

**Stoichiometric Reactions of Acylnickel(II) Complexes with
Electrophiles and the Catalytic Synthesis of Ketones**

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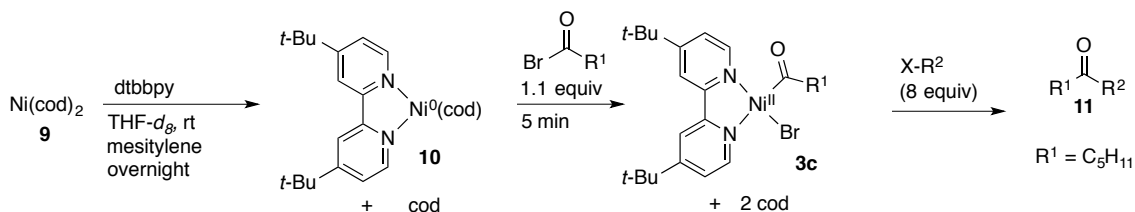
Supporting Information

Table of Contents

I.	Supplementary Tables and Figure	S3
	Table S1 – Full product distribution for Table 2	S3
	Table S2 – Full product distribution for Table 3	S4
	Pictures of the the reaction of 1c with electrophiles	S5
II.	Spectra	S7
	dtbbpy ¹ H NMR	S8
	Ni(cod) ₂ ¹ H NMR	S9
	Compound 3 ¹ H NMR	S10
	Compound 3 ¹ H paramagnetic NMR	S11
	Compound 1b ¹ H NMR	S12
	Compound 1b ¹ H paramagnetic NMR	S13
	Compound 1c ¹ H NMR	S14
	Compound 1c ¹ H paramagnetic NMR	S15
	Compound 22 ¹ H NMR	S16
	Compound 22 ¹³ C NMR	S17
	Compound 23 ¹ H NMR	S18
	Compound 23 ¹³ C NMR	S19
	Compound 24 ¹ H NMR	S20
	Compound 24 ¹³ C NMR	S21
	Compound 25 ¹ H NMR	S22
	Compound 25 ¹³ C NMR	S23
	Compound 25 ¹⁹ F NMR	S24
	Compound 26 ¹ H NMR	S25
	Compound 26 ¹³ C NMR	S26
	Compound 26 ¹⁹ F NMR	S27
	Compound 27 ¹ H NMR	S28
	Compound 27 ¹³ C NMR	S29

I. Supplementary Tables

Table S1. Full Data From Table 2.^a



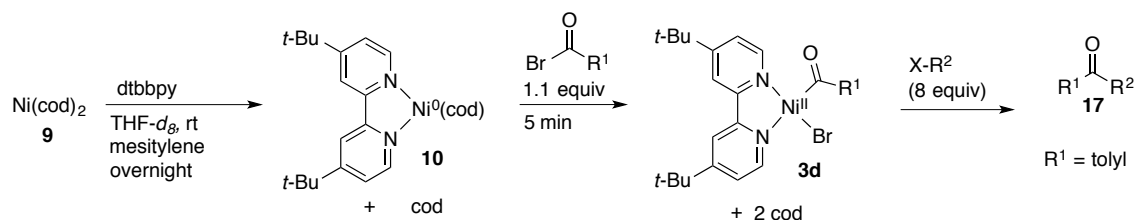
X-R ₂ time, temp	R ₁ -R ₂	R ₁ -C(=O)-R ₂	R ₁ -C(=O)-R ₂	R ₁ -R ₁	R ₁ -C(=O)-R ₁	R ₁ -C(=O)-R ₁	R ₂ -R ₂	R ₂ -C(=O)-R ₂	R ₂ -C(=O)-R ₂
 < 14 h, 60 °C)	ND	12	ND	ND	3	11	23	8	11
 < 5 mins, rt.	ND	54	ND	ND	1	3	15	ND	ND
Br- <i>n</i> -octyl < 14 h, 60 °C	ND	17	ND	ND	<1	4	ND	12	ND
I- <i>n</i> -octyl < 12 h, 60 °C	ND	33	ND	ND	3	2	0	18	ND

As above but with zinc flake (8.4 eq):

X-R ₂ time, temp	R ₁ -R ₂	R ₁ -C(=O)-R ₂	R ₁ -C(=O)-R ₂	R ₁ -R ₁	R ₁ -C(=O)-R ₁	R ₁ -C(=O)-R ₁	R ₂ -R ₂	R ₂ -C(=O)-R ₂	R ₂ -C(=O)-R ₂
 < 12 h, 60 °C)	ND	22	ND	ND	3	ND	461	13	ND
 5 mins, rt.	ND	44	ND	ND	<1	<1	613	ND	ND
Br- <i>n</i> -octyl < 14 h, 60 °C	ND	31	ND	ND	3	2	165	20	ND

^a R¹ = C₅H₁₁. ND = not detected by GC analysis. In all cases, yields are calculated vs. amount of Ni(cod)₂ added in the first step. Yields are *uncorrected* GC yields vs. mesitylene internal standard, so >100% total yield for all products could be observed. For reactions with added reductant, >100% yields are possible because the nickel can turnover.

Table S2. Full Data From Table 3.



X-R ₂ time, temp	R ₁ -R ₂		R ₁ -C(=O)-R ₂		R ₁ -C(=O)-C(=O)-R ₂		R ₁ -R ₁		R ₁ -C(=O)-R ₁		R ₁ -C(=O)-C(=O)-R ₁		R ₂ -R ₂		R ₂ -C(=O)-R ₂		R ₂ -C(=O)-C(=O)-R ₂		R ¹ -H	
	Ph-Br < 12 h, 60 °C)	3	25	4	1	23	8	5	21	ND	1									
Ph-Cl < 12 h, 60 °C)	ND	94	ND	ND	5	2	21	ND	ND	7										
I-n-octyl 1h, rt.	ND	60	ND	3	5	<1	ND	8	ND	2										

With Zinc -325 mesh flake 20 mg, 8.4 mmol:

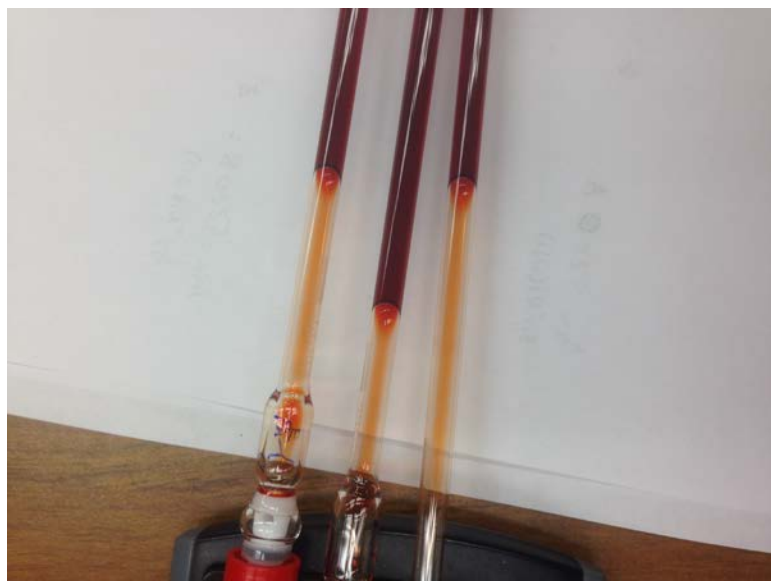
X-R ₂ time, temp	R ₁ -R ₂		R ₁ -C(=O)-R ₂		R ₁ -C(=O)-C(=O)-R ₂		R ₁ -R ₁		R ₁ -C(=O)-R ₁		R ₁ -C(=O)-C(=O)-R ₁		R ₂ -R ₂		R ₂ -C(=O)-R ₂		R ₂ -C(=O)-C(=O)-R ₂		R ¹ -H	
	Ph-Br < 12 h, 60 °C)	35	25	4	6	30	ND	500	26	ND	1									
Ph-Cl < 12 h, 60 °C)	ND	87	ND	ND	ND	ND	612	ND	ND	3										
I-n-octyl 1h, rt.	ND	58	ND	<1	ND	<1	ND	58	ND	4										

^a R¹ = p-tolyl. ND = not detected by GC analysis. In all cases, yields are calculated vs. amount of Ni(cod)₂ added in the first step. Yields are *uncorrected* GC yields vs. mesitylene internal standard, so >100% total yield for all products could be observed. For reactions with added reductant, >100% yields are possible because the nickel can turnover.

Figure S1. Pictures of the formation and reaction of $(dtbbpy)Ni^{II}(C(O)tolyl)(Br)$ (**1c**) with RX (Table 3).



Complex **1c** in THF- d_8 .



Reaction mixtures immediately after adding in DMA and the electrophile (RX).

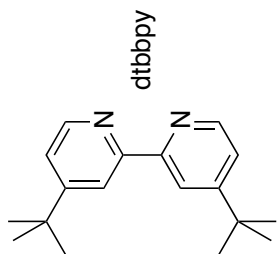


Reaction colors after 1 h reaction time.



Reaction mixtures after completion.

II. Spectra

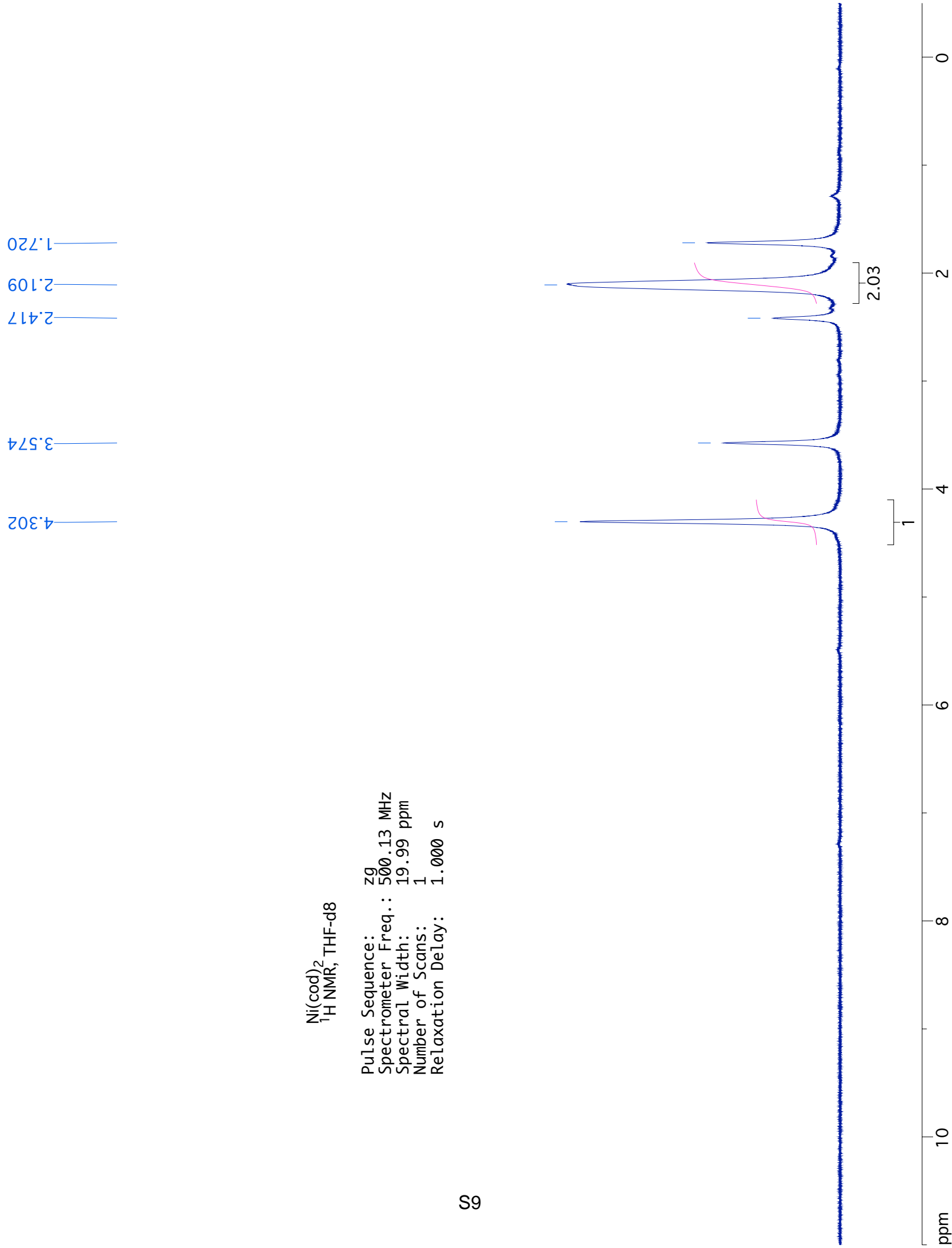


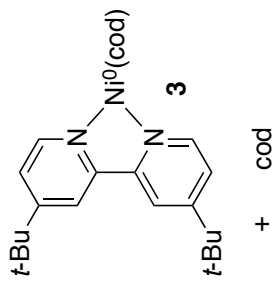
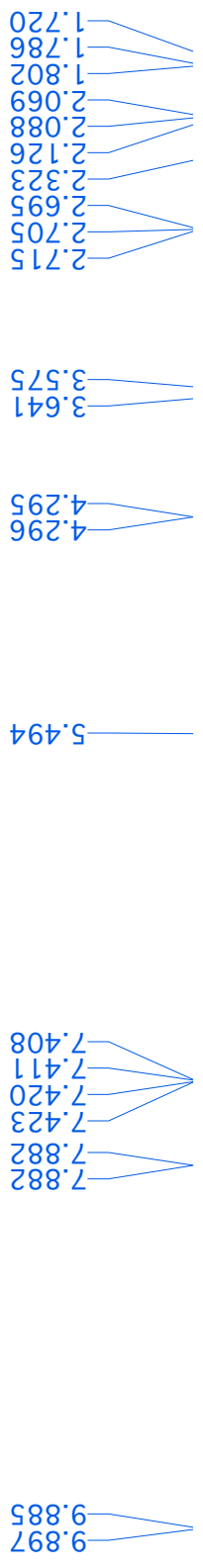
¹H NMR, THF-d8

Pulse Sequence: zg
 Spectrometer Freq.: 500.13 MHz
 Spectral Width: 19.99 ppm
 Number of Scans: 2
 Relaxation Delay: 12.000 s

$\text{Ni}(\text{cod})_2$
 ^1H NMR, THF-d8

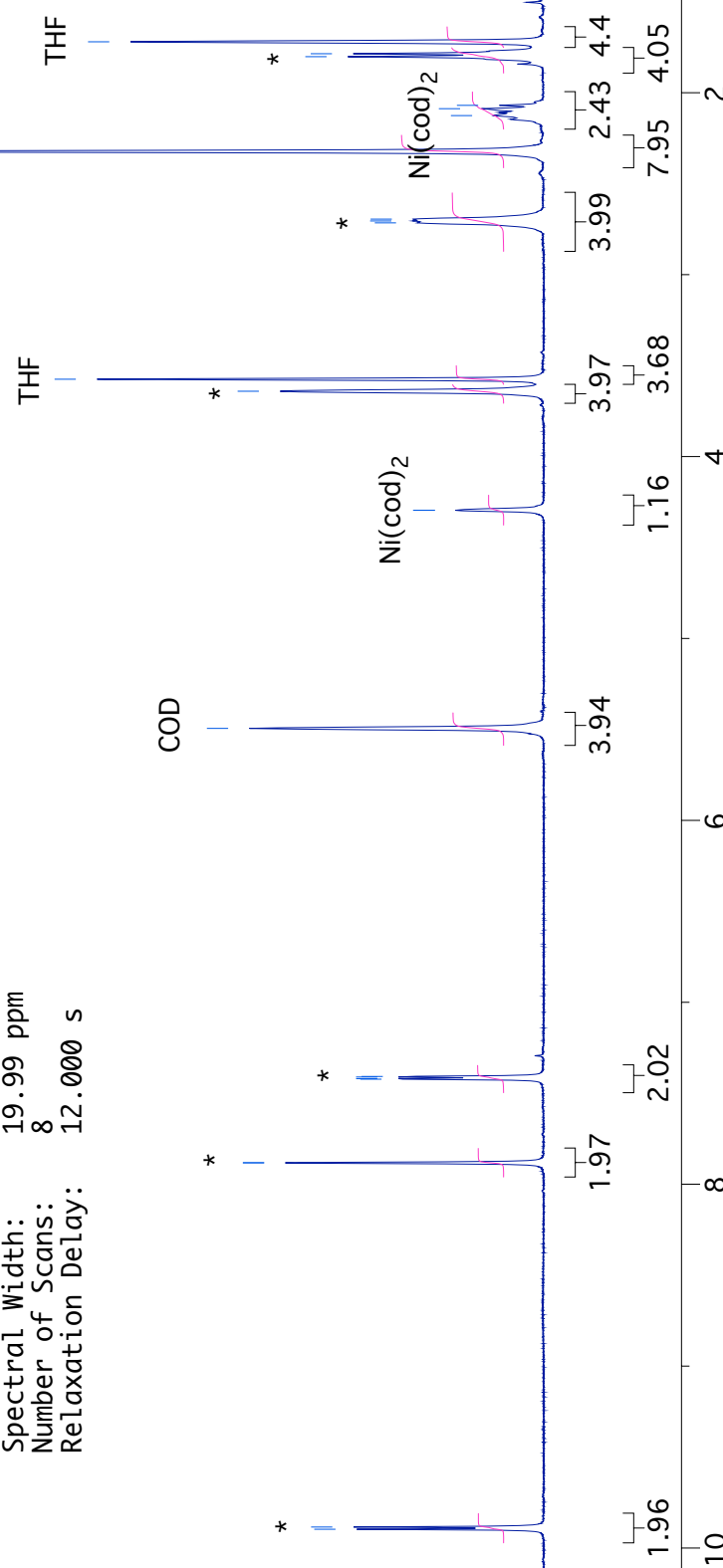
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Spectral Width: 19.99 ppm
Number of Scans: 1
Relaxation Delay: 1.000 s

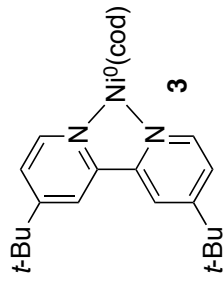




¹H NMR, THF-d8

Pulse Sequence: zg
 Spectrometer Freq.: 500.13 MHz
 Spectral Width: 19.99 ppm
 Number of Scans: 8
 Relaxation Delay: 12.000 s



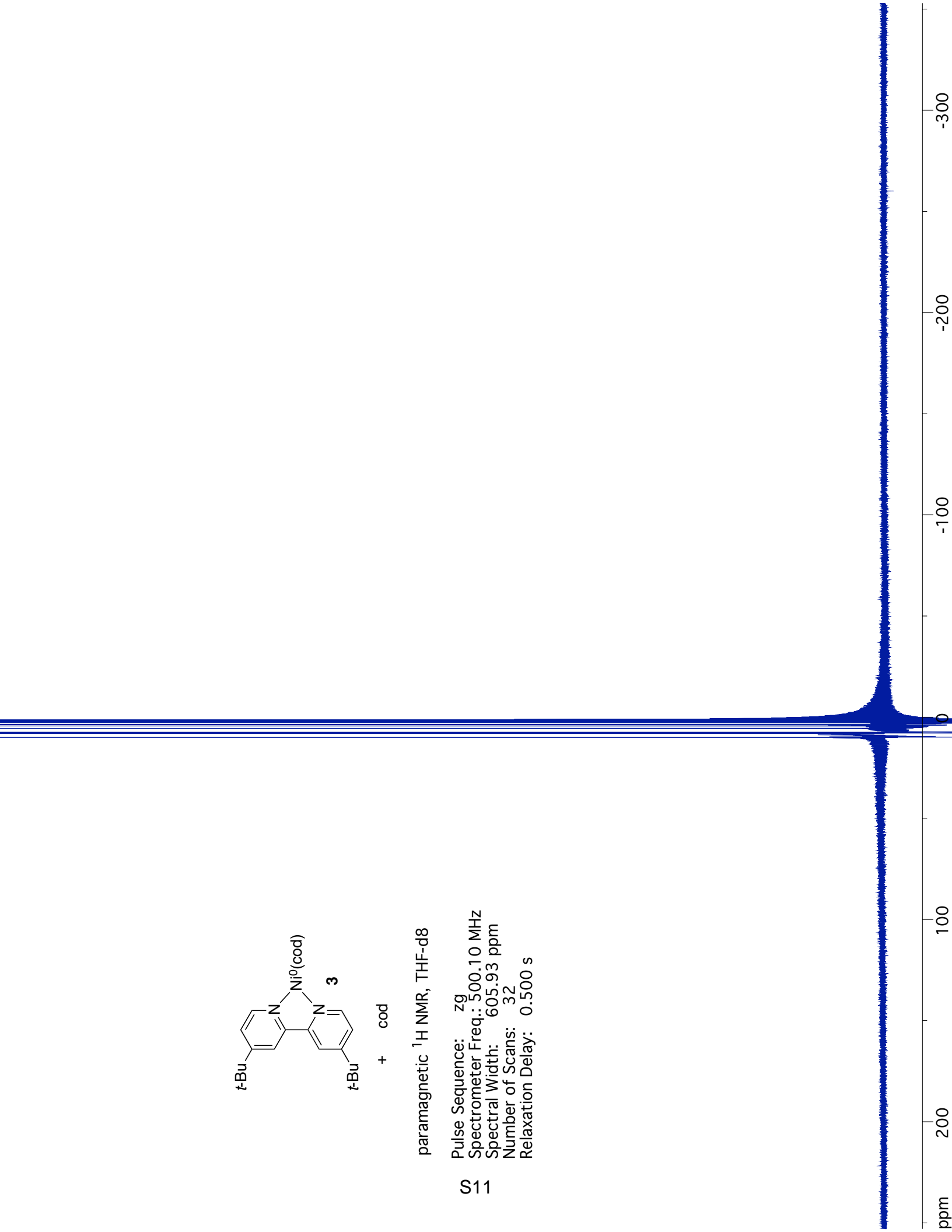


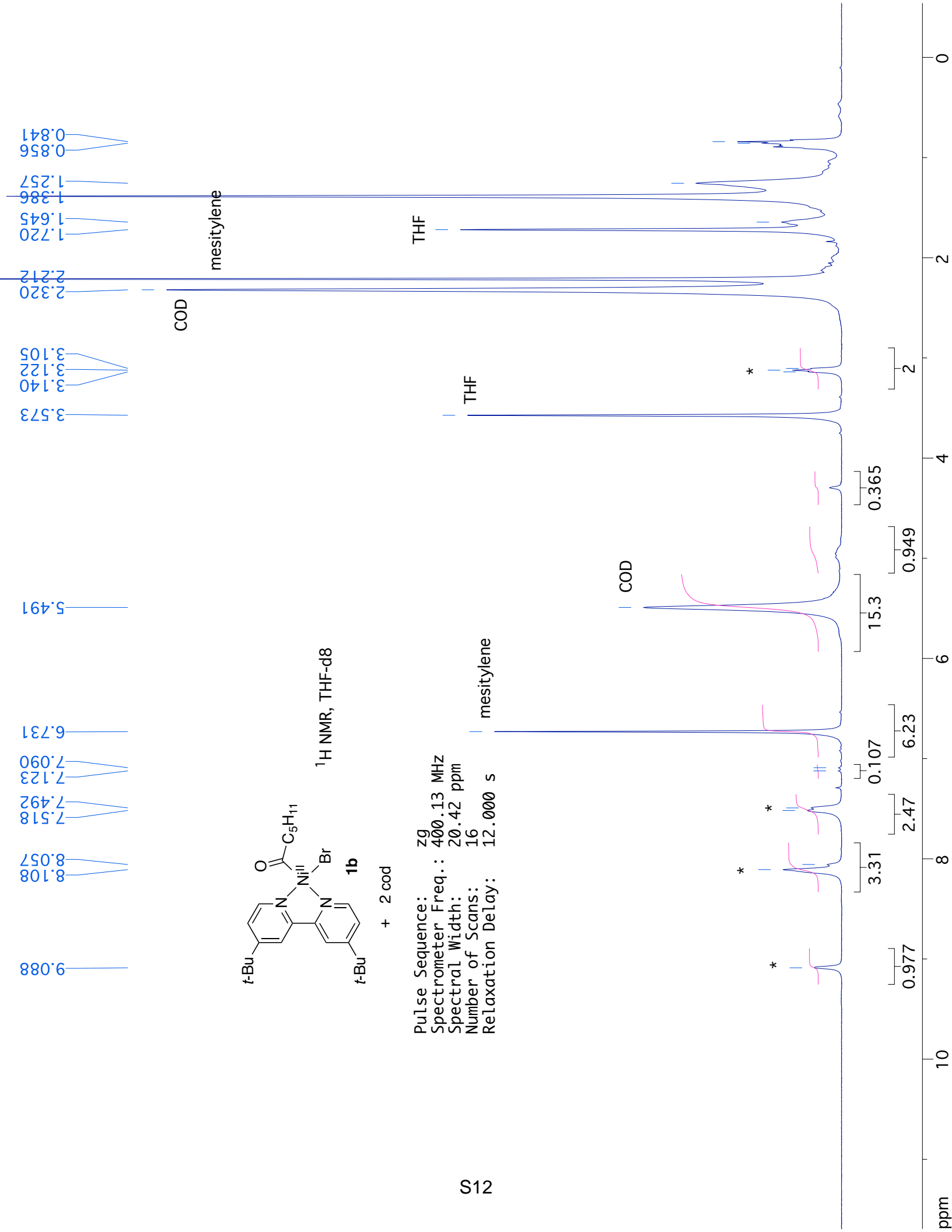
+ cod

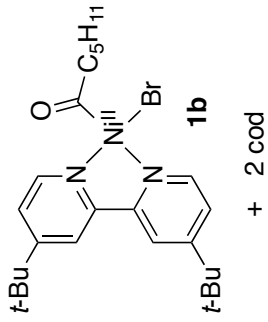
paramagnetic ^1H NMR, THF-d8

S11

Pulse Sequence: zg
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Spectral Width: 605.93 ppm
Number of Scans: 32
Relaxation Delay: 0.500 s



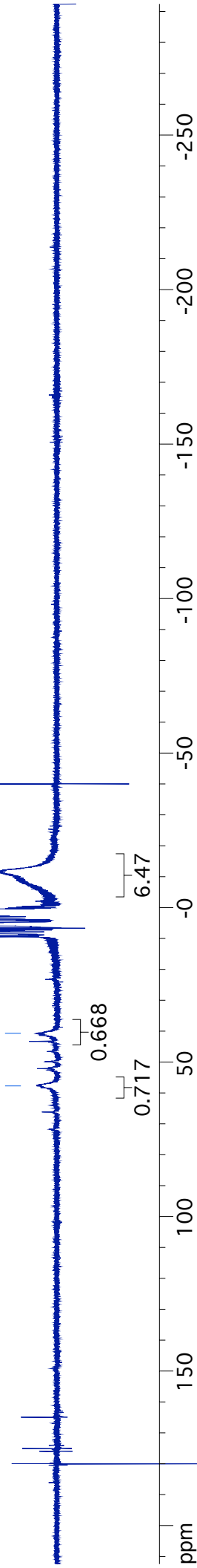


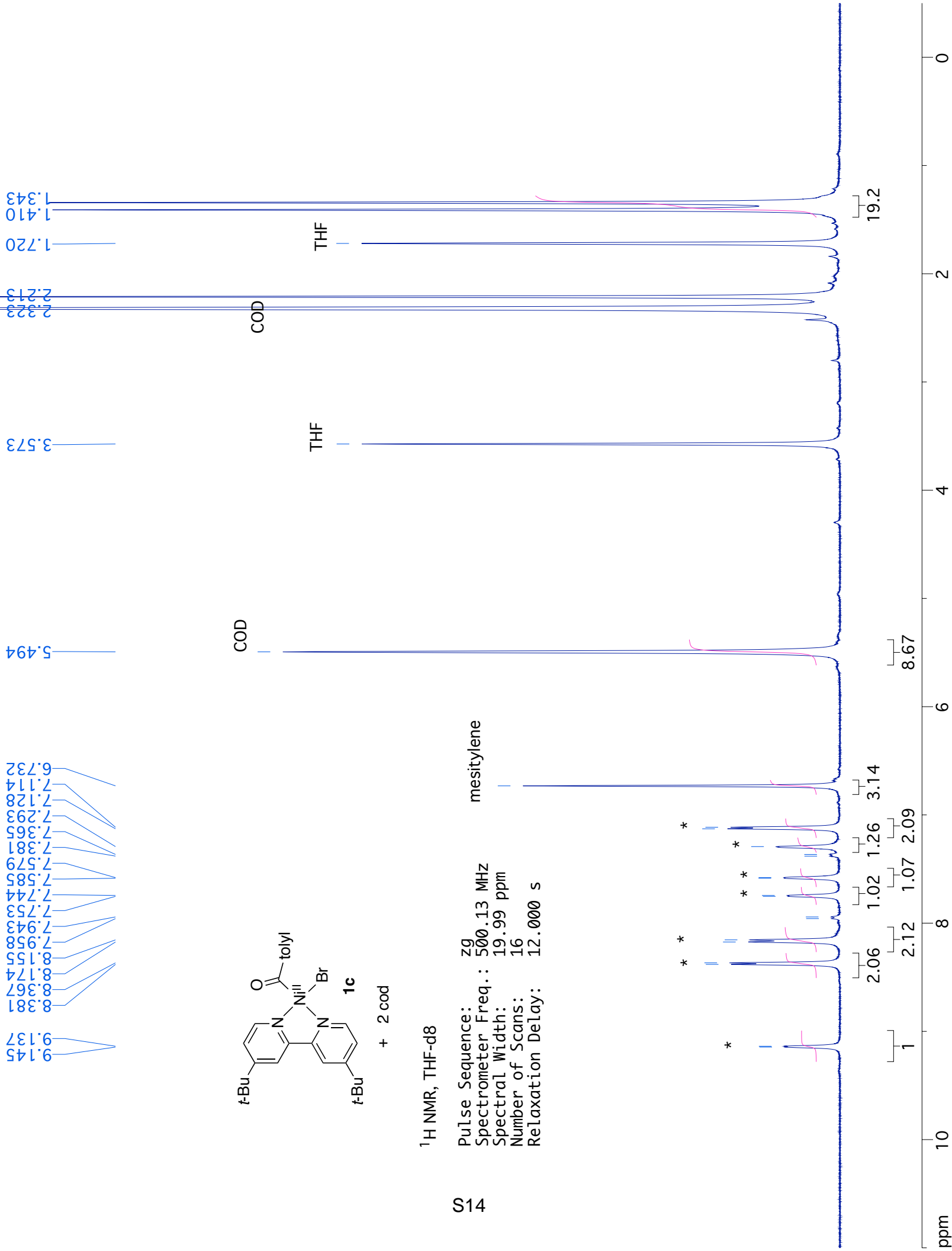


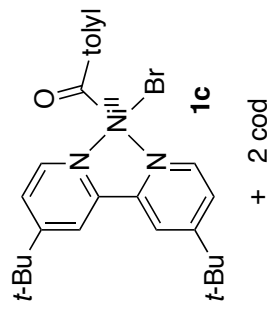
paramagnetic ¹H NMR, THF-d8

Pulse Sequence: zg
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 Spectral Width: 504.91 ppm
 Number of Scans: 355
 Relaxation Delay: 0.150 s

57.729
 40.679
 -11.440



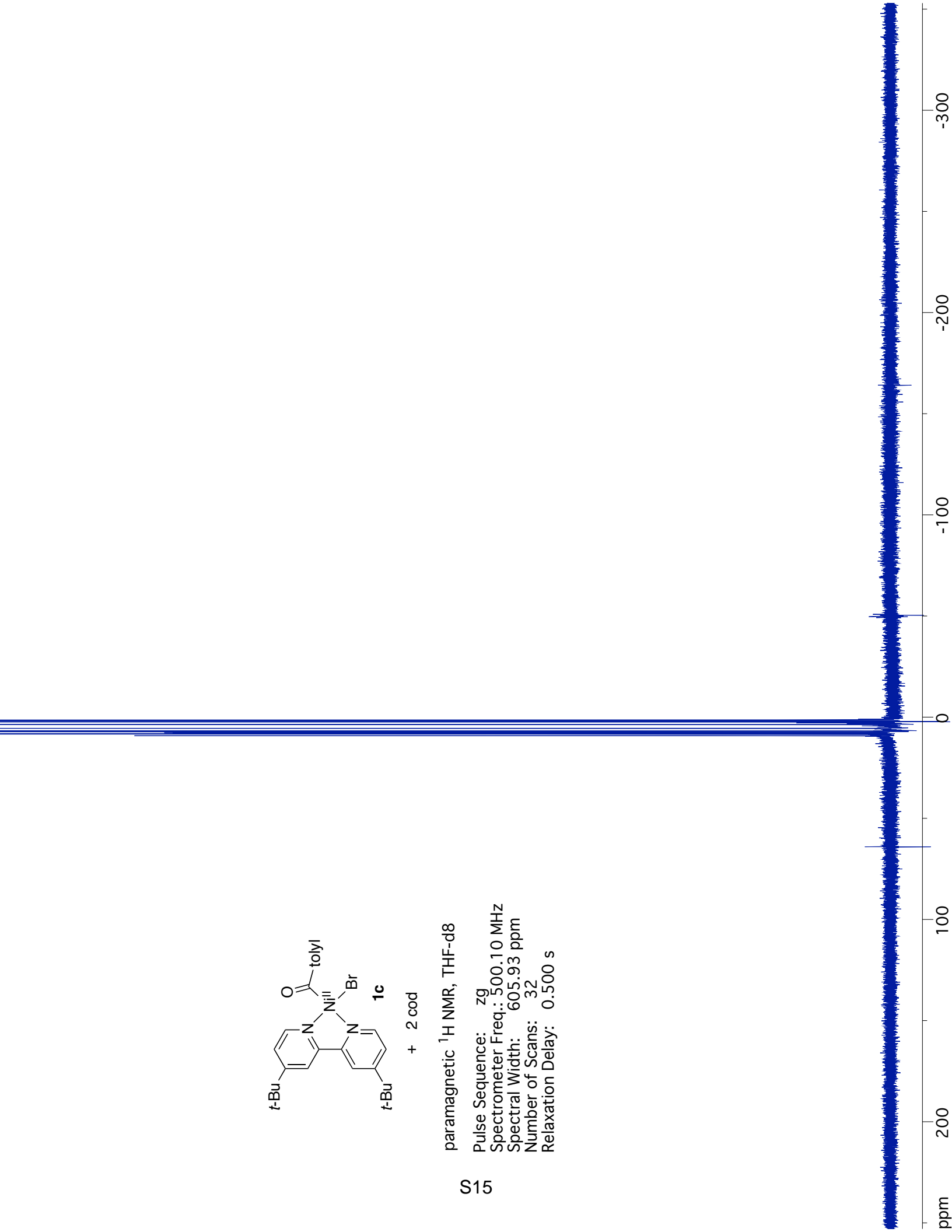




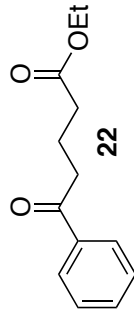
paramagnetic ^1H NMR, THF-d8

S15

Pulse Sequence: zg
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Spectral Width: 605.93 ppm
Number of Scans: 32
Relaxation Delay: 0.500 s



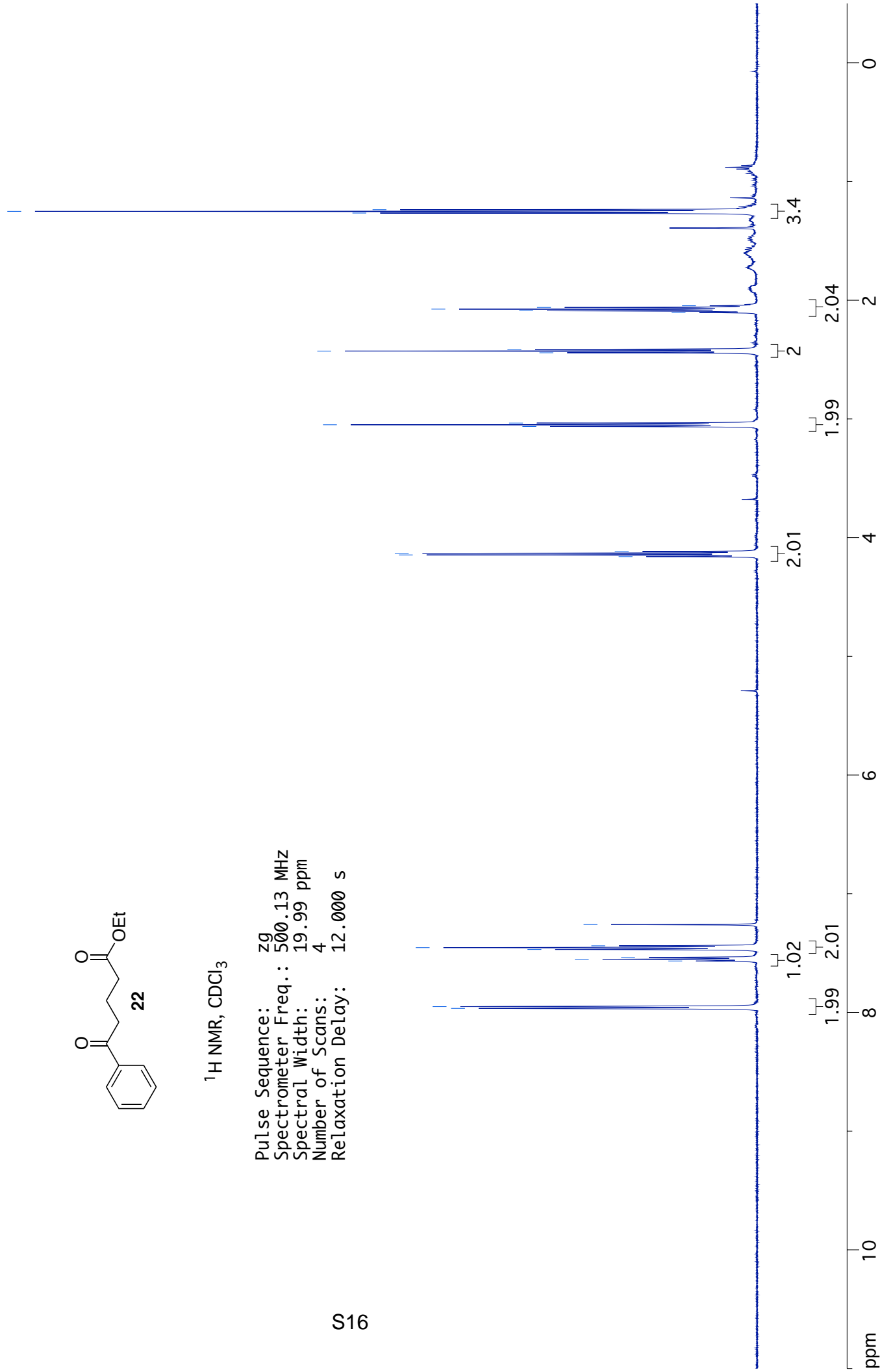
7.966
7.951
7.567
7.552
7.537
7.470
7.454
7.439
7.260

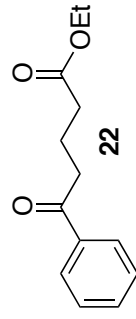


¹H NMR, CDCl₃

Pulse Sequence: zg
Spectrometer Freq.: 500.13 MHz
Spectral Width: 19.99 ppm
Number of Scans: 4
Relaxation Delay: 12.000 s

4.160
4.146
4.131
4.117
3.063
3.049
3.035
2.443
2.428
2.414
2.104
2.089
2.075
2.061
2.046
1.266
1.252
1.237





¹³C NMR, CDCl₃

Pulse Sequence: zgdc
Spectrometer Freq.: 125.77 MHz
Spectral Width: 301.18 ppm
Number of Scans: 200
Relaxation Delay: 2.000 s

S15

ppm

150

100

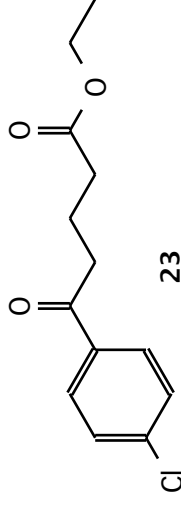
50

0

-50

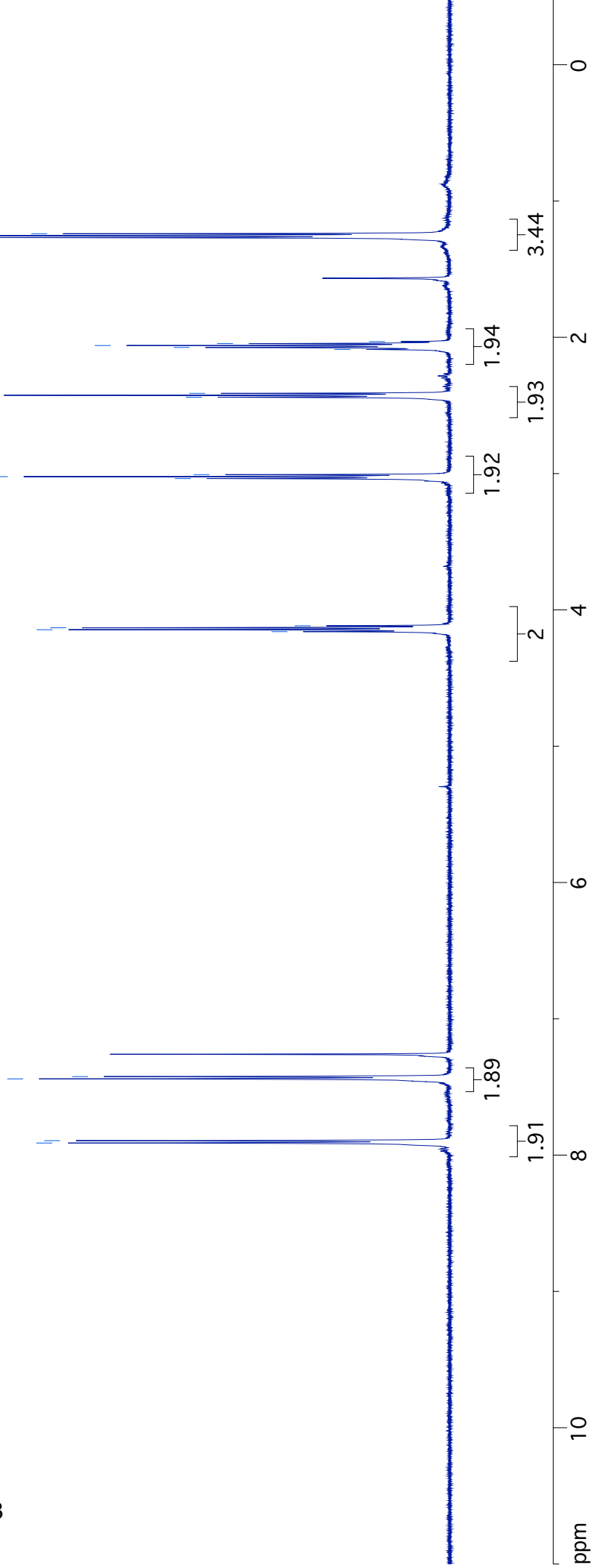
1.240
 1.254
 1.269
 2.032
 2.046
 2.060
 2.075
 2.089
 2.411
 2.426
 2.440
 3.008
 3.022
 3.037
 4.160
 4.145
 4.131
 4.117

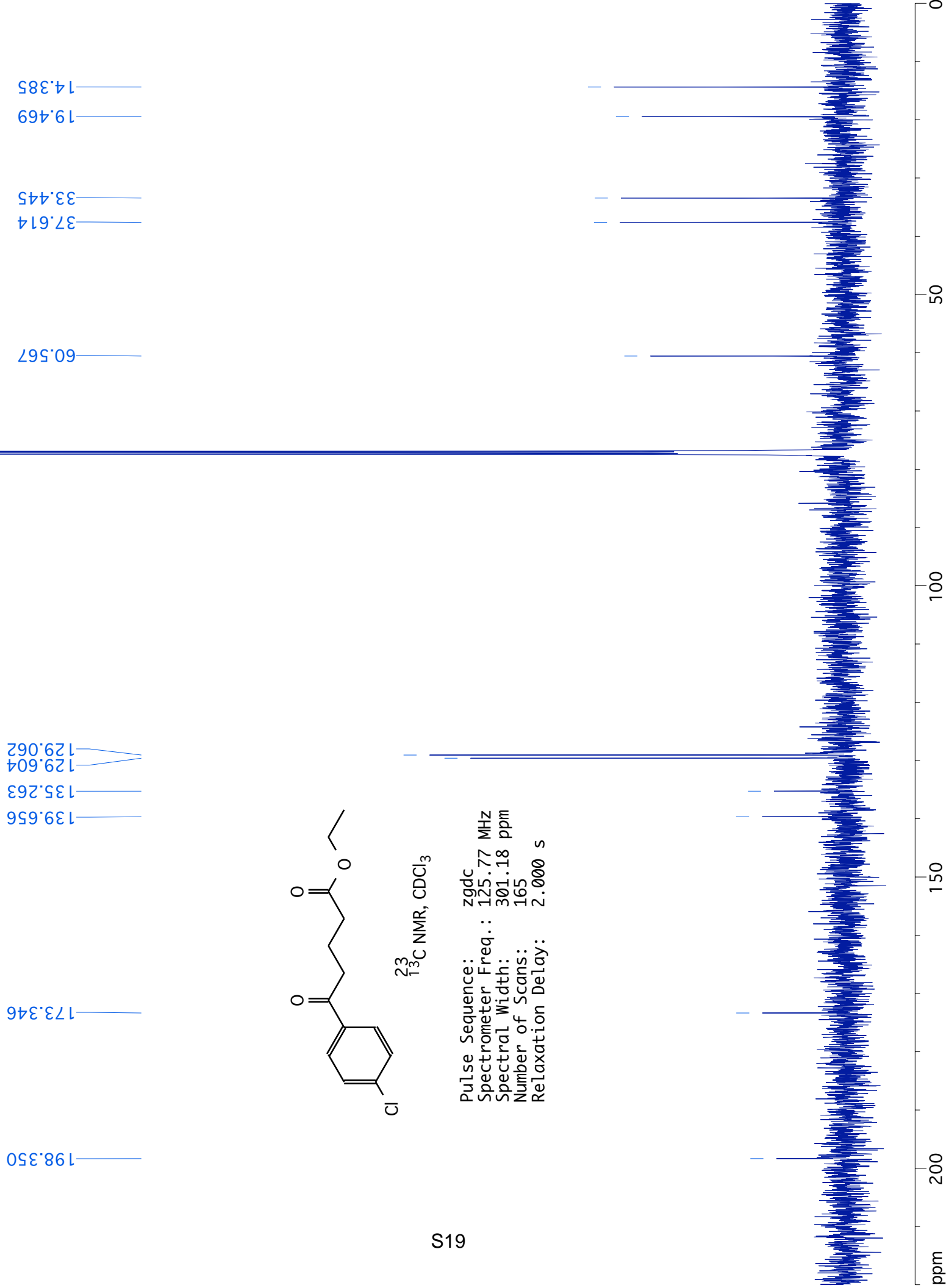
7.911
 7.894
 7.441
 7.424



23
¹H NMR, CDCl₃

Pulse Sequence: zg
 Spectrometer Freq.: 500.13 MHz
 Spectral Width: 19.99 ppm
 Number of Scans: 5
 Relaxation Delay: 10.000 s

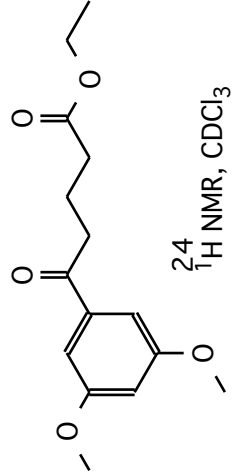




1.238
 1.252
 1.267
 2.026
 2.040
 2.054
 2.069
 2.083
 2.401
 2.416
 2.430
 2.987
 3.002
 3.016

3.831
 4.115
 4.129
 4.143
 4.158

6.638
 6.643
 6.647
 7.092
 7.096



Pulse Sequence: zg
 Spectrometer Freq.: 500.13 MHz
 Spectral Width: 19.99 ppm
 Number of Scans: 8
 Relaxation Delay: 10.000 s

1.87
 1.89
 3.39
 5.94
 1.98

0.965
 1.87

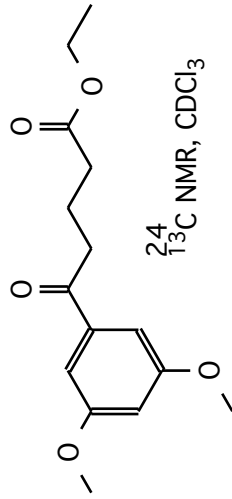
14.751
20.000
33.785
38.001
55.867
60.622

105.847
105.290

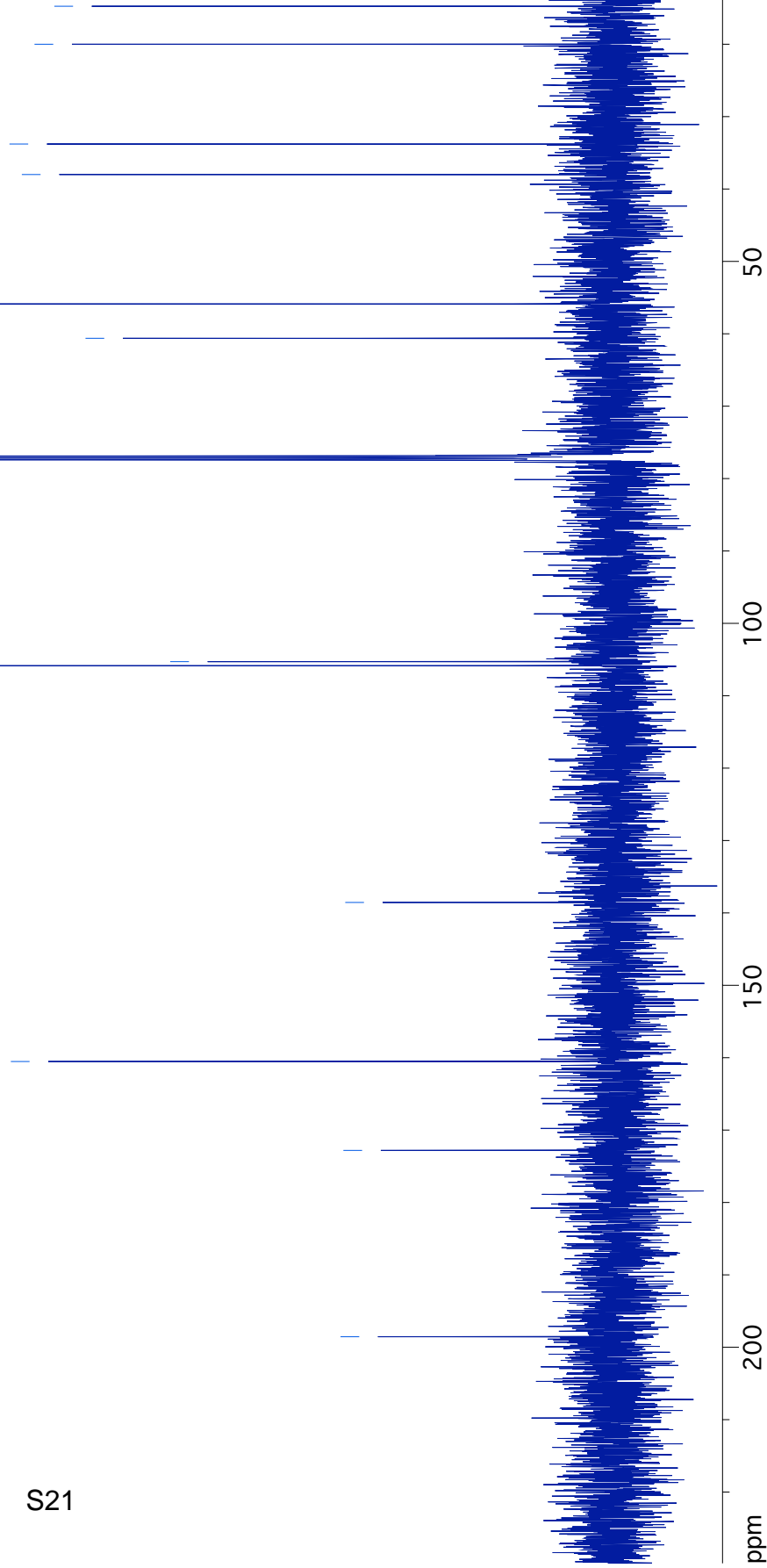
138.554

160.527
172.806

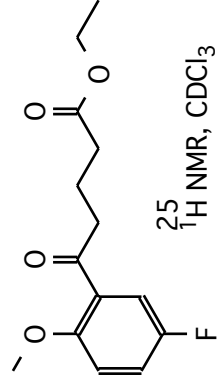
198.549



Pulse Sequence: zgdc
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Spectral Width: 299.41 ppm
Number of Scans: 93
Relaxation Delay: 2.000 s

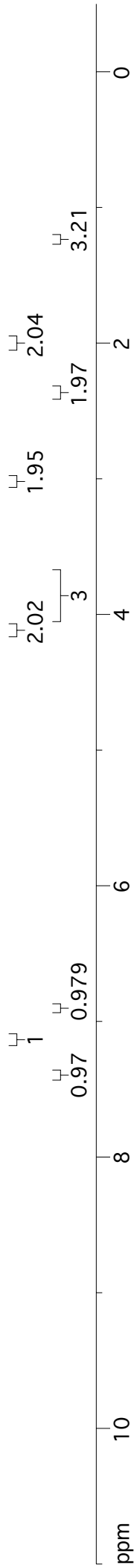


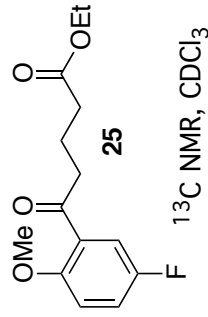
7.410
7.403
7.392
7.385
7.159
7.152
7.144
7.141
7.137
7.134
7.126
7.119
6.913
6.905
6.895
6.887



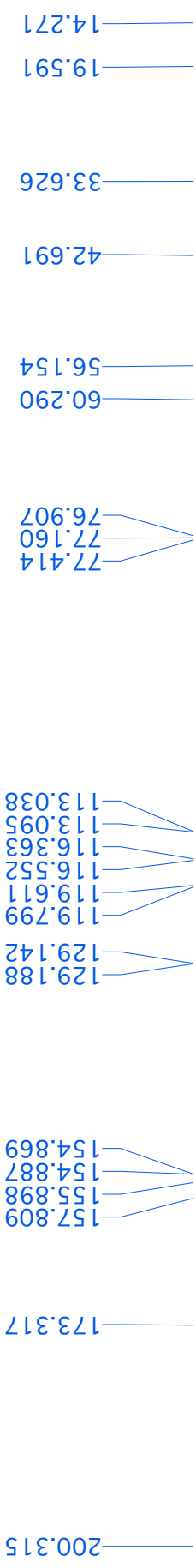
Pulse Sequence: zg
Spectrometer Freq.: 400.05 MHz
Spectral Width: 20.03 ppm
Number of Scans: 8
Relaxation Delay: 10.000 s

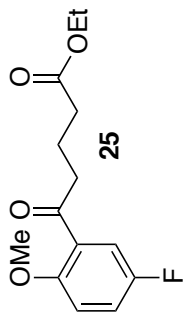
4.139
4.125
4.111
4.096
3.869
3.036
3.022
3.008
2.387
2.372
2.357
2.029
2.015
2.001
1.986
1.972
1.248
1.233
1.219





Pulse Sequence: zgdc
 Spectrometer Freq.: 125.77 MHz
 Spectral Width: 301.18 ppm
 Number of Scans: 118
 Relaxation Delay: 2.000 s





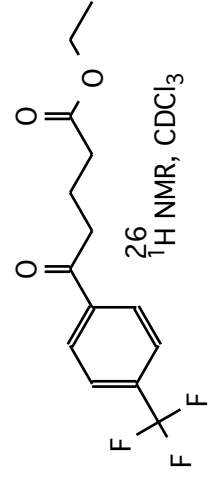
¹⁹F NMR, CDCl₃

Pulse Sequence: zg
Spectrometer Freq.: 376.48 MHz
Spectral Width: 265.62 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

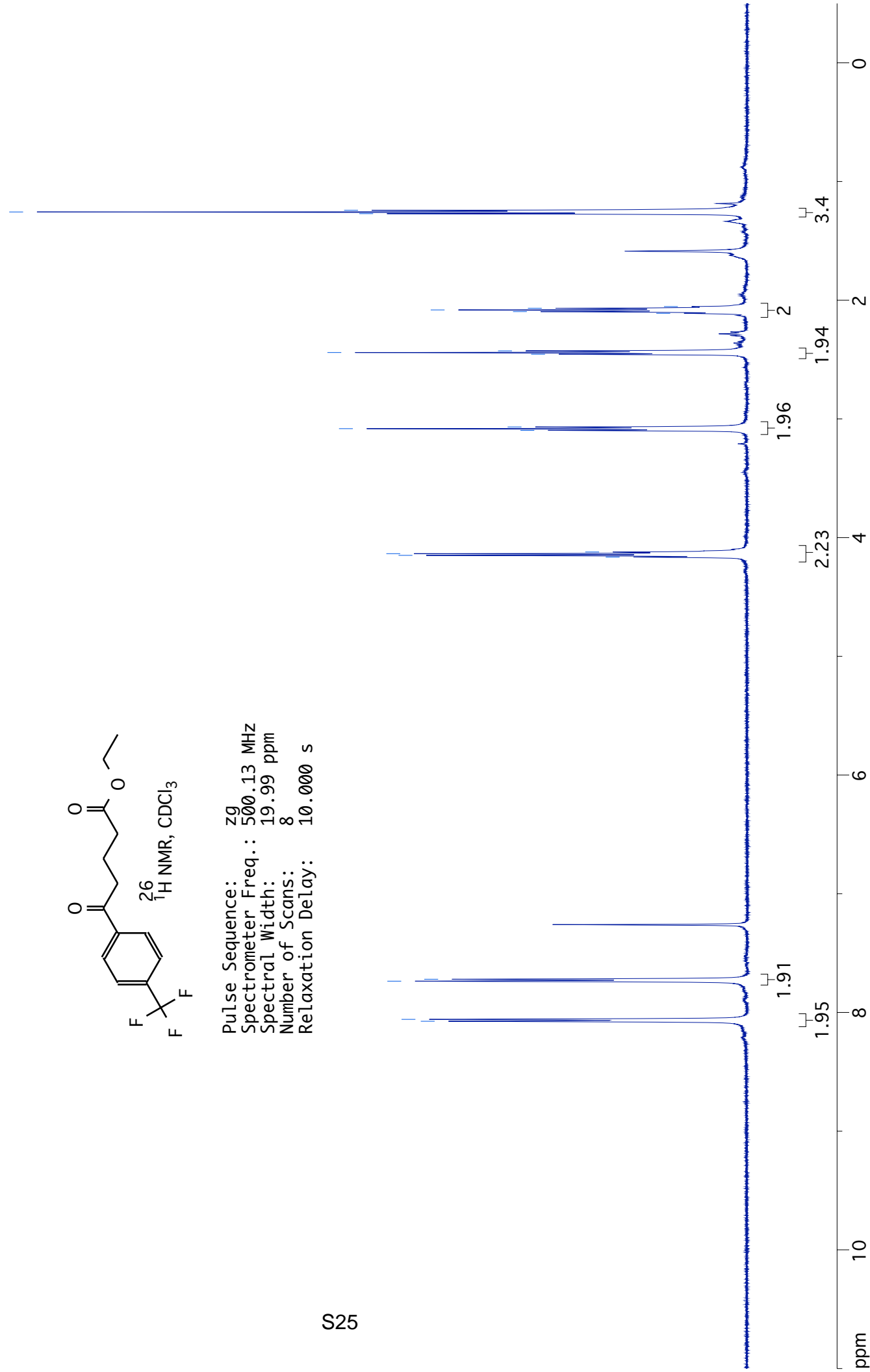
663.09

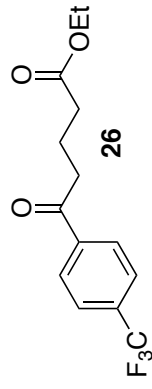
1.242
 1.256
 1.271
 2.054
 2.067
 2.082
 2.096
 2.110
 2.427
 2.441
 2.455
 3.068
 3.082
 3.096
 4.121
 4.135
 4.149
 4.164

8.074
 8.058
 7.737
 7.720



Pulse Sequence: zg
 Spectrometer Freq.: 500.13 MHz
 Spectral Width: 19.99 ppm
 Number of Scans: 8
 Relaxation Delay: 10.000 s

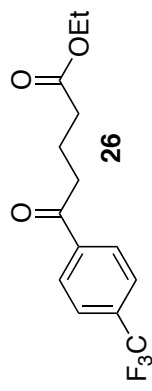




¹³C NMR, CDCl₃

Pulse Sequence: zgdc
Spectrometer Freq.: 100.60 MHz
Spectral Width: 299.41 ppm
Number of Scans: 1461
Relaxation Delay: 2.000 s





¹⁹F NMR, CDCl₃

Pulse Sequence: zg
Spectrometer Freq.: 376.50 MHz
Spectral Width: 199.70 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

-0.035

ppm

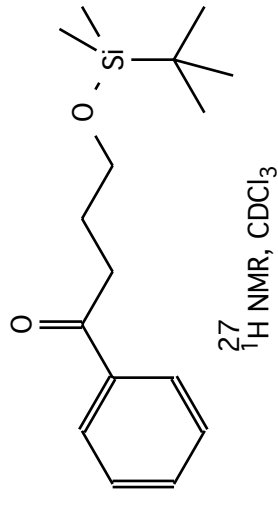
150

100

50

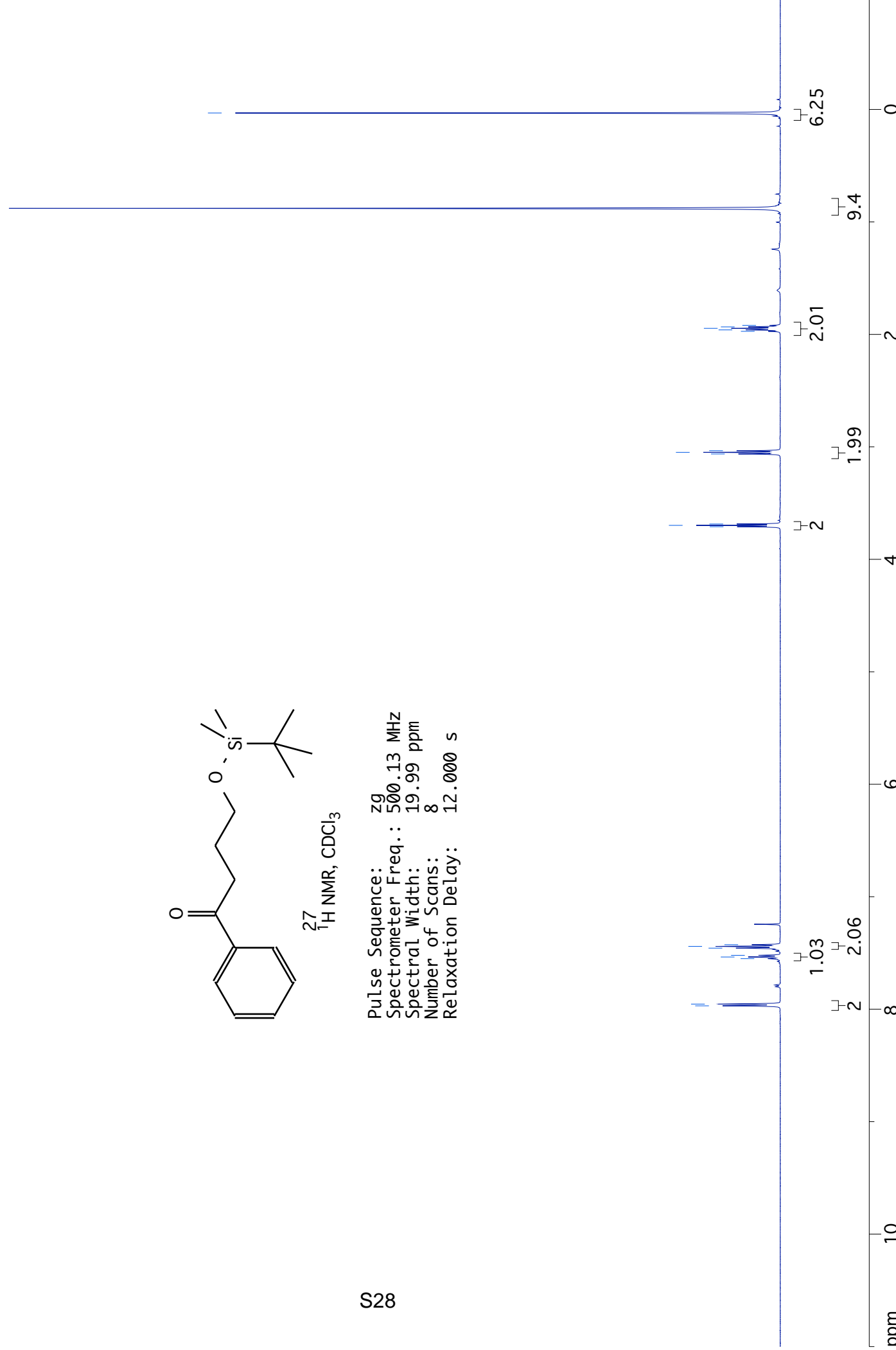
-0

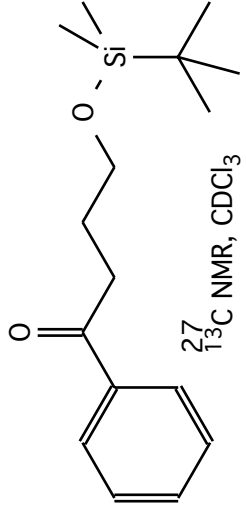
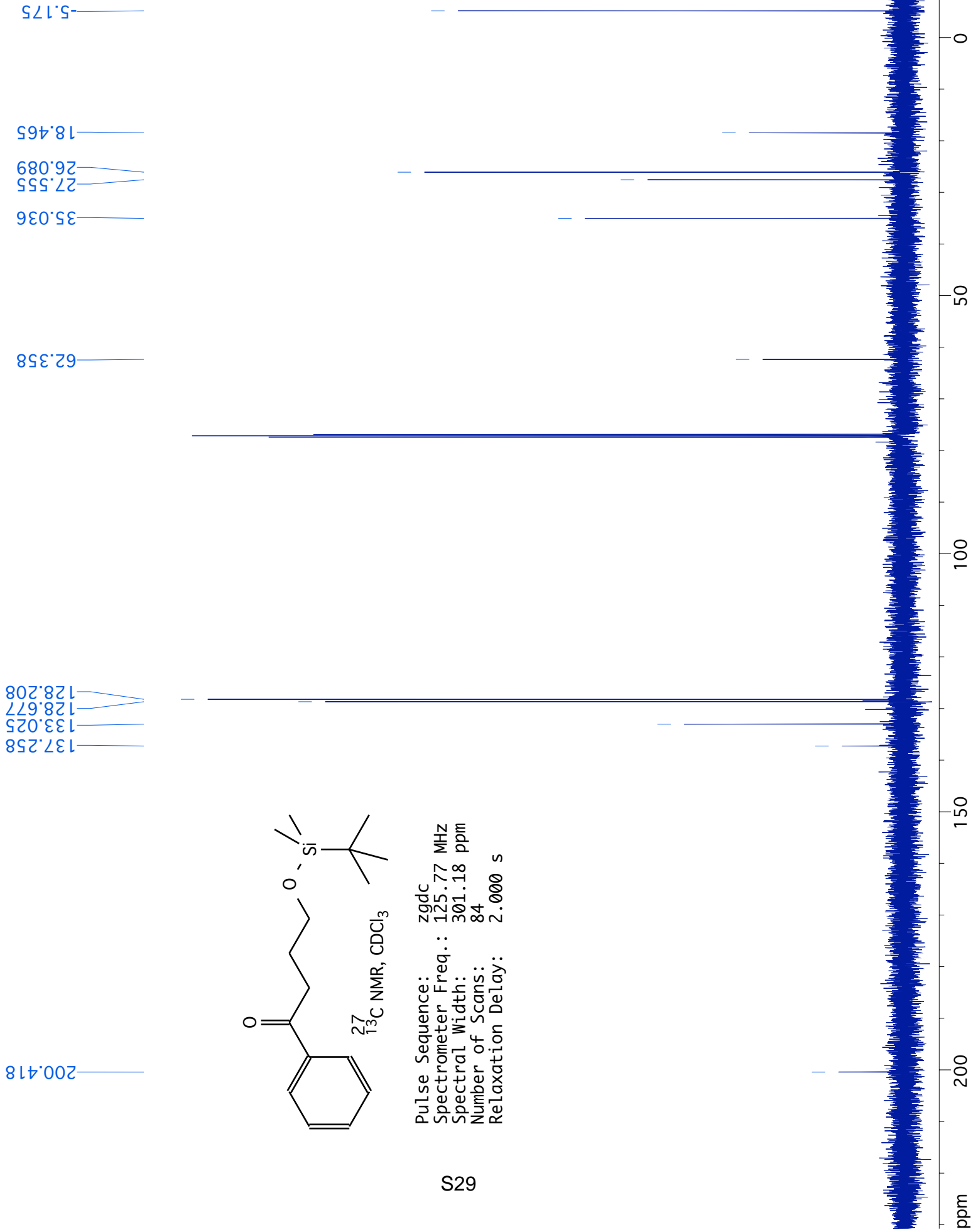
7.970
7.955
7.551
7.536
7.521
7.457
7.442
7.426



Pulse Sequence: zg
Spectrometer Freq.: 500.13 MHz
Spectral Width: 19.99 ppm
Number of Scans: 8
Relaxation Delay: 12.000 s

3.710
3.698
3.686
3.063
3.049
3.034
1.973
1.960
1.946
1.933
1.920
-0.879
0.031





Pulse Sequence: zgdc
 Spectrometer Freq.: 125.77 MHz
 Spectral Width: 301.18 ppm
 Number of Scans: 84
 Relaxation Delay: 2.000 s