

Supplementary Material

Diastereoselective photochemical radical addition of a cyclic ether to olefins: addition of THF radicals to dialkyl maleates

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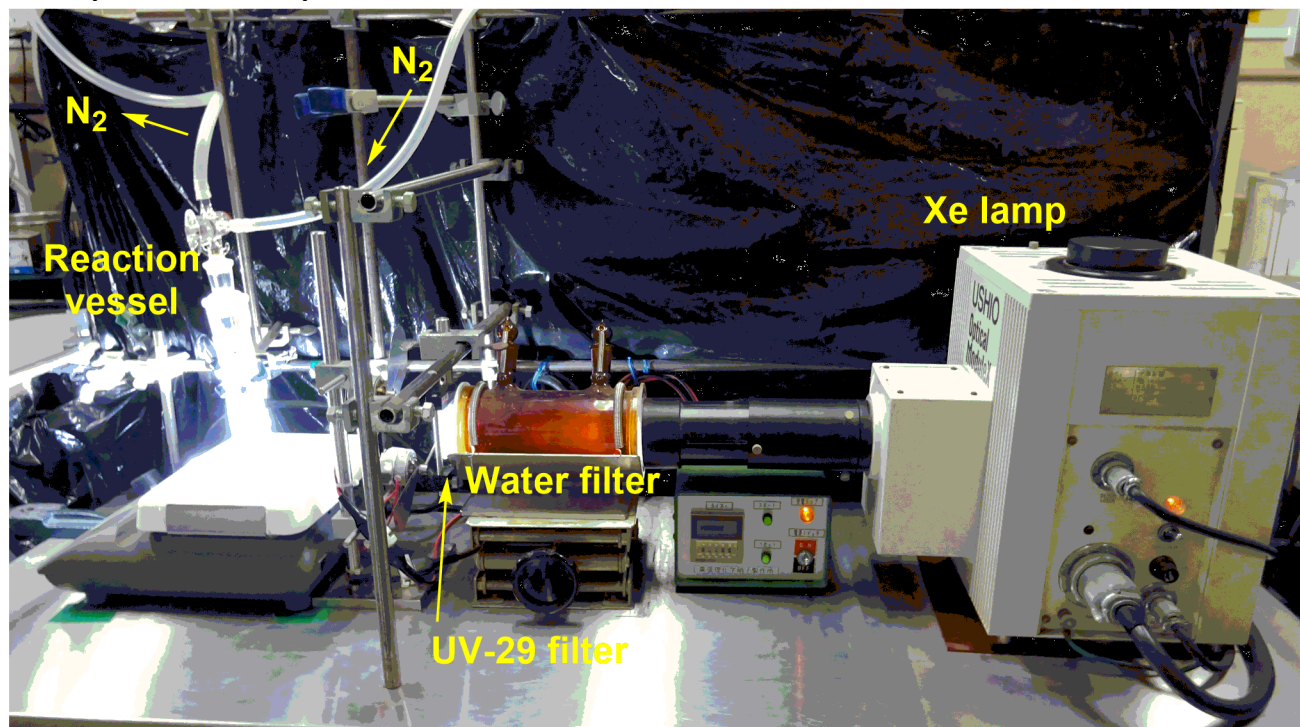
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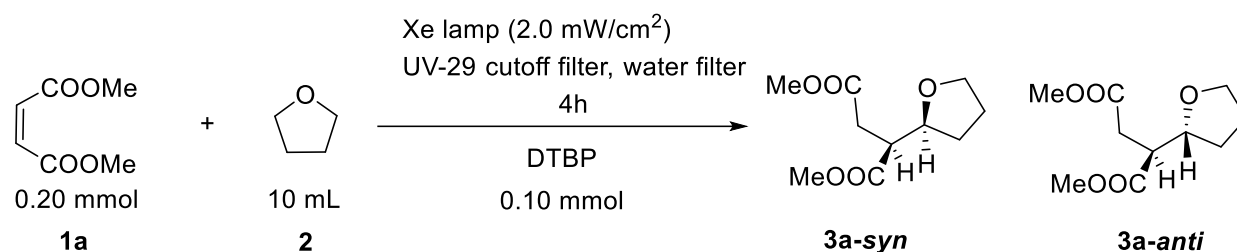
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1. Experimental

1.1. Experimental setup



1.2. Experimental details of the reactions in Table 1

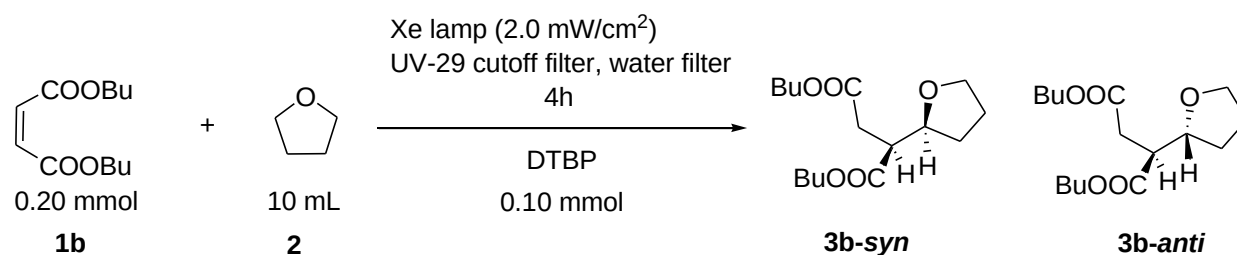
1.2.1. Entry 1: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (**3a-syn/anti**)^{S1-S3}

Run 1

Dimethyl maleate (**1a**, 28.87 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3a**: 100 % (*syn* / *anti* = 61 / 39) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a**, 28.79 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3a**: 95 % (*syn* / *anti* = 60 / 35) (conversion: 100 %) (NMR, CDCl₃).

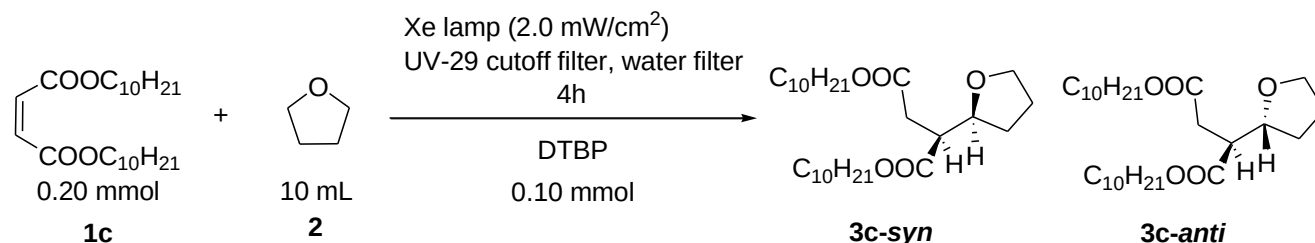
1.2.2. Entry 2: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dibutyl ester (**3b-syn/anti**)

Run 1

Dibutyl maleate (**1b**, 45.52 mg, 0.20 mmol) and DTBP (15.14 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3b**: 100 % (*syn* / *anti* = 64 / 36) (conversion: 100 %) (NMR, CDCl₃).

Run 2

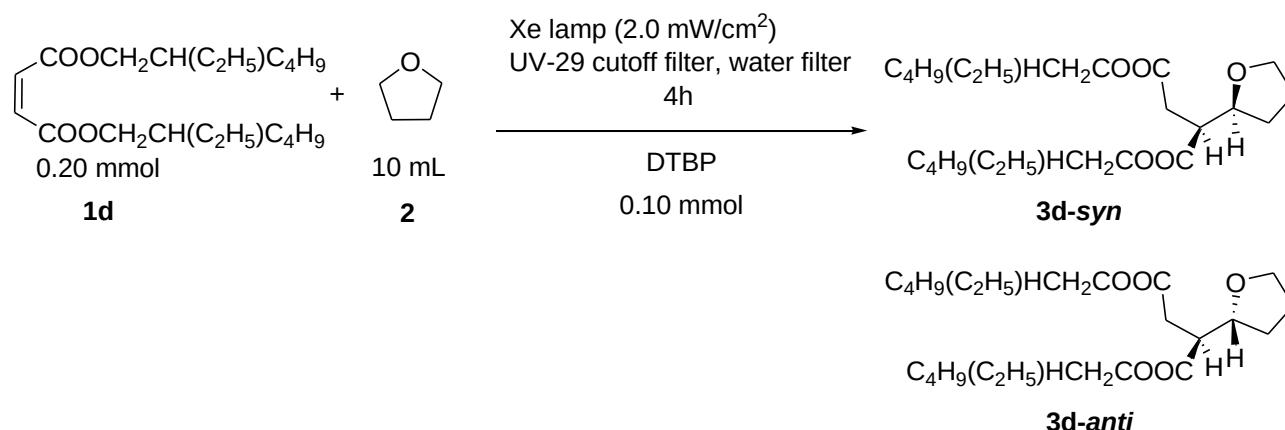
Dibutyl maleate (**1b**, 45.61 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3b**: 100 % (*syn* / *anti* = 65 / 35) (conversion: 100 %) (NMR, CDCl₃).

1.2.3. Entry 3: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-didecyl ester (3c-syn/anti**)****Run 1**

Didecyl maleate (**1c**, 79.08 mg, 0.20 mmol) and DTBP (14.86 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3c**: 86 % (*syn* / *anti* = 60 / 26) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Didecyl maleate (**1c**, 79.56 mg, 0.20 mmol) and DTBP (14.85 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3c**: 89 % (*syn* / *anti* = 60 / 29) (conversion: 100 %) (NMR, CDCl₃).

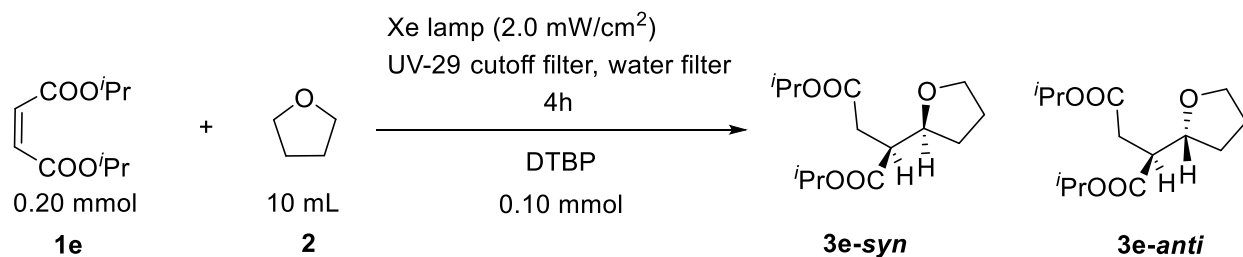
1.2.4. Entry 4: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-bis(2-ethylhexyl) ester (3d-syn/anti**)****Run 1**

Bis (2-ethylhexyl) maleate (**1d**, 68.07 mg, 0.20 mmol) and DTBP (14.79 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3d**: 99 % (*syn* / *anti* = 67 / 32) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Bis (2-ethylhexyl) maleate (**1d**, 68.18 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3d**: 96 % (*syn* / *anti* = 62 / 34) (conversion: 100 %) (NMR, CDCl₃).

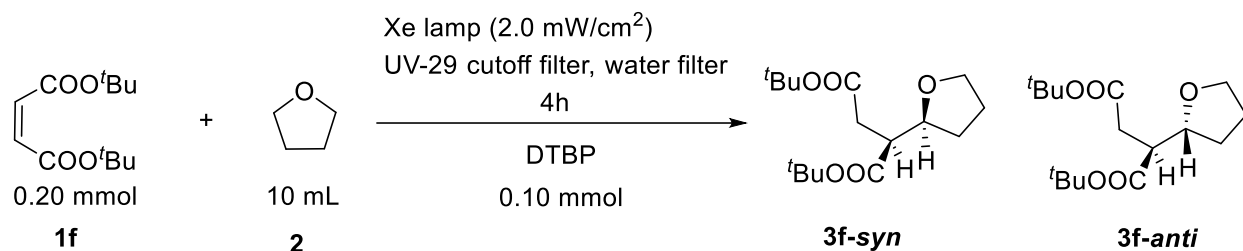
1.2.5. Entry 5: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-diisopropyl ester (3e-syn/anti**)**^{S3}

**Run 1**

Diisopropyl maleate (**1e**, 40.32 mg, 0.20 mmol) and DTBP (14.60 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3e**: 91 % (*syn* / *anti* = 61 / 30) (conversion: 100 %) (NMR, CDCl₃).

Run 2

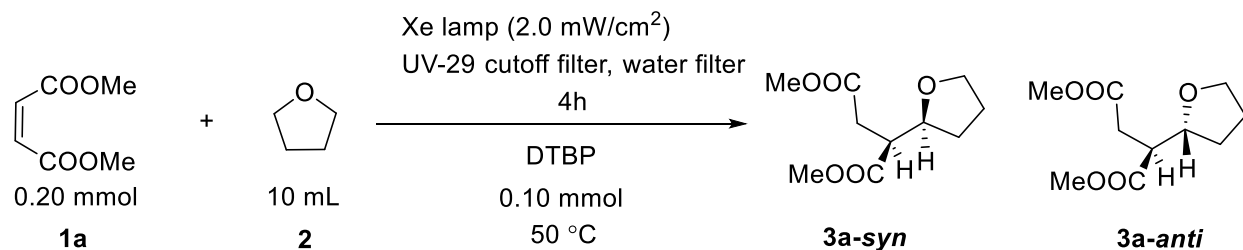
Diisopropyl maleate (**1e**, 68.07 mg, 0.20 mmol) and DTBP (14.79 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3e**: 96 % (*syn* / *anti* = 64 / 32) (conversion: 100 %) (NMR, CDCl₃).

1.2.6. Entry 6: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4- di-*tert*-butyl ester (3f-syn/anti**)****Run 1**

Di-*tert*-butyl maleate (**1f**, 45.50 mg, 0.20 mmol) and DTBP (14.51 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3f**: 96 % (*syn* / *anti* = 67 / 29) (conversion: 100 %) (NMR, CDCl₃).

Run 2

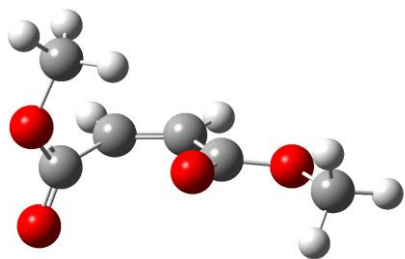
Di-*tert*-butyl maleate (**1f**, 45.59 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3f**: 96 % (*syn* / *anti* = 67 / 29) (conversion: 100 %) (NMR, CDCl₃).

1.3. Reaction of 1a and 2 at 50 °C (3a-cis-syn/anti**)^{S1-S3}**

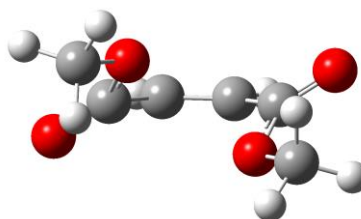
Dimethyl maleate (**1a**, 28.84 mg, 0.20 mmol) and DTBP (14.56 mg, 0.10 mmol) in THF (**2**, 10 mL). Irradiation time: 4h. Irradiation temperature: 50 °C. Yield of **3a**: 100 % (*syn* / *anti* = 61 / 38) (conversion: 100 %) (NMR, CDCl₃).

References

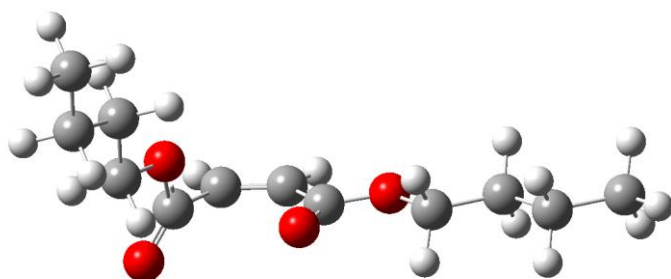
- S1. Hayakawa, M.; Shimizu, R.; Omori, H.; Shiota, H.; Uchida, K.; Mashimo, H.; Xu, H.; Yamada, R.; Niino, S.; Wakame, Y.; Liu, C.; Aoyama, T.; Ouchi, A., *Tetrahedron*, **2020**, 76, 131557.
- S2. Rohe, S.; Morris, A. O.; McCallum, T.; Barriault, L., *Angew. Chem. Int. Ed.*, **2018**, 57, 15664–15669.
- S3. Papadopoulos, G. N.; Kokotou, M. G.; Spiliopoulou, N.; Nikitas, N. F.; Voutyritsa, E.; Tzaras, D. I.; Kaplaneris, N.; Kokotos, C. G., *ChemSusChem*, **2020**, 13, 5934–5944.

2. Calculated stable conformers and energies of maleic acid and its dialkyl esters. ^{S4, S5}

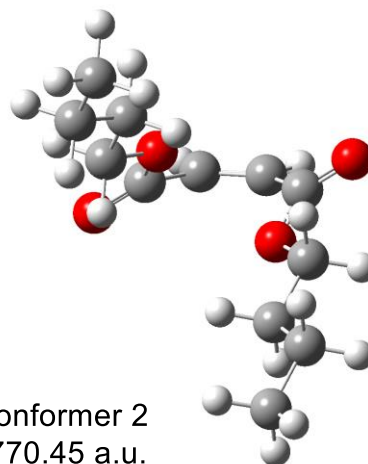
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-534.50 a.u.



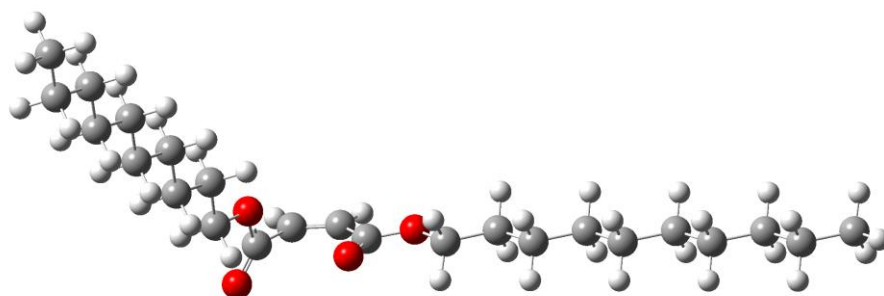
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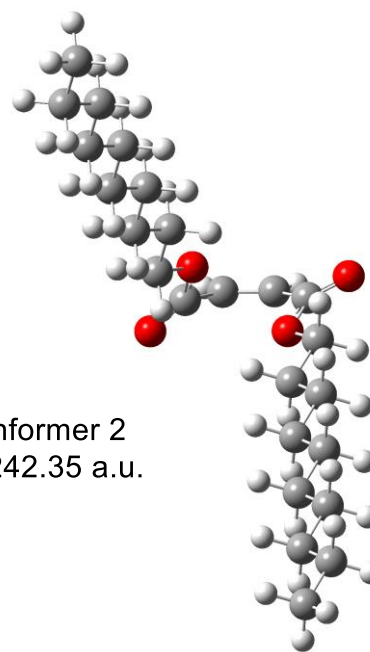
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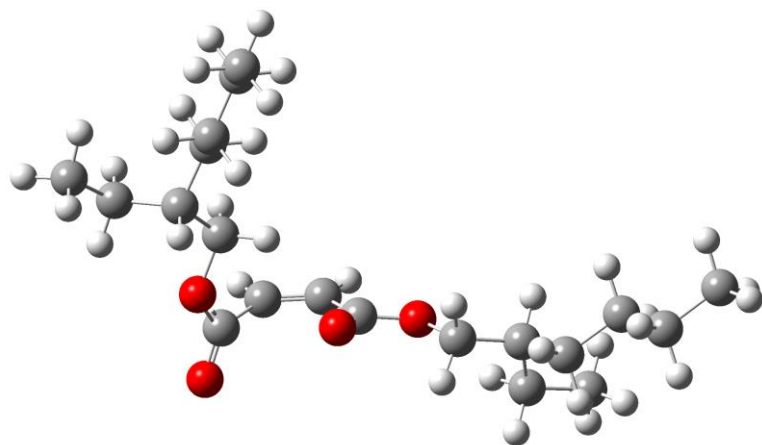
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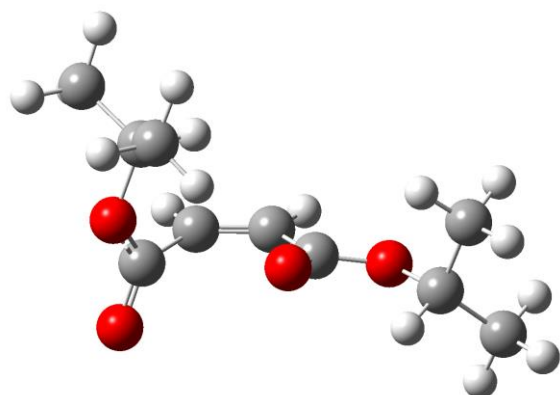
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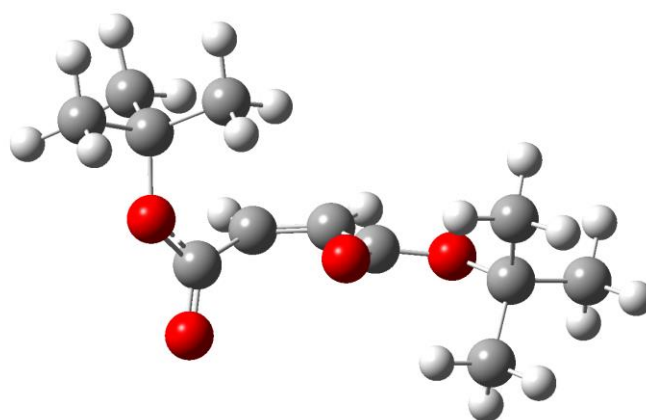
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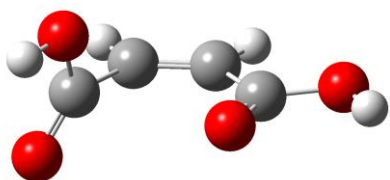
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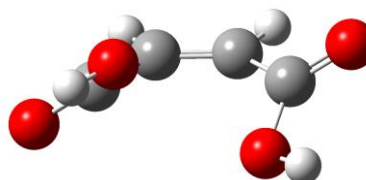
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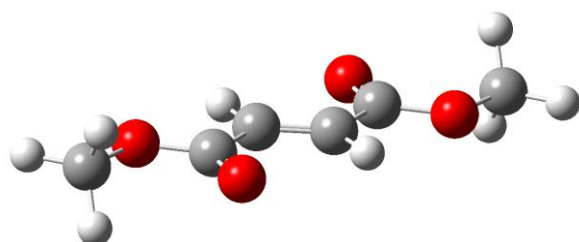
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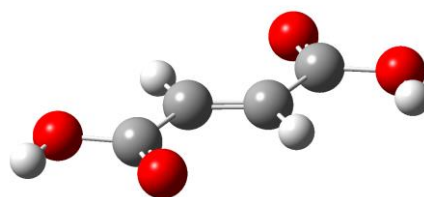
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-455.88 a.u.



1g conformer 2
-455.88 a.u.



1h -534.51 a.u.

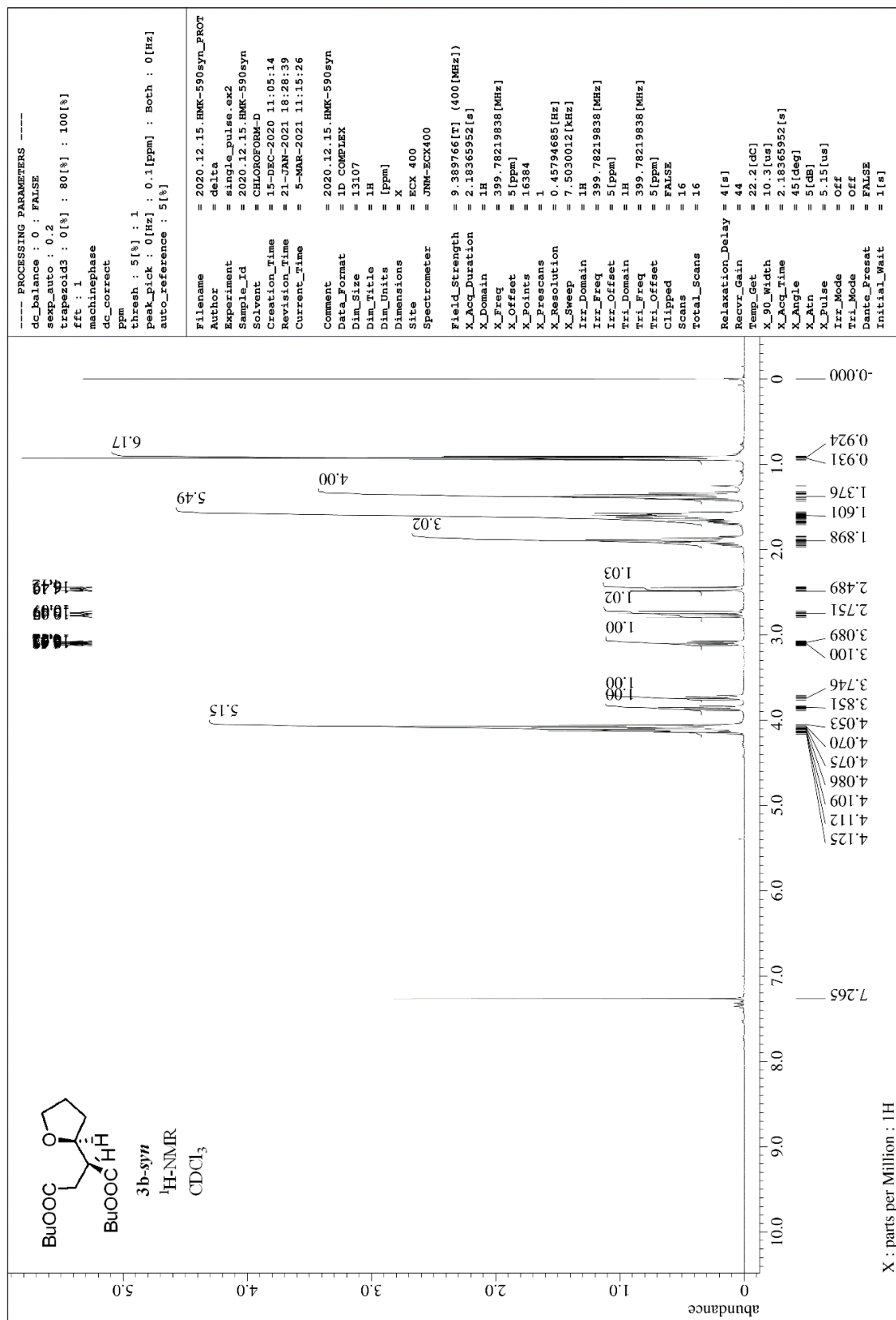


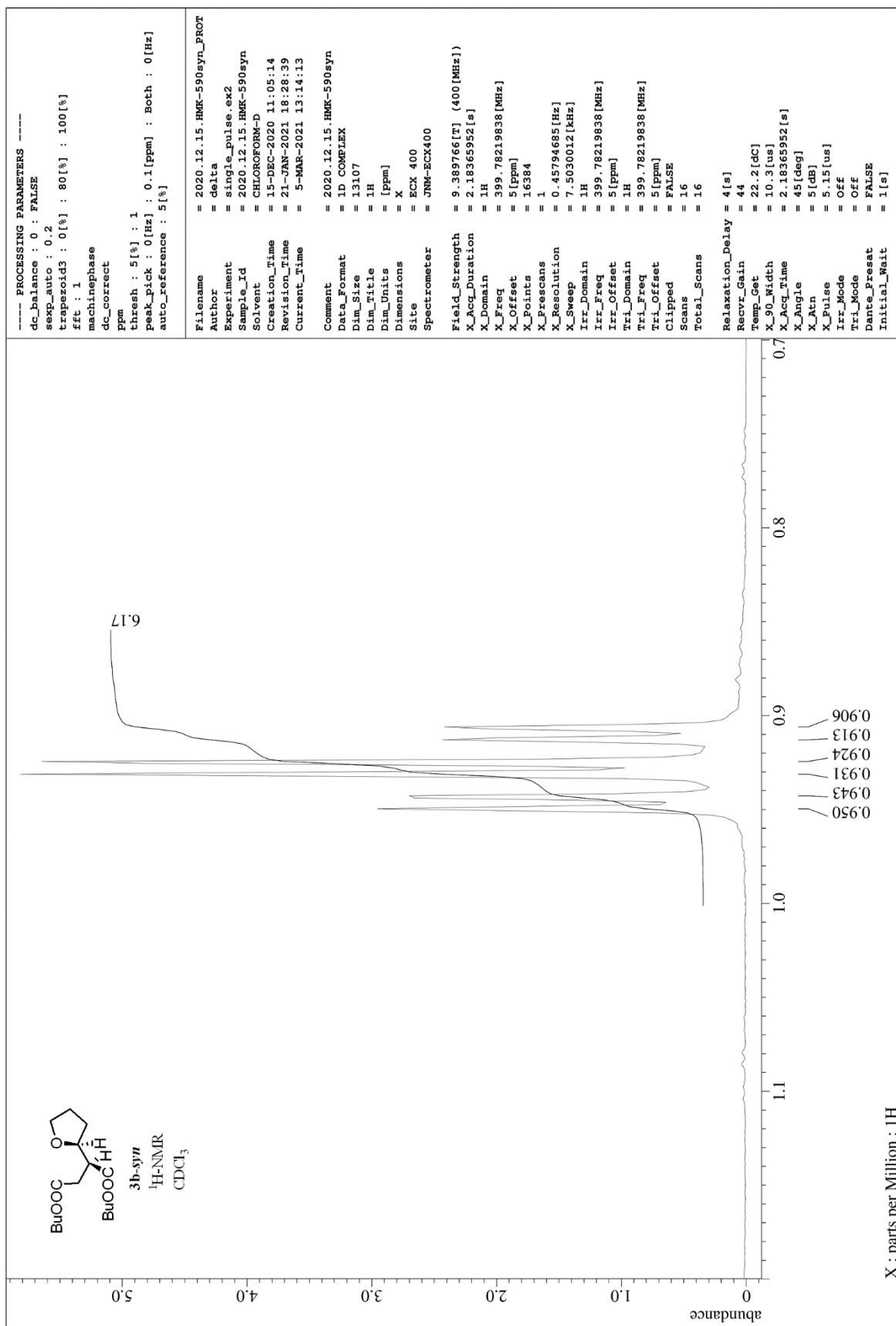
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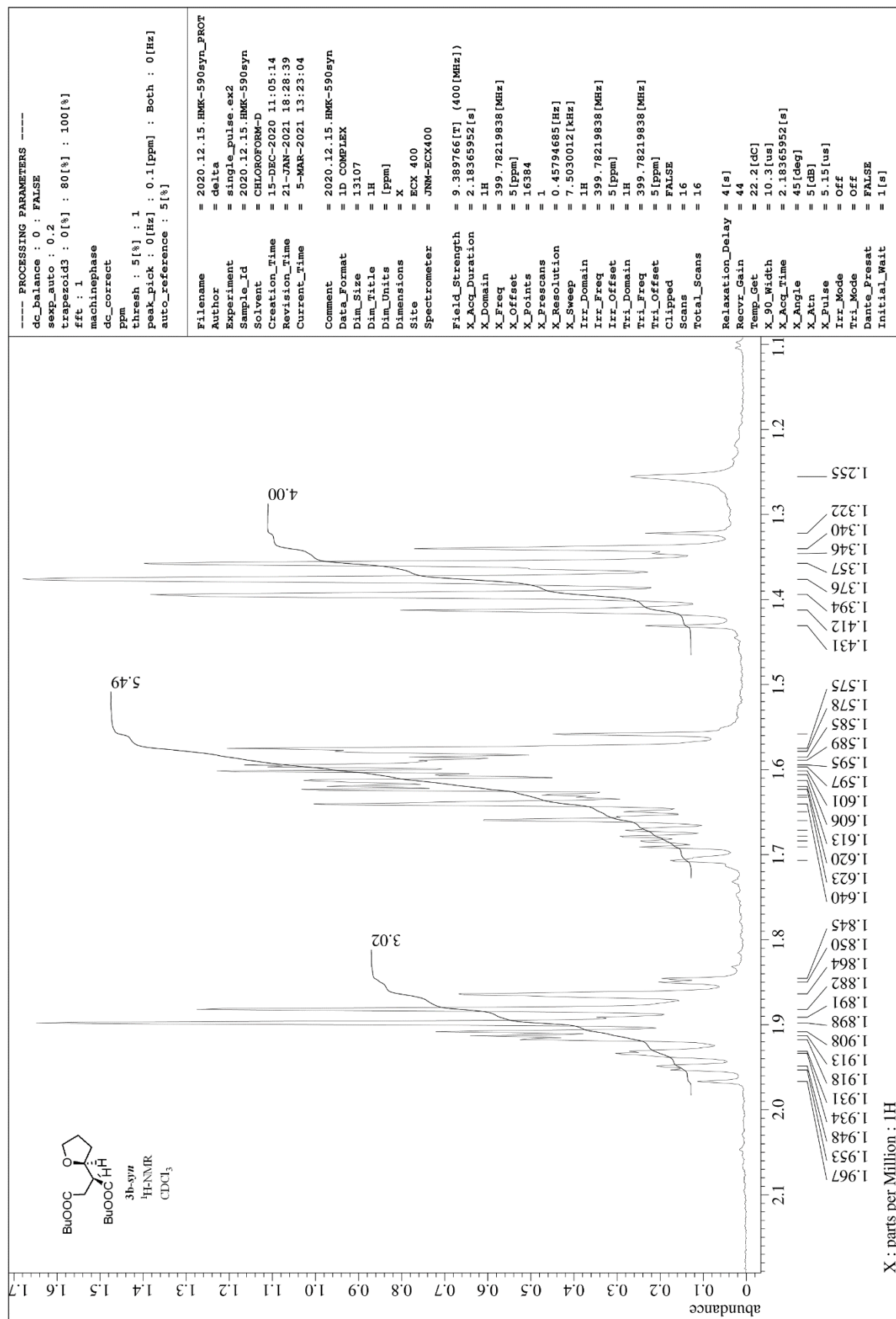
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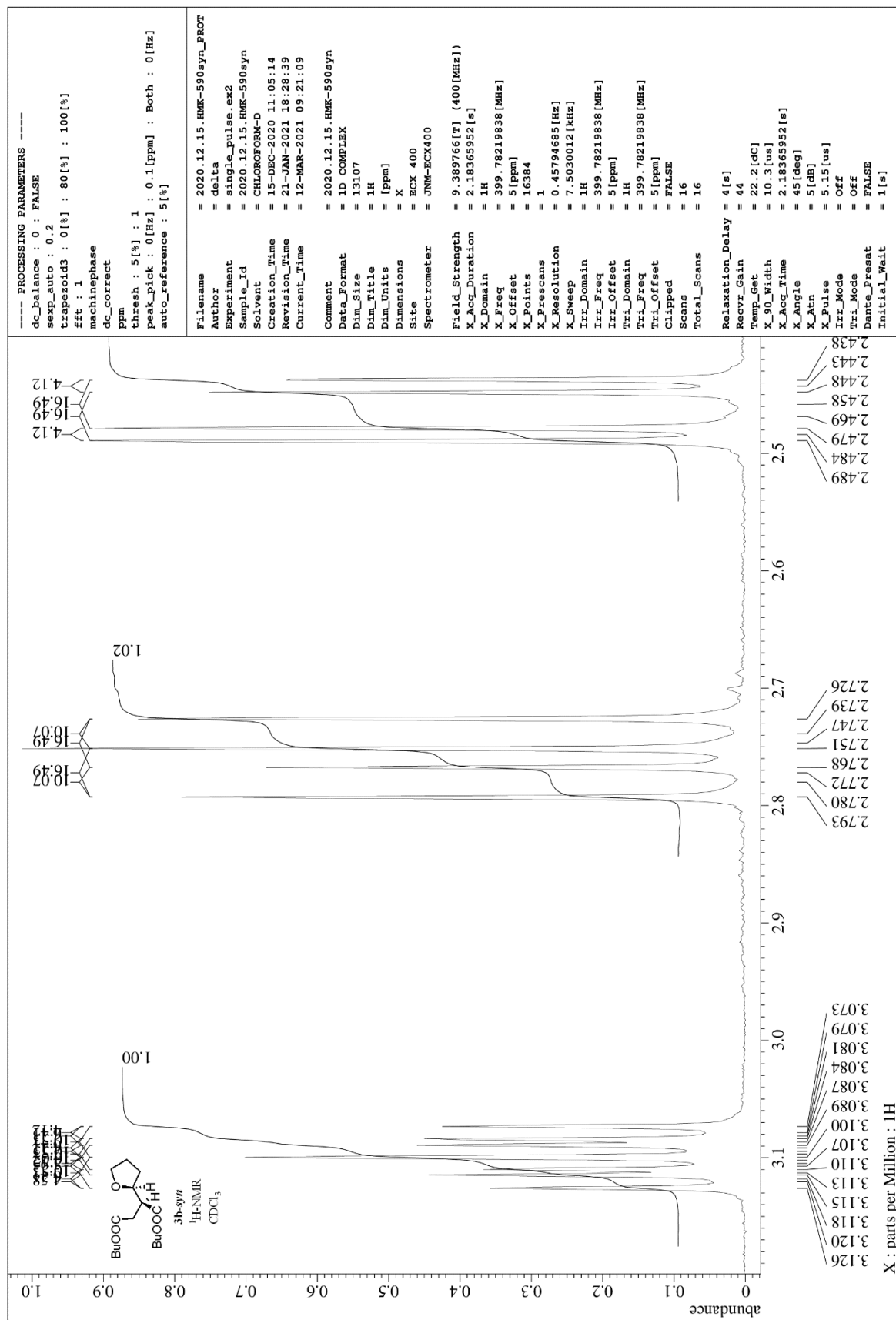
- S4. Stable conformations were calculated by B3LYP/6-31++G(d,p) using Gaussian 16; Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- S5. Graphics were prepared using GausView 6; GaussView, Version 6, Dennington, Roy; Keith, Todd A.; Millam, John M. Semichem Inc., Shawnee Mission, KS, 2016.

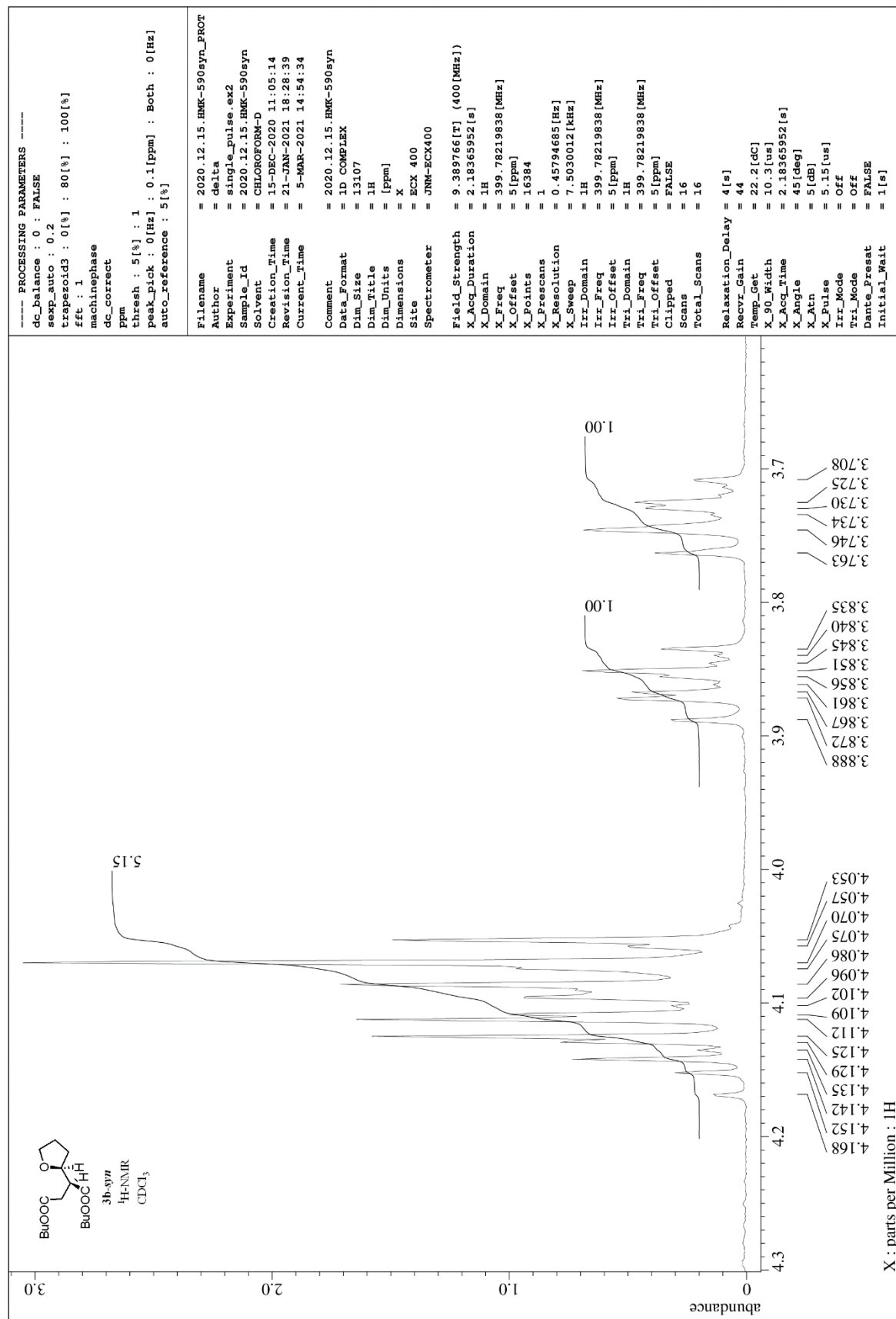
3. ^1H -NMR and ^{13}C -NMR spectra.

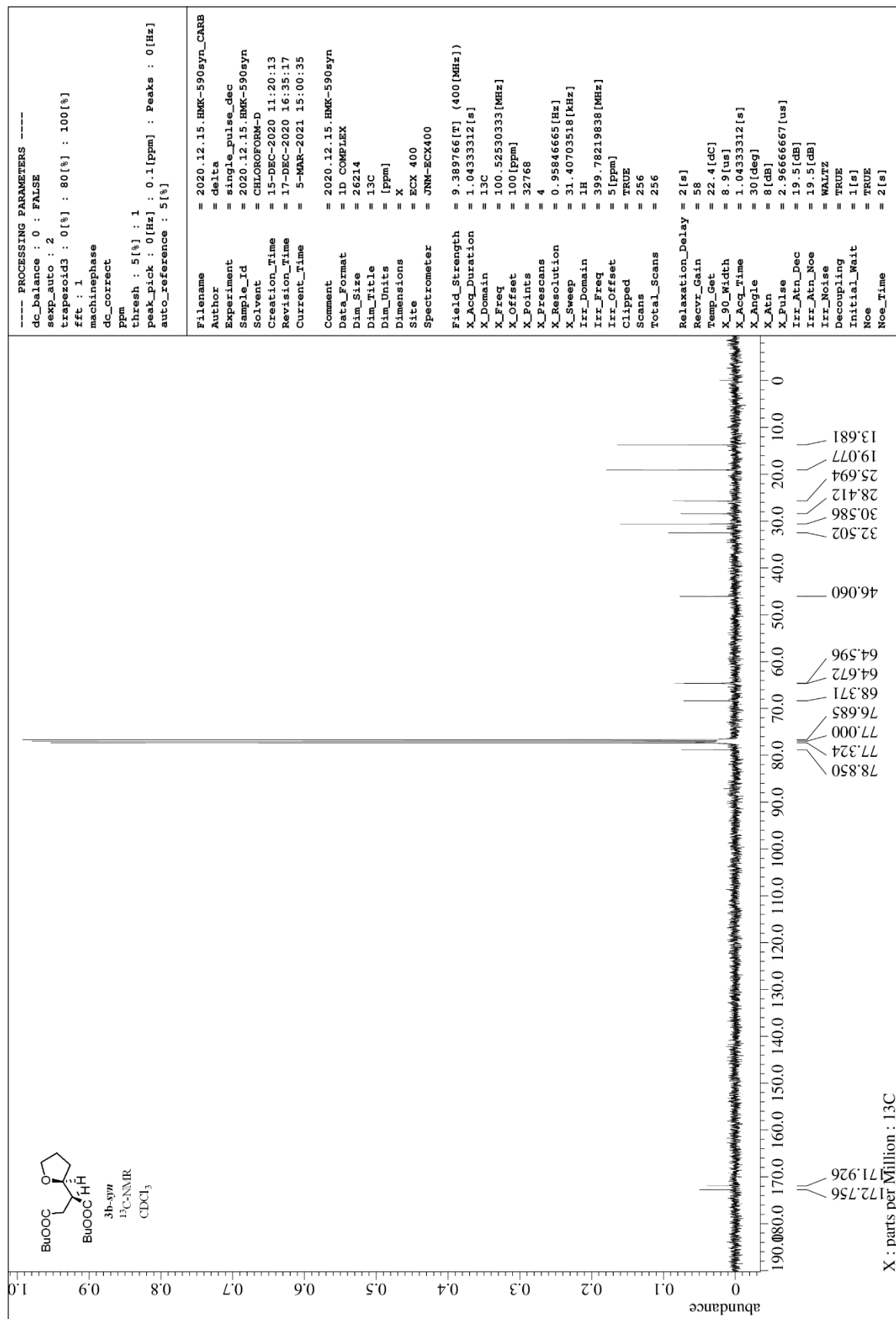


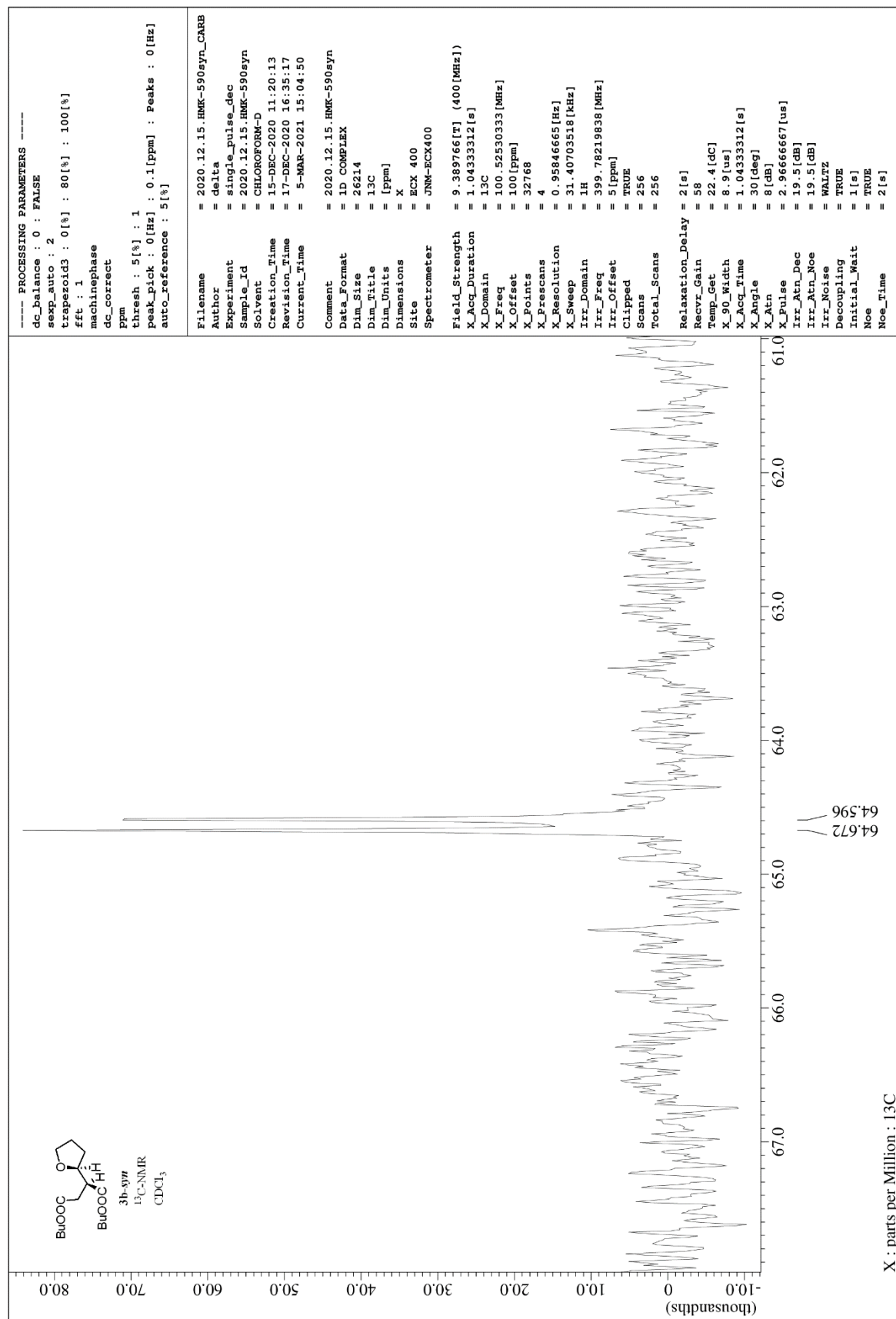


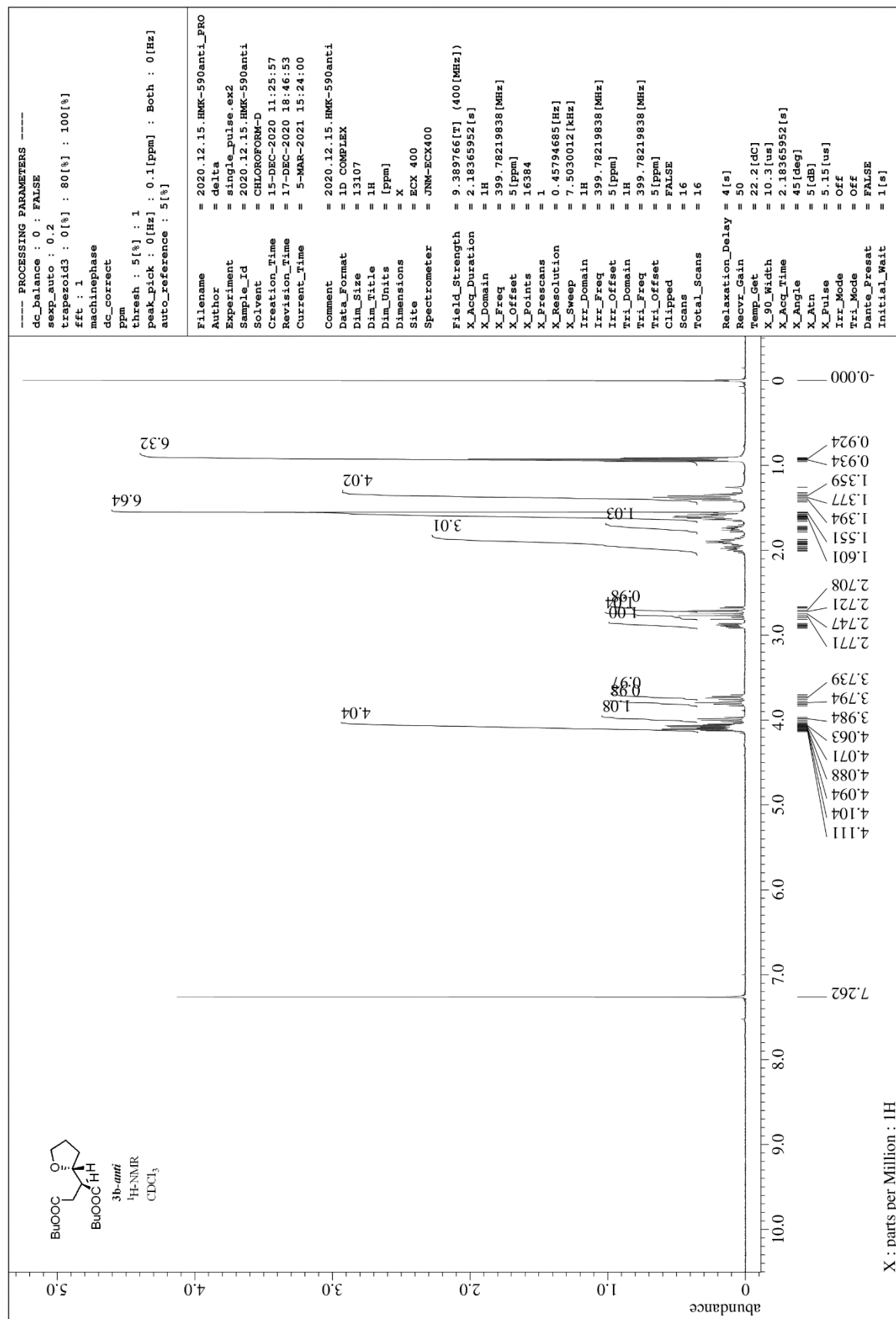


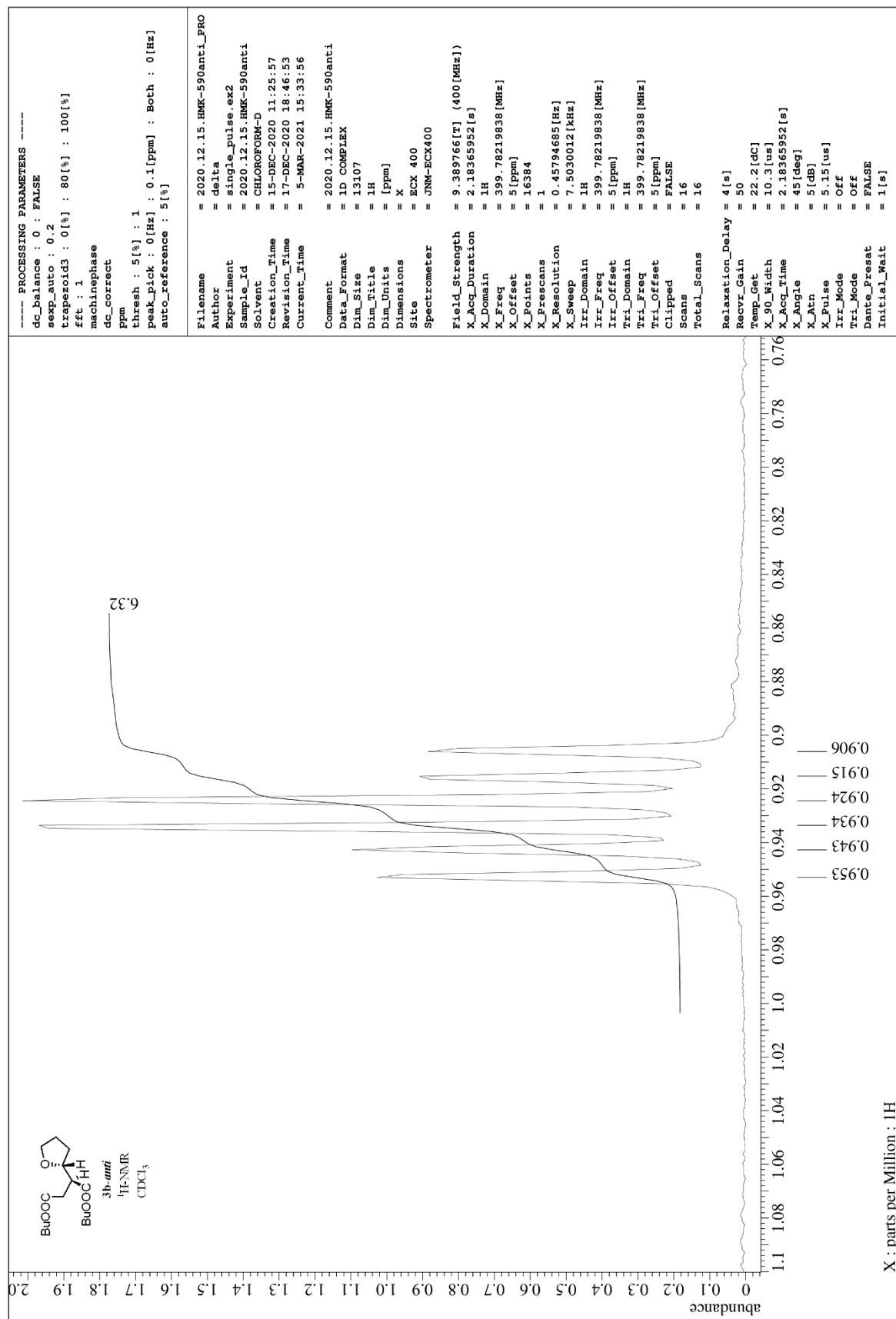


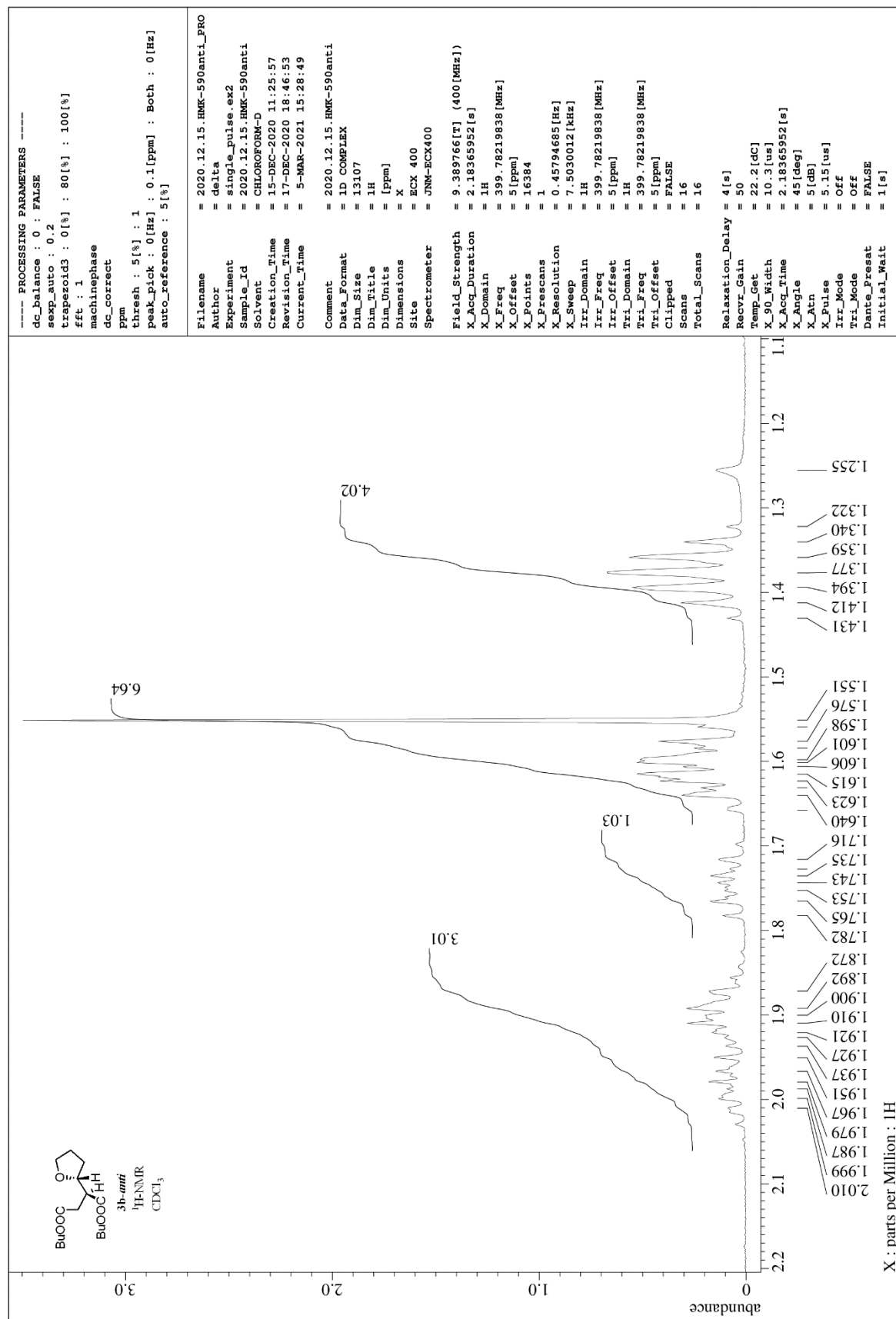


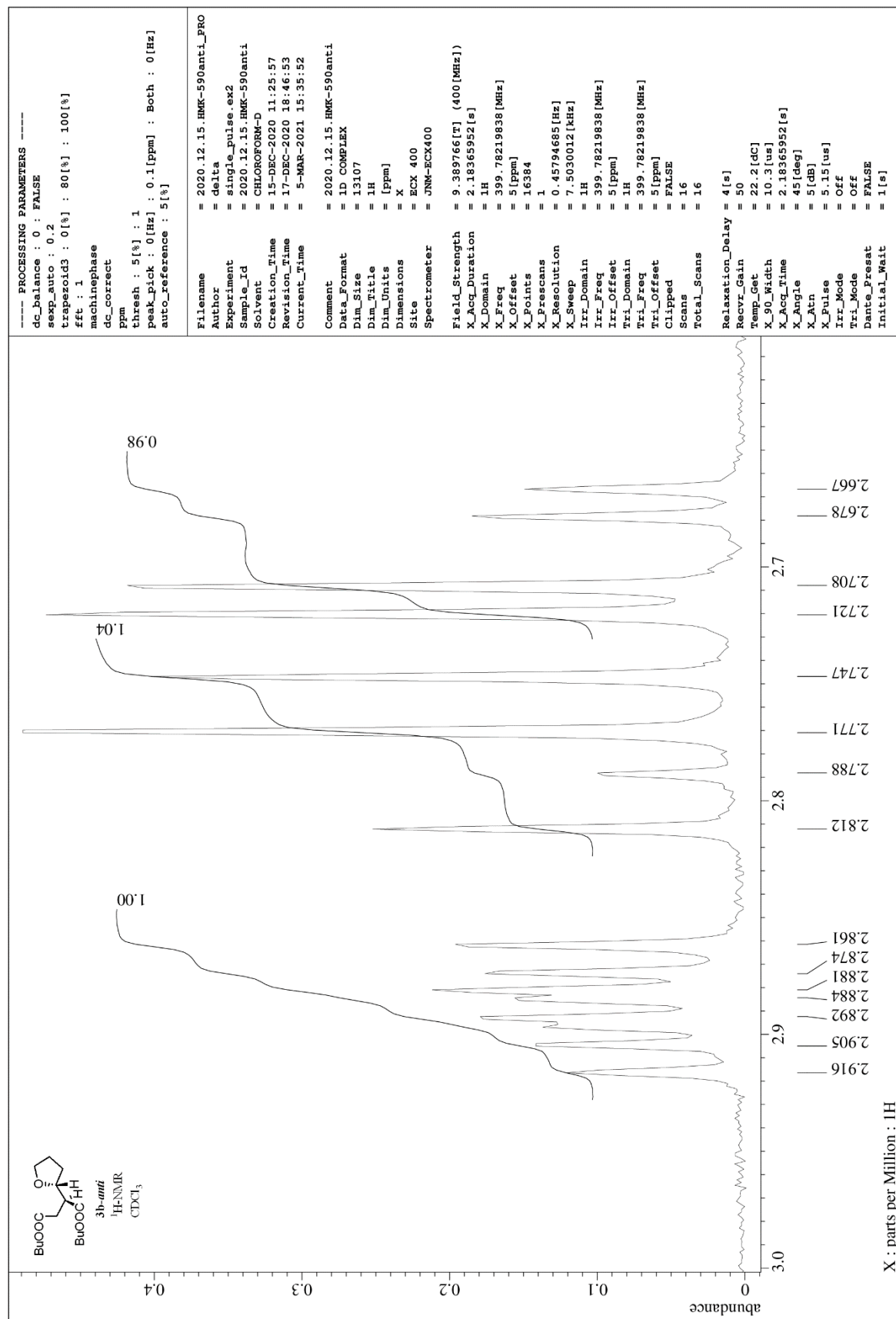


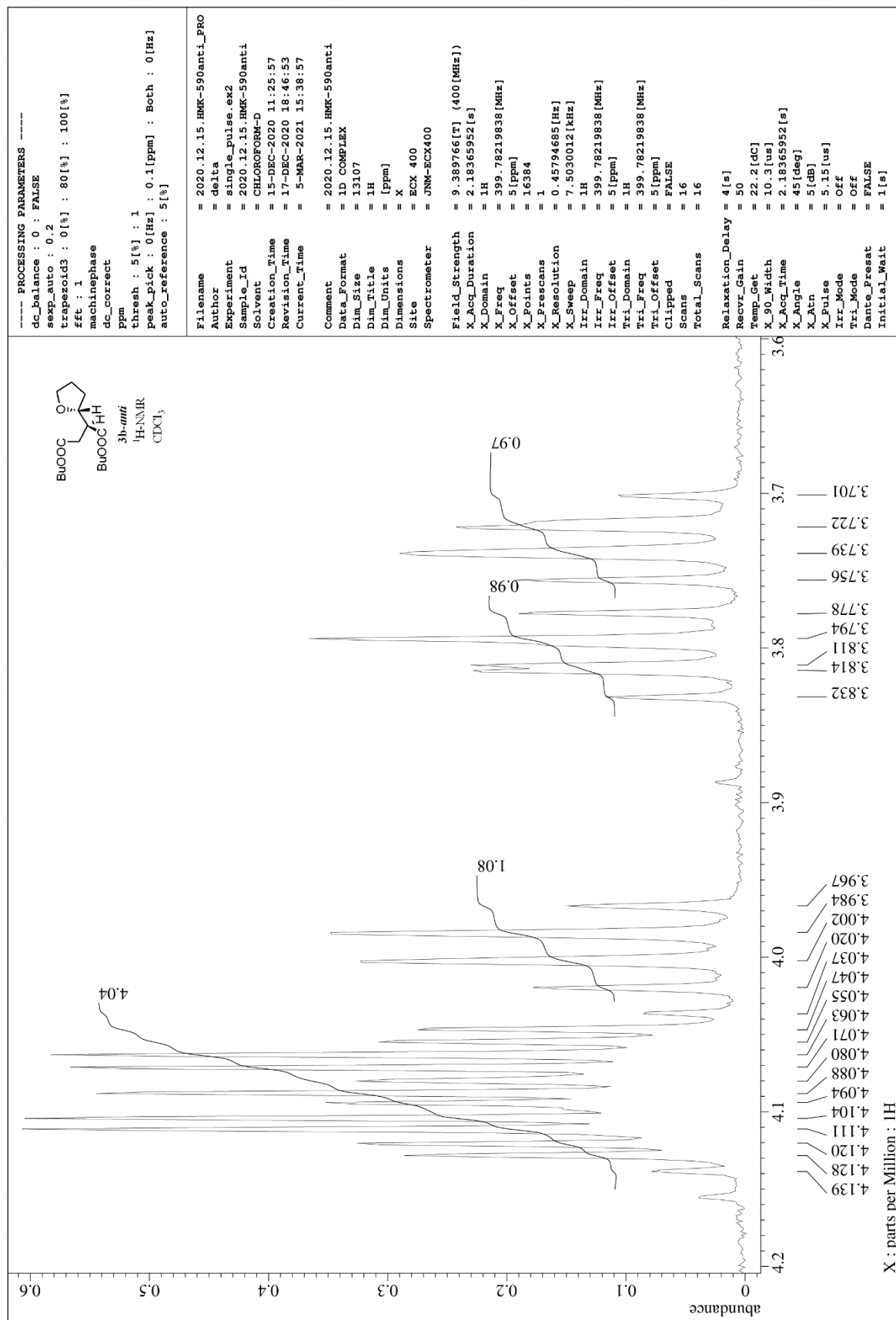


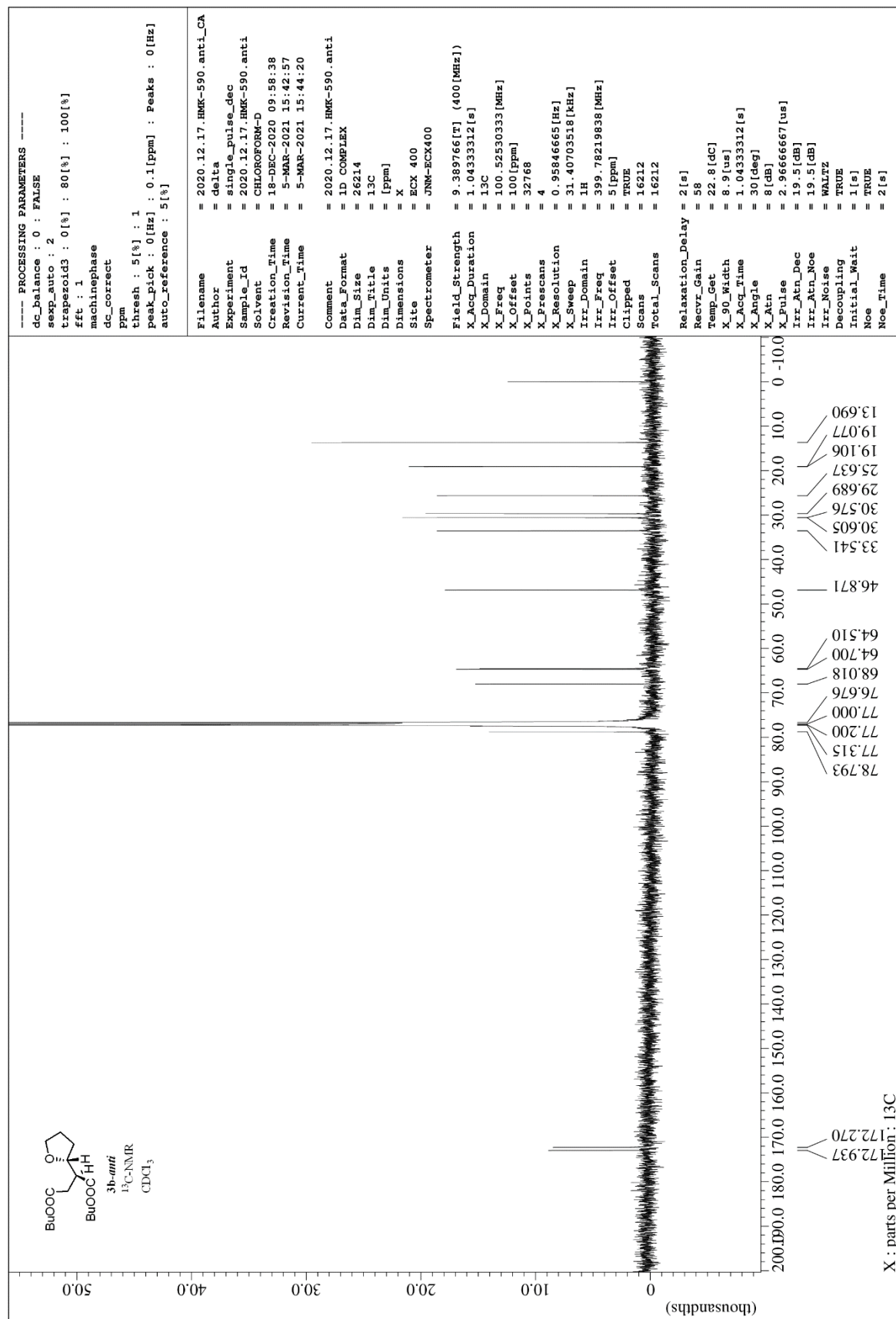


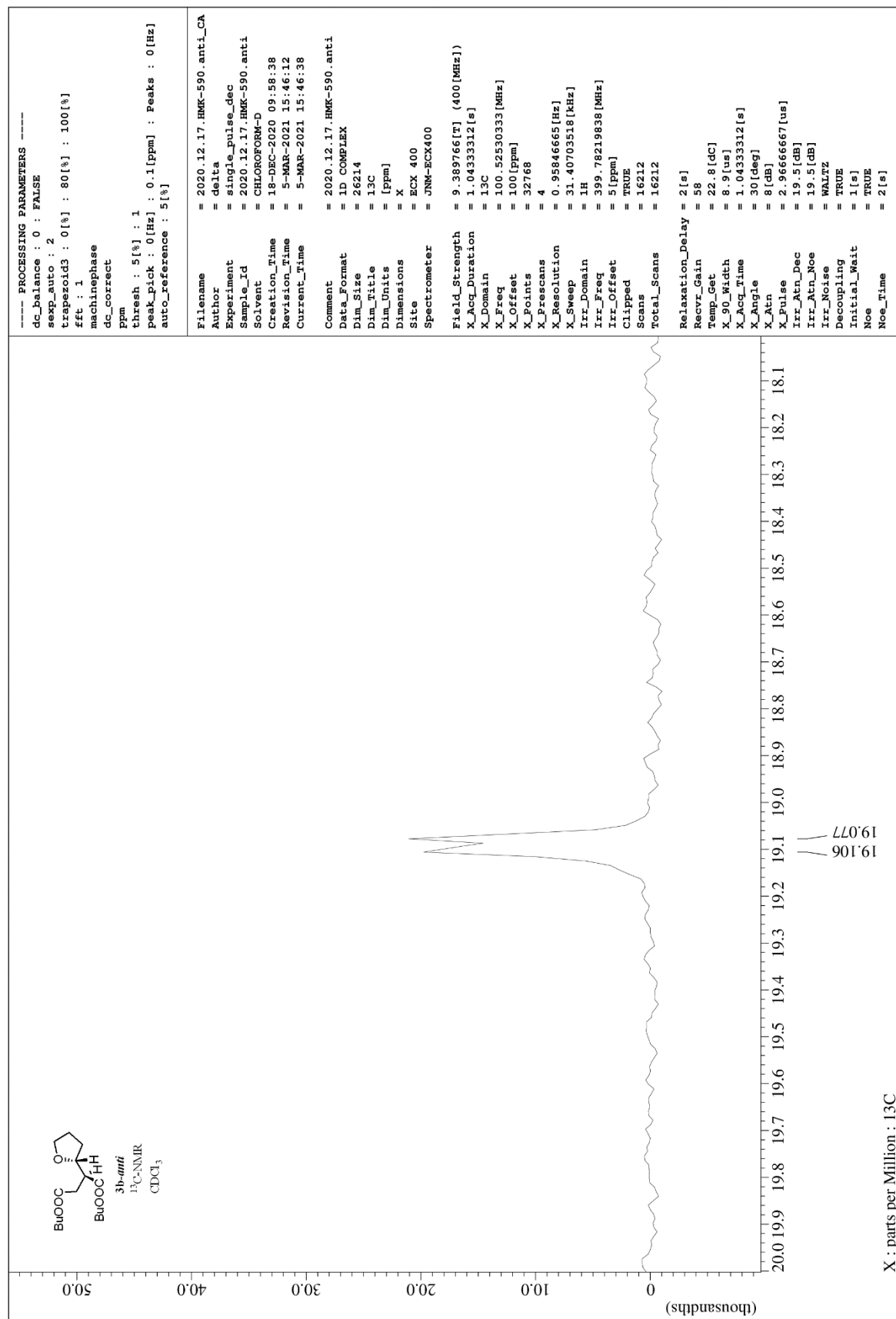


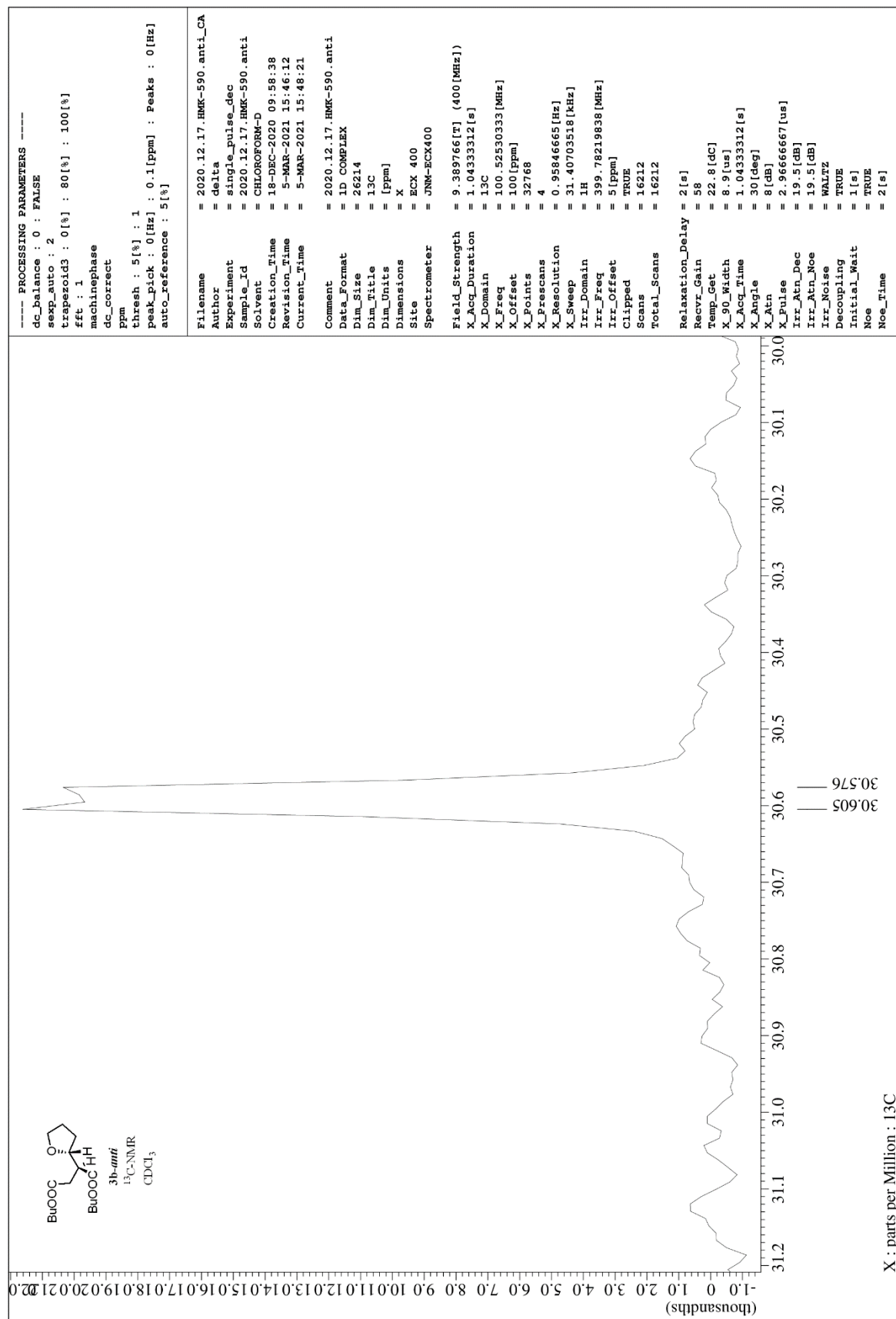


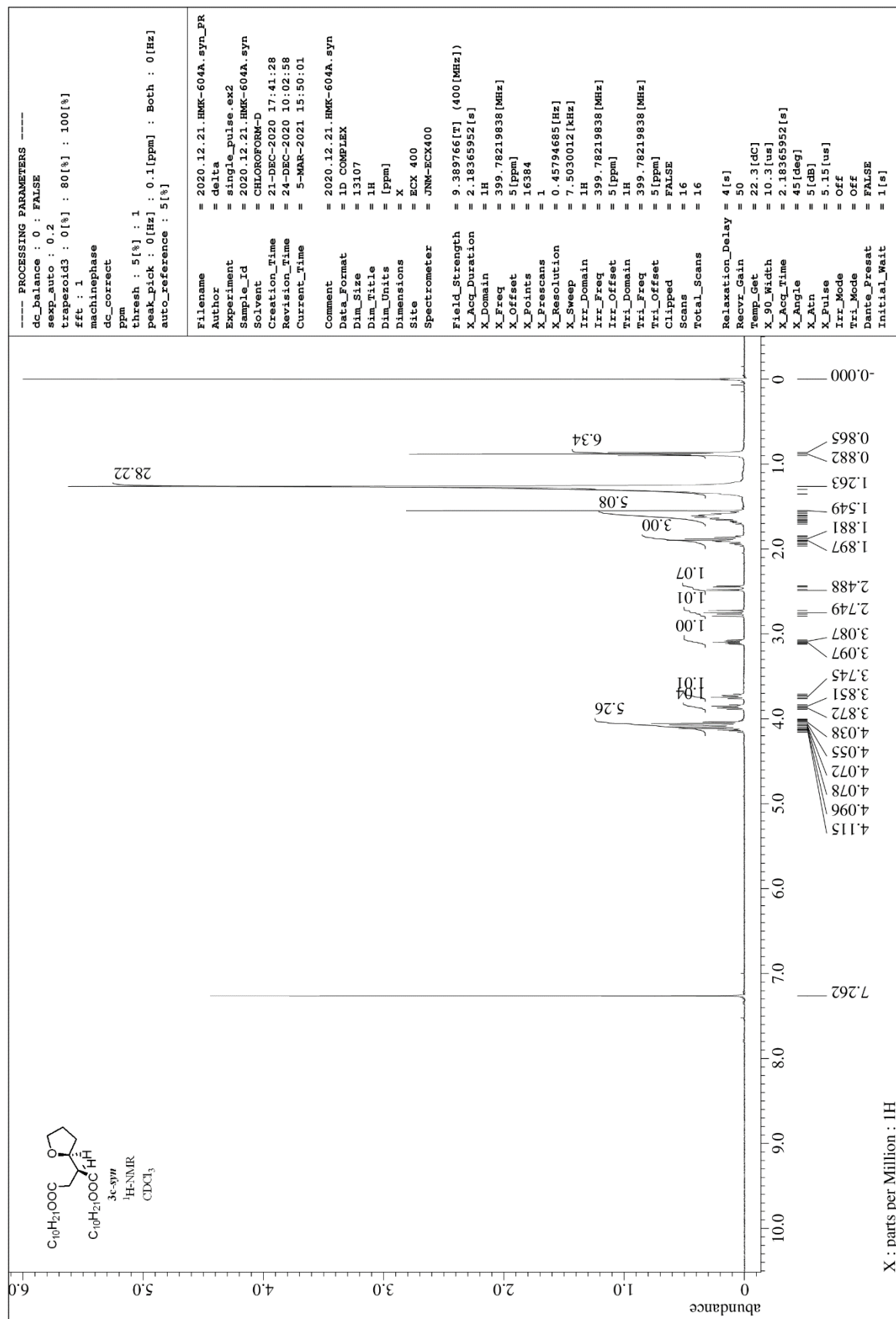


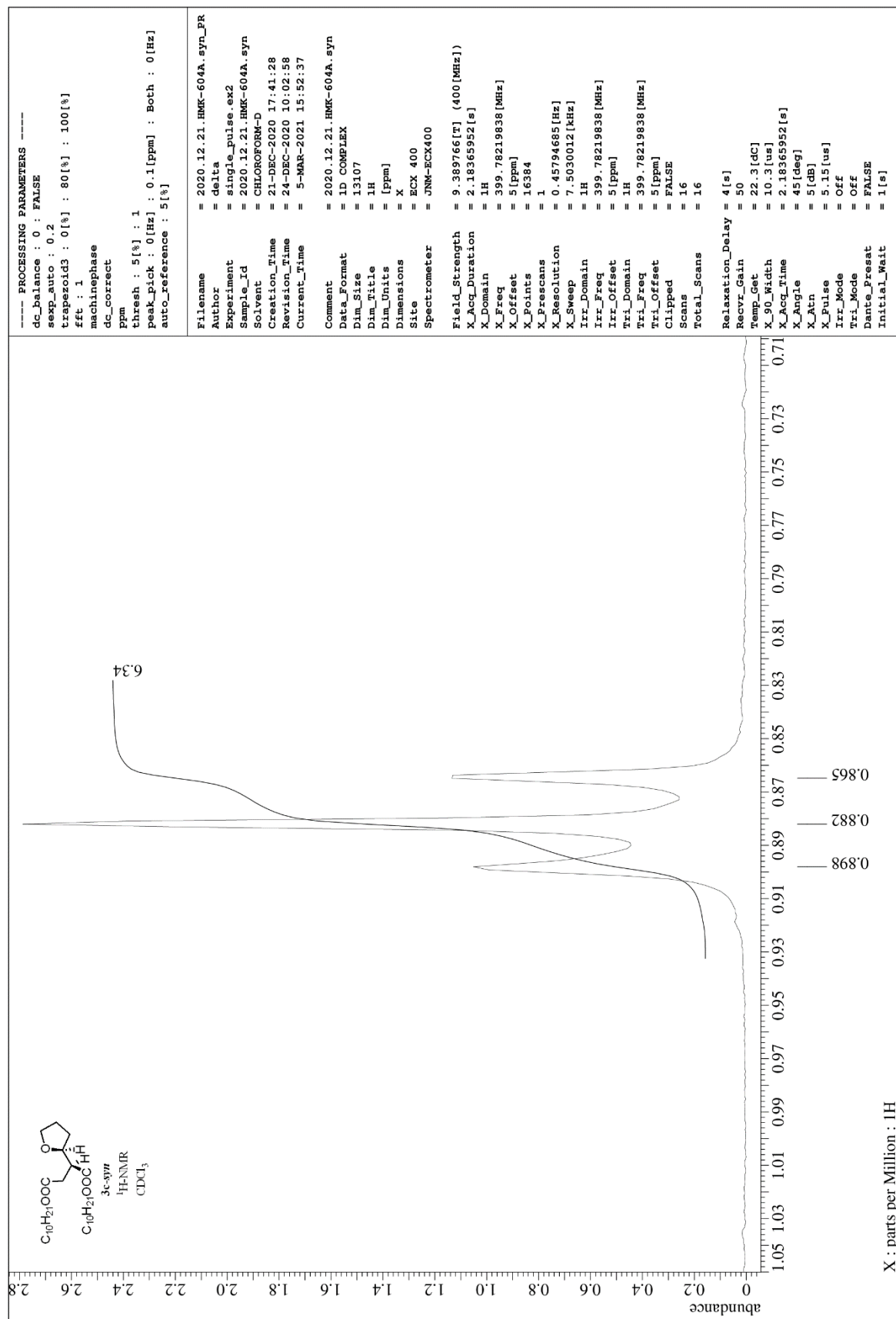


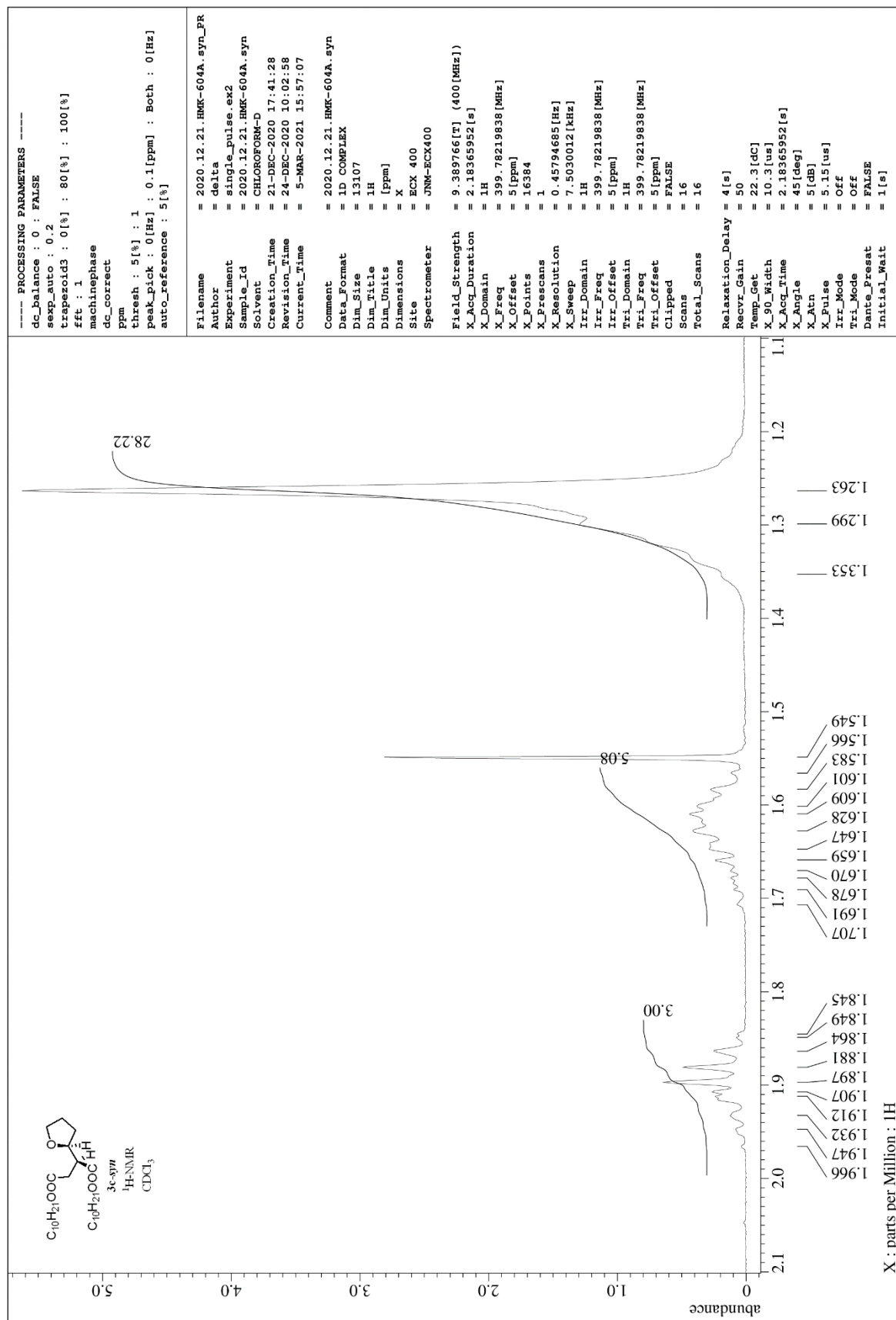


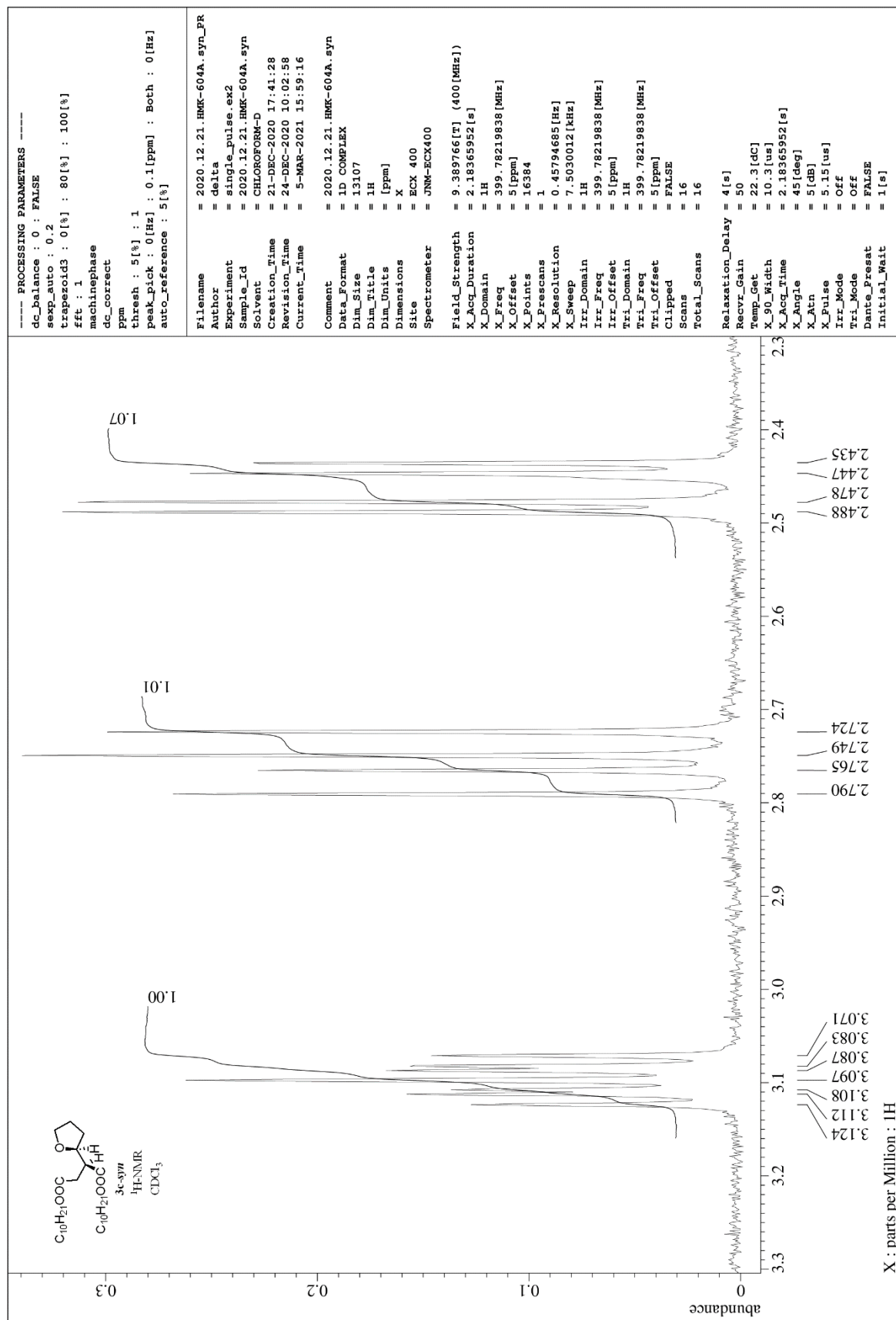


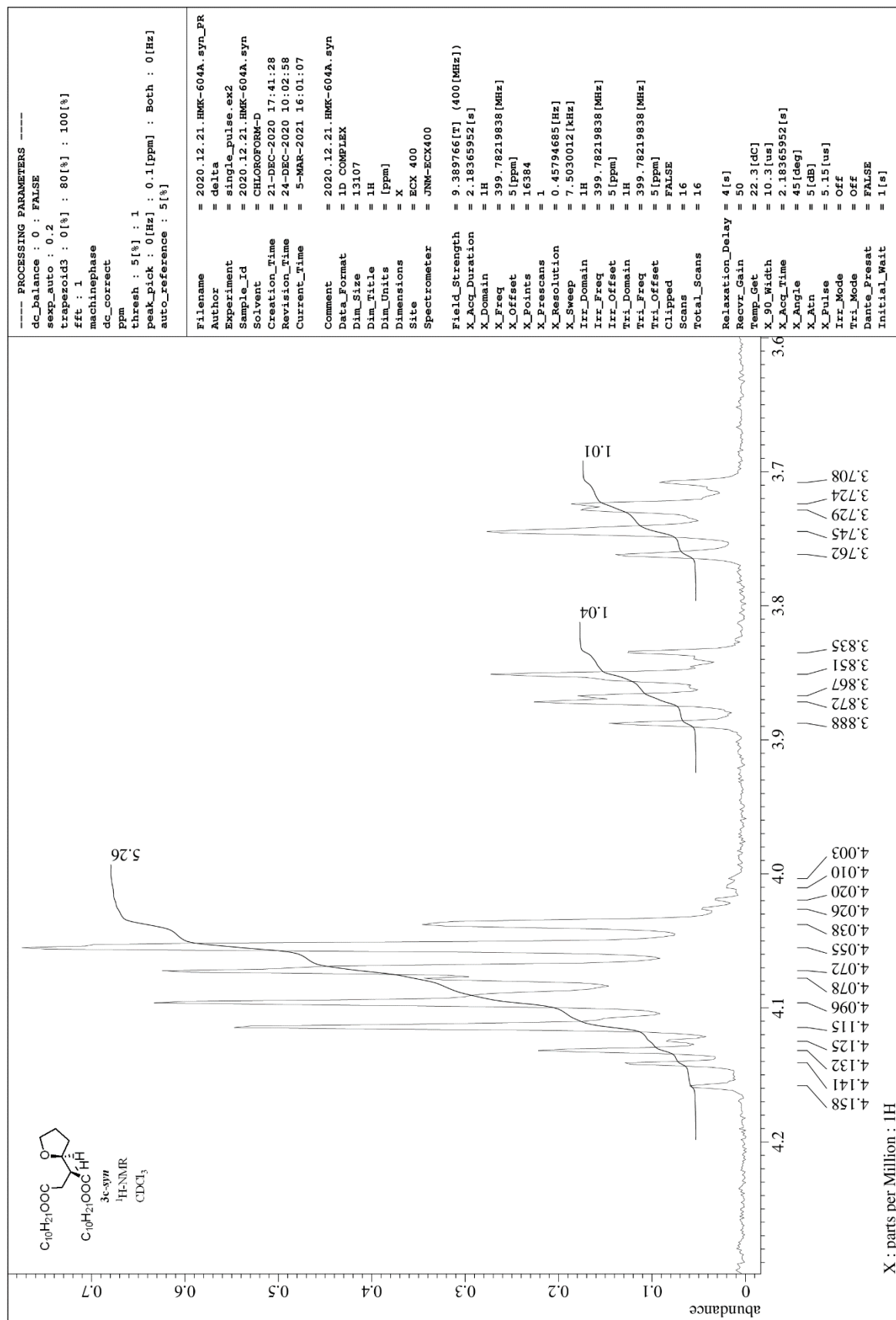


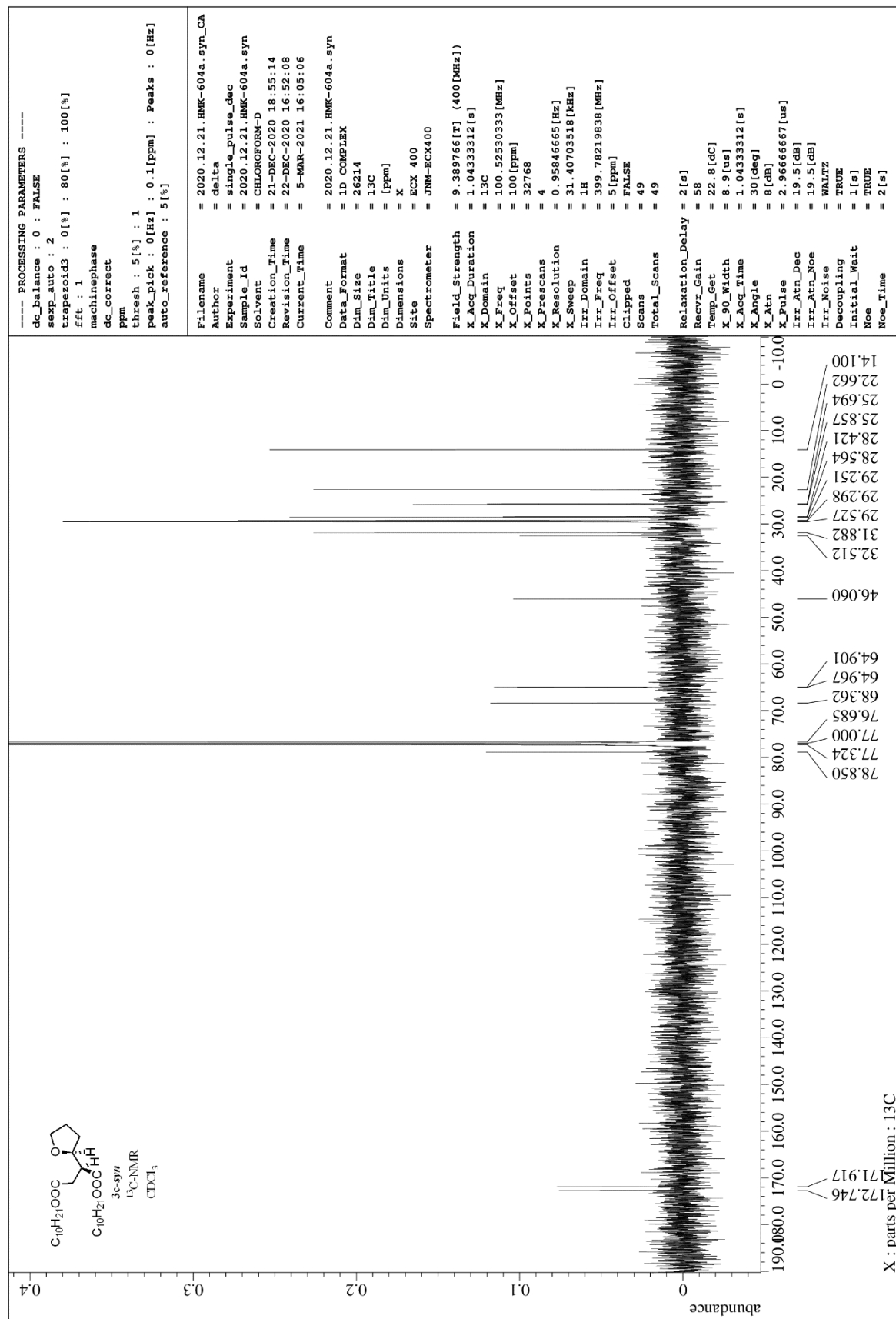


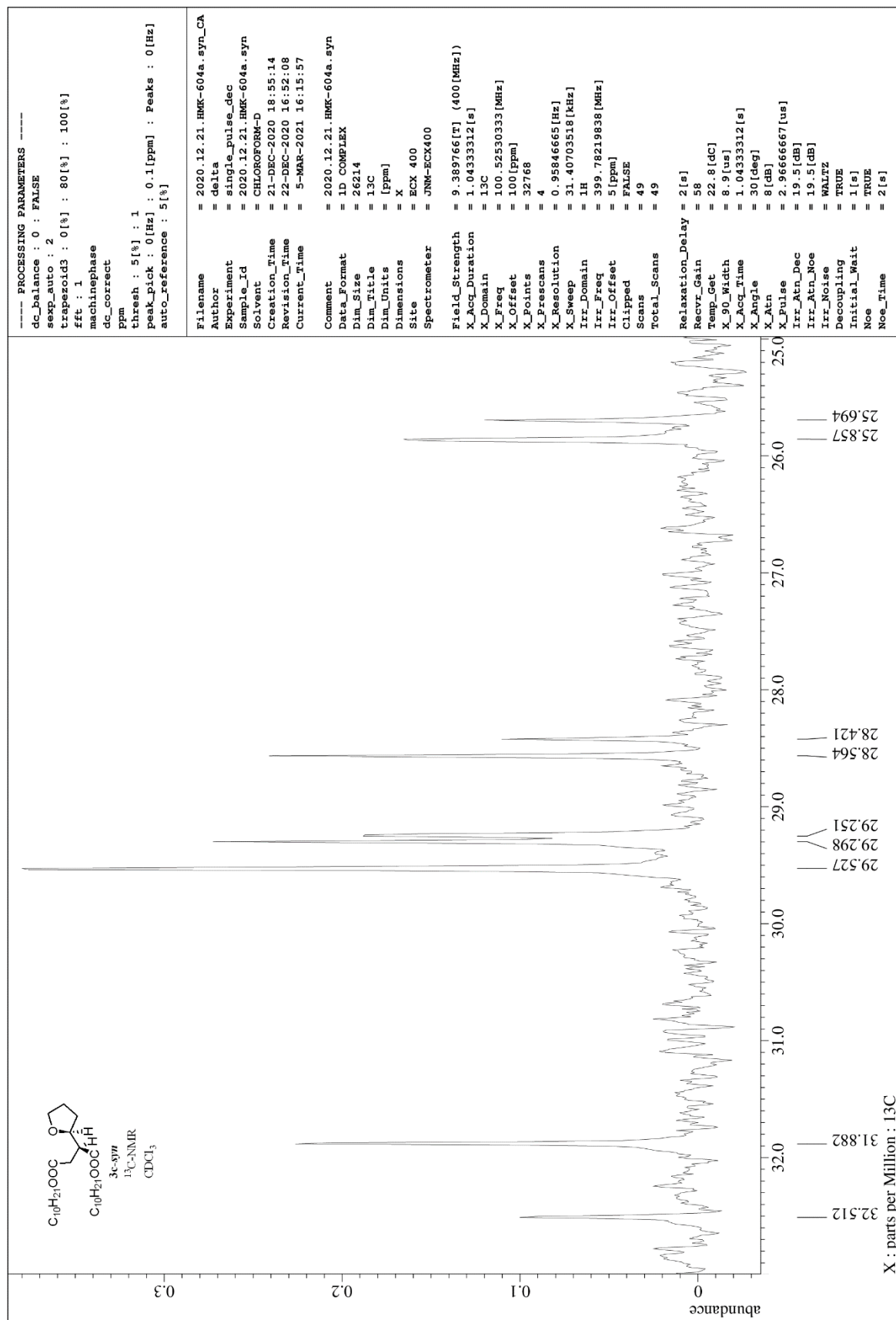


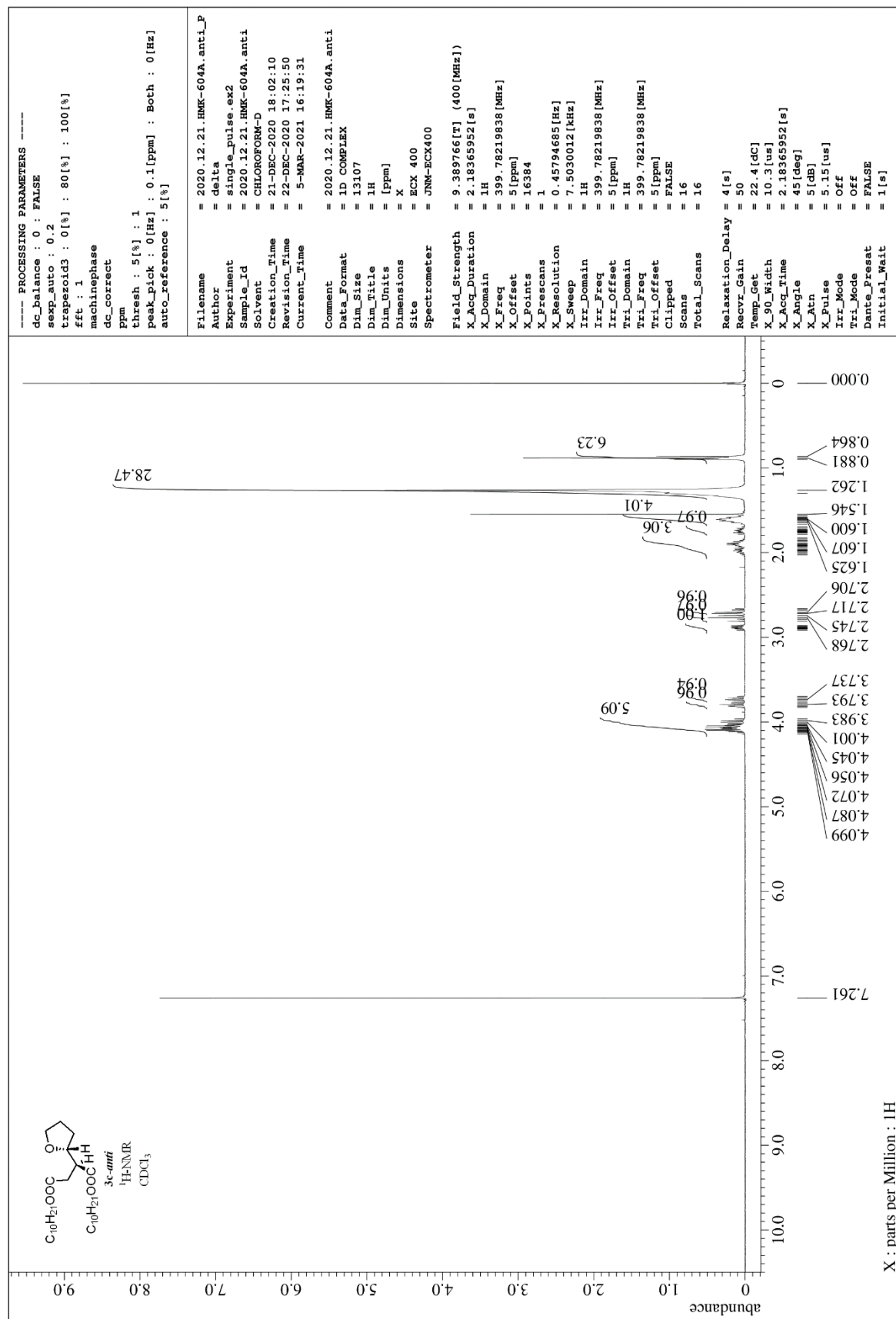


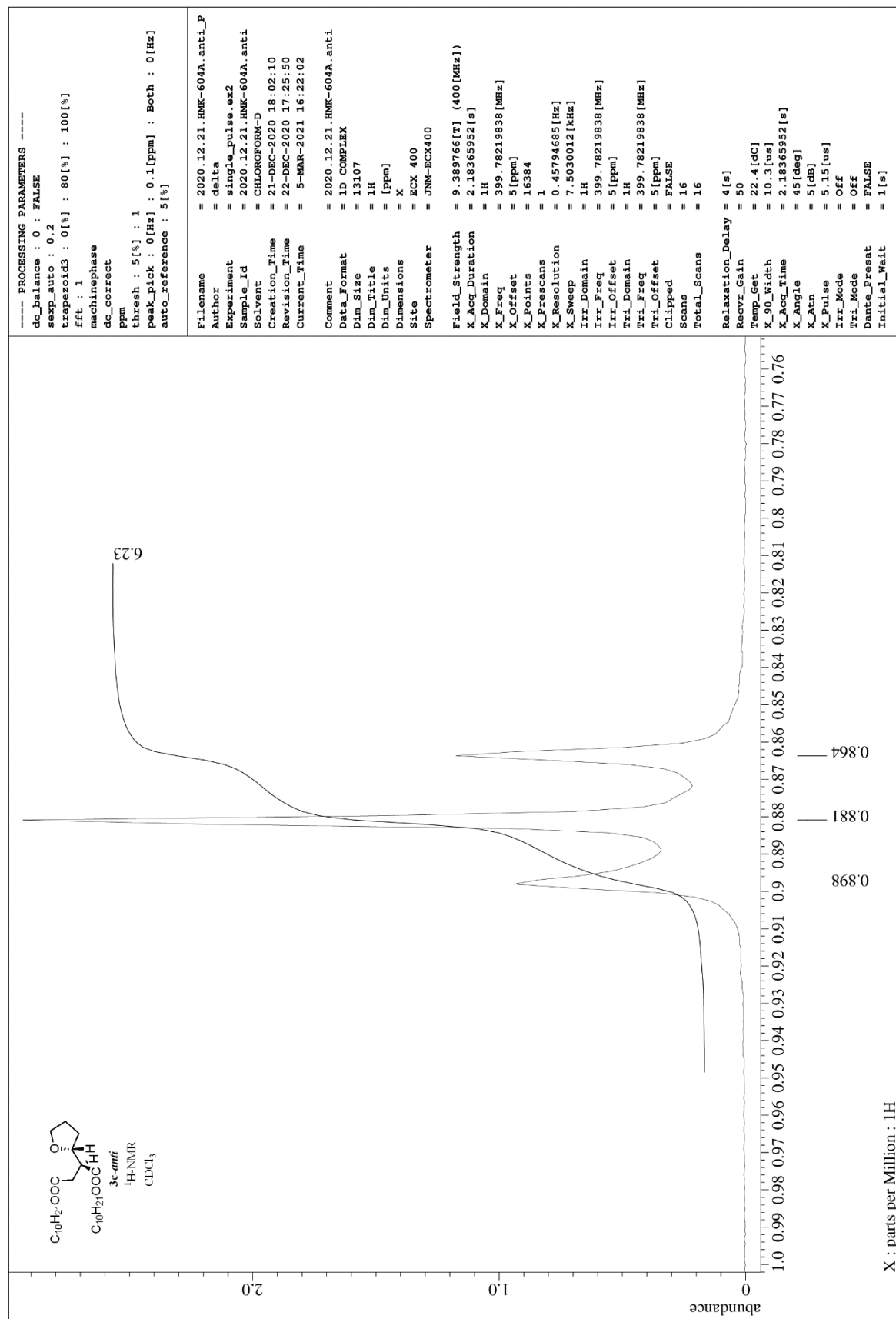


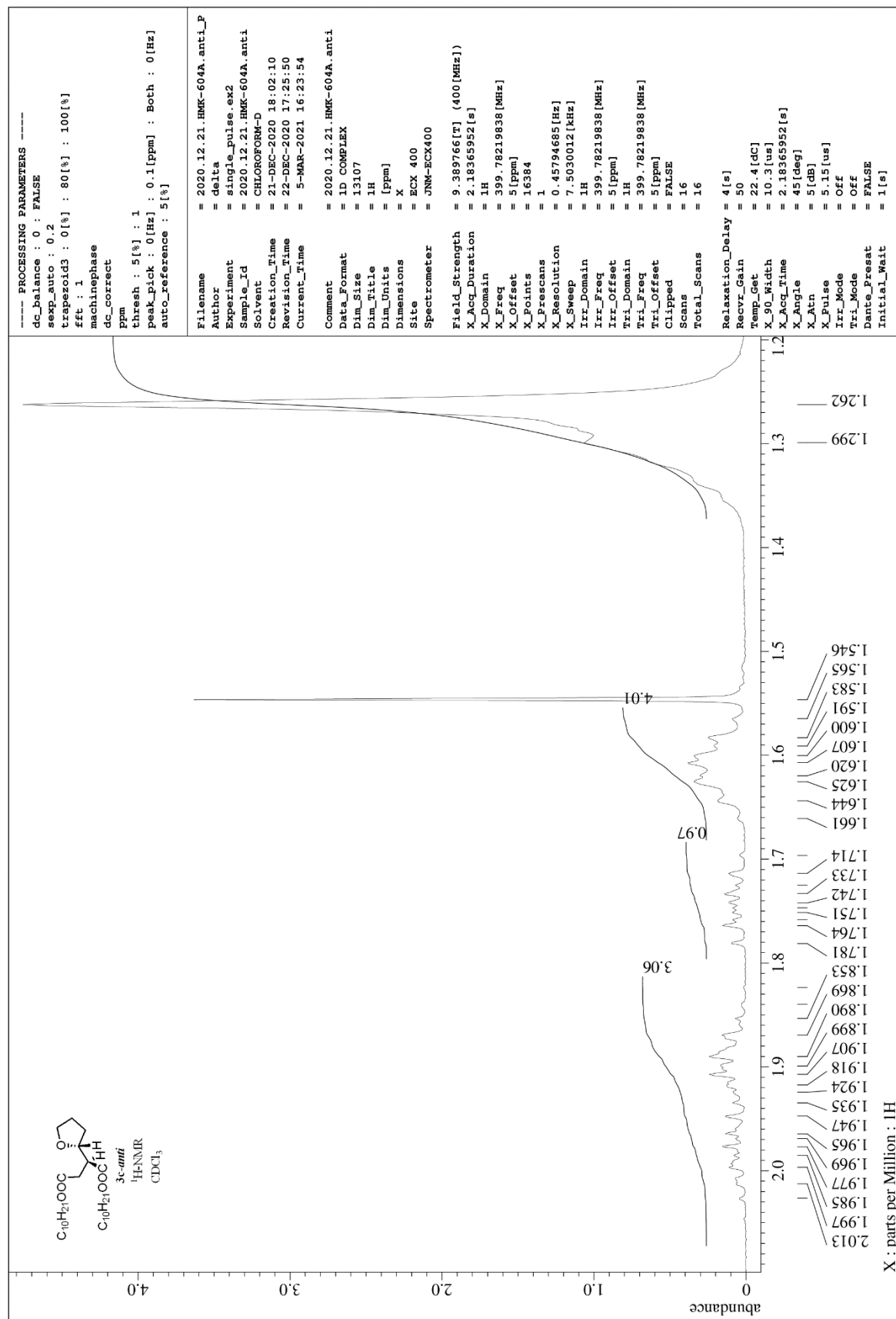


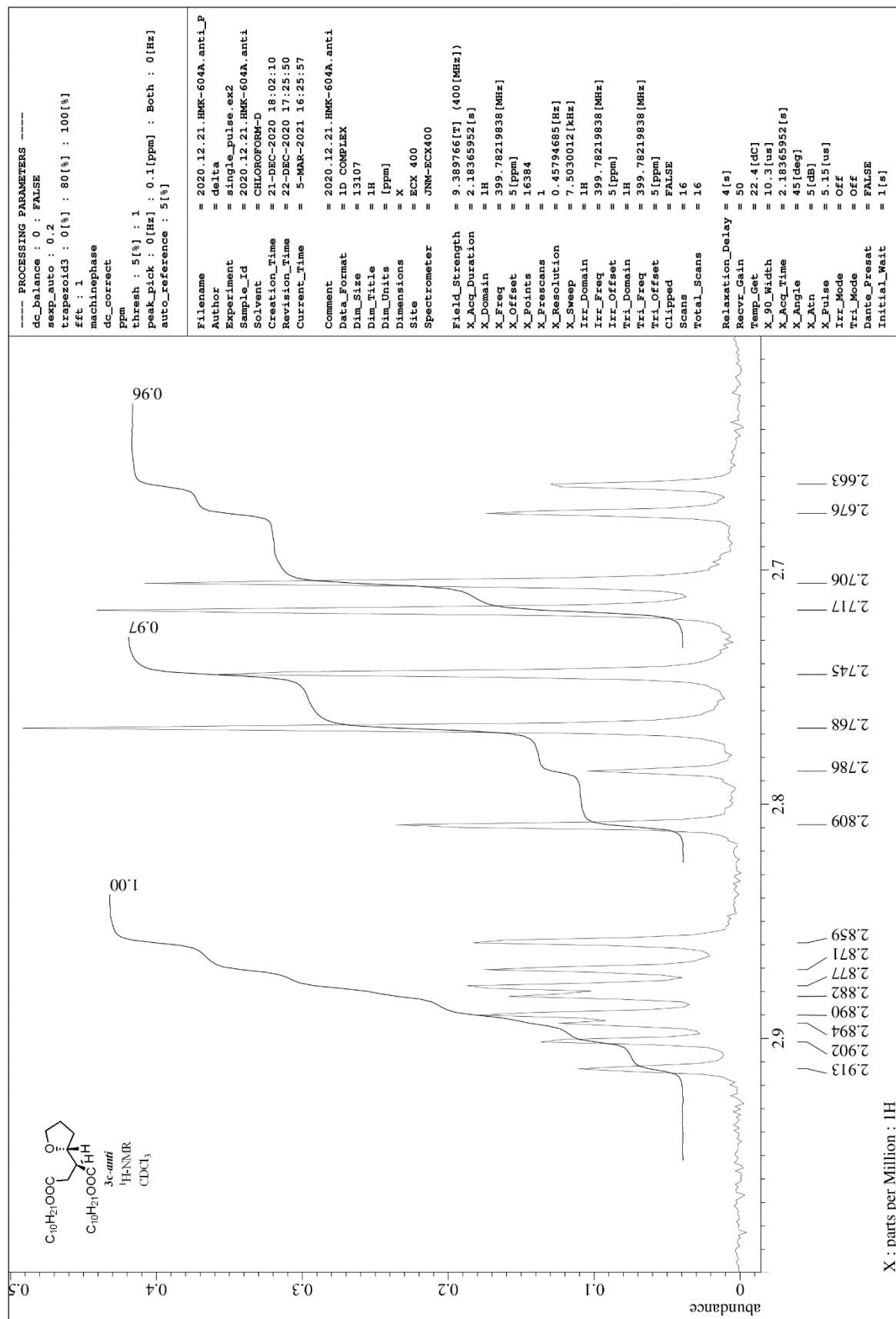


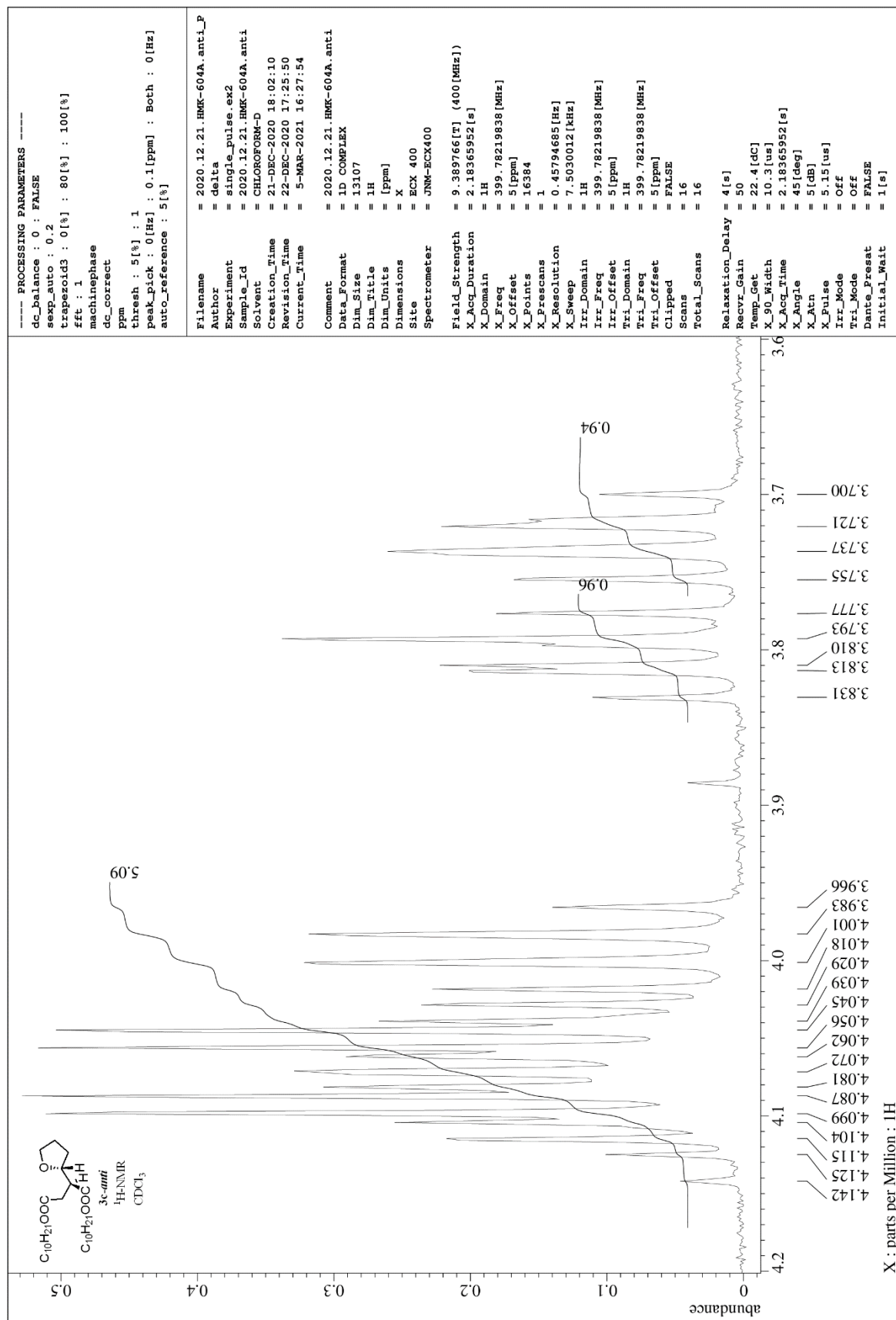


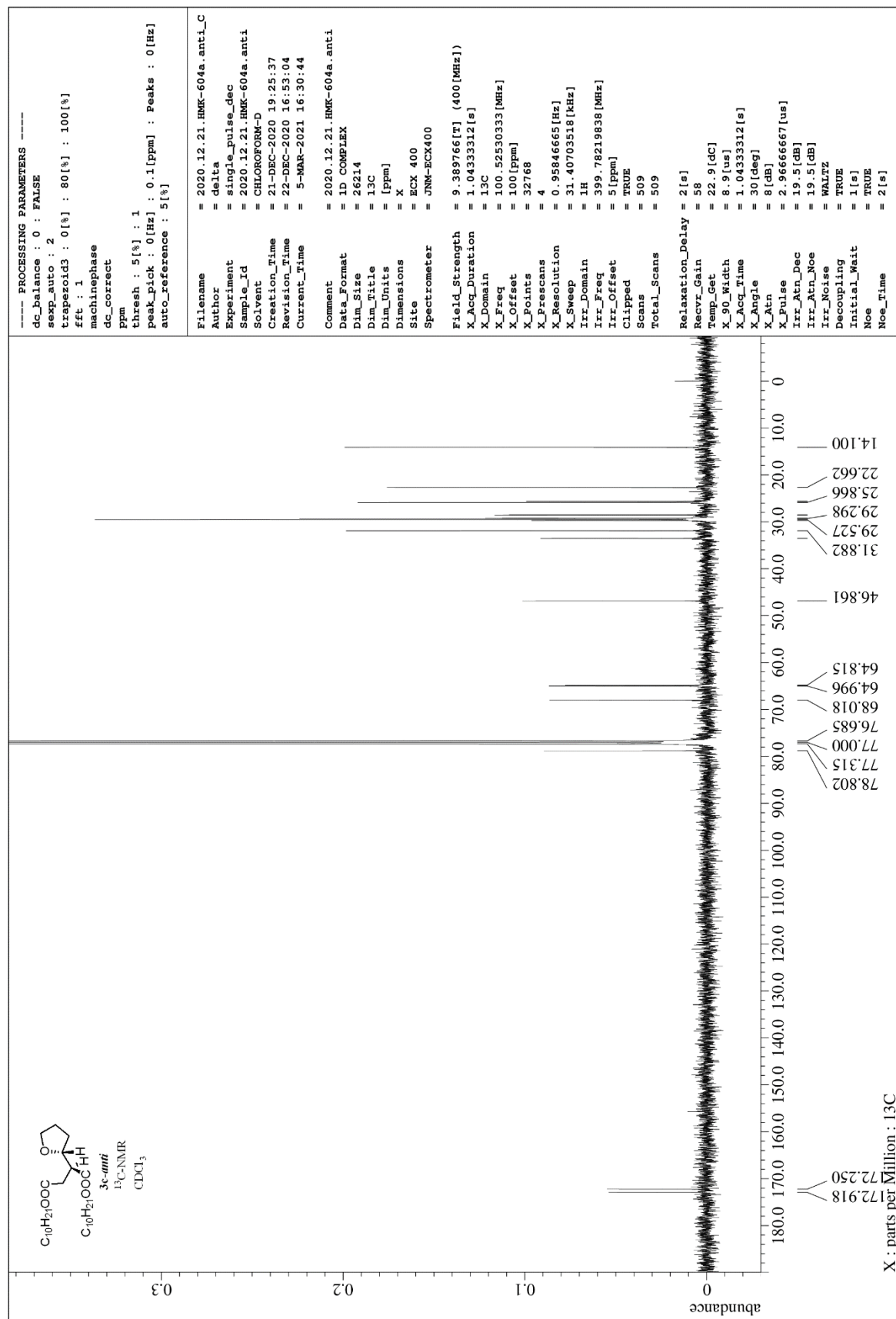


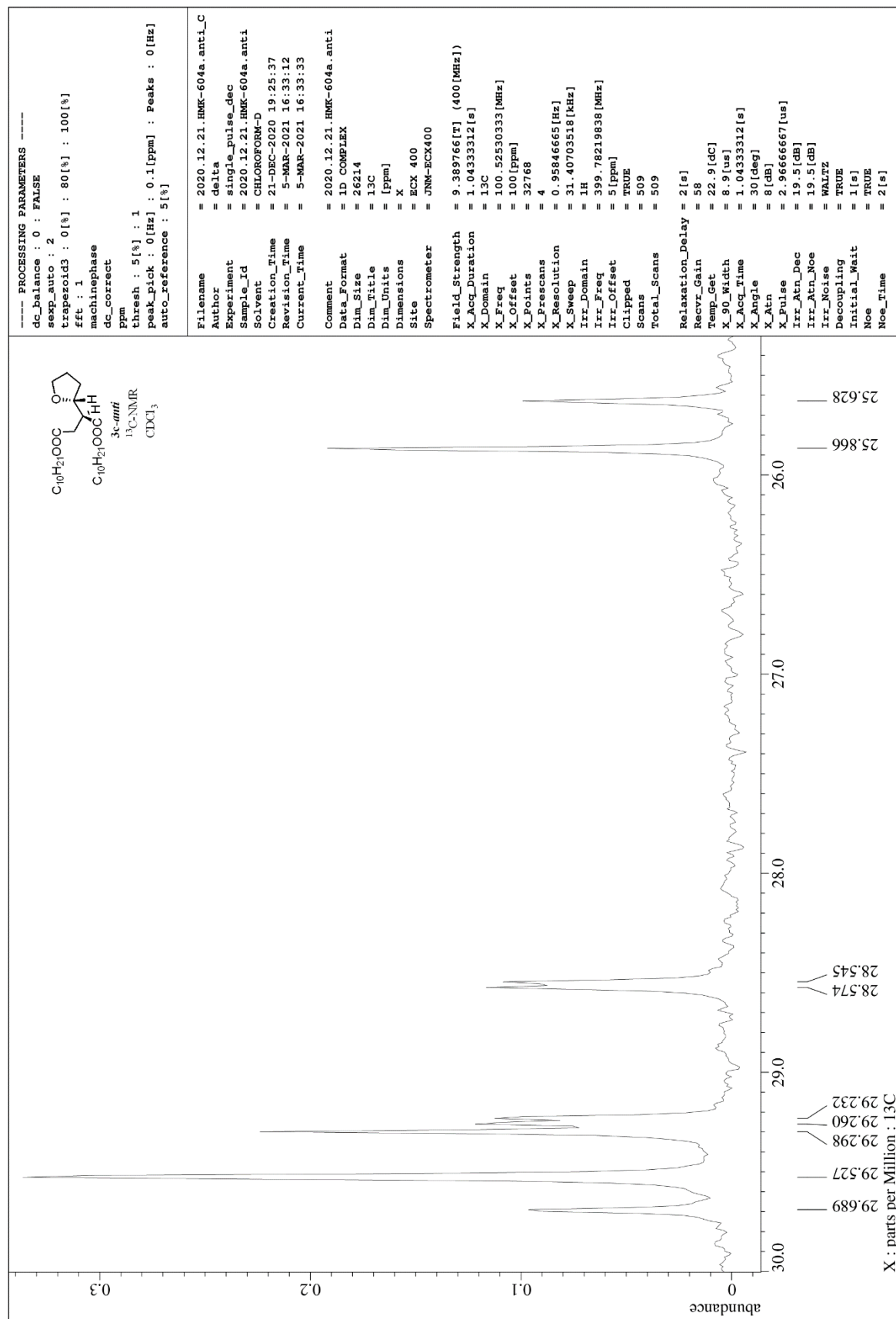


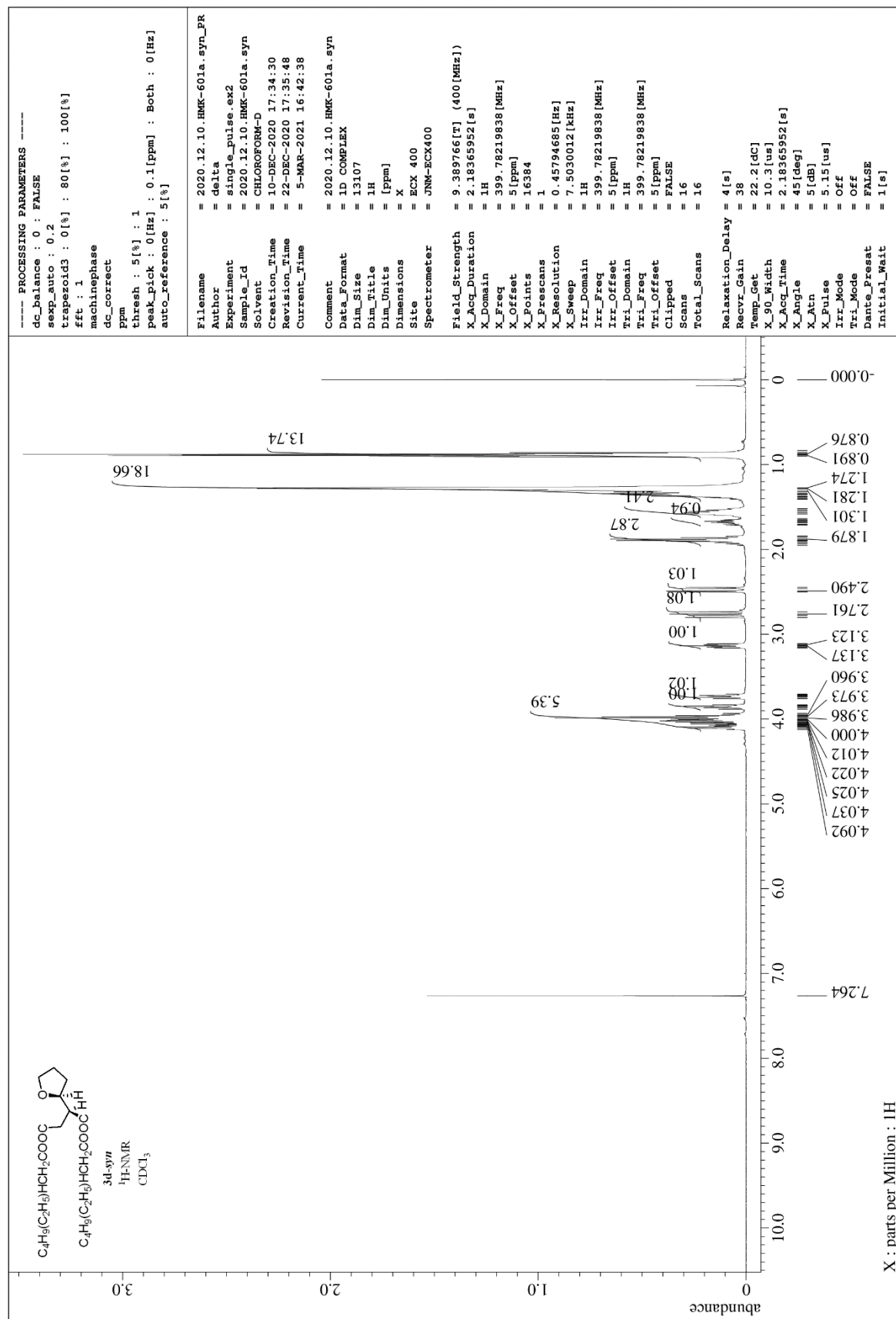


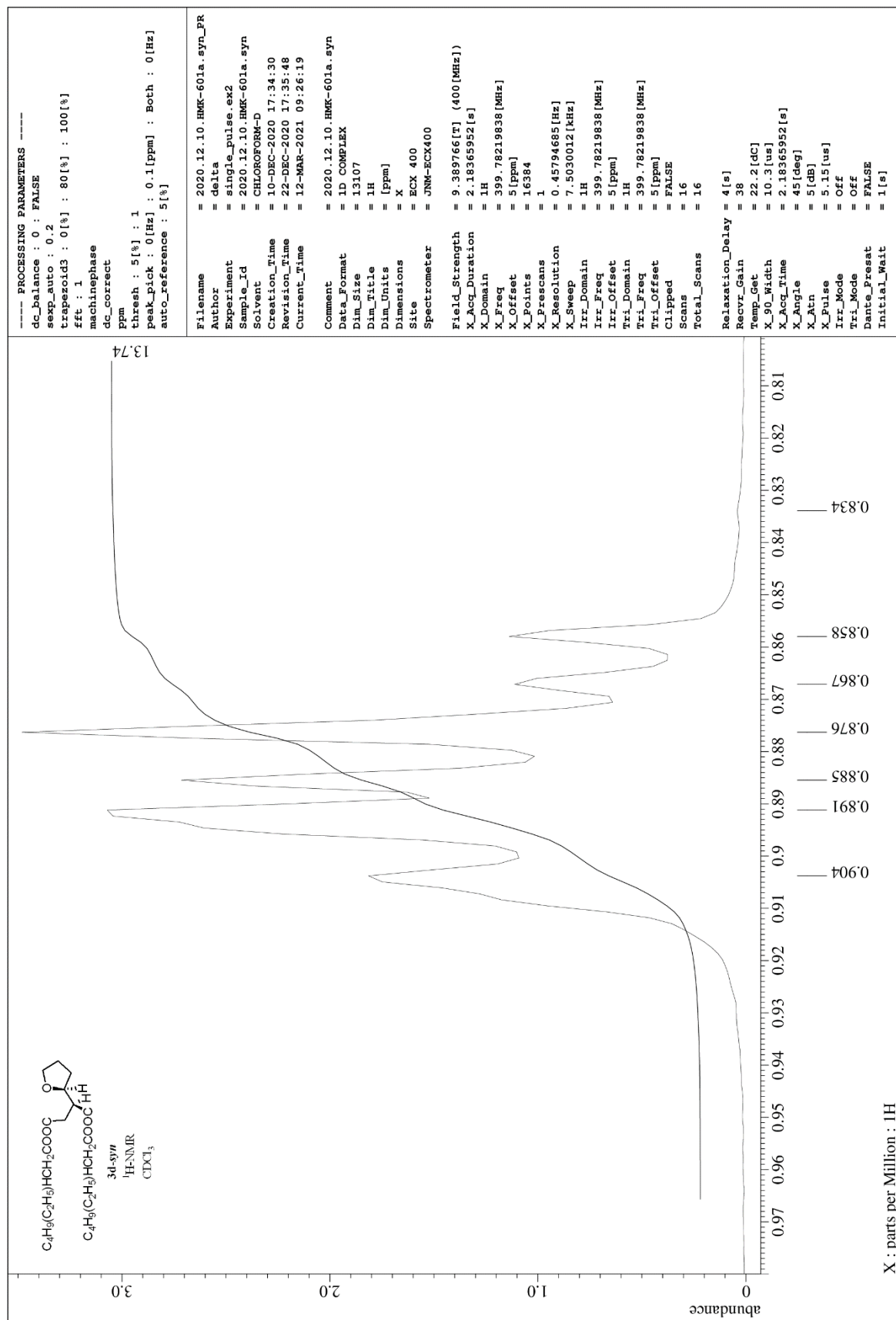


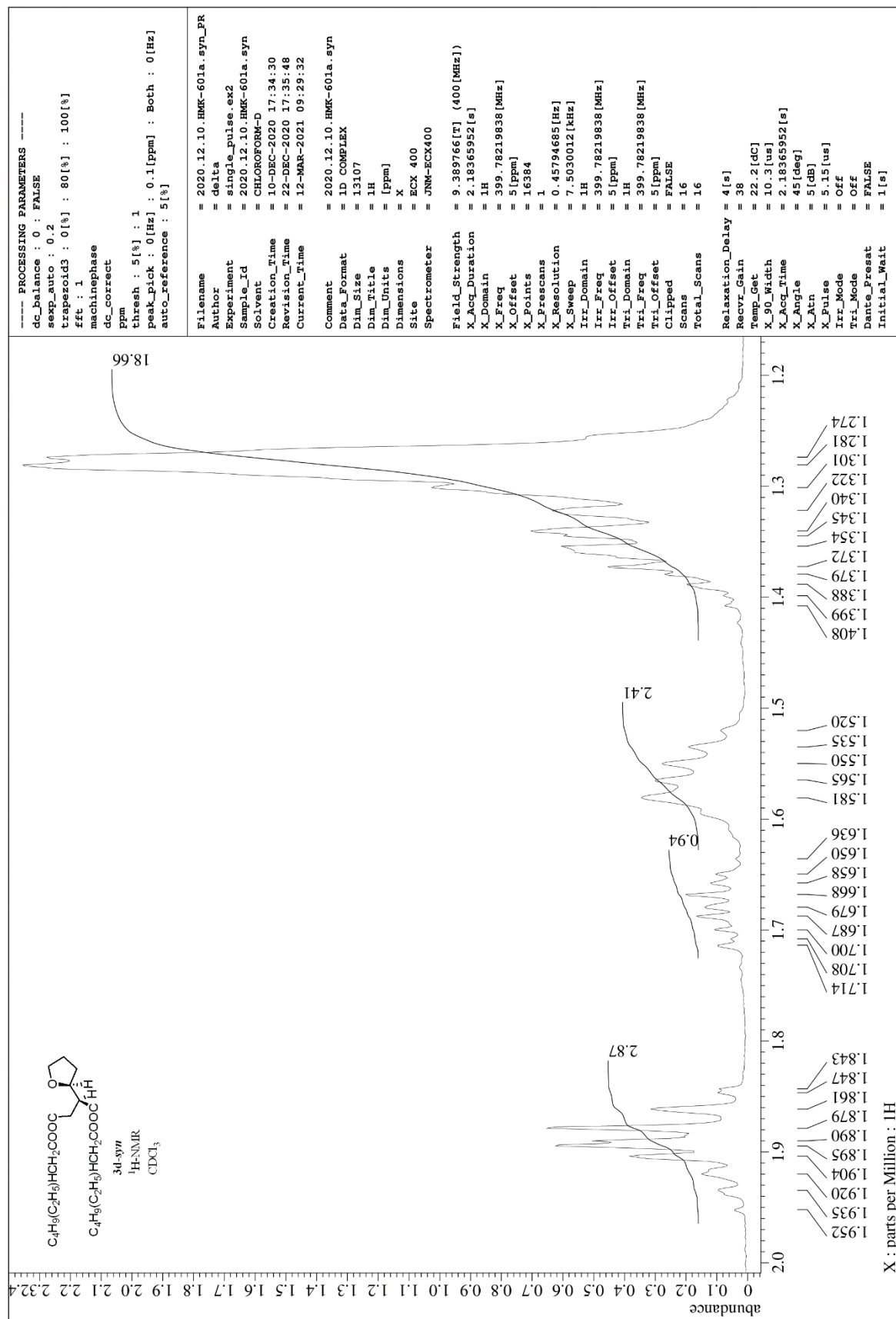


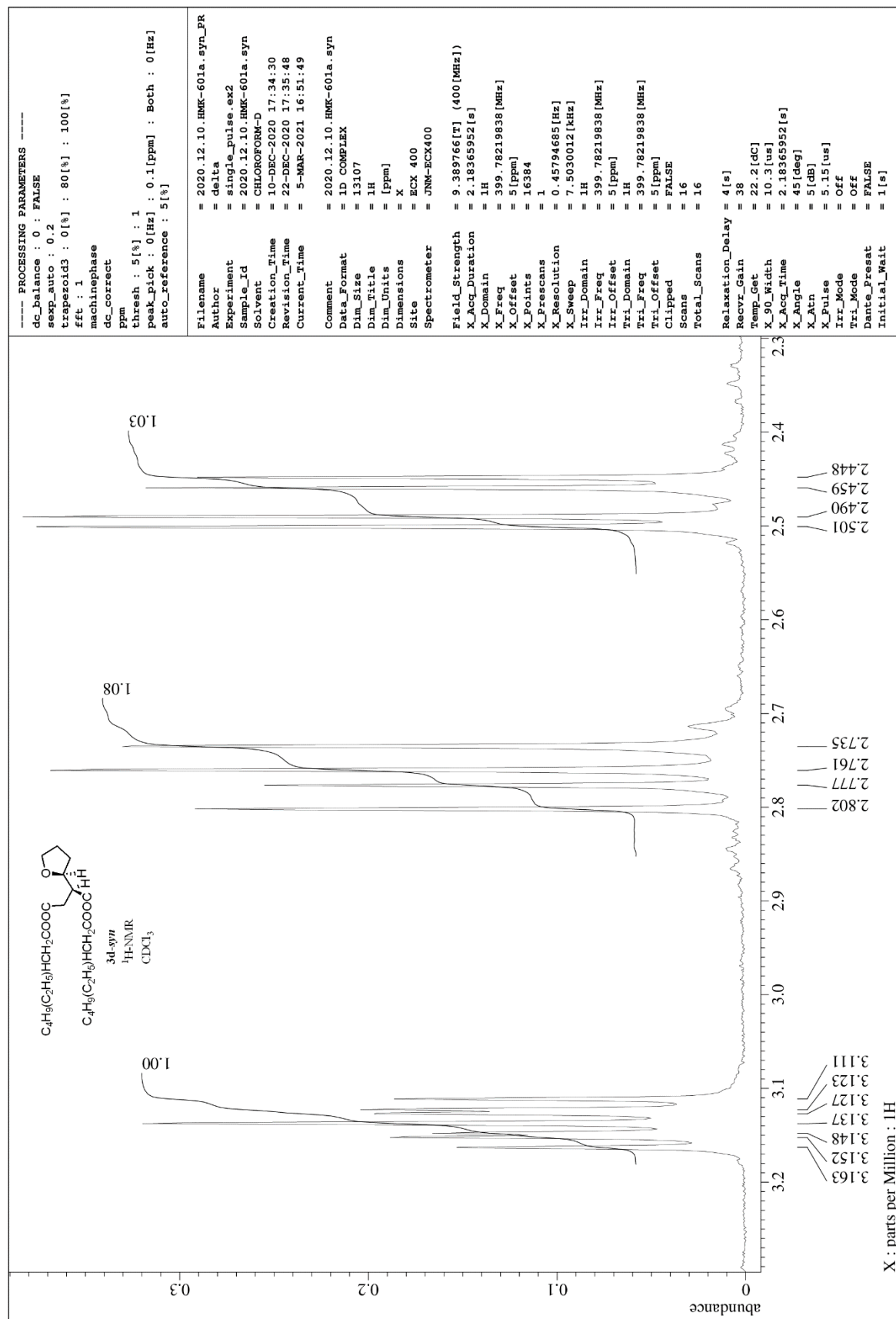


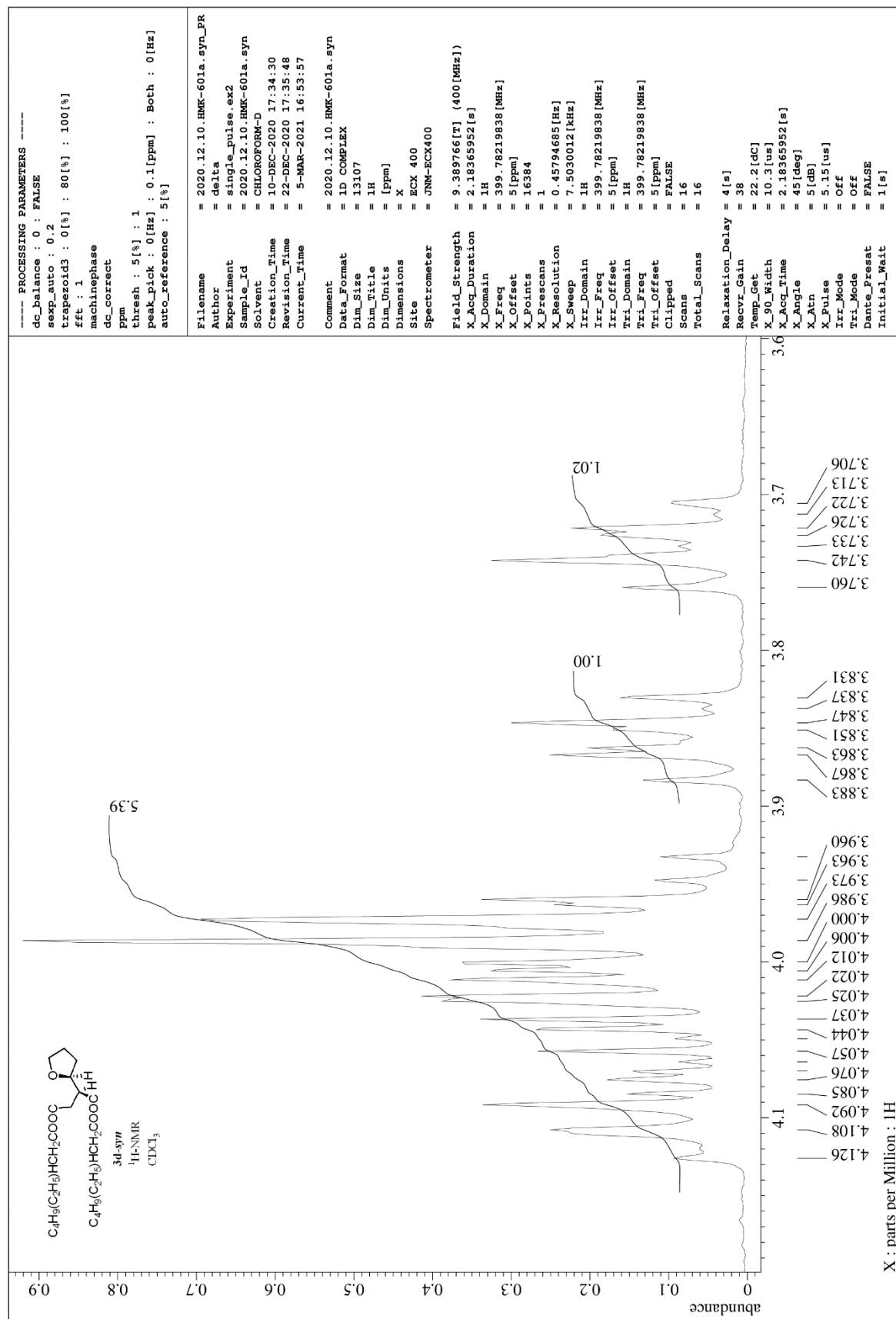


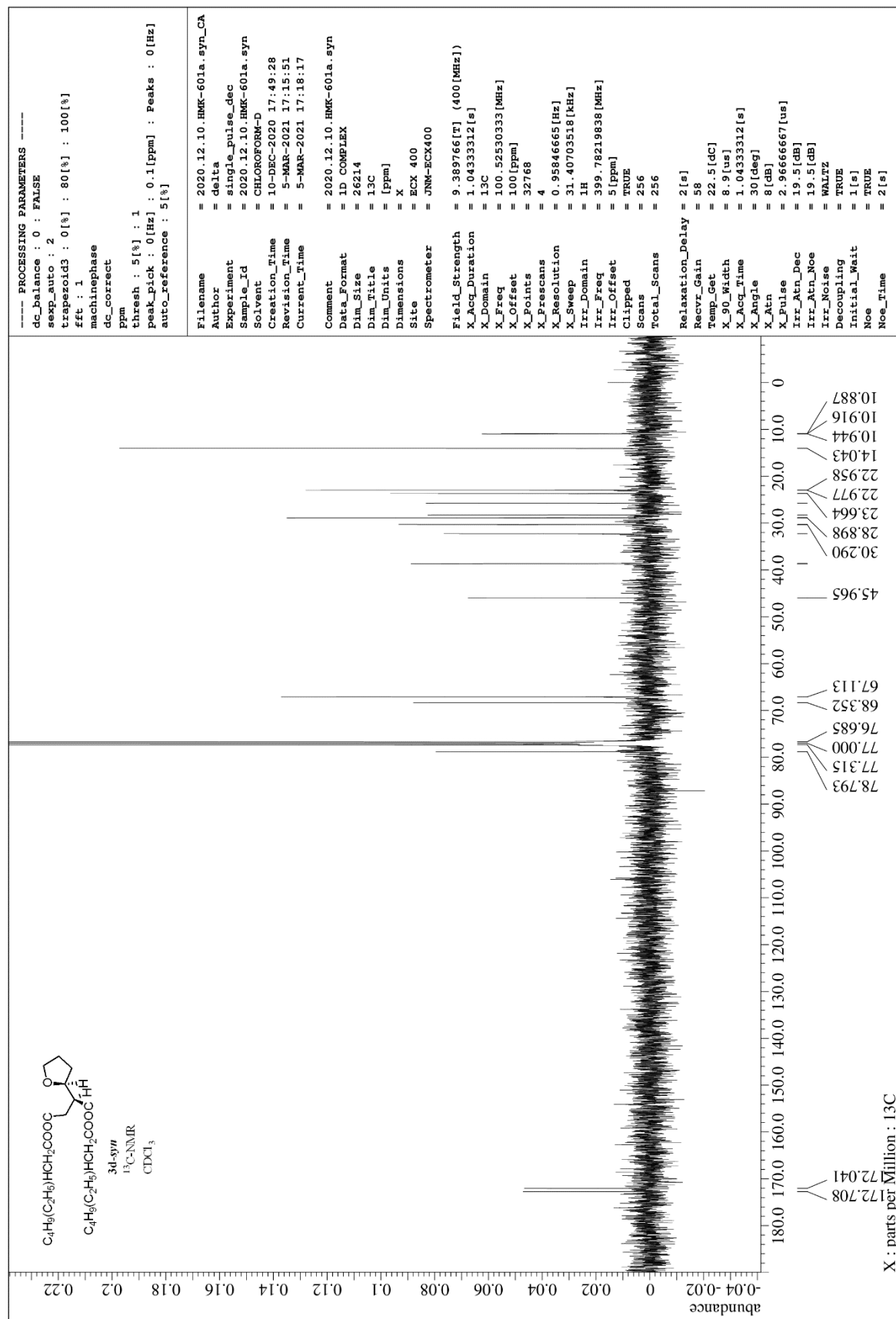


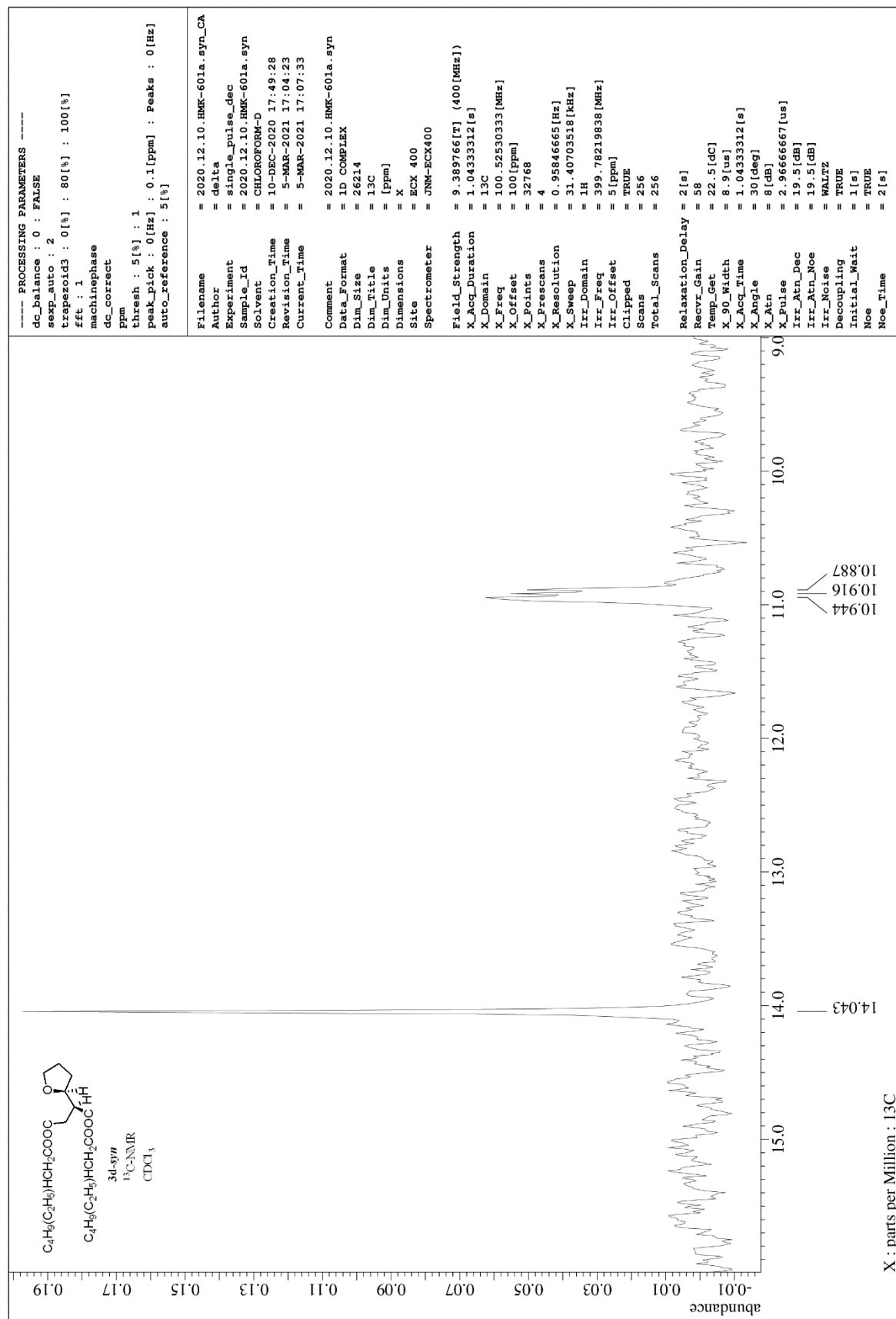


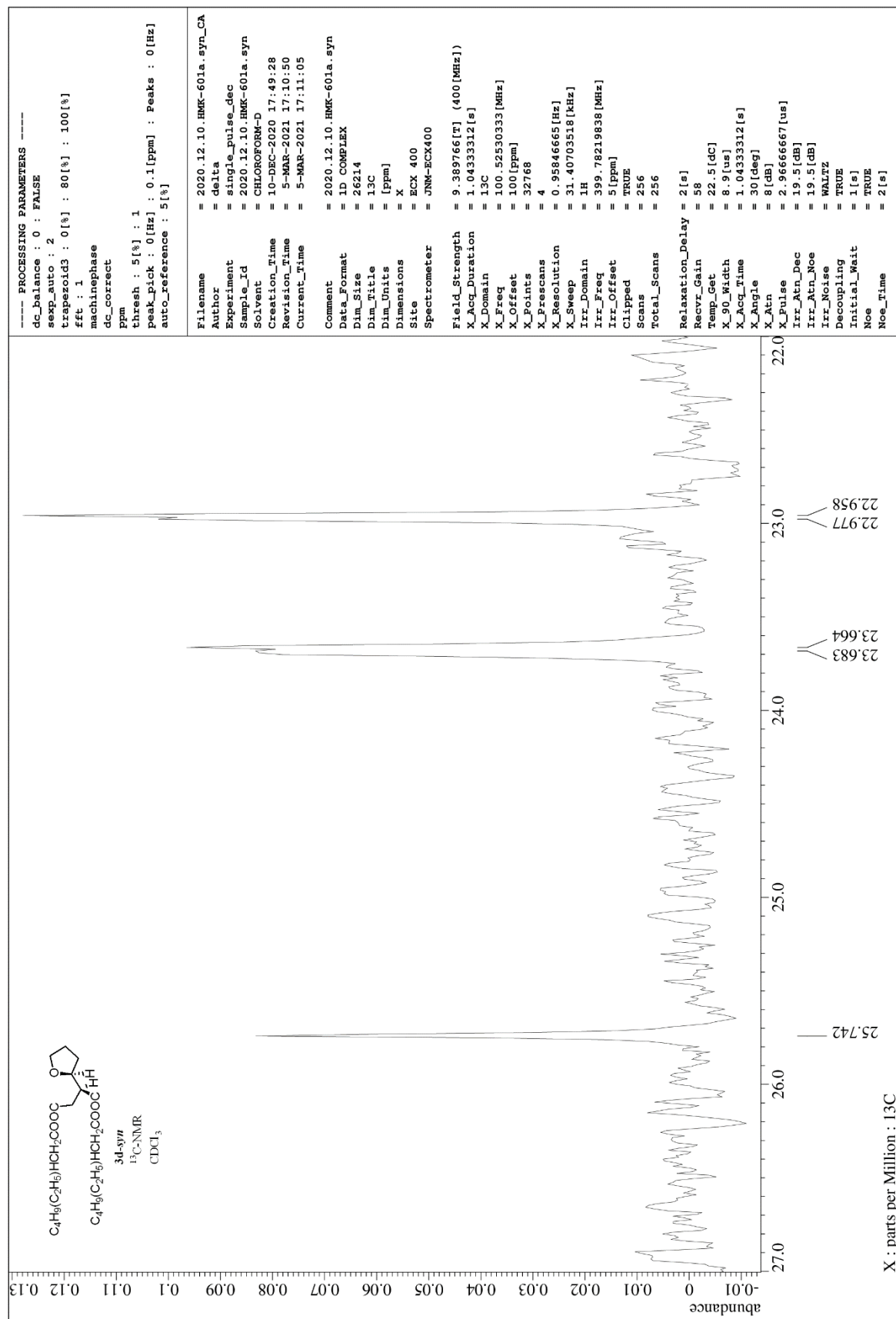


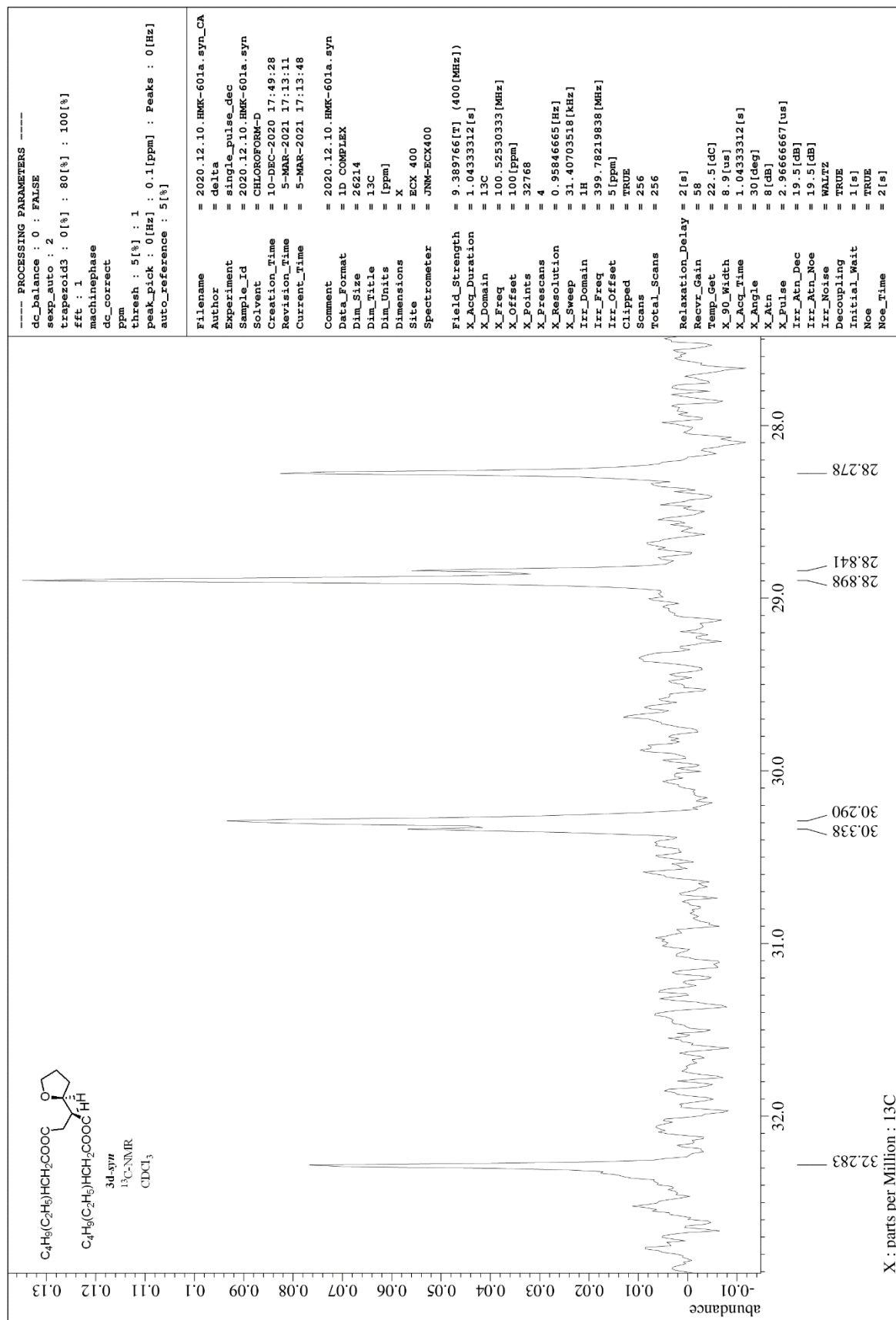


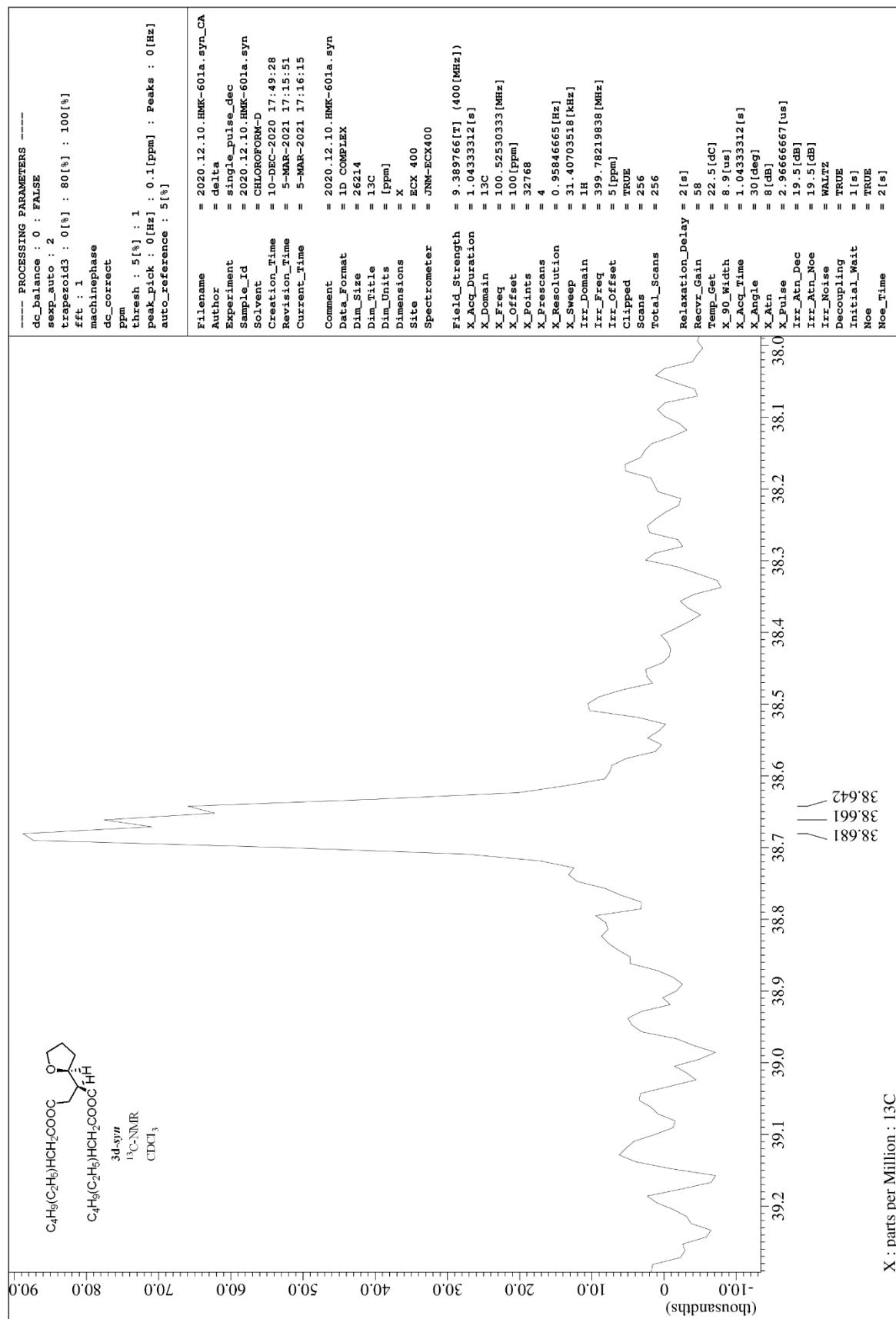


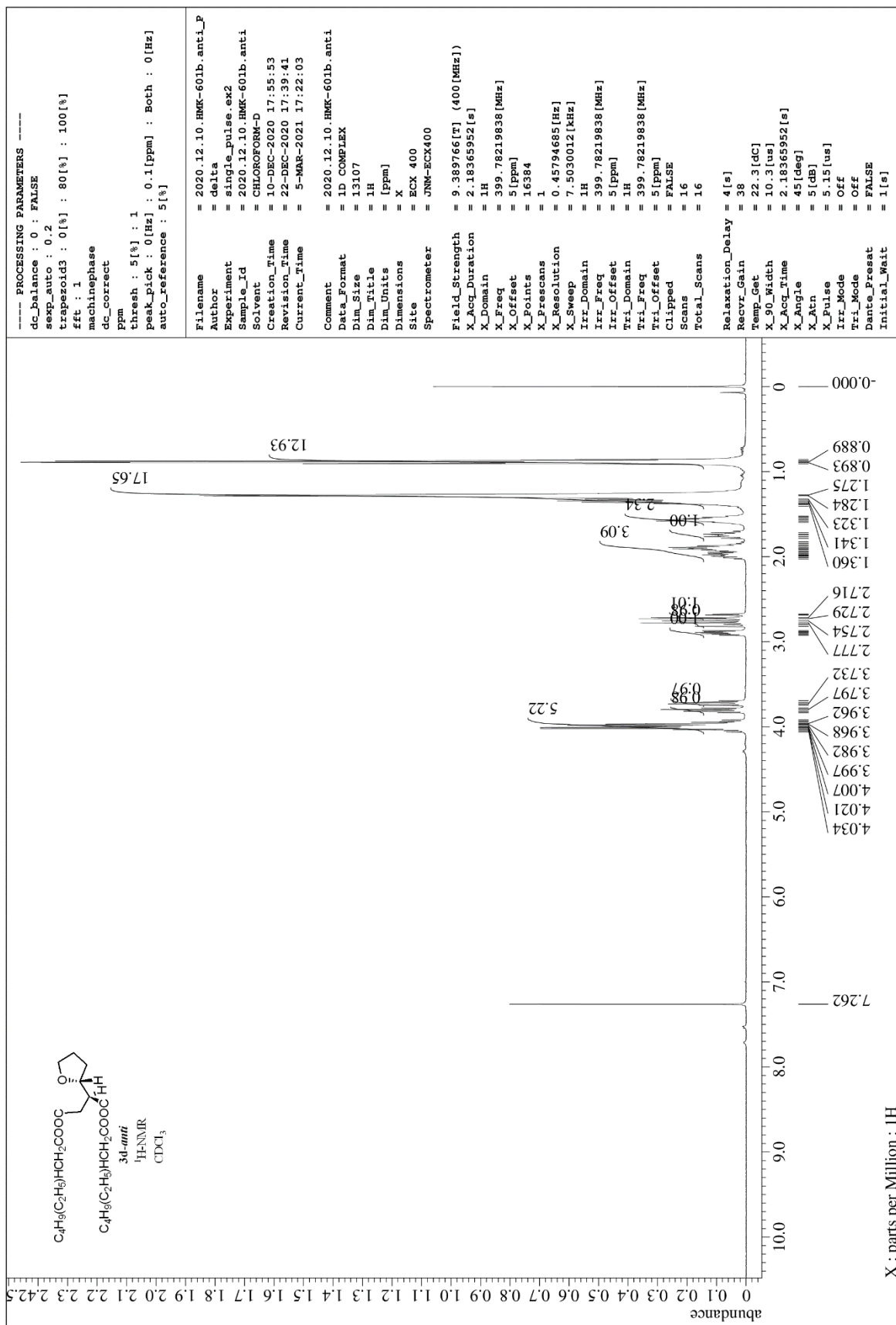


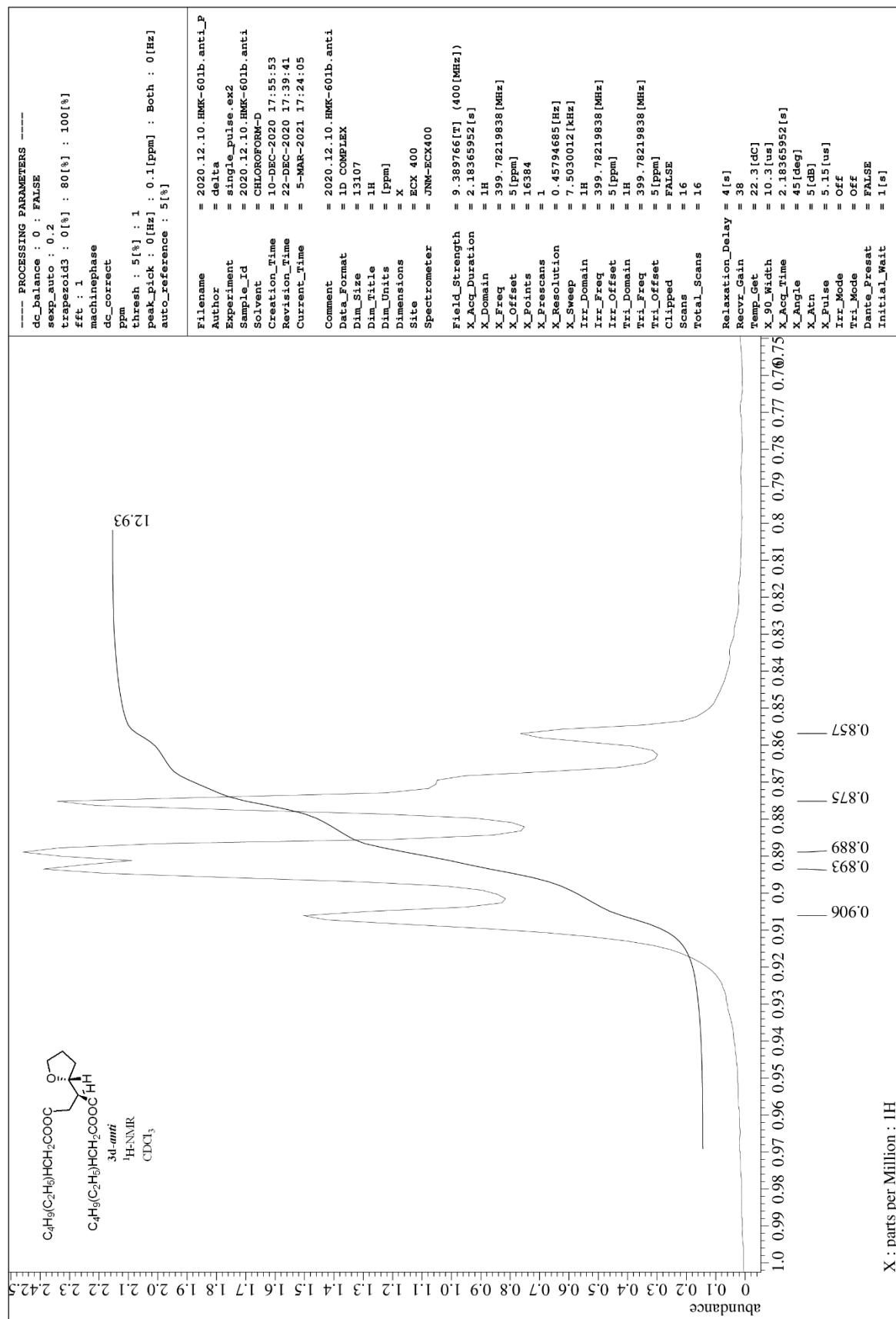


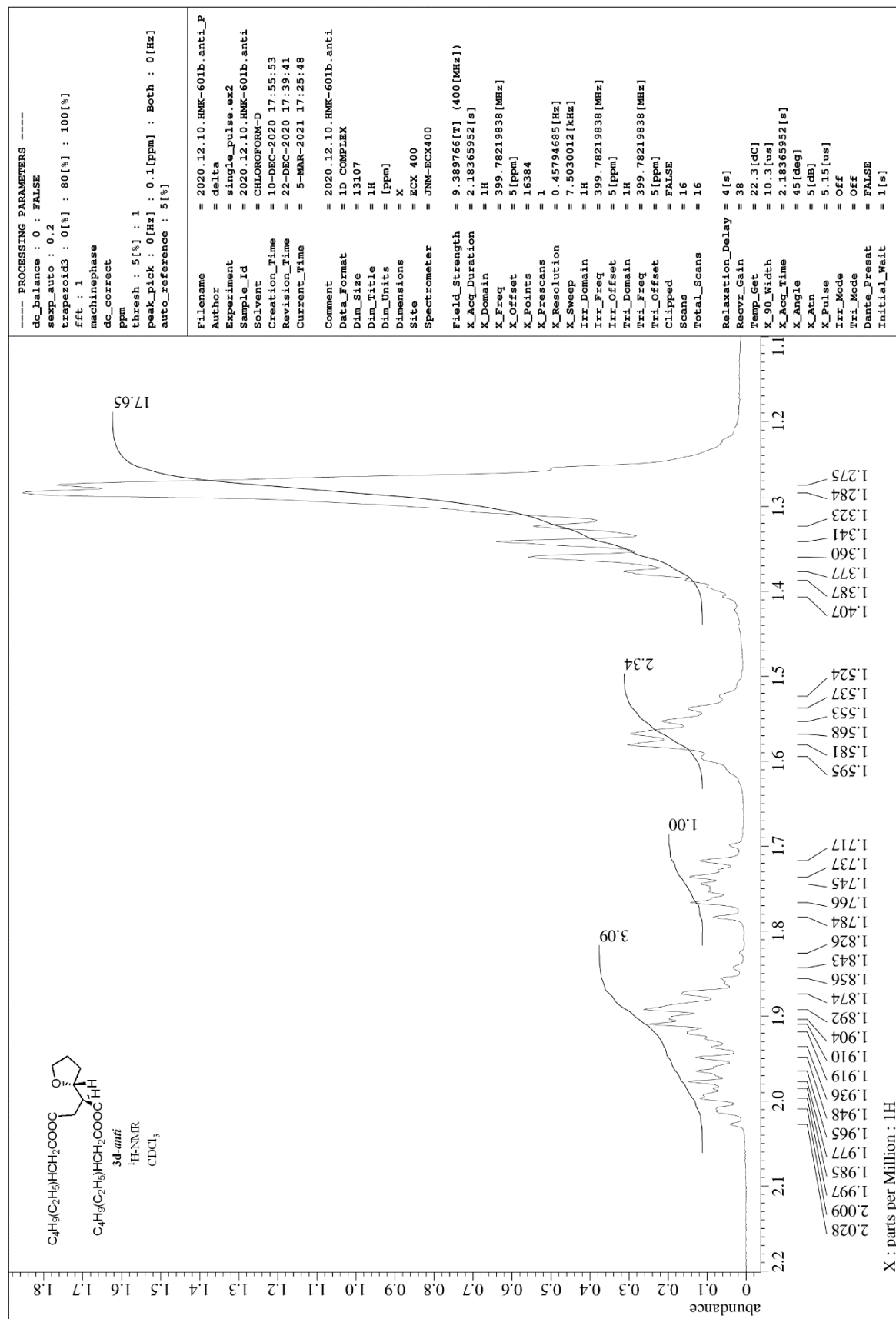


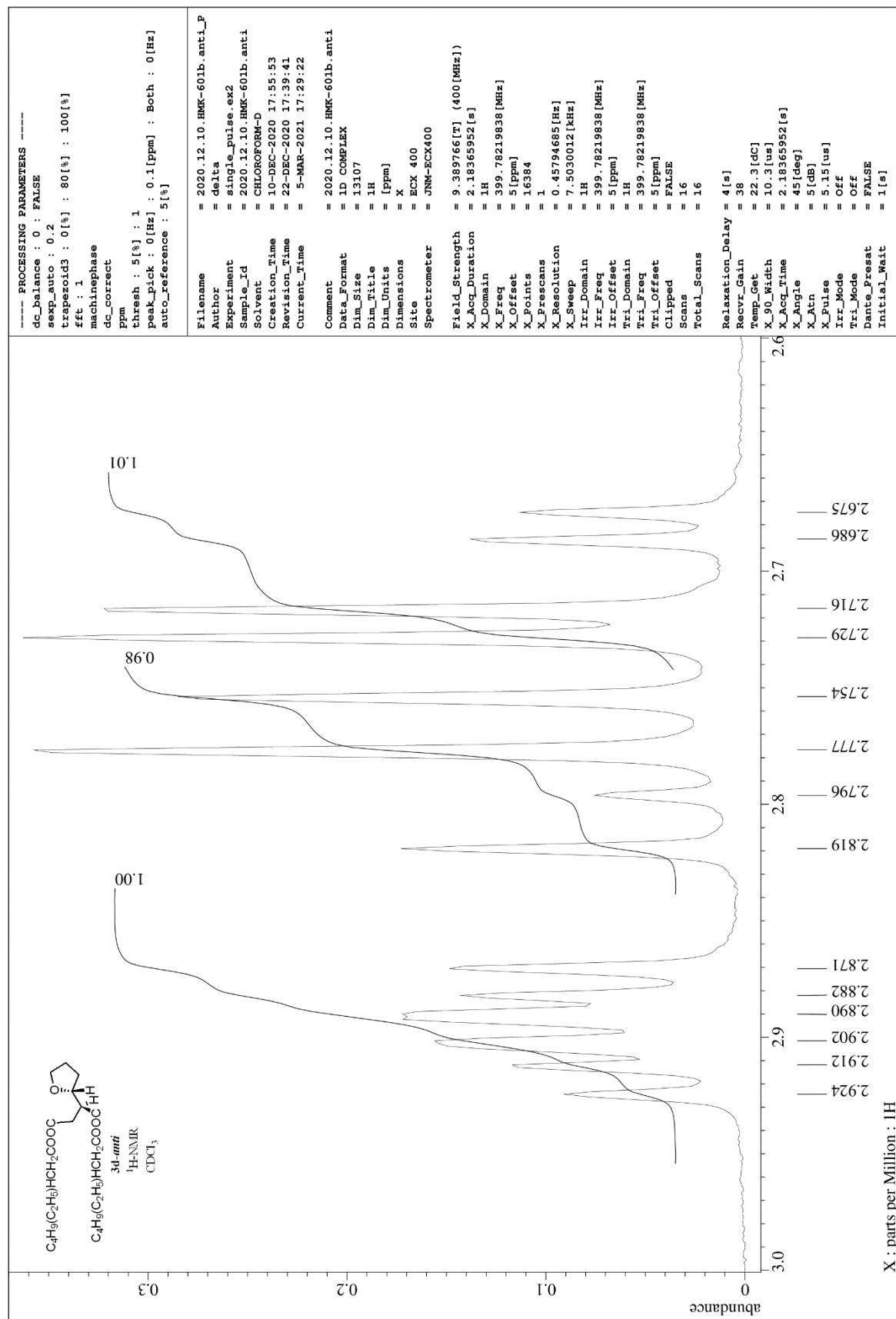


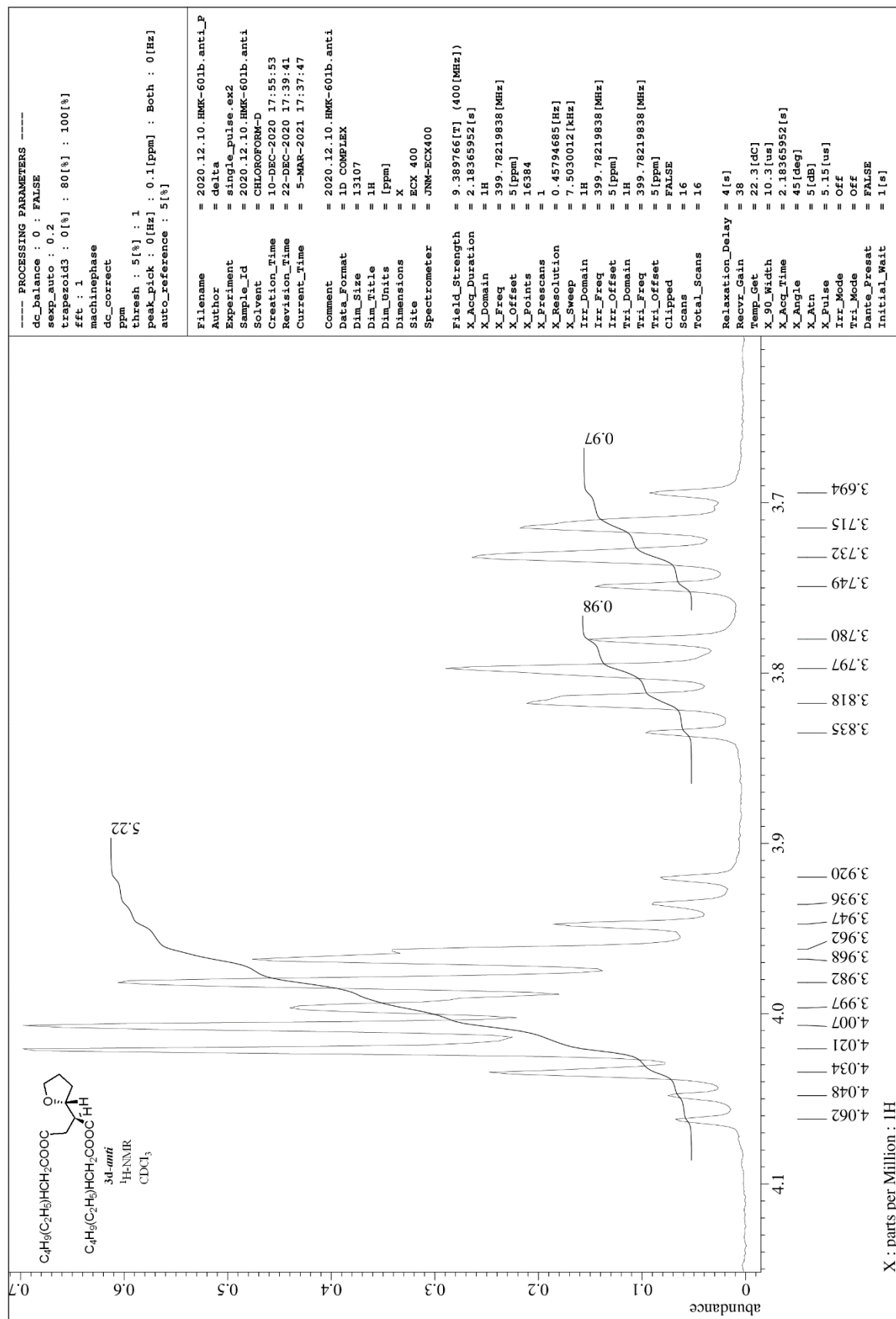


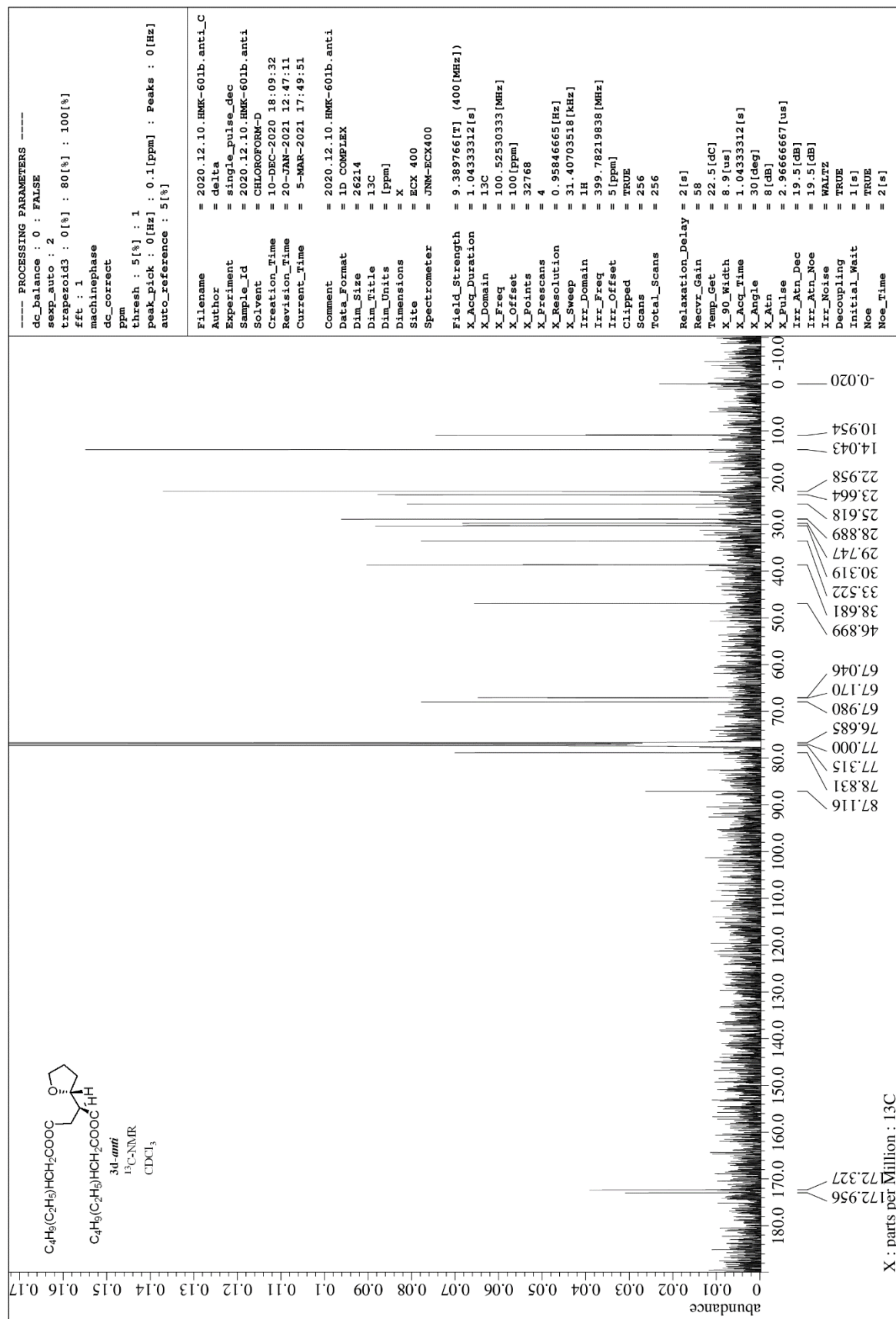


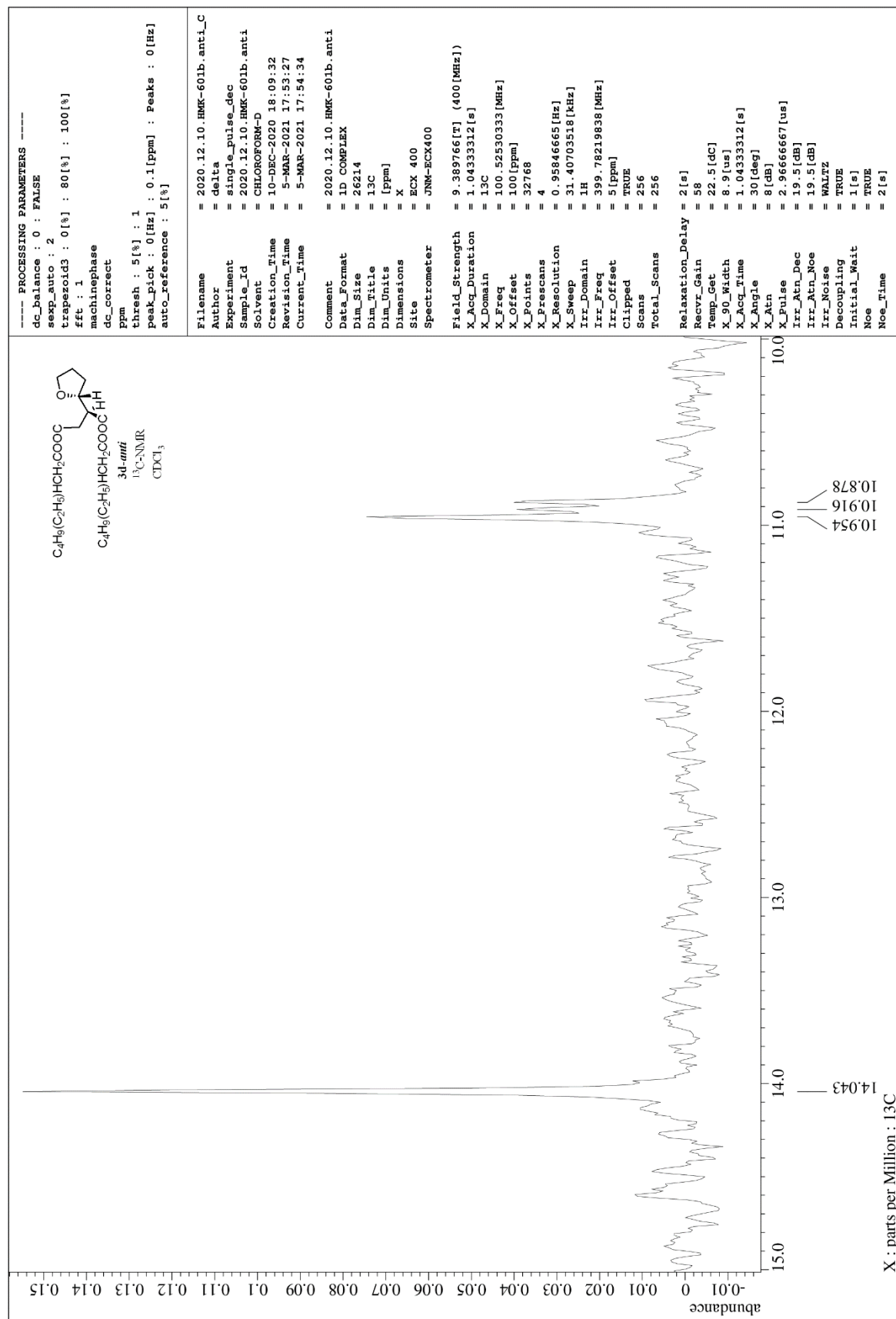


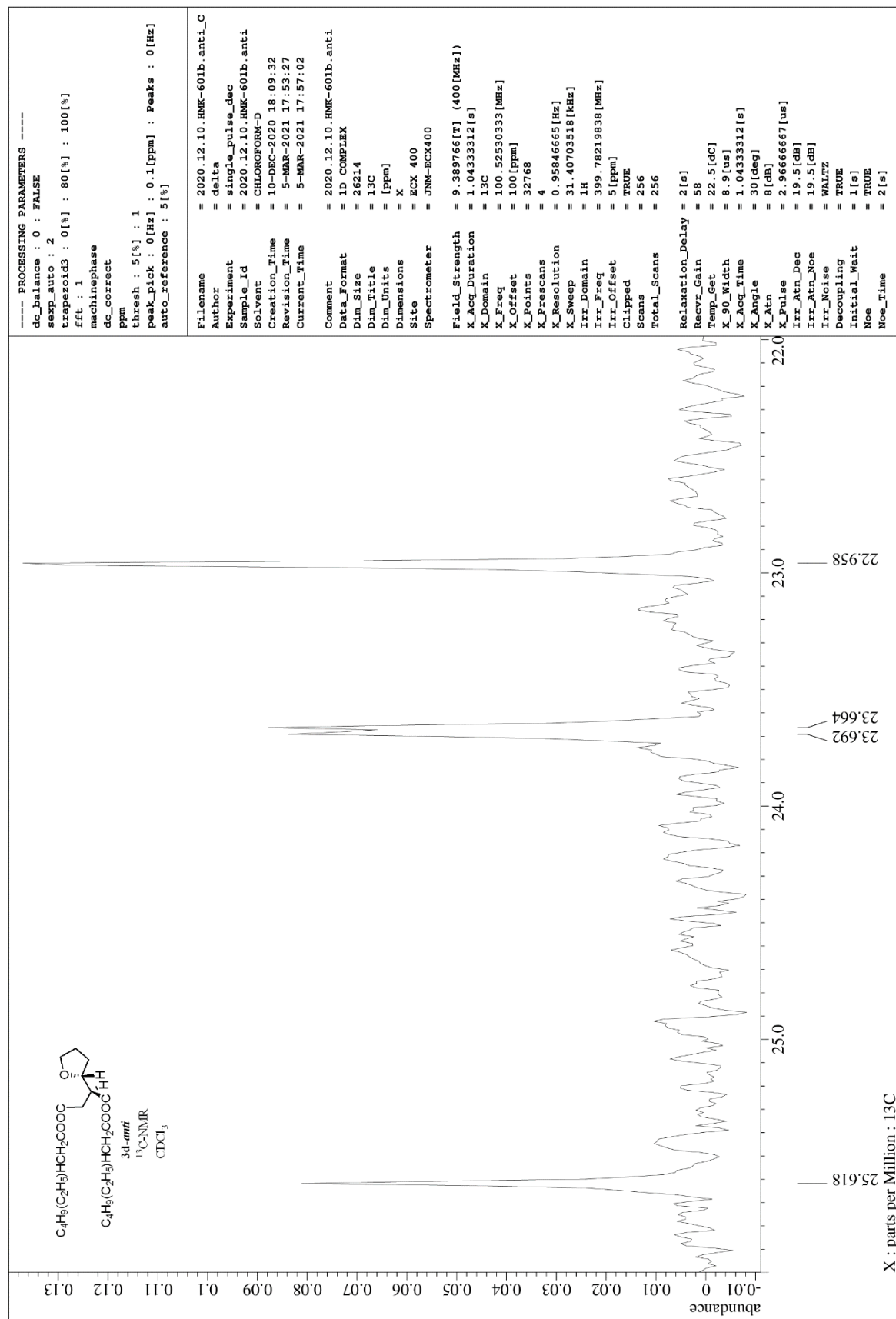


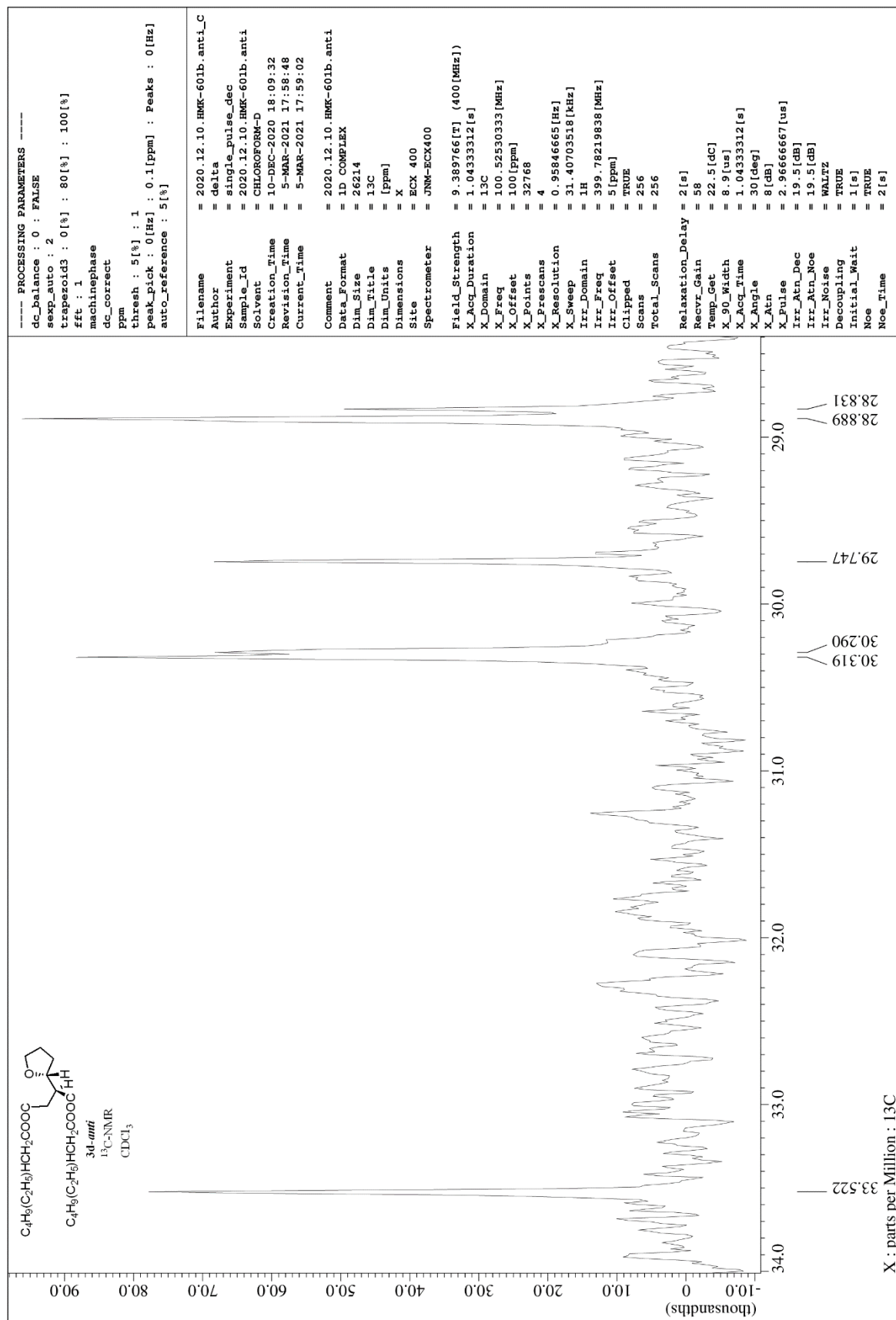


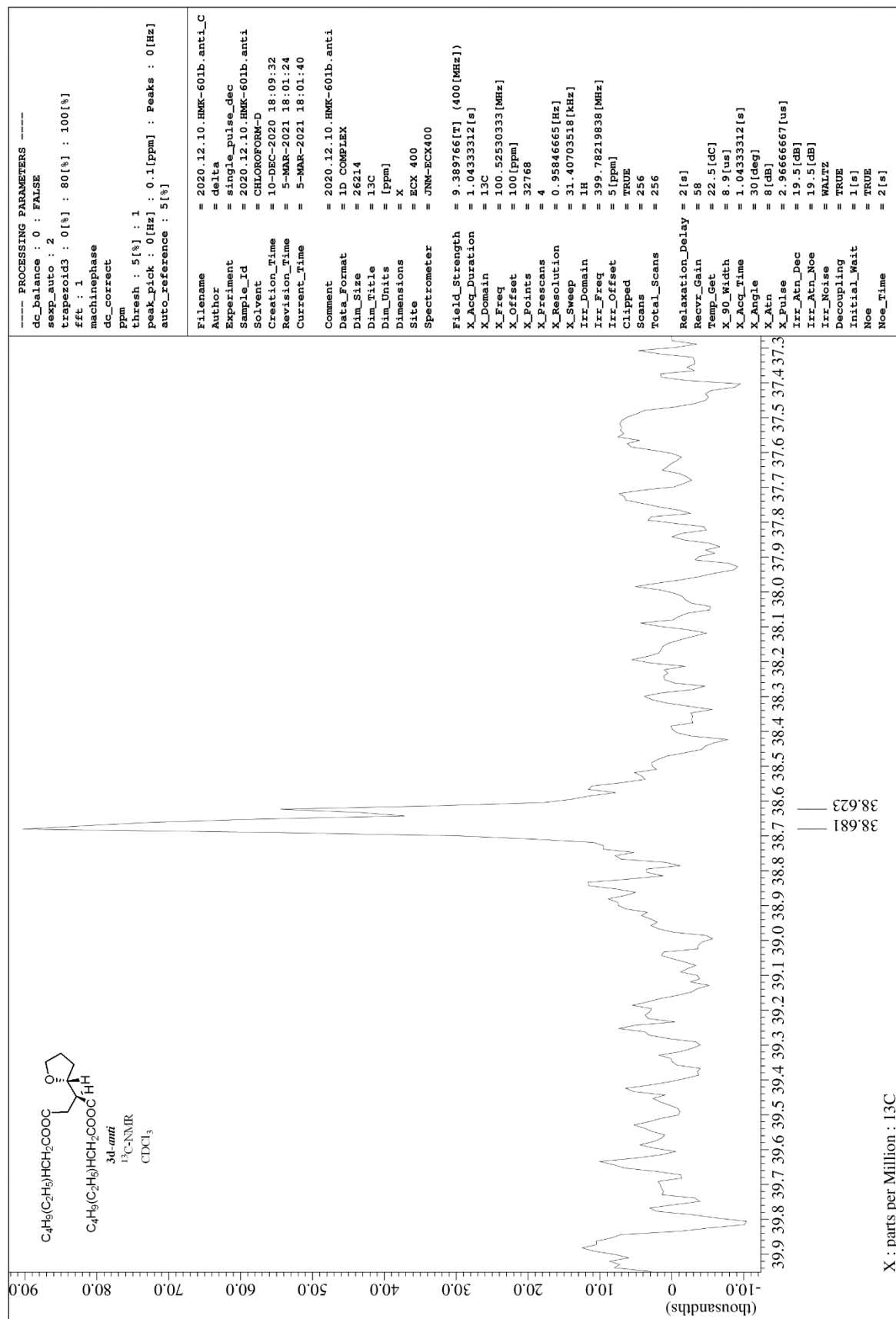


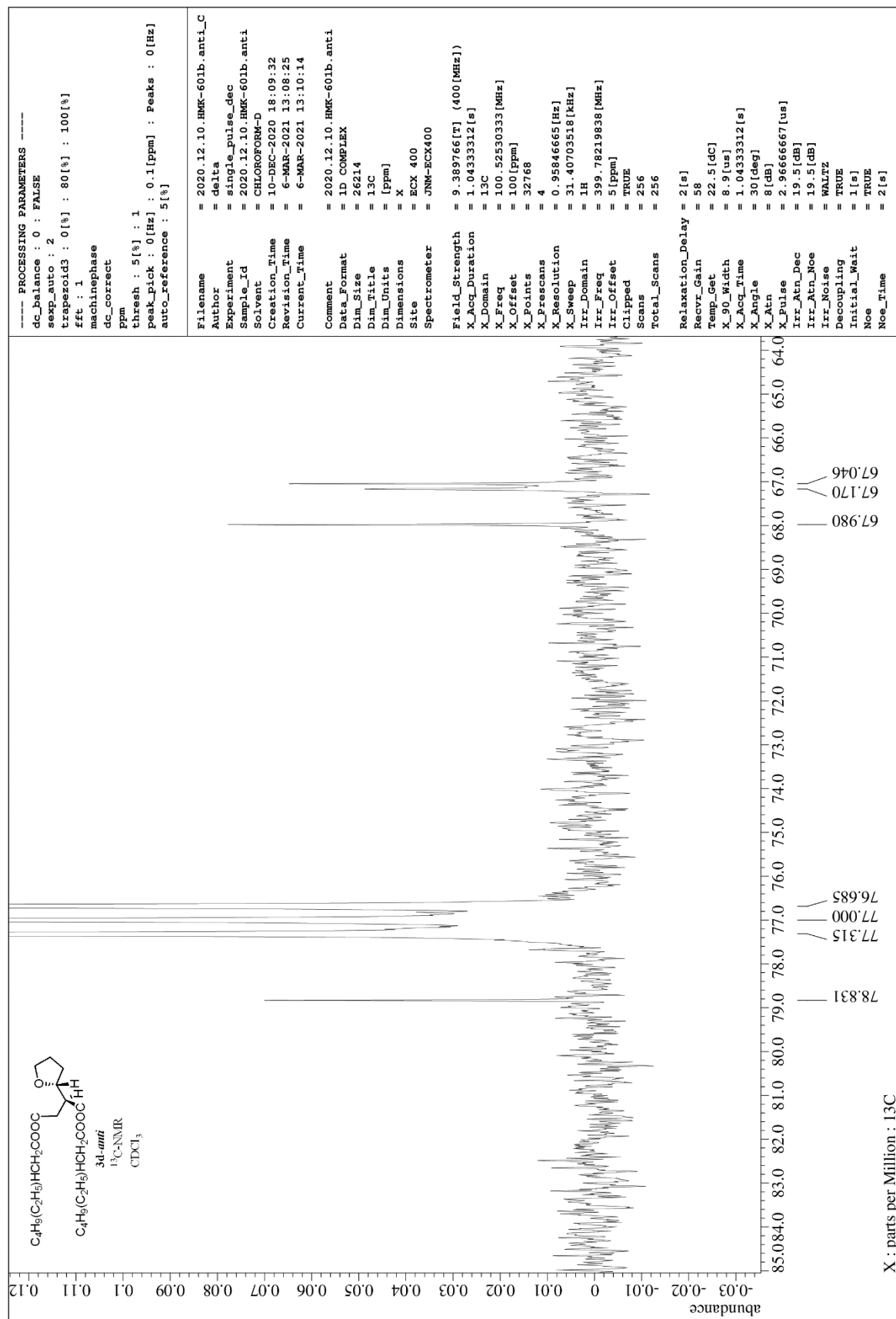


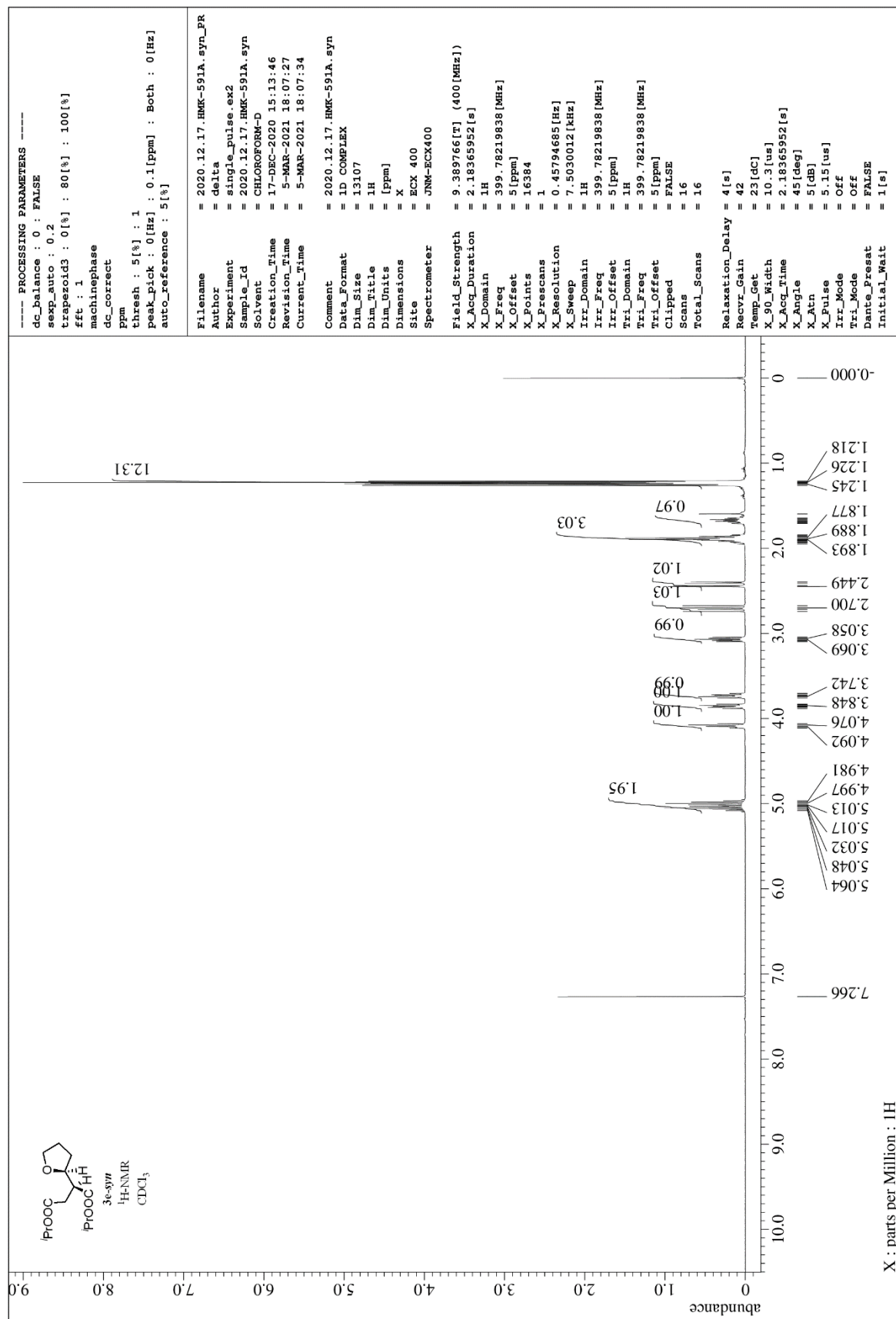


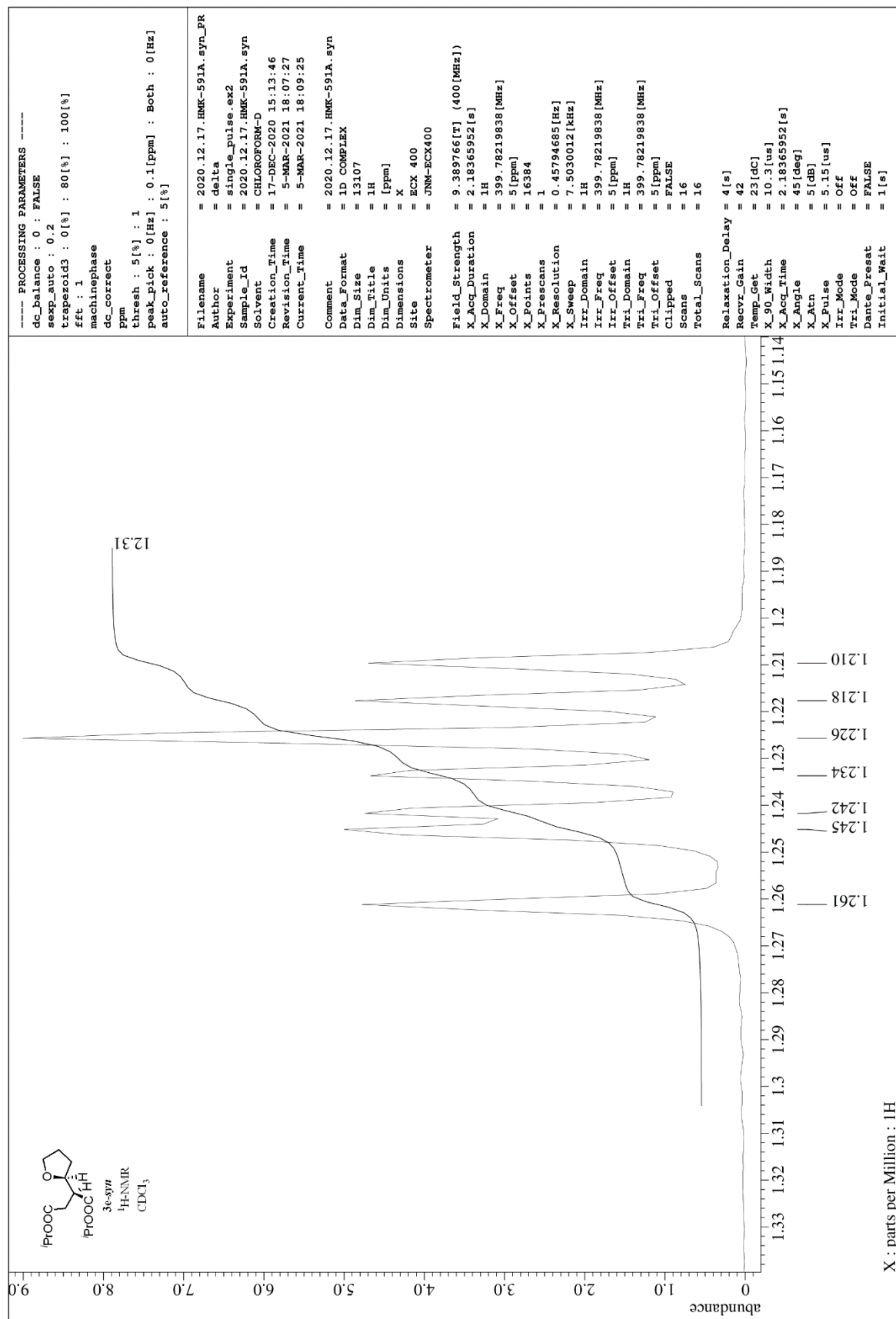


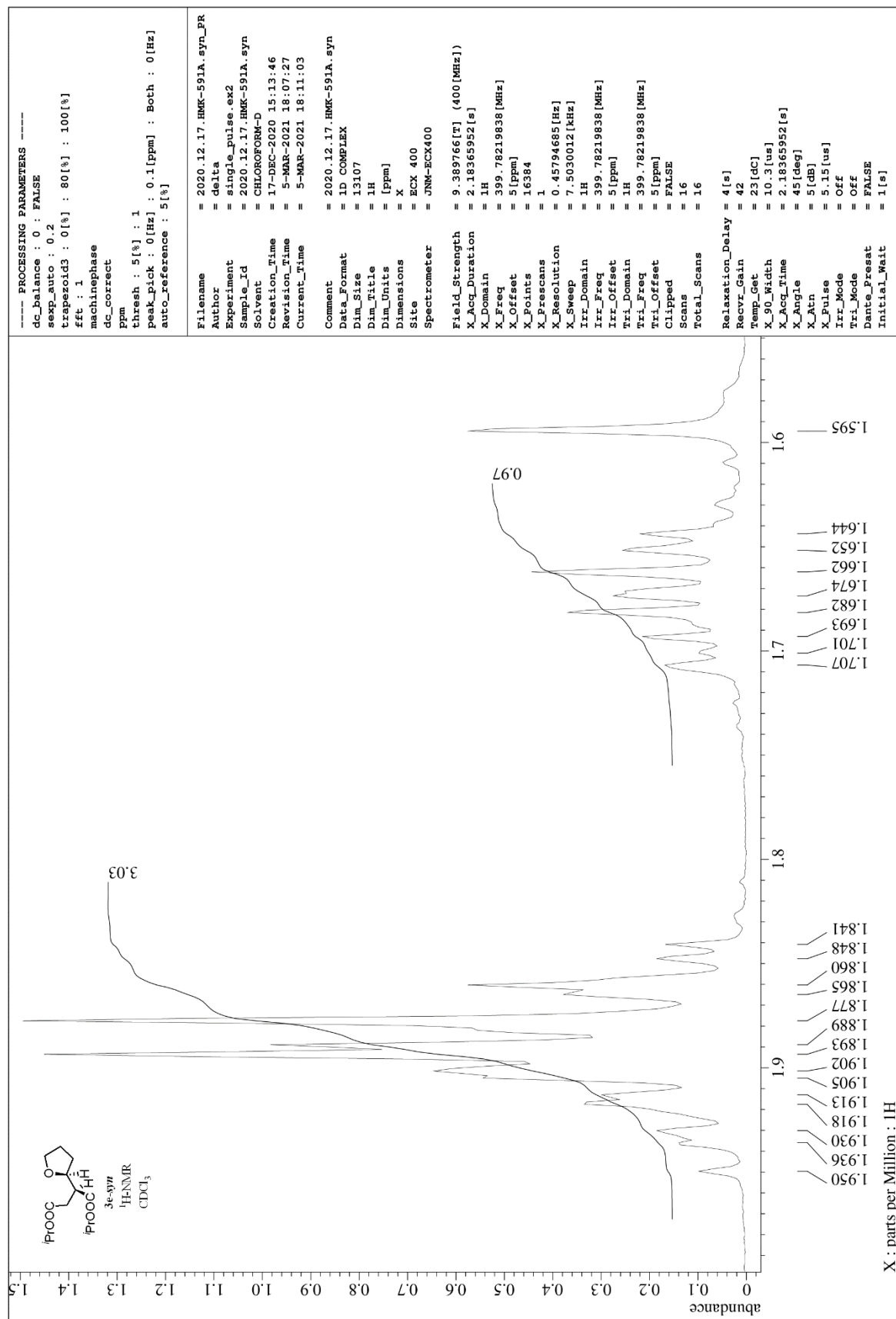


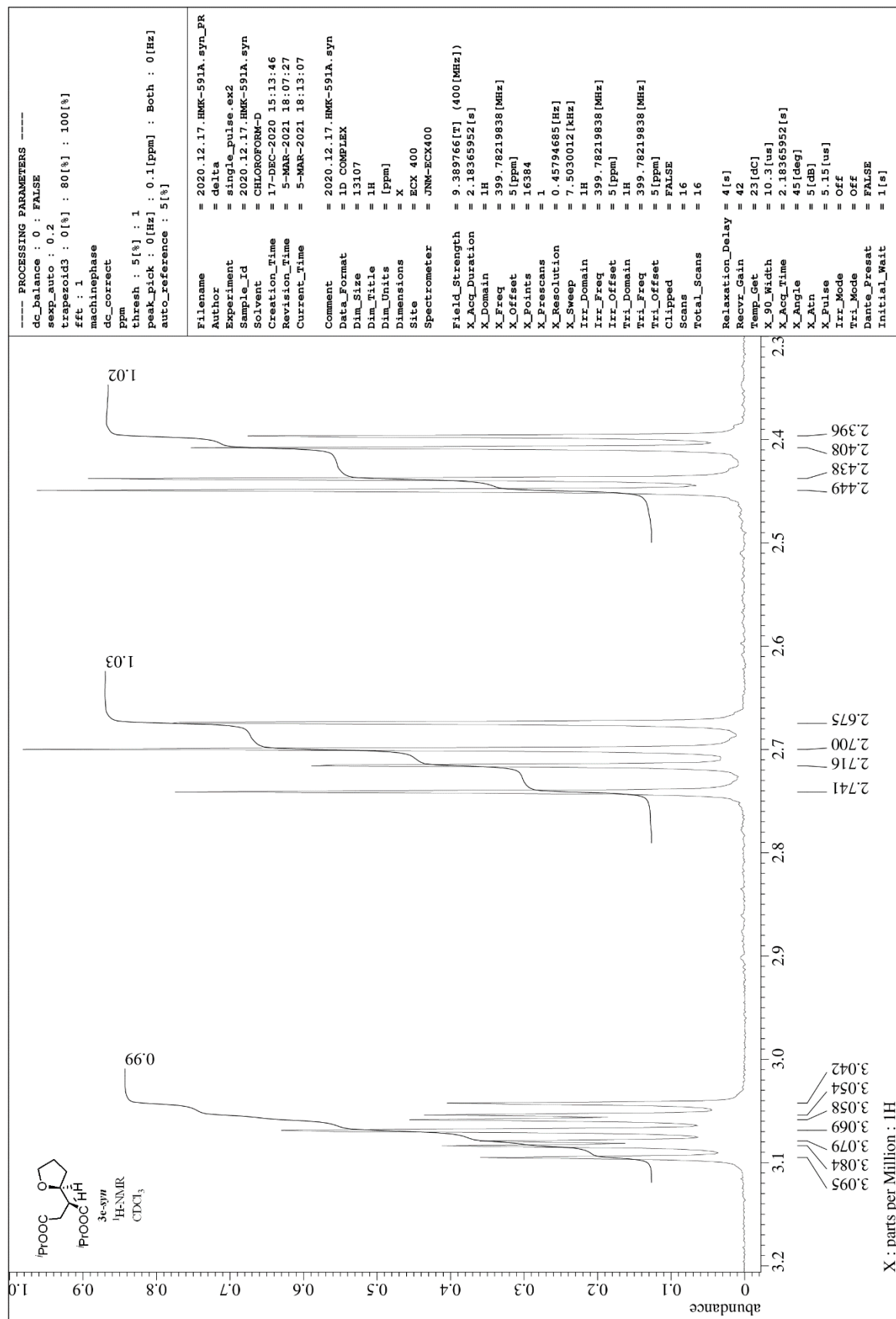


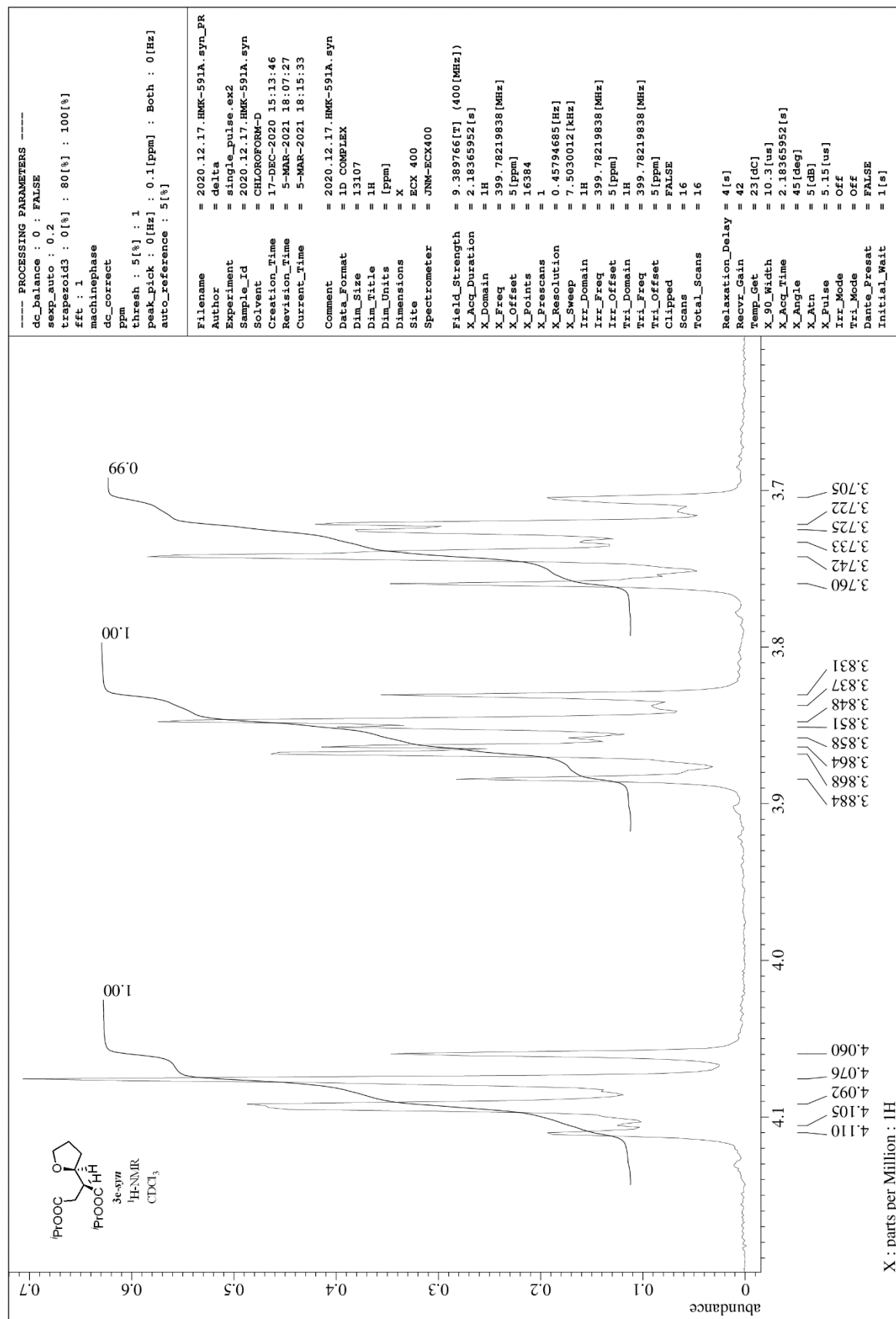


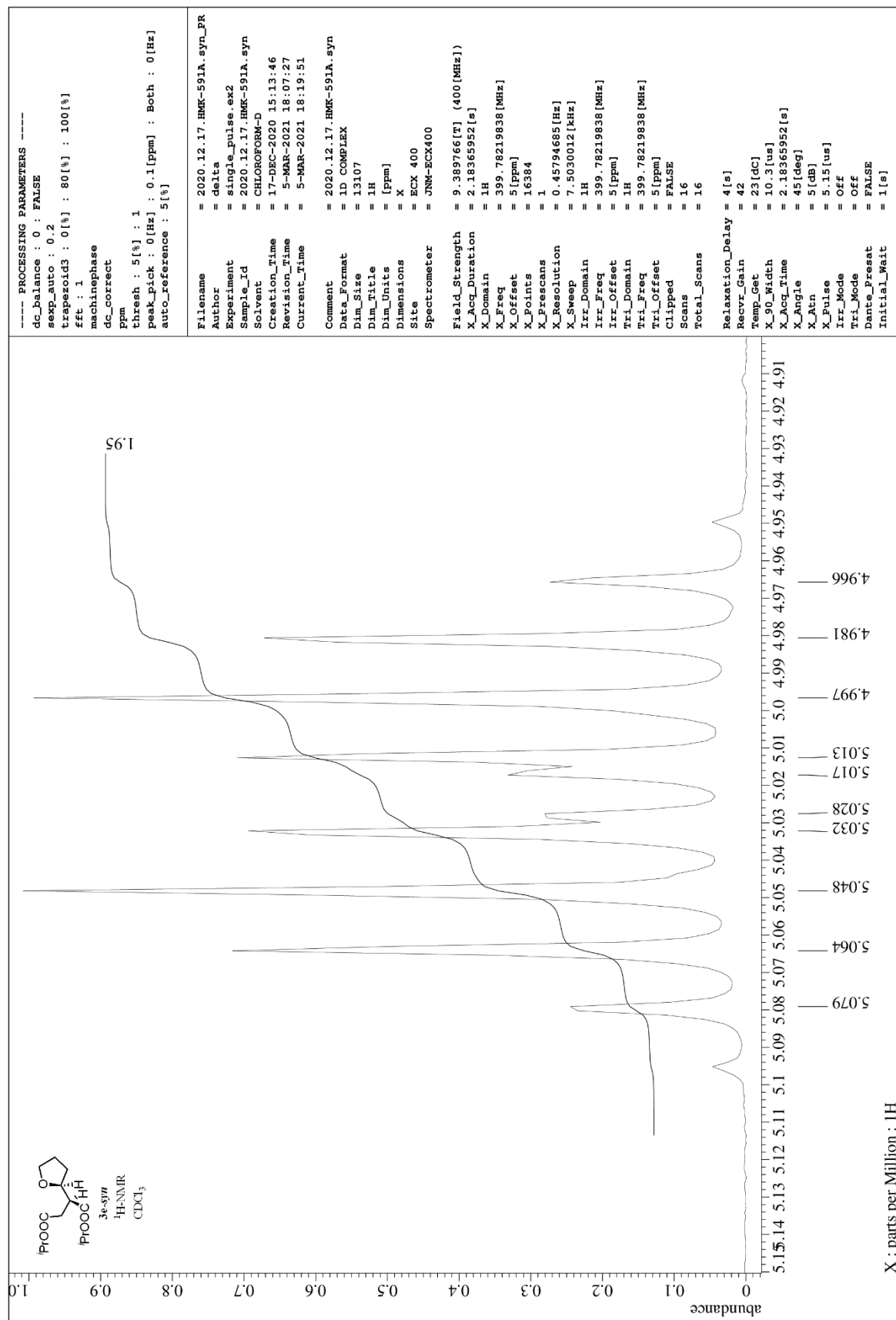


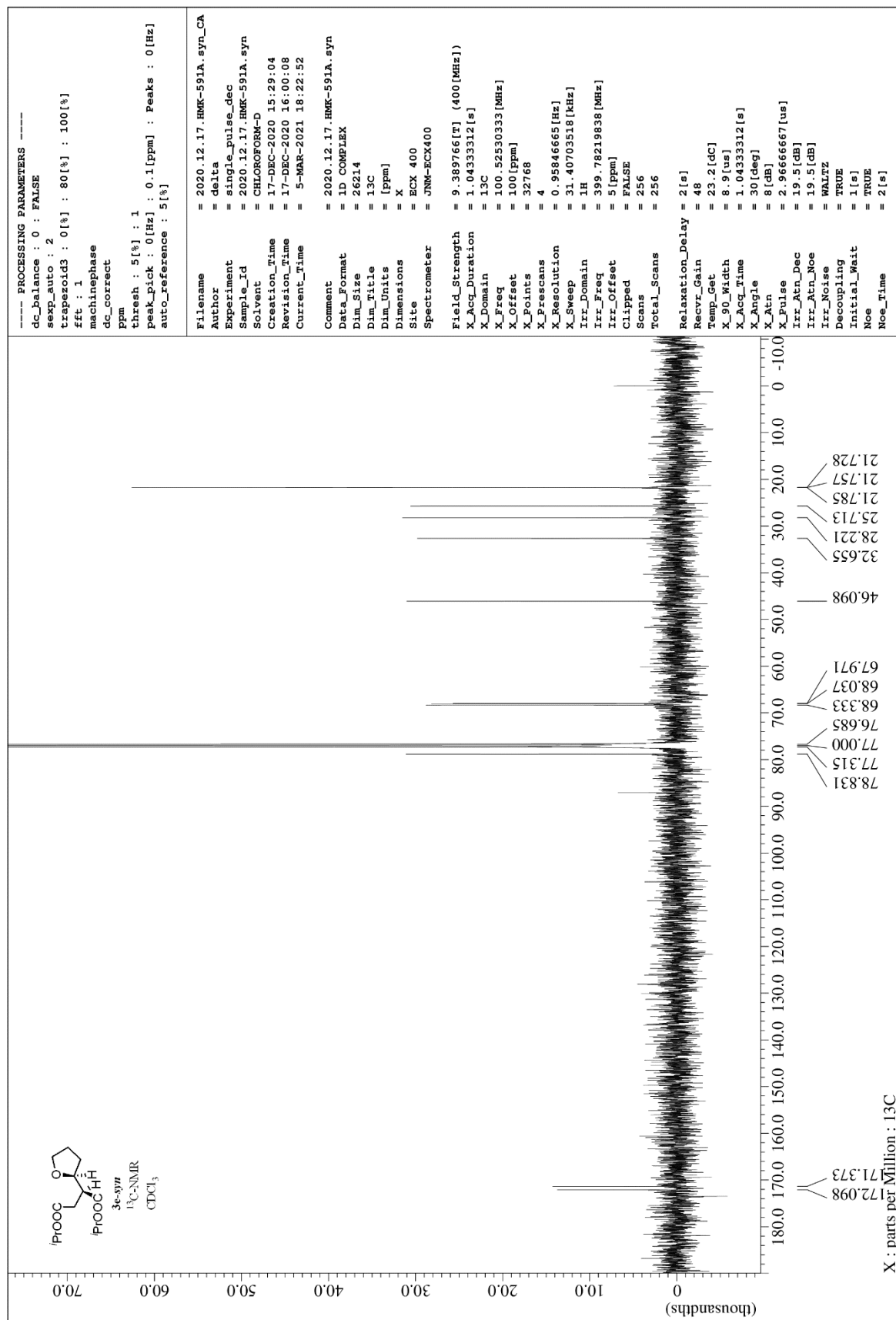


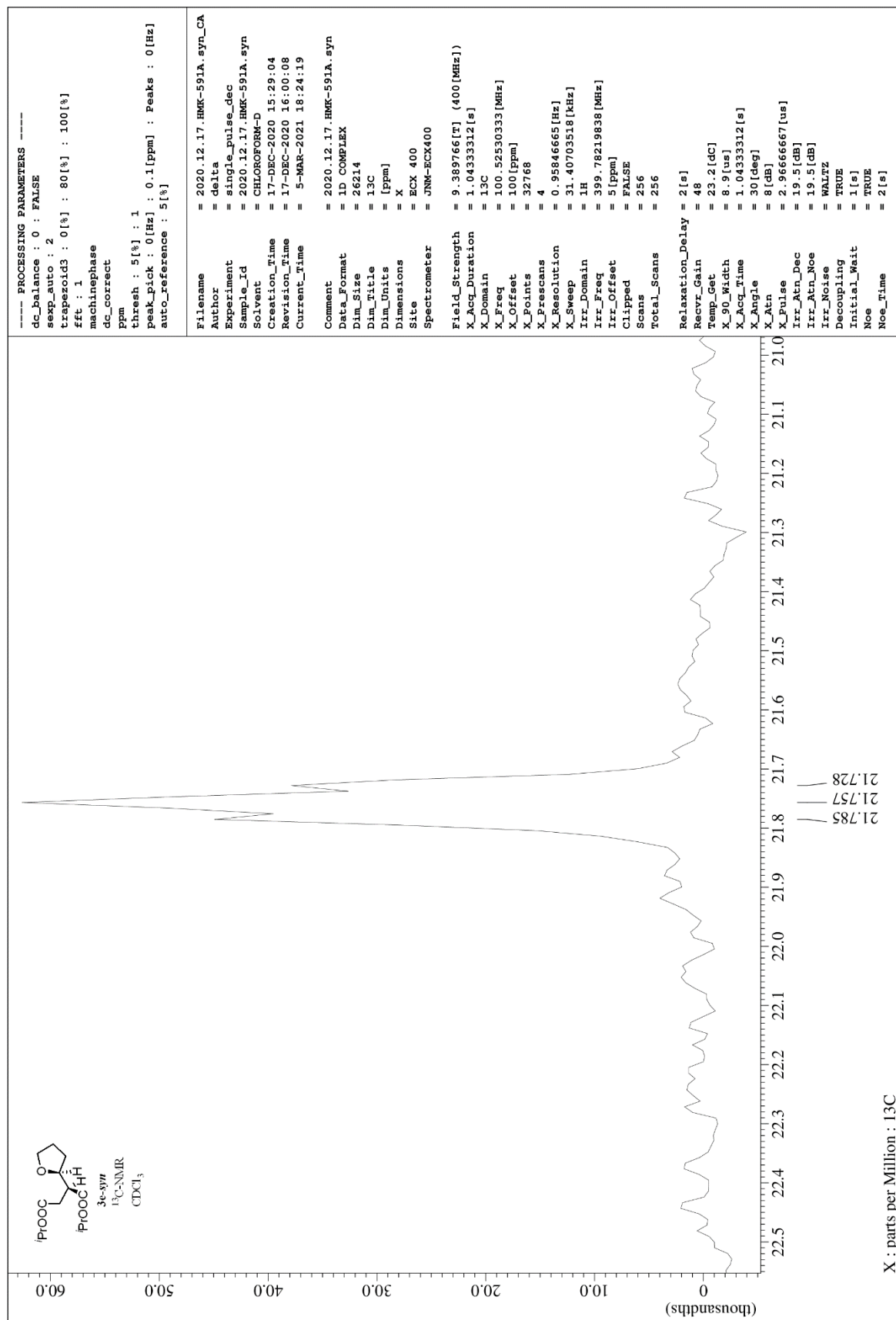












X : parts per Million : 13C

