

**O-Heterocycle Synthesis via Intramolecular C–H Alkoxylation Catalyzed by Iron
Acetylacetonate**

Supporting Information

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General consideration	7
Characterization and physical measurement	8
Table S1. Fe-catalyst optimization	9
Table S2. Catalytic condition optimization	10
Figure S1. Proposed hydride abstraction pathway	11
Figure S2. Analysis of intramolecular competition experiment	12
Figure S3. Analysis of isotope-labelling experiment	14
Figure S4. Analysis of CHD quenching experiment	15
Figure S5. Hammett analysis	20
<i>Analysis for constructing Hammett plot²</i>	21
Figure S6. Analysis of reaction concentration profiles	34
Figure S7. Analysis of radical clock substrate	38
α-Diazo-β-ketoesters synthesis	44
Spectroscopic details for α-diazo-β-ketoesters and the corresponding products	46
<i>Methyl 2-diazo-3-oxo-6-phenylhexanoate (1)</i>	46
<i>Methyl 2-diazo-6-methyl-3-oxoheptanoate (8)</i>	47
<i>Methyl 2-diazo-3-oxoheptanoate (S2)</i>	48

<i>Methyl 2-diazo-3-oxohexanoate (S3)</i>	49
<i>Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (S5)</i>	50
<i>Phenethyl 2-diazo-7-methyl-3-oxooctanoate (S7)</i>	56
<i>Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (I2)</i>	62
<i>3-Diazo-octane-2,4-dione (S8)</i>	65
<i>Methyl 2-diazo-3-oxo-7-phenylheptanoate (S9)</i>	68
<i>Methyl 2-diazo-3-oxooctanoate (S10)</i>	69
<i>Methyl 2-diazo-6-methyl-3-oxo-4-propylheptanoate (S12)</i>	70
<i>Methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (S14)</i>	71
<i>Methyl 6-(4-bromophenyl)-2-diazo-3-oxohexanoate (S16)</i>	77
<i>Methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (S17)</i>	83
<i>Methyl 2-diazo-6-(4-methoxyphenyl)-3-oxohexanoate (S20)</i>	91
<i>Methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (S22)</i>	97
<i>Methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (S24)</i>	103
<i>Methyl 6-(benzo[d]thiazol-2-yl)-2-diazo-3-oxohexanoate (S26)</i>	109
<i>Methyl 6-(benzo[d]thiazol-2-yl)-2-diazo-3-oxohexanoate (S28)</i>	112
<i>Methyl 2-diazo-6-(1-methyl-1H-indol-3-yl)-3-oxohexanoate (S30)</i>	118
<i>Methyl 7-cyano-2-diazo-3-oxoheptanoate (S32)</i>	124
<i>Methyl 2-diazo-6-methoxy-3-oxohexanoate (S34)</i>	127
<i>Methyl 2-diazo-4-ethoxy-3-oxobutanoate (S36)</i>	130
<i>Methyl 2-diazo-5-(1,3-dioxolan-2-yl)-3-oxopentanoate (S38)</i>	133
<i>Methyl 2-diazo-4-isopropoxy-3-oxobutanoate (S40)</i>	139
<i>Methyl 5-cyclopropyl-2-diazo-3-oxopentanoate (31)</i>	145
<i>Methyl 5-cyclobutyl-2-diazo-3-oxopentanoate (S43)</i>	148
<i>Ethyl 5-cyclopentyl-2-diazo-3-oxopentanoate (S44)</i>	151
<i>Methyl 5-cyclohexyl-2-diazo-3-oxopentanoate (S46)</i>	154
<i>tert-Butyl 4-(4-diazo-5-methoxy-3,5-dioxopentyl)piperidine-1-carboxylate (S48)</i>	157
<i>Ethyl 3-cyclopentyl-2-diazo-3-oxopropanoate (S50)</i>	163
<i>Ethyl 2-diazo-5-(2,3-dihydrobenzofuran-2-yl)-3-oxopentanoate (S52)</i>	169
<i>Ethyl 5-(chroman-2-yl)-2-diazo-3-oxopentanoate (S54)</i>	175
<i>Ethyl 4-cyclobutyl-2-diazo-3-oxobutanoate (S55)</i>	181
<i>Ethyl 4-cyclopentyl-2-diazo-3-oxobutanoate (S56)</i>	184

<i>Ethyl 4-cyclohexyl-2-diazo-3-oxobutanoate (S57)</i>	187
<i>Methyl trans-4-(4-((tert-butoxycarbonyl)amino)cyclohexyl)-2-diazo-3-oxobutanoate (S59)</i>	190
<i>Methyl 2-diazo-3-oxo-4-(tetrahydrofuran-3-yl)butanoate (S61)</i>	196
<i>Methyl 4-(adamantan-1-yl)-2-diazo-3-oxobutanoate (S63)</i>	202
<i>Methyl 2-diazo-4-(6-fluoro-2,3-dihydro-1H-inden-1-yl)-3-oxobutanoate (S65)</i>	208
<i>Methyl 2-diazo-4-(2,3-dihydro-1H-inden-2-yl)-3-oxobutanoate (S67)</i>	216
<i>Dimethyl 2,10-bis(diazo)-3,9-dioxoundecanedioate (S69)</i>	222
<i>Methyl (6R)-2-diazo-6-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxoheptanoate (S71)</i>	225
<i>Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (S72)</i>	229
<i>Methyl 6-cyclopropyl-2-diazo-3-oxohexanoate (6)</i>	230
Procedure for catalytic C–H alkoxylation	231
Characterization of (Z)-2-alkylidene tetrahydrofuran	234
<i>Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (2)</i>	234
<i>Solid-state molecular structure for methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (2)</i>	239
<i>Methyl (Z)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (3)</i>	240
<i>Methyl (E)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (3')</i>	244
<i>Methyl (Z)-2-(5-methyldihydrofuran-2(3H)-ylidene)acetate (4)</i>	247
<i>Methyl (Z)-2-(dihydrofuran-2(3H)-ylidene)acetate (5)</i>	253
<i>Phenethyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (10)</i>	257
<i>Phenethyl (Z)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (11)</i>	261
<i>(Z)-1-(5-Methyldihydrofuran-2(3H)-ylidene)propan-2-one (13)</i>	265
<i>Methyl (Z)-2-(5-ethyldihydrofuran-2(3H)-ylidene)acetate (14)</i>	269
<i>Methyl (Z)-2-(5-benzylidihydrofuran-2(3H)-ylidene)acetate (15):</i>	274
<i>Solid-state molecular structure for methyl (Z)-2-(5-benzylidihydrofuran-2(3H)-ylidene)acetate (15)</i>	279
<i>Methyl (Z)-2-(5-(4-fluorophenyl)dihydrofuran-2(3H)-ylidene)acetate (16)</i>	280
<i>Methyl (Z)-2-(5-(4-bromophenyl)dihydrofuran-2(3H)-ylidene)acetate (17):</i>	286
<i>Methyl (Z)-2-(5-(p-tolyl)dihydrofuran-2(3H)-ylidene)acetate (18)</i>	291
<i>Methyl (Z)-2-(5-(4-methoxyphenyl)dihydrofuran-2(3H)-ylidene)acetate (19)</i>	296
<i>Methyl (Z)-2-(5-(furan-2-yl)dihydrofuran-2(3H)-ylidene)acetate (20)</i>	301
<i>Methyl (Z)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21)</i>	306

<i>Solid-state molecular structure of methyl (Z)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21)</i>	311
<i>Methyl (E)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21')</i>	312
<i>Methyl (Z)-2-(5-(pyridin-2-yl)dihydrofuran-2(3H)-ylidene)acetate (22)</i>	315
<i>Methyl (Z)-2-(5-(benzo[d]thiazol-2-yl)dihydrofuran-2(3H)-ylidene)acetate (23)</i>	319
<i>Methyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (24)</i>	323
<i>Solid-state molecular structure of methyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (24)</i>	329
<i>Methyl (Z)-2-(5-(cyanomethyl)dihydrofuran-2(3H)-ylidene)acetate (25)</i>	331
<i>Methyl (Z)-2-(5-methoxydihydrofuran-2(3H)-ylidene)acetate (26)</i>	335
<i>Methyl (Z)-2-(2-methyl-1,3-dioxolan-4-ylidene)acetate (27):</i>	339
<i>Methyl (Z)-2-(2,2-dimethyl-1,3-dioxolan-4-ylidene)acetate (28)</i>	343
<i>Methyl 5-(2-hydroxy-1,3-dioxolan-2-yl)-3-oxopentanoate (29)</i>	347
<i>Methyl (Z)-2-((5S)-5-((3R,5R,8R,9S,10S,13S,17S)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (30)</i>	351
<i>Methyl (Z)-2-(5-oxaspiro[3.4]octan-6-ylidene)acetate (32)</i>	355
<i>Ethyl (Z)-2-(1-oxaspiro[4.4]nonan-2-ylidene)acetate (33)</i>	359
<i>Methyl (Z)-2-(1-oxaspiro[4.5]decan-2-ylidene)acetate (34)</i>	363
<i>tert-Butyl (Z)-2-(2-methoxy-2-oxoethylidene)-1-oxa-8-azaspiro[4.5]decane-8-carboxylate (35)</i>	367
<i>Methyl (Z)-2-(1,6-dioxaspiro[4.4]nonan-2-ylidene)acetate (36)</i>	371
<i>Ethyl (Z)-2-(3',4'-dihydro-5'H-spiro[chromane-2,2'-furan]-5'-ylidene)acetate (37)</i>	377
<i>Ethyl (Z)-2-(3',4'-dihydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-ylidene)acetate (38)</i>	381
<i>Solid-state molecular structure for ethyl (Z)-2-(3',4'-dihydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-ylidene)acetate (38)</i>	386
<i>Dimethyl 2,2'-(1,6-dioxaspiro[4.4]nonane-2,7-diylidene)(2Z,2'Z)-diacetate (39)</i>	391
<i>Solid-state molecular structure for methyl dimethyl 2,2'-(1,6-dioxaspiro[4.4]nonane-2,7-diylidene)(2Z,2'Z)-diacetate (39)</i>	395
<i>Ethyl (Z)-2-(2-oxabicyclo[3.2.0]heptan-3-ylidene)acetate (40)</i>	396
<i>Ethyl (Z)-2-(hexahydro-2H-cyclopenta[b]furan-2-ylidene)acetate (41):</i>	400
<i>Ethyl (Z)-2-(hexahydrobenzofuran-2(3H)-ylidene)acetate (42)</i>	404
<i>Methyl (Z)-2-((3ar,9s)-hexahydro-4H-3a,7:5,9-dimethanocycloocta[b]furan-2(3H)-ylidene)acetate (43)</i>	408

<i>Solid-state molecular structure for methyl (E)-2-((3ar,9s)-hexahydro-4H-3a,7:5,9-dimethanocycloocta[b]furan-2(3H)-ylidene)acetate (43)</i>	413
<i>Methyl (Z)-trans-2-(6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44)</i>	414
<i>Solid-state molecular structure for methyl (Z)-trans-2-(6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44)</i>	415
<i>Methyl (E)-trans-2-(6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44')</i>	418
<i>Methyl (Z)-2-(tetrahydrofuro[2,3-b]furan-2(3H)-ylidene)acetate (45)</i>	421
<i>Methyl (Z)-2-(3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan-2-ylidene)acetate (46)</i>	425
<i>Methyl (Z)-2-(5-fluoro-3,3a,8,8a-tetrahydro-2H-indeno[2,1-b]furan-2-ylidene)acetate (47)</i>	430
<i>Solid-state molecular structure for methyl (Z)-2-(5-fluoro-3,3a,8,8a-tetrahydro-2H-indeno[2,1-b]furan-2-ylidene)acetate (47)</i>	436
Reactivity of (Z)-2-alkylidene tetrahydrofuran	437
1. Bromination	437
<i>Solid-state molecular structure for methyl (Z)-2-bromo-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (S74)</i>	440
2. Alkene reduction	441
X-ray Diffraction Techniques	444
Table S3. X-ray Diffraction Experimental Details	447
Computational Methods	452
<i>Structural optimization and electronic structure calculation of Fe stabilized vinyl C-radical</i>	453
<i>Molecular geometry of Fe stabilized vinyl C-radical with S = 3</i>	453
<i>Molecular geometry of Fe stabilized vinyl C-radical with S = 2</i>	456
<i>MO description and spin density plot of the Fe stabilized vinyl C-radical</i>	459
<i>Potential energy surface for transformation catalyzed by Fe(acac)₂</i>	461
1. Optimization of the starting substrates, products, Fe(acac) ₂ and intermediates	461
2. Location of N ₂ -loss transition state	461
3. Location of HAA transition state	462
4. Location of RR transition state	462
5. Different potential modes of N ₂ loss	463
6. Coordinates of optimized geometries	463
7. Summary figure of the potential energy surface.....	519

8. <i>Results using other functionals</i>	520
References	521

General consideration

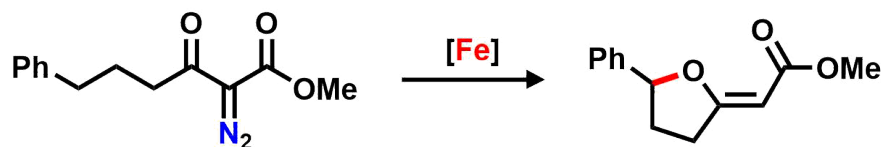
All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. All glassware was oven dried overnight and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, and hexanes were dried over 4 Å molecular sieves (Strem) prior to use in the box. Chloroform-*d* and dichloromethane-*d*₂ was purchased from Cambridge Isotope Labs and used as received. Benzene-*d*₆ and tetrahydrofuran-*d*₈ were purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use. Dichloromethane, ethyl acetate and hexanes were purchased from Aldrich and used as received outside the box. Compounds *p*-ABSA, triethyl amine, sodium hydroxide, hydrochloric acid (12 M), CDI, methyl potassium malonate, magnesium chloride, phenylbutyric acid, octane-2,4-dione, methyl 3-(2-methylphenyl)-3-oxopropanoate, 5-phenylvaleric acid, methyl 3-oxooctanoate, methyl 3-oxo-6-methyl-heptanoate, lithocholic acid, 5-hexenoic acid, 4-(*p*-tolyl)butyric acid, 4-(*p*-bromophenyl)butyric acid, 4-(*p*-fluorophenyl)butyric acid, 4-(*p*-methoxyphenyl)butyric acid 2-thiophenebutanoic acid, 1,4-cyclohexadiene, ethyl 3-cyclohexyl-3-oxopropanoate, ethyl 3-cyclopentyl-3-oxopropanoate, ethyl 5-cyclopentyl-3-oxopentanoate, ethyl 5-cyclohexyl-3-oxopentanoate, 1-Boc-piperidin-4-ylpropionic acid, furan, 4-(1-methyl-1H-indol-3-yl)butanoic acid, 3-cyclobutylpropanoic acid, 3-cyclopropylpropanoic acid, 3-tetrahydro-2-furanylpropanoic acid and methyl acetoacetate were purchased from Aldrich and used as received. Compound 4-(furan-2-yl)butanoic acid¹ was prepared according to previously published procedures. Compounds ferrous acetylacetonate was purchased from AstaTech and used as received in the drybox. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum

while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

Characterization and physical measurement

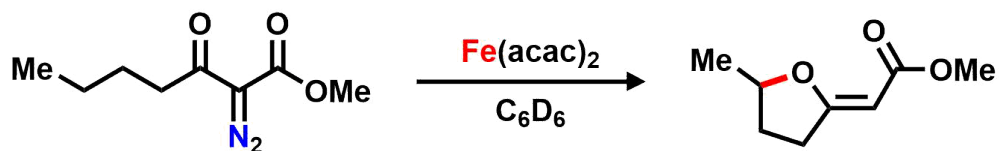
^1H , ^{13}C , and ^{19}F NMR were recorded on Varian Unity/Inova 500 MHz- and JEOL 400 MHz- spectrometers. ^1H and ^{13}C NMR chemical shifts are reported relative to SiMe_4 using the chemical shift of residual solvent peaks as reference. ^{19}F NMR chemical shifts are reported relative to an external standard of boron trifluoride diethyl etherate.

Table S1. Fe-catalyst optimization



Entry	Cat.	Cat. loading (mol%)	Solvent	Temp. (°C) ^a	Time	Conversion (%) ^b	NMR yield (%)
1	(^t BuCl _L)Fe(OEt ₂)Cl	10	C ₆ D ₆	80	12 h	> 99	64
2	Fe(acac) ₂	30	C ₆ D ₆	25	3 h	> 99	58
		10	C ₆ D ₆	60	20 min	> 99	74
3	FeHMDS ₂	20	C ₆ D ₆	80	36 h	90	60
4	Fe(OAc) ₂	1 equiv	C ₆ D ₆	80	60 h	75	34
5	Fe(acac) ₃	10	C ₆ D ₆	100	90 h	45	18
6	None	N/A	C ₆ D ₆	100	24 h	No productive reaction observed Slow decomposition of substrates at elevated temperature	
7	Zn(acac) ₂	1 equiv	C ₆ D ₆	100	24 h		
8	Zn(OTf) ₂	1 equiv	C ₆ D ₆	100	24 h		
9	FeCl ₂	1 equiv	C ₆ D ₆	100	24 h		
10	FeCp ₂	20	C ₆ D ₆	100	24 h		
11	Fe(OTf) ₂	1 equiv	C ₆ D ₆	100	24 h		
12	Fe(OTf) ₃	1 equiv	C ₆ D ₆	100	24 h		
13	Fe nanopowder (60-80 nm)	1 equiv	C ₆ D ₆	100	24 h		
14	Fe(acac) ₂	10	d ₈ -THF	100	24 h		
15	Fe(OTf) ₂	1 equiv	d ₈ -THF	100	24 h		
16	FeCl ₂	1 equiv	d ₈ -THF	100	24 h		

- a. Reaction is carried out in a sealed J-young tube with 20 mg of the substrate in 2 ml of solvent.
- b. Calculated by the amount of substrate consumed in the NMR spectrum of the crude reaction mixture.

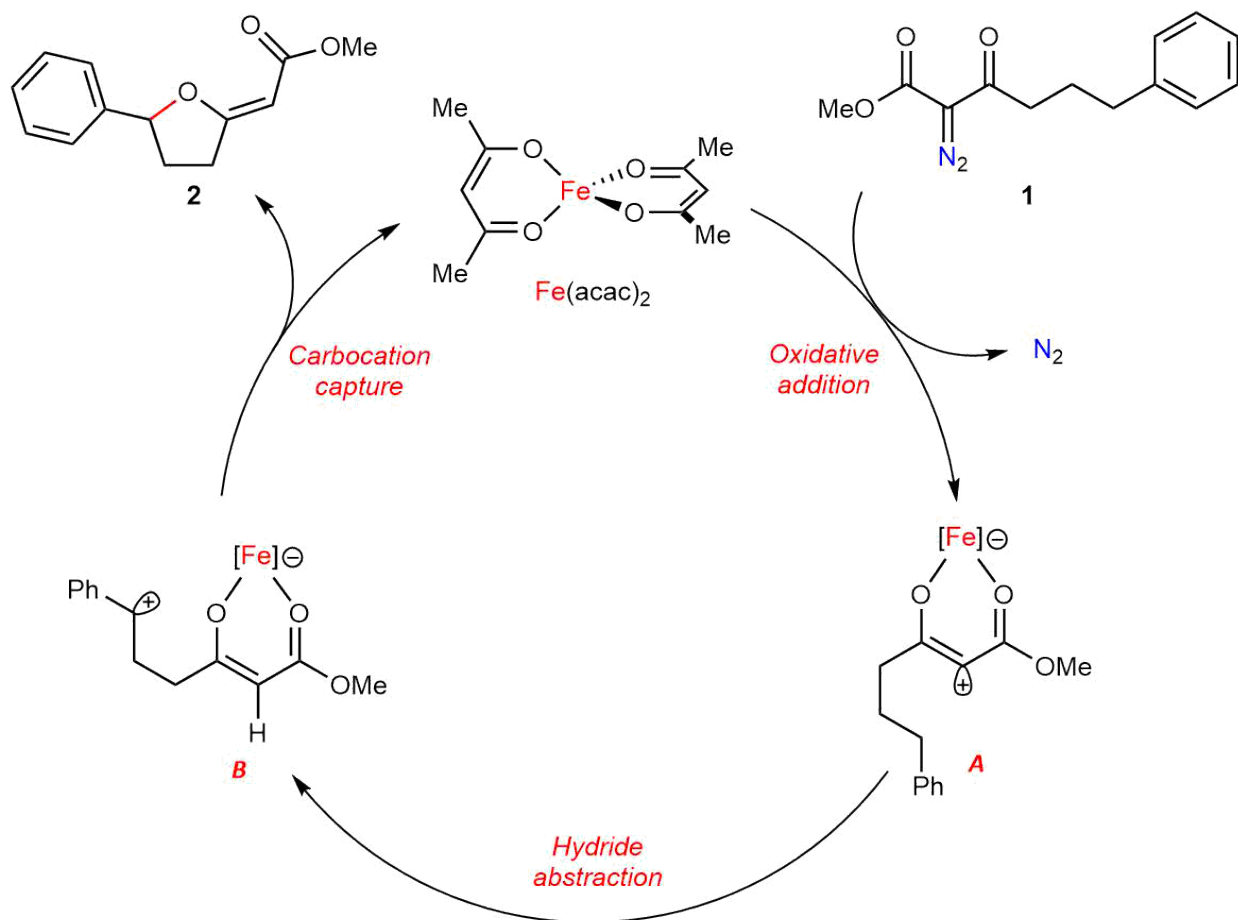
Table S2. Catalytic condition optimization

Entry	Cat. loading (mol%)	Temp. ($^{\circ}\text{C}$) ^a	Time	Conversion (%) ^b	NMR yield (%)
1	30	25	12 h	> 99	88
2	10	40	40 min	78	68
3	10	60	20 min	> 99	83
4	20	60	20 min	> 99	82
5	10	80	20 min	> 99	88
6	10	100	20 min	> 99	90

- Reaction is carried out in a sealed J-young tube with 20 mg of the substrate in 2 ml of solvent.
- Calculated by the amount of substrate consumed in the NMR spectrum of the crude reaction mixture.

Since full conversion is achieved with both 30 mol% and 10 mol% of $\text{Fe}(\text{acac})_2$ at room temperature ($25\text{ }^{\circ}\text{C}$) and $60\text{ }^{\circ}\text{C}$, respectively, these two setups will be used as the default catalytic conditions for substrate screening. Although heightened NMR yield is observed with higher reaction temperature, the increase (7%) is not significant enough to justify the harsher reaction condition ($100\text{ }^{\circ}\text{C}$). However, with substrates where the C–H bonds are harder to activate (ie. primary alkyl or electron deficient ones), further elevated temperature of $100\text{ }^{\circ}\text{C}$ is required for the cyclization to take place. It is also worth noting that increased catalyst loading (entry 3-4) with reaction conditions that already provides full conversion does not increase the NMR yield. Crude NMRs for condition screening can be found along with the characterization data.

Figure S1. Proposed hydride abstraction pathway

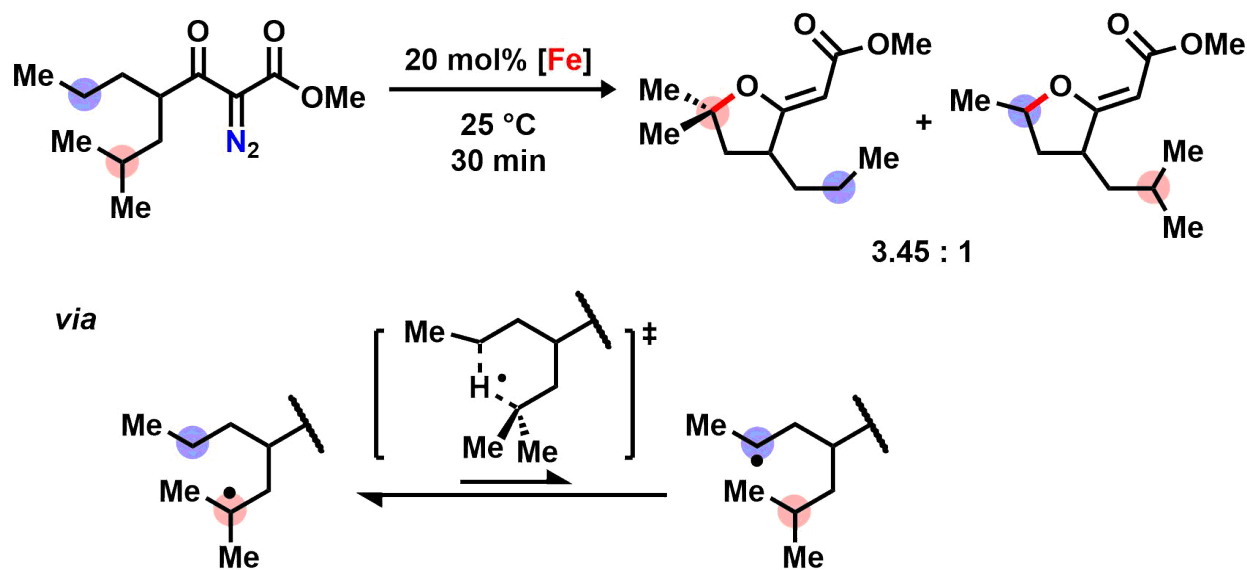


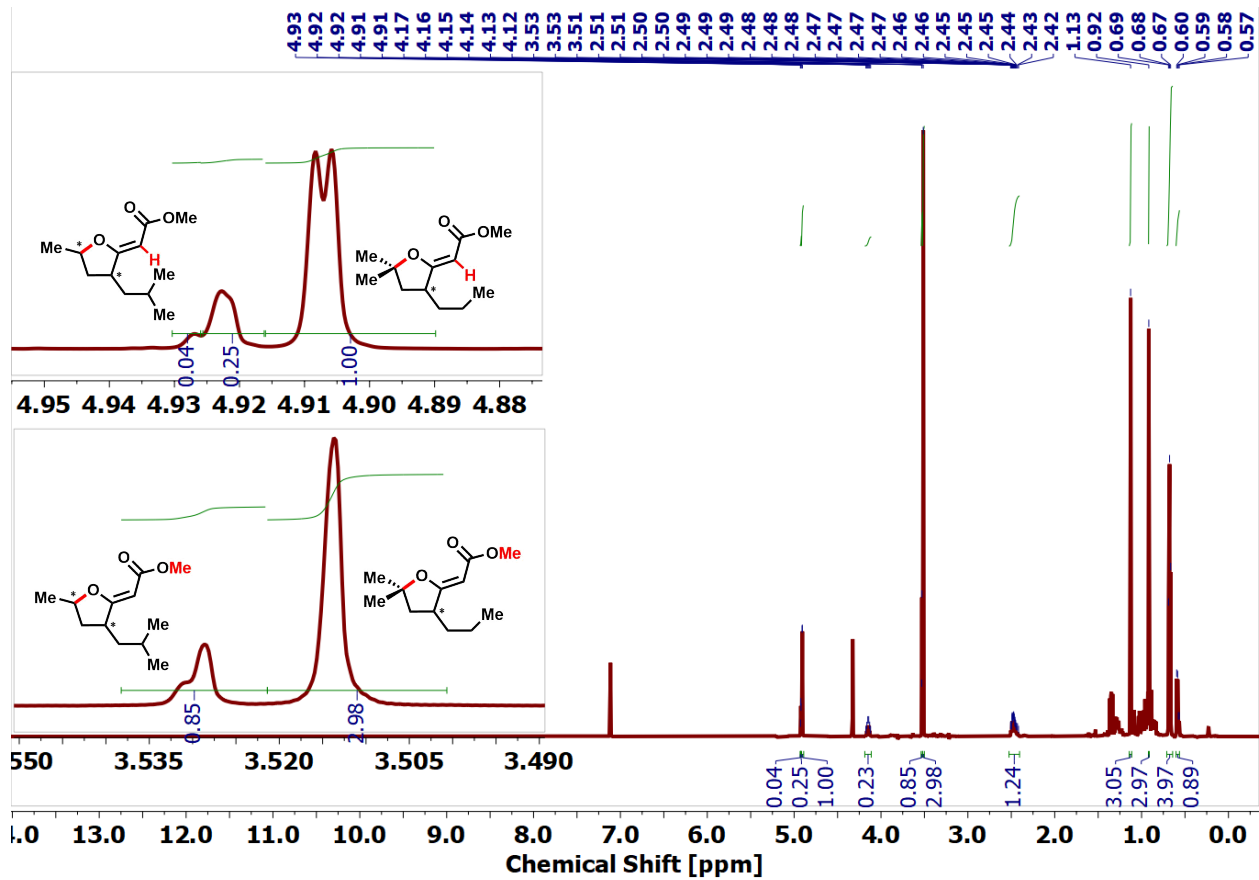
Proposed alternative mechanism via C–H heterolysis. *Fe*-center remains ferrous state throughout as a Lewis-acid catalyst. The mechanism is unlikely due to:

1. Redox-innocent $\text{Zn}(\text{acac})_2$ as a Lewis acid with similar coordination sphere does not mediate the alkoxylation reaction (*vide supra*).
2. Only a small, negative slope ($\rho = -0.30$) is observed in the Hammett analysis (*vide infra*).
3. Spin density distribution of the optimized structure of intermediate A shows strong spin delocalization on the vinyl-C, inconsistent with the vinyl carbocation electronic structure proposed.

Figure S2. Analysis of intramolecular competition experiment

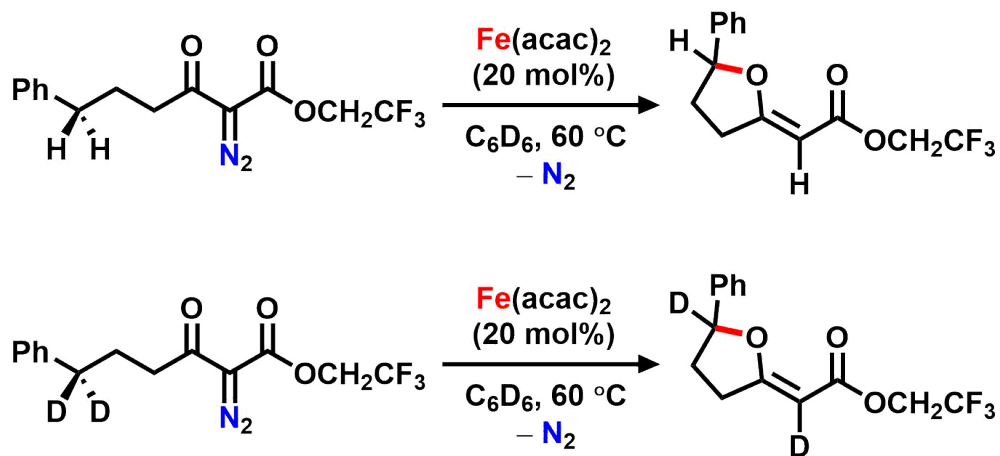
With both secondary and tertiary C–H bonds poised for activation, the substrate herein can be fully cyclized at room temperature (25 °C) upon treatment of 20 mol% of Fe(acac)₂ within 30 min. Despite short reaction time, both products resulting from the activation of secondary and tertiary C–H bonds are observed in the final reaction mixture by ¹H NMR spectroscopy with a ratio of 3.45:1. Given the long reaction time (12 h) and higher catalyst loading (30 mol%) of Fe(acac)₂ required to fully convert secondary C–H bonds at room temperature (*vide infra*), we hypothesized that the 1,5-HAT between the initially generated tertiary carbon radical and the secondary C–H bonds is responsible for the formation a mixture of products, and therefore this experiment is not conclusive toward the intramolecular chemoselectivity between activation of secondary and tertiary C–H bonds





^1H NMR spectrum upon acidic workup followed by a silica plug.

Figure S3. Analysis of isotope-labelling experiment



^1H NMR spectra after purification by silica column chromatography:

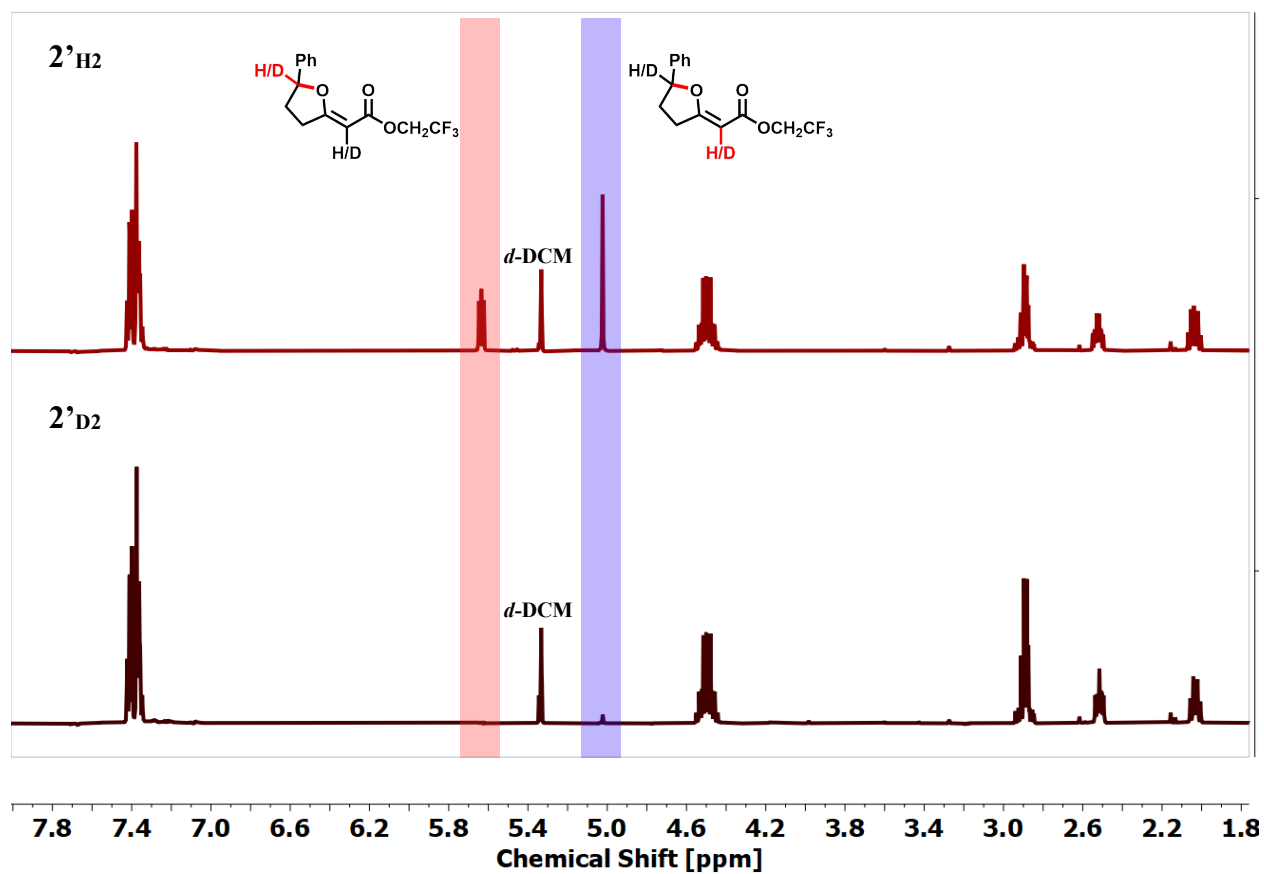
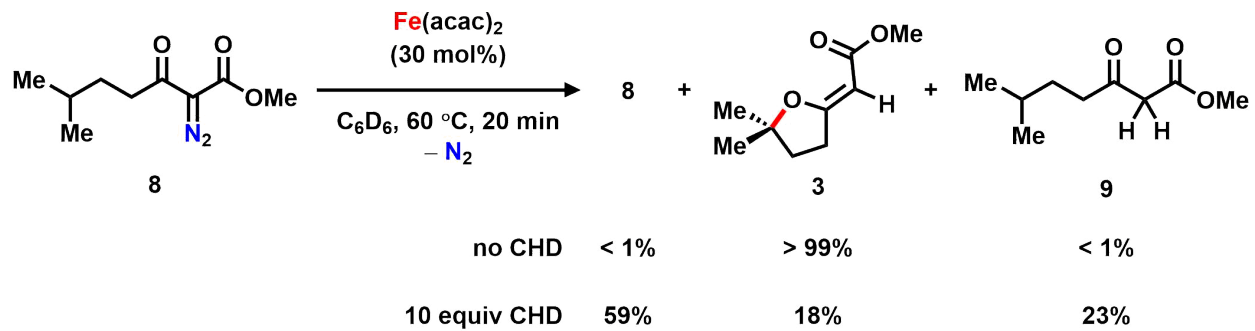
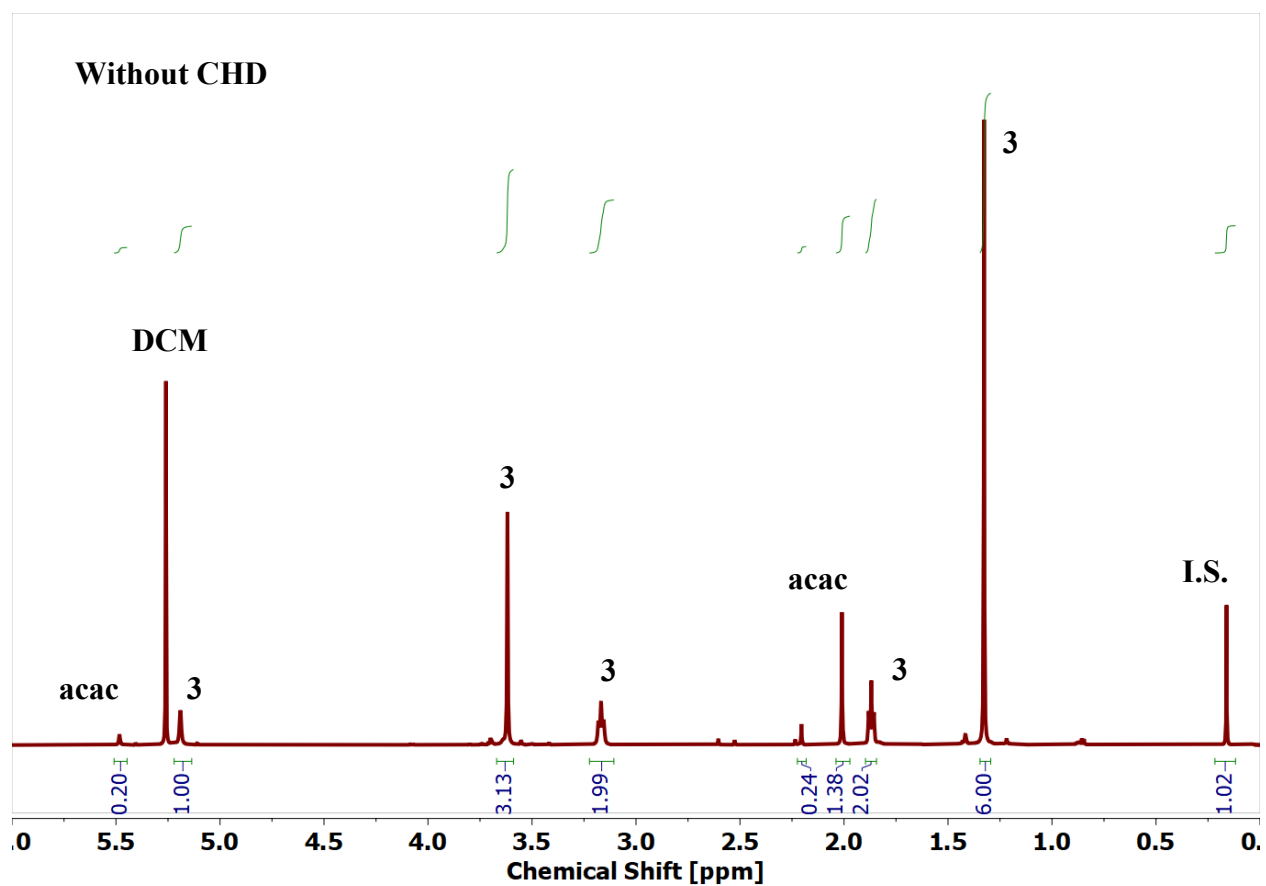
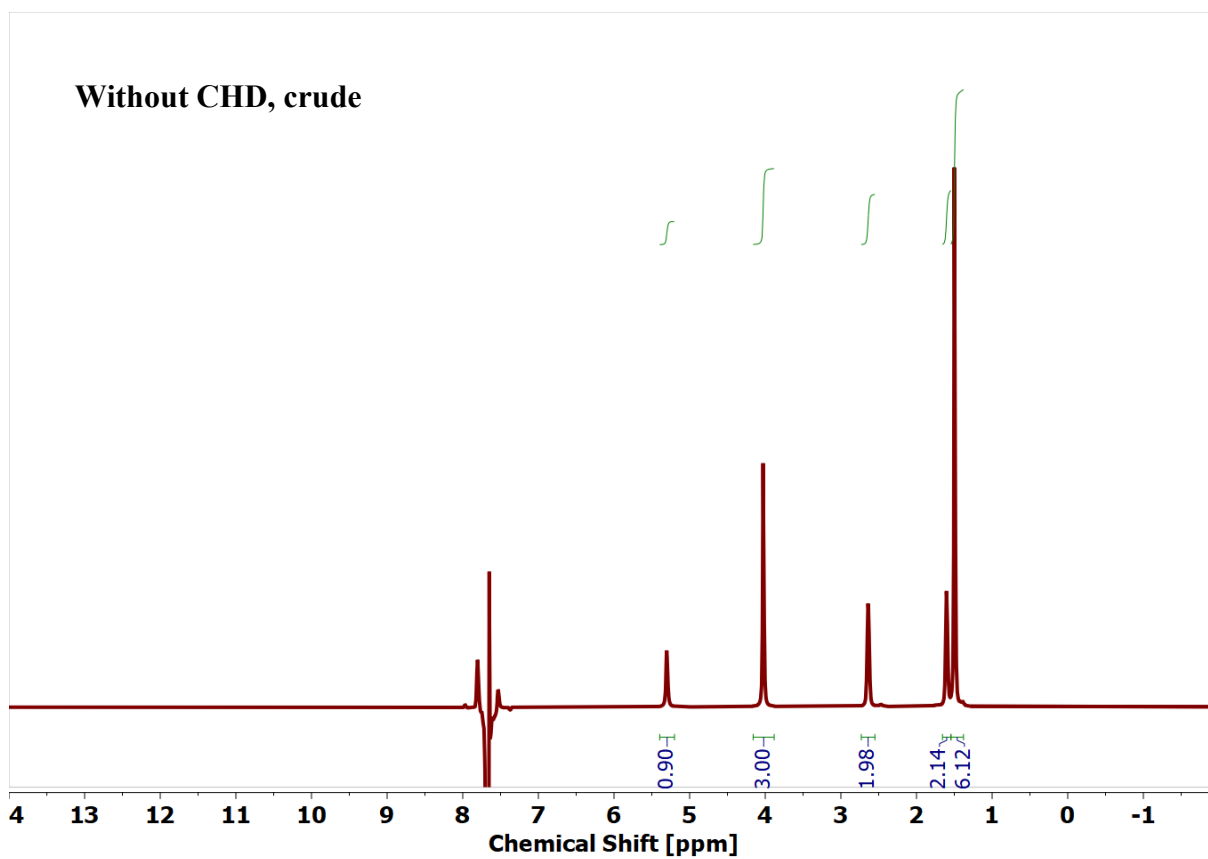
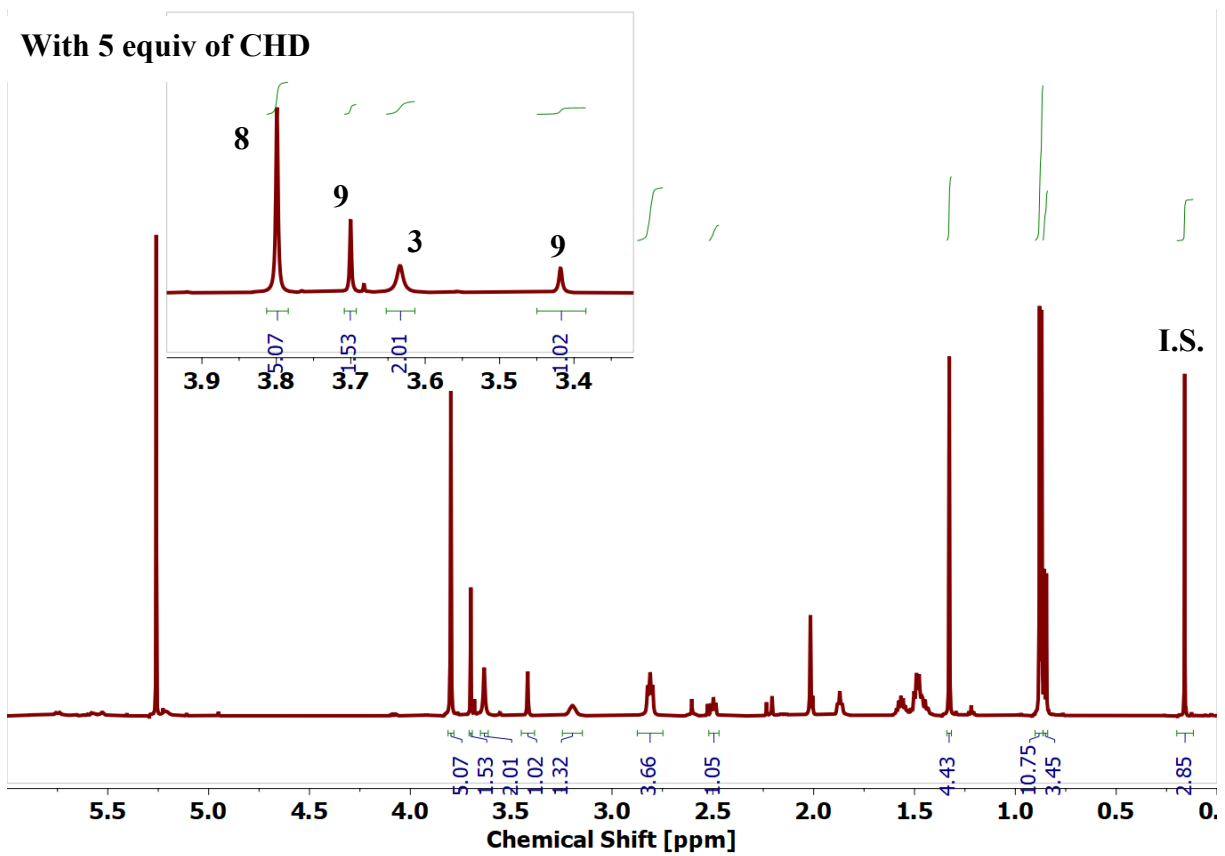


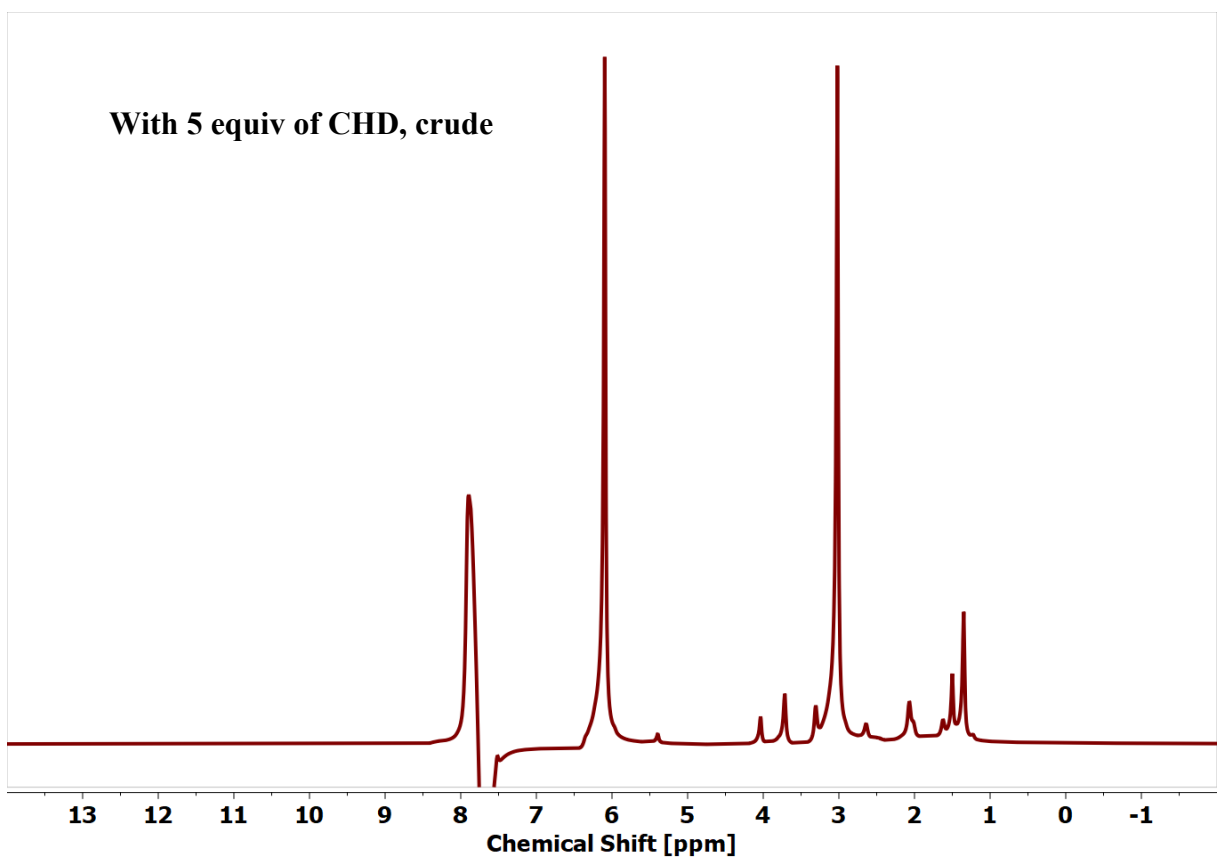
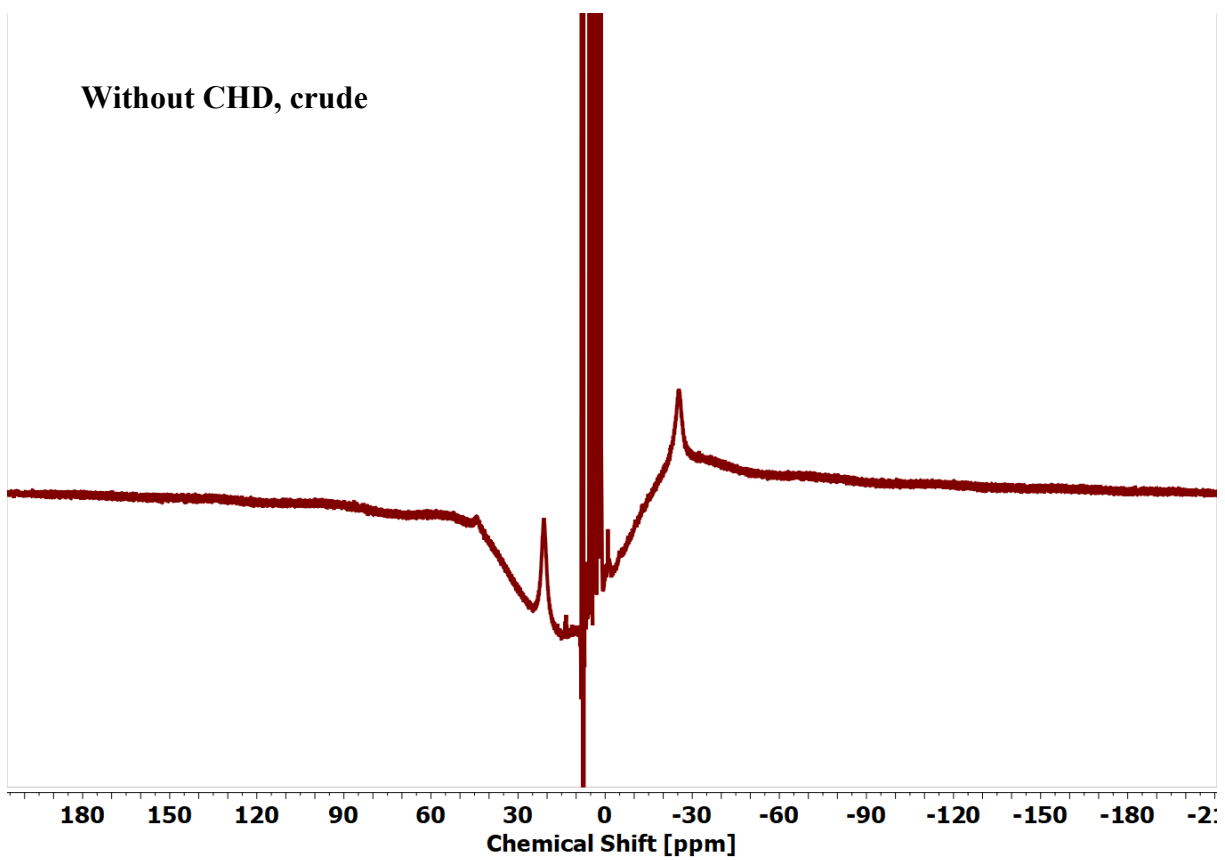
Figure S4. Analysis of CHD quenching experiment

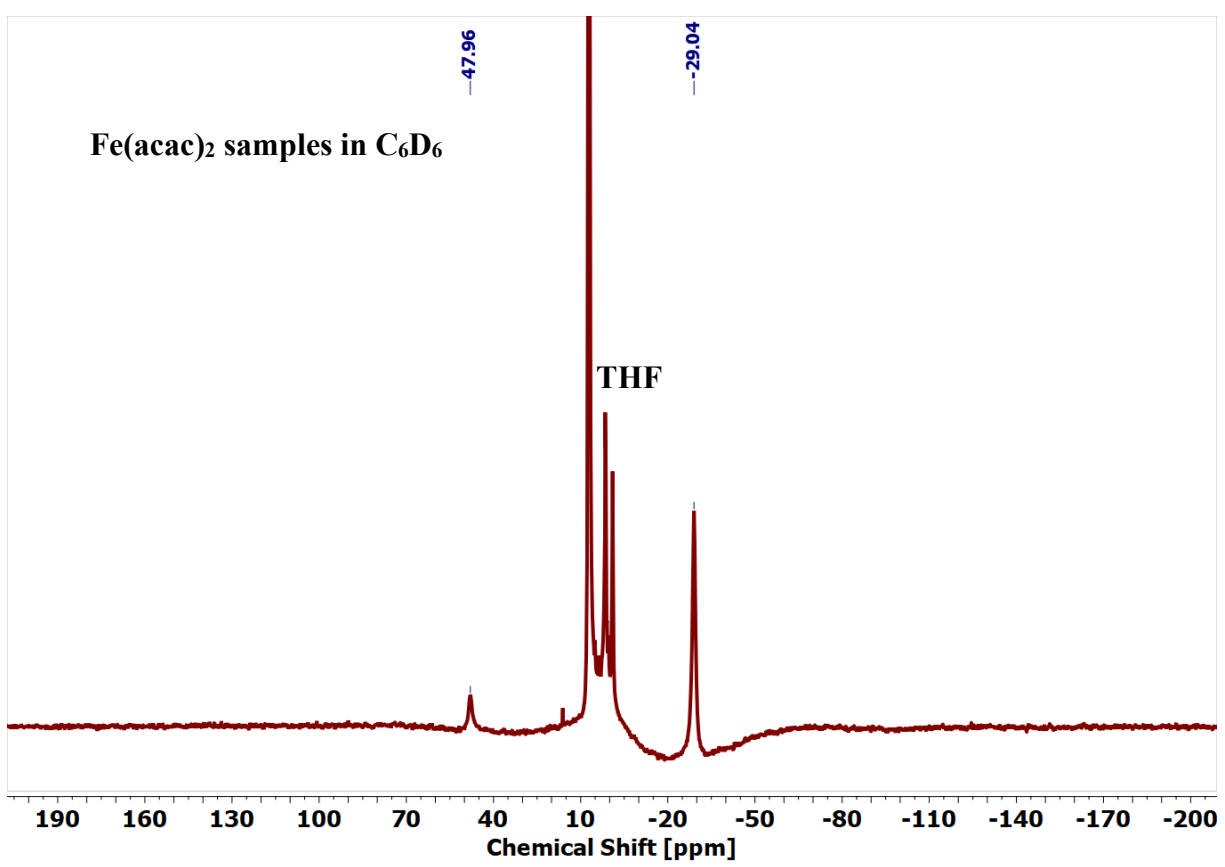
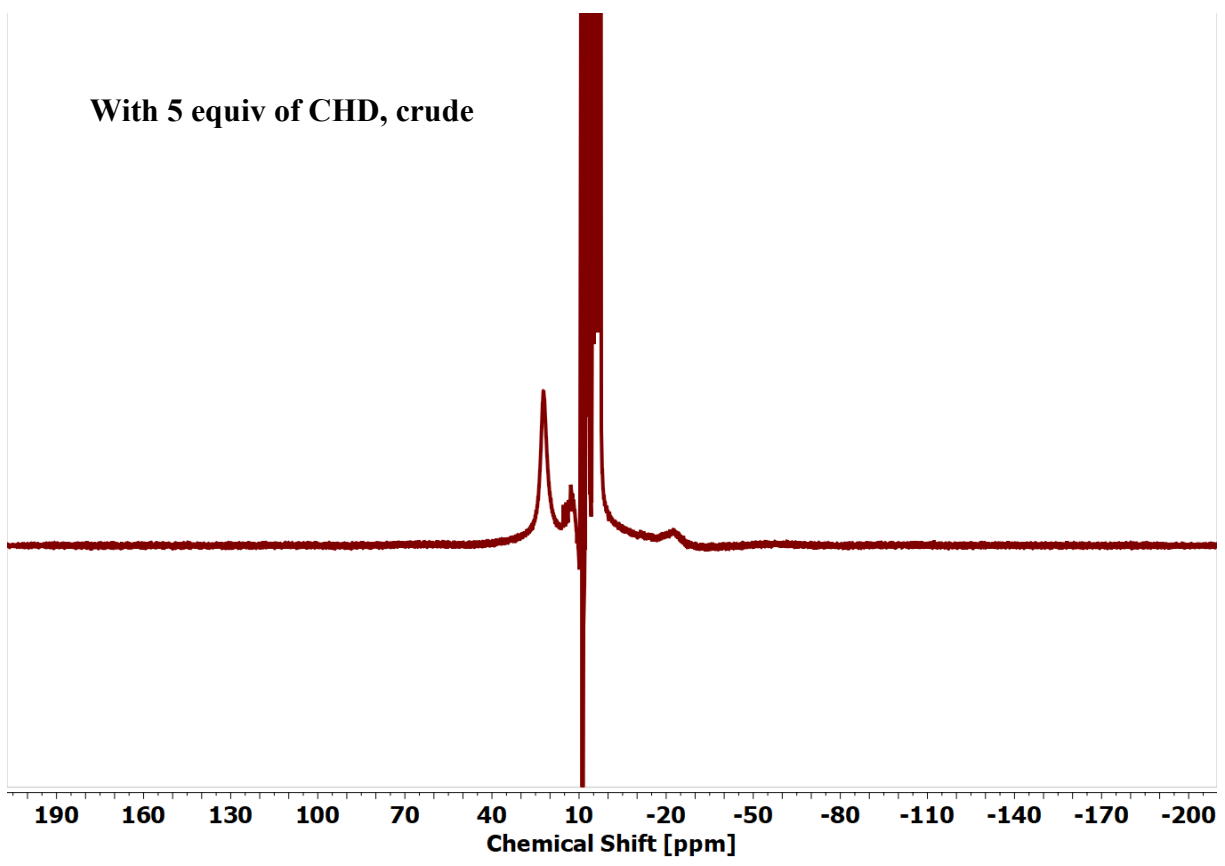


^1H NMR spectra after quick acidic workup:









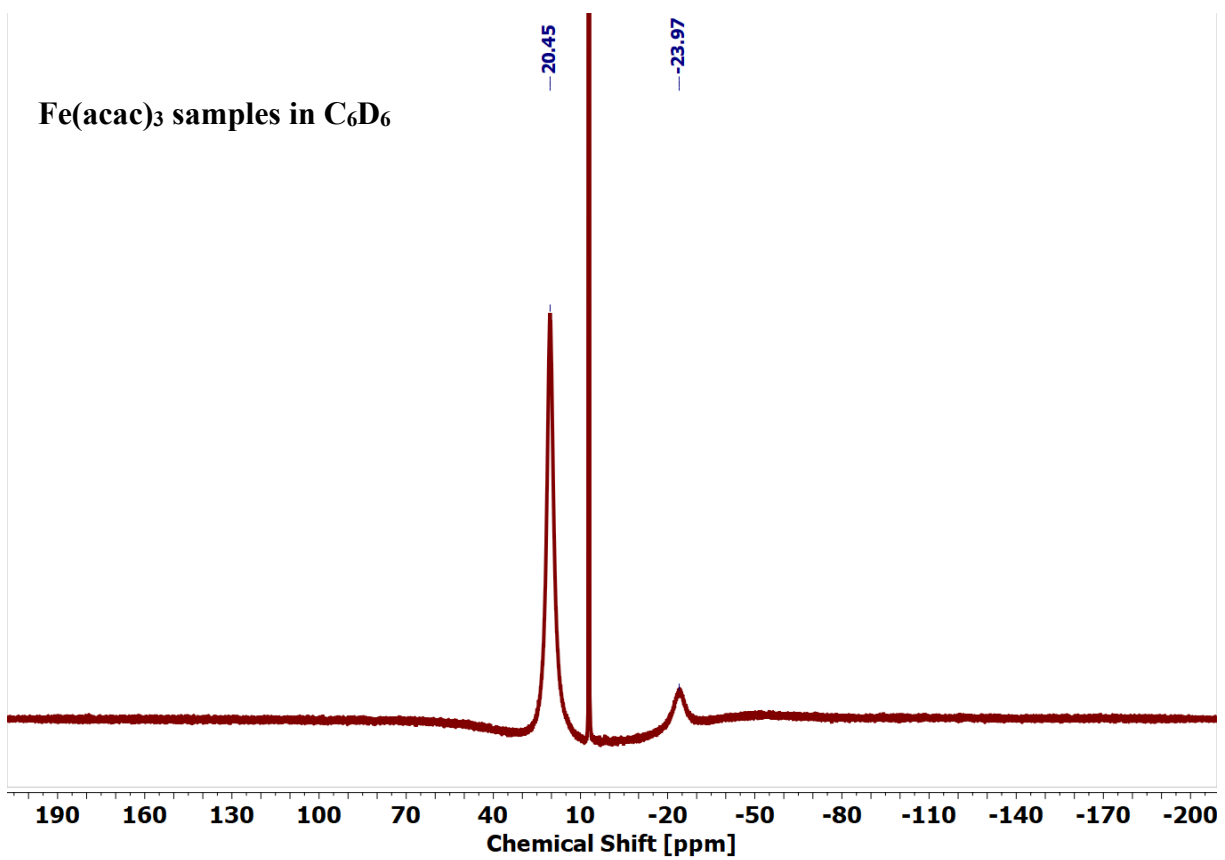
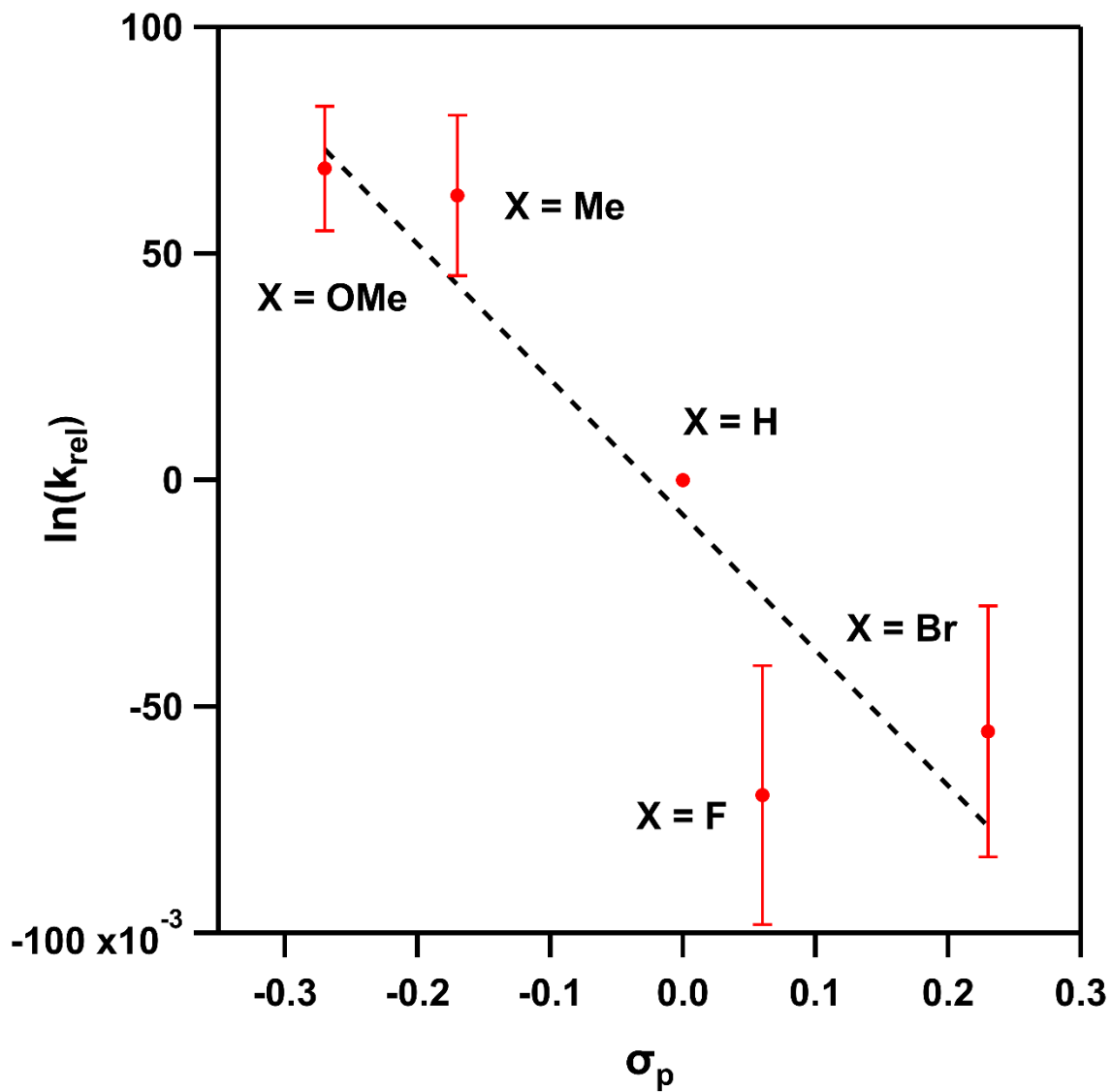
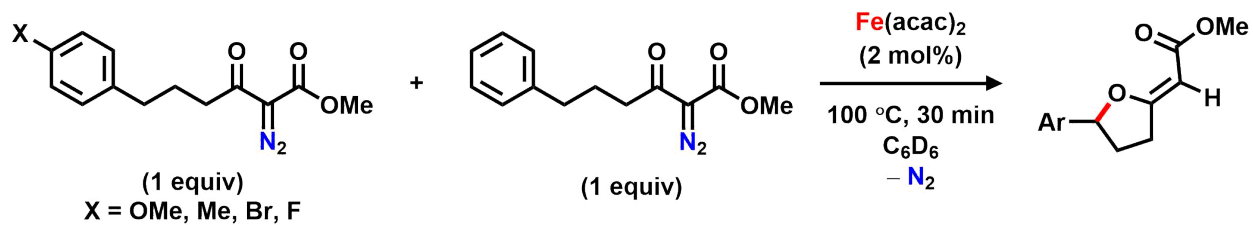
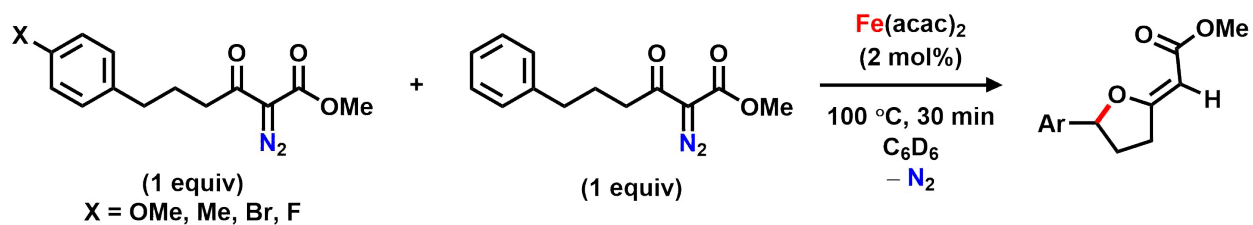


Figure S5. Hammett analysis

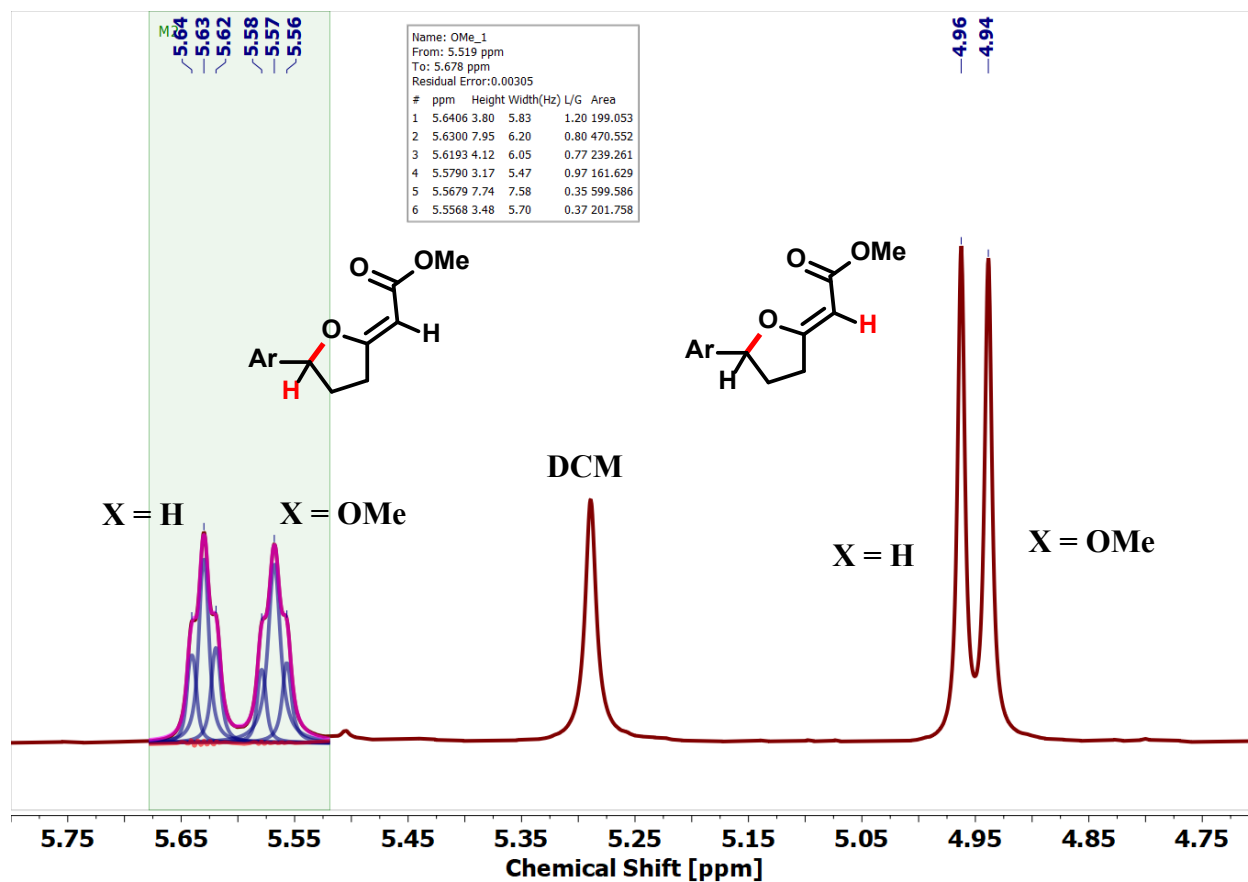


Analysis for constructing Hammett plot²



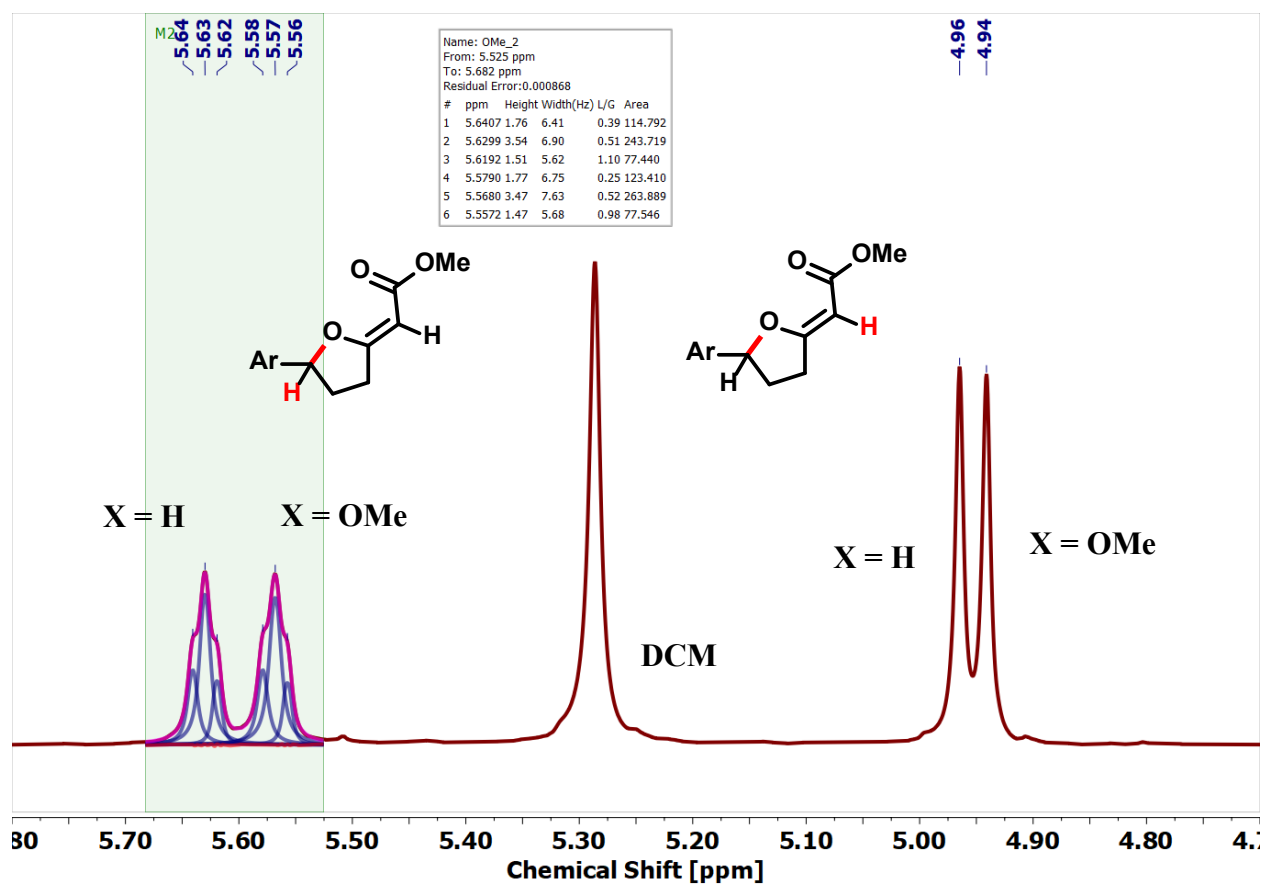
X	σ_p	$k_{\text{rel}}(1)$	$k_{\text{rel}}(2)$	$k_{\text{rel}}(3)$	$k_{\text{rel}}(\text{avg})$	$\ln(k_{\text{rel}})$
OMe	-0.27	1.060	1.066	1.088	1.071 ± 0.015	0.069 ± 0.014
Me	-0.17	1.069	1.044	1.081	1.065 ± 0.019	0.063 ± 0.018
F	0.06	0.903	0.943	0.953	0.933 ± 0.027	-0.070 ± 0.029
Br	0.23	0.965	0.956	0.916	0.946 ± 0.026	-0.056 ± 0.028

X = OMe (run 1)



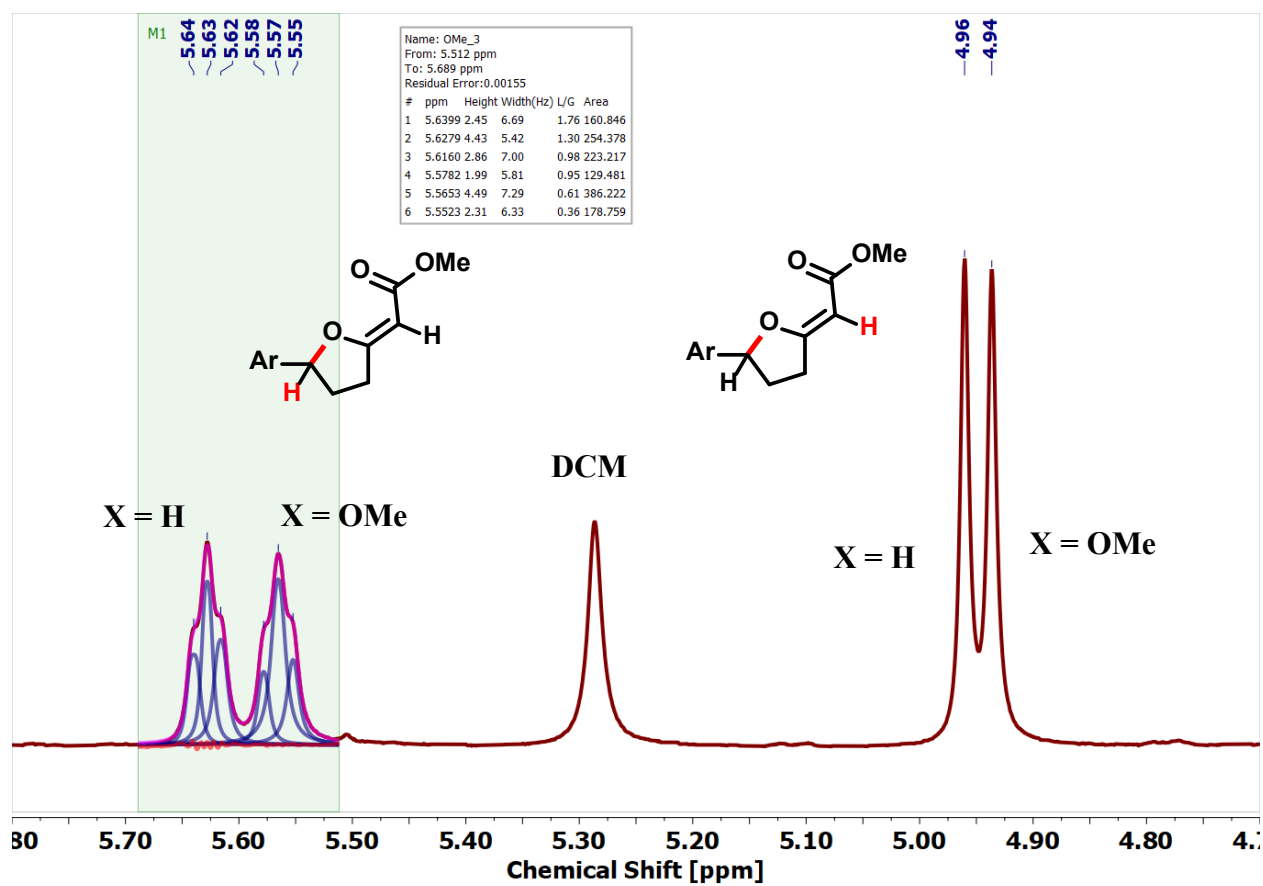
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	908.866	1.060	0.31%
5.57 (t)	962.973		

X = OMe (run 2)



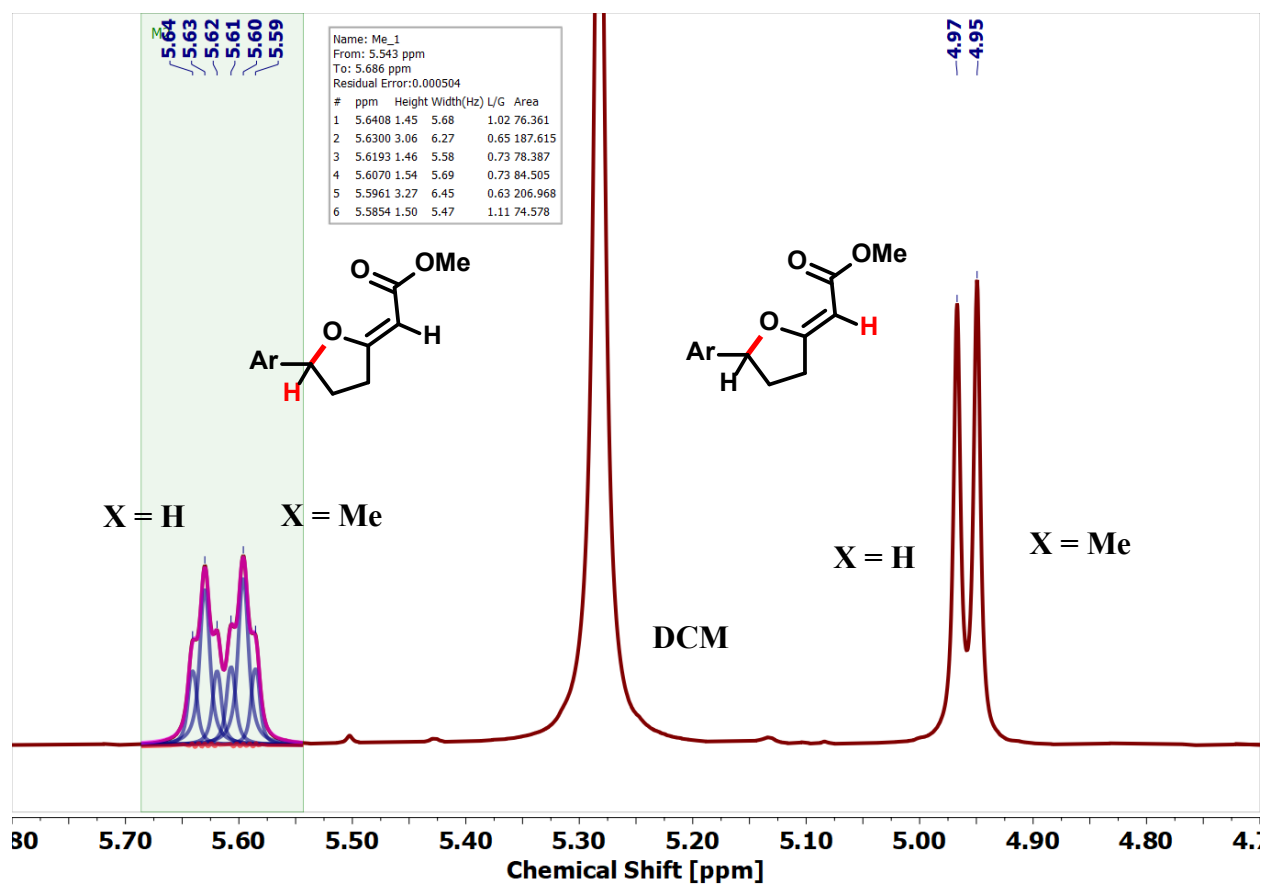
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	435.951	1.066	0.09%
5.57 (t)	464.845		

X = OMe (run 3)



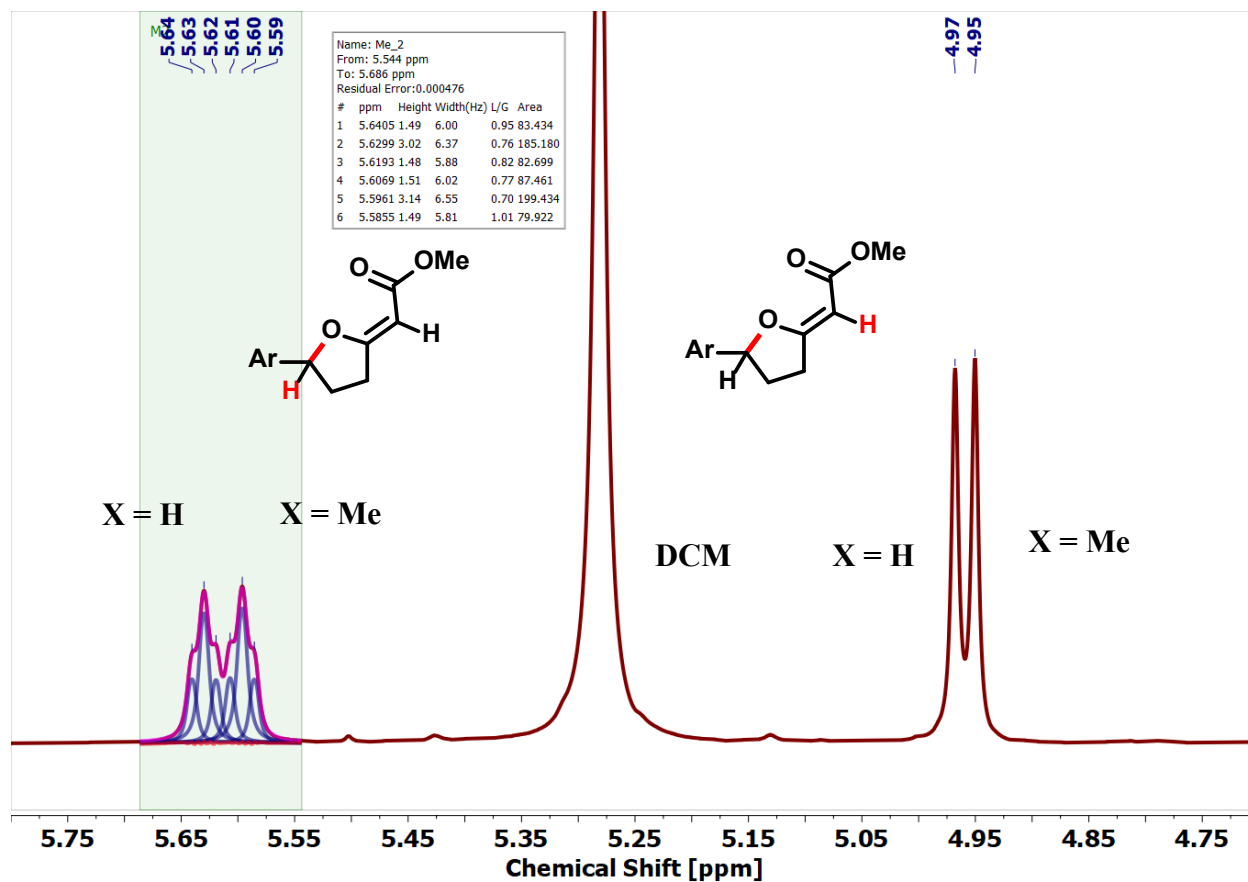
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	638.441	1.088	0.16%
5.57 (t)	694.462		

X = Me (run 1)



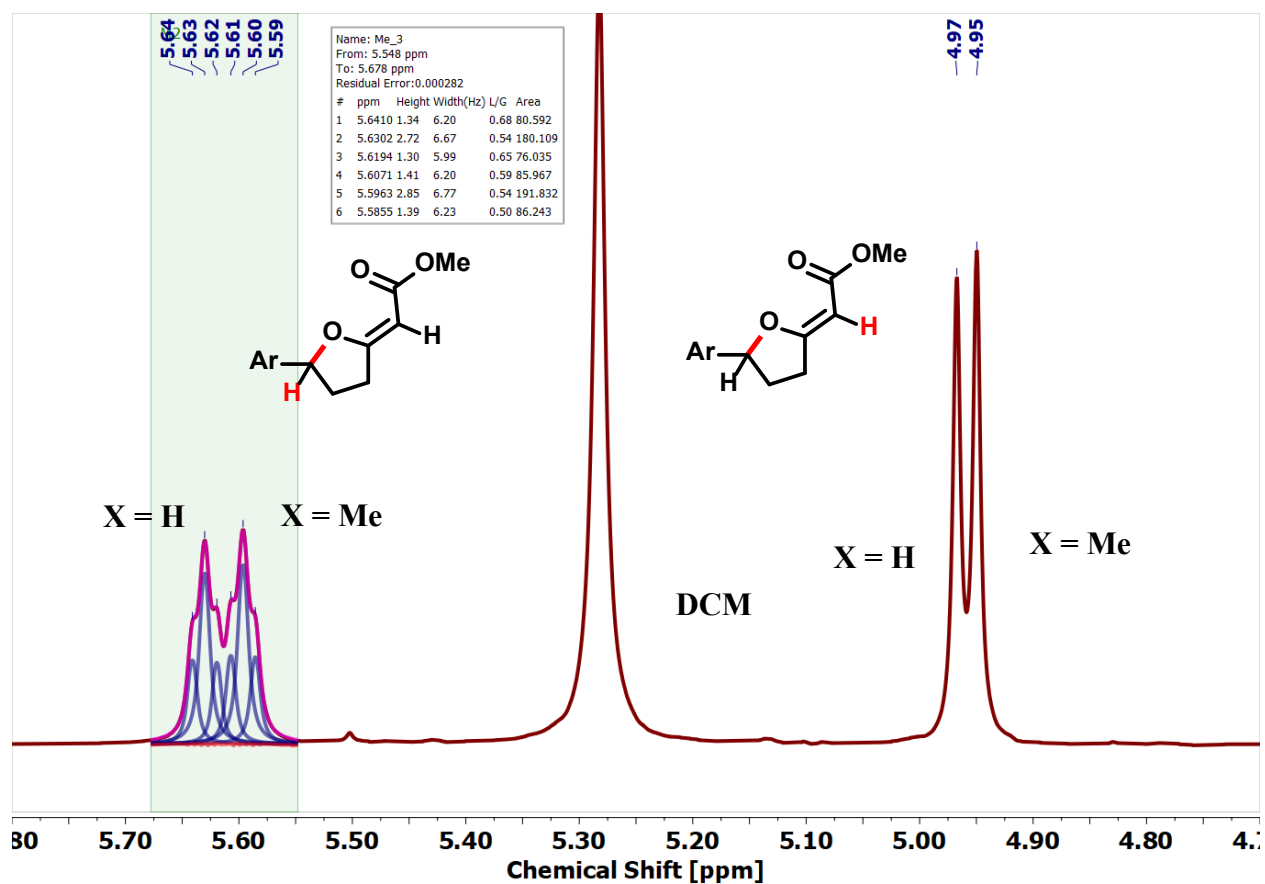
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	342.363	1.069	0.05%
5.60 (t)	366.051		

X = Me (run 2)



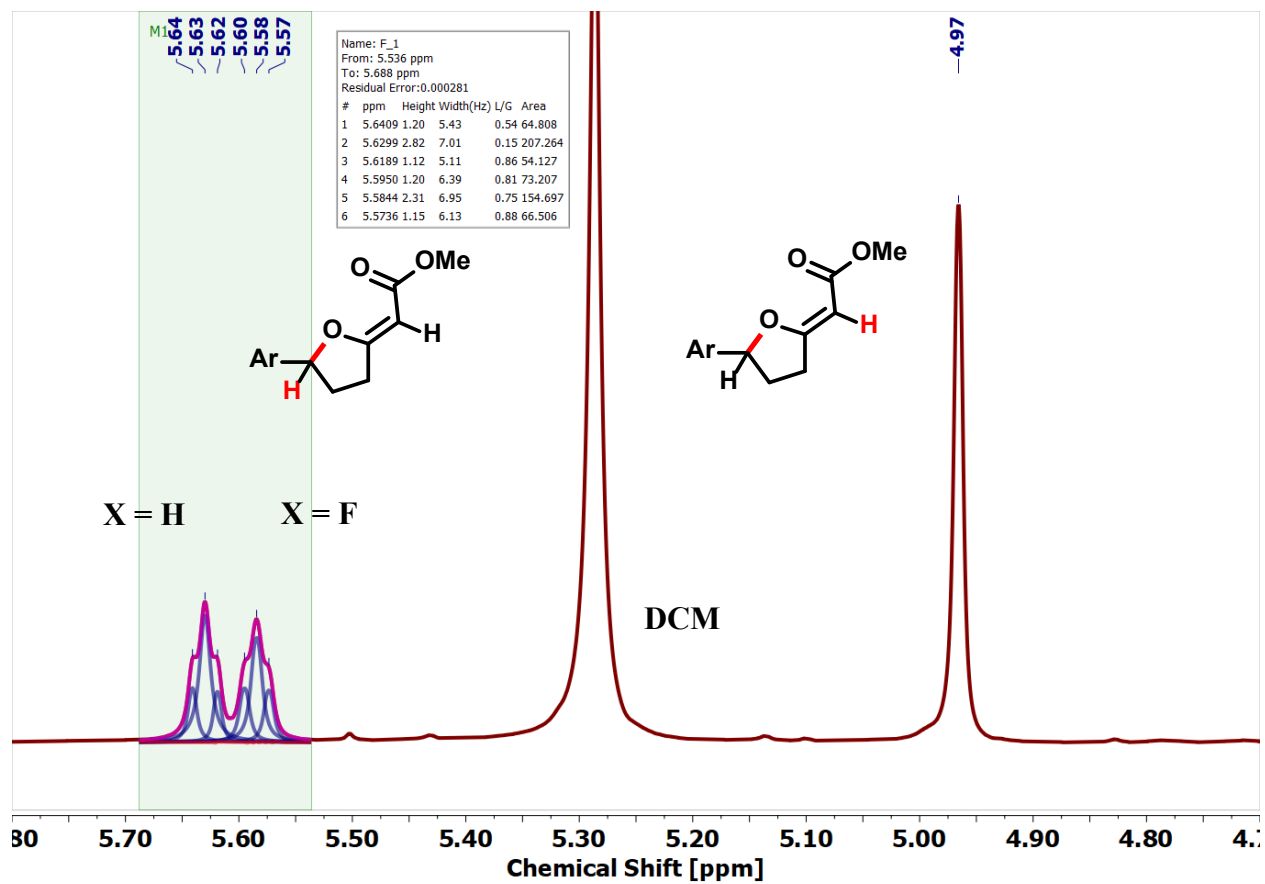
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	351.313	1.044	0.05%
5.60 (t)	366.817		

X = Me (run 3)



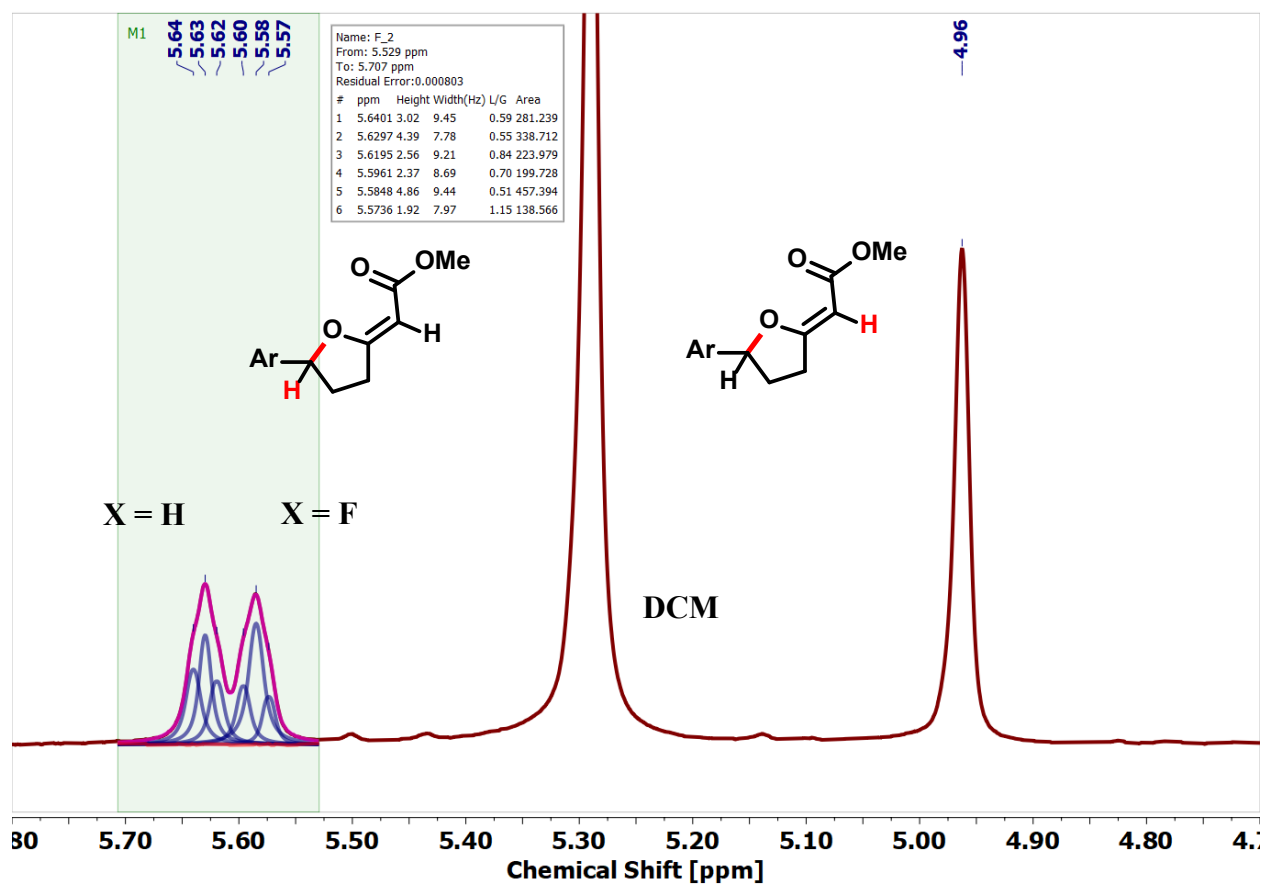
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	336.736	1.081	0.03%
5.60 (t)	364.042		

X = F (run 1)



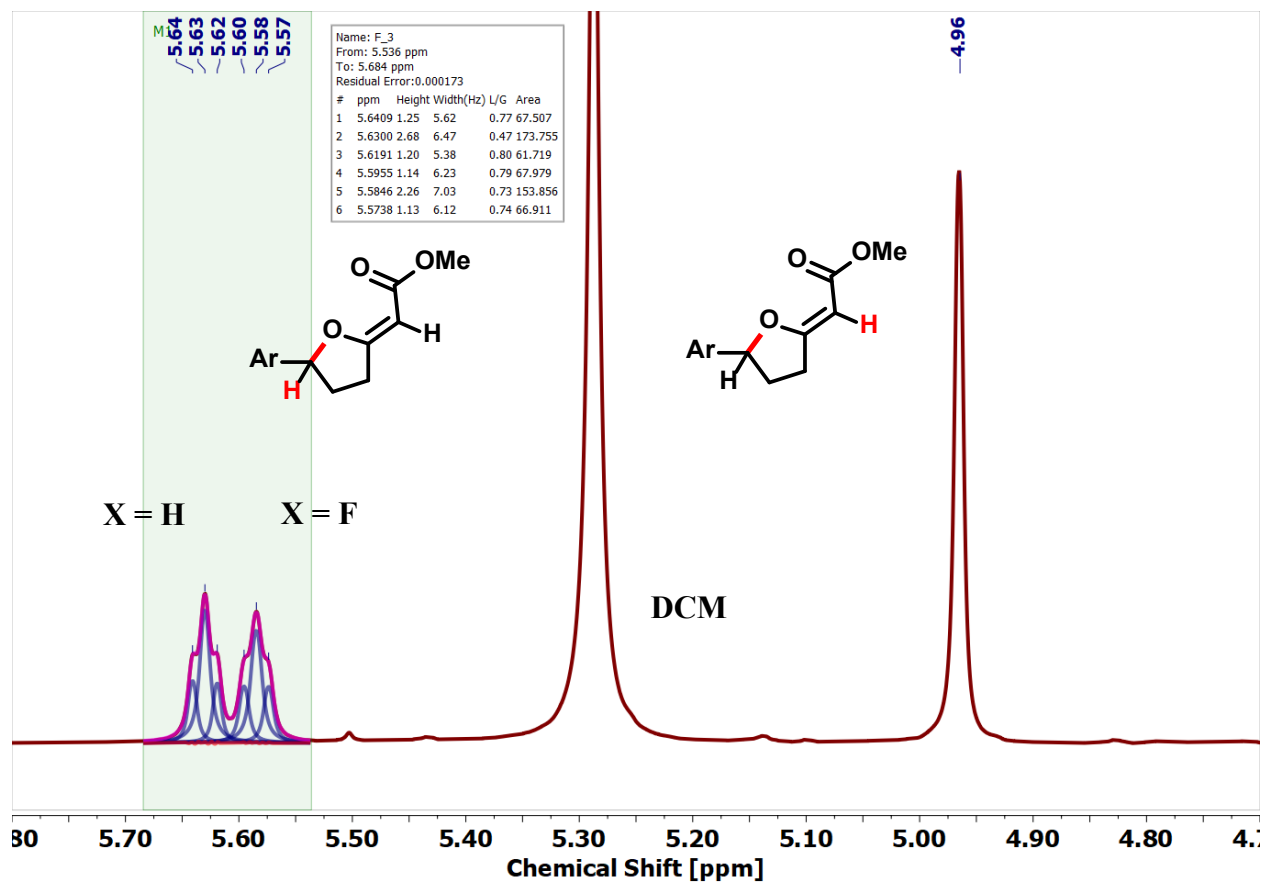
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	326.199	0.903	0.03%
5.58 (t)	294.41		

X = F (run 2)



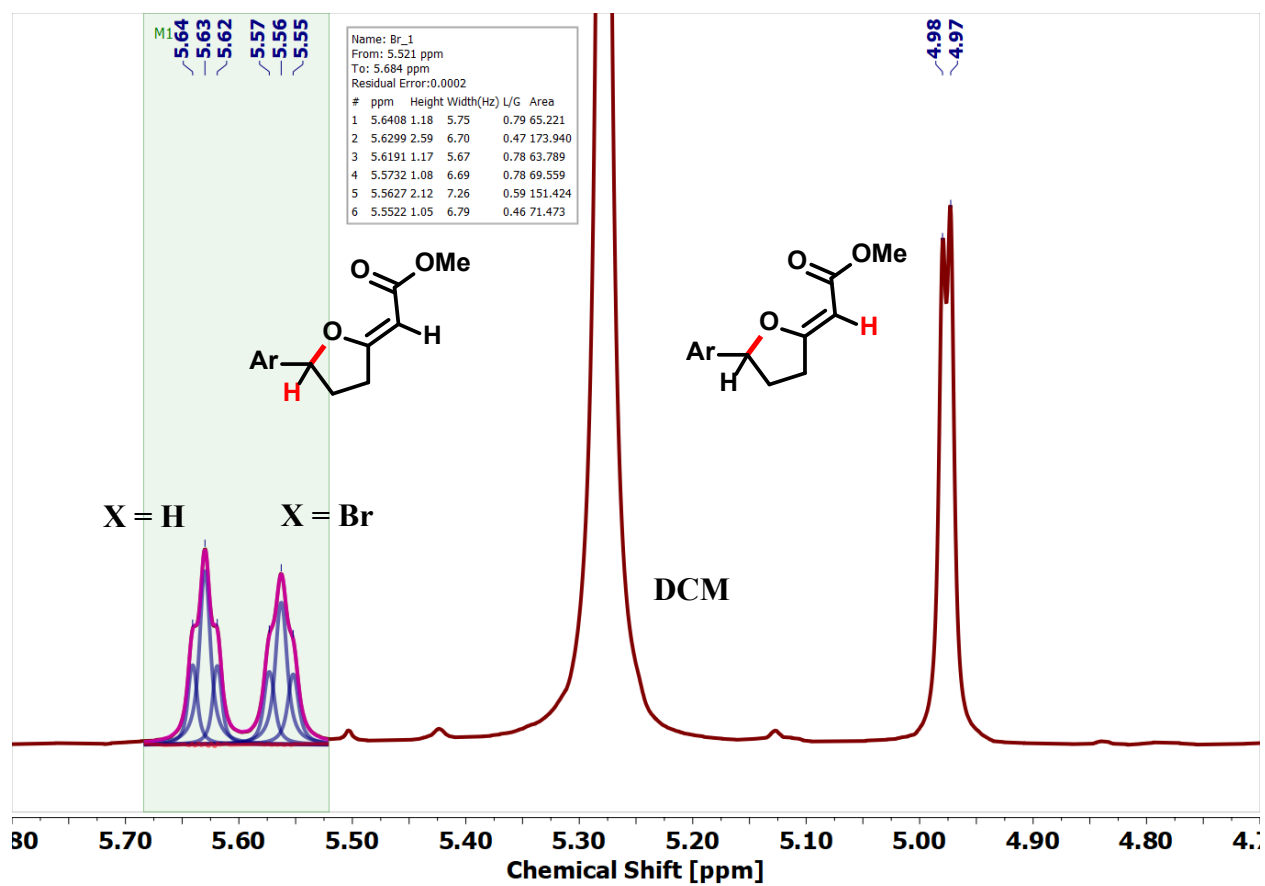
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	843.93	0.943	0.08%
5.58 (t)	795.688		

X = F (run 3)



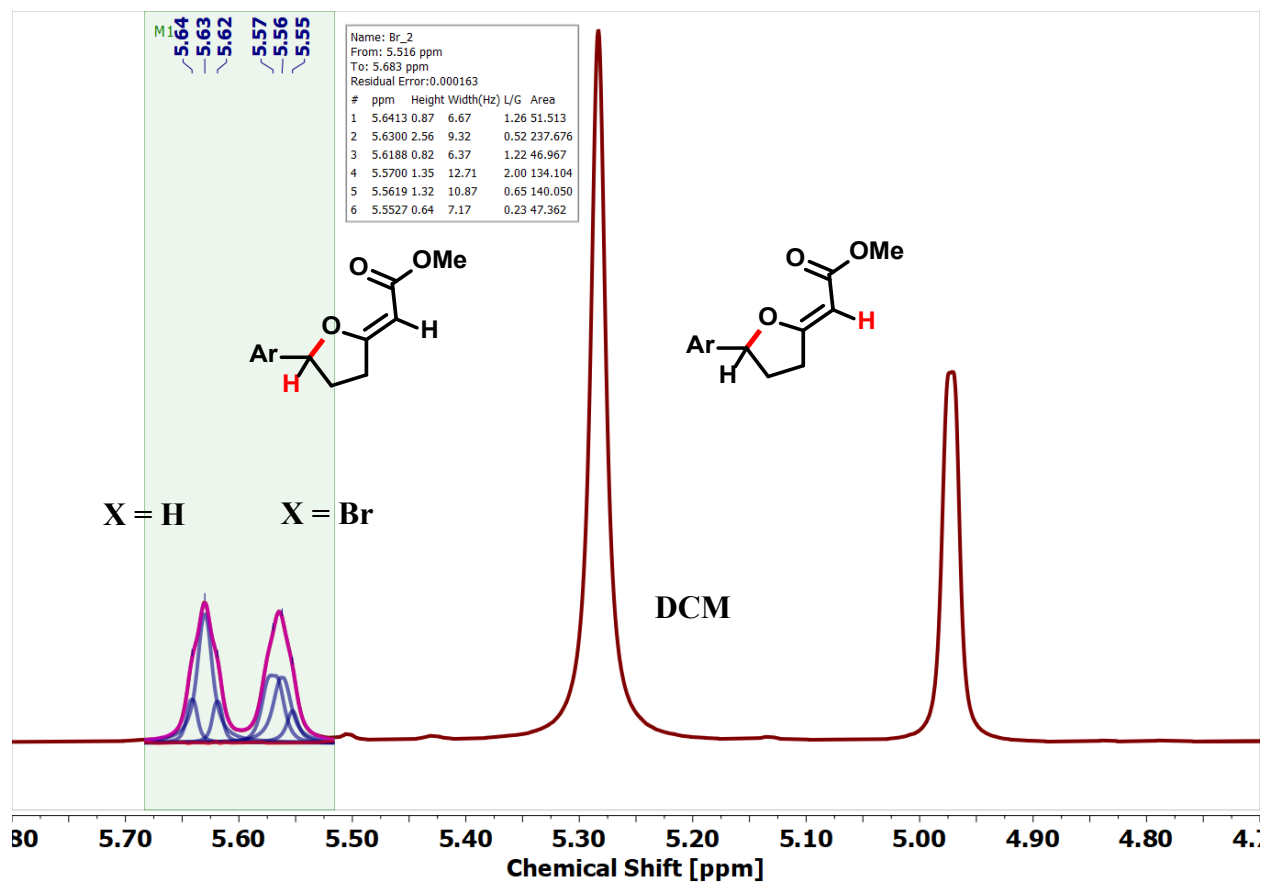
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	302.981	0.953	0.02%
5.58 (t)	288.746		

X = Br (run 1)



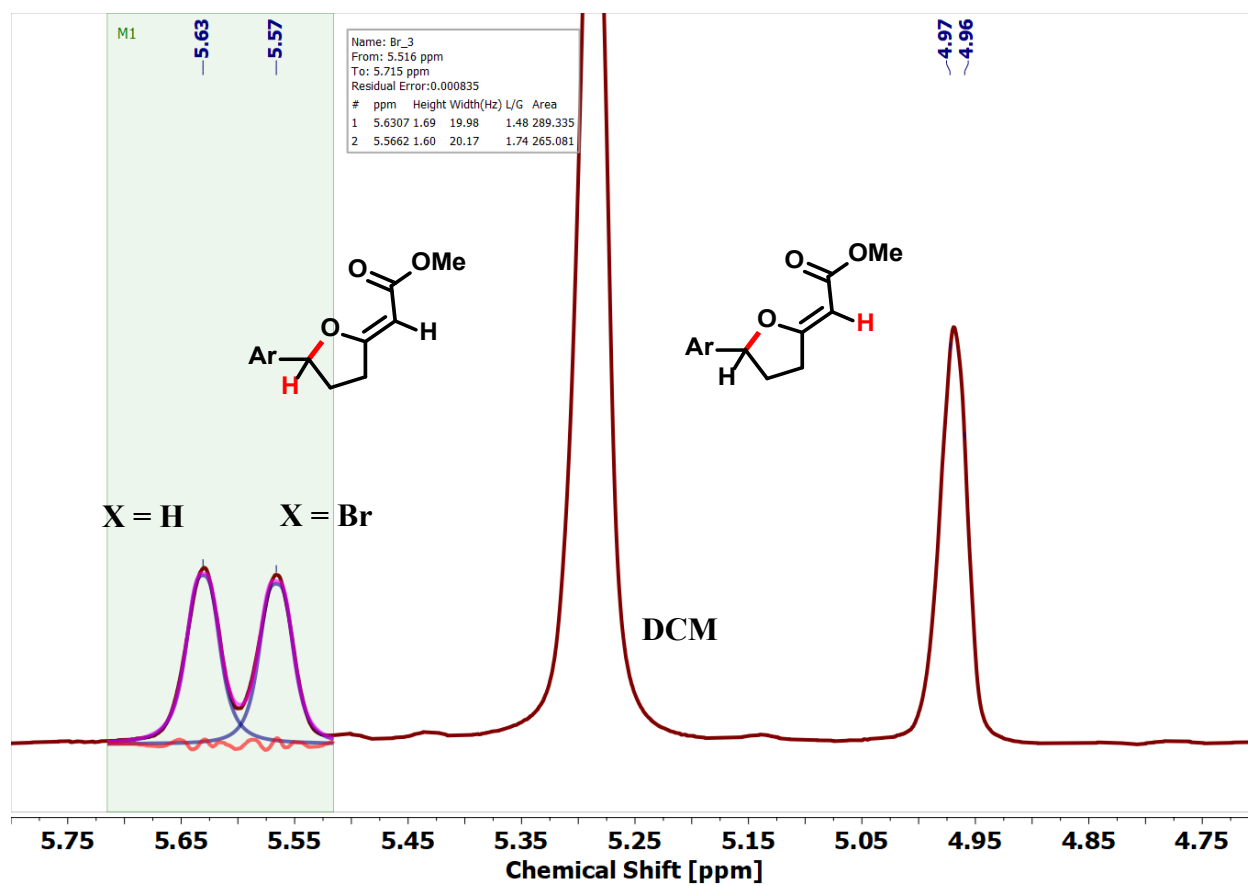
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	302.95	0.965	0.02%
5.56 (t)	292.456		

X = Br (run 2)



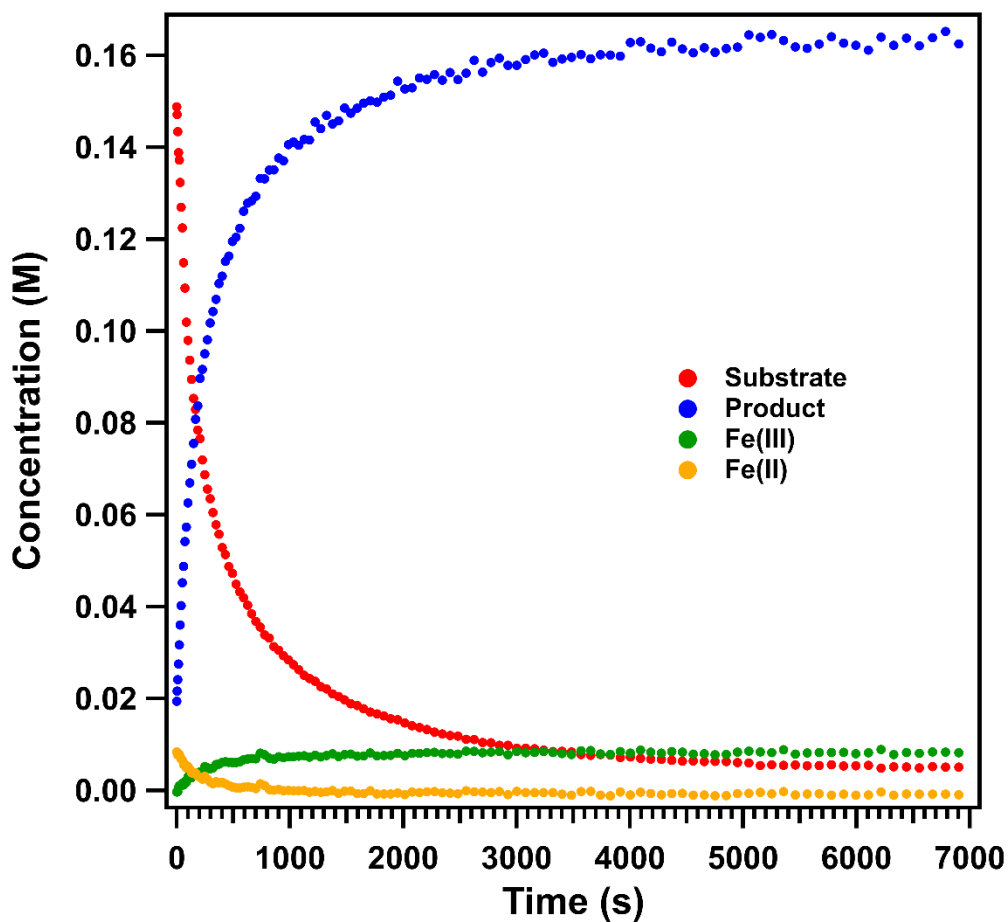
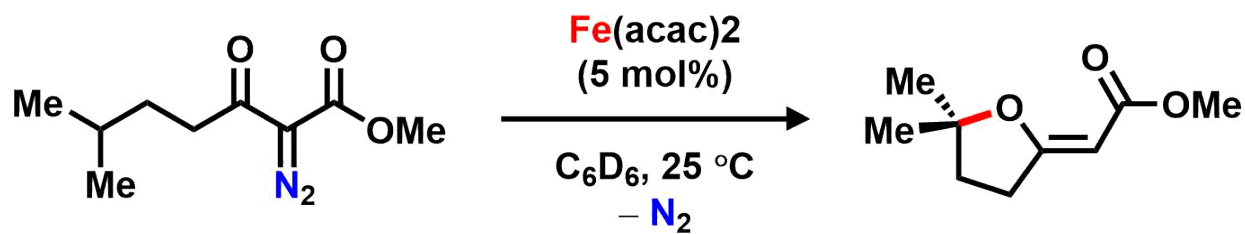
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (t)	336.156	0.956	0.02%
5.56 (t)	321.516		

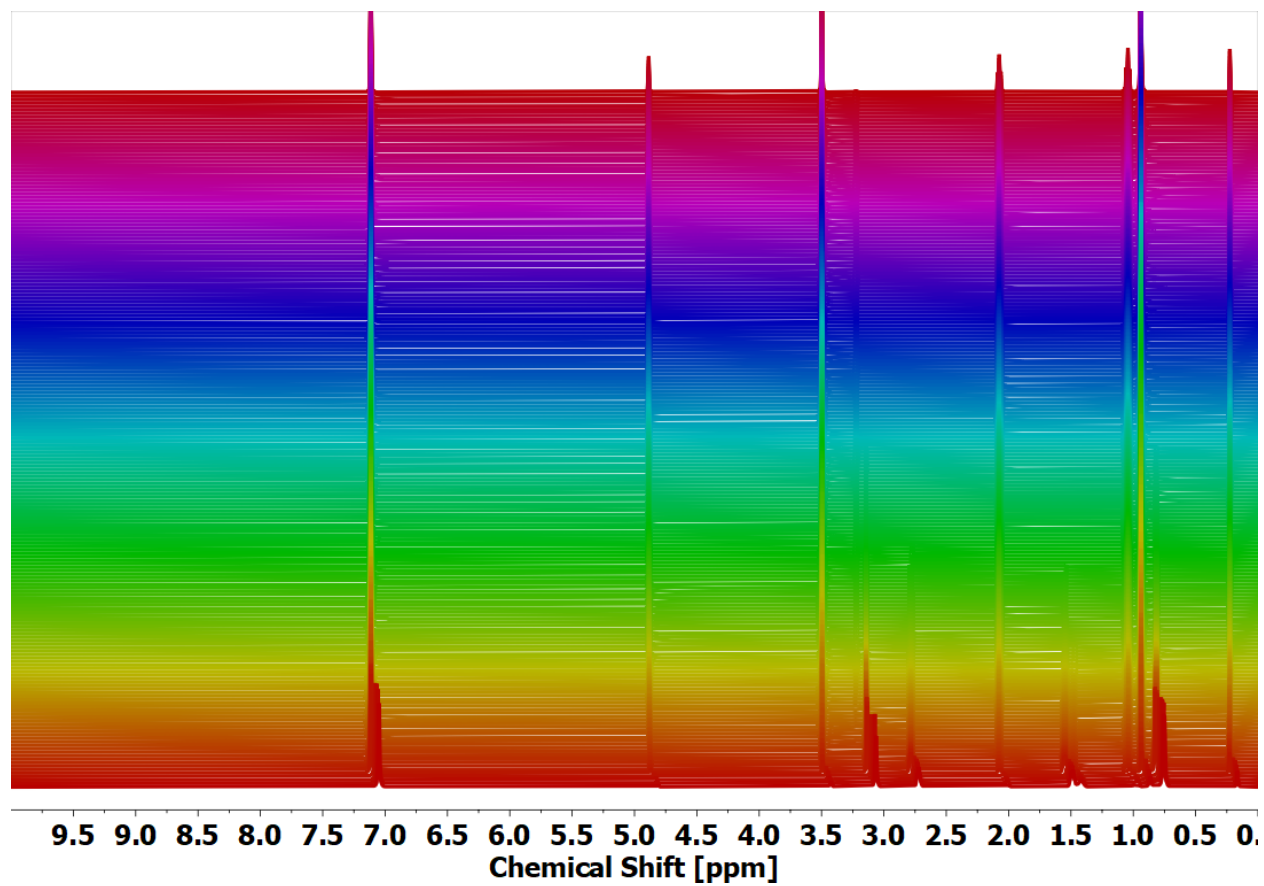
X = Br (run 3)



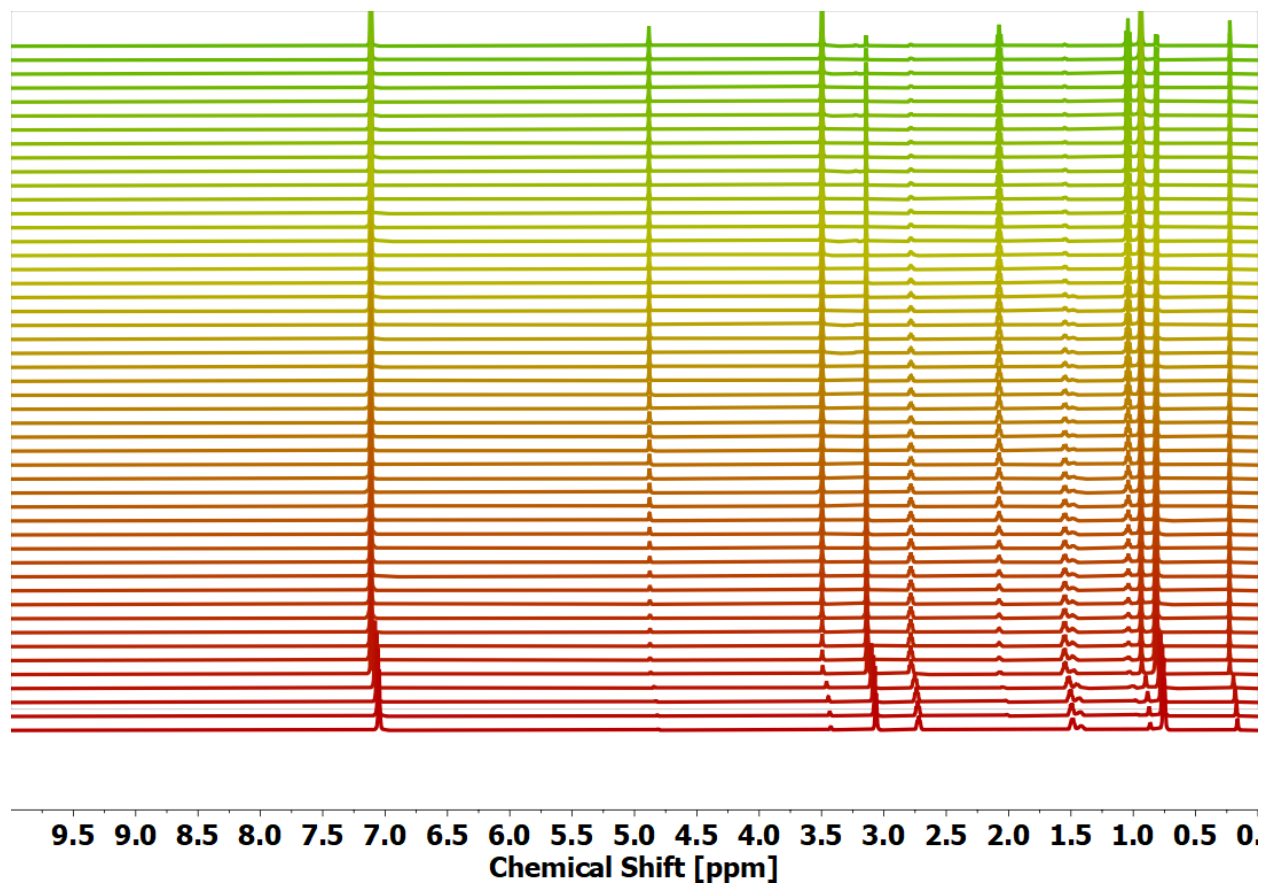
Chemical Shift (ppm)	Area	k_{rel}	Residue
5.63 (apparent s.)	289.335	0.916	0.08%
5.57 (apparent s.)	265.081		

Figure S6. Analysis of reaction concentration profiles

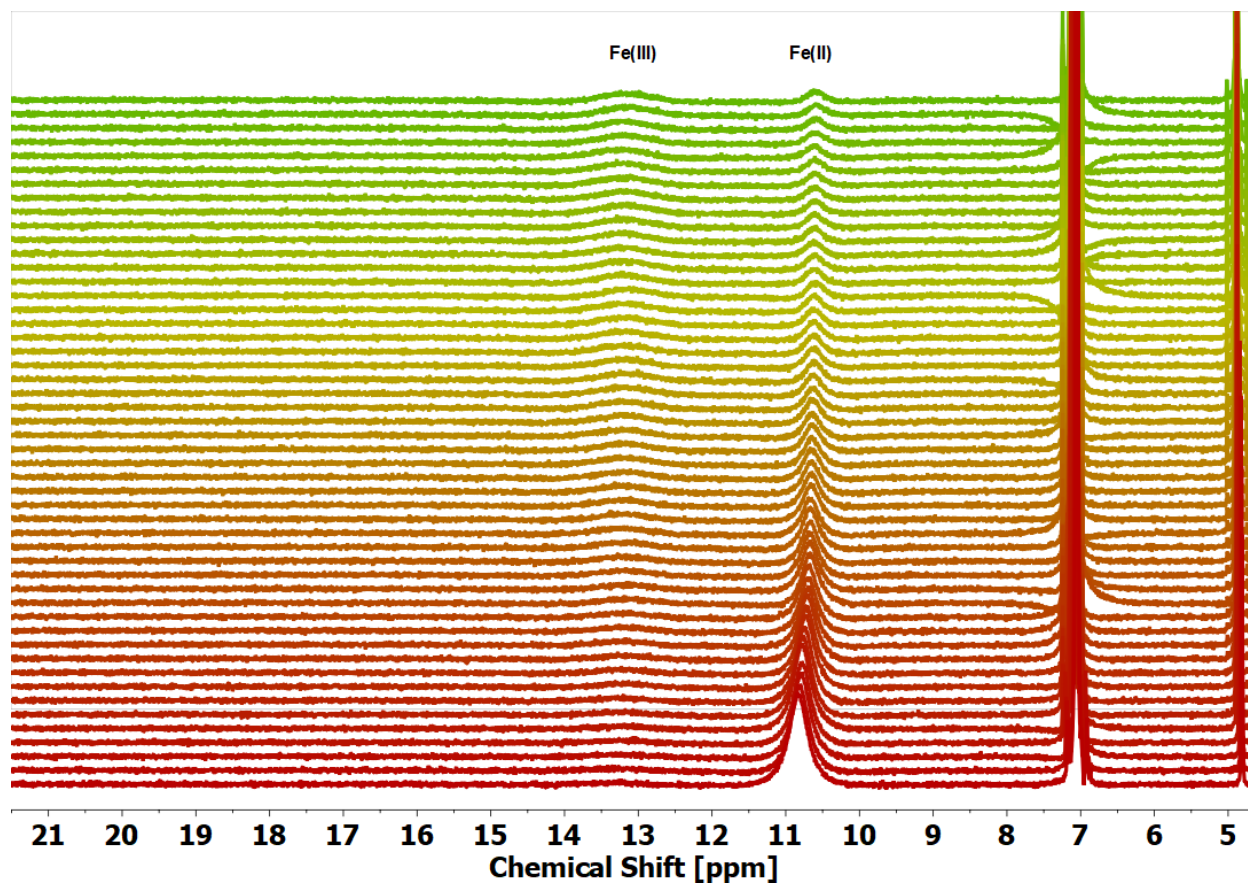




Full NMR stack for the transformation.

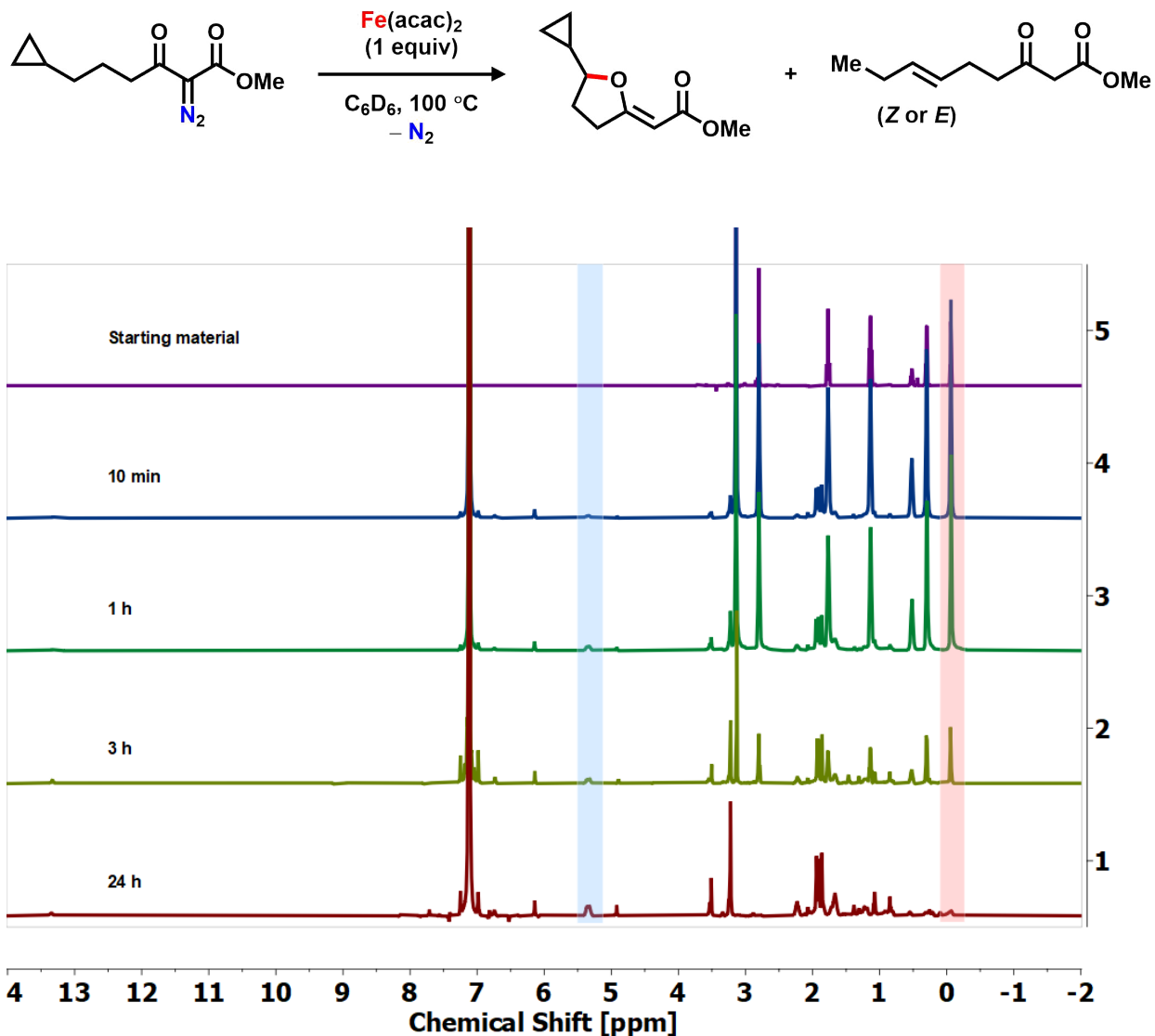


First 50 spectra in the full NMR stack showing the formation of product and disappearance of starting material.

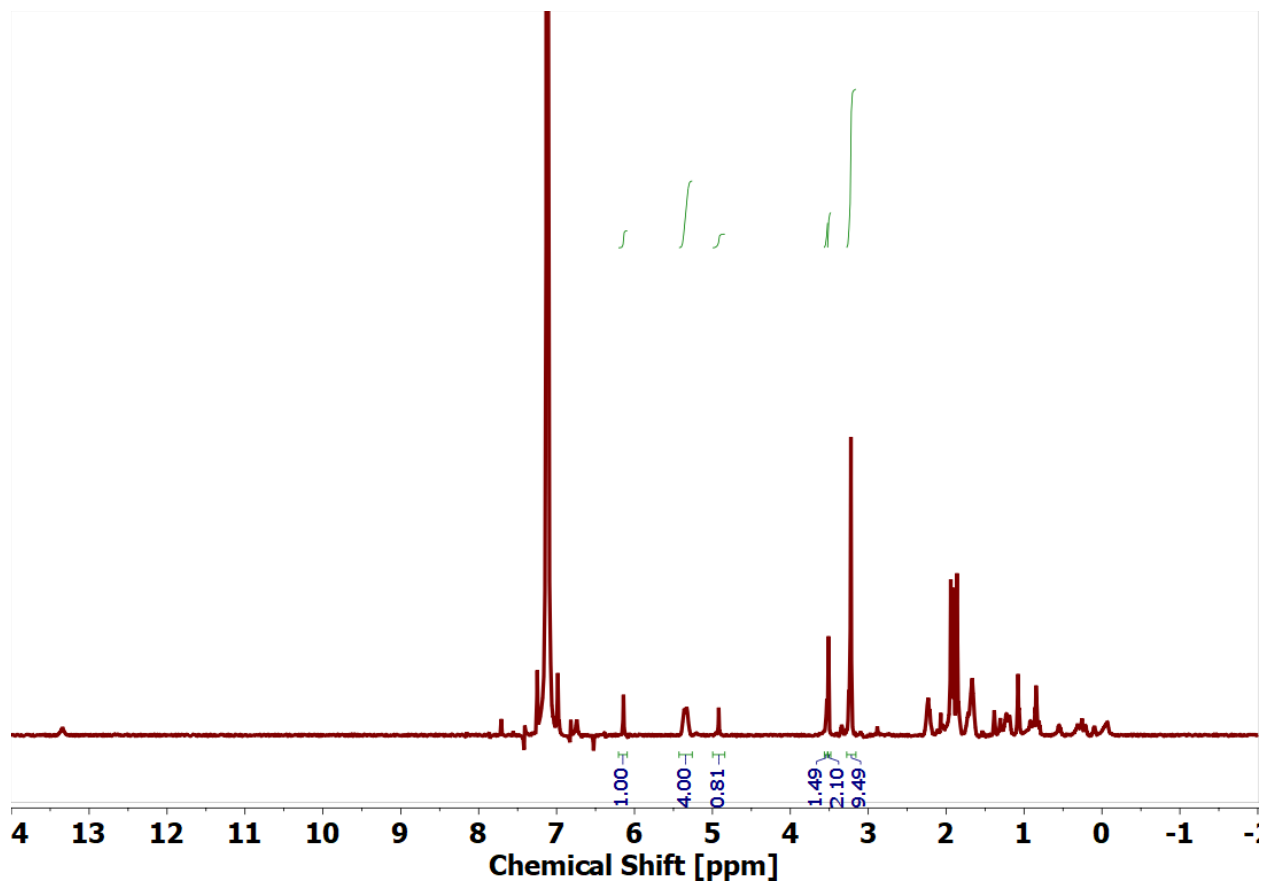


First 50 spectra in the full NMR stack showing the formation of a Fe(III) species and quick disappearance of Fe(acac)₂.

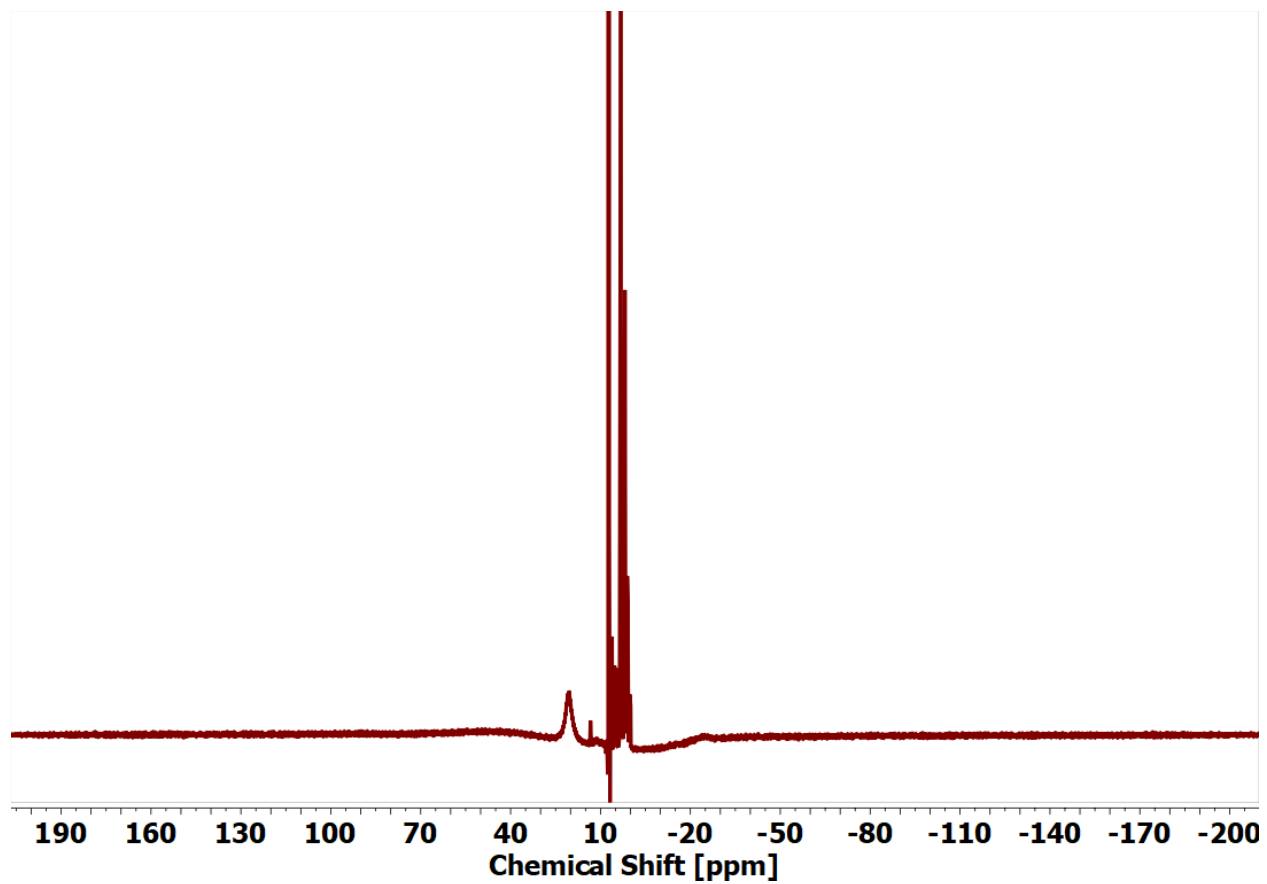
Figure S7. Analysis of radical clock substrate



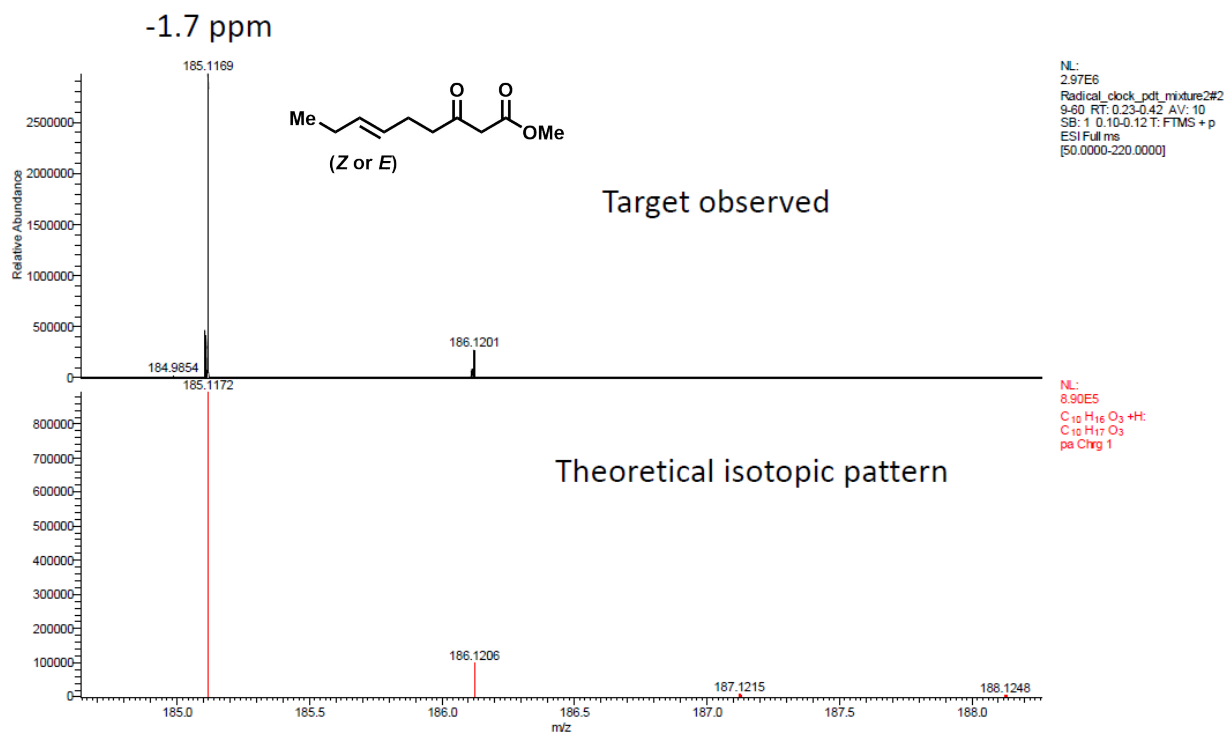
The ¹H NMR stack for the above transformation at 10 min, 1 h, 3 h, and 24 h at room temperature. The highlighted region in red shows the olefin peaks growing in during the reaction due to cyclopropyl ring opening while the highlighted region in blue (< 0 ppm) shows the disappearance of cyclopropyl groups. The formation of cyclized product and ring-opened olefins is further supported by high resolution mass spectrometry and fragmentation pattern from electron ionization. However, due to the complexity of the reaction, a numerical product distribution cannot be derived.



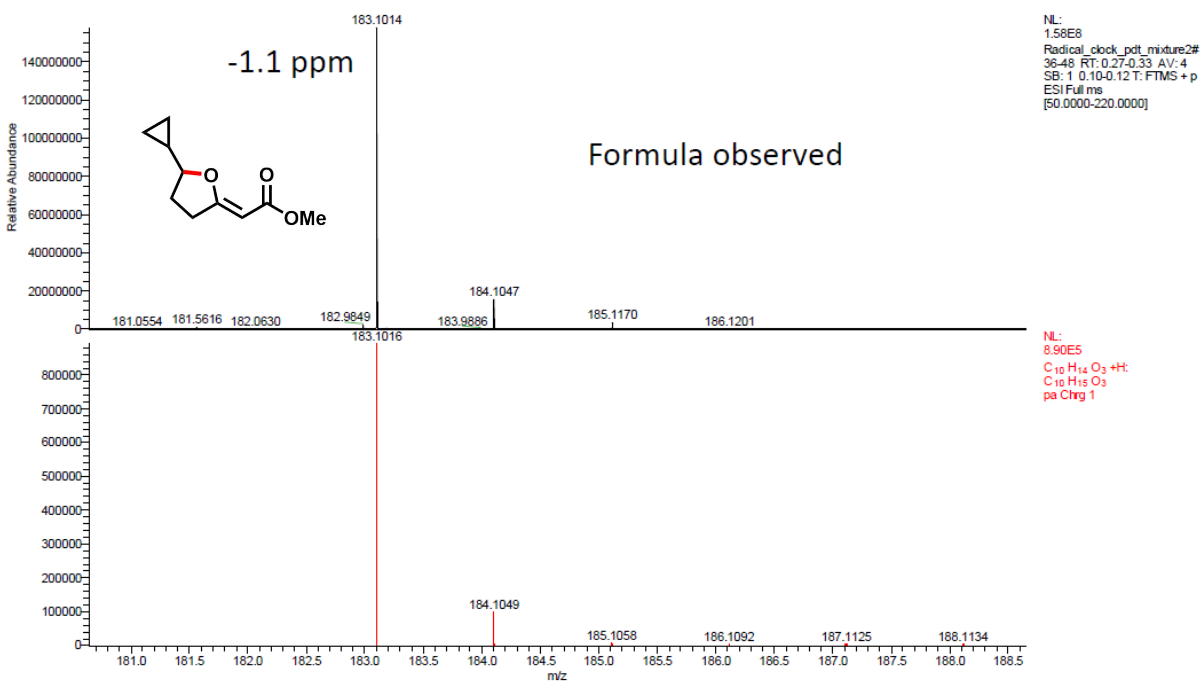
Diamagnetic region of the final ^1H NMR spectrum after 24 h of the reaction at room temperature.



Paramagnetic region of the final ^1H NMR spectrum after 24 h of the reaction at room temperature.

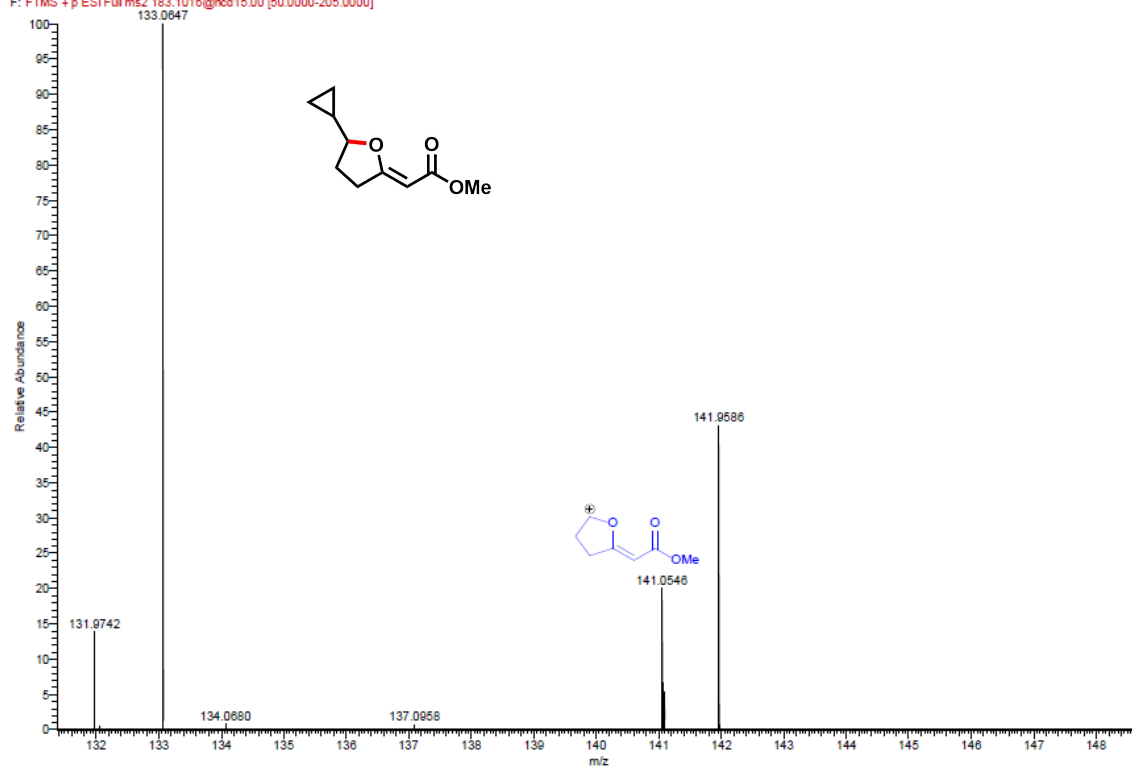


High resolution mass spectrum (ESI⁺-MS) for the ring-opening product



High resolution mass spectrum (ESI⁺-MS) for the cyclization product.

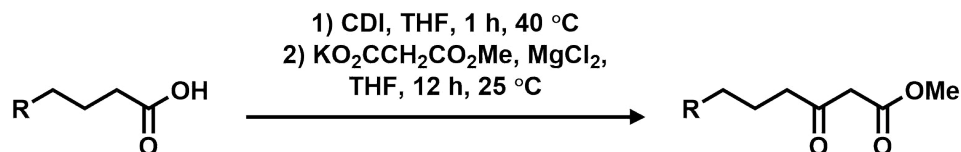
Radical_clock_pdt_mixture2 #48-60 RT: 0.36-0.42 AV: 2 NL: 4.38E6
F: FTMS +p ESI Full ms2 183.1016@hcd15.00 [50.0000-205.0000]



Fragmentation pattern (EI-MS) verifying the presence of the cyclization product.

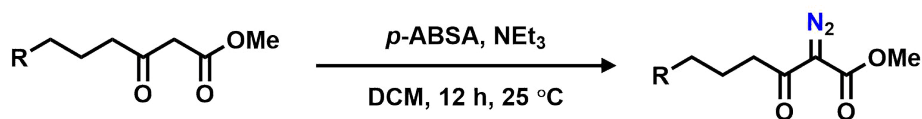
α -Diazo- β -ketoesters synthesis

Procedure A: Synthesis of 1,3-ketoesters derivatives from carboxylic acid



Procedure was adapted following a previous literature report.³ Potassium monomethyl malonate (1.5 eq) and MgCl_2 (1 eq) were dissolved in anhydrous THF (25 mL). The suspension was stirred at 65 °C for 3 hours, cooled to room temperature, and stirred for an additional 1 hour. Separately, the butyric acid (1 eq) and carbonyl diimidazole (1.1 eq) were dissolved in anhydrous THF (10 mL) and stirred at 45 °C for 1 hour. The acyl imidazole solution was then transferred via syringe to the magnesium malonate solution and stirred at room temperature overnight. A 1 M solution of HCl (5 mL) was added dropwise to the reaction mixture. The quenched reaction mixture was extracted into EtOAc (2 x 50 mL), washed with brine, dried with sodium sulfate, and concentrated under reduced pressure. The resulting oil was further purified by SiO_2 chromatography (10–20% EtOAc in Hexanes) to give the β -ketoesters as either yellow oils or white solids. The product was transferred using dichloromethane due to its high solubilizing ability and volatility.

Procedure B: Synthesis of α -diazo- β -ketoesters



Procedure was adapted following a previous literature report.³ The respective β -ketoester (1 eq) and *para*-acetamidobenzenesulfonyl azide (1.5 eq) were dissolved in CH_2Cl_2 (20 mL) and cooled

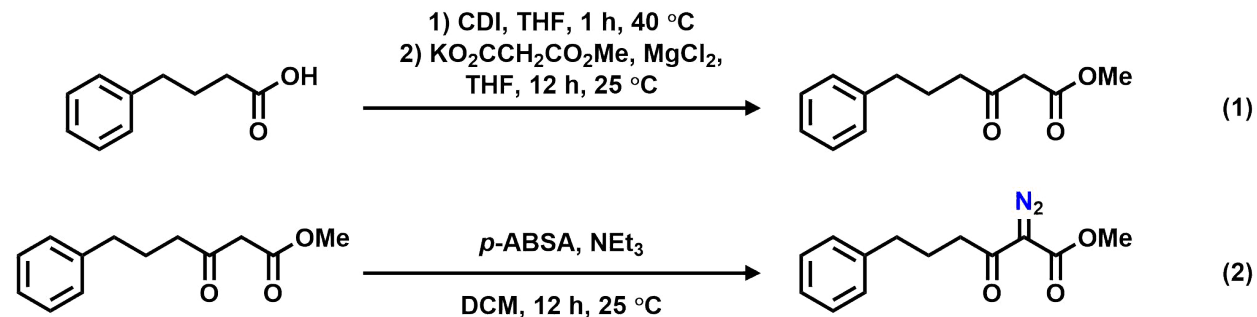
to 0 °C. Triethylamine (1.8 eq) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with CH₂Cl₂ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO₂ chromatography (10–20% EtOAc in Hexanes) to give the diazo products as yellow oils or white/off-white solids. The product was transferred using dichloromethane due to its high solubilizing ability and volatility.

Drying: The resulting *α*-diazo-*β*-ketoesters was brought into a N₂-filled glovebox, dissolved in either hexanes or Et₂O and let sit over 4 Å molecular sieves overnight. The solution was then filtered through a short silica plug and concentrated to provide dry, degassed substrate for catalysis.

Note: 1. The keto-esters prepared always appear as a mixture of their keto and enol forms in CDCl₃. The characterization data provided are for the keto form while satisfactory data for the enols cannot be consistently obtained due to their low concentration (est. < 10%) as well as the overlapping signals with the major keto form. The level of tautomerization is recorded in the data presented using the integration of both the enol- and vinyl-H in the ¹H NMR spectra.

Spectroscopic details for α -diazo- β -ketoesters and the corresponding products

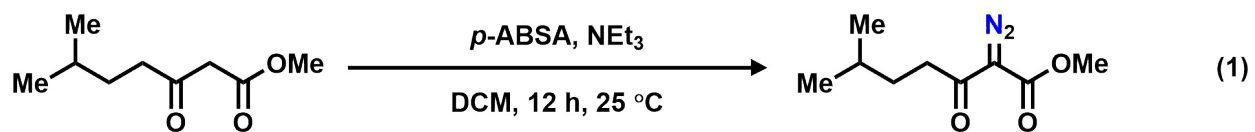
Methyl 2-diazo-3-oxo-6-phenylhexanoate (1)



1. Methyl 3-oxo-6-phenylhexanoate (S1): Synthesized following previously reported procedure.³

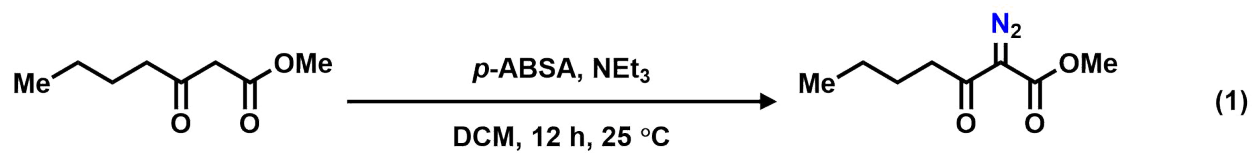
2. Methyl 2-diazo-3-oxo-6-phenylhexanoate (1): Synthesized following previously reported procedure.³

Methyl 2-diazo-6-methyl-3-oxoheptanoate (8)



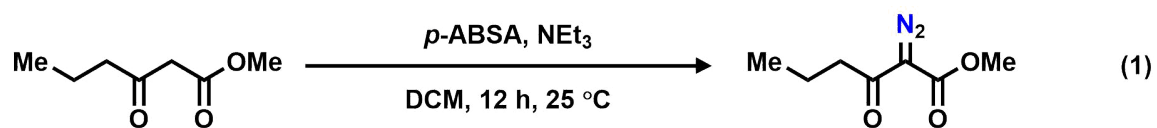
1. Methyl 2-diazo-6-methyl-3-oxoheptanoate (8): Synthesized following previously reported procedure.⁴

Methyl 2-diazo-3-oxoheptanoate (S2)



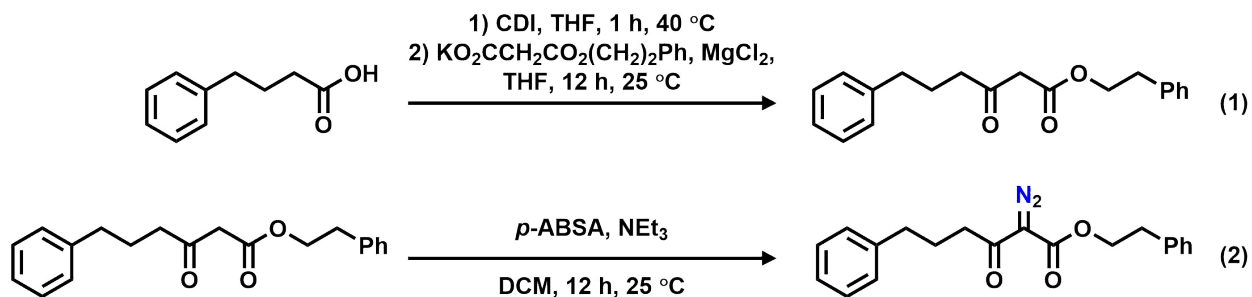
1. Methyl 2-diazo-3-oxoheptanoate (S2): Synthesized following previously reported procedure.⁵

Methyl 2-diazo-3-oxohexanoate (S3)

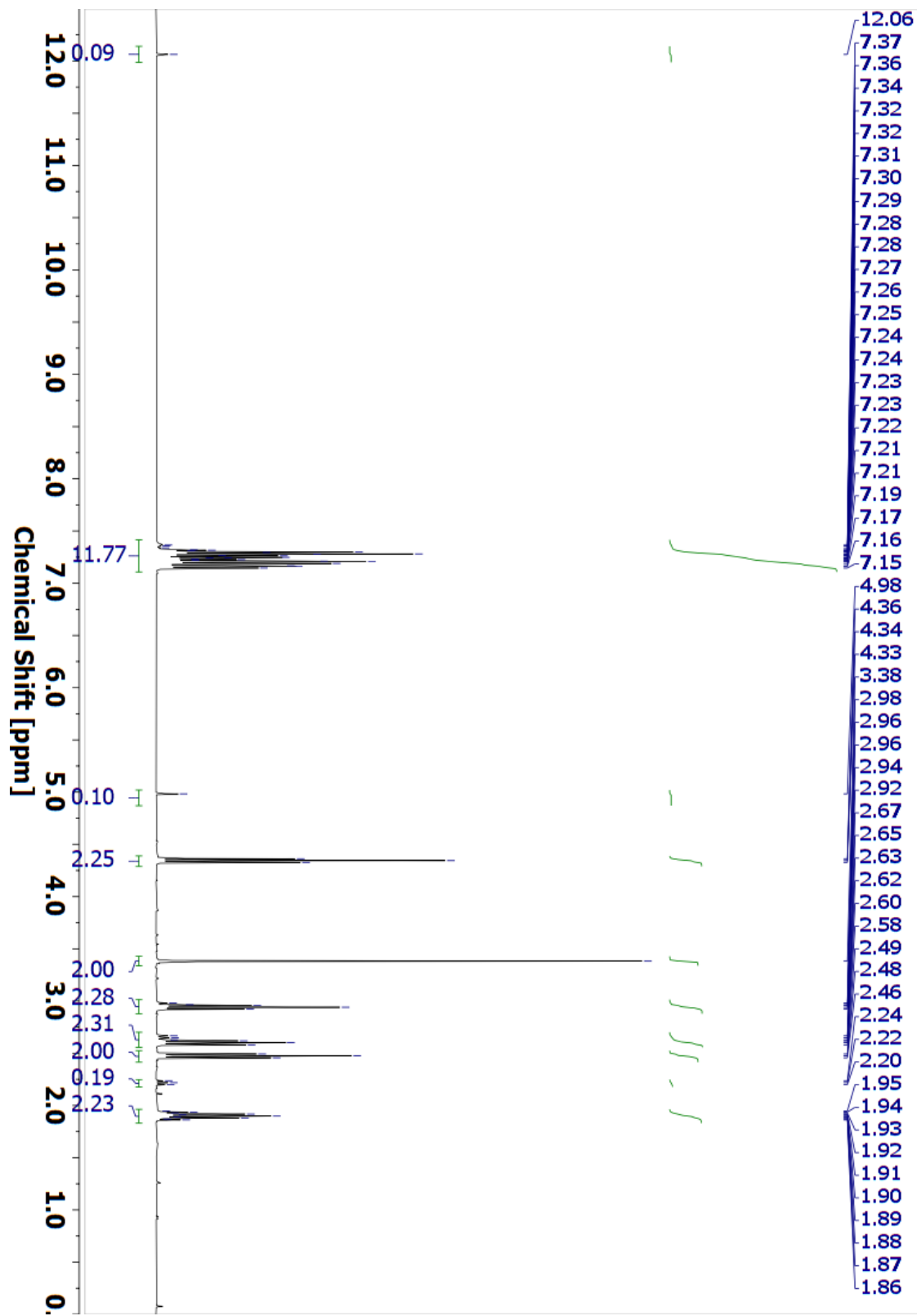


1. Methyl 2-diazo-3-oxohexanoate (S3): Synthesized following previously reported procedure.⁶

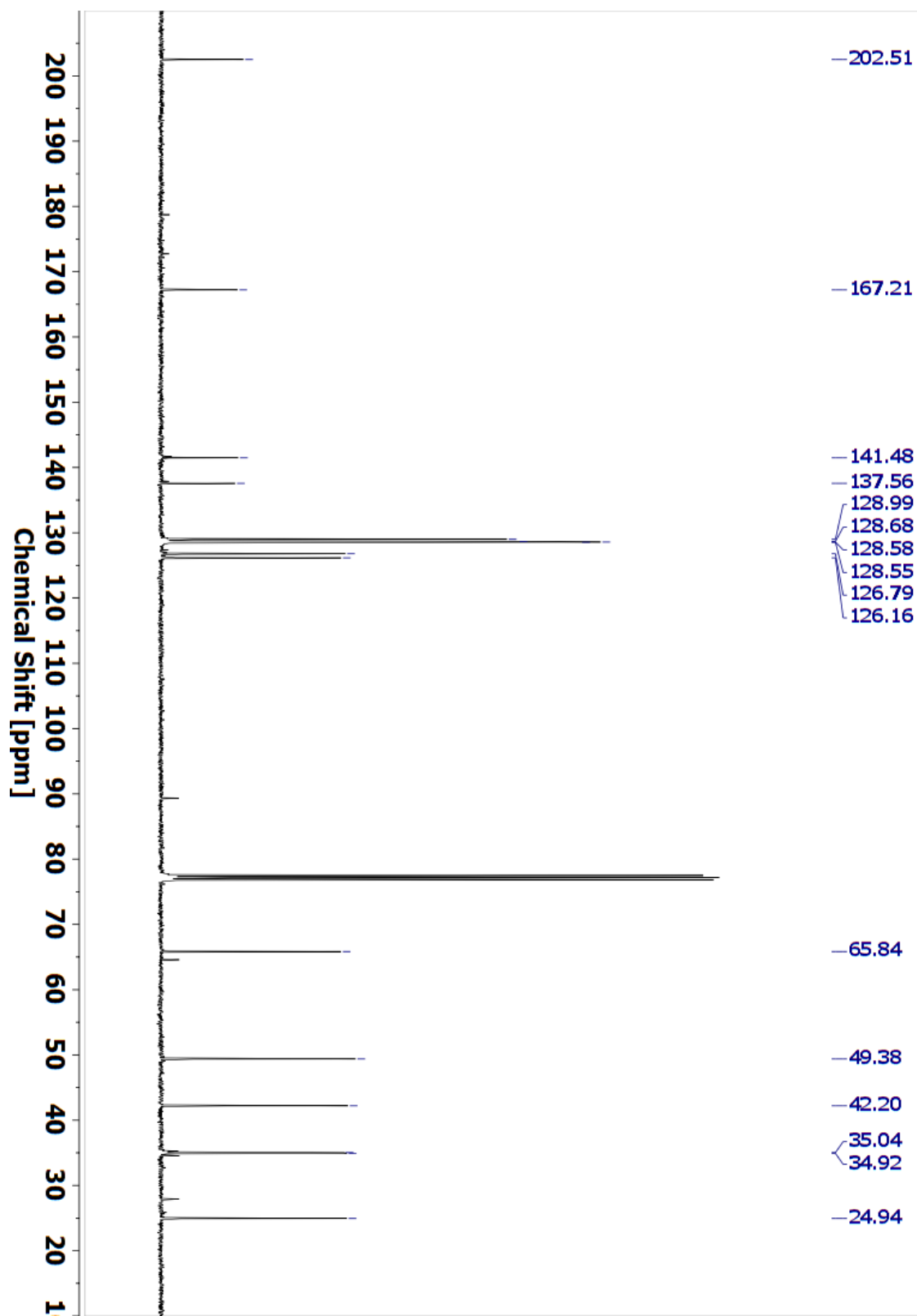
Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (S5)



1. Phenethyl 3-oxo-6-phenylhexanoate (S4): Synthesized following Procedure A: The reaction was run on 10.0 mmol scale to give 2.02 g (65% yield, 8.3% tautomerization) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.11 (m, 10H), 4.34 (t, *J* = 7.0 Hz, 2H), 3.38 (s, 2H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.4 Hz, 2H), 1.97–1.83 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 202.51, 167.21, 141.48, 137.56, 128.99, 128.68, 128.58, 128.55, 126.79, 126.16, 65.84, 49.38, 42.20, 35.04, 34.92, 24.94. HRMS (ESI⁺) *m/z* Calc. 311.1642 [C₂₀H₂₂O₃+H]⁺, Found. 311.1640 [M+H]⁺.

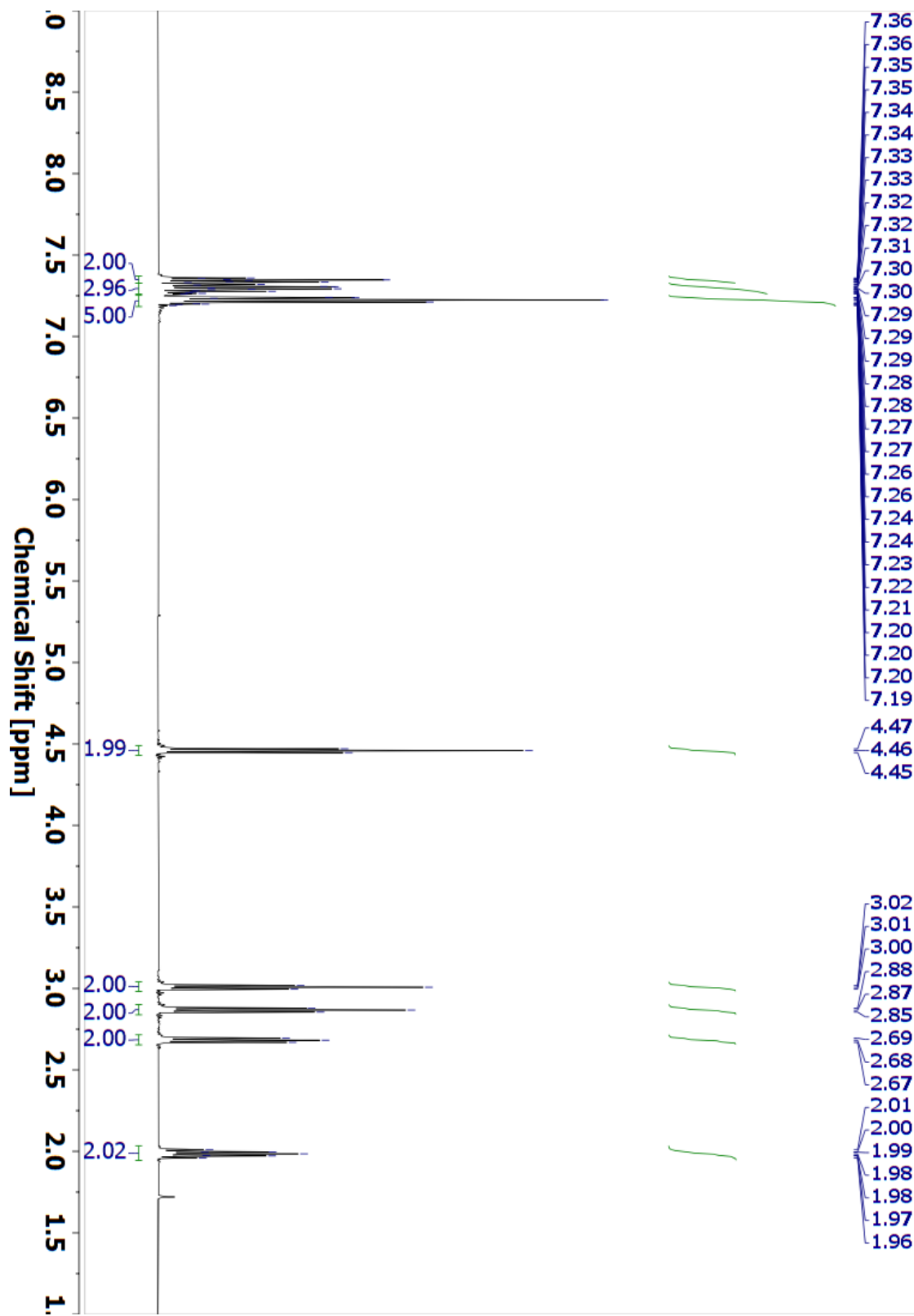


^1H NMR spectrum of isolated product in CDCl_3

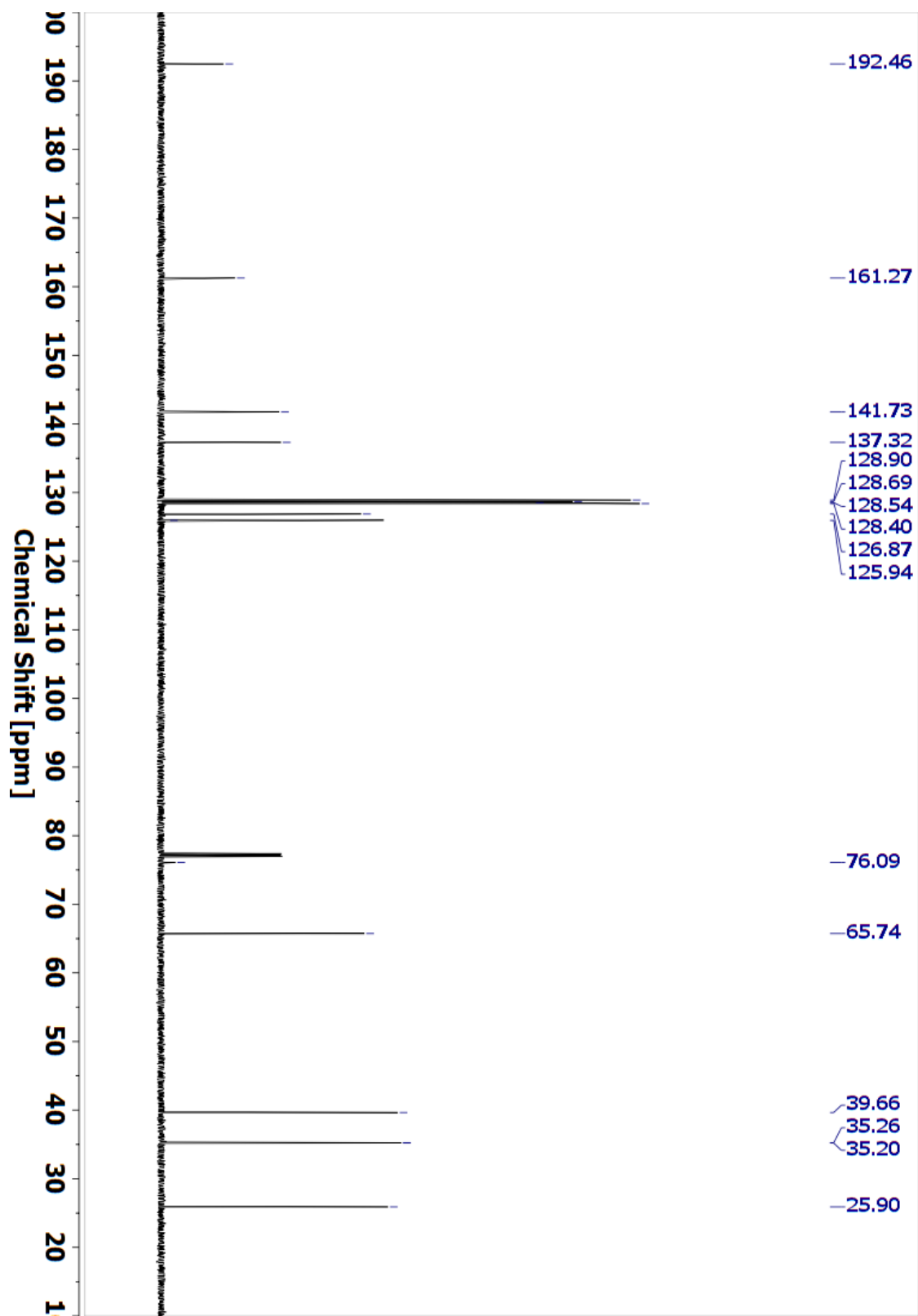


^{13}C NMR spectrum of isolated product in CDCl_3

2. Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (S5): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 1.38 g (82% yield) of product as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.37–7.33 (m, 2H), 7.33–7.26 (m, 3H), 7.25–7.19 (m, 5H), 4.46 (t, *J* = 6.9 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.71–2.65 (m, 2H), 1.98 (p, *J* = 7.3 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 192.46, 161.27, 141.73, 137.32, 128.90, 128.69, 128.54, 128.40, 126.87, 125.94, 76.09, 65.74, 39.66, 35.26, 35.20, 25.90. HRMS (ESI⁺) *m/z* Calc. 337.1547 [C₂₀H₂₀N₂O₃+H]⁺, Found. 337.1546 [M+H]⁺.

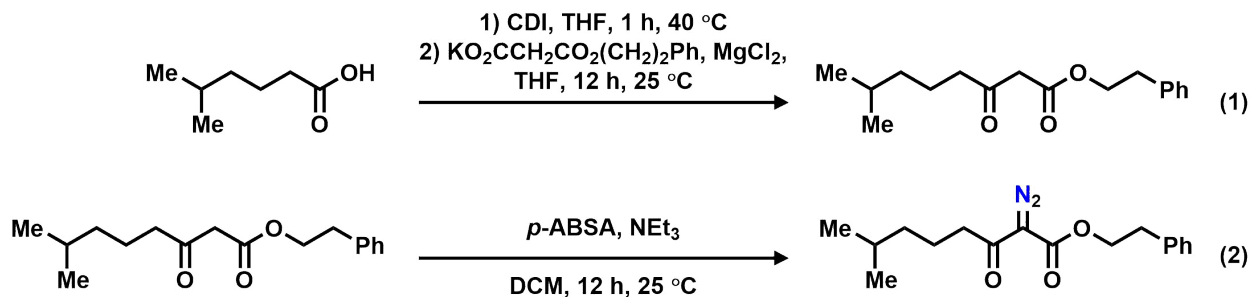


^1H NMR spectrum of isolated product in CDCl_3

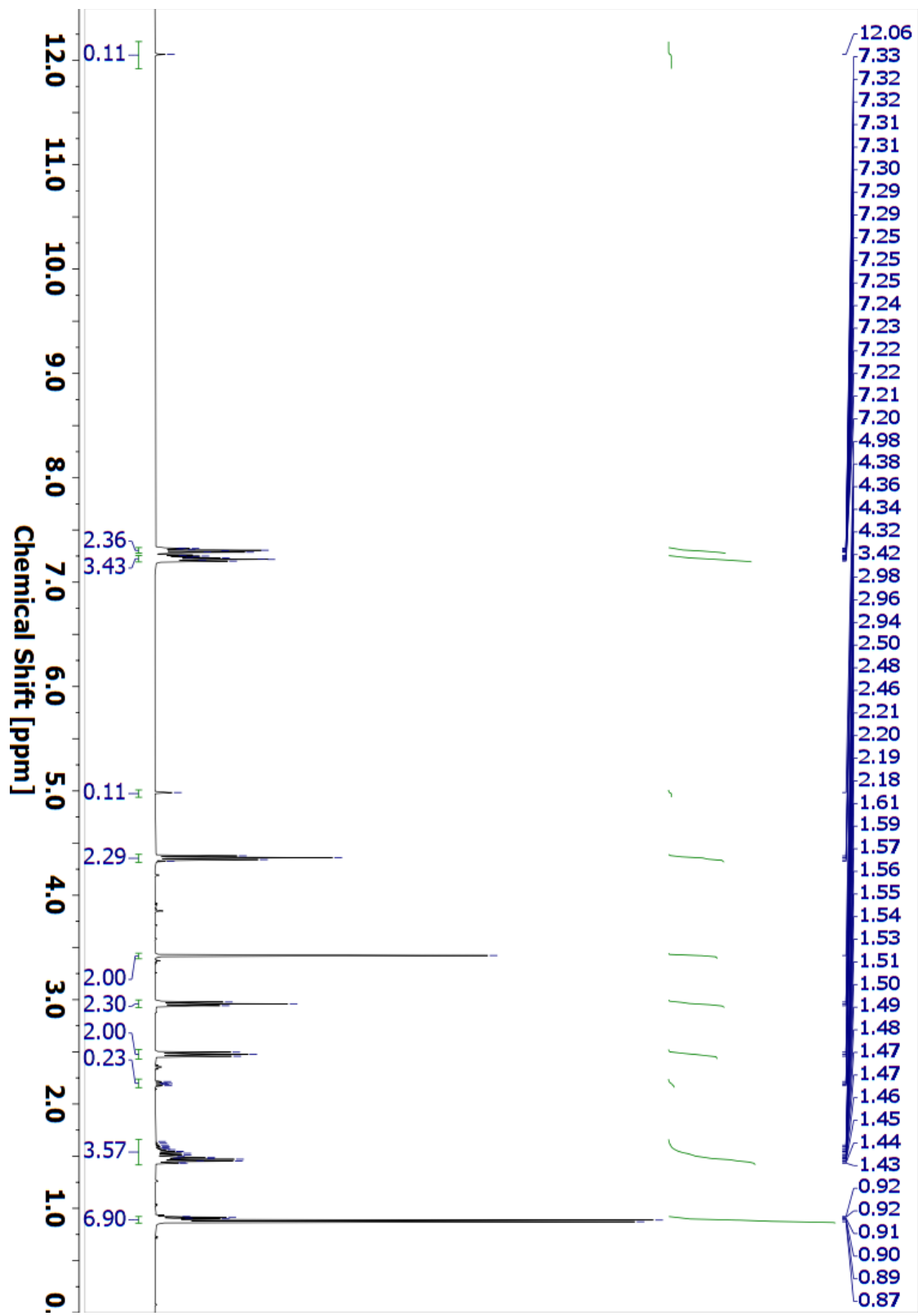


¹³C NMR spectrum of isolated product in CDCl₃

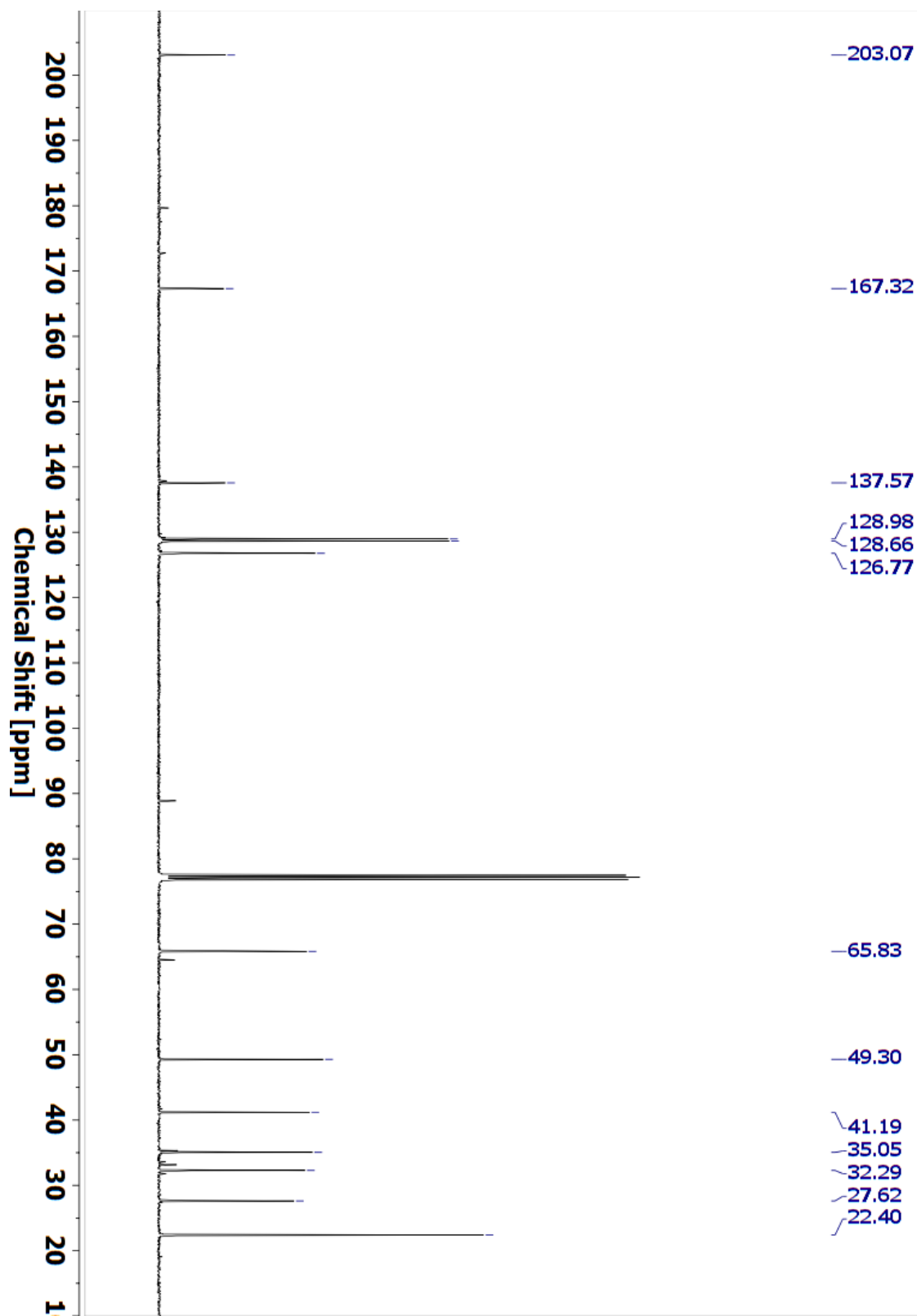
Phenethyl 2-diazo-7-methyl-3-oxooctanoate (S7)



1. Phenethyl 7-methyl-3-oxooctanoate (S6): Synthesized following Procedure A: The reaction was run on 10.0 mmol scale to give 1.96 g (71% yield, 9.9% tautomerization) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.27 (m, 2H), 7.26–7.19 (m, 3H), 4.36 (t, *J* = 7.0 Hz, 2H), 3.42 (s, 2H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.55–2.42 (m, 2H), 1.61–1.40 (m, 3H), 0.88 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 203.07, 167.32, 137.57, 128.98, 128.66, 126.77, 65.83, 49.30, 41.19, 35.05, 32.29, 27.62, 22.40. HRMS (ESI⁺) *m/z* Calc. 263.1642 [C₁₆H₂₂O₃+H]⁺, Found. 263.1643 [M+H]⁺.

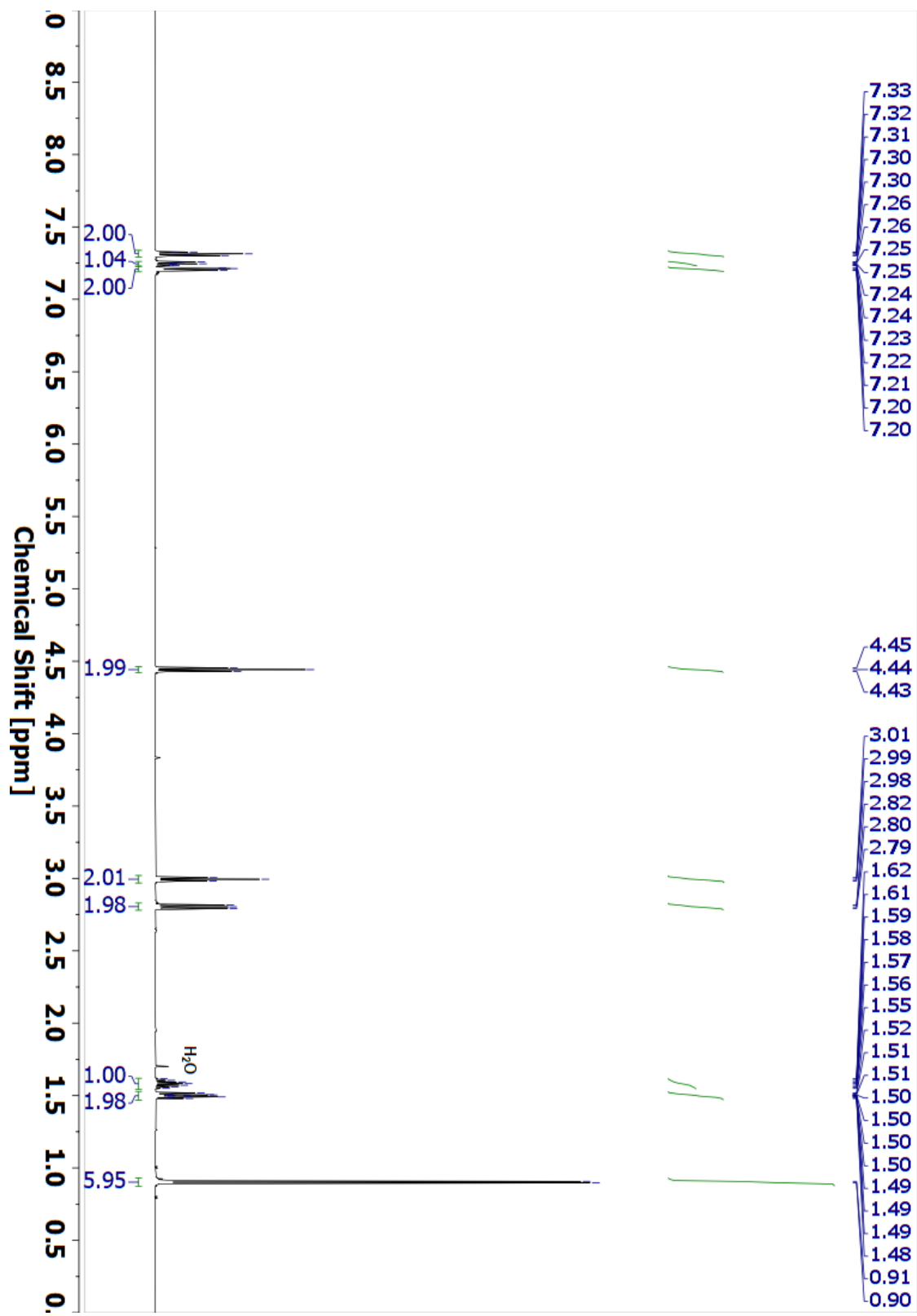


^1H NMR spectrum of isolated product in CDCl_3

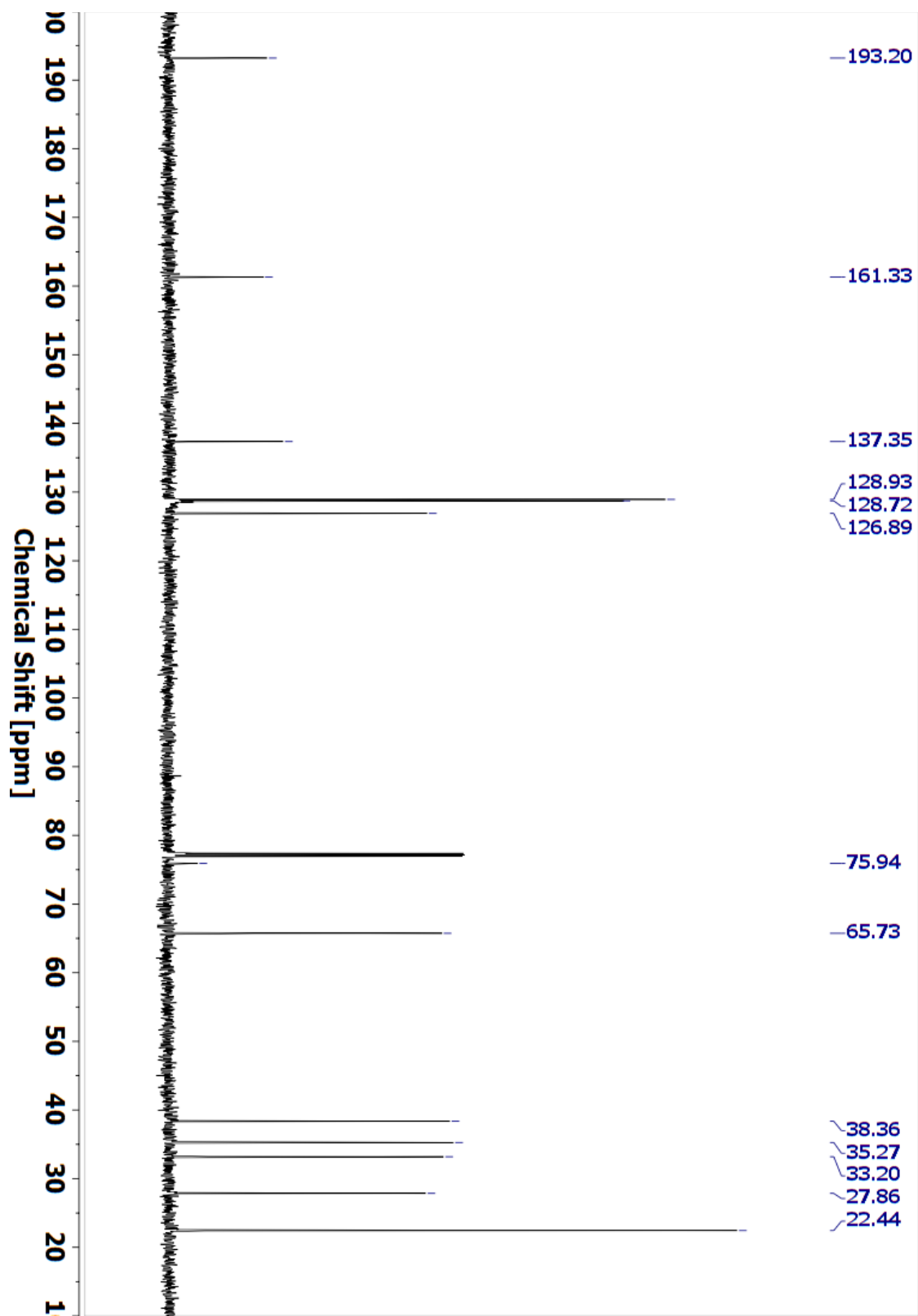


^{13}C NMR spectrum of isolated product in CDCl_3

2. Phenethyl 2-diazo-7-methyl-3-oxooctanoate (S7): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 1.36 g (90% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.34–7.29 (m, 2H), 7.27–7.23 (m, 1H), 7.23–7.19 (m, 2H), 4.44 (t, $J = 6.9$ Hz, 2H), 2.99 (t, $J = 6.9$ Hz, 2H), 2.84–2.77 (m, 2H), 1.63–1.54 (m, 1H), 1.54–1.45 (m, 2H), 0.90 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.20, 161.33, 137.35, 128.93, 128.72, 126.89, 75.94, 65.73, 38.36, 35.27, 33.20, 27.86, 22.44. HRMS (ESI $^+$) m/z Calc. 289.1547 [$\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_3 + \text{H}$] $^+$, Found. 289.1547 [$\text{M} + \text{H}$] $^+$.

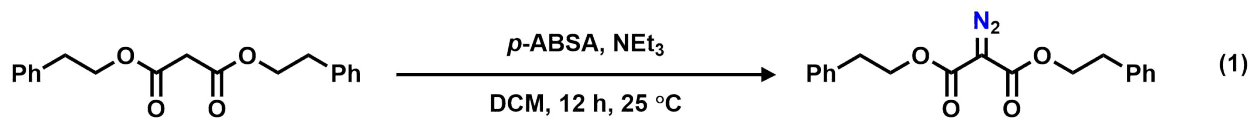


^1H NMR spectrum of isolated product in CDCl_3

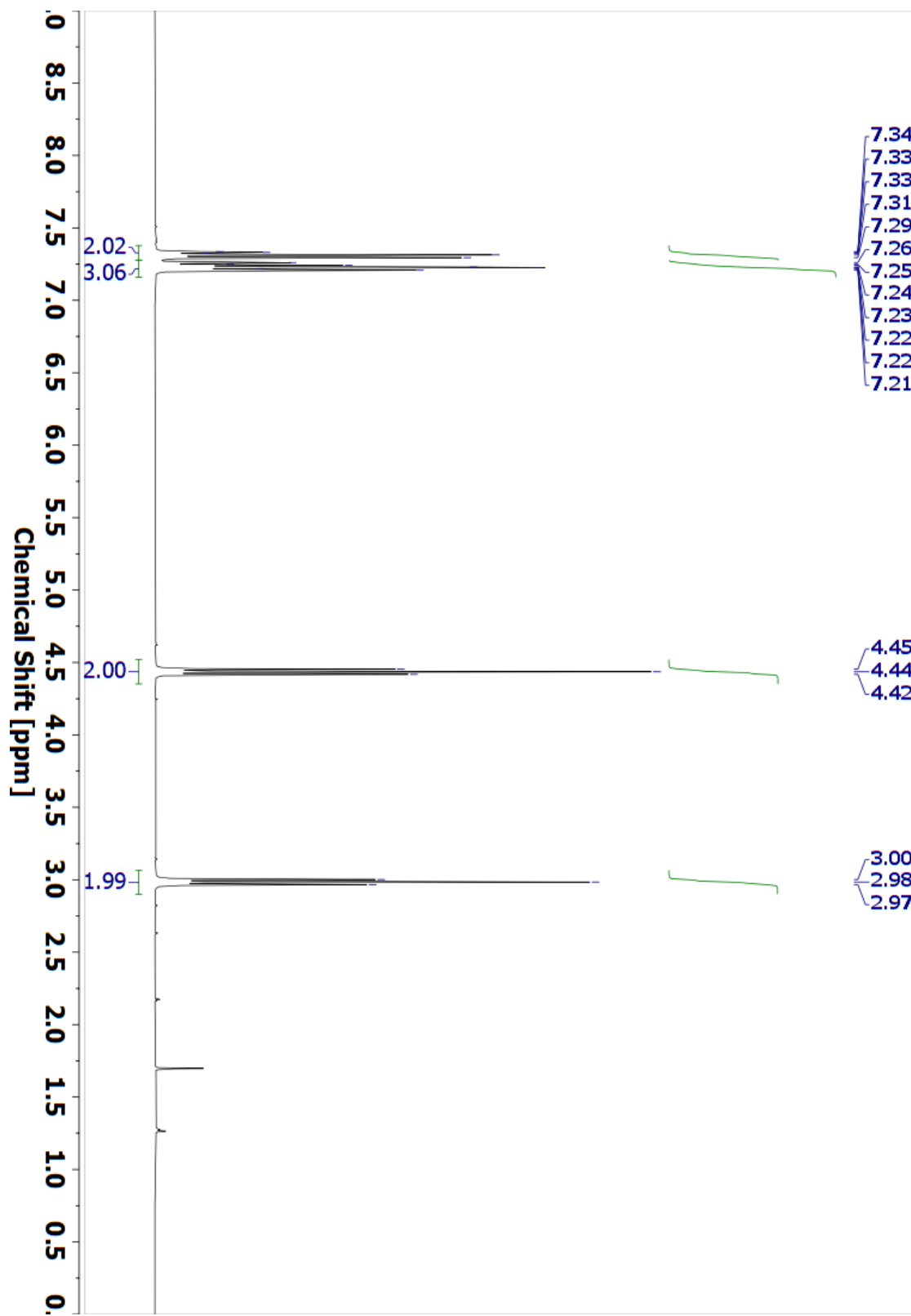


^{13}C NMR spectrum of isolated product in CDCl_3

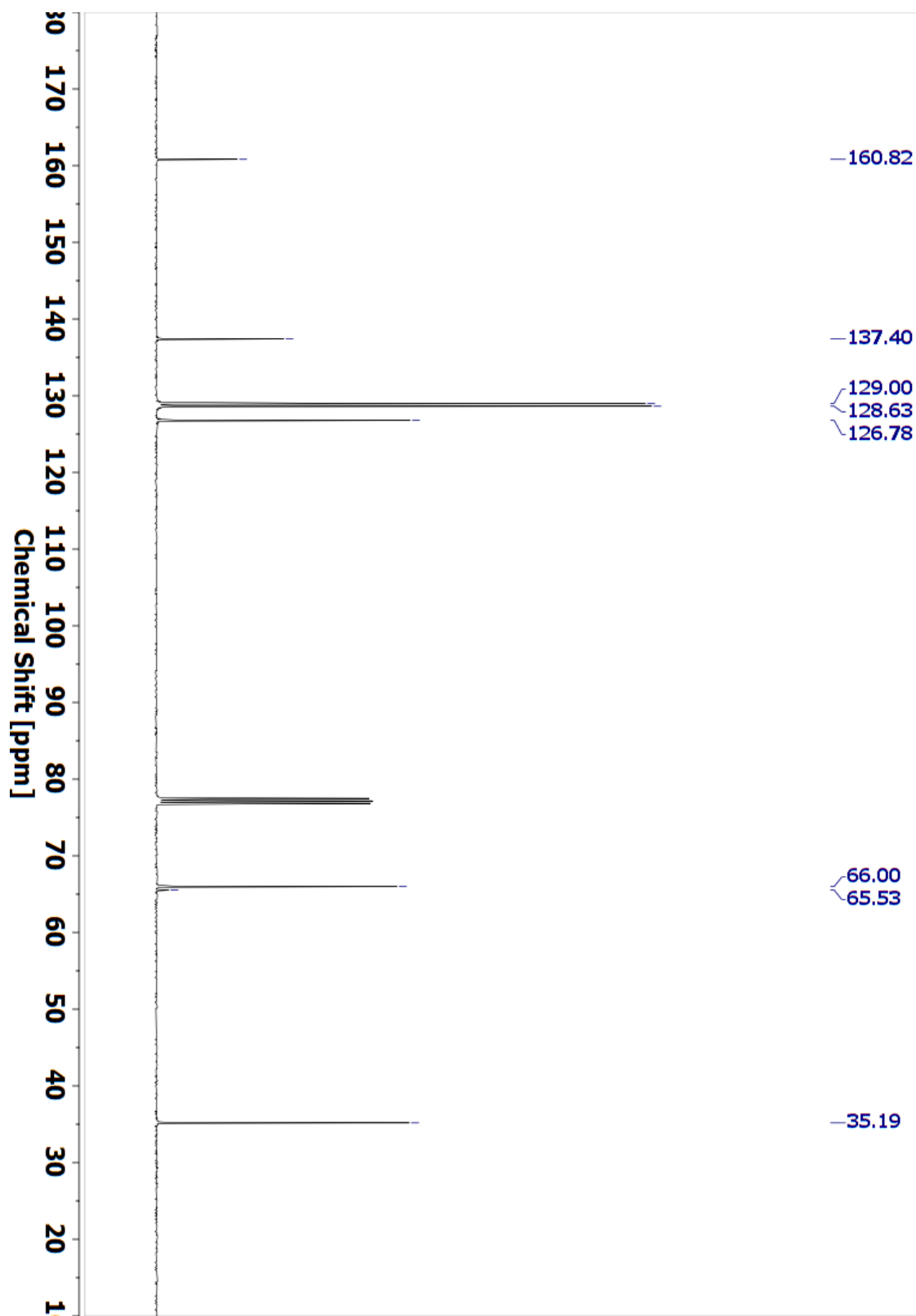
Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (12)



1. Phenethyl 2-diazo-3-oxo-6-phenylhexanoate (12): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 1.54 g (91% yield) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.28 (m, 2H), 7.28–7.15 (m, 3H), 4.44 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 160.82, 137.40, 129.00, 128.63, 126.78, 66.00, 65.53, 35.19. HRMS (ESI⁺) *m/z* Calc. 339.1339 [C₁₉H₁₈N₂O₄+H]⁺, Found. 339.1339 [M+H]⁺.

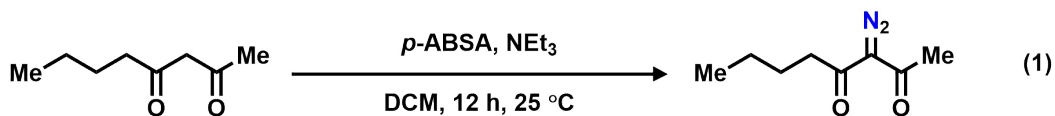


^1H NMR spectrum of isolated product in CDCl_3

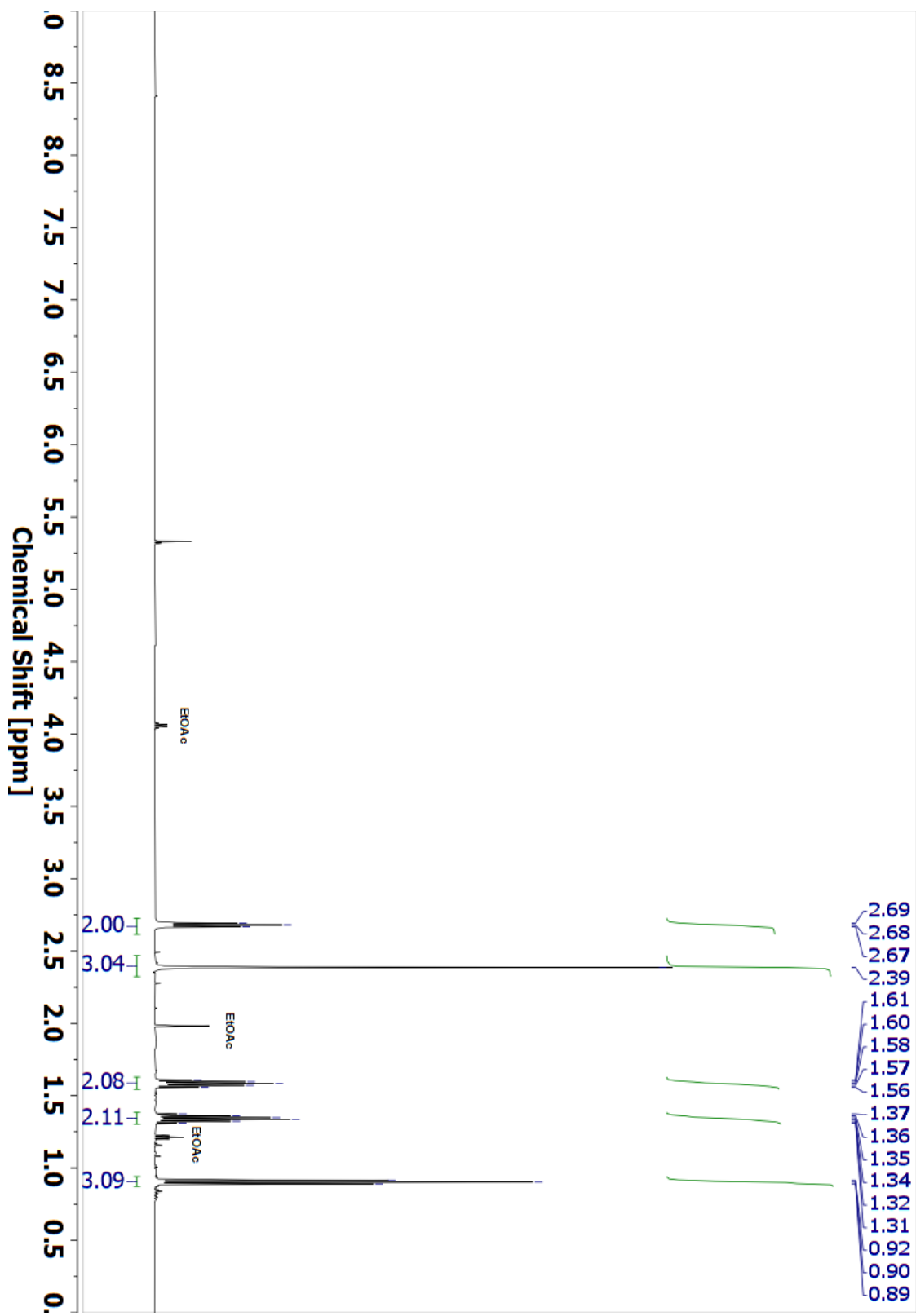


¹³C NMR spectrum of isolated product in CDCl₃

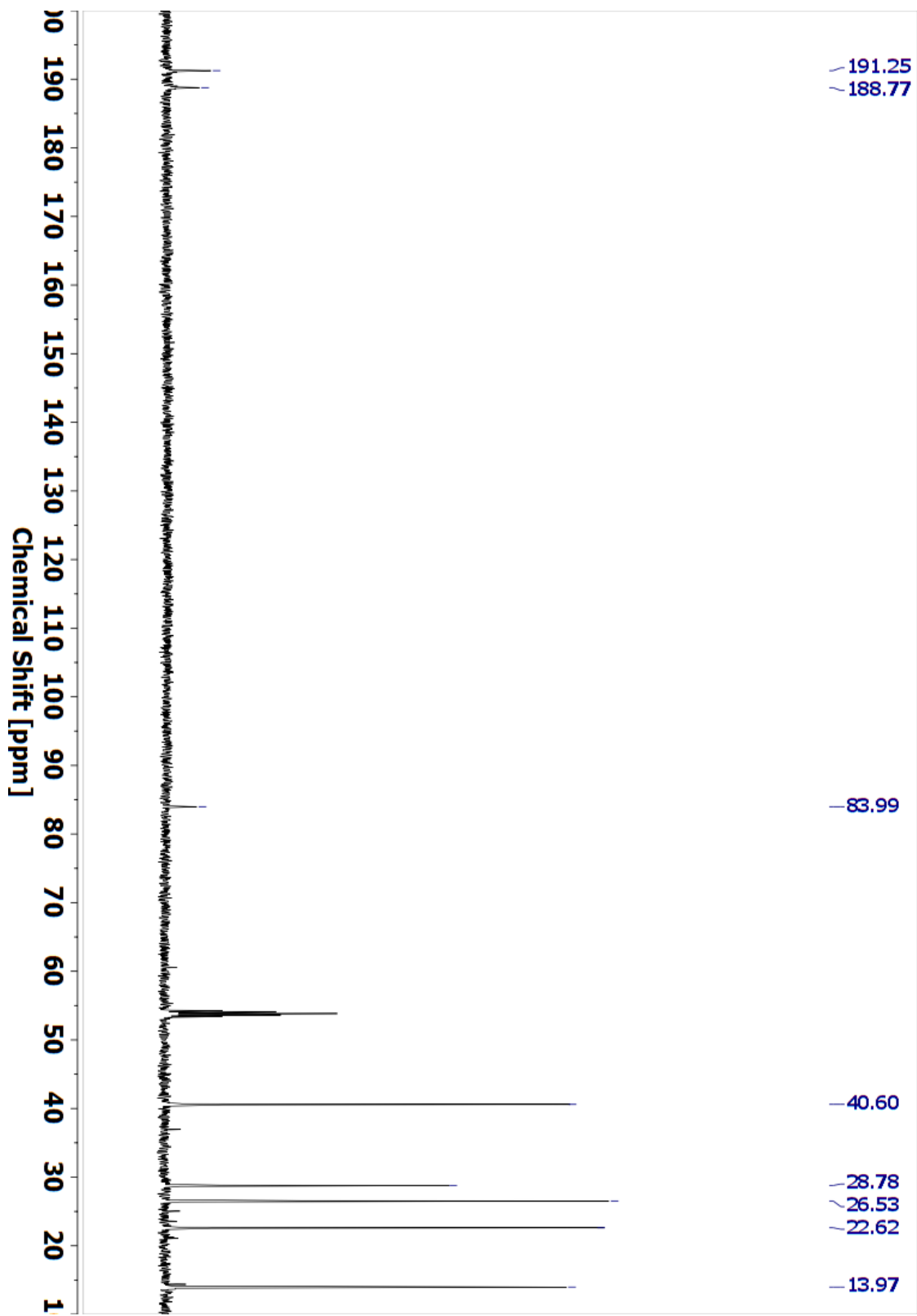
3-Diazoctane-2,4-dione (S8)



1. 3-Diazoctane-2,4-dione (S8): Synthesized following Procedure B: The reaction was run on 10.00 mmol scale to give 1.03 g (61% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 2.68 (t, $J = 7.5$ Hz, 2H), 2.39 (s, 3H), 1.65–1.52 (m, 2H), 1.43–1.28 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 191.25, 188.77, 83.99, 40.60, 28.78, 26.53, 22.62, 13.97. HRMS (ESI $^+$) m/z Calc. 191.0791 [$\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2 + \text{Na}$] $^+$, Found. 191.0815 [$\text{M} + \text{Na}$] $^+$.

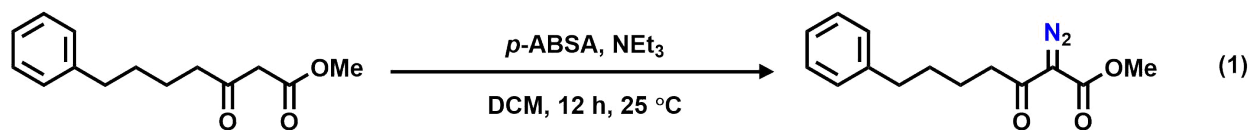


^1H NMR spectrum of isolated product in CD_2Cl_2



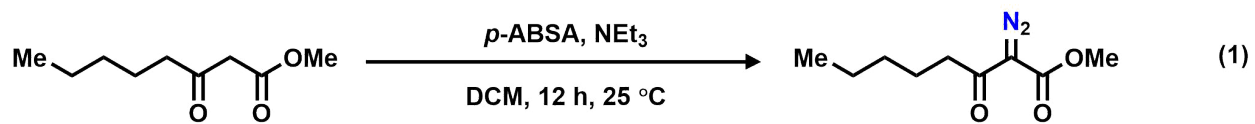
¹³C NMR spectrum of isolated product in CD₂Cl₂

Methyl 2-diazo-3-oxo-7-phenylheptanoate (S9)



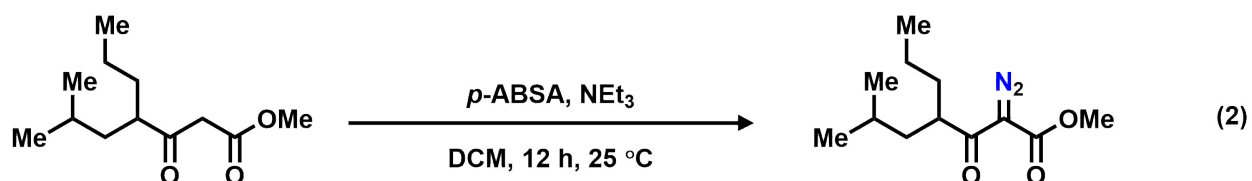
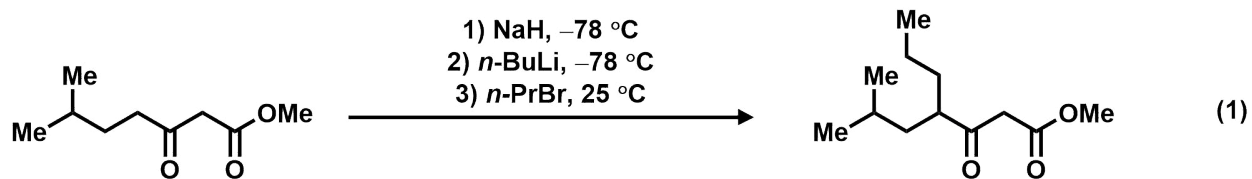
1. Methyl 2-diazo-3-oxo-7-phenylheptanoate (S9): Synthesized following previously reported procedure.⁷

Methyl 2-diazo-3-oxooctanoate (S10)



1. Methyl 2-diazo-3-oxooctanoate (S10): Synthesized following previously reported procedure.⁶

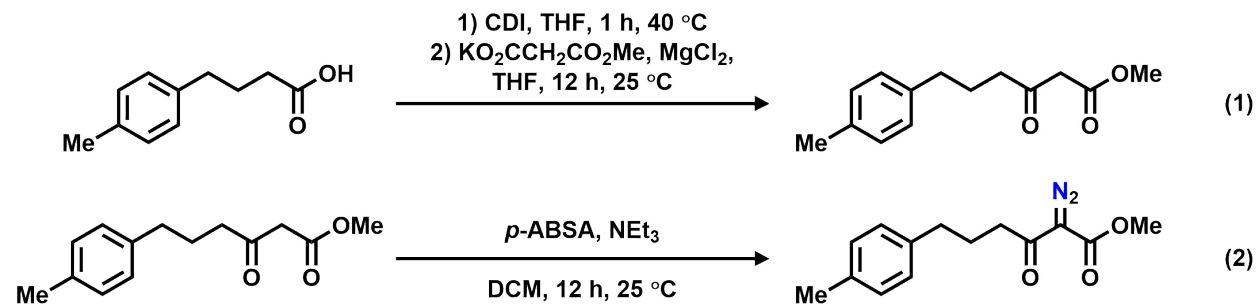
Methyl 2-diazo-6-methyl-3-oxo-4-propylheptanoate (S12)



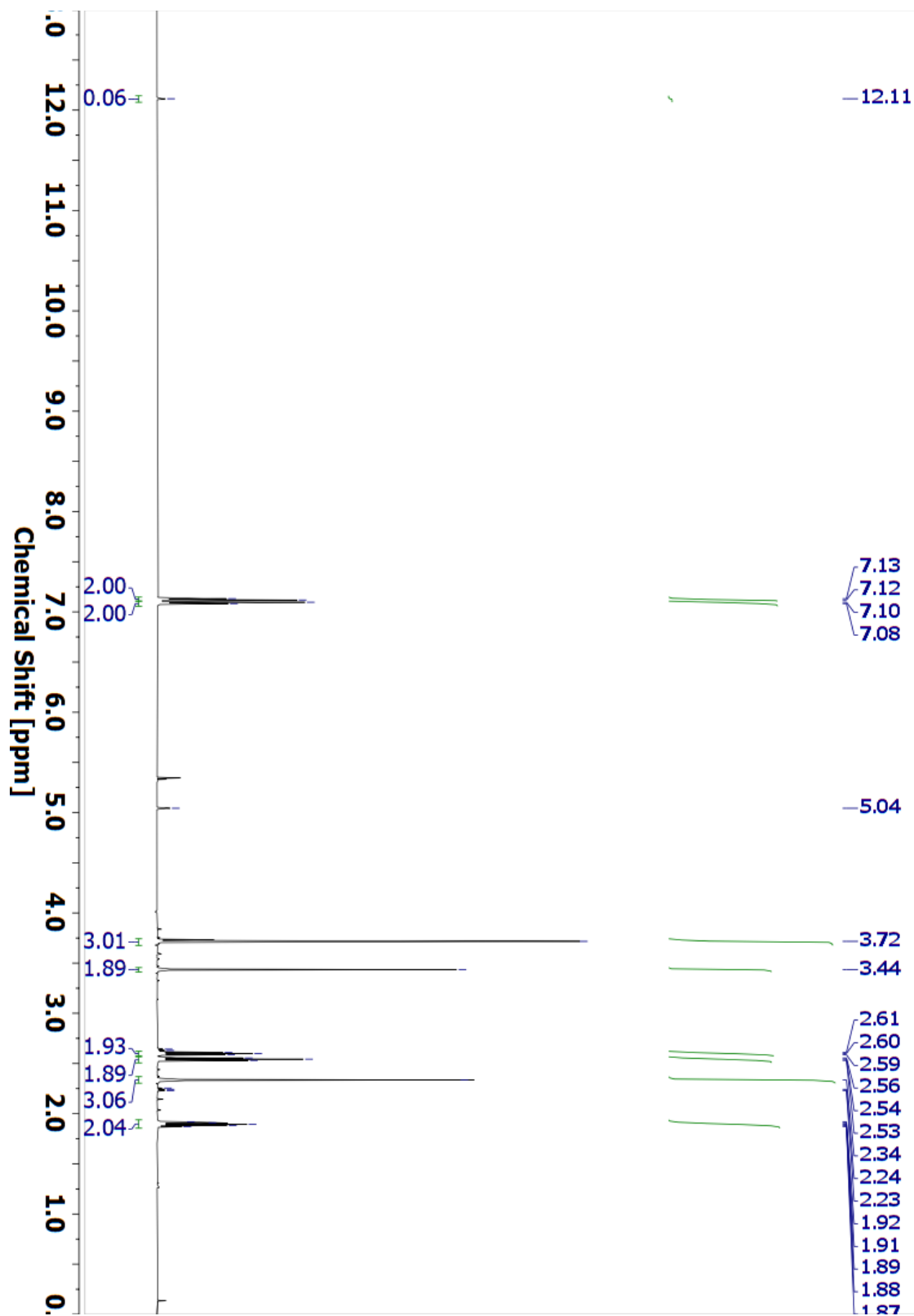
1. Methyl 6-methyl-3-oxo-4-propylheptanoate (S11): Synthesized following previously reported procedure.⁸

2. Methyl 2-diazo-6-methyl-3-oxo-4-propylheptanoate (S12): Synthesized following previously reported procedure.⁸

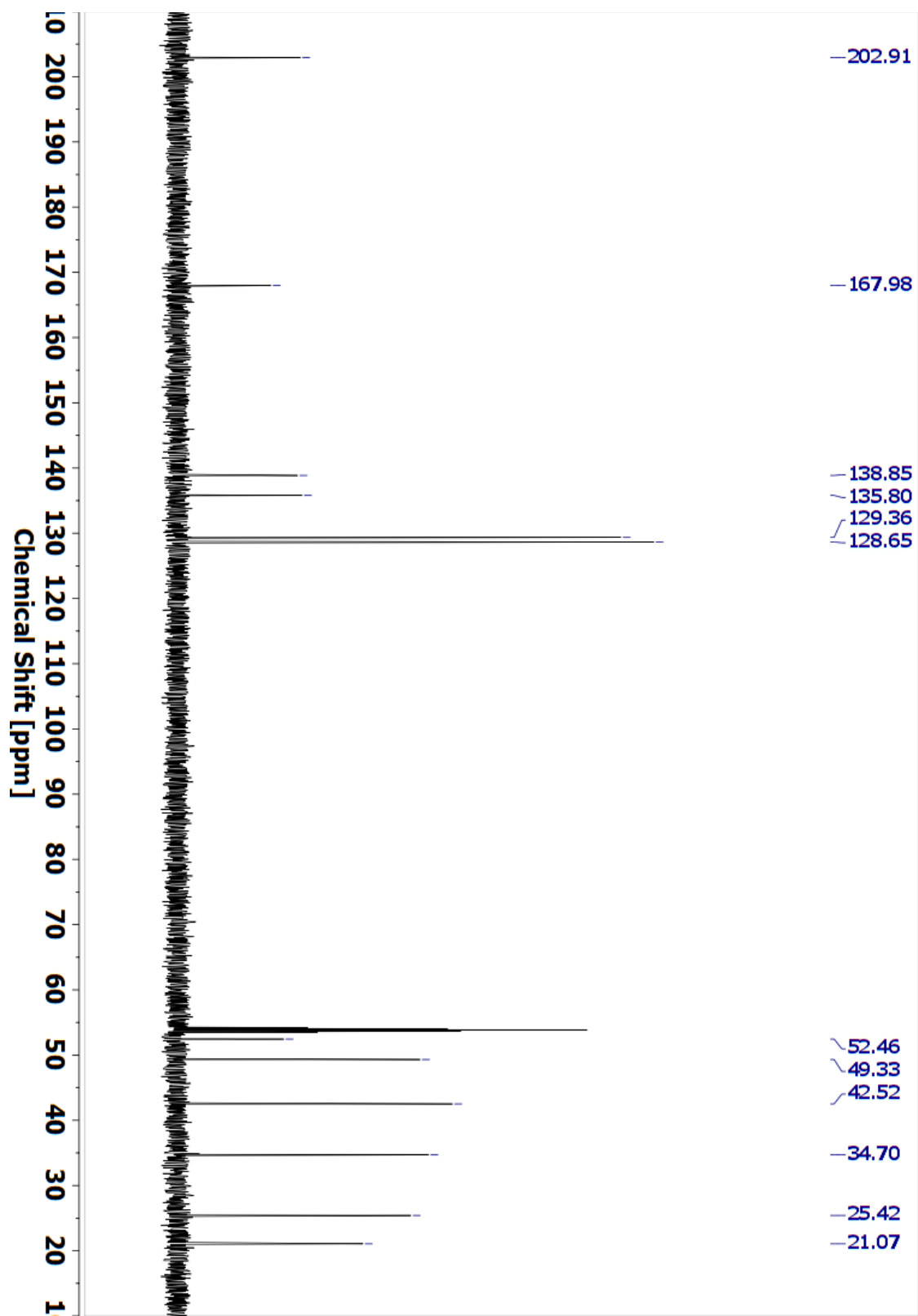
Methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (S14)



1. Methyl 3-oxo-6-(*p*-tolyl)hexanoate (S13): Synthesized following Procedure A: The reaction was run on 30.00 mmol scale to give 3.21 g (46% yield, 5.7% tautomerization) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.13 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 3.72 (s, 3H), 3.44 (s, 3H), 2.60 (t, $J = 7.6$ Hz, 2H), 2.54 (t, $J = 7.3$ Hz, 2H), 1.99–1.81 (m, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 202.91, 167.98, 138.85, 135.80, 129.36, 128.65, 52.46, 49.33, 42.52, 34.70, 25.42, 21.07. HRMS (ESI $^+$) m/z Calc. 257.1148 [$\text{C}_{14}\text{H}_{18}\text{O}_3+\text{Na}$] $^+$, Found 257.1164 [$\text{M}+\text{Na}$] $^+$.

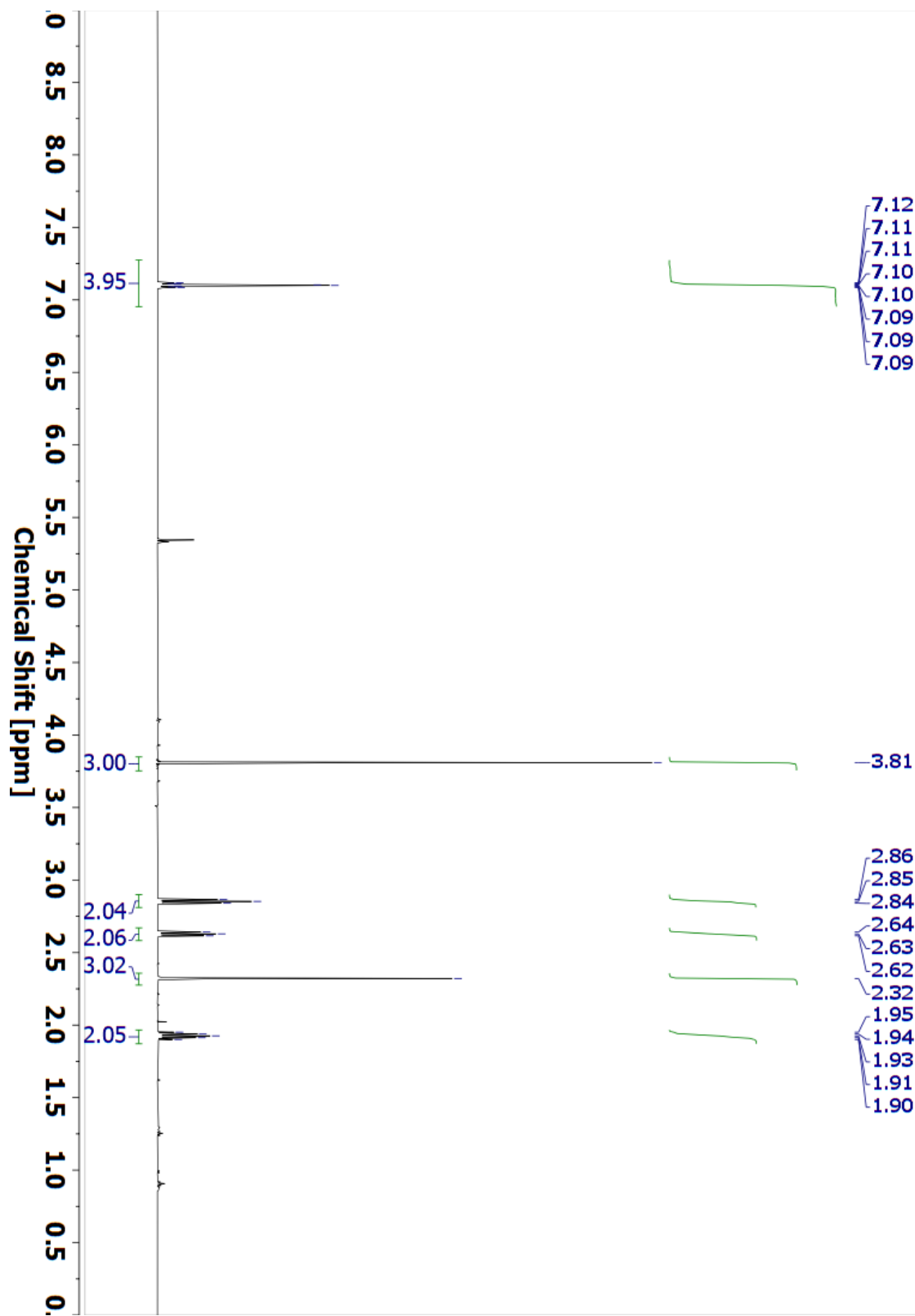


^1H NMR spectrum of isolated product in CD_2Cl_2

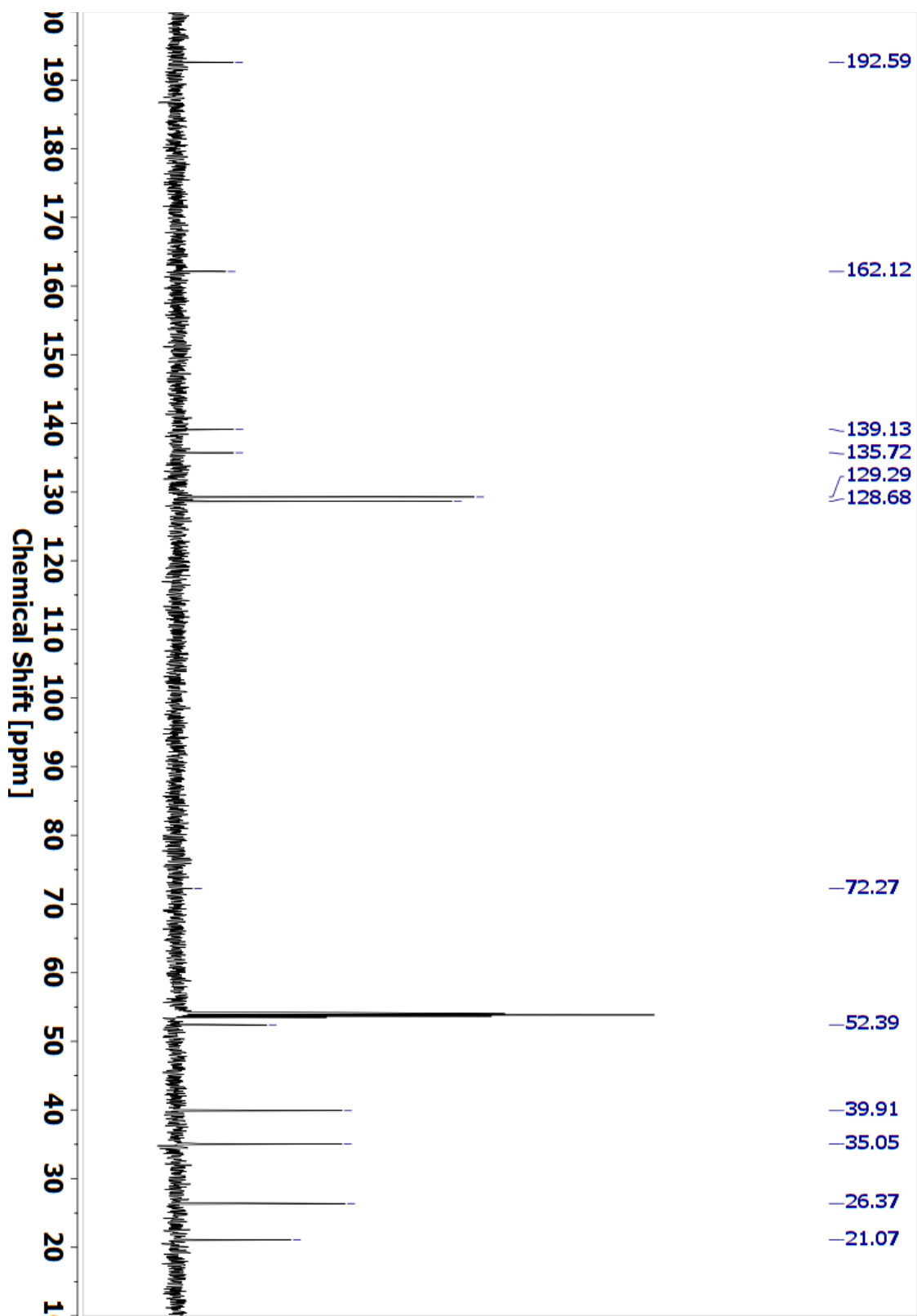


^{13}C NMR spectrum of isolated product in CD_2Cl_2

2. Methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (S14): Synthesized following Procedure B: The reaction was run on 10.00 mmol scale to give 2.02 g (78% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.27–6.95 (m, 4H), 3.81 (s, 3H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.71–2.57 (m, 2H), 2.32 (s, 2H), 1.98–1.86 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 192.59, 162.12, 139.13, 135.72, 129.29, 128.68, 72.27, 52.39, 39.91, 35.05, 26.37, 21.07. HRMS (ESI⁺) *m/z* Calc. 283.1053 [C₁₄H₁₆N₂O₃+Na]⁺, Found. 283.1052 [M+Na]⁺.

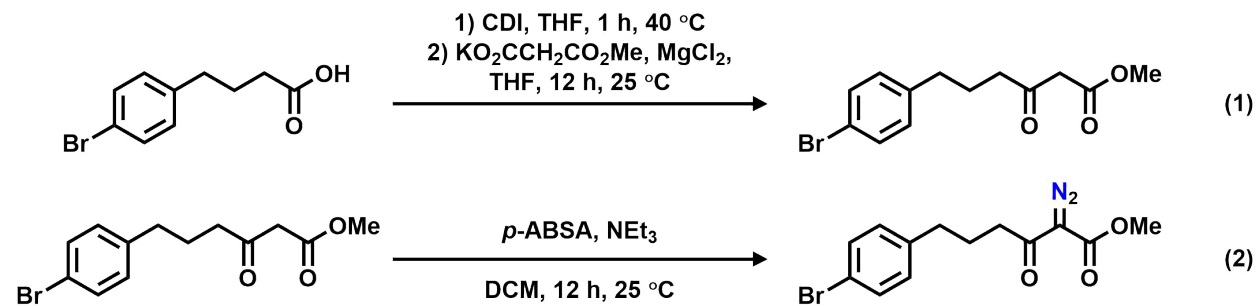


^1H NMR spectrum of isolated product in CD_2Cl_2

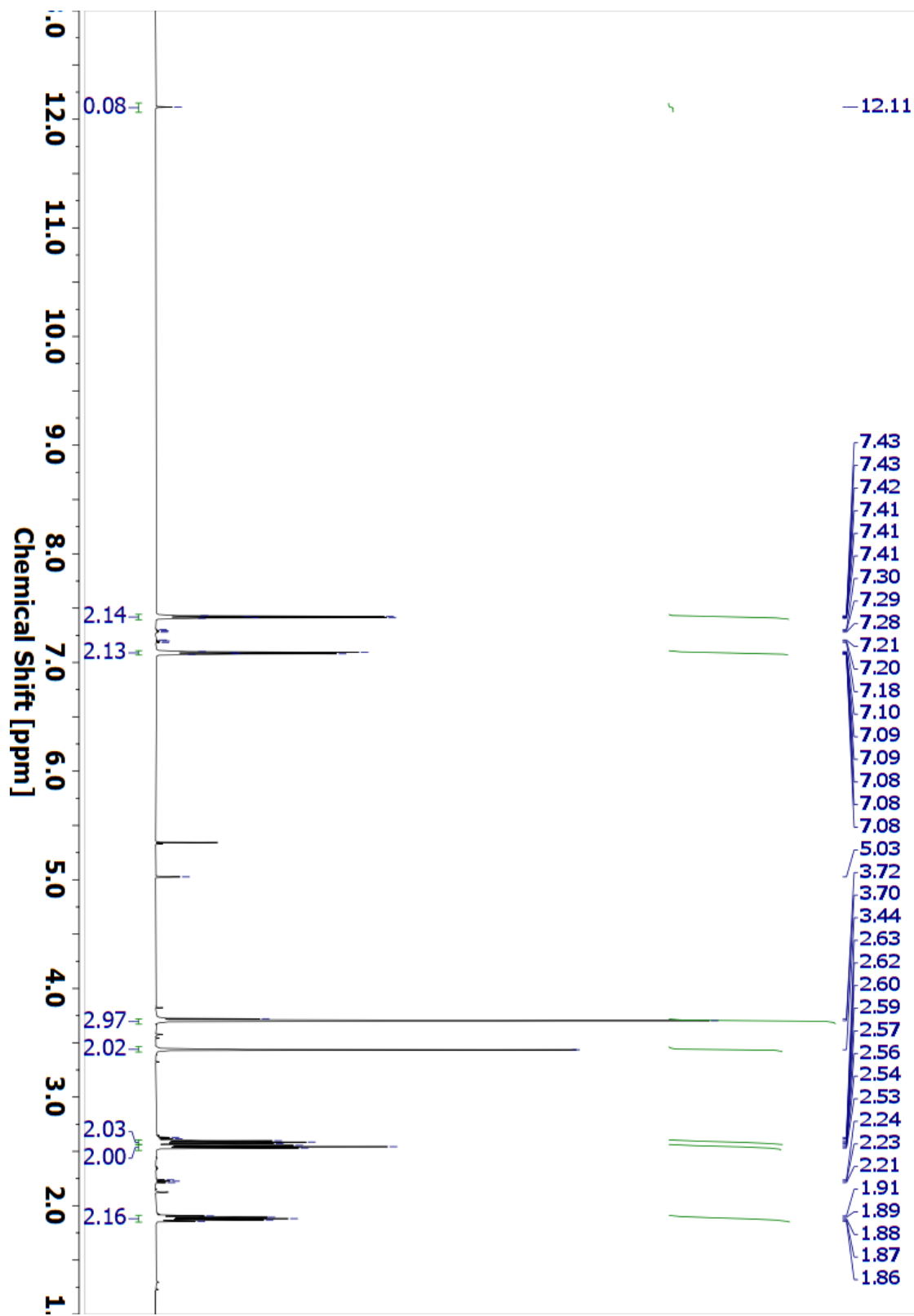


^{13}C NMR spectrum of isolated product in CD_2Cl_2

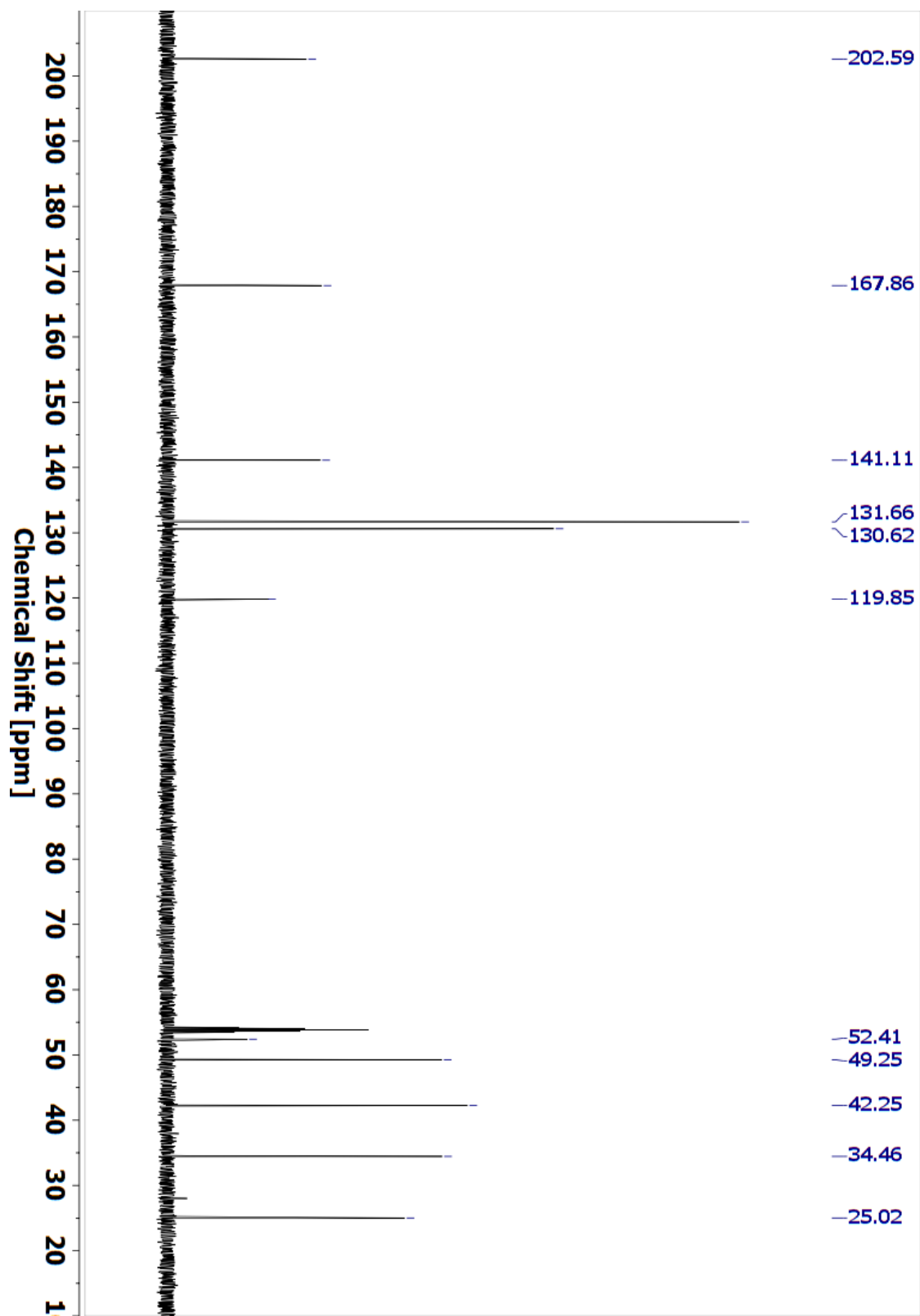
Methyl 6-(4-bromophenyl)-2-diazo-3-oxohexanoate (S16)



1. Methyl 6-(4-bromophenyl)-3-oxohexanoate (S15): Synthesized following Procedure A: The reaction was run on 30.00 mmol scale to give 3.36 g (37% yield, 7.4% tautomerization) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.45–7.39 (m, 2H), 7.12–7.06 (m, 2H), 3.70 (s, 3H), 3.44 (s, 2H), 2.61–2.56 (m, 2H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.95–1.83 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 202.59, 167.86, 141.11, 131.66, 130.62, 119.85, 52.41, 49.25, 42.25, 34.46, 25.02. HRMS (ESI⁺) *m/z* Calc. 321.0097 [C₁₃H₁₅BrO₃+Na]⁺, Found 321.0108 [M+Na]⁺.

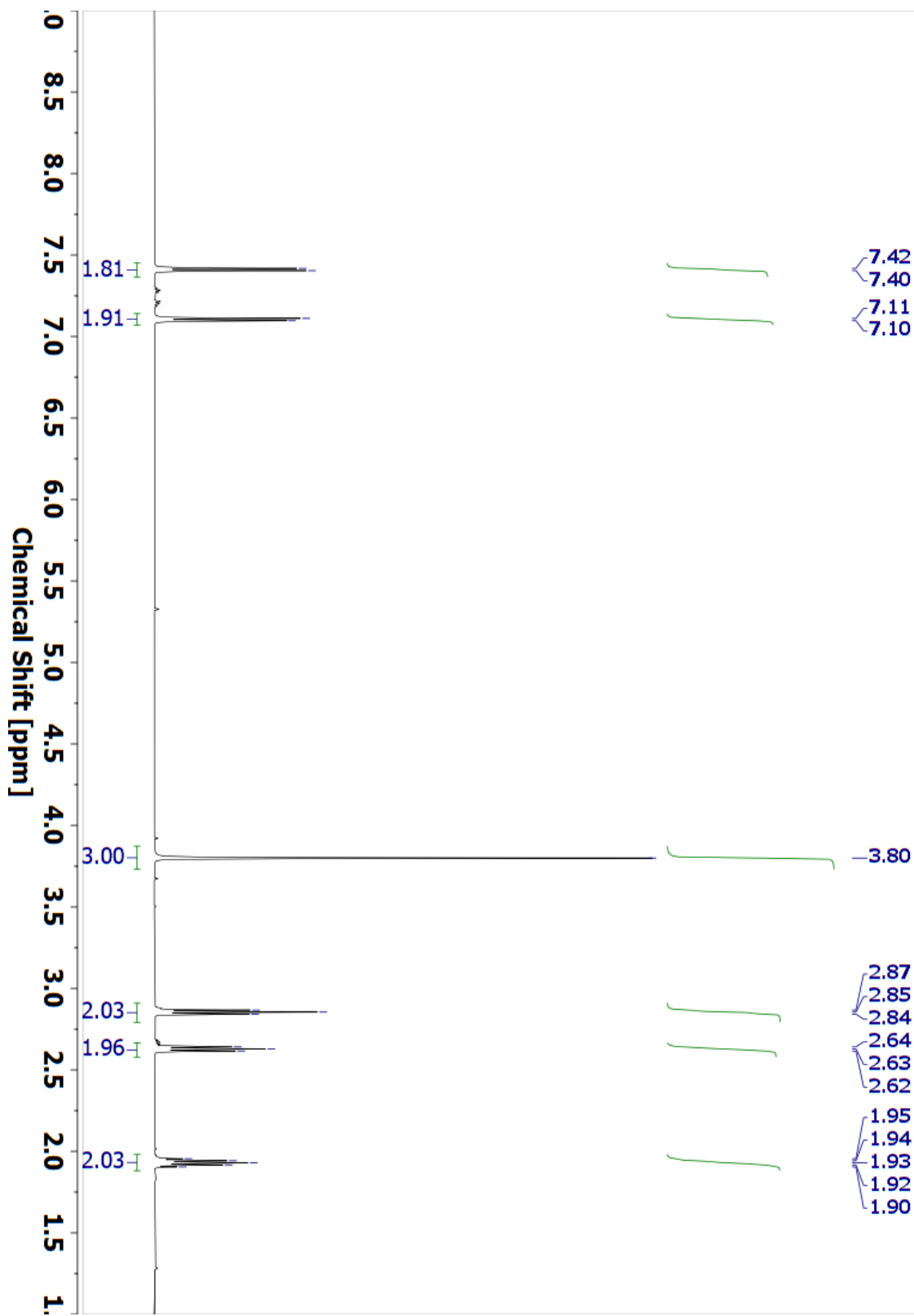


^1H NMR spectrum of isolated product in CD_2Cl_2

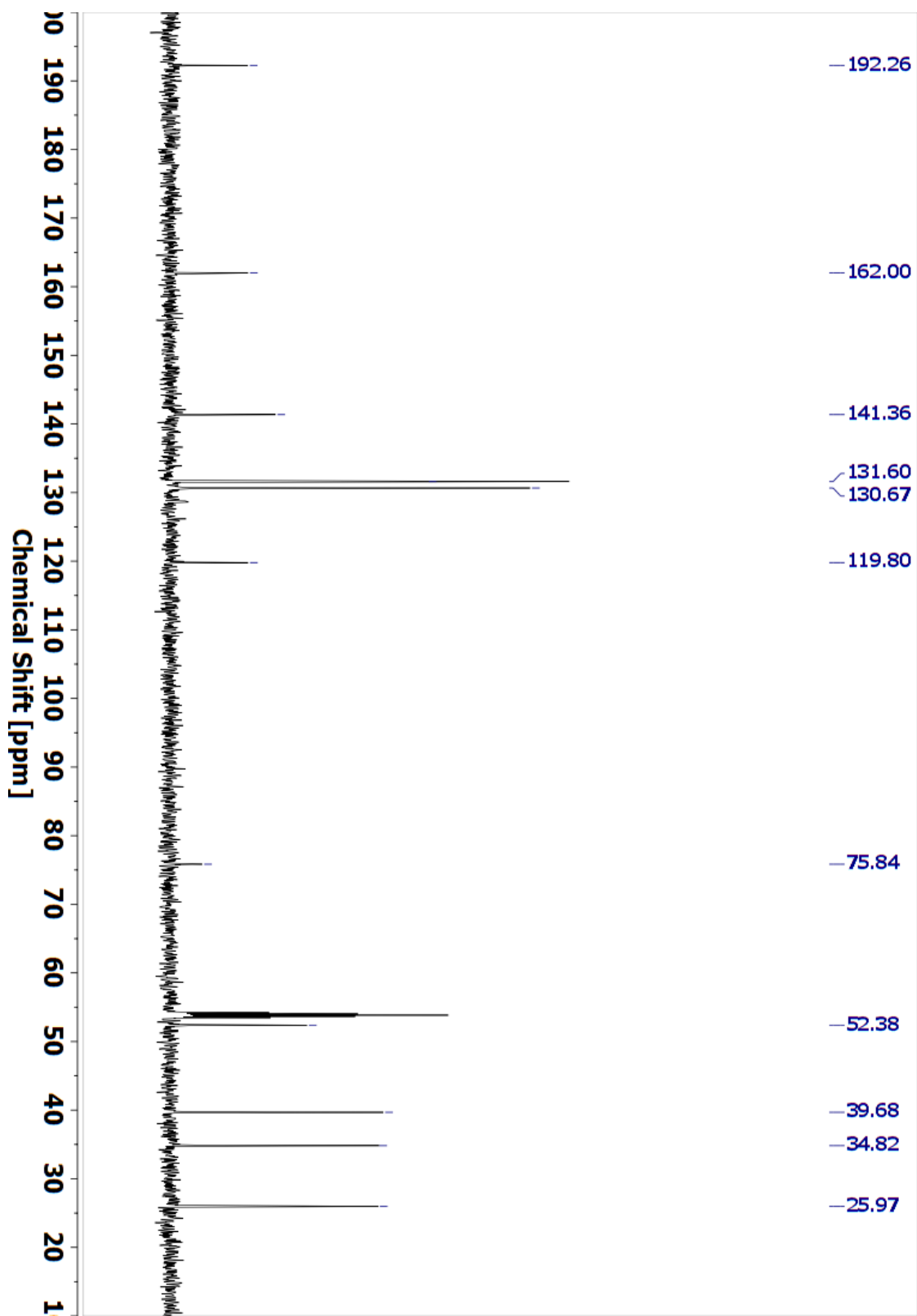


^{13}C NMR spectrum of isolated product in CD_2Cl_2

2. Methyl 6-(4-bromophenyl)-2-diazo-3-oxohexanoate (S16): Synthesized following Procedure B: The reaction was run on 10.00 mmol scale to give 1.90 g (58% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.06–1.85 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 192.26, 162.00, 141.36, 131.60, 130.67, 119.80, 75.84, 52.38, 39.68, 34.82, 25.97. HRMS (ESI⁺) *m/z* Calc. 325.0182 [C₁₃H₁₃BrN₂O₃+H]⁺, Found. 325.0184 [M+H]⁺.

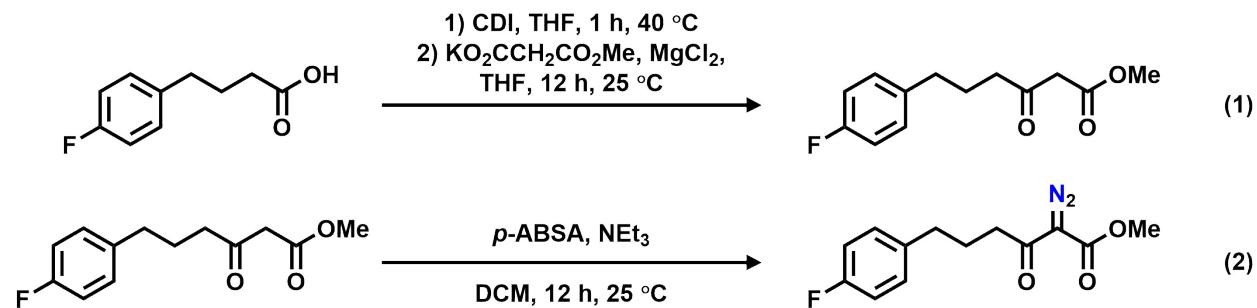


^1H NMR spectrum of isolated product in CD_2Cl_2

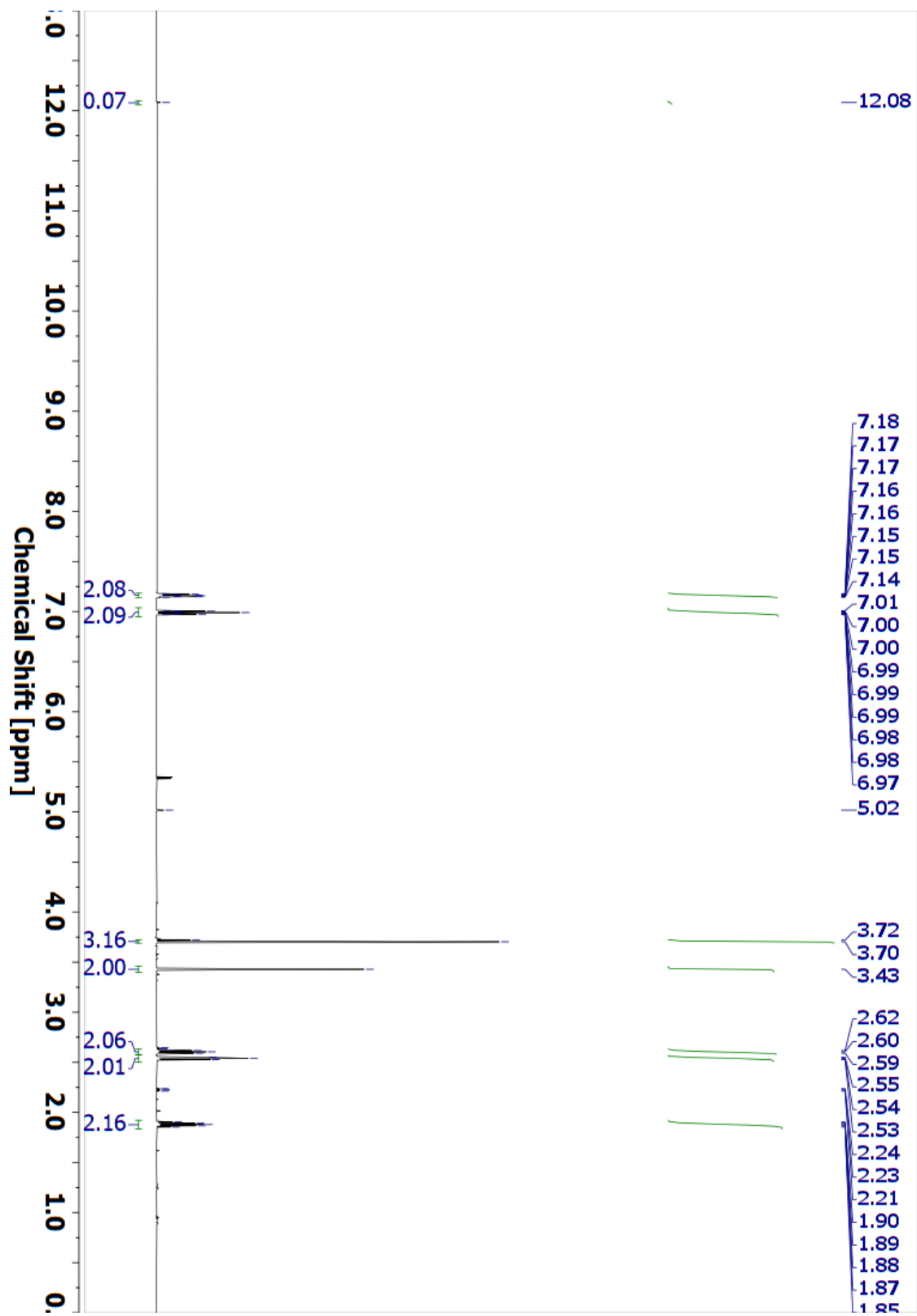


¹³C NMR spectrum of isolated product in CD₂Cl₂

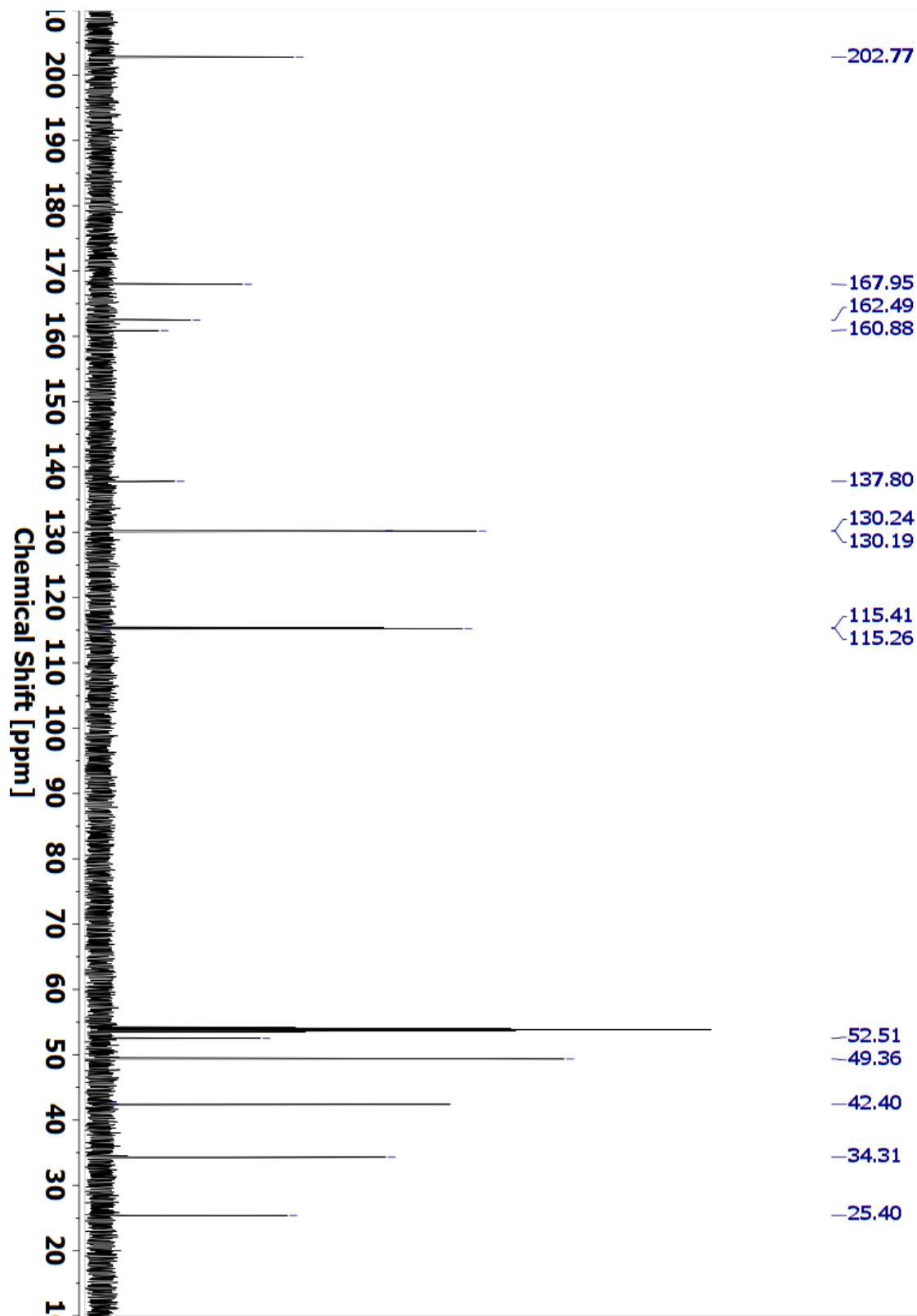
Methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (S17)



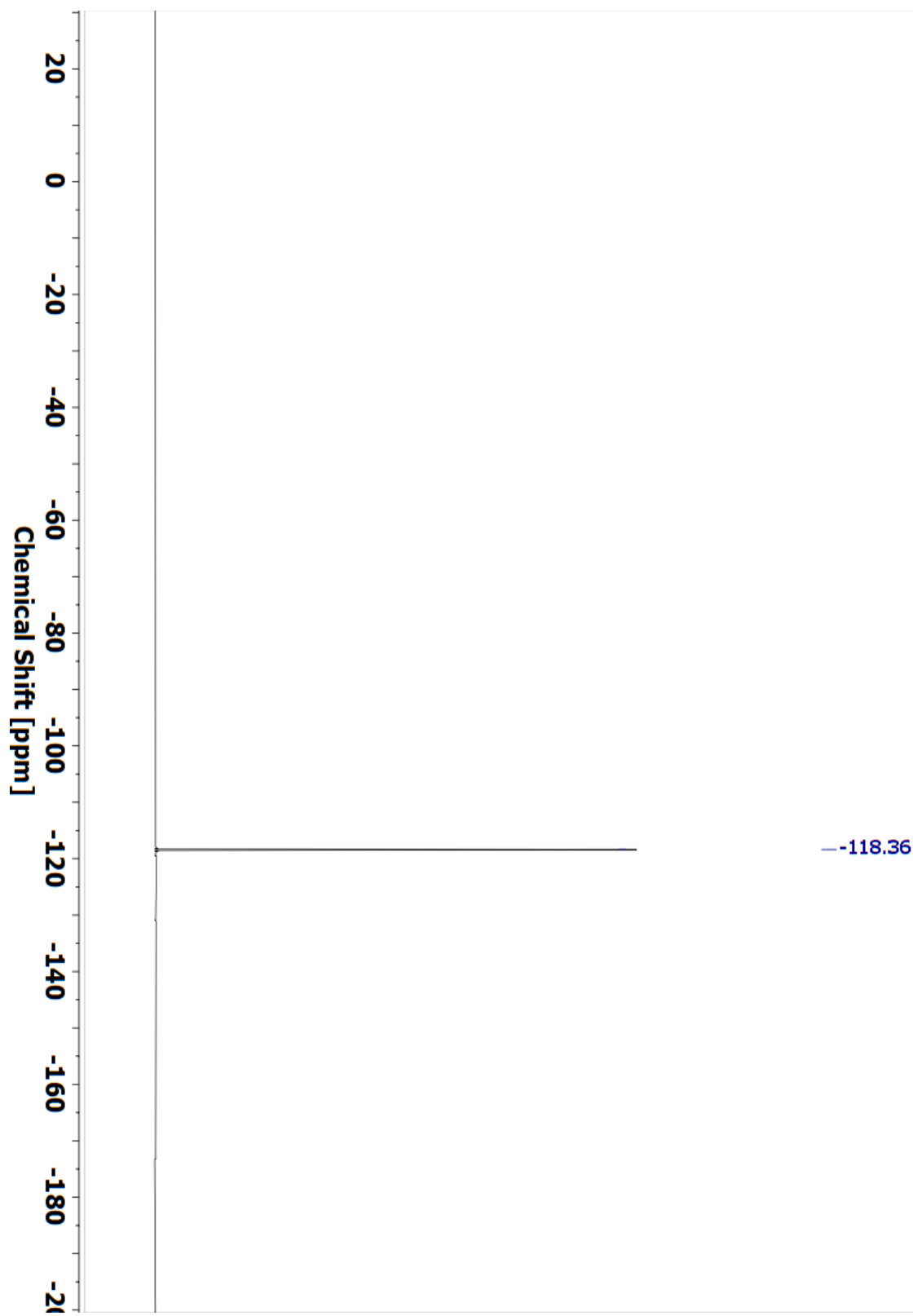
1. Methyl 6-(4-fluorophenyl)-3-oxohexanoate (S17): Synthesized following Procedure A: The reaction was run on 30.00 mmol scale to give 3.86 g (54% yield, 7.4% tautomerization) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.23–7.11 (m, 2H), 7.07–6.89 (m, 2H), 3.70 (s, 3H), 3.43 (s, 2H), 2.66–2.57 (m, 2H), 2.54 (t, $J = 7.3$ Hz, 2H), 2.00–1.76 (m, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 202.77, 167.95, 161.69 (d, $J = 242.8$ Hz), 137.80, 130.22 (d, $J = 8.1$ Hz), 115.33 (d, $J = 22.5$ Hz), 52.51, 49.36, 42.40, 34.31, 25.40. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -118.36. HRMS (ESI⁺) m/z Calc. 261.0897 [$\text{C}_{13}\text{H}_{15}\text{FO}_3 + \text{Na}$]⁺, Found 261.0894 [$\text{M} + \text{Na}$]⁺.



^1H NMR spectrum of isolated product in CD_2Cl_2

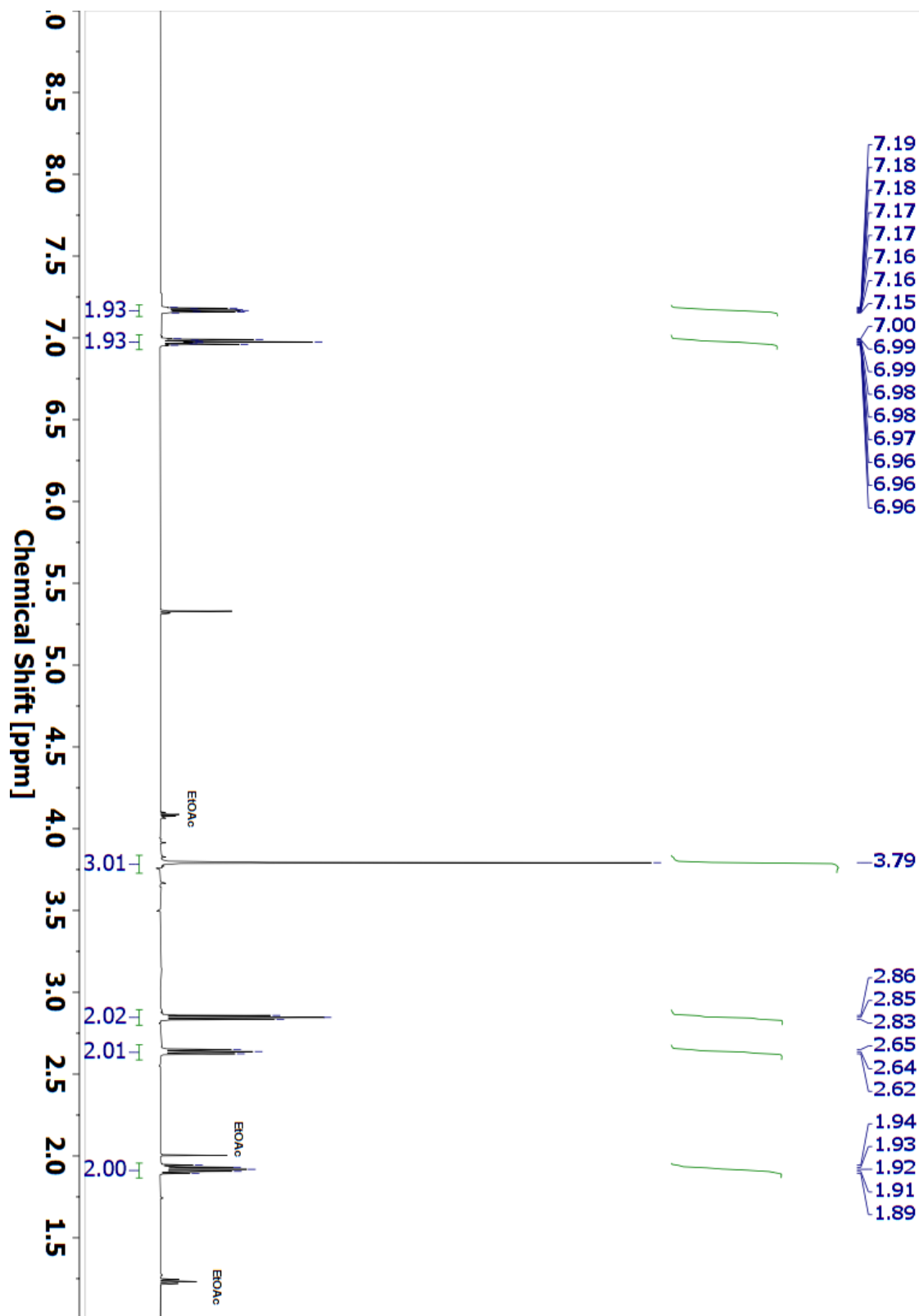


^{13}C NMR spectrum of isolated product in CD_2Cl_2

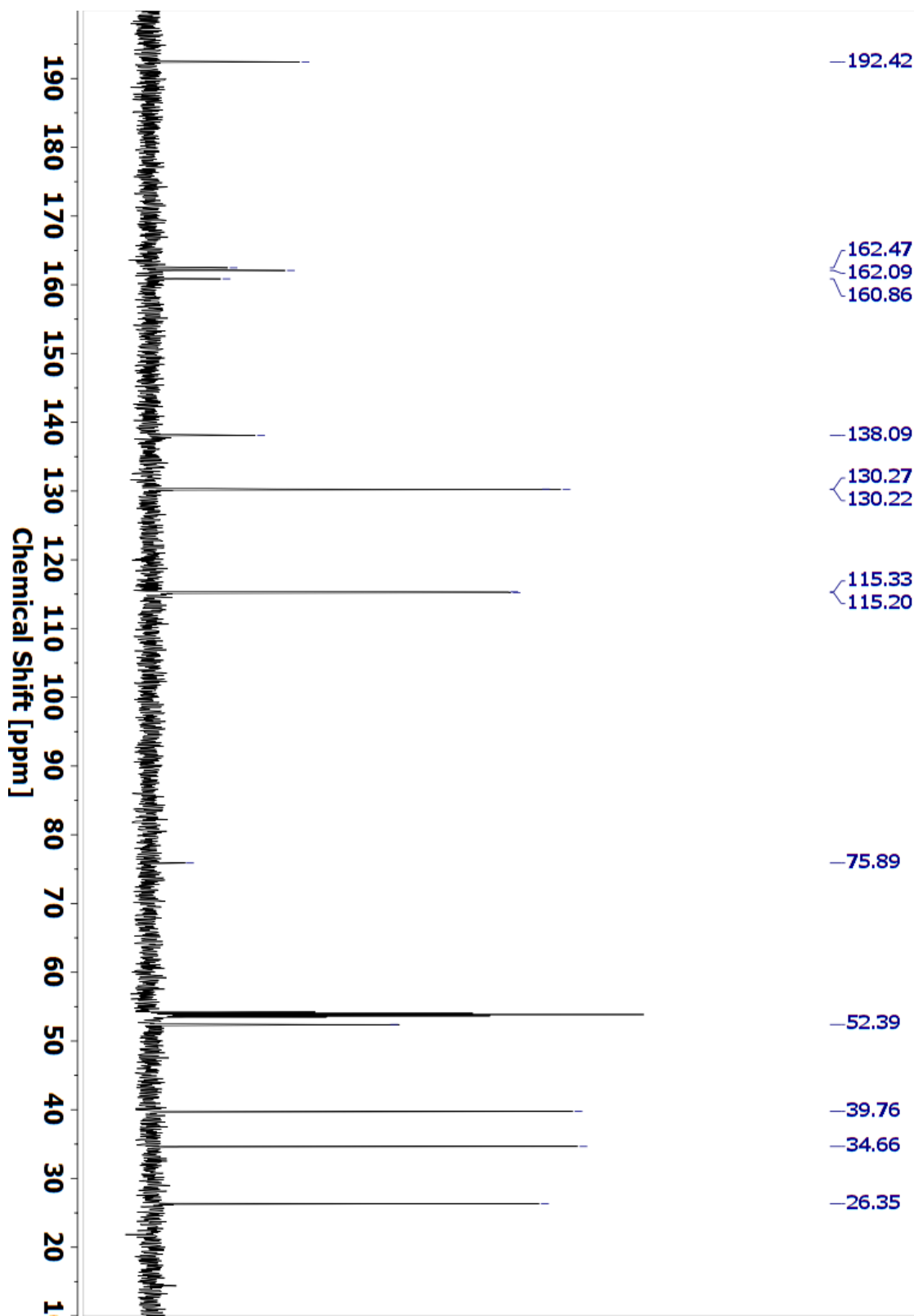


^{19}F NMR spectrum of isolated product in CD_2Cl_2

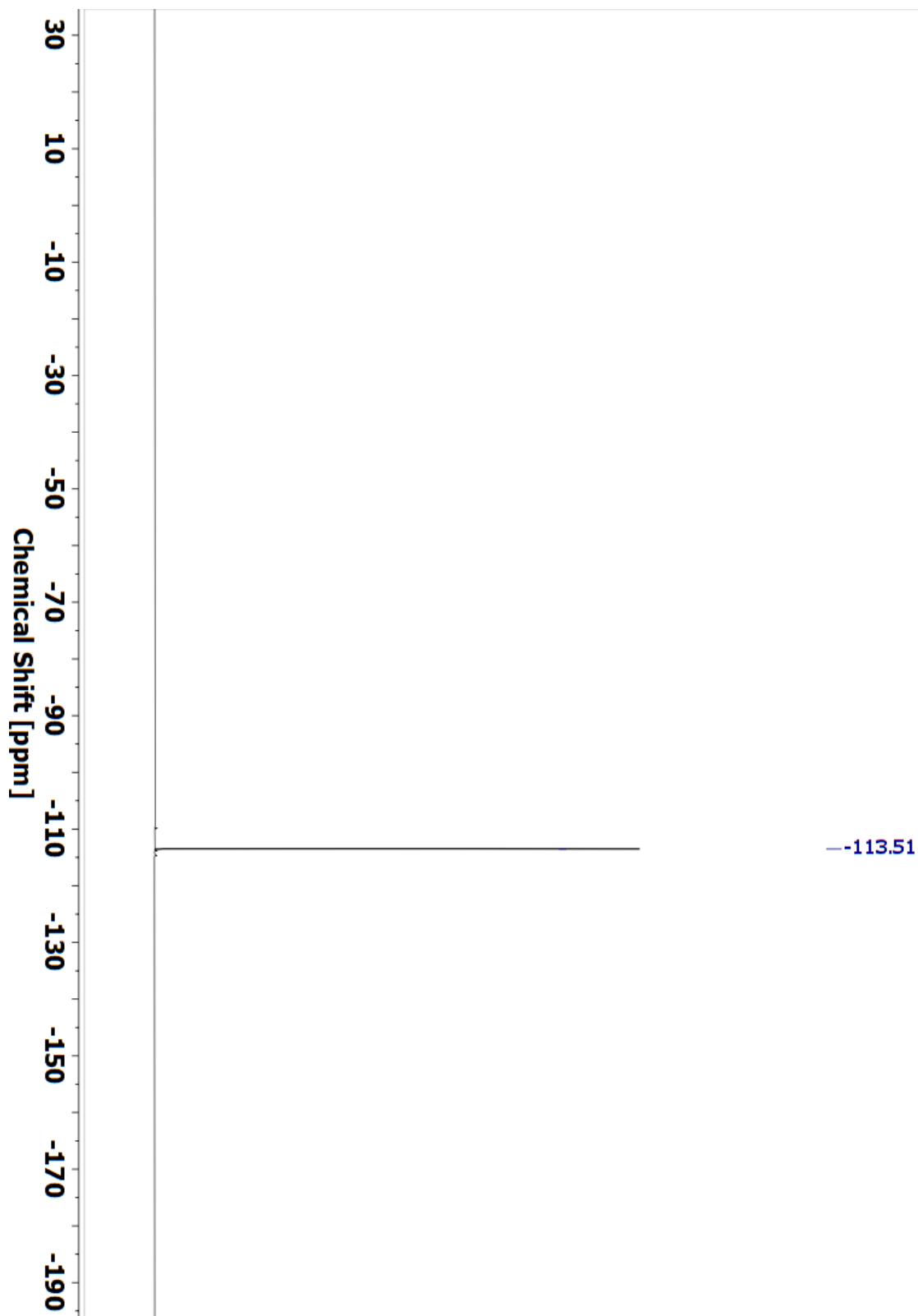
2. Methyl 2-diazo-6-(4-fluorophenyl)-3-oxohexanoate (S18): Synthesized following Procedure B: The reaction was run on 10.00 mmol scale to give 1.59 g (60% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.21–7.12 (m, 2H), 7.05–6.90 (m, 2H), 3.79 (s, 3H), 2.90–2.79 (m, 2H), 2.73–2.59 (m, 2H), 1.96–1.84 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 192.42, 162.09, 161.67 (d, *J* = 243.5 Hz), 138.09, 130.25 (d, *J* = 7.5 Hz), 115.27 (d, *J* = 20.8 Hz), 75.89, 52.39, 39.76, 34.66, 26.35. ¹⁹F NMR (471 MHz, CD₂Cl₂) δ -113.51. HRMS (ESI⁺) *m/z* Calc. 287.0802 [C₁₃H₁₃FN₂O₃+Na]⁺, Found. 287.0823 [M+Na]⁺.



^1H NMR spectrum of isolated product in CD_2Cl_2

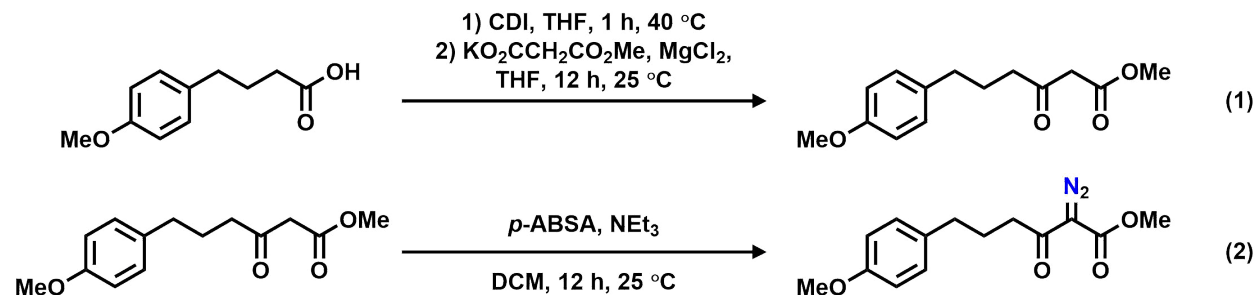


^{13}C NMR spectrum of isolated product in CD_2Cl_2



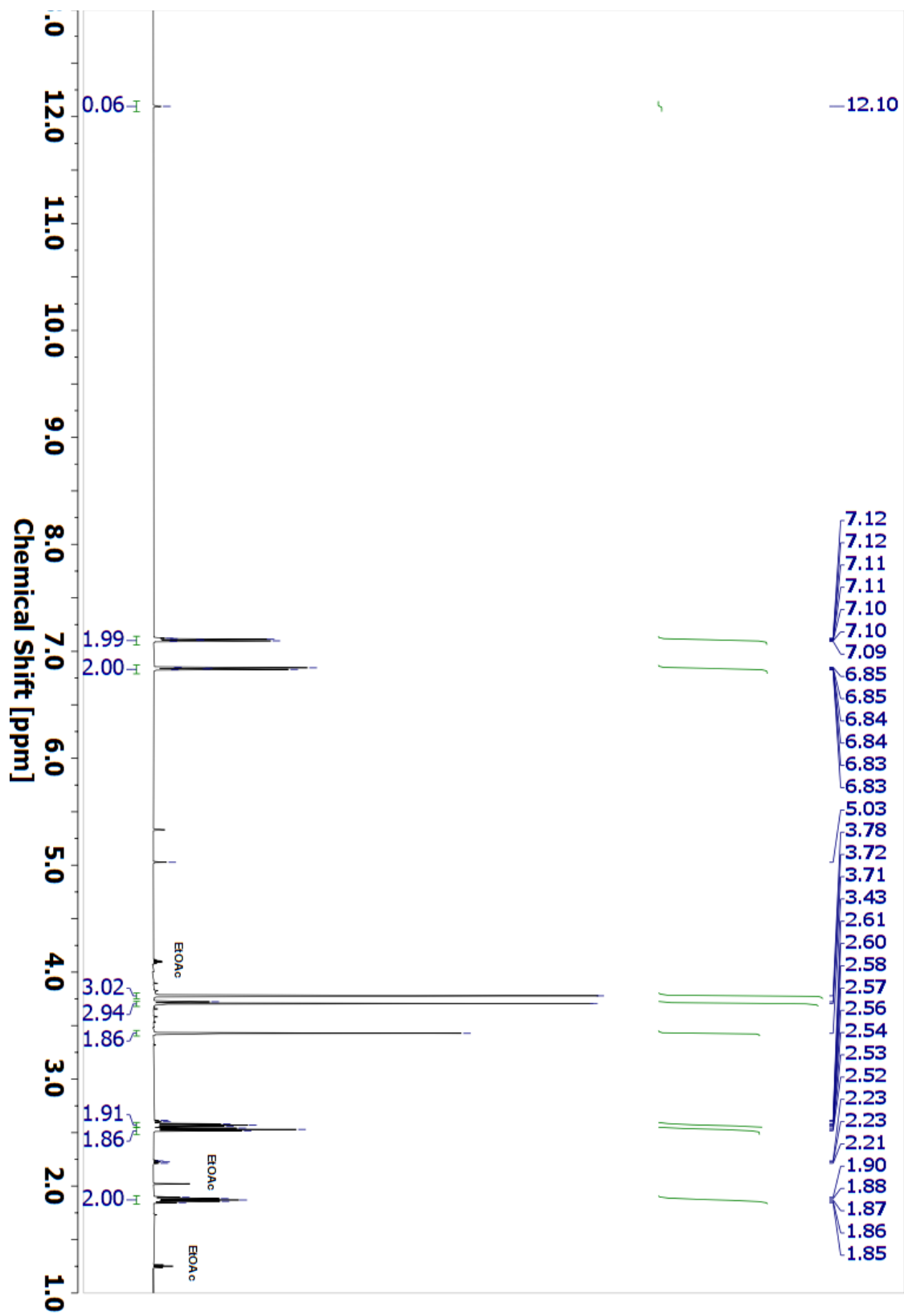
^{19}F NMR spectrum of isolated product in CD_2Cl_2

Methyl 2-diazo-6-(4-methoxyphenyl)-3-oxohexanoate (S20)

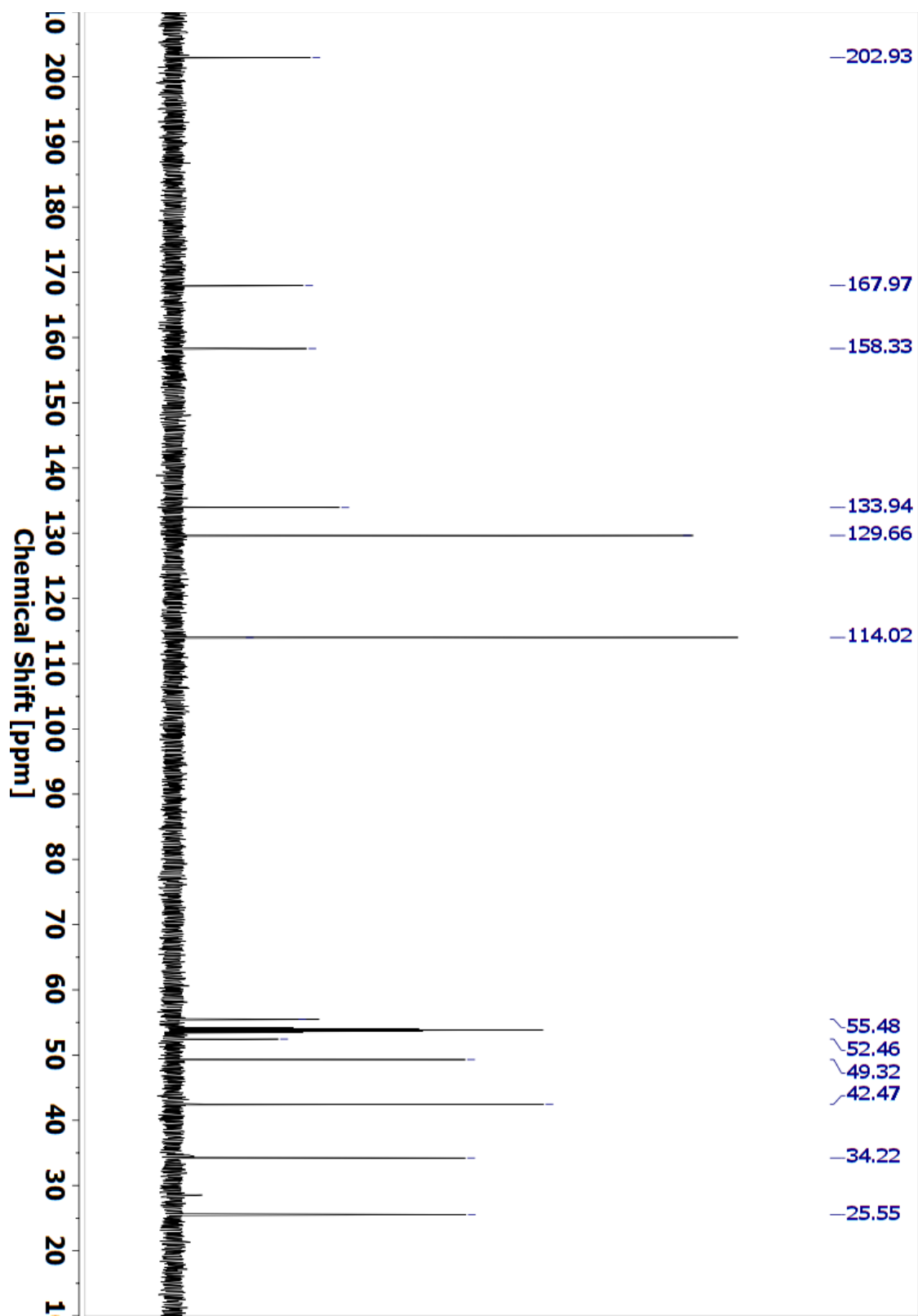


1. Methyl 6-(4-methoxyphenyl)-3-oxohexanoate (S19): Synthesized following Procedure A:

The reaction was run on 30.00 mmol scale to give 3.17 g (42% yield, 5.7% tautomerization) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.15–7.06 (m, 2H), 6.88–6.79 (m, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 3.43 (s, 2H), 2.60–2.55 (m, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 1.93–1.78 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 202.93, 167.97, 158.33, 133.94, 129.66, 114.02, 55.48, 52.46, 49.32, 42.47, 34.22, 25.55. HRMS (ESI+) *m/z* Calc. 273.1097 [C₁₄H₁₈O₄+Na]⁺, Found 273.1062 [M+Na]⁺

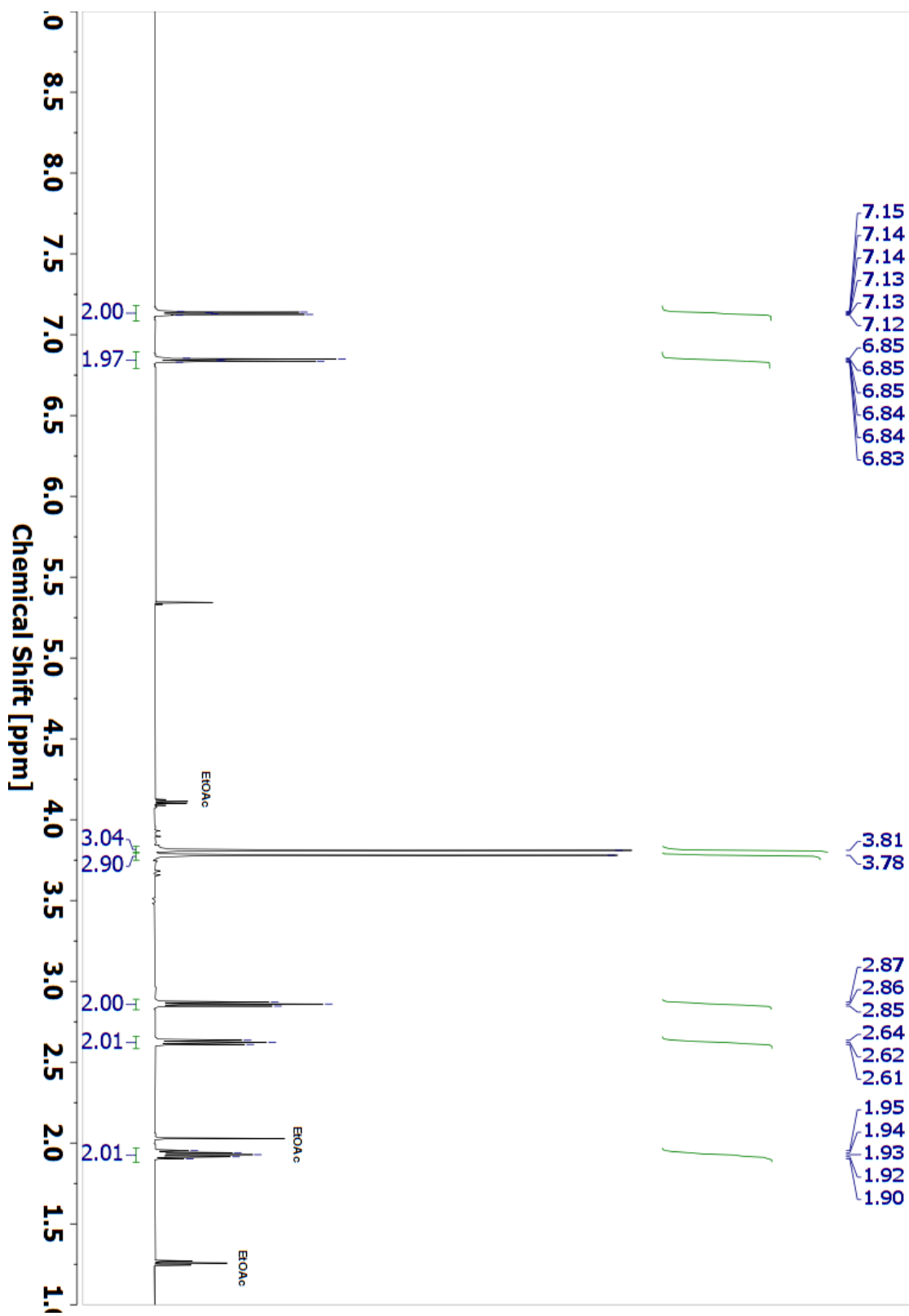


^1H NMR spectrum of isolated product in CD_2Cl_2

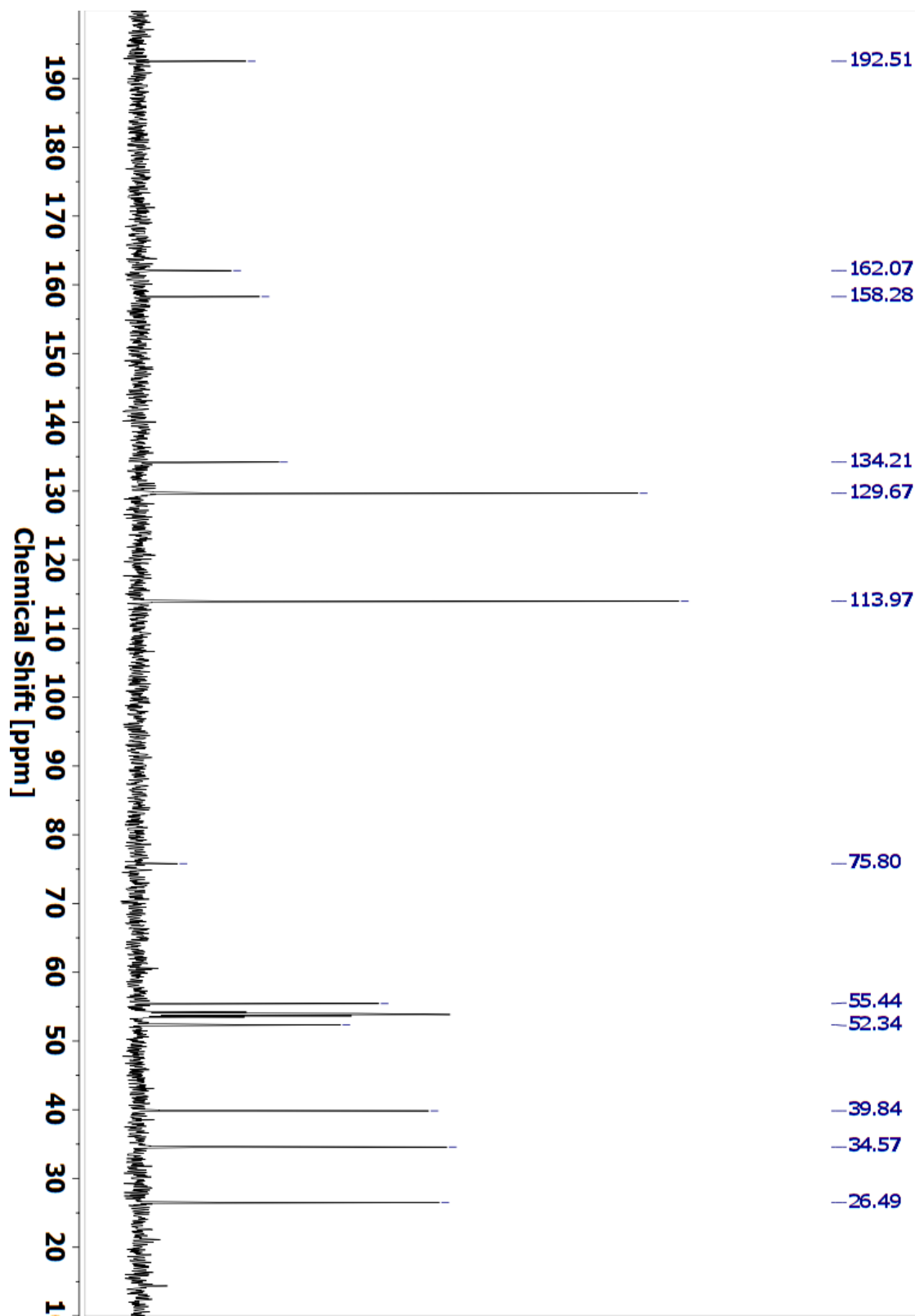


¹³C NMR spectrum of isolated product in CD₂Cl₂

2. Methyl 2-diazo-6-(4-methoxyphenyl)-3-oxohexanoate (S20): Synthesized following Procedure B: The reaction was run on 10.00 mmol scale to give 1.77 g (64% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.26–7.06 (m, 2H), 6.95–6.62 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.93–2.80 (m, 2H), 2.74–2.51 (m, 2H), 1.95–1.87 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 192.51, 162.07, 158.28, 134.21, 129.67, 113.97, 75.80, 55.44, 52.34, 39.84, 34.57, 26.49. HRMS (ESI⁺) m/z Calc. 299.1002 [C₁₄H₁₆N₂O₄+Na]⁺, Found 299.0905 [M+Na]⁺.

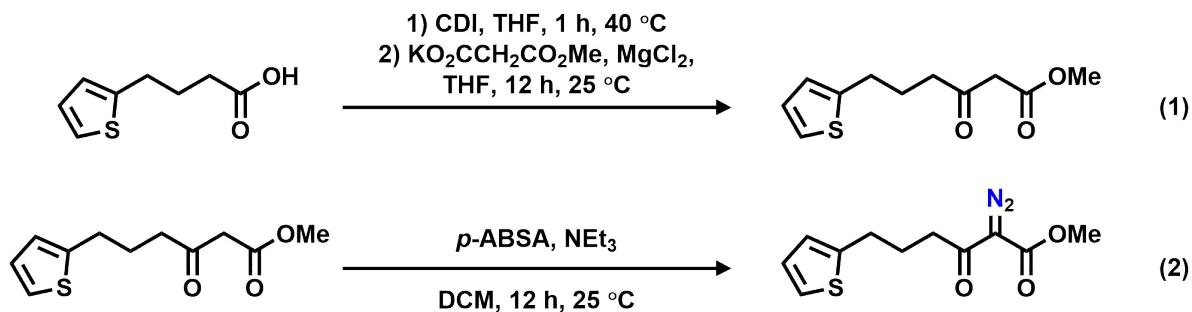


^1H NMR spectrum of isolated product in CD_2Cl_2

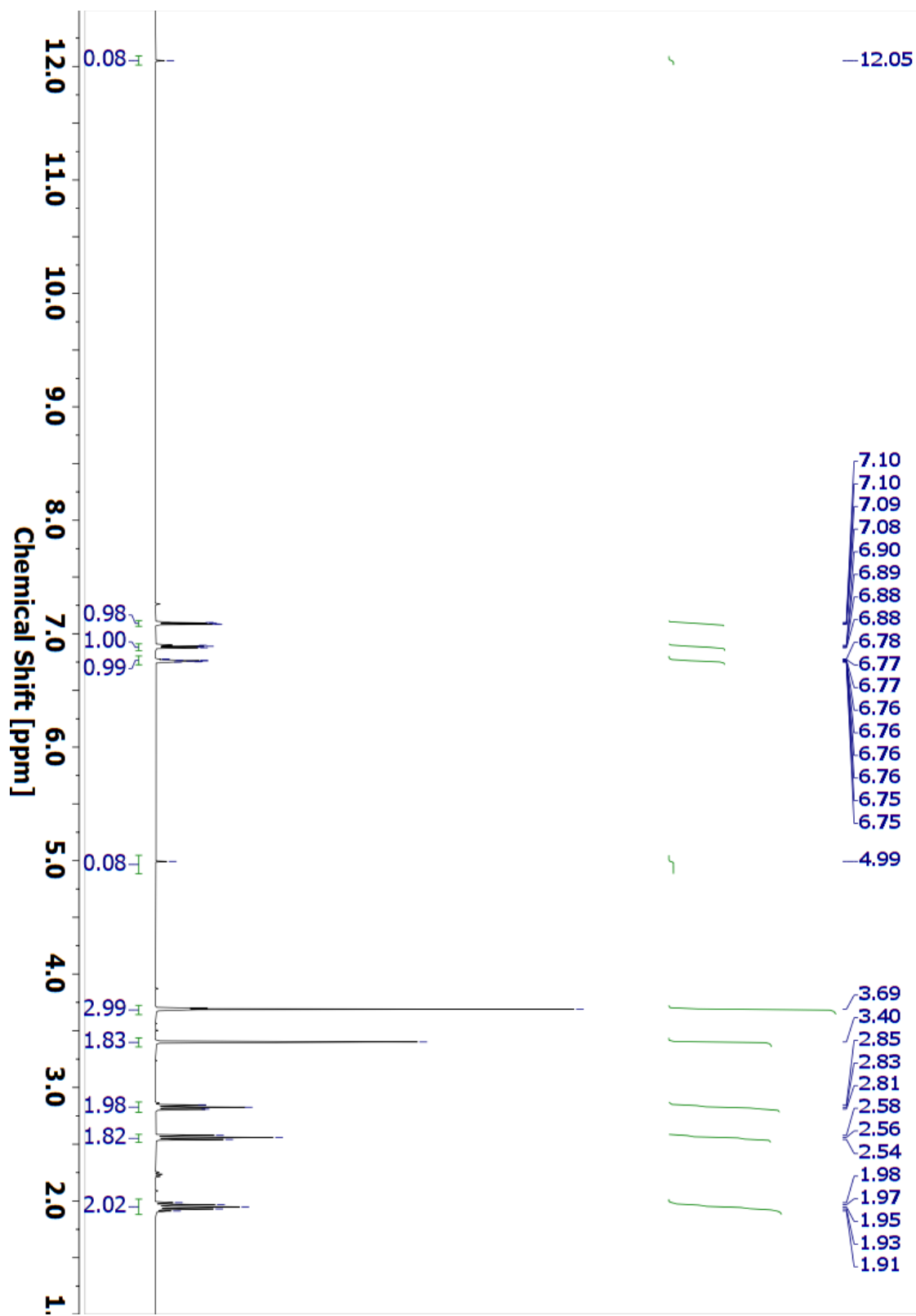


^{13}C NMR spectrum of isolated product in CD_2Cl_2

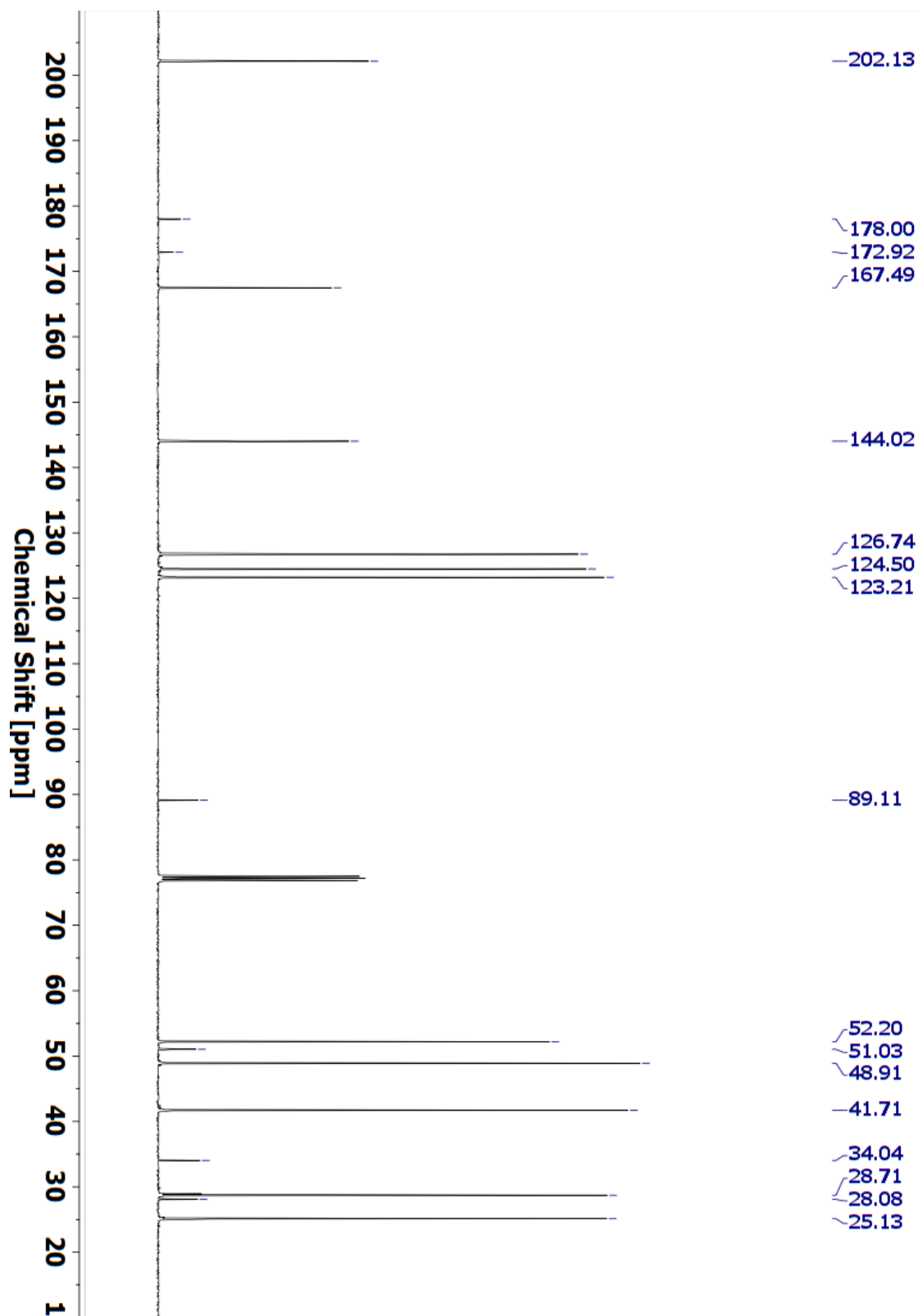
Methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (S22)



1. Methyl 3-oxo-6-(thiophen-2-yl)hexanoate (S21): Synthesized following Procedure A: The reaction was run on 10.0 mmol scale to give 1.34 g (59% yield, 7.4% tautomerization) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.09 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.3 Hz, 1H), 6.79–6.72 (m, 1H), 3.69 (s, 3H), 3.40 (s, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.00–1.88 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 202.13, 167.49, 144.02, 126.74, 124.50, 123.21, 52.20, 48.91, 41.71, 28.71, 25.13. HRMS (ESI⁺) *m/z* Calc. 249.0556 [C₁₁H₁₄O₃S+Na]⁺, Found. 249.0554 [M+Na]⁺.



^1H NMR spectrum of isolated product in CD_2Cl_2

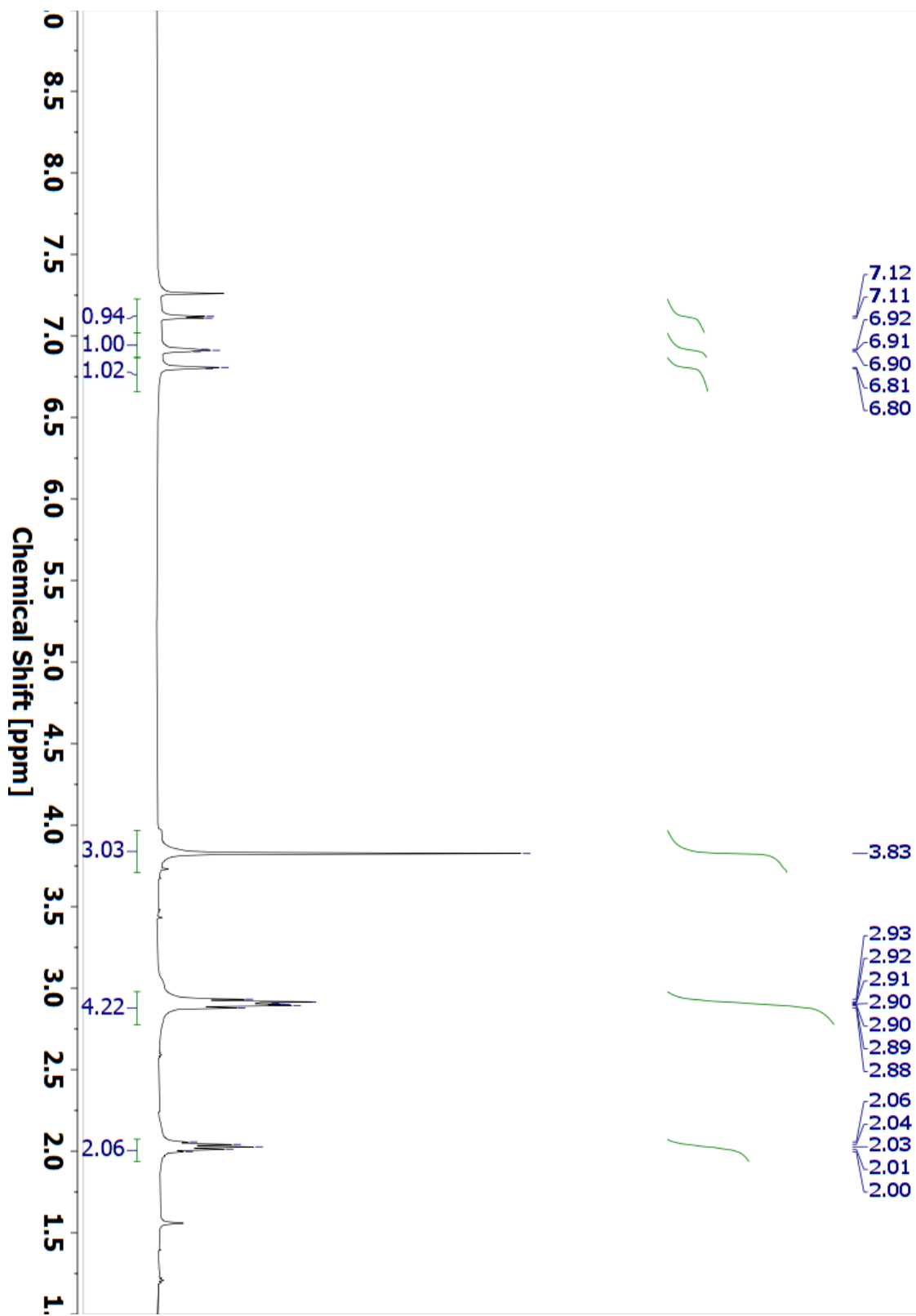


^{13}C NMR spectrum of isolated product in CD_2Cl_2

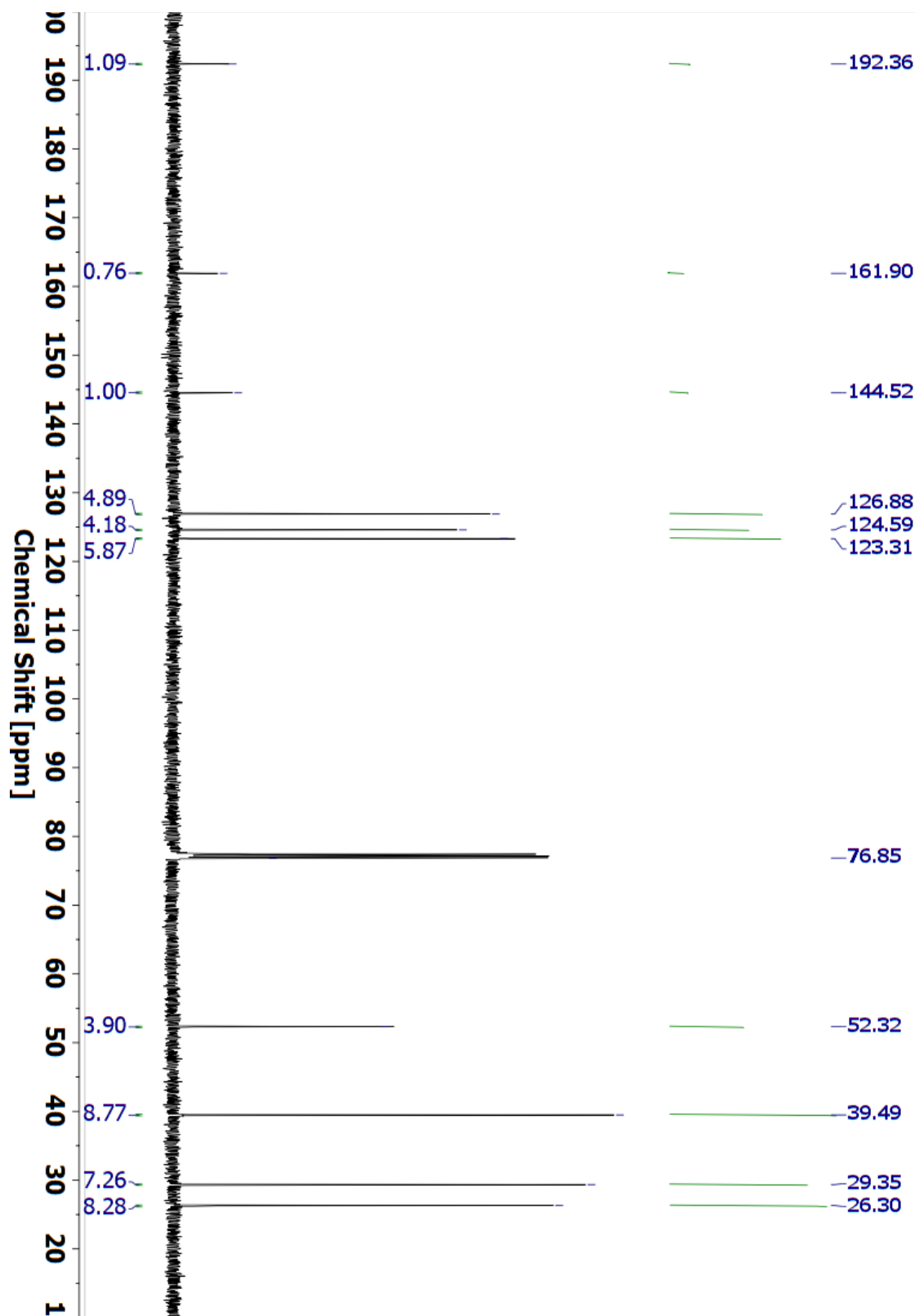
2. Methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (S22): Synthesized following Procedure B:

The reaction was run on 5.00 mmol scale to give 0.96 g (76% yield) of product as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 7.11 (d, $J = 5.1$ Hz, 1H), 7.02–6.87 (m, 1H), 6.80 (d, $J = 3.5$ Hz, 1H), 3.83 (s, 3H), 3.00–2.73 (m, 4H), 2.13–1.85 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 192.36, 161.90, 144.52, 126.88, 124.59, 123.31, 76.85, 52.32, 39.49, 29.35, 26.30. HRMS (ESI $^+$) m/z Calc. 253.0641 [$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3\text{S}+\text{H}$] $^+$, Found 253.0642 [$\text{M}+\text{H}$] $^+$.

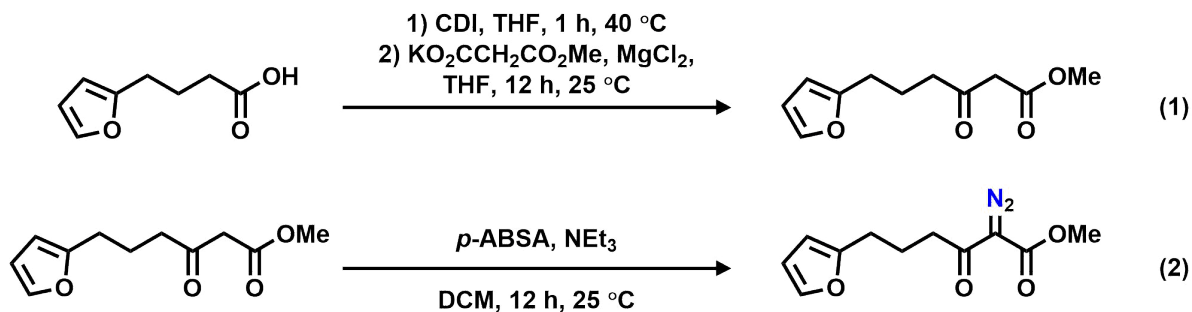


^1H NMR spectrum of isolated product in CD_2Cl_2

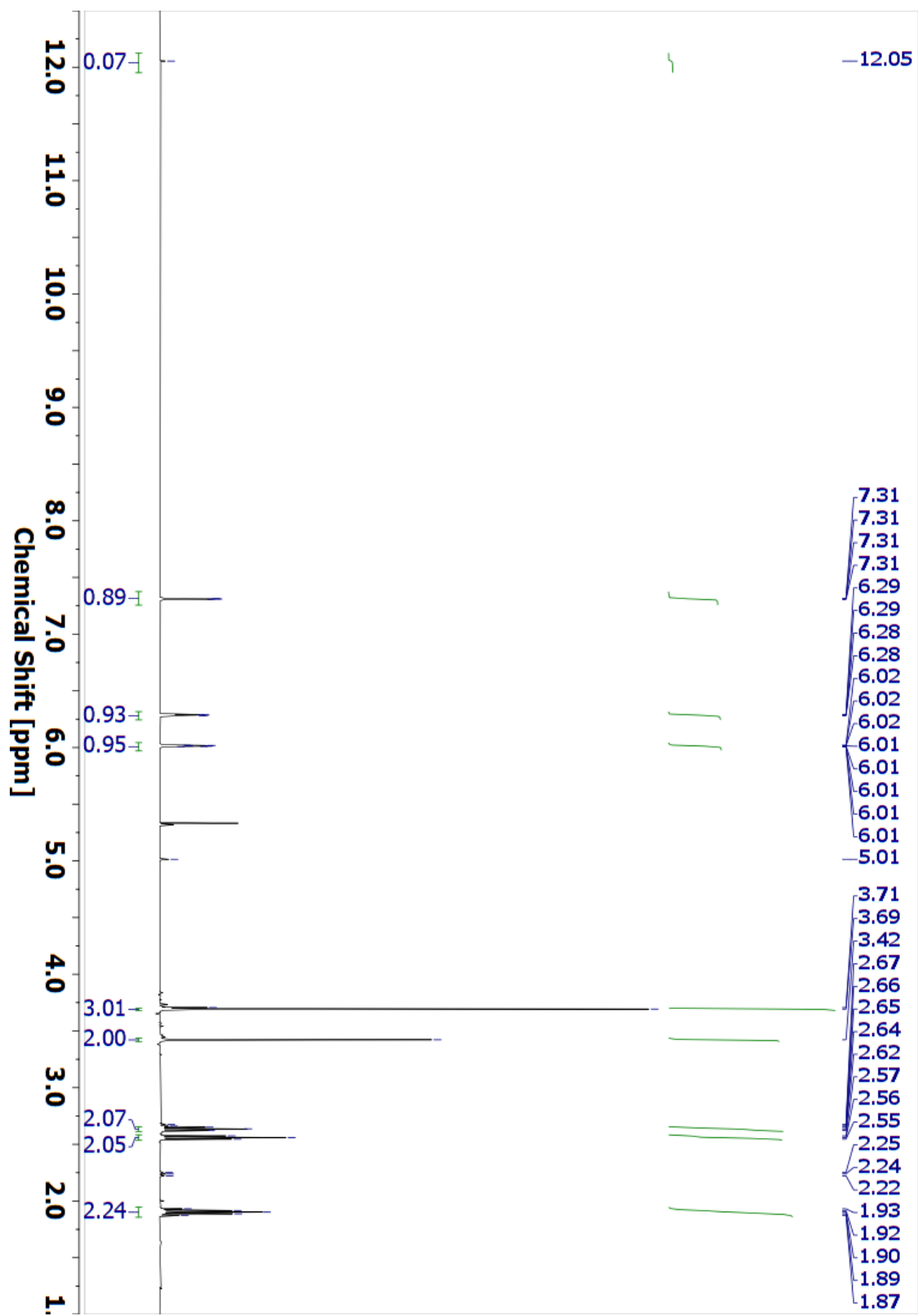


^{13}C NMR spectrum of isolated product in CD_2Cl_2

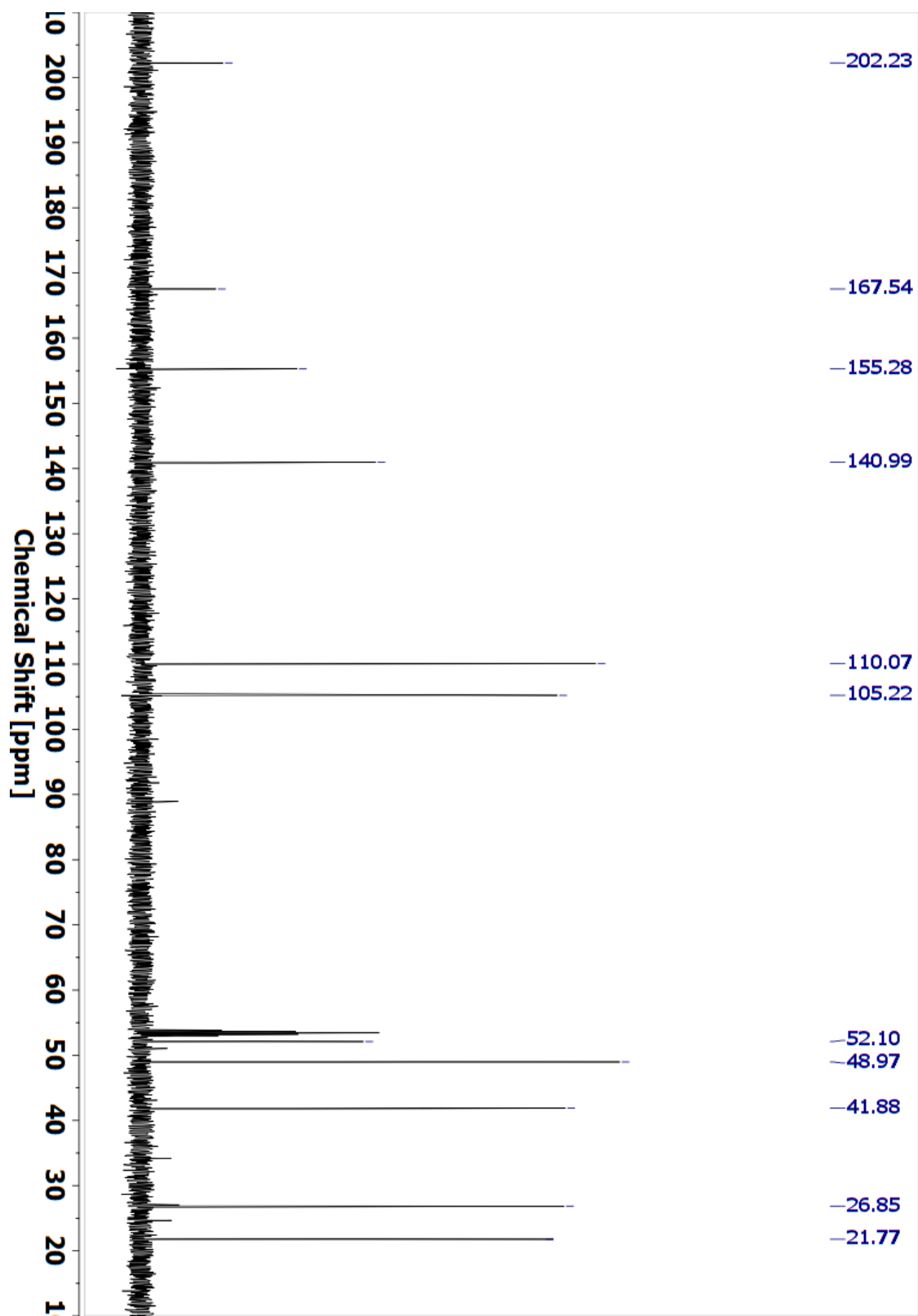
Methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (S24)



1. Methyl 6-(furan-2-yl)-3-oxohexanoate (S23): Synthesized following Procedure A: The reaction was run on 10.00 mmol scale to give 1.33 g (63% yield, 6.5% tautomerization) of product as a colorless oil. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.31 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.06–5.96 (m, 1H), 3.69 (s, 3H), 3.42 (s, 2H), 2.68–2.60 (m, 2H), 2.56 (t, *J* = 7.3 Hz, 2H), 1.97–1.85 (m, 2H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 202.23, 167.54, 155.28, 140.99, 110.07, 105.22, 52.10, 48.97, 41.88, 26.85, 21.77. HRMS (ESI⁺) *m/z* Calc. 233.0784 [C₁₁H₁₄O₄+Na]⁺, Found. 233.0782 [M+Na]⁺.



^1H NMR spectrum of isolated product in CD_2Cl_2

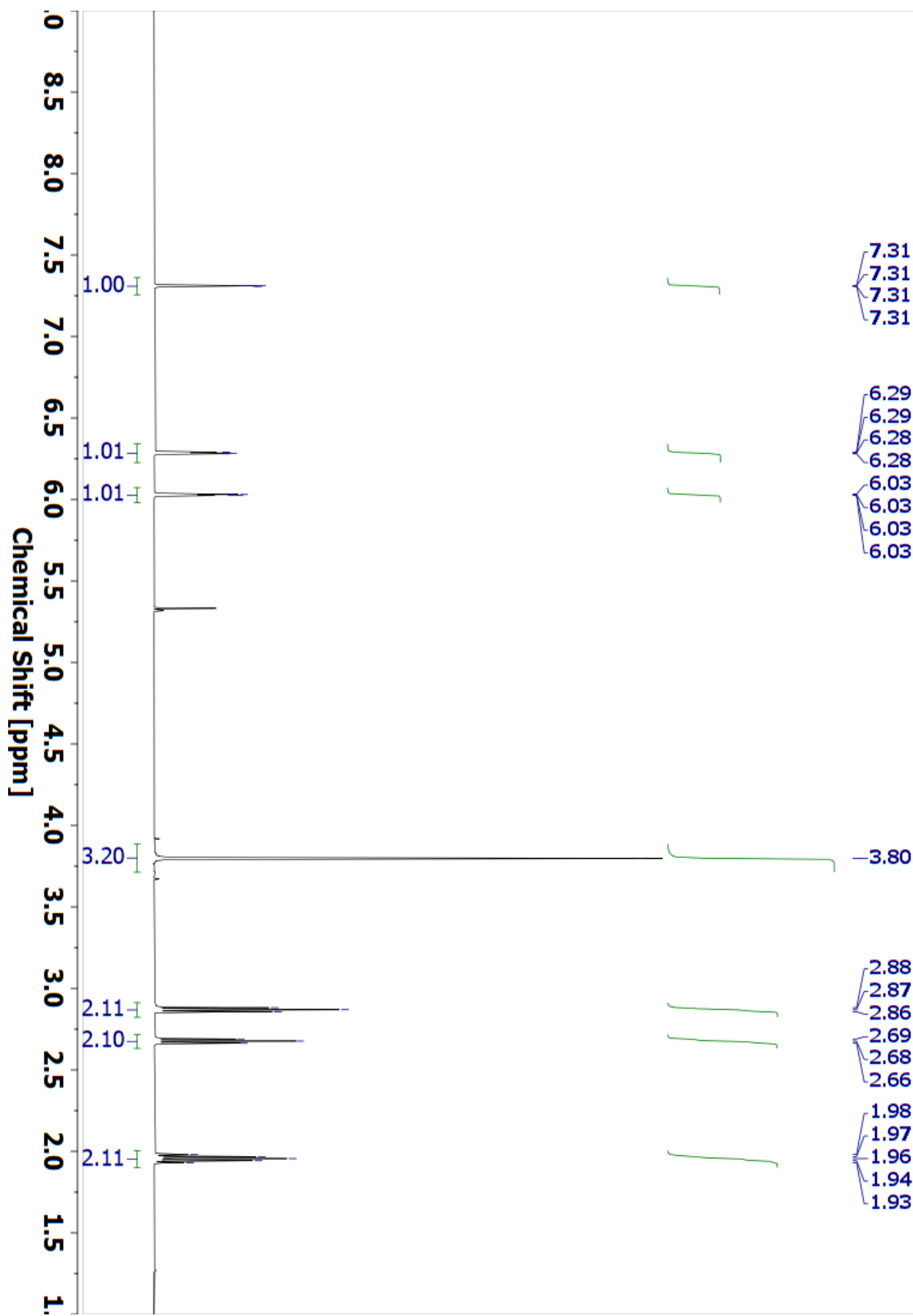


^{13}C NMR spectrum of isolated product in CD_2Cl_2

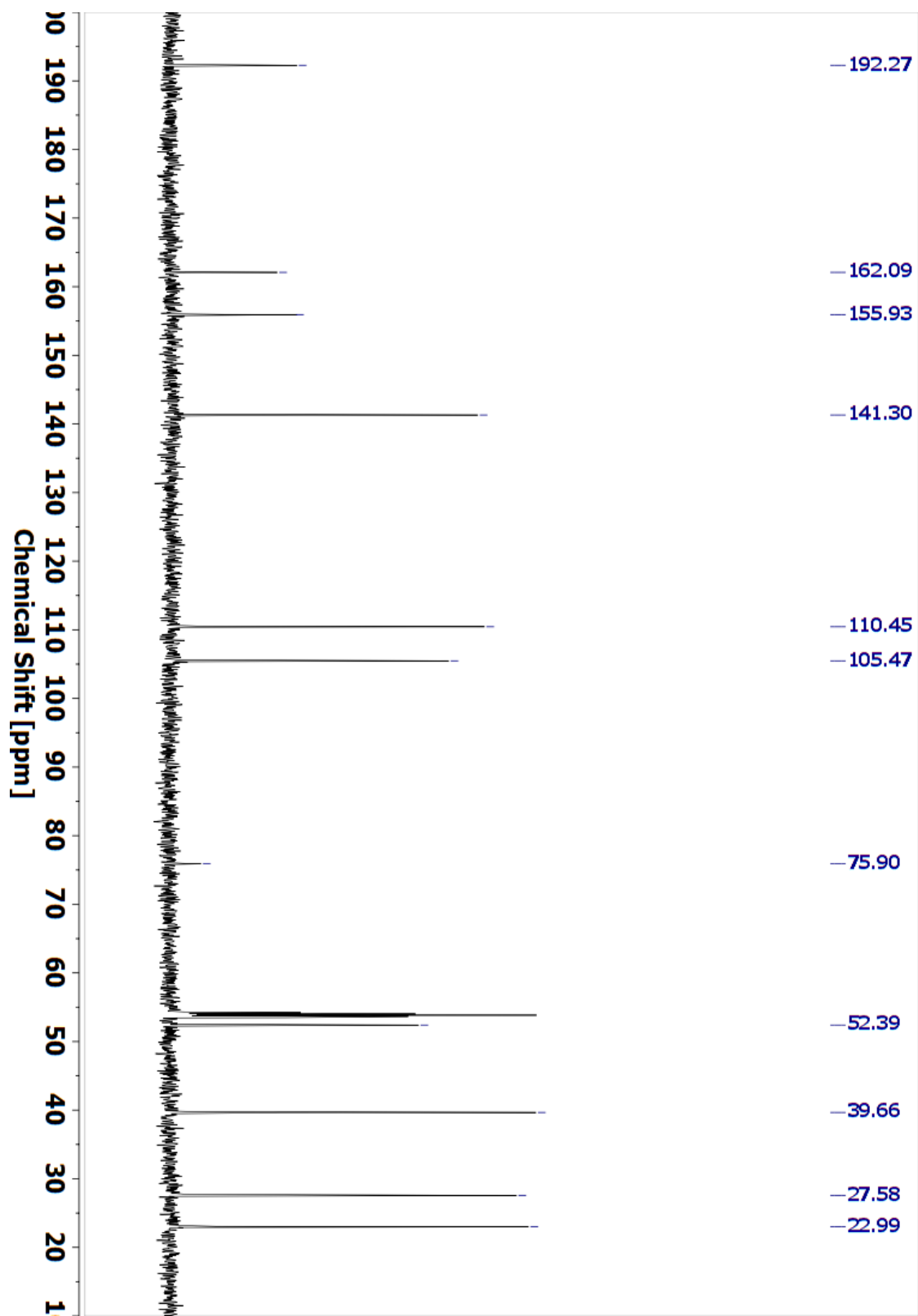
2. Methyl 2-diazo-6-(furan-2-yl)-3-oxohexanoate (S24): Synthesized following Procedure B:

The reaction was run on 5.00 mmol scale to give 0.99 g (84% yield) of product as a colorless oil.

^1H NMR (600 MHz, CD_2Cl_2) δ 7.31 (dd, $J = 1.8, 0.9$ Hz, 1H), 6.29 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.03 (dd, $J = 3.2, 0.9$ Hz, 1H), 3.80 (s, 3H), 2.87 (t, $J = 7.3$ Hz, 2H), 2.68 (t, $J = 7.6$ Hz, 2H), 2.10–1.85 (m, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 192.27, 162.09, 155.93, 141.30, 110.45, 105.47, 75.90, 52.39, 39.66, 27.58, 22.99. HRMS (ESI $^+$) m/z Calc. 237.0870 [$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4 + \text{H}$] $^+$, Found. 237.0870 [$\text{M} + \text{H}$] $^+$.

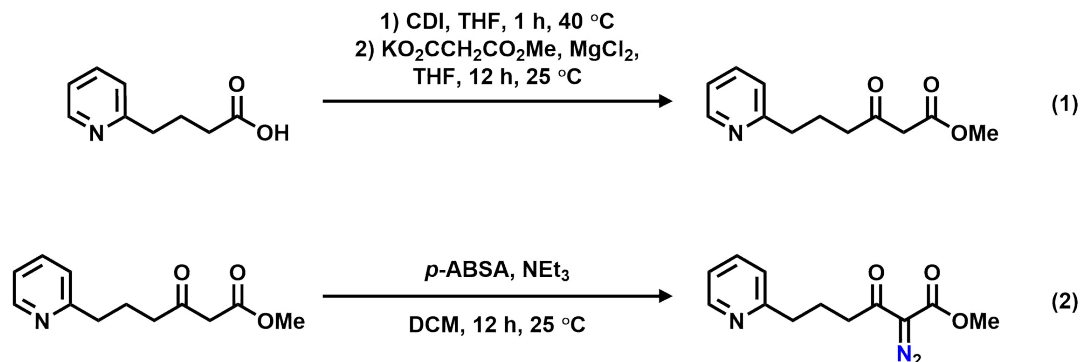


^1H NMR spectrum of isolated product in CD_2Cl_2



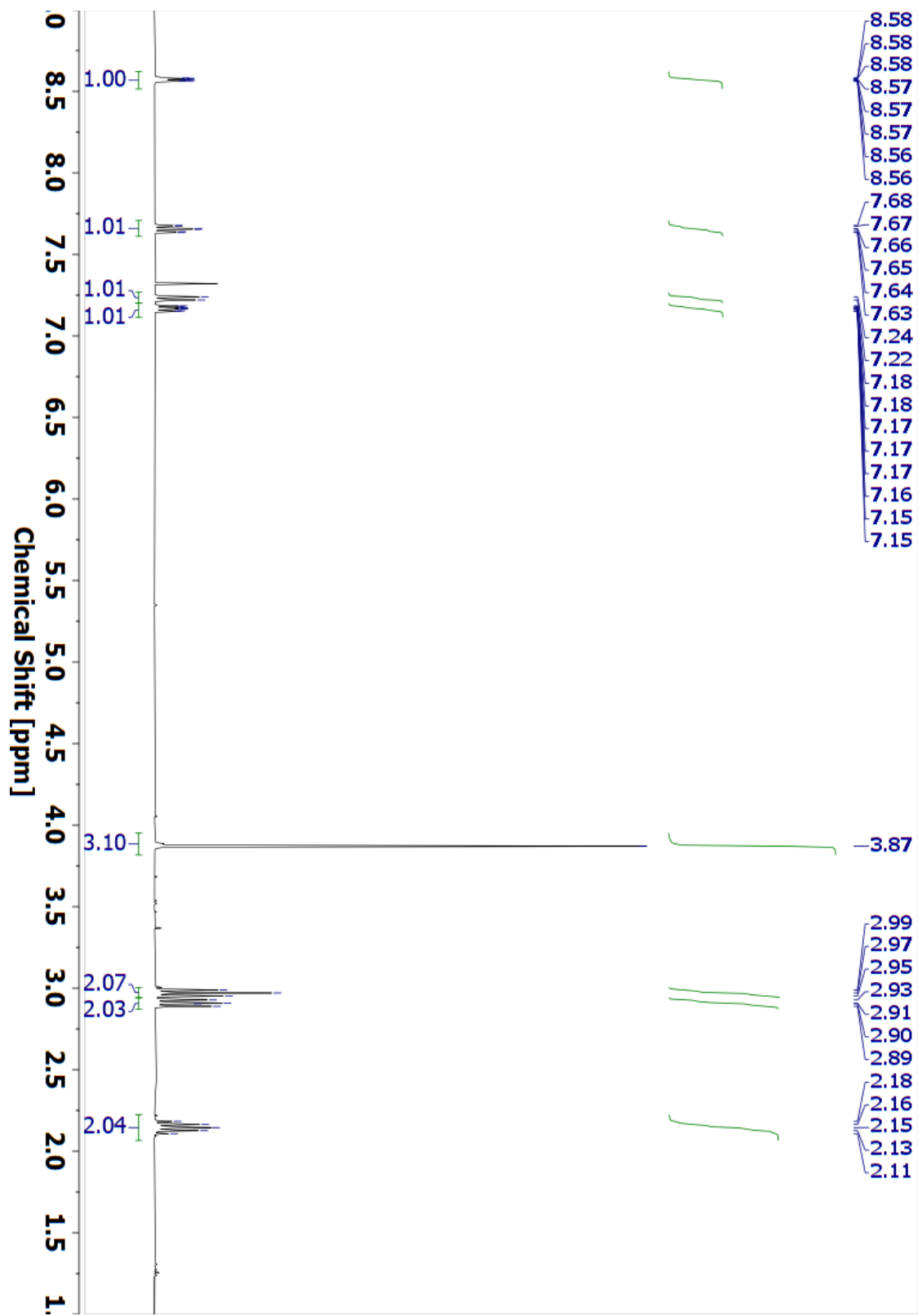
^{13}C NMR spectrum of isolated product in CD_2Cl_2

Methyl 6-(benzo[d]thiazol-2-yl)-2-diazo-3-oxohexanoate (S26)

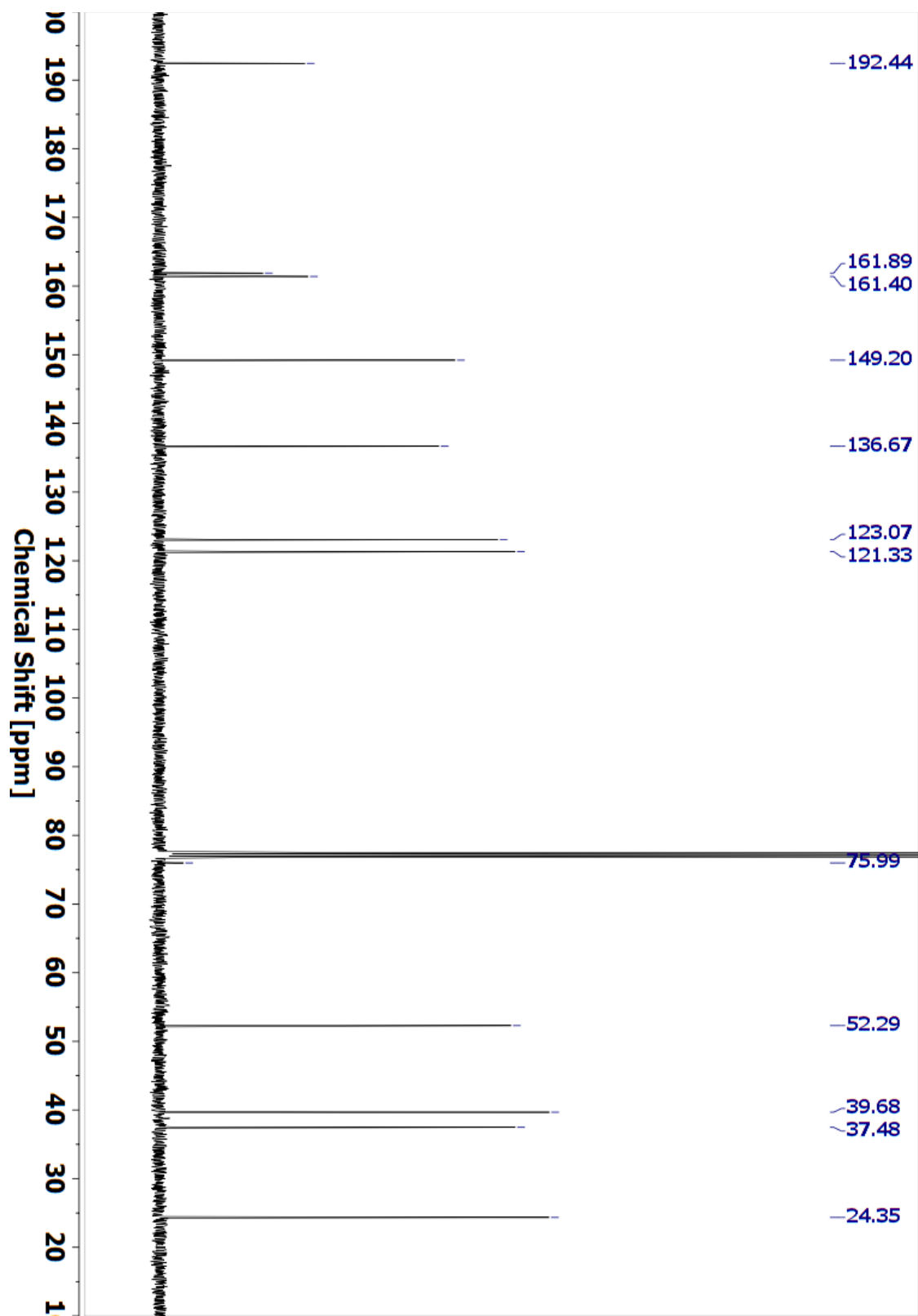


1. Methyl 3-oxo-6-(pyridin-2-yl)hexanoate (S25): Synthesized following Procedure A: The product is passed through a silica plug with a mixture of EtOAc and hexanes (8 : 2 v:v) and directly used in the next step.

2. Methyl 2-diazo-3-oxo-6-(pyridin-2-yl)hexanoate (S26): Synthesized following Procedure B assuming full conversion from the previous step with 10.0 mmol of starting material: The reaction yielded give 0.86 g (35% yield overall) of final product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.51 (ddd, $J = 4.9, 1.9, 1.1$ Hz, 1H), 7.60 (td, $J = 7.7, 1.9$ Hz, 1H), 7.17 (d, $J = 7.7$ Hz, 1H), 7.11 (ddd, $J = 7.7, 4.9, 1.1$ Hz, 1H), 3.81 (s, 3H), 2.91 (t, $J = 7.3$ Hz, 2H), 2.88–2.80 (m, 2H), 2.15–2.01 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.44, 161.89, 161.40, 149.20, 136.67, 123.07, 121.33, 75.99, 52.29, 39.68, 37.48, 24.35. HRMS (ESI $^+$) m/z Calc. 248.1030 [$\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3 + \text{H}$] $^+$, Found. 248.1032 [$\text{M} + \text{H}$] $^+$.

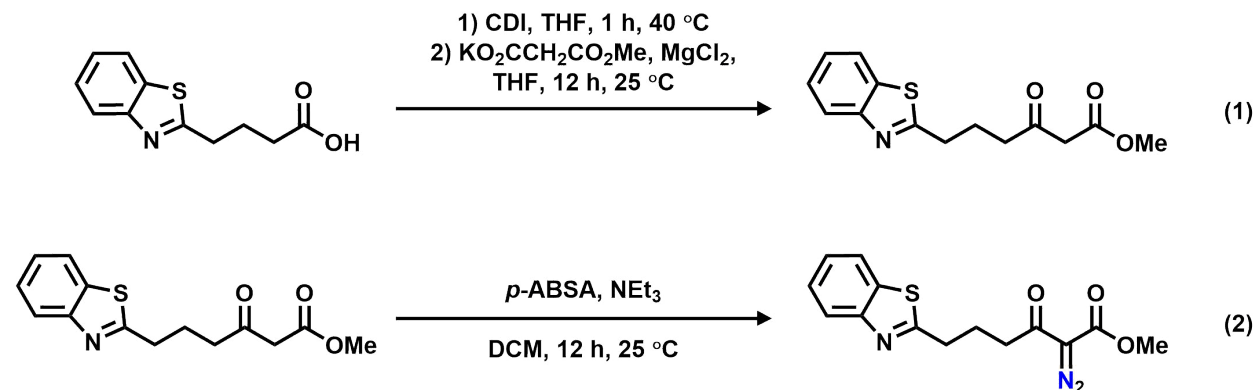


^1H NMR spectrum of isolated product in CDCl_3



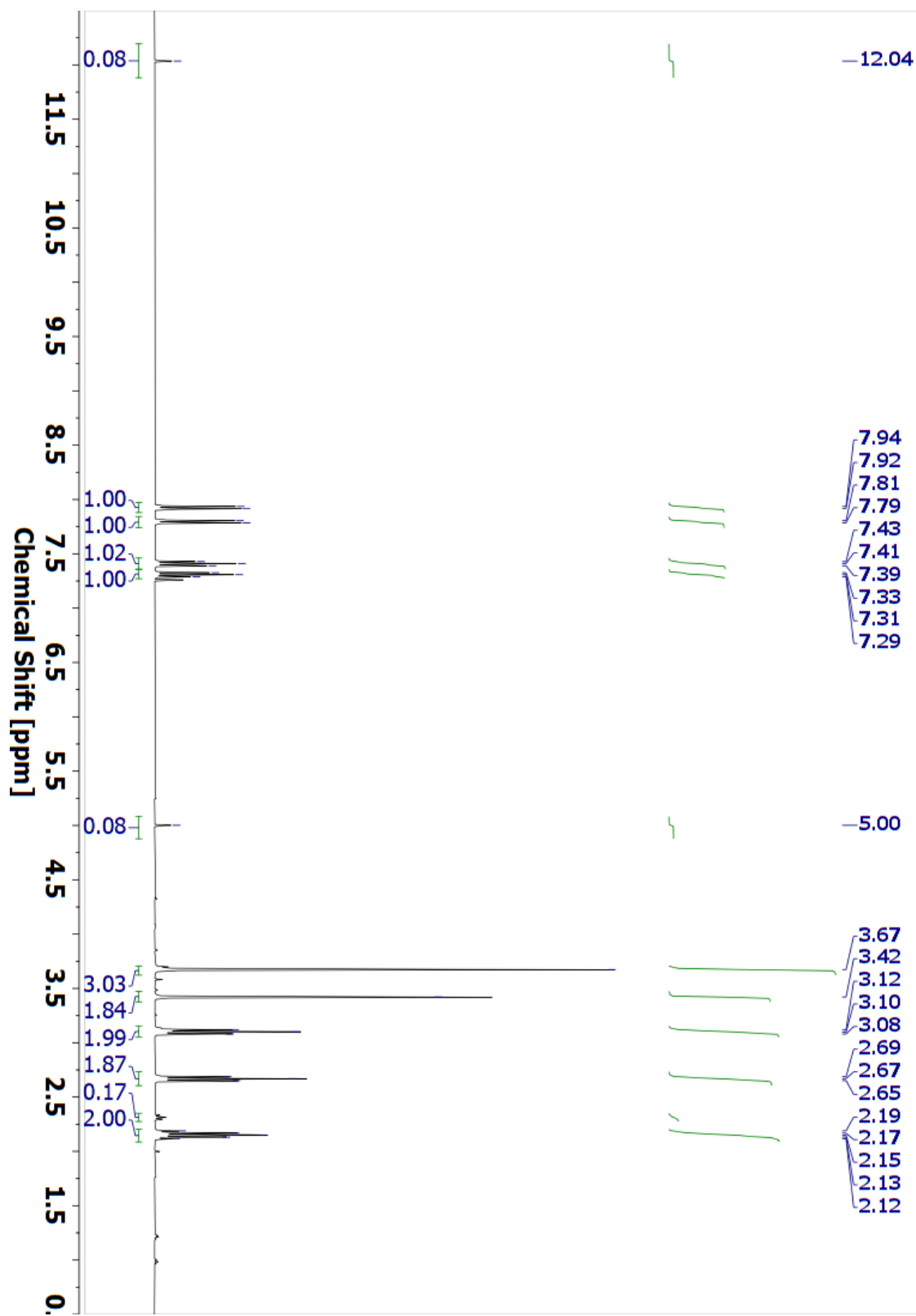
¹³C NMR spectrum of isolated product in CDCl₃

Methyl 6-(benzo[d]thiazol-2-yl)-2-diazo-3-oxohexanoate (S28)

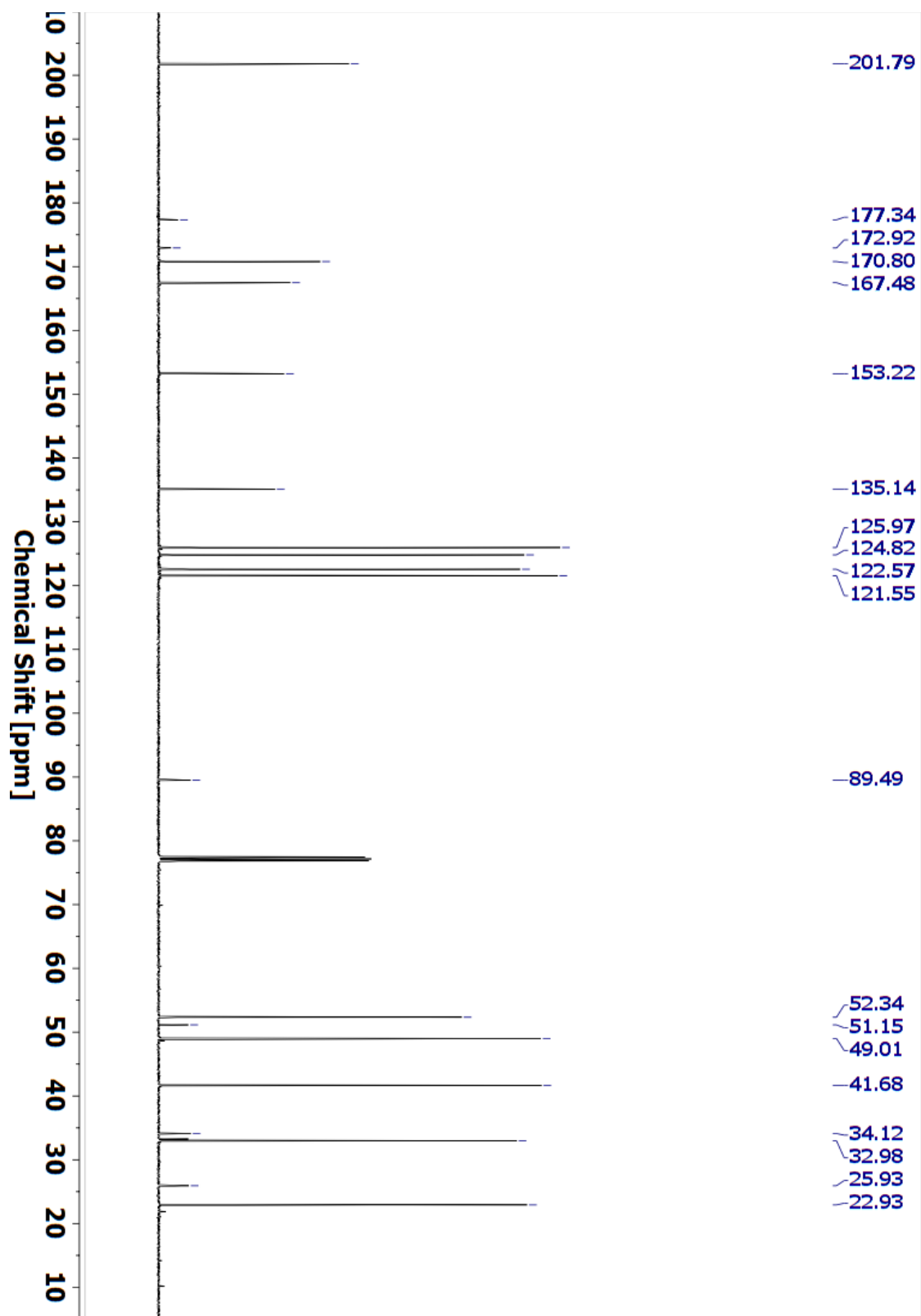


1. Methyl 6-(benzo[d]thiazol-2-yl)-3-oxohexanoate (S27): Synthesized following Procedure A:

The reaction was run on 5.00 mmol scale to give 0.70 g (51% yield, 7.4% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.46–7.36 (m, 1H), 7.35–7.26 (m, 1H), 3.67 (s, 3H), 3.42 (s, 2H), 3.10 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.1$ Hz, 2H), 2.21–2.07 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.79, 170.80, 167.48, 153.22, 135.14, 125.97, 124.82, 122.57, 121.55, 52.34, 49.01, 41.68, 32.98, 22.93. HRMS (ESI^+) m/z Calc. 278.0845 [$\text{C}_{14}\text{H}_{15}\text{NO}_3\text{S}+\text{H}$] $^+$, Found. 278.0844 [$\text{M}+\text{H}$] $^+$.

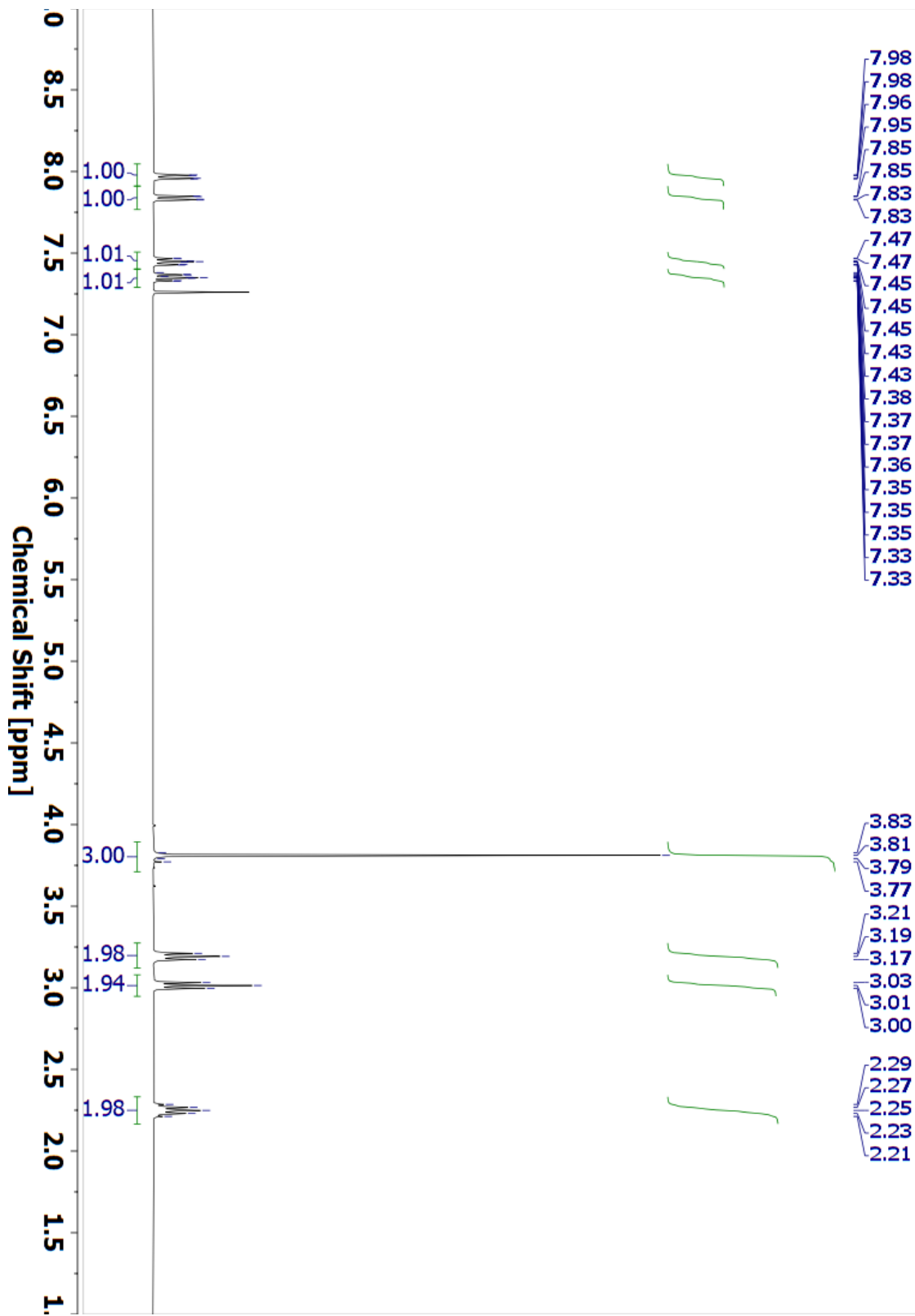


¹H NMR spectrum of isolated product in CDCl₃

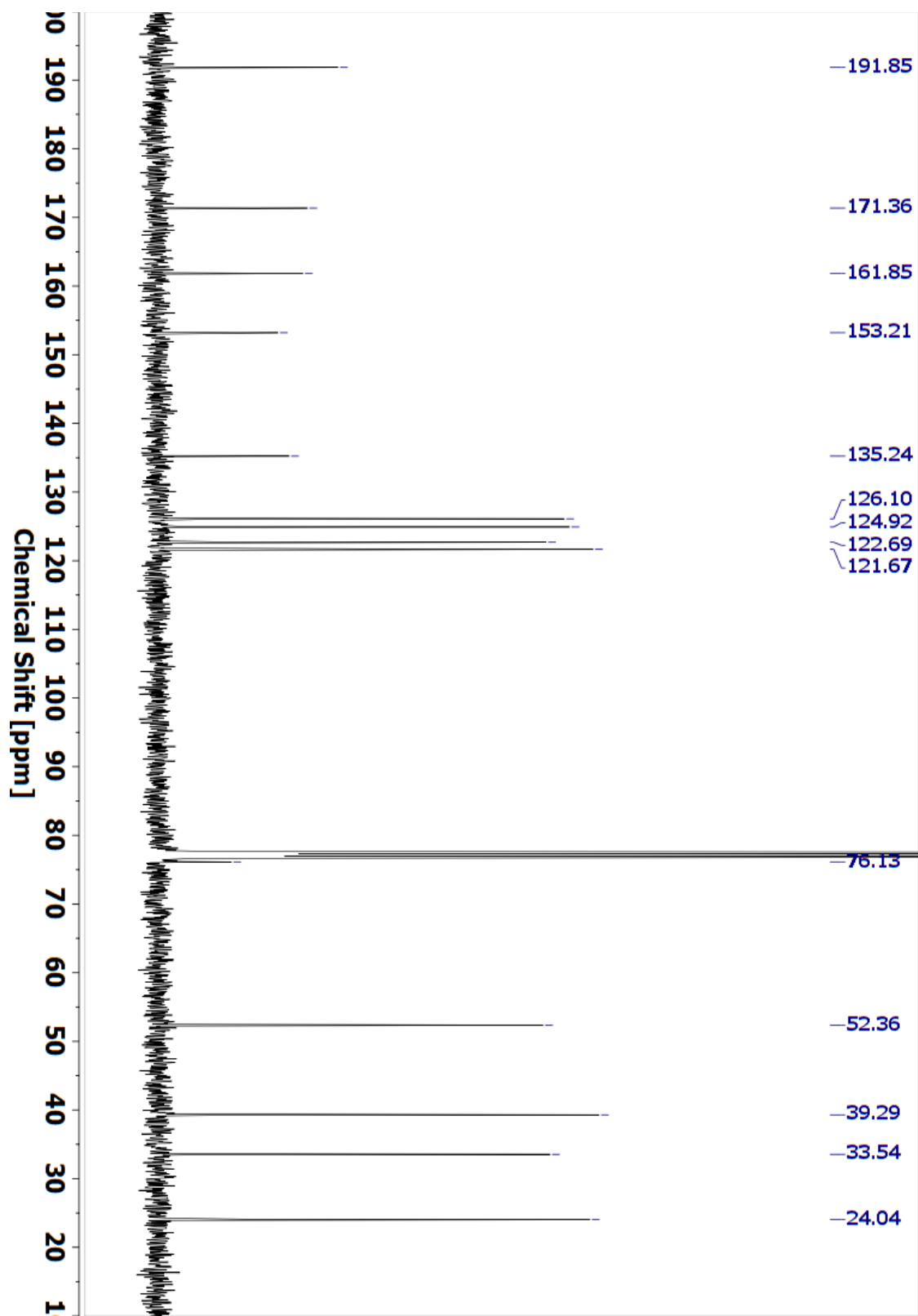


^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 6-(benzo[d]thiazol-2-yl)-2-diazo-3-oxohexanoate (S28): Synthesized following Procedure B: The reaction was run on 2.00 mmol scale to give 0.40 g (66% yield) of product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.84 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.45 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.35 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 3.81 (s, 3H), 3.19 (t, $J = 7.6$ Hz, 2H), 3.01 (t, $J = 7.1$ Hz, 2H), 2.29–2.19 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.85, 171.36, 161.85, 153.21, 135.24, 126.10, 124.92, 122.69, 121.67, 76.13, 52.36, 39.29, 33.54, 24.04. HRMS (ESI $^+$) m/z Calc. 304.0750 [$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3\text{S}+\text{H}$] $^+$, Found. 304.0749 [$\text{M}+\text{H}$] $^+$.

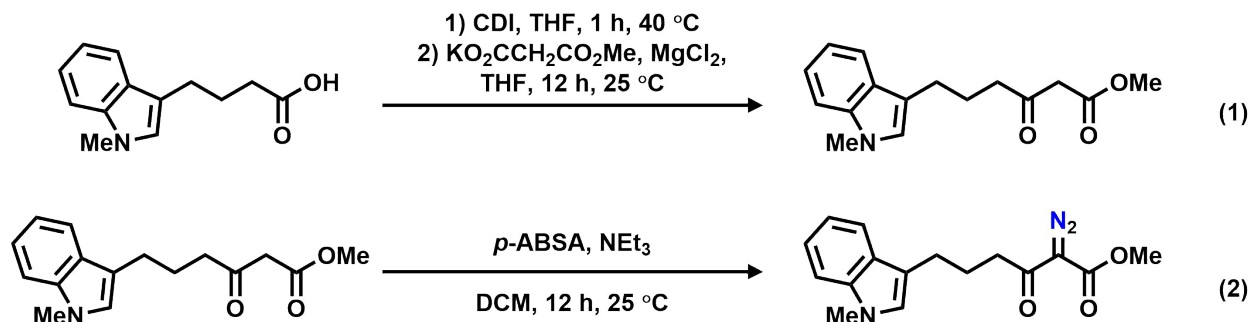


^1H NMR spectrum of isolated product in CDCl_3



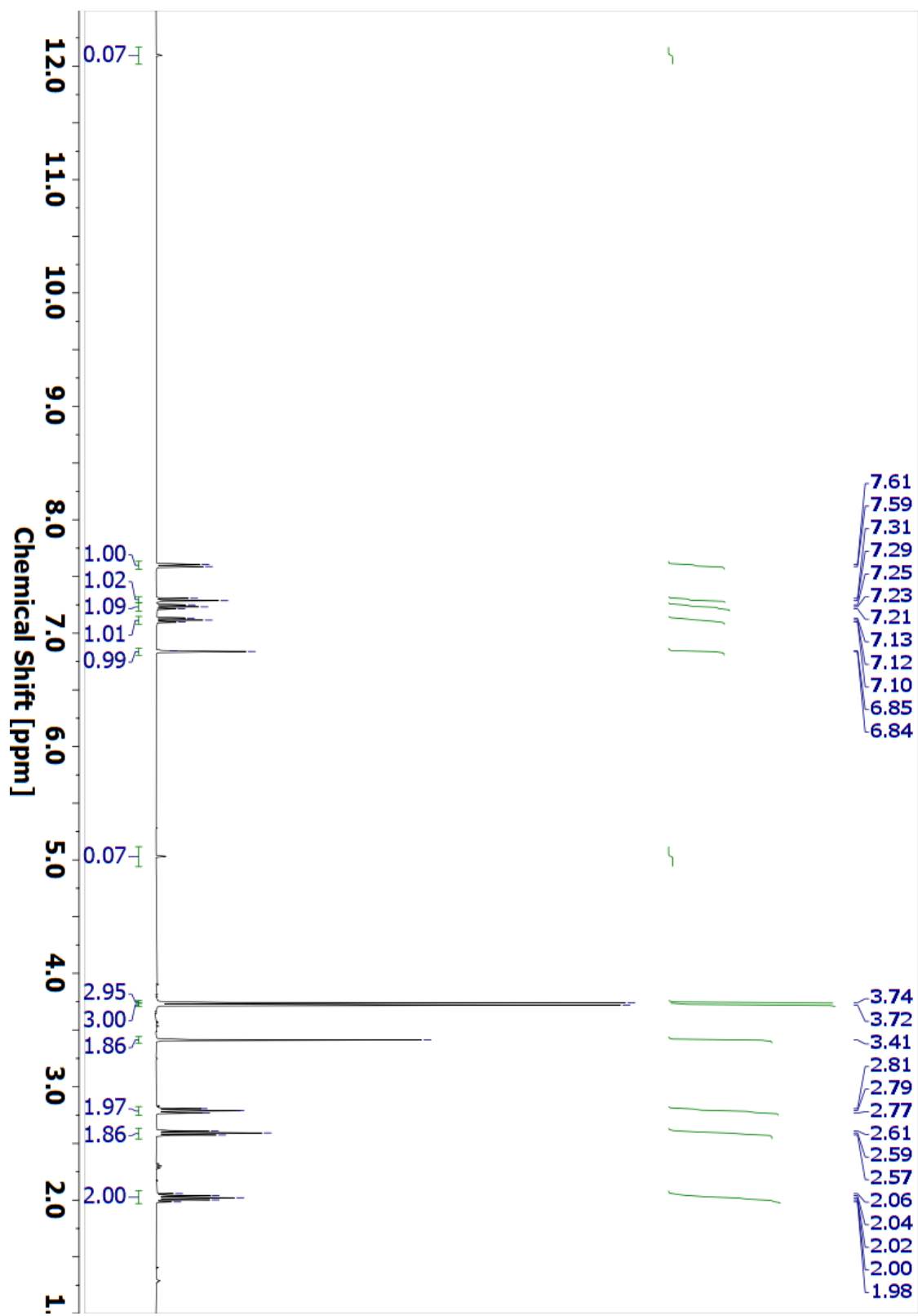
¹³C NMR spectrum of isolated product in CDCl₃

Methyl 2-diazo-6-(1-methyl-1H-indol-3-yl)-3-oxohexanoate (S30)

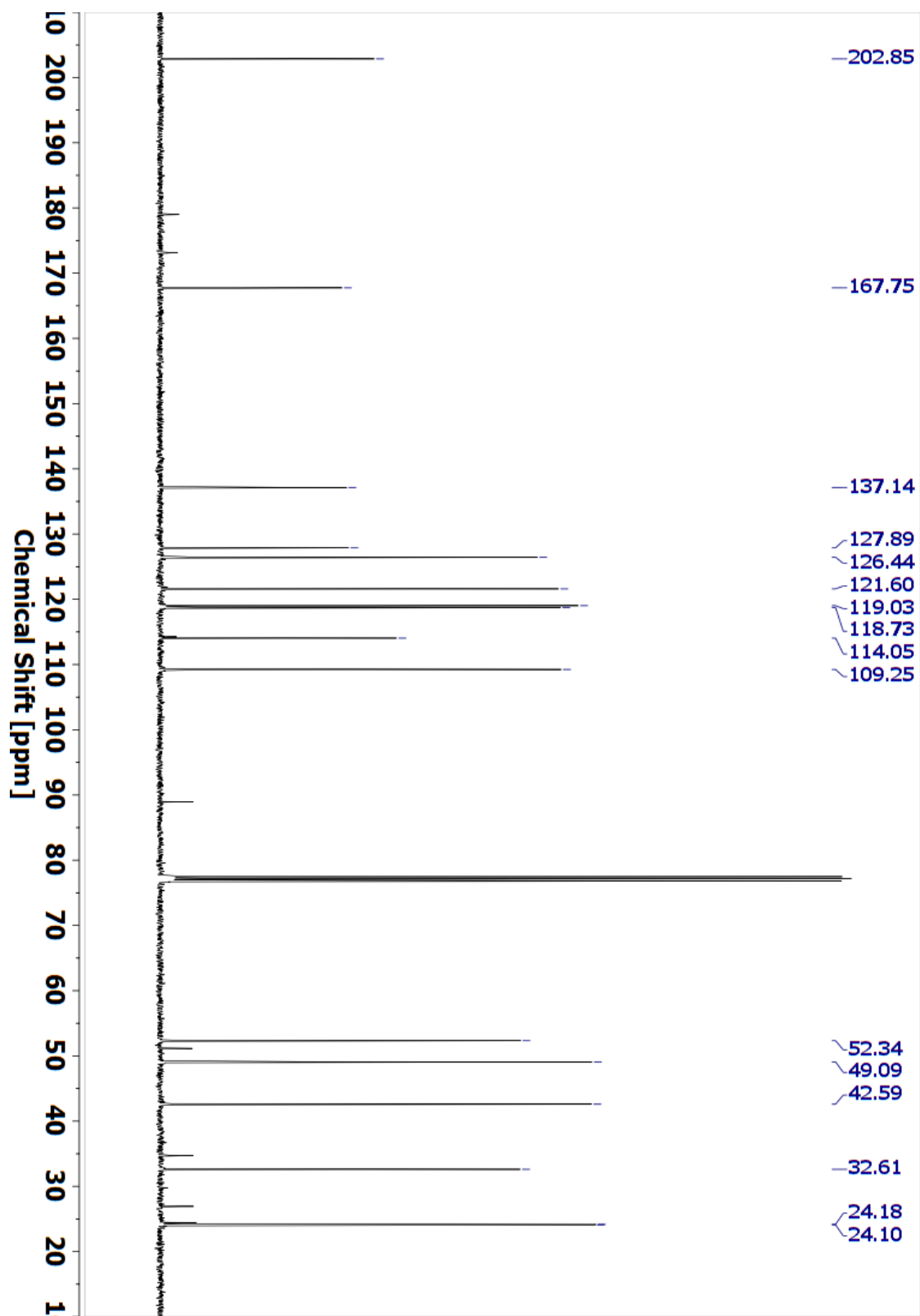


1. Methyl 6-(1-methyl-1H-indol-3-yl)-3-oxohexanoate (S29): Synthesized following Procedure

A: The reaction was run on 10.00 mmol scale to give 1.61 g (59% yield, 6.5% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.1$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 1H), 7.23 (t, $J = 6.9$ Hz, 1H), 7.12 (t, $J = 6.9$ Hz, 1H), 6.84 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.41 (s, 2H), 2.79 (t, $J = 7.5$ Hz, 2H), 2.59 (t, $J = 7.4$ Hz, 2H), 2.02 (p, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.85, 167.75, 137.14, 127.89, 126.44, 121.60, 119.03, 118.73, 114.05, 109.25, 52.34, 49.09, 42.59, 32.61, 24.18, 24.10. HRMS (ESI^+) m/z Calc. 274.1438 $[\text{C}_{16}\text{H}_{19}\text{NO}_3 + \text{H}]^+$, Found. 274.1437 $[\text{M} + \text{H}]^+$.

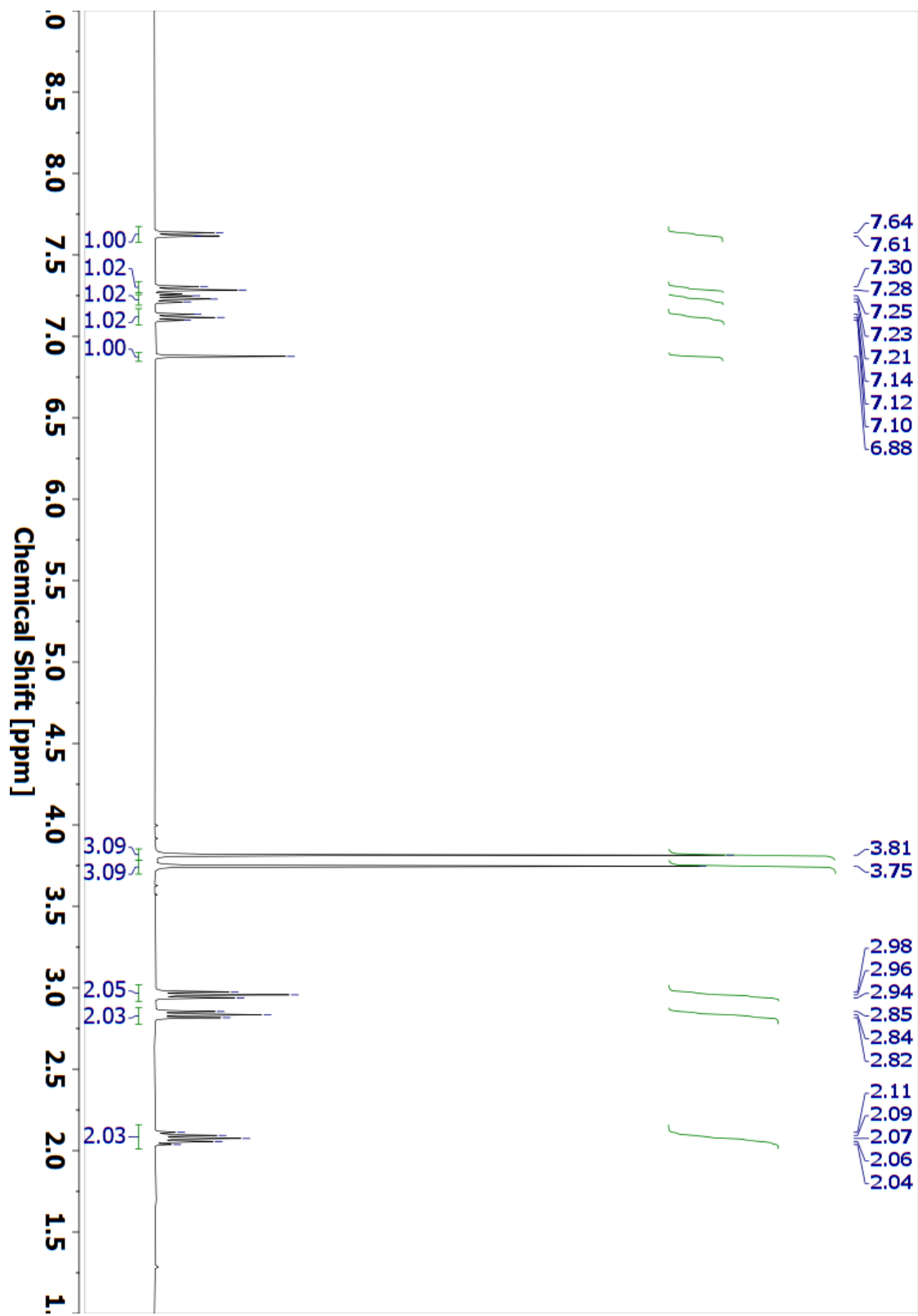


^1H NMR spectrum of isolated product in CDCl_3

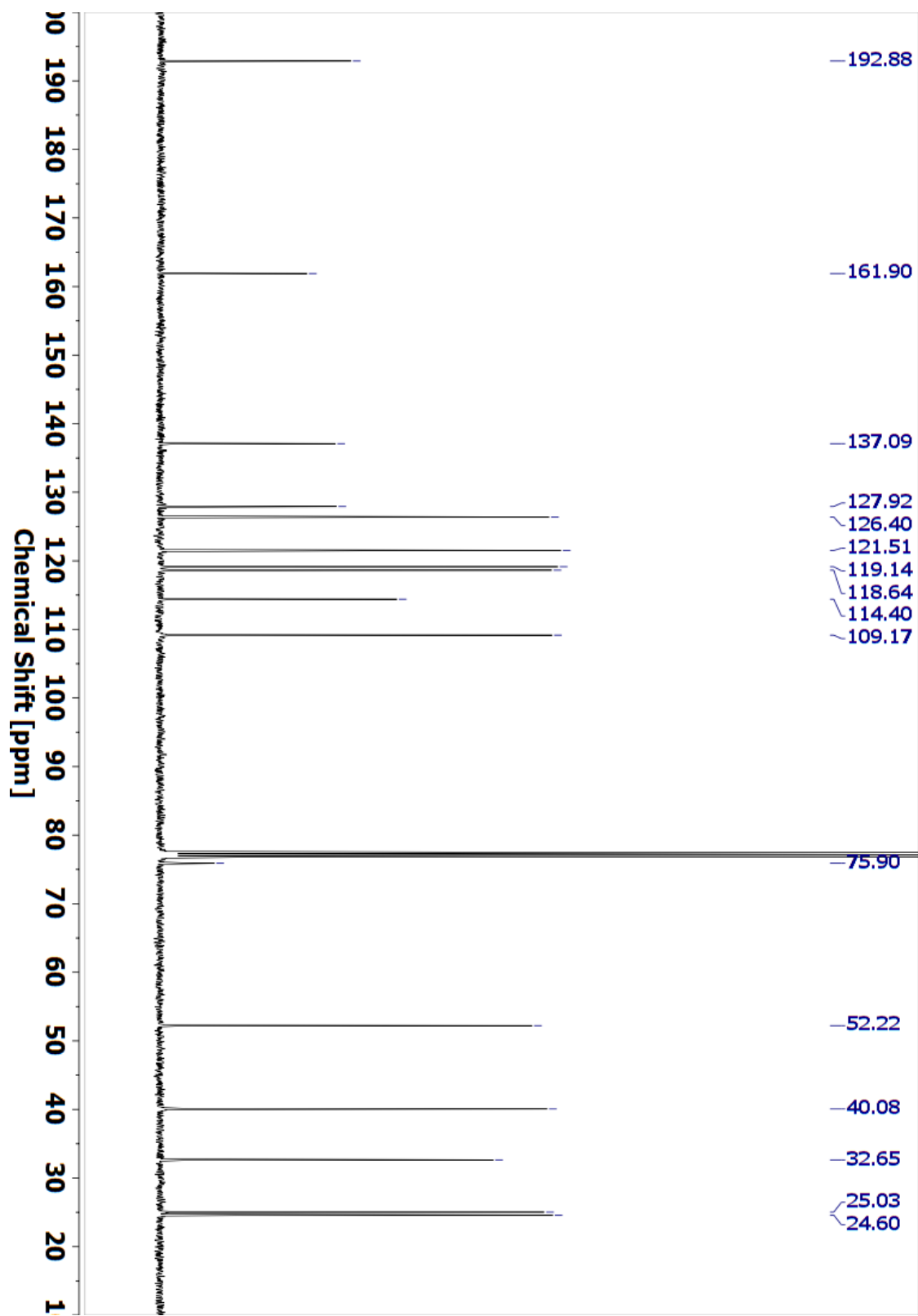


¹³C NMR spectrum of isolated product in CDCl₃

2. Methyl 2-diazo-6-(1-methyl-1H-indol-3-yl)-3-oxohexanoate (S30): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 1.15 g (77% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 8.9$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.25–7.20 (m, 1H), 7.14–7.07 (m, 1H), 6.88 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.96 (t, $J = 7.5$ Hz, 2H), 2.84 (t, $J = 7.5$ Hz, 2H), 2.07 (p, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.88, 161.90, 137.09, 127.92, 126.40, 121.51, 119.14, 118.64, 114.40, 109.17, 75.90, 52.22, 40.08, 32.65, 25.03, 24.60. HRMS (ESI $^+$) m/z Calc. 300.1343 [$\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_3 + \text{H}$] $^+$, Found. 300.1341 [$\text{M} + \text{H}$] $^+$.

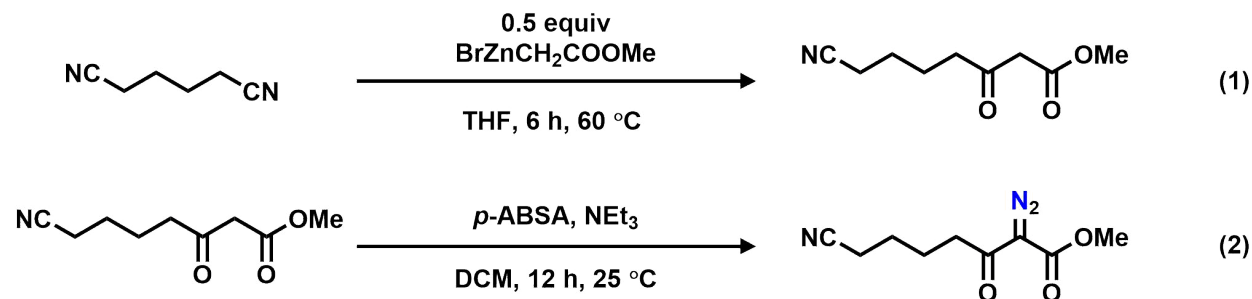


^1H NMR spectrum of isolated product in CDCl_3



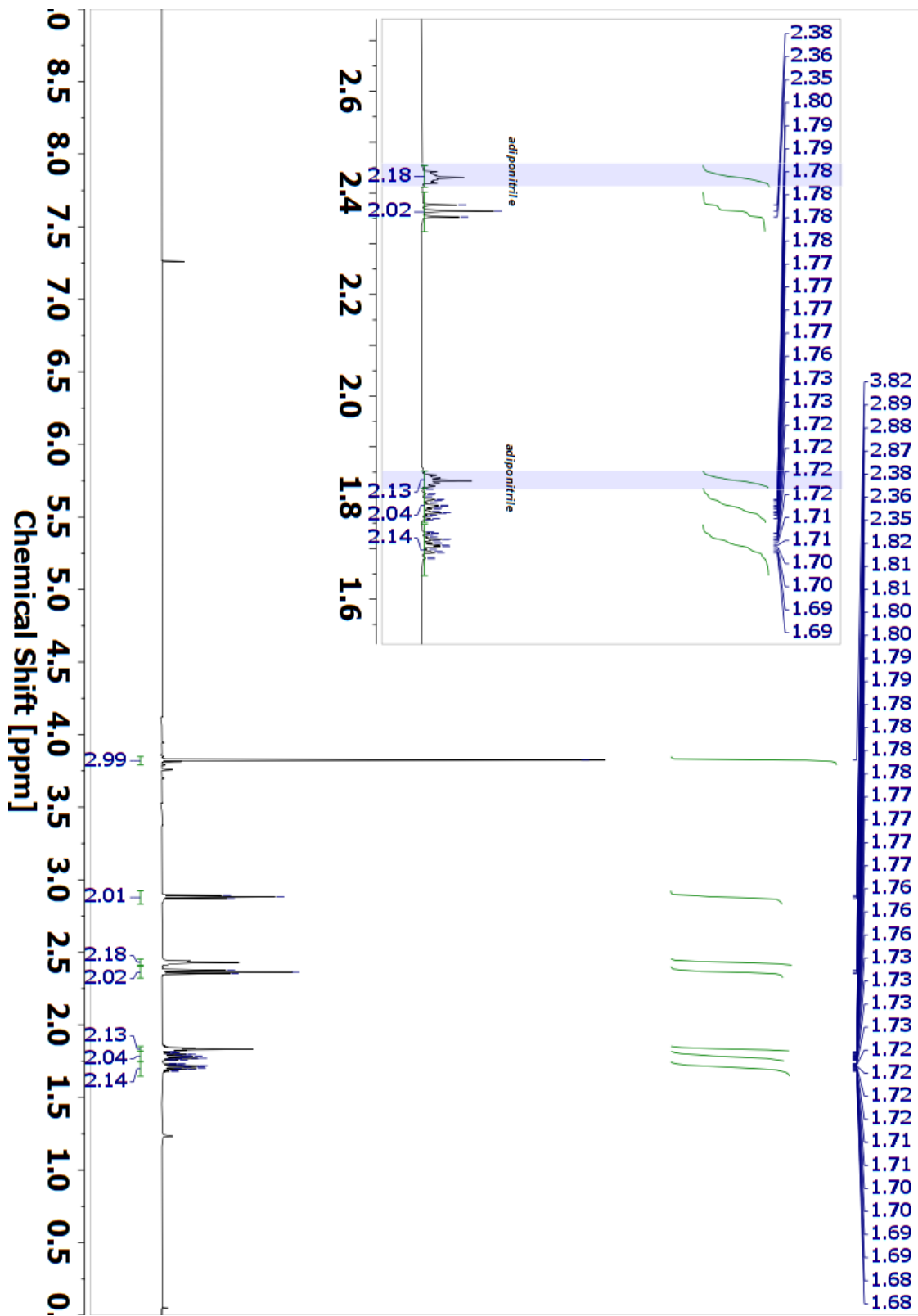
¹³C NMR spectrum of isolated product in CDCl₃

Methyl 7-cyano-2-diazo-3-oxoheptanoate (S32)

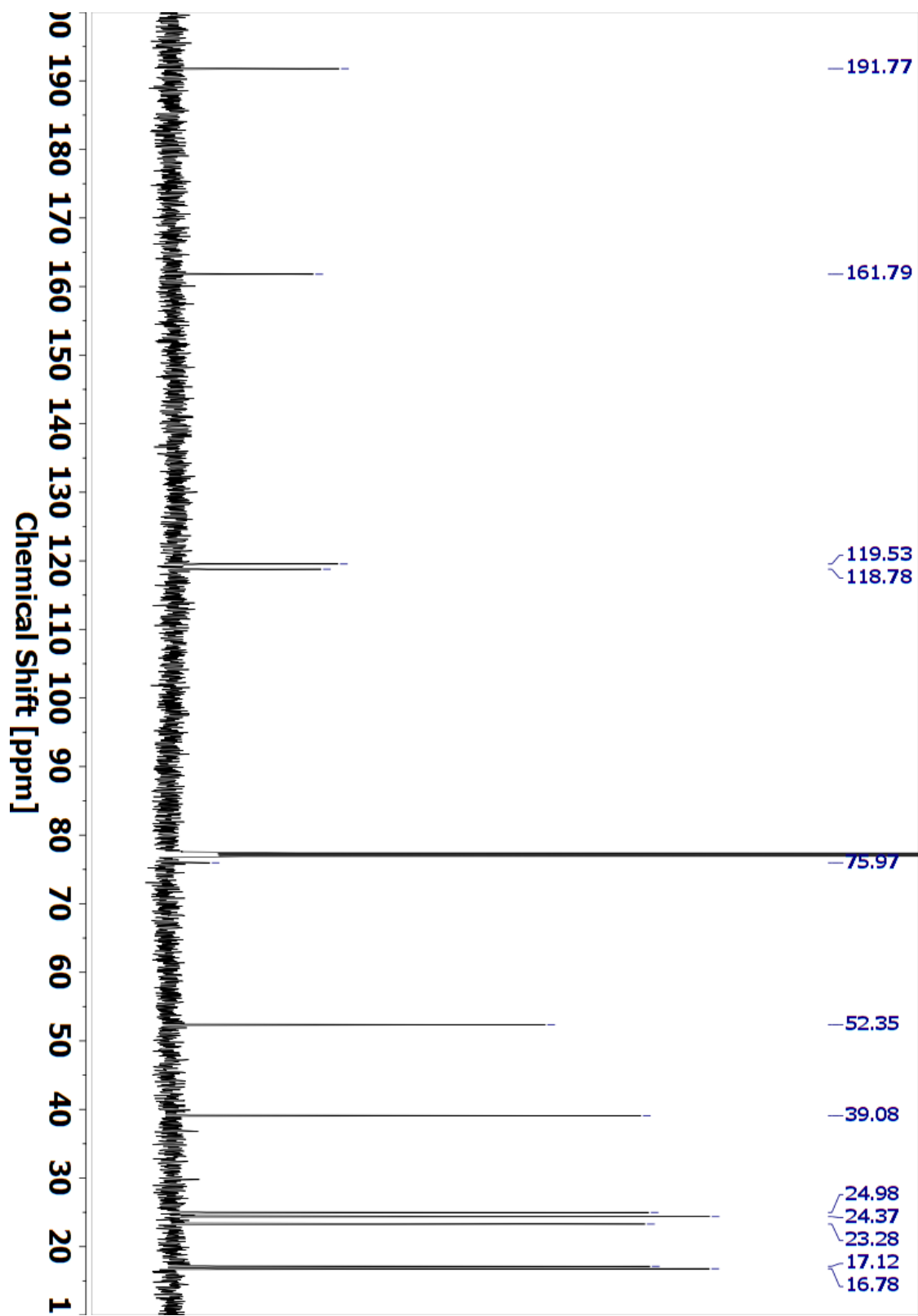


1. Methyl 7-cyano-3-oxoheptanoate (S31): Synthesized following reported literature procedure with 0.5 equiv of methyl 2-bromoacetate using 10.0 mmol of starting material.⁹ The product after purification by column chromatography is an inseparable (1.5:1) mixture of methyl 7-cyano-3-oxoheptanoate and adiponitrile.

2. Methyl 7-cyano-2-diazo-3-oxoheptanoate (S32): Synthesized following Procedure B. The product mixture obtained from previous step was used directly to give 0.80 g (38% yield over two steps) of product as a light-yellow oil. The product after purification by column chromatography is an inseparable (2:1) mixture of methyl 7-cyano-2-diazo-3-oxoheptanoate and adiponitrile. Cyclization of methyl 7-cyano-2-diazo-3-oxoheptanoate is observed despite the presence of adiponitrile as an impurity. ^1H NMR (600 MHz, CDCl_3) δ 3.82 (s, 3H), 2.88 (t, $J = 7.1$ Hz, 2H), 2.36 (t, $J = 7.1$ Hz, 2H), 1.82–1.75 (m, 2H), 1.74–1.66 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.77, 161.79, 119.53, 75.97, 52.35, 39.08, 24.98, 23.28, 17.12. HRMS (ESI^+) m/z Calc. 210.0873 [$\text{C}_9\text{H}_{11}\text{N}_3\text{O}_3+\text{H}$] $^+$, Found. 210.0875 [$\text{M}+\text{e}$] $^+$ Adiponitrile¹⁰: ^1H NMR (600 MHz, CDCl_3) δ 2.46–2.40 (m, 4H), 1.86–1.82 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 118.78, 24.37, 16.78.

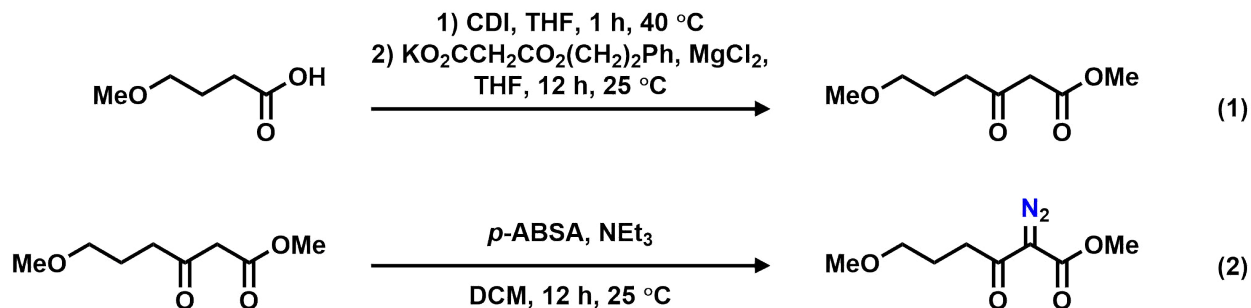


^1H NMR spectrum of isolated product in CDCl_3



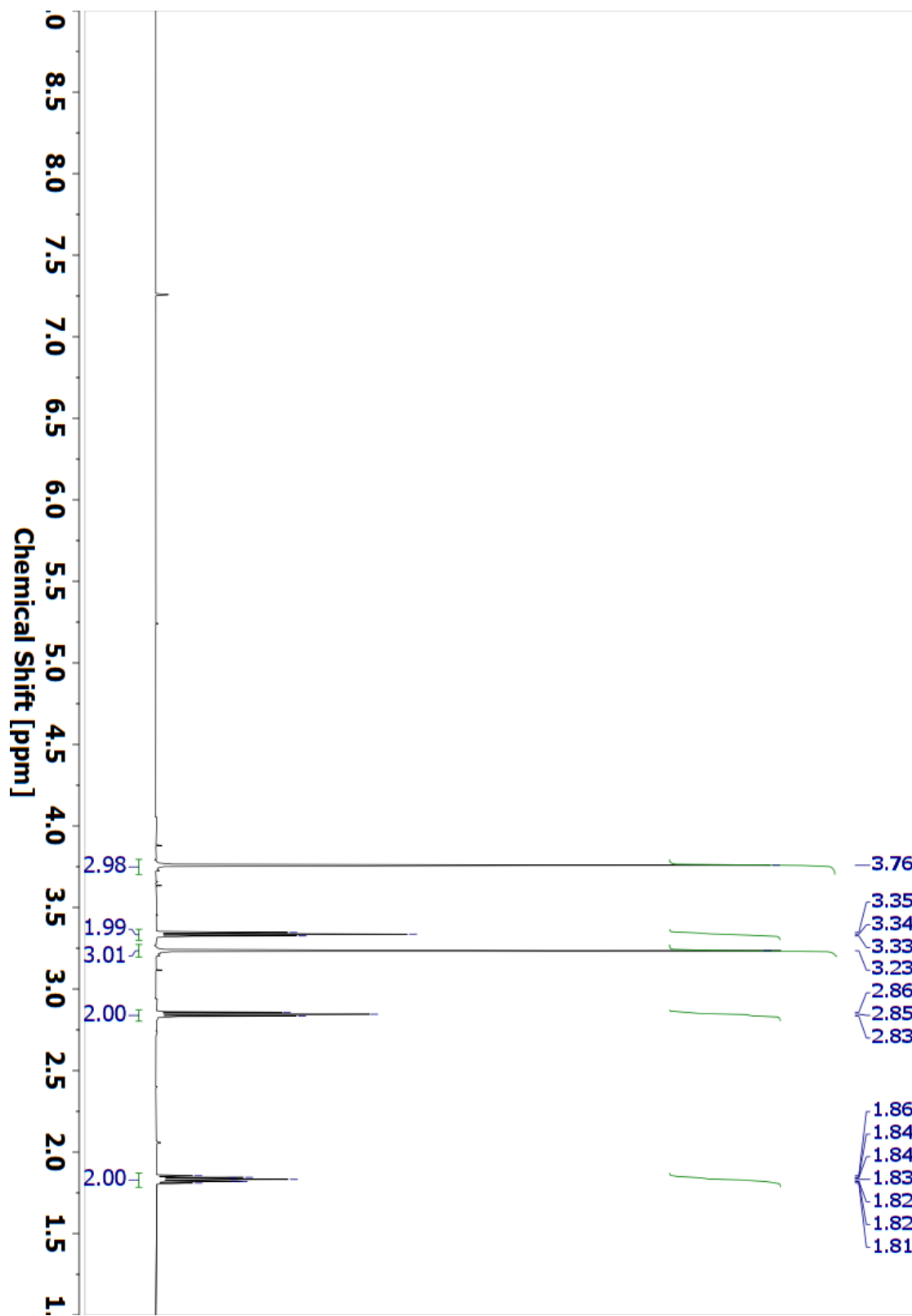
¹³C NMR spectrum of isolated product in CDCl₃

Methyl 2-diazo-6-methoxy-3-oxohexanoate (S34)

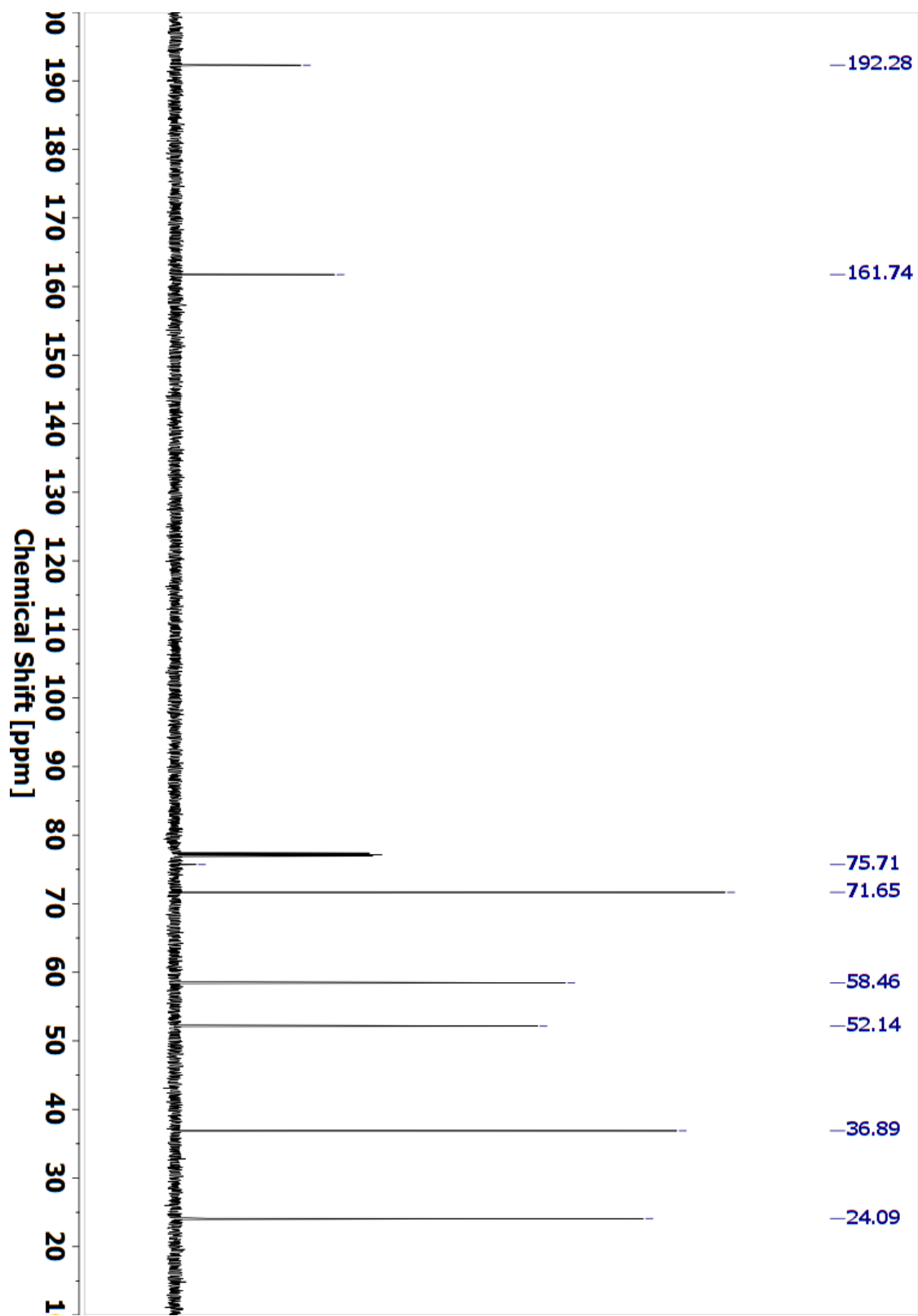


1. Methyl 6-methoxy-3-oxohexanoate (S33): Synthesized following Procedure A. Spectroscopic feature is consistent with reported value.¹¹

2. Methyl 2-diazo-6-methoxy-3-oxohexanoate (S34): Synthesized following Procedure B. Spectroscopic feature is consistent with reported value.¹¹ The reaction was run on 5.00 mmol scale to give 0.64 g (64% yield) of product as a light yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 3.76 (s, 3H), 3.34 (t, $J = 6.3$ Hz, 2H), 3.23 (s, 3H), 2.85 (t, $J = 7.3$ Hz, 2H), 1.90–1.78 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 192.28, 161.74, 75.71, 71.65, 58.46, 52.14, 36.89, 24.09. HRMS (ESI⁺) m/z Calc. 201.0870 [$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4 + \text{H}$]⁺, Found. 201.0871 [$\text{M} + \text{e}$]⁺.

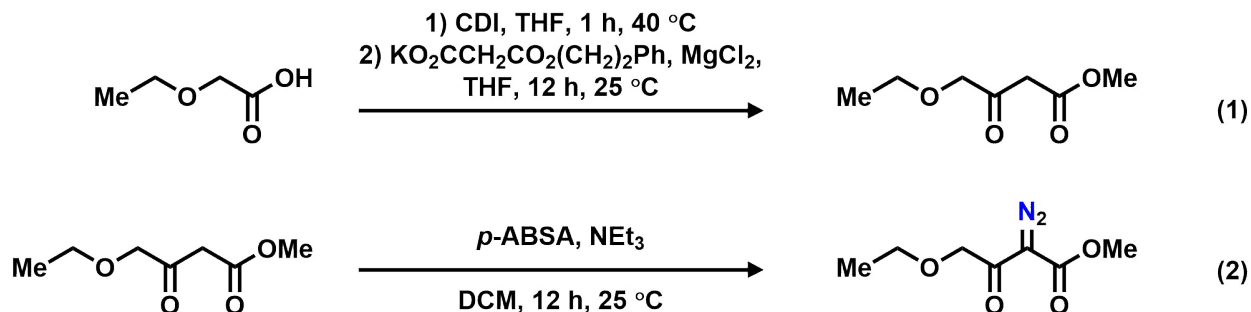


^1H NMR spectrum of isolated product in CDCl_3



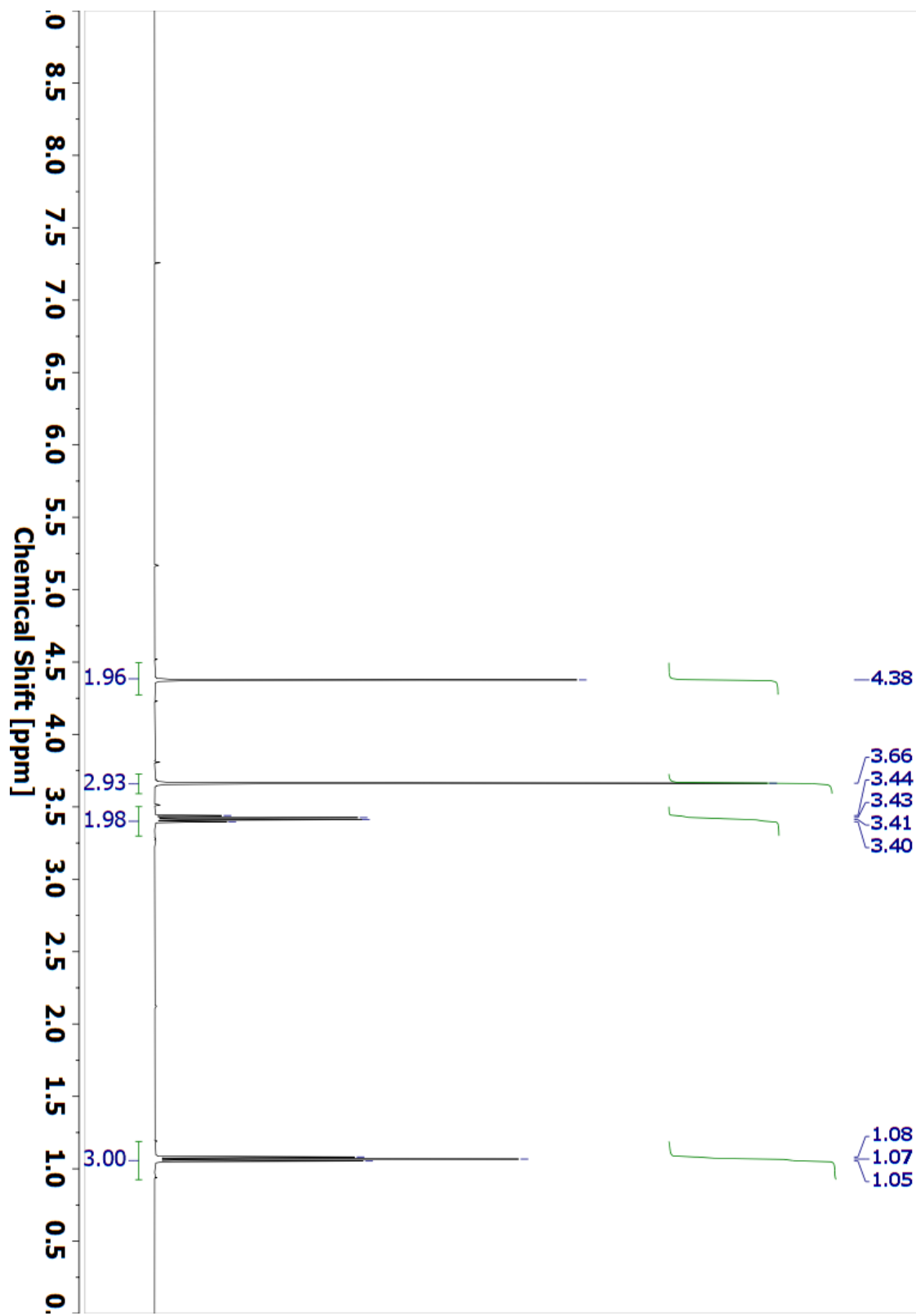
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl 2-diazo-4-ethoxy-3-oxobutanoate (S36)

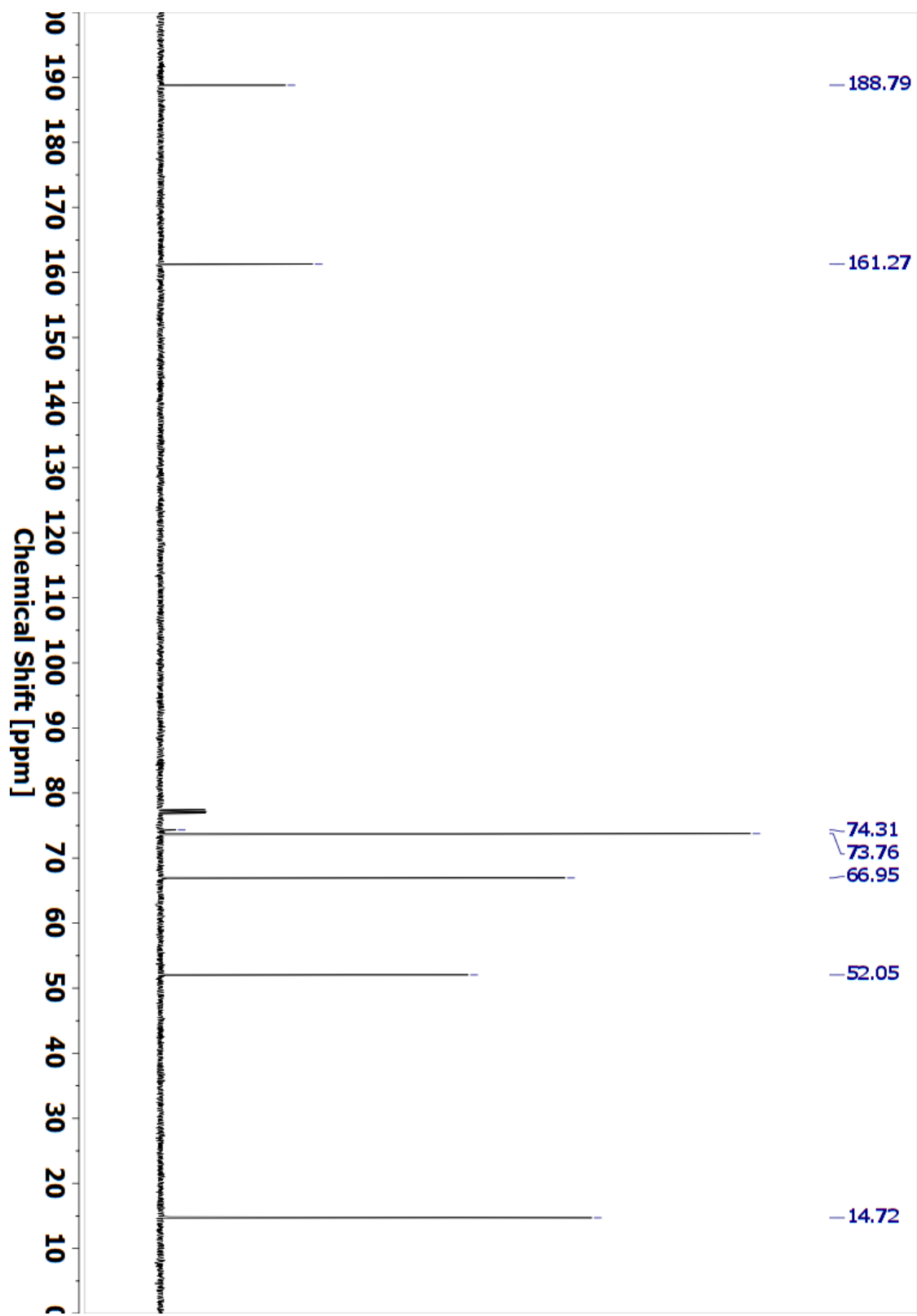


1. Methyl 4-ethoxy-3-oxobutanoate (S35): Synthesized following Procedure A. Spectroscopic feature is consistent with reported value.¹²

2. Methyl 2-diazo-4-ethoxy-3-oxobutanoate (S36): Synthesized following Procedure B. Spectroscopic feature is consistent with reported value.¹² The reaction was run on 5.00 mmol scale to give 0.40 g (43% yield) of product as a light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 4.38 (s, 2H), 3.66 (s, 3H), 3.42 (q, $J = 7.0$ Hz, 2H), 1.07 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.79, 161.27, 74.31, 73.76, 66.95, 52.05, 14.72.

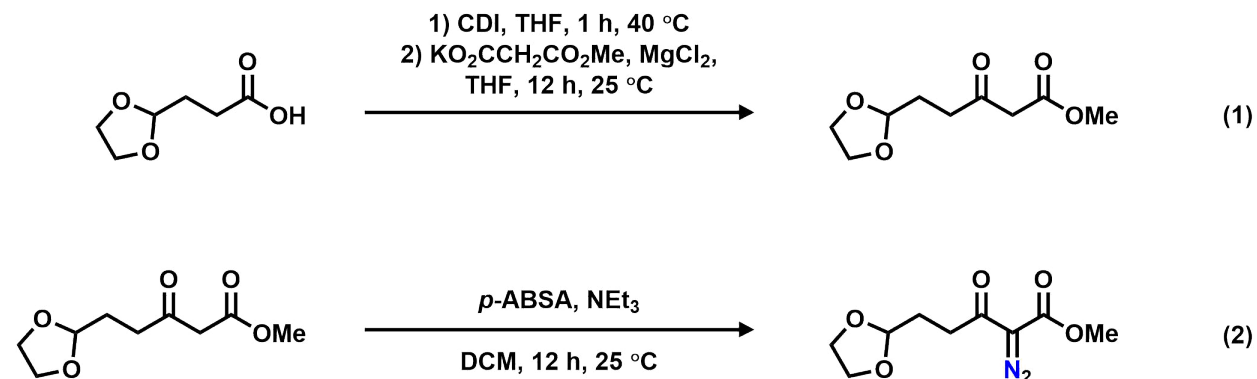


^1H NMR spectrum of isolated product in CDCl_3



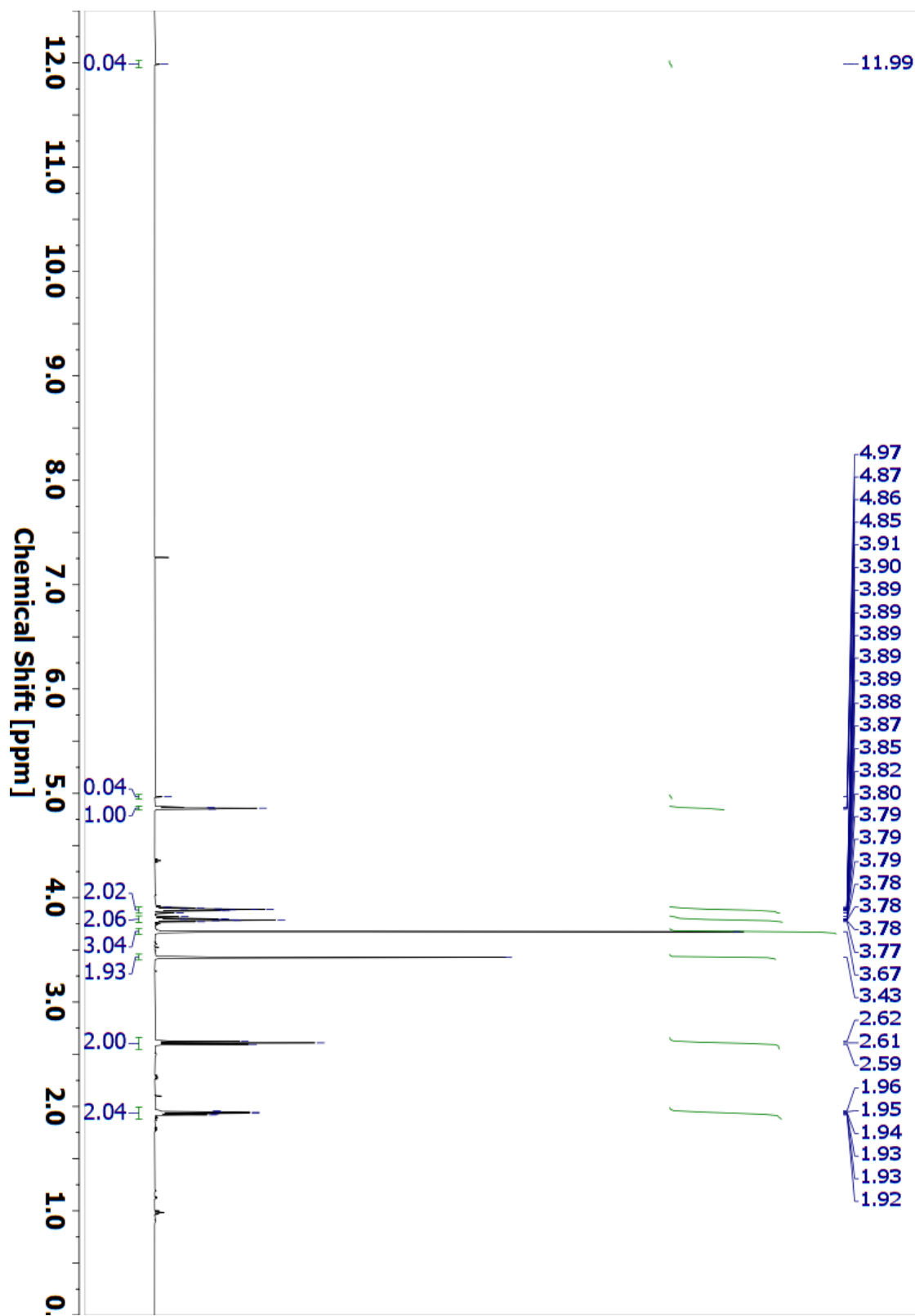
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl 2-diazo-5-(1,3-dioxolan-2-yl)-3-oxopentanoate (S38)

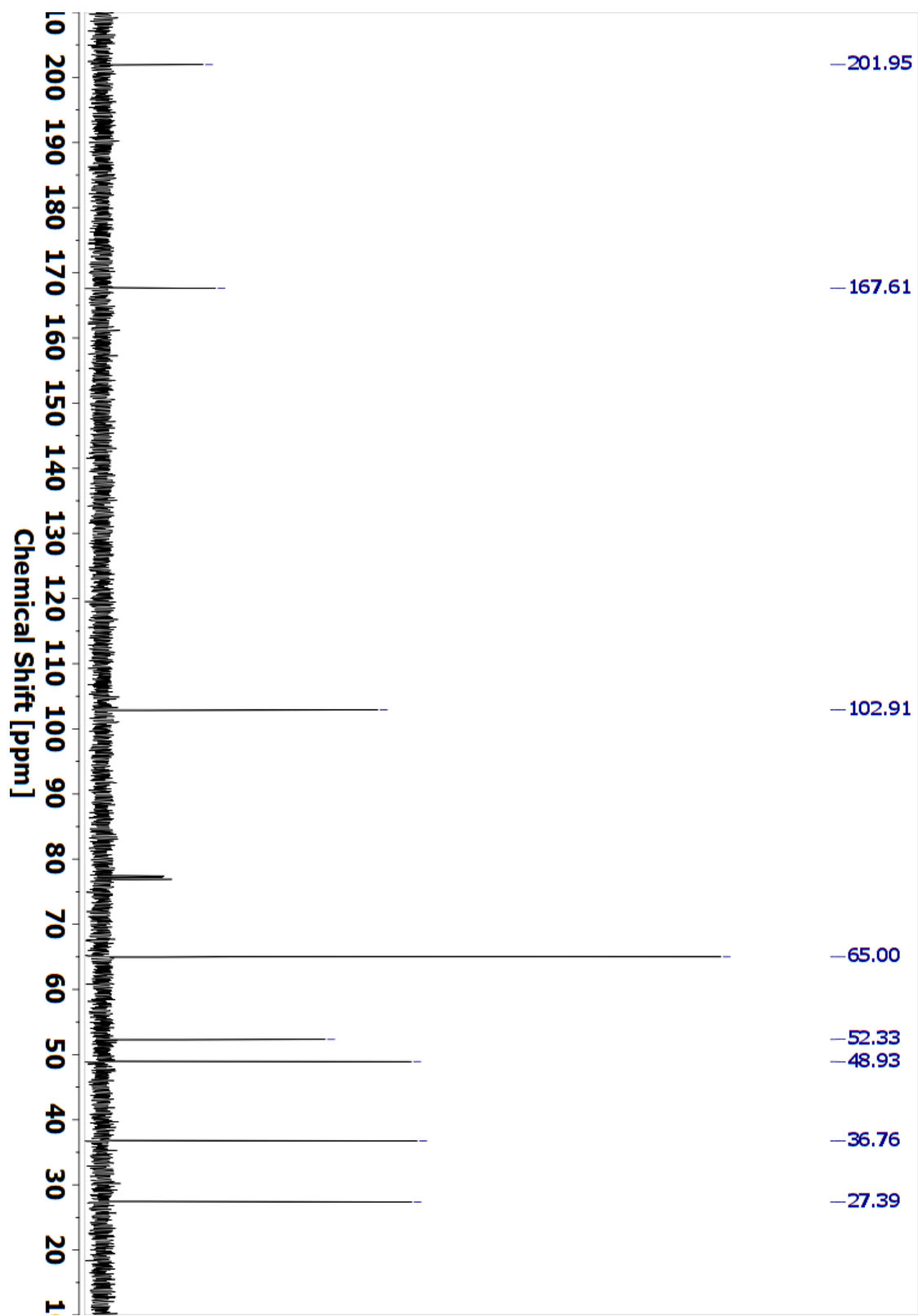


1. Methyl 5-(1,3-dioxolan-2-yl)-3-oxopentanoate (S37): Synthesized following Procedure A:

The reaction was run on 10.00 mmol scale to give 1.23 g (61% yield, 3.8% tautomerization) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 4.86 (t, $J = 4.2$ Hz, 1H), 3.93–3.84 (m, 2H), 3.82–3.74 (m, 2H), 3.67 (s, 3H), 3.43 (s, 2H), 2.61 (t, $J = 7.3$ Hz, 2H), 1.94 (td, $J = 7.3, 4.2$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.95, 167.61, 102.91, 65.00, 52.33, 48.93, 36.76, 27.39. HRMS (ESI $^+$) m/z Calc. 203.0914 [$\text{C}_9\text{H}_{14}\text{O}_5 + \text{H}$] $^+$, Found. 203.0915 [$\text{M} + \text{H}$] $^+$.

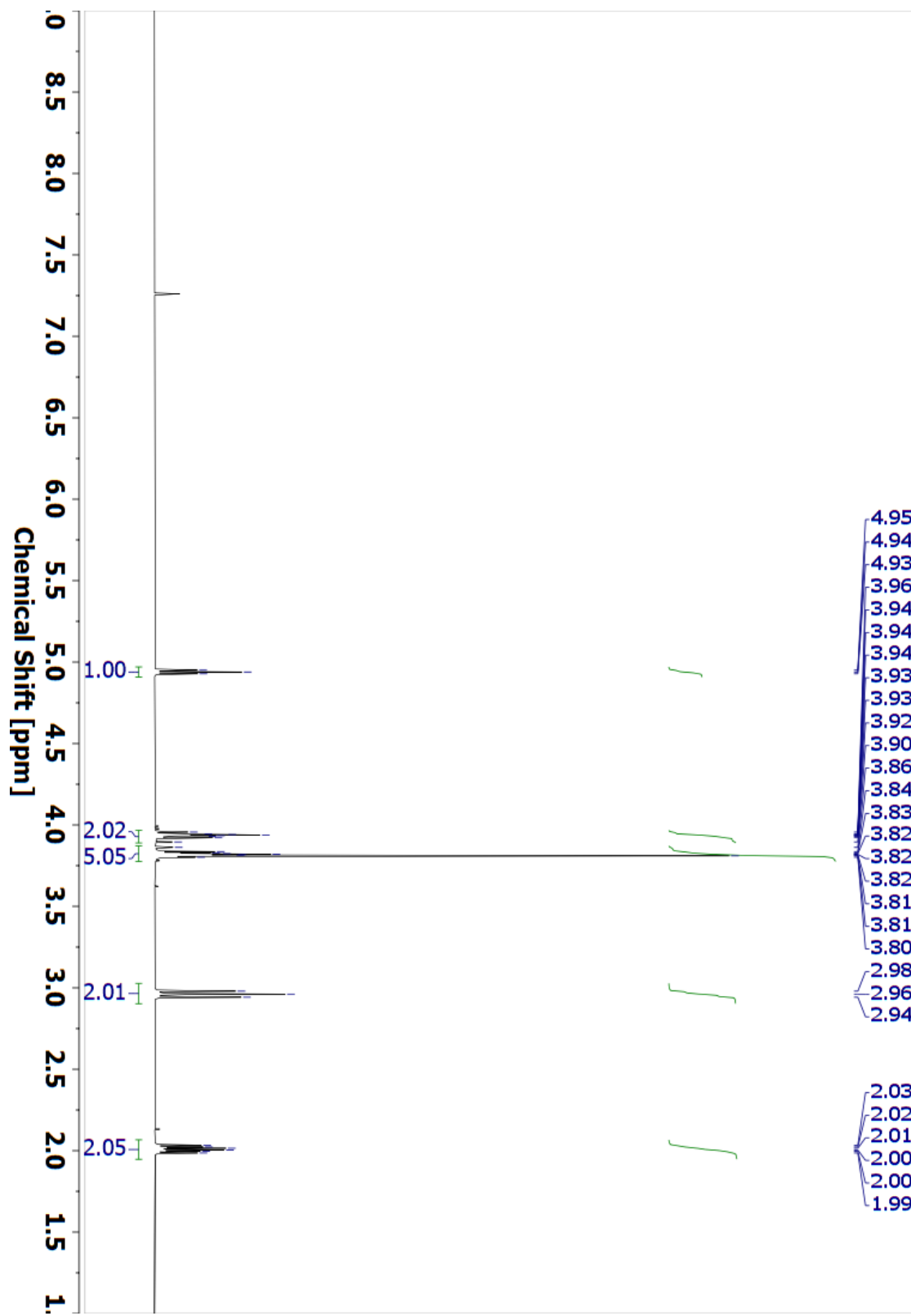


^1H NMR spectrum of isolated product in CDCl_3

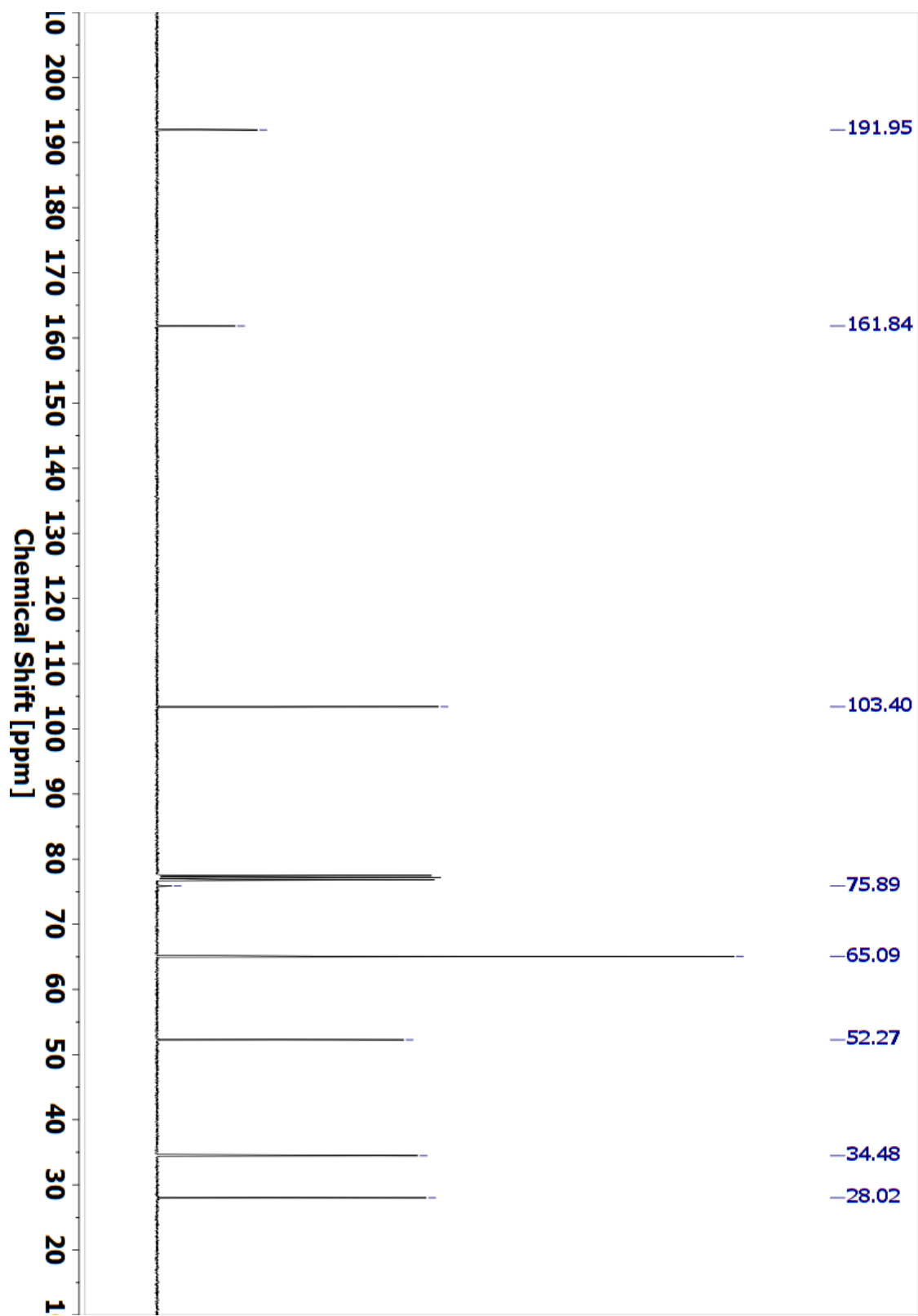


^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 2-diazo-5-(1,3-dioxolan-2-yl)-3-oxopentanoate (S38): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.97 g (85% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.94 (t, $J = 4.4$ Hz, 1H), 3.96–3.88 (m, 2H), 3.88–3.76 (m, 5H), 2.96 (t, $J = 7.4$ Hz, 2H), 2.01 (td, $J = 7.4, 4.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.95, 161.84, 103.40, 75.89, 65.09, 52.27, 34.48, 28.02. HRMS (ESI^+) m/z Calc. 229.0819 $[\text{C}_9\text{H}_{12}\text{N}_2\text{O}_5+\text{H}]^+$, Found. 229.0821 $[\text{M}+\text{H}]^+$.

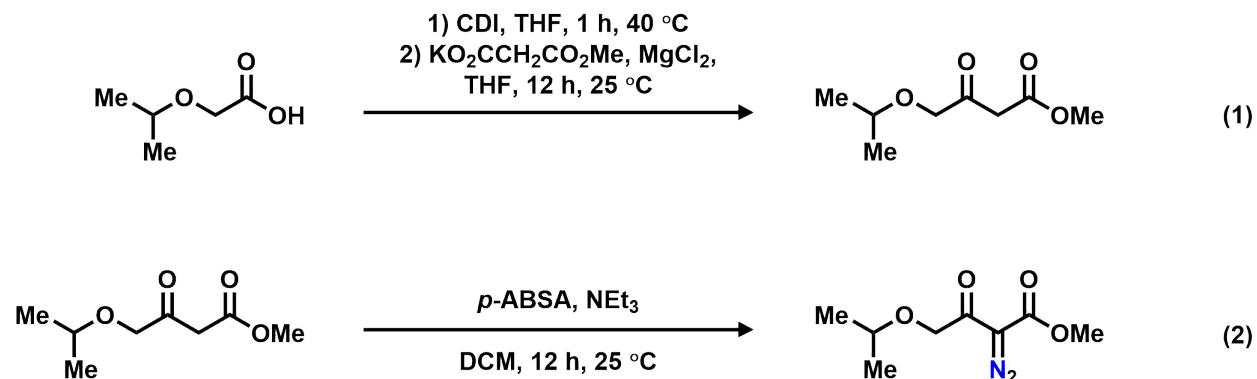


^1H NMR spectrum of isolated product in CDCl_3

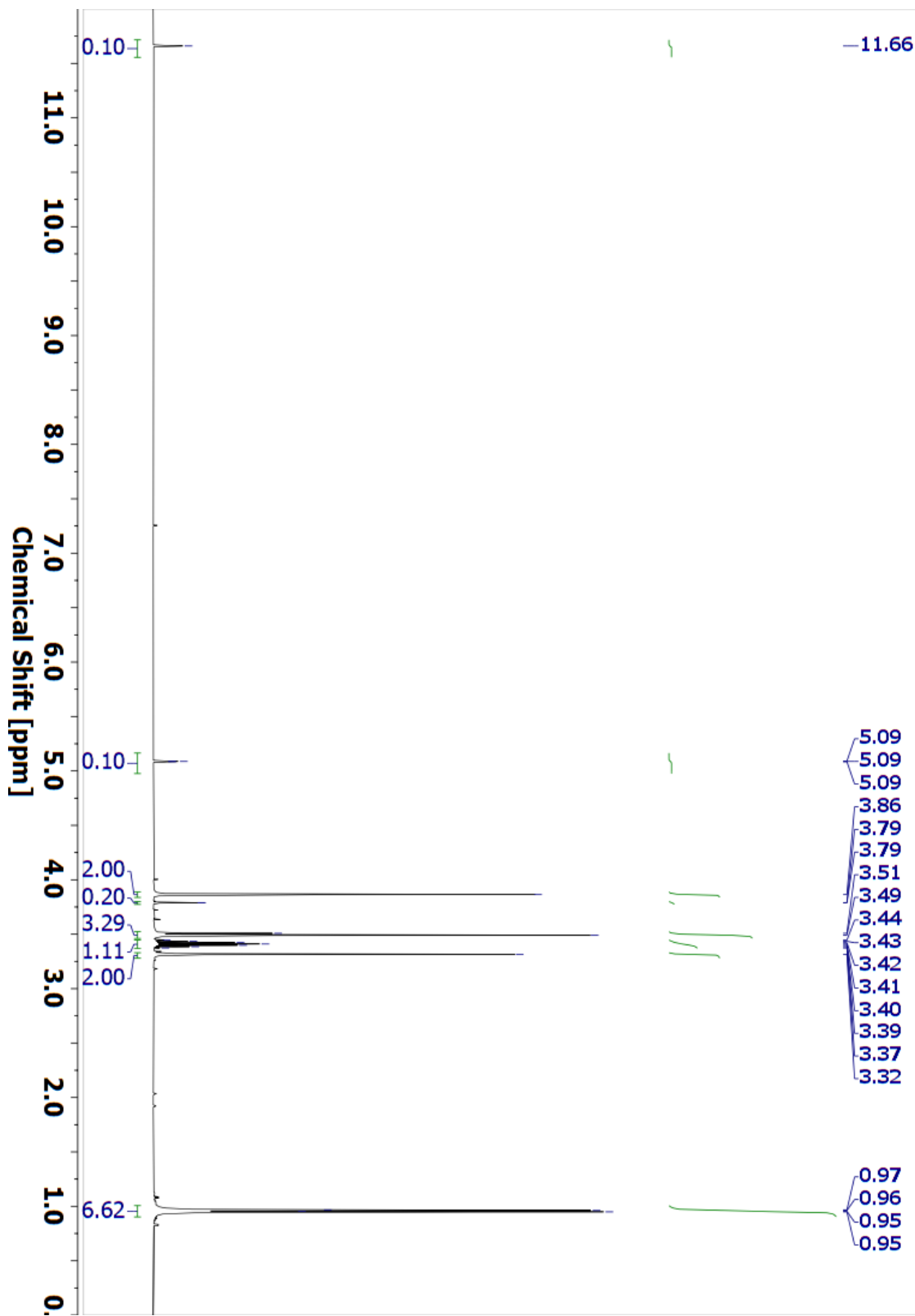


^{13}C NMR spectrum of isolated product in CDCl_3

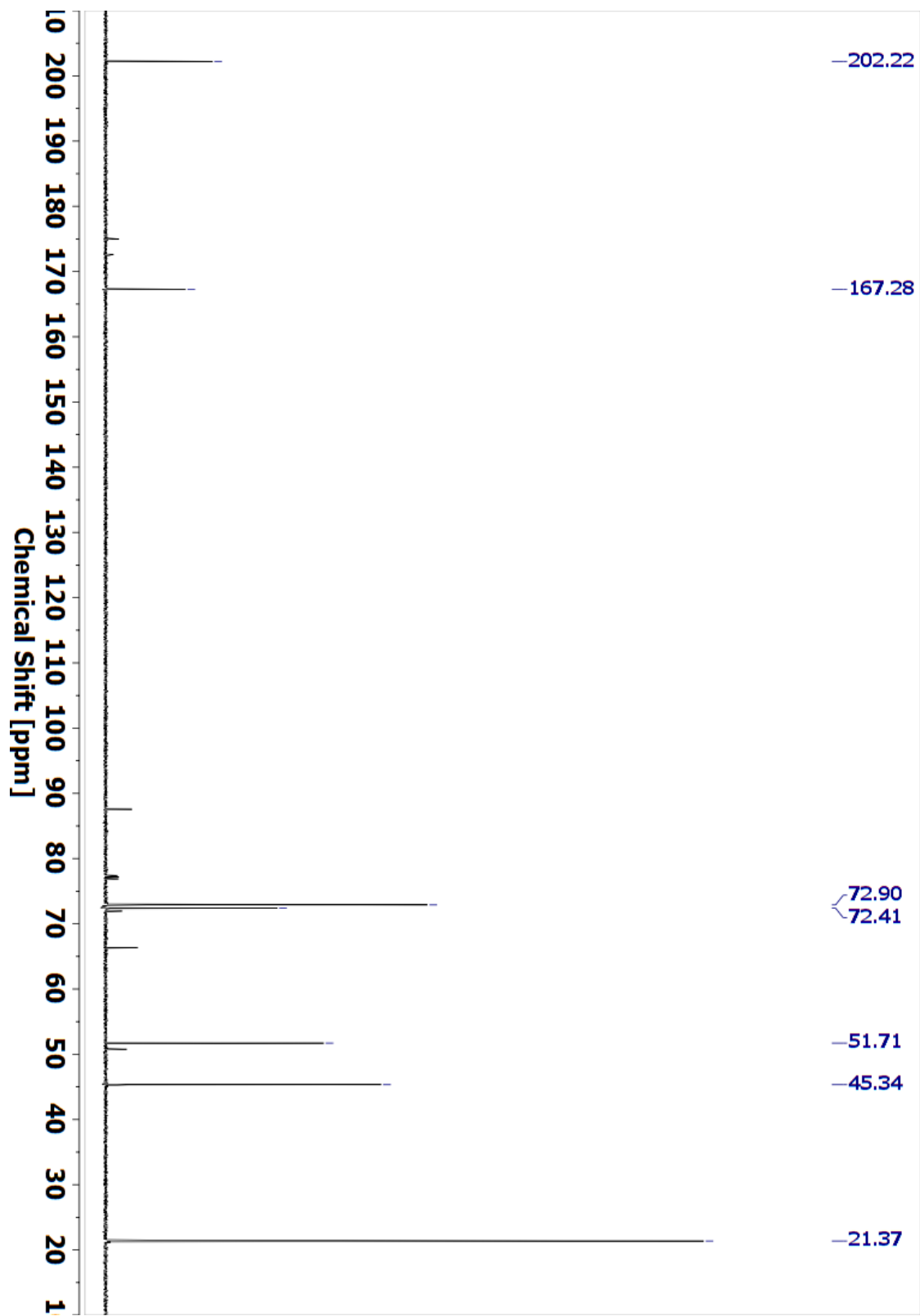
Methyl 2-diazo-4-isopropoxy-3-oxobutanoate (S40)



1. Methyl 4-isopropoxy-3-oxobutanoate (S39): Synthesized following Procedure A: The reaction was run on 10.00 mmol scale to give 1.15 g (66% yield, 9.1% tautomerization) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 3.86 (s, 2H), 3.49 (s, 3H), 3.45–3.36 (m, 1H), 3.32 (s, 2H), 0.96 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 202.22, 167.28, 72.90, 72.41, 51.71, 45.34, 21.37. HRMS (ESI $^+$) m/z Calc. 175.0965 [$\text{C}_8\text{H}_{14}\text{O}_4 + \text{H}$] $^+$, Found. 175.0966 [$\text{M} + \text{H}$] $^+$.



^1H NMR spectrum of isolated product in CDCl_3



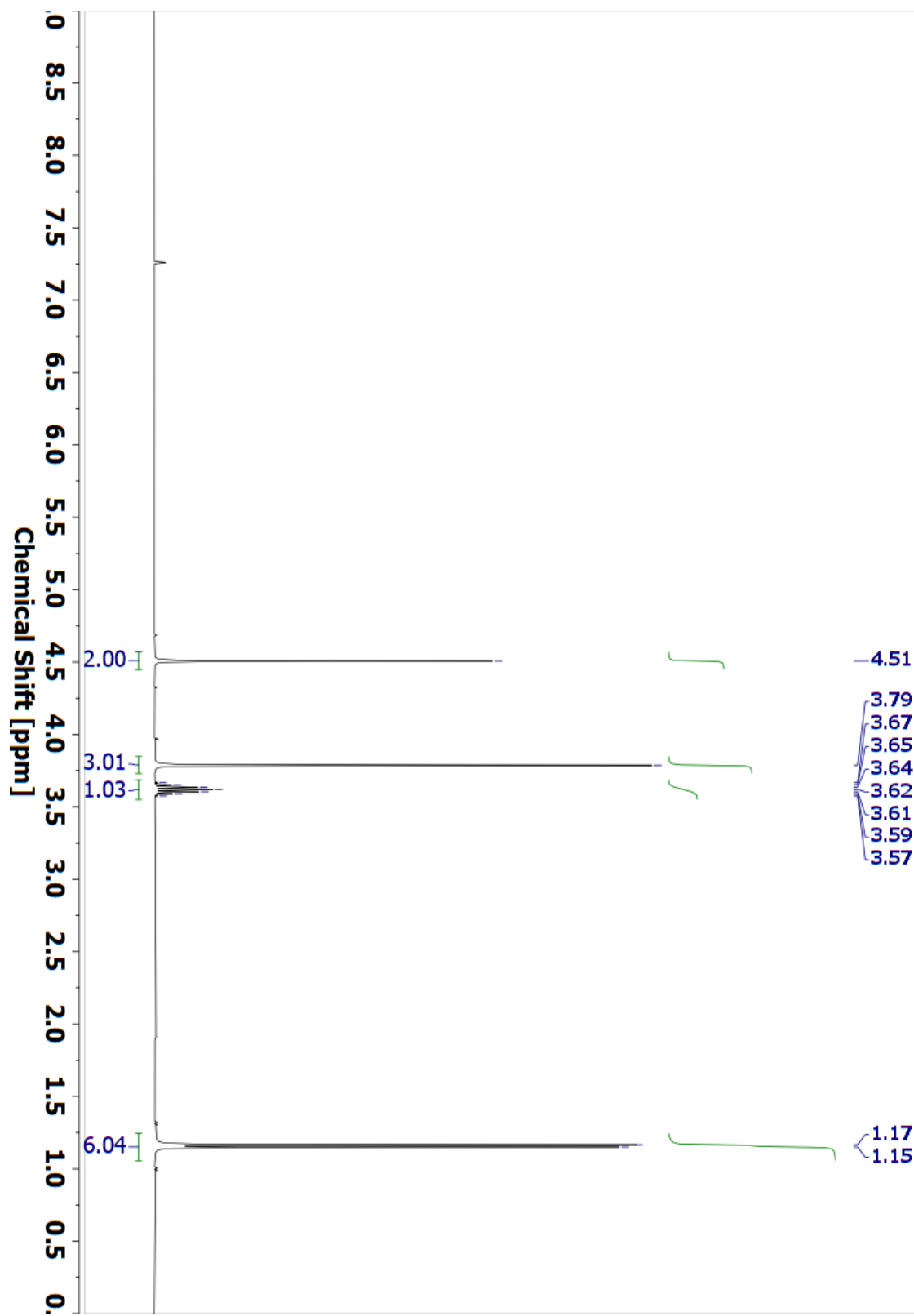
^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 2-diazo-4-isopropoxy-3-oxobutanoate (S40): Synthesized following Procedure B:

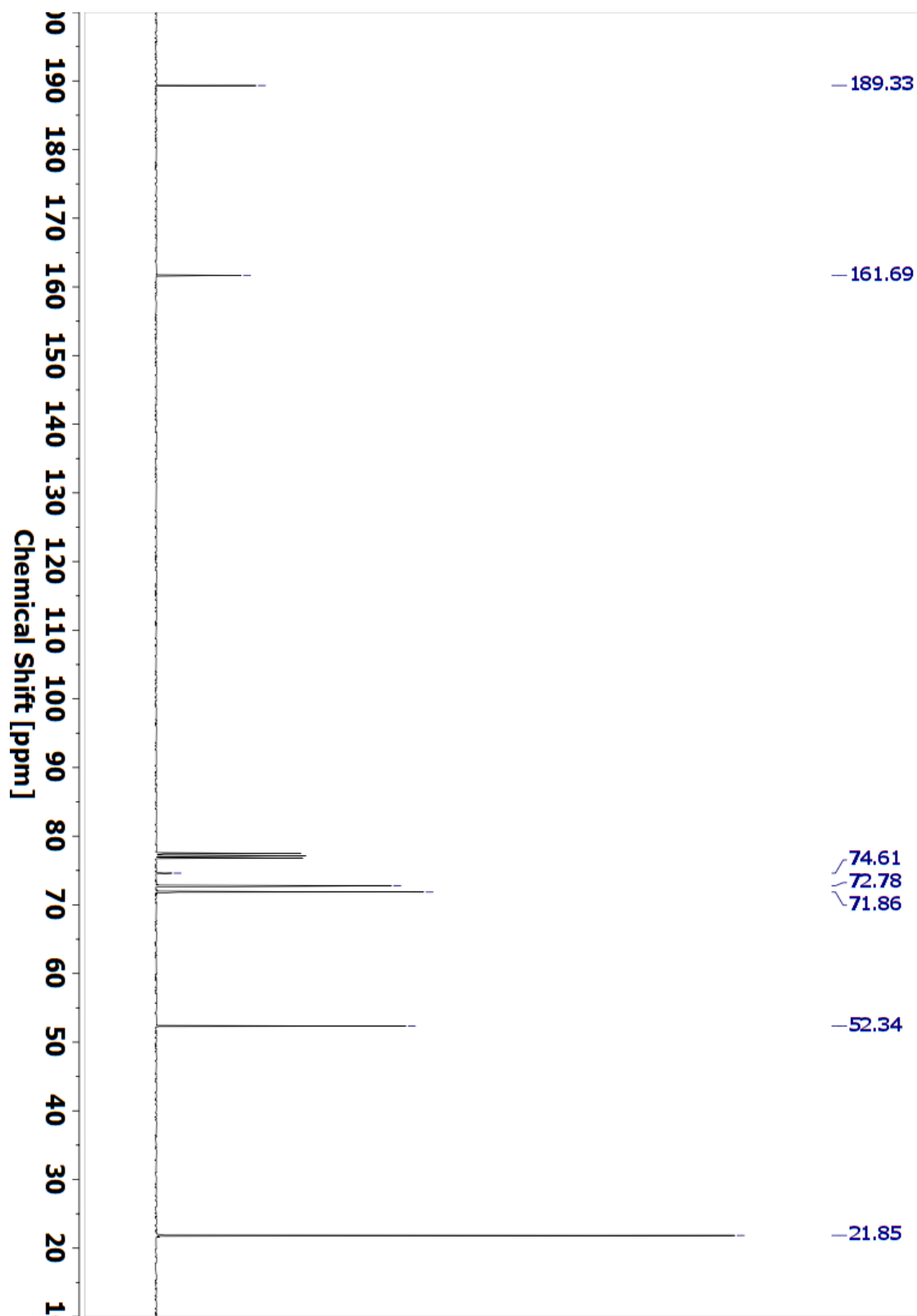
The reaction was run on 5.00 mmol scale to give 0.74 g (74% yield) of product as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 4.51 (s, 2H), 3.79 (s, 3H), 3.62 (hept, $J = 6.1$ Hz, 1H), 1.16 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 189.33, 161.69, 74.61, 72.78, 71.86, 52.34, 21.85.

HRMS (ESI $^+$) m/z Calc. 201.0870 [$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4 + \text{H}$] $^+$, Found. 201.0871 [$\text{M} + \text{H}$] $^+$.

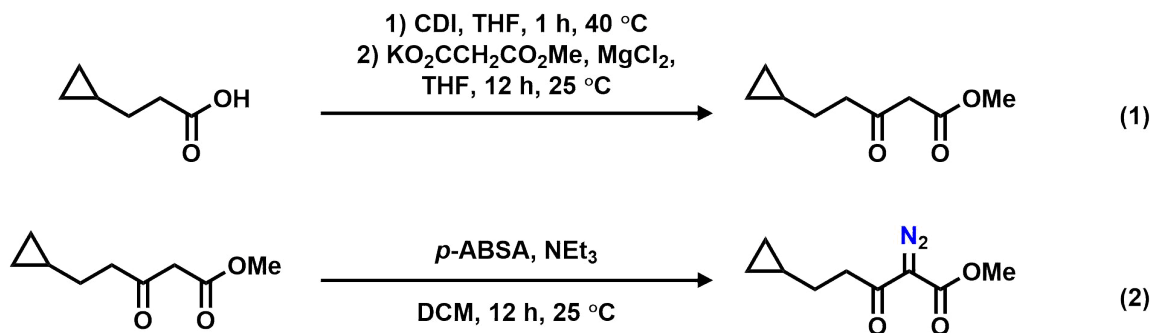


^1H NMR spectrum of isolated product in CDCl_3



¹³C NMR spectrum of isolated product in CDCl₃

Methyl 5-cyclopropyl-2-diazo-3-oxopentanoate (31)

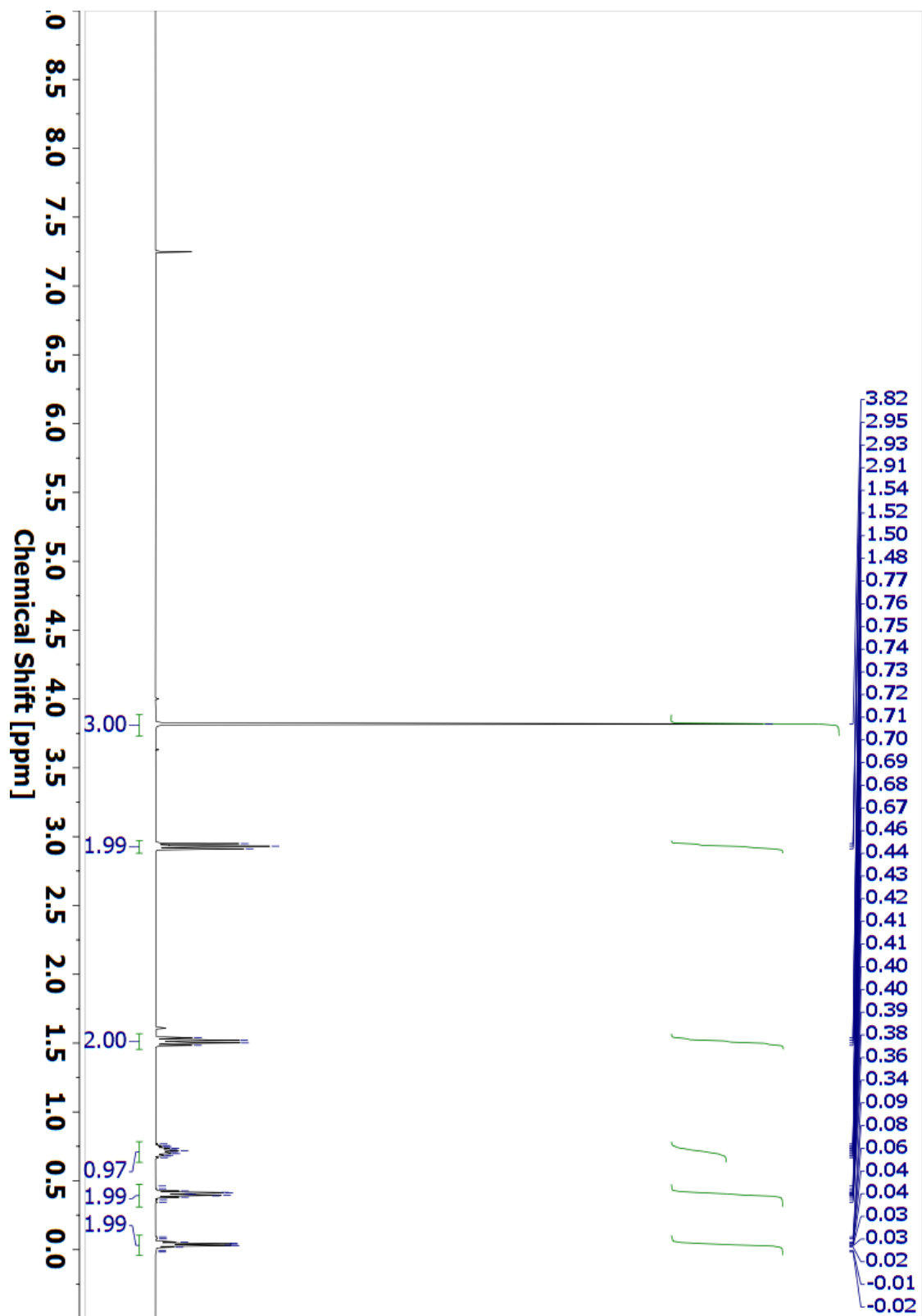


1. Methyl 5-cyclopropyl-3-oxopentanoate (S41): Synthesized following previously reported procedure.¹³

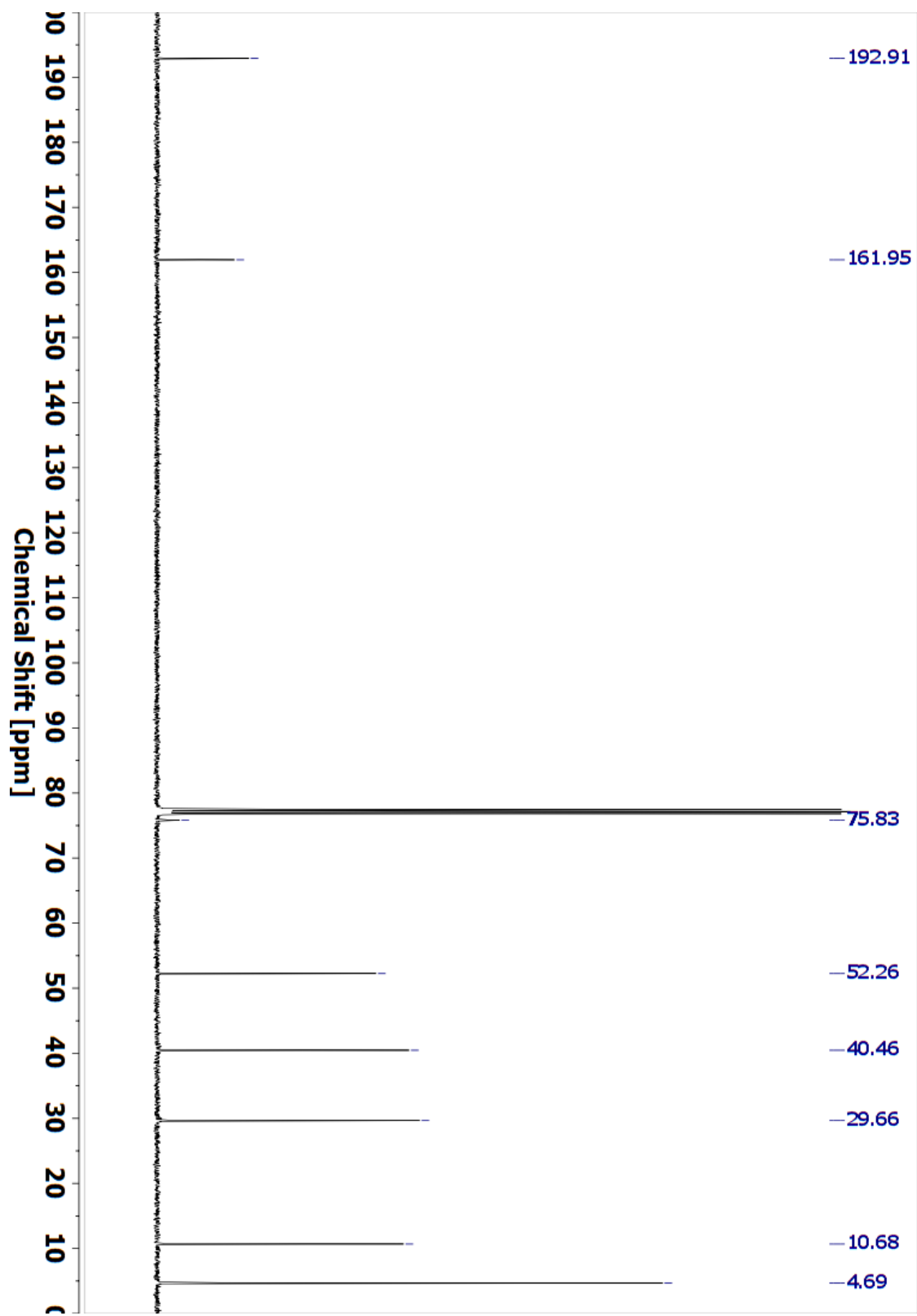
2. Methyl 5-cyclopropyl-2-diazo-3-oxopentanoate (31): Synthesized following Procedure B:

The reaction was run on 5.00 mmol scale to give 0.61 g (58% yield) of product as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.82 (s, 3H), 3.14–2.84 (m, 2H), 1.68–1.29 (m, 2H), 0.85–0.62 (m, 1H), 0.52–0.28 (m, 2H), 0.13–0.13 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.91, 161.95, 75.83, 52.26, 40.46, 29.66, 10.68, 4.69. HRMS (ESI⁺) m/z Calc. 197.0921 [C₉H₁₂N₂O₃+H]⁺, Found. 197.0921 [M+H]⁺.

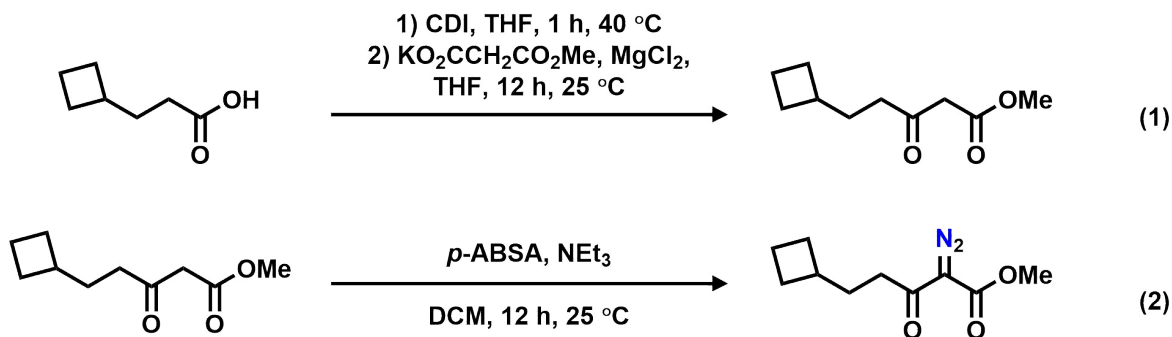


^1H NMR spectrum of isolated product in CDCl_3



¹³C NMR spectrum of isolated product in CDCl₃

Methyl 5-cyclobutyl-2-diazo-3-oxopentanoate (S43)

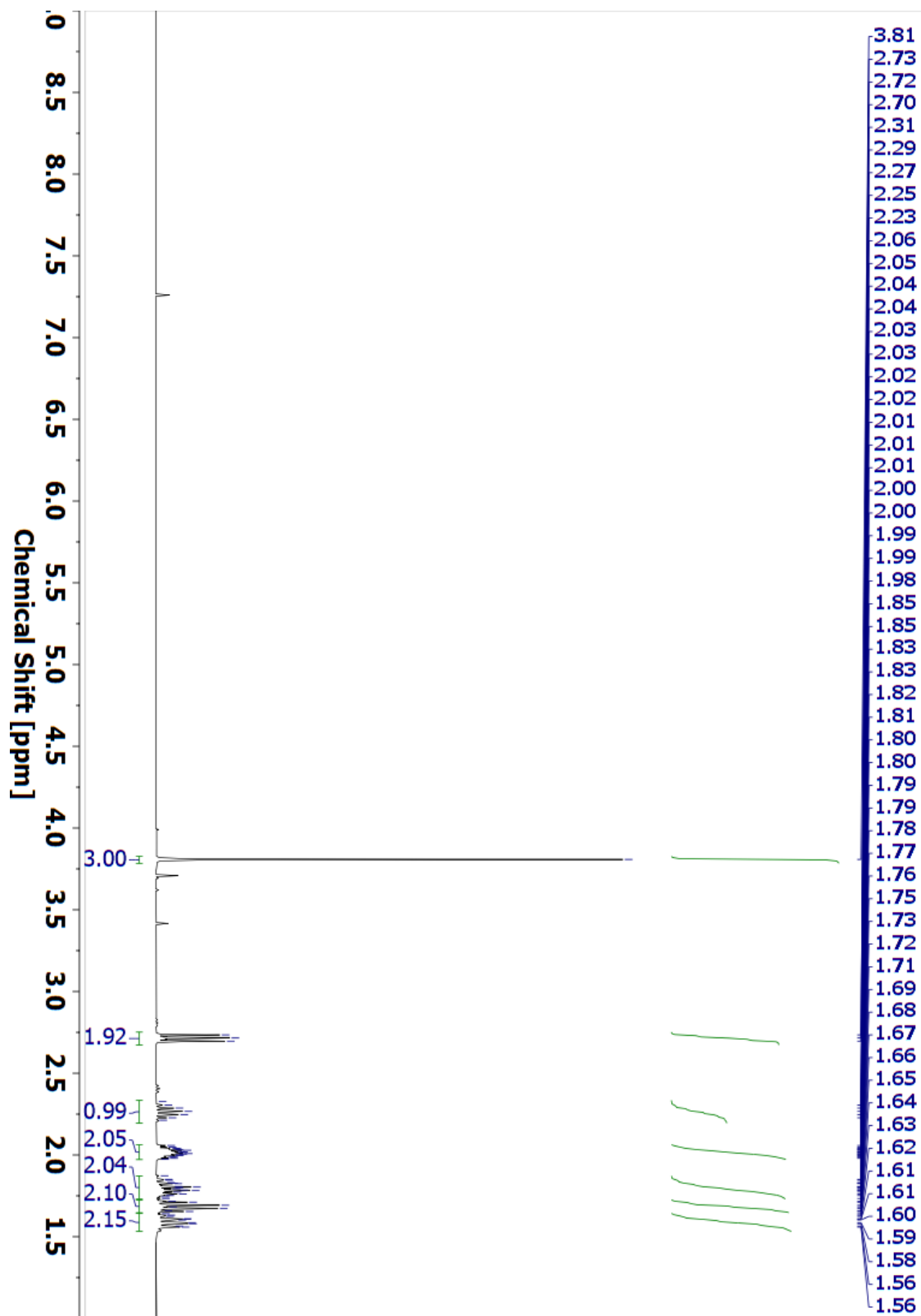


1. Methyl 5-cyclobutyl-3-oxopentanoate (S42): Synthesized following previously reported procedure.¹³

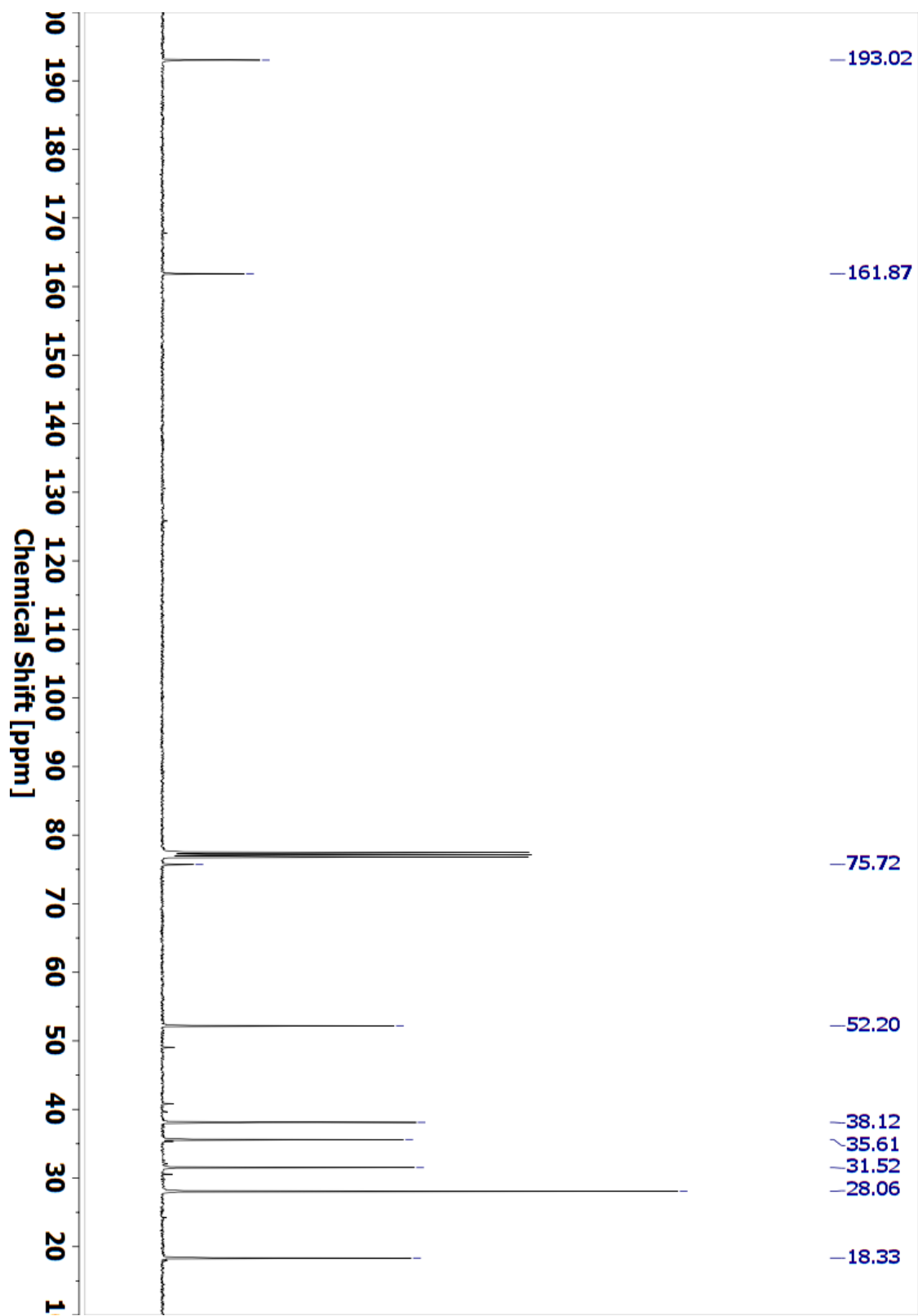
2. Methyl 5-cyclobutyl-2-diazo-3-oxopentanoate (S43): Synthesized following Procedure B:

The reaction was run on 5.00 mmol scale to give 0.83 g (79% yield) of product as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.81 (s, 3H), 2.76–2.67 (m, 2H), 2.27 (p, *J* = 7.7 Hz, 1H), 2.07–1.96 (m, 2H), 1.88–1.74 (m, 2H), 1.73–1.65 (m, 2H), 1.64–1.53 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.02, 161.87, 75.72, 52.20, 38.12, 35.61, 31.52, 28.06, 18.33. HRMS (ESI⁺) *m/z* Calc. 211.1077 [C₁₀H₁₄N₂O₃+H]⁺, Found. 211.1077 [M+H]⁺.

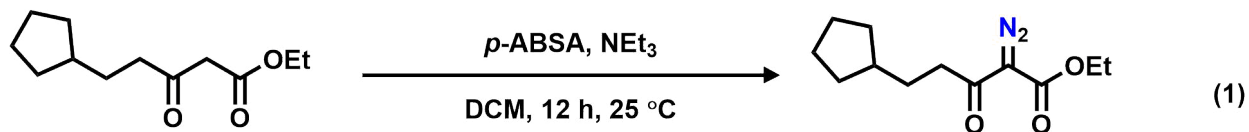


^1H NMR spectrum of isolated product in CDCl_3

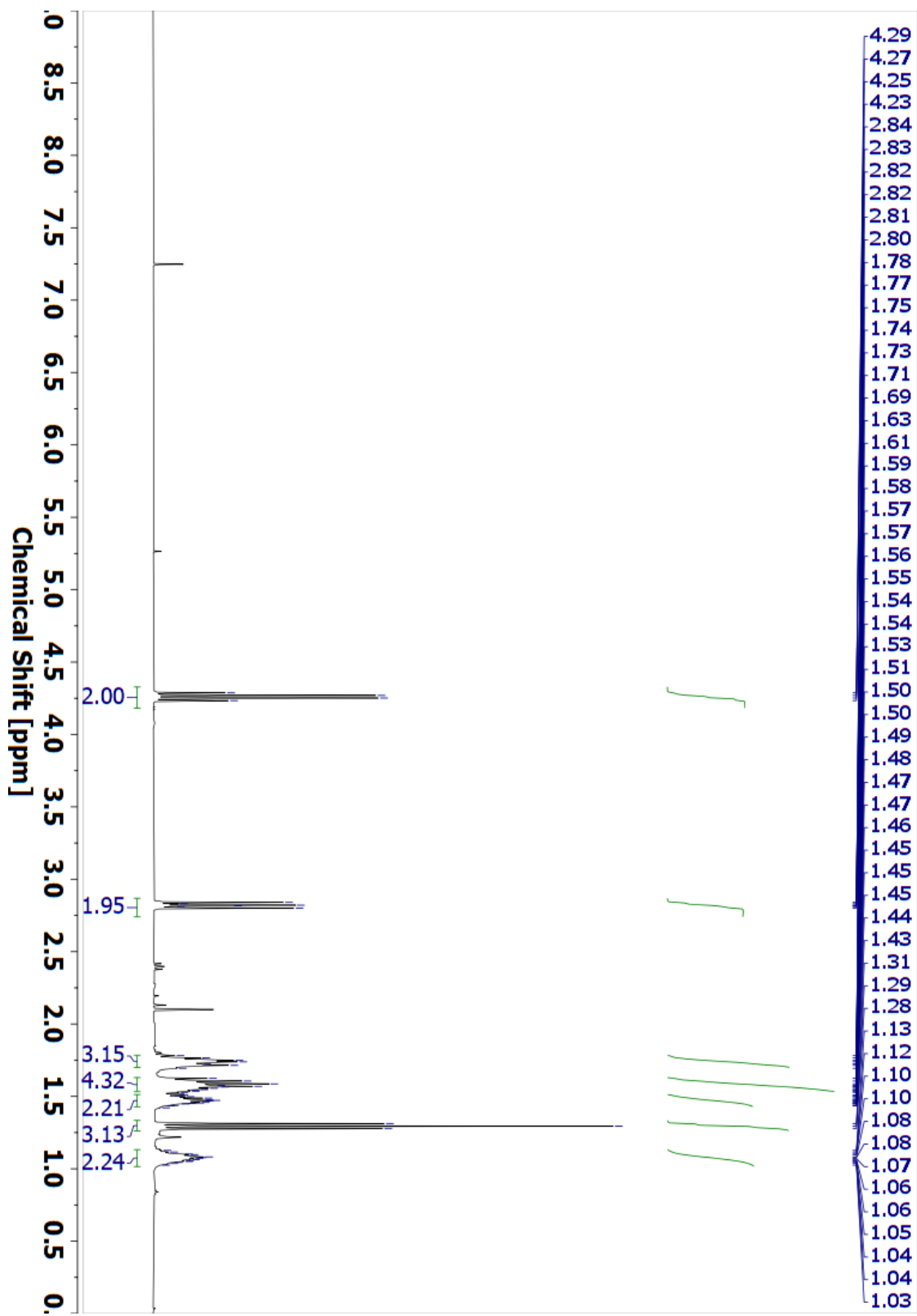


^{13}C NMR spectrum of isolated product in CDCl_3

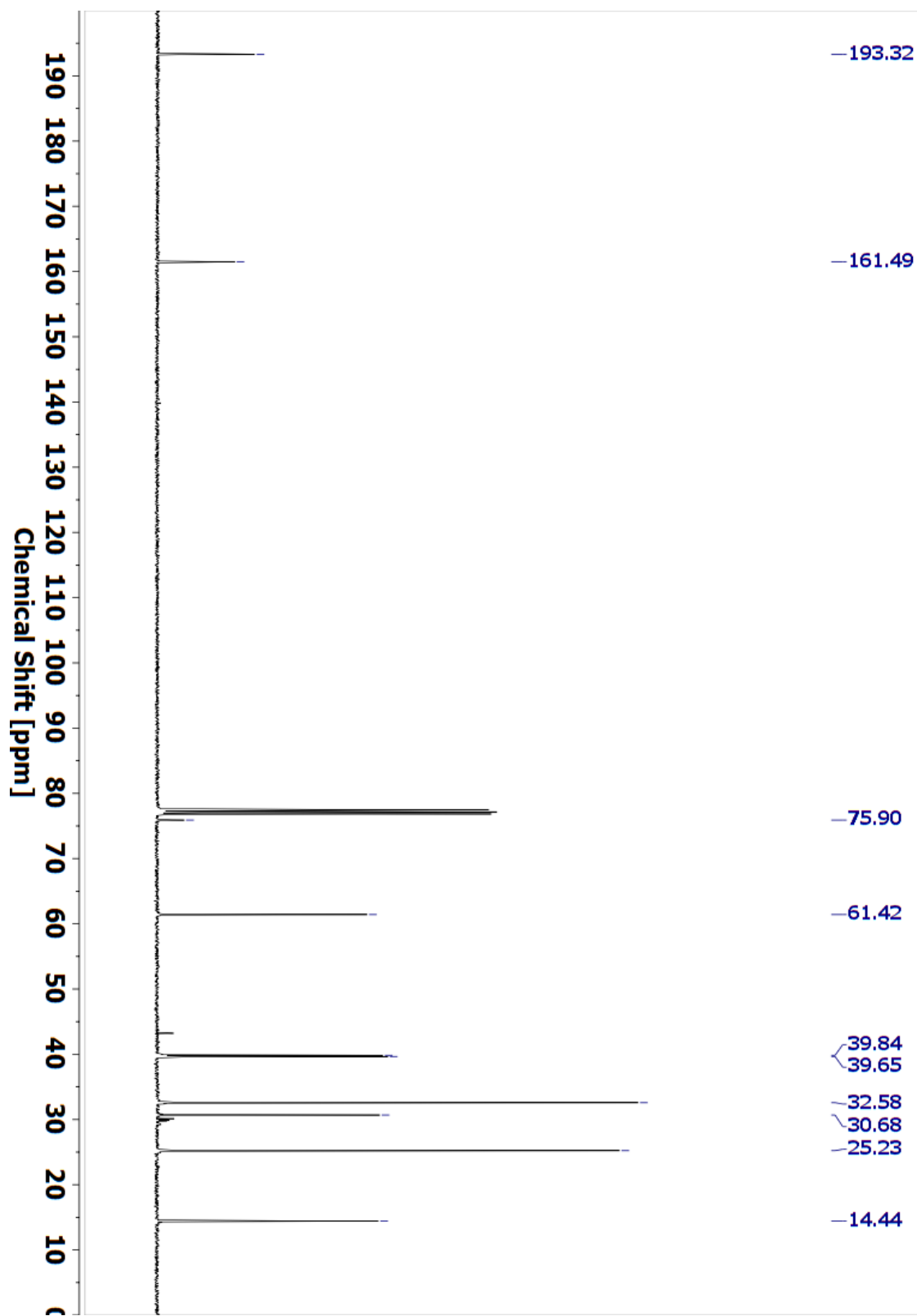
Ethyl 5-cyclopentyl-2-diazo-3-oxopentanoate (S44)



1. Ethyl 5-cyclopentyl-2-diazo-3-oxopentanoate (S44): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.96 g (81% yield) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.26 (q, *J* = 7.1 Hz, 2H), 2.87–2.75 (m, 2H), 1.83–1.66 (m, 3H), 1.64–1.52 (m, 4H), 1.52–1.40 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18–0.95 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.32, 161.49, 75.90, 61.42, 39.84, 39.65, 32.58, 30.68, 25.23, 14.44. HRMS (ESI⁺) *m/z* Calc. 239.1390 [C₁₂H₁₈N₂O₃+H]⁺, Found. 239.1390 [M+H]⁺.

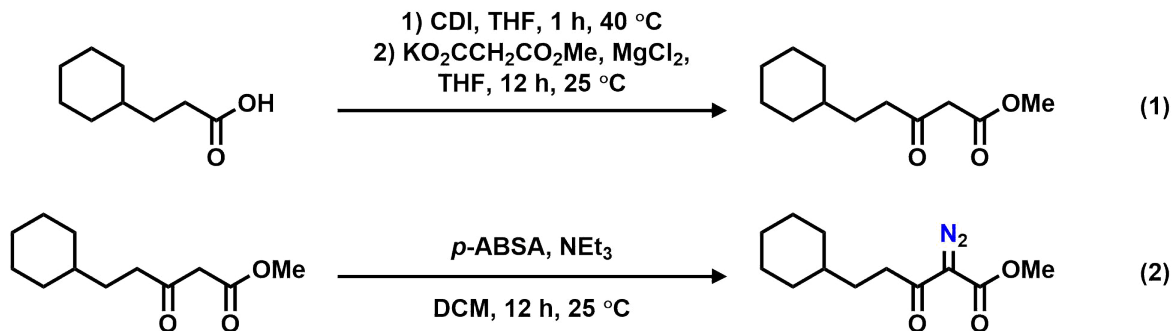


^1H NMR spectrum of isolated product in CDCl_3



^{13}C NMR spectrum of isolated product in CDCl_3

Methyl 5-cyclohexyl-2-diazo-3-oxopentanoate (S46)

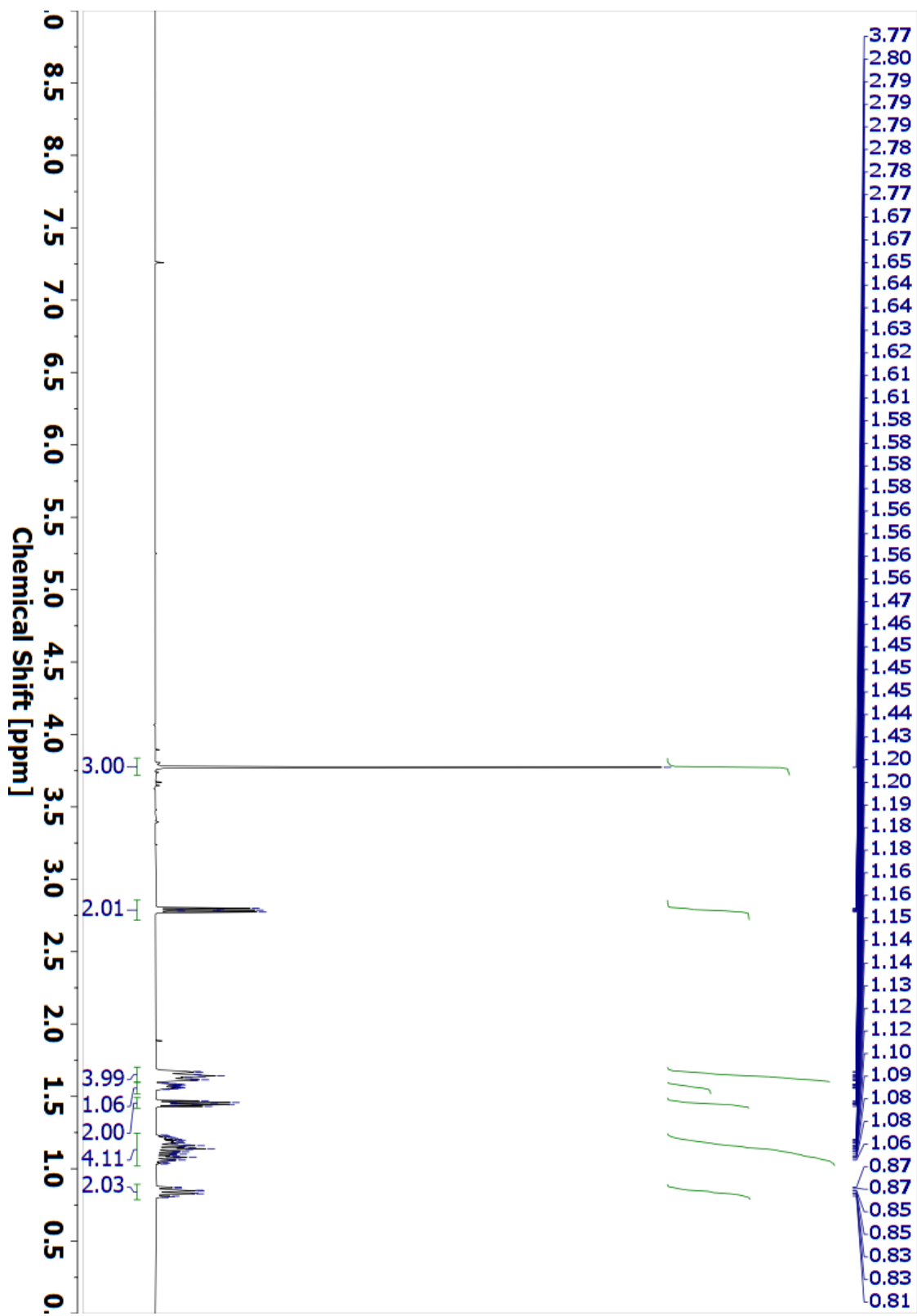


1. Methyl 5-cyclohexyl-3-oxopentanoate (S45): Synthesized following previously reported procedure.¹³

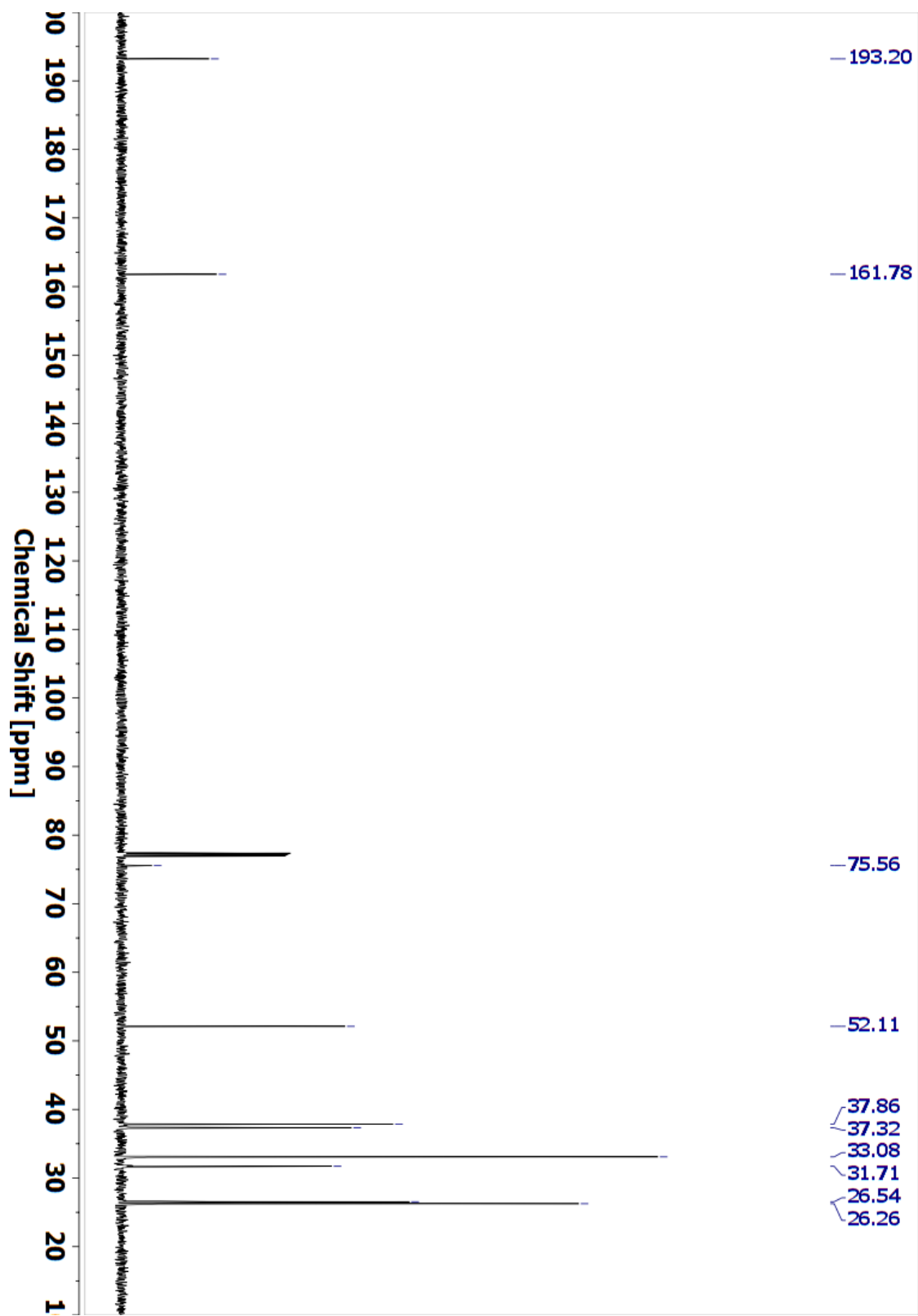
2. Methyl 5-cyclohexyl-2-diazo-3-oxopentanoate (S46): Synthesized following Procedure B:

The reaction was run on 5.00 mmol scale to give 0.87 g (73% yield) of product as a colorless oil.

^1H NMR (600 MHz, CDCl_3) δ 3.77 (s, 3H), 2.84–2.72 (m, 2H), 1.71–1.60 (m, 4H), 1.60–1.53 (m, 1H), 1.49–1.40 (m, 2H), 1.25–1.02 (m, 4H), 0.93–0.77 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.20, 161.78, 75.56, 52.11, 37.86, 37.32, 33.08, 31.71, 26.54, 26.26. HRMS (ESI⁺) m/z Calc. 239.1390 [$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3+\text{H}$]⁺, Found 239.1390 [$\text{M}+\text{H}$]⁺.

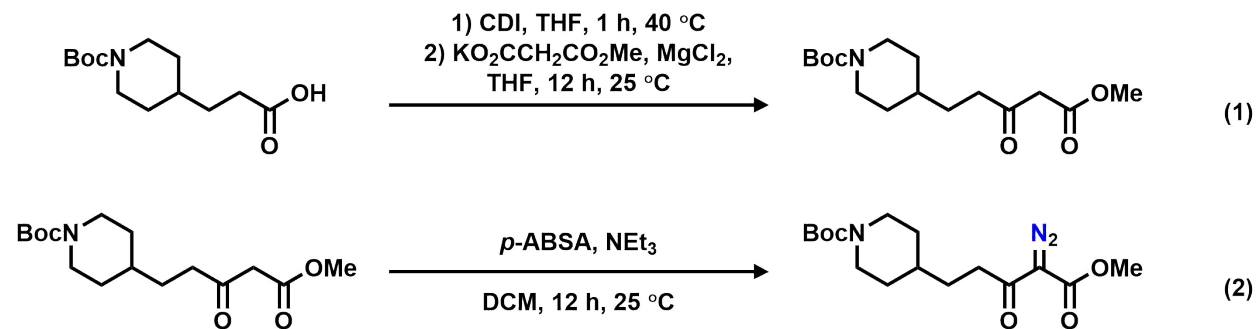


^1H NMR spectrum of isolated product in CDCl_3

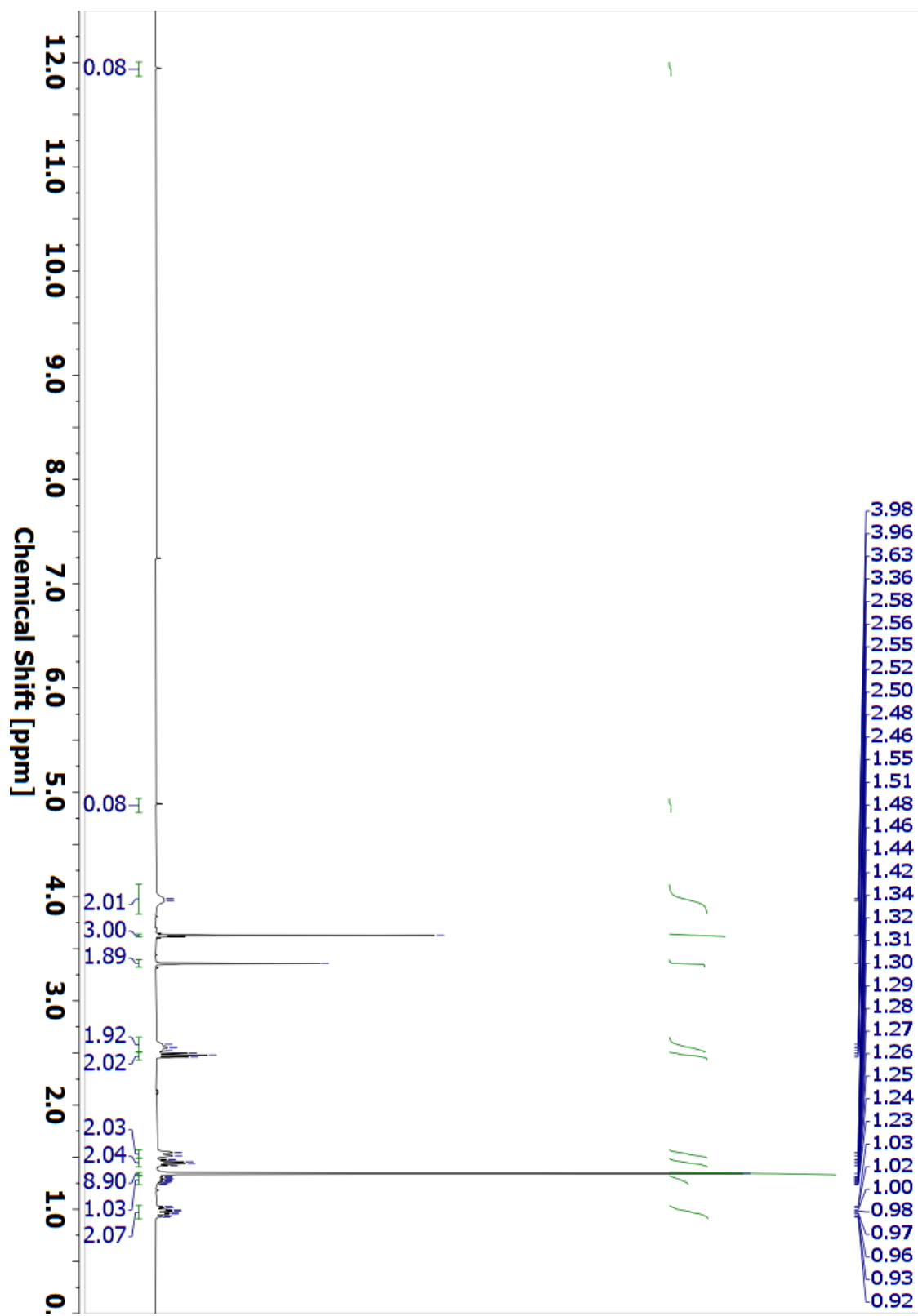


¹³C NMR spectrum of isolated product in CDCl₃

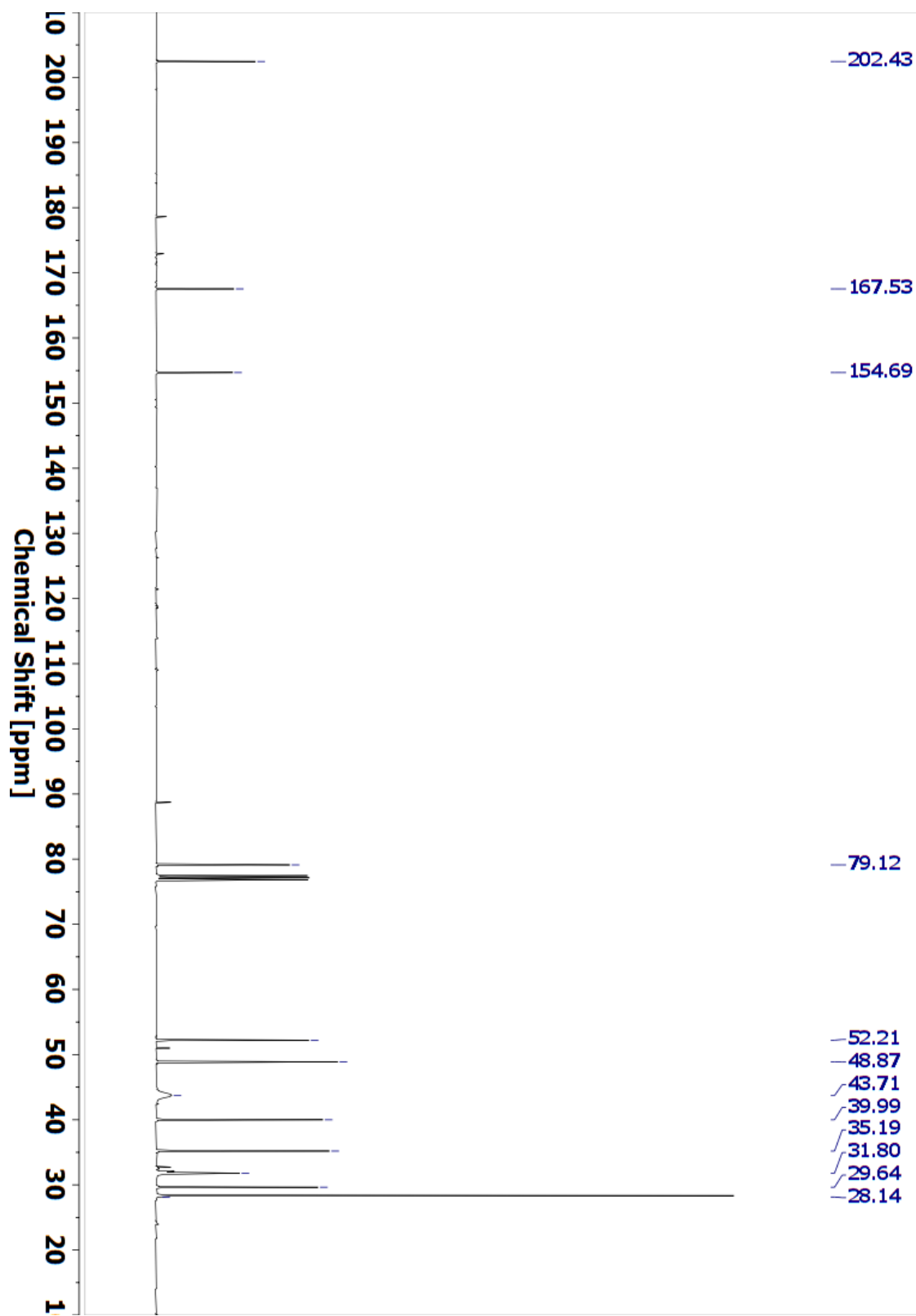
tert-Butyl 4-(4-diazo-5-methoxy-3,5-dioxopentyl)piperidine-1-carboxylate (S48)



1. *tert*-butyl 4-(5-methoxy-3,5-dioxopentyl)piperidine-1-carboxylate (S47): Synthesized following Procedure A: The reaction was run on 10.0 mmol scale to give 1.85 g (59% yield, 7.4% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.10–3.83 (m, 2H), 3.63 (s, 3H), 3.36 (s, 2H), 2.64–2.51 (m, 2H), 2.48 (t, $J = 7.5$ Hz, 2H), 1.59–1.50 (m, 2H), 1.50–1.40 (m, 2H), 1.34 (s, 9H), 1.32–1.22 (m, 1H), 1.08–0.90 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.43, 167.53, 154.69, 79.12, 52.21, 48.87, 43.71, 39.99, 35.19, 31.80, 29.64, 28.14. HRMS (ESI $^+$) m/z Calc. 314.1962 [$\text{C}_{16}\text{H}_{27}\text{NO}_5 + \text{H}$] $^+$, Found. 314.1959 [$\text{M} + \text{H}$] $^+$.



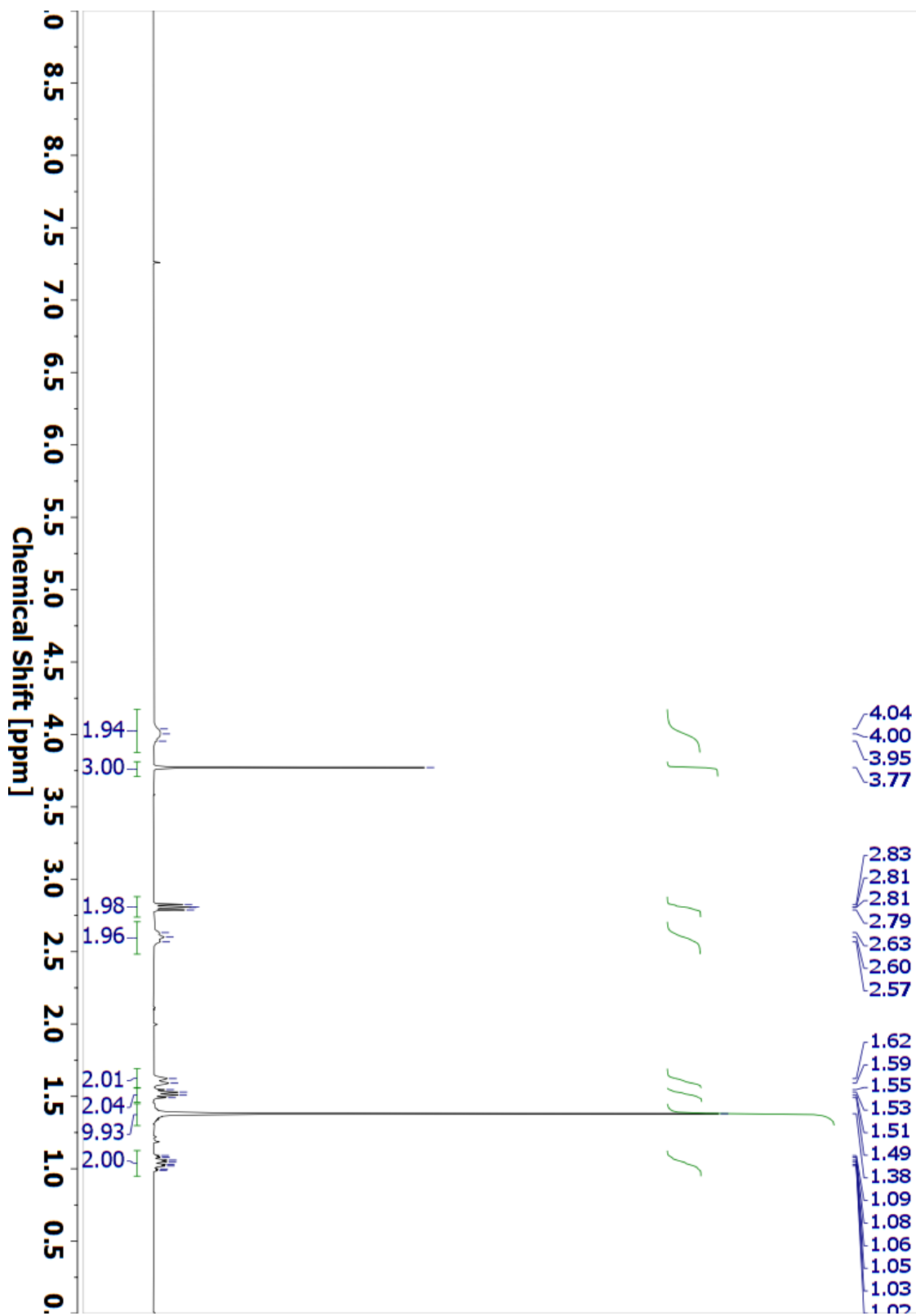
^1H NMR spectrum of isolated product in CDCl_3



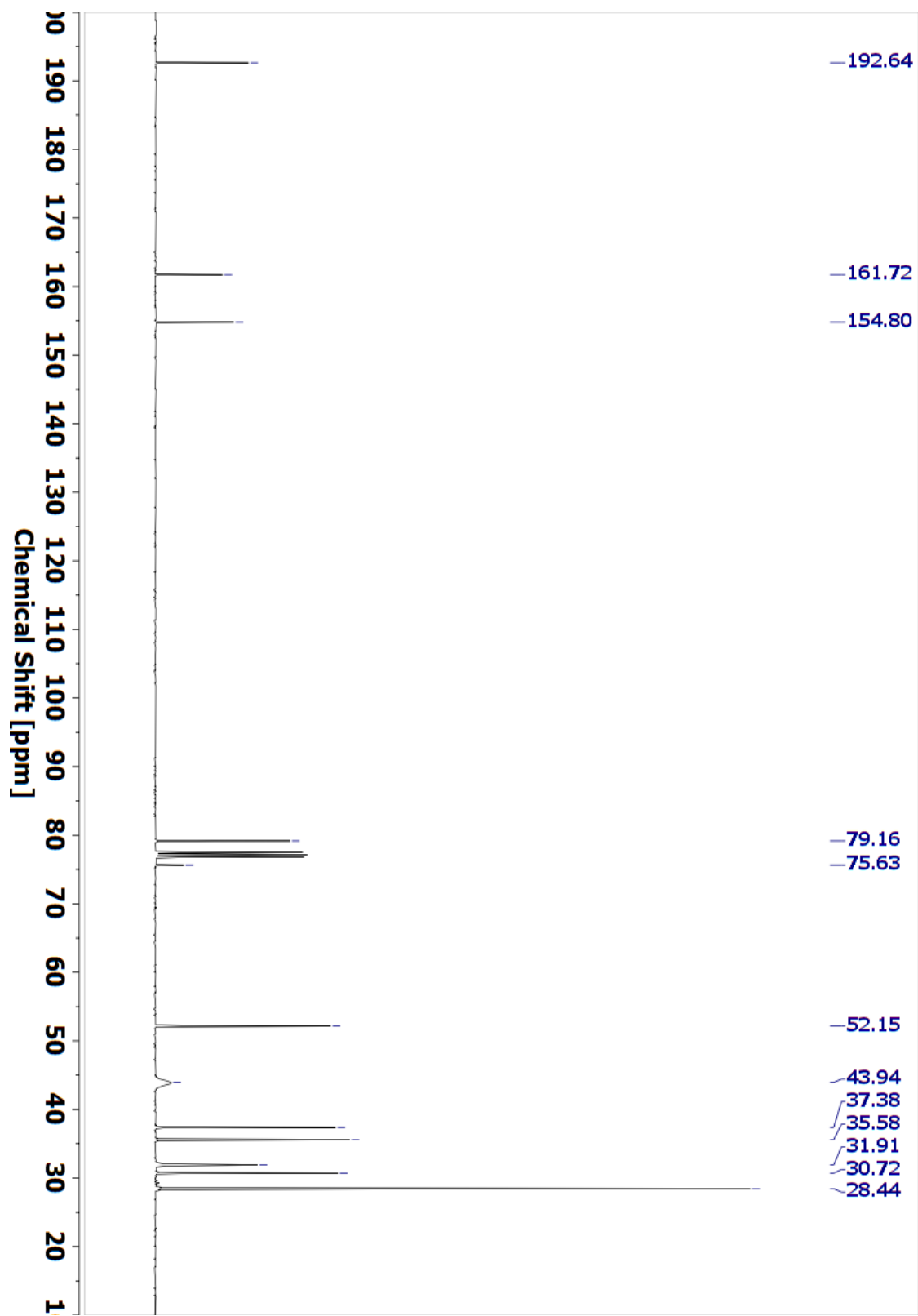
^{13}C NMR spectrum of isolated product in CDCl_3

2. *tert*-Butyl 4-(4-diazo-5-methoxy-3,5-dioxopentyl)piperidine-1-carboxylate (S48):

Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 1.40 g (83% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.17–3.87 (m, 2H), 3.77 (s, 3H), 2.81 (dd, $J = 8.2, 7.1$ Hz, 2H), 2.71–2.48 (m, 2H), 1.61 (d, $J = 12.7$ Hz, 2H), 1.56–1.46 (m, 2H), 1.45–1.30 (m, 10H), 1.04 (qd, $J = 12.6, 4.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.64, 161.72, 154.80, 79.16, 75.63, 52.15, 43.94, 37.38, 35.58, 31.91, 30.72, 28.44. HRMS (ESI $^+$) m/z Calc. 340.1867 [$\text{C}_{16}\text{H}_{25}\text{N}_3\text{O}_5 + \text{H}$] $^+$, Found. 340.1865 [$\text{M} + \text{H}$] $^+$.

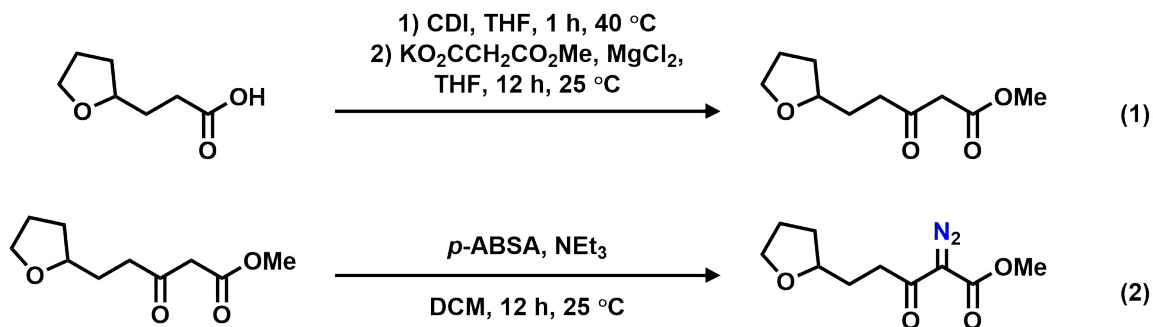


^1H NMR spectrum of isolated product in CDCl_3



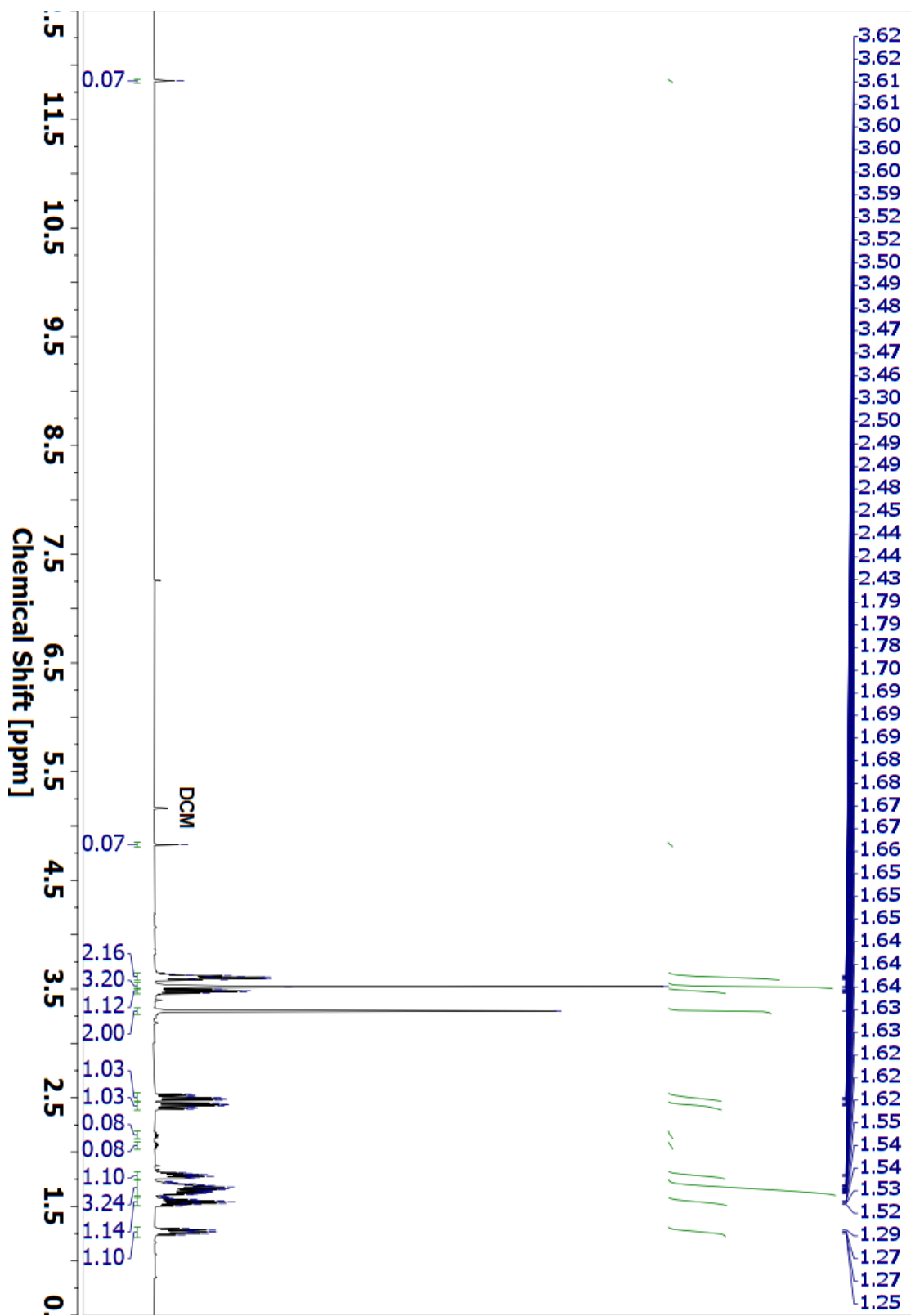
^{13}C NMR spectrum of isolated product in CDCl_3

Ethyl 3-cyclopentyl-2-diazo-3-oxopropanoate (S50)

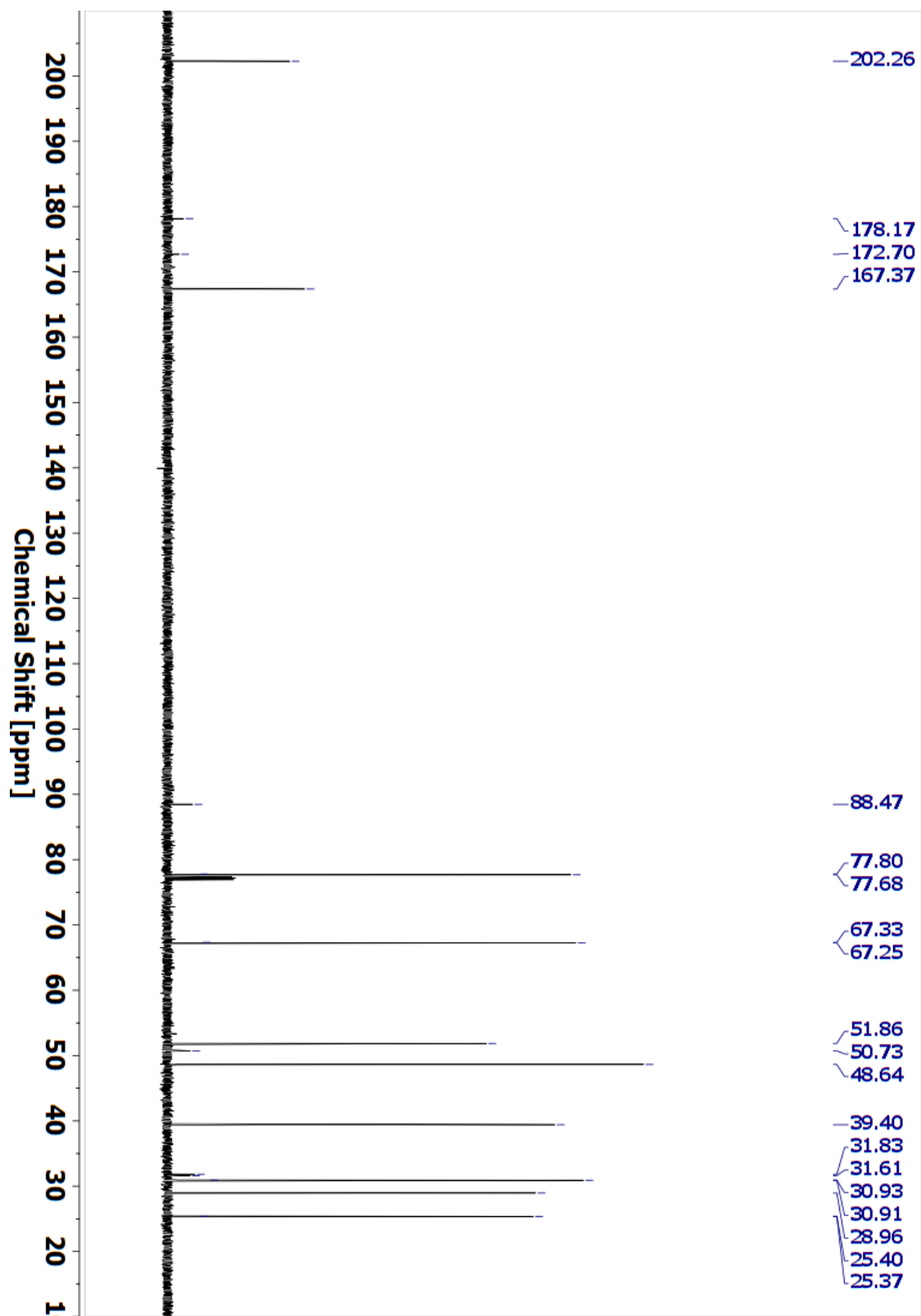


1. Methyl 3-oxo-5-(tetrahydrofuran-2-yl)pentanoate (S49): Synthesized following Procedure

A: The reaction was run on 10.00 mmol scale to give 1.54 g (77% yield, 6.5% tautomerization) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 3.65–3.58 (m, 2H), 3.52 (s, 3H), 3.50–3.45 (m, 1H), 3.30 (s, 2H), 2.50 (ddd, $J = 17.8, 8.6, 5.9$ Hz, 1H), 2.42 (ddd, $J = 17.8, 8.4, 6.4$ Hz, 1H), 1.85–1.74 (m, 1H), 1.74–1.59 (m, 3H), 1.59–1.49 (m, 1H), 1.31–1.22 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 202.26, 167.37, 77.80, 67.25, 51.86, 48.64, 39.40, 30.91, 28.96, 25.37. HRMS (ESI $^+$) m/z Calc. 201.1121 [$\text{C}_{10}\text{H}_{16}\text{O}_4+\text{H}$] $^+$, Found. 201.1119 [$\text{M}+\text{H}$] $^+$.

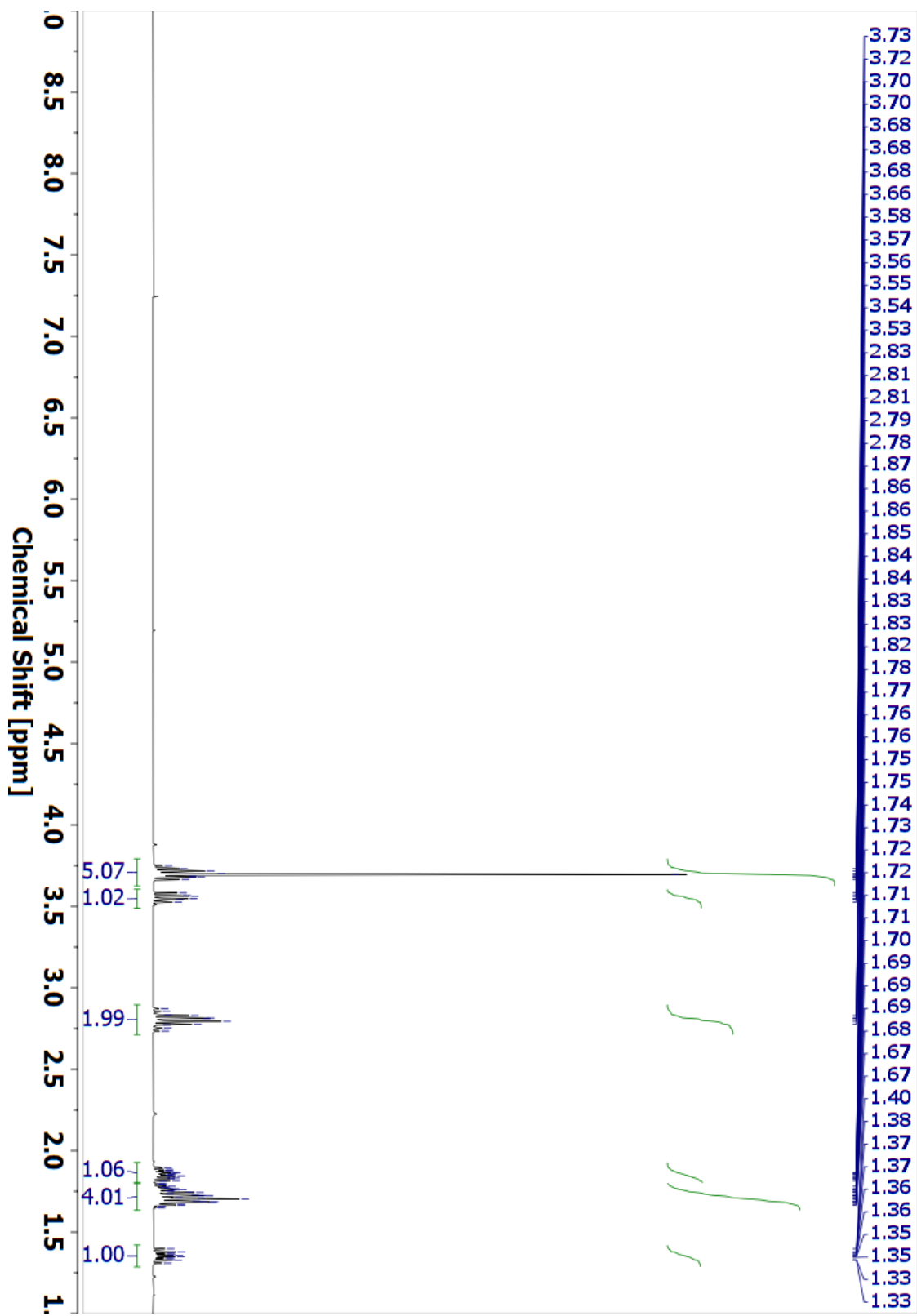


^1H NMR spectrum of isolated product in CDCl_3

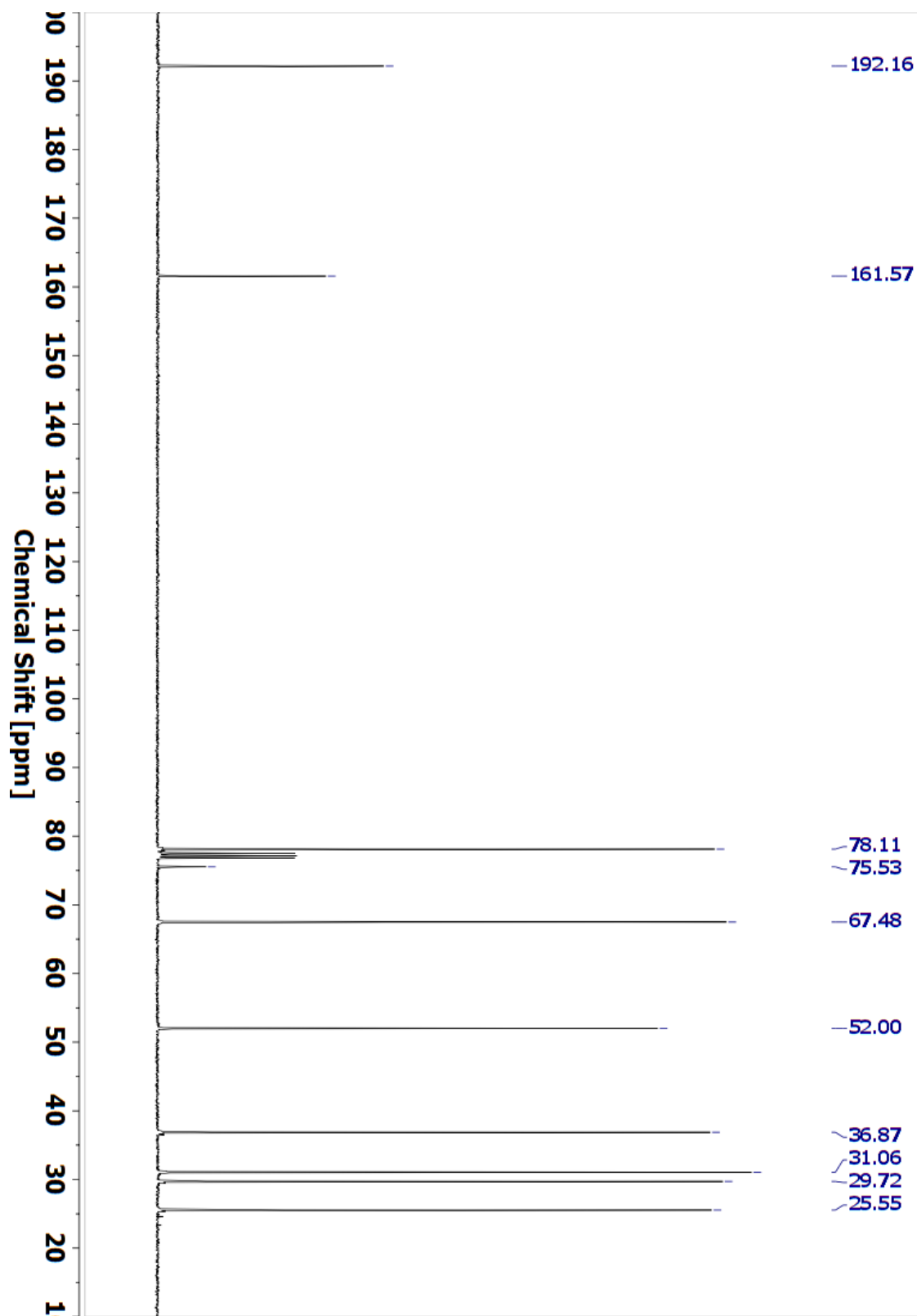


^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 2-diazo-3-oxo-5-(tetrahydrofuran-2-yl)pentanoate (S50): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.70 g (62% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 3.79–3.62 (m, 5H), 3.60–3.50 (m, 1H), 2.90–2.70 (m, 2H), 1.93–1.80 (m, 1H), 1.79–1.62 (m, 4H), 1.42–1.29 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.16, 161.57, 78.11, 75.53, 67.48, 52.00, 36.87, 31.06, 29.72, 25.55. HRMS (ESI $^+$) m/z Calc. 227.1026 [$\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4+\text{H}$] $^+$, Found. 227.1026 [$\text{M}+\text{H}$] $^+$.

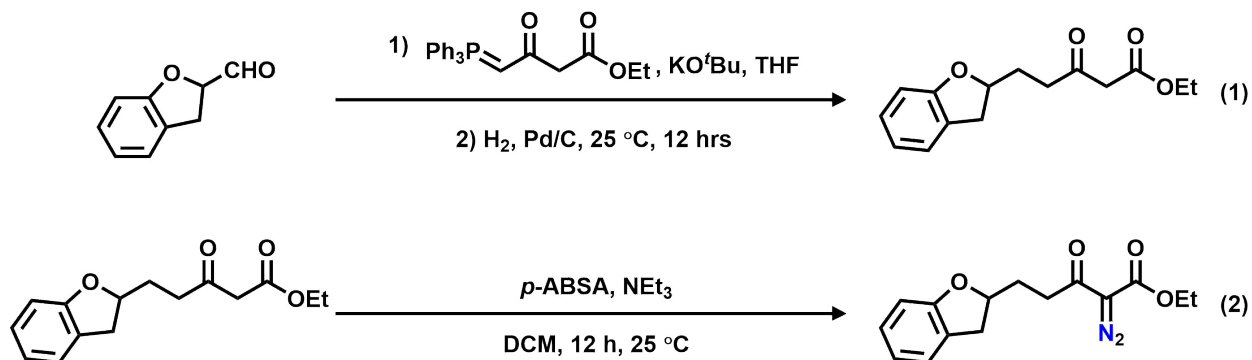


^1H NMR spectrum of isolated product in CDCl_3

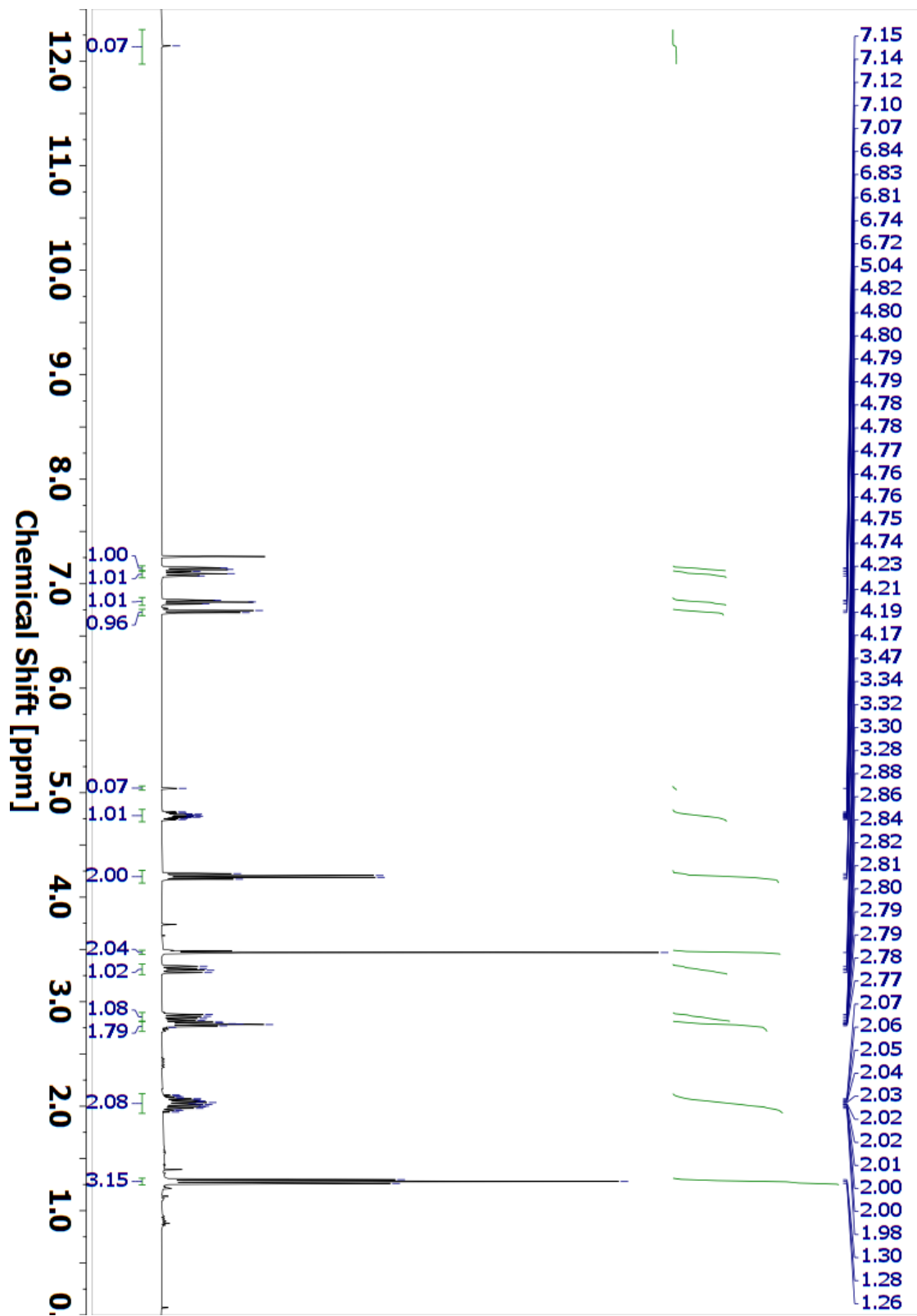


¹³C NMR spectrum of isolated product in CDCl₃

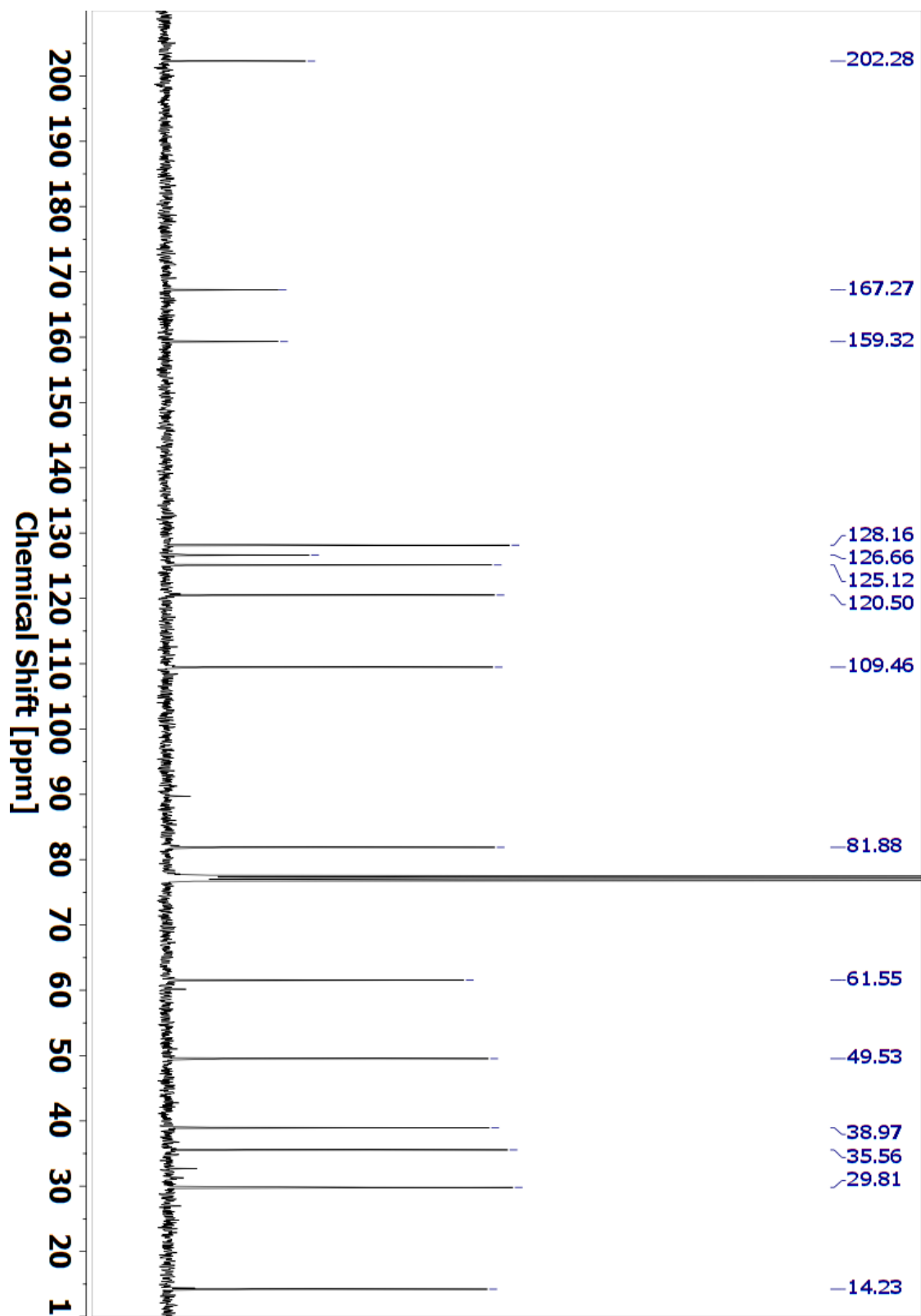
Ethyl 2-diazo-5-(2,3-dihydrobenzofuran-2-yl)-3-oxopentanoate (S52)



1. Ethyl 5-(2,3-dihydrobenzofuran-2-yl)-3-oxopentanoate (S51): Synthesized following literature procedure.¹⁴ The reaction was run on 5.00 mmol scale to give 0.72 g (55% yield, 6.5% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 6.0$ Hz, 1H), 7.12–7.06 (m, 1H), 6.86–6.78 (m, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.85–4.70 (m, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.47 (s, 2H), 3.31 (dd, $J = 15.6, 9.1$ Hz, 1H), 2.85 (dd, $J = 15.6, 7.3$ Hz, 1H), 2.81–2.74 (m, 2H), 2.13–1.93 (m, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.28, 167.27, 159.32, 128.16, 126.66, 125.12, 120.50, 109.46, 81.88, 61.55, 49.53, 38.97, 35.56, 29.81, 14.23. HRMS (ESI⁺) m/z Calc. 263.1278 [$\text{C}_{15}\text{H}_{18}\text{O}_4 + \text{H}$]⁺, Found. 263.1280 [$\text{M} + \text{H}$]⁺.

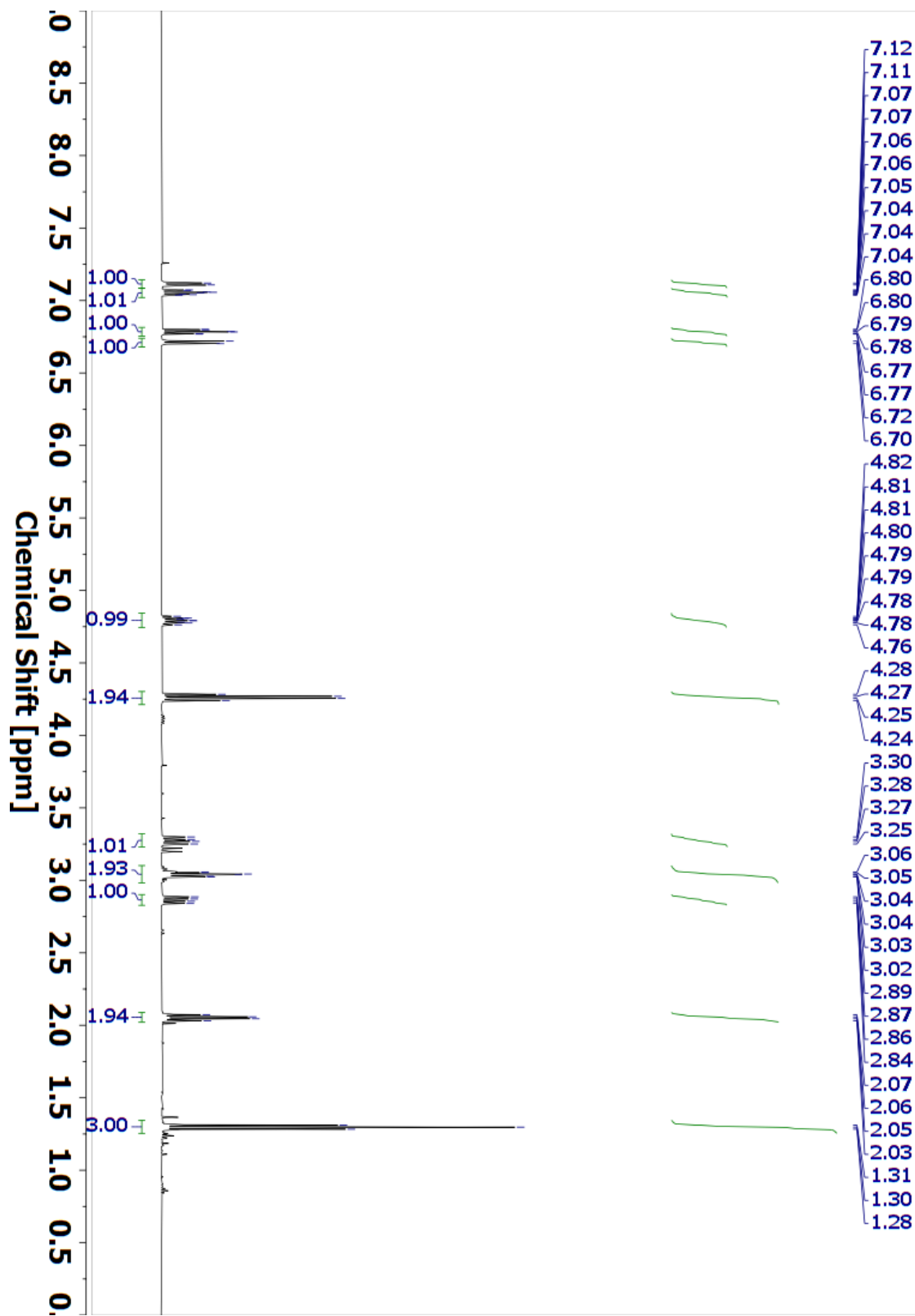


^1H NMR spectrum of isolated product in CDCl_3

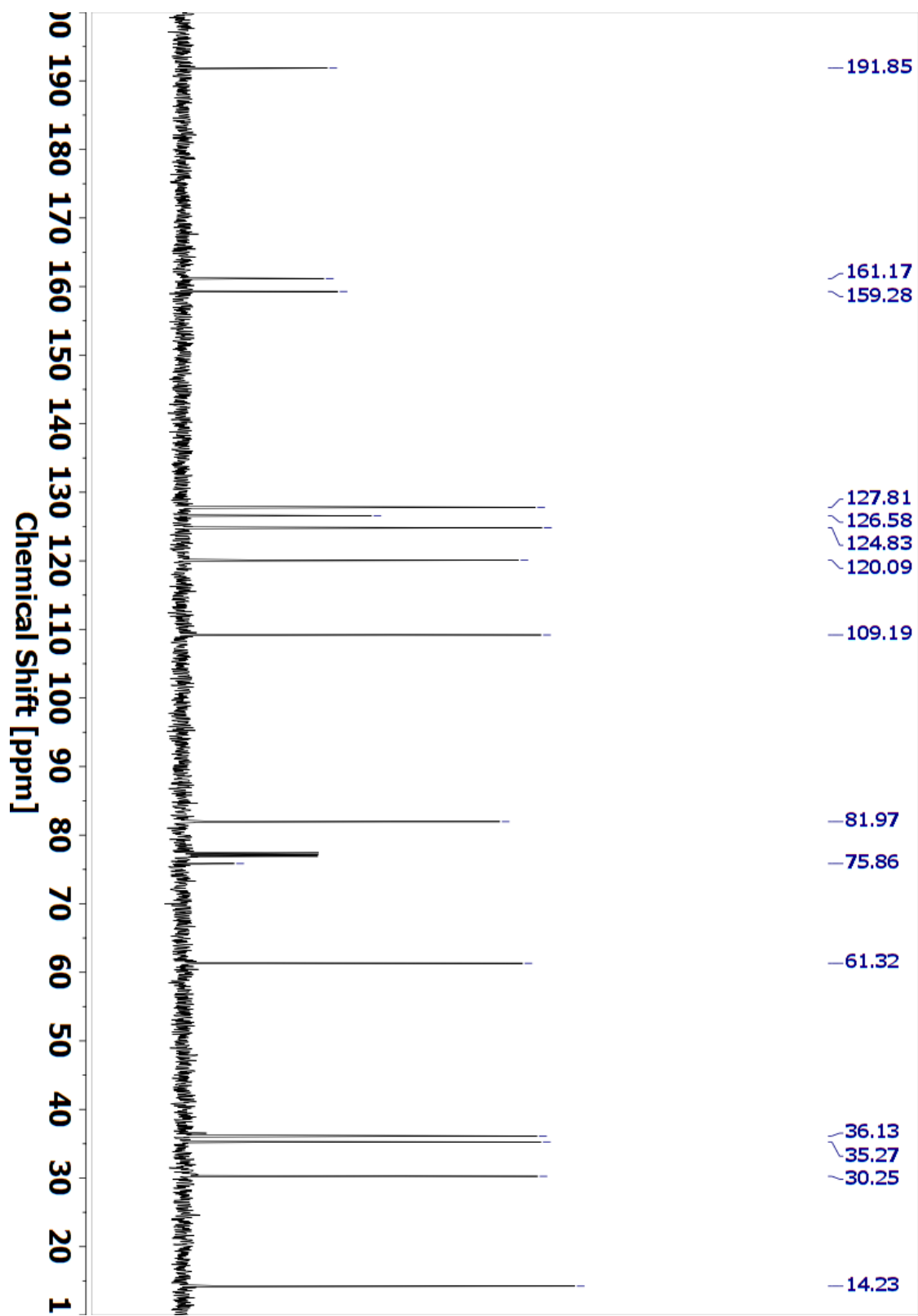


^{13}C NMR spectrum of isolated product in CDCl_3

2. Ethyl 2-diazo-5-(2,3-dihydrobenzofuran-2-yl)-3-oxopentanoate (S52): Synthesized following Procedure B: The reaction was run on 2.00 mmol scale to give 0.40 g (70% yield) of product as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, *J* = 6.4 Hz, 1H), 7.09–7.00 (m, 1H), 6.88–6.74 (m, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 4.84–4.74 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 15.5, 9.0 Hz, 1H), 3.04 (td, *J* = 7.3, 2.3 Hz, 2H), 2.86 (dd, *J* = 15.5, 7.3 Hz, 1H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 191.85, 161.17, 159.28, 127.81, 126.58, 124.83, 120.09, 109.19, 81.97, 75.86, 61.32, 36.13, 35.27, 30.25, 14.23. HRMS (ESI⁺) *m/z* Calc. 289.1183 [C₁₅H₁₆N₂O₄+H]⁺, Found. 289.1186 [M+H]⁺.

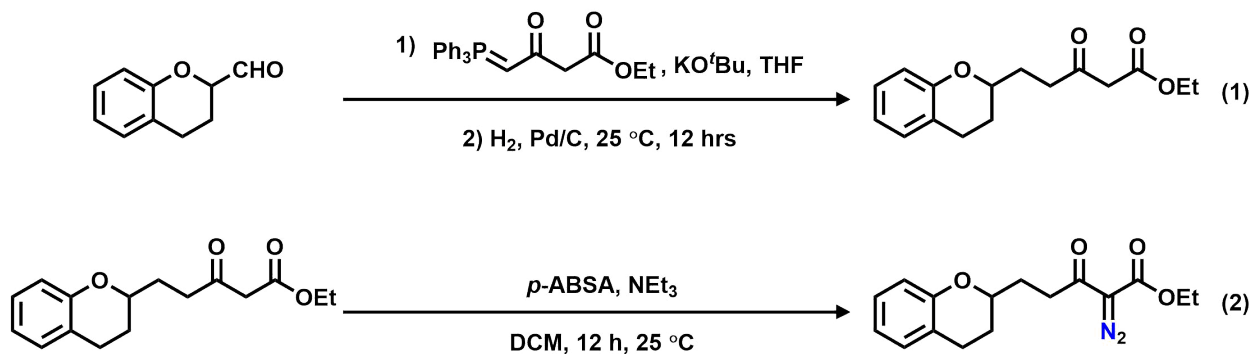


^1H NMR spectrum of isolated product in CDCl_3



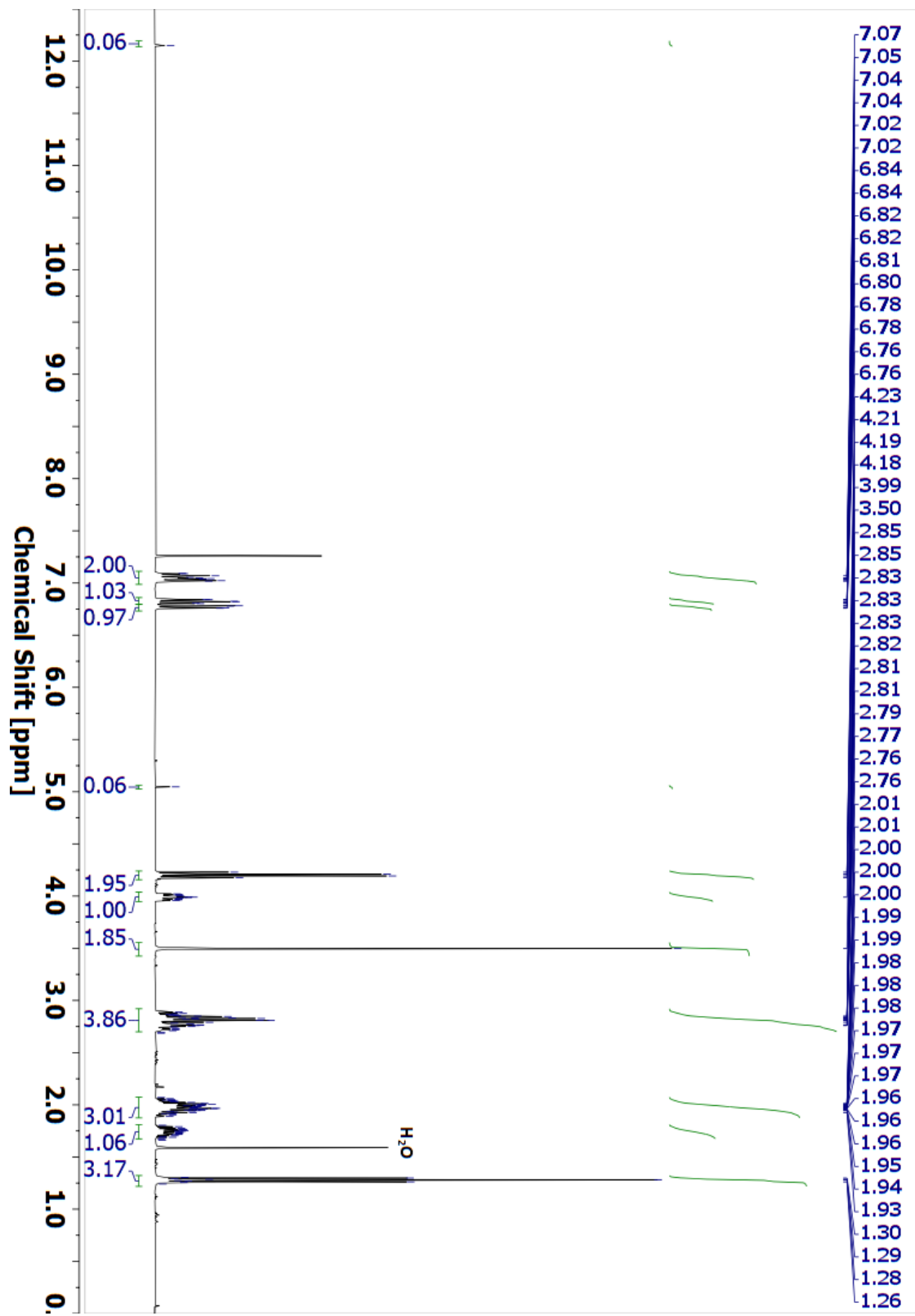
^{13}C NMR spectrum of isolated product in CDCl_3

Ethyl 5-(chroman-2-yl)-2-diazo-3-oxopentanoate (S54)

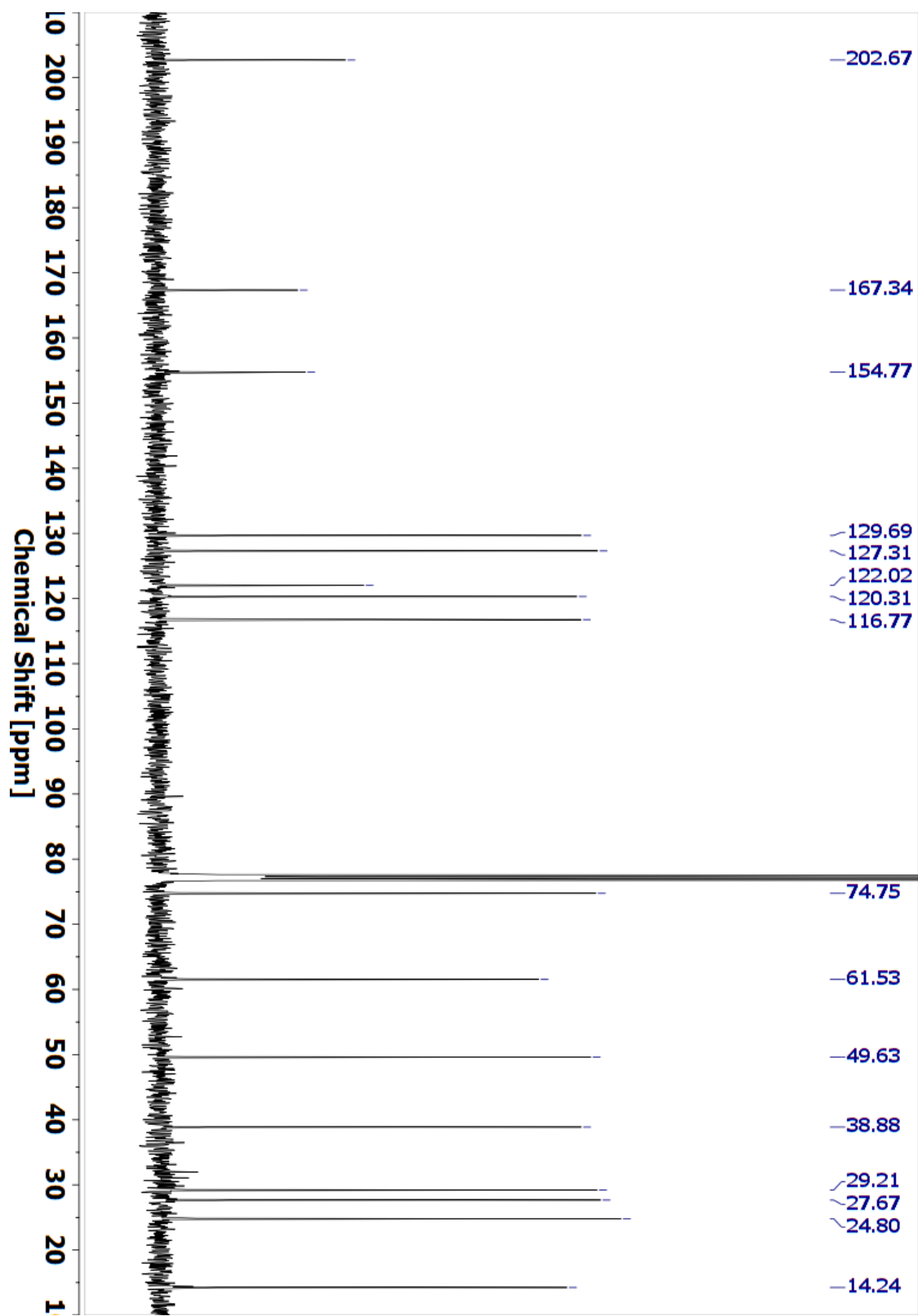


1. Ethyl 5-(chroman-2-yl)-3-oxopentanoate (S53): Synthesized following literature procedure.¹⁴

The reaction was run on 5.00 mmol scale to give 0.68 g (49% yield, 5.7% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.12–6.97 (m, 2H), 6.82 (td, $J = 7.4, 1.3$ Hz, 1H), 6.77 (dd, $J = 8.1, 1.4$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 4.04–3.94 (m, 1H), 3.50 (s, 2H), 2.91–2.67 (m, 4H), 2.08–1.87 (m, 3H), 1.83–1.66 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.67, 167.34, 154.77, 129.69, 127.31, 122.02, 120.31, 116.77, 74.75, 61.53, 49.63, 38.88, 29.21, 27.67, 24.80, 14.24. HRMS (ESI⁺) m/z Calc. 277.1434 [$\text{C}_{16}\text{H}_{20}\text{O}_4+\text{H}$]⁺, Found. 277.1437 [$\text{M}+\text{H}$]⁺.



¹H NMR spectrum of isolated product in CDCl₃

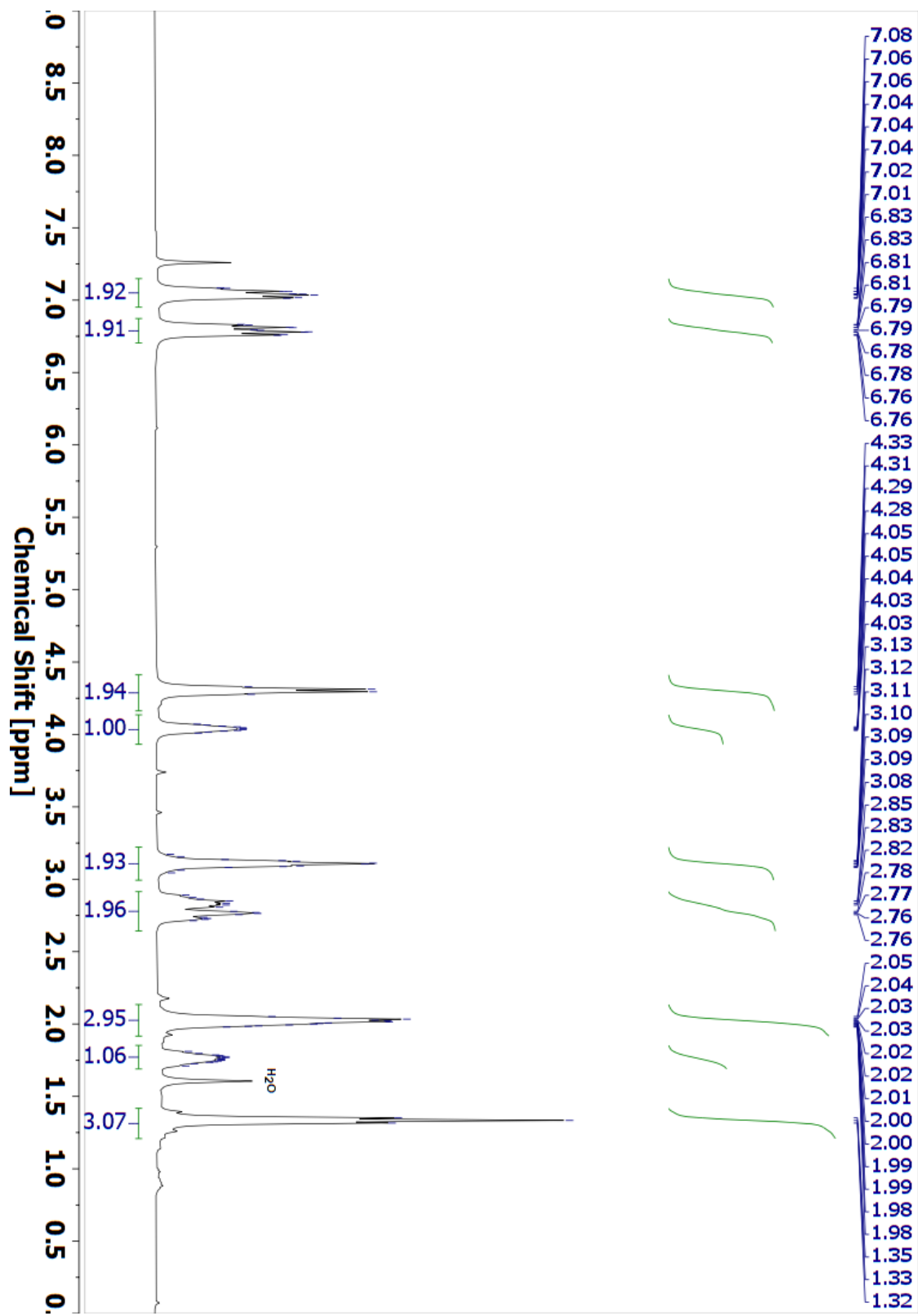


^{13}C NMR spectrum of isolated product in CDCl_3

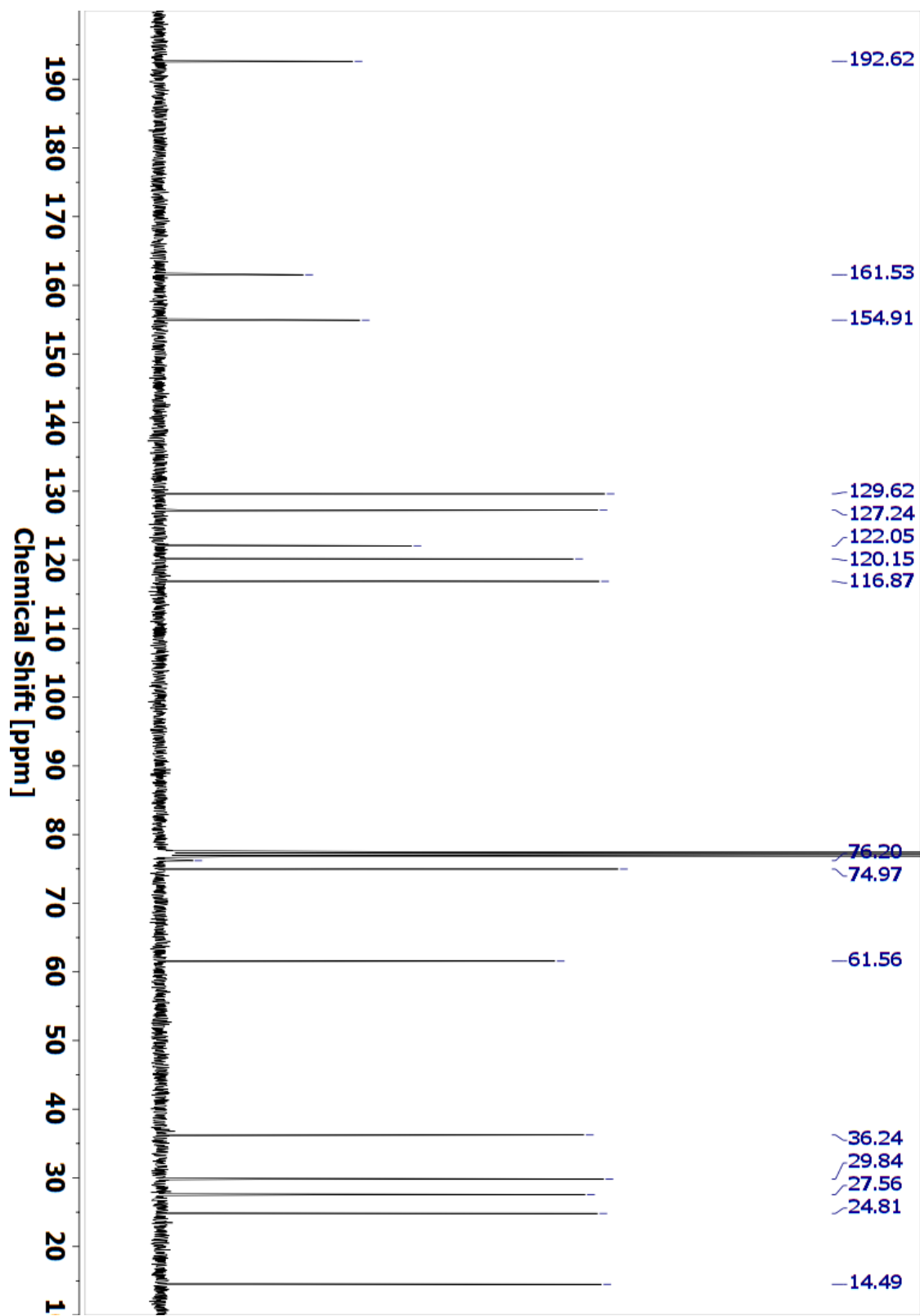
2. Ethyl 5-(chroman-2-yl)-2-diazo-3-oxopentanoate (S54): Synthesized following Procedure B:

The reaction was run on 2.00 mmol scale to give 0.46 g (77% yield) of product as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.10–6.99 (m, 2H), 6.85–6.74 (m, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.06–4.02 (m, 1H), 3.15–3.07 (m, 2H), 2.91–2.69 (m, 2H), 2.08–1.96 (m, 3H), 1.83–1.69 (m, 1H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.62, 161.53, 154.91, 129.62, 127.24, 122.05, 120.15, 116.87, 76.20, 74.97, 61.56, 36.24, 29.84, 27.56, 24.81, 14.49. HRMS (ESI $^+$) m/z Calc. 303.1339 [$\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4+\text{H}$] $^+$, Found. 303.1343 [$\text{M}+\text{H}$] $^+$.

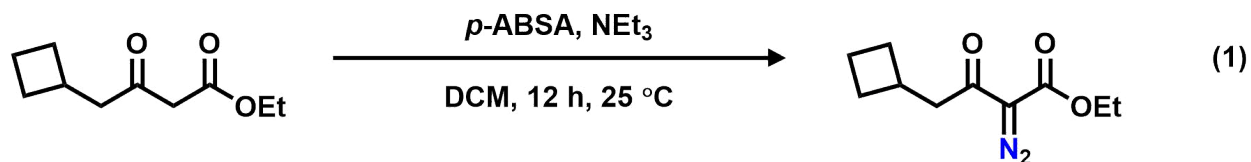


^1H NMR spectrum of isolated product in CDCl_3

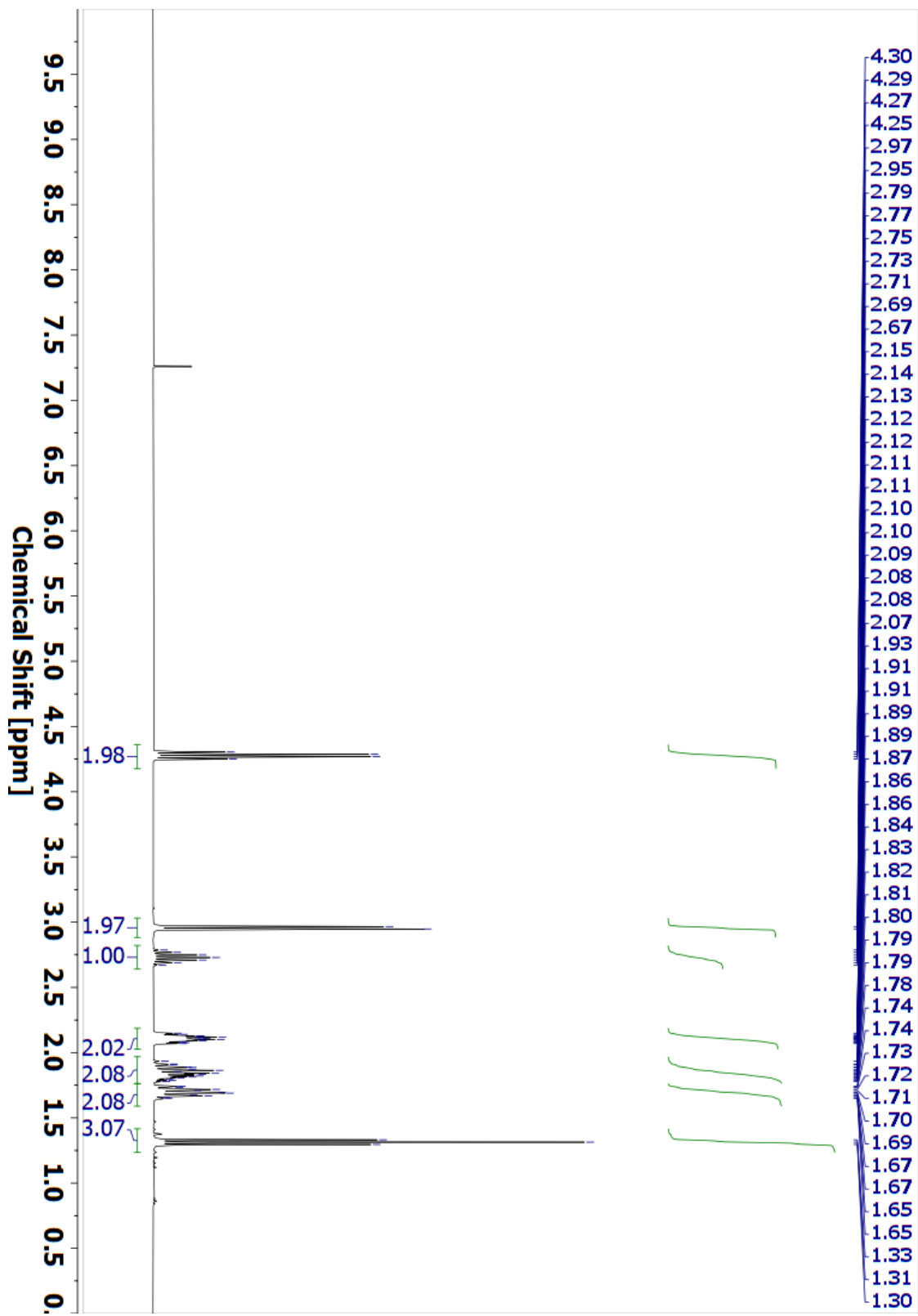


¹³C NMR spectrum of isolated product in CDCl₃

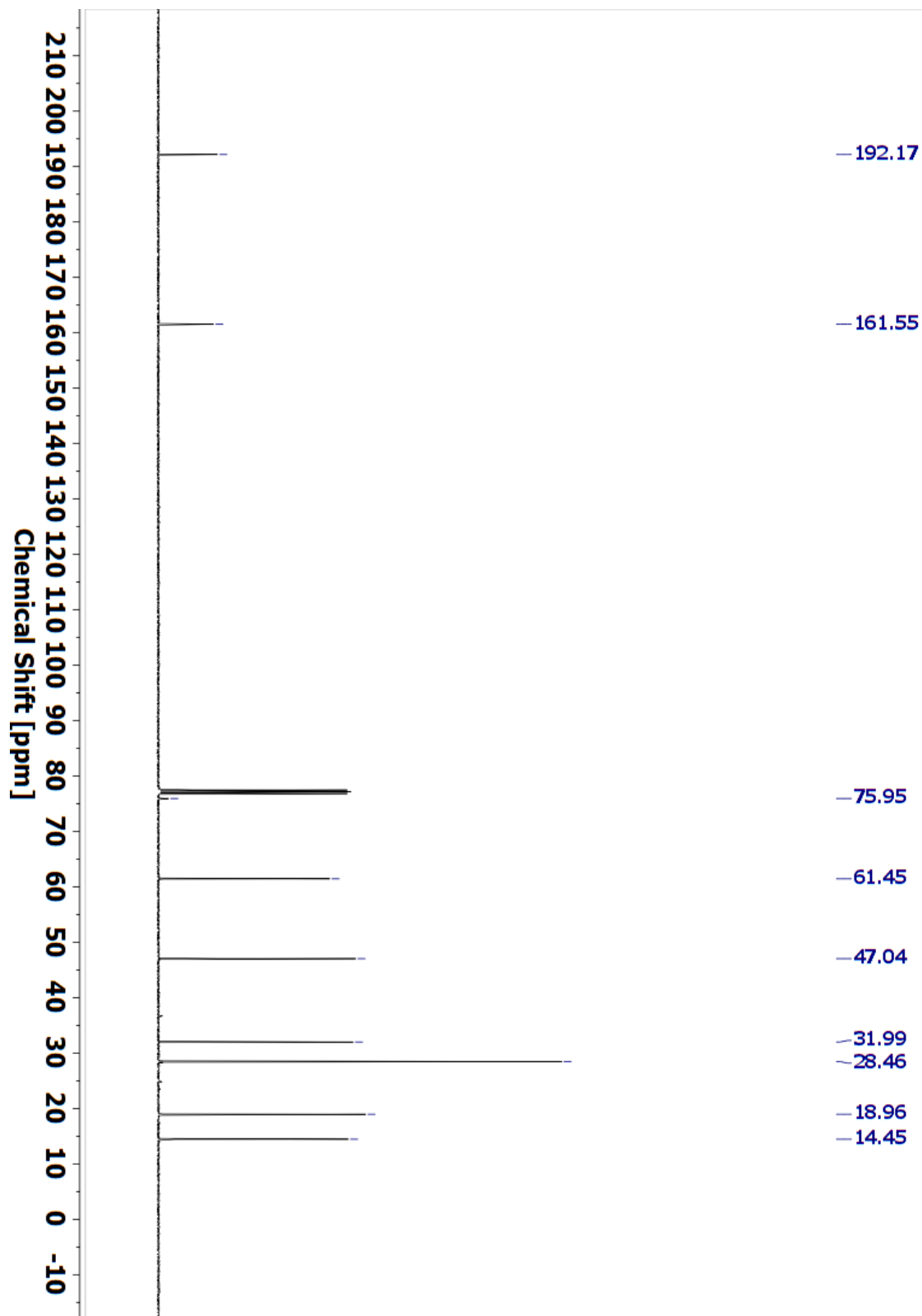
Ethyl 4-cyclobutyl-2-diazo-3-oxobutanoate (S55)



1. Ethyl 4-cyclobutyl-2-diazo-3-oxobutanoate (S55): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.71 g (67% yield) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.28 (q, *J* = 7.1 Hz, 2H), 2.96 (d, *J* = 7.3 Hz, 2H), 2.73 (hept, *J* = 7.4 Hz, 1H), 2.17–2.05 (m, 2H), 1.94–1.76 (m, 2H), 1.76–1.61 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.17, 161.55, 75.95, 61.45, 47.04, 31.99, 28.46, 18.96, 14.45. HRMS (ESI⁺) *m/z* Calc. 211.1077 [C₁₀H₁₄N₂O₃+H]⁺, Found. 211.1079 [M+H]⁺.

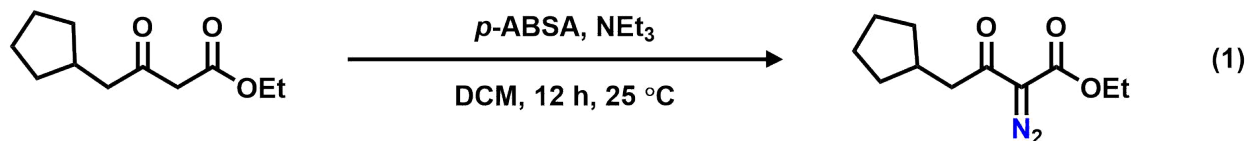


^1H NMR spectrum of isolated product in CDCl_3

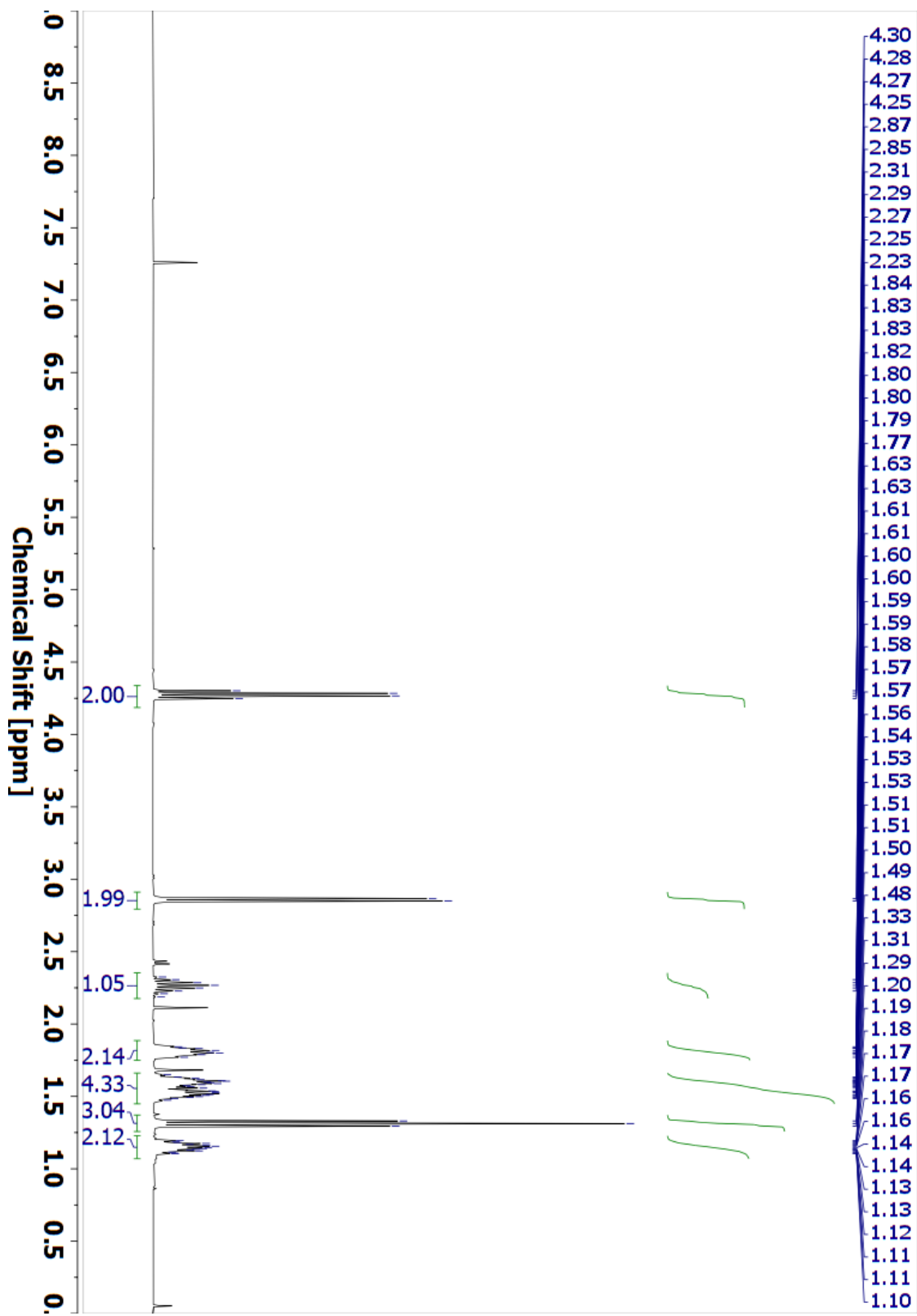


^{13}C NMR spectrum of isolated product in CDCl_3

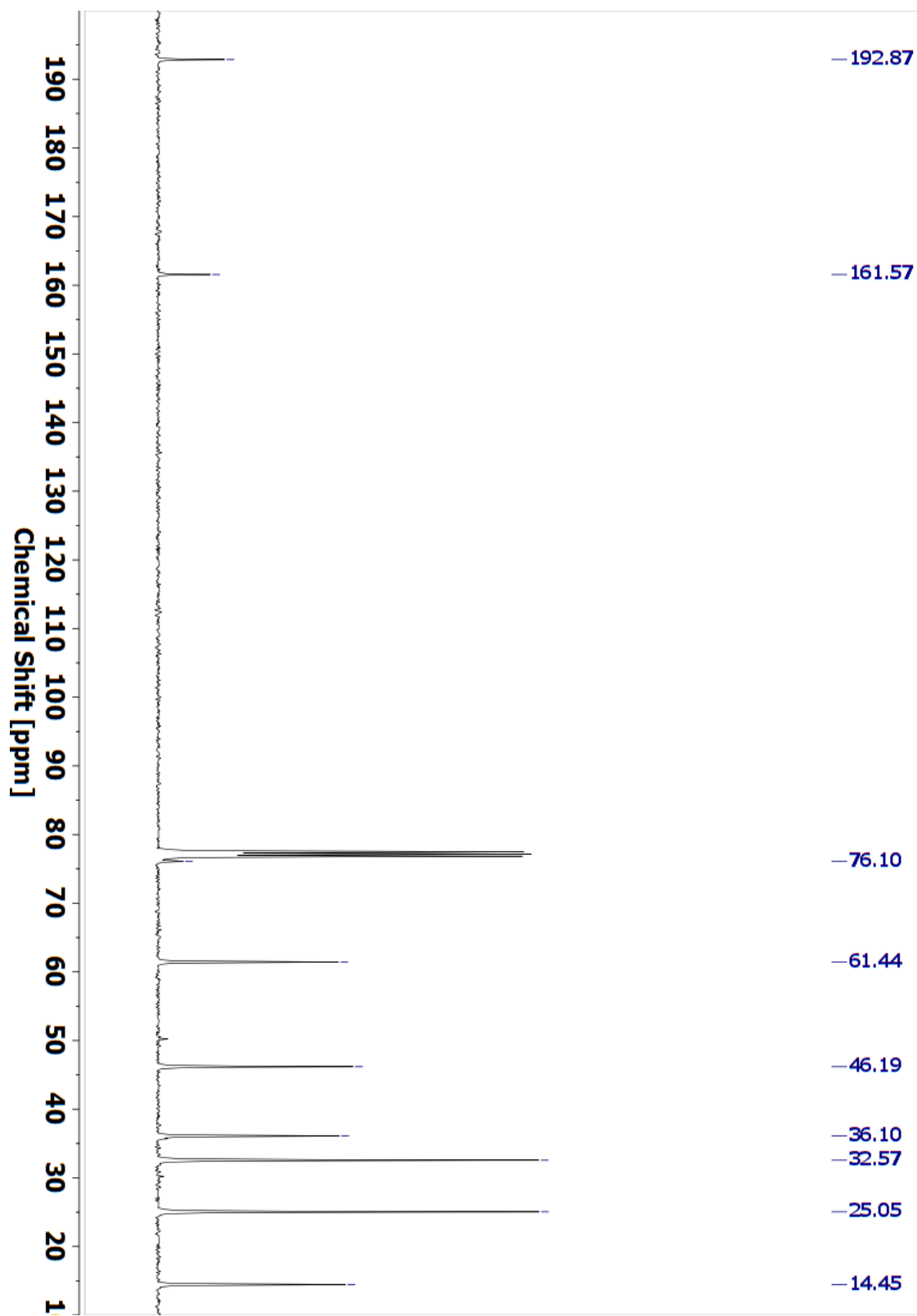
Ethyl 4-cyclopentyl-2-diazo-3-oxobutanoate (S56)



1. Ethyl 4-cyclopentyl-2-diazo-3-oxobutanoate (S56): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.55 g (49% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.27 (q, $J = 7.1$ Hz, 2H), 2.86 (d, $J = 7.1$ Hz, 2H), 2.37–2.17 (m, 1H), 1.88–1.74 (m, 2H), 1.68–1.43 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.23–1.08 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.87, 161.57, 76.10, 61.44, 46.19, 36.10, 32.57, 25.05, 14.45. HRMS (ESI^+) m/z Calc. 225.1234 [$\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}$] $^+$, Found. 225.1236 [$\text{M} + \text{H}$] $^+$.

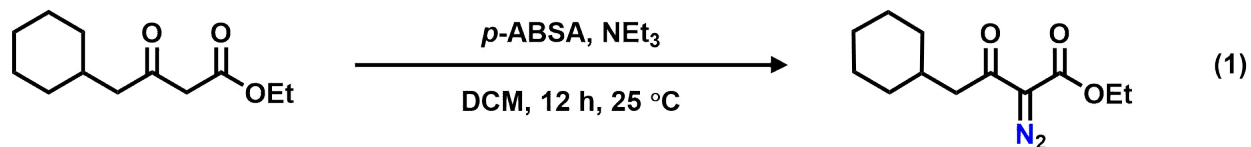


^1H NMR spectrum of isolated product in CDCl_3

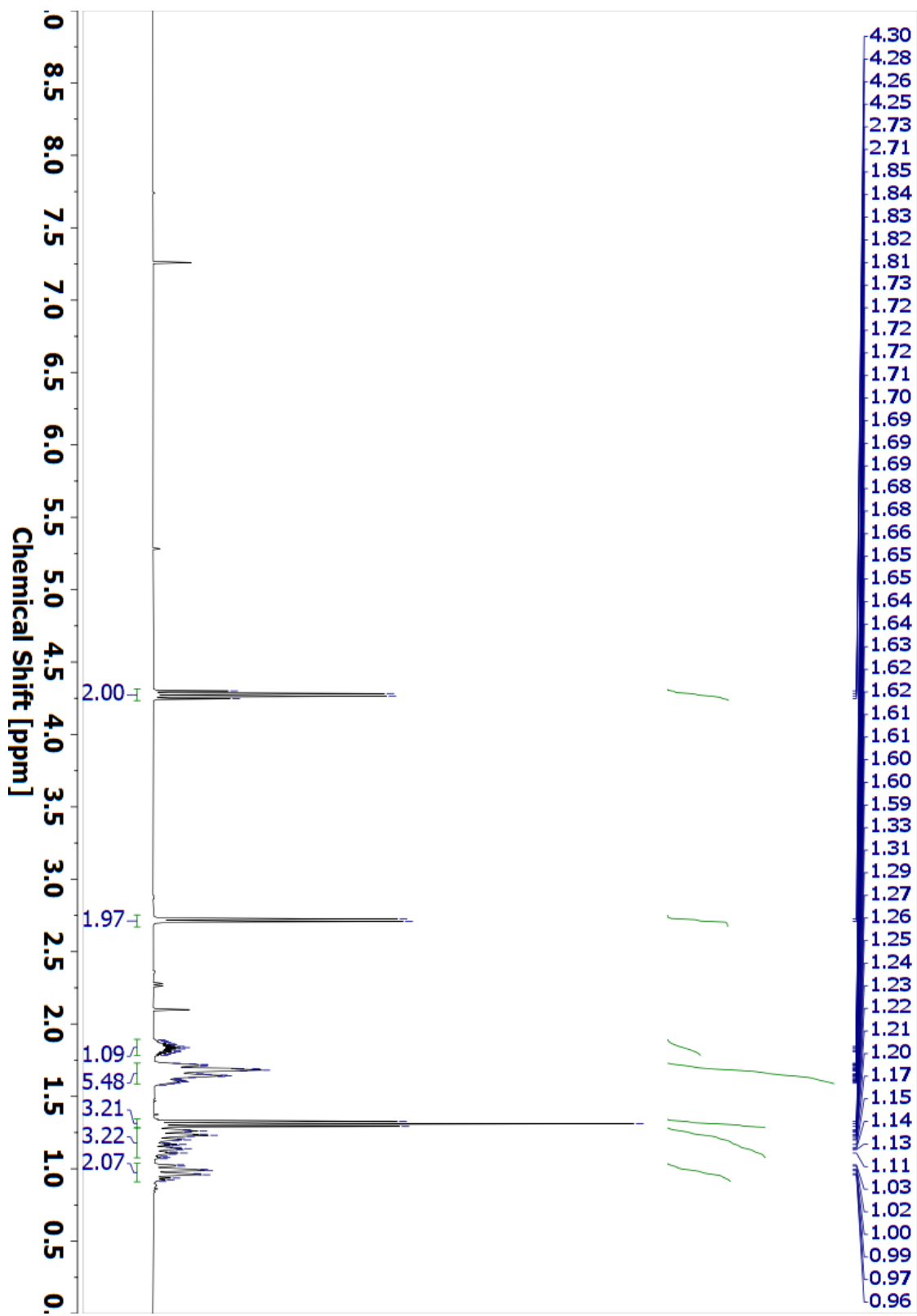


^{13}C NMR spectrum of isolated product in CDCl_3

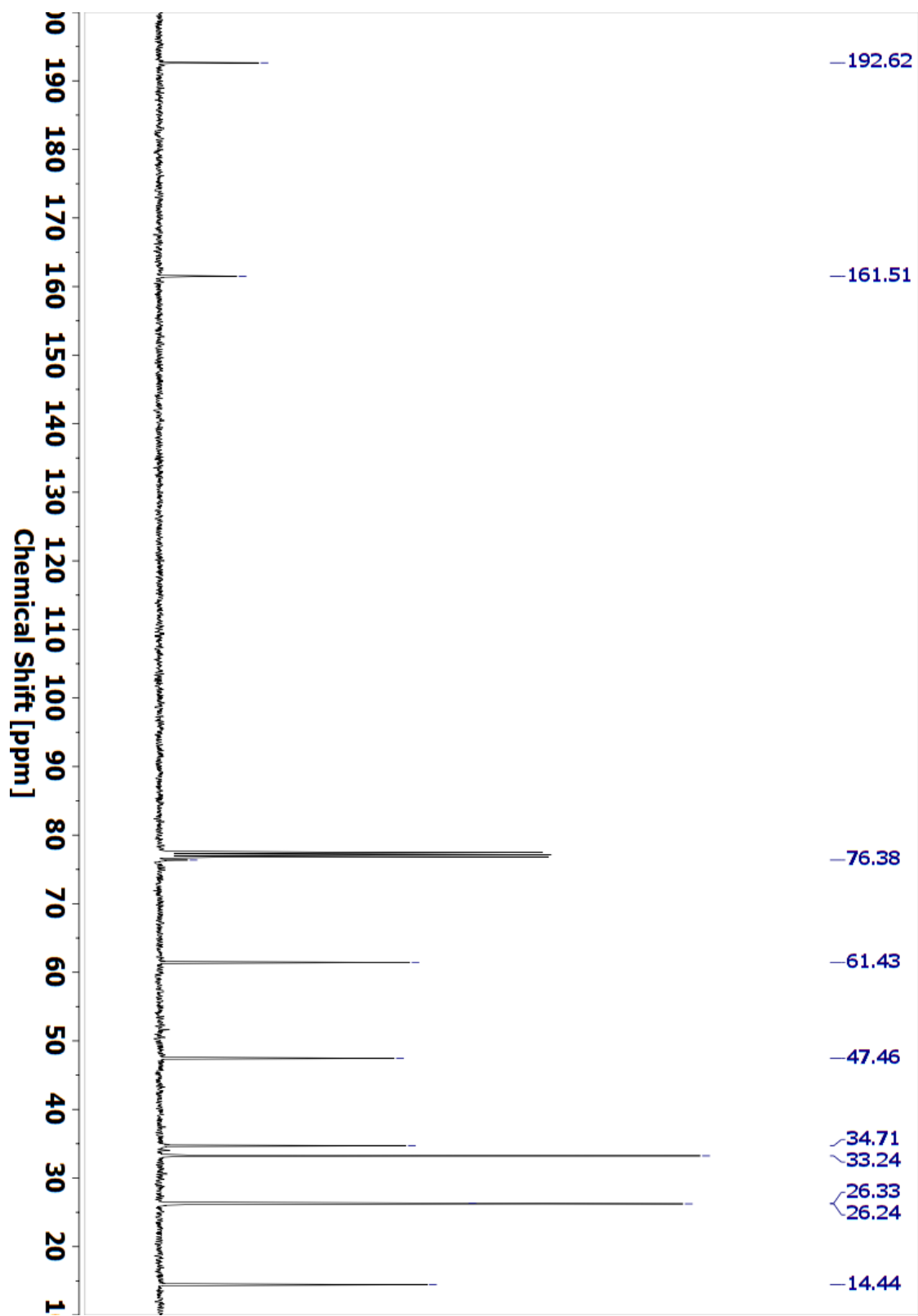
Ethyl 4-cyclohexyl-2-diazo-3-oxobutanoate (S57)



1. Ethyl 4-cyclohexyl-2-diazo-3-oxobutanoate (S57): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.66 g (55% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.27 (q, $J = 7.1$ Hz, 2H), 2.72 (d, $J = 6.9$ Hz, 2H), 1.91–1.76 (m, 1H), 1.74–1.56 (m, 5H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.27–1.05 (m, 3H), 1.05–0.89 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.62, 161.51, 76.38, 61.43, 47.46, 34.71, 33.24, 26.33, 26.24, 14.44. HRMS (ESI $^+$) m/z Calc. 239.1390 [$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3 + \text{H}$] $^+$, Found. 239.1393 [$\text{M} + \text{H}$] $^+$.

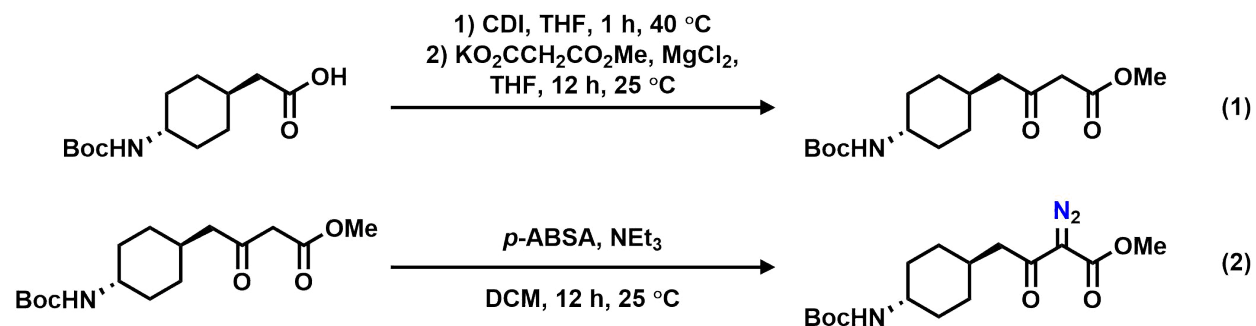


^1H NMR spectrum of isolated product in CDCl_3



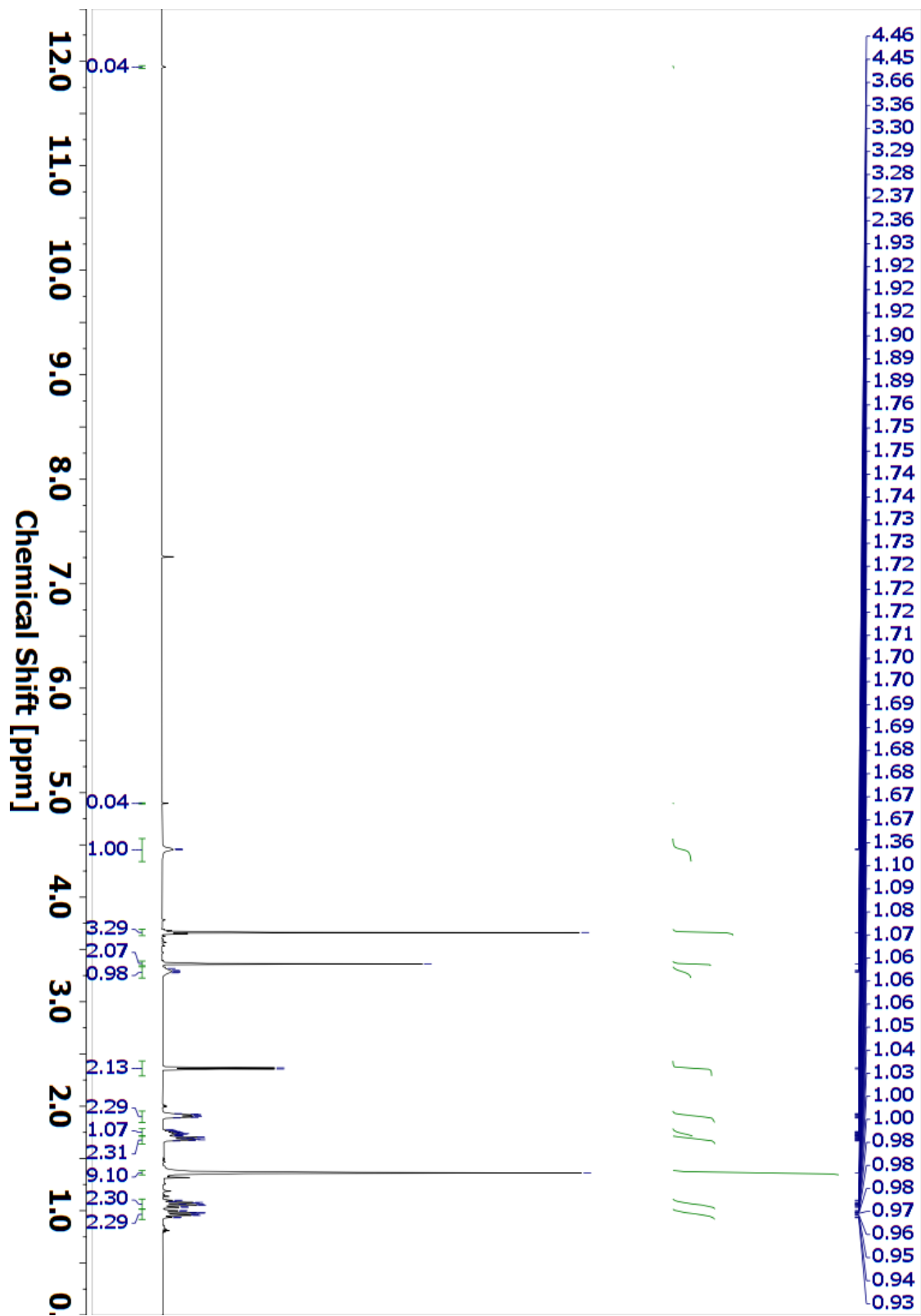
¹³C NMR spectrum of isolated product in CDCl₃

Methyl trans-4-(4-((tert-butoxycarbonyl)amino)cyclohexyl)-2-diazo-3-oxobutanoate (S59)

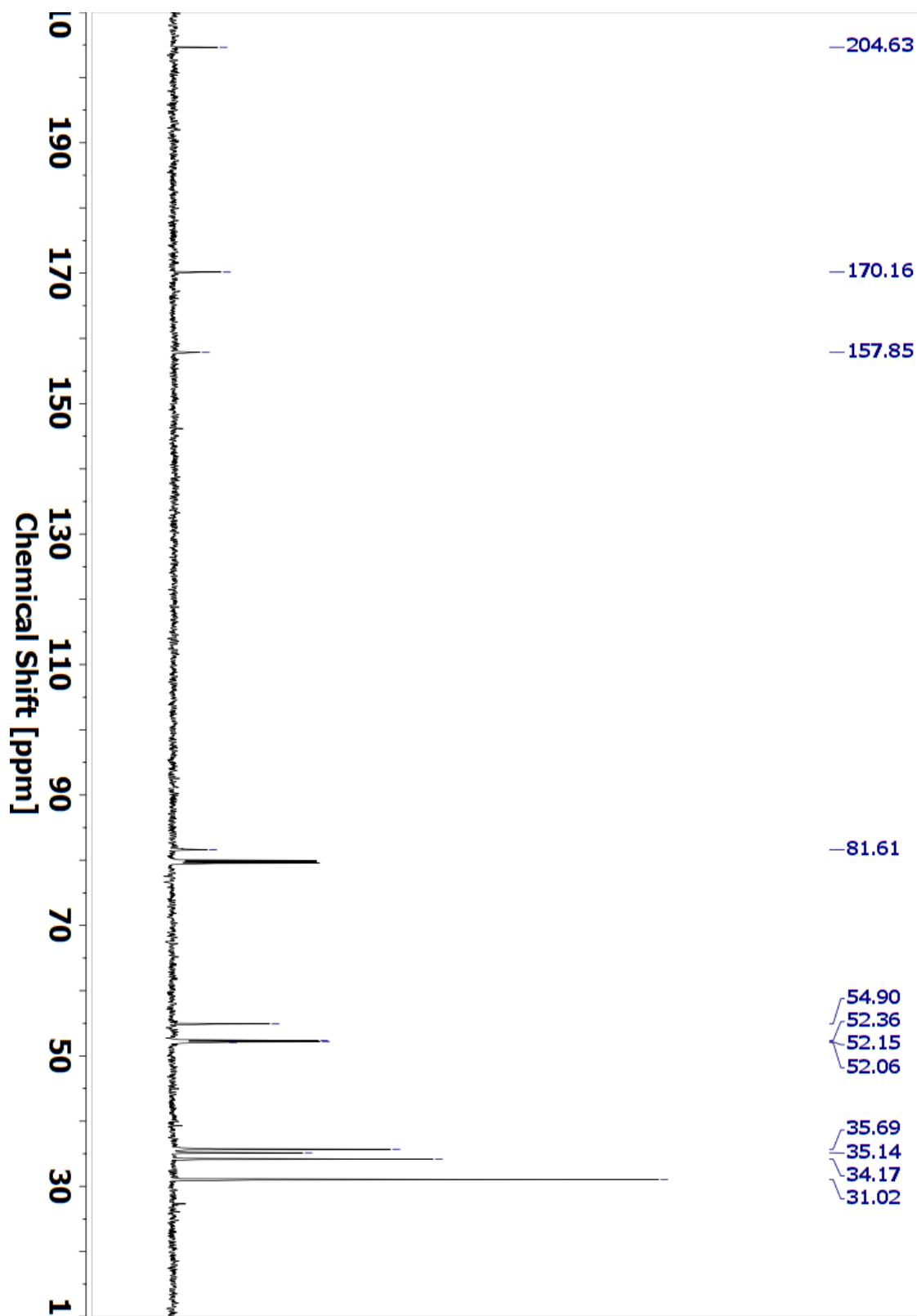


1. Methyl *trans*-4-(4-((tert-butoxycarbonyl)amino)cyclohexyl)-3-oxobutanoate (S58):

Synthesized following Procedure A: The reaction was run on 5.00 mmol scale to give 0.75 g (48% yield, 3.8% tautomerization) of product as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 4.46 (d, $J = 5.3$ Hz, 1H), 3.66 (s, 3H), 3.36 (s, 2H), 3.33–3.23 (m, 1H), 2.36 (d, $J = 6.6$ Hz, 2H), 1.94–1.88 (m, 2H), 1.78–1.71 (m, 1H), 1.71–1.66 (m, 2H), 1.36 (s, 9H), 1.11–1.02 (m, 2H), 1.01–0.92 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 204.63, 170.16, 157.85, 81.61, 54.90, 52.36, 52.15, 52.06, 35.69, 35.14, 34.17, 31.02. HRMS (ESI $^+$) m/z Calc. 336.1781 [$\text{C}_{16}\text{H}_{27}\text{NO}_5 + \text{H}$] $^+$, Found. 336.1782 [$\text{M} + \text{H}$] $^+$.



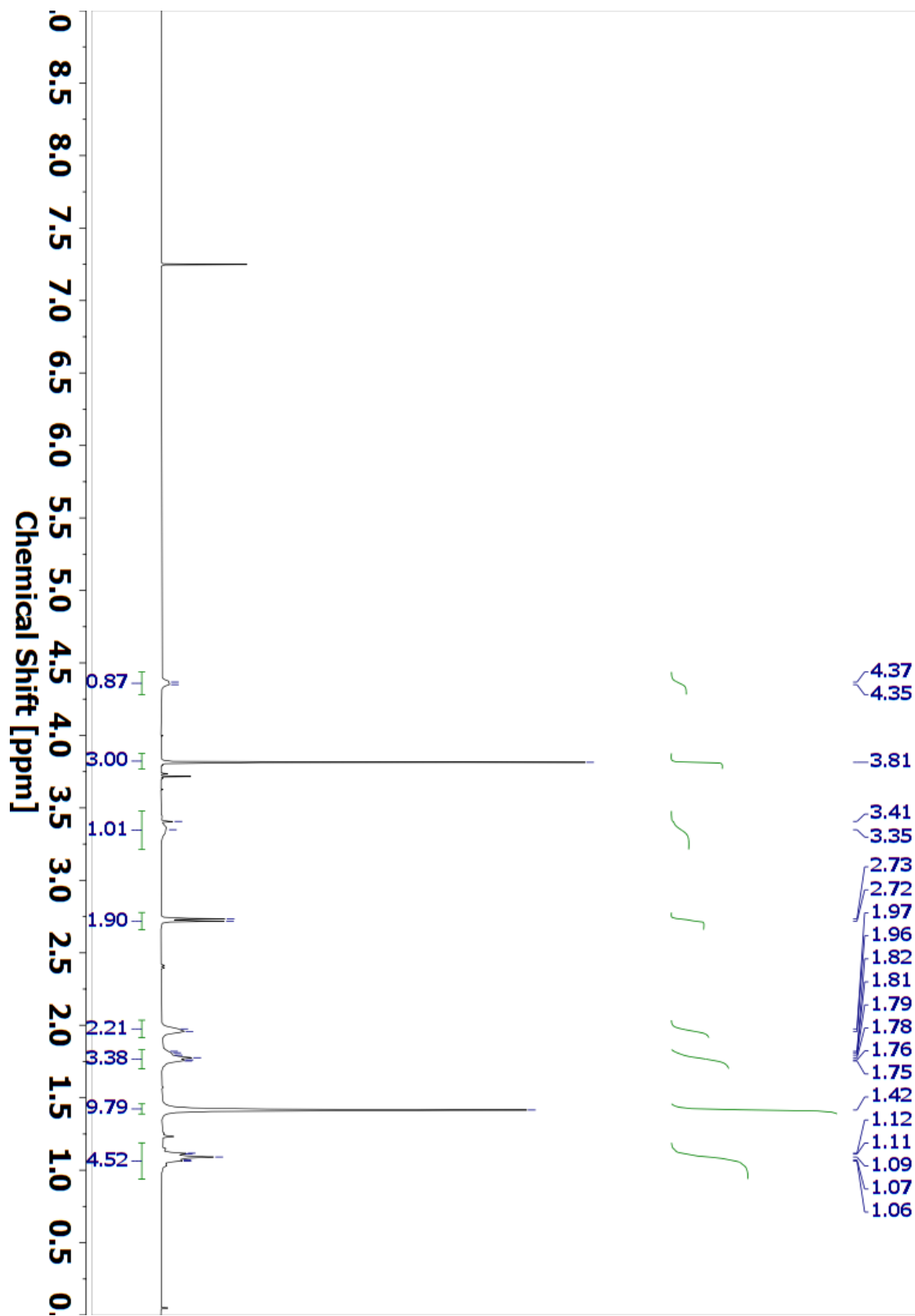
^1H NMR spectrum of isolated product in CDCl_3



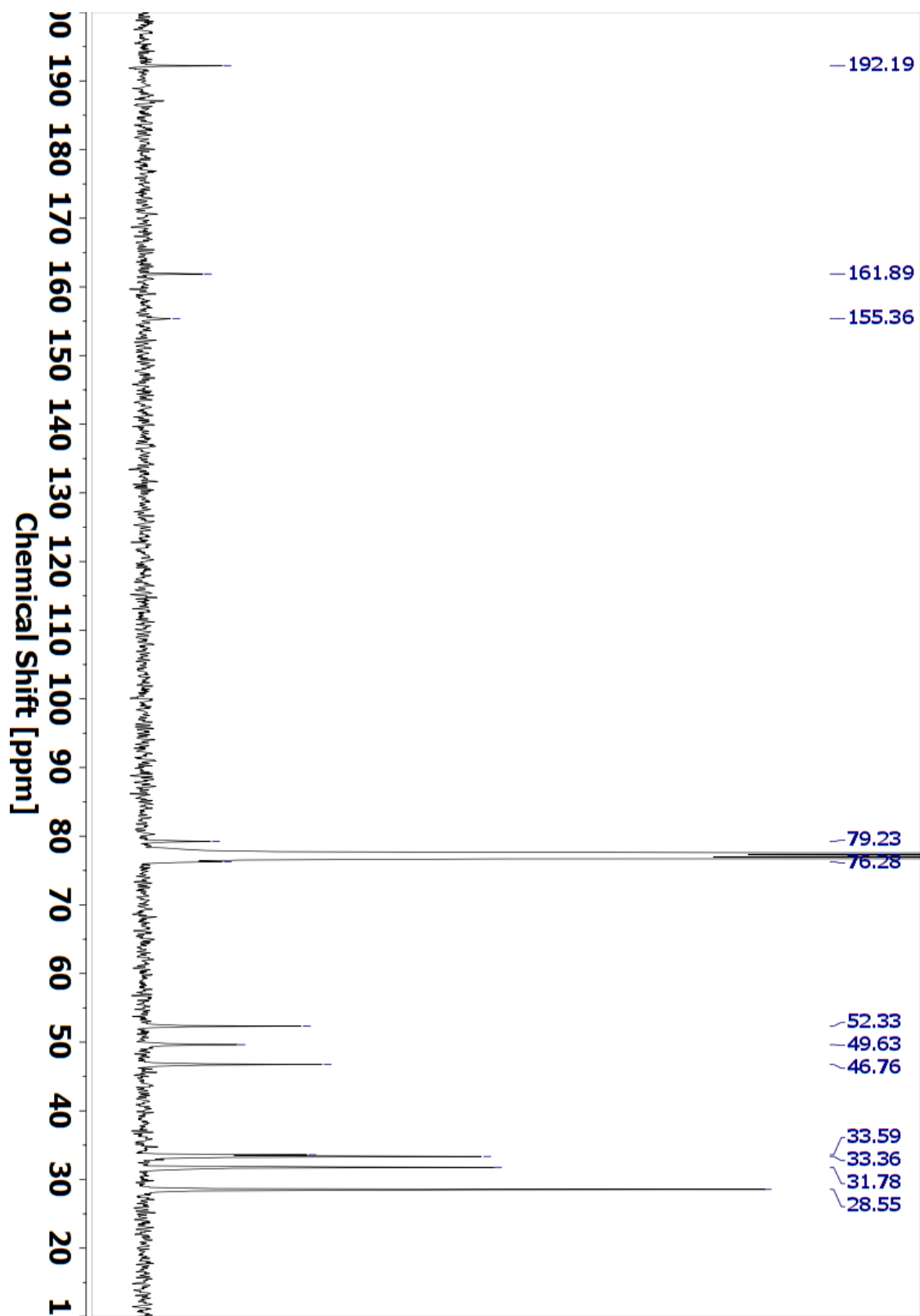
¹³C NMR spectrum of isolated product in CDCl₃

2. Methyl *trans*-4-(4-((*tert*-butoxycarbonyl)amino)cyclohexyl)-2-diazo-3-oxobutanoate (S59):

Synthesized following Procedure B: The reaction was run on 2.00 mmol scale to give 0.45 g (66% yield) of product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 4.36 (d, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 3.38 (br. s, 1H), 2.73 (d, *J* = 6.5 Hz, 2H), 2.06–1.89 (m, 2H), 1.85–1.65 (m, 3H), 1.42 (s, 9H), 1.16–0.95 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 192.19, 161.89, 155.36, 79.23, 76.28, 52.33, 49.63, 46.76, 33.59, 33.36, 31.78, 28.55. HRMS (ESI⁺) *m/z* Calc. 340.1867 [C₁₆H₂₅N₃O₅+H]⁺, Found. 340.1870 [M+H]⁺.

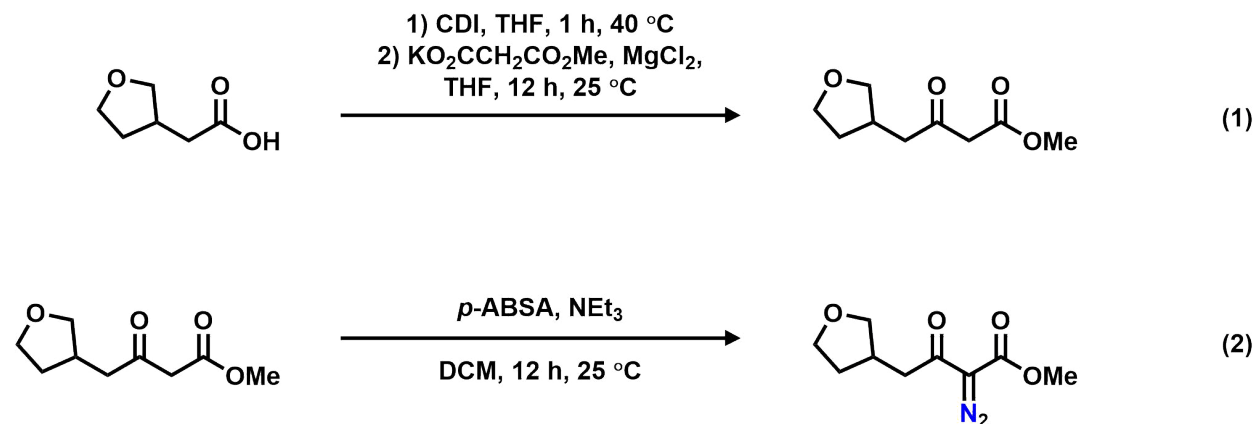


^1H NMR spectrum of isolated product in CDCl_3



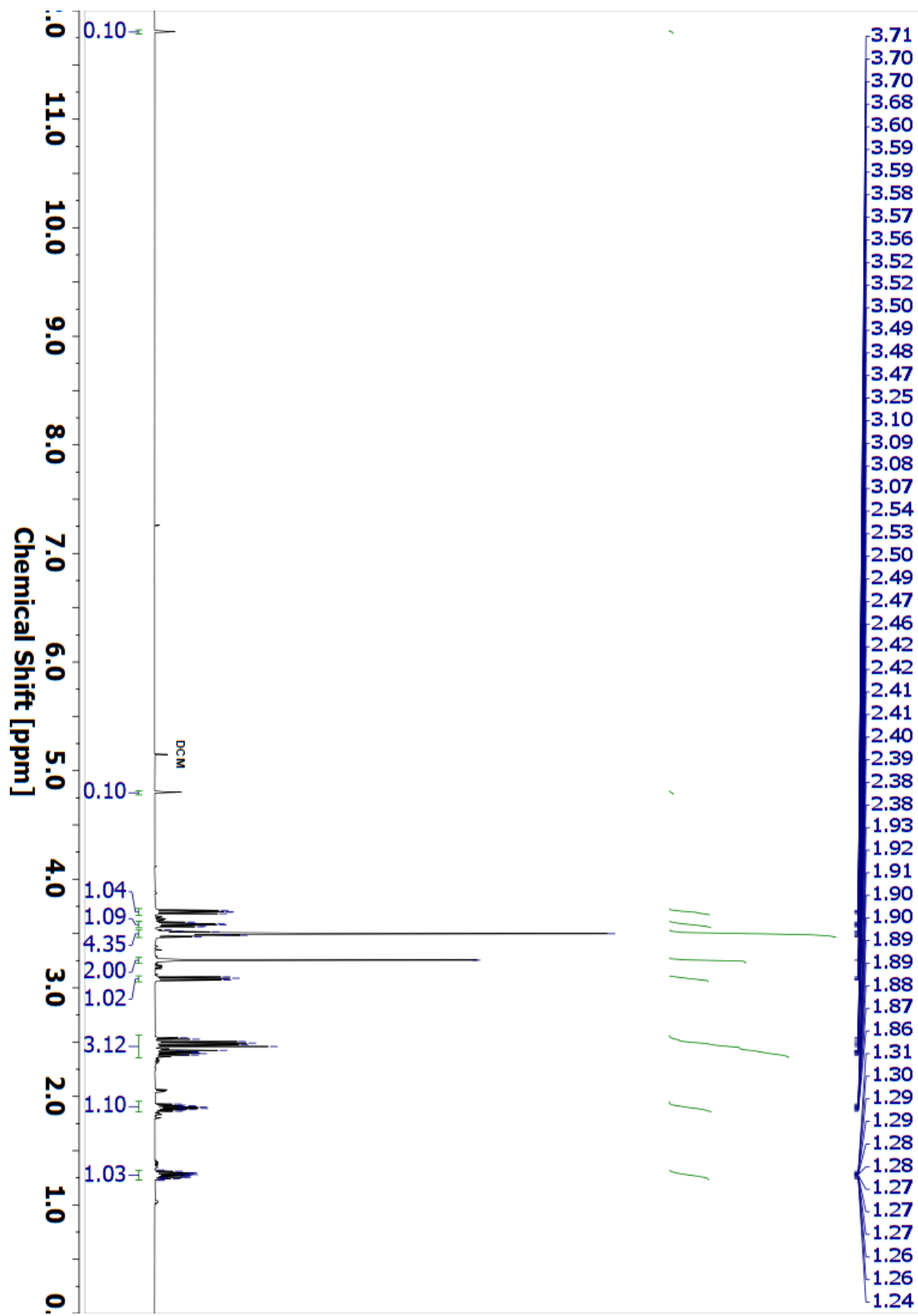
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl 2-diazo-3-oxo-4-(tetrahydrofuran-3-yl)butanoate (S61)

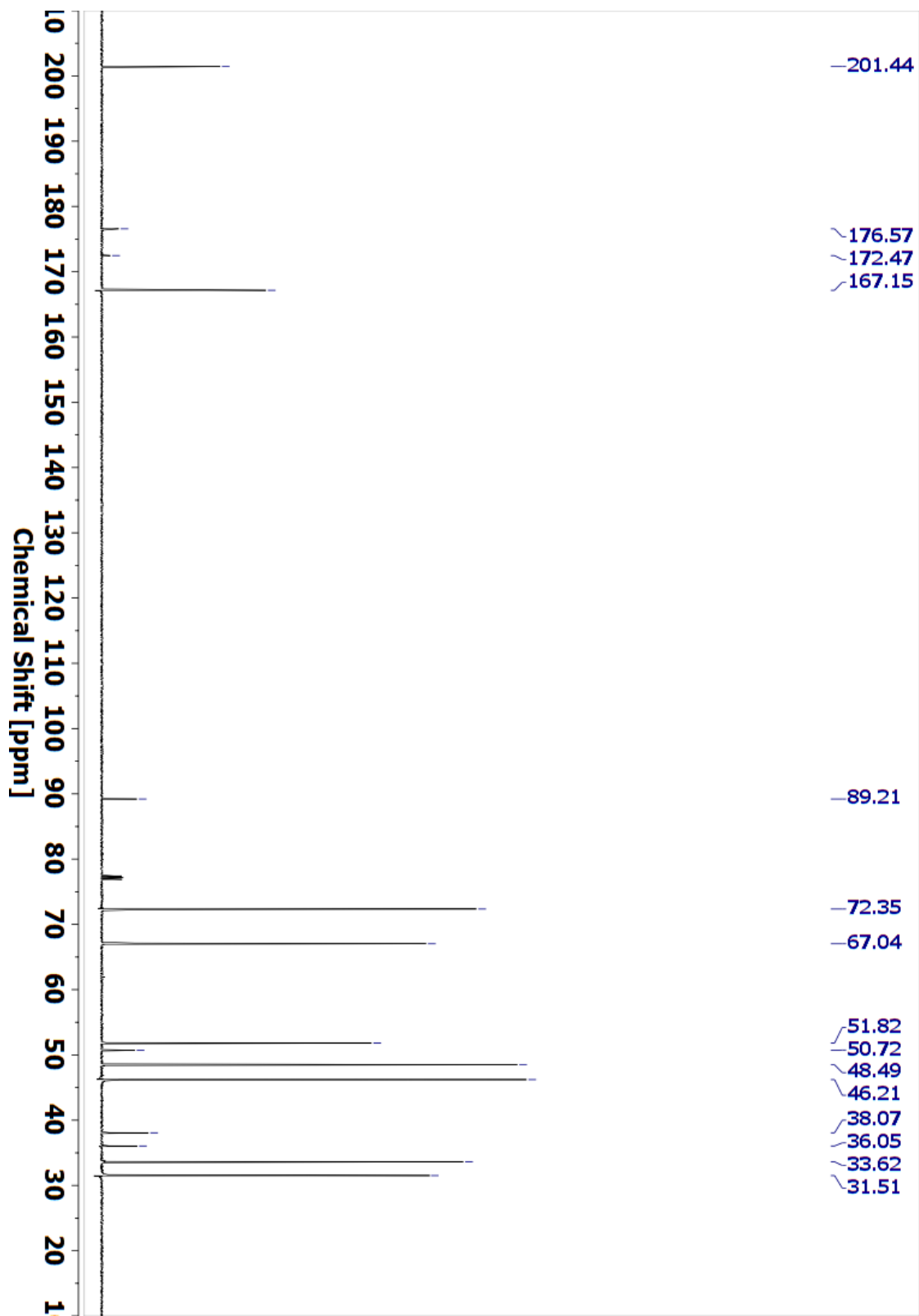


1. Methyl 3-oxo-4-(tetrahydrofuran-3-yl)butanoate (S60): Synthesized following Procedure A:

The reaction was run on 10.00 mmol scale to give 0.80 g (43% yield, 9.1% tautomerization) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 3.70 (dd, $J = 8.6, 6.5$ Hz, 1H), 3.61–3.55 (m, 1H), 3.54–3.46 (m, 4H), 3.25 (s, 2H), 3.09 (dd, $J = 8.6, 6.5$ Hz, 1H), 2.57–2.35 (m, 3H), 1.96–1.84 (m, 1H), 1.33–1.22 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.44, 167.15, 72.35, 67.04, 51.82, 48.49, 46.21, 33.62, 31.51. HRMS (ESI $^+$) m/z Calc. 187.0965 [$\text{C}_9\text{H}_{14}\text{O}_4 + \text{H}$] $^+$, Found. 187.0966 [$\text{M} + \text{H}$] $^+$.

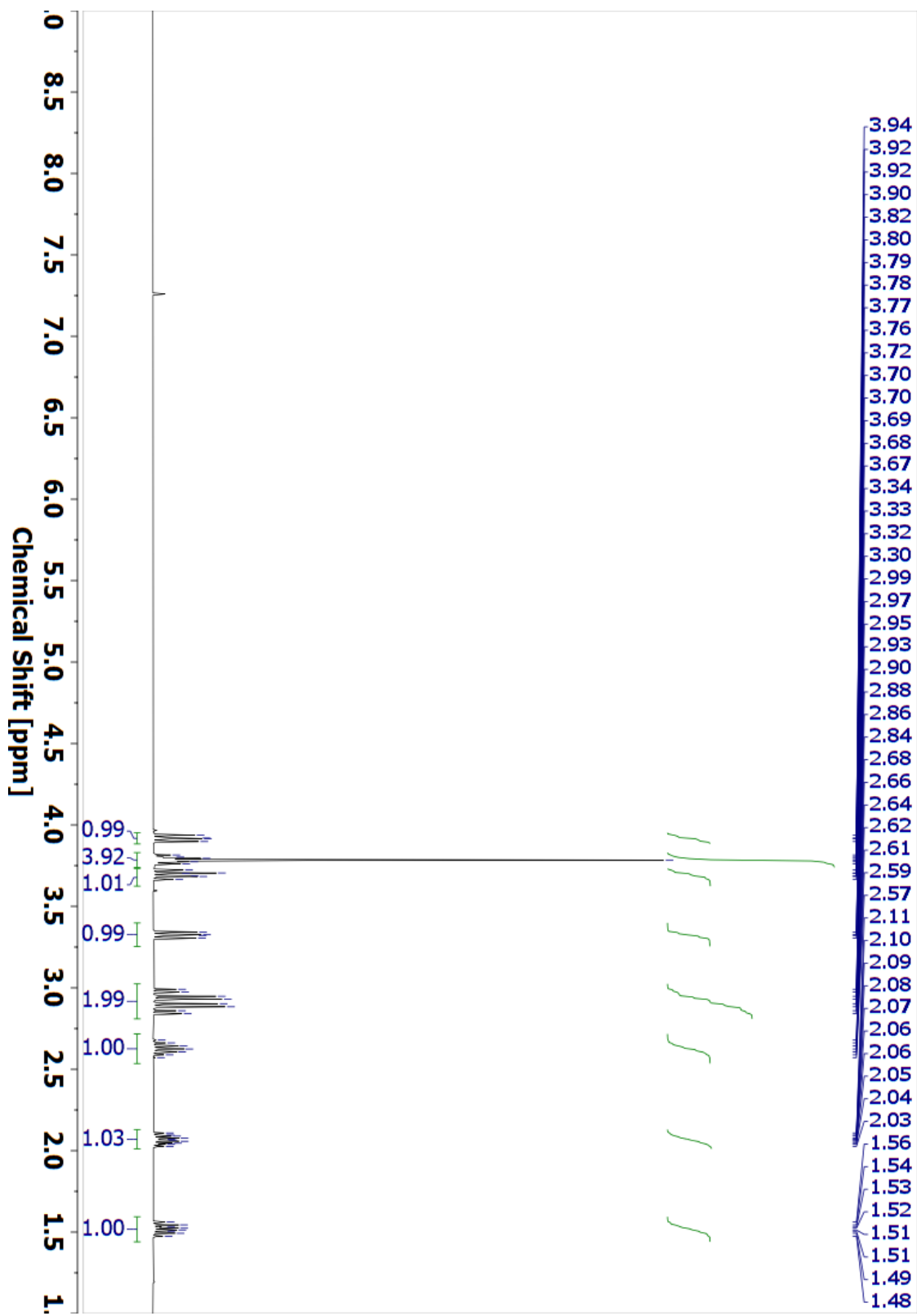


^1H NMR spectrum of isolated product in CDCl_3

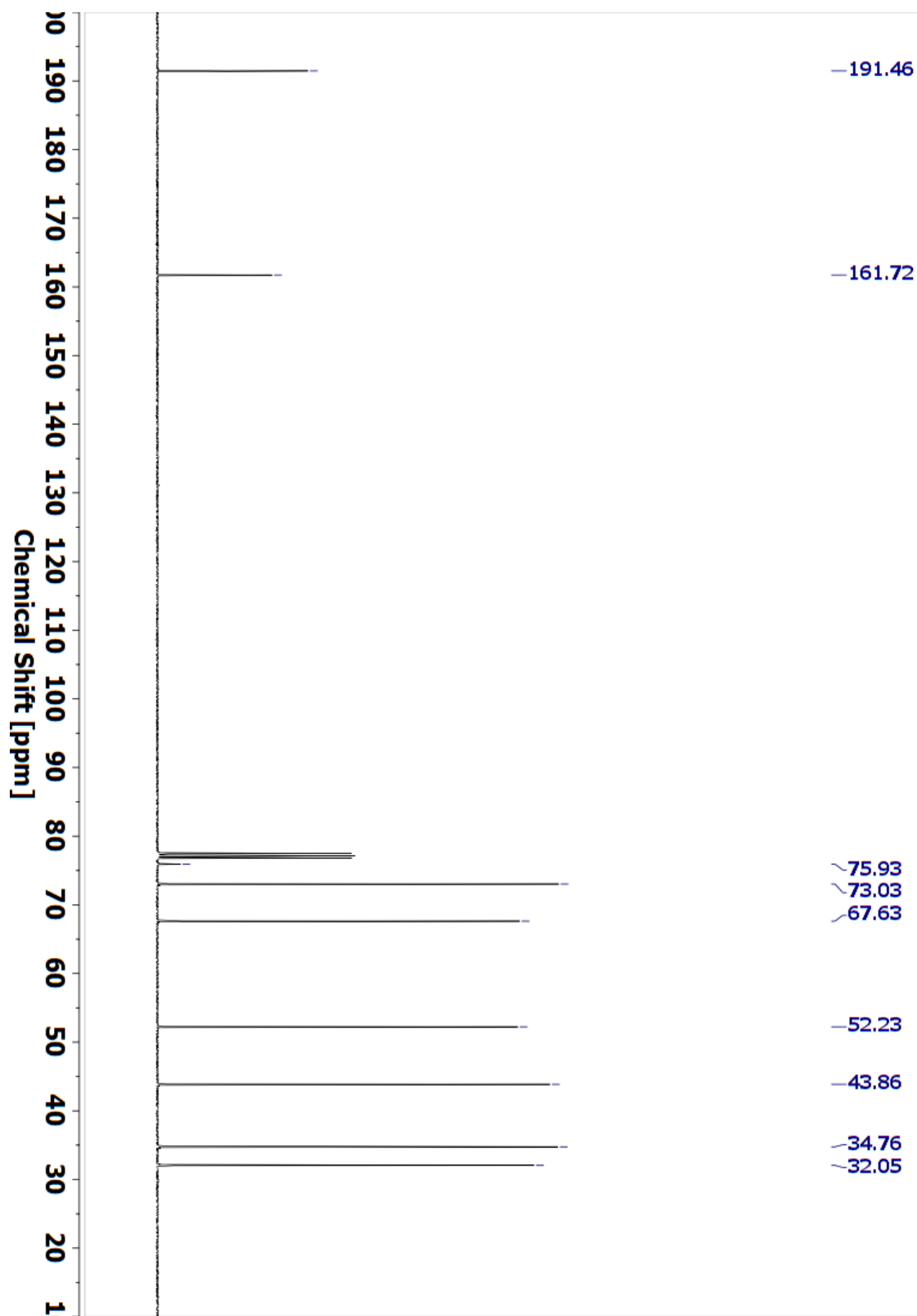


^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 2-diazo-3-oxo-4-(tetrahydrofuran-3-yl)butanoate (S61): Synthesized following Procedure B: The reaction was run on 4.00 mmol scale to give 0.45 g (71% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 3.92 (dd, $J = 8.6, 7.1$ Hz, 1H), 3.84–3.74 (m, 4H), 3.74–3.64 (m, 1H), 3.32 (dd, $J = 8.6, 6.6$ Hz, 1H), 3.01–2.81 (m, 2H), 2.70–2.55 (m, 1H), 2.13–2.00 (m, 1H), 1.58–1.45 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.46, 161.72, 75.93, 73.03, 67.63, 52.23, 43.86, 34.76, 32.05. HRMS (ESI $^+$) m/z Calc. 213.0870 [$\text{C}_9\text{H}_{12}\text{N}_2\text{O}_4+\text{H}$] $^+$, Found. 213.0871 [$\text{M}+\text{H}$] $^+$.

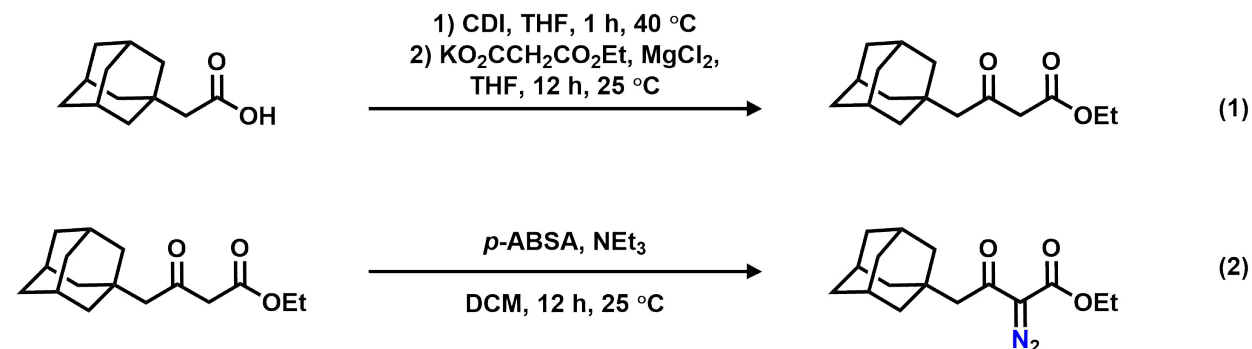


^1H NMR spectrum of isolated product in CDCl_3

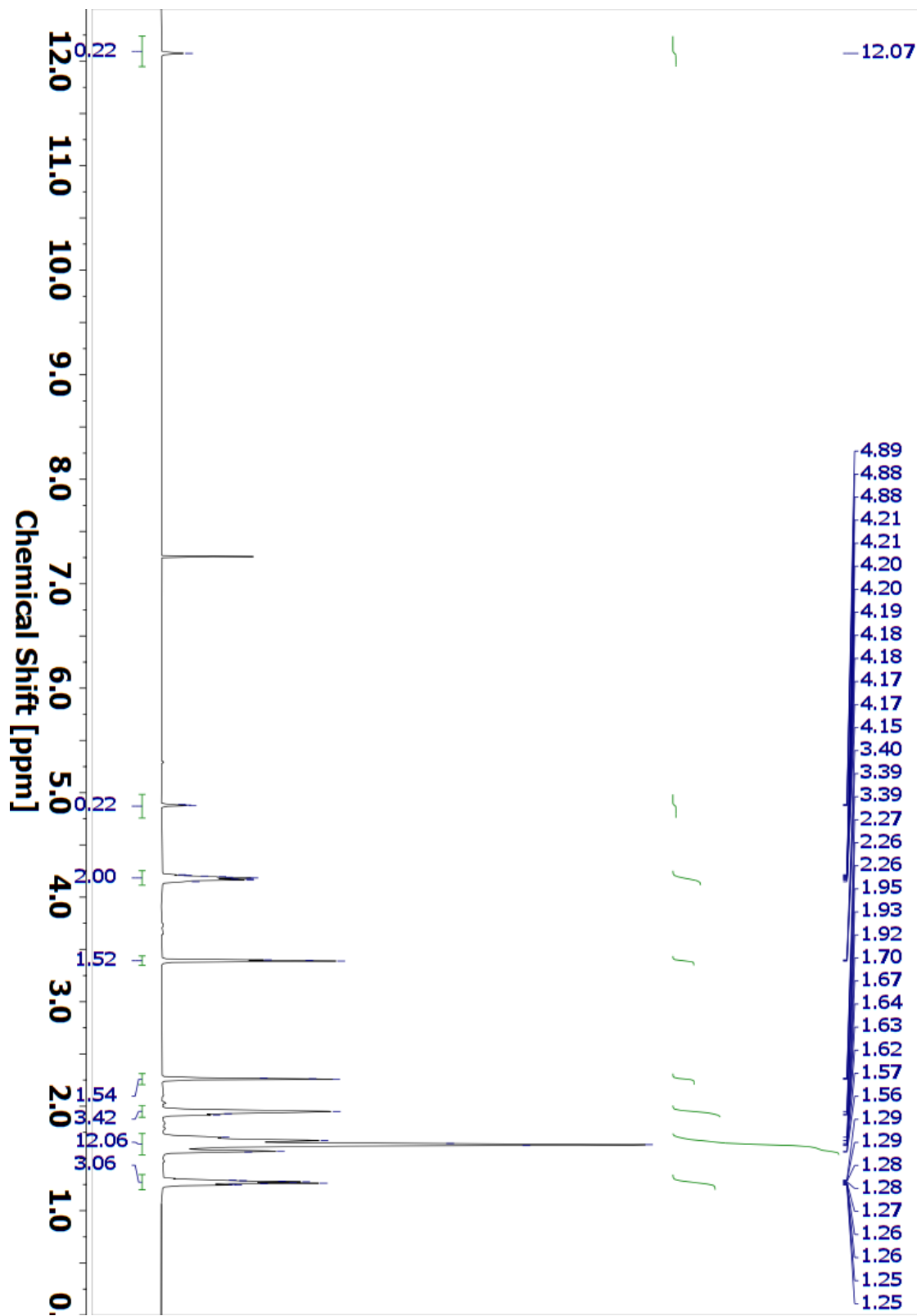


^{13}C NMR spectrum of isolated product in CDCl_3

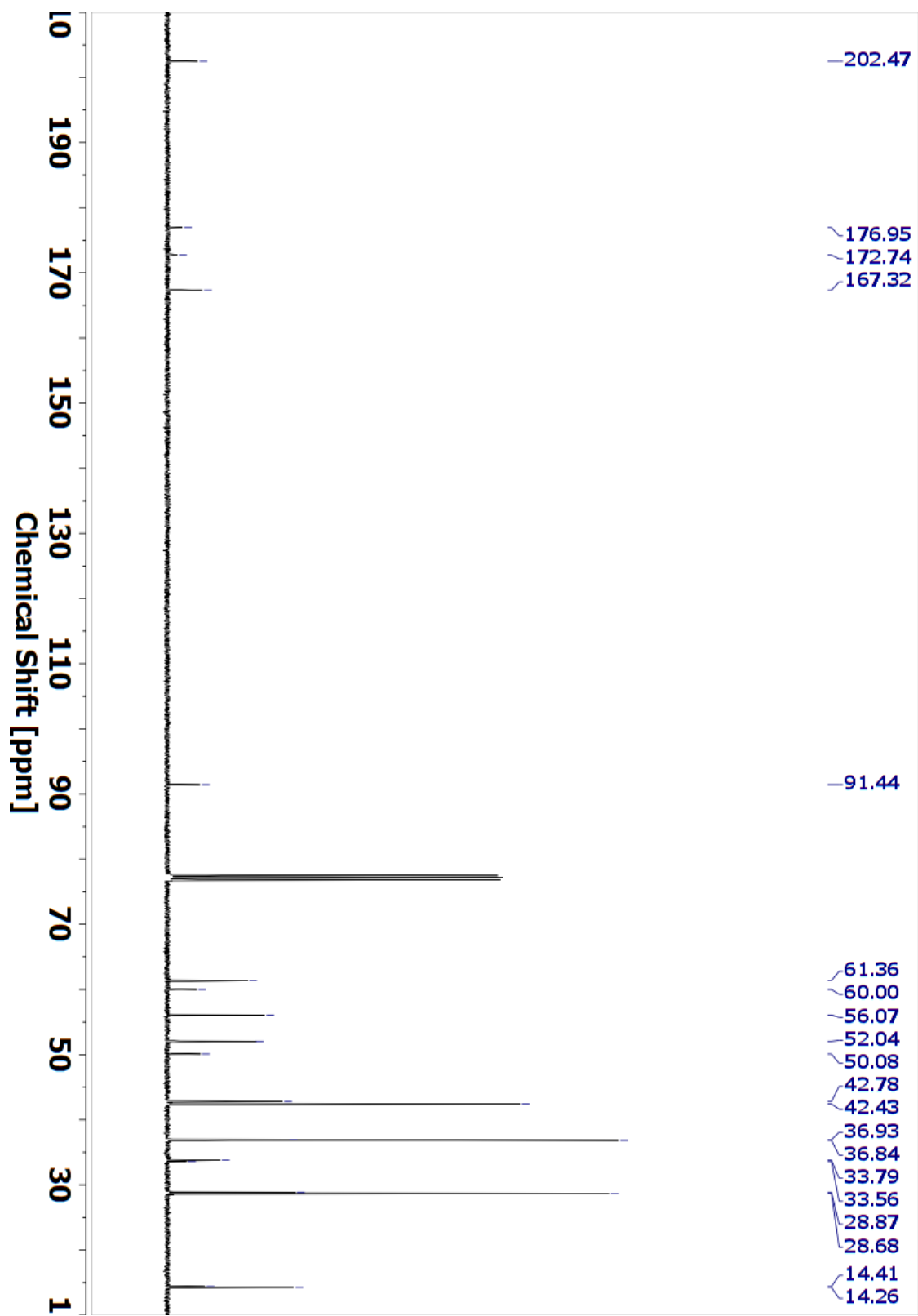
Methyl 4-(adamantan-1-yl)-2-diazo-3-oxobutanoate (S63)



1. Methyl 4-(adamantan-1-yl)-3-oxobutanoate (S62): Synthesized following Procedure A: The reaction was run on 10.00 mmol scale to give 1.90 g (72% yield, 22% tautomerization) of product as a white solid. Keto form: ¹H NMR (400 MHz, CDCl₃) δ 4.25–4.08 (m, 2H), 3.42–3.37 (m, 2H), 2.29–2.23 (m, 2H), 2.00–1.87 (m, 3H), 1.75–1.54 (m, 12H), 1.32–1.18 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 202.47, 167.32, 61.36, 56.07, 52.04, 42.43, 36.84, 33.79, 28.68, 14.26. Enol form: ¹H NMR (400 MHz, CDCl₃) δ 12.07 (s, 1H), 4.91–4.84 (m, 1H), 4.25–4.08 (m, 2H), 2.29–2.23 (m, 2H), 2.00–1.87 (m, 3H), 1.75–1.54 (m, 12H), 1.32–1.18 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.95, 172.74, 91.44, 60.00, 50.08, 42.78, 36.93, 33.56, 28.87, 14.41. HRMS (ESI⁺) *m/z* Calc. 265.1798 [C₁₆H₂₄O₃+H]⁺, Found. 265.1801 [M+H]⁺.



^1H NMR spectrum of isolated product in CDCl_3

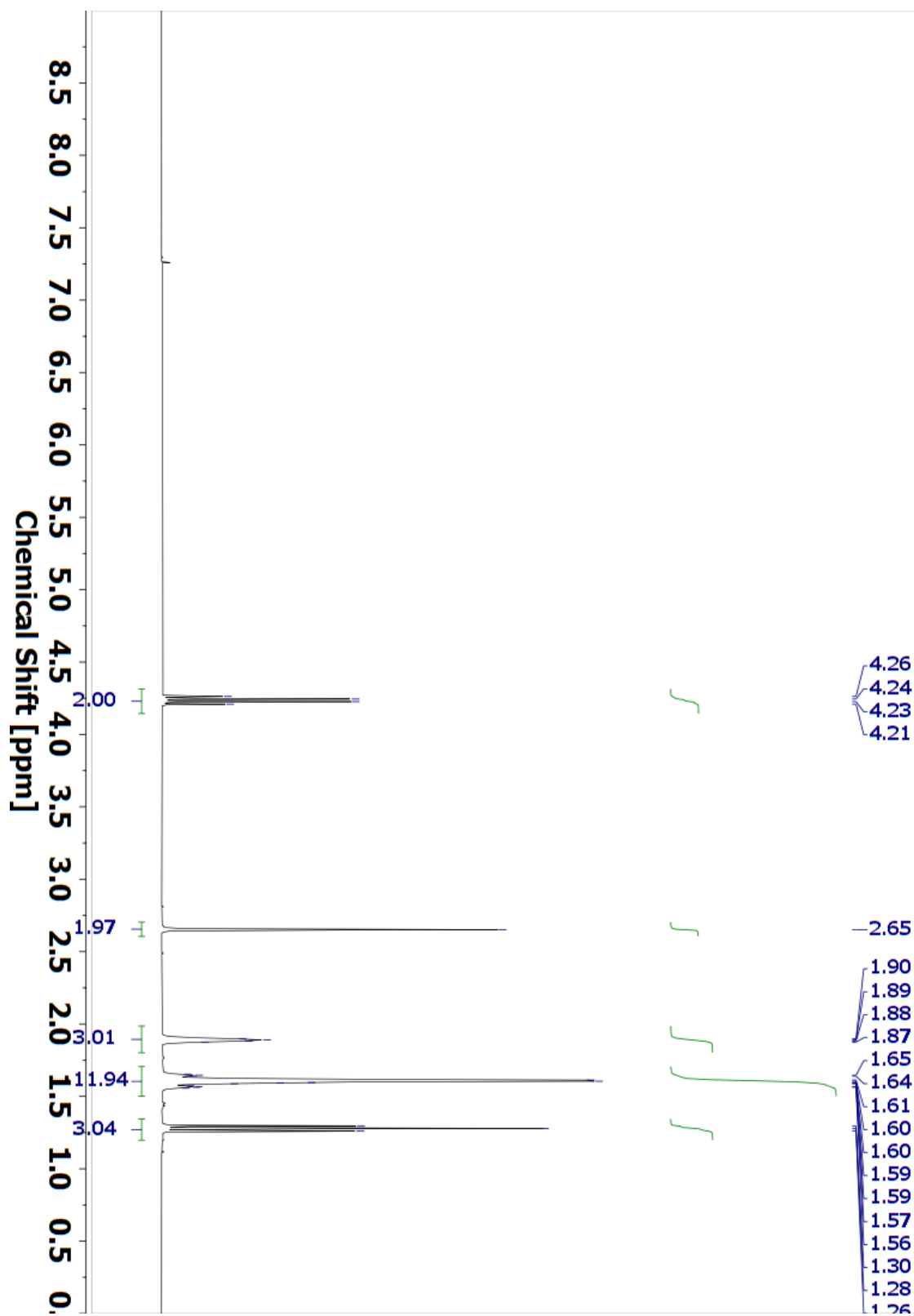


¹³C NMR spectrum of isolated product in CDCl₃

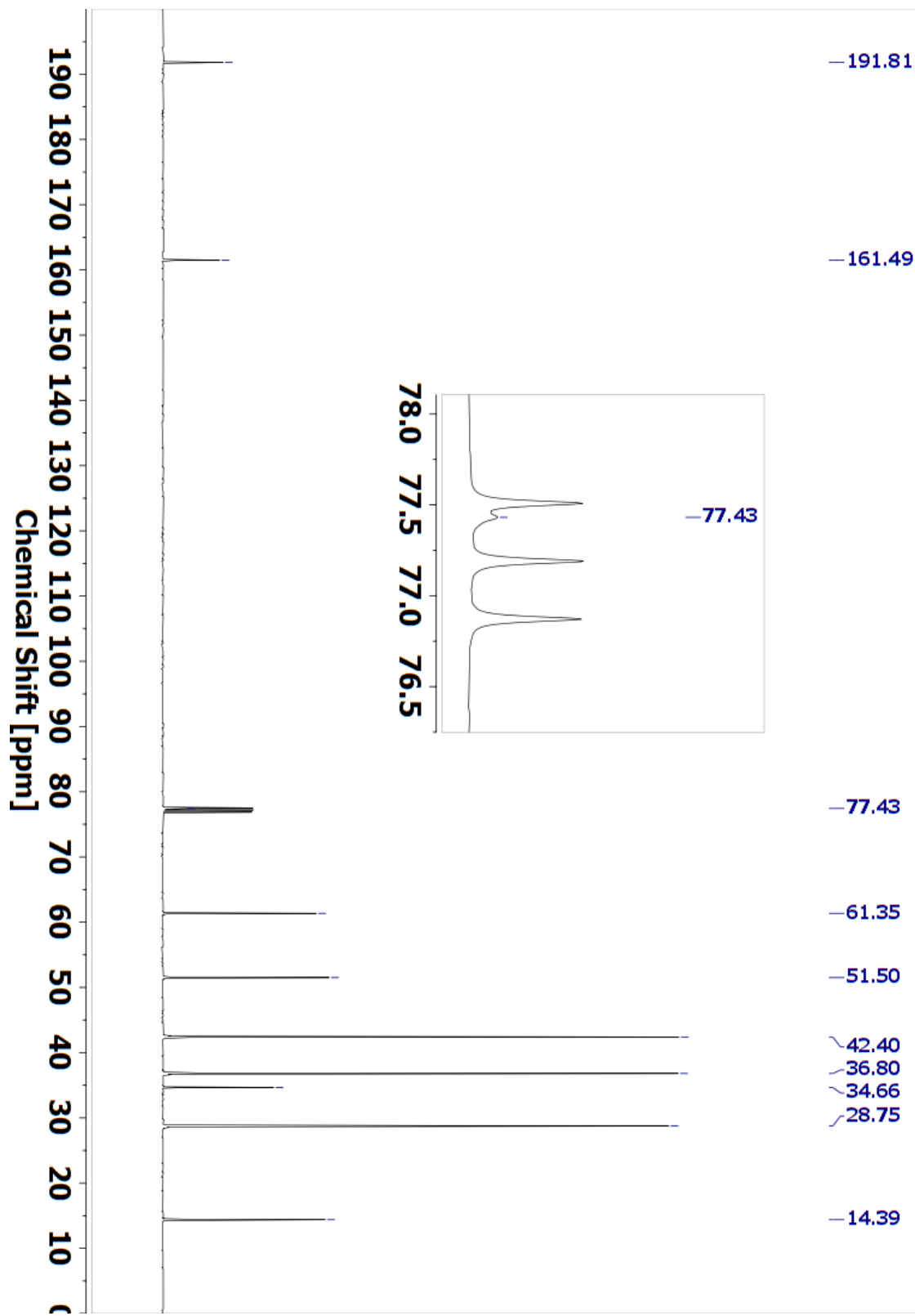
2. Methyl 4-(adamantan-1-yl)-2-diazo-3-oxobutanoate (S63): Synthesized following Procedure

A: The reaction was run on 5.00 mmol scale to give 1.20 g (83% yield) of product as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 4.24 (q, $J = 7.1$ Hz, 2H), 2.65 (s, 2H), 1.98–1.81 (m, 3H), 1.70–1.52 (m, 12H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.81, 161.49, 77.43, 61.35, 51.50, 42.40, 36.80, 34.66, 28.75, 14.39. HRMS (ESI $^+$) m/z Calc. 291.1703 $[\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3+\text{H}]^+$, Found. 291.1706 $[\text{M}+\text{H}]^+$.

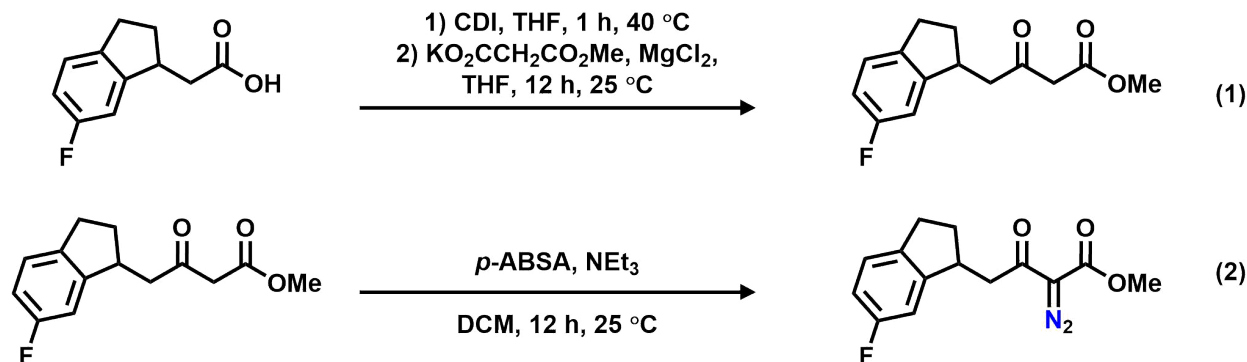


^1H NMR spectrum of isolated product in CDCl_3

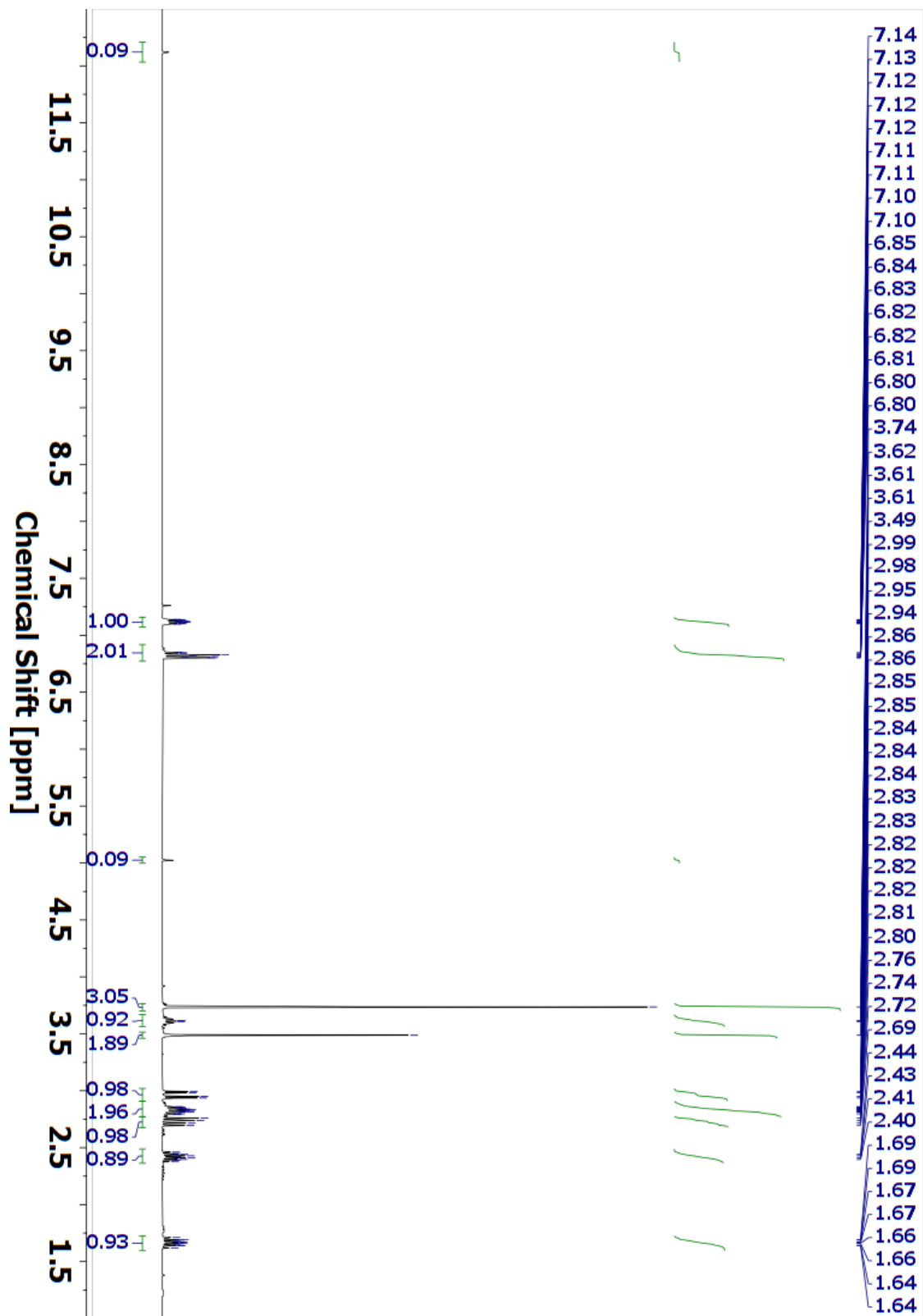


^{13}C NMR spectrum of isolated product in CDCl_3

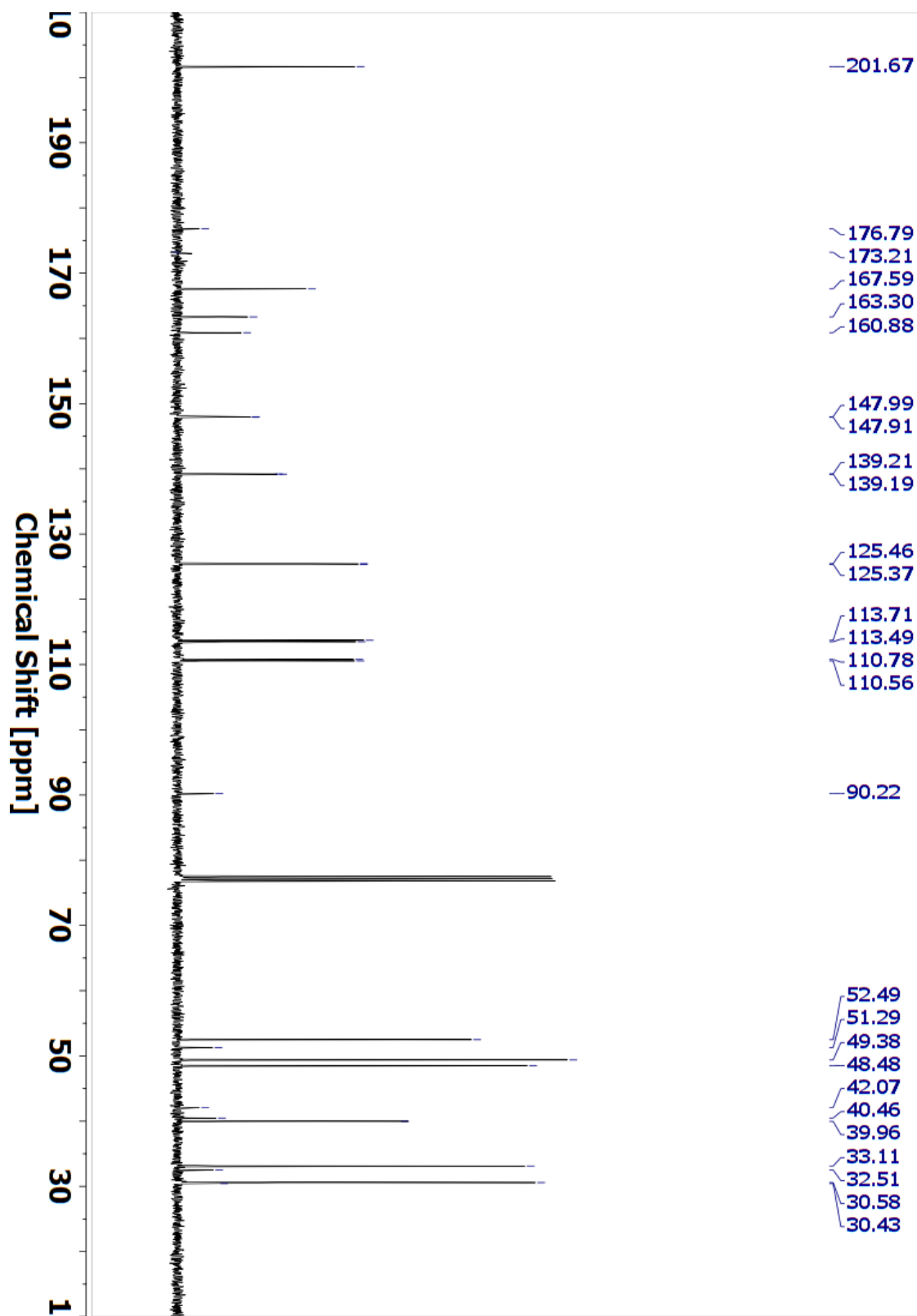
Methyl 2-diazo-4-(6-fluoro-2,3-dihydro-1H-inden-1-yl)-3-oxobutanoate (S65)



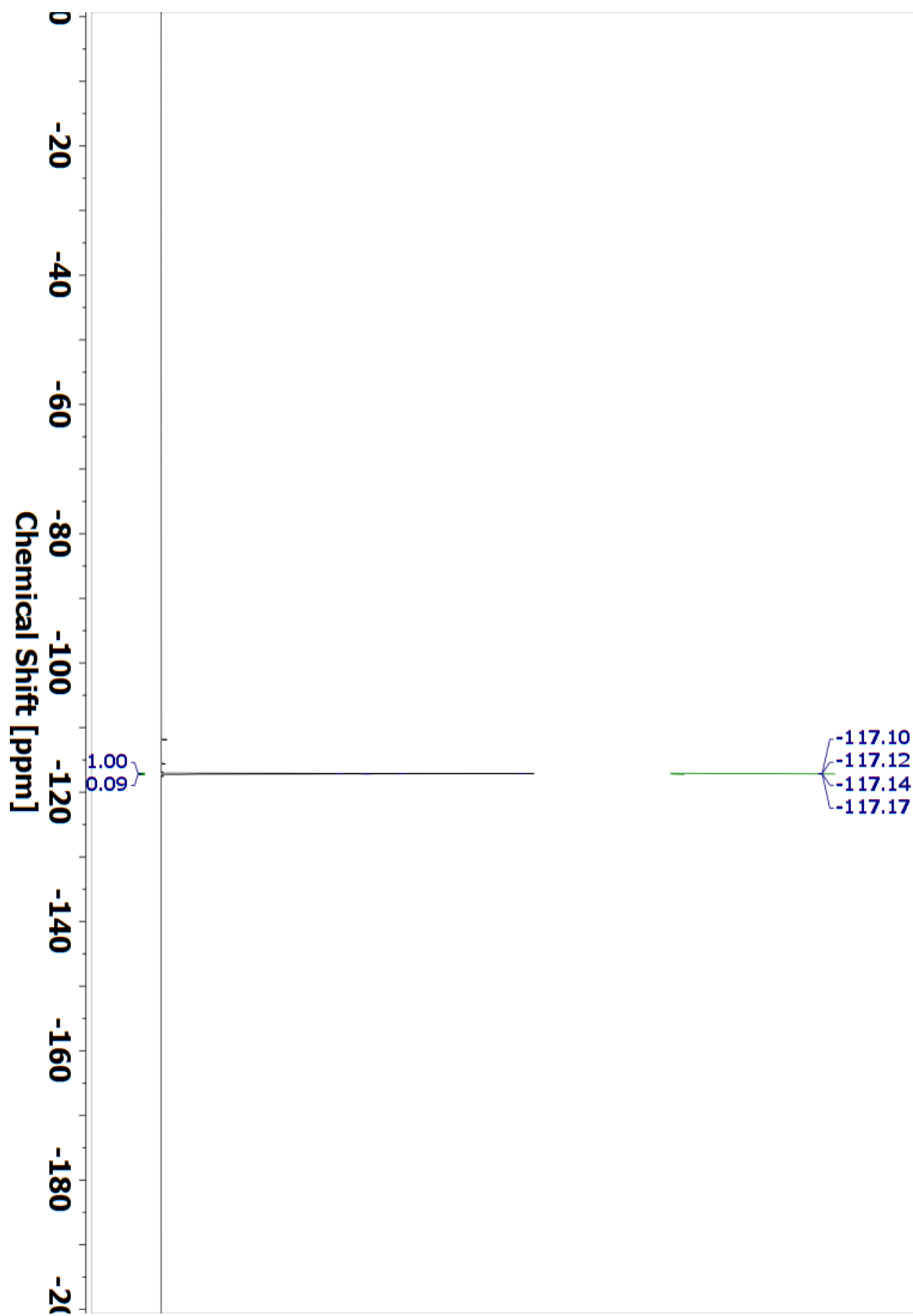
1. Methyl 4-(6-fluoro-2,3-dihydro-1H-inden-1-yl)-3-oxobutanoate (S64): Synthesized following Procedure A: The reaction was run on 10.0 mmol scale to give 1.33 g (53% yield, 9.1% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.17–7.06 (m, 1H), 6.91–6.76 (m, 2H), 3.74 (s, 3H), 3.67–3.56 (m, 1H), 3.49 (s, 2H), 2.97 (dd, $J = 17.7, 5.5$ Hz, 1H), 2.91–2.77 (m, 2H), 2.73 (dd, $J = 17.7, 8.3$ Hz, 1H), 2.51–2.35 (m, 1H), 1.73–1.59 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.67, 167.59, 162.09 (d, $J = 242.7$ Hz), 147.95 (d, $J = 7.7$ Hz), 139.20 (d, $J = 2.4$ Hz), 125.42 (d, $J = 8.7$ Hz), 113.60 (d, $J = 22.2$ Hz), 110.67 (d, $J = 22.2$ Hz), 52.49, 49.38, 48.48, 39.96, 33.11, 30.58. ^{19}F NMR (376 MHz, CDCl_3) δ -117.07–-117.18 (m). HRMS (ESI $^+$) m/z Calc. 251.1078 [$\text{C}_{14}\text{H}_{15}\text{NO}_3 + \text{H}$] $^+$, Found. 251.1081 [$\text{M} + \text{H}$] $^+$.



^1H NMR spectrum of isolated product in CDCl_3

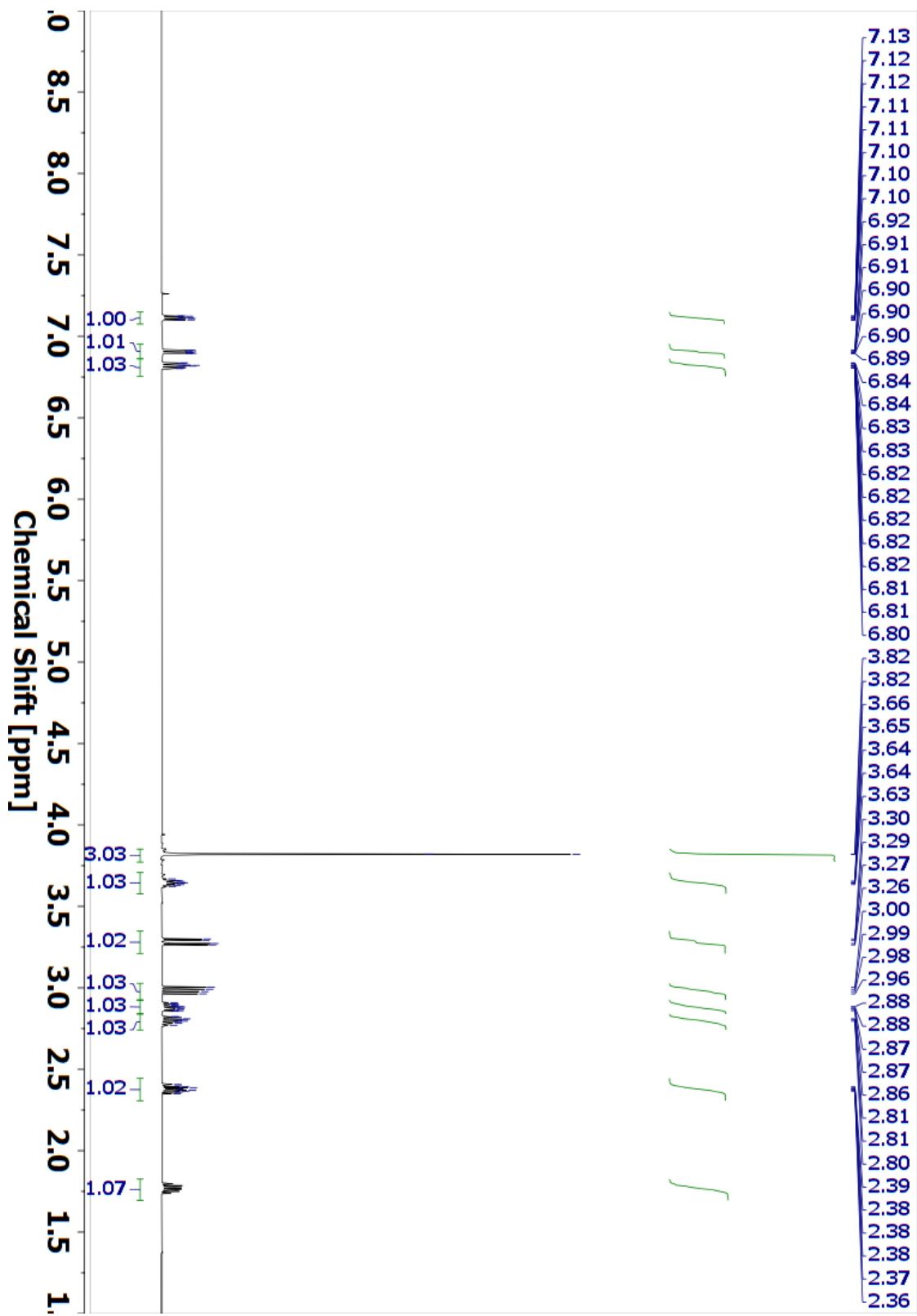


¹³C NMR spectrum of isolated product in CDCl₃

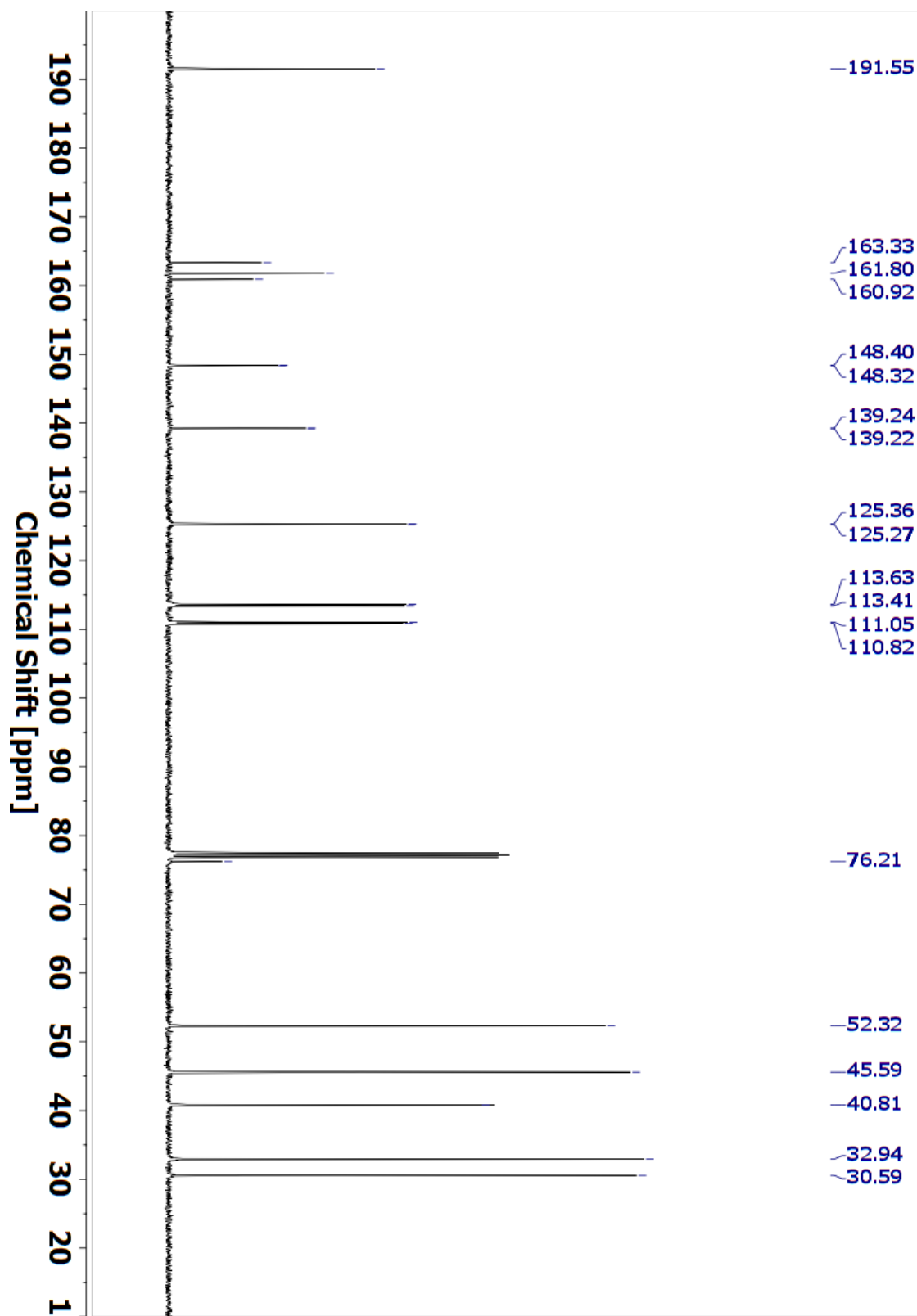


^{19}F NMR spectrum of isolated product in CDCl_3

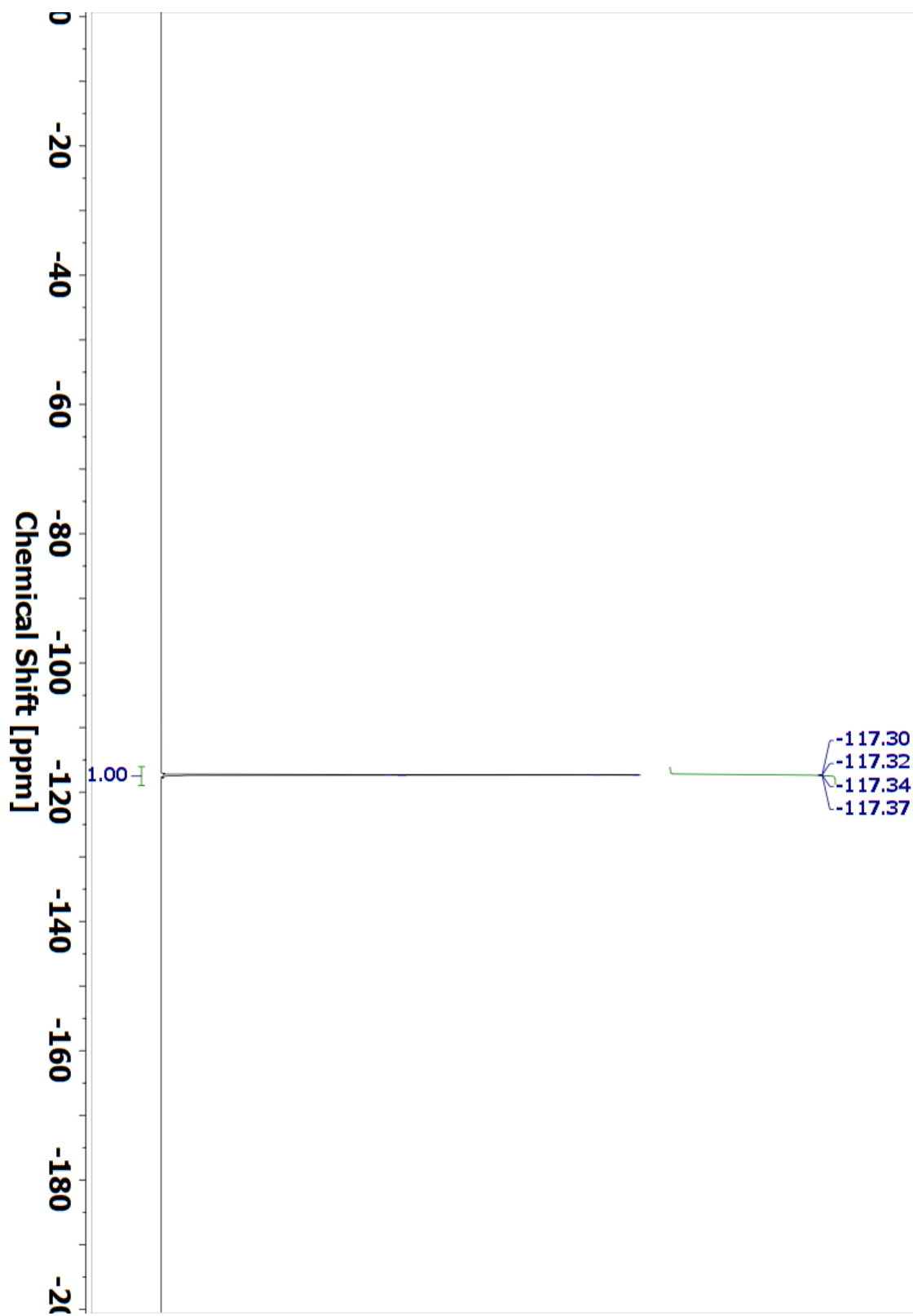
2. Methyl 2-diazo-4-(6-fluoro-2,3-dihydro-1H-inden-1-yl)-3-oxobutanoate (S65): Synthesized following Procedure A: The reaction was run on 5.00 mmol scale to give 0.93 g (67% yield) of product as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.14–7.08 (m, 1H), 6.94–6.88 (m, 1H), 6.85–6.79 (m, 1H), 3.82 (s, 3H), 3.69–3.60 (m, 1H), 3.28 (dd, $J = 16.6, 5.3$ Hz, 1H), 2.98 (dd, $J = 16.6, 8.7$ Hz, 1H), 2.92–2.84 (m, 1H), 2.84–2.74 (m, 1H), 2.47–2.31 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.55, 162.13 (d, $J = 242.3$ Hz), 161.80, 148.36 (d, $J = 7.7$ Hz), 139.23 (d, $J = 2.4$ Hz), 125.32 (d, $J = 8.7$ Hz), 113.52 (d, $J = 22.2$ Hz), 110.94 (d, $J = 22.2$ Hz), 76.21, 52.32, 45.59, 40.81, 32.94, 30.59. ^{19}F NMR (376 MHz, CDCl_3) δ -117.02–-117.63 (m). HRMS (ESI $^+$) m/z Calc. 277.0983 [$\text{C}_{14}\text{H}_{15}\text{FO}_3 + \text{H}$] $^+$, Found. 277.0.984 [$\text{M} + \text{H}$] $^+$.



^1H NMR spectrum of isolated product in CDCl_3

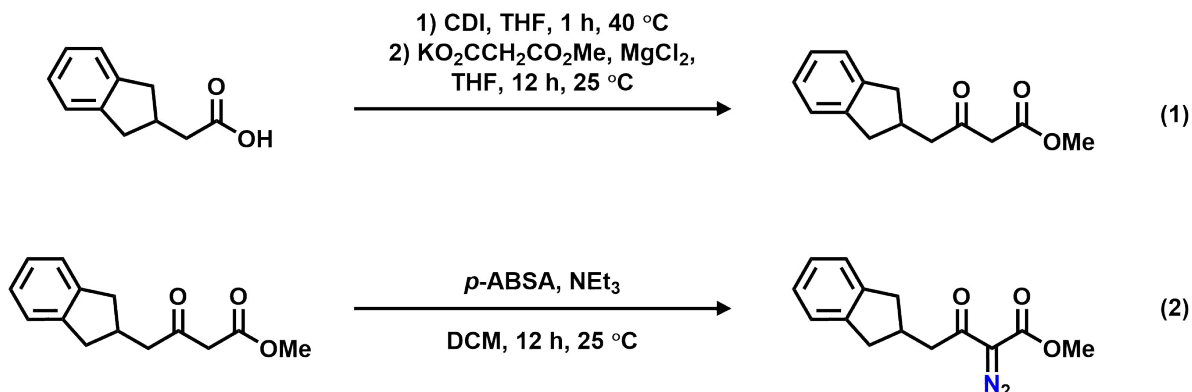


^{13}C NMR spectrum of isolated product in CDCl_3

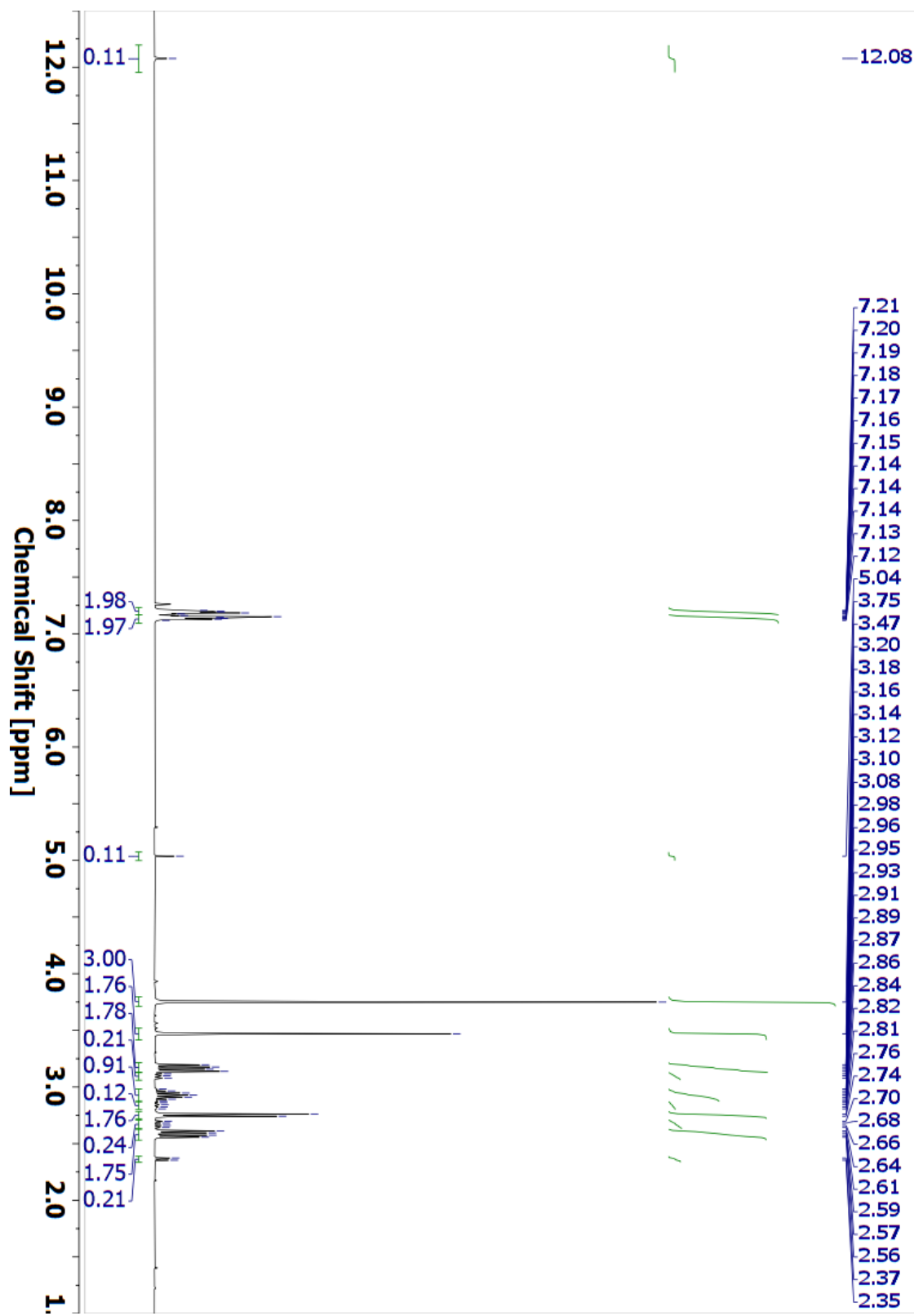


^{19}F NMR spectrum of isolated product in CDCl_3

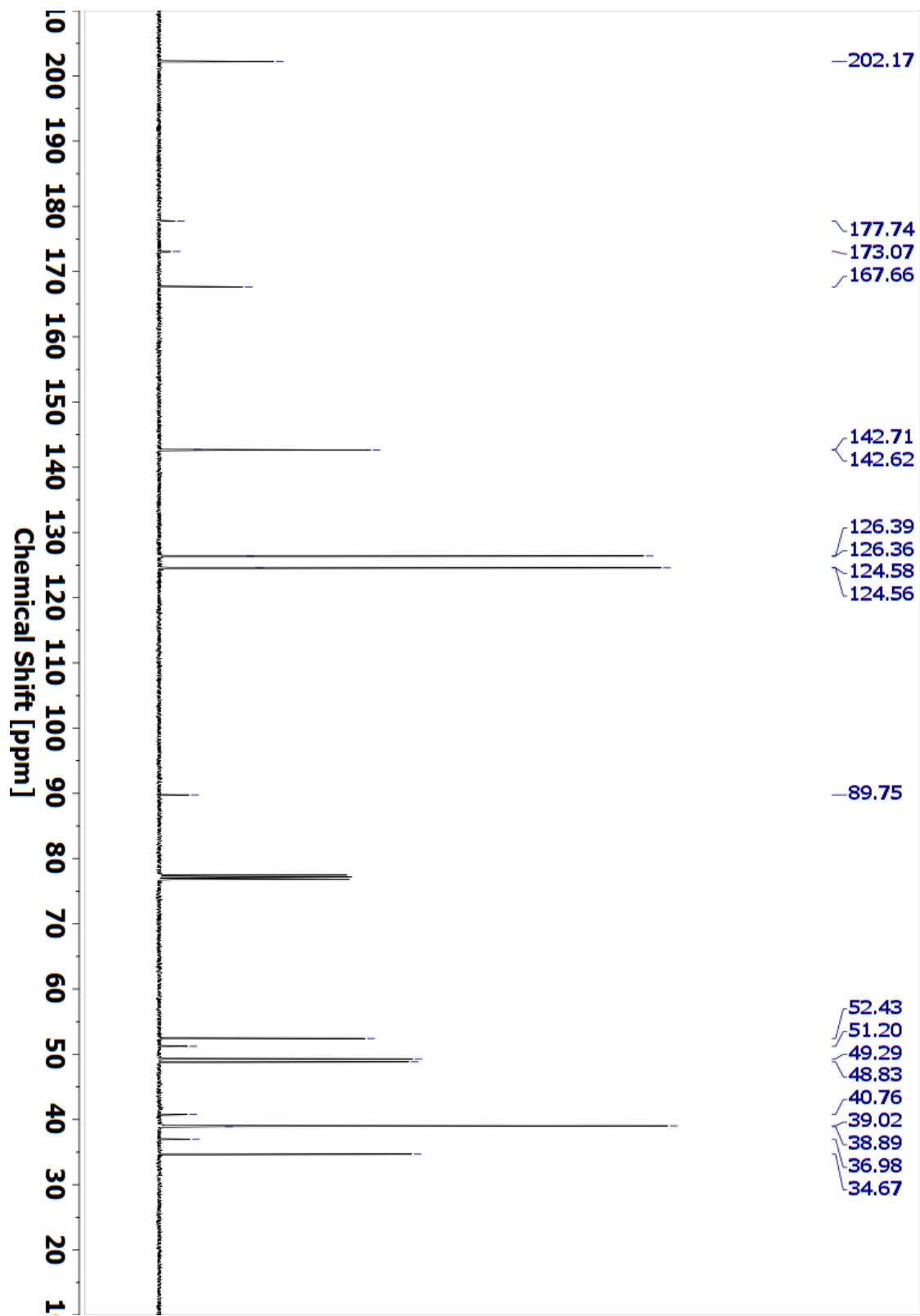
Methyl 2-diazo-4-(2,3-dihydro-1H-inden-2-yl)-3-oxobutanoate (S67)



1. Methyl 4-(2,3-dihydro-1H-inden-2-yl)-3-oxobutanoate (S66): Synthesized following Procedure A. The reaction was run on 10.0 mmol scale to give 1.46 g (63% yield, 11.1% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (*keto form*) 7.24–7.17 (m, 2H), 7.17–7.09 (m, 2H), 3.75 (s, 3H), 3.47 (s, 2H), 3.17 (dd, $J = 15.3, 7.8$ Hz, 2H), 2.98–2.87 (m, 1H), 2.75 (d, $J = 7.1$ Hz, 2H), 2.58 (dd, $J = 15.4, 7.1$ Hz, 2H); (*enol form*) 12.08 (s, 1H), 7.23–7.17 (m, 2H), 7.17–7.09 (m, 2H), 5.04 (s, 1H), 3.75 (s, 3H), 3.12–3.06 (m, 2H), 2.87–2.80 (m, 1H), 2.67 (dd, $J = 15.4, 7.1$ Hz, 2H), 2.36 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ (*keto form*) 202.17, 167.66, 142.62, 126.39, 124.56, 52.43, 49.29, 48.83, 39.02, 34.67; (*enol form*) 177.74, 173.07, 142.71, 126.36, 124.58, 89.75, 51.20, 40.76, 38.89, 36.98. HRMS (ESI^+) m/z Calc. 233.1172 [$\text{C}_{14}\text{H}_{16}\text{O}_3 + \text{H}$] $^+$, Found. 233.1173 [$\text{M} + \text{H}$] $^+$.

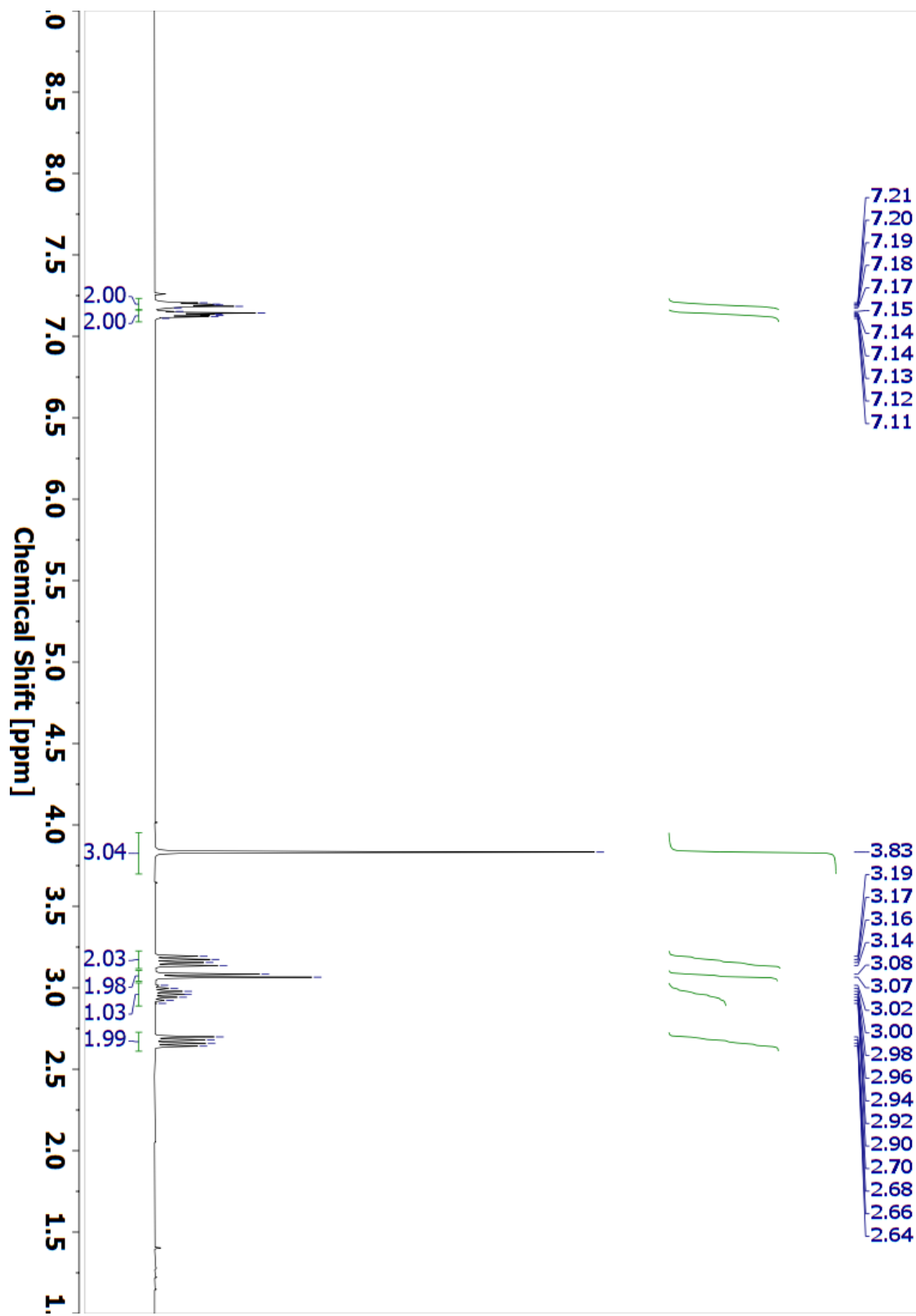


^1H NMR spectrum of isolated product in CDCl_3

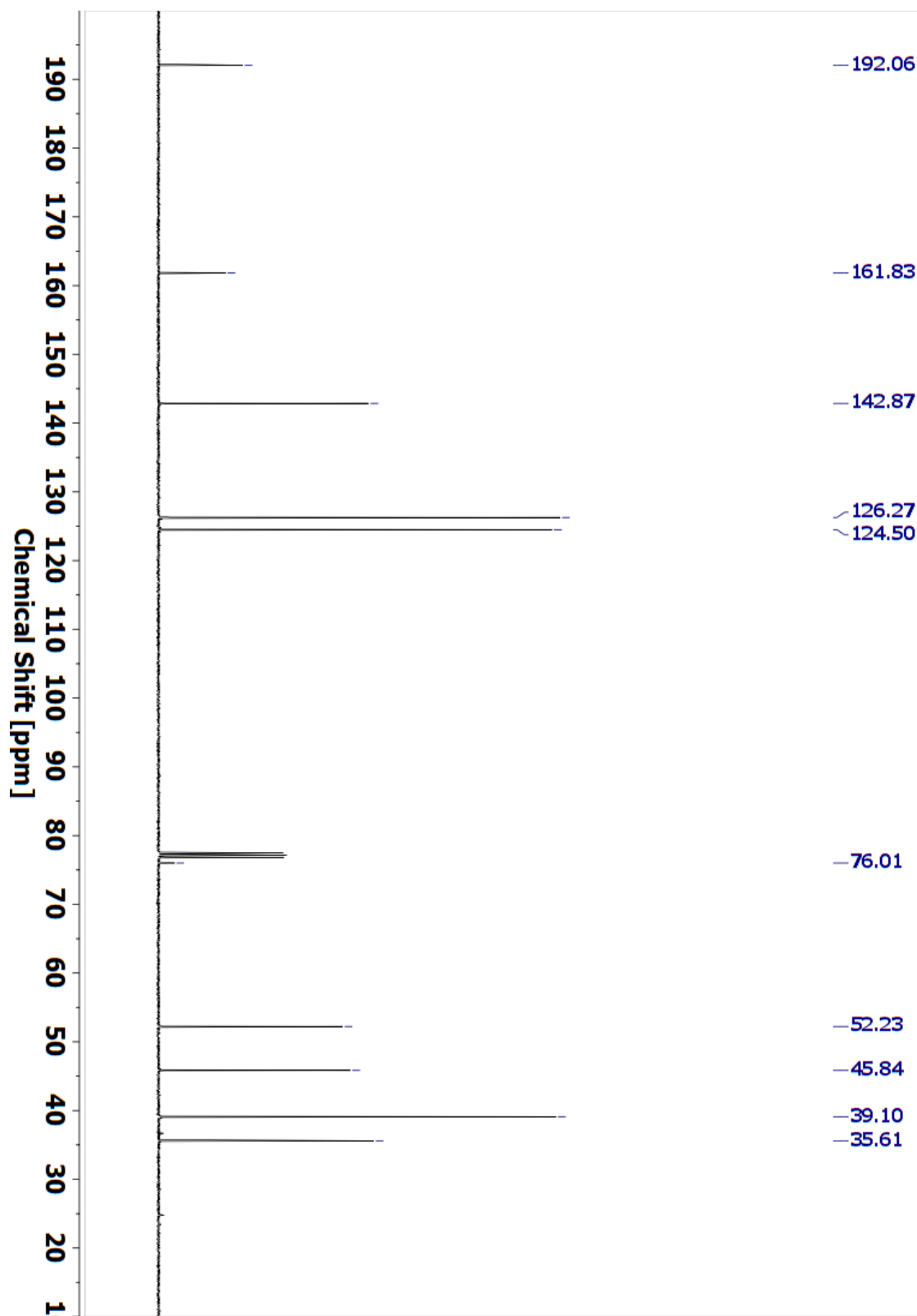


^{13}C NMR spectrum of isolated product in CDCl_3

2. Methyl 2-diazo-4-(2,3-dihydro-1H-inden-2-yl)-3-oxobutanoate (S67): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.91 g (70% yield) of product as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.19 (dd, *J* = 5.4, 3.4 Hz, 2H), 7.13 (dd, *J* = 5.4, 3.4 Hz, 2H), 3.83 (s, 3H), 3.16 (dd, *J* = 15.3, 7.8 Hz, 2H), 3.07 (d, *J* = 7.3 Hz, 2H), 3.03–2.88 (m, 1H), 2.67 (dd, *J* = 15.3, 7.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.06, 161.83, 142.87, 126.27, 124.50, 76.01, 52.23, 45.84, 39.10, 35.61. HRMS (ESI⁺) *m/z* Calc. 259.1077 [C₁₄H₁₄N₂O₃+H]⁺, Found. 259.1081 [M+H]⁺.

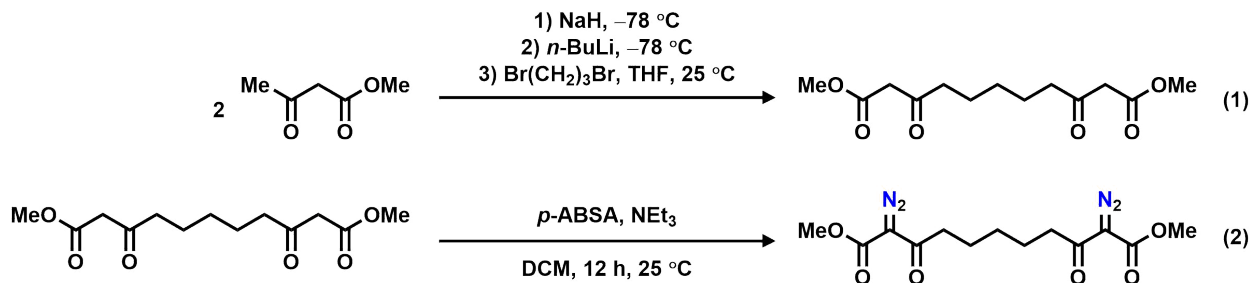


^1H NMR spectrum of isolated product in CDCl_3



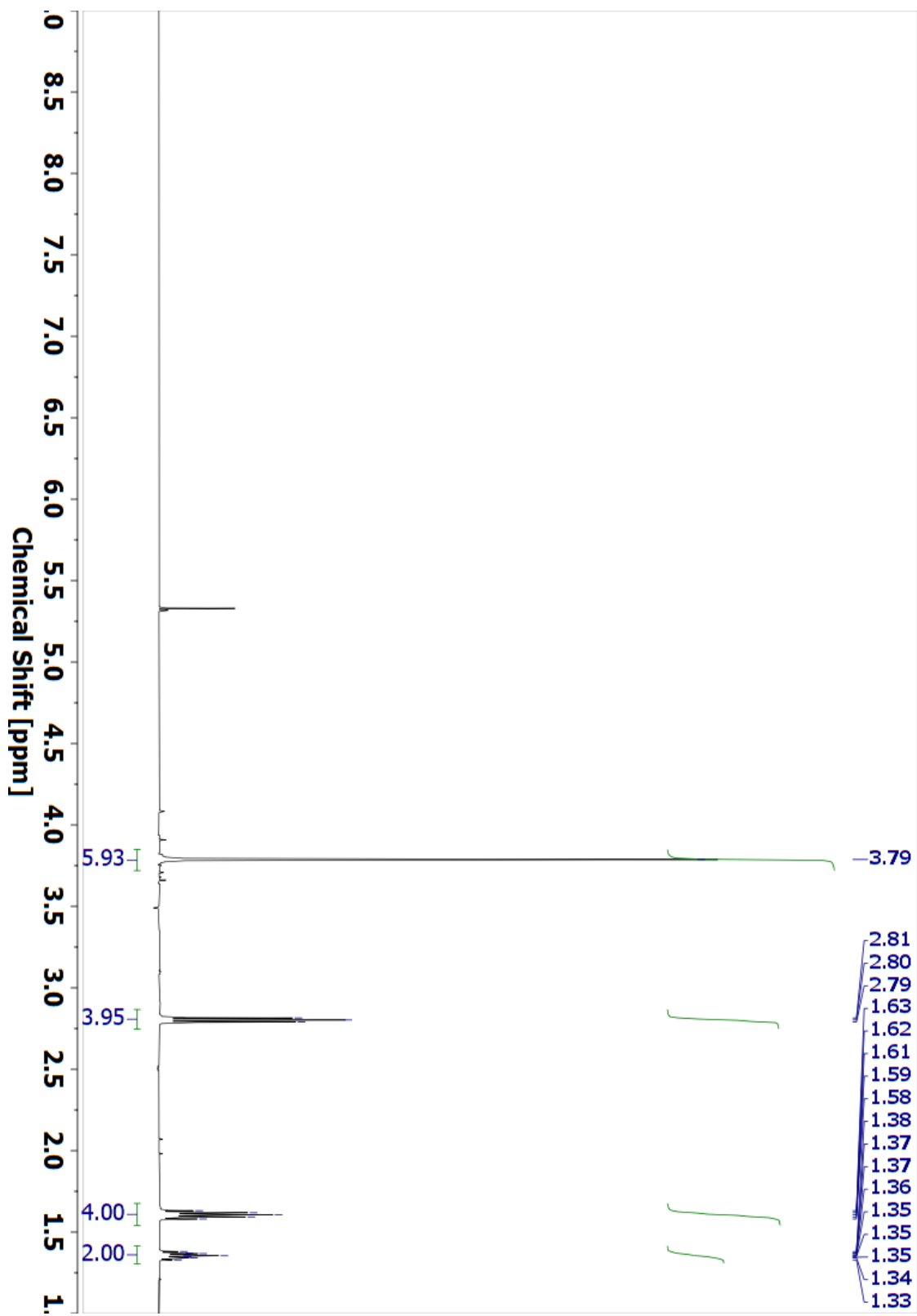
^{13}C NMR spectrum of isolated product in CDCl_3

Dimethyl 2,10-bis(diazo)-3,9-dioxoundecanedioate (S69)

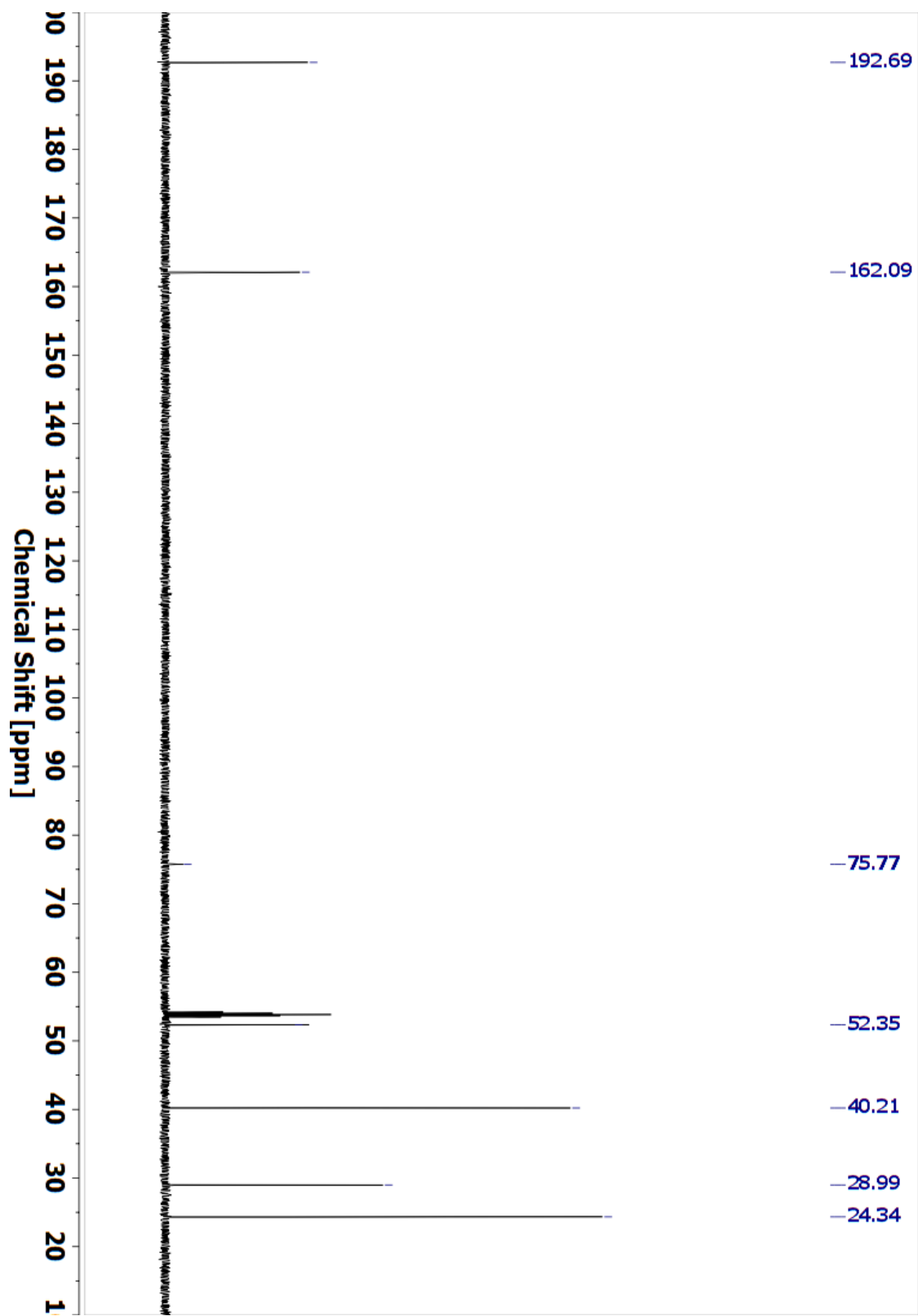


1. Dimethyl 3,9-dioxoundecanedioate (S68): Synthesized following previously reported procedure.¹⁵

2. Dimethyl 2,10-bis(diazo)-3,9-dioxoundecanedioate (S69): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.83 g (51% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 3.79 (s, 6H), 2.94–2.67 (m, 4H), 1.68–1.54 (m, 4H), 1.42–1.30 (m, 2H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 192.69, 162.09, 75.77, 52.35, 40.21, 28.99, 24.34. HRMS (ESI⁺) *m/z* Calc. 325.1143 [C₁₃H₁₆N₄O₆+H]⁺, Found. 325.1142 [M+H]⁺.

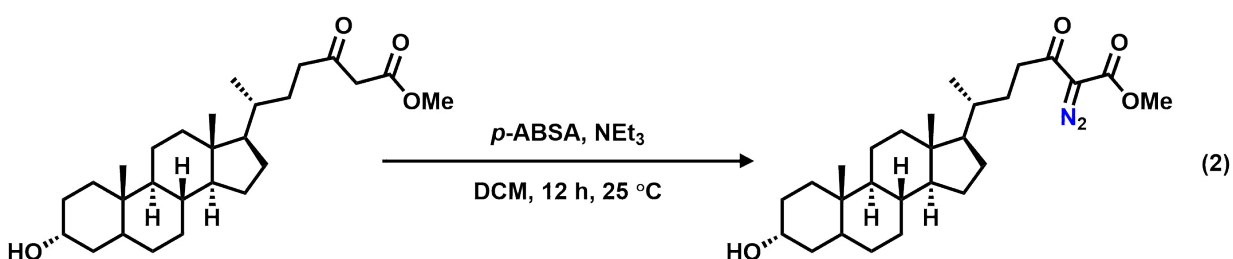
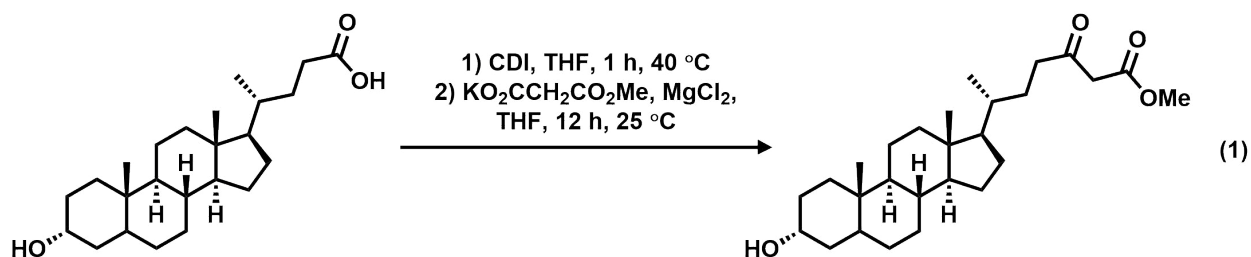


^1H NMR spectrum of isolated product in CD_2Cl_2



^{13}C NMR spectrum of isolated product in CD_2Cl_2

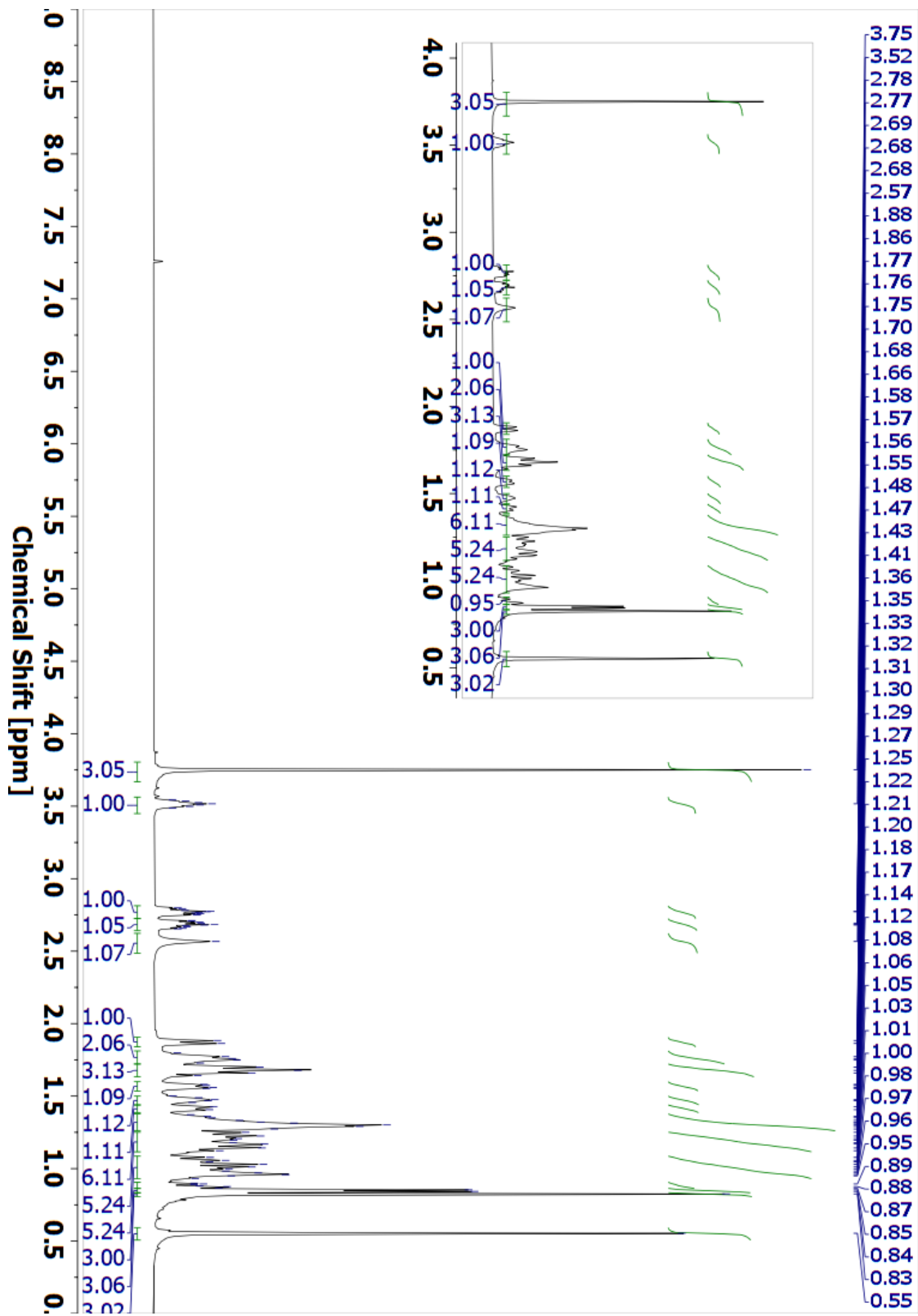
Methyl (6R)-2-diazo-6-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadeca-hydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxoheptanoate (S71)



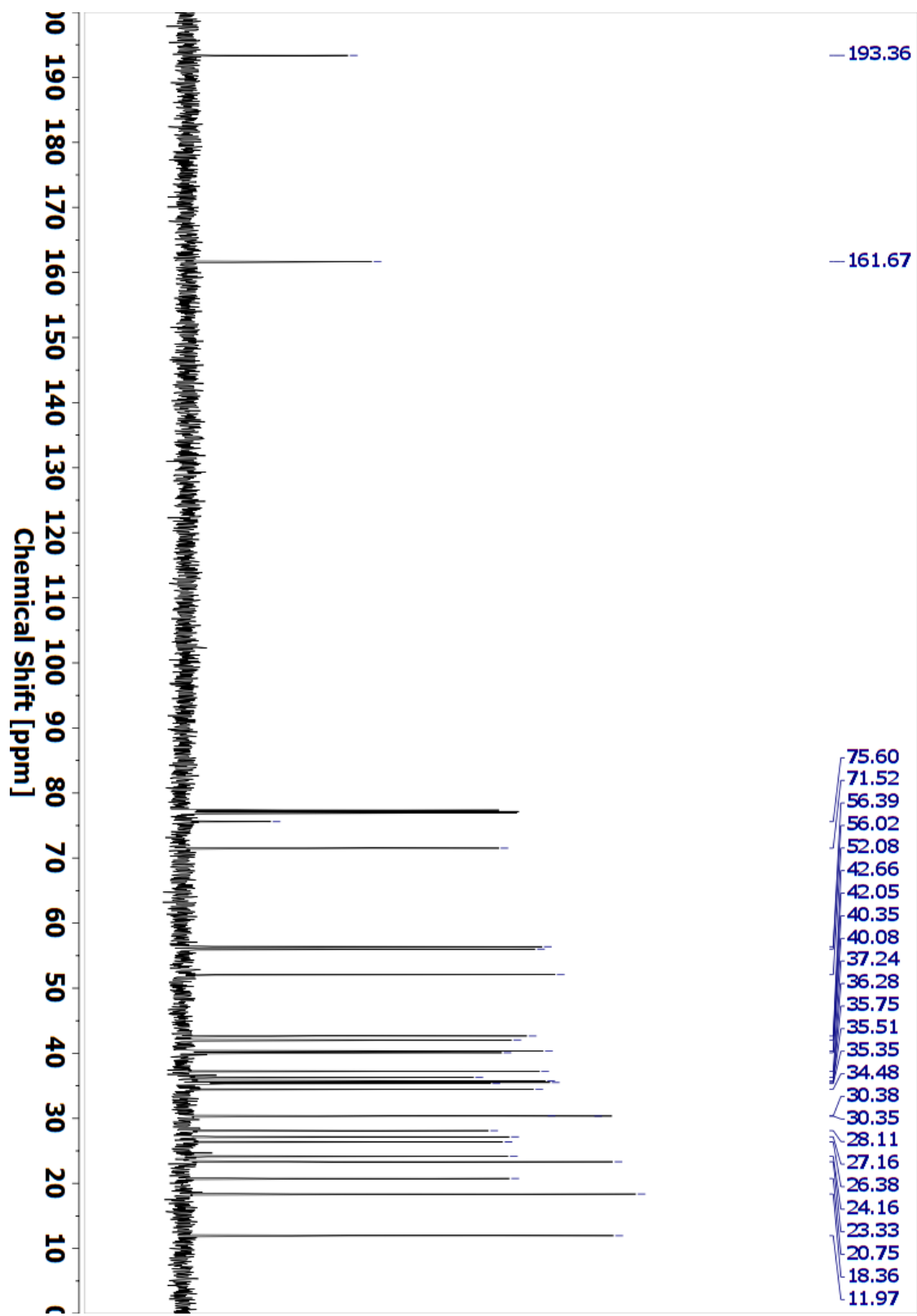
1. Methyl (6R)-6-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxoheptanoate (S70): Synthesized following Procedure A using 10.0 mmol of starting material: The product was directly carried on to the diazo-transfer due to its high viscosity as a thick oil. HRMS (ESI⁺) m/z Calc. 433.3312 [C₂₇H₄₄O₄+H]⁺, Found. 433.3310 [M+H]⁺.

2. Methyl (6R)-2-diazo-6-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxoheptanoate (S71): Synthesized following Procedure B: The product mixture from previous reaction is directly subjected to the reaction condition, providing 2.26 g (49% yield over two steps) of product as a colorless solid. ¹H NMR (600 MHz, CDCl₃) δ 3.75 (s, 3H), 3.57–3.45 (m, 1H), 2.82–2.73 (m, 1H), 2.73–2.64 (m, 1H), 2.57 (s, 1H), 1.87 (d, *J* = 12.0 Hz, 1H), 1.80–1.72 (m, 2H), 1.72–1.61 (m, 3H), 1.60–1.54 (m, 1H), 1.52–1.45 (m, 1H), 1.47–1.36 (m, 1H), 1.38–1.26 (m, 6H), 1.24–1.10 (m, 5H), 1.09–0.92 (m, 5H), 0.92–

0.86 (m, 1H), 0.85 (d, $J = 6.5$ Hz, 3H), 0.82 (s, 3H), 0.55 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.36, 161.67, 75.60, 71.52, 56.39, 56.02, 52.08, 42.66, 42.05, 40.35, 40.08, 37.24, 36.28, 35.75, 35.51, 35.35, 34.48, 30.38, 30.35, 28.11, 27.16, 26.38, 24.16, 23.33, 20.75, 18.36, 11.97. HRMS (ESI $^+$) m/z Calc. 459.3217 [$\text{C}_{27}\text{H}_{42}\text{N}_2\text{O}_4+\text{H}$] $^+$, Found. 459.3213 [$\text{M}+\text{H}$] $^+$. Elemental analysis was conducted due to the complexity of the NMR spectra for bulk purity assessment. Anal. Calc. for $\text{C}_{27}\text{H}_{42}\text{N}_2\text{O}_4$: C 70.71, H 9.23, N, 6.11; Found C 70.51, H 9.12, N, 5.99.

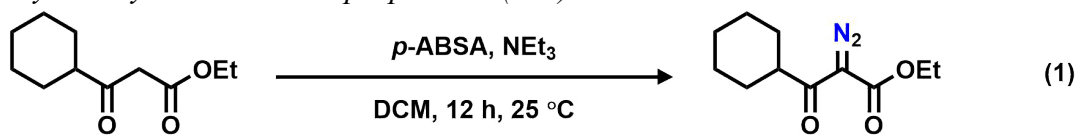


^1H NMR spectrum of isolated product in CDCl_3



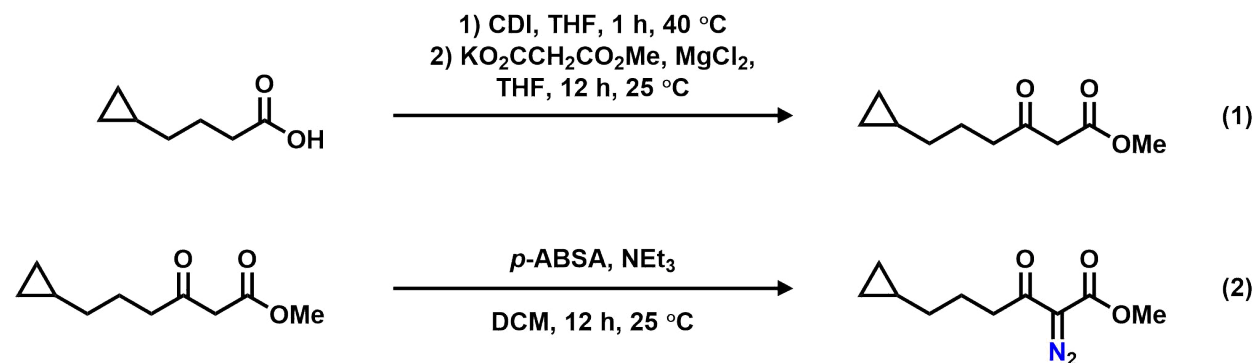
^{13}C NMR spectrum of isolated product in CDCl_3

Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (S72)



1. Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (S72): Synthesized following previously reported procedure.¹⁶

Methyl 6-cyclopropyl-2-diazo-3-oxohexanoate (6)



1. Methyl 5-(1,3-dioxolan-2-yl)-3-oxopentanoate (S73): Synthesized following reported procedure.¹³

2. Methyl 6-cyclopropyl-2-diazo-3-oxohexanoate (6): Synthesized following Procedure B: The reaction was run on 5.00 mmol scale to give 0.79 g (75% yield) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 3H), 2.86–2.78 (m, 2H), 1.74–1.62 (m, 2H), 1.24–1.14 (m, 2H), 0.68–0.51 (m, 1H), 0.39–0.30 (m, 2H), –0.03–0.08 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.85, 161.79, 75.62, 52.12, 39.94, 34.15, 24.38, 10.60, 4.38. HRMS (ESI⁺) m/z Calc. 211.1077 [$\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4+\text{H}$]⁺, Found. 211.1080 [$\text{M}+\text{H}$]⁺.

Procedure for catalytic C–H alkoxylation

Preparation of Fe(acac)₂ stock solution: In a 20 mL scintillation vial under N₂ atmosphere, Fe(acac)₂ (ca. 100 mg, freshly grounded) was added followed by 5 mL of dry C₆D₆. The suspension was brought to boiling (b.p. 80.1 °C) for 5 min. The suspension was then cooled back down to room temperature and filtered. The filtrate was used as a stock solution for the catalysis.

Concentration measurement: Four stock solutions were prepared and 1 mL of solution was taken from each. The samples were transferred into individual vials and all the volatiles were removed *in vacuo*. The mass of remaining solid from each sample was obtained and the concentration of the stock solution was calculated as 11.0(8) mg/mL (43(3) mM). (standard deviation was used as error bars)

Catalysis setup: Procedure C (at 25 °C): In a scintillation vial with a stir bar under N₂ atmosphere, 20.0 mg of diazo substrate in C₆D₆ was added followed by specified amount of Fe(acac)₂ stock solution. Additional C₆D₆ was further added to bring the total volume to 2 mL. The reaction was stirred at room temperature with the reaction progress checked by TLC and NMR spectroscopy till no further consumption of diazo substrate was observed, and the product mixture was directly purified by column chromatography with a pentane/diethyl ether mixture to yield the corresponding 2-alkylidene dihydrofuran product.

Procedure D (heating required): In a J-young NMR tube under N₂ atmosphere, 20.0 mg of diazo substrate in C₆D₆ was added followed by specified amount of Fe(acac)₂ stock solution. Additional C₆D₆ was further added to bring the total volume to 2 mL. The J-young NMR tube was then capped and heated to specified reaction temperatures. The progress of the reaction was monitored by ¹H- or ¹⁹F-NMR spectroscopy till no further consumption of diazo substrate was observed, and the

product mixture was directly purified by column chromatography with a pentane/diethyl ether mixture to yield the corresponding 2-alkylidene dihydrofuran product.

Product isomerization (Z → E): Procedure E: In a scintillation vial under N₂ atmosphere, product in *Z*-form in DCM was added followed by 10 mol% of Sc(OTf)₃. The mixture is stirred at room temperature for 24 h, and the volatiles is removed *in vacuo* to provide the product in its *E*-form.

Note: 1. The product is sometimes accompanied by a small quantity of water, potentially due to hydrogen bonding with the ethereal and carbonyl oxygen atoms. Attempts of eliminating the water contamination by prolonged exposure to high vacuum is unsuccessful, often lead to product decomposition and/or isomerization.

2. For certain substrates olefin isomerization is observed in polar solvents (chloroform, dichloromethane, water, acetonitrile etc.). The *Z*-conformation is observed in the initial reaction mixture (C₆D₆) and stable at least for 24h, while isomerization takes place during the purification and characterization processes.

3. The *Z*- and *E*-form of the product are readily isolable from each other by silica column chromatography, with the *Z*-isomer having a much lower *R_f* value potentially due to the hydrogen chelating with the ethereal and carbonyl oxygen atoms.

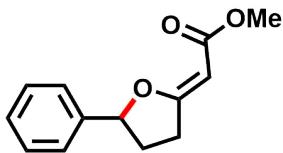
4. Some substrates were tested both at room (25 °C) and elevated temperatures (60-100 °C). The isolated yield is based on the condition that provides the higher NMR yield (referenced to Si(SiMe₃)₄ as internal standard). Detailed information is offered in sections for each individual substrate.

5. For certain substrates, the scale of the reaction is increased 10- to 15-fold (200-300 mg per run) to demonstrate the scalability of the method. Detailed information can be found within sections for each individual substrate.

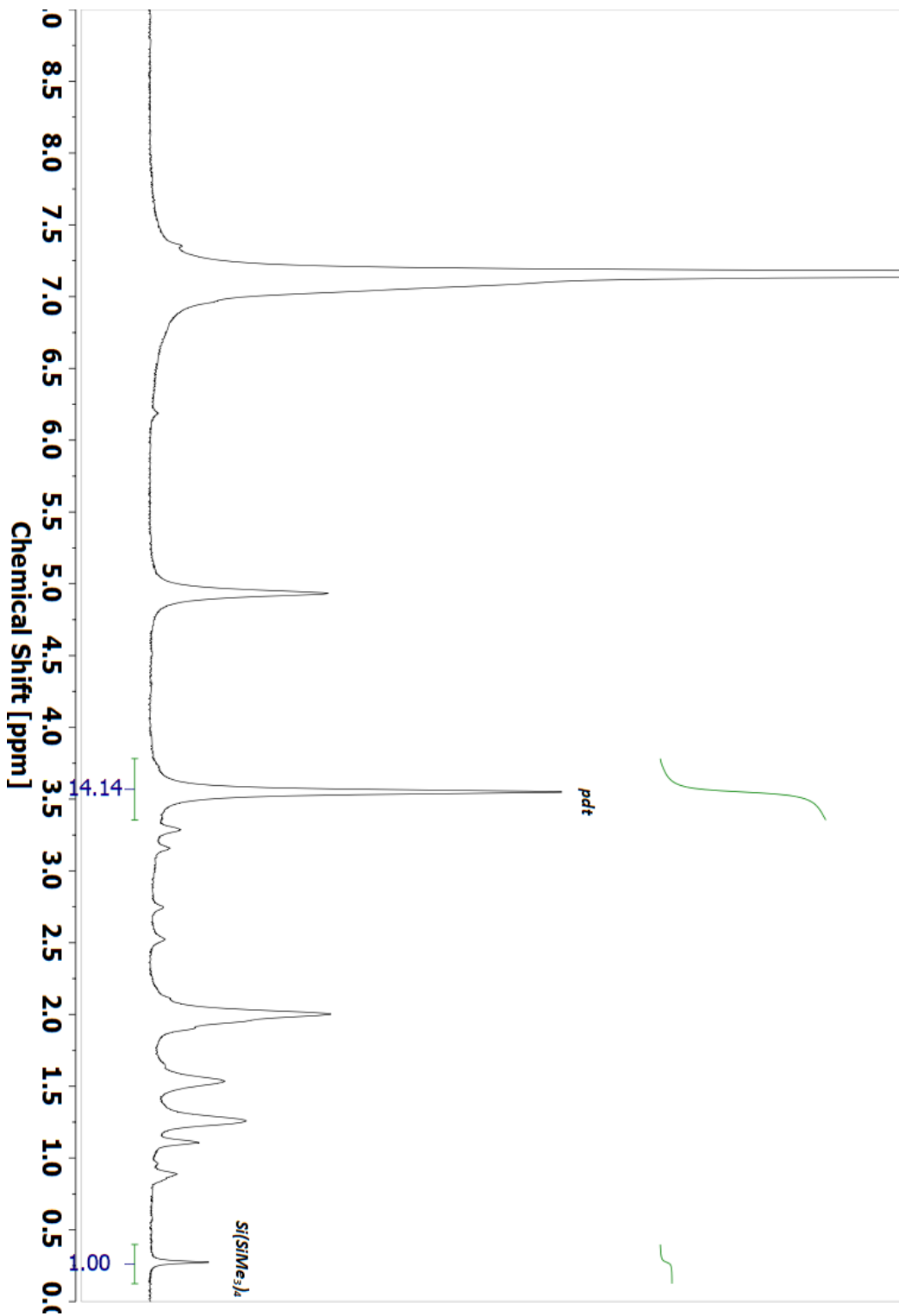
6. For fused bicyclic structures formed, excellent chemoselectivity is observed (*syn* : *anti* > 99 : 1) as verified by both $^2J_{\text{H-H}}$ coupling constants in the ^1H NMR spectrum and solid-state structures of the product.

Characterization of (Z)-2-alkylidene tetrahydrofuran

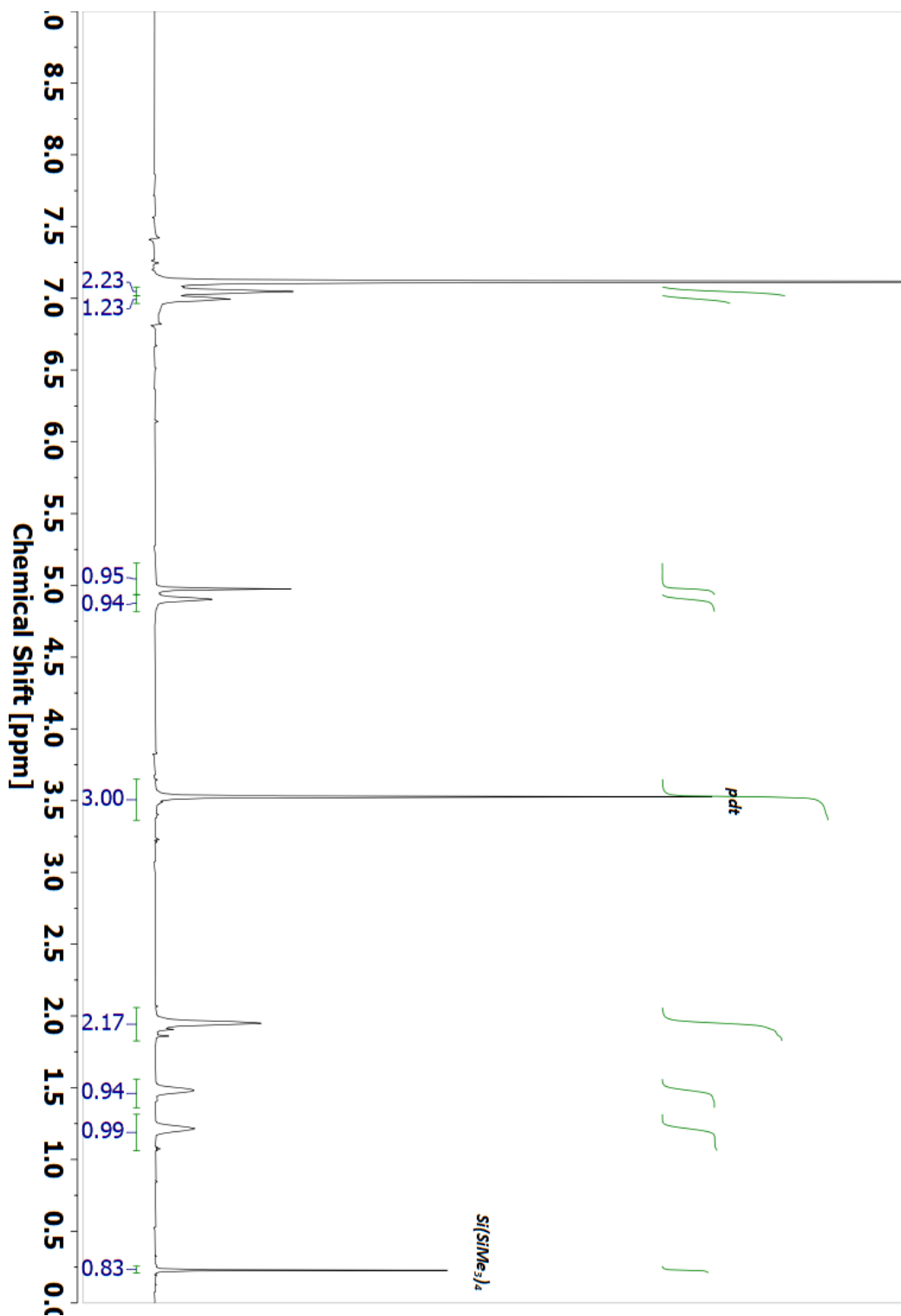
Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (2)



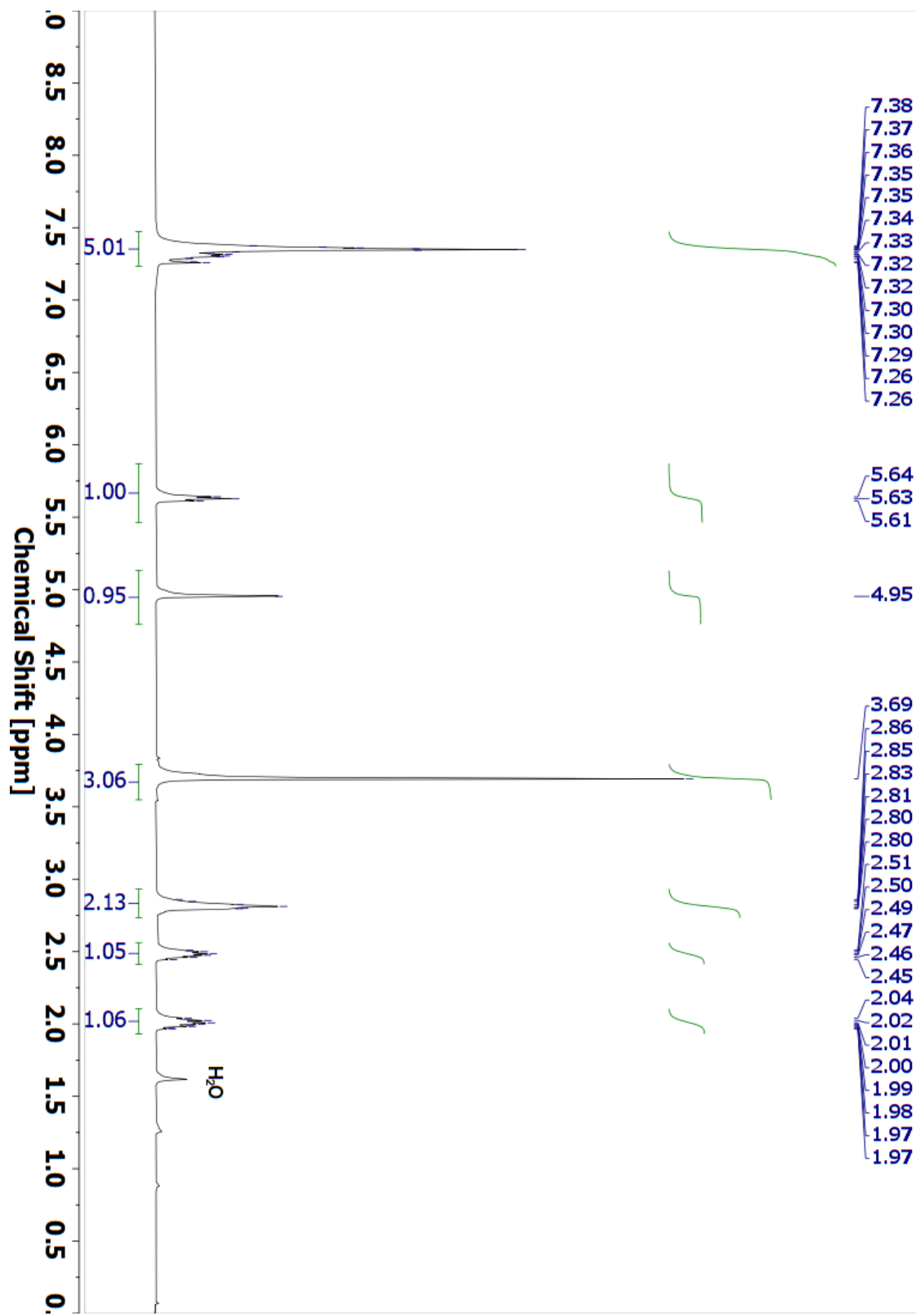
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 58% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 74% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.8 mg (61% yield) of product as a white solid. Crystals suitable for X-ray diffraction analysis is grown from slowly cooling down a saturated boiling hexanes solution. ^1H NMR (500 MHz, CDCl_3) δ 7.50–7.03 (m, 5H), 5.63 (t, $J = 7.0$ Hz, 1H), 4.95 (s, 1H), 3.69 (s, 3H), 2.99–2.67 (m, 2H), 2.63–2.31 (m, 1H), 2.07–1.78 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.57, 166.40, 140.03, 128.72, 128.19, 125.53, 88.35, 86.84, 50.87, 32.20, 31.84. HRMS (ESI $^+$) m/z Calc. 241.0835 $[\text{C}_{13}\text{H}_{14}\text{O}_3 + \text{Na}]^+$, Found. 241.0850 $[\text{M} + \text{Na}]^+$.



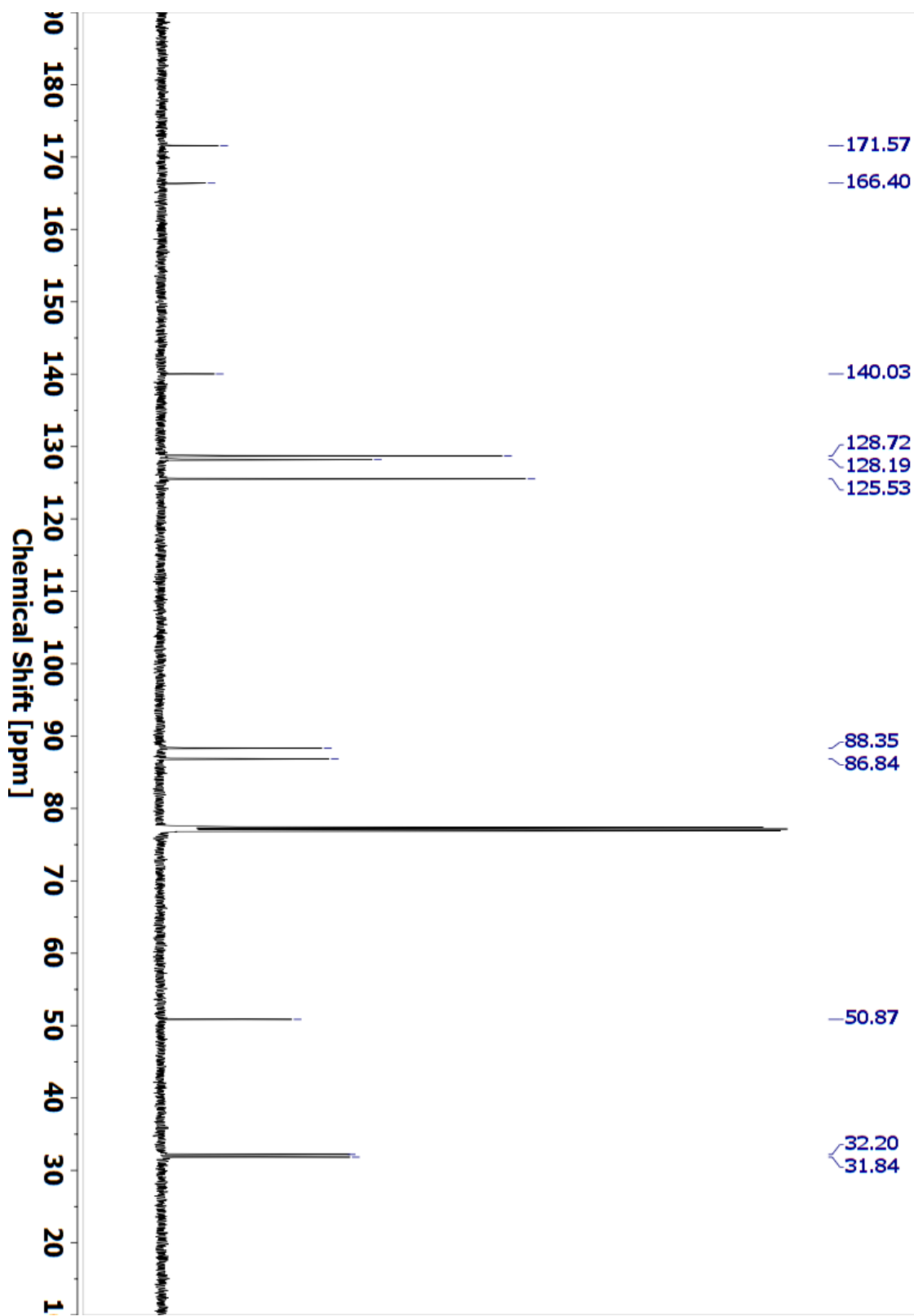
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.1 mg Si(SiMe₃)₄ as internal standard).



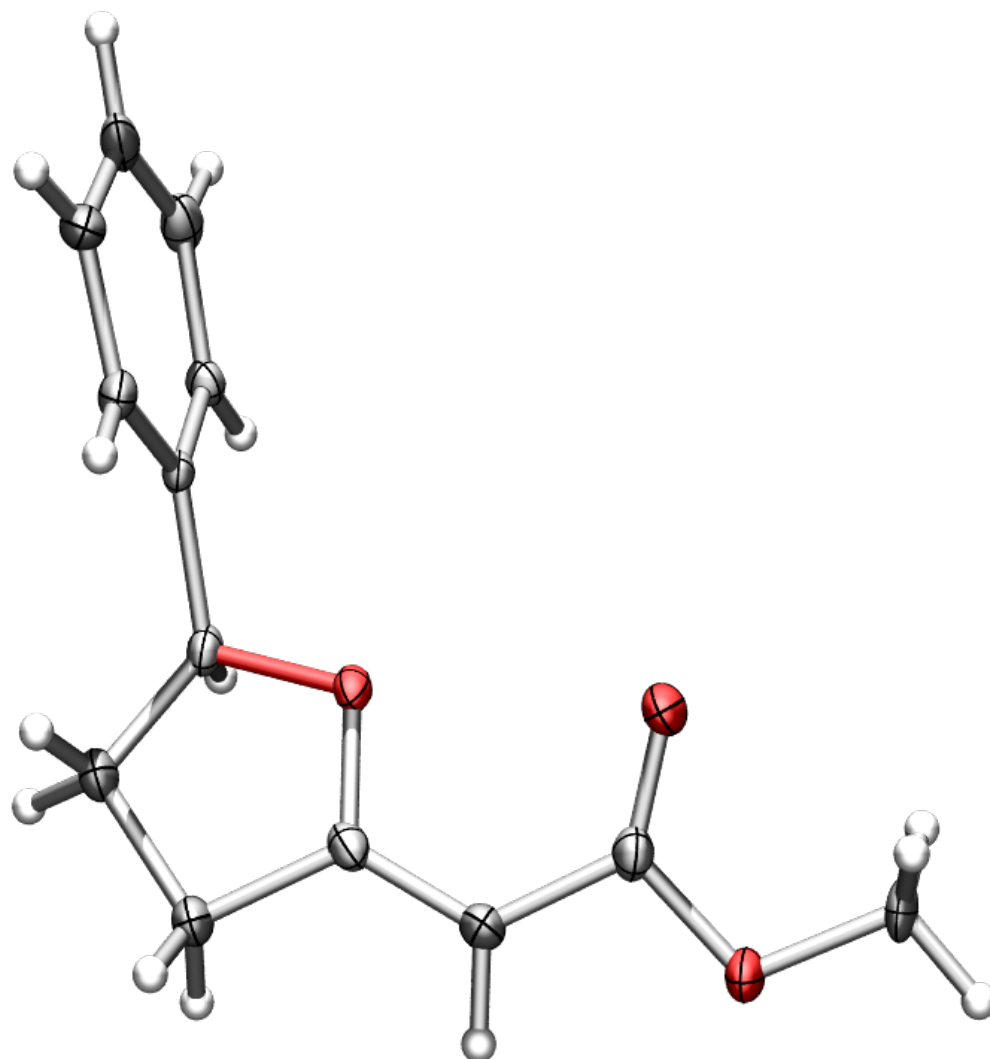
Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% $\text{Fe}(\text{acac})_2$ after 20 min (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



¹H NMR spectrum of isolated product in CDCl₃

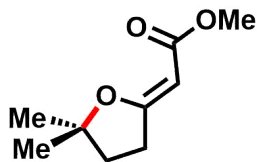


¹³C NMR spectrum of isolated product in CDCl₃



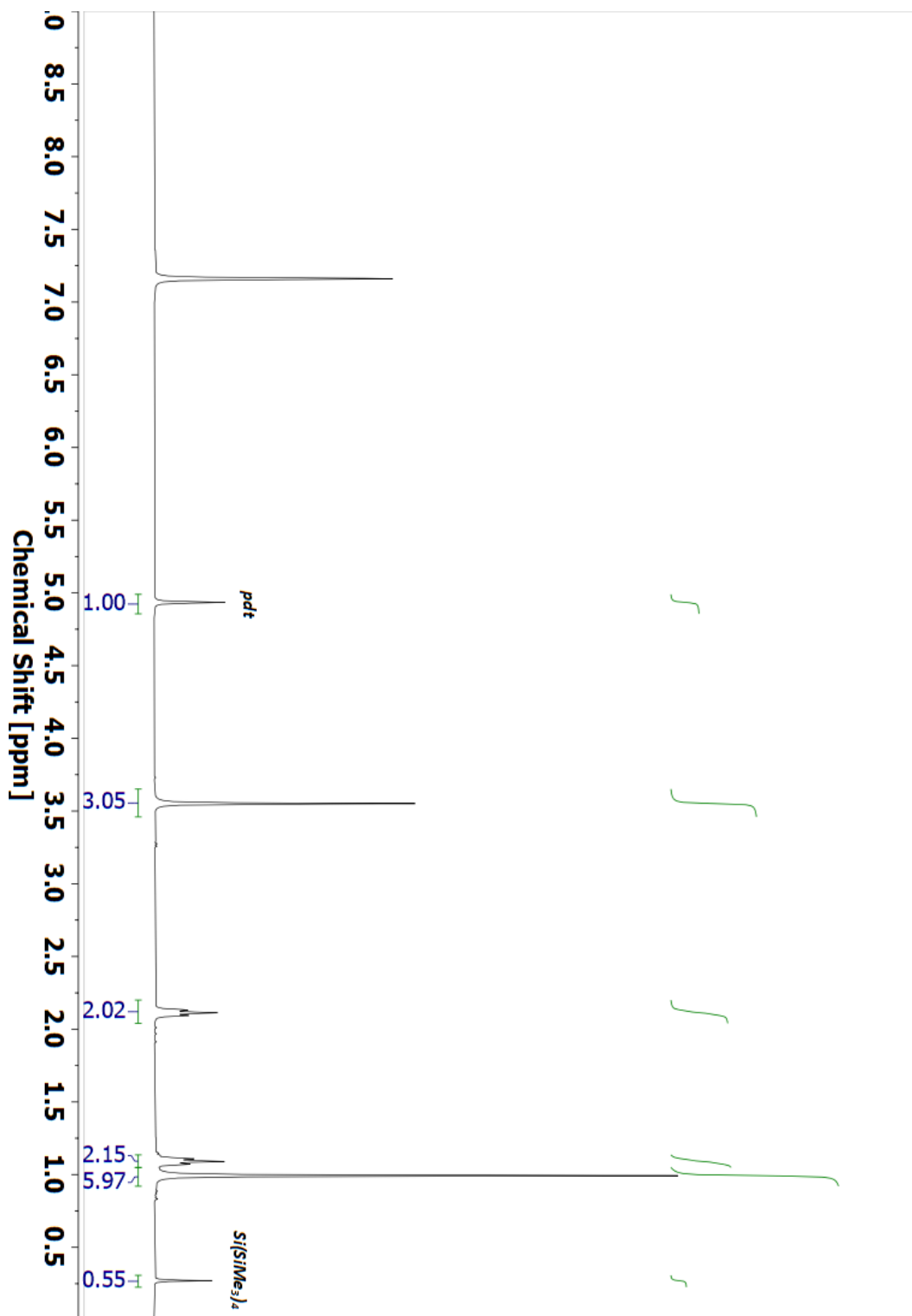
Solid-state molecular structure for methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (2) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white. Disorder is omitted for clarity.

Methyl (Z)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (3)

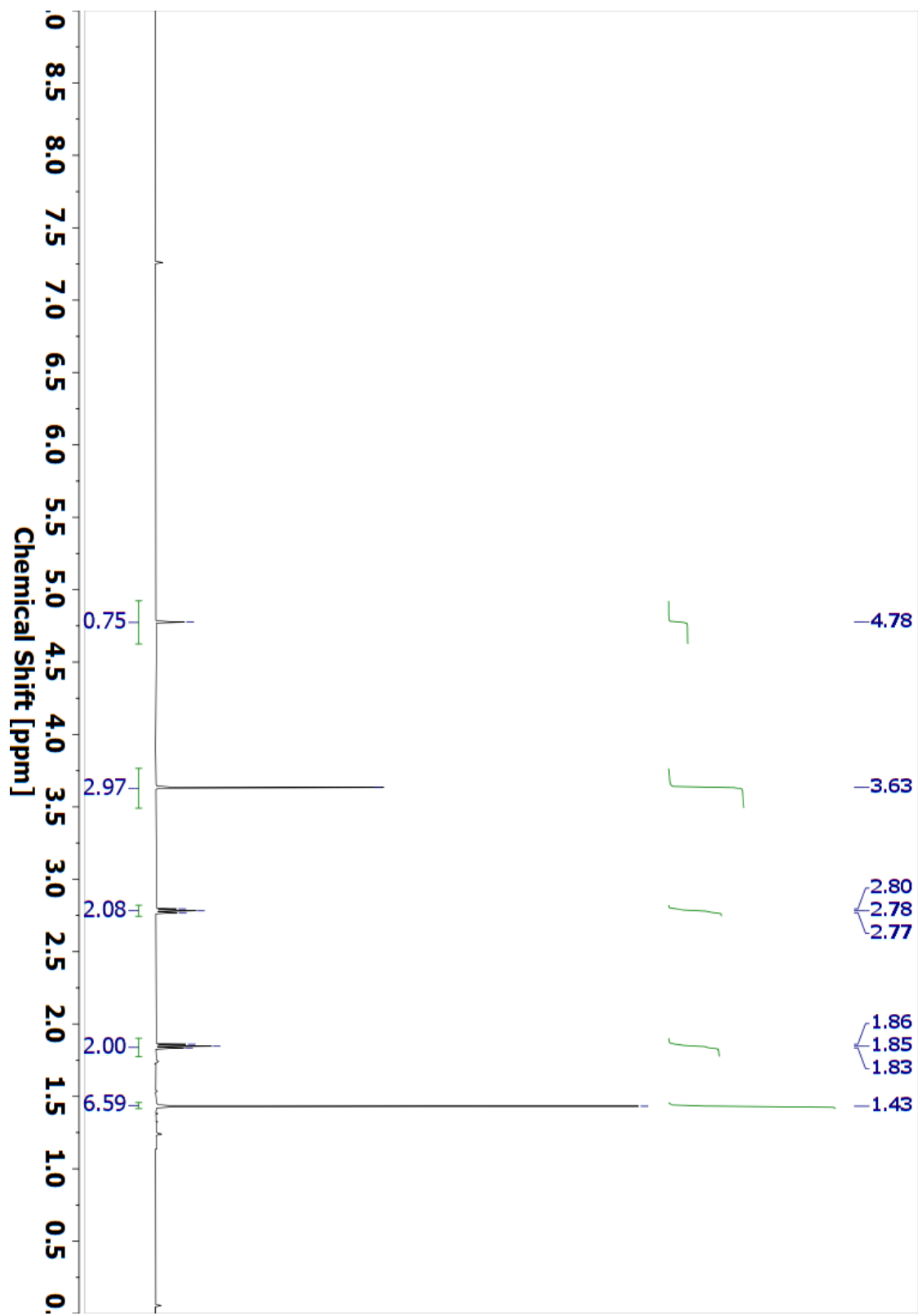


The reaction was carried out at 25 °C with 5 mol% catalyst loading following procedure C (3 h, 86% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.0 mg (70% yield) of product as colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 4.78 (s, 1H), 3.63 (s, 3H), 2.78 (t, $J = 7.8$ Hz, 2H), 1.85 (t, $J = 7.8$ Hz, 2H), 1.43 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.83, 166.52, 90.50, 87.16, 50.59, 35.33, 32.60, 27.31. HRMS (ESI $^+$) m/z Calc. 171.1016 [$\text{C}_9\text{H}_{14}\text{O}_3+\text{H}$] $^+$, Found. 171.1014 [$\text{M}+\text{H}$] $^+$.

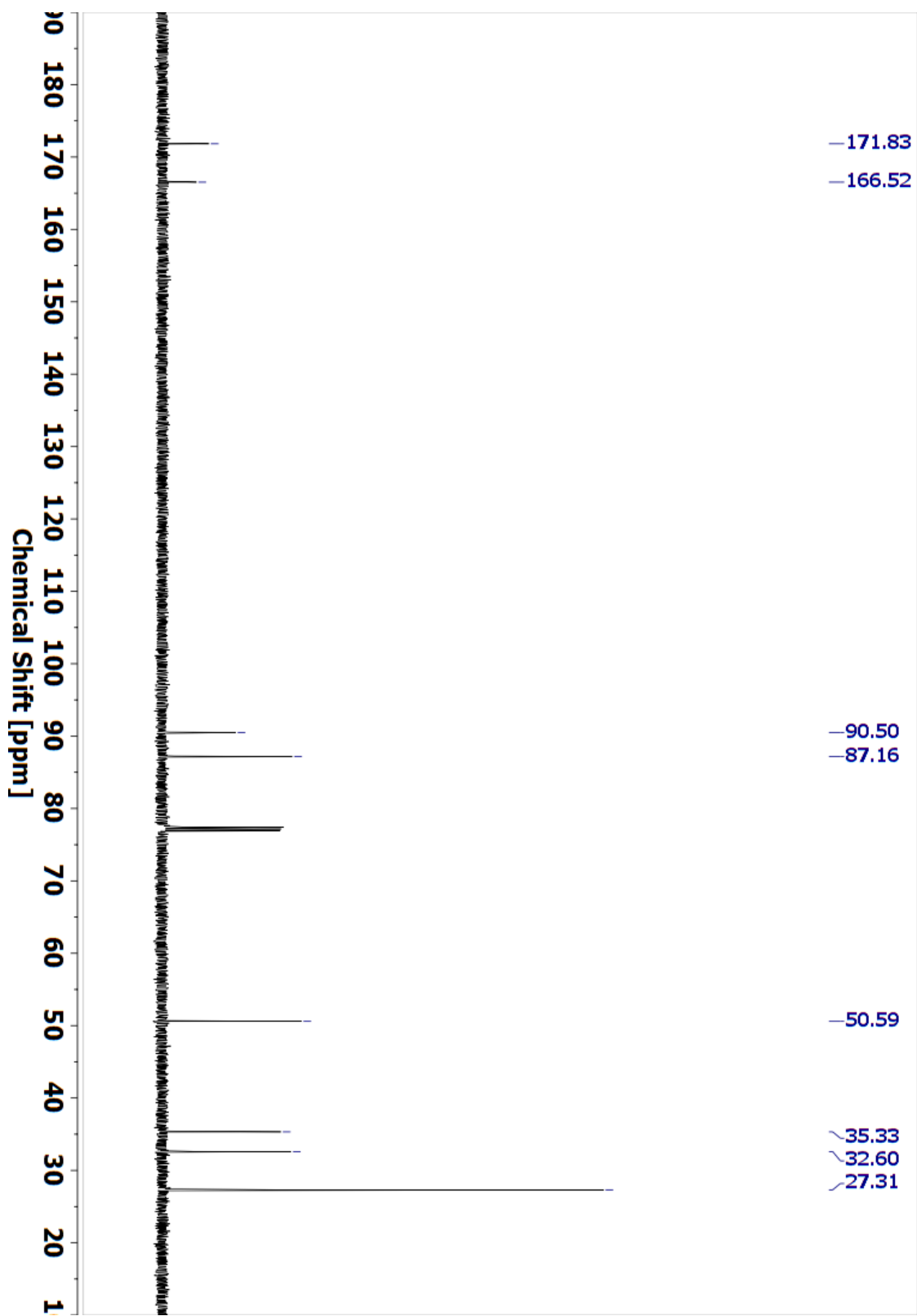
Scale-up: The reaction was carried out at 25 °C with 5 mol% catalyst loading following procedure C for 3 h with 250 mg of α -diazo- β -ketoester in 25 ml of benzene to give 203 mg (95% yield) of product as a colorless oil.



Crude NMR spectrum for reaction carried out at 25 °C with 5 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

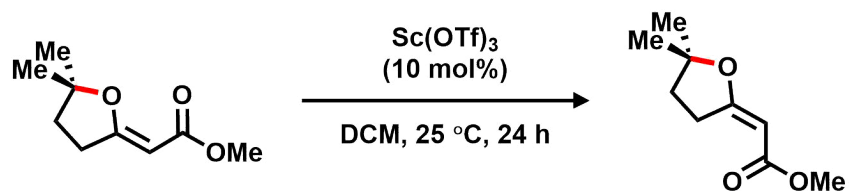


^1H NMR spectrum of isolated product in CDCl_3

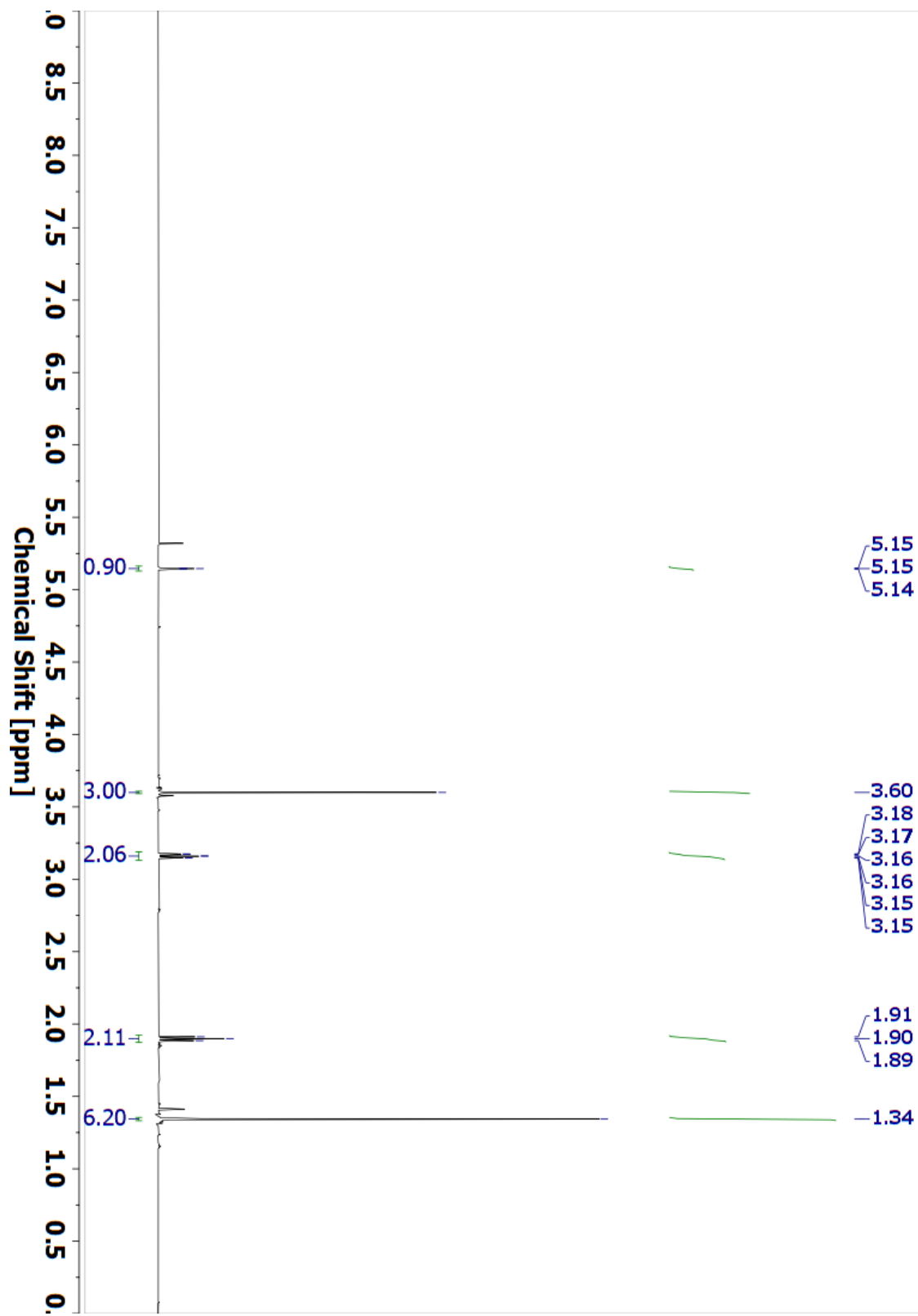


¹³C NMR spectrum of isolated product in CDCl₃

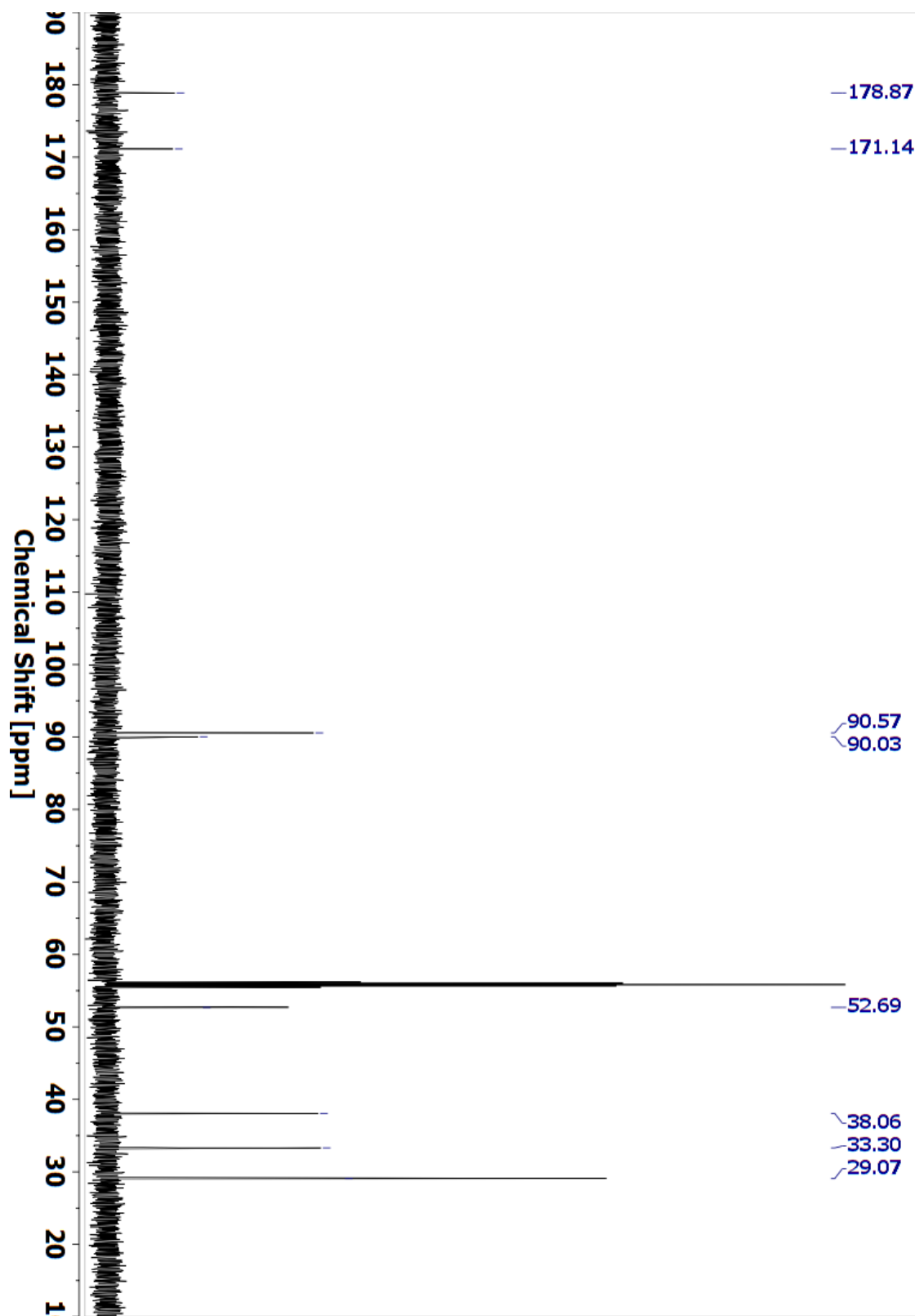
Methyl (E)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (3')



The reaction was run on 20.0 mg scale of starting material following procedure E to give 12.1 mg (60% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 5.15 (t, *J* = 1.8 Hz, 1H), 3.60 (s, 3H), 3.16 (td, *J* = 7.9, 1.8 Hz, 2H), 1.90 (t, *J* = 7.9 Hz, 2H), 1.34 (s, 6H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 178.87, 171.14, 90.57, 90.03, 52.69, 38.06, 33.30, 29.07.

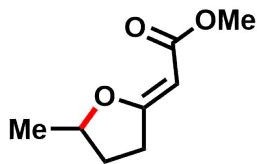


^1H NMR spectrum of isolated product in CD_2Cl_2

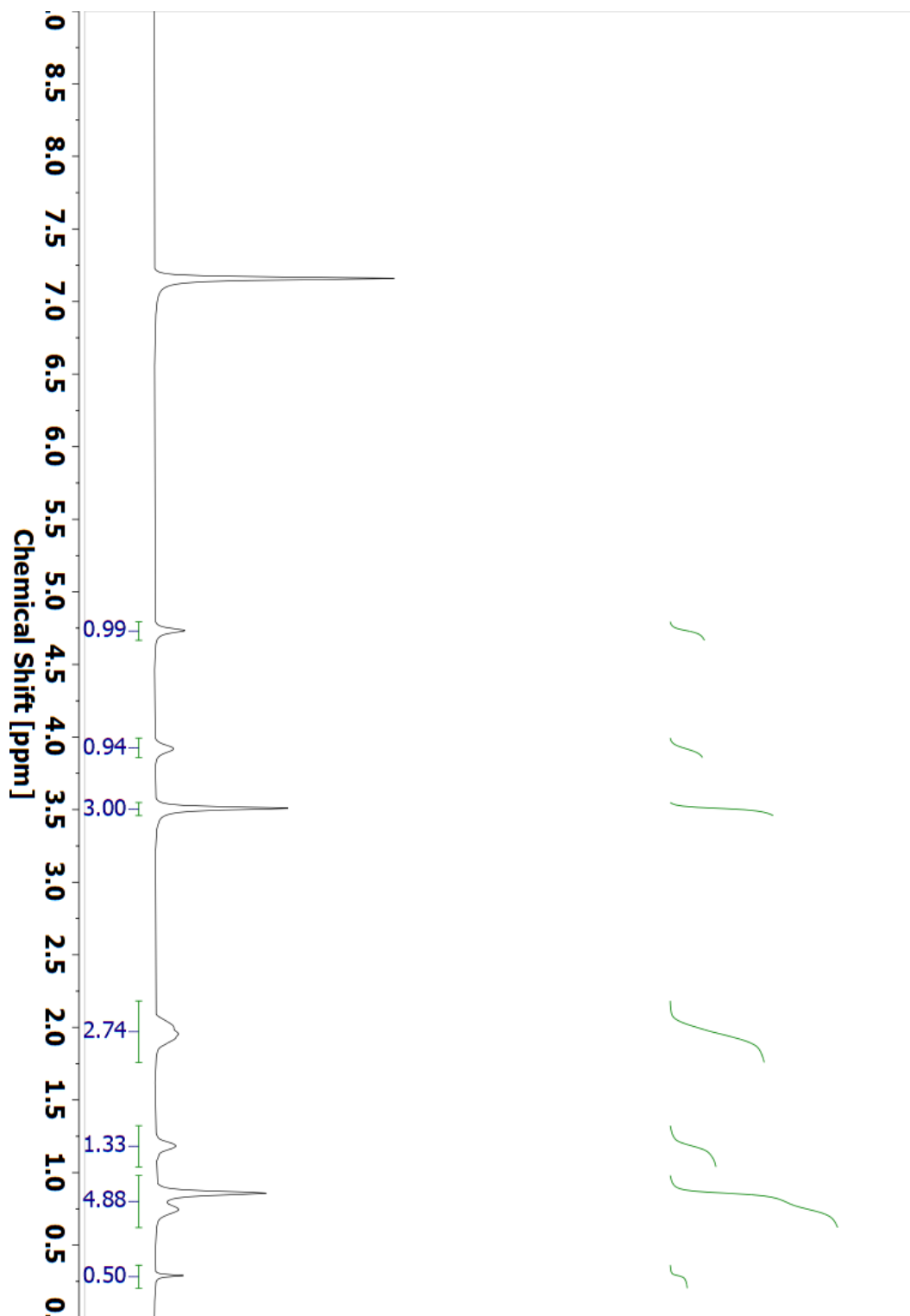


^{13}C NMR spectrum of isolated product in CD_2Cl_2

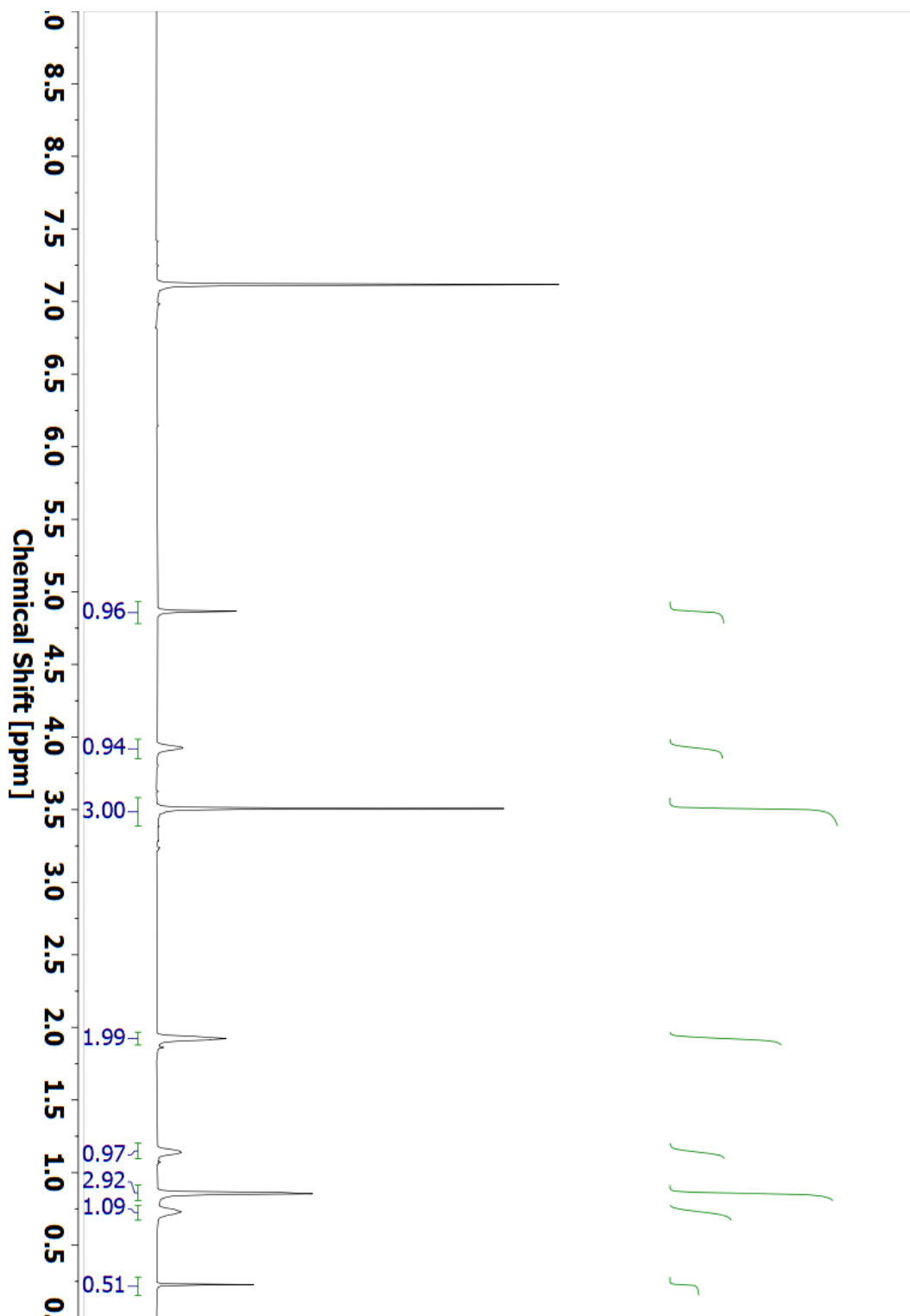
Methyl (Z)-2-(5-methyldihydrofuran-2(3H)-ylidene)acetate (4)



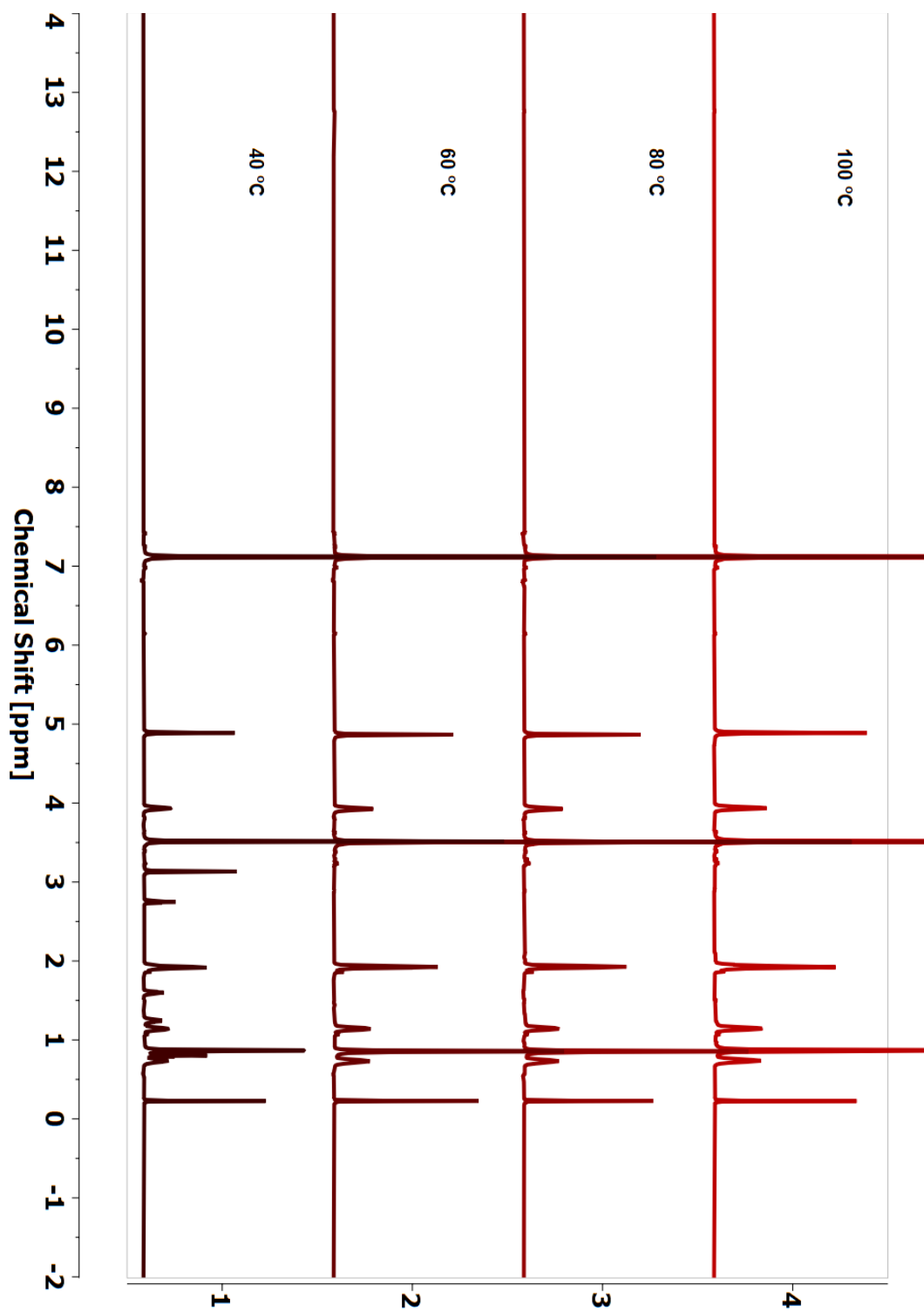
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 88% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 83% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.7 mg (63% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 4.78 (s, 1H), 4.73–4.64 (m, 1H), 3.59 (s, 3H), 2.78–2.65 (m, 2H), 2.19–2.10 (m, 1H), 1.68–1.56 (m, 1H), 1.41 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 172.58, 166.28, 87.25, 83.49, 50.62, 32.94, 30.76, 20.61. HRMS (ESI $^+$) m/z Calc. 157.0859 [$\text{C}_8\text{H}_{12}\text{O}_3 + \text{H}$] $^+$, Found. 157.0859 [$\text{M} + \text{H}$] $^+$.



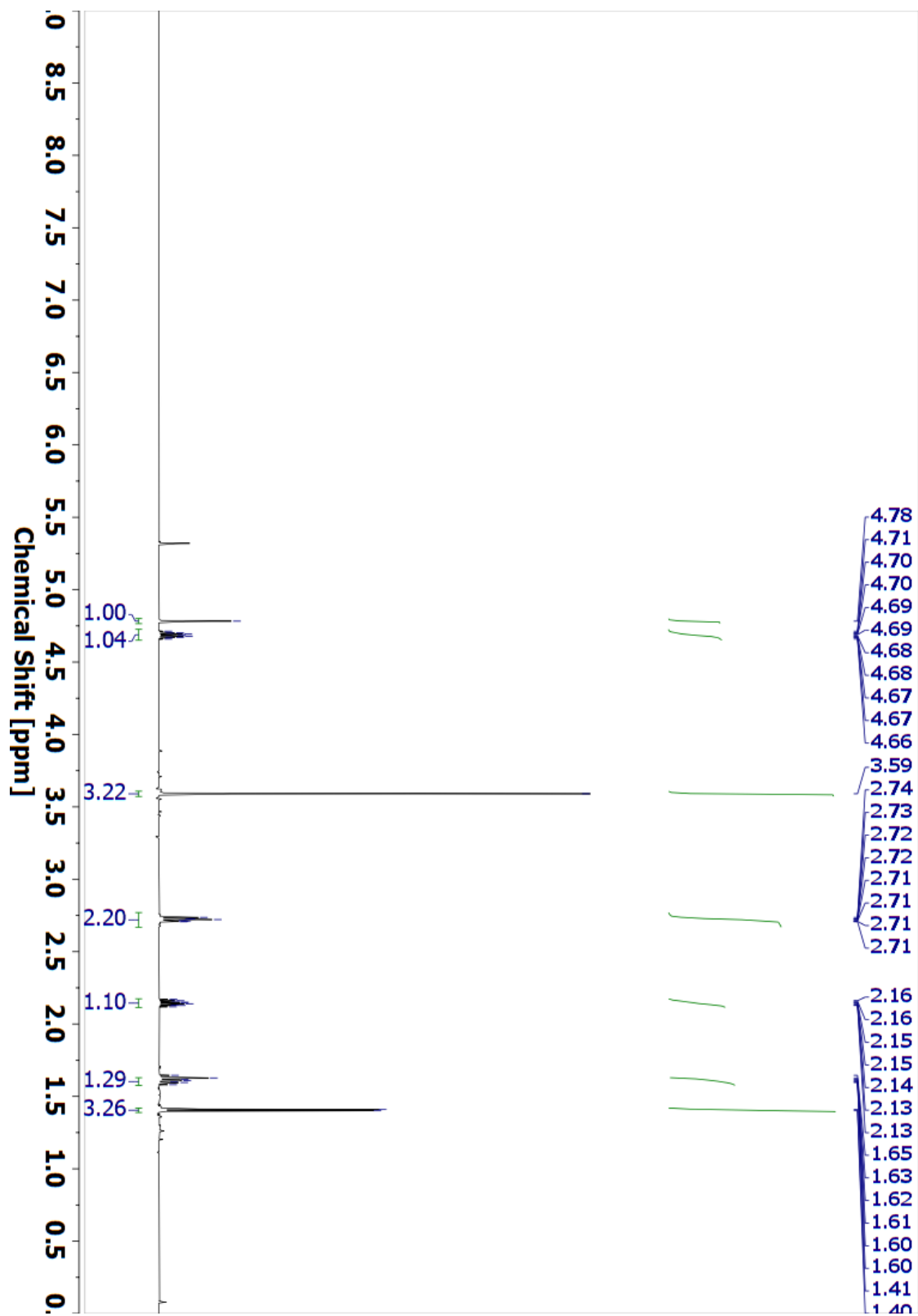
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).



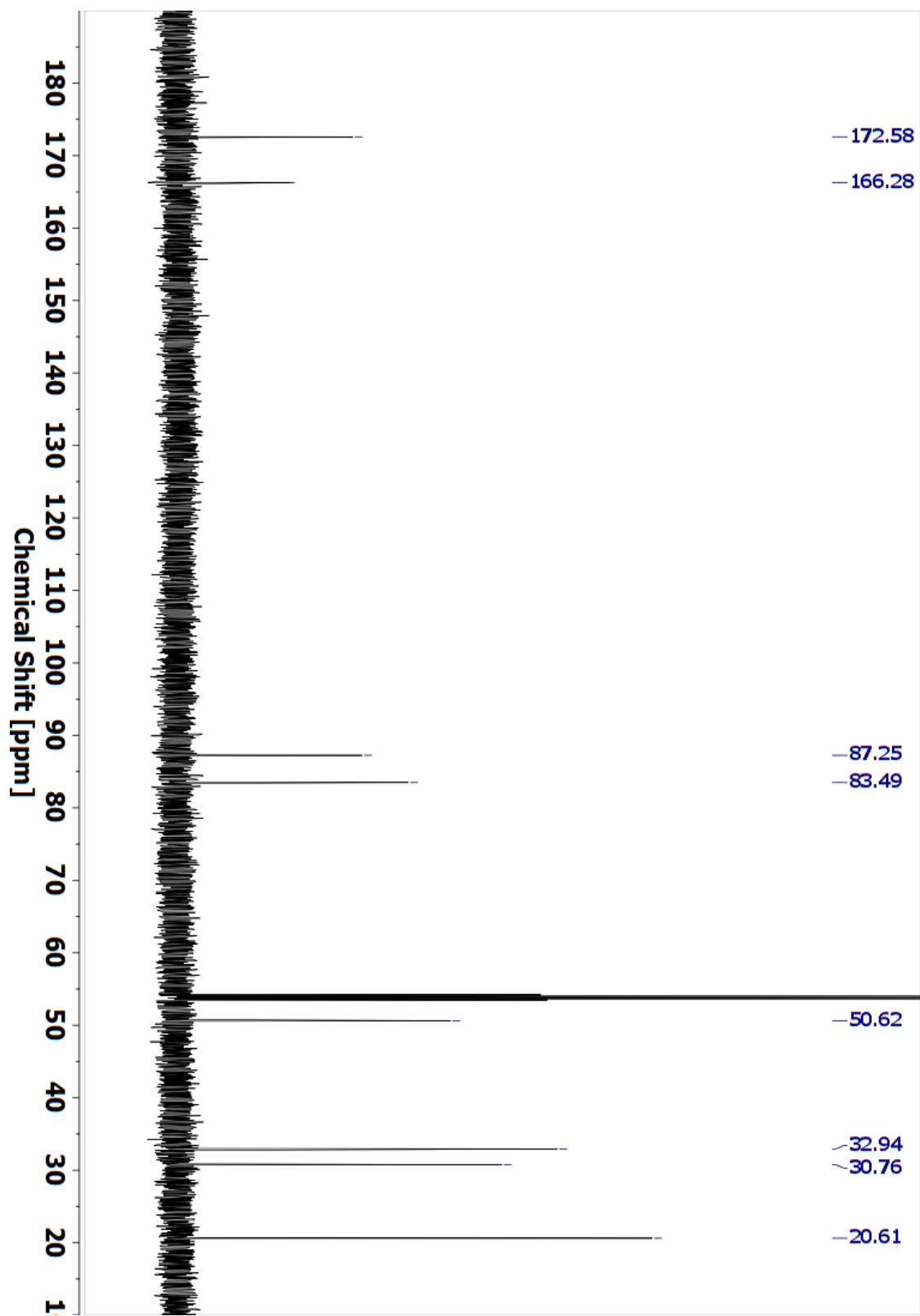
Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).



Diamagnetic region of the crude NMR spectrum for reaction carried out at 40, 60, 80 and 100 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard), showing at least 60 °C is required to achieve full conversion of the starting material.

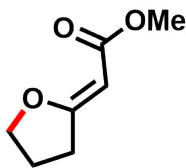


¹H NMR spectrum of isolated product in CD₂Cl₂

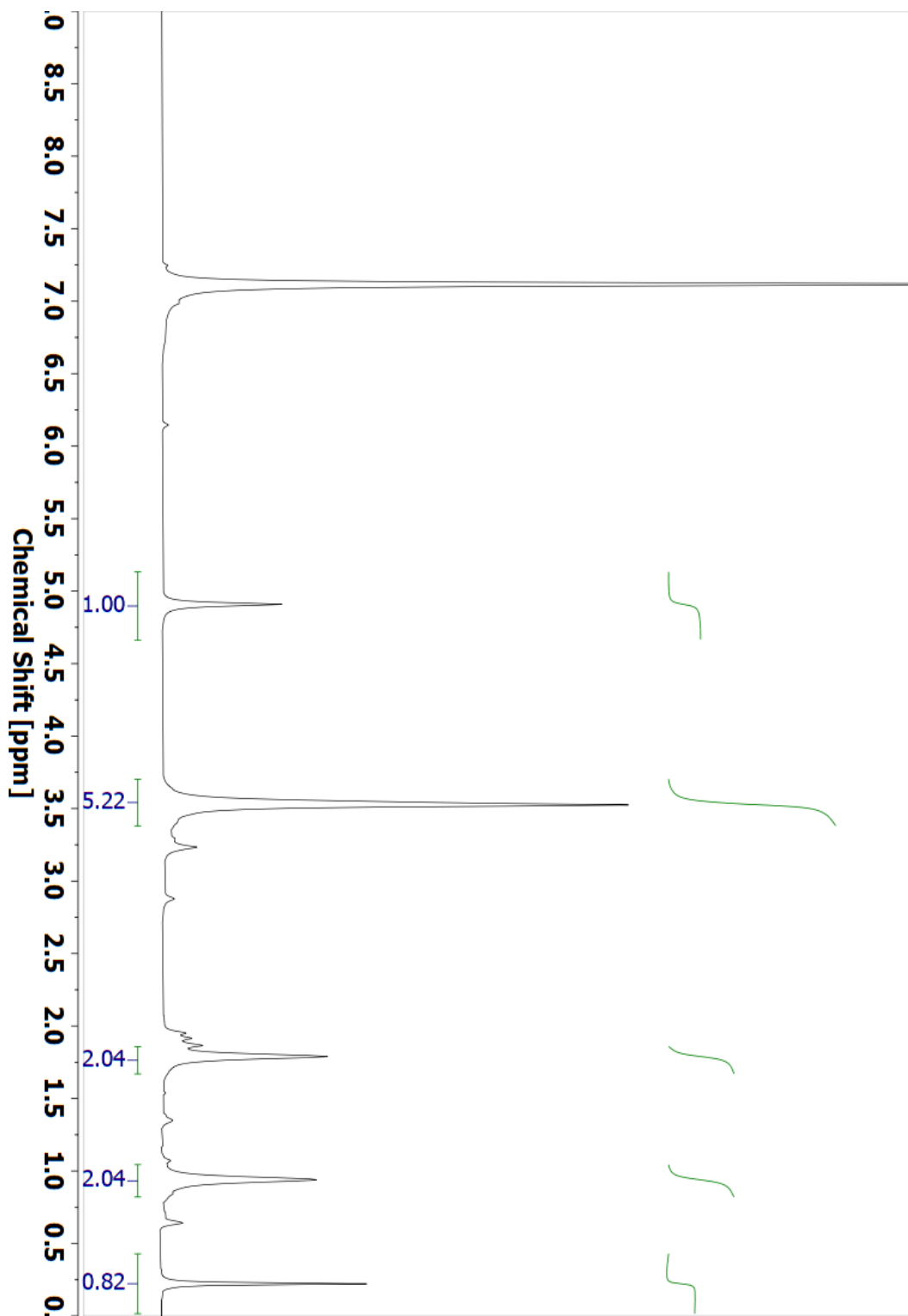


^{13}C NMR spectrum of isolated product in CD_2Cl_2

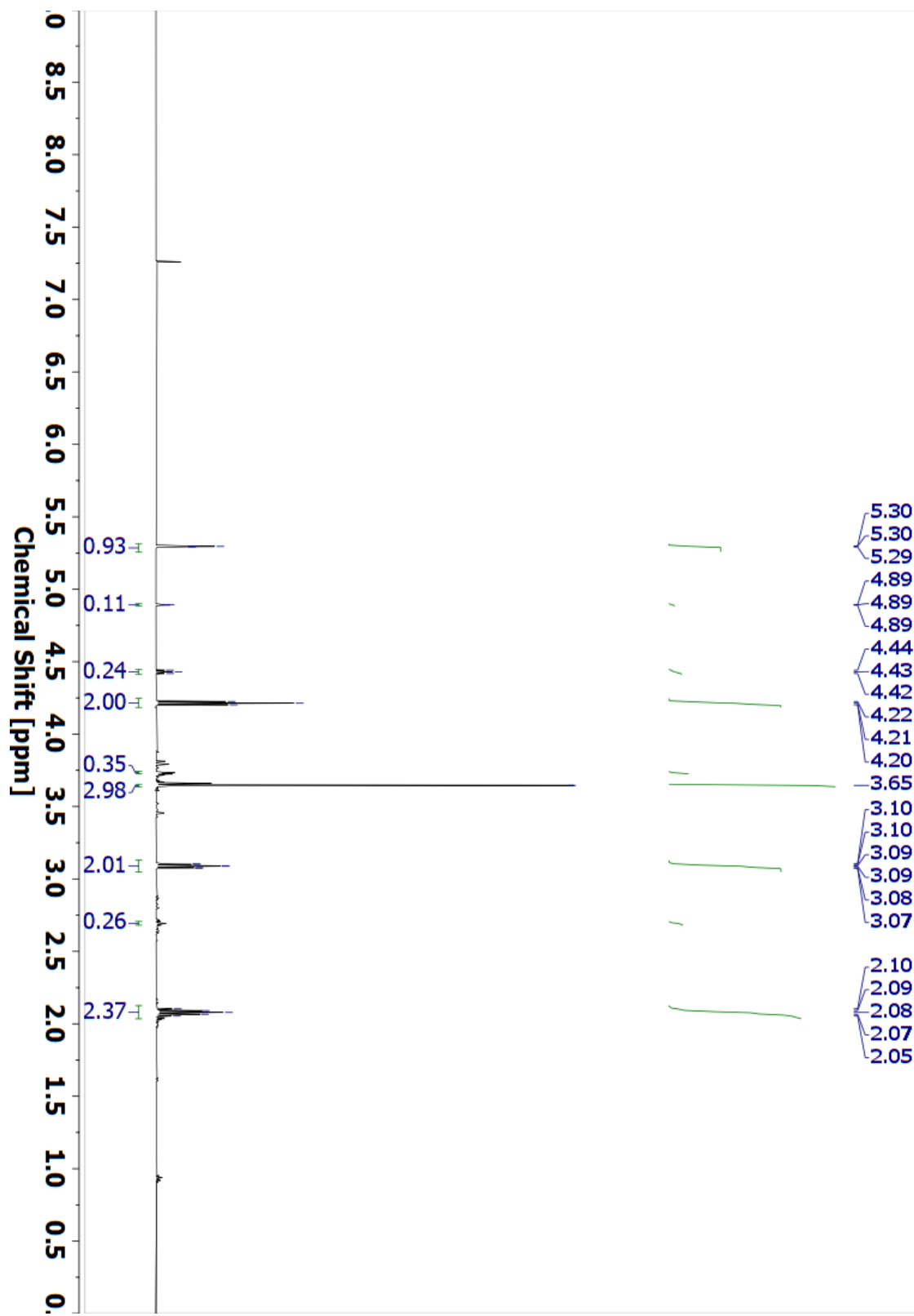
Methyl (Z)-2-(dihydrofuran-2(3H)-ylidene)acetate (5)



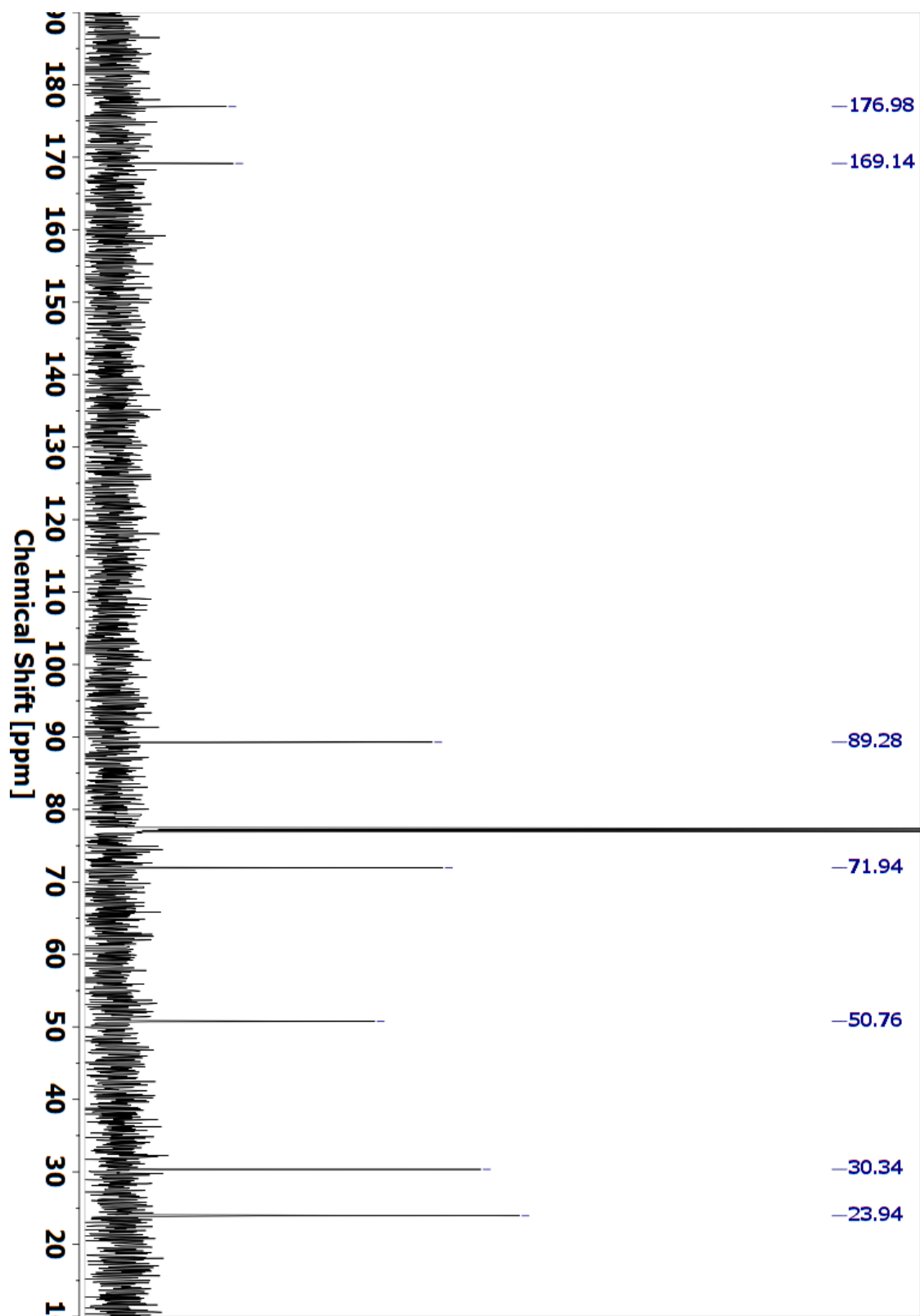
The reaction was carried out at 100 °C with 30 mol% catalyst loading following procedure D (20 h, 49% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 4.4 mg (26% yield, 89% *E*- : 11% *Z*-isomer) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 5.30 (t, $J = 1.8$ Hz, 1H), 4.21 (t, $J = 7.0$ Hz, 2H), 3.65 (s, 3H), 3.09 (td, $J = 7.8, 1.8$ Hz, 2H), 2.11–2.05 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ (*E*-isomer) 176.98, 169.14, 89.28, 71.94, 50.76, 30.34, 23.94. The spectroscopic features match the reported data.¹⁷ Despite the formation of a single species (*Z*-isomer), quick isomerization of the product in polar solvent CDCl_3 resulted in a mixture with a majority of the *E*-isomer. The same ratio is also reported previously.¹⁷



Crude NMR spectrum for reaction carried out at 100 °C with 30 mol% Fe(acac)₂ after 20 min
(0.5 mg Si(SiMe₃)₄ as internal standard).

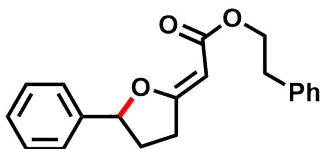


^1H NMR spectrum of isolated product in CDCl_3 (89% *E*- : 11% *Z*-isomer)

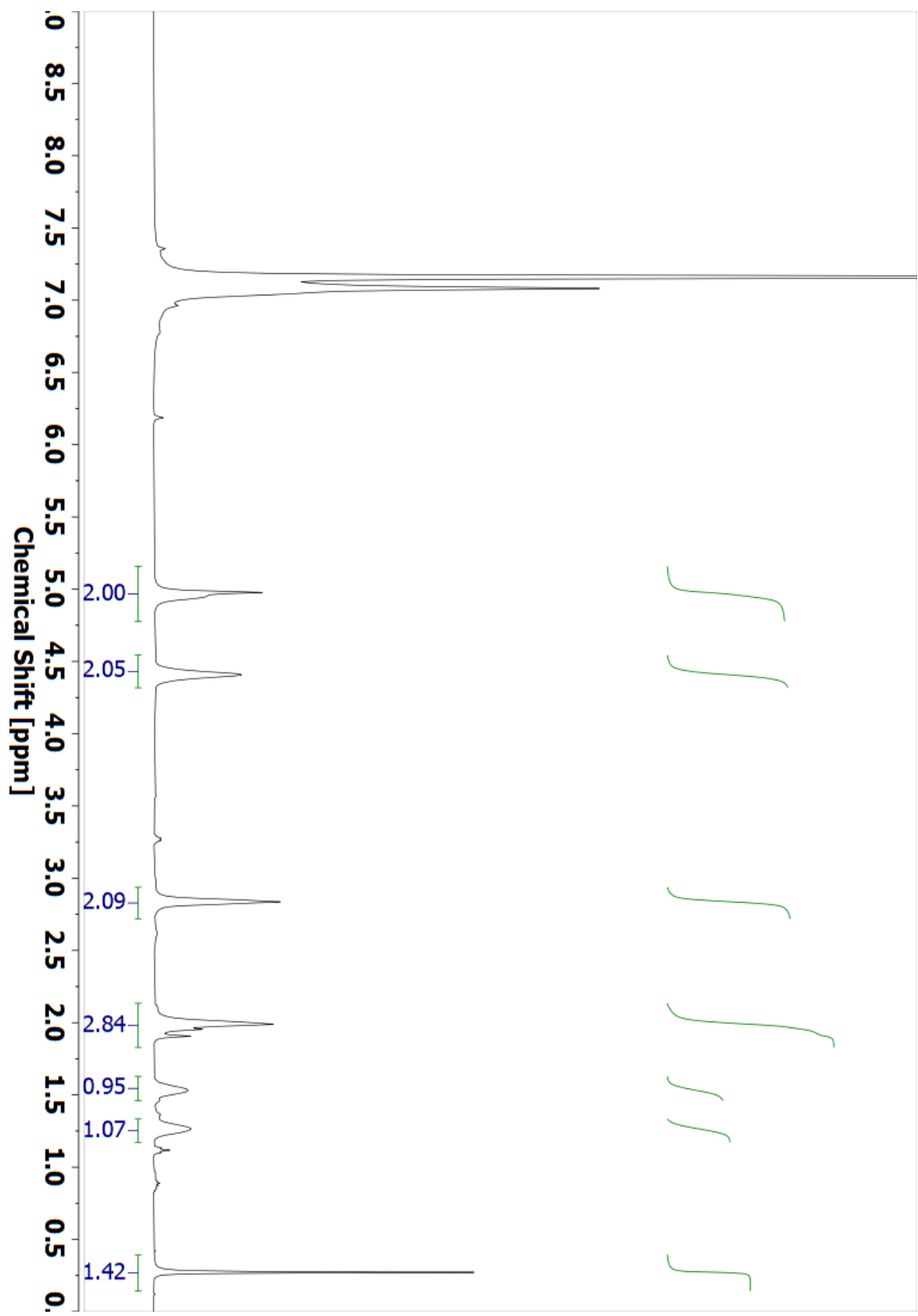


¹³C NMR spectrum of isolated product in CDCl₃

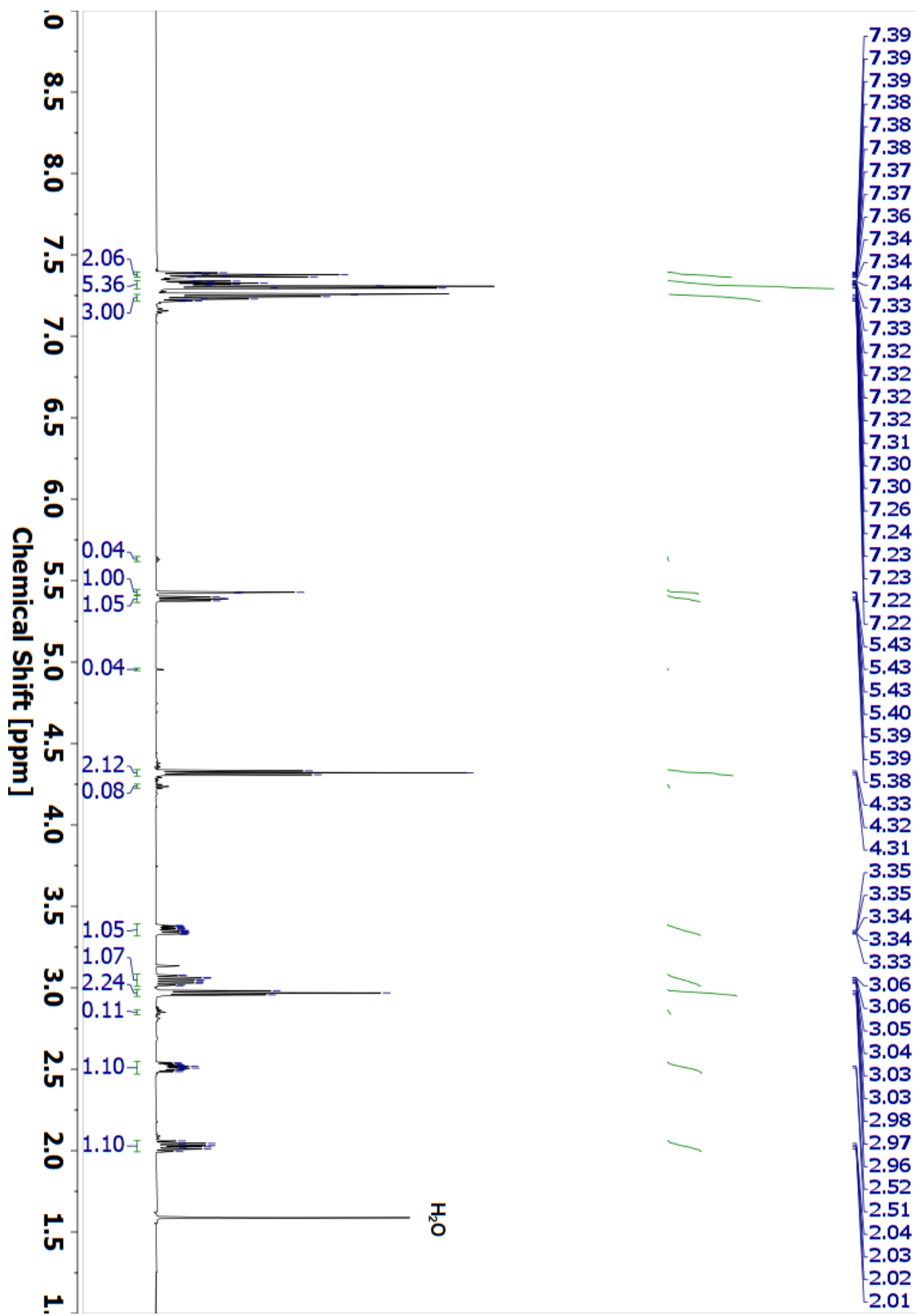
Phenethyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (10)



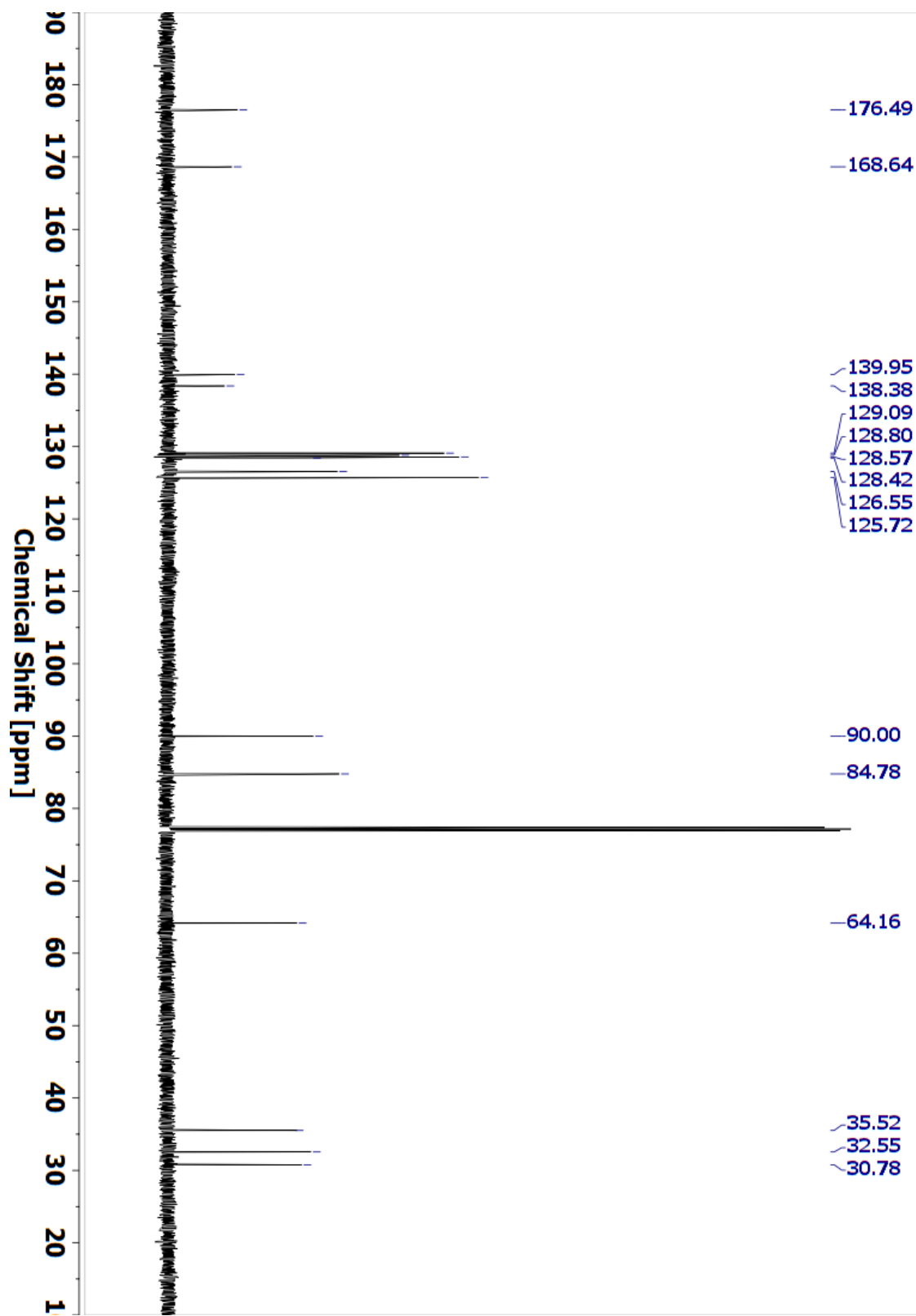
The reaction was carried out at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 61% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.1 mg (55% yield, 96% *Z*- : 4% *E*-isomer) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.36 (m, 2H), 7.34–7.29 (m, 5H), 7.26–7.21 (m, 3H), 5.43 (t, J = 1.8 Hz, 1H), 5.39 (dd, J = 8.4, 6.5 Hz, 1H), 4.32 (t, J = 7.1 Hz, 2H), 3.36 (dddd, J = 18.3, 8.7, 4.2, 1.6 Hz, 1H), 3.09–2.99 (m, 1H), 2.97 (t, J = 7.1 Hz, 2H), 2.55–2.47 (m, 1H), 2.07–1.99 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.49, 168.64, 139.95, 138.38, 129.09, 128.80, 128.57, 128.42, 126.55, 125.72, 90.00, 84.78, 64.16, 35.52, 32.55, 30.78. HRMS (ESI $^+$) m/z Calc. 309.1485 [$\text{C}_{20}\text{H}_{20}\text{O}_3+\text{H}$] $^+$, Found. 309.1487 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

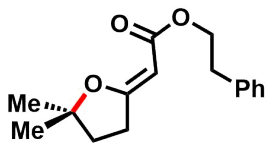


¹H NMR spectrum of isolated product in CDCl₃ (96% *Z*- : 4% *E*-isomer)

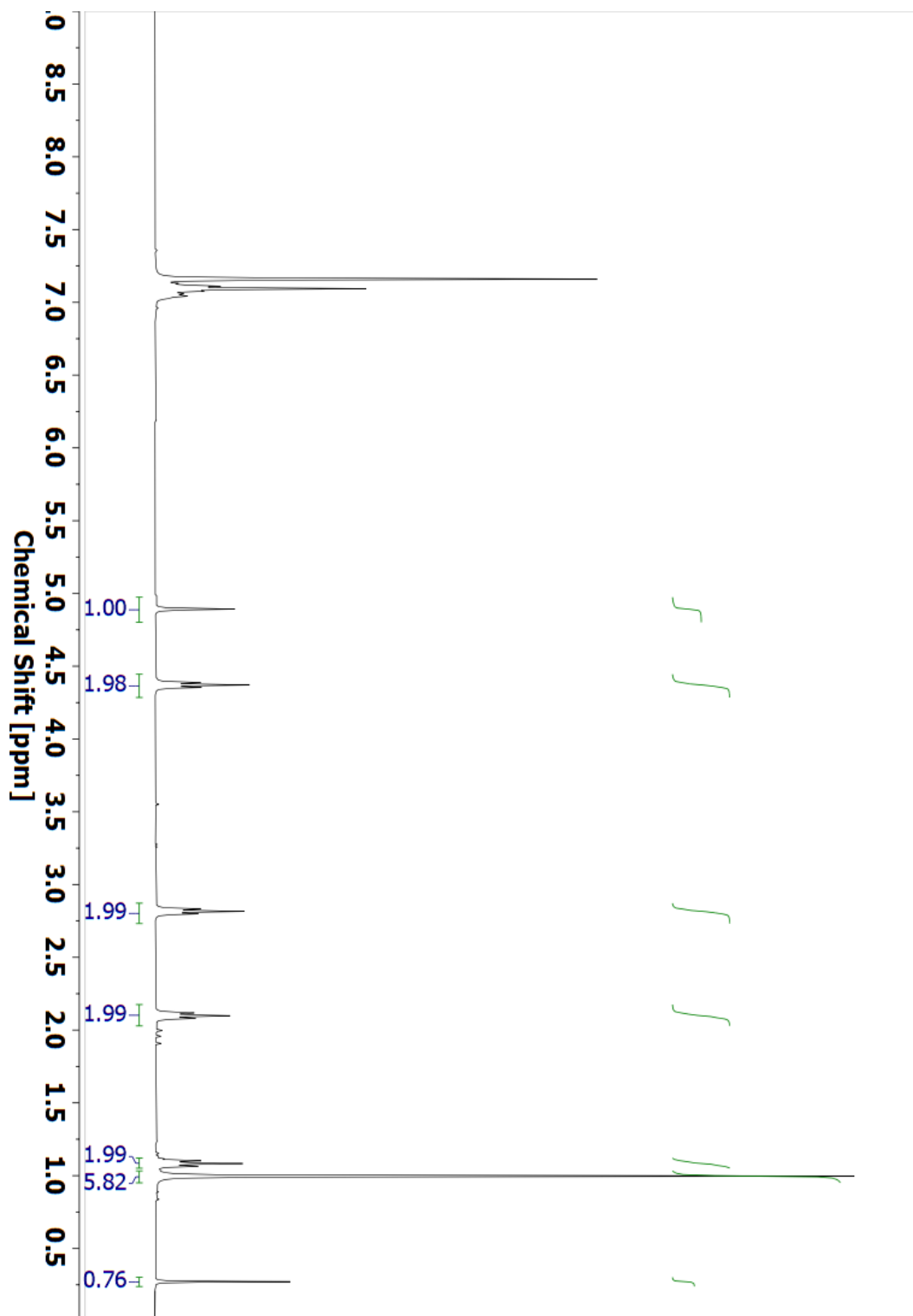


¹³C NMR spectrum of isolated product in CDCl₃

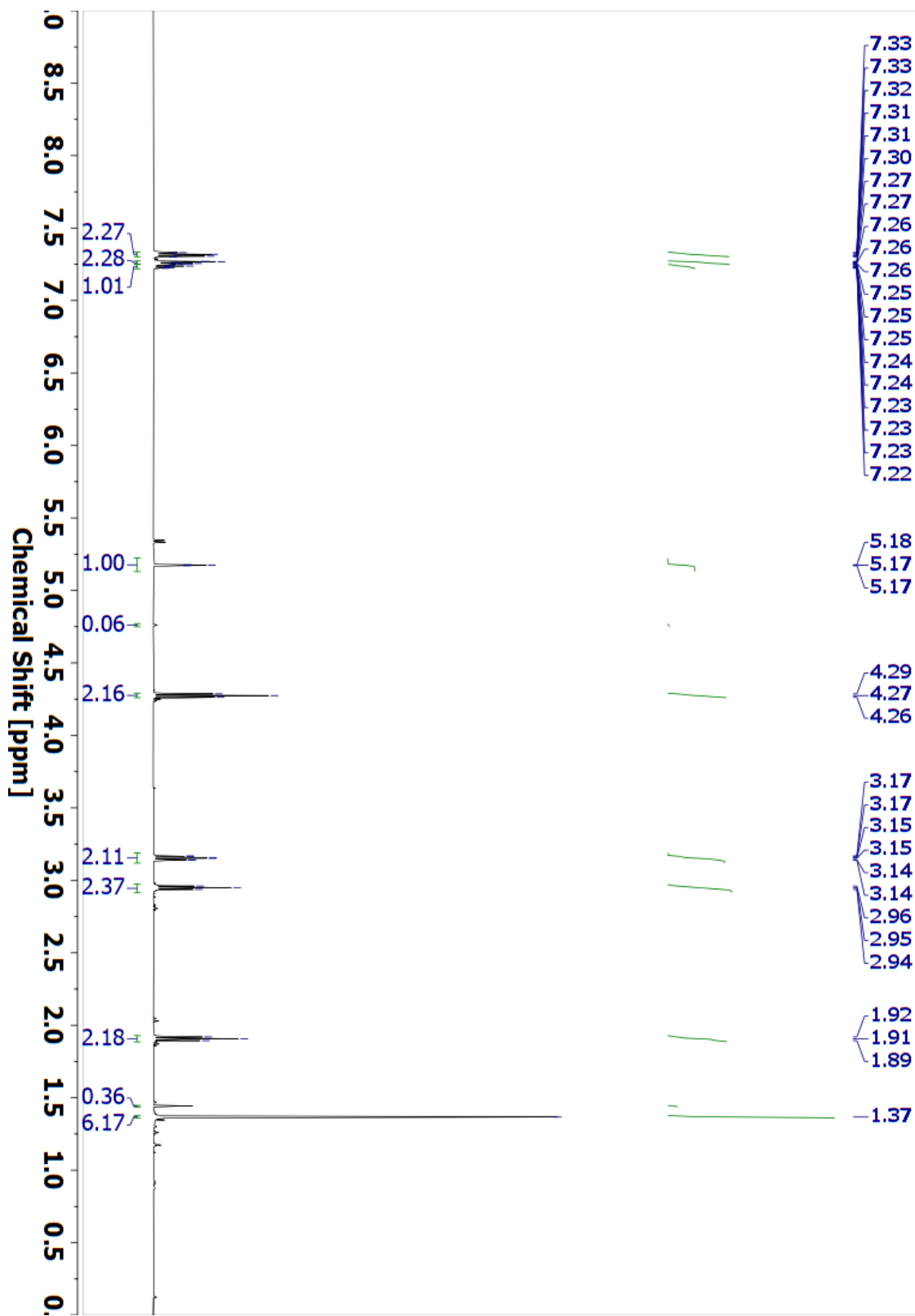
Phenethyl (Z)-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (11)



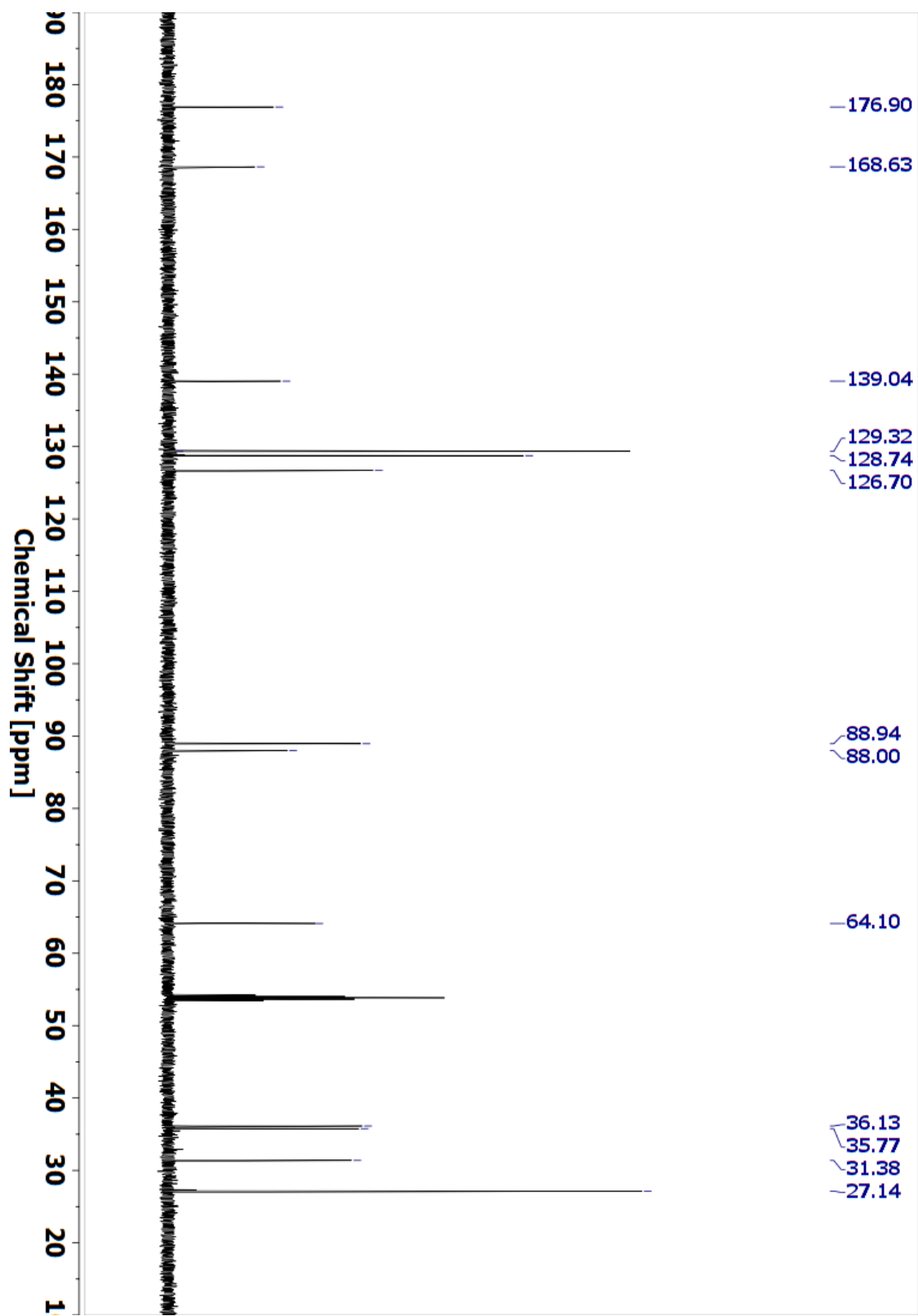
The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 96% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.3 mg (68% yield, 96% *Z*- : 4% *E*-isomer) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.34–7.30 (m, 2H), 7.28–7.25 (m, 2H), 7.25–7.22 (m, 1H), 5.17 (t, *J* = 1.8 Hz, 1H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.15 (td, *J* = 7.9, 1.8 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 1.91 (t, *J* = 7.8 Hz, 2H), 1.37 (s, 6H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 176.90, 168.63, 139.04, 129.32, 128.74, 126.70, 88.94, 88.00, 64.10, 36.13, 35.77, 31.38, 27.14. HRMS (ESI⁺) *m/z* Calc. 261.1485 [C₁₆H₂₀O₃+H]⁺, Found. 261.1485 [M+H]⁺.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

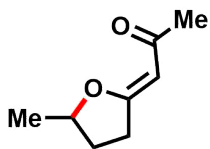


¹H NMR spectrum of isolated product in CD₂Cl₂ (96% Z- : 4% E-isomer)

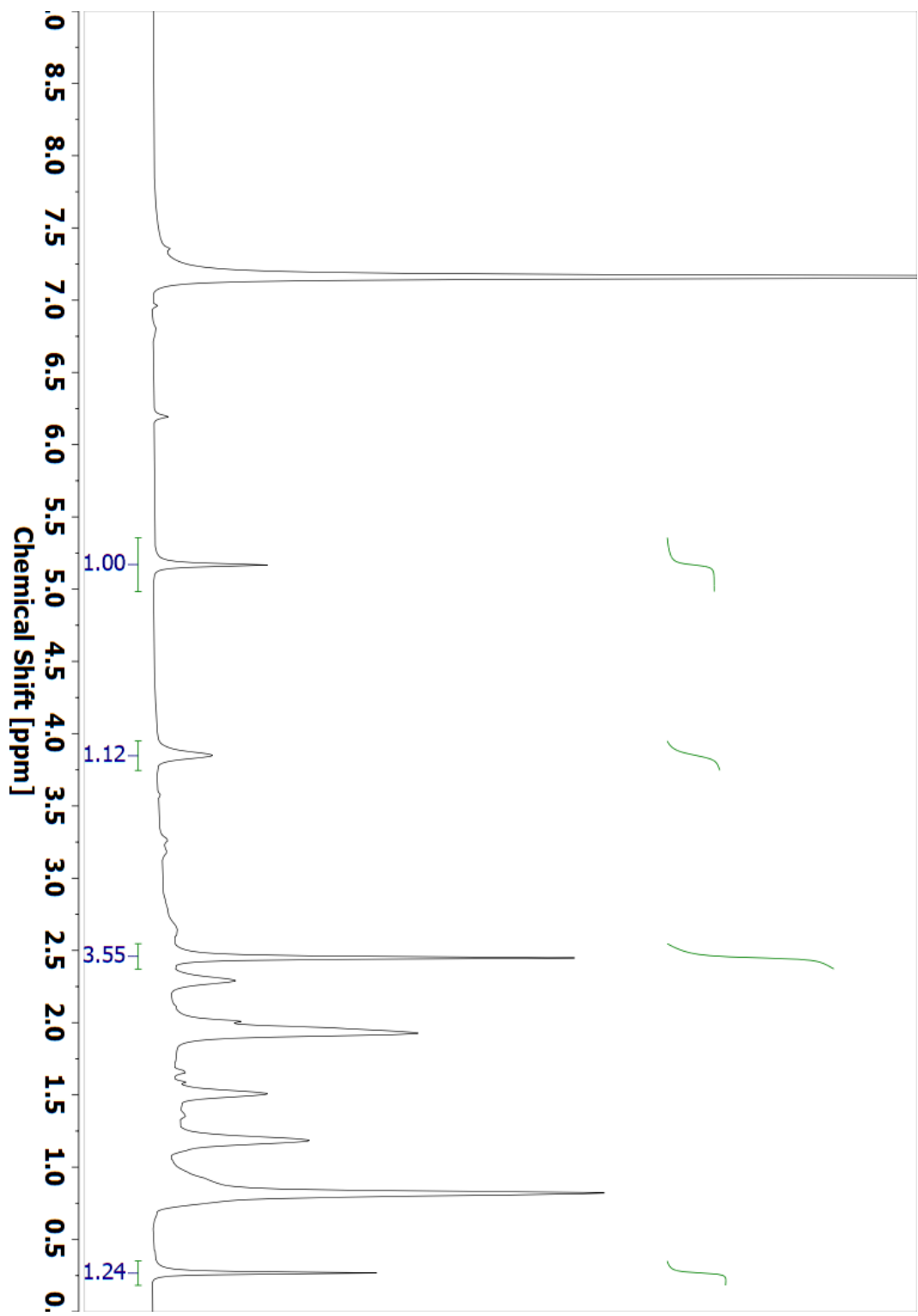


^{13}C NMR spectrum of isolated product in CD_2Cl_2

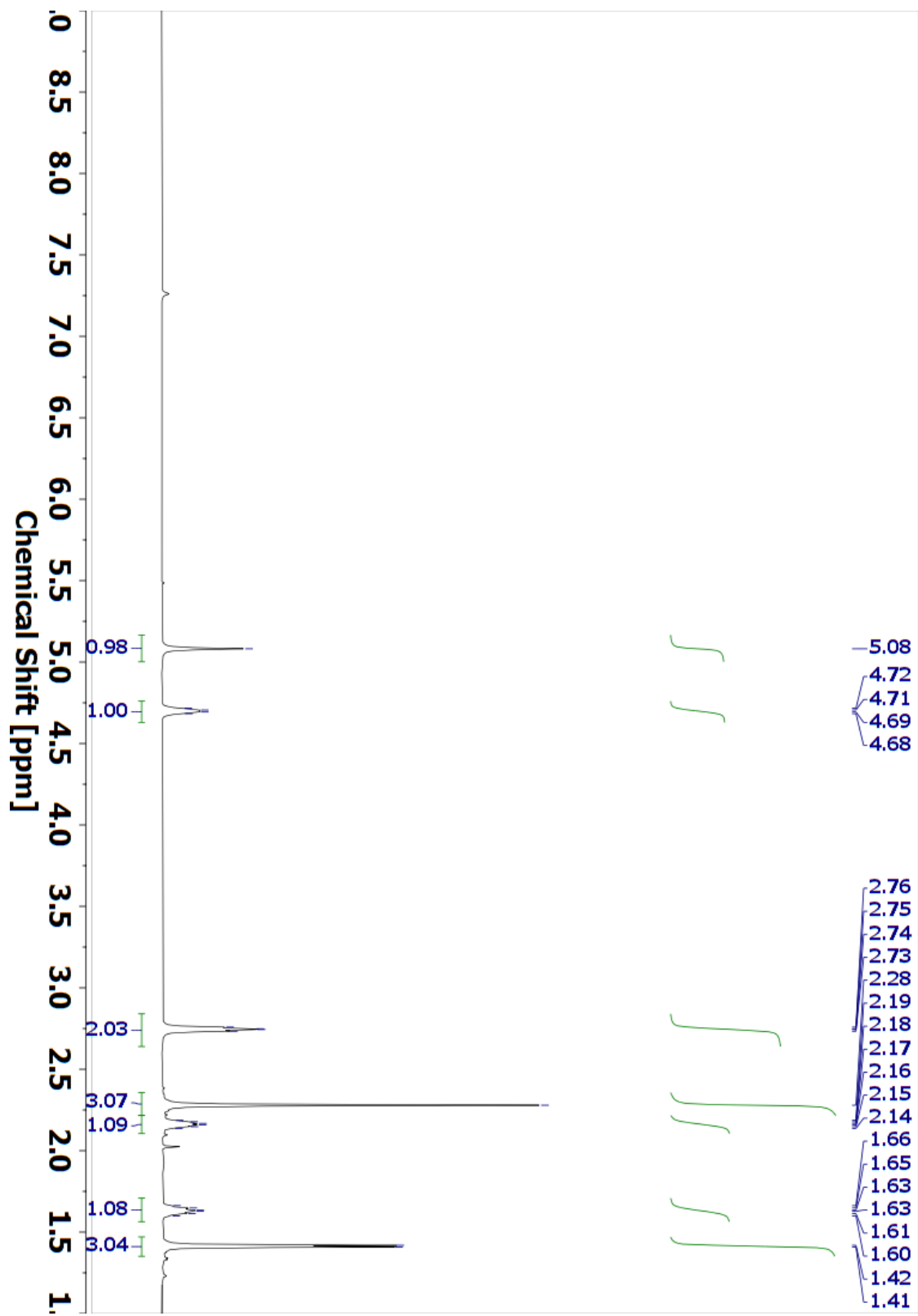
(Z)-1-(5-Methyldihydrofuran-2(3H)-ylidene)propan-2-one (13)



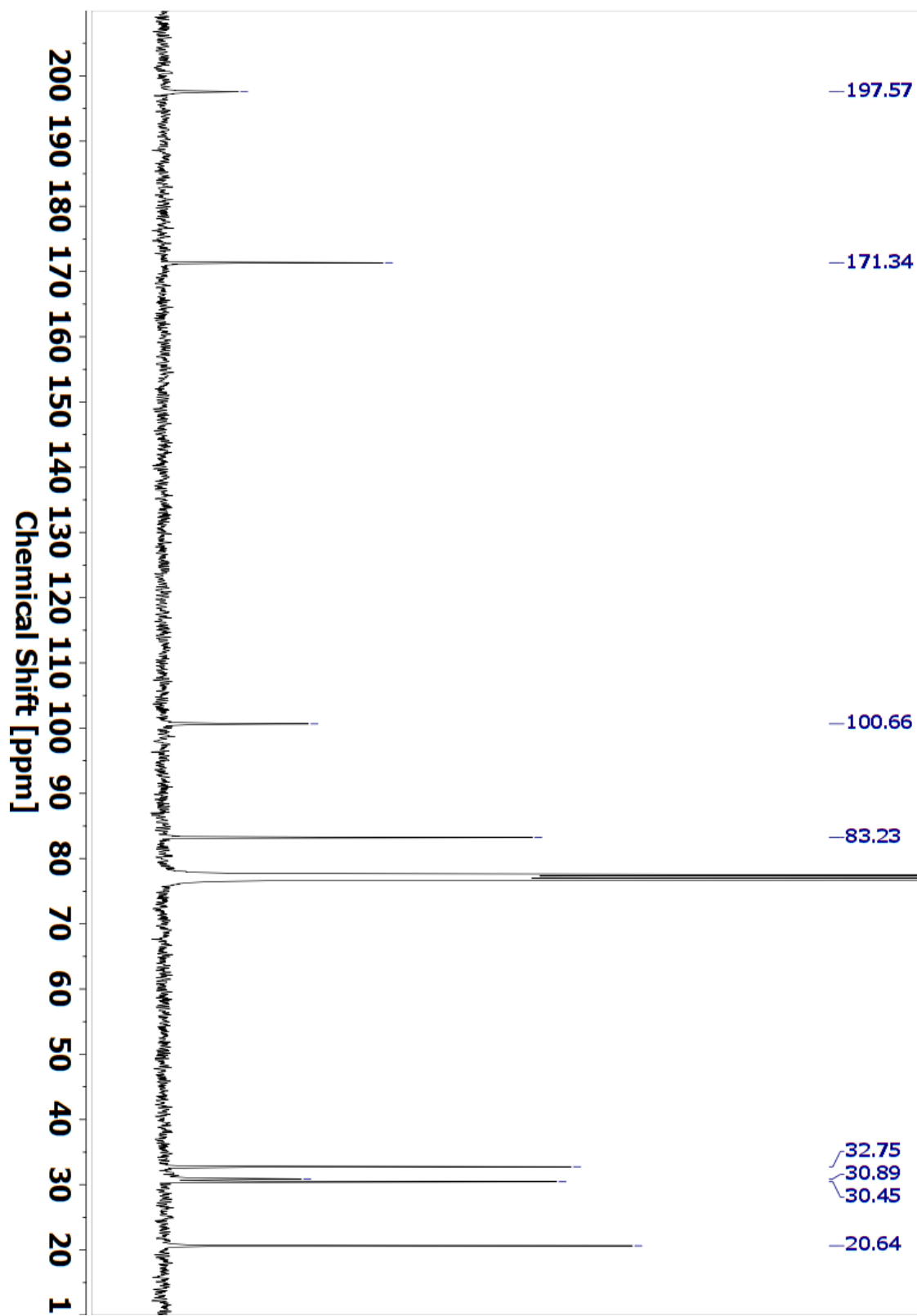
The reaction was carried out at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 32% NMR yield) with 20.0 mg of α -diazo- β -dione to give 4.0 mg (24% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 5.08 (s, 1H), 4.73–4.67 (m, 1H), 2.77–2.72 (m, 2H), 2.28 (s, 3H), 2.19–2.13 (m, 1H), 1.68–1.58 (m, 1H), 1.41 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.57, 171.34, 100.66, 83.23, 32.75, 30.89, 30.45, 20.64. HRMS (ESI+) m/z Calc. 141.0910 [$\text{C}_8\text{H}_{12}\text{O}_2+\text{H}$] $^+$, Found 141.0906 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).

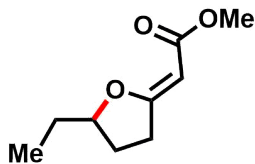


^1H NMR spectrum of isolated product in CDCl_3

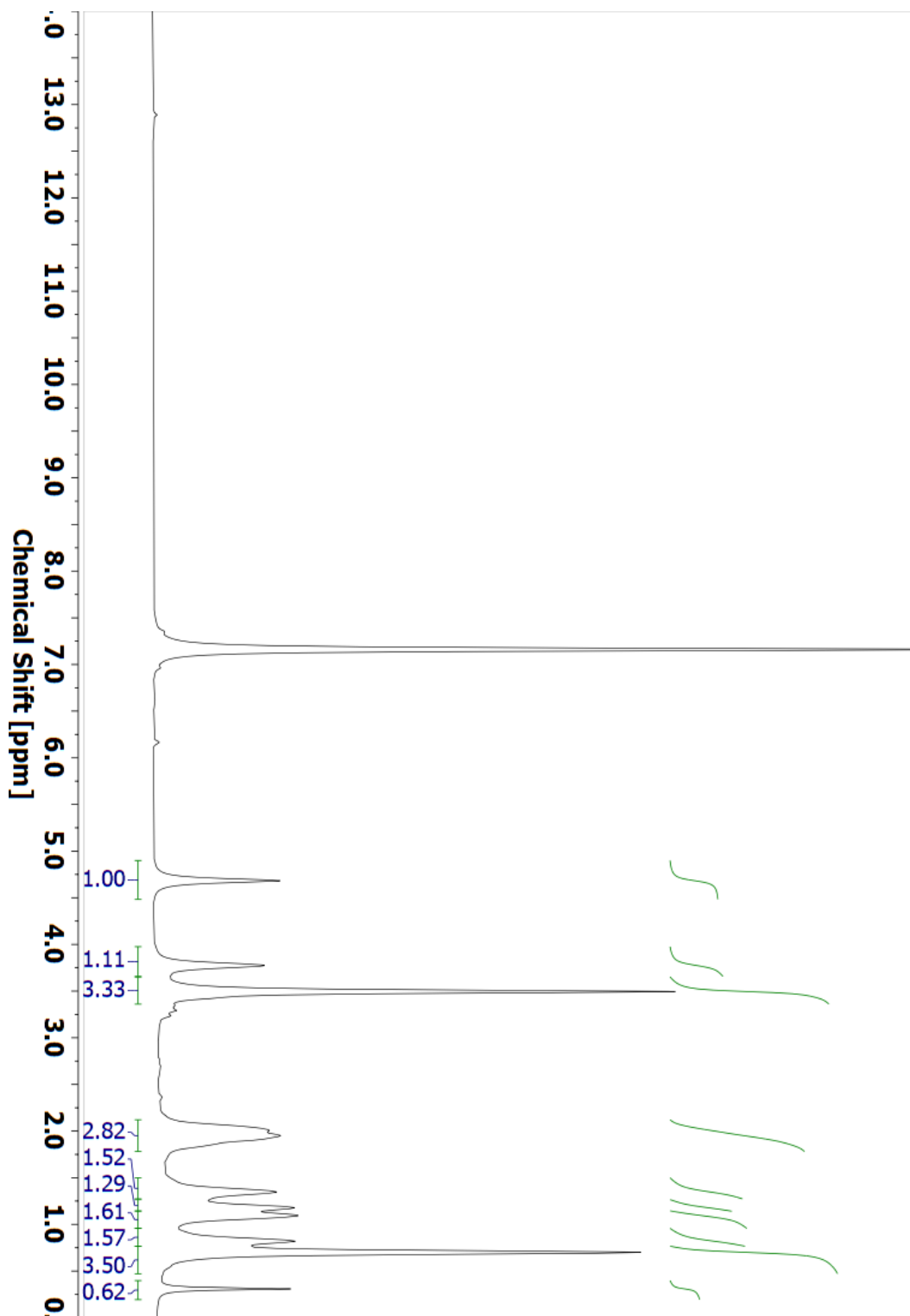


^{13}C NMR spectrum of isolated product in CDCl_3

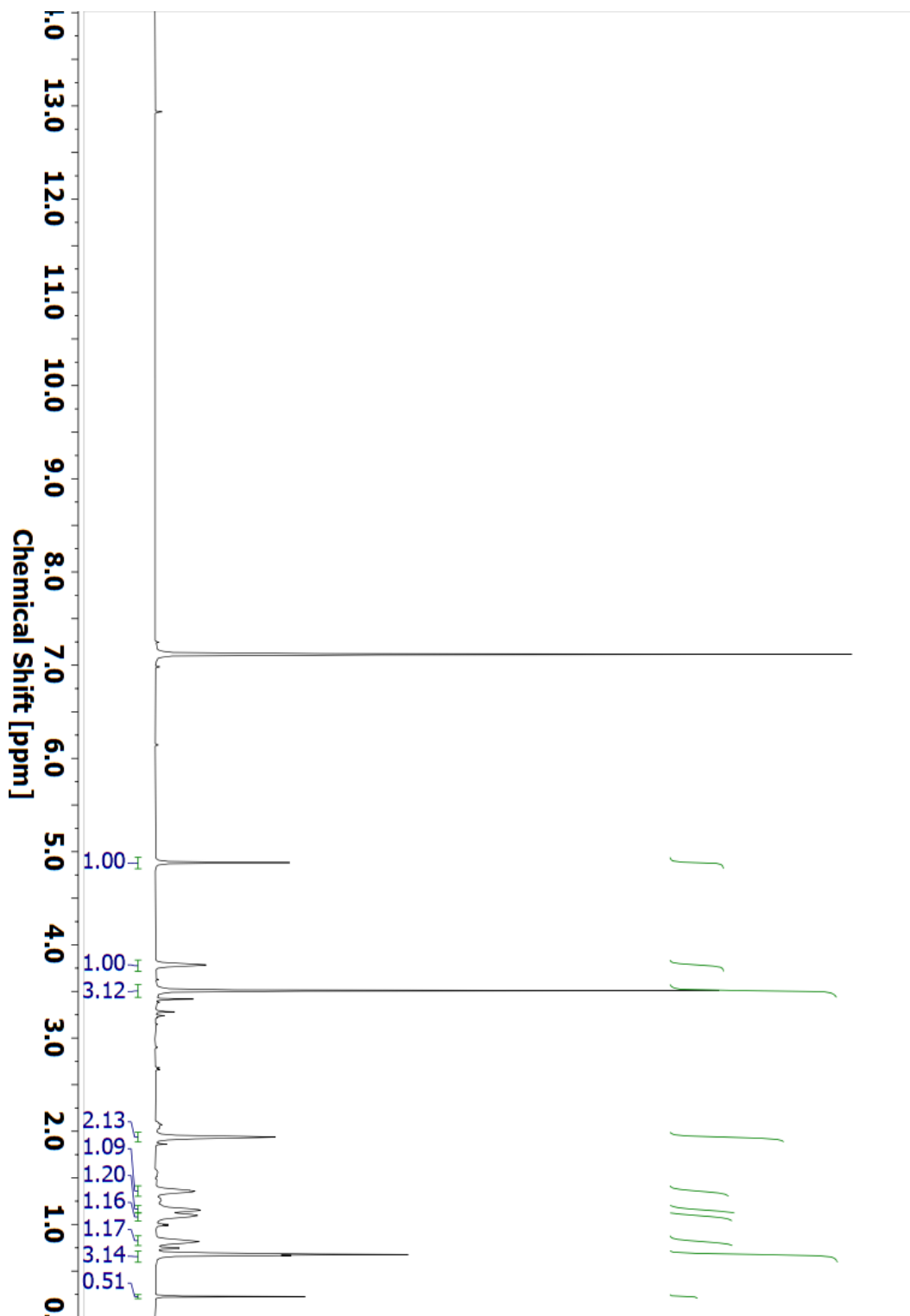
Methyl (Z)-2-(5-ethylidihydrofuran-2(3H)-ylidene)acetate (14)



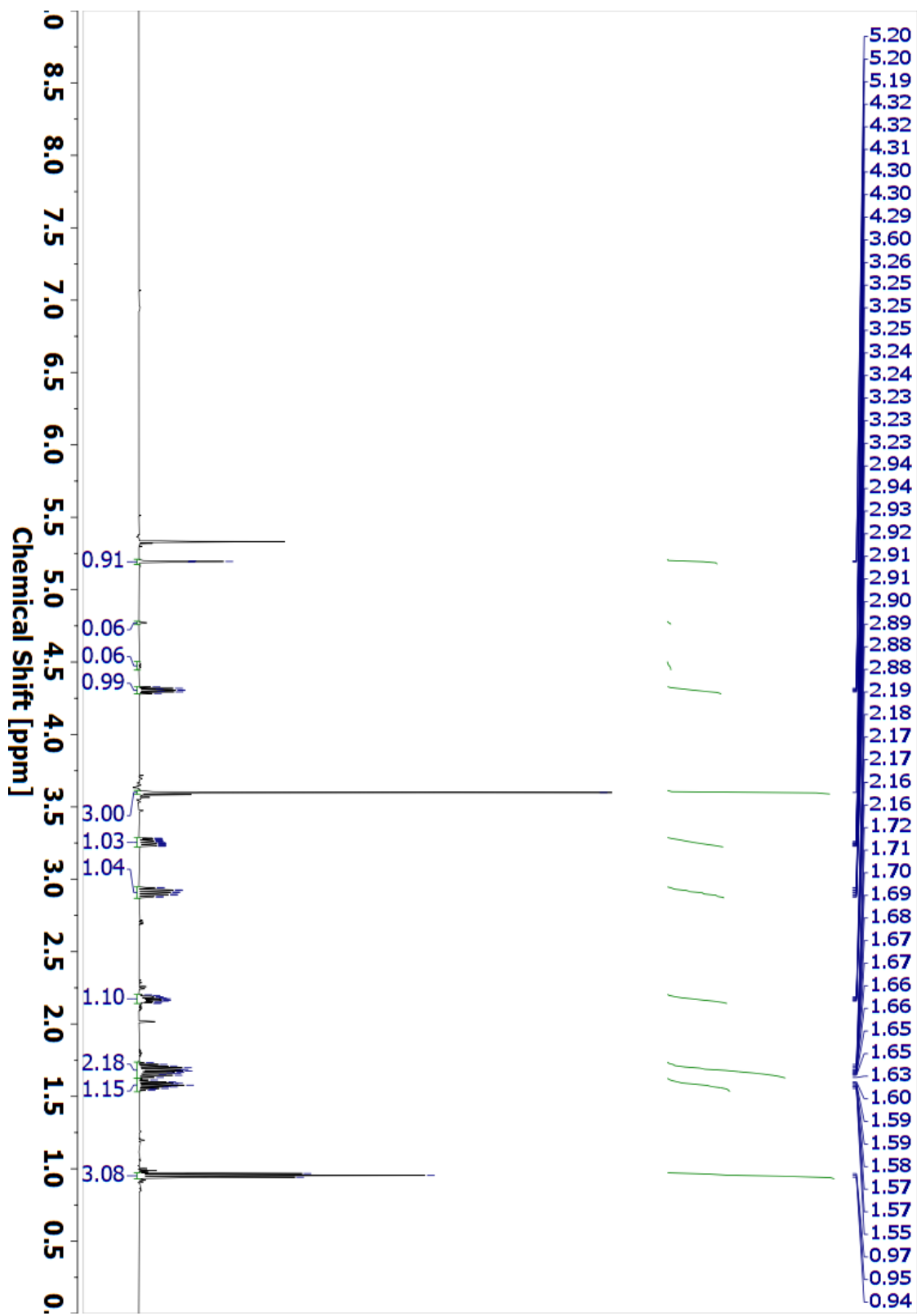
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 77% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 94% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 11.8 mg (69% yield, 94% *Z*- : 6% *E*-isomer) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 5.20 (t, $J = 2.0$ Hz, 1H), 4.34–4.27 (m, 1H), 3.60 (s, 3H), 3.26 (dddd, $J = 18.5, 9.1, 3.9, 1.5$ Hz, 1H), 2.96–2.86 (m, 1H), 2.22–2.13 (m, 1H), 1.74–1.62 (m, 2H), 1.62–1.53 (m, 1H), 0.95 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 179.35, 171.08, 90.58, 88.05, 52.71, 33.00, 31.10, 30.22, 11.96. HRMS (ESI $^+$) m/z Calc. 171.1016 [$\text{C}_9\text{H}_{14}\text{O}_3 + \text{H}$] $^+$, Found. 171.1014 [$\text{M} + \text{H}$] $^+$.



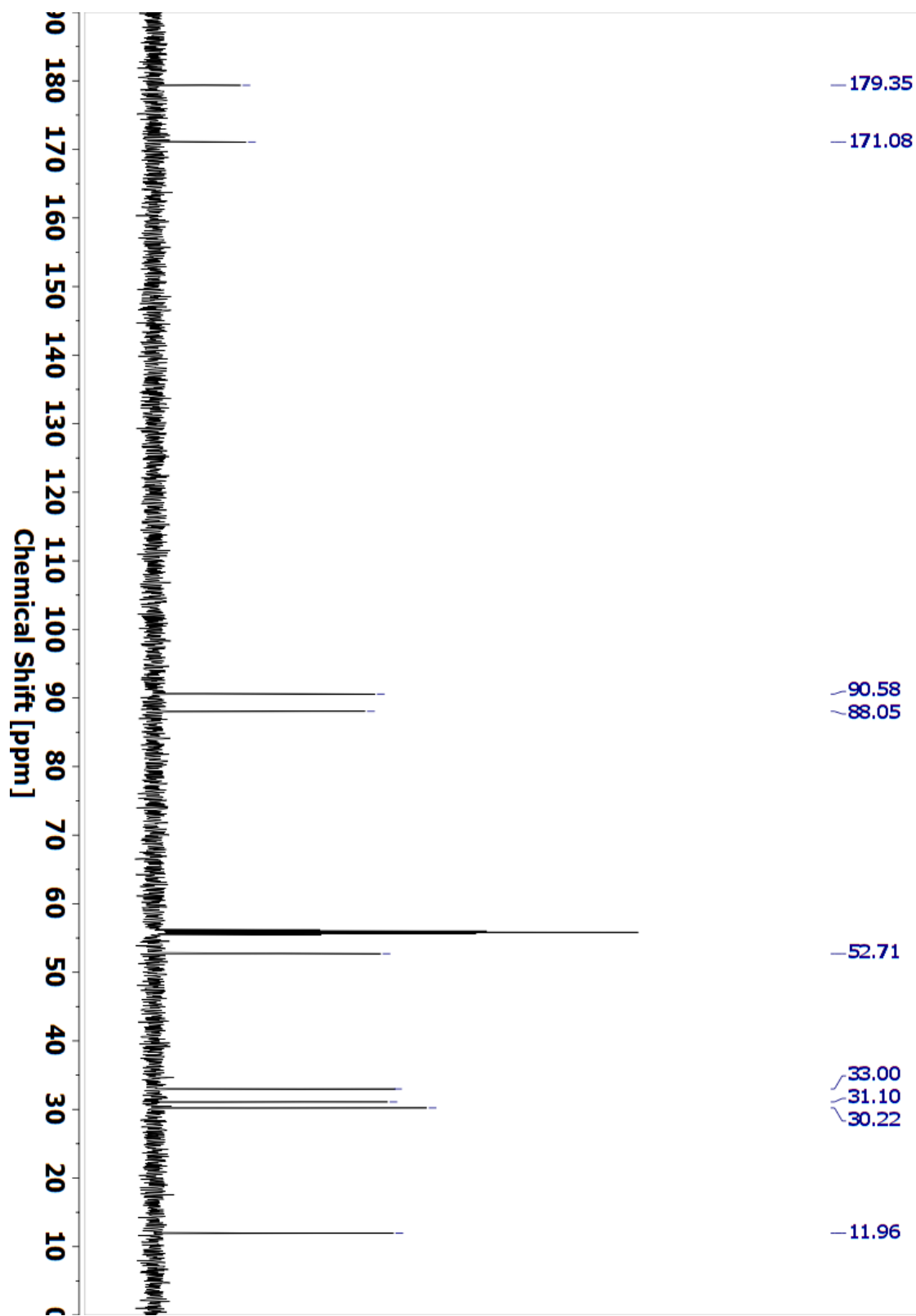
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).

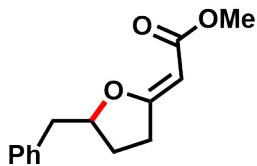


^1H NMR spectrum of isolated product in CD_2Cl_2 (96% *Z*- : 4% *E*-isomer)

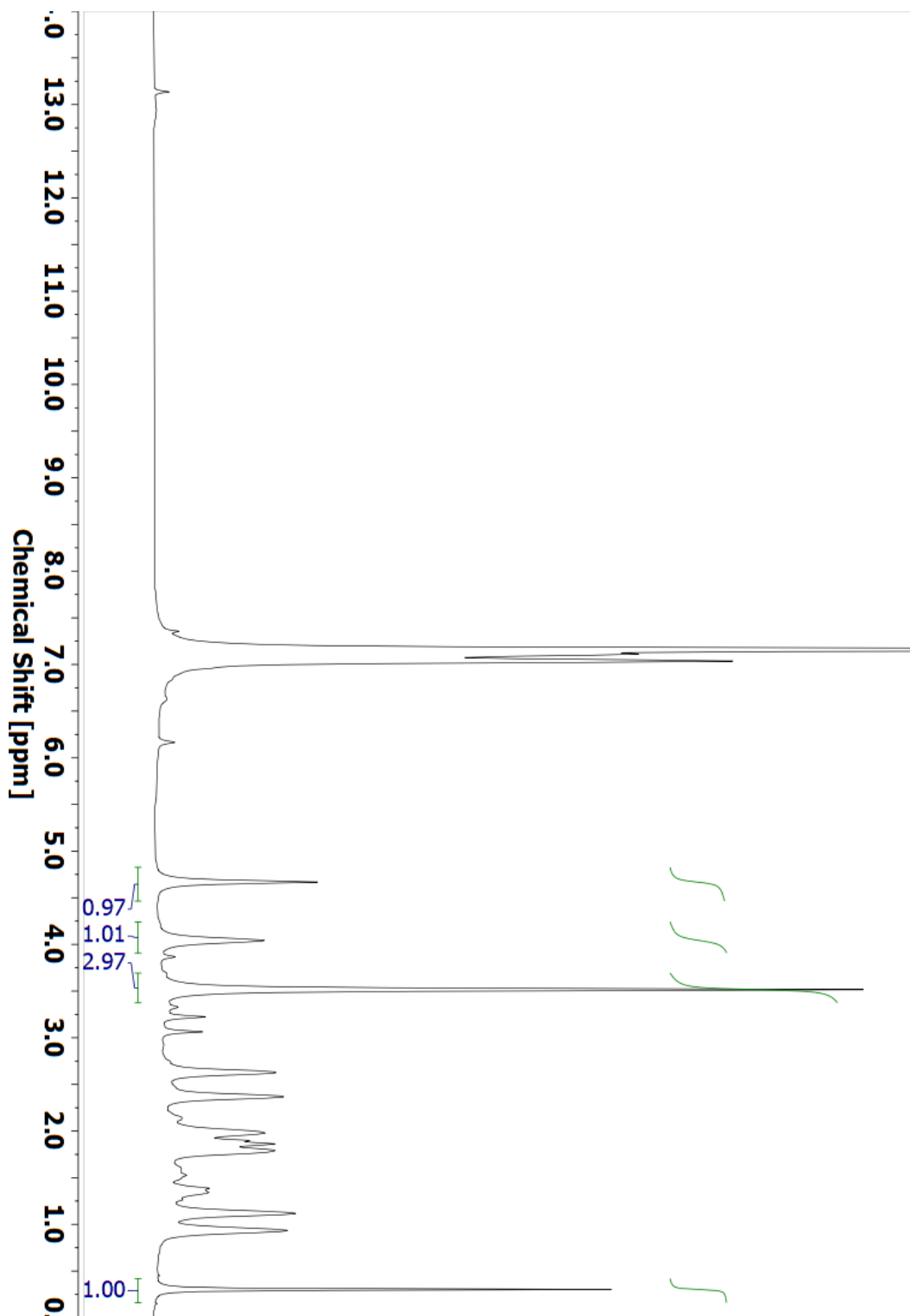


^{13}C NMR spectrum of isolated product in CD_2Cl_2

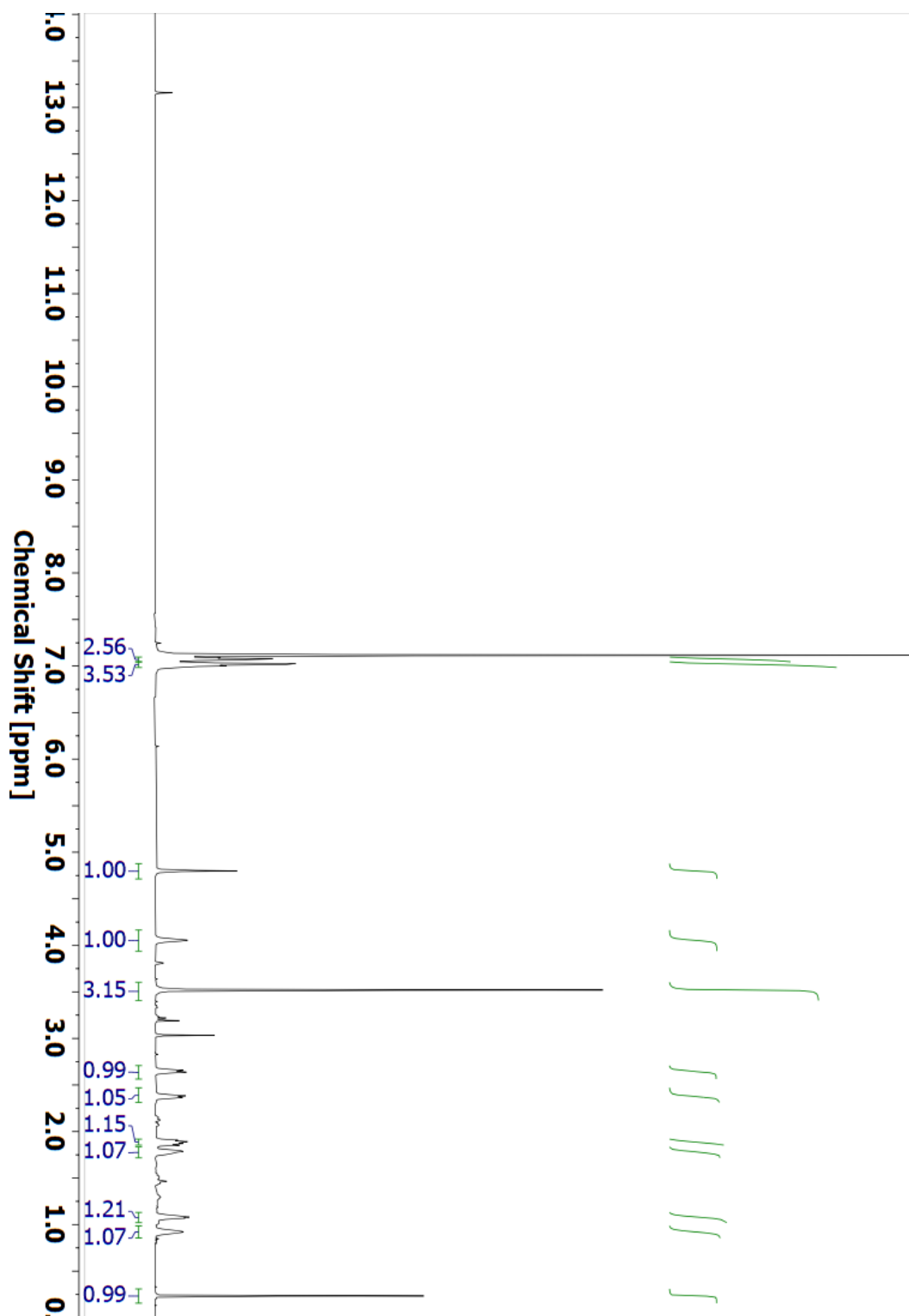
Methyl (Z)-2-(5-benzylidihydrofuran-2(3H)-ylidene)acetate (15):



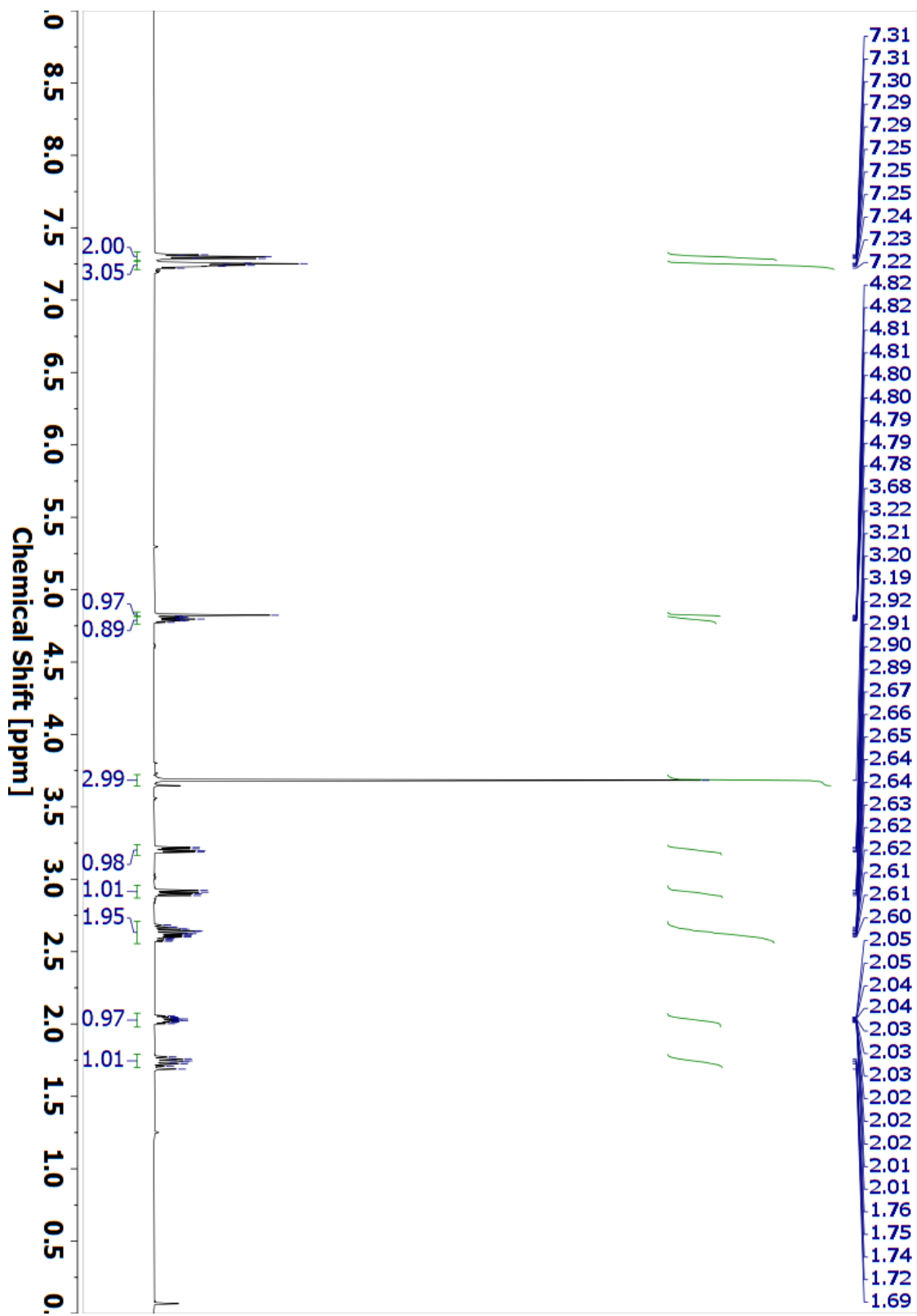
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 63% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 66% NMR yield) with 20.0 mg of σ -diazo- β -ketoester to give 9.3 mg (52% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.33–7.27 (m, 2H), 7.27–7.21 (m, 3H), 4.82 (s, 1H), 4.81–4.76 (m, 1H), 3.68 (s, 3H), 3.20 (dd, $J = 13.7, 5.4$ Hz, 1H), 2.91 (dd, $J = 13.7, 7.3$ Hz, 1H), 2.73–2.55 (m, 2H), 2.07–1.98 (m, 1H), 1.80–1.70 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.99, 169.04, 137.66, 129.72, 128.86, 127.05, 89.14, 84.97, 50.80, 41.31, 30.76, 29.13. HRMS (ESI $^+$) m/z Calc. 233.1172 [$\text{C}_{14}\text{H}_{16}\text{O}_3+\text{H}$] $^+$, Found. 233.1171 [$\text{M}+\text{H}$] $^+$.



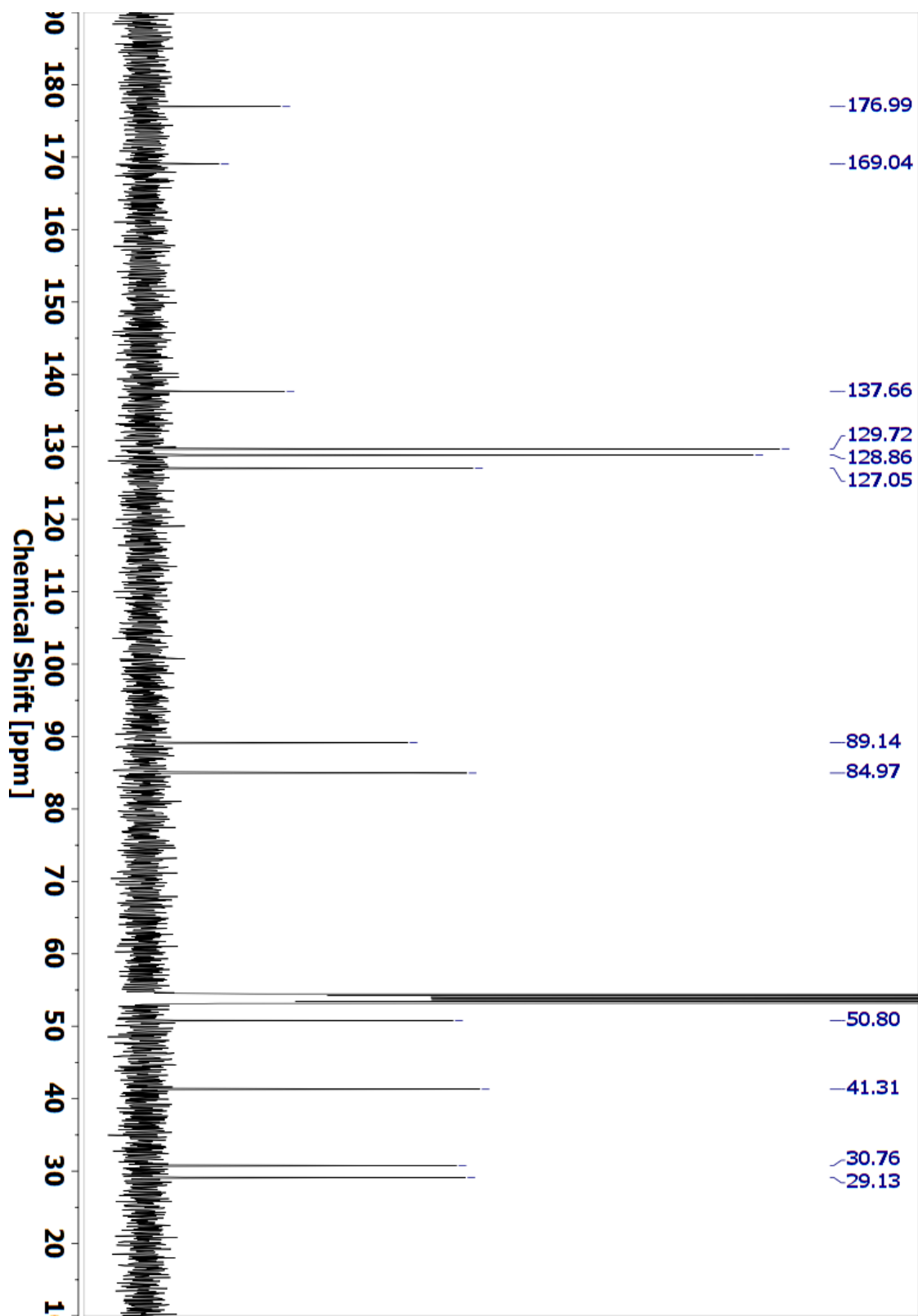
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).



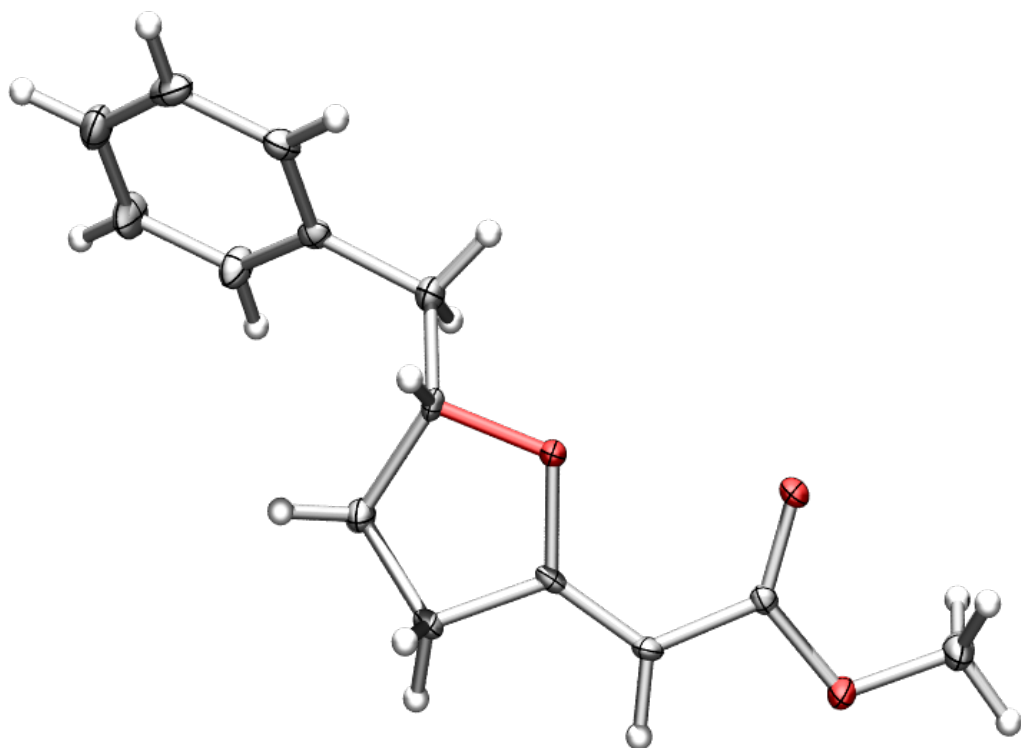
Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 1 h (0.5 mg Si(SiMe₃)₄ as internal standard).



^1H NMR spectrum of isolated product in CD_2Cl_2

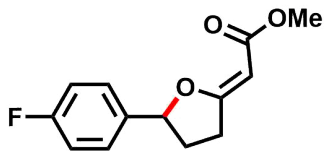


¹³C NMR spectrum of isolated product in CD₂Cl₂

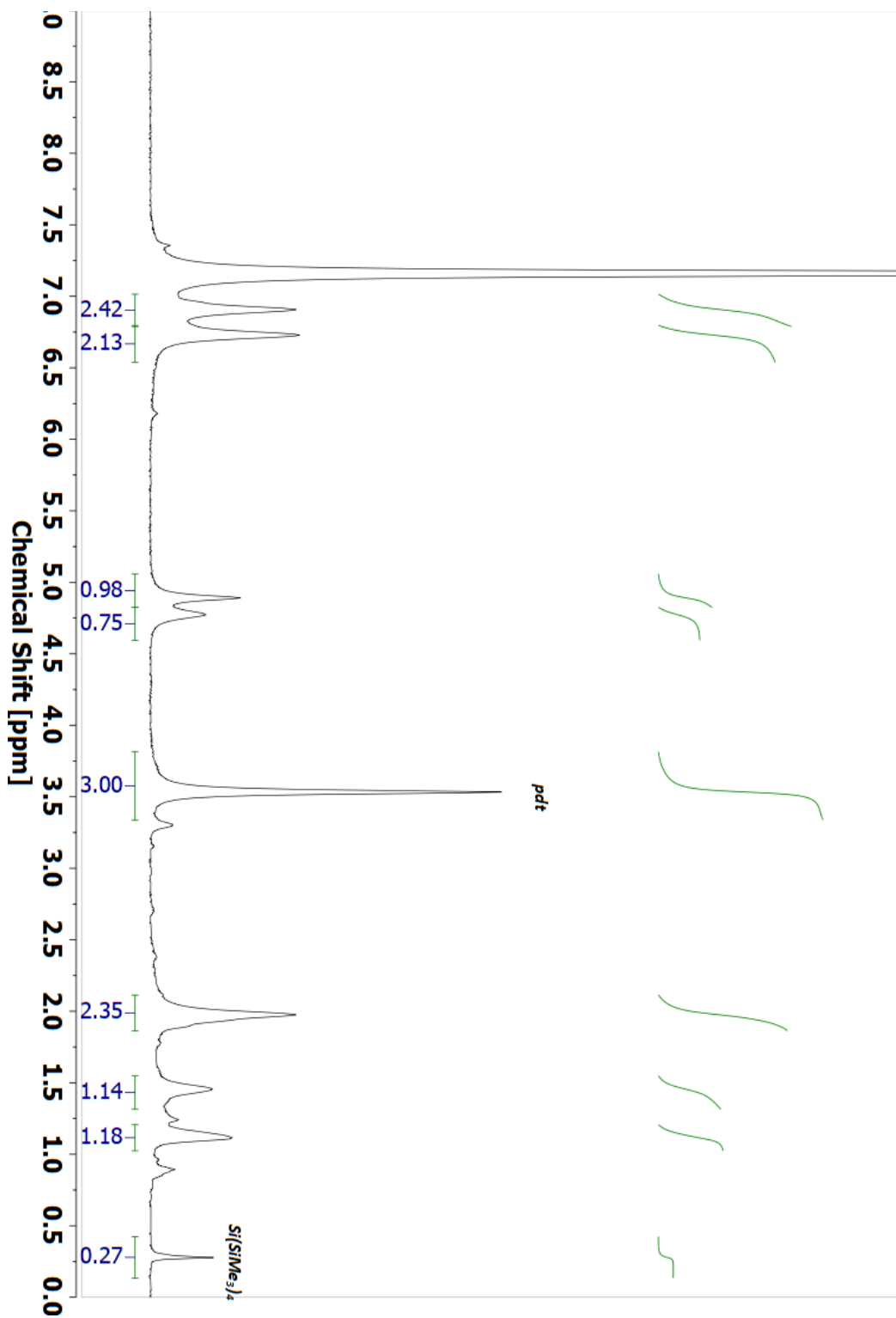


Solid-state molecular structure for methyl (Z)-2-(5-benzylidihydrofuran-2(3H)-ylidene)acetate (15) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white. Only one molecule is displayed here for clarity.

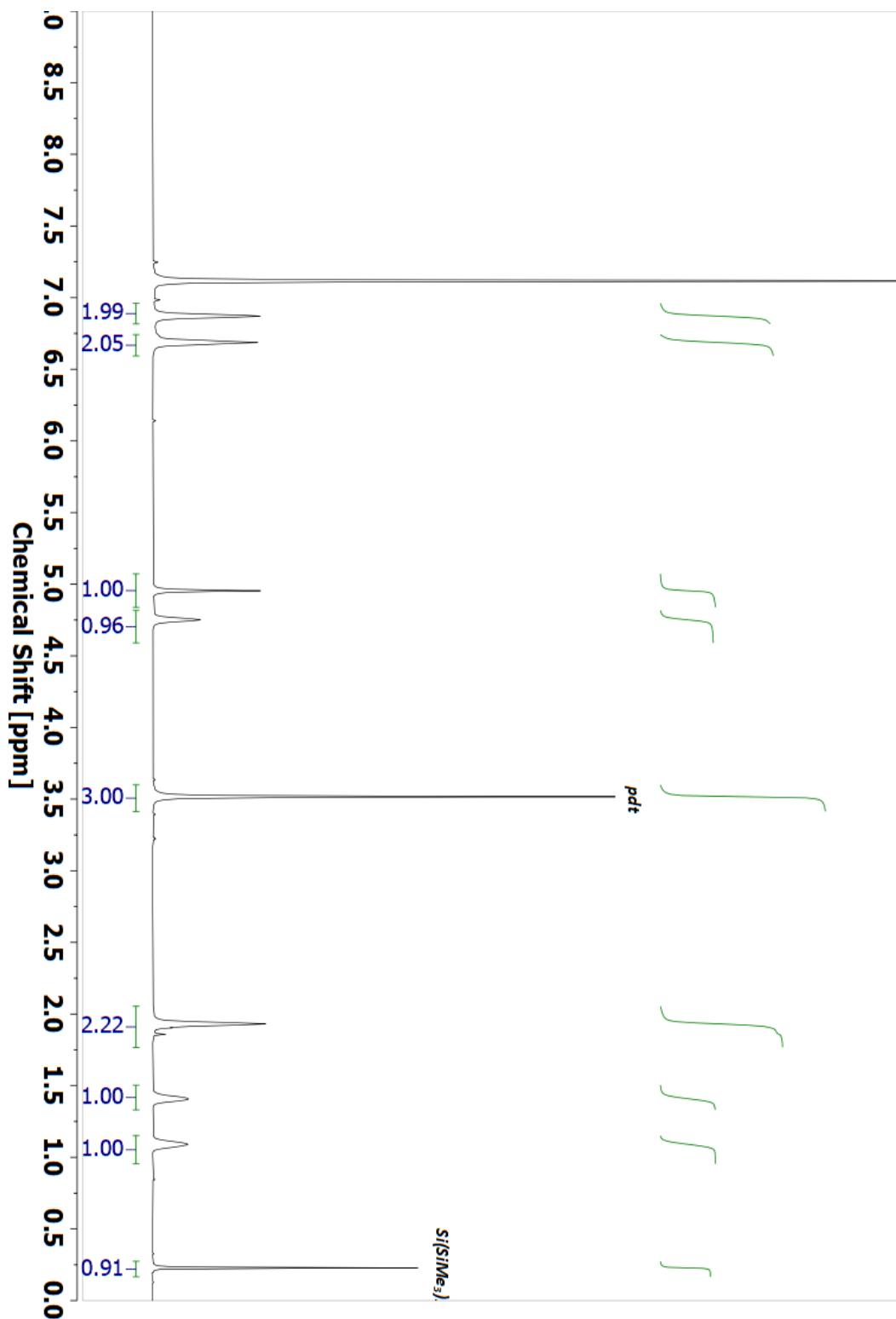
Methyl (Z)-2-(5-(4-fluorophenyl)dihydrofuran-2(3H)-ylidene)acetate (16)



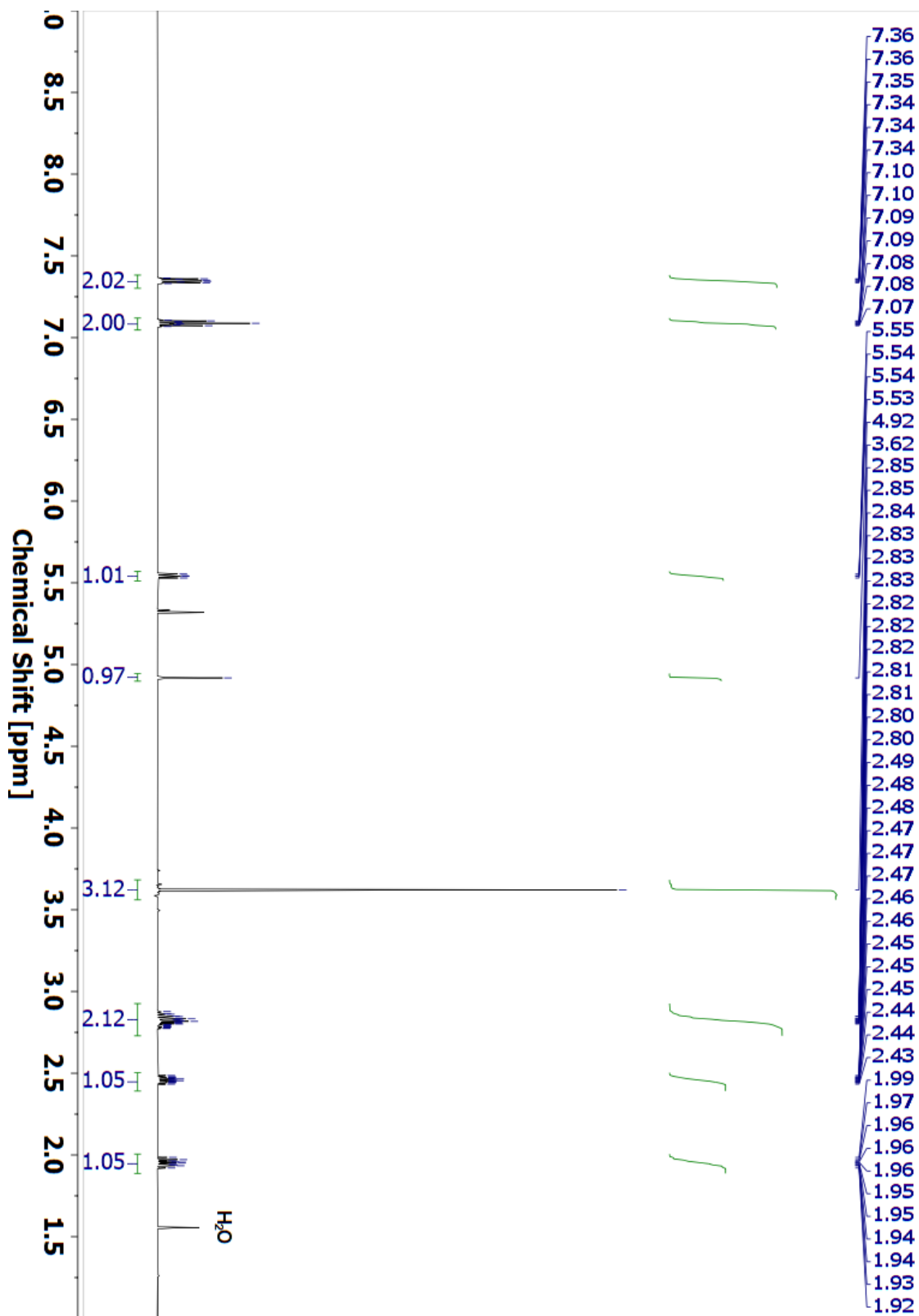
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 49% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 73% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.9 mg (61% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.37–7.32 (m, 2H), 7.12–7.06 (m, 2H), 5.54 (dd, $J = 8.4, 6.2$ Hz, 1H), 4.92 (s, 1H), 3.62 (s, 3H), 2.91–2.73 (m, 2H), 2.53–2.39 (m, 1H), 2.03–1.87 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.70, 166.11, 162.99 (d, $J = 246.0$ Hz), 136.28 (d, $J = 3.4$ Hz), 127.92 (d, $J = 8.2$ Hz), 115.83 (d, $J = 21.6$ Hz), 88.34, 86.62, 50.78, 32.62, 32.15. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -114.77. HRMS (ESI+) m/z Calc. 237.0921 [$\text{C}_{13}\text{H}_{13}\text{FO}_3+\text{H}$] $^+$, Found 237.0914 [$\text{M}+\text{H}$] $^+$.



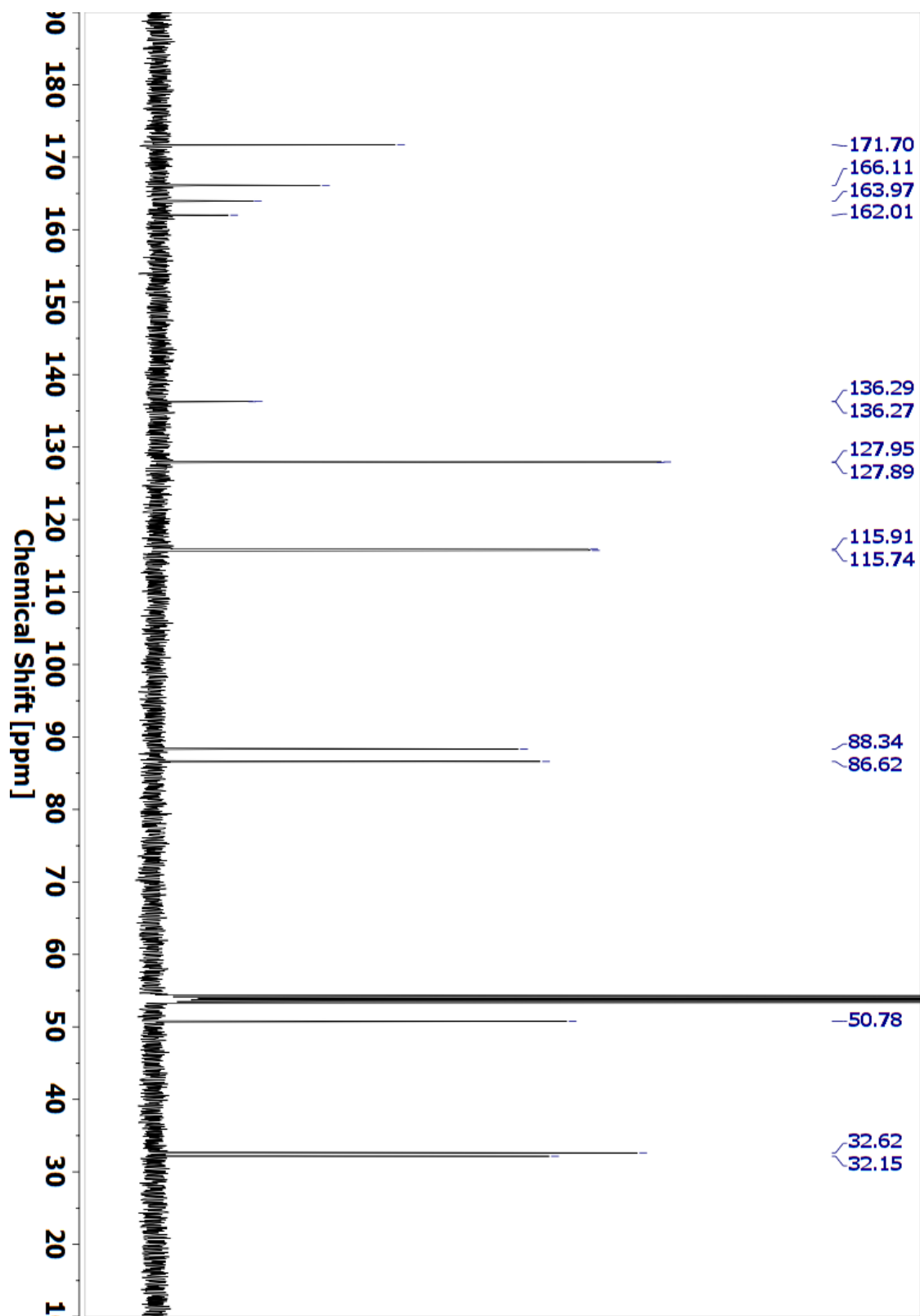
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.1 mg Si(SiMe₃)₄ as internal standard).



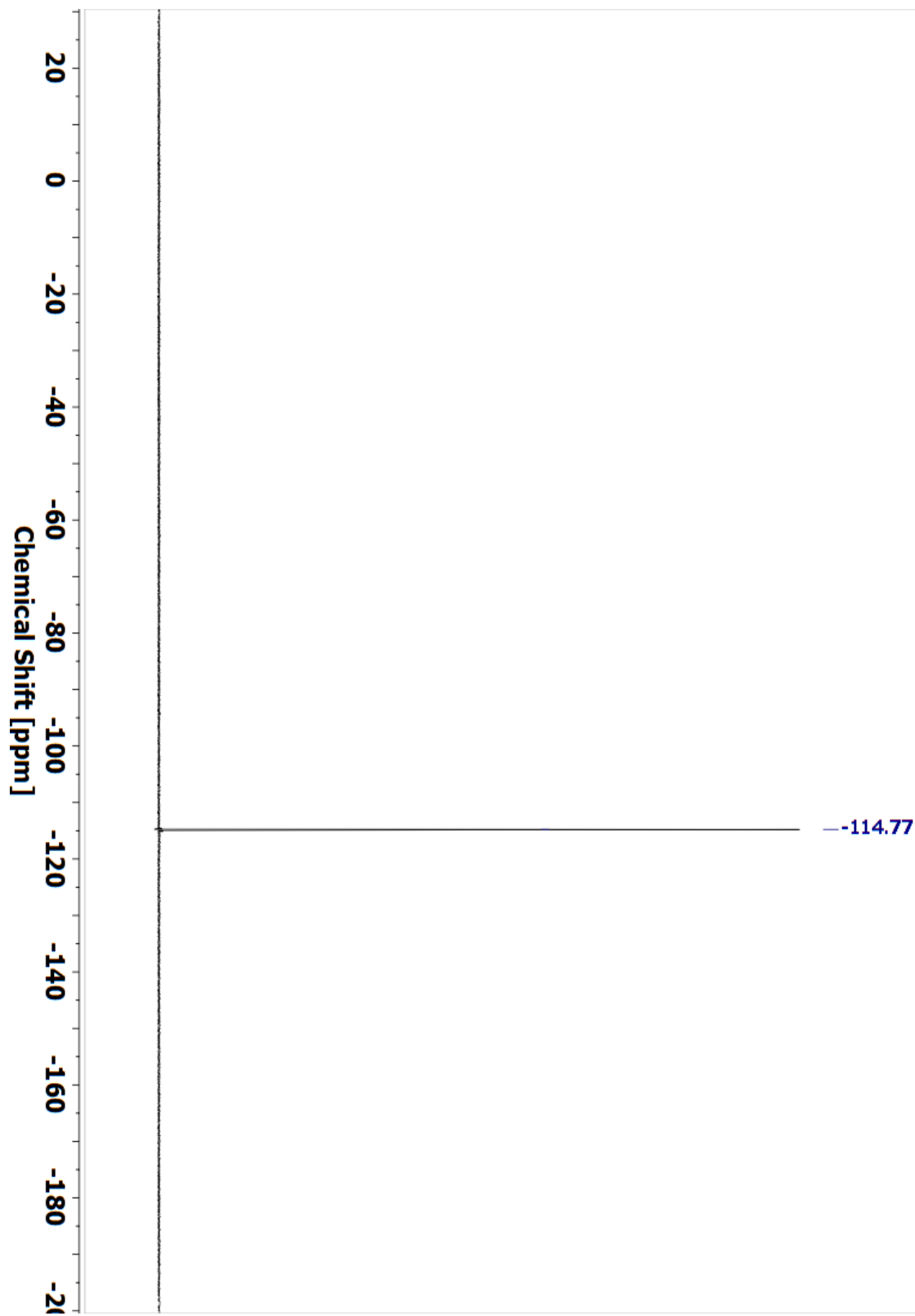
Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% $\text{Fe}(\text{acac})_2$ after 20 min (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



^1H NMR spectrum of isolated product in CD_2Cl_2

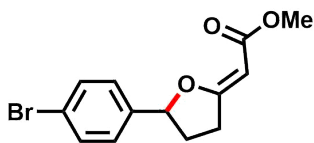


^{13}C NMR spectrum of isolated product in CD_2Cl_2

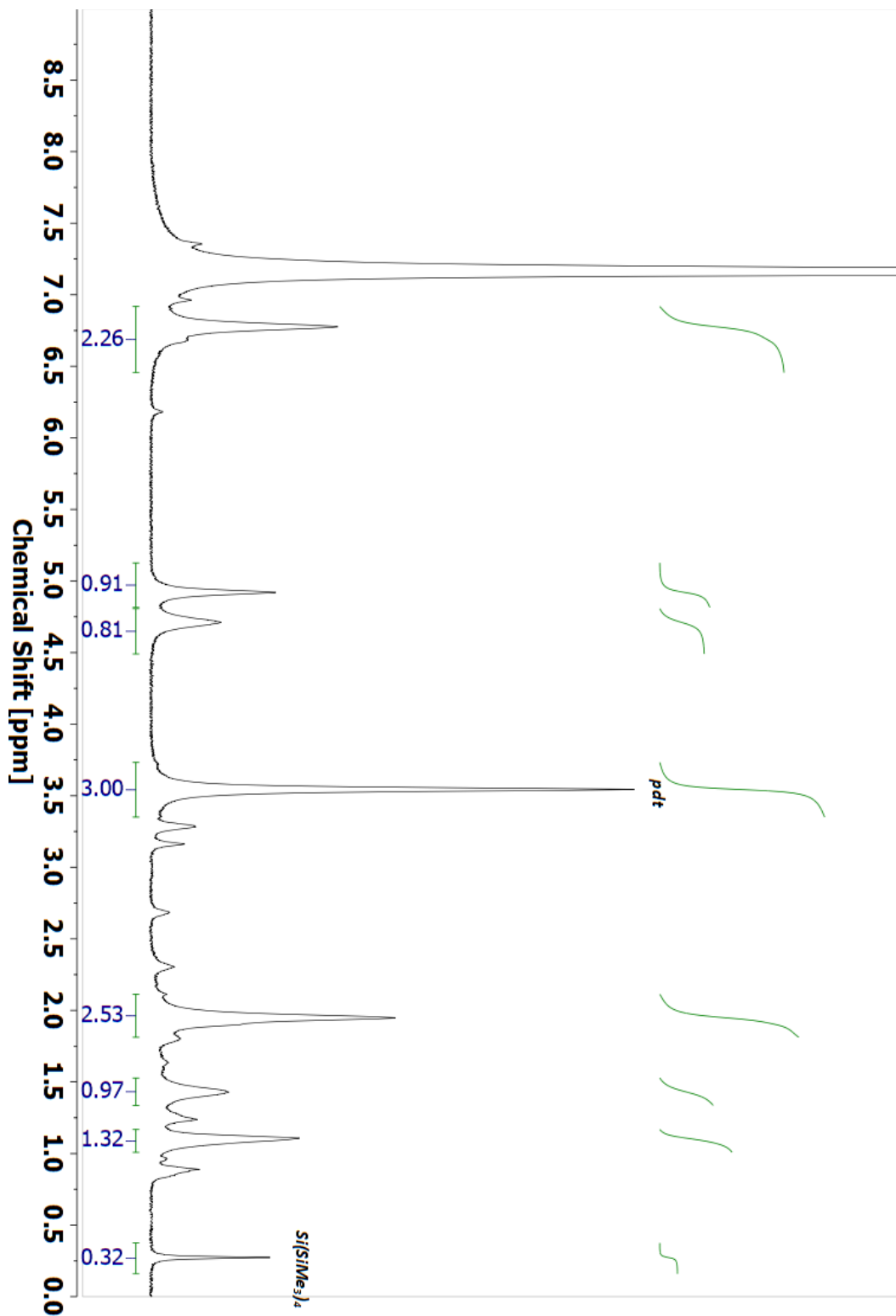


^{19}F NMR spectrum of isolated product in CD_2Cl_2

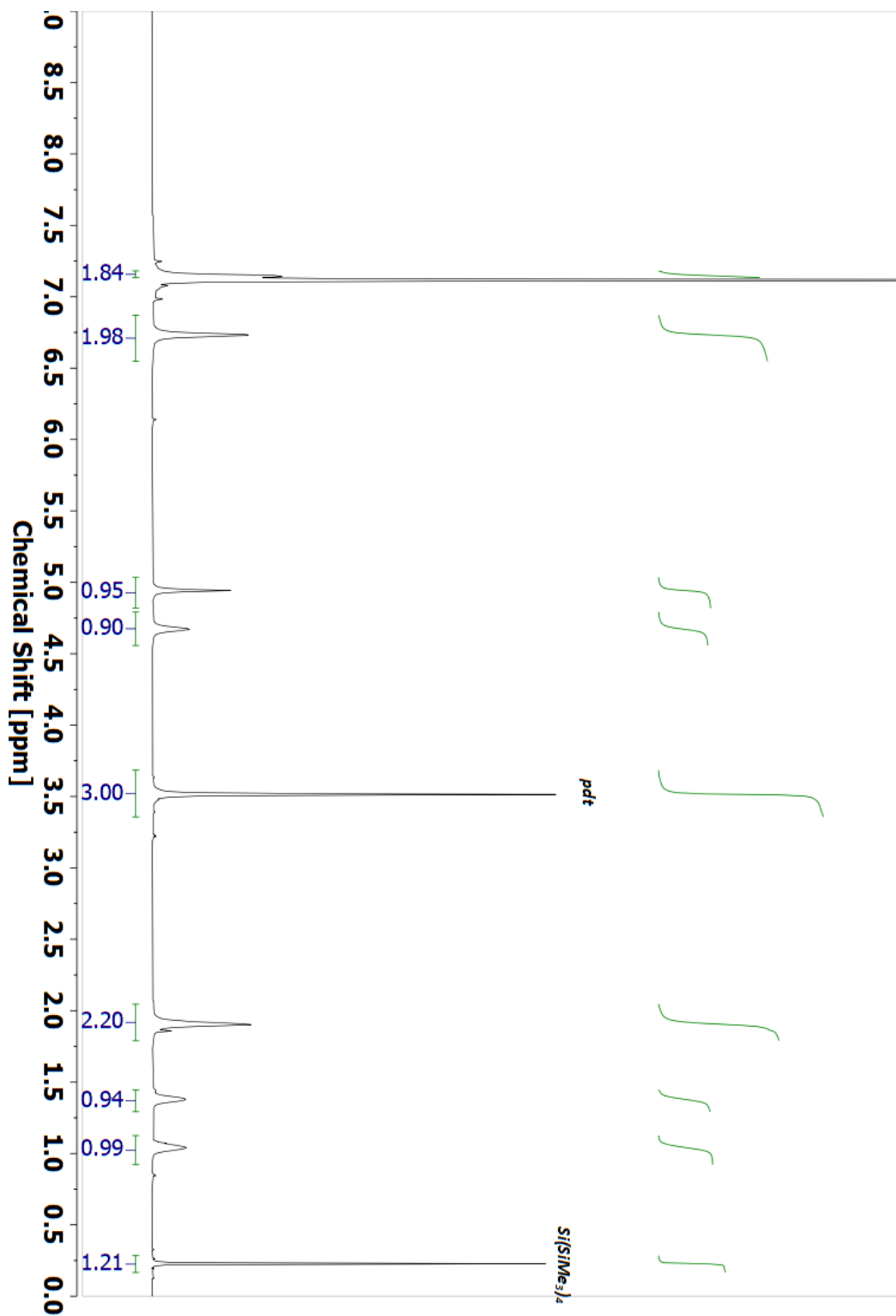
Methyl (Z)-2-(5-(4-bromophenyl)dihydrofuran-2(3H)-ylidene)acetate (17):



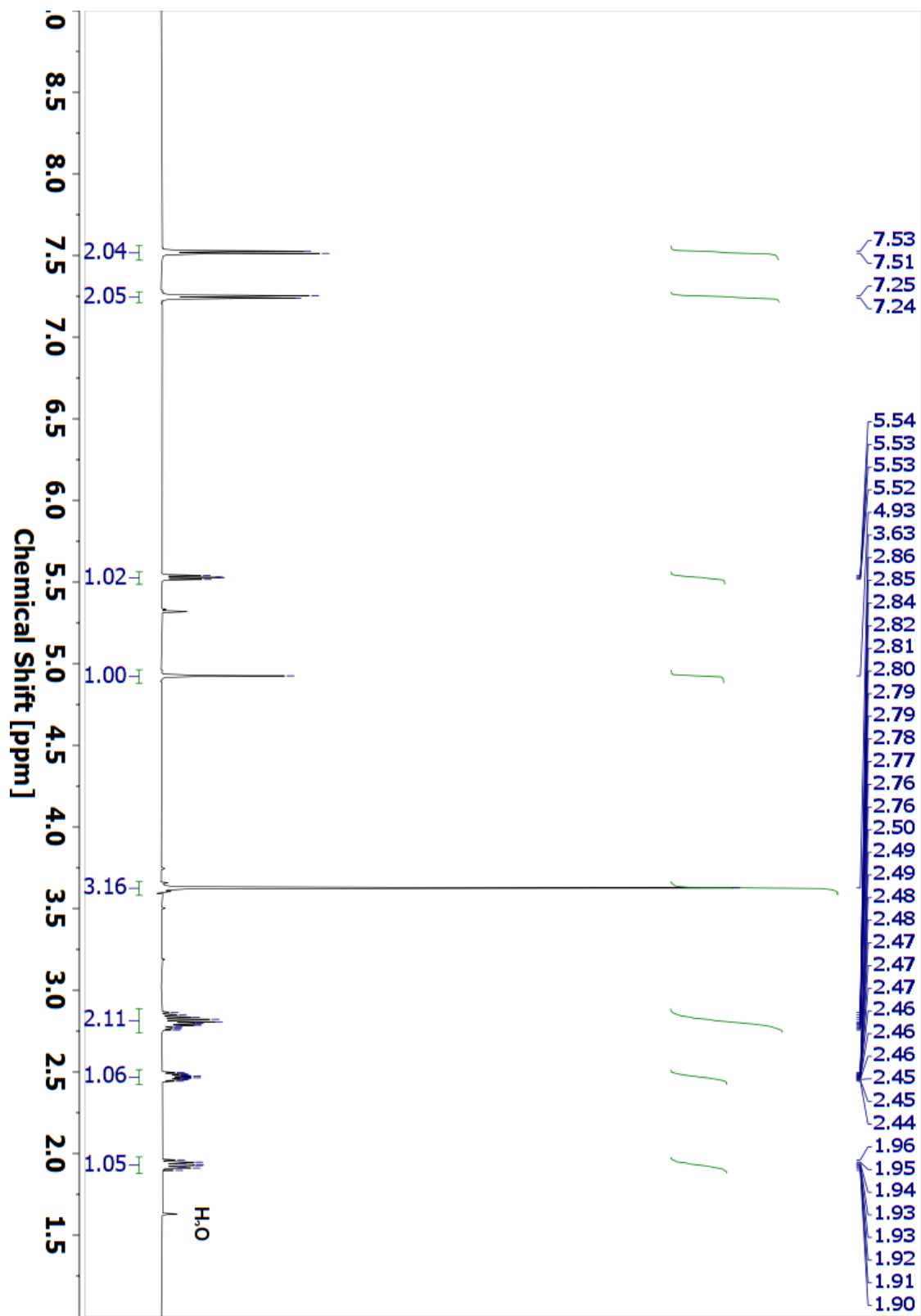
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 52% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 68% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 11.9 mg (65% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.52 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 5.53 (dd, J = 8.1, 6.3 Hz, 1H), 4.93 (s, 1H), 3.63 (s, 3H), 2.89–2.74 (m, 2H), 2.51–2.42 (m, 1H), 1.98–1.88 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.59, 166.07, 139.65, 132.08, 127.71, 122.28, 88.49, 86.39, 50.80, 32.46, 32.04. HRMS (ESI $^+$) m/z Calc. 297.0121 [$\text{C}_{13}\text{H}_{13}\text{BrO}_3+\text{H}$] $^+$, Found 297.0127 [$\text{M}+\text{H}$] $^+$.



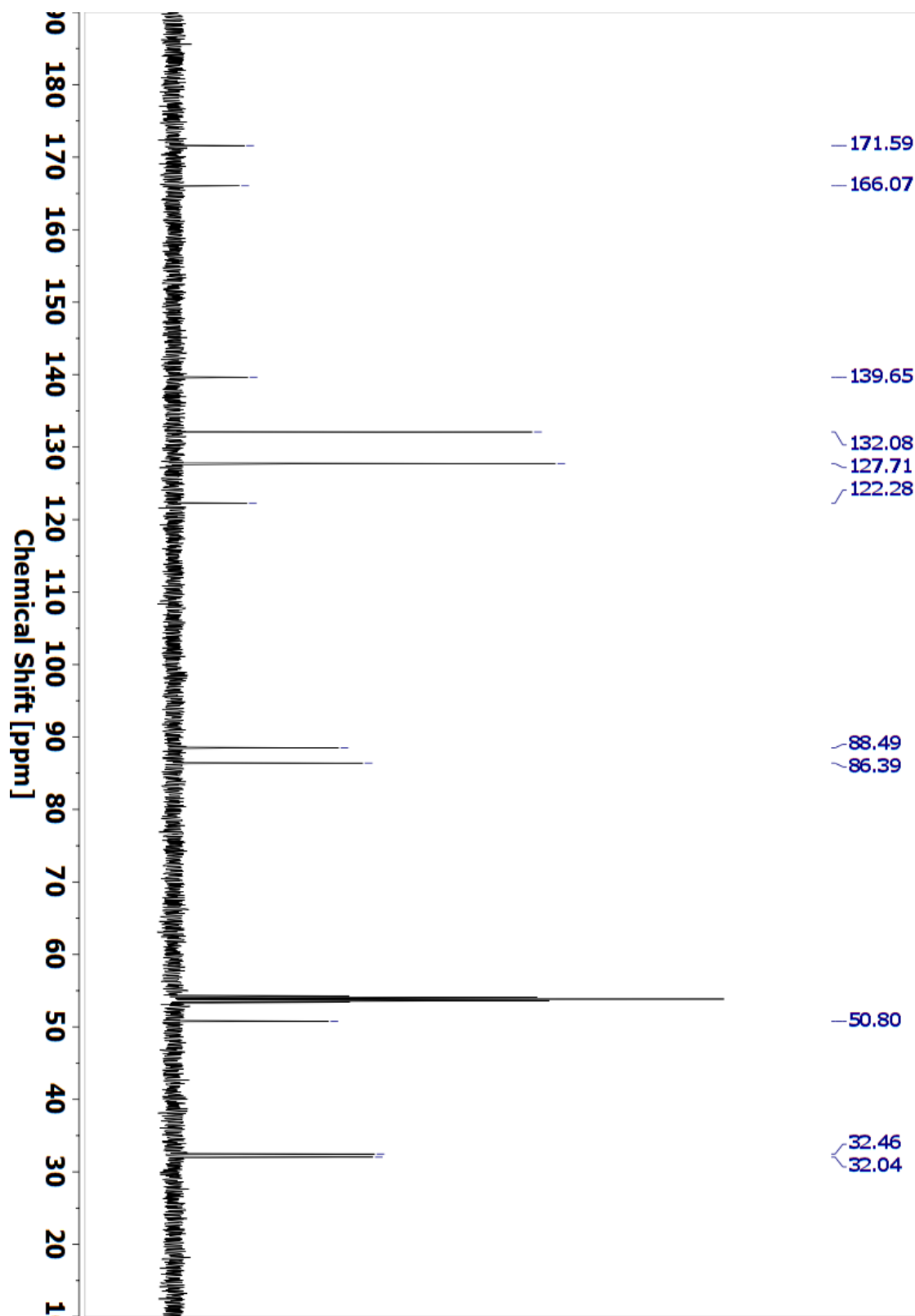
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.1 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).

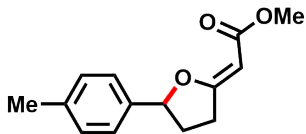


^1H NMR spectrum of isolated product in CD_2Cl_2

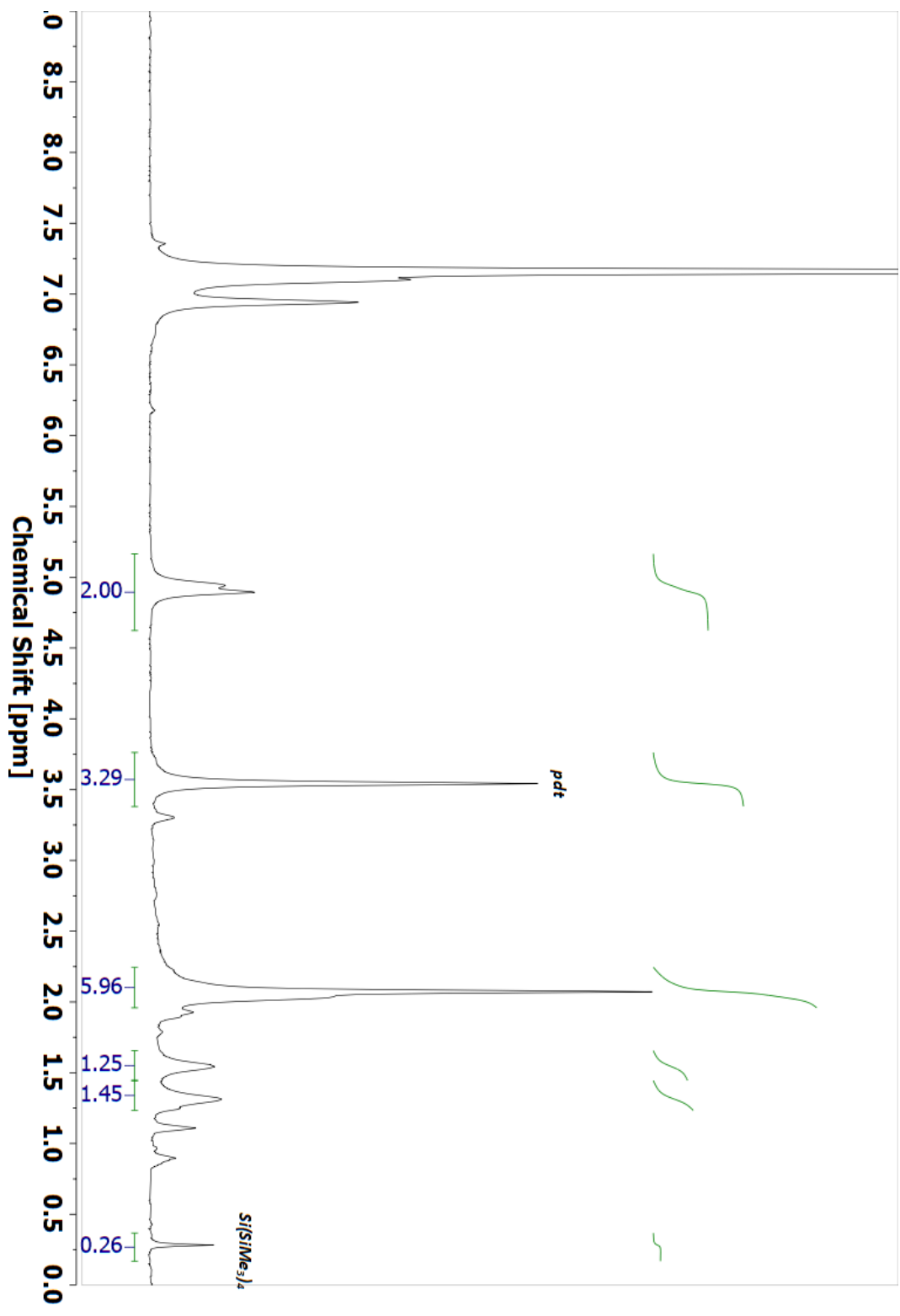


^{13}C NMR spectrum of isolated product in CD_2Cl_2

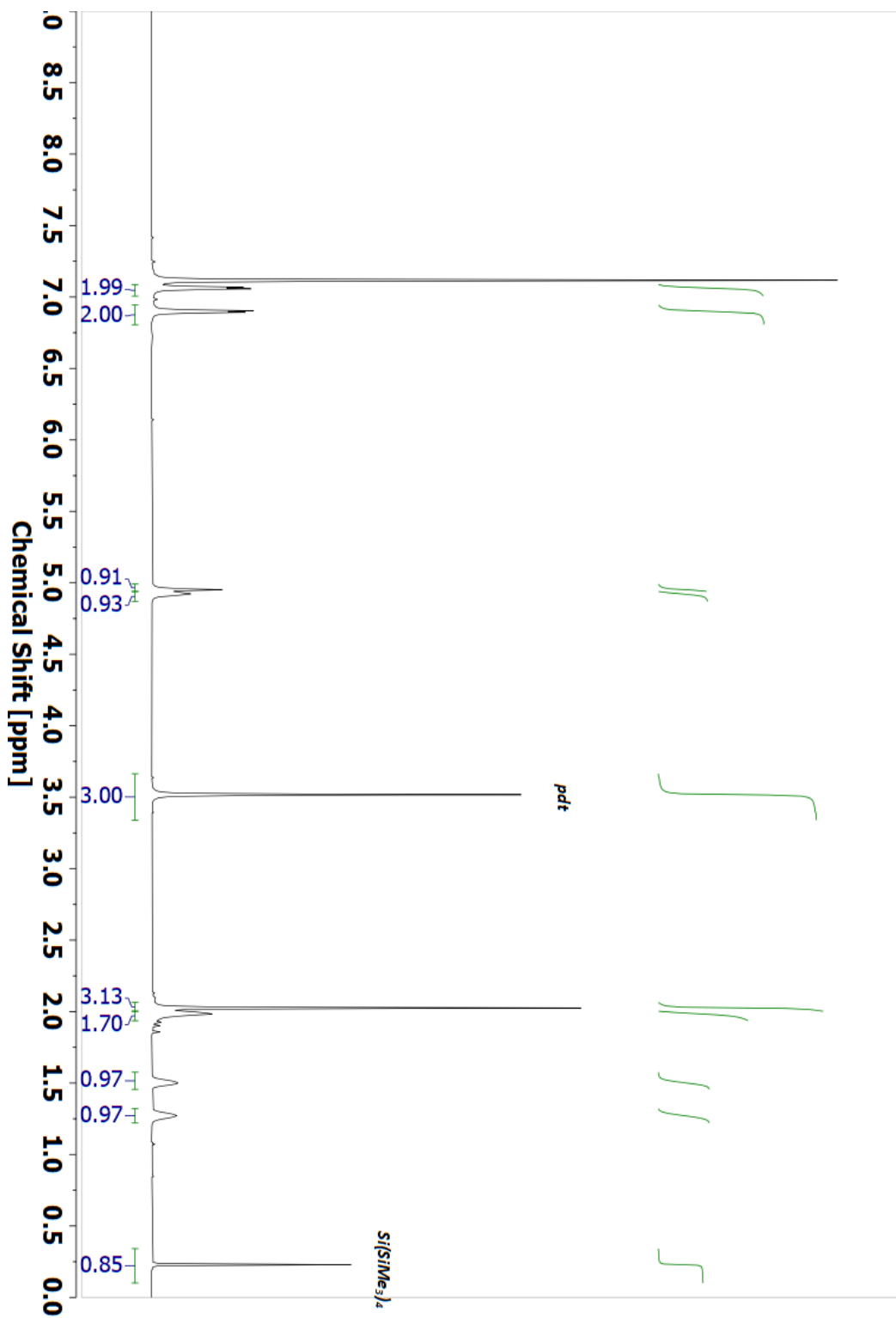
Methyl (Z)-2-(5-(p-tolyl)dihydrofuran-2(3H)-ylidene)acetate (18)



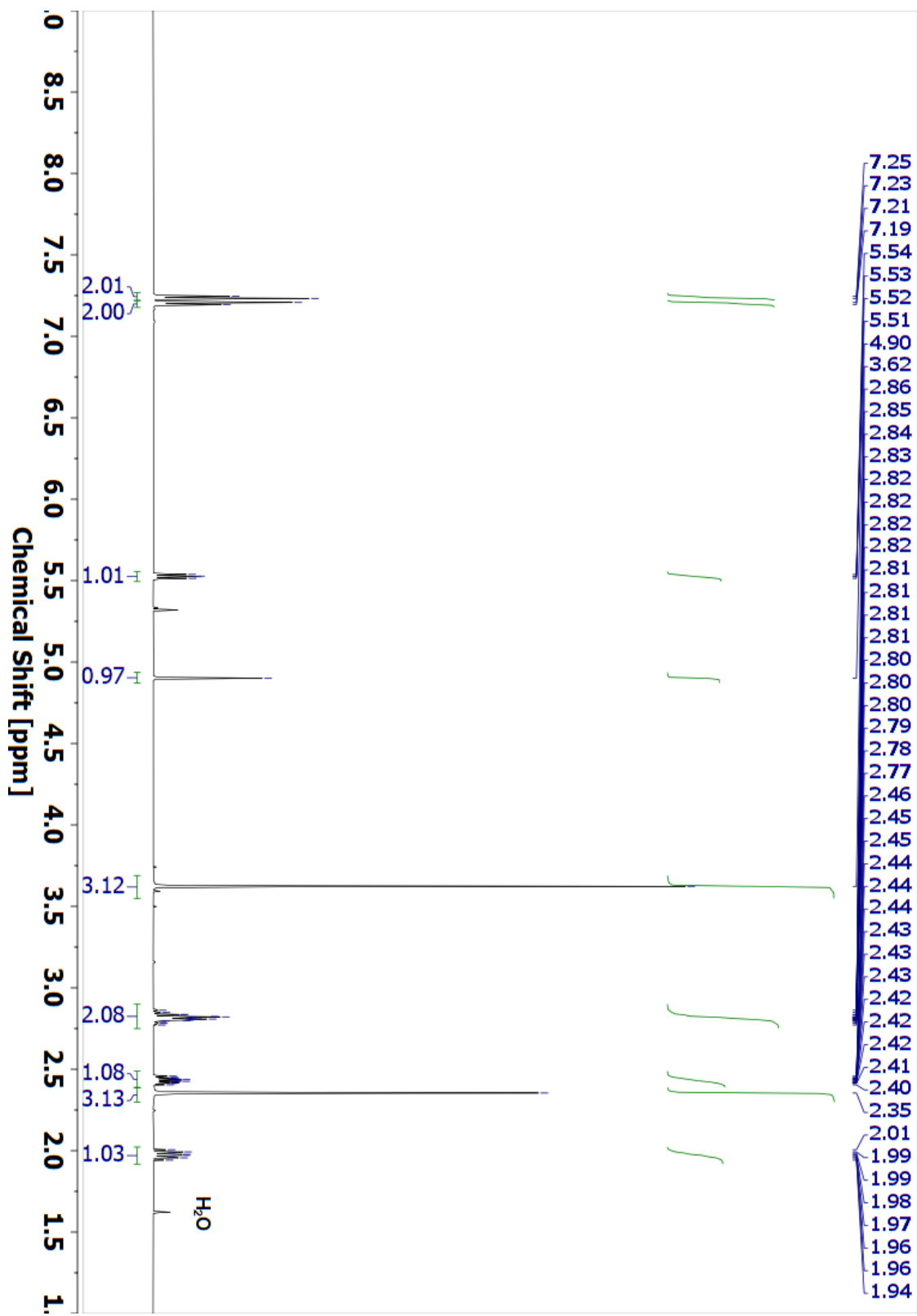
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 55% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 77% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.6 mg (59% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.24 (d, $J = 8.1$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H), 5.53 (dd, $J = 8.3, 6.2$ Hz, 1H), 4.90 (s, 1H), 3.62 (s, 3H), 2.93–2.69 (m, 2H), 2.49–2.37 (m, 1H), 2.35 (s, 3H), 2.07–1.91 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.05, 166.18, 138.59, 137.25, 129.62, 126.05, 87.99, 87.39, 50.74, 32.73, 31.98, 21.26. HRMS (ESI $^+$) m/z Calc. 255.0992 [$\text{C}_{14}\text{H}_{16}\text{O}_3 + \text{Na}$] $^+$, Found 255.1004 [$\text{M} + \text{Na}$] $^+$.



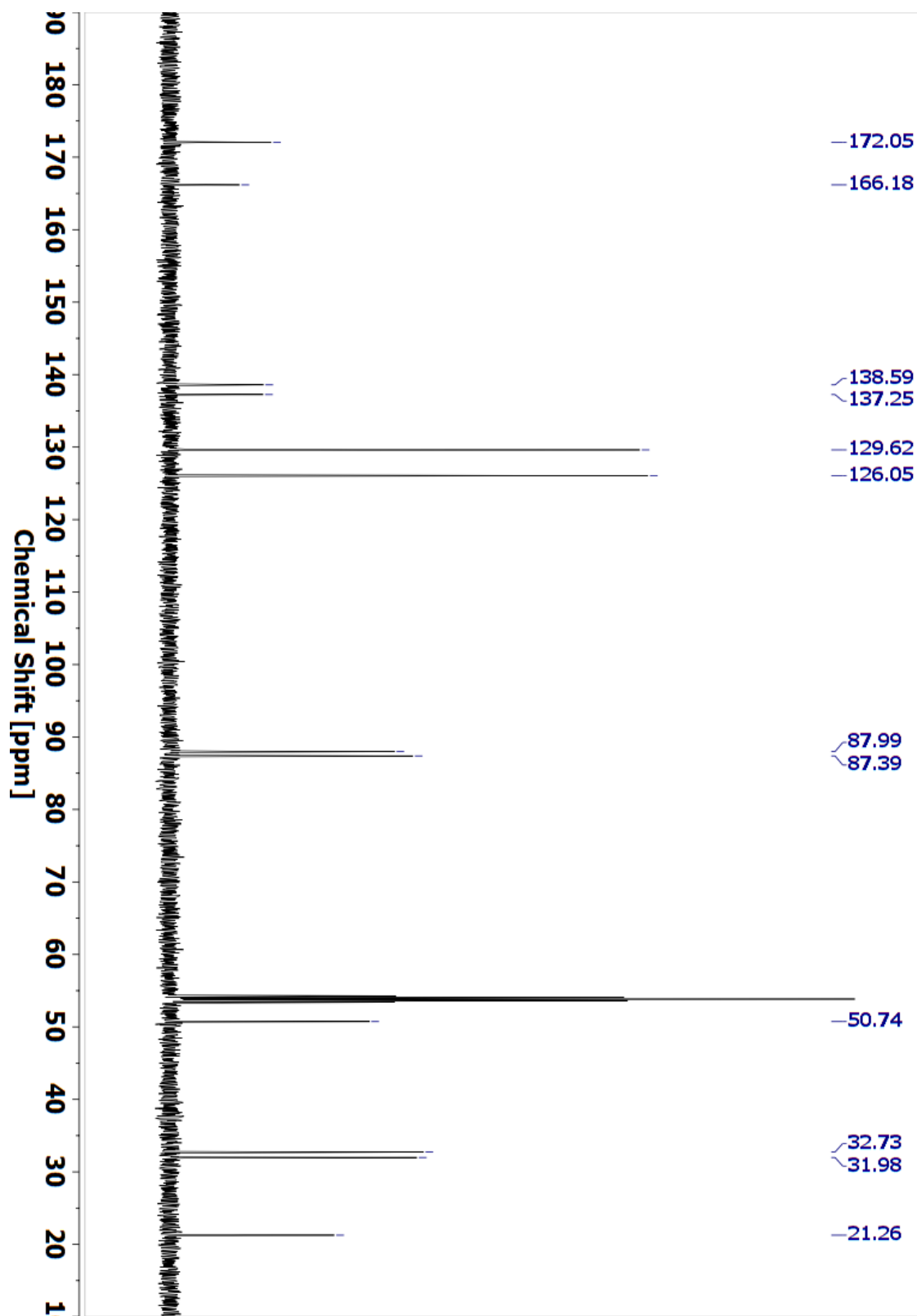
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.1 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% $\text{Fe}(\text{acac})_2$ after 20 min (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).

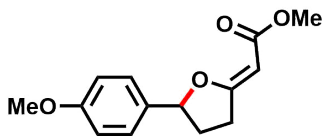


^1H NMR spectrum of isolated product in CD_2Cl_2

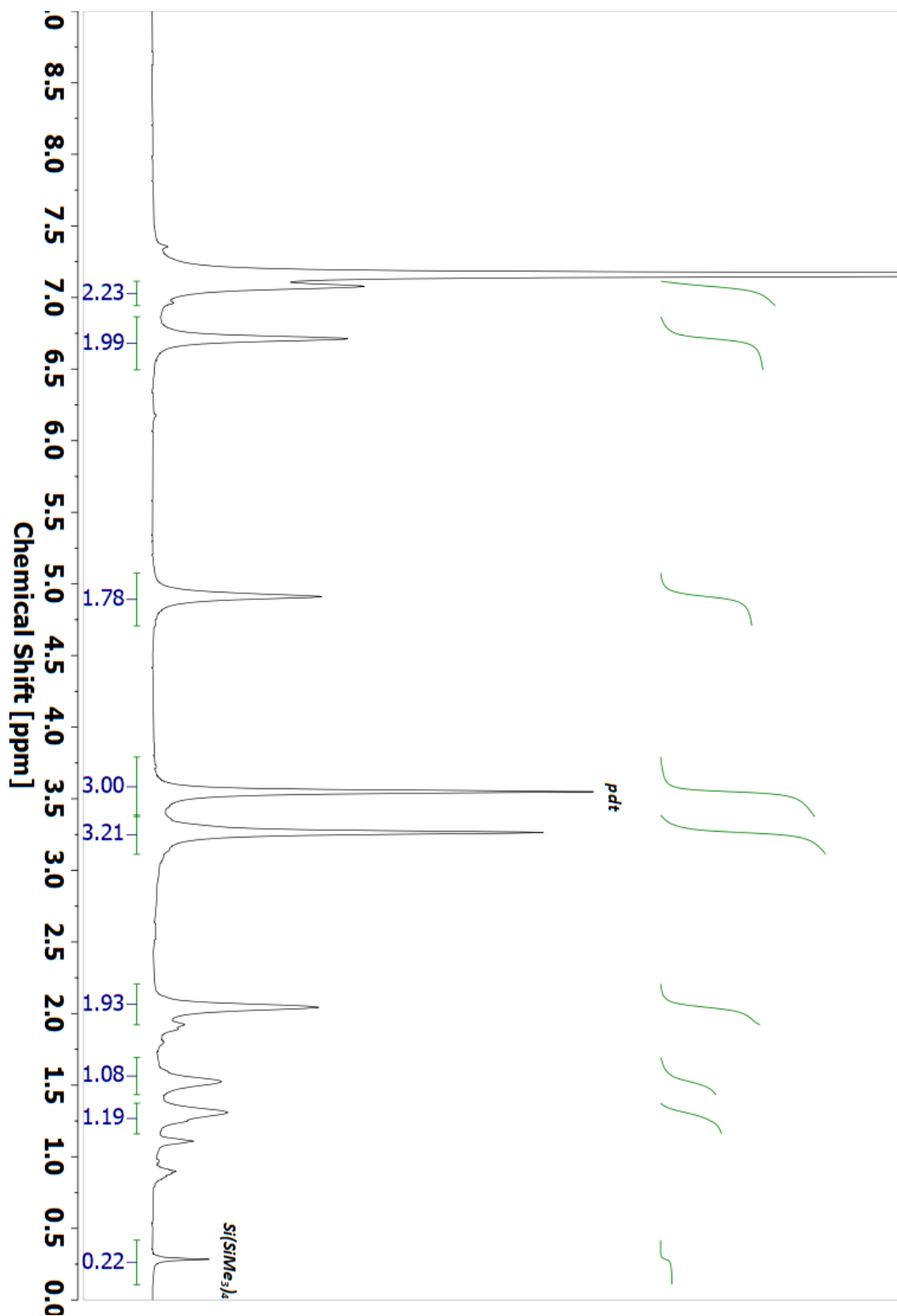


^{13}C NMR spectrum of isolated product in CD_2Cl_2

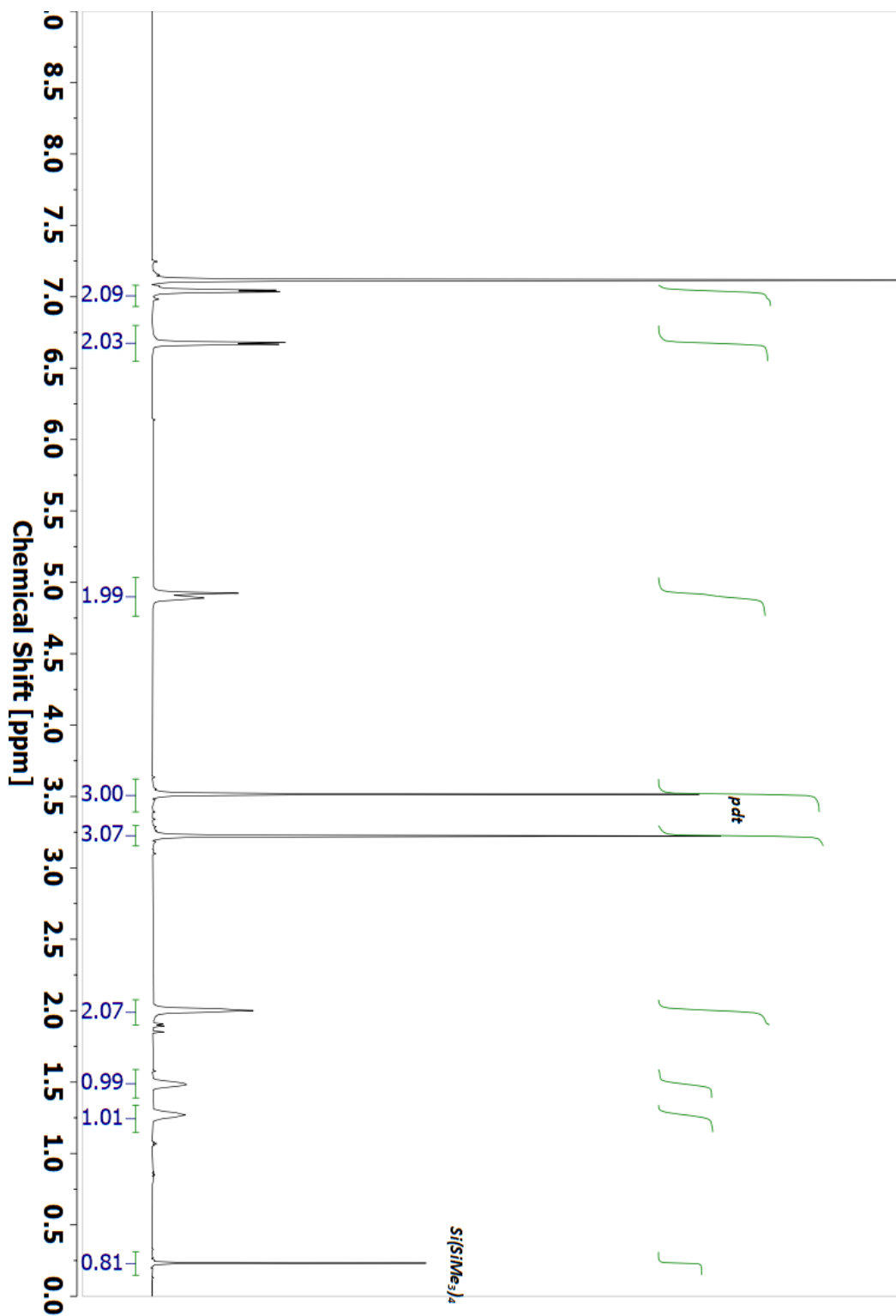
Methyl (Z)-2-(5-(4-methoxyphenyl)dihydrofuran-2(3H)-ylidene)acetate (19)



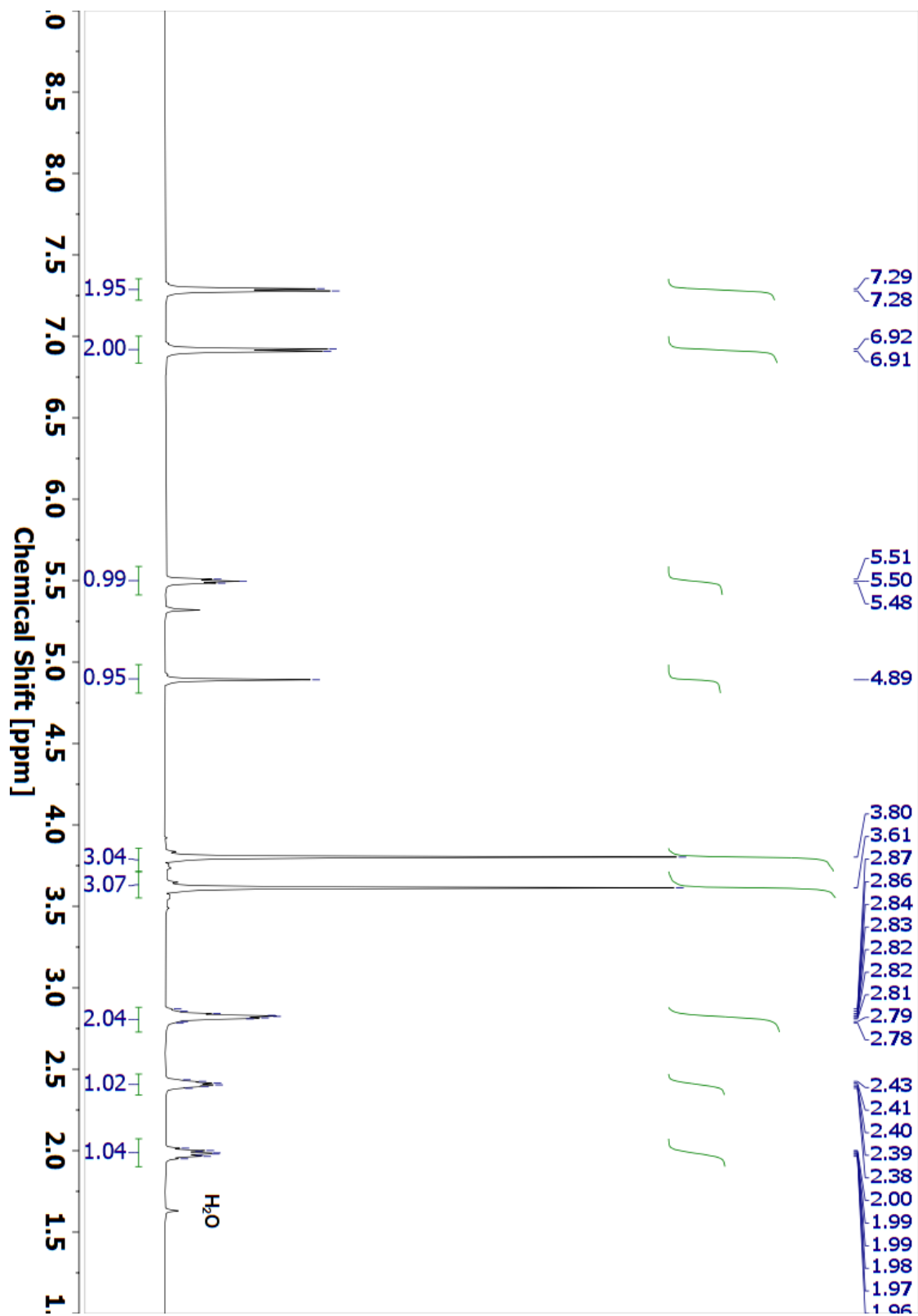
The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 64% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 86% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.0 mg (56% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.29 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 5.59–5.41 (m, 1H), 4.89 (s, 1H), 3.80 (s, 3H), 3.61 (s, 3H), 2.98–2.68 (m, 2H), 2.48–2.32 (m, 1H), 2.07–1.90 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.01, 166.18, 160.17, 132.06, 127.66, 114.33, 87.91, 87.37, 55.67, 50.72, 32.87, 31.91. HRMS (ESI $^+$) m/z Calc. 249.1121 [$\text{C}_{14}\text{H}_{16}\text{O}_4+\text{H}$] $^+$, Found. 249.1119 [$\text{M}+\text{H}$] $^+$.



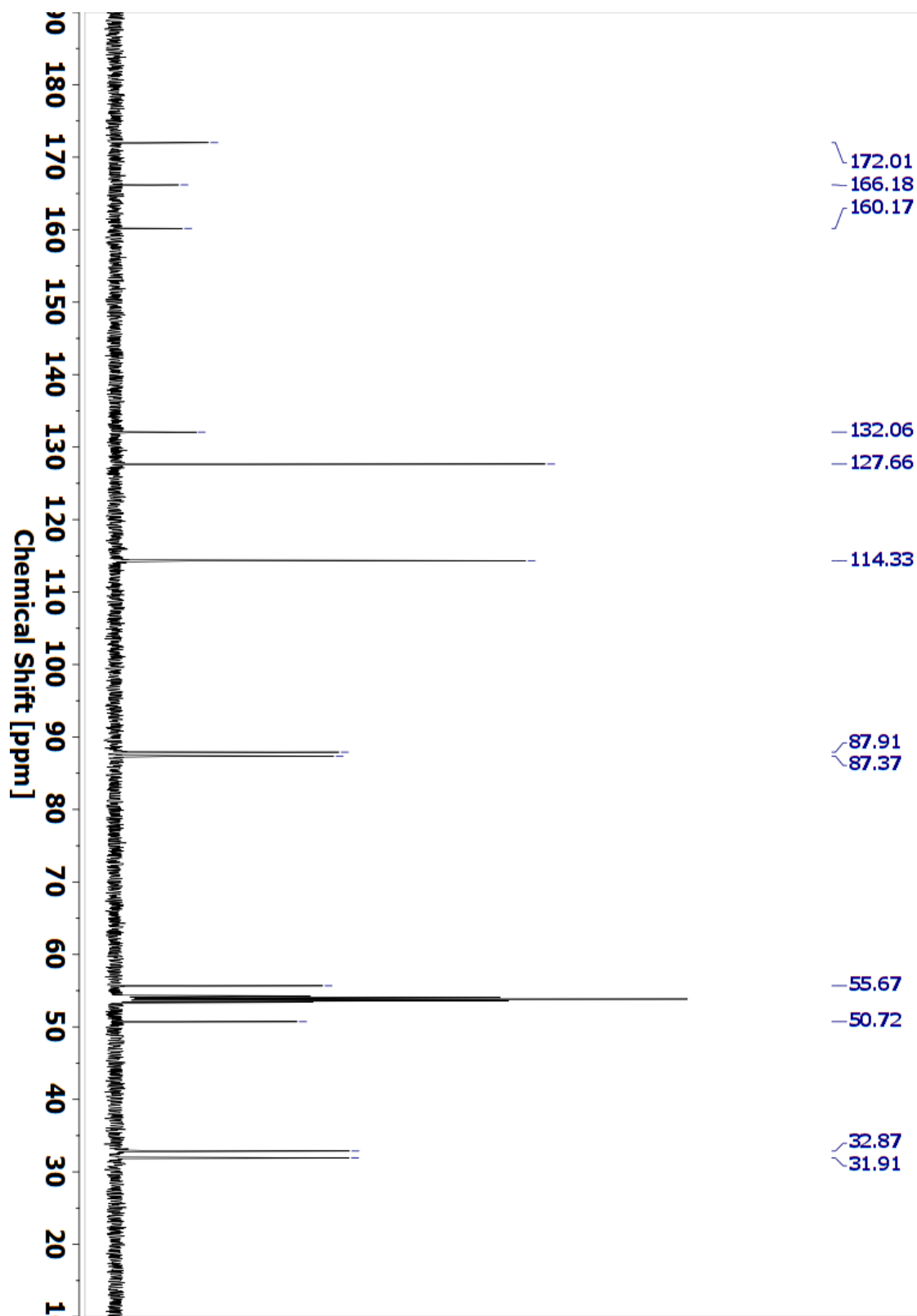
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.1 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).

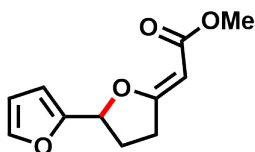


^1H NMR spectrum of isolated product in CD_2Cl_2



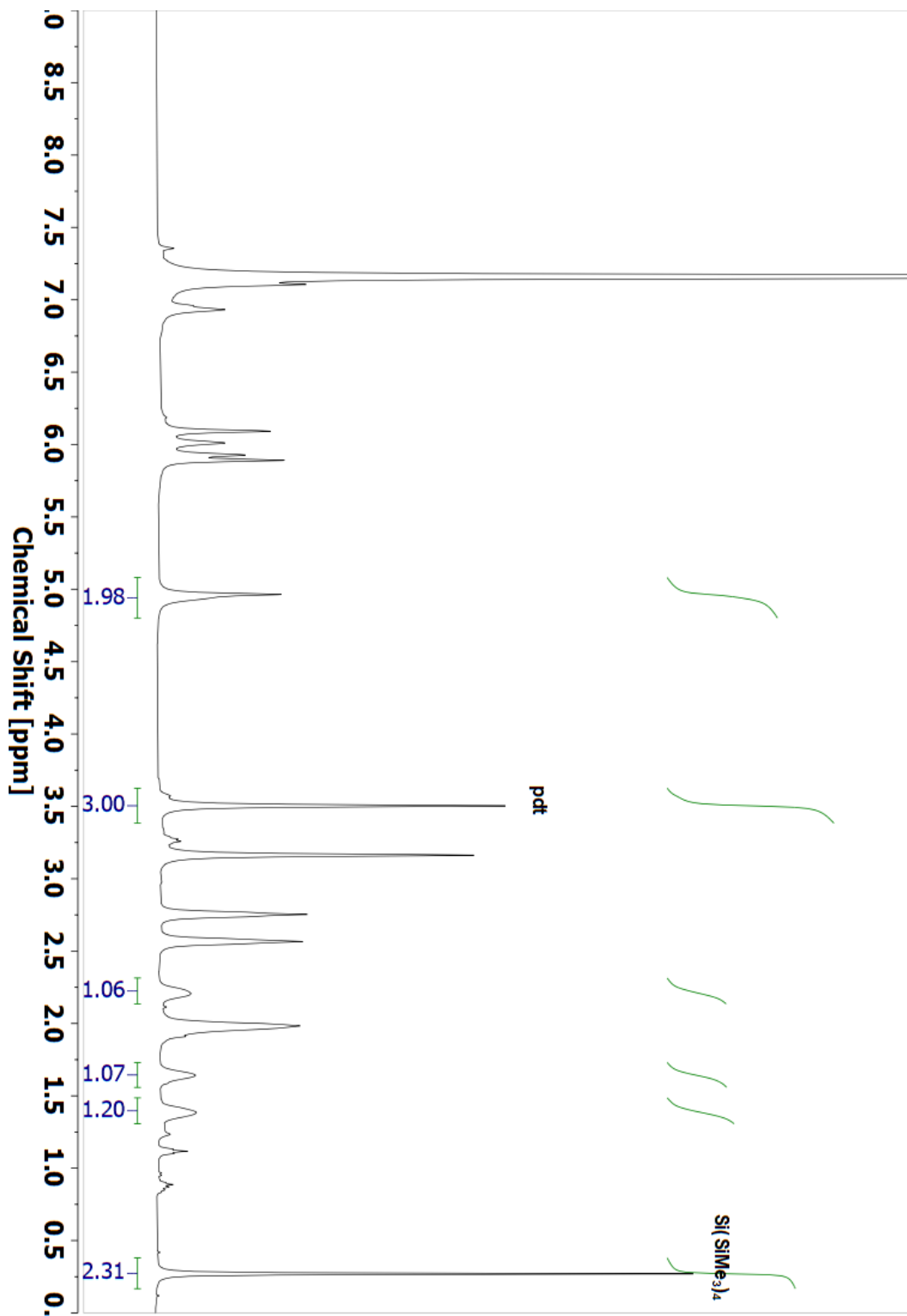
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl (Z)-2-(5-(furan-2-yl)dihydrofuran-2(3H)-ylidene)acetate (20)

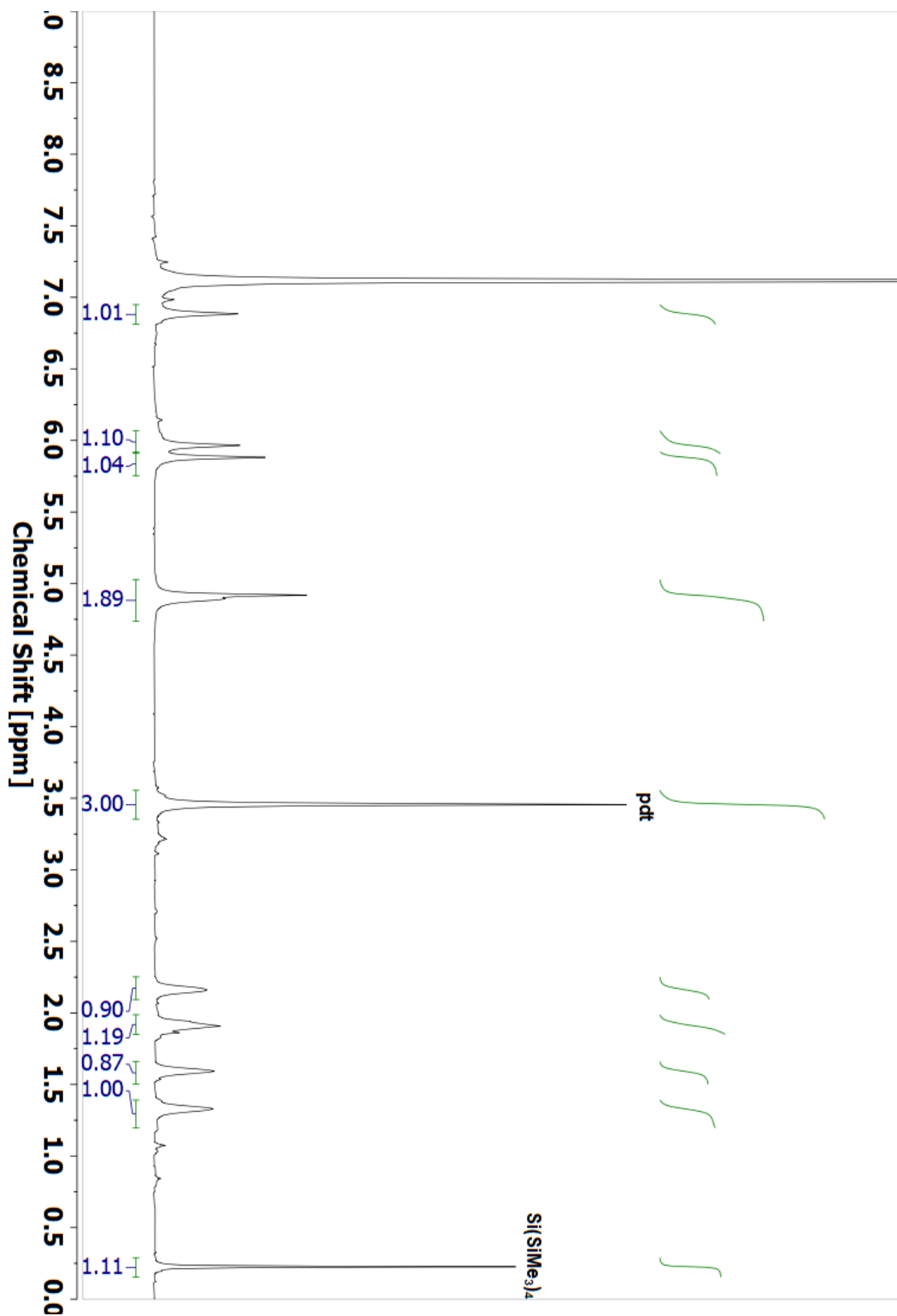


The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 25% NMR yield) and (2) at 60 °C with 20 mol% catalyst loading following procedure D (20 min, 50% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 7.9 mg (45% yield) of product as white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.40 (dd, $J = 1.9, 0.7$ Hz, 1H), 6.40 (dd, $J = 3.2, 0.7$ Hz, 1H), 6.34 (dd, $J = 3.2, 1.9$ Hz, 1H), 5.59 (t, $J = 6.9$ Hz, 1H), 4.91 (t, $J = 1.3$ Hz, 1H), 3.64 (s, 3H), 3.01–2.91 (m, 1H), 2.83–2.76 (m, 1H), 2.35–2.27 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.06, 166.23, 151.32, 143.27, 110.49, 109.47, 88.35, 80.19, 50.84, 32.33, 27.62. HRMS (ESI $^+$) m/z Calc. 209.0808 [$\text{C}_{11}\text{H}_{12}\text{O}_4+\text{H}$] $^+$, Found. 209.0807 [$\text{M}+\text{H}$] $^+$.

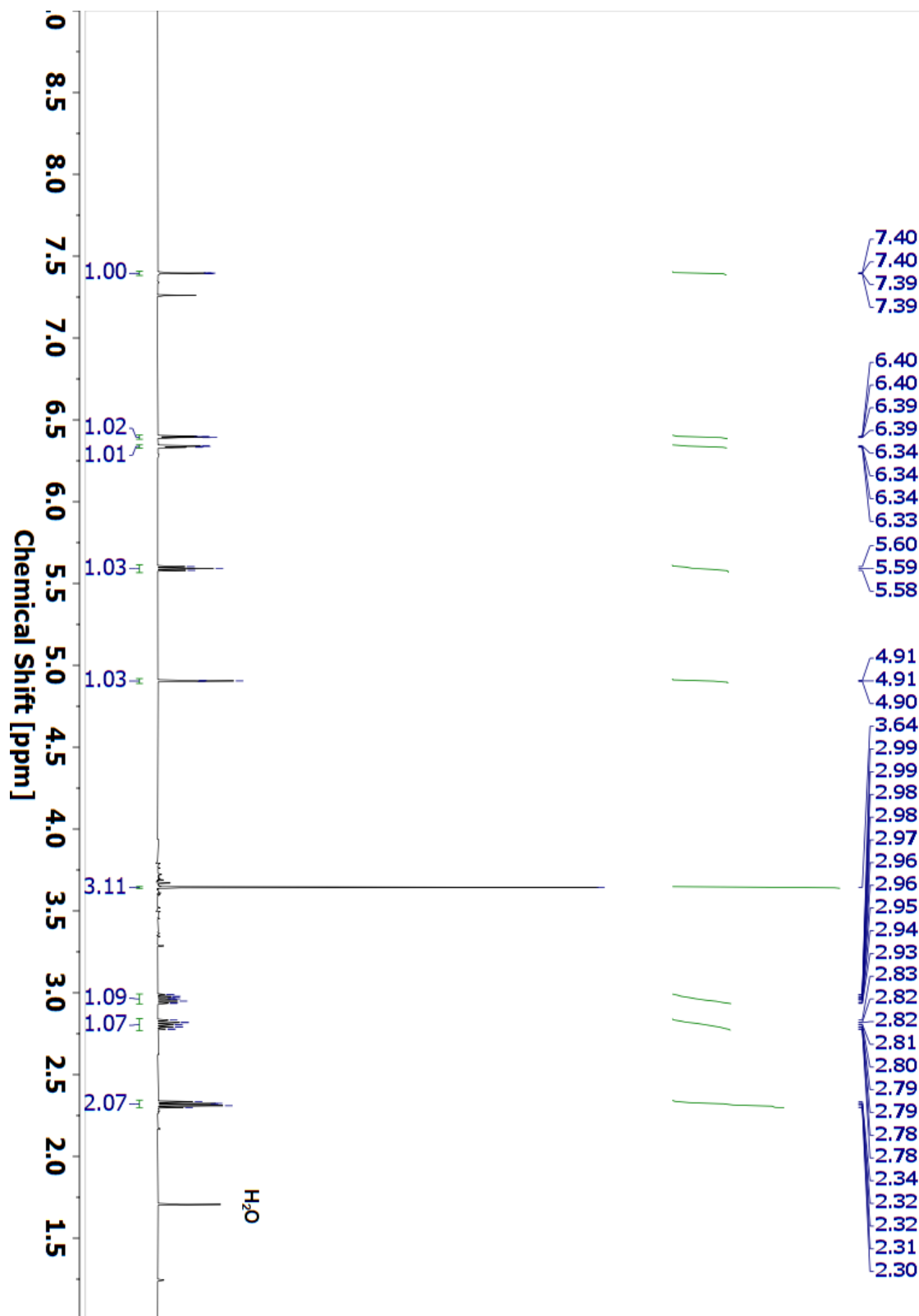
Scale-up: The reaction was carried out at 60 °C with 20 mol% catalyst loading following procedure D for 1 h with 200 mg of α -diazo- β -ketoester in 20 ml of benzene to give 113 mg (64% yield) of product as a white solid.



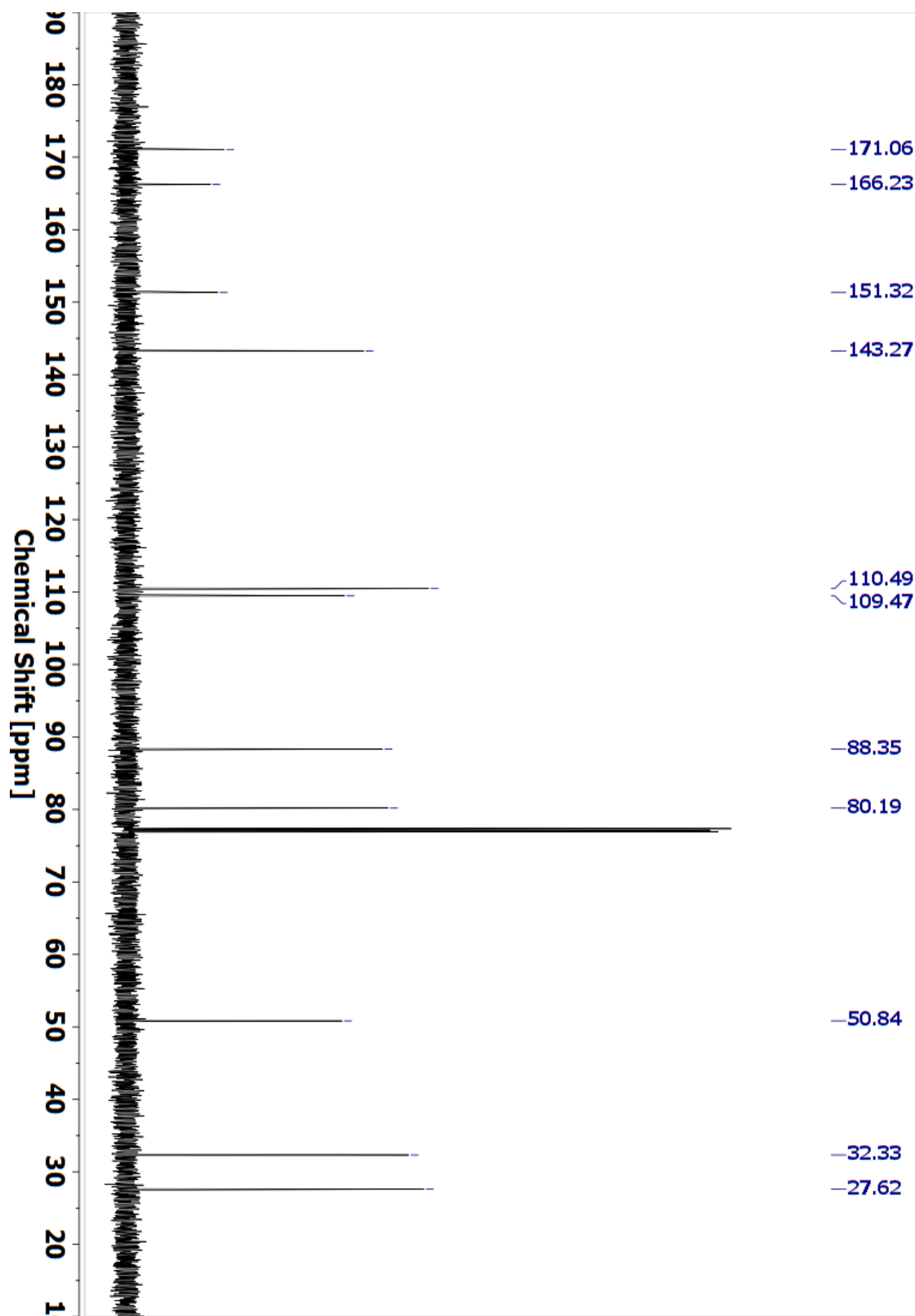
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 20 mol% Fe(acac)₂ after 12 h (0.5 mg Si(SiMe₃)₄ as internal standard).

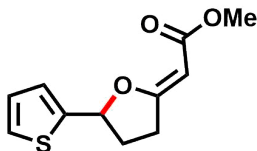


¹H NMR spectrum of isolated product in CDCl₃



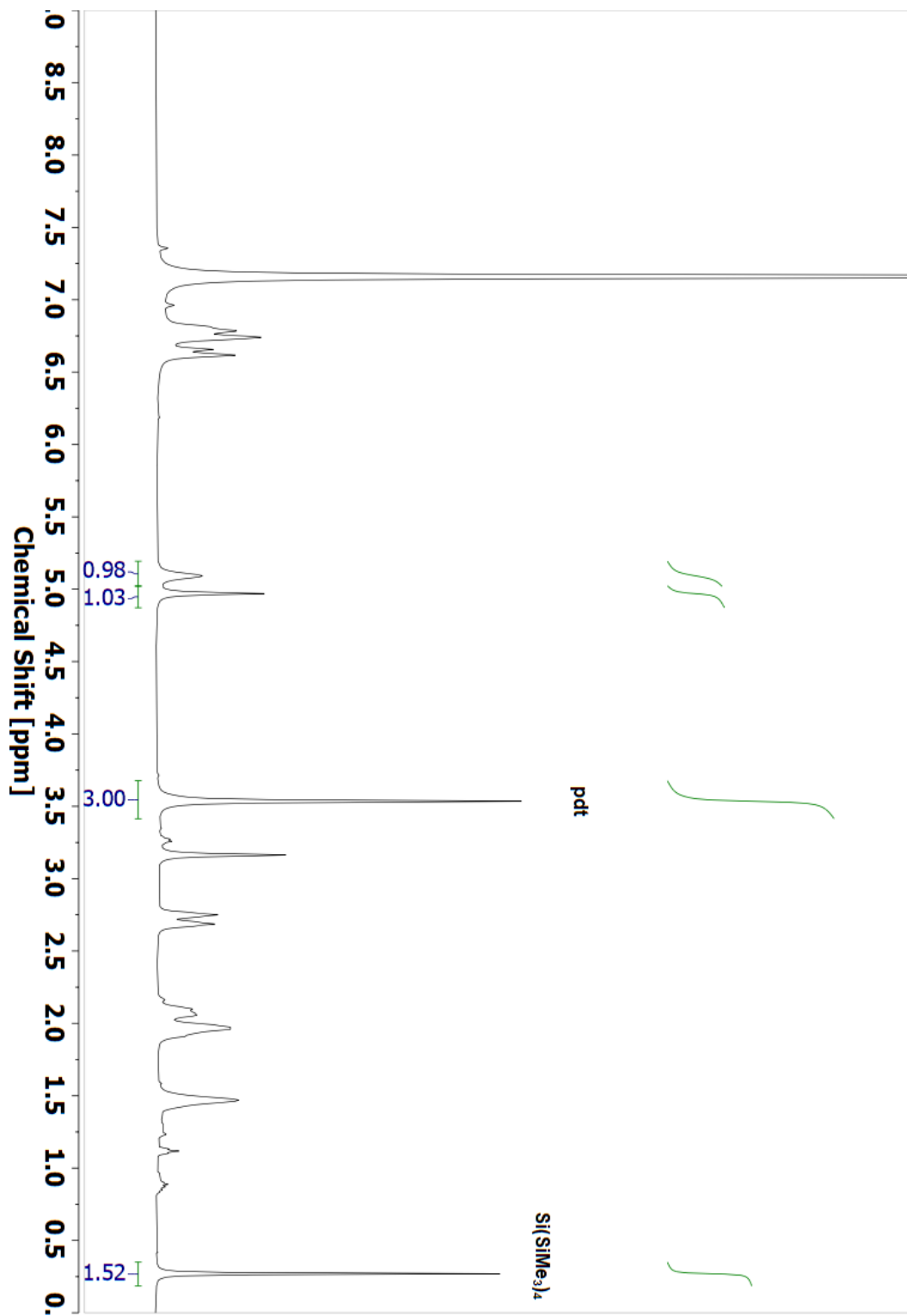
¹³C NMR spectrum of isolated product in CDCl₃

Methyl (Z)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21)

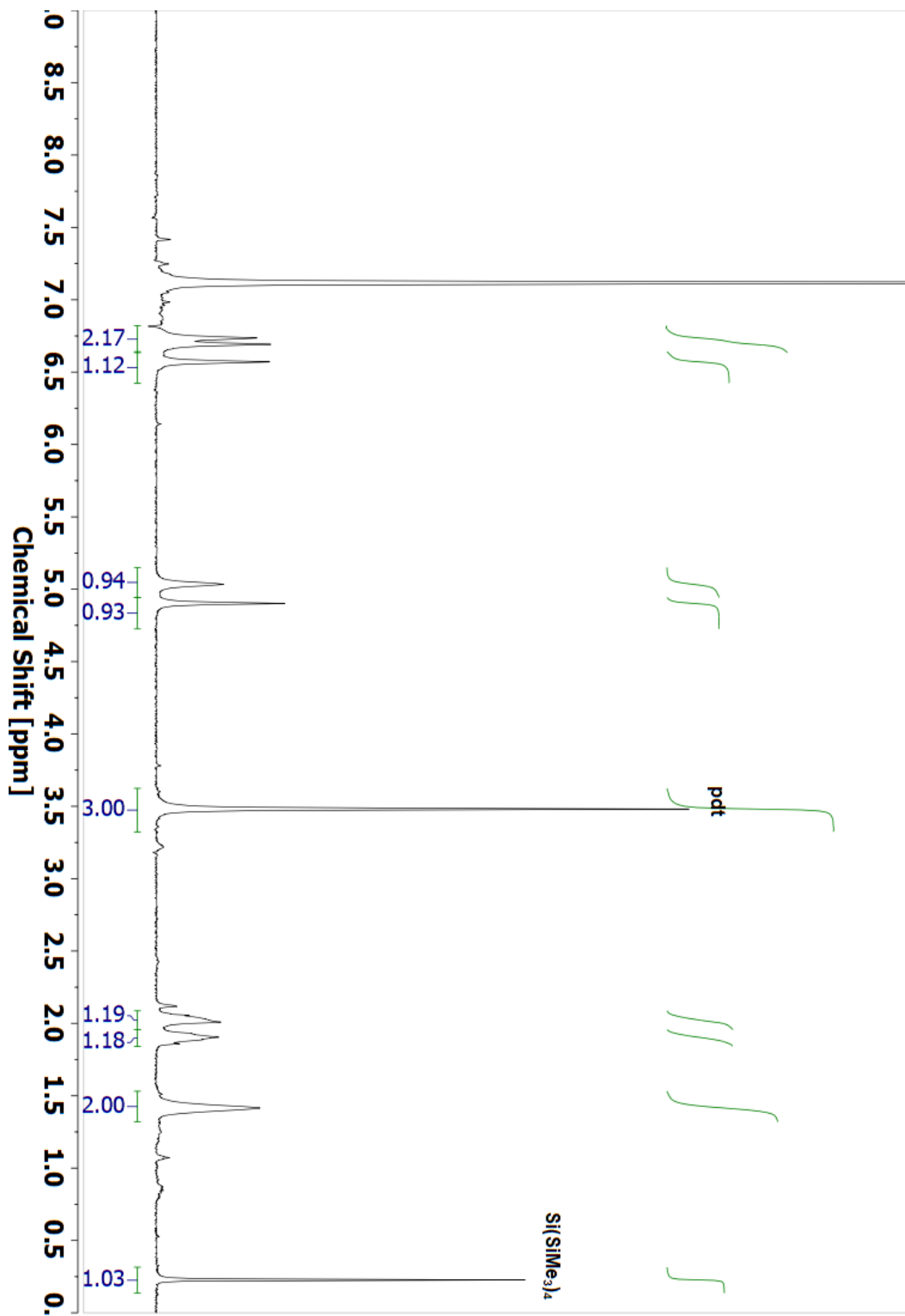


The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (12 h, 41% NMR yield) and (2) at 60 °C with 20 mol% catalyst loading following procedure D (20 min, 57% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 9.3 mg (52% yield) of product as white solid. Crystals suitable for single crystal X-ray diffraction study is obtained by storing a concentrated hexanes solution at -30 °C for 48 h. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.36 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.17–7.08 (m, 1H), 7.03 (dd, $J = 5.0, 3.5$ Hz, 1H), 5.89–5.70 (m, 1H), 4.89 (t, $J = 1.3$ Hz, 1H), 3.61 (s, 3H), 2.95–2.78 (m, 2H), 2.56–2.42 (m, 1H), 2.26–2.06 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 171.01, 165.98, 142.64, 127.29, 126.49, 88.44, 88.42, 83.21, 50.78, 32.75, 32.01. HRMS (ESI+) m/z Calc. 225.0580 [$\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}+\text{H}$] $^+$, Found 225.0584 [$\text{M}+\text{H}$] $^+$.

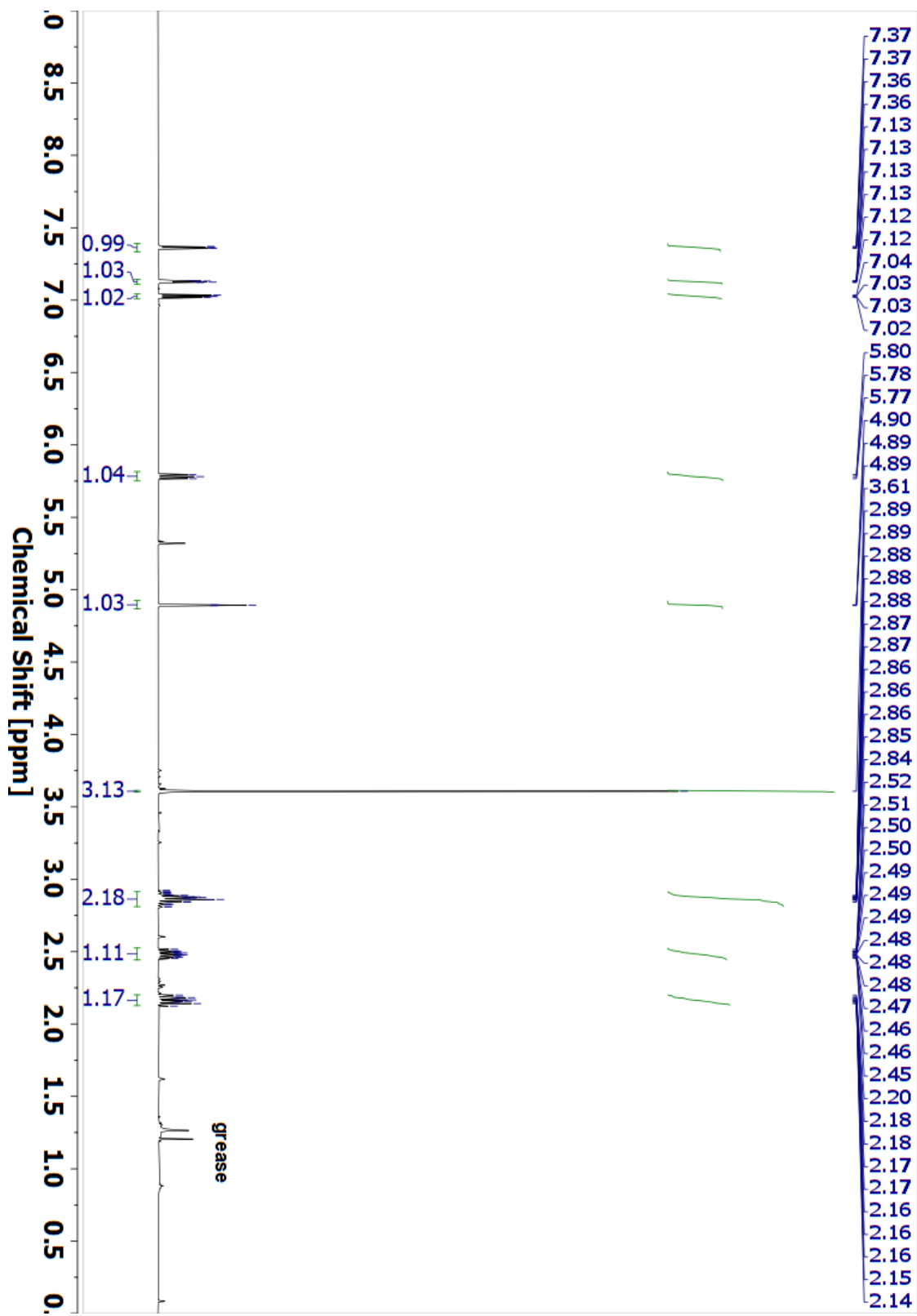
Scale-up: The reaction was carried out at 60 °C with 20 mol% catalyst loading following procedure D for 1 h with 200 mg of α -diazo- β -ketoester in 20 ml of benzene to give 131 mg (74% yield) of product as a white solid.



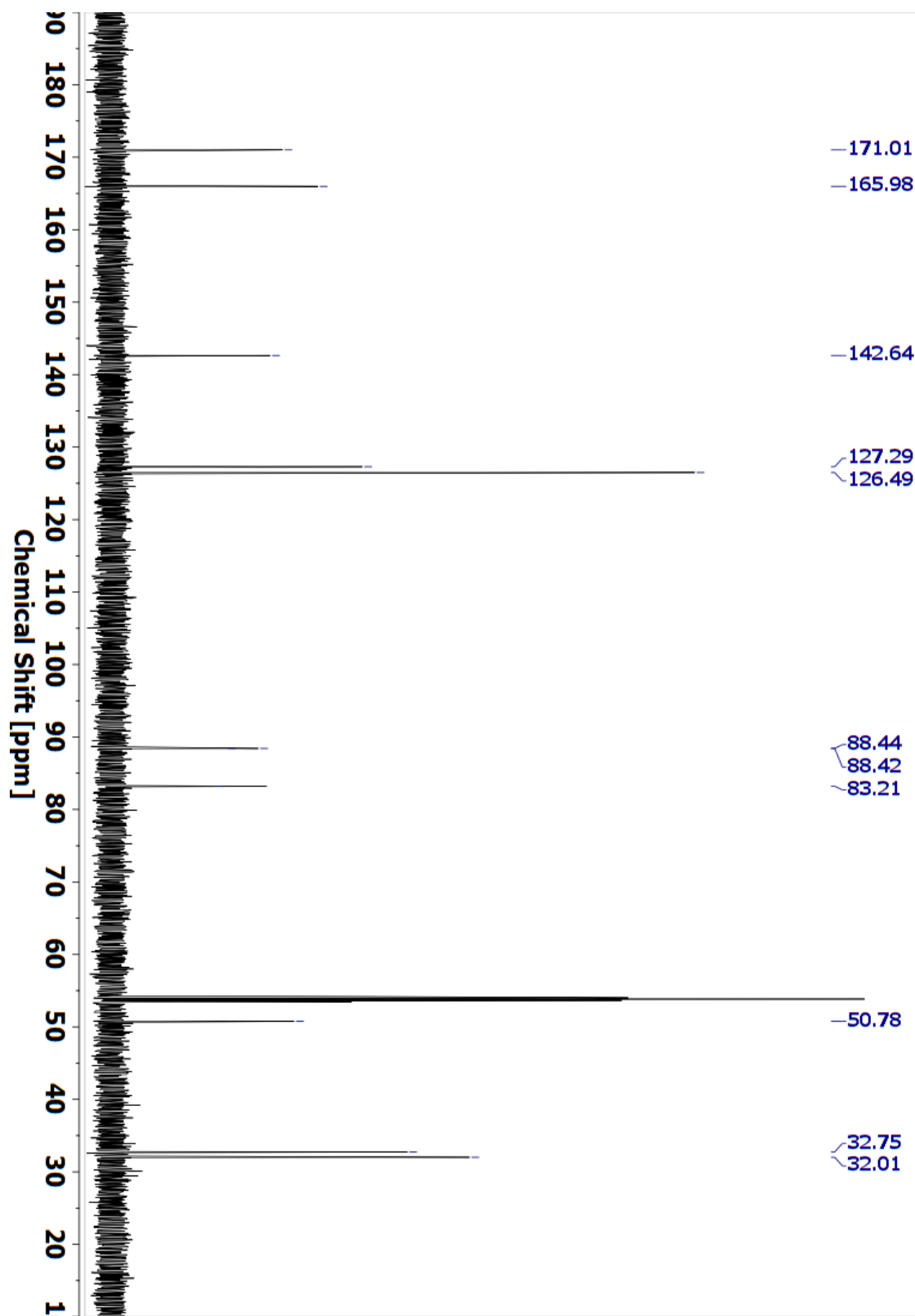
Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% $\text{Fe}(\text{acac})_2$ after 12 h (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



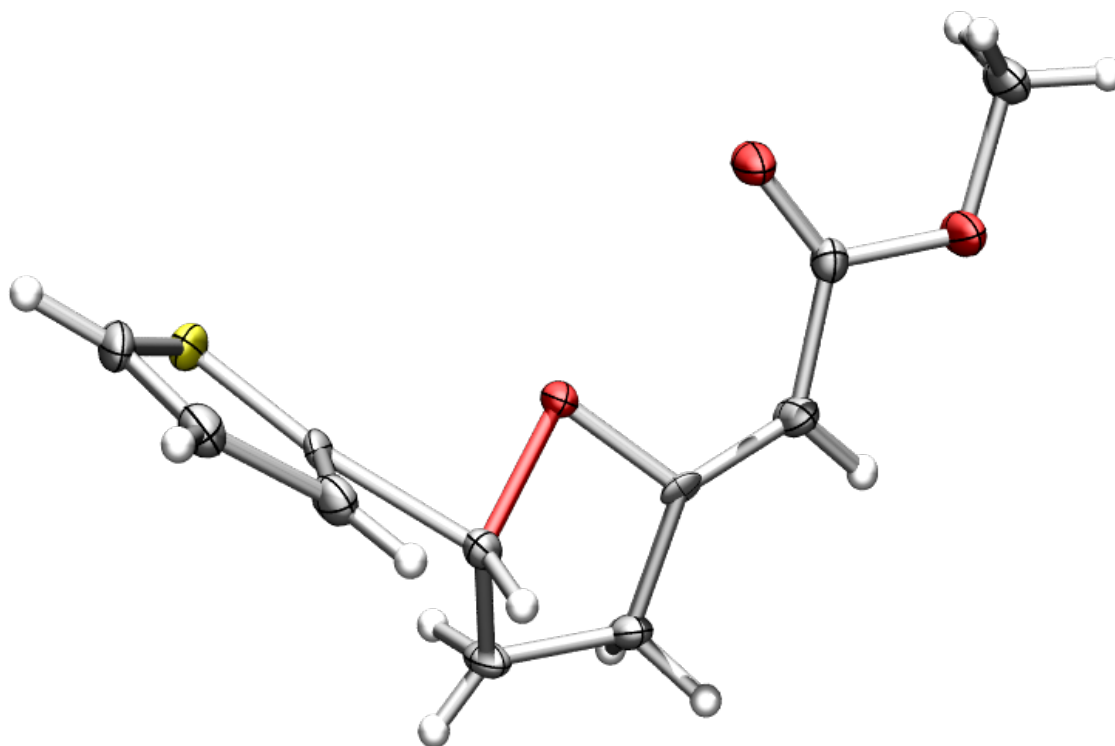
Crude NMR spectrum for reaction carried out at 60 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 20 min (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



^1H NMR spectrum of isolated product in CD_2Cl_2

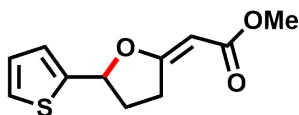


¹³C NMR spectrum of isolated product in CD₂Cl₂

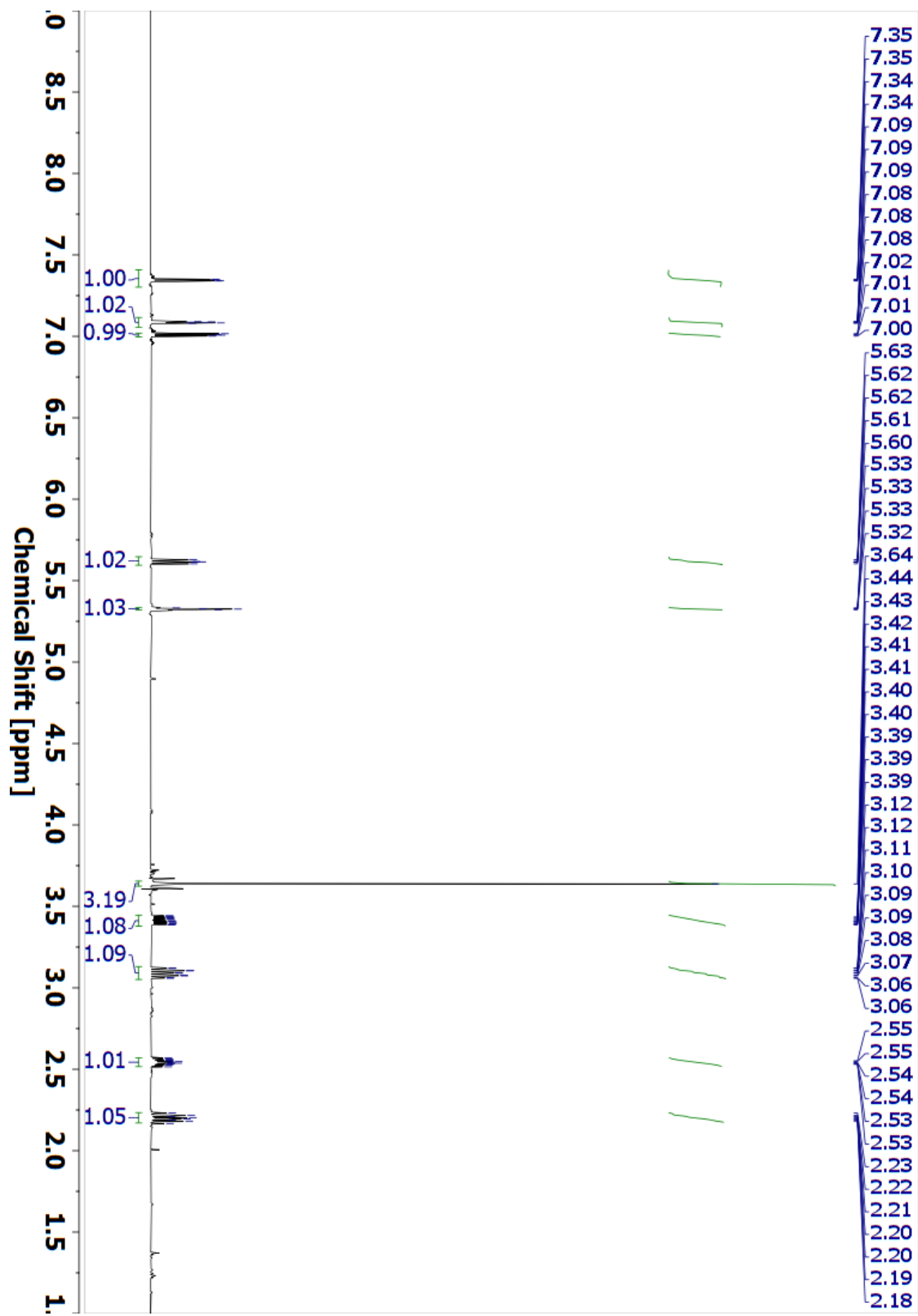


Solid-state molecular structure of methyl (Z)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white, sulfur = yellow. Only one rotational disordered thiophene fragments is shown here for clarity.

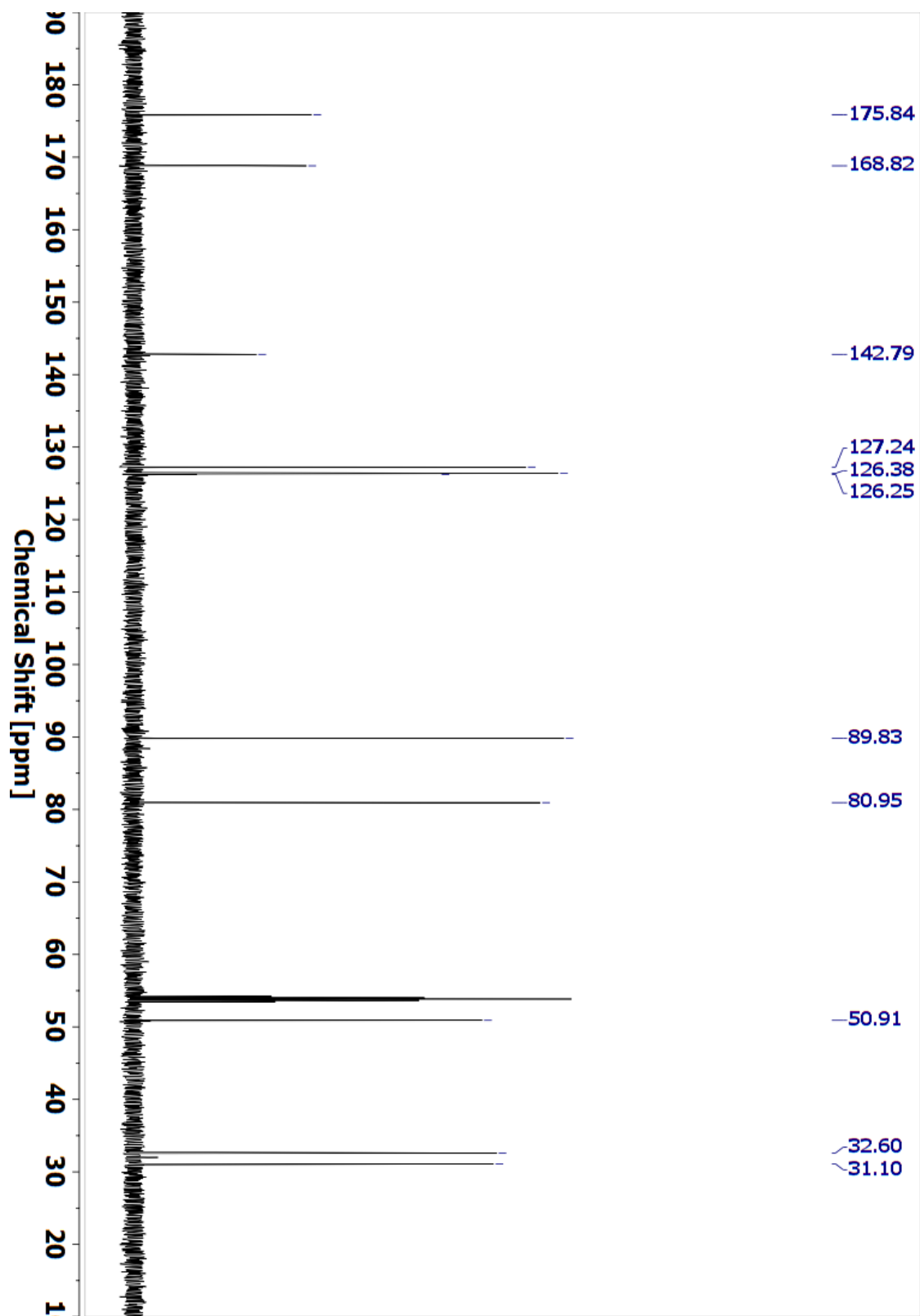
Methyl (E)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21')



The reaction was carried out following procedure E with 5.0 mg of starting material, giving quantitative conversion. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.35 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.11–7.05 (m, 1H), 7.01 (dd, $J = 5.1, 3.5$ Hz, 1H), 5.65–5.57 (m, 1H), 5.32 (t, $J = 2.0$ Hz, 1H), 3.64 (s, 3H), 3.45–3.36 (m, 1H), 3.17–3.04 (m, 1H), 2.58–2.50 (m, 1H), 2.26–2.14 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 175.84, 168.82, 142.79, 127.24, 126.38, 126.25, 89.83, 80.95, 50.91, 32.60, 31.10.

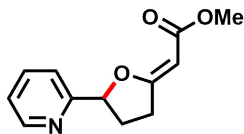


^1H NMR spectrum of isolated product in CD_2Cl_2

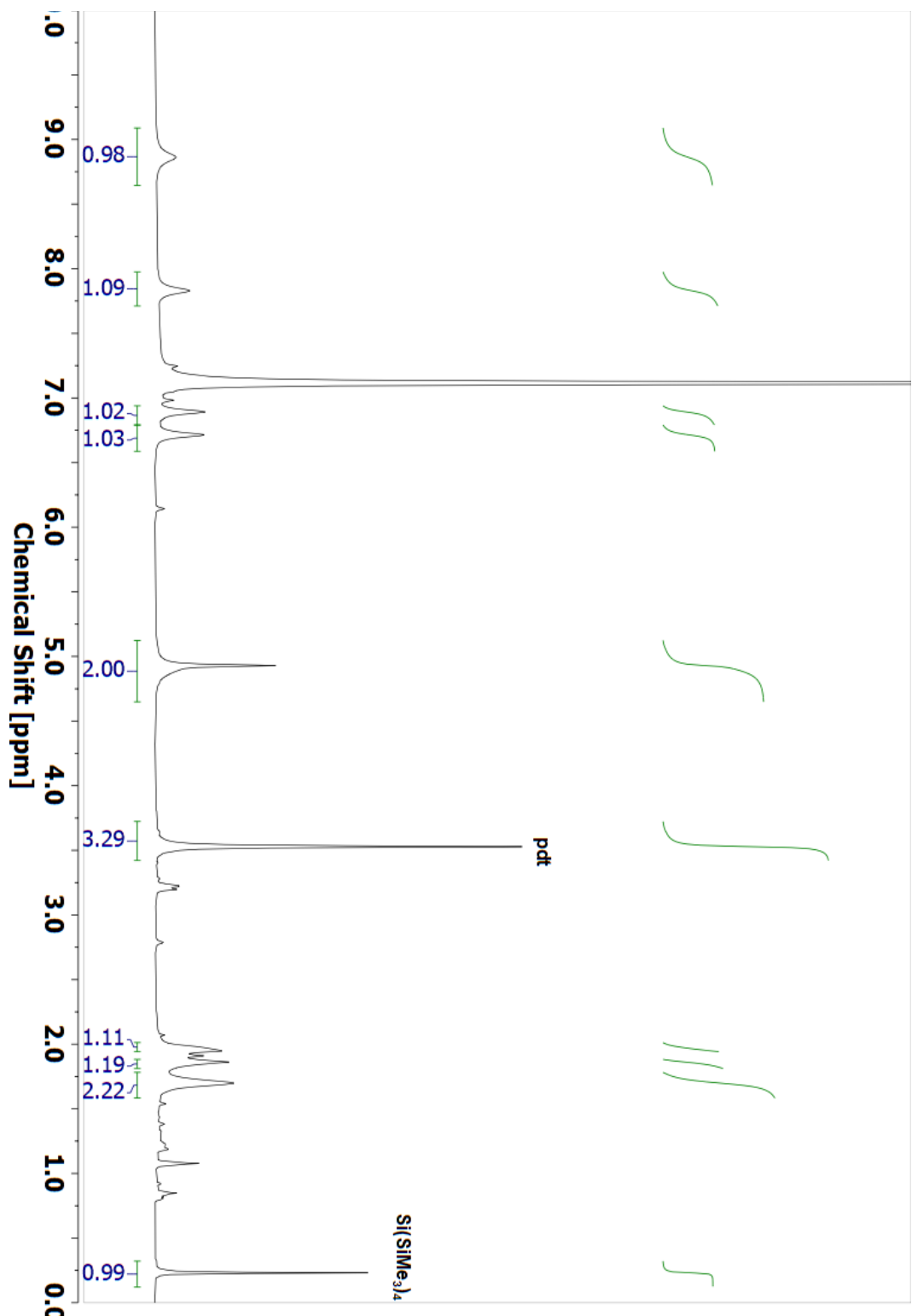


^{13}C NMR spectrum of isolated product in CD_2Cl_2

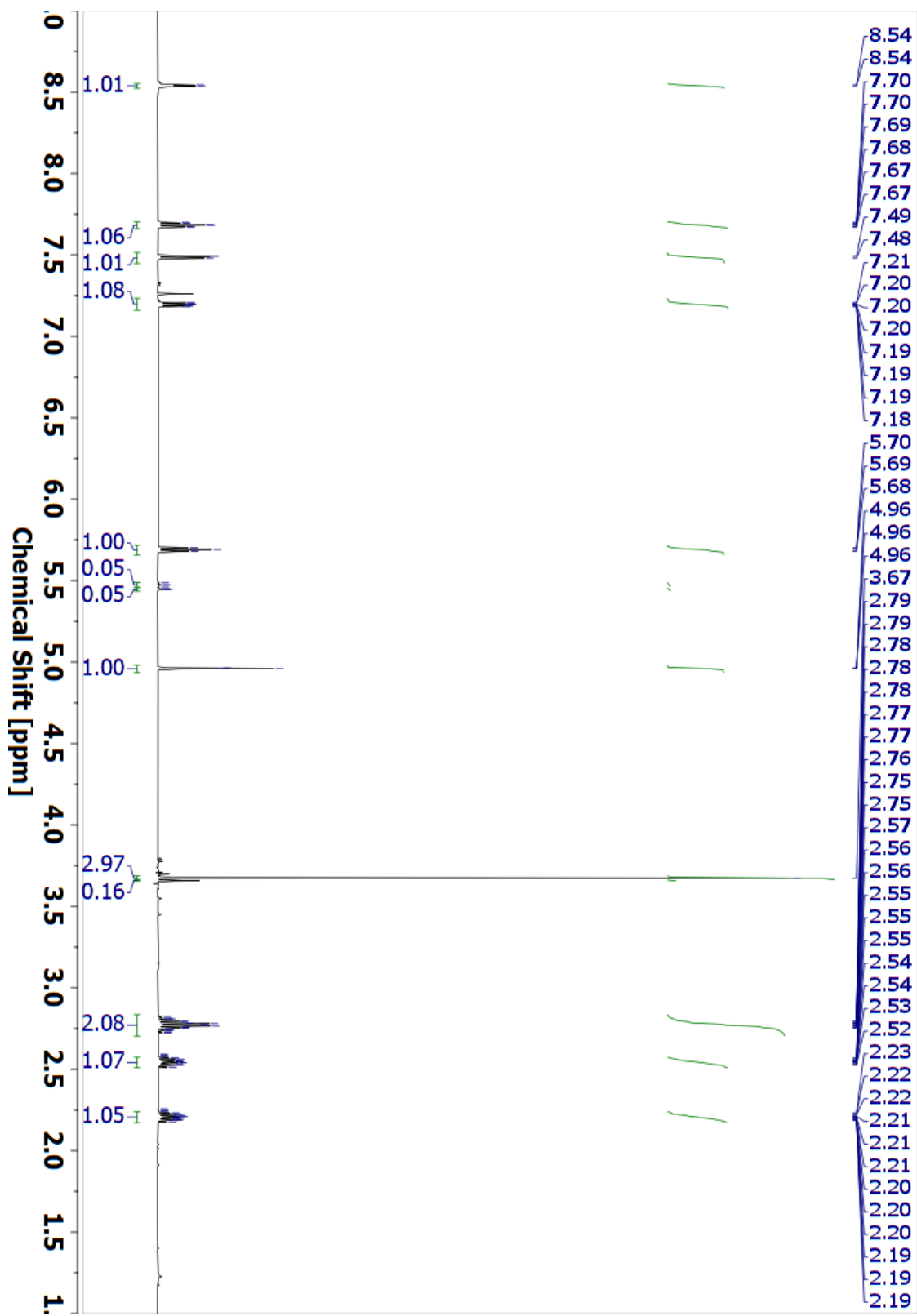
Methyl (Z)-2-(5-(pyridin-2-yl)dihydrofuran-2(3H)-ylidene)acetate (22)



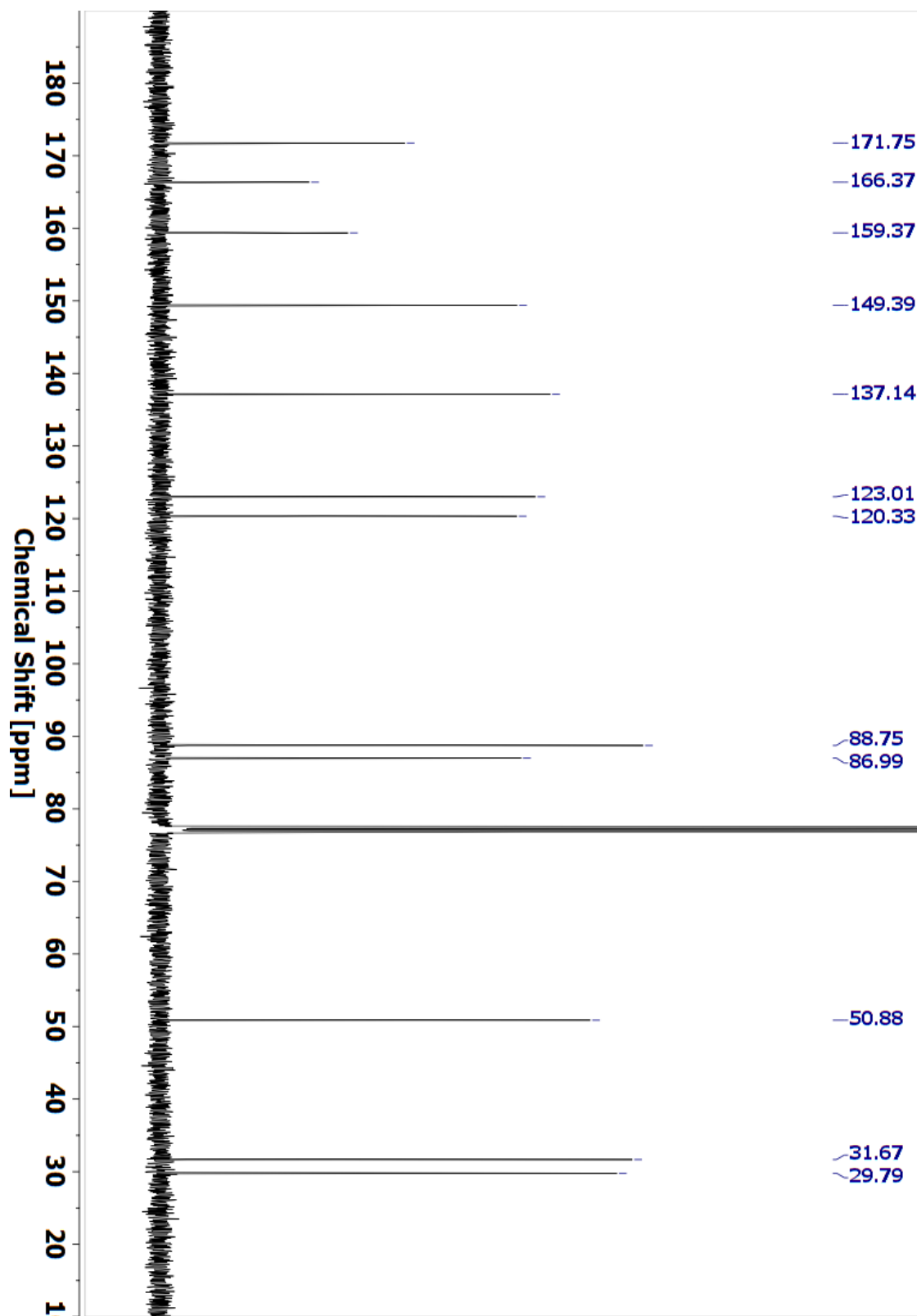
The reaction was carried out at 100 °C with 30 mol% catalyst loading following procedure D (20 min, 62% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 9.8 mg (55% yield, 95% *Z*- : 5% *E*-isomer) of product as white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.54 (d, $J = 4.8$ Hz, 1H), 7.71–7.66 (m, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.19 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H), 5.69 (t, $J = 6.7$ Hz, 1H), 4.96 (t, $J = 1.3$ Hz, 1H), 3.67 (s, 3H), 2.83–2.70 (m, 2H), 2.60–2.50 (m, 1H), 2.26–2.16 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.75, 166.37, 159.37, 149.39, 137.14, 123.01, 120.33, 88.75, 86.99, 50.88, 31.67, 29.79. HRMS (ESI $^+$) m/z Calc. 220.0968 [$\text{C}_{12}\text{H}_{13}\text{NO}_3 + \text{H}$] $^+$, Found. 220.0971 [$\text{M} + \text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 100 °C with 30 mol% Fe(acac)₂ after 20 min
(0.5 mg Si(SiMe₃)₄ as internal standard).

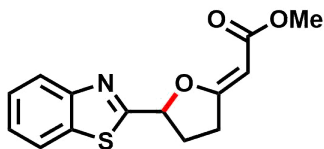


¹H NMR spectrum of isolated product in CDCl₃ (95% Z- : 5% E-isomer)



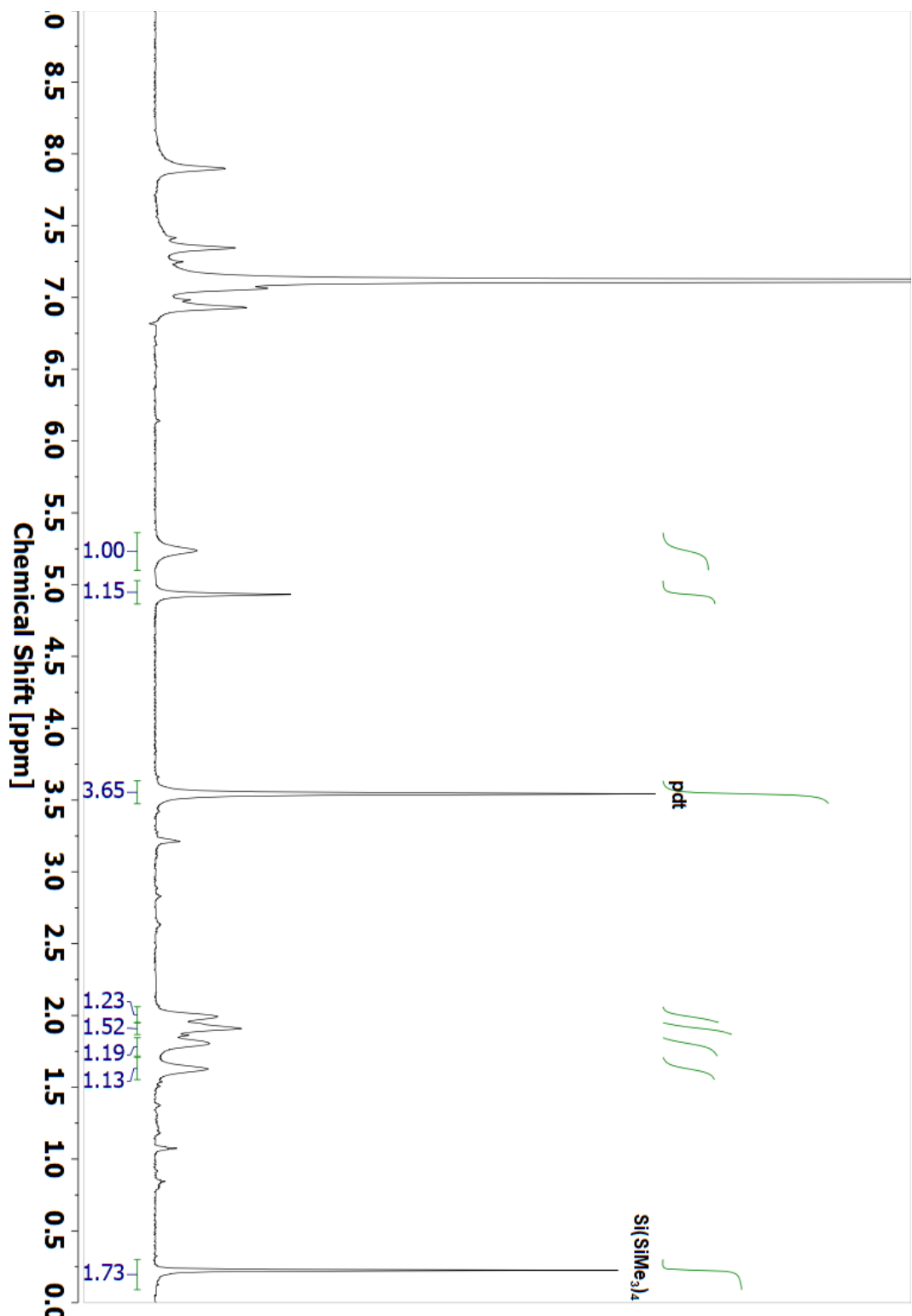
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl (Z)-2-(5-(benzo[d]thiazol-2-yl)dihydrofuran-2(3H)-ylidene)acetate (23)

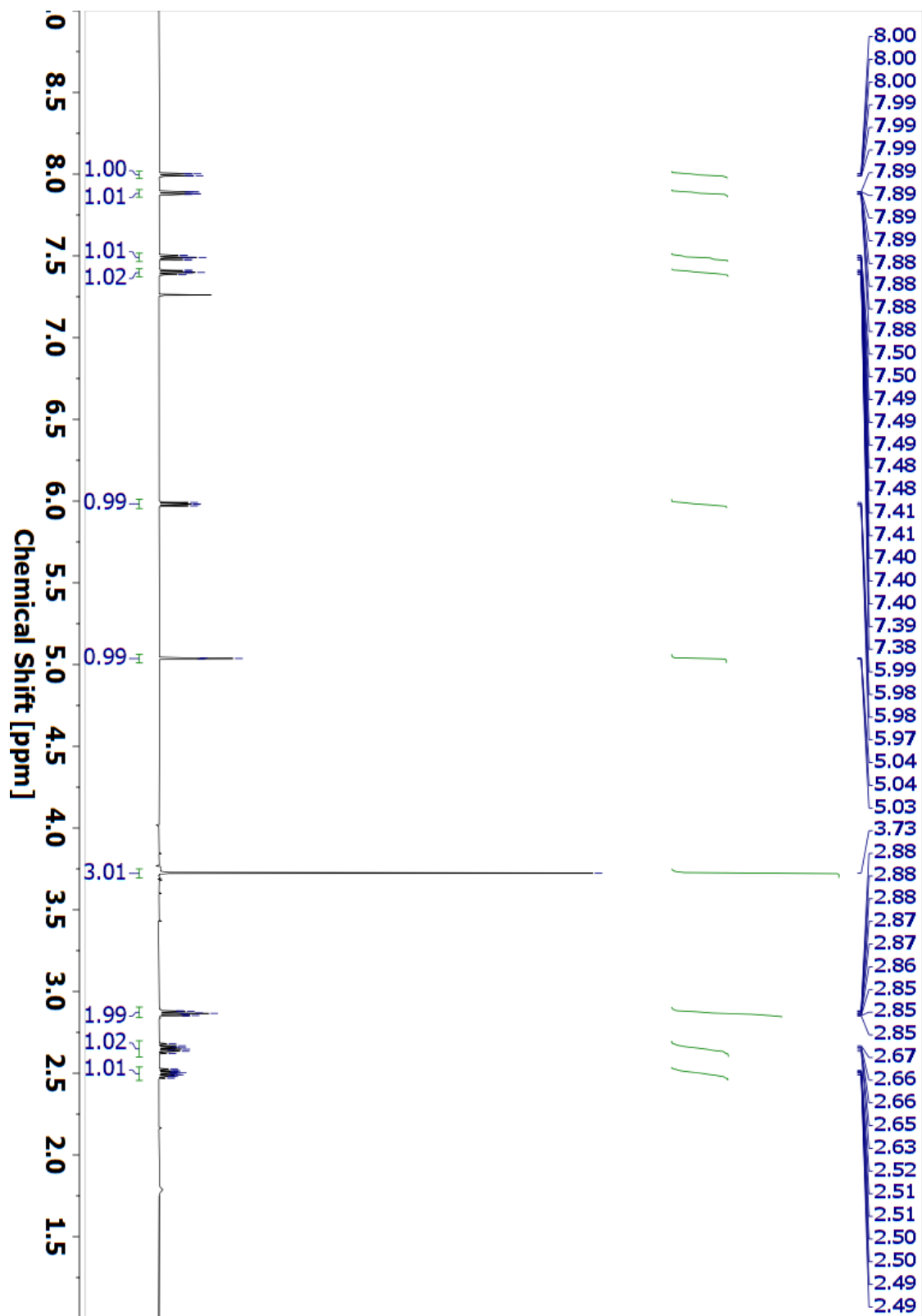


The reaction was carried out at 100 °C with 30 mol% catalyst loading following procedure D (20 min, 50% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 8.5 mg (47% yield) of product as white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.02–7.97 (m, 1H), 7.91–7.86 (m, 1H), 7.52–7.46 (m, 1H), 7.43–7.37 (m, 1H), 5.98 (dd, $J = 7.4, 5.5$ Hz, 1H), 5.04 (t, $J = 1.4$ Hz, 1H), 3.73 (s, 3H), 2.91–2.82 (m, 1H), 2.70–2.60 (m, 1H), 2.54–2.45 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.83, 170.03, 165.90, 153.31, 134.96, 126.33, 125.43, 123.17, 121.94, 90.05, 84.19, 50.99, 31.27, 29.89. HRMS (ESI⁺) m/z Calc. 276.0689 [$\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}+\text{H}$]⁺, Found. 276.0693 [$\text{M}+\text{H}$]⁺.

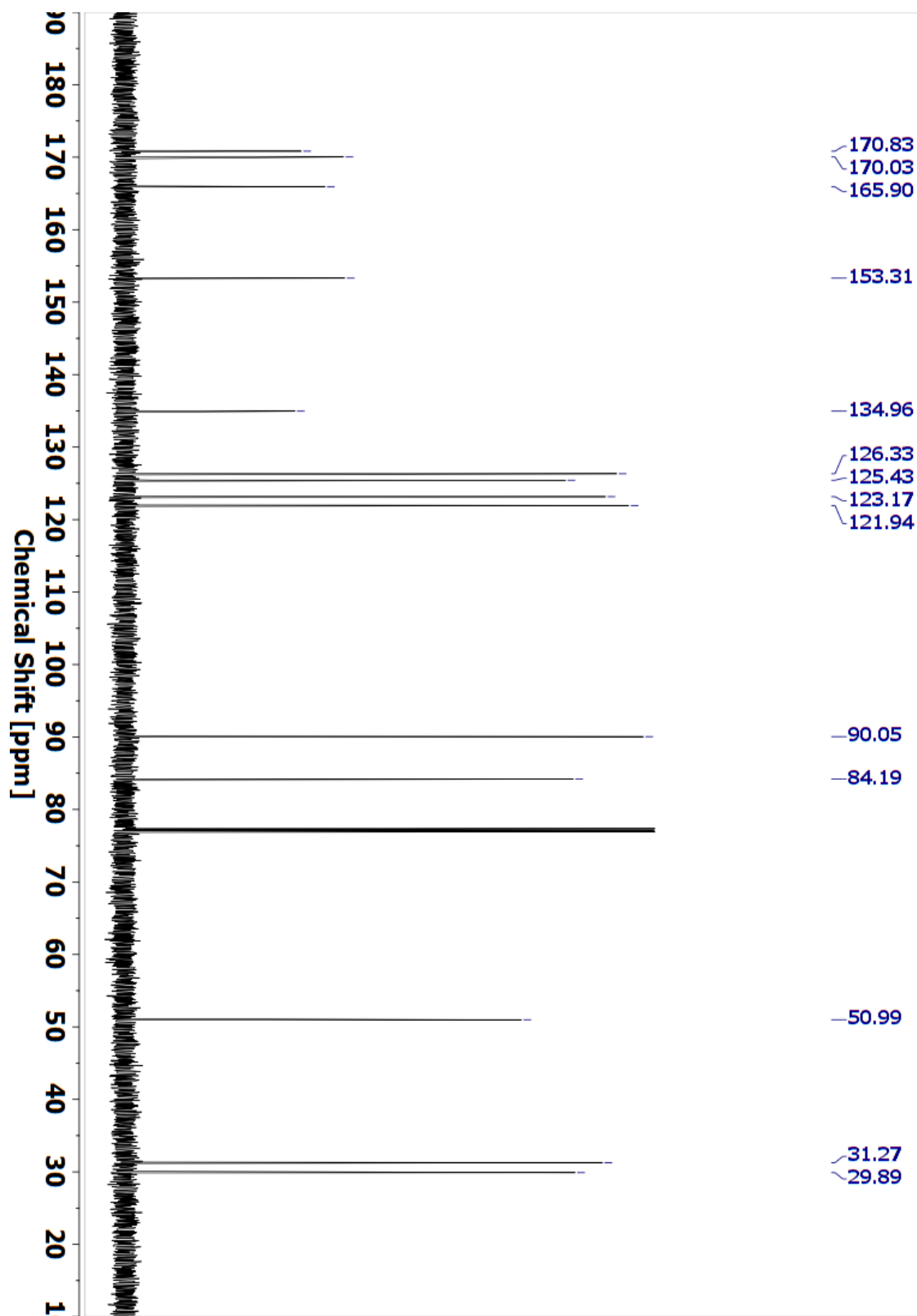
Scale-up: The reaction was carried out at 100 °C with 30 mol% catalyst loading following procedure D for 1 h with 110 mg of α -diazo- β -ketoester in 11 ml of benzene to give 62 mg (64% yield) of product as a white solid.



Crude NMR spectrum for reaction carried out at 100 °C with 30 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).

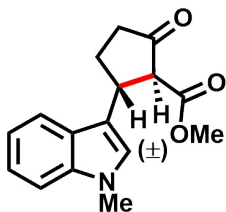


^1H NMR spectrum of isolated product in CDCl_3

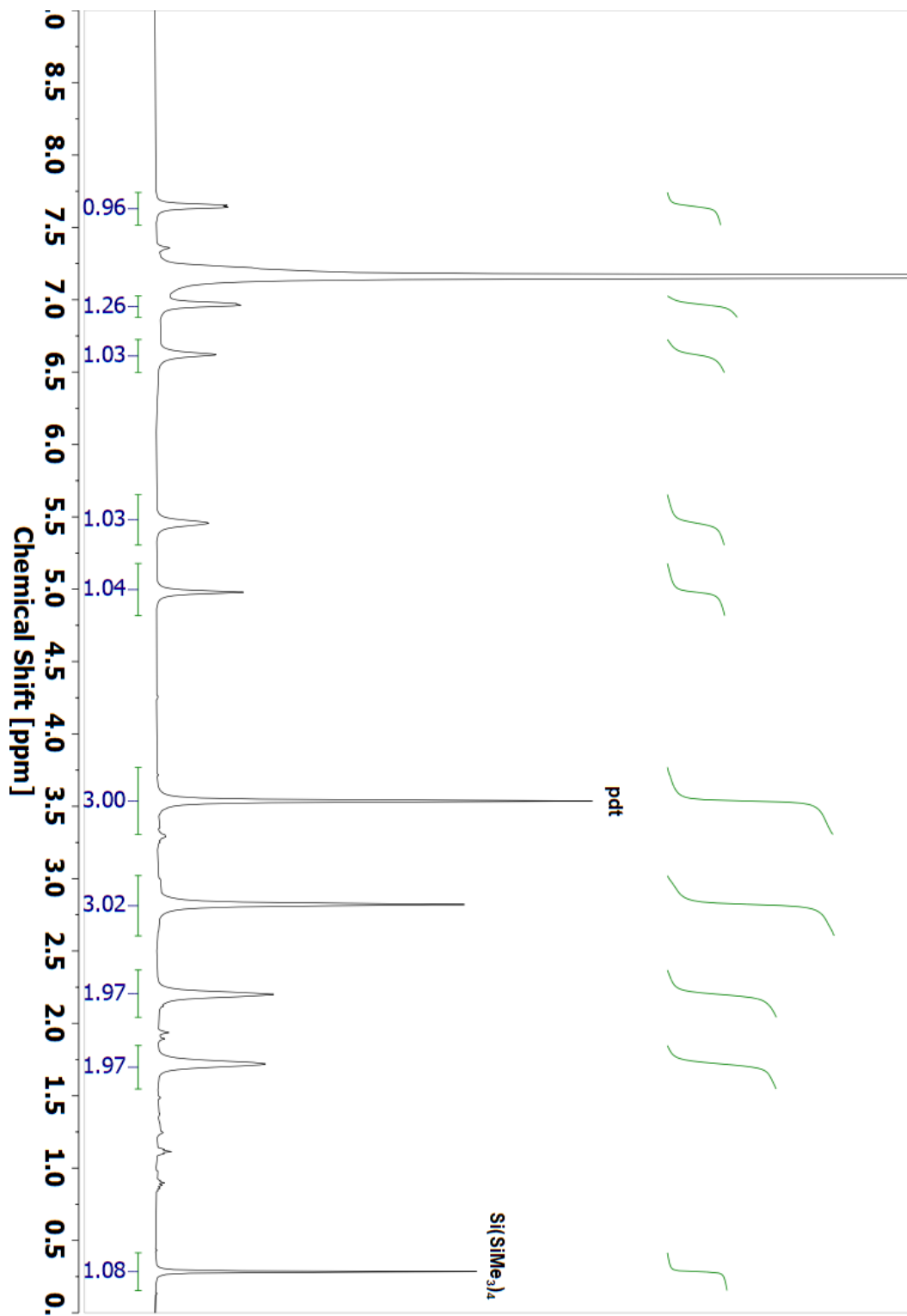


¹³C NMR spectrum of isolated product in CDCl₃

Methyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (24)

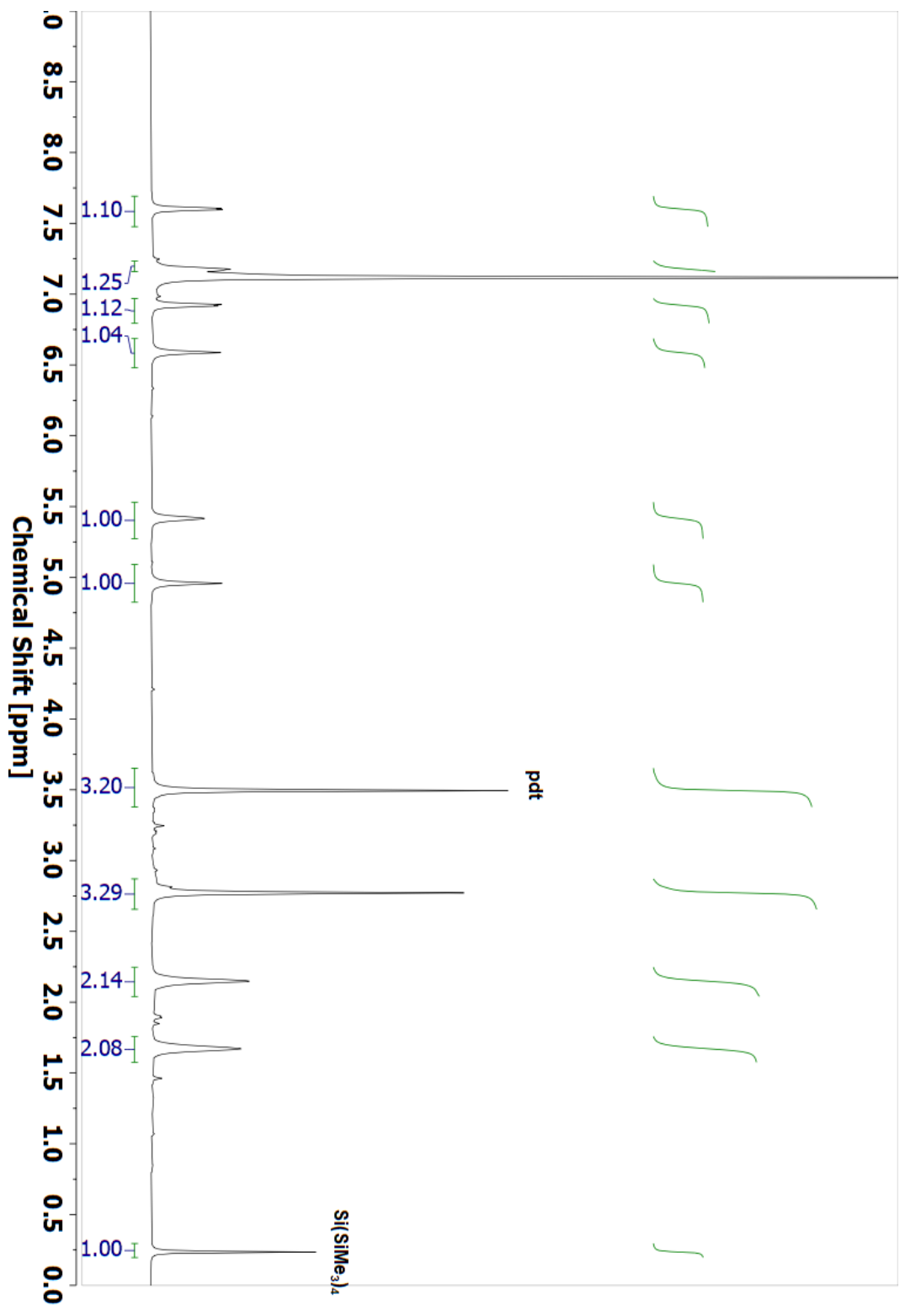


The reaction was carried out under two sets conditions: (1) at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 72% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 76% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.7 mg (70% yield) of product as white solid. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.59 (d, $J = 8.2$ Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.95 (s, 1H), 4.03 (td, $J = 11.8, 5.9$ Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.42 (d, $J = 11.8$ Hz, 1H), 2.66–2.44 (m, 3H), 2.17–2.03 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 211.70, 170.18, 137.81, 127.21, 125.77, 122.20, 119.47, 119.32, 115.35, 109.88, 62.56, 52.68, 39.10, 38.99, 33.01, 29.03. HRMS (ESI^+) m/z Calc. 312.1805 [$\text{C}_{16}\text{H}_{17}\text{NO}_3 + \text{H}$] $^+$, Found. 312.1804 [$\text{M} + \text{H}$] $^+$.

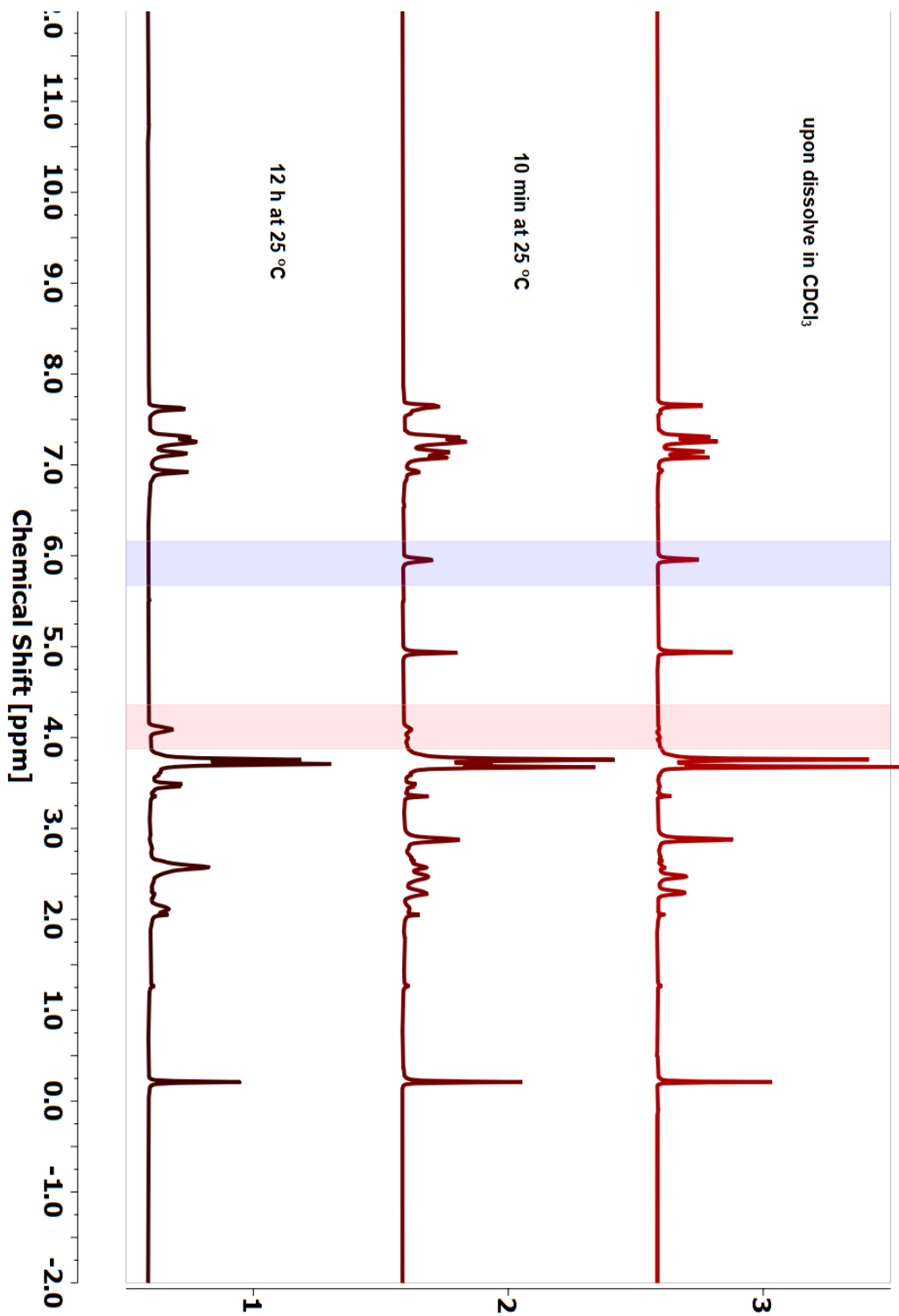


Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.5 mg

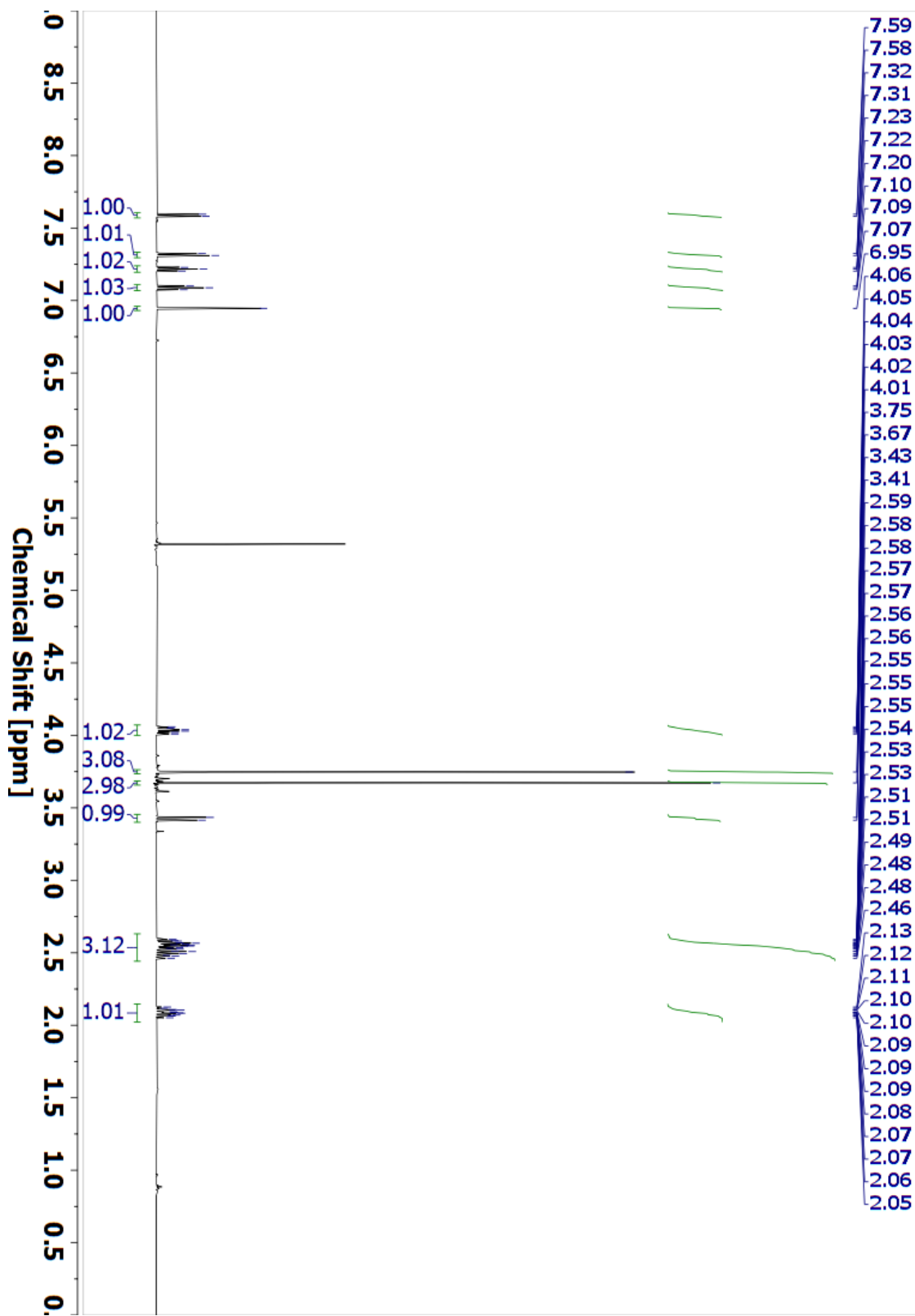
Si(SiMe₃)₄ as internal standard).



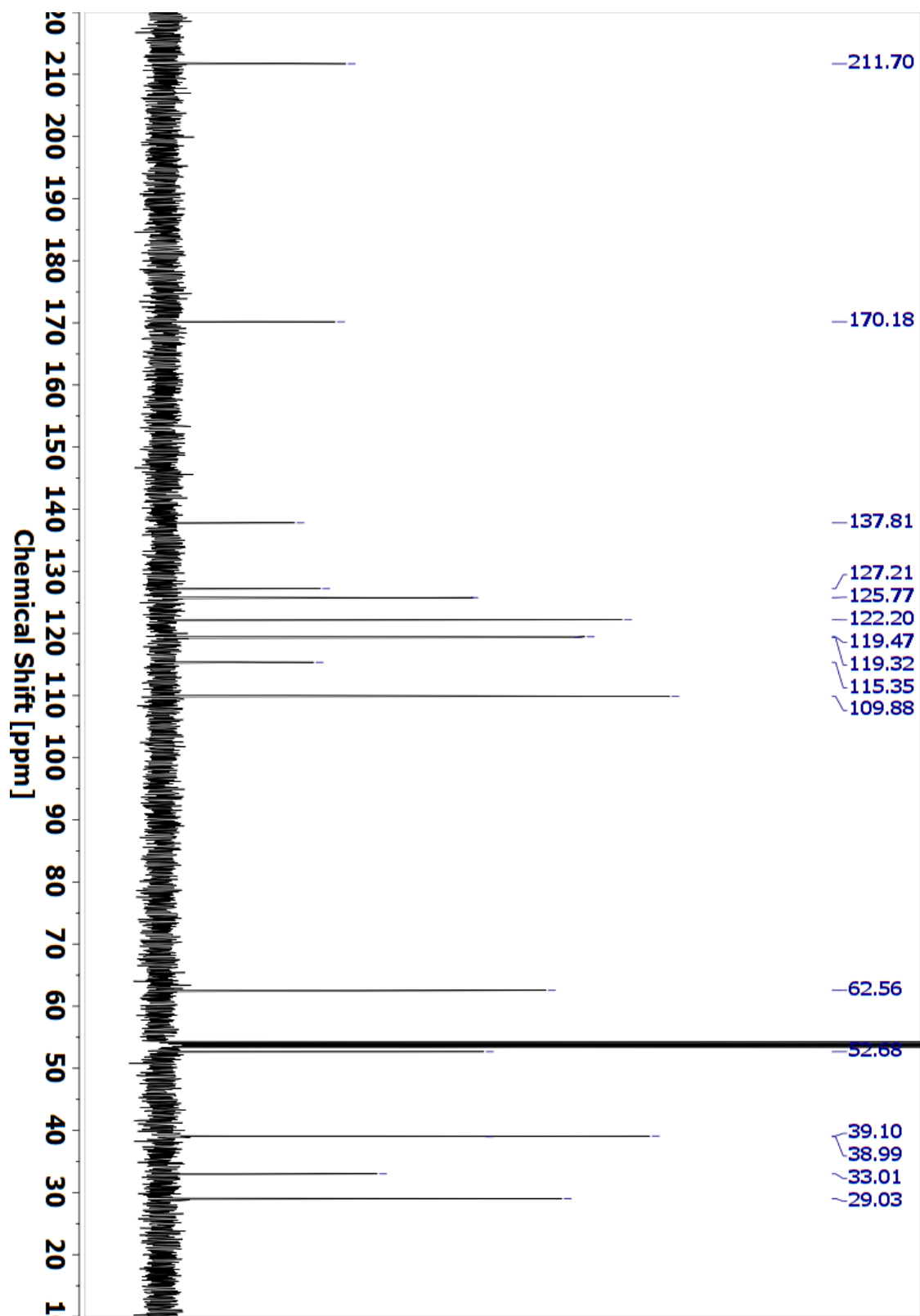
Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).



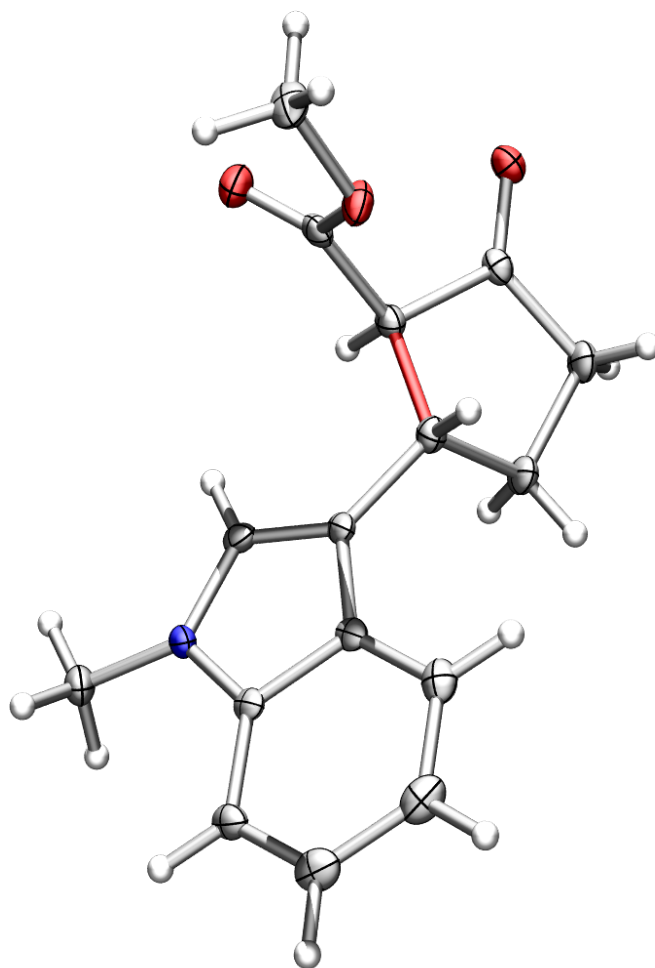
Crude sample dissolved in CDCl_3 and stand at 25 °C, showing the isomerization from 2-alkylidene dihydrofuran to substituted cyclopentanone derivative.



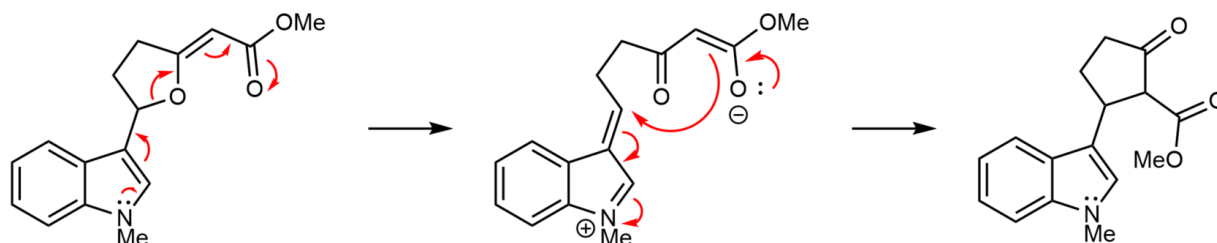
^1H NMR spectrum of isolated product in CD_2Cl_2



^{13}C NMR spectrum of isolated product in CD_2Cl_2

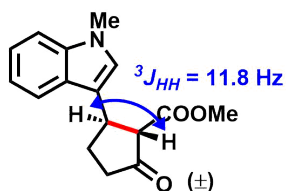


Solid-state molecular structure of methyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (24) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, nitrogen = blue, hydrogen = white.



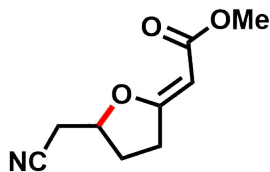
Proposed mechanism for product isomerization

Product **24** is generated exclusively as the *trans*- isomer, as suggested by the $^3J_{HH}$ coupling constants shown below:

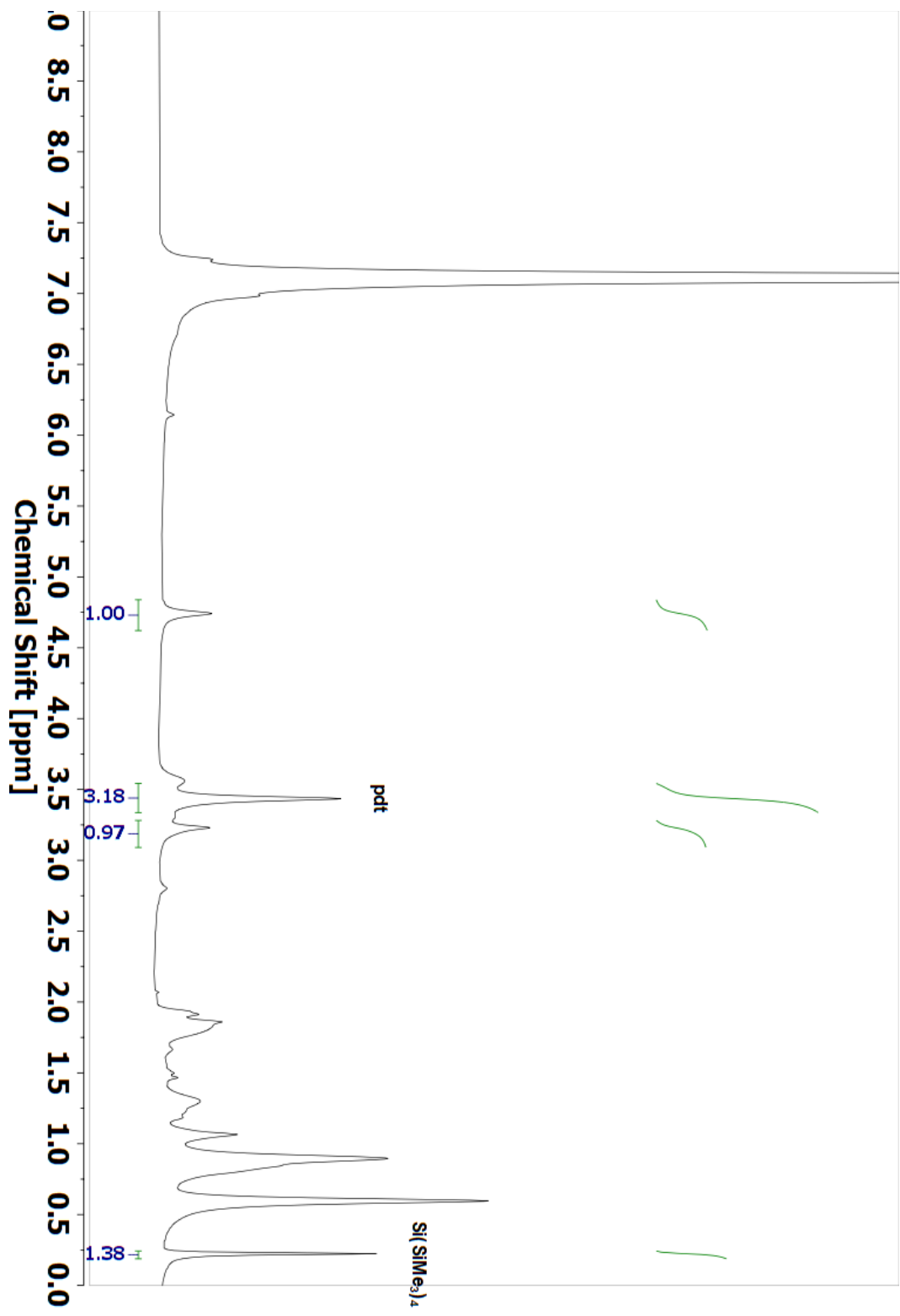


The *trans*- configuration is also the direct result of the nucleophilic attack of the β -keto-ester anion to the 3-alkylidene-indolium intermediate in the proposed mechanism. Similar results were also observed in previous study (*Science* **2018**, 362, 564).

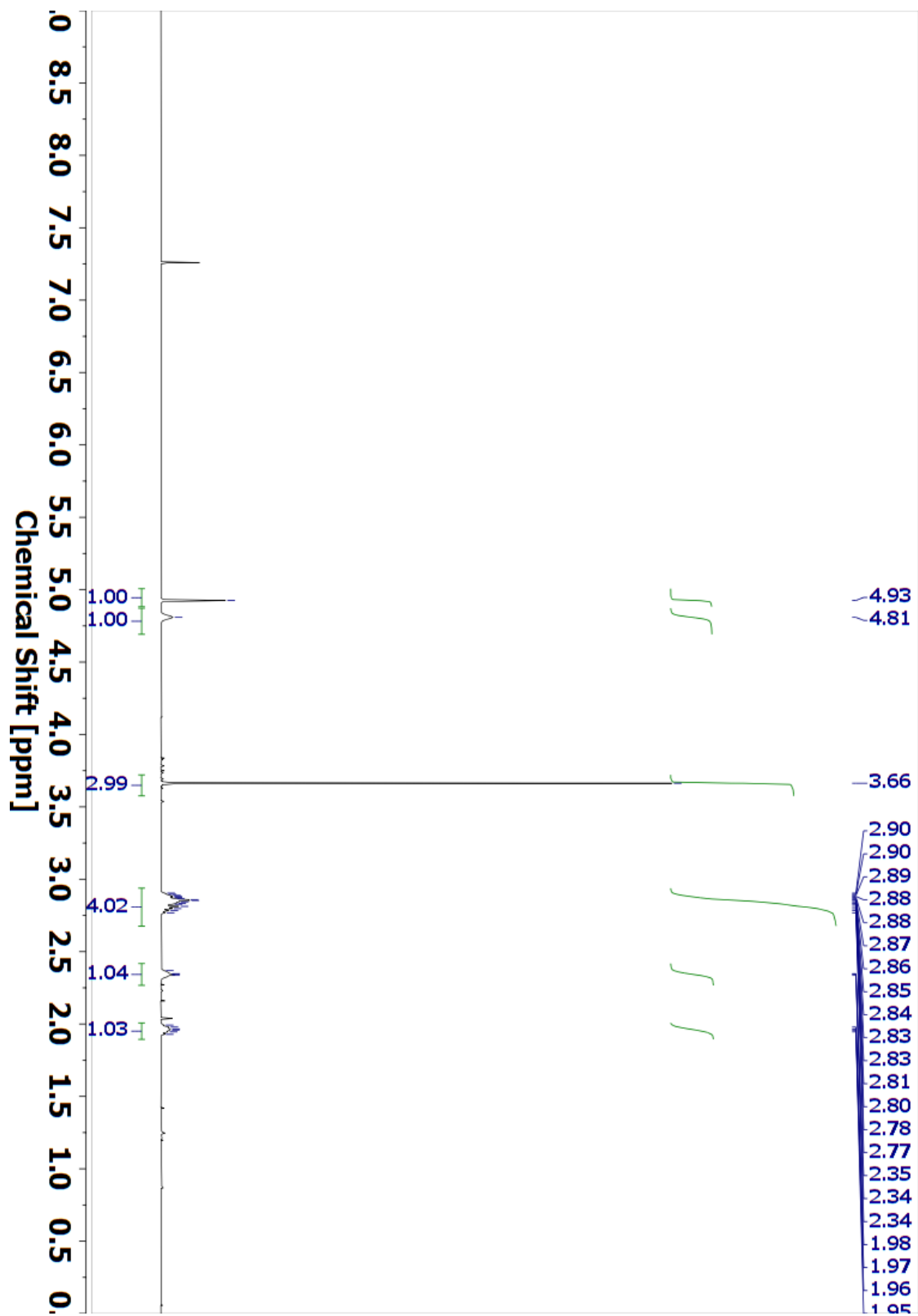
Methyl (Z)-2-(5-(cyanomethyl)dihydrofuran-2(3H)-ylidene)acetate (25)



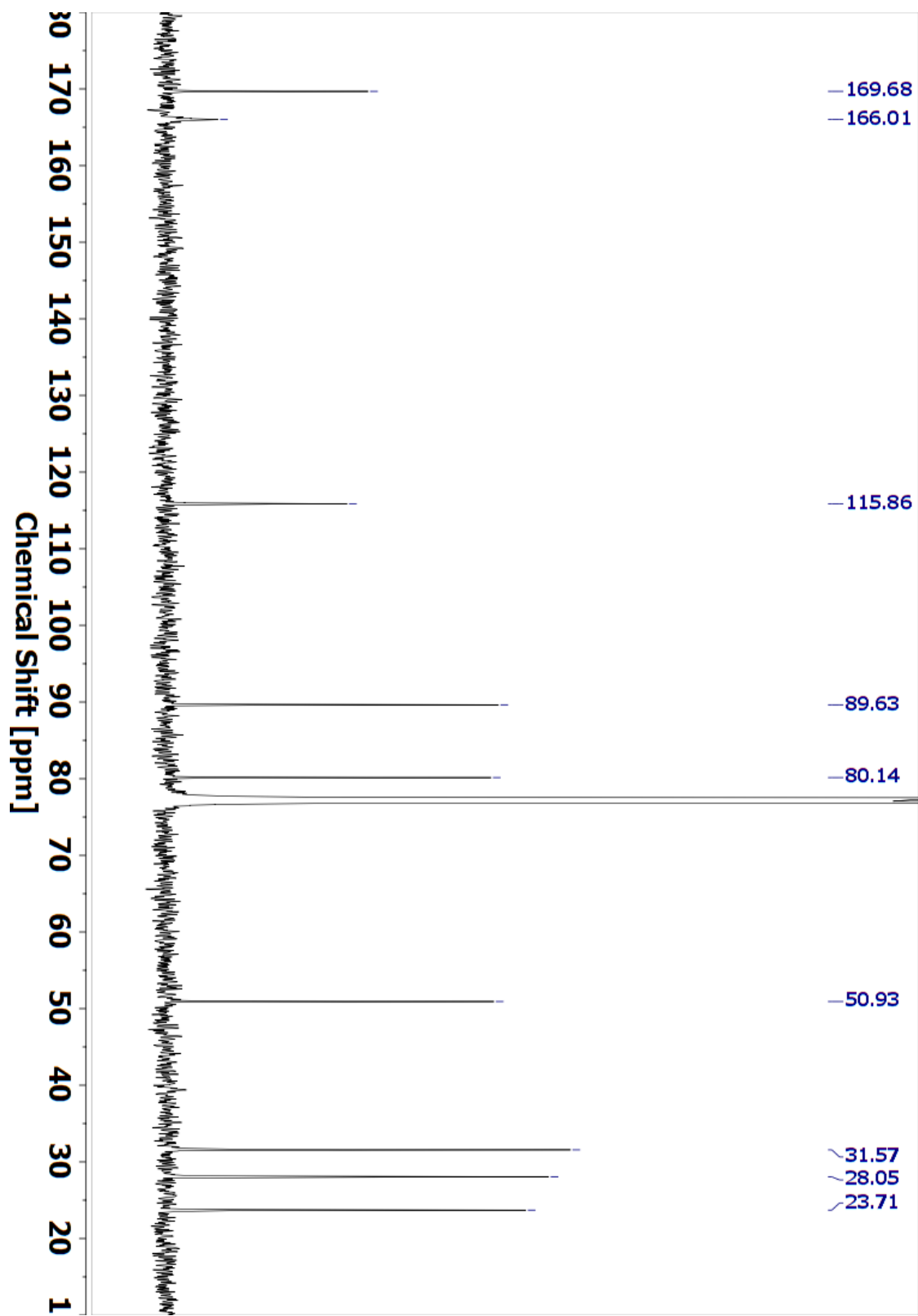
The reaction was carried out at 100 °C with 30 mol% catalyst loading (per substrate) following procedure D (20 min, 56% NMR yield) with 20.0 mg of α -diazo- β -ketoester (2:1 mixture of substrate and adiponitrile) to give 5.2 mg (45% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 4.93 (s, 1H), 4.81 (s, 1H), 3.66 (s, 3H), 3.08–2.71 (m, 4H), 2.48–2.21 (m, 1H), 2.01–1.89 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.68, 166.01, 115.86, 89.63, 80.14, 50.93, 31.57, 28.05, 23.71. HRMS (ESI $^+$) m/z Calc. 182.0812 [$\text{C}_9\text{H}_{11}\text{NO}_3+\text{H}$] $^+$, Found. 182.0814 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 100 °C with 30 mol% Fe(acac)₂ after 20 min
(0.5 mg Si(SiMe₃)₄ as internal standard).

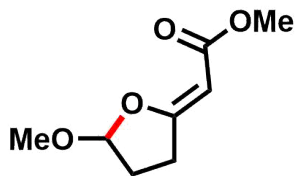


^1H NMR spectrum of isolated product in CDCl_3



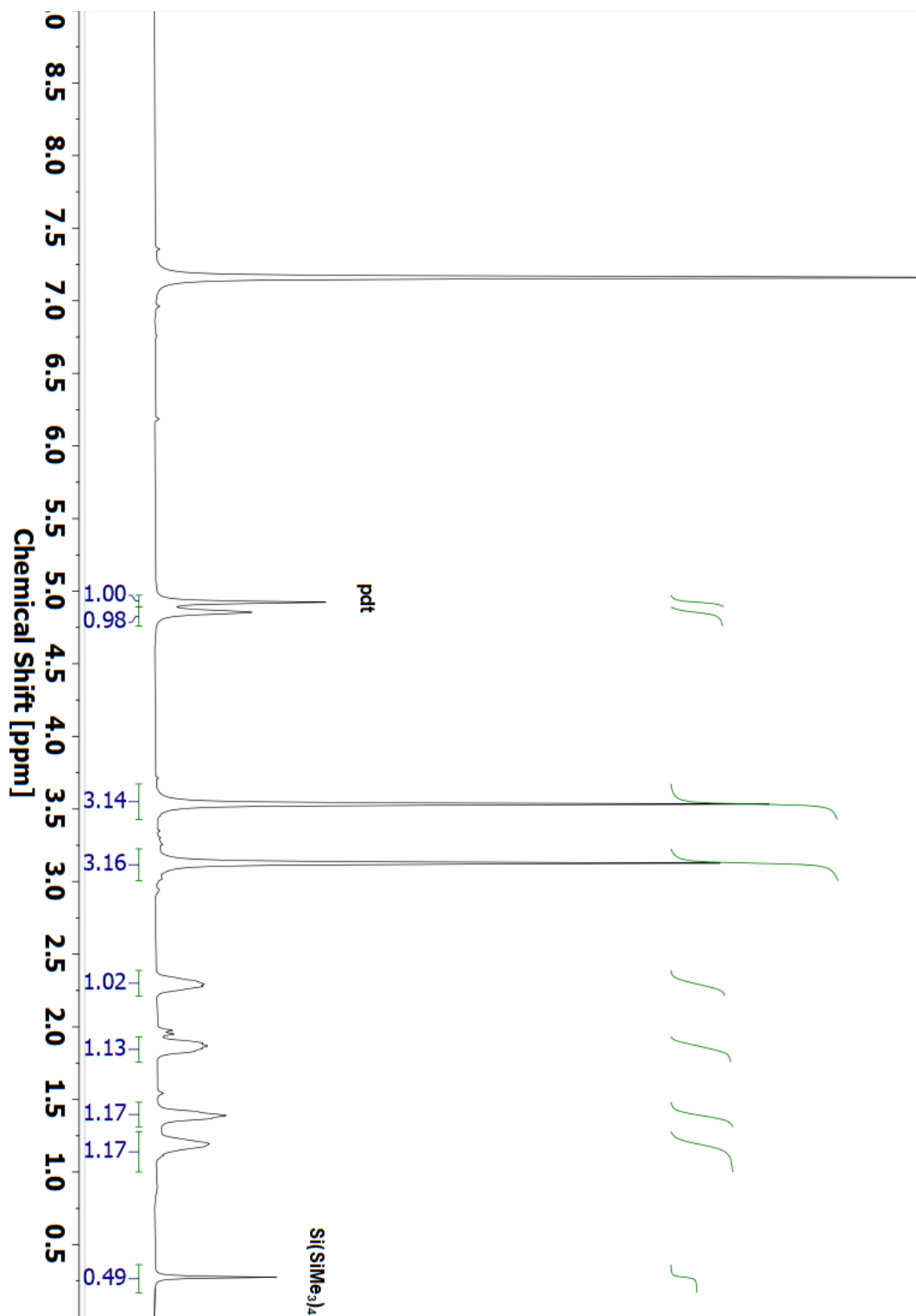
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl (Z)-2-(5-methoxydihydrofuran-2(3H)-ylidene)acetate (26)

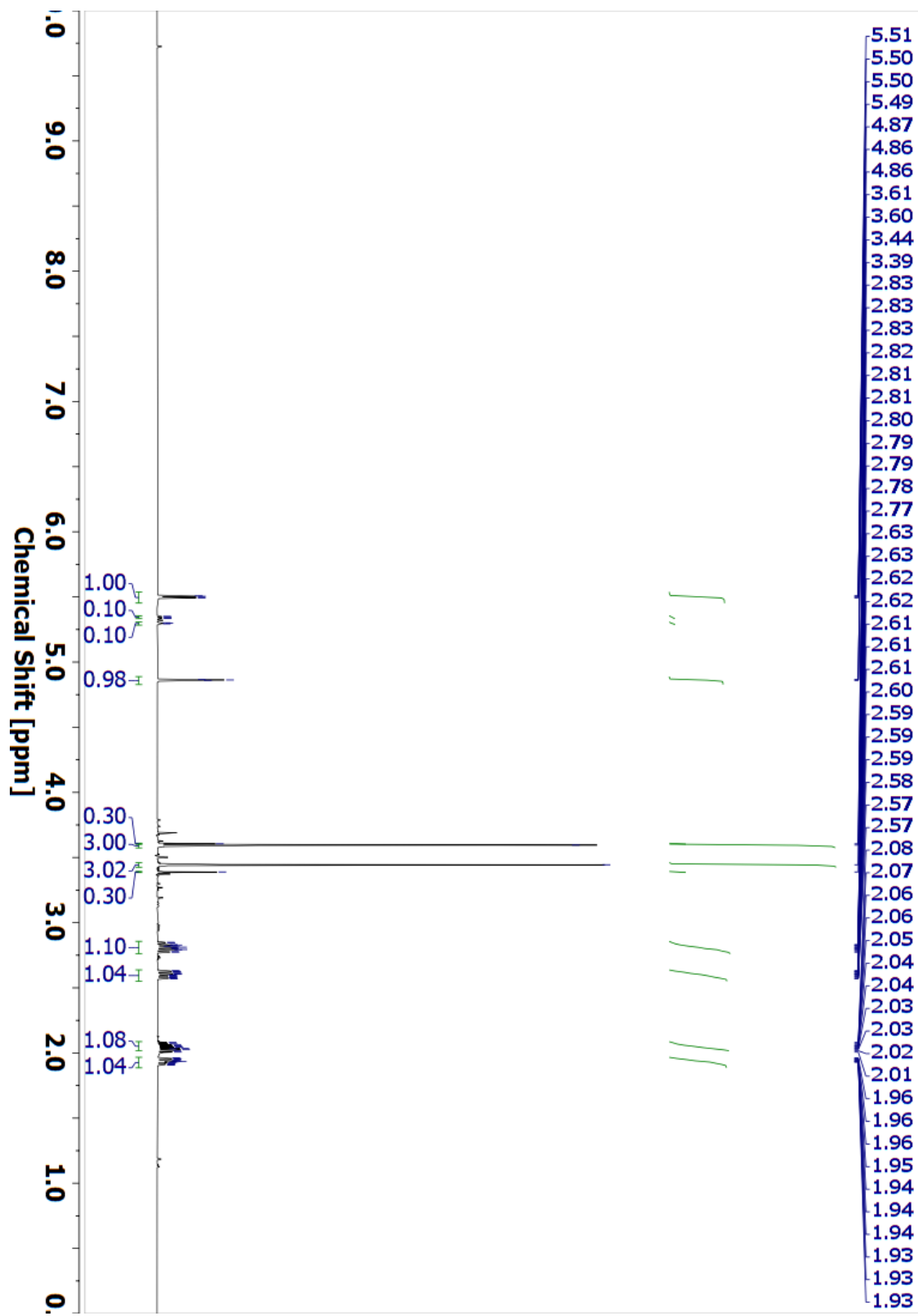


The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C (3 h, 99% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.7 mg (62% yield, 91% *Z*- : 9% *E*-isomer) of product as a colorless oil. ¹H NMR (500 MHz, CD₂Cl₂) δ 5.50 (dd, *J* = 5.3, 1.7 Hz, 1H), 4.86 (t, *J* = 1.5 Hz, 1H), 3.60 (s, 3H), 3.44 (s, 3H), 2.87–2.76 (m, 1H), 2.66–2.54 (m, 1H), 2.11–1.98 (m, 1H), 1.98–1.88 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 170.94, 165.88, 110.27, 89.14, 56.42, 50.67, 30.03, 29.43. HRMS (ESI⁺) *m/z* Calc. 173.0808 [C₈H₁₂O₄+H]⁺, Found. 173.0810 [M+H]⁺.

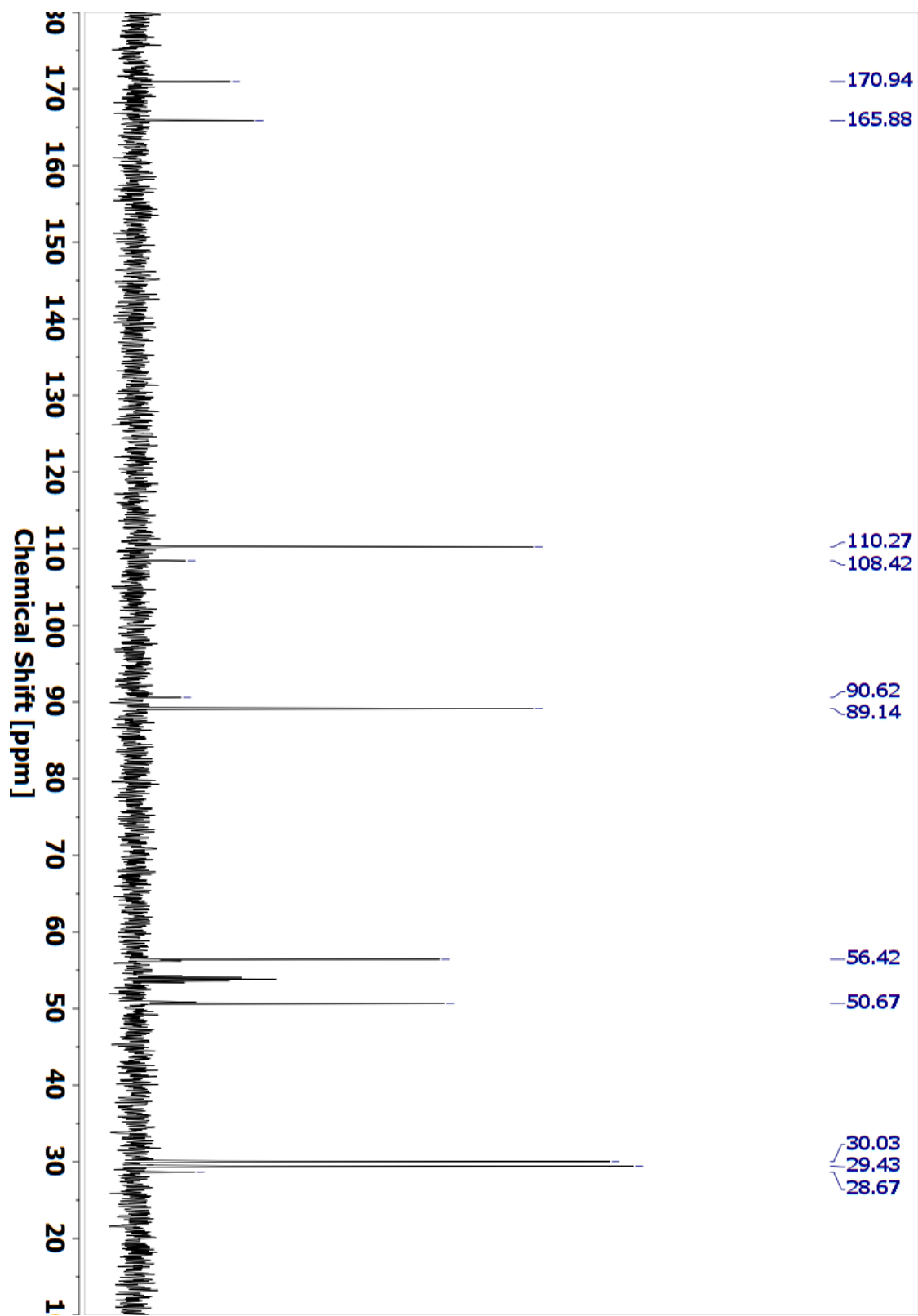
Scale-up: The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C for 3 h with 300 mg of α -diazo- β -ketoester in 30 ml of benzene to give 192 mg (74% yield) of product as a white solid.



Crude NMR spectrum for reaction carried out at 25 °C with 15 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

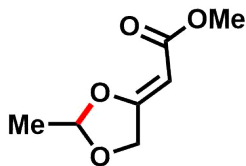


^1H NMR spectrum of isolated product in CD_2Cl_2 (91% *Z*- : 9% *E*-isomer)

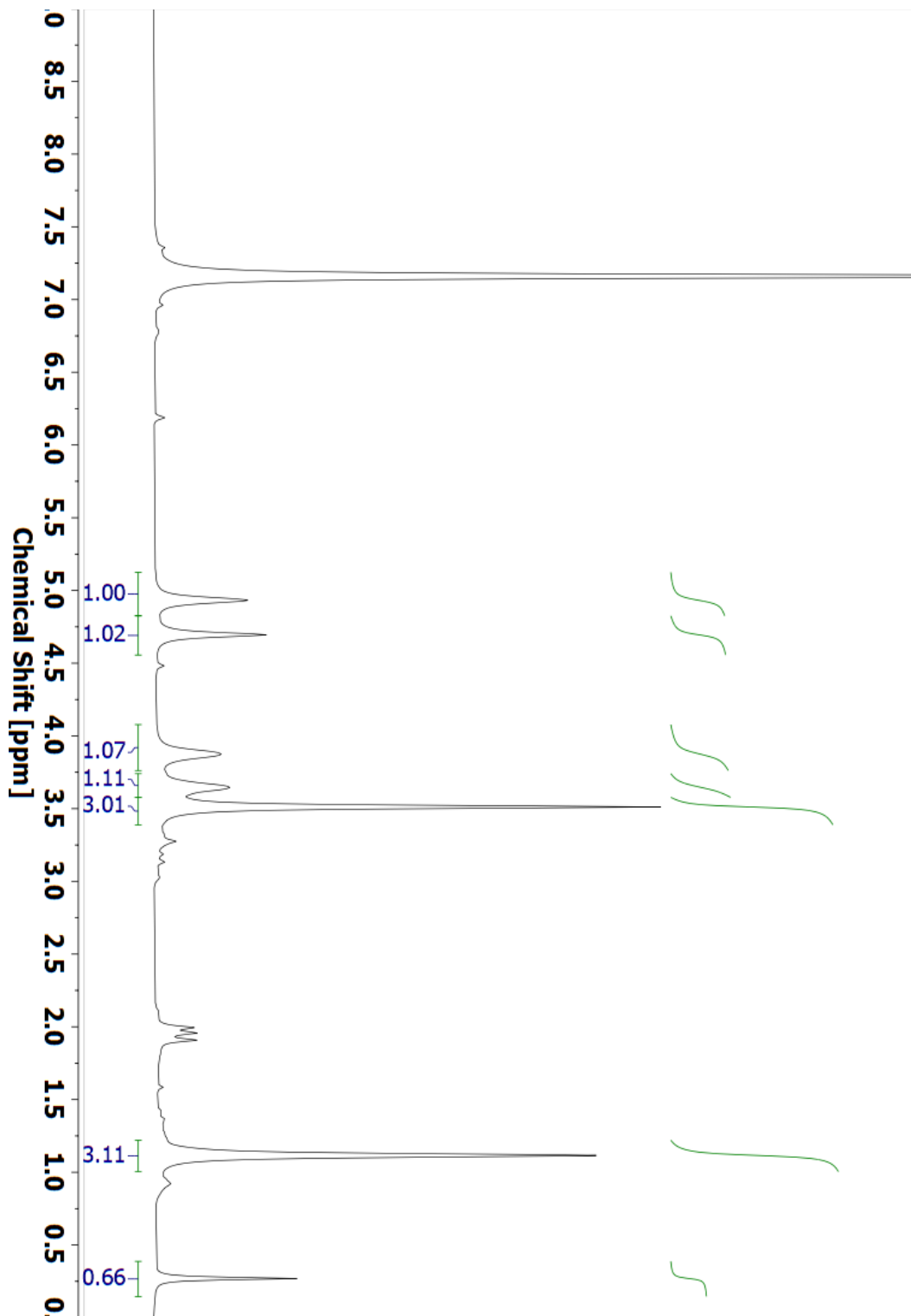


¹³C NMR spectrum of isolated product in CD₂Cl₂

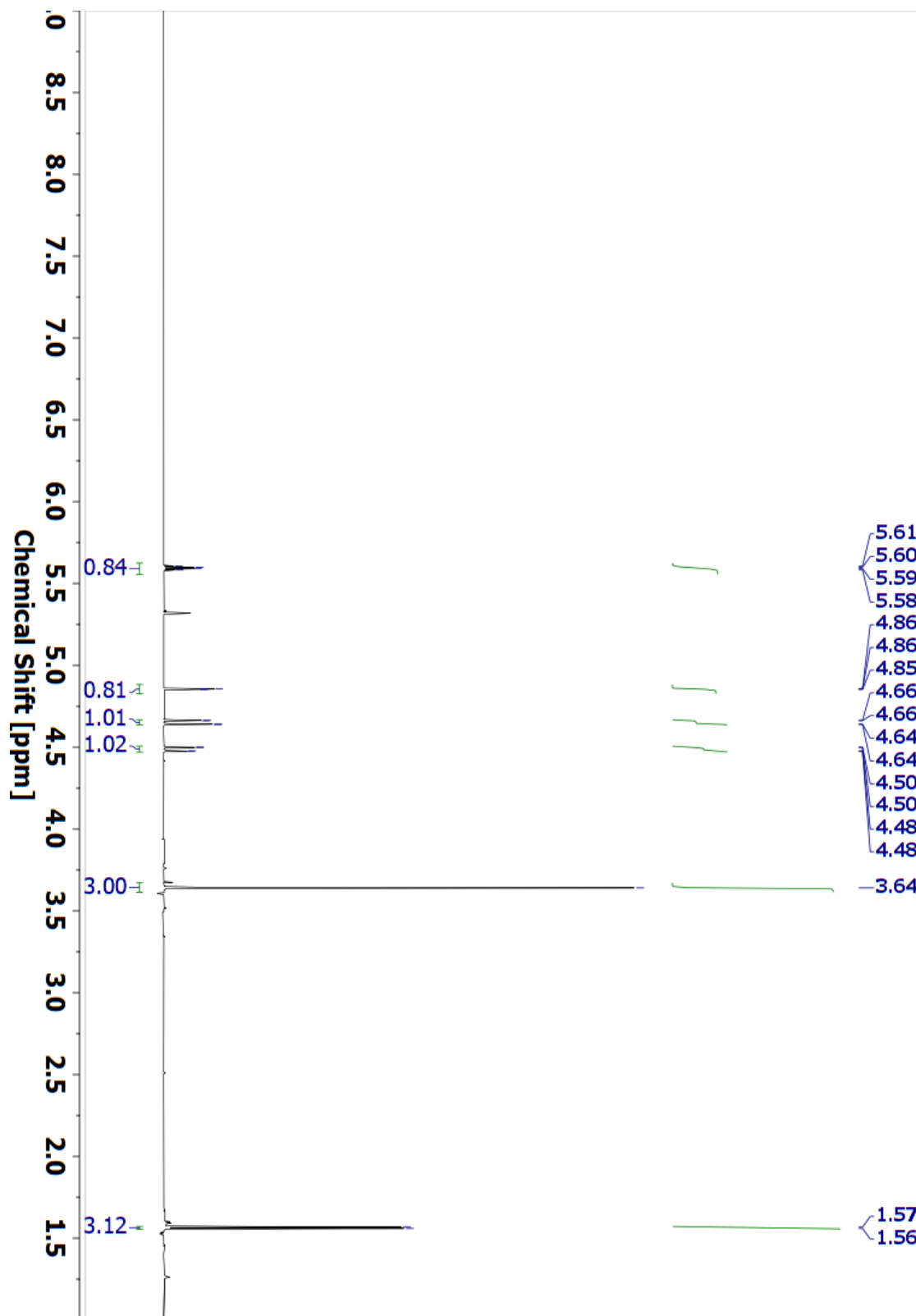
Methyl (Z)-2-(2-methyl-1,3-dioxolan-4-ylidene)acetate (27):



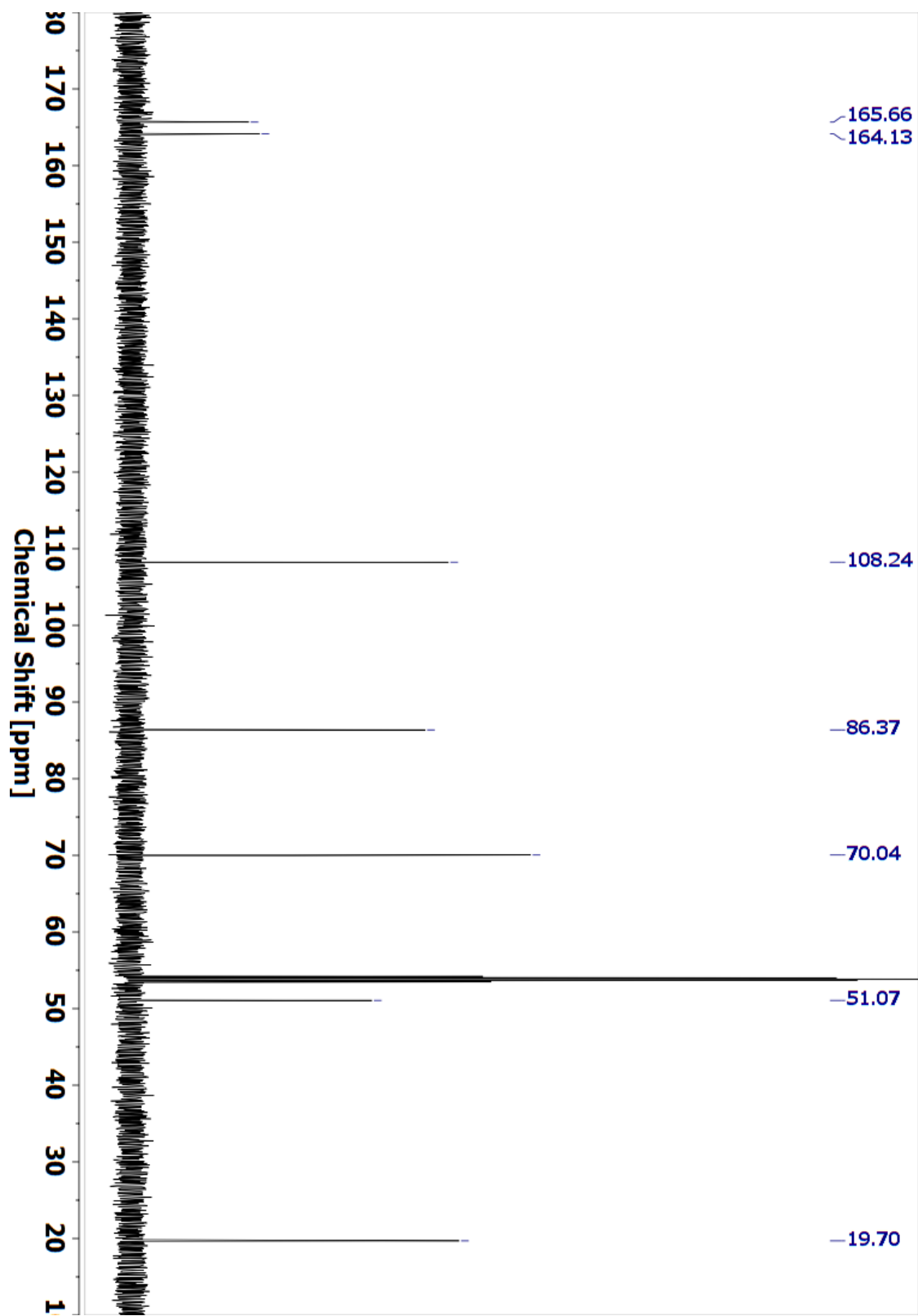
The reaction was carried out at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 67% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 10.7 mg (58% yield) of product as a white solid. ^1H NMR (600 MHz, CD_2Cl_2) δ 5.60 (q, $J = 5.0$ Hz, 1H), 4.86 (t, $J = 1.2$ Hz, 1H), 4.65 (dd, $J = 13.6, 1.2$ Hz, 1H), 4.49 (dd, $J = 13.6, 1.2$ Hz, 1H), 3.64 (s, 3H), 1.56 (d, $J = 5.0$ Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 165.66, 164.13, 108.24, 86.37, 70.04, 51.07, 19.70. HRMS (ESI $^+$) m/z Calc. 159.0652 [$\text{C}_7\text{H}_{10}\text{O}_4+\text{H}$] $^+$, Found. 159.0653 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

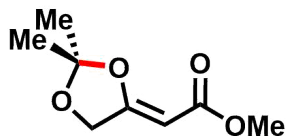


^1H NMR spectrum of isolated product in CD_2Cl_2

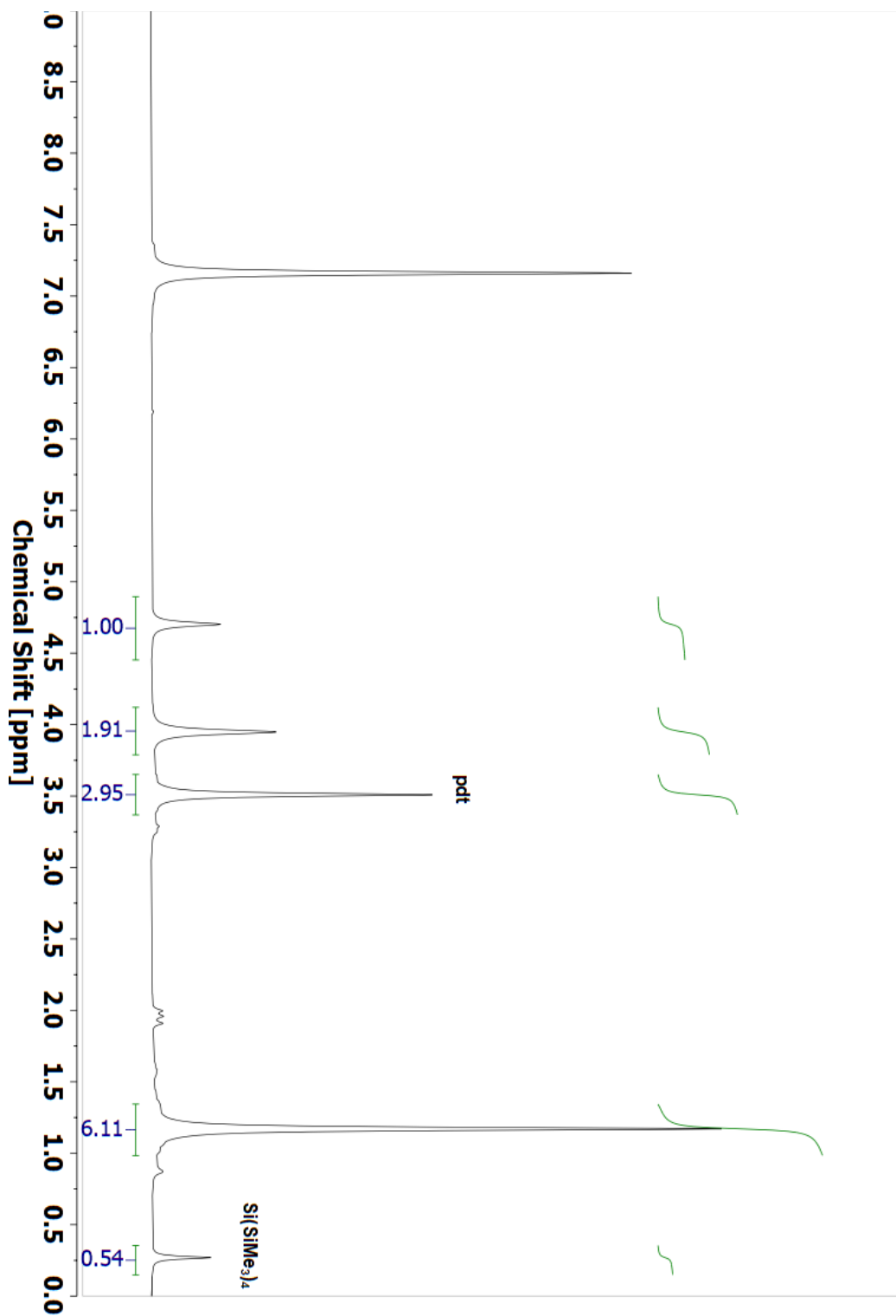


¹³C NMR spectrum of isolated product in CD₂Cl₂

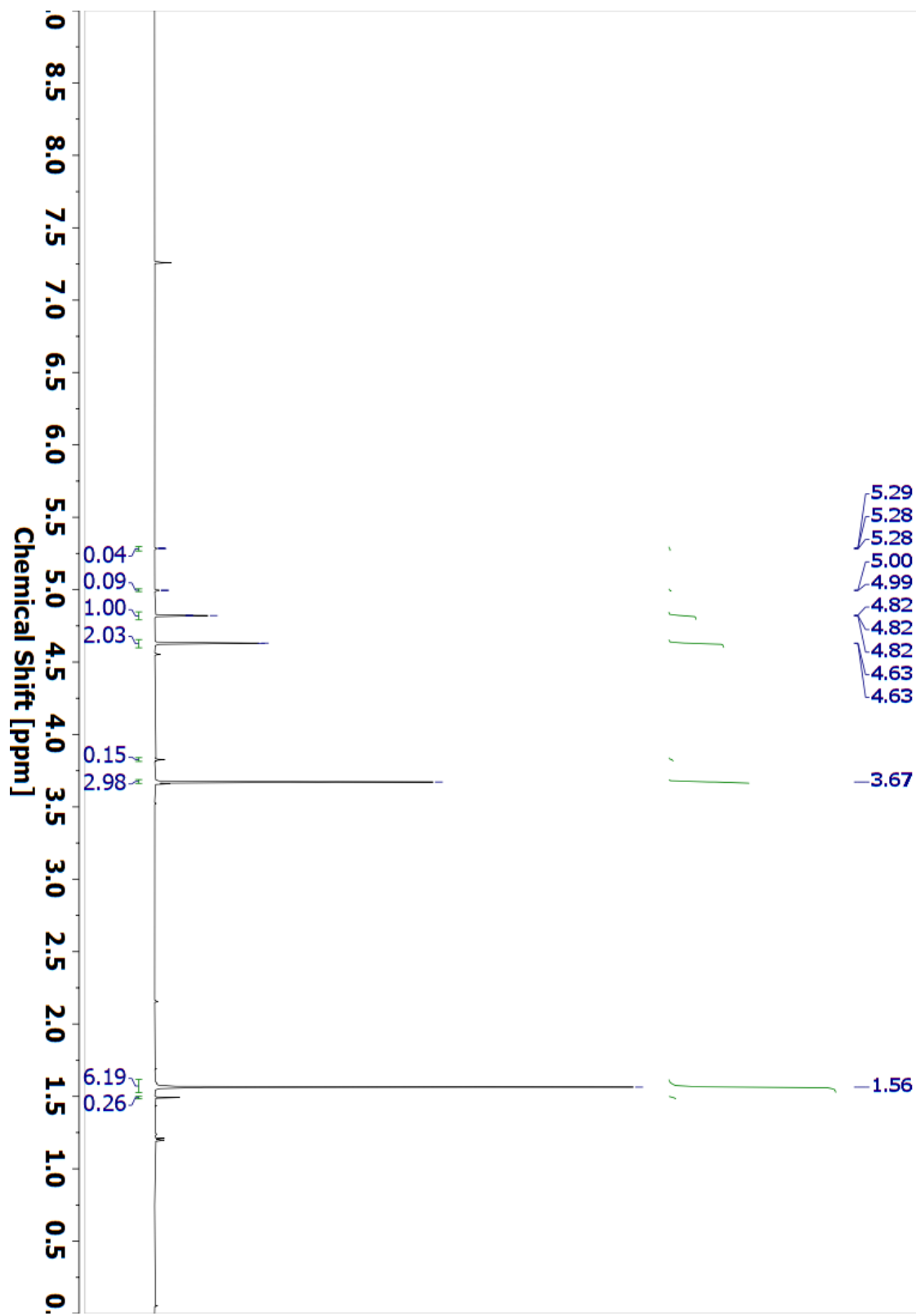
Methyl (Z)-2-(2,2-dimethyl-1,3-dioxolan-4-ylidene)acetate (28)



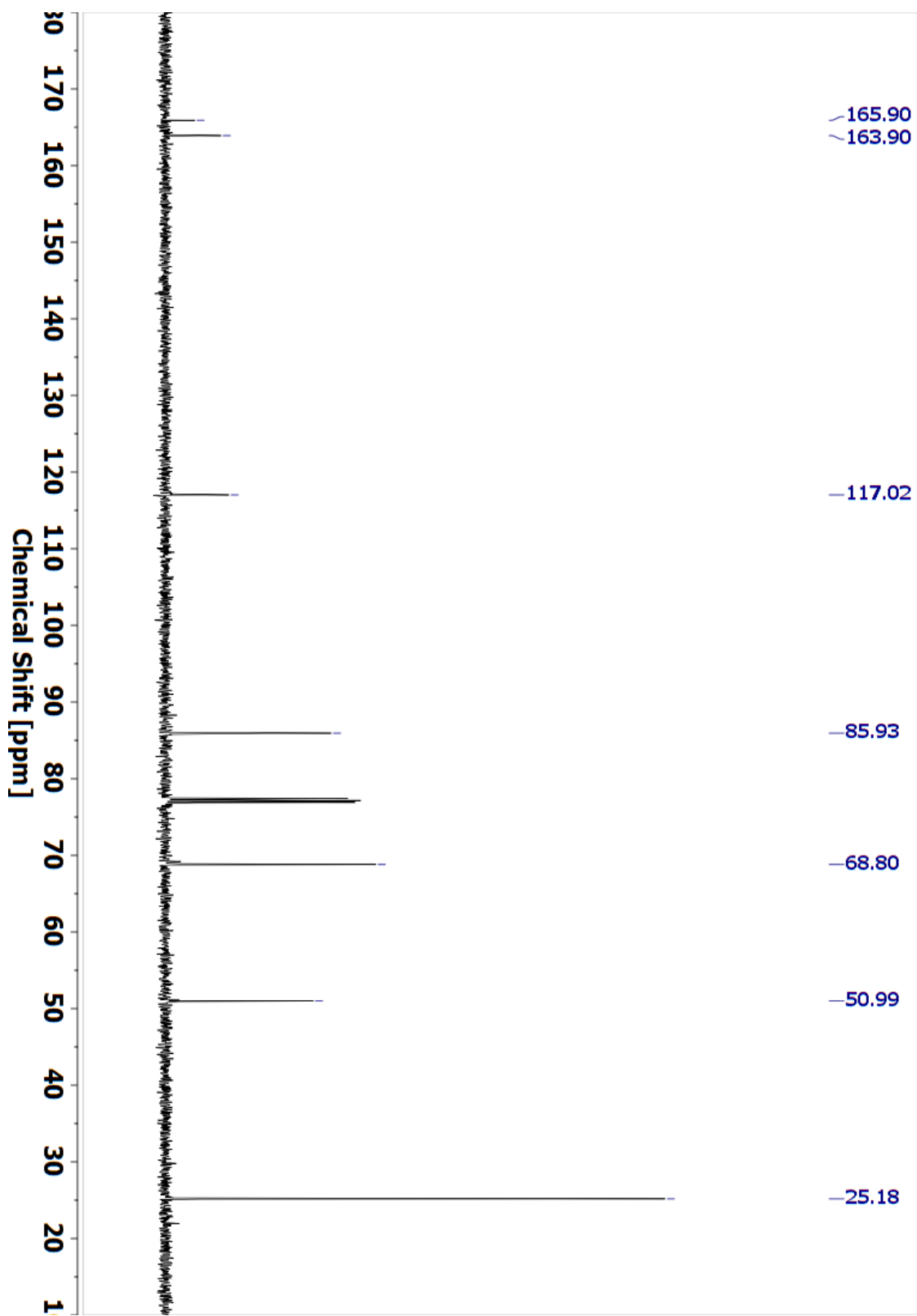
The reaction was carried out at 25 °C with 30 mol% catalyst loading following procedure C (3 h, 89% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 13.3 mg (77% yield, 96% Z- : 4% E-isomer) of product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 4.82 (t, $J = 1.3$ Hz, 1H), 4.63 (d, $J = 1.3$ Hz, 2H), 3.67 (s, 3H), 1.56 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.90, 163.90, 117.02, 85.93, 68.80, 50.99, 25.18. HRMS (ESI $^+$) m/z Calc. 173.0808 [$\text{C}_8\text{H}_{12}\text{O}_4 + \text{H}$] $^+$, Found. 173.0810 [$\text{M} + \text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 30 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

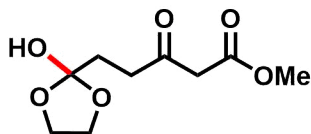


¹H NMR spectrum of isolated product in CDCl₃ (96% Z- : 4% E-isomer)



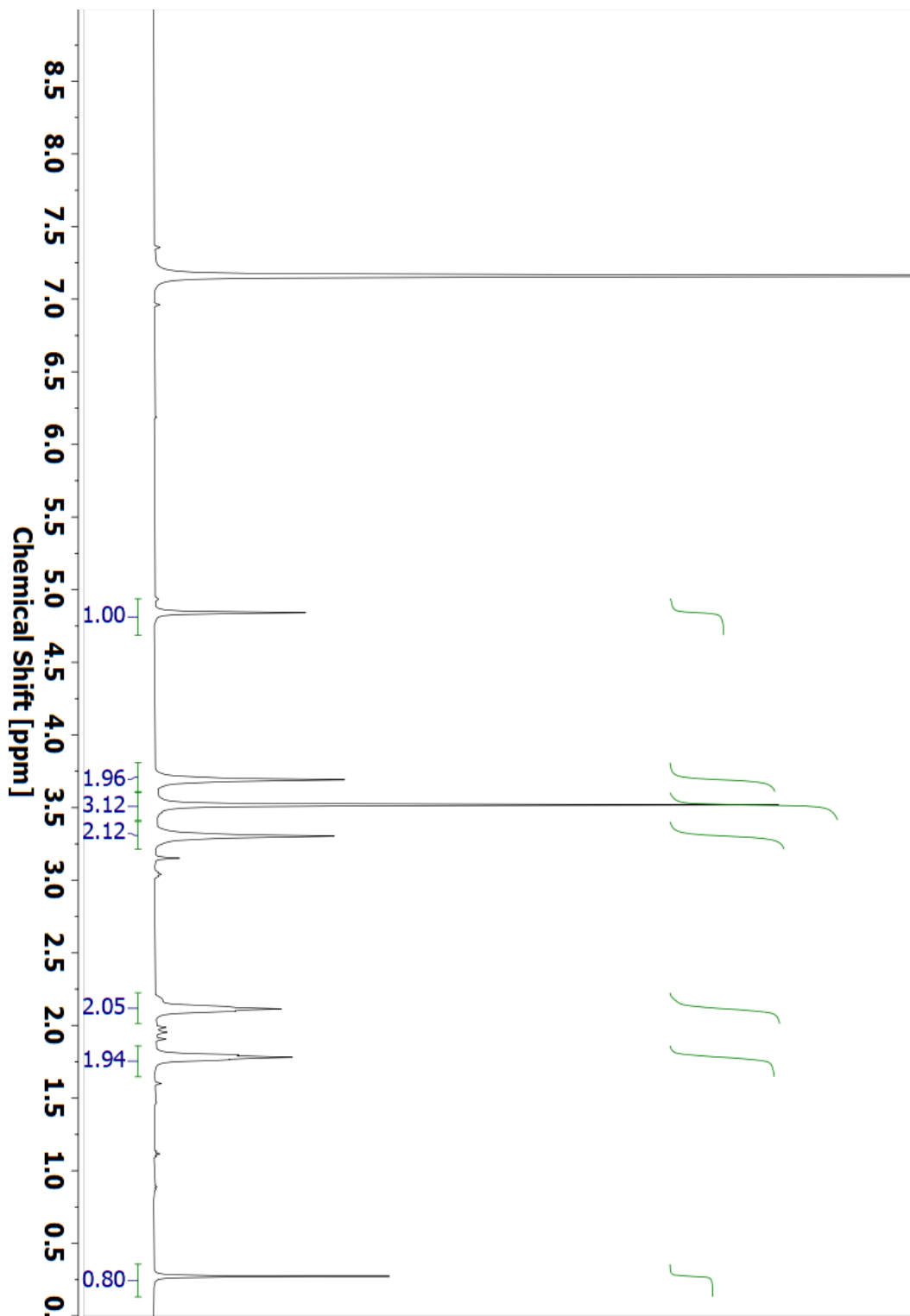
^{13}C NMR spectrum of isolated product in CDCl_3

Methyl 5-(2-hydroxy-1,3-dioxolan-2-yl)-3-oxopentanoate (29)

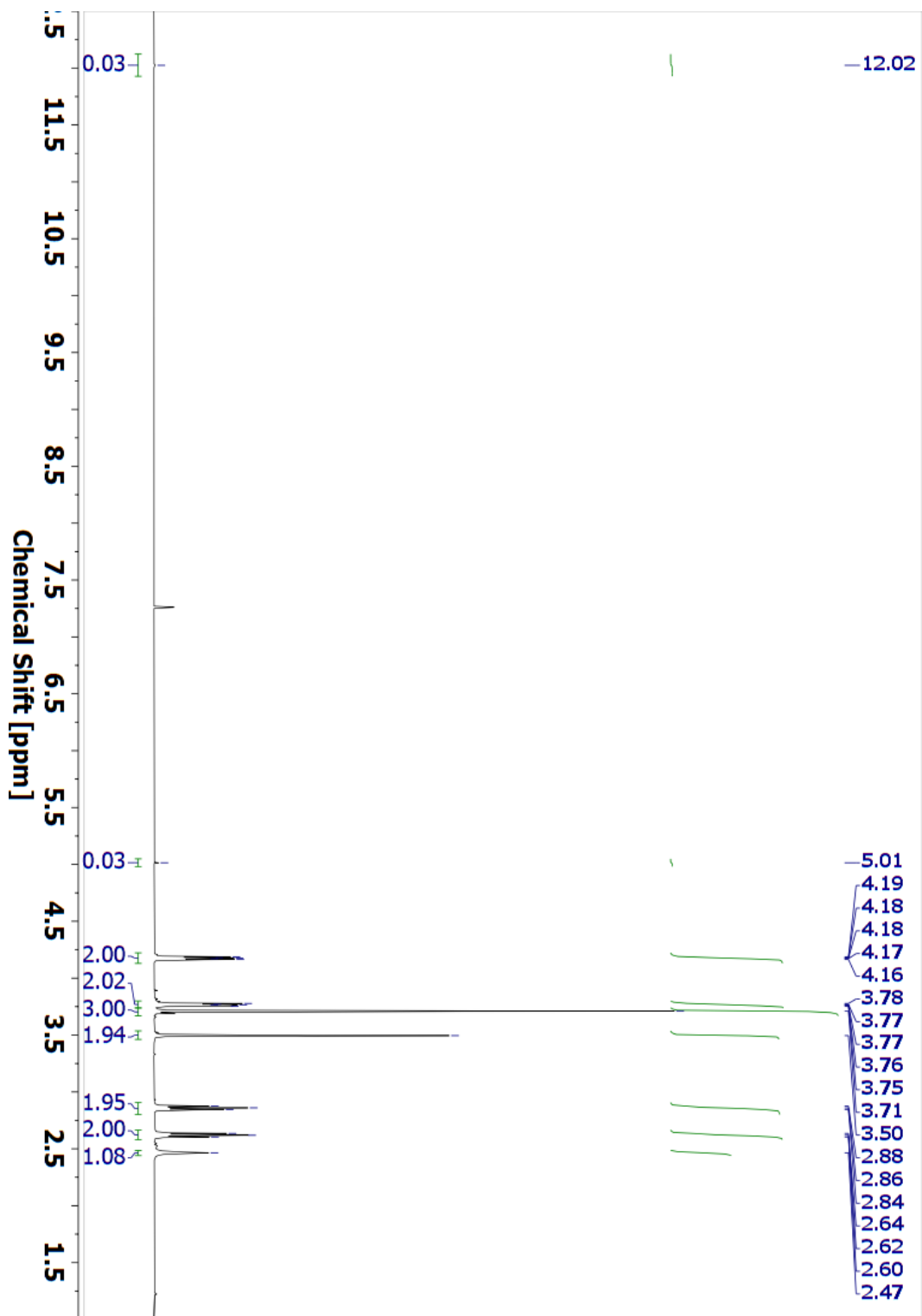


The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 70% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 7.3 mg (41% yield, 2.9% tautomerization) of product as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.22–4.14 (m, 2H), 3.82–3.73 (m, 2H), 3.71 (s, 3H), 3.50 (s, 2H), 2.86 (t, $J = 6.4$ Hz, 2H), 2.62 (t, $J = 6.4$ Hz, 2H), 2.47 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.36, 172.58, 167.63, 66.43, 60.94, 52.54, 48.93, 37.55, 27.99. HRMS (ESI $^+$) m/z Calc. 219.0863 [$\text{C}_9\text{H}_{14}\text{O}_6+\text{H}$] $^+$, Found. 219.0865 [$\text{M}+\text{H}$] $^+$.

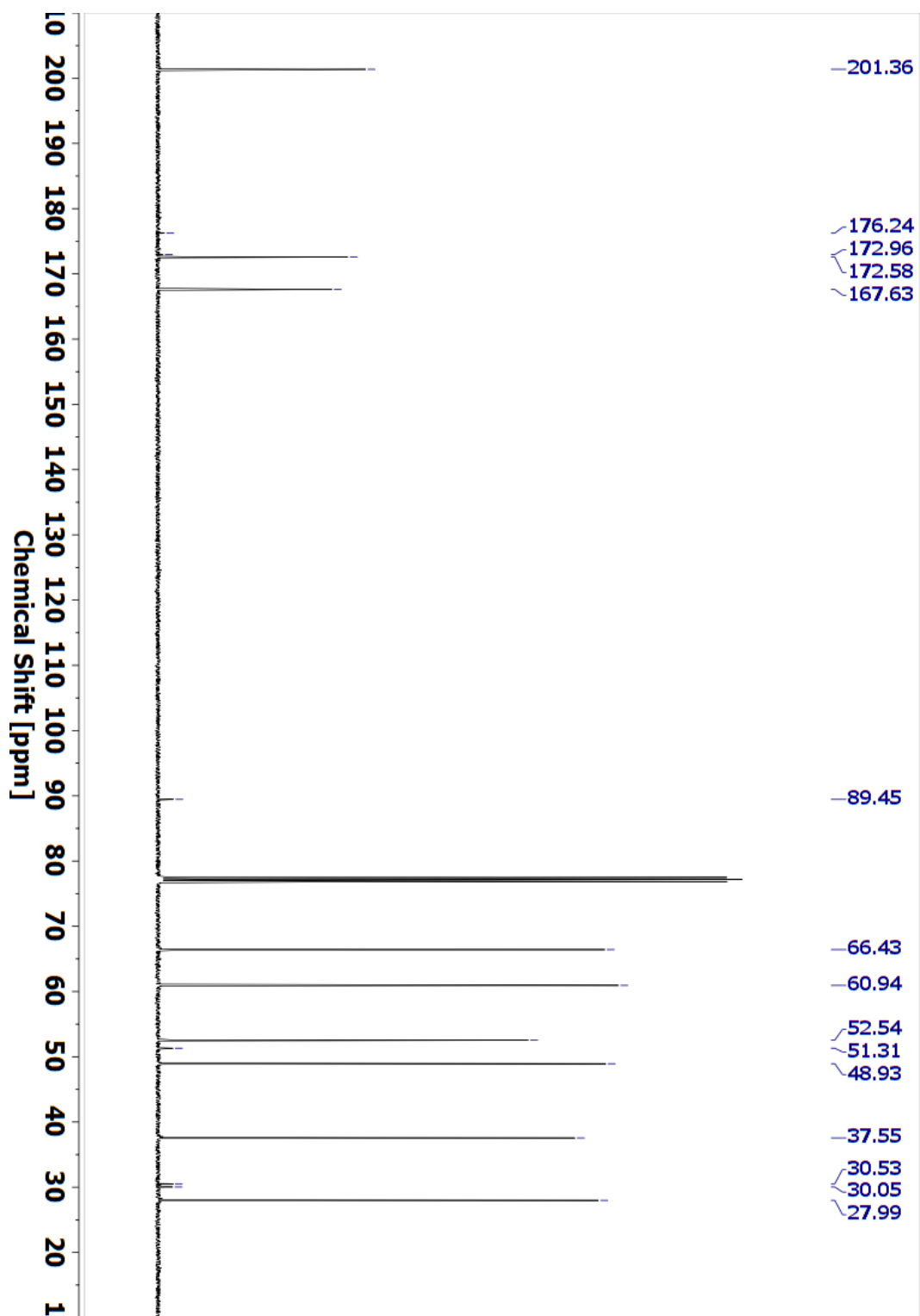
Crude ^1H NMR exhibits features expected for the cyclized product **29'** (methyl (Z)-2-(1,4,6-trioxaspiro[4.4]nonan-7-ylidene)acetate). Rapid hydrolyzation, however, prohibits the isolation of this species. The ring-opened alcohol compound is isolated instead, as shown in the purified ^1H and ^{13}C NMR spectra below.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

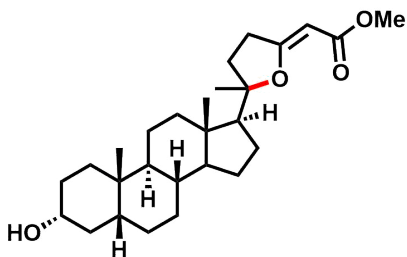


^1H NMR spectrum of isolated product in CDCl_3 (Minor peaks at ~ 12 ppm suggests small amount of conversion to the corresponding fully deprotected carboxylic acid)

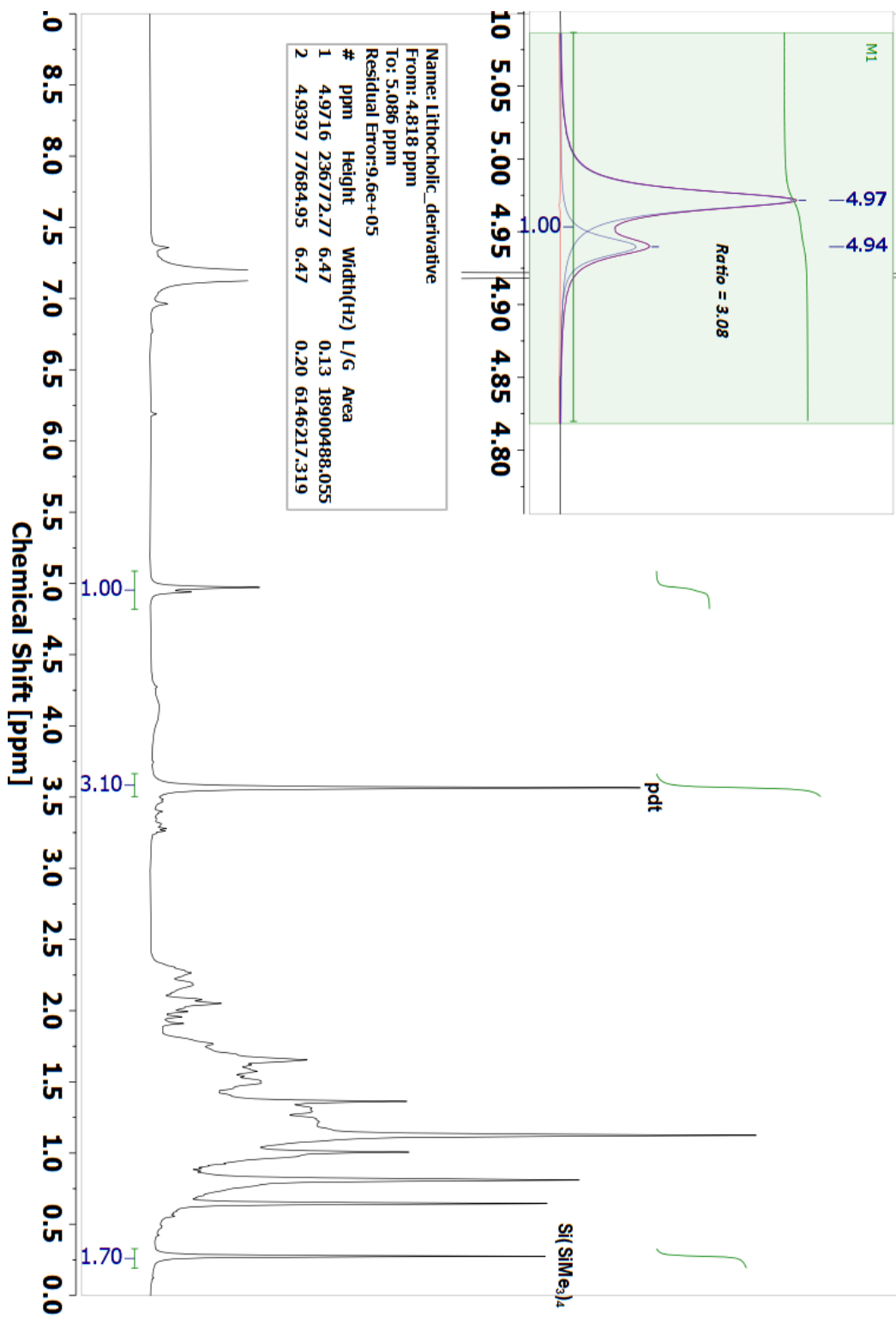


^{13}C NMR spectrum of isolated product in CDCl_3

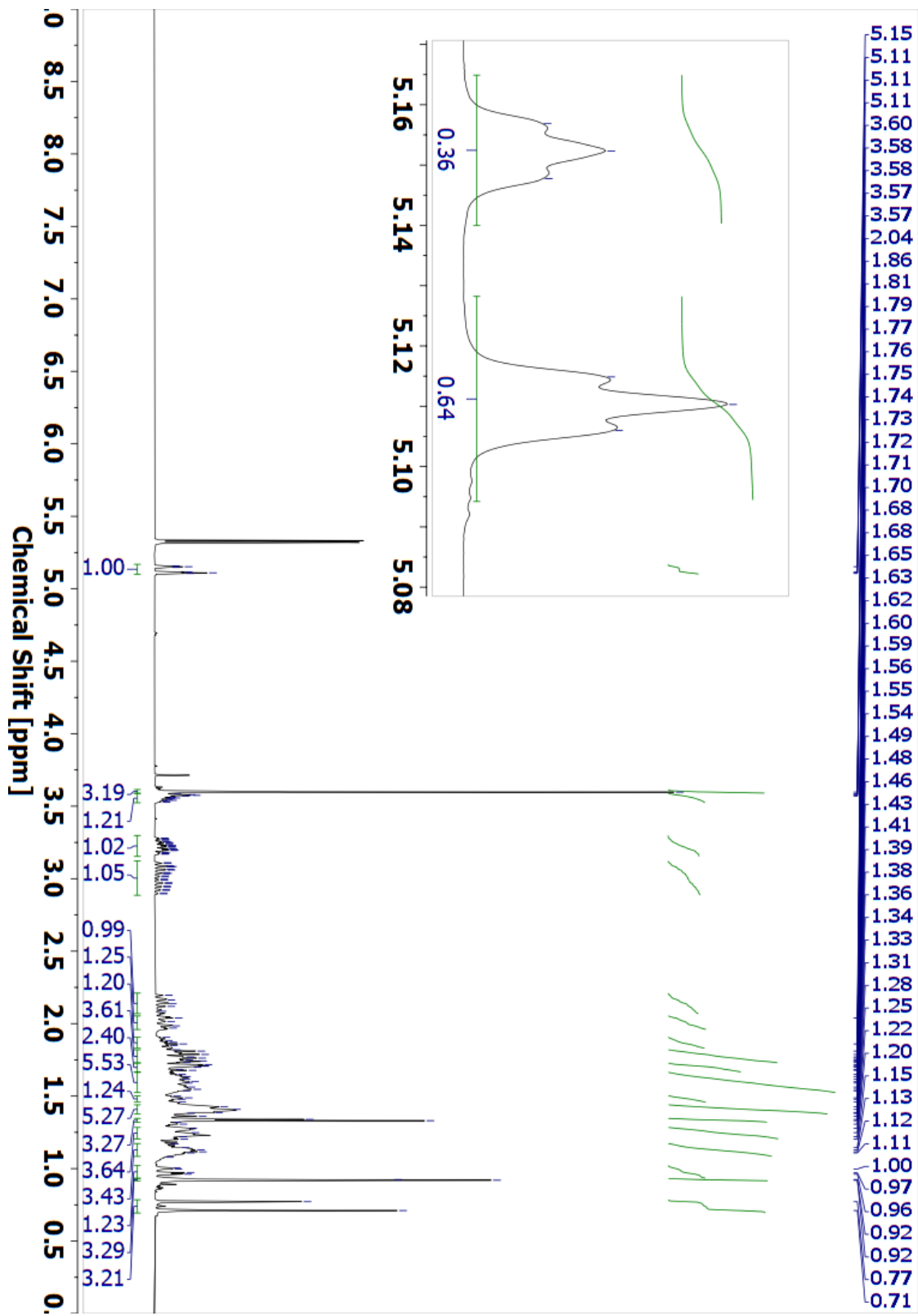
Methyl (Z)-2-((5S)-5-((3R,5R,8R,9S,10S,13S,17S)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (30)



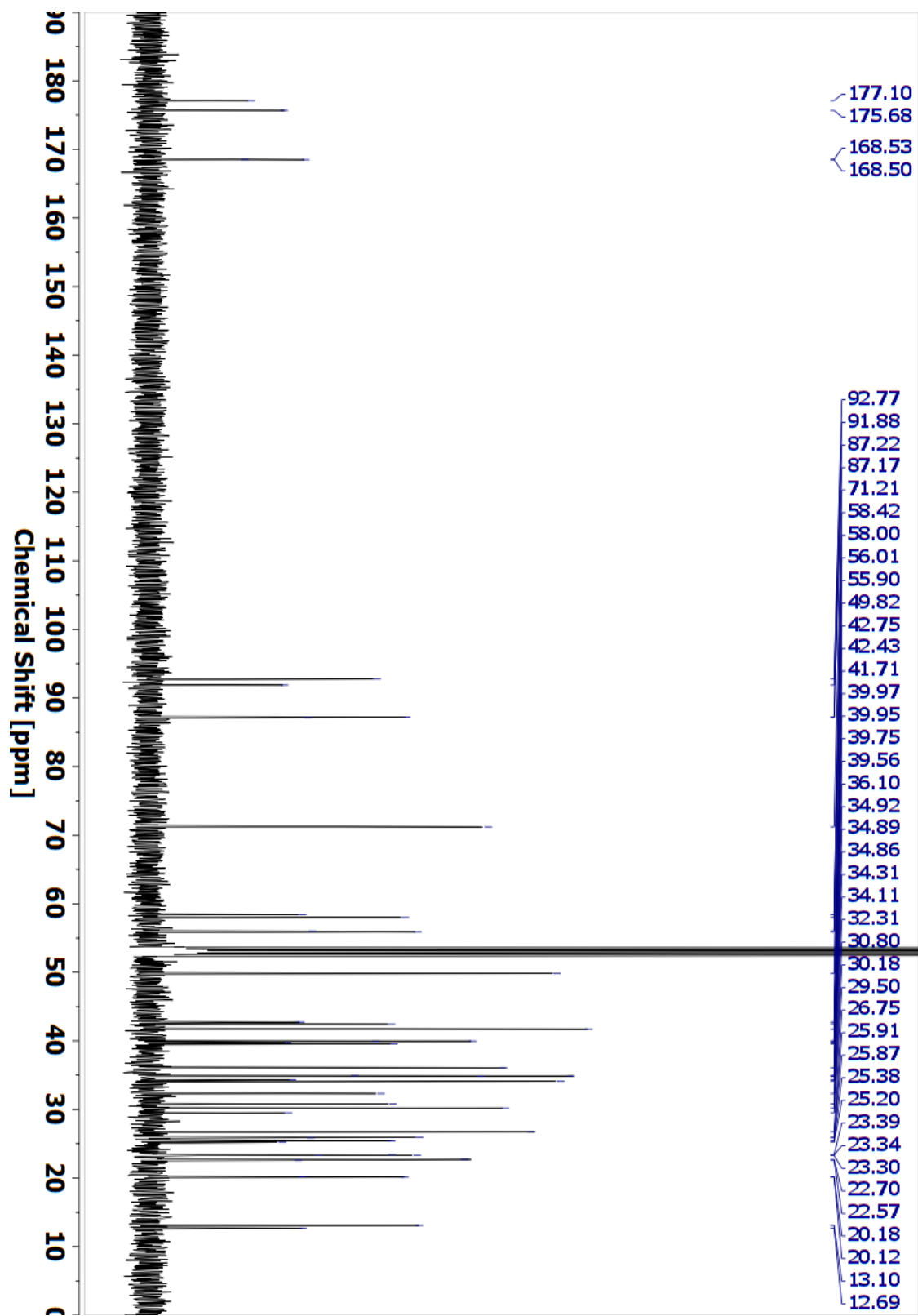
The reaction was carried out at 25 °C with 20 mol% catalyst loading following procedure C (3 h, 71% NMR yield, diastereomer ratio 3.08:1) with 20.0 mg of α -diazo- β -ketoester to give 10.9 mg (58% yield) of product as a white solid. ^1H NMR (400 MHz, CD_2Cl_2) δ 5.15 (t, $J = 1.8$ Hz, 0.36H, minor), 5.11 (t, $J = 1.8$ Hz, 0.64H), 3.60 (s, 3H), 3.59–3.52 (m, 1H), 3.30–3.16 (m, 1H), 3.12–2.89 (m, 1H), 2.22–2.09 (m, 1H), 2.07–1.95 (m, 1H), 1.92–1.83 (m, 1H), 1.82–1.73 (m, 3H), 1.73–1.67 (m, 2H), 1.66–1.52 (m, 5H), 1.51–1.46 (m, 1H), 1.45–1.37 (m, 5H), 1.34 (s, 1.08H, minor), 1.33 (s, 1.92H, major), 1.29–1.20 (m, 3H), 1.17–1.08 (m, 3H), 1.02–0.94 (m, 1H), 0.92 (s, 1.08H, minor), 0.92 (s, 1.92H, major), 0.77 (s, 1.08H, minor), 0.71 (s, 1.92H, major). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 177.10, 175.68, 168.53, 168.50, 92.77, 91.88, 87.22, 87.17, 71.21, 58.42, 58.00, 56.01, 55.90, 49.82, 42.75, 42.43, 41.71, 39.97, 39.95, 39.75, 39.56, 36.10, 34.92, 34.89, 34.86, 34.31, 34.11, 32.31, 30.80, 30.18, 29.50, 26.75, 25.91, 25.87, 25.38, 25.20, 23.39, 23.34, 23.30, 22.70, 22.57, 20.18, 20.12, 13.10, 12.69. Not all ^{13}C NMR peaks are resolved due to the structural similarities between the two diastereomers. HRMS (ESI $^+$) m/z Calc. 431.3156 [$\text{C}_{27}\text{H}_{42}\text{O}_4 + \text{H}$] $^+$, Found. 431.3151 [$\text{M} + \text{H}$] $^+$. Elemental analysis was conducted due to the complexity of the NMR spectra for bulk purity assessment. Anal. Calc. for $\text{C}_{27}\text{H}_{42}\text{O}_4$: C 75.31, H 9.83; Found C 74.95, H 9.69



Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 3 h (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).

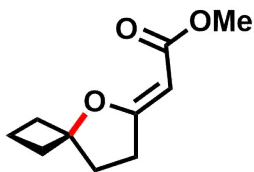


^1H NMR spectrum of isolated product in CD_2Cl_2

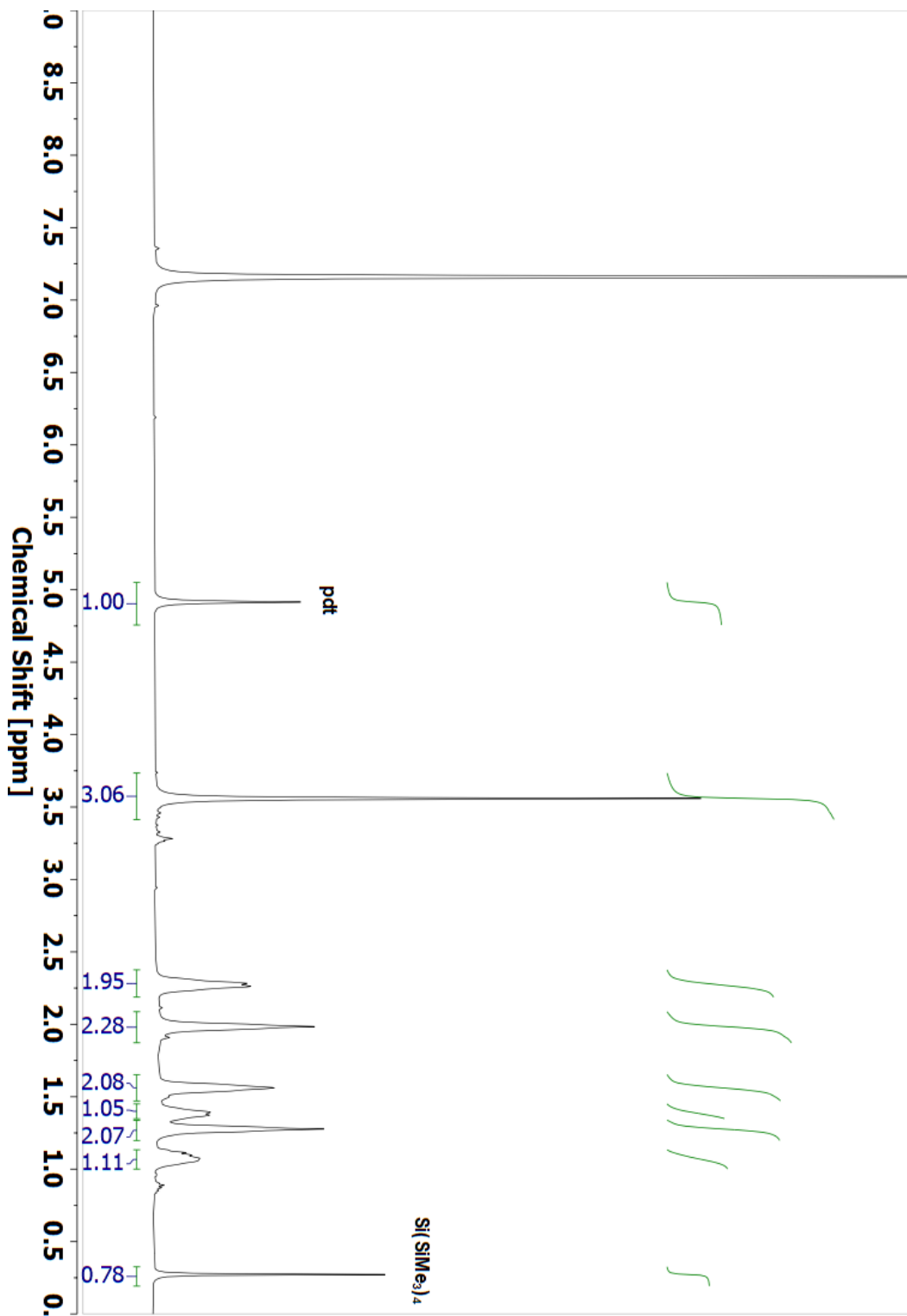


^{13}C NMR spectrum of isolated product in CD_2Cl_2

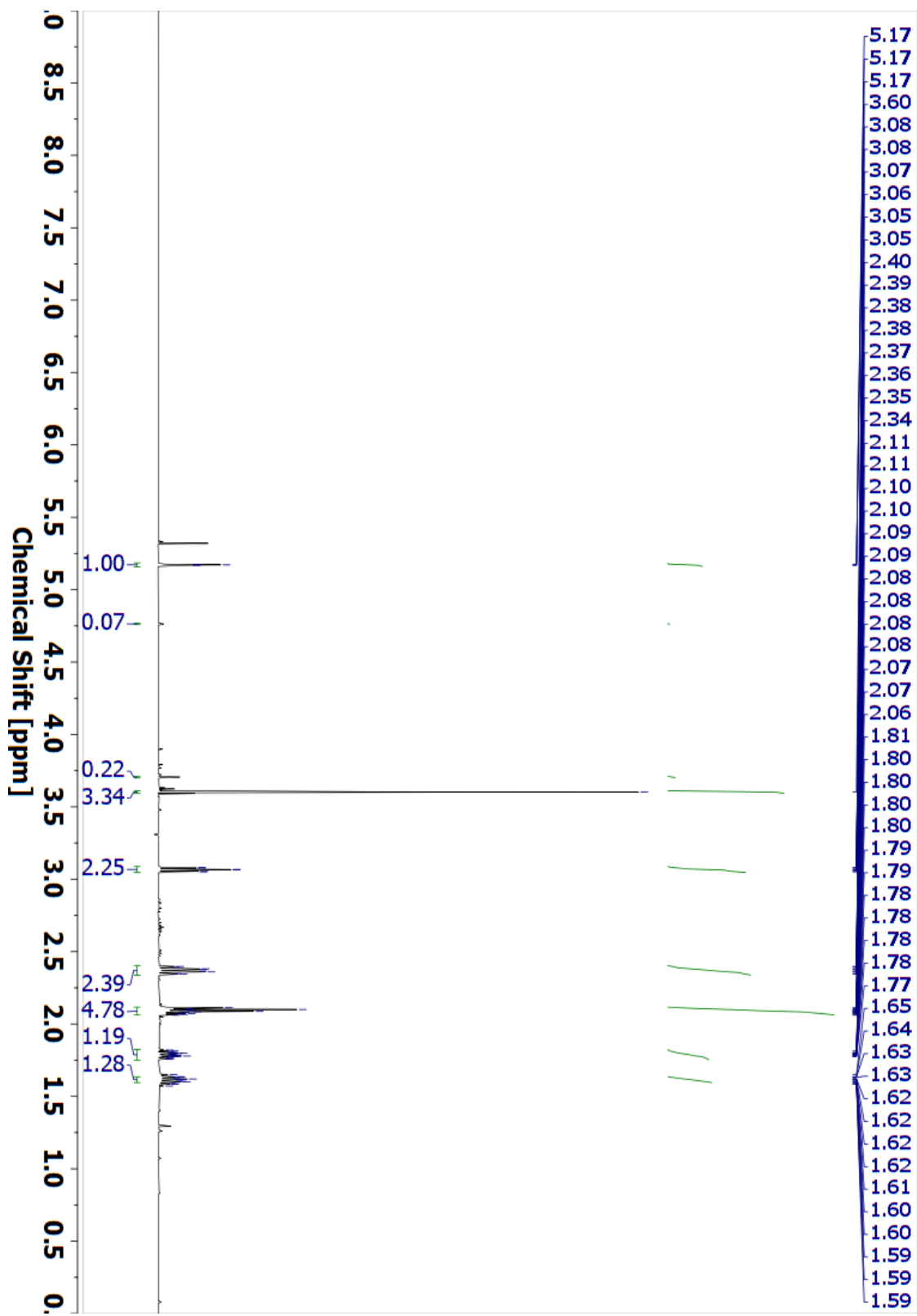
Methyl (Z)-2-(5-oxaspiro[3.4]octan-6-ylidene)acetate (32)



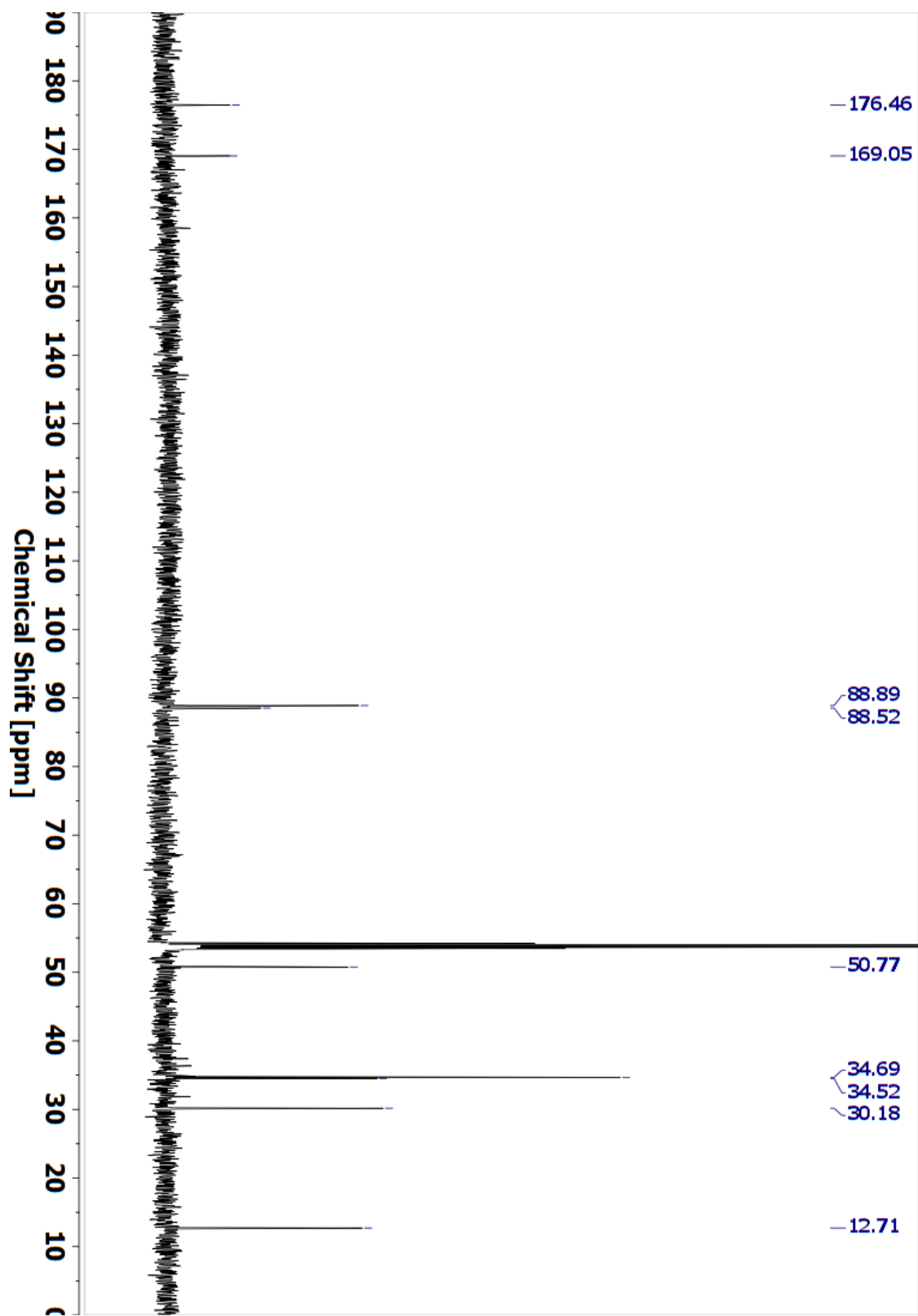
The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 66% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 9.9 mg (57% yield, 94% *Z*- : 6% *E*- isomer) of **36** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 5.17 (t, J = 1.8 Hz, 1H), 3.60 (s, 3H), 3.07 (td, J = 7.6, 1.8 Hz, 2H), 2.42–2.31 (m, 2H), 2.13–2.04 (m, 4H), 1.85–1.74 (m, 1H), 1.68–1.56 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 176.46, 169.05, 88.89, 88.52, 50.77, 34.69, 34.52, 30.18, 12.71. HRMS (ESI $^+$) m/z Calc. 183.1016 [$\text{C}_{10}\text{H}_{14}\text{O}_3+\text{H}$] $^+$, Found. 183.1018 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

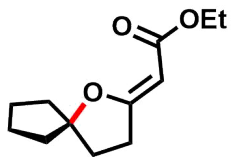


¹H NMR spectrum of isolated product in CD₂Cl₂ (94% *Z*- : 6% *E*-isomer)

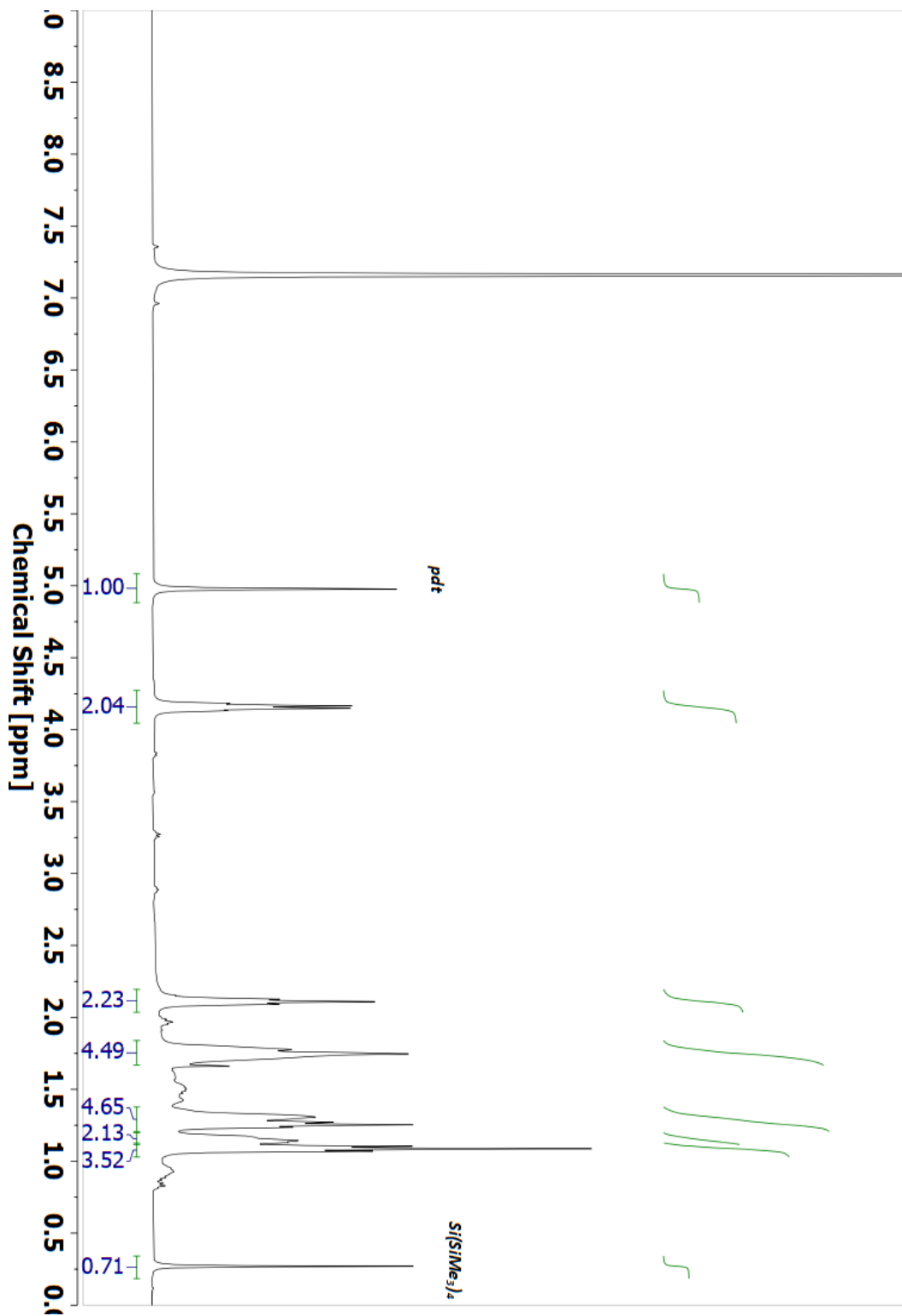


¹³C NMR spectrum of isolated product in CD₂Cl₂

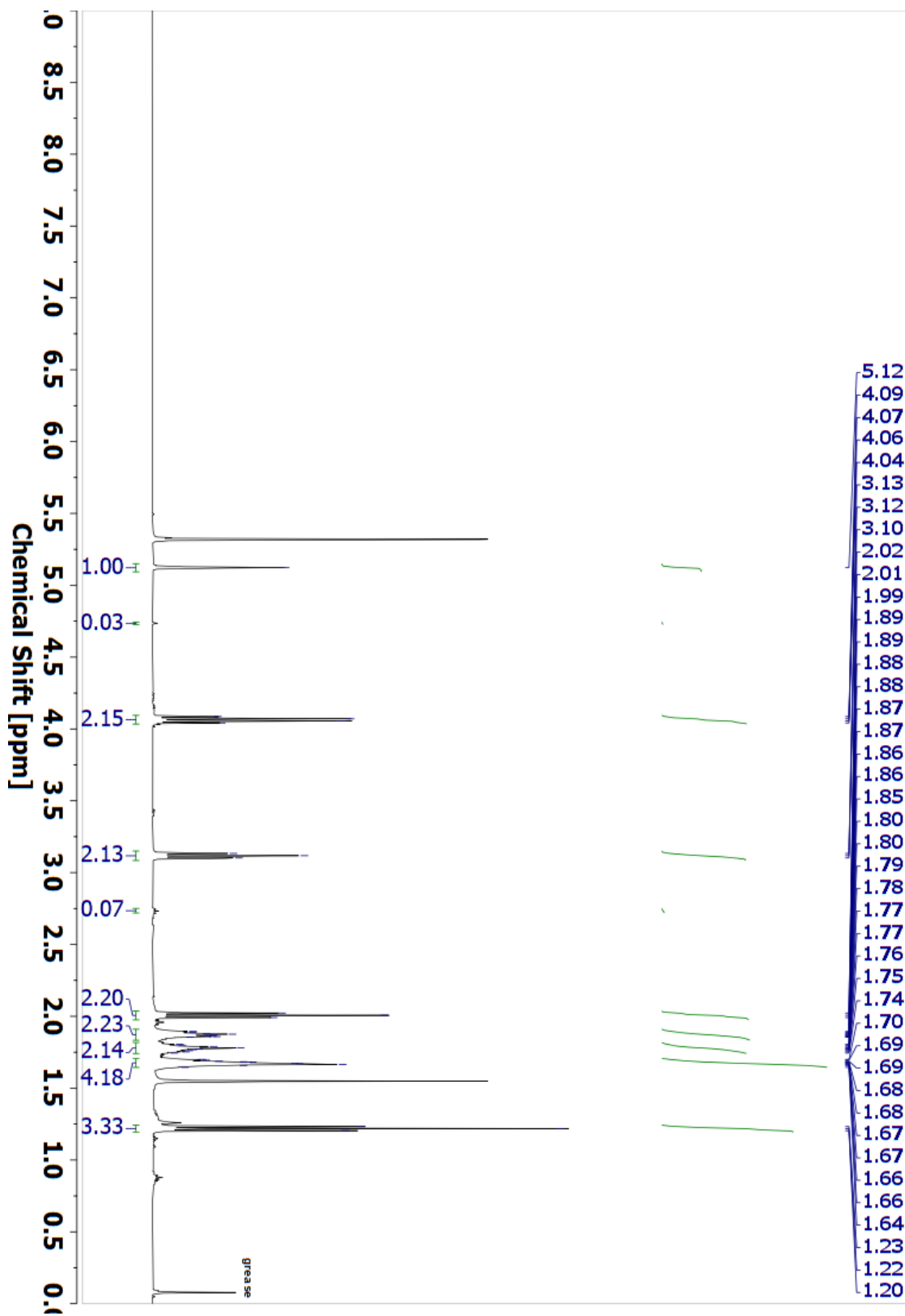
Ethyl (Z)-2-(1-oxaspiro[4.4]nonan-2-ylidene)acetate (33)



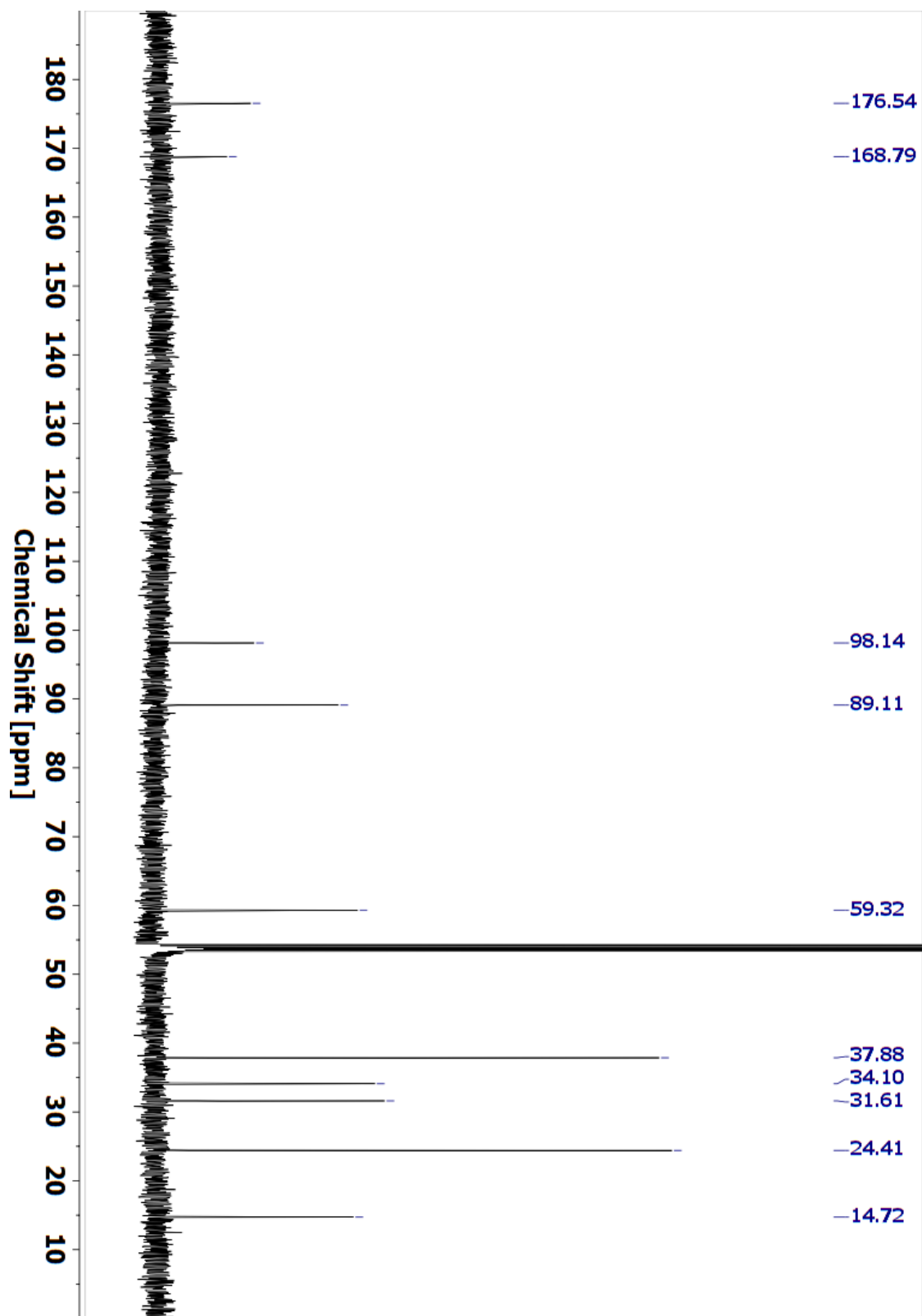
The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 83% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 13.4 mg (76% yield, 97% *Z*- : 3% *E*-isomer) of product as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 5.12 (s, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.12 (t, $J = 7.8$ Hz, 2H), 2.01 (t, $J = 7.8$ Hz, 2H), 1.91–1.83 (m, 2H), 1.82–1.74 (m, 2H), 1.71–1.63 (m, 4H), 1.22 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 176.54, 168.79, 98.14, 89.11, 59.32, 37.88, 34.10, 31.61, 24.41, 14.72. HRMS (ESI $^+$) m/z Calc. 211.1329 [$\text{C}_{12}\text{H}_{18}\text{O}_3 + \text{H}$] $^+$, Found. 211.1327 [$\text{M} + \text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

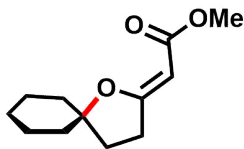


¹H NMR spectrum of isolated product in CD₂Cl₂ (97% *Z*- : 3% *E*-isomer)



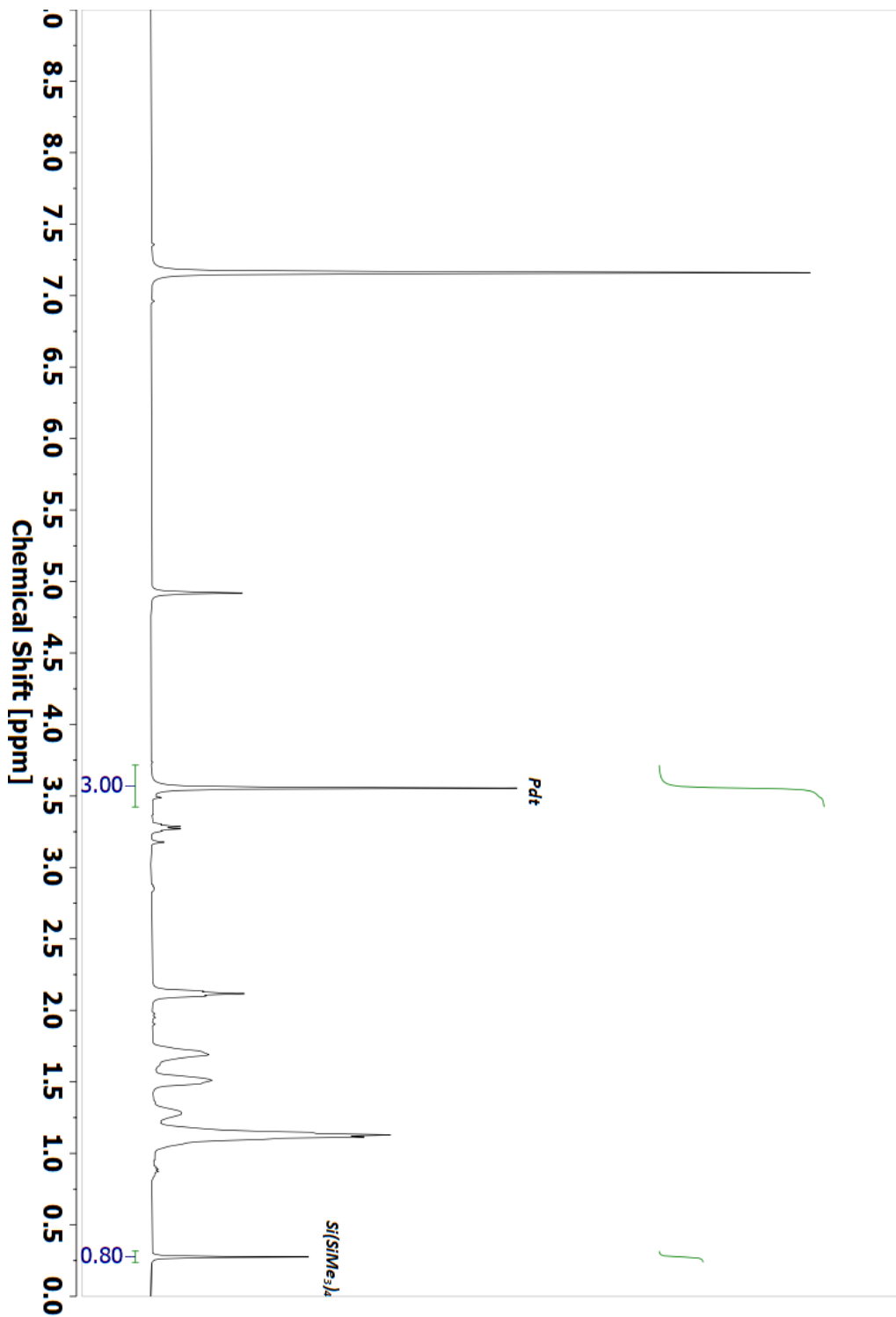
^{13}C NMR spectrum of isolated product in CD_2Cl_2

Methyl (Z)-2-(1-oxaspiro[4.5]decan-2-ylidene)acetate (34)

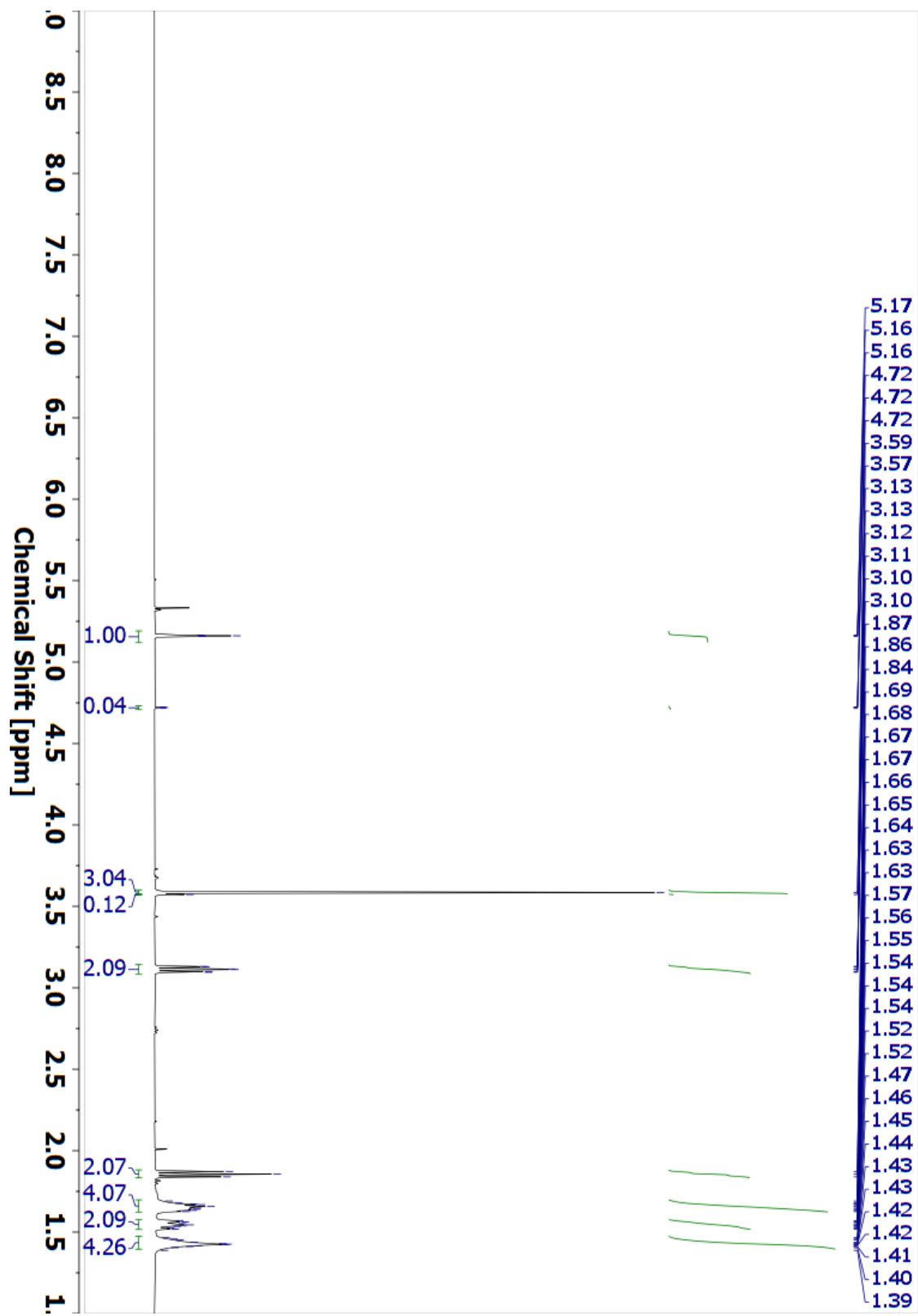


The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (1 h, 74% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 11.2 mg (64% yield, 96% *Z* : 4% *E*-isomer) of product as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 5.16 (t, $J = 1.8$ Hz, 1H), 3.59 (s, 3H), 3.11 (td, $J = 8.0, 1.8$ Hz, 2H), 1.86 (t, $J = 8.0$ Hz, 2H), 1.71–1.61 (m, 4H), 1.58–1.51 (m, 2H), 1.47–1.39 (m, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 176.80, 169.15, 89.97, 88.52, 50.62, 36.57, 33.90, 30.63, 25.56, 23.69. HRMS (ESI $^+$) m/z Calc. 211.1329 [$\text{C}_{12}\text{H}_{18}\text{O}_3+\text{H}$] $^+$, Found. 211.1331 [$\text{M}+\text{H}$] $^+$.

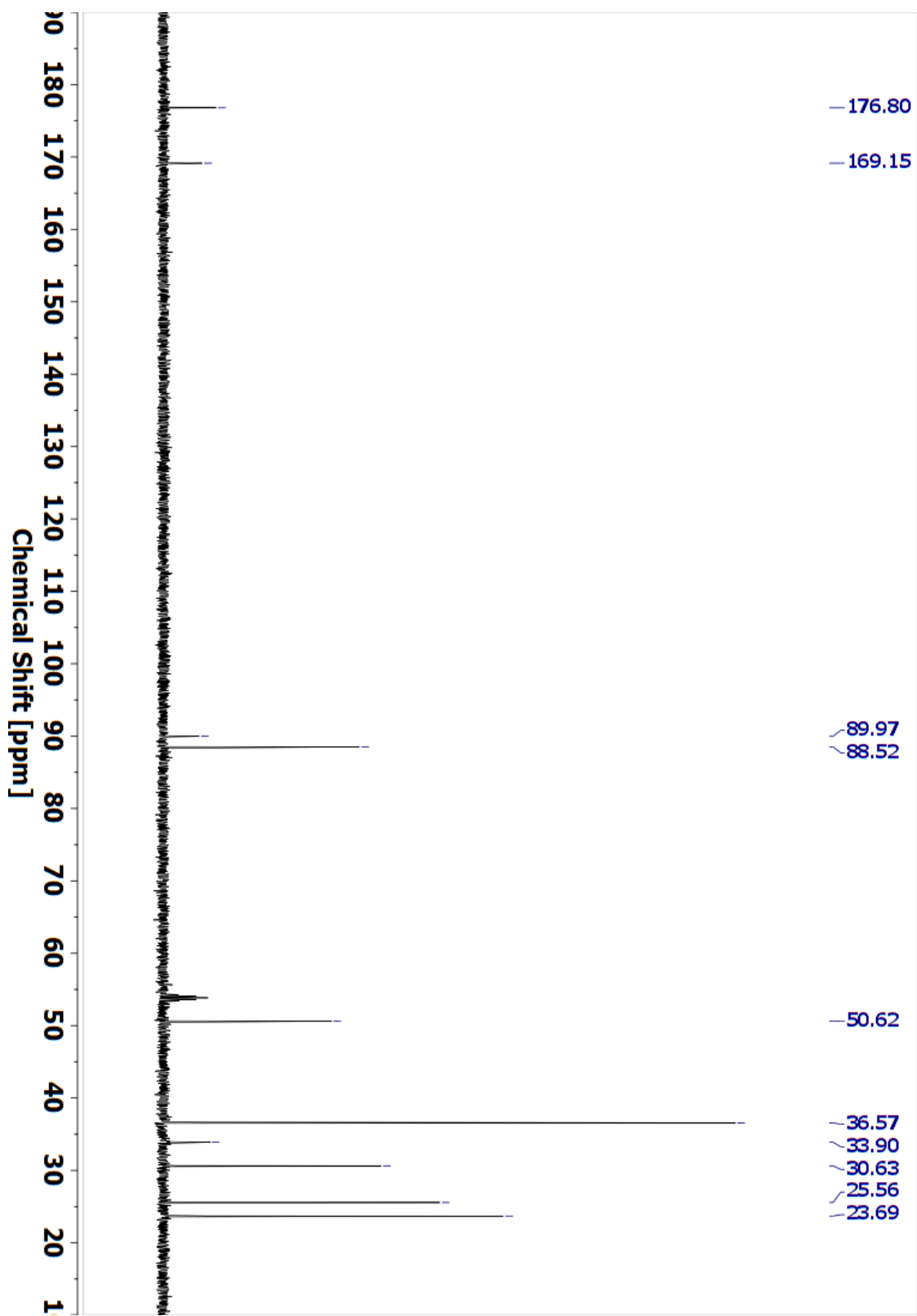
Scale-up: The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C for 1 h with 300 mg of α -diazo- β -ketoester in 30 ml of benzene to give 218 mg (82% yield) of product as a white solid.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 1 h (0.5 mg Si(SiMe₃)₄ as internal standard).

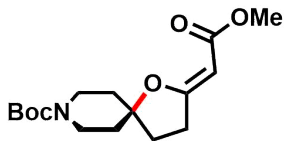


^1H NMR spectrum of isolated product in CD_2Cl_2 (96% Z- : 4% E-isomer)

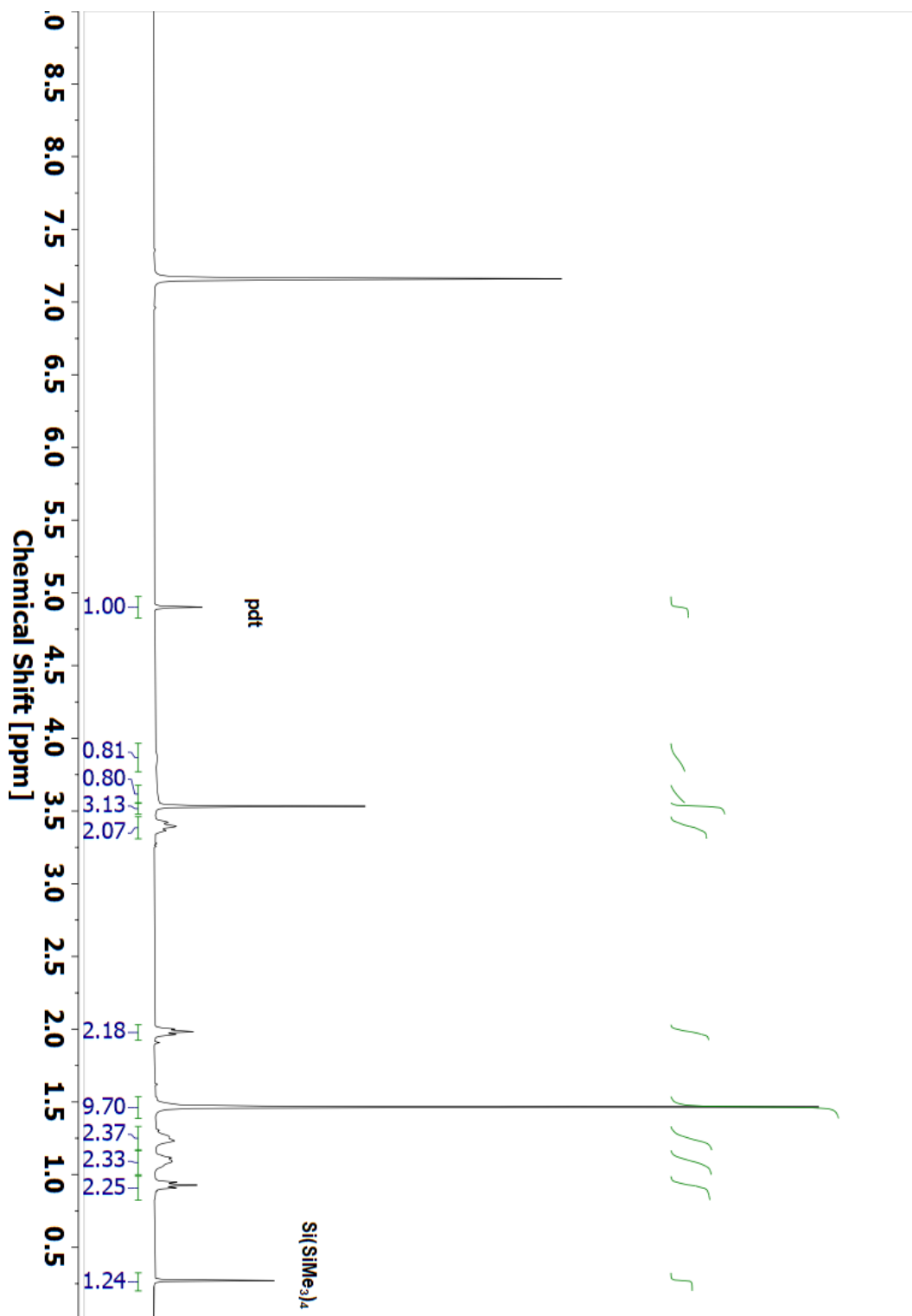


¹³C NMR spectrum of isolated product in CD₂Cl₂

tert-Butyl (Z)-2-(2-methoxy-2-oxoethylidene)-1-oxa-8-azaspiro[4.5]decane-8-carboxylate (35)

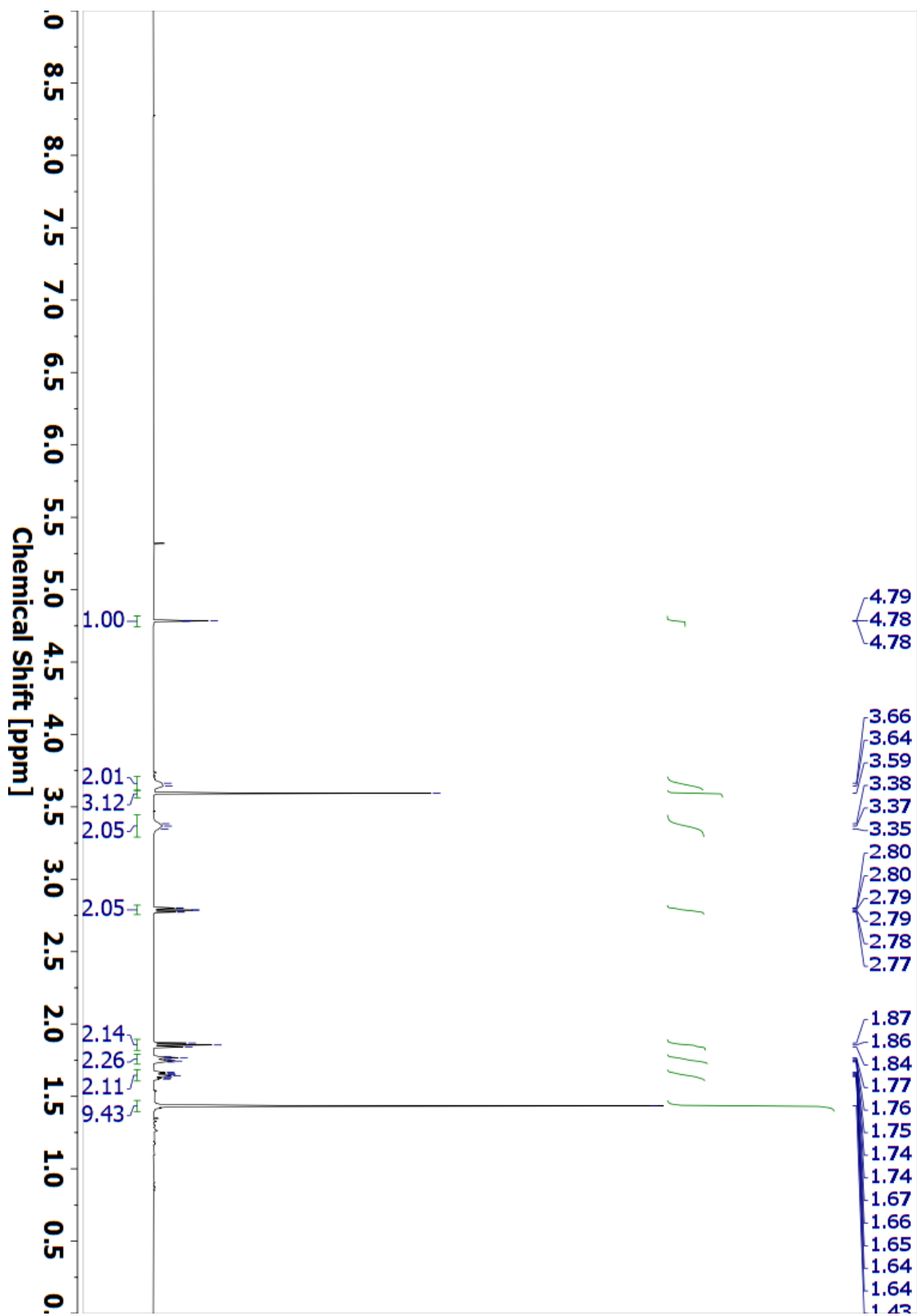


The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 71% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 9.3 mg (51% yield) of product as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 4.78 (t, $J = 1.4$ Hz, 1H), 3.65 (d, $J = 11.7$ Hz, 2H), 3.59 (s, 3H), 3.45 – 3.27 (m, 2H), 2.79 (td, $J = 7.9, 1.4$ Hz, 2H), 1.86 (t, $J = 7.9$ Hz, 2H), 1.79–1.71 (m, 2H), 1.65 (td, $J = 9.8, 5.0$ Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 171.16, 166.20, 154.86, 89.76, 88.12, 88.09, 79.63, 50.63, 35.98, 33.44, 31.67, 28.50. HRMS (ESI $^+$) m/z Calc. 312.1805 [$\text{C}_{16}\text{H}_{25}\text{NO}_5 + \text{H}$] $^+$, Found. 312.1804 [$\text{M} + \text{H}$] $^+$.

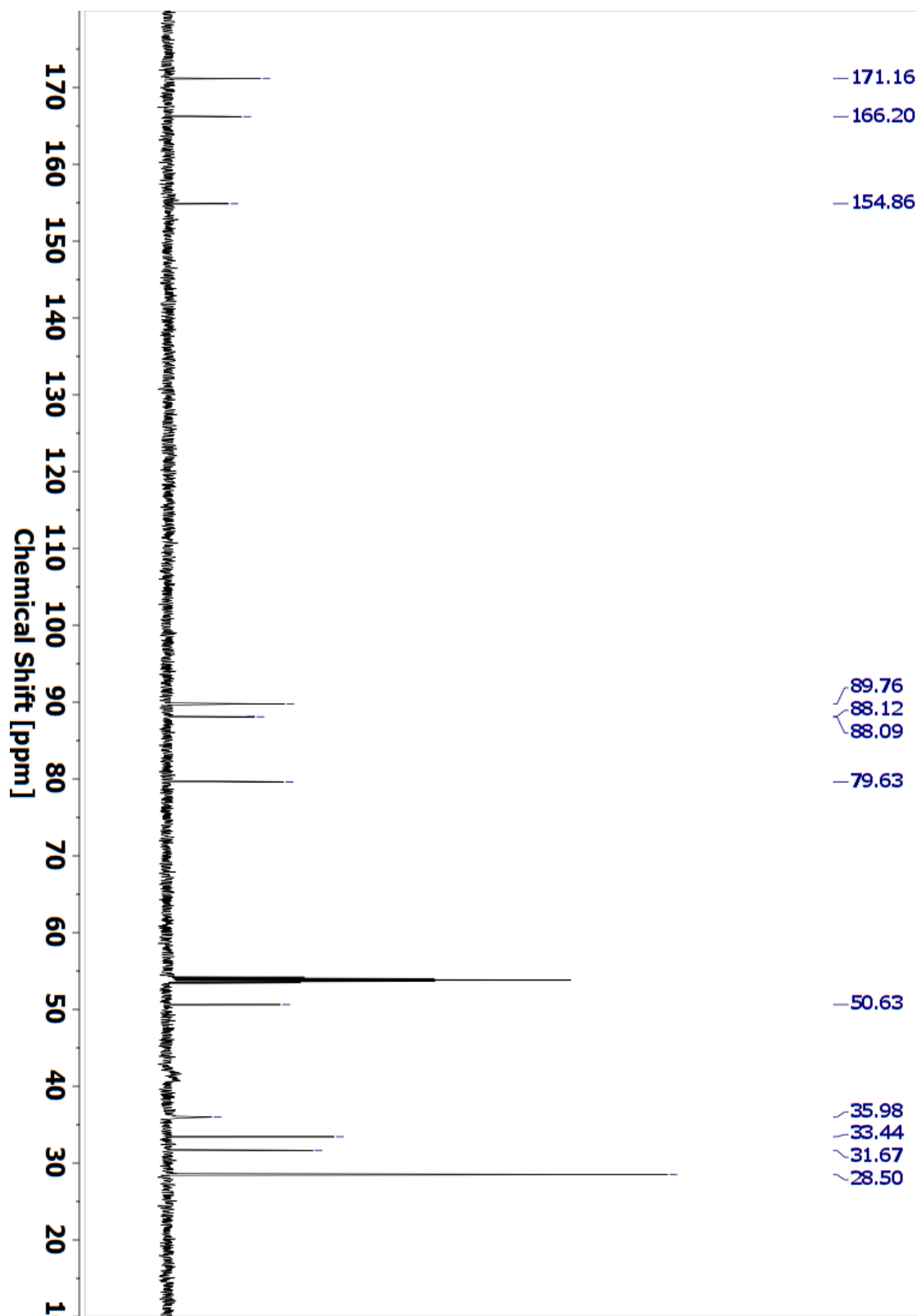


Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% $\text{Fe}(\text{acac})_2$ after 3 h (0.5 mg

$\text{Si}(\text{SiMe}_3)_4$ as internal standard).

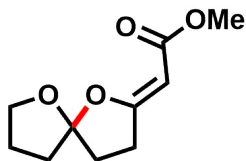


^1H NMR spectrum of isolated product in CD_2Cl_2

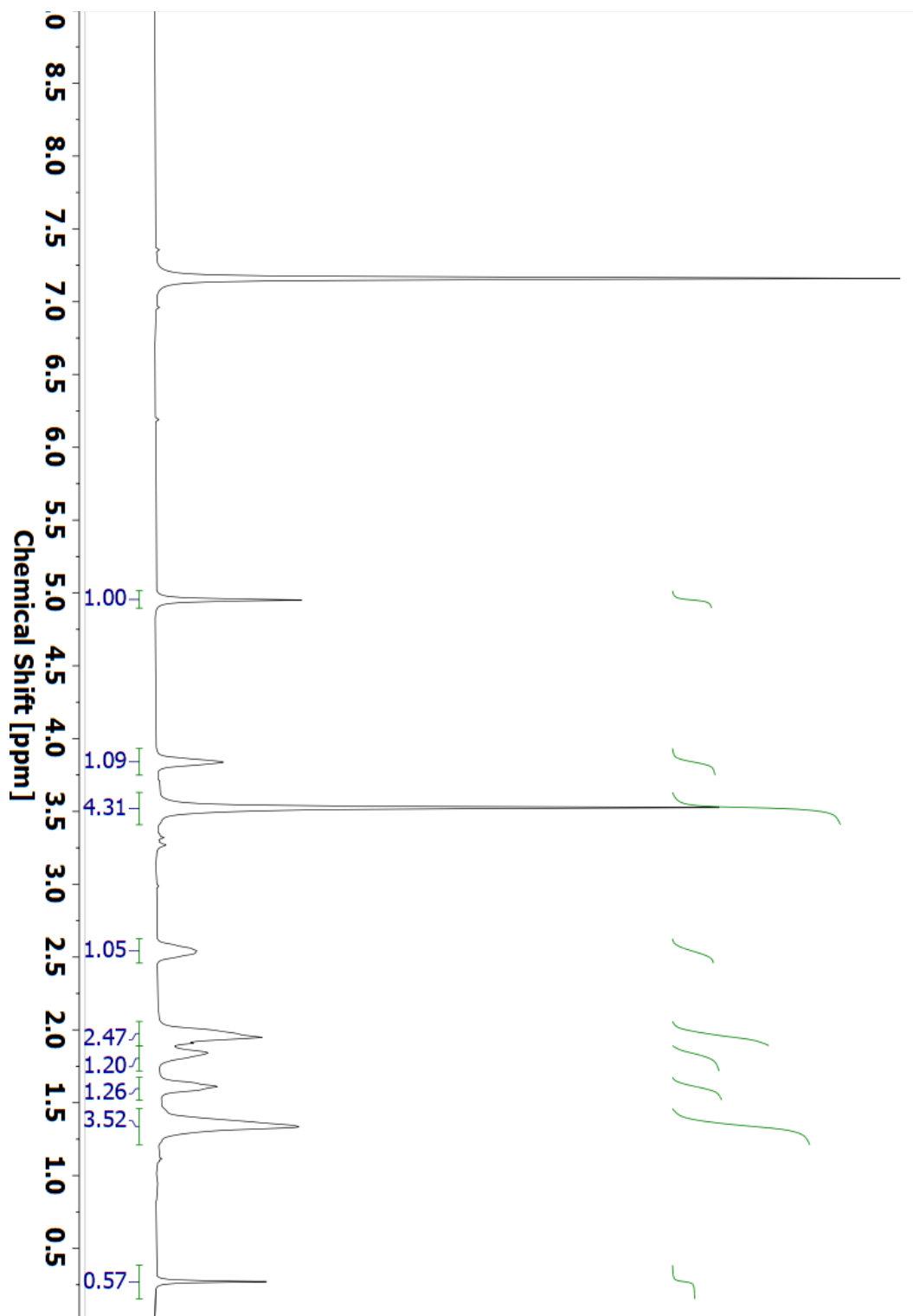


^{13}C NMR spectrum of isolated product in CD_2Cl_2

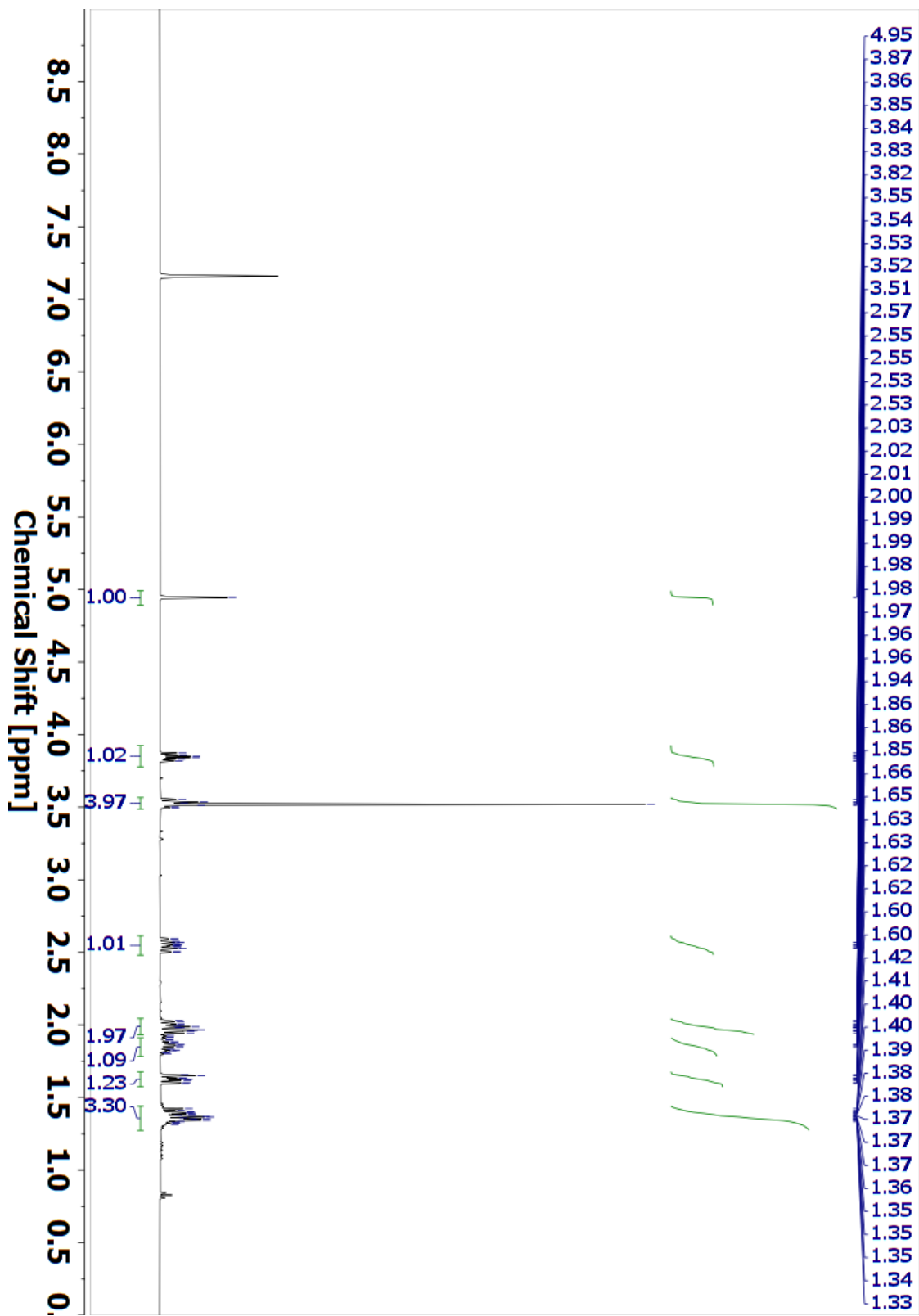
Methyl (Z)-2-(1,6-dioxaspiro[4.4]nonan-2-ylidene)acetate (36)



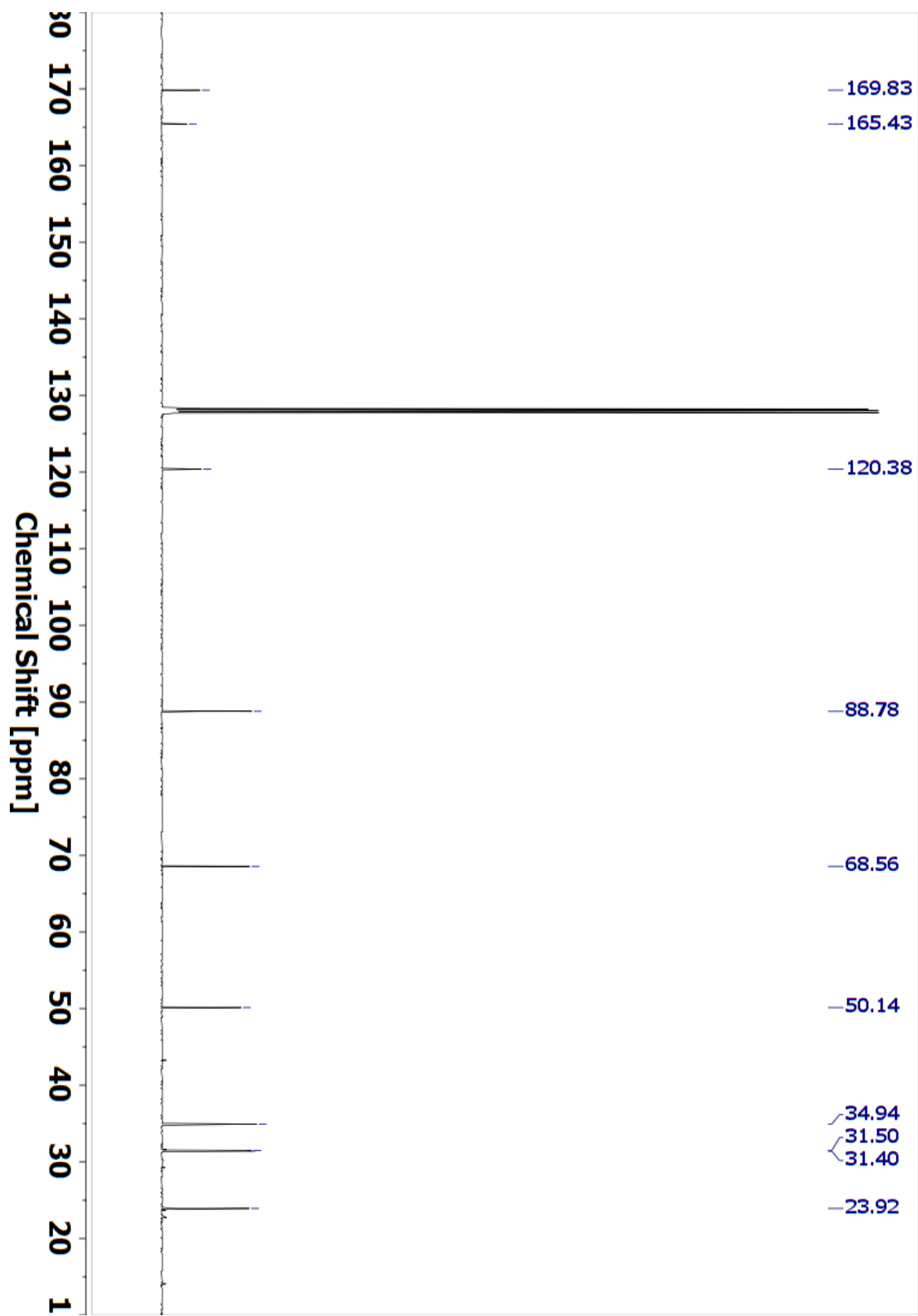
The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C (3 h, 77% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.6 mg (72% yield) of product as a colorless oil. ^1H NMR (400 MHz, C_6D_6) δ 4.95 (s, 1H), 3.85 (td, $J = 8.4, 5.1$ Hz, 1H), 3.59–3.43 (s, 4H), 2.64–2.47 (m, 1H), 2.06–1.92 (m, 2H), 1.92–1.78 (m, 1H), 1.63 (ddd, $J = 12.6, 8.4, 2.1$ Hz, 1H), 1.47–1.20 (m, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 169.83, 165.43, 120.38, 88.78, 68.56, 50.14, 34.94, 31.50, 31.40, 23.92. ^1H NMR (600 MHz, CDCl_3) δ 5.26 (t, $J = 1.9$ Hz, 1H), 4.08–4.02 (m, 1H), 4.01–3.92 (m, 1H), 3.66 (s, 3H), 3.37–3.24 (m, 1H), 3.19–3.05 (m, 1H), 2.31–2.17 (m, 2H), 2.17–2.07 (m, 2H), 2.07–1.95 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.38, 168.87, 119.33, 89.72, 69.21, 50.79, 35.33, 32.33, 30.46, 24.32. HRMS (ESI $^+$) m/z Calc. 200.0998 [$\text{C}_{10}\text{H}_{14}\text{O}_4+\text{H}$] $^+$, Found. 200.1033 [$\text{M}+\text{H}$] $^+$.



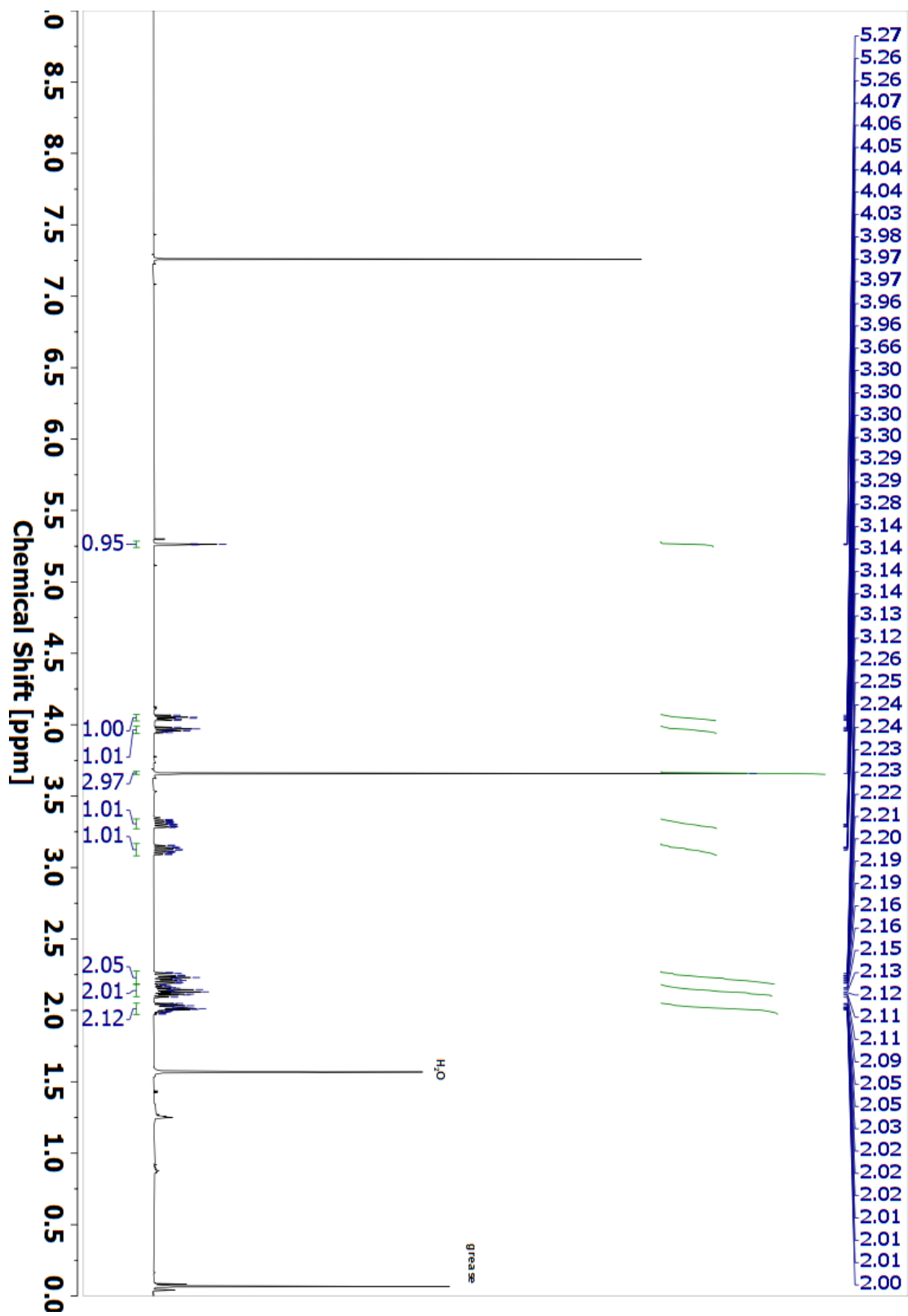
Crude NMR spectrum for reaction carried out at 25 °C with 15 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).



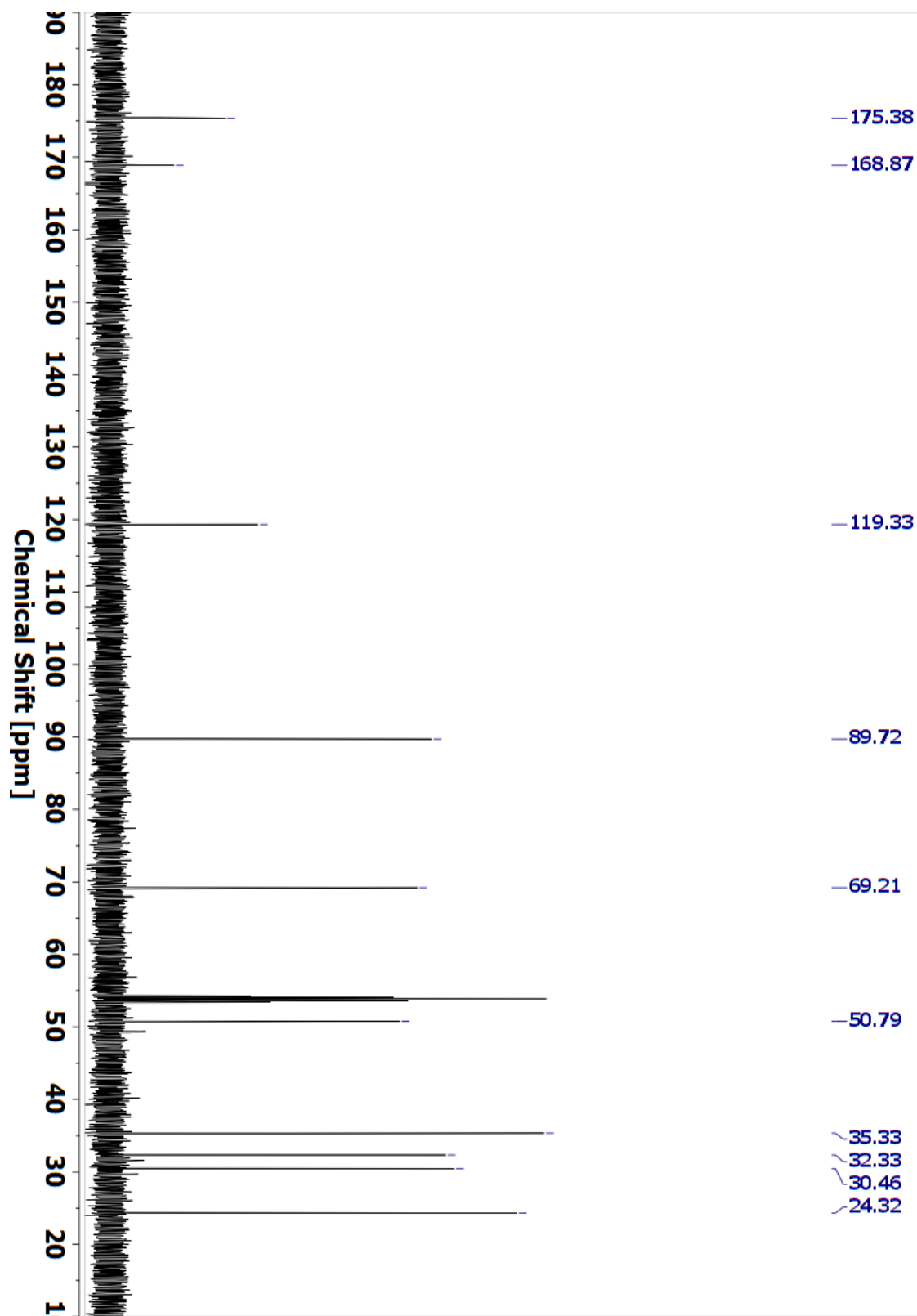
^1H NMR spectrum of isolated product in C_6D_6



¹³C NMR spectrum of isolated product in C₆D₆

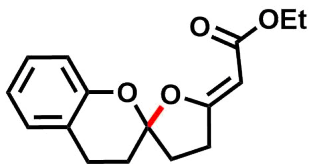


¹H NMR spectrum of isolated product in CDCl₃

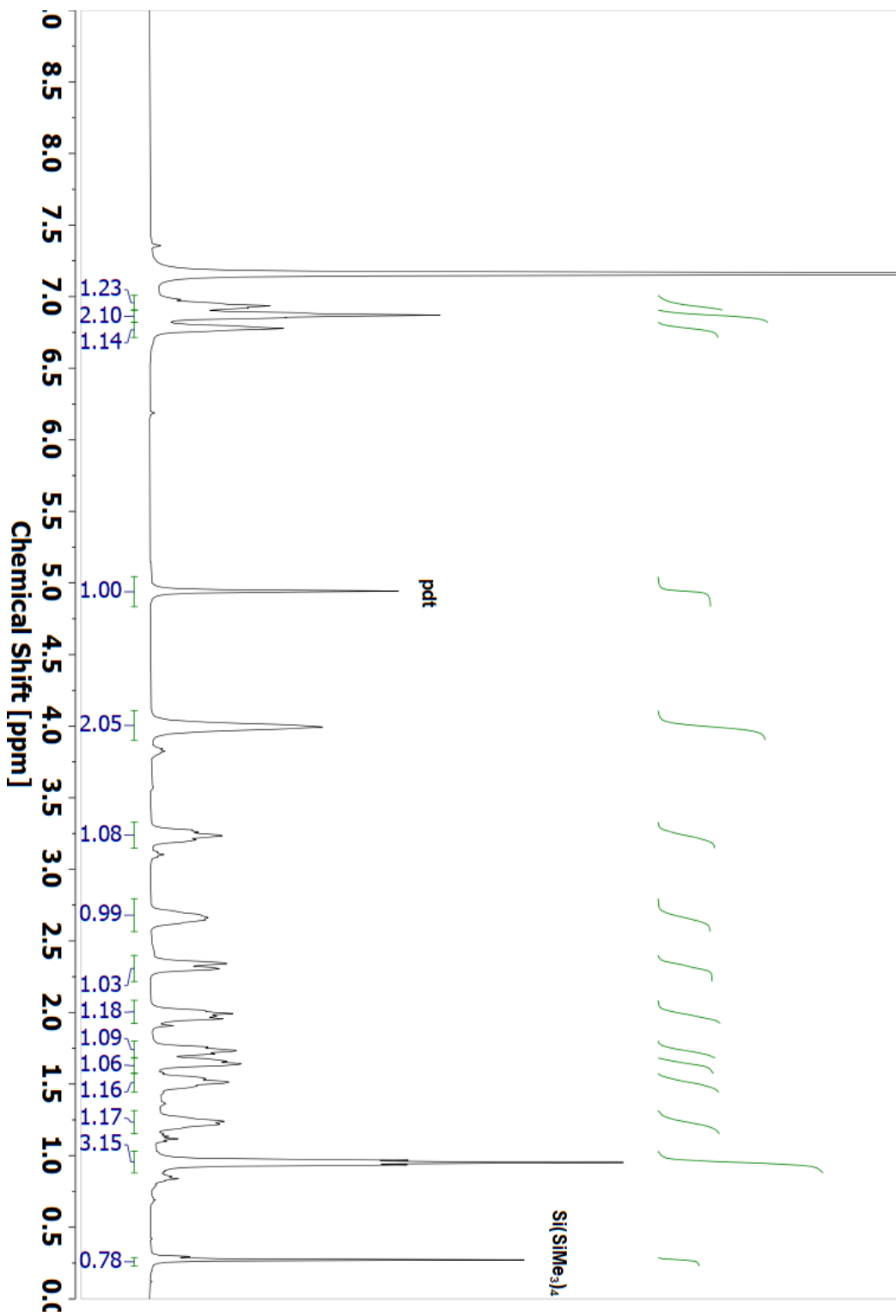


¹³C NMR spectrum of isolated product in CD₂Cl₂

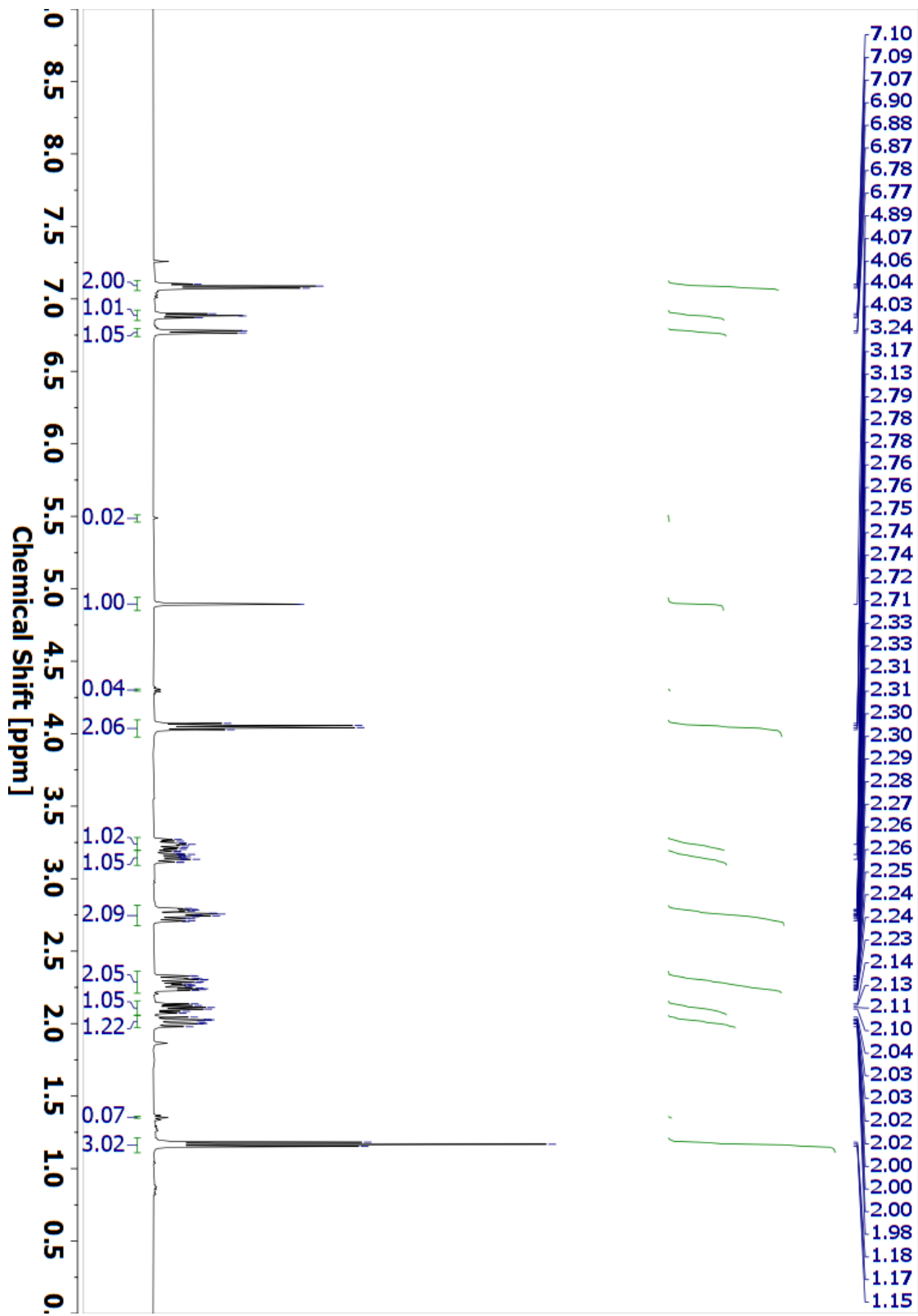
Ethyl (Z)-2-(3',4'-dihydro-5'H-spiro[chromane-2,2'-furan]-5'-ylidene)acetate (37)



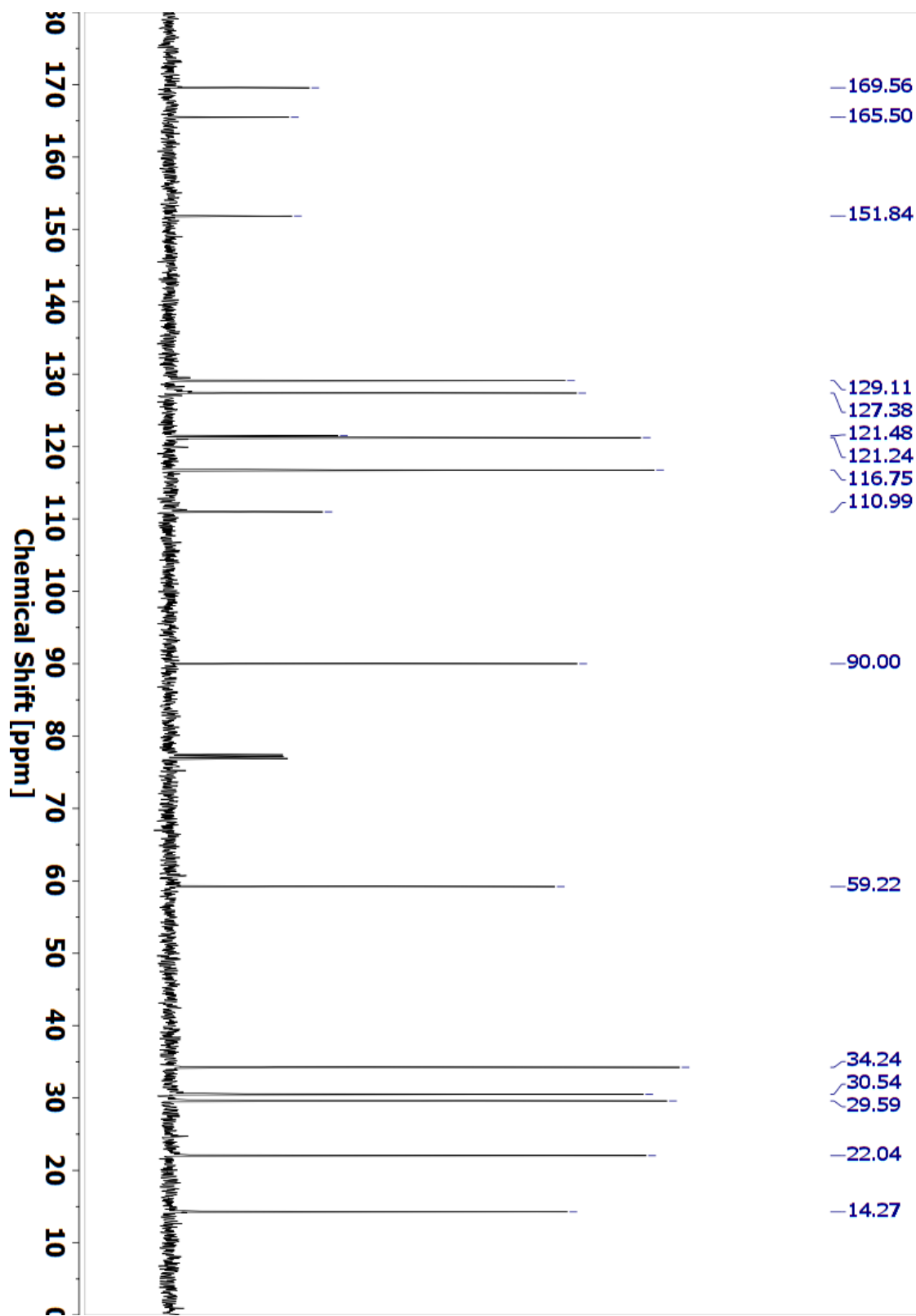
The reaction was carried out at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 94% NMR yield) with 20.0 mg of σ -diazo- β -ketoester to give 11.6 mg (64% yield, 98% Z- : 2% E-isomer) of product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.12–7.05 (m, 2H), 6.88 (t, $J = 6.8$ Hz, 1H), 6.77 (d, $J = 7.3$ Hz, 1H), 4.89 (s, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 3.30–3.20 (m, 1H), 3.20–3.10 (m, 1H), 2.83–2.69 (m, 2H), 2.35–2.19 (m, 2H), 2.16–2.06 (m, 1H), 2.06–1.95 (m, 1H), 1.17 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.56, 165.50, 151.84, 129.11, 127.38, 121.48, 121.24, 116.75, 110.99, 90.00, 59.22, 34.24, 30.54, 29.59, 22.04, 14.27. HRMS (ESI $^+$) m/z Calc. 275.1278 [$\text{C}_{16}\text{H}_{18}\text{O}_4+\text{H}$] $^+$, Found. 275.1280 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

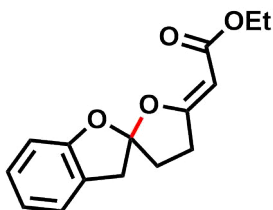


^1H NMR spectrum of isolated product in CDCl_3 (98% *Z*- : 2% *E*-isomer)

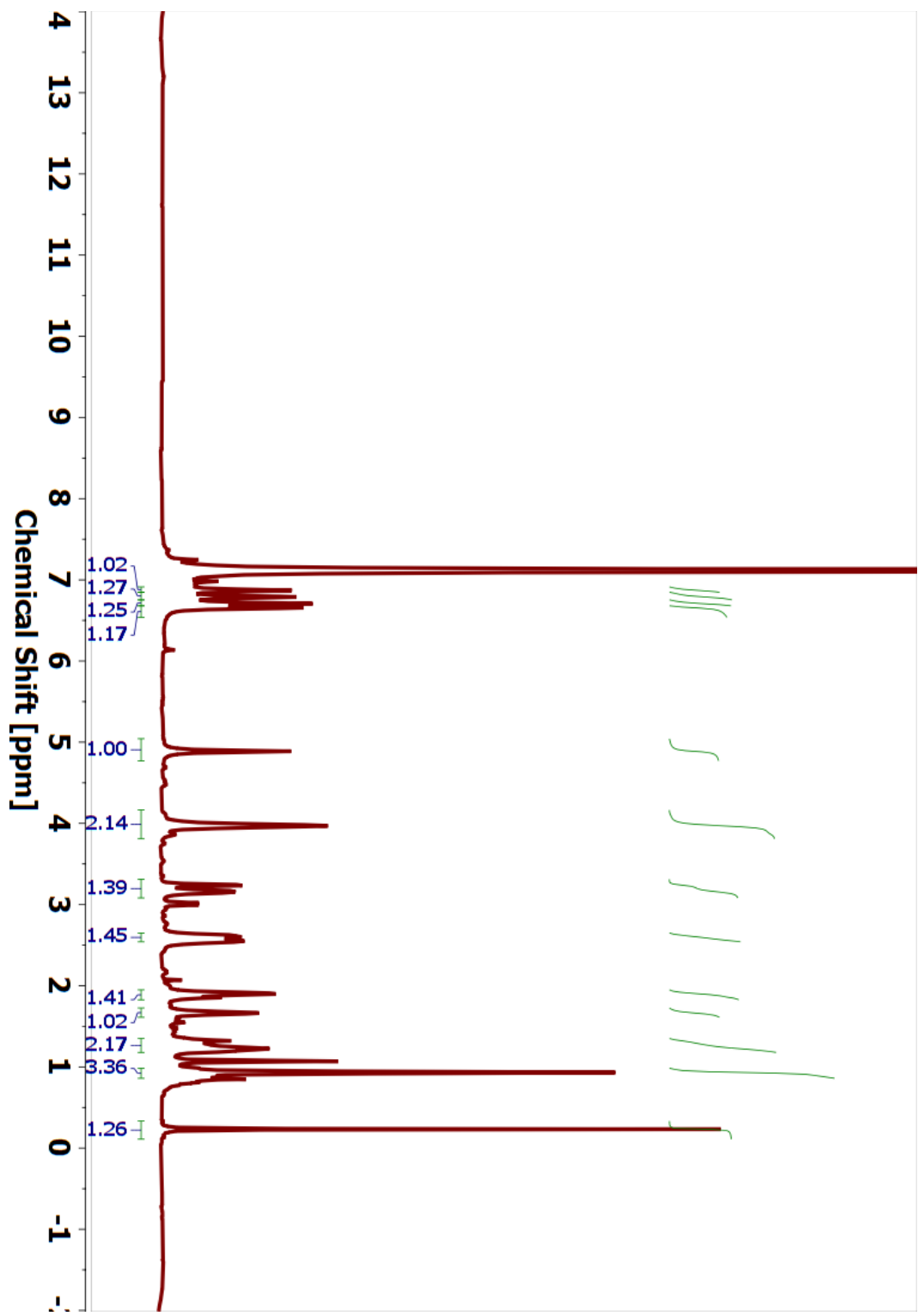


^{13}C NMR spectrum of isolated product in CDCl_3

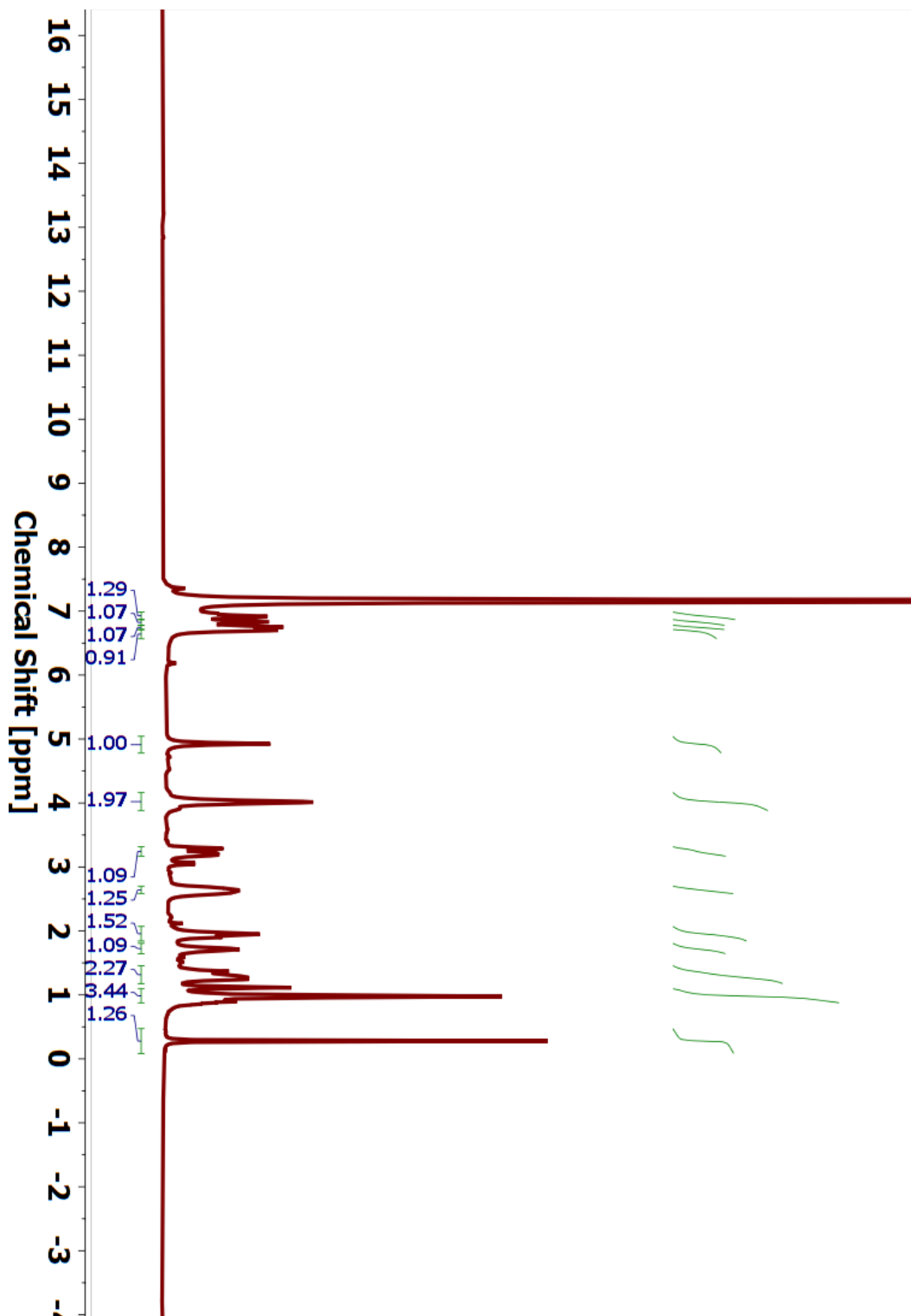
Ethyl (Z)-2-(3',4'-dihydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-ylidene)acetate (38)



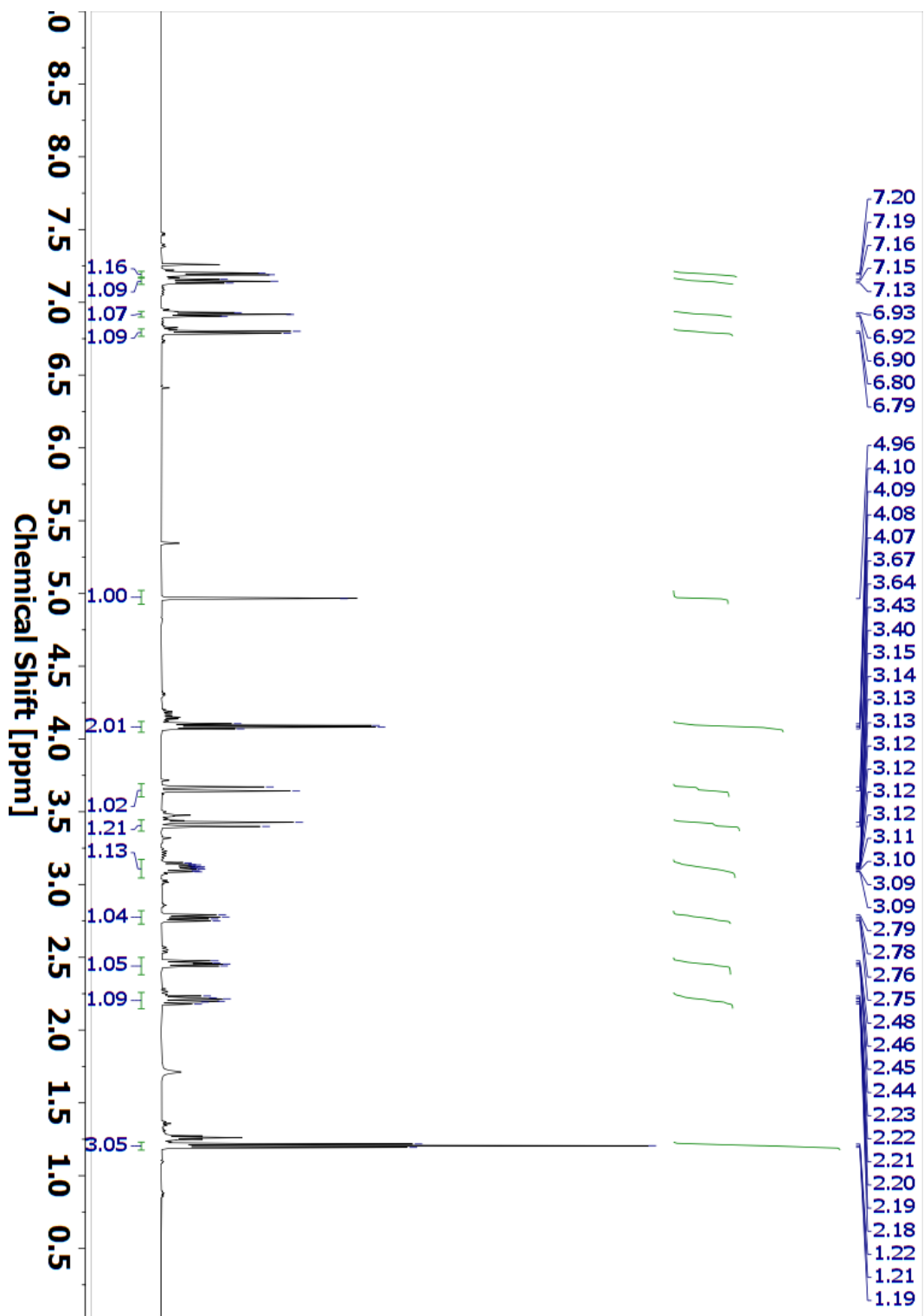
The reaction was carried out at 25 °C with 20 mol% catalyst loading following procedure C (3 h, 58% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 8.5 mg (47% yield) of product as a white crystalline solid suitable for single-crystal X-ray diffraction analysis. ^1H NMR (600 MHz, CDCl_3) δ 7.20 (d, $J = 7.3$ Hz, 1H), 7.17–7.10 (m, 1H), 6.95–6.89 (m, 1H), 6.79 (d, $J = 8.1$ Hz, 1H), 4.96 (s, 1H), 4.09 (q, $J = 7.1$ Hz, 2H), 3.66 (d, $J = 17.0$ Hz, 2H), 3.41 (d, $J = 17.0$ Hz, 1H), 3.21–3.06 (m, 1H), 2.77 (dd, $J = 16.7, 8.7$ Hz, 1H), 2.46 (dd, $J = 13.0, 8.3$ Hz, 1H), 2.26–2.16 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.65, 167.87, 160.04, 130.92, 127.35, 127.30, 124.16, 123.64, 112.35, 92.92, 61.98, 41.58, 36.46, 33.49, 17.01. ***The cyclized product is tabulated in the main manuscript to match the bulk product conformation upon isolation from column chromatography, as confirmed by rapid crystallization from non-polar hexanes.***



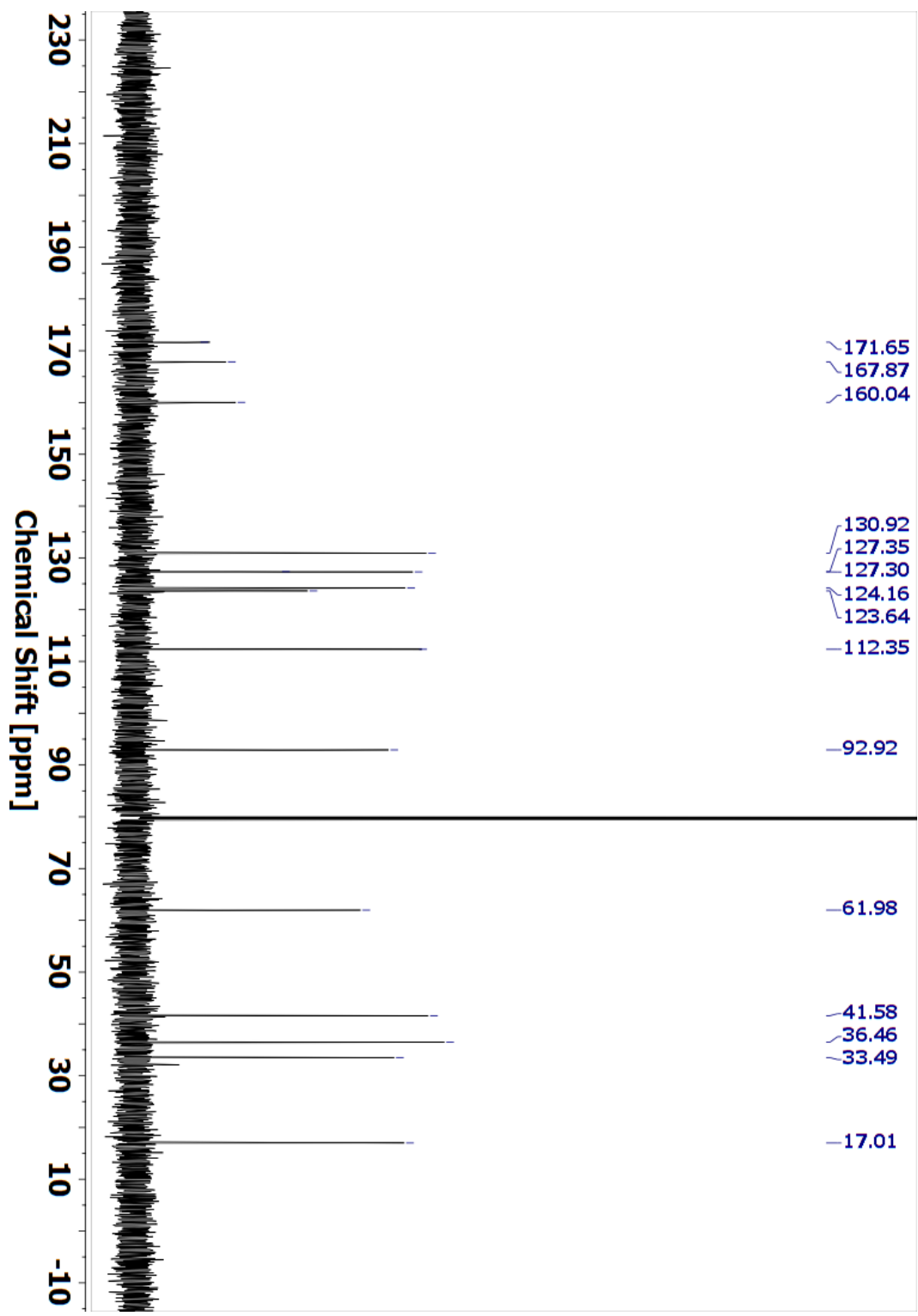
Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 3 h (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



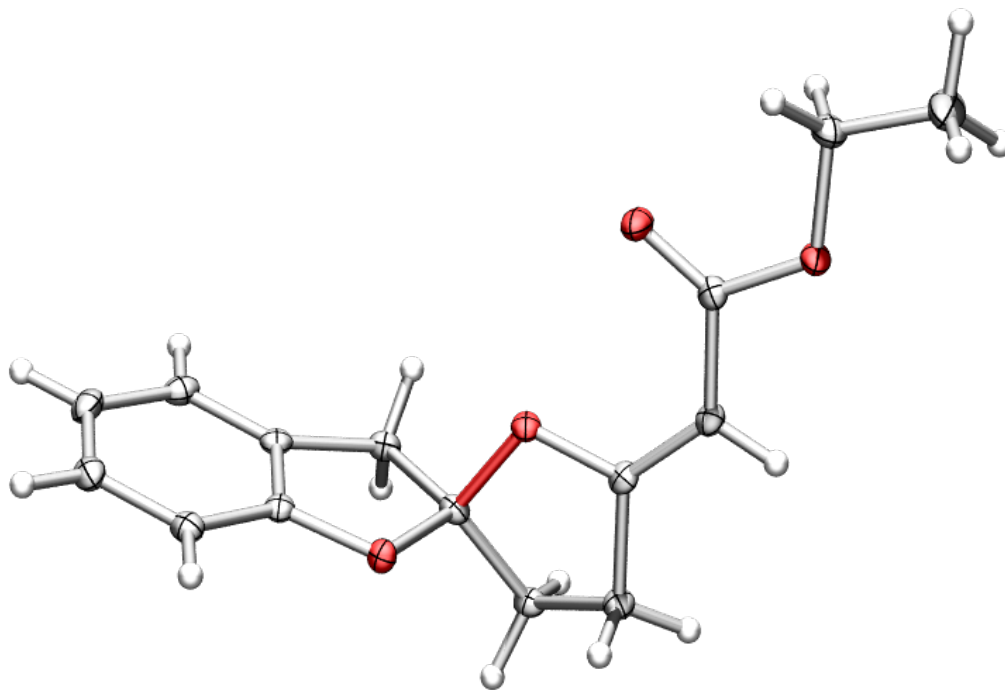
Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 24 h, showing no sign of isomerization (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).



^1H NMR spectrum of isolated product in CDCl_3 , showing small degree of isomerization upon dissolving in CDCl_3 (< 20 min)

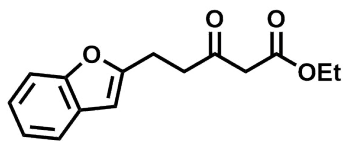


^{13}C NMR spectrum of isolated product in CDCl_3 , showing significant amount of isomerization upon dissolving in CDCl_3 (< 20 min)

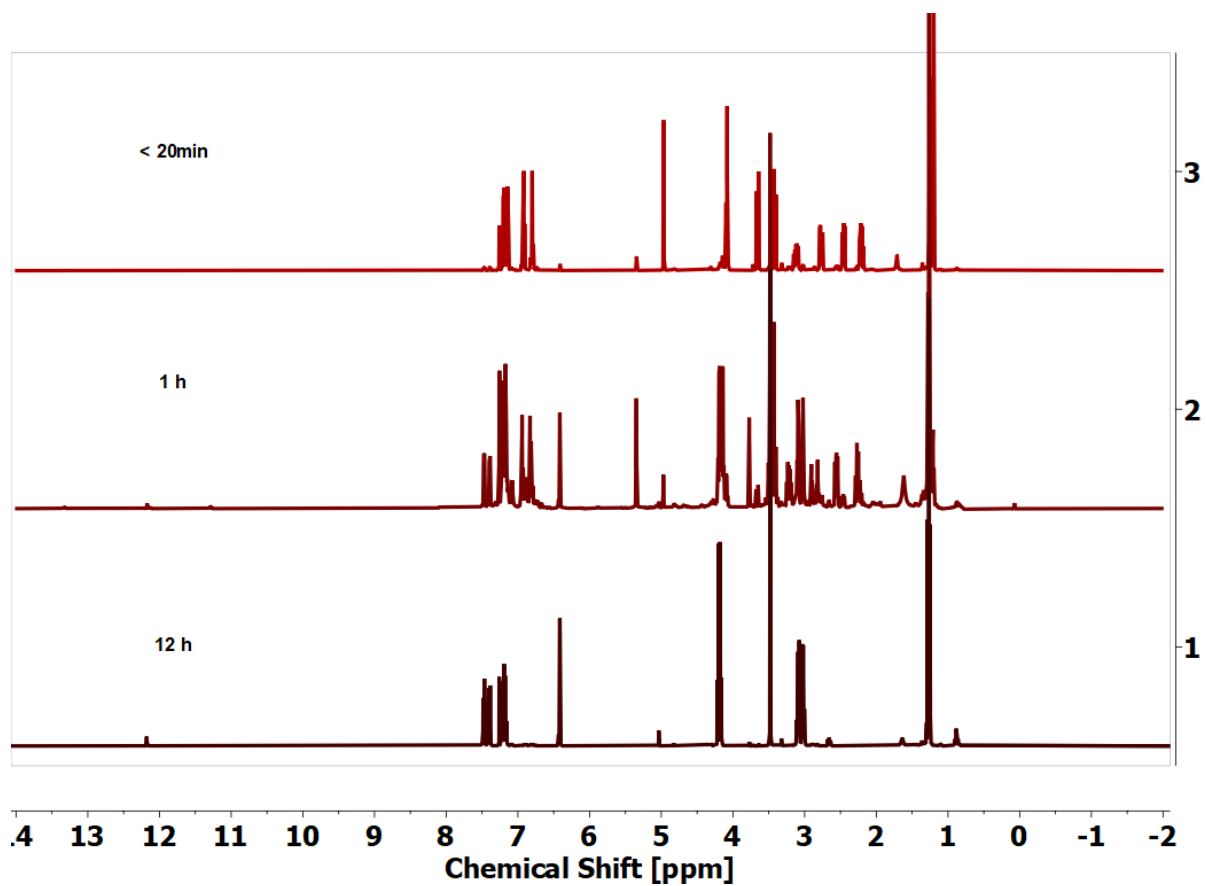


Solid-state molecular structure for ethyl (Z)-2-(3',4'-dihydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-ylidene)acetate (38) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white.

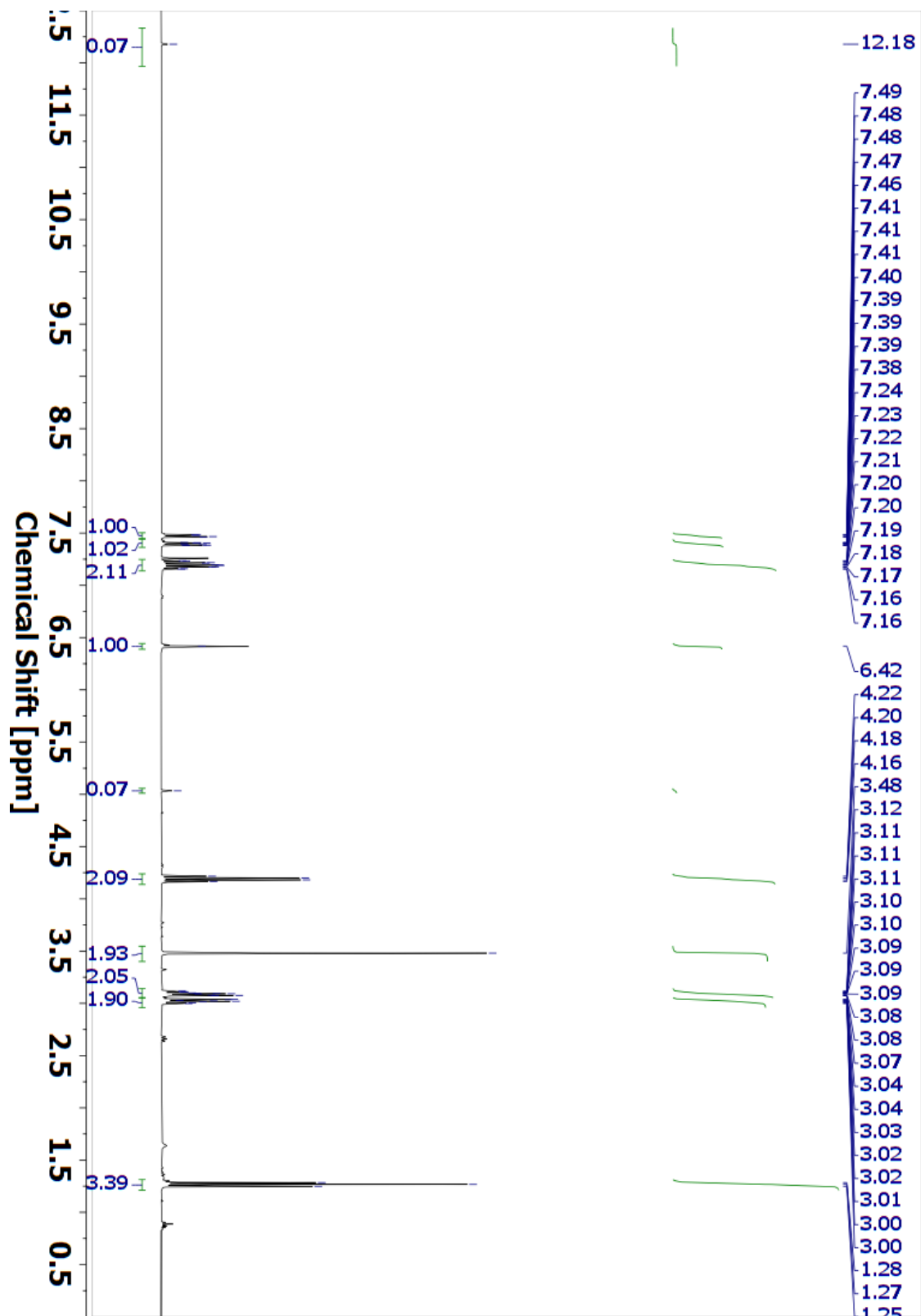
Despite the stability of the product in solid state (verified by unit cell measurement) and anhydrous condition in C_6D_6 (verified by crude NMR sample at room temperature for 24h), quick isomerization is observed upon dissolving in $CDCl_3$, leading to the formation of ethyl 5-(benzofuran-2-yl)-3-oxopentanoate (6.5% tautomerization).



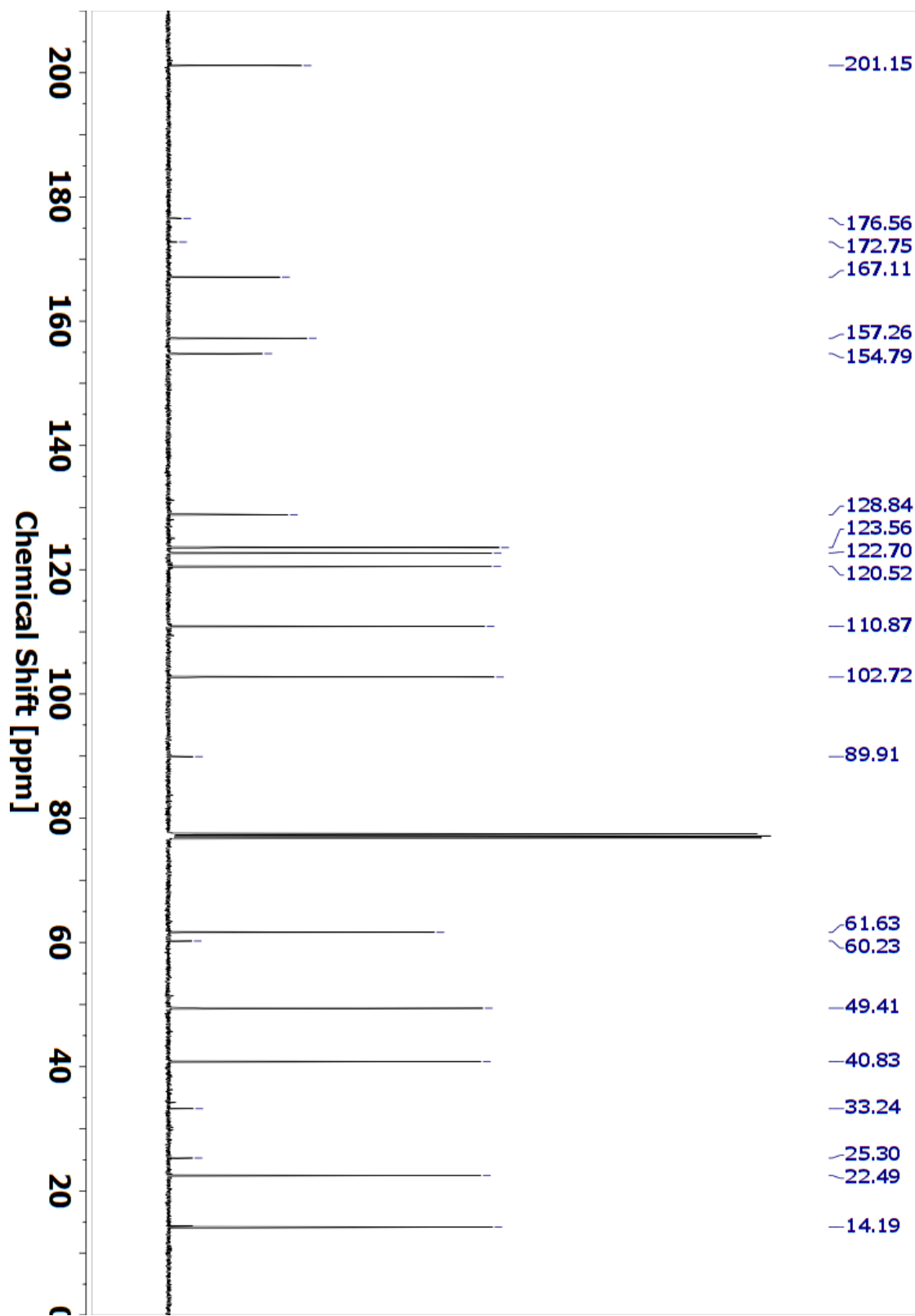
1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.44 (m, 1H), 7.44–7.36 (m, 1H), 7.24–7.14 (m, 2H), 6.42 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.48 (s, 2H), 3.15–3.05 (m, 2H), 3.05–2.95 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (keto form) 201.15, 167.11, 157.26, 154.79, 128.84, 123.56, 122.70, 120.52, 110.87, 102.72, 61.63, 49.41, 40.83, 22.49, 14.19. HRMS (ESI $^+$) m/z Calc. 261.1121 [$C_{15}H_{16}O_4+H$] $^+$, Found. 261.1125 [$M+H$] $^+$.



^1H NMR spectrum of isolated product in CDCl_3 , showing complete isomerization after 12 h

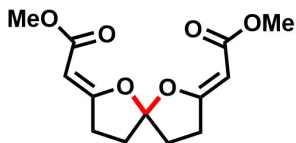


^1H NMR spectrum of isolated product in CDCl_3

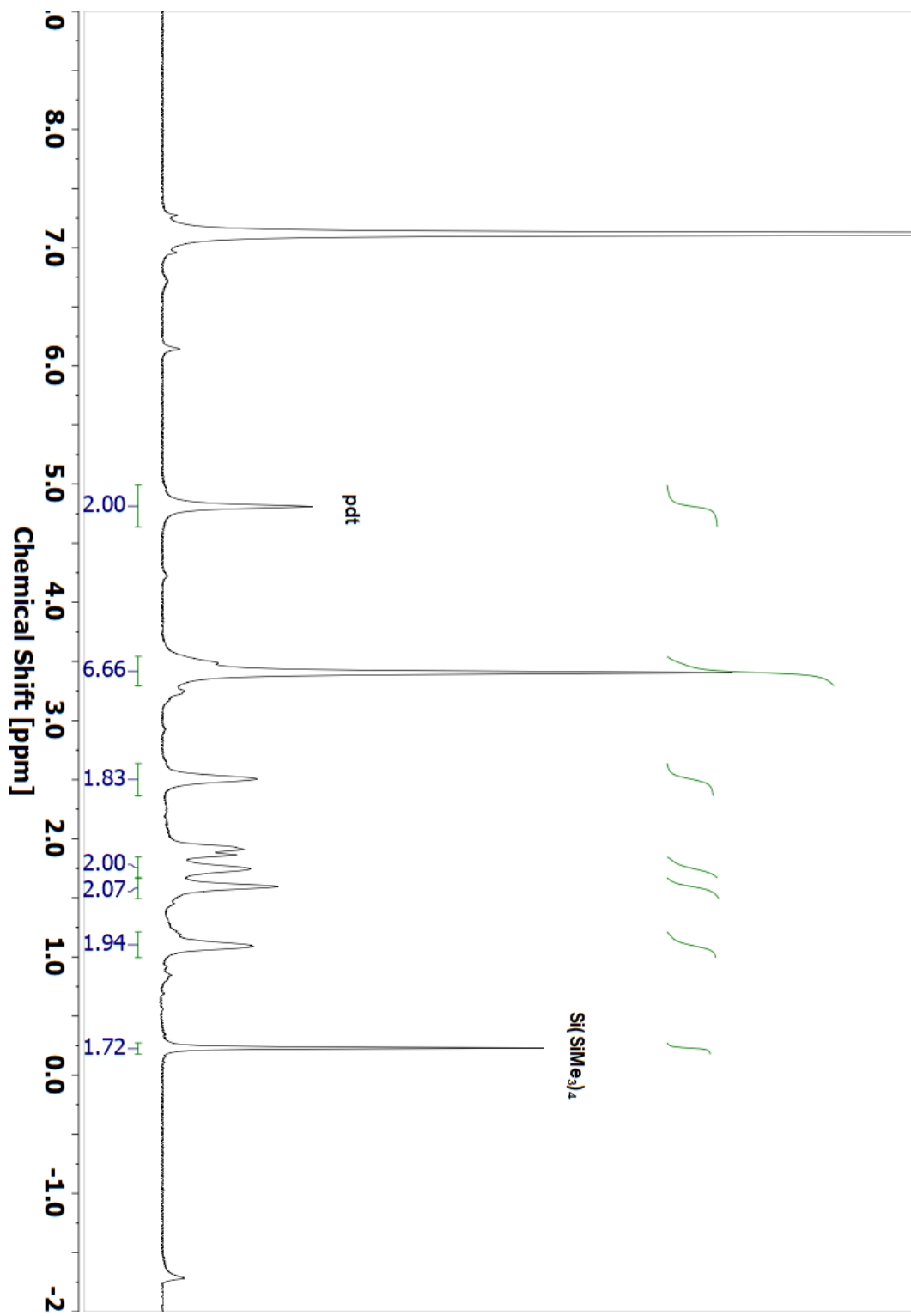


^{13}C NMR spectrum of isolated product in CDCl_3

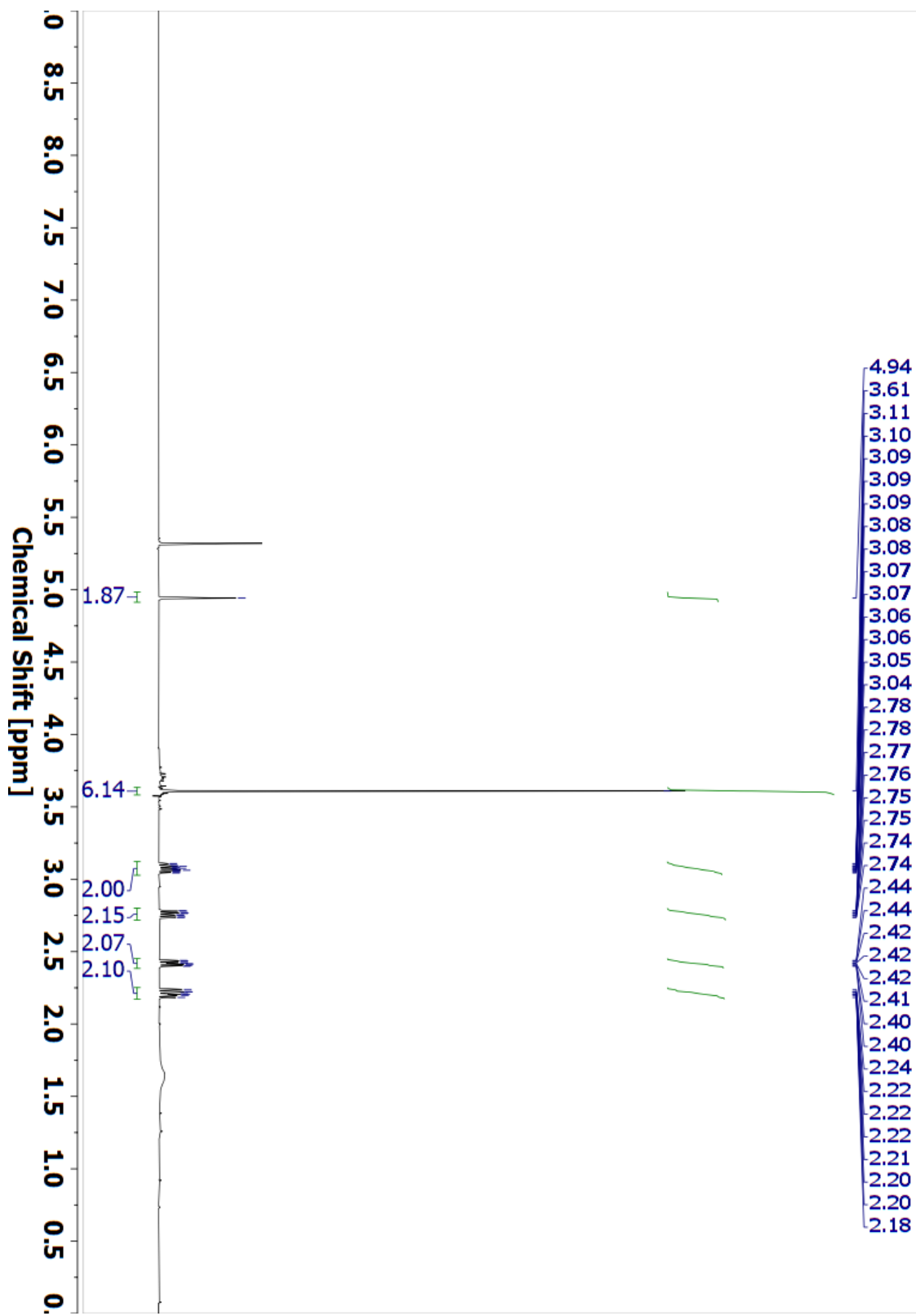
Dimethyl 2,2'-(1,6-dioxaspiro[4.4]nonane-2,7-diylidene)(2Z,2'Z)-diacetate (39)



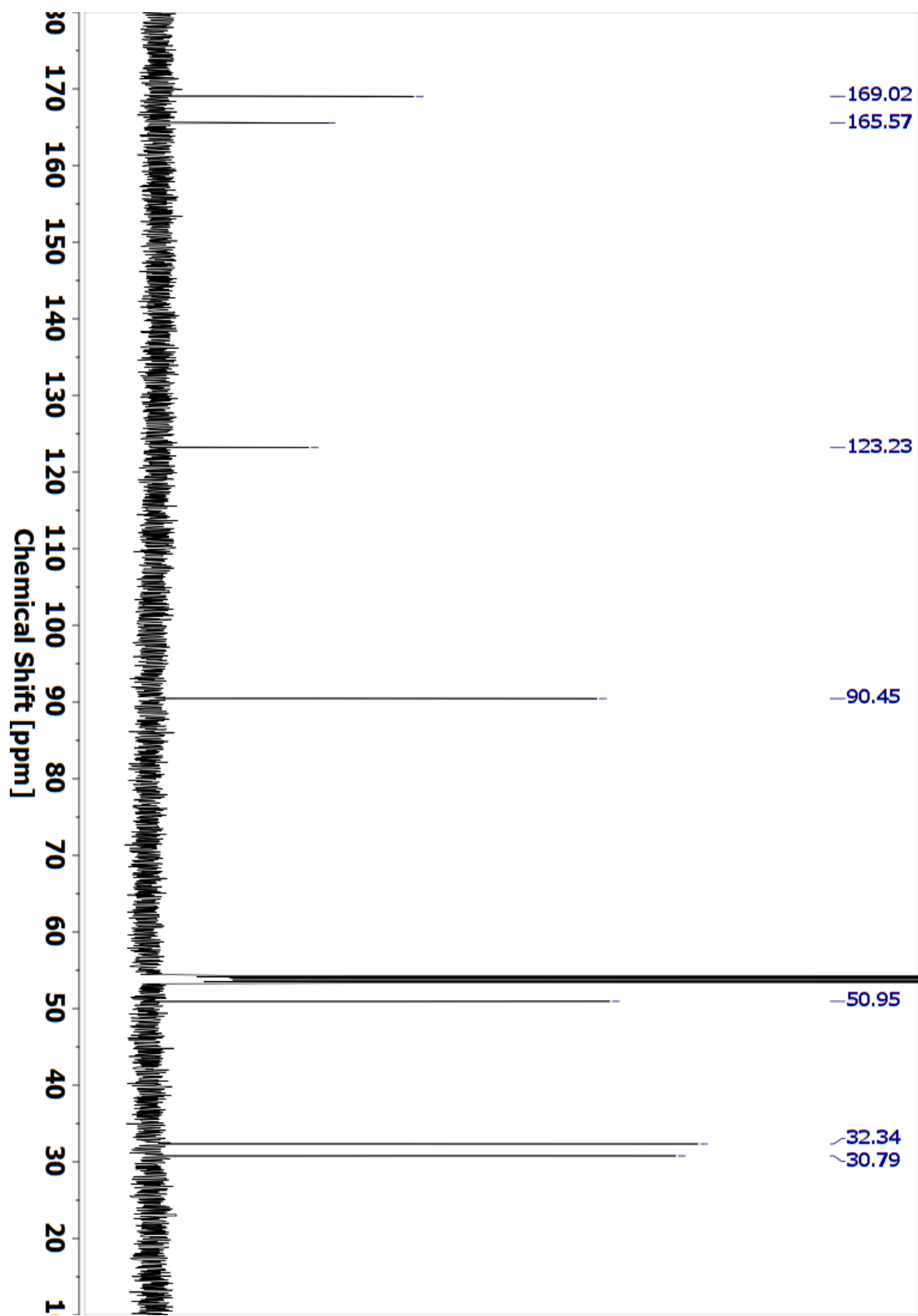
The reaction was carried out at 60 °C with 30 mol% catalyst loading following procedure D (40 min, 48% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 7.0 mg (43% yield) of product as a white solid. ^1H NMR (600 MHz, CD_2Cl_2) δ 4.94 (s, 2H), 3.61 (s, 6H), 3.19–2.98 (m, 2H), 2.76 (ddd, $J = 17.0, 8.8, 2.2$ Hz, 2H), 2.42 (ddd, $J = 13.4, 8.8, 2.2$ Hz, 2H), 2.21 (ddd, $J = 13.4, 11.2, 8.8$ Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 169.02, 165.57, 123.23, 90.45, 50.95, 32.34, 30.79. HRMS (ESI $^+$) m/z Calc. 269.1018 [$\text{C}_{13}\text{H}_{16}\text{O}_6+\text{H}$] $^+$, Found. 269.1020 [$\text{M}+\text{H}$] $^+$.



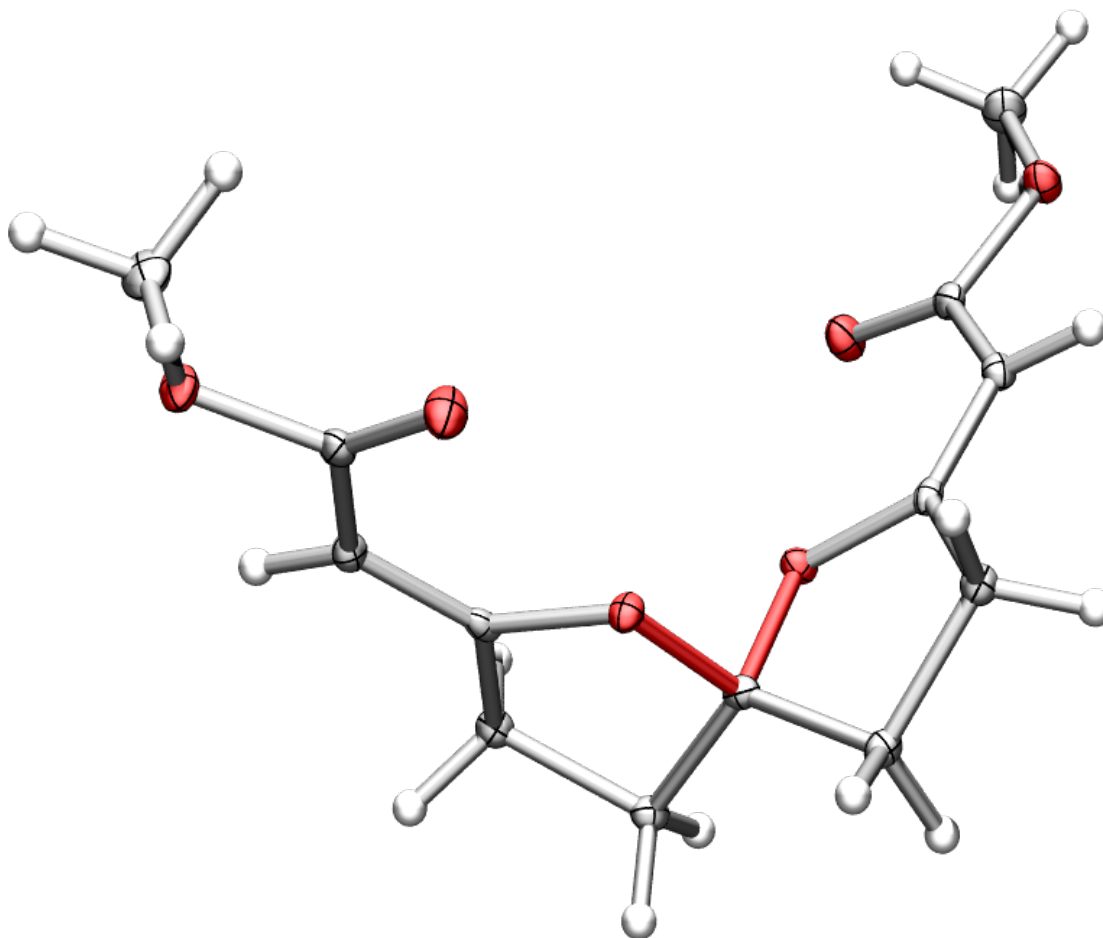
Crude NMR spectrum for reaction carried out at 60 °C with 30 mol% Fe(acac)₂ after 40 min (0.5 mg Si(SiMe₃)₄ as internal standard).



^1H NMR spectrum of isolated product in CD_2Cl_2

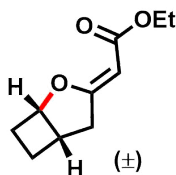


¹³C NMR spectrum of isolated product in CD₂Cl₂

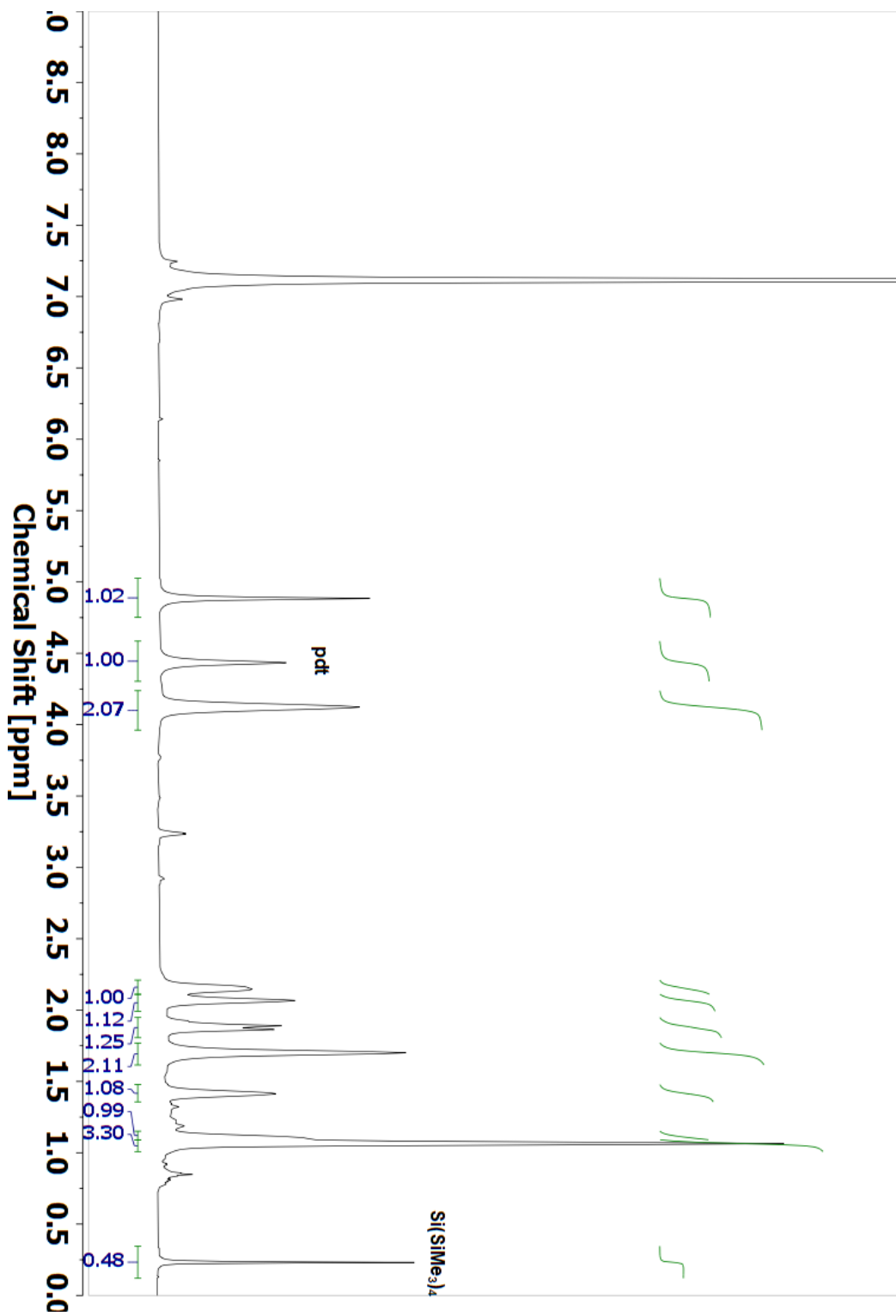


Solid-state molecular structure for methyl dimethyl 2,2'-(1,6-dioxaspiro[4.4]nonane-2,7-diylidene)(2Z,2'Z)-diacetate (39) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white, fluorine = green.

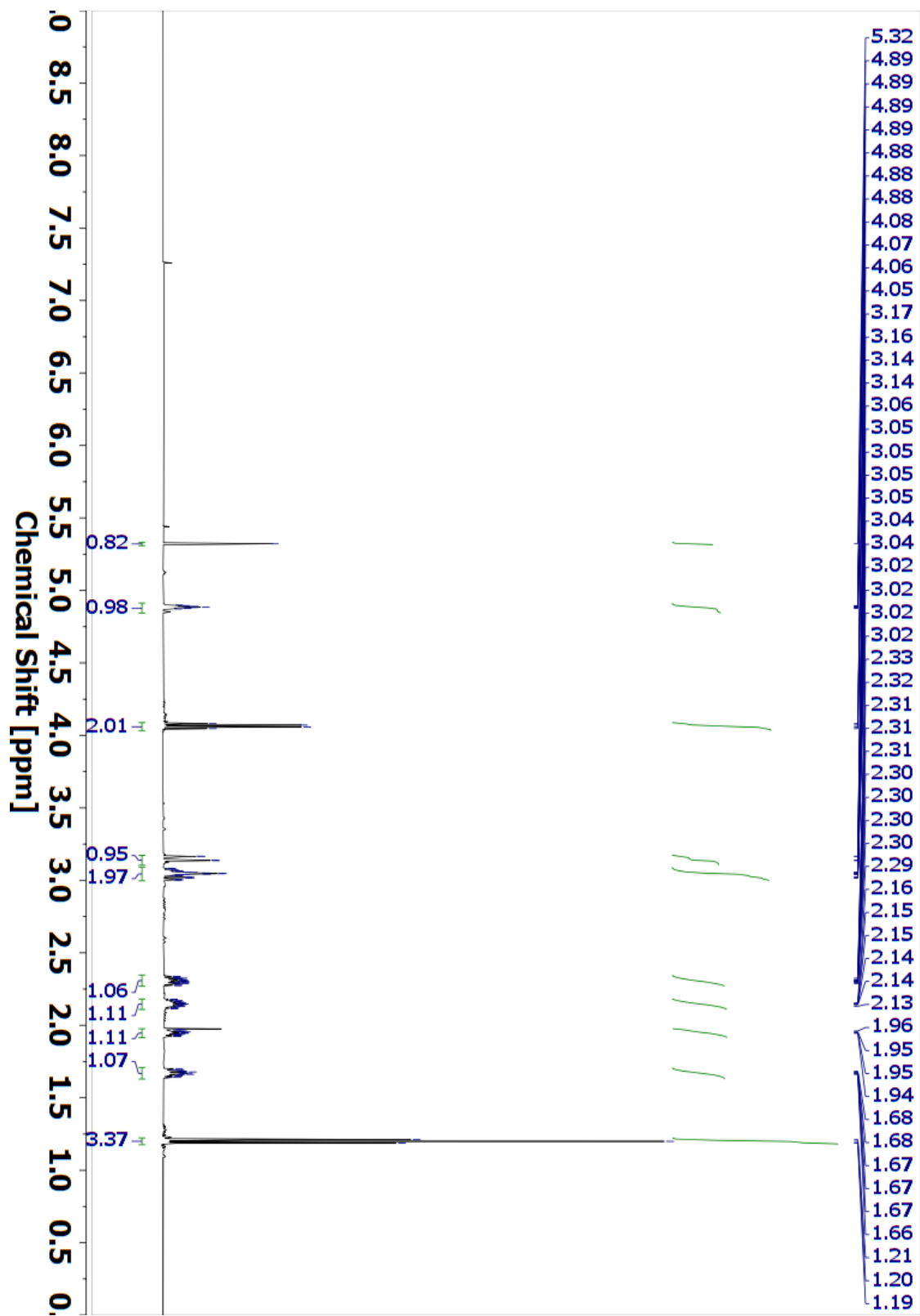
Ethyl (Z)-2-(2-oxabicyclo[3.2.0]heptan-3-ylidene)acetate (40)



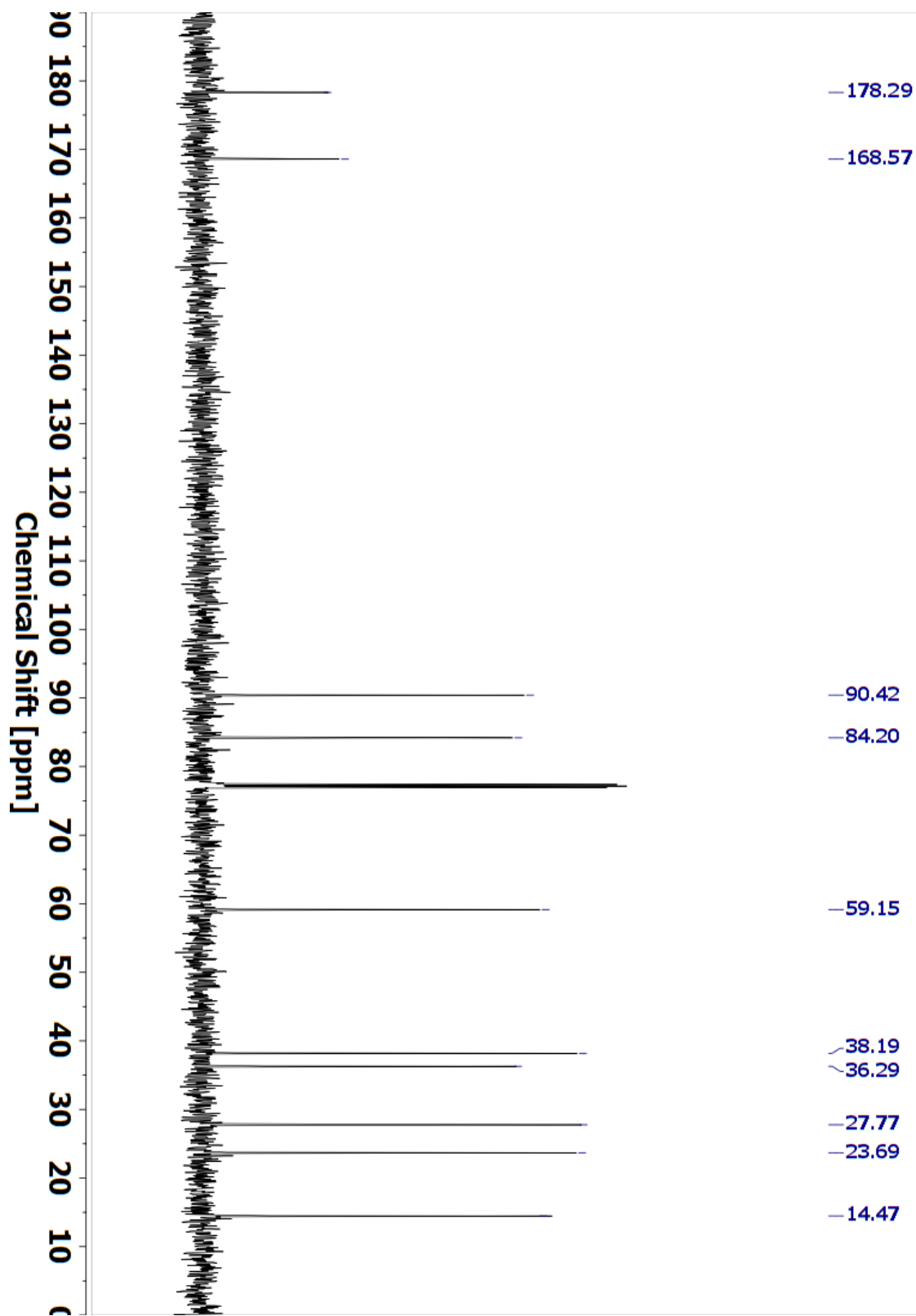
The reaction was carried out at 25 °C with 20 mol% catalyst loading following procedure C (3 h, >99% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 13.5 mg (78% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 5.32 (s, 1H), 5.01–4.73 (m, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.19–3.10 (m, 1H), 3.09–2.96 (m, 2H), 2.37–2.26 (m, 1H), 2.19–2.09 (m, 1H), 1.99–1.91 (m, 1H), 1.72–1.63 (m, 1H), 1.20 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 178.29, 168.57, 90.42, 84.20, 59.15, 38.19, 36.29, 27.77, 23.69, 14.47. HRMS (ESI $^+$) m/z Calc. 183.1016 [$\text{C}_{10}\text{H}_{14}\text{O}_3 + \text{H}$] $^+$, Found. 183.1016 [$\text{M} + \text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 3 h (0.5 mg $\text{Si}(\text{SiMe}_3)_4$ as internal standard).

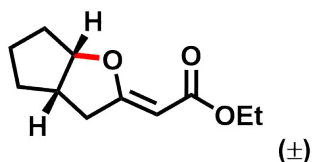


^1H NMR spectrum of isolated product in CDCl_3



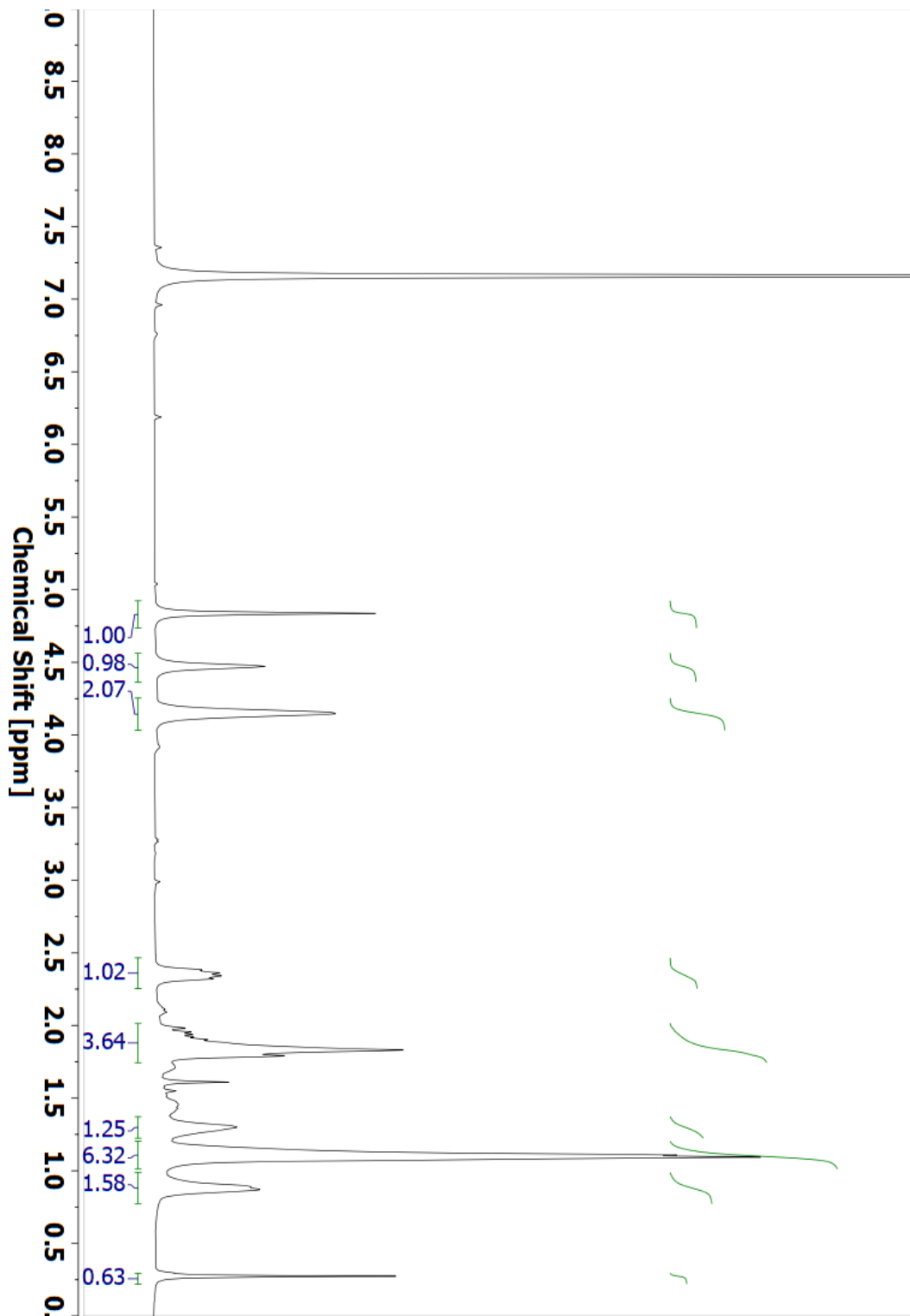
^{13}C NMR spectrum of isolated product in CDCl_3

Ethyl (Z)-2-(hexahydro-2H-cyclopenta[b]furan-2-ylidene)acetate (41):

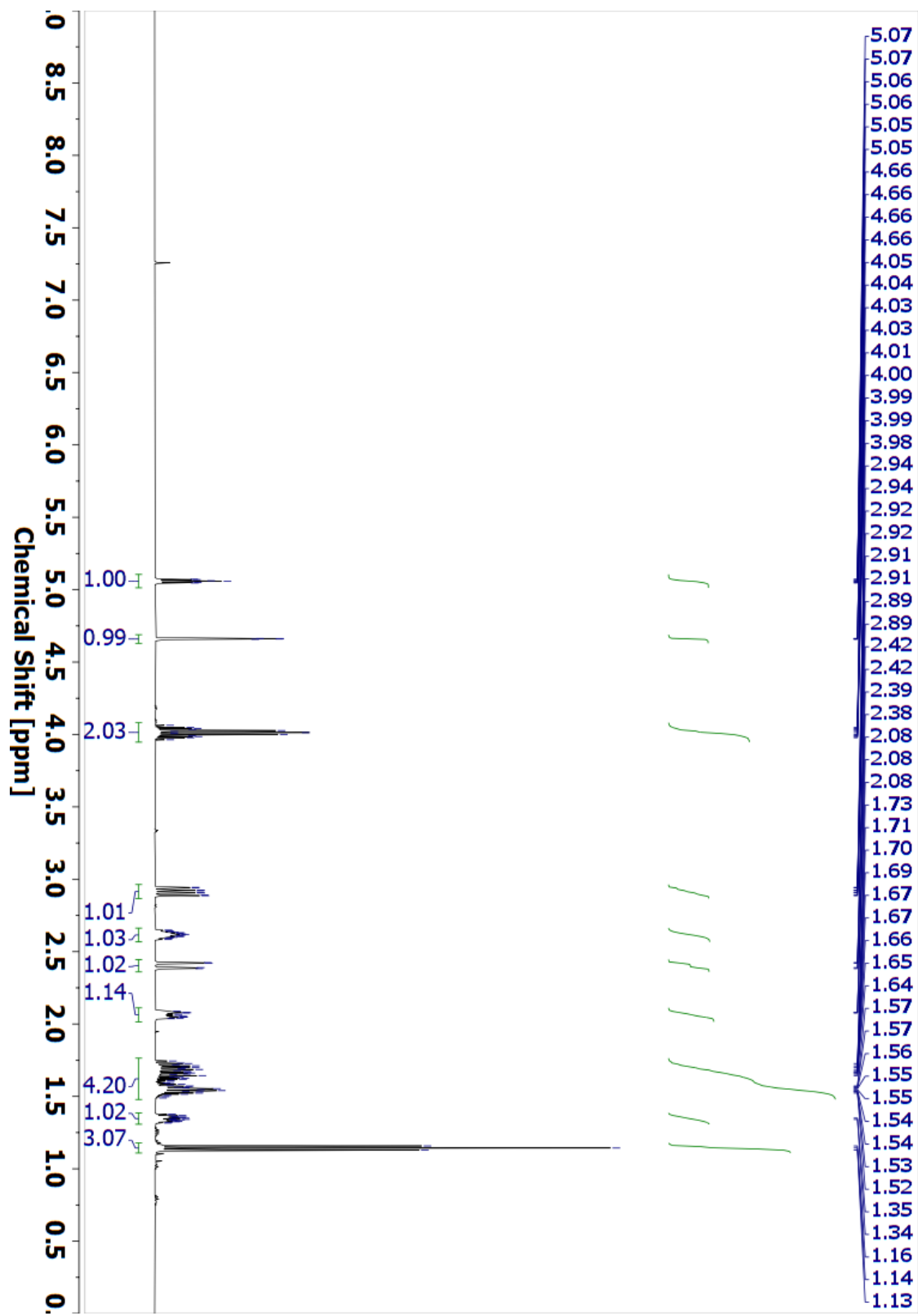


The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C (3 h, 81% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.8 mg (73% yield) of product as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 5.06 (td, $J = 6.1, 5.7, 1.4$ Hz, 1H), 4.66 (dd, $J = 1.7, 1.0$ Hz, 1H), 4.09–3.94 (m, 2H), 2.92 (ddd, $J = 17.4, 9.4, 1.7$ Hz, 1H), 2.68–2.56 (m, 1H), 2.40 (dd, $J = 17.4, 2.8$ Hz, 1H), 2.10–2.02 (m, 1H), 1.76–1.48 (m, 4H), 1.39–1.31 (m, 1H), 1.14 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.75, 165.81, 93.39, 86.95, 58.81, 39.77, 39.09, 33.70, 32.61, 23.79, 14.33. HRMS (ESI $^+$) m/z Calc. 197.1172 [$\text{C}_{11}\text{H}_{16}\text{O}_3 + \text{H}$] $^+$, Found. 197.1174 [$\text{M} + \text{H}$] $^+$.

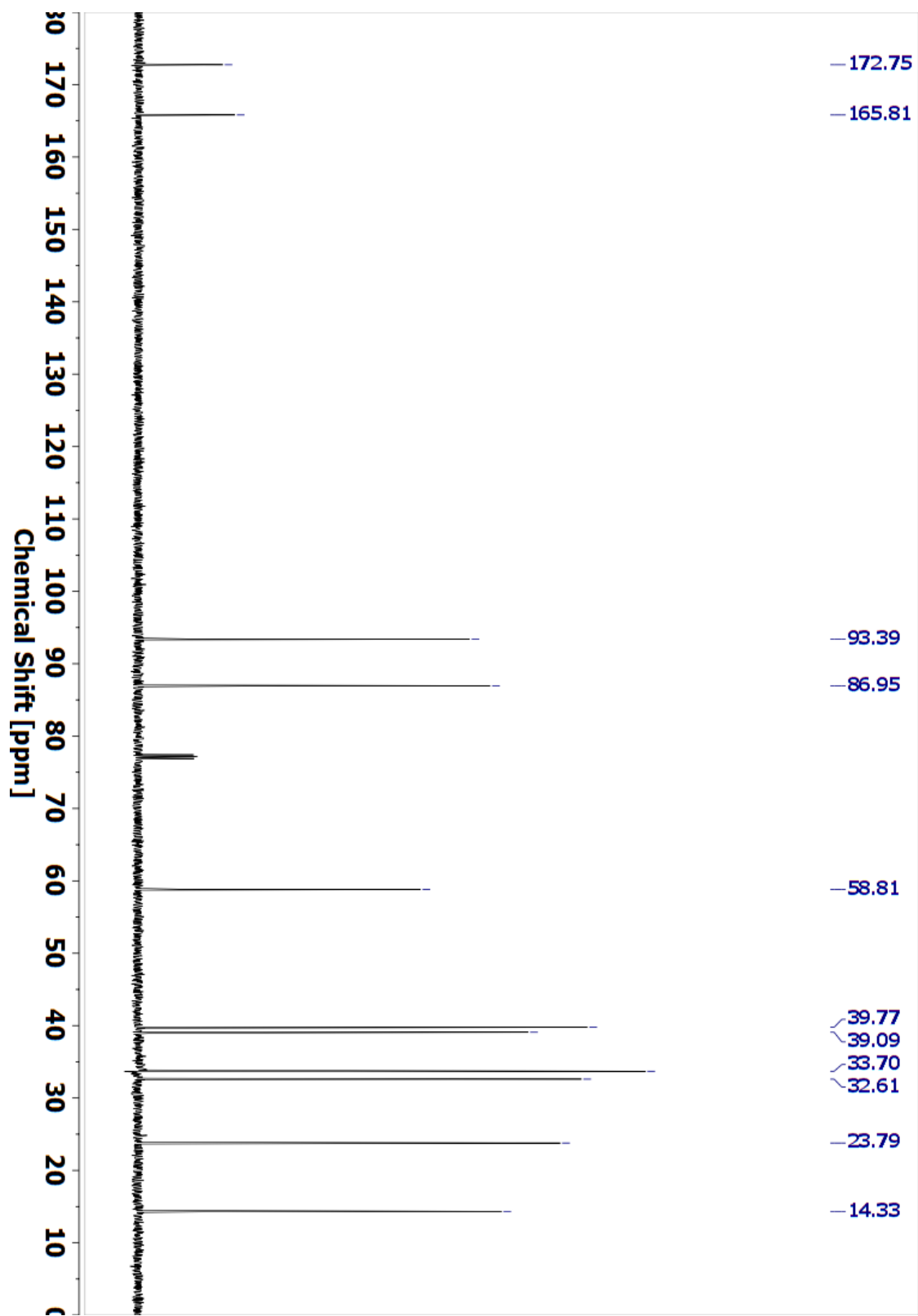
Scale-up: The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C for 3 h with 250 mg of α -diazo- β -ketoester in 25 ml of benzene to give 180 mg (82% yield) of product as a colorless oil.



Crude NMR spectrum for reaction carried out at 25 °C with 15 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

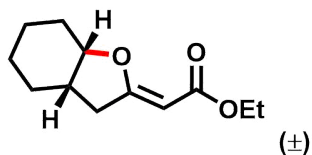


^1H NMR spectrum of isolated product in CDCl_3



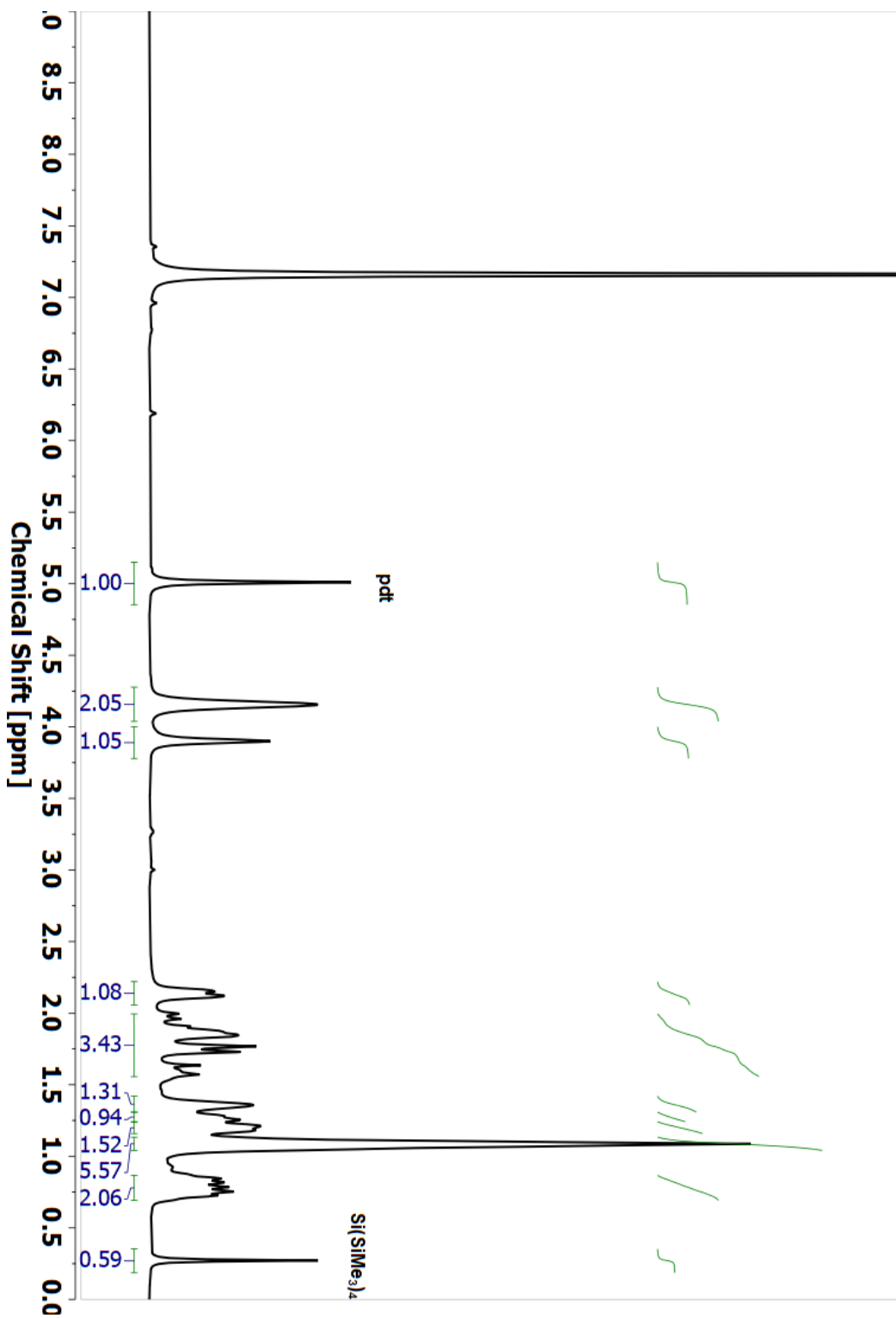
¹³C NMR spectrum of isolated product in CDCl₃

Ethyl (Z)-2-(hexahydrobenzofuran-2(3H)-ylidene)acetate (42)

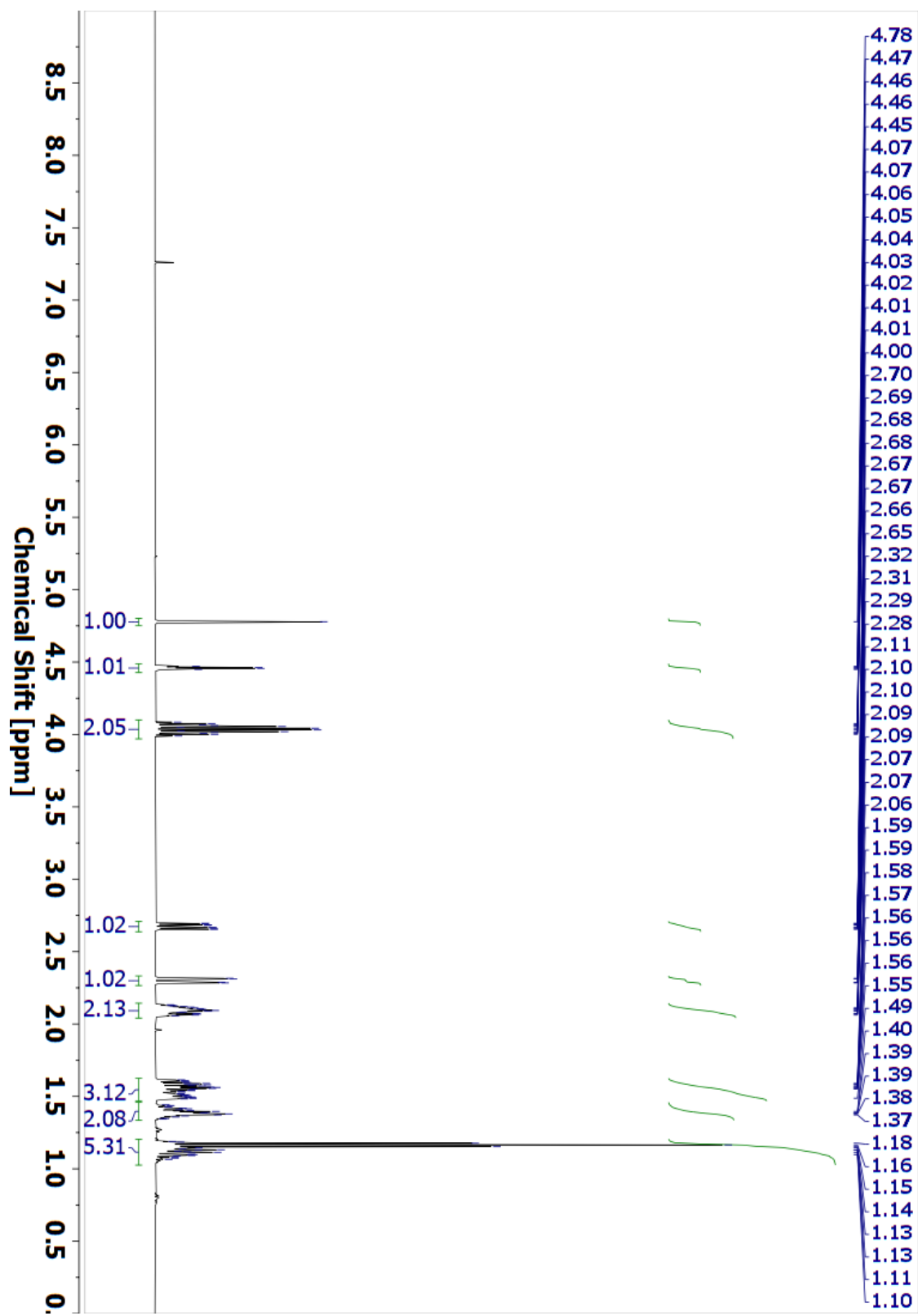


The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C (3 h, 93% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.2 mg (69% yield) of product as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 4.78 (s, 1H), 4.46 (q, $J = 4.1$ Hz, 1H), 4.10–3.97 (m, 2H), 2.67 (ddd, $J = 16.1, 6.6, 1.8$ Hz, 1H), 2.30 (dd, $J = 16.1, 2.8$ Hz, 1H), 2.15–2.04 (m, 2H), 1.63–1.46 (m, 3H), 1.45–1.33 (m, 2H), 1.24–1.02 (m, 5H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.18, 165.71, 88.79, 83.83, 58.88, 39.68, 34.74, 27.54, 26.37, 22.91, 20.05, 14.36. HRMS (ESI $^+$) m/z Calc. 211.1329 [$\text{C}_{12}\text{H}_{18}\text{O}_3+\text{H}$] $^+$, Found. 211.1330 [$\text{M}+\text{H}$] $^+$.

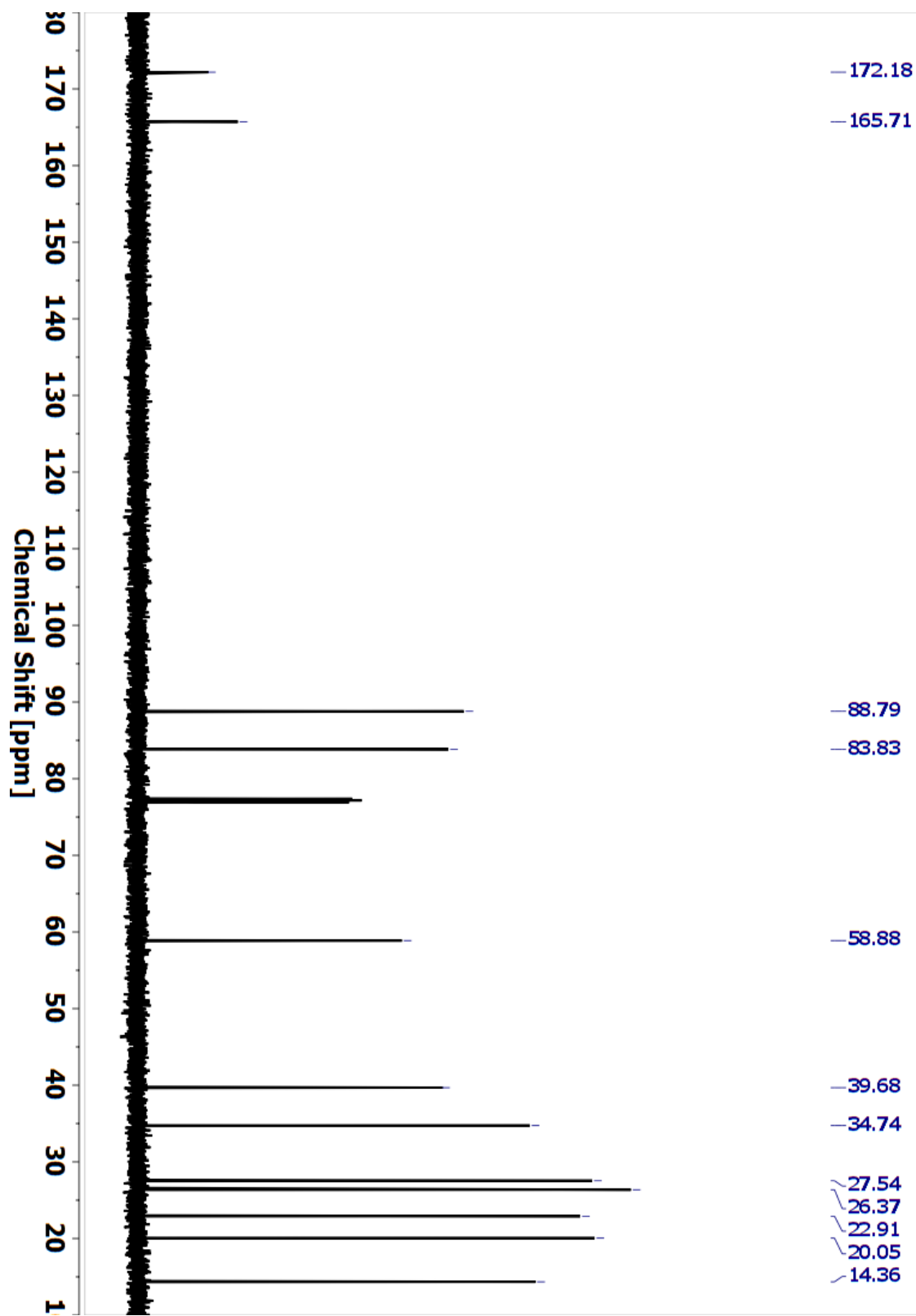
Scale-up: The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C for 3 h with 250 mg of α -diazo- β -ketoester in 25 ml of benzene to give 186 mg (84% yield) of product as a colorless oil.



Crude NMR spectrum for reaction carried out at 25 °C with 15 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

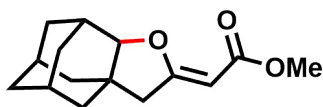


^1H NMR spectrum of isolated product in CDCl_3

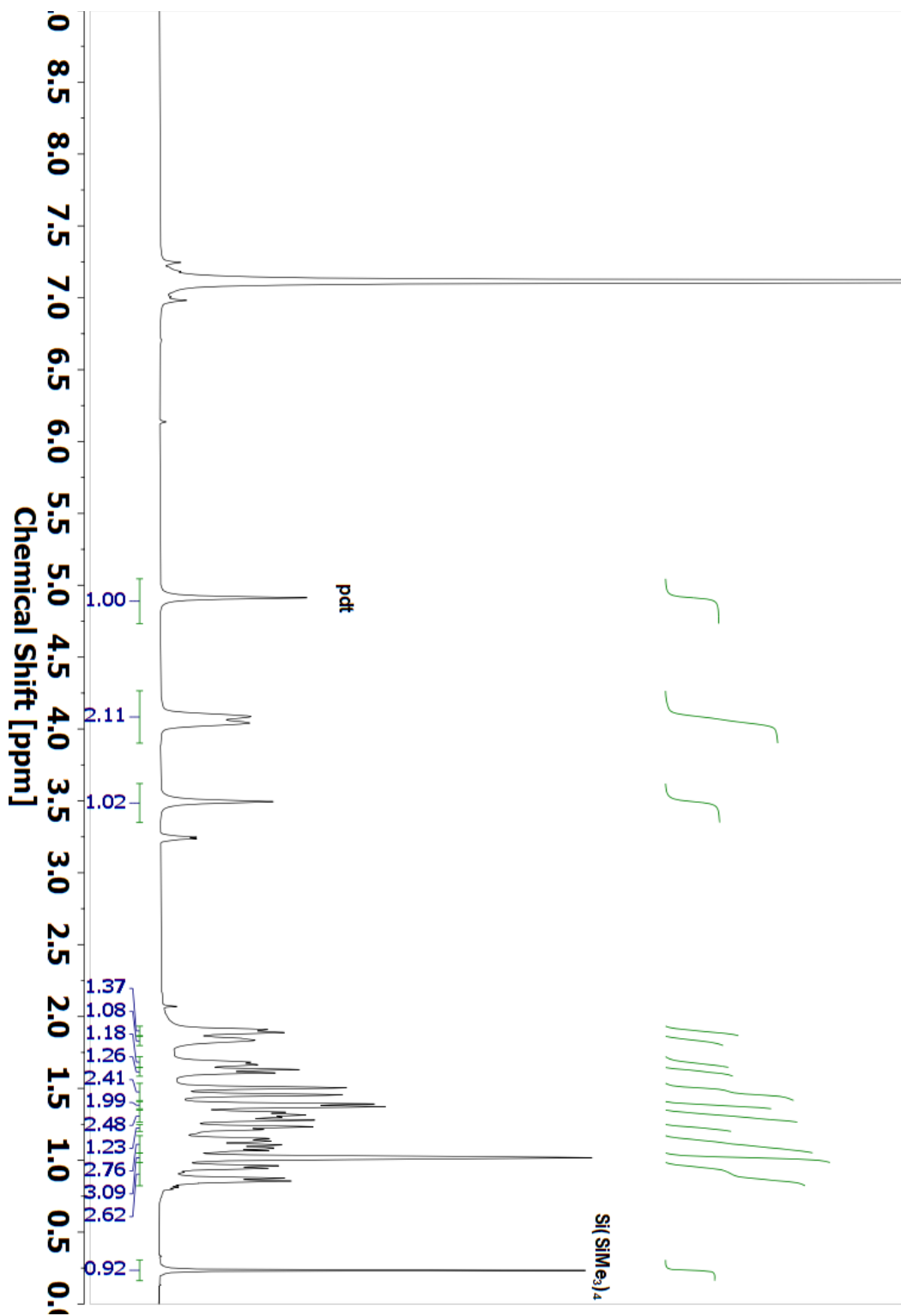


¹³C NMR spectrum of isolated product in CDCl₃

Methyl (Z)-2-((3ar,9s)-hexahydro-4H-3a,7:5,9-dimethanocycloocta[b]furan-2(3H)-ylidene)acetate (43)

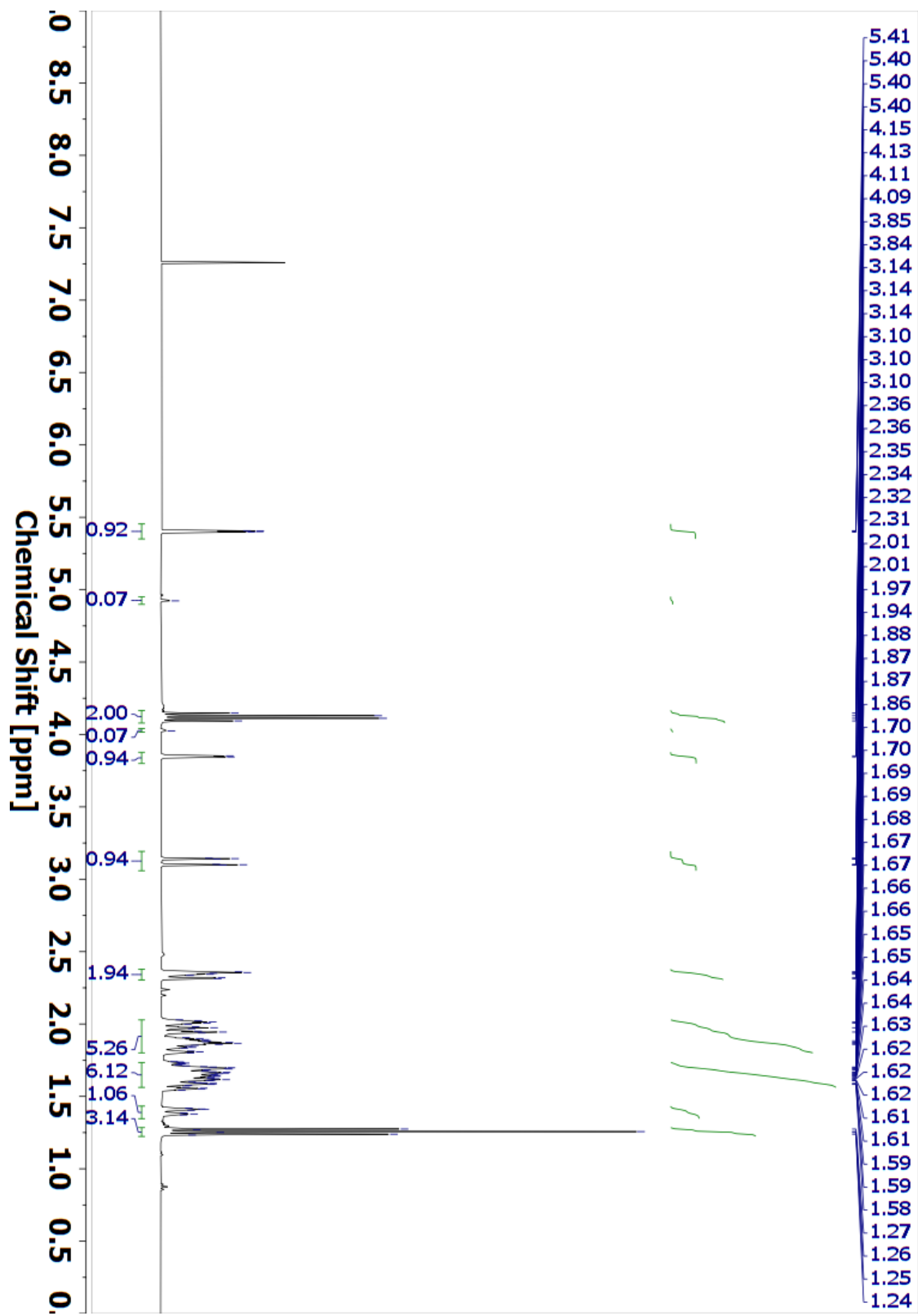


The reaction was carried out at 25 °C with 20 mol% catalyst loading following procedure C (3 h, 80% NMR yield) with 20.0 mg of σ -diazo- β -ketoester to give 12.3 mg (68% yield, 93% *Z*- : 7% *E*-isomer) of product as a crystalline white solid. Single crystal suitable for X-ray diffraction analysis is obtained by slow vapor diffusion of pentane into a concentrated CDCl₃ solution at room temperature over a week. The solid-state structure reflects the product in its *E*-form, potentially due to isomerization in polar solvent during crystallization. The olefin geometry of the bulk product upon separation using column chromatography for NMR analysis is confirmed as the *Z*-form via 2D-NOESY spectroscopy. ¹H NMR (400 MHz, CDCl₃) δ 5.40 (dd, J = 2.4, 1.1 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.85 (d, J = 3.0 Hz, 1H), 3.20–3.08 (m, 1H), 2.39–2.27 (m, 2H), 2.07–1.76 (m, 5H), 1.77–1.50 (m, 6H), 1.45–1.36 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 178.65, 171.22, 95.08, 91.48, 61.83, 46.97, 42.05, 41.05, 39.35, 38.85, 38.81, 32.87, 32.25, 31.37, 29.88, 17.11. HRMS (ESI⁺) m/z Calc. 263.1642 [C₁₆H₂₂O₃+H]⁺, Found. 263.1643 [M+H]⁺. *The Z-product is tabulated in the main manuscript to match the bulk product conformation upon isolation from column chromatography, as confirmed by 2D-NOESY NMR study.*

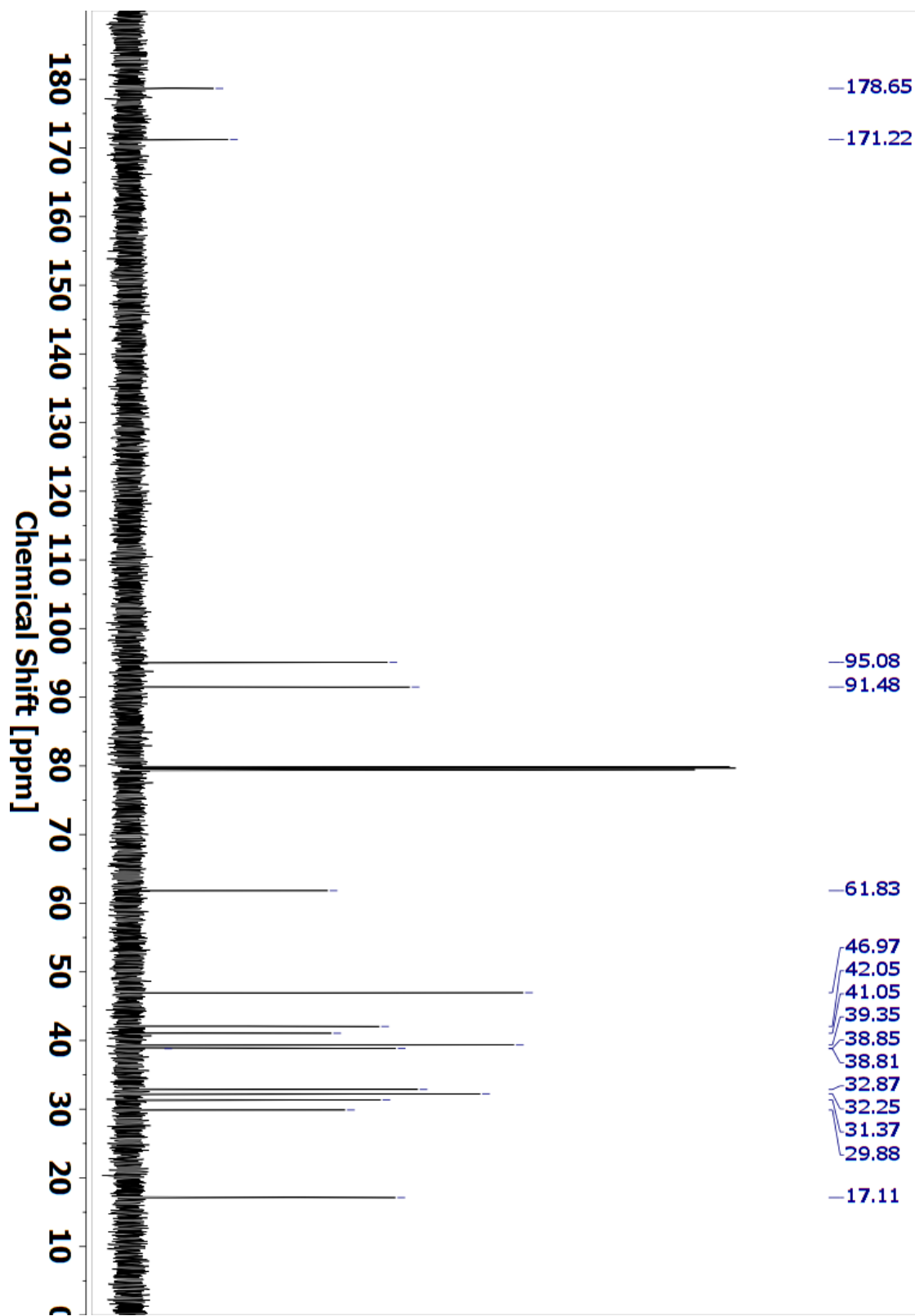


Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% $\text{Fe}(\text{acac})_2$ after 3 h (0.5 mg

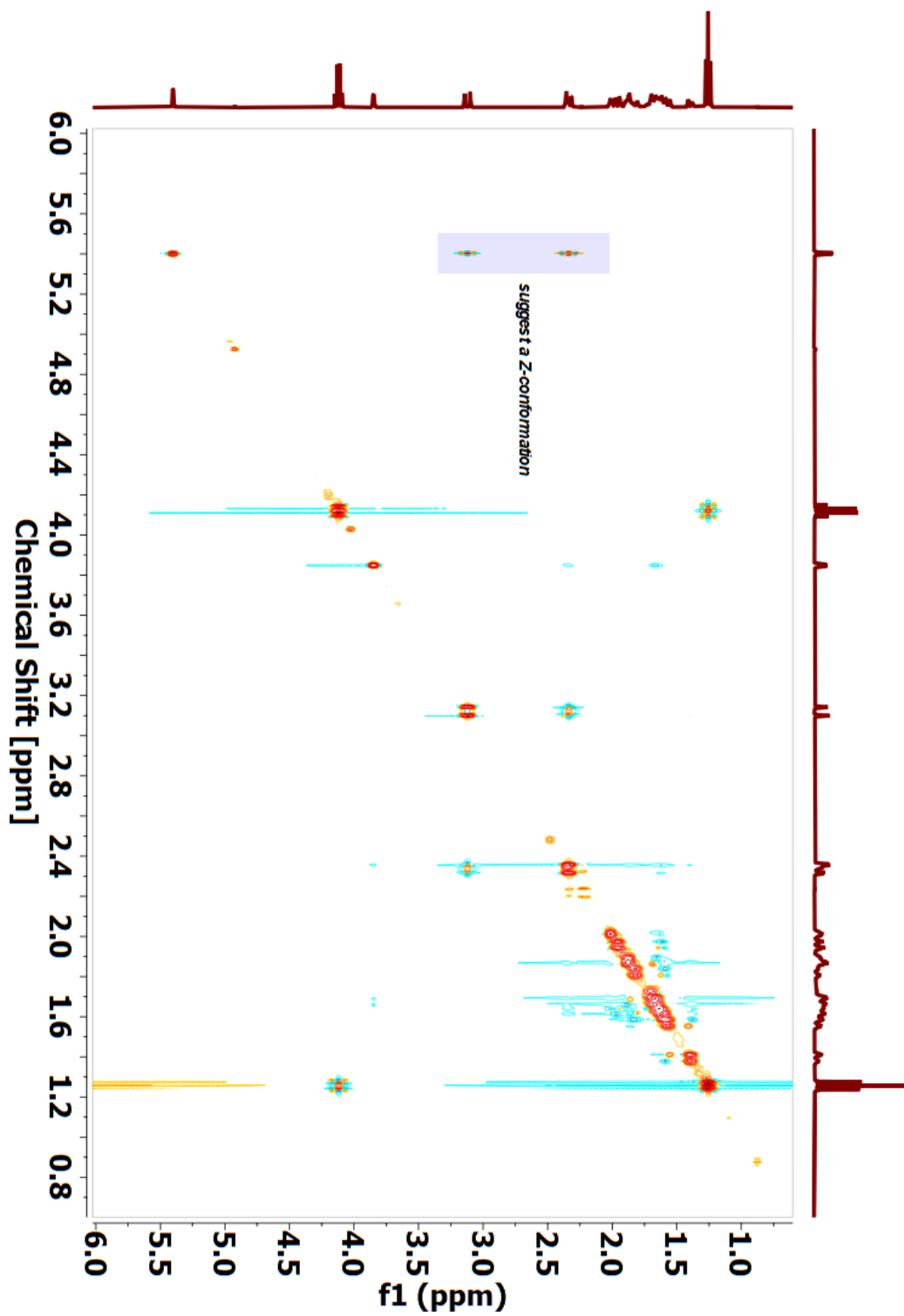
$\text{Si}(\text{SiMe}_3)_4$ as internal standard).



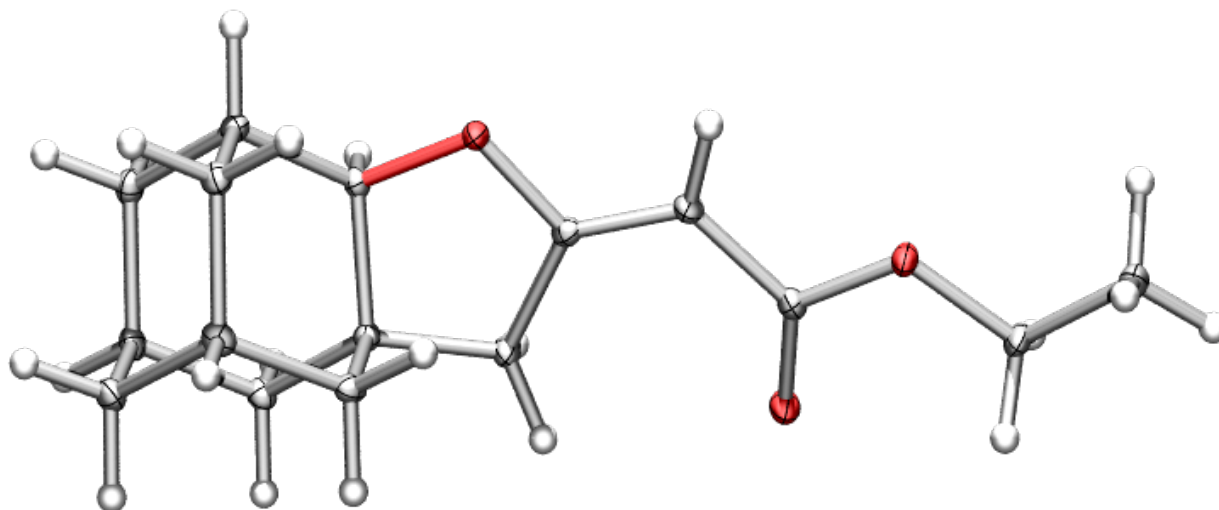
¹H NMR spectrum of isolated product in CDCl₃ (93% Z- : 7% E-isomer)



^{13}C NMR spectrum of isolated product in CDCl_3

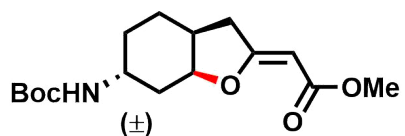


2D-NOESY spectrum of isolated product in CDCl_3 , highlighted cross peak suggests a *Z*-conformation (interaction between vinyl CH and CH_2 unit in the THF motif).

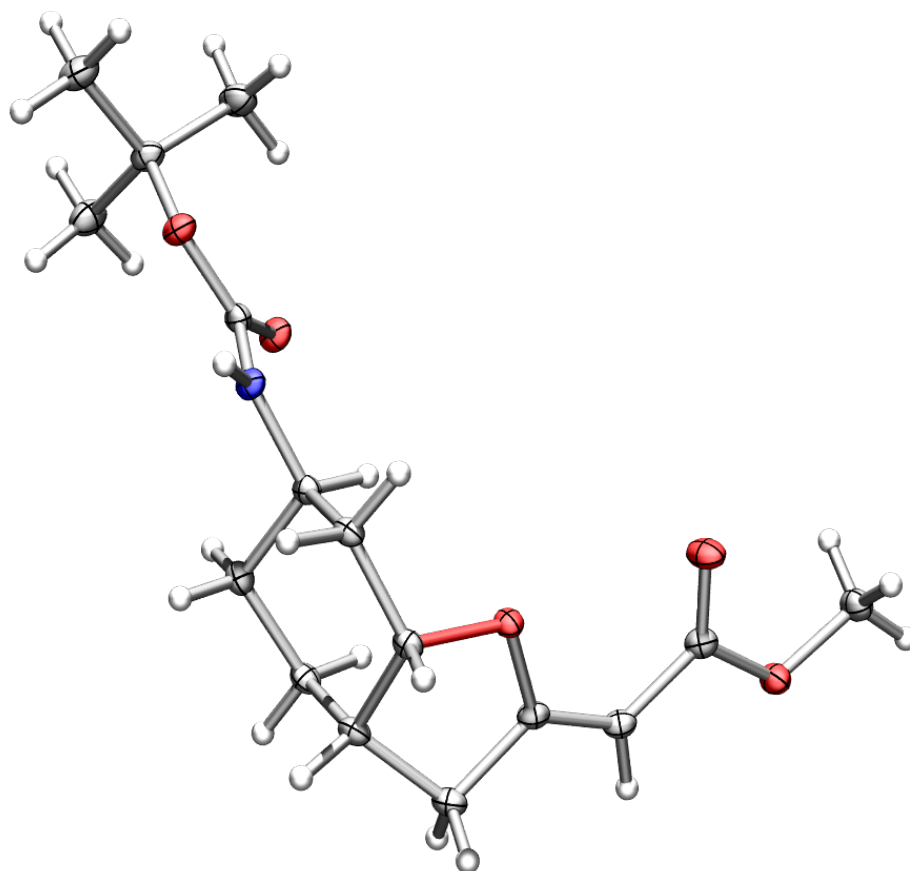


Solid-state molecular structure for methyl (E)-2-((3ar,9s)-hexahydro-4H-3a,7:5,9-dimethanocycloocta[b]furan-2(3H)-ylidene)acetate (43) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white.

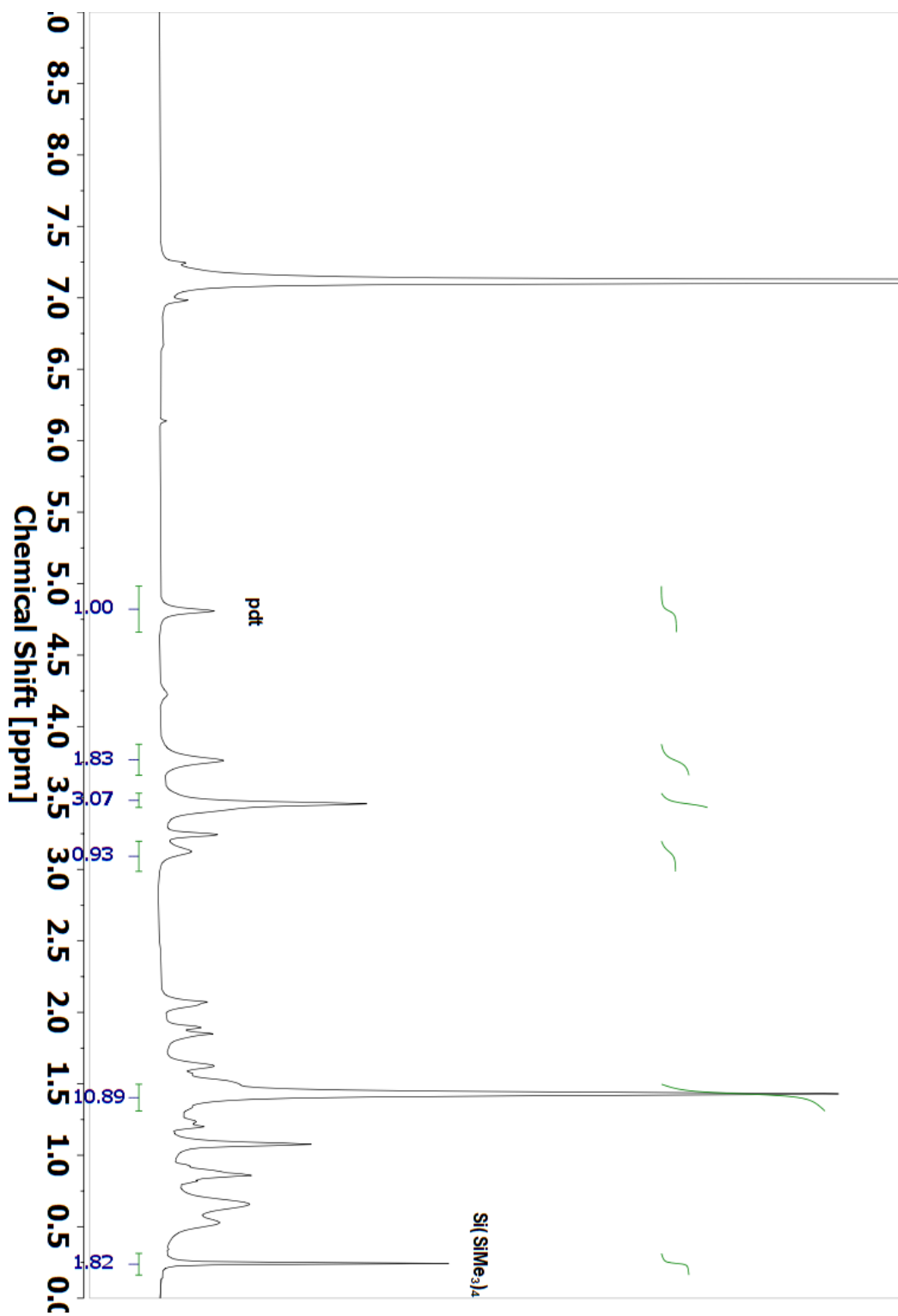
Methyl (Z)-trans-2-(6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44)



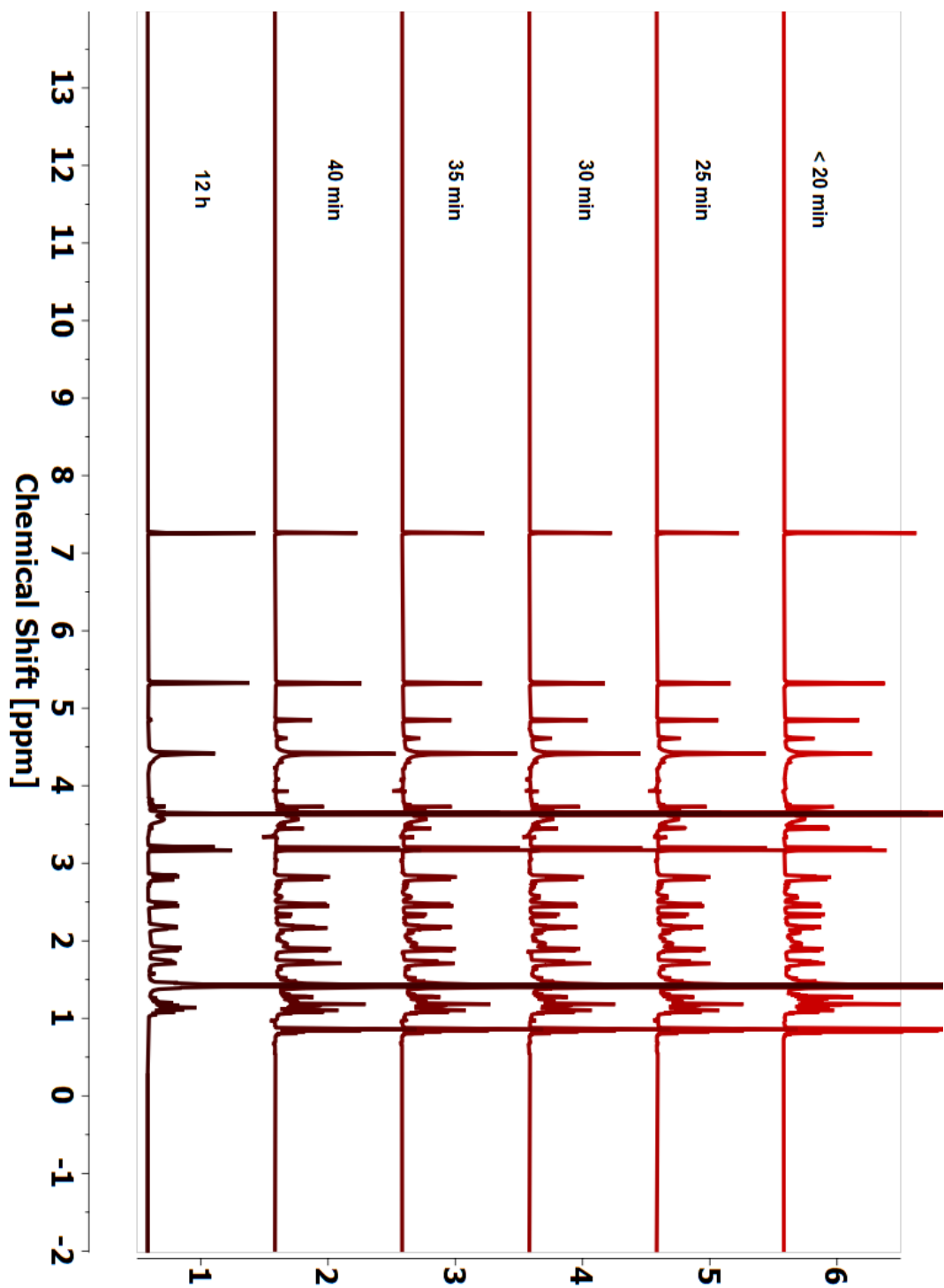
The reaction was carried out at 25 °C with 20 mol% catalyst loading following procedure C (3 h, 48% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 7.9 mg (43% yield) of product after recrystallization from boiling hexanes as a white crystalline solid suitable for single-crystal X-ray diffraction analysis. Unfortunately, despite the solid-state structure from XRD confirms the product as the kinetically stable Z-isomer, no satisfactory NMR data was obtained for the Z-product due to extremely *rapid* olefin isomerization of the product in polar solvent such as CDCl₃ at room temperature. Corresponding NMR data for the E-isomer is provided below instead. *The Z-product is tabulated in the main manuscript to match the bulk product conformation upon isolation from column chromatography, as confirmed by rapid crystallization from non-polar hexanes.*



Solid-state molecular structure for methyl (Z)-trans-2-(6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white.

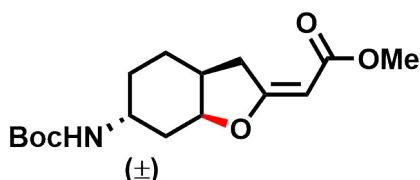


Crude NMR spectrum for reaction carried out at 25 °C with 20 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

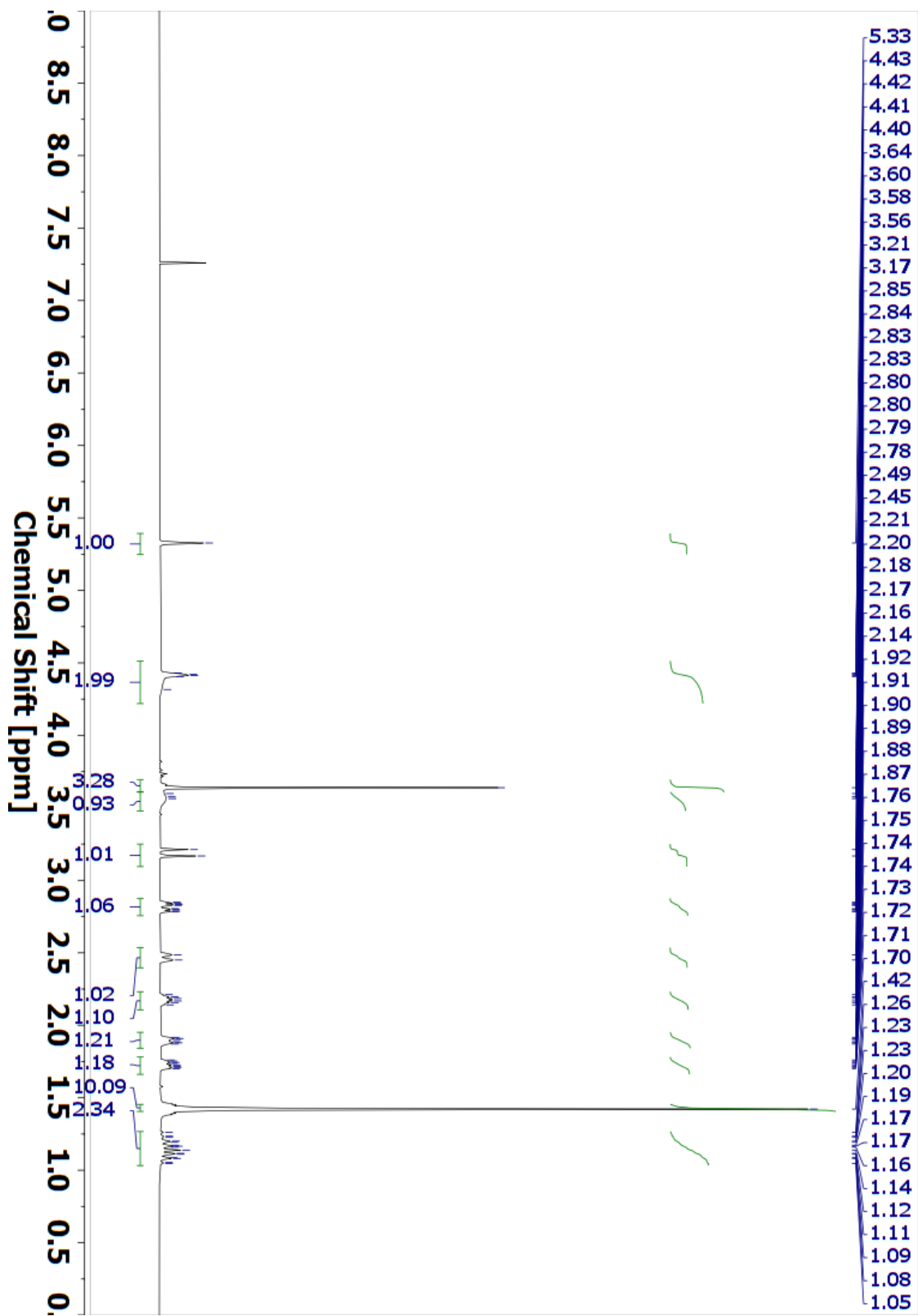


¹H NMR spectrum of isolated product in CDCl₃, showing olefin isomerization in 12 h at room temperature

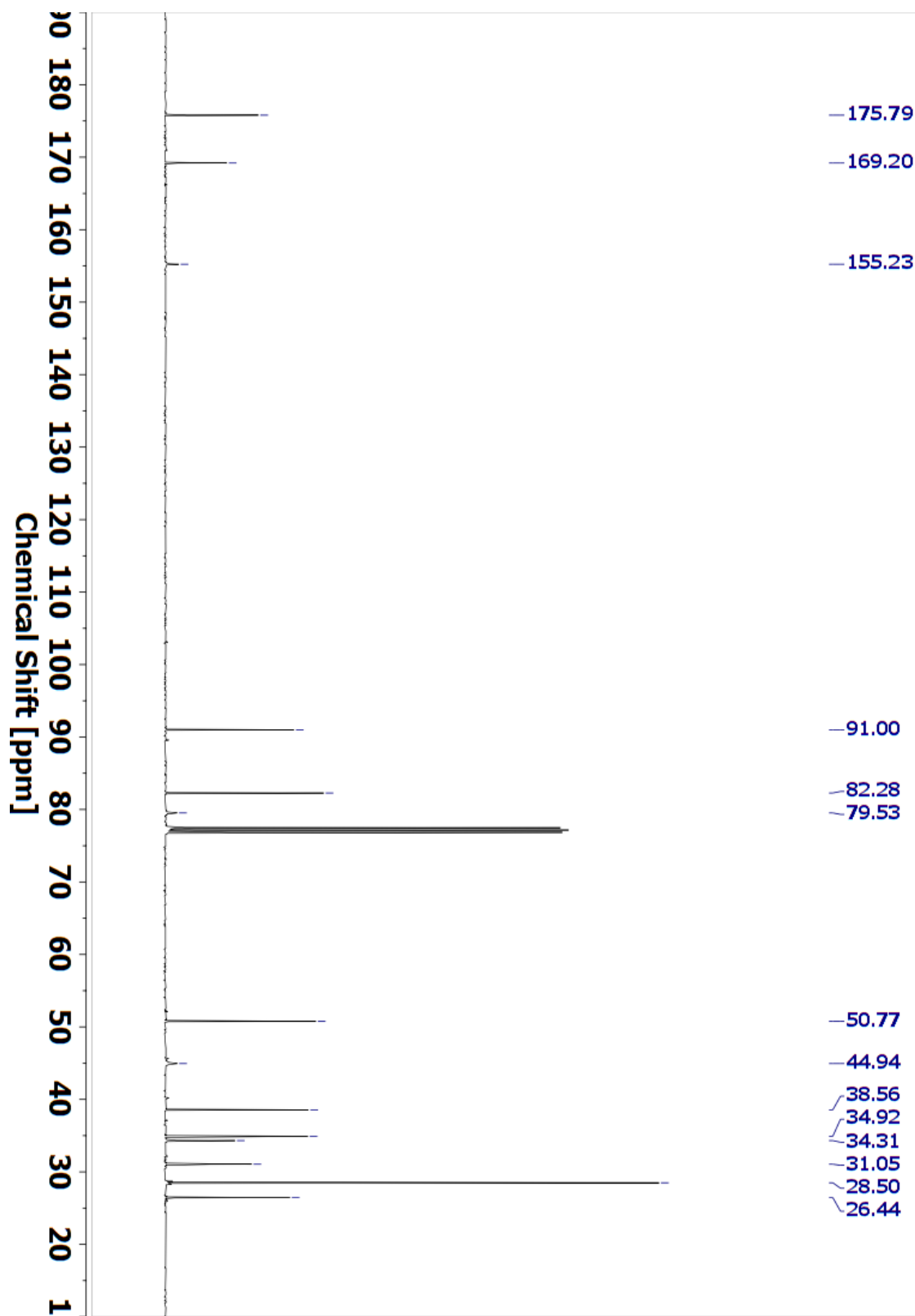
Methyl (*E*)-*trans*-2-(6-((*tert*-butoxycarbonyl)amino)hexahydrobenzofuran-2(3*H*)-ylidene)acetate (44')



Despite the stability of the product in solid state (verified by unit cell measurement) and non-polar solvents such as pentane and hexanes, quick olefin isomerization is observed upon dissolving in CDCl_3 , leading to the formation of methyl (*E*)-*trans*-2-(6-((*tert*-butoxycarbonyl)amino)hexahydrobenzofuran-2(3*H*)-ylidene)acetate. ^1H NMR (400 MHz, CDCl_3) δ 5.33 (s, 1H), 4.55–4.21 (m, 2H), 3.64 (s, 3H), 3.61–3.47 (m, 1H), 3.19 (d, $J = 17.8$ Hz, 1H), 2.87–2.76 (m, 1H), 2.47 (d, $J = 14.4$ Hz, 1H), 2.23–2.12 (m, 1H), 1.94–1.85 (m, 1H), 1.78–1.68 (m, 1H), 1.52–1.30 (m, 10H), 1.28–0.99 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.79, 169.20, 155.23, 91.00, 82.28, 79.53, 50.77, 44.94, 38.56, 34.92, 34.31, 31.05, 28.50, 26.44. HRMS (ESI $^+$) m/z Calc. 312.1805 $[\text{C}_{16}\text{H}_{25}\text{NO}_5 + \text{H}]^+$, Found. 312.1807 $[\text{M} + \text{H}]^+$.

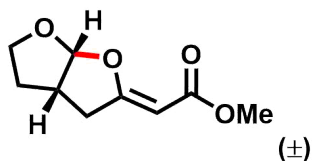


^1H NMR spectrum of isolated product in CDCl_3

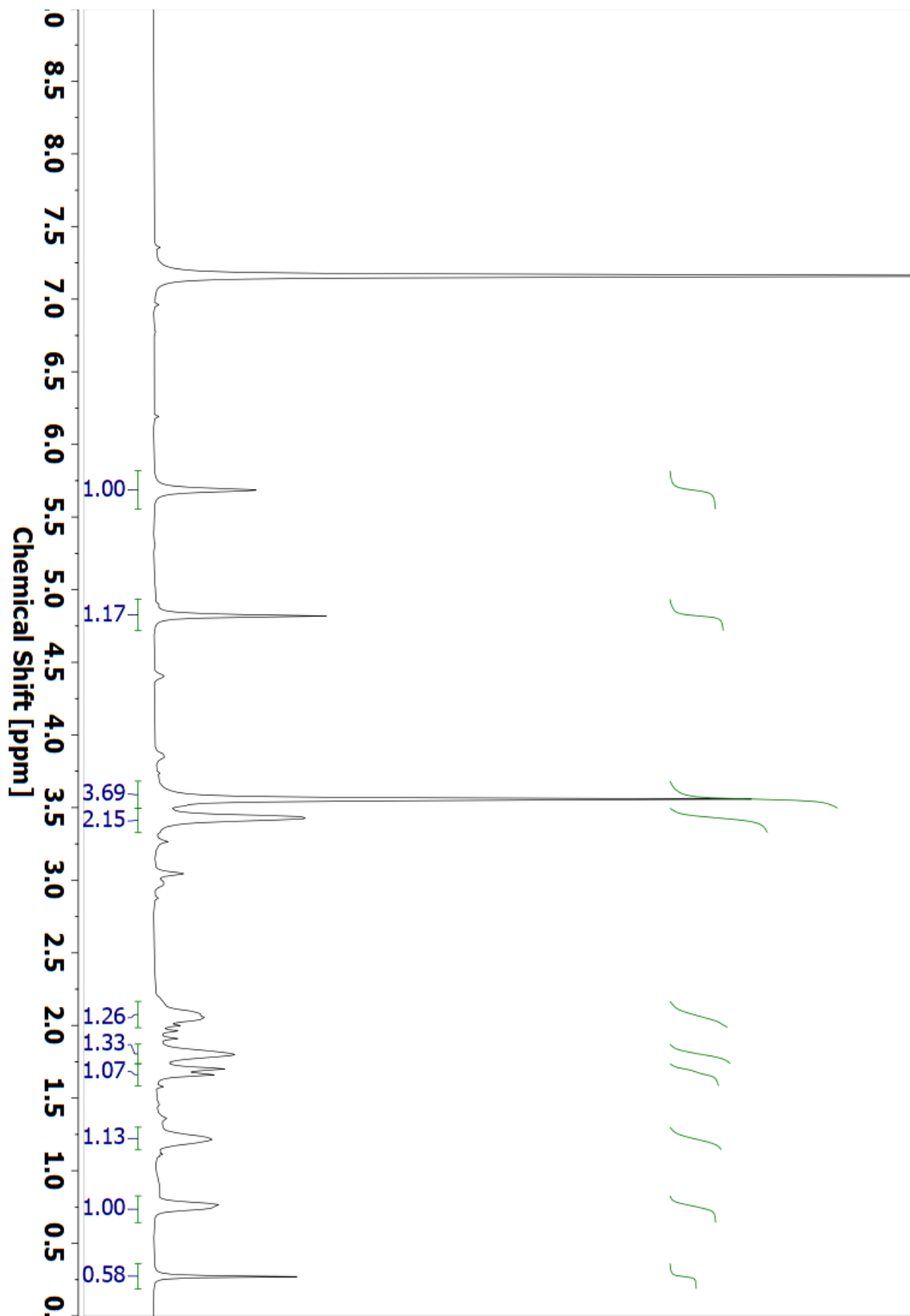


^{13}C NMR spectrum of isolated product in CDCl_3

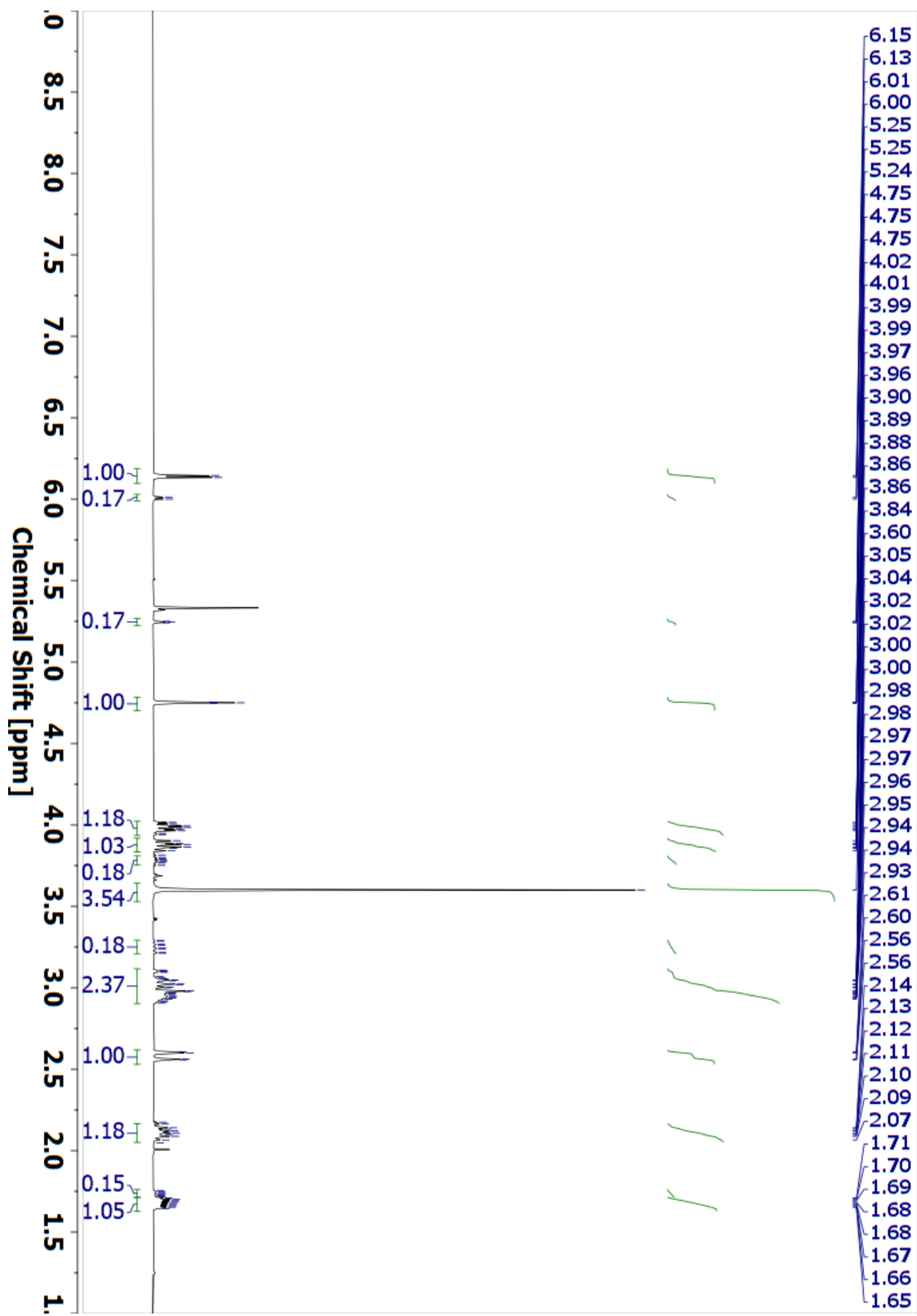
Methyl (Z)-2-(tetrahydrofuro[2,3-b]furan-2(3H)-ylidene)acetate (45)



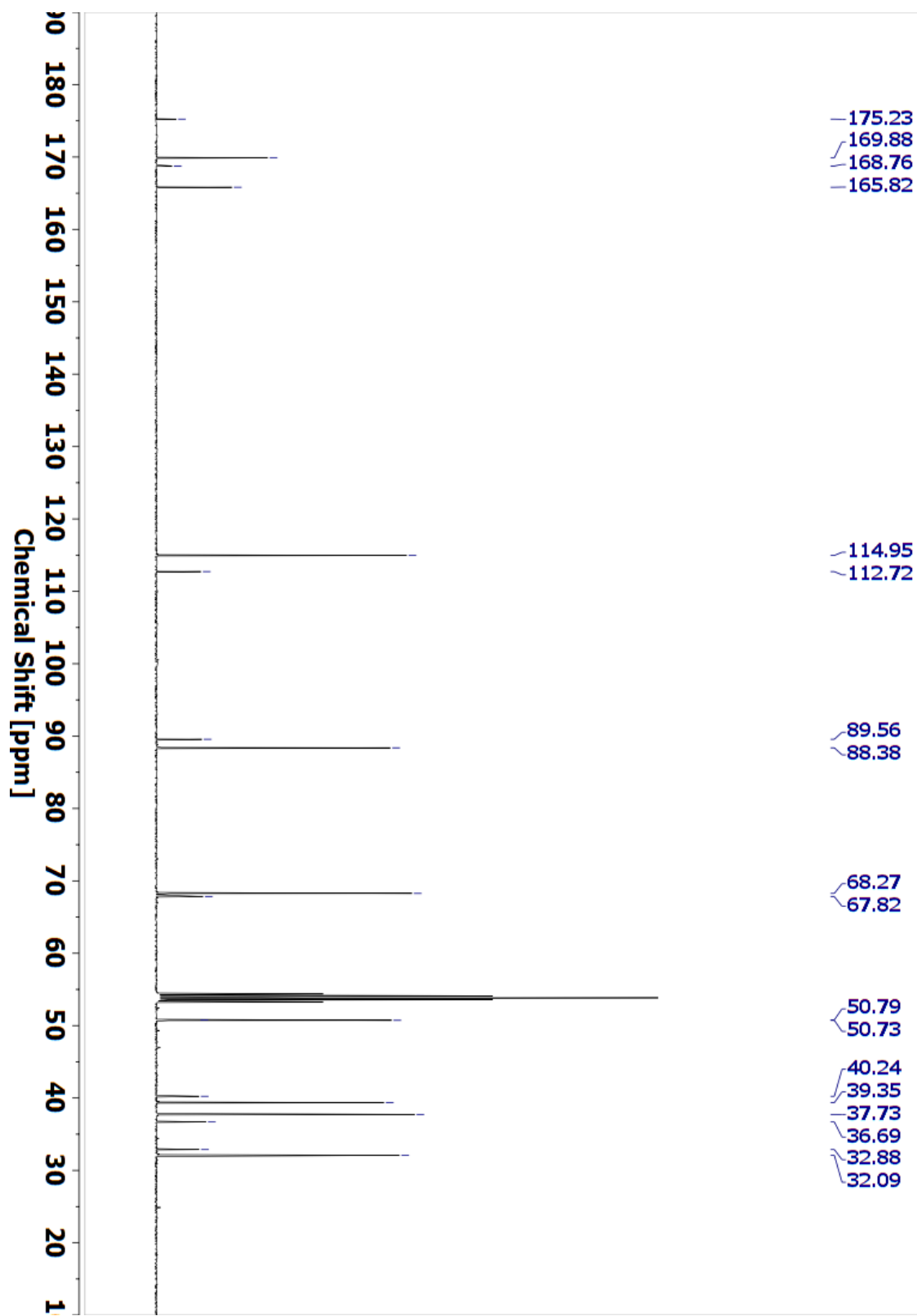
The reaction was carried out at 25 °C with 15 mol% catalyst loading following procedure C (3 h, 89% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 9.9 mg (73% yield, 85% Z- : 15% E-isomer) of product as a colorless oil. Z-isomer: ^1H NMR (400 MHz, CD_2Cl_2) δ 6.14 (d, $J = 4.8$ Hz, 1H), 4.75 (t, $J = 1.3$ Hz, 1H), 4.03–3.95 (m, 1H), 3.91–3.83 (m, 1H), 3.60 (s, 3H), 3.08–2.89 (m, 2H), 2.58 (dd, $J = 17.3, 1.9$ Hz, 1H), 2.20–2.04 (m, 1H), 1.77–1.62 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.88, 165.82, 114.95, 88.38, 68.27, 50.73, 39.35, 37.73, 32.09. E-isomer: ^1H NMR (400 MHz, CD_2Cl_2) δ 6.01 (d, $J = 5.0$ Hz, 1H), 5.25 (t, $J = 1.8$ Hz, 1H), 4.03–3.94 (m, 1H), 3.82–3.74 (m, 1H), 3.60 (s, 3H), 3.31–3.20 (m, 1H), 3.12–2.89 (m, 2H), 2.17–2.05 (m, 1H), 1.77–1.70 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 175.23, 168.76, 112.72, 89.56, 67.82, 50.79, 40.24, 36.69, 32.88. HRMS (ESI $^+$) m/z Calc. 185.0808 [$\text{C}_9\text{H}_{12}\text{O}_4+\text{H}$] $^+$, Found. 185.0810 [$\text{M}+\text{H}$] $^+$.



Crude NMR spectrum for reaction carried out at 25 °C with 15 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).

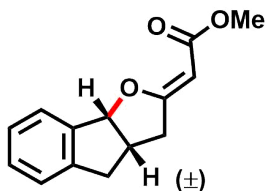


^1H NMR spectrum of isolated product in CD_2Cl_2 (85% *Z*- : 15% *E*-isomer)

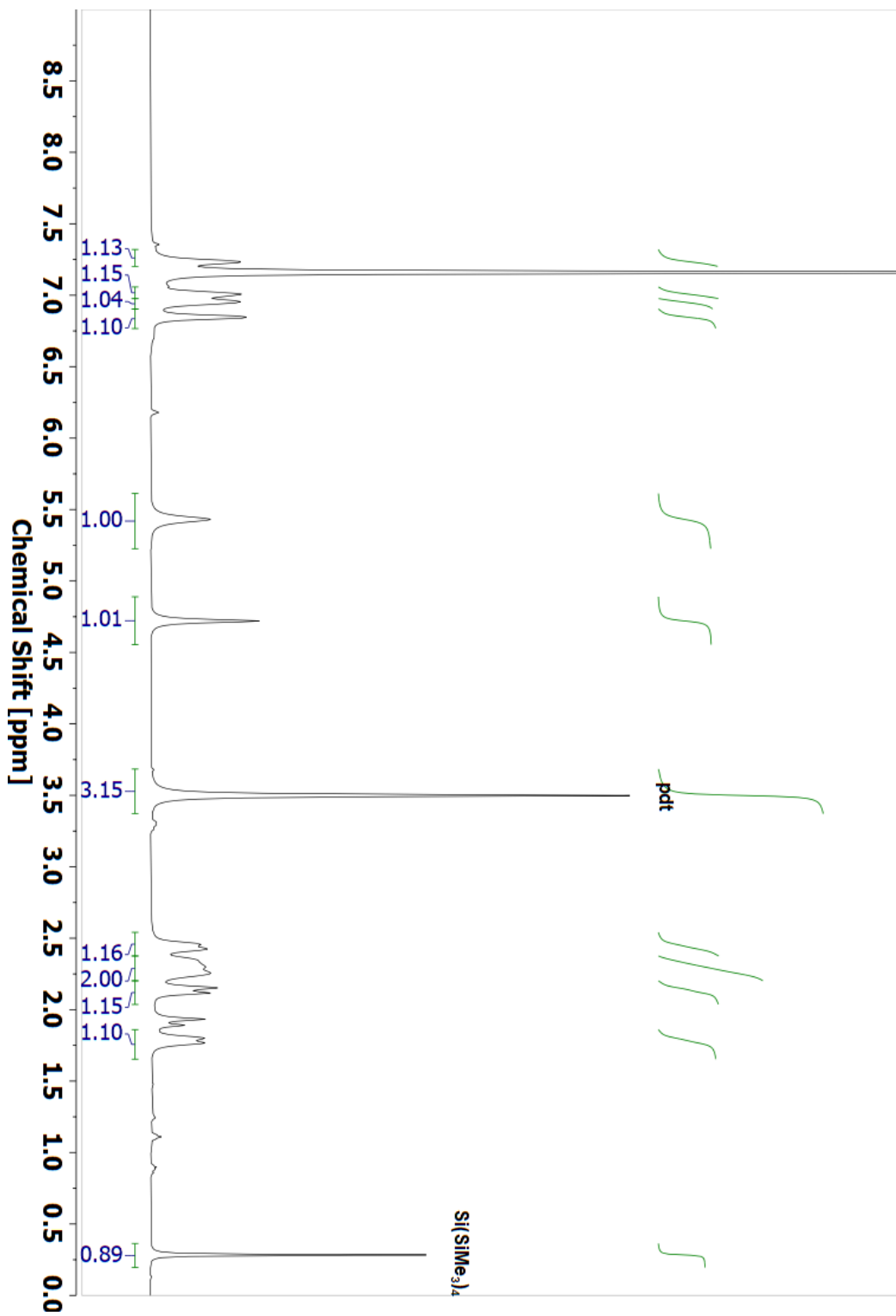


^{13}C NMR spectrum of isolated product in CD_2Cl_2

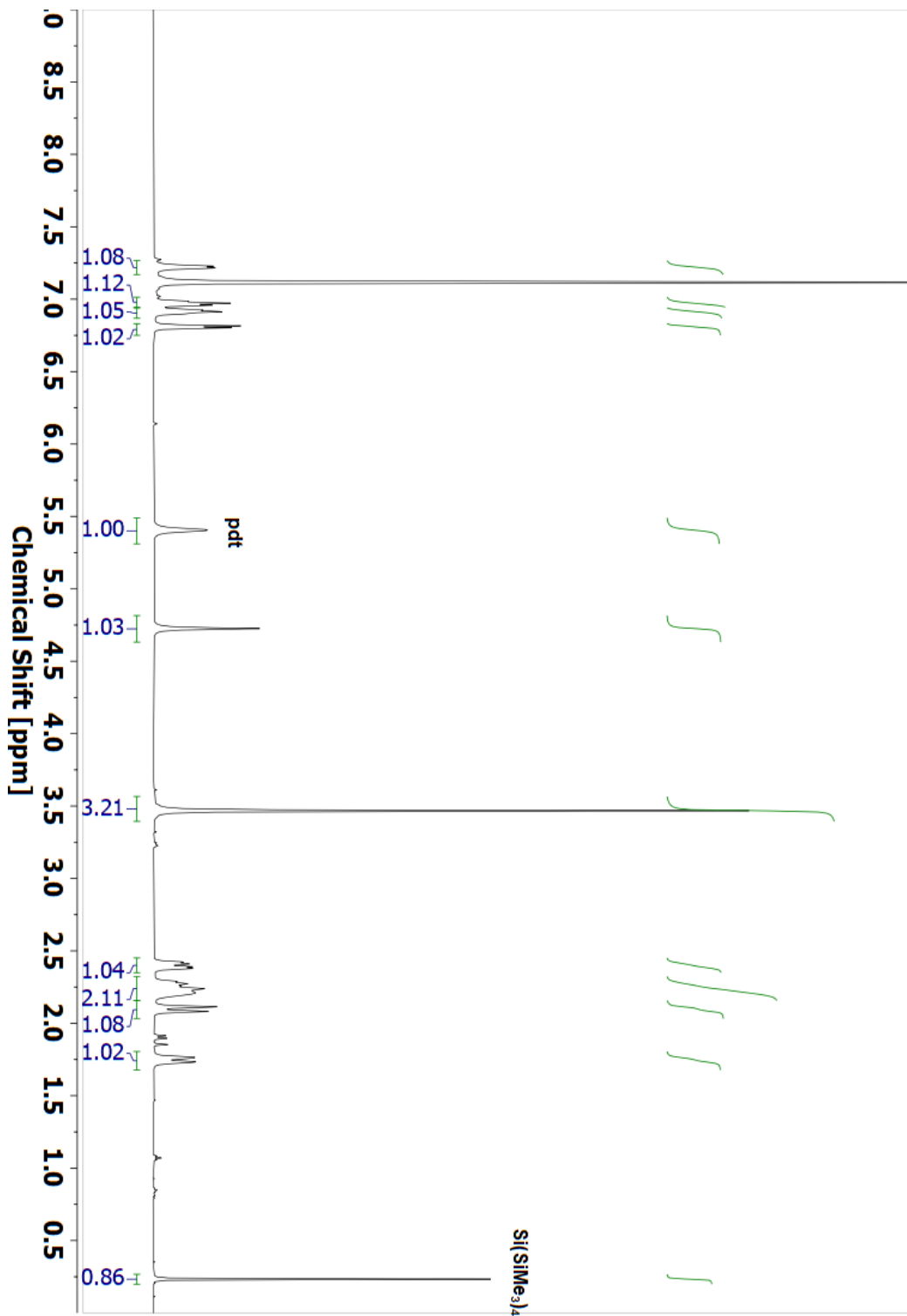
Methyl (Z)-2-(3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan-2-ylidene)acetate (46)



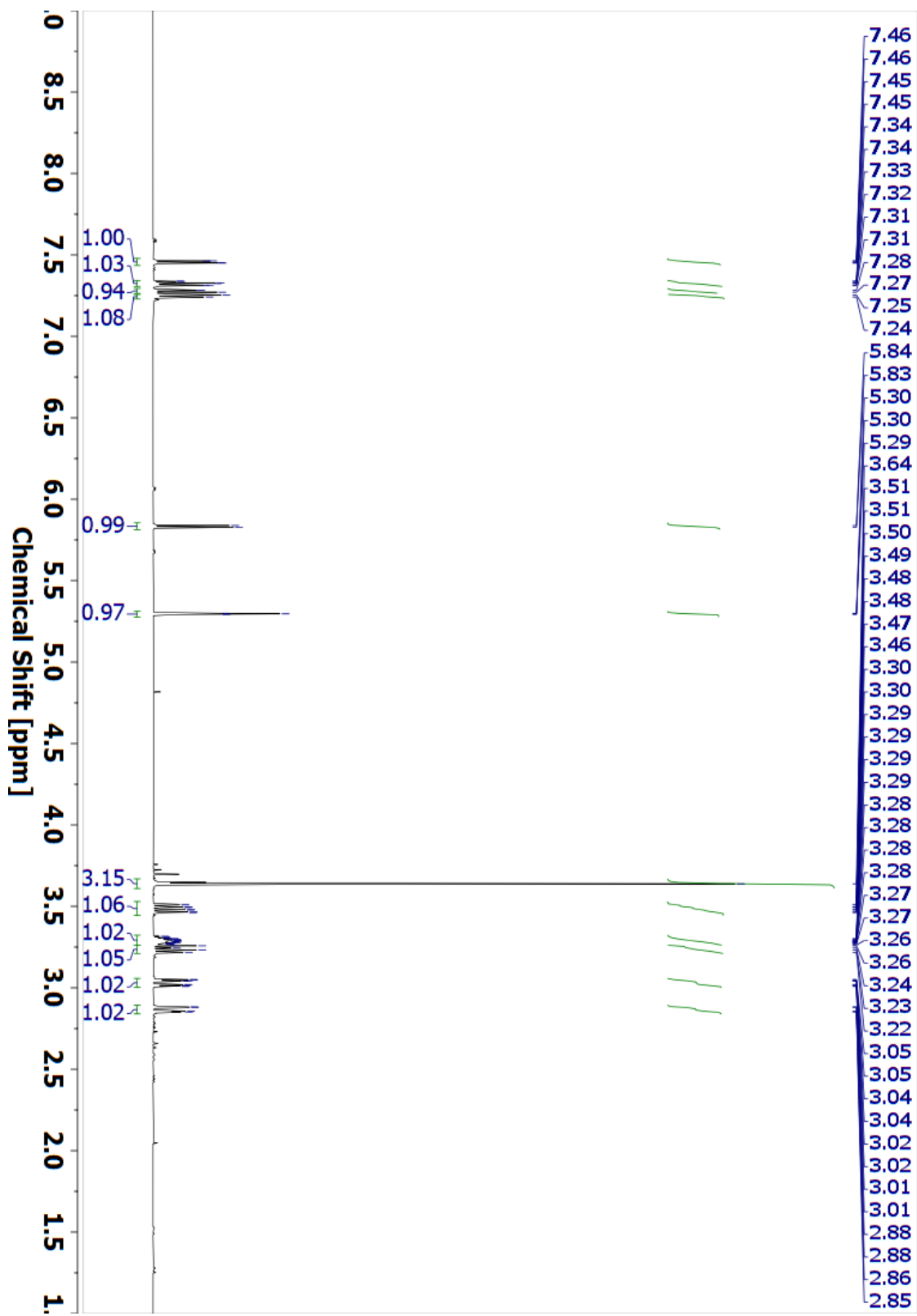
The reaction was carried out under two sets conditions: (1) at 25 °C with 10 mol% catalyst loading following procedure C (3 h, 73% NMR yield) and (2) at 60 °C with 10 mol% catalyst loading following procedure D (20 min, 75% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 12.5 mg (70% yield) of product as white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.46 (dd, $J = 7.4$, 1.2 Hz, 1H), 7.33 (td, $J = 7.4$, 1.2 Hz, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 5.83 (d, $J = 6.7$ Hz, 1H), 5.30 (t, $J = 1.8$ Hz, 1H), 3.64 (s, 3H), 3.49 (ddd, $J = 18.6$, 9.4, 1.8 Hz, 1H), 3.35–3.26 (m, 1H), 3.26–3.20 (m, 1H), 3.03 (ddd, $J = 18.6$, 4.8, 1.8 Hz, 1H), 2.87 (dd, $J = 16.0$, 3.4 Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.65, 169.00, 142.85, 139.45, 129.73, 127.32, 125.94, 125.33, 91.55, 89.36, 50.62, 39.76, 37.86, 37.68. HRMS (ESI^+) m/z Calc. 231.1016 [$\text{C}_{14}\text{H}_{14}\text{O}_3+\text{H}$] $^+$, Found. 231.1016 [$\text{M}+\text{H}$] $^+$.



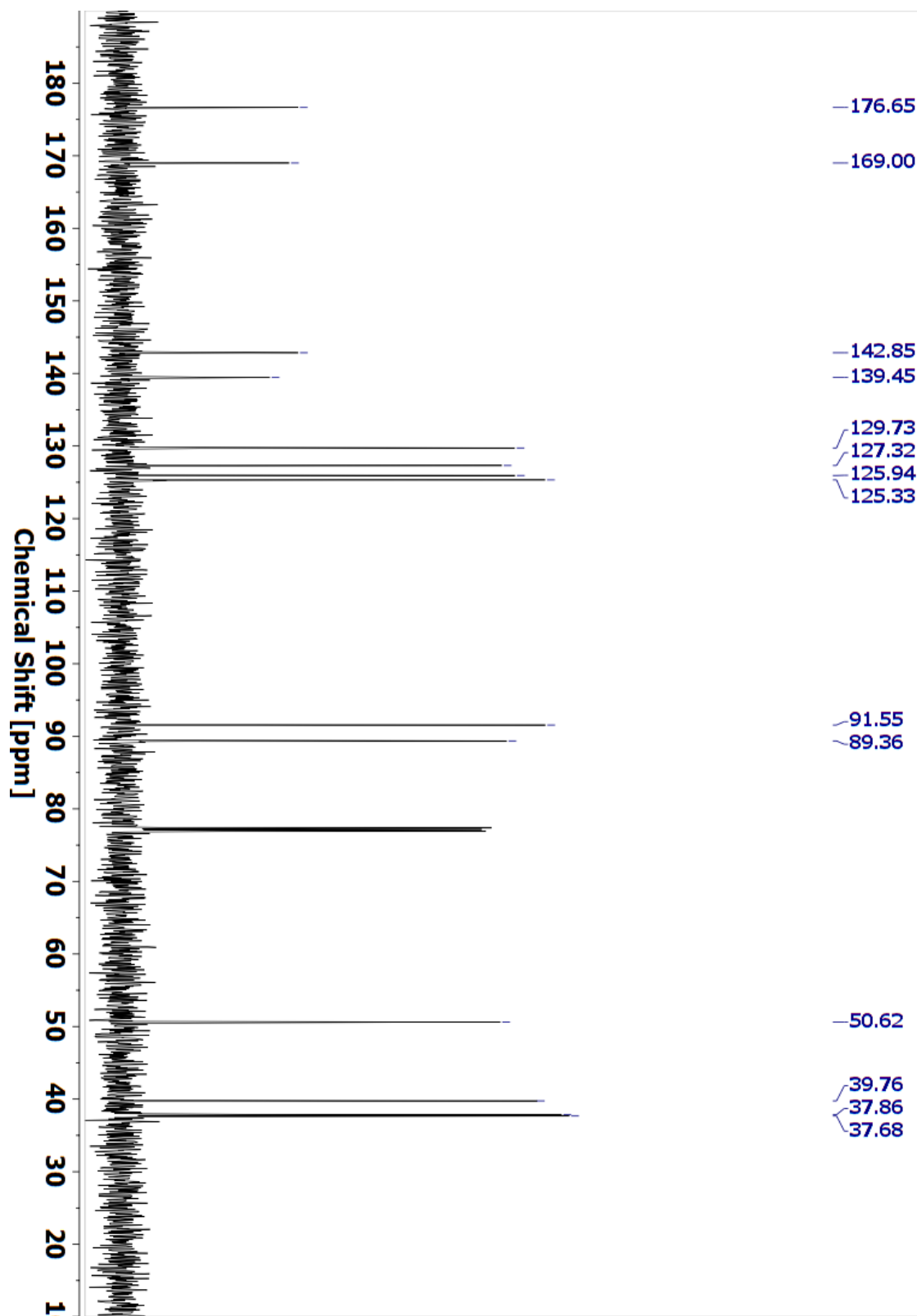
Crude NMR spectrum for reaction carried out at 25 °C with 10 mol% Fe(acac)₂ after 3 h (0.5 mg Si(SiMe₃)₄ as internal standard).



Crude NMR spectrum for reaction carried out at 60 °C with 10 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).

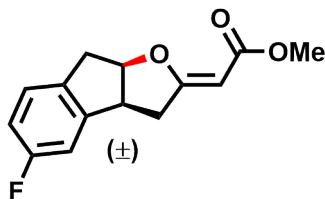


^1H NMR spectrum of isolated product in CDCl_3

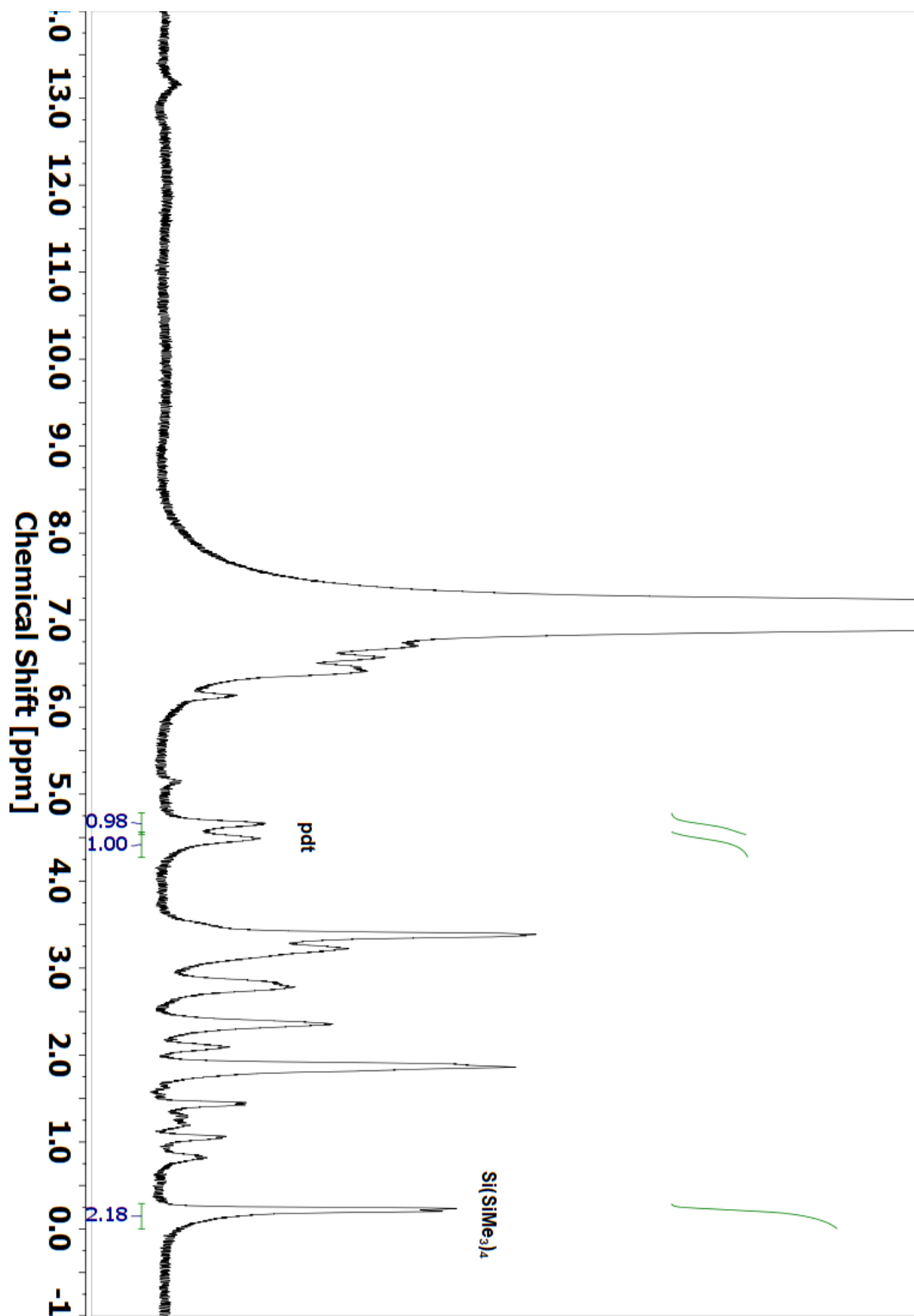


^{13}C NMR spectrum of isolated product in CDCl_3

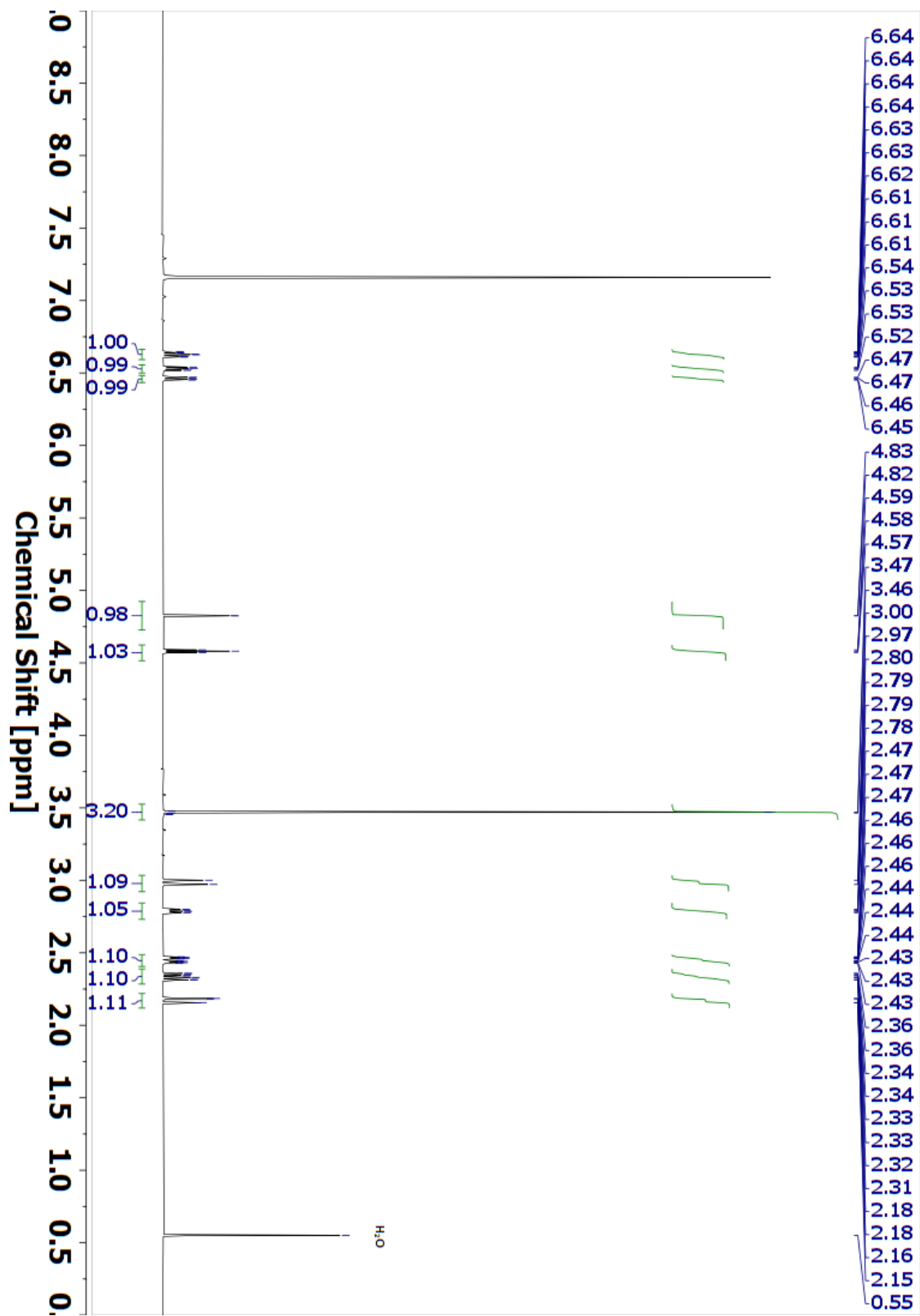
Methyl (Z)-2-(5-fluoro-3,3a,8,8a-tetrahydro-2H-indeno[2,1-b]furan-2-ylidene)acetate (47)



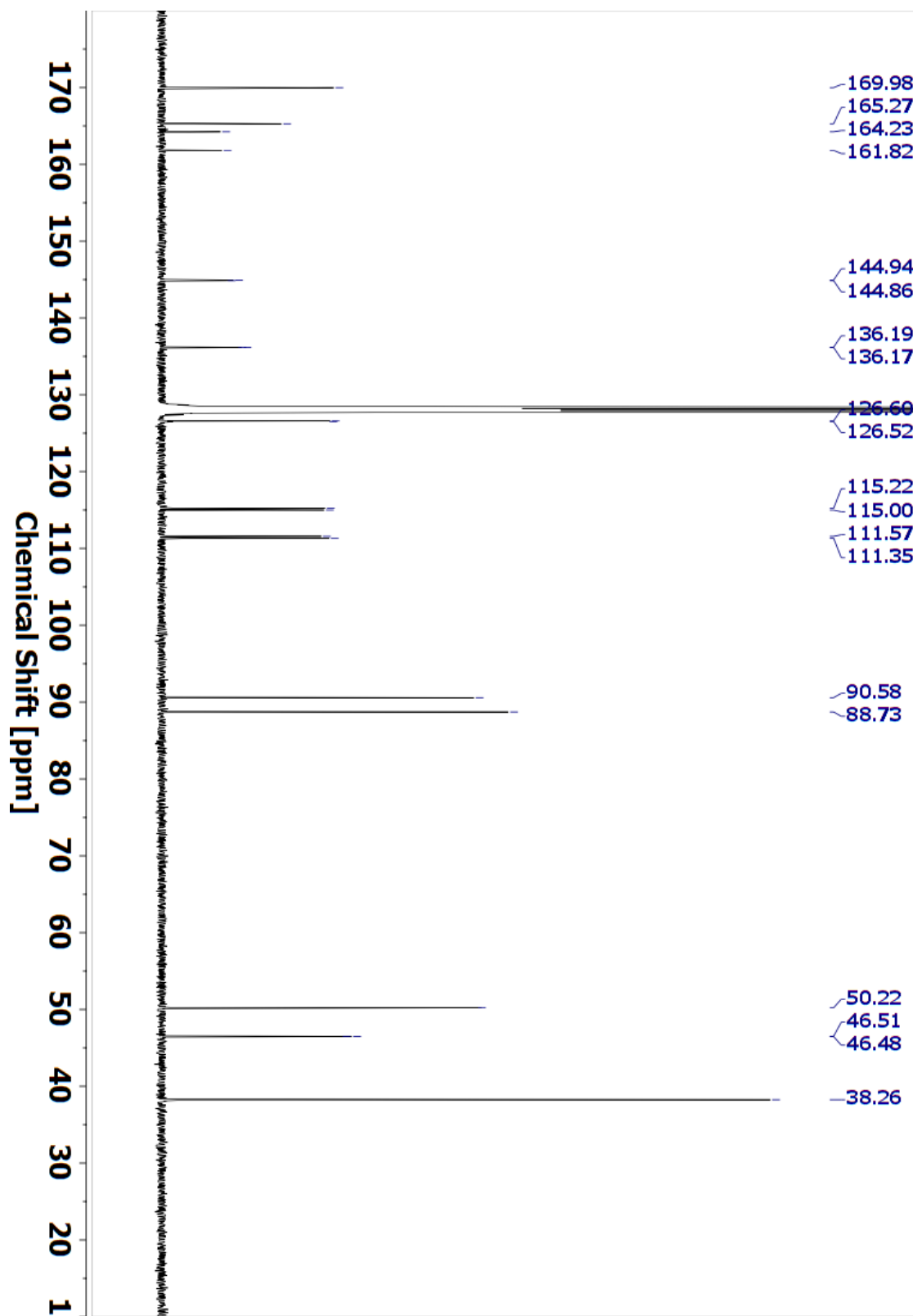
The reaction was carried out at 100°C with 50 mol% catalyst loading following procedure D (20 min, 32% NMR yield) with 20.0 mg of α -diazo- β -ketoester to give 4.5 mg (25% yield) of product as a white crystalline solid. Crystal suitable for single-crystal X-ray diffraction analysis is grown from a pentane/diethyl ether mixture at -30 °C overnight. ^1H NMR (600 MHz, C_6D_6) δ 6.67–6.60 (m, 1H), 6.53 (dd, $J = 8.4, 5.2$ Hz, 1H), 6.46 (dd, $J = 8.7, 2.4$ Hz, 1H), 4.83 (d, $J = 1.6$ Hz, 1H), 4.58 (t, $J = 5.3$ Hz, 1H), 3.47 (s, 3H), 2.99 (d, $J = 17.3$ Hz, 1H), 2.79 (dd, $J = 8.7, 5.3$ Hz, 1H), 2.45 (ddt, $J = 17.3, 5.5, 1.7$ Hz, 1H), 2.34 (ddd, $J = 17.0, 8.7, 1.8$ Hz, 1H), 2.17 (dd, $J = 17.1, 1.2$ Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 169.98, 165.27, 163.02 (d, $J = 243.4$ Hz), 144.90 (d, $J = 7.6$ Hz), 136.18 (d, $J = 2.5$ Hz), 126.56 (d, $J = 8.7$ Hz), 115.11 (d, $J = 22.5$ Hz), 111.46 (d, $J = 22.2$ Hz), 90.58, 88.73, 50.22, 46.51, 46.48, 38.26. ^{19}F NMR (471 MHz, C_6D_6) δ -116.00. HRMS (ESI $^+$) m/z Calc. 249.0921 [$\text{C}_{14}\text{H}_{13}\text{FO}_3+\text{H}$] $^+$, Found. 249.0923 [$\text{M}+\text{H}$] $^+$.



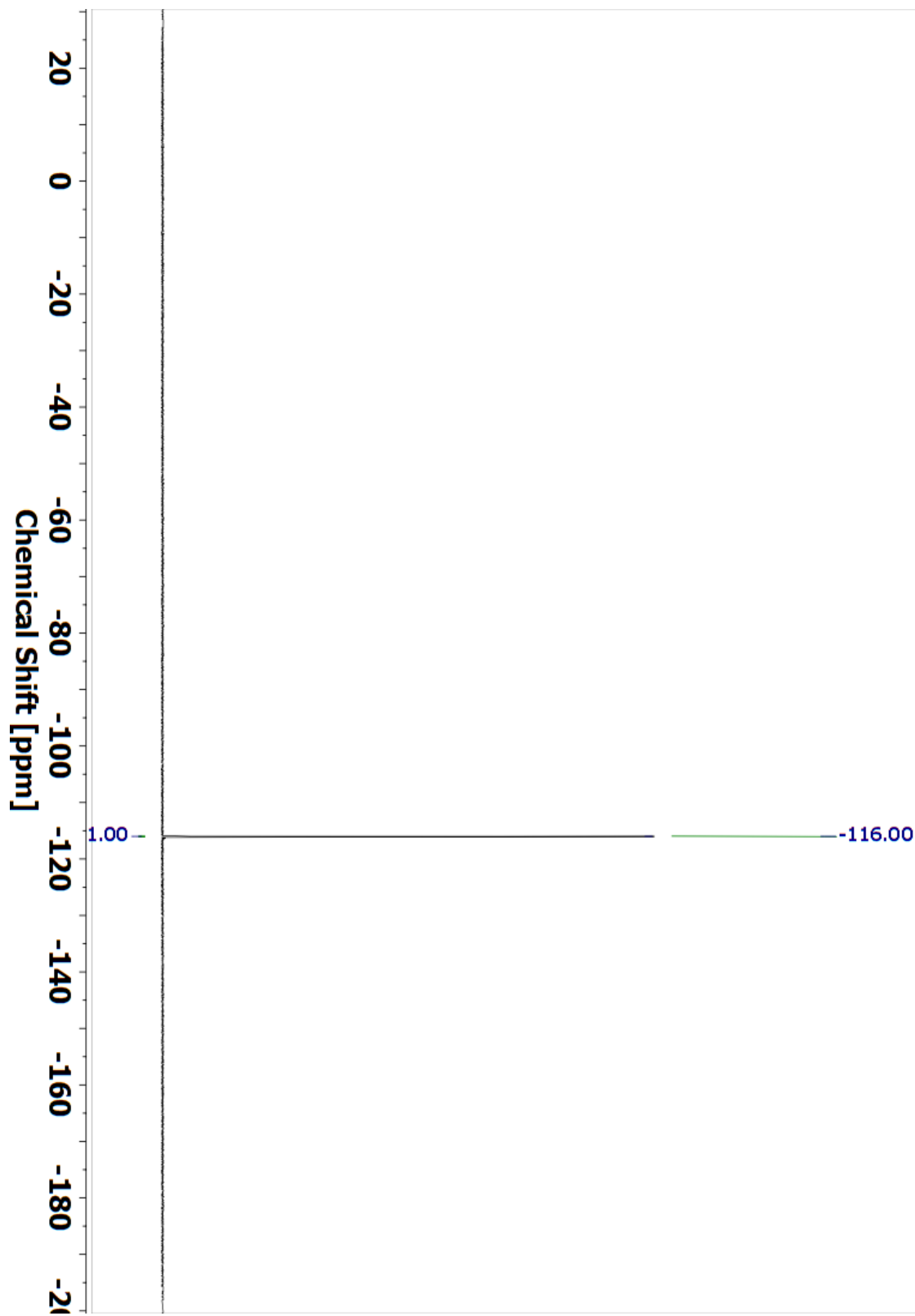
Crude NMR spectrum for reaction carried out at 100 °C with 50 mol% Fe(acac)₂ after 20 min (0.5 mg Si(SiMe₃)₄ as internal standard).



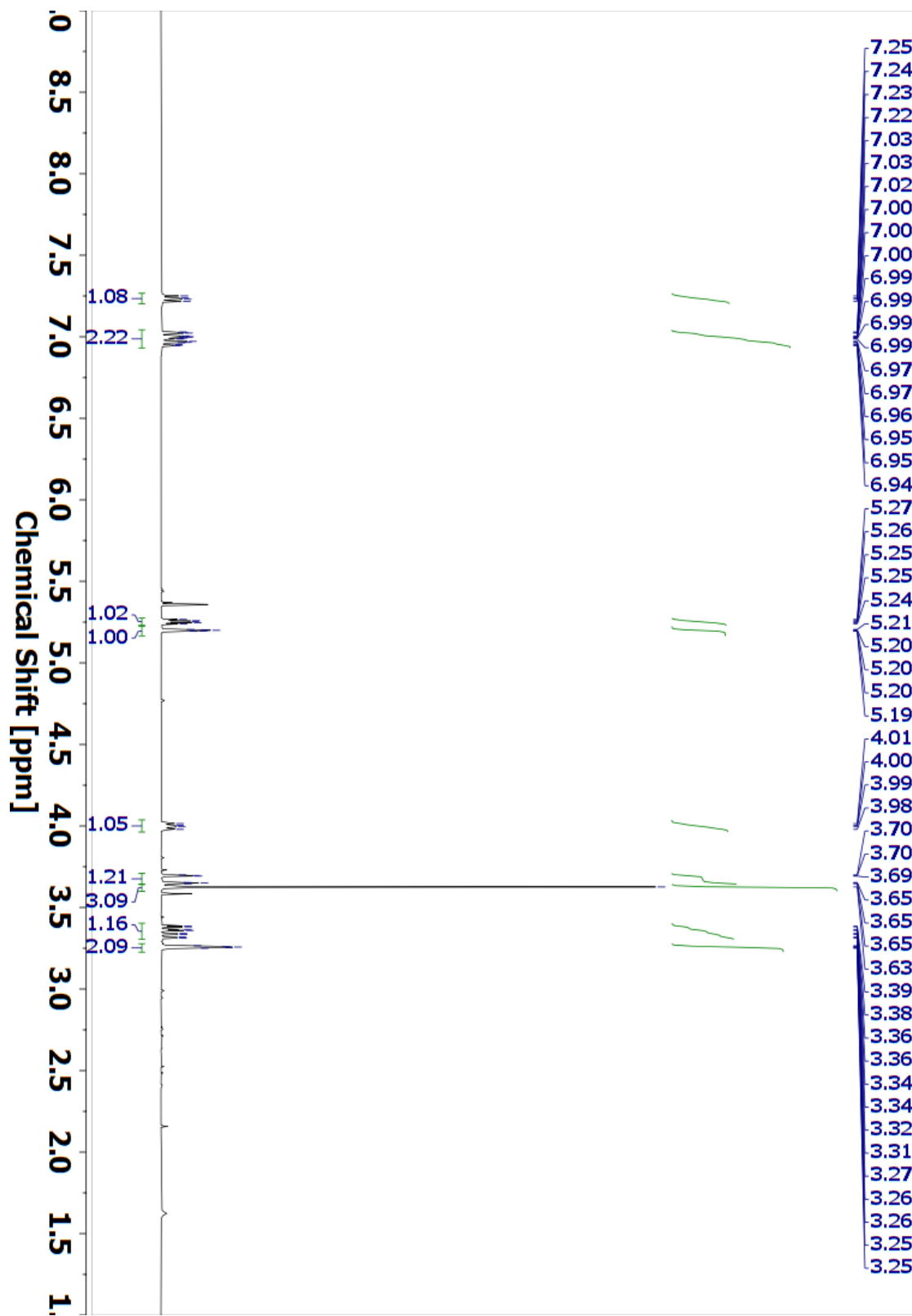
¹H NMR spectrum of isolated product in C₆D₆.



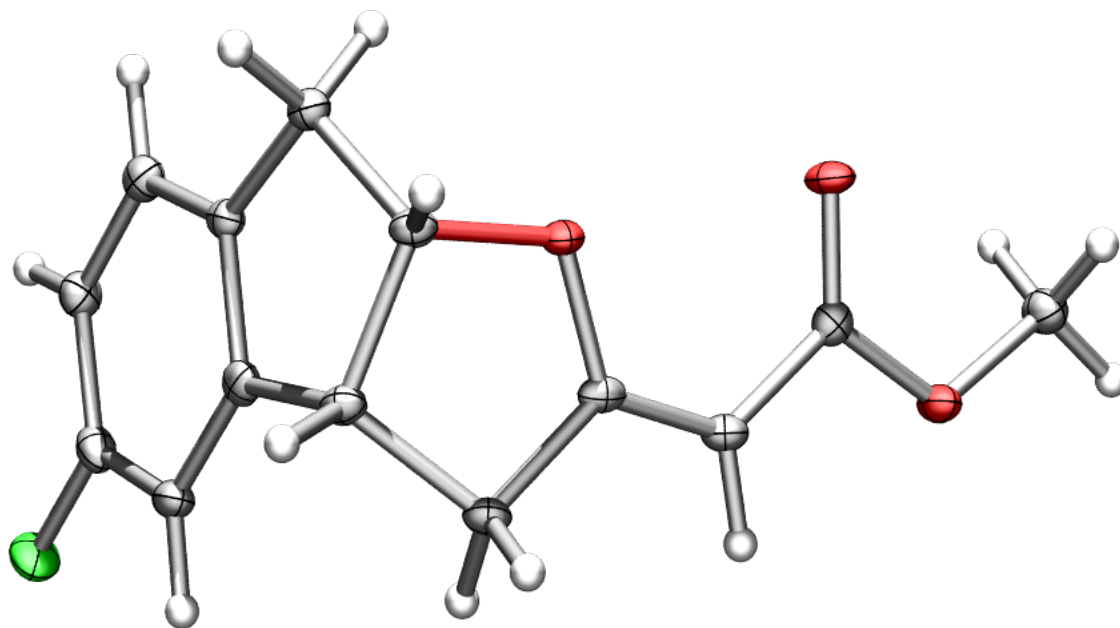
^{13}C NMR spectrum of isolated product in C_6D_6 .



^{19}F NMR spectrum of isolated product in C_6D_6 .



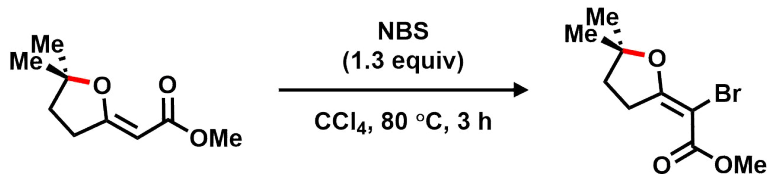
^1H NMR spectrum of isolated product in CD_2Cl_2 .



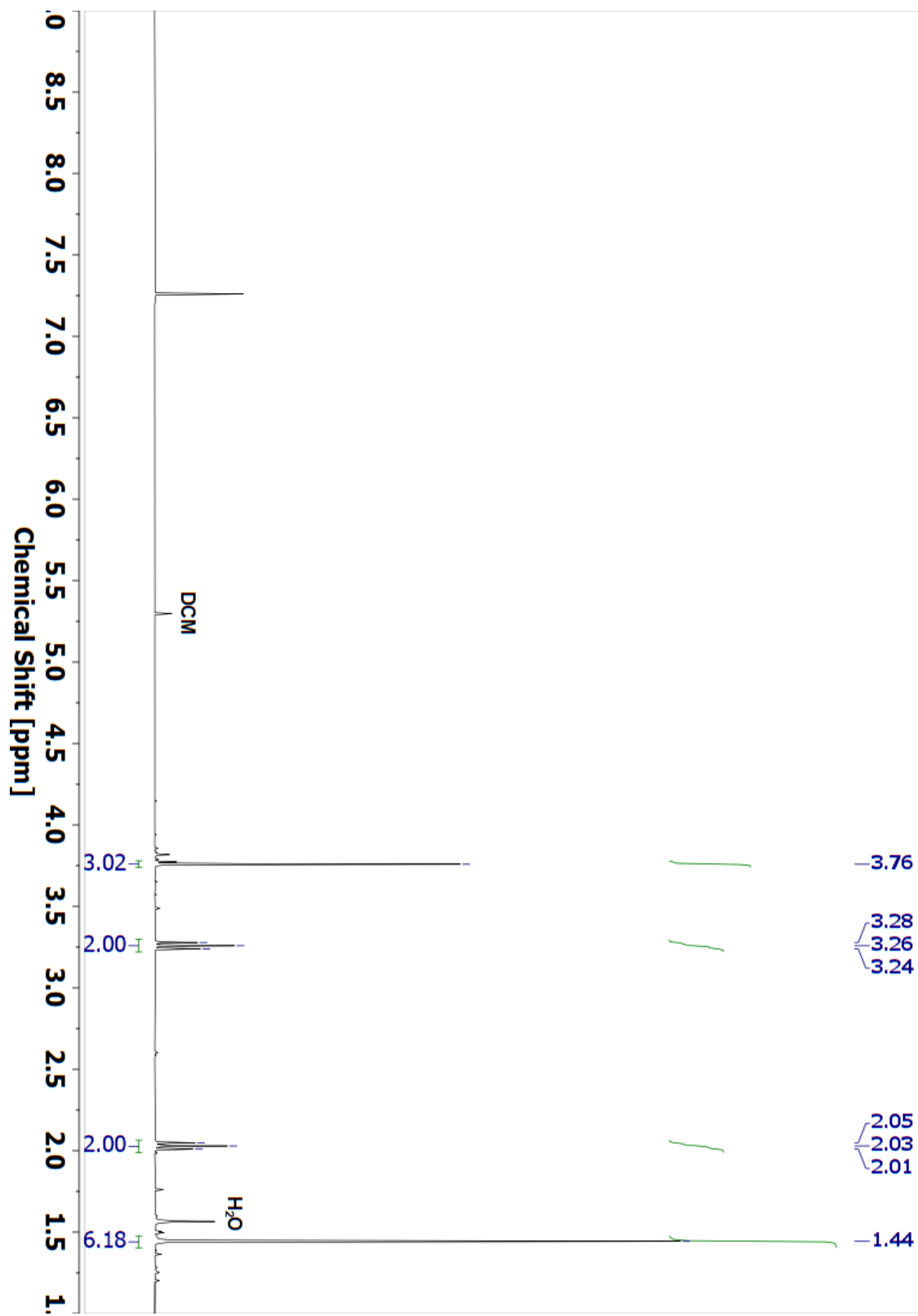
Solid-state molecular structure for methyl (Z)-2-(5-fluoro-3,3a,8,8a-tetrahydro-2H-indeno[2,1-b]furan-2-ylidene)acetate (47) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white, fluorine = green.

Reactivity of (Z)-2-alkylidene tetrahydrofuran

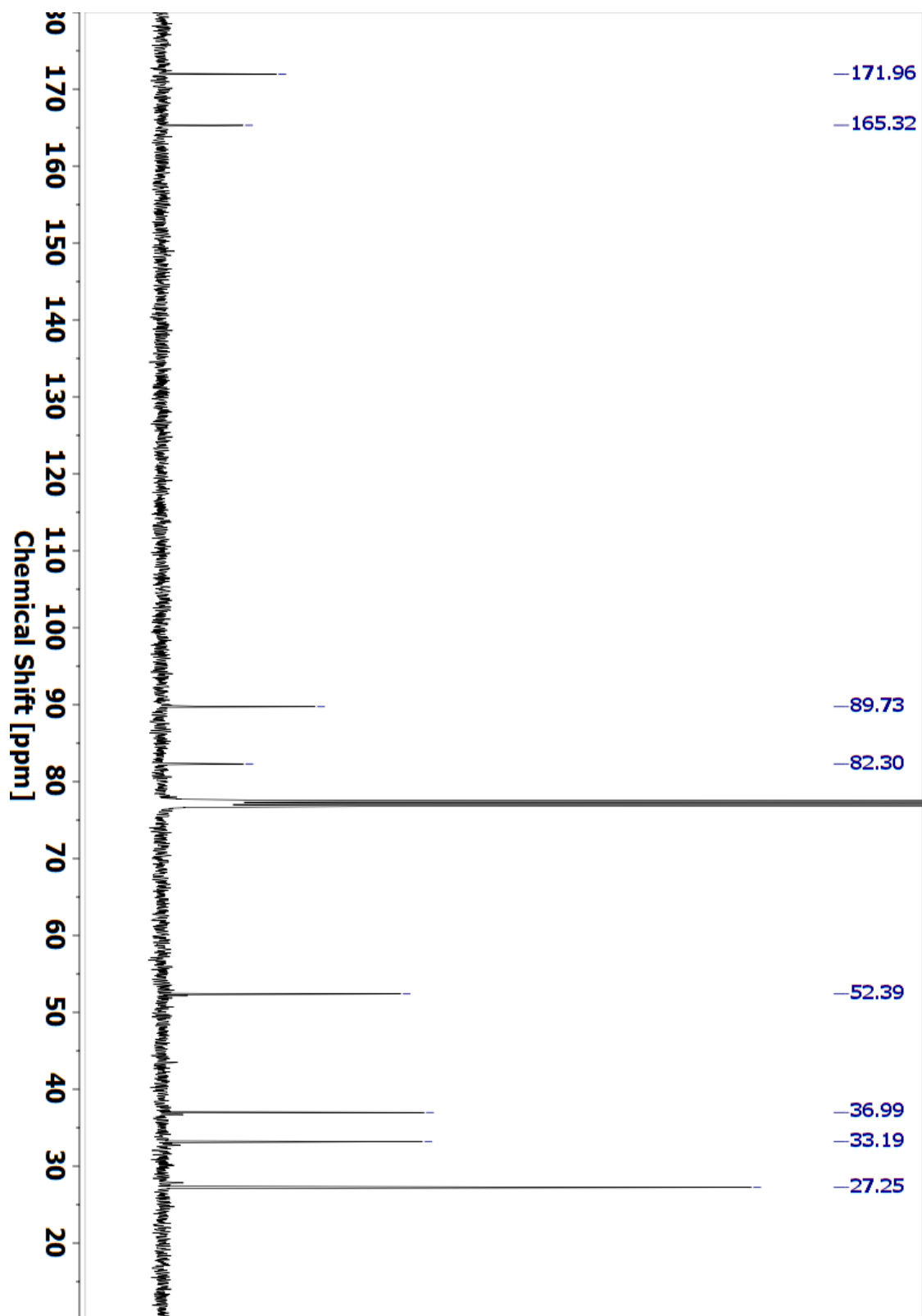
1. Bromination



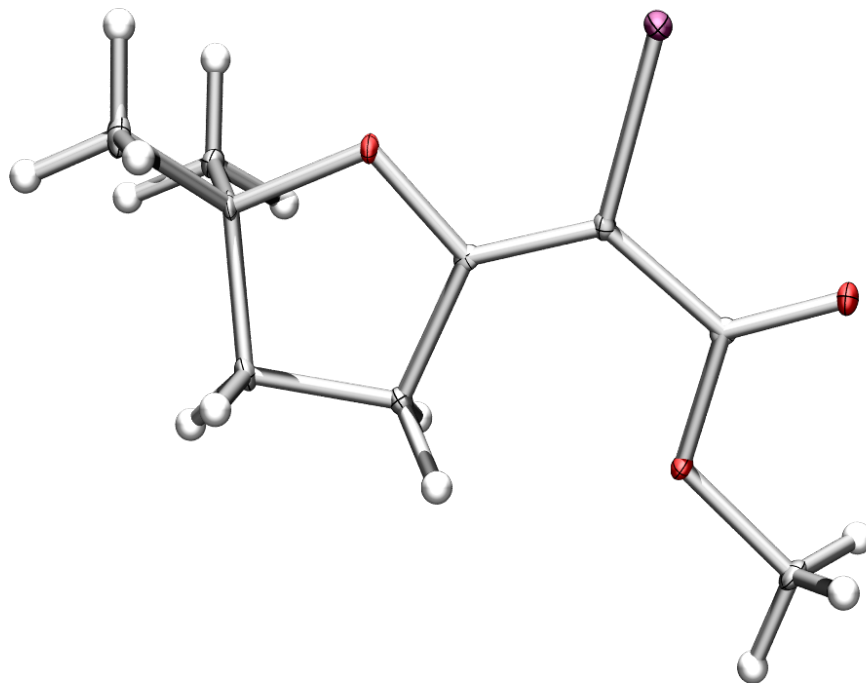
Methyl (Z)-2-bromo-2-(5,5-dimethyltetrahydrofuran-2(3H)-ylidene)acetate (S74): The reaction was carried out using a modified literature procedure in a J-young tube.¹⁸ The reaction was run on 0.18 mmol scale of starting material **8** (30 mg) to give 18.2 mg (41% yield) of product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 3.76 (s, 3H), 3.26 (t, *J* = 7.8 Hz, 2H), 2.03 (t, *J* = 7.8 Hz, 2H), 1.44 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 171.96, 165.32, 89.73, 82.30, 52.39, 36.99, 33.19, 27.25. HRMS (ESI⁺) *m/z* Calc. 249.0121 [C₉H₁₃BrO₃+H]⁺, Found. 249.0124 [M+H]⁺.



^1H NMR spectrum of isolated product in CDCl_3

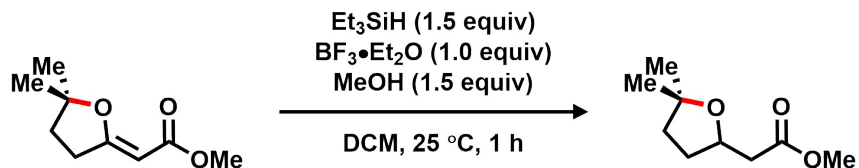


^{13}C NMR spectrum of isolated product in CDCl_3

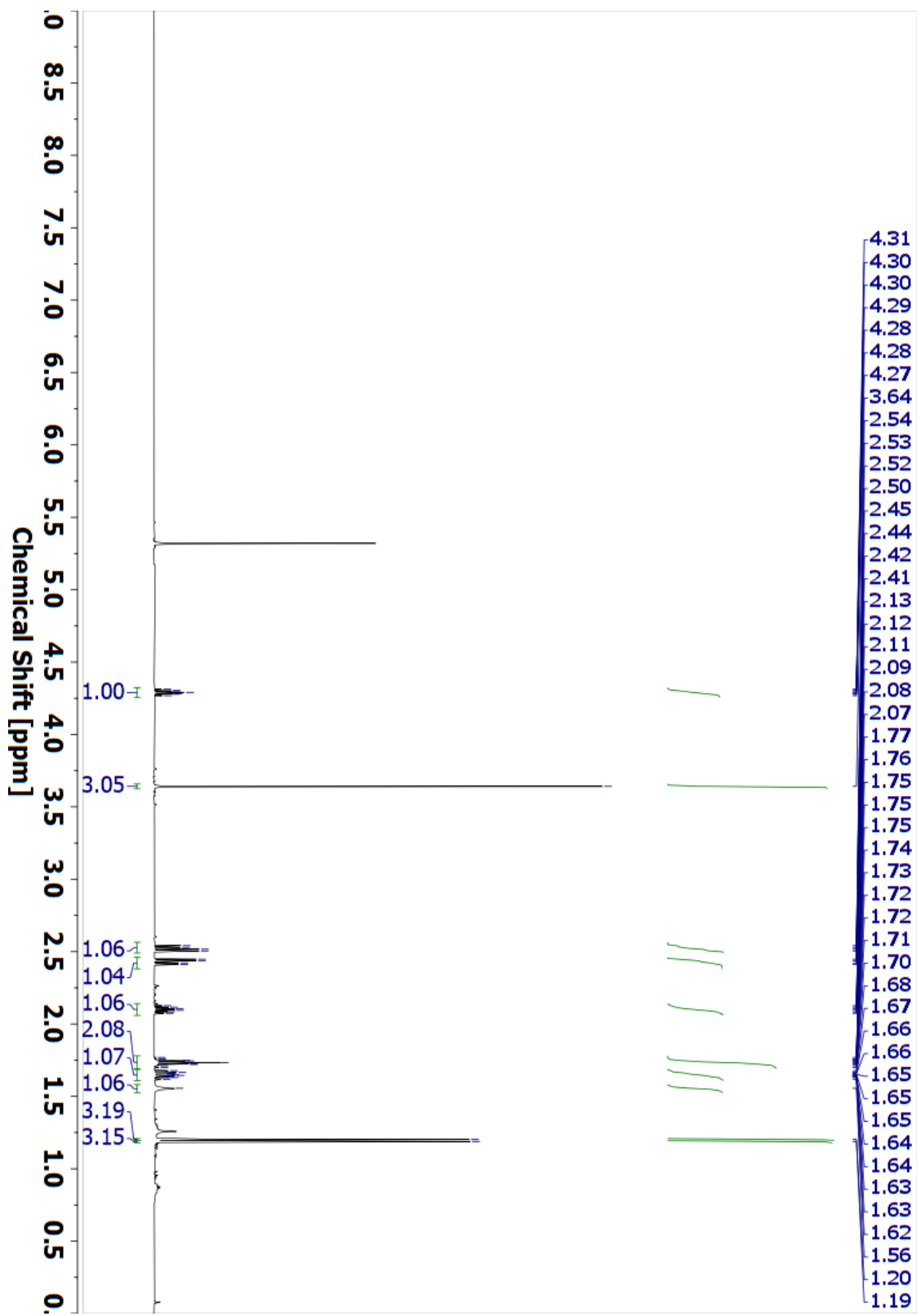


Solid-state molecular structure for methyl (Z)-2-bromo-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (S74) with thermal ellipsoids at 50% probability level. carbon = gray, oxygen = red, hydrogen = white, bromine = maroon.

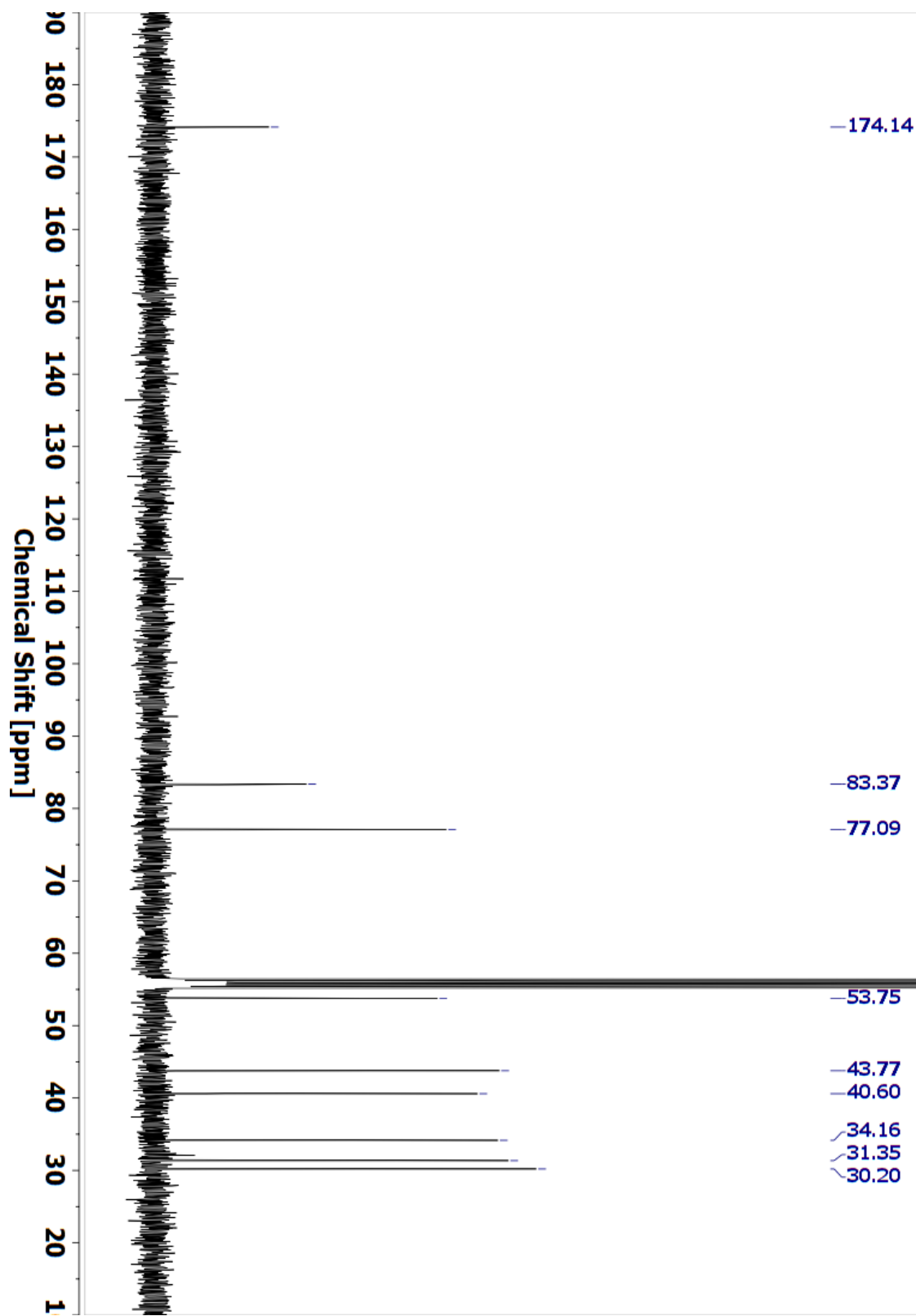
2. Alkene reduction



Methyl 2-(5,5-dimethyltetrahydrofuran-2-yl)acetate (S75): The reaction was carried out using a modified literature procedure in a J-young tube.¹⁹ The reaction was run on 0.12 mmol scale of starting material **8** (20 mg) to give 12.1 mg (60% yield) of product as a colorless oil. ¹H NMR (600 MHz, CD₂Cl₂) δ 4.33–4.25 (m, 1H), 3.64 (s, 3H), 2.52 (dd, *J* = 15.1, 7.2 Hz, 1H), 2.43 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.15–2.06 (m, 1H), 1.77–1.69 (m, 2H), 1.69–1.58 (m, 1H), 1.56 (s, 1H), 1.20 (s, 3H), 1.19 (s, 3H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 174.14, 83.37, 77.09, 53.75, 43.77, 40.60, 34.16, 31.35, 30.20. HRMS (ESI⁺) *m/z* Calc. 173.1172 [C₉H₁₆O₃+H]⁺, Found. 173.1174 [M+H]⁺.



^1H NMR spectrum of isolated product in CD_2Cl_2



^{13}C NMR spectrum of isolated product in CD_2Cl_2

X-ray Diffraction Techniques

The structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo K α (0.71073 Å) or Cu K α (1.54178 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of ϕ and/or ω scans.

Data was integrated using SAINT and scaled with multi-scan absorption correction using SADABS.²⁰⁻²¹ The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014²² and SHELXL-2014²³ with the OLEX 2 interface.²⁴ All non-H atoms, including the disorder fragments, were located in difference Fourier maps, and then refined anisotropically. The restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI/SAME and EADP instructions of SHELXL-2014)²³ as well as the restraints of the atomic displacement parameters (SIMU/RIGU instructions of SHELXL-2014)²⁵ if necessary, have been applied for the disorder refinement.²⁶ Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups).

Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (2): The structure for **2** was solved in the monoclinic space group $P2_1/c$. The structure displays full-molecule disorder and was refined using restraints and constraints. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2003790)

Methyl (Z)-2-(5-benzylidihydrofuran-2(3H)-ylidene)acetate (15): The structure for **15** was solved in the triclinic space group $P-1$. The structure exhibits pseudo-merohedral twinning and is

refined by applied the twin law obtained by Platon/TwinRotMat. There are four molecules per asymmetric unit ($Z' = 4$) and eight per unit cell ($Z = 8$). (CCDC: 2003791)

Methyl (Z)-2-(5-(thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (21): The structure for **21** was solved in the monoclinic space group $P2_1/c$. The structure displaces three-part full-molecule disorder and was refined using restraints and constraints. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2031360)

Methyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (24): The structure for **24** was solved in the monoclinic space group $P2_1/n$. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2003792)

Methyl (Z)-2-(3',4'-dihydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-ylidene)acetate (38): The structure for **38** was solved in the monoclinic space group $P2_1/n$. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2031365)

Dimethyl 2,2'-(1,6-dioxaspiro[4.4]nonane-2,7-diylidene)(2Z,2'Z)-diacetate (39): The structure for **39** was solved in the orthorhombic space group $Pbcn$. There is half of a molecule per asymmetric unit ($Z' = 0.5$) and four per unit cell ($Z = 4$). (CCDC: 2003793)

Ethyl (E)-2-(hexahydro-4H-3a,7:5,9-dimethanocycloocta[b]furan-2(3H)-ylidene)acetate (43): The structure for **43** was solved in the triclinic space group $P-1$. There is one molecule per asymmetric unit ($Z' = 1$) and two per unit cell ($Z = 2$). (CCDC: 2031361)

Methyl 2-((Z)-6-((tert-butoxycarbonyl)amino)hexahydrobenzofuran-2(3H)-ylidene)acetate (44): The structure for **44** was solved in the monoclinic space group $P2_1/c$. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2031364)

Methyl (Z)-2-(6-fluoro-3,3a,8,8a-tetrahydro-2H-indeno[2,1-b]furan-2-ylidene)acetate (47):

The structure for **47** was solved in the monoclinic space group $P2_1$. There is one molecule per asymmetric unit ($Z' = 1$) and two per unit cell ($Z = 2$). The structure is refined with inversion twinning (Flack (x)=0.47(10), Hooft(y)=0.46(9), Parsons (z) =0.49(9)). The absence of higher symmetry was further confirmed by Platon/Addsym.²⁷ (CCDC: 2031363)

Methyl (Z)-2-bromo-2-(5,5-dimethyldihydrofuran-2(3H)-ylidene)acetate (S74): The structure for **S74** was solved in the monoclinic space group $P2_1/c$. There is one molecule per asymmetric unit ($Z' = 1$) and four per unit cell ($Z = 4$). (CCDC: 2031362)

Table S3. X-ray Diffraction Experimental Details

	2	15
Moiety Formula	C ₁₃ H ₁₄ O ₃	C ₁₄ H ₁₆ O ₃
FW	218.24	232.27
Crystal System	Monoclinic	Triclinic
Space Group (Z)	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
a (Å)	5.4040(6)	7.6903(16)
b (Å)	20.1133(19)	11.498(2)
c (Å)	10.3898(10)	28.286(6)
α (°)	90	78.369(3)
β (°)	97.569(3)	89.269(3)
γ (°)	90	86.275(3)
Volume (Å³)	1119.5(2)	2444.7(9)
Calc. ρ (mg/m³)	1.295	1.262
μ (cm⁻¹)	0.091	0.088
Reflections	1977	8610
Completeness (to 2θ)	0.996	0.995
GOF on F²	1.153	1.037
R₁, wR₂^c [I > 2σ(I)]	0.0856, 0.1868	0.0539, 0.1225

	21	24
Moiety Formula	C ₁₁ H ₁₂ O ₃ S	C ₁₆ H ₁₇ NO ₃
FW	224.27	271.31
Crystal System	Monoclinic	Monoclinic
Space Group (Z)	<i>P2₁/c</i>	<i>P2₁/n</i>
a (Å)	5.3530(3)	11.4079(8)
b (Å)	19.559(1)	7.1440(4)
c (Å)	10.3792(6)	17.6523(11)
α (°)	90	90
β (°)	99.693(5)	103.663(2)
γ (°)	90	90
Volume (Å³)	1071.18(10)	1397.92(15)
Calc. ρ (mg/m³)	1.390	1.289
μ (mm⁻¹)	0.285	0.089
Reflections	1897	2483
Completeness (to 2θ)	1.000	0.999
GOF on F²	1.217	1.120
R₁, wR₂^c [I > 2σ(I)]	0.0687, 0.1297	0.0653, 0.1548

	38	43
Moiety Formula	C ₁₅ H ₁₆ O ₄	C ₁₆ H ₂₂ O ₃
FW	260.28	262.33
Crystal System	Monoclinic	Triclinic
Space Group (Z)	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
a (Å)	5.5819(4)	6.4688(14)
b (Å)	26.694(2)	10.659(2)
c (Å)	8.9893(6)	10.746(2)
α (°)	90	72.406(3)
β (°)	96.297(4)	82.229(3)
γ (°)	90	73.296(3)
Volume (Å³)	1331.33(17)	675.6(2)
Calc. ρ (mg/m³)	1.299	1.290
μ (mm⁻¹)	0.774	0.087
Reflections	2347	2383
Completeness (to 2θ)	0.995	0.998
GOF on F²	1.053	1.035
R₁, wR₂^c [I > 2σ(I)]	0.0378, 0.0974	0.0347, 0.0869

	44	47
Moiety Formula	C ₁₆ H ₂₅ NO ₅	C ₁₄ H ₁₃ FO ₃
FW	311.37	248.24
Crystal System	Monoclinic	Monoclinic
Space Group (Z)	<i>P2₁/c</i>	<i>P2₁</i>
a (Å)	27.0114(10)	4.7394(2)
b (Å)	6.0386(3)	10.4283(3)
c (Å)	10.1563(4)	11.7914(5)
α (°)	90	90
β (°)	92.246(2)	96.080(2)
γ (°)	90	90
Volume (Å³)	1655.33(12)	579.50(4)
Calc. ρ (mg/m³)	1.249	1.423
μ (mm⁻¹)	0.761	0.924
Reflections	2915	1898
Completeness (to 2θ)	0.998	1.75/0.93
GOF on F²	1.097	1.172
R₁, wR₂^c [I > 2σ(I)]	0.0476, 0.1260	0.048, 0.1291

	39	S74
Moiety Formula	C ₁₃ H ₁₆ O ₆	C ₉ H ₁₃ BrO ₃
FW	268.26	249.09
Crystal System	Orthorhombic	Monoclinic
Space Group (Z)	<i>Pbcn</i>	<i>P2₁/c</i>
a (Å)	5.7778(4)	8.8485(10)
b (Å)	10.0009(6)	6.7391(7)
c (Å)	22.4445(13)	16.7732(18)
α (°)	90	90
β (°)	90	98.086 (2)
γ (°)	90	90
Volume (Å³)	1296.92(14)	990.26(19)
Calc. ρ (mg/m³)	1.374	1.671
μ (mm⁻¹)	0.109	4.124
Reflections	1145	1752
Completeness (to 2θ)	1.000	1.000
GOF on F²	1.125	1.050
R₁, wR₂^c [I > 2σ(I)]	0.0402, 0.0926	0.219, 0.0577

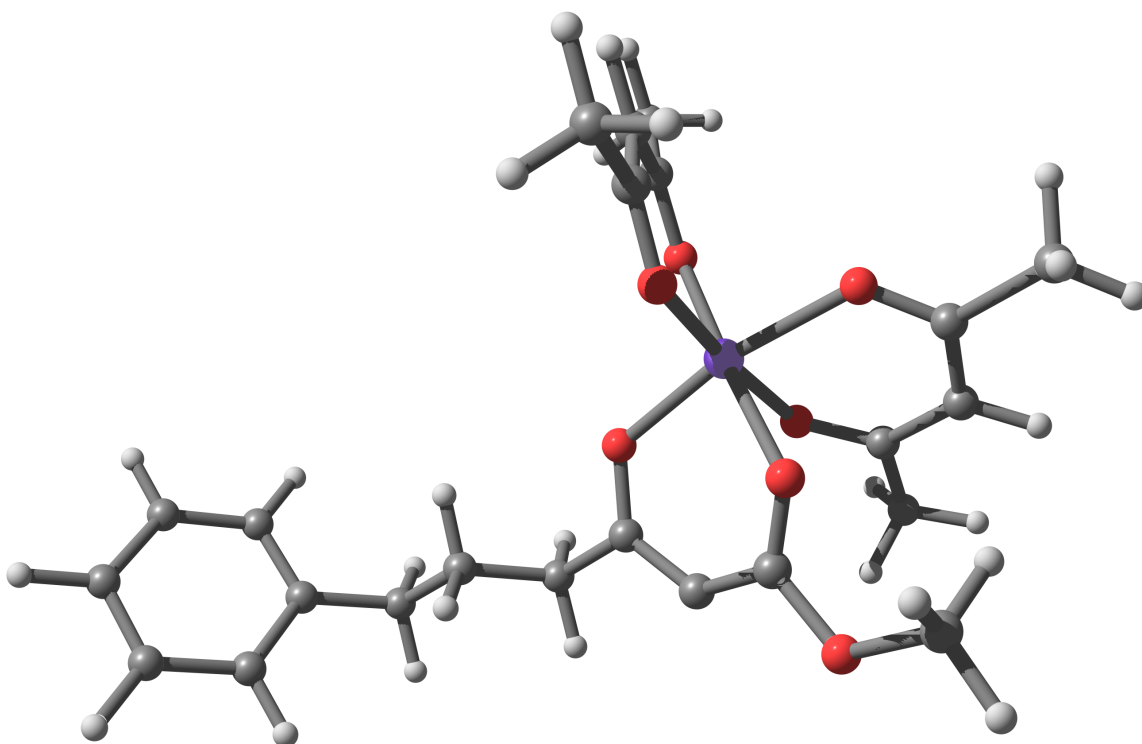
Computational Methods

All calculations employed the Orca program package.²⁸ Structures created and first optimized with MM (molecular mechanics) simulation employing a UFF forcefield²⁹, followed by modeling using quantum mechanics (QM). All QM calculations were conducted with the def2-TZVP (Fe, O)/def2-SVP (C, H) basis sets and the W06 density fitting function of Aldrich and co-workers'.³⁰⁻³¹ Frequency calculations were performed at the same level of theory in order to confirm the optimized structures were minima on the potential energy surfaces. The calculations were carried out using BP86 GGA functional³²⁻³³ benchmarked with a variety of other functionals such as B3LYP,^{25, 34-36} PBE³⁷ and TPSS.³⁸ The D3BJ dispersion correction is incorporated in every calculation.³⁹ All calculated transition states possess one imaginary frequency while all minimization calcs exhibited zero. All calculations assumed 298.15 K and 1 atm.

Structural optimization and electronic structure calculation of Fe stabilized vinyl C-radical

The calculation is carried out on both the HS ($S = 3$, ferromagnetic coupling) and LS ($S = 2$, anti-ferromagnetic coupling) surfaces. The result shown here reflects the optimized geometry of substrate with benzylic C–H bonds.

Molecular geometry of Fe stabilized vinyl C-radical with $S = 3$

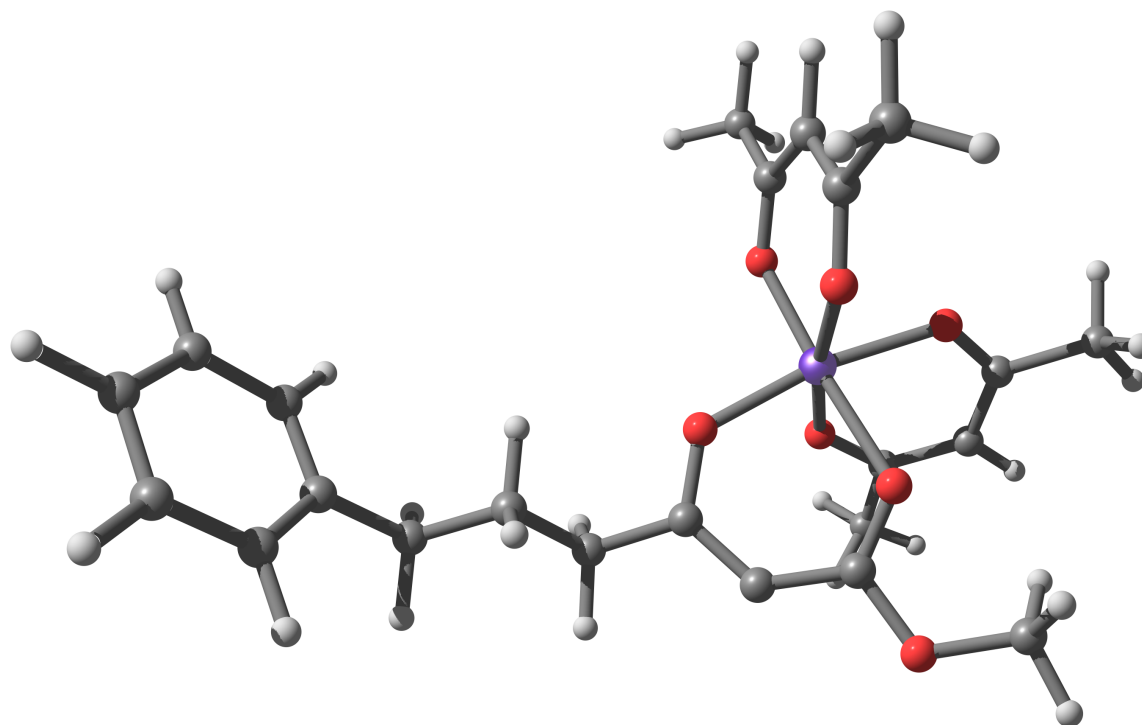


26	1.738710000	3.944234000	3.605448000
6	-0.232305000	0.467804000	5.280356000
6	0.202208000	1.913733000	5.169622000
6	0.133480000	2.761096000	6.303882000
6	0.412089000	4.147669000	6.264914000
6	0.241477000	4.995072000	7.505031000
6	3.702293000	3.753091000	5.853242000
6	3.911560000	5.133106000	5.672118000
6	3.643894000	5.933726000	4.589939000

6	4.173260000	7.342992000	4.513014000
6	2.902706000	1.504342000	0.237688000
6	2.124110000	2.539821000	1.018616000
6	0.930799000	3.083319000	0.481061000
6	0.179772000	4.104627000	1.101837000
6	-1.032674000	4.688975000	0.413577000
8	0.609669000	2.284324000	4.014585000
8	0.819283000	4.772678000	5.220587000
8	3.116060000	3.017405000	5.016028000
8	2.942962000	5.515677000	3.577180000
8	2.626985000	2.876491000	2.147570000
8	0.461714000	4.615435000	2.248101000
1	0.637353000	-0.186646000	5.064639000
1	-0.995595000	0.252937000	4.505179000
1	-0.638530000	0.214539000	6.277531000
1	-0.236563000	2.335176000	7.245966000
1	1.234989000	5.398448000	7.792100000
1	-0.403092000	5.866797000	7.273827000
1	-0.184734000	4.434237000	8.357779000
1	3.305016000	8.022749000	4.368027000
1	4.649985000	7.608375000	5.478528000
1	2.993843000	0.583702000	0.849429000
1	3.932807000	1.876269000	0.063543000
1	2.434356000	1.255563000	-0.732011000
1	0.599180000	2.727633000	-0.502497000
1	-1.919117000	4.561222000	1.068193000
1	-1.231643000	4.224187000	-0.569376000
1	-0.887030000	5.780628000	0.280492000
6	5.164825000	7.517291000	3.350560000
1	6.031797000	6.838310000	3.495268000

1	4.679275000	7.203624000	2.403903000
6	5.666998000	8.965535000	3.219460000
1	6.138957000	9.273867000	4.167273000
1	4.804660000	9.634390000	3.065875000
6	3.916757000	1.821489000	7.187892000
1	4.409421000	1.223002000	6.397631000
1	4.334792000	1.571527000	8.179065000
1	2.826994000	1.625032000	7.159642000
6	6.648645000	9.127780000	2.084784000
6	8.012752000	8.819048000	2.265812000
6	6.216619000	9.538369000	0.807622000
6	8.921271000	8.917299000	1.200244000
1	8.364815000	8.497311000	3.259262000
6	7.121800000	9.641137000	-0.261115000
1	5.153701000	9.784705000	0.653447000
6	8.478178000	9.329943000	-0.068301000
1	9.982699000	8.671972000	1.361119000
1	6.766165000	9.970467000	-1.249764000
1	9.189447000	9.412184000	-0.904550000
8	4.177572000	3.230272000	7.005911000

Molecular geometry of Fe stabilized vinyl C-radical with $S = 2$



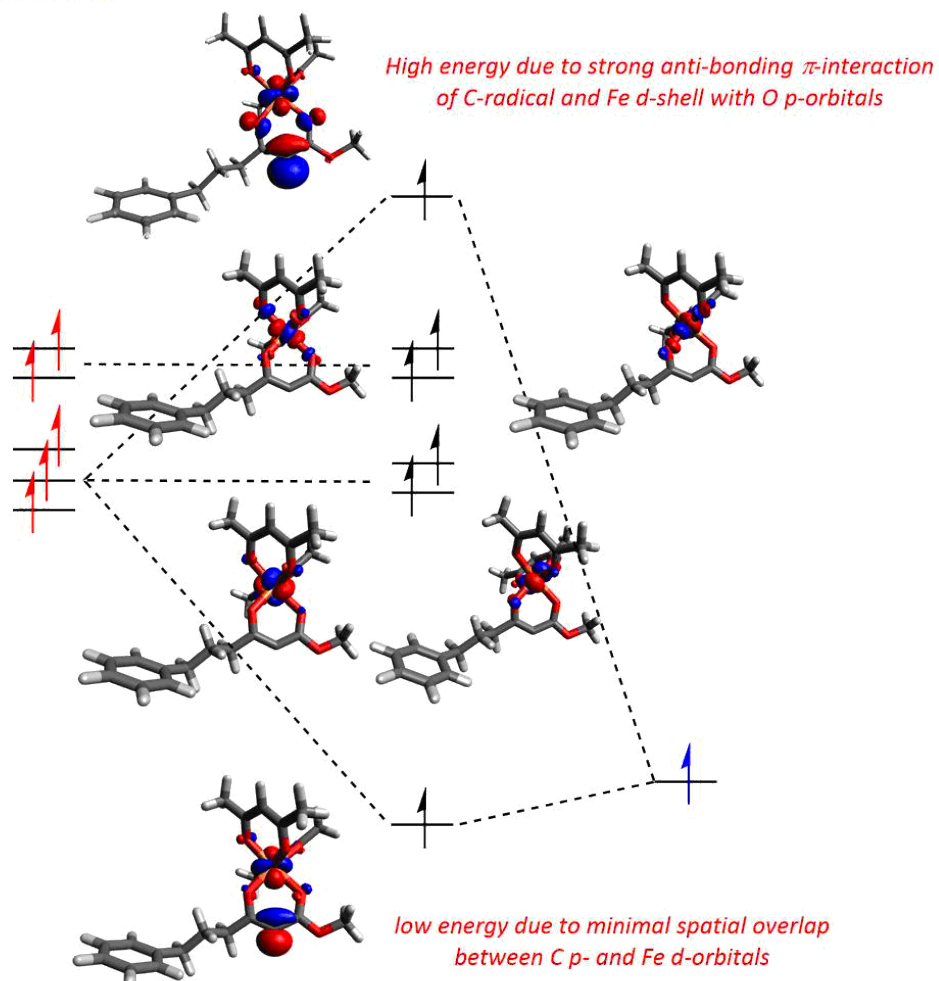
26	1.862704000	3.940162000	3.661835000
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6	0.095353000	1.996486000	5.088366000
6	0.016380000	2.829438000	6.232627000
6	0.383784000	4.195761000	6.233910000
6	0.178376000	5.037781000	7.473410000
6	3.764694000	3.588059000	5.962707000
6	4.187975000	4.910766000	5.757191000
6	3.919002000	5.768907000	4.723851000
6	4.489674000	7.162516000	4.683926000
6	2.987048000	1.380005000	0.376035000
6	2.265833000	2.491386000	1.106127000
6	1.145390000	3.121085000	0.509946000
6	0.454502000	4.210645000	1.083345000

6	-0.676225000	4.878066000	0.333921000
8	0.592342000	2.356650000	3.965614000
8	0.895361000	4.807161000	5.228448000
8	3.084191000	2.942235000	5.119832000
8	3.167258000	5.411540000	3.721085000
8	2.746890000	2.805678000	2.250916000
8	0.728604000	4.719111000	2.232453000
1	0.399569000	-0.125019000	4.969451000
1	-1.167795000	0.426822000	4.327017000
1	-0.916033000	0.340224000	6.115677000
1	-0.437317000	2.415789000	7.143156000
1	1.167315000	5.399351000	7.823854000
1	-0.417580000	5.936591000	7.215953000
1	-0.319569000	4.486279000	8.292784000
1	3.634843000	7.873149000	4.741884000
1	5.116271000	7.322988000	5.584921000
1	2.956630000	0.461758000	0.997916000
1	4.055750000	1.652418000	0.258640000
1	2.551709000	1.164412000	-0.616848000
1	0.828251000	2.777363000	-0.482586000
1	-1.593900000	4.846558000	0.956261000
1	-0.879132000	4.405173000	-0.644356000
1	-0.430496000	5.948669000	0.179128000
6	5.290560000	7.430108000	3.399809000
1	6.139469000	6.717060000	3.333396000
1	4.646691000	7.229988000	2.519606000
6	5.826469000	8.870525000	3.332617000
1	6.469988000	9.060980000	4.207786000
1	4.980385000	9.573244000	3.405194000
6	3.637063000	1.667685000	7.323501000

1	4.048887000	0.982600000	6.557300000
1	3.982795000	1.372737000	8.329972000
1	2.530573000	1.647718000	7.264425000
6	6.602114000	9.132094000	2.064760000
6	7.975824000	8.824476000	1.986714000
6	5.959553000	9.635664000	0.915374000
6	8.690249000	9.013949000	0.792962000
1	8.490327000	8.432081000	2.878762000
6	6.669672000	9.828813000	-0.280530000
1	4.886675000	9.882255000	0.963796000
6	8.038398000	9.517624000	-0.345821000
1	9.762939000	8.768916000	0.751737000
1	6.152271000	10.227700000	-1.167003000
1	8.597344000	9.671271000	-1.281880000
8	4.129277000	3.011744000	7.128289000

MO description and spin density plot of the Fe stabilized vinyl C-radical

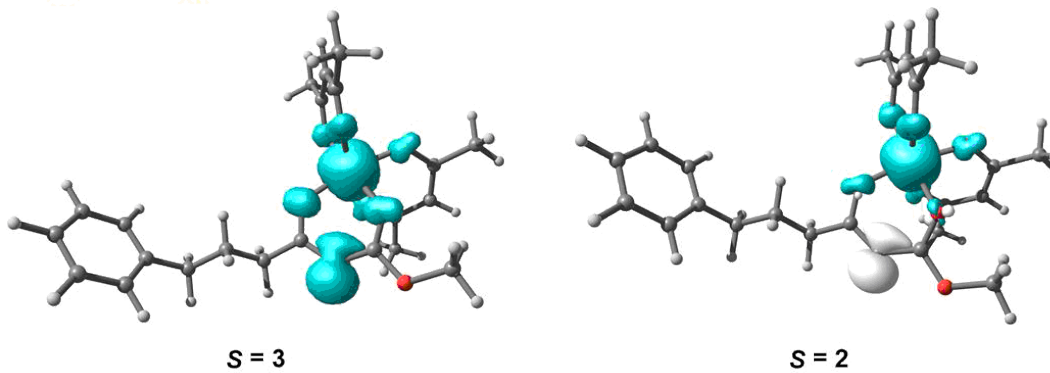
MO analysis



Fe 3d-orbital $\{O_h\}$

Vinyl C-based p-orbital

Spin density plot



Energy comparison

	$S = 3$ (hatee/mol)	$S = 2$ (hatee/mol)	Septet-Quintet (kcal/mol)
Electronic energy	-2683.75162681	-2683.75177580	0.093491225
Total enthalpy	-2683.26054630	-2683.26094101	0.247680525
Total entropy	-0.10107473	-0.10118925	0.0718613
Final Gibbs free energy	-2683.36162104	-2683.36213026	0.31953555

The small difference between the ferro- and anti-ferromagnetic coupling is 0.09 kcal/mol in electronic energy and 0.32 kcal/mol in Gibbs free energy. The small magnitude of the energy gap suggests the vinyl-C based radical and the Fe-center are not interacting strongly at room temperature, possibly due to the large spatial separation between the two atoms. The preference toward the quintet state is estimated around 1.72 to 1 comparing to the septet state using Boltzmann distribution. The spin density plot indeed also shows a change in sign of the vinyl radical between the septet and quintet states.

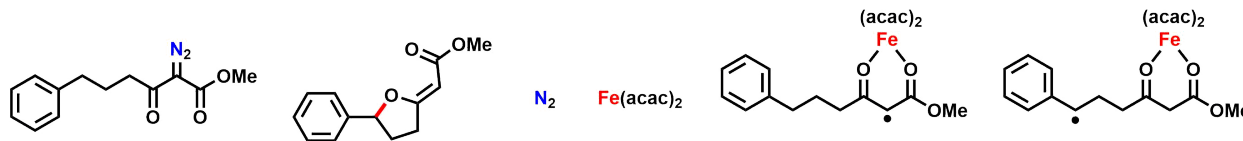
The spin density shown here further corroborates a radical-type mechanism since a hydride type mechanism would locate most spin density on the Fe-center while leaving the vinyl-C cationic in nature (Fe^{II} – vinyl carbocation vs. Fe^{III} – vinyl radical).

Potential energy surface for transformation catalyzed by $Fe(acac)_2$

The calculation is carried out using the following methodology (The calculation involves the potential surfaces of converting benzylic, tertiary, secondary, and diazo-malonate substrates. The method shown herein is only regarding the benzylic substrate with BP86 functional as an example, while the other three substrates were carried out using the same procedure. The results for benzylic substrate were benchmarked with PBE, TPSSh and B3LYP functionals.):

1. Optimization of the starting substrates, products, $Fe(acac)_2$ and intermediates

Model of the following molecules were built using Avogadro followed by optimization using UFF prior to be subjected to QM calculations.



All the optimized structures were then subjected to frequency calculations to ensure the establishment of a minima on the global surface.

Note: Both the α -diazo- β -ketoester substrates and cyclized 2-alkylidene dihydrofuran cannot form a stable adduct with $Fe(acac)_2$. Dissociation is observed during the optimization for every substrate surveyed.

2. Location of N_2 -loss transition state

Due to the instability of a substrate adduct with $Fe(acac)_2$, the transition state is located by bring a nitrogen molecule toward the vinyl C-atom from 3 to 1.2 Å in 10×0.2 Å steps (relaxed surface scan), and the geometry corresponding to the highest energy is subjected to transition state search. If the transition state search does not provide satisfactory result, a full, exact hessian calculation is

performed for transition state optimization. Frequency calculation is then carried out using the transition state obtained to ensure the presence of all but one positive vibration modes with positive frequency. Coordinates of optimized transition state geometry is provided below.

3. Location of HAA transition state

The “C–H bond” indicated in this paragraph specifically refers to the C–H bond to be activated. The conformation of the Fe(acac)₂ bound vinyl radical where the C–H bond is closest to the Fe center is first optimized using MM with a UFF force field. The H atom is then brought toward the vinyl radical from 1.9 to 1 Å in 10×0.1 Å steps (relax surface scan). Transition state search is performed using the point closest to the peak of the energy curve. If the calculation does not converge or more than one negative frequency was found, a full, exact hessian calculation is carried out to find the saddle point for the transition state. Frequency calculation is then carried out using the transition state obtained to ensure the presence of all but one positive vibration modes with positive frequency. Coordinates of optimized transition state geometry is provided below.

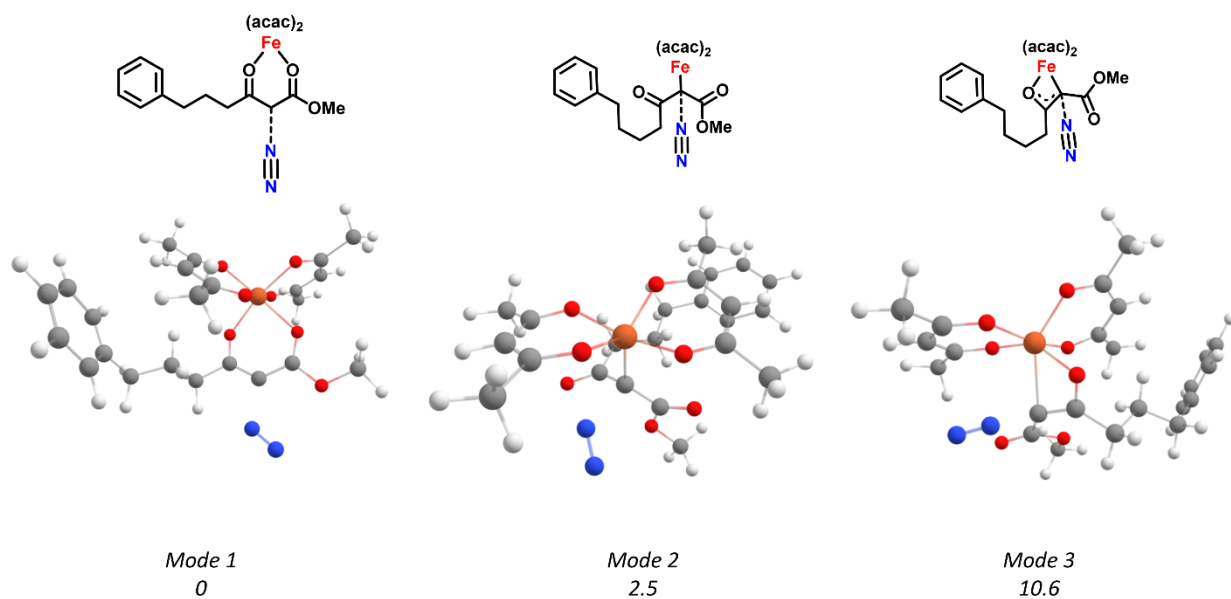
4. Location of RR transition state

Due to the instability of a product adduct with Fe(acac)₂ using QM calculations, the adduct is first optimized using MM with a UFF force field. The C- and O-atom is then separated to 2 Å while the C-atom is brought closer to the O-atom to 1.4 Å in 8×0.1 Å steps (relaxed surface scan). Transition state search is performed using the point closest to the peak of the energy curve. If the calculation does not converge or more than one negative frequency was found, a full, exact hessian calculation is carried out to find the saddle point for the transition state. Frequency calculation is then carried out using the transition state obtained to ensure the presence of all but one positive

vibration modes with positive frequency. Coordinates of optimized transition state geometry is provided below.

5. Different potential modes of N_2 loss

The following additional two potential N_2 loss modes are proposed and subjected TS search. The relative energy is calculated and listed below (in kcal/mol).



The result confirms the most favorable transition state being *Mode 1* (chelation through oxygen atoms).

6. Coordinates of optimized geometries

A. BP86

$Fe(acac)_2$

Fe	1.089053	4.237113	3.206328
C	-2.853794	5.339398	4.357688

C	-1.346285	5.242273	4.405625
C	-0.622841	5.861073	5.452106
C	0.783665	5.836172	5.598736
C	1.444380	6.541809	6.760608
C	2.653441	0.398300	2.258703
C	2.339160	1.869072	2.108086
C	2.779144	2.581020	0.967823
C	2.546938	3.954532	0.722057
C	3.075069	4.606436	-0.535321
O	-0.803888	4.570768	3.441907
O	1.590727	5.234058	4.785914
O	1.660588	2.392060	3.077769
O	1.894135	4.737562	1.518755
H	-3.292831	4.320583	4.362447
H	-3.165450	5.815003	3.404469
H	-3.270620	5.917650	5.203290
H	-1.200609	6.404324	6.212407
H	2.033753	5.810508	7.352285
H	2.163489	7.295630	6.377826
H	0.714811	7.041602	7.424979
H	1.708654	-0.174857	2.355932
H	3.224573	0.235875	3.196458
H	3.234437	-0.002028	1.406757
H	3.347058	2.021258	0.212109
H	2.234080	5.064162	-1.096368
H	3.605353	3.892681	-1.193249
H	3.765014	5.431960	-0.262727

Dinitrogen

N	-0.981799	0.333305	0.004363
N	0.120929	0.333305	0.004363

a-Diazo- β -ketoester Substrates

Benzylic:

C	5.975366	1.601920	5.564648
C	5.678544	3.050129	5.635020
C	5.531957	3.943803	4.448412
C	5.225708	5.407339	4.738706
O	6.140594	0.969316	4.546372
O	5.654884	3.501475	3.319894
H	4.300315	5.455622	5.355703
H	6.031956	5.809105	5.394193
C	5.079373	6.254640	3.476359
H	6.001850	6.176556	2.866362
H	4.269545	5.841139	2.840840
C	4.788949	7.732251	3.794137
H	5.604650	8.139497	4.414926
H	3.869975	7.803044	4.399343
C	6.323493	-0.341195	6.866168
H	7.306117	-0.553270	6.401877
H	6.335268	-0.609821	7.936873
H	5.542469	-0.913754	6.329485
C	4.636612	8.563534	2.543329
C	5.765310	9.117768	1.906382
C	3.370036	8.754728	1.955188
C	5.633805	9.842002	0.710982
H	6.761484	8.978878	2.356585
C	3.232948	9.479006	0.760064
H	2.479133	8.329703	2.444871
C	4.365760	10.023767	0.132808
H	6.526401	10.268201	0.228002
H	2.235284	9.619859	0.316349

H	4.260905	10.588973	-0.805577
O	6.036833	1.073997	6.825014
N	5.533117	3.574143	6.834010
N	5.396259	4.064143	7.852574

Tertiary:

C	6.022003	1.569328	5.580238
C	5.682961	3.008556	5.636590
C	5.431629	3.868240	4.441510
C	5.089100	5.325575	4.719670
O	6.145945	0.917214	4.568462
O	5.501748	3.401685	3.318211
H	4.206728	5.346590	5.395945
H	5.920344	5.771556	5.312452
C	4.838648	6.136101	3.450170
H	5.713244	6.017791	2.777871
H	3.980756	5.697530	2.896421
C	4.582353	7.633912	3.697298
H	5.445996	8.033331	4.262935
C	6.504611	-0.331912	6.900834
H	7.463625	-0.528410	6.383462
H	6.586958	-0.575371	7.974478
H	5.709675	-0.937291	6.423716
O	6.175913	1.073634	6.846361
N	5.592725	3.556474	6.830080
N	5.501577	4.067341	7.843485
C	4.510998	8.383084	2.360571
H	5.436857	8.240571	1.766814
H	3.661657	8.012563	1.747950
H	4.365560	9.471831	2.513151
C	3.315386	7.885308	4.526087

H	2.421048	7.479207	4.007366
H	3.363631	7.416895	5.529182
H	3.147393	8.970387	4.679910

Secondary:

C	5.990070	1.575759	5.600799
C	5.726985	3.031413	5.637650
C	5.484510	3.880253	4.433290
C	5.226082	5.358565	4.689722
O	6.057842	0.900547	4.598851
O	5.497819	3.390530	3.317693
H	4.379255	5.447927	5.407149
H	6.106571	5.776309	5.229108
C	4.942085	6.155911	3.418543
H	5.793482	6.039667	2.715805
H	4.067251	5.712499	2.897820
C	4.689355	7.641617	3.698040
H	5.566880	8.071329	4.212400
H	3.847514	7.743282	4.405620
C	6.405941	-0.323907	6.946220
H	7.344506	-0.576510	6.415633
H	6.496184	-0.552809	8.022430
H	5.573556	-0.897406	6.494211
O	6.145878	1.094900	6.872278
N	5.700240	3.605026	6.822245
N	5.665682	4.137680	7.827940
C	4.392112	8.442633	2.429868
H	5.238238	8.388414	1.713587
H	3.493866	8.048059	1.911199
H	4.207472	9.512449	2.653744

Diazo-malonate substrate

C	5.769758	1.522762	5.375458
C	5.570198	2.986153	5.341512
C	5.436919	3.781462	4.104350
O	5.257738	5.098967	4.414875
O	5.848346	0.806535	4.402043
O	5.479217	3.333923	2.979812
C	5.106642	5.984021	3.272437
H	6.002712	5.897988	2.624316
H	4.231994	5.658131	2.672645
C	4.928307	7.403281	3.806909
H	5.812542	7.671379	4.421980
H	4.044882	7.428488	4.478104
C	6.041276	-0.337551	6.831945
H	6.974889	-0.636932	6.332994
H	5.213409	-0.867137	6.338189
C	4.755913	8.387739	2.669239
C	5.879091	8.958027	2.034923
C	3.472113	8.707429	2.181365
C	5.724488	9.826745	0.943112
H	6.888840	8.720805	2.406844
C	3.313260	9.576657	1.090404
H	2.584938	8.271910	2.668505
C	4.439858	10.137501	0.466829
H	6.612245	10.265006	0.462504
H	2.303215	9.818548	0.726094
H	4.316201	10.817556	-0.389868
O	5.851961	1.093836	6.668591
N	5.503475	3.624455	6.494319
N	5.444082	4.173189	7.486122
C	6.082378	-0.622034	8.328377

H	6.910481	-0.042460	8.784793
H	5.138552	-0.265891	8.789127
C	6.269046	-2.102902	8.581751
C	5.156692	-2.967212	8.649654
C	7.560645	-2.655854	8.703276
C	5.328787	-4.347292	8.840348
C	7.736916	-4.035435	8.894311
C	6.620732	-4.885373	8.963765
H	4.141228	-2.548739	8.558862
H	8.439499	-1.992540	8.655302
H	4.448422	-5.005565	8.898046
H	8.752156	-4.449105	8.994926
H	6.757953	-5.966430	9.120177

Cyclized Products

Benzylic

O	-3.608908	0.951715	-0.319499
C	-4.649283	-0.029062	-0.635266
C	-4.073756	-1.361992	-0.128558
C	-2.567288	-1.155450	-0.334627
C	-2.421838	0.332435	-0.122459
C	-1.284209	0.984265	0.216796
C	-1.167410	2.425739	0.409906
O	-2.048108	3.266850	0.335527
O	0.141098	2.744029	0.715082
C	0.371429	4.146659	0.932733
C	-5.953188	0.383011	-0.009631
C	-7.162973	0.087890	-0.664944
C	-8.391857	0.395472	-0.058979
C	-8.416936	1.013503	1.202177
C	-7.209567	1.321222	1.853717

C	-5.981554	1.005141	1.253684
H	-4.750979	-0.045696	-1.734607
H	-4.492274	-2.226663	-0.675562
H	-4.315596	-1.478093	0.946165
H	-2.270868	-1.408265	-1.375844
H	-1.924792	-1.741670	0.347517
H	-0.385258	0.386613	0.356148
H	1.447540	4.243286	1.164842
H	-0.240621	4.522893	1.776730
H	0.116452	4.735979	0.029169
H	-7.140930	-0.381625	-1.661214
H	-9.333111	0.161022	-0.578817
H	-9.378722	1.264750	1.674267
H	-7.224896	1.815901	2.836509
H	-5.034697	1.260941	1.750637

Tertiary

O	-3.636469	0.918956	-0.241249
C	-4.676166	-0.032373	-0.699052
C	-4.070586	-1.407911	-0.356684
C	-2.560561	-1.160814	-0.475265
C	-2.440117	0.307822	-0.137004
C	-1.297831	0.944059	0.222679
C	-1.182806	2.370227	0.499795
O	-2.061832	3.216563	0.472236
O	0.128386	2.672597	0.817076
C	0.360661	4.062076	1.101726
H	-4.442118	-2.202508	-1.029960
H	-4.337360	-1.682902	0.682816
H	-2.197536	-1.333308	-1.510438
H	-1.945360	-1.790064	0.194024

H	-0.391540	0.345949	0.298754
H	1.439457	4.148308	1.326025
H	-0.240693	4.395600	1.971161
H	0.094761	4.696283	0.232217
C	-5.938094	0.302162	0.081179
H	-6.751833	-0.399100	-0.191475
H	-5.754743	0.226085	1.170326
H	-6.276355	1.332037	-0.144077
C	-4.855468	0.183914	-2.201584
H	-3.929807	-0.054061	-2.760867
H	-5.671893	-0.457060	-2.590271
H	-5.113141	1.240728	-2.405568

Secondary

O	-3.642895	0.938851	-0.226022
C	-4.678390	-0.014412	-0.644575
C	-4.077679	-1.385970	-0.322281
C	-2.577039	-1.135153	-0.529575
C	-2.441091	0.324457	-0.159863
C	-1.292157	0.953214	0.187687
C	-1.173072	2.371572	0.505593
O	-2.054997	3.214577	0.527056
O	0.144074	2.666767	0.800751
C	0.380547	4.046999	1.125655
H	-4.788409	0.108658	-1.737370
H	-4.489463	-2.185143	-0.966413
H	-4.289392	-1.645204	0.735074
H	-2.295947	-1.268778	-1.596771
H	-1.913800	-1.782984	0.072287
H	-0.383634	0.354926	0.226173
H	1.463581	4.127780	1.330534

H	-0.203325	4.350547	2.017613
H	0.095914	4.708194	0.282615
C	-5.969672	0.343008	0.058597
H	-6.779043	-0.343245	-0.262845
H	-5.850265	0.261227	1.157198
H	-6.276989	1.378488	-0.183644

Malonate derivative

O	-3.676295	1.100363	-0.106771
C	-4.661685	0.129322	-0.570491
C	-4.023567	-1.189717	-0.119185
O	-2.611799	-0.881279	-0.101639
C	-2.497782	0.467187	0.058411
C	-1.312093	1.053278	0.352418
C	-1.130802	2.491177	0.463214
O	-1.969359	3.367995	0.321295
O	0.186607	2.762352	0.772780
C	0.499628	4.165145	0.905233
C	-6.016543	0.410549	0.013957
C	-7.169104	0.128041	-0.742471
C	-8.444367	0.315821	-0.185238
C	-8.572216	0.801091	1.126613
C	-7.421882	1.095619	1.879653
C	-6.147033	0.897455	1.329158
H	-4.694083	0.193258	-1.671093
H	-4.191296	-2.026982	-0.819888
H	-4.354861	-1.471993	0.901391
H	-0.459447	0.397891	0.508374
H	-0.164410	4.628482	1.664708
H	0.299931	4.685013	-0.055579
H	-7.067117	-0.237467	-1.776525

H	-9.341162	0.092423	-0.782458
H	-9.570909	0.959814	1.560922
H	-7.518784	1.489161	2.902504
H	-5.244962	1.143530	1.907766
C	1.971473	4.275939	1.305001
H	2.123949	3.731826	2.260410
H	2.591779	3.766535	0.539079
C	2.395311	5.721499	1.448362
C	2.199143	6.413247	2.662081
C	2.943966	6.425577	0.356357
C	2.546944	7.767670	2.784140
C	3.294418	7.779965	0.473914
C	3.096843	8.455983	1.689445
H	1.771860	5.878137	3.525818
H	3.104008	5.899254	-0.598731
H	2.389739	8.288884	3.741354
H	3.726883	8.309888	-0.388886
H	3.374595	9.516681	1.785106

Fe(acac)₂ stabilized vinyl C-based radicals

Tertiary (*S* = 2)

Fe	1.916415	3.807051	3.663892
C	-0.601398	0.649914	5.237611
C	0.003737	2.032932	5.120988
C	-0.089836	2.938336	6.207142
C	0.336264	4.286649	6.144205
C	0.112862	5.211171	7.320123
C	3.682639	3.540545	6.071449
C	4.159821	4.834423	5.812510
C	3.981840	5.633194	4.713079
C	4.613916	6.996121	4.610571

C	3.114573	1.080446	0.539832
C	2.391216	2.238723	1.190985
C	1.322601	2.876901	0.514573
C	0.632698	4.003547	1.012137
C	-0.444227	4.666486	0.183413
O	0.568676	2.299011	4.003568
O	0.918939	4.812569	5.129912
O	3.034151	2.863148	5.226833
O	3.271082	5.234464	3.696174
O	2.820526	2.579381	2.348709
O	0.863676	4.549141	2.152786
H	0.199437	-0.105996	5.103574
H	-1.329032	0.495594	4.414591
H	-1.104868	0.480608	6.207945
H	-0.602688	2.600789	7.117560
H	1.100382	5.550680	7.695298
H	-0.427834	6.117422	6.981022
H	-0.446085	4.732854	8.145976
H	3.790666	7.736036	4.495048
H	5.136814	7.219742	5.560996
H	3.005929	0.181973	1.181921
H	4.199119	1.307417	0.488032
H	2.736491	0.853201	-0.473472
H	1.046025	2.504261	-0.479675
H	-1.391097	4.678678	0.760969
H	-0.611168	4.161067	-0.785476
H	-0.167269	5.725002	0.001844
C	5.561141	7.098344	3.402568
H	6.411811	6.394930	3.541062
H	5.011981	6.749817	2.503549

C	6.109121	8.513177	3.145721
H	5.241437	9.193050	3.051629
C	3.393444	1.717649	7.536724
H	3.824552	0.969126	6.843978
H	3.662543	1.476052	8.580274
H	2.293058	1.738733	7.406170
O	3.953279	3.027231	7.290988
C	6.881701	8.549624	1.820594
H	7.761928	7.873507	1.857640
H	6.245393	8.224125	0.972494
H	7.253855	9.569635	1.594665
C	6.987656	9.016796	4.298598
H	6.436250	9.064825	5.258695
H	7.860157	8.344882	4.444837
H	7.378364	10.033729	4.091224

Secondary ($S = 2$)

Fe	1.898460	3.805220	3.623162
C	-0.557201	0.649256	5.290393
C	0.030269	2.036607	5.142396
C	-0.054533	2.957638	6.215715
C	0.355374	4.309590	6.123874
C	0.140516	5.250741	7.288019
C	3.704761	3.592631	6.010072
C	4.158174	4.890643	5.728601
C	3.952453	5.671060	4.621244
C	4.556278	7.043711	4.490467
C	3.039712	1.025330	0.528839
C	2.329085	2.196271	1.170997
C	1.245069	2.818630	0.504646
C	0.565288	3.955806	0.993143

C	-0.526145	4.604904	0.172543
O	0.573180	2.291271	4.011222
O	0.915275	4.824639	5.091551
O	3.052917	2.895209	5.185100
O	3.240388	5.244648	3.616174
O	2.784134	2.563143	2.311244
O	0.817643	4.522152	2.119011
H	0.249808	-0.099712	5.154272
H	-1.296381	0.474637	4.482081
H	-1.042805	0.489278	6.271300
H	-0.548011	2.629071	7.140005
H	1.129621	5.612740	7.637274
H	-0.421725	6.142105	6.943668
H	-0.394679	4.778864	8.133060
H	3.720988	7.760143	4.327855
H	5.053224	7.317038	5.443429
H	2.945882	0.140407	1.191586
H	4.122389	1.252386	0.448466
H	2.639858	0.777071	-0.471175
H	0.949426	2.426136	-0.476424
H	-1.465441	4.618514	0.762453
H	-0.703970	4.089547	-0.788953
H	-0.256402	5.662738	-0.022975
C	5.542752	7.133596	3.313009
H	6.388353	6.434084	3.490399
H	5.033236	6.777180	2.393193
C	6.081525	8.550606	3.094816
H	6.571725	8.902927	4.019233
H	5.234146	9.236443	2.923080
C	3.471805	1.783610	7.503733

H	3.906214	1.032564	6.815990
H	3.760008	1.562014	8.546496
H	2.369488	1.782525	7.389244
O	4.004855	3.099097	7.231246
C	7.063941	8.641271	1.925621
H	7.943573	7.984665	2.087237
H	6.586985	8.323258	0.975365
H	7.438944	9.674545	1.782781

Malonate Derivative ($S = 2$)

Fe	2.864394	3.002254	3.771420
C	0.820704	-0.078179	5.919586
C	1.381738	1.298120	5.658617
C	1.573033	2.201185	6.728048
C	2.048152	3.527466	6.575849
C	2.169557	4.426831	7.786232
C	5.476124	2.551667	5.222427
C	5.938209	3.800785	4.846605
C	5.368505	4.679064	3.939017
O	6.027063	5.834776	3.685225
C	4.065036	1.763756	-0.159784
C	3.301970	2.530414	0.896941
C	2.628271	3.729318	0.557378
C	1.802802	4.448860	1.451467
C	1.068714	5.683892	0.982030
O	1.652732	1.570646	4.430468
O	2.403890	4.045945	5.459884
O	4.382129	2.049878	4.798375
O	4.268915	4.453316	3.336276
O	3.306793	2.016032	2.071281
O	1.614855	4.122673	2.680556

H	1.536059	-0.834184	5.540236
H	-0.122319	-0.206668	5.350148
H	0.639563	-0.267880	6.993122
H	1.295810	1.859766	7.733171
H	3.235421	4.706028	7.917729
H	1.612426	5.367907	7.606124
H	1.798976	3.951388	8.713069
H	3.696851	0.718380	-0.190042
H	5.135572	1.717612	0.128760
H	3.976986	2.215653	-1.165126
H	2.693173	4.081219	-0.480815
H	0.004334	5.623047	1.285184
H	1.139029	5.835852	-0.111318
H	1.499131	6.569255	1.494641
C	5.376667	6.712771	2.732507
H	5.372468	6.234087	1.731245
H	4.319918	6.864061	3.029812
C	6.140005	8.033405	2.711662
H	7.192078	7.843062	2.453574
H	6.124860	8.469772	3.722277
C	5.650271	0.595099	6.549982
H	6.510171	-0.023176	6.872453
H	5.142269	0.099895	5.701530
C	5.510093	8.977675	1.714865
C	6.036138	9.116255	0.415104
C	4.341561	9.692666	2.050148
C	5.413092	9.950575	-0.527378
H	6.950520	8.565829	0.142063
C	3.713109	10.524062	1.109864
H	3.921634	9.596200	3.064655

C	4.247849	10.655221	-0.183279
H	5.841723	10.052427	-1.536287
H	2.801412	11.074627	1.388391
H	3.757874	11.308727	-0.921240
O	6.242320	1.836374	6.086060
C	4.675039	0.870901	7.691588
H	5.233031	1.266965	8.566678
H	3.995847	1.685813	7.362186
C	3.799829	-0.288209	8.120421
C	2.903679	-0.102072	9.197621
C	3.799263	-1.538044	7.468471
C	2.029204	-1.120860	9.601055
C	2.926257	-2.564343	7.871720
C	2.034716	-2.360179	8.935226
H	2.896336	0.864922	9.726098
H	4.483333	-1.723372	6.627197
H	1.341101	-0.949853	10.443517
H	2.945180	-3.531149	7.345545
H	1.351264	-3.163449	9.249962

Tertiary ($S = 3$)

Fe	1.893906	3.804777	3.636358
C	-0.610455	0.673849	5.291281
C	-0.000617	2.052193	5.147801
C	-0.074971	2.972473	6.223472
C	0.357188	4.316674	6.136110
C	0.168408	5.257162	7.304451
C	3.631912	3.554538	6.051067
C	4.003609	4.891157	5.816438
C	3.907126	5.651174	4.676855
C	4.564368	7.005130	4.584301

C	3.072844	1.046590	0.526474
C	2.352136	2.209707	1.172027
C	1.289324	2.851069	0.488681
C	0.602279	3.980854	0.981801
C	-0.463630	4.652962	0.146371
O	0.550052	2.301217	4.019957
O	0.923788	4.825983	5.103244
O	3.027083	2.835864	5.210824
O	3.253405	5.241853	3.630120
O	2.778201	2.552214	2.329960
O	0.827048	4.521808	2.126485
H	0.184687	-0.087697	5.155156
H	-1.350734	0.512905	4.481100
H	-1.100681	0.519514	6.270807
H	-0.572137	2.648458	7.147306
H	1.169714	5.574355	7.663281
H	-0.352128	6.173865	6.961865
H	-0.392079	4.801198	8.141753
H	3.757151	7.751931	4.411823
H	5.034367	7.241235	5.558800
H	2.964749	0.152112	1.173892
H	4.157365	1.272619	0.470411
H	2.692493	0.814142	-0.484956
H	1.015778	2.477896	-0.506287
H	-1.414300	4.675582	0.717241
H	-0.628550	4.149023	-0.823493
H	-0.174229	5.708302	-0.034678
C	5.578037	7.076144	3.429926
H	6.433986	6.399925	3.649415
H	5.091025	6.675151	2.517073

C	6.109233	8.490664	3.137790
H	5.235757	9.129544	2.907548
C	3.528690	1.695430	7.497552
H	4.007242	0.998303	6.783072
H	3.841934	1.463313	8.530758
H	2.428313	1.618632	7.392344
O	3.962802	3.052855	7.261816
C	7.017779	8.468504	1.902859
H	7.911629	7.834618	2.082488
H	6.490387	8.057100	1.017903
H	7.375609	9.485246	1.642327
C	6.840410	9.103789	4.339030
H	6.180843	9.203653	5.223907
H	7.707951	8.476322	4.635963
H	7.226565	10.114835	4.098184

Secondary ($S = 3$)

Fe	1.849812	3.790896	3.620142
C	-0.576256	0.660258	5.380094
C	0.009649	2.044379	5.198732
C	-0.066123	2.986853	6.254672
C	0.342504	4.336010	6.132565
C	0.146487	5.299794	7.280417
C	3.630142	3.613566	6.017798
C	3.974741	4.952267	5.753414
C	3.850035	5.687845	4.600893
C	4.482871	7.049814	4.469614
C	3.130151	1.058084	0.520466
C	2.366636	2.196021	1.161789
C	1.299859	2.814558	0.463333
C	0.570739	3.918256	0.953872

C	-0.505149	4.561475	0.108666
O	0.540265	2.277191	4.057591
O	0.891514	4.830894	5.083533
O	3.024558	2.869628	5.201471
O	3.189373	5.247123	3.571099
O	2.760936	2.538285	2.330702
O	0.760681	4.456715	2.106237
H	0.226696	-0.092447	5.241222
H	-1.330645	0.474237	4.588586
H	-1.044171	0.517538	6.372123
H	-0.547681	2.675534	7.191020
H	1.143761	5.653486	7.615279
H	-0.404891	6.192765	6.923287
H	-0.388683	4.850161	8.137383
H	3.662469	7.780388	4.293012
H	4.968208	7.321191	5.429017
H	3.031352	0.154091	1.156043
H	4.209472	1.312160	0.490625
H	2.777771	0.826581	-0.501279
H	1.054311	2.441987	-0.539214
H	-1.470224	4.520568	0.654434
H	-0.621225	4.076857	-0.878001
H	-0.264889	5.634700	-0.035026
C	5.486261	7.118535	3.306616
H	6.317593	6.405209	3.496689
H	4.983910	6.768305	2.380550
C	6.052420	8.525485	3.092250
H	6.536989	8.871458	4.022061
H	5.219083	9.225418	2.909053
C	3.584020	1.780926	7.501177

H	4.053342	1.079288	6.785083
H	3.927593	1.570426	8.529293
H	2.482544	1.686563	7.426806
O	3.990209	3.140963	7.232615
C	7.050232	8.597881	1.935130
H	7.917742	7.928335	2.108867
H	6.580464	8.285060	0.979613
H	7.442975	9.624886	1.794365

Malonate Derivative ($S = 3$)

Fe	2.860317	2.994711	3.420056
C	0.869967	-0.042777	5.657377
C	1.409909	1.336585	5.360914
C	1.701598	2.223073	6.423025
C	2.173133	3.547328	6.245488
C	2.427968	4.427892	7.446827
C	5.148323	2.593601	5.236411
C	5.585567	3.884409	4.972751
C	5.220937	4.708809	3.915520
O	5.844837	5.907449	3.825159
C	3.930384	1.600715	-0.497216
C	3.219991	2.431721	0.546800
C	2.554875	3.625032	0.176433
C	1.798008	4.415055	1.071477
C	1.088450	5.655187	0.578417
O	1.584619	1.619394	4.118792
O	2.428699	4.072713	5.104978
O	4.313630	1.969848	4.503323
O	4.336314	4.405384	3.049353
O	3.260232	1.973982	1.744595
O	1.657055	4.153636	2.322217

H	1.560054	-0.795524	5.224554
H	-0.108406	-0.178267	5.153157
H	0.762740	-0.233876	6.741033
H	1.504245	1.876158	7.444742
H	3.513260	4.657991	7.483115
H	1.899136	5.393666	7.322508
H	2.119683	3.957275	8.398771
H	3.528765	0.567374	-0.476671
H	5.006101	1.530956	-0.234271
H	3.828677	2.015931	-1.516984
H	2.586020	3.926831	-0.878953
H	0.037628	5.647374	0.930310
H	1.113486	5.755101	-0.522843
H	1.571940	6.546129	1.030521
C	5.349947	6.781101	2.779889
H	5.630047	6.369363	1.788435
H	4.243079	6.818227	2.824429
C	5.955636	8.163999	2.996058
H	7.052720	8.095025	2.955380
H	5.686819	8.514588	4.004255
C	4.978816	0.753194	6.724927
H	5.491303	-0.093635	6.222434
H	3.933201	0.780242	6.366375
C	5.441030	9.122096	1.947229
C	6.177710	9.372893	0.772544
C	4.179497	9.734883	2.097558
C	5.669917	10.218092	-0.227850
H	7.165014	8.901284	0.645687
C	3.667156	10.578608	1.099283
H	3.595268	9.547997	3.013029

C	4.411908	10.822226	-0.067710
H	6.261776	10.407629	-1.136743
H	2.682444	11.051728	1.233533
H	4.013459	11.485064	-0.851182
O	5.635021	1.992446	6.352043
C	5.009027	0.618795	8.249227
H	6.037121	0.390065	8.600707
H	4.722210	1.594250	8.690119
C	4.027760	-0.450028	8.679635
C	2.790034	-0.099682	9.257774
C	4.287764	-1.814312	8.430512
C	1.834702	-1.079521	9.572642
C	3.334316	-2.797474	8.739925
C	2.102107	-2.433078	9.308976
H	2.579416	0.960530	9.470702
H	5.252278	-2.111108	7.988309
H	0.877533	-0.783774	10.029015
H	3.555674	-3.856540	8.535644
H	1.354862	-3.203278	9.553601

In Situ generated C(sp³)-based radical

Benzylic ($S = 2$)

Fe	1.634354	3.785997	4.424154
C	-0.523555	0.188312	4.948791
C	-0.125447	1.629283	5.168410
C	-0.817431	2.430673	6.100830
C	-0.486251	3.774523	6.365651
C	-1.256384	4.565627	7.396626
C	4.262913	3.680644	5.902051
C	4.628646	4.900609	5.251923
C	3.731210	5.729014	4.601212

C	4.211974	7.033899	4.004738
C	4.341340	3.232830	1.270906
C	3.026621	3.602814	1.917930
C	2.054260	4.324455	1.204548
C	0.763199	4.656231	1.704317
C	-0.219883	5.379289	0.805229
O	0.866020	2.025617	4.451627
O	0.462527	4.431100	5.791121
O	3.130194	3.160341	5.960927
O	2.463440	5.503104	4.419892
O	2.904499	3.186767	3.136557
O	0.351644	4.375780	2.877335
H	0.330936	-0.471852	5.203102
H	-0.743590	0.028530	3.873791
H	-1.402240	-0.104682	5.551667
H	-1.648785	1.980476	6.657916
H	-0.551618	4.962047	8.155453
H	-1.727495	5.443238	6.908790
H	-2.036506	3.962556	7.895988
H	5.665256	5.216499	5.338589
H	3.617023	7.864401	4.438540
H	5.273129	7.205127	4.268531
H	4.443868	2.128674	1.241134
H	5.173429	3.614133	1.897493
H	4.435413	3.635068	0.245642
H	2.293718	4.611002	0.172593
H	-1.153270	4.785634	0.728915
H	0.179805	5.566854	-0.208477
H	-0.493149	6.346656	1.273502
C	4.038248	7.032411	2.460327

H	4.553702	6.141391	2.048840
H	2.960381	6.889190	2.244200
C	4.542687	8.278526	1.823742
H	3.884489	9.152740	1.841020
C	5.007424	1.846713	7.197236
H	4.567604	1.115472	6.490969
H	5.968775	1.474167	7.593832
H	4.288595	2.013996	8.023465
C	5.828321	8.448735	1.259680
C	6.811141	7.403436	1.238086
C	6.199297	9.706862	0.676135
C	8.067383	7.609455	0.666276
H	6.573248	6.427521	1.684865
C	7.456573	9.900085	0.106183
H	5.462386	10.525769	0.681608
C	8.404229	8.853657	0.093478
H	8.803782	6.790157	0.665081
H	7.710505	10.875343	-0.337296
H	9.396127	9.007256	-0.356900
O	5.317642	3.082660	6.527383

Tertiary ($S = 2$)

Fe	1.895960	3.805280	3.655081
C	-0.479105	0.600092	5.337894
C	0.085232	1.997499	5.192841
C	0.021021	2.901444	6.281597
C	0.407829	4.260825	6.196843
C	0.214215	5.180773	7.382015
C	3.745861	3.574330	5.970543
C	4.189128	4.915009	5.815697
C	3.936910	5.657850	4.666173

C	4.537717	7.029810	4.505571
C	2.939776	1.103474	0.453748
C	2.248694	2.258391	1.145059
C	1.144102	2.894934	0.527949
C	0.481939	4.020773	1.065447
C	-0.634109	4.689901	0.295112
O	0.588937	2.276092	4.049160
O	0.927680	4.800244	5.156552
O	3.088301	2.894134	5.143277
O	3.241483	5.237151	3.661454
O	2.739887	2.600391	2.277643
O	0.770756	4.558620	2.196148
H	0.333403	-0.135710	5.167487
H	-1.239157	0.427106	4.548860
H	-0.933598	0.419527	6.330041
H	-0.437935	2.552221	7.215979
H	1.209834	5.539158	7.716417
H	-0.357544	6.076369	7.065775
H	-0.300601	4.692145	8.230230
H	4.784251	5.347570	6.616269
H	3.728408	7.728773	4.209762
H	4.963126	7.379862	5.466505
H	2.885635	0.208247	1.106774
H	4.015200	1.343040	0.326497
H	2.497483	0.865863	-0.530952
H	0.816792	2.524937	-0.451761
H	-1.554212	4.689634	0.914674
H	-0.842873	4.197279	-0.672111
H	-0.369251	5.751945	0.116168
C	5.640174	7.035802	3.397137

H	6.438655	6.325985	3.702333
H	5.176333	6.632312	2.471965
C	6.210465	8.394718	3.155627
C	3.621366	1.663454	7.357780
H	4.038629	0.973170	6.599270
H	3.964092	1.378299	8.368401
H	2.515197	1.636079	7.294717
O	4.104075	3.006899	7.153489
C	7.307456	8.897149	4.033995
H	6.918286	9.376182	4.969501
H	7.984464	8.080646	4.360699
H	7.918230	9.676001	3.529012
C	5.415086	9.378437	2.363348
H	4.853629	8.890620	1.539715
H	4.652344	9.908810	2.990245
H	6.054730	10.174215	1.926639

Secondary ($S = 2$)

Fe	1.664450	3.718525	4.452530
C	-1.139657	0.595605	4.984619
C	-0.497197	1.951034	5.169982
C	-1.099169	2.921147	5.998678
C	-0.544748	4.195036	6.232903
C	-1.225073	5.168441	7.166687
C	4.147463	3.295711	6.117852
C	4.736698	4.415295	5.454491
C	4.026481	5.326078	4.691546
C	4.736550	6.510998	4.077943
C	4.372702	2.525132	1.478214
C	3.116422	3.153167	2.037165
C	2.310883	3.981615	1.235620

C	1.072614	4.551168	1.646741
C	0.270986	5.379769	0.662650
O	0.603229	2.115741	4.525060
O	0.548645	4.634894	5.711478
O	2.949049	2.946421	6.103197
O	2.759415	5.274855	4.405044
O	2.876837	2.842805	3.269322
O	0.566672	4.410426	2.807567
H	-0.430065	-0.194730	5.303123
H	-1.341350	0.430574	3.906665
H	-2.080922	0.493844	5.554181
H	-2.039997	2.663722	6.500990
H	-0.523176	5.447975	7.978503
H	-1.464101	6.100204	6.615114
H	-2.151377	4.756094	7.605978
H	5.796591	4.589219	5.623985
H	4.128362	7.419038	4.266656
H	5.727023	6.653611	4.552829
H	4.287015	1.419656	1.523481
H	5.233721	2.808478	2.117030
H	4.568657	2.832875	0.434608
H	2.638903	4.157413	0.202923
H	-0.767746	4.995271	0.616851
H	0.708225	5.386527	-0.353199
H	0.210464	6.422562	1.037499
C	4.897918	6.322889	2.536624
H	5.505047	5.406239	2.368477
H	3.889410	6.121198	2.121487
C	5.532748	7.490839	1.869547
H	4.898032	8.342249	1.610126

C	4.506875	1.447447	7.549644
H	4.035382	0.740712	6.838656
H	5.364992	0.972270	8.058218
H	3.744386	1.761144	8.289541
O	5.050292	2.585676	6.855644
C	7.009129	7.667292	1.826346
H	7.426168	8.026007	2.802145
H	7.531097	6.708576	1.614042
H	7.322620	8.410329	1.064955

Malonate Derivative ($S = 2$)

Fe	2.792557	3.062743	3.432199
C	0.746274	-0.022593	5.746411
C	1.247711	1.343366	5.326206
C	1.410903	2.353269	6.321546
C	1.857090	3.660108	6.068919
C	1.927880	4.683589	7.176521
C	4.970933	2.955396	5.277097
C	5.421056	4.257371	5.074924
C	5.043716	5.007618	3.933640
O	5.645271	6.235669	3.882260
C	3.724348	1.093473	-0.169650
C	2.984681	2.016454	0.769169
C	1.884937	2.771638	0.315720
C	1.168110	3.667299	1.136339
C	0.002735	4.452509	0.582560
O	1.521120	1.504312	4.093605
O	2.239906	4.108640	4.915053
O	4.184787	2.279491	4.523371
O	4.254965	4.672899	3.015712
O	3.453361	2.039750	1.969744

O	1.424436	3.893488	2.377555
H	1.623545	-0.683671	5.916245
H	0.141488	-0.470968	4.934984
H	0.166335	0.008411	6.687850
H	1.103053	2.113918	7.347711
H	2.982639	5.007914	7.292531
H	1.344092	5.582697	6.894551
H	1.553698	4.290401	8.139468
H	6.106285	4.696764	5.794231
H	3.676748	0.056727	0.222097
H	4.795788	1.378857	-0.192213
H	3.313710	1.116932	-1.195552
H	1.577758	2.664145	-0.732347
H	-0.904097	4.229939	1.180939
H	-0.194103	4.222898	-0.480523
H	0.203120	5.537971	0.694559
C	5.261344	7.063143	2.765374
H	5.595890	6.583864	1.816432
H	4.148288	7.104768	2.704583
C	5.868184	8.404731	2.959590
H	6.366644	8.582934	3.913990
C	4.821481	1.056422	6.696398
H	5.261885	0.268934	6.049113
H	3.740167	1.113351	6.468018
C	5.815505	9.442540	2.004643
C	5.166067	9.287773	0.734409
C	6.421621	10.712364	2.284776
C	5.133401	10.337175	-0.185725
H	4.686640	8.330670	0.481173
C	6.382268	11.751731	1.356860

H	6.922574	10.852710	3.255255
C	5.738561	11.575500	0.112811
H	4.629757	10.194917	-1.154517
H	6.856192	12.716012	1.596921
H	5.708980	12.397768	-0.618215
O	5.435041	2.333088	6.396456
C	5.030344	0.747929	8.178400
H	6.107189	0.589634	8.393166
H	4.701037	1.626556	8.770282
C	4.214629	-0.469668	8.554311
C	2.862348	-0.330002	8.932595
C	4.750260	-1.769412	8.446537
C	2.068645	-1.454941	9.203706
C	3.959246	-2.898622	8.715356
C	2.615433	-2.744983	9.094256
H	2.430770	0.680073	9.017158
H	5.803399	-1.896849	8.148143
H	1.018428	-1.324624	9.506465
H	4.396305	-3.905467	8.628862
H	1.996031	-3.629011	9.308755

Benzylic ($S = 3$)

Fe	1.670706	3.678001	3.363037
C	0.035918	0.646346	5.983268
C	0.423873	2.033870	5.518088
C	0.520658	3.091941	6.454741
C	0.760399	4.439778	6.094400
C	0.758023	5.521172	7.151572
C	3.987941	3.904225	5.212022
C	4.250476	5.237353	4.792548
C	3.700862	5.776461	3.634331

C	4.122472	7.149348	3.169126
C	2.228719	0.644132	0.338901
C	1.601021	1.831187	1.035494
C	0.340443	2.316805	0.610256
C	-0.291593	3.455763	1.156641
C	-1.603125	3.947296	0.586682
O	0.636781	2.158122	4.261438
O	0.986418	4.837029	4.896596
O	3.248202	3.064627	4.641641
O	2.860725	5.166010	2.866295
O	2.287099	2.340116	1.990806
O	0.179494	4.147476	2.131847
H	0.870857	-0.052307	5.767750
H	-0.835902	0.293350	5.396269
H	-0.206329	0.605834	7.061524
H	0.309606	2.870104	7.509342
H	1.766100	5.984410	7.183356
H	0.046907	6.320923	6.861669
H	0.498390	5.141985	8.157350
H	4.947848	5.826497	5.382991
H	3.210571	7.757614	2.996428
H	4.728218	7.656878	3.944822
H	2.359487	-0.176979	1.073526
H	3.242421	0.921009	-0.014077
H	1.627660	0.280149	-0.514555
H	-0.150938	1.809549	-0.229976
H	-2.378247	3.914906	1.380404
H	-1.942034	3.351871	-0.280789
H	-1.496448	5.009371	0.286769
C	4.934221	7.060194	1.842265

H	5.810870	6.399709	2.014480
H	4.297802	6.554950	1.088499
C	5.364897	8.400720	1.352948
H	4.700973	8.923850	0.659222
C	4.358231	2.213612	6.823294
H	4.682003	1.454701	6.084925
H	4.929664	2.107921	7.762291
H	3.272660	2.091125	7.008131
C	6.520717	9.089988	1.788065
C	7.441701	8.533350	2.737201
C	6.810647	10.402348	1.285247
C	8.568344	9.247469	3.147807
H	7.258070	7.528852	3.144414
C	7.940411	11.104703	1.701283
H	6.116468	10.850028	0.556011
C	8.830646	10.535632	2.637424
H	9.260055	8.798088	3.877768
H	8.138354	12.109492	1.297516
H	9.721888	11.091400	2.965154
O	4.640050	3.546459	6.349676

Tertiary ($S = 3$)

Fe	1.895930	3.805291	3.655056
C	-0.479095	0.600106	5.337922
C	0.085233	1.997517	5.192856
C	0.021035	2.901462	6.281610
C	0.407853	4.260840	6.196854
C	0.214270	5.180785	7.382033
C	3.745828	3.574341	5.970522
C	4.189074	4.915029	5.815685
C	3.936858	5.657868	4.666161

C	4.537667	7.029828	4.505561
C	2.939841	1.103566	0.453683
C	2.248711	2.258439	1.145022
C	1.144087	2.894943	0.527930
C	0.481870	4.020741	1.065450
C	-0.634225	4.689815	0.295137
O	0.588916	2.276105	4.049163
O	0.927693	4.800260	5.156558
O	3.088284	2.894134	5.143252
O	3.241443	5.237164	3.661435
O	2.739898	2.600439	2.277609
O	0.770672	4.558588	2.196155
H	0.333415	-0.135693	5.167512
H	-1.239156	0.427110	4.548898
H	-0.933575	0.419545	6.330077
H	-0.437906	2.552239	7.215999
H	1.209898	5.539169	7.716411
H	-0.357499	6.076381	7.065810
H	-0.300525	4.692155	8.230261
H	4.784185	5.347595	6.616262
H	3.728377	7.728781	4.209678
H	4.963019	7.379905	5.466510
H	2.885756	0.208327	1.106697
H	4.015250	1.343188	0.326418
H	2.497543	0.865947	-0.531013
H	0.816784	2.524946	-0.451782
H	-1.554327	4.689464	0.914701
H	-0.842956	4.197204	-0.672098
H	-0.369441	5.751883	0.116222
C	5.640199	7.035779	3.397199

H	6.438660	6.325978	3.702484
H	5.176425	6.632247	2.472012
C	6.210506	8.394684	3.155665
C	3.621356	1.663463	7.357759
H	4.038639	0.973187	6.599254
H	3.964081	1.378315	8.368382
H	2.515188	1.636069	7.294689
O	4.104043	3.006916	7.153470
C	7.307447	8.897142	4.034082
H	6.918227	9.376133	4.969589
H	7.984474	8.080656	4.360790
H	7.918208	9.676029	3.529138
C	5.415188	9.378364	2.363278
H	4.853804	8.890506	1.539620
H	4.652388	9.908765	2.990081
H	6.054866	10.174123	1.926584

Secondary ($S = 3$)

Fe	1.929821	3.778390	3.571554
C	-0.502996	0.712972	5.422682
C	0.084819	2.090327	5.200474
C	0.023381	3.058693	6.232178
C	0.432738	4.404455	6.071171
C	0.243016	5.396182	7.197554
C	3.772507	3.653303	5.903897
C	4.245686	4.972076	5.668154
C	4.011008	5.647651	4.474971
C	4.649982	6.992120	4.229183
C	2.955882	0.910532	0.509120
C	2.274787	2.104610	1.141286
C	1.185867	2.728338	0.484295

C	0.535235	3.886681	0.963088
C	-0.563892	4.535896	0.152680
O	0.603528	2.291784	4.047101
O	0.971247	4.872731	5.006228
O	3.102708	2.937616	5.117662
O	3.301982	5.185777	3.499373
O	2.758772	2.489740	2.263035
O	0.821260	4.471536	2.070958
H	0.297032	-0.045140	5.296111
H	-1.264388	0.508711	4.642547
H	-0.962482	0.597145	6.422094
H	-0.450164	2.772800	7.180677
H	1.241415	5.751047	7.527410
H	-0.302402	6.284280	6.819903
H	-0.295680	4.969675	8.064119
H	4.852692	5.438547	6.440248
H	3.859647	7.702103	3.909443
H	5.103402	7.378911	5.162672
H	2.876885	0.044137	1.197718
H	4.036982	1.126816	0.387963
H	2.523054	0.640184	-0.471210
H	0.863137	2.319321	-0.481371
H	-1.490572	4.572845	0.761211
H	-0.768481	4.006427	-0.795747
H	-0.284121	5.586318	-0.066767
C	5.731705	6.898609	3.105488
H	6.496911	6.159468	3.430508
H	5.235739	6.480944	2.205162
C	6.373498	8.207573	2.805597
H	5.867166	8.883812	2.112083

C	3.609477	1.833029	7.405201
H	4.014092	1.090464	6.690485
H	3.947163	1.603475	8.431464
H	2.503006	1.822781	7.343075
O	4.117351	3.152717	7.120152
C	7.492595	8.737789	3.629856
H	7.147561	9.117805	4.625240
H	8.245922	7.950587	3.856196
H	8.012096	9.584474	3.137785

Malonate Derivative ($S = 3$)

Fe	2.847769	2.853187	3.445264
C	1.071620	-0.285919	5.708515
C	1.493318	1.129412	5.392230
C	1.686110	2.057208	6.440045
C	2.062094	3.410094	6.245409
C	2.210148	4.330982	7.435120
C	5.168699	2.657013	5.257796
C	5.614923	3.966060	5.021583
C	5.133165	4.688103	3.918194
O	5.673363	5.928988	3.758614
C	4.117040	1.603276	-0.449418
C	3.327884	2.374335	0.583665
C	2.652554	3.564994	0.222376
C	1.811325	4.287467	1.099837
C	1.069883	5.510321	0.608066
O	1.671323	1.401836	4.146879
O	2.309213	3.932256	5.102400
O	4.355163	1.996186	4.543333
O	4.260169	4.308970	3.080993
O	3.311055	1.869818	1.763296

O	1.610137	3.972846	2.328898
H	1.871082	-0.978638	5.372388
H	0.159936	-0.544553	5.132999
H	0.895715	-0.445589	6.788247
H	1.489468	1.714193	7.463482
H	3.269048	4.657559	7.494216
H	1.601993	5.243892	7.277521
H	1.919270	3.852951	8.388923
H	6.337478	4.421839	5.691838
H	3.750169	0.557500	-0.484153
H	5.179808	1.558738	-0.133567
H	4.053850	2.050637	-1.458569
H	2.732306	3.908031	-0.817696
H	-0.012831	5.399845	0.821975
H	1.216671	5.696889	-0.472232
H	1.417312	6.394626	1.181945
C	5.100165	6.702003	2.682195
H	5.298398	6.188844	1.712128
H	3.990847	6.713148	2.792073
C	5.678121	8.068372	2.721952
H	6.405359	8.280657	3.507221
C	5.037746	0.821149	6.759727
H	5.561450	-0.019882	6.258834
H	3.992408	0.831756	6.401278
C	5.319354	9.085928	1.811071
C	4.366077	8.871427	0.759784
C	5.903823	10.391472	1.914652
C	4.026912	9.900579	-0.120547
H	3.895006	7.883976	0.644576
C	5.556393	11.410412	1.029003

H	6.636547	10.578274	2.715603
C	4.615016	11.176330	0.003230
H	3.291535	9.712311	-0.918545
H	6.018961	12.404095	1.131758
H	4.340758	11.983240	-0.692894
O	5.670350	2.067976	6.381586
C	5.060279	0.687949	8.285242
H	6.075512	0.417088	8.644604
H	4.811090	1.675166	8.723107
C	4.029231	-0.335076	8.711171
C	2.834404	0.068089	9.343010
C	4.191716	-1.701593	8.397824
C	1.826445	-0.861342	9.647198
C	3.184572	-2.633797	8.694446
C	1.995749	-2.216284	9.317262
H	2.698074	1.129801	9.603213
H	5.121130	-2.040932	7.912902
H	0.903781	-0.524586	10.144601
H	3.329333	-3.694721	8.437958
H	1.206612	-2.946759	9.552137

N₂ loss Transition State

Benzylic

Fe	1.974474	4.147104	4.465141
C	-0.681435	0.960016	3.637472
C	-0.168016	2.227357	4.280667
C	-0.961951	2.932161	5.211003
C	-0.527859	4.096672	5.872612
C	-1.413738	4.781587	6.886231
C	4.146433	3.246521	6.420607
C	4.777329	4.479296	6.089059

C	4.224149	5.585331	5.494279
C	5.012983	6.832869	5.158858
C	5.097477	3.613830	1.690494
C	3.779111	4.134433	2.212705
C	3.055886	5.093684	1.482991
C	1.790667	5.610077	1.869538
C	1.113731	6.647736	0.999241
O	1.013747	2.574815	3.914591
O	0.616326	4.666231	5.699575
O	2.986708	2.928180	6.080238
O	2.981184	5.639021	5.093399
O	3.413552	3.620988	3.343537
O	1.160995	5.258972	2.923789
H	-0.010727	0.117482	3.902864
H	-0.644168	1.066969	2.533951
H	-1.713053	0.717007	3.950254
H	-1.958412	2.540491	5.449521
H	-0.871322	4.866868	7.849555
H	-1.625312	5.815365	6.545557
H	-2.367834	4.247317	7.044784
H	4.411987	7.709926	5.478725
H	5.980253	6.851071	5.691580
H	4.979419	2.556632	1.374043
H	5.847700	3.626048	2.506384
H	5.462457	4.211753	0.835557
H	3.506096	5.468300	0.555120
H	0.100172	6.295951	0.720293
H	1.692309	6.878261	0.086412
H	0.979908	7.578407	1.587980
C	5.186858	6.847090	3.632831

H	5.800977	5.975037	3.327359
H	4.191541	6.684903	3.178444
C	5.784897	8.114486	3.002174
H	6.838203	8.241984	3.298469
H	5.237172	9.001691	3.357017
C	4.282583	1.144132	7.482102
H	4.004121	0.601615	6.557790
H	5.042692	0.579466	8.051392
H	3.371426	1.295818	8.093072
C	5.655969	7.987228	1.502619
C	6.582826	7.223348	0.764162
C	4.528861	8.505458	0.833855
C	6.382373	6.971437	-0.602659
H	7.468751	6.812263	1.273960
C	4.326830	8.262829	-0.534609
H	3.792365	9.095248	1.402703
C	5.249536	7.486621	-1.256808
H	7.117524	6.372582	-1.162978
H	3.443453	8.682288	-1.040820
H	5.090745	7.289534	-2.328142
O	4.901251	2.406350	7.165329
N	6.633848	4.707095	6.489823
N	7.305383	3.865355	6.840697

Tertiary

Fe	1.840474	4.055164	4.509087
C	-0.778216	0.767105	4.065867
C	-0.239491	2.066030	4.618725
C	-0.949752	2.771924	5.613367
C	-0.488130	3.971215	6.189515
C	-1.276623	4.654990	7.280850

C	4.266880	3.324662	6.186289
C	4.782357	4.595585	5.795587
C	4.090877	5.666544	5.269028
C	4.748566	6.999276	4.994723
C	4.828589	3.743965	1.589406
C	3.496689	4.161517	2.164729
C	2.707545	5.134295	1.527268
C	1.414276	5.539921	1.962640
C	0.640926	6.561100	1.153869
O	0.883410	2.439501	4.115412
O	0.606464	4.573604	5.869060
O	3.082023	2.957456	6.027621
O	2.835749	5.627922	4.926407
O	3.179905	3.545876	3.258794
O	0.835513	5.091907	3.006457
H	-0.046210	-0.044495	4.255085
H	-0.886970	0.854548	2.965552
H	-1.751705	0.493219	4.510833
H	-1.898719	2.354225	5.971134
H	-0.635202	4.770075	8.178034
H	-1.549546	5.677021	6.949156
H	-2.193650	4.101162	7.551238
H	3.973933	7.770991	5.172816
H	5.591907	7.173202	5.688451
H	4.819861	2.654500	1.383588
H	5.618443	3.925080	2.346103
H	5.075758	4.289788	0.660877
H	3.097510	5.571119	0.599333
H	-0.360835	6.156568	0.906167
H	1.159561	6.855166	0.223035

H	0.477658	7.463222	1.778527
C	5.235782	7.059932	3.535724
H	6.017584	6.283127	3.396454
H	4.394707	6.783524	2.863717
C	5.802720	8.420843	3.096649
H	6.623270	8.686713	3.788577
C	4.653472	1.220427	7.178548
H	4.249495	0.678549	6.301507
H	5.518645	0.682731	7.605802
H	3.849312	1.325755	7.933059
O	5.161595	2.511094	6.788770
N	6.515275	4.987805	6.083961
N	7.311221	4.215575	6.369567
C	6.391229	8.301550	1.684419
H	6.829818	9.261153	1.342558
H	7.186306	7.528825	1.638178
H	5.602342	8.017054	0.955686
C	4.751319	9.535182	3.150987
H	3.890722	9.295453	2.491099
H	4.354992	9.692761	4.173444
H	5.175158	10.501963	2.811105

Secondary

Fe	1.790598	4.021844	4.381347
C	-0.856357	0.760812	3.913636
C	-0.322732	2.067439	4.453262
C	-1.063467	2.809452	5.398363
C	-0.609280	4.018015	5.960347
C	-1.434246	4.744424	6.995913
C	4.111455	3.297566	6.201583
C	4.654907	4.546919	5.796723

C	4.025241	5.616445	5.205145
C	4.735354	6.924263	4.939097
C	4.923754	3.621426	1.634338
C	3.568108	4.063355	2.131872
C	2.831795	5.042986	1.443141
C	1.517185	5.463058	1.794604
C	0.799464	6.475712	0.926160
O	0.824771	2.412696	3.987497
O	0.507380	4.595591	5.671105
O	2.933932	2.932266	5.987423
O	2.788773	5.593732	4.787946
O	3.179096	3.460012	3.209613
O	0.873512	5.031194	2.806053
H	-0.146694	-0.055262	4.159591
H	-0.913693	0.817257	2.807407
H	-1.853034	0.513902	4.321742
H	-2.032443	2.414337	5.727031
H	-0.828773	4.883843	7.914266
H	-1.683543	5.757208	6.620015
H	-2.366933	4.207918	7.246838
H	3.965556	7.722186	4.968423
H	5.483409	7.127275	5.728473
H	4.910169	2.530297	1.437455
H	5.674320	3.799325	2.430955
H	5.227817	4.155879	0.716097
H	3.281070	5.465770	0.535528
H	-0.176083	6.060289	0.602908
H	1.384363	6.773285	0.036434
H	0.577949	7.376942	1.533608
C	5.416821	6.910879	3.558244

H	6.188059	6.109917	3.543674
H	4.663724	6.638718	2.788747
C	6.064225	8.249857	3.195798
H	6.810378	8.514945	3.963870
H	5.297976	9.043752	3.228923
C	4.423883	1.227405	7.289202
H	4.067402	0.654393	6.411250
H	5.257275	0.700054	7.787055
H	3.577554	1.366838	7.989982
O	4.965565	2.498710	6.881415
N	6.480378	4.939363	6.200931
N	7.233171	4.155618	6.520472
C	6.725112	8.229772	1.815701
H	7.184228	9.207142	1.564026
H	7.524061	7.460796	1.763430
H	5.985027	7.993468	1.023020

Malonate Derivative

Fe	2.905189	3.795714	3.695110
C	-0.743995	1.712638	4.104663
C	0.262998	2.824952	4.276096
C	-0.078198	3.998669	4.983992
C	0.824341	5.052520	5.218531
C	0.409973	6.267252	6.012544
C	5.107439	2.699841	5.478159
C	5.994232	3.514583	4.739891
C	5.653769	4.599329	3.950534
O	6.648747	5.344711	3.413742
C	5.549277	1.865967	1.143637
C	4.436104	2.817884	1.504836
C	4.085044	3.881834	0.659389

C	2.996388	4.774656	0.894233
C	2.681628	5.839890	-0.130024
O	1.409465	2.597842	3.738563
O	2.048584	5.080157	4.808219
O	3.852915	2.784169	5.454981
O	4.447390	4.966615	3.692507
O	3.867253	2.554349	2.642055
O	2.265338	4.741993	1.937843
H	-0.343339	0.783789	4.558454
H	-0.884368	1.508298	3.024181
H	-1.720346	1.951481	4.563958
H	-1.092191	4.081531	5.394503
H	1.078946	6.376243	6.889745
H	0.546720	7.175709	5.390925
H	-0.639044	6.211329	6.355037
H	5.194433	0.819954	1.235960
H	6.373960	1.993927	1.876401
H	5.936811	2.037363	0.122754
H	4.637454	3.981544	-0.284113
H	1.588492	5.999412	-0.187111
H	3.087160	5.602790	-1.131695
H	3.125706	6.798243	0.212898
C	6.204611	6.404201	2.526508
H	7.115488	6.672841	1.960581
H	5.452854	5.992874	1.827684
C	5.626701	7.616373	3.293552
H	6.406362	8.381490	3.424957
H	5.338641	7.276167	4.295904
C	4.824419	0.867442	6.957877
H	4.144330	0.380695	6.228722

H	4.191581	1.439731	7.667911
C	4.420356	8.206266	2.601595
C	4.570155	9.120763	1.538442
C	3.119370	7.813091	2.978901
C	3.447286	9.638446	0.870897
H	5.581011	9.439678	1.237421
C	1.997078	8.332342	2.315819
H	2.989360	7.077916	3.786046
C	2.154833	9.248464	1.261603
H	3.583293	10.354517	0.045247
H	0.990343	8.004156	2.616278
H	1.273856	9.653841	0.741229
O	5.710990	1.771920	6.258903
N	7.886857	3.256727	4.845201
N	8.364351	2.383499	5.382634
C	5.695845	-0.156656	7.683685
H	6.345685	-0.664355	6.941547
H	6.365085	0.375898	8.390501
C	4.841875	-1.167132	8.417969
C	4.432561	-2.360082	7.786407
C	4.387658	-0.910816	9.728562
C	3.598926	-3.275749	8.447980
C	3.553336	-1.823316	10.393788
C	3.156553	-3.009769	9.754507
H	4.780084	-2.574419	6.763101
H	4.700055	0.016708	10.235148
H	3.295655	-4.205216	7.941956
H	3.214157	-1.608491	11.418620
H	2.506849	-3.729591	10.275967

HAA Transition State

Benzylic

Fe	-2.469402	-0.487334	-1.185418
O	-3.587035	-0.225164	-2.700757
O	-2.007754	1.547458	-1.206542
O	-1.010525	-0.903267	-2.352899
O	-1.456015	-0.871823	0.383484
O	-3.159472	-2.648812	-1.283869
O	-3.942691	-0.082344	-0.058420
C	-5.119745	-0.646935	-0.197170
C	-5.334096	-1.872883	-0.761050
C	-4.398164	-2.822738	-1.237546
C	0.182285	-1.238773	-2.011721
C	0.622519	-1.399521	-0.680259
C	-0.213932	-1.215554	0.437551
C	-4.269702	0.849138	-2.944242
C	-3.980835	2.119831	-2.421044
C	-2.846708	2.416697	-1.608602
O	-4.949173	-3.993916	-1.648200
C	-4.010450	-4.966452	-2.148794
C	-6.278653	0.195742	0.300634
C	-7.501180	-0.617781	0.741552
C	-7.989989	-1.546846	-0.370536
C	-8.980614	-2.597571	-0.000615
C	-10.189444	-2.735589	-0.718145
C	-11.123086	-3.727654	-0.379574
C	-10.860801	-4.609064	0.682757
C	-9.655158	-4.491824	1.398502
C	-8.725846	-3.498278	1.059774
C	-5.444776	0.636103	-3.868453
C	-2.587980	3.848636	-1.186083

C	1.129769	-1.463920	-3.167088
C	0.314552	-1.425142	1.837172
H	1.664175	-1.698583	-0.507710
H	-4.631957	2.951909	-2.719738
H	-4.620321	-5.830871	-2.466597
H	-3.294904	-5.267720	-1.358753
H	-3.439685	-4.556955	-3.005194
H	-6.546355	0.894524	-0.524785
H	-5.897375	0.832847	1.123706
H	-8.317208	0.065616	1.058822
H	-7.231623	-1.221340	1.633014
H	-8.330309	-0.967026	-1.243475
H	-10.396562	-2.045442	-1.551929
H	-12.062512	-3.811428	-0.947790
H	-11.591642	-5.387792	0.950185
H	-9.437978	-5.184529	2.226614
H	-7.778196	-3.423063	1.614861
H	-6.147570	-0.079012	-3.390379
H	-5.099947	0.163812	-4.810324
H	-5.974617	1.577394	-4.103339
H	-3.279428	4.569802	-1.659941
H	-1.542281	4.123561	-1.430537
H	-2.690844	3.919981	-0.083142
H	1.173611	-0.546267	-3.788943
H	2.149168	-1.729721	-2.832568
H	0.735437	-2.273289	-3.815478
H	1.365956	-1.766016	1.844393
H	-0.320083	-2.168304	2.361267
H	0.232594	-0.475604	2.404860
H	-6.991760	-2.052894	-0.728492

Tertiary

Fe	-5.039785	2.605708	-0.119516
O	-4.371914	3.421924	-1.827136
O	-5.749239	4.401541	0.381179
O	-3.202644	2.996326	0.706184
O	-5.469848	1.736697	1.685892
O	-4.171261	0.748826	-0.703685
O	-6.761136	1.867201	-0.741459
C	-7.126542	0.623605	-0.630899
C	-6.214949	-0.405058	-0.575863
C	-4.814311	-0.327997	-0.560745
C	-2.599713	2.281101	1.579158
C	-3.234734	1.320248	2.405225
C	-4.635475	1.118518	2.436512
C	-4.107741	4.660399	-2.032516
C	-4.523409	5.716303	-1.187441
C	-5.337933	5.540648	-0.045539
O	-4.151880	-1.494921	-0.384259
C	-2.715274	-1.374900	-0.304957
C	-8.612473	0.341608	-0.573377
C	-8.959389	-0.784267	0.415330
C	-8.247109	-2.107187	0.104811
C	-3.313020	4.959866	-3.284167
C	-5.800228	6.739277	0.752041
C	-1.109067	2.516817	1.706337
C	-5.240115	0.114459	3.392862
H	-2.614509	0.760628	3.118449
H	-4.245182	6.740597	-1.467209
H	-2.344854	-2.397579	-0.112972
H	-2.430107	-0.692468	0.520550

H	-2.297838	-0.985188	-1.253626
H	-8.961077	0.087673	-1.598365
H	-9.119741	1.285850	-0.295182
H	-10.061297	-0.940175	0.433553
H	-8.670344	-0.451867	1.434860
H	-3.846090	4.545466	-4.163968
H	-2.337695	4.435535	-3.227536
H	-3.138662	6.041148	-3.434776
H	-5.466753	7.698242	0.314613
H	-5.411074	6.656297	1.787388
H	-6.906914	6.728601	0.824304
H	-0.923212	3.590278	1.914207
H	-0.640689	1.904167	2.499128
H	-0.623135	2.291963	0.734310
H	-4.499574	-0.328776	4.084674
H	-5.710981	-0.695027	2.796337
H	-6.051037	0.597780	3.973938
H	-7.162973	-1.769627	-0.121636
C	-8.203605	-3.047470	1.302757
H	-9.230008	-3.357356	1.598540
H	-7.629674	-3.968642	1.077514
H	-7.737284	-2.560326	2.182876
C	-8.758380	-2.788921	-1.161042
H	-8.158133	-3.688255	-1.404503
H	-9.813838	-3.113769	-1.032197
H	-8.717928	-2.115538	-2.040327

Secondary

Fe	1.790598	4.021844	4.381347
C	-0.856357	0.760812	3.913636
C	-0.322732	2.067439	4.453262

C	-1.063467	2.809452	5.398363
C	-0.609280	4.018015	5.960347
C	-1.434246	4.744424	6.995913
C	4.111455	3.297566	6.201583
C	4.654907	4.546919	5.796723
C	4.025241	5.616445	5.205145
C	4.735354	6.924263	4.939097
C	4.923754	3.621426	1.634338
C	3.568108	4.063355	2.131872
C	2.831795	5.042986	1.443141
C	1.517185	5.463058	1.794604
C	0.799464	6.475712	0.926160
O	0.824771	2.412696	3.987497
O	0.507380	4.595591	5.671105
O	2.933932	2.932266	5.987423
O	2.788773	5.593732	4.787946
O	3.179096	3.460012	3.209613
O	0.873512	5.031194	2.806053
H	-0.146694	-0.055262	4.159591
H	-0.913693	0.817257	2.807407
H	-1.853034	0.513902	4.321742
H	-2.032443	2.414337	5.727031
H	-0.828773	4.883843	7.914266
H	-1.683543	5.757208	6.620015
H	-2.366933	4.207918	7.246838
H	3.965556	7.722186	4.968423
H	5.483409	7.127275	5.728473
H	4.910169	2.530297	1.437455
H	5.674320	3.799325	2.430955
H	5.227817	4.155879	0.716097

H	3.281070	5.465770	0.535528
H	-0.176083	6.060289	0.602908
H	1.384363	6.773285	0.036434
H	0.577949	7.376942	1.533608
C	5.416821	6.910879	3.558244
H	6.188059	6.109917	3.543674
H	4.663724	6.638718	2.788747
C	6.064225	8.249857	3.195798
H	6.810378	8.514945	3.963870
H	5.297976	9.043752	3.228923
C	4.423883	1.227405	7.289202
H	4.067402	0.654393	6.411250
H	5.257275	0.700054	7.787055
H	3.577554	1.366838	7.989982
O	4.965565	2.498710	6.881415
N	6.480378	4.939363	6.200931
N	7.233171	4.155618	6.520472
C	6.725112	8.229772	1.815701
H	7.184228	9.207142	1.564026
H	7.524061	7.460796	1.763430
H	5.985027	7.993468	1.023020

Malonate Derivative

Fe	-2.976123	-0.081006	-2.016430
O	-3.255361	0.927705	-3.729419
O	-2.101632	1.547716	-1.290284
O	-1.358668	-1.068459	-2.694577
O	-2.718621	-1.141344	-0.287466
O	-4.055880	-1.689104	-2.783853
O	-4.771802	0.532152	-1.223400
C	-5.646371	-0.282055	-0.785972

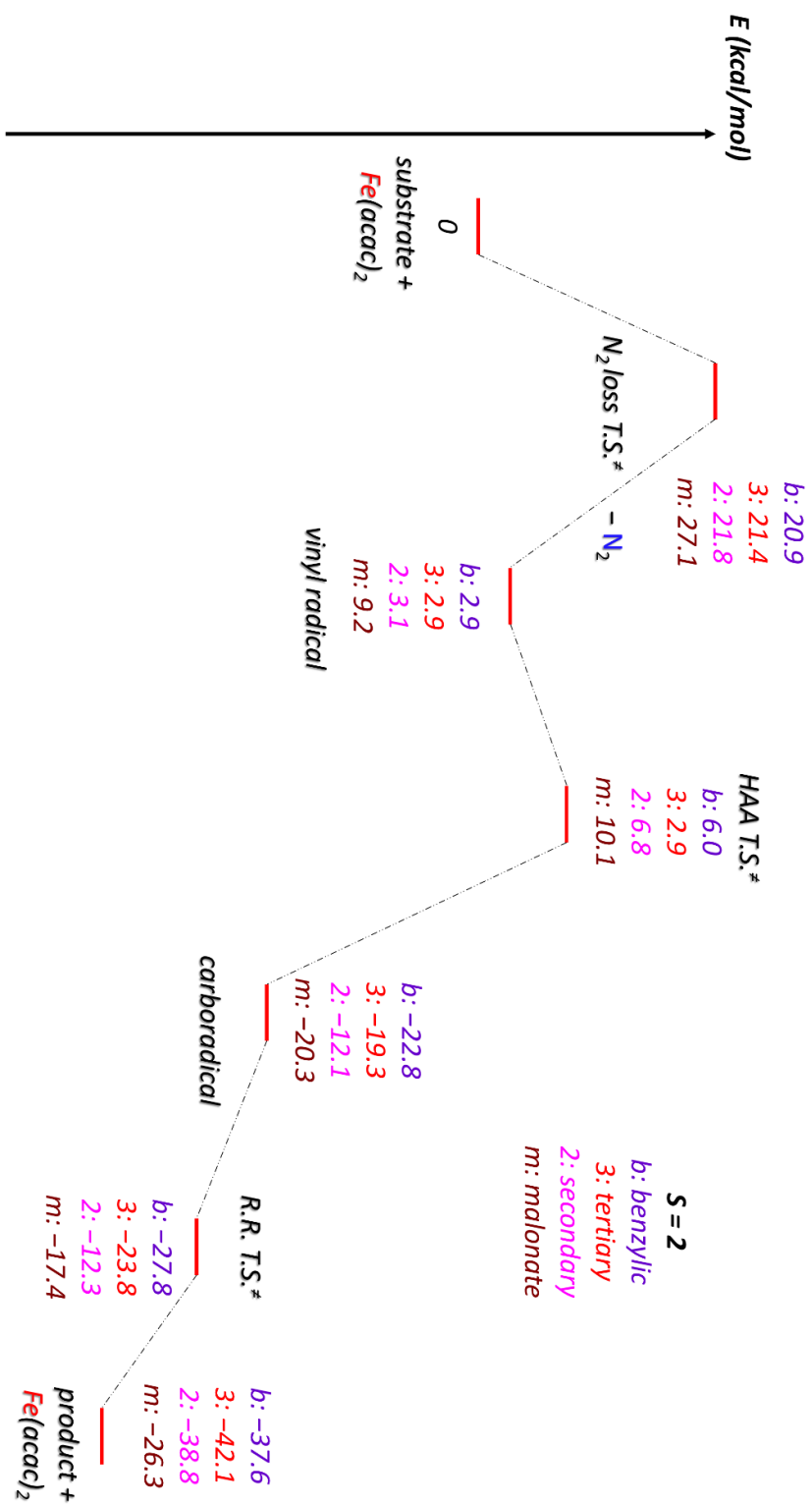
C	-5.739341	-1.622007	-1.147068
C	-4.987131	-2.255453	-2.134702
C	-1.059687	-2.283883	-2.406855
C	-1.518387	-2.960715	-1.252182
C	-2.304600	-2.352551	-0.242398
C	-3.337121	2.200667	-3.859353
C	-2.919392	3.129479	-2.875761
C	-2.305032	2.763098	-1.657597
O	-5.274231	-3.558198	-2.377487
C	-4.365039	-4.241917	-3.276712
O	-6.532694	0.261588	0.095370
C	-7.302044	-0.660877	0.902772
C	-8.060461	-1.688806	0.073963
C	-8.646436	-2.836195	0.815018
C	-10.002986	-3.189601	0.634576
C	-10.559816	-4.282009	1.316159
C	-9.767895	-5.048052	2.188571
C	-8.413518	-4.714424	2.369586
C	-7.858207	-3.622100	1.689412
C	-3.908780	2.689462	-5.171209
C	-1.823848	3.823147	-0.694464
C	-0.168768	-2.996514	-3.398668
C	-2.725111	-3.144218	0.974862
H	-1.190634	-3.996577	-1.097574
H	-3.032084	4.199389	-3.095327
H	-3.347336	-3.824947	-3.149008
H	-4.677400	-4.058679	-4.326275
H	-7.986618	-0.018540	1.490232
H	-6.605986	-1.169922	1.601594
H	-8.782788	-1.206663	-0.599946

H	-10.625158	-2.591977	-0.050431
H	-11.619471	-4.538649	1.163349
H	-10.202596	-5.908313	2.719809
H	-7.782754	-5.317476	3.041089
H	-6.791233	-3.384414	1.819640
H	-4.941515	2.300392	-5.281585
H	-3.317409	2.266725	-6.008417
H	-3.924024	3.792611	-5.249356
H	-1.967689	4.848986	-1.081243
H	-0.750314	3.657866	-0.471106
H	-2.372153	3.713433	0.263477
H	0.754041	-2.404754	-3.563532
H	0.096249	-4.019921	-3.077181
H	-0.693604	-3.052618	-4.374569
H	-2.258608	-4.145164	1.023142
H	-3.829839	-3.254965	0.943893
H	-2.482148	-2.573053	1.893264
H	-7.185252	-2.077514	-0.635348
C	-4.380715	-5.731284	-2.933939
H	-4.188218	-5.838510	-1.846349
H	-5.384199	-6.160114	-3.134359
C	-3.314999	-6.452923	-3.729030
C	-1.997321	-6.548640	-3.233363
C	-3.588847	-6.971683	-5.010965
C	-0.982334	-7.150618	-3.993180
C	-2.575901	-7.572530	-5.776249
C	-1.268684	-7.662925	-5.269887
H	-1.768703	-6.146911	-2.233302
H	-4.612926	-6.905186	-5.413091
H	0.037824	-7.224463	-3.585349

H -2.809978 -7.973037 -6.774278

H -0.474394 -8.134804 -5.867952

7. Summary figure of the potential energy surface



8. Results using other functionals

To benchmark the result obtained using BP86 functional, the N₂ loss and HAA transition states are reproduced with PBE, TPSS, and B3LYP functionals with D3BJ dispersion correction. The difference between the N₂ loss and HAA transition state is calculated and listed in the table below. The result from BP86, PBE and TPSS are consistent within 1 kcal/mol whereas the hybrid functional B3LYP revealed a larger gap between the two barriers by 2 kcal/mol comparing to the BP86 result. Overall, the result obtained using BP86 can be reproduced with other functionals with similar results.

Functionals	$\Delta\Delta G^\ddagger$ (N ₂ loss–HAA)	Difference compared to BP86
BP86	14.6	0
PBE	15.1	0.5
TPSS	15.3	0.7
B3LYP	16.6	2.0

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