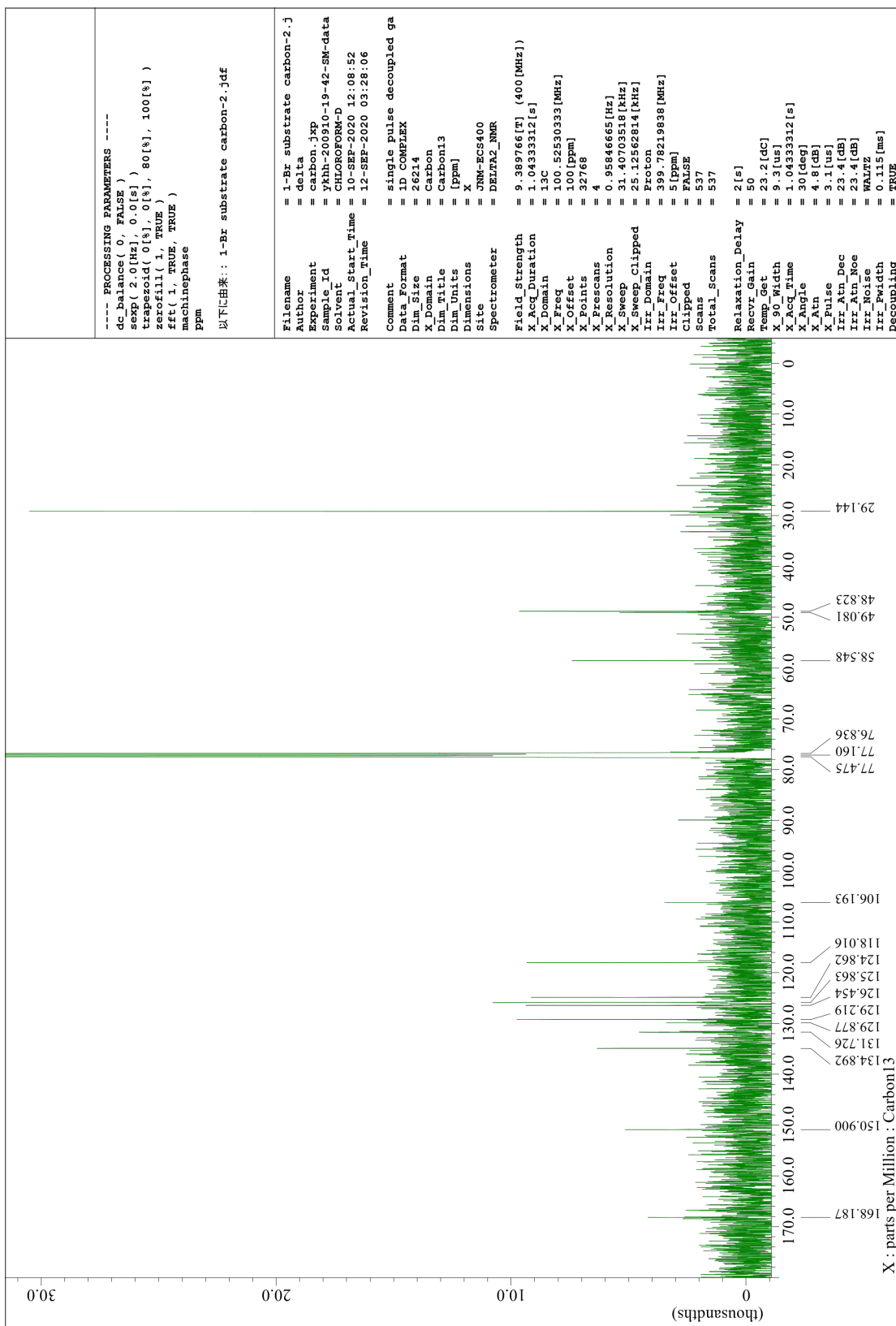


# Supporting Information

1g

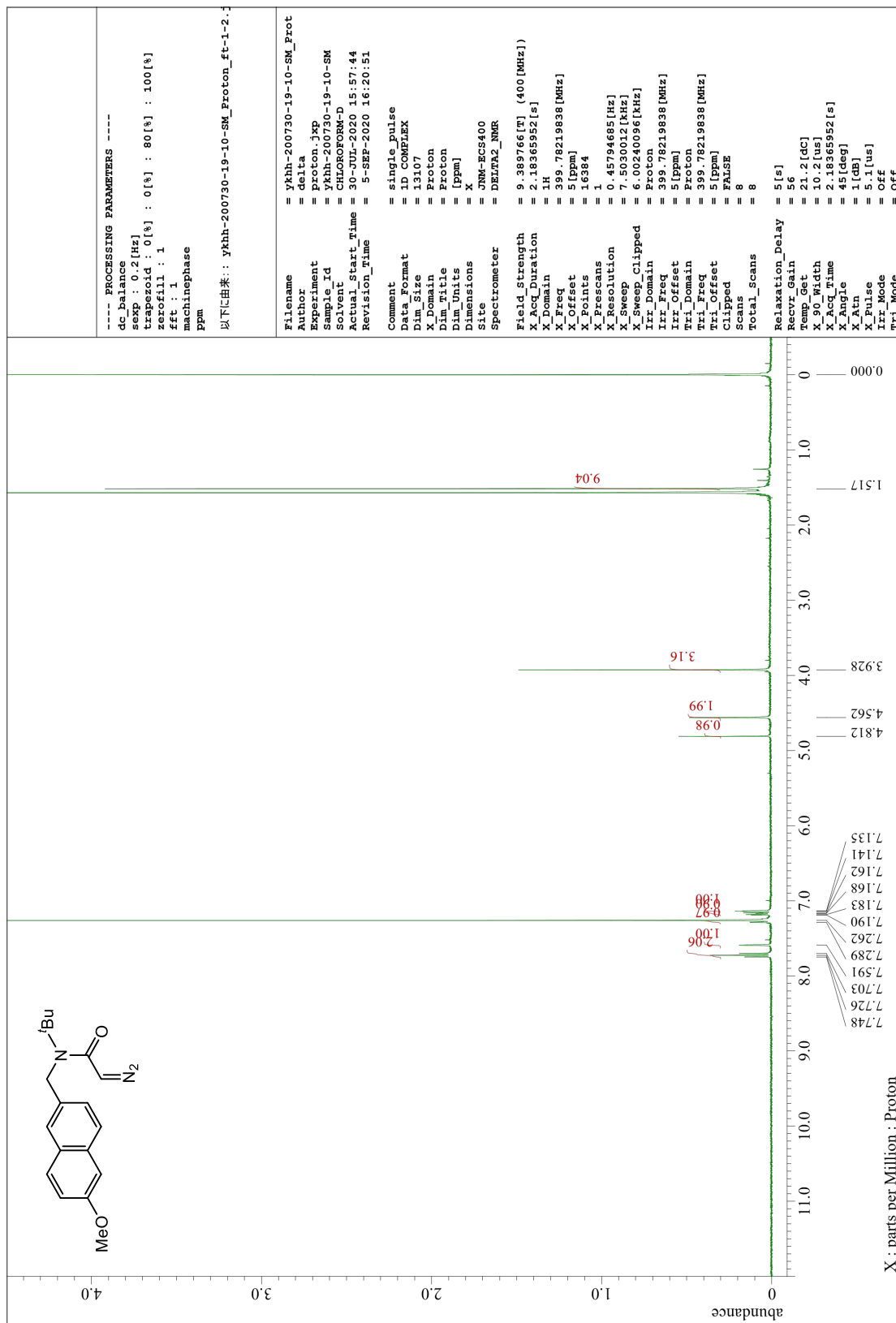


# Supporting Information

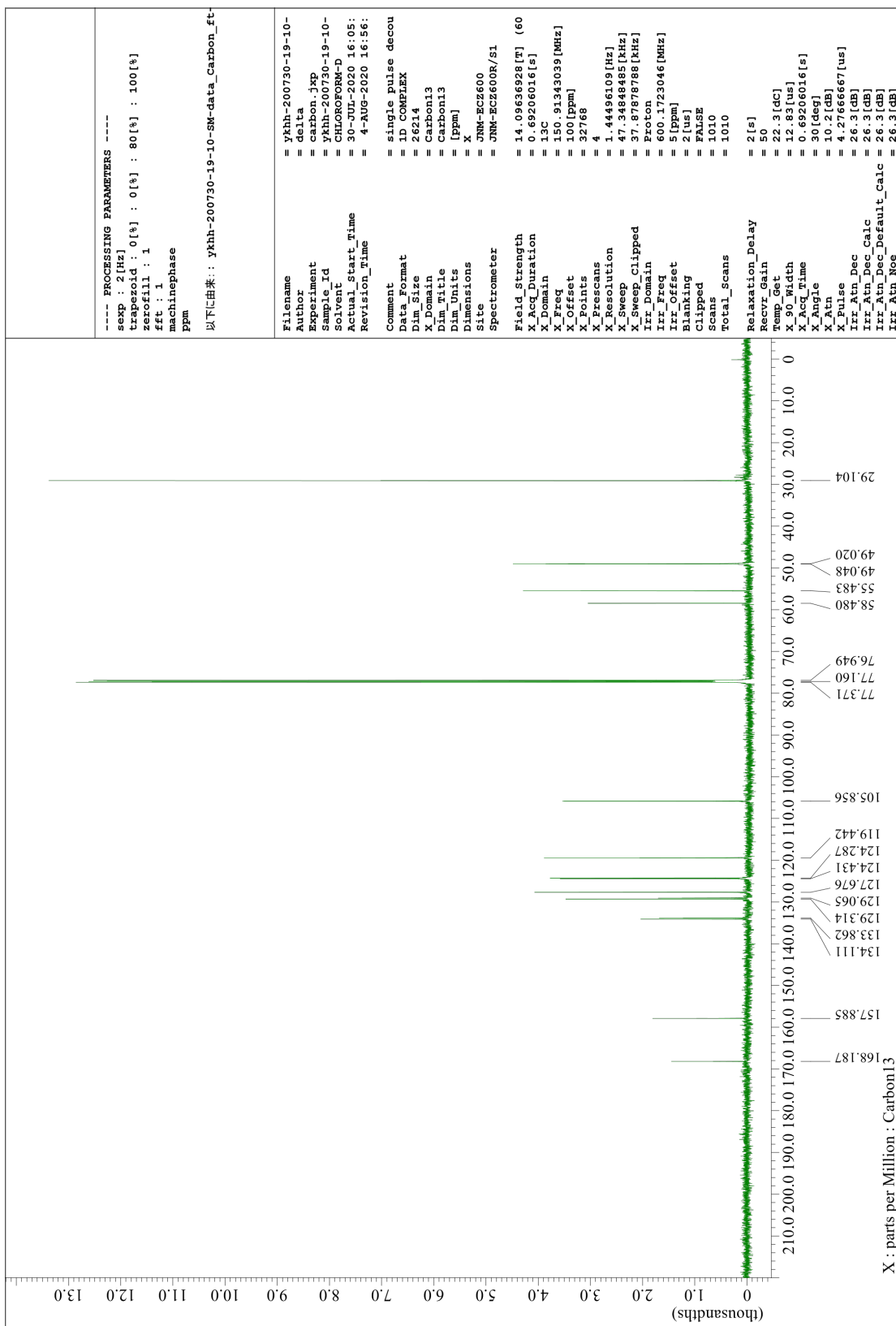


# Supporting Information

1h

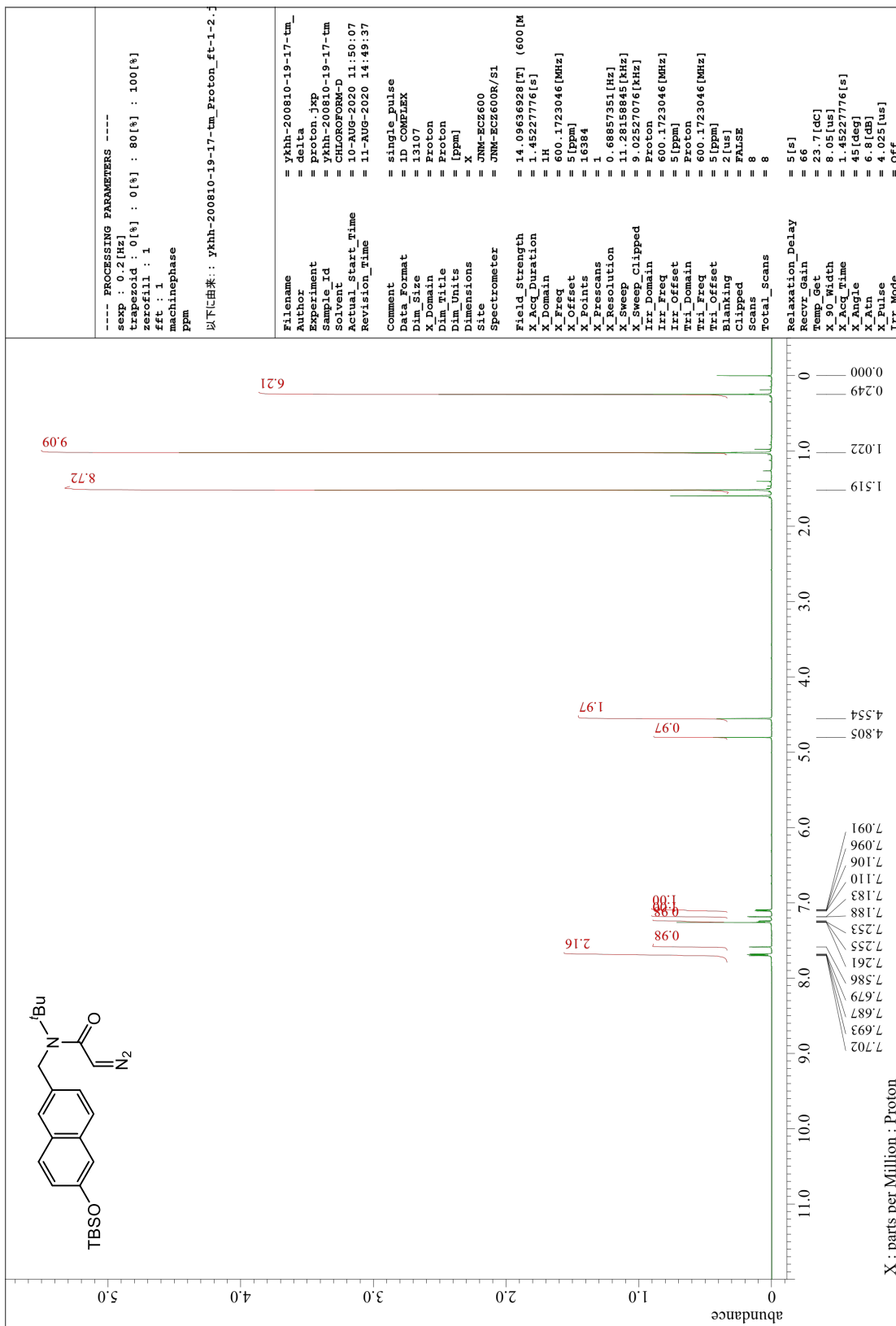


# Supporting Information



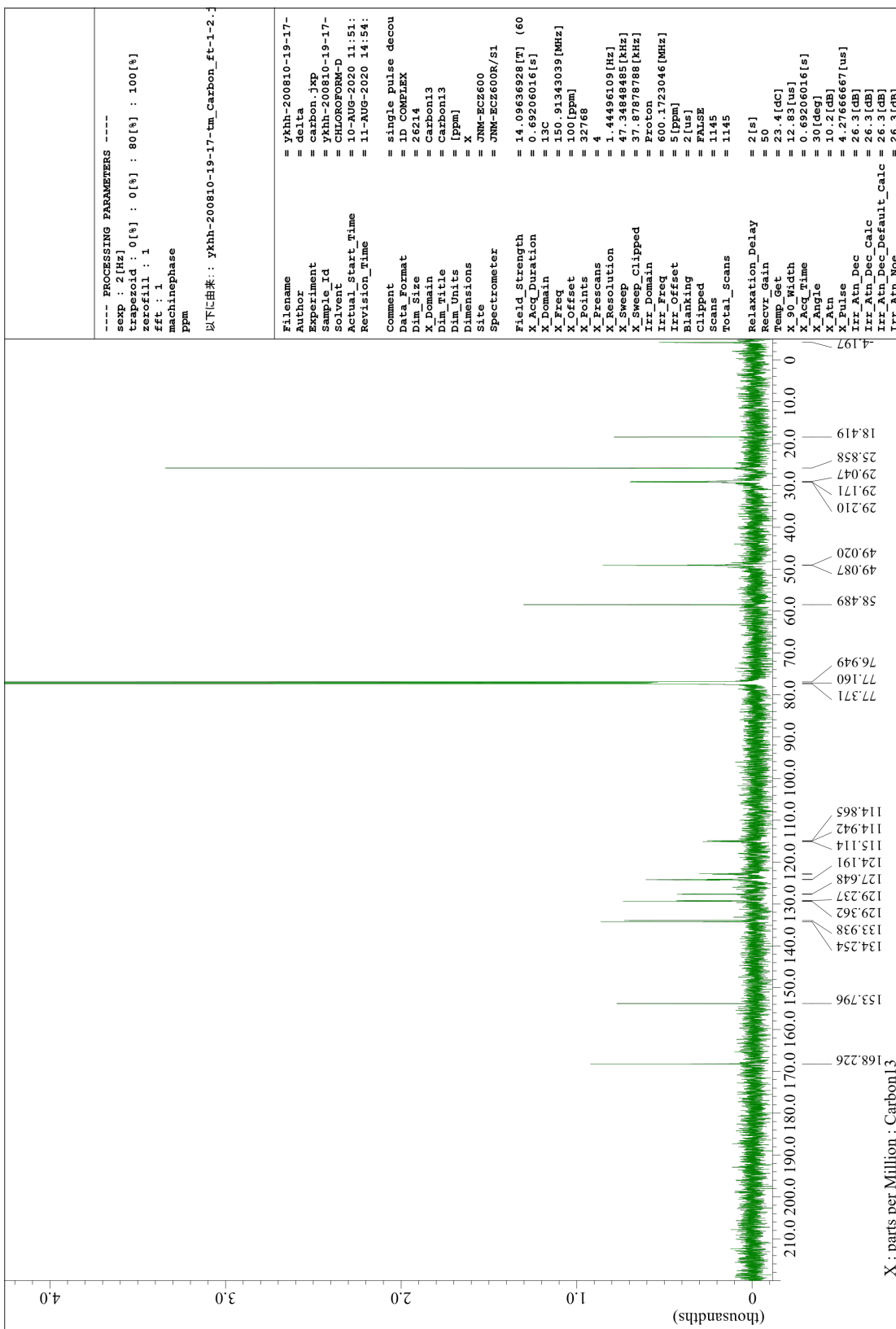
# Supporting Information

1i



S162

# Supporting Information



## Supporting Information

### 8. [References](#)

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