Electronic Supplementary Material (ESI) for ChemComm.

- SUPPORTING INFORMATION -

Halocarbocyclization versus Dihalogenation: Substituent Directed Iodine(III) Catalyzed Halogenations

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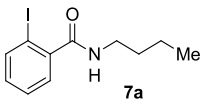
1. General Information

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use**.** Reagents were purchased at the highest commercial quality and used without further purification, except NBS which was recrystrallized from water prior to use. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on Merck silica gel aluminium plates with F-254 indicator using UV light as the visualizing agent and an acidic mixture of anisaldehyde, phosphomolybdic acid, or ceric ammonium molybdate, and heat as developing agents. Silica gel Merck 60 (particle size 0.63 – 0.2 mm) was used for flash column chromatography. Solvent mixtures are understood as volume/volume. NMR spectra were recorded on Varian Mercury 300, VNMR 400, and VNMR 600 spectrometers. The spectra were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, $CHCl_3$ @ 77.00 ppm ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, q = quartet, m = multiplet, br = broad. In addition, the following abbreviations were used: EtOAc = ethyl acetate, DCM = dichloromethane, NBS = *N*-bromosuccinimide, TLC = thin layer chromatography, rt = room temperature, sat = saturated. Melting points were determined on a Büchi M-560 melting point apparatus. Mass spectra (MS-EI, 70 eV) were conducted on a Finnigan MAT SSQ 700 and spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Diastereomeric ratios were determined by ^{1}H-NMR spectra of the crude product.

2. Catalyst Synthesis

At 0 °C thionyl chloride (2.88 g, 1.8 mL, 24.2 mmol, 2.0 equiv.) was added to a solution of 2-iodobenzoic acid (3.00 g, 12.1 mmol, 1 equiv.) in 24.8 mL dry toluene (0.5M). The mixture was heated to reflux for 4 h and the solvent was removed *in vacuo*, re-dissolved in 10 mL DCM and added to a solution of NEt_3 (2.45 g, 3.40 mL, 24.2 mmol, 2.0 equiv.) and *n*butylamine (0.97 g, 13.3 mmol, 1.1 equiv.) in DCM (65.0 mL, 0.2M) at 0 °C. After being stirred overnight, water was added and the organic layer was washed with 10% aq. HCl and 5% aq. NaOH, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 80:20) to afford 2-iodobenzamide **7a** (2.90 g, 9.56 mmol, 79% yield) as a white solid.

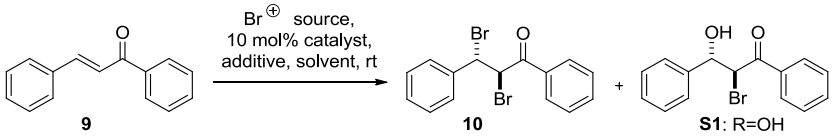


7a

m.p. = 75 °C (EtOAc); $\mathbf{R_f}$ = 0.13 (silica gel, hexane/EtOAc 80:20); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H, CH), 7.41 – 7.34 (m, 2H, CH), 7.08 (ddd, *J* = 8.0, 6.7, 2.5 Hz, 1H, CH), 5.73 (br, 1H, NH), 3.48 (d, *J* = 7.1 Hz, 1H, NCH_2), 3.44 (d, *J* = 7.1 Hz, 1H, NCH_2), 1.67 – 1.59 (m, 2H, CH_2), 1.45 (dq, *J* = 14.4, 7.3 Hz, 2H, CH_2), 0.97 (t, *J* = 7.3 Hz, 3H, Me) ppm.[1]

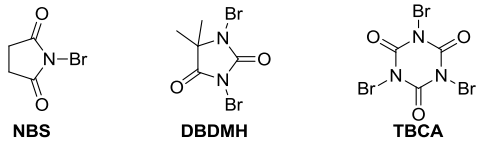
3. Optimization of the Reaction Conditions

Table S1. Evaluation of the optimum reaction conditions in iodine(III)-mediated dibrominations



9 10 **S1**: R=OH

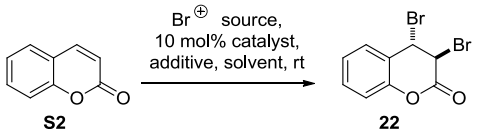
entry	Br ⊕ source	catalyst (10 mol%)	solvent	additive	time	conversion	**10** : **S1**
1	NBS	**7a**	DCM	NH_4Cl_{aq} [a]	2 h	>99%	1 : 0
2	NBS	**7a**	EtOAc	NH_4Cl_{aq} [a]	1 h	>99%	1 : 3.5
3	NBS	**7a**	MeCN	NH_4Cl_{aq} [a]	0.5 h	>99%	1 : 1.8
4	NBS	-	MeCN	-	5 h	<5%	1 : 1
5	NBS	**7a**	MeOH	NH_4Cl_{aq} [a]	0.5 h	>99%	1 : 1.8
6	NBS	**7a**	acetone	NH_4Cl_{aq} [a]	0.5 h	>99%	1 : 6
7	NBS	**7a**	NMP	NH_4Cl_{aq} [a]	24 h	-	-
8	NBS	**7a**	DCM	-	5 h	-	-
9	NBS	**7a**	DCM	H_2O [a]	24 h	-	-
10	NBS	-	DCM	NH_4Cl_{aq} [a]	5 h	12%	1 : 0
11	NBS	**7a**	DCM	NH_4Cl_{solid} [b]	5 h	60%	1 : 0
12	NBS	**7a**	DCM	TFA [b]	1 h	>99%	1 : 0
13	NBS	**7a**	DCM	acidic acid [b]	5 h	43%	1 : 0
12	DBDMH	**7a**	DCM	NH_4Cl_{aq} [a]	5 h	>99%	1 : 0.4
13	TBCA	**7a**	DCM	NH_4Cl_{aq} [a]	2 h	>99%	1 : 0



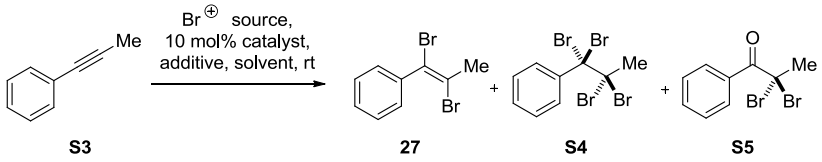
The reactions were carried out using chalcone (**9**, 208 mg, 1 mmol, 1.0 eq.) and NBS (392 mg, 2.20 mmol, 2.2 eq.) in a 0.2 M solution at rt. [a]1 drop of additive was used. [b]10 mol% of additive was used.

4. Control Experiments for Dibromination Reactions

Table S2. Dibromination reactions of coumarin (**S2**) and phenylmethylacetylene (**S3**) with and without **7a**



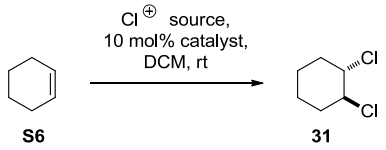
entry	Br⊕ source	catalyst (10 mol%)	solvent	additive	time	conversion
1	NBS	**7a**	DCM	NH_4Cl_{aq}	16 h	>99%
2	NBS	**-**	DCM	NH_4Cl_{aq} [a]	16 h	-
3	KBr/oxone	**7a**	DCM	-	12 h	>99%
4	KBr/oxone	**-**	DCM	-	12 h	-



entry	Br⊕ source	catalyst (10 mol%)	solvent	additive	time	conversion	**27:S4:S5**
1	NBS	**7a**	DCM	NH_4Cl_{aq}	3 h	>99%	1:0:0
2	NBS	**-**	DCM	NH_4Cl_{aq}	22 h	23%	1:traces:0.1
3	KBr/oxone	**7a**	DCM	-	1 h	>99%	1:0:traces
4	KBr/oxone	**-**	DCM	-	22 h	62%	1:0.4:0.2

5. Control Experiments for Dichlorination Reactions

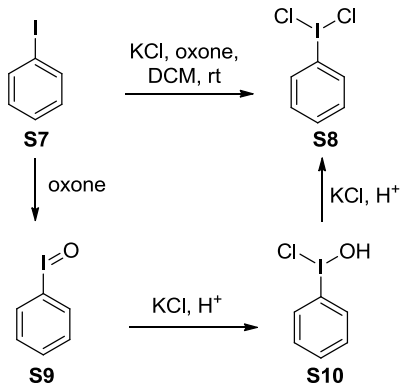
Table S3. Dichlorination reactions of cyclohexene (**S6**)



entry	Cl⊕ source	catalyst (10 mol%)	time	conversion
1	KCl/oxone	**7a**	<5 min	>99%/98%[a]
2	$PhICl_2$ (**S8**)	-	30 min	>99%
3	KCl/oxone	PhI (**S7**)	1 h	>99%

[a]isolated yield

Using PhI (**S7**) as catalyst instead of **7a** also led to a complete conversion of starting material **S6**, albeit a longer reaction time was needed (<5 min vs. 1h, Table S3, entry 1 and 3). Treatment of cyclohexene (**S6**) with $PhICl_2$ (**S8**) resulted, as expected, likewise in the formation of the desired product **31**. Here an extended reaction time of 30 min (entry 2) was necessary to achieve complete conversion of **S6**. An explanation for the observed dichlorination triggered by the addition of iodobenzene (**S7**) might be that **S7** is oxidized by oxone giving the corresponding iodine(III) compound **S9**, which reacts with chloride affording $PhICl_2$ (**S8**, Scheme S1) through PhIClOH (**S10**). Both in situ generated compounds **S8** and **S10** can, in principle, undergo the observed dichlorination of **S6** yielding **31**.



Scheme S1. Possible in situ formation of **S8**

In order to prove this hypothesis **S7** was treated with KCl/oxone in DCM (procedure see 6.4) giving a single product. The NMR spectra of the isolated compound were in full agreement with that of **S8**

obtained by the standard procedure using NaOCl/HCl and the physical and spectroscopic data described in literature.[2] Furthermore, reaction of the obtained **S8** with cyclohexene (**S6**) again delivered **31**.

6. General Procedures for the Halogenation Reactions

6.1 Using NBS (Procedure A)

To a solution of starting material (1.00 mmol, 1.0 equiv.) and iodoamide **7a** (30.3 mg, 0.10 mmol, 0.10 equiv.) in DCM (5 mL, 0.2 M) NBS (392 mg, 2.20 mmol, 2.2 equiv.) and 1 drop sat. NH_4Cl solution were added. The reaction mixture was stirred until all starting material was consumed, which was monitored by TLC. The orange suspension was diluted with DCM (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous phase was additionally extracted with DCM or EtOAc (2 x 20 mL), the combined organic layers dried over anhydrous $MgSO_4$, and the solvent removed. The residue was purified by filtration over a short silica pad to afford the corresponding halogenated products.

6.2 Using Potassium Bromide and Oxone (Procedure B)

To a solution of starting material (1.00 mmol, 1.0 equiv.) and iodoamide **7a** (30.3 mg, 0.10 mmol, 0.10 equiv.) in DCM (5 mL, 0.2 M) KBr (357 mg, 3.00 mmol, 3.0 equiv.) and additionally grinded, wet oxone (676 mg, 1.10 mmol, 1.1 equiv.) were added. The reaction mixture was stirred at rt (using alkenes as substrates) and 0 °C (using alkynes as starting material), respectively, until all starting material was consumed, which was monitored by TLC. The orange suspension was diluted with DCM (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous phase was additionally extracted with DCM or EtOAc (2 x 20 mL), the combined organic layers dried over anhydrous $MgSO_4$, and the solvent removed. The residue was purified by filtration over a short silica pad to afford the corresponding halogenated products.

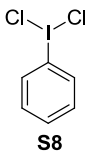
6.3 Using Potassium Chloride and Oxone

To a solution of starting material (1.00 mmol, 1.0 equiv.) and iodoamide **7a** (30.3 mg, 0.10 mmol, 0.10 equiv.) in DCM (5 mL, 0.2 M) KCl (373 mg, 5.00 mmol, 5.0 equiv.) and additionally grinded, wet oxone (676 mg, 1.10 mmol, 1.1 equiv.) were added. The reaction mixture was stirred at rt until all starting material was consumed, which was monitored by TLC. The suspension was diluted with DCM (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous phase was additionally extracted with DCM or

EtOAc (2 x 20 mL), the combined organic layers dried over anhydrous $MgSO_4$, and the solvent removed. The residue was purified by filtration over a short silica pad to afford the corresponding halogenated products.

6.4 Formation of $PhICl_2$ using Potassium Chloride and Oxone

Iodobenzene (**S7**, 204 mg, 1.00 mmol) was dissolved in 5 mL DCM (0.2M). KCl (373 mg, 5.00 mmol, 5.0 equiv.) and grinded, wet oxone (676 mg, 1.10 mmol, 1.1 equiv.) were added to the solution at 0°C and stirred at rt for 3 h. The reaction mixture was diluted with 20 mL DCM and washed with 10 mL H_2O (3x) and brine (2x 5 mL). The organic layer was dried using $NaSO_4$ and the solvent removed in the absence of light, obtaining $PhICl_2$ (**S8**) as a yellow solid (269 mg, 0.98 mmol, 98%).

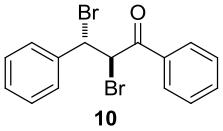


S8

(Dichloroiodo)benzene (S8):[2b] yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.17 (m, 2H, C_{ar}-H), 7.62 – 7.59 (m, 1H, C_{ar}-H), 7.51 – 7.46 (m, 2H, C_{ar}-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.0 (CH), 132.3 (CH), 131.7 (CH), 125.5 (CI) ppm.

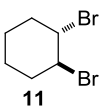
7. Physical and Spectroscopic Data

7.1 Brominated Products



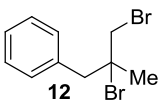
10

(*trans*)-3,4-Dibromo-4-phenylbutan-2-one (10):[3] **A:** 2 h; **B:** 30 min; white solid; **m.p**. = 157 °C (DCM), lit.[3] 156 – 158 °C (hexane/DCM); $\mathbf{R_f}$ = 0.67 (silica gel, hexane/EtOAc 70:30); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.2 Hz, 2H, CH), 7.60 (t, *J* = 7.4 Hz, 1H, CH), 7.51 – 7.44 (m, 4H, CH), 7.40 – 7.31 (m, 3H, CH), 5.76 (d, *J* = 11.3 Hz, 1H, CH), 5.58 (d, *J* = 11.3 Hz, 1H, CH) ppm.



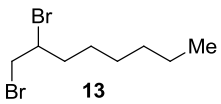
11

(*trans*)-1,2-Dibromocyclohexane (11):[5] **A:** 2 h; **B:** 5 min; colorless oil; $\mathbf{R_f}$ = 0.49 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 4.46 – 4.44 (m, 2H, CHBr), 2.51 – 2.41 (m, 2H, CH_2), 1.96 – 1.76 (m, 4H, CH_2), 1.56 – 1.46 (m, 2H, CH_2) ppm.



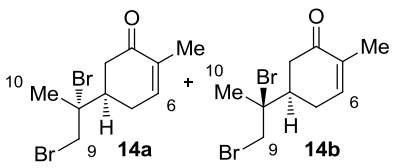
12

1,2-Dibromo-2-methyl-3-phenylpropane (12): A: 3 h, **B:** 40 min; yellow oil; $\mathbf{R_f}$ = 0.51 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.42 – 7.30 (m, 5H, CH), 3.82 (d, *J* = 10.2 Hz, 1H, $BnCH_2$), 3.74 (d, *J* = 10.2 Hz, 1H, $BnCH_2$), 3.28 (d, *J* = 14.3 Hz, 1H, CH_2Br), 3.22 (d, *J* = 14.4 Hz, 1H, CH_2Br), 1.91 (s, 3H, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 136.1 (C_{ar}-H), 131.0 (C_{ar}-H), 128.2 (C_{ar}-H), 127.4 (C_{ar}-H), 66.71 (C_q), 47.25 (CH_2Br), 42.32 (CH_2Br), 30.85 (Me) ppm; **IR** (film) 3061, 3030, 2973, 2926, 2315, 1951, 1886, 1810, 1600, 1494, 1449, 1378, 1213, 1081, 1036, 740, 700, 545 cm $^{-1}$; **MS** (EI, 70 eV): *m/z* (%) = 293/291/289 (20/41/20) [M^+], 213/211 (16/18) [M-Br^+], 171/169 (15/15), 91 (100) [$C_7H_7^+$].



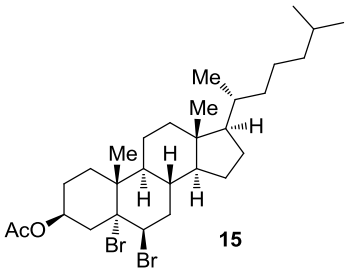
13

1,2-Dibromooctane (13):[6] **A:** 1 h; **B:** 15 min; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.17 (ddd, *J* = 13.2, 9.3, 3.8 Hz, 1H,CHBr), 3.84 (dd, *J* = 10.2, 4.4 Hz, 1H, CH_2Br), 3.62 (dd, *J* = 10.0, 9.9 Hz, 1H, CH_2Br), 2.19 – 2.08 (m, 1H, CH_2), 1.84 – 1.72 (m, 1H, CH_2), 1.64 – 1.50 (m, 1H,CH_2), 1.49 – 1.24 (m, 7H, CH_2), 0.89 (t, *J* = 6.8 Hz, 3H, CH_3) ppm.



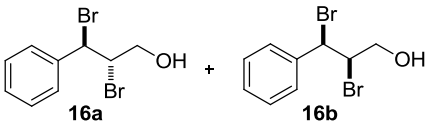
14a **14b**

(4*R*,8*R*)-8,9-Dibromo-p-menth-6-en-2-one (14a) and (4*R*,8*S*)-8,9-dibromo-p-menth-6-en-2-one (14b):[7] **A:** 5 h, **B:** 3.5 h; ~1:1 ratio of diastereomers; colorless oil; $\mathbf{R_f}$ = 0.27 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 6.74 (m, 2H, 6-CH), 3.96 (d, *J* = 10.4 Hz, 1H, 9-CH_2), 3.94 (d, *J* = 10.4 Hz, 1H, 9-CH_2), 3.85 (d, *J* = 10.4 Hz, 1H, 9-CH_2), 3.81 (d, *J* = 10.4 Hz, 9-CH_2), 2.03 – 1.78 (m, 5H), 2.67 – 2.29 (m, 10H), 1.88 (s, 3H, 7-CH_3), 1.86 (s, 3H, 7-CH_3), 1.79 (bs, 6H, 10-CH_3) ppm.



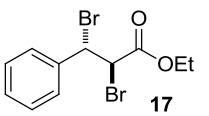
15

5α,6β-Dibromocholestan-3β-yl acetate (15):[8] **A:** 5 h, **B:** 3.5 h; white solid; **m.p**. = 111 °C (Hex:EtOAc), lit.[7] 109 – 111 °C; $\mathbf{R_f}$ = 0.50 (silica gel, hexanes/EtOAc 90:10); α_D = -55.8° (c = 1.0, $CHCl_3$), lit. -44.5° (c = 3.59, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 5.48 (m, 1H, 3α-CH), 4.82 (dd, *J* = 4.2, 1.9 Hz, 1H, 6α-CH), 2.66 (ddd, *J* = 15.7, 12.2, 4.4 Hz, 1H, CH), 2.58 (dd, *J* = 13.9, 10.3 Hz, 1H, CH), 2.04 (s, 3H, $OCOCH_3$), 2.03 – 1.78 (m, 5H), 1.74 – 1.49 (m, 7H), 1.46 (s, 3H, 19-CH_3), 1.38 – 1.00 (m, 13H), 0.91 (d, *J* = 6.5 Hz, 3H, 21-CH_3), 2x 0.86 (each d, *J* = 6.6 Hz, 3H, 26- and 27-CH_3), 0.70 (s, 3H, 18-CH_3) ppm.



16a **16b**

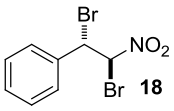
(*trans*)-2,3-Dibromo-3-phenylpropan-1-ol (16a) and (*cis*)-2,3-Dibromo-3-phenylpropan-1-ol (16b):[9] **A:** 2 h, **B:** 1 h; 85:15 ratio of diastereomers (**16a**:**16b**); white solid; ; **m.p**. = 69 °C (Hex:EtOAc), lit.[9] 68 - 70 °C; $\mathbf{R_f}$ = 0.64 (silica gel, hexanes/EtOAc 90:10); **^{1}H NMR of 5a** (400 MHz, $CDCl_3$) δ = 7.50 – 7.33 (m, 5H, CH), 5.27 (d, *J* = 11.1 Hz, 1H, 3-CH), 4.71 (ddd, *J* = 11.1, 4.4, 2.7 Hz, 1H, 2-CH), 4.33 (dd, *J* = 12.8, 4.4 Hz, 1H, CH_2), 4.25 (dd, *J* = 12.7, 2.7 Hz, 1H, CH_2), 2.28 (br, 1H, OH) ppm. **^{1}H NMR of 5b** (400 MHz, $CDCl_3$) δ = 7.50 – 7.30 (m, 5H), 5.37 (d, *J* = 6.5 Hz, 1H, 3-CH), 4.54 – 4.48 (m, 1H, 2-CH), 3.94 (dd, *J* = 12.3, 4.6 Hz, 1H,CH_2), 3.68 (dd, *J* = 12.3, 6.1 Hz, 1H, CH_2), 2.28 (br, 1H, OH).



17

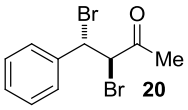
(*trans*)-2,3-Dibromo-3-phenyl-propionic acid ethyl ester (17):[11] **A:** 2 h; **B:** 1 h; white solid; **m.p**. = 73 °C (DCM); $\mathbf{R_f}$ = 0.47 (silica gel, hexane/EtOAc 95:5); **^{1}H NMR** (300 MHz,

$CDCl_3$) δ = 7.43 – 7.35 (m, 5H, CH), 5.35 (d, *J* = 11.8 Hz, 1H, CHBr), 4.83 (d, *J* = 11.8 Hz, 1H, CHBr), 4.36 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.38 (t, *J* = 7.1 Hz, 3H, CH_3) ppm.



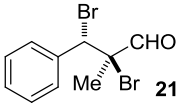
18

(*trans*)-1,2-Dibromo-2-phenyl-1-nitroethane (18):[5] **A:** 3 h, **B:** 1 h; white solid; **m.p**. = 95 °C (DCM), lit[4] 89 °C; $\mathbf{R_f}$ = 0.48 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.50 – 7.35 (m, 5H, CH), 6.33 (d, *J* = 10.9 Hz, 1H, 1-CH), 5.49 (d, *J* = 10.9 Hz, 1H, 2-CH) ppm.



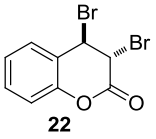
20

(*trans*)-3,4-Dibromo-3-phenylbutan-2-one (20):[12] **A:** 2 h; **B:** 1 h; white solid; **m.p**. = 122 °C (DCM), lit[9] 126-128 °C; $\mathbf{R_f}$ = 0.63 (silica gel, hexane/EtOAc 80:20); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 5H, CH), 5.34 (d, *J* = 11.7 Hz, 1H, CH), 4.96 (d, *J* = 11.7 Hz, 1H, CH), 2.48 (s, 3H, CH_3) ppm.



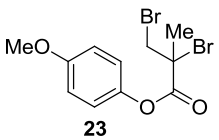
21

(*trans*)-2,3-dibromo-3-phenyl-propanal (21):[3] **A:** 2 h; **B:** 1 h; colorless oil; $\mathbf{R_f}$ = 0.32 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.34 (s, 1H, CHO), 7.53 – 7.47 (m, 2H, CH), 7.42 – 7.37 (m, 3H, CH), 5.45 (s, 1H, CHBr), 1.96 (s, 3H, CH_3) ppm.



22

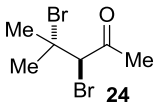
(*trans*)-3,4-Dibromo-3,4-dihydrocoumarin (22):[13] **A:** 6 h; **B:** 3.5 h; white solid; **m.p**. = 98 °C (DCM), lit[13] 94-97 °C (Et_2O/hexane); $\mathbf{R_f}$ = 0.23 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.47 – 7.37 (m, 2H, CH), 7.26 – 7.15 (m, 2H, CH), 5.35 (d, *J* = 2.6 Hz, 1H, CHBr), 4.96 (d, *J* = 2.6 Hz, 1H, CHBr) ppm.



23

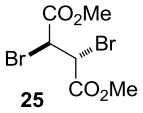
2,3-Dibromo-2-methylpropanoic acid-4-methoxyphenyl ester (23): A: 12 h; **B:** 3.5 h; colorless oil; $\mathbf{R_f}$ = 0.50 (silica gel, hexanes/EtOAc 90:10); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.08 (m, 2H, CH), 6.92 (m, 2H, CH), 4.39 (d, *J* = 9.9 Hz, 1H, CH_2), 3.83 (d, *J* = 9.9 Hz, 1H, CH_2), 3.81 (s, 3H, OMe), 2.14 (s, 3H, Me); **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 167.9 (C=O), 157.8 (C_{ar}-O), 144.1 (C_{ar}-O), 122.0 (C_{ar}-H), 114.7 (C_{ar}-H), 55.76 (OMe), 55.25 (C_q), 38.13 (CH_2), 26.51 (Me) ppm; **IR** (film) 3498, 3050, 2938, 2340, 2049, 1873, 1759, 1600, 1504, 1449, 1382,

1289, 1250, 1190, 1074, 1038, 951, 875, 818, 748, 605, 518 cm $^{-1}$; **MS** (EI, 70 eV): *m*/*z* (%) = 354/352/350 (53/100/53) [M^+], 273/271 (2/2) [M-Br^+], 231/229/227 (6/11/6) [$C_4H_5Br_2O^+$], 203/201/199 (12/23/12) [$C_3H_5Br_2^+$], 124 (100) [$C_7H_8O_2^+$].



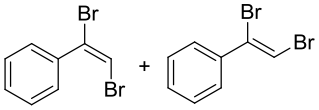
24

3,4-Dibromo-4-methylpentan-2-one (24): A: 12 h; **B:** 5 h; colorless oil; R_f = 0.51 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.69 (s, 1H, CHBr), 2.38 (s, 3H,$COCH_3$), 1.98 (s, 3H, CH_3), 1.91 (s, 3H, CH_3) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.6, 62.11, 59.67, 34.35, 29.74, 28.69 ppm; **IR** (film) 2934, 1730, 1452, 1359, 1193, 1155, 1101, 703 cm $^{-1}$; **MS** (EI, 70 eV): *m*/*z* (%) = 259/257/255 (3/5/3) [M^+], 231 (15), 179/177 (8/9) [M^+-Br], 136/134 (26/26), 121/123 (29/30), 55 (100).



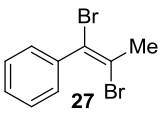
25

(*meso*)-2,3-Dibromosuccinic acid methyl ester (25):[15] **A:** 24 h; **B:** 12 h; colorless oil; R_f = 0.34 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.69 (s, 2H, CH), 3.86 (s, 6H, OCH_3) ppm.



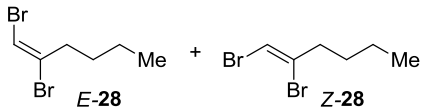
E-**26** *Z*-**26**

1,2-Dibromo-1-phenylethen (26):[16] **A:** 1 h; **B:** 10 min; 65:35 ratio of *E*:*Z*; yellow liquid; R_f = 0.90 (silica gel, pentane); *E* isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H, CH), 6.81 (s, 1H, vinyl-CH) ppm; *Z* isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 5H, CH), 7.06 (s, 1H, vinyl-CH) ppm.

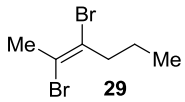


27

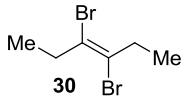
(*E*)-1,2-Dibromo-1-phenylpropene (27):[6] **A:** 1 h; **B:** 10 min; colorless liquid; R_f = 0.81 (silica gel, pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H, CH), 2.61 (s, 3H, CH_3) ppm.



1,2-Dibromo-1-phenylethen (28):[5] **A:** 1 h; **B:** 20 min; 94:6 ratio of *E*:*Z*; colorless liquid; $\mathbf{R_f}$ = 0.85 (silica gel, pentane); *E* isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.40 (d, *J* = 0.6 Hz, 1H, vinyl-CH), 2.61 (d, *J* = 7.3 Hz, 1H, $CBrCH_2$), 2.58 (d, *J* = 7.3 Hz, 1H, $CBrCH_2$), 1.62 – 1.53 (m, 2H, CH_2), 1.38 – 1.26 (m, 6H, CH_2), 0.90 (t, *J* = 6.5 Hz, 3H, CH_3) ppm; *Z* isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.57 – 6.55 (m, 1H, vinyl-CH), 2.50 (t, *J* = 7.3 Hz, 1H, $CBrCH_2$), 1.62 – 1.53 (m, 2H, CH_2), 1.38 – 1.26 (m, 6H, CH_2), 0.90 (t, *J* = 6.5 Hz, 3H, CH_3) ppm.

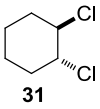


2,3-Dibromohex-2-ene (29):[17] **A:** 1 h; **B:** 20 min; yellow liquid; $\mathbf{R_f}$ = 0.74 (silica gel, pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.64 (ddd, *J* = 8.4, 6.5, 0.9 Hz, 2H, allyl-CH_2), 2.42 (t, *J* = 0.9 Hz, 3H, allyl-CH_3), 1.68 – 1.55 (m, 2H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3) ppm.



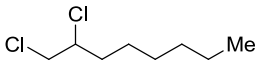
3,4-Dibromohex-3-ene (30):[18] **A:** 1 h; **B:** 20 min; yellow liquid; $\mathbf{R_f}$ = 0.76 (silica gel, pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.67 (q, *J* = 7.4 Hz, 4H, CH_2), 1.11 (t, *J* = 7.4 Hz, 6H, CH_3) ppm.

7.2 Chlorinated Products



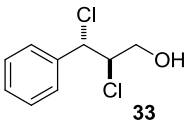
31

(*trans*)-1,2-Dichlorocycohexen (32):[5] 5 min; colorless liquid; $\mathbf{R_f}$ = 0.89 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.01 – 3.99 (m, 2H, CHCl), 2.33 – 2.26 (m, 2H, CH_2), 1.78 – 1.69 (m, 4H, CH_2), 1.43 – 1.38 (m, 2H, CH_2) ppm.



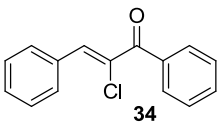
32

1,2-Dichlorooctane (32):[19] 15 min; colorless liquid; $\mathbf{R_f}$ = 0.64 (silica gel, hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.00 (dddd, *J* = 8.9, 7.5, 5.1, 3.9 Hz, 1H,CHCl), 3.76 (dd, *J* = 11.3, 5.2 Hz, 1H, CH_2Cl), 3.65 (dd, *J* = 11.3, 7.4 Hz, 1H, CH_2Cl), 2.03 – 1.93 (m, 1H, CH_2), 1.77 – 1.66 (m, 1H, CH_2), 1.60 – 1.49 (m, 1H,CH_2), 1.47 – 1.24 (m, 7H, CH_2), 0.89 (t, *J* = 6.8 Hz, 3H, CH_3) ppm.



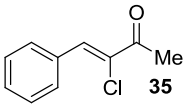
33

(*trans*)-2,3-Dichloro-3-phenylpropan-1-ol (33):[20] 1 h; colorless oil; $\mathbf{R_f}$ = 0.41 (silica gel, hexanes/EtOAc 80:20); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 1H, CH), 5.10 (d, *J* = 9.5 Hz, 1H, 3-CH), 4.43 (ddd, *J* = 9.5, 4.8, 3.2 Hz, 1H, 2-CH), 4.19 (ddd, *J* = 12.1, 7.2, 4.8 Hz, 1H, CH_2), 4.09 (ddd, *J* = 12.4, 6.6, 3.1 Hz, 1H, CH_2), 2.11 (t, *J* = 7.0 Hz, 1H) ppm.



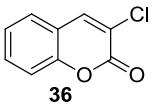
34

(*Z*)-2-Chloro-1,3-diphenylpropan-1-one (34):[21] 20 min; colorless oil; $\mathbf{R_f}$ = 0.61 (silica gel, hexanes/EtOAc 90:10); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 4H, CH), 7.63 – 7.57 (m, 1H, CH), 7.53 – 7.42 (m, 6H, CH) ppm.



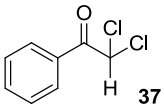
35

(*Z*)-2-Chloro-1-phenylbutan-3-one (35):[22] 20 min; yellow oil; $\mathbf{R_f}$ = 0.63 (silica gel, hexanes/EtOAc 90:10); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H, C_{ar}-H), 7.76 (s, 1H, C_{benzyl}-H), 7.49 – 7.40 (m, 3H, C_{ar}-H), 2.56 (s, 3H, Me) ppm.



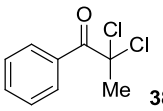
36

3-Chlorocoumarin (36):[23] 5 h; white solid; **m.p**. = 123 °C (Hex:EtOAc), lit.[19] 121 °C; $\mathbf{R_f}$ = 0.48 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.88 (s, 1H, 4-CH), 7.57 (ddd, *J* = 7.1, 1.5 Hz, 1H, CH), 7.47 (dd, *J* = 7.8, 1.6 Hz, 1H, CH), 7.38 – 7.30 (m, 2H, CH) ppm.



37

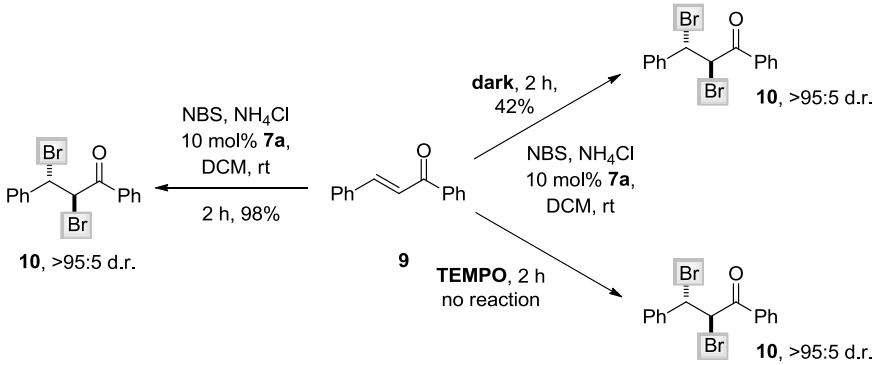
2,2-Dichloro-1-phenylethan-1-one (37):[24] 3 h; yellow oil; $\mathbf{R_f}$ = 0.51 (silica gel, hexanes/EtOAc 90:10); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 1.0 Hz, 2H, CH), 7.66 (t, *J* = 7.4 Hz, 1H, CH), 7.53 (t, *J* = 7.8 Hz, 2H, CH), 6.69 (s, 1H, $CHCl_2$) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.0 (C=O), 134.7 (C_{ar}-H) , 131.5 (C_{ar}-C), 129.9 (C_{ar}-H), 129.1 (C_{ar}-H), 67.92 (CH) ppm.



38

2,2-Dichloro-1-phenylpropan-1-one (38):[25] 18 h; colorless oil; $\mathbf{R_f}$ = 0.54 (silica gel, hexanes/EtOAc 95:5); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 – 8.31 (m, 2H, CH), 7.64 – 7.53 (m, 1H, CH), 7.62 – 7.58 (m, 1H, CH), 7.50 – 7.45 (m, 2H, CH), 2.36 (s, 3H, CH_3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2 (C=O), 133.7 (C_{ar}-C) , 131.4 (C_{ar}-H), 131.3 (C_{ar}-H), 128.3 (C_{ar}-H), 82.86 (C_q), 34.43 (Me) ppm.

8. Studies on the Reaction Mechanism of Dibrominations using NBS



Reaction in the Dark:

To a solution of chalcone (**9**, 208 mg, 1.00 mmol, 1.0 equiv.) and iodoamide **7a** (30.3 mg, 0.10 mmol, 0.1 equiv.) in DCM (5 mL, 0.2 M) NBS (392 mg, 2.20 mmol, 2.2 equiv.) and 1 drop sat. NH_4Cl solution were added. The reaction mixture was stirred for 2 h in the dark (amber vial wrapped with tin foil). The suspension was diluted with DCM (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous phase was additionally extracted with EtOAc (2 x 20 mL), the combined organic layers were dried over anhydrous $MgSO_4$, and the solvent removed. The residue was purified by column chromatography (SiO_2, hexane: DCM 1:0 → 2:1) to afford the corresponding halogenated products **10** (155 mg, 0.42 mmol, 42%).

Addition of the Radical Scavenger TEMPO:

To a solution of chalcone (**9**, 208 mg, 1.00 mmol, 1.0 equiv.) and iodoamide **7a** (30.3 mg, 0.10 mmol, 0.1 equiv.) in DCM (5 mL, 0.2 M) NBS (392 mg, 2.20 mmol, 2.2 equiv.), 1 drop sat. NH_4Cl solution and TEMPO (344 mg, 2.20 mmol, 2.2 equiv) were added. The reaction mixture was stirred for 2 h. The suspension was diluted with DCM (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous phase was additionally extracted with EtOAc (2 x 20 mL), the combined organic layers dried over anhydrous $MgSO_4$, and the solvent removed. The ^1H NMR of the crude mixture showed no formation of **10**.

9. Literature

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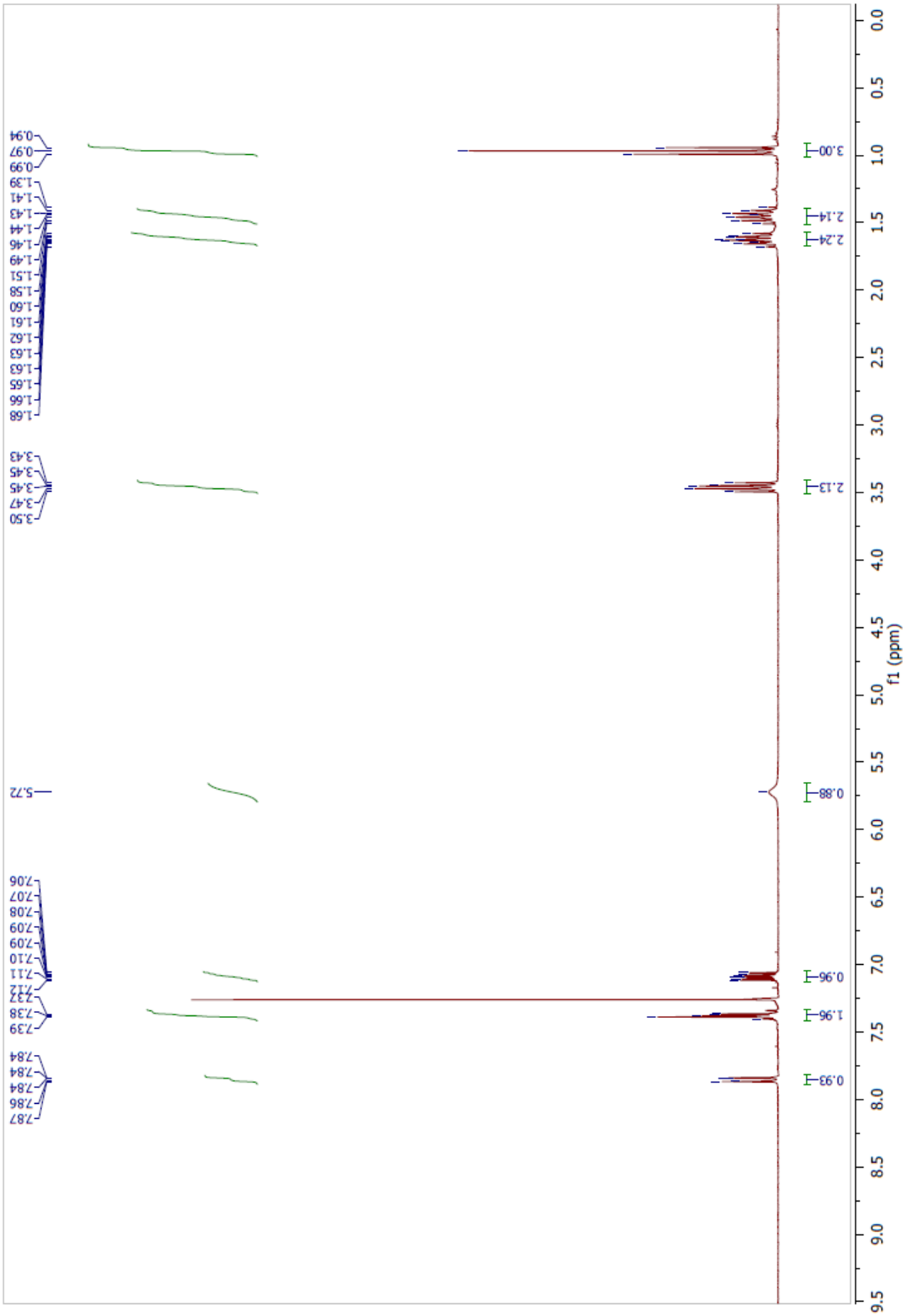
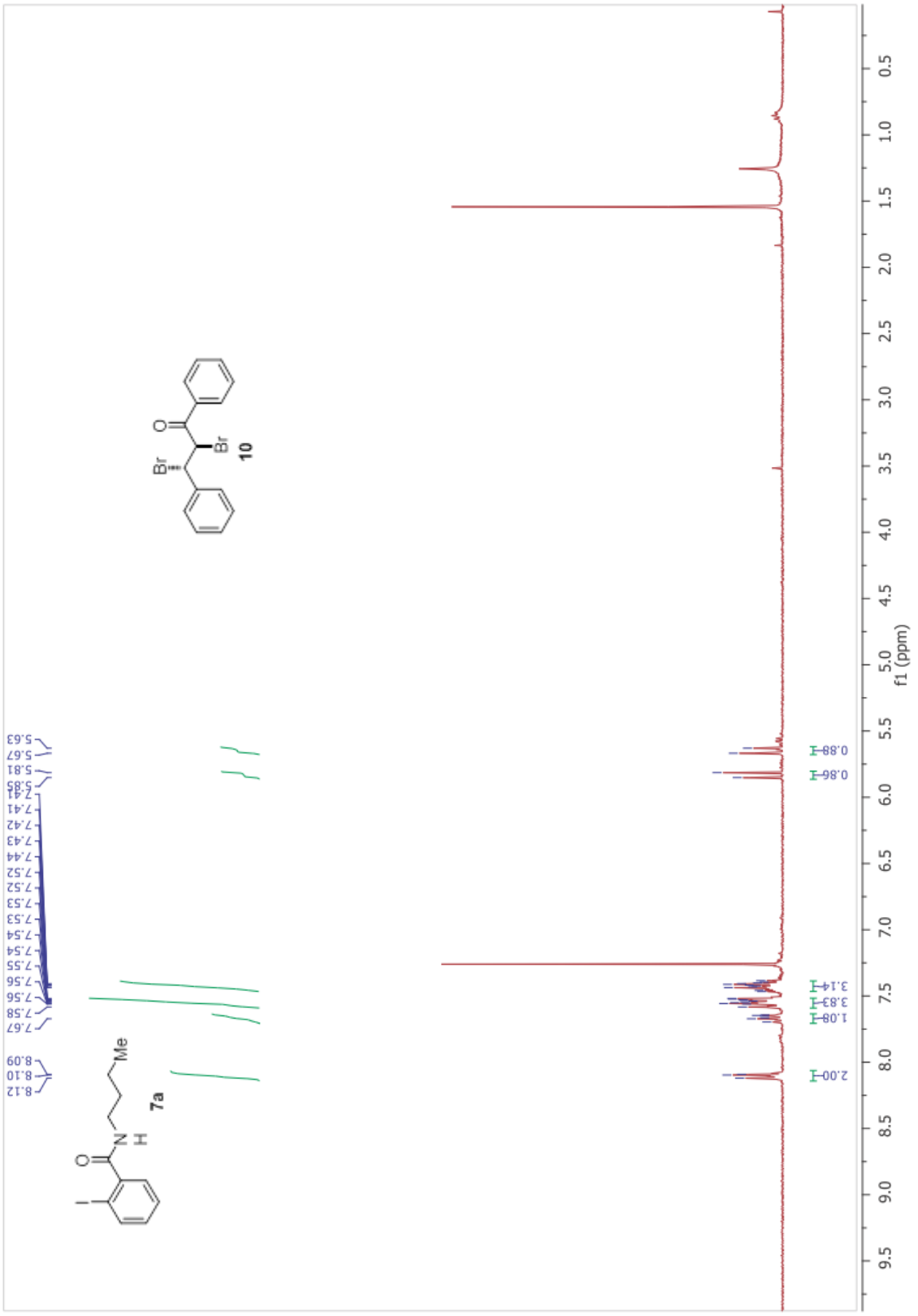
10. NMR Spectra

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8.09
7.67
7.58
7.56
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.44
7.43
7.42
7.41
7.41
5.85
5.81
5.67
5.63
Me
N
H
O
I
7a
Br
Br
O
10
0.88
0.86
3.14
3.83
1.08
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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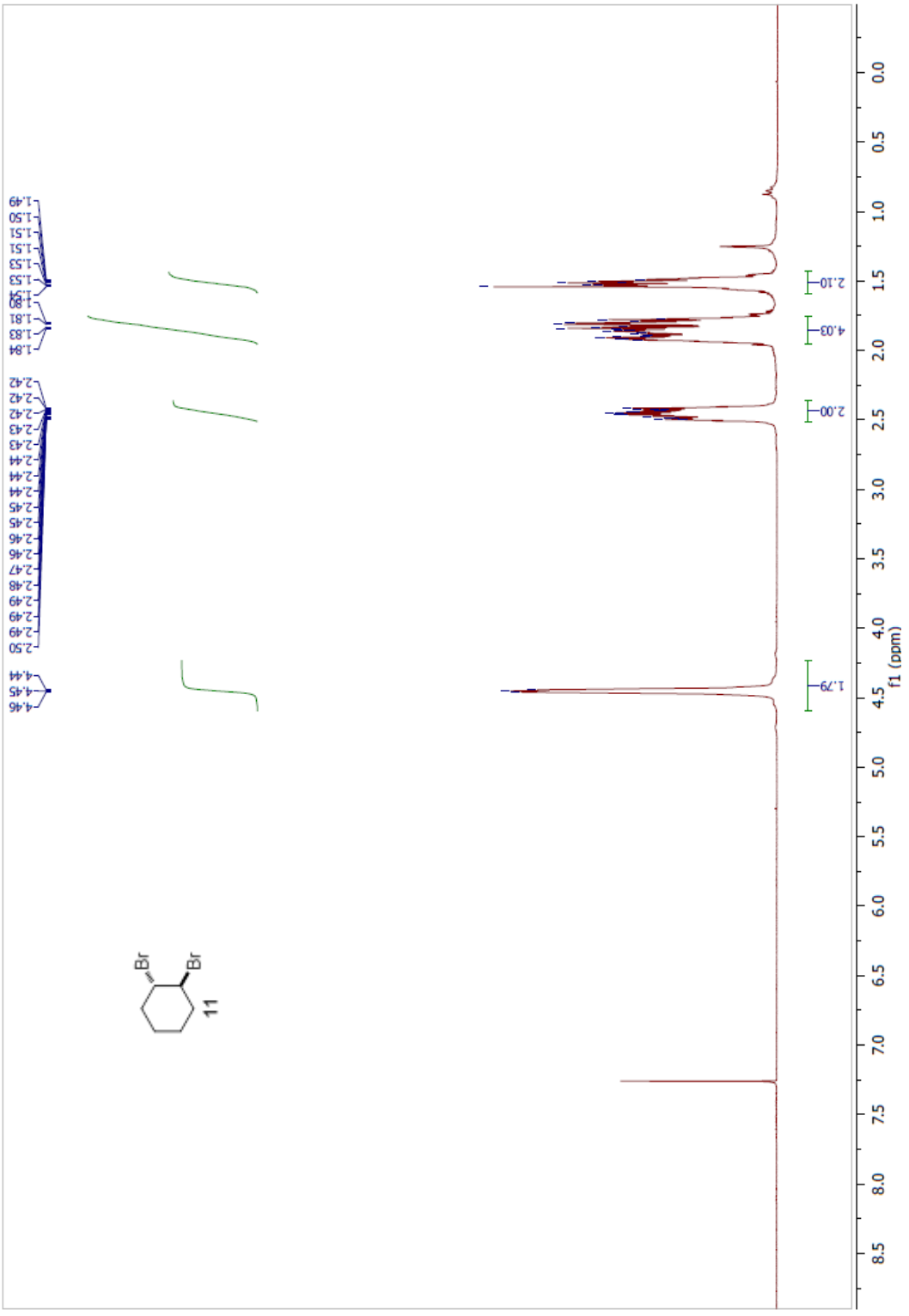
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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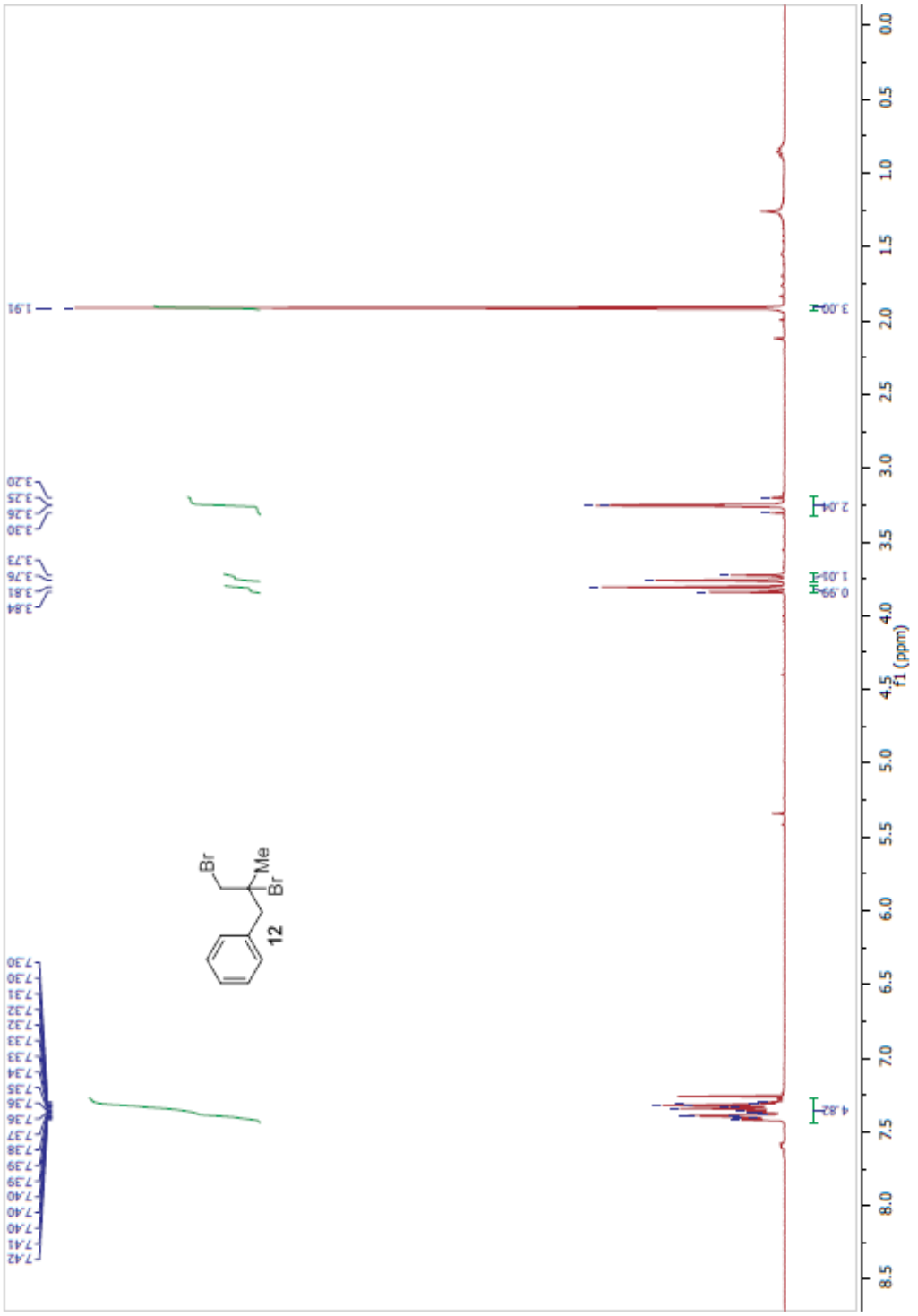
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Br
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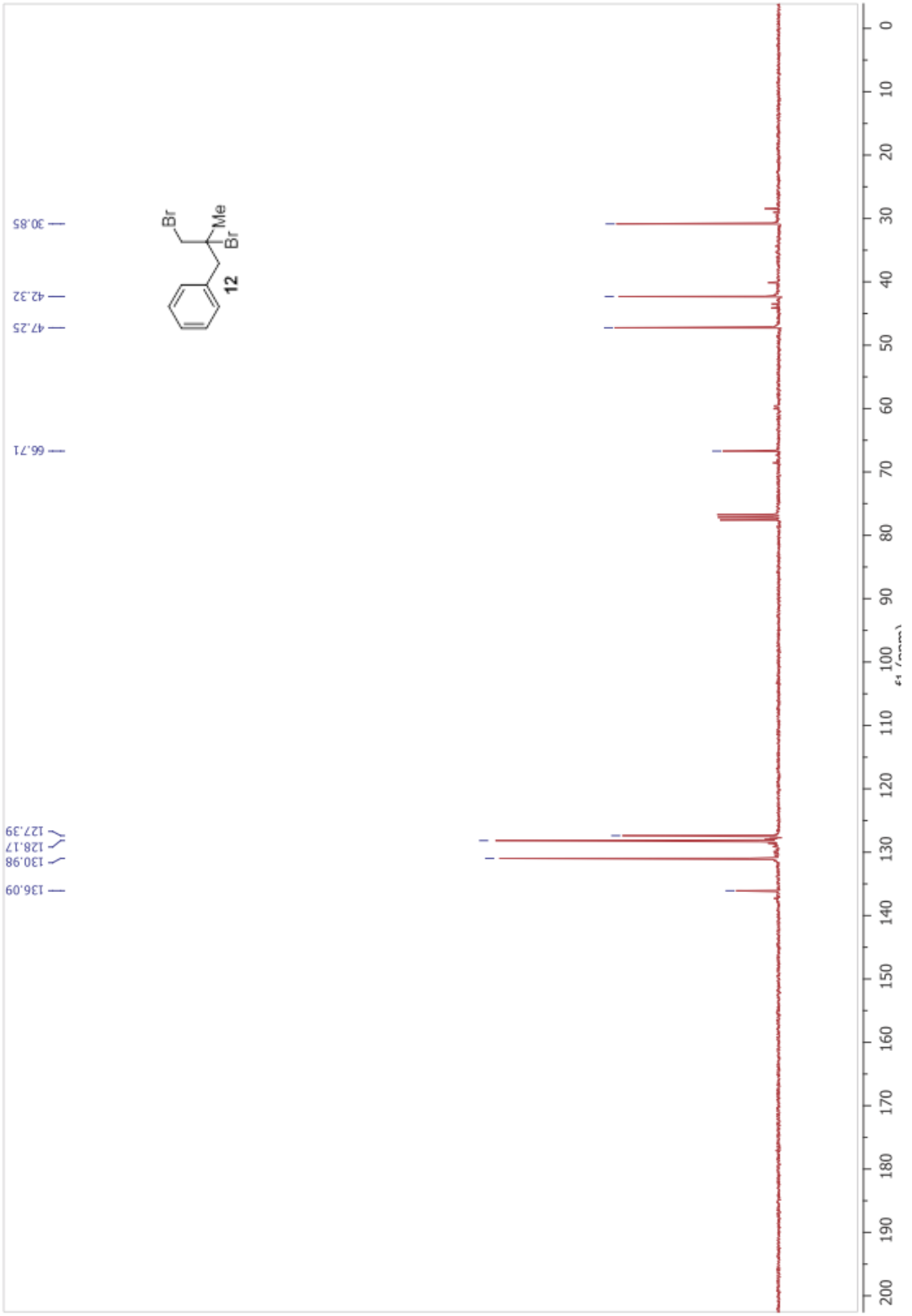
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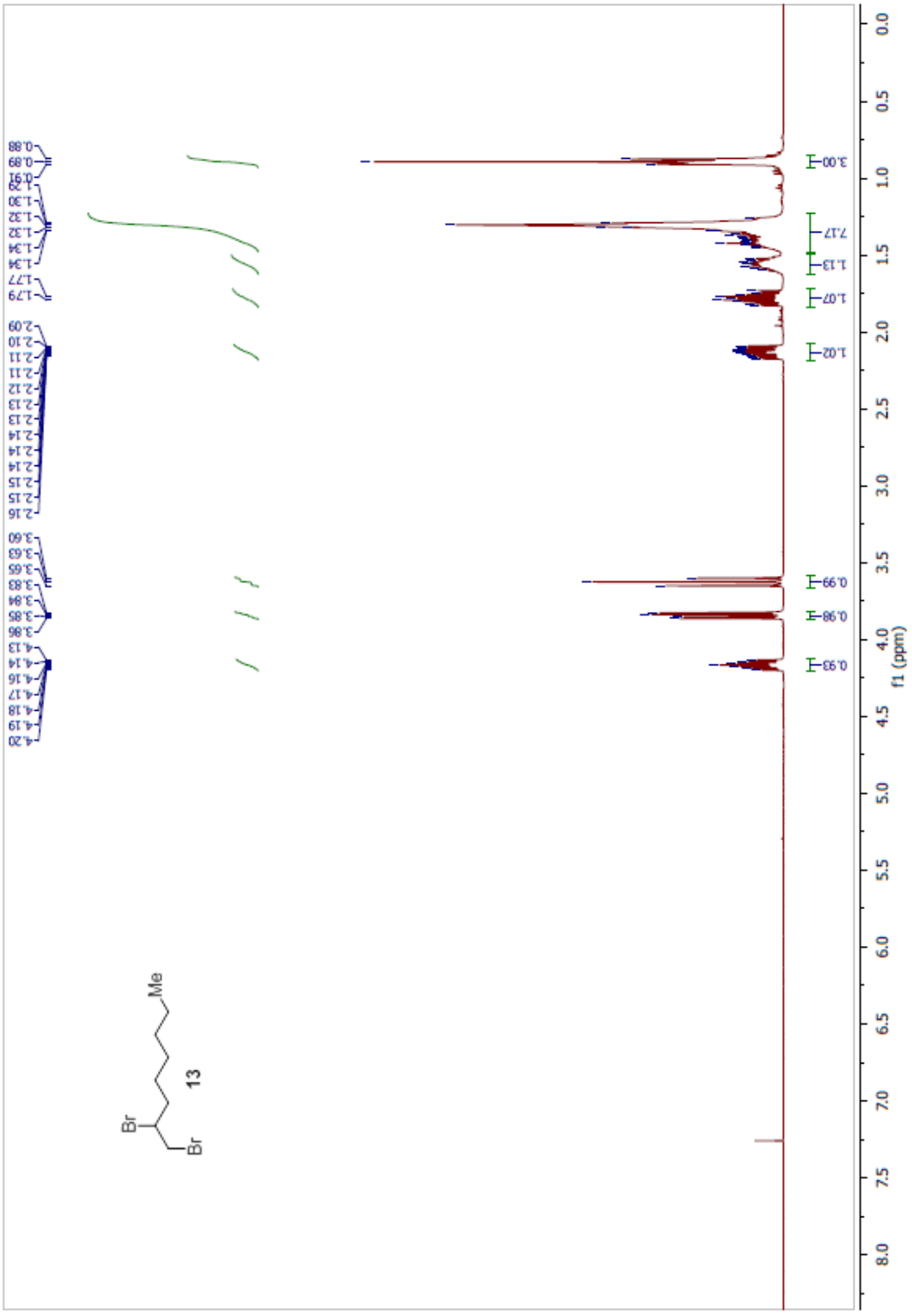
42.32
47.25
66.71
127.39
128.17
130.98
136.09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Br
Br
13
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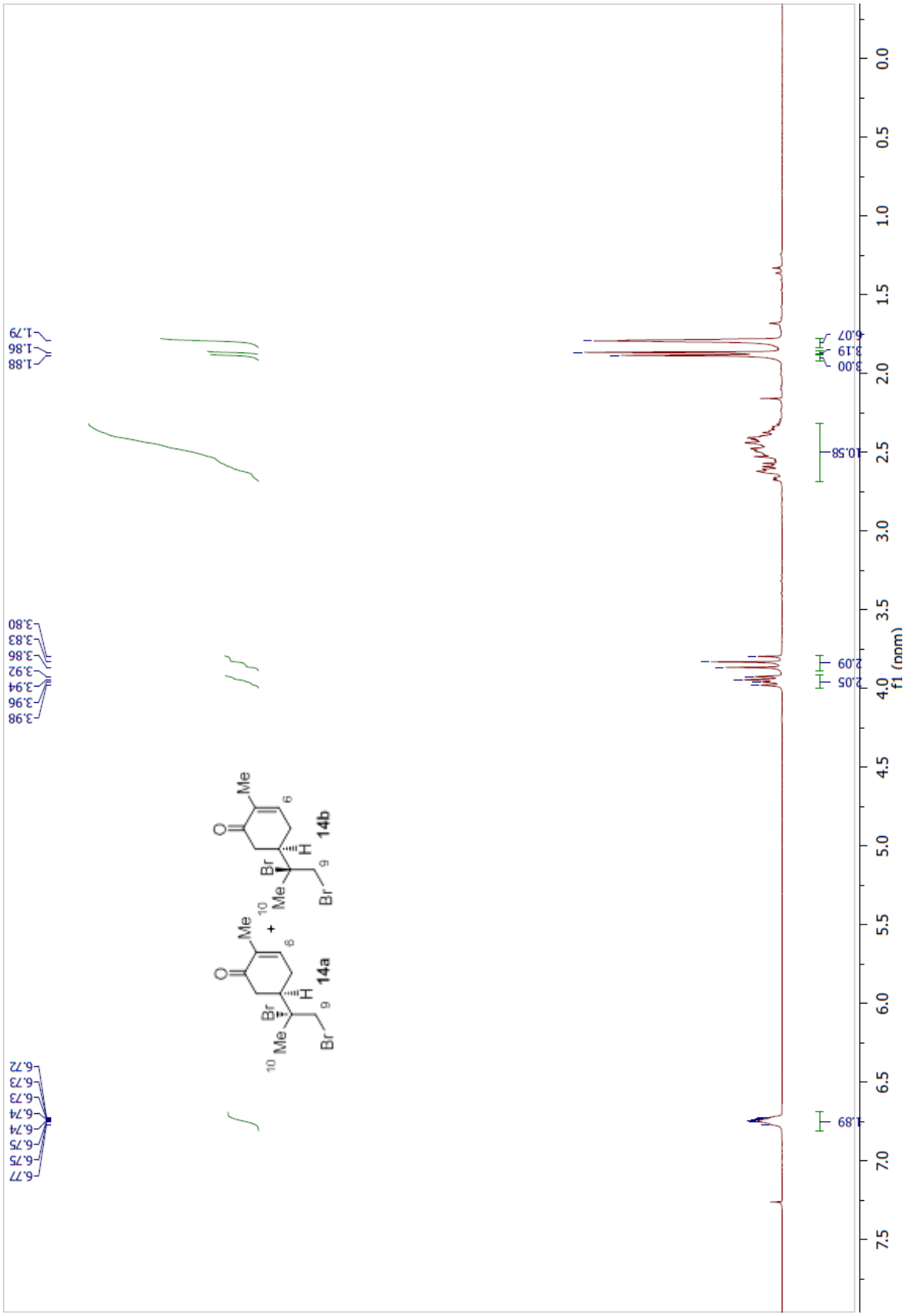
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6.75
6.75
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6.74
6.73
6.73
6.72
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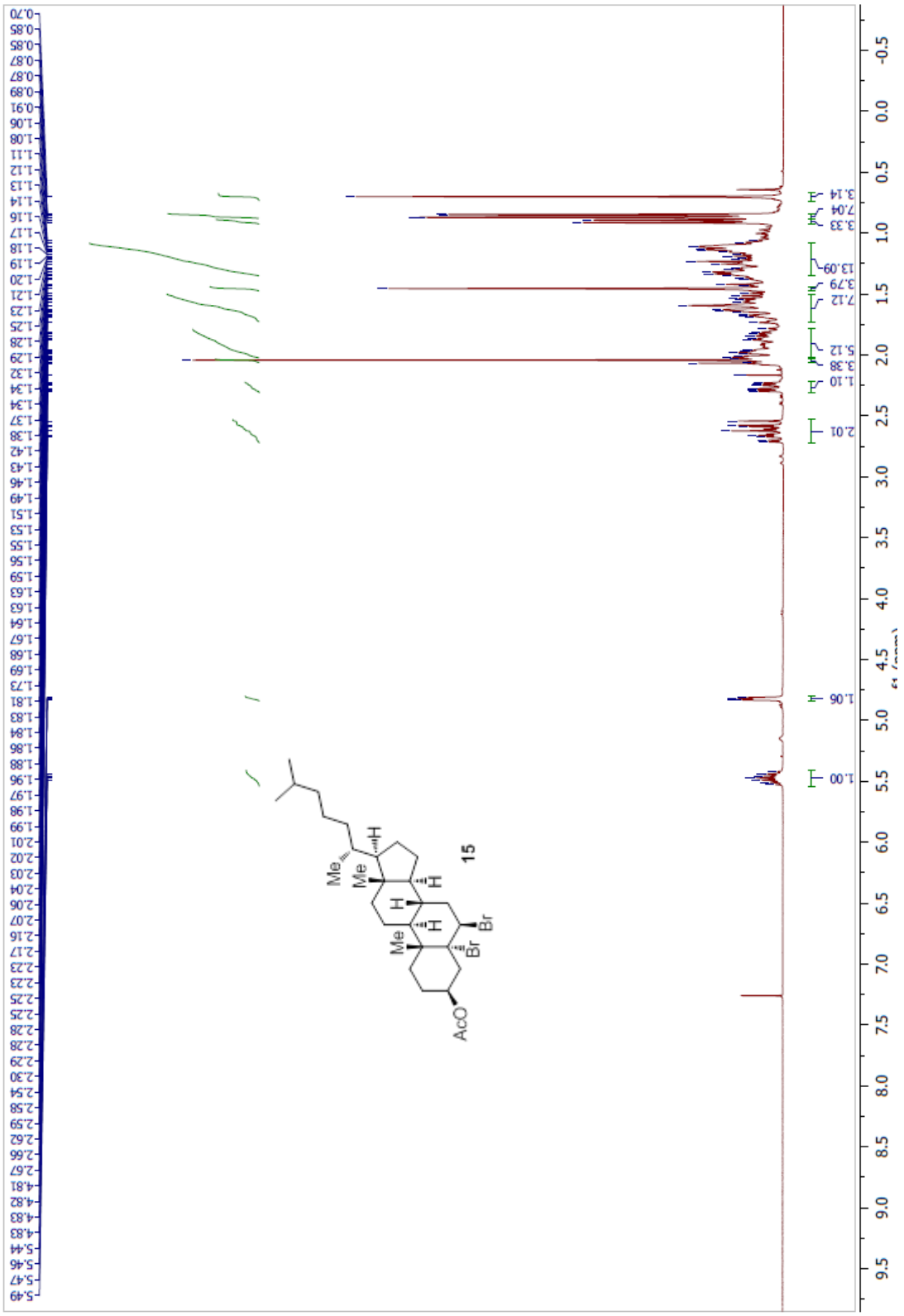
3.96
3.94
3.92
3.86
3.83
3.80
1.88
1.86
1.79
1.89
2.09
2.05
10.58
6.07
3.19
3.00
f1 (ppm)
14a
14b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AcO
Br
Br
Me
Me
H
H
H
H
H
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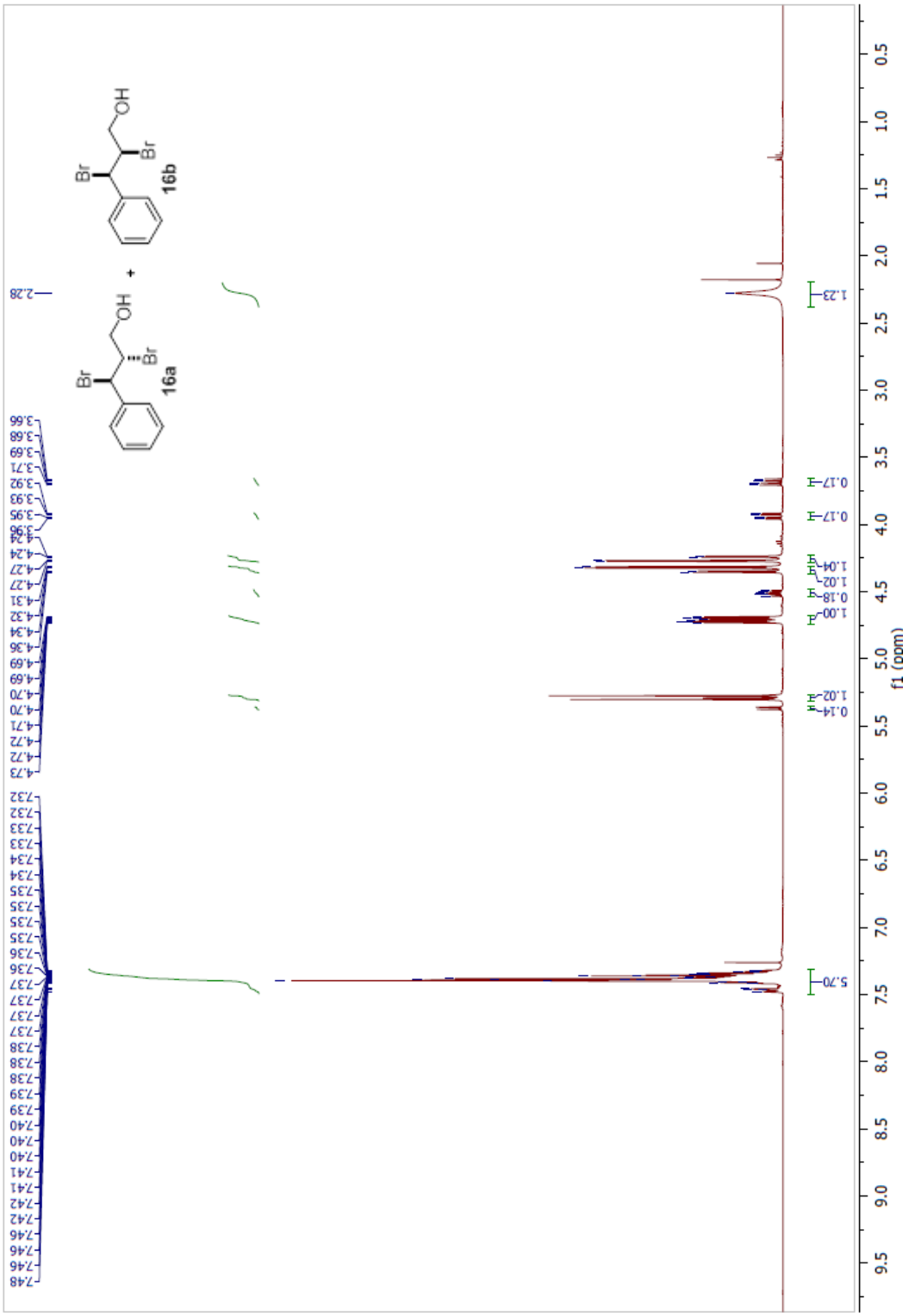
5.12
7.12
3.79
13.09
3.33
7.04
3.14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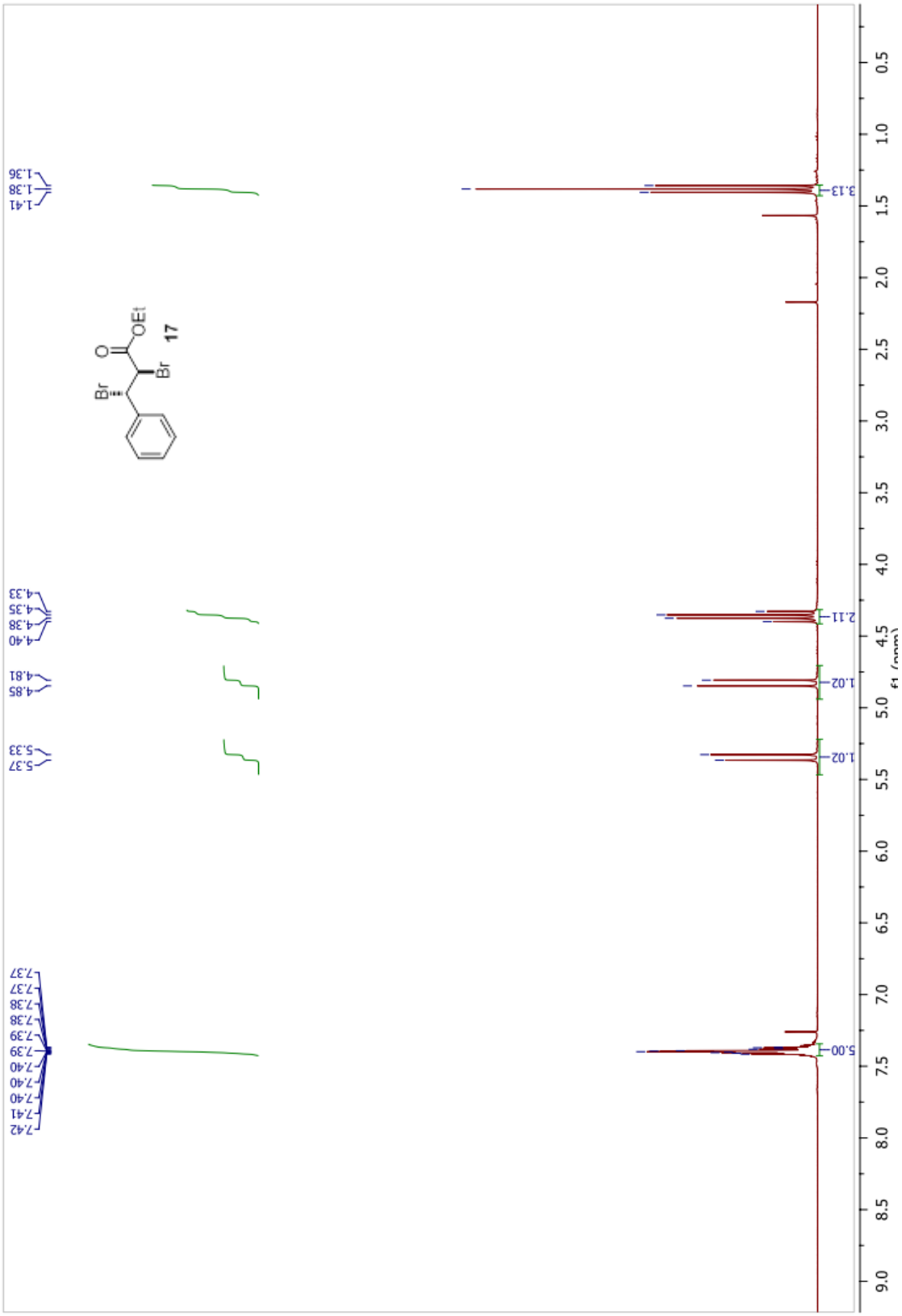
+
Br
OH
Br
16a
f1 (ppm)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Br
Br
O
OEt
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1.38
1.41
4.33
4.35
4.38
4.40
4.81
4.85
5.33
5.37
7.37
7.37
7.38
7.38
7.39
7.39
7.40
7.40
7.40
7.41
7.42
3.13
2.11
1.02
1.02
5.00
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
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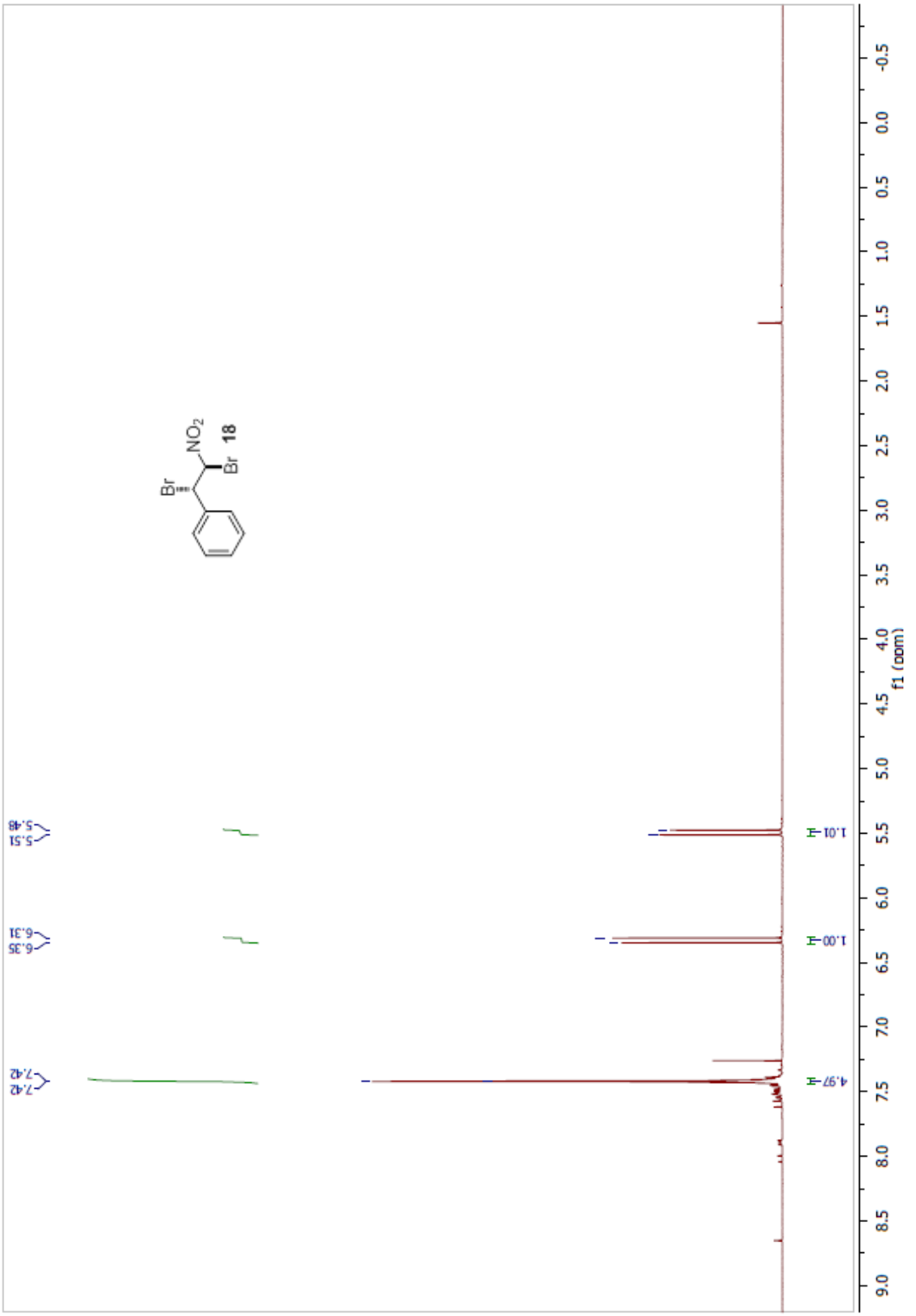
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)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NO2
Br
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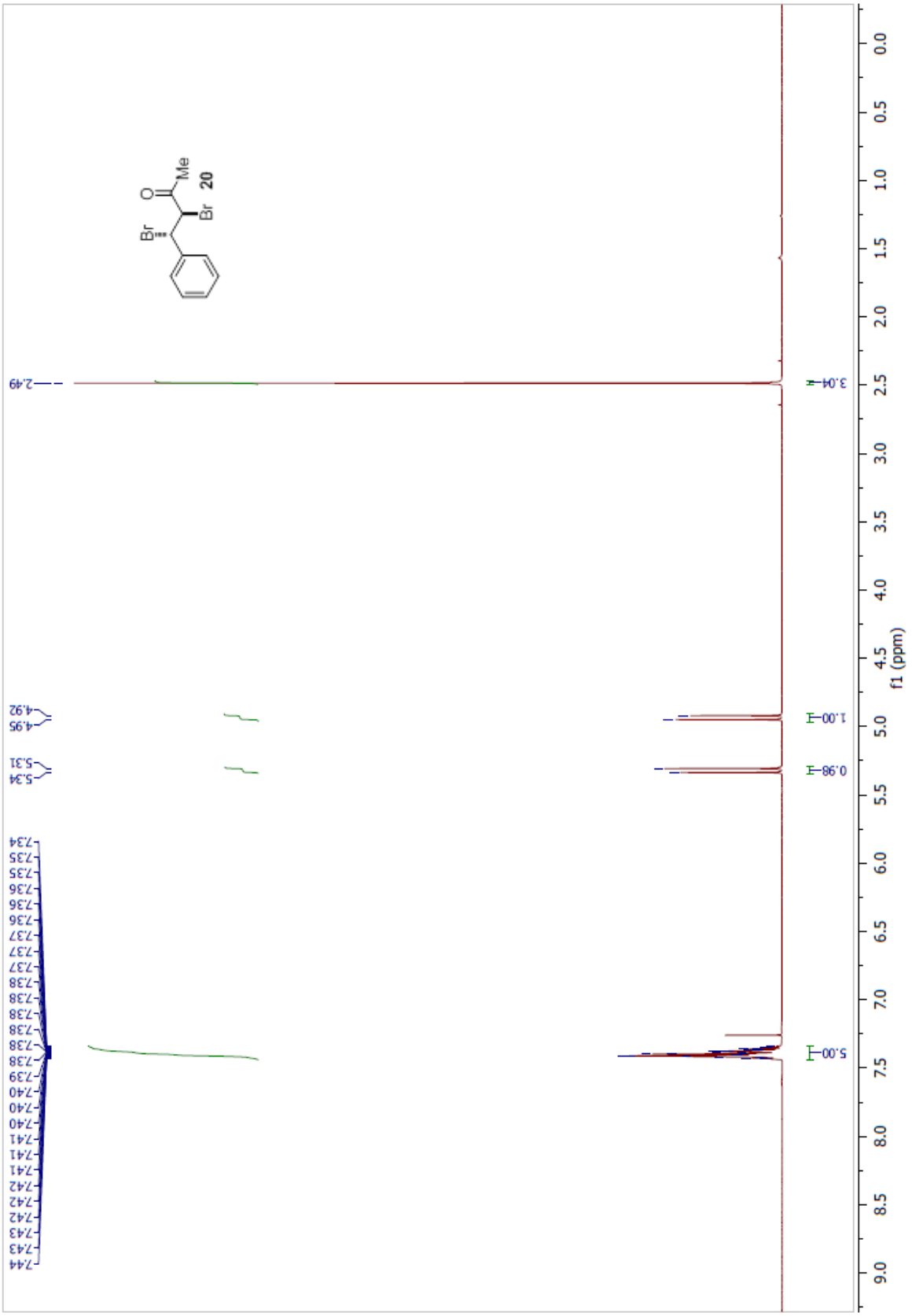
6.35
6.31
5.51
5.48
4.97
1.00
1.01
f1 (ppm)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O
Me
Br
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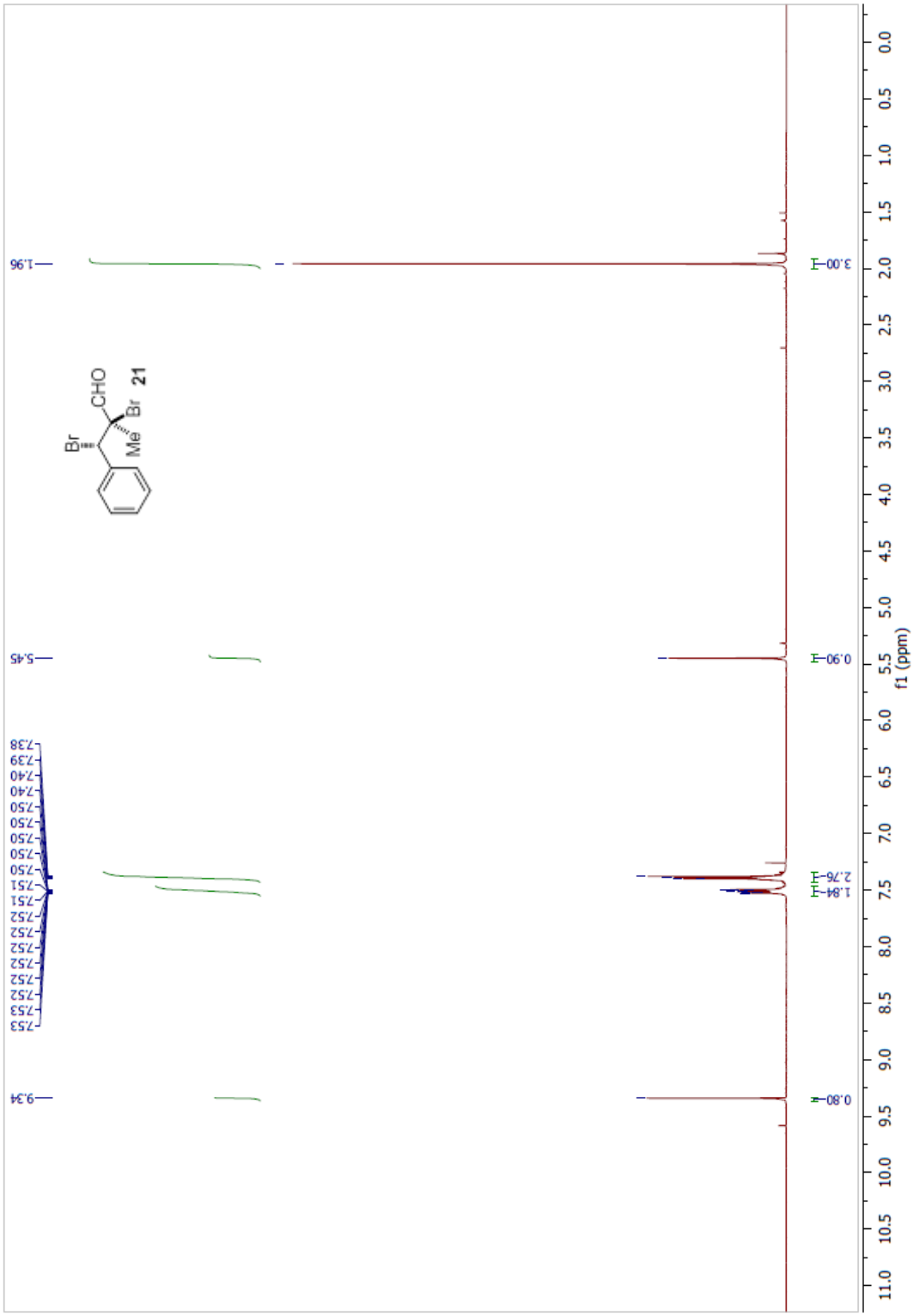
4.92
5.34
5.31
1.00
0.98
5.00
f1 (ppm)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Me
Br
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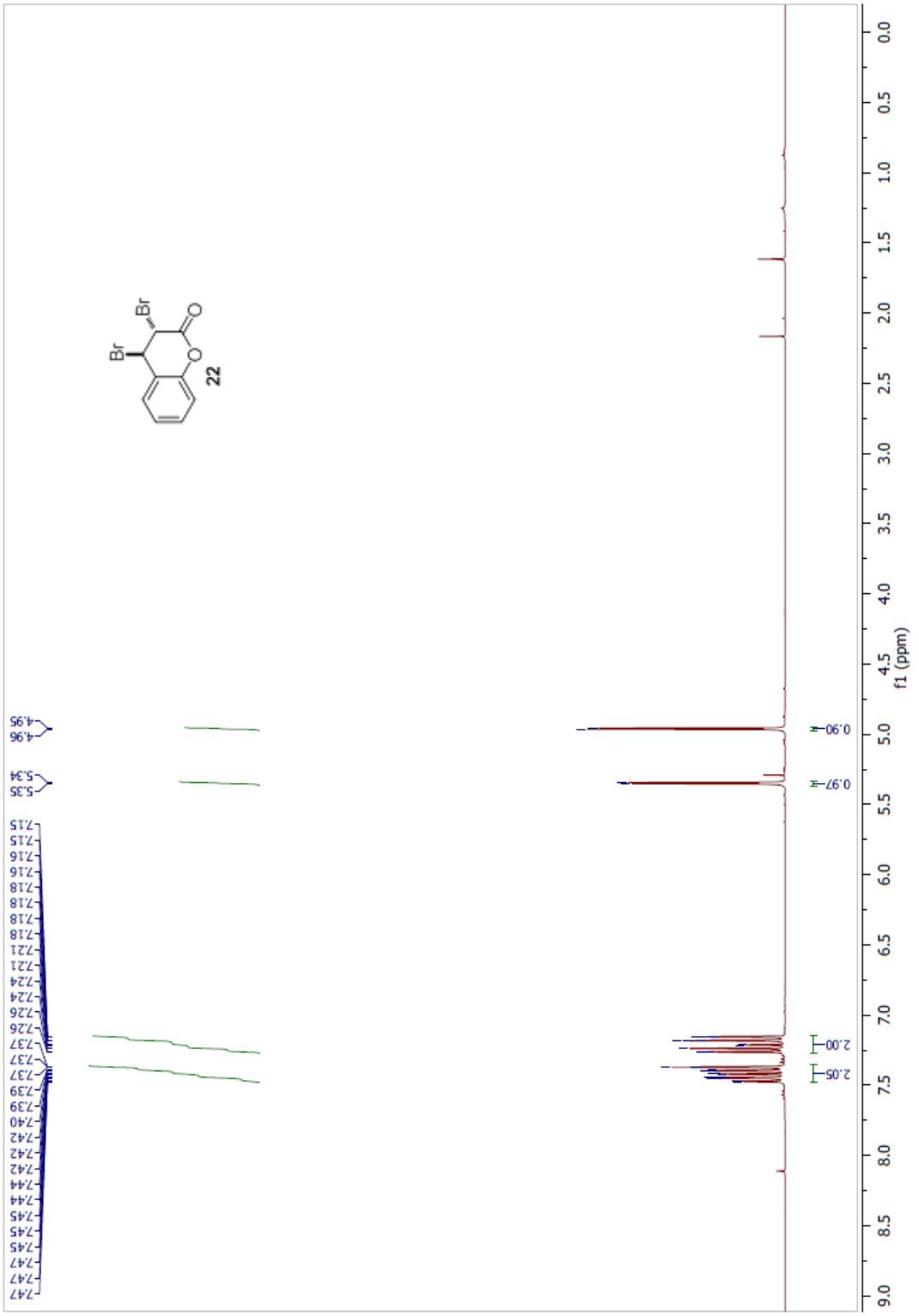
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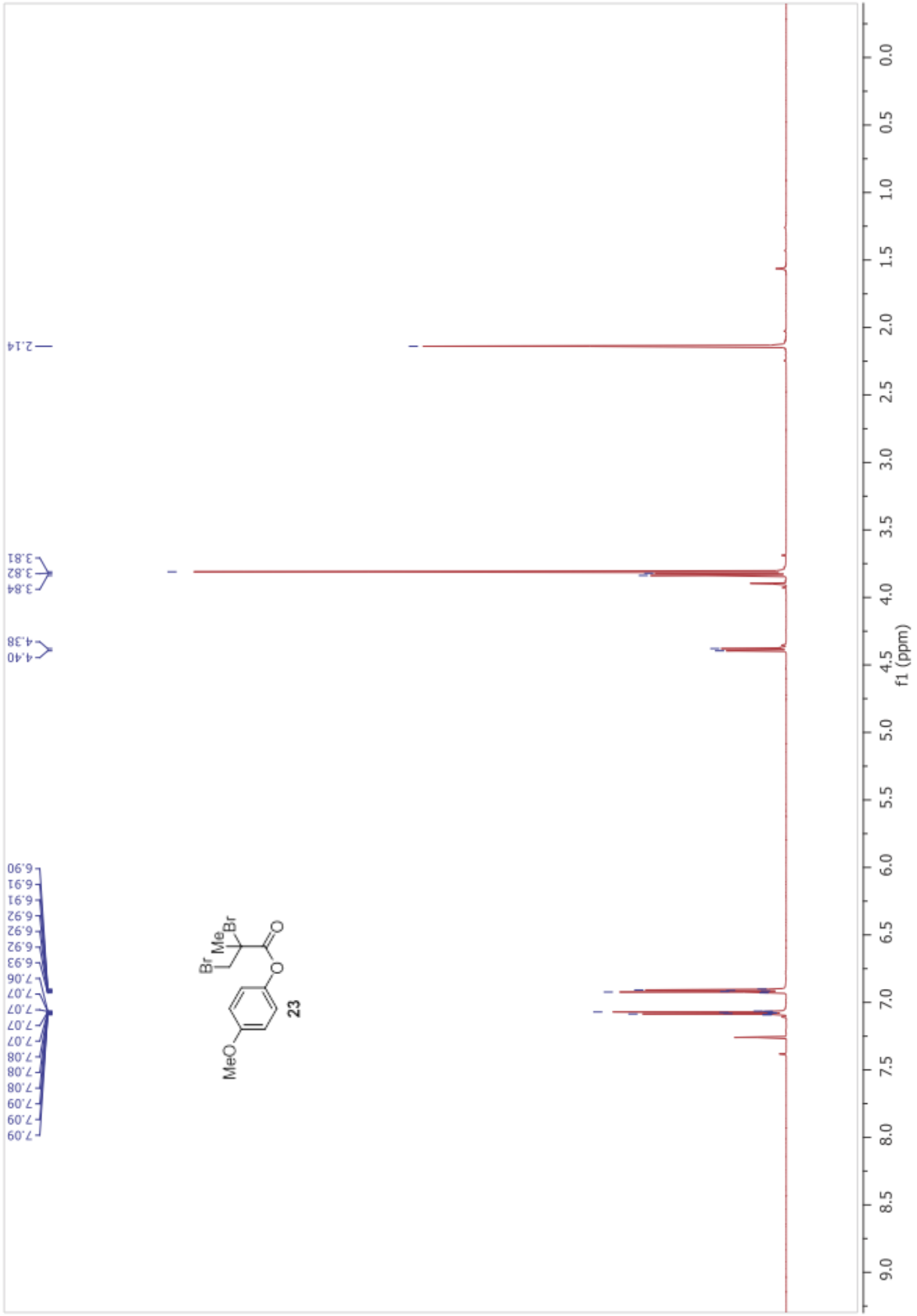
Br
O
O
22
f1 (ppm)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6.91
6.92
6.92
6.92
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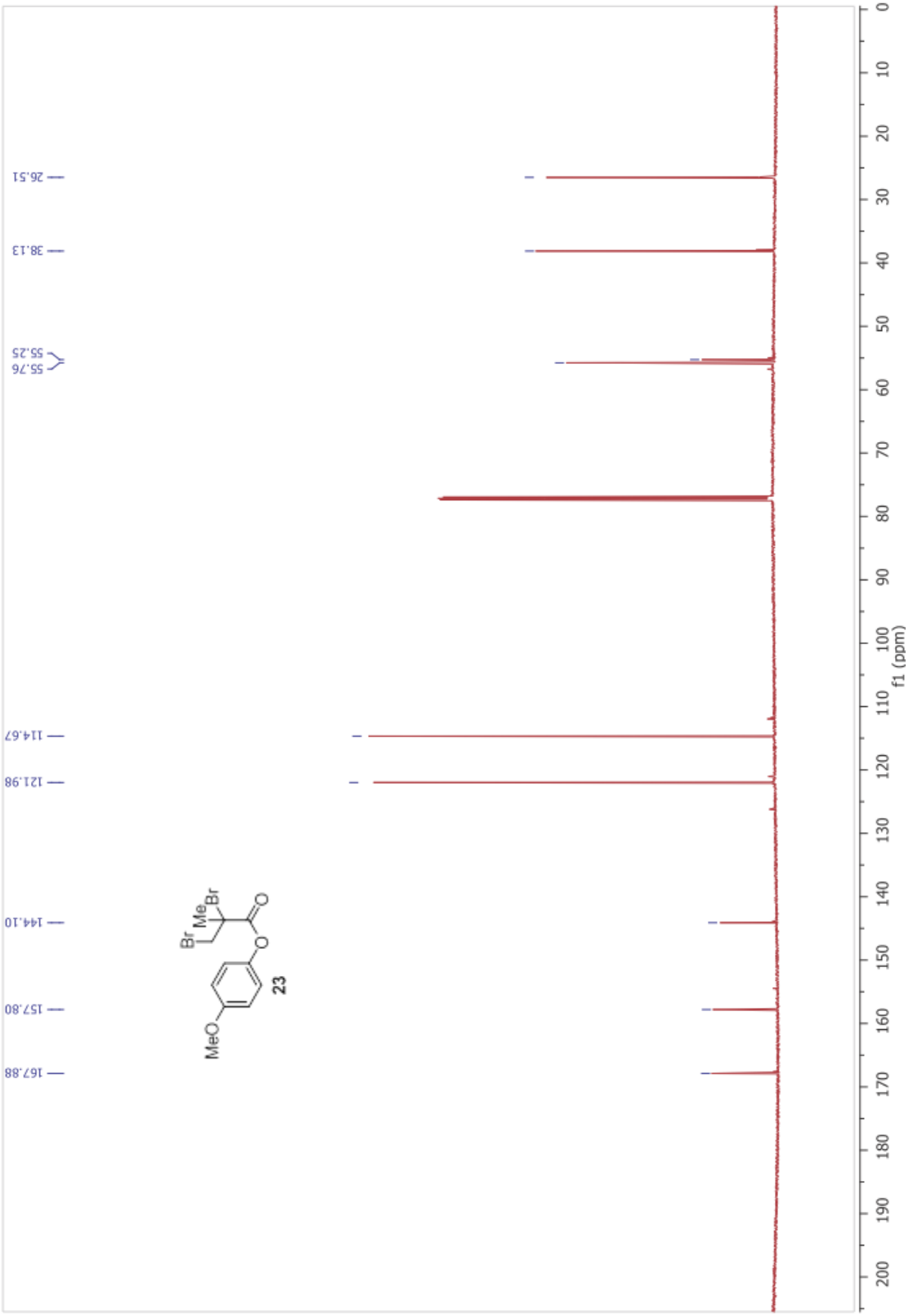
7.06
7.07
7.07
7.07
7.07
7.07
7.08
7.08
7.08
7.09
7.09
7.09
Br
Me
Br
O
O
MeO
23
f1 (ppm)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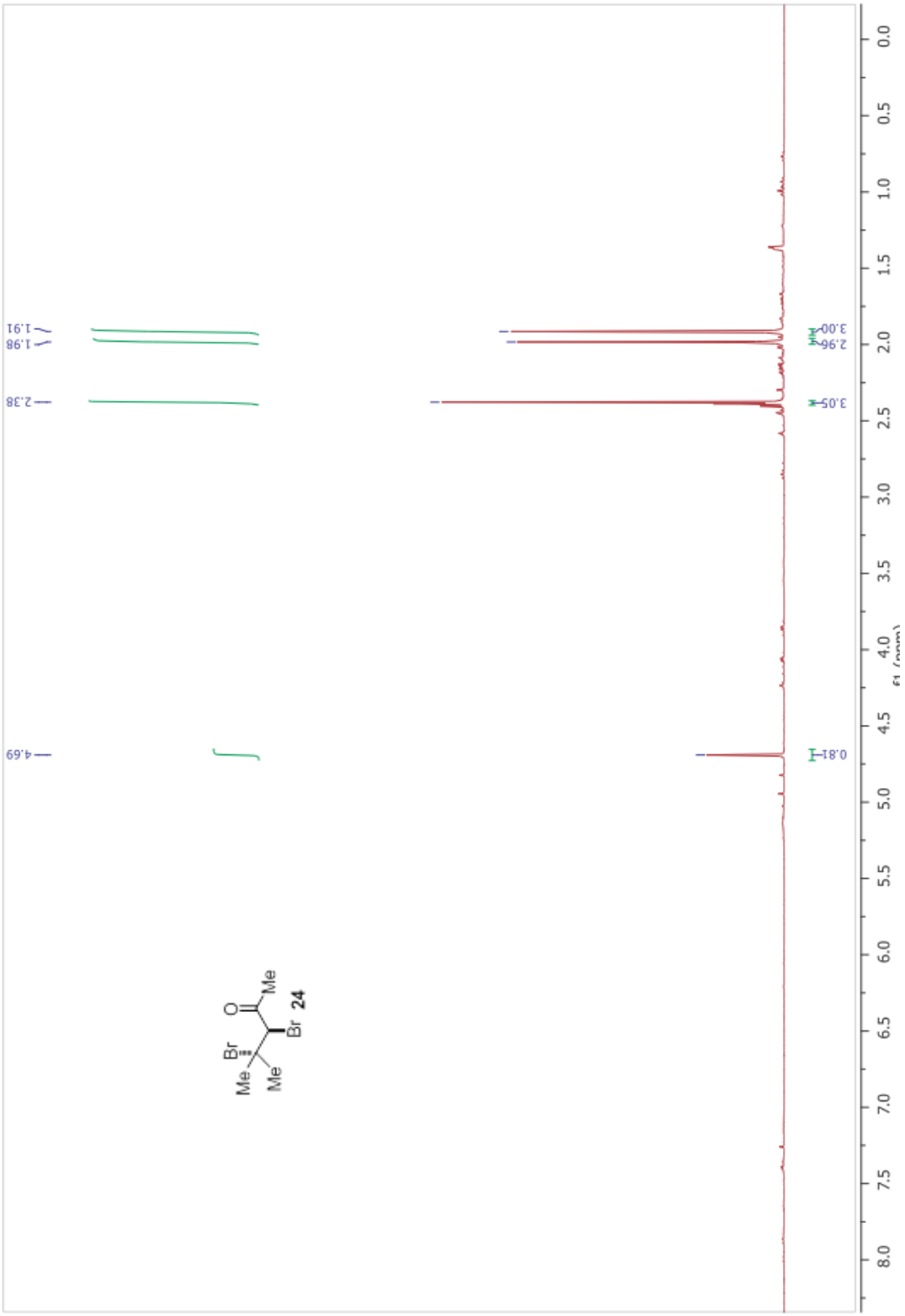
Me
Br
O
O
MeO
23
f1 (ppm)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2.96
3.00
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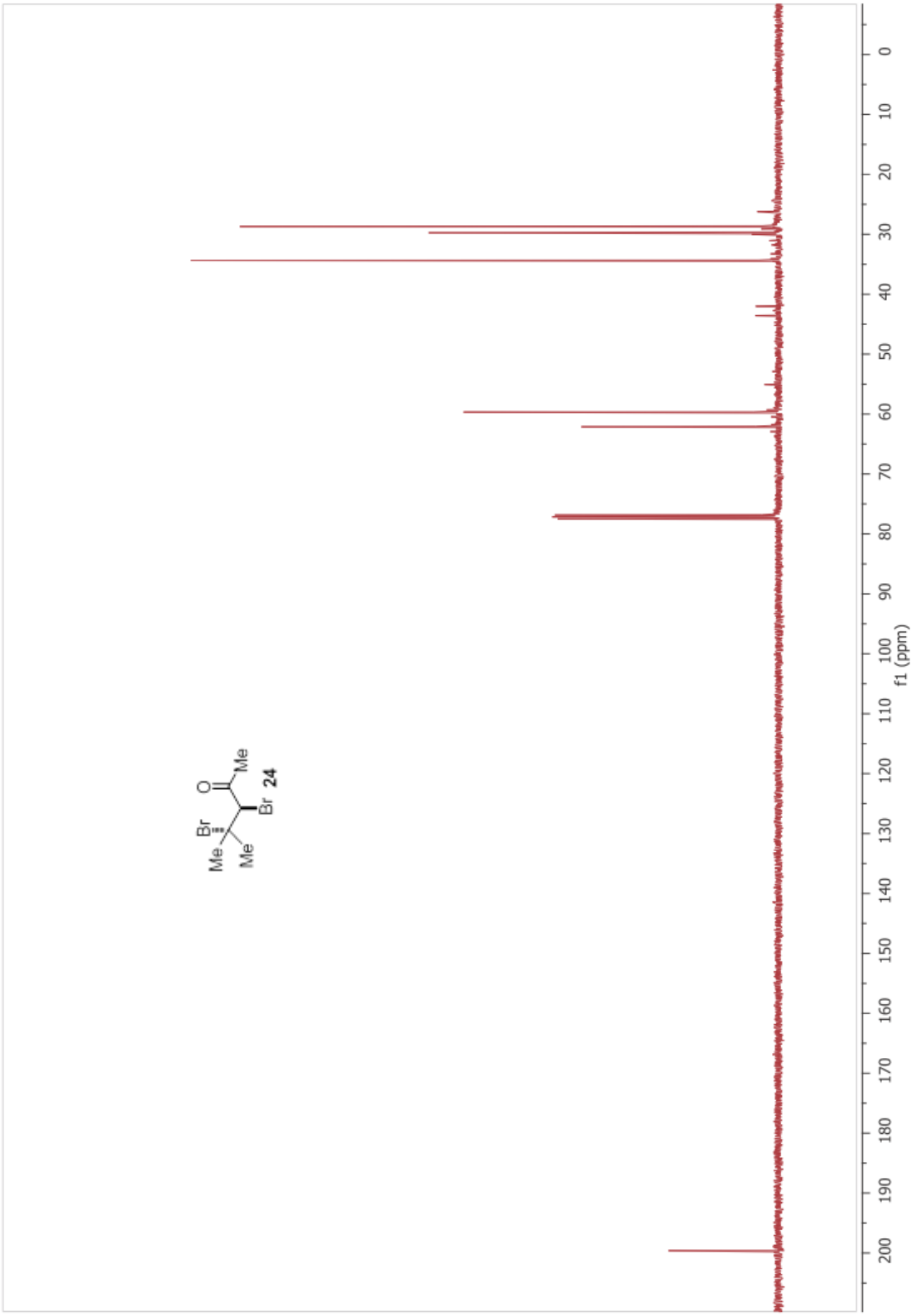
O
Br
Me
Me
Br
24
f1 (ppm)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O
Me
Me
Br
Me
24
0
10
20
30
40
50
60
70
80
90
100
110
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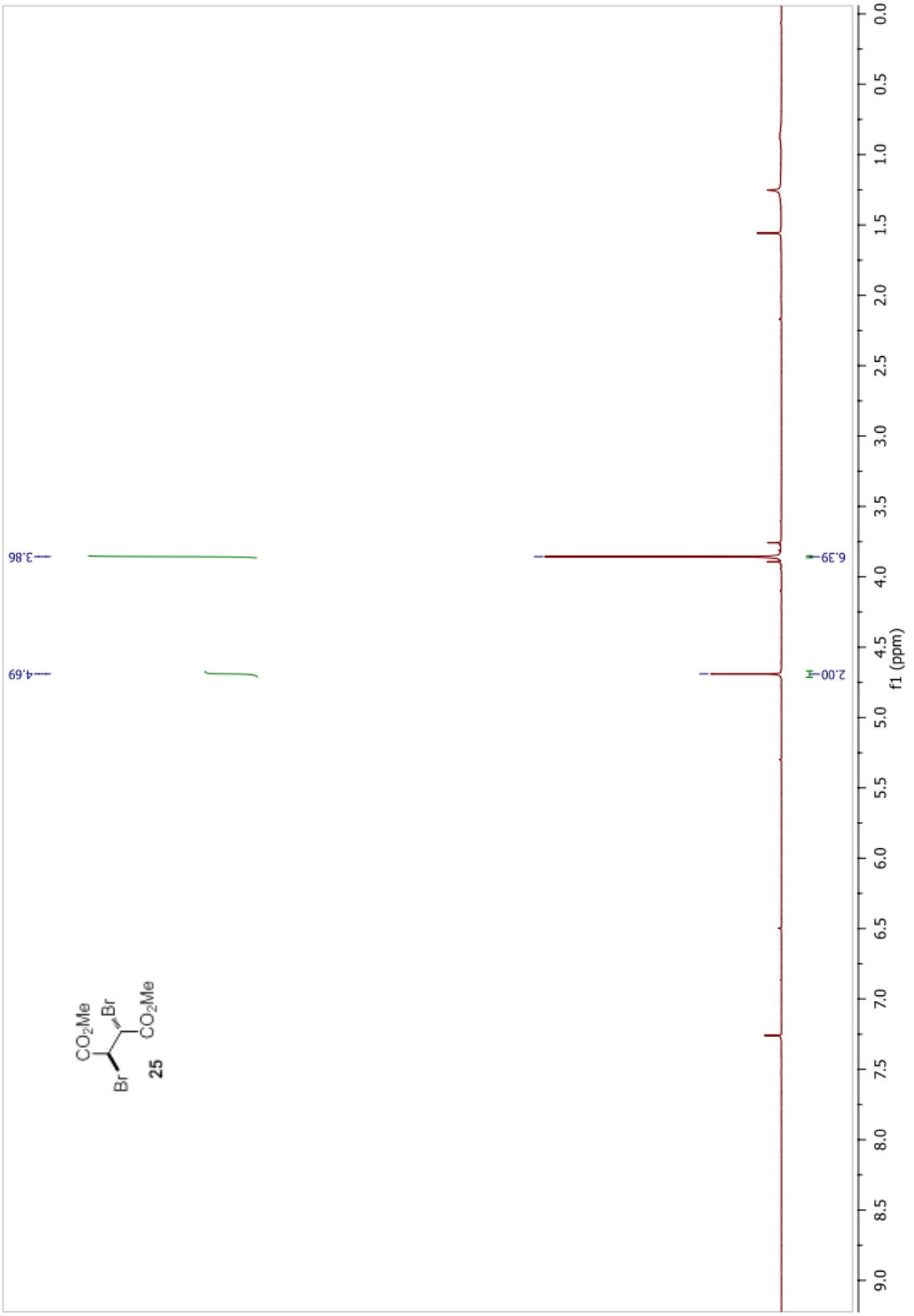
140
150
160
170
180
190
200
f1 (ppm)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f1 (ppm)
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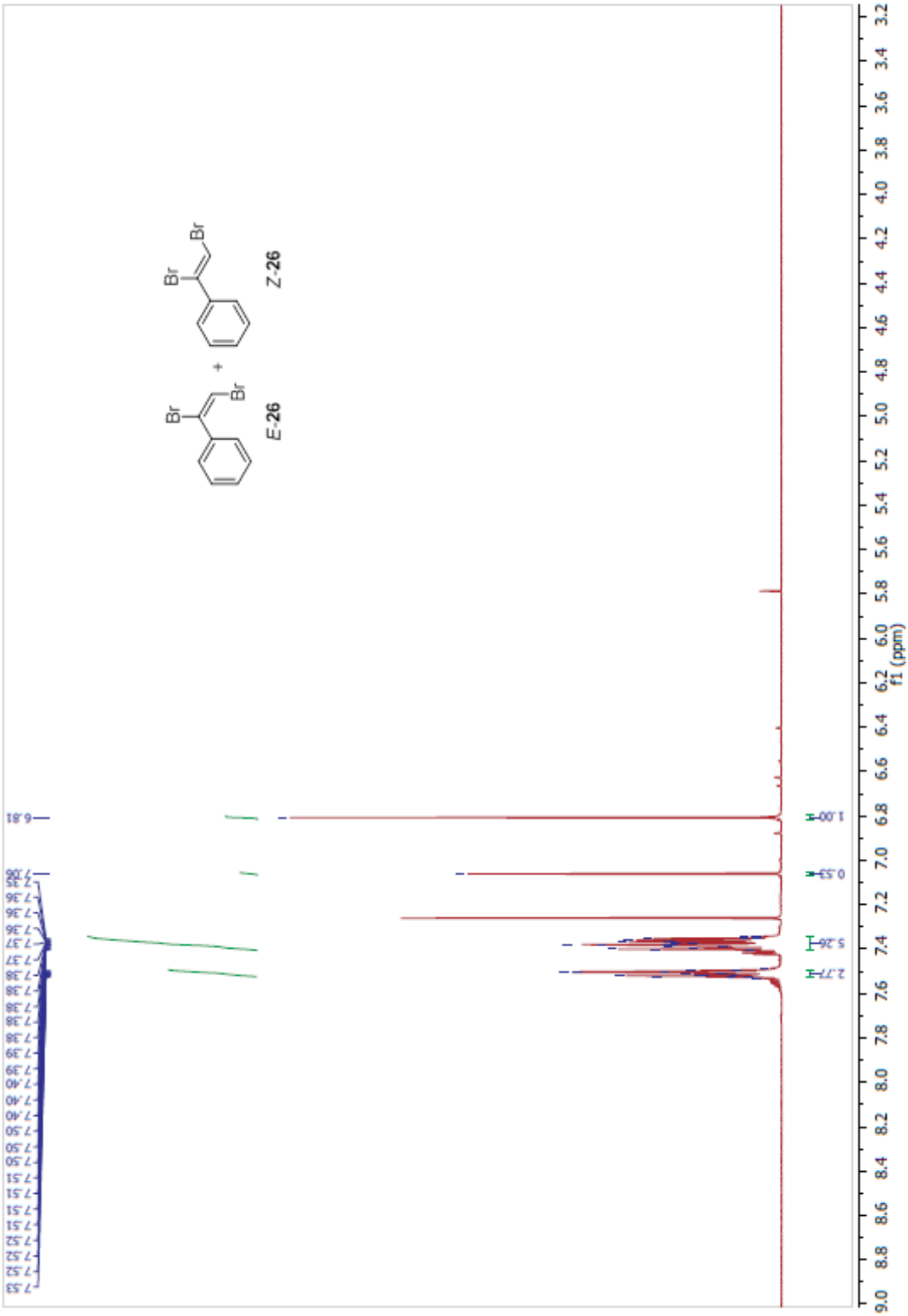
Br
CO2Me
Br
25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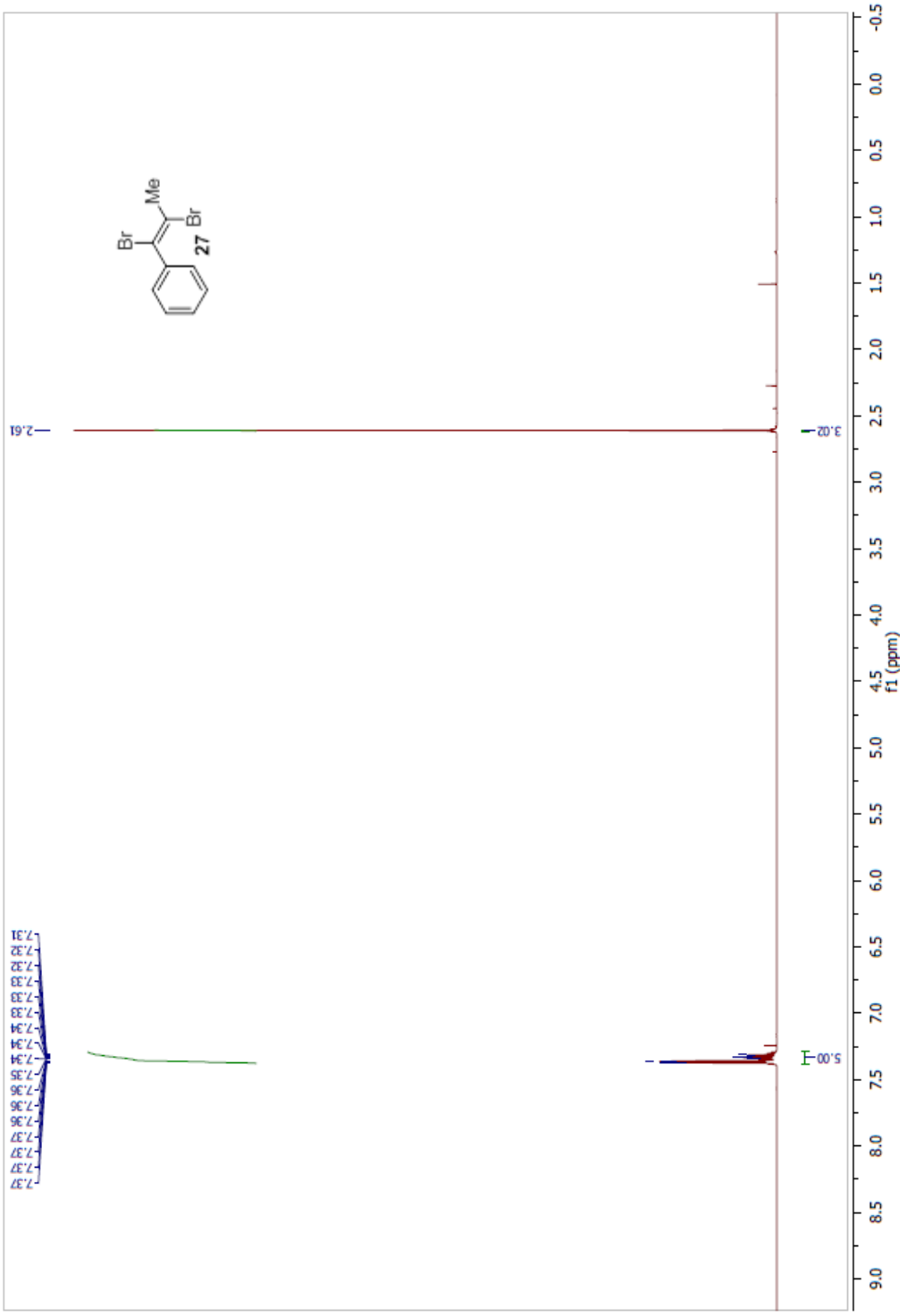
Br
Z-26
+
Br
Br
E-26
f1 (ppm)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Br
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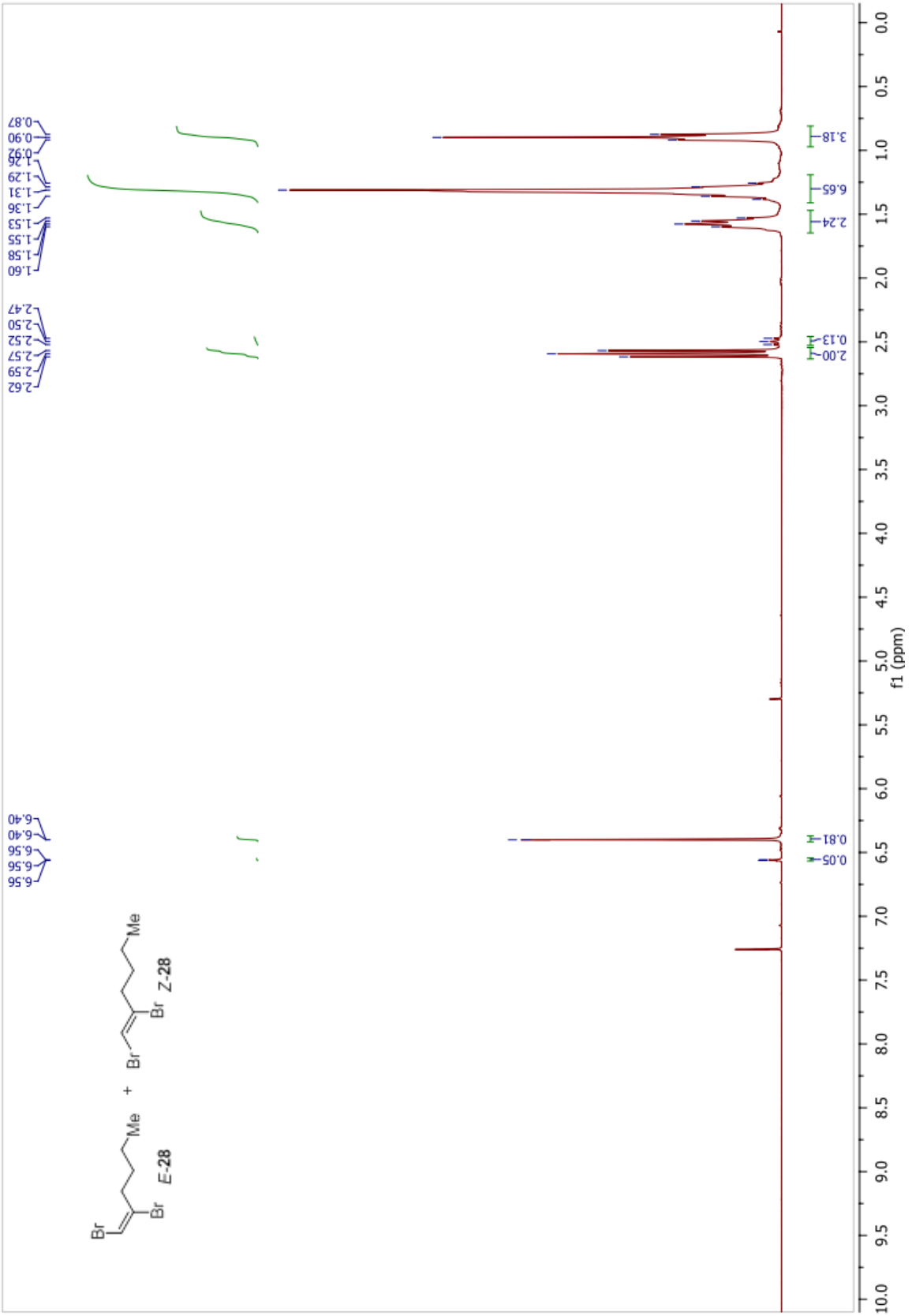
7.32
7.33
7.33
7.33
7.34
7.34
7.34
7.35
7.36
7.36
7.36
7.37
7.37
7.37
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)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2.57
2.52
2.50
2.47
1.60
1.58
1.55
1.53
1.36
1.31
1.29
1.26
0.92
0.90
0.87
0.81
0.05
2.00
0.13
2.24
6.65
3.18
f1 (ppm)
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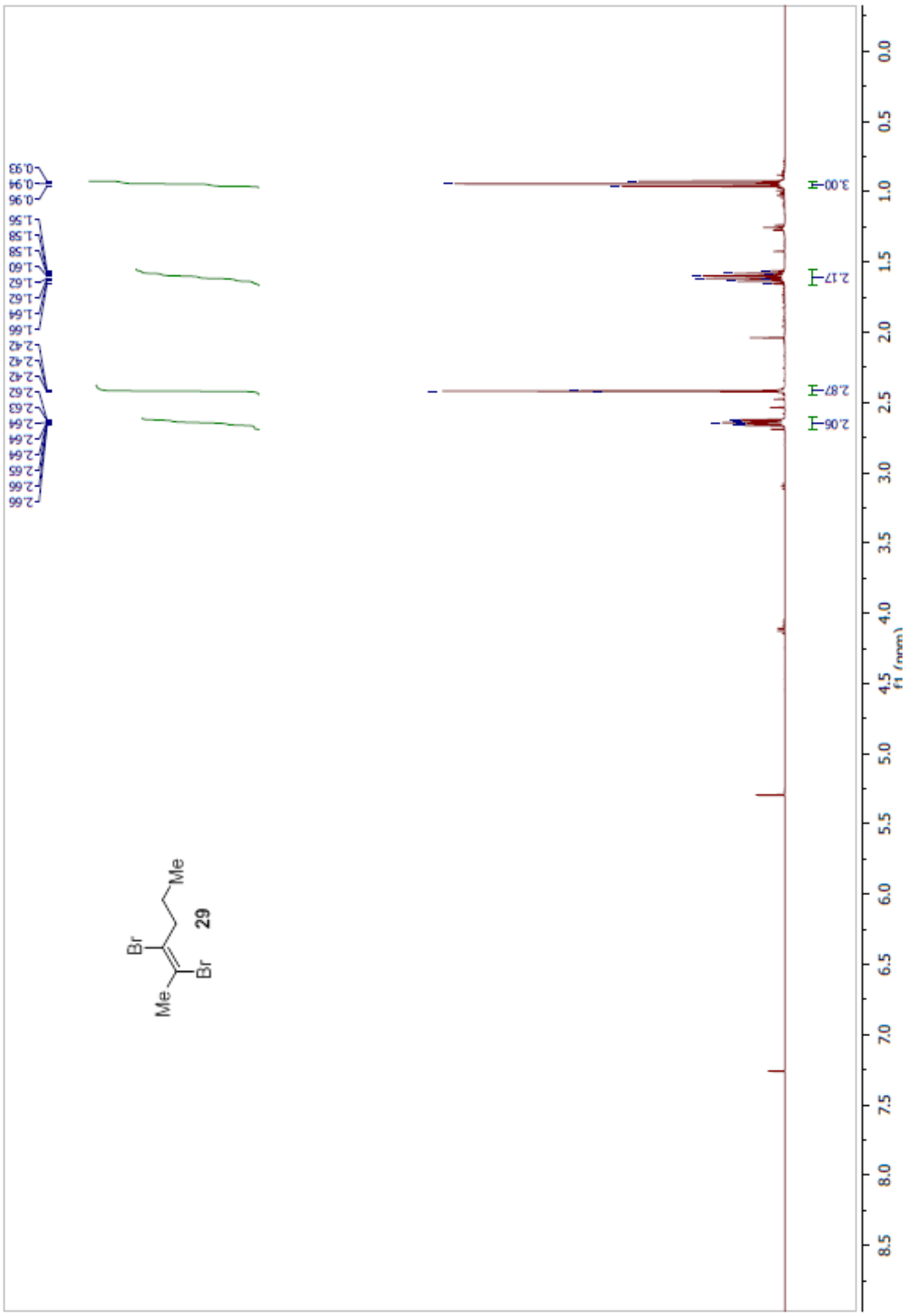
Me
Br
E-28
+
Br
Br
Me
Z-28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1.60
1.62
1.62
1.64
1.66
2.42
2.42
2.42
2.62
2.63
2.64
2.64
2.64
2.65
2.66
2.66
3.00
2.17
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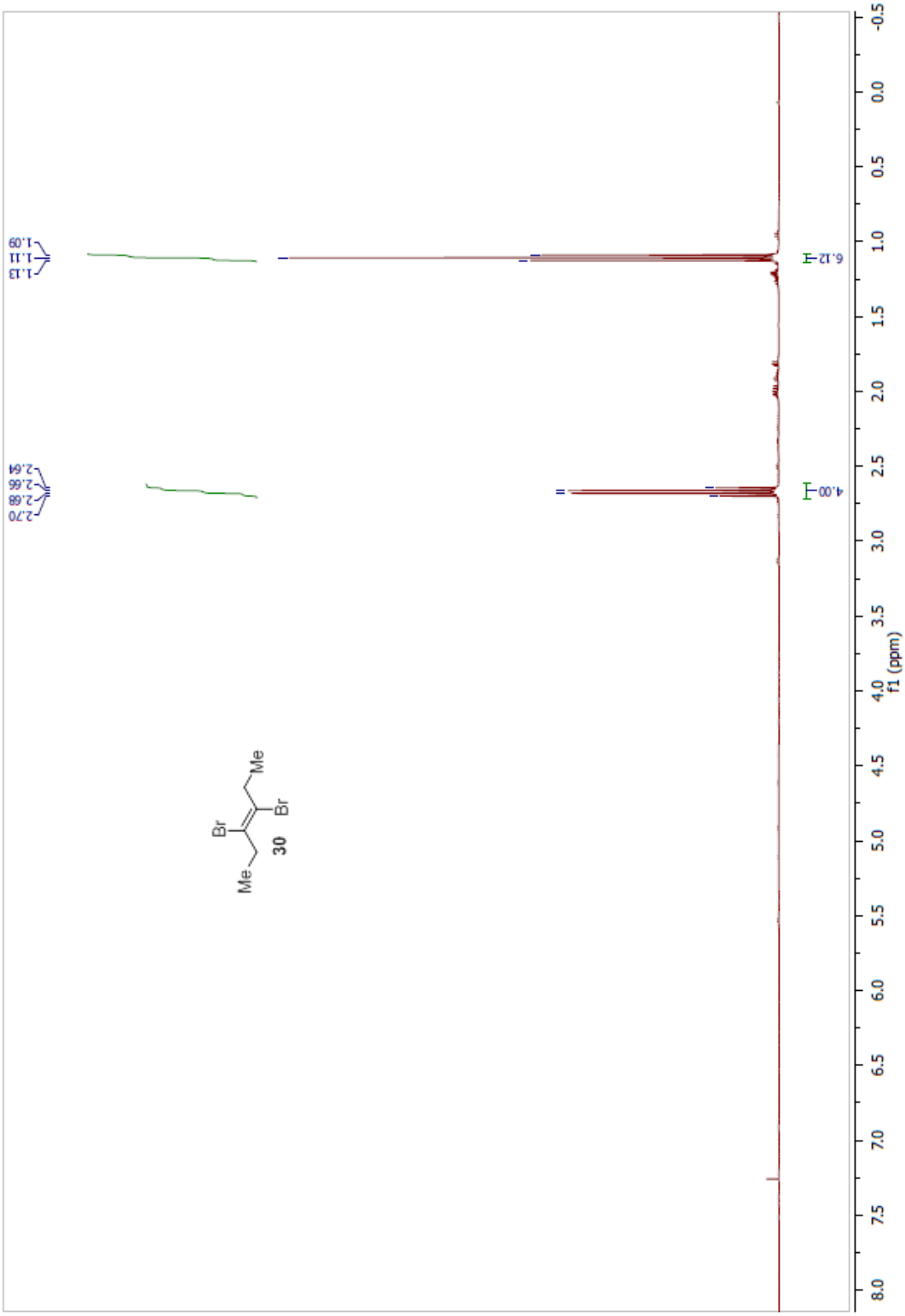
2.06
Me
Br
Br
Me
29
f1 (ppm)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1.13
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2.70
6.12
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Me
Br
Br
Me
30
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
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4.5
5.0
5.5
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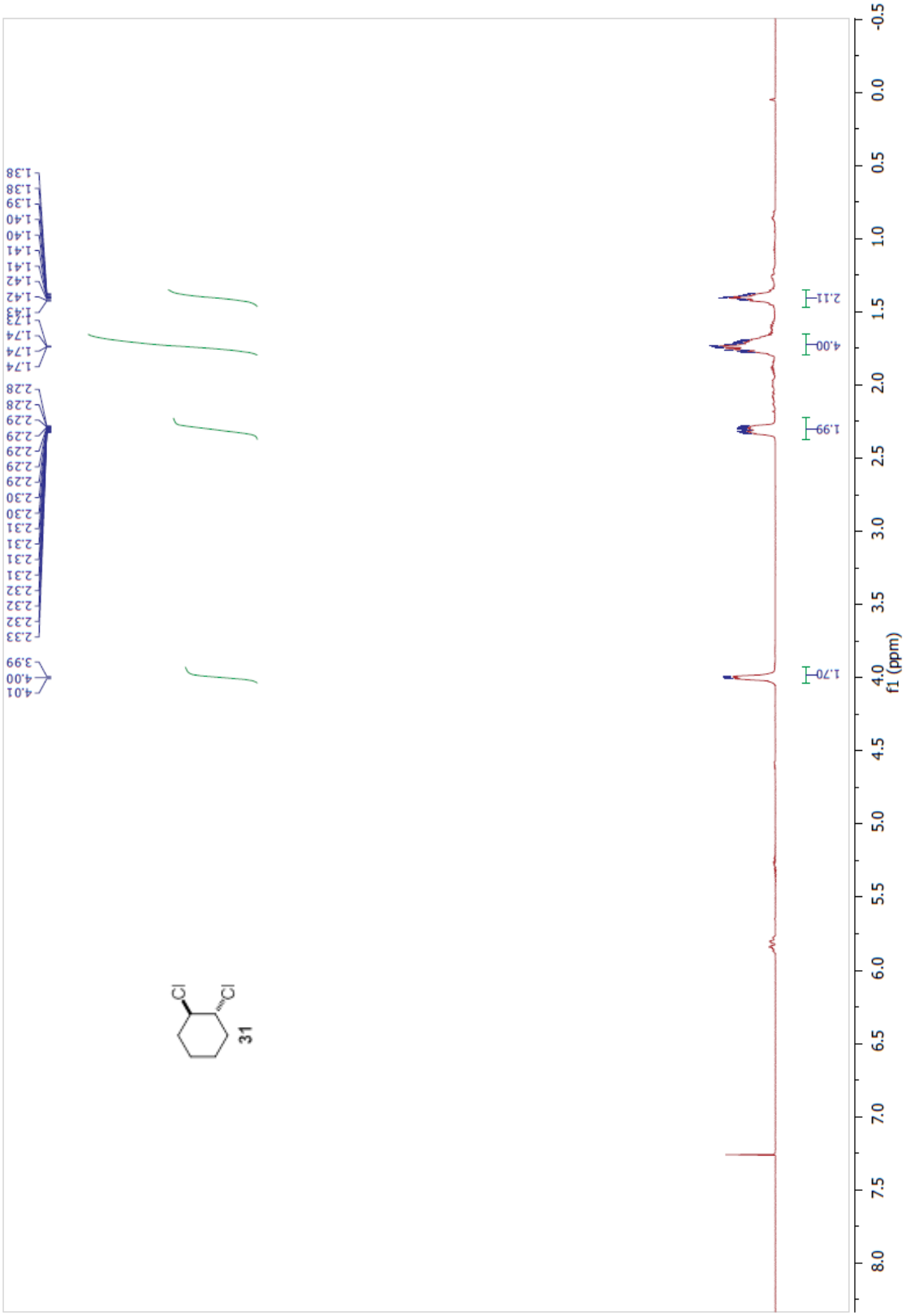
6.5
7.0
7.5
8.0
f1 (ppm)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Cl
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1.38
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1.39
1.40
1.40
1.41
1.41
1.42
1.42
1.43
1.73
1.74
1.74
2.28
2.28
2.29
2.29
2.29
2.29
2.30
2.30
2.31
2.31
2.31
2.31
2.32
2.32
2.32
2.33
3.99
4.00
4.01
2.11
4.00
1.99
1.70
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0.0
0.5
1.0
1.5
2.0
2.5
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3.5
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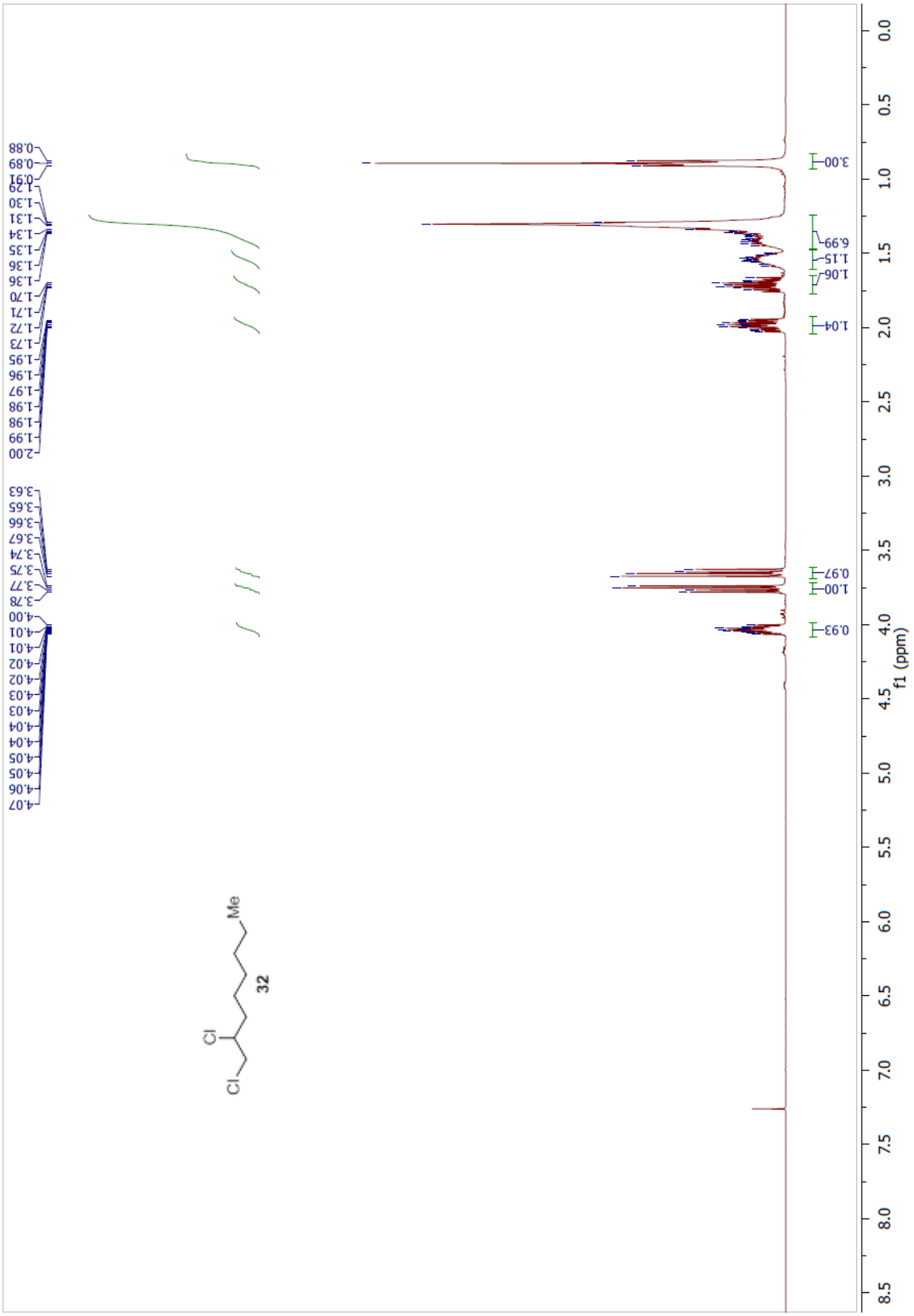
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)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32
Cl
Cl
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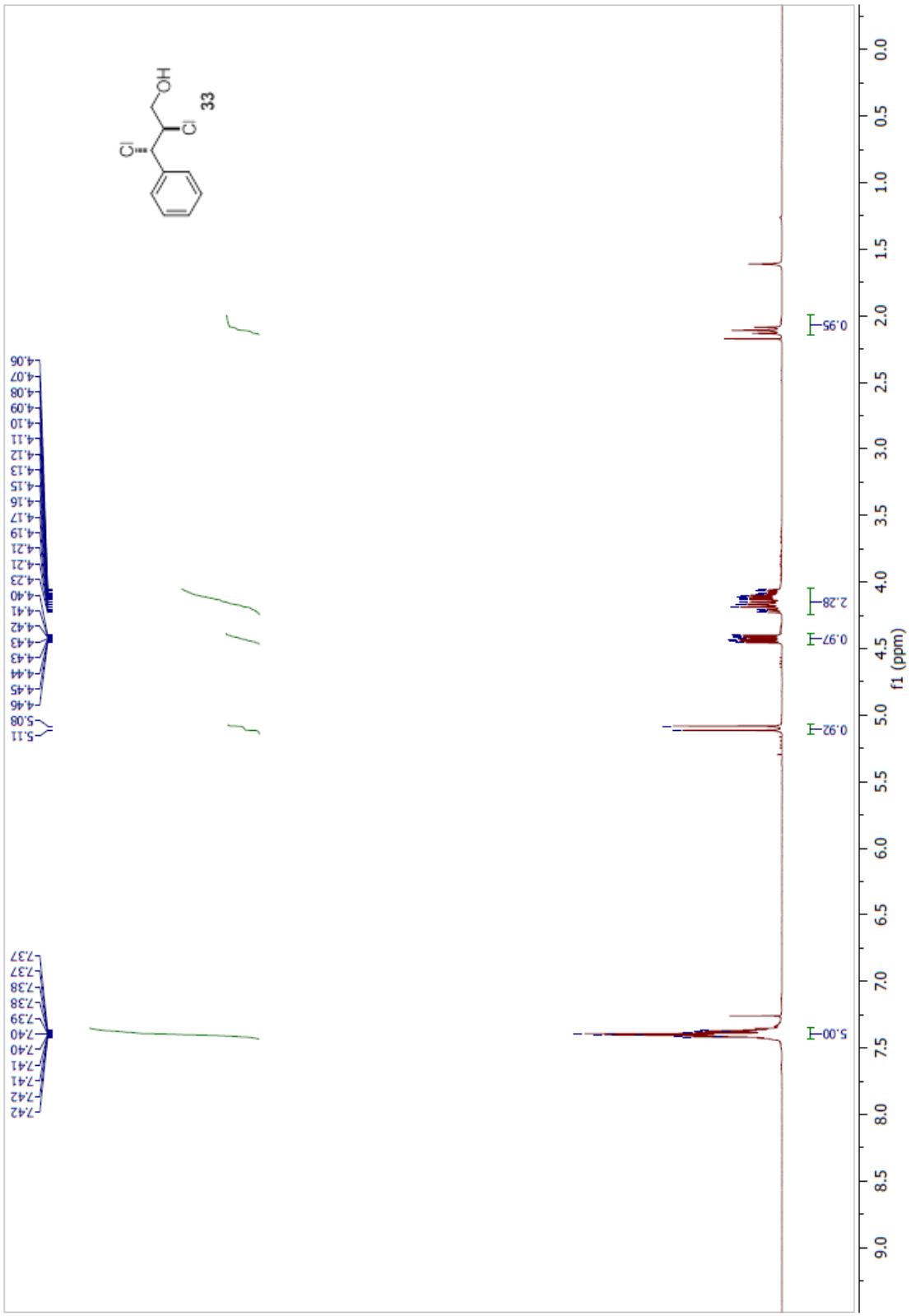
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Cl
Cl
33
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7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
5.11
5.08
4.46
4.45
4.44
4.43
4.42
4.41
4.40
4.23
4.21
4.21
4.19
4.17
4.16
4.15
4.13
4.12
4.11
4.10
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4.08
4.07
4.06
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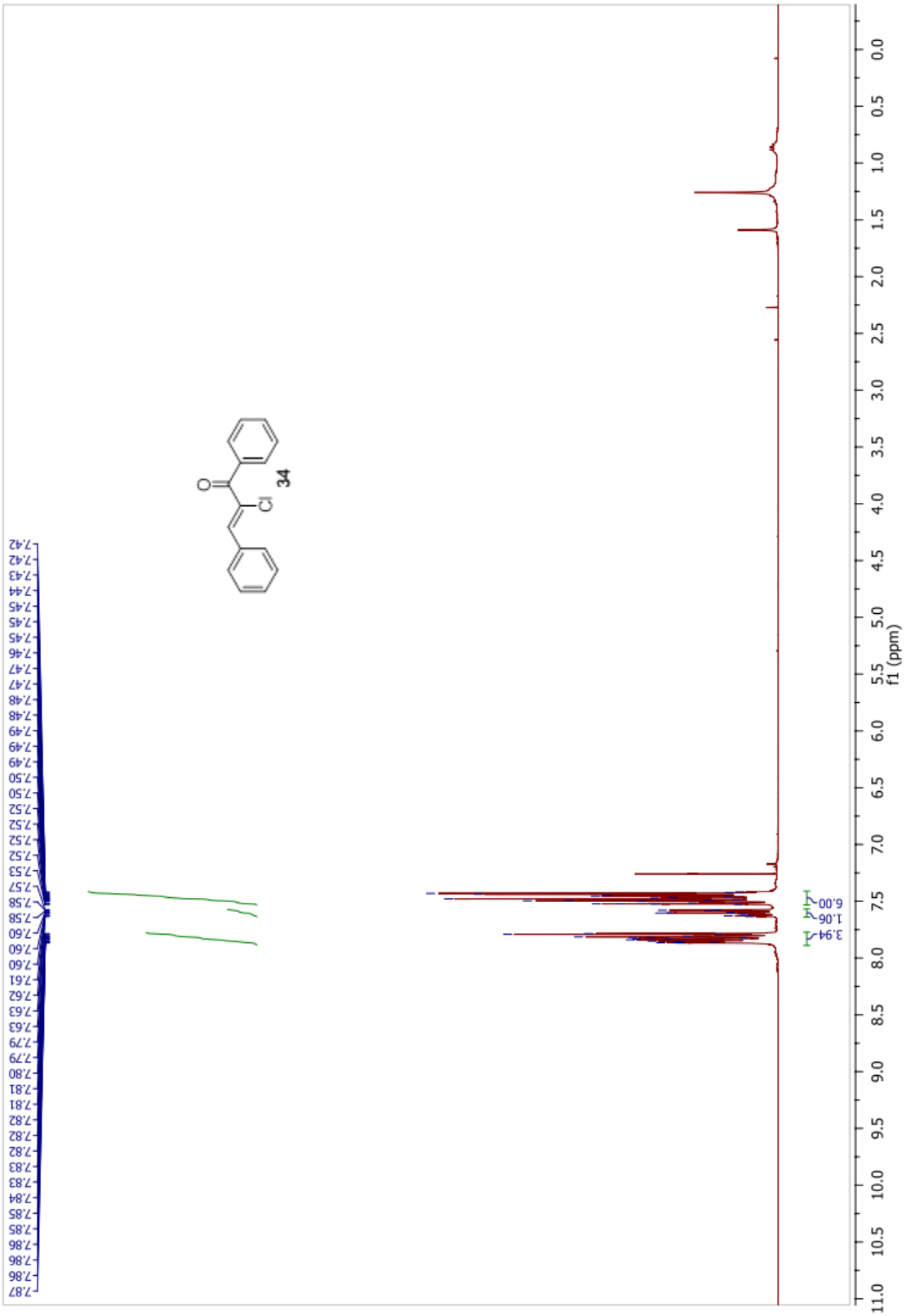
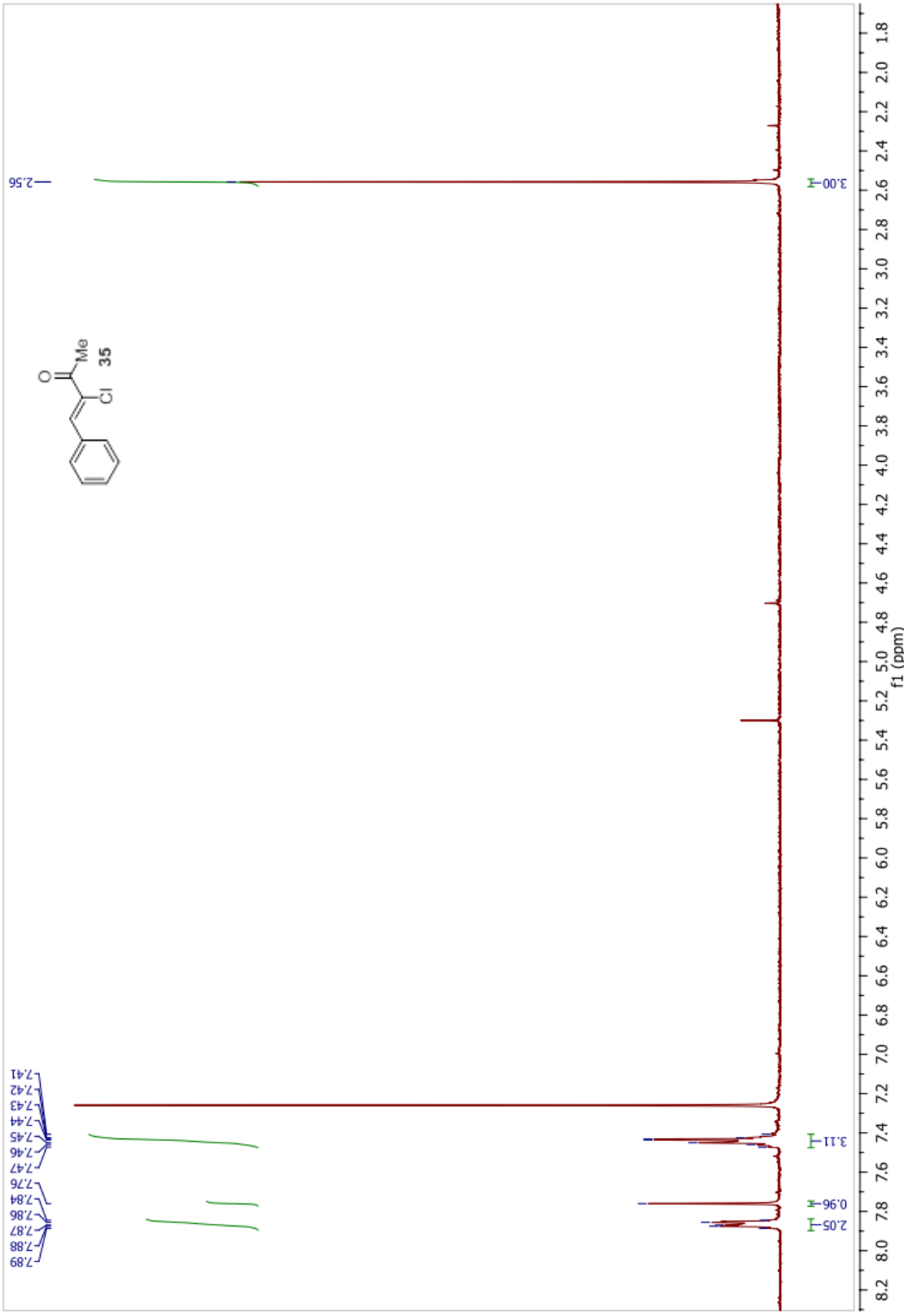
2.28
0.95
f1 (ppm)


34
Cl
O
f1 (ppm)
6.00
1.06
3.94


2.56
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2.05
7.41
7.42
7.43
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7.45
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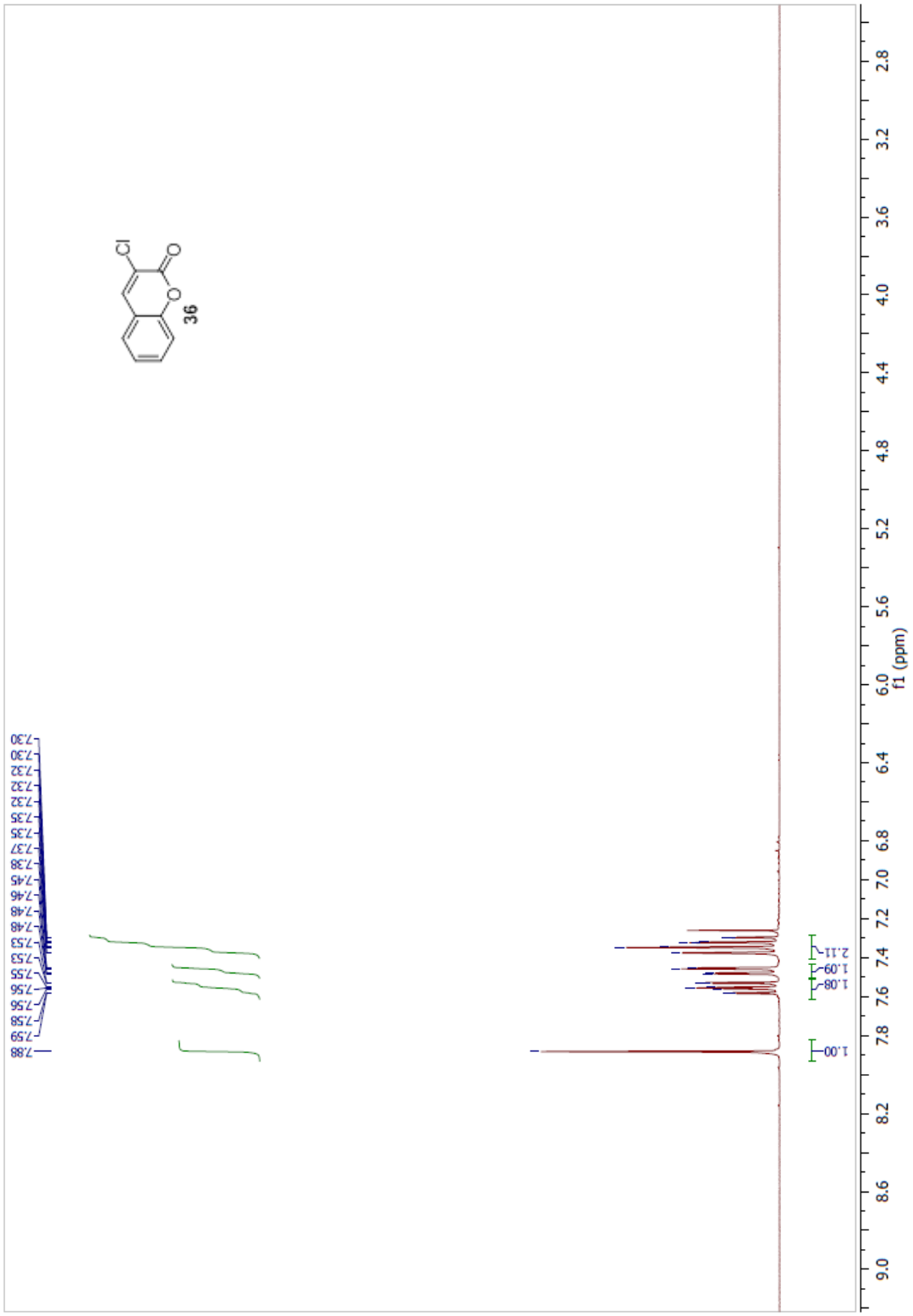
7.76
7.84
7.86
7.87
7.88
7.89
O
Me
Cl
35
f1 (ppm)


Cl
O
O
36
7.88
7.59
7.58
7.56
7.56
7.55
7.53
7.53
7.48
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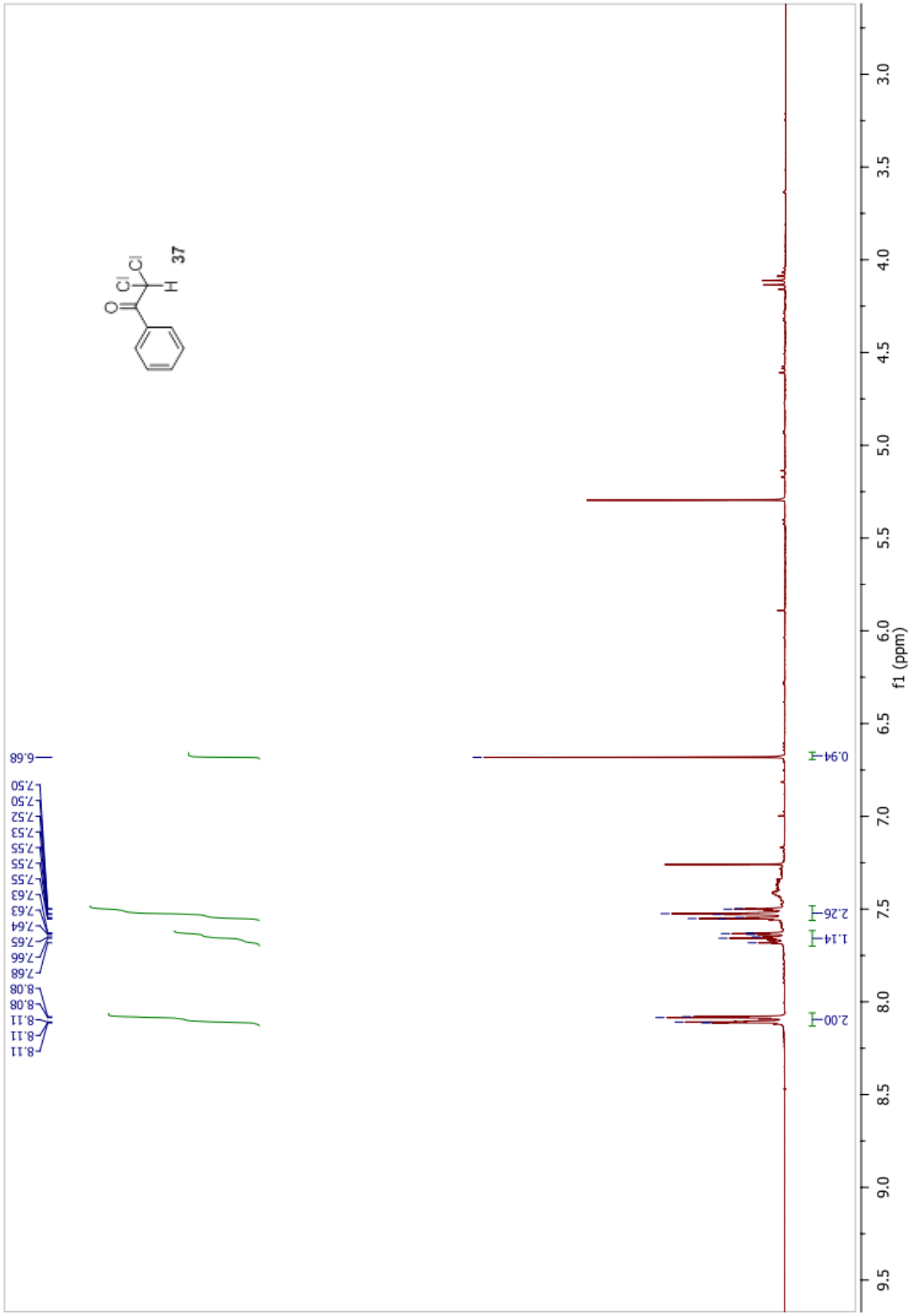
7.46
7.45
7.38
7.37
7.35
7.32
7.32
7.30
7.30
1.00
2.11
1.09
1.08
9.0
8.6
8.2
7.8
7.6
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
f1 (ppm)


37
Cl
Cl
O
H
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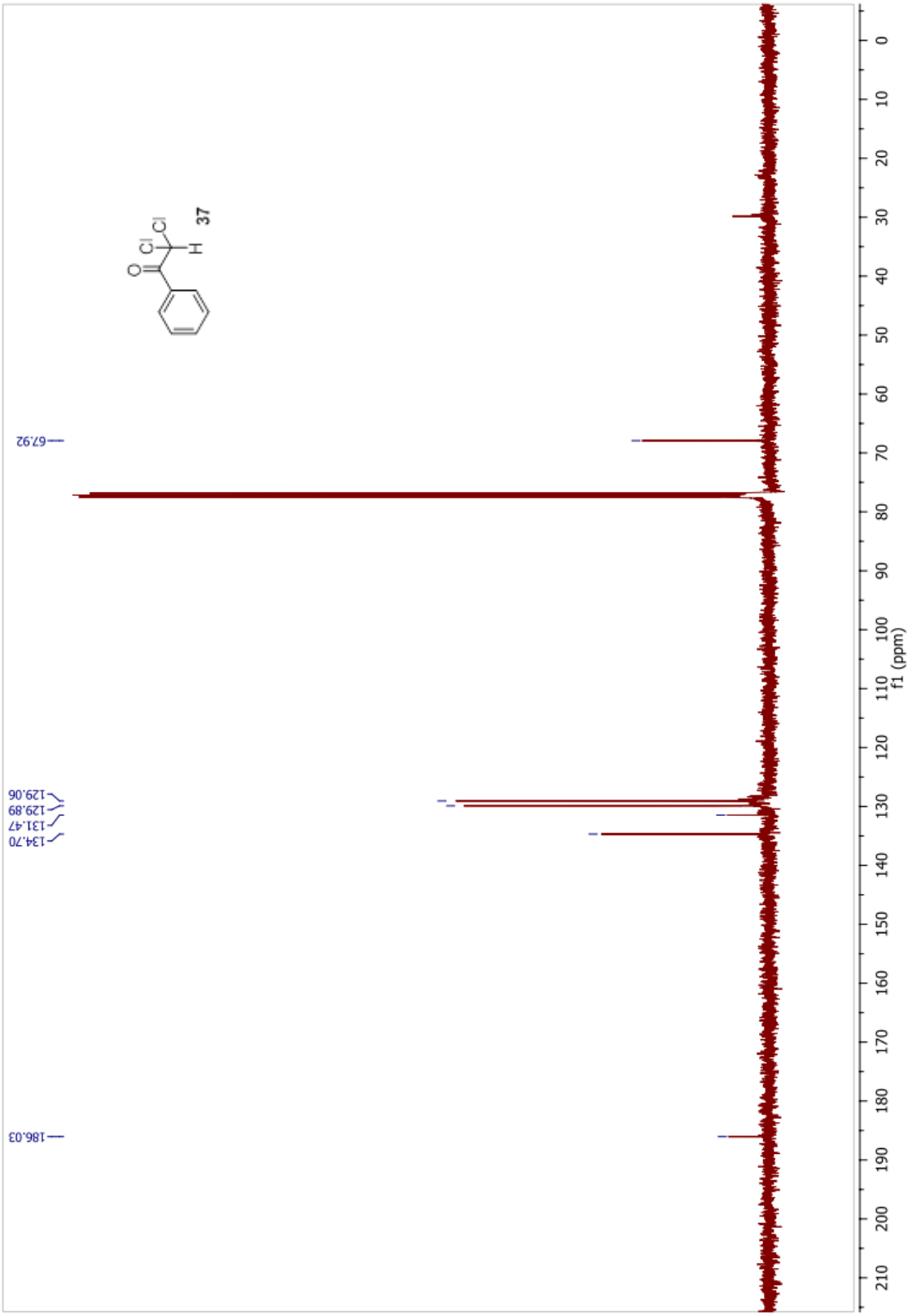
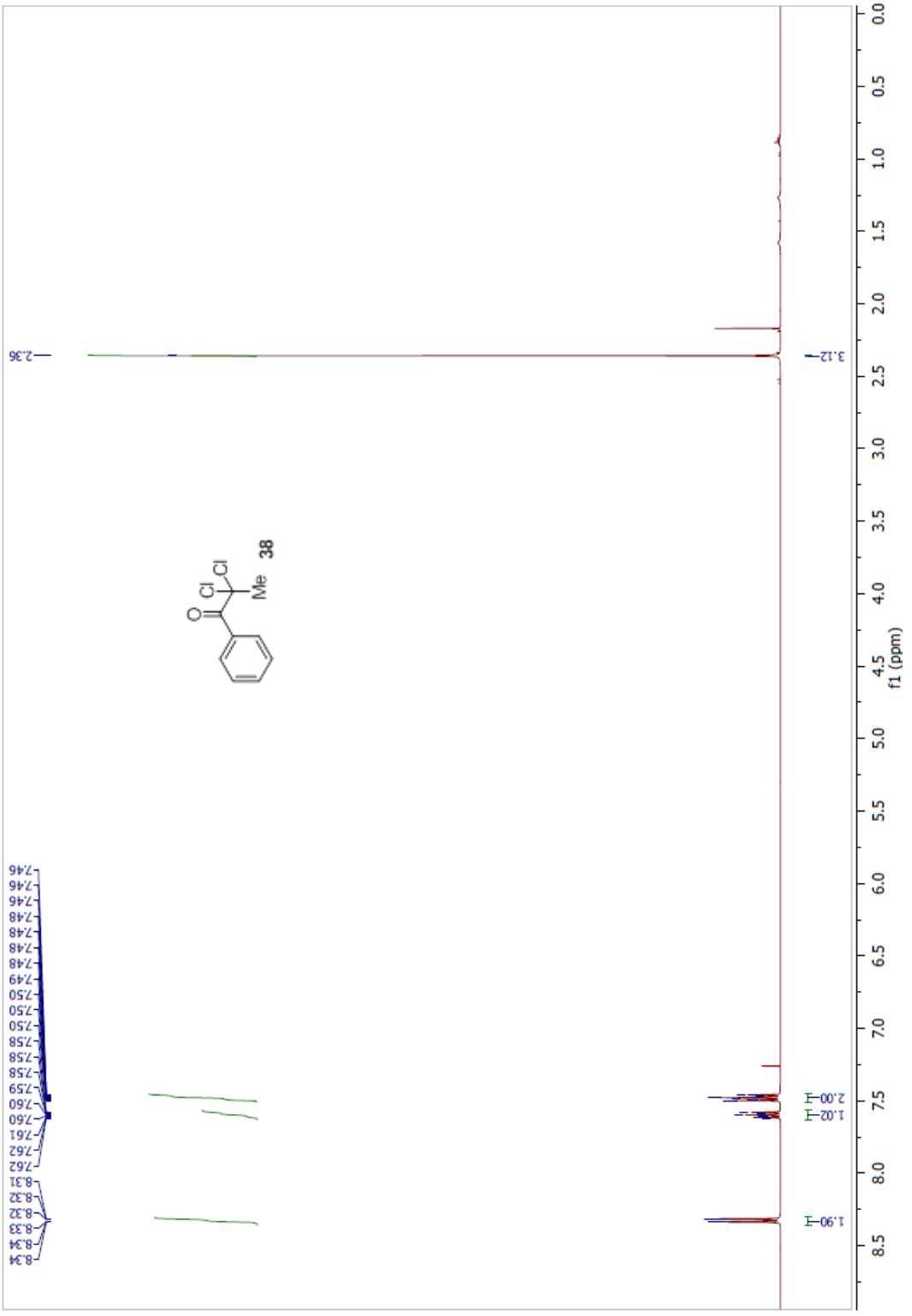
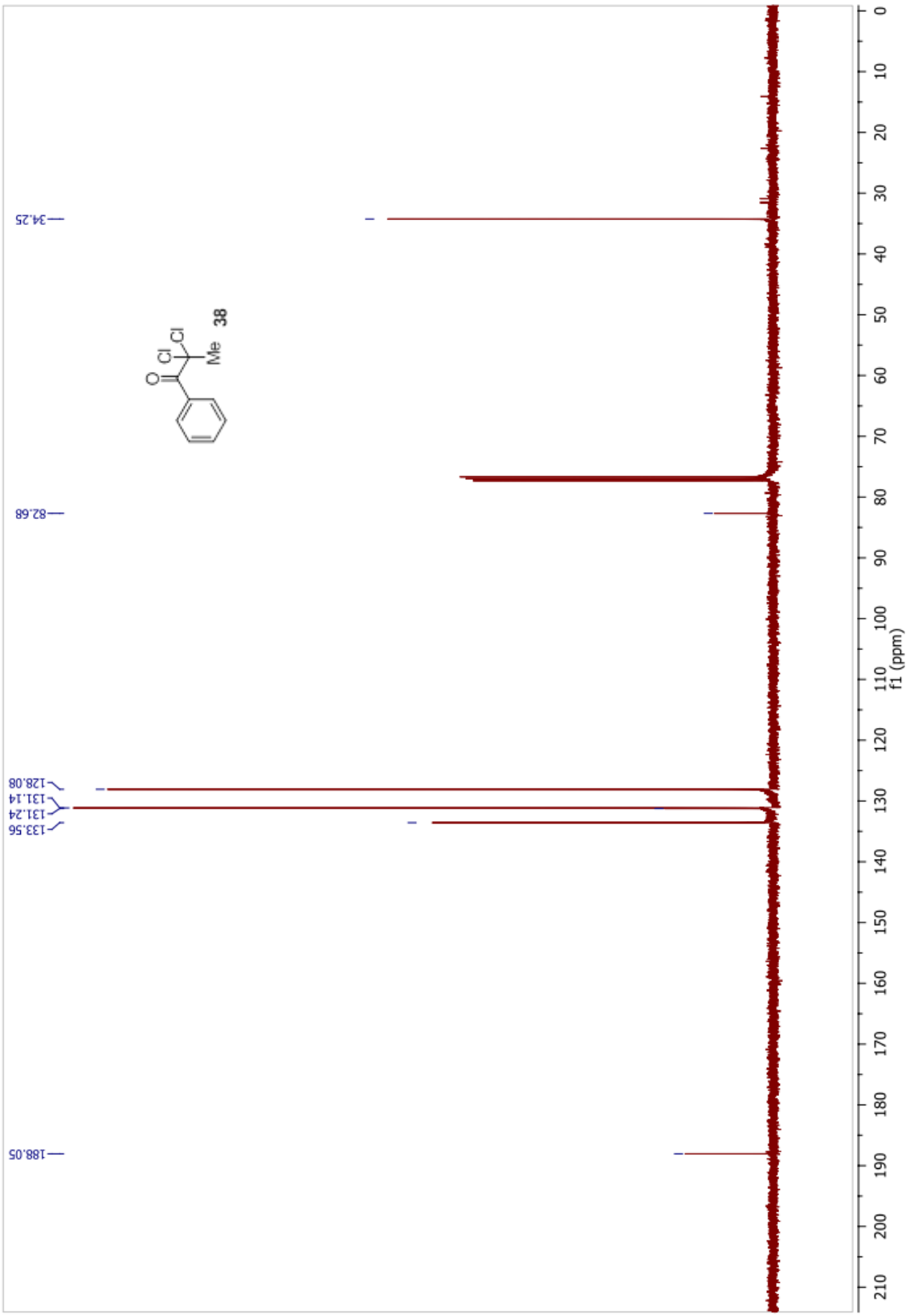
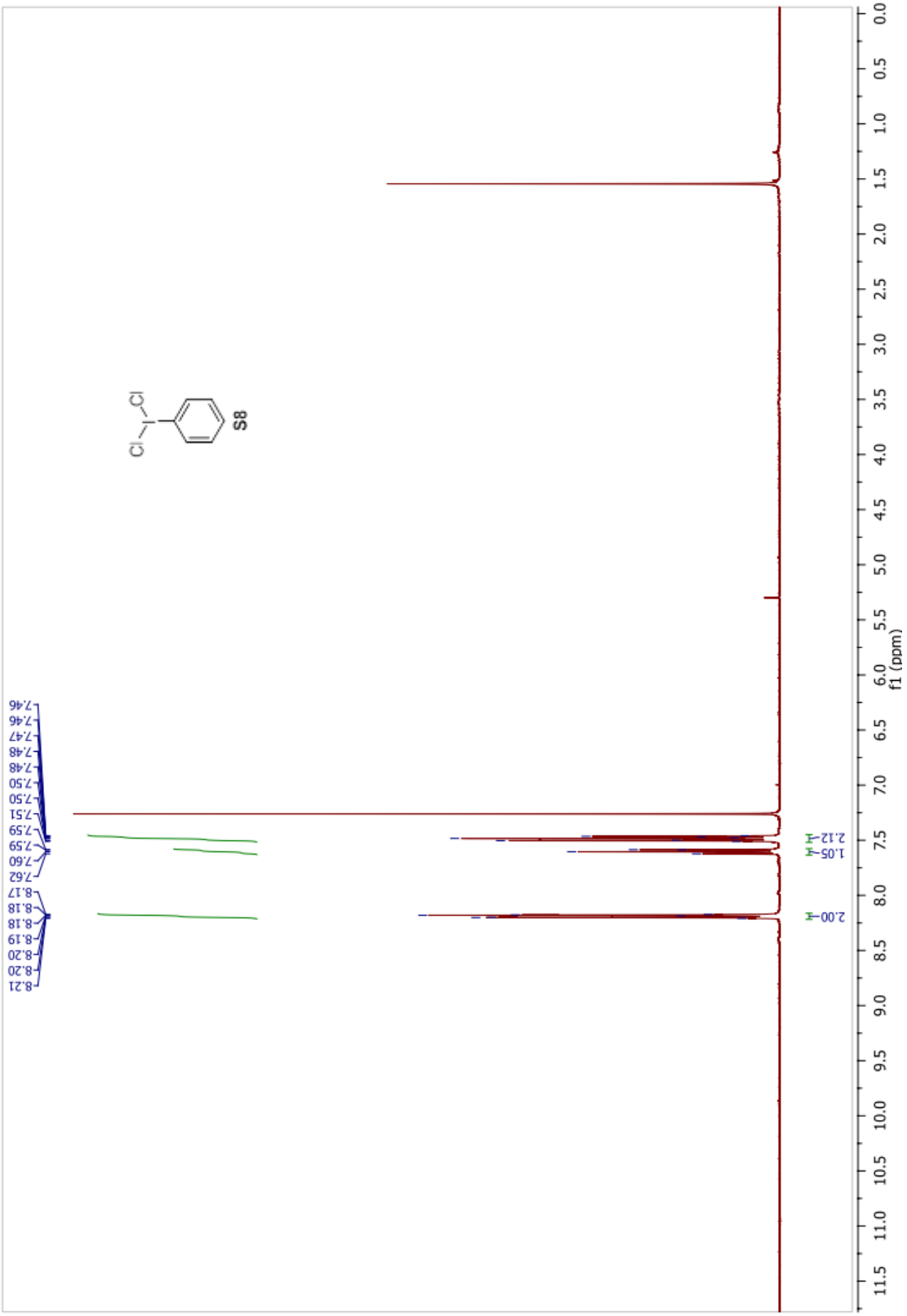
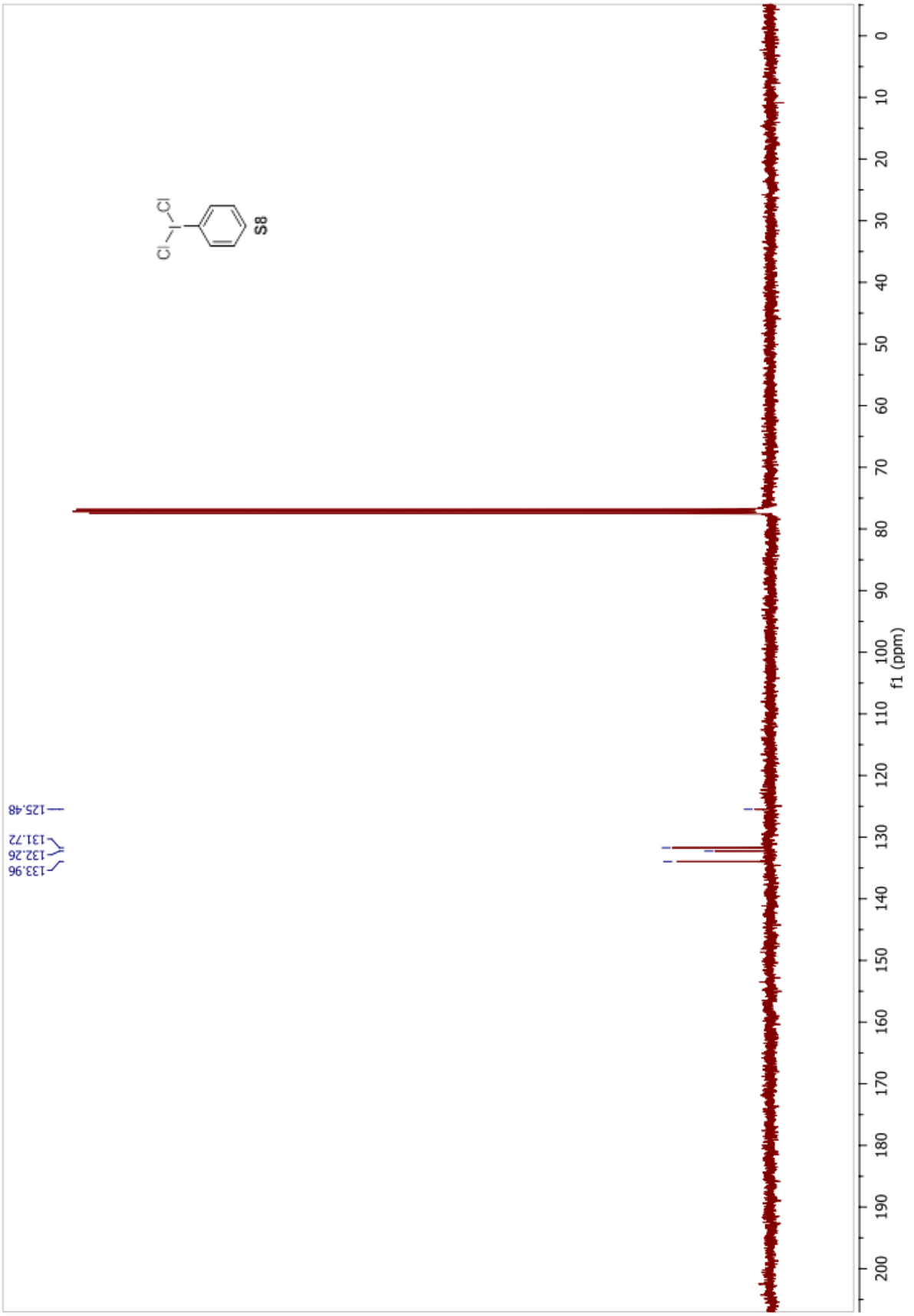
7.50
7.50
7.52
7.53
7.55
7.55
7.55
7.63
7.63
7.64
7.65
7.66
7.68
8.08
8.08
8.11
8.11
8.11
0.94
2.26
1.14
2.00
f1 (ppm)


37
Cl
Cl
O
H
186.03
134.70
131.47
129.89
129.06
67.92
f1 (ppm)


38
Cl
Cl
Me
O
2.36
3.12
2.00
1.02
1.90
f1 (ppm)


38
Cl
Cl
Me
O
34.25
82.68
128.08
131.14
131.24
133.56
188.05
f1 (ppm)


S8
Cl
I
Cl
8.21
8.20
8.20
8.19
8.18
8.18
8.17
7.62
7.60
7.59
7.59
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.46
2.12
1.05
2.00
f1 (ppm)


S8
Cl
Cl
125.48
131.72
132.26
133.96
f1 (ppm)