

**B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed metal-free hydrogenation of 2-oxazolones**

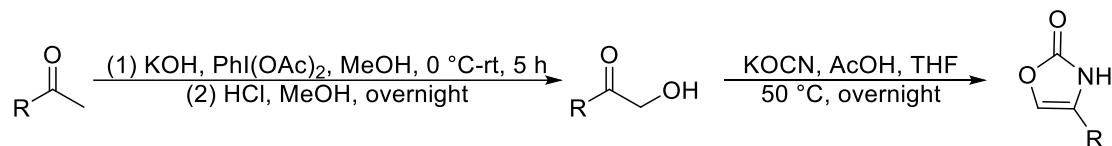
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**Supporting Information**

**General consideration:** All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on Bruker AV 400 and 500 at ambient temperature with  $\text{CDCl}_3$  and  $d_6$ -DMSO as solvent and TMS as internal standard. Chemical shifts ( $\delta$ ) were given in ppm, referenced to the residual proton resonance of TMS (0), to the carbon resonance of the  $\text{CDCl}_3$  (77.23) and  $d_6$ -DMSO (39.53). Coupling constants ( $J$ ) were given in Hertz (Hz). IR spectrums were recorded on Perkin-Elmer-983 spectrometer. Optical rotations were measured with Rudolph-Autopol-VI automatic polarimeter. High resolution mass spectra (HRMS) were recorded on Thermo Fisher Exactive orbitrap mass instrument (ESI). Column chromatography was performed on silica gel (200-300 mesh). All solvents were purified by conventional methods, distilled before use. Commercially available reagents were used without further purification.

### Representative procedure for the synthesis of 1



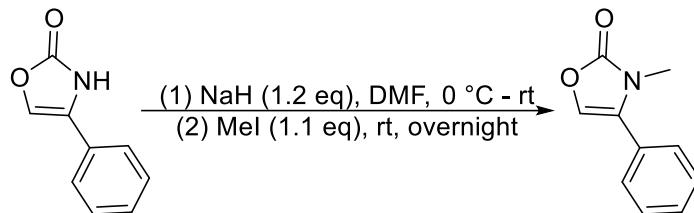
### Representative procedure for the synthesis of 4-(*p*-tolyl)oxazol-2(3*H*)-one (1):

To a stirred solution of the corresponding *p*-methylacetophenone (3.4 g, 1.0 eq, 25.0 mmol) and powdered potassium hydroxide (7.7 g, 5.5 eq, 137.5 mmol) in 50.0 mL methanol was added iodobenzene diacetate (9.1 g, 1.1 eq, 35.0 mmol) slowly at 0 °C. The reaction mixture was kept at room temperature until TLC indicated the total consumption of the *p*-methylacetophenone. Then the whole reaction mixture was concentrated. The residue was shaken with water and ethyl acetate. The combined

organic layer was evaporated under reduced pressure. The residue was dissolved in a mixture of 12.5 mL methanol and 12.5 mL aqueous hydrochloric acid (2.0 M) and then stirred overnight at room temperature. Water (100 mL) was added and the mixture was extracted with ethyl acetate ( $2 \times 100$  mL). The organic layers were washed with water ( $3 \times 150$  mL) and brine (150 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure. The crude product 2-hydroxy-1-*p*-tolyl-ethanone was used directly for the next step without further purifications.

To a stirred solution of 2-hydroxy-1-*p*-tolyl-ethanone (25.0 mmol, 1.0 eq.) and KOCN (4.1 g, 2.0 eq, 50.0 mmol) in 60 mL tetrahydrofuran was added AcOH (3.6 g, 2.4 eq, 60.0 mmol) slowly at 50 °C. The reaction was stirred at this temperature for 12 h until TLC indicated the total consumption of the 2-hydroxy-1-*p*-tolyl-ethanone, and then poured into ice cooled  $\text{H}_2\text{O}$  and the resulting precipitate was collected by filtration to obtain crude product, was passed through a silica gel column to give the desired products **1d** (1.5 g, 34% yield).

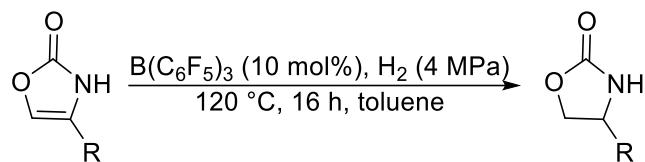
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To a solution of **1a** (322.1 mg, 2.0 mmol) in 4.0 mL DMF was added sodium hydride (96.0 mg, 2.4 mmol, 60% purity) portionwise at 0 °C under  $\text{N}_2$ . The mixture was stirred at 0 °C for 1 h before MeI (312.3 mg, 2.2 mmol) was added. The mixture was stirred at room temperature until full consumption of the starting material indicated by TLC.

Then the reaction was quenched with water and was added EtOAc. The organic layers were washed twice with 5 wt % aqueous LiCl solution to remove DMF, followed by additional washing with brine. After drying over Na<sub>2</sub>SO<sub>4</sub>, the crude product was purified by column chromatography (petroleum ether/EA = 3/1) on silica gel to provide the desired products **1v** as white solid (65.0 mg, 18% yield).

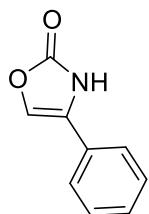
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#### Representative procedure for asymmetric hydrogenation of 4-phenyloxazol-2(3H)-one **1** (Scheme 2):

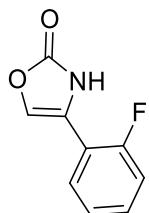
To a stainless-steel autoclave, were added 4-phenyloxazol-2(3H)-one (**1a**) (80.6 mg, 0.50 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**2a**) (25.6 mg, 0.05 mmol) and dry toluene (5.0 mL) in a nitrogen atmosphere glovebox. The resulting mixture was stirred at 120 °C in an oil bath for 16 h. The solvent was removed under reduced pressure. The crude residue was purified by flash chromatography on silica gel (200-300 mesh) to give the desired product **3a** as a white solid (79.2 mg, 97% yield). (**1e**, **1f**, **1i**, **1j**, **1k** was carried out with DCM as solvent; **1s** was carried out with oxazolidinone (1.0 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.1 mmol) in toluene (10.0 mL); **3u** was carried out with 20 mol % B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>).

#### Characterization of substrates



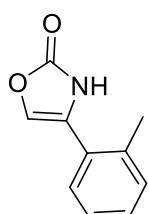
**4-phenyloxazol-2(3H)-one (1a).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.67 (s, 1H), 7.48-7.41 (m, 4H), 7.39-7.32 (m, 1H), 7.12 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  158.4, 129.5, 129.2, 128.4, 126.5, 124.4, 124.1.

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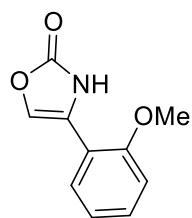
**4-(2-fluorophenyl)oxazol-2(3H)-one (1b).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.61 (s, 1H), 7.52-7.45 (m, 1H), 7.37-7.31 (m, 1H), 7.31-7.24 (m, 2H), 7.20-7.13 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.6 (d,  $J = 255.0$  Hz), 157.7, 130.2 (d,  $J = 8.8$  Hz), 127.9 (d,  $J = 15.0$  Hz), 126.0 (d,  $J = 2.5$  Hz), 125.3 (d,  $J = 3.8$  Hz), 122.7, 116.4 (d,  $J = 21.3$  Hz), 114.9 (d,  $J = 12.5$  Hz);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -111.0.

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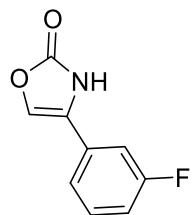


**4-(*o*-tolyl)oxazol-2(3*H*)-one (**1c**).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.06 (s, 1H), 7.40-7.35 (m, 1H), 7.31-7.26 (m, 3H), 6.92 (s, 1H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  157.6, 135.9, 131.5, 129.2, 127.5, 127.2, 126.9, 126.2, 125.9, 21.4.

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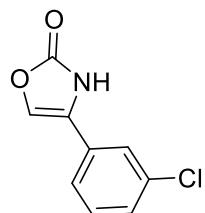


**4-(*o*-methoxyphenyl)-4-oxazoline-2-one (**1d**).** white solid; m.p. 194-196 °C. IR (film): 3051, 1762, 1508  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.13 (s, 1H), 7.55-7.48 (m, 2H), 7.36-7.28 (m, 1H), 7.14-7.08 (m, 1H), 7.05-6.98 (m, 1H), 3.89 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  155.9, 155.4, 129.0, 127.4, 125.4, 123.4, 120.4, 115.2, 111.3, 55.4; HRMS (ESI) m/z: [M+H] $^+$  Calcd for  $\text{C}_{10}\text{H}_{10}\text{NO}_3$  192.0655; Found 192.0660.



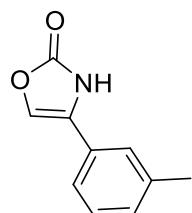
**4-(3-fluorophenyl)oxazol-2(3*H*)-one (**1e**).** white solid; m.p. 158-161 °C. IR (film): 3162, 3093, 1782, 1760, 1467  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.38 (s, 1H), 7.77 (s, 1H), 7.51-7.39 (m, 3H), 7.21-7.14 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -

DMSO, ppm):  $\delta$  162.4 (d,  $J$ = 241.3 Hz), 155.7, 131.0 (d,  $J$ = 8.8 Hz), 129.1 (d,  $J$ = 8.8 Hz), 126.1 (d,  $J$ = 3.8 Hz), 125.7, 120.0 (d,  $J$ = 2.5 Hz), 114.9 (d,  $J$ = 20.0 Hz), 110.7 (d,  $J$ = 23.8 Hz);  $^{19}\text{F}$  NMR (377 MHz,  $d_6$ -DMSO, ppm)  $\delta$  -112.3; HRMS (ESI) m/z: [M-H]<sup>-</sup> Calcd for C<sub>9</sub>H<sub>5</sub>NO<sub>2</sub>F 178.0310; Found 178.0296.



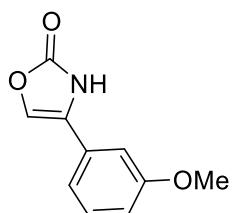
**4-(3-chlorophenyl)-4-oxazoline-2-one (1f).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.37 (s, 1H), 7.79 (m, 1H), 7.67 (s, 1H), 7.55-7.35 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  155.9, 133.9, 130.7, 129.0, 128.0, 126.0, 125.9, 123.7, 122.4.

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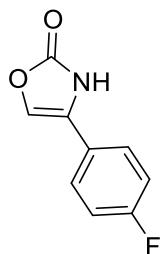
**4-(m-tolyl)oxazol-2(3H)-one (1g).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.28 (s, 1H), 7.64 (s, 1H), 7.41 (s, 1H), 7.38-7.28 (m, 2H), 7.19-7.13 (m, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  155.9, 138.1, 128.9, 128.7, 127.2, 126.7, 124.5, 124.4, 121.1, 20.9.

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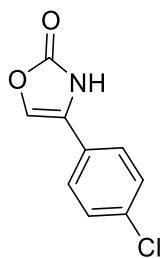
**4-(3-methoxyphenyl)-4-oxazoline-2-one (1h).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.31 (s, 1H), 7.69-7.65 (m, 1H), 7.35-7.28 (m, 1H), 7.15-7.10 (m, 2H), 6.92-6.86 (m, 1H), 3.77 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  159.7, 156.0, 130.0, 128.1, 127.1, 124.9, 116.3, 114.1, 109.6, 55.2.

Z. Liu, W. Zhang, S. Guo and J. Zhu, *J. Org. Chem.*, 2019, **84**, 11945–11957.



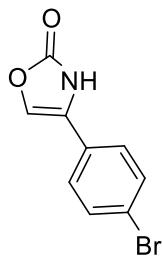
**4-(4-fluorophenyl)oxazol-2(3H)-one (1i).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.39 (s, 1H), 7.78 (s, 1H), 7.51-7.39 (m, 3H), 7.21-7.14 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  162.4 (d,  $J = 241.3$  Hz), 155.7, 131.0 (d,  $J = 8.8$  Hz), 129.1 (d,  $J = 10.0$  Hz), 126.1 (d,  $J = 2.5$  Hz), 125.7, 120.0 (d,  $J = 2.5$  Hz), 114.9 (d,  $J = 21.3$  Hz), 110.7 (d,  $J = 23.8$  Hz);  $^{19}\text{F}$  NMR (377 MHz,  $d_6$ -DMSO, ppm)  $\delta$  -112.9.

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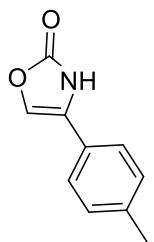
**4-(4-chlorophenyl)-4-oxazoline-2-one (1j).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.37 (s, 1H), 7.74-7.70 (m, 1H), 7.57 (d,  $J = 8.5$  Hz, 2H), 7.54-7.47 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  155.8, 132.6, 128.9, 126.1, 125.7, 125.6, 125.1.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.



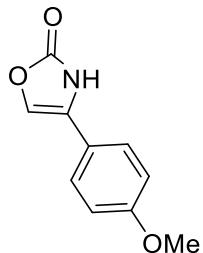
**4-(4-bromophenyl)oxazol-2(3H)-one (1k).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.37 (s, 1H), 7.74 (s, 1H), 7.64 (d,  $J = 8.5$  Hz, 2H), 7.51 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  155.8, 131.8, 126.2, 126.1, 125.9, 125.2, 121.1.

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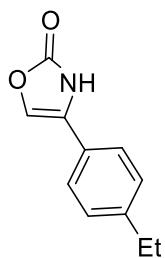
**4-(*p*-tolyl)oxazol-2(3*H*)-one (**1l**).** yellow solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.43 (s, 1H), 7.32 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.07 (s, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  158.2, 139.3, 130.1, 128.4, 124.4, 123.7, 123.6, 21.5.

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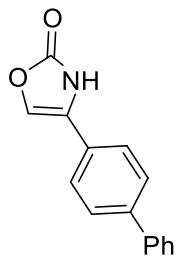
**4-(4-methoxyphenyl)oxazol-2(3*H*)-one (**1m**).** yellow solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.61 (s, 1H), 7.37 (d,  $J = 8.5$  Hz, 2H), 7.02 (s, 1H), 6.95 (d,  $J = 8.5$  Hz, 2H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  160.4, 158.3, 128.2, 126.0, 122.9, 119.0, 115.0, 55.6.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.



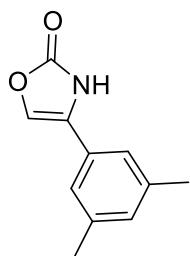
**4-(4-ethylphenyl)oxazol-2(3H)-one (**1n**).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.47 (s, 1H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.07 (s, 1H), 2.67 (q,  $J = 7.5$  Hz, 2H), 1.24 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  158.2, 145.7, 129.0, 128.4, 124.5, 123.9, 123.6, 28.9, 15.5.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.

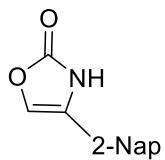


**4-([1,1'-biphenyl]-4-yl)oxazol-2(3H)-one(**1o**).** white solid;  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  11.40 (s, 1H), 7.82-7.60 (m, 7H), 7.55-7.44 (m, 2H), 7.43-7.30 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  156.0, 139.8, 139.2, 128.9, 127.7, 127.0, 126.5, 125.9, 124.8, 124.5.

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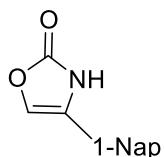


**4-(3,5-dimethylphenyl)oxazol-2(3H)-one (1p).** white solid; m.p. 140-142 °C. IR (film): 3141, 1727, 1641, 1456 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO, ppm): δ 11.19 (s, 1H), 7.59 (s, 1H), 7.18 (s, 2H), 6.96 (s, 1H), 2.27 (s, 6H); <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO, ppm): δ 156.0, 138.0, 129.8, 127.3, 126.7, 124.4, 124.3, 121.8, 20.8; HRMS (ESI) m/z: [M-H]<sup>-</sup> Calcd for C<sub>11</sub>H<sub>10</sub>NO<sub>2</sub> 188.0717; Found 188.0704.



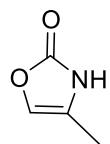
**4-(naphthalen-2-yl)oxazol-2(3H)-one (1q).** white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 10.08 (s, 1H), 7.92-7.82 (m, 4H), 7.56-7.47 (m, 3H), 7.23 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 156.0, 132.8, 132.5, 128.6, 127.8, 127.7, 127.3, 127.0, 126.5, 125.4, 124.3, 122.5, 122.1.

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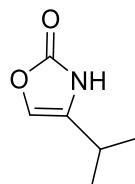
**4-(1'-Naphthyl)-4-oxazolin-2-one (1r).** white solid; m.p. 167-169 °C. IR (film): 3048, 1790, 1747, 1509 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 9.52 (s, 1H), 8.11 (d, *J* =

8.0 Hz, 1H), 7.91 (d,  $J$  = 7.5 Hz, 2H), 7.61-7.51 (m, 4H), 7.06 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, ppm):  $\delta$  157.1, 134.1, 130.9, 130.3, 129.1, 127.6, 126.9, 126.8, 126.6, 126.2, 125.6, 124.4, 124.1; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub> 212.0706; Found 212.0707.



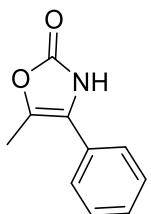
**4-methyloxazol-2(3H)-one (1s).** yellow solid;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  9.65 (s, 1H), 6.54-6.51 (m, 1H), 2.02 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  158.1, 124.7, 123.2, 9.3.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.



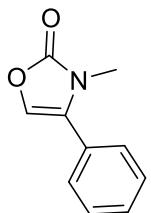
**4-isopropylloxazol-2-one (1t).** yellow solid;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  10.14 (s, 1H), 6.49 (s, 1H), 2.69 (septet,  $J$  = 6.5 Hz, 1H), 1.19 (d,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  158.6, 133.9, 122.9, 24.6, 20.4.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.



**5-methyl-4-phenyl-1,3-oxazol-2(3H)-one (1u).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.42 (s, 1H), 7.47-7.38 (m, 4H), 7.36-7.30 (m, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  157.4, 133.8, 129.3, 128.3, 127.8, 126.0, 121.9, 11.6.

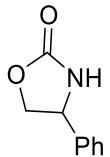
Z. Liu, W. Zhang, S. Guo and J. Zhu, *J. Org. Chem.*, 2019, **84**, 11945–11957.



**3-methyl-4-phenyloxazol-2(3H)-one (1v).** white solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.52-7.44 (m, 3H), 7.39-7.33 (m, 2H), 6.84 (s, 1H), 3.23 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  156.6, 130.2, 129.7, 129.3, 128.3, 126.8, 123.9, 29.5.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.

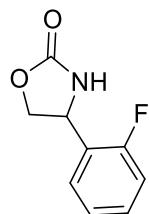
### Characterization of products:



**4-phenyloxazolidin-2-one (3a).** white solid; 79.2 mg, 97% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.43-7.38 (m, 2H), 7.38-7.31 (m, 3H), 6.11 (s, 1H), 4.98-4.92 (m, 1H),

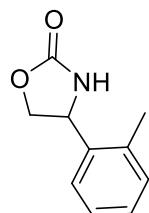
4.75-4.69 (m, 1H), 4.18 (dd,  $J = 8.5, 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.9, 139.7, 129.4, 129.0, 126.2, 72.7, 56.6.

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**2-fluorophenylloxazolidin-2-one (3b).** white solid; 85.3 mg, 93% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$ ; 7.46-7.40 (m, 1H), 7.37-7.30 (m, 1H), 7.24-7.19 (m, 1H), 7.11-7.05 (m, 1H), 6.24 (s, 1H), 5.30-5.25 (m, 1H), 4.84-4.78 (m, 1H), 4.22 (dd,  $J = 8.5, 6.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  160.4 (d,  $J = 245.0$  Hz), 159.9, 130.4 (d,  $J = 7.9$  Hz), 127.0 (d,  $J = 13.8$  Hz), 126.9 (d,  $J = 3.8$  Hz), 125.1 (d,  $J = 2.5$  Hz), 116.0 (d,  $J = 20.0$  Hz), 71.6, 50.5 (d,  $J = 3.8$  Hz);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -119.5.

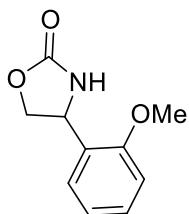
H. Lebel, L. M. Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. D. Leduc, E. Azek and M. Ernzerhof, *Org. Biomol. Chem.*, 2017, **15**, 4144–4158.



**4-(3-methylphenyl)-oxazolidine-2-one (3c).** white solid; 83.1 mg, 94% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.44 (d,  $J = 7.5$  Hz, 1H), 7.31-7.27 (m, 1H), 7.25-

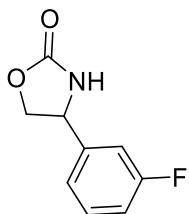
7.22 (m, 1H), 7.19 (d,  $J = 7.5$  Hz, 1H), 5.48 (s 1H), 5.25-5.19 (m, 1H), 4.82-4.76 (m, 1H), 4.14-4.09 (m, 1H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.7, 137.6, 134.9, 131.2, 128.6, 127.2, 125.0, 71.8, 53.3, 19.2.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.



**4-(2-methoxyphenyl)oxazolidin-2-one (3d).** white solid, 93.6 mg, 97% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.36-7.26 (m, 2H), 7.05-6.95 (m, 1H), 6.89 (d,  $J = 7.5$  Hz, 1H), 5.95 (s, 1H), 5.28-5.19 (m, 1H), 4.83-4.74 (m, 1H), 4.24-4.08 (m, 1H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  160.4, 156.7, 128.6, 128.1, 125.7, 121.1, 110.7, 71.7, 55.6, 51.6.

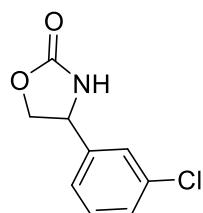
H. Lebel, L. M. Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. D. Leduc, E. Azek and M. Ernzerhof, *Org. Biomol. Chem.*, 2017, **15**, 4144–4158.



**3-fluorophenoxyoxazolidin-2-one (3e).** white solid; 81.1 mg, 89% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.43-7.33 (m, 1H), 7.17-7.02 (m, 3H), 5.81 (s, 1H), 5.02-4.92 (m, 1H), 4.80-4.71 (m, 1H), 4.22-4.14 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$

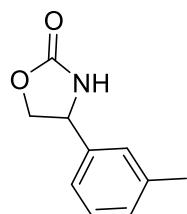
163.4 (d,  $J = 247.0$  Hz), 160.0, 142.3 (d,  $J = 7.0$  Hz), 131.1 (d,  $J = 8.0$  Hz), 121.8 (d,  $J = 3.0$  Hz), 116.0 (d,  $J = 21.0$  Hz), 113.2 (d,  $J = 22.0$  Hz), 72.4, 56.1;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -111.1.

N. Wan, J. Tian, X. Zhou, H. Wang, B. Cui, W. Han and Y. Chen, *Adv. Synth. Catal.*, 2019, **361**, 4651–4655.



**4-(3-chlorophenyl)oxazolidin-2-one (3f).** white solid; 94.6 mg, 97% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.35-7.31 (m, 3H), 7.25-7.20 (m, 1H), 6.35 (s, 1H), 4.96-4.91 (m, 1H), 4.75-4.70 (m, 1H), 4.15 (dd,  $J = 8.5, 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.9, 141.9, 135.4, 130.8, 129.2, 126.5, 124.3, 72.4, 56.1.

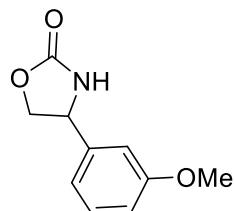
H. Lebel, L. M. Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. D. Leduc, E. Azek and M. Ernzerhof, *Org. Biomol. Chem.*, 2017, **15**, 4144–4158.



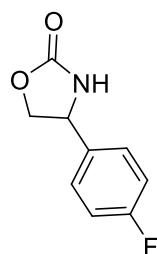
**4-(3-methylphenyl)-oxazolidine-2-one (3g).** white solid; 82.4 mg, 93% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.32-7.25 (m, 1H), 7.20-7.10 (m, 3H), 5.65 (s, 1H), 4.94-4.86 (m, 1H), 4.75-4.68 (m, 1H), 4.22-4.15 (m, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (125

MHz, CDCl<sub>3</sub>, ppm): δ 159.7, 139.7, 139.3, 129.8, 129.3, 126.8, 123.3, 72.8, 56.5, 21.6.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.



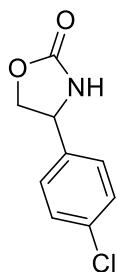
**4-(3-methoxyphenyl)oxazolidin-2-one (3h).** white solid, 94.8 mg, 98% yield, m.p. 59–61 °C. IR (film): 3279, 2919, 2839, 1750, 1604, 1459 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.33–7.28 (m, 1H), 6.99–6.85 (m, 3H), 5.98 (s, 1H), 4.94–4.89 (m, 1H), 4.73–4.68 (m, 1H), 4.17 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 160.6, 159.9, 141.3, 130.5, 118.4, 114.4, 117.7, 72.6, 56.5, 55.5; HRMS (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>N Na 2126.0631; Found 216.0634.



**4-fluorophenylloxazolidin-2-one (3i).** white solid; 84.0 mg, 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ; 7.35–7.29 (m, 2H), 7.13–7.05 (m, 2H), 6.48 (s, 0.7H), 6.04 (s, 0.2H), 4.98–4.92 (m, 1H), 4.75–4.68 (m, 1H), 4.18–4.11 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 163.1 (d, *J* = 246.3 Hz ), 160.0, 135.6 (d, *J* = 3.8 Hz), 128.0 (d, *J* = 7.5 Hz), 116.3 (d, *J* = 21.3 Hz), 72.7, 55.9; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>, ppm) δ -112.9.

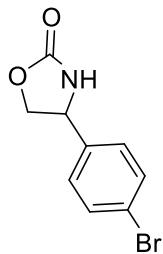
Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS*

*Catal.*, 2020, **10**, 11153–11161.



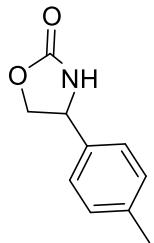
**4-(4-chlorophenyl)oxazolidin-2-one (3j).** white solid; 95.9 mg, 98% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.37 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 6.34 (s, 1H), 4.96-4.90 (m, 1H), 4.74-4.68 (m, 1H), 4.12 (dd,  $J = 8.5, 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.9, 138.2, 135.0, 129.6, 127.6, 72.5, 56.0.

H. Lebel, L. M. Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. D. Leduc, E. Azek and M. Ernzerhof, *Org. Biomol. Chem.*, 2017, **15**, 4144–4158.



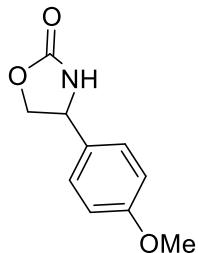
**4-(4-bromophenyl)oxazolidin-2-one (3k).** white solid; 112.0 mg, 92% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.56-7.50 (m, 2H), 7.25-7.19 (m, 2H), 6.30-5.96 (m, 1H), 4.96-4.90 (m, 1H), 4.72 (dd,  $J = 17.0, 8.5$  Hz, 1H), 4.14 (dd,  $J = 16.0, 9.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.7, 138.7, 132.6, 127.9, 123.1, 72.4, 56.1.

N. Wan, J. Tian, X. Zhou, H. Wang, B. Cui, W. Han and Y. Chen, *Adv. Synth. Catal.*, 2019, **361**, 4651–4655.



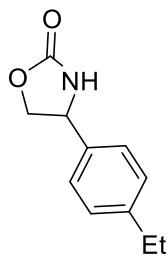
**4-(*p*-tolyl)oxazolidin-2-one (**3i**).** white solid; 89.8 mg, 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.25-7.18 (m, 4H), 5.57 (s, 1H), 4.94-4.88 (m, 1H), 4.74-4.67 (m, 1H), 4.19-4.14 (m, 1H), 2.36 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 159.7, 139.0, 136.7, 130.1, 126.2, 72.9, 56.4, 21.3.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.



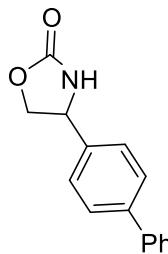
**4-(4-methoxyphenyl)oxazolidin-2-one (**3m**).** white solid; 88.9 mg, 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 1H), 4.92-4.87 (m, 1H), 4.72-4.67 (m, 1H), 4.19-4.14 (m, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 160.3, 159.5, 131.5, 127.6, 114.9, 72.9, 56.2, 55.6.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.

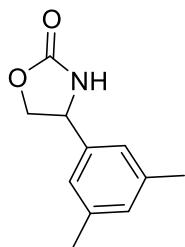


**4-(4-ethylphenyl)oxazol-2(3H)-one (3n).** white solid; 88.7 mg, 93% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.27-7.19 (m, 4H), 6.36 (br, 1H), 4.95-4.88 (m, 1H), 4.75-4.65 (m, 1H), 4.20-4.12 (m, 1H), 2.64 (q,  $J = 7.6$  Hz, 2H), 1.23 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.8, 145.3, 136.9, 128.9, 126.3, 72.8, 56.4, 28.7, 15.6.

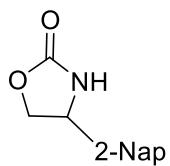
Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.



**4-(biphenyl-4-yl)oxazolidin-2-one (3o).** white solid; 115.5 mg, 96% yield, m.p. 202–204 °C. IR (film): 2919, 1736, 1701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.63 (d,  $J = 8.5$  Hz, 2H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.48-7.35 (m, 5H), 5.53 (s, 1H), 5.02-4.97 (m, 1H), 4.80-4.74 (m, 1H), 4.27-4.21 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.5, 142.3, 140.5, 138.5, 129.1, 128.2, 127.9, 127.3, 126.7, 72.7, 56.4; HRMS (ESI) m/z: [M-H]<sup>-</sup> Calcd for  $\text{C}_{15}\text{H}_{12}\text{NO}_2$  238.0863; Found 238.0863.



**4-(3,5-dimethylphenyl)-2-oxazolidinone (3p).** white solid; 89.0 mg, 93% yield, m.p. 127-130 °C. IR (film): 3275, 2919, 1752 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 6.98 (s, 1H), 6.93 (s, 2H), 5.48 (s, 1H), 4.90-4.82 (m, 1H), 4.75-4.65 (m, 1H), 4.21-4.14 (m, 1H), 2.32 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 159.6, 139.7, 139.2, 130.7, 124.0, 72.8, 56.5, 21.4; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub> 192.1019; Found 192.1024.

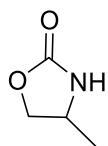


**4-(naphthalen-2-yl)oxazolidin-2-one (3q).** white solid; 96.4 mg, 91% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.87-7.81 (m, 2H), 7.78 (s, 1H), 7.56-7.50 (m, 2H), 7.48-7.43 (m, 1H), 5.48 (s, 1H), 5.14-5.09 (m, 1H), 4.83-4.78 (m, 1H), 4.29 (dd, *J* = 9.0, 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 159.6, 136.9, 133.7, 133.4, 129.7, 128.1, 128.0, 127.1, 126.9, 125.7, 123.4, 72.6, 56.7.

Q. Wang, X. Tan, Z. Zhu, X.-Q. Dong and X. Zhang, *Tetrahedron Lett.*, 2016, **57**, 658–662.

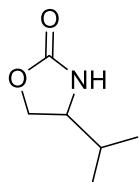


**4-(1-Naphthyl)-2-oxazolidone (3r).** white solid, 104.7 mg, 98% yield, m.p. 137-139 °C. IR (film): 3275, 3060, 1751, 1406 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO, ppm): δ 8.31 (s, 1H), 8.02-7.96 (m, 2H), 7.95-7.86 (m, 1H), 7.62-7.54 (m, 4H), 5.77-5.71 (m, 1H), 5.04-4.95 (m, 1H), 4.00-3.93 (m, 1H); <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO, ppm): δ 158.9, 136.7, 133.4, 129.7, 128.7, 128.1, 126.5, 125.9, 125.4, 122.6, 121.9, 70.8, 52.0; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub> 214.0863; Found 214.0866.



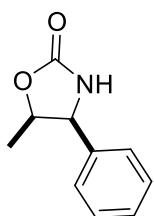
**4-methyloxazolidin-2-one (3s).** yellow oil; 94.0 mg, 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 5.97 (s, 1H), 4.51-4.46 (m, 1H), 4.02-3.91 (m, 2H), 1.27 (d, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 160.3, 72.0, 48.5, 20.8.

Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.



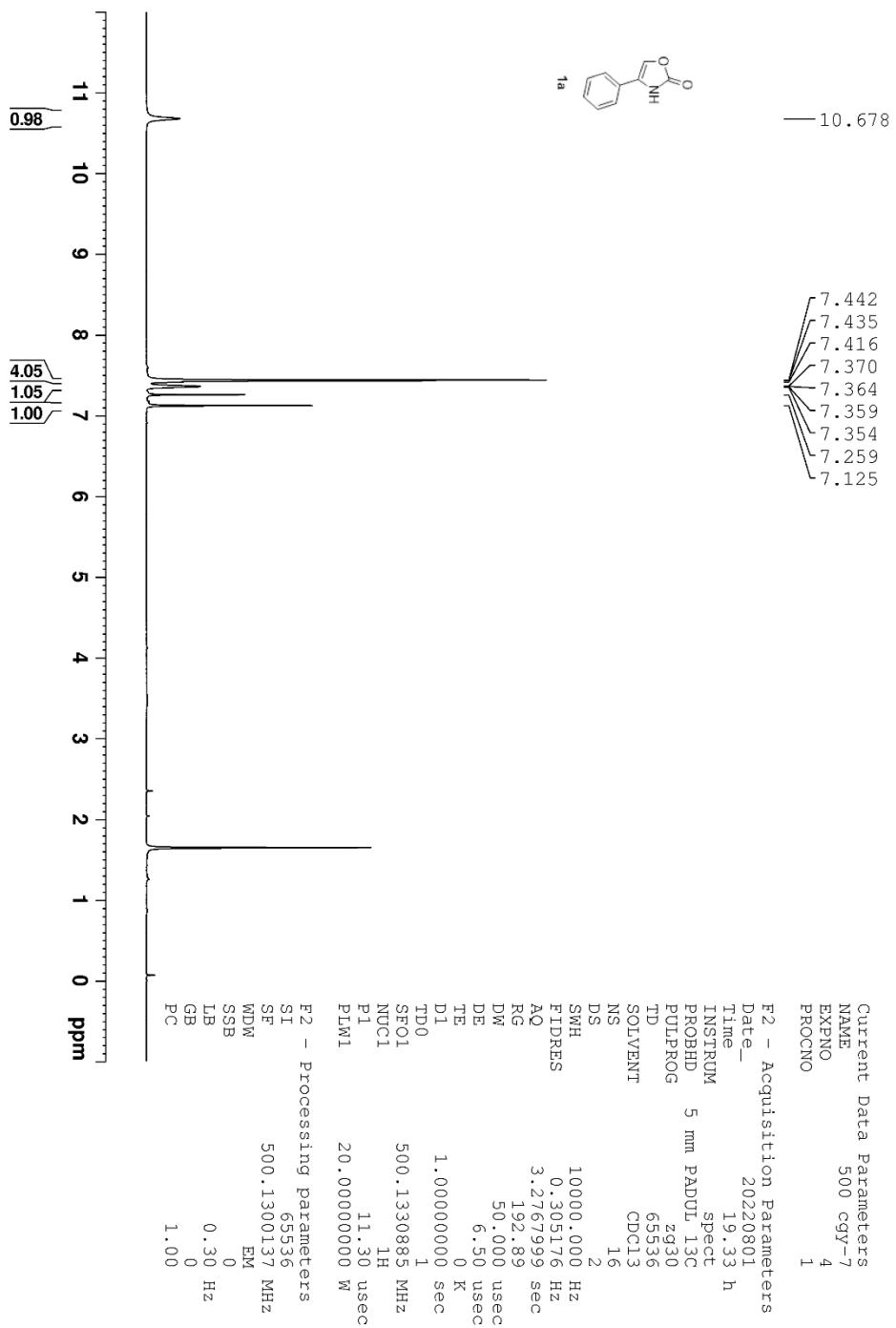
**4-isopropyl-1,3-oxazolidin-2-one (3t).** yellow oil; 58.4 mg, 89% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 6.04 (s, 1H), 4.47-4.41 (m, 1H), 4.13-4.08 (m, 1H), 3.60 (dd, *J* = 14.5, 6.0 Hz, 1H), 1.76-1.69 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 160.2, 68.8, 58.5, 32.8, 18.2, 17.8.

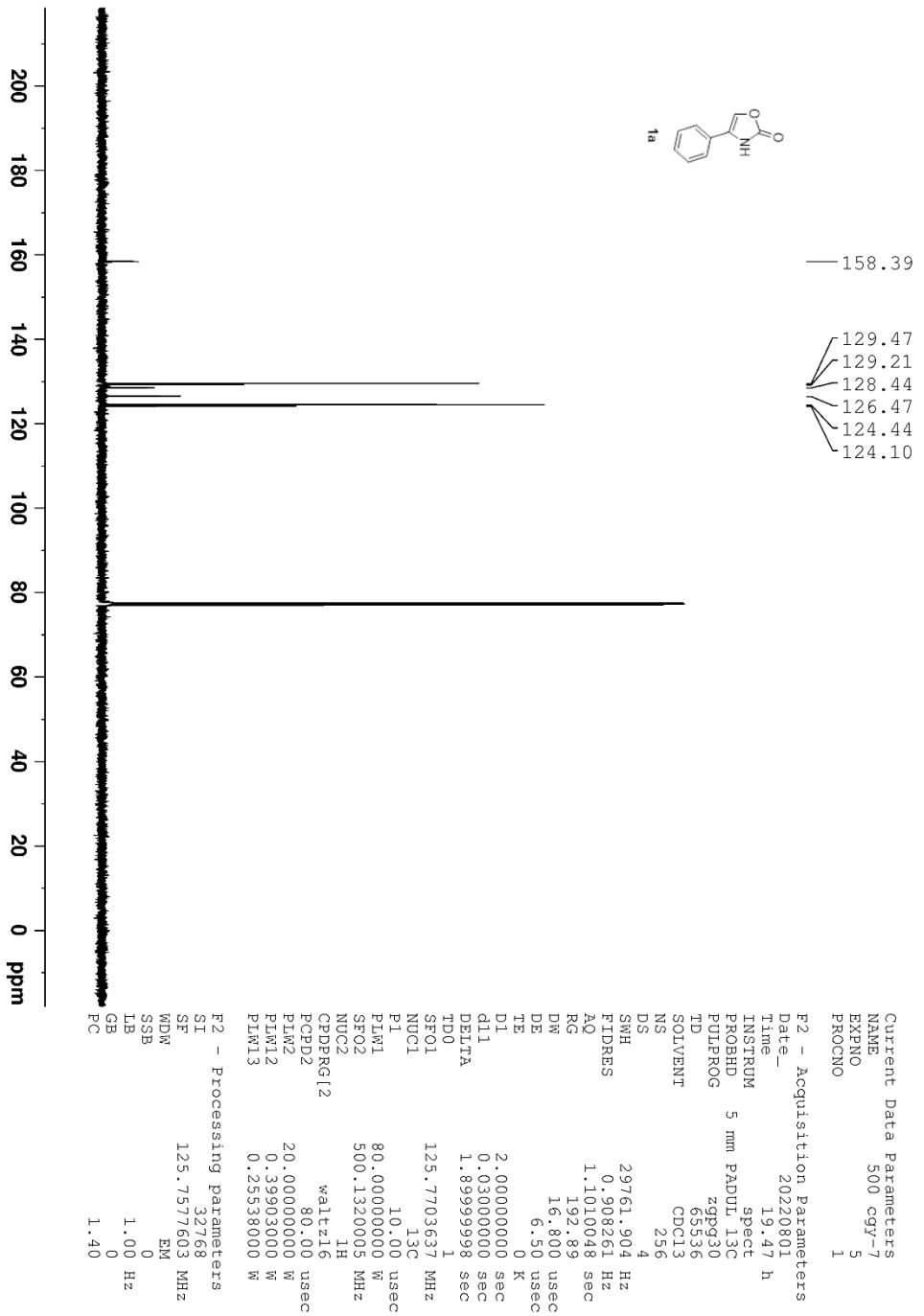
Y. Liu, Z. Yi, X. Yang, H. Wang, C. Yin, M. Wang, X.-Q. Dong and X. Zhang, *ACS Catal.*, 2020, **10**, 11153–11161.

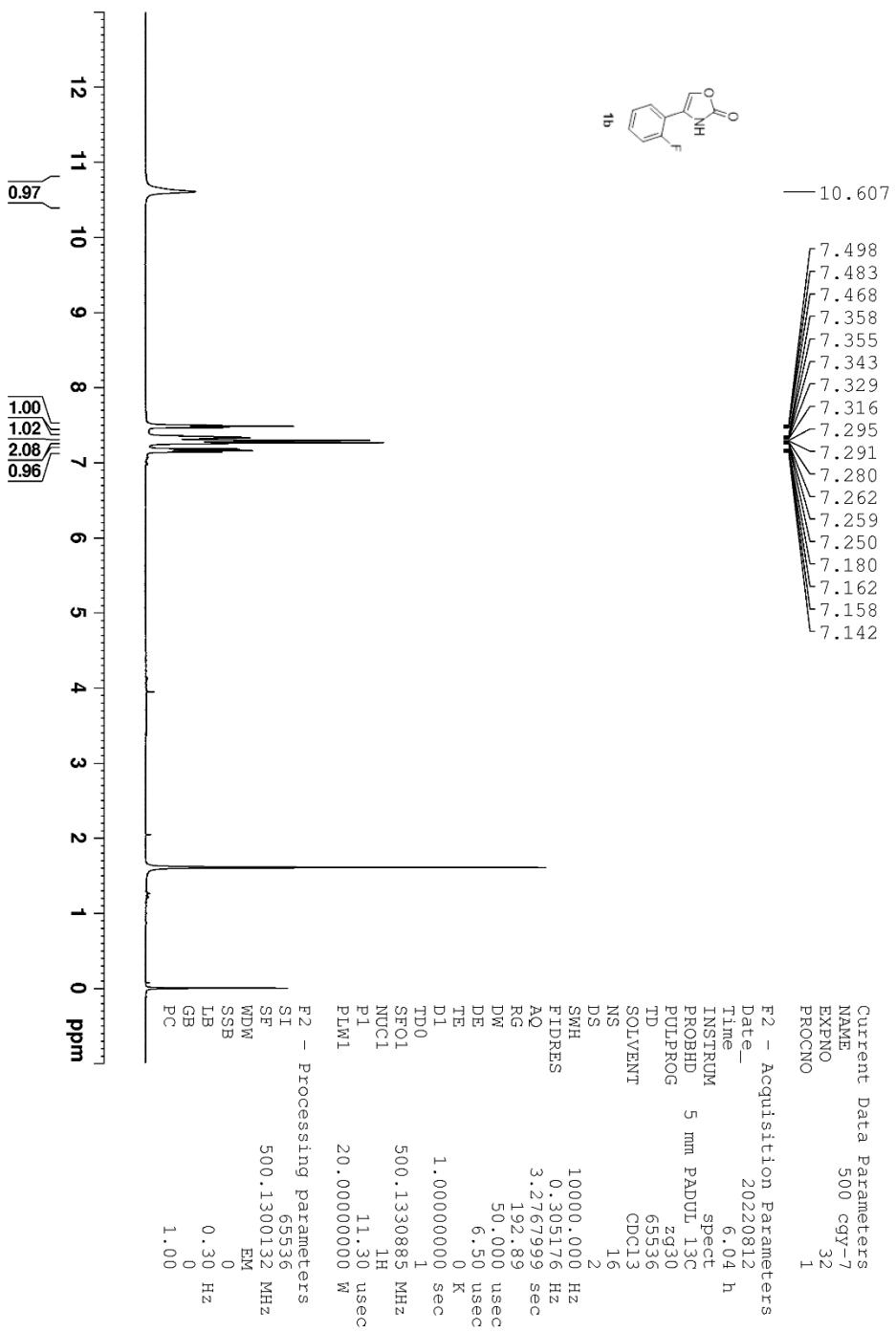


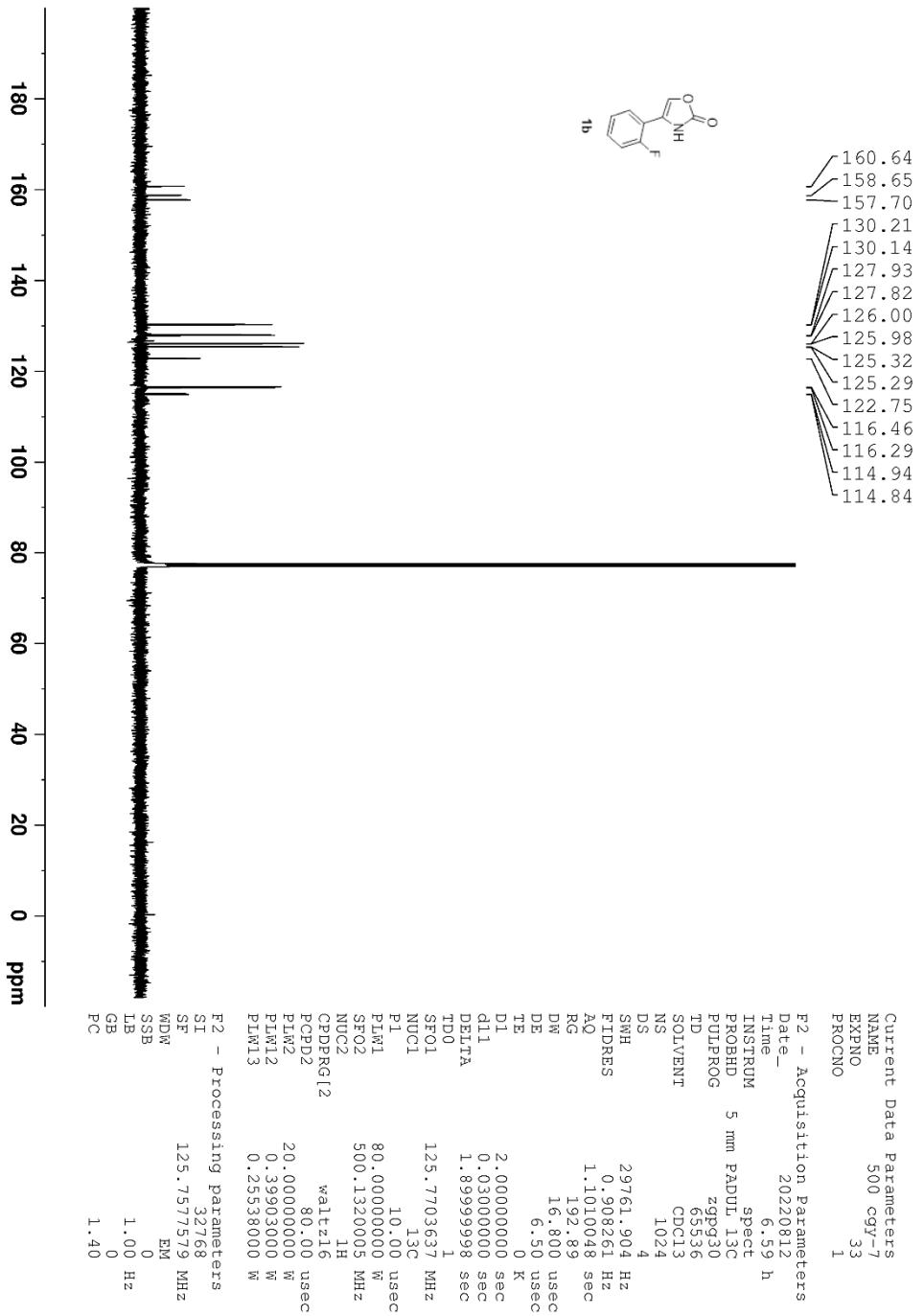
**syn-5-methyl-4-phenyloxazolidin-2-one (3u).** white solid, 62.3 mg, 70% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.41-7.33 (m, 3H), 7.23-7.17 (m, 2H), 5.86 (s, 1H), 5.02-4.94 (m, 1H), 4.91-4.88 (d,  $J = 8.0$  Hz, 1H), 0.92-0.89 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  160.1, 136.6, 129.1, 129.0, 127.1, 77.7, 60.2, 16.7.

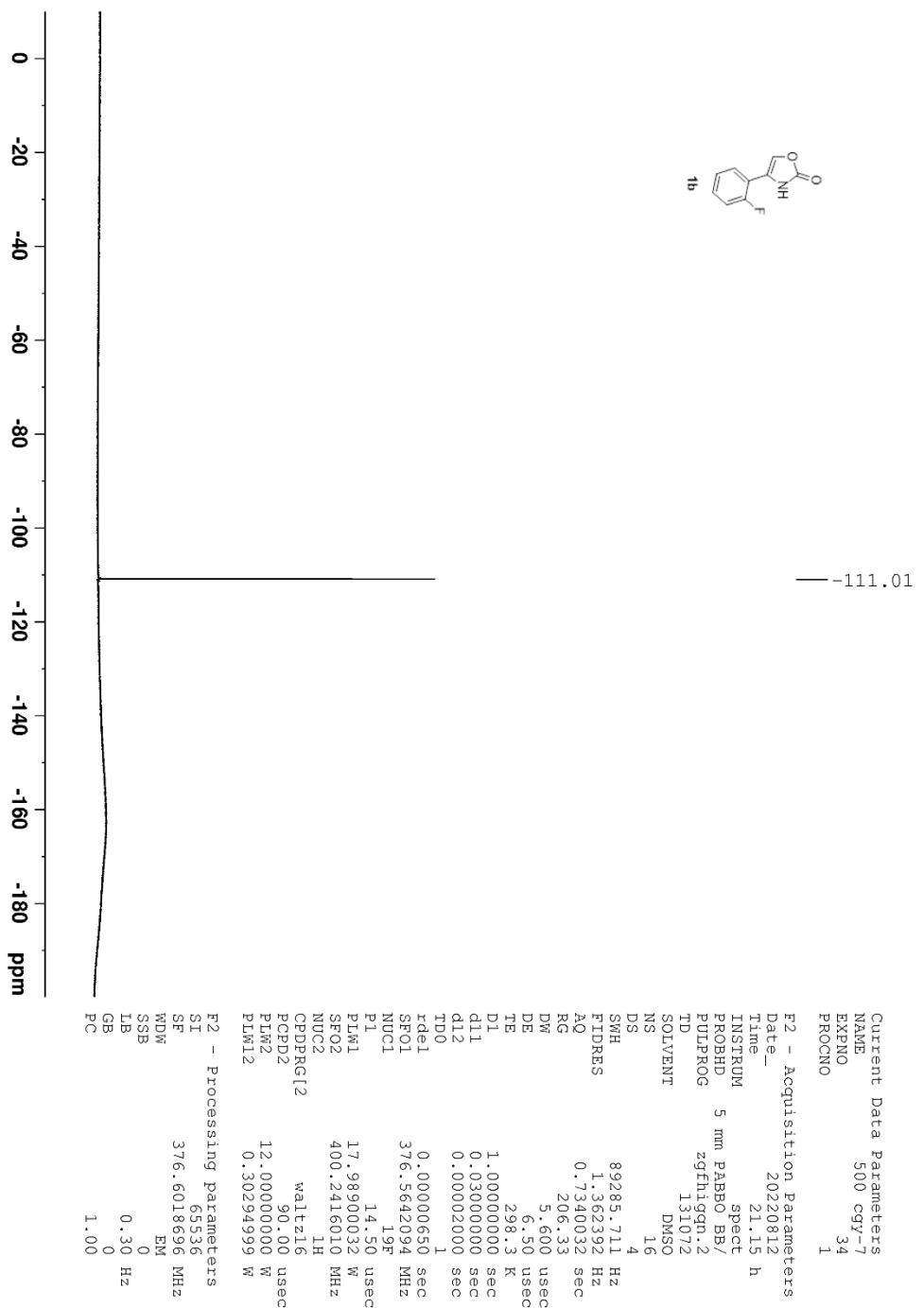
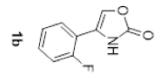
H. Lebel, L. M. Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. D. Leduc, E. Azek and M. Ernzerhof, *Org. Biomol. Chem.*, 2017, **15**, 4144–4158.

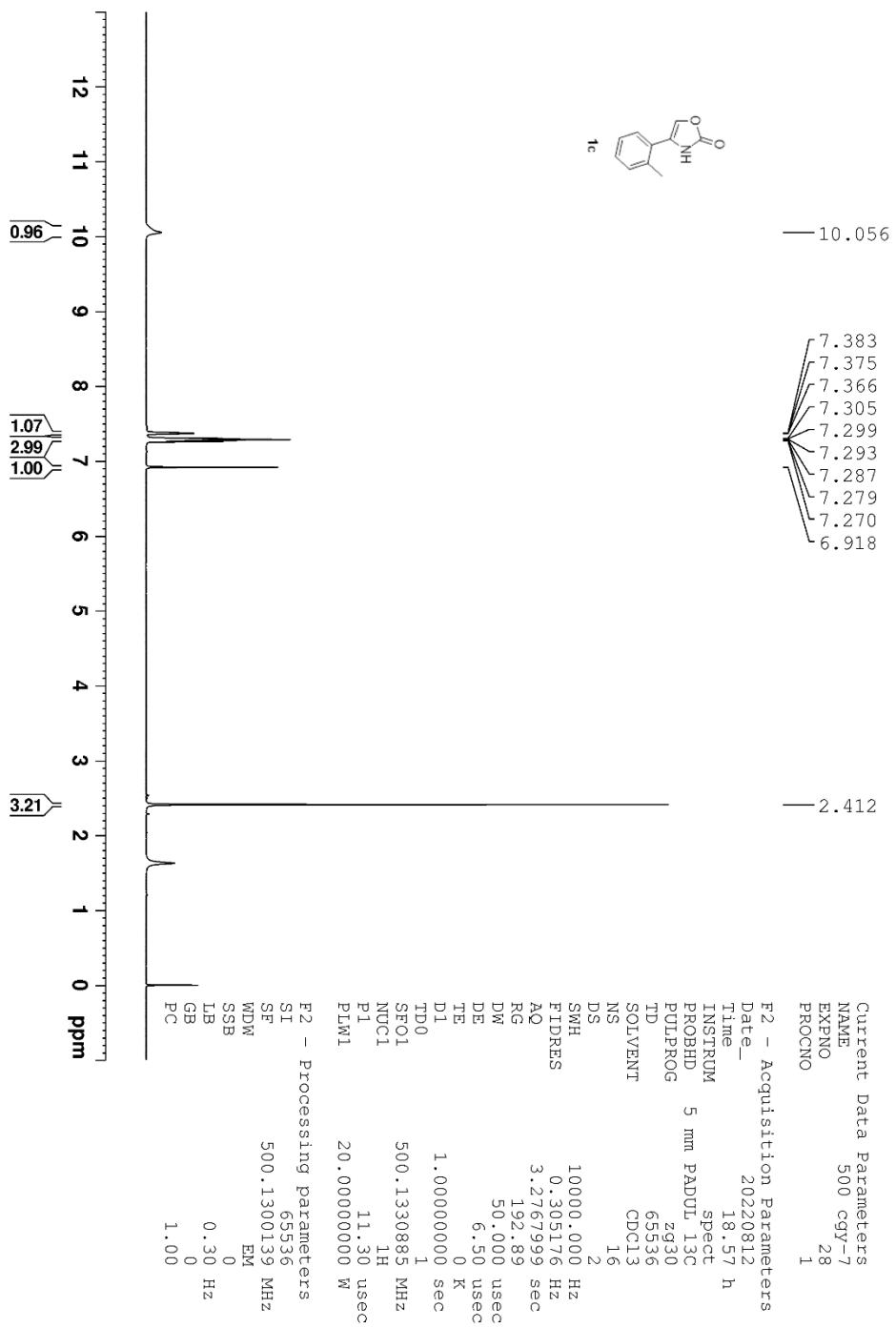


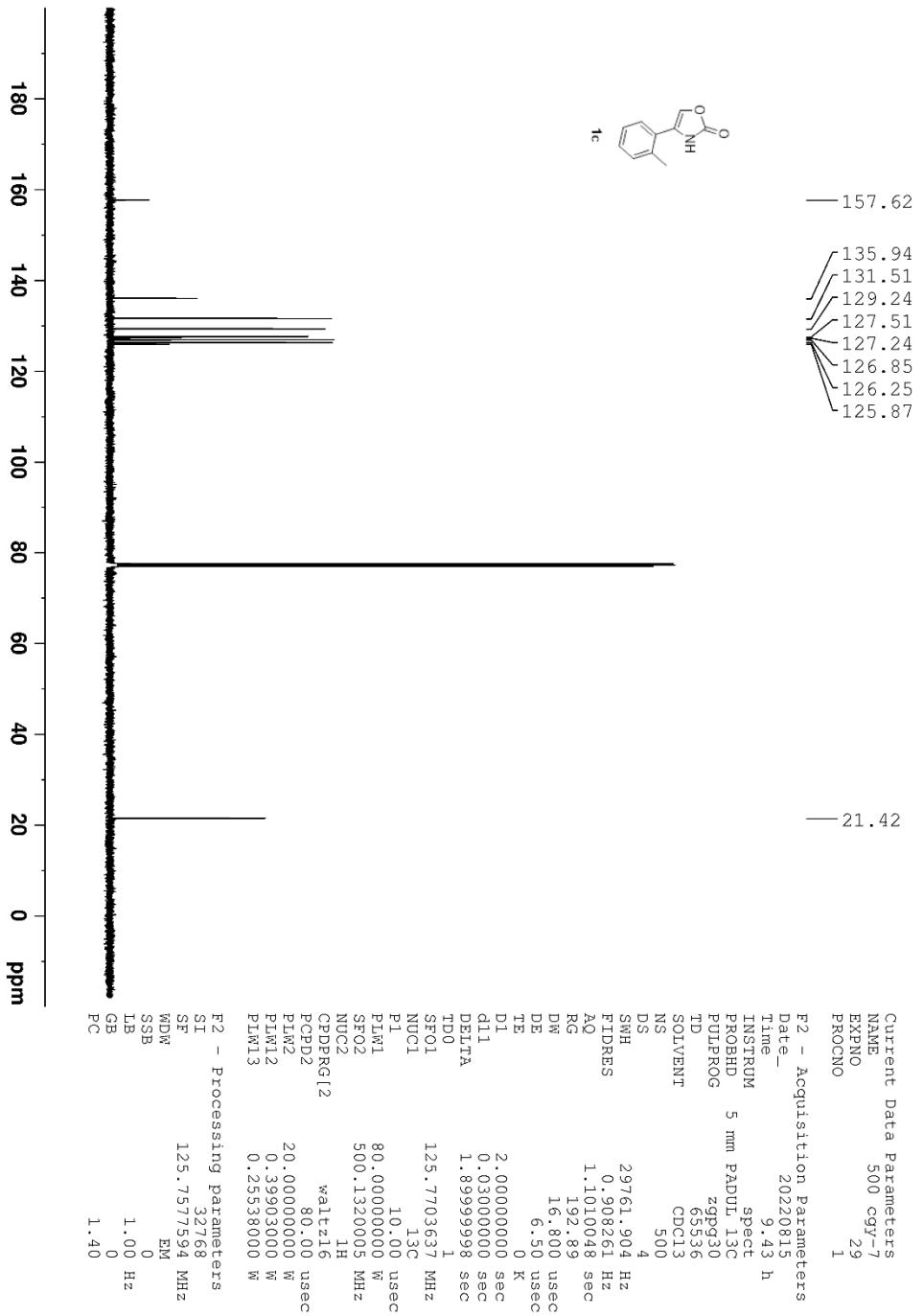


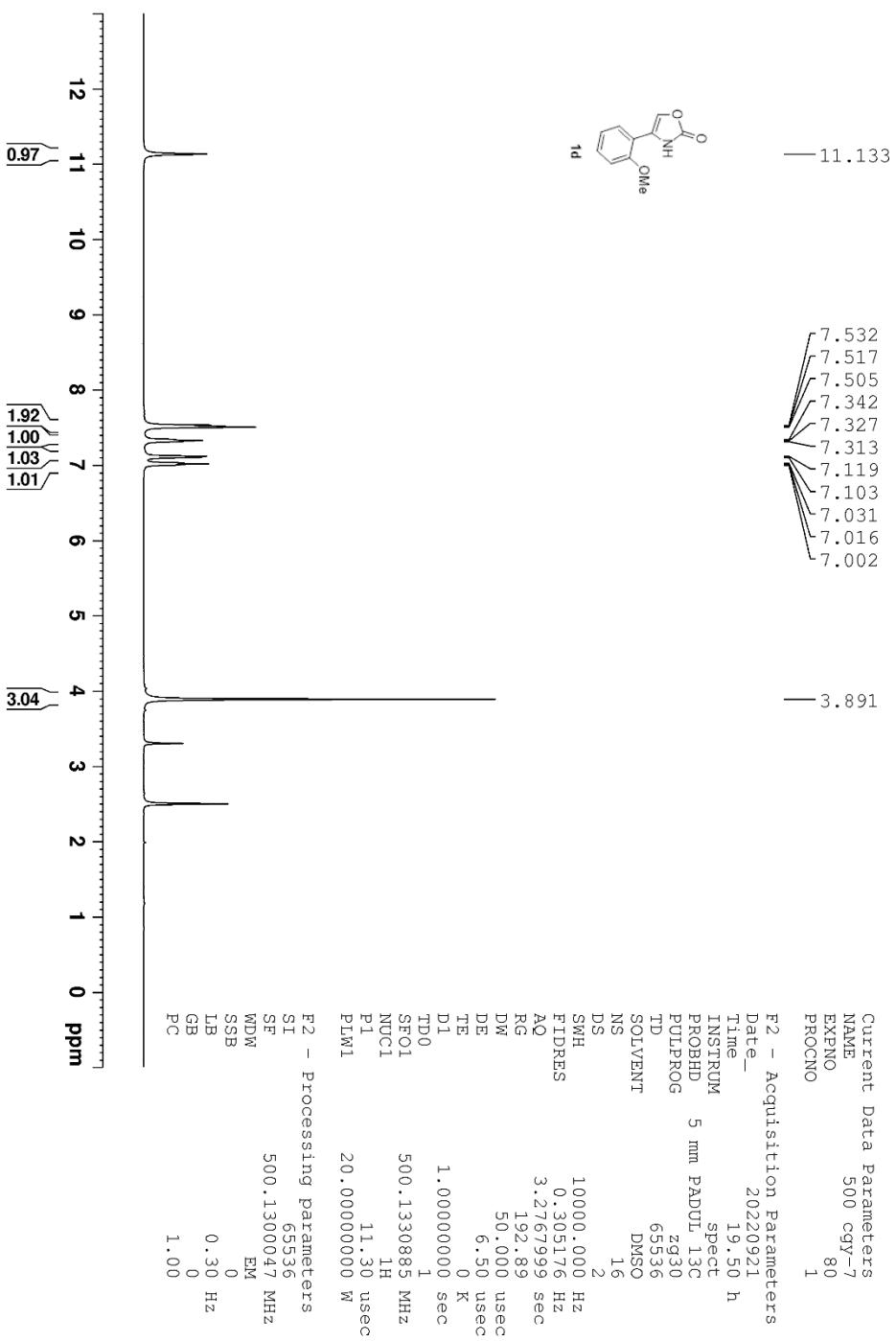


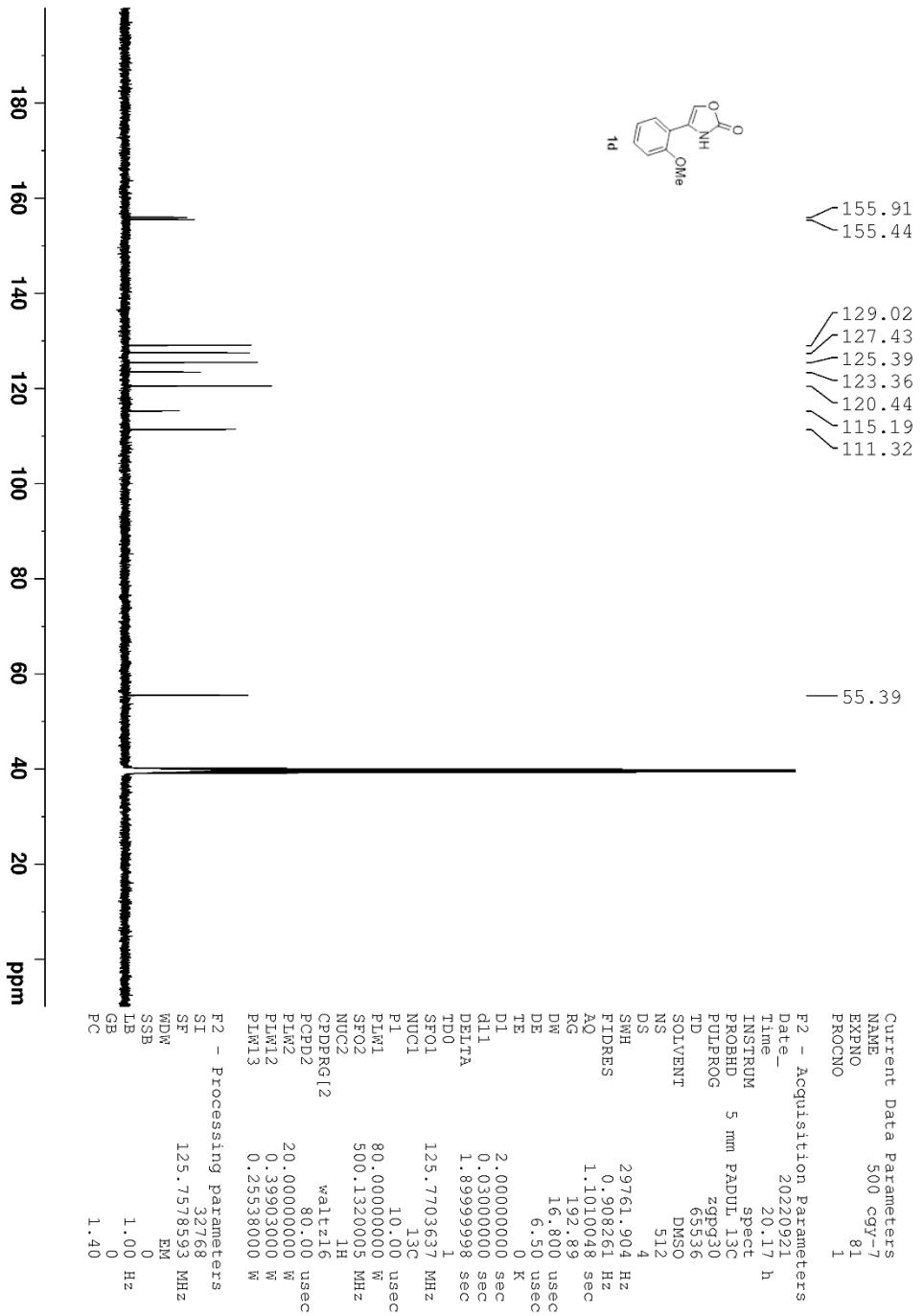


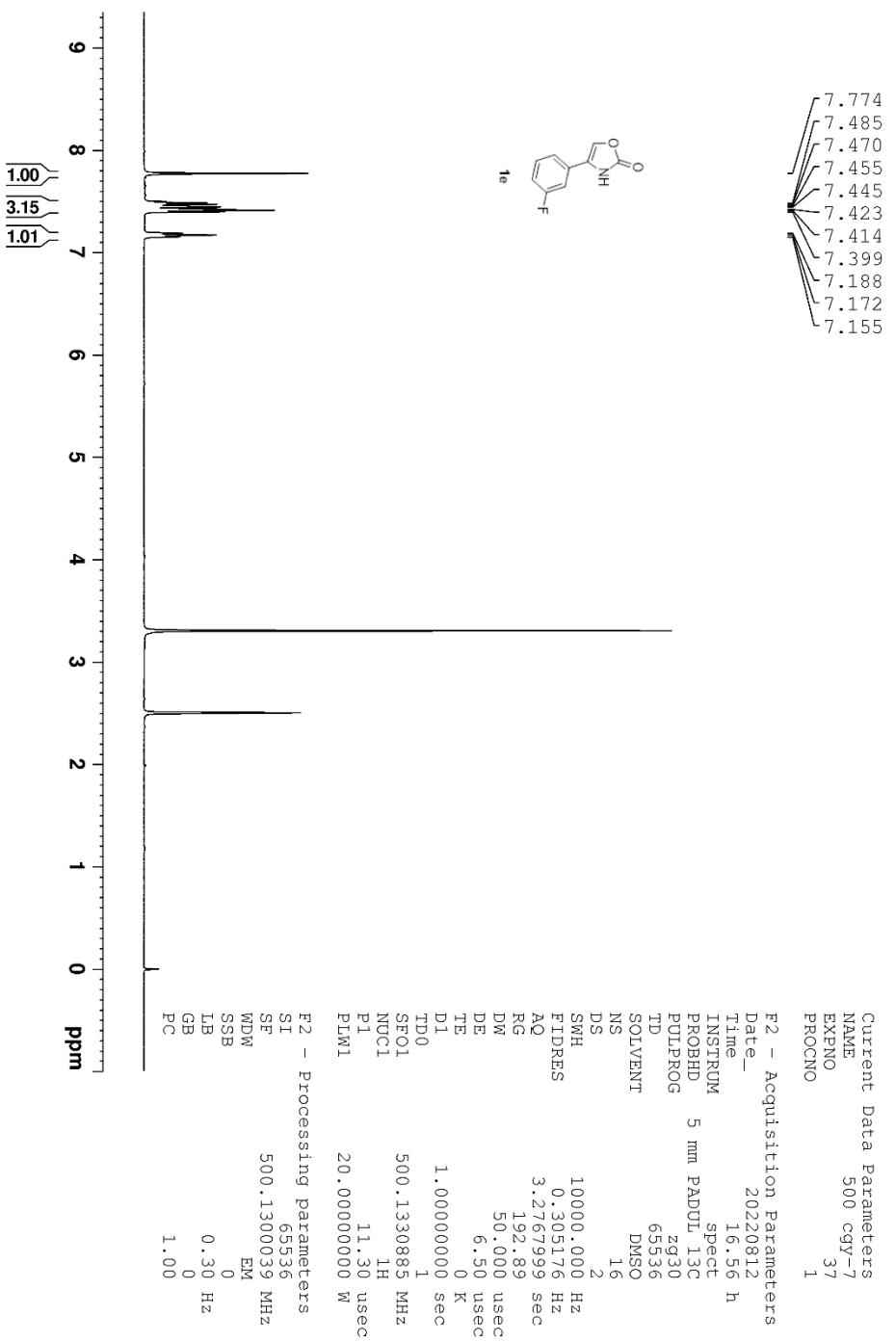


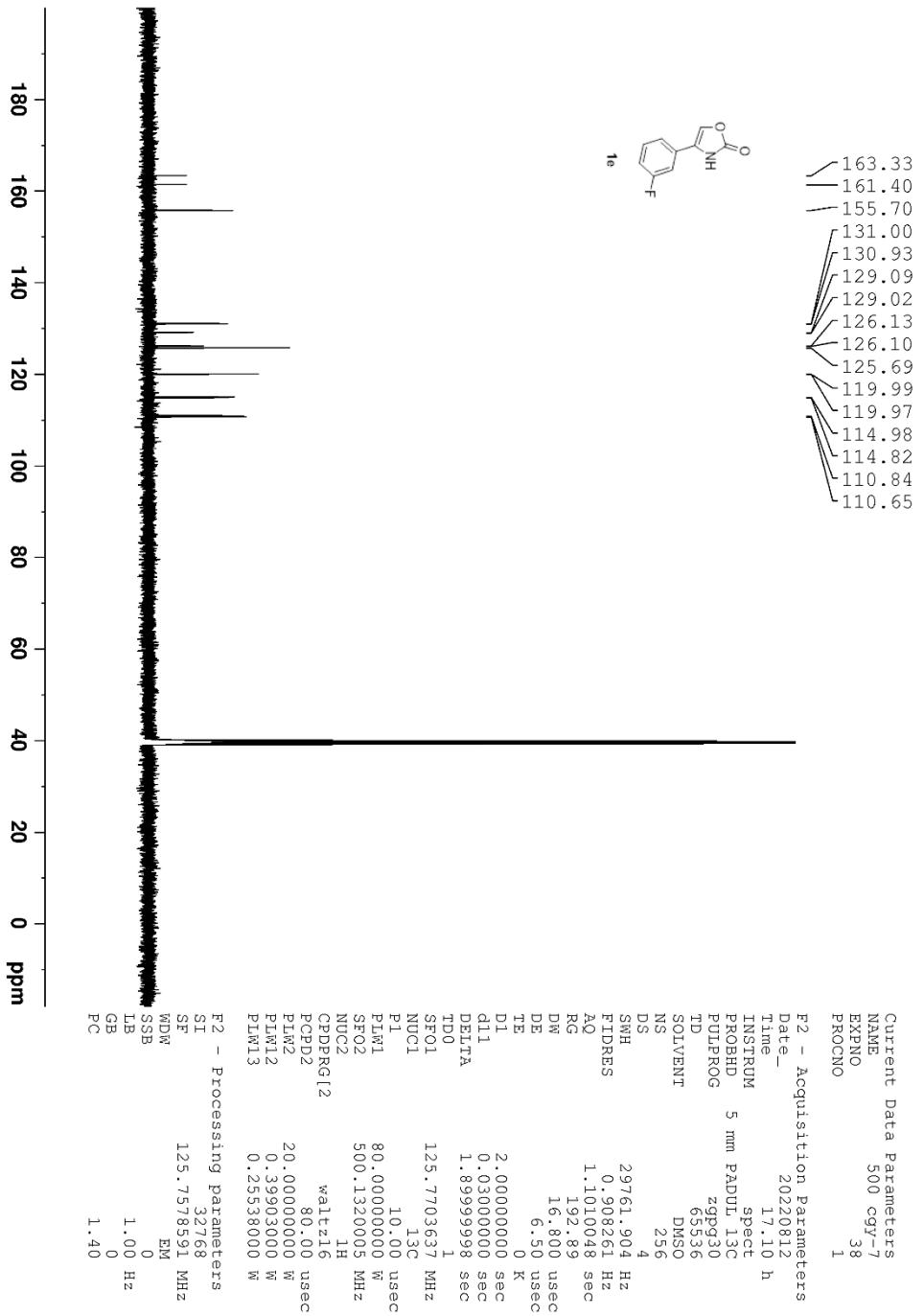


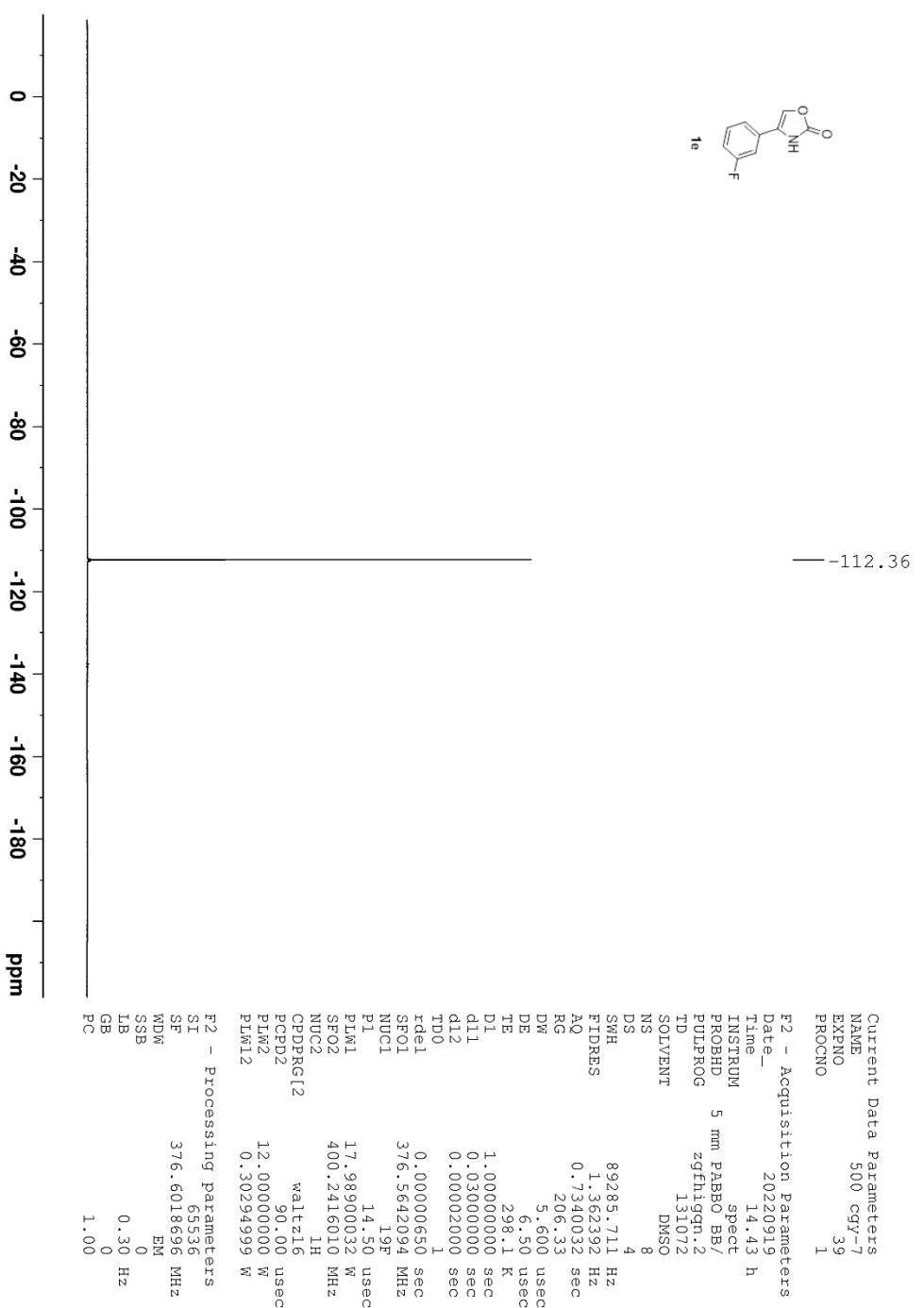


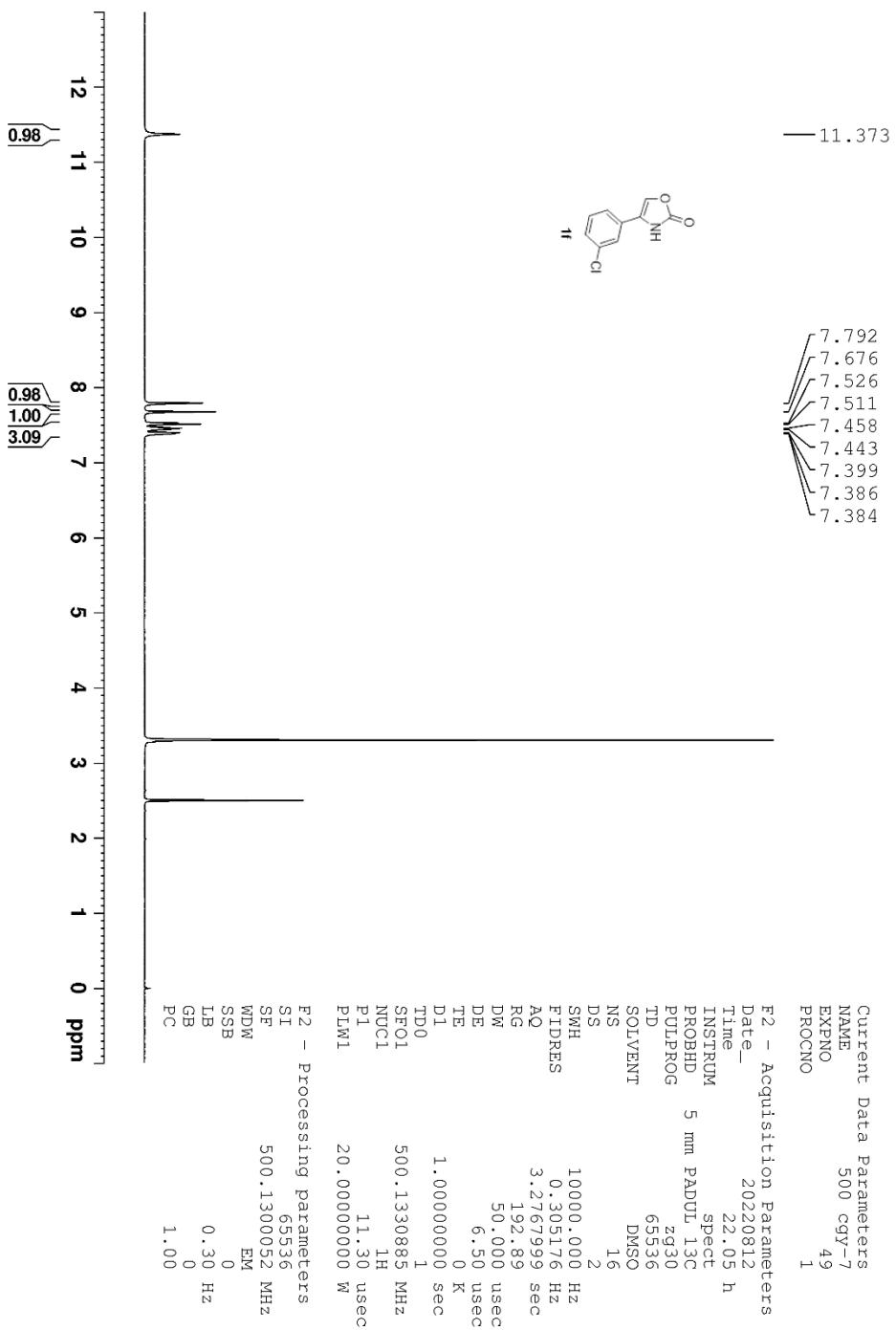


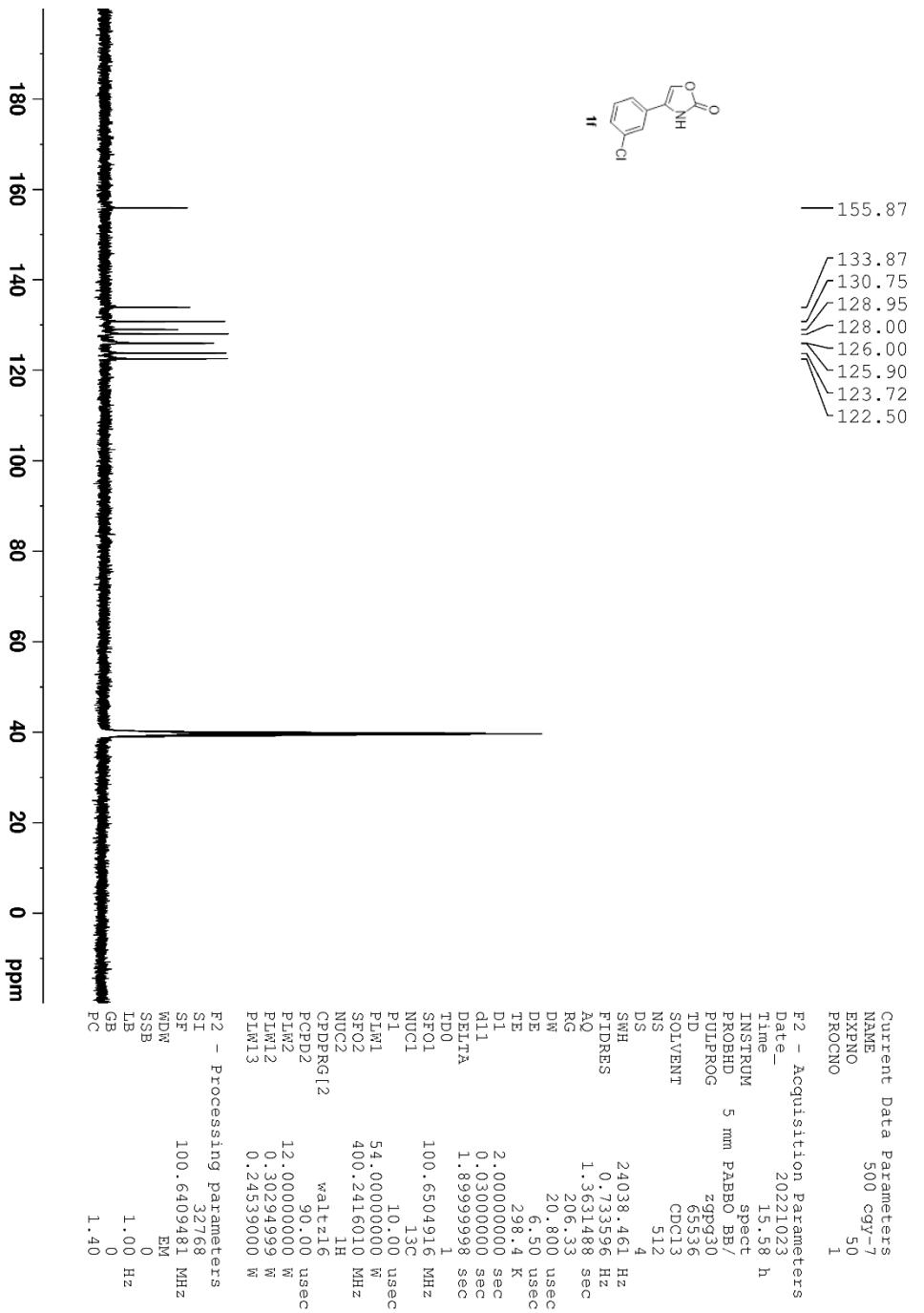


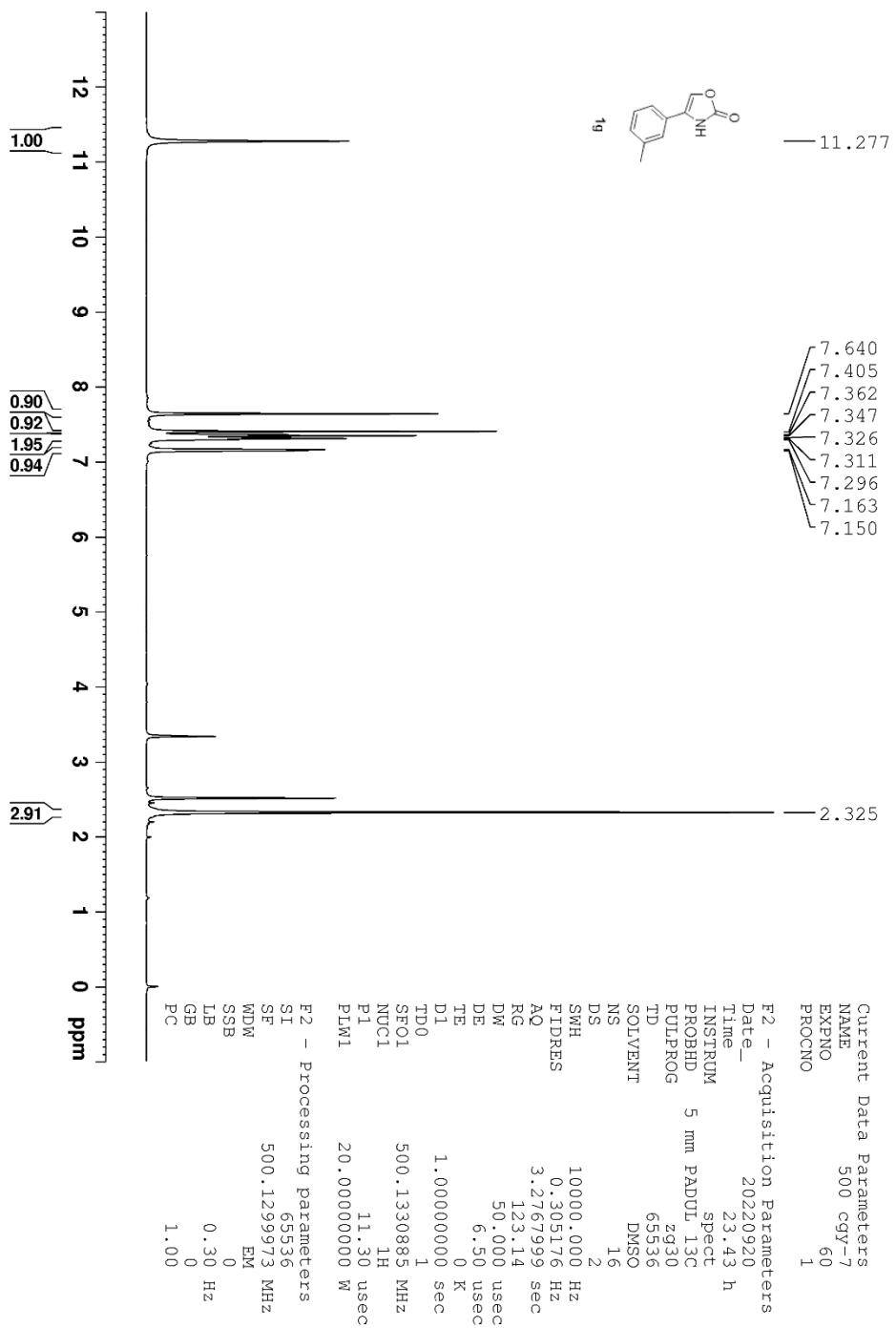


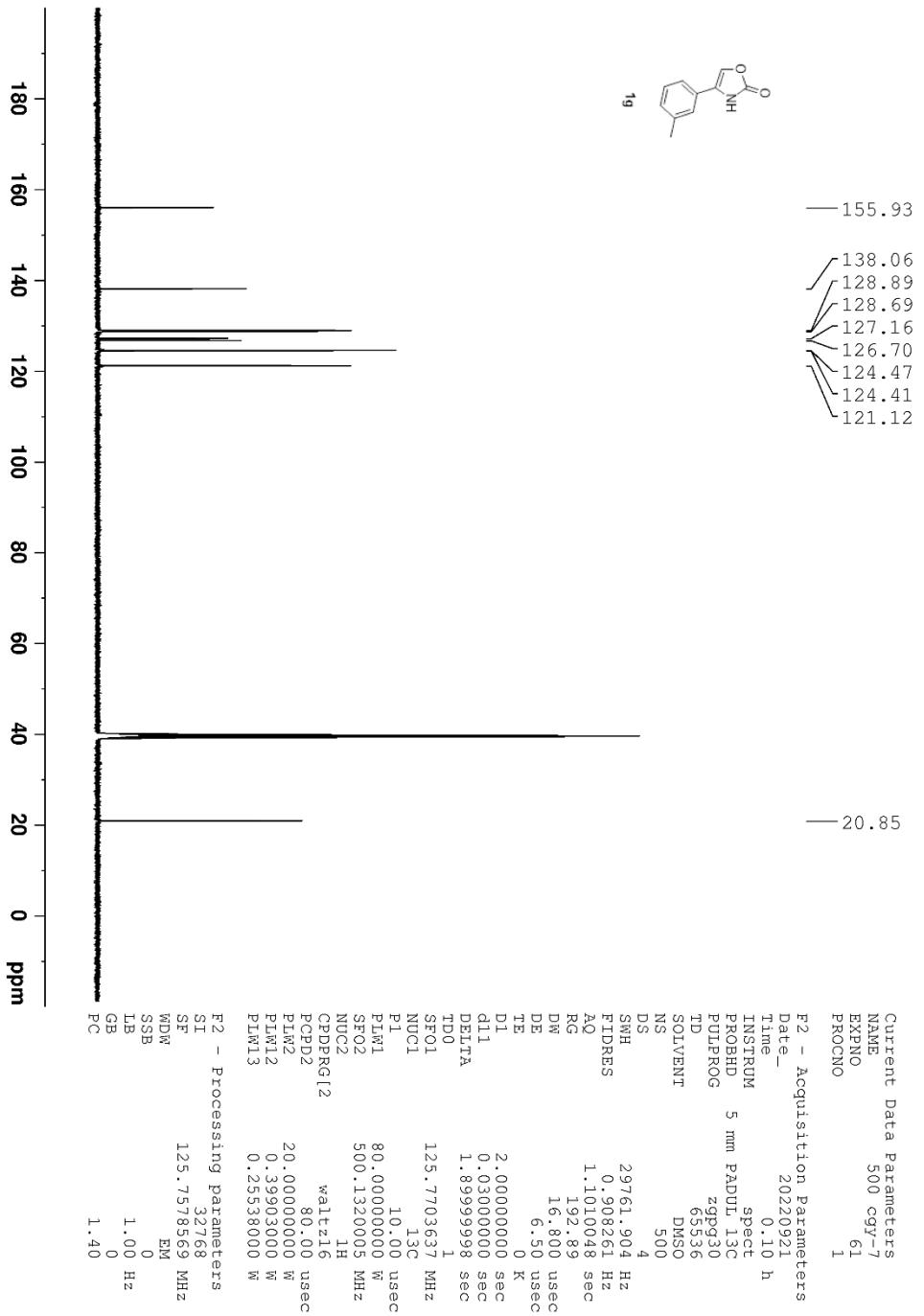


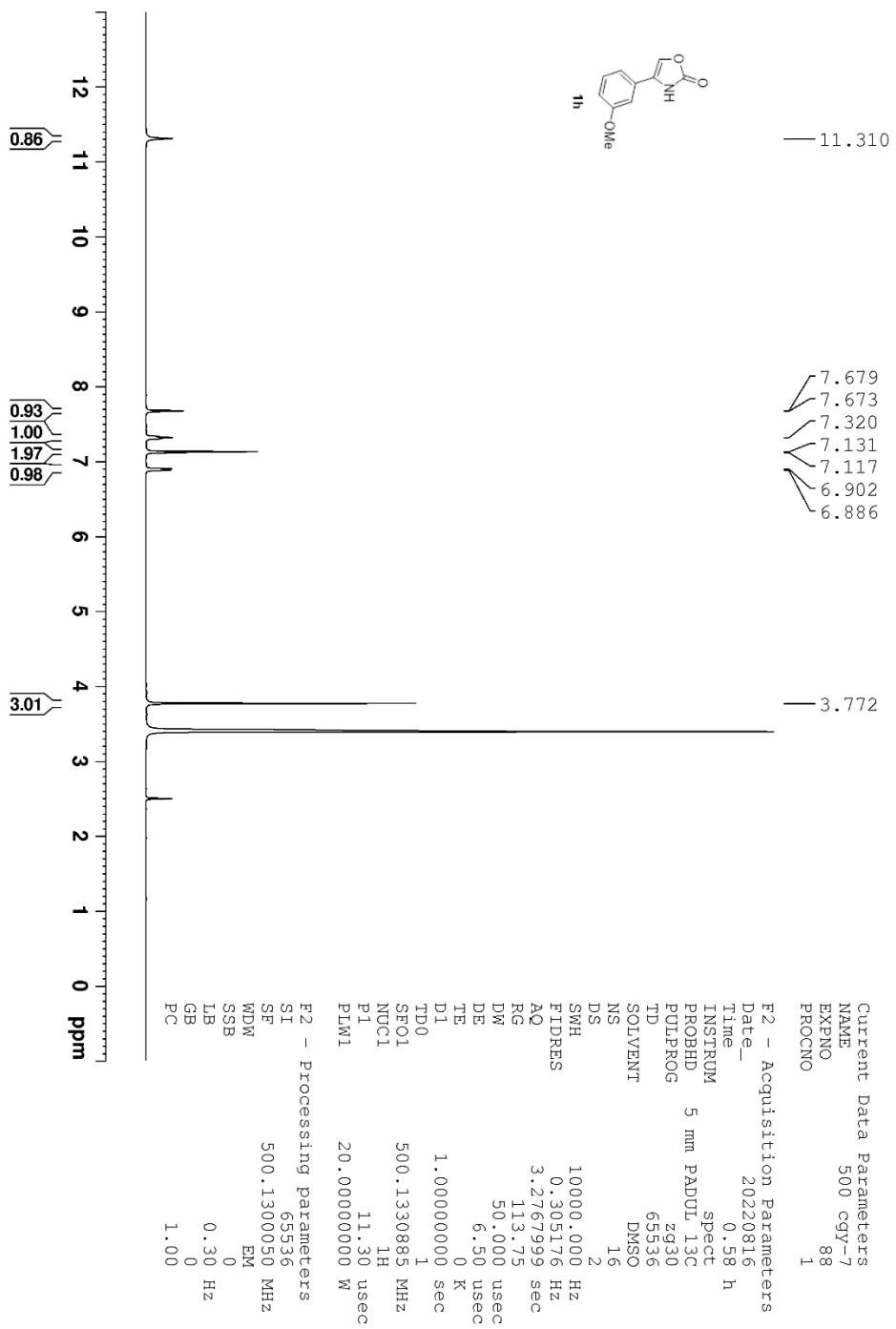


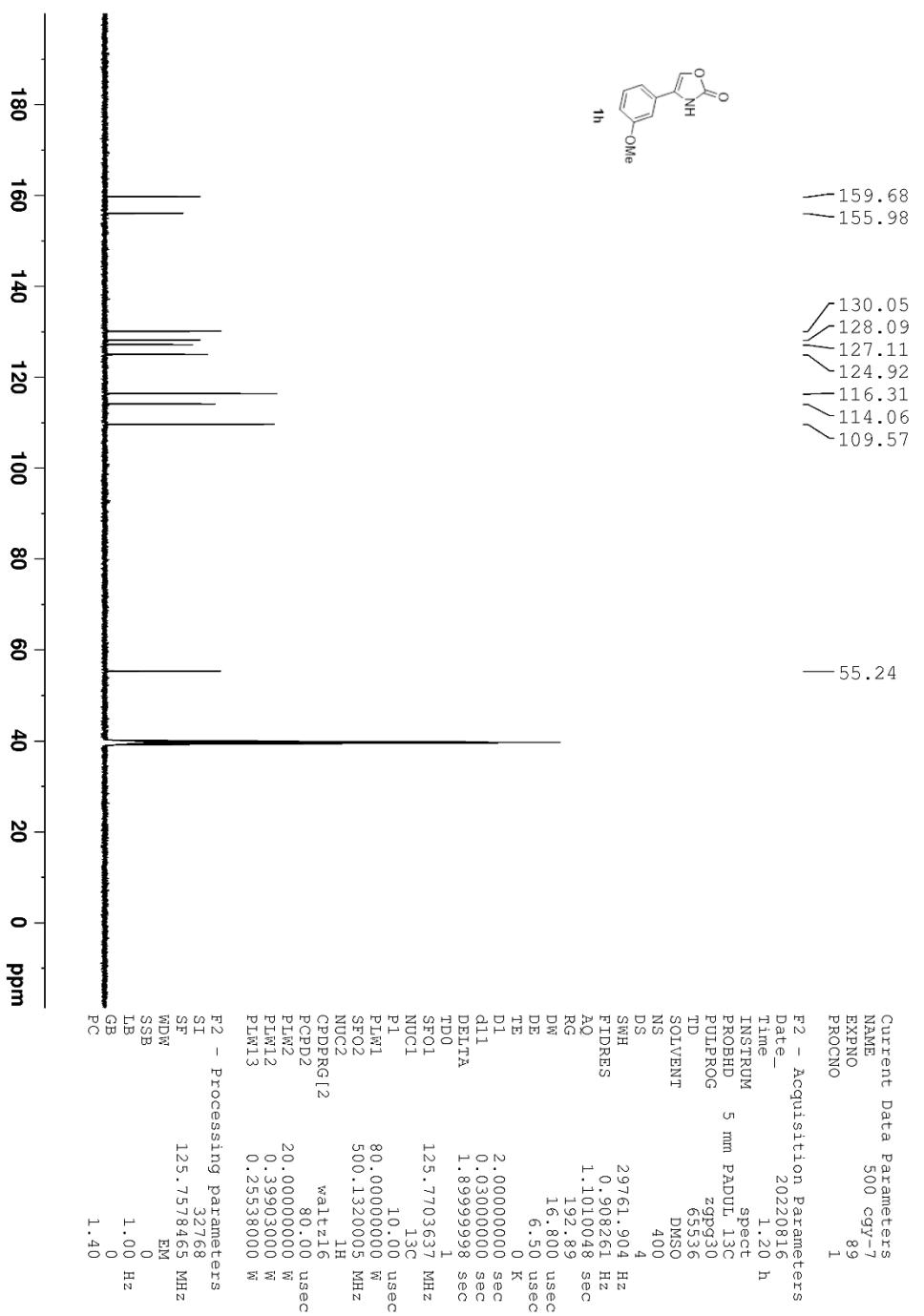


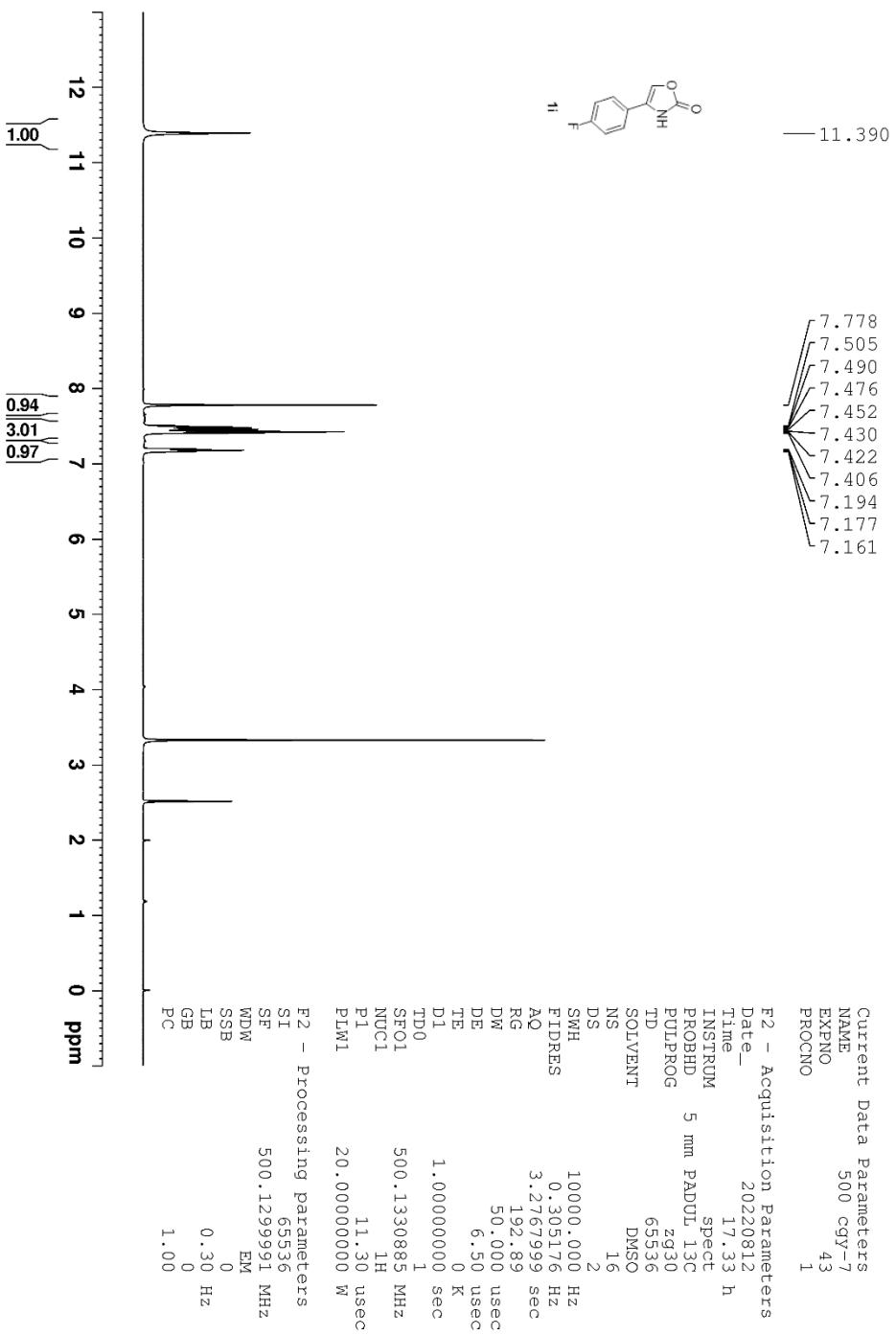


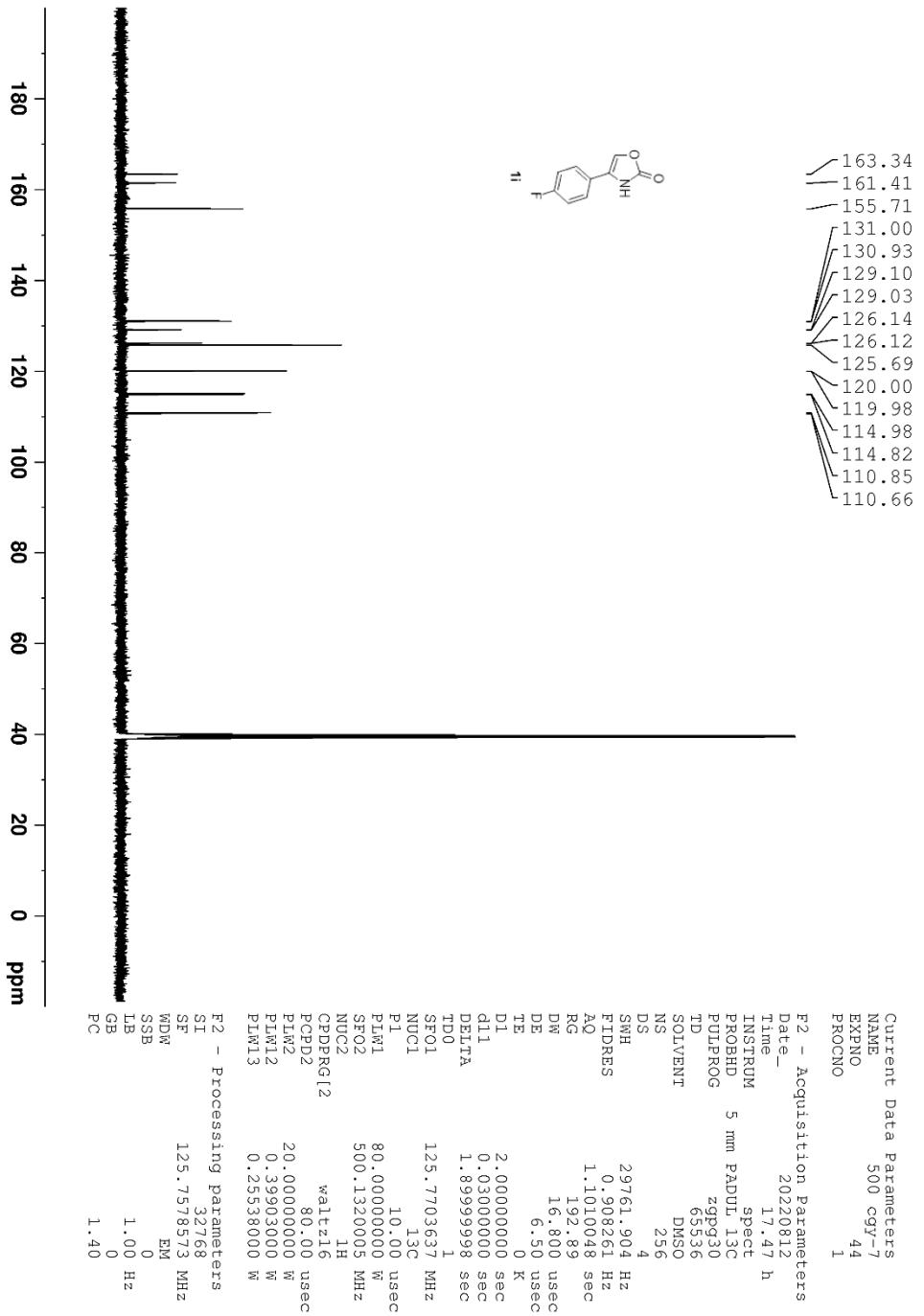


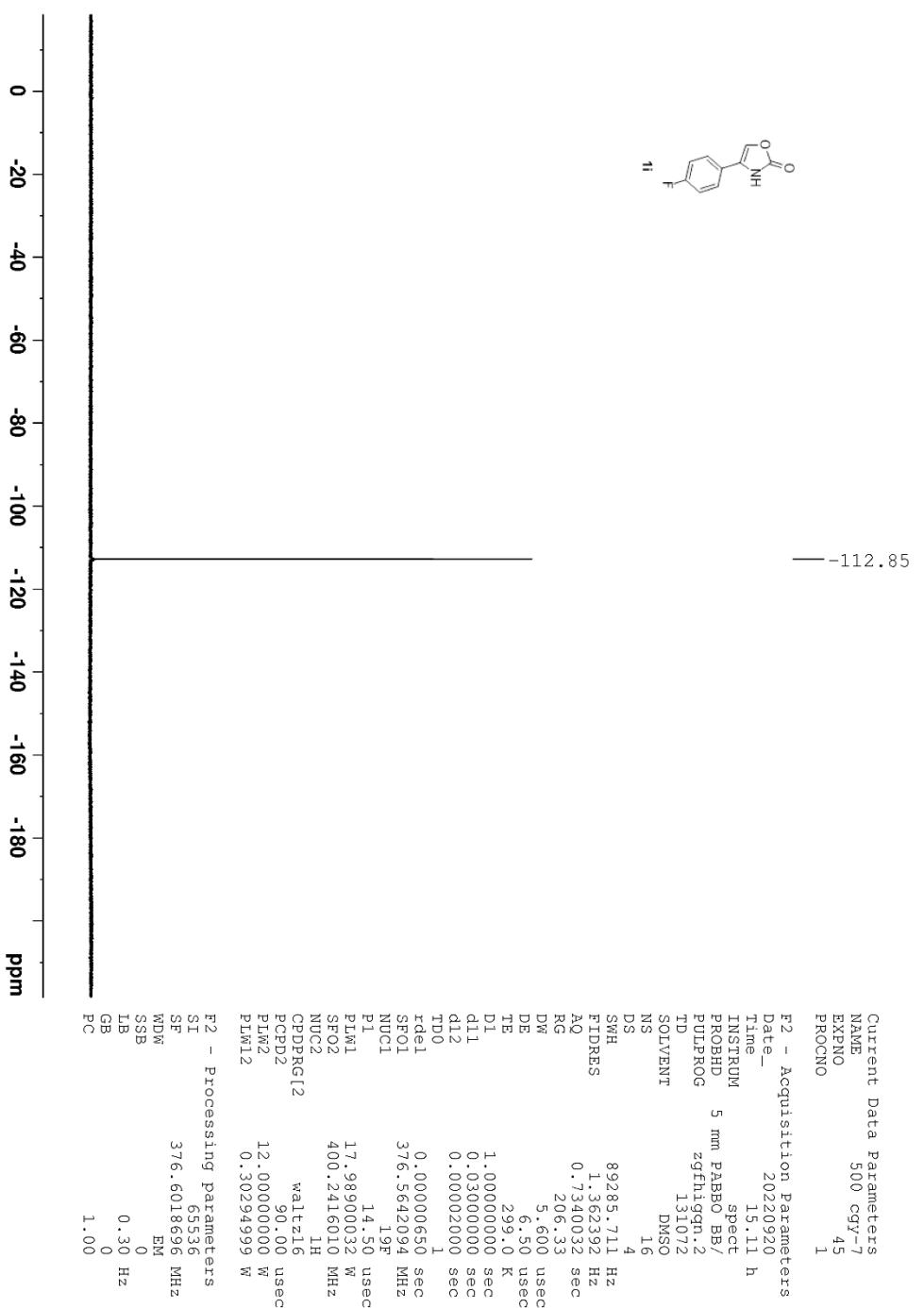


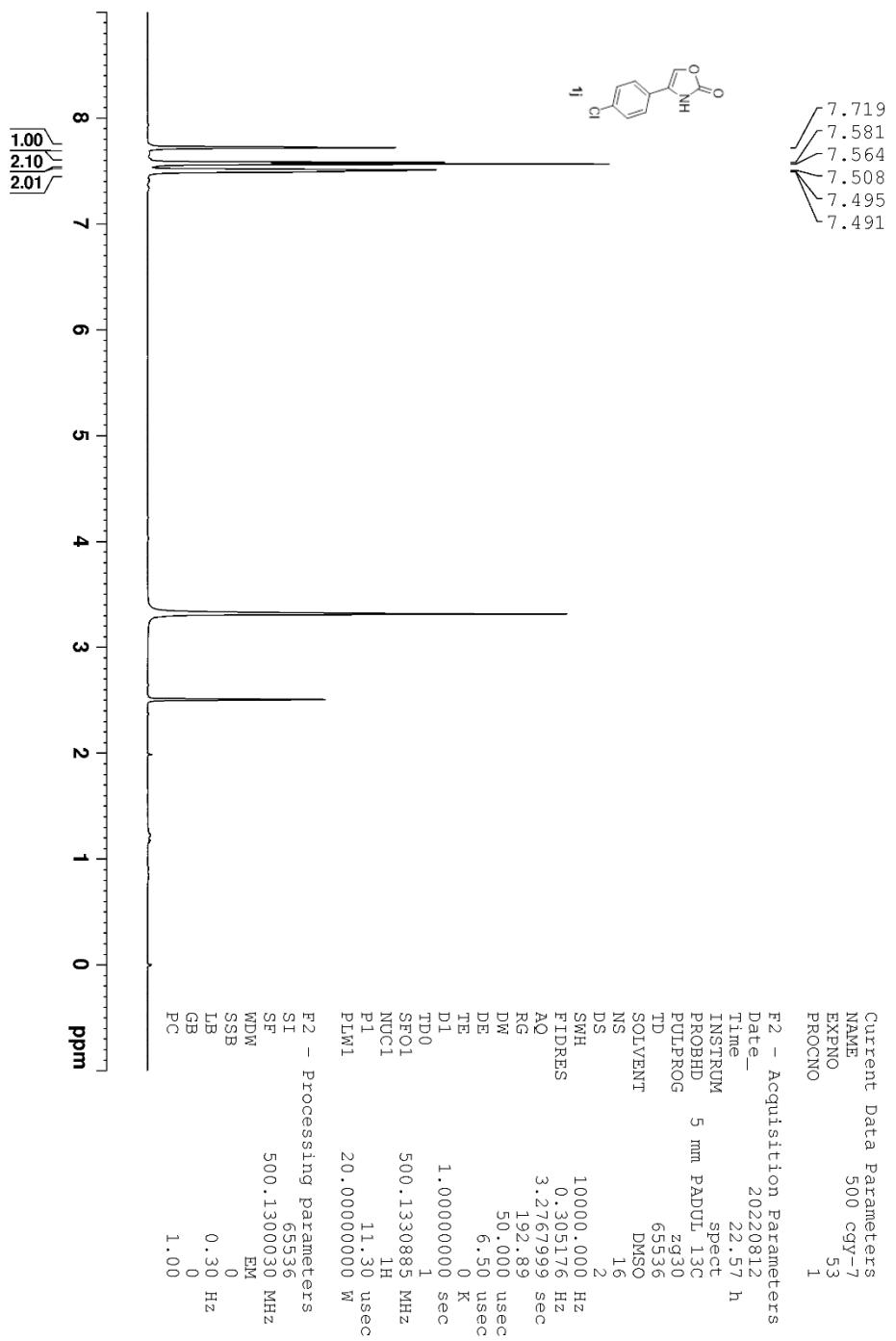


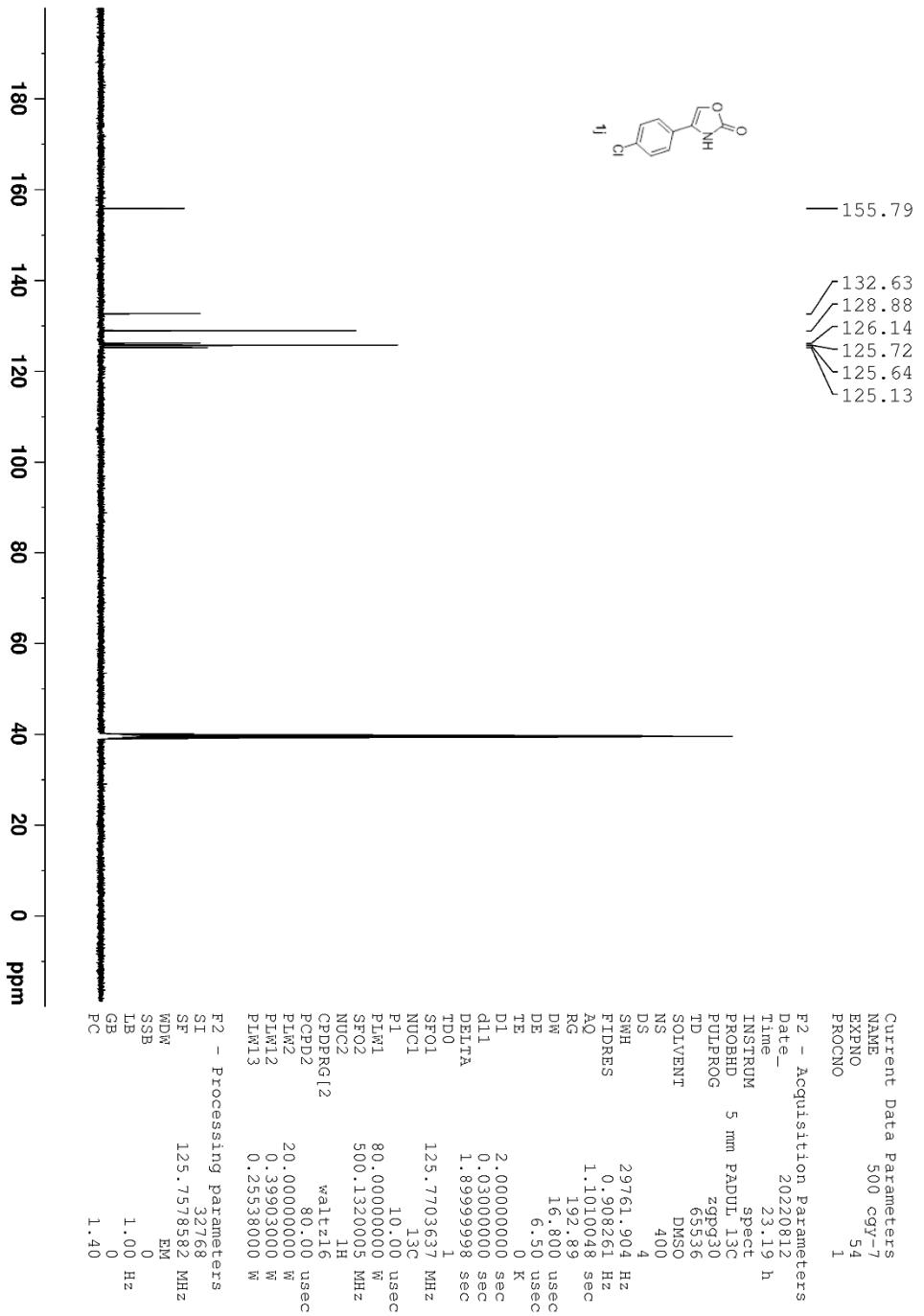


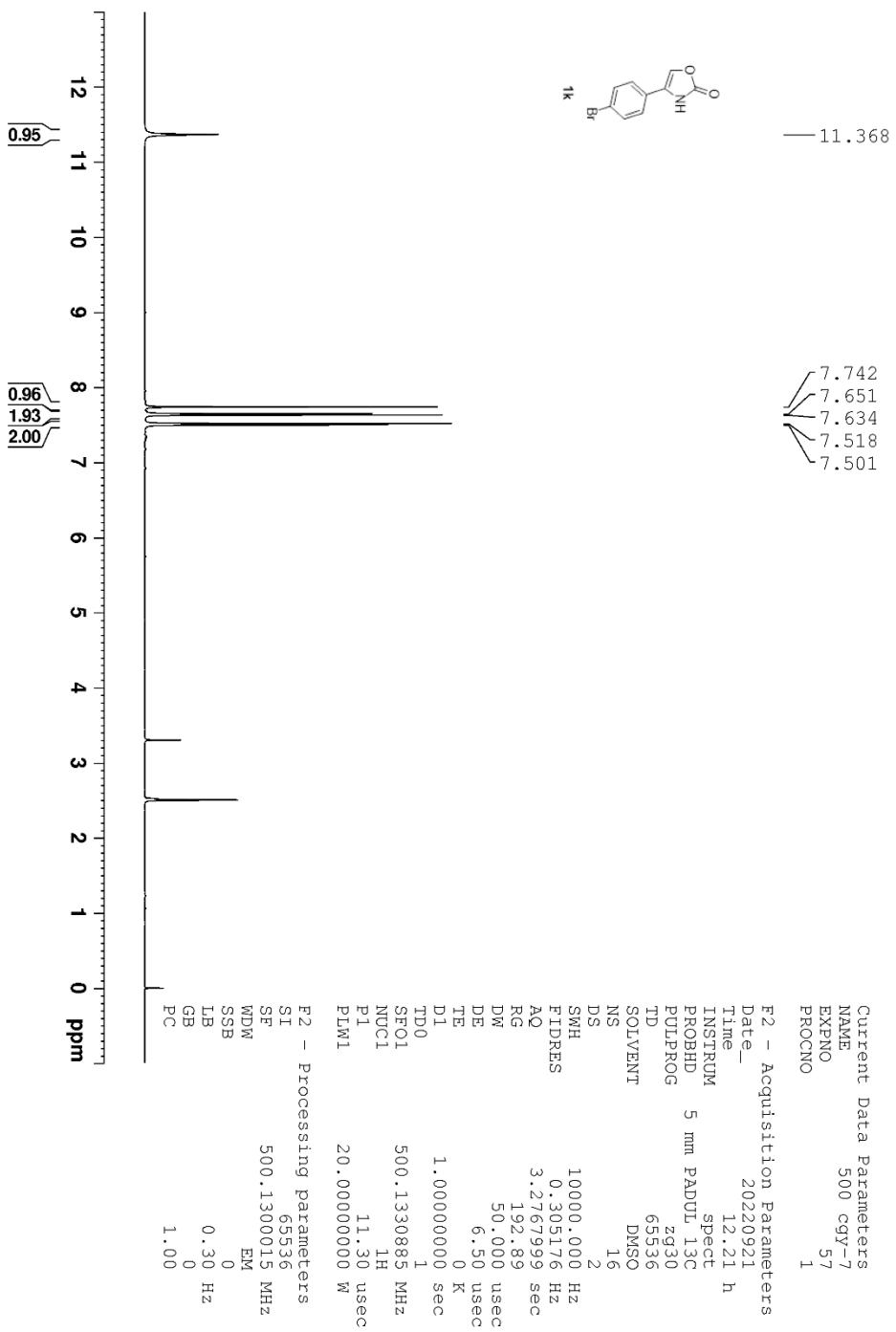


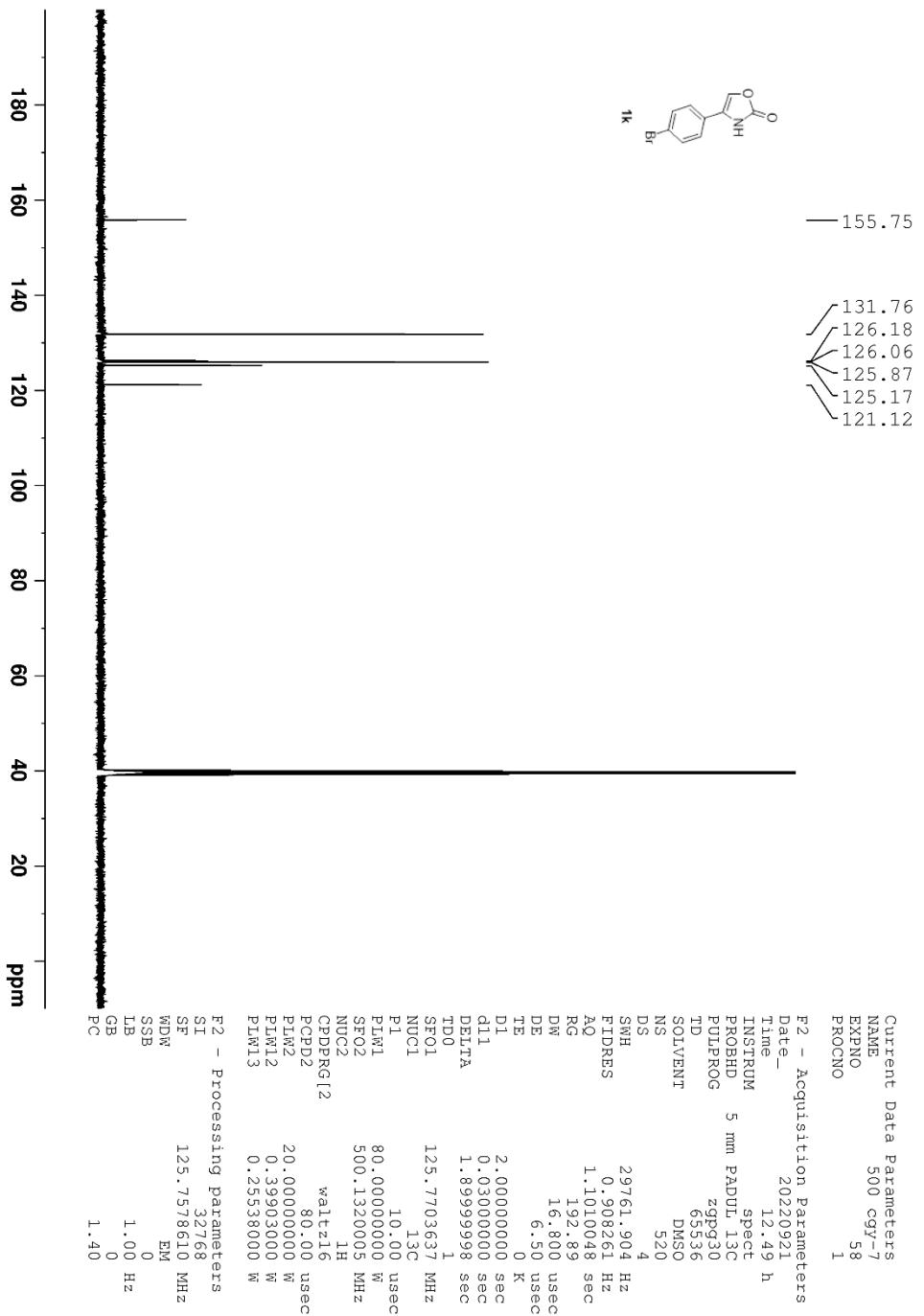


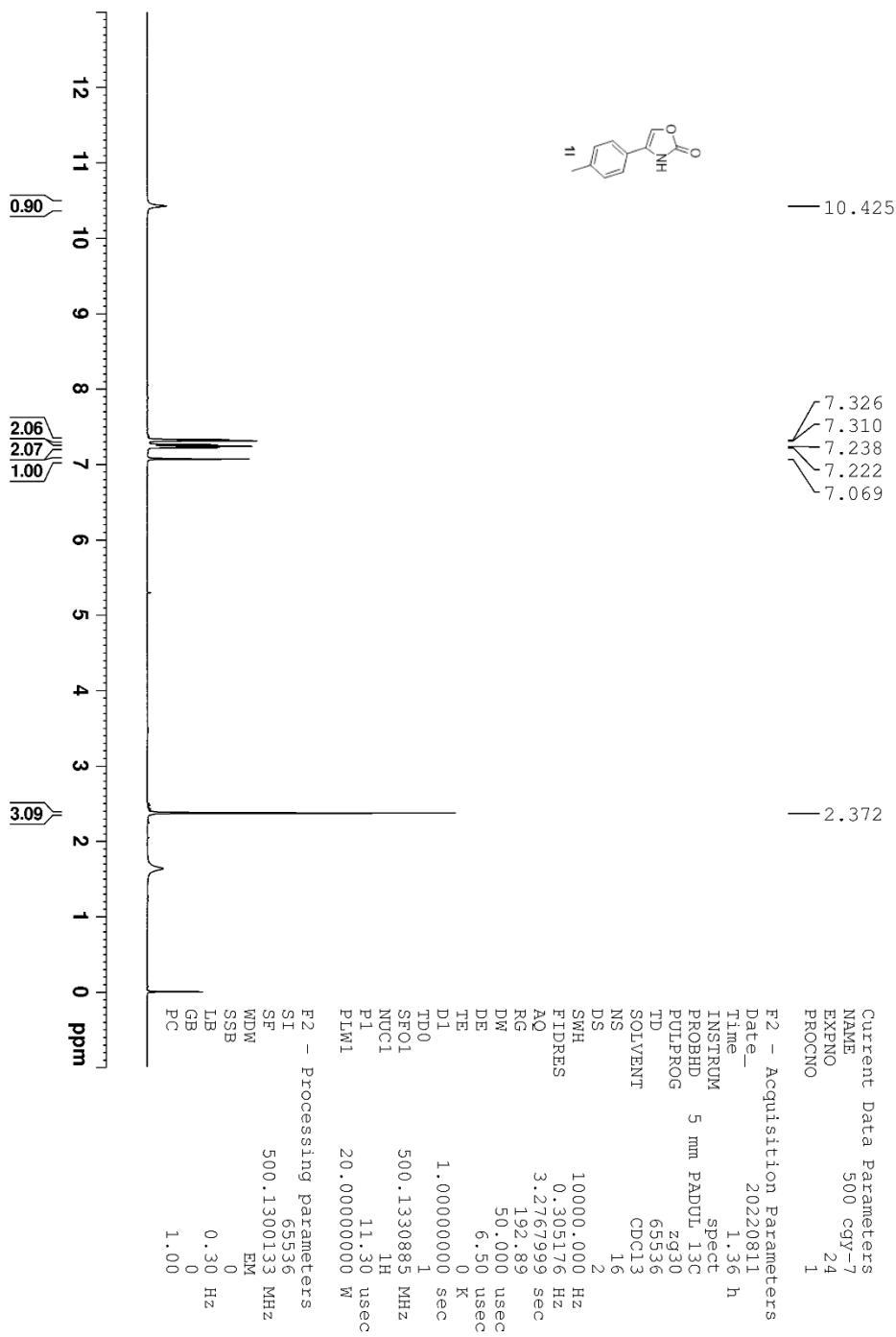


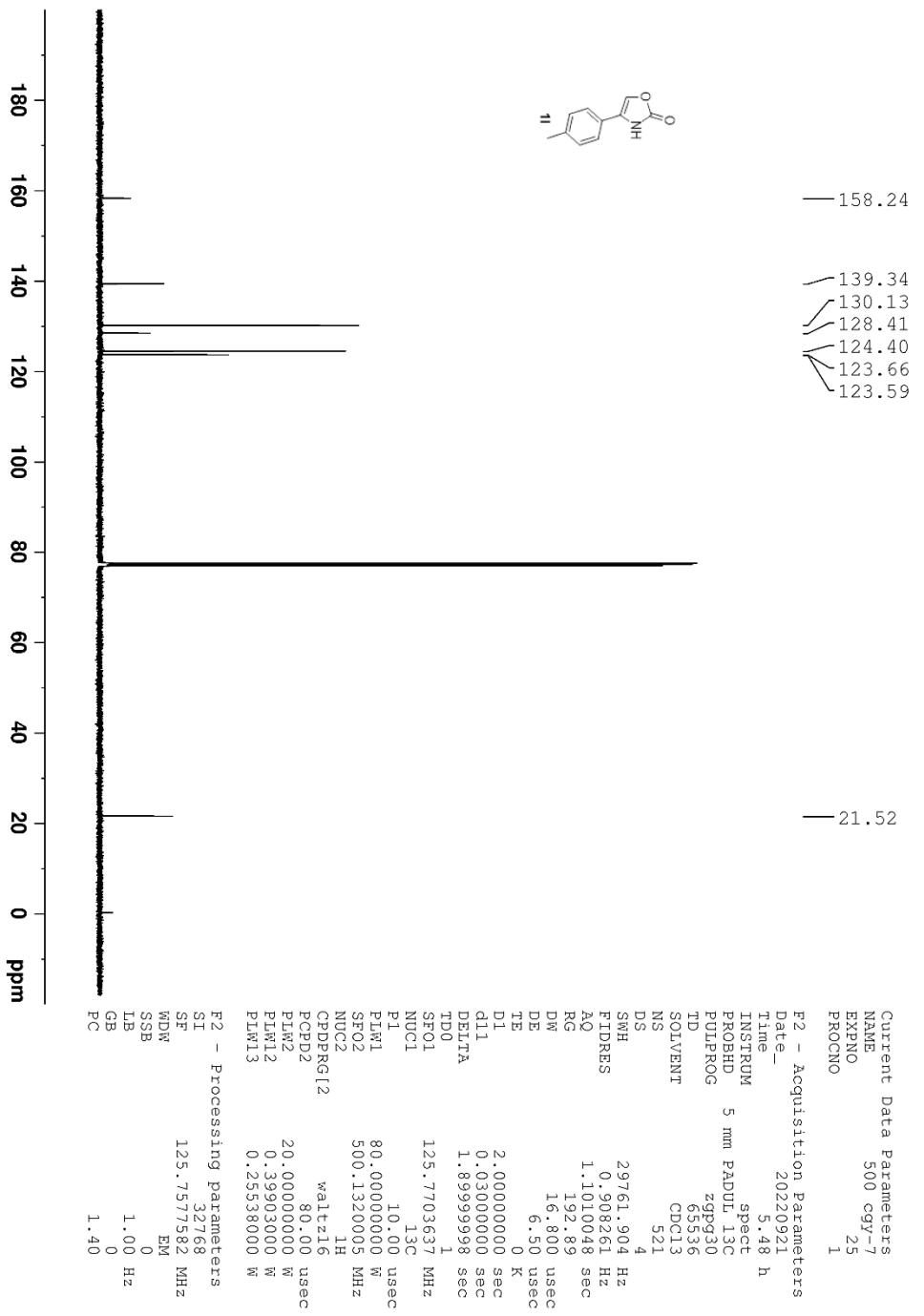


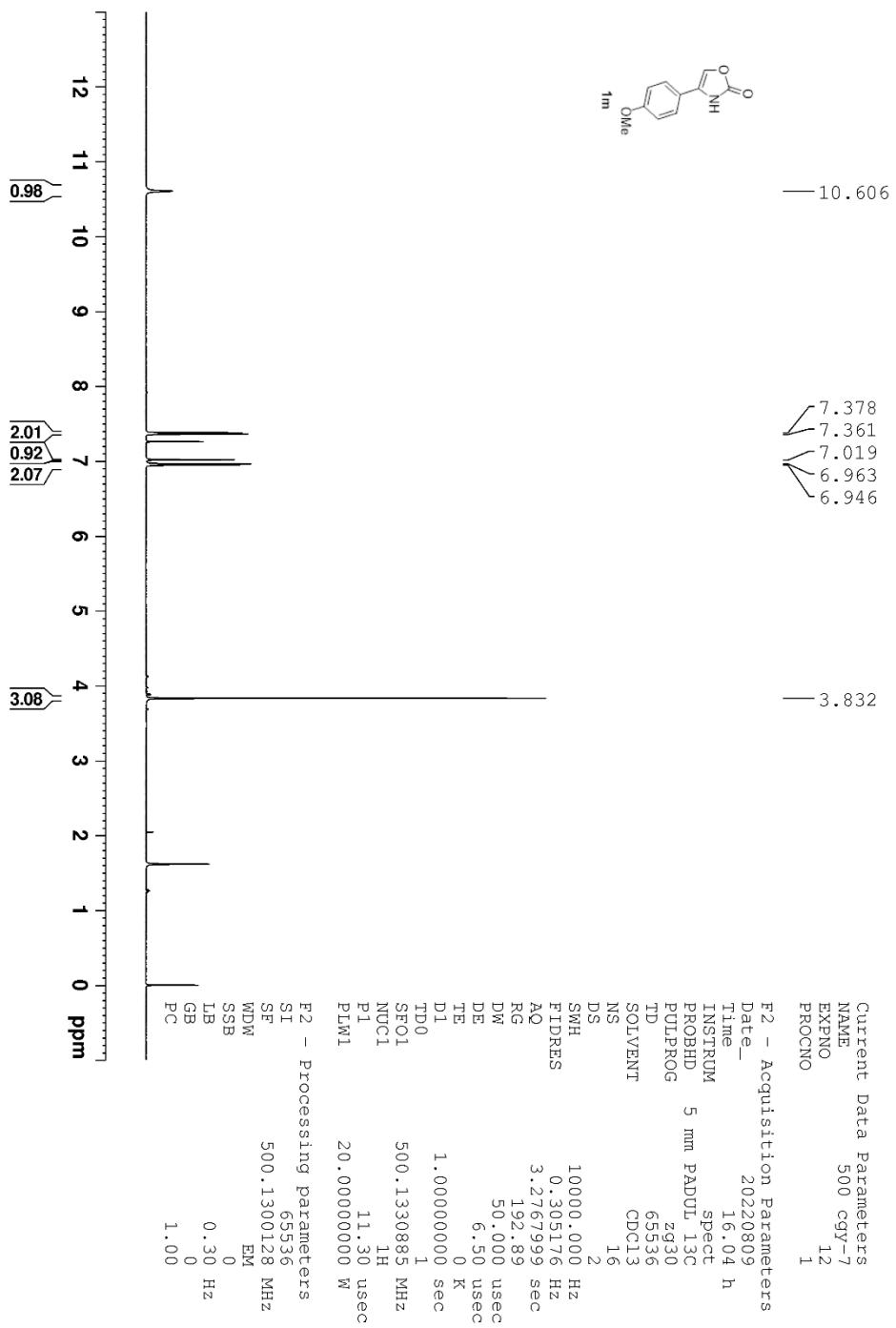


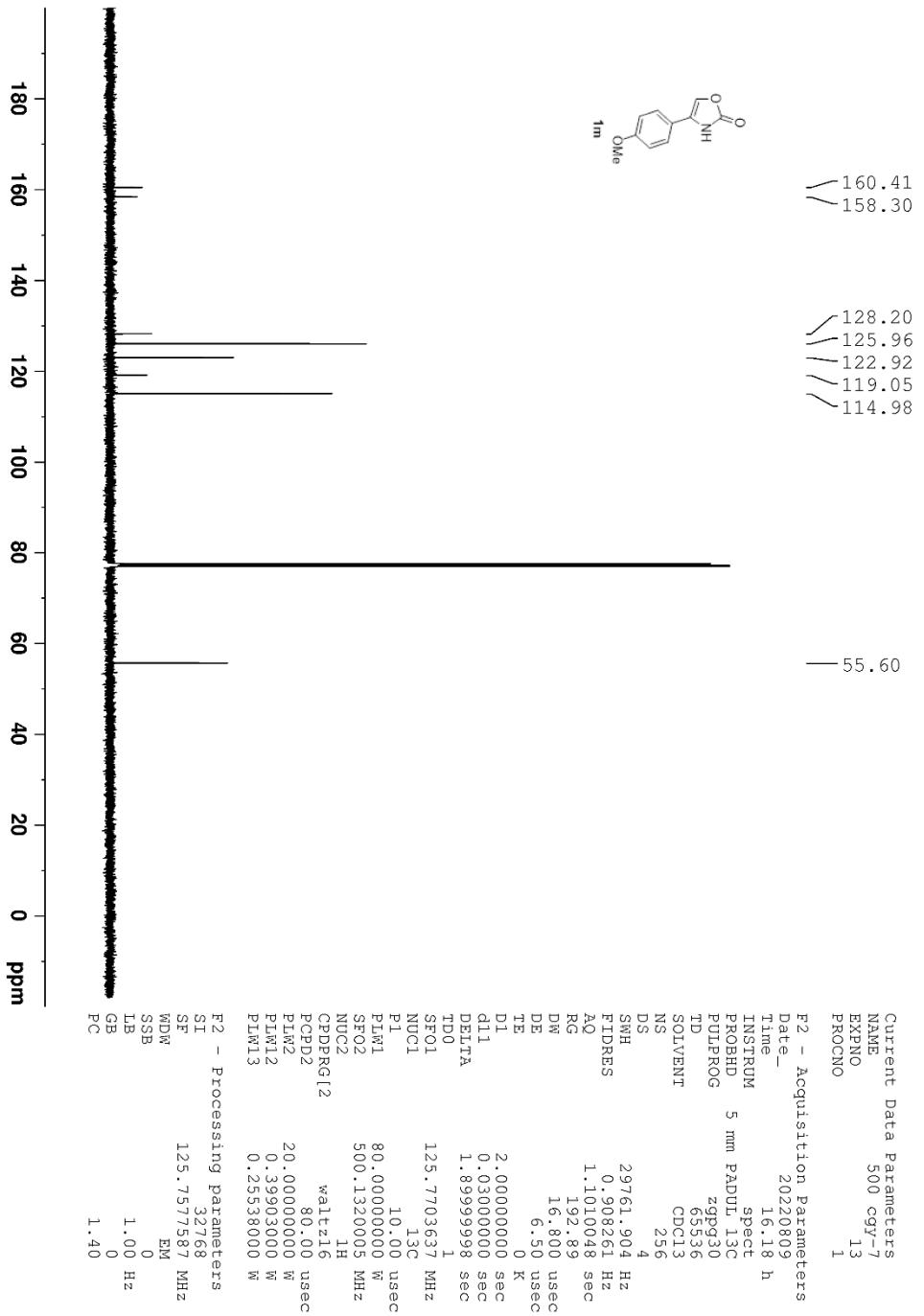


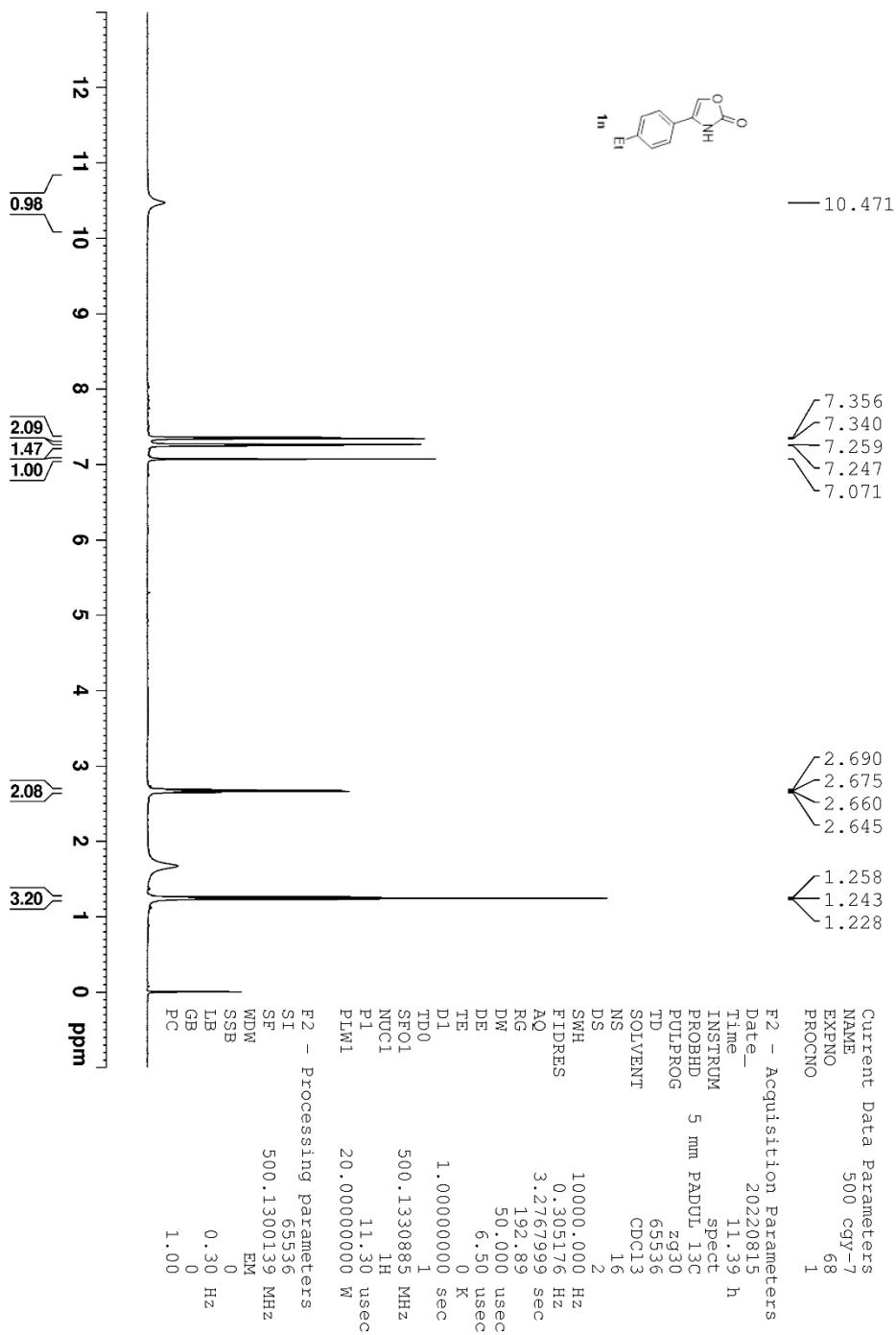


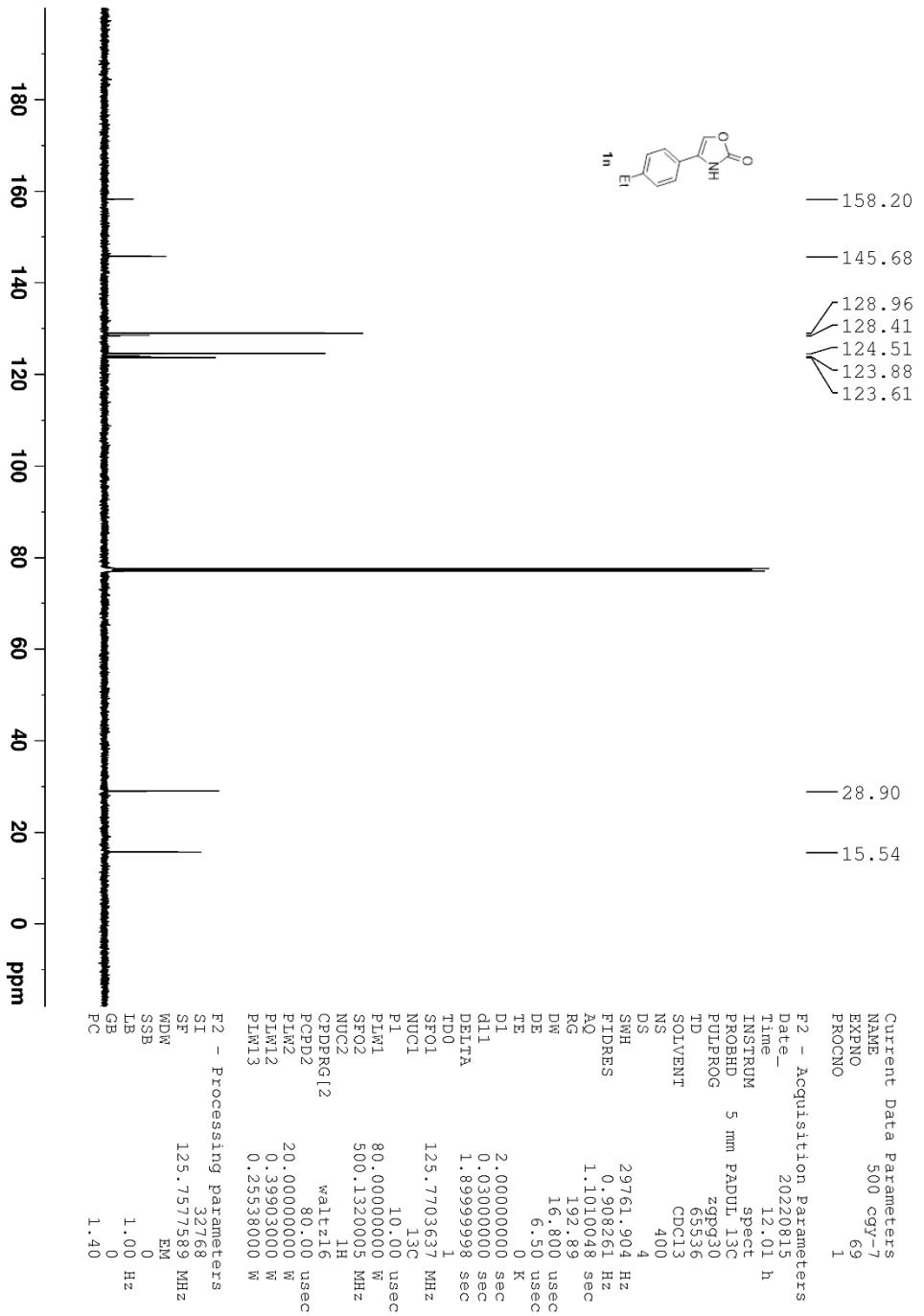


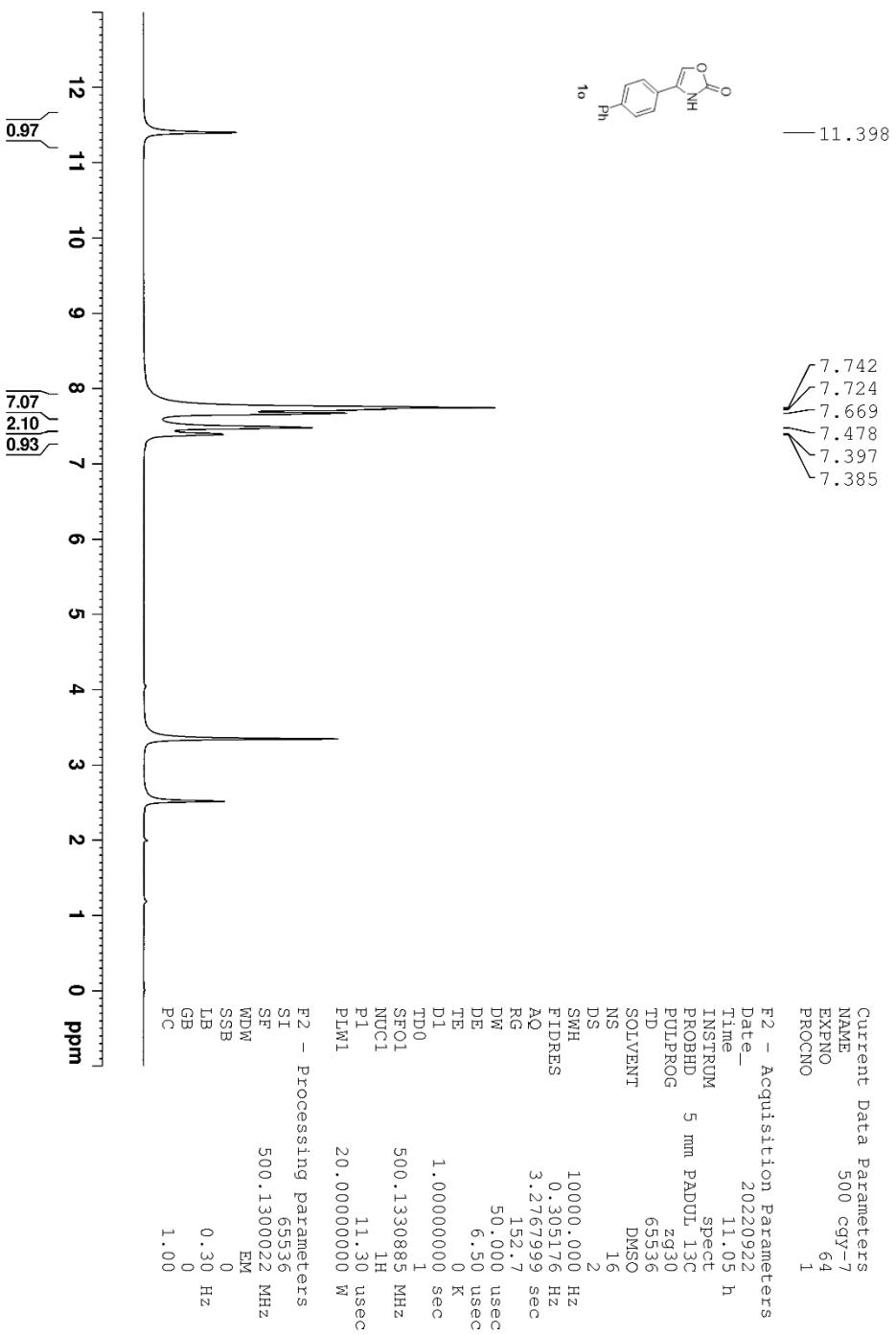


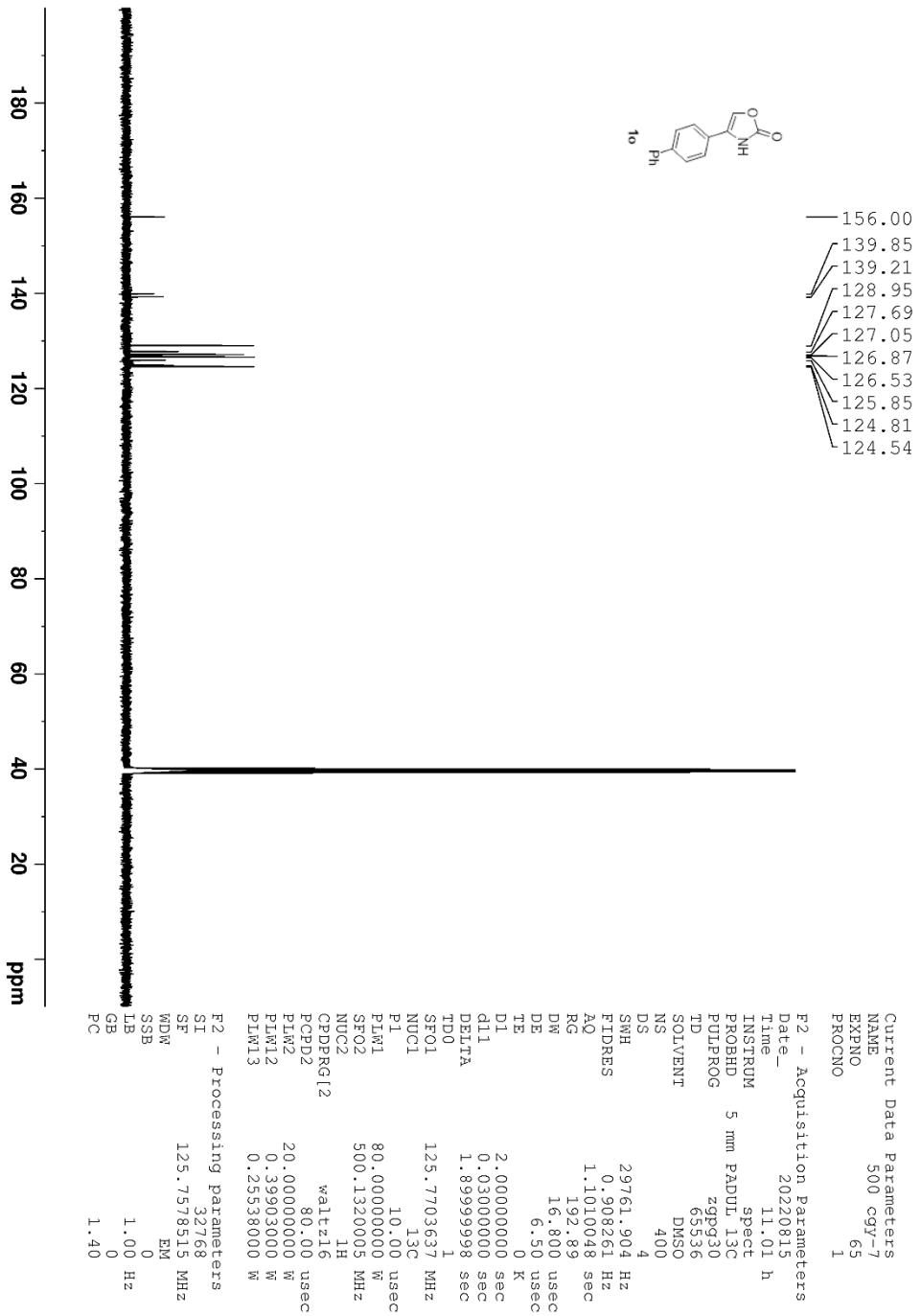


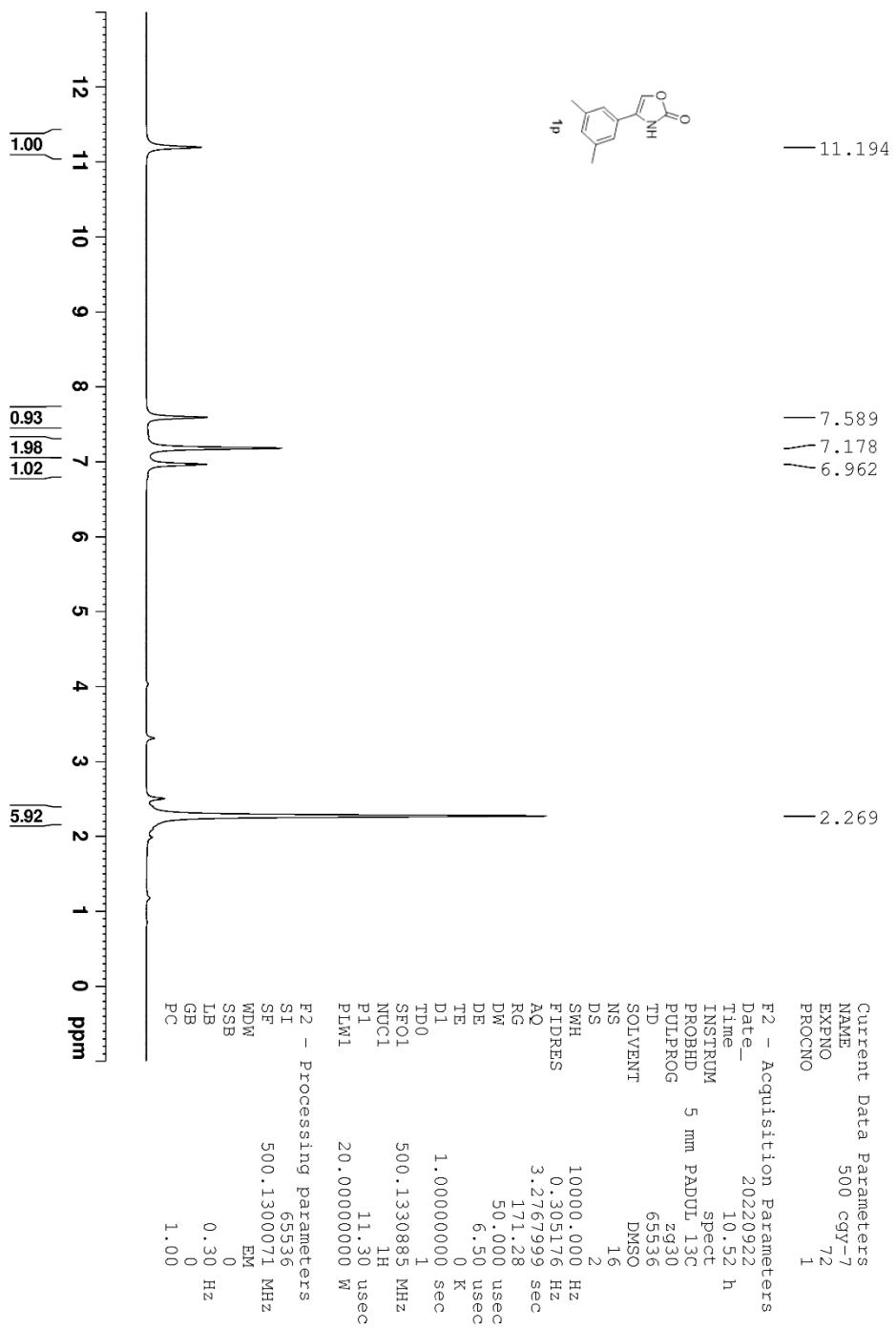


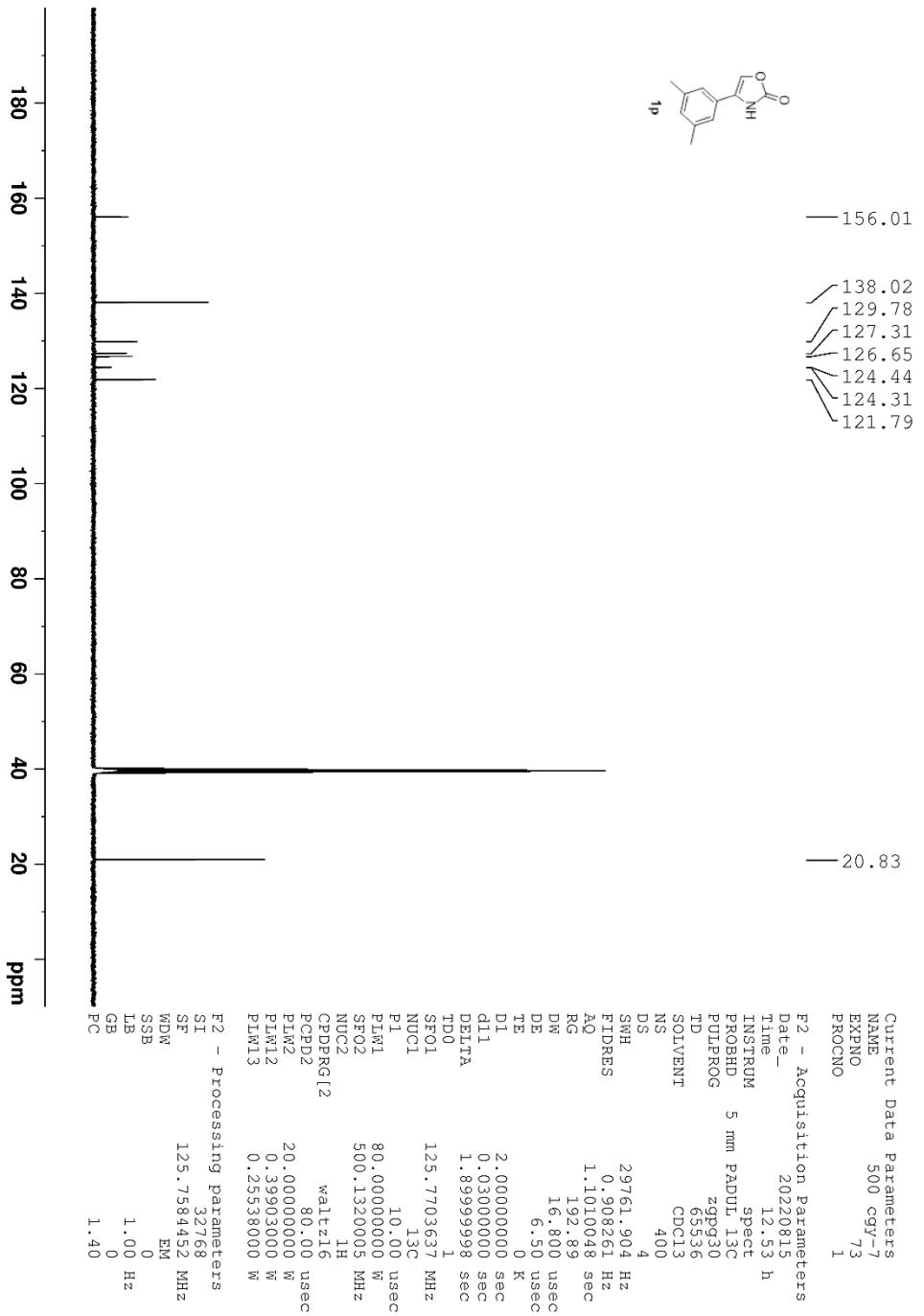


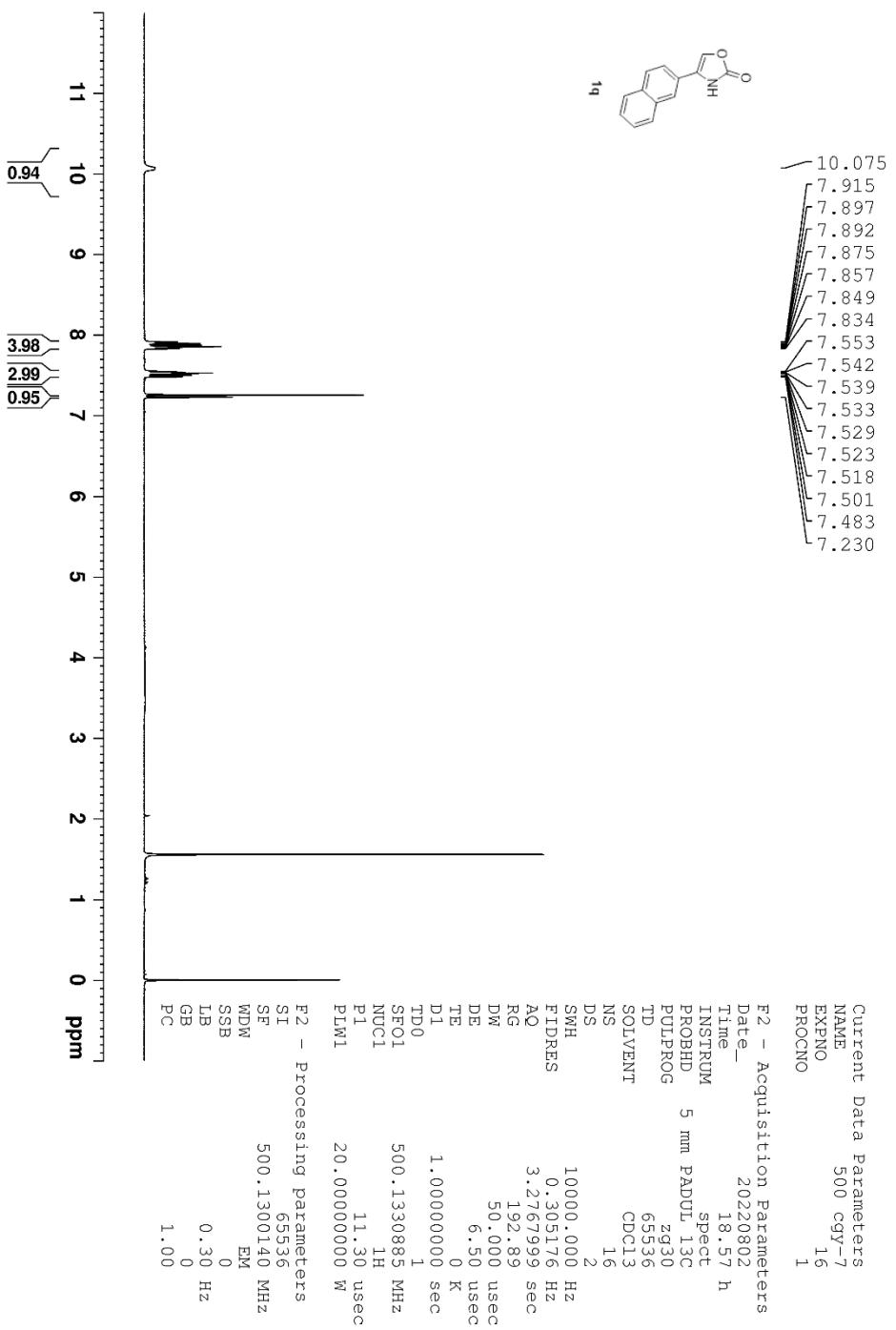


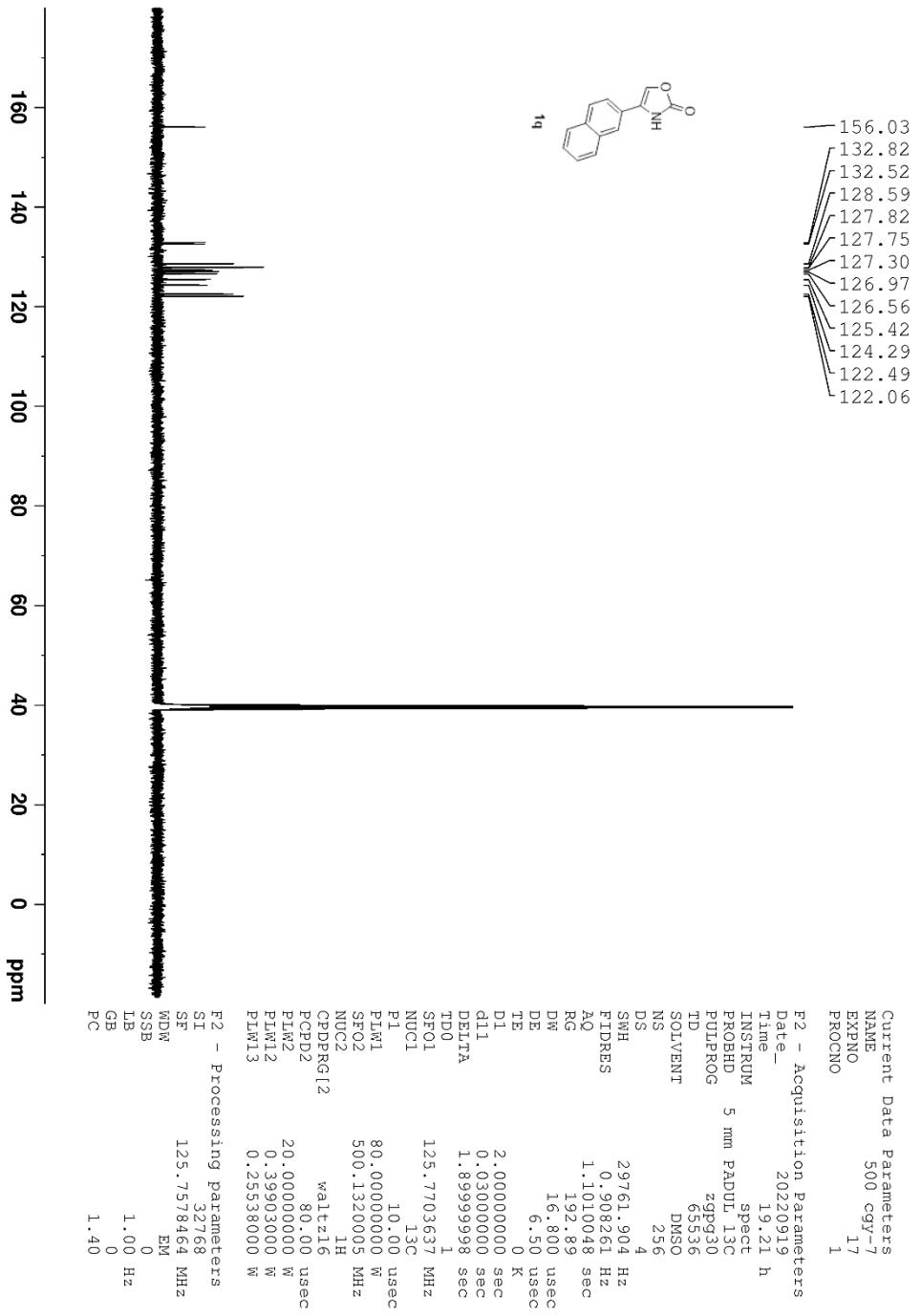


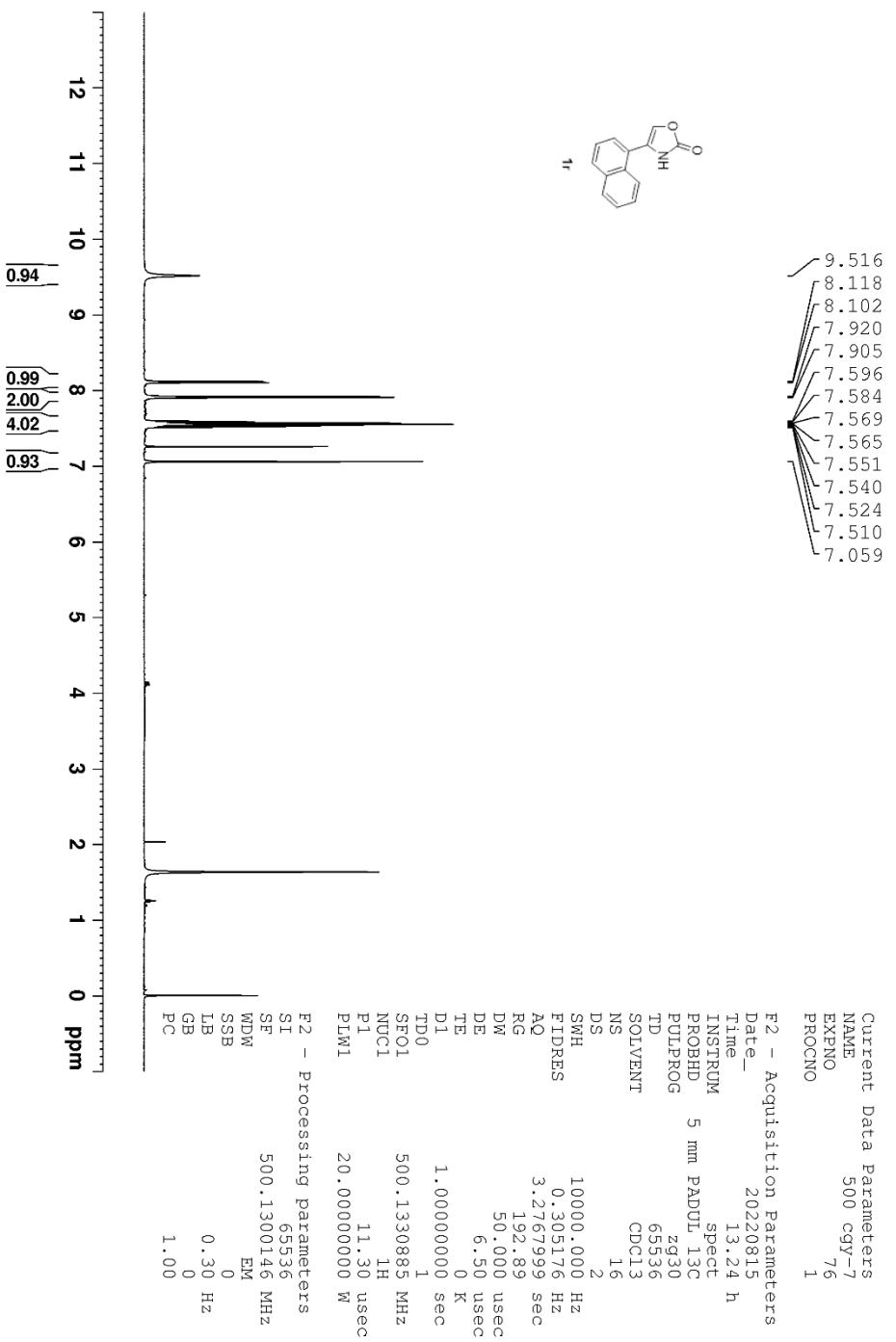


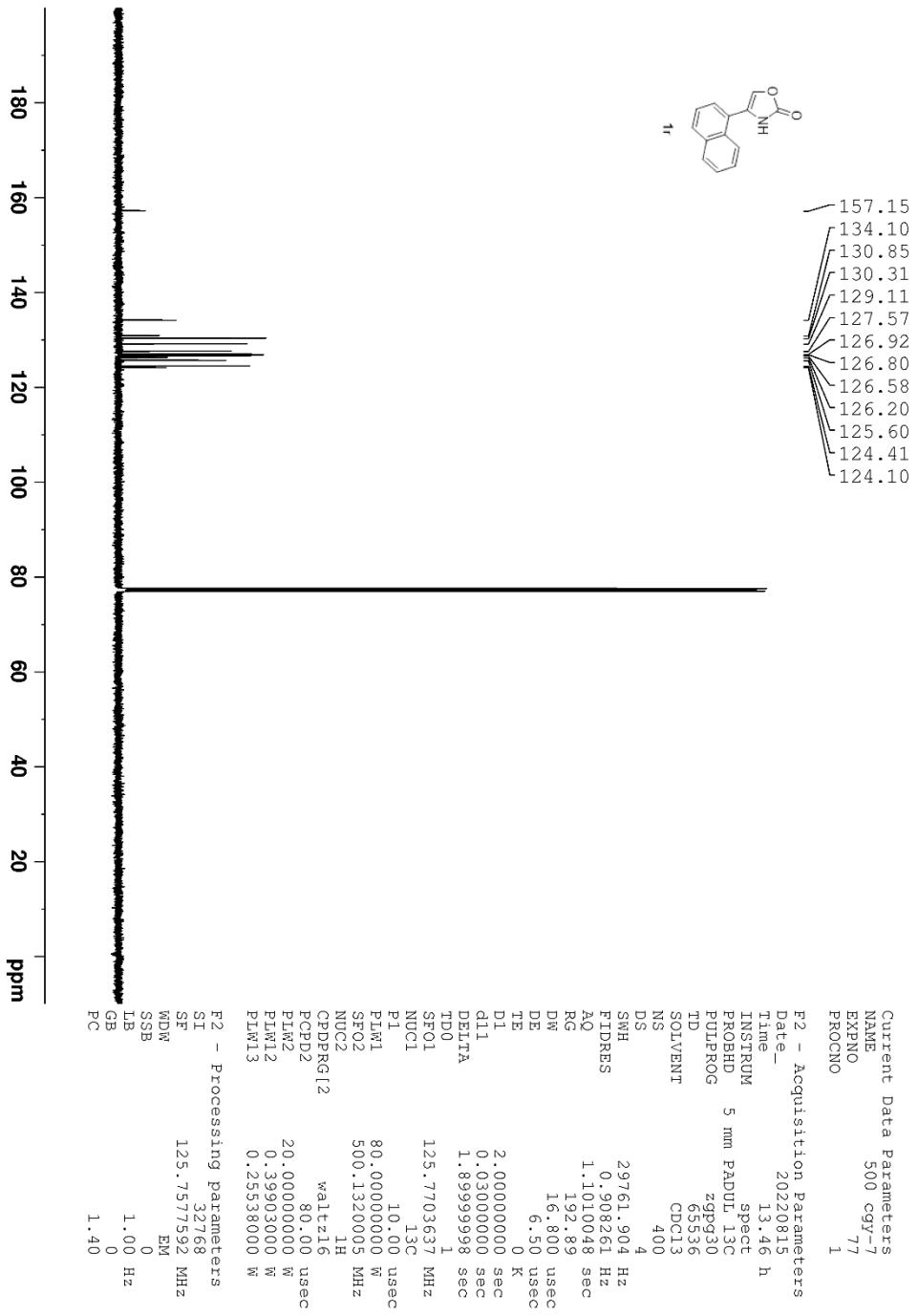


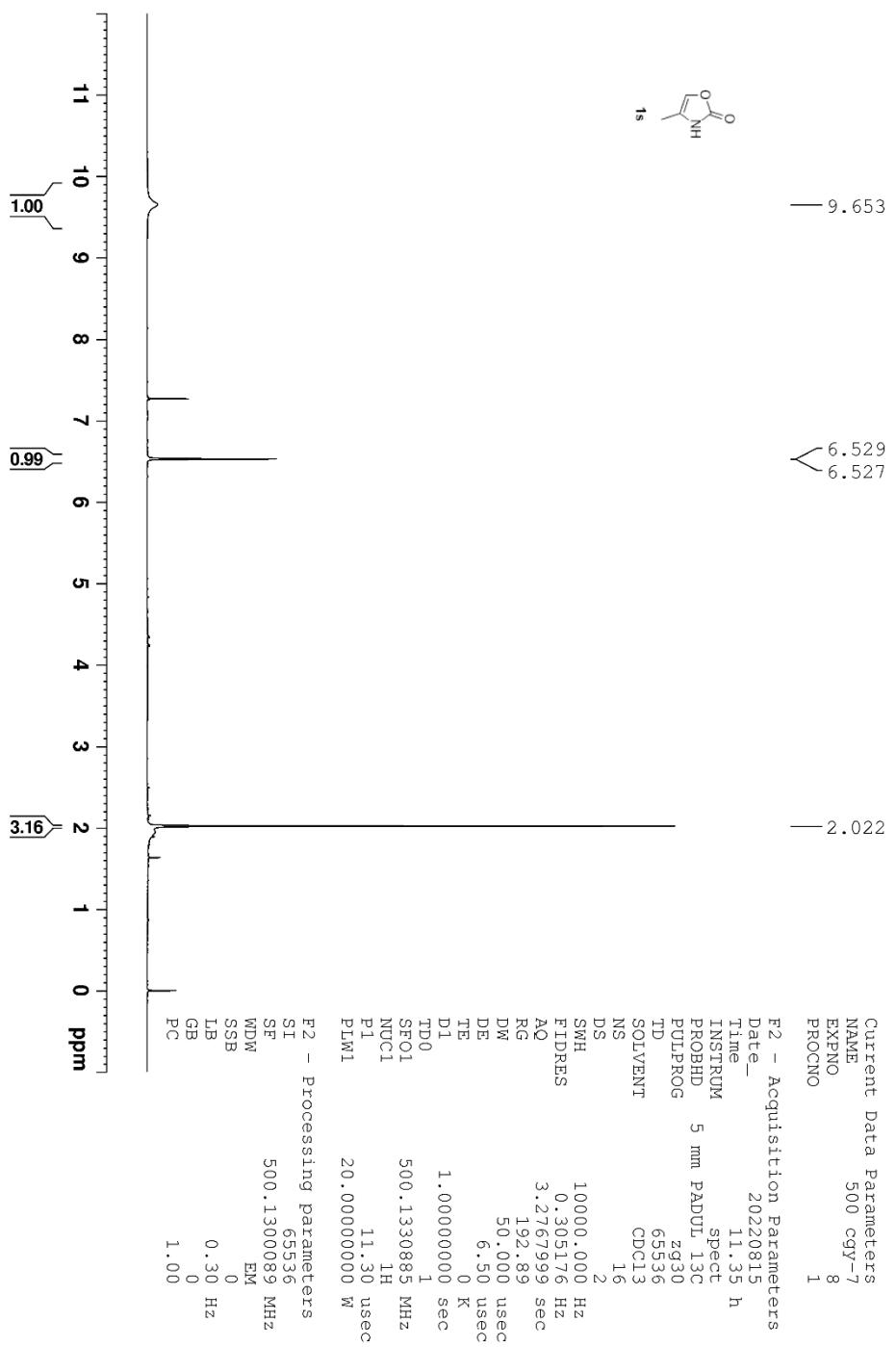


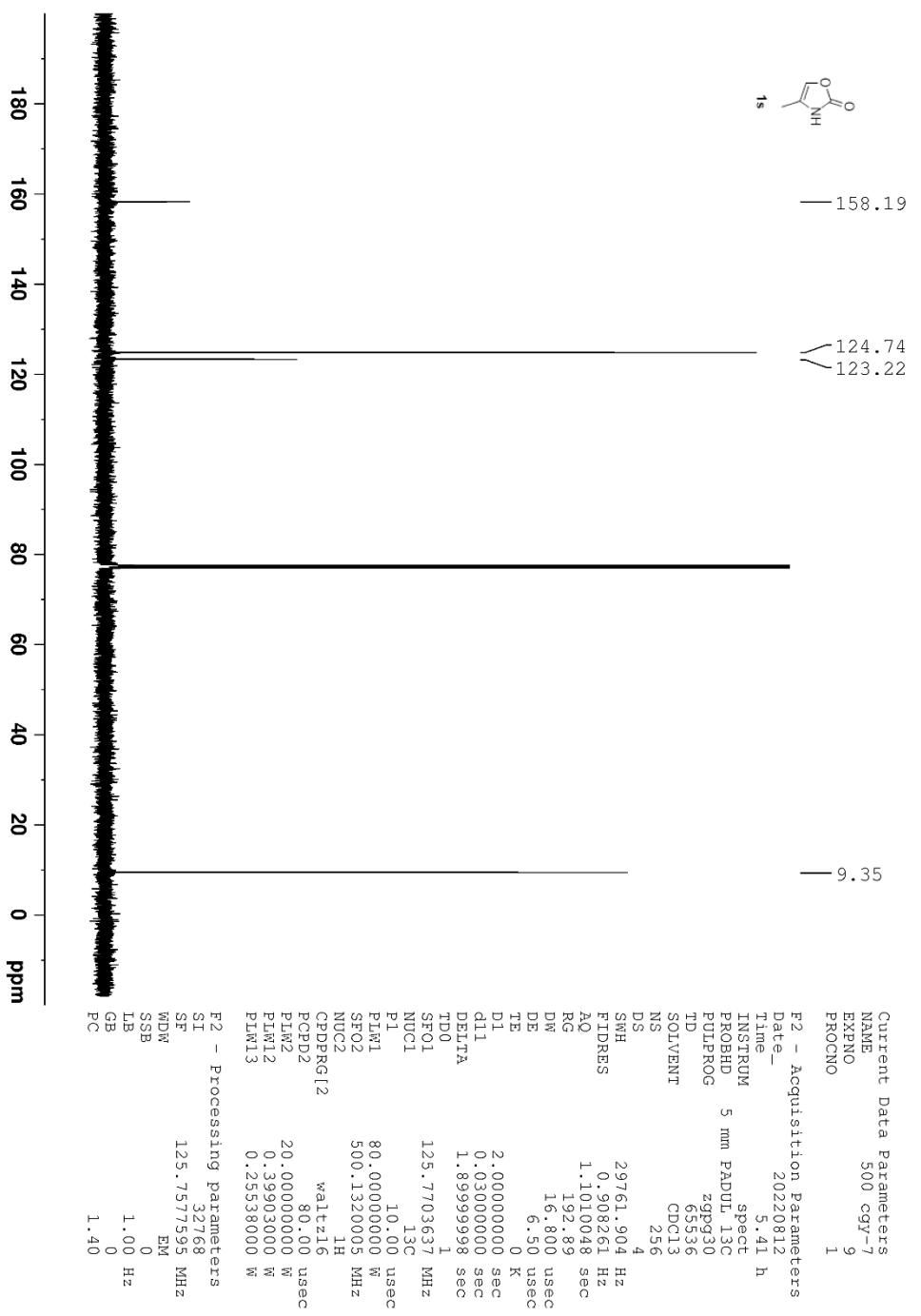


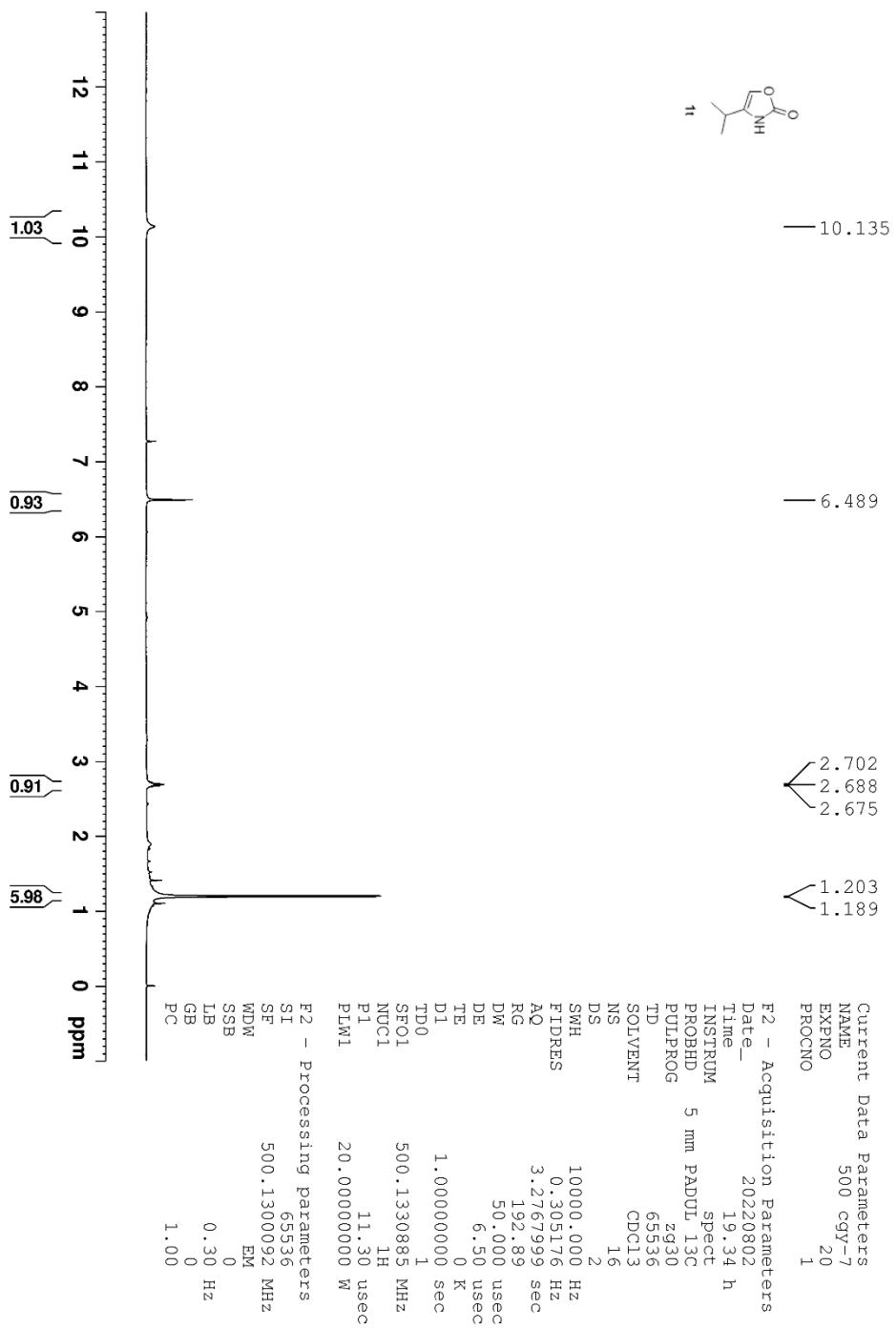


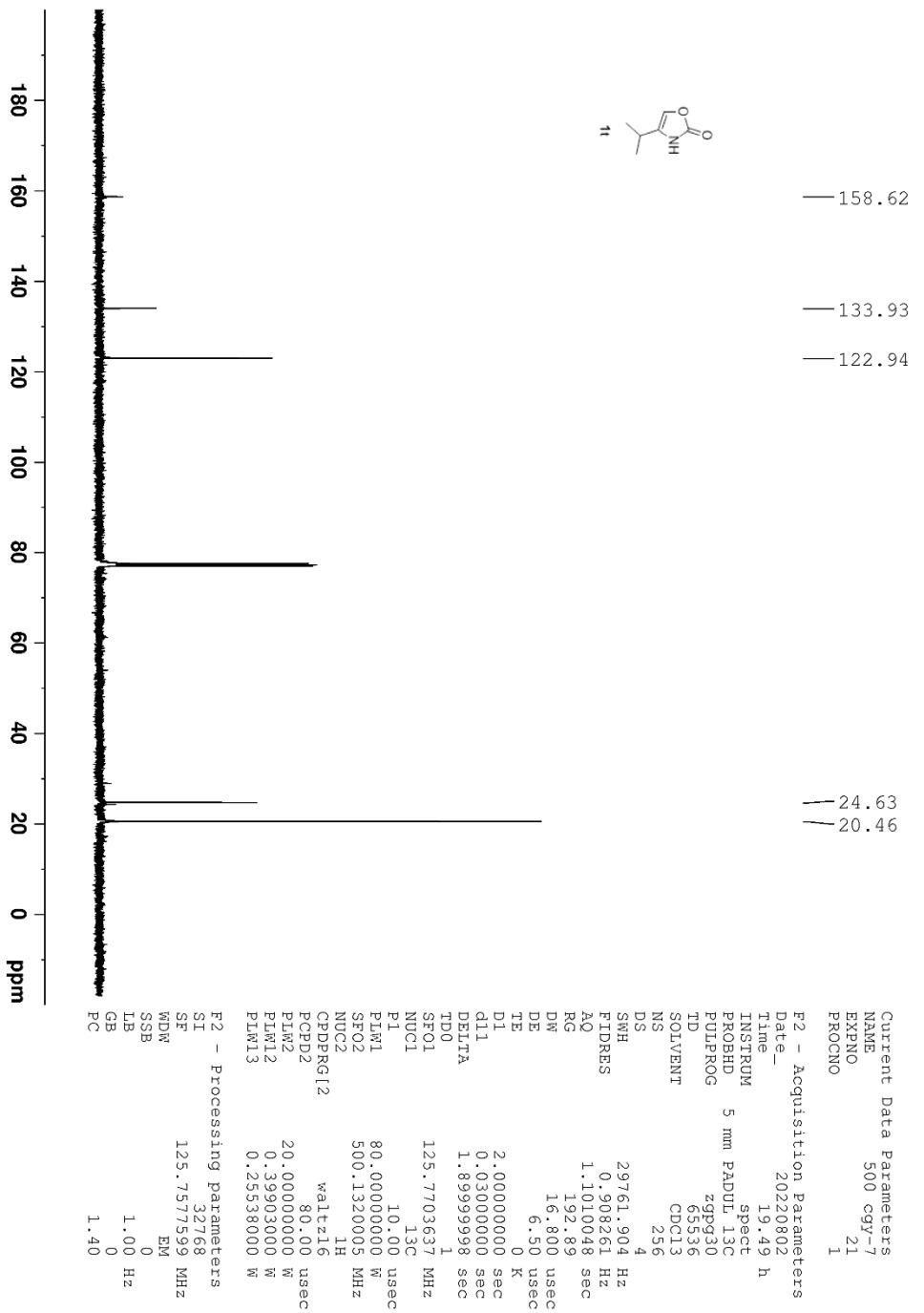


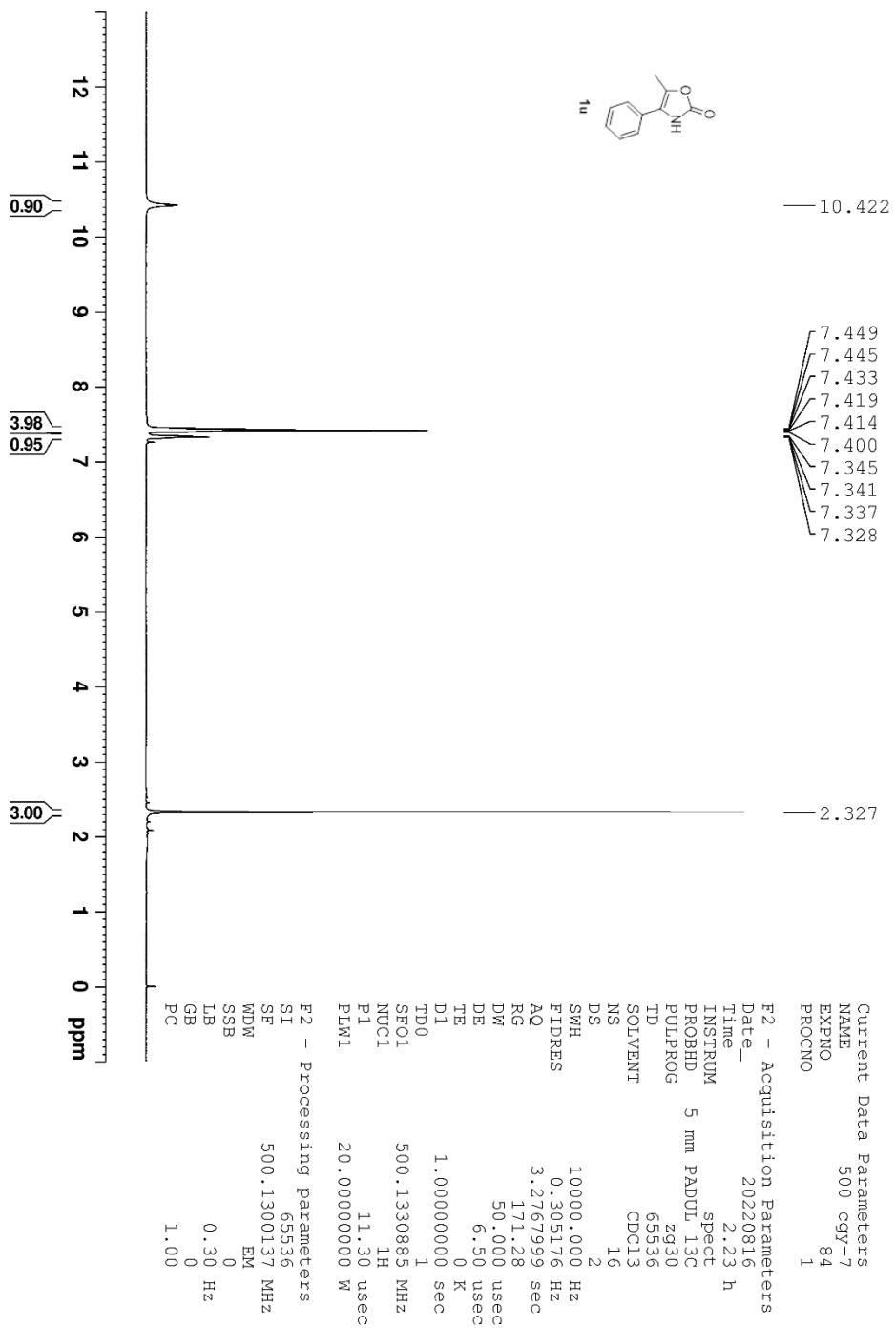


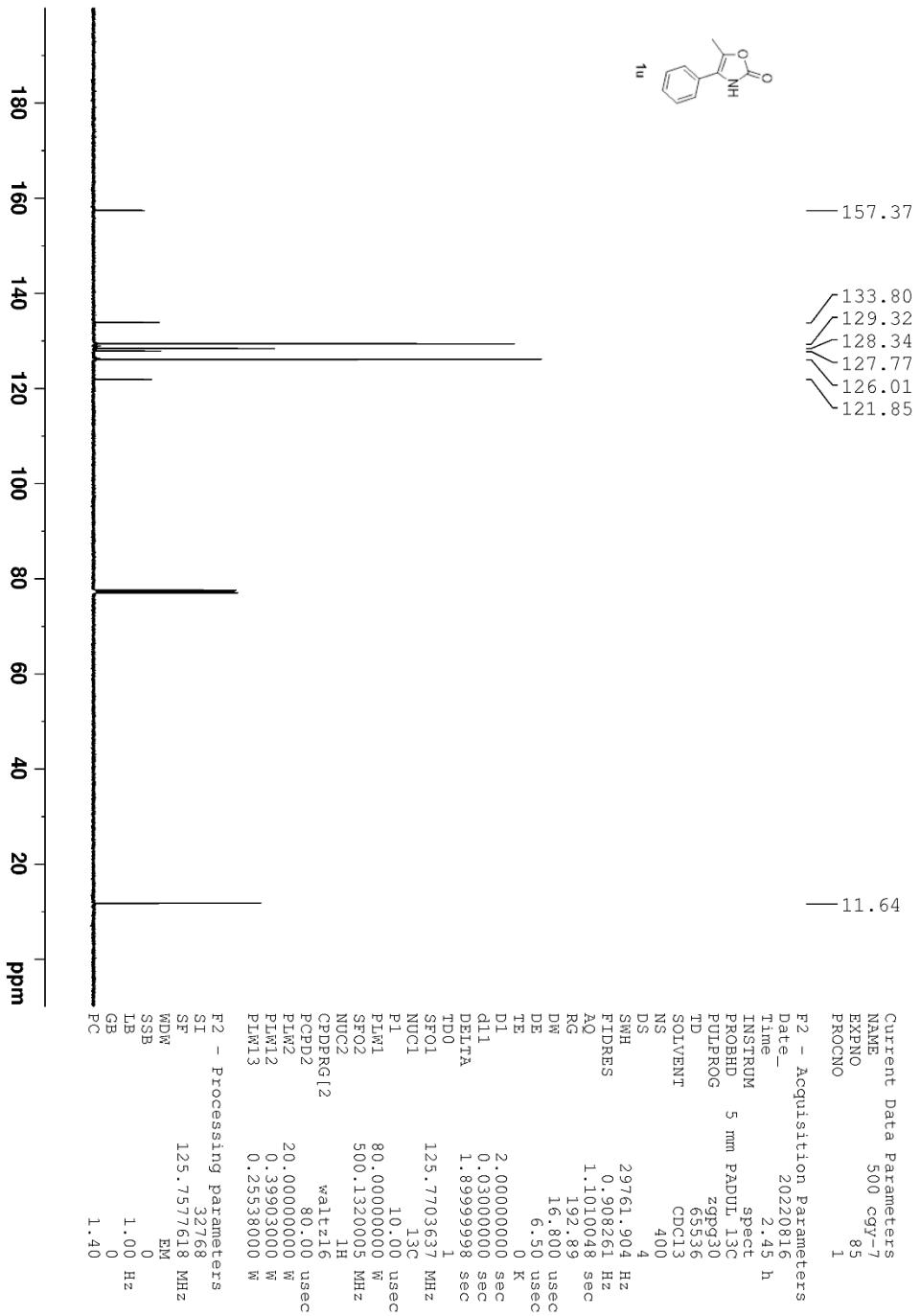


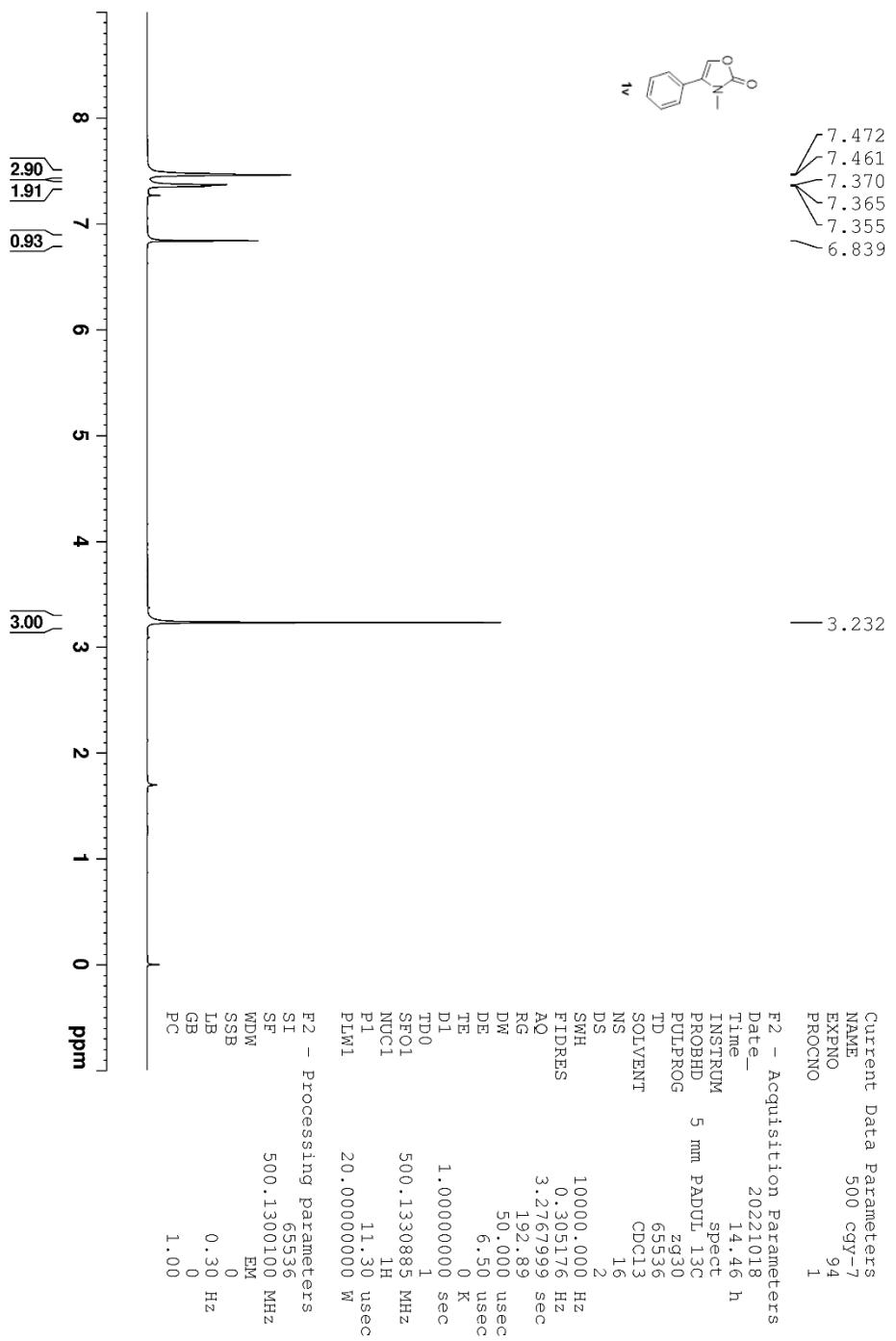


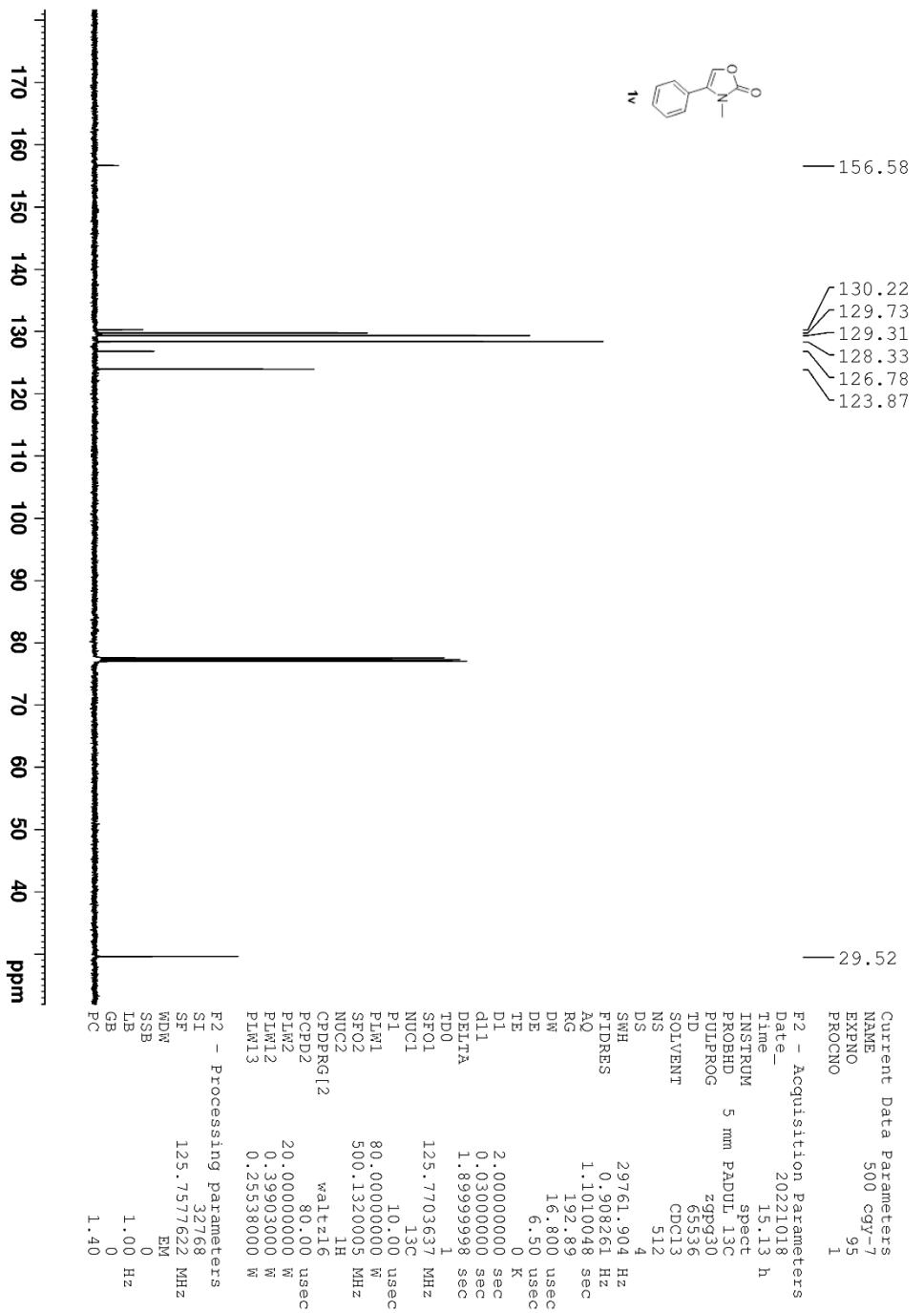


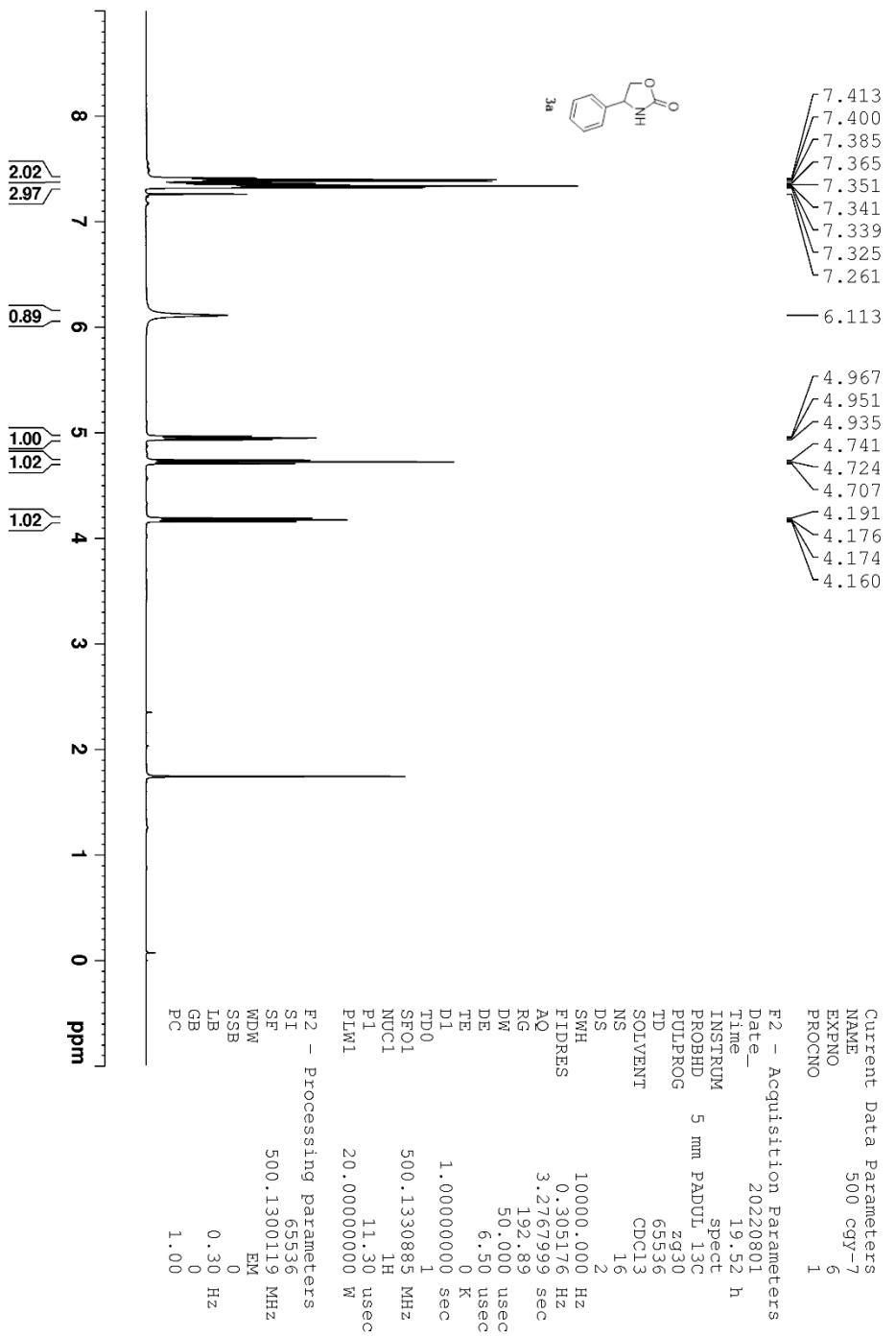


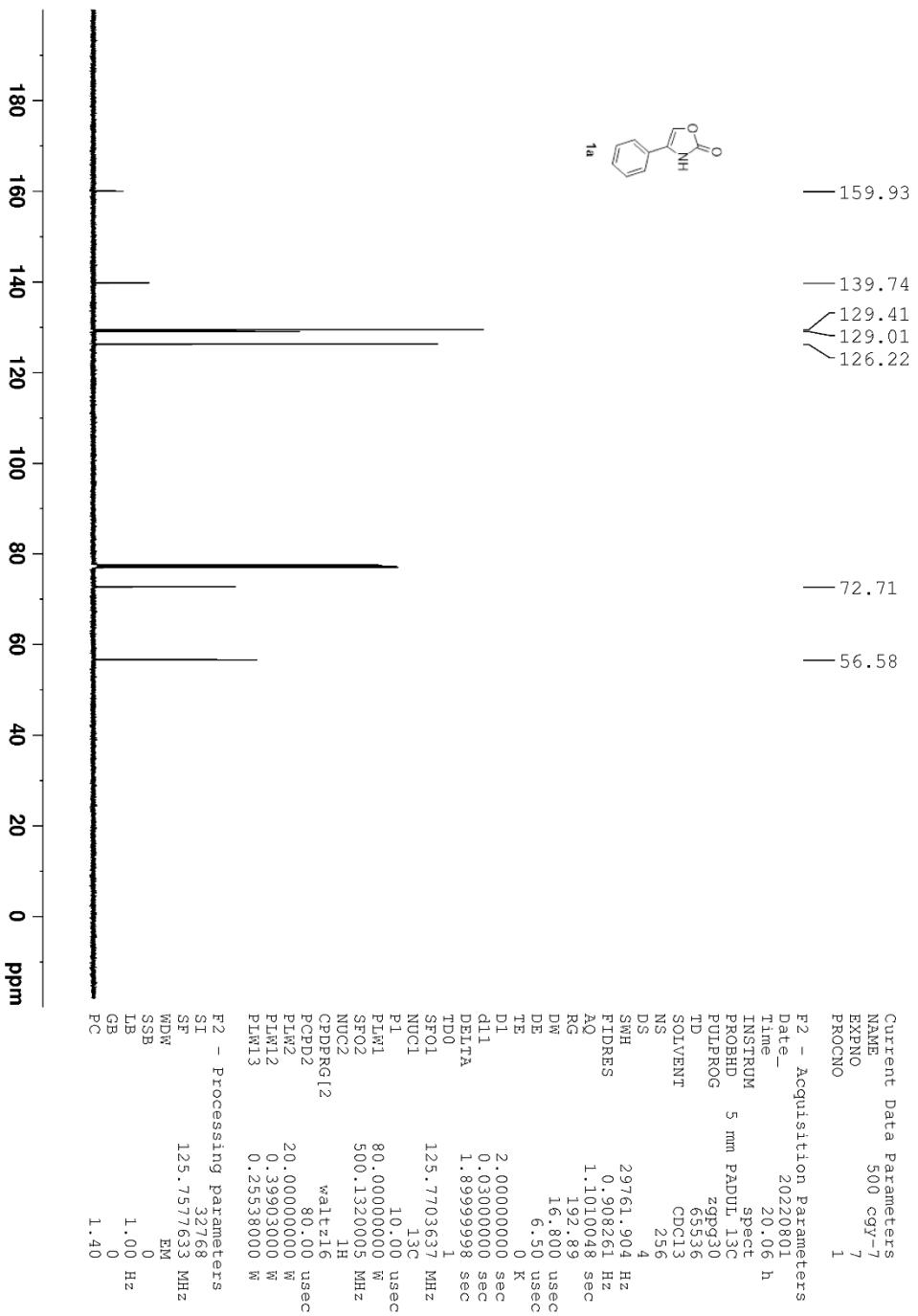


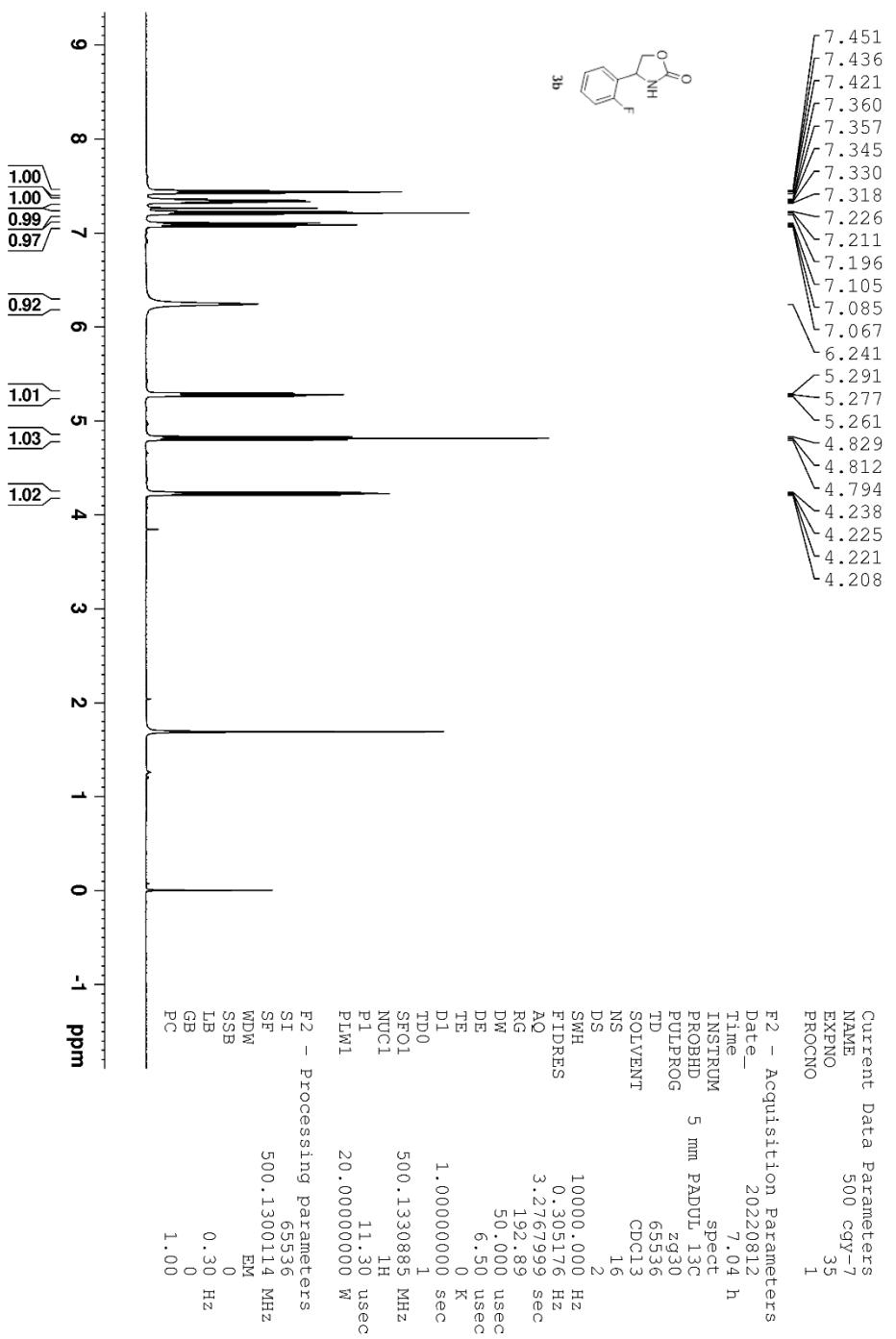


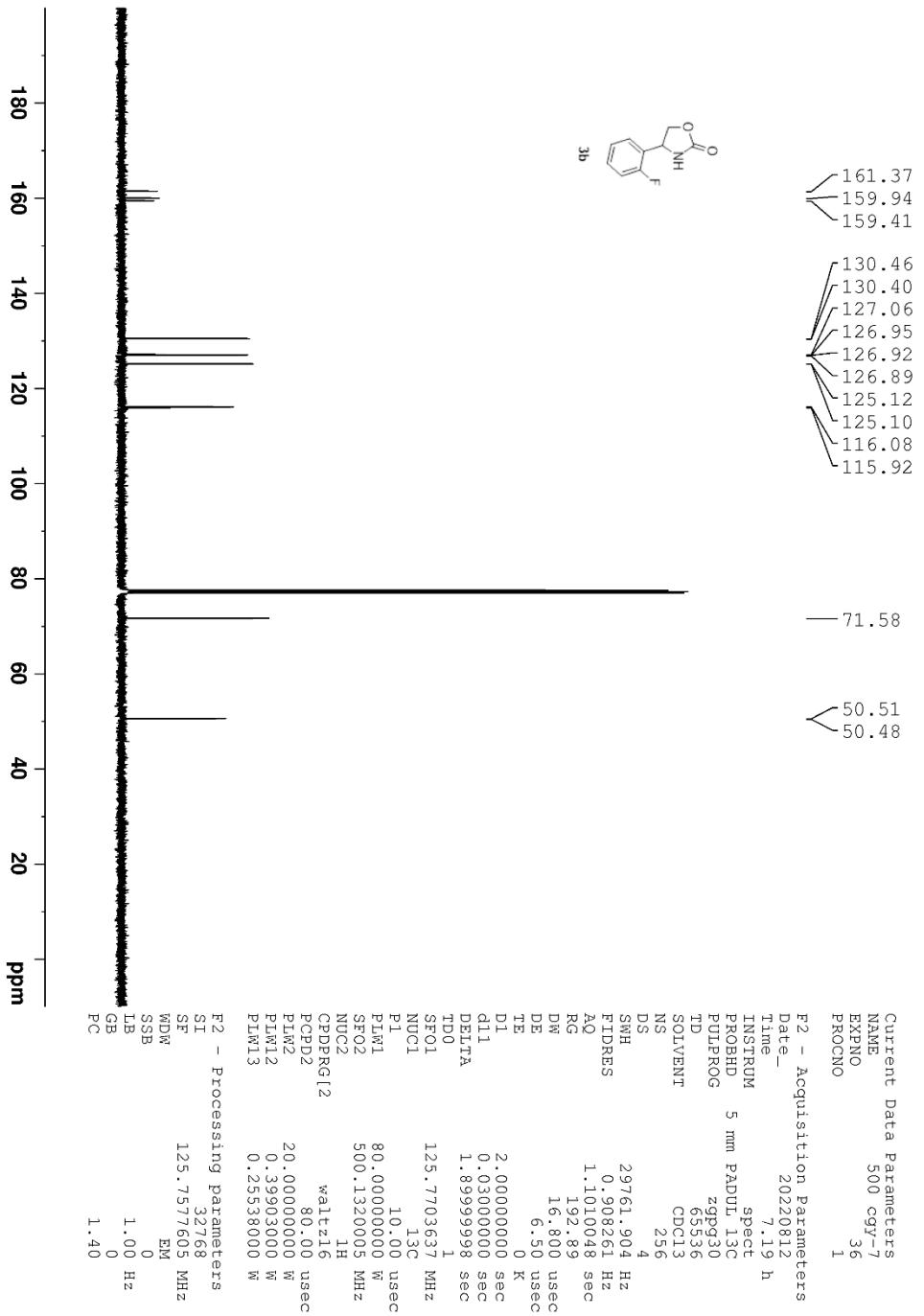


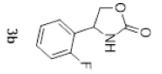






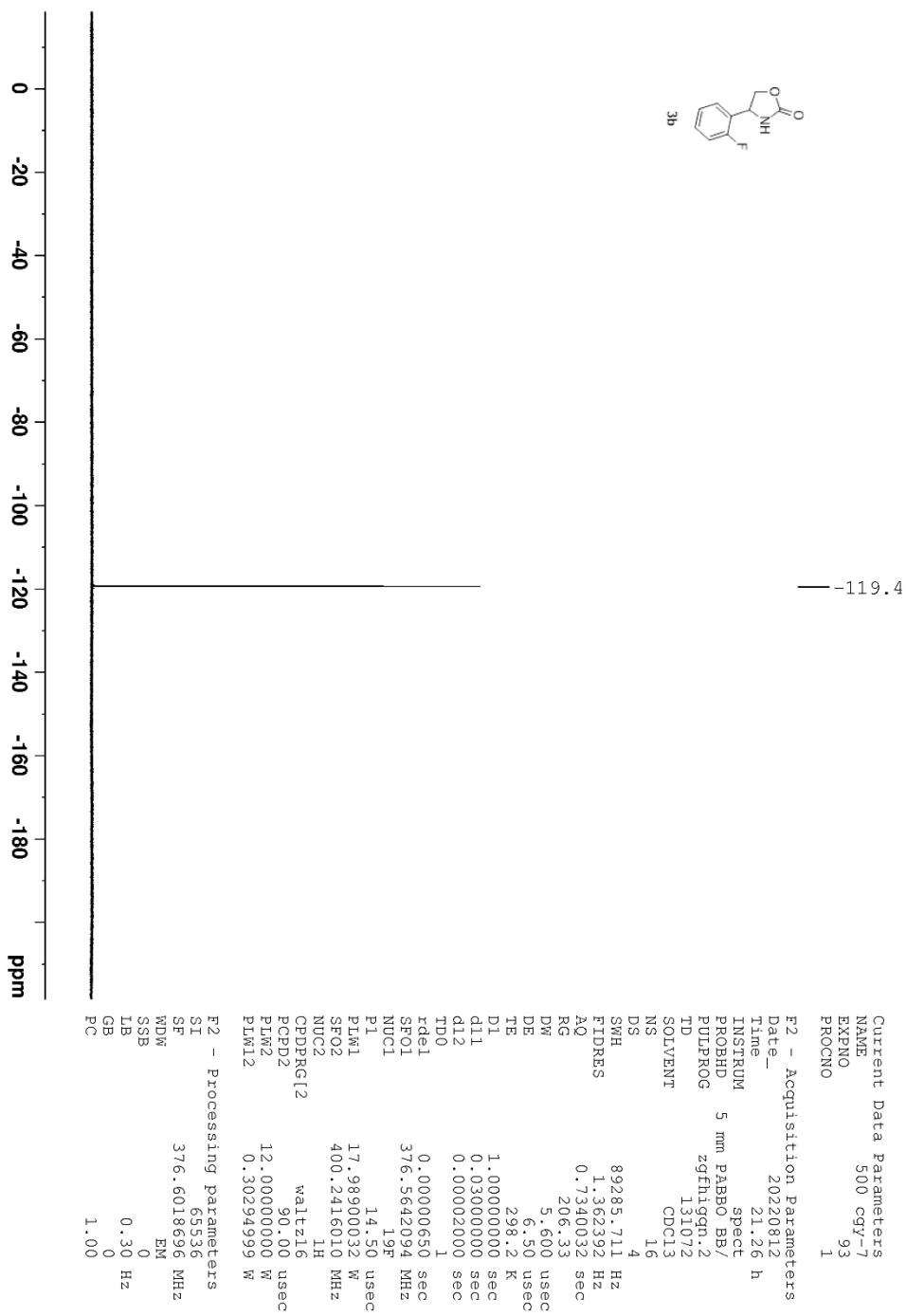


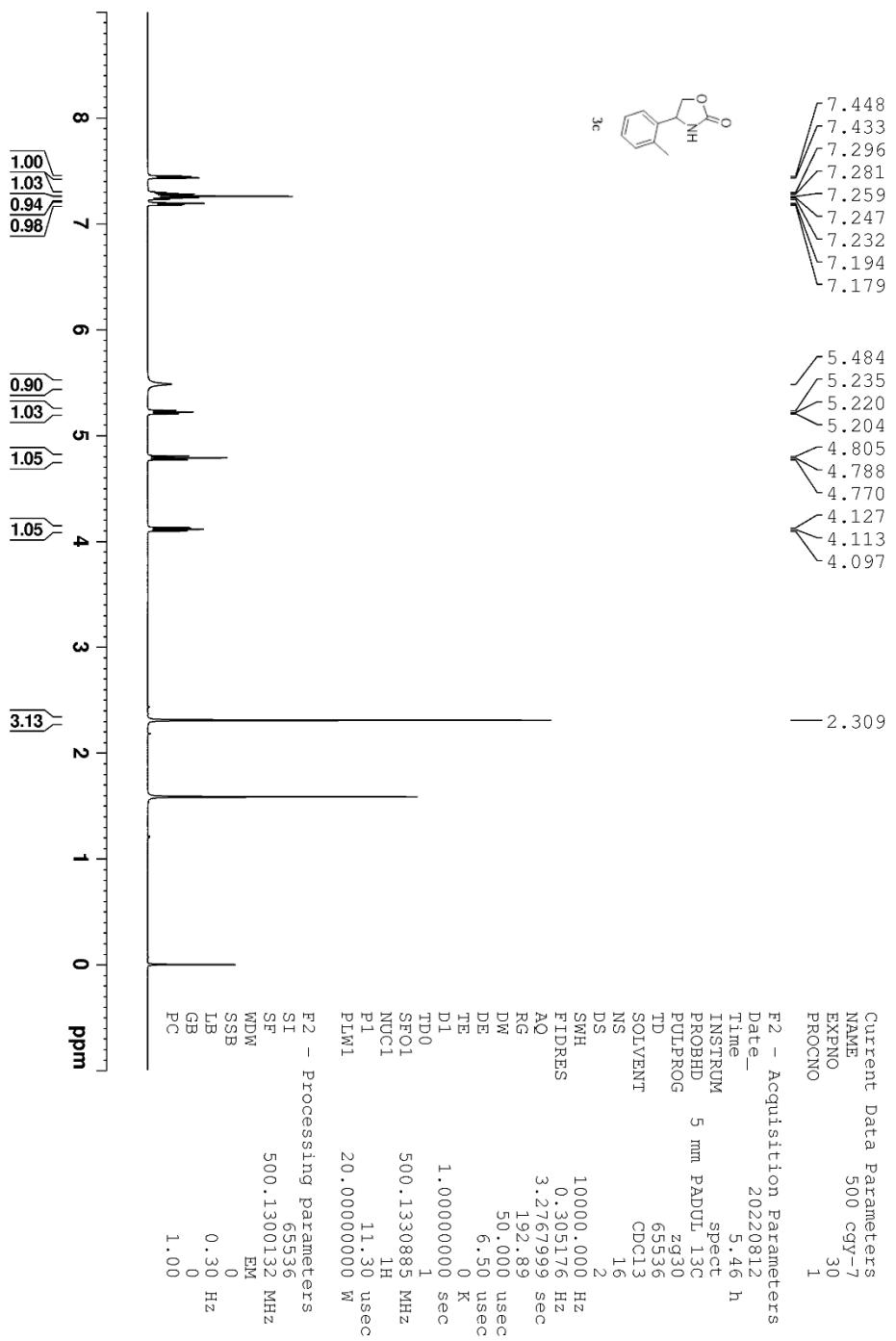


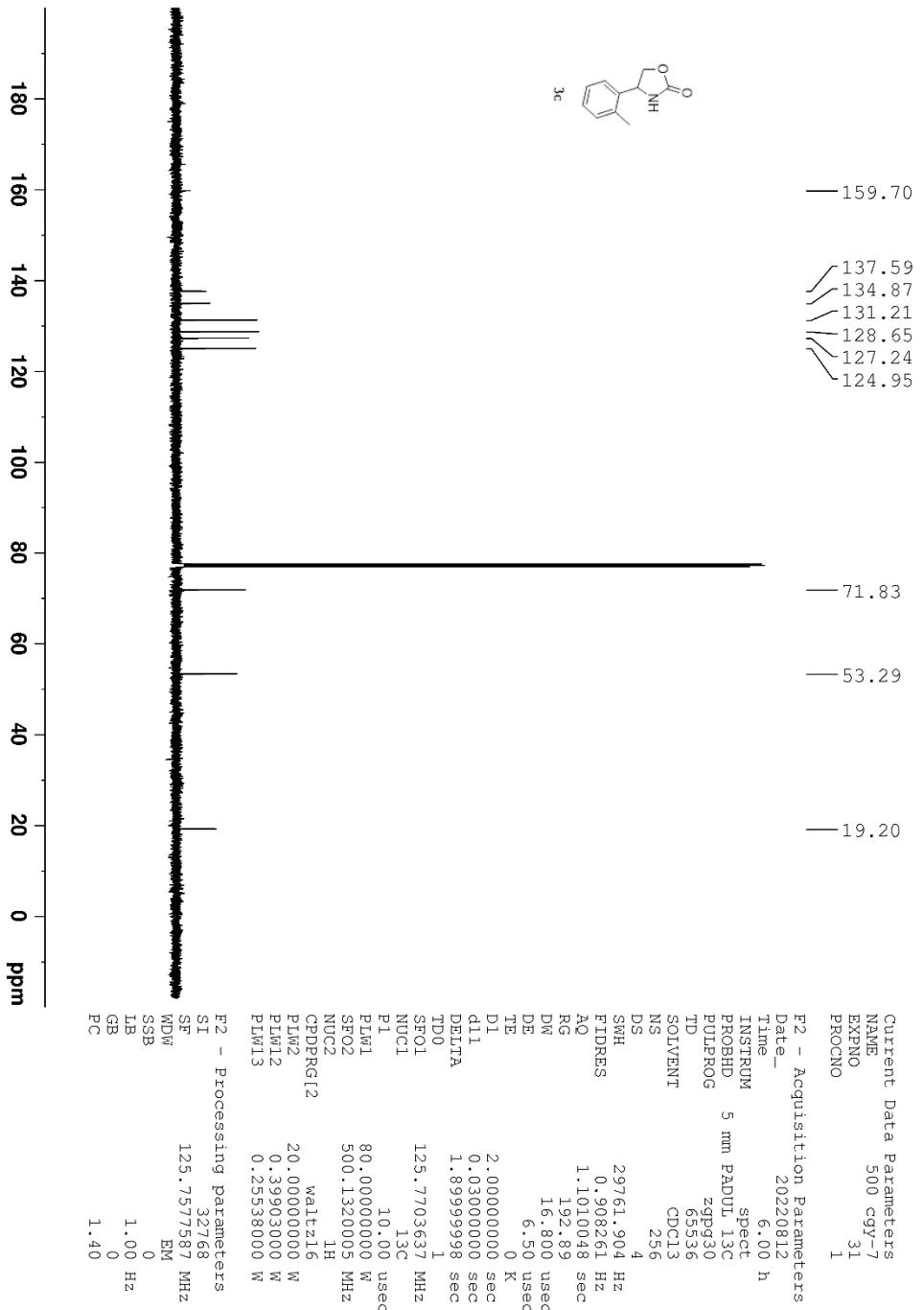


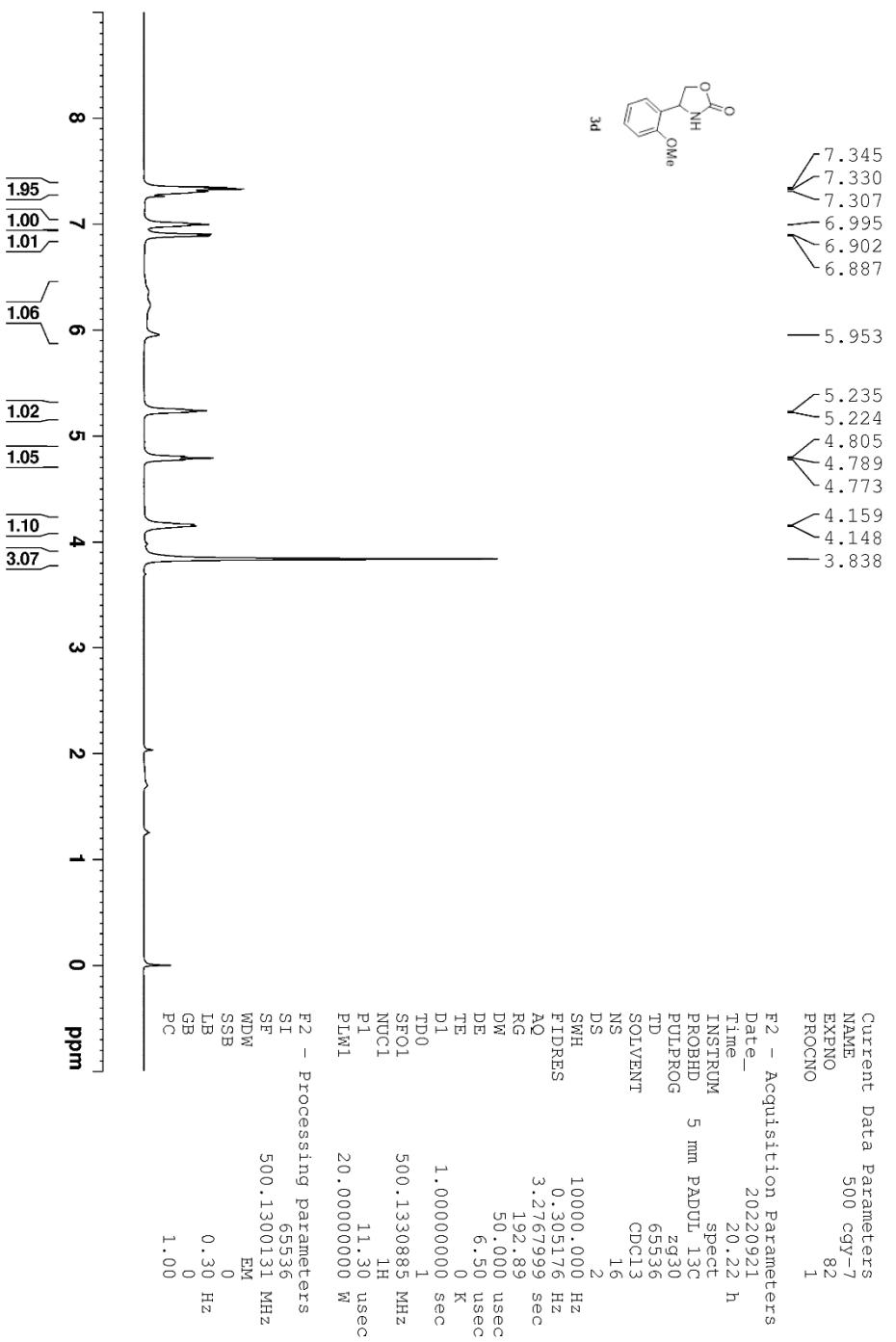
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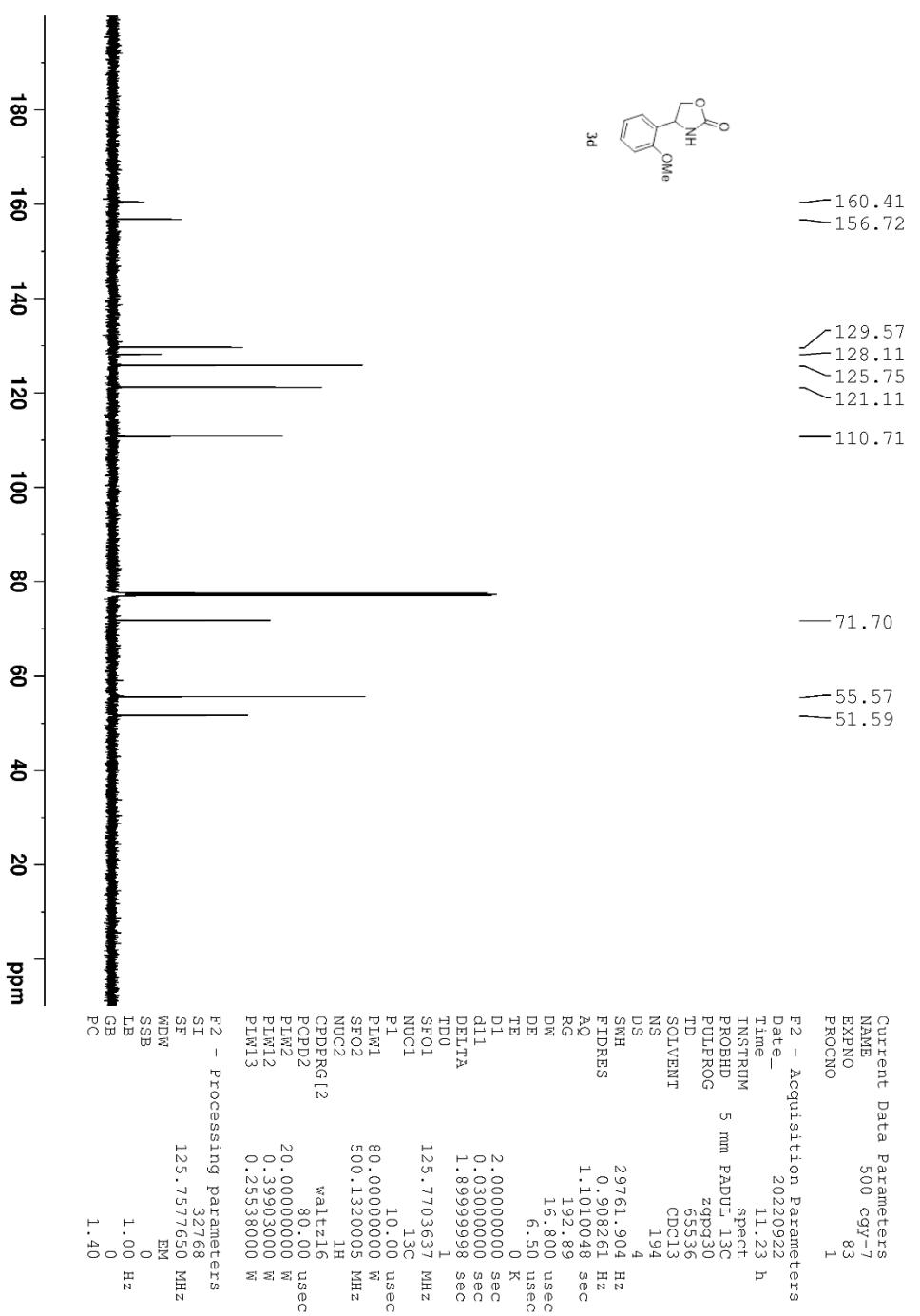
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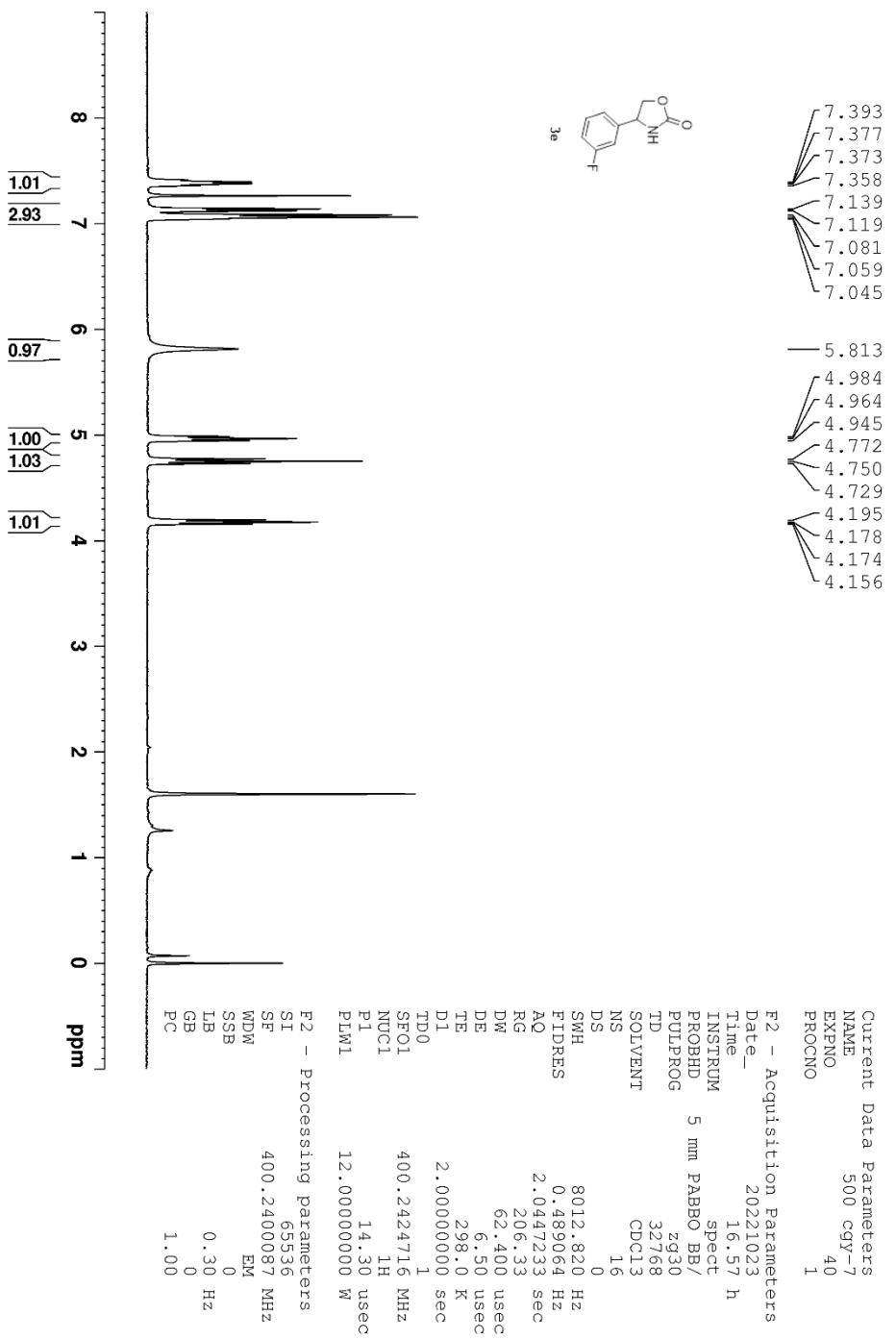


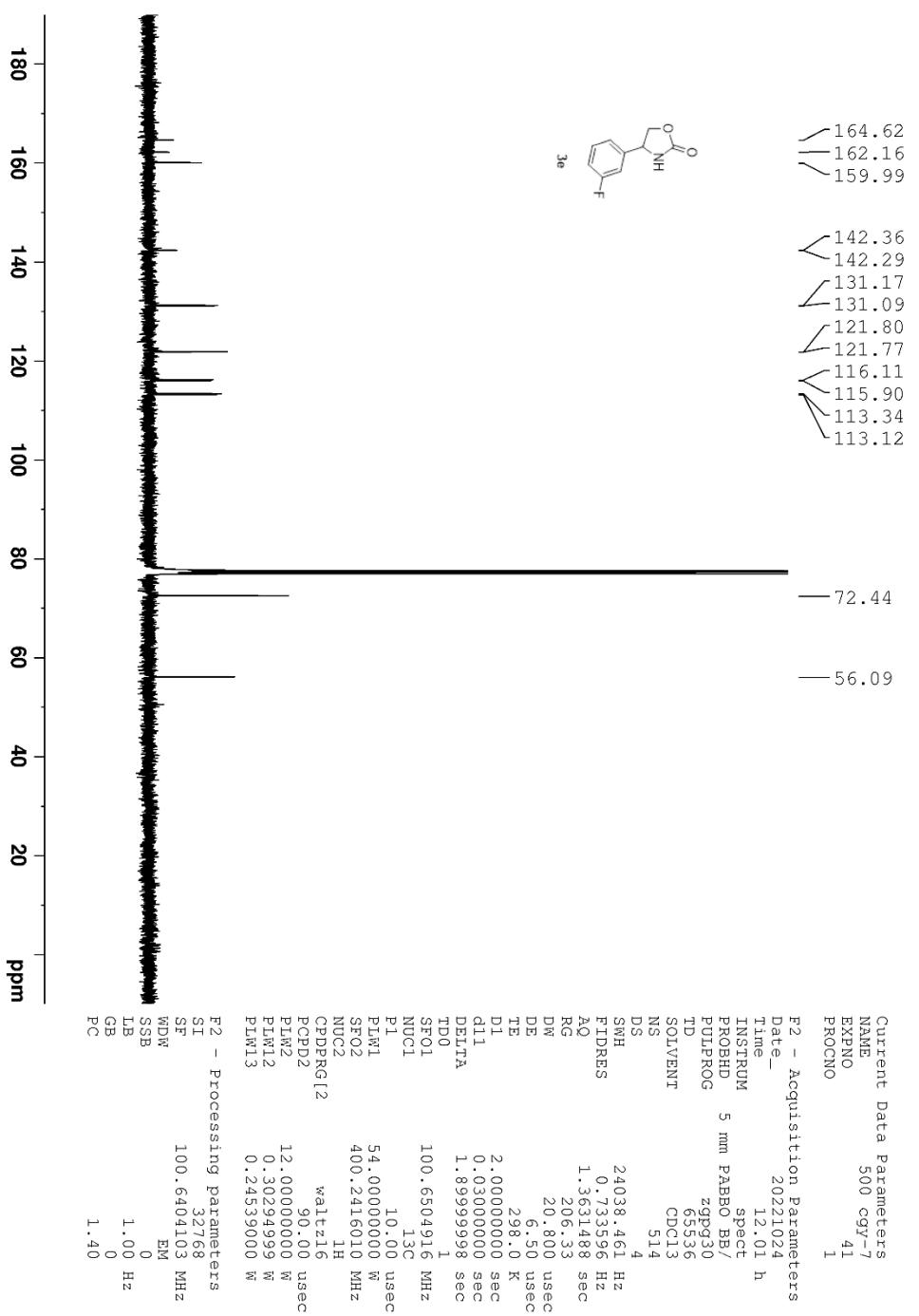


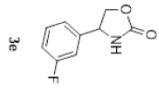












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