Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Organocatalytic Enantioselective Allylic Alkylation of α-Aryl γ-Lactones: An Approach to Densely Functionalized Quaternary Stereocentres

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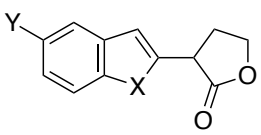
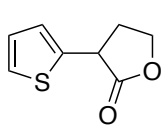
1) General Informations

Solvents and commercially available reagents were purchased from standard chemical suppliers (Fisher, Sigma-Aldrich, ABCR) and used as received without further purification or drying. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2, DMF, MeCN, toluene). Reactions were performed under an atmosphere of dry argon. TLC analyses were done using aluminium sheets coated with silica gel 60 F254. Flash column chromatography (FC) was carried out using silica gel 60 Å (0.04–0.06 mm). NMR spectra were recorded with 250 MHz (BBFO + Z-GRD Probe) (^{1}H: 250 MHz and ^{13}C: 63 MHz), 500 MHz (BBFO + Z-GRD Probe) (^{1}H: 500 MHz, ^{13}C: 126 MHz and ^{19}F: 471 MHz) and 600 MHz (CPTCI Z-GRD CryoProbe) (^{1}H: 600 MHz and ^{13}C: 151 MHz) spectrometers in $CDCl_3$ or DMSO-d_6. Chemical shifts are given in ppm, calibrated to the residual solvent peak, and coupling constants *J* are expressed in hertz (multiplicity: standard abbreviations). In the ^{13}C NMR data, reported signal multiplicities are related to C–F coupling. High-resolution mass spectra (HRMS) were performed on Q-TOF Micro micromass positive ESI (EV = 30 V).

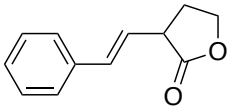
Known lactones were synthesised according to literature: **1a-1j**,[1] **1k,**[2] **1l-1x,**[3] **1'a and 1'b,**[4] **1'c**[5] and **1'd**.[6]



1a : X= O, Y=H
1b : X=NH, Y=H
1c : X=S, Y=H
1d : X=CH_2, Y=H
1e : X=NH, Y=OMe



1f



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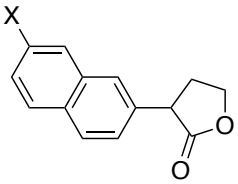
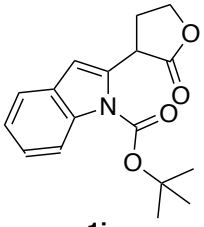


1h : X=H
1i : X=OMe



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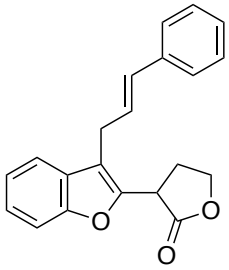

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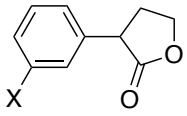

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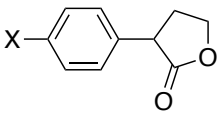
1m : X=Br
1n : X=F
1o : X=OMe
1p : X=Me
1q : X=H



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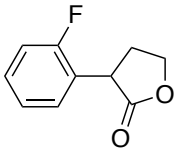
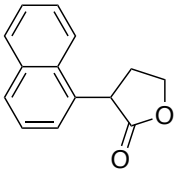
1s : X=Br
1t : X=F
1u : X=OMe
1v : X=Me



1w



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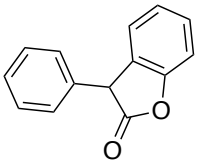
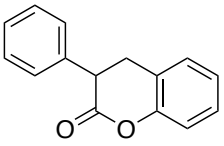
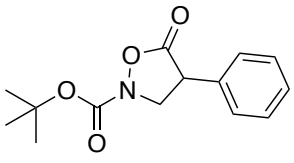


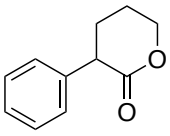
1'a



1'b



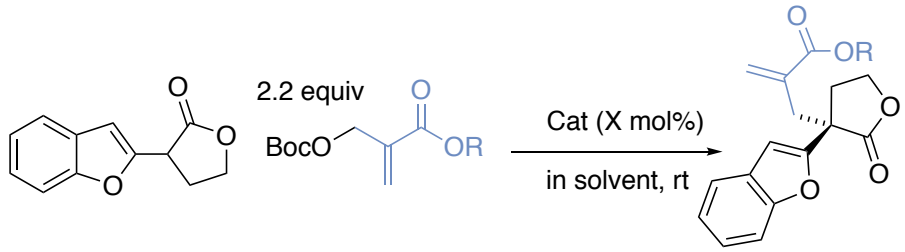
1'c



1'd

2) Asymmetric Allylic Alkylation of benzofuroyl-lactone

a) Optimisation of the general procedure



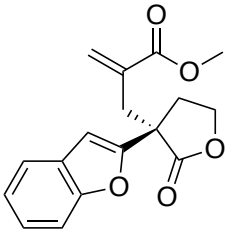
1a **3a-3f**

General Procedure for Asymmetric Allylic Alkylation of lactone 1a: Catalyst was added to a mixture of MBH carbonate (0.55 mmol) and **1a** (0.25 mmol) in solvent (1 mL). The reaction was followed by TLC analysis until total consumption of the starting lactone. The resulting mixture was then purified on SiO_2.

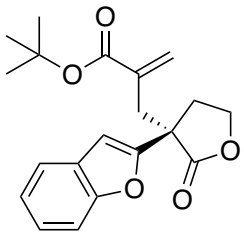
Screening of catalyst							
Catalyst	X mol %	Solvent	R	Time (h)	Lactone	Yield (%)	er
DMAP	5	$CHCl_3$	CH_3	2	**3a**	97	-
$(DHQ)_2PHAL$	10	$CHCl_3$	CH_3	6	**3a**	90	55/45
$(DHQD)_2PHAL$	10	$CHCl_3$	CH_3	7	**3a**	87	54/46
Hydroquinine	10	$CHCl_3$	CH_3	1	**3a**	90	69/31
Hydroquinidine	10	$CHCl_3$	CH_3	2	**3a**	89	69/31
C_1	5	$CHCl_3$	CH_3	6	**3a**	93	70/30
C_2	5	$CHCl_3$	CH_3	20	**3a**	97	66/34
C_3	5	$CHCl_3$	CH_3	1.5	**3a**	98	60/40
C_4	5	$CHCl_3$	CH_3	2	**3a**	96	88/12
C_5	5	$CHCl_3$	CH_3	24	**3a**	98	82/18
C_6	**5**	**$CHCl_3$**	**CH_3**	**3.5**	**3a**	**96**	**90/10**
C_7	5	$CHCl_3$	CH_3	4	**3a**	97	60/40
Screening of solvents							
C_6	**5**	**$CHCl_3$**	**CH_3**	**3.5**	**3a**	**96**	**90/10**
C_6	5	MTBE	CH_3	4	**3a**	97	73/27
C_6	5	DCE	CH_3	3.5	**3a**	98	84/16
C_6	5	Benzene	CH_3	2.5	**3a**	97	87/13
C_6	5	*o*-xylene	CH_3	2.5	**3a**	95	87/13
C_6	5	*m*-xylene	CH_3	2.5	**3a**	94	82/18
C_6	5	Mesitylene	CH_3	3.5	**3a**	87	84/16
C_6	5	EtOAc	CH_3	4	**3a**	80	74/25
C_6	5	1,4-dioxane	CH_3	4	**3a**	90	73/27
C_6	5	THF	CH_3	4	**3a**	85	66/34
C_6	5	Ph-CF_3	CH_3	3	**3a**	97	86/14
Screening of MBH carbonate adduct							
C_6	**10**	**$CHCl_3$**	***t*Bu**	**5**	**3b**	**93**	**93/7**
C_6	10	$CHCl_3$	2-adamantyl	8.5	**3c**	90	92/8
C_6	10	$CHCl_3$	1-adamantyl	8.5	**3d**	92	91/9
C_6	10	$CHCl_3$	Bn	12	**3e**	96	91/9
C_6	10	$CHCl_3$	CH_2-*t*Bu	6.5	**3f**	96	92/8

b) MBH carbonate Screening

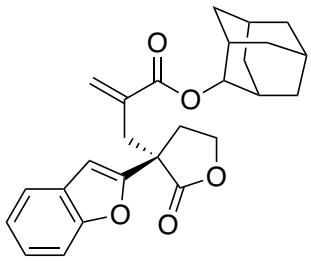
General Procedure for Asymmetric Allylic Alkylation on lactone 1a : Unless specified **C_6** (10 mol %) was added to a mixture of MBH carbonate (0.55 mmol, 2.2 equiv) and **1a** (0.25 mmol) unless specified in $CHCl_3$ (1 mL). The reaction was followed by TLC analysis until total consumption of the starting lactone. The resulting mixture was then purified with column chromatography.



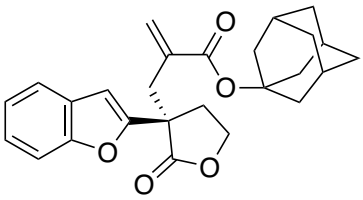
Compound **3a** (72 mg, 96%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 6.71 (s, 1H), 6.25 (s, 1H), 5.54 (s, 1H), 4.38 (td, *J* = 9.0, 8.0 Hz, 1H), 4.30 (td, *J* = 9.0, 7.0 Hz, 1H), 3.65 (s, 3H), 3.31 (d, *J* = 13.5 Hz, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.78 (ddd, *J* = 13.5, 7.0, 4.0 Hz, 1H), 2.55 (dt, *J* = 13.5, 9.0 Hz, 1H).**^{13}C NMR (126 MHz, Chloroform-*d*)** δ 175.9, 167.5, 155.0, 154.2, 135.2, 130.3, 128.0, 124.6, 123.2, 121.3, 111.3, 104.8, 66.0, 52.3, 49.1, 36.9, 32.6. **IR (neat)** ν_{max} 3010, 2955, 2919, 2852, 1769, 1713, 1630, 1453, 1280, 1197, 1164, 1021, 952, 806, 757, 616, 464 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{17}H_{16}NaO_5$ [M + Na]$^+$ 323.0895, found 323.0894. **$[\alpha]^{20}_D$** = +55 (*c* 0.5; $CHCl_3$), er (90:10). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 12.7 min, t_R (minor) = 18.4 min.



Compound **3b** (79 mg, 93%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.0 Hz, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 6.72 (s, 1H), 6.17 (s, 1H), 5.46 (s, 1H), 4.37 (td, *J* = 9.0, 8.0 Hz, 1H), 4.30 (ddd, *J* = 9.0, 8.0, 7.0 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 2.97 (d, *J* = 14.0 Hz, 1H), 2.78 (ddd, *J* = 13.5, 8.0, 4.5 Hz, 1H), 2.55 (dt, *J* = 13.5, 9.0 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 175.9, 166.2, 155.0, 154.5, 136.7, 129.3, 128.0, 124.5, 123.1, 121.2, 111.3, 104.6, 81.3, 77.4, 65.9, 49.2, 36.5, 32.6, 28.0. **IR (neat)** ν_{max} 3058, 2982, 2911, 1766, 1705, 1625, 1455, 1391, 1158, 1021, 948, 794, 745, 700, 439 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{22}NaO_5$ [M + Na]$^+$ 365.1365, found 365.1368. **$[\alpha]^{20}_D$** = +41 (*c* 0.5; $CHCl_3$), er (93:7). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 6.4 min, t_R (minor) = 8.4 min.

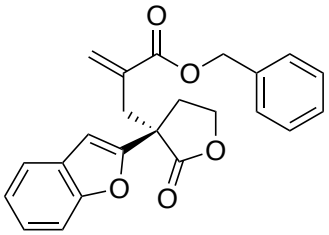


Compound **3c** (94 mg, 90%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.27 (td, *J* = 7.5, 1.0 Hz, 1H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 6.71 (s, 1H), 6.30 (s, 1H), 5.56 (s, 1H), 4.94 (s, 1H), 4.37 (ddd, *J* = 9.0, 8.0, 4.0 Hz, 1H), 4.29 (td, *J* = 9.0, 7.0 Hz, 1H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.0 Hz, 1H), 2.78 (ddd, *J* = 13.0, 7.0, 4.0 Hz, 1H), 2.57 (dt, *J* = 13.0, 8.0 Hz, 1H), 2.04 – 1.93 (m, 4H), 1.88 – 1.73 (m, 8H), 1.63 – 1.56 (m, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.0, 166.5, 155.0, 154.5, 136.0, 129.8, 128.0, 124.6, 123.2, 121.3, 111.4, 104.7, 78.0, 66.1, 49.4, 37.5, 36.7, 36.4, 32.5, 32.1, 32.0, 27.3, 27.1. **IR (neat)** ν_{max} 2960, 1761, 1700, 1633, 1377, 1285, 1172, 1027, 928, 739, 632, 433 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{26}H_{29}O_5$ [M + H]$^+$ 421.2014, found 421.2015. **$[\alpha]^{20}_D$** = +38 (*c* 0.5; $CHCl_3$), er (92:8). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.9 min, t_R (minor) = 10.5 min.

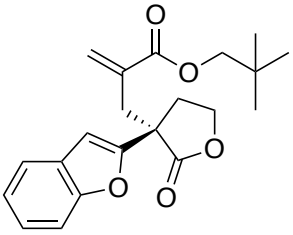


Compound **3d** (96 mg, 92%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 6.71 (s, 1H), 6.17 (s, 1H), 5.46 (s, 1H), 4.36 (ddd, *J* = 9.0, 8.0, 4.5 Hz, 1H), 4.29 (td, *J* = 9.0, 7.0 Hz, 1H), 3.26 (d, *J* = 14.0 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 2.77 (ddd, *J* = 13.5, 7.0, 4.5 Hz, 1H), 2.55 (dt, *J* = 13.5, 8.0 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 6H), 1.64 (s, 6H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.0, 165.9, 155.0, 154.5, 136.7, 129.3, 128.1, 124.5, 123.1, 121.2, 111.4,

104.6, 81.4, 65.9, 49.2, 41.2, 36.5, 36.2, 32.6, 30.9. **IR (neat)** ν_{max} 2909, 2849, 1763, 1714, 1452, 1169, 1157, 1011, 813, 749, 688 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{26}H_{28}NaO_5$ $[M + Na]^+$ 443.1833, found 443.1834. **$[\alpha]^{20}_D$** = +40 (*c* 0.5; $CHCl_3$), er (92:8). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.3 min, t_R (minor) = 9.7 min.



Compound **3e** (90 mg, 96%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.30 – 7.26 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 6.30 (s, 1H), 5.56 (s, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.5 Hz, 1H), 4.32 (ddd, *J* = 9.0, 8.0, 4.0 Hz, 1H), 4.26 (td, *J* = 9.0, 7.0 Hz, 1H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.74 (ddd, *J* = 13.5, 7.0, 4.0 Hz, 1H), 2.51 (dt, *J* = 13.5, 8.0 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 175.9, 166.9, 155.0, 154.2, 135.8, 135.2, 130.6, 128.7, 128.5, 128.3, 128.1, 124.7, 123.2, 121.3, 111.4, 104.8, 77.4, 67.0, 66.0, 49.2, 36.9, 32.6. **IR (neat)** ν_{max} 3661, 2971, 2901, 1769, 1714, 1453, 1158, 1066, 1026, 953, 749, 697, 436 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{23}H_{20}NaO_5$ $[M + Na]^+$ 399.1210, found 399.1208. **$[\alpha]^{20}_D$** = +44 (*c* 0.5; $CHCl_3$), er (91:9). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 9.8 min, t_R (minor) = 12.3 min.

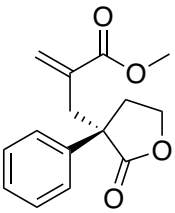


Compound **3f** (85 mg, 96%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 6.71 (s, 1H), 6.27 (s, 1H), 5.56 (s, 1H), 4.37 (ddd, *J* = 9.0, 8.0, 4.0 Hz, 1H), 4.29 (td, *J* = 9.0, 7.0 Hz, 1H), 3.81 (d, *J* = 10.5 Hz, 1H), 3.76 (d, *J* = 10.5 Hz, 1H), 3.31 (d, *J* = 14.0 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.78 (ddd, *J* = 13.5, 7.0, 4.0 Hz, 1H), 2.56 (dt, *J* = 13.5, 8.0 Hz, 1H), 0.95 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.0, 167.2, 155.0, 154.3, 135.4, 130.0, 128.0, 124.6, 123.2, 121.2, 111.4, 104.7, 74.5, 66.0, 49.3, 36.7, 32.4, 31.6, 26.6. **IR (neat)** ν_{max} 2958, 1771, 1712, 1577, 1453, 1371, 1163, 1026, 750 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{21}H_{24}NaO_5$ $[M + Na]^+$ 379.1524, found 379.1521. **$[\alpha]^{20}_D$** = +41 (*c* 0.5; $CHCl_3$), er (92:8). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.0 min, t_R (minor) = 9.4 min.

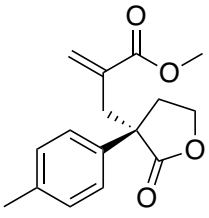
3) Asymmetric Allylic Alkylation of α-aryl-γ-lactones

a) Substrate scope

All lactones were alkylated according to the general procedure of AAA.

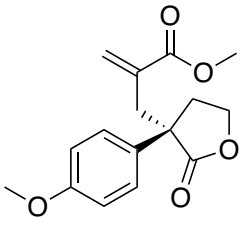


Compound **4** (37 mg, 58%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 98:2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.19 (s, 1H), 5.41 (s, 1H), 4.27 (ddd, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.01 (td, *J* = 9.0, 6.0 Hz, 1H), 3.67 (s, 3H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.63 (ddd, *J* = 13.5, 6.0, 3.0 Hz, 1H), 2.46 (ddd, *J* = 13.5, 10.0, 8.0 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.4, 167.8, 138.2, 135.6, 130.2, 128.8, 127.8, 126.7, 126.7, 65.4, 52.07, 52.14, 39.7, 33.5. **IR (neat)** ν_{max} 2951, 1762, 1715, 1627, 1444, 1193, 1151, 1023, 957, 699, 506 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{15}H_{16}NaO_4$ $[M + Na]^+$ 283.0945, found 283.0946. **$[\alpha]^{20}_D$** = +59 (*c* 0.5; $CHCl_3$), er (89:11). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 75:25, 254 nm, 1 mL/min), t_R (major) = 12.6 min, t_R (minor) = 17.3 min.

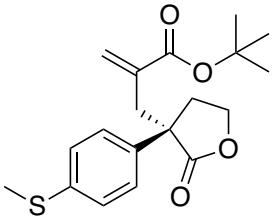


Compound **5** (28 mg, 41%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.33 (m, 2H), 7.16 (m, 2H), 6.19 (s, 1H), 5.43 (s, 1H), 4.26 (ddd, *J* = 9.0, 8.0, 2.5, 1H), 4.01 (td, *J* = 9.5, 6.0 Hz, 1H), 3.69 (s, 3H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.61 (ddd, *J* = 13.5, 6.0, 2.5 Hz, 1H), 2.44 (ddd, *J* = 13.5, 10.0, 8.0 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.6, 167.9, 137.6, 135.7, 135.2, 130.2, 129.5, 126.6, 65.4, 52.2, 52.0, 39.7, 33.6, 21.0. **IR (neat)** ν_{max} 2951, 1765, 1716, 1627, 1513, 1439, 1285, 1195, 1154,

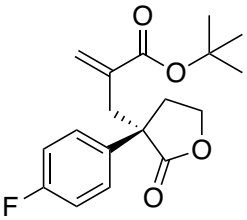
1022, 813, 751 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{16}H_{18}NaO_4$ $[M + Na]^+$ 297.1103, found 297,1102**. [α] $^{20}_D$** = +57 (*c* 0.25; $CHCl_3$), er (82:18**).** The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 11.0 min, t_R (minor) = 14.0 min.



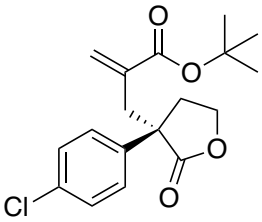
The reaction was carried on 0.5 mmol scale and **6** (26 mg, 18%) was obtained as a white powder after two silica gel column chromatographies (Petroleum ether/EtOAc 90:10 then CH_2Cl_2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.36 (m, 2H), 6.88 (m, 2H), 6.19 (s, 1H), 5.40 (s, 1H), 4.28 (td, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.02 (td, *J* = 10.0, 9.0, 6.0 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.04 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.60 (ddd, *J* = 13.5, 6.0, 3.0 Hz, 1H), 2.44 (ddd, *J* = 13.5, 10.0, 8.0 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.7, 167.9, 159.1, 135.6, 130.3, 129.9, 128.0, 114.1, 65.4, 55.4, 52.2, 51.5, 39.8, 33.6. **IR (neat)** ν_{max} 2951, 2838, 1762, 1704, 1599, 1582, 1247, 1144, 1024, 848, 699 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{16}H_{18}NaO_5$ $[M + Na]^+$ 313.1052, found 313.1053. **[α] $^{20}_D$** = +41 (*c* 0.5; $CHCl_3$), er (86:14). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 14.1 min, t_R (minor) = 18.3 min.



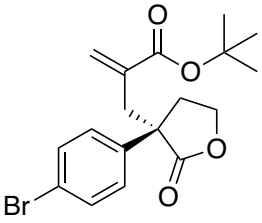
Compound **7** (88 mg, 92%) was obtained as a brown oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.36 (m, 2H), 7.22 (m, 2H), 6.13 (s, 1H), 5.38 (s, 1H), 4.27 (ddd, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.00 (td, *J* = 9.0, 6.0 Hz, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.84 (d, *J* = 14.0 Hz, 1H), 2.58 (ddd, *J* = 13.0, 6.0, 3.0 Hz, 1H), 2.46 (m, 1H), 2.45 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.4, 166.5, 138.3, 137.1, 135.3, 129.4, 127.3, 126.7, 81.1, 65.4, 52.0, 39.4, 33.7, 28.1, 15.7. **IR (neat)** ν_{max} 2976, 2922, 1763, 1705, 1438, 1367, 1145, 1024, 815 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{19}H_{24}NaO_4S$ $[M + Na]^+$ 371.1294, found 317.1293. **[α] $^{20}_D$** = +51 (*c* 0.25; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 8.7 min, t_R (minor) = 11.4 min.



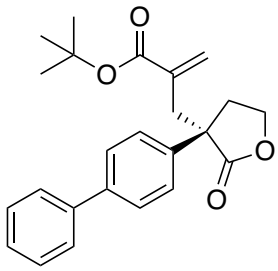
Compound **8** (64 mg, 80%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.45 (m, 2H), 7.06 (m, 2H), 6.13 (s, 1H), 5.36 (s, 1H), 4.31 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 4.03 (td, *J* = 9.0, 6.0 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 2.60 (ddd, *J* = 13.5, 6.0, 3.5 Hz, 1H), 2.50 (ddd, *J* = 13.5, 9.0, 7.5 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.4, 166.5, 163.1 (d, *J* = 246.9 Hz) 137.0, 134.5 (d, *J* = 3.5 Hz), 129.4, 128.6 (d, *J* = 8.5 Hz), 115.7 (d, *J* = 21.5 Hz), 81.2, 65.3, 51.8, 39.7, 33.9, 28.2, 28.1, 28.1. **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -114.8 (dq, *J* = 9.0, 4.5 Hz).**IR (neat)** ν_{max} 2980, 1766, 1707, 1626, 1604, 1477, 1509, 1368, 1227, 1144, 1025, 815, 683 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{18}H_{21}FNaO_4$ $[M + Na]^+$ 343.1322., found 343.1318. **[α] $^{20}_D$** = +55 (*c* 0.5; $CHCl_3$), er (93:7). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.9 min, t_R (minor) = 7.3 min.



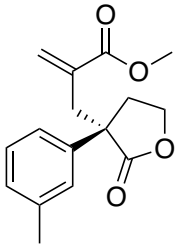
Compound **9** (82 mg, 98%) was obtained as a brown oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.41 (m, 2H), 7.32 (m, 2H), 6.14 (s, 1H), 5.37 (s, 1H), 4.29 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 4.03 (td, *J* = 9.0, 6.5 Hz, 1H), 3.00 (d, *J* = 14.0 Hz, 1H), 2.84 (d, *J* = 14.0 Hz, 1H), 2.58 (ddd, *J* = 13.0, 6.5, 3.5 Hz, 1H), 2.49 (ddd, *J* = 13.0, 9.0, 7.5 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.1, 166.5, 137.4, 136.9, 133.8, 129.5, 129.0, 128.9, 128.3, 81.2, 65.3, 51.9, 39.6, 33.7, 28.14, 28.09, 28.0. **IR (neat)** ν_{max} 2980, 1754, 1709, 1626, 1492, 1339, 1163, 1146, 1128, 1024, 974, 831, 502 cm^{-1}. **ESI-HRMS** m/z calcd for $C_{18}H_{21}ClNaO_4$ $[M + Na]^+$ 359.1026, found 359.1028. **[α] $^{20}_D$** = +55 (*c* 0.5; $CHCl_3$), er (87:13). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.9 min, t_R (minor) = 7.2 min.



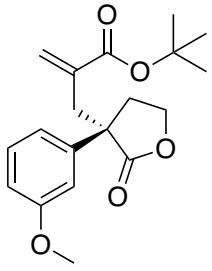
Compound **10** (87 mg, 92%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.48 (m, 2H), 7.34 (m, 2H), 6.14 (s, 1H), 5.37 (s, 1H), 4.29 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 4.02 (td, *J* = 9.0, 6.0 Hz, 1H), 3.00 (d, *J* = 13.5 Hz, 1H), 2.83 (d, *J* = 13.5, 1H), 2.57 (ddd, *J* = 13.0, 6.0, 3.5 Hz, 1H), 2.49 (ddd, *J* = 13.0, 9.0, 7.5 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.0, 166.4, 137.9, 136.9, 132.0, 129.5, 128.7, 122.0, 81.2, 65.3, 51.9, 39.5, 33.7, 28.0. **IR (neat)** ν_{max} 2978, 2912, 1755, 1709, 1626, 1588, 1487, 1339, 1163, 1145, 1128, 1023, 1007, 758, 733, 498 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{18}H_{21}BrNaO_4$ [M + Na]$^+$ 403.0521, found 403.0521. **[α] $^{20}_D$** = +17 (*c* 0.5; $CHCl_3$), er (91:9). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 6.3 min, t_R (minor) = 7.6 min. Recrystallization in hexane led to compound **10** (69 mg, 74%) with er (>99:1) mp 82−84 °C.



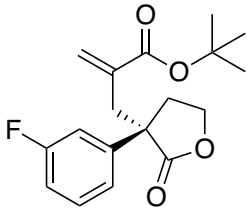
Compound **11** (69 mg, 73%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 98:2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.61 – 7.55 (m, 4H), 7.53 (m, 2H), 7.44 (m, 2H), 7.36 (m, 1H), 6.17 (s, 1H), 5.45 (s, 1H), 4.30 (ddd, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.06 (td, *J* = 9.0, 6.0 Hz, 1H), 3.11 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 14.0 Hz, 1H), 2.67 (ddd, *J* = 13.5, 6.0, 3.0 Hz, 1H), 2.51 (ddd, *J* = 13.5, 9.0, 8.0 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.5, 166.6, 140.7, 140.4, 137.8, 137.2, 129.4, 129.0, 127.6, 127.5, 127.24, 127.16, 81.1, 65.4, 52.3, 39.5, 33.8, 28.1. **IR (neat)** ν_{max} 2979, 2931, 1753, 1708, 1630, 1486, 1441, 1391, 1366, 1273, 1152, 1027, 960, 695 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{24}H_{26}NaO_4$ [M + Na]$^+$ 401.1729, found 401.1732**. [α] $^{20}_D$** = +74 (*c* 0.5; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.5 min, t_R (minor) = 10.5 min.



Compound **12** (48 mg, 70%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26 – 7.18 (m, 3H), 7.10 (m, 1H), 6.21 (s, 1H), 5.47 (s, 1H), 4.26 (td, *J* = 8.5, 2.5 Hz, 1H), 4.00 (td, *J* = 9.5, 6.0 Hz, 1H), 3.69 (s, 3H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.61 (ddd, *J* = 13.5, 6.0, 2.5 Hz, 1H), 2.44 (ddd, *J* = 13.5, 10.0, 8.0 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.5, 168.0, 138.6, 138.3, 135.7, 130.3, 128.7, 128.6, 127.4, 123.7, 65.4, 52.4, 52.2, 39.6, 33.6, 21.7. **IR (neat)** ν_{max} 2987, 2901, 1764, 1715, 1587, 1627, 1438, 1371, 1193, 1159, 1024, 703, 439 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{16}H_{18}NaO_4$ [M + Na]$^+$ 297.1103, found 297.1105**. [α] $^{20}_D$** = +62 (*c* 0.25; $CHCl_3$), er (86:14). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 9.7 min, t_R (minor) = 13.2 min.

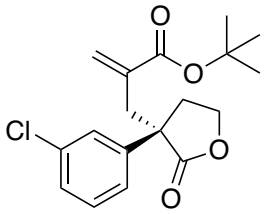


Compound **13** (35 mg, 43%) was obtained as a colourless oil after two silica gel column chromatographies (Petroleum ether/EtOAc 90:10 then CH_2Cl_2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.26 (m, 1H), 7.10 – 6.96 (m, 2H), 6.82 (ddd, *J* = 9.0, 2.5, 1.0 Hz, 1H), 6.14 (s, 1H), 5.41 (s, 1H), 4.26 (ddd, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.02 (td, *J* = 9.0, 6.0 Hz, 1H), 3.80 (s, 3H), 3.04 (d, *J* = 14.0 Hz, 1H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.60 (ddd, *J* = 13.5, 6.0, 3.0 Hz, 1H), 2.46 (ddd, *J* = 13.5, 9.0, 8.0 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.4, 166.6, 160.0, 140.4, 137.2, 129.8, 129.3, 119.0, 113.0, 112.9, 81.0, 65.4, 55.4, 52.5, 39.4, 33.8, 28.1. **IR (neat)** ν_{max} 2975, 1764, 1704, 1599, 1582, 1247, 1144, 1024, 848, 699 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{19}H_{24}NaO_5$ [M + Na]$^+$ 355.1521, found 355.1523. **[α] $^{20}_D$** = +67 (*c* 0.5; $CHCl_3$), er (95:5). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.7 min, t_R (minor) = 10.6 min.

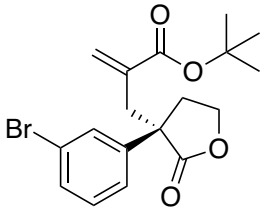


Compound **14** (64 mg, 80%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.22 (td, *J* = 8.0, 6,0 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.89 (tdd, *J* = 8.0, 2.5, 1.0 Hz, 1H), 6.05 (s, 1H), 5.28 (s, 1H), 4.19 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 3.94 (td, *J* = 9.0, 6.5 Hz, 1H), 2.92 (d, *J* = 14.0 Hz, 1H), 2.76 (d, *J* = 14.0, Hz, 1H), 2.49 (ddd, *J* = 13.0, 6.5, 3.5 Hz, 1H), 2.40 (ddd, *J* = 13.0, 9.0, 7.5 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.0, 166.4, 163.0 (d, *J* = 246.5 Hz), 141.5 (d, *J* = 7.0 Hz), 136.9, 130.4 (d, *J* = 8.0 Hz), 129.5, 122.5 (d, *J* = 3.0 Hz), 114.8 (d, *J* = 21.0 Hz), 114.2 (d, *J* = 23.0 Hz), 81.2, 65.3, 52.1, 39.5, 33.7, 28.1. **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -111.8 (ddd, *J* = 10.5, 8.5, 6.0 Hz). **IR (neat)** ν_{max} 2977, 1765, 1705, 1614, 1586, 1393, 1368,

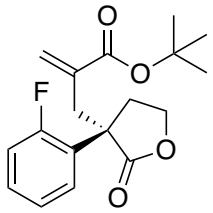
1146, 1024, 696, 456 cm^{-1}. **ESI-HRMS** *m*/*z* calcd for $C_{18}H_{21}FNaO_4$ [M + Na]$^+$ 343.1322, found 343.1321**.** **[α] $^{20}_D$** = +62 (*c* 0.5; $CHCl_3$), er (92:8). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.9 min, t_R (minor) = 7.3 min.



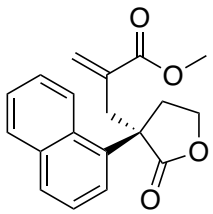
Compound **15** (82 mg, 98%) was obtained as a brown oil after silica gel column chromatography (Petroleum ether/EtOAc 80:20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.46 (t, *J* = 2.0 Hz, 1H), 7.37 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.26 (m, 2H), 6.15 (s, 1H), 5.40 (s, 1H), 4.29 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 4.04 (td, *J* = 9.0, 6.5 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.85 (d, *J* = 14.0 Hz, 1H), 2.59 (ddd, *J* = 14.0, 6.5, 4.0 Hz, 1H), 2.50 (ddd, *J* = 13.0, 9.0, 8.0 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.9, 166.4, 141.0, 136.9, 134.9, 130.1, 129.6, 128.1, 128.0, 127.1, 125.1, 81.3, 81.2, 65.3, 52.2, 39.5, 33.7, 28.1. **IR (neat)** ν_{max} 2977, 2932, 1765, 1707, 1571, 1367, 1146, 1024, 695 cm^{-1}. **ESI-HRMS** *m*/*z* calcd for $C_{18}H_{21}ClNaO_4$ [M + Na]$^+$ 359.1026, found 359.1028. **[α] $^{20}_D$** = +73 (*c* 0.5; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.7 min, t_R (minor) = 7.0 min.



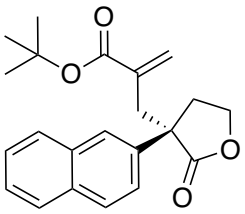
Compound **16** (79 mg, 83%) was obtained as a brown oil after silica gel column chromatography (Petroleum ether/EtOAc 80:20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.63 (t, *J* = 2.0 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 5.43 (s, 1H), 4.31 (ddd, *J* = 9.0, 7.5, 3.5 Hz, 1H), 4.06 (td, *J* = 9.0, 6.0 Hz, 1H), 3.04 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5, 1H), 2.61 (ddd, *J* = 13.0, 6.0, 3.5 Hz, 1H), 2.52 (ddd, *J* = 13.0, 9.0, 7.5 Hz, 1H), 1.49 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.8, 166.4, 141.3, 136.9, 131.0, 130.4, 129.9, 129.6, 125.6, 123.0, 81.3, 65.3, 52.2, 39.5, 33.7, 28.1. **IR (neat)** ν_{max} 2973, 2909, 1759, 1702, 1627, 1403, 1367, 1343, 1166, 1150, 1024, 945, 783, 703 cm^{-1}. **ESI-HRMS** *m*/*z* calcd for $C_{18}H_{21}BrNaO_4$ [M + Na]$^+$ 403.0521, found 403.0522. **[α] $^{20}_D$** = +61 (*c* 0.5; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.8 min, t_R (minor) = 7.1 min.



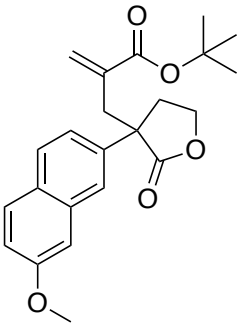
Compound **17** (52 mg, 65%) was obtained as a colourless oil after silica gel column chromatography (CH_2Cl_2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.51 (td, *J* = 8.0, 1.5 Hz, 1H), 7.34 – 7.23 (m, 1H), 7.15 – 7.05 (m, 2H), 6.23 (s, 1H), 5.51 (s, 1H), 4.24 (ddd, *J* = 9.0, 7.5, 5.5 Hz, 1H), 4.11 (dt, *J* = 9.0, 7.5 Hz, 1H), 3.26 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H), 2.68 –2.59 (m, 2H), 1.50 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.7, 166.5, 161.4 (d, *J* = 247.0 Hz), 137.1, 129.9, 129.7 (d, *J* = 9.0 Hz), 128.7 (d, *J* = 3.5 Hz), 127.6 (d, *J* = 10.5 Hz), 124.3 (d, *J* = 3.5 Hz), 116.8 (d, *J* = 23.0 Hz), 81.3, 65.7, 50.9, 36.8 (d, *J* = 3.0 Hz), 34.1 (d, *J* = 5.5 Hz), 28.1. **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -110.2 (m). **IR (neat)** ν_{max} 2977, 2931, 1768, 1708, 1489, 1368, 1146, 757 cm^{-1}. **ESI-HRMS** *m*/*z* calcd for $C_{18}H_{21}FNaO_4$ [M + Na]$^+$ 343.1322, found 343.1320. **[α] $^{20}_D$** = +19 (*c* 0.5; $CHCl_3$), er (78:22). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 6.5 min, t_R (minor) = 8.8 min.



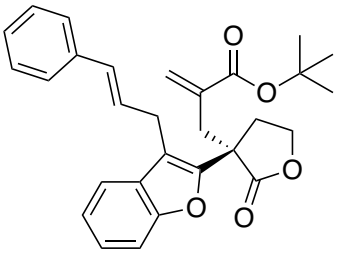
The reaction was carried on 0.5 mmol scale and compound **18** (20 mg, 12%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.71 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.5, 6.5, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.5, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.38 (dd, *J* = 8.0, 7.5 Hz, 1H) 6.43 (s, 1H), 5.95 (s, 1H), 4.20 (td, *J* = 8.5, 1.5 Hz, 1H), 3.89 (s, 3H), 3.85 (ddd, *J* = 11.0, 9.0, 5.5 Hz, 1H), 3.76 (d, *J* = 14.0 Hz, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.98 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.52 (ddd, *J* = 13.0, 11.0, 8.5 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 179.4, 168.6, 135.8, 135.4, 134.8, 132.0, 130.1, 130.0, 129.5, 126.3, 125.7, 125.5, 125.4, 125.1, 65.8, 55.9, 52.5, 36.8, 33.3. **IR (neat)** ν_{max} 2951, 1766, 1710, 1626, 1599, 1440, 1170, 1147, 1028, 805, 776, 730 cm^{-1}. **ESI-HRMS** *m*/*z* calcd for $C_{19}H_{18}NaO_4$ [M + Na]$^+$ 333.1103, found 333.1105. **[α] $^{20}_D$** = +30 (*c* 0.36; $CHCl_3$), er (73:27).). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.4 min, t_R (minor) = 10.6 min.



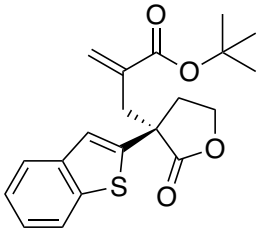
Compound **19** (74 mg, 96%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.90 – 7.74 (m, 4H), 7.62 (d, *J* = 11.0 Hz, 1H), 7.56 – 7.45 (m, 2H), 6.15 (s, 1H), 5.44 (s, 1H), 4.31 (ddd, *J* = 9.0, 8.0, 3.0 Hz, 1H), 4.03 (ddd, *J* = 10.0, 9.0, 6.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.74 (ddd, *J* = 13.0, 6.0, 3.0 Hz, 1H), 2.56 (ddd, *J* = 13.0, 10.0, 8.0 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.5, 166.6, 137.2, 136.1, 133.2, 132.7, 129.4, 128.9, 128.3, 127.6, 126.6, 126.5, 125.6, 124.7, 81.1, 65.4, 52.9, 39.3, 33.9, 28.1. **IR (neat)** ν_{max} 3671, 2979, 2901, 1757, 1703, 1628, 1365, 1157, 1140, 1020, 945, 817, 759, 475 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{22}H_{24}NaO_4$ $[M + Na]^+$ 375.1572, found 375.1574. **[α] $^{20}_D$** = +81 (*c* 0.5; $CHCl_3$), er (93:7). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.0 min, t_R (minor) = 9.6 min.



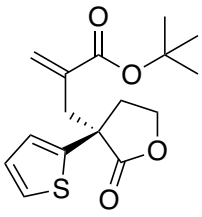
Compound **20** (93 mg, 98%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.58 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.16 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.14 (s, 1H), 5.42 (s, 1H), 4.30 (dt, *J* = 9.0, 8.0, 1H), 4.03 (ddd, *J* = 9.5, 8.0, 6.0 Hz, 1H), 3.91 (s, 3H), 3.14 (d, *J* = 14.0 Hz, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.72 (ddd, *J* = 13.0, 6.0, 2.5 Hz, 1H), 2.53 (ddd, *J* = 13.0, 9.0, 8.0 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 178.6, 166.6, 158.2, 137.2, 133.9, 133.6, 129.8, 129.4, 128.6, 127.7, 125.4, 125.2, 119.4, 105.5, 81.1, 65.5, 55.5, 52.7, 39.3, 33.8, 28.0. **IR (neat)** ν_{max} 3059, 2976, 2918, 1758, 1700, 1604, 1262, 1161, 1019, 846, 819, 668, 471 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{23}H_{26}NaO_5$ $[M + Na]^+$ 405.1678, found 405.1682. **[α] $^{20}_D$** = + 86 (*c* 0.5; $CHCl_3$), er (93:7). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 9.1 min, t_R (minor) = 13.2 min.



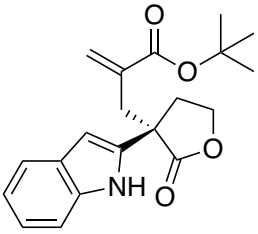
Compound **21** (100 mg, 88%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 95:5).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.24 – 7.11 (m, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.33 (m, 1H), 6.16 (s, 1H), 5.56 (s, 1H), 4.33 (td, *J* = 8.0, 2.5 Hz, 1H), 4.19 (td, *J* = 9.5, 6.0 Hz, 1H), 3.76 (d, *J* = 6.5 Hz, 2H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.04 (d, *J* = 14.0 Hz, 1H), 2.99 (ddd, *J* = 13.5, 6.0, 2.5 Hz, 1H), 2.47 (ddd, *J* = 13.5, 10.0, 8.0 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.1, 166.4, 153.4, 148.3, 137.4, 137.0, 131.3, 130.0, 129.1, 128.6, 128.5, 127.3, 127.24, 127.16, 126.3, 124.6, 122.8, 120.1, 115.6, 111.2, 81.2, 66.3, 49.7, 36.5, 33.7, 28.0, 27.0. **IR (neat)** ν_{max} 2976, 1770, 1705, 1453, 1367, 1145, 1024, 960, 848, 746, 691 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{29}H_{30}NaO_5$ $[M + Na]^+$ 481.1991, found 481.1992. **[α] $^{20}_D$** = +35 (*c* 0.5; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 6.1 min, t_R (minor) = 7.5 min.



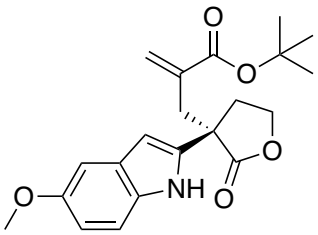
Compound **22** (87 mg, 98%) was obtained as a white powder after silica gel column chromatography (CH_2Cl_2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.78 (m, 1H), 7.71 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.27 (s, 1H), 6.18 (s, 1H), 5.45 (s, 1H), 4.38 (ddd, *J* = 9.0, 7.5, 4.0 Hz, 1H), 4.25 (td, *J* = 9.0, 6.5 Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.68 (ddd, *J* = 13.5, 6.5, 4.0 Hz, 1H), 2.61 (ddd, *J* = 13.5, 8.5, 7.5 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.2, 166.3, 143.3, 139.5, 139.4, 136.6, 129.6, 124.7, 124.6, 123.8, 122.6, 122.3, 81.3, 65.9, 50.6, 39.9, 35.1, 28.1. **IR (neat)** ν_{max} 2951,1766, 1713, 1635, 1590, 1473, 1434, 1369, 1148, 1025, 956, 751 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{22}SNaO_4$ $[M + Na]^+$ 381.1136, found 381.1138. **[α] $^{20}_D$** = +66 (*c* 0.5; $CHCl_3$), er (95:5). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.4 min, t_R (minor) = 11.4 min. Recrystallization in hexane led to compound **22** (62 mg, 70%) with er (>99:1) mp 91–93 °C.



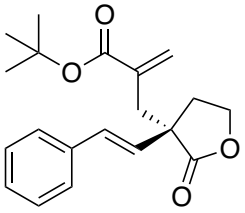
Compound **23** (74 mg, 96%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.22 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.00 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.13 (s, 1H), 5.32 (s, 1H), 4.35 (ddd, *J* = 9.0, 7.5, 4.5 Hz, 1H), 4.22 (td, *J* = 9.0, 6.5 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.60 – 2.53 (m, 2H), 1.45 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 177.6, 166.3, 142.5, 136.6, 129.3, 127.0, 125.6, 125.2, 81.1, 65.8, 49.9, 40.3, 35.0, 28.0. **IR (neat)** ν_{max} 2976, 1765, 1704, 1626, 1393, 1218, 1151, 1025, 849, 530 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{16}H_{20}NaO_4S$ [M + Na]$^+$ 331.0980, found 331.0980. **[α] $^{20}_D$** = +65 (*c* 0.5; $CHCl_3$), er (96:4). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.8 min, t_R (minor) = 10.6 min.



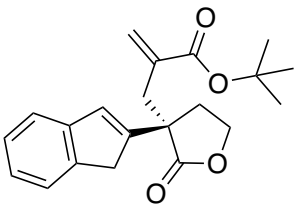
Compound **24** (76 mg, 90%) was obtained as a brown solid after silica gel column chromatography (Petroleum ether/EtOAc 80:20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.97 (bs, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.17 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.33 (s, 1H), 6.13 (s, 1H), 5.20 (s, 1H), 4.46 (ddd, *J* = 9.0, 7.5, 6.0 Hz, 1H), 4.36 (ddd, *J* = 9.0, 7.5, 6.5 Hz, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.74 (ddd, *J* = 13.0, 7.5, 6.0 Hz, 1H), 2.60 (ddd, *J* = 13.1, 7.5, 6.5 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.8, 166.1, 136.5, 136.4, 135.5, 129.2, 127.8, 122.4, 120.4, 120.1, 111.3, 100.9, 81.3, 77.4, 66.6, 47.9, 39.1, 32.9, 27.9. **IR (neat)** ν_{max} 3440, 2981, 1754, 1704, 1624, 1444, 1341, 1148, 1019, 968, 789, 742, 472, 442 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{23}NNaO_4$ [M + Na]$^+$ 364.1523, found 364.1522. **[α] $^{20}_D$** = +27 (*c* 0.5; $CHCl_3$), er (78:22). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 6.0 min, t_R (minor) = 6.5 min.



Compound **25** (91 mg, 98%) was obtained as a brown solid after silica gel column chromatography (Petroleum ether/EtOAc 80:20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.83 (bs, 1H), 7.24 (s, 1H), 7.00 (s, 1H), 6.84 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.24 (s, 1H), 6.13 (s, 1H), 5.20 (s, 1H), 4.46 (m, 1H), 4.36 (dt, *J* = 9.0, 7.0 Hz, 1H), 3.83 (s, 3H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H), 2.72 (dt, *J* = 13.5, 6.5 Hz, 1H), 2.58 (dt, *J* = 13.5, 7.0 Hz, 1H), 1.37 (s, 9H).**^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.8, 166.2, 154.4, 136.4, 136.2, 131.7, 129.3, 128.2, 112.6, 112.0, 102.3, 100.7, 81.3, 66.6, 56.0, 48.0, 39.2, 33.0, 28.0. **IR (neat)** ν_{max} 3412, 3375, 2980, 1758, 1742, 1703, 1625, 1589, 1487, 1297, 1203, 1178, 1149, 1024, 711, 552, 461 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{21}H_{25}NNaO_5$ [M + Na]$^+$ 394.1631, found 394.1630. **[α] $^{20}_D$** = +22 (*c* 0.5; $CHCl_3$), er (78:22). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 8.4 min, t_R (minor) = 11.8 min.



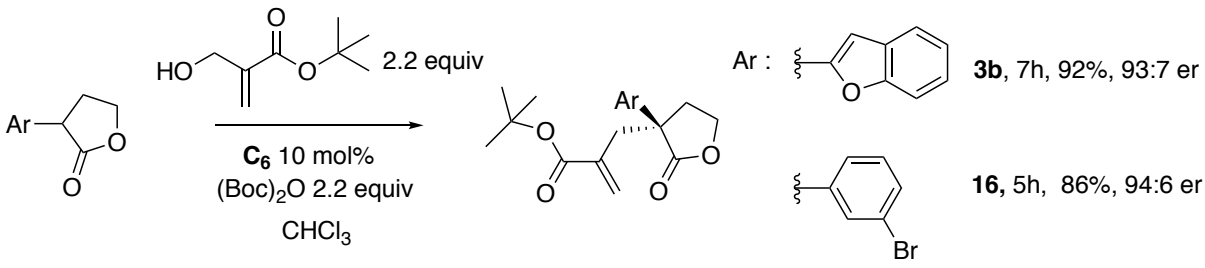
Compound **26** (68 mg, 84%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.39 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.24 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.30 – 6.11 (m, 2H), 5.63 (s, 1H), 4.31 (ddd, *J* = 9.0, 7.5, 4.5 Hz, 1H), 4.23 (ddd, *J* = 9.0, 8.0, 7.0 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 2.45 – 2.22 (m, 2H), 1.45 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.5, 166.5, 137.1, 136.3, 131.2, 129.2, 128.8, 128.7, 128.2, 126.6, 81.3, 65.6, 50.0, 37.7, 32.6, 28.1. **IR (neat)** ν_{max} 2980, 2927, 1752, 1700, 1366, 1343, 1154, 1211, 1019, 850, 739, 691 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{24}NaO_4$ [M + Na]$^+$ 351.1572, found 351.1576. **[α] $^{20}_D$** = +26 (*c* 0.5; $CHCl_3$), er (70:30). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 7.3 min, t_R (minor) = 8.6 min.



Compound **27** (73 mg, 86%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.23 (m, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.78 (s, 1H), 6.17 (s, 1H), 5.54 (s, 1H), 4.32 (td, *J* = 9.5, 3.0 Hz, 1H), 4.21 (td, *J* = 9.0, 6.5 Hz, 1H), 3.67 – 3.32 (m, 2H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.80 (d, *J* = 14.0 Hz, 1H), 2.54 (ddd, *J* = 13.5, 6.5, 3.0 Hz, 1H), 2.42 (ddd, *J* = 13.5, 9.5, 8.0 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.9, 166.4, 145.4, 143.8, 143.3, 137.5, 129.5, 128.6, 126.6, 125.1, 123.8, 123.7, 121.1, 81.2, 65.7, 50.2, 38.9, 37.7, 32.9, 27.9. **IR (neat)** ν_{max} 3000,

2979, 1764, 1697, 1366, 1298, 1154, 1022, 754, 717, 411 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{21}H_{24}NaO_4$ $[M + Na]^+$ 363.1572, found 363.1574. **[α] $^{20}_D$** = +55 (*c* 0.5; $CHCl_3$), er (76:24). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.6 min, t_R (minor) = 10.2 min.

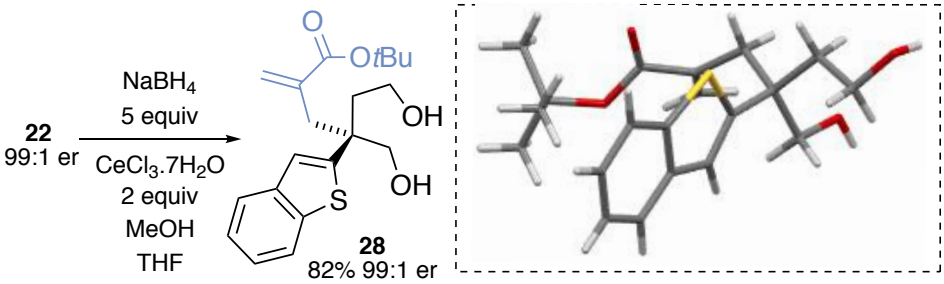
b) *In situ* activation



General procedure for *in situ* activation : Boc_2O (0.55 mmol) was added to a mixture of MBH alcohol (0.55 mmol) and lactone (**1a** or **1m**) (0.25 mmol) in $CHCl_3$ (1 mL). Then **C_6** (10 mol%) was added to the reaction mixture. The reaction was followed by TLC analysis until total consumption of the starting lactone. The resulting mixture was then purified on silica gel column chromatography.
Compound **3b** (78 mg, 92%) was obtained after silica gel column chromatography (Petroluem ether/EtOAc 90:10).
Compound **16** (81 mg, 86%) was obtained after silica gel column chromatography (Petroluem ether/EtOAc 80:20).

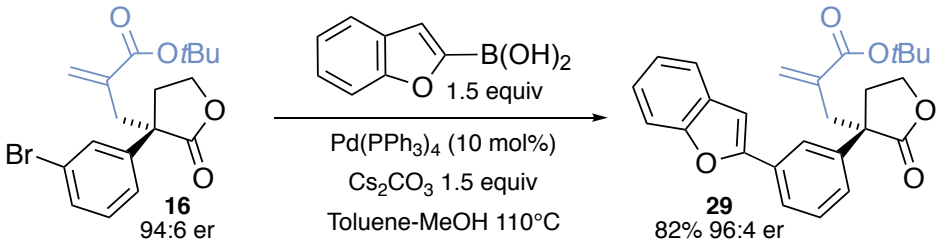
c) Synthetically useful transformations of α-quaternary γ-Lactones

Selective reduction of lactone ring: access to acyclic quaternary stereocenter



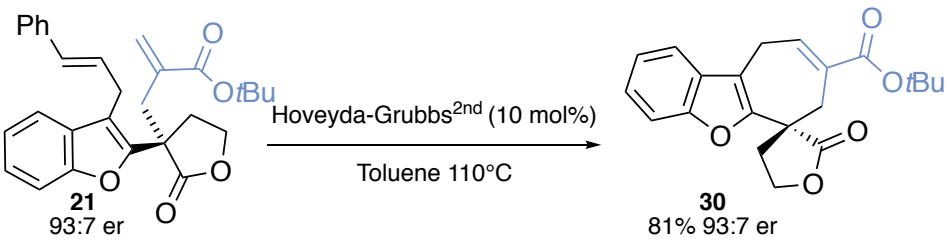
$CeCl_3 \bullet 7H_2O$ (128 mg, 0.50 mmol, 2 equiv) was added to a solution of **22** (93 mg, 0.25 mmol) in MeOH:THF 4:1 (2 mL) at 0°C. After 10 minutes stirring, $NaBH_4$ (48 mg, 1.25 mmol, 5 equiv) was slowly added to the reaction mixture over a period of 20 minutes and the reaction was stirred for another 10 minutes. The resulting mixture was quenched with glacial acetic acid and concentrated under reduce pressure. The residue was dissolved in EtOAc and washed with saturated aqueous solution of $NaHCO_3$ and brine. The organic layer was dried with Na_2SO_4. Compound **28** (77 mg, 82%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.94 (s, 1H), 6.06 (s, 1H), 5.21 (s, 1H), 4.05 (bs, 1H), 3.83 (m, 2H), 3.71 (m, 2H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H), 2.36 (bs, 1H), 2.24 (m, 1H), 2.05 (dt, *J* = 14.5, 6.0 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 168.4, 149.7, 139.8, 138.7, 136.8, 129.6, 124.3, 124.1, 123.4, 122.2, 121.1, 81.8, 65.1, 59.1, 47.1, 41.6, 39.7, 28.0. **IR (neat)** ν_{max} 3298, 2973, 1708, 1632, 1459, 1313, 1156, 1048, 1005, 823, 754, 560, 430 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{26}NaO_4S$ $[M + Na]^+$ 385.1450, found 385.1449. **[α] $^{20}_D$** = -32 (*c* 0.25; $CHCl_3$), er (99:1). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 5.4 min, t_R (minor) = 6.3 min. Single crystal was obtained by diffusion of pentane in EtOAc. mp 128−130 °C.

Cross coupling reaction : access to polyaromatic compound



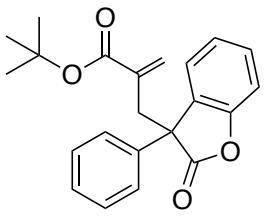
$Pd(PPh_3)_4$ (40 mg, 0.035 mmol, 10 mol%) was added to a round bottom flask previously flushed with argon and filled with **16** (100 mg, 0.35 mmol), benzofuroylboronic acid (84 mg, 0.52 mmol, 1.5 equiv) and Cs_2CO_3 (169 mg, 0.52 mmol, 1.5 equiv) in THF:MeOH 95:5 (3.7 mL). The reaction was refluxed for 18 hours. then the reaction was allowed to cool to room temperature. Compound **29** (120 mg, 82%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 90:10). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.96 (m, 1H), 7.79 (dt, *J* = 6.5, 2.0 Hz, 1H), 7.59 (d, *J* = 8.0, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.30 (m, 1H), 7.22 (d, *J* = 1.0 Hz, 1H), 7.07 (s, 1H), 6.18 (s, 1H), 5.46 (s, 1H), 4.32 (ddd, *J* = 9.5, 8.0, 3.0 Hz, 1H), 4.08 (td, *J* = 9.0, 6.0 Hz, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.95 (d, *J* = 1.0 Hz, 1H), 2.72 (ddd, *J* = 13.5, 6.0, 3.0 Hz, 1H), 2.56 (ddd, *J* = 13.5, 9.5, 8.0 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.3, 166.6, 155.5, 155.1, 139.7, 137.1, 131.2, 129.6, 129.4, 129.2, 127.0, 124.6, 124.4, 123.19, 123.17, 121.12, 111.4, 102.1, 81.2, 65.5, 52.6, 39.5, 33.9, 28.1. **IR (neat)** ν_{max} 2974, 1761, 1703, 1623, 1451, 1176, 1144, 1021, 792, 733, 703, 693, 453 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{26}H_{26}NaO_5$ $[M + Na]^+$ 441.1678, found 441.1678. **[α] $^{20}_D$** = +68 (*c* 0.5; $CHCl_3$), er (94:6). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 6.7 min, t_R (minor) = 9.2 min.

Ring closing metathesis : access to spirocyclic lactone

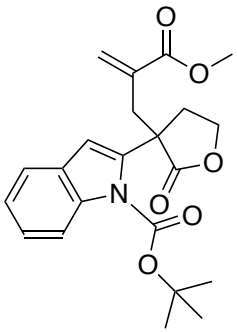


Hoveyda-Grubbs 2nd generation (7.8 mg, 0.0125 mmol, 10 mol%) was added to a solution of **21** (228 mg, 0.50 mmol) in Toluene (7 mL) and the solution was heated at 110°C for 2 hours then allowed to cool to room temperature. Compound **30** (143 mg, 81%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 98:2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.45 (m, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.21 (m, 2H), 4.62 (td, *J* = 8.5, 5.0 Hz, 1H), 4.55 (dt, *J* = 9.0, 8.0 Hz, 1H), 3.64 (dd, *J* = 18.0, 5.0 Hz, 1H), 3.87 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.67 (dt, *J* = 13.0, 8.0 Hz, 1H), 2.42 (ddd, *J* = 13.0, 8.0, 5.0 Hz, 1H), 1.51 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.7, 166.2, 153.1, 151.5, 143.2, 132.9, 128.5, 124.7, 122.8, 118.8, 113.7, 111.3, 81.3, 66.2, 47.2, 33.7, 30.3, 28.2, 21.9. **IR (neat)** ν_{max} 2970, 1770, 1702, 1455, 1368, 1224, 1196, 1169, 1102, 1023, 871, 744, 434 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{21}H_{22}NaO_5^+$ $[M + Na]^+$ 377.1366, found 377.1365. **[α] $^{20}_D$** = +54 (*c* 0.25; $CHCl_3$), er (93:7). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 254 nm, 1 mL/min), t_R (major) = 12.6 min, t_R (minor) = 21.0 min.

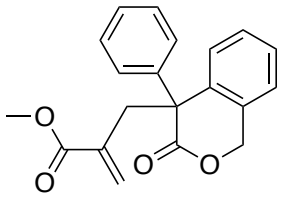
d) Other chiral lactones synthesized according to the general procedure of AAA



Compound **31** (66 mg, 76%) was obtained as a colourless oil after silica gel column chromatography (Petroleum ether/EtOAc 98:2).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.15 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 1H), 5.47 (s, 1H), 3.48 (d, *J* = 13.5 Hz, 1H), 3.29 (d, *J* = 13.5 Hz, 1H), 1.20 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 177.7, 165.7, 153.1, 138.9, 136.9, 129.2, 128.9, 128.4, 128.3, 128.0, 127.1, 126.8, 124.1, 110.7, 80.9, 56.7, 38.7, 27.9. **IR (neat)** ν_{max} 2977, 2934, 1799, 1707, 1597, 1367, 1345, 1229, 1145, 1060, 881, 760, 734, 694, 450 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{22}H_{22}NaO_4$ [M + Na]$^+$ 373.1416, found 373.1419**. [α] $^{20}_D$** = +80 (*c* 0.5; $CHCl_3$), er (92:8). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (minor) = 7.3 min, t_R (major) = 9.3 min.

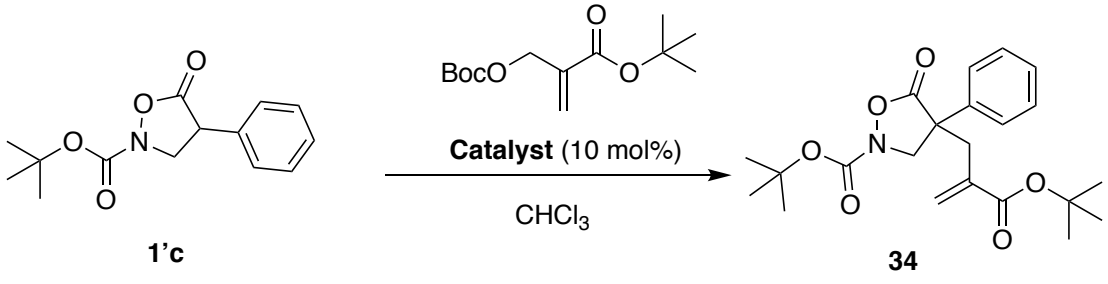


Compound **32** (19 mg, 20%) was obtained as a brown solid after silica gel column chromatography (Petroleum ether/EtOAc 98:2).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.29 (m, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (s, 1H), 6.42 (s, 1H), 5.85 (s, 1H), 4.40 (ddd, *J* = 10.0, 9.0, 3.5 Hz, 1H), 4.10 (q, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.45 (d, *J* = 13.5 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 2.80 (ddd, *J* = 13.0, 10.0, 8.0 Hz, 1H), 2.49 (ddd, *J* = 12.5, 8.5, 3.5 Hz, 1H), 1.70 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.6, 168.1, 151.2, 139.7, 136.5, 135.2, 131.6, 128.6, 124.7, 123.0, 120.8, 115.8, 110.8, 85.1, 65.9, 52.4, 50.3, 38.4, 33.4, 28.3. **IR (neat)** ν_{max} 2978, 1766, 1722, 1627, 1558, 1453, 1368, 1326, 1125, 1154, 1012, 844, 766, 675, 437 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{22}H_{25}NNaO_6$ [M + Na]$^+$ 422.1580, found 422.1580. **[α] $^{20}_D$** = +13 (*c* 0.25; $CHCl_3$), er (81:19). The enantiomeric ratio was determined by HPLC with a CHIRALCEL Whelk column (hexane/isopropanol = 60:40, 230 nm, 1 mL/min), t_R (major) = 18.4 min, t_R (minor) = 20.4 min.



Compound **33** (62 mg, 78%) was obtained as a white powder after silica gel column chromatography (Petroleum ether/EtOAc 98:2). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.23 – 7.11 (m, 6H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 5.43 (s, 1H), 3.61 (s, 3H), 3.39 (d, *J* = 16.5 Hz, 1H), 3.26 – 3.18 (m, 2H), 3.13 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 170.7, 168.0, 151.0, 136.6, 135.6, 130.4, 128.6, 128.2, 127.8, 126.9, 124.5, 122.3, 116.1, 52.1, 50.3, 40.3, 32.1. **IR (neat)** ν_{max} 2950, 2926, 2848, 1747, 1715, 1456, 1225, 1198, 1171, 1134, 962, 747, 693, 492, 456 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{20}H_{18}NaO_4$ [M + Na]$^+$ 345.1103, found 345.1103. **[α] $^{20}_D$** = +18 (*c* 0.25; $CHCl_3$), er (79:21). The enantiomeric ratio was determined by HPLC with a CHIRALCEL IC column (hexane/isopropanol = 65:35, 230 nm, 1 mL/min), t_R (major) = 7.1 min, t_R (minor) = 7.6 min.

4) Studies on related lactone analogues

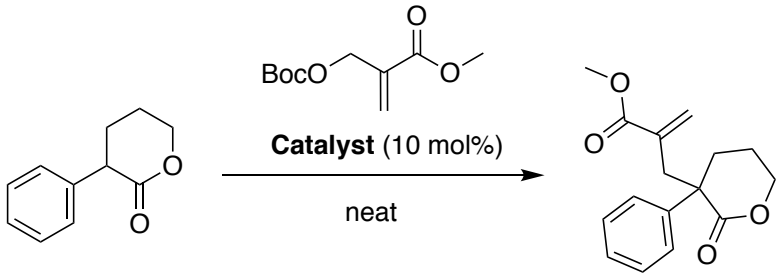


1'c **34**

Catalyst = DMAP : 98% yield
C_6 : no reaction

DMAP (3 mg, 0.025 mmol, 10 mol%) was added to a solution of **1'c** (65 mg, 0.25 mmol) and MBH carbonate (142 mg, 0.55 mmol, 2.2 equiv) in $CHCl_3$ (1 mL) and the solution was stirred under argon for 5 hours. Compound **34** (98 mg, 98%) was obtained as a brown oil after silica gel column chromatography (CH_2Cl_2). **^{1}H NMR (500 MHz,**

Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 6.17 (s, 1H), 5.49 (s, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 1.46 (s, 9H), 1.25 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 175.4, 166.2, 156.0, 136.5, 136.2, 130.1, 129.11, 129.06, 128.5, 126.91, 126.86, 83.9, 81.5, 58.1, 53.8, 38.7, 28.1, 27.8. **IR (neat)** ν_{max} 2978, 2934, 1793, 1749, 1704, 1629, 1449, 1368, 1255, 1140, 847, 697 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{22}H_{29}NNaO_6$ [M + Na]$^+$ 426.1893, found 426.1890.



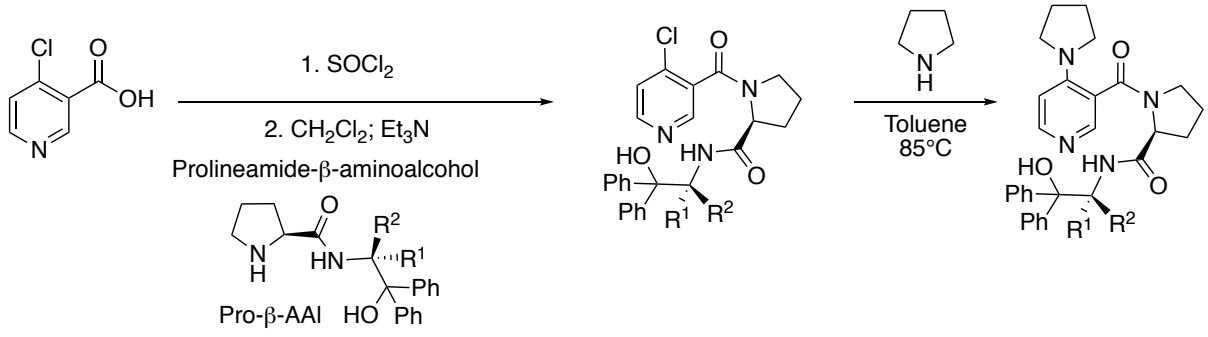
1'd **35**

Catalyst = DMAP : 98% yield
C_6 : no reaction

DMAP (3 mg, 0.025 mmol, 10 mol%) was added to a mixture of **1'd** (44 mg, 0.25 mmol) and MBH carbonate (142 mg, 0.55 mmol, 2.2 equiv) and stirred under argon for 24h. Compound **35** (43 mg, 63%) was obtained as a colourless oil after two silica gel column chromatographies (CH_2Cl_2 then Petroleum ether/EtOAc 95:5). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.39 – 7.28 (m, 5H), 6.18 (s, 1H), 5.36 (s, 1H), 4.17 (dt, *J* = 11.0, 6.5 Hz, 1H), 3.92 (dt, *J* = 11.0, 6.5 Hz, 1H), 3.59 (s, 3H), 3.08 (d, *J* = 14.0 Hz, 1H), 2.97 (d, *J* = 14.0 Hz, 1H), 2.52 (m, 1H), 1.97 – 1.87 (m, 2H), 1.75 (m, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 174.2, 168.2, 139.2, 136.1, 130.1, 129.0, 127.7, 126.5, 67.7, 52.4, 52.0, 41.4, 27.2, 19.4. **IR (neat)** ν_{max} 2950, 1717, 1626, 1599, 1495, 1445, 1268, 1193, 1149, 1090, 975, 815, 762, 724, 700, 541 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{16}H_{18}NaO_4$ [M + Na]$^+$ 297.1103, found 297.1105**.**

5) Catalysts Synthesis C_2-C_7

Catalysts **C_2** to **C_7** were synthesized according to procedure described by Dàlaigh and Connon.[7] Pro-beta-β-AAl were synthesized according procedure described in literature,[8] **Pro-β-AAl$_5$**, **Pro-β-AAl$_6$** are known compounds.

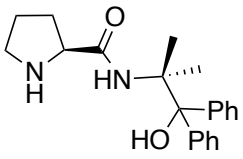


Pro-β-AAl$_3$ R_1= R_2= CH_3
Pro-β-AAl$_4$ R_1= H, R_2= *t*Bu
Pro-β-AAl$_5$ R_1= H, R_2= Bn
Pro-β-AAl$_6$ R_1= H, R_2= *i*Bu
Pro-β-AAl$_7$ R_1= *i*Bu, R_2= H

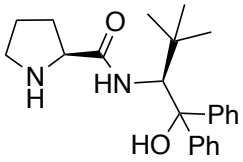
ClPy$_3$ R_1= R_2= CH_3
ClPy$_4$ R_1= H, R_2= *t*Bu
ClPy$_5$ R_1= H, R_2= Bn
ClPy$_6$ R_1= H, R_2= *i*Bu
ClPy$_7$ R_1= *i*Bu, R_2= H

C_3 R_1= R_2= CH_3
C_4 R_1= H, R_2= *t*Bu
C_5 R_1= H, R_2= Bn
C_6 R_1= H, R_2= *i*Bu
C_7 R_1= *i*Bu, R_2= H

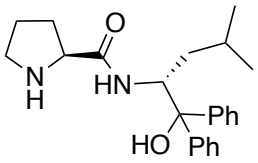
a) New Prolineamide-β-aminoalcohols



Pro-β-AAl$_3$ (2.2 g, 67%) was obtained after recrystallization from EtOAc. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.20 (bs, 1H), 7.67 (bs, 2H), 7.55 (bs, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.14 (m, 2H), 3.45 (bs, 1H), 2.91 (dt, *J* = 10.0, 7.0 Hz, 1H), 2.76 (m, 1H), 1.96 – 1.74 (m, 2H), 1.50 (s, 3H), 1.41 (s, 3H) 1.35-1.55 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.0, 146.4, 145.1, 128.4, 128.3, 127.3, 126.7, 126.6, 82.5, 61.9, 60.3, 47.4, 30.2, 26.3, 24.8. **IR (neat)** ν_{max} 3370, 3157, 2887, 1632, 1518, 1471, 1391, 1286, 1048, 1002, 755, 700, 589, 445 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{21}H_{25}N_2O$ [M – H_2O]$^+$ 321.1967, found 321.1965. **[α] $^{20}_D$** = -72 (*c* 0.5; $CHCl_3$).



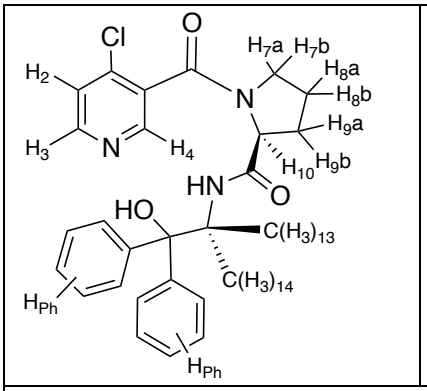
Pro-β-AAl$_4$ (1.9 g, 79%) was obtained after recrystallization from EtOAc. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.18 (bs, 1H), 7.63 (bs, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.68 (bs, 1H), 2.88 (dt, *J* = 10.0, 7 Hz, 1H), 2.79 (dt, *J* = 10.0, 7 Hz, 1H), 1.86 (m, 1H), 1.76 (m, 1H), 1.58 – 1.36 (m, 2H), 0.88 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 174.8, 148.8, 146.9, 128.1, 127.9, 126.6, 126.3, 125.7, 125.3, 60.8, 47.4, 38.2, 30.4, 29.9, 26.2. **IR (neat)** ν_{max} 3370, 3156, 2970, 1640, 1512, 1392, 1173, 755, 706, 694 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{23}H_{31}N_2O_2$ [M + H]$^+$ 367.2386, found 367.2384. **[α] $^{20}_D$** = -113 (*c* 0.5; $CHCl_3$).

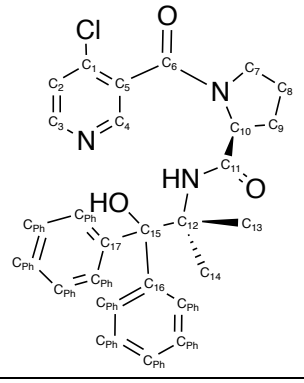


Pro-β-AAl$_7$ (1.8 g, 81%) was obtained after recrystallization from EtOAc. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.83 (d, *J* = 9.5 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.18 (m, 1H), 7.12 (m, 1H), 4.95 (m, 1H), 3.90 (bs,1H) 3.55 (dd, *J* = 9.5, 5.0Hz, 1H), 2.79 (dt, *J* = 10.5, 7.0 Hz, 1H), 2.47 (dt, *J* = 10.5, 6.5 Hz, 1H), 1.94 – 1.73 (m, 2H), 1.65 – 1.50 (m, 2H), 1.49 – 1.33 (m, 2H), 1.30 – 1.09 (m, 2H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 175.4, 145.8, 145.2, 128.4, 128.1, 127.0, 126.7, 125.7, 81.4, 60.4, 54.2, 47.1, 39.1, 30.4, 25.9, 25.3, 24.1, 21.7. **IR (neat)** ν_{max} 3417, 3336, 3269, 2956, 2874, 1630, 1522, 1446, 1152, 1061, 743, 692 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{23}H_{31}N_2O_2$ [M + H]$^+$ 367.2386, found 367.2383. **[α] $^{20}_D$** = -6 (*c* 0.5; $CHCl_3$).

b) ClPy intermediates

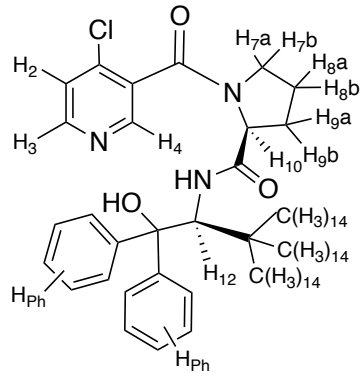
Compounds **ClPy** are present as a mixture of two rotamers in slow exchange in DMSO. The presence of two rotameric forms (*vs* diastereoisomeric forms) of compounds **ClPy** in DMSO-d_6 is unambiguously highlighted by the presence in the 2D NOESY spectrum of compound **ClPy$_3$** and **ClPy$_6$** (recorded at 323K and 353K) of cross peaks of the same sign as the diagonal peaks.

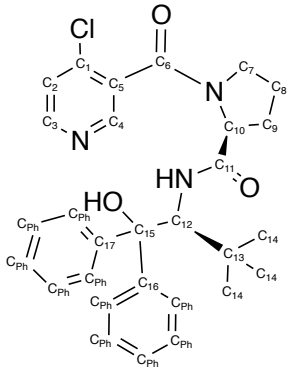




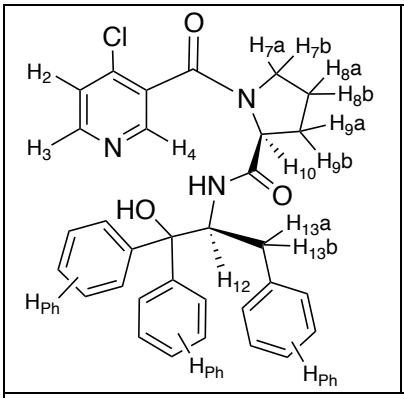
Chloropyridine **ClPy$_3$** (0.6 g, 80%) was obtained after column chromatography (CH_2Cl_2/MeOH 93:7) as a white solid. Ratio of rotamers *Rot1*/*Rot2*: 1/1.4. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.59 (d, *J* = 5.5 Hz, H_3 *Rot1*), 8.57 (d, *J* = 5.5 Hz, H_3 *Rot2*), 8.48 (s, H_4 *Rot1*), 8.37 (s, H_4 *Rot2*), 7.65 (d, *J* = 5.5 Hz, H_2 *Rot1*), 7.62 (d, *J* = 5.5 Hz, H_2 *Rot2*), 7.55 – 7.10 (m, H_{Ph}), 4.43 (dd, *J* = 8.5, 4.5 Hz, H_{10} *Rot1*), 4.05 (d, *J* = 5.5 Hz, H_{10} *Rot2*), 3.40-3.50 (m, H_{7a}-H_{7b} *Rot1*), 3.20 – 3.12 (m, H_{7a}-H_{7b} *Rot1*), 3.12 – 3.05 (m, H_{7a}-H_{7b} *Rot2*), 1.89 – 1.76 (m, H_{9a} *Rot1-Rot2*), 1.68 – 1.54 (m, H_{8a} *Rot1-Rot2*), 1.40 (s, $H_{13\text{-}14}$ *Rot1-Rot2*), 1.32 (s, $H_{13\text{-}14}$ *Rot1-Rot2*),1.53 – 1.30 (m, H_{8b} *Rot1-Rot2*), 1.10 (s, $H_{13\text{-}14}$ *Rot1-Rot2*), 1.02 (s, $H_{13\text{-}14}$ *Rot1-Rot2*), 1.05 – 0.90 (m, H_{9b} *Rot1-Rot2*).**^{13}C NMR (126 MHz, DMSO-d_6)** δ

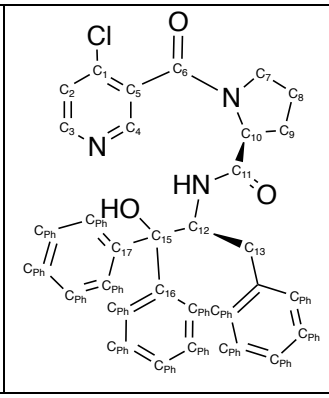
171.9 and 171.8 (C_{11} *Rot1-Rot2*), 163.5 and 163.3 (C_6 *Rot1-Rot2*), 151.1 and 150.8 (C_3 *Rot1-Rot2*), 148.4 and 148.0 (C_4 *Rot1-Rot2*), 146.2, 146.1, 144.9 and 144.4 ($C_{17\text{-}16}$ *Rot1-Rot2*), 139.2 (C_1 *Rot1-Rot2*), 132.5 and 132.3 (C_5 *Rot1-Rot2*), 128.2 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 127.1 (C_{Ph}), 127.08 (C_{Ph}), 127.03 (C_{Ph}), 126.5 (C_{Ph}), 124.74 and 124.66 (C_2 *Rot1-Rot2*), 81.7 and 81.6 (C_{15} *Rot1-Rot2*), 61.5 and 61.4 (C_{12} *Rot1-Rot2*), 60.3 and 59.5 (C_{10} *Rot1-Rot2*), 48.3 and 46.6 (C_7 *Rot1-Rot2*), 30.9 and 28.9 (C_9 *Rot1-Rot2*), 27.8, 24.2, 23.2 ($C_{13\text{-}14}$ *Rot1-Rot2*), 23.9 and 22.1 (C_8 *Rot1-Rot2*). **IR (neat)** ν_{max} 3266, 3065, 2986, 2882, 1623, 1442, 1391, 1156, 753, 702 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{27}H_{28}N_3O_3NaCl$ $[M + Na]^+$ 500.1717, found 500.1718. **$[\alpha]^{20}_D$** = -96 (*c* 0.5; $CHCl_3$)





Chloropyridine **$ClPy_4$** (1 g, 90%) was obtained after column chromatography (CH_2Cl_2/MeOH 93:7) as a white solid. Ratio of rotamers *Rot1*/*Rot2*: 1/1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.59 (d, *J* = 5.5 Hz, H_3 *Rot1*), 8.50 (d, *J* = 5.5 Hz, H_3 *Rot2*), 8.48 (s, H_4 *Rot1*), 8.41 (s, H_4 *Rot2*), 7.69 (d, *J* = 10.0 Hz, NH, *Rot1*), 7.65 (d, *J* = 5.5 Hz, H_2 *Rot1*), 7.64 – 7.61 (m, H_{Ph}), 7.59 – 7.53 (m, H_2 *Rot2* H_{Ph}), 7.49 – 7.44 (m, H_{Ph}), 7.32 (d, *J* = 10.0 Hz, NH), 7.26 – 7.15 (m, H_{Ph}), 7.12 – 7.03 (m, H_{Ph}), 5.53 (s, OH, *Rot1*), 5.30 (s, OH, *Rot2*), 4.94 (d, *J* = 10.0 Hz, H_{12} *Rot1*), 4.72 (d, *J* = 10.0 Hz, H_{12} *Rot2*), 4.23 (dd, *J* = 8.5, 3.5 Hz, H_{10} *Rot1*), 4.03 – 3.93 (m, H_{10} *Rot2*), 3.66 – 3.48 (m, H_{7a}-H_{7b} *Rot1*), 3.40-3.33 (m, H_{7a}-H_{7b} *Rot1*), 3.26 – 3.15 (m, H_{7a}-H_{7b} *Rot2*), 3.15 – 3.03 (m, H_{7a}-H_{7b} *Rot2*), 1.76 – 1.32 (m, $H_{8a\text{-}8b}$, H_{9a} *Rot1-Rot2*), 0.79 (s, H_{14}, *Rot1*), 0.72 (m, H_{9b}, *Rot1*), 0.42 (s, H_{14}, *Rot2*), 0.34 (m, H_{9b}, *Rot2*). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 169.7 and 169.5 (C_{11} *Rot1-Rot2*), 163.5 and 163.0 (C_6 *Rot1-Rot2*), 151.2 and 150.8 (C_3 *Rot1-Rot2*) , 149.6 and 149.3 ($C_{17\text{-}16}$ *Rot1-Rot2*), 148.8 and 148.0 (C_4 *Rot1-Rot2*), 147.0 and 146.7 ($C_{17\text{-}16}$ *Rot1-Rot2*), 139.2 (C_1 *Rot1-Rot2*), 132.9 and 132.4 (C_5 *Rot1-Rot2*), 127.73 (C_{Ph}), 127.71 (C_{Ph}), 127.68 (C_{Ph}), 127.6 (C_{Ph}), 126.0 (C_{Ph}), 125.94 (C_{Ph}), 125.85 (C_{Ph}), 125.80 (C_{Ph}), 125.3 (C_{Ph}), 125.2 (C_{Ph}), 124.8 and 124.7 (C_2 *Rot1-Rot2*), 124.5 (C_{Ph}), 81.7 and 79.2 (C_{15} *Rot1-Rot2*), 60.5 (C_{10} *Rot1-Rot2*), 60.2 and 60.1 (C_{12} *Rot1-Rot2*), 59.4 (C_{10} *Rot1-Rot2*), 48.2 and 46.6 (C_7 *Rot1-Rot2*), 37.3 and 36.5 (C_{13} *Rot1-Rot2*), 30.8 (C_9 *Rot1-Rot2*), 29.6 and 29.4 (C_{14} *Rot1-Rot2*), 28.4 (C_9 *Rot1-Rot2*), 24.1 and 22.1 (C_8 *Rot1-Rot2*). **IR (neat)** ν_{max} 3341, 3063, 2956, 2875, 1669, 1633, 1446, 1065, 745, 705, 458 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{29}H_{32}N_3O_3NaCl$ $[M + Na]^+$ 528.2030, found 528.2029. **$[\alpha]^{20}_D$** = -116 (*c* 0.5; $CHCl_3$).

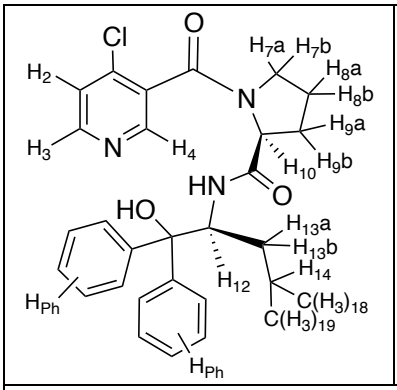


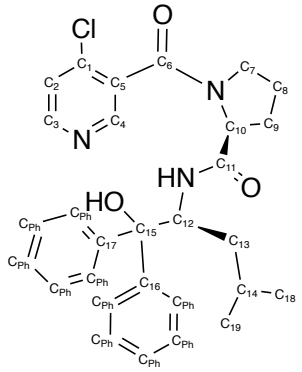


Chloropyridine **$ClPy_5$** (250 mg, 67%) was obtained after column chromatography (CH_2Cl_2/MeOH 99:1) as a white solid. Ratio of rotamers *Rot1*/*Rot2*: 1.2/1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.59 (d, *J* = 5.5 Hz, H_3 *Rot1*), 8.55 (d d, *J* = 5.5 Hz, H_3 *Rot2*), 8.38 (s, H_4 *Rot1*), 8.16 (s, H_4 *Rot2*), 7.85 (d, *J* = 10.0 Hz, NH, *Rot2*), 7.69 – 7.00

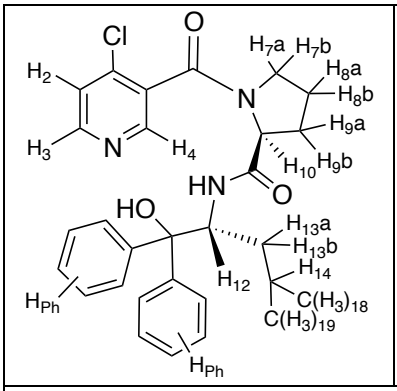
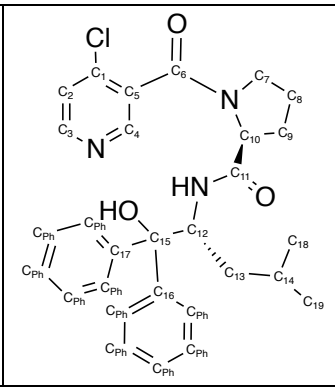
(m, H_{Ph}), 6.88 (d, *J* = 7.0 Hz, H_{Ph}), 6.11 (s, 0H, *Rot1*), 5.82 (s, OH, *Rot2*), 5.26 – 4.91 (m, H_{12} *Rot1-Rot2*), 4.36 (dd, *J* = 8.5, 3.5 Hz, H_{10} *Rot1*), 3.93 (d, *J* = 8.0 Hz, H_{10} *Rot2*), 3.45 – 3.36 (m, H_{7a} *Rot2*), 3.37 – 3.28 (m, H_{7b} *Rot2*), 3.12 – 3.05 (m, H_{7a} *Rot1*), 3.05 – 2.99 (m, H_{7b} *Rot2*), 2.78 (dd, *J* = 14.5, 10.0 Hz, H_{13a} *Rot1*), 2.68 (d, *J* = 14.5 Hz, H_{13b} *Rot1*), 2.62 (d, *J* = 12.5 Hz, H_{13a} *Rot2*), 2.42 (dd, *J* = 14.5, 9.0 Hz, H_{13b} *Rot2*), 1.70 – 1.59 (m, H_{8a} *Rot1-Rot2*), 1.56 – 1.49 (m, H_{9a} *Rot1-Rot2*), 1.48 – 1.39 (m, H_{9b} *Rot1*), 1.25 – 1.12 (m, H_{9b} *Rot2*), 0.96 – 0.87 (m, H_{8b} *Rot1*), 0.87 – 0.78 (m, H_{8b} *Rot2*).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 170.3 and 169.7(C_{11} *Rot1-Rot2)*, 163.3 and 163.2 (C_6 *Rot1-Rot2*), 151.0 and 150.7 (C_3 *Rot1-Rot2*), 148.0 and 147.9 (C_4 *Rot1-Rot2*), 146.4 146.3, 146.0, 145.8 ($C_{17\text{-}16}$ *Rot1-Rot2*), 139.5, 139.3, 139.1 ($C_{1\text{-}18}$ *Rot1-Rot2),* 132.7 and 132.2 (C_5 *Rot1-Rot2)*, 129.3 (C_{Ph}), 128.9 (C_{Ph}), 128.5 (C_{Ph}), 128.4 (C_{Ph}), 128.2 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 127.5 (C_{Ph}), 127.43 (C_{Ph}), 126.36 (C_{Ph}), 126.4 (C_{Ph}), 126.04 (C_{Ph}), 126.00 (C_{Ph}), 125.9 (C_{Ph}), 125.7 (C_{Ph}), 125.6 (C_{Ph}), 125.5 (C_{Ph}), 125.32 (C_{Ph}), 125.25 (C_{Ph}), 124.7 (C_{Ph}), 124.5 (C_{Ph}), 80.6 and 80.5 (C_{15} *Rot1-Rot2*), 60.7 and 59.1 (C_{10} *Rot1-Rot2*), 57.0 and 56.5 (C_{12} *Rot1-Rot2*), 47.9 and 45.7 (C_7 *Rot1-Rot2*), 36.4 and 36.1 (C_{13} *Rot1-Rot2*), 31.0 and 28.7 (C_8 *Rot1-Rot2*), 23.6 and 21.5 (C_9 *Rot1-Rot2*). **IR (neat)** ν_{max} 3301, 3068, 3035, 1633, 1446, 1061, 746, 697 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{32}H_{30}N_3ClNaO_3$ $[M + Na]^+$ 562.1873, found 562.1877. **[α] $^{20}_D$** = -91 (*c* 0.5; $CHCl_3$).





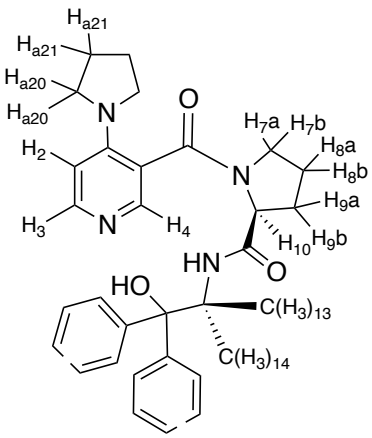
Chloropyridine **ClPy$_6$** (1.6 g, 73%) was obtained after column chromatography (CH_2Cl_2/MeOH 93:7) as a white solid. Ratio of rotamers *Rot1*/*Rot2*: 1/2. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.59 (d, *J* = 5.5 Hz, H_3 *Rot1*), 8.51 (d, *J* = 5.5 Hz, H_3 *Rot2*), 8.48 (s, H_4 *Rot1*), 8.34 (s, H_4 *Rot2*), 7.65 (d, *J* = 5.5 Hz, H_2 *Rot1*), 7.60 (d, *J* = 10.0 Hz, NH), 7.58 (d, *J* = 5.5 Hz, H_2 *Rot2*), 7.56 – 7.50 (m, H_{Ph}), 7.50 – 7.41 (m, H_{Ph}), 7.33 – 7.24 (m, H_{Ph}), 7.24 – 7.01 (m, H_{Ph}), 5.69 (s, OH, *Rot1*), 5.47 (s, OH, *Rot2*), 5.05 (d, *J* = 10.5 Hz, H_{12}), 4.88 (d, *J* = 10.5 Hz, H_{12}), 4.32 (dd, *J* = 7.5, 3.5 Hz, H_{10} *Rot1*), 4.22 – 4.04 (m, H_{10} *Rot2*), 3.63 – 3.40 (m, H_{7a} *Rot2*), 3.37 – 3.31 (m, H_{7b} *Rot2*), 3.20 – 3.15 (m, H_{7a} *Rot1*), 3.11 – 3.06 (m, H_{7b} *Rot1*), 1.74 – 1.50 (m, H_{8a}, H_{9a} *Rot1-Rot2*, H_{13a} *Rot1*), 1.32 – 1.23 (m, H_{8b} *Rot1*), 1.21 – 1.13 (m, H_{13a} *Rot2*), 0.98 – 0.92 (m, H_{13b} *Rot1*), 0.92 – 0.88 (m, H_{9b} *Rot2*), 0.84-0.78 (m, H_{13b} *Rot2*), 0.86 (d, *J* = 6.5 Hz, H_{18} *Rot1*), 0.80 (d, *J* = 6.5 Hz, H_{18} *Rot2*), 0.77 (d, *J* = 6.5 Hz, H_{19} *Rot1*), 0.67-0.65 (m, H_{9b} *Rot2*), 0.61 (d, *J* = 6.5 Hz, H_{19} *Rot2*).**^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 170.24 and 170.18 (C_{11} *Rot1-Rot2*), 163.6, and 163.0 (C_6 *Rot1-Rot2*), 151.1 and 150.6 (C_3 *Rot1-Rot2*), 148.6 and 148.0 (C_4 *Rot1-Rot2*), 147.0, 146.7, 146.1, 146.0 ($C_{17\text{-}16}$ *Rot1-Rot2*), 139.2 (C_1 *Rot1-Rot2*), 132.8 and 132.4 (C_5 *Rot1-Rot2*), 128.1 (C_{Ph}), 127.5 (C_{Ph}), 126.31 (C_{Ph}), 126.27 (C_{Ph}), 126.0 (C_{Ph}), 125.9 (C_{Ph}), 125.5 (C_{Ph}), 125.23 (C_{Ph}), 125.20, (C_{Ph}) 124.8 and 124.5 (C_2 *Rot1-Rot2*), 80.3 and 80.1 (C_{15} *Rot1-Rot2*), 60.2 and 59.2 (C_{10} *Rot1-Rot2*), 52.7 and 52.4 (C_{12} *Rot1-Rot2*), 48.2 and 46.5 (C_7 *Rot1-Rot2*), 39.1 and 38.5 (C_{13} *Rot1-Rot2*), 31.5 and 28.9 (C_9 *Rot1-Rot2*), 24.3 and 24.1 (C_{18} *Rot1-Rot2*), 24.0(C_8 *Rot1*), 23.8 and 23.6 (C_{14} *Rot1-Rot2*), 22.0 (C_8 *Rot2*), 21.7 and 21.3 (C_{19} *Rot1-Rot2*). **IR (neat)** ν_{max} 3409, 2953, 1642, 1388, 1265, 1083, 746, 702, 680 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{29}H_{32}N_3O_3NaCl$ $[M + Na]^+$ 528.2030, found 528.2026. **[α] $^{20}_D$** = -82 (*c* 0.5; $CHCl_3$)

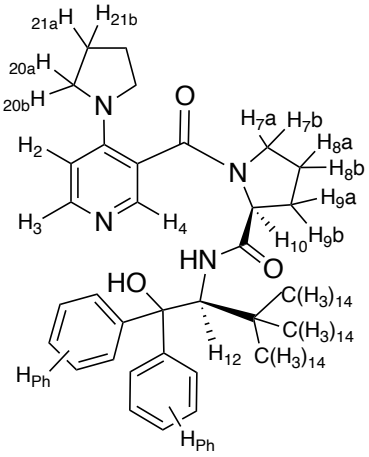
Chloropyridine **ClPy$_7$** (0.73 g, 96%) was obtained after column chromatography (CH_2Cl_2/MeOH 93:7) as a white solid. Ratio of rotamers *Rot1*/*Rot2*: 2/1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.62 (d, *J* = 5.5 Hz, H_3 *Rot1*), 8.57 (d, *J* = 5.5 Hz, H_3 *Rot2*), 8.55 (s, H_4 *Rot1*), 8.49 (s, H_4 *Rot2*), 7.70 (d, *J* = 5.5 Hz, H_2 *Rot1*), 7.61 (d, *J* = 5.5 Hz, H_2 *Rot2*), 7.56 – 7.45 (m, H_{Ph}), 7.34 – 7.04 (m, H_{Ph}), 6.83 (d, *J* = 9 Hz, NH), 6.08 (s, OH, *Rot2*), 6.01 (s, OH, *Rot1*), 5.07 (t, *J* = 10.0 Hz, H_{12} *Rot1*), 4.89 (bs, H_{12} *Rot2*), 4.33 (dd, *J* = 9.0, 3.5 Hz, H_{10} *Rot1*), 3.91 (d, *J* = 10.0 Hz, H_{10} *Rot2*), 3.46 – 3.39 (m, H_{7a} *Rot2*), 3.29 – 3.22 (m, H_{7b} *Rot2*), 3.14 – 2.96 (m, H_{7a}-H_{7b} *Rot1*), 1.98 – 1.76 (m, H_{9a}, *Rot1-Rot2*), 1.67 – 1.41 (m, H_{13a} *Rot1-Rot2,* H_{8a}, *Rot1-Rot2,* H_{9b} *Rot2*), 1.32 – 1.18 (m, H_{9b} *Rot1*), 1.15 – 1.04 (m, H_{8b}, *Rot1*), 1.03 – 0.91 (m, H_{13b} *Rot1-Rot2*), 0.88 (d, *J* = 6.5 Hz, H_{18} *Rot1*), 0.78 – 0.73 (m, H_{18} *Rot2,* H_{19}, *Rot1*), 0.69 (d, *J* = 6.5 Hz, H_{19} *Rot2*), 0.65-0.55 (m, H_{8b} *Rot2*).**^{13}C NMR (126 MHz, DMSO-d_6)** δ 170.3 and 169.9 (C_{11} *Rot1-Rot2*), 164.05 and 164.00 (C_6 *Rot1-Rot2*), 151.3 and 151.2 (C_3 *Rot1-Rot2*), 148.2 and 147.9 (C_4 *Rot1-Rot2*), 147.1, 146.7, 146.0 and 145.8 (C_{17-16} *Rot1-Rot2*), 139.1 and 139.02 (C_1 *Rot1-Rot2*) , 132.3 and 132.2 (C_5 *Rot1-Rot2*), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 127.8 (C_{Ph}), 127.5 (C_{Ph}), 126.3 (C_{Ph}), 126.22 (C_{Ph}), 126.19 (C_{Ph}), 126.0 (C_{Ph}), 125.4 (C_{Ph}), 125.2 (C_{Ph}), 125.1 (C_{Ph}), 125.0 (C_{Ph}),, 124.6 (C_2 *Rot1-Rot2*), 80.1 and 79.8 (C_{15} *Rot1-Rot2*), 61.6 and 60.1 (C_{10} *Rot1-Rot2*), 53.9 and 52.7 (C_{12} *Rot1-Rot2*), 48.1 and 46.0 (C_7 *Rot1-Rot2*), 39.1 and 38.8 (C_{13} *Rot1-Rot2*), 31.2 and 28.9 (C_9 *Rot1-Rot2*), 24.2 (C_{18} *Rot1-Rot2*), 24.0 and 23.8 (C_{14} *Rot1-Rot2*), 23.4 (C_8 *Rot1*), 21.5 and 21.2 (C_{19} *Rot1-Rot2*), 21.0 (C_8 *Rot2*). **IR (neat)** ν_{max} 3490, 3295, 2934, 2882, 1658, 1612, 1545, 1389, 1130, 837, 740, 705, 690 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{29}H_{32}N_3O_3NaCl$ $[M + Na]^+$ 528.2030, found 528.2029. **[α] $^{20}_D$** = -78 (*c* 0.5; $CHCl_3$).

c) Catalysts C_3 to C_7

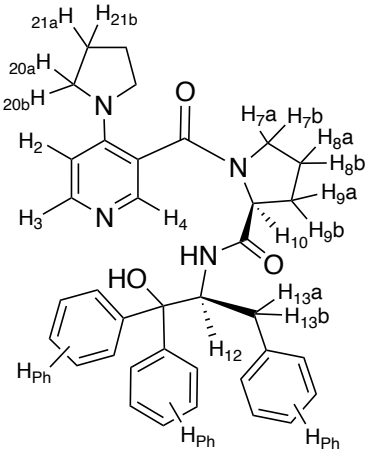
Compounds **C_3** to **C_7** are present as a mixture of three to four rotamers in slow exchange in DMSO-d_6. The presence of four rotameric forms (*vs* diastereoisomeric forms) of compounds **C_6** at 383K in DMSO-d_6 is unambiguously highlighted by the presence in the 2D NOESY spectrum of cross peaks of the same sign as the diagonal peaks.



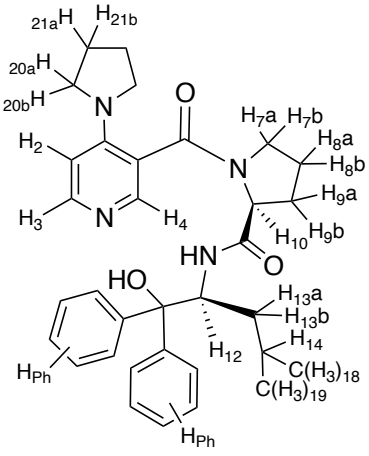
Catalyst **C_3** (0.253 g, 78%) was obtained after column chromatography (CH_2Cl_2/MeOH 93:7) as a white solid. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.09 – 8.03 (m, H_3) *Rot1-Rot2-Rot3*; 7.99 – 7.94 (m, H_4) *Rot1-Rot2-Rot3*; 7.75 – 6.85 (m, H_{Ph}, NH) *Rot1-Rot2-Rot3*; 6.61 – 6.48 (m, H_2) *Rot1-Rot2-Rot3*; 4.60 – 4.09 (m, H_{10}) *Rot1-Rot2-Rot3*; 3.75 – 2.82 (m, 2H), (m, H_7, H_{13}, H_{20}) *Rot1-Rot2-Rot3*; 1.96 – 1.82, 1.73 – 1.61, 1.59 – 1.49, 1.42 – 1.15 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3*; 1.44 (bs, H_{13-14}), 1.38 (bs, H_{13-14}), 1.20 (bs, H_{13-14}), 1.14 (bs, H_{13-14}) *Rot1-Rot2-Rot3*. **^{13}C NMR (126 MHz, DMSO-d_6)** δ 171.8, 171.6, 167.3, 148.2, 147.3, 145.7, 144.8, 144.4, 127.9, 127.8, 127.7, 127.6, 126.4, 126.4, 125.9, 117.3, 108.0, 81.5, 78.6, 61.1, 60.7, 59.4, 48.6, 48.1, 48.0, 46.1, 40.1, 40.0, 39.95, 39.93, 39.8, 39.7, 39.6, 39.5, 39.44, 39.35, 39.2, 39.0, 30.3, 28.4, 26.6, 26.2, 24.5, 24.1, 23.4, 23.0, 21.6. **IR (neat)** ν_{max} 3207, 2972, 2877, 1615, 1589, 1416, 1378, 1198, 754, 701 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{31}H_{37}N_4O_3$ $[M + H]^+$ 513.2866, found 513.2870. **[α] $^{20}_D$** = -65 (*c* 0.5; $CHCl_3$)



Catalyst **C_4** (0.195 g, 90%) was obtained after column chromatography (CH_2Cl_2/MeOH 85:15) as a white solid. Ratio of rotamers *Rot1*/*Rot2*/*Rot3*/*Rot4*: 0.4/1/0.3/0.6. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.11 – 7.96 (m, H_3-H_4) *Rot1-Rot2-Rot3-Rot4*; 7.78 – 6.97 (m, H_{Ph}, NH) *Rot1-Rot2-Rot3-Rot4*; 6.59-6.50 (m, H_2), 6.44 (d, *J* = 6.5 Hz, , H_2) *Rot1-Rot2-Rot3-Rot4*; 5.56 (s, OH), 5.54 (s, OH), 5.35 (s, OH), 5.35 (s, OH) *Rot1-Rot2-Rot3-Rot4*; 4.94 (d, *J* = 10.5 Hz, H_{12}), 4.90 (d, *J* = 10.5 Hz, H_{12}), 4.76 (d, *J* = 10.5 Hz, H_{12}), 4.72 (d, *J* = 10.5 Hz, H_{12}) *Rot1-Rot2-Rot3-Rot4*; 4.26 (dd, *J* = 8.0, 2.5 Hz, H_{10}), 4.20 (d, *J* = 7.0 Hz, H_{10}), 4.16 (dd, *J* = 7.0, 5.0 Hz, H_{10}), 3.95 (d, *J* = 8.5 Hz, H_{10}) *Rot1-Rot2-Rot3-Rot4*; 3.69 – 2.96 (m, H_7, H_{20}) *Rot1-Rot2-Rot3-Rot4*; 1.99 – 1.17 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3-Rot4*; 0.95-0.15 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3-Rot4*; 0.78 (s, H_{13}), 0.51 (s, H_{13}), 0.41 (s, H_{13}) *Rot1-Rot2-Rot3-Rot4* **^{13}C NMR (151 MHz, DMSO-d_6)** δ 170.5, 170.2, 169.9, 169.8, 167.6, 167.2, 166.6, 166.5, 149.8, 149.7, 149.5, 149.4, 149.0, 148.8, 148.5, 148.3, 148.1, 147.7, 147.1, 146.9, 146.8, 146.7, 127.7, 127.6, 127.5, 125.9, 125.8, 125.3, 125.2, 124.7, 124.4, 118.0, 117.7, 117.3, 115.9, 108.8, 108.6, 108.3, 81.7, 81.6, 81.5, 61.5, 60.3, 60.0, 59.6, 59.3, 49.3, 49.0, 48.7, 48.6, 48.5, 47.1, 46.2, 44.8, 39.9, 39.8, 39.7, 39.5, 39.4, 39.2, 39.1, 37.3, 36.7, 36.6, 31.4, 30.4, 30.0, 29.60, 29.57, 29.4, 29.2, 28.5, 28.4, 25.2, 25.1, 24.2, 23.9, 23.7, 22.3, 22.2, 22.0. **IR (neat)** ν_{max} 3345, 2953, 1672, 1630, 1595, 1171, 1065, 807, 748, 706, 697 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{33}H_{41}N_4O_3$ $[M + H]^+$ 541.3179, found 541.3180. **[α] $^{20}_D$** = -113 (*c* 0.5; $CHCl_3$).

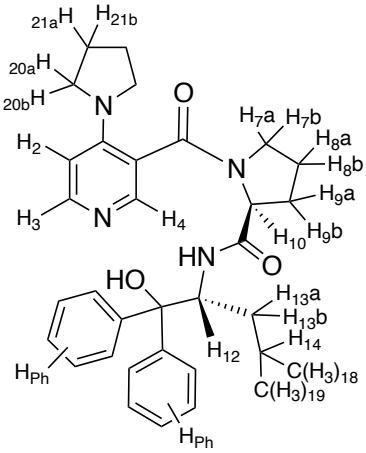


Catalyst **C_5** (0.154 g, 72%) was obtained after column chromatography (CH_2Cl_2/MeOH 95:5) as a white solid. Ratio of 3 rotamers undetermined. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.13 – 8.00 (m, H_3) *Rot1-Rot2-Rot3;* 8.00 – 7.85 (m, H_4) *Rot1-Rot2-Rot3*; 7.66 – 7.00 (m, H_{Ph}, NH) *Rot1-Rot2-Rot3*; 6.62 – 6.48 (m, H_2) *Rot1-Rot2-Rot3*; 5.89 (bs, 0H), 5.80 (bs, 0H) *Rot1-Rot2-Rot3*; 5.19 – 4.93 (m, H_{12}) *Rot1-Rot2-Rot3*; 4.49 (d, *J* = 7.5 Hz, H_{10}), 4.37 – 4.29 (m, H_{10}); 4.10 (d, *J* = 7.5 Hz, H_{10}) *Rot1-Rot2-Rot3*; 3.28 – 2.67 (m, H_7, H_{13}, H_{20}) *Rot1-Rot2-Rot3*; 2.09 – 0.78 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3* **^{13}C NMR (126 MHz, DMSO-d_6)** δ 171.2, 170.6, 170.3, 167.9, 166.3, 165.9, 148.9, 148.6, 148.3, 147.6, 146.7, 146.6, 146.4, 146.0, 139.6, 129.0, 128.9, 128.7, 128.4, 128.2, 128.1, 127.8, 127.7, 127.5, 126.4, 126.0, 125.6, 125.4, 117.4, 108.4, 80.9, 80.42, 80.36, 61.2, 59.2, 56.3, 48.9, 48.8, 48.6, 48.5, 48.4, 41.5, 36.6, 35.9, 28.9, 28.8, 25.2, 25.1, 23.7, 23.6, 22.1, 17.2. **IR (neat)** ν_{max} 2952, 2870, 1635, 1590, 1507, 1408, 1062, 746, 702, 465 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{36}H_{39}N_4O_3$ $[M + H]^+$ 575.3022, found 575.3026. **[α] $^{20}_D$** = -35 (*c* 0.25; $CHCl_3$)



Catalyst **C_6** was obtained after column chromatography (CH_2Cl_2/MeOH 85:15) as a white solid (0.195 g, 91%). Ratio of rotamers *Rot1*/*Rot2*/*Rot3*/*Rot4*: 3/2.7/1/1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.08 (d, *J* = 5.5 Hz, H_3), 8.05 (d, *J* = 5.5 Hz, H_3), 8.03 – 7.98 (m, H_3-H_4) *Rot1-Rot2-Rot3-Rot4***;** 7.63 – 7.02 (m, H_{Ph}, NH) *Rot1-Rot2-Rot3-Rot4***;** 6.58 – 6.53 (m, H_2), 6.51 (d, *J* = 6.0 Hz, H_2), 6.48 (d, *J* = 6.0 Hz, H_2) *Rot1-Rot2-Rot3-Rot4***;** 5.77 (s, OH), 5.55 (s, OH), 5.47 (s, OH), 5.43 (s, OH) *Rot1-Rot2-Rot3-Rot4***;** 5.06 (t, *J* = 10.5 Hz, H_{12}), 5.01 (t, *J* = 10.5 Hz, H_{12}), 4.92 (t, *J* = 10.5 Hz, H_{12})**;** 4.85 (t, *J* = 10.5 Hz, H_{12}) *Rot1-Rot2-Rot3-Rot4***;** 4.42 (dd, *J* = 8.0, 3.5 Hz, H_{10}), 4.26 – 4.15 (m, H_{10}), 4.04 (d, *J* = 8.0 Hz, H_{10}) *Rot1-Rot2-Rot3-Rot4***;** 3.58 – 2.97 (m, H_7, H_{20}) *Rot1-Rot2-Rot3-Rot4***;** 2.04 – 1.10 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3-Rot4***;** 1.0-0.46 (m, H_8, H_9, H_{21}) *Rot1-Rot2-Rot3-Rot4***;** 0.85 (d, *J* = 6.0 Hz, $H_{18\text{-}19}$), 0.82 (d, *J* = 6.0 Hz, $H_{18\text{-}19}$), 0.76 (d, *J* = 6.0 Hz, $H_{18\text{-}19}$), 0.66 (d, *J* = 6.0 Hz, $H_{18\text{-}19}$), 0.54 (d, *J* = 6.0 Hz, $H_{18\text{-}19}$) *Rot1-Rot2-Rot3-Rot4.***^{13}C NMR (151 MHz, DMSO-d_6)** δ 171.0, 170.6, 167.7, 167.4, 167.0, 166.6, 166.5, 149.1, 148.8, 148.6, 148.4, 148.14, 148.09, 147.9, 147.8, 147.4, 147.2, 147.1, 146.9, 146.8, 146.11, 146.06, 145.9, 131.6, 128.7, 128.13, 128.11, 127.54, 127.50, 126.3, 126.2, 126.1, 126.0, 125.5, 125.4, 125.2, 125.1, 117.9, 117.6, 117.3, 115.9, 108.5, 108.4, 108.2, 80.32, 80.27, 80.20, 61.0, 60.3, 59.4, 59.3, 53.0, 52.4, 52.19, 52.15, 49.4, 49.2, 49.0, 48.7, 48.5, 48.4, 47.4, 46.2, 40.1, 38.8, 38.6, 31.5, 30.7, 29.0, 28.9, 25.3, 25.2, 25.1, 24.5, 24.4, 24.32, 24.28, 24.1, 23.9, 23.8, 23.6, 23.3, 22.3, 22.2, 21.8, 21.6, 21.5, 21.3. **IR (neat)** ν_{max} 3314, 2956, 2870, 1682, 1604, 1585, 1429, 1246, 1062, 974,

807, 747, 709, 637 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{33}H_{41}N_4O_3$ $[M + H]^+$ 541.3179, found 541.3177. **[α] $^{20}_D$** = -70 (*c* 0.5; $CHCl_3$).



Catalyst **C_7** (0.130 g, 40%) was obtained after column chromatography (CH_2Cl_2/MeOH 85:15) as a white solid. Ratio of rotamers *Rot1*/*Rot2/Rot3*: 1/0.6/0.4. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.16–7.86 (m, H_3-H_4) *Rot1-Rot2-Rot3*; 7.65 – 6.91 (m, H_{Ph}, NH) *Rot1-Rot2-Rot3*; 6.57 (d, *J* = 6.0 Hz, H_2), 6.53 (d, *J* = 6.0 Hz, H_2) *Rot1-Rot2-Rot3*; 6.24 (bs, OH), 6.07 (bs, OH), 6.02 (bs, OH) *Rot1-Rot2-Rot3*; 5.05 (s, H_{12}), 4.99 (s, H_{12}), 4.82 (s, H_{12}) *Rot1-Rot2-Rot3*; 4.34 – 4.18 (m, H_{10}), 4.00 (d, *J* = 8.5 Hz, H_{10}) *Rot1-Rot2-Rot3*; 3.59 – 2.90 (m, H_7, H_{20}), 2.11 – 0.53 (m, H_8, H_9, H_{13}, H_{18}, H_{19}, H_{21}) *Rot1-Rot2-Rot3*.**^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 172.6, 171.0, 169.4, 169.0, 167.7, 149.7, 149.6, 148.8, 148.6, 148.5, 148.2, 147.9, 147.4, 146.5, 146.4, 128.5, 128.3, 127.9, 126.7, 126.5, 126.2, 125.9, 125.6, 125.5, 118.0, 117.8, 108.9, 80.5, 80.5, 62.3, 60.8, 54.0, 53.2, 49.3, 49.0, 48.8, 46.6, , 30.8, 29.3, 25.5, 24.72, 24.67 24.3, 24.2, 24.1, 22.0, 21.8, 21.1. **IR (neat)** ν_{max} 3350, 2958, 2927, 2872, 1677, 1632, 1513, 1378, 1064, 749, 699 cm^{-1}. **ESI-HRMS** *m/z* calcd for $C_{33}H_{41}N_4O_3$ $[M + H]^+$ 541.3179, found 541.3174. **[α] $^{20}_D$** = -78 (*c* 0.5; $CHCl_3$).

6) References

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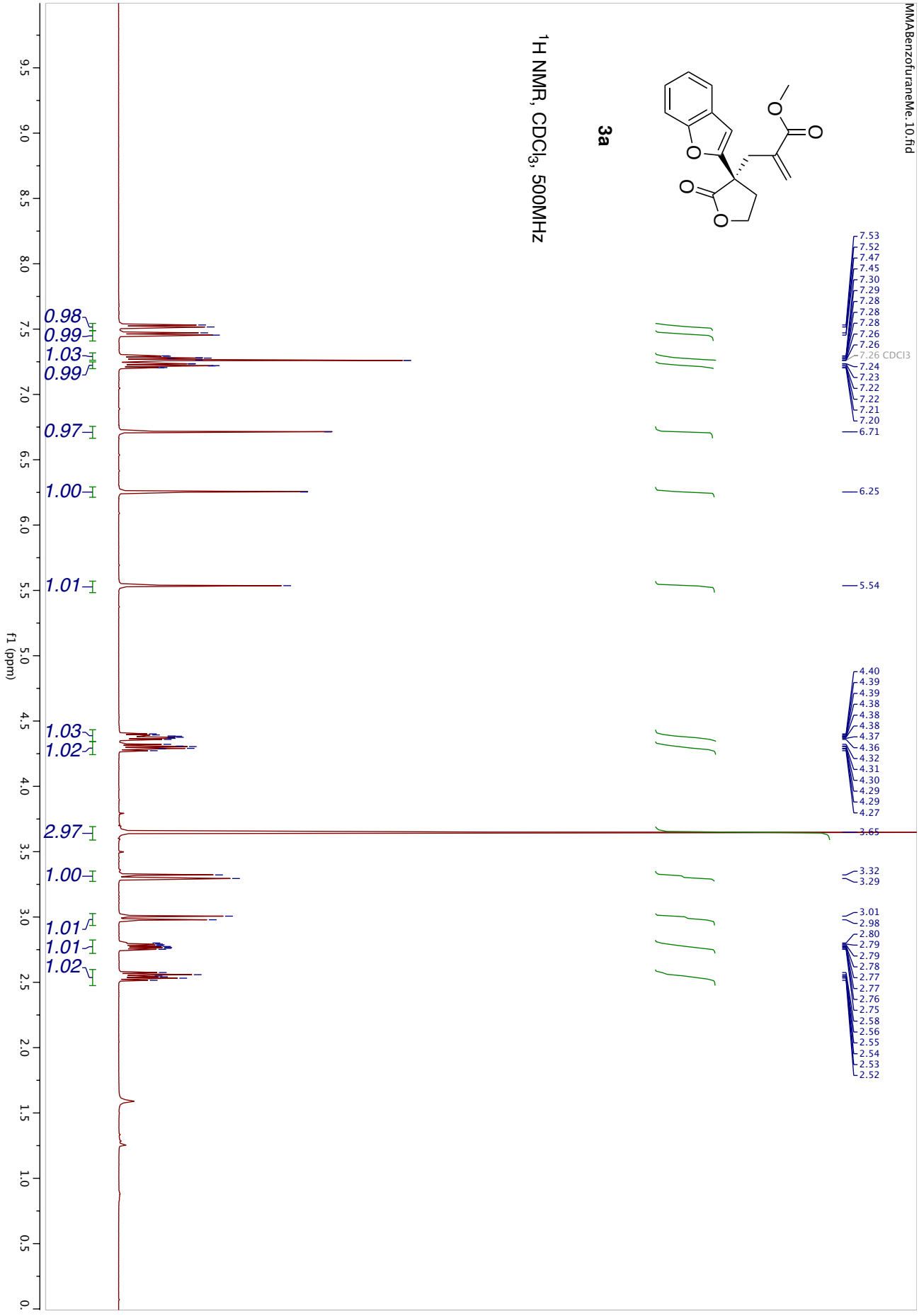
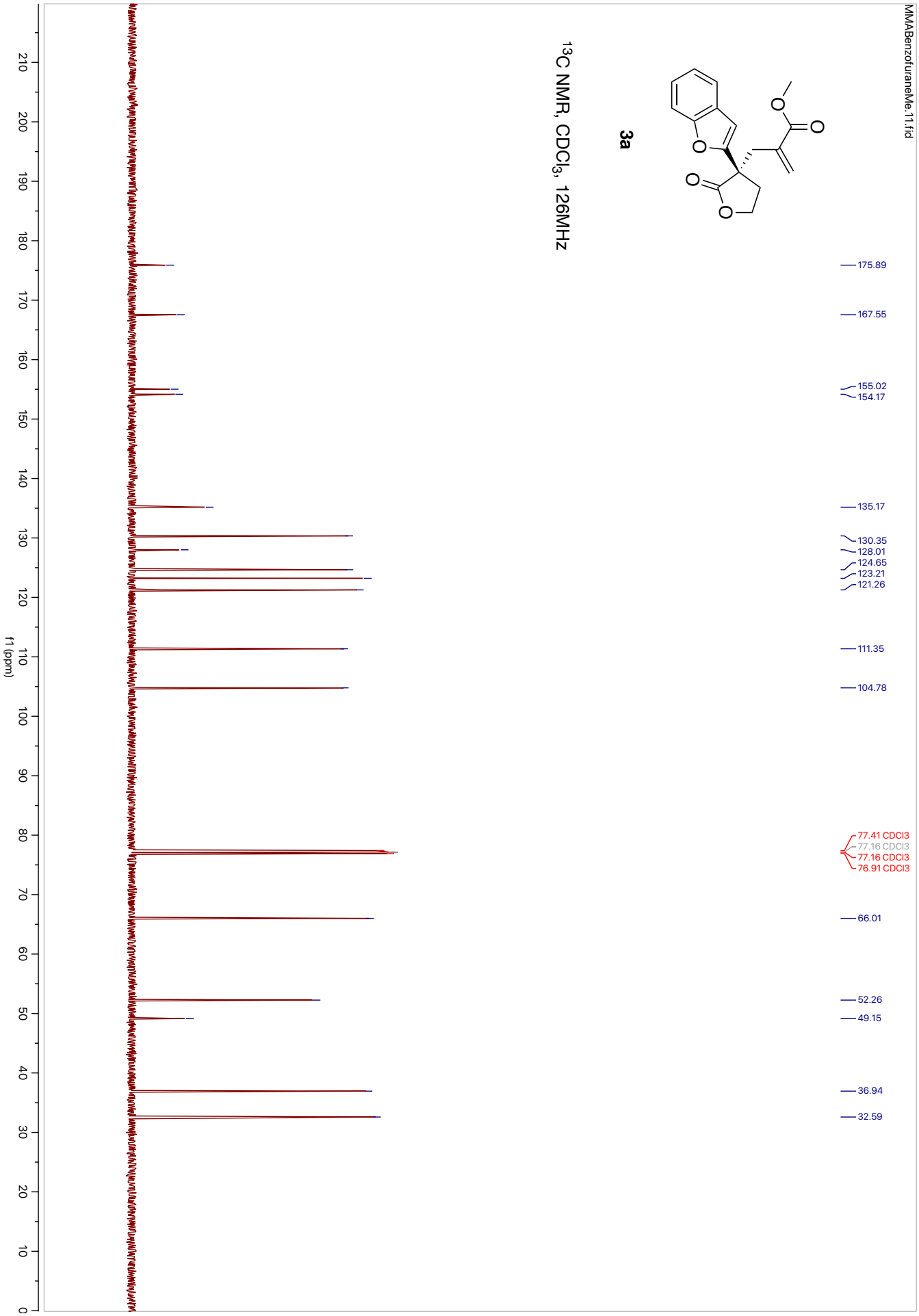
7) ^{1}H & ^{13}C NMR spectra

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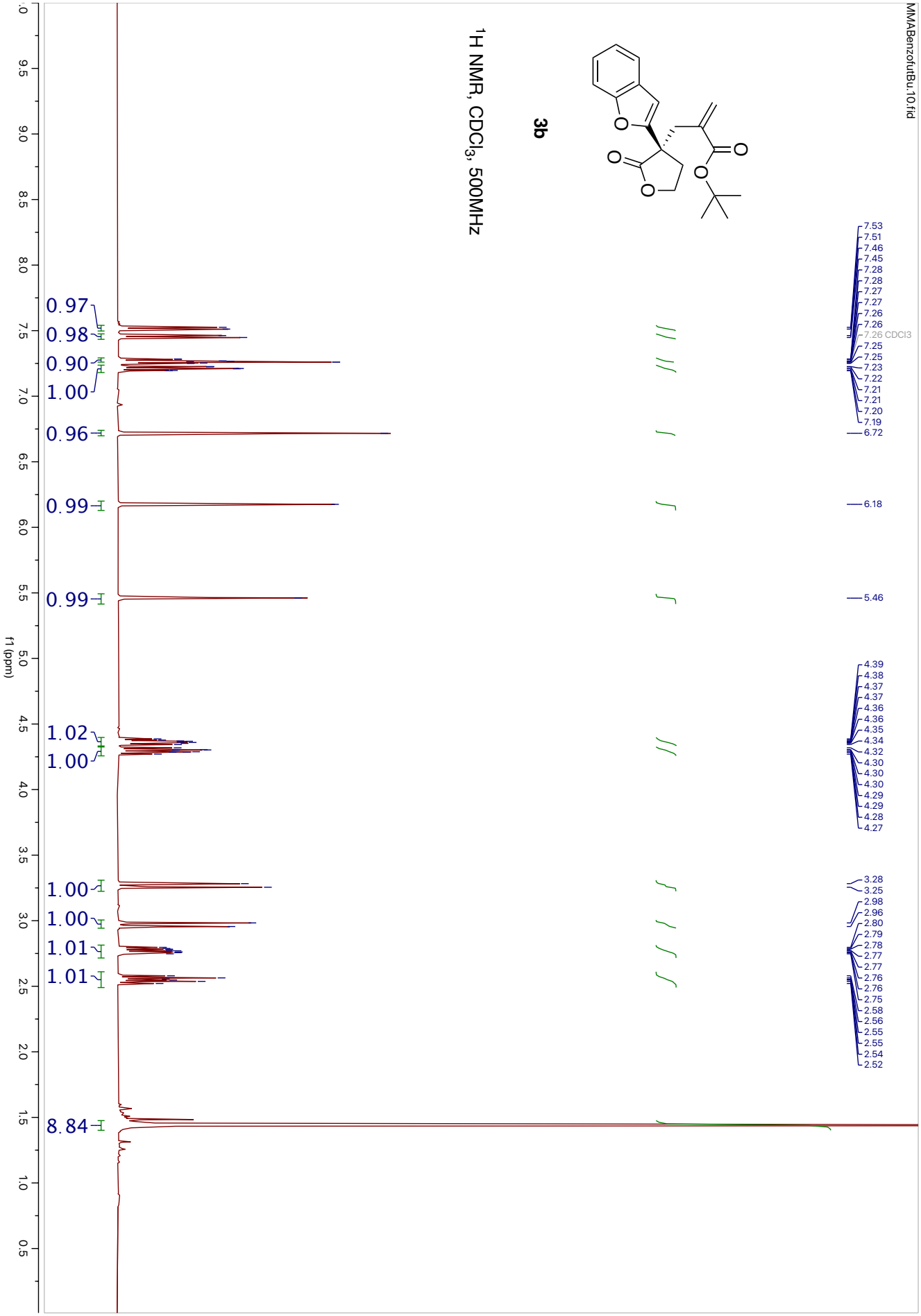
3a
175.89
167.55
155.02
154.17
135.17
130.35
128.01
124.65
123.21
121.26
111.35
104.78
77.41 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
66.01
52.26
49.15
36.94
32.59
f1 (ppm)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3b
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0.98
0.90
1.00
0.96
0.99
0.99
1.02
1.00
1.00
1.00
1.01
1.01
8.84
7.53
7.51
7.46
7.45
7.28
7.28
7.27
7.27
7.26
7.26
7.26 CDCl3
7.25
7.25
7.23
7.22
7.21
7.21
7.20
7.19
6.72
6.18
5.46
4.39
4.38
4.37
4.37
4.36
4.36
4.35
4.34
4.32
4.30
4.30
4.30
4.29
4.29
4.28
4.27
3.28
3.25
2.98
2.96
2.80
2.79
2.78
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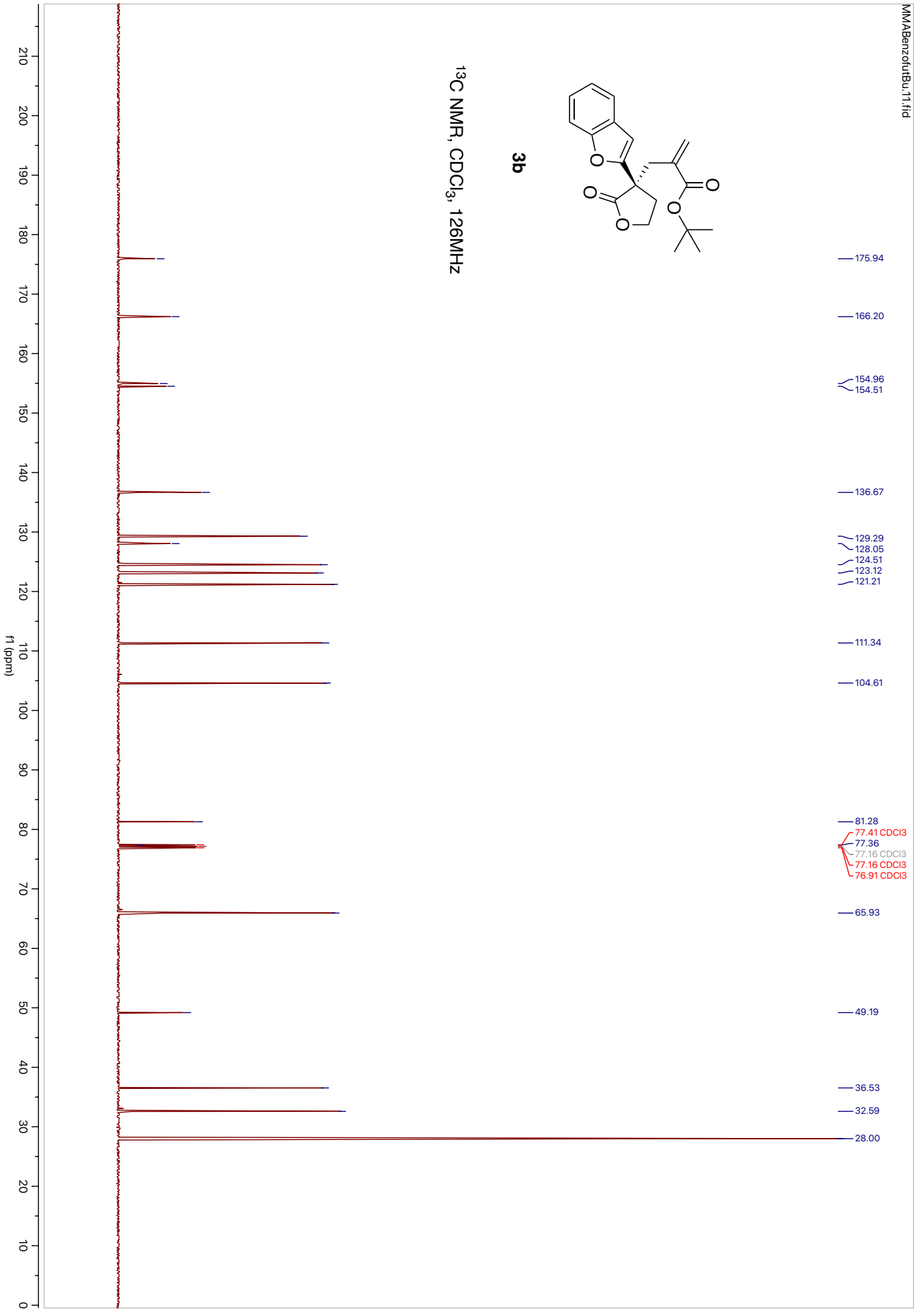
2.55
2.54
2.52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^{13}C NMR, $CDCl_3$, 126MHz
3b
f1 (ppm)
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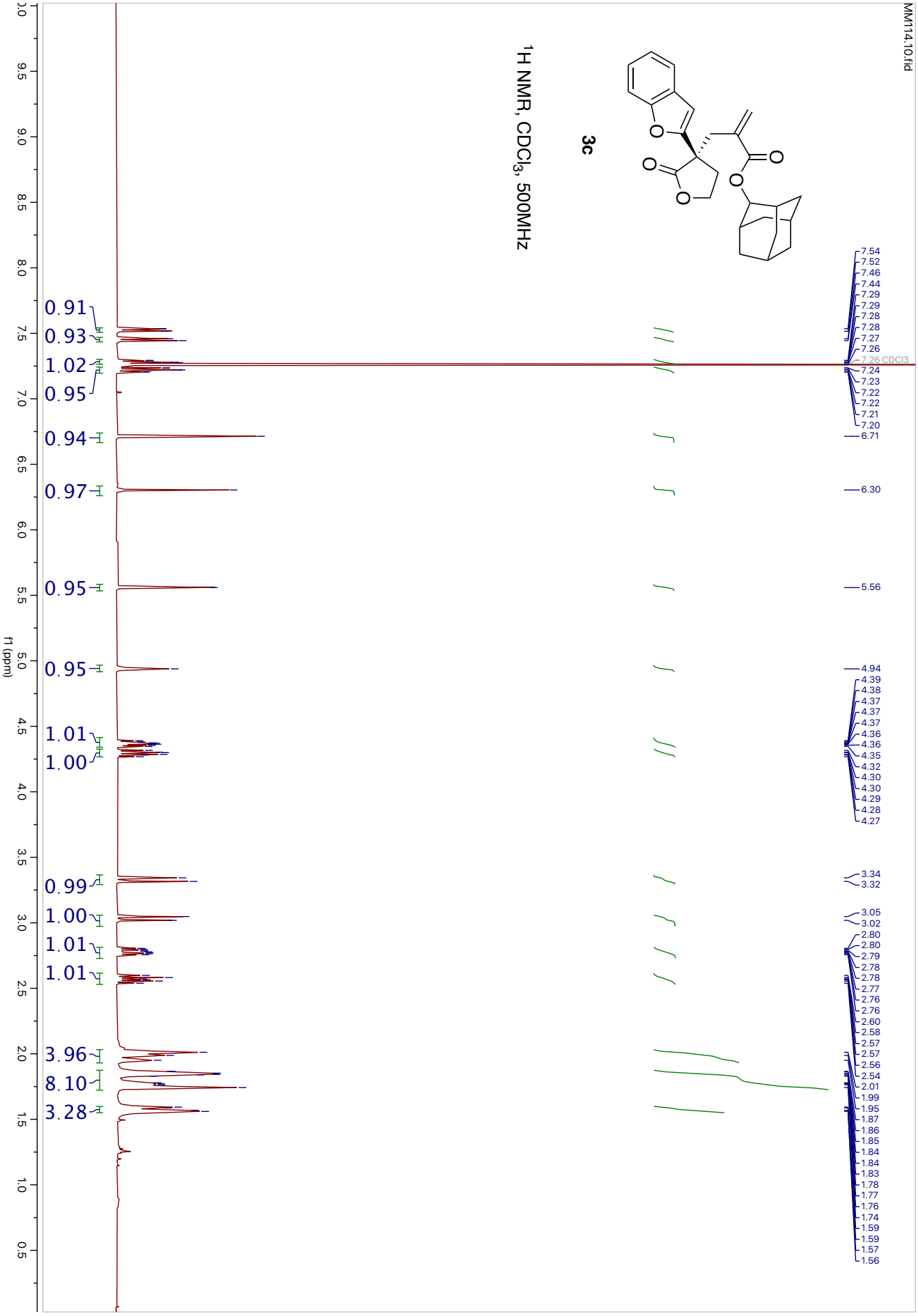
166.20
154.96
154.51
136.67
129.29
128.05
124.51
123.12
121.21
111.34
104.61
81.28
77.41 CDCl3
77.36
77.16 CDCl3
76.91 CDCl3
65.93
49.19
36.53
32.59
28.00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3c
f1 (ppm)
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0.93
1.02
0.95
0.94
0.97
0.95
0.95
1.01
1.00
0.99
1.00
1.01
1.01
3.96
8.10
3.28
7.54
7.52
7.46
7.44
7.29
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
7.24
7.23
7.22
7.22
7.21
7.20
6.71
6.30
5.56
4.94
4.39
4.38
4.37
4.37
4.37
4.36
4.36
4.35
4.32
4.30
4.30
4.29
4.28
4.27
3.34
3.32
3.05
3.02
2.80
2.80
2.79
2.78
2.78
2.77
2.76
2.76
2.60
2.58
2.57
2.57
2.56
2.54
2.01
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1.95
1.87
1.86
1.85
1.84
1.84
1.83
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1.77
1.76
1.74
1.59
1.59
1.57
1.56

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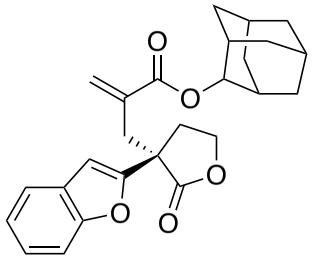
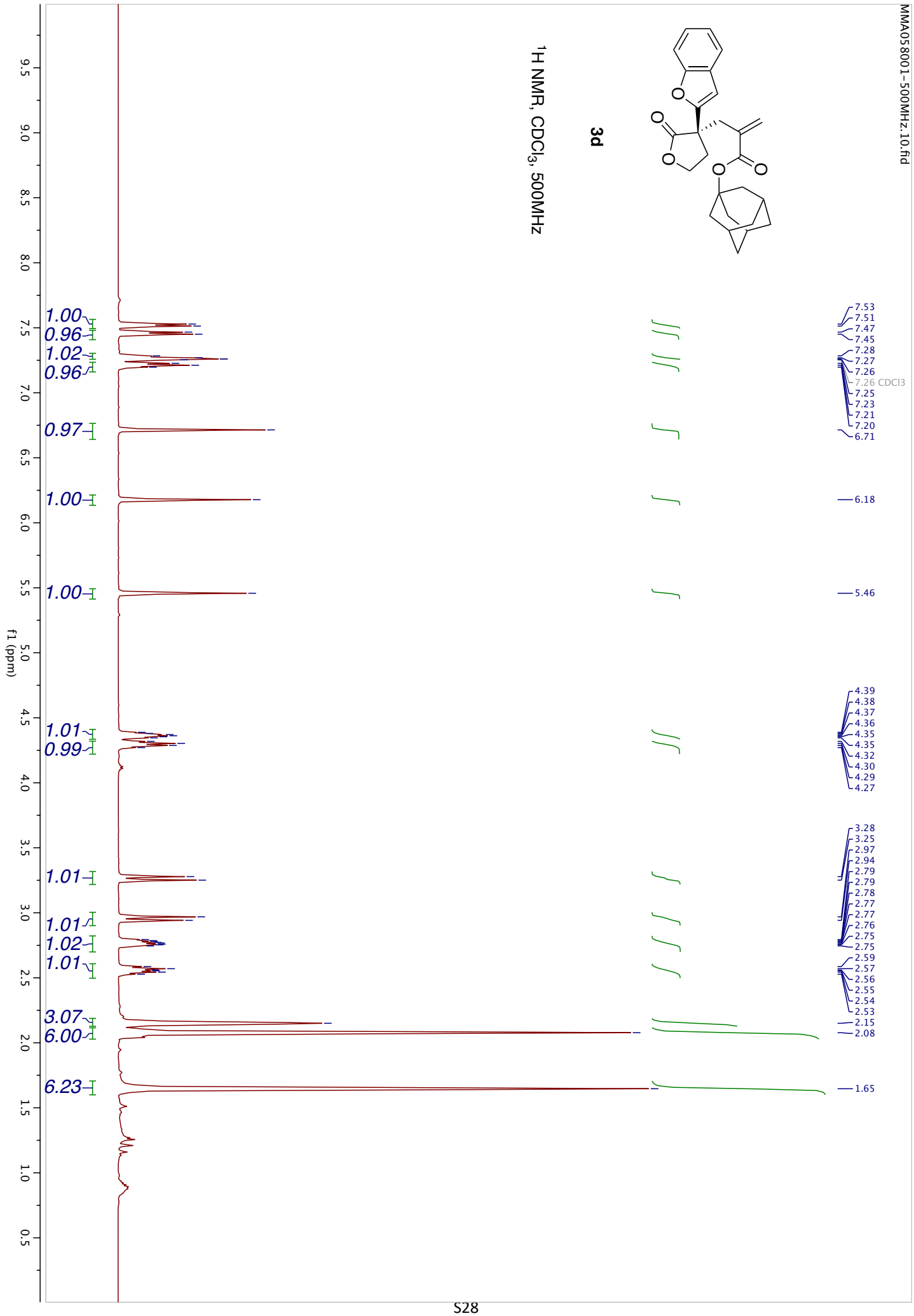


3c

^{13}C NMR, $CDCl_3$, 126MHz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3d
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f1 (ppm)
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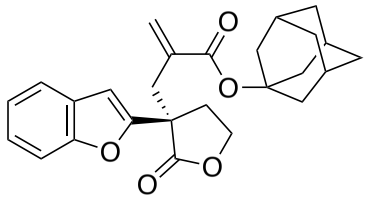
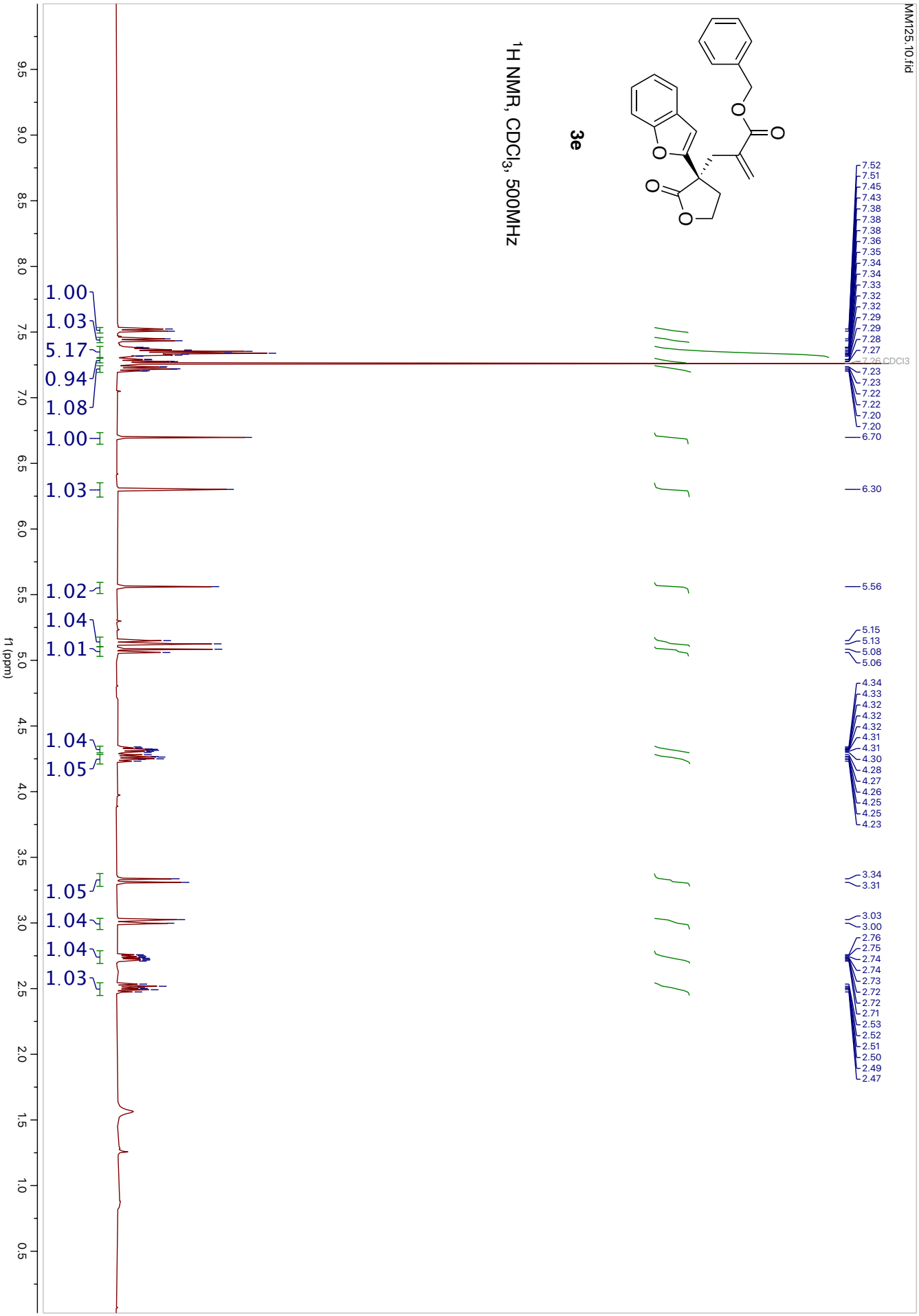
0.96
1.02
0.96
0.97
1.00
1.00
1.01
0.99
1.01
1.01
1.02
1.01
3.07
6.00
6.23
7.53
7.51
7.47
7.45
7.28
7.27
7.26
7.26 CDCl3
7.25
7.23
7.21
7.20
6.71
6.18
5.46
4.39
4.38
4.37
4.36
4.35
4.35
4.32
4.30
4.29
4.27
3.28
3.25
2.97
2.94
2.79
2.79
2.78
2.77
2.77
2.76
2.75
2.75
2.59
2.57
2.56
2.55
2.54
2.53
2.15
2.08
1.65

MMA058001-500MHz.21.fid



3d

^{13}C NMR, $CDCl_3$, 126MHz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3e
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1.08
1.00
1.03
1.02
1.04
1.01
1.04
1.05
1.05
1.04
1.04
1.03
7.52
7.51
7.45
7.43
7.38
7.38
7.38
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.29
7.29
7.28
7.27
7.26 CDCl3
7.23
7.23
7.22
7.22
7.20
7.20
6.70
6.30
5.56
5.15
5.13
5.08
5.06
4.34
4.33
4.32
4.32
4.32
4.31
4.31
4.30
4.28
4.27
4.26
4.25
4.25
4.23
3.34
3.31
3.03
3.00
2.76
2.75
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2.72
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2.52
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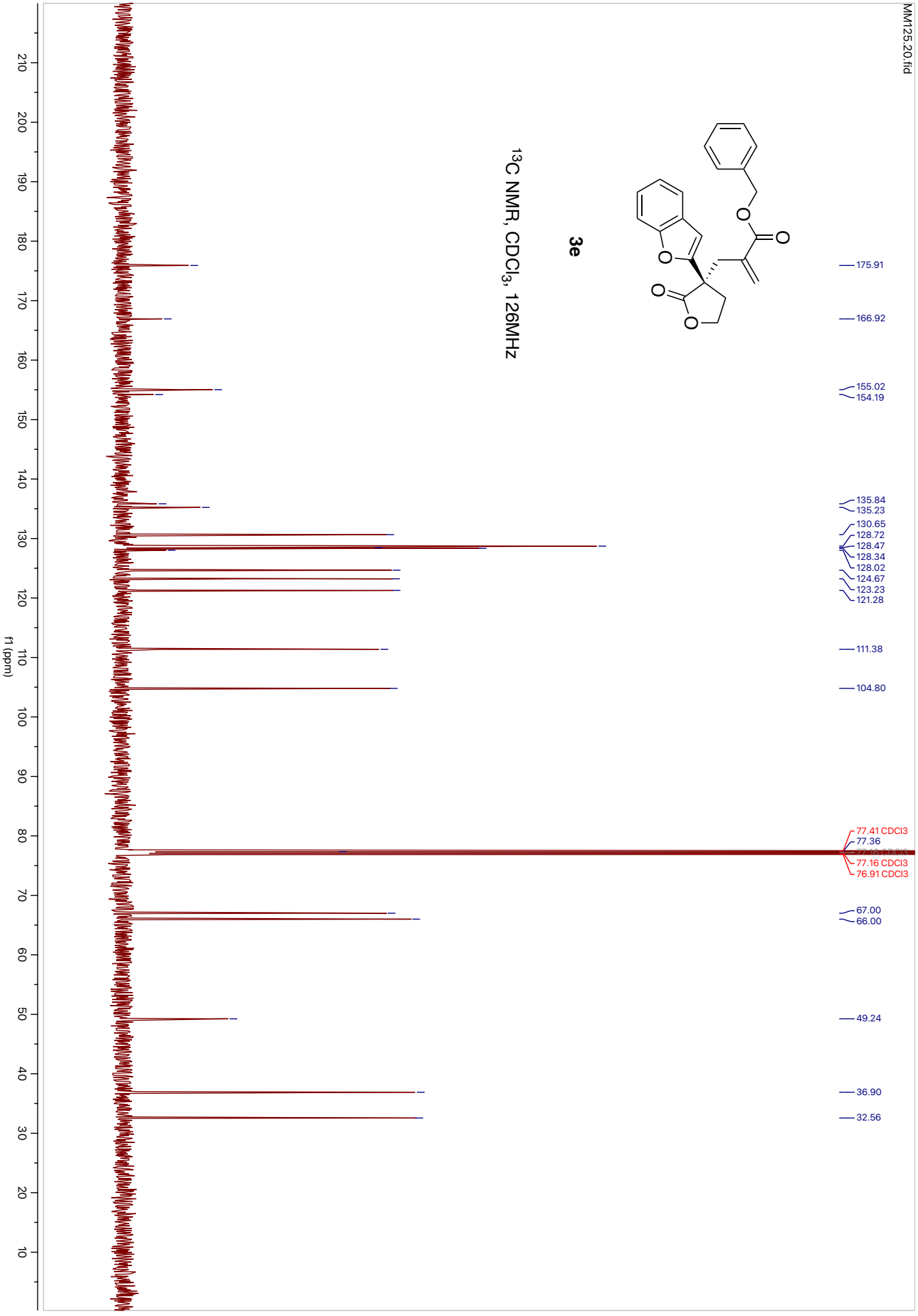
2.49
2.47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^{13}C NMR, $CDCl_3$, 126MHz
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135.23
130.65
128.72
128.47
128.34
128.02
124.67
123.23
121.28
111.38
104.80
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77.36
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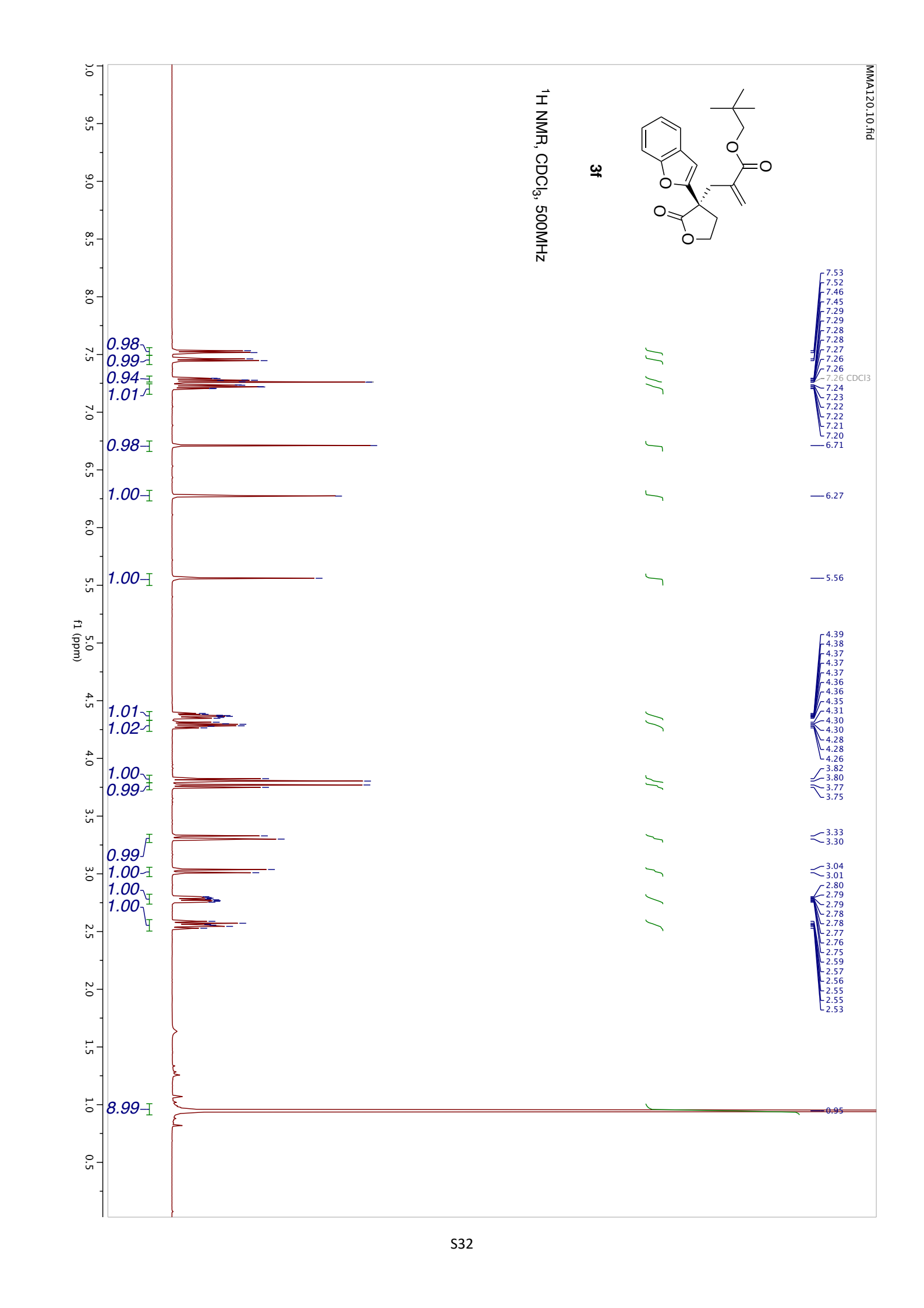
36.90
32.56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7.28
7.28
7.27
7.26
7.26
7.26 CDCl3
7.24
7.23
7.22
7.22
7.21
7.20
6.71
6.27
5.56
4.39
4.38
4.37
4.37
4.37
4.36
4.36
4.35
4.31
4.30
4.30
4.28
4.28
4.26
3.82
3.80
3.77
3.75
3.33
3.30
3.04
3.01
2.80
2.79
2.79
2.78
2.78
2.77
2.76
2.75
2.59
2.57
2.56
2.55
2.55
2.53
0.95
0.98
0.99
0.94
1.01
0.98
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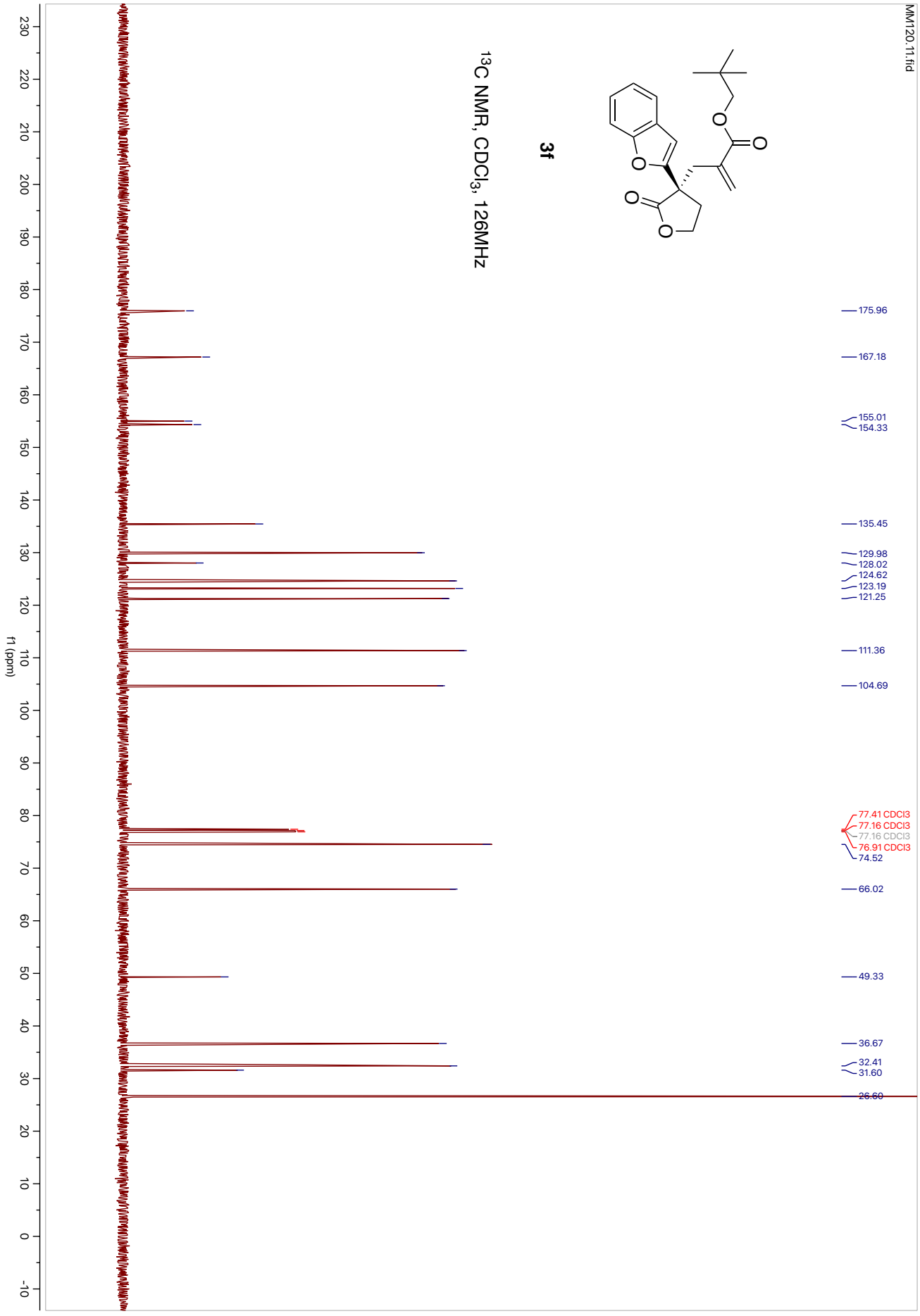
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3f
^{13}C NMR, $CDCl_3$, 126MHz
f1 (ppm)
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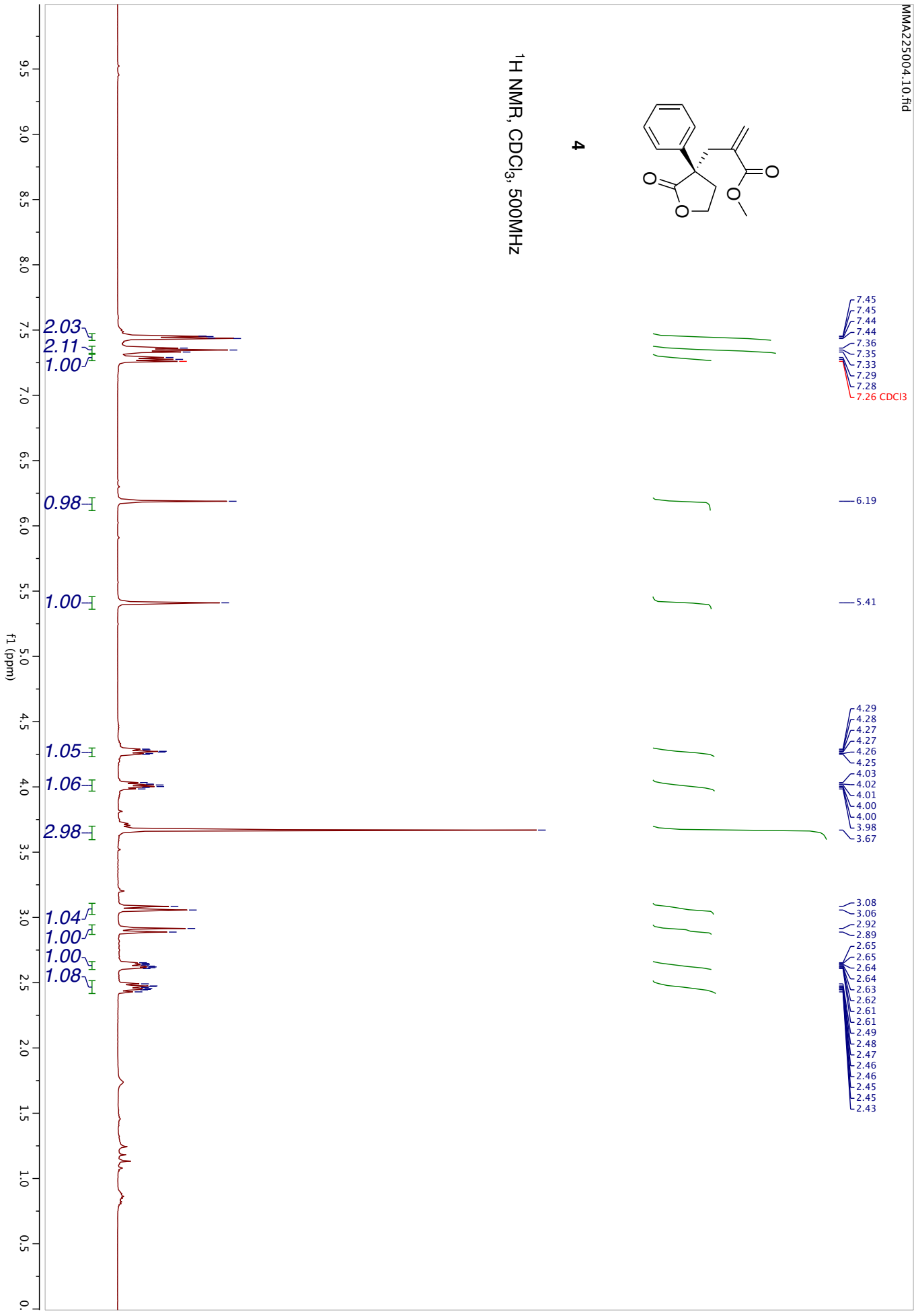
167.18
155.01
154.33
135.45
129.98
128.02
124.62
123.19
121.25
111.36
104.69
77.41 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
74.52
66.02
49.33
36.67
32.41
31.60
26.60


MMA225004.10.fid
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^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
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1.05
1.06
2.98
1.04
1.00
1.00
1.08
7.45
7.45
7.44
7.44
7.36
7.35
7.33
7.29
7.28
7.26 CDCl3
6.19
5.41
4.29
4.28
4.27
4.27
4.26
4.25
4.03
4.02
4.01
4.00
4.00
3.98
3.67
3.08
3.06
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2.89
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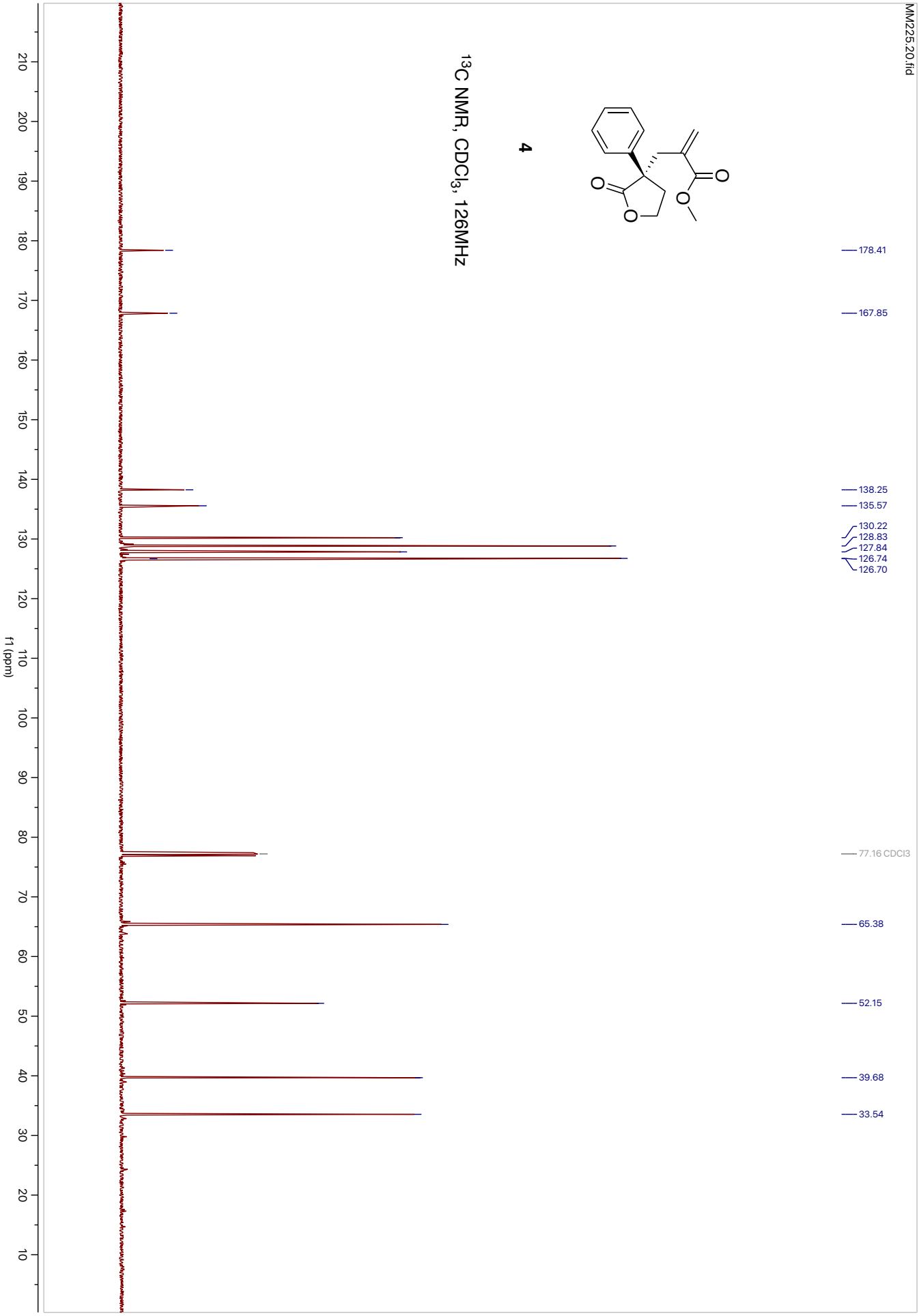
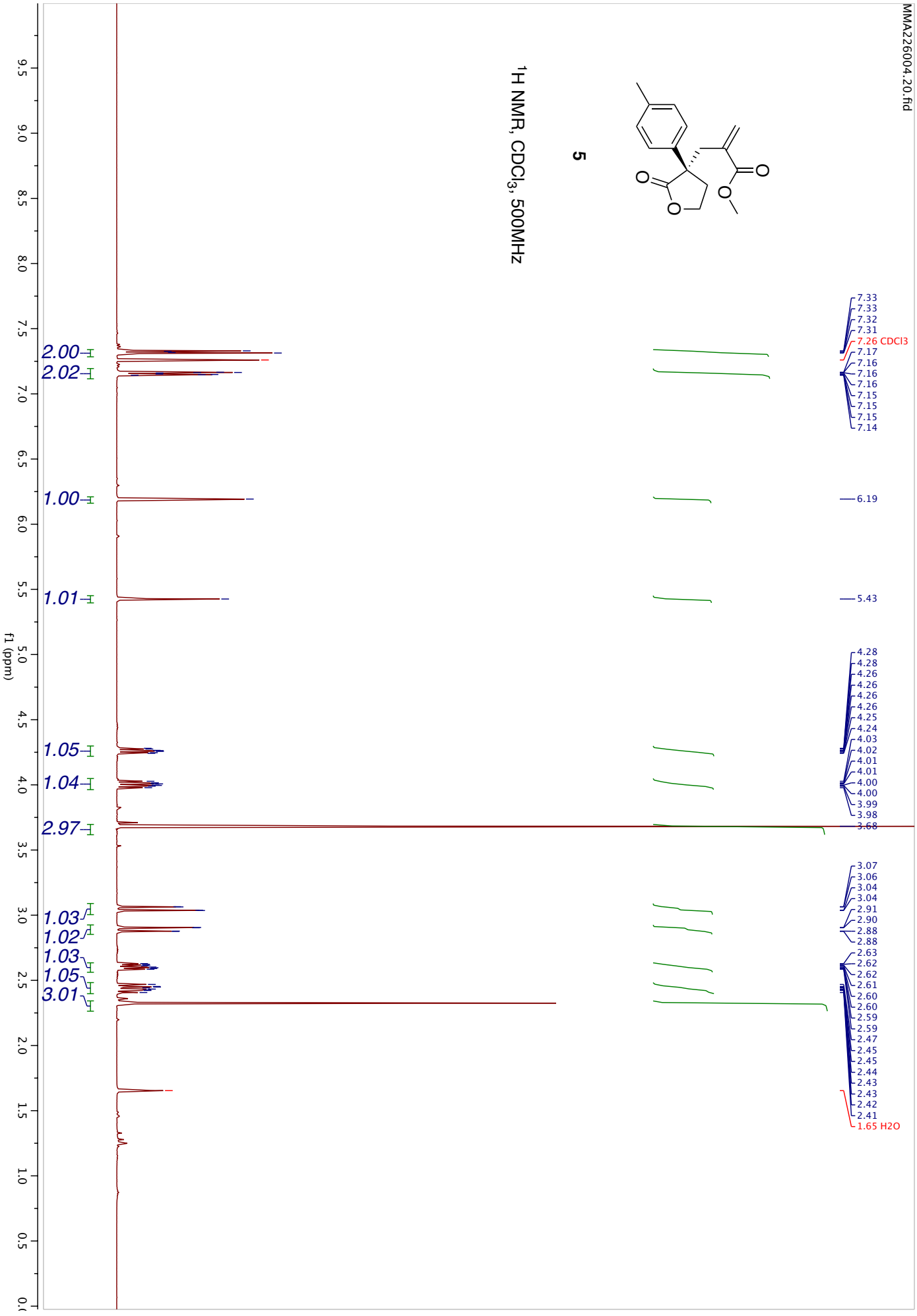
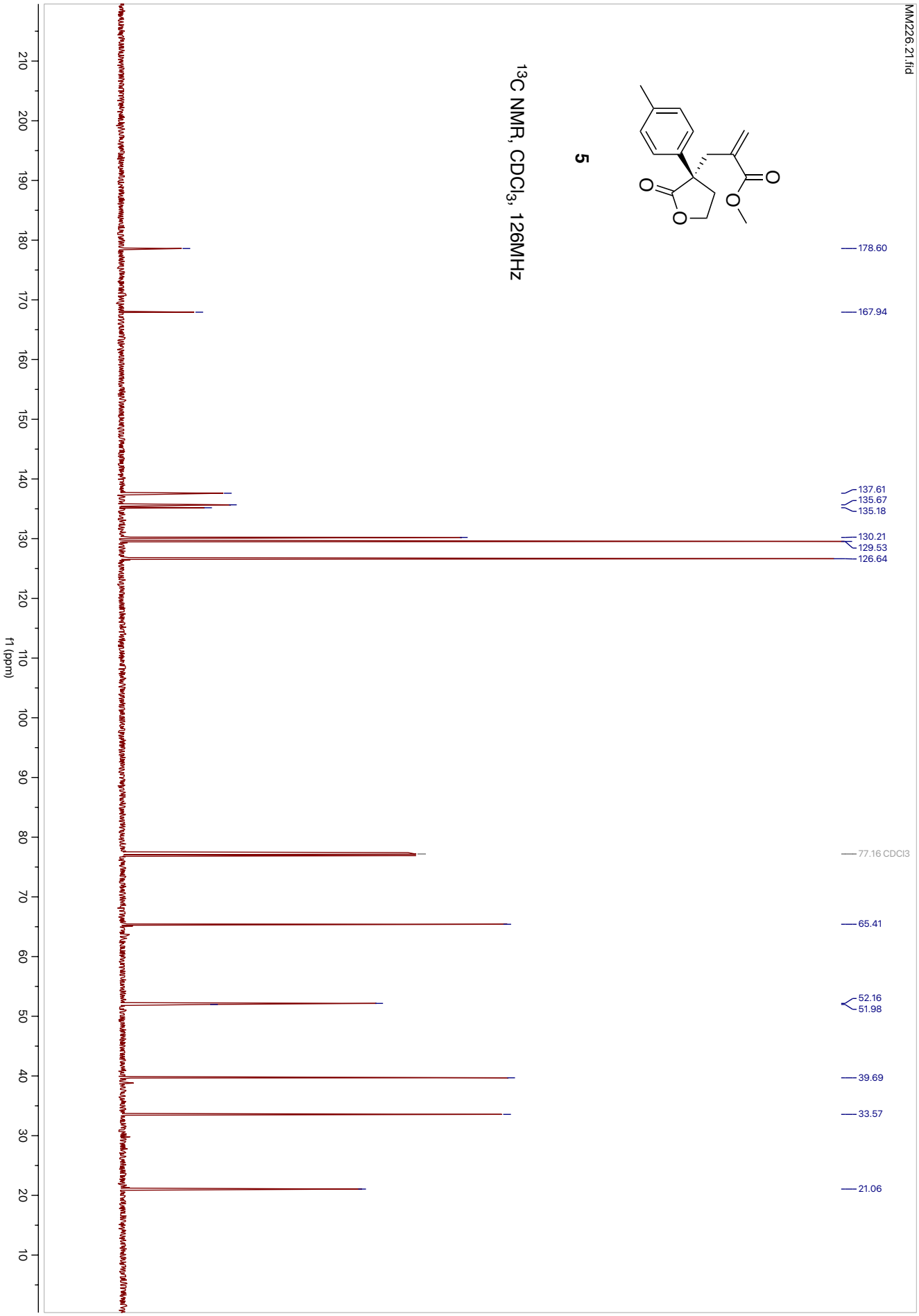
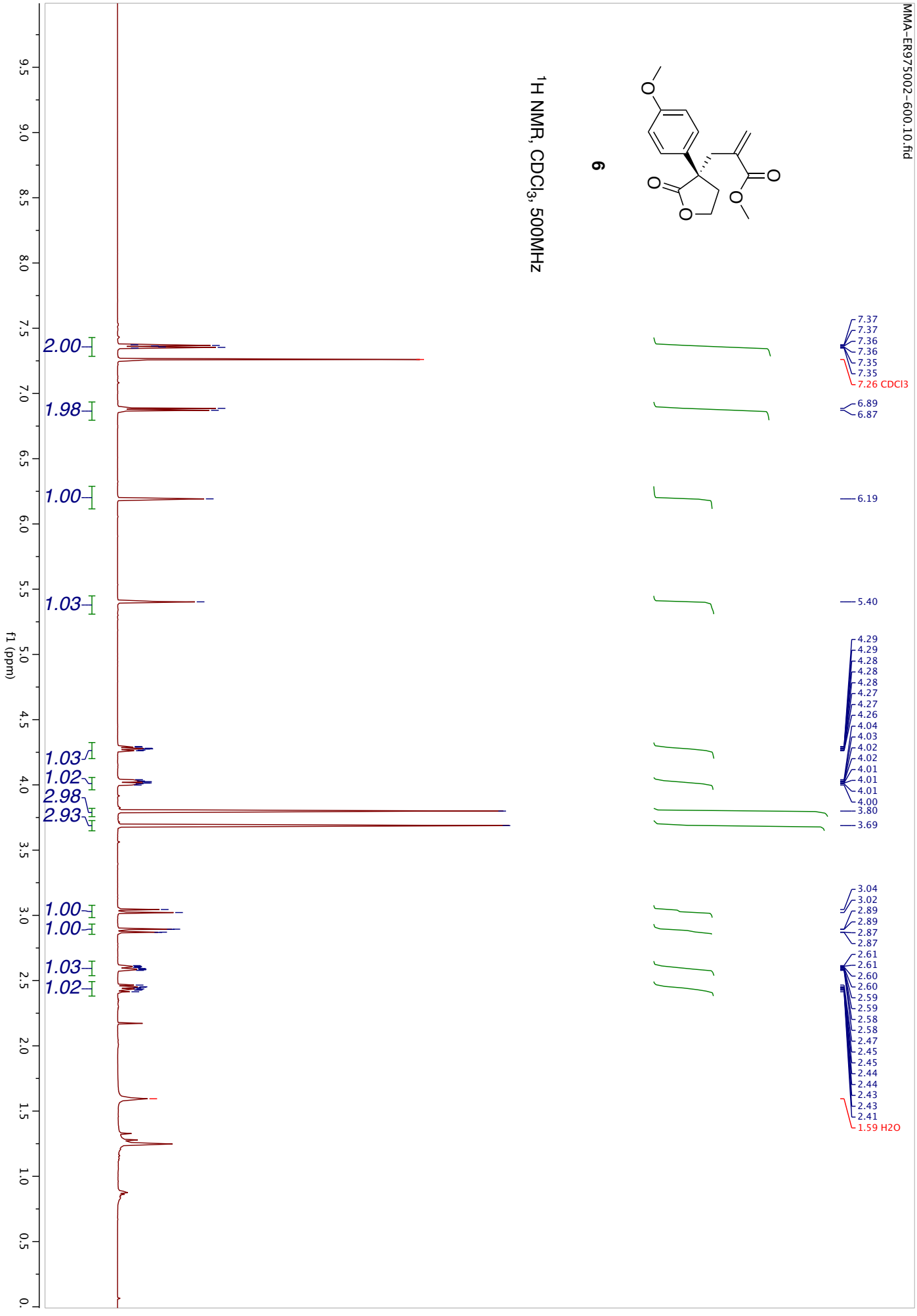
2.65
2.64
2.64
2.63
2.62
2.61
2.61
2.49
2.48
2.47
2.46
2.46
2.45
2.45
2.43


MM225.20.fid
4
^{13}C NMR, $CDCl_3$, 126MHz
178.41
167.85
138.25
135.57
130.22
128.83
127.84
126.74
126.70
77.16 CDCl3
65.38
52.15
39.68
33.54
f1 (ppm)


MMA226004-20.fid
^{1}H NMR, $CDCl_3$, 500MHz
5
f1 (ppm)
2.00
2.02
1.00
1.01
1.05
1.04
2.97
1.03
1.02
1.03
1.05
3.01
7.26 CDCl3
1.65 H2O


MM226.21.fid
^{13}C NMR, $CDCl_3$, 126MHz
5
178.60
167.94
137.61
135.67
135.18
130.21
129.53
126.64
77.16 CDCl3
65.41
52.16
51.98
39.69
33.57
21.06
f1 (ppm)


MMA-ER975002-600.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
6
f1 (ppm)
2.00
1.98
1.00
1.03
1.03
1.02
2.98
2.93
1.00
1.00
1.03
1.02
7.37
7.37
7.36
7.36
7.35
7.35
7.26 CDCl3
6.89
6.87
6.19
5.40
4.29
4.29
4.28
4.28
4.28
4.27
4.27
4.26
4.04
4.03
4.02
4.02
4.01
4.01
4.01
4.00
3.80
3.69
3.04
3.02
2.89
2.89
2.87
2.87
2.61
2.61
2.60
2.60
2.59
2.59
2.58
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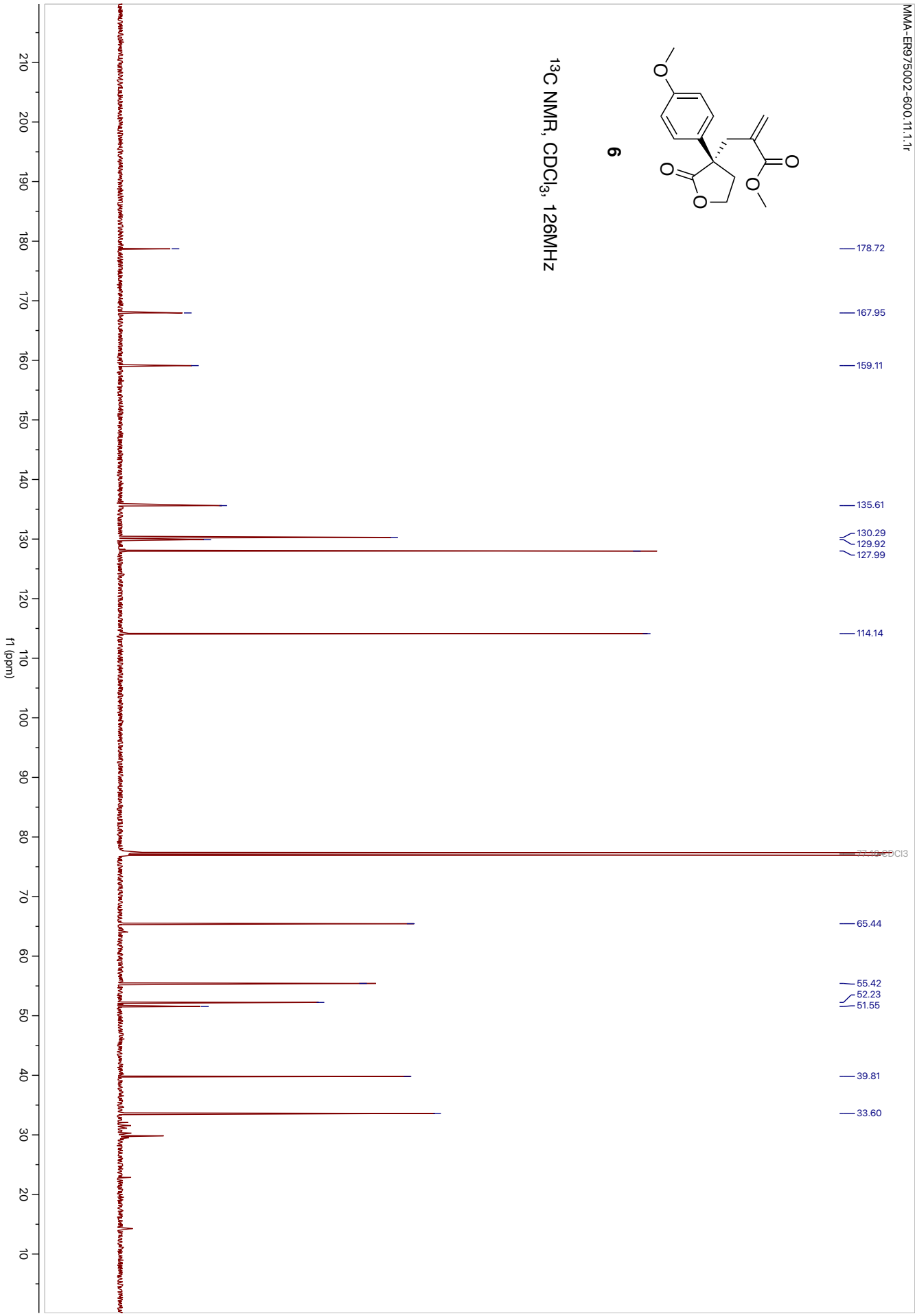
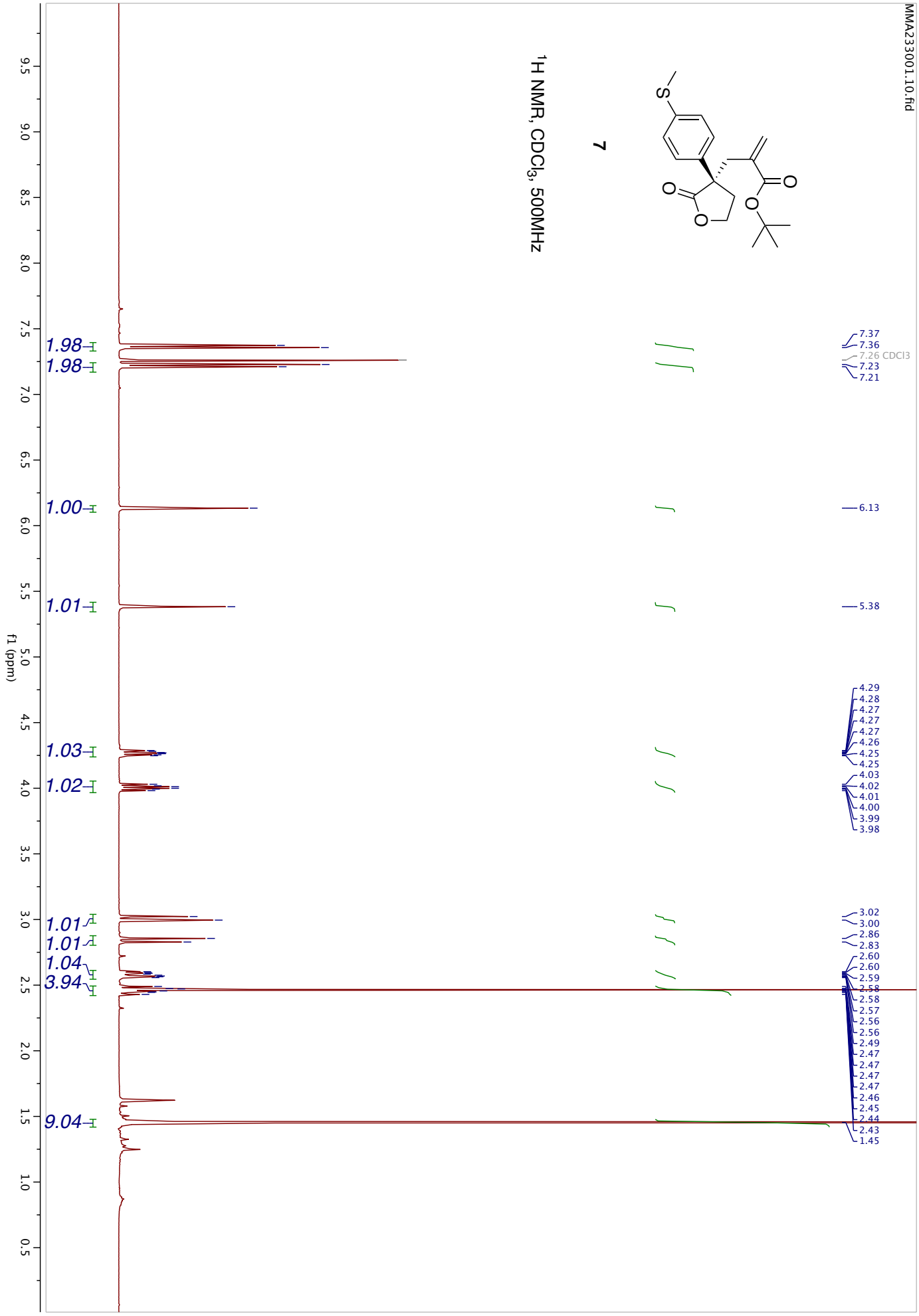
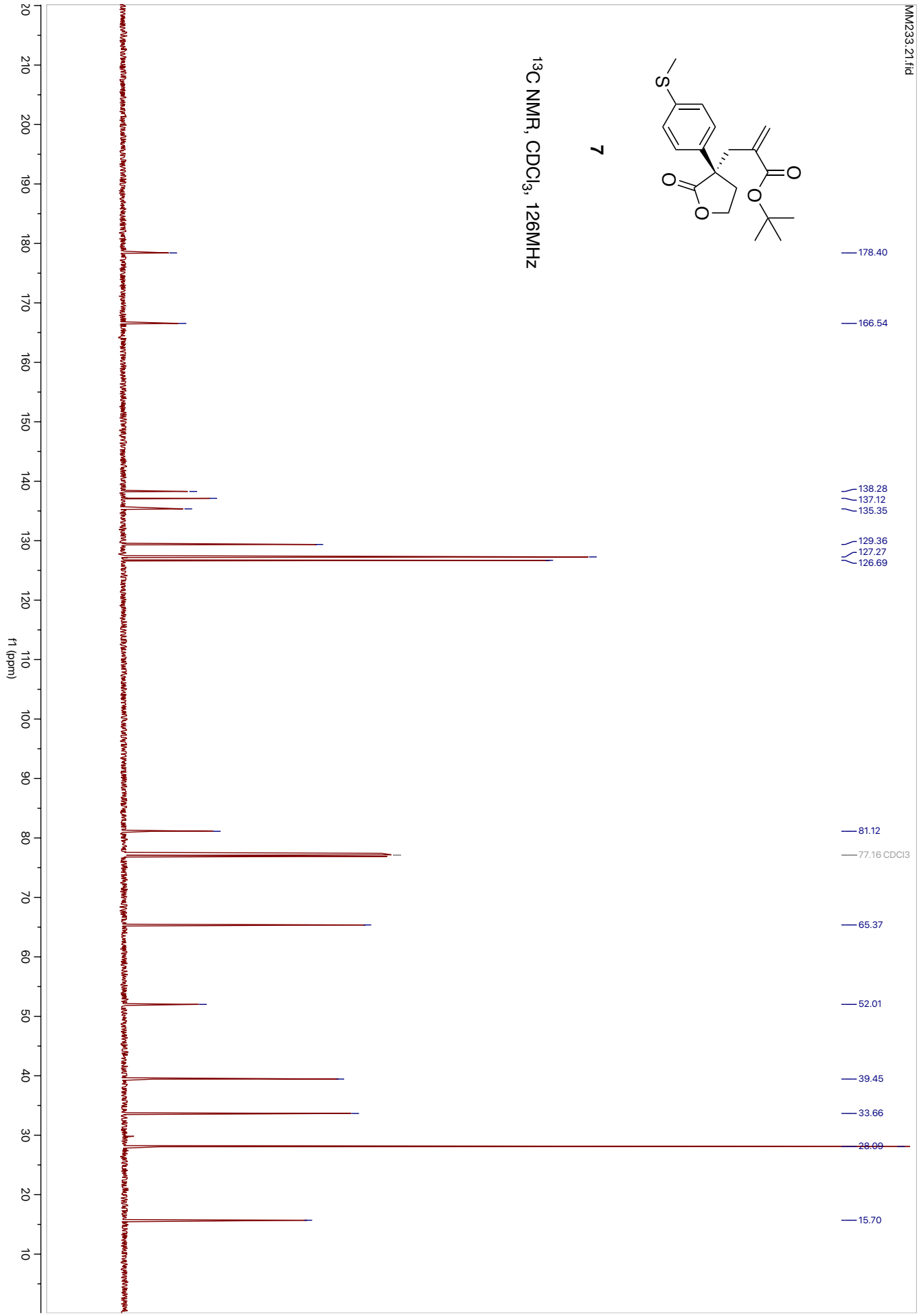
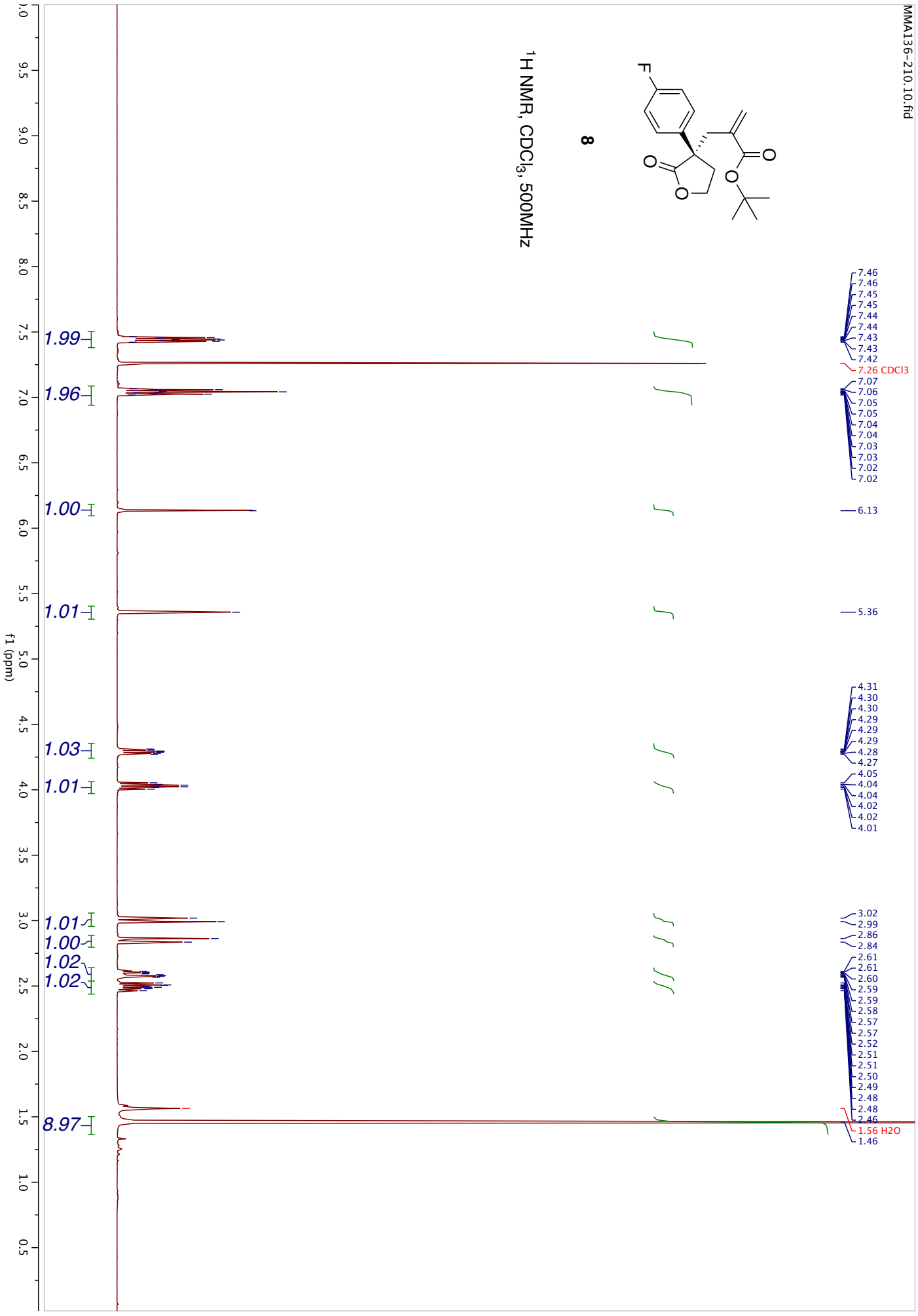
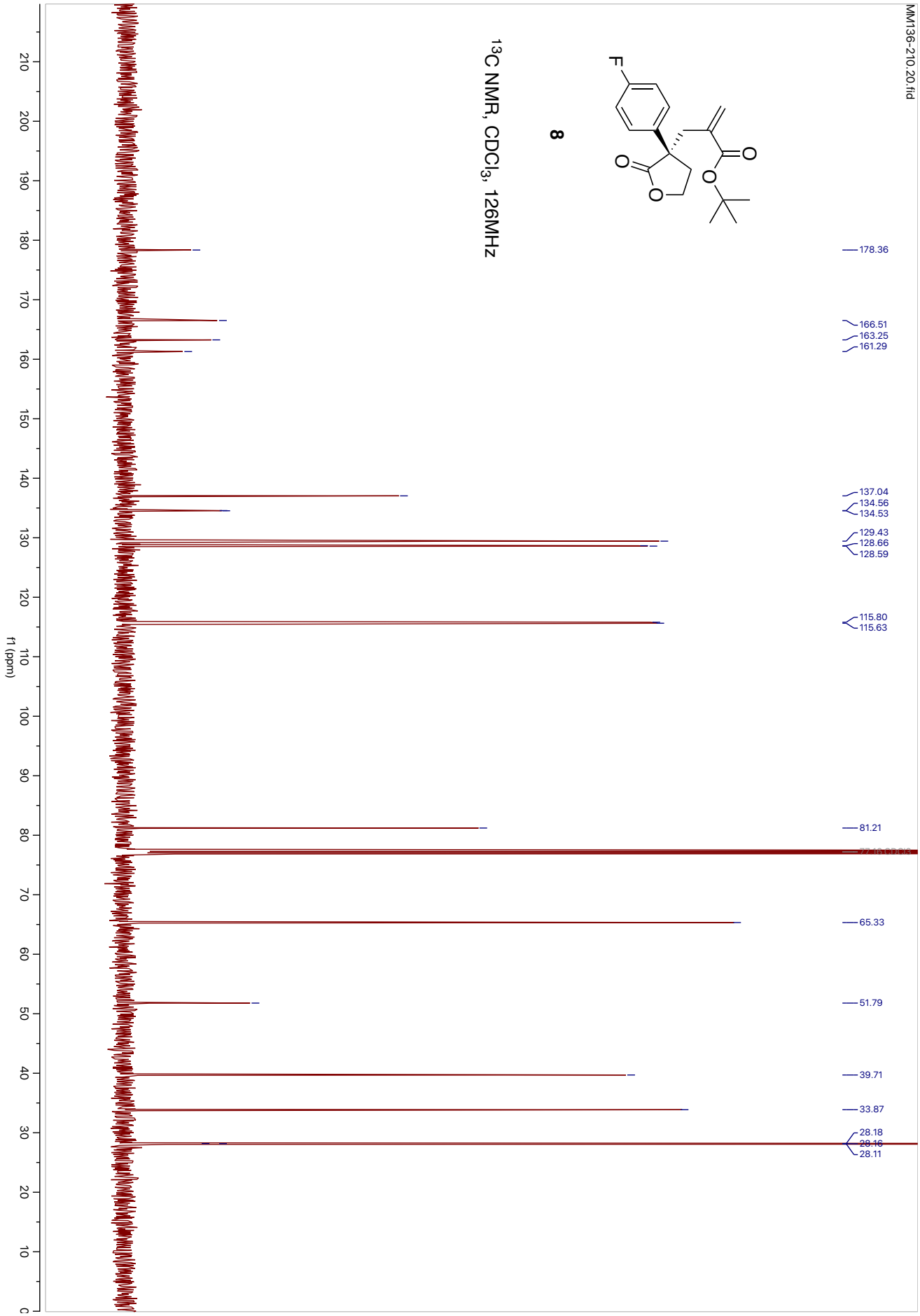
2.47
2.45
2.45
2.44
2.44
2.43
2.43
2.41
1.59 H2O


MMA-ER975002-600.11.1.1r
^{13}C NMR, $CDCl_3$, 126MHz
6
178.72
167.95
159.11
135.61
130.29
129.92
127.99
114.14
77.48
CDCl3
65.44
55.42
52.23
51.55
39.81
33.60
f1 (ppm)

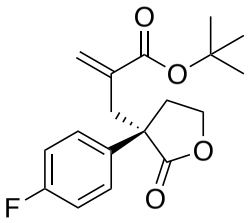

MMA233001.10.fid
7
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
1.98
1.98
1.00
1.01
1.03
1.02
1.01
1.01
1.04
3.94
9.04
7.37
7.36
7.26 CDCl3
7.23
7.21
6.13
5.38
4.29
4.28
4.27
4.27
4.27
4.26
4.25
4.25
4.03
4.02
4.01
4.00
3.99
3.98
3.02
3.00
2.86
2.83
2.60
2.60
2.59
2.58
2.58
2.57
2.56
2.56
2.49
2.47
2.47
2.47
2.47
2.46
2.45
2.44
2.43
1.45


MM233.21.fid
7
^{13}C NMR, $CDCl_3$, 126MHz
178.40
166.54
138.28
137.12
135.35
129.36
127.27
126.69
81.12
77.16 CDCl3
65.37
52.01
39.45
33.66
28.09
15.70
f1 (ppm)


MMA136-210.10.fid
8
^{1}H NMR, $CDCl_3$, 500MHz
F
O
O
O
O
f1 (ppm)
1.99
1.96
1.00
1.01
1.03
1.01
1.01
1.00
1.02
1.02
8.97
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.26 CDCl3
7.07
7.06
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
6.13
5.36
4.31
4.30
4.30
4.29
4.29
4.29
4.28
4.27
4.05
4.04
4.04
4.02
4.02
4.01
3.02
2.99
2.86
2.84
2.61
2.61
2.60
2.59
2.59
2.58
2.57
2.57
2.52
2.51
2.51
2.50
2.49
2.48
2.48
2.46
1.56 H2O
1.46

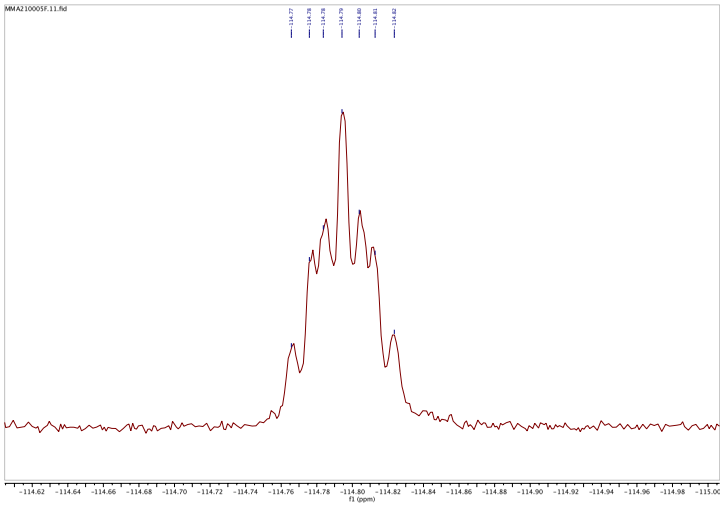

MM136-210.20.fid
178.36
166.51
163.25
161.29
137.04
134.56
134.53
129.43
128.66
128.59
115.80
115.63
81.21
65.33
51.79
39.71
33.87
28.18
28.16
28.11
f1 (ppm)
^{13}C NMR, $CDCl_3$, 126MHz
8
F
O
O
O
O

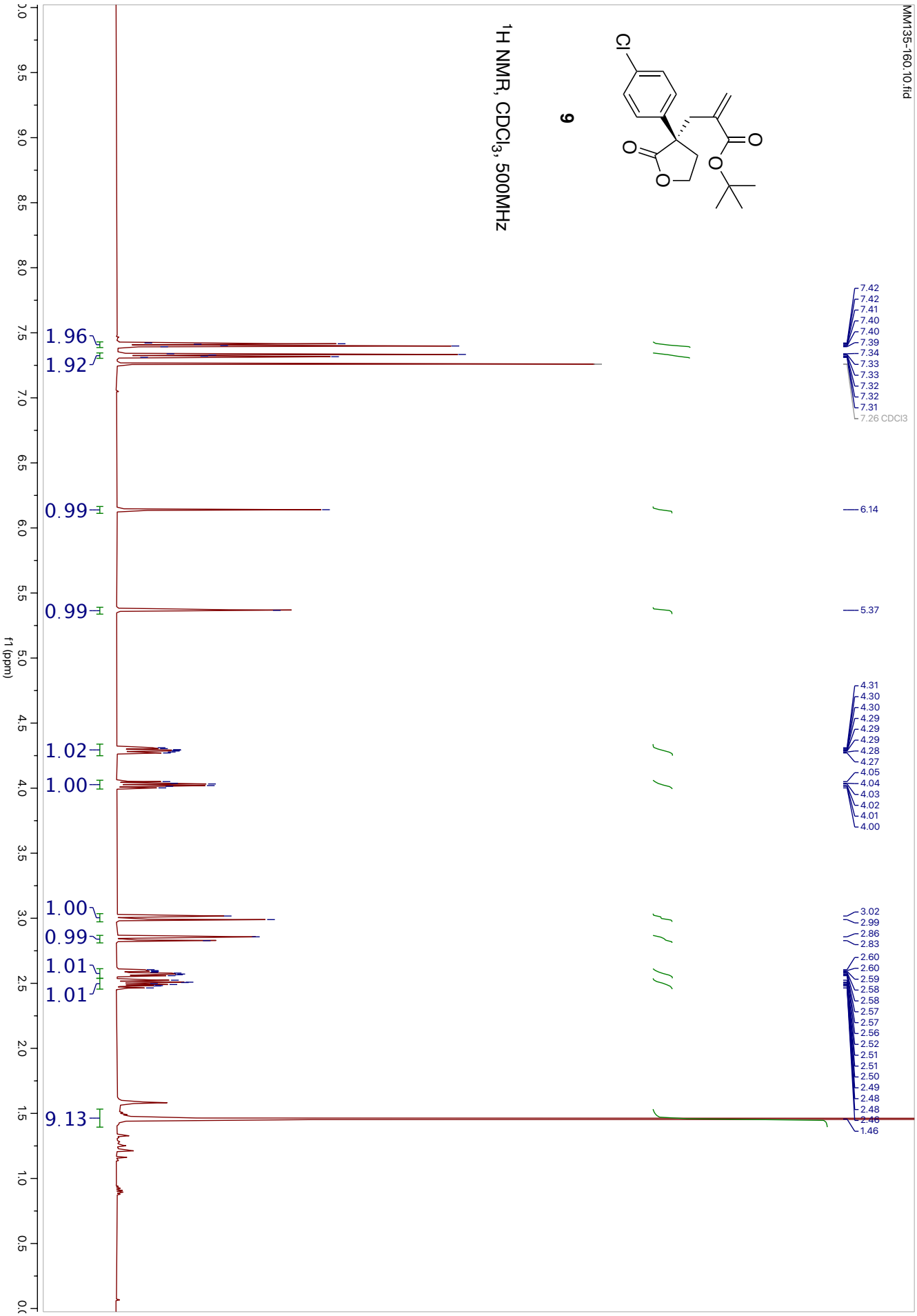
MMA210005F.11.fid

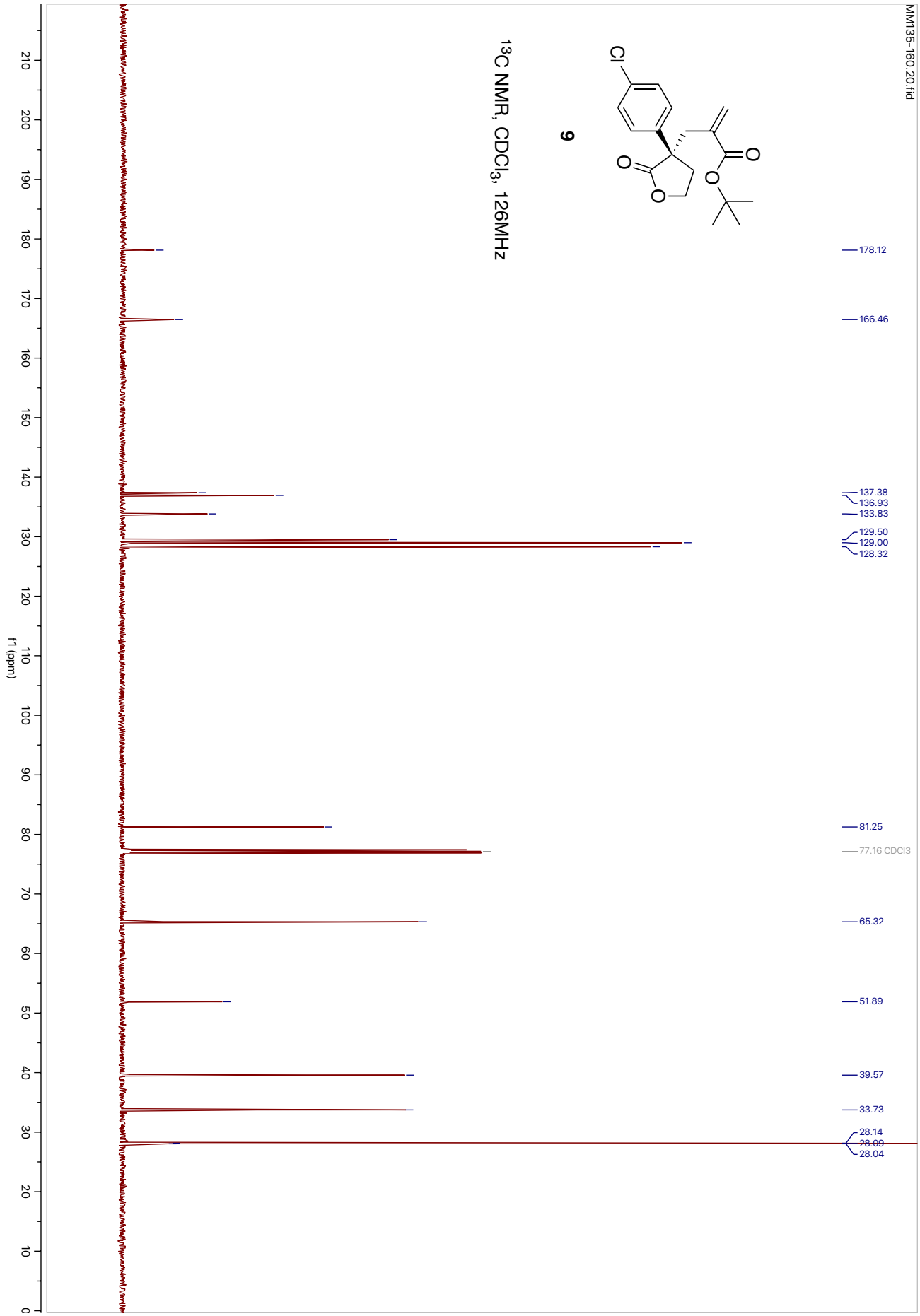


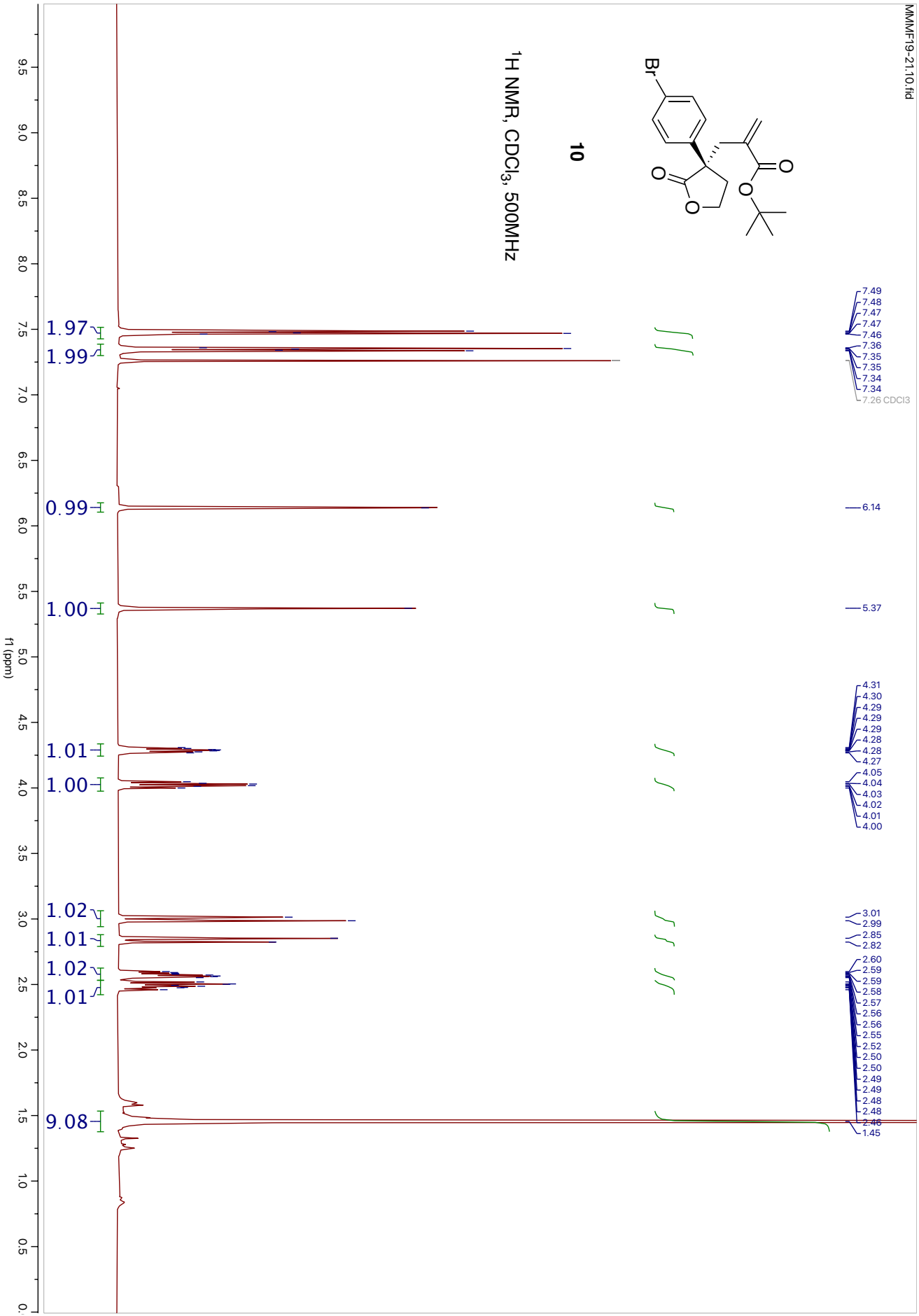
8

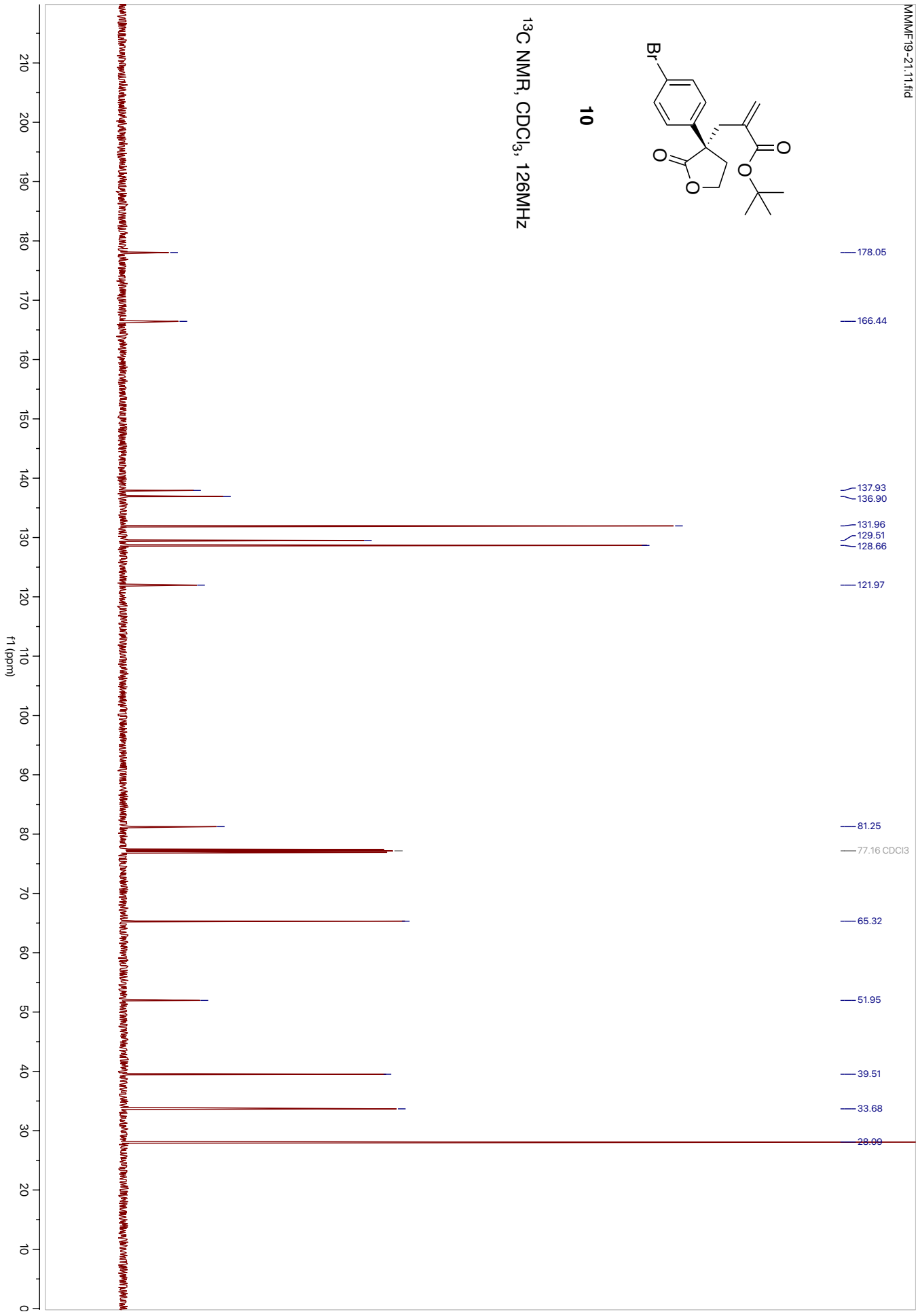
^{19}F NMR, $CDCl_3$, 471MHz

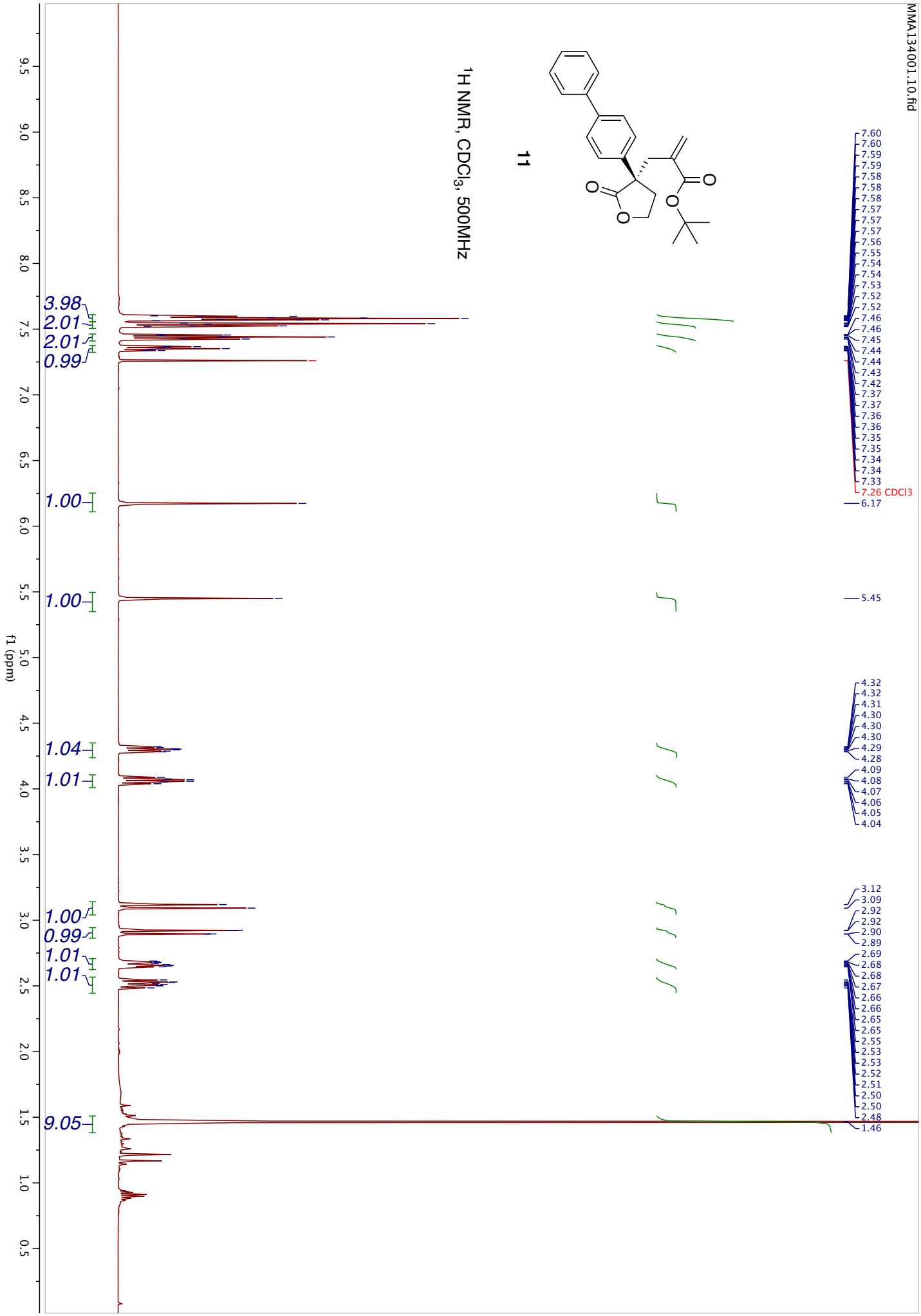


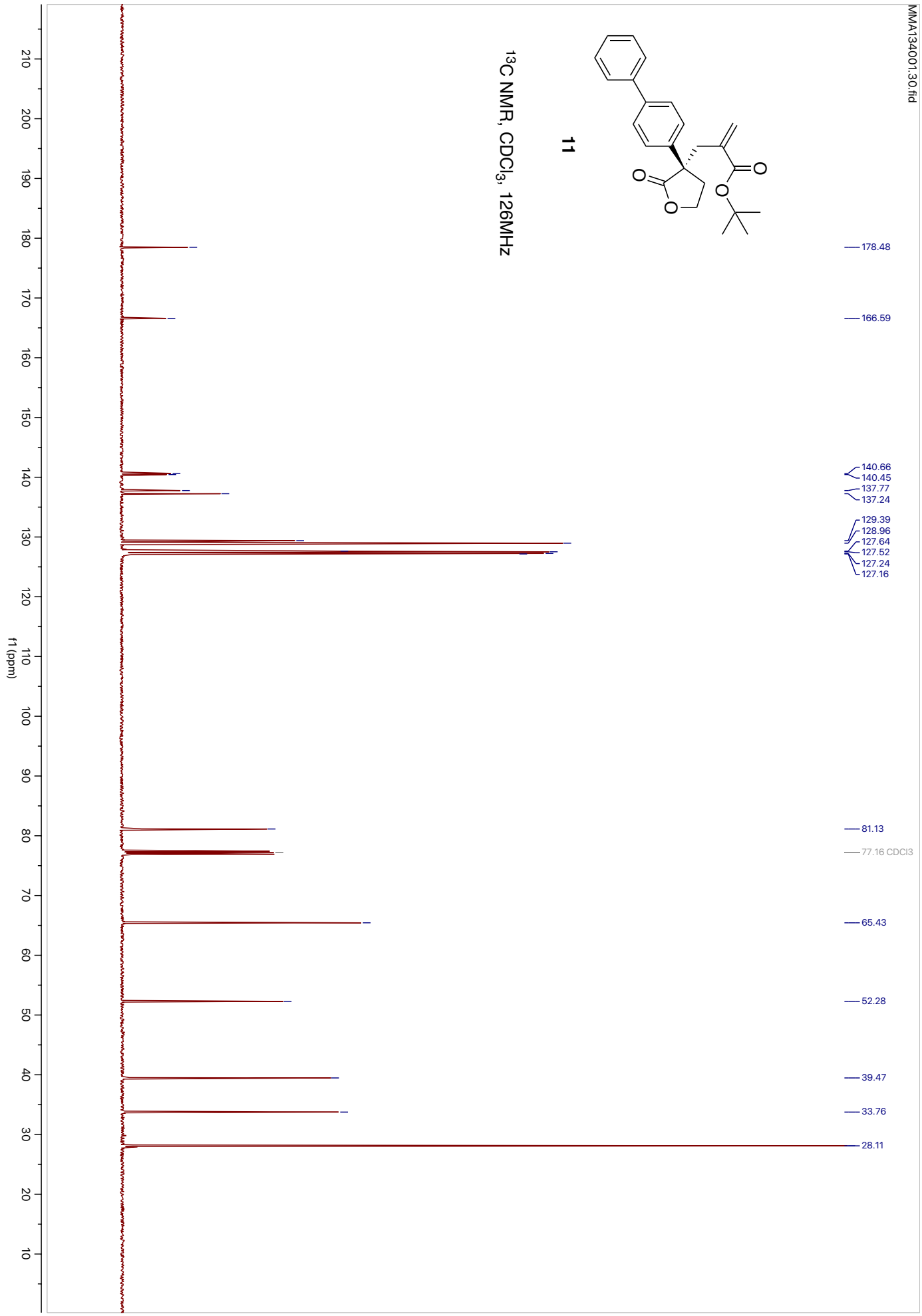

MM135-160.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
9
Cl
O
O
O
O
f1 (ppm)
1.96
1.92
0.99
0.99
1.02
1.00
1.00
0.99
1.01
1.01
9.13
7.42
7.42
7.41
7.40
7.40
7.39
7.34
7.33
7.33
7.32
7.32
7.31
7.26 CDCl3
6.14
5.37
4.31
4.30
4.30
4.29
4.29
4.29
4.28
4.27
4.05
4.04
4.03
4.02
4.01
4.00
3.02
2.99
2.86
2.83
2.60
2.60
2.59
2.58
2.58
2.57
2.57
2.56
2.52
2.51
2.51
2.50
2.49
2.48
2.48
2.46
1.46

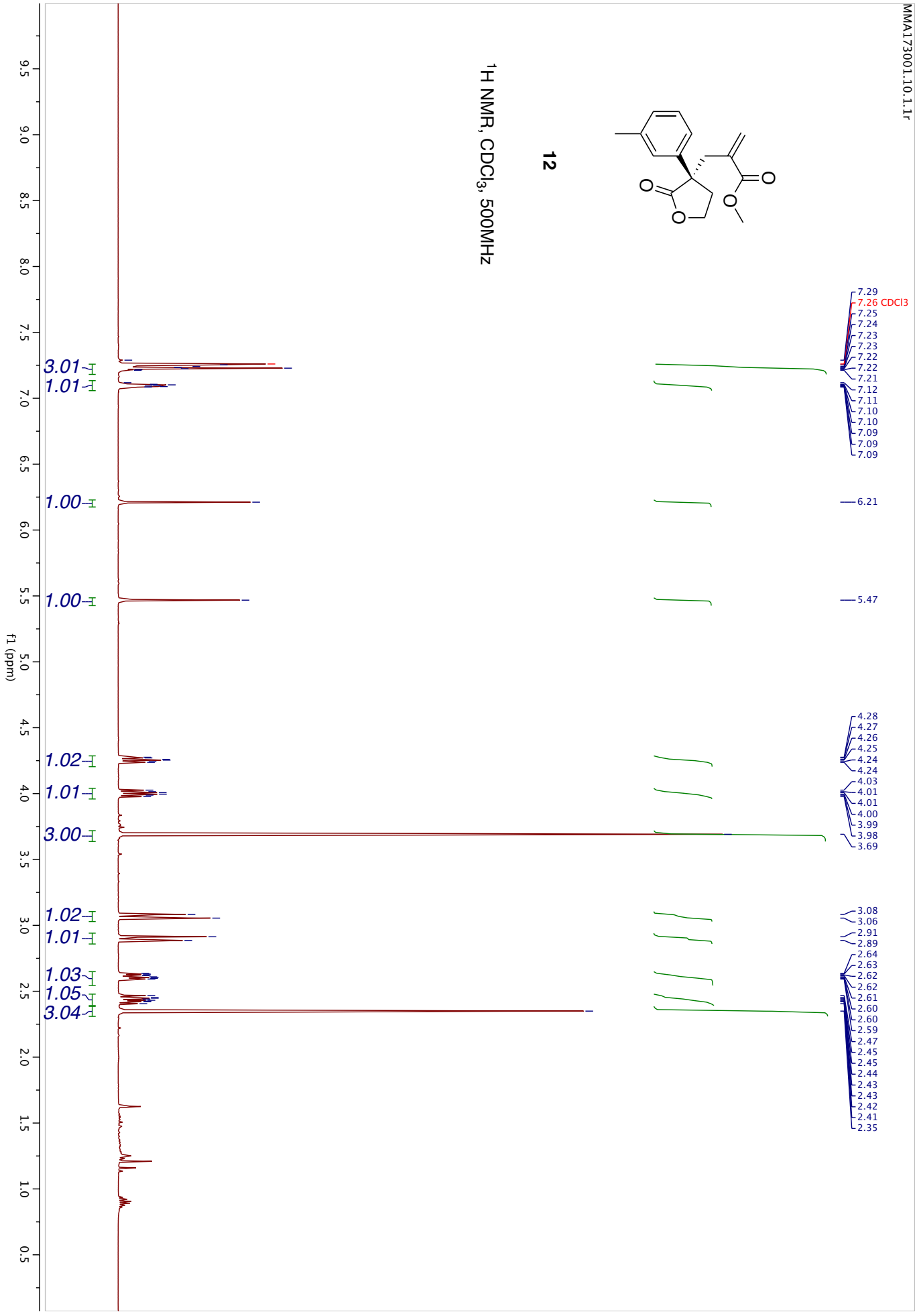

MM135-160.20.fid
^{13}C NMR, $CDCl_3$, 126MHz
9
Cl
O
O
O
178.12
166.46
137.38
136.93
133.83
129.50
129.00
128.32
81.25
77.16 CDCl3
65.32
51.89
39.57
33.73
28.14
28.09
28.04
f1 (ppm)

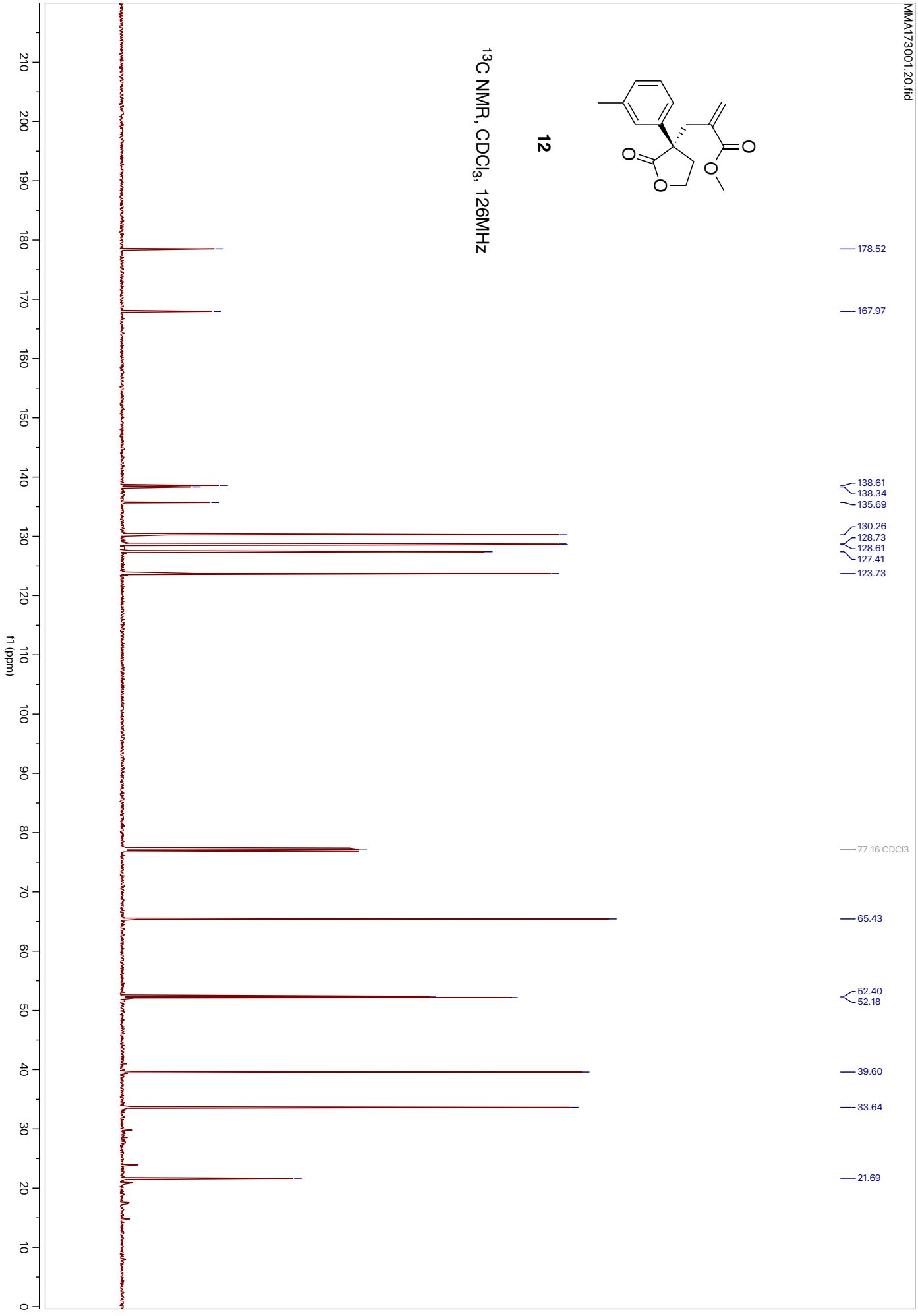

MMMF19-21.10.fid
10
^{1}H NMR, $CDCl_3$, 500MHz
Br
O
O
O
O
f1 (ppm)
1.97
1.99
0.99
1.00
1.01
1.00
1.02
1.01
1.02
1.01
9.08
7.49
7.48
7.47
7.47
7.46
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
6.14
5.37
4.31
4.30
4.29
4.29
4.29
4.28
4.28
4.27
4.05
4.04
4.03
4.02
4.01
4.00
3.01
2.99
2.85
2.82
2.60
2.59
2.59
2.58
2.57
2.56
2.56
2.55
2.52
2.50
2.50
2.49
2.49
2.48
2.48
2.46
1.45

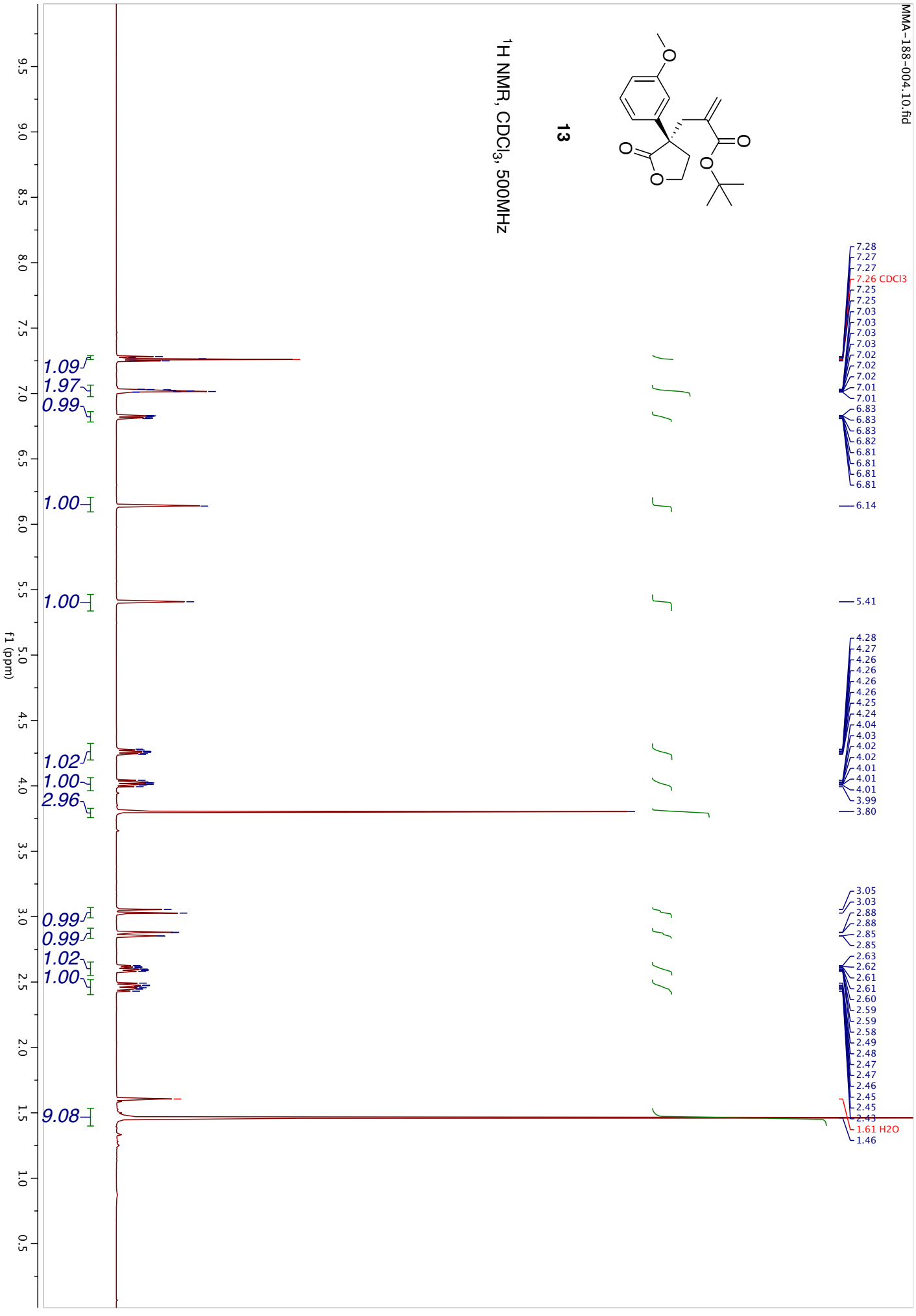

MMMF19-21.11.fid
10
^{13}C NMR, $CDCl_3$, 126MHz
Br
O
O
O
O
178.05
166.44
137.93
136.90
131.96
129.51
128.66
121.97
81.25
77.16 CDCl3
65.32
51.95
39.51
33.68
28.09
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

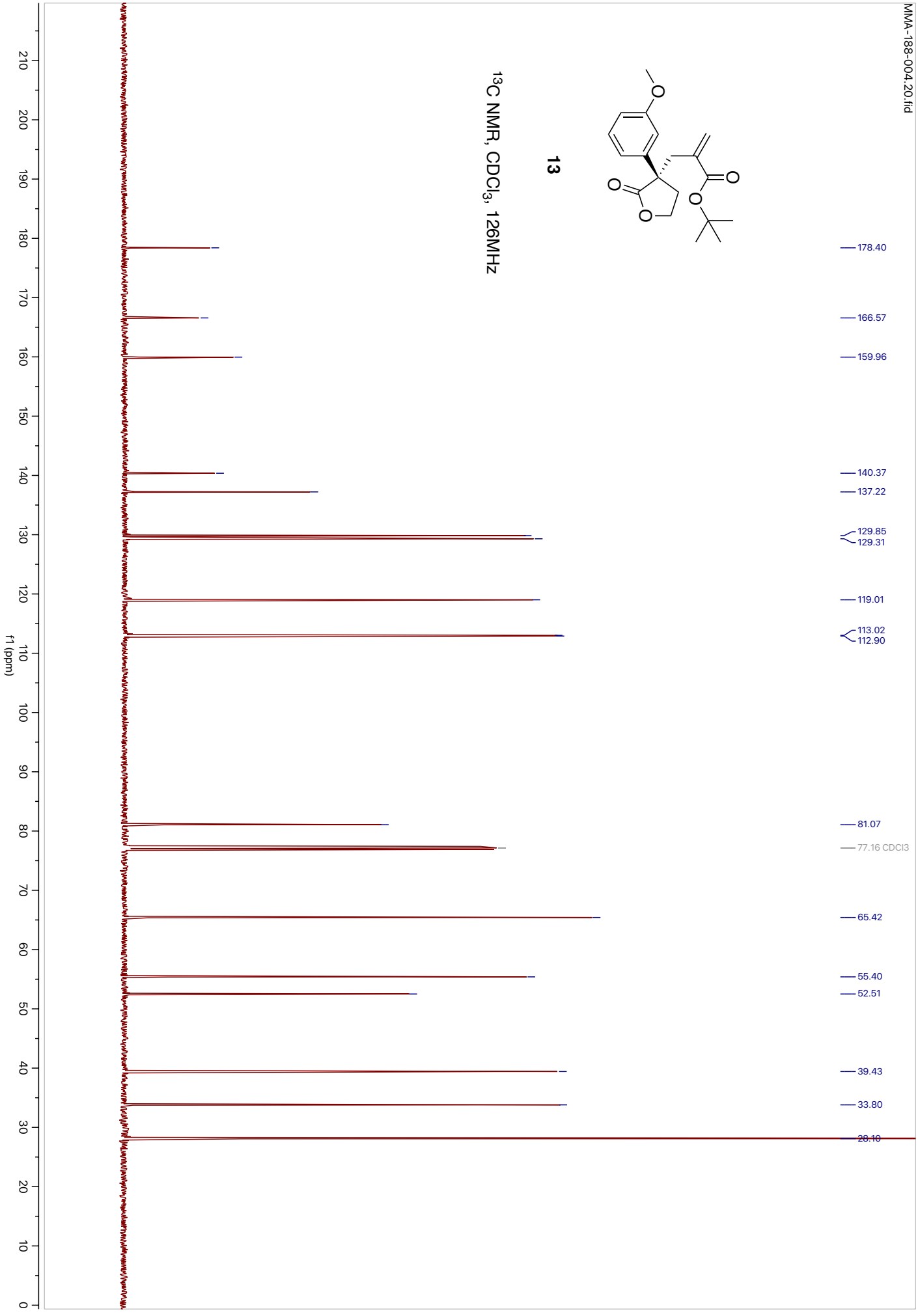

MMA134001.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
11
f1 (ppm)
3.98
2.01
2.01
0.99
1.00
1.00
1.04
1.01
1.00
0.99
1.01
1.01
9.05
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.53
7.52
7.46
7.45
7.44
7.43
7.42
7.37
7.36
7.35
7.34
7.33
7.26 CDCl3
6.17
5.45
4.32
4.31
4.30
4.29
4.28
4.09
4.08
4.07
4.06
4.05
4.04
3.12
3.09
2.92
2.90
2.89
2.69
2.68
2.67
2.66
2.65
2.55
2.53
2.52
2.51
2.50
2.48
1.46

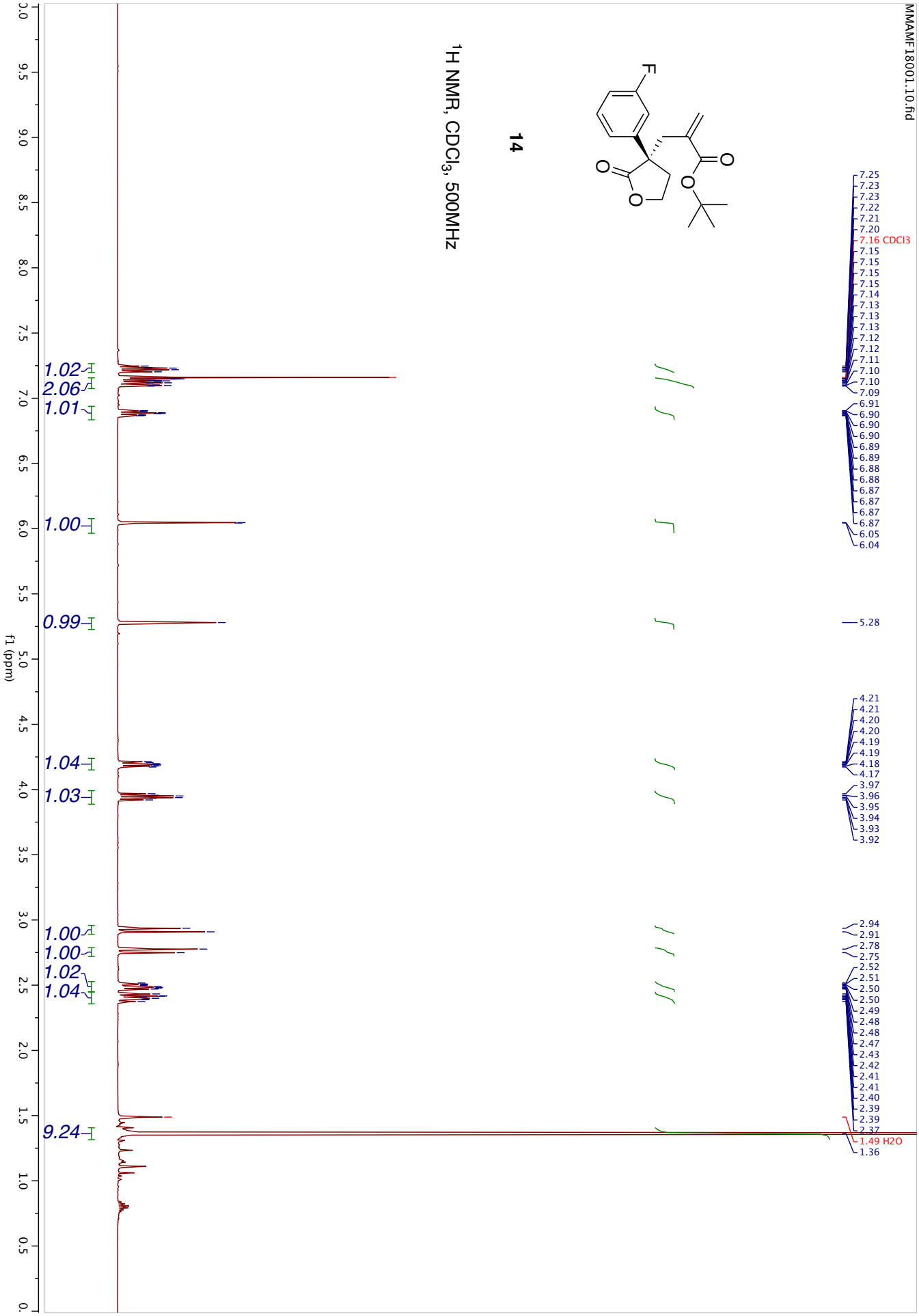

MMA134001.30.fid
^{13}C NMR, $CDCl_3$, 126MHz
11
178.48
166.59
140.66
140.45
137.77
137.24
129.39
128.96
127.64
127.52
127.24
127.16
81.13
77.16 CDCl3
65.43
52.28
39.47
33.76
28.11
f1 (ppm)

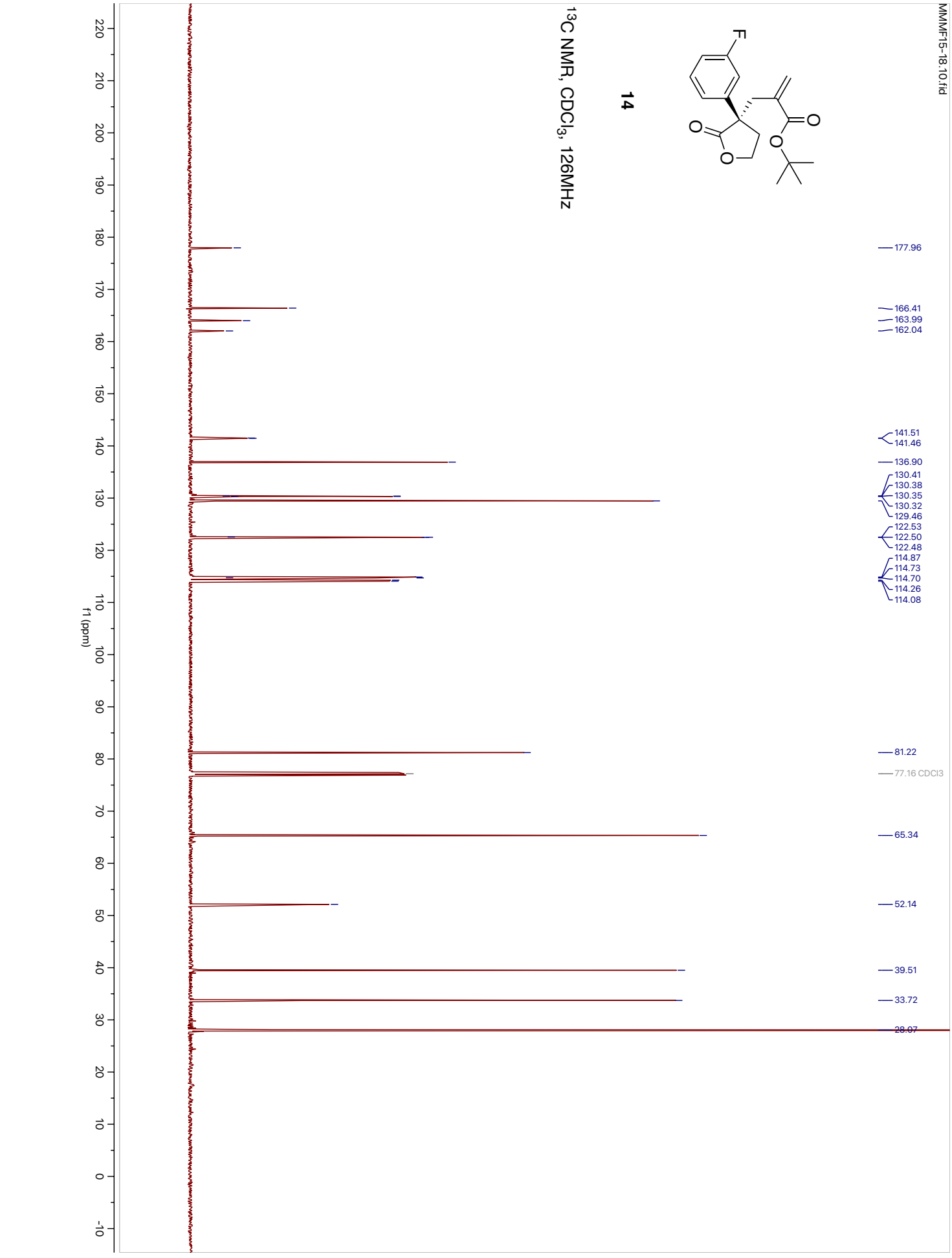

MMA173001.10.1.1r
12
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
3.01
1.01
1.00
1.00
1.02
1.01
3.00
1.02
1.01
1.03
1.05
3.04
7.29
7.26 CDCl3
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.12
7.11
7.10
7.10
7.09
7.09
7.09
6.21
5.47
4.28
4.27
4.26
4.25
4.24
4.24
4.03
4.01
4.01
4.00
3.99
3.98
3.69
3.08
3.06
2.91
2.89
2.64
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.47
2.45
2.45
2.44
2.43
2.43
2.42
2.41
2.35


MMA173001.20.fid
12
^{13}C NMR, $CDCl_3$, 126MHz
178.52
167.97
138.61
138.34
135.69
130.26
128.73
128.61
127.41
123.73
77.16 CDCl3
65.43
52.40
52.18
39.60
33.64
21.69
f1 (ppm)

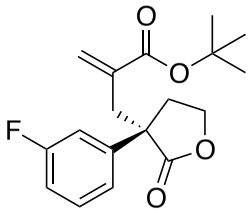

MMA-188-004.10.fid
13
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
1.09
1.97
0.99
1.00
1.00
1.02
1.00
2.96
0.99
0.99
1.02
1.00
9.08
7.28
7.27
7.27
7.26 CDCl3
7.25
7.25
7.03
7.03
7.03
7.03
7.02
7.02
7.02
7.01
7.01
6.83
6.83
6.83
6.82
6.81
6.81
6.81
6.81
6.14
5.41
4.28
4.27
4.26
4.26
4.26
4.26
4.25
4.24
4.04
4.03
4.02
4.02
4.01
4.01
4.01
3.99
3.80
3.05
3.03
2.88
2.88
2.85
2.85
2.63
2.62
2.61
2.61
2.60
2.59
2.59
2.58
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.43
1.61 H2O
1.46


MMA-188-004.20.fid
13
^{13}C NMR, $CDCl_3$, 126MHz
178.40
166.57
159.96
140.37
137.22
129.85
129.31
119.01
113.02
112.90
81.07
77.16 CDCl3
65.42
55.40
52.51
39.43
33.80
28.10
f1 (ppm)


MMAMF18001.10.fid
14
^{1}H NMR, $CDCl_3$, 500MHz
F
O
O
O
O
f1 (ppm)
1.02
2.06
1.01
1.00
0.99
1.04
1.03
1.00
1.00
1.02
1.04
9.24
7.25
7.23
7.23
7.22
7.21
7.20
7.16 CDCl3
7.15
7.15
7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
6.91
6.90
6.90
6.90
6.89
6.89
6.88
6.88
6.87
6.87
6.87
6.87
6.05
6.04
5.28
4.21
4.21
4.20
4.20
4.19
4.19
4.18
4.17
3.97
3.96
3.95
3.94
3.93
3.92
2.94
2.91
2.78
2.75
2.52
2.51
2.50
2.50
2.49
2.48
2.48
2.47
2.43
2.42
2.41
2.41
2.40
2.39
2.39
2.37
1.49 H2O
1.36

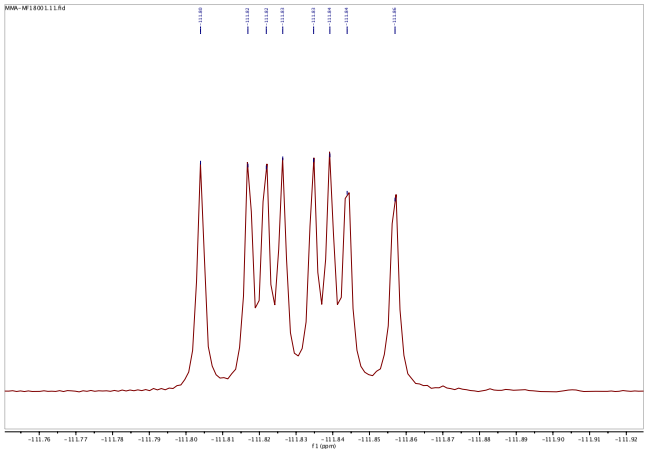

MMMF15-18.10.fid
14
^{13}C NMR, $CDCl_3$, 126MHz
177.96
166.41
163.99
162.04
141.51
141.46
136.90
130.41
130.38
130.35
130.32
129.46
122.53
122.50
122.48
114.87
114.73
114.70
114.26
114.08
81.22
77.16 CDCl3
65.34
52.14
39.51
33.72
28.07
f1 (ppm)

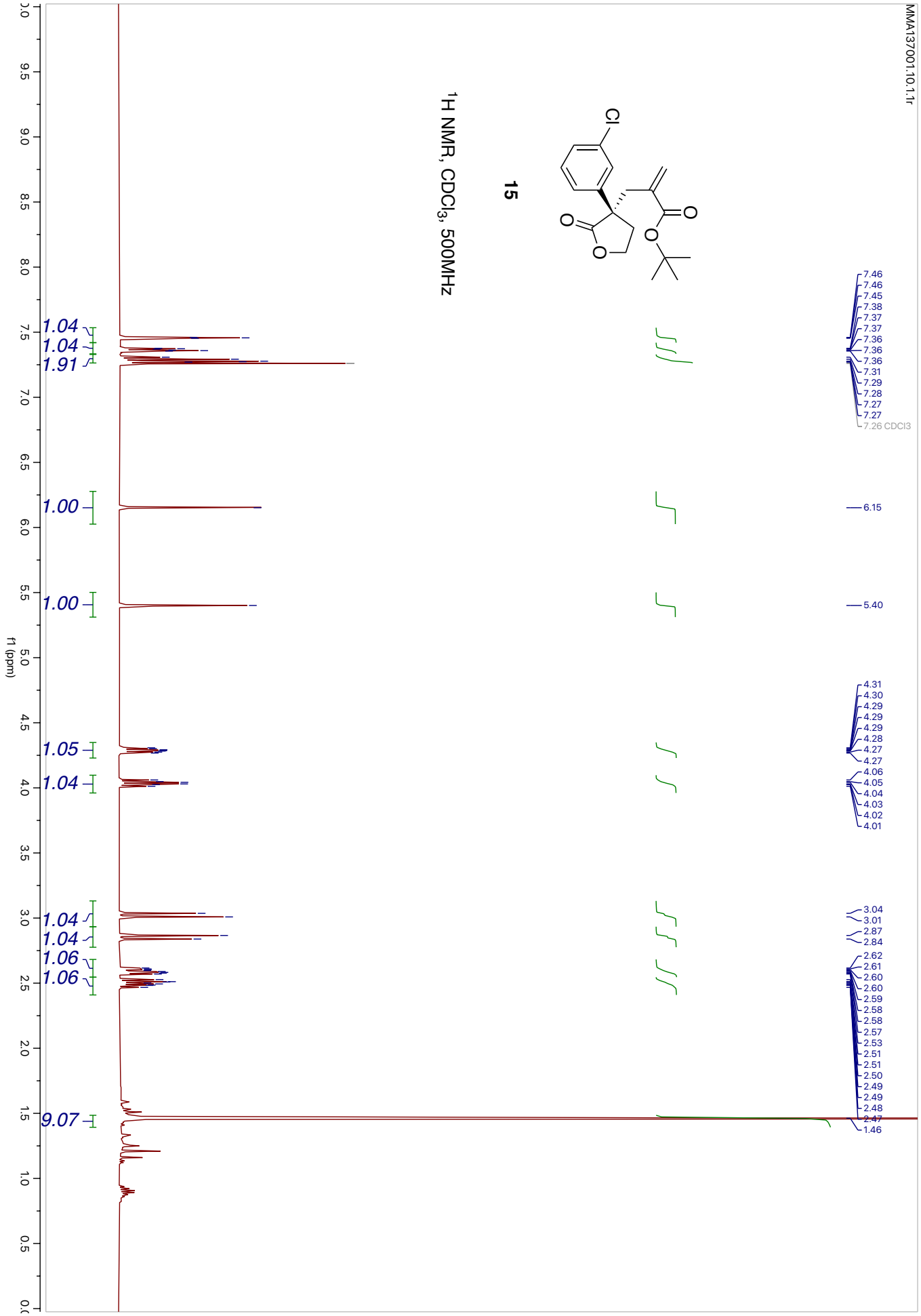
MMA-MF18001.11.fid

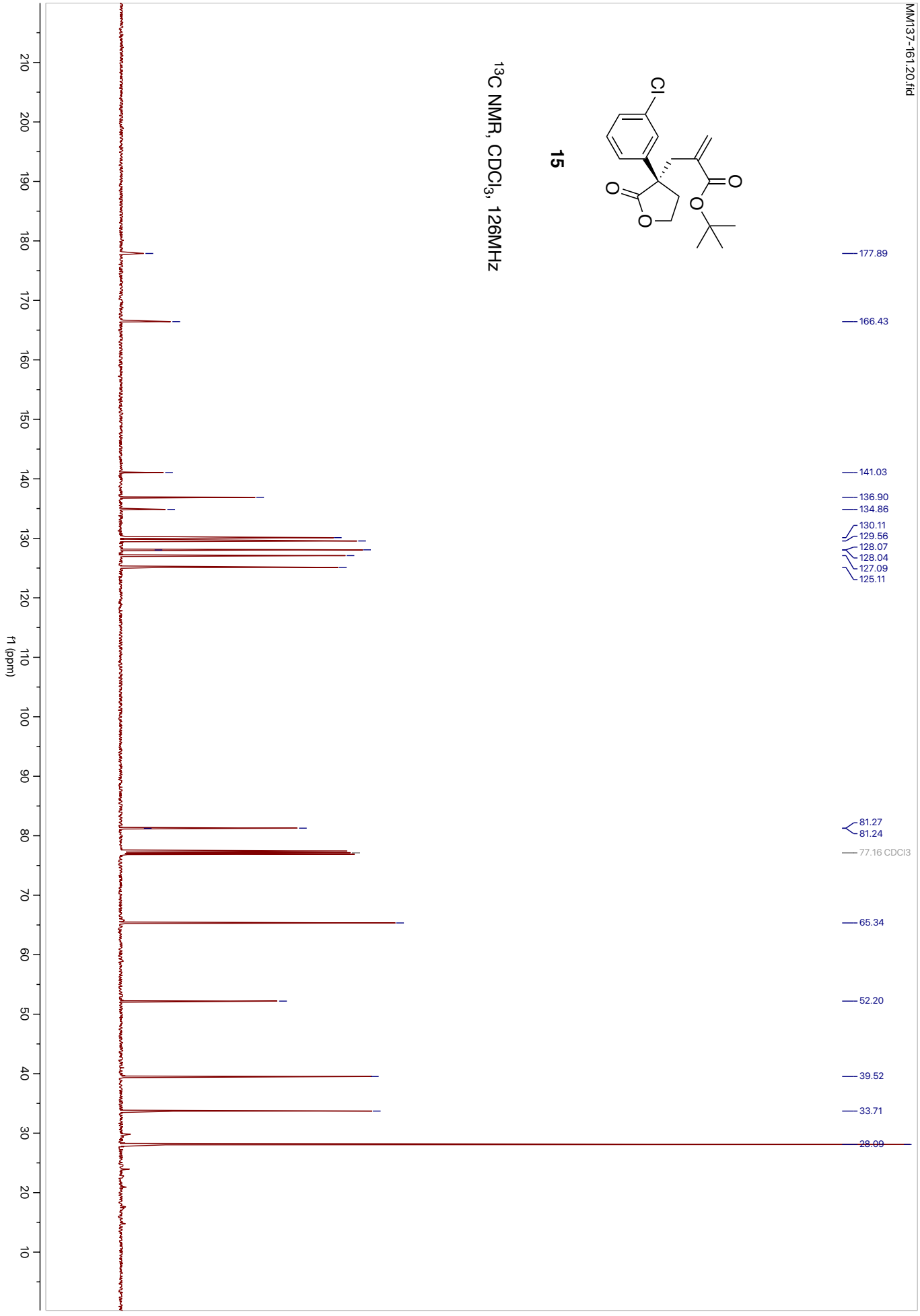


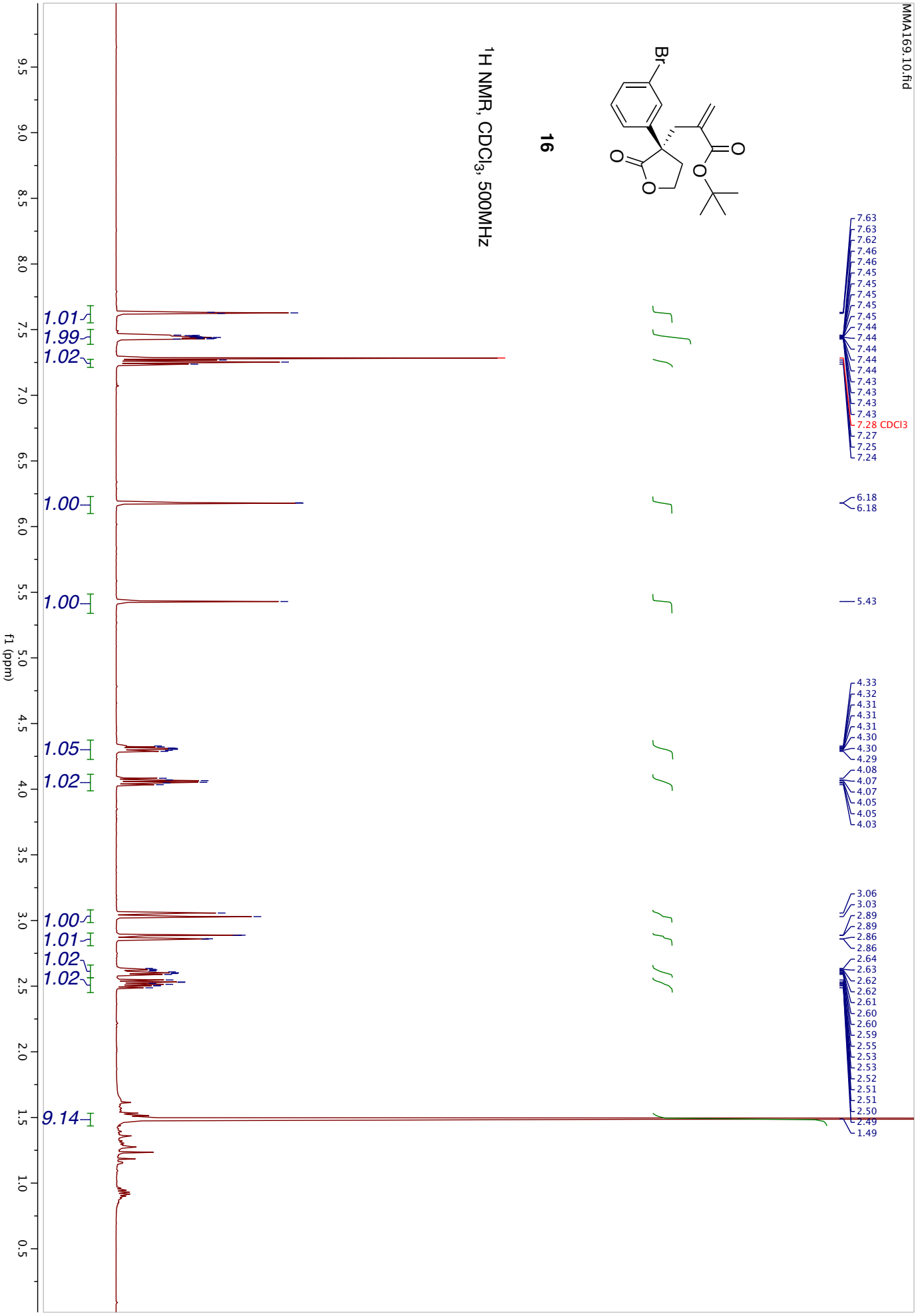
14

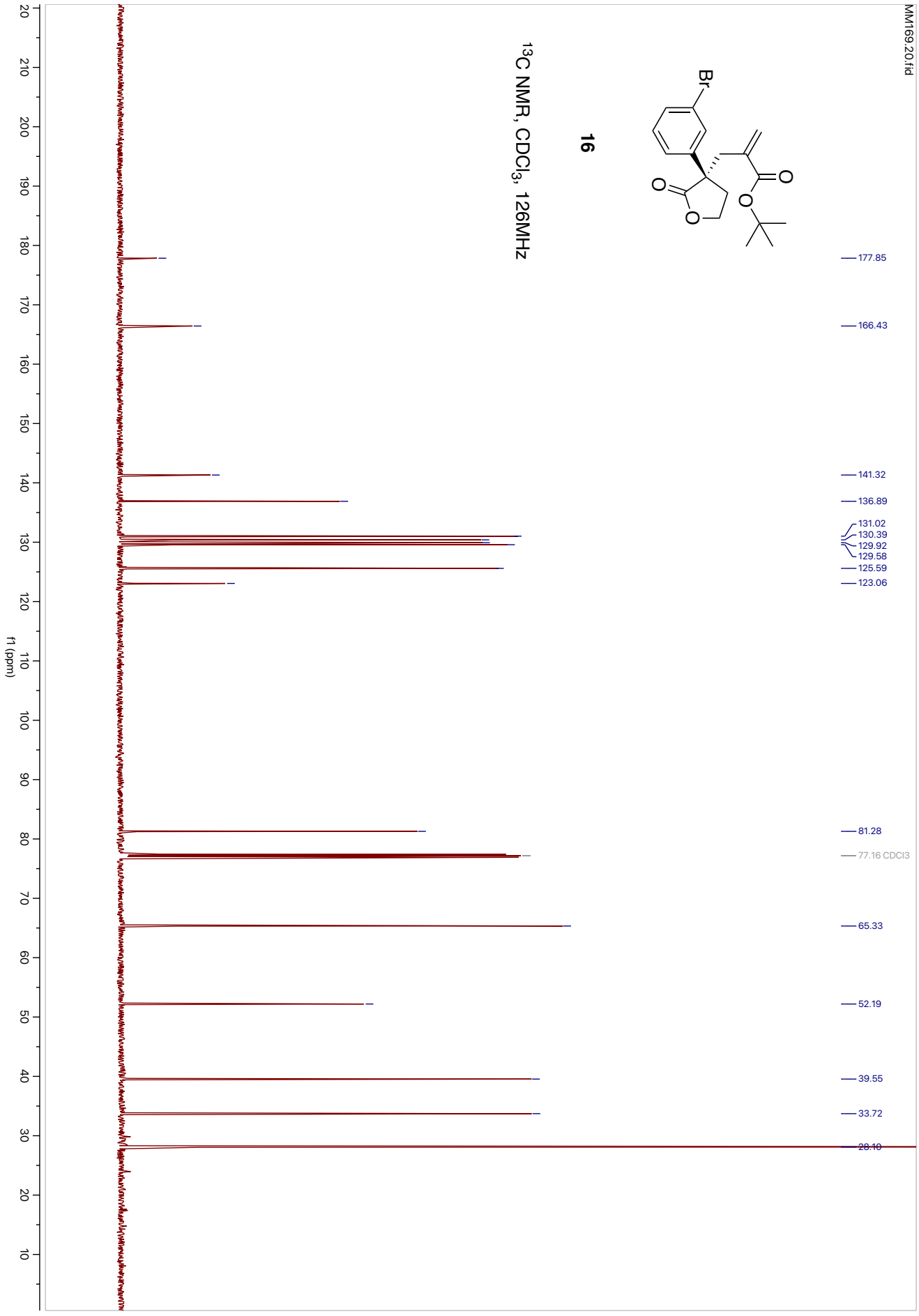
^{19}F NMR, $CDCl_3$, 471MHz

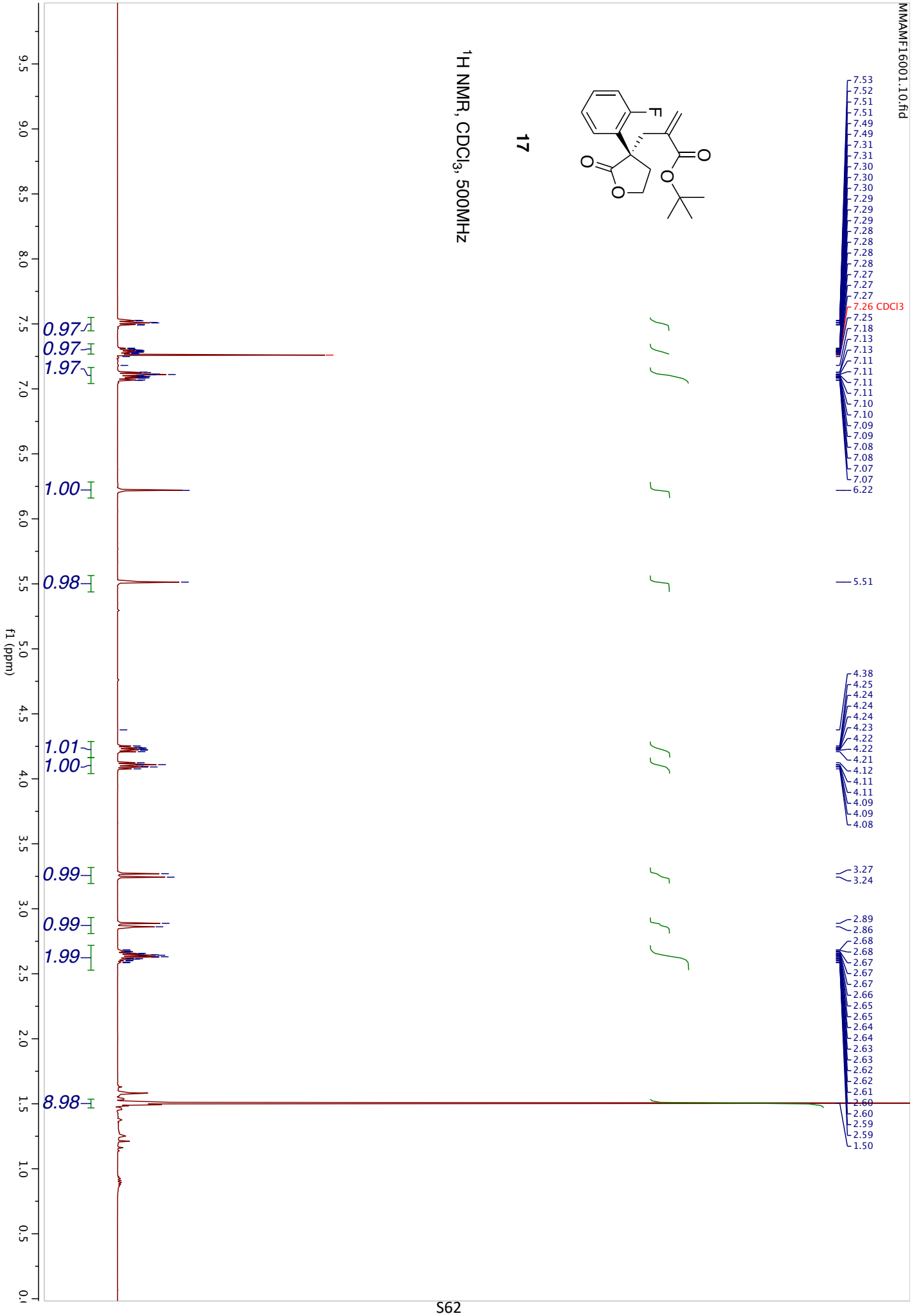


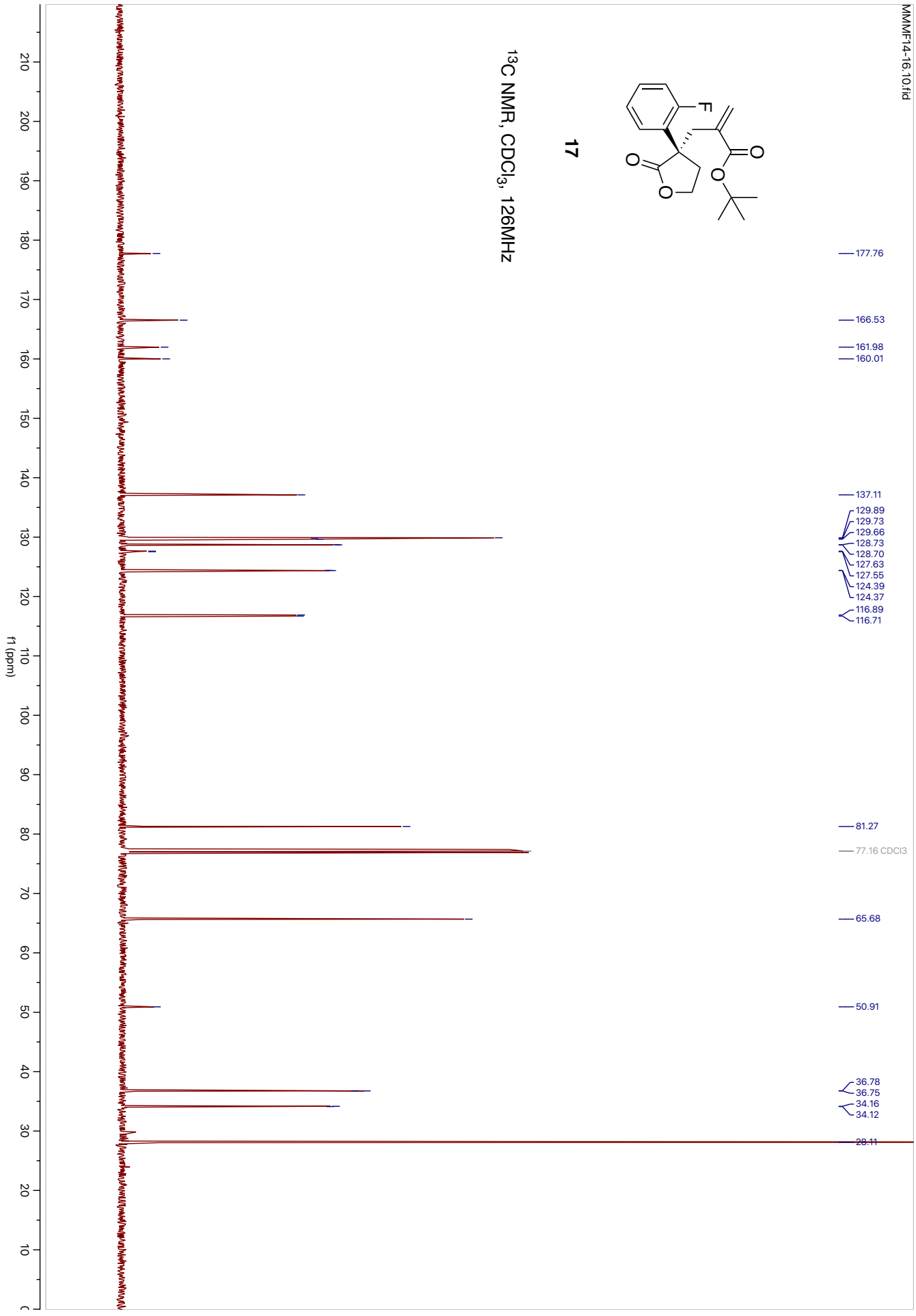

MMA137001.10.1.1r
15
^{1}H NMR, $CDCl_3$, 500MHz
Cl
O
O
O
O
f1 (ppm)
1.04
1.04
1.91
1.00
1.00
1.05
1.04
1.04
1.04
1.06
1.06
9.07
7.46
7.46
7.45
7.38
7.37
7.37
7.36
7.36
7.36
7.31
7.29
7.28
7.27
7.27
7.26 CDCl3
6.15
5.40
4.31
4.30
4.29
4.29
4.29
4.28
4.27
4.27
4.06
4.05
4.04
4.03
4.02
4.01
3.04
3.01
2.87
2.84
2.62
2.61
2.60
2.60
2.59
2.58
2.58
2.57
2.53
2.51
2.51
2.50
2.49
2.49
2.48
2.47
1.46


MM137-161.20.fid
15
^{13}C NMR, $CDCl_3$, 126MHz
Cl
O
O
O
O
177.89
166.43
141.03
136.90
134.86
130.11
129.56
128.07
128.04
127.09
125.11
81.27
81.24
77.16 CDCl3
65.34
52.20
39.52
33.71
28.09
f1 (ppm)

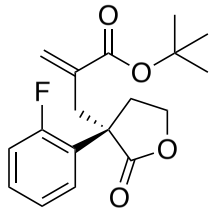

MMA169.10.fid
16
^{1}H NMR, $CDCl_3$, 500MHz
Br
O
O
O
O
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.01
1.99
1.02
1.00
1.00
1.05
1.02
1.00
1.01
1.02
1.02
9.14
7.63
7.63
7.62
7.46
7.46
7.45
7.45
7.45
7.45
7.45
7.44
7.44
7.44
7.44
7.44
7.44
7.43
7.43
7.43
7.43
7.28 CDCl3
7.27
7.25
7.24
6.18
6.18
5.43
4.33
4.32
4.31
4.31
4.31
4.30
4.30
4.29
4.08
4.07
4.07
4.05
4.05
4.03
3.06
3.03
2.89
2.89
2.86
2.86
2.64
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.55
2.53
2.53
2.52
2.51
2.51
2.50
2.49
1.49


MM169.20.fid
16
^{13}C NMR, $CDCl_3$, 126MHz
Br
O
O
O
O
177.85
166.43
141.32
136.89
131.02
130.39
129.92
129.58
125.59
123.06
81.28
77.16 CDCl3
65.33
52.19
39.55
33.72
28.10
f1 (ppm)


MMAMF16001.10.fid
17
^{1}H NMR, $CDCl_3$, 500MHz
F
O
O
O
O
f1 (ppm)
0.97
0.97
1.97
1.00
0.98
1.01
1.00
0.99
0.99
1.99
8.98
7.53
7.52
7.51
7.51
7.49
7.49
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
7.25
7.18
7.13
7.13
7.11
7.11
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.07
6.22
5.51
4.38
4.25
4.24
4.24
4.24
4.23
4.22
4.22
4.21
4.12
4.11
4.11
4.09
4.09
4.08
3.27
3.24
2.89
2.86
2.68
2.68
2.67
2.67
2.67
2.66
2.65
2.65
2.64
2.64
2.63
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.59
1.50

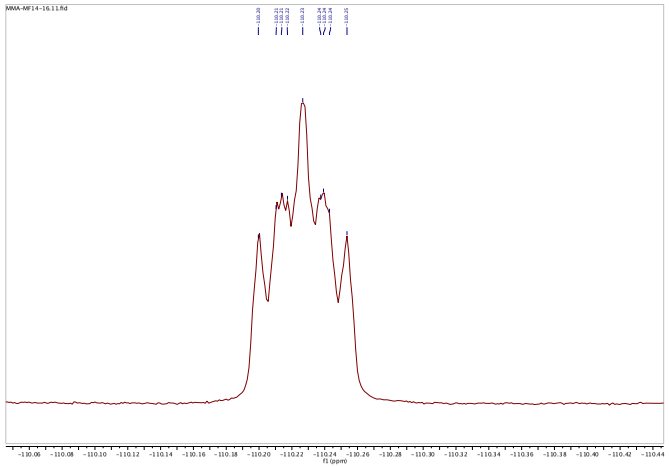

MMMF14-16.10.fid
^{13}C NMR, $CDCl_3$, 126MHz
17
F
O
O
O
O
177.76
166.53
161.98
160.01
137.11
129.89
129.73
129.66
128.73
128.70
127.63
127.55
124.39
124.37
116.89
116.71
81.27
77.16 CDCl3
65.68
50.91
36.78
36.75
34.16
34.12
28.11
f1 (ppm)

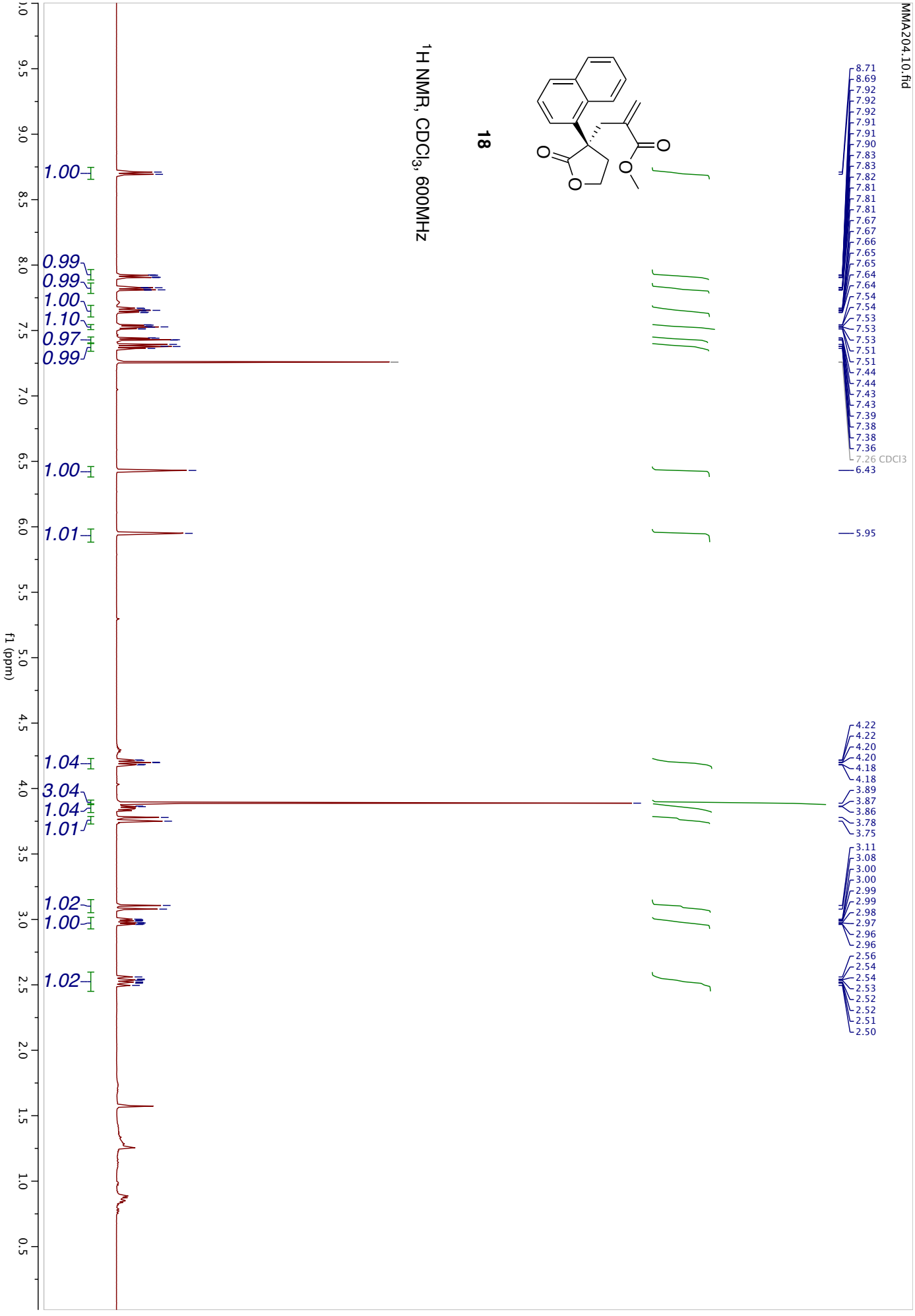
MMA-MF14-16.11.fid

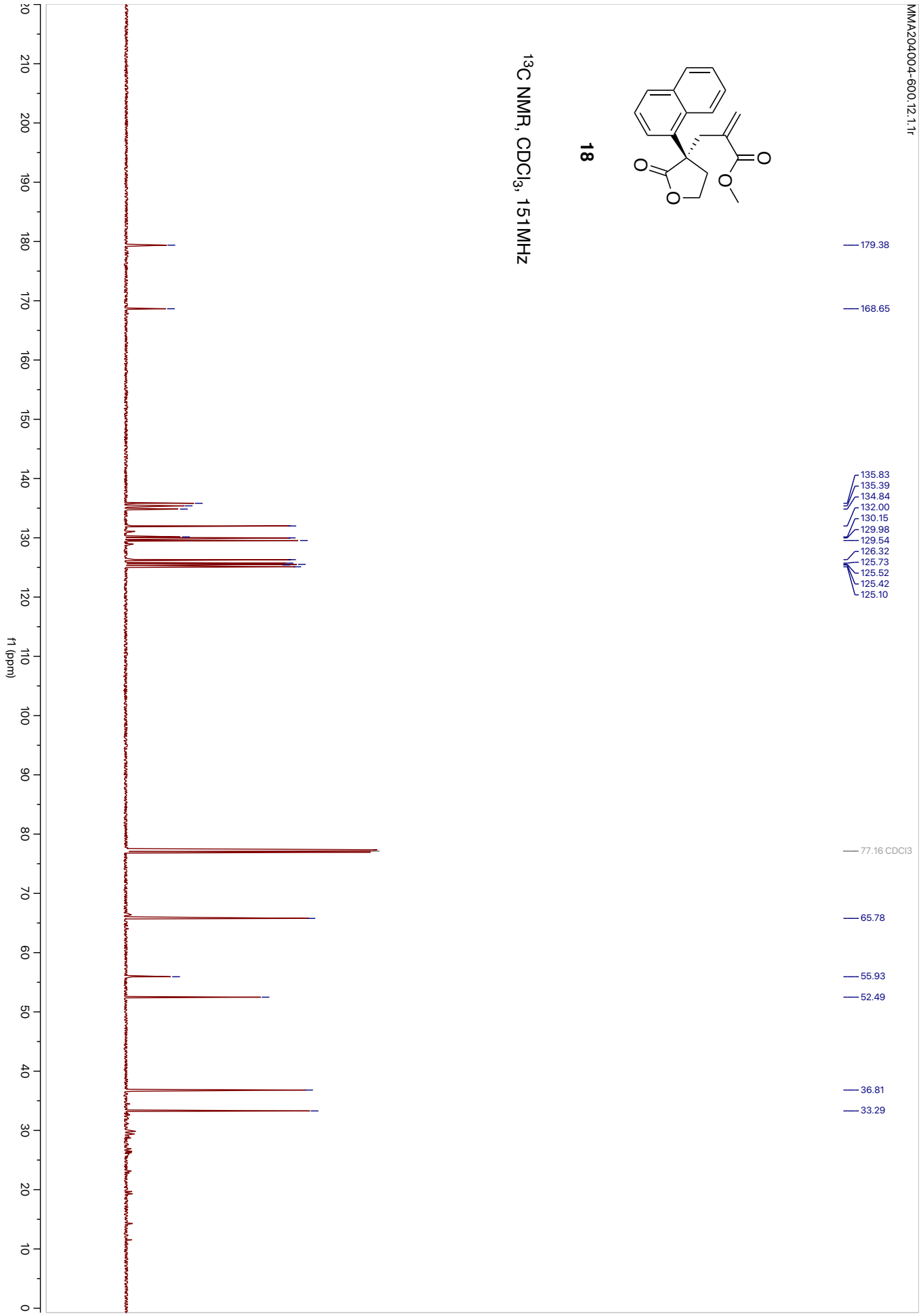


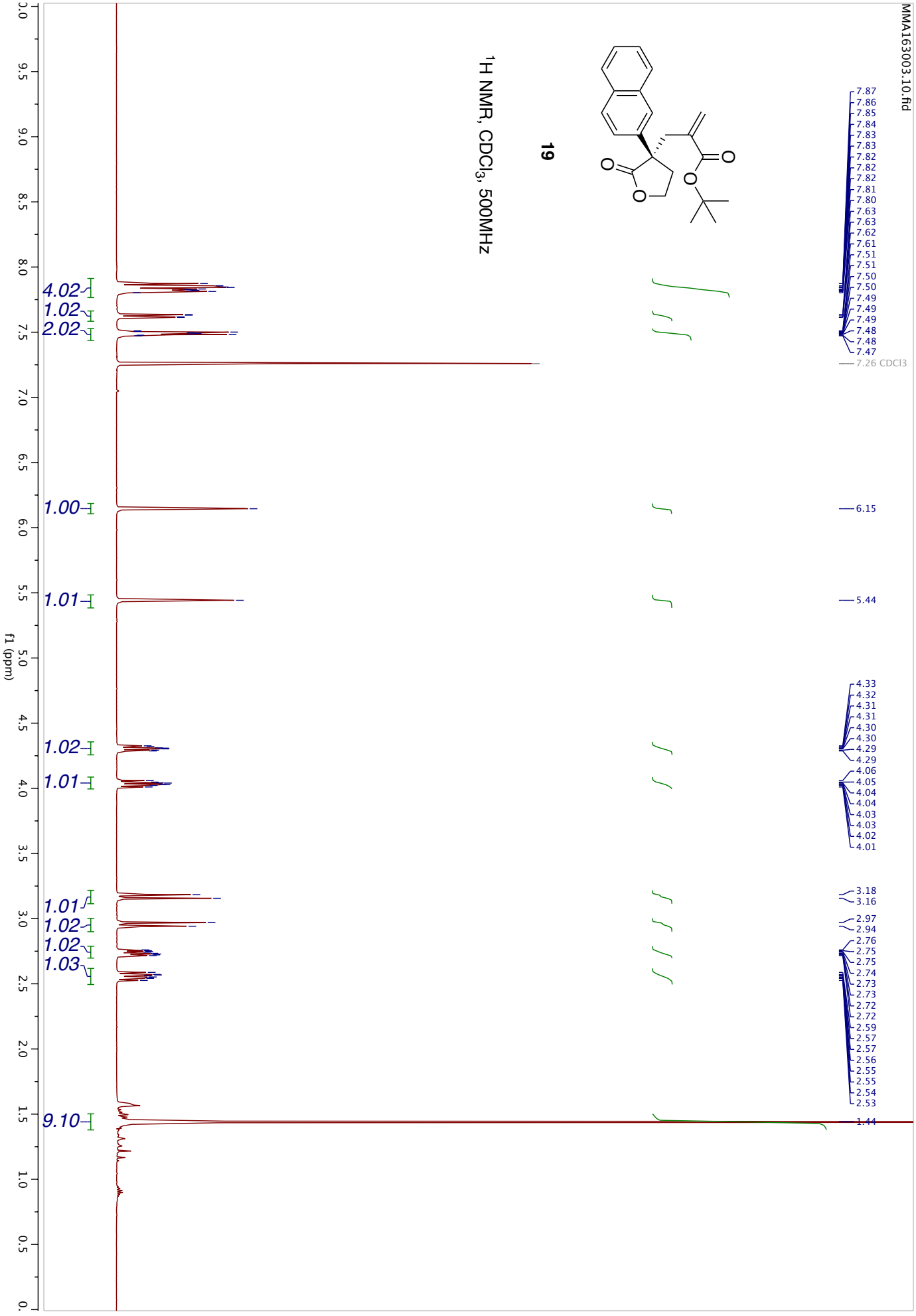
17

^{19}F NMR, $CDCl_3$, 471MHz

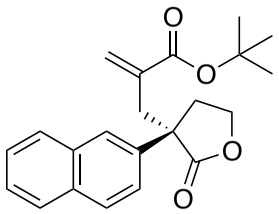



MMA204.10.fid
18
^{1}H NMR, $CDCl_3$, 600MHz
f1 (ppm)
1.00
0.99
0.99
1.00
1.10
0.97
0.99
1.00
1.01
1.04
3.04
1.04
1.01
1.02
1.00
1.02
8.71
8.69
7.92
7.92
7.92
7.91
7.91
7.90
7.83
7.83
7.82
7.81
7.81
7.81
7.67
7.67
7.66
7.65
7.65
7.64
7.64
7.54
7.54
7.53
7.53
7.53
7.51
7.51
7.44
7.44
7.43
7.43
7.39
7.38
7.38
7.36
7.26 CDCl3
6.43
5.95
4.22
4.22
4.20
4.20
4.18
4.18
3.89
3.87
3.86
3.78
3.75
3.11
3.08
3.00
3.00
2.99
2.99
2.98
2.97
2.96
2.96
2.56
2.54
2.54
2.53
2.52
2.52
2.51
2.50


MMA204004-600.12.1.1r
18
^{13}C NMR, $CDCl_3$, 151MHz
179.38
168.65
135.83
135.39
134.84
132.00
130.15
129.98
129.54
126.32
125.73
125.52
125.42
125.10
77.16 CDCl3
65.78
55.93
52.49
36.81
33.29
f1 (ppm)

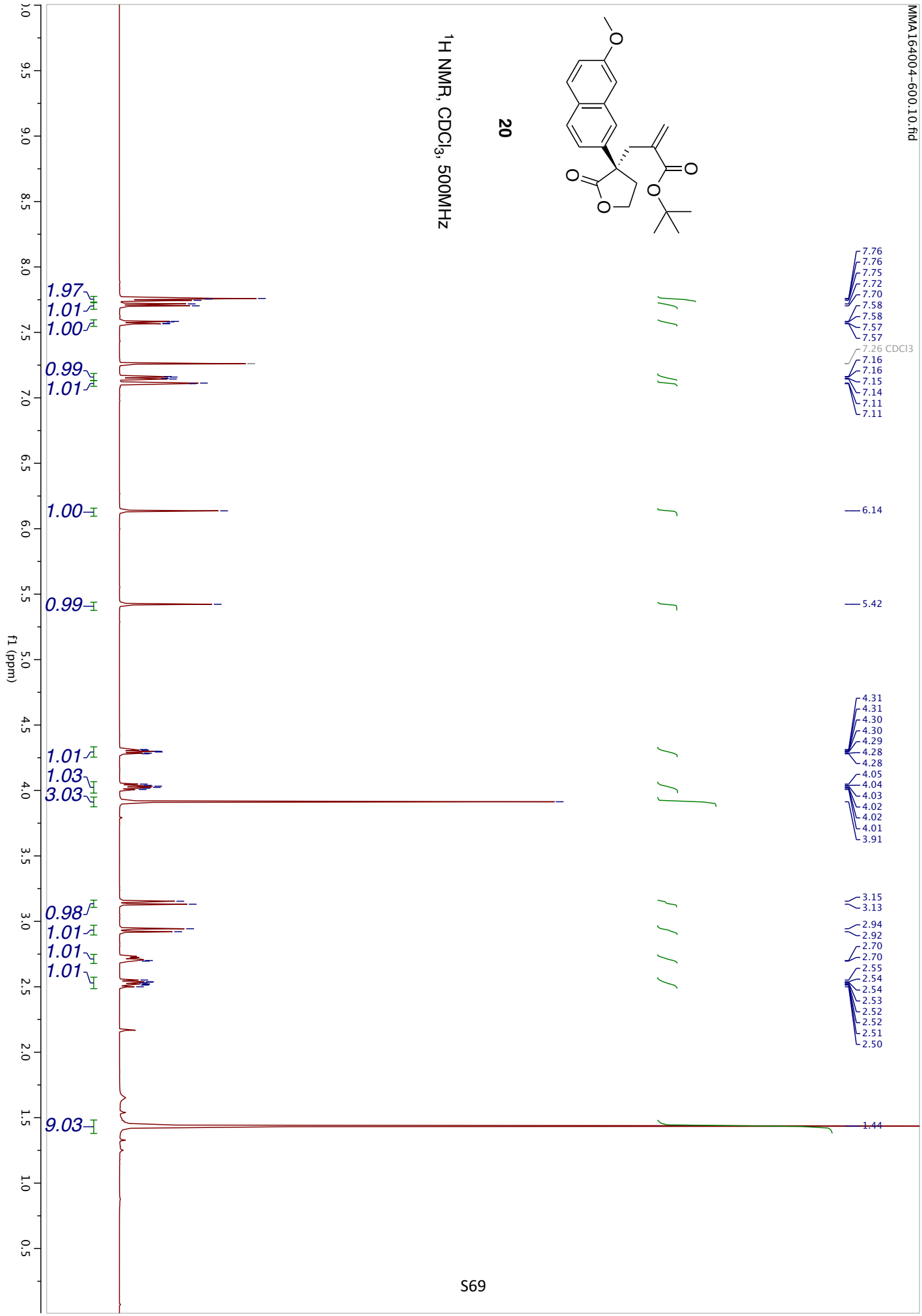

MMA163003.10.fid
19
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
4.02
1.02
2.02
1.00
1.01
1.02
1.01
1.01
1.02
1.02
1.03
9.10
7.87
7.86
7.85
7.84
7.83
7.83
7.82
7.82
7.82
7.81
7.80
7.63
7.63
7.62
7.61
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.26 CDCl3
6.15
5.44
4.33
4.32
4.31
4.31
4.30
4.30
4.29
4.29
4.06
4.05
4.04
4.04
4.03
4.03
4.02
4.01
3.18
3.16
2.97
2.94
2.76
2.75
2.75
2.74
2.73
2.73
2.72
2.72
2.59
2.57
2.57
2.56
2.55
2.55
2.54
2.53
1.44

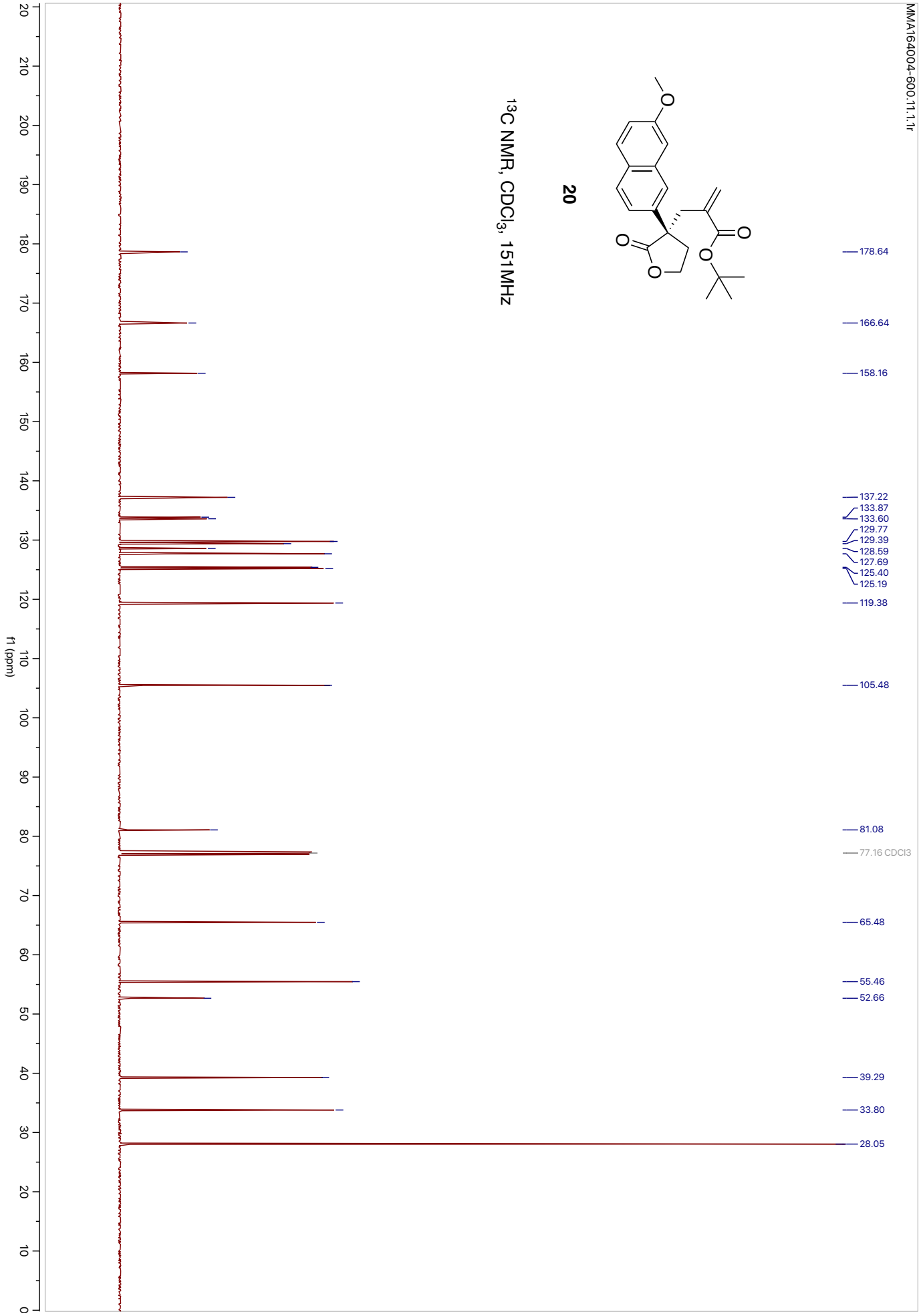
MMA163002.10.fid

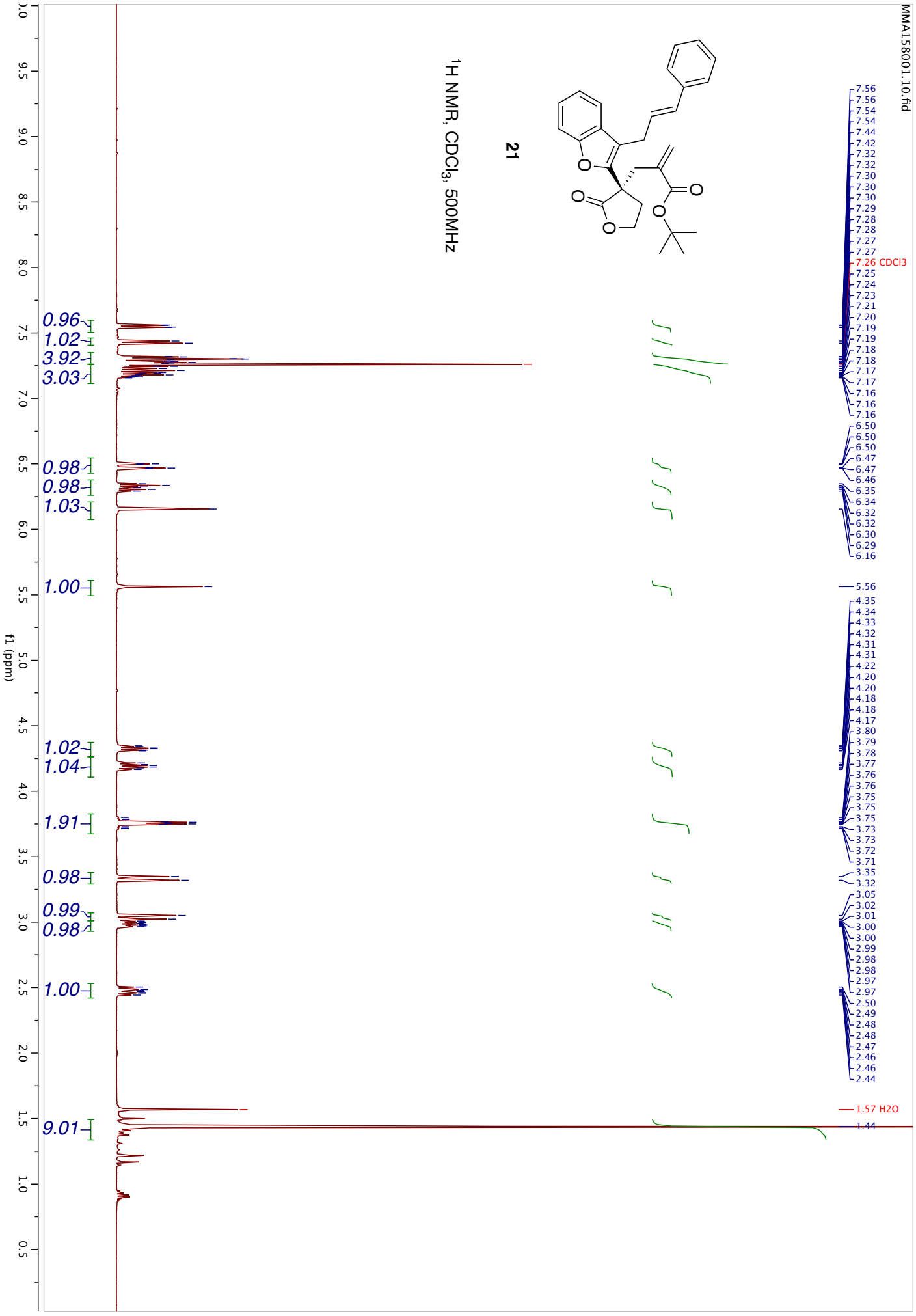


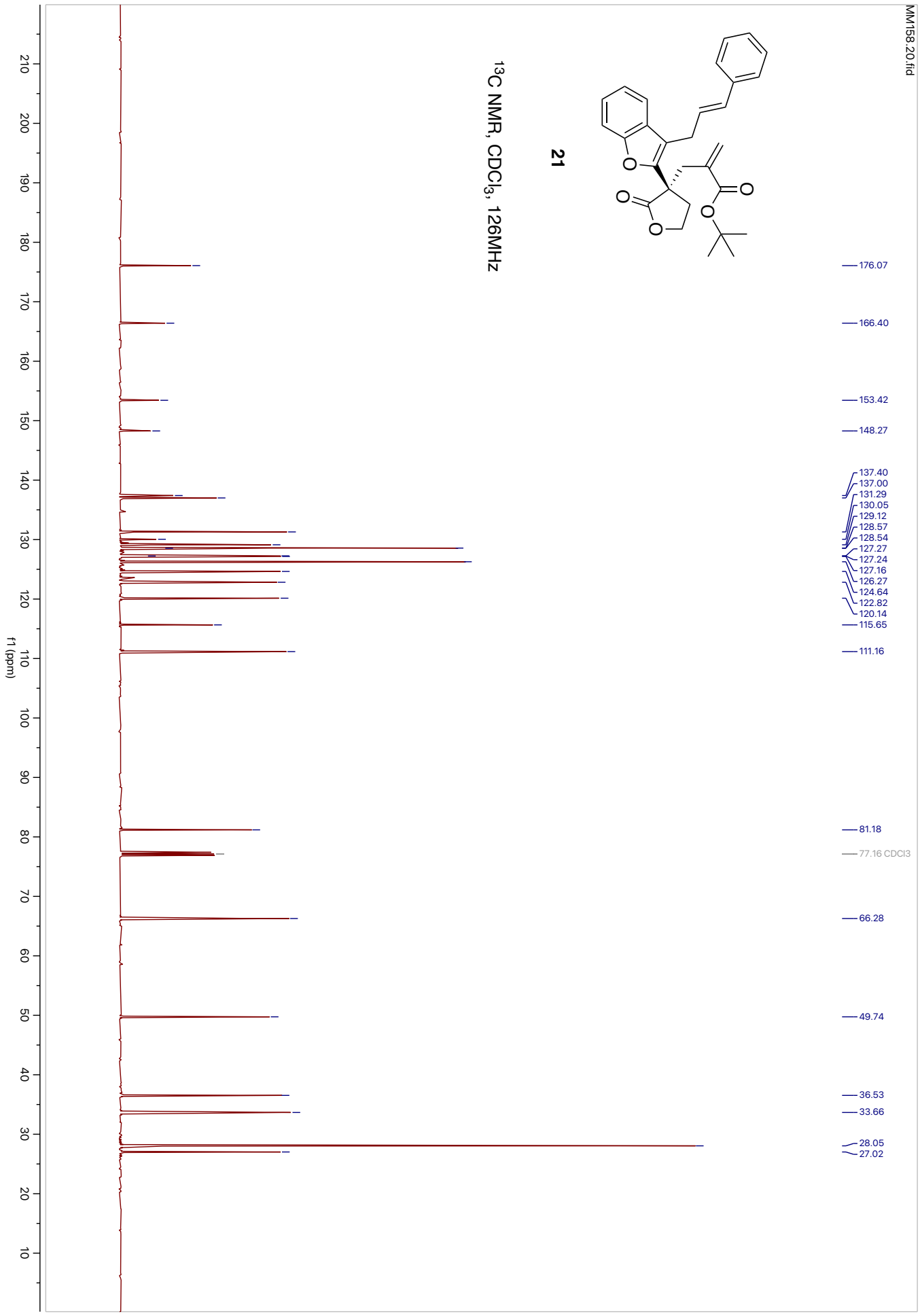
19

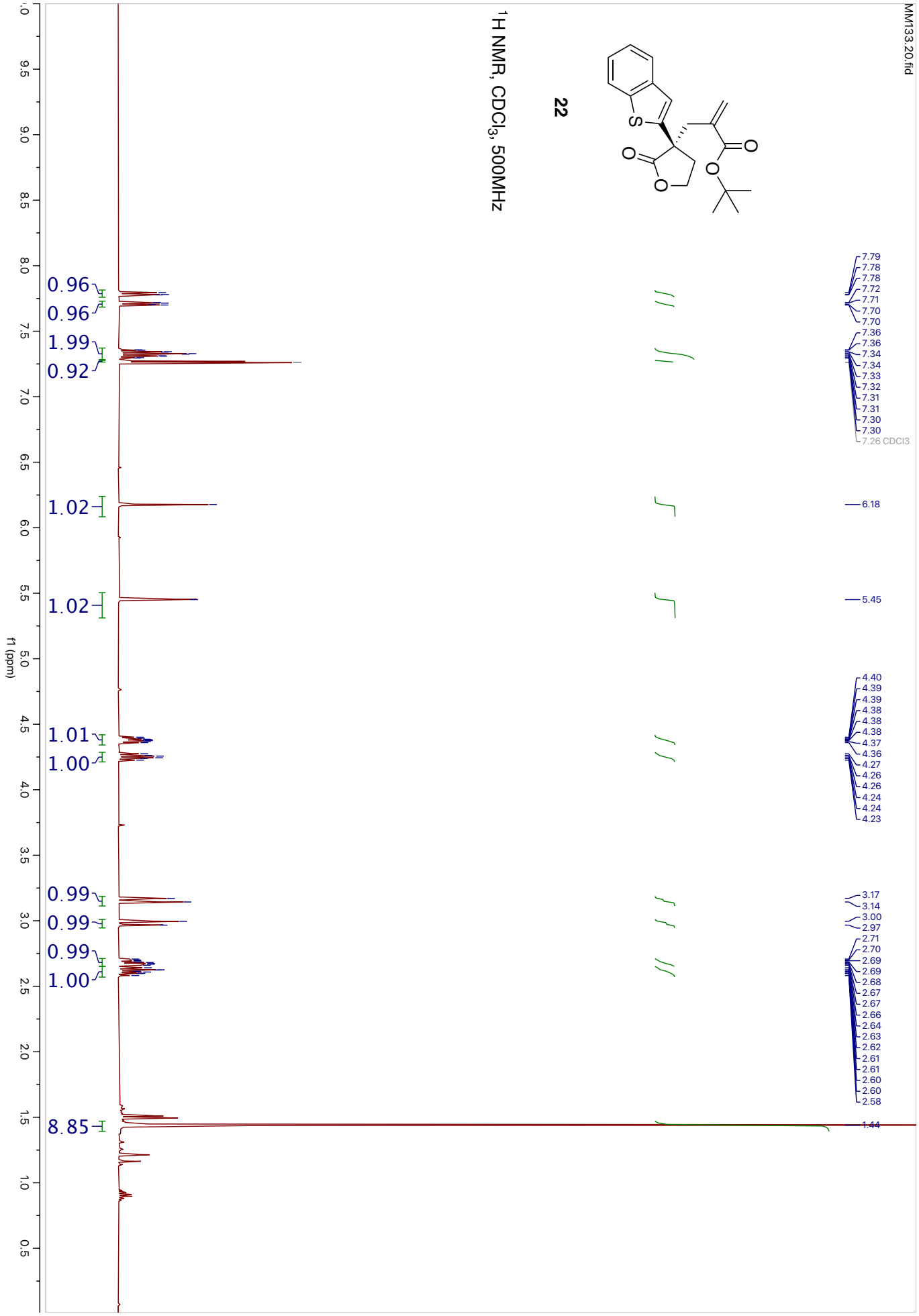
^{13}C NMR, $CDCl_3$, 126MHz

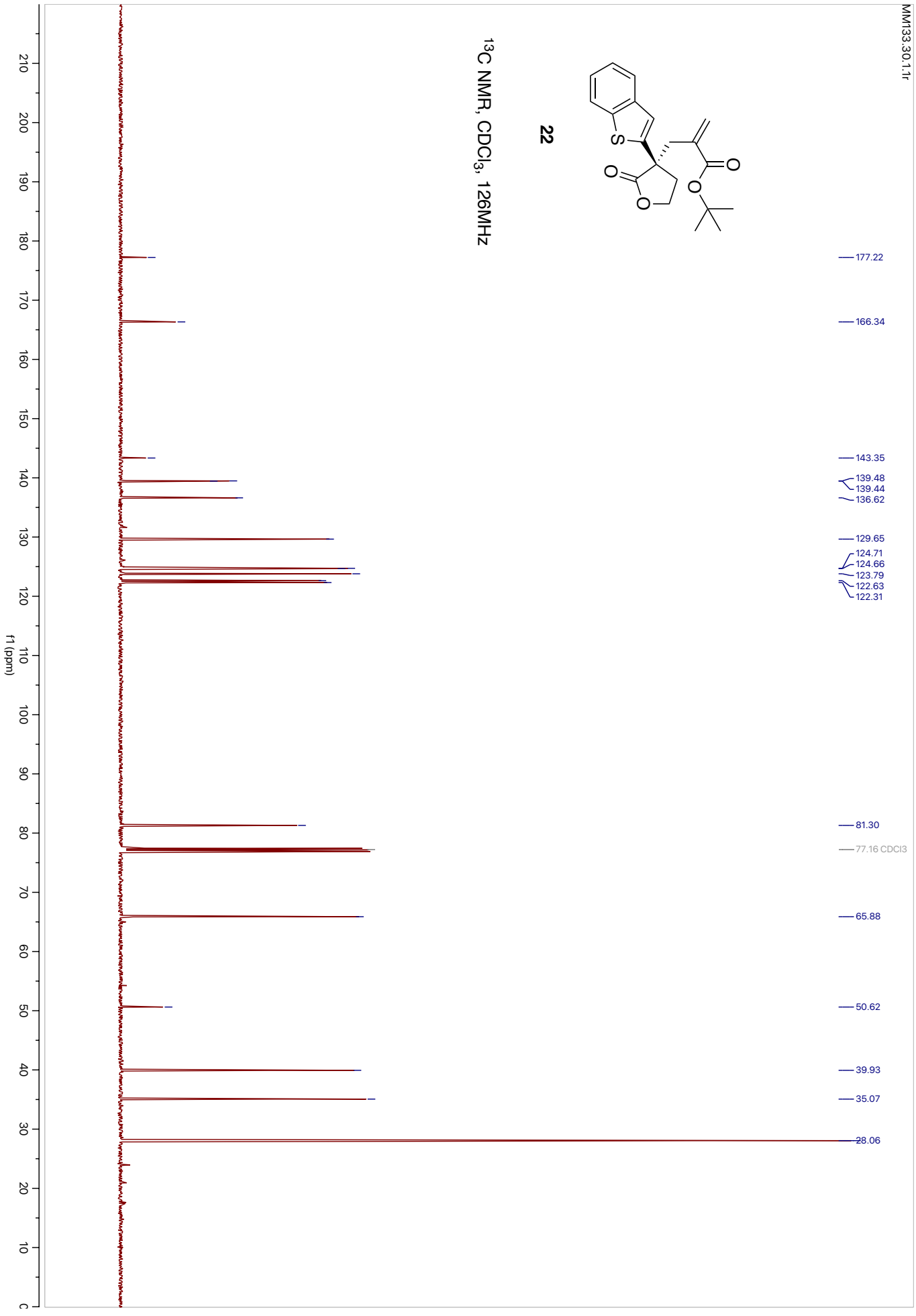

MMA164004-600.10.fid
20
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
1.97
1.01
1.00
0.99
1.01
1.00
0.99
1.01
1.03
3.03
0.98
1.01
1.01
1.01
9.03
7.76
7.76
7.75
7.72
7.70
7.58
7.58
7.57
7.57
7.26 CDCl3
7.16
7.16
7.15
7.14
7.11
7.11
6.14
5.42
4.31
4.31
4.30
4.30
4.29
4.28
4.28
4.05
4.04
4.03
4.02
4.02
4.01
3.91
3.15
3.13
2.94
2.92
2.70
2.70
2.55
2.54
2.54
2.53
2.52
2.52
2.51
2.50
1.44

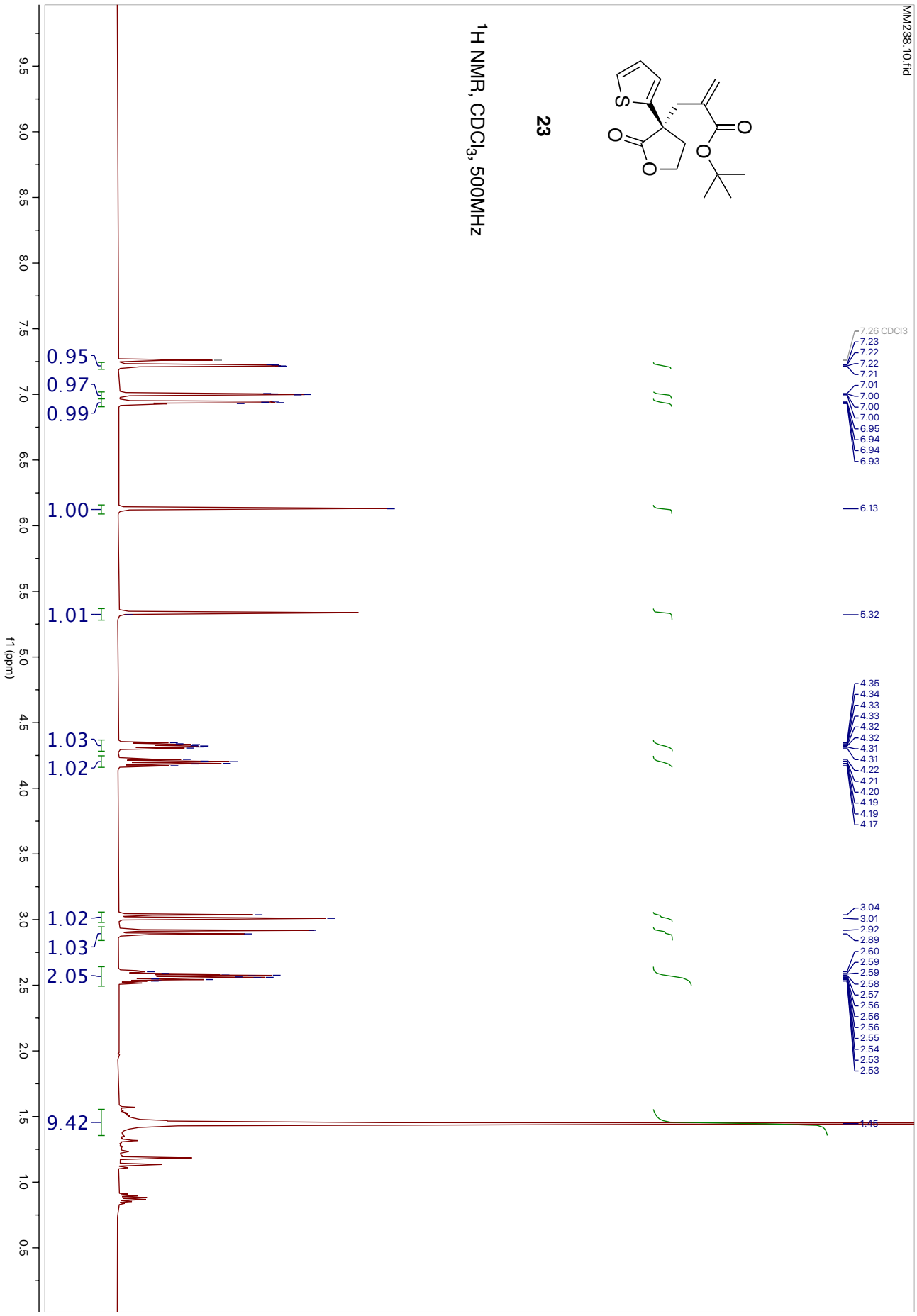

MMA164004-600.11.1.1r
20
^{13}C NMR, $CDCl_3$, 151MHz
f1 (ppm)
178.64
166.64
158.16
137.22
133.87
133.60
129.77
129.39
128.59
127.69
125.40
125.19
119.38
105.48
81.08
77.16 CDCl3
65.48
55.46
52.66
39.29
33.80
28.05

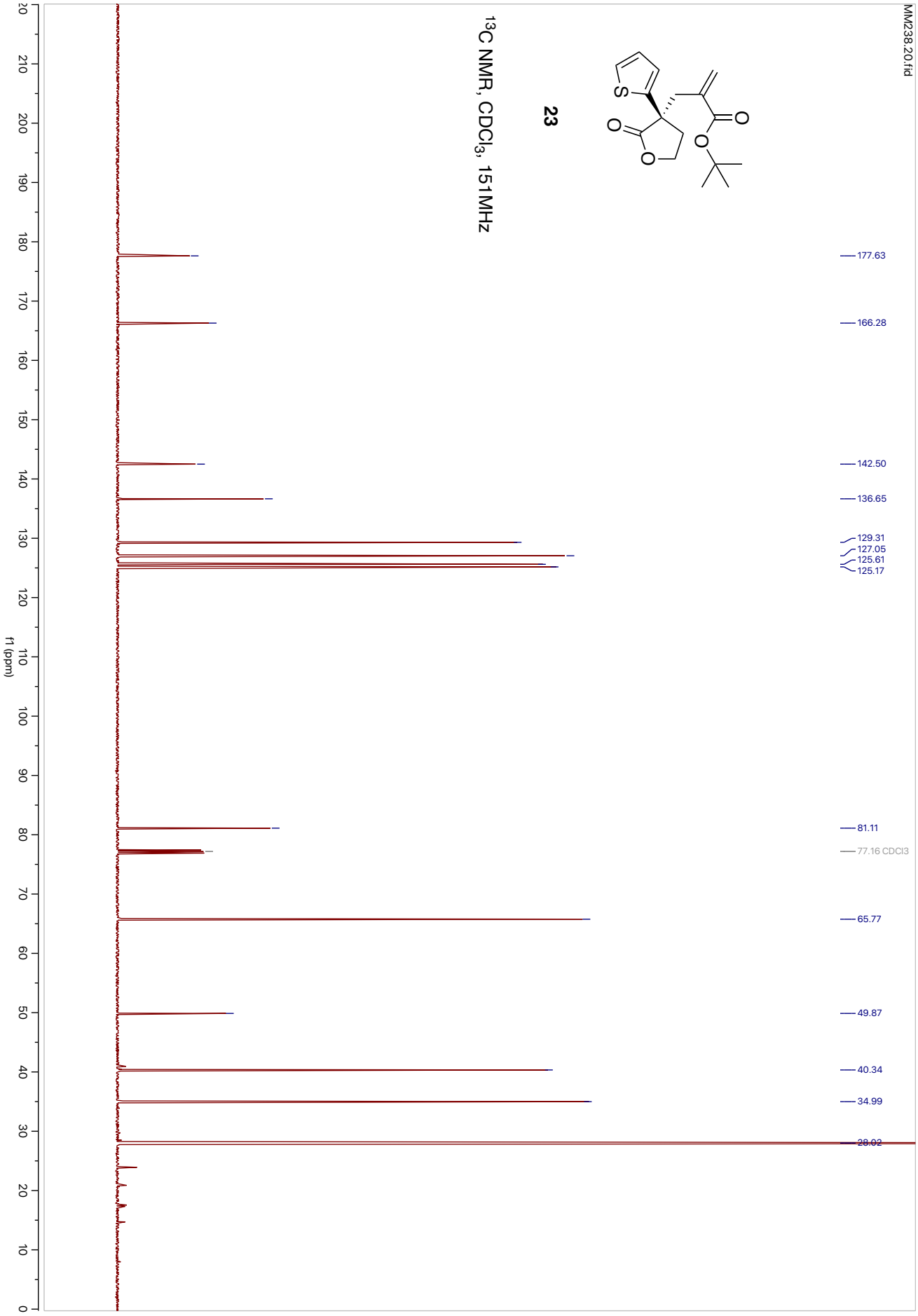

MMA158001.10.fid
21
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
0.96
1.02
3.92
3.03
0.98
0.98
1.03
1.00
1.02
1.04
1.91
0.98
0.99
0.98
1.00
9.01
7.26 CDCl3
1.57 H2O

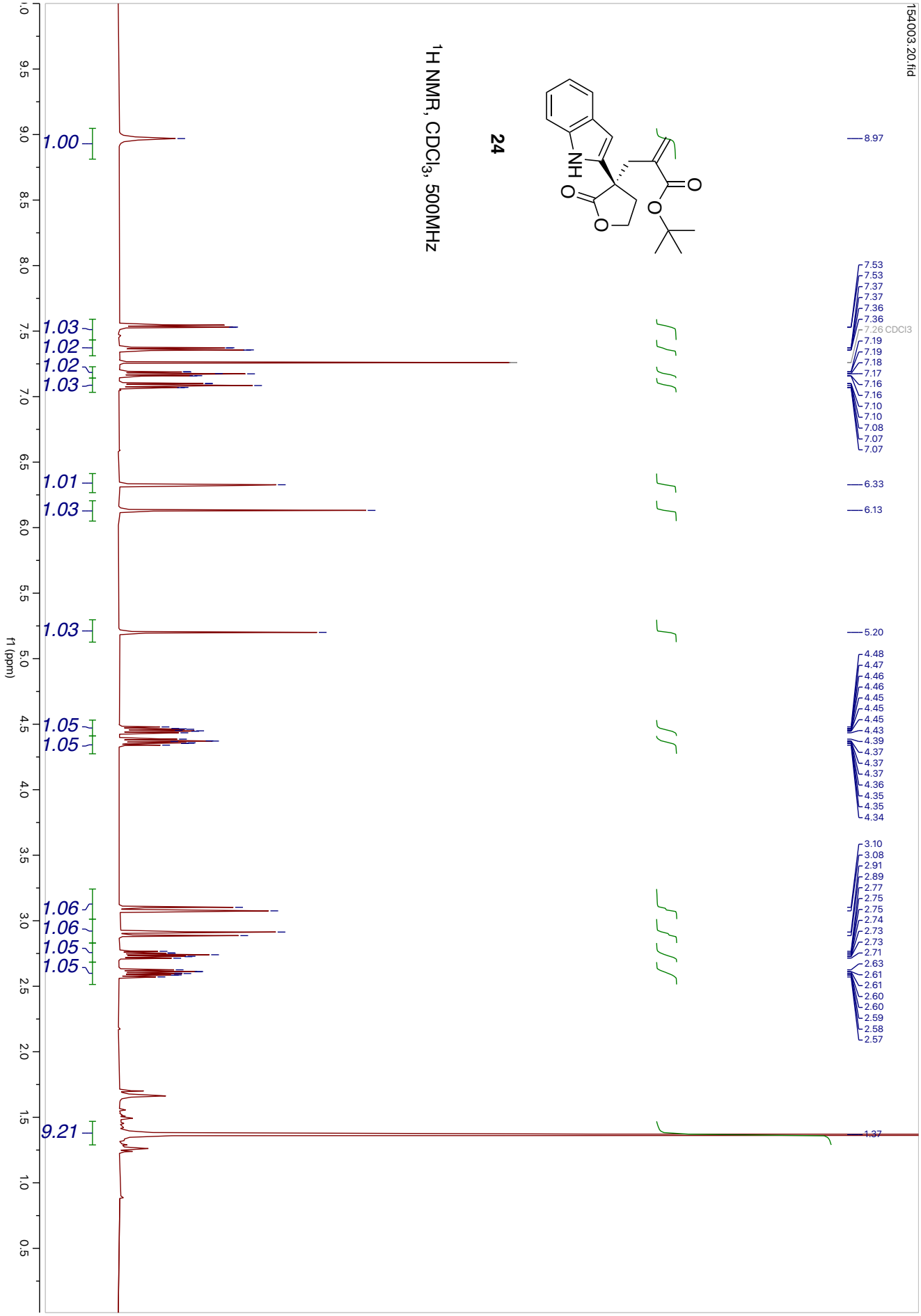

MM158.20.fid
21
^{13}C NMR, $CDCl_3$, 126MHz
f1 (ppm)
176.07
166.40
153.42
148.27
137.40
137.00
131.29
130.05
129.12
128.57
128.54
127.27
127.24
127.16
126.27
124.64
122.82
120.14
115.65
111.16
81.18
77.16 CDCl3
66.28
49.74
36.53
33.66
28.05
27.02

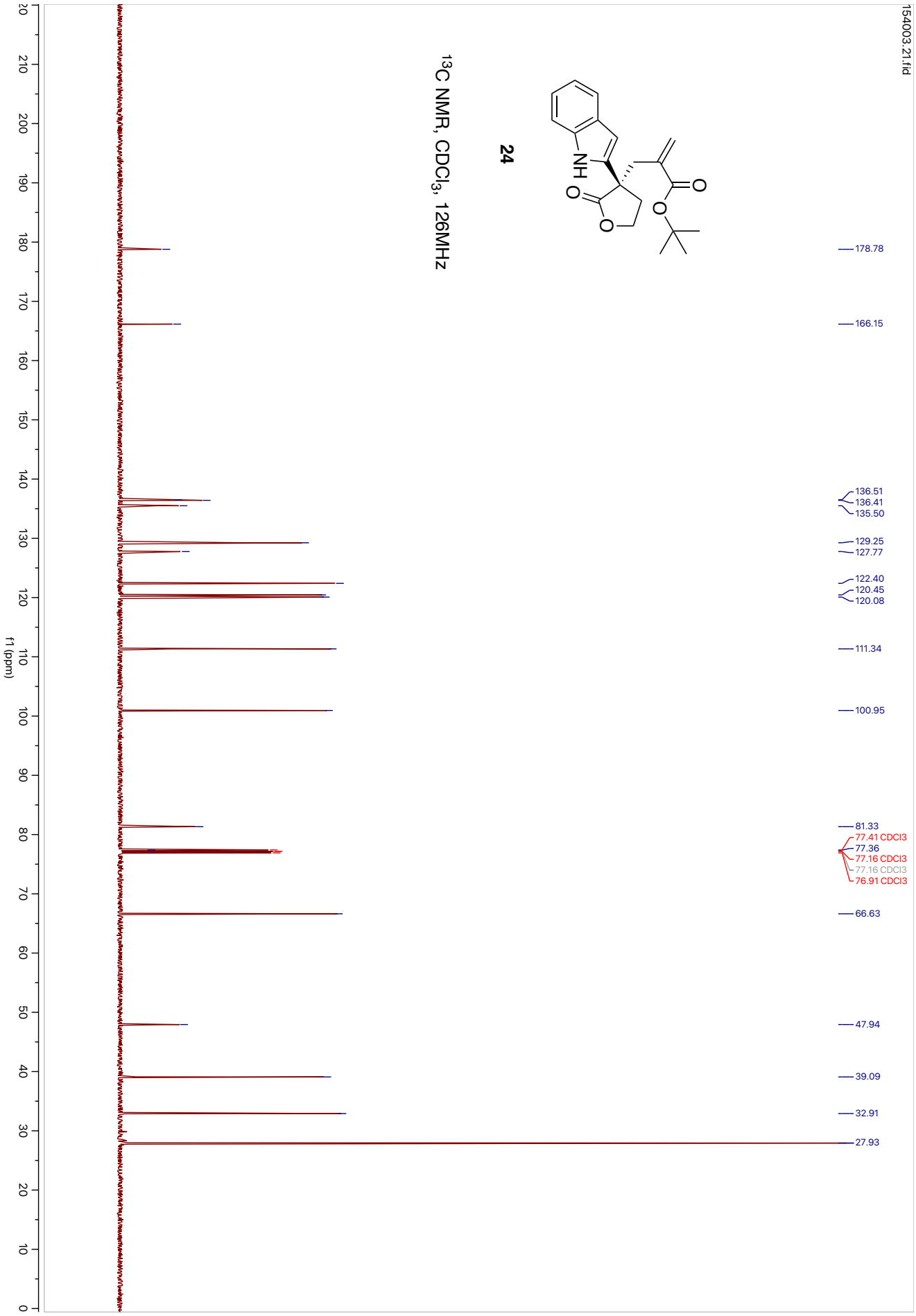

MM133.20.fid
^{1}H NMR, $CDCl_3$, 500MHz
22
f1 (ppm)
0.96
0.96
1.99
0.92
1.02
1.02
1.01
1.00
0.99
0.99
0.99
1.00
8.85
7.79
7.78
7.78
7.72
7.71
7.70
7.70
7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.26 CDCl3
6.18
5.45
4.40
4.39
4.39
4.38
4.38
4.38
4.37
4.36
4.27
4.26
4.26
4.24
4.24
4.23
3.17
3.14
3.00
2.97
2.71
2.70
2.69
2.69
2.68
2.67
2.67
2.66
2.64
2.63
2.62
2.61
2.61
2.60
2.60
2.58
1.44

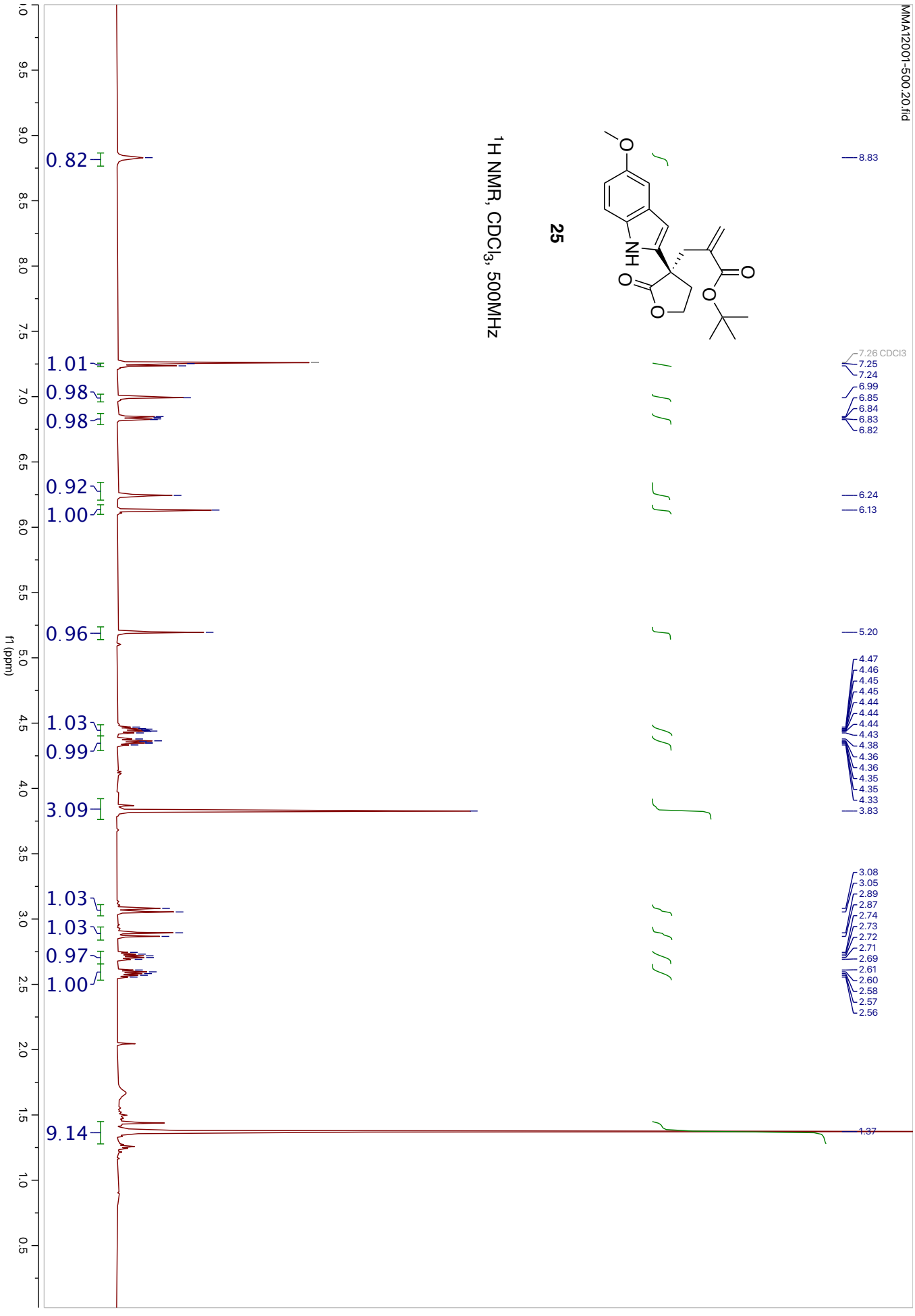

MM133.30.1.1r
22
^{13}C NMR, $CDCl_3$, 126MHz
177.22
166.34
143.35
139.48
139.44
136.62
129.65
124.71
124.66
123.79
122.63
122.31
81.30
77.16 CDCl3
65.88
50.62
39.93
35.07
28.06
f1 (ppm)

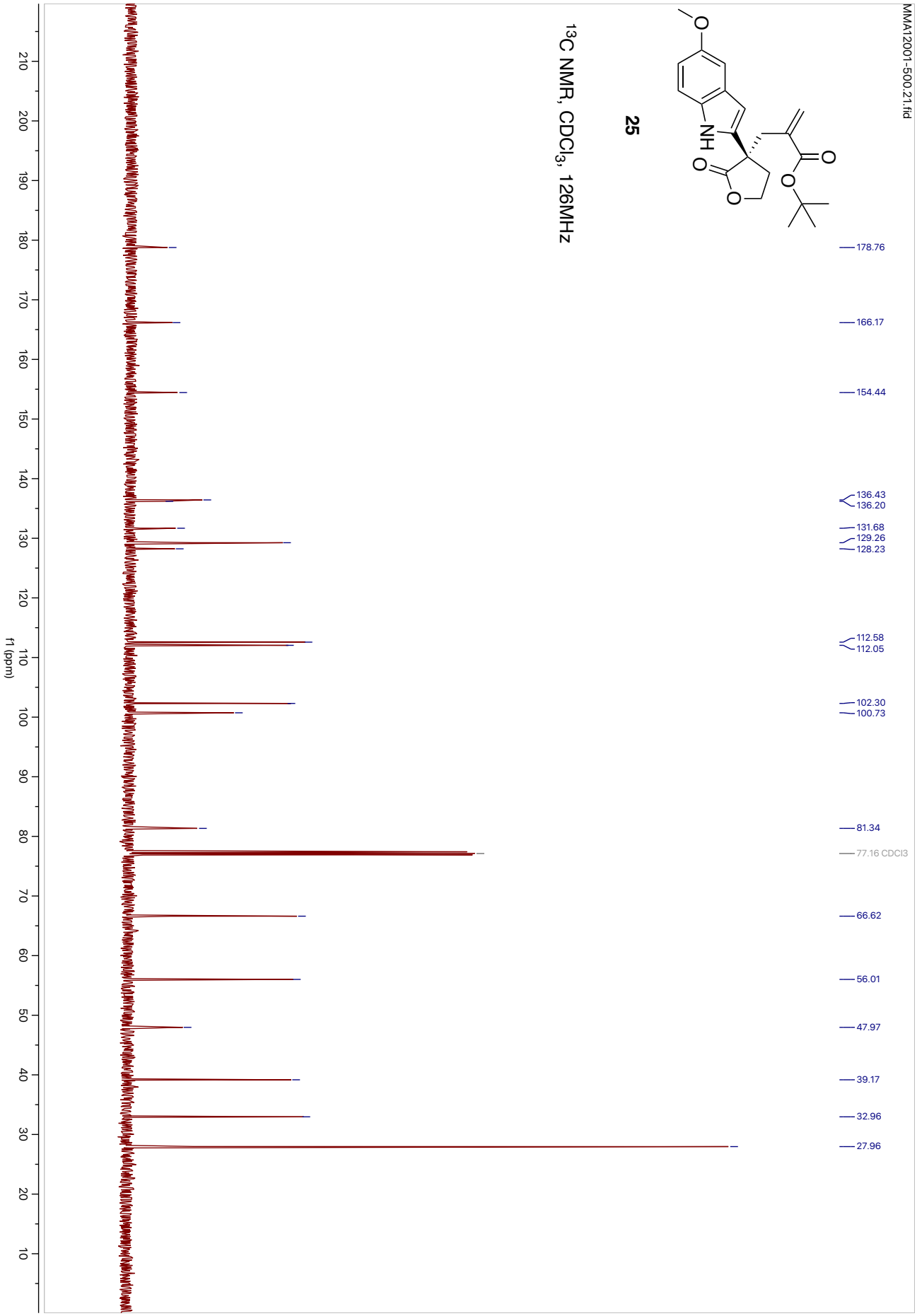

MM238.10.fid
23
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
0.95
0.97
0.99
1.00
1.01
1.03
1.02
1.02
1.03
2.05
9.42
7.26 CDCl3
7.23
7.22
7.22
7.21
7.01
7.00
7.00
7.00
6.95
6.94
6.94
6.93
6.13
5.32
4.35
4.34
4.33
4.33
4.32
4.32
4.31
4.31
4.22
4.21
4.20
4.19
4.19
4.17
3.04
3.01
2.92
2.89
2.60
2.59
2.59
2.58
2.57
2.56
2.56
2.56
2.55
2.54
2.53
2.53
1.45

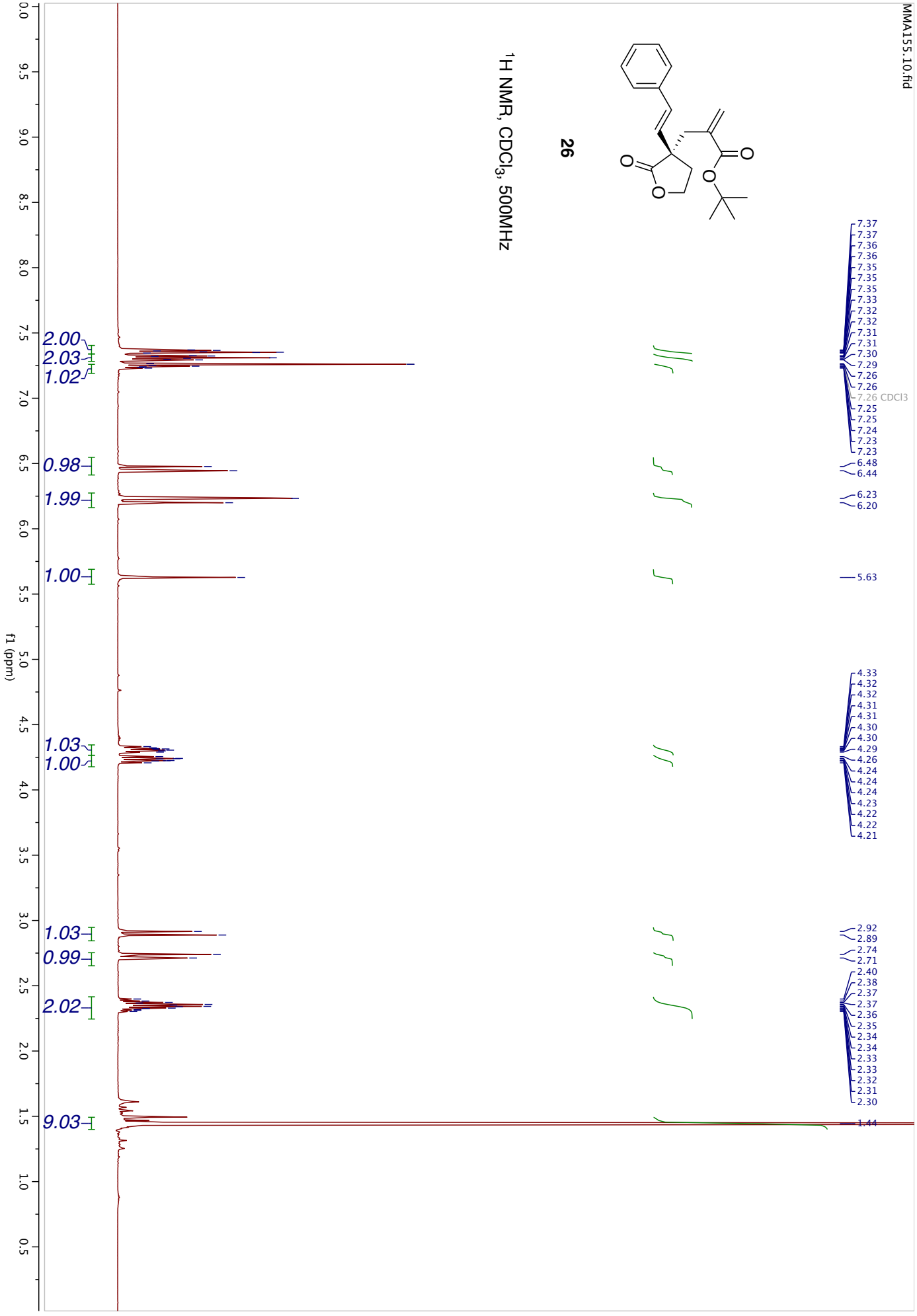

MM238.20.fid
23
^{13}C NMR, $CDCl_3$, 151MHz
177.63
166.28
142.50
136.65
129.31
127.05
125.61
125.17
81.11
77.16 CDCl3
65.77
49.87
40.34
34.99
28.02
f1 (ppm)

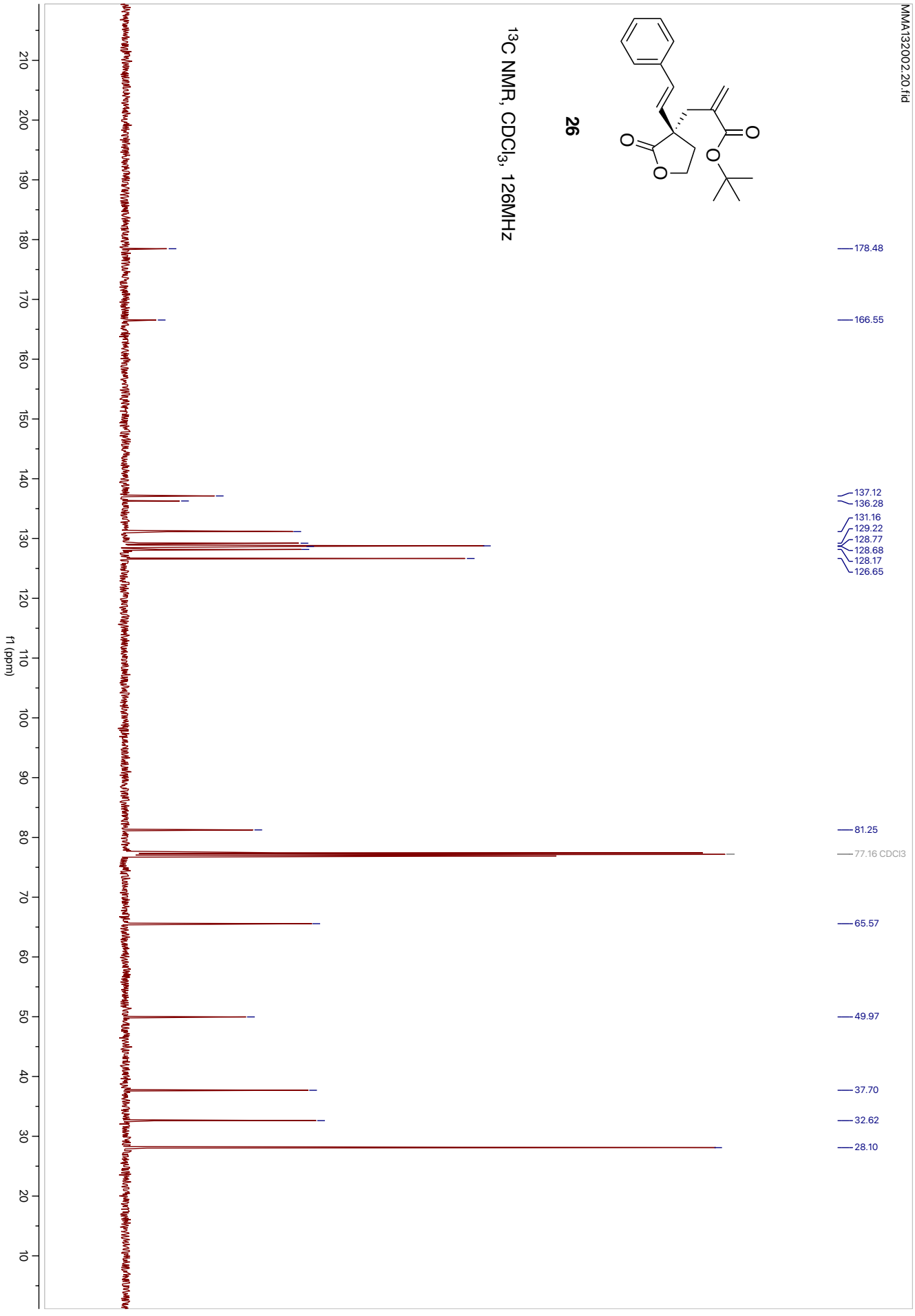

154003.20.fid
24
1H NMR, CDCl3, 500MHz
NH
O
O
O
O
f1 (ppm)
1.00
1.03
1.02
1.02
1.03
1.01
1.03
1.03
1.05
1.05
1.06
1.06
1.05
1.05
9.21
8.97
7.53
7.53
7.37
7.37
7.36
7.36
7.26 CDCl3
7.19
7.19
7.18
7.17
7.16
7.16
7.10
7.10
7.08
7.07
7.07
6.33
6.13
5.20
4.48
4.47
4.46
4.46
4.45
4.45
4.45
4.43
4.39
4.37
4.37
4.37
4.36
4.35
4.35
4.34
3.10
3.08
2.91
2.89
2.77
2.75
2.75
2.74
2.73
2.73
2.71
2.63
2.61
2.61
2.60
2.60
2.59
2.58
2.57
1.37

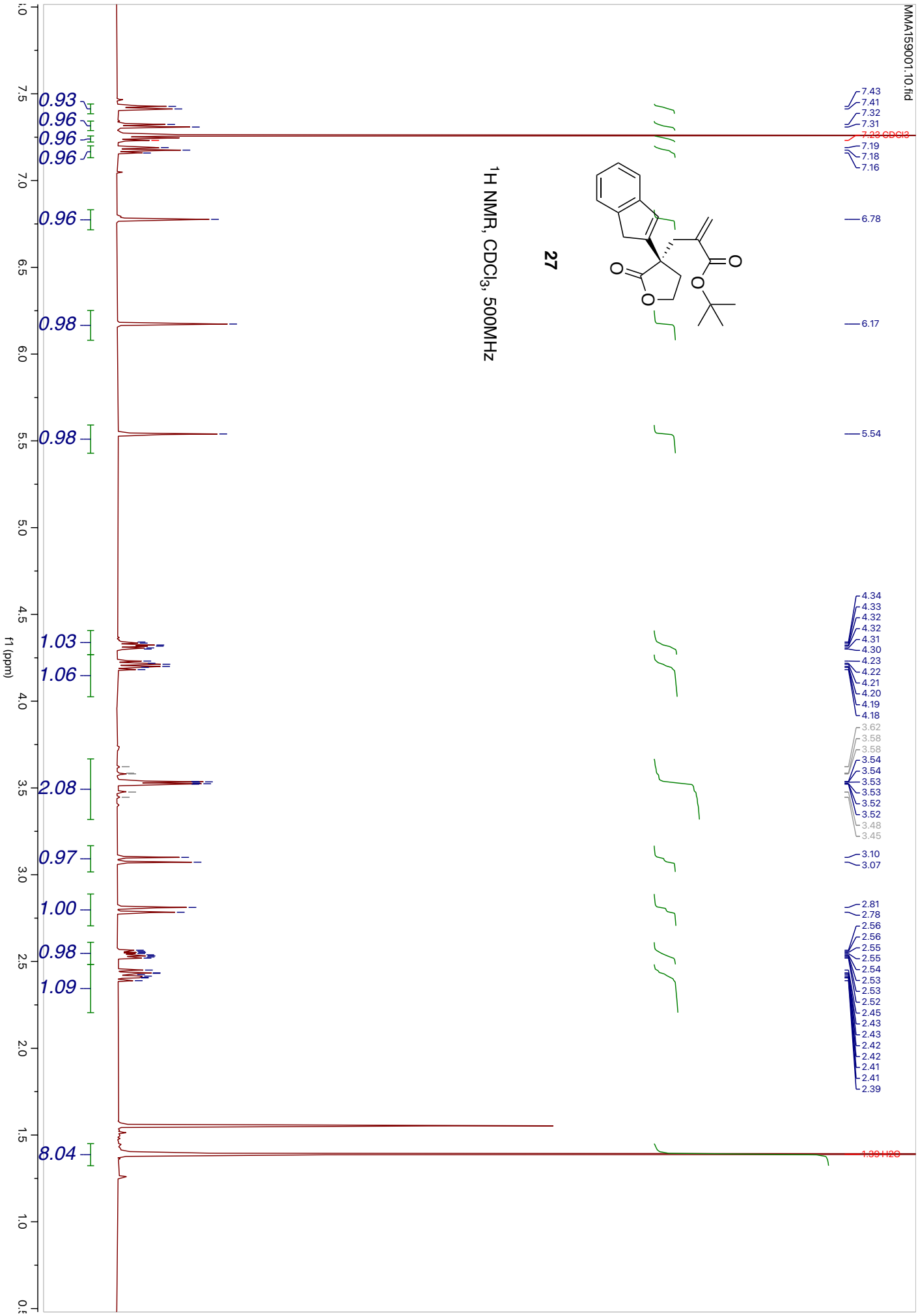

154003.21.fid
24
^{13}C NMR, $CDCl_3$, 126MHz
NH
O
O
O
O
178.78
166.15
136.51
136.41
135.50
129.25
127.77
122.40
120.45
120.08
111.34
100.95
81.33
77.41 CDCl3
77.36
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
66.63
47.94
39.09
32.91
27.93
f1 (ppm)

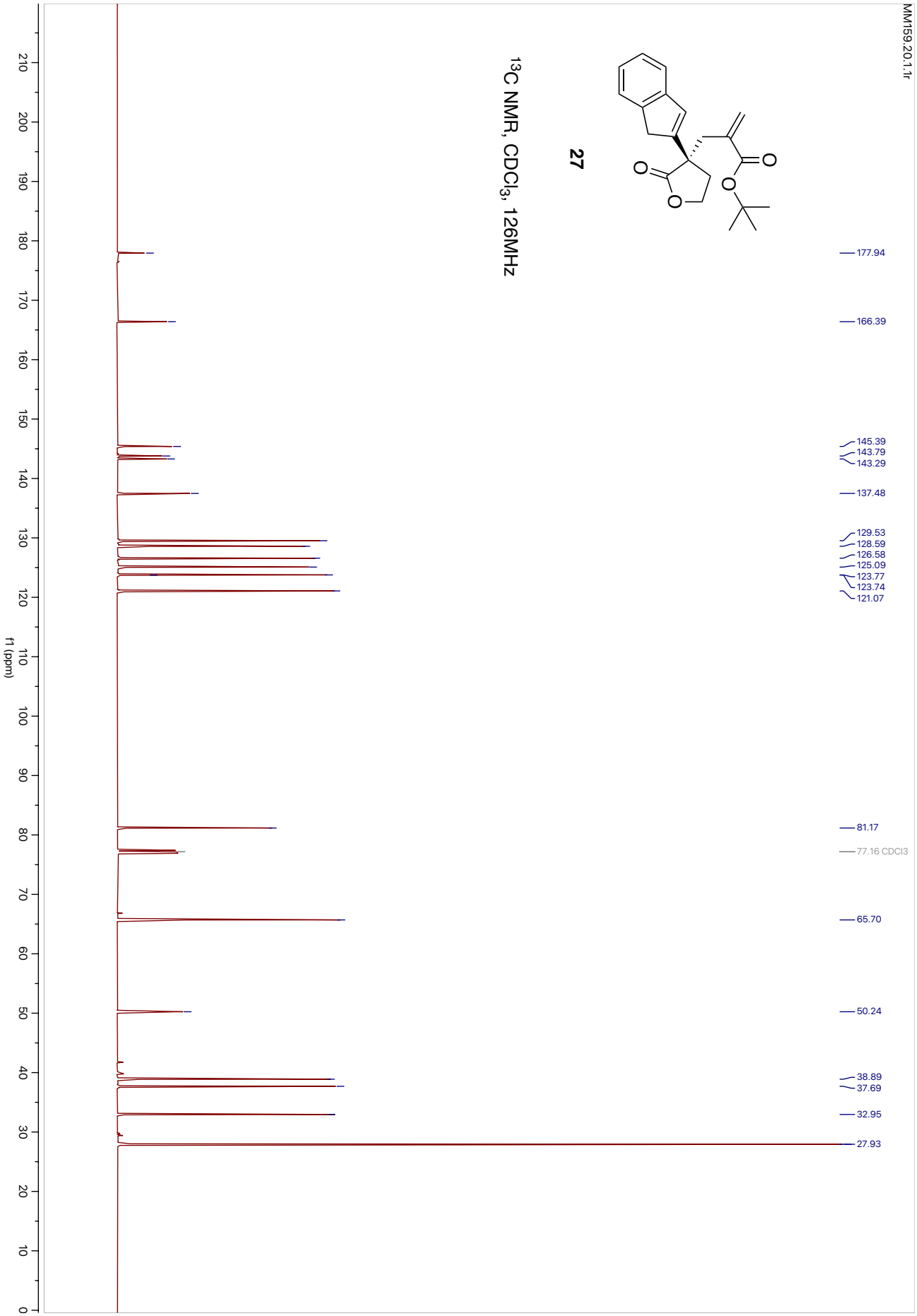

MMA12001-500.20.fid
25
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
0.82
1.01
0.98
0.98
0.92
1.00
0.96
1.03
0.99
3.09
1.03
1.03
0.97
1.00
9.14
8.83
7.26 CDCl3
7.25
7.24
6.99
6.85
6.84
6.83
6.82
6.24
6.13
5.20
4.47
4.46
4.45
4.45
4.44
4.44
4.44
4.43
4.38
4.36
4.36
4.35
4.35
4.33
3.83
3.08
3.05
2.89
2.87
2.74
2.73
2.72
2.71
2.69
2.61
2.60
2.58
2.57
2.56
1.37

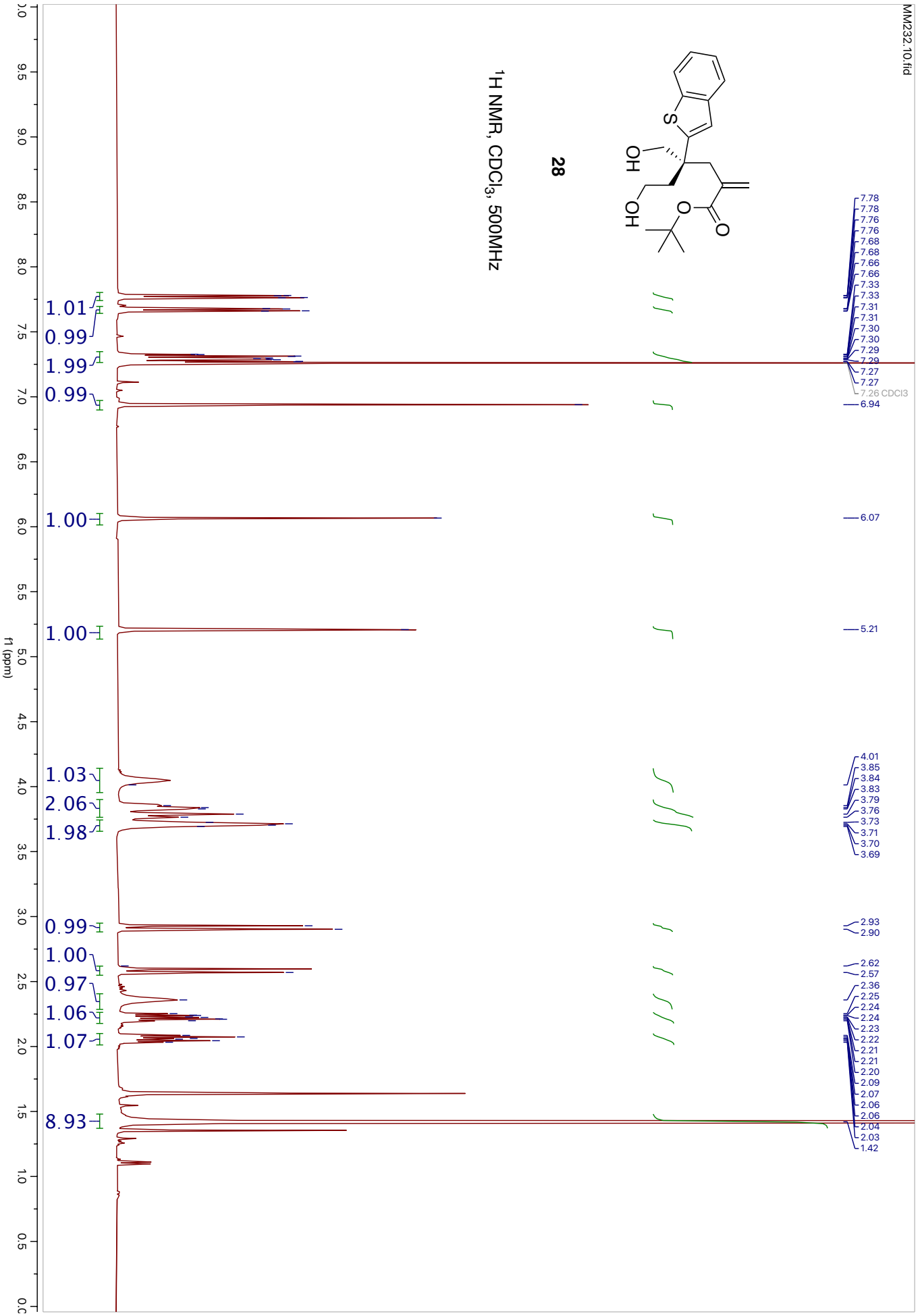

MMA12001-500.21.fid
25
^{13}C NMR, $CDCl_3$, 126MHz
178.76
166.17
154.44
136.43
136.20
131.68
129.26
128.23
112.58
112.05
102.30
100.73
81.34
77.16 CDCl3
66.62
56.01
47.97
39.17
32.96
27.96
f1 (ppm)

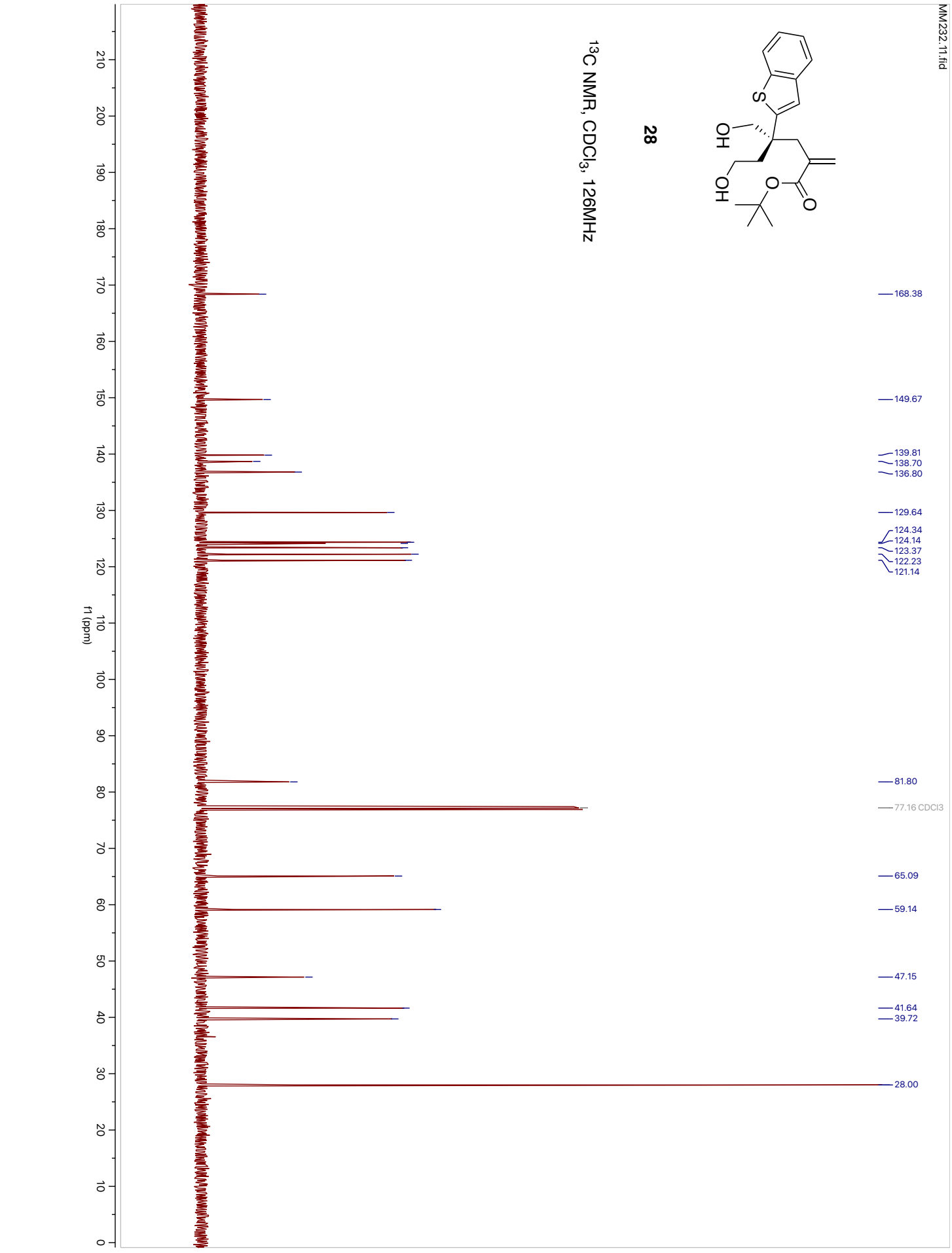

MMA155.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
26
f1 (ppm)
2.00
2.03
1.02
0.98
1.99
1.00
1.03
1.00
1.03
0.99
2.02
9.03
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
7.26
7.26 CDCl3
7.25
7.25
7.24
7.23
7.23
6.48
6.44
6.23
6.20
5.63
4.33
4.32
4.32
4.31
4.31
4.30
4.30
4.29
4.26
4.24
4.24
4.24
4.23
4.22
4.22
4.21
2.92
2.89
2.74
2.71
2.40
2.38
2.37
2.37
2.36
2.35
2.34
2.34
2.33
2.33
2.32
2.31
2.30
1.44

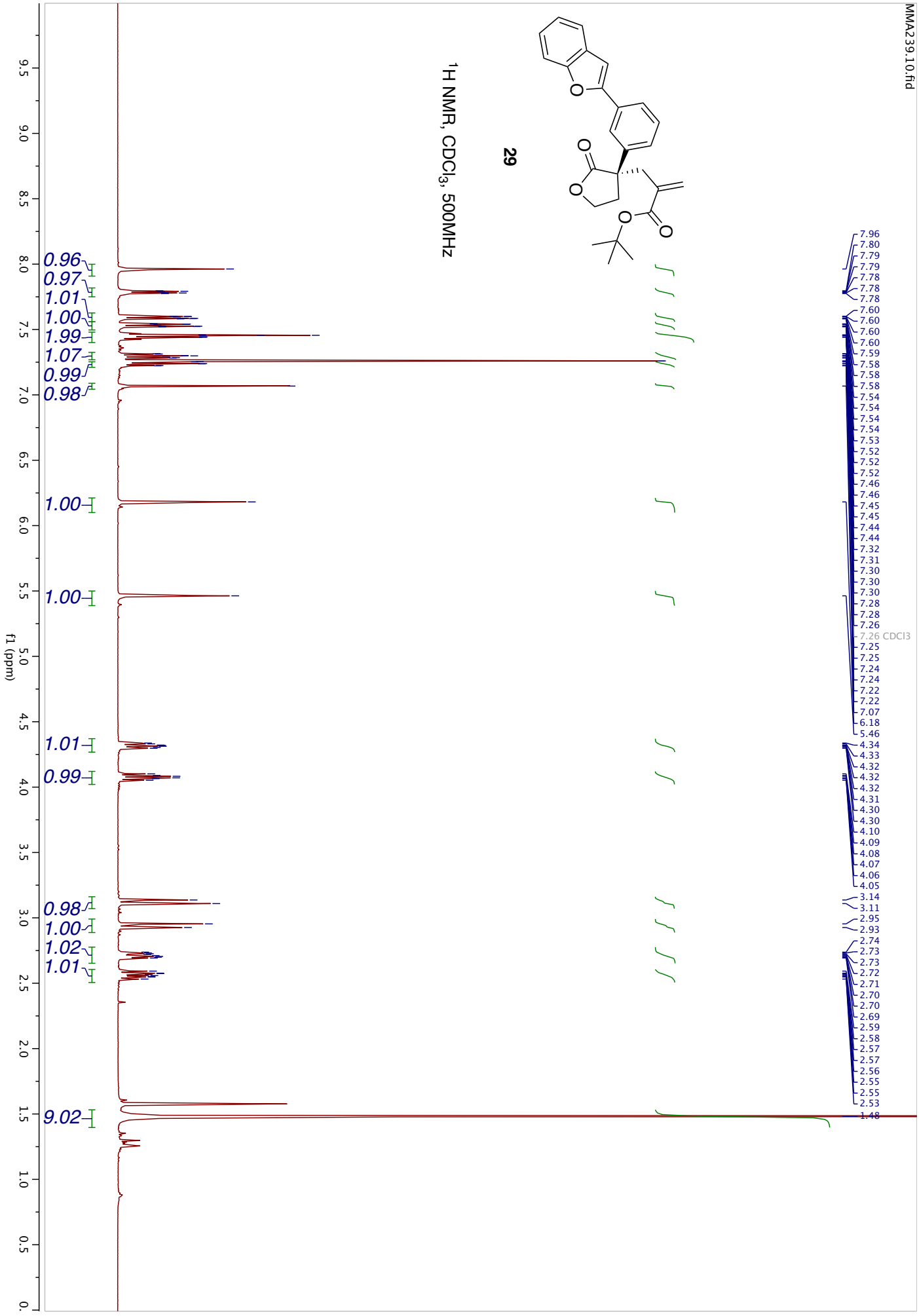

MMA132002.20.fid
^{13}C NMR, $CDCl_3$, 126MHz
26
178.48
166.55
137.12
136.28
131.16
129.22
128.77
128.68
128.17
126.65
81.25
77.16 CDCl3
65.57
49.97
37.70
32.62
28.10
f1 (ppm)

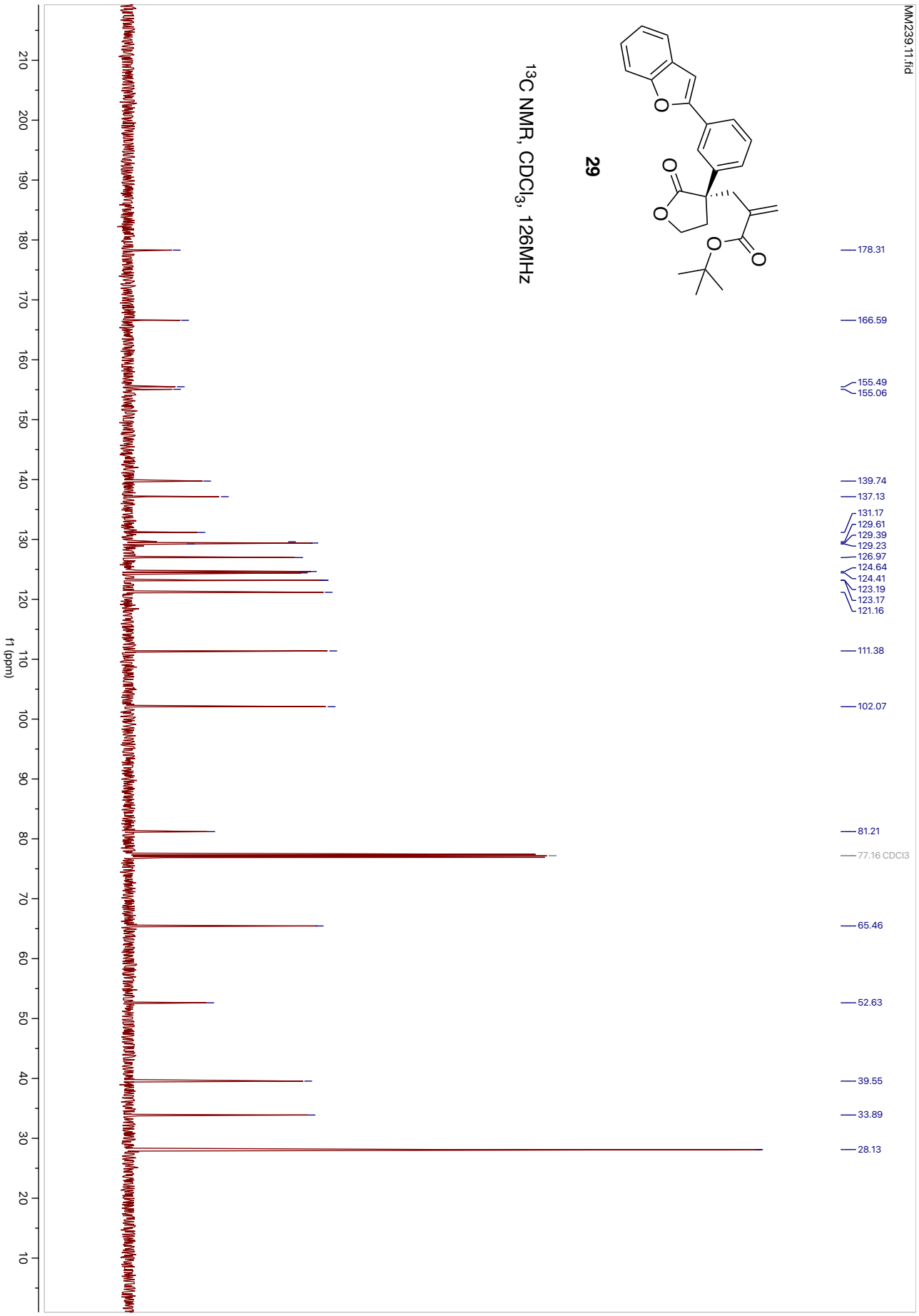

MMA159001.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
27
f1 (ppm)
0.93
0.96
0.96
0.96
0.96
0.98
0.98
1.03
1.06
2.08
0.97
1.00
0.98
1.09
8.04
7.43
7.41
7.32
7.31
7.26 CDCl3
7.19
7.18
7.16
6.78
6.17
5.54
4.34
4.33
4.32
4.32
4.31
4.30
4.23
4.22
4.21
4.20
4.19
4.18
3.62
3.58
3.58
3.54
3.54
3.53
3.53
3.52
3.52
3.48
3.45
3.10
3.07
2.81
2.78
2.56
2.56
2.55
2.55
2.54
2.53
2.53
2.52
2.45
2.43
2.43
2.42
2.42
2.41
2.41
2.39
1.30 H2O

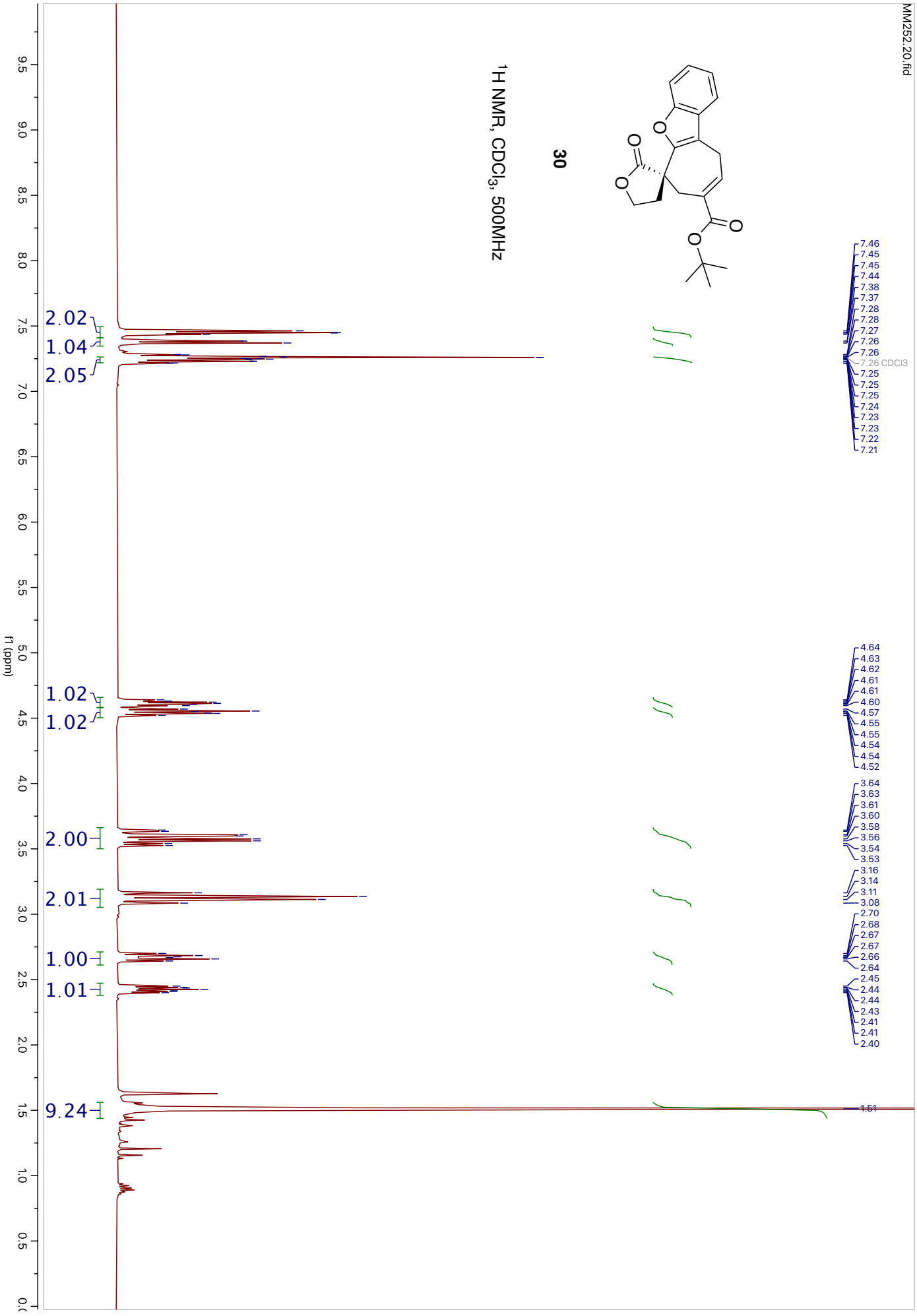

MM159.20.1.1r
27
^{13}C NMR, $CDCl_3$, 126MHz
177.94
166.39
145.39
143.79
143.29
137.48
129.53
128.59
126.58
125.09
123.77
123.74
121.07
81.17
77.16 CDCl3
65.70
50.24
38.89
37.69
32.95
27.93
f1 (ppm)

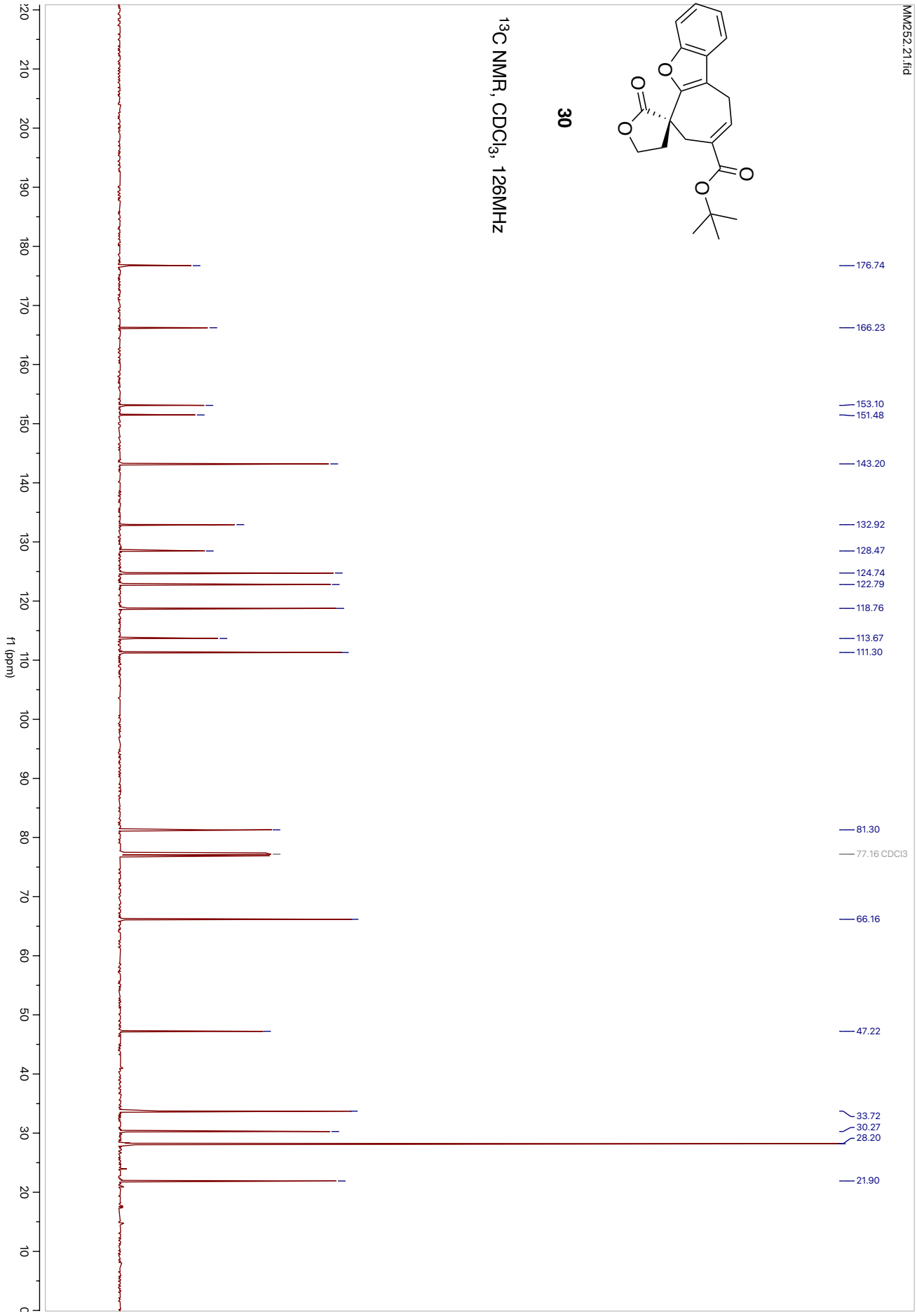

MM232.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
28
OH
OH
O
O
S
f1 (ppm)
1.01
0.99
1.99
0.99
1.00
1.00
1.03
2.06
1.98
0.99
1.00
0.97
1.06
1.07
8.93
7.78
7.78
7.76
7.76
7.68
7.68
7.66
7.66
7.33
7.33
7.31
7.31
7.30
7.30
7.29
7.29
7.27
7.27
7.26 CDCl3
6.94
6.07
5.21
4.01
3.85
3.84
3.83
3.79
3.76
3.73
3.71
3.70
3.69
2.93
2.90
2.62
2.57
2.36
2.25
2.24
2.24
2.23
2.22
2.21
2.21
2.20
2.09
2.07
2.06
2.06
2.04
2.03
1.42

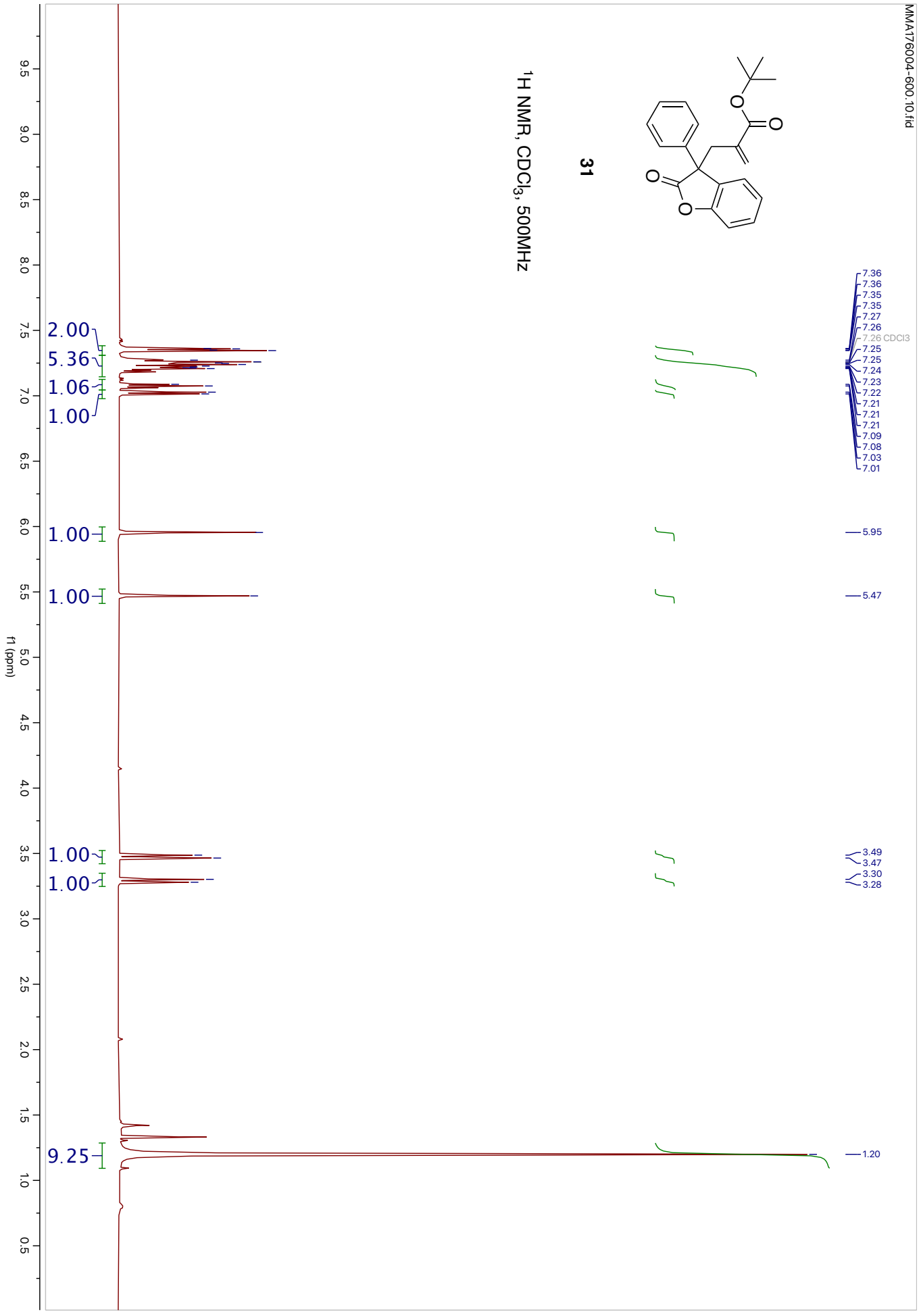

MM232.11.fid
28
^{13}C NMR, $CDCl_3$, 126MHz
OH
OH
S
O
O
168.38
149.67
139.81
138.70
136.80
129.64
124.34
124.14
123.37
122.23
121.14
81.80
77.16 CDCl3
65.09
59.14
47.15
41.64
39.72
28.00
f1 (ppm)

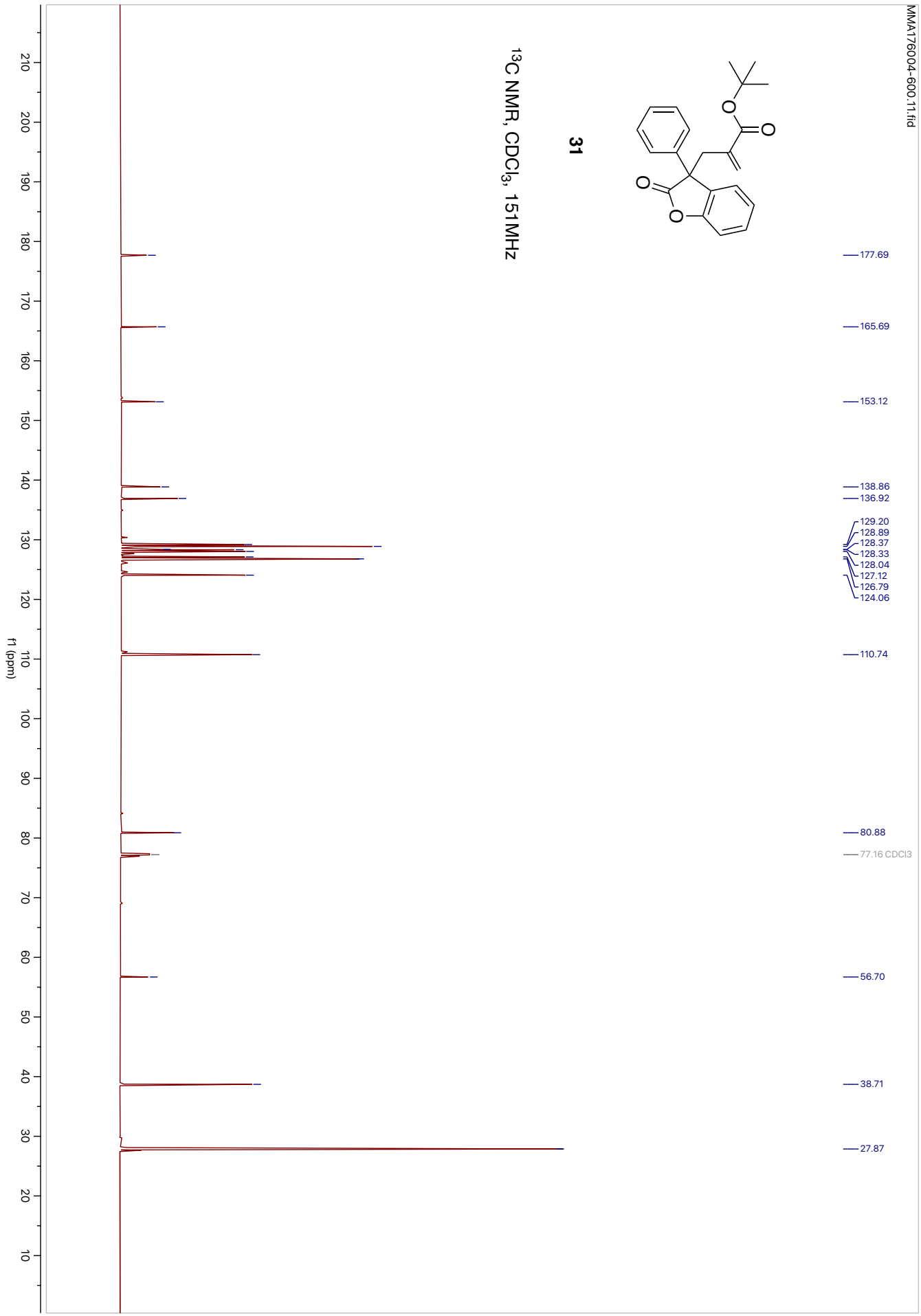

MMA239.10.fid
29
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
0.96
0.97
1.01
1.00
1.99
1.07
0.99
0.98
1.00
1.00
1.01
0.99
0.98
1.00
1.02
1.01
9.02
7.26 CDCl3

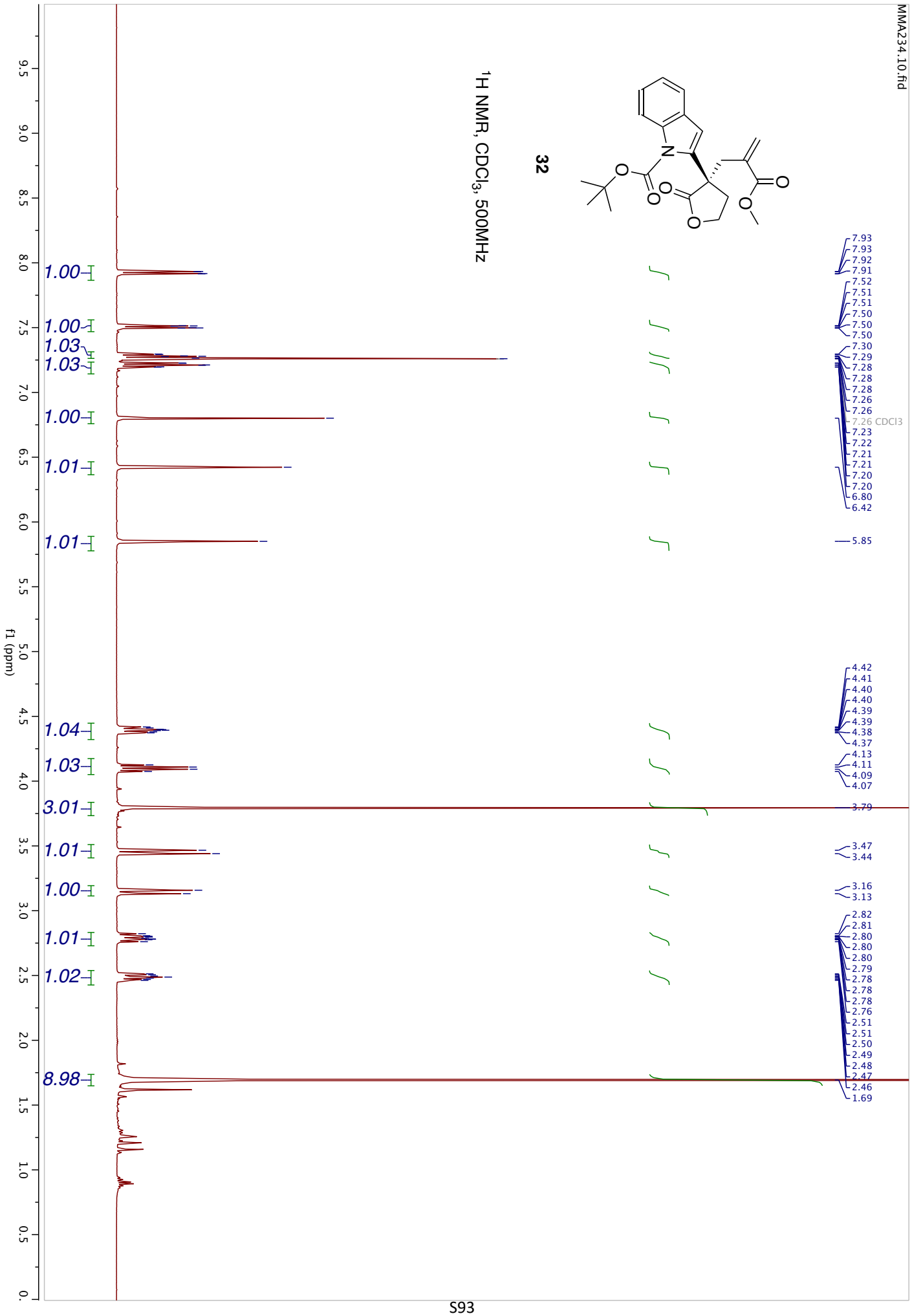

MM239.11.fid
178.31
166.59
155.49
155.06
139.74
137.13
131.17
129.61
129.39
129.23
126.97
124.64
124.41
123.19
123.17
121.16
111.38
102.07
81.21
77.16 CDCl3
65.46
52.63
39.55
33.89
28.13
f1 (ppm)
29
13C NMR, CDCl3, 126MHz

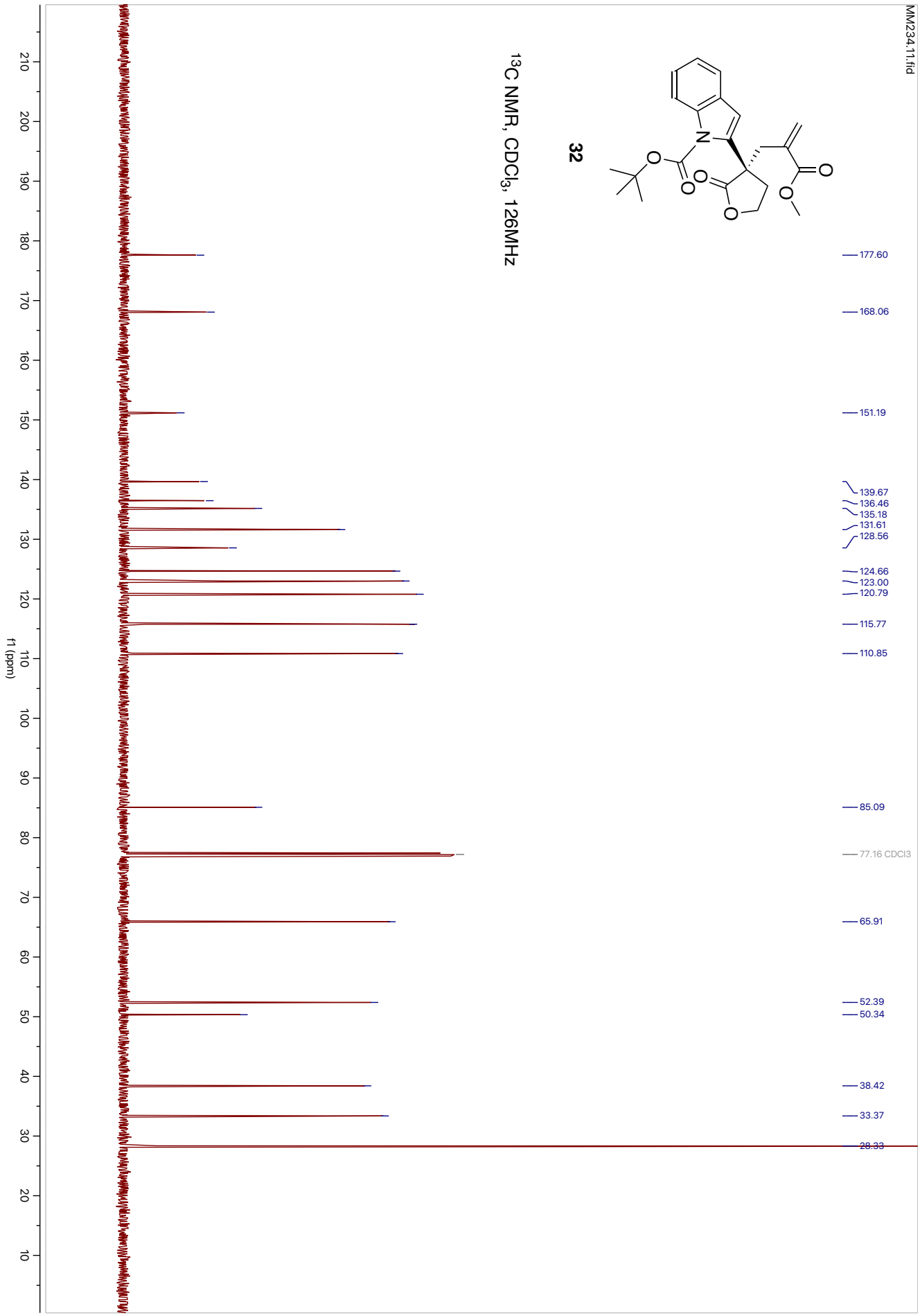

MM252.20.fid
30
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
2.02
1.04
2.05
1.02
1.02
2.00
2.01
1.00
1.01
9.24
7.46
7.45
7.45
7.44
7.38
7.37
7.28
7.28
7.27
7.26
7.26
7.26 CDCl3
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.21
4.64
4.63
4.62
4.61
4.61
4.60
4.57
4.55
4.55
4.54
4.54
4.52
3.64
3.63
3.61
3.60
3.58
3.56
3.54
3.53
3.16
3.14
3.11
3.08
2.70
2.68
2.67
2.67
2.66
2.64
2.45
2.44
2.44
2.43
2.41
2.41
2.40
1.51


MM252.21.fid
30
^{13}C NMR, $CDCl_3$, 126MHz
f1 (ppm)
176.74
166.23
153.10
151.48
143.20
132.92
128.47
124.74
122.79
118.76
113.67
111.30
81.30
77.16 CDCl3
66.16
47.22
33.72
30.27
28.20
21.90

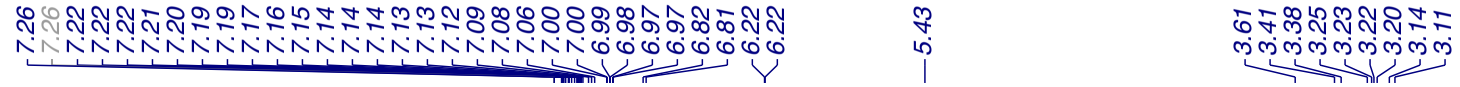

MMA176004-600.10.fid
31
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
2.00
5.36
1.06
1.00
1.00
1.00
1.00
9.25
7.36
7.36
7.35
7.35
7.27
7.26
7.26 CDCl3
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.21
7.09
7.08
7.03
7.01
5.95
5.47
3.49
3.47
3.30
3.28
1.20

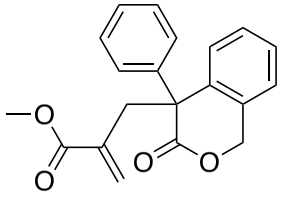

MMA176004-600.11.fid
31
^{13}C NMR, $CDCl_3$, 151MHz
f1 (ppm)
177.69
165.69
153.12
138.86
136.92
129.20
128.89
128.37
128.33
128.04
127.12
126.79
124.06
110.74
80.88
77.16 CDCl3
56.70
38.71
27.87


MMA234.10.fid
^{1}H NMR, $CDCl_3$, 500MHz
32
f1 (ppm)
1.00
1.00
1.03
1.03
1.00
1.01
1.01
1.04
1.03
3.01
1.01
1.00
1.01
1.02
8.98
7.93
7.93
7.92
7.91
7.52
7.51
7.51
7.50
7.50
7.50
7.30
7.29
7.28
7.28
7.28
7.26
7.26
7.26 CDCl3
7.23
7.22
7.21
7.21
7.20
7.20
6.80
6.42
5.85
4.42
4.41
4.40
4.40
4.39
4.39
4.38
4.37
4.13
4.11
4.09
4.07
3.79
3.47
3.44
3.16
3.13
2.82
2.81
2.80
2.80
2.80
2.79
2.78
2.78
2.78
2.78
2.76
2.51
2.51
2.50
2.49
2.48
2.47
2.46
1.69


MM234.11.fid
^{13}C NMR, $CDCl_3$, 126MHz
32
177.60
168.06
151.19
139.67
136.46
135.18
131.61
128.56
124.66
123.00
120.79
115.77
110.85
85.09
77.16 CDCl3
65.91
52.39
50.34
38.42
33.37
28.33
f1 (ppm)

ERM54002.10.fid

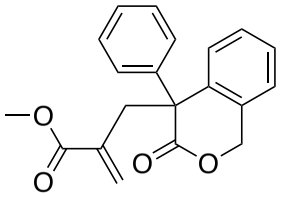




33

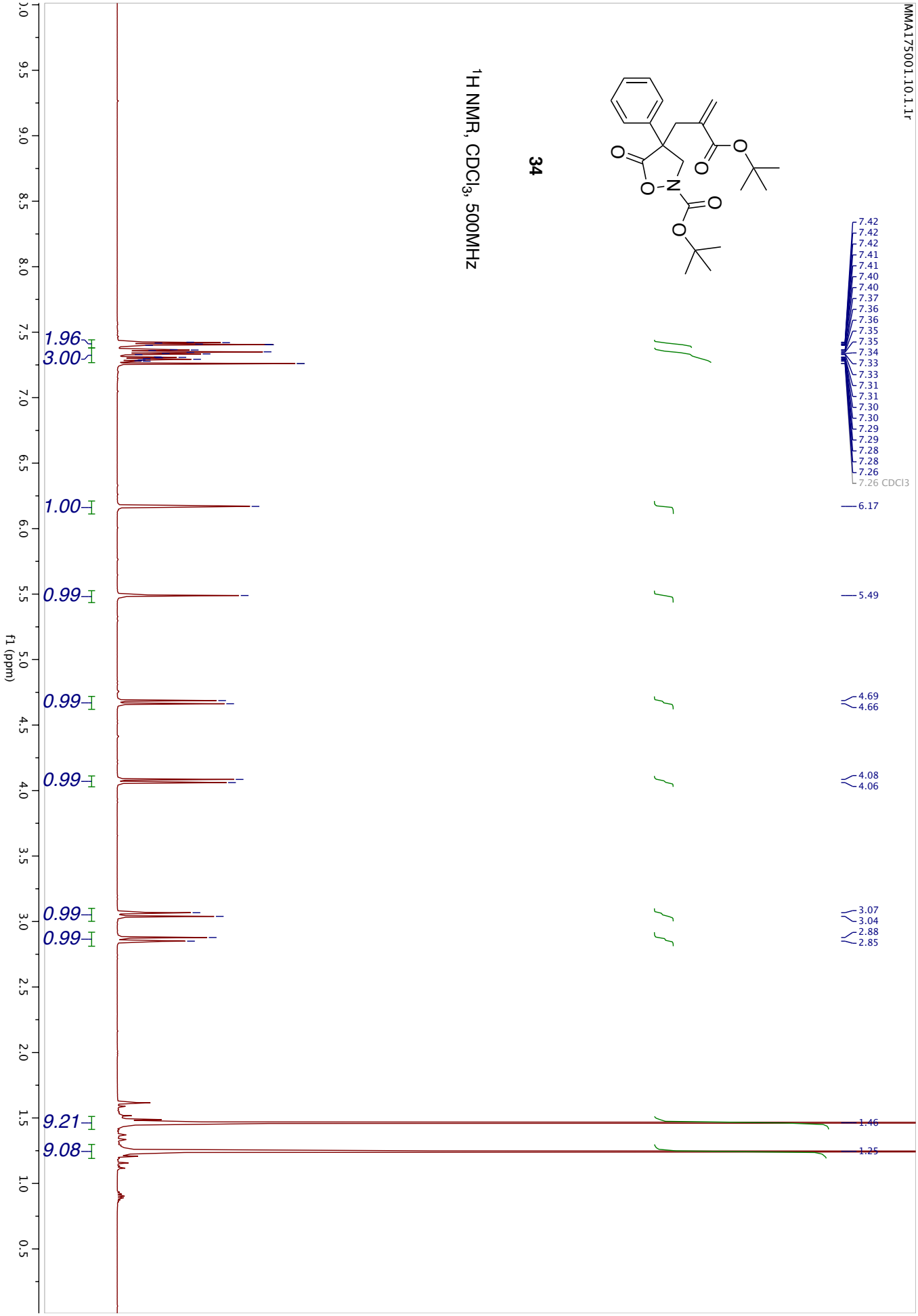
^{1}H NMR, $CDCl_3$, 500MHz

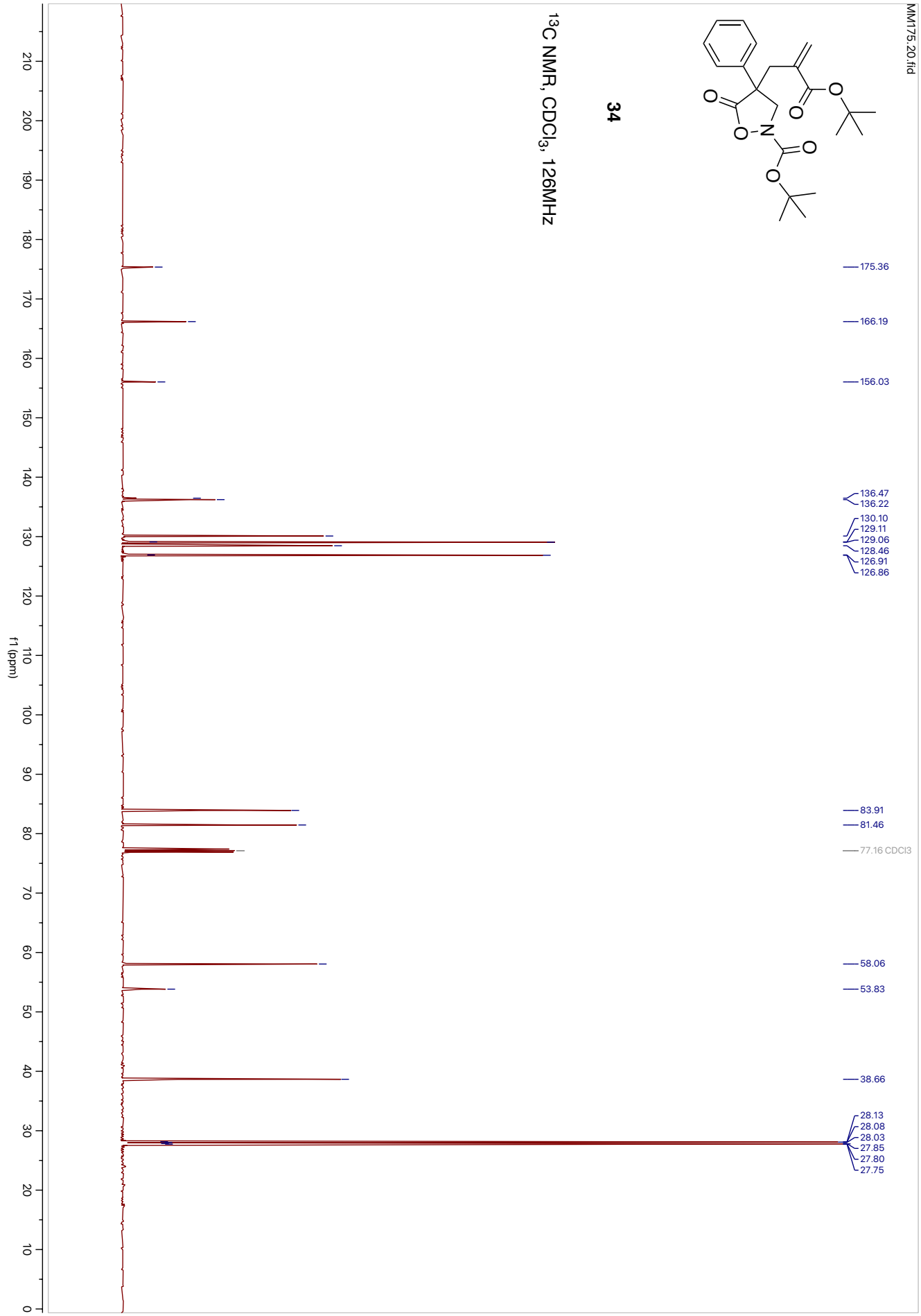
ERM54002.11.fid

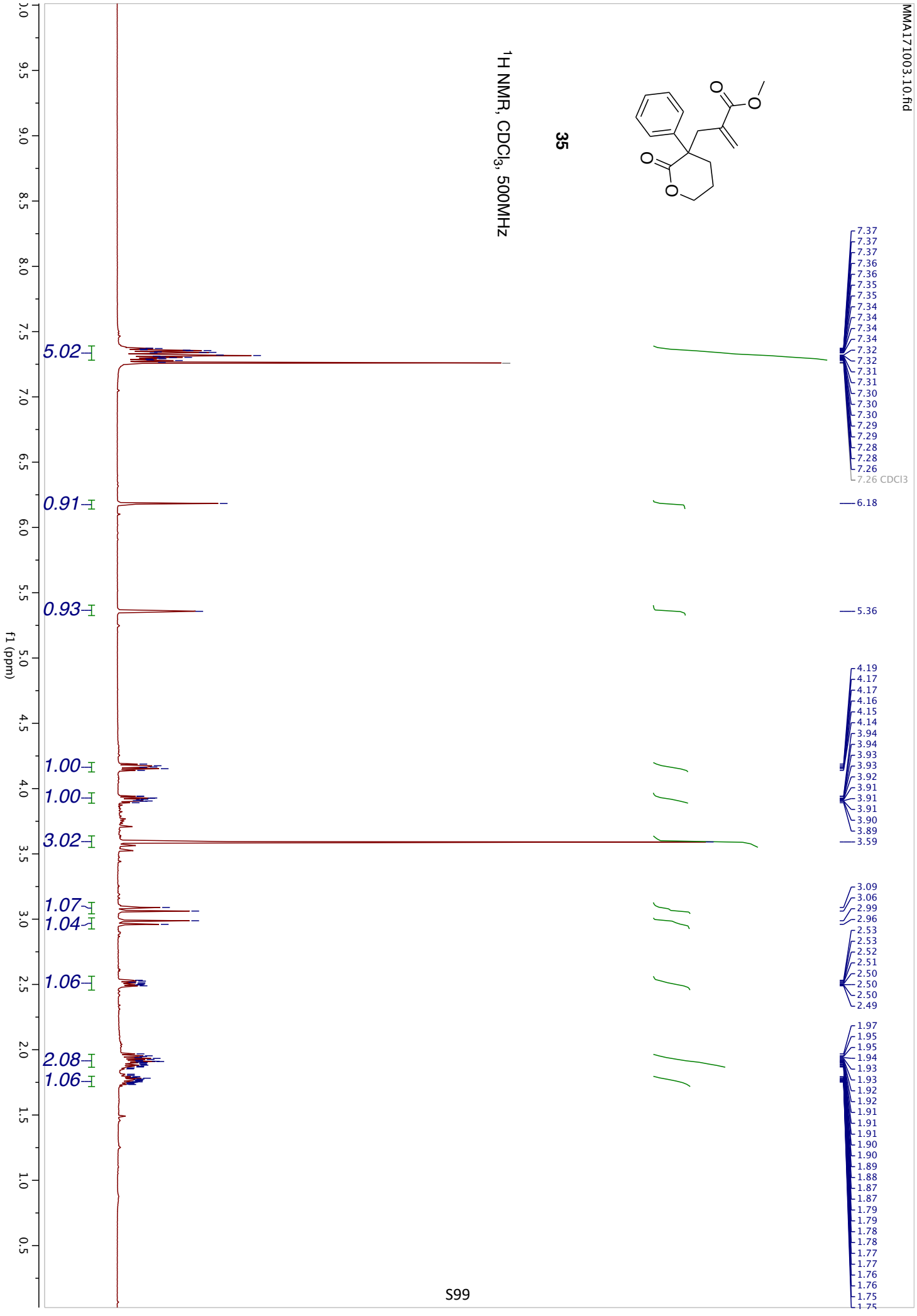


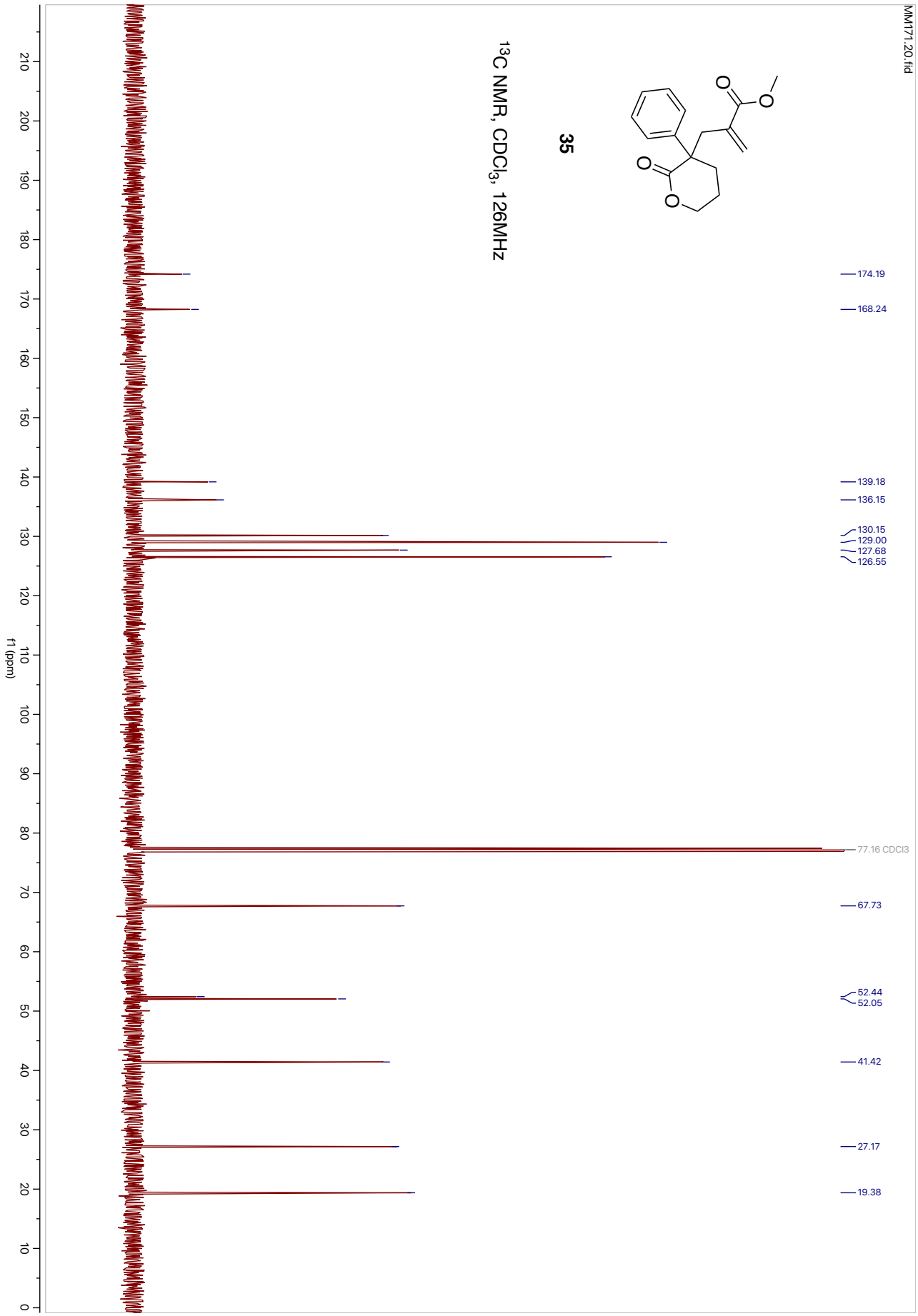
33

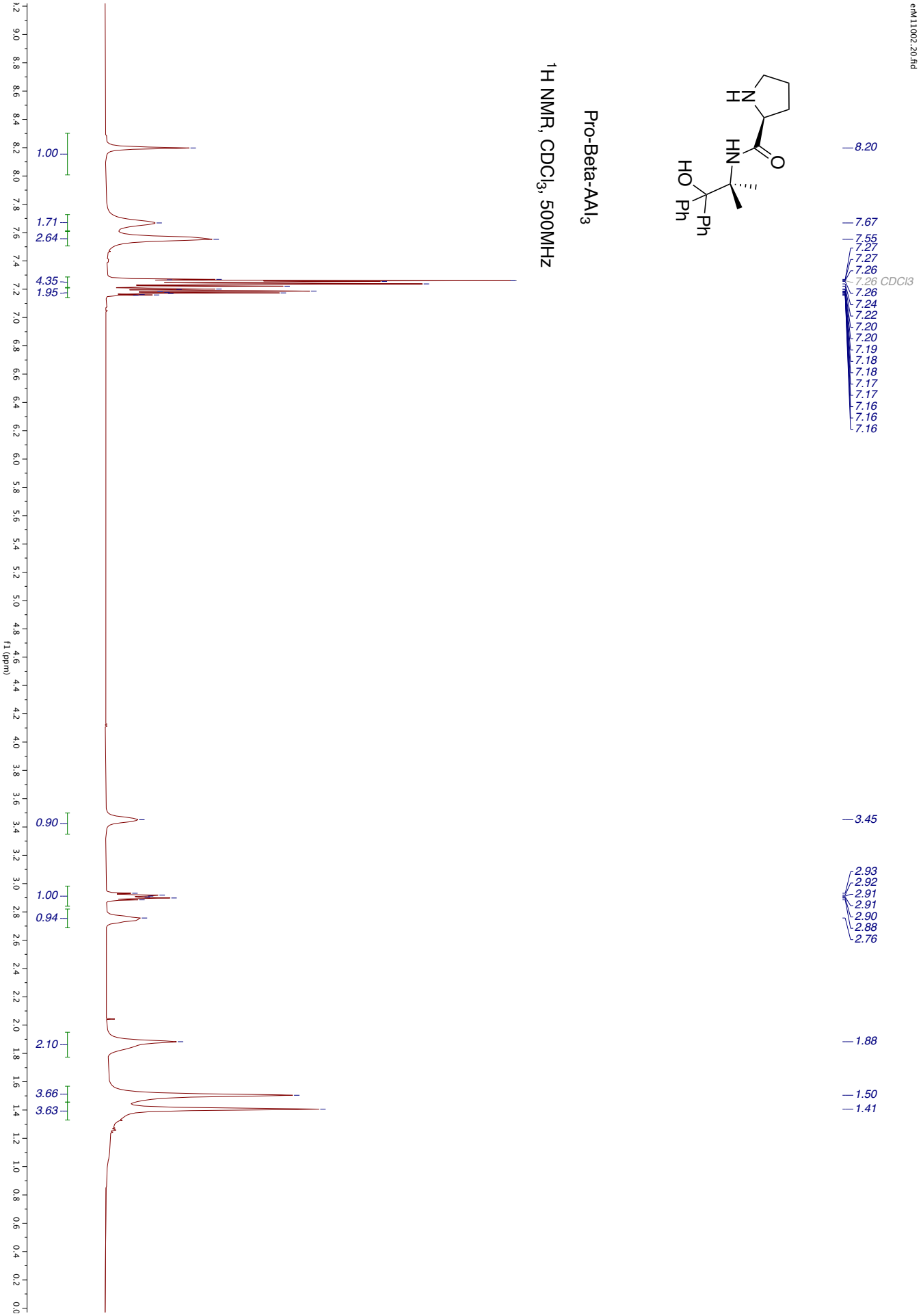
^{13}C NMR, $CDCl_3$, 126MHz

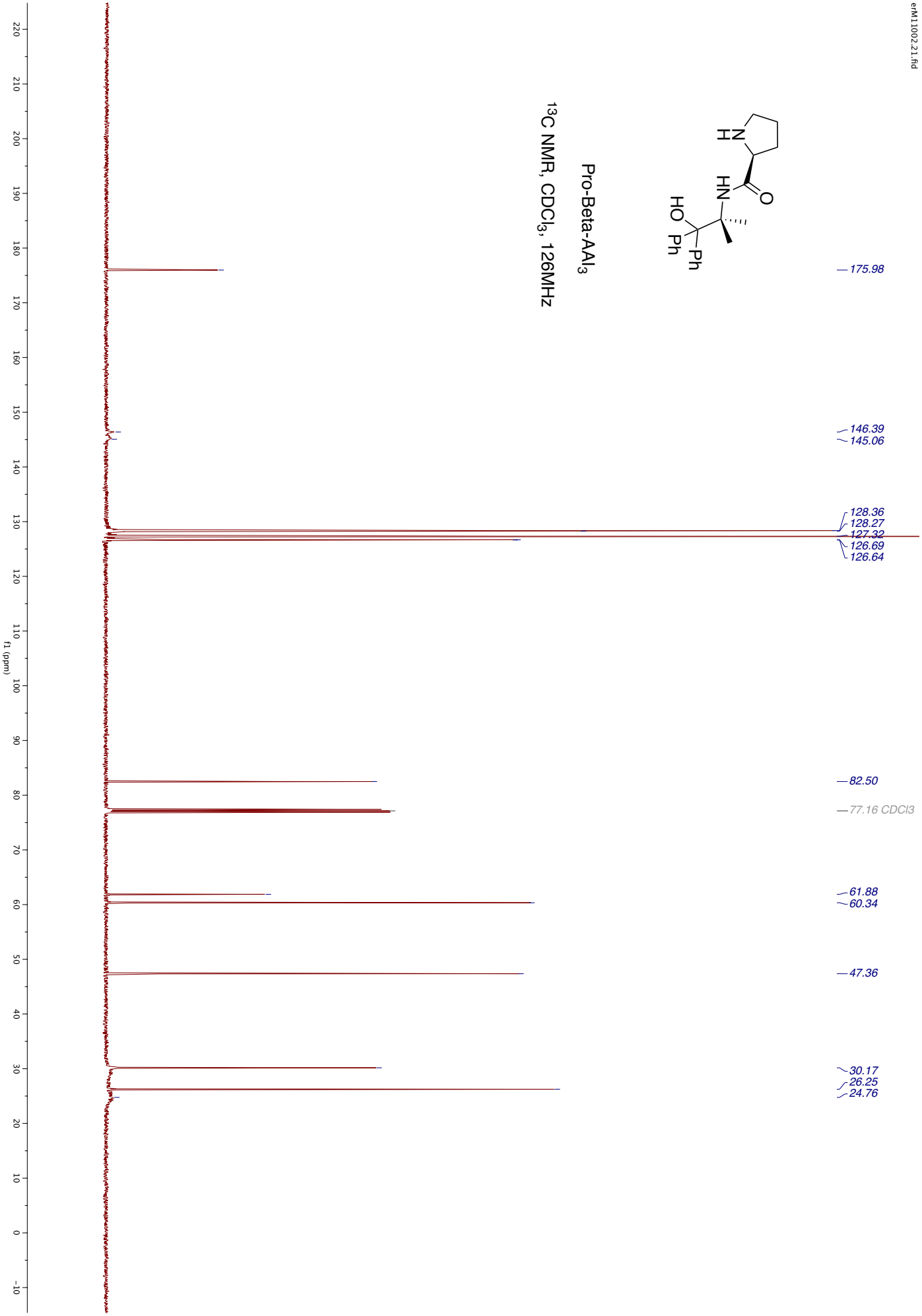

MMA175001.10.1.1r
34
^{1}H NMR, $CDCl_3$, 500MHz
f1 (ppm)
1.96
3.00
1.00
0.99
0.99
0.99
0.99
0.99
9.21
9.08
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.26 CDCl3
6.17
5.49
4.69
4.66
4.08
4.06
3.07
3.04
2.88
2.85
1.46
1.25

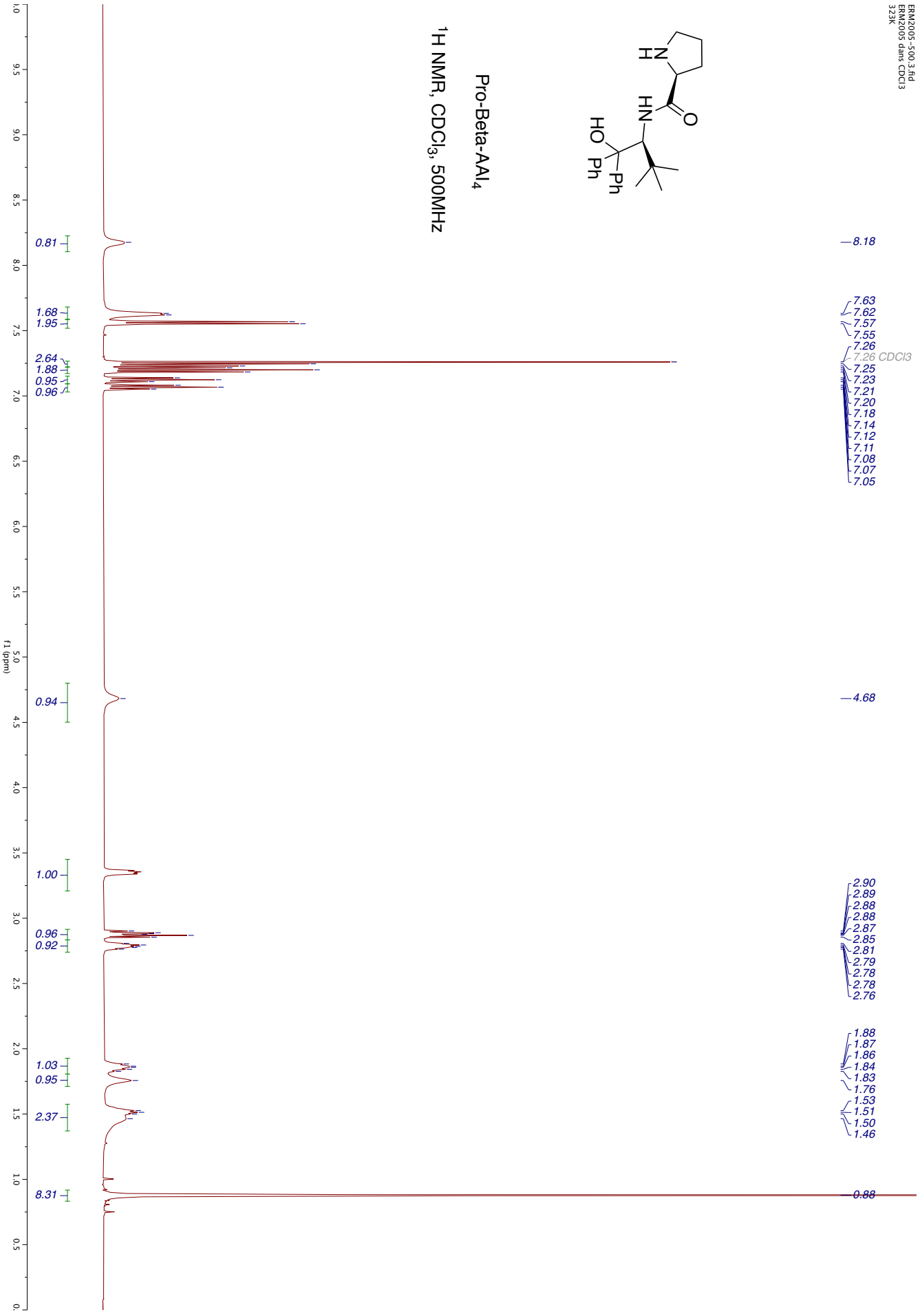

MM175.20.fid
34
^{13}C NMR, $CDCl_3$, 126MHz
175.36
166.19
156.03
136.47
136.22
130.10
129.11
129.06
128.46
126.91
126.86
83.91
81.46
77.16 CDCl3
58.06
53.83
38.66
28.13
28.08
28.03
27.85
27.80
27.75
f1 (ppm)

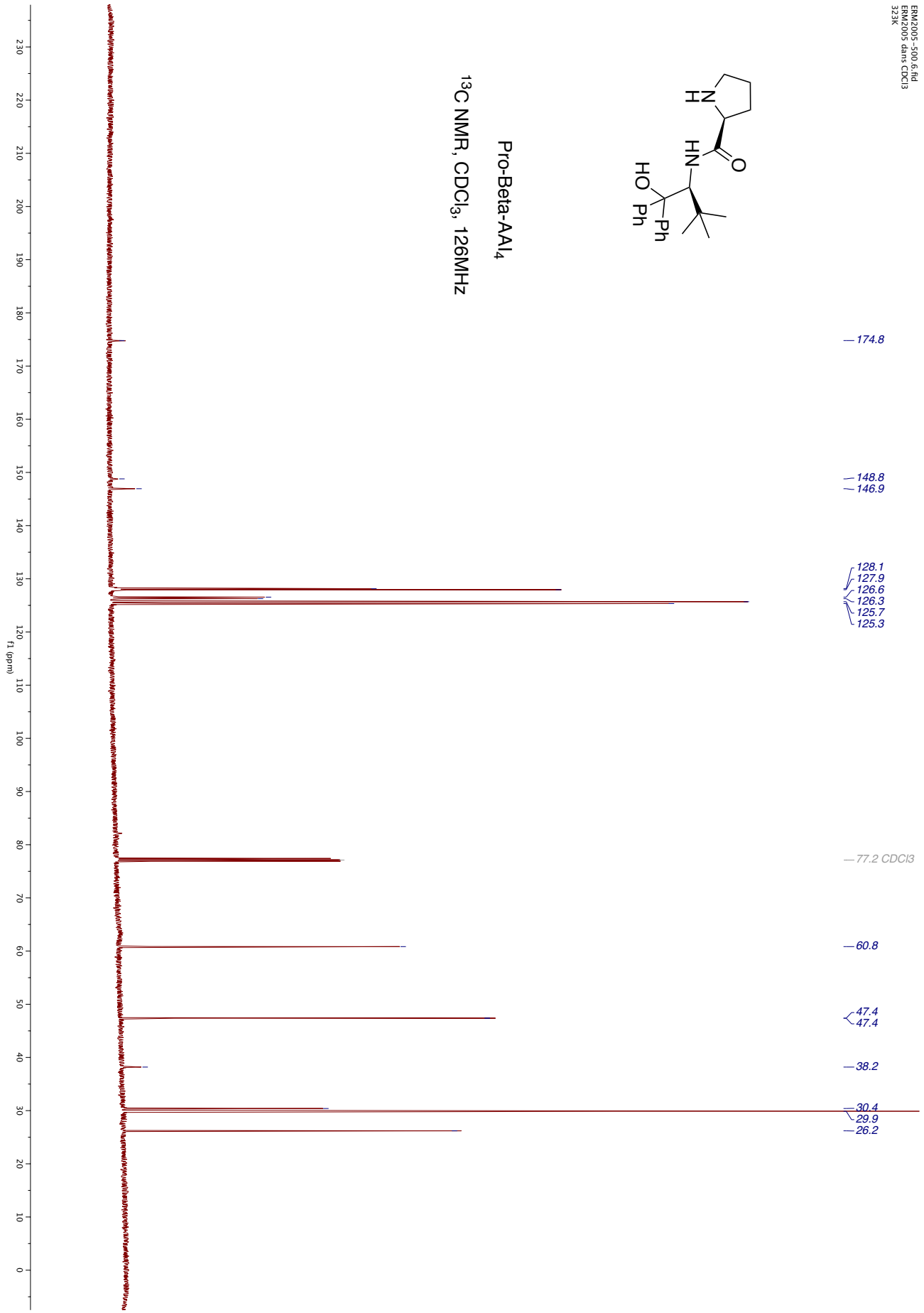

MMA171003.10.fid
35
^{1}H NMR, CDCl$_3$, 500MHz
f1 (ppm)
5.02
0.91
0.93
1.00
1.00
3.02
1.07
1.04
1.06
2.08
1.06
7.26 CDCl3
6.18
5.36
3.59

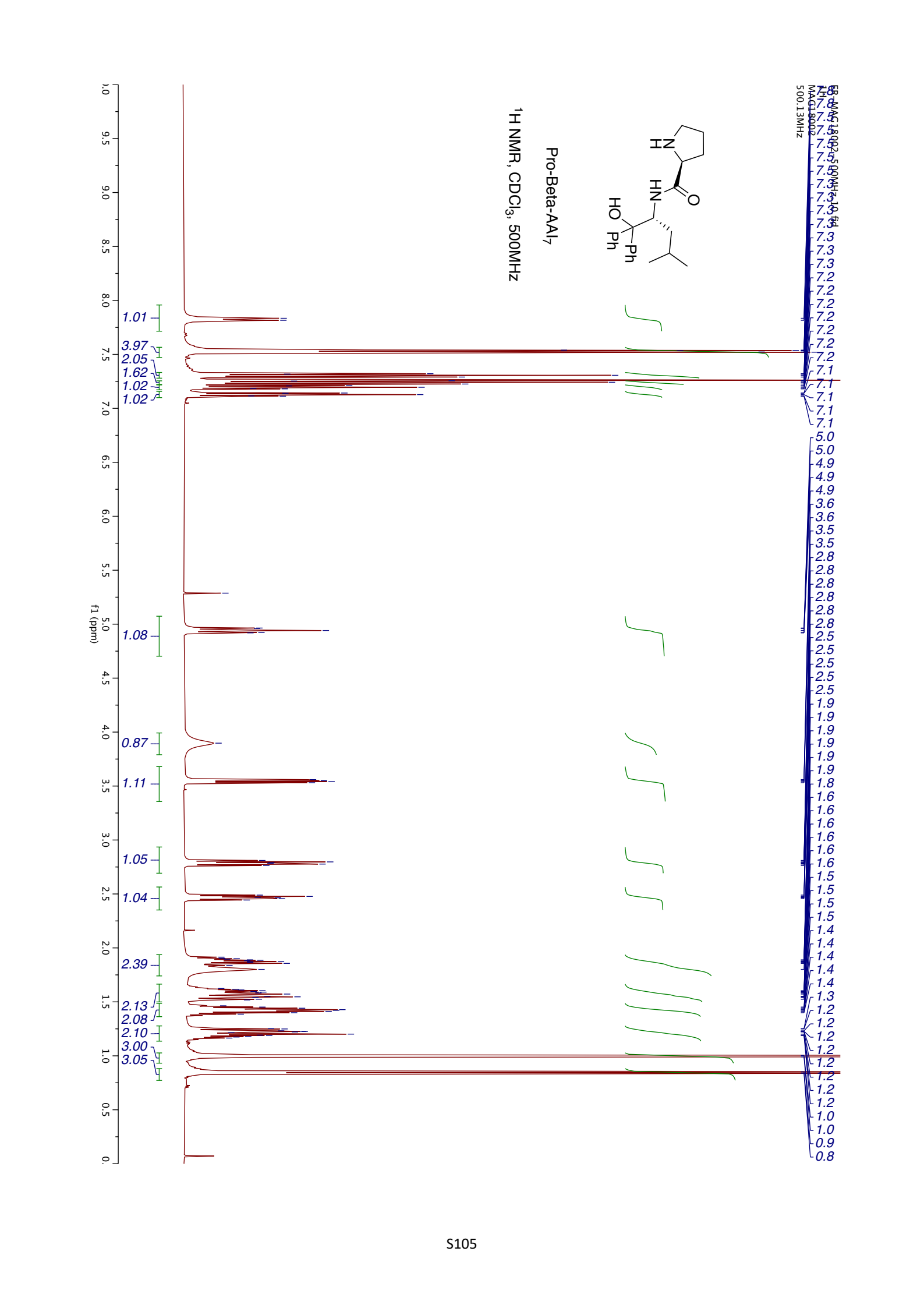

MM171.20.fid
35
^{13}C NMR, $CDCl_3$, 126MHz
174.19
168.24
139.18
136.15
130.15
129.00
127.68
126.55
77.16 CDCl3
67.73
52.44
52.05
41.42
27.17
19.38
f1 (ppm)

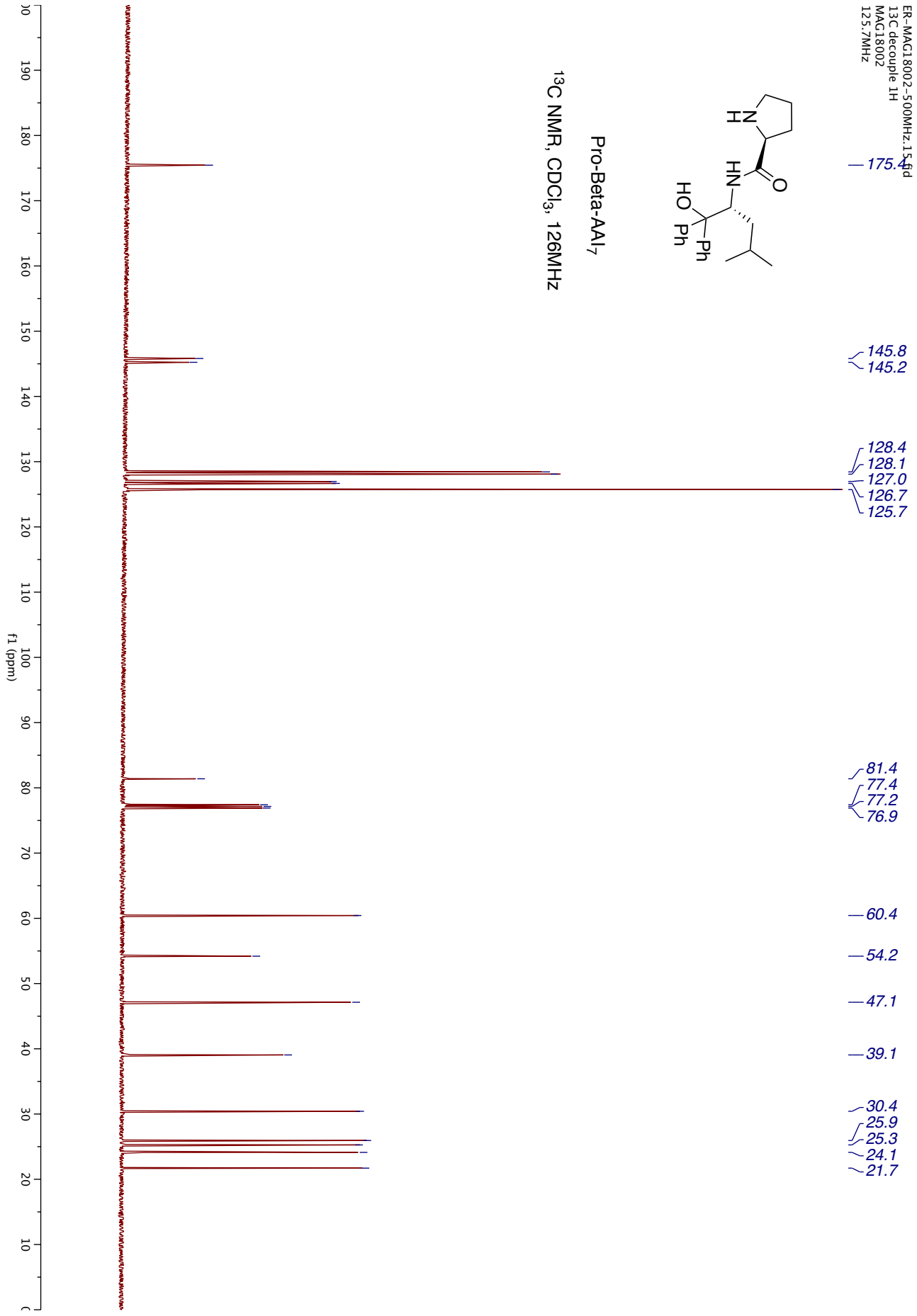

Pro-Beta-AAl3
1H NMR, CDCl3, 500MHz
efM11002.20.fid
f1 (ppm)
1.00
1.71
2.64
4.35
1.95
0.90
1.00
0.94
2.10
3.66
3.63
8.20
7.67
7.55
7.27
7.27
7.26
7.26 CDCl3
7.26
7.24
7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.16
3.45
2.93
2.92
2.91
2.91
2.90
2.88
2.76
1.88
1.50
1.41

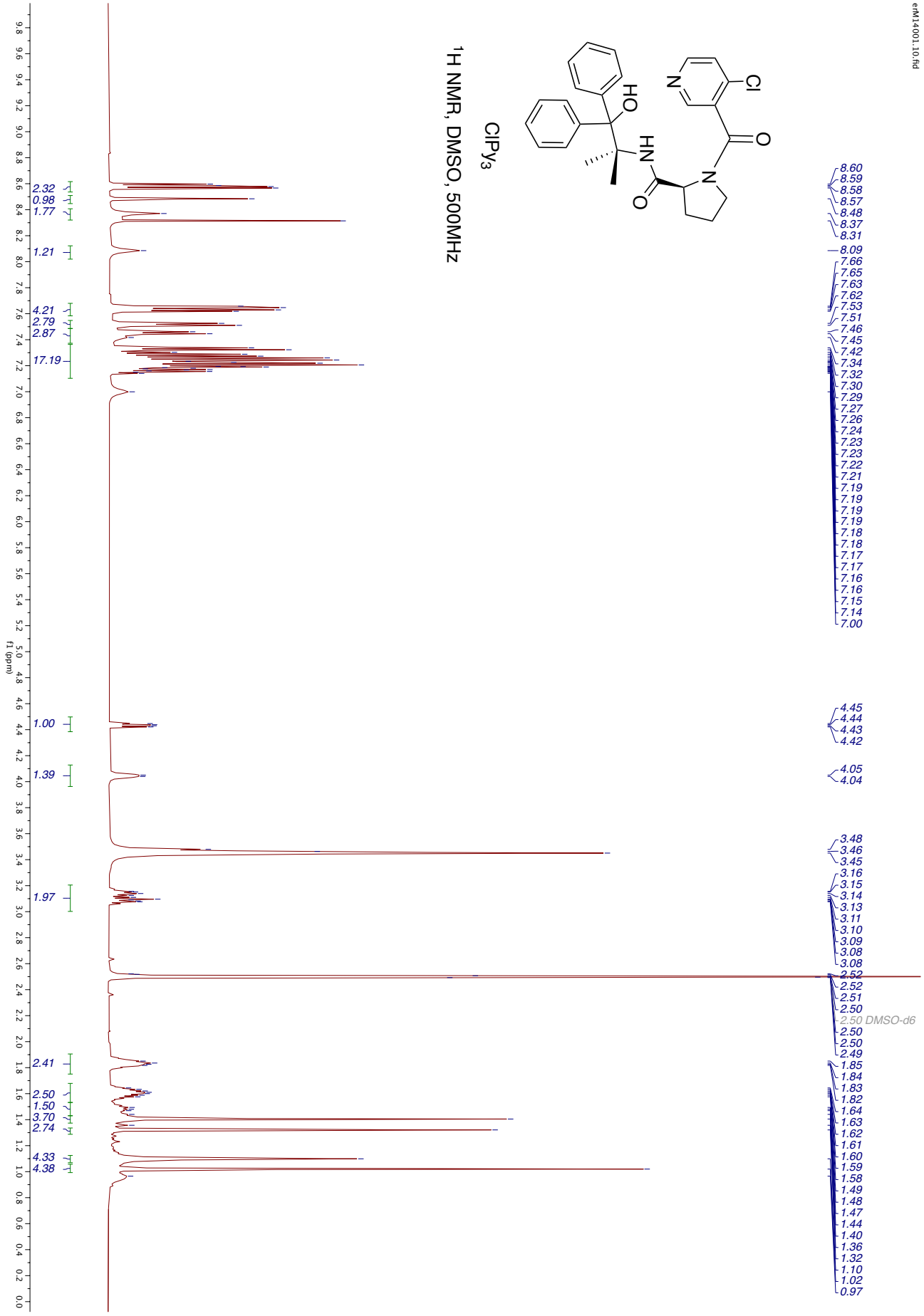

erM11002.21.fid
Pro-Beta-AAl3
13C NMR, CDCl3, 126MHz
N
H
HN
O
HO
Ph
Ph
175.98
146.39
145.06
128.36
128.27
127.32
126.69
126.64
82.50
77.16 CDCl3
61.88
60.34
47.36
30.17
26.25
24.76
f1 (ppm)

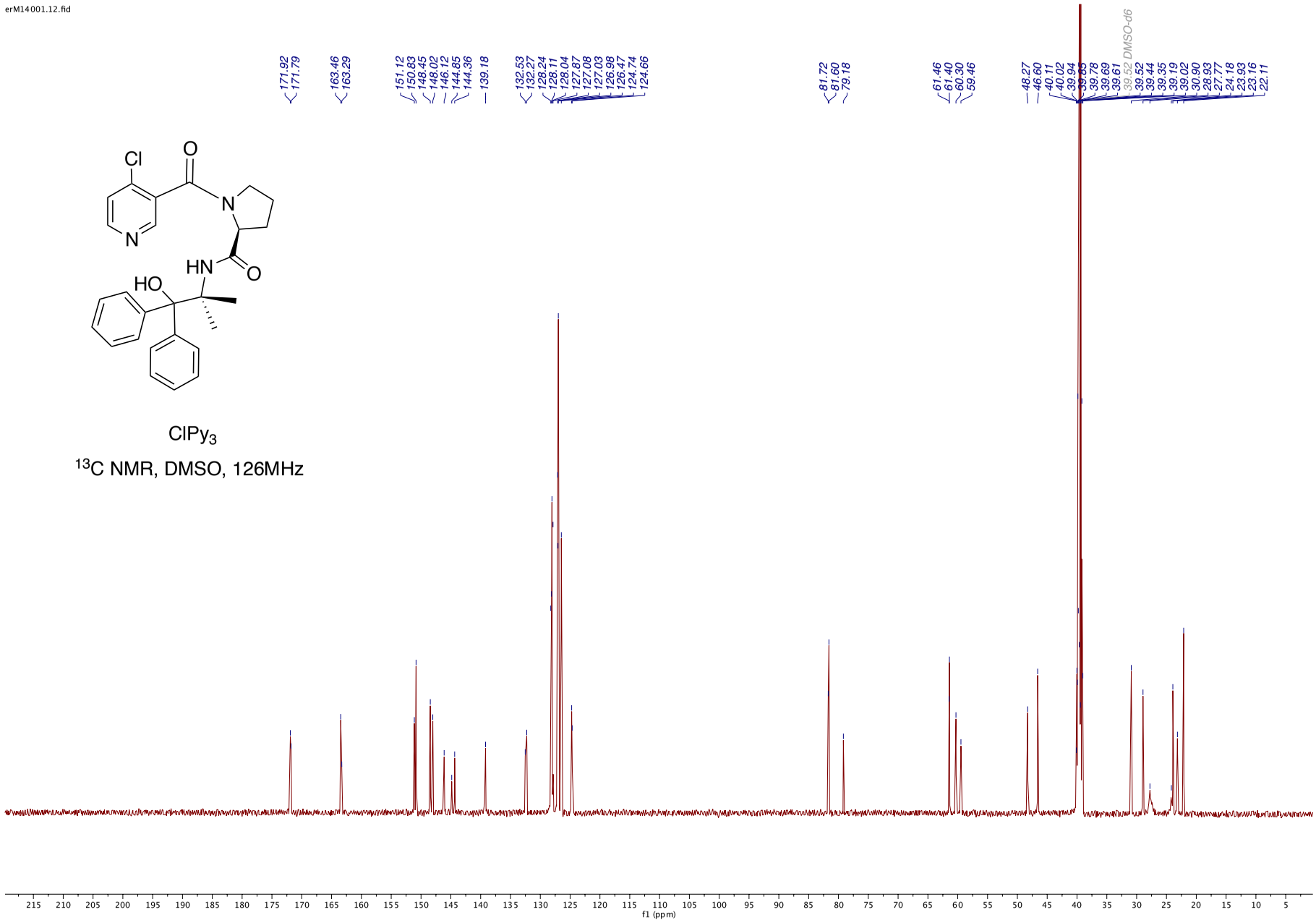

EBM2005-500.3.fid
EBM2005 dans CDCl3
323K
Pro-Beta-AAl4
1H NMR, CDCl3, 500MHz
f1 (ppm)
0.81
1.68
1.95
2.64
1.88
0.95
0.96
0.94
1.00
0.96
0.92
1.03
0.95
2.37
8.31
8.18
7.63
7.62
7.57
7.55
7.26
7.26 CDCl3
7.25
7.23
7.21
7.20
7.18
7.14
7.12
7.11
7.08
7.07
7.05
4.68
2.90
2.89
2.88
2.88
2.87
2.85
2.81
2.79
2.78
2.78
2.76
1.88
1.87
1.86
1.84
1.83
1.76
1.53
1.51
1.50
1.46
0.88


ERM2005-500.6.fid
ERM2005 d4m3 CDCl3
323K
Pro-Beta-AAl_4
^{13}C NMR, $CDCl_3$, 126MHz
HN
HN
O
HO
Ph
Ph
174.8
148.8
146.9
128.1
127.9
126.6
126.3
125.7
125.3
77.2 CDCl3
60.8
47.4
47.4
38.2
30.4
29.9
26.2
f1 (ppm)


Pro-Beta-AAl7
1H NMR, CDCl3, 500MHz
HO
Ph
Ph
HN
H
N
O
f1 (ppm)
1.01
3.97
2.05
1.62
1.02
1.02
1.08
0.87
1.11
1.05
1.04
2.39
2.13
2.08
2.10
3.00
3.05

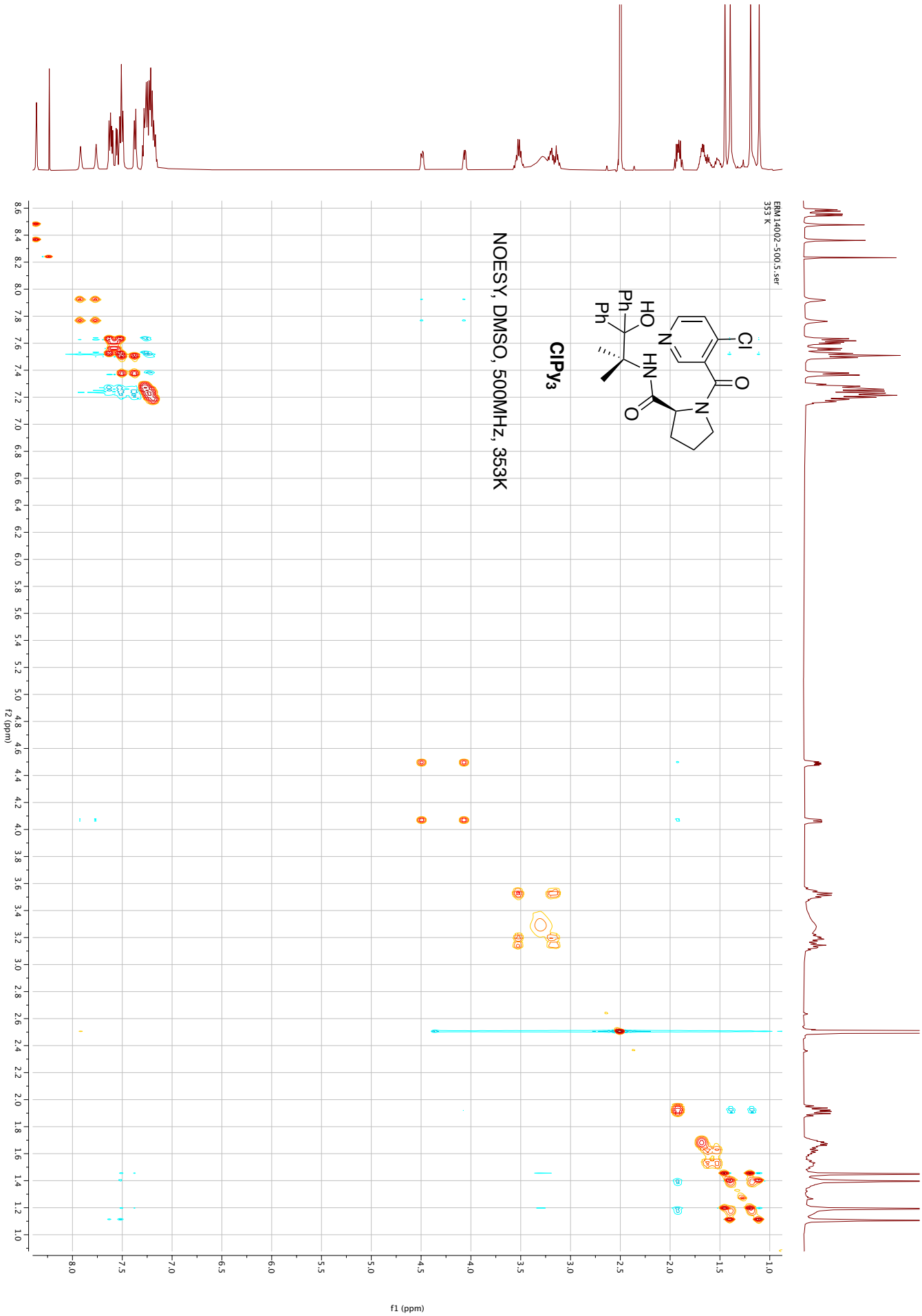

ER-MAG18002-500MHz.15.fid
13C decouple 1H
MAG18002
125.7MHz
Pro-Beta-AA$_7$
^{13}C NMR, CDCl$_3$, 126MHz
175.4
145.8
145.2
128.4
128.1
127.0
126.7
125.7
81.4
77.4
77.2
76.9
60.4
54.2
47.1
39.1
30.4
25.9
25.3
24.1
21.7
f1 (ppm)

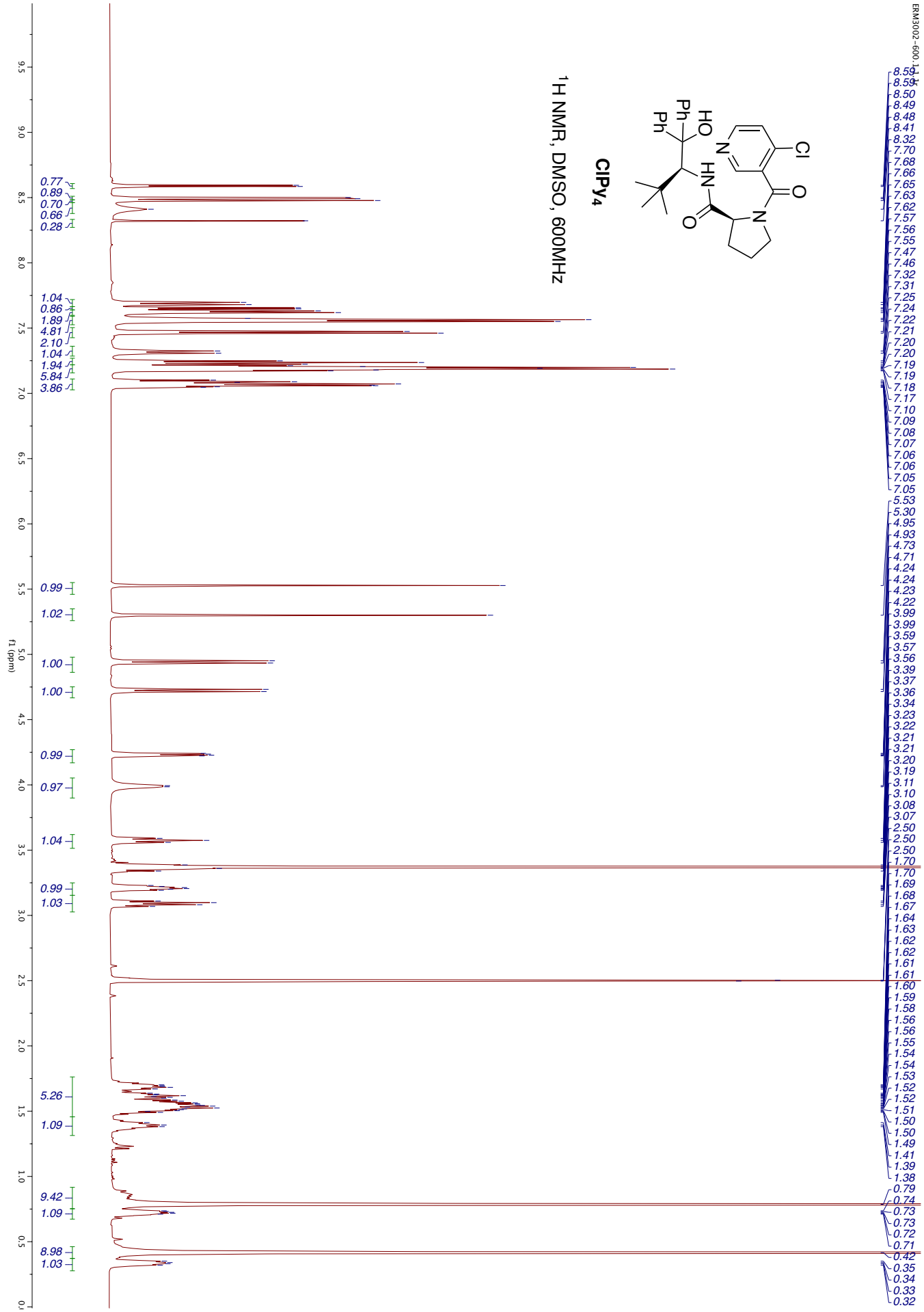

erM14001.10.fid
^{1}H NMR, DMSO, 500MHz
ClPy$_3$
HO
HN
O
N
Cl
f1 (ppm)
2.32
0.98
1.77
1.21
4.21
2.79
2.87
17.19
1.00
1.39
1.97
2.41
2.50
1.50
3.70
2.74
4.33
4.38
8.60
8.59
8.58
8.57
8.48
8.37
8.31
8.09
7.66
7.65
7.63
7.62
7.53
7.51
7.46
7.45
7.42
7.34
7.32
7.30
7.29
7.27
7.26
7.24
7.23
7.23
7.22
7.21
7.19
7.19
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.00
4.45
4.44
4.43
4.42
4.05
4.04
3.48
3.46
3.45
3.16
3.15
3.14
3.13
3.11
3.10
3.09
3.08
3.08
2.52
2.52
2.51
2.50
2.50 DMSO-d6
2.50
2.50
2.49
1.85
1.84
1.83
1.82
1.64
1.63
1.62
1.61
1.60
1.59
1.58
1.49
1.48
1.47
1.44
1.40
1.36
1.32
1.10
1.02
0.97



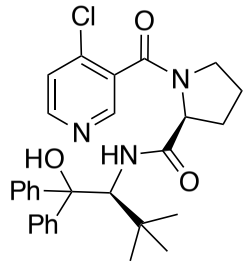
$ClPy_3$

^{13}C NMR, DMSO, 126MHz


ERM14002-500S.ser
353 K
NOESY, DMSO, 500MHz, 353K
ClPy3
HO
Ph
Ph
Cl
N
HN
O
O
N
f2 (ppm)
f1 (ppm)

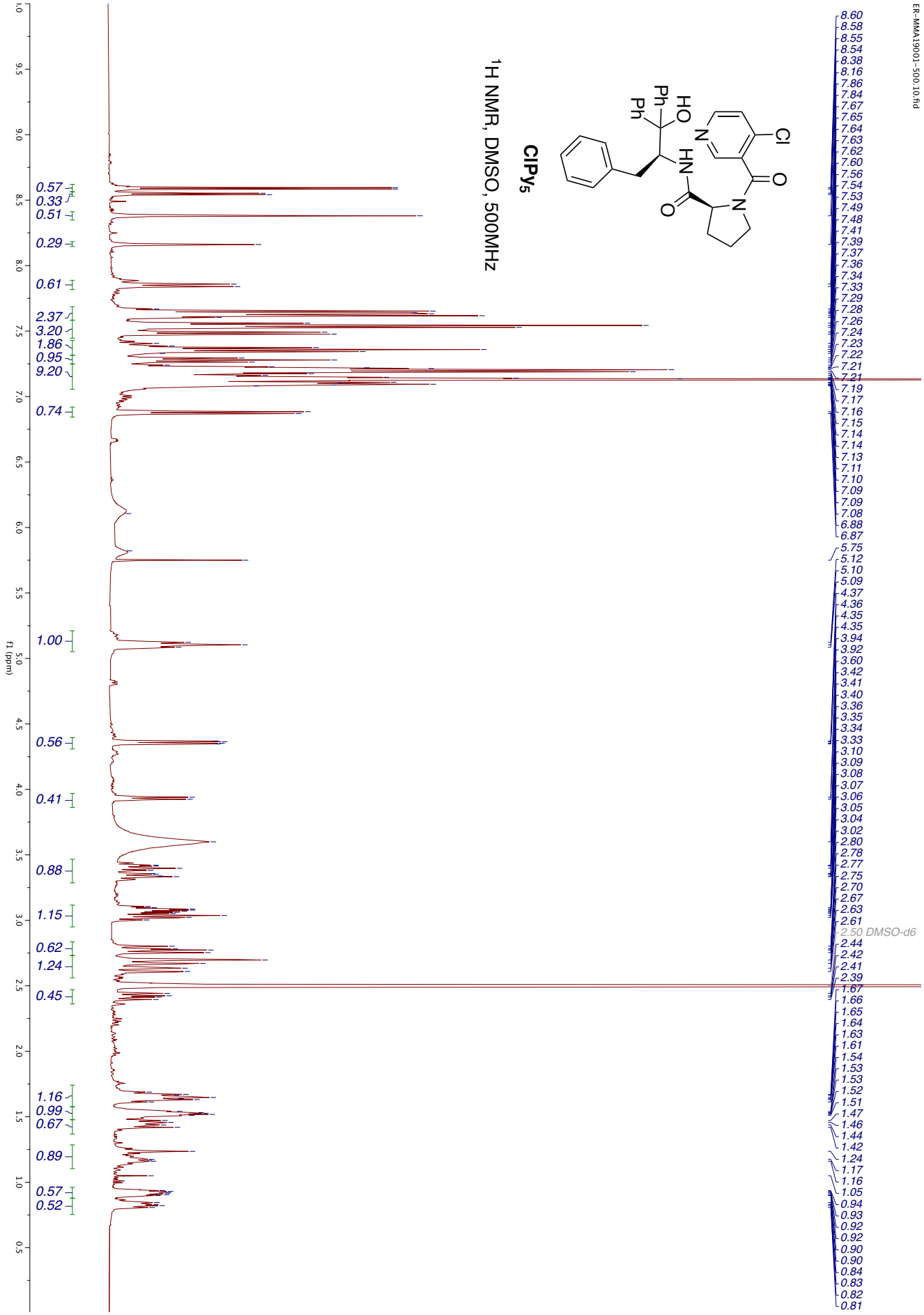

^{1}H NMR, DMSO, 600MHz
ClPy$_4$
Cl
O
N
HN
HO
Ph
Ph
Ph
f1 (ppm)

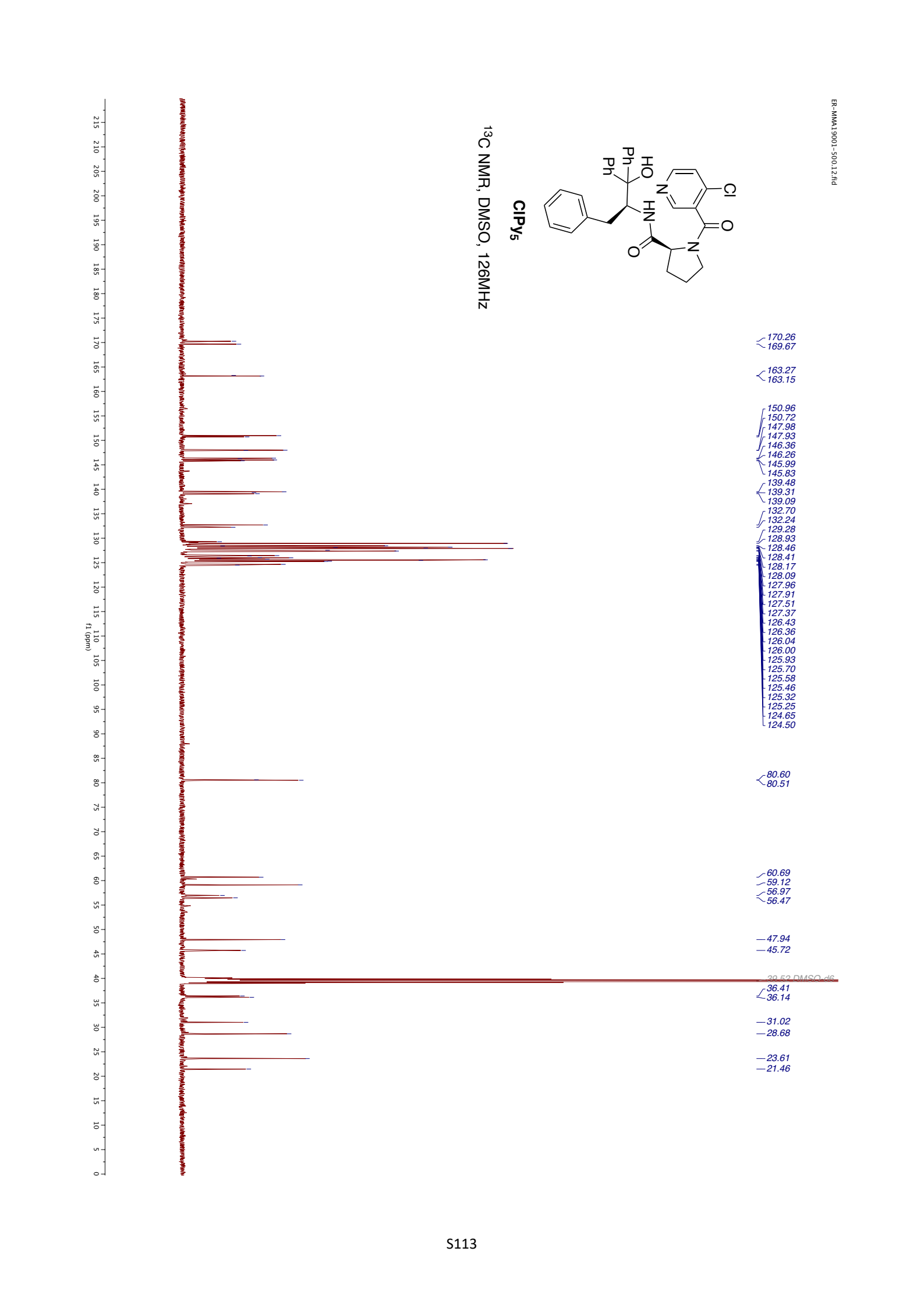
ERM3002-600.2.1.1r

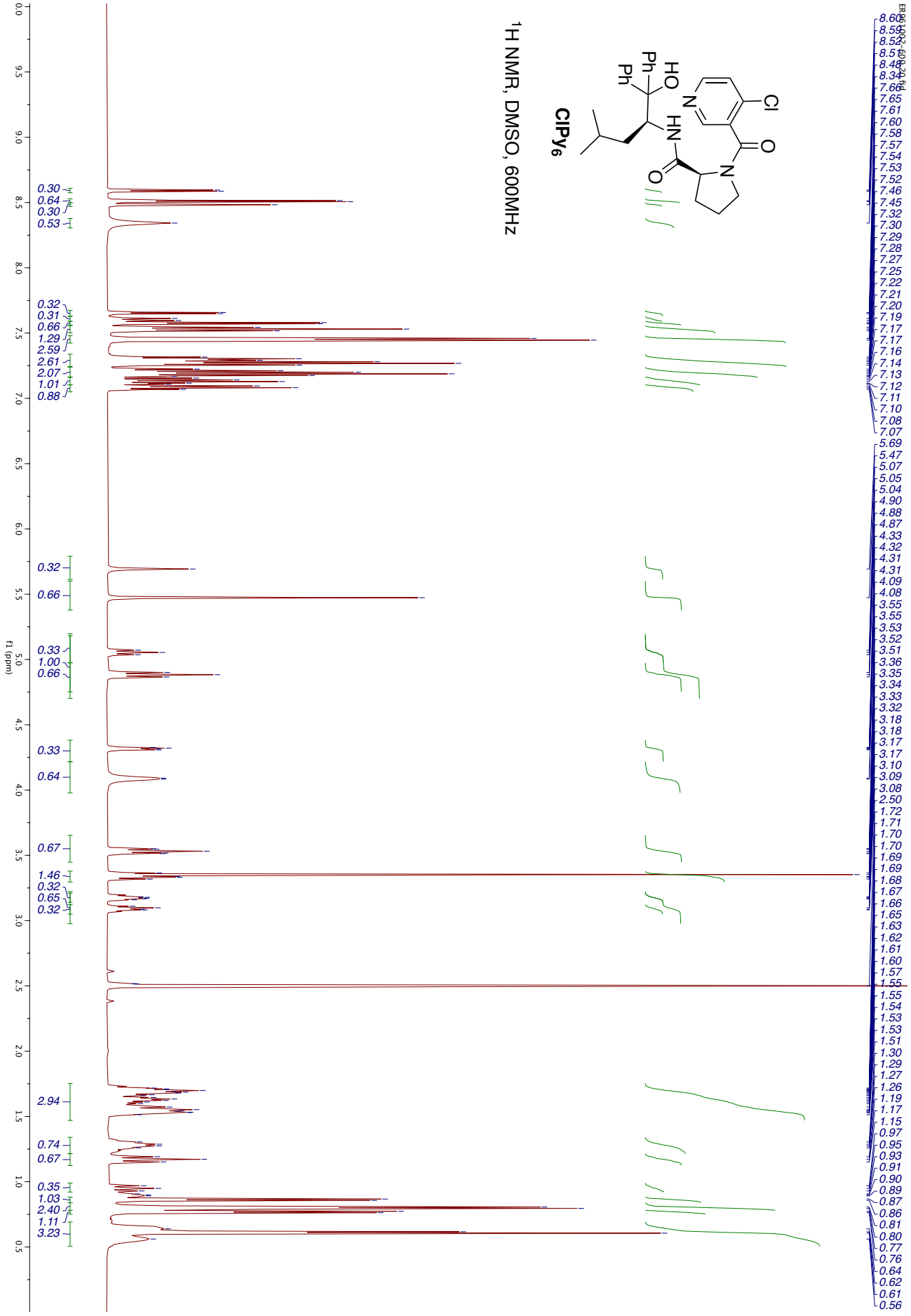


ClPy$_4$

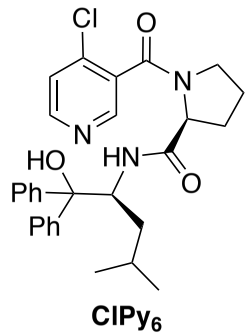
^{13}C NMR, DMSO, 151MHz


^{1}H NMR, DMSO, 500MHz
ClPy$_5$
ER-MMA19001-500.10.fid
f1 (ppm)
2.50 DMSO-d6


ER-MMA19001-500.1.fid
^{13}C NMR, DMSO, 126MHz
ClPy$_5$
HO
Ph
Ph
HN
N
O
O
Cl
N
f1 (ppm)
170.26
169.67
163.27
163.15
150.96
150.72
147.98
147.93
146.36
146.26
145.99
145.83
139.48
139.31
139.09
132.70
132.24
129.28
128.93
128.46
128.41
128.17
128.09
127.96
127.91
127.51
127.37
126.43
126.36
126.04
126.00
125.93
125.70
125.58
125.46
125.32
125.25
124.65
124.50
80.60
80.51
60.69
59.12
56.97
56.47
47.94
45.72
39.52 DMSO-d6
36.41
36.14
31.02
28.68
23.61
21.46

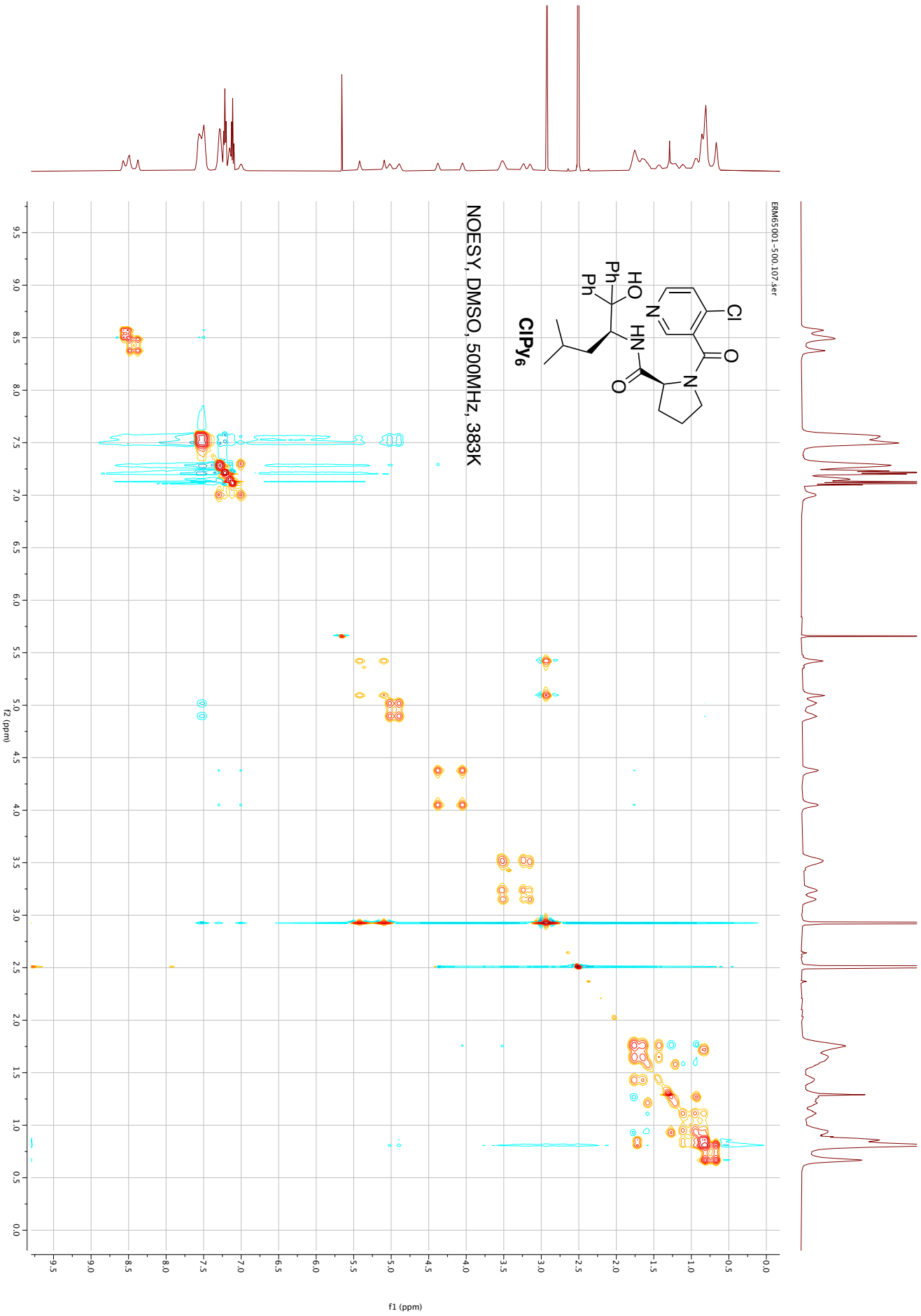

^{1}H NMR, DMSO, 600MHz
ClPy$_6$
f1 (ppm)

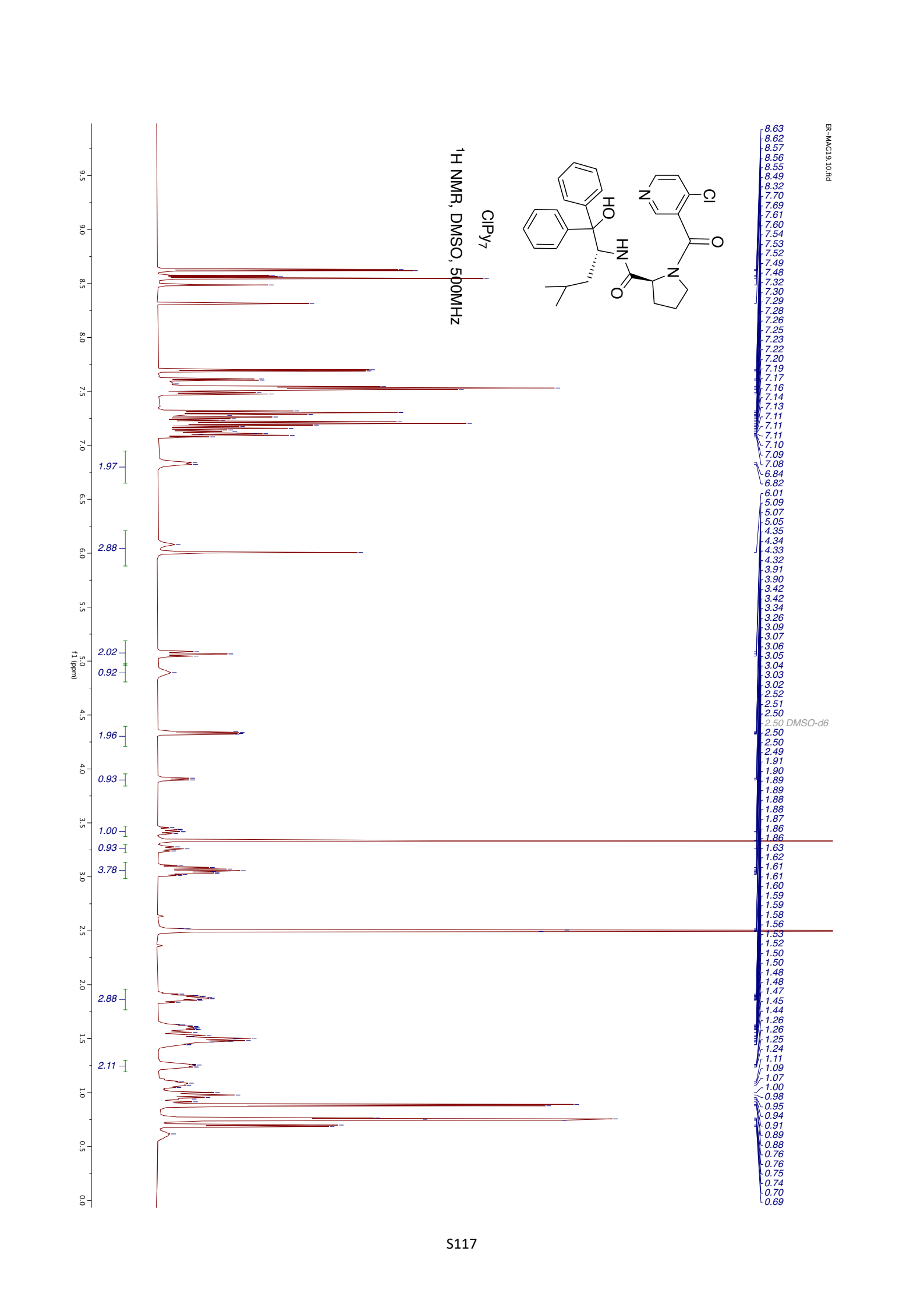
ER961002-600.27.1.1r



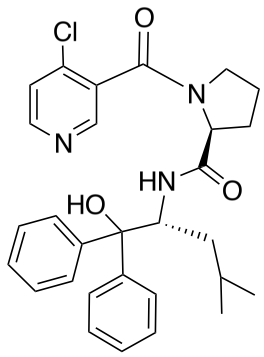
ClPy$_6$

^{13}C NMR, DMSO, 151MHz


NOESY, DMSO, 500MHz, 383K
ClPy6
ERM65001-500.107.ser
f1 (ppm)
f2 (ppm)

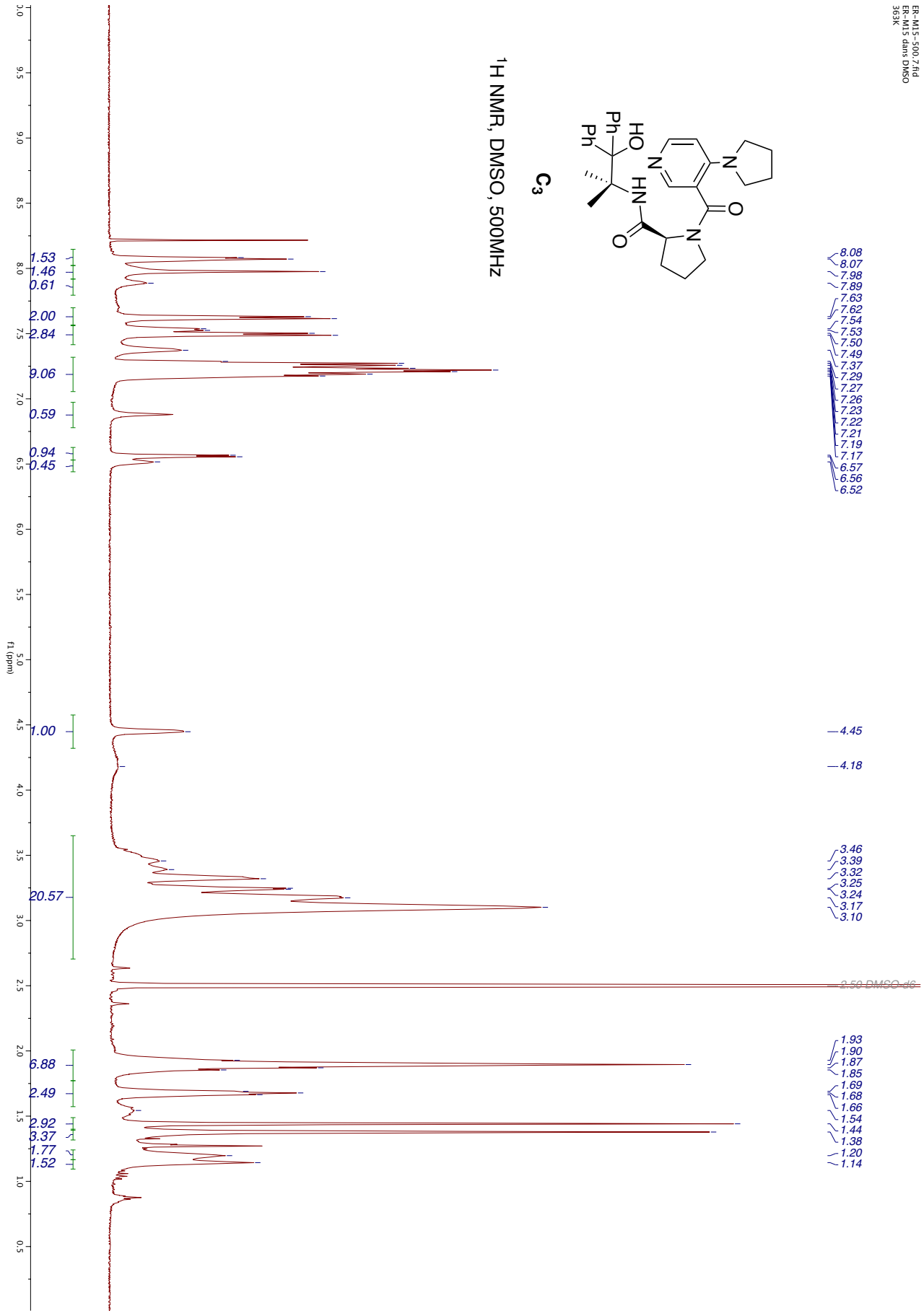

ClPy7
1H NMR, DMSO, 500MHz
ER-MAG19-10.fid
2.50 DMSO-d6
f1 (ppm)

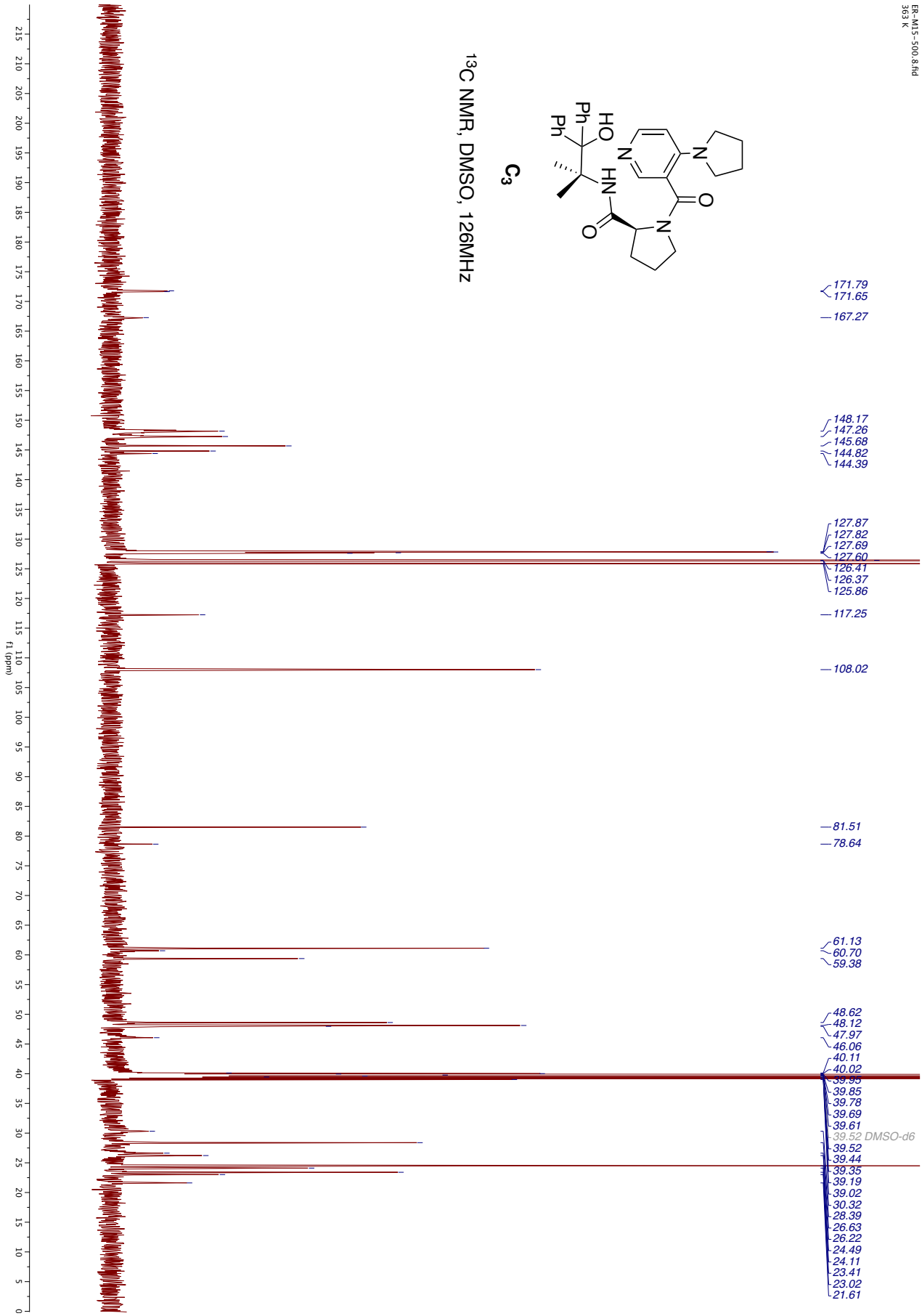
ER-MAG19.12.fid



$ClPy_7$

^{13}C NMR, DMSO, 126MHz


ER-M15-500.7.fid
ER-M15 dans DMSO
363K
^{1}H NMR, DMSO, 500MHz
C_3
HO
Ph
Ph
HN
O
N
N
O
N
O
f1 (ppm)
1.53
1.46
0.61
2.00
2.84
9.06
0.59
0.94
0.45
1.00
20.57
6.88
2.49
2.92
3.37
1.77
1.52
8.08
8.07
7.98
7.89
7.63
7.62
7.54
7.53
7.50
7.49
7.37
7.29
7.27
7.26
7.23
7.22
7.21
7.19
7.17
6.57
6.56
6.52
4.45
4.18
3.46
3.39
3.32
3.25
3.24
3.17
3.10
2.50 DMSO-d6
1.93
1.90
1.87
1.85
1.69
1.68
1.66
1.54
1.44
1.38
1.20
1.14


EB-M15-500.8.fid
363 K
^{13}C NMR, DMSO, 126MHz
C3
HO
Ph
Ph
HN
O
N
N
O
N
f1 (ppm)
171.79
171.65
167.27
148.17
147.26
145.68
144.82
144.39
127.87
127.82
127.69
127.60
126.41
126.37
125.86
117.25
108.02
81.51
78.64
61.13
60.70
59.38
48.62
48.12
47.97
46.06
40.11
40.02
39.85
39.78
39.69
39.61
39.52 DMSO-d6
39.52
39.44
39.35
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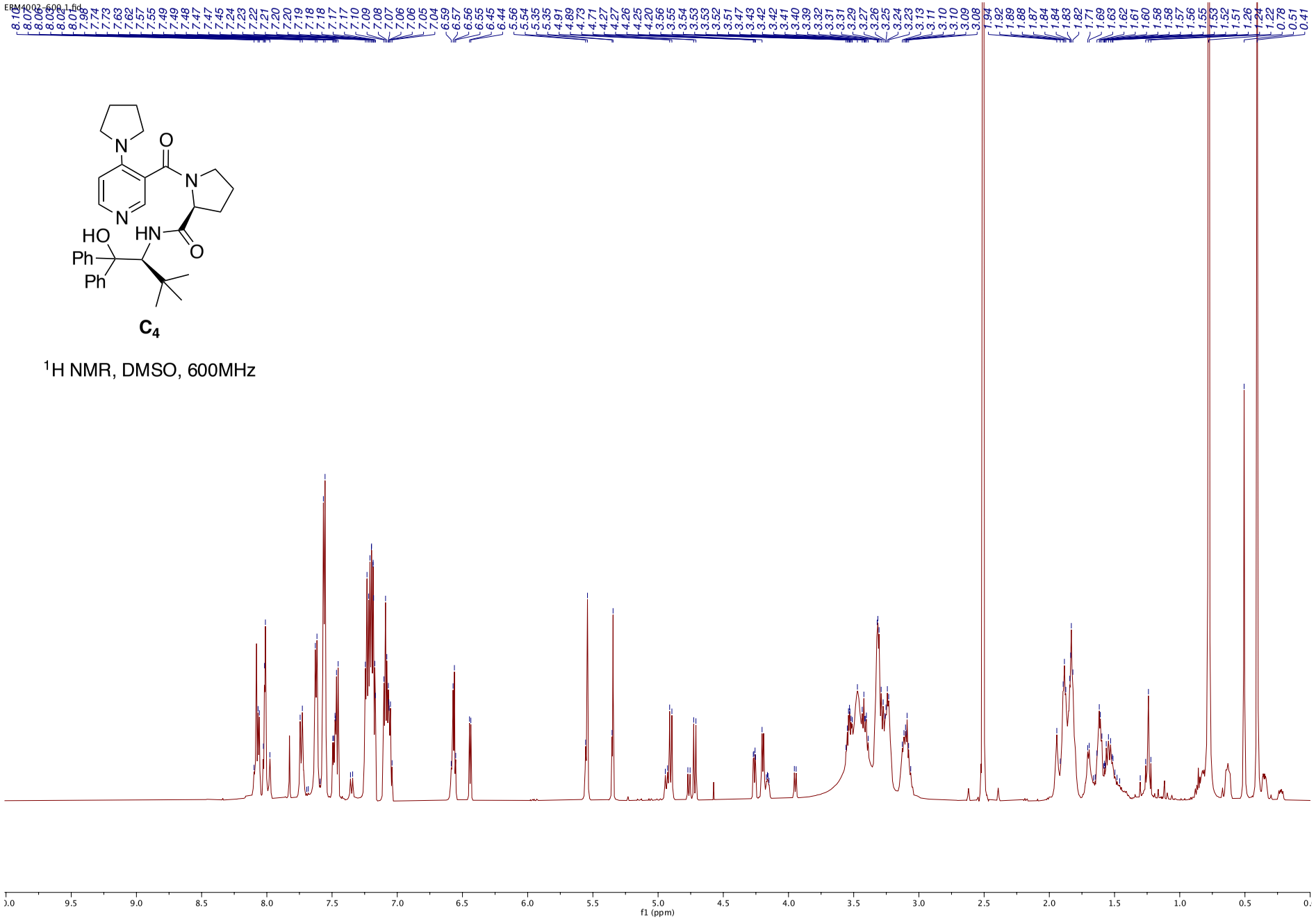
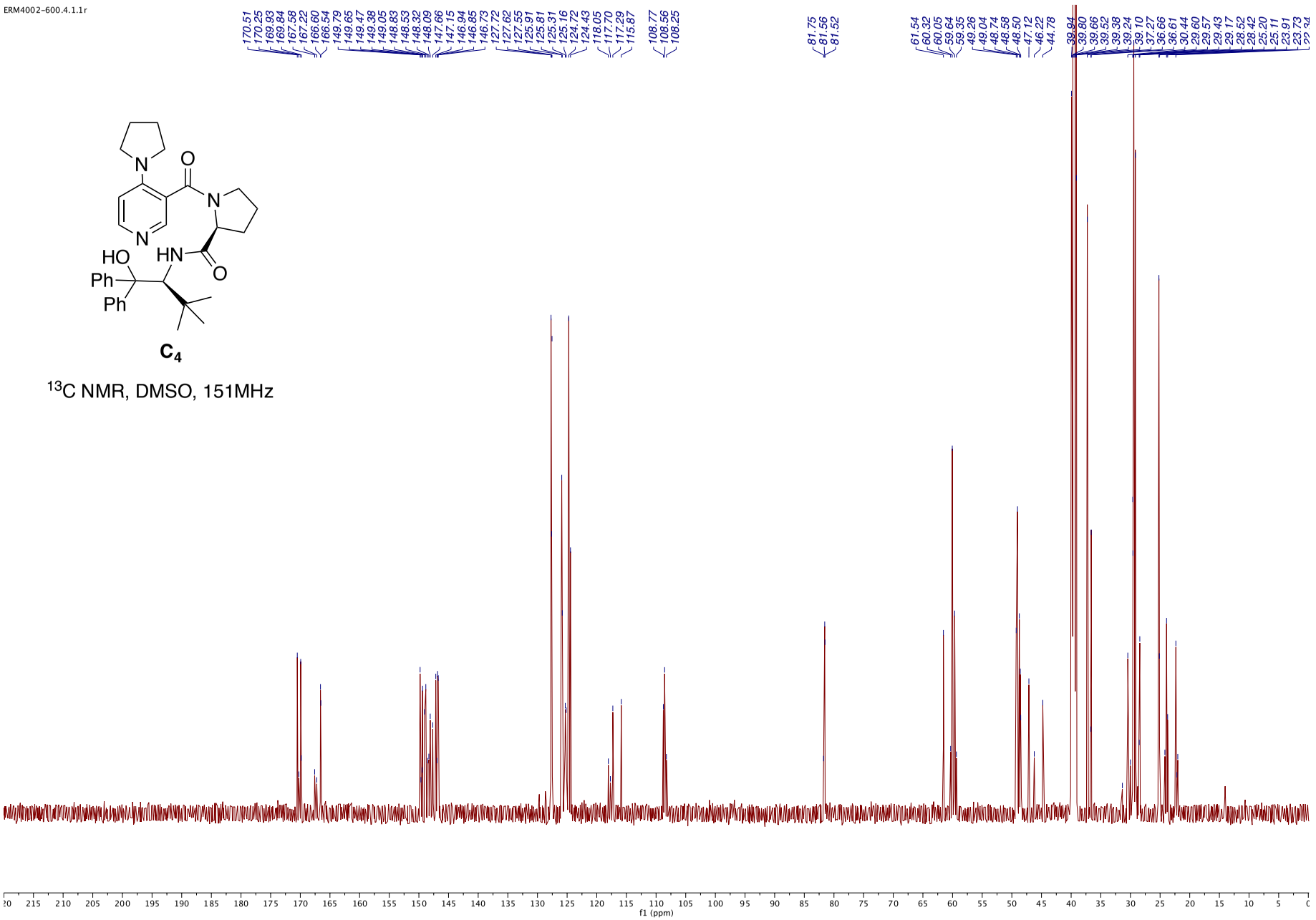
39.02
30.32
28.39
26.63
26.22
24.49
24.11
23.41
23.02
21.61



C_4

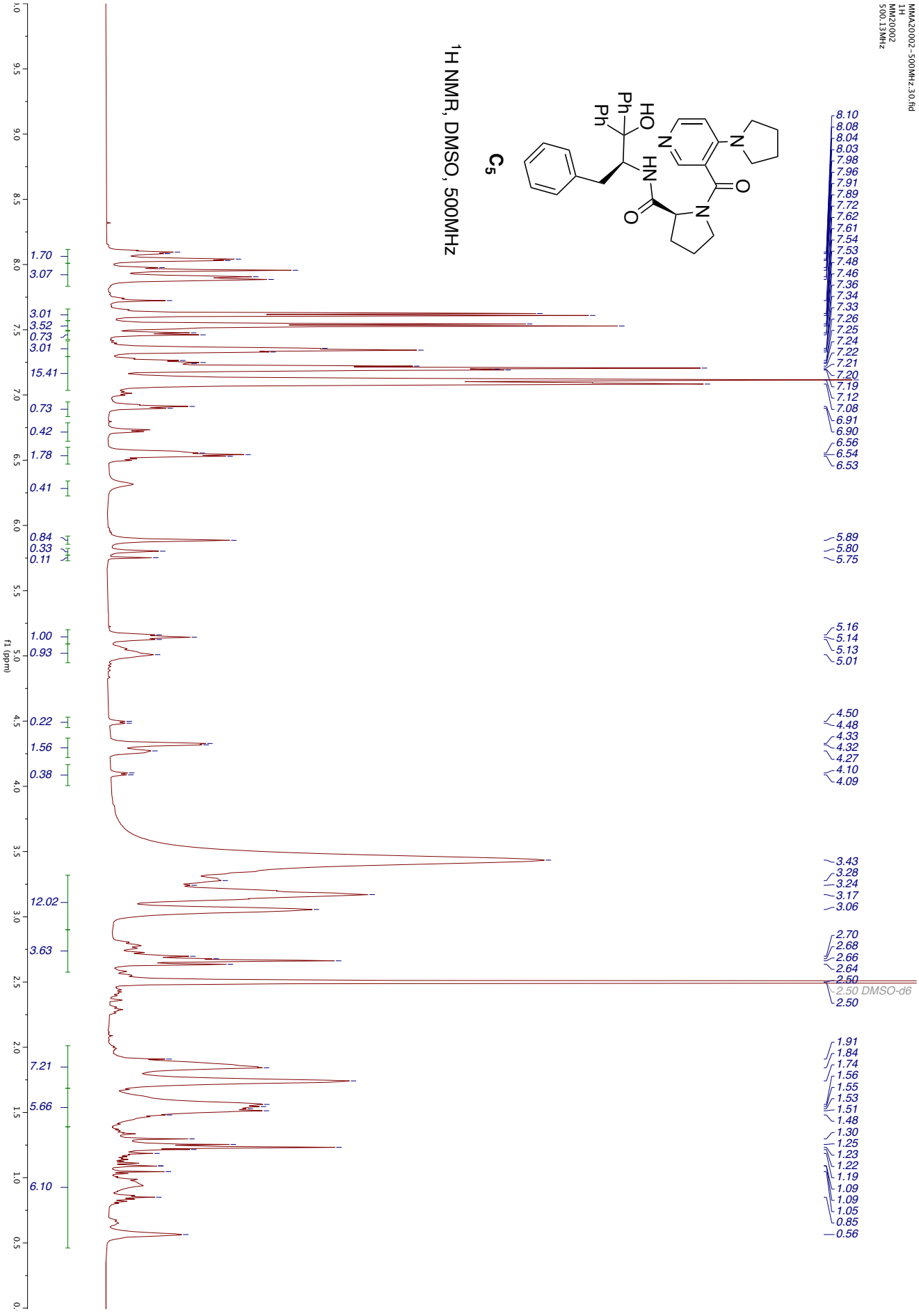
^{1}H NMR, DMSO, 600MHz

ERM4002-600.4.1.1r

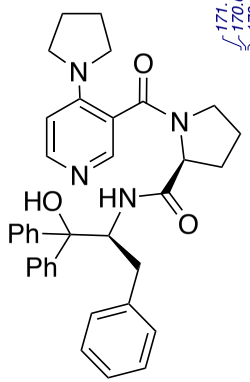


C$_4$

^{13}C NMR, DMSO, 151MHz


MMA20002-500MHz-30.fid
1H
MMA20002
500.13MHz
^{1}H NMR, DMSO, 500MHz
C5
HO
Ph
Ph
HN
O
N
N
O
N
O
f1 (ppm)
8.10
8.08
8.04
8.03
7.98
7.96
7.91
7.89
7.72
7.62
7.61
7.54
7.53
7.48
7.46
7.36
7.34
7.33
7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.12
7.08
6.91
6.90
6.56
6.54
6.53
5.89
5.80
5.75
5.16
5.14
5.13
5.01
4.50
4.48
4.33
4.32
4.27
4.10
4.09
3.43
3.28
3.24
3.17
3.06
2.70
2.68
2.66
2.64
2.50
2.50 DMSO-d6
2.50
1.91
1.84
1.74
1.56
1.55
1.53
1.51
1.48
1.30
1.25
1.23
1.22
1.19
1.09
1.09
1.05
0.85
0.56
1.70
3.07
3.01
3.52
0.73
3.01
15.41
0.73
0.42
1.78
0.41
0.84
0.33
0.11
1.00
0.93
0.22
1.56
0.38
12.02
3.63
7.21
5.66
6.10

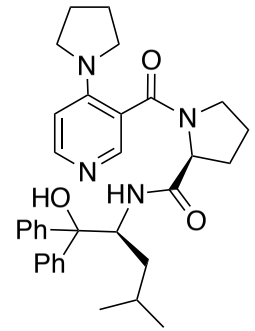
MMA20002-500MHz.35.fid
13C decouple 1H
MM20002
125.7MHz



C$_5$

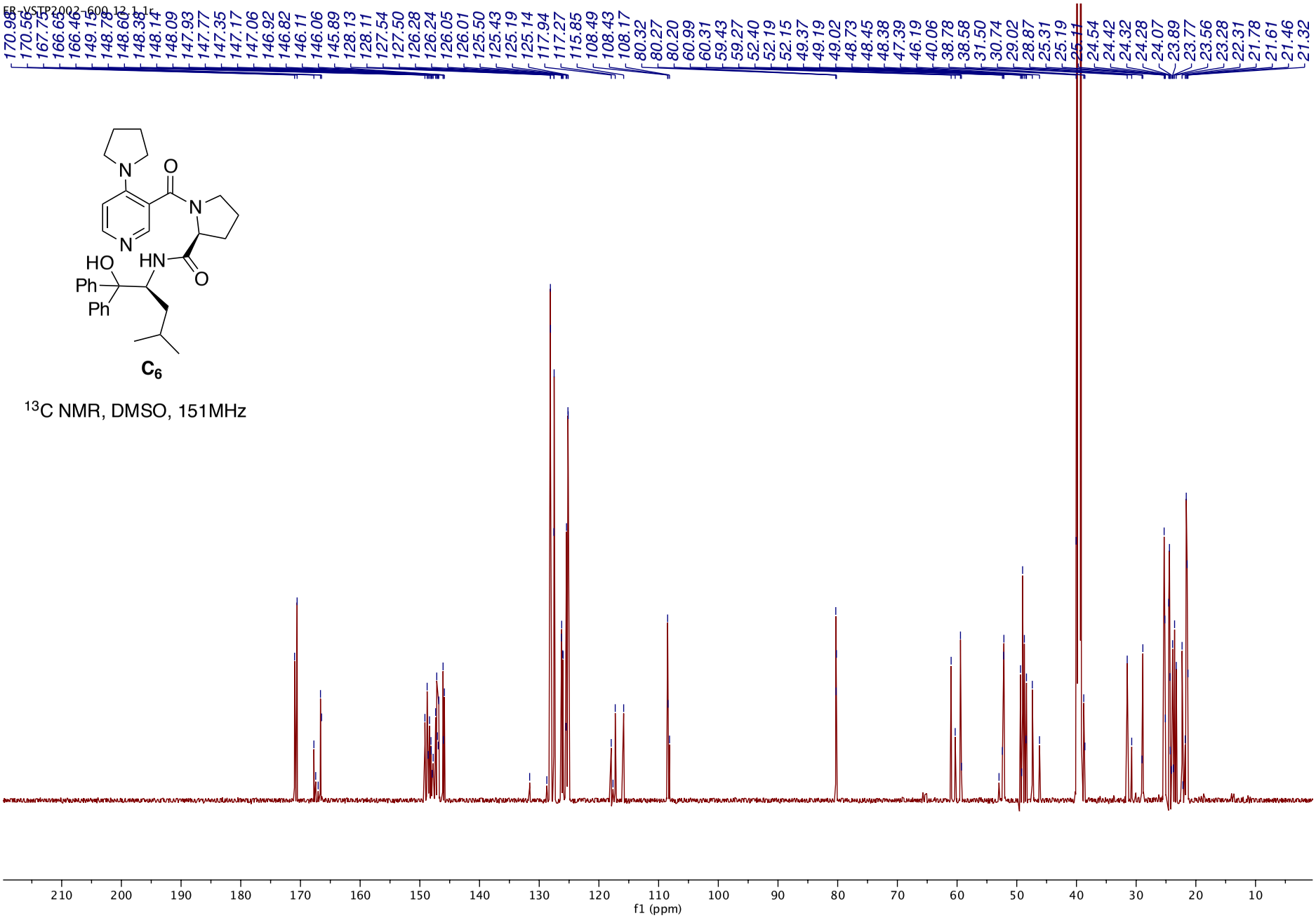
^{13}C NMR, DMSO, 126MHz

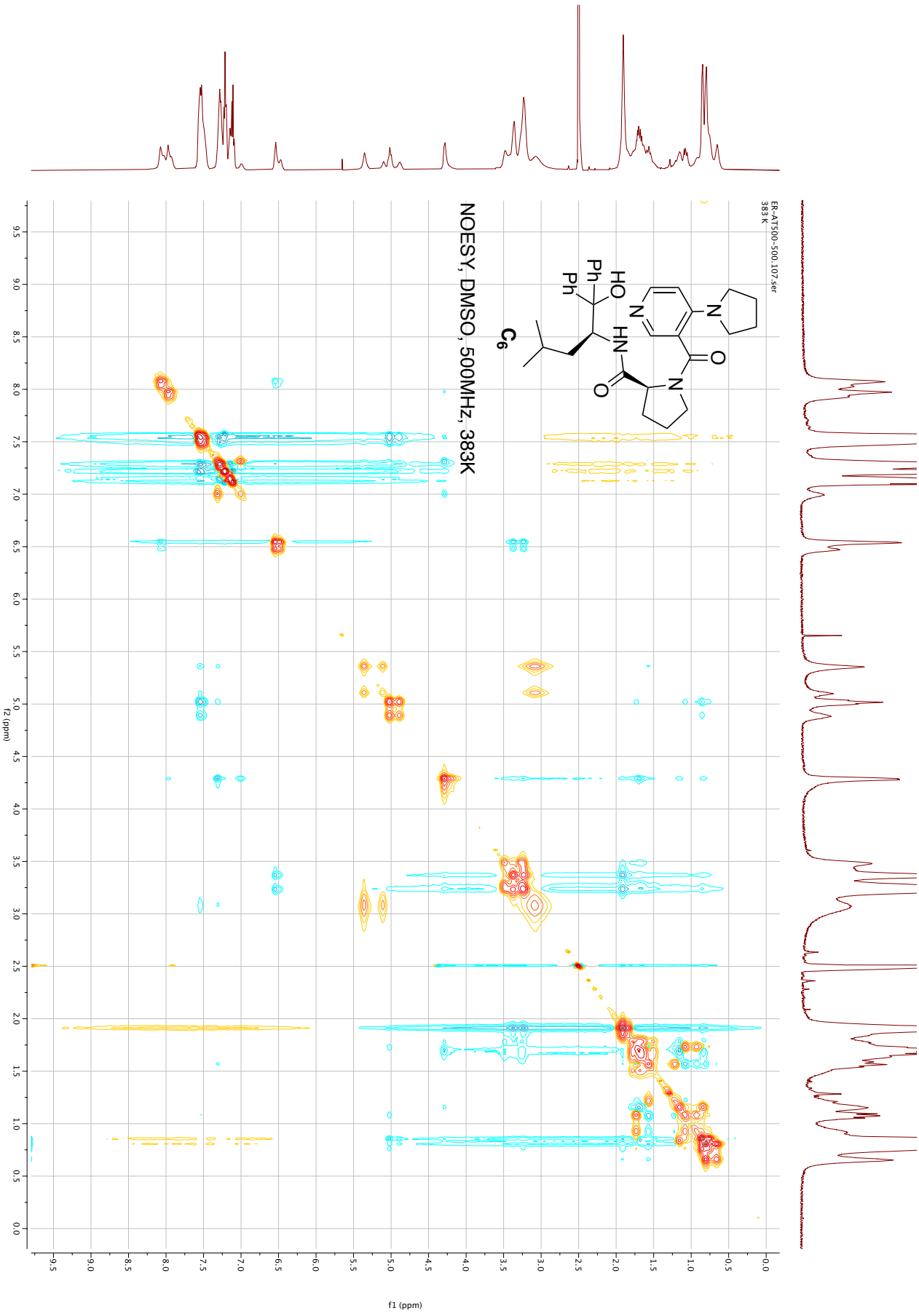
ER-VSTP2002-600.10.fid



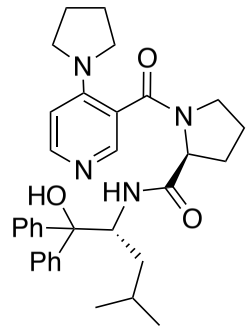
C$_6$

^{1}H NMR, DMSO, 600MHz


EB-VSTP2002-600.12.1.1r
170.98
170.56
167.75
166.65
166.46
149.15
148.78
148.60
148.38
148.14
148.09
147.93
147.77
147.35
147.17
147.06
146.92
146.82
146.11
146.06
145.89
128.13
128.11
127.54
127.50
126.28
126.24
126.05
126.01
125.50
125.43
125.19
125.14
117.94
117.27
115.85
108.49
108.43
108.17
80.32
80.27
80.20
60.99
60.31
59.43
59.27
52.40
52.19
52.15
49.37
49.19
49.02
48.73
48.45
48.38
47.39
46.19
40.06
38.78
38.58
31.50
30.74
29.02
28.87
25.31
25.19
25.11
24.54
24.42
24.32
24.28
24.07
23.89
23.77
23.56
23.28
22.31
21.78
21.61
21.46
21.32
N
O
N
N
HO
HN
O
Ph
Ph
C6
13C NMR, DMSO, 151MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

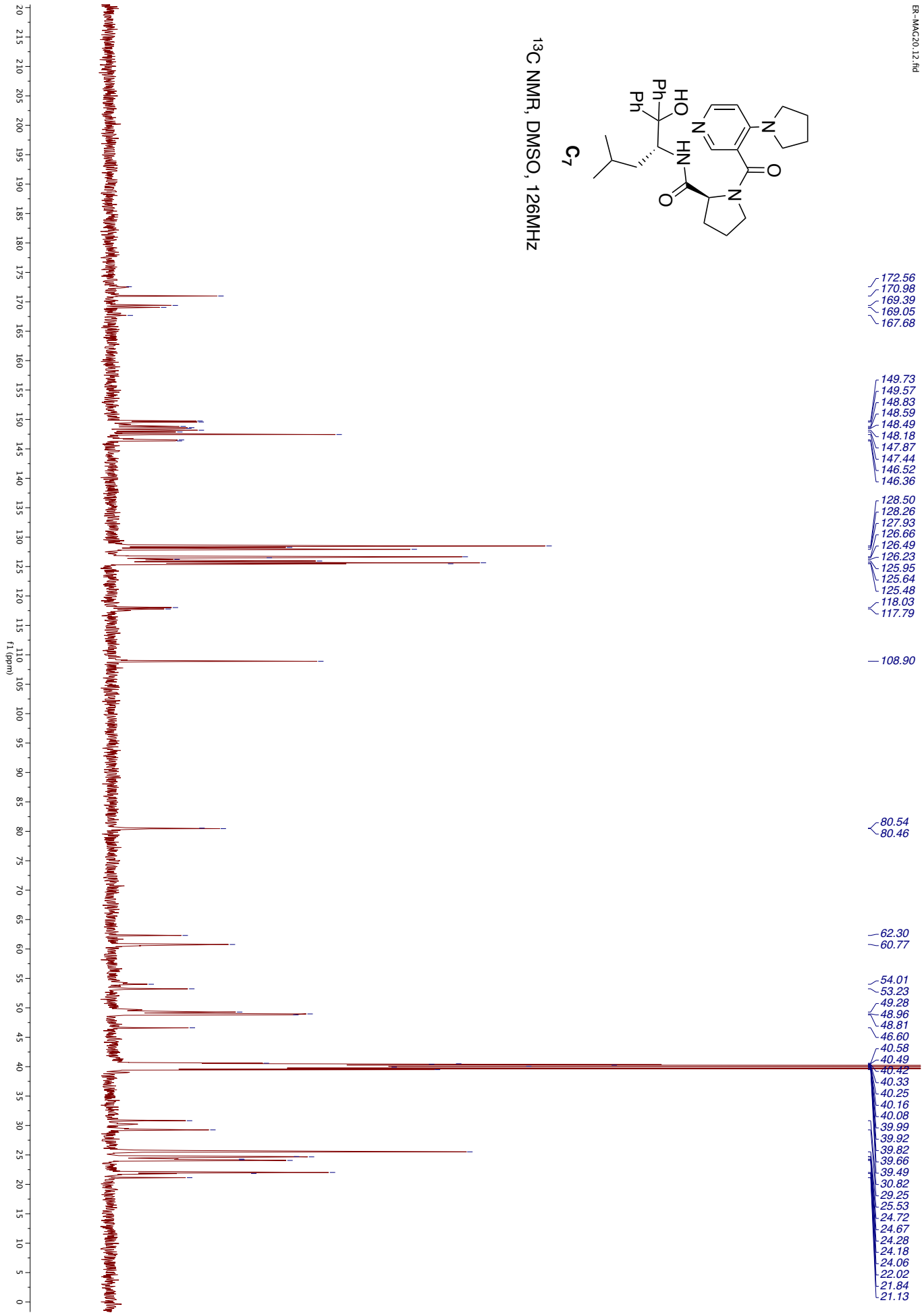

NOESY, DMSO, 500MHz, 383K
ER-AT500-500.107.ser
383 K
HO
Ph
Ph
HN
O
O
N
N
N
C6
f2 (ppm)
f1 (ppm)

ER-MAG20.10.fid

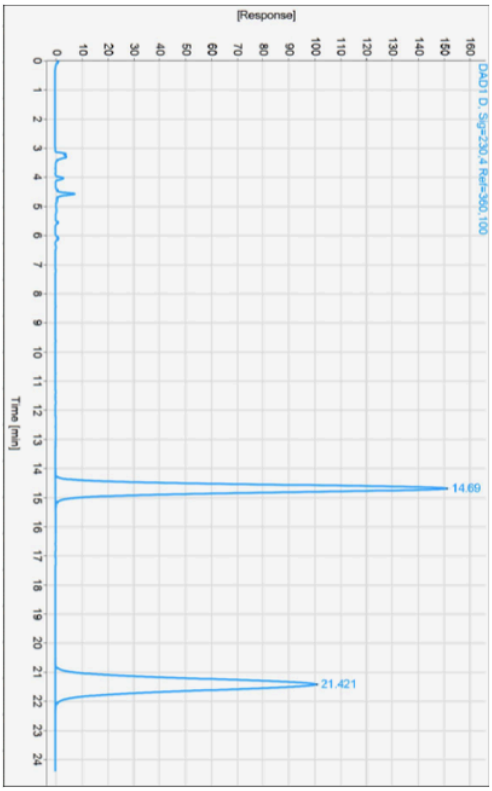


C_7

^{1}H NMR, DMSO, 500MHz

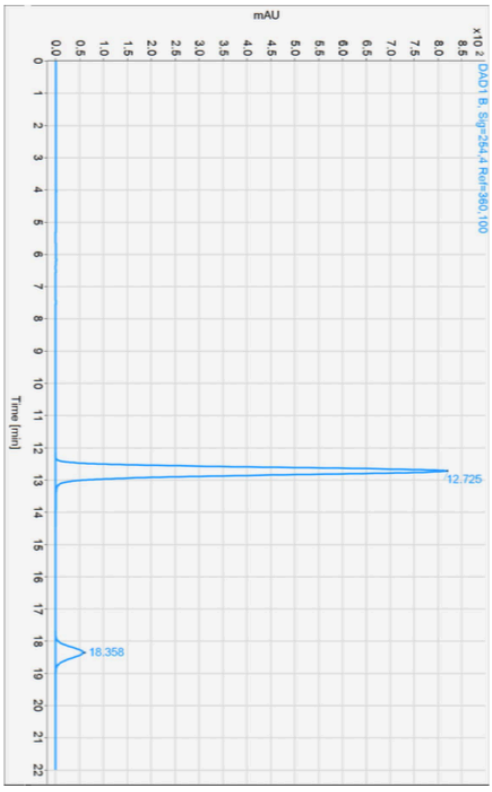

ER-MAC20.12.fid
^{13}C NMR, DMSO, 126MHz
C7
HO
Ph
Ph
HN
O
N
N
O
N
f1 (ppm)
172.56
170.98
169.39
169.05
167.68
149.73
149.57
148.83
148.59
148.49
148.18
147.87
147.44
146.52
146.36
128.50
128.26
127.93
126.66
126.49
126.23
125.95
125.64
125.48
118.03
117.79
108.90
80.54
80.46
62.30
60.77
54.01
53.23
49.28
48.96
48.81
46.60
40.58
40.49
40.42
40.33
40.25
40.16
40.08
39.99
39.92
39.82
39.66
39.49
30.82
29.25
25.53
24.72
24.67
24.28
24.18
24.06
22.02
21.84
21.13

8) Chiral HPLC analyses



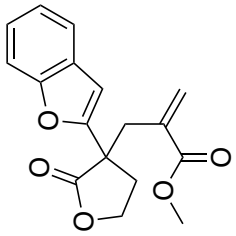
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
14.690		0.2973	2866.4448	151.1211	50.0061	0.92570	13450.26166
21.421		0.4439	2865.7400	100.7290	49.9939	0.92555	12803.48029
	Sum		5732.1848				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
12.725		0.2645	13905.2354	817.2411	90.5985	0.87100	12310.19104
18.358		0.3906	1442.9592	57.5397	9.4015	0.93388	11940.65704
	Sum		15348.1946				



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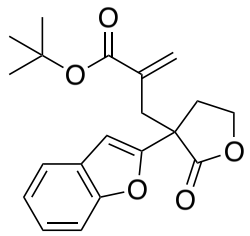

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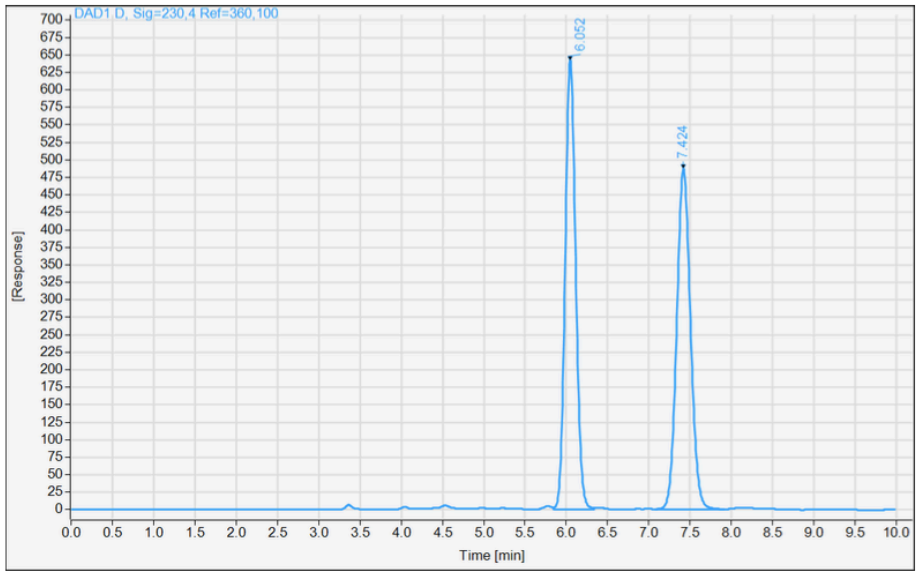
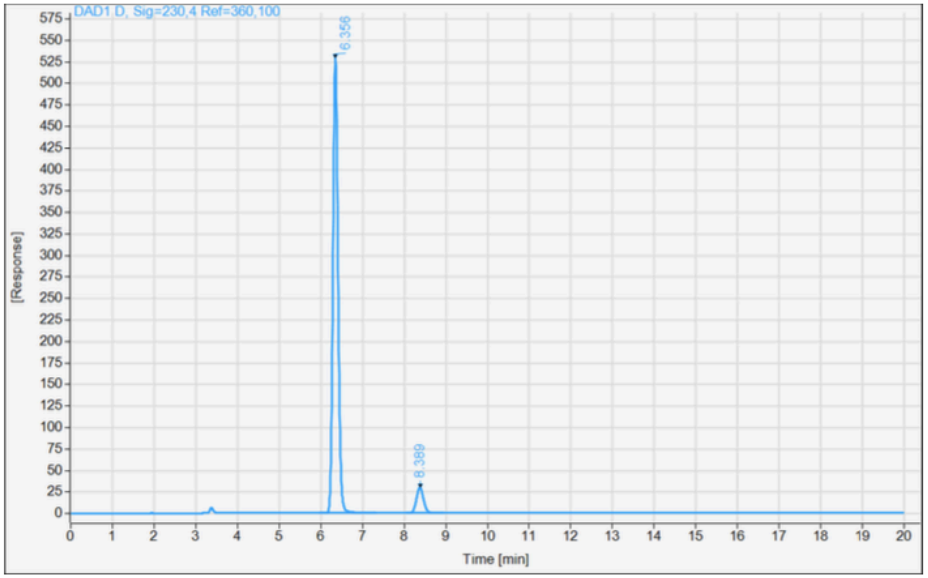


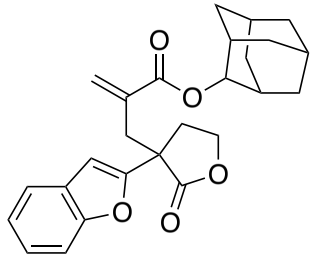


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.052		0.1372	5690.7769	643.5863	49.7951	0.89738	10238.87743
7.424		0.1832	5737.6201	487.7328	50.2049	0.90688	8641.20704
		Sum	11428.3970				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.356		0.1313	4504.9175	529.5228	92.7706	0.85506	11967.65918
8.389		0.1841	351.0576	29.6544	7.2294	0.90881	10868.36488
		Sum	4855.9751				



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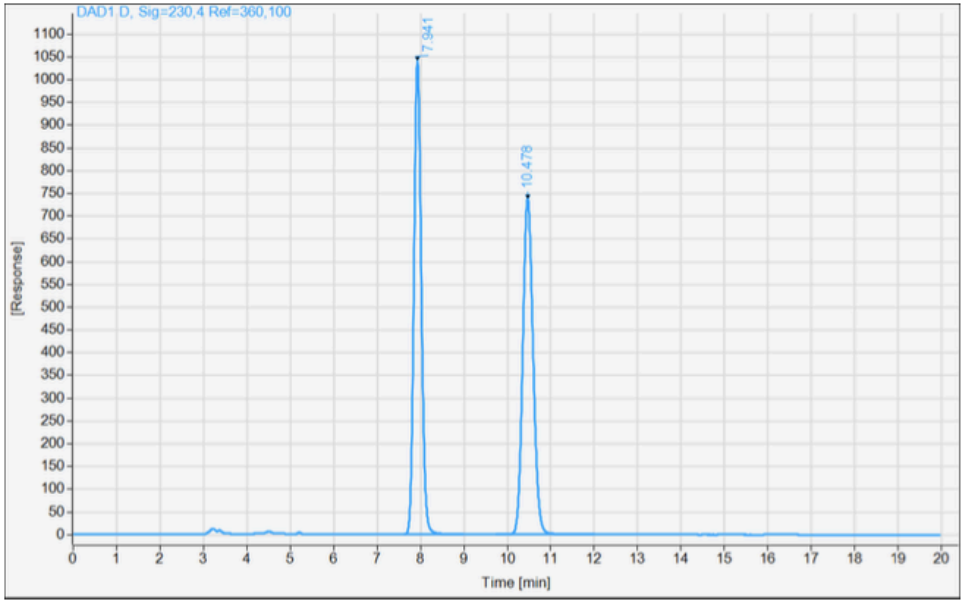
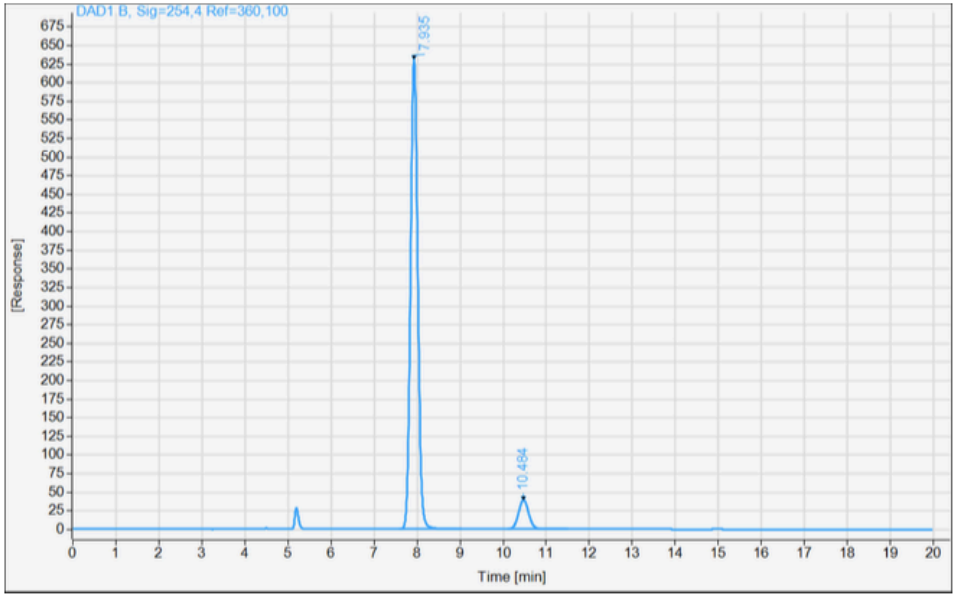


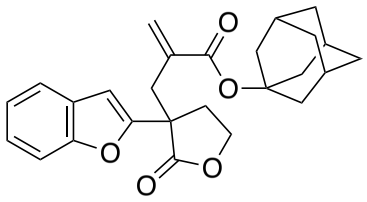


Signal: DAD1 D, Sig=230,4 Ref=360,100

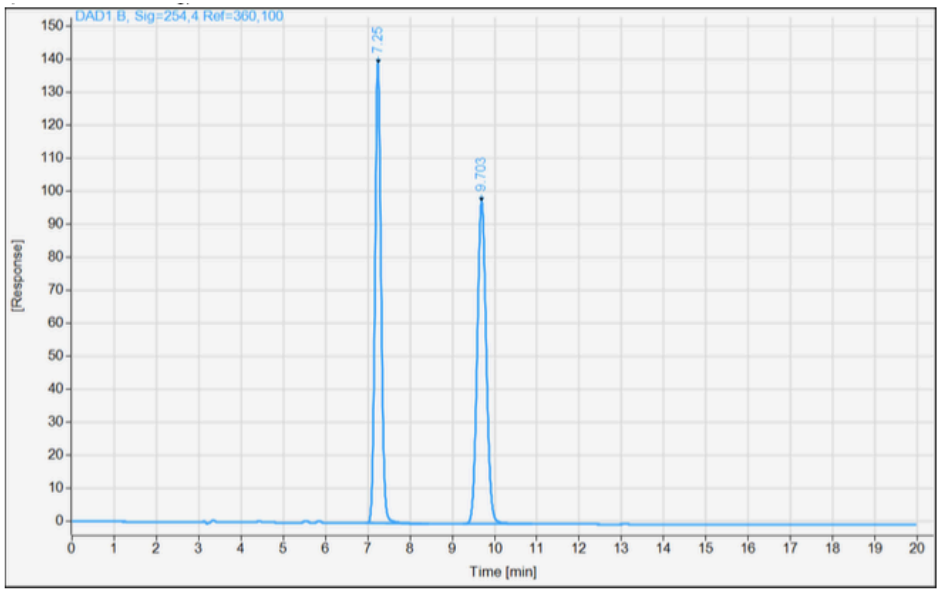
RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.941		0.1839	12308.3926	1041.0049	50.1939	0.85601	9832.56658
10.478		0.2568	12213.2939	738.8644	49.8061	0.86040	8872.92294
		Sum	24521.6865				

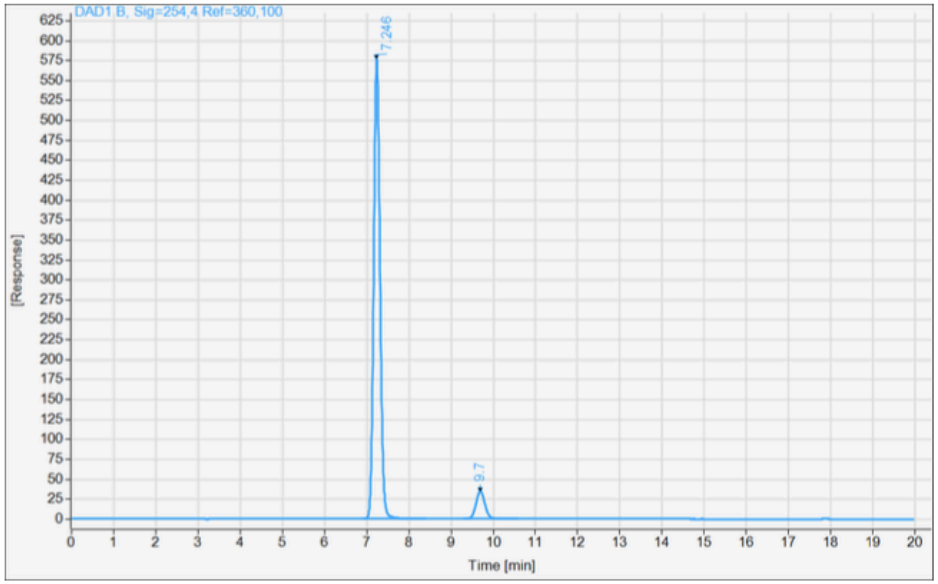
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.935		0.1834	7431.2817	630.9387	92.0041	0.88318	9884.74447
10.484		0.2562	645.8362	39.1934	7.9959	0.91754	9079.05798
		Sum	8077.1180				



3d



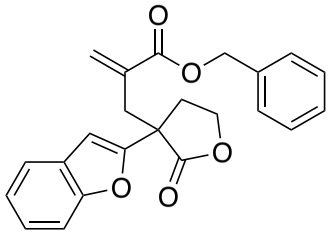


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.250		0.1612	1448.3514	139.4538	49.9694	0.88818	10925.52588
9.703		0.2310	1450.1257	97.7894	50.0306	0.91388	9536.53835
		Sum	2898.4772				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.246		0.1611	5991.4976	577.2426	92.1518	0.87946	10633.88991
9.700		0.2292	510.2703	34.3673	7.8482	0.91289	9530.37855
		Sum	6501.7679				



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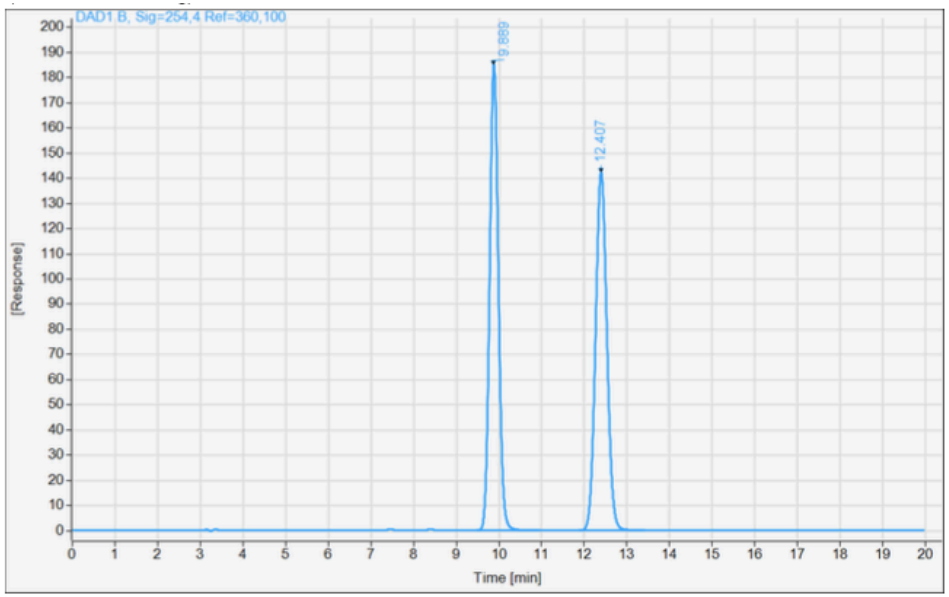
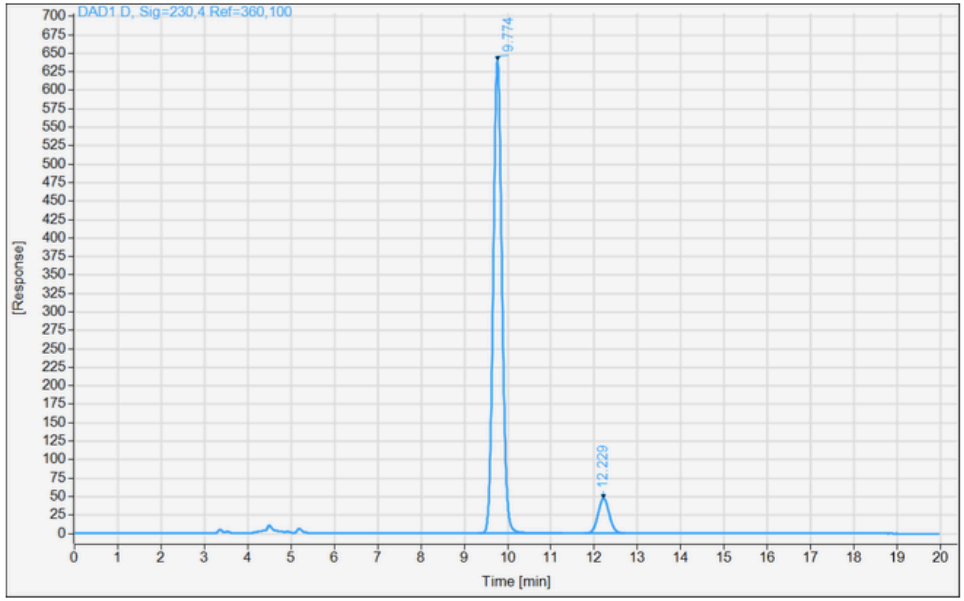


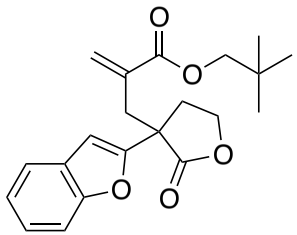


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
9.889		0.2226	2640.7830	184.9764	50.0690	0.90565	10394.45288
12.407		0.2877	2633.4995	142.4079	49.9310	0.92686	9902.95747
		Sum	5274.2825				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
9.774		0.2195	8973.1191	640.4260	91.4429	0.89156	10660.48980
12.229		0.2783	839.6883	47.0371	8.5571	0.94183	10550.43911
		Sum	9812.8074				



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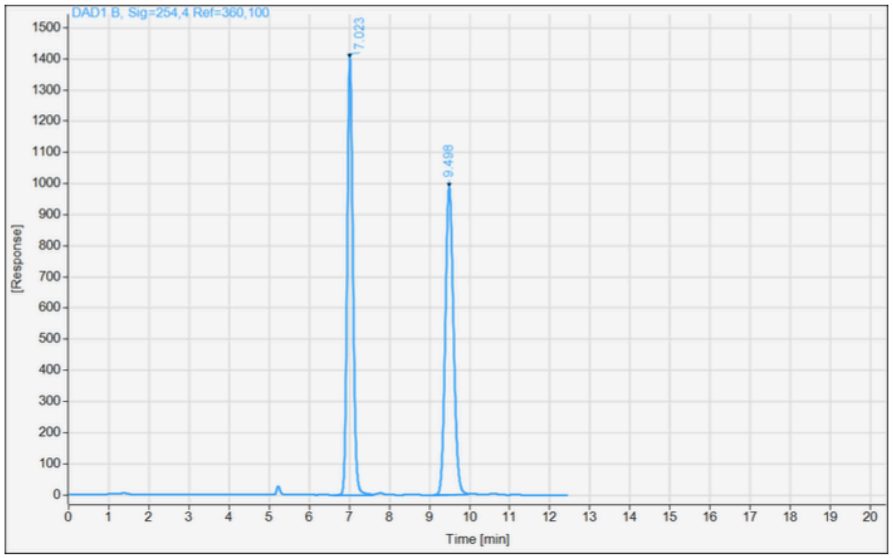
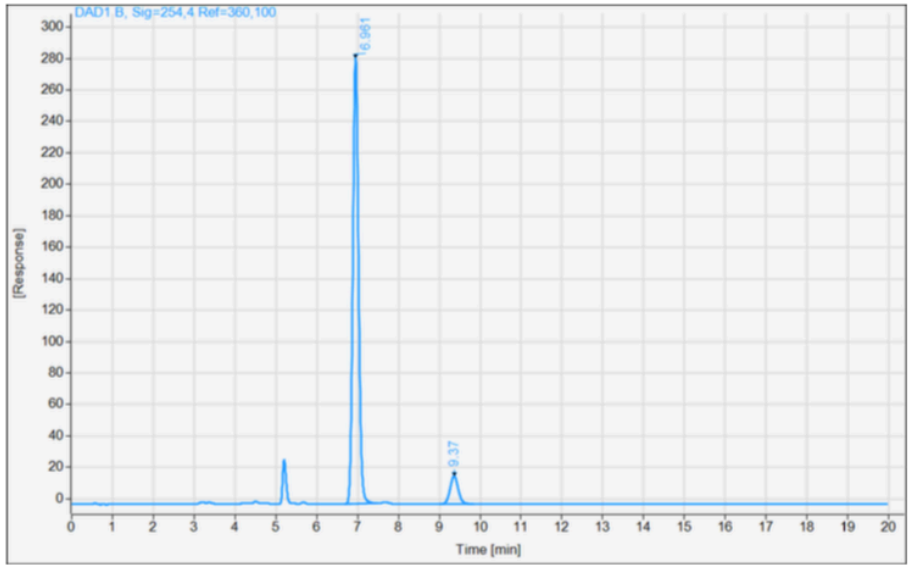


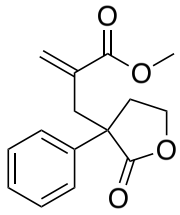


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.023		0.1544	14007.4326	1404.2224	49.9940	0.85245	10807.80813
9.498		0.2212	14010.8193	989.6196	50.0060	0.85849	9916.87309
		Sum	28018.2520				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.961		0.1483	2730.4839	283.6491	91.9454	0.88234	11343.98884
9.370		0.2127	239.1968	17.5838	8.0546	0.92975	10478.10625
		Sum	2969.6807				



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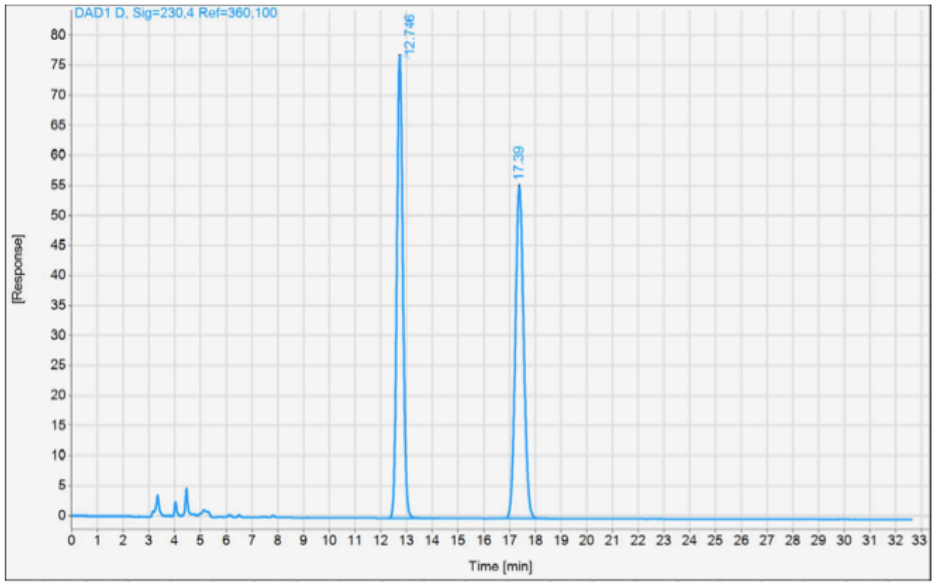
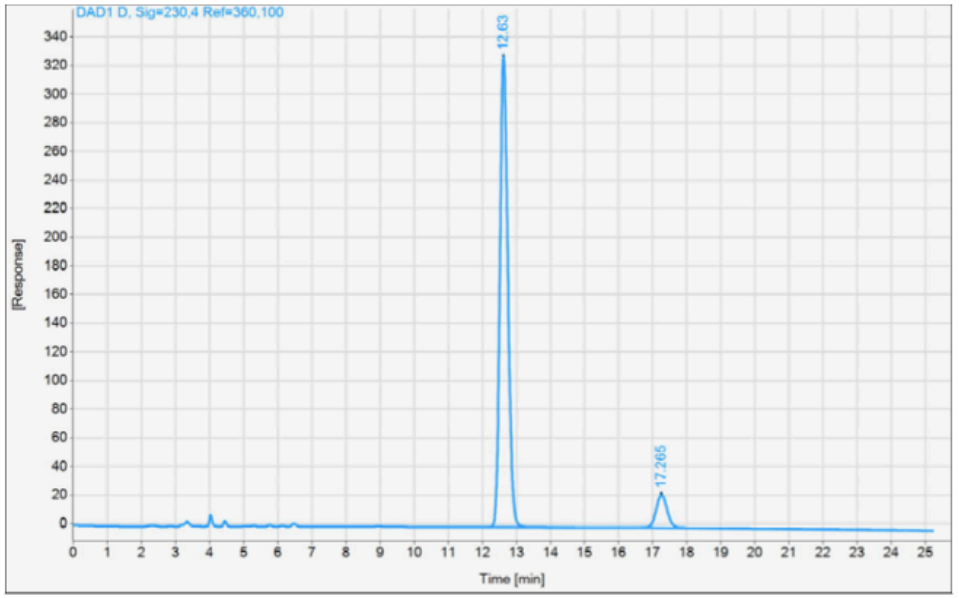


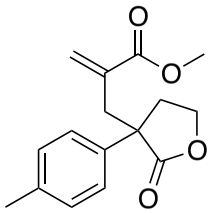


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
12.746		0.2529	1245.2408	76.9230	49.9945	0.88646	13752.67018
17.390		0.3511	1245.5153	55.2370	50.0055	0.88680	13322.16454
		Sum	2490.7561				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
12.630		0.2492	5326.6440	328.4647	89.0656	0.79603	13509.14194
17.265		0.4204	653.9423	22.9541	10.9344	0.54392	13606.17162
		Sum	5980.5863				



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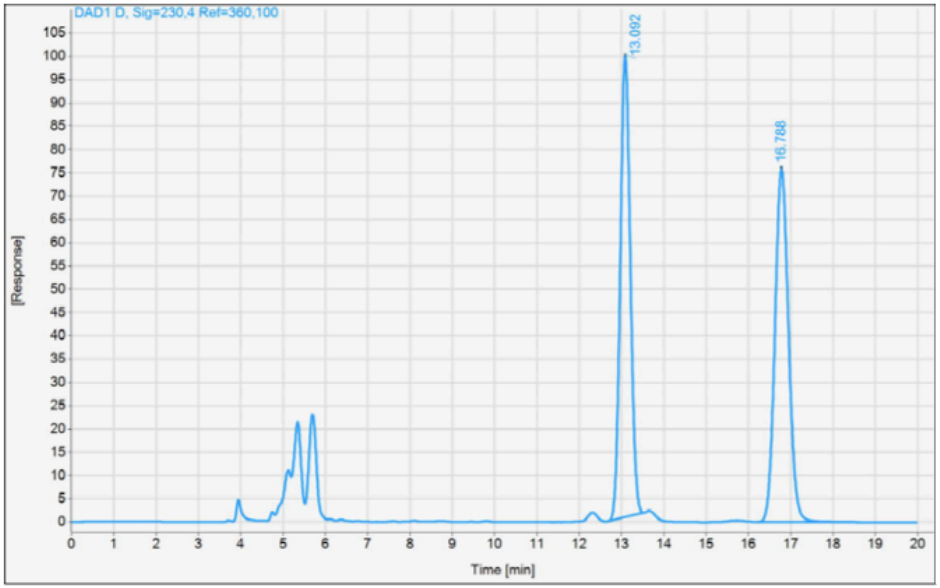
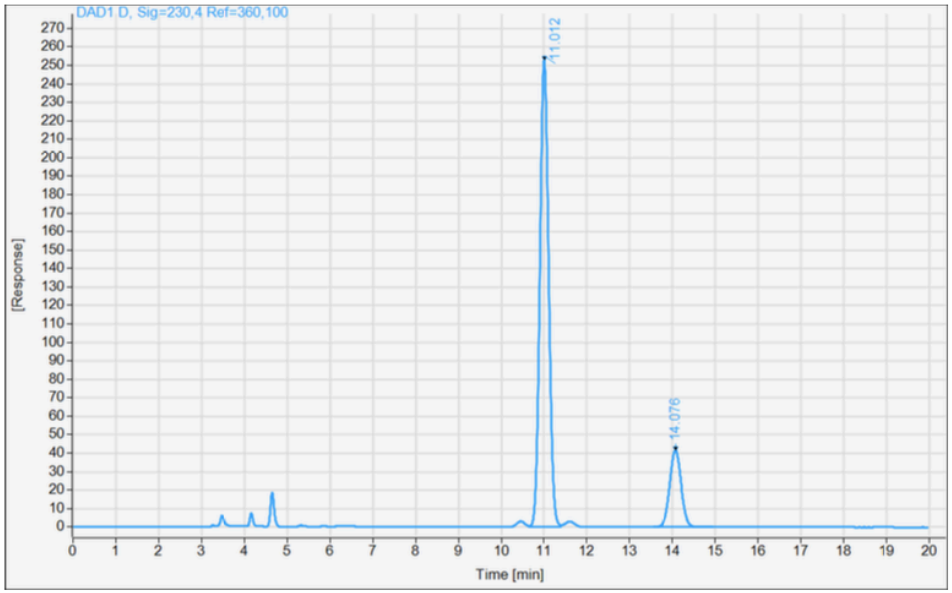


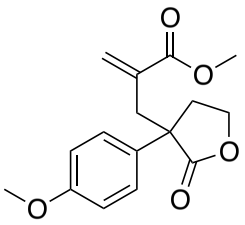


Signal: DAD1 D, Sig=230,4 Ref=360,100

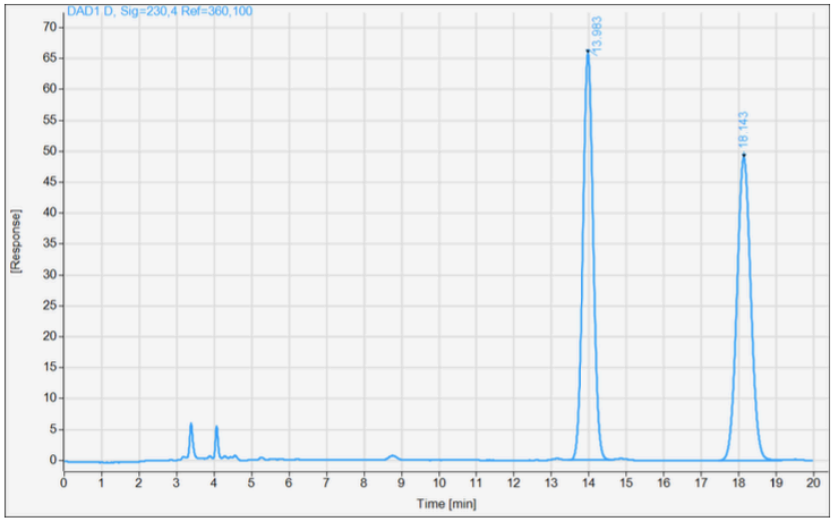
RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
13.092		0.2584	1631.6307	98.9276	49.0155	0.91564	13773.62910
16.788		0.3473	1697.1743	75.7738	50.9845	0.88804	12370.65061
		Sum	3328.8051				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
11.012		0.2221	3600.1526	252.8005	82.0707	0.91317	13359.00432
14.076		0.2942	786.4933	41.6720	17.9293	0.94926	12609.52791
		Sum	4386.6459				

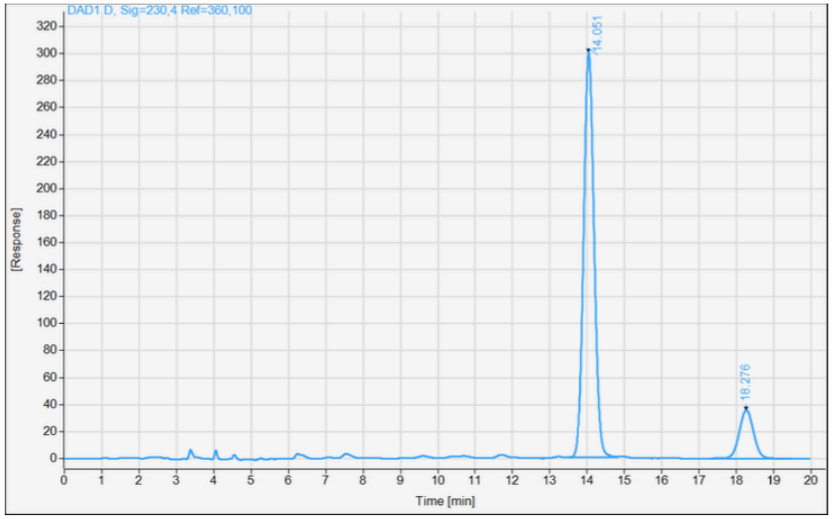


6



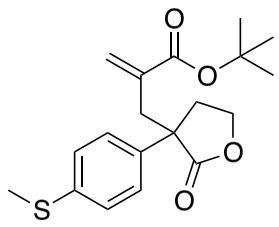
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
13.983		0.2966	1255.2262	65.7974	49.9291	0.94449	11943.97143
18.143		0.3996	1258.7911	49.0177	50.0709	0.94175	11212.19356
		Sum	2514.0173				



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
14.051		0.3027	5835.8379	300.2712	86.0289	0.90739	11447.64144
18.276		0.4118	947.7438	35.9212	13.9711	0.95529	10702.00009
		Sum	6783.5817				



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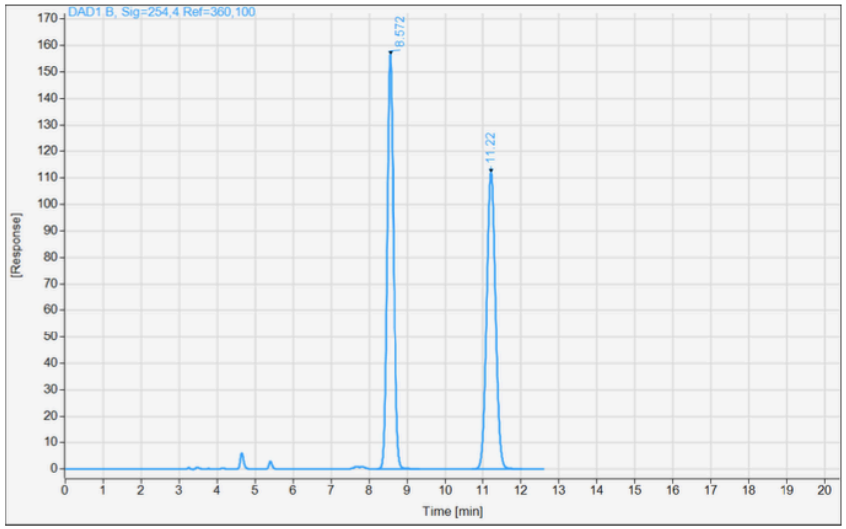
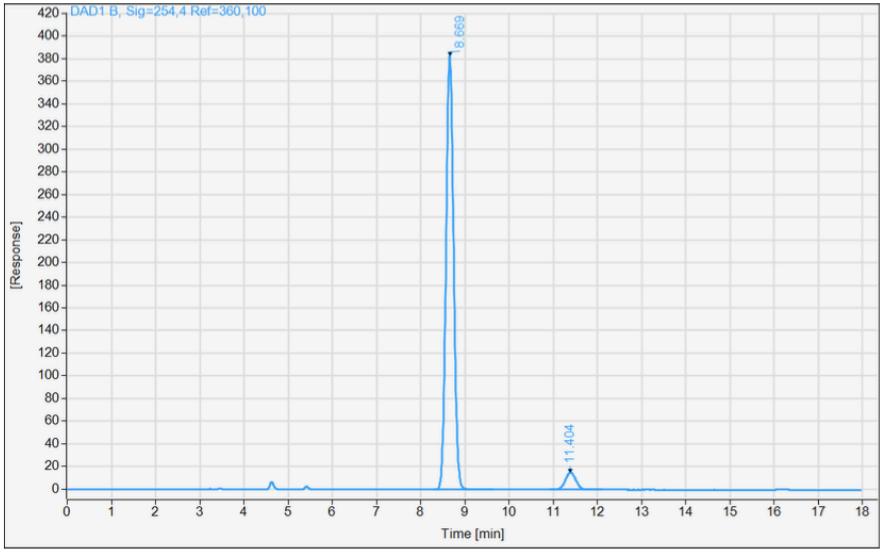


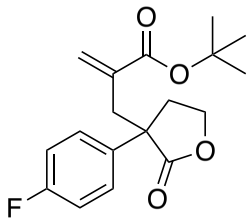
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
8.572		0.1811	1812.0188	156.4583	49.9910	0.93232	12152.76108
11.220		0.2527	1812.6711	112.0981	50.0090	0.93654	10729.53270
		Sum	3624.6899				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
8.669		0.1853	4572.8198	383.0768	94.7362	0.92195	11866.98092
11.404		0.2587	254.0800	15.2283	5.2638	0.94878	10449.15646
		Sum	4826.8998				



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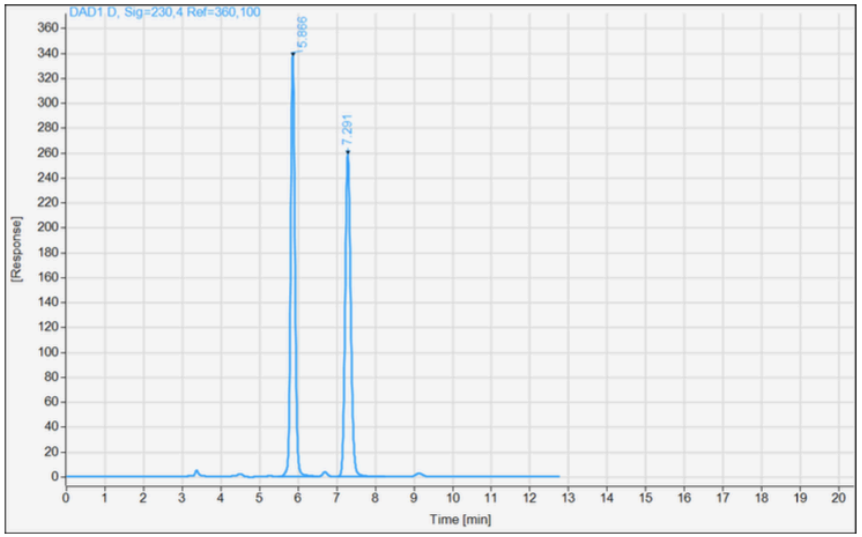
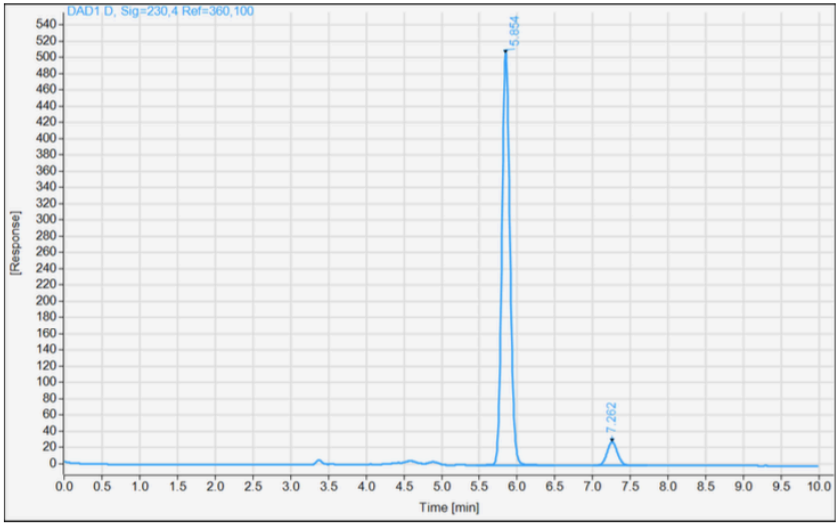


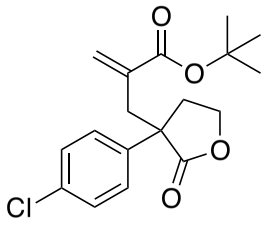


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.866		0.1206	2626.1509	338.0829	50.3643	0.87289	12114.89516
7.291		0.1565	2588.1570	259.2168	49.6357	0.83973	11515.78628
		Sum	5214.3079				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.854		0.1147	3773.7341	507.9380	93.1808	0.86844	13815.43121
7.262		0.1478	276.1698	28.8108	6.8192	0.92019	12882.84115
		Sum	4049.9039				



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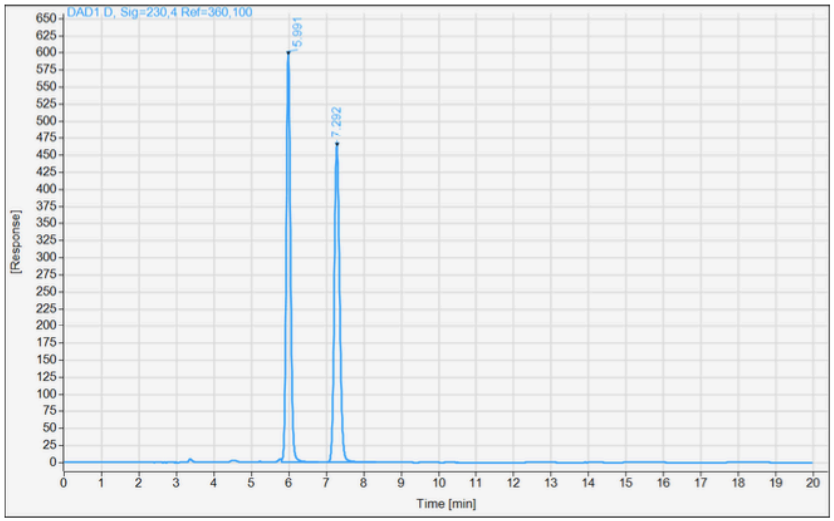
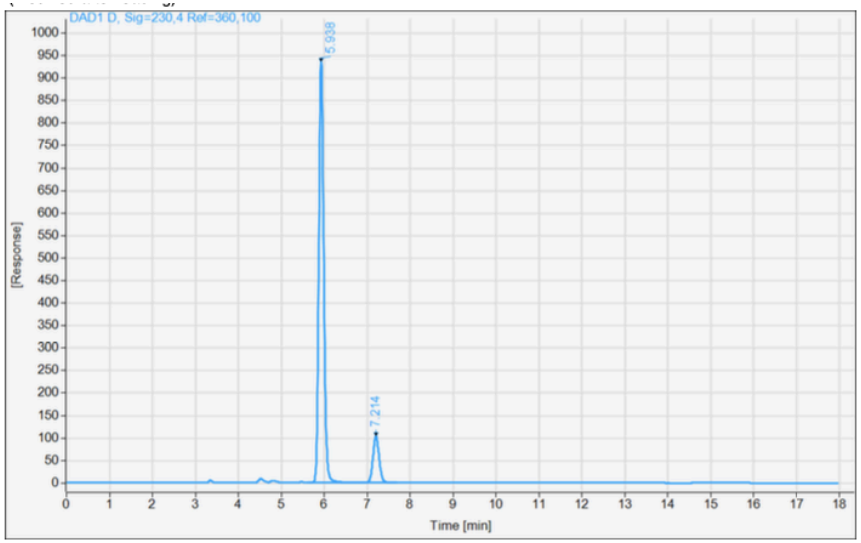


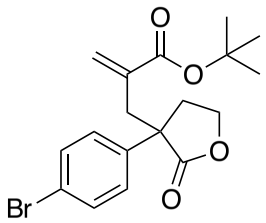


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.991		0.1195	4690.6875	598.2744	50.0019	0.84887	12296.04940
7.292		0.1582	4690.3379	462.9823	49.9981	0.86504	11312.36169
		Sum	9381.0254				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.938		0.1224	7428.3589	937.6635	87.7774	0.82649	11859.47270
7.214		0.1553	1034.3605	102.8338	12.2226	0.89747	11106.96998
		Sum	8462.7194				



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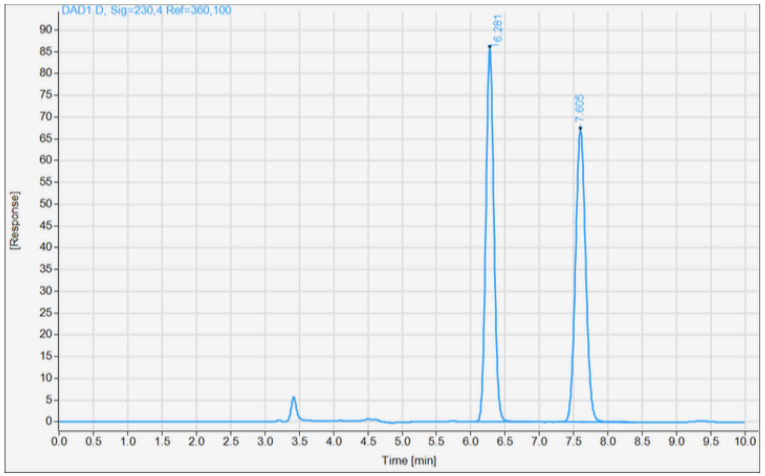
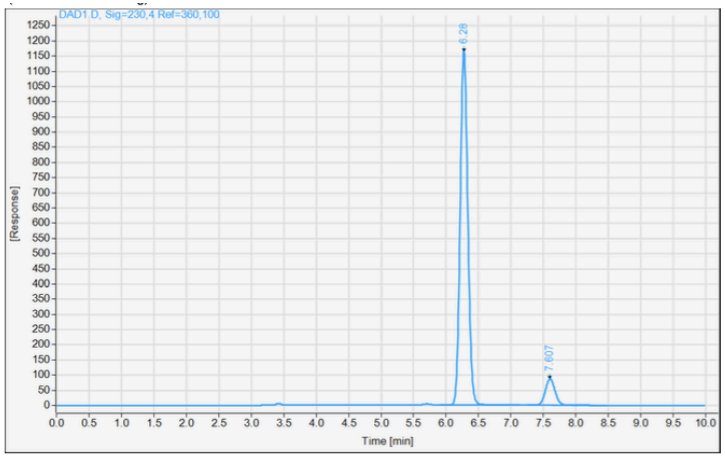


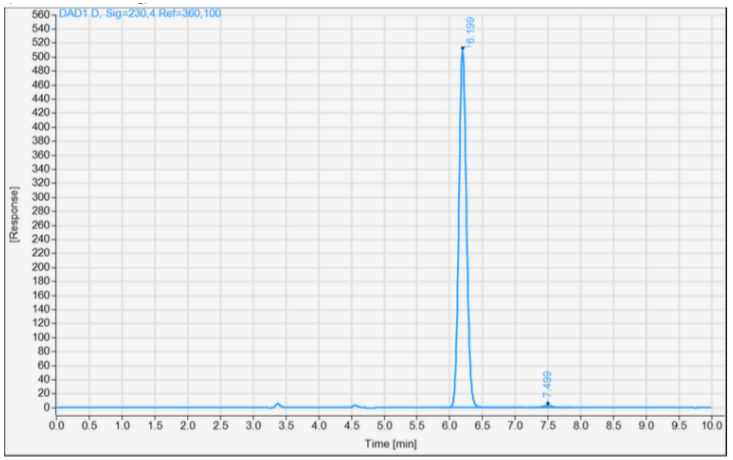
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.281		0.1246	695.0865	85.7003	50.0057	0.90894	13153.07942
7.605		0.1609	694.9285	67.0400	49.9943	0.92148	11952.42053
		Sum	1390.0150				



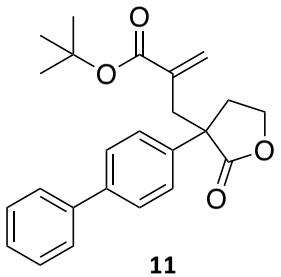
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.280		0.1269	9487.3467	1166.3707	91.3569	0.89675	13076.08278
7.607		0.1608	897.5807	86.6628	8.6431	0.91806	11740.29854
		Sum	10384.9274				



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.199		0.1260	4110.6421	510.3123	99.2609	0.90015	12980.22930
7.499		0.1596	30.6073	2.9858	0.7391	0.94573	11919.12763
		Sum	4141.2494				



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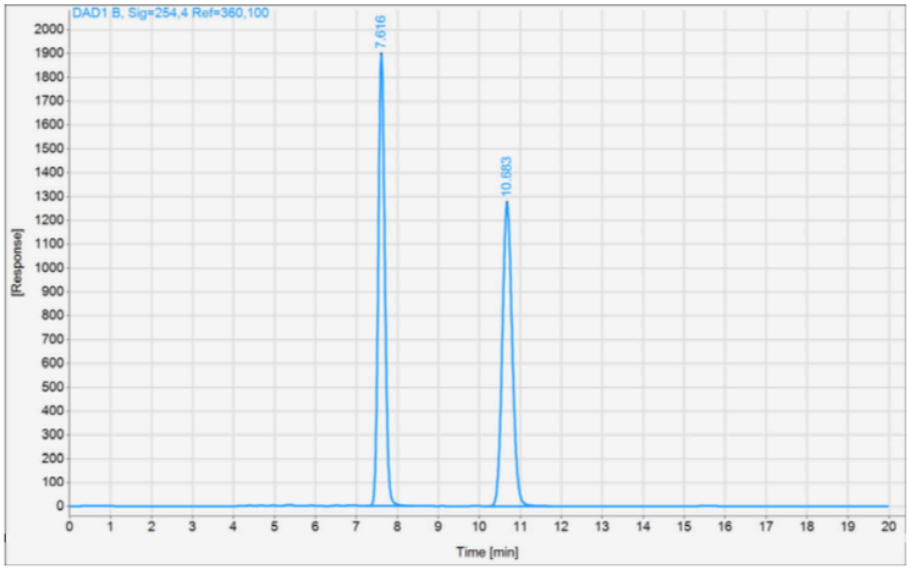
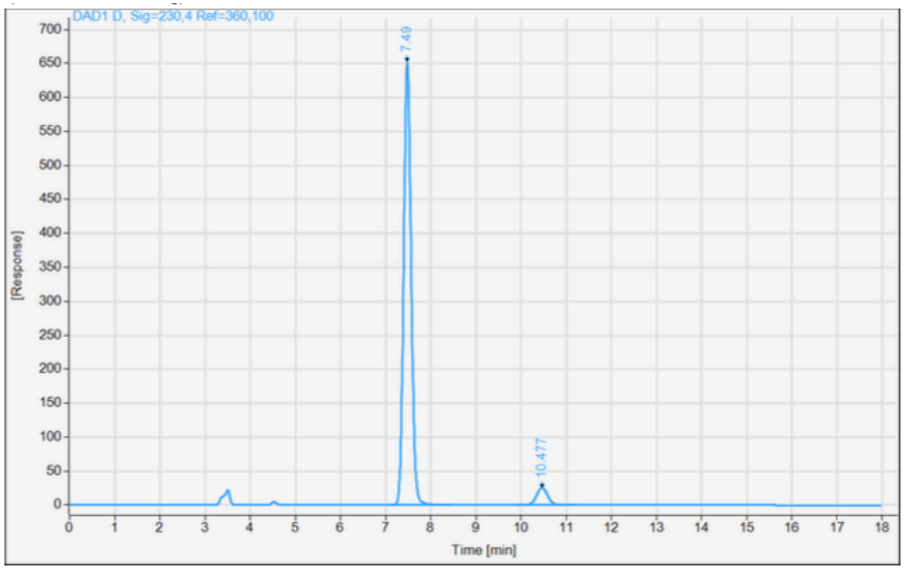


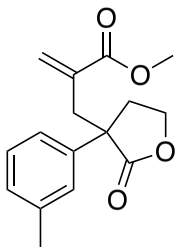


Signal: DAD1 B, Sig=254,4 Ref=360,100

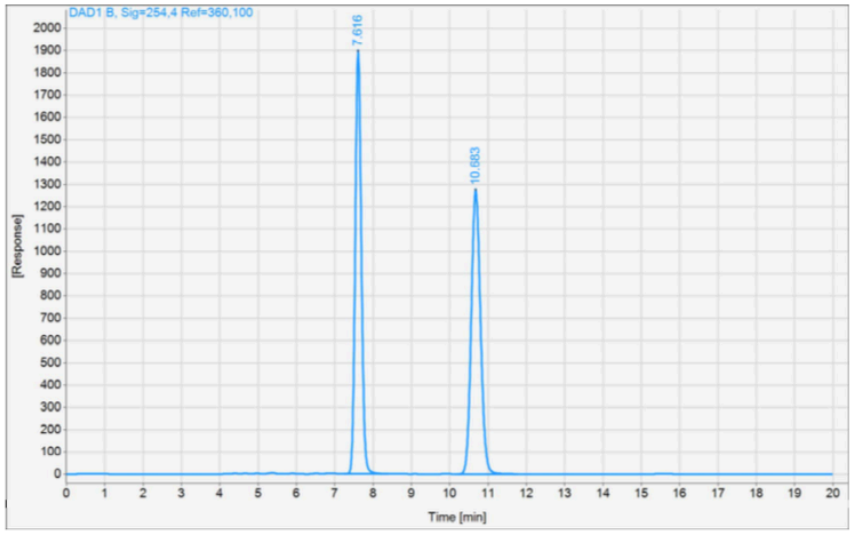
RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.616		0.1741	21086.1504	1891.5137	49.6688	0.87156	10226.43950
10.683		0.2626	21367.3223	1268.0287	50.3312	0.87831	8830.89411
		Sum	42453.4727				

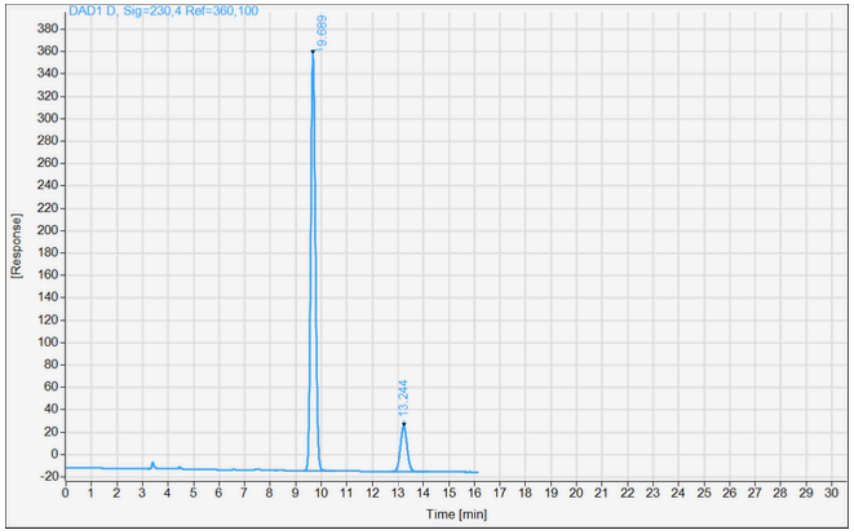
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.490		0.1780	7492.7451	652.5090	94.4373	0.87474	9320.30286
10.477		0.2662	441.3475	25.7217	5.5627	0.97229	7880.32354
		Sum	7934.0926				



12



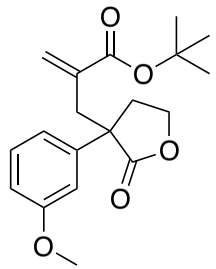


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.616		0.1741	21086.1504	1891.5137	49.6688	0.87156	10226.43950
10.683		0.2626	21367.3223	1268.0287	50.3312	0.87831	8830.89411
		Sum	42453.4727				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
9.689		0.1974	4708.7891	372.6505	86.5045	0.86863	13308.41485
13.244		0.2845	734.6171	40.3389	13.4955	0.93321	11784.25921
		Sum	5443.4061				



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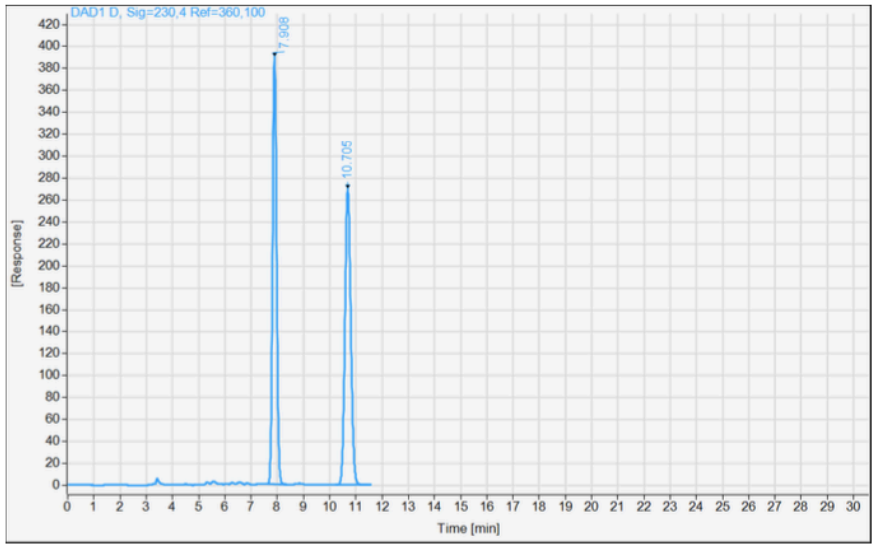
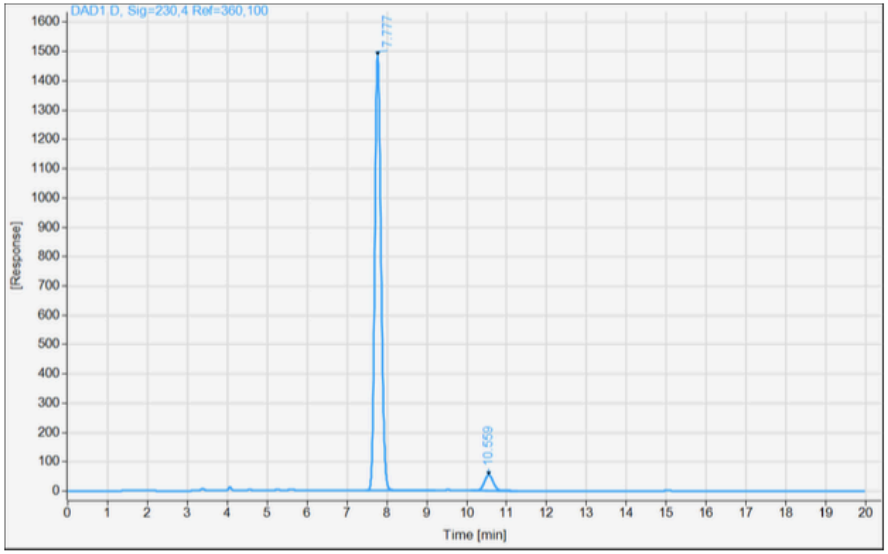


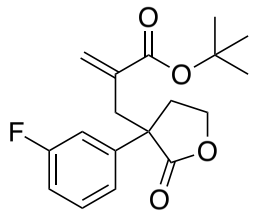


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.908		0.1660	4145.6665	390.1014	49.8042	0.89761	12167.88565
10.705		0.2425	4178.2676	270.0149	50.1958	0.88135	10620.92705
		Sum	8323.9341				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.777		0.1684	16104.5059	1485.9576	95.0695	0.79461	11563.50061
10.559		0.2395	835.2170	54.2721	4.9305	0.93427	10461.86243
		Sum	16939.7228				



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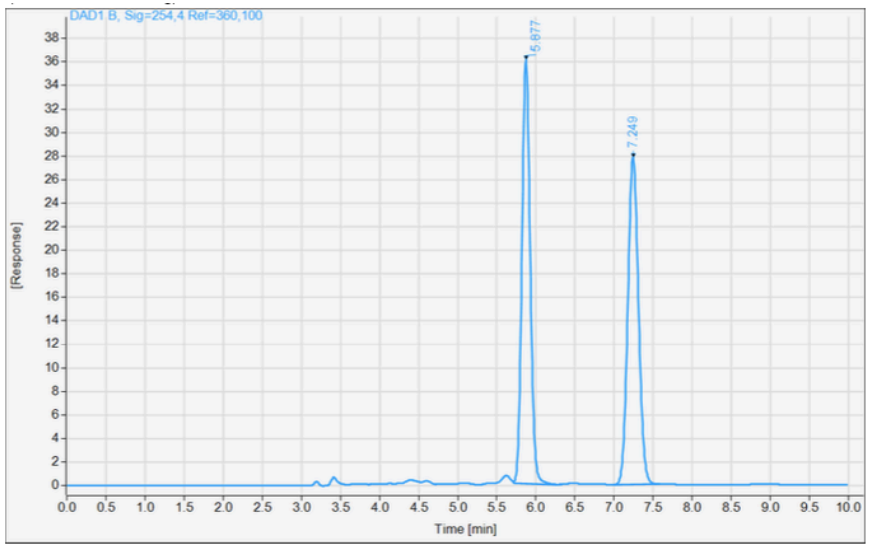
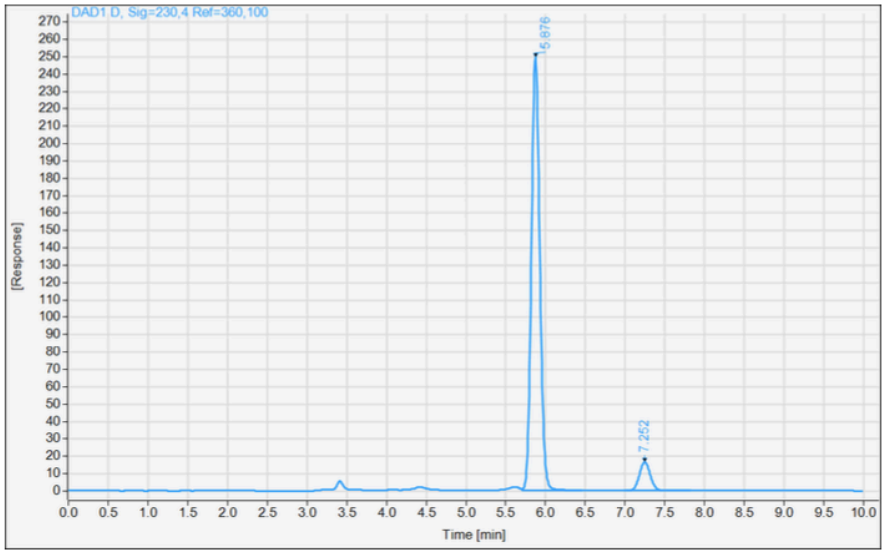


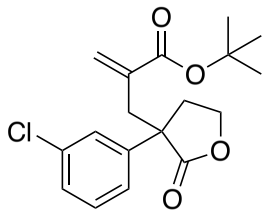


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.877		0.1158	265.1658	36.0691	50.0635	0.88008	13741.63827
7.249		0.1487	264.4926	27.8815	49.9365	0.90875	12719.55208
		Sum	529.6584				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.876		0.1160	1838.9967	249.5007	92.1779	0.87680	13830.51718
7.252		0.1465	156.0549	16.4714	7.8221	0.91704	12756.37880
		Sum	1995.0516				



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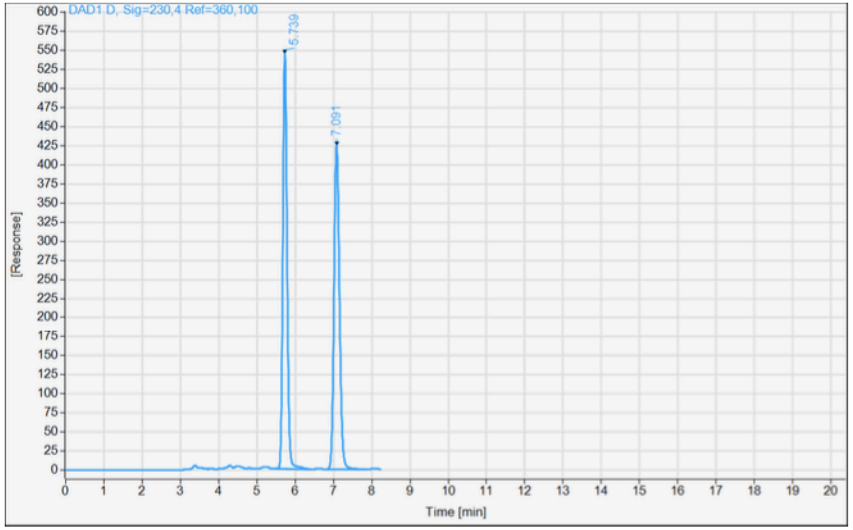
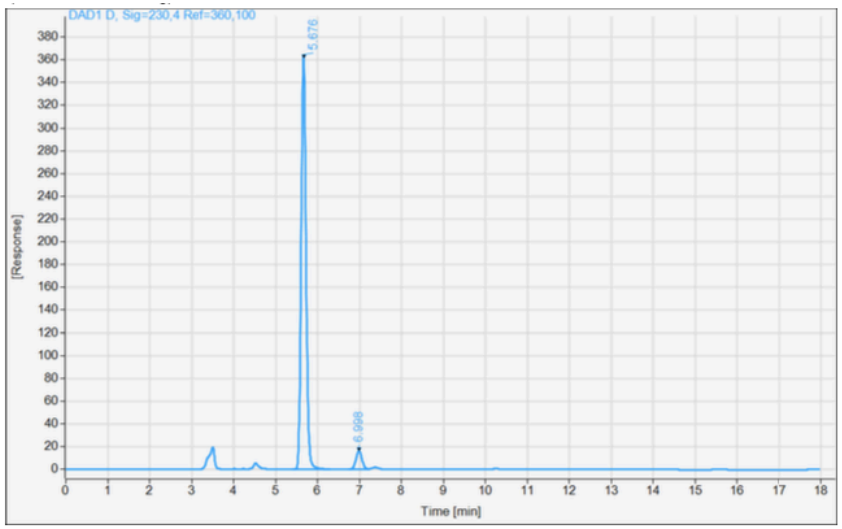


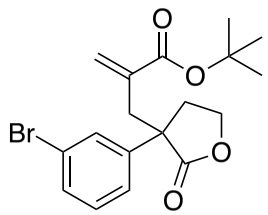


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.739		0.1173	4180.5220	546.1414	50.0488	0.82362	12079.93880
7.091		0.1525	4172.3628	425.2188	49.9512	0.84364	11310.96061
		Sum	8352.8848				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.676		0.1238	2909.7524	362.0874	94.6900	0.85973	10806.76620
6.998		0.1582	163.1709	16.1117	5.3100	0.95537	10001.76198
		Sum	3072.9233				



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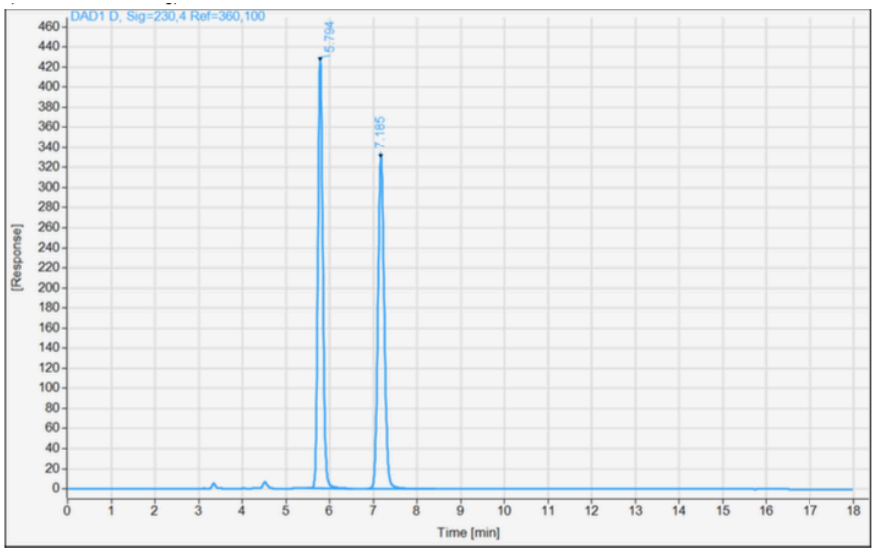
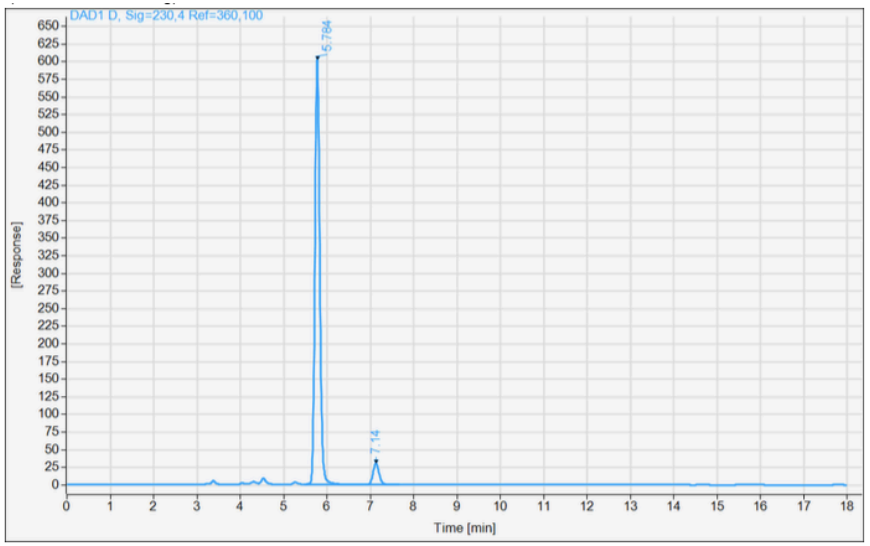


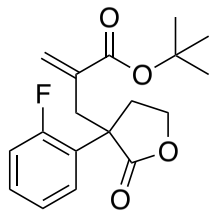


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5
5.794		0.1206	3314.3298	426.6456	49.9125	0.84832	11936.483
7.185		0.1575	3325.9558	330.2408	50.0875	0.86516	11136.446
		Sum	6640.2856				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.784		0.1186	4684.9600	603.5703	94.0786	0.83502	11839.67882
7.140		0.1526	294.8775	30.0244	5.9214	0.87792	11356.40041
		Sum	4979.8374				



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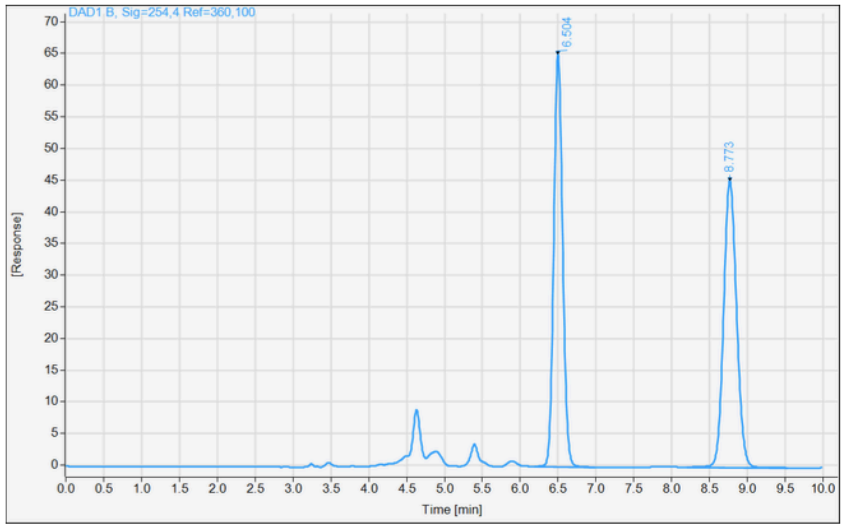
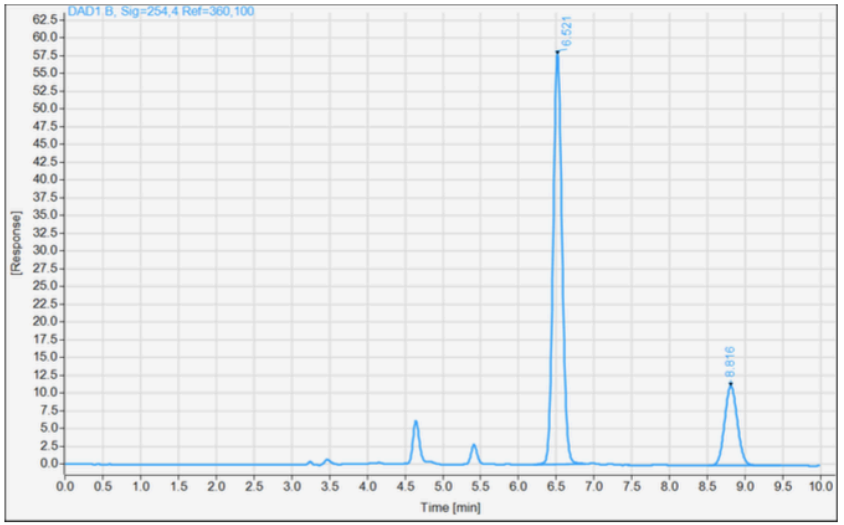


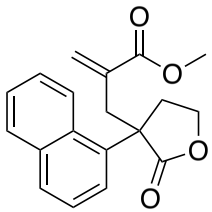
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.504		0.1273	532.1602	65.1660	49.7348	0.89179	14142.28546
8.773		0.1846	537.8362	45.2582	50.2652	0.87973	12232.63883
		Sum	1069.9963				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.521		0.1276	473.9244	57.8298	78.0878	0.90021	14040.09100
8.816		0.1842	132.9878	11.2287	21.9122	0.90708	12556.91180
		Sum	606.9122				



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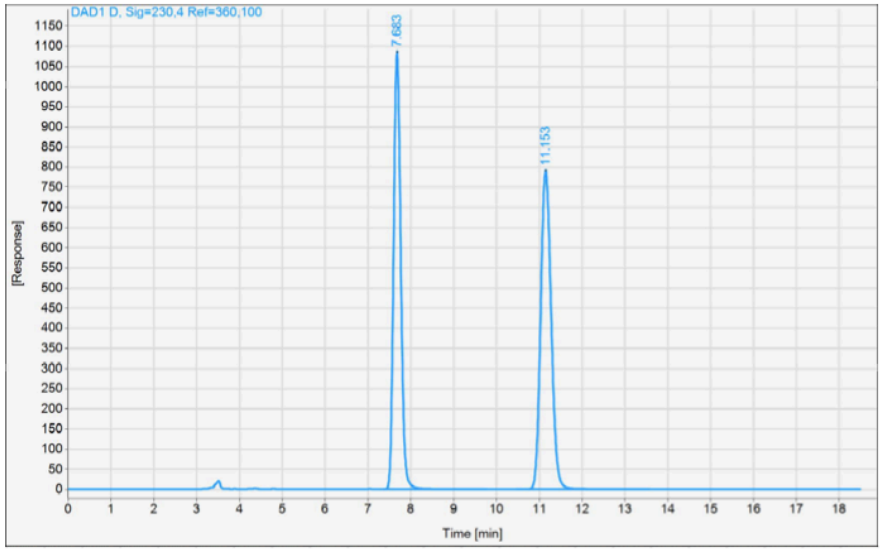
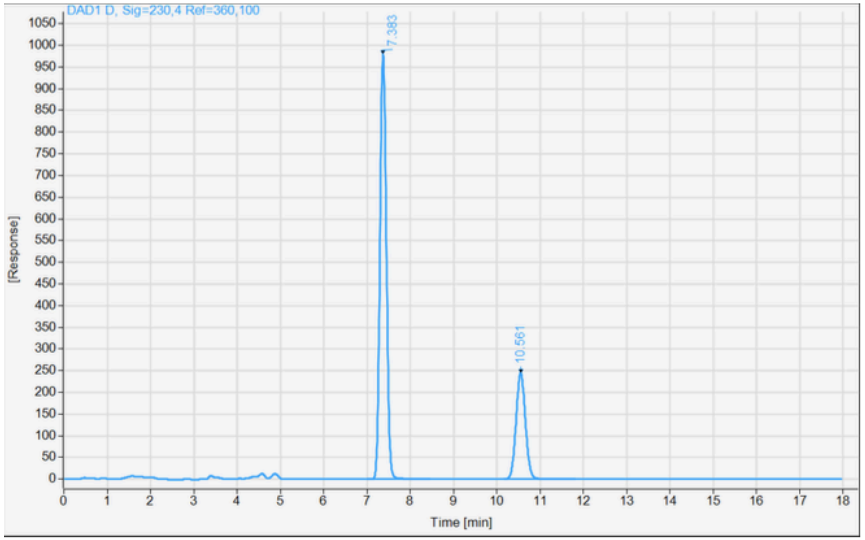


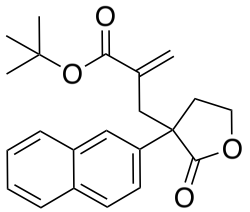
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.683		0.1837	12580.8740	1081.7837	48.2838	0.84415	9823.29254
11.153		0.2675	13475.2217	788.0290	51.7162	0.84510	9708.83627
		Sum	26056.0957				



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.383		0.1615	10043.3906	980.4279	73.1926	0.90345	12248.40780
10.561		0.2356	3678.4685	244.4605	26.8074	0.91788	11310.89351
		Sum	13721.8591				



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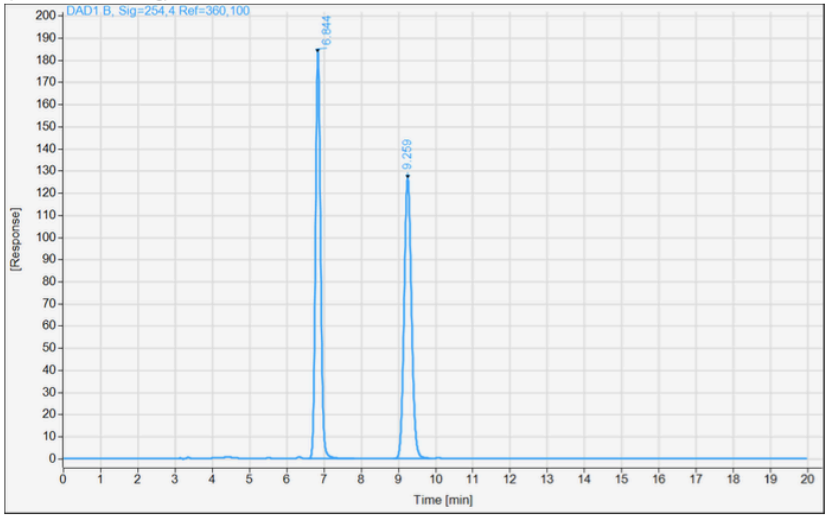
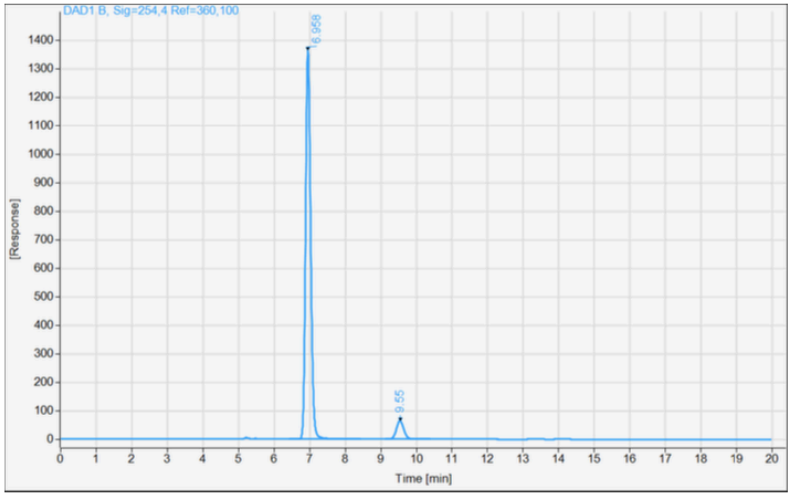


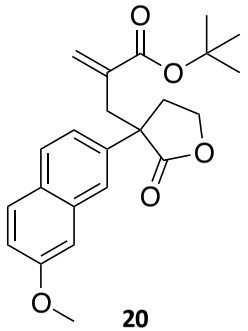
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.844		0.1471	1748.2592	183.6079	50.1225	0.86250	11119.68493
9.259		0.2142	1739.7170	126.7346	49.8775	0.88354	9836.16618
		Sum	3487.9762				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.958		0.1536	13510.2666	1363.7803	93.5862	0.79052	10668.71722
9.550		0.2245	925.9073	64.1164	6.4138	0.88810	9537.42011
		Sum	14436.1739				



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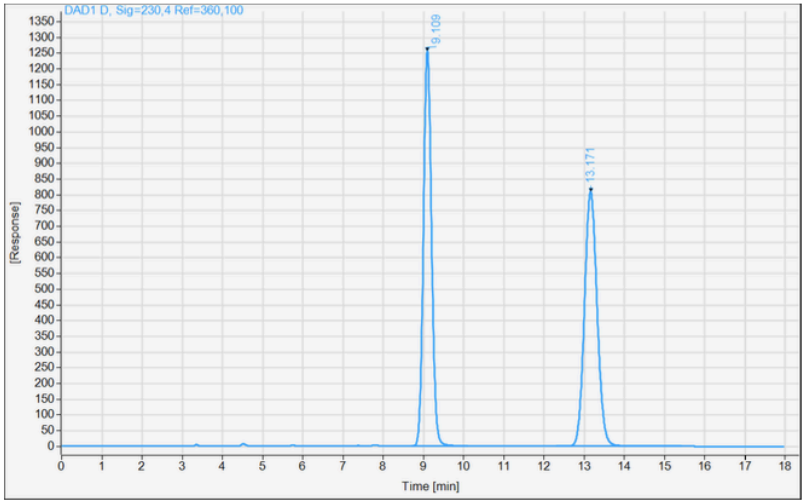
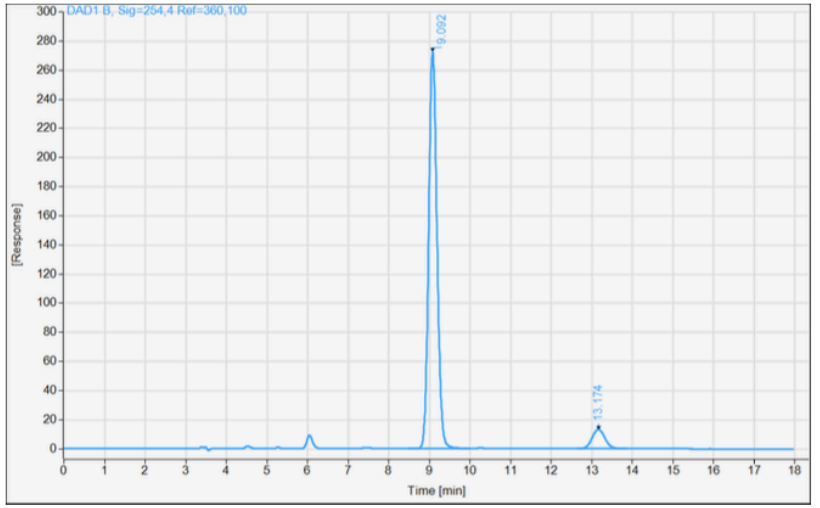


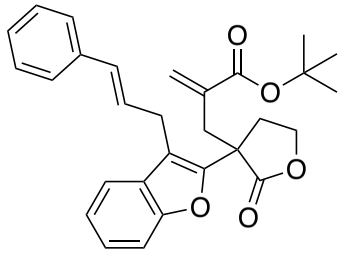
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
9.109		0.2178	17640.4297	1256.1188	49.8570	0.88815	9197.78202
13.171		0.3416	17741.6113	809.8153	50.1430	0.89000	7969.19624
		Sum	35382.0410				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
9.092		0.2217	3874.5991	272.7282	92.9888	0.87512	8931.18163
13.174		0.3398	292.1373	13.3255	7.0112	0.91586	7925.10977
		Sum	4166.7365				



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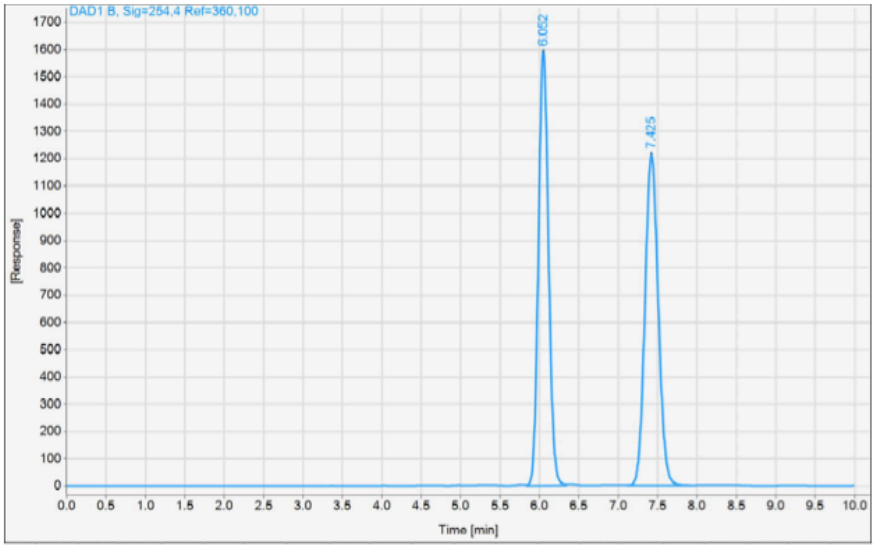
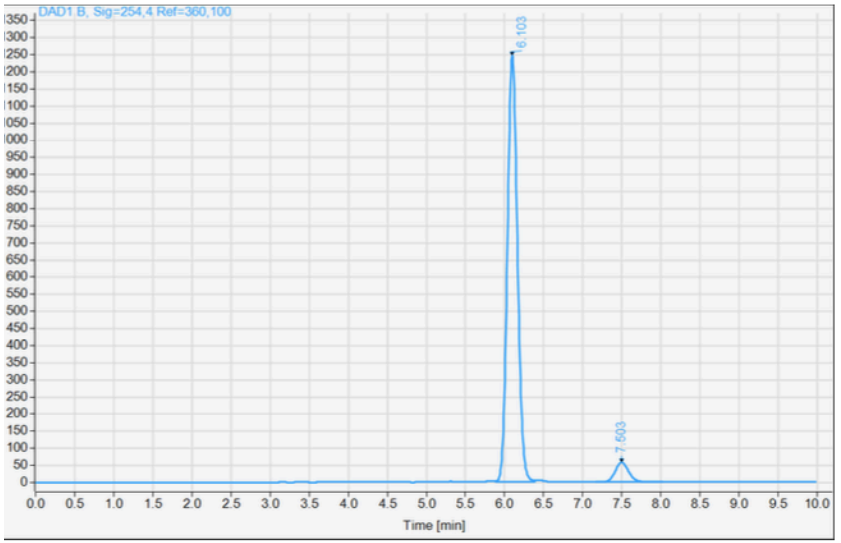


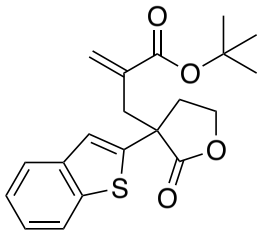


Signal: DAD1 B, Sig=254,4 Ref=360,100

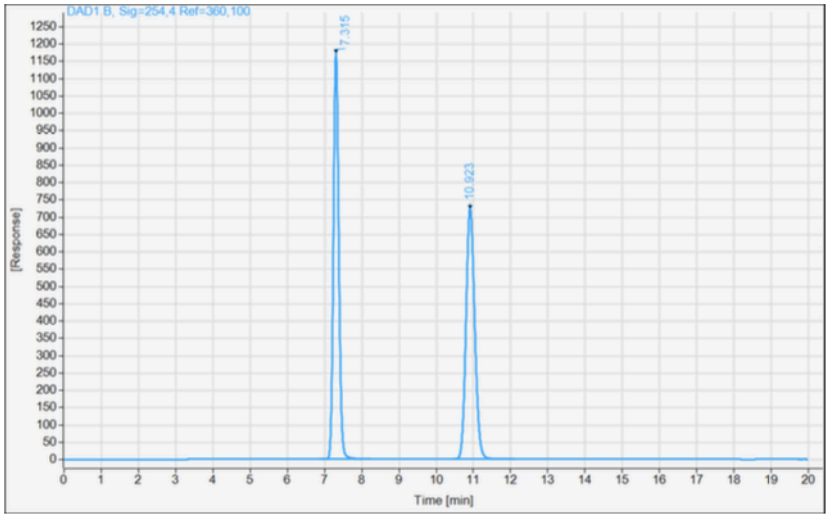
RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.052		0.1397	14148.1924	1591.5295	49.8615	0.89255	10183.61076
7.425		0.1829	14226.7627	1212.2290	50.1385	0.90226	8745.67880
		Sum	28374.9551				

gnal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.103		0.1406	11184.6963	1247.2041	94.1013	0.89535	10123.27816
7.503		0.1884	701.1074	57.4403	5.8987	0.88762	7807.14495
		Sum	11885.8037				

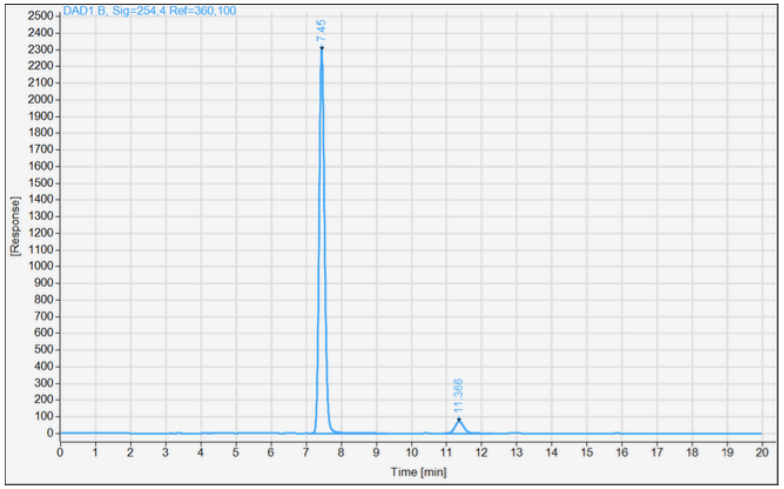


22



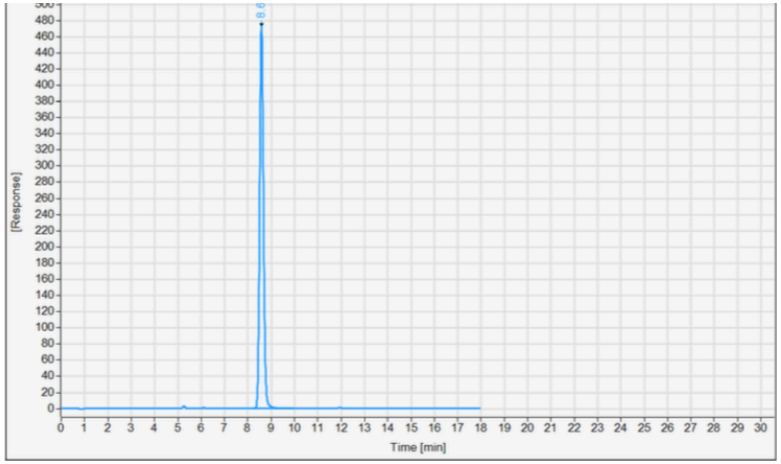
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.315		0.1550	11762.3398	1173.2529	49.9647	0.85297	11549.95841
10.923		0.2517	11778.9805	724.3193	50.0353	0.84106	9867.67265
		Sum	23541.3203				



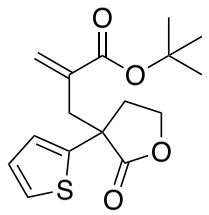
Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.450		0.1675	24723.5137	2297.7817	95.2602	0.80939	10654.58557
11.366		0.2706	1230.1450	70.8205	4.7398	0.91382	9491.26876
		Sum	25953.6587				



Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
8.600		0.1769	5383.4653	472.5024	100.0000	0.86281	12398.33476
		Sum	5383.4653				



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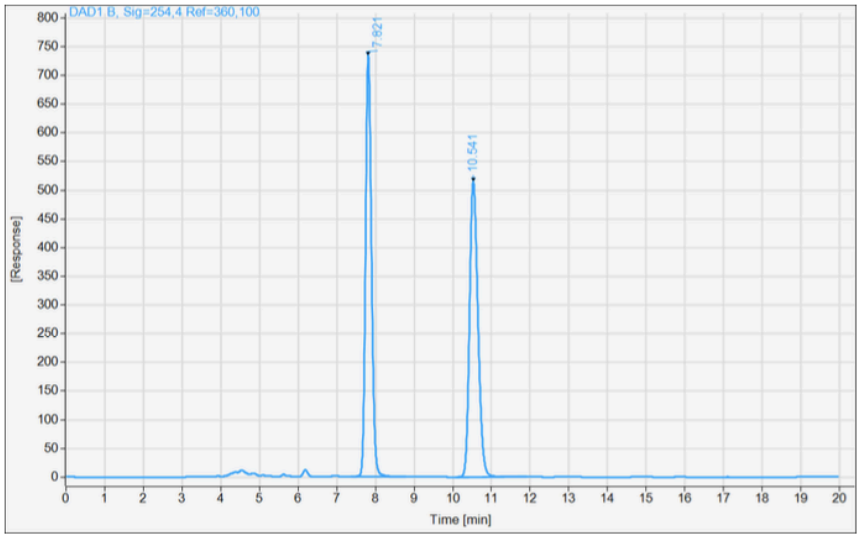
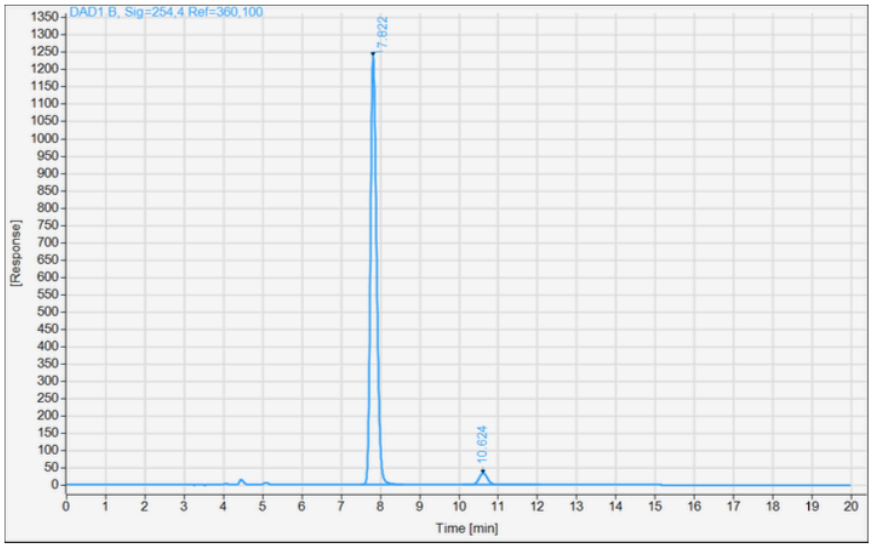


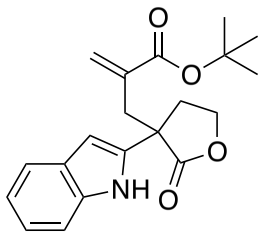


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.821		0.1662	7816.7192	734.0186	50.1433	0.80193	11693.37830
10.541		0.2340	7772.0400	515.0472	49.8567	0.75055	10765.67830
		Sum	15588.7593				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.822		0.1682	13407.2598	1239.3901	96.1965	0.72618	11427.59868
10.624		0.2402	530.1111	33.9449	3.8035	0.87124	10305.22410
		Sum	13937.3708				



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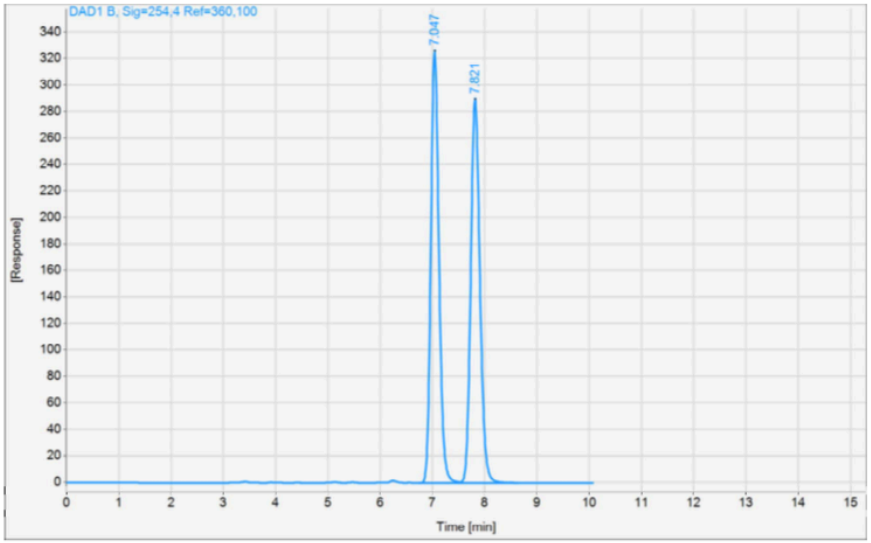
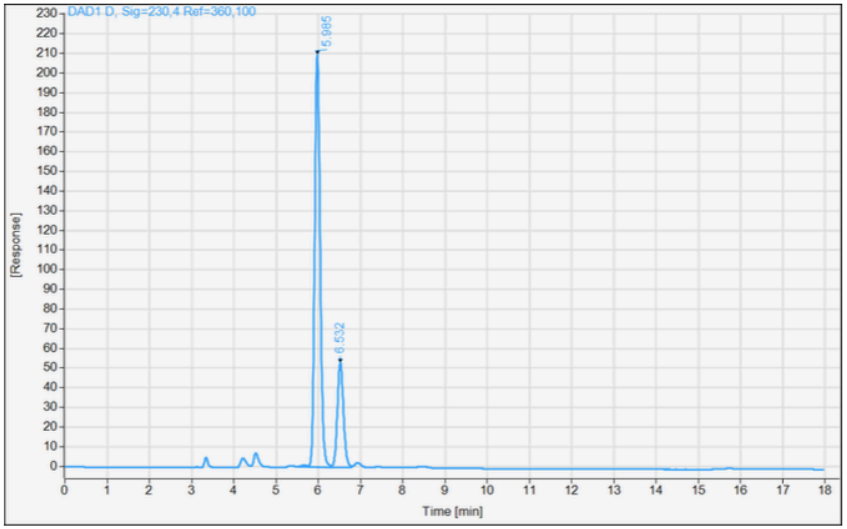


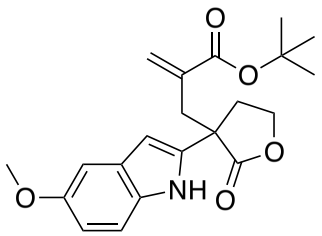


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.047		0.1688	3538.9133	325.5475	49.9806	0.82041	8831.82272
7.821		0.1889	3541.6580	289.0828	50.0194	0.83200	8760.96666
		Sum	7080.5713				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.985		0.1410	1891.4562	210.1532	77.9365	0.84204	9590.78972
6.532		0.1548	535.4642	53.4885	22.0635	0.89207	9041.70189
		Sum	2426.9204				



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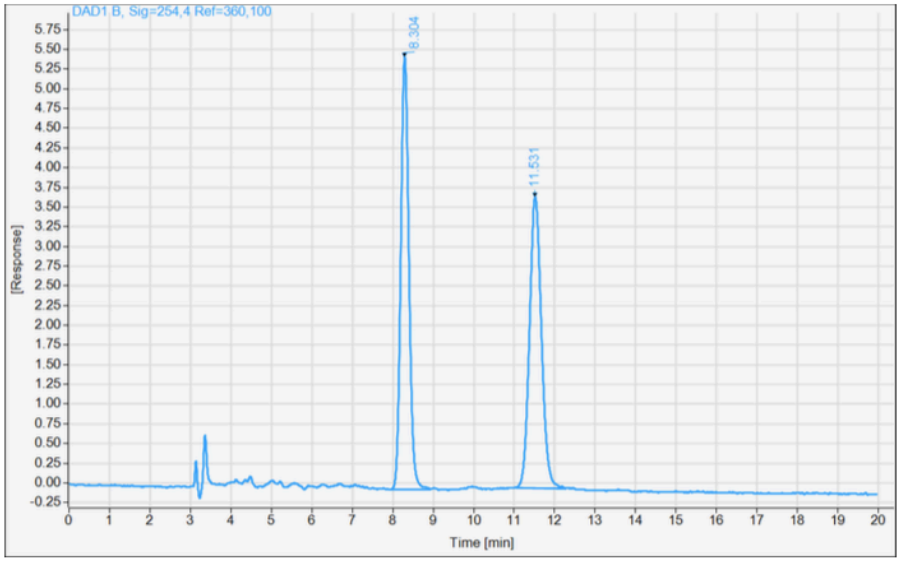
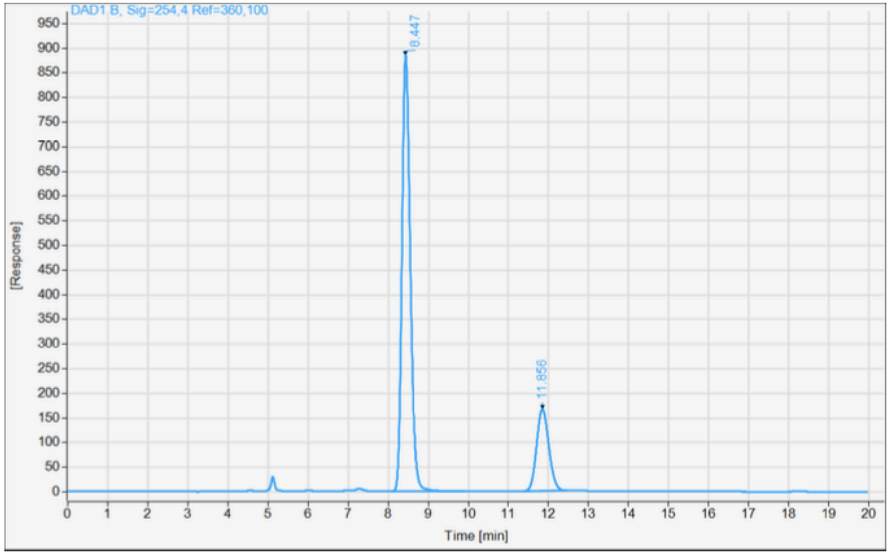


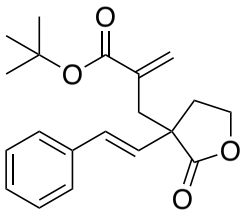


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
8.304		0.2171	76.7579	5.4892	49.9548	0.86994	7623.82966
11.531		0.3269	76.8967	3.6930	50.0452	0.88728	6532.92612
		Sum	153.6546				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
8.447		0.2248	12811.3740	885.3228	78.4617	0.75097	7343.05126
11.856		0.3308	3516.8044	166.2202	21.5383	0.85266	6845.63822
		Sum	16328.1785				



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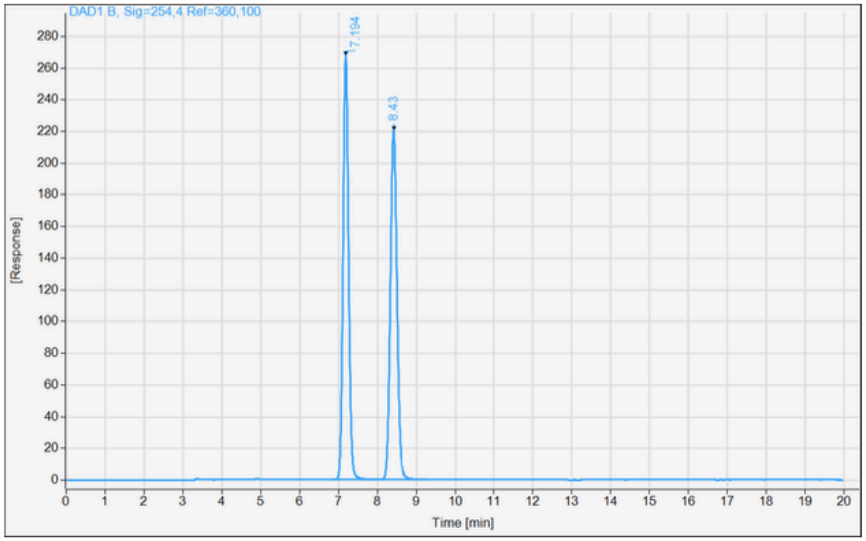
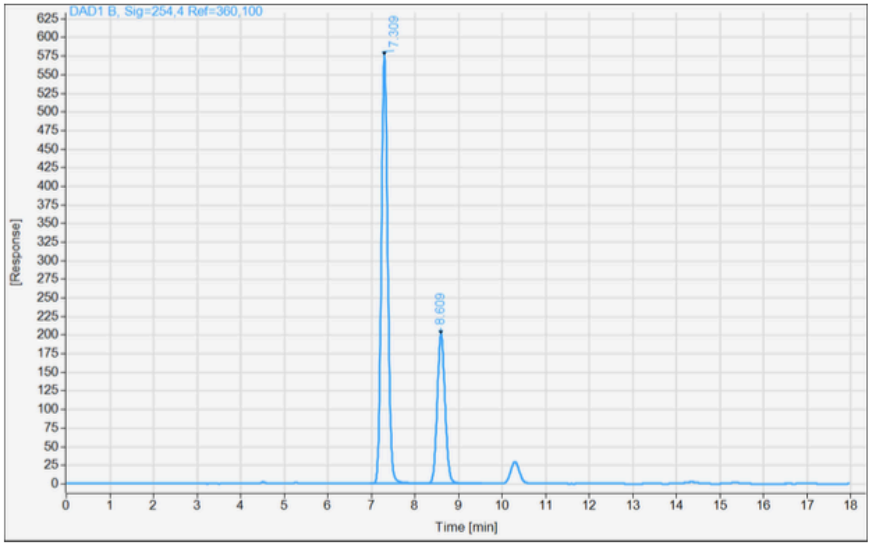


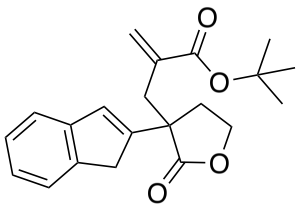


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.194		0.1524	2624.7322	267.7464	50.0563	0.88772	11614.36585
8.430		0.1843	2618.8281	220.8525	49.9437	0.90387	10982.56012
		Sum	5243.5603				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.309		0.1595	5899.9473	576.0099	70.2124	0.87621	11052.41697
8.609		0.1932	2503.0500	201.0611	29.7876	0.90190	10394.23448
		Sum	8402.9973				



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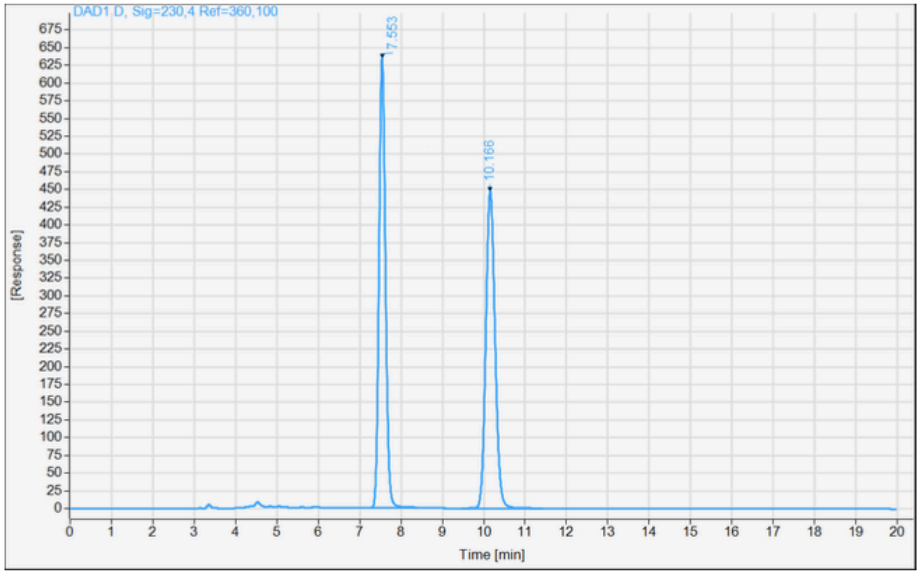
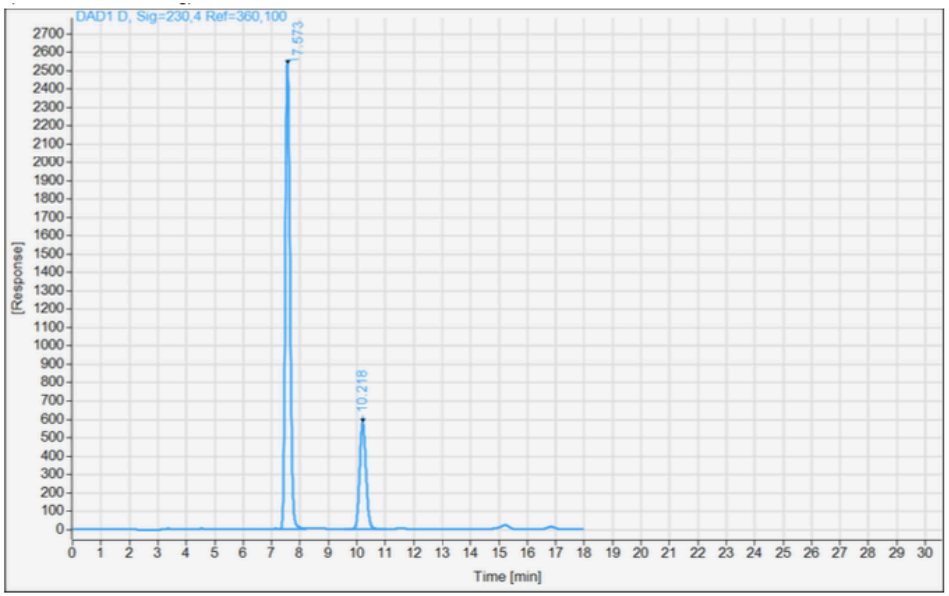


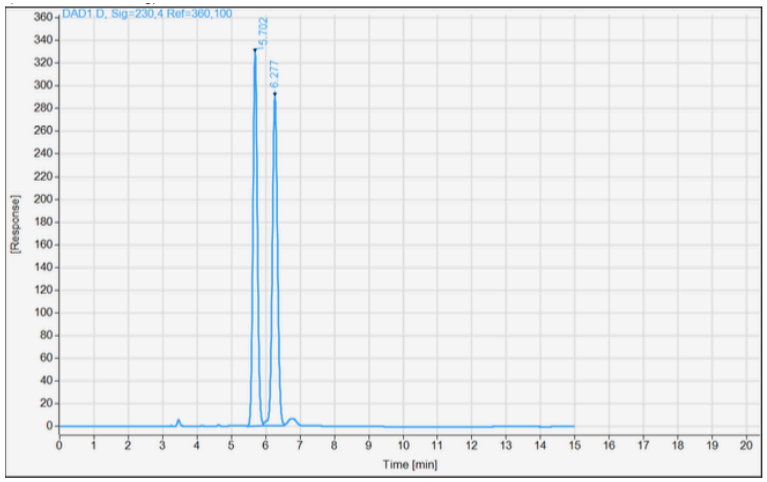


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.553		0.1680	6850.8760	634.5551	49.7415	0.85917	10590.72170
10.166		0.2405	6922.0830	447.3504	50.2585	0.86268	9493.79648
		Sum	13772.9590				

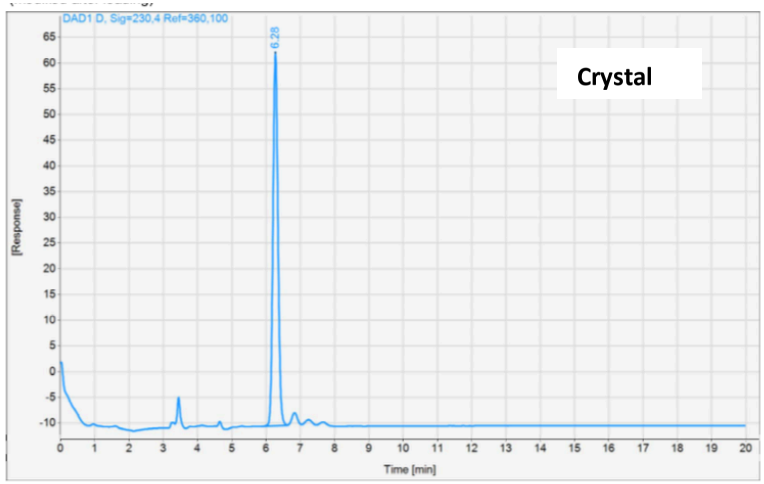
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.573		0.1840	29530.3008	2532.8662	76.6259	0.78171	9859.55626
10.218		0.2414	9007.9629	579.2330	23.3741	0.85965	9465.68526
		Sum	38538.2637				



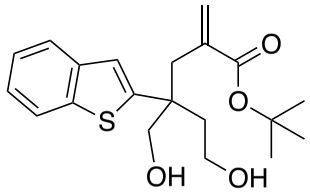
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.702		0.1402	2944.7375	329.5786	49.3522	0.90503	8875.23422
6.277		0.1614	3022.0410	290.4424	50.6478	0.95694	7918.80717
		Sum	5966.7786				



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.280		0.1870	732.9597	69.5306	100.0000	0.92806	8295.47826
		Sum	732.9597				



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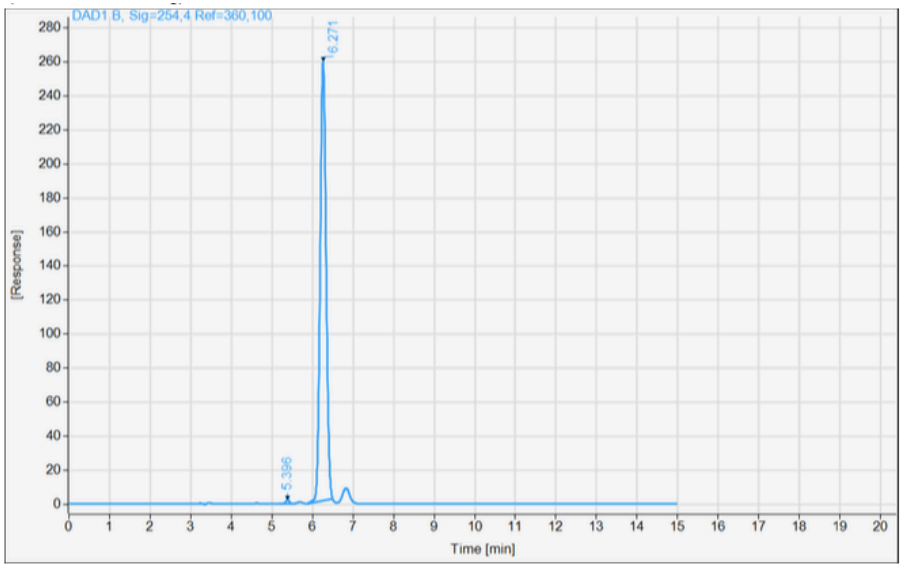
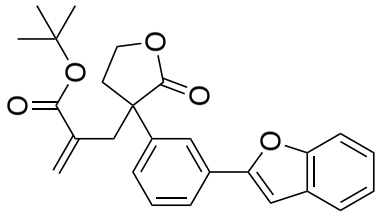


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
5.396		0.0859	13.8572	2.5301	0.5268	0.90647	20649.17983
6.271		0.1582	2616.7231	258.3056	99.4732	0.93188	8501.92474
		Sum	2630.5804				



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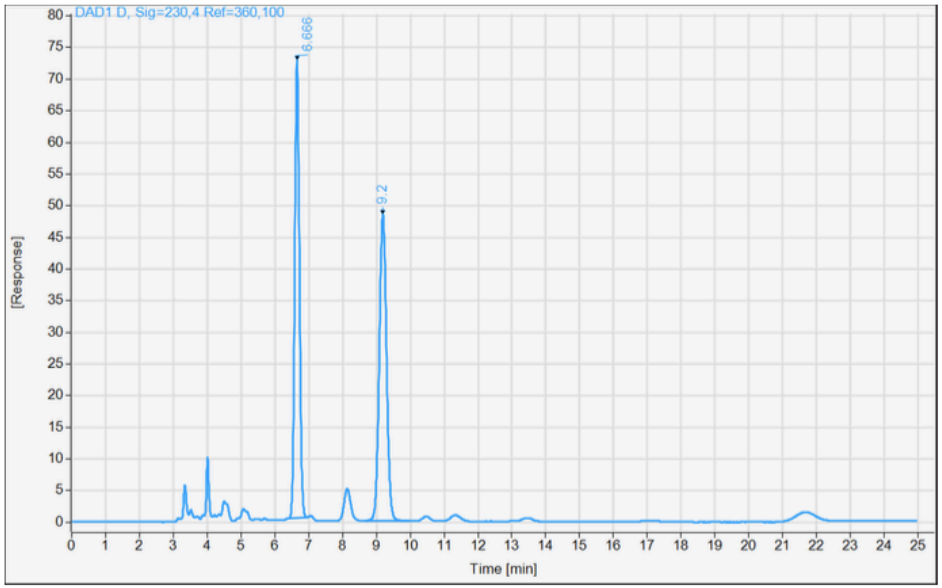
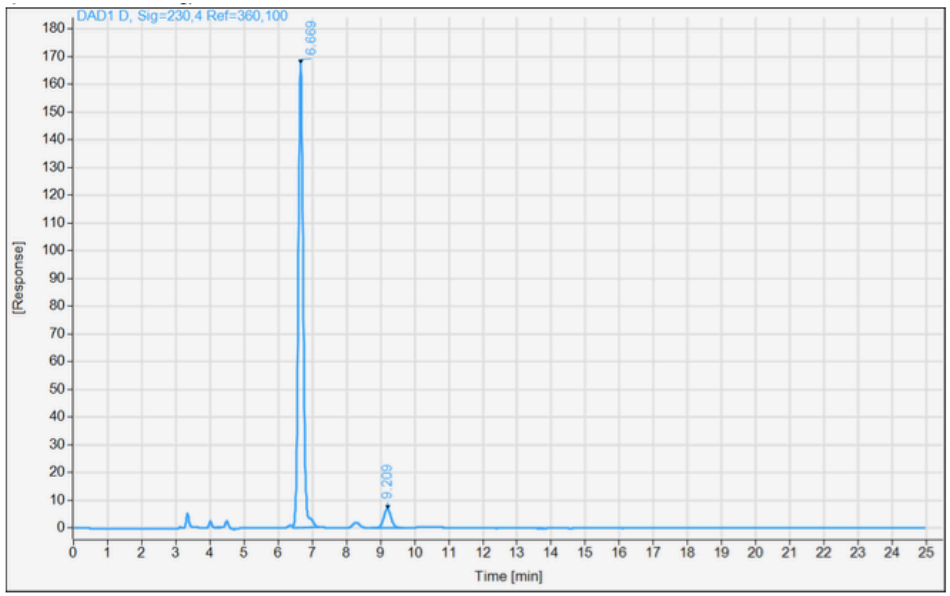


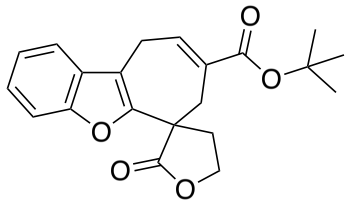


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.666		0.1498	693.4621	72.3958	48.8650	0.91617	10516.76545
9.200		0.2323	725.6775	48.5744	51.1350	0.93583	8149.94153
		Sum	1419.1396				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
6.669		0.1512	1653.1013	167.3738	94.2597	0.87647	9999.86238
9.209		0.2242	100.6713	6.8223	5.7403	0.93355	8561.78438
		Sum	1753.7727				



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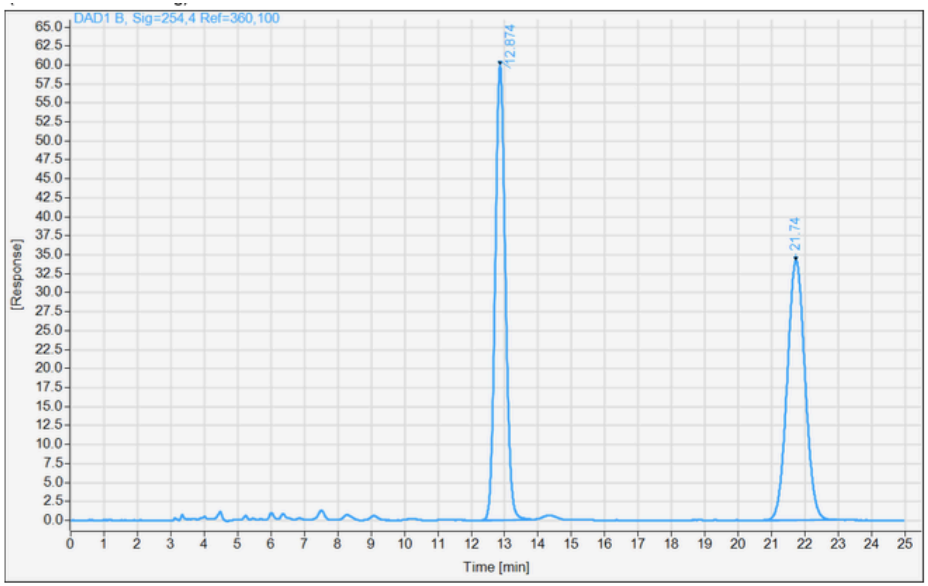
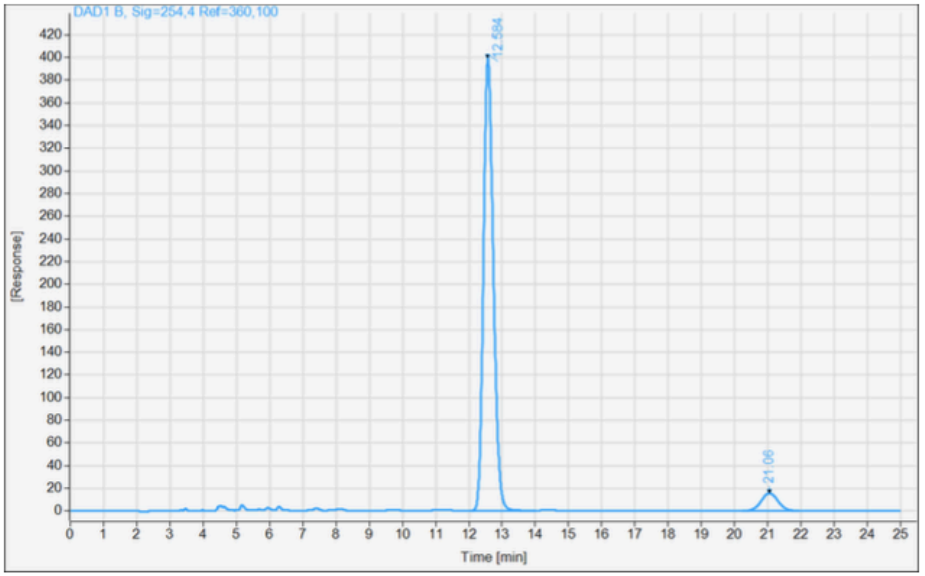


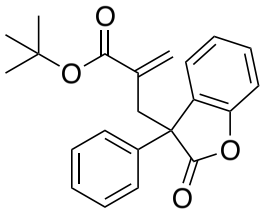


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
12.874		0.3286	1266.4113	59.9124	50.0126	0.87726	8071.28756
21.740		0.5756	1265.7744	34.2151	49.9874	0.93652	7667.81331
		Sum	2532.1857				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
12.584		0.3221	8281.7617	399.1203	93.6209	0.77317	8046.43187
21.060		0.5642	564.2995	15.6667	6.3791	0.95572	7449.37601
		Sum	8846.0612				



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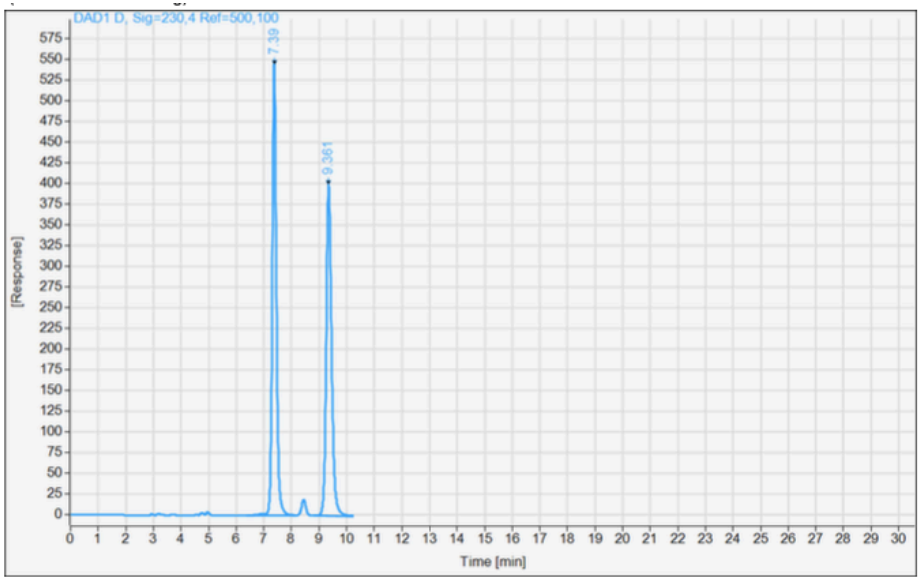
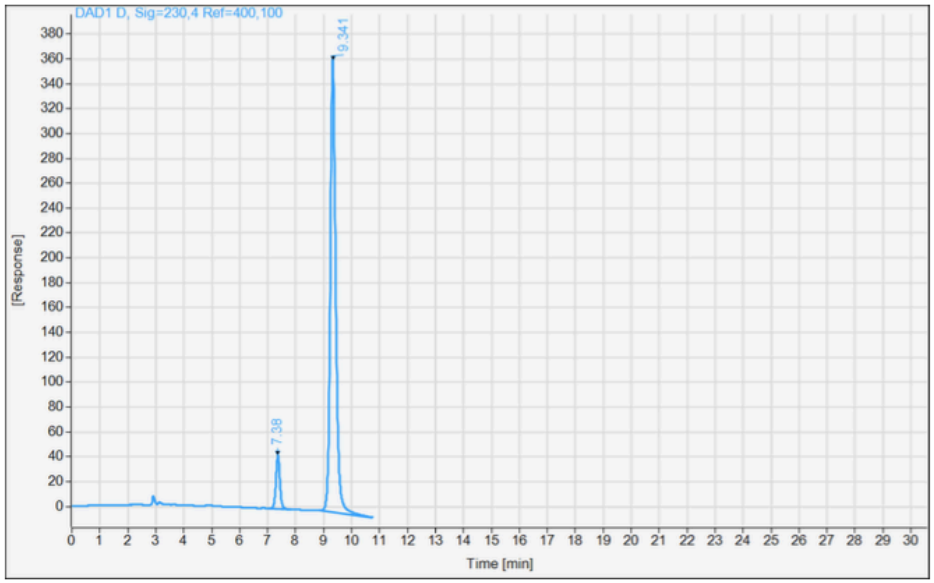


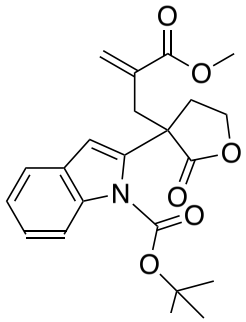


Signal: DAD1 D, Sig=230,4 Ref=500,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.390		0.1585	5732.4268	545.7640	51.5359	0.82273	9300.17044
9.361		0.2049	5390.7368	400.7188	48.4641	0.74911	8999.72718
		Sum	11123.1636				

Signal: DAD1 D, Sig=230,4 Ref=400,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.380		0.1514	431.7875	43.6650	8.0004	0.92676	10697.50391
9.341		0.2051	4965.3071	364.0334	91.9996	0.73256	8956.92783
		Sum	5397.0946				



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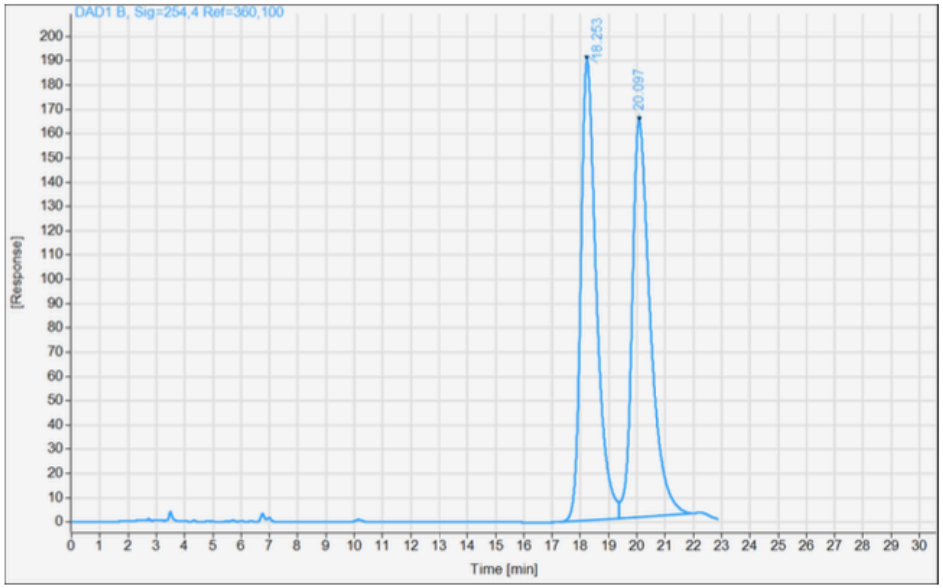
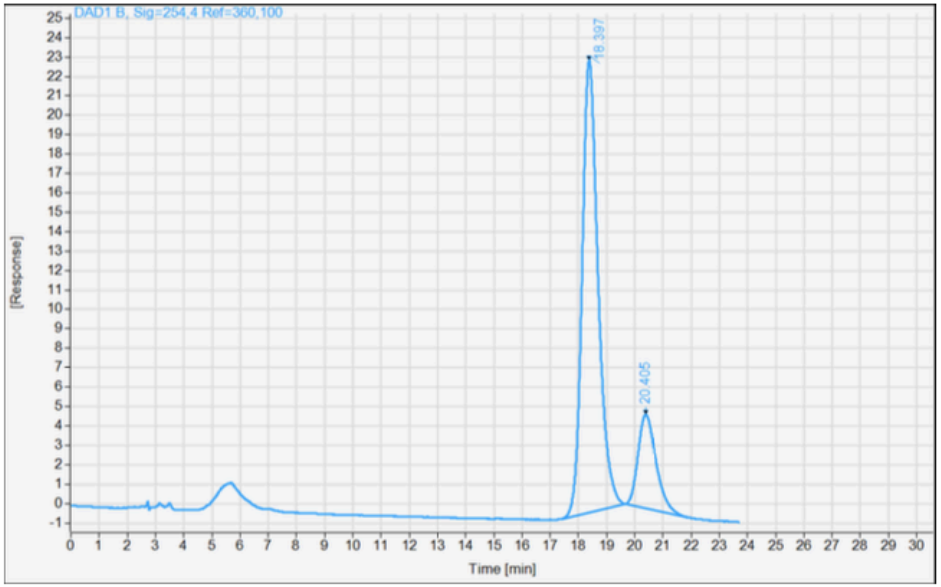


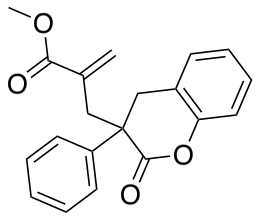


Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
18.253		0.5749	7269.8843	189.7704	49.8898	0.62273	3559.34420
20.097		0.6679	7302.0093	163.2285	50.1102	0.58970	3139.34215
		Sum	14571.8936				

Signal: DAD1 B, Sig=254,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
18.397		0.5969	916.9159	23.3091	81.0142	0.75010	3795.09627
20.405		0.6138	214.8805	4.8412	18.9858	0.69912	4485.99009
		Sum	1131.7964				



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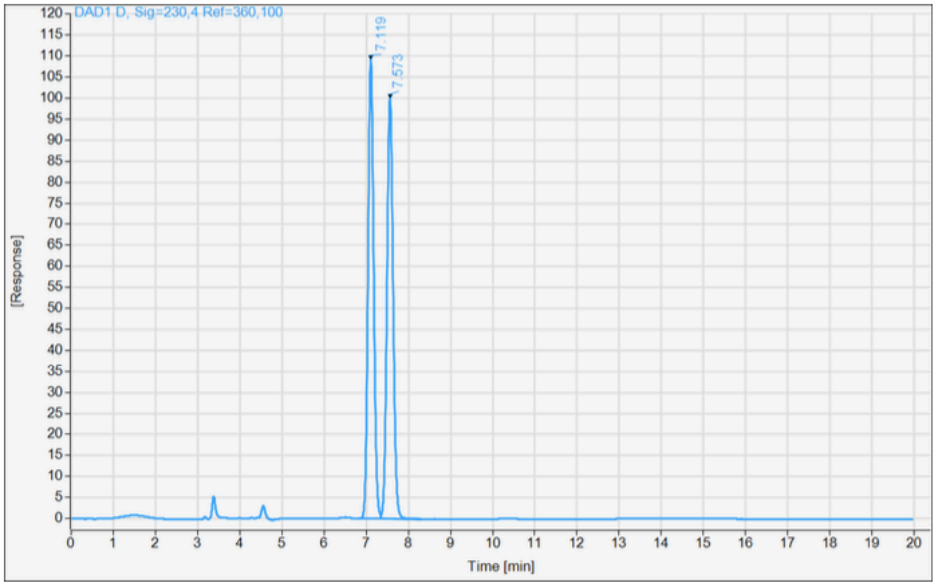

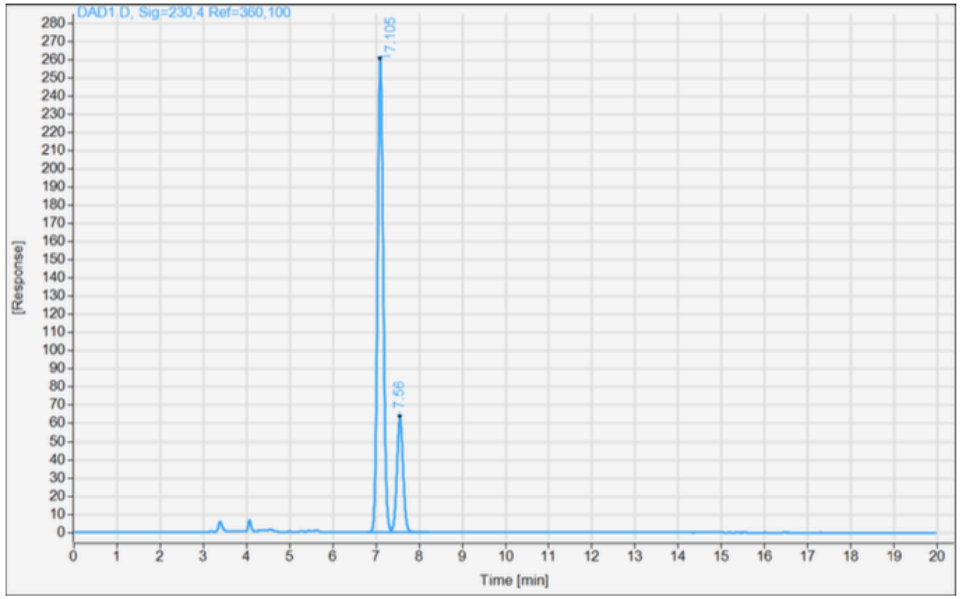

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.119		0.1447	1018.3293	109.2939	50.1053	0.91345	12787.34804
7.573		0.1581	1014.0506	100.1861	49.8947	0.91251	12235.19698
		Sum	2032.3799				

Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Compound_Name	Width [min]	Area	Height	Area%	Peak_Symmetry	Peak_Plate5Sigma
7.105		0.1439	2400.7185	259.5074	79.2389	0.90533	12900.58982
7.560		0.1556	629.0054	62.4196	20.7611	0.92344	12116.03377
		Sum	3029.7239				