Transition Metal-Free, Chemoselective Arylation of Thioamides Yielding Aryl Thioimidates or *N*-Aryl Thioamides

Piret Villo,[a,b] Gabriella Kervefors,[a] and Berit Olofsson*[a]

[a] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm (Sweden)

[b] Institute of Technology, University of Tartu, 50 411 Tartu, Estonia.

berit.olofsson@su.se

Electronic Supplimentary Information

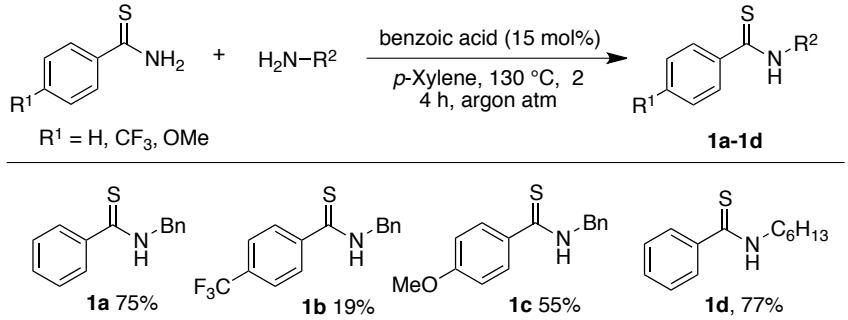
1 General information

All reactions were carried out in non-dried glassware unless otherwise stated. Toluene, THF, acetonitrile, CH_2Cl_2 and DMF were dried using VAC purification system, stored under argon, and over activated 4Å molecular sieved, when needed. *t*BuOLi, *t*BuONa, *t*BuOK were stored under argon in a desiccator. All diaryliodonium salts were synthesized according to procedures described in Section 2.1. Thioamides were synthesized according to protocols in literature (Section 2.2), except for pyrrolidine-2-thione, thiobenzamide, *N,N*-dimethylthioacetamide, and 2-mercaptopyridine which were purchased. *m*CPBA (77% active oxidant) was purchased from commercial supplier, and dried at rt on high vacuum for 3-4 h, and titrated by iodometric titration prior to use.[1] TfOH was stored and handled under argon, using Hamilton syringes and oven-dried metal syringes. All other solvents and reagents were purchased from commercial suppliers and used without further purification. Anhydrous toluene was degassed using the freeze-thaw method.

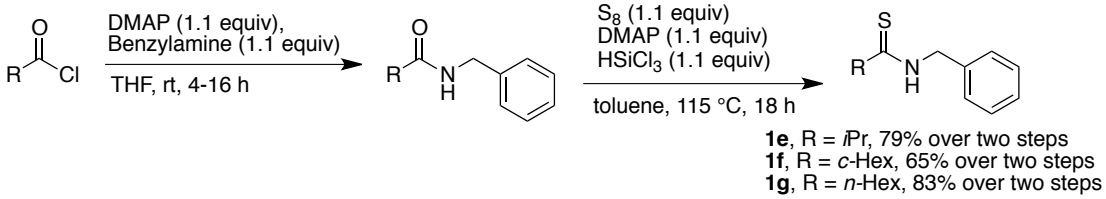
TLC analysis was performed on pre-coated silica gel 60 F_{254} plates using UV light and phosphomolybdic acid stain (solution in EtOH). Column chromatography was conducted by flash column chromatography using 40-60 μm, 230-400 mesh, 60Å silica gel as stationary phase. Alternatively, automated flash system Teledyne ISCO CombiFlash Rf 200 with RediSep Rf columns was used. Melting points were measured using a STUART SMP3 and are reported uncorrected. All NMR spectra were recorded using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K using $CDCl_3$, CD_3OD or DMSO-d_6 as solvents. Chemical shifts are given in ppm either relative to tetramethylsilane (TMS) as internal standard or to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26; CD_3OD 3.31; DMSO-d_6 2.50, CD_3CN 1.93; ^{13}C NMR: $CDCl_3$ δ 77.16; CD_3OD 49.00, DMSO-d_6 39.52) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. High resolution mass analyses were obtained using a Bruker microTOF ESI or APCI. GC-MS analyses were performed using a Shimadzu GC-2010 Plus gas chromatograph (column HP-5MS 30 m x 0.25 mm x 0.25 uM) connected to a GCMS-QP2020 mass spectrometer. Analytical data is given if the compound is novel or not fully characterized in the literature.

2 Synthesis of Starting Materials

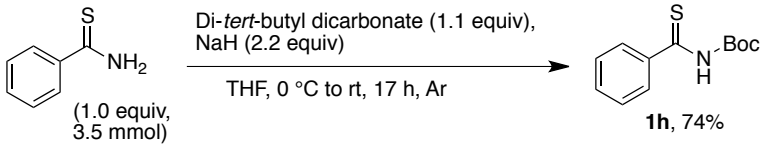
2.1 Synthesis of Thioamides and Thiolactams 1



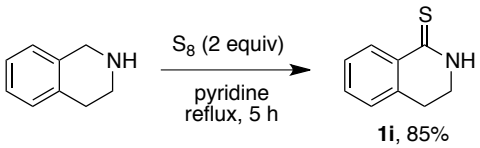
Thioamides **1a-1d** were synthesized according to a literature procedure.[2] The analytical data matched those previously reported for **1a**,[3] **1b-1c**,[4] and **1d**.[5]



Thioamide **1e, 1f** and **1g** were synthesized from a corresponding amide according to a literature procedure.[4] The analytical data for **1e** and **1g** matched those previously reported.[4] Analytical data for **1f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 4.83 (d, J = 5.1 Hz, 2H), 2.52 (tt, J = 11.8, 3.4 Hz, 1H), 1.96–1.87 (m, 2H), 1.85–1.77 (m, 2H), 1.72–1.55 (m, 3H), 1.36–1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.40, 136.43, 129.04, 128.32, 128.18, 55.07, 50.02, 33.01, 26.04, 25.69. HRMS (ESI): calcd for $C_{14}H_{19}NNaS$ $[M+Na]^+$: 256.1130; found 256.1130.



Thioamide **1h** was synthesized according to a literature procedure.[6] **1h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.80–7.59 (m, 2H), 7.55–7.44 (m, 1H), 7.44–7.32 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 149.1, 142.2, 131.6, 128.1, 127.1, 83.5, 27.9. HRMS (ESI): calcd for $C_{12}H_{14}NO_2S$ $[M-H]^-$: 236.0751; found 236.0751.

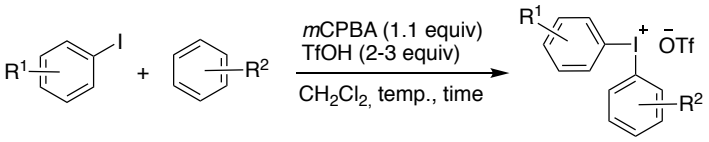
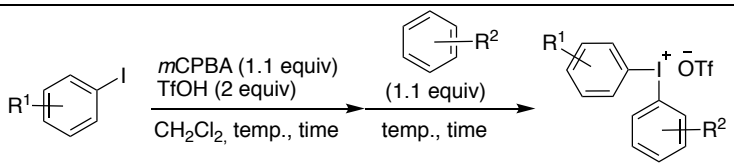
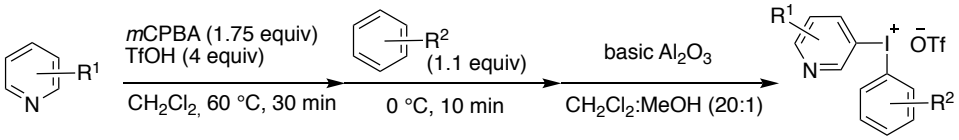
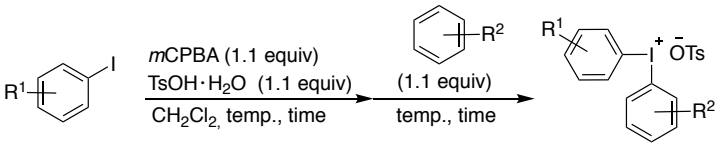
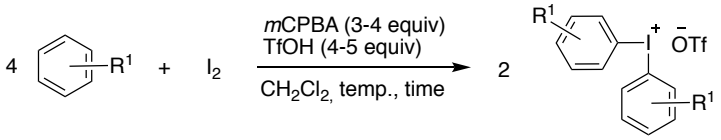
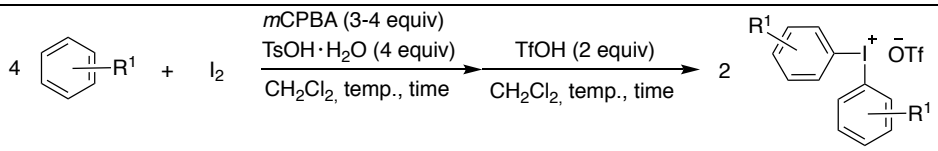
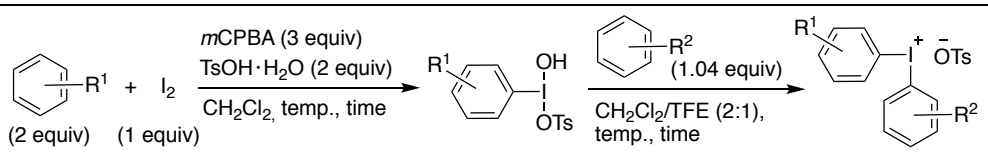
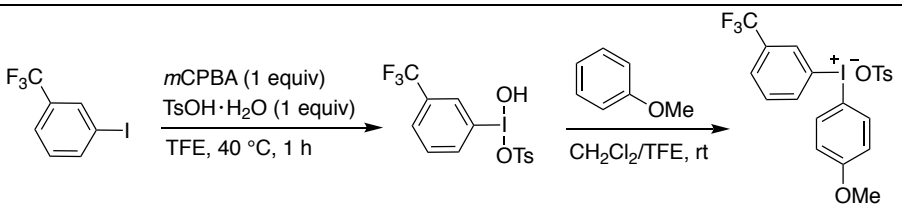


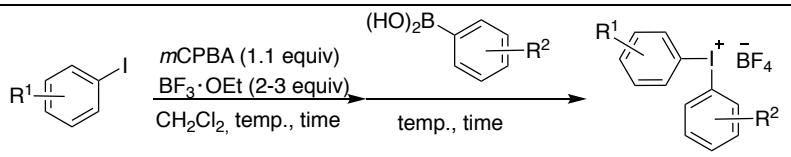
Thioamide **1i** was synthesized according to a literature procedure.[7] The analytical data matched those previously reported.[8]

2.2 Synthesis of Diaryliodonium Salts 2

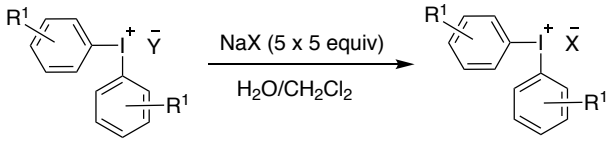
The general methods developed in our group were used for synthesis of diaryliodonium salts featured in the arylation of thioamides (Table S1). No precautions were taken to avoid air or moisture. In unsymmetric diaryliodonium salts, the substrates should be selected such that an aryl group with electron-withdrawing substituents is introduced as the ArI, and the other aryl group as ArH. See Table S2 for synthetic details and references to analytical data.

Table S1. General methods to synthesize diaryliodonium salts

1[9]	
2[10]	
3[11]	
4[10]	
5[9]	
6[11]	
7[12]	
8[10, 13]	

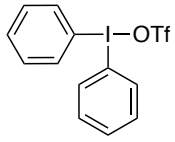
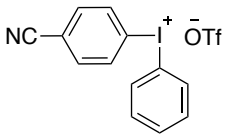
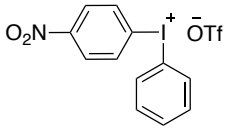
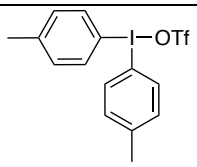
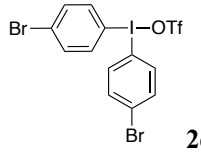
9[14]	

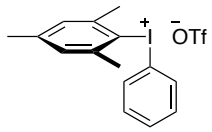
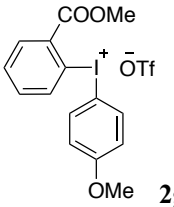
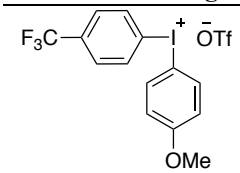
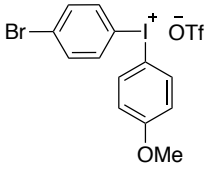
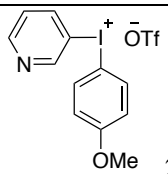
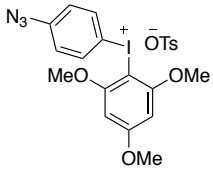
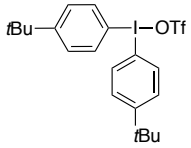
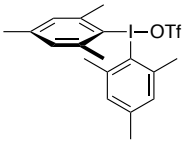
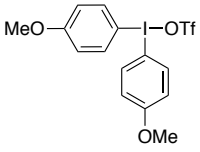
Anion exchange:

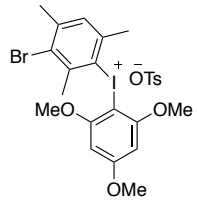
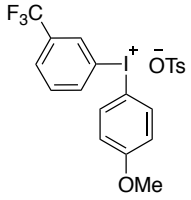
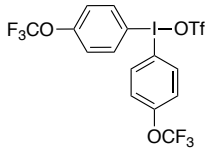
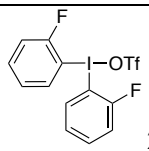


NaX (85 mmol) was dissolved in H_2O (100 mL). Diaryliodonium salt (3.4 mmol) was dissolved in CH_2Cl_2 (20 mL) and washed 5 times with 20 mL of the prepared aqueous solution. The organic layer was concentrated without drying. To the crude was added Et_2O, and the mixture was stirred at rt or at 0 °C until precipitation occurrred. The solid was filtered and washed with Et_2O, followed by drying under vacuum. The method was used to exchange BF_4 to OTs using NaOTs, and OTs to OTf using NaOTf.

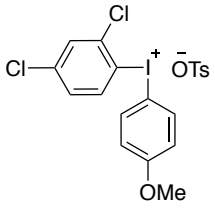
Table S2. Synthesized diaryliodonium salts.

Ar_2IX	Method	Acid (equiv)	Temp. [°C]	Time	Yield [%]	Ref.
 **2a**	1	3	Acid addition at 0 °C, then run at rt	1.5 h	95	[9]
 **2b**	1	2	Acid addition at 0 °C, then run at rt	17 h	79	[15]
 **2c**	1	2	Acid addition at 0 °C, then run at rt	17 h	88	[15]
 **2d**	1	2	Acid addition at 0 °C, then run at rt	1 h	78	[9]
 **2e**	1	3	Acid addition at 0 °C, then run at rt	3 h	90	[9]

 **2f**	1	2	r.t.	1	66	[9]
 **2g**	1	1	1) 0 °C 2) 40 °C	10 min + 3 h	70	[10]
 **2h**	2	2	Acid addition at 0 °C, then run at rt	30 min +30 min	89	[9]
 **2i**	2	2	1) Acid addition at 0 °C, then run at rt; 2) 0 °C	50 min + 50 min	68	[9]
 **2j**	3	4	1) 60 °C 2) 0 °C	30 min + 10 min	79	[10, 16]
 **2l**	4	1.1	r.t. + 40 °C	15 min+ 4 h	14	[17]
 **2m**	5	5	Acid addition at 0 °C, then run at rt	2 h	43	[9]
 **2n**	5	4	Acid addition at 0 °C, then run at rt	1.5 h	31	[9]
 **2o**	6	$TsOH \cdot H_2O$ (4), TfOH (2)	rt	20 h, 1 h	57	[10]

 **2p**	7	2	1) r.t., 2) addition at 0 °C then r.t.	1 h + 1 h	88	[12]
 **2q**	8	1	1) 40 °C 2) r.t.	1 h +24 h	94	[13, 18]
 **2r**	9, then anion exchange	2.5	1) r.t. 2) addition at 0 °C, then r.t.	1 h +40 min	57	[14]
 **2s**	9, then anion exchange	2.5	r.t.	30 min +15 min	85	[14]

(2,4-Dichlorophenyl)(4-methoxyphenyl)-λ^3-iodaneyl 4-methylbenzenesulfonate

 **2k**

To a stirred solution of 2,4-dichloroiodobenzene (100 μL, 0.737 mmol) and *m*CPBA (0.810 mmol, 160 mg, 87% active oxidant) in CH_2Cl_2 (8 mL) was added $TsOH·H_2O$ (210 mg, 1,105 mmol) portion wise at room temperature. The mixture was warmed at 40 °C for 5 min. After that anisole (88 μL, 0.810 mmol) was added to the solution at r.t, followed by stirring the reaction for 2 h at rt. Then the solution was concentrated to dryness, added Et_2O (*ca* 4 mL) and stirred on ice-bath. The precipitation was filtrated and washed with Et_2O to yield white solid as product (312 mg, 77%). ^{1}H NMR (400 MHz, CD_3OD) δ 8.34 (d, *J* = 8.6 Hz, 1H), 8.12–8.06 (m, 2H), 7.86 (d, *J* = 2.3 Hz, 1H), 7.71–7.66 (m, 2H), 7.47 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.24–7.19 (m, 2H), 7.09–7.04 (m, 2H), 3.84 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, CD_3OD) δ 163.3, 142.2, 140.2, 140.1, 139.0, 137.9, 137.3, 130.1, 130.1, 128.4, 125.5, 117.5, 115.9, 103.6, 54.9, 19.9 ppm. HRMS (ESI): calcd for $C_{13}H_{10}Cl_2IO$ $[M\text{-}OTs]^+$: 378.9148; found 378.9151.

3 Optimization of the Arylation of Thioamides

3.1 Screening of Reaction Conditions

Extensive optimization studies were performed. Base, anions and solvents were screened at rt. (Tables S3-S5). The stoichiometry and concentration effects are detailed in Table S6. The addition of aryne traps (furan or piperidine), and radical trap (DPE) excluded radical or aryne mechanisms (Table S6). The temperature was finally varied in Table S7.

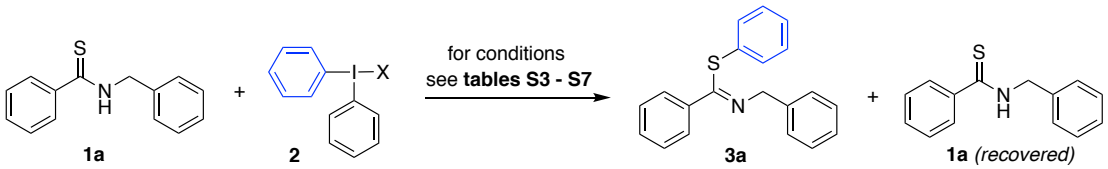


Table S3. Base screening in toluene at r.t. (X = OTf)

Salt (equiv)	Base (equiv)	solvent	Temp. [°C]	Time [h]	Yield **3a** [%][a]	Recovered thio-amide **1a** [%][a]
1.5	-	toluene	rt	24	n.o.	Quant.
2.0	NaH (1.5)	toluene	rt	24	25 [b]	61
2.0	NaH (1.5)	toluene	rt	24	34	43
1.5	NaH (1.5)	toluene	rt	24	39	49
1.5	NaH (1.5)	toluene	rt	16	40	29
1.5	NaH (1.1)	toluene	rt	16	27	33
1.5	NaH (1.5)	toluene	rt	1	6	94
1.5	NaO*t*Bu (1.5)	toluene	rt	1	27	43
1.5	NaO*t*Bu (1.2)	toluene	rt	1	29	45
1.5	NaO*t*Bu (1.1)	toluene	rt	1	22	48
1.5	*n*BuLi (1.2)	toluene	rt	1	20	72
1.5	NaO*t*Bu (1.2)	toluene	rt	16	28	39
1.5	*t*BuOK (1.2)	toluene	rt	16	27	33
1.5	**LiO*t*Bu (1.2)**	**toluene**	**rt**	**16**	**40**	**26**
1.5	Et_3N (1.2)	toluene	rt	16	3	Quant.
1.5	TMG (1.2)	toluene	rt	16	39	58
1.5	NH_3 in MeOH (excess)	toluene	rt	16	6	89
1.5	NH_3 (25% aq., excess)	toluene	rt	16	34	26
1.5	NaOH (1.2)	toluene	rt	16	34	39
1.5	Na_2CO_3 (1.2)	toluene	rt	16	traces	95
1.5	Cs_2CO_3 (1.2)	toluene	rt	16	4	86

[a] Isolated yields
[b] Reaction was run under argon atmosphere
n.o. – not observed; n.d. – not determined; TMG – 1,1,3,3-tetramethylguanidine

Table S4. Diaryliodonium counterion (X) screening in toluene at rt.

Counter -ion **X**	Salt (equiv)	Base (equiv)	solvent	Temp. [°C]	Time [h]	Yield **3a** [%][a]	Recovered thioamide **1a** [%][a]
OTf	**1.5**	**NaO*t*Bu (1.2)**	**toluene**	**rt**	**1**	**29**	**45**
OTs	**1.5**	**NaO*t*Bu (1.2)**	**toluene**	**rt**	**1**	**29**	**48**
Br	**1.5**	**NaO*t*Bu (1.2)**	**toluene**	**rt**	**1**	**29**	**28**
BF_4	1.5	NaO*t*Bu (1.2)	toluene	rt	1	25	57
PF_6	1.5	NaO*t*Bu (1.2)	toluene	rt	1	18	75
TFA	1.5	NaO*t*Bu (1.2)	toluene	rt	1	19	50

[a] Isolated yields

Table S5. Solvent screening at rt. (X = OTf)

Salt (equiv)	Base (equiv)	solvent	Temp. [°C]	Time [h]	Yield **3a** [%][a]	Recovered thioamide **1a** [%][a]
1.5	**LiO*t*Bu (1.2)**	**toluene**	**rt**	**16**	**40**	**26**
1.5	LiO*t*Bu (1.2)	CH_3CN	rt	16	23	46
1.5	LiO*t*Bu (1.2)	THF	rt	16	21	55
1.5	LiO*t*Bu (1.2)	2Me-THF	rt	16	19	55
1.5	LiO*t*Bu (1.2)	DMF	rt	16	21	53
1.5	LiO*t*Bu (1.2)	pentane	rt	16	17	n.d.
1.5	**LiO*t*Bu (1.2)**	**CH_2Cl_2**	**rt**	**16**	**55**	**36**
1.5	**LiO*t*Bu (1.2)**	**EtOAc**	**rt**	**16**	**37**	**41**
1.5	**LiO*t*Bu (1.2)**	***i*PrOAc**	**rt**	**16**	**36**	**42**

[a] Isolated yields

Table S6. Screening for reagent loading, concentration effect and additives (X = OTf)

Additive (equiv)	Salt (equiv)	Base (equiv)	solvent	Temp [°C]	Time [h]	Yield **3a** [%][a]	Recovered **1a** [%][a]
-	1.5	LiO*t*Bu (2.0)	toluene	rt	16	42	11
-	1.5	LiO*t*Bu (1.5)	toluene	rt	16	42	14
-	1.5	LiO*t*Bu (1.2)	toluene	rt	16	40	26
-	1.5	LiO*t*Bu (1.1)	toluene	rt	16	38	41
-	1.5	LiO*t*Bu (1.1)	toluene	rt	16	38	25
-	1.5	LiO*t*Bu (1.0)	toluene	rt	16	23	39
-	2.0	LiO*t*Bu (1.1)	toluene	rt	16	37	31
-	**1.1**	**LiO*t*Bu (1.1)**	**Toluene (0.2 M)**	**rt**	**16**	**42**	**25**
-	1.1	LiO*t*Bu (1.1)	Toluene (0.4 M)	rt	16	30	14
-	1.1	LiO*t*Bu (1.1)	Toluene (0.1 M)	rt	16	40	38
DPE (1.0)	1.1	LiO*t*Bu (1.1)	toluene	rt	16	38	50
Furan (5)	1.1	LiO*t*Bu (1.2)	toluene	rt	16	28 [b]	58
Piperidine (1.0)	1.1	LiO*t*Bu (1.1)	toluene	80	1	78 [c]	n.d.

[a] Isolated yields

[b] ^{1}H NMR of the crude reaction mixture showed no evidence of formed Diels-Alder adducts. Low yield could be explained by high loading of furane that can interfere with the reaction outcome via other mechanisms.

[c] ^{1}H NMR yield was determined with 1,3,5-trimethoxybenzene as internal standard. No arylated piperidine was observed in crude ^{1}H NMR.

n.d. – not determined

Table S7. Temperature and reaction time screening, X = OTf

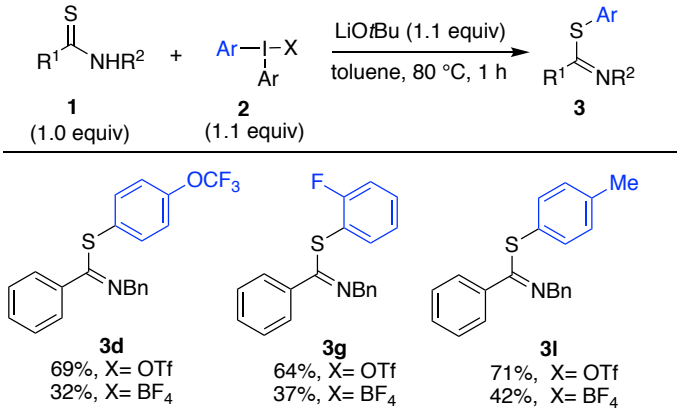
Salt (equiv)	Base (equiv)	solvent	Temp. [°C]	Time [h]	Yield **3a** [%][a]	Recovered thioamide **1a** [%][a]
1.1	LiO*t*Bu (1.1)	toluene	rt	16	42	25
1.1	LiO*t*Bu (1.1)	toluene	40	16	61	20
1.1	LiO*t*Bu (1.1)	toluene	60	16	64	17
1.1	LiO*t*Bu (1.1)	toluene	80	16	71	5
1.1	LiO*t*Bu (1.1)	toluene	reflux	16	80	13
1.1	LiO*t*Bu (1.1)	toluene	70	1	71	30
1.1	LiO*t*Bu (1.1)	toluene	80	1	75	17
1.1	LiO*t*Bu (1.1)	toluene	reflux	1	70	n.d.
1.1	LiO*t*Bu (1.1)	toluene	80	5	73	14
1.1	LiO*t*Bu (1.1)	toluene	80	0.5	71	16

1.1	LiO*t*Bu (1.1)	toluene	80	1	79 [b]	14
1.1	**LiO*t*Bu (1.1)**	**toluene**	**80**	**1**	**91** [c]	n.d
1.5	NaO*t*Bu (1.2)	toluene	40	23	48	19
1.5	TMG (1.2)	toluene	reflux	1	56	10
1.1	Cs_2CO_3 (1.1)	EtOAc	80	16	47	26
1.1	Cs_2CO_3 (1.1)	*i*PrOAc	90	16	51	21
1.1	LiO*t*Bu (1.1)	*i*PrOAc	80	1	57	39
1.1	LiO*t*Bu (1.2)	*i*PrOAc	90	1	78	20
1.1	LiO*t*Bu (1.1)	CH_2Cl_2	reflux	1	37	52
1.1	LiO*t*Bu (1.2)	*i*PrOAc	90	16	81	n.d.

[a] Isolated yields
[b] under argon atmosphere
[c] degassed anhydrous toluene
n.d. – not determined

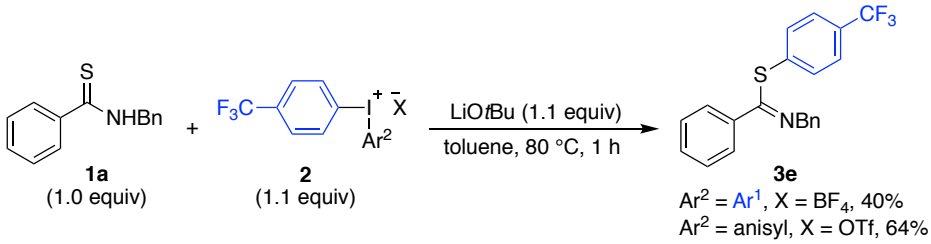
3.2 Effect of the Counterion in Diaryliodonium Salts

A preliminary comparison of counterions OTf, OTs, Br, PF_6, BF_4 and TFA was performed in the optimization (Table S4). The superiority of the commonly used OTf over BF_4 was further confirmed by reactions at 80 °C under our optimized conditions (Scheme S1).



Scheme S1. Effect of the counterion X.

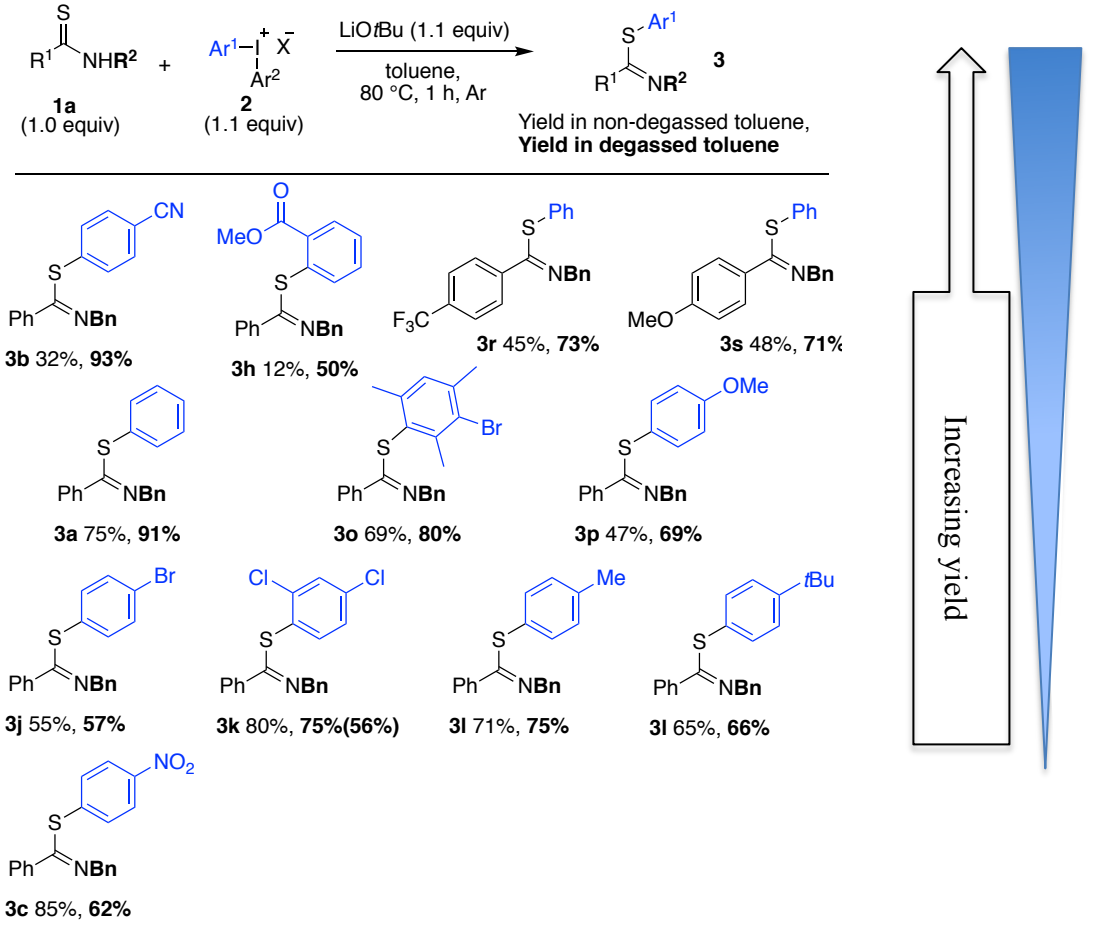
A considerable increase in yield was detected when the effects of the counterion X (here BF_4 vs OTf) and the dummy group (here anisyl) work in favour of the expected product **3e** (Scheme S2).



Scheme S2. Combined effect of counterion X and dummy group.

3.3 Effect of Degassing the Toluene

Towards the end of the project, we discovered a positive effect on the reaction yield upon degassing the toluene. Especially the yields of **3b**, **3h**, and **3r** increased considerably as well as thioimidates **3s, 3a, 3o, 3p** (Scheme S3). The positive effect icluded both electron rich (*e.g.* **3p**) or electron deficient aryl transfer (*e.g.* **3b)**. The yields of some thioimidates were, on the other hand, almost not affected by the degassed solvent (*e.g.* **3j, 3k, 3l, 3m**). Surprisingly, **3c** even gave a somewhat lower yield compared to reactions in non-degassed toluene. The reason behind the general yield increase was not explored, but degassing is presumed to suppress desulfurization and hydolysis processes of the formed thioimidates.



Scheme S3. Effect of degassed toluene on the yield of thioimidates **3**.

4 Chemoselectivity Studies

Byproducts often form in the synthesis of symmetric diaryliodonium salts with either two electron withdrawing or two electron donating aryl groups. Unsymmetric diaryliodonium salts are often easier to synthesize, as the electronic properties can be better matched to get good reactivity, as exemplified in Figure S1. Furthermore, the preparation cost can be considerably decreased when a precious aryl group should be introduced, or when a substitution pattern that cannot be reached by electrophilic aromatic substitution (Methods 1-8) is desired, as boronic acids (Method 9) can be avoided.

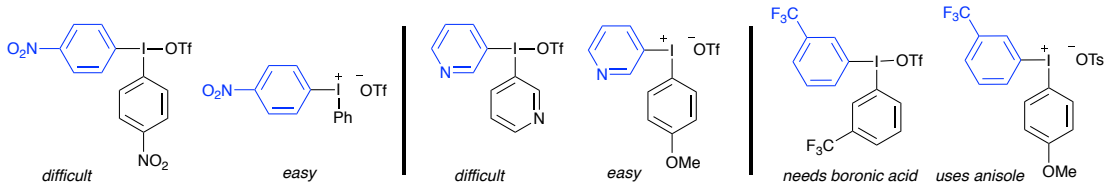


Figure S1. Ease of synthesis of symmetric and unsymmetric iodonium salts.

Unsymmetric iodonium salts are highly useful reagents when one aryl group is chemoselectively transferred to the nucleophile. The chemoselectivity can depend both on the sterics and electronics, and under transition metal-free reaction conditions, the more electron deficient aryl is preferably transferred.[10, 12, 19] *Ortho*-substituted aryl groups are often preferred in the ligand coupling, a feature that is referred to as the ''*ortho*-effect''.[20] Considering these aspects and the nature of the nucleophile, the non-transferable aryl moiety or the "dummy group" can be specifically chosen to aid the transfer of the desired aryl to the nucleophile under metal-free conditions.[21] In this project, we have employed the three dummy groups depicted in Figure S2. The phenyl group is used in reactions where a strongly electron withdrawing aryl group should be transferred, e.g. NO_2 and CN. Complete chemoselectivity is often not reached with the Ph dummy in transfer of aryl groups with weaker EWG substituents, such as CF_3 and halides, for which the anisyl dummy is suitable. The latter dummy can also be used in transfer of aryl groups with weakly EDG substituents. The TMP dummy is suitable in transfer of EDG aryls, and salts with a TMP dummy sometimes give superior yields in synthesis or arylations compared to the corresponding anisyl salts.[22]

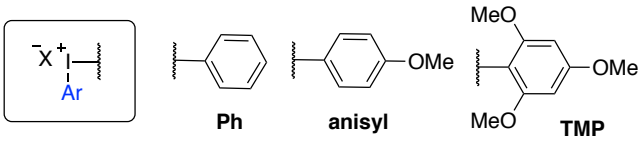
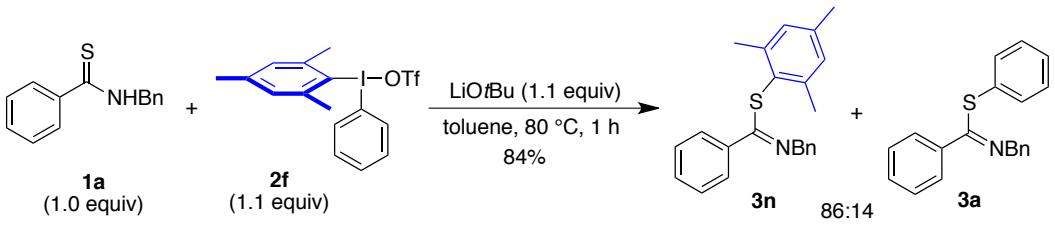


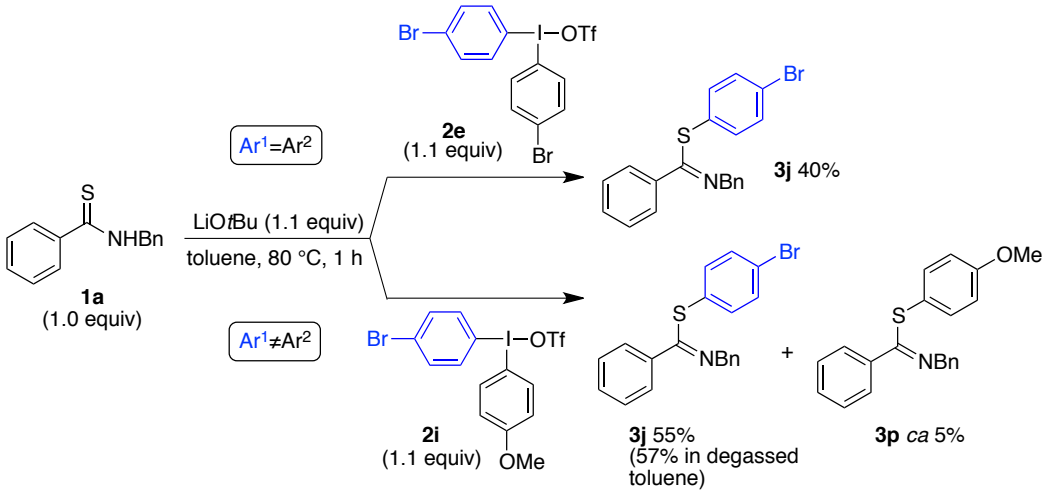
Figure S2. Employed dummy groups.

We observed a considerable *ortho*-effect for the S-arylation of thioamides, as exemplified in Scheme S4. The arylation with mesityl(phenyl)iodonium triflate (**2f**) delivered a mixture of mesitylated and phenylated products **3n** and **3a** in a 86:14 ratio and overall yield of 84% in favor of **3n**, with 16% of thioamide **1a** recovered. In comparison, a reaction with symmetric dimesityliodonium triflate **2n** gave 73% yield under the same conditions, i.e. **3n** was formed in similar yields with both salts.



Scheme S4. Chemoselectivity study.

To achieve complete chemoselectivity, we investigated the anisyl as group as dummy by comparing arylations of **1a** with a symmetric **2e** and an unsymmetric *p*-Br salt **2i** (Scheme S5). Indeed, employment of the anisyl salt **2i** increased the yield considerably compared to the symmetric salt **2e**, giving **3j** in 55% and 40% respectively. The observed chemoselectivity with the unsymmetric salt was also good, with < 5% of **3p** isolated. (Product **3p** can be obtained in 69% with the symmetric dianisyliodonium triflate **2o**.)



Scheme S5. Comparison of symmetric and unsymmetric salts.

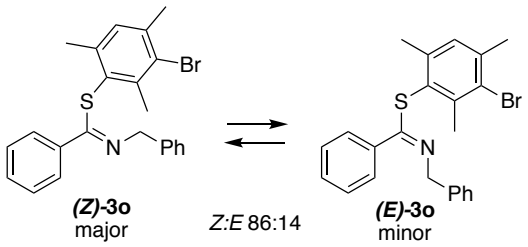
5 Structure Analysis of Thioimidates 3

5.1 Determination of the *Z/E*–Ratio

Throughout the optimization and scope studies, the major product was isolated together with an inseparable minor product by column chromatography. While the thioamides can easily hydrolyze to the corresponding amides,[23] such species were not formed according to comparison with literature NMR data.

Schmidt and coworkers reported the synthesis of thioimidates from indazolium salts and thiophenols, and observed the products to be an *Z:E* mixture with ratios up to 5:1.[24] The extra set of signals for the N-C*H*$_3$ of the *E* isomer in ^{1}H and ^{13}C NMR spectra were shifted upfield from the major *Z* isomer. Single-crystal X-ray analysis confirmed the *Z* configuration of the imine bond.

The NMR data of the major and minor products formed in the synthesis of acyclic aryl thioimidates **3a-3s, 3v** are in agreement with the formation of *Z*- and *E*-isomers. The minor *E*-isomer was observed as an extra set of NMR signals upfield for the methylene signals in N-C*H*$_2$-Ph. This hypothesis was also supported by NOESY analysis that did not show any correlation between the methylene and the aromatic backbone, which would be expected for the *E* isomer.[25] The *Z:E* ratios were determined by integrating the methylene signals N–C*H*$_2$-Ph for both isomers in the ^{1}H NMR spectrum of the isolated product and ranged from 86:14 up to 96:4. The ratios stayed constant independent of the reaction conditions (various solvents, bases and reaction temperatures). The minor isomer is not fully characterized due to overlapping of signals in the aromatic area. Thioimidate **3o**, furnished with a bulky *S*-aryl moiety, gave the lowest *Z:E* ratio of 86:14 (Scheme S6).



Scheme S6. *E* and *Z* isomers of thioimidate **3o**.

As the *Z:E* ratio of **3o** was lower than for the other thioimidates **3**, the carbonyl group S-*C*=N was also observable for the minor isomer (Figure S3). The shifts of the carbonyl group of both the major (162.59 ppm) and minor (165.00 ppm) counterpart are observable in the thioimidate area, which is high field from a thioamide carbonyl region (203 ppm).

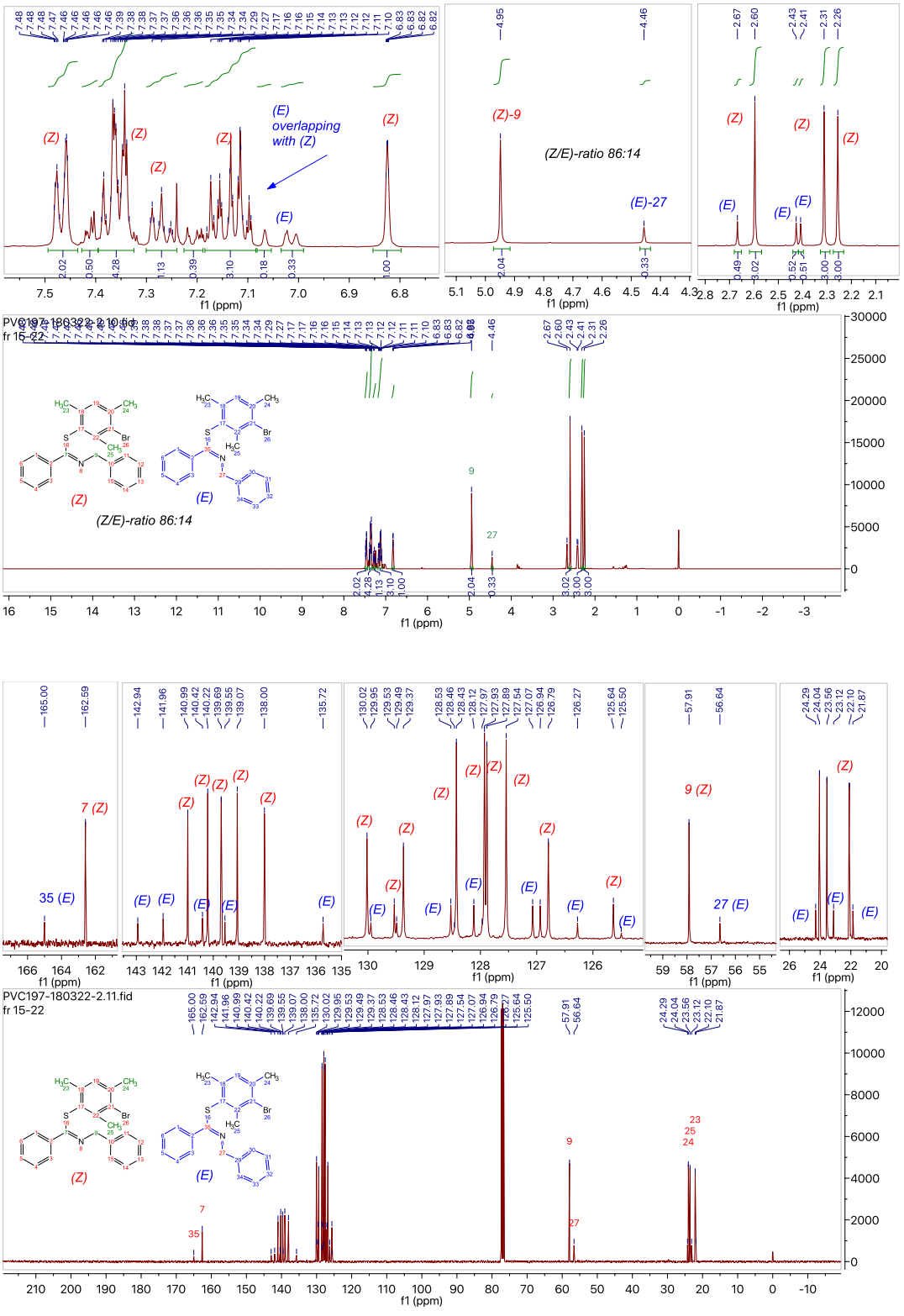


Figure S3. ^{1}H and ^{13}C NMR of thioimidate **3o**.

Other thioimidates **3a-3s, 3v** have been analyzed in analogy with **3o** (Figure S4). No significant alterations in the *Z:E* ratios were detected when the arylation was run at room temperature or elevated temperature. Compounds **3w**, **3x**, **3y** and **4b** only gave one set of signals by NMR analysis.

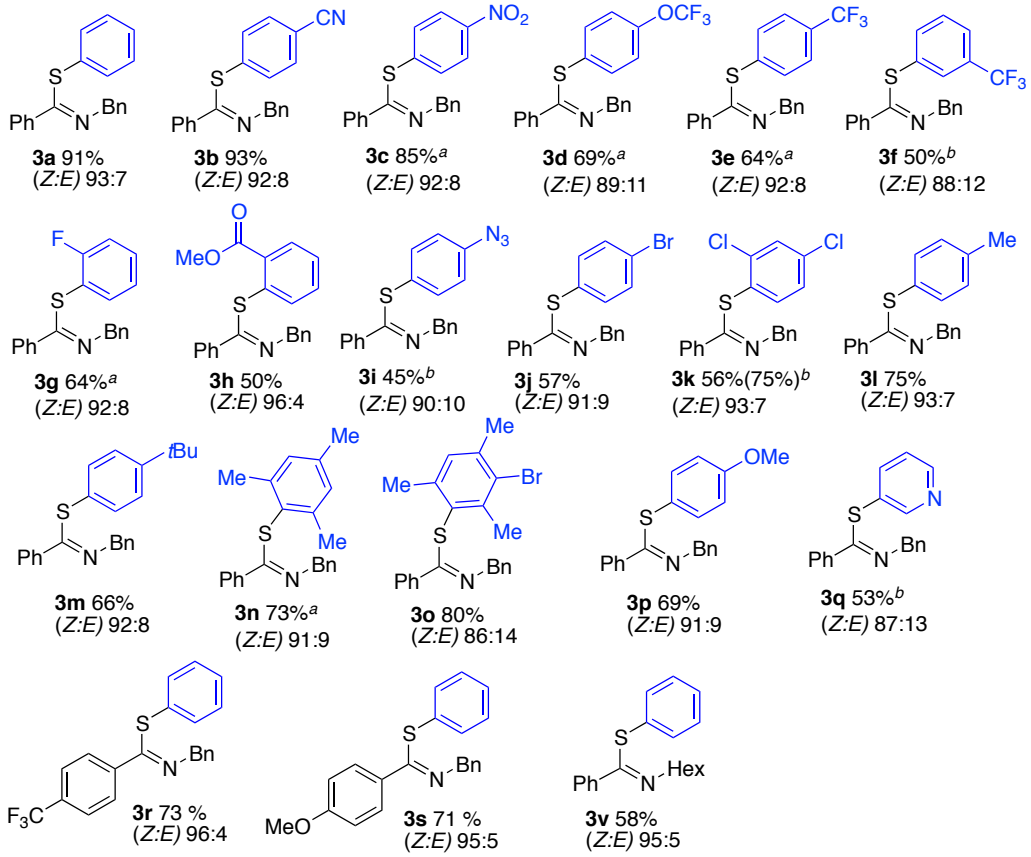
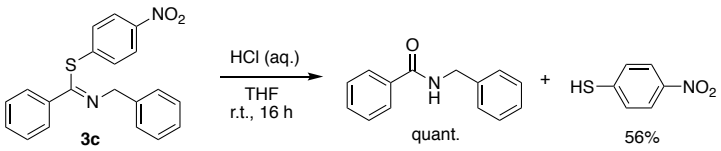


Figure S4. *Z:E* ratios for aryl thioimidates **3a-3s** and **3v**.

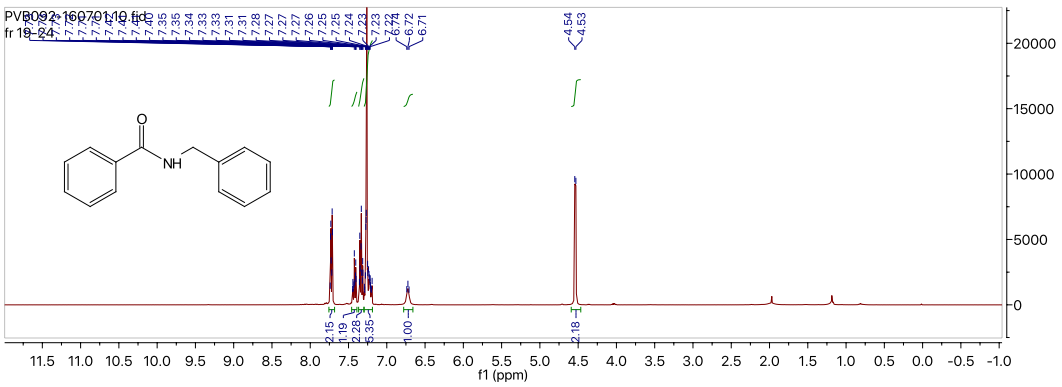
Thioimidates **3t, 3u** and **4a** were isolated as *S*- and *N*-arylated mixtures instead (see Section 5.3).

5.2 Hydrolysis of Thioimidate

In order to further confirm the formation of *S*-arylated thioimidates, product **3c** was subjected to hydrolysis under acidic conditions (Scheme S7).[26] Two major products were isolated and identified as the corresponding amide and *p*-NO_2 thiophenol, which are both reported compounds (^{1}H, ^{13}C NMR spectra shown in Figure S5).[27]



Scheme S7. Hydrolysis of thioimidate **3c**



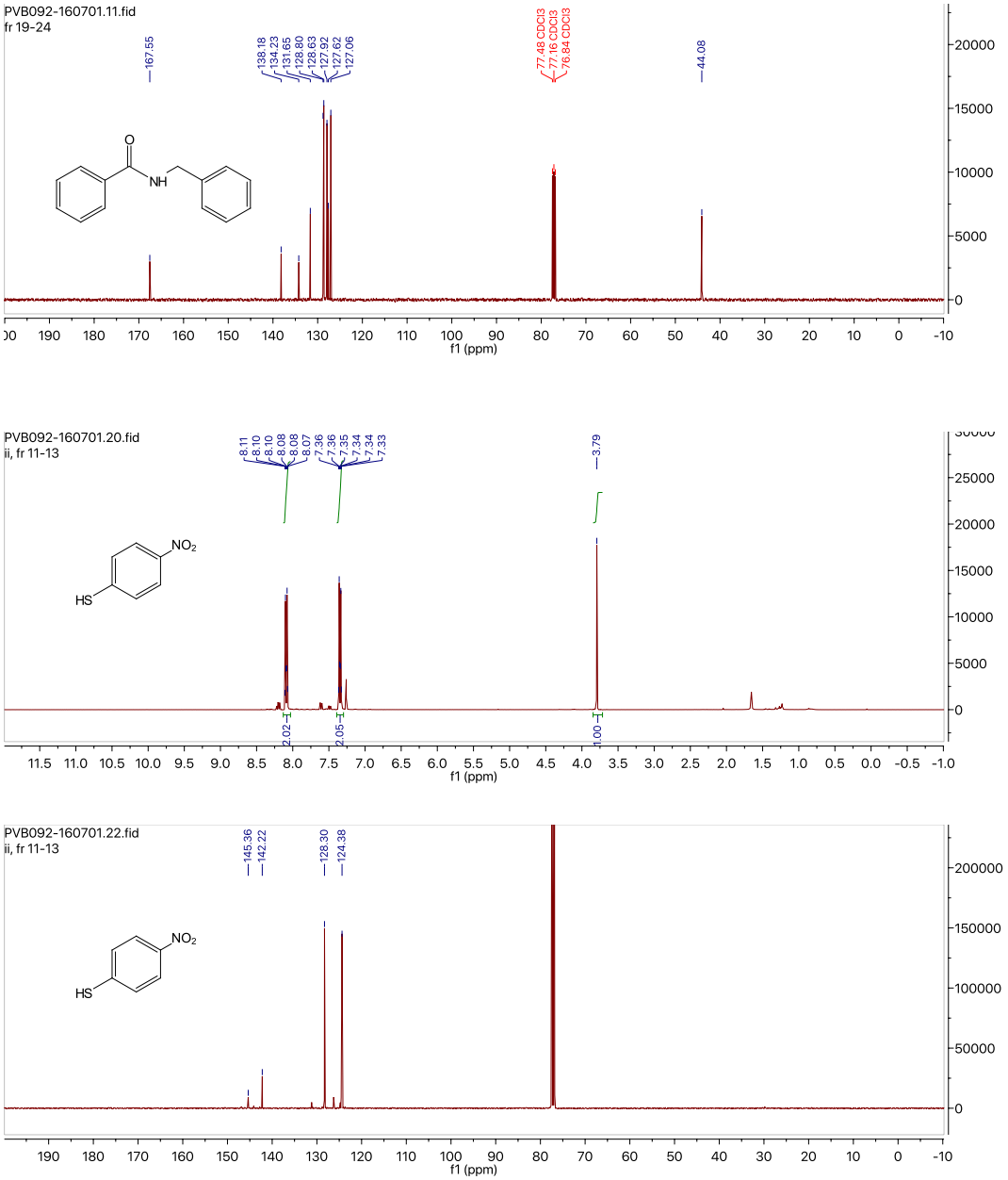
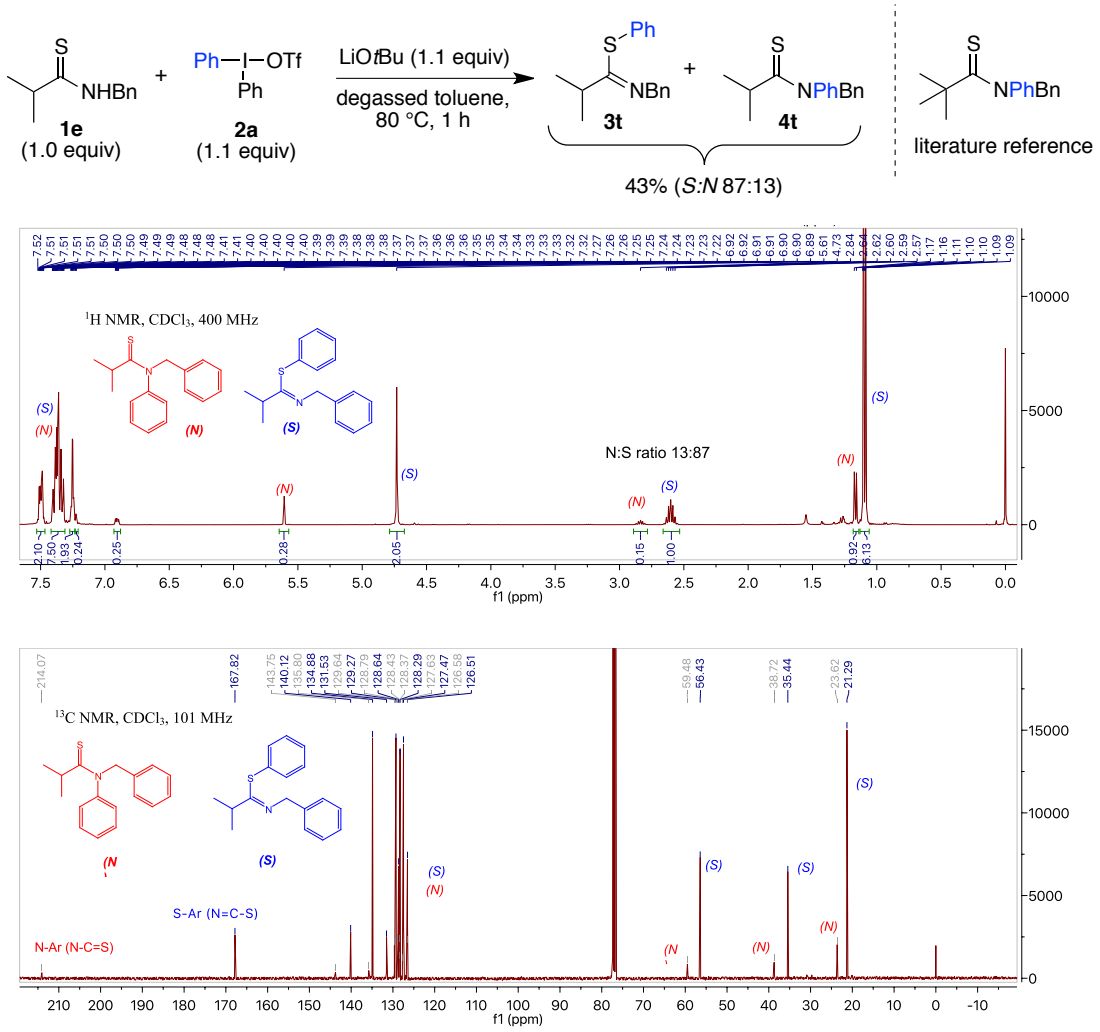


Figure S5. ^{1}H and ^{13}C NMR spectra for amide and thiophenol from hydrolysis of **3c**.

5.3 *S/N*-Arylation Products of Thioamides 1e, 1f and Pyrrolidine-2-thione

In general, the acyclic thioamides delivered *S*-arylated products with no observed *N*-arylations. The exceptions were alkyl thioamides **1e** and **1f**. Thioamide **1e** gave the *S*-arylated **3t** as major product with a minor *N*-arylated product **4t** in 43% overall yield (Scheme S8). No *E/Z*-mixture was detected, only one set of signals was observed for both products in ^{1}H and ^{13}C NMR analysis. The carbonyl signal in ^{13}C NMR for thioimidate **3t** is at 167.8 ppm, whereas the carbonyl signal in **4t** is at 214.0 ppm, which is characteristic for a thioamide. For a similar thioamide (*t*Bu instead of *i*Pr),

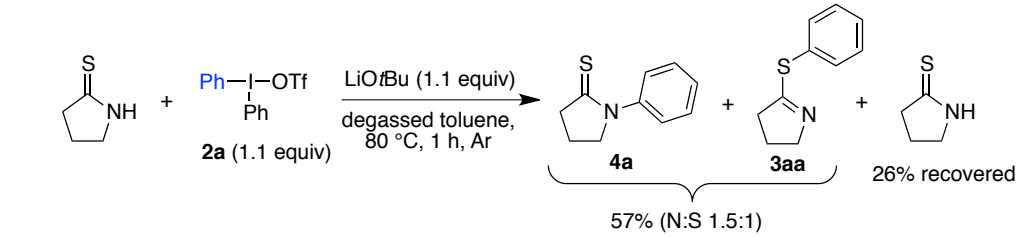
the reported carbonyl signal is at 217.0 ppm.[28] The ratio of *S:N*-arylation (87:13) is assessed by ^{1}H NMR integration as shown from –C*H*-*i*Pr signals at 2.60 ppm (**3t**) and 2.84 ppm (**4t**). A substantial shift is also seen for the –CH_2-Ph protons at 4.73 ppm (**3t**) and 5.61 ppm (**4t**), for the reported *t*Bu thioamide the corresponding signals are at 5.65 ppm.[28] Thioamide **1f** bearing cyclo-hexyl instead on *i*-Pr followed suit, giving a *S:N* mixture 5:1 of arylation products in 32% yield (**3u**). On the other hand, **1g** with linear *n*-hexyl substitution, gave only traces of arylation products, with mostly starting material **1g** recovered (29%) along with the corresponding amide (51%), indicating that the alkylated thioamide is much more prone to hydrolysis compared to arylated substrates.

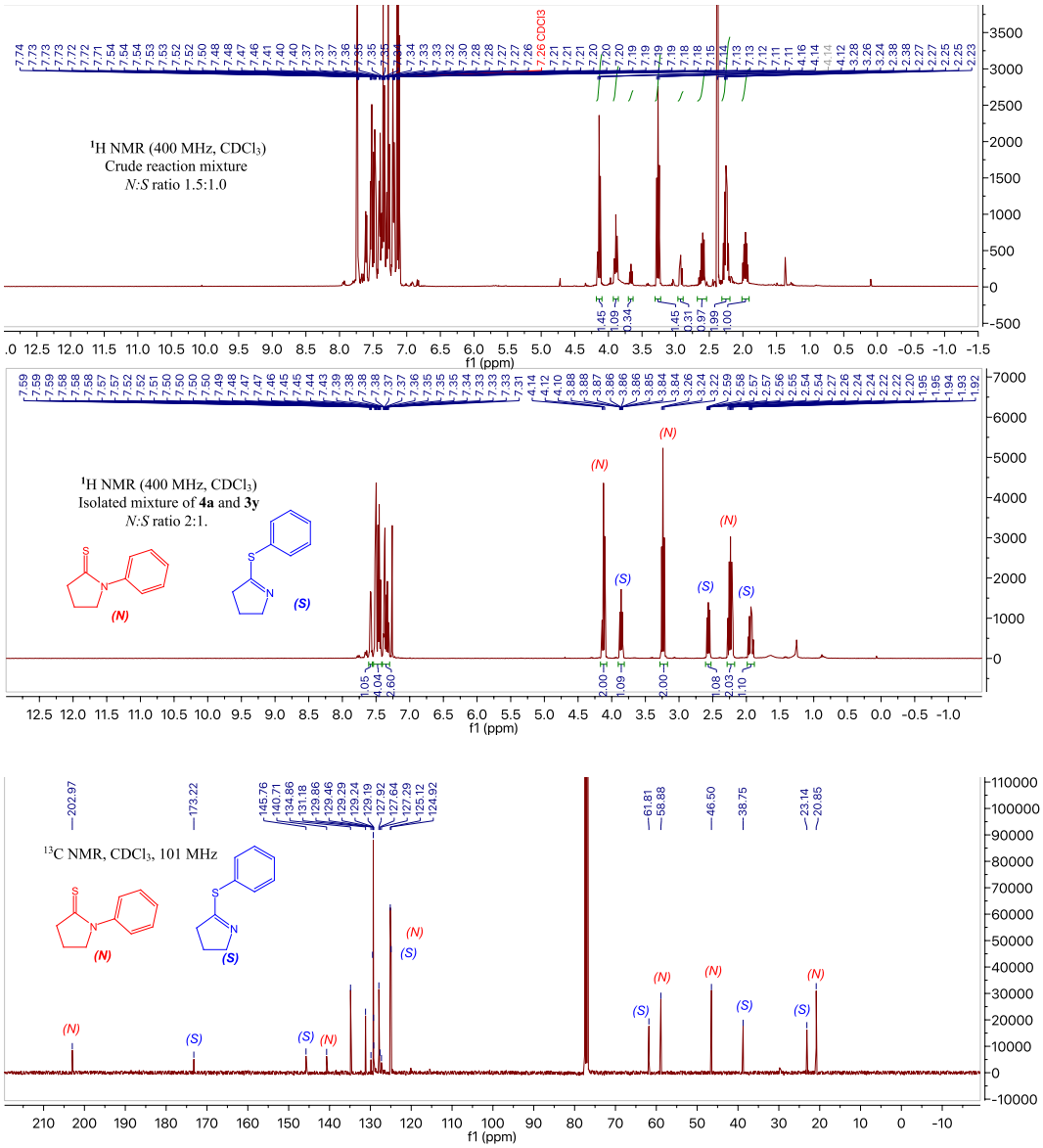


Scheme S8. ^{1}H and ^{13}C NMR of N- and S-arylated products of thioamide **1e**. A reported *t*Bu thioamide is shown as comparison.[28]

Interestingly, reactions with thiolactams gave predominantly *N*-arylated products. Pyrrolidine-2-thione gave a mixture of *N*-arylated **4a** (major) and *S*-arylated product **3aa** (minor) (Scheme S9), which matches the literature data on **4a**.[29] The products were difficult to separate by flash chromatography and were thus isolated together. The *N:S* ratio was measured from the crude reaction mixture (*N:S* 1.5:1) after evaporation of toluene. Some of minor isomer was lost during purification, giving *N:S*

2:1 for the isolated **4a**,**3aa** mixture. The isolated mixture of **4a** and **3aa** was investigated by GC-MS, which showed two major signals with the same mass (Figure S6). The *N/S* mixture was observed also under different reaction conditions, *e.g.*, at room temperature, at 0 °C and after shorter and longer reaction times.





Scheme S9. ^{1}H, ^{13}C NMR of the *N/S* mixture from arylation of pyrrolidine-2-thione.

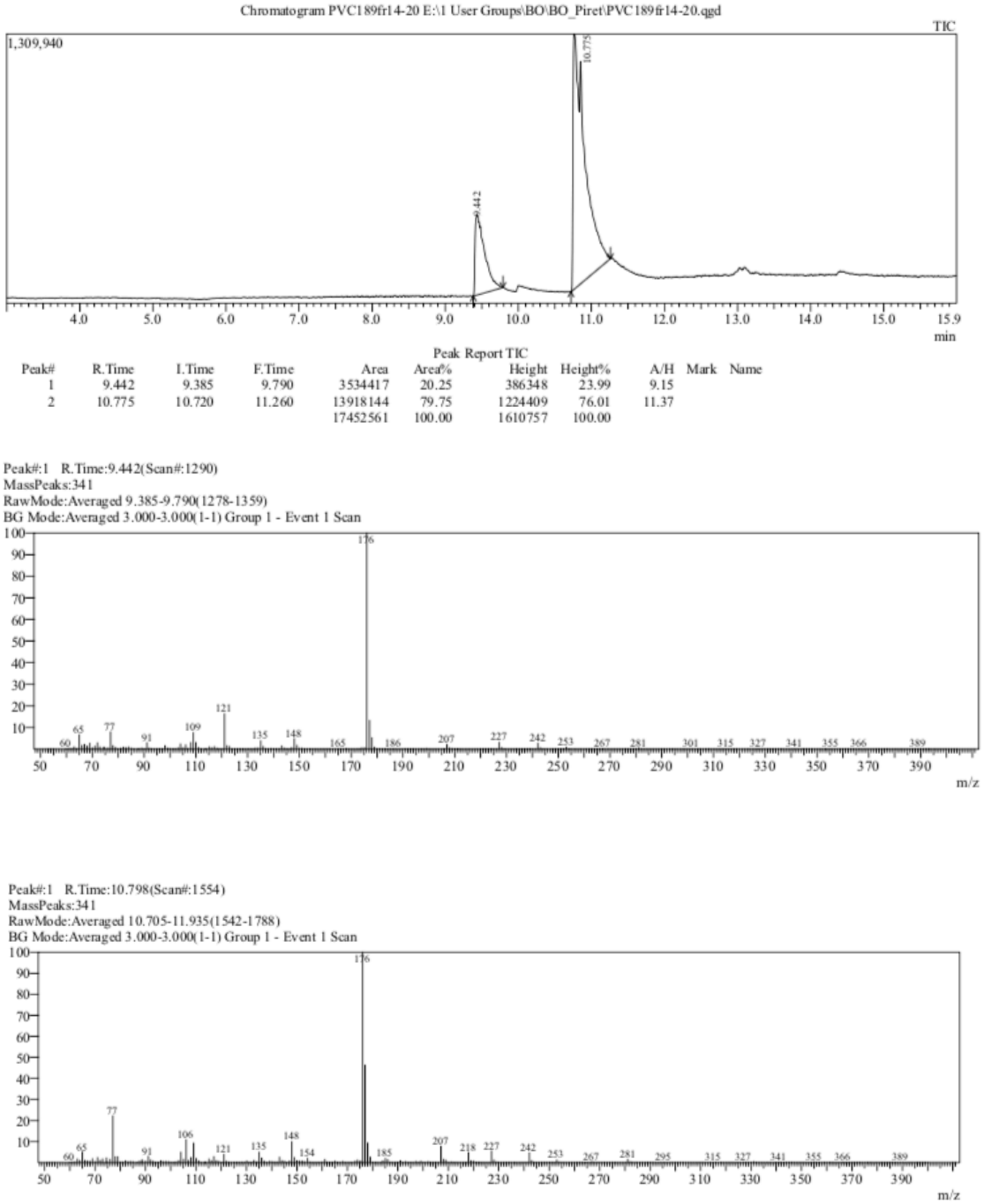
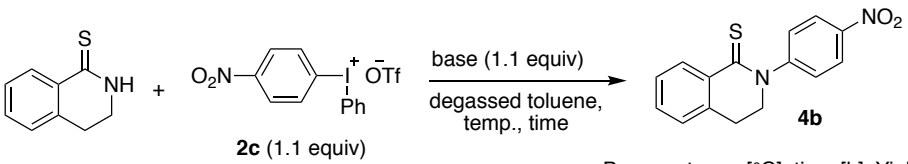


Figure S6. GC-MS analysis of the *N/S* mixture from arylation of pyrrolidine-2-thione.

Isoquinoline-1-thione delivered the *N*-arylated thiolactam **4b** in high yields already at room temperature (Scheme S10). In this case, the yield can be further improved by adding the base to a stirred solution of thiolactam and **2c** in toluene after 5 min. This effect was not observed for other substrates. LiO*t*Bu gave 76-95% isolated yield of **4b**, and NaO*t*Bu gave 81%, whereas reactions with K_2CO_3 only resulted in recovered starting material [conditions: Ph_2IOTf (1.1 equiv), K_2CO_3 (1.1 equiv), 80 °C, 1 h].



Base	temp. [°C]	time [h]	Yield [%]
NaO*t*Bu	r.t.	1	81
LiO*t*Bu	r.t.	1	76
LiO*t*Bu	r.t.	16	95

Scheme S10. Arylation of isoquinoline-1-thione.

6 Preliminary Mechanistic Studies

We have recently published a mechanistic study of *O*-arylations with diaryliodonium salts, based on experimental techniques and calculations. We demonstrated that reactions under basic conditions can result in aryne formation already at room temperature.[30] We used two approaches to identify arynes:

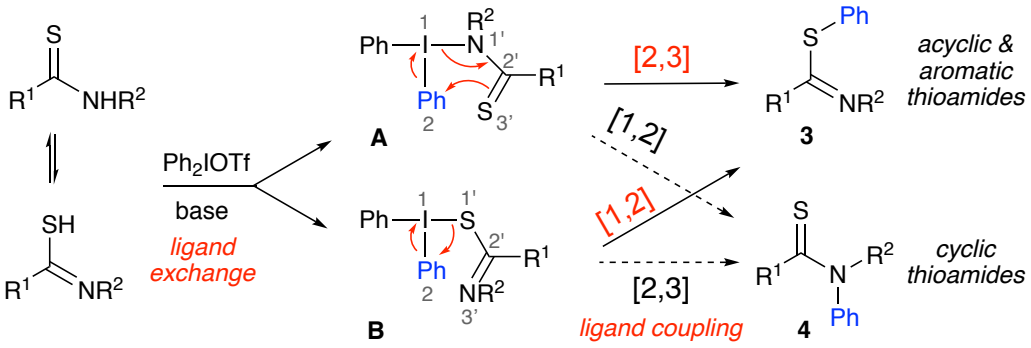
1) arylations with EDG-substituted iodonium salts (e.g. *para*-alkyl) gives regioisomers when arynes are involved.

2) furan was added as an aryne trap, resulting in cycloaddition products in the presence of arynes.

Preliminary mechanistic investigations in the arylation of thioamides revealed that arynes could not be identified using the approaches above. Furthermore, addition of radical scavengers (piperidine and 1,1-diphenylethylene, respectively) had negligible effect on the reaction outcome (see Table S6). Hence both an aryne pathway and a radical mechanism can be excluded.

We have previously studied the mechanisms in arylation of other nucleophiles with two nucleophilic atoms (enolates and nitrite) using a combination of experimental and theoretical techniques.[31] Those studies revealed the possibility of two different intermediates that could be converted to product via different types of ligand coupling, either with a 3-membered TS or with a larger TS. We have been unable to observe intermediates in any arylations by NMR due to the heterogeneous reactions, apart from in a recently described synthesis of Phenoxazine, where the T-shaped intermediate was stable to workup.[32]

Based on previous studies, we propose that the reaction proceeds by deprotonation and ligand exchange to provide T-shaped intermediate **A** and/or **B** (Scheme S11). *I-N* intermediate **A** could form the *S*-arylated thioimidate **3** via a [2,3] rearrangement, whereas *I-S* intermediate **B** would undergo a [1,2] rearrangement to yield **3**. Alternatively, intermediates **A** and **B** could yield *N*-aryl thioamide **4** through [1,2] and [2,3] rearrangement, respectively.



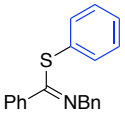
Scheme S11. Mechanistic possibilities.

7 Synthesis of Aryl Thioimidates 3

7.1 General Procedure for Arylation of Thioamides

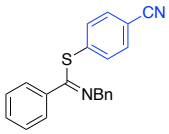
Thioamide **1** (0.12 mmol, 1 equiv), diaryliodonium salt **2** (1.1 equiv) and LiO*t*Bu (1.1 equiv) were weighed into an oven dried 4 mL microwave vial. The reaction vessel was evacuated and backfilled with argon three times, and the solids were then dissolved in degassed, anhydrous toluene (1.9 mL) under argon. The reaction was stirred at 80 °C for 1 h. After that the reaction mixture was brought to room temperature, and transported directly onto a silica gel column with a small amount of CH_2Cl_2. The mixture was purified by flash column chromatography (2% EtOAc in pentane or Et_2O in pentane).

7.2 Synthetic Details and Analytical Data



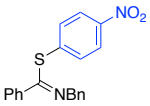
Phenyl (*Z*)-*N*-benzylbenzimidothioate (3a)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2a** as yellow oil, *Z:E* ratio 93:7. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.62 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.38 (m, 2H), 7.34–7.29 (m, 1H), 7.25 (m, 5H), 7.19–7.14 (m, 3H), 5.04 (bs, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 139.6, 138.2, 132.6, 132.6, 129.5, 129.1, 128.9, 128.4, 127.89, 127.8, 127.4, 126.8, 58.6. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (s, 2H, N-C*H*$_2$-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 56.9 ppm. HRMS (ESI): calcd $C_{20}H_{18}NS$ $[M+H]^+$: 304.1154, found 304.1153.



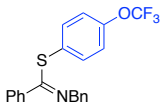
4-Cyanophenyl (*Z*)-*N*-benzylbenzimidothioate (3b)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2b** as beige oil, *Z:E* ratio 92:8. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.65 (m, 2H), 7.47–7.34 (m, 6H), 7.32–7.20 (m, 6H), 5.03 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 140.2, 138.94, 137.6, 132.3, 131.3, 130.4, 129.2, 128.6, 128.3, 127.8, 127.1, 118.3, 110.4, 59.4. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H, N-C*H*$_2$-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 57.12. HRMS (ESI): calcd $C_{21}H_{17}N_2S$ $[M+H]^+$: 329.1107, found 329.1105.



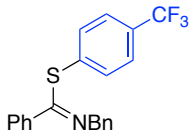
4-Nitrophenyl (*Z*)-*N*-benzylbenzimidothioate (3c)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2c** as yellow oil, *Z:E* ratio 92:7. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (app.d, 2H), 7.76 (app. d, 2H), 7.44 (app. d, 2H), 7.38 (m, 2H), 7.34–7.24 (m, 6H), 5.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 146.2, 142.6, 138.8, 137.5, 130.9, 130.5, 129.2, 128.5, 128.3, 127.8, 127.1, 123.8, 59.5.
Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (s, 2H, N-C*H*$_2$-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 57.2. HRMS (ESI): calcd $C_{20}H_{17}N_2O_2S$ $[M+H]^+$: 349.1005, found 349.1003.



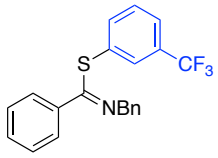
4-(Trifluoromethoxy)phenyl (*Z*)-*N*-benzylbenzimidothioate (3d)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2r** as yellow oil, *Z:E* ratio 89:11. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.50–7.45 (m, 2H), 7.43–7.36 (m, 2H), 7.34–7.28 (m, 1H), 7.27–7.21 (m, 5H), 7.03–6.97 (m, 2H), 5.02 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 148.7, 139.5, 137.9, 134.2, 131.5, 129.8, 129.2, 128.7, 128.1, 128.0, 127.1, 123.0 (q, J = 258.3 Hz), 121.5, 58.9. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 2H, N-CH_2-Ph). HRMS (ESI): calcd $C_{21}H_{17}F_3NOS$ $[M+H]^+$: 388.0977, found 388.0975.



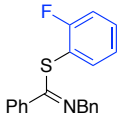
4-(Trifluoromethyl)phenyl (*Z*)-*N*-benzylbenzimidothioate (3e)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2h** as yellow oil, *Z:E* ratio 92:8. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.67 (m, 2H), 7.44 (m, 2H), 7.40–7.34 (m, 4H), 7.32–7.21 (m, 6H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 139.3, 138.2, 137.9, 135.1, 131.6, 130.3, 129.3, 128.7, 128.3, 128.0, 127.1, 125.9 (q, J = 3.7 Hz), 123.9 (q, J = 272.1 Hz), 59.3. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H, N-CH_2-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 57.1. HRMS (ESI): calcd $C_{21}H_{17}F_3NS$ $[M+H]^+$: 372.1028, found 372.1028.



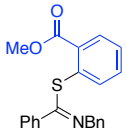
3-(Trifluoromethyl)phenyl (*Z*)-*N*-benzylbenzimidothioate (3f)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2q** as yellow oil, *Z:E* ratio 88:12. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 2H), 7.45 (dd, J = 7.2, 1.7 Hz, 3H), 7.40–7.32 (m, 4H), 7.32–7.26 (m, 1H), 7.24–7.16 (m, 4H), 5.01 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 139.2, 137.6, 135.5 (q, J = 0.9 Hz), 134.2, 131.3 (q, J = 32.5 Hz), 129.8, 129.2, 129.1, 129.1, 128.5, 128.0, 127.9, 126.9, 124.0 (q, J = 3.7 Hz), 123.4 (q, J = 272.9 Hz), 58.9. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H, N-CH_2-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.9. HRMS (ESI): calcd $C_{21}H_{17}F_3NS$ $[M+H]^+$: 372.1028, found 372.1016. The isolated **3f** contained *ca* 5% 4-iodoanisole, the yield 50% is calculated from the isolated mixture. Characteristic signal for 4-iodoanisole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H, OCH_3).

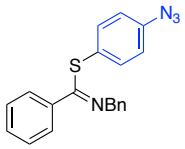


2-Fluorophenyl (*Z*)-*N*-benzylbenzimidothioate (3g)

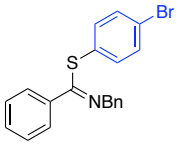
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2s** as yellow oil, *Z:E* ratio 92:8. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2H), 7.50–7.45 (m, 2H), 7.41–7.35 (m, 2H), 7.32–7.25 (m, 2H), 7.21–7.11 (m, 4H), 6.97–6.92 (m, 1H), 6.91–6.86 (m, 1H), 5.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 160.6 (d, J = 93.5 Hz), 139.6, 138.0, 135.6, 130.5 (d, J = 7.9 Hz), 129.6, 128.9, 128.6, 128.1, 127.9, 127.0, 124.6 (d, J = 3.9 Hz), 119.9 (d, J = 18.2 Hz), 115.9 (d, J = 22.6 Hz), 58.8. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H, N-CH_2-Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 57.1. HRMS (ESI): calcd $C_{20}H_{17}FNS$ $[M+H]^+$: 322.1060, found 322.1062.



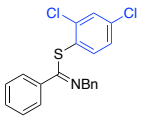
Methyl (*Z*)-2-([(benzylimino)(phenyl)methyl]thio)benzoate (3h)
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2g** as beige oil, *Z:E* ratio 96:4. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 1H), 7.81–7.75 (m, 2H), 7.50–7.42 (m, 2H), 7.35 (m, 2H), 7.30–7.20 (m, 4H), 7.15 (ddd, *J* = 7.1, 4.3, 2.0 Hz, 2H), 7.11–7.07 (m, 1H), 5.05 (s, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 160.2, 139.6, 138.4, 136.0, 132.2, 131.9, 131.1, 130.1, 130.0, 129.1, 128.4, 128.0, 127.9, 126.8, 126.2, 59.2, 52.4. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 2H, N-C*H*$_2$-Ph), 3.78 (s, 3H, COOC*H*$_3$). HRMS (ESI): calcd $C_{22}H_{20}NO_2S$ $[M+H]^+$: 362.1209, found 362.1207.



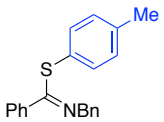
4-Azidophenyl (*Z*)-*N*-benzylbenzimidothioate (3i)
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2l** as yellow oil, *Z:E* ratio 90:10. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 2H), 7.48–7.42 (m, 2H), 7.40–7.33 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 4H), 6.82–6.75 (m, 2H), 4.99 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 139.6, 139.5, 137.9, 134.4, 129.6, 129.1, 128.5, 128.5, 127.9, 127.9, 126.9, 119.5, 58.5. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{20}H_{17}N_4S$ $[M+H]^+$: 345.1168, found 345.1169.
The isolated **3i** contained *ca* 5% TMP-I, the yield 45% is calculated from the isolated mixture. Characteristic signal for TMP-I: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 2H), 3.77 (s, 6H, OC*H*$_3$).



4-Bromophenyl (*Z*)-*N*-benzylbenzimidothioate (3j)
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2e** or **2i** as yellow oil, *Z:E* ratio 91:9. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.56 (m, 2H), 7.46–7.42 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.20 (m, 6H), 7.10–7.03 (m, 2H), 4.99 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 139.4, 137.8, 133.8, 132.0, 131.8, 129.8, 129.1, 128.5, 128.0, 127.9, 126.9, 121.7, 58.8. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{20}H_{17}BrNS$ $[M+H]^+$: 382.0260, found 382.0261.

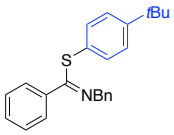


2,4-Dichlorophenyl (*Z*)-*N*-benzylbenzimidothioate (3k)
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2k** as yellow oil in 56% yield, *Z:E* ratio 93:7. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.56 (m, 2H), 7.48–7.43 (m, 2H), 7.41–7.34 (m, 2H), 7.31–7.14 (m, 6H), 6.99 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 139.3, 137.7, 137.1, 135.5, 134.5, 130.6, 129.9, 129.7, 128.9, 128.5, 127.9, 127.9, 127.4, 126.9, 58.9. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H, N-C*H*$_2$-Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.9. HRMS (ESI): calcd $C_{20}H_{16}Cl_2NS$ $[M+H]^+$: 372.0375, found 372.0376.
A parallel reaction gave the isolated **3k** contaiminated with *ca* 32% 4-iodoanisole, the yield 75% for **3k** was calculated from the isolated mixture. Characteristic signal for 4-iodoanisole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H, OC*H*$_3$) ppm.



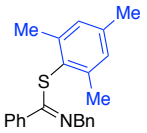
***p*-Tolyl (*Z*)-*N*-benzylbenzimidothioate (3l)**
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2d** as beige waxy solid in 75% yield, *Z:E* ratio 93:7. **(*Z*) isomer:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.44–7.40 (m,

4H), 7.39–7.33 (m, 2H), 7.31–7.25 (m, 1H), 7.22–7.10 (m, 5H), 6.99–6.93 (m, 2H), 4.97 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 167.7, 140.4, 139.7, 139.2, 134.9, 130.8, 130.5, 130.1, 129.6, 129.1, 129.0, 128.8, 128.1, 59.1, 21.0. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{21}H_{20}NS$ $[M+H]^+$: 318.1311, found 318.1313.



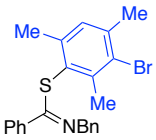
4-(*tert*-Butyl)phenyl (*Z*)-*N*-benzylbenzimidothioate (3m)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2m** as yellow oil in 66% yield, *Z:E* ratio 92:8. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 2H), 7.45 (m, 2H), 7.40–7.33 (m, 2H), 7.30–7.24 (m, 1H), 7.21–7.11 (m, 7H), 4.97 (s, 2H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 150.8, 139.8, 138.3, 132.4, 129.3, 129.1, 128.9, 128.4, 127.9, 127.7, 126.8, 125.9, 58.5, 34.5, 31.1. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{24}H_{25}NS$ $[M+H]^+$: 360.1780, found 360.1780.



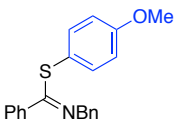
Mesityl (*Z*)-*N*-benzylbenzimidothioate (3n)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2n** or **2f**. as yellow oil in 73% yield, *Z:E* ratio 91:9. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.43–7.37 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.22–7.13 (m, 3H), 6.79 (s, 2H), 4.98 (s, 2H), 2.40 (s, 6H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 141.4, 140.1, 138.7, 138.5, 129.4, 129.2, 128.5, 128.2, 128.1, 127.6, 127.5, 126.8, 57.9, 22.2, 21.0. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{23}H_{24}NS$ $[M+H]^+$: 346.1624, found 346.1623.



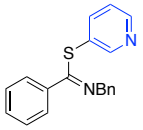
3-Bromo-2,4,6-trimethylphenyl (*Z*)-*N*-benzylbenzimidothioate (3o)

Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2p** as beige oil, in 80% yield, *Z:E* ratio 86:14. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.44–7.31 (m, 4H), 7.31–7.22 (m, 1H), 7.21–7.08 (m, 3H), 6.82 (s, 1H), 4.95 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 140.9, 140.2, 139.7, 139.1, 138.0, 130.0, 129.5, 129.4, 128.4, 127.9, 127.9, 127.5, 126.8, 125.6, 57.9, 24.0, 23.6, 22.1. Characteristic signals for **(*E*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 2H, N-C*H*$_2$-Ph), 2.67 (s, 3H, C*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 2.41 (s, 3H, C*H*$_3$). HRMS (ESI): calcd $C_{23}H_{23}BrNS$ $[M+H]^+$: 424.0729, found 424.0715.



4-Methoxyphenyl (*Z*)-*N*-benzylbenzimidothioate (3p)

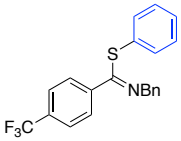
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2o** as beige waxy solid in 69% yield, *Z:E* ratio 91:9. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.42 (m, 4H), 7.41–7.32 (m, 2H), 7.31–7.21 (m, 1H), 7.21–7.11 (m, 5H), 6.73–6.58 (m, 2H), 4.97 (s, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 159.4, 139.8, 138.2, 135.0, 129.2, 128.9, 128.4, 127.9, 127.7, 126.8, 122.6, 114.5, 58.2, 55.2. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 2H, N-C*H*$_2$-Ph), 3.80 (s, 3H, OC*H*$_3$). HRMS (ESI): calcd $C_{21}H_{20}NOS$ $[M+H]^+$: 334.1260, found 334.1258.



Pyridin-3-yl (*Z*)-*N*-benzylbenzimidothioate (3q)

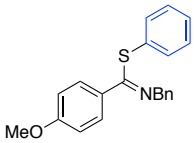
Synthesized according to the general procedure using thioamide **1a** and diaryliodonium salt **2j** as yellow oil in 53% yield, *Z:E* ratio 87:13. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.32 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.57–7.50 (m, 2H), 7.48–7.43 (m, 3H), 7.40–7.33 (m, 3H), 7.31–7.26 (m, 1H), 7.23–7.15 (m, 2H), 7.02 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 152.7, 148.3, 139.9, 139.2, 137.4, 130.1, 129.8, 129.1, 128.5, 128.1, 127.9, 126.9, 123.5, 58.8. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (m, 1H), 8.55 (m, 1H), 4.50 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{19}H_{17}N_2S$ $[M+H]^+$: 305.1107, found 305.1113.

The yield 53% is calculated from an isolated mixture of **3q** and the corresponding amide, which is the product of hydrolysis of **3q**. Characteristic signals for the corresponding amide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 6.52 (bs, 1H, N*H*), 4.64 (d, *J* = 5.7 Hz, 2H). Compound **3q** seems to be more prone to hydrolysis than other isolated thioimidates **3**, and even when NMR analysis is carried out directly after isolation, the corresponding amide signals are always observed. Also, the amide signals increase over time.



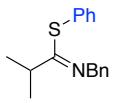
Phenyl (*Z*)-*N*-benzyl-4-(trifluoromethyl)benzimidothioate (3r)

Synthesized according to the general procedure using thioamide **1b** and diaryliodonium salt **2a**.as yellow oil in 73% yield, *Z:E* ratio 96:4. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 2H), 7.48–7.41 (m, 4H), 7.41–7.35 (m, 2H), 7.33–7.26 (m, 1H), 7.23–7.18 (m, 2H), 7.14 (dp, *J* = 4.4, 1.5 Hz, 3H), 5.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 141.5, 139.3, 132.8, 131.7, 131.2 (q, *J* = 32.6 Hz), 129.4, 129.2, 128.5, 127.9, 127.9, 127.0, 124.8 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.4 Hz), 58.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 2H, N-C*H*$_2$-Ph). HRMS (ESI): calcd $C_{21}H_{17}F_3NS$ $[M+H]^+$: 372.1028, found 372.1034.



Phenyl (*Z*)-*N*-benzyl-4-methoxybenzimidothioate (3s)

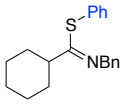
Synthesized according to the general procedure using thioamide **1c** and diaryliodonium salt **2a** as yellow oil in 71% yield, *Z:E* ratio 95:5. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.61 (m, 2H), 7.47–7.40 (m, 2H), 7.38–7.32 (m, 2H), 7.29–7.19 (m, 3H), 7.18–7.10 (m, 3H), 6.79–6.67 (m, 2H), 4.98 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 160.1, 139.9, 133.3, 131.9, 131.0, 130.8, 128.9, 128.4, 127.9, 127.0, 126.7, 113.2, 58.7, 55.2. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 2H, N-C*H*$_2$-Ph), 3.81 (s, 3H, OC*H*$_3$). HRMS (ESI): calcd $C_{21}H_{20}NOS$ $[M+H]^+$: 334.1260, found 334.1262.



Phenyl (*Z*)-*N*-benzyl-2-methylpropanimidothioate (3t)

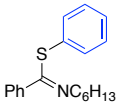
Synthesized according to the general procedure using thioamide **1e** and diaryliodonium salt **2a** as beige oil in 45% yield; *S:N* ratio 6:1. **Major isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.47 (m, 2H), 7.42–7.31 (m, 6H), 7.28–7.23 (m, 2H), 4.73 (s, 2H), 2.60 (hept, *J* = 6.7 Hz, 1H), 1.10 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 140.1, 134.9, 131.5, 129.3, 128.6, 128.3, 127.5, 126.5, 56.4, 35.4, 21.3. **Minor isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.21 (m, 9H, signals overlapping with aromatic signals of major product), 6.90 (m, 1H), 5.61 (s. 1H), 2.84 (hept, *J* = 6.6 Hz, 1H), 1.17

(d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.1, 143.8, 135.8, 129.6, 128.8, 128.4, 128.4, 127.6, 126.6, 59.5, 38.7, 23.6. HRMS (ESI): calcd $C_{17}H_{20}NS$ $[M+H]^+$: 270.1311, found 270.1309.



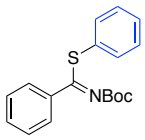
(*Z*)-Phenyl *N*-benzylcyclohexanecarbimidothioate (3u)

Synthesized according to the general procedure using thioamide **1f** and diaryliodonium salt **2a** as beige oil in 32% yield; *S:N* ratio 5:1. **Major isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 2H), 7.30–7.19 (m, 6H), 7.17–7.12 (m, 2H), 4.61 (s, 2H), 2.11 (tt, J = 11.5, 3.3 Hz, 1H), 1.75–1.65 (m, 2H), 1.60–1.48 (m, 2H), 1.46–1.34 (m, 3H), 1.10–0.95 (m, 1H), 0.89–0.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 140.29, 135.00, 131.71, 129.36, 128.77, 128.43, 127.63, 126.65, 56.67, 45.62, 31.87, 26.23, 26.02. Characteristic signals for **minor isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49, 2.34. ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.45, 59.47, 49.95, 33.80. HRMS (ESI): calcd $C_{20}H_{24}NS$ $[M+H]^+$: 310.1624, found 310.1625.



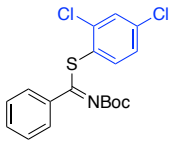
Phenyl (*Z*)-*N*-hexylbenzimidothioate (3v)

Synthesized according to the general procedure using thioamide **1d** and diaryliodonium salt **2a** as beige oil in 58% yield, *Z:E* ratio 95:5. **(*Z*) isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.44 (m, 2H), 7.23–7.14 (m, 5H), 7.13–7.04 (m, 3H), 3.77 (t, J = 6.9 Hz, 2H), 1.89–1.74 (m, 2H), 1.57–1.41 (m, 2H), 1.40–1.32 (m, 4H), 1.00–0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 138.3, 132.8, 132.7, 129.1, 128.9, 128.7, 127.8, 127.2, 55.1, 31.7, 30.6, 27.3, 22.8, 14.1. Characteristic signals for **(*E*) isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (t, 2H, N-CH_2). HRMS (ESI): calcd $C_{19}H_{24}NS$ $[M+H]^+$: 298.1624, found 298.1630.



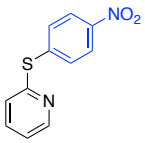
Phenyl (*Z*)-*N*-(tert-butoxycarbonyl)benzimidothioate (3w)

Synthesized according to the general procedure using thioamide **1h** and diaryliodonium salt **2a** as orange oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.59 (m, 2H), 7.50–7.42 (m, 2H), 7.41–7.34 (m, 1H), 7.33–7.26 (m, 5H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 159.6, 136.0, 134.1, 130.9, 129.9, 129.1, 128.9, 128.3, 128.2, 82.3, 27.9. HRMS (ESI): calcd $C_{18}H_{19}NNaO_2S$ $[M+Na]^+$: 336.1029, found 336.1026.



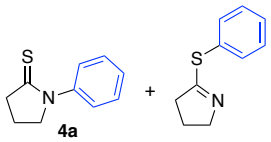
2,4-Dichlorophenyl (*Z*)-*N*-(tert-butoxycarbonyl)benzimidothioate (3x)

Synthesized according to the general procedure using thioamide **1h** and diaryliodonium salt **2k** as yellow oil in 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.61 (m, 2H), 7.48 (d, J = 8.3 Hz, 1H), 7.44–7.38 (m, 2H), 7.37–7.31 (m, 2H), 7.18 (dd, J = 8.3, 2.2 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 159.4, 138.9, 137.4, 136.3, 135.8, 131.5, 130.2, 128.5, 128.5, 128.4, 127.8, 82.7, 28.0. HRMS (ESI): calcd $C_{18}H_{17}Cl_2NNaO_2S$ $[M+Na]^+$: 404.0249, found 404.0251.



2-[(4-Nitrophenyl)thio]pyridine (3y)

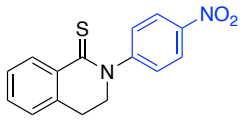
Synthesized according to the general procedure using pyridine-2-thiol and diaryliodonium salt **2c** as yellow oil in 78% yield. Analytical data is in agreement with data reported in literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.9 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 2H), 7.62 (m, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 150.4, 146.9, 142.3, 137.3, 131.8, 124.8, 124.1, 121.9.



4a

1-Phenylpyrrolidine-2-thione[29] (4a)

Synthesized according to the general procedure using pyrrolidine-2-thione and diaryliodonium salt **2a** as yellow waxy solid. *N:S* ratio 2:1. **4a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.48–7.42 (m, 2H), 7.36–7.30 (m, 1H), 4.12 (m, 2H), 3.24 (m, 2H), 2.31–2.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 140.7, 129.5, 129.3, 125.1, 58.9, 46.5, 20.9. **Minor isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.30 (m, 5H, signals overlapping with major isomer), 3.86 (m, 2H), 2.57 (m, 2H), 1.93 (m, , 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 140.7, 134.9, 129.5, 124.9, 61.8, 38.8, 23.1. HRMS (ESI): calcd $C_{10}H_{11}NNaS$ $[M+Na]^+$: 200.0504, found 200.0507.



2-(4-Nitrophenyl)-3,4-dihydroisoquinoline-1(2*H*)-thione (4b)

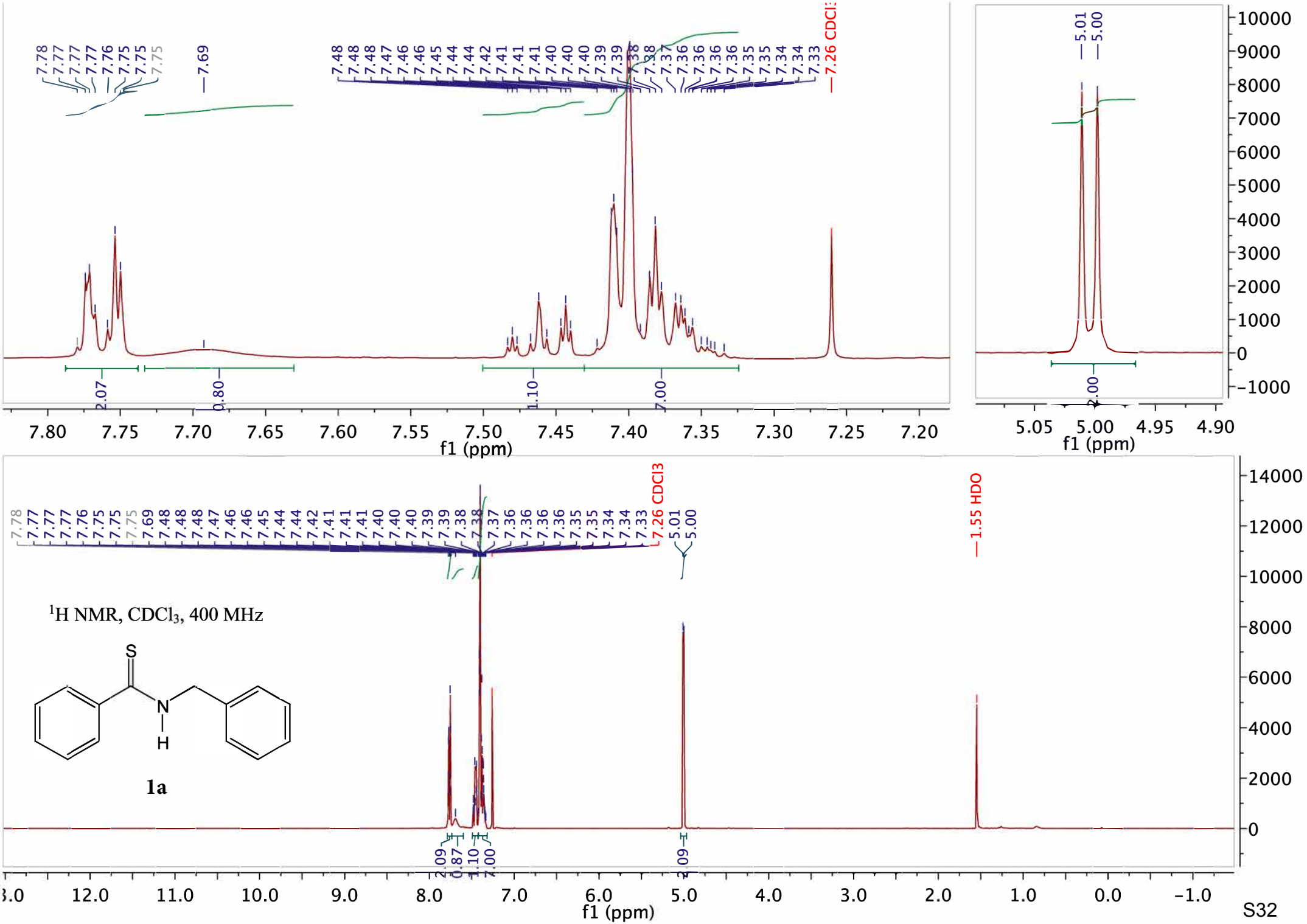
Synthesized according to the general procedure using thioamide **1i** and diaryliodonium salt **2c** as yellow waxy solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.39–8.31 (m, 2H), 7.59–7.52 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.38 (m, 1H), 7.22 (m, 1H), 4.04–3.95 (m, 2H), 3.21 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 152.8, 146.7, 133.8, 132.9, 132.8, 132.6, 128.2, 127.6, 127.0, 125.3, 52.2, 28.6. HRMS (ESI): calcd $C_{15}H_{12}N_2O_2S$ $[M+H]^+$: 307.0512, found 307.0508.

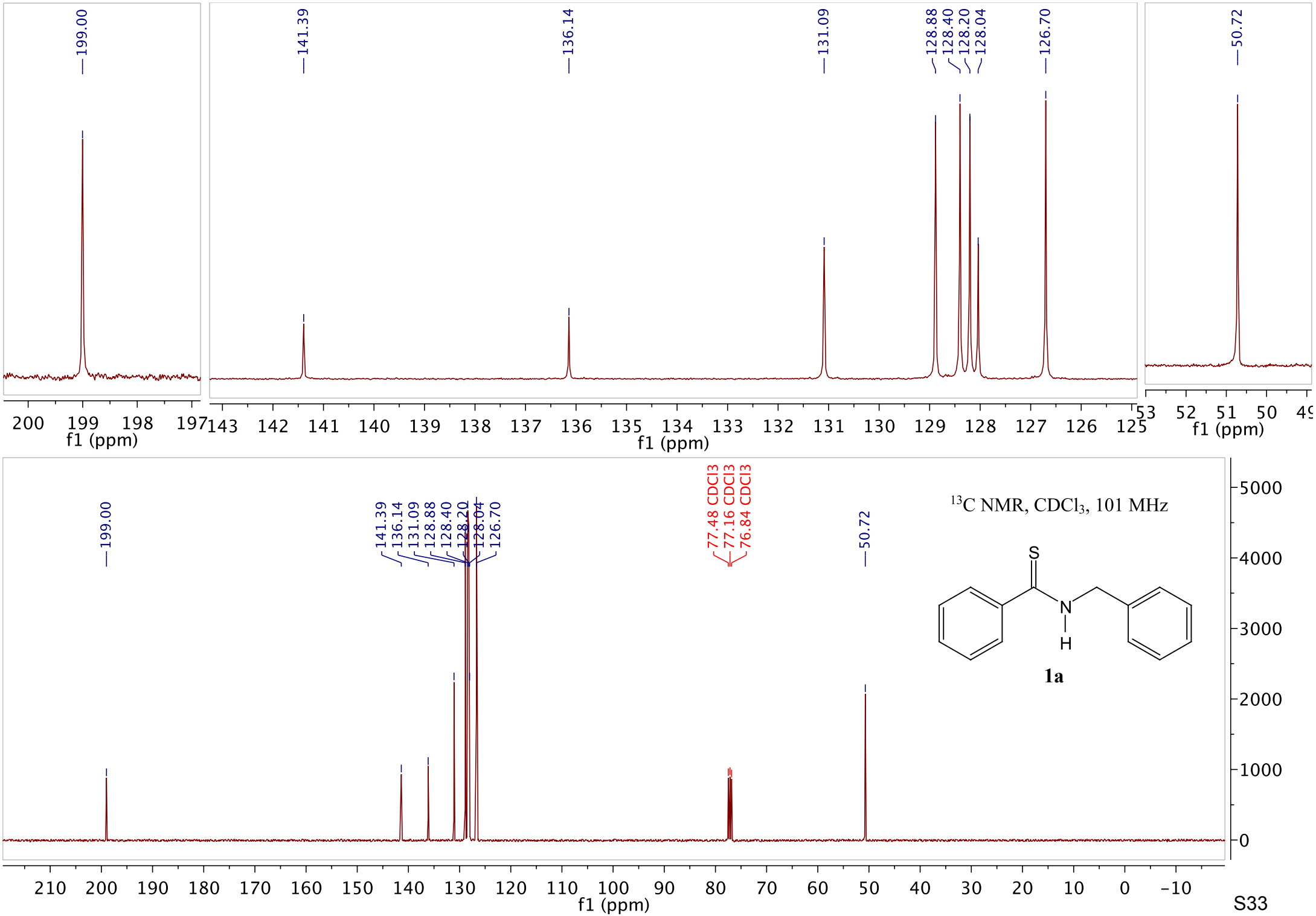
8 References

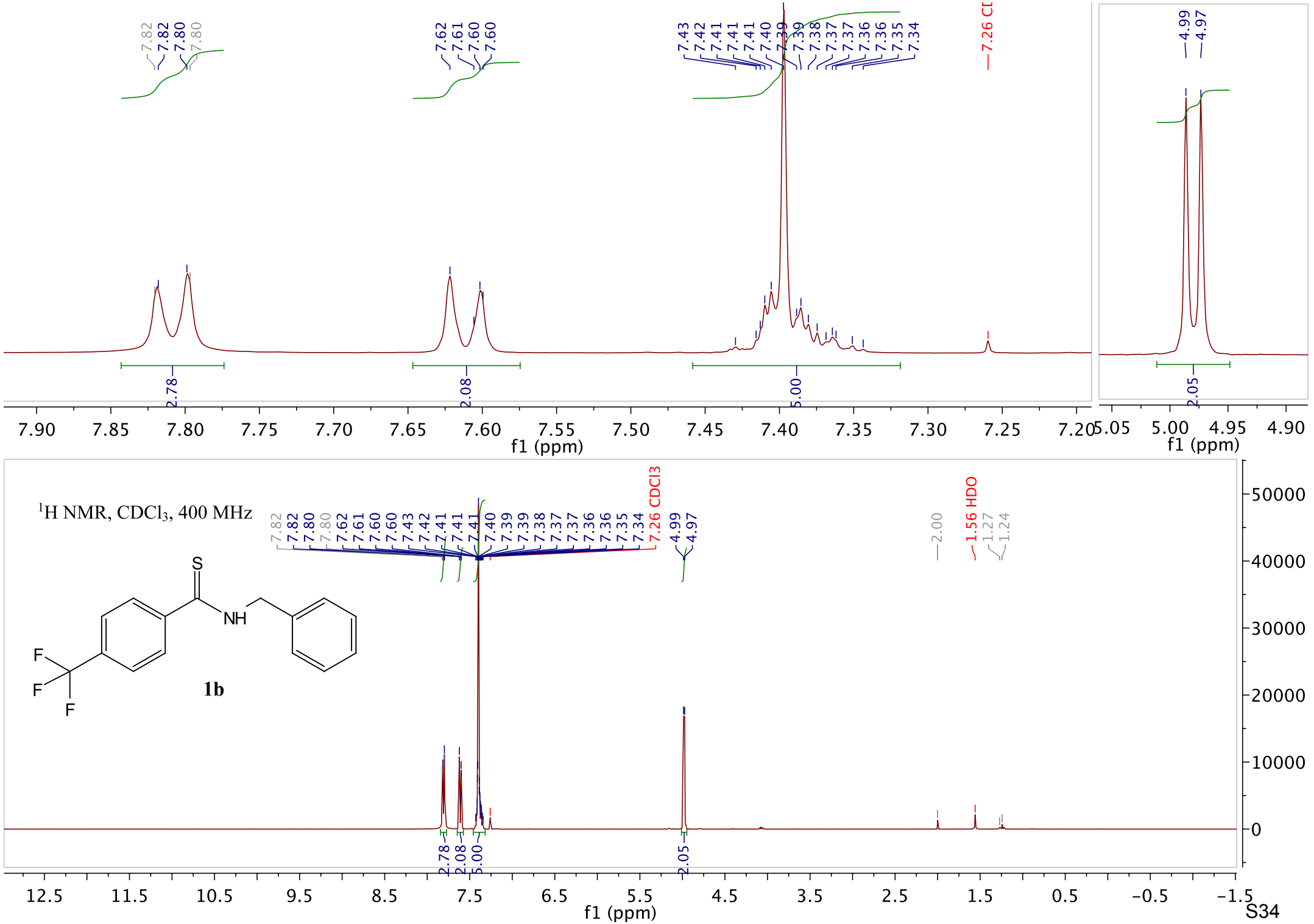
1. (a) A. I. Vogel, B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, Longman, 1978; (b) R. N. McDonald, R. N. Steppel and J. E. Dorsey, *Org. Syn.*, 1970, **50**, 15-18.
2. J. W. Wu, Y. D. Wu, J. J. Dai and H. J. Xu, *Adv. Synth. Catal.*, 2014, **356**, 2429-2436.
3. A. B. Charette and M. Grenon, *J. Org. Chem.*, 2003, **68**, 5792-5794.
4. F. Shibahara, R. Sugiura and T. Murai, *Org. Lett.*, 2009, **11**, 3064-3067.
5. T. Guntreddi, R. Vanjari and K. N. Singh, *Org. Lett.*, 2014, **16**, 3624-3627.
6. H. K. Lee, L. N. Ten and C. S. Pak, *Bull. Korean Chem. Soc.*, 1998, **19**, 1148-1149.
7. K. I. Ajzert and K. Takacs, *Liebigs Ann. Chem.*, 1987, 1061-1063.
8. M. Milen, P. Abranyi-Balogh, A. Dancso and G. Keglevich, *J. Sulfur Chem.*, 2012, **33**, 33-41.
9. M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal.*, 2007, **349**, 2610-2618.
10. N. Jalalian, T. B. Petersen and B. Olofsson, *Chem. - Eur. J.*, 2012, **18**, 14140-14149, S14140/14141-S14140/14163.
11. M. Zhu, N. Jalalian and B. Olofsson, *Synlett*, 2008, 592-596.
12. E. Lindstedt, E. Stridfeldt and B. Olofsson, *Org. Lett.*, 2016, **18**, 4234-4237.
13. N. Jalalian and B. Olofsson, *Org. Synth.*, 2013, **90**, 1-9.
14. M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.*, 2008, **73**, 4602-4607.
15. R. Ghosh, E. Lindstedt, N. Jalalian and B. Olofsson, *ChemistryOpen*, 2014, **3**, 54-57.
16. M. Bielawski, J. Malmgren, L. M. Pardo, Y. Wikmark and B. Olofsson, *ChemistryOpen*, 2014, **3**, 19-22.
17. G. L. Tolnai, U. J. Nilsson and B. Olofsson, *Angew. Chem., Int. Ed.*, 2016, **55**, 11226-11230.
18. E. A. Merritt, V. M. T. Carneiro, L. F. Silva, Jr. and B. Olofsson, *J. Org. Chem.*, 2010, **75**, 7416-7419.
19. F. Tinnis, E. Stridfeldt, H. Lundberg, H. Adolfsson and B. Olofsson, *Org. Lett.*, 2015, **17**, 2688-2691.
20. Y. Yamada and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1860-1863.

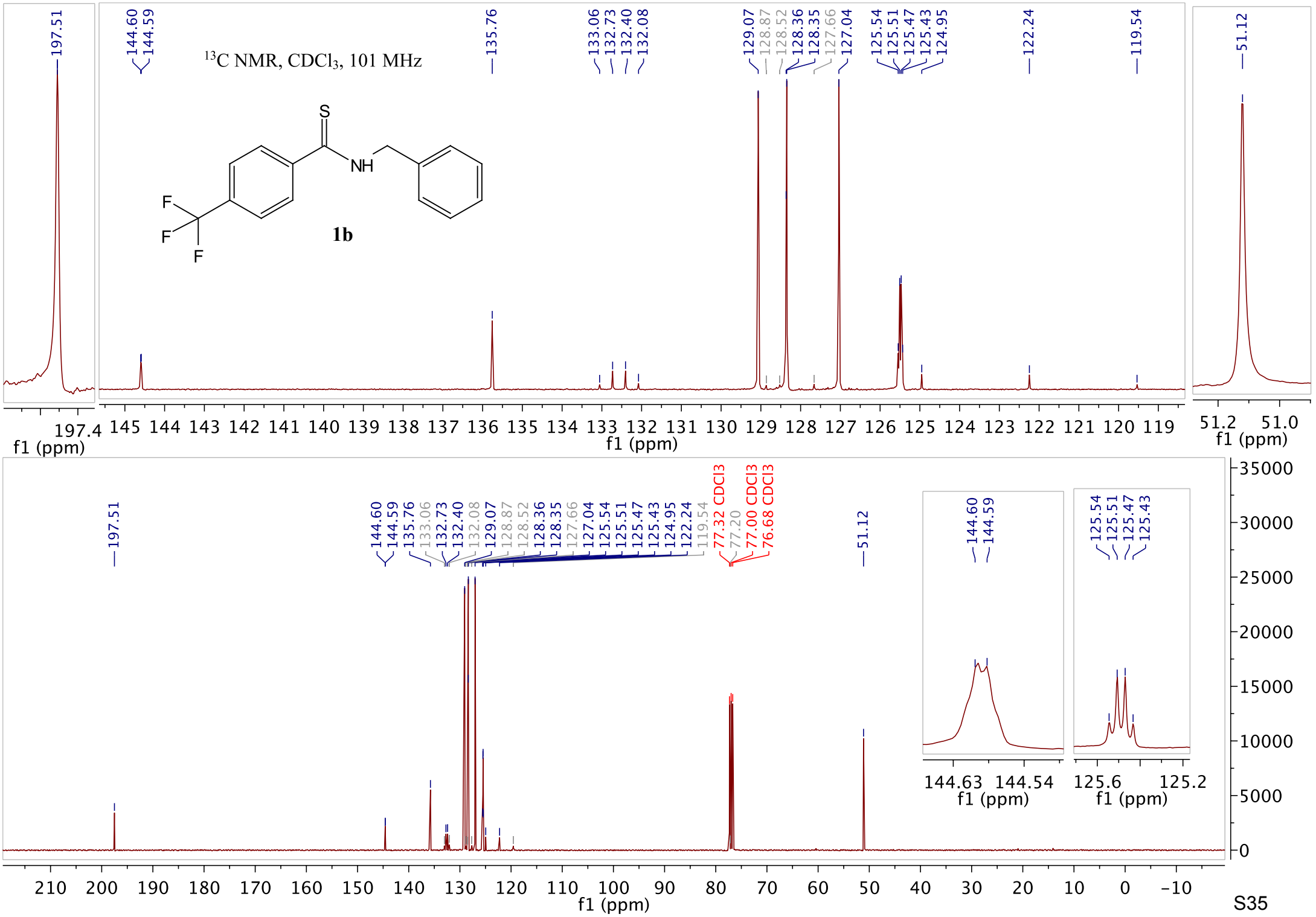
21. (a) D. R. Stuart, *Chem. - Eur. J.*, 2017, **23**, 15852-15863; (b) J. Malmgren, S. Santoro, N. Jalalian, F. Himo and B. Olofsson, *Chem. - Eur. J.*, 2013, **19**, 10334-10342.
22. (a) E. Lindstedt, M. Reitti and B. Olofsson, *J. Org. Chem.*, 2017, **82**, 11909-11914; (b) E. Lindstedt, E. Stridfeldt and B. Olofsson, *Org. Lett.*, 2016, **18**, 4234-4237.
23. (a) W. Walter and J. Krohn, *Chem. Ber.*, 1969, **102**, 3786-3794; (b) R. K. Chaturvedi, A. E. MacMahon and G. L. Schmir, *J. Amer. Chem. Soc.*, 1967, **89**, 6984-6993.
24. Z. Guan, M. Nieger and A. Schmidt, *Eur. J. Org. Chem.*, 2015, **2015**, 4710-4719.
25. (a) W. Walter and C. O. Meese, *Chem. Ber.*, 1976, **109**, 922-946; (b) W. Walter, W. Ruback and C. O. Meese, *Chem. Ber.*, 1980, **113**, 171-182.
26. K. Kobayashi, M. Kuroda and Y. Kanbe, *Helv. Chim. Acta*, 2013, **96**, 1894-1904.
27. (a) L. U. Nordstrom, H. Vogt and R. Madsen, *J. Am. Chem. Soc.*, 2008, **130**, 17672-17673; (b) C. G. Andrews, R. F. Langler and D. R. Branch, *J. Sulfur Chem.*, 2009, **30**, 22-28.
28. J. E. Spangler, Y. Kobayashi, P. Verma, D.-H. Wang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2015, **137**, 11876-11879.
29. J. P. Michael, G. D. Hosken and A. S. Howard, *Tetrahedron*, 1988, **44**, 3025-3036.
30. E. Stridfeldt, E. Lindstedt, M. Reitti, J. Blid, P.-O. Norrby and B. Olofsson, *Chem. Eur. J.*, 2017, 13249-13258.
31. (a) P.-O. Norrby, T. B. Petersen, M. Bielawski and B. Olofsson, *Chem. Eur. J.*, 2010, **16**, 8251-8254; (b) M. Reitti, P. Villo and B. Olofsson, *Angew. Chem. Int. Ed.*, 2016, **55**, 8928-8932; (c) J. Malmgren, S. Santoro, N. Jalalian, F. Himo and B. Olofsson, *Chem. Eur. J.*, 2013, **19**, 10334-10342.
32. G. Kervefors, A. Becker, C. Dey and B. Olofsson, *Beilstein J. Org. Chem.*, 2018, **14**, 1491-1497.
33. Y. Goriya and C. V. Ramana, *Tetrahedron*, 2010, **66**, 7642-7650.

9 Copies of NMR Spectra

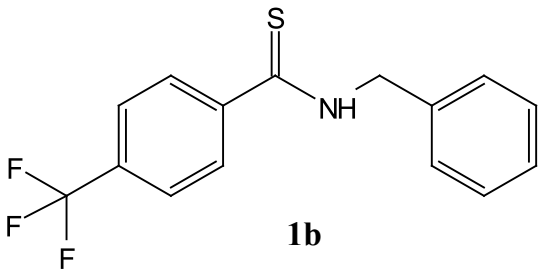

7.78 7.77 7.77 7.77 7.76 7.75 7.75 7.75
7.69
7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33
7.26 CDCl3
2.07
0.80
1.10
7.00
f1 (ppm)
5.01
5.00
2.00
f1 (ppm)
1.55 HDO
^{1}H NMR, $CDCl_3$, 400 MHz
S
N
H
1a
f1 (ppm)
S32


199.00
141.39
136.14
131.09
128.88
128.40
128.20
128.04
126.70
50.72
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
13C NMR, CDCl3, 101 MHz
S
N
H
1a
f1 (ppm)

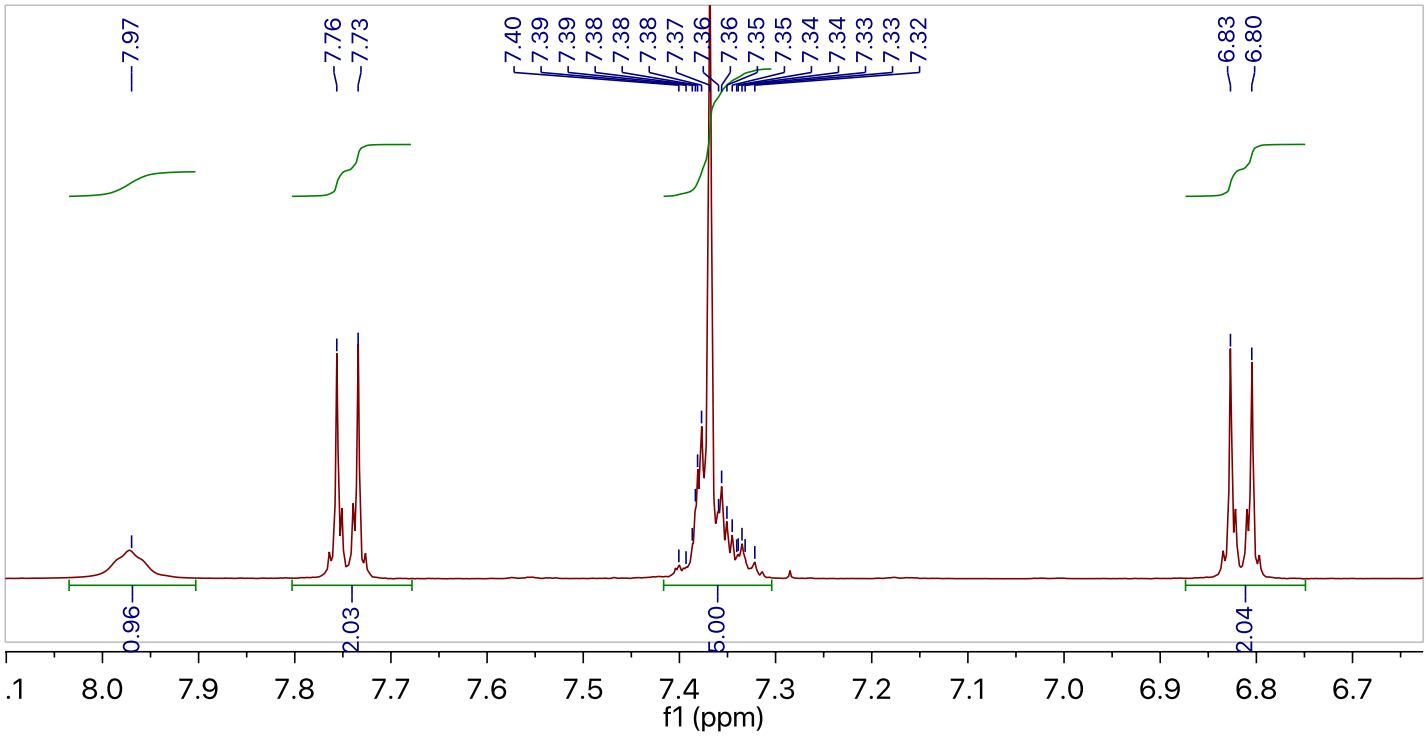

^{1}H NMR, $CDCl_3$, 400 MHz
S
NH
F
F
F
1b
7.26 CDCl3
1.56 HDO
f1 (ppm)

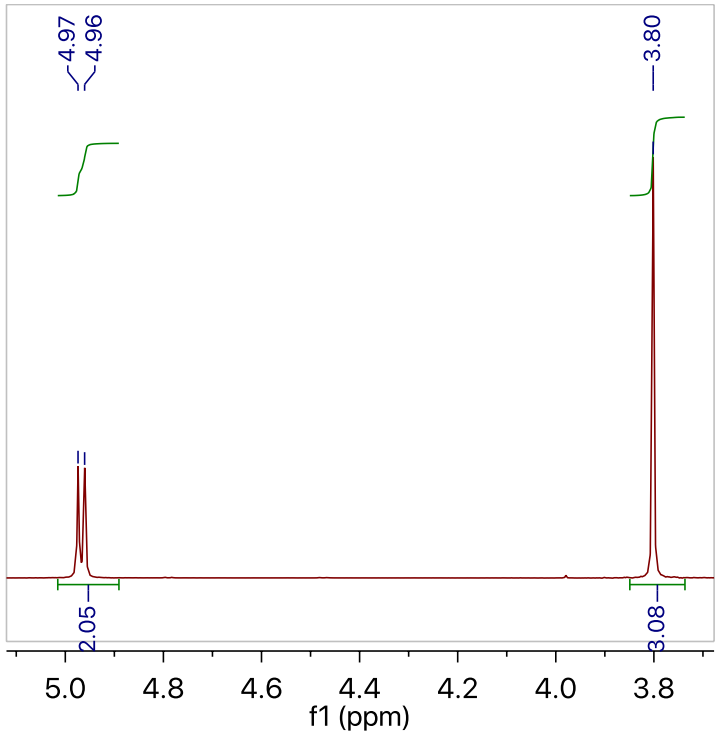

^{13}C NMR, $CDCl_3$, 101 MHz
1b
f1 (ppm)
S35

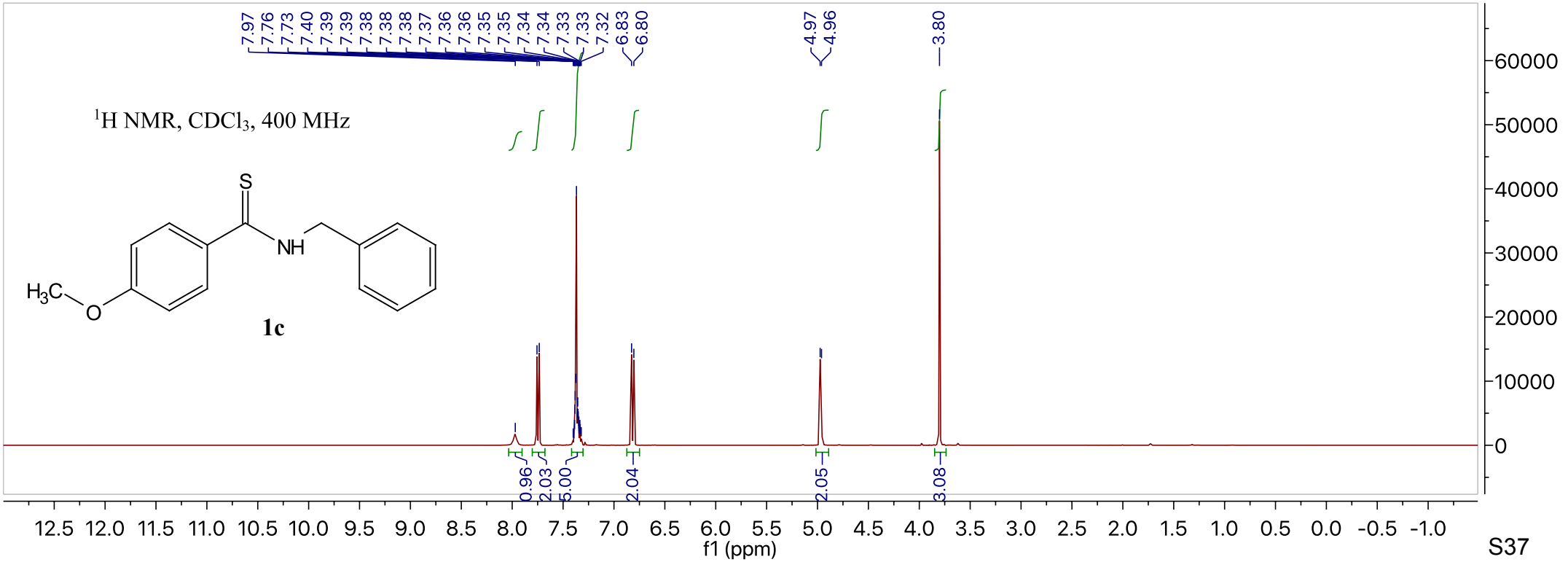
^{19}F NMR (376 MHz, $CDCl_3$)

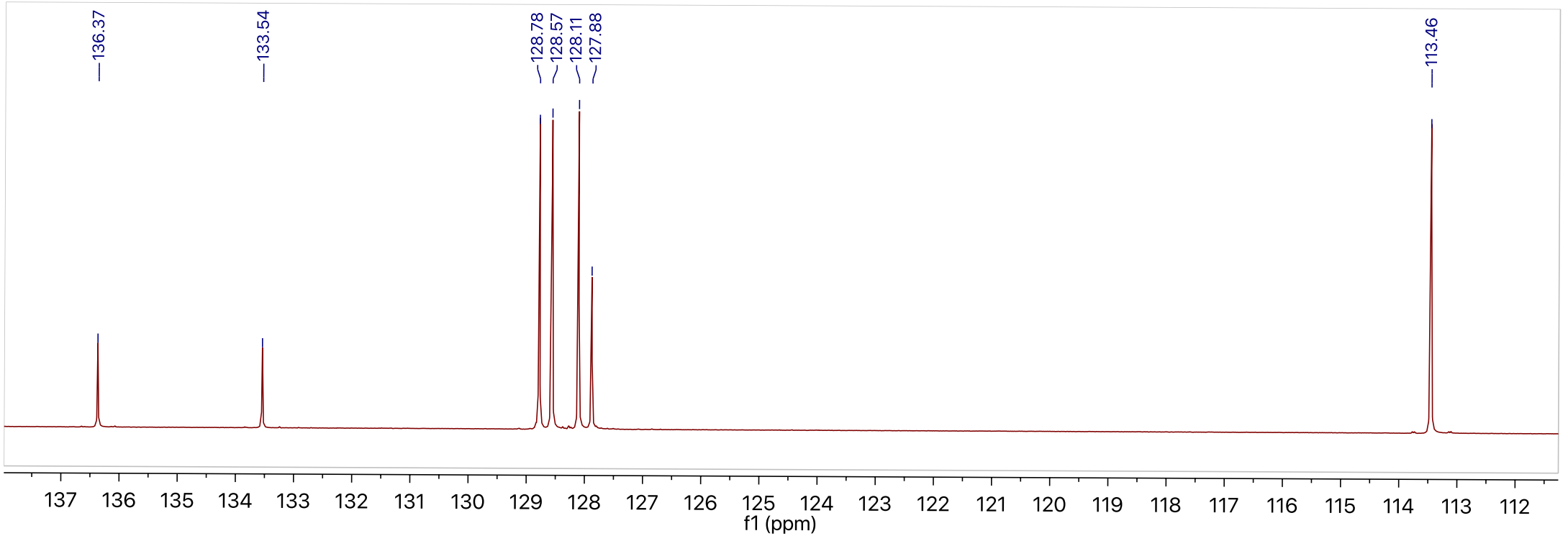


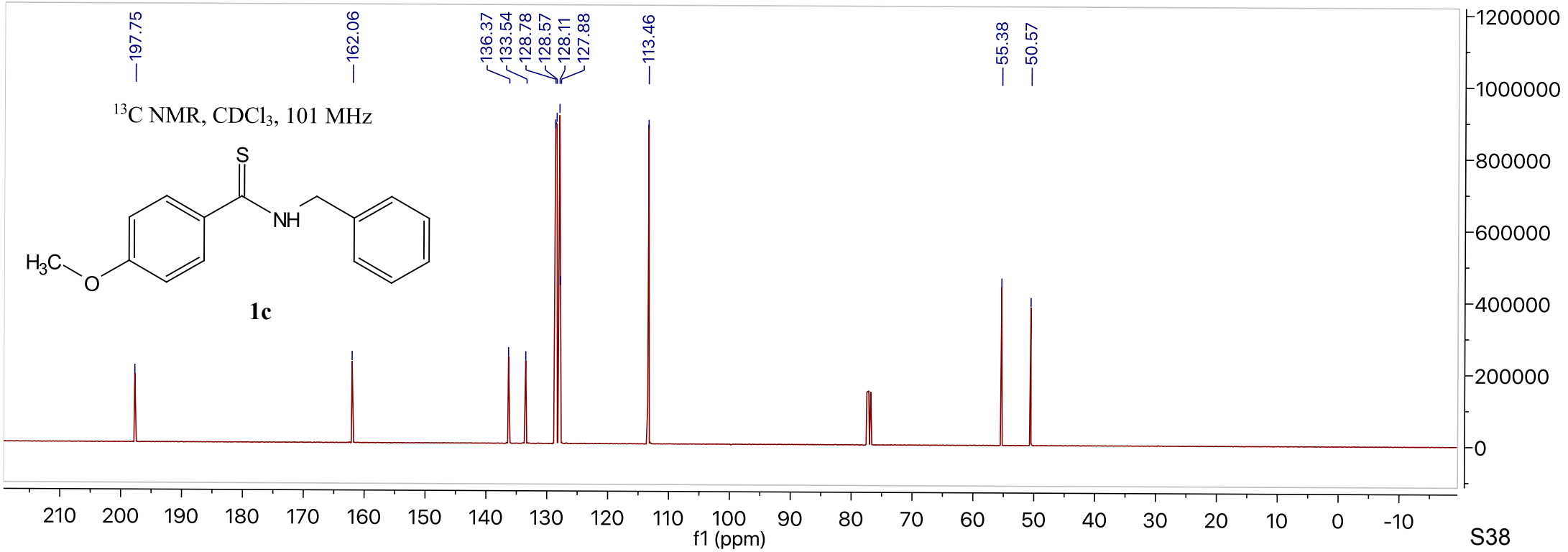
1b

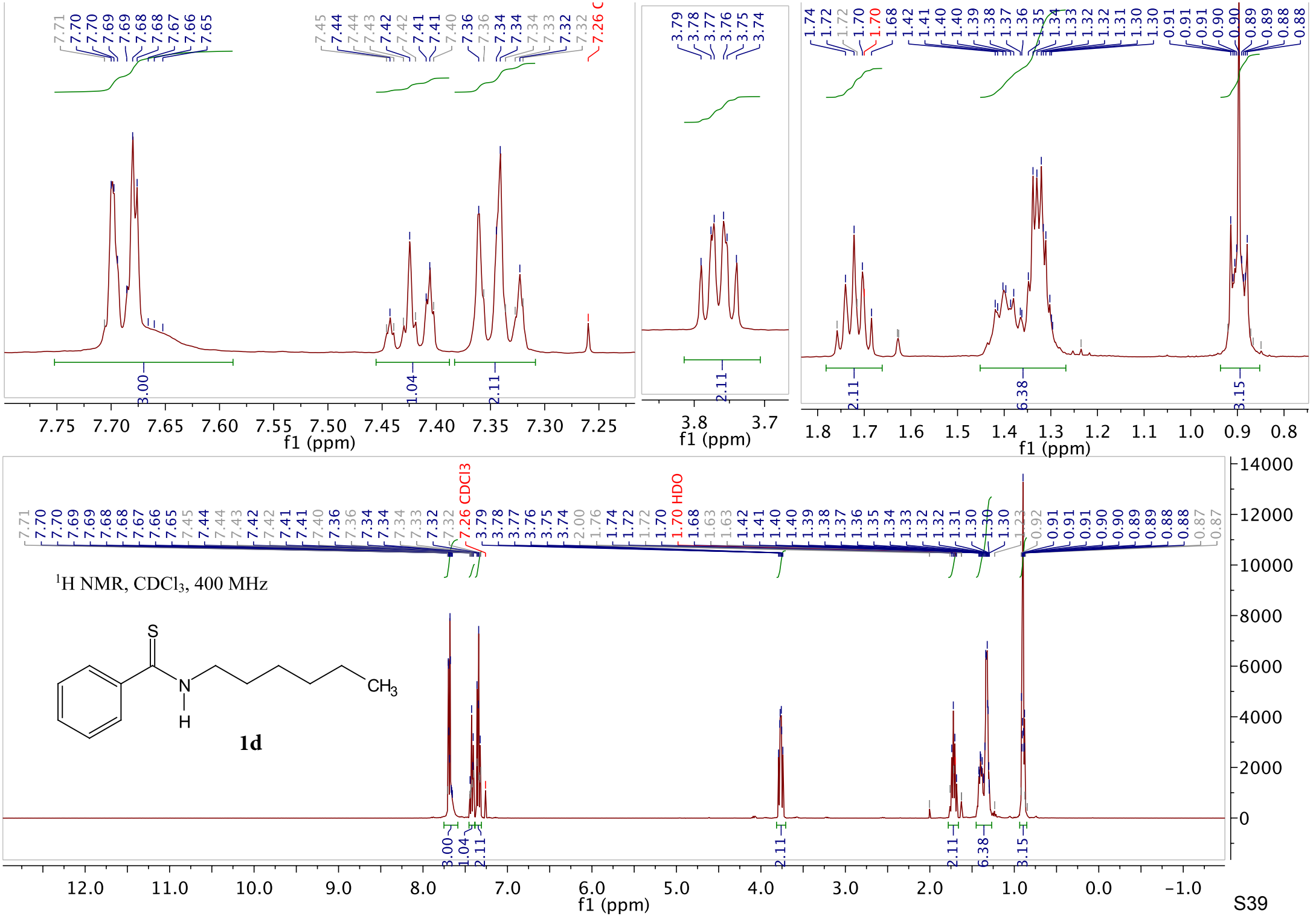

7.97
7.76
7.73
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
6.83
6.80
0.96
2.03
5.00
2.04
f1 (ppm)

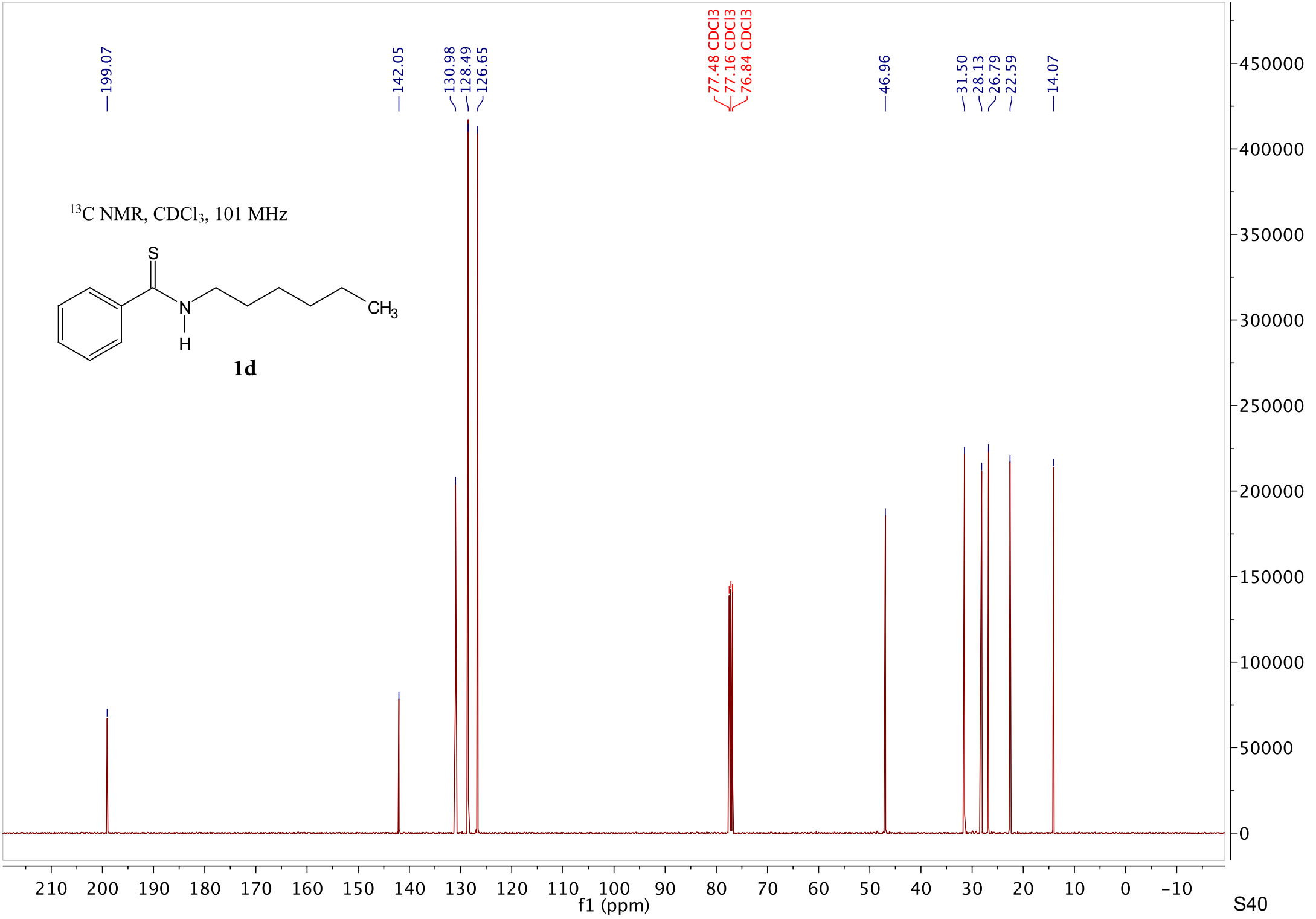

4.97
4.96
3.80
2.05
3.08
f1 (ppm)

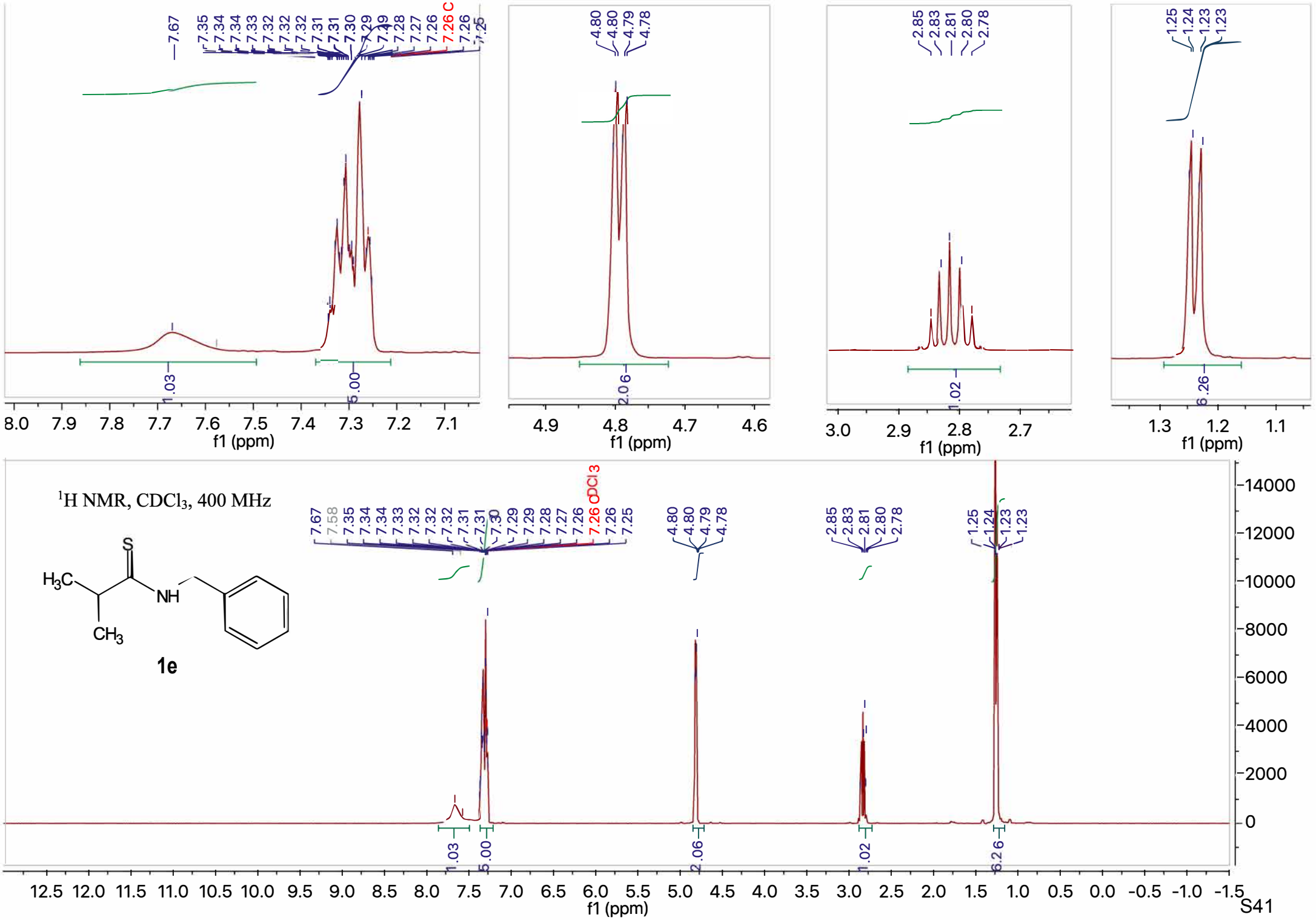

7.97
7.76
7.73
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
6.83
6.80
4.97
4.96
3.80
^{1}H NMR, $CDCl_3$, 400 MHz
S
NH
H_3C
O
1c
0.96
2.03
5.00
2.04
2.05
3.08
f1 (ppm)

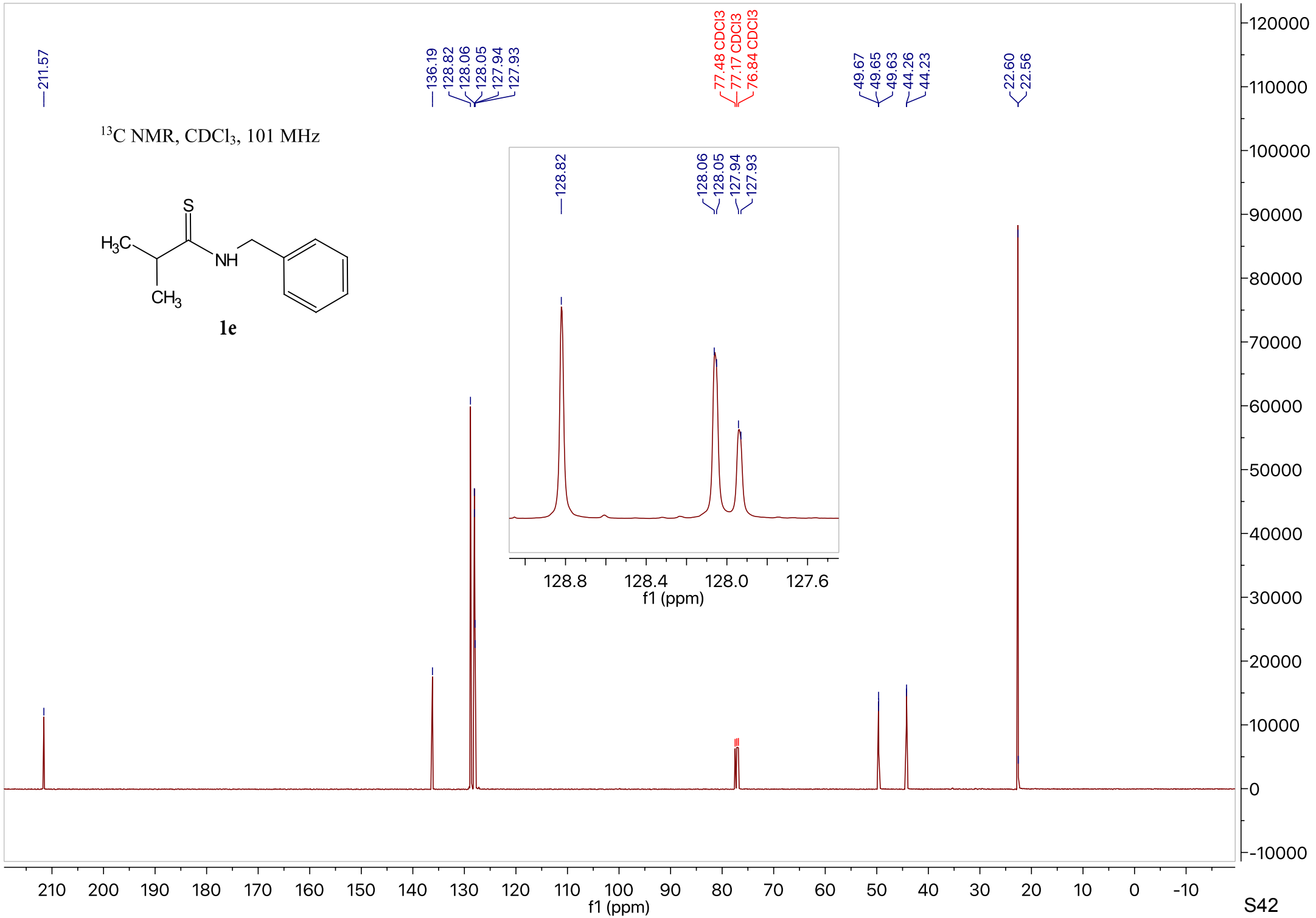

136.37
133.54
128.78
128.57
128.11
127.88
113.46
137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112
f1 (ppm)

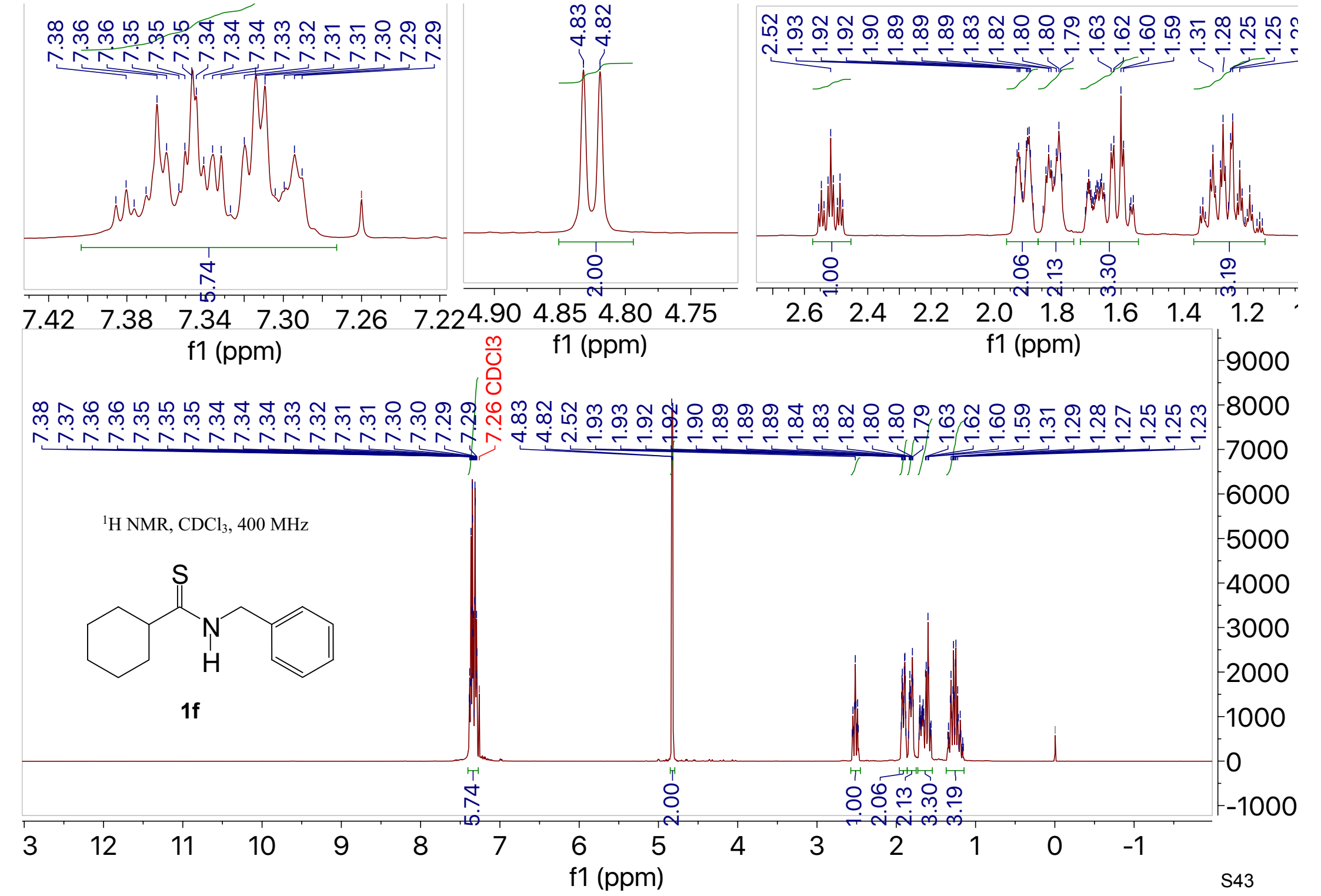

197.75
162.06
136.37
133.54
128.78
128.57
128.11
127.88
113.46
55.38
50.57
^{13}C NMR, CDCl$_3$, 101 MHz
S
NH
H$_3$C
O
1c
1200000
1000000
800000
600000
400000
200000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

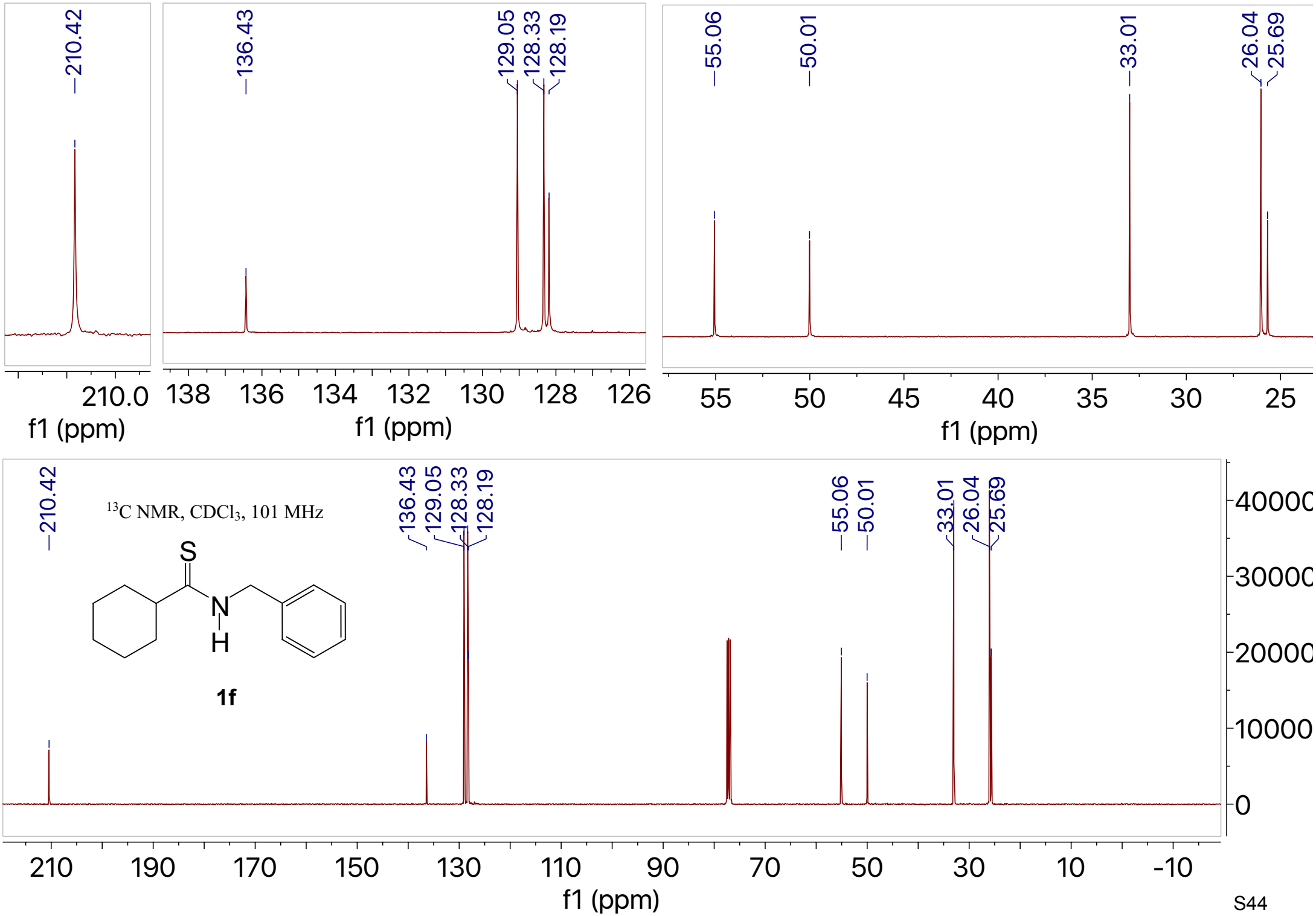

^{1}H NMR, $CDCl_3$, 400 MHz
S
N
H
CH_3
1d
7.26 CDCl3
1.70 HDO
f1 (ppm)

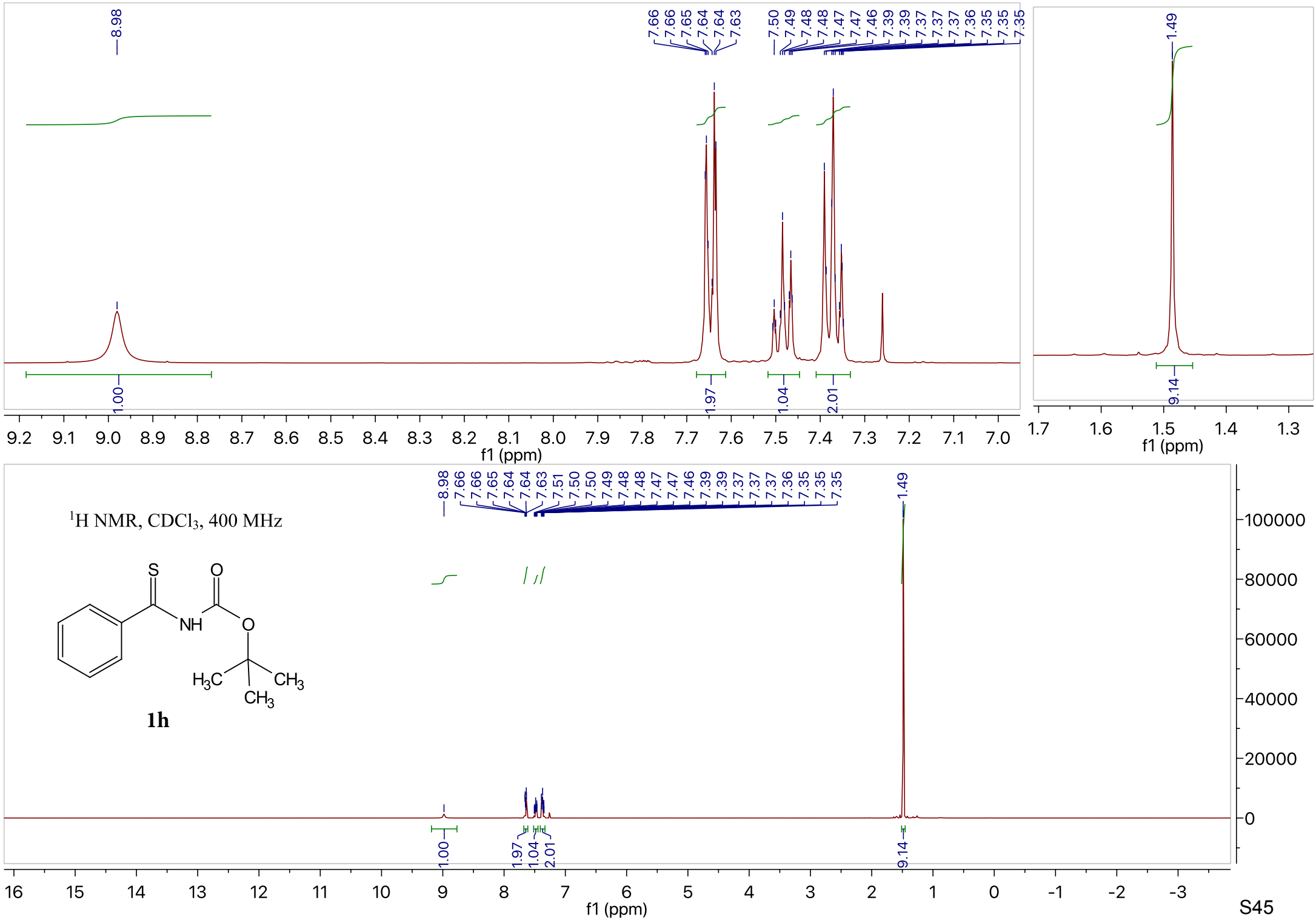

199.07
142.05
130.98
128.49
126.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
46.96
31.50
28.13
26.79
22.59
14.07
13C NMR, CDCl3, 101 MHz
S
N
H
CH3
1d
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

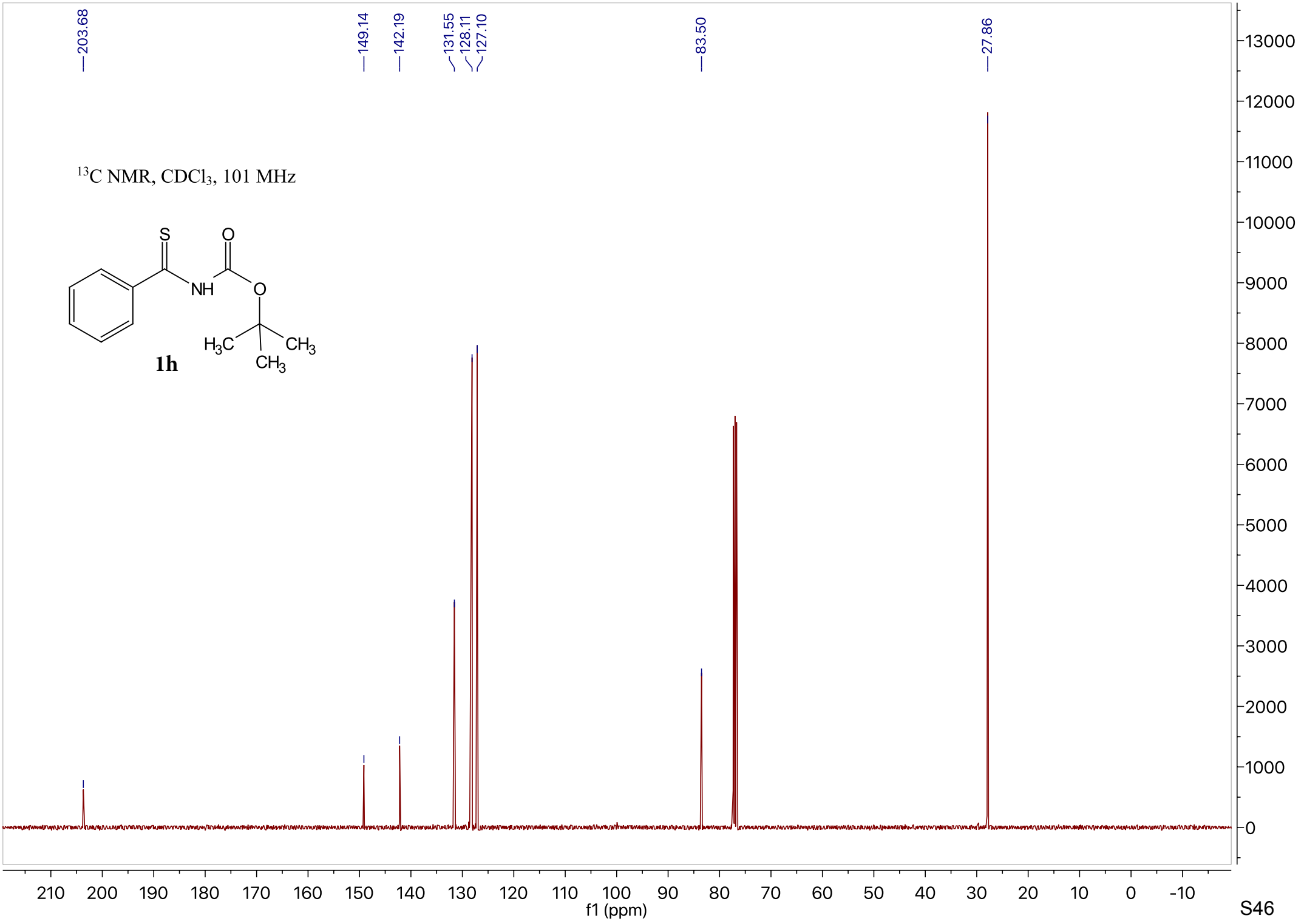

^{1}H NMR, $CDCl_3$, 400 MHz
1e
f1 (ppm)


211.57
136.19
128.82
128.06
128.05
127.94
127.93
77.48 CDCl3
77.17 CDCl3
76.84 CDCl3
49.67
49.65
49.63
44.26
44.23
22.60
22.56
13C NMR, CDCl3, 101 MHz
S
H3C
NH
CH3
1e
128.82
128.06
128.05
127.94
127.93
128.8
128.4
128.0
127.6
f1 (ppm)
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.38 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29
5.74
7.42 7.38 7.34 7.30 7.26 7.22
f1 (ppm)
4.83 4.82
2.00
4.90 4.85 4.80 4.75
f1 (ppm)
2.52 1.93 1.92 1.92 1.90 1.89 1.89 1.89 1.83 1.82 1.80 1.80 1.79 1.63 1.62 1.60 1.59 1.31 1.28 1.25 1.25
1.00 2.06 2.13 3.30 3.19
2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)
7.38 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29
7.26 CDCl3
4.83 4.82 2.52 1.93 1.93 1.92 1.92 1.90 1.89 1.89 1.89 1.84 1.83 1.82 1.80 1.80 1.79 1.63 1.62 1.60 1.59 1.31 1.29 1.28 1.27 1.25 1.25 1.23
1H NMR, CDCl3, 400 MHz
S
N
H
1f
5.74
2.00
1.00 2.06 2.13 3.30 3.19
9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
3 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

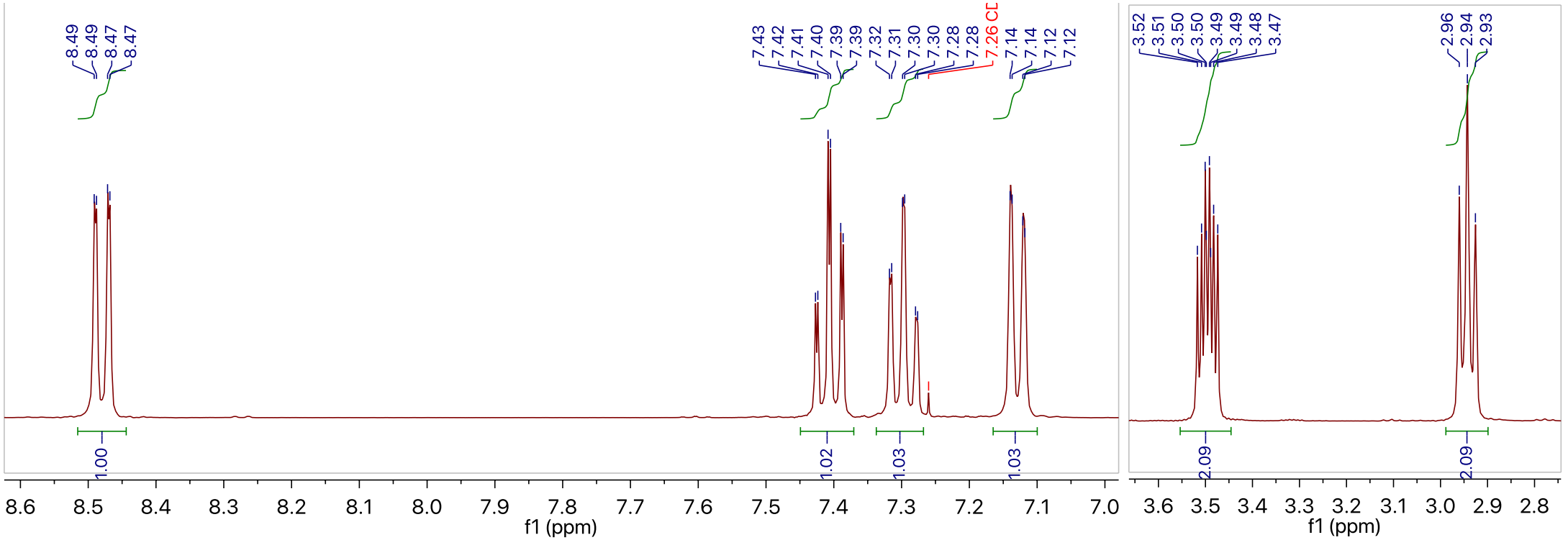

210.42
136.43
129.05
128.33
128.19
55.06
50.01
33.01
26.04
25.69
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
S
N
H
1f
40000
30000
20000
10000
0

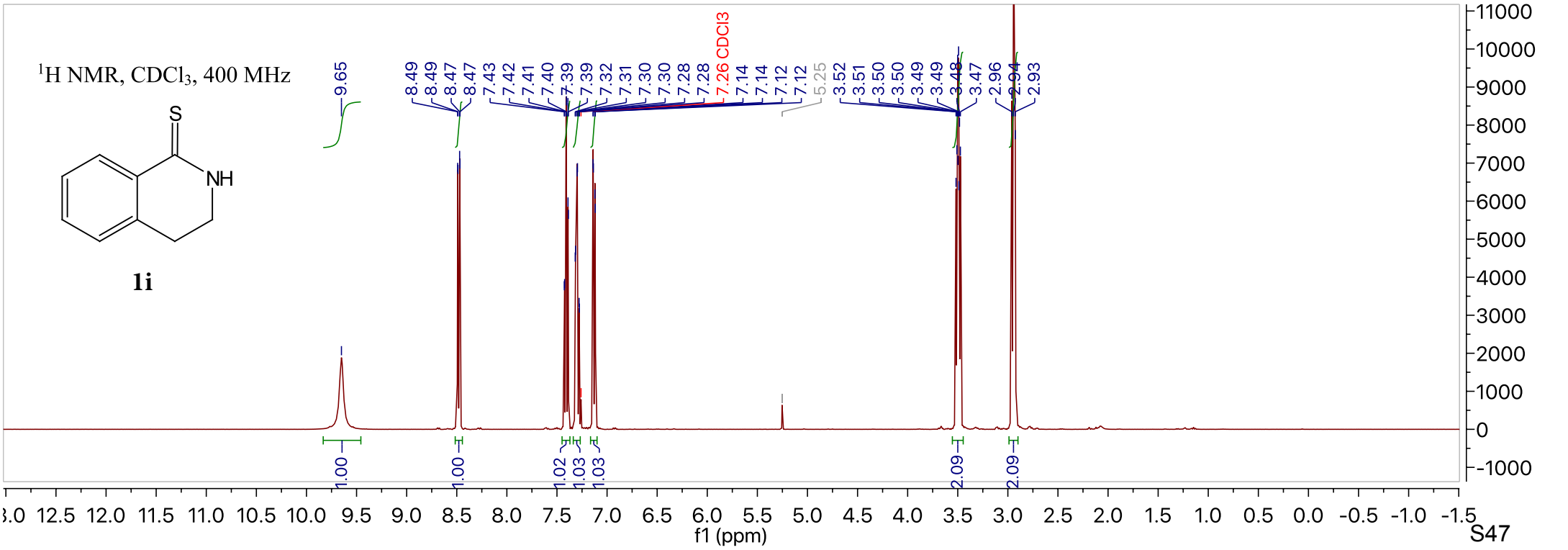

8.98
7.66 7.66 7.65 7.64 7.64 7.63
7.50 7.49 7.48 7.48 7.47 7.47 7.46 7.39 7.39 7.37 7.37 7.37 7.36 7.35 7.35 7.35
1.49
1.00
1.97
1.04
2.01
9.14
f1 (ppm)
1H NMR, CDCl3, 400 MHz
S
O
NH
O
H3C
CH3
CH3
1h
100000
80000
60000
40000
20000
0

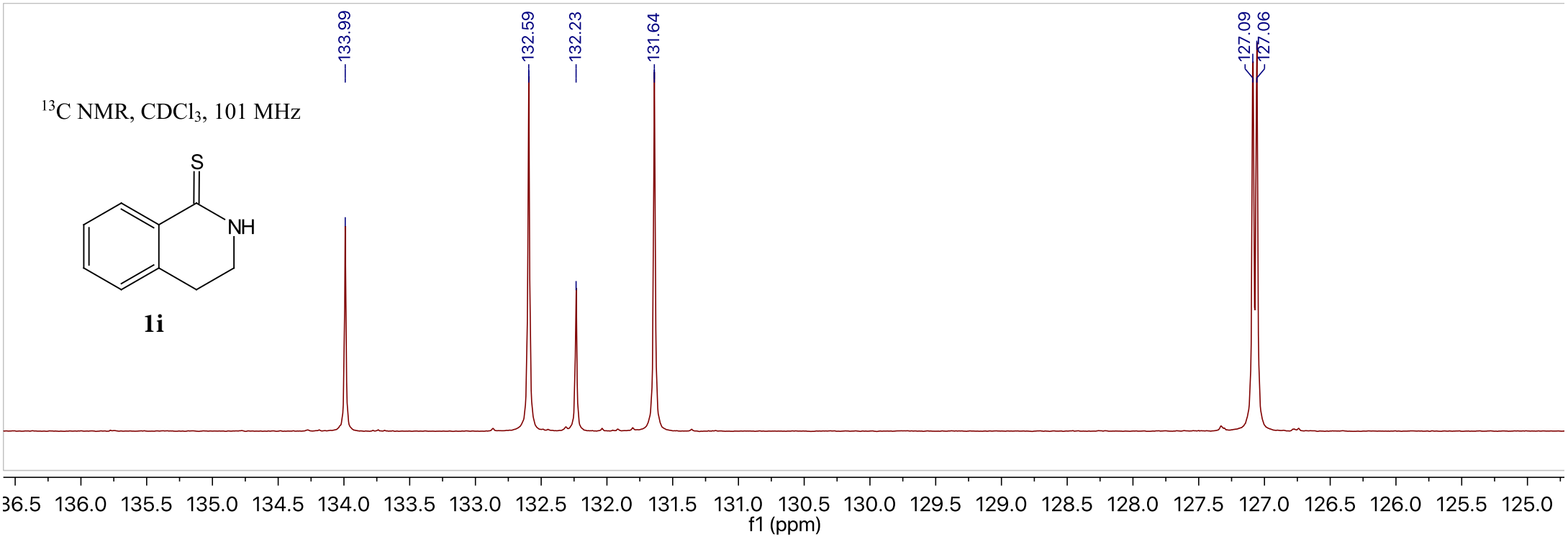


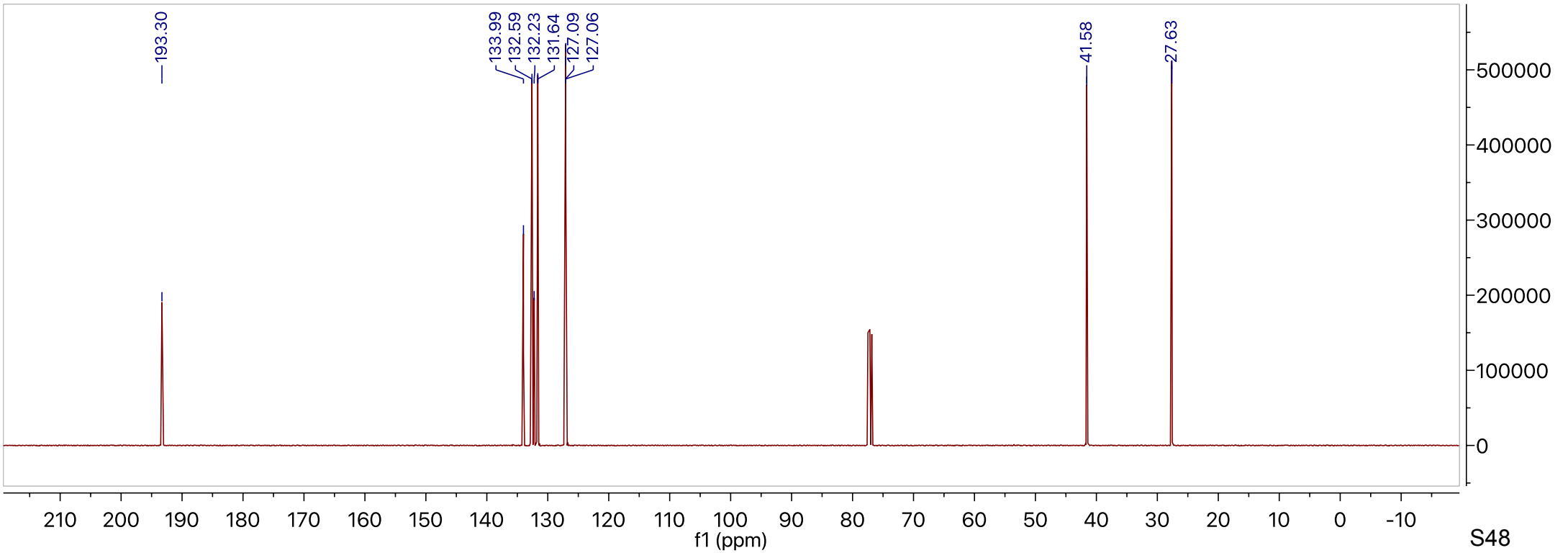
^{13}C NMR, $CDCl_3$, 101 MHz

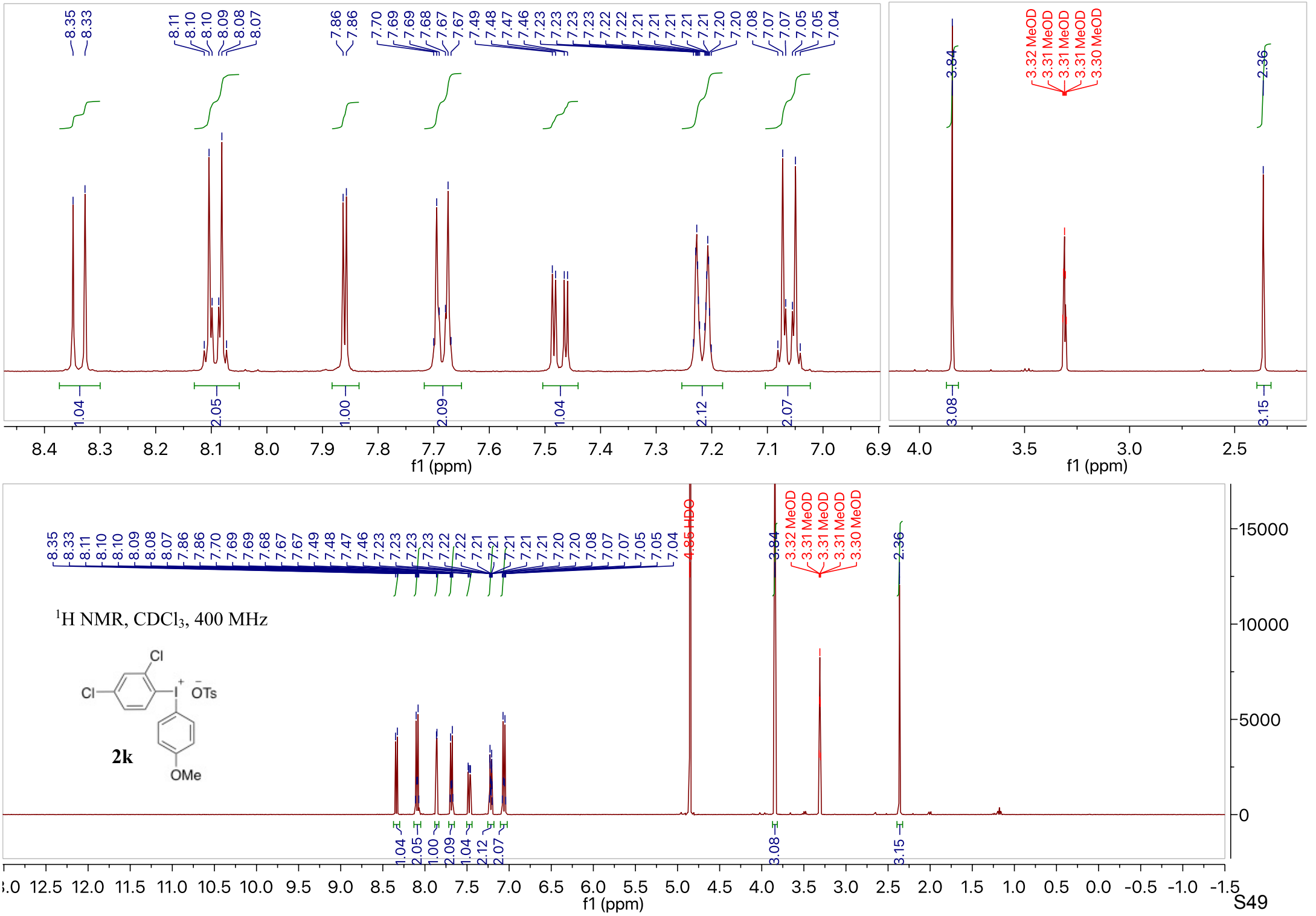
1h

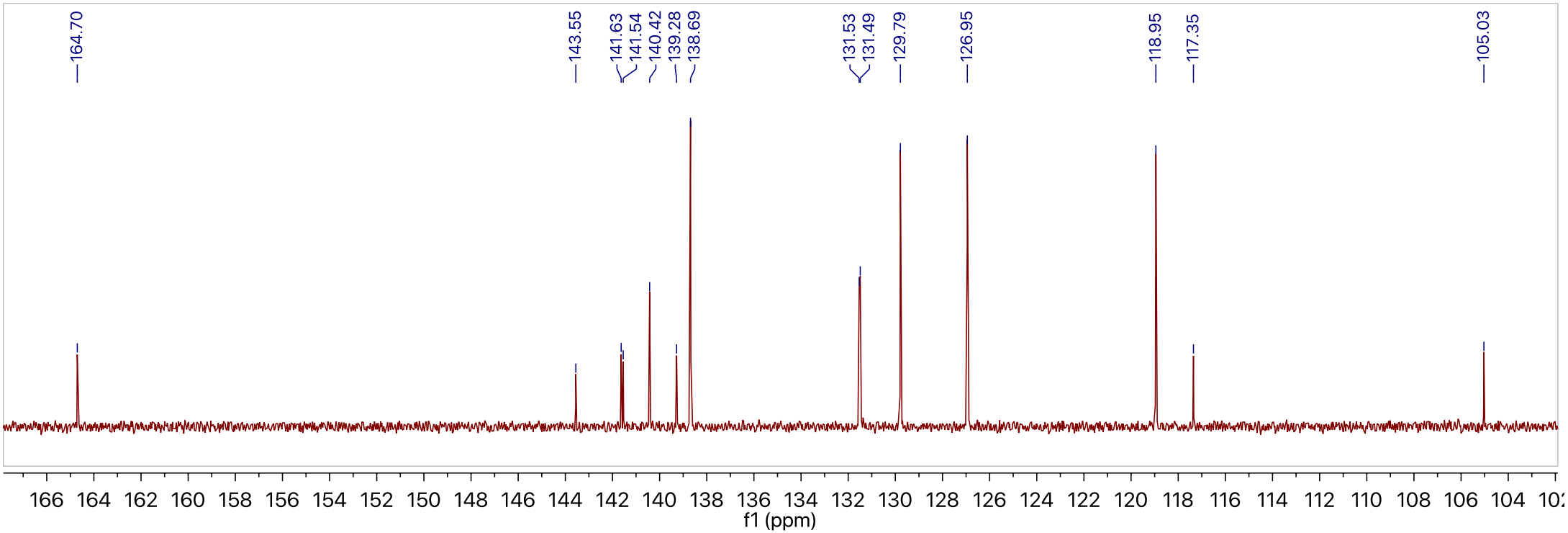

8.49
8.49
8.47
8.47
7.43
7.42
7.41
7.40
7.39
7.39
7.32
7.31
7.30
7.30
7.28
7.28
7.26 CD
7.14
7.14
7.12
7.12
3.52
3.51
3.50
3.50
3.49
3.49
3.48
3.47
2.96
2.94
2.93
1.00
1.02
1.03
1.03
2.09
2.09
f1 (ppm)
f1 (ppm)

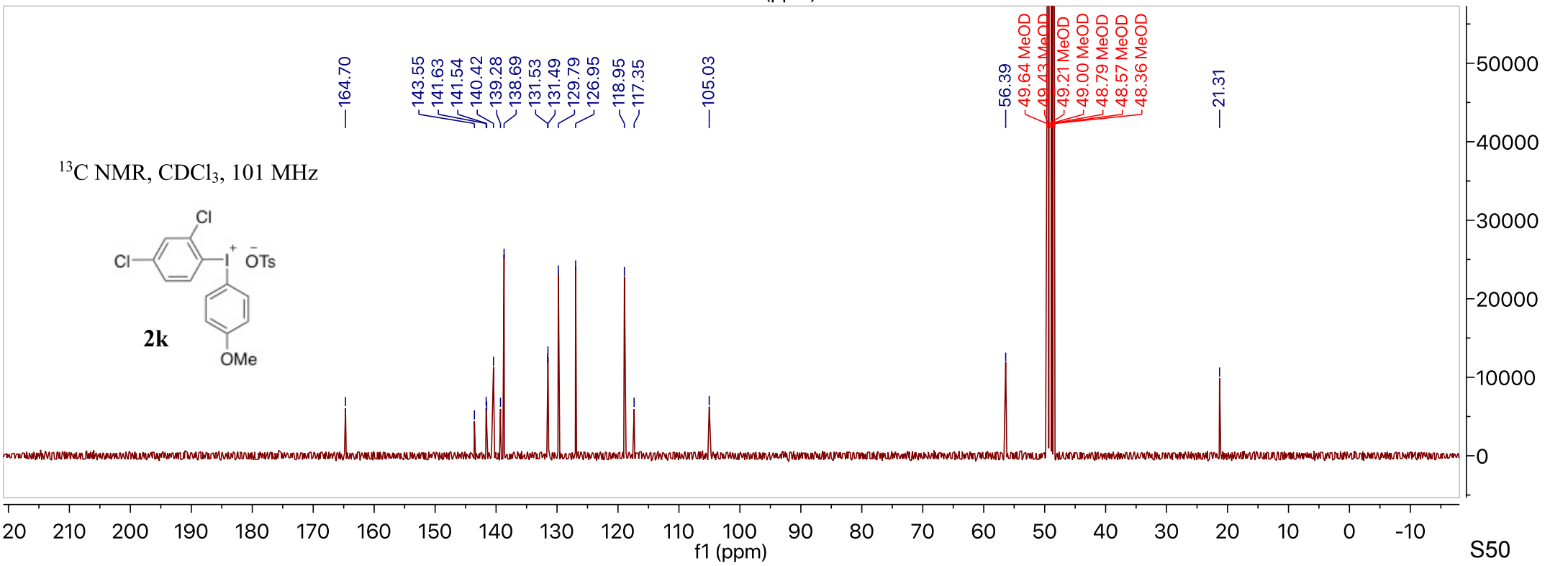

^{1}H NMR, $CDCl_3$, 400 MHz
S
NH
1i
9.65
8.49
8.49
8.47
8.47
7.43
7.42
7.41
7.40
7.39
7.39
7.32
7.31
7.30
7.30
7.28
7.28
7.26 CDCl3
7.14
7.14
7.12
7.12
5.25
3.52
3.51
3.50
3.50
3.49
3.49
3.48
3.47
2.96
2.94
2.93
1.00
1.00
1.02
1.03
1.03
2.09
2.09
f1 (ppm)

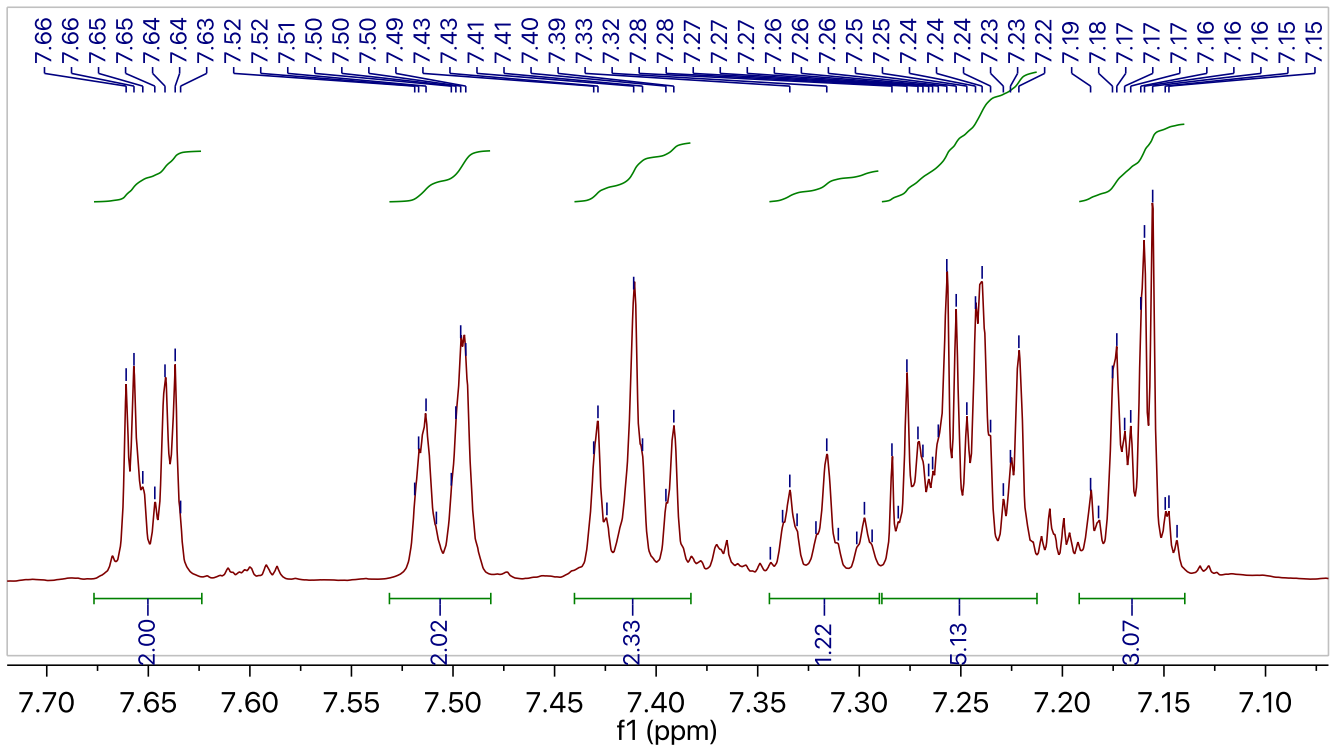

133.99
132.59
132.23
131.64
127.09
127.06
^{13}C NMR, $CDCl_3$, 101 MHz
S
NH
1i
136.5 136.0 135.5 135.0 134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0
f1 (ppm)

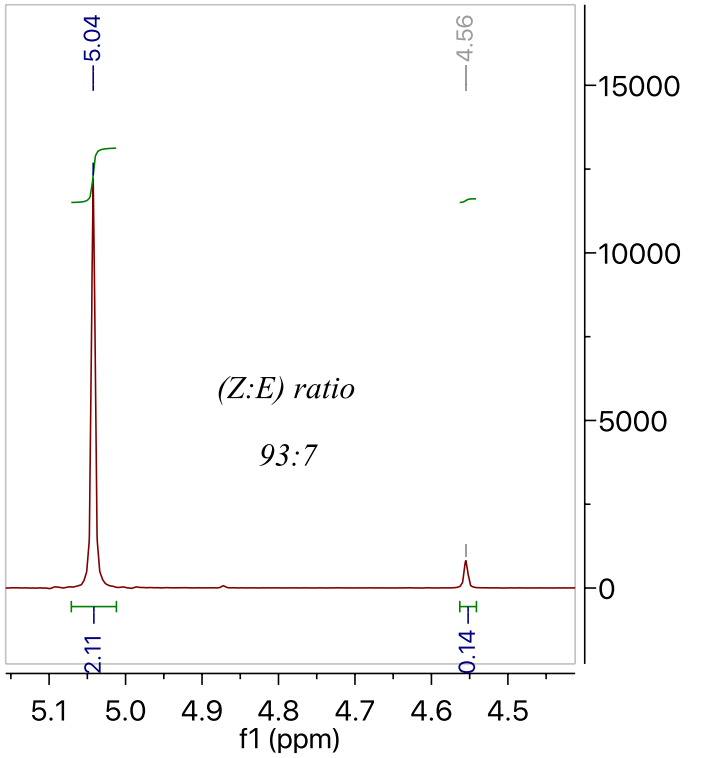

193.30
133.99
132.59
132.23
131.64
127.09
127.06
41.58
27.63
500000
400000
300000
200000
100000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

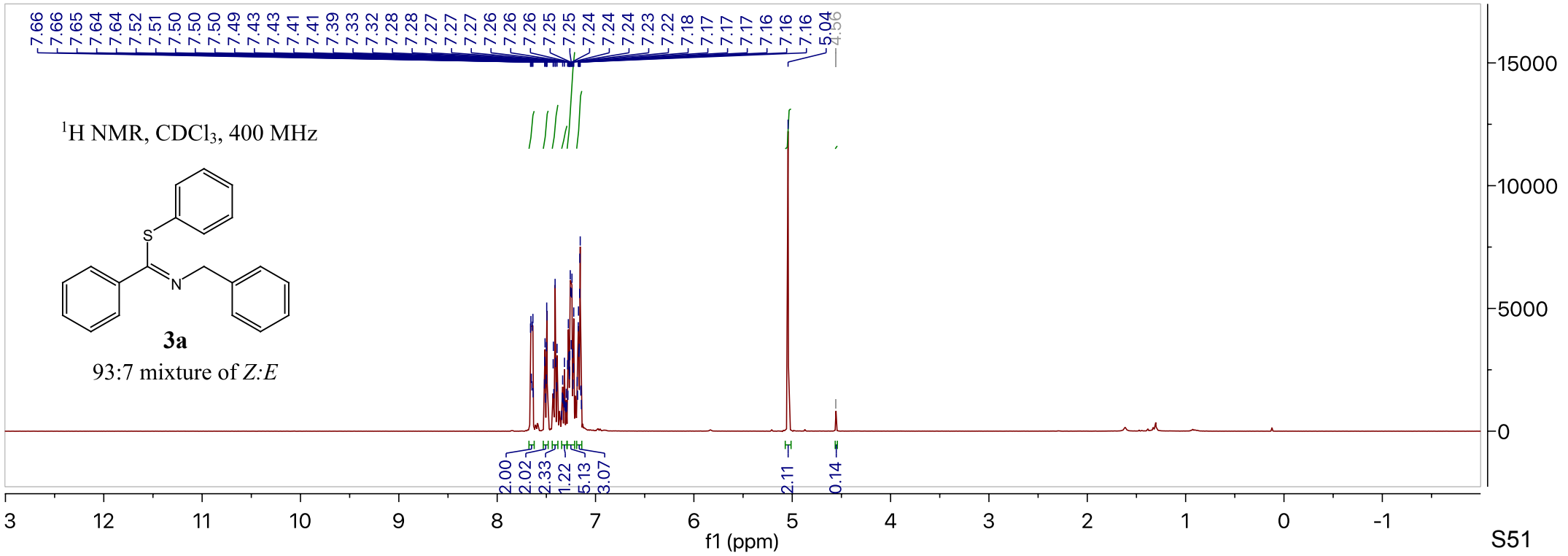

8.35
8.33
8.11
8.10
8.10
8.09
8.08
8.07
7.86
7.86
7.70
7.69
7.69
7.68
7.67
7.67
7.49
7.48
7.47
7.46
7.23
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.20
7.08
7.07
7.07
7.05
7.05
7.04
1.04
2.05
1.00
2.09
1.04
2.12
2.07
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
3.84
3.32 MeOD
3.31 MeOD
3.31 MeOD
3.31 MeOD
3.30 MeOD
2.36
3.08
3.15
4.0
3.5
3.0
2.5
f1 (ppm)
^{1}H NMR, $CDCl_3$, 400 MHz
Cl
Cl
I
OTs
OMe
2k
4.85 HDO
15000
10000
5000
0
f1 (ppm)

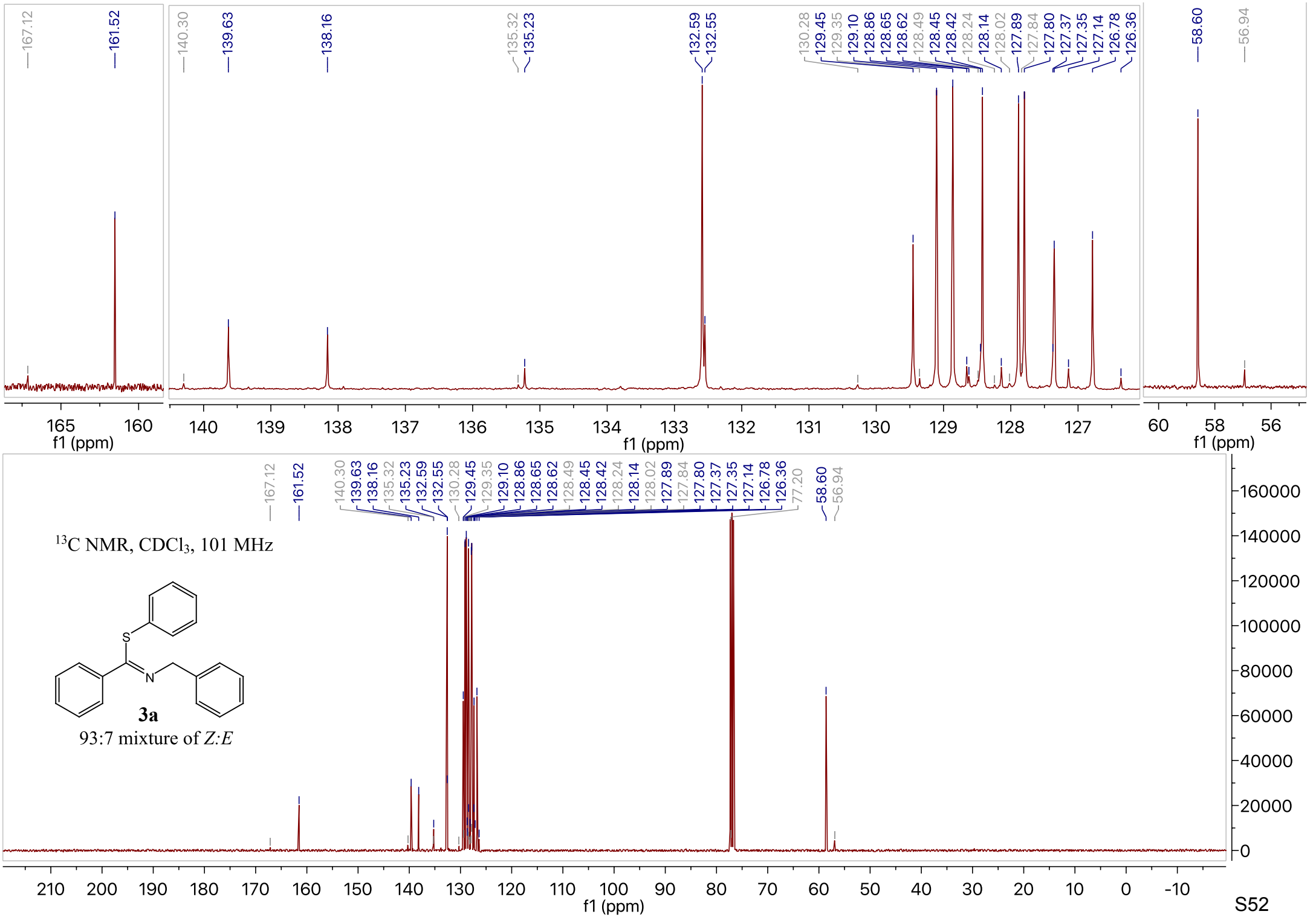

164.70
143.55
141.63
141.54
140.42
139.28
138.69
131.53
131.49
129.79
126.95
118.95
117.35
105.03
166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104
f1 (ppm)

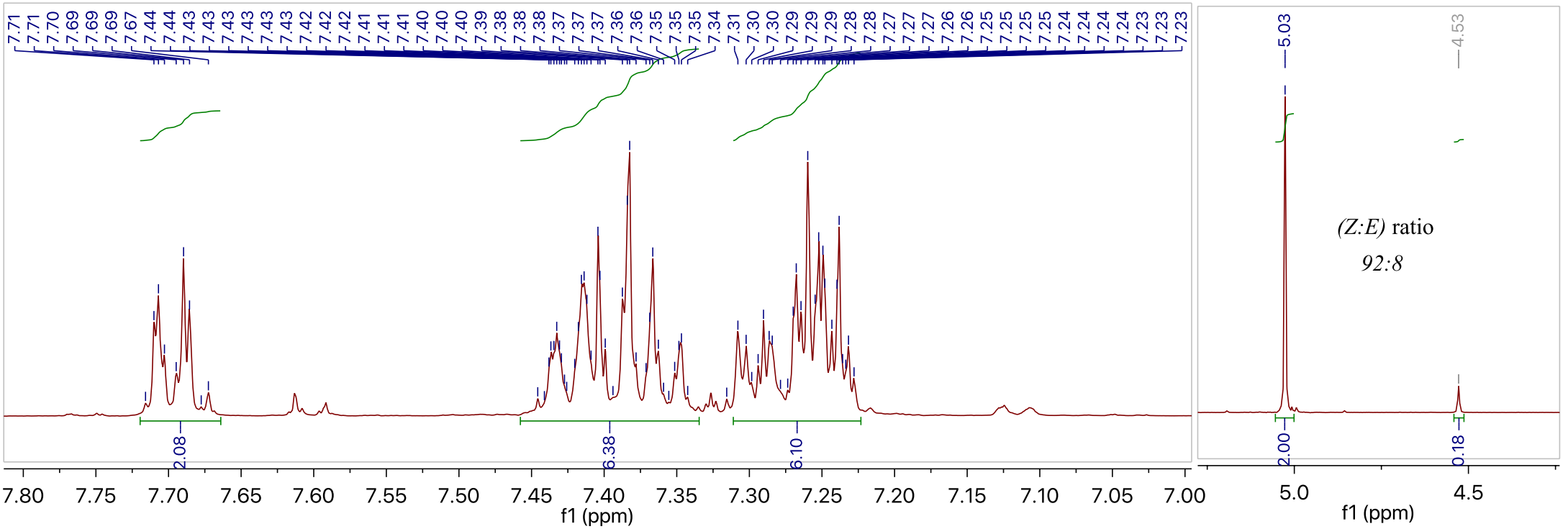

164.70
143.55
141.63
141.54
140.42
139.28
138.69
131.53
131.49
129.79
126.95
118.95
117.35
105.03
56.39
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
21.31
^{13}C NMR, $CDCl_3$, 101 MHz
Cl
Cl
I
OTs
OMe
2k
50000
40000
30000
20000
10000
0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.66 7.66 7.65 7.65 7.64 7.64 7.63 7.52 7.52 7.51 7.50 7.50 7.50 7.49 7.43 7.43 7.41 7.41 7.40 7.39 7.33 7.32 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.19 7.18 7.17 7.17 7.17 7.16 7.16 7.16 7.15 7.15
2.00 2.02 2.33 1.22 5.13 3.07
10000 8000 6000 4000 2000 0
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)

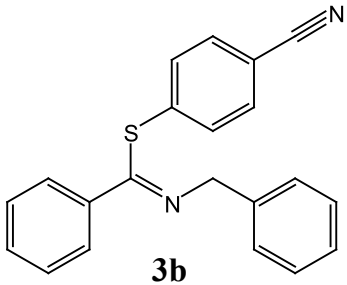

5.04
4.56
(Z:E) ratio
93:7
2.11 0.14
15000 10000 5000 0
5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)


7.66 7.66 7.65 7.64 7.64 7.52 7.51 7.50 7.50 7.50 7.49 7.43 7.43 7.41 7.41 7.39 7.33 7.32 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.22 7.18 7.17 7.17 7.17 7.16 7.16 5.04 4.56
^{1}H NMR, $CDCl_3$, 400 MHz
S
N
3a
93:7 mixture of Z:E
2.00 2.02 2.33 1.22 5.13 3.07 2.11 0.14
15000 10000 5000 0
3 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


167.12
161.52
140.30
139.63
138.16
135.32
135.23
132.59
132.55
130.28
129.45
129.35
129.10
128.86
128.65
128.62
128.49
128.45
128.42
128.24
128.14
128.02
127.89
127.84
127.80
127.37
127.35
127.14
126.78
126.36
77.20
58.60
56.94
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3a
93:7 mixture of *Z:E*

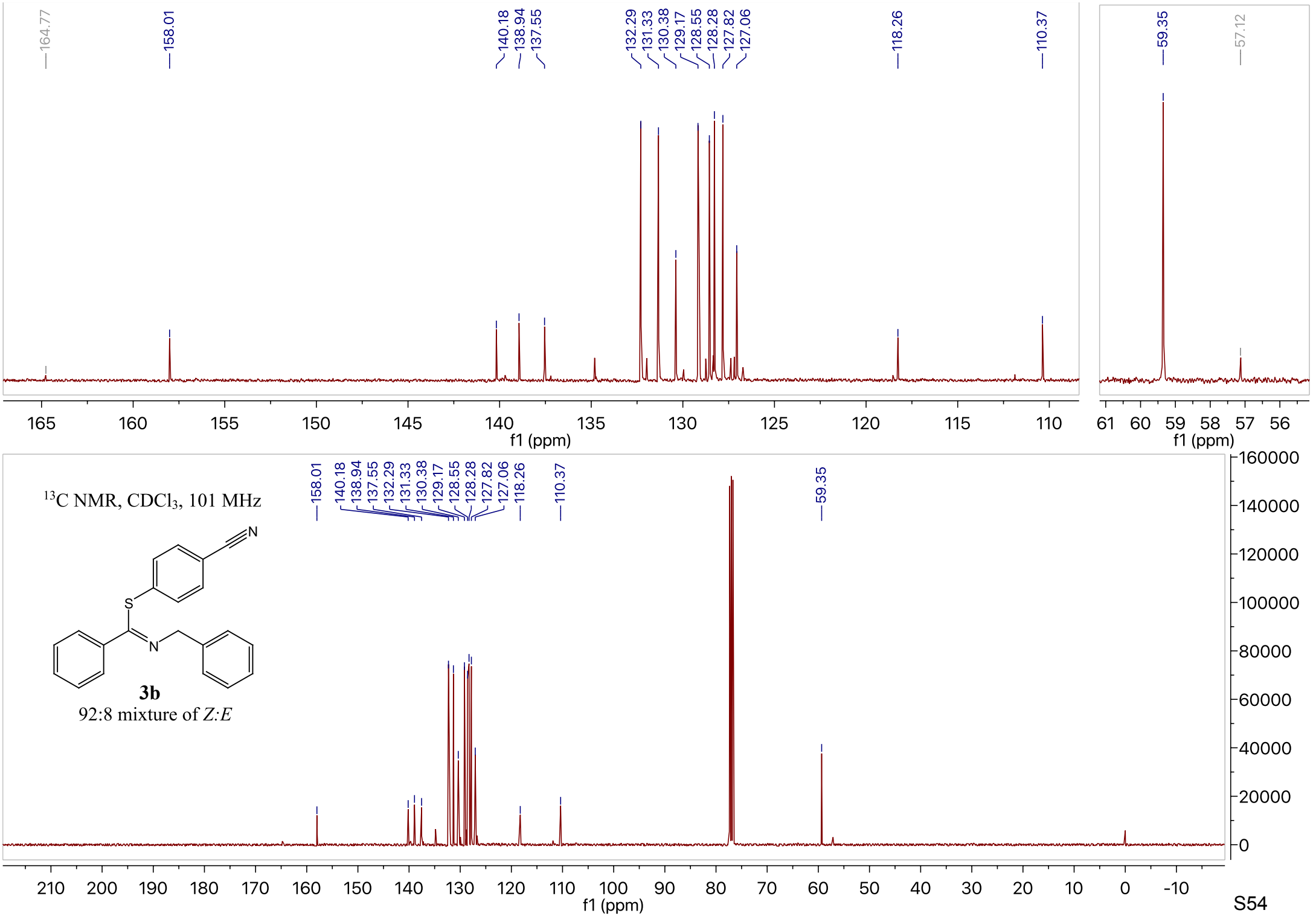


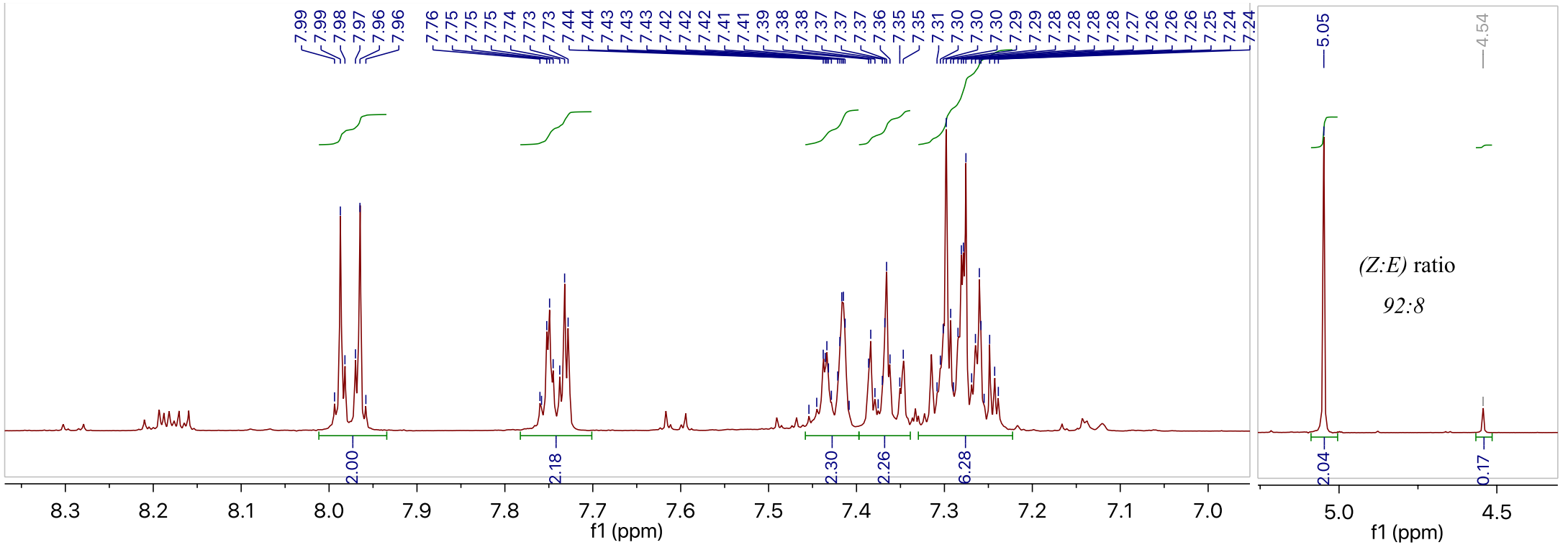
^{1}H NMR, $CDCl_3$, 400 MHz



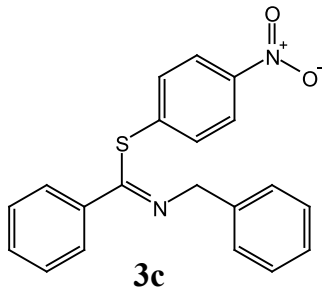
3b

92:8 mixture of *Z:E*


164.77
158.01
140.18
138.94
137.55
132.29
131.33
130.38
129.17
128.55
128.28
127.82
127.06
118.26
110.37
59.35
57.12
f1 (ppm)
^{13}C NMR, CDCl$_3$, 101 MHz
3b
92:8 mixture of Z:E

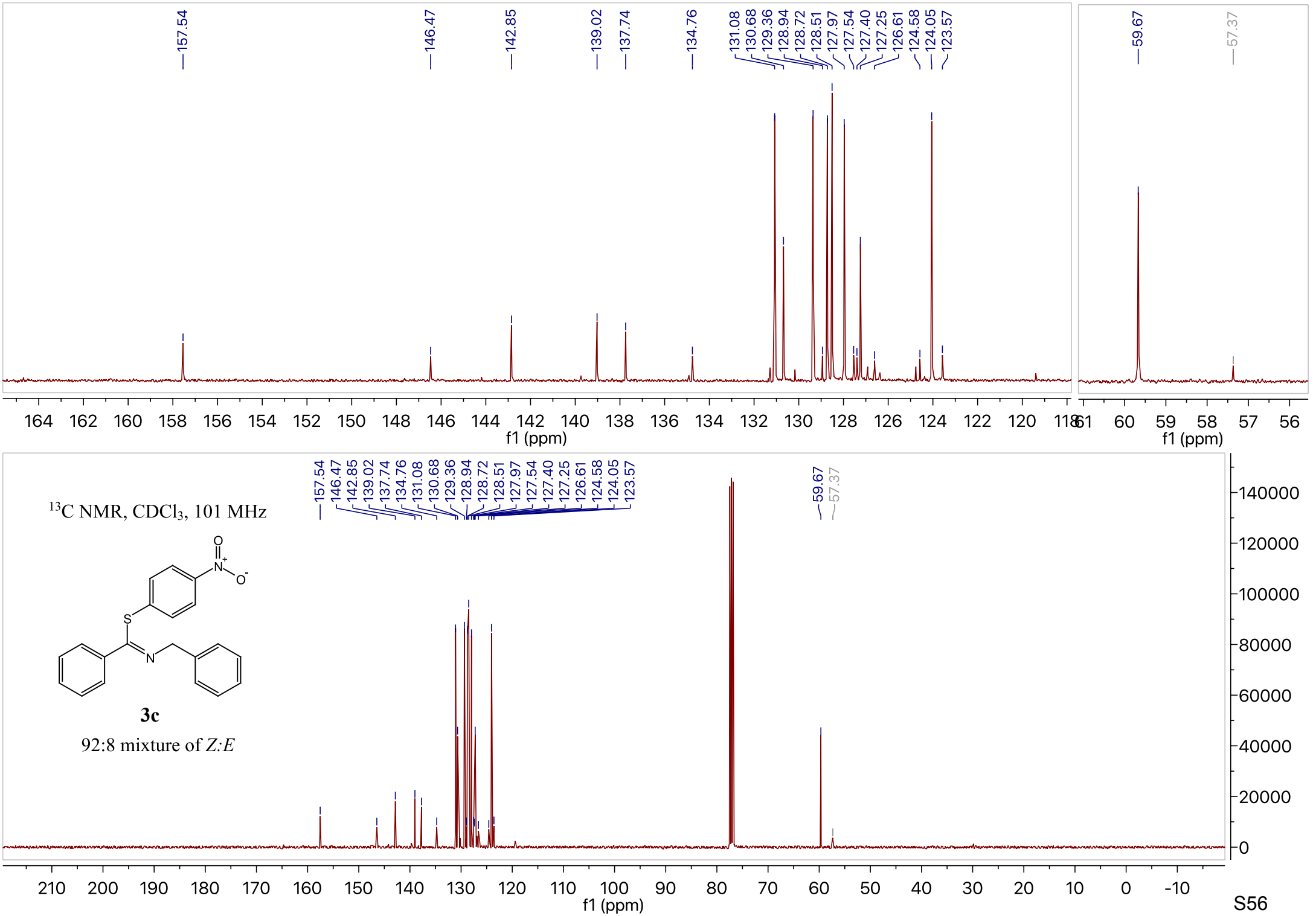


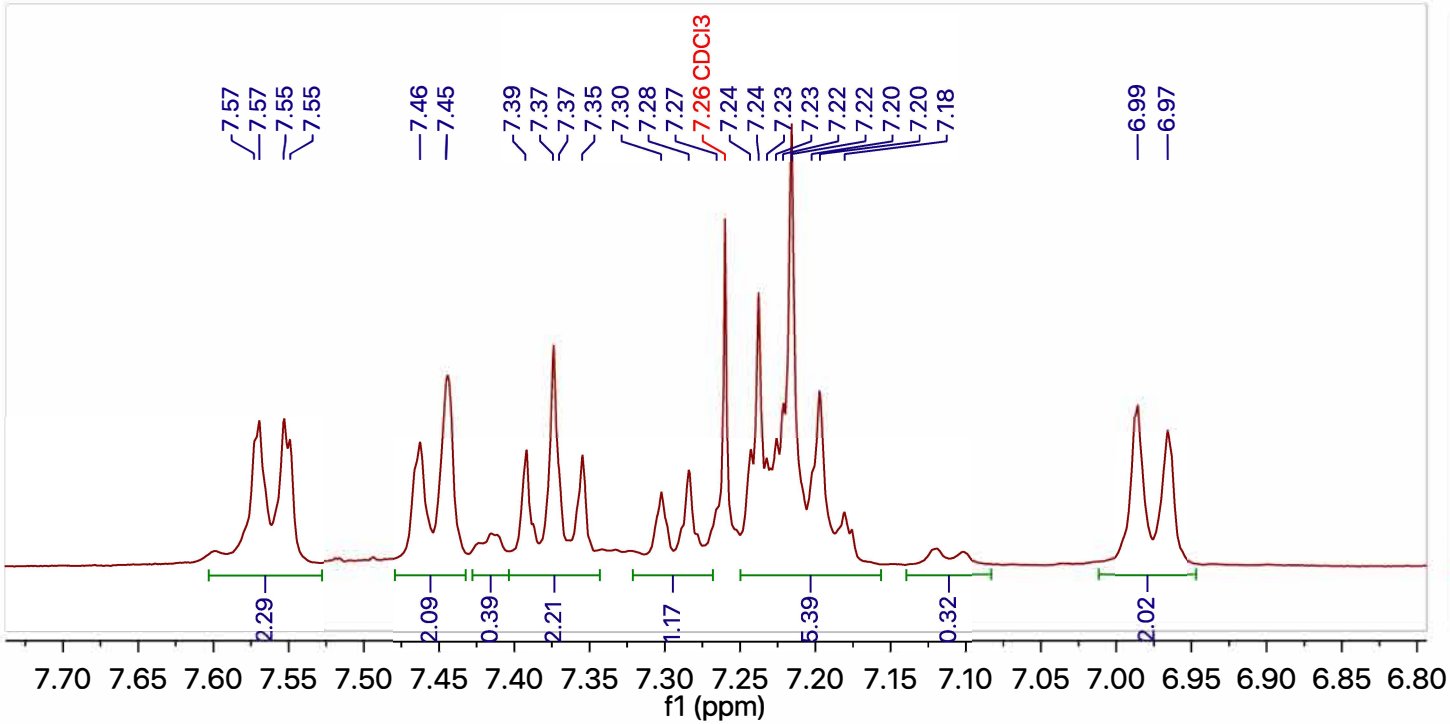
^{1}H NMR, $CDCl_3$, 400 MHz

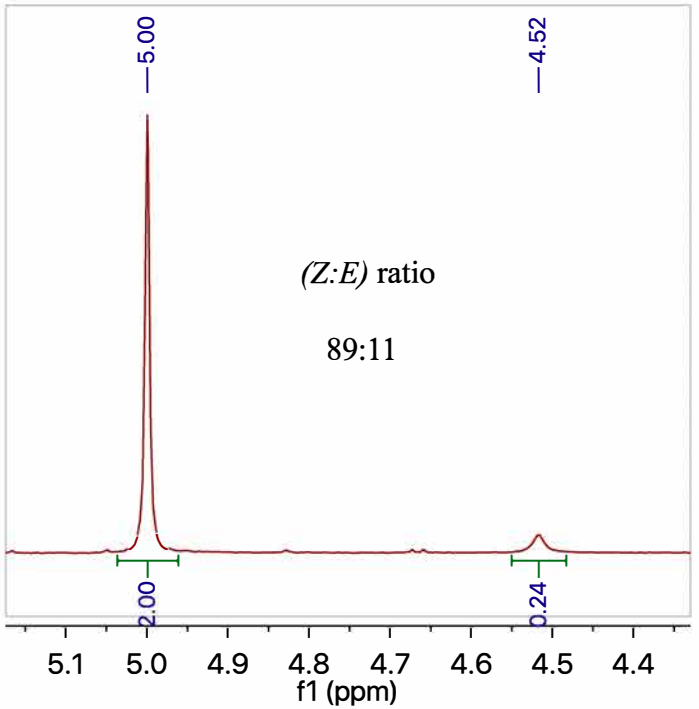


3c

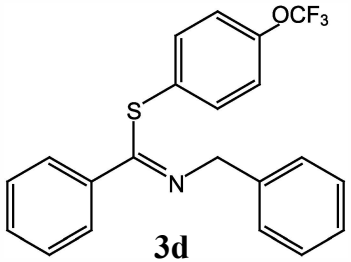
92:8 mixture of *Z:E*


157.54
146.47
142.85
139.02
137.74
134.76
131.08
130.68
129.36
128.94
128.72
128.51
127.97
127.54
127.40
127.25
126.61
124.58
124.05
123.57
59.67
57.37
f1 (ppm)
^{13}C NMR, CDCl$_3$, 101 MHz
3c
92:8 mixture of *Z:E*



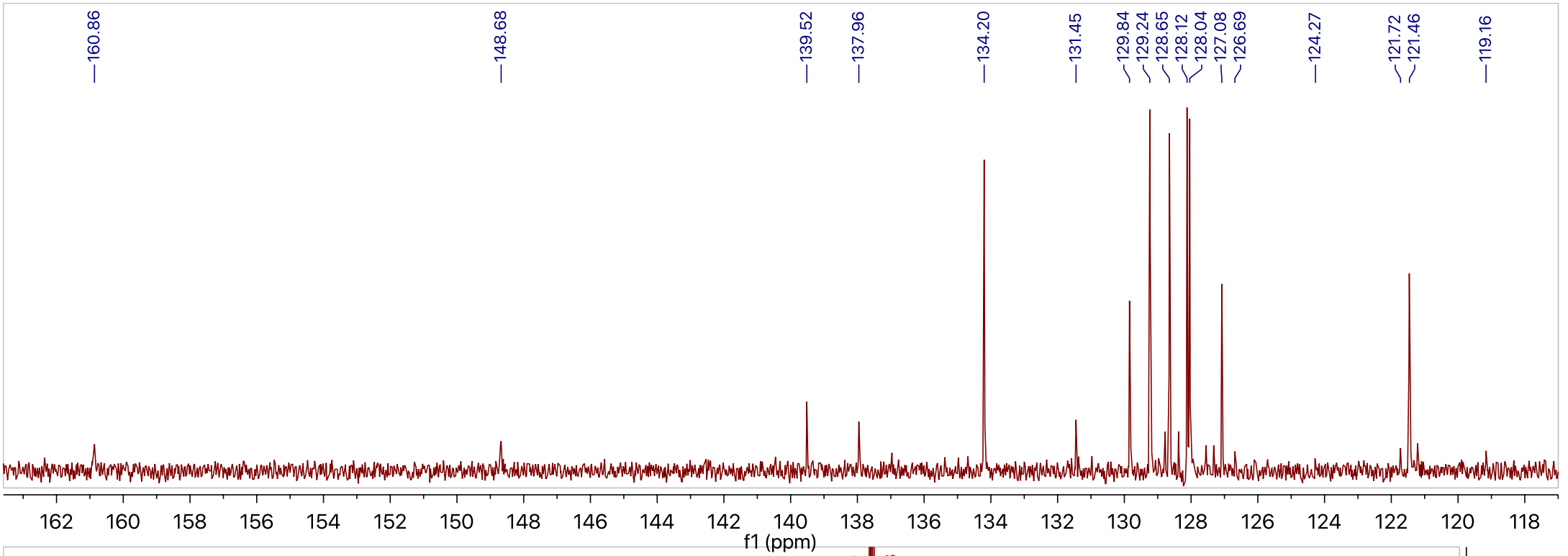


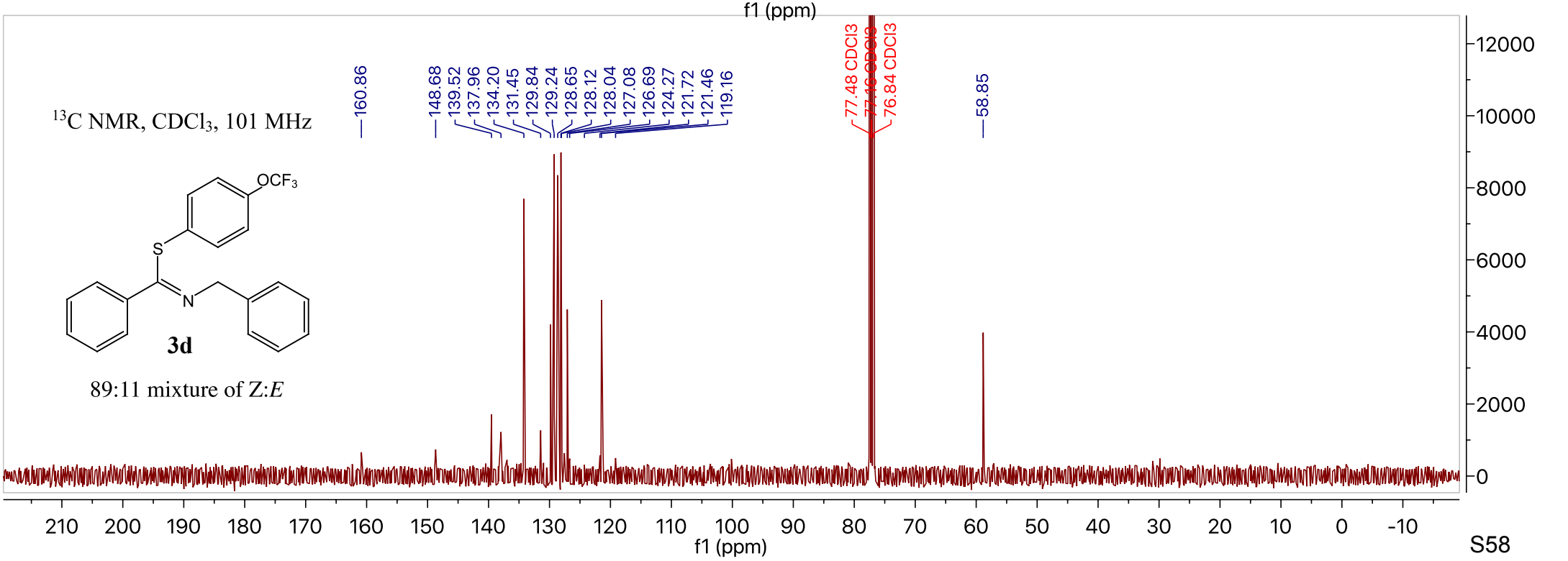
^{1}H NMR, $CDCl_3$, 400 MHz



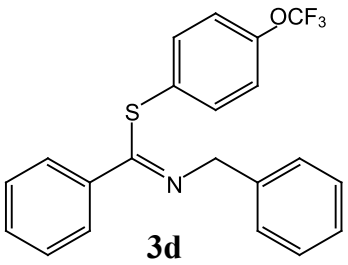
3d

89:11 mixture of Z:*E*


160.86
148.68
139.52
137.96
134.20
131.45
129.84
129.24
128.65
128.12
128.04
127.08
126.69
124.27
121.72
121.46
119.16
f1 (ppm)

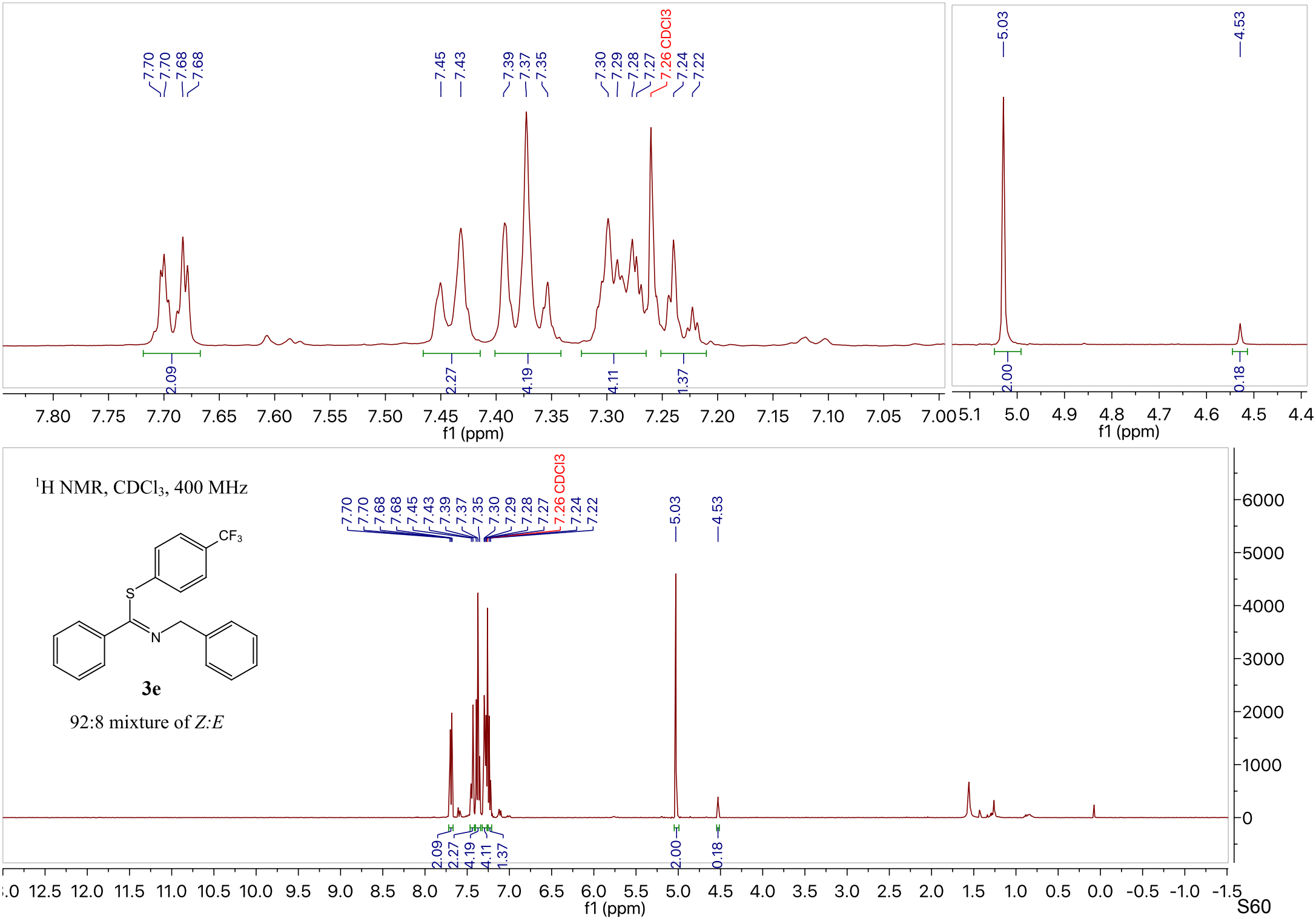

^{13}C NMR, $CDCl_3$, 101 MHz
160.86
148.68
139.52
137.96
134.20
131.45
129.84
129.24
128.65
128.12
128.04
127.08
126.69
124.27
121.72
121.46
119.16
77.48 CDCl3
76.84 CDCl3
58.85
OCF3
S
N
3d
89:11 mixture of Z:E
f1 (ppm)

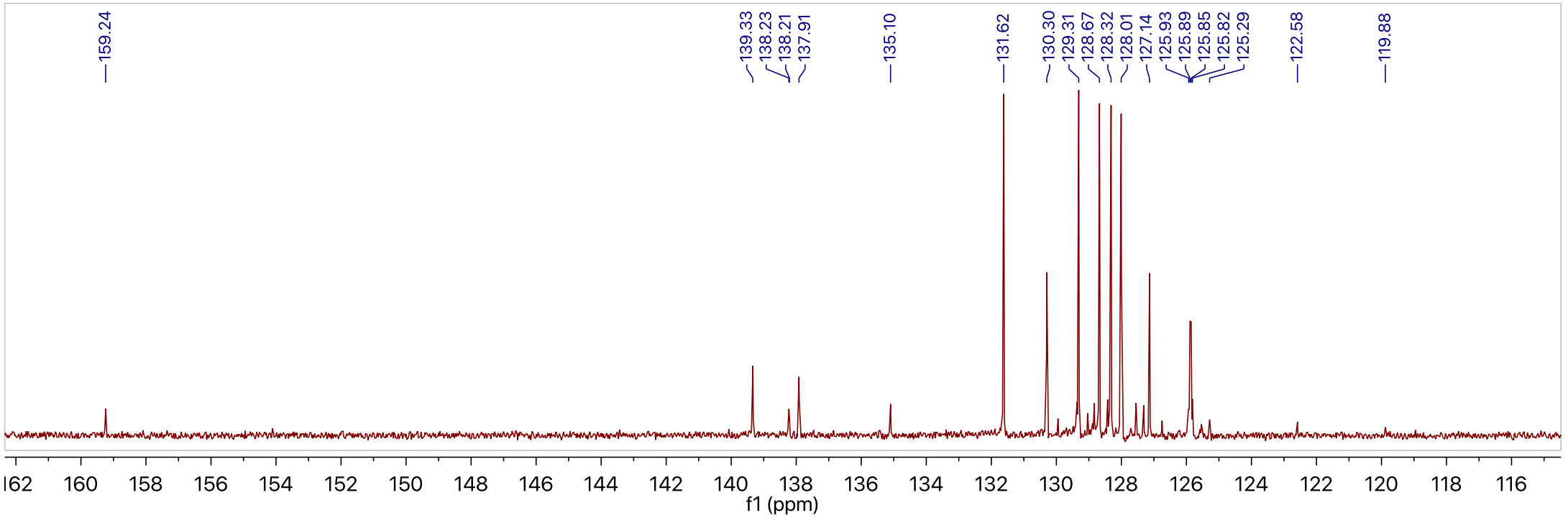
^{19}F NMR (376 MHz, $CDCl_3$)

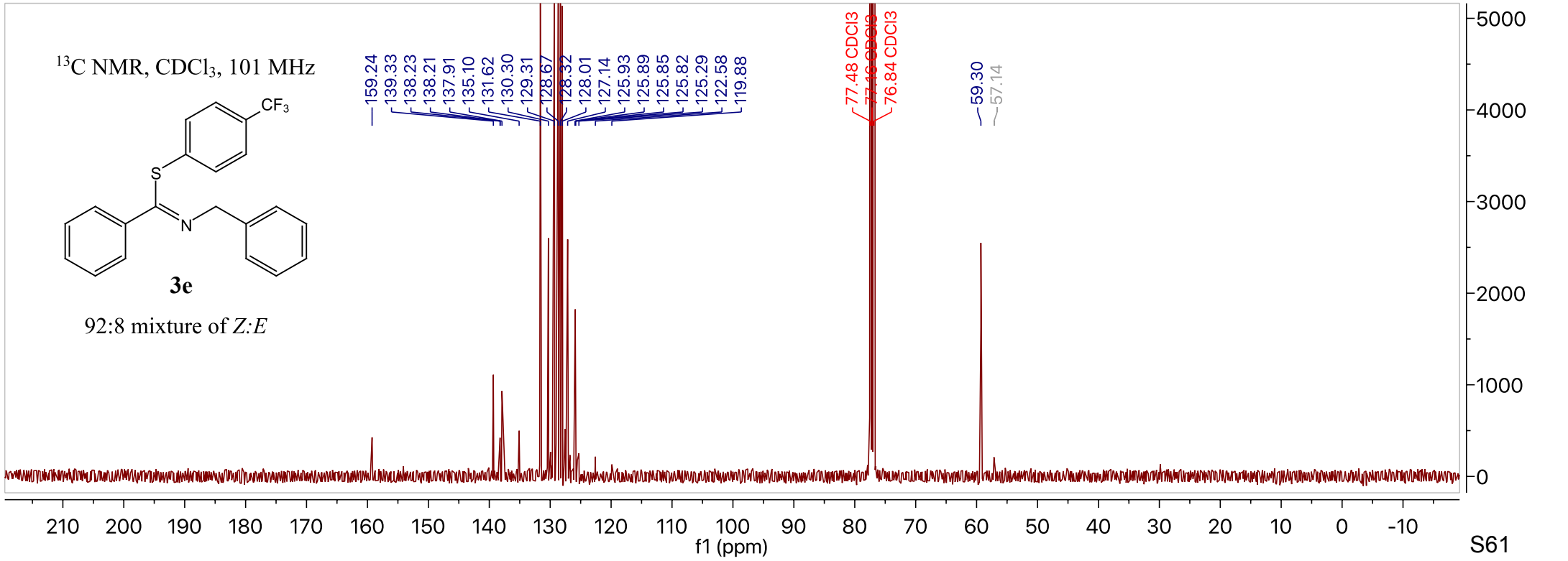


3d

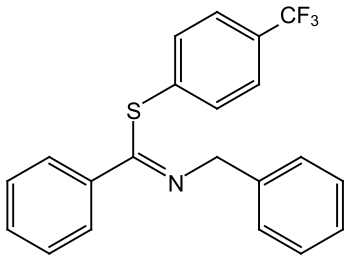
89:11 mixture of Z:*E*


7.70
7.70
7.68
7.68
7.45
7.43
7.39
7.37
7.35
7.30
7.29
7.28
7.27
7.26 CDCl3
7.24
7.22
5.03
4.53
2.09
2.27
4.19
4.11
1.37
2.00
0.18
f1 (ppm)
^{1}H NMR, $CDCl_3$, 400 MHz
CF_3
S
N
3e
92:8 mixture of *Z:E*


159.24
139.33
138.23
138.21
137.91
135.10
131.62
130.30
129.31
128.67
128.32
128.01
127.14
125.93
125.89
125.85
125.82
125.29
122.58
119.88
162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)

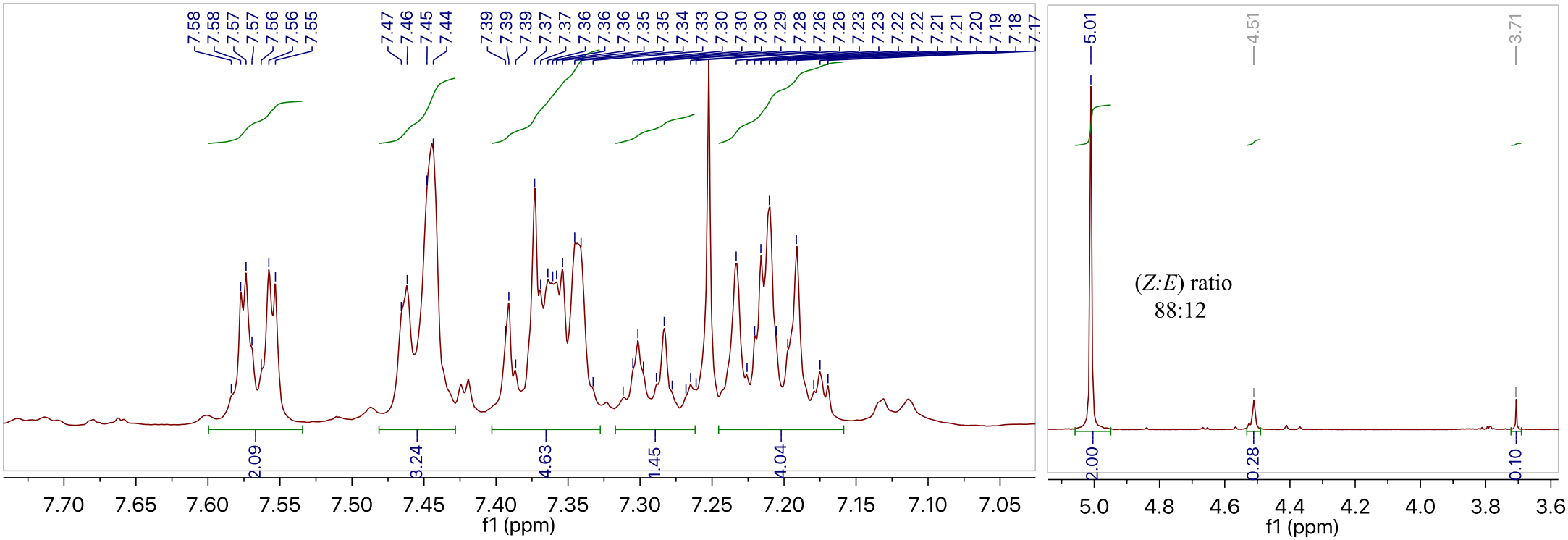

^{13}C NMR, CDCl$_3$, 101 MHz
CF$_3$
S
N
3e
92:8 mixture of *Z:E*
159.24
139.33
138.23
138.21
137.91
135.10
131.62
130.30
129.31
128.67
128.32
128.01
127.14
125.93
125.89
125.85
125.82
125.29
122.58
119.88
77.48 CDCl3
76.84 CDCl3
59.30
57.14
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

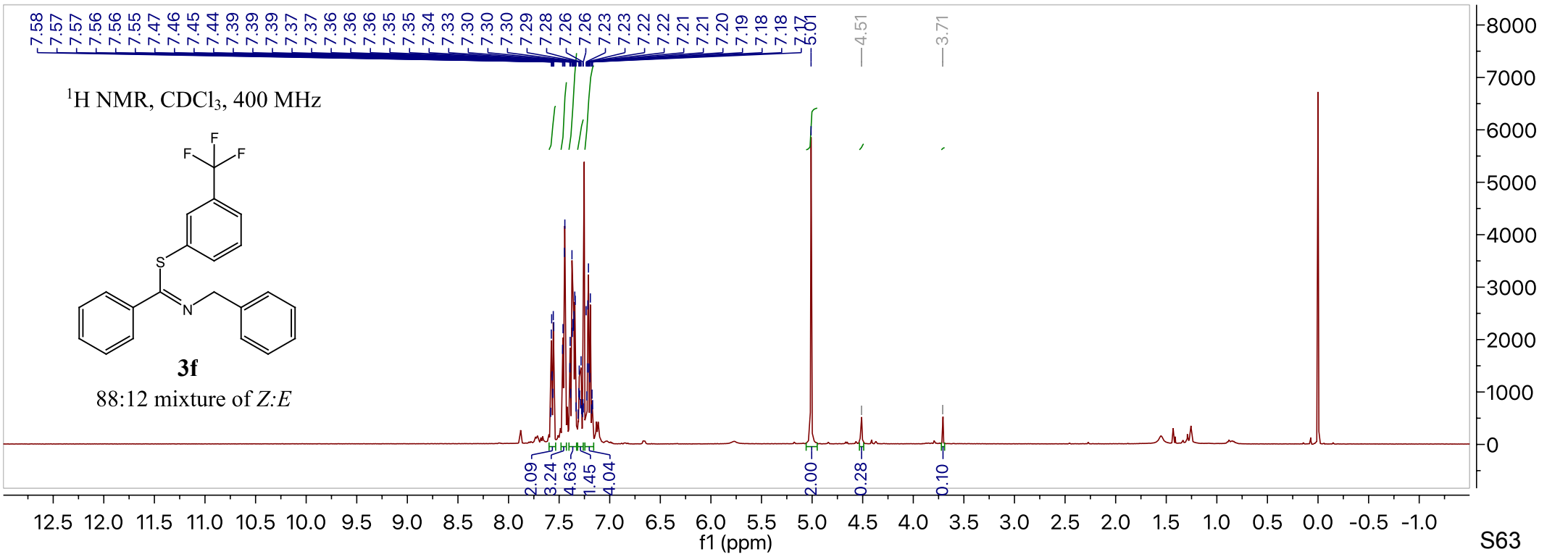
^{19}F NMR (376 MHz, $CDCl_3$)

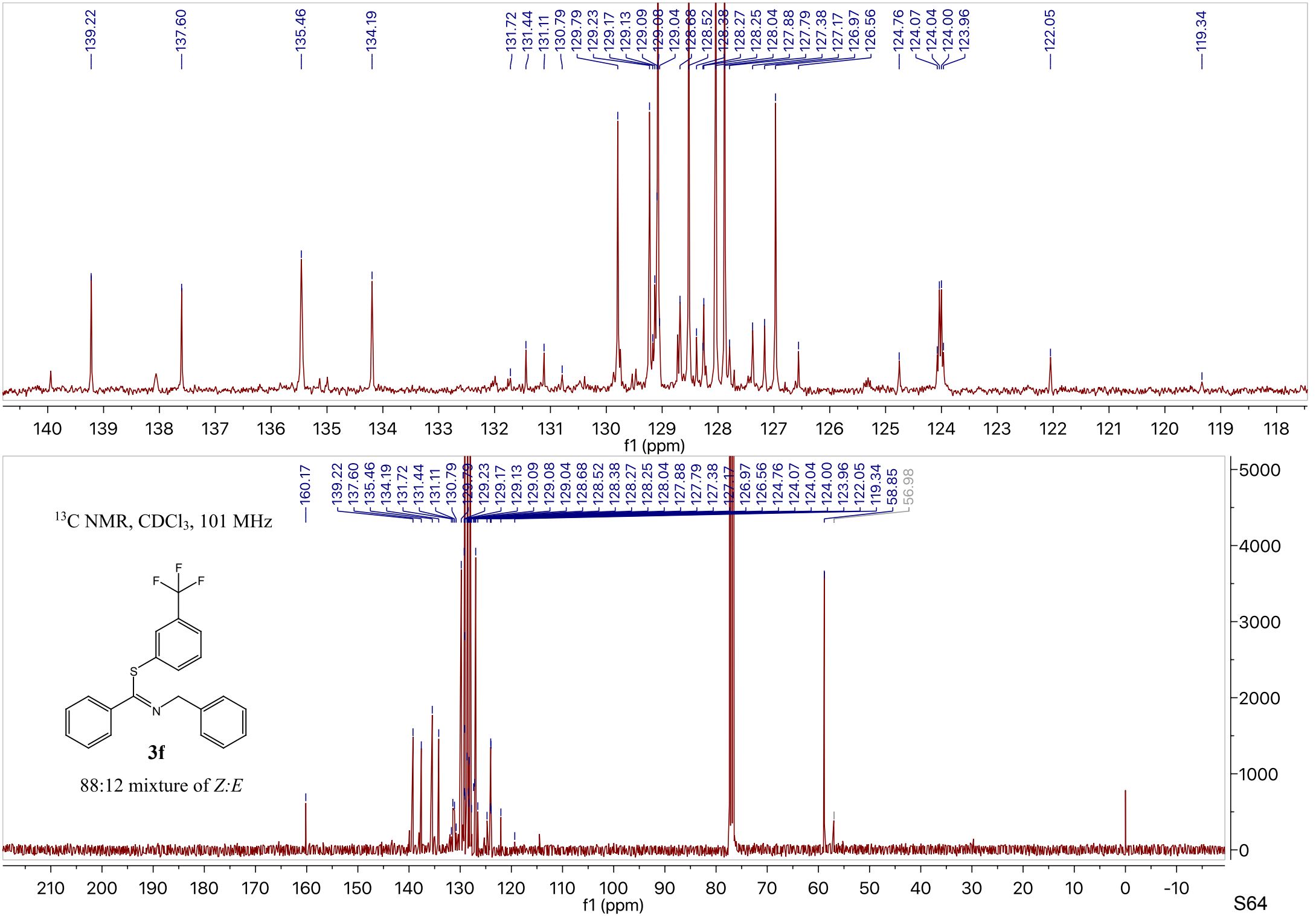


3e

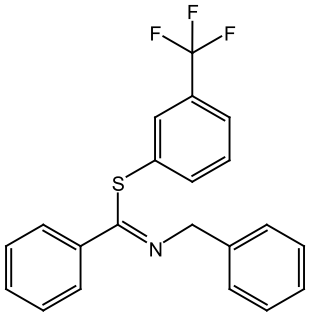
92:8 mixture of *Z*:*E*


(Z:E) ratio
88:12
f1 (ppm)


1H NMR, CDCl3, 400 MHz
3f
88:12 mixture of Z:E
f1 (ppm)

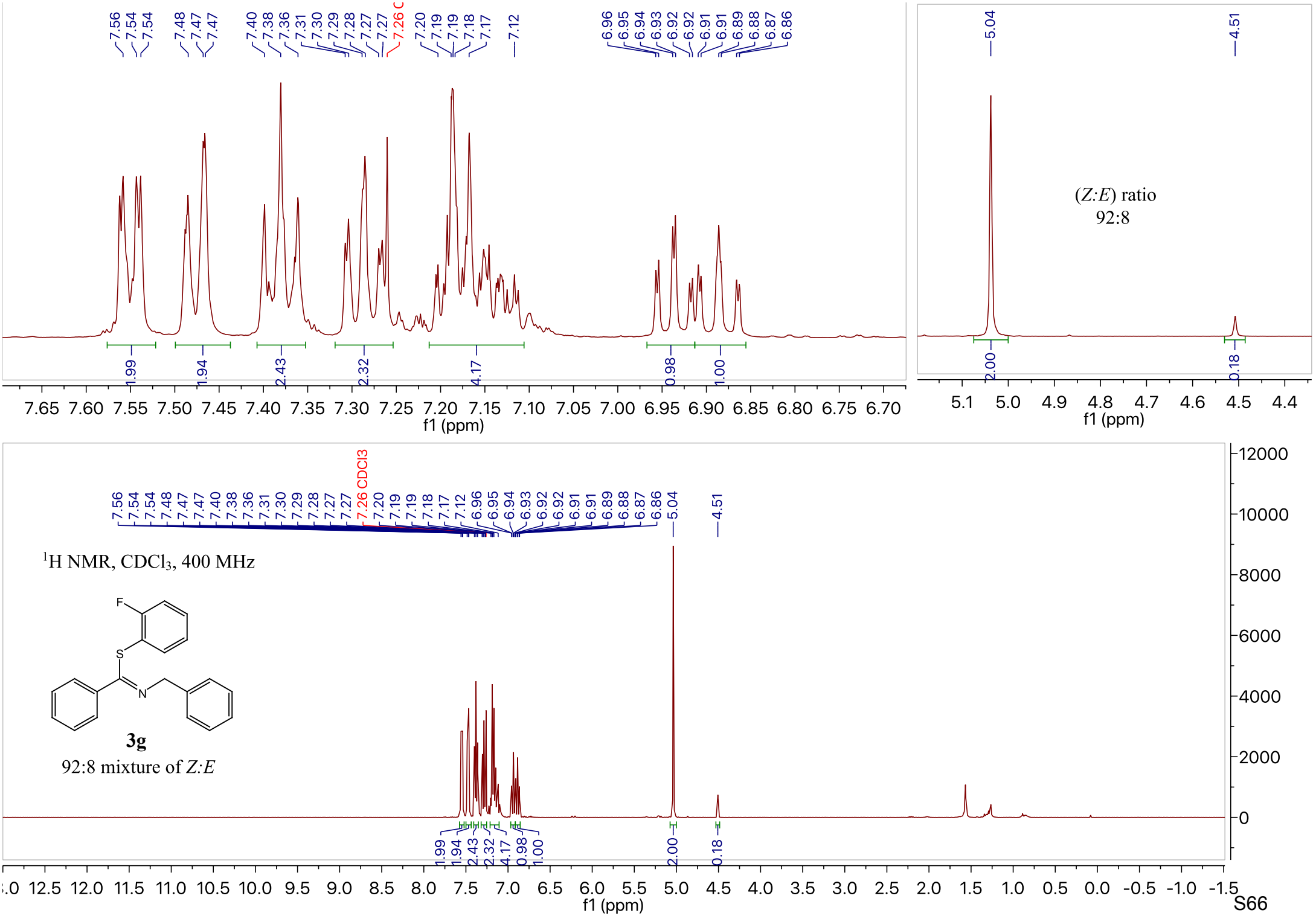

139.22
137.60
135.46
134.19
131.72
131.44
131.11
130.79
129.79
129.23
129.17
129.13
129.09
129.08
129.04
128.68
128.52
128.38
128.27
128.25
128.04
127.88
127.79
127.38
127.17
126.97
126.56
124.76
124.07
124.04
124.00
123.96
122.05
119.34
f1 (ppm)
160.17
58.85
56.98
^{13}C NMR, $CDCl_3$, 101 MHz
3f
88:12 mixture of *Z:E*
f1 (ppm)

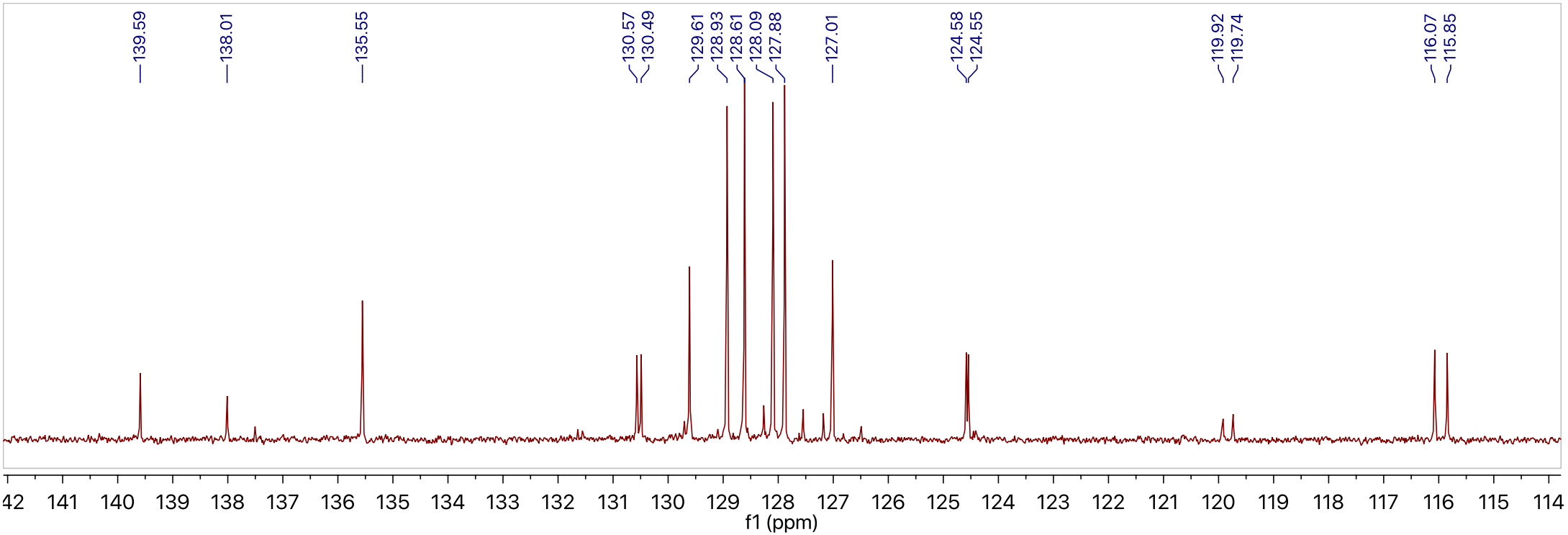
^{19}F NMR (376 MHz, $CDCl_3$)

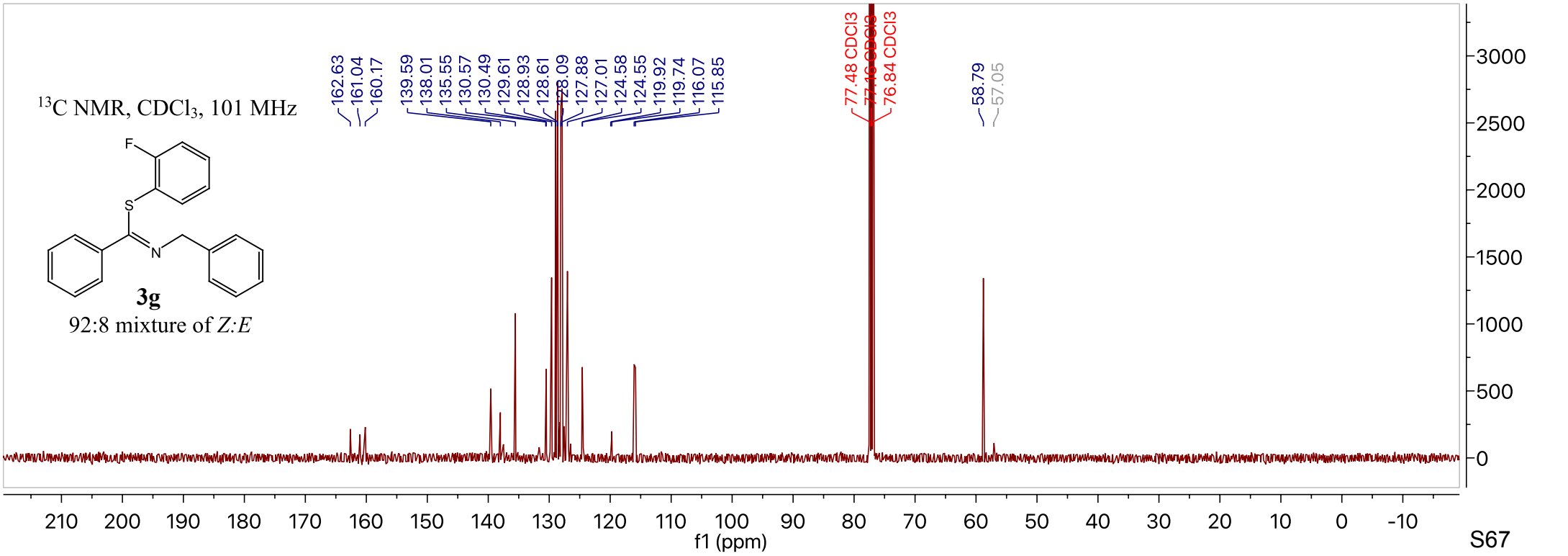


3f

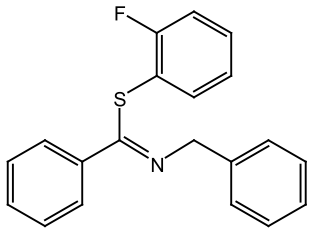
88:12 mixture of *Z:E*


7.56 7.54 7.54 7.48 7.47 7.47 7.40 7.38 7.36 7.31 7.30 7.29 7.28 7.27 7.27 7.26 C 7.20 7.19 7.19 7.18 7.17 7.12 6.96 6.95 6.94 6.93 6.92 6.92 6.91 6.91 6.89 6.88 6.87 6.86
1.99 1.94 2.43 2.32 4.17 0.98 1.00
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (ppm)
5.04 4.51
(Z:E) ratio
92:8
2.00 0.18
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)
7.26 CDCl3
1H NMR, CDCl3, 400 MHz
F
S
N
3g
92:8 mixture of Z:E
12000 10000 8000 6000 4000 2000 0
f1 (ppm)


139.59
138.01
135.55
130.57
130.49
129.61
128.93
128.61
128.09
127.88
127.01
124.58
124.55
119.92
119.74
116.07
115.85
42 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114
f1 (ppm)

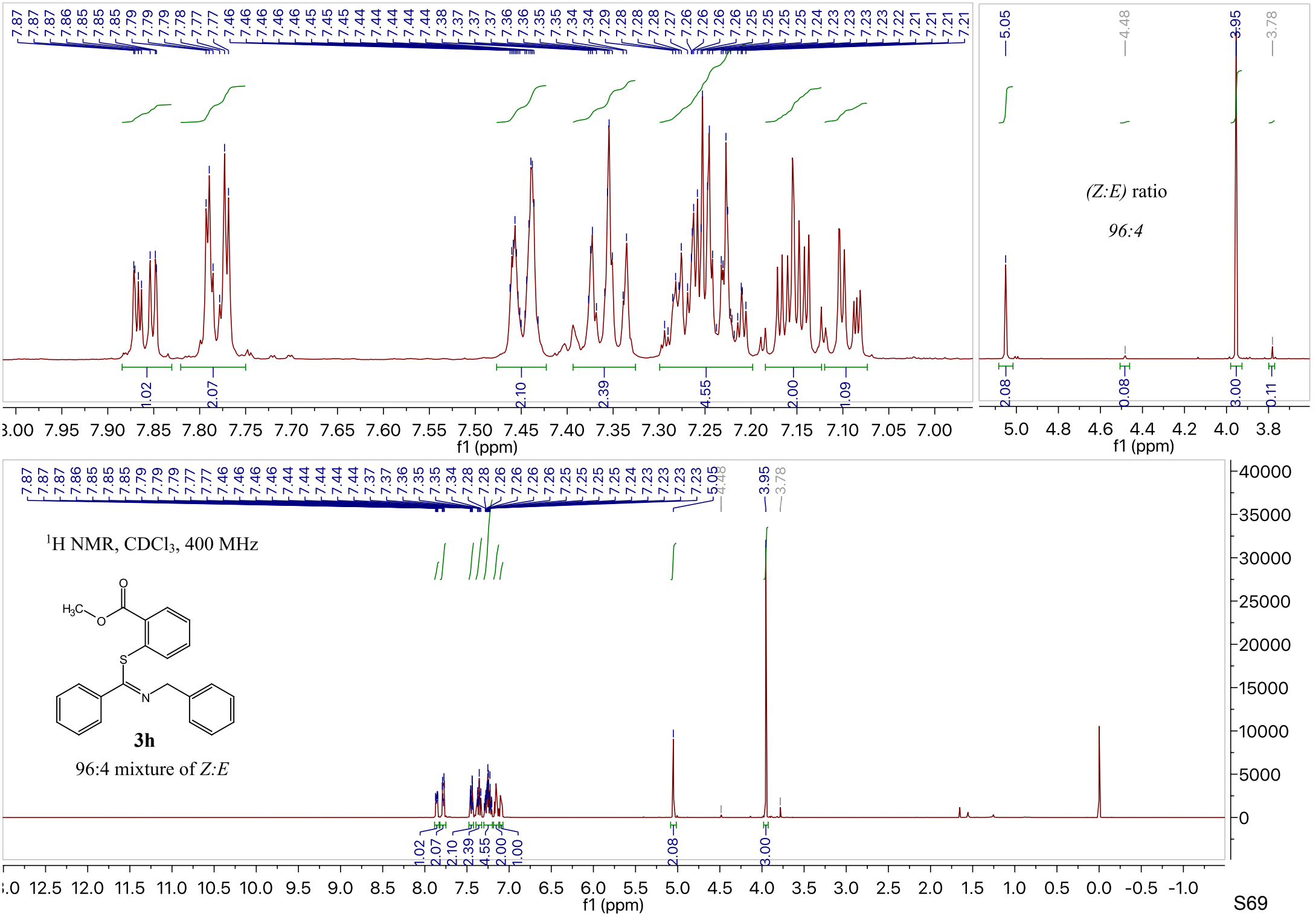

^{13}C NMR, $CDCl_3$, 101 MHz
F
S
N
3g
92:8 mixture of *Z:E*
162.63
161.04
160.17
139.59
138.01
135.55
130.57
130.49
129.61
128.93
128.61
128.09
127.88
127.01
124.58
124.55
119.92
119.74
116.07
115.85
77.48 CDCl3
76.84 CDCl3
58.79
57.05
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

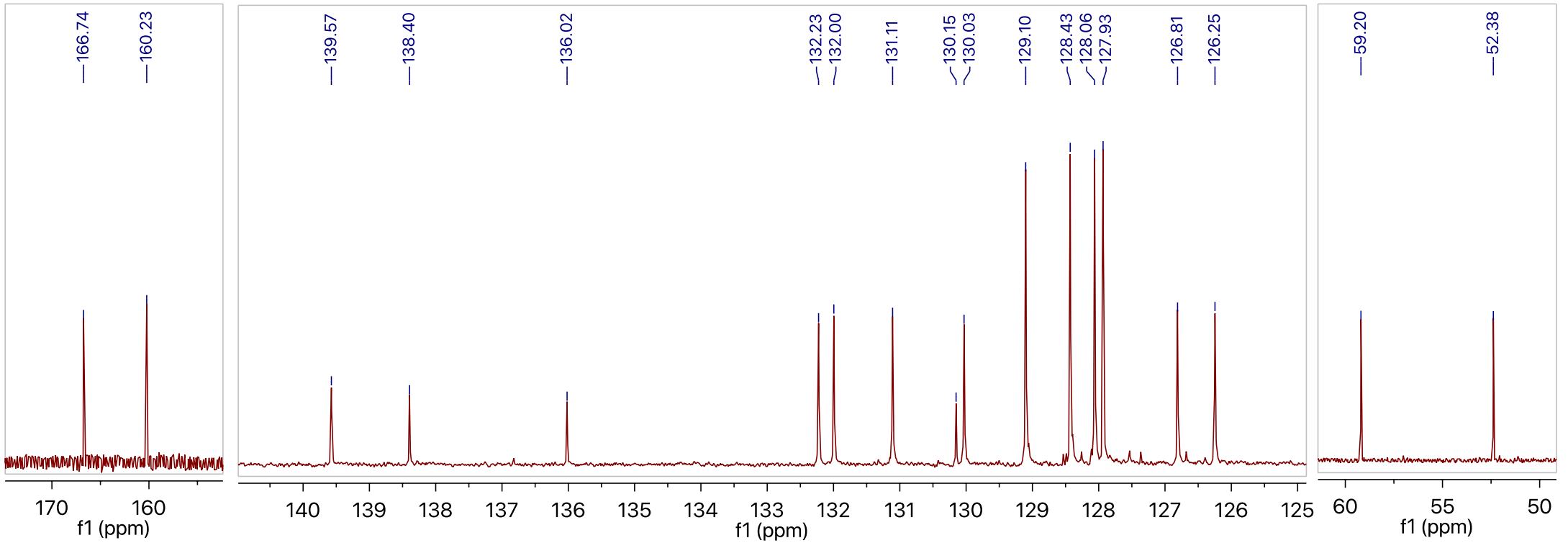
^{19}F NMR (376 MHz, $CDCl_3$)



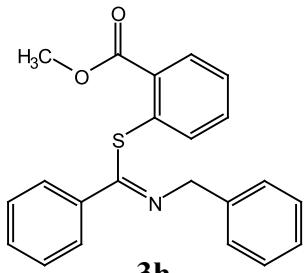
3g

92:8 mixture of *Z:E*


(Z:E) ratio
96:4
^{1}H NMR, $CDCl_3$, 400 MHz
3h
96:4 mixture of Z:E
f1 (ppm)

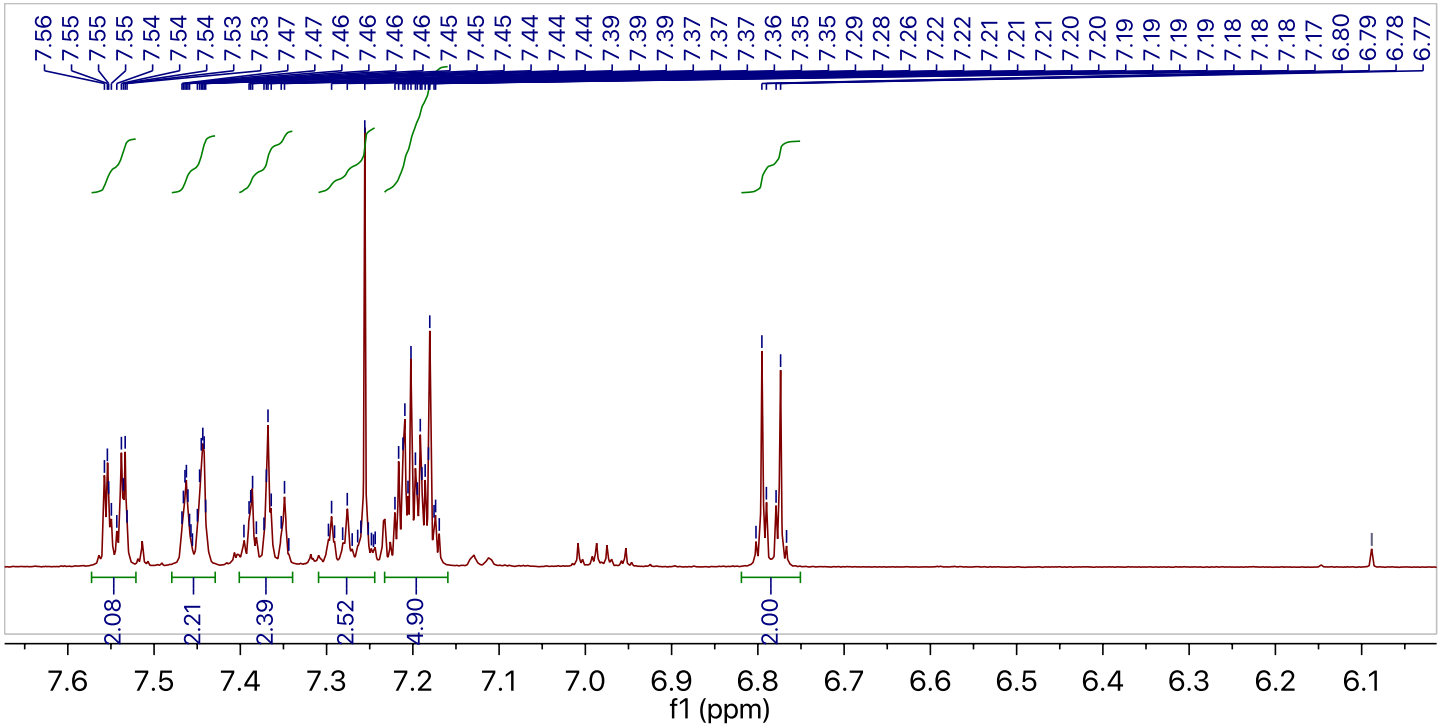


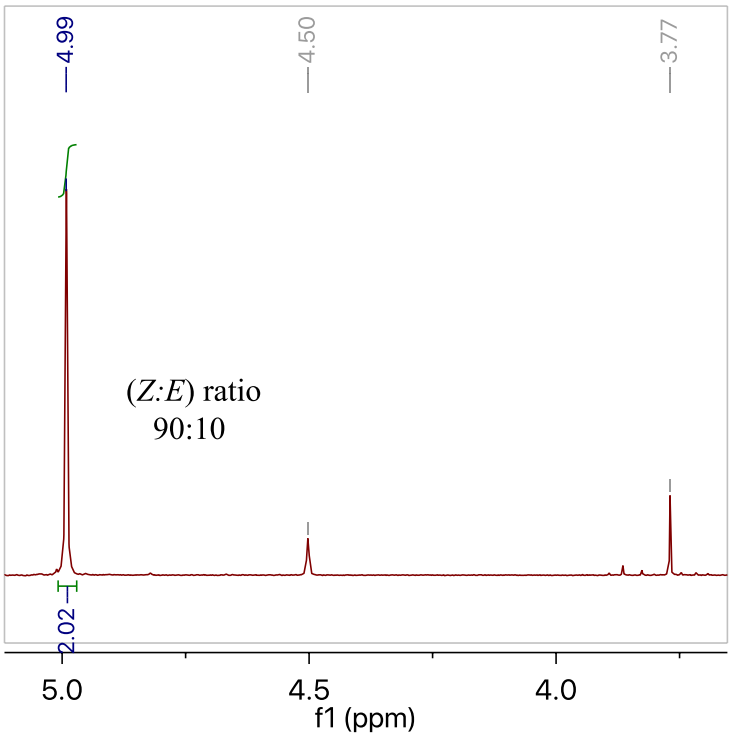
^{13}C NMR, $CDCl_3$, 101 MHz



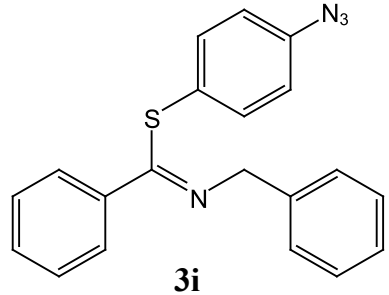
3h

96:4 mixture of *Z:E*



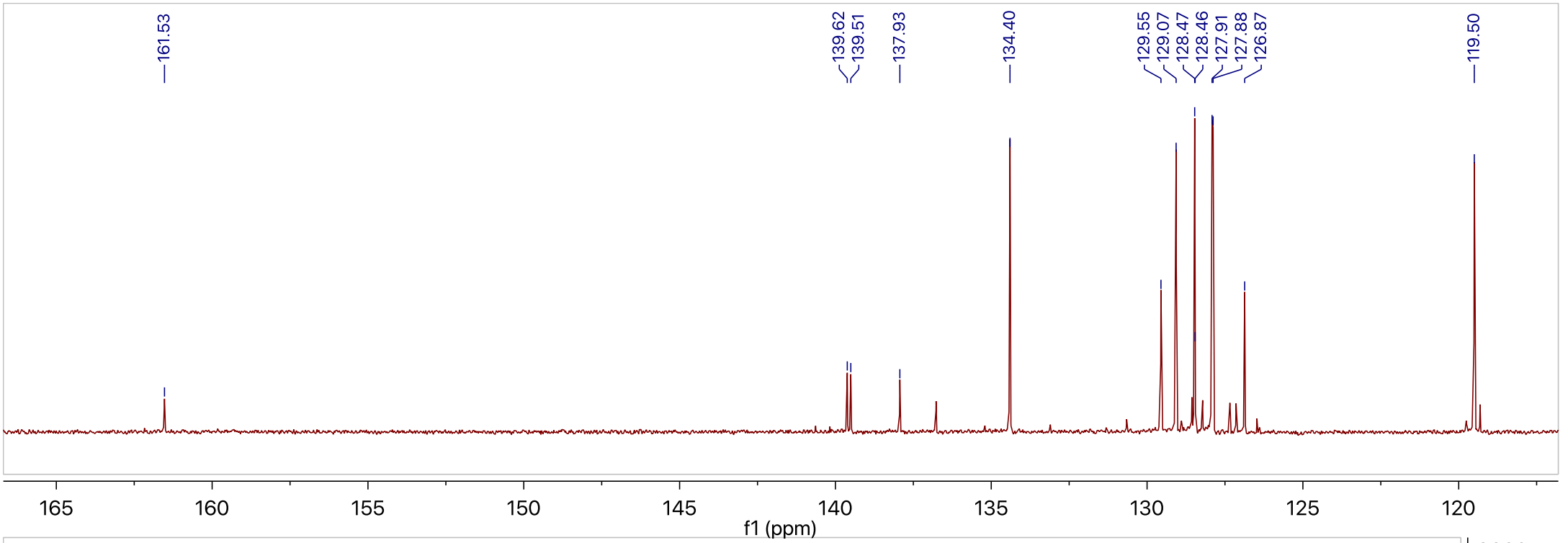


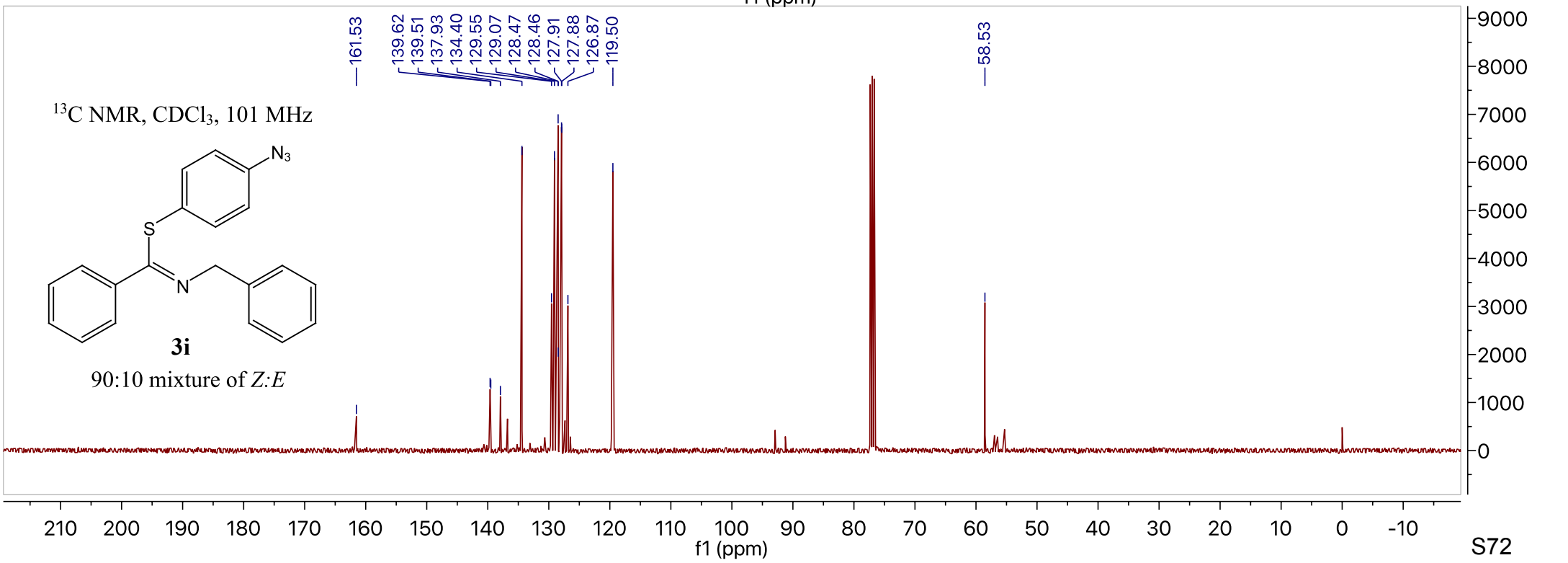
^{1}H NMR, $CDCl_3$, 400 MHz

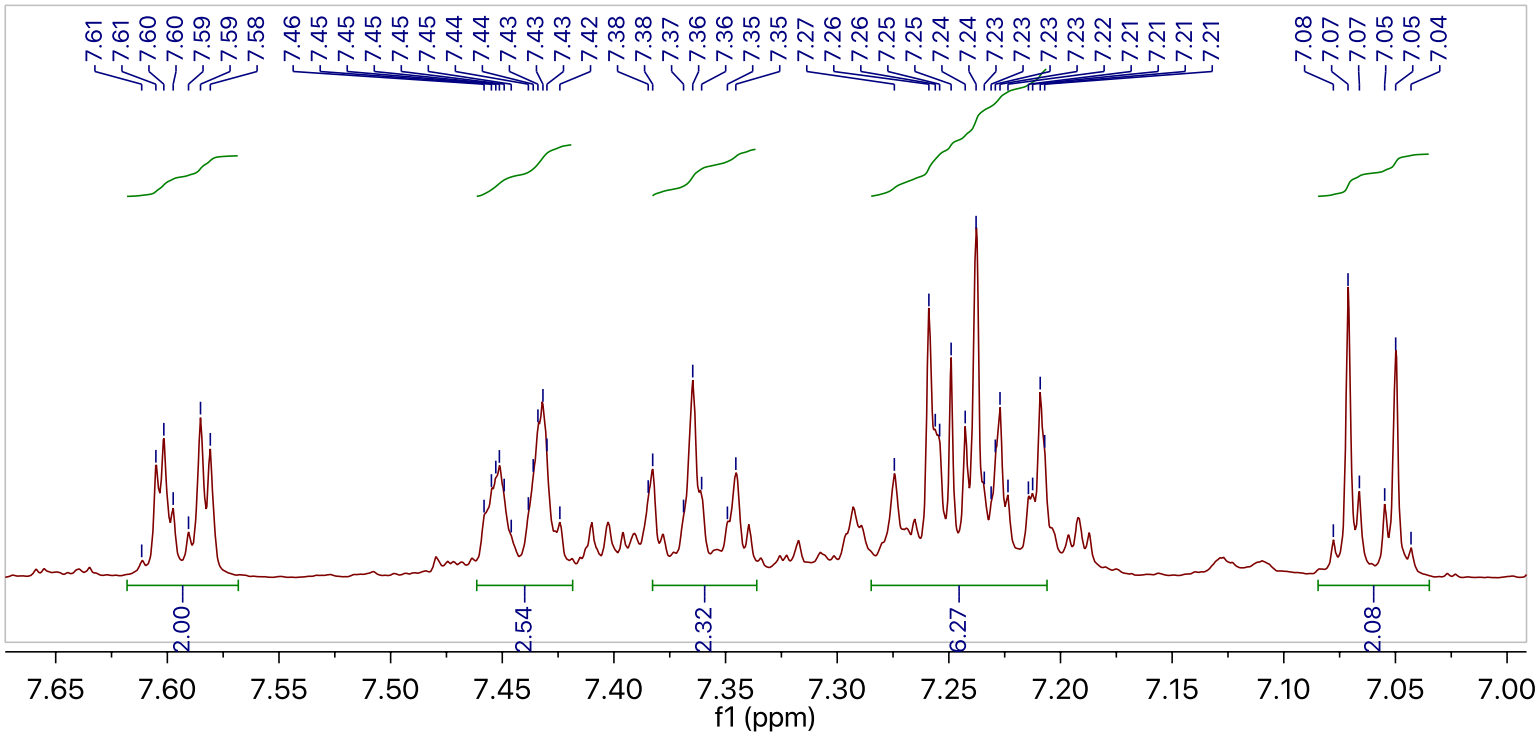


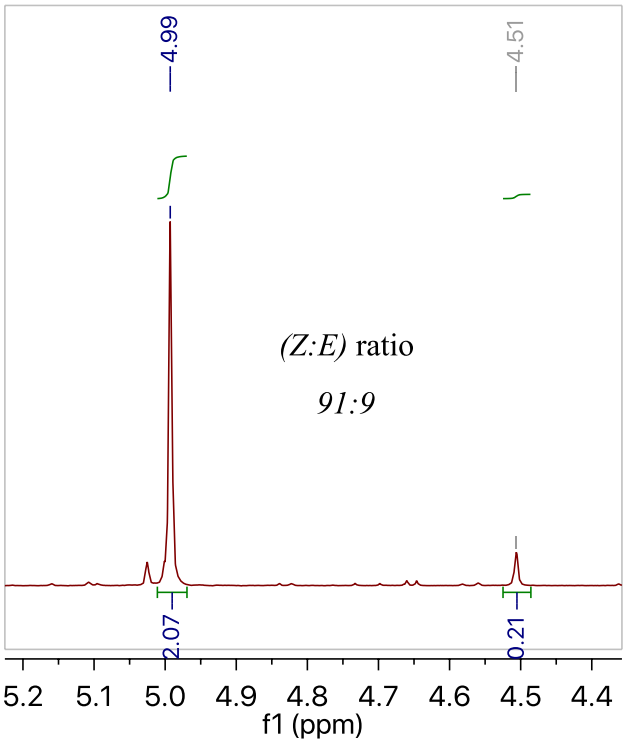
3i

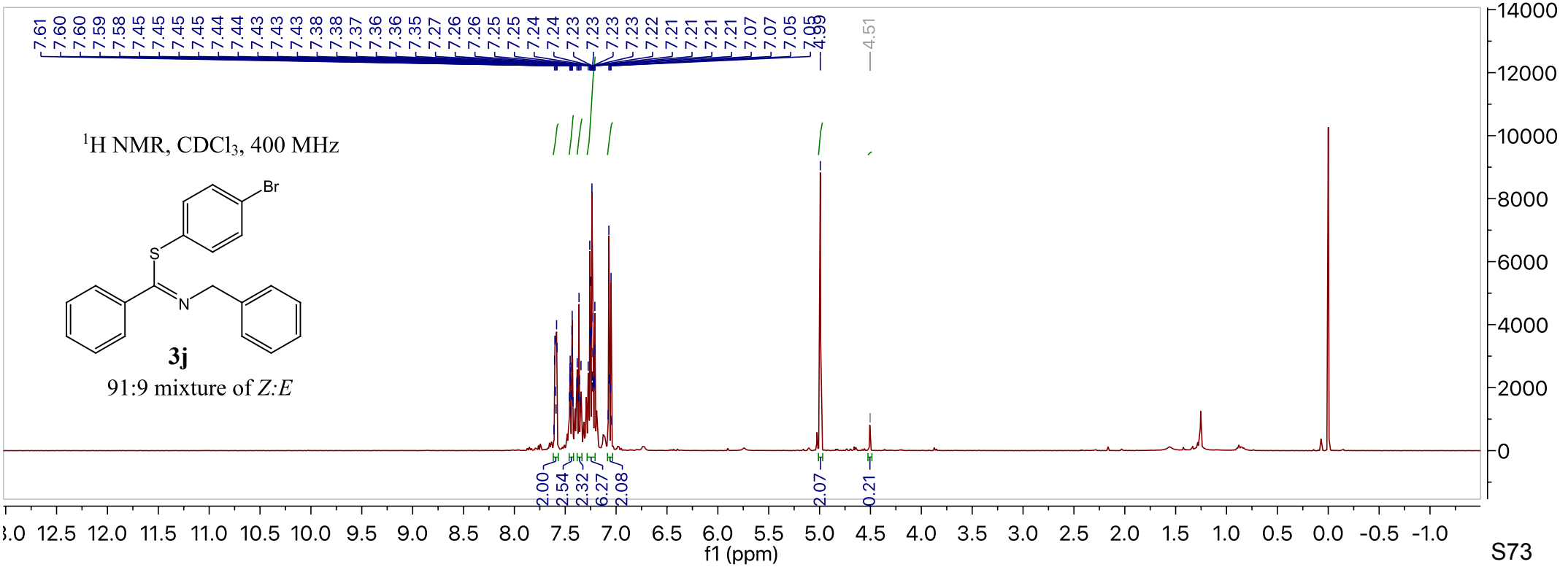
90:10 mixture of *Z:E*

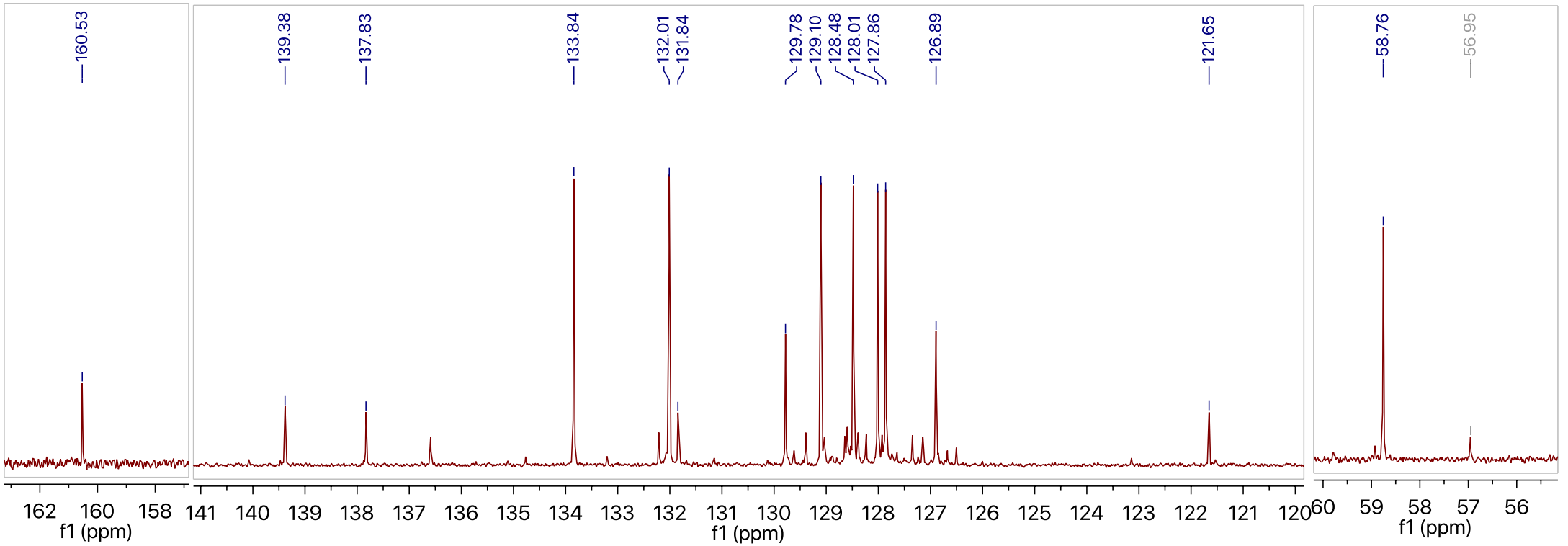

161.53
139.62
139.51
137.93
134.40
129.55
129.07
128.47
128.46
127.91
127.88
126.87
119.50
165
160
155
150
145
140
135
130
125
120
f1 (ppm)


161.53
139.62
139.51
137.93
134.40
129.55
129.07
128.47
128.46
127.91
127.88
126.87
119.50
58.53
^{13}C NMR, CDCl$_3$, 101 MHz
N$_3$
S
N
3i
90:10 mixture of *Z:E*
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

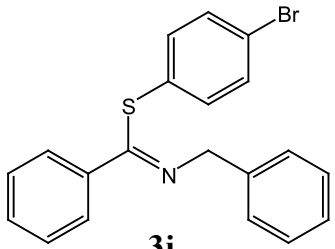

7.61 7.61 7.60 7.60 7.59 7.59 7.58
7.46 7.45 7.45 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42
7.38 7.38 7.37 7.36 7.36 7.35 7.35
7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.21 7.21 7.21
7.08 7.07 7.07 7.05 7.05 7.04
2.00
2.54
2.32
6.27
2.08
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)


4.99
4.51
(Z:E) ratio
91:9
2.07
0.21
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)


7.61 7.60 7.60 7.59 7.58 7.45 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.38 7.38 7.37 7.36 7.36 7.35 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.23 7.23 7.22 7.21 7.21 7.21 7.21 7.07 7.07 7.05 7.05 4.99
4.51
1H NMR, CDCl3, 400 MHz
Br
S
N
3j
91:9 mixture of Z:E
2.00
2.54
2.32
6.27
2.08
2.07
0.21
14000
12000
10000
8000
6000
4000
2000
0
f1 (ppm)

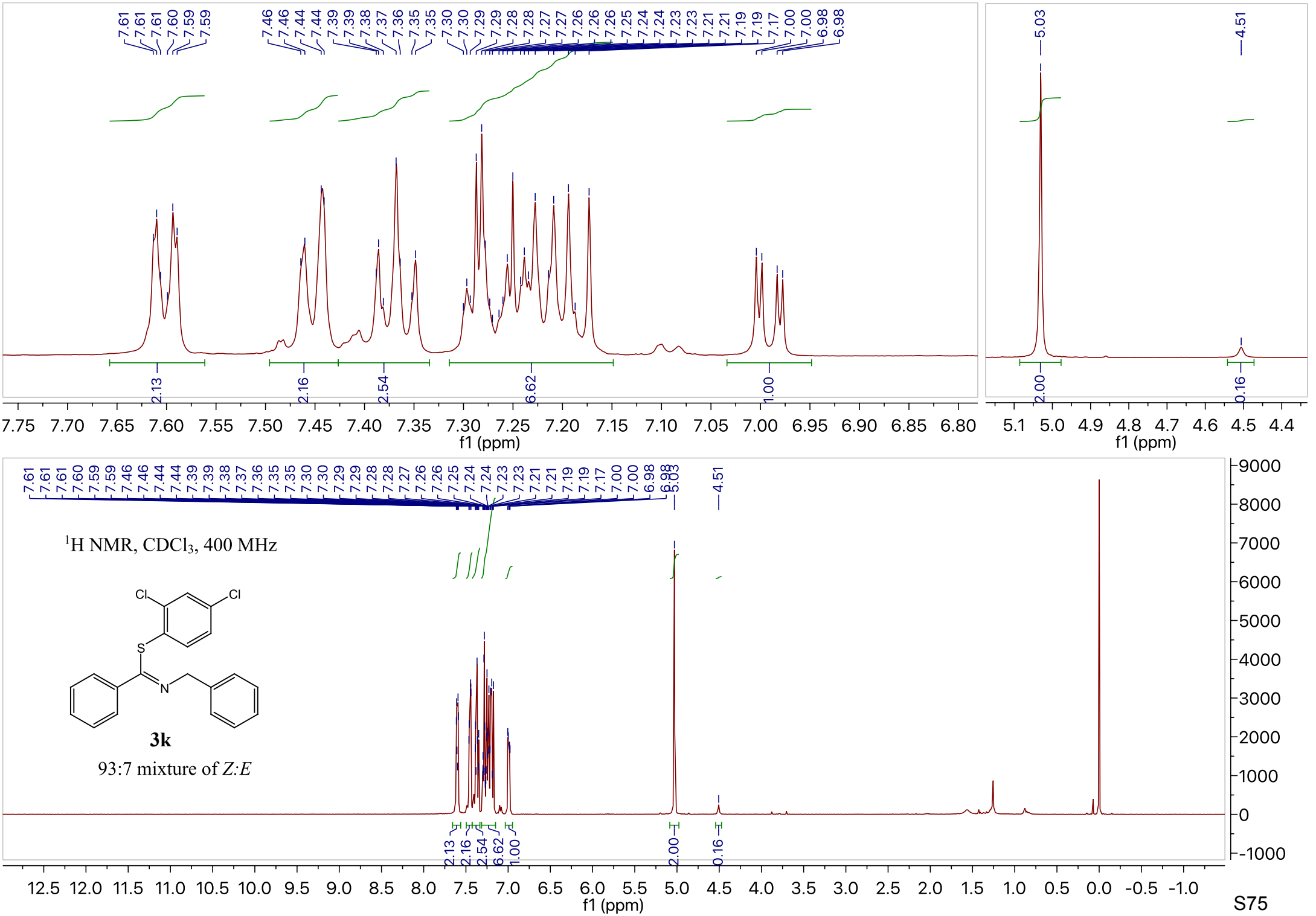


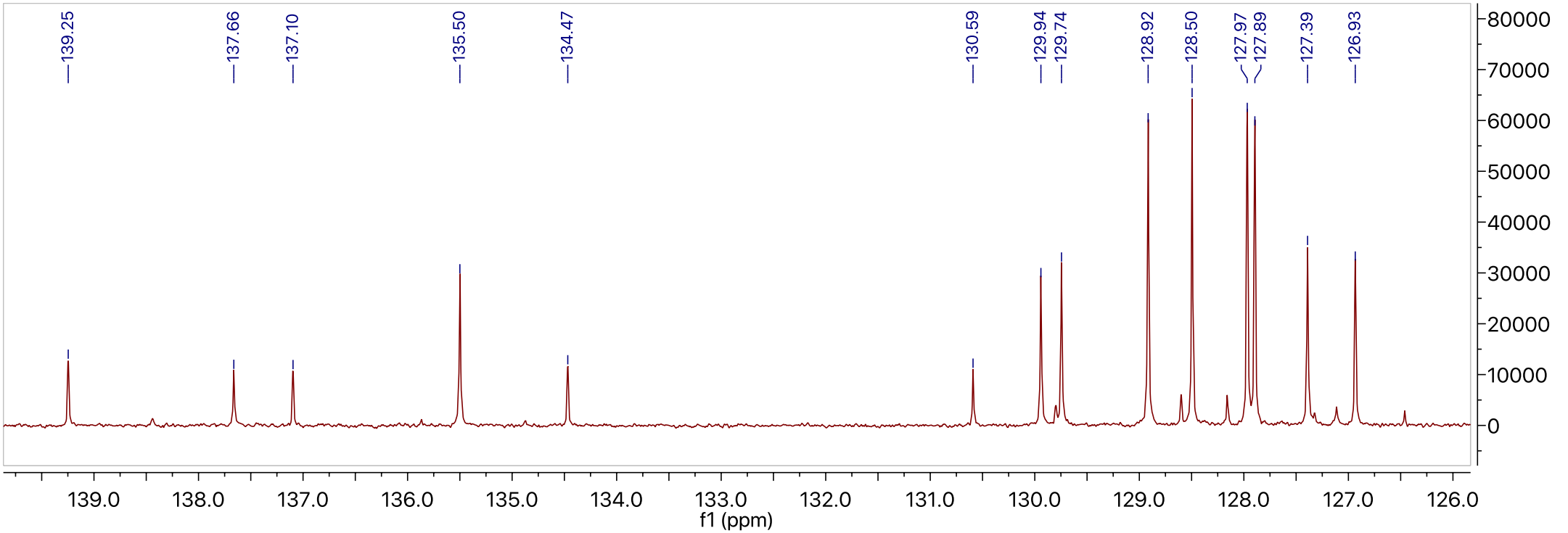
^{13}C NMR, $CDCl_3$, 101 MHz

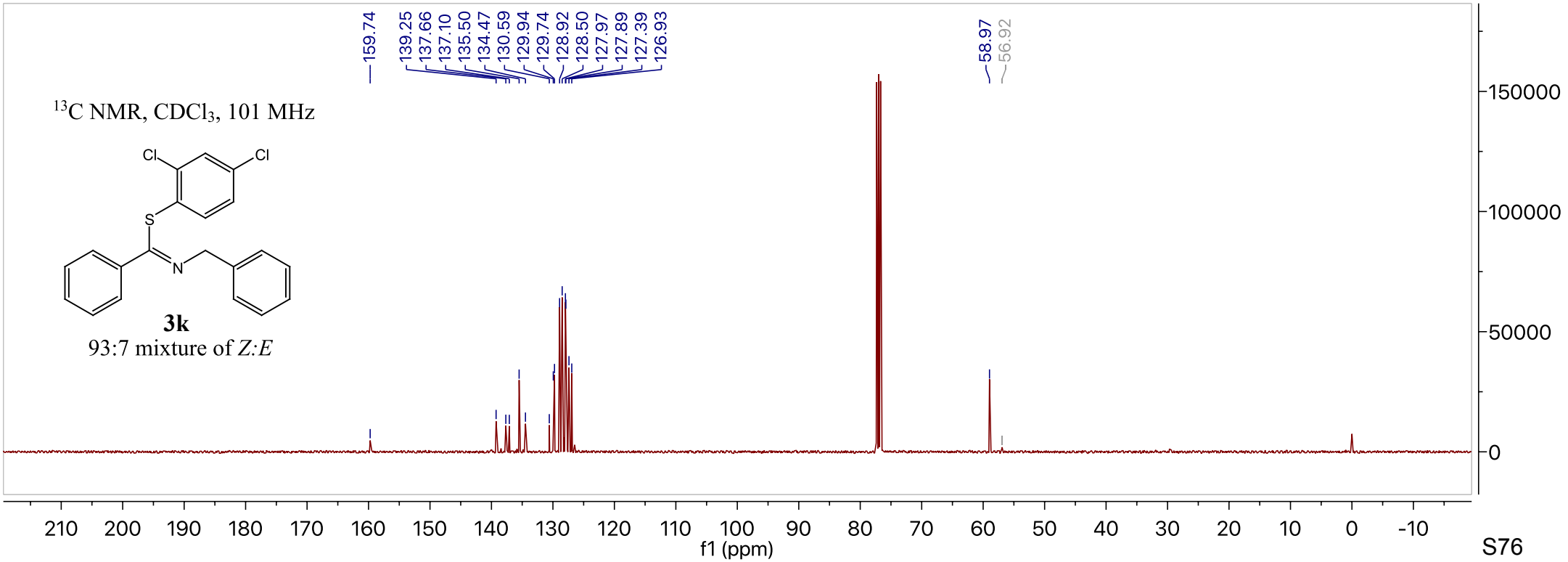


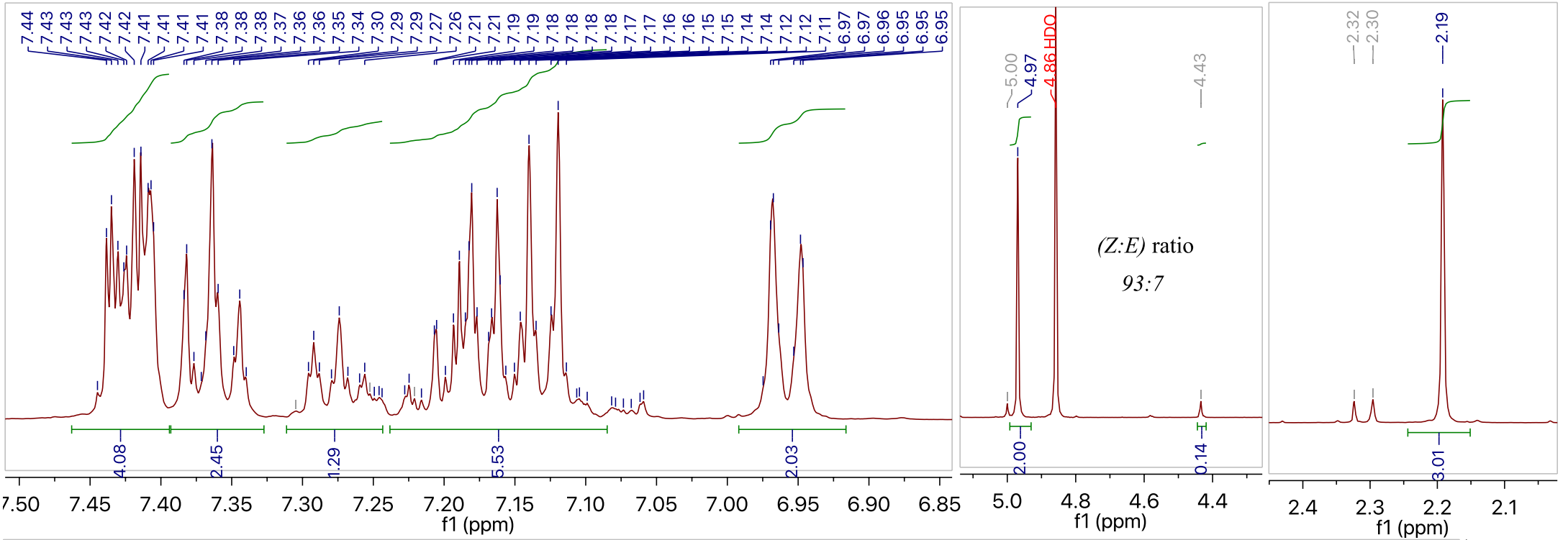
3j

91:9 mixture of *Z:E*

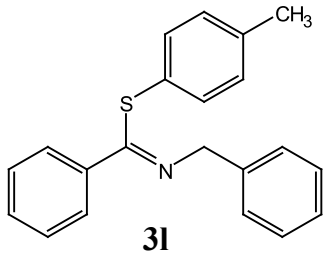

^{1}H NMR, $CDCl_3$, 400 MHz
Cl
Cl
S
N
3k
93:7 mixture of *Z:E*
f1 (ppm)


139.25
137.66
137.10
135.50
134.47
130.59
129.94
129.74
128.92
128.50
127.97
127.89
127.39
126.93
80000
70000
60000
50000
40000
30000
20000
10000
0
139.0
138.0
137.0
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.0
126.0
f1 (ppm)


159.74
139.25
137.66
137.10
135.50
134.47
130.59
129.94
129.74
128.92
128.50
127.97
127.89
127.39
126.93
58.97
56.92
^{13}C NMR, CDCl$_3$, 101 MHz
Cl
Cl
S
N
3k
93:7 mixture of *Z:E*
150000
100000
50000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

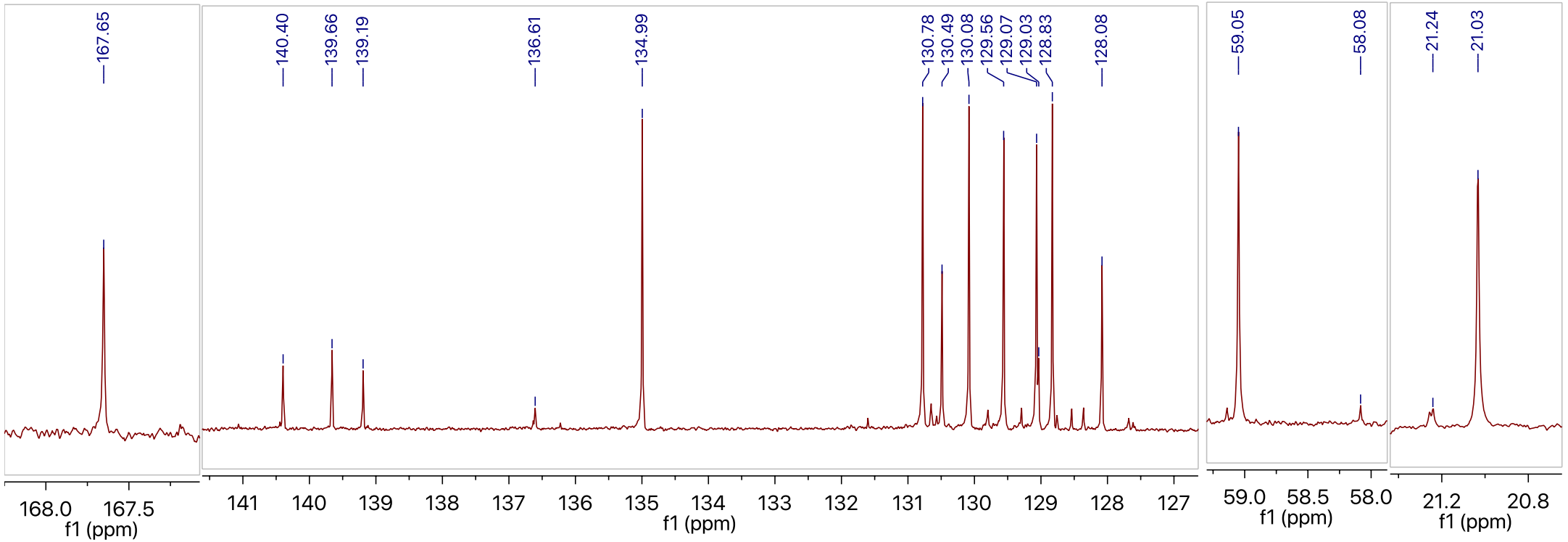


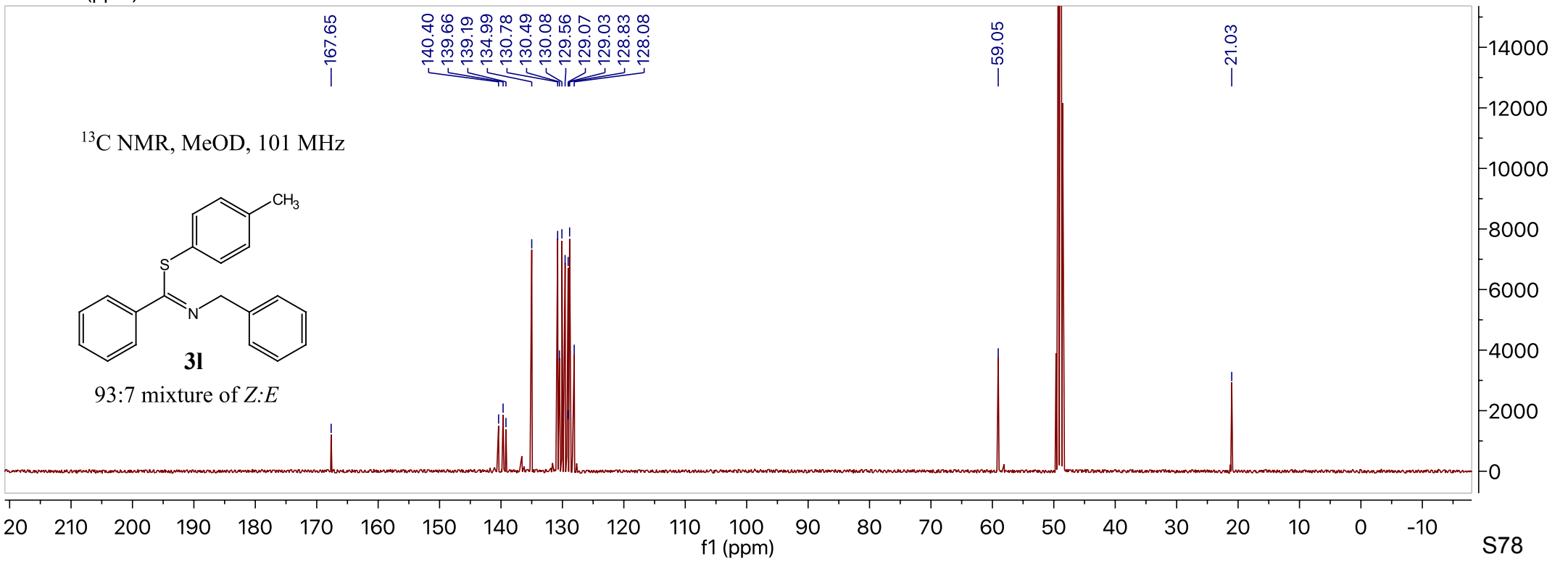
^{1}H NMR, $MeOD_3$, 400 MHz

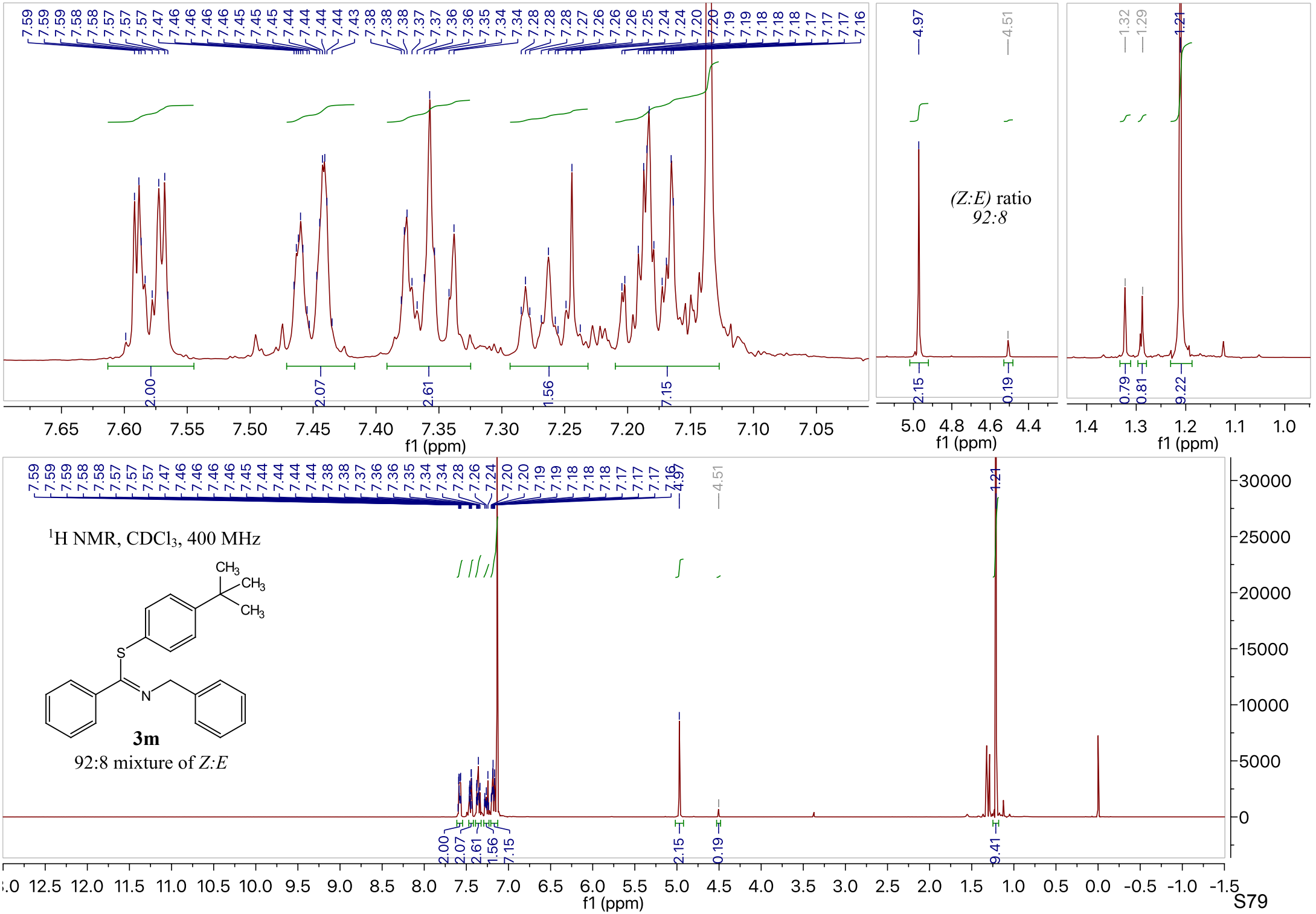


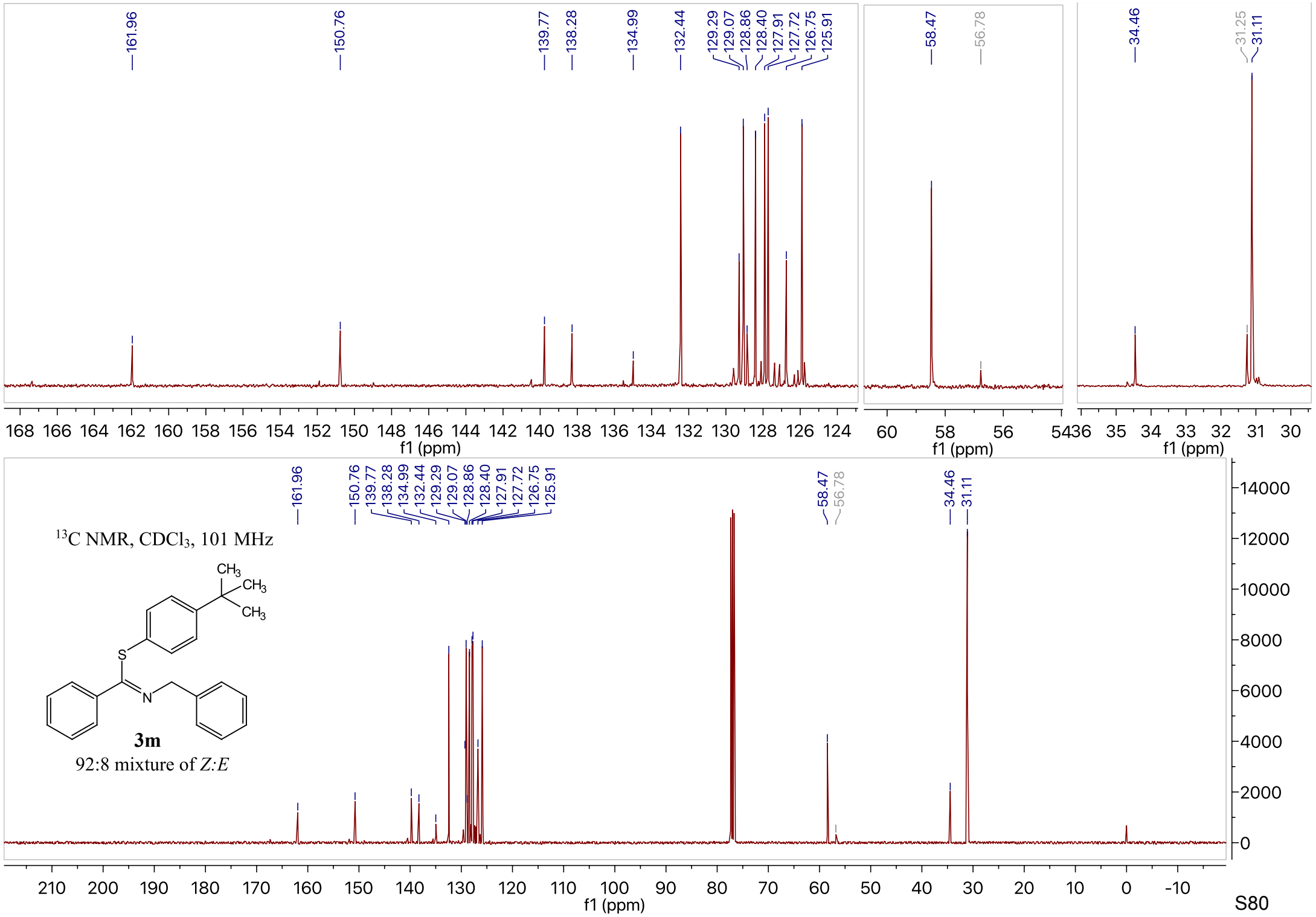
3l

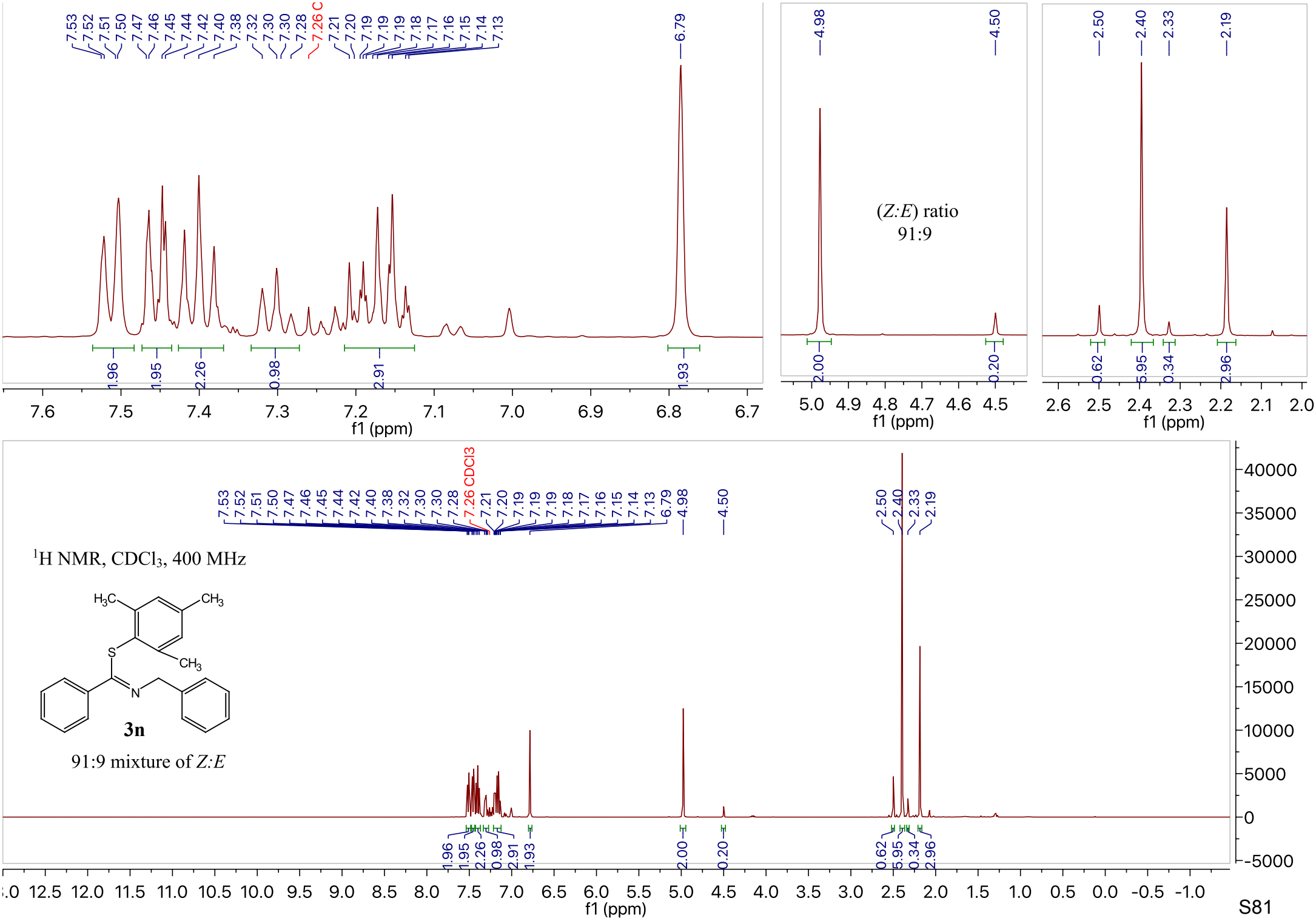
93:7 mixture of *Z:E*

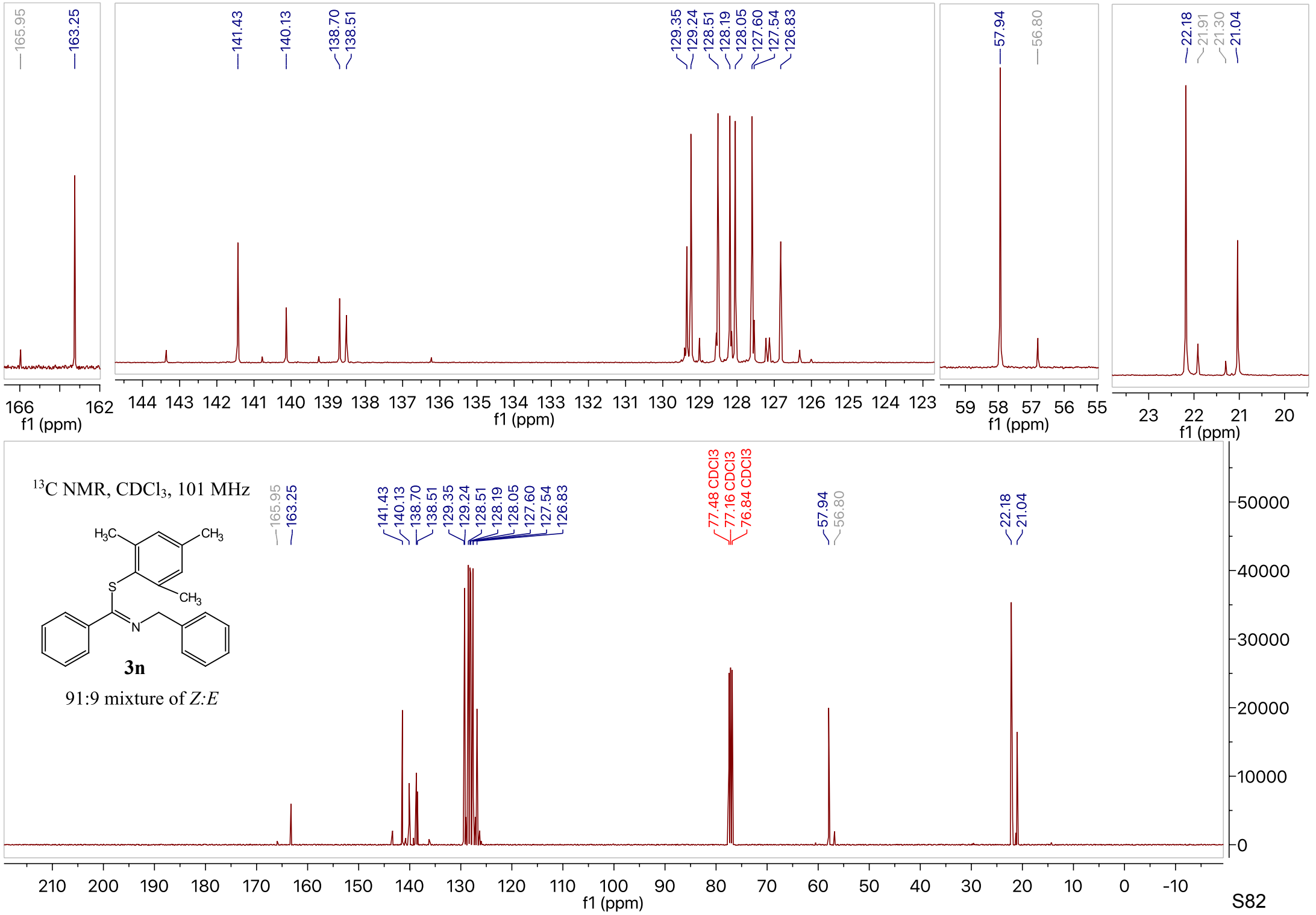

167.65
140.40
139.66
139.19
136.61
134.99
130.78
130.49
130.08
129.56
129.07
129.03
128.83
128.08
59.05
58.08
21.24
21.03
f1 (ppm)

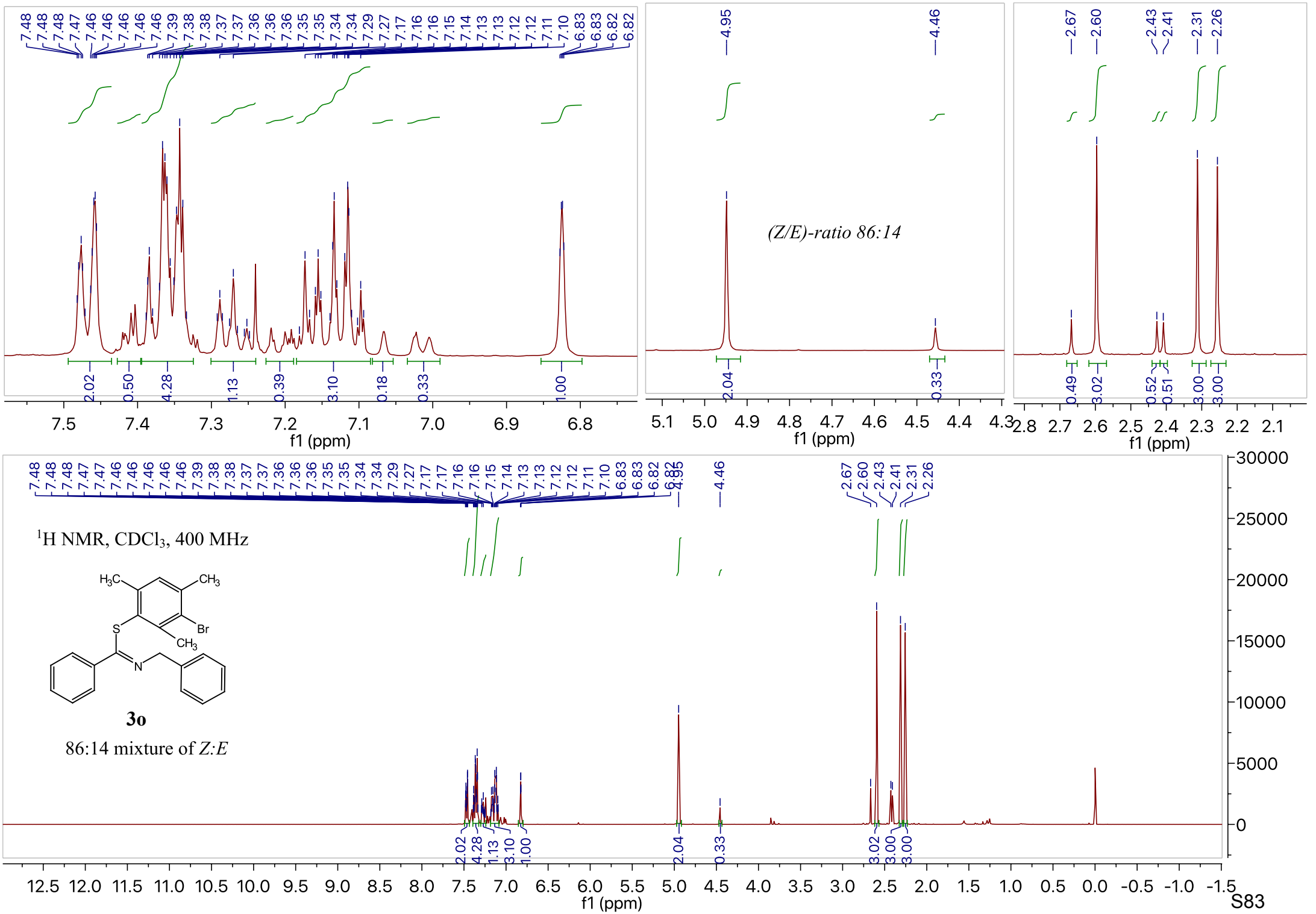

167.65
140.40
139.66
139.19
134.99
130.78
130.49
130.08
129.56
129.07
129.03
128.83
128.08
59.05
21.03
^{13}C NMR, MeOD, 101 MHz
CH3
S
N
3l
93:7 mixture of Z:E
f1 (ppm)

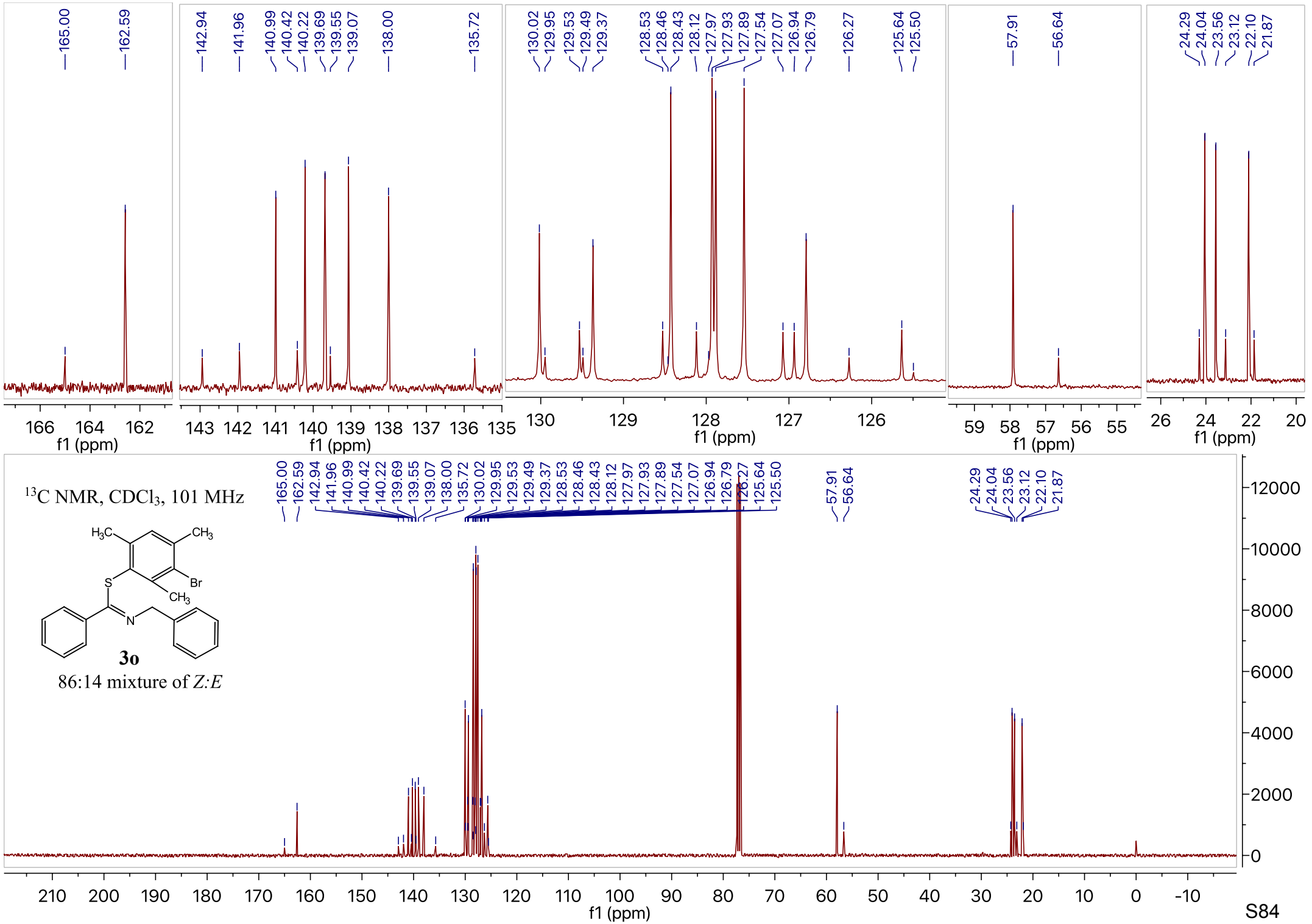

(Z:E) ratio
92:8
1H NMR, CDCl3, 400 MHz
3m
92:8 mixture of Z:E
f1 (ppm)

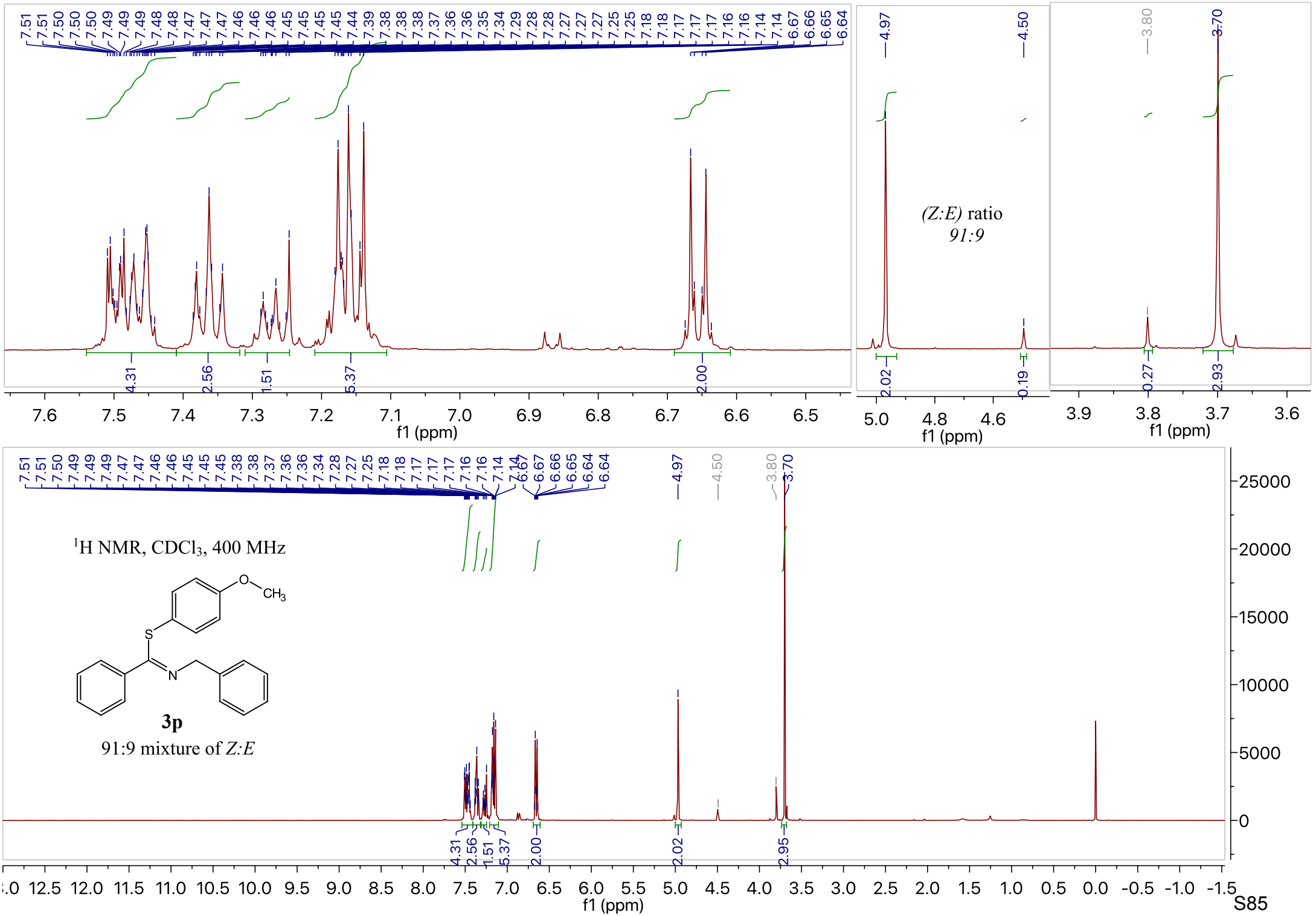

161.96
150.76
139.77
138.28
134.99
132.44
129.29
129.07
128.86
128.40
127.91
127.72
126.75
125.91
58.47
56.78
34.46
31.25
31.11
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3m
92:8 mixture of Z:E

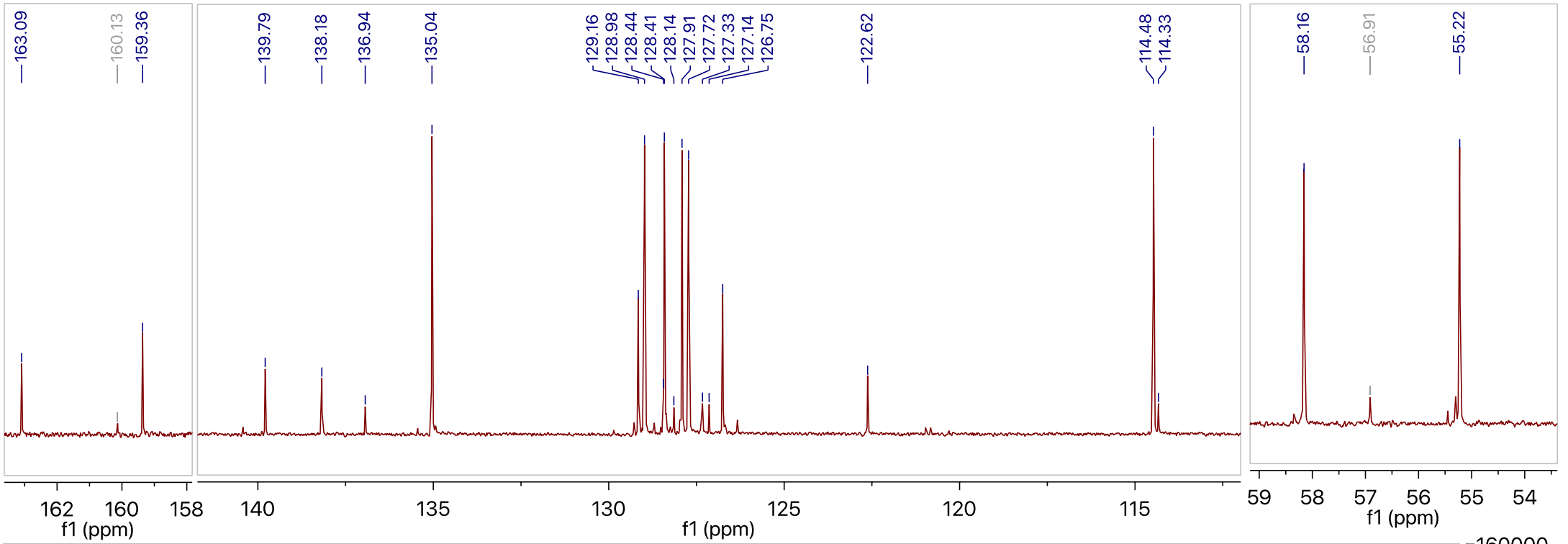

7.53 7.52 7.51 7.50 7.47 7.46 7.45 7.44 7.42 7.40 7.38 7.32 7.30 7.30 7.28 7.26 C 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.16 7.15 7.14 7.13 6.79
1.96 1.95 2.26 0.98 2.91 1.93
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.98 4.50
2.00 0.20
5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)
(Z:E) ratio
91:9
2.50 2.40 2.33 2.19
0.62 5.95 0.34 2.96
2.6 2.5 2.4 2.3 2.2 2.1 2.0
f1 (ppm)
7.53 7.52 7.51 7.50 7.47 7.46 7.45 7.44 7.42 7.40 7.38 7.32 7.30 7.30 7.28 7.26 CDCl3 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.16 7.15 7.14 7.13 6.79 4.98 4.50 2.50 2.40 2.33 2.19
1H NMR, CDCl3, 400 MHz
H3C CH3 S CH3 N
3n
91:9 mixture of Z:E
1.96 1.95 2.26 0.98 2.91 1.93 2.00 0.20 0.62 5.95 0.34 2.96
40000 35000 30000 25000 20000 15000 10000 5000 0 -5000
.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

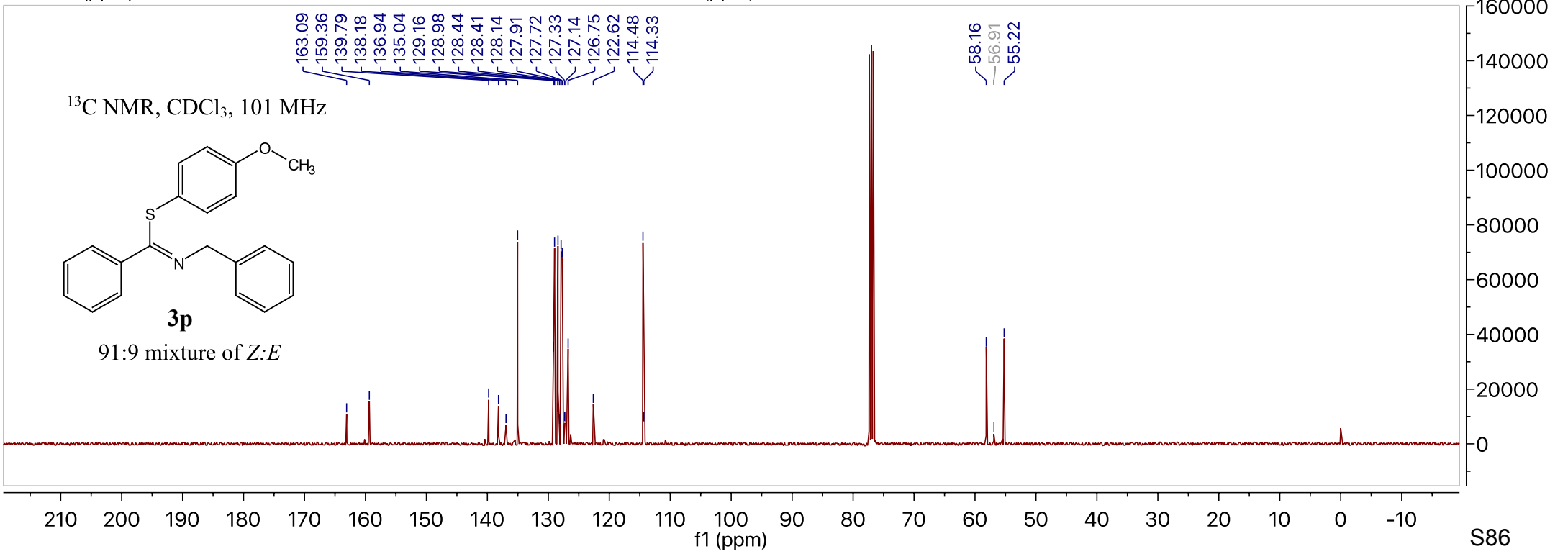

^{13}C NMR, $CDCl_3$, 101 MHz
3n
91:9 mixture of *Z:E*
165.95
163.25
141.43
140.13
138.70
138.51
129.35
129.24
128.51
128.19
128.05
127.60
127.54
126.83
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.94
56.80
22.18
21.04
f1 (ppm)

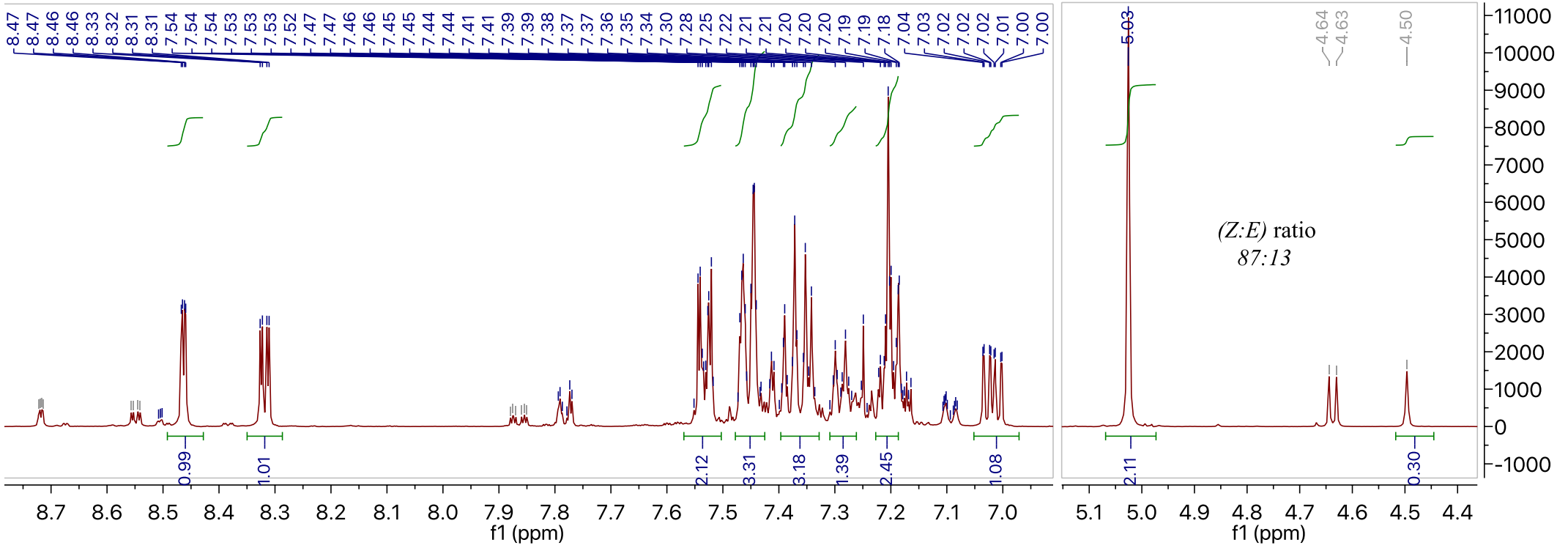

(Z/E)-ratio 86:14
1H NMR, CDCl3, 400 MHz
3o
86:14 mixture of Z:E
f1 (ppm)

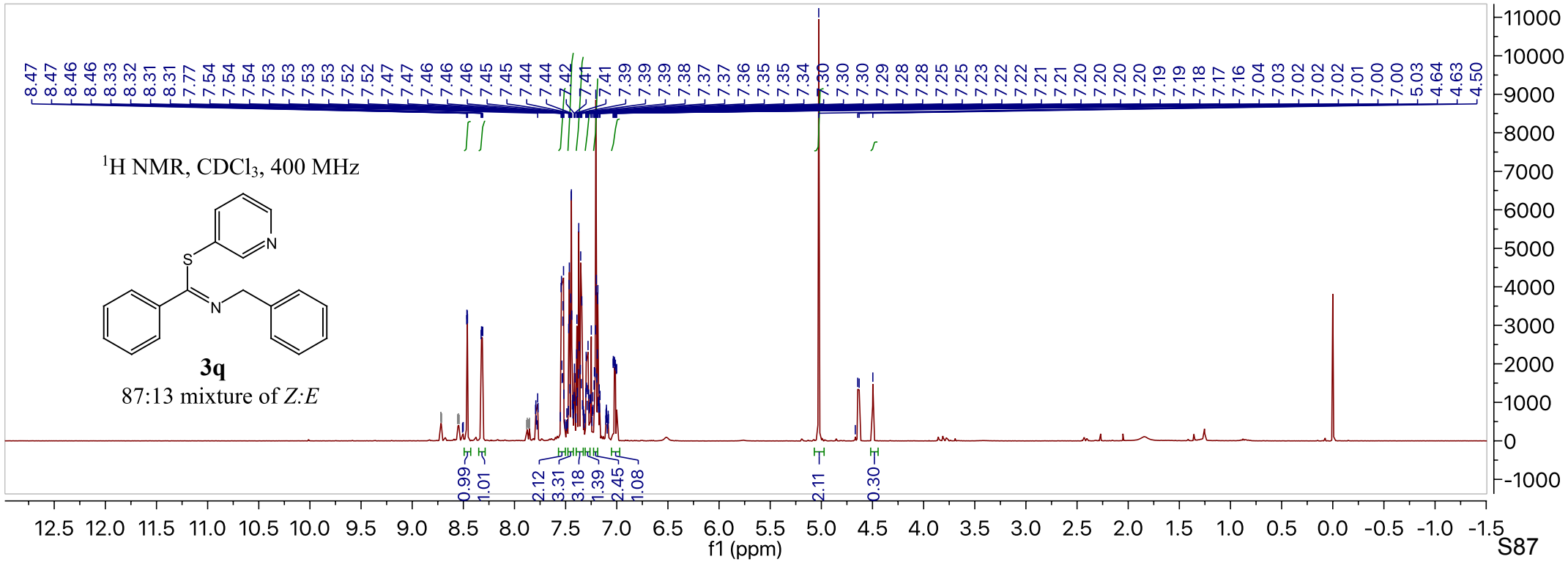

^{13}C NMR, $CDCl_3$, 101 MHz
3o
86:14 mixture of *Z:E*
f1 (ppm)

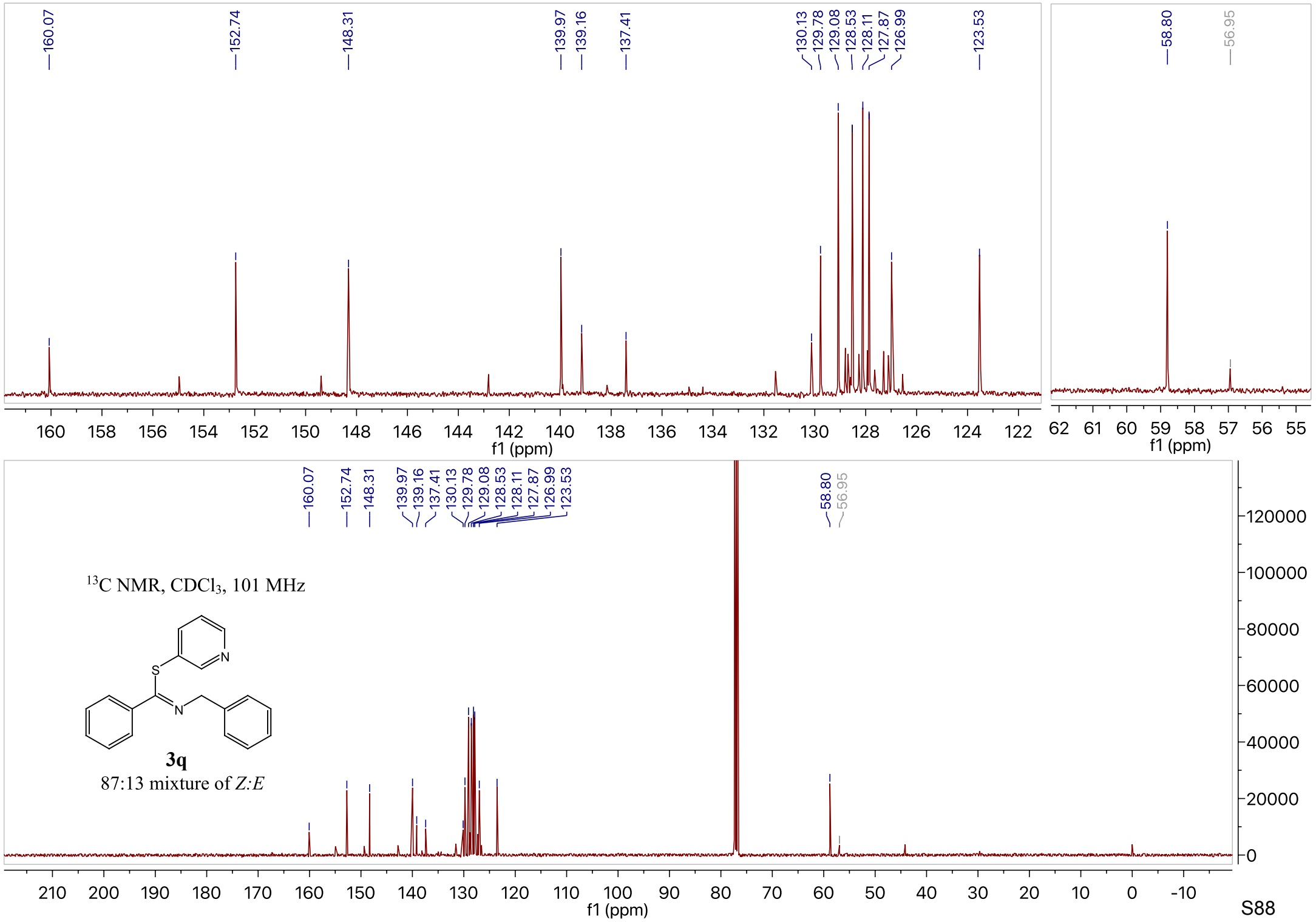

(Z:E) ratio
91:9
1H NMR, CDCl3, 400 MHz
3p
91:9 mixture of Z:E
f1 (ppm)

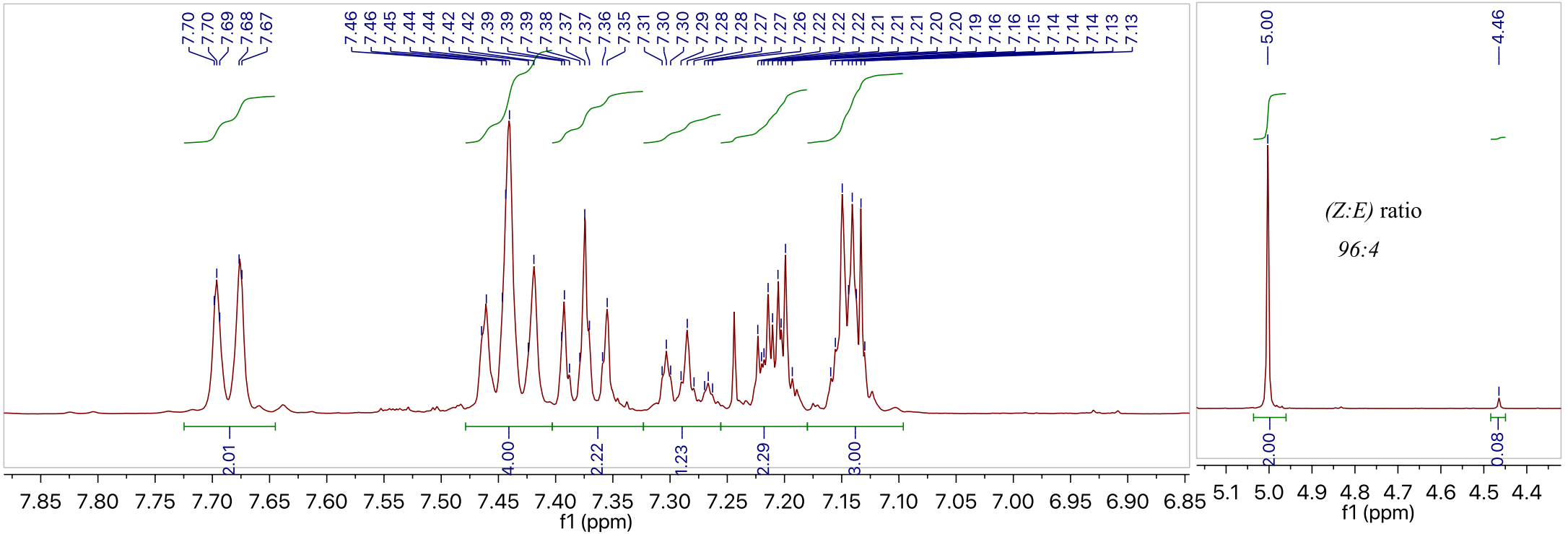

163.09
160.13
159.36
139.79
138.18
136.94
135.04
129.16
128.98
128.44
128.41
128.14
127.91
127.72
127.33
127.14
126.75
122.62
114.48
114.33
58.16
56.91
55.22
f1 (ppm)

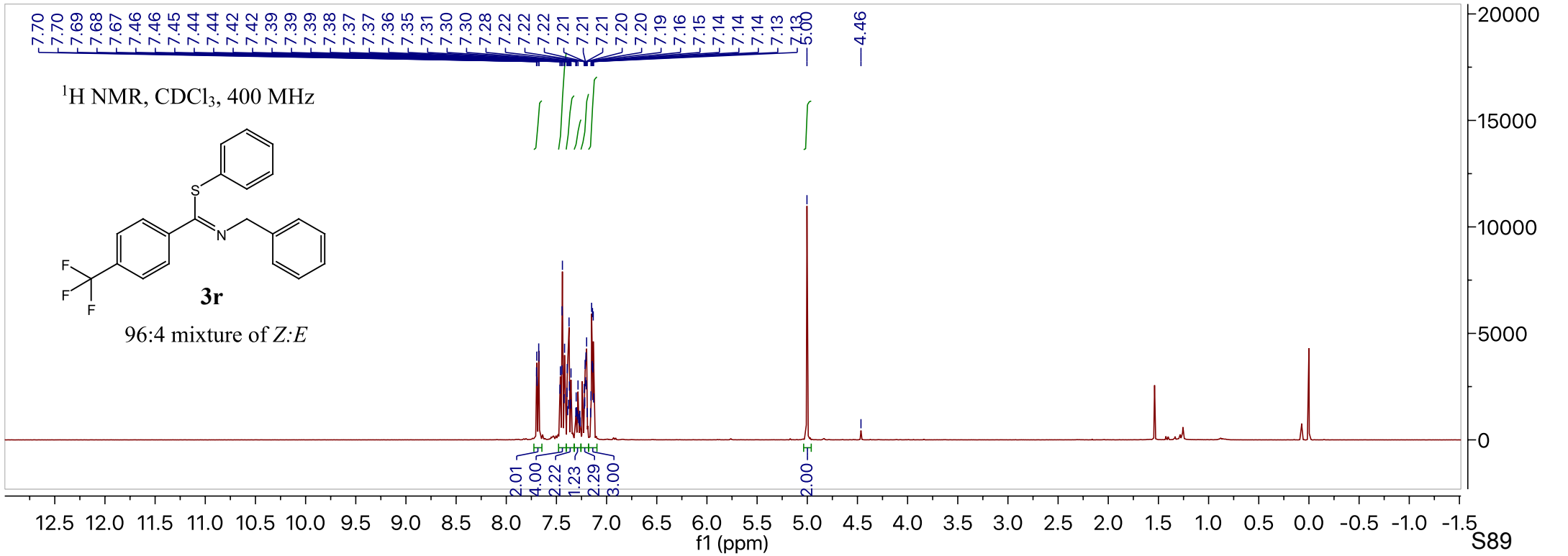

163.09
159.36
139.79
138.18
136.94
135.04
129.16
128.98
128.44
128.41
128.14
127.91
127.72
127.33
127.14
126.75
122.62
114.48
114.33
58.16
56.91
55.22
^{13}C NMR, $CDCl_3$, 101 MHz
O
CH_3
S
N
3p
91:9 mixture of *Z:E*
f1 (ppm)

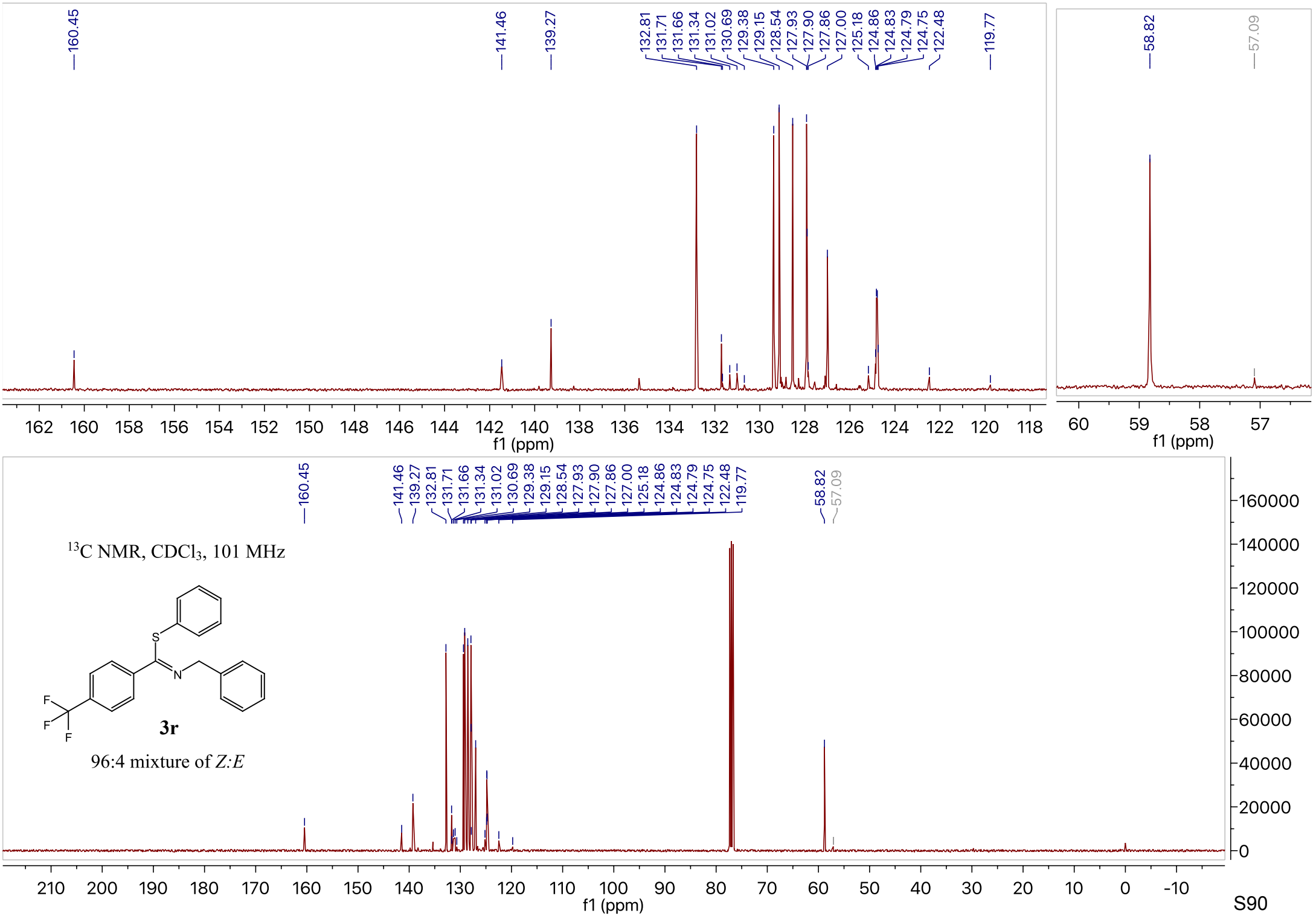

(Z:E) ratio
87:13
f1 (ppm)


^{1}H NMR, $CDCl_3$, 400 MHz
3q
87:13 mixture of Z:E
f1 (ppm)

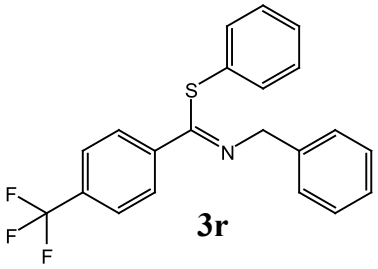

160.07
152.74
148.31
139.97
139.16
137.41
130.13
129.78
129.08
128.53
128.11
127.87
126.99
123.53
58.80
56.95
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3q
87:13 mixture of Z:E


(Z:E) ratio
96:4
f1 (ppm)

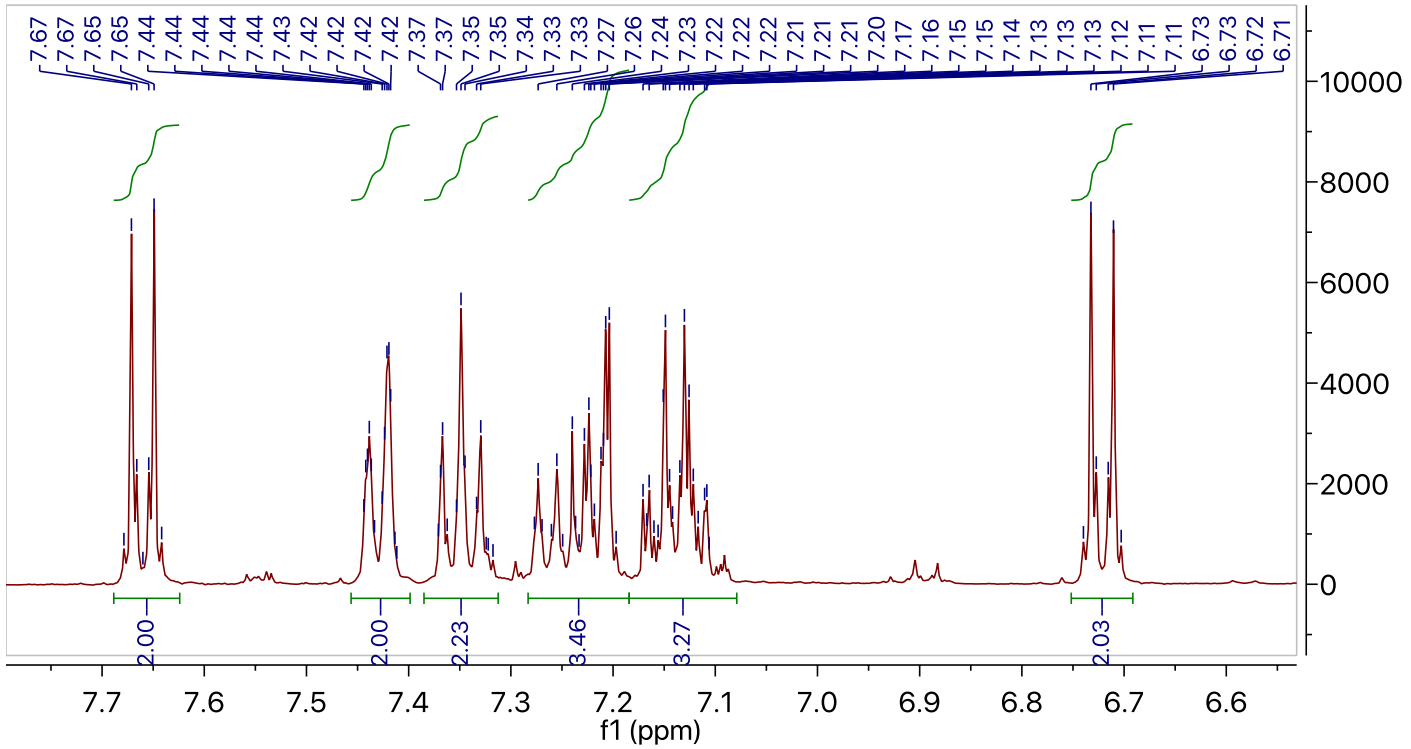

^{1}H NMR, $CDCl_3$, 400 MHz
3r
96:4 mixture of Z:E
f1 (ppm)

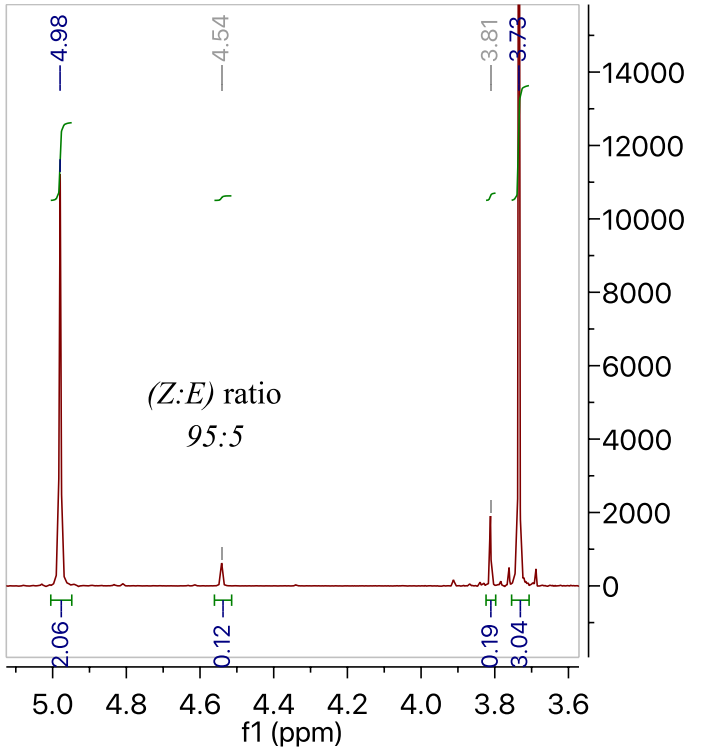

160.45
141.46
139.27
132.81
131.71
131.66
131.34
131.02
130.69
129.38
129.15
128.54
127.93
127.90
127.86
127.00
125.18
124.86
124.83
124.79
124.75
122.48
119.77
58.82
57.09
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3r
96:4 mixture of *Z*:*E*

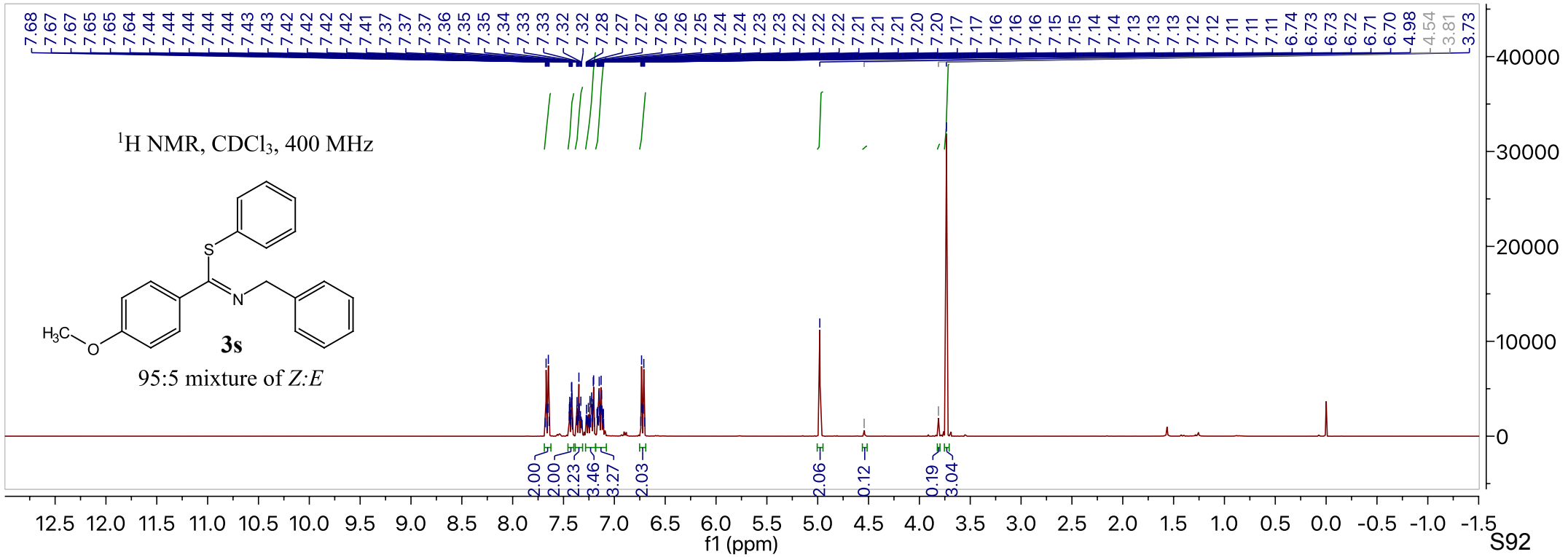
^{19}F NMR (376 MHz, $CDCl_3$)

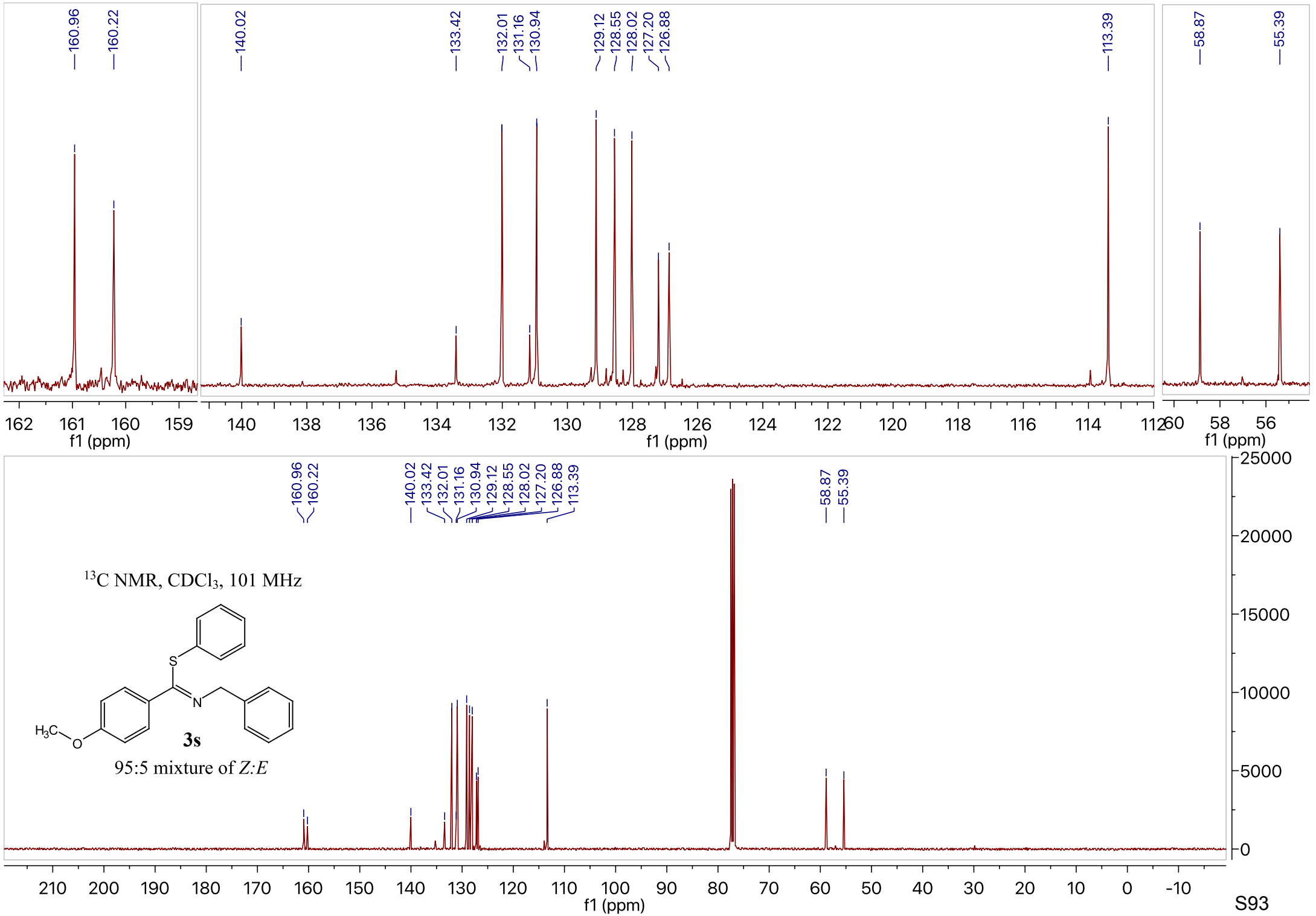


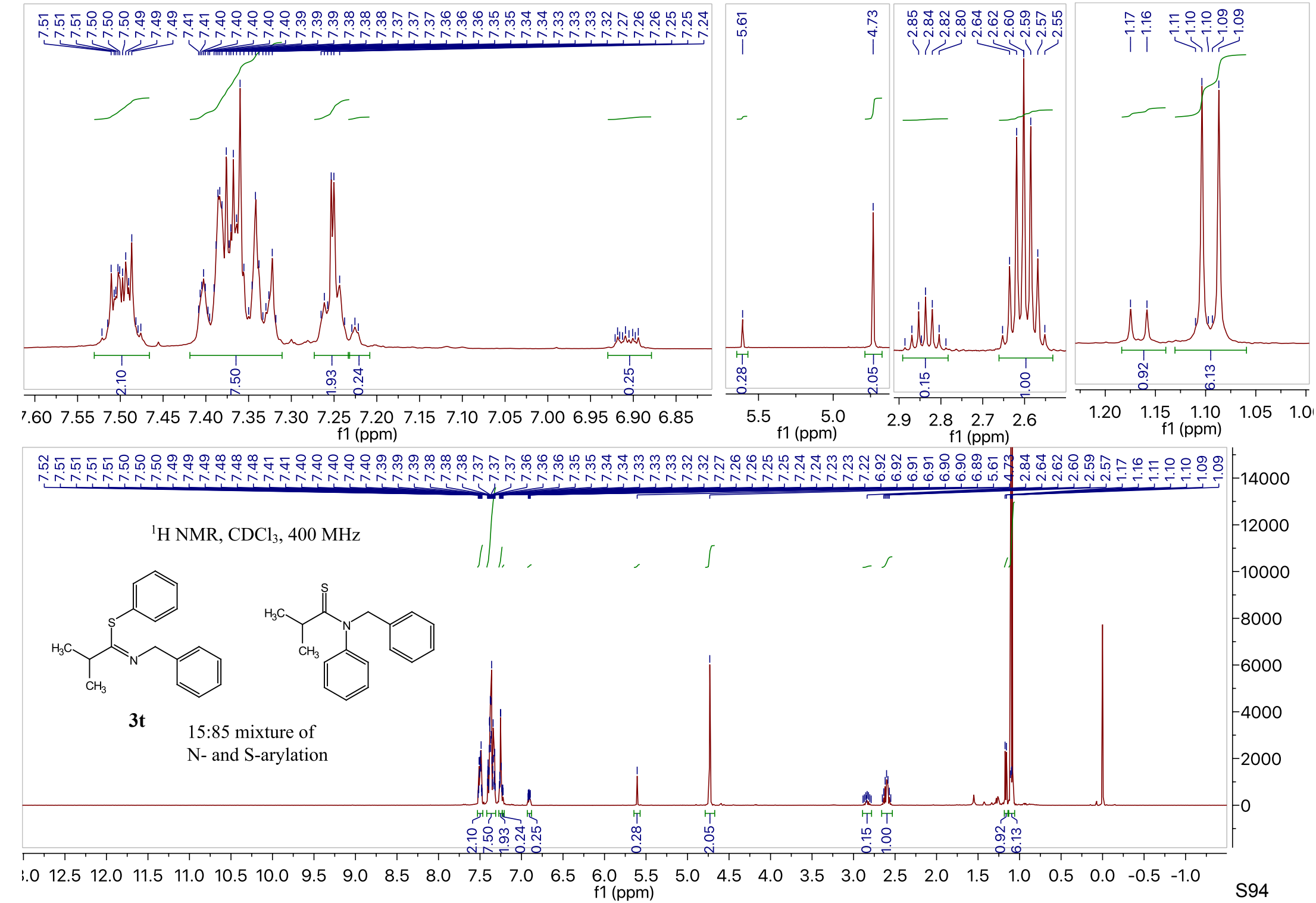
3r

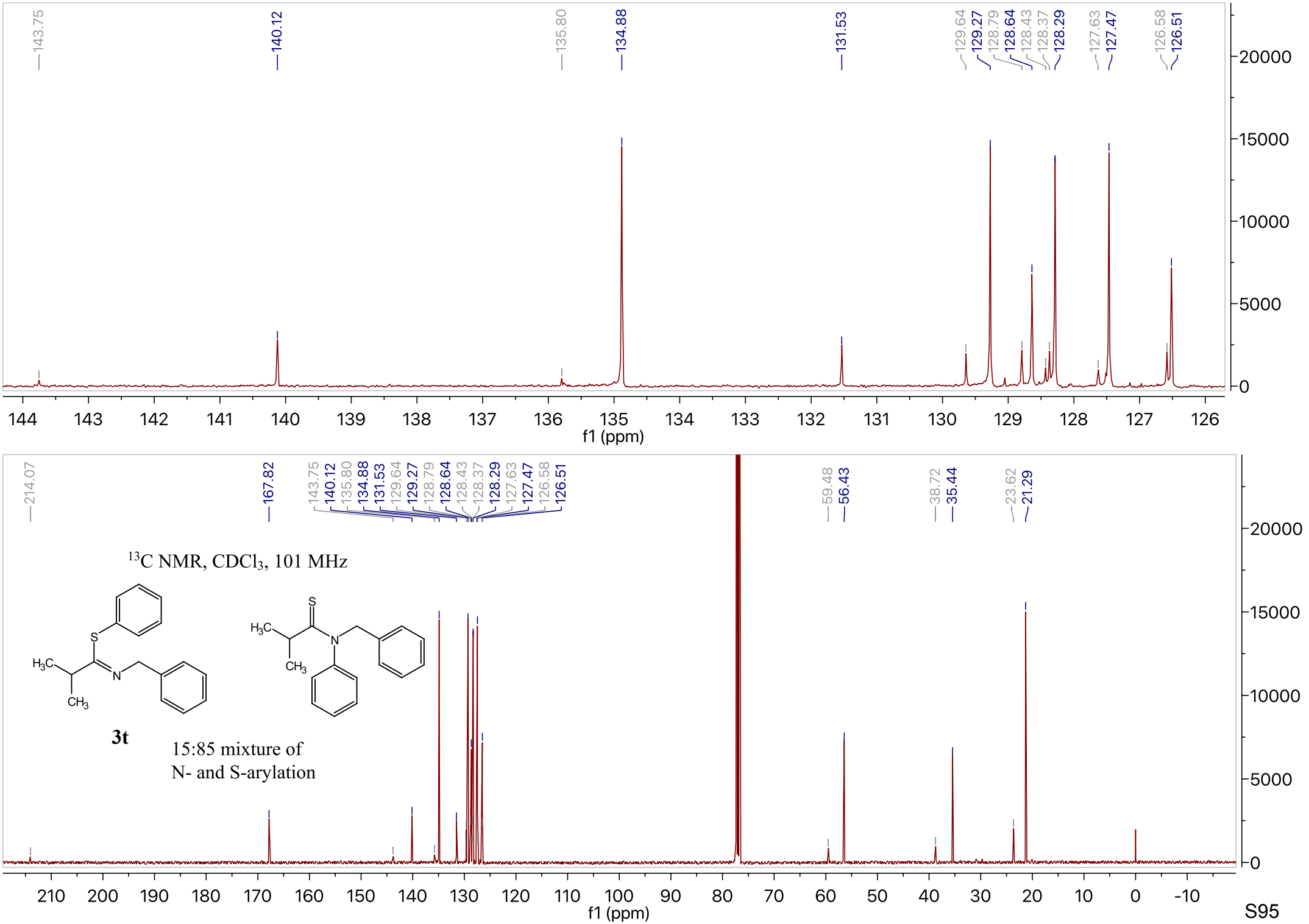

f1 (ppm)

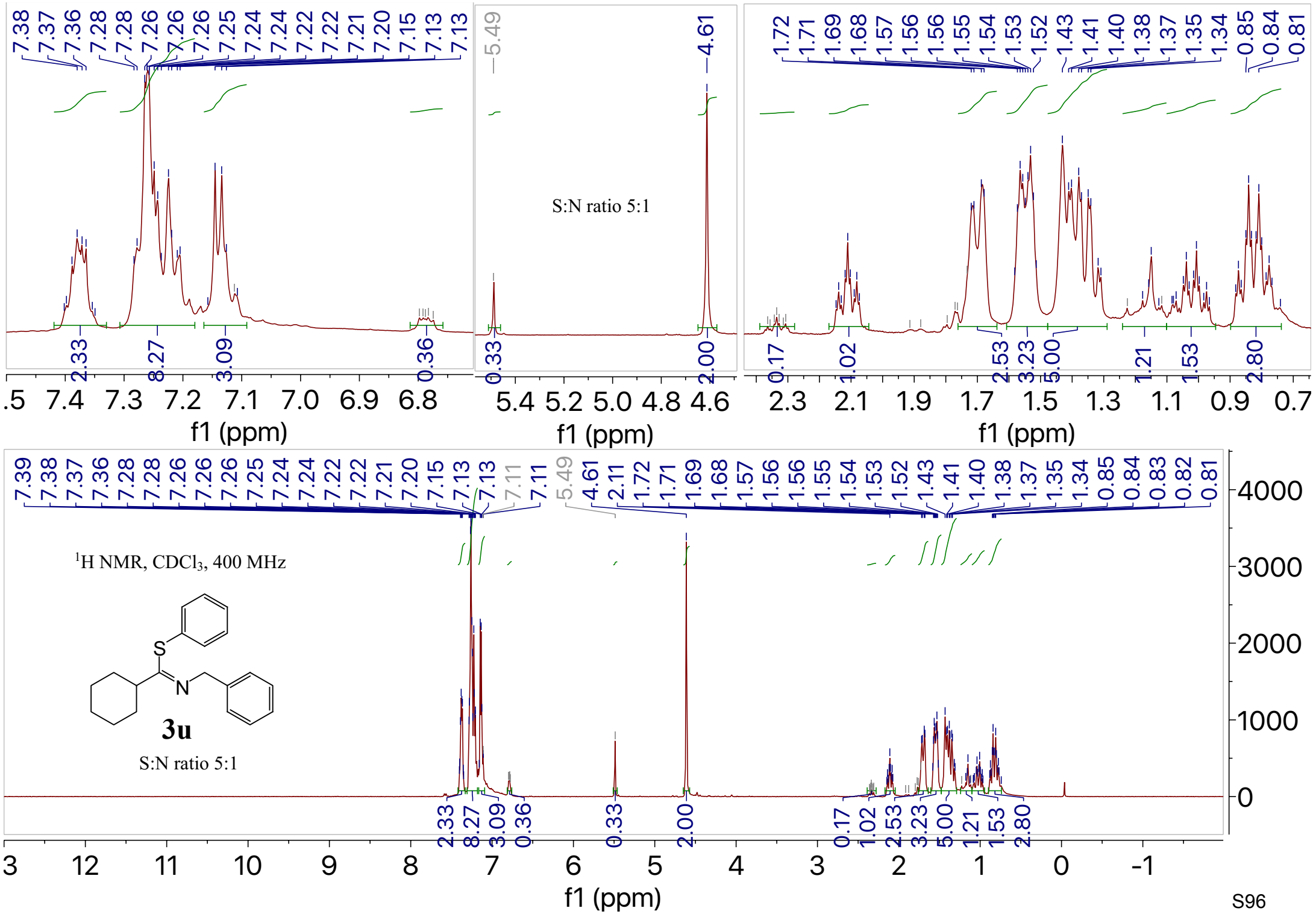

(Z:E) ratio
95:5
f1 (ppm)

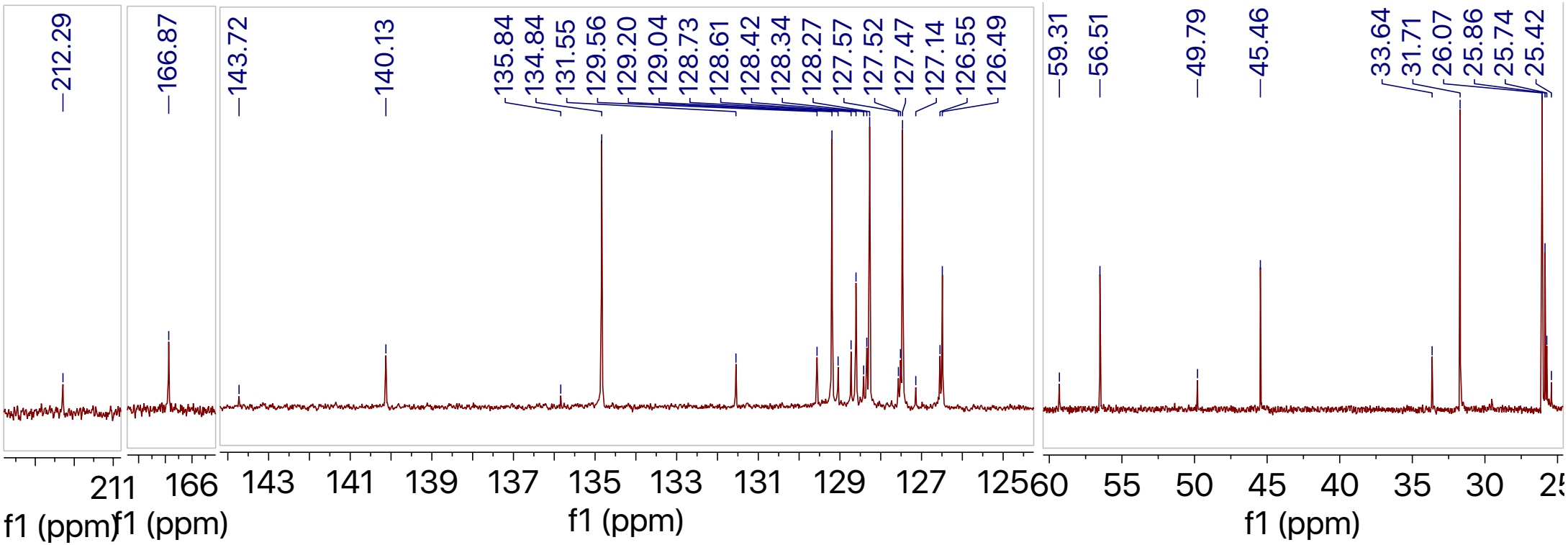

1H NMR, CDCl3, 400 MHz
3s
95:5 mixture of Z:E
f1 (ppm)

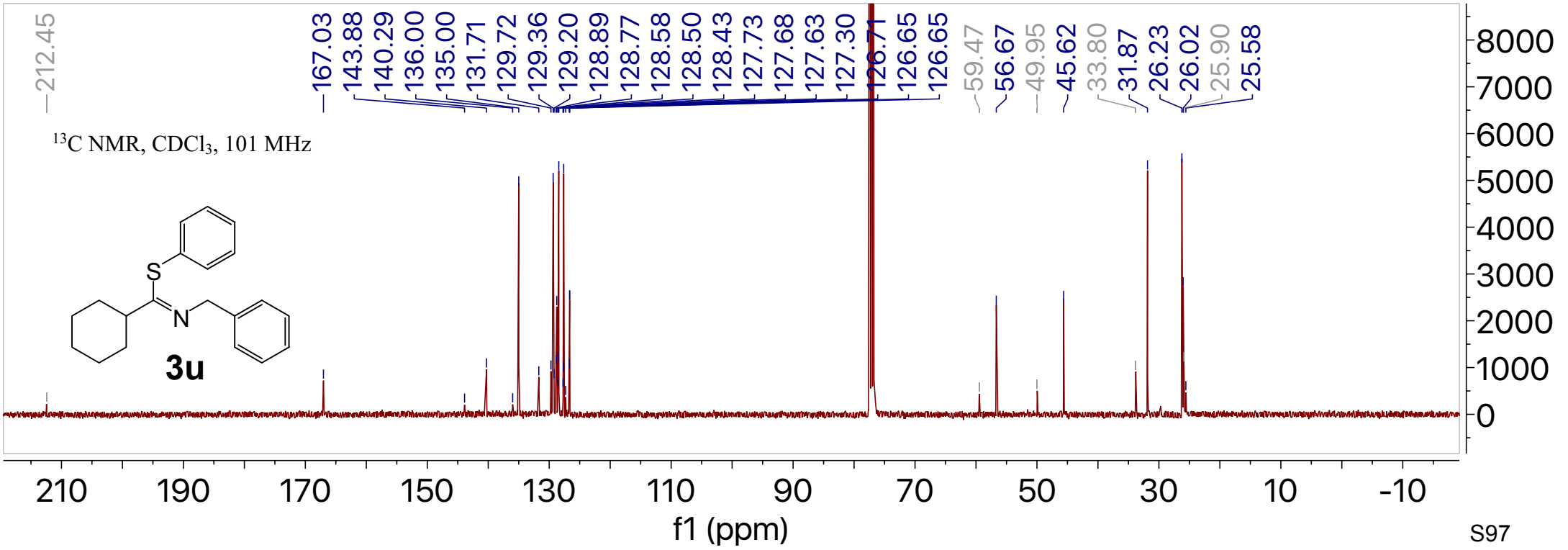

160.96
160.22
140.02
133.42
132.01
131.16
130.94
129.12
128.55
128.02
127.20
126.88
113.39
58.87
55.39
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3s
95:5 mixture of *Z:E*

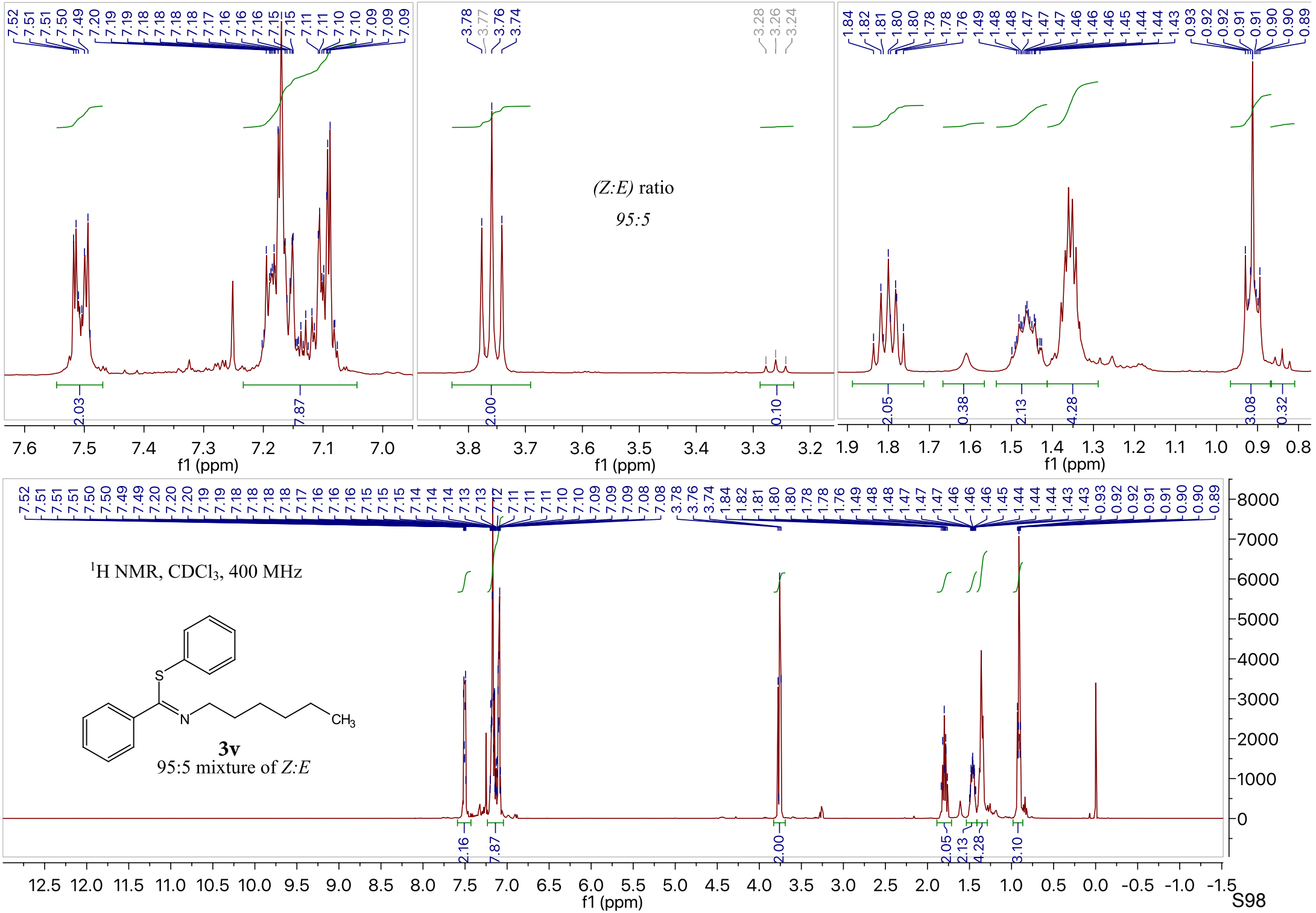

^{1}H NMR, $CDCl_3$, 400 MHz
3t
15:85 mixture of
N- and S-arylation
f1 (ppm)

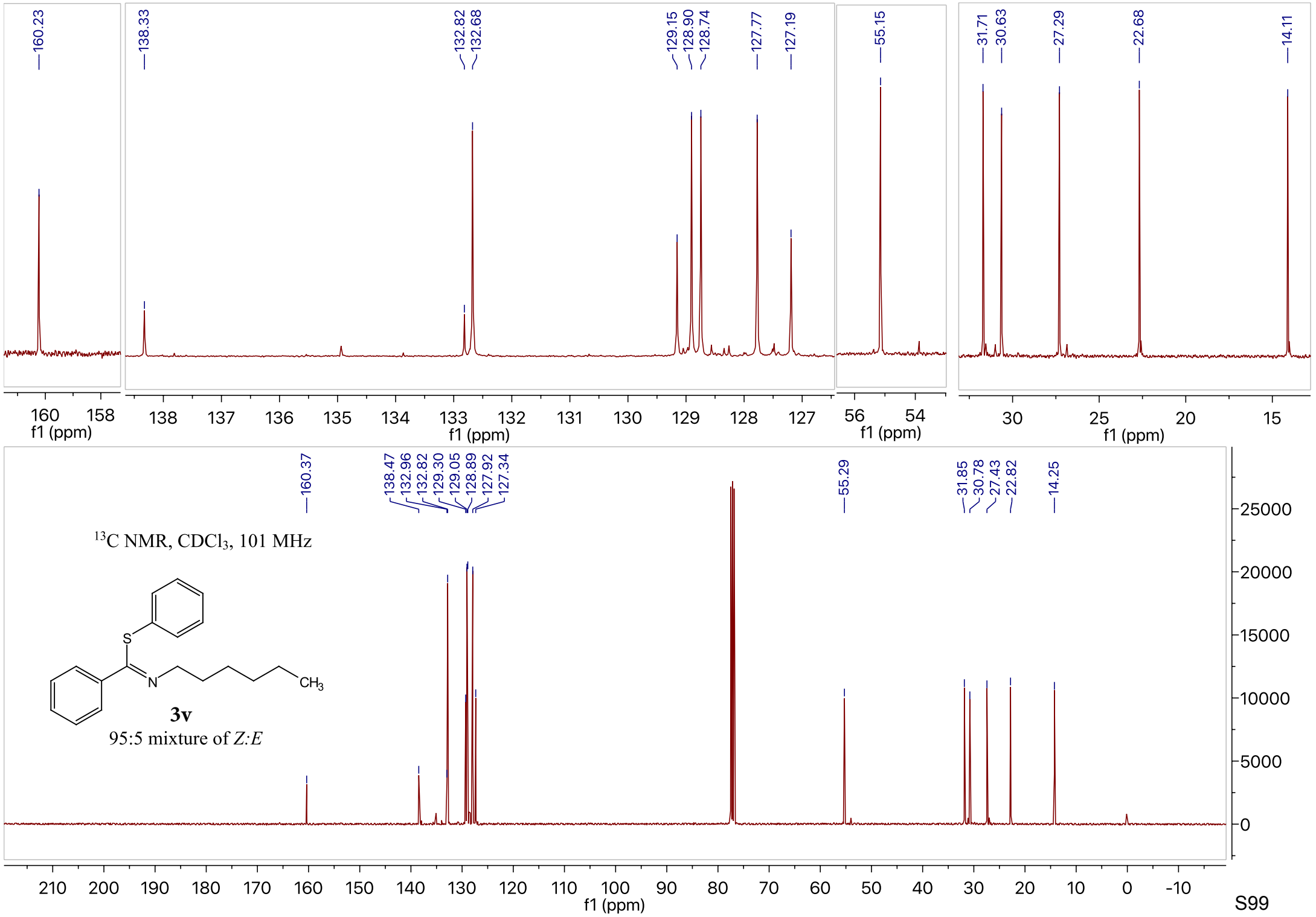

143.75
140.12
135.80
134.88
131.53
129.64
129.27
128.79
128.64
128.43
128.37
128.29
127.63
127.47
126.58
126.51
20000
15000
10000
5000
0
144
143
142
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
f1 (ppm)
214.07
167.82
59.48
56.43
38.72
35.44
23.62
21.29
^{13}C NMR, $CDCl_3$, 101 MHz
3t
15:85 mixture of
N- and S-arylation
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

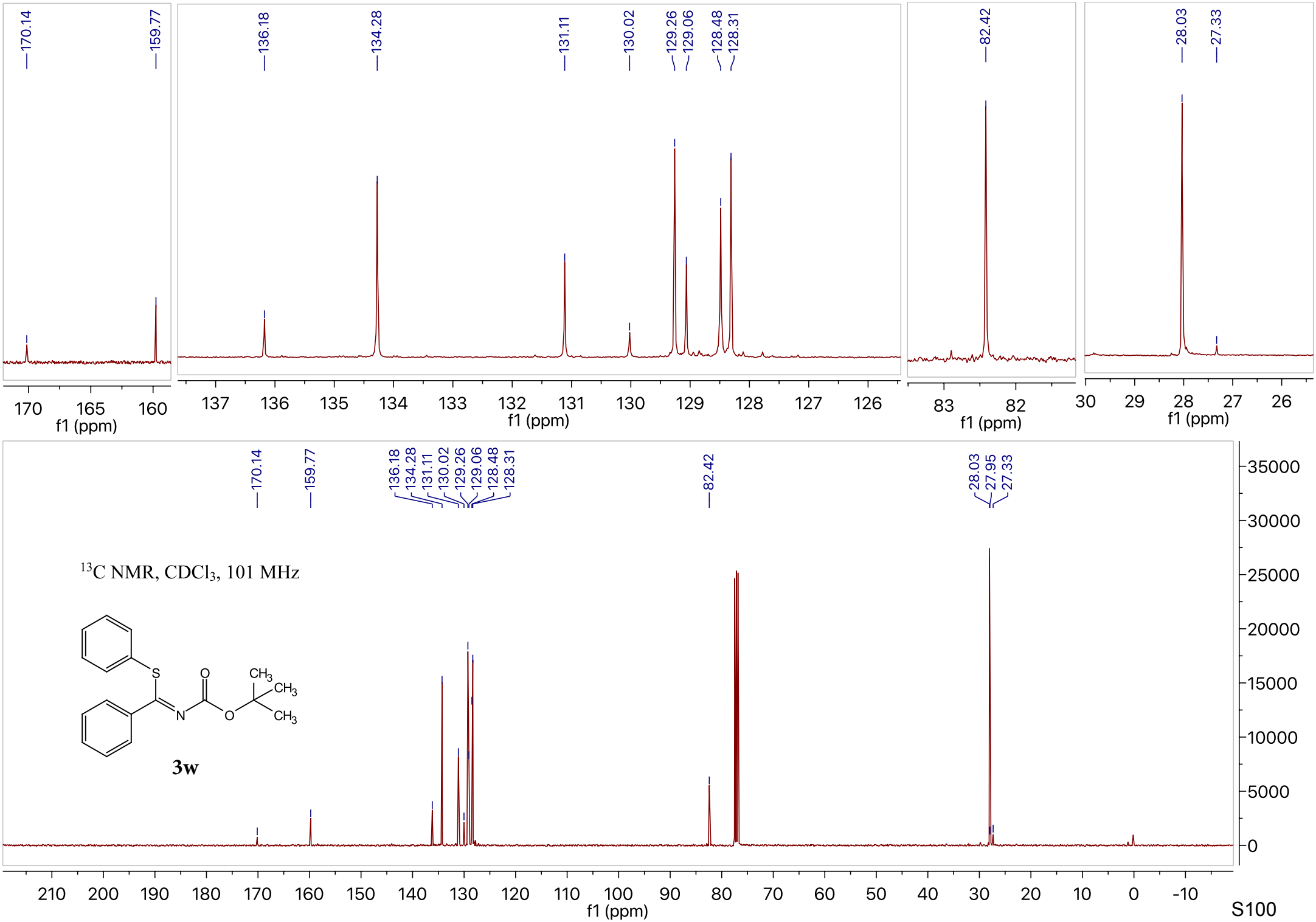

S:N ratio 5:1
f1 (ppm)
f1 (ppm)
f1 (ppm)
^{1}H NMR, $CDCl_3$, 400 MHz
3u
S:N ratio 5:1
f1 (ppm)

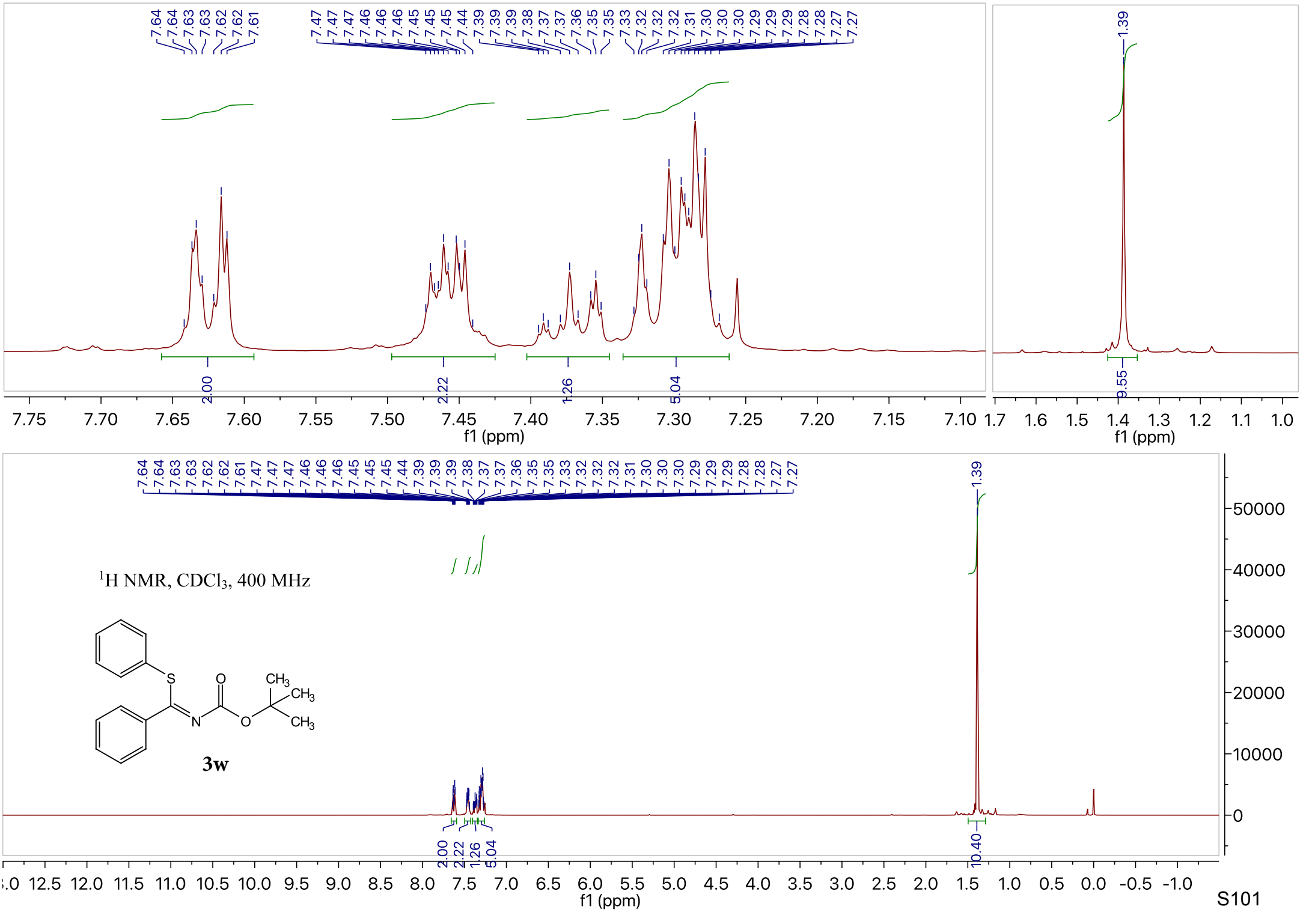

212.29
166.87
143.72
140.13
135.84
134.84
131.55
129.56
129.20
129.04
128.73
128.61
128.42
128.34
128.27
127.57
127.52
127.47
127.14
126.55
126.49
59.31
56.51
49.79
45.46
33.64
31.71
26.07
25.86
25.74
25.42
f1 (ppm)

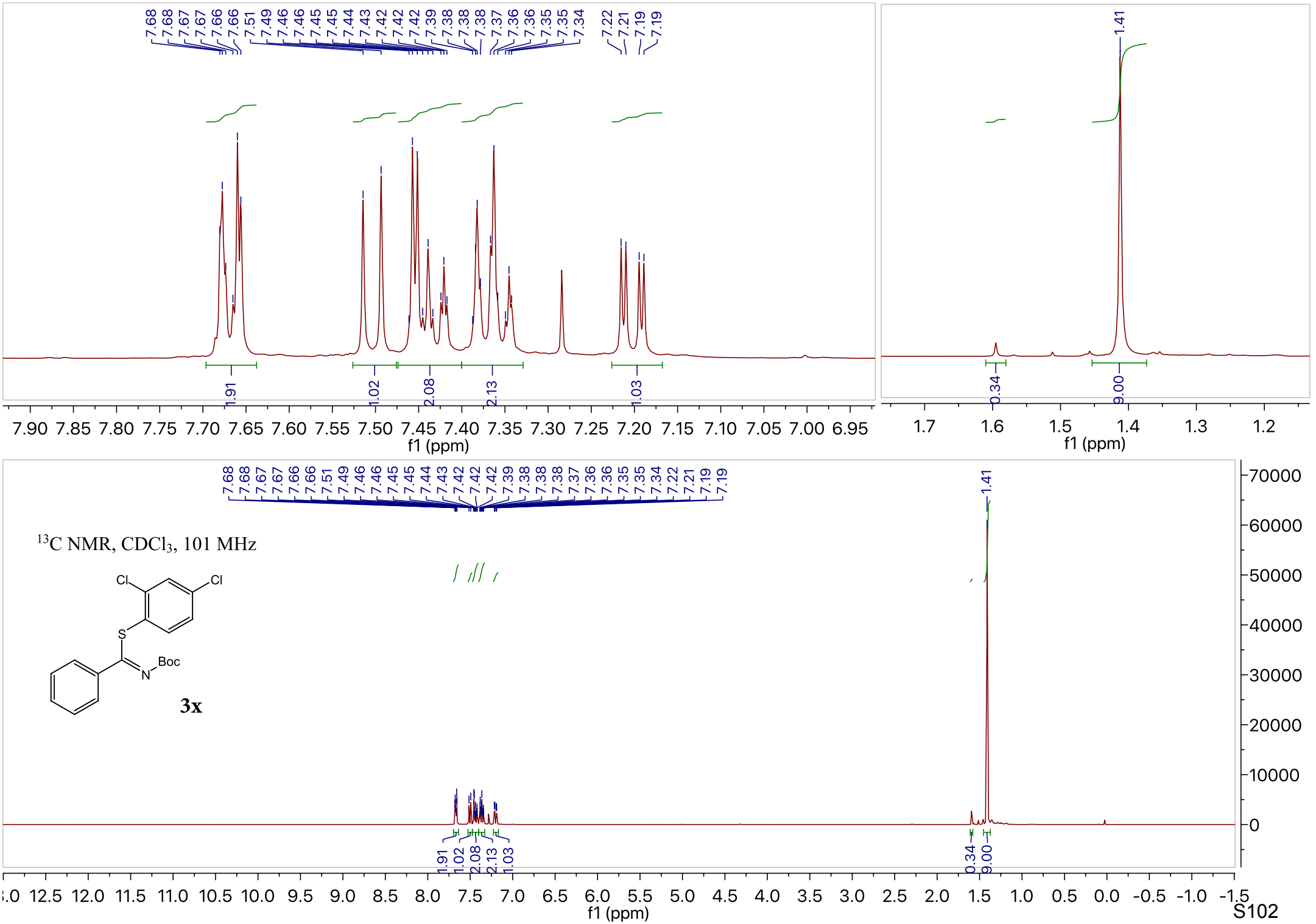

212.45
167.03
143.88
140.29
136.00
135.00
131.71
129.72
129.36
129.20
128.89
128.77
128.58
128.50
128.43
127.73
127.68
127.63
127.30
126.71
126.65
126.65
59.47
56.67
49.95
45.62
33.80
31.87
26.23
26.02
25.90
25.58
13C NMR, CDCl3, 101 MHz
S
N
3u
f1 (ppm)

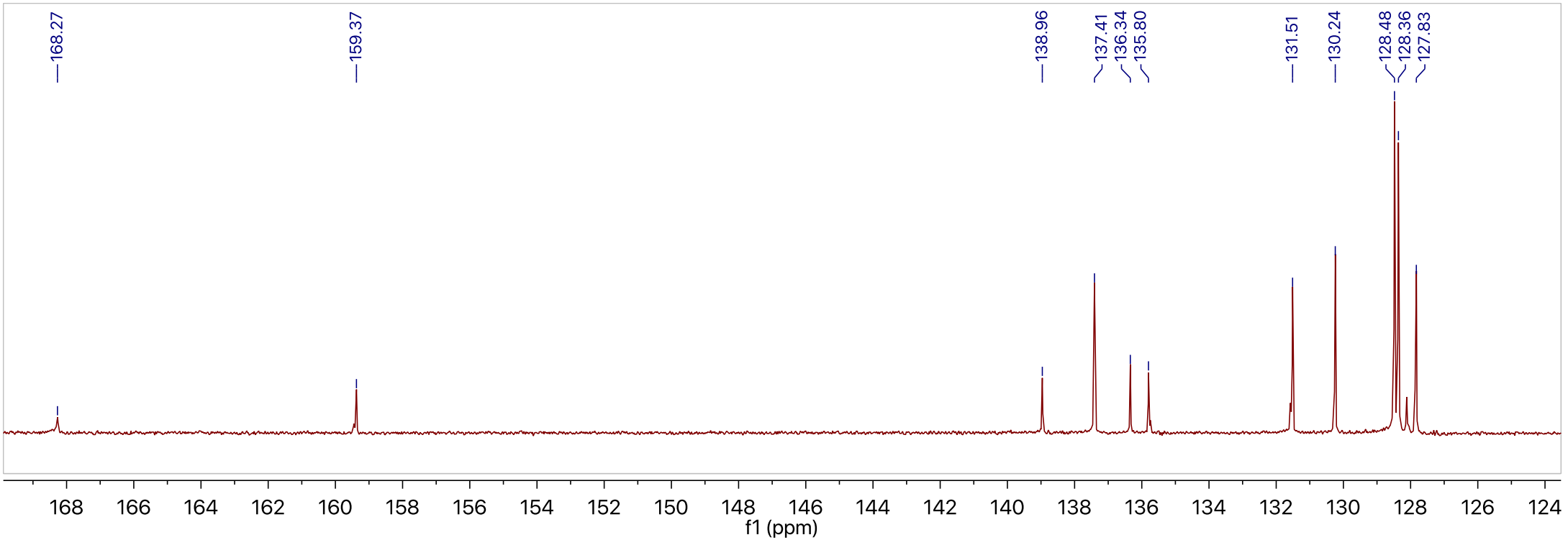

(Z:E) ratio
95:5
1H NMR, CDCl3, 400 MHz
S
N
CH3
3v
95:5 mixture of Z:E
f1 (ppm)

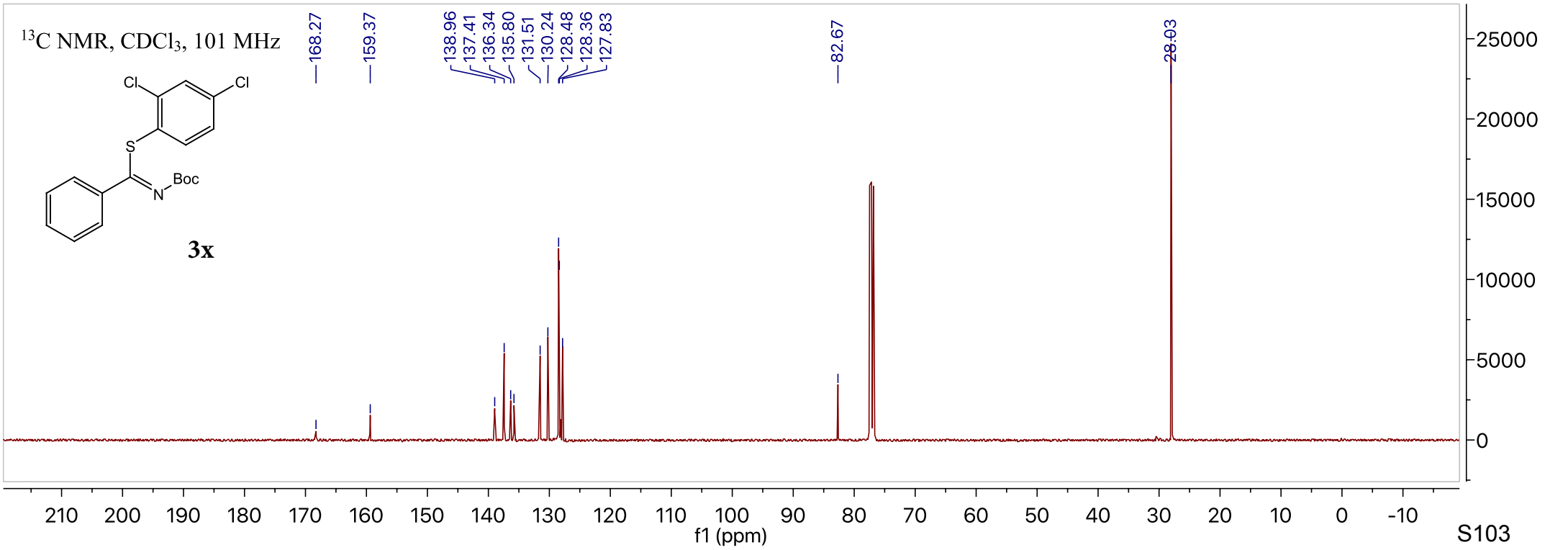

160.23
138.33
132.82
132.68
129.15
128.90
128.74
127.77
127.19
55.15
31.71
30.63
27.29
22.68
14.11
f1 (ppm)
160.37
138.47
132.96
132.82
129.30
129.05
128.89
127.92
127.34
55.29
31.85
30.78
27.43
22.82
14.25
^{13}C NMR, $CDCl_3$, 101 MHz
S
N
CH_3
3v
95:5 mixture of *Z:E*
25000
20000
15000
10000
5000
0
f1 (ppm)

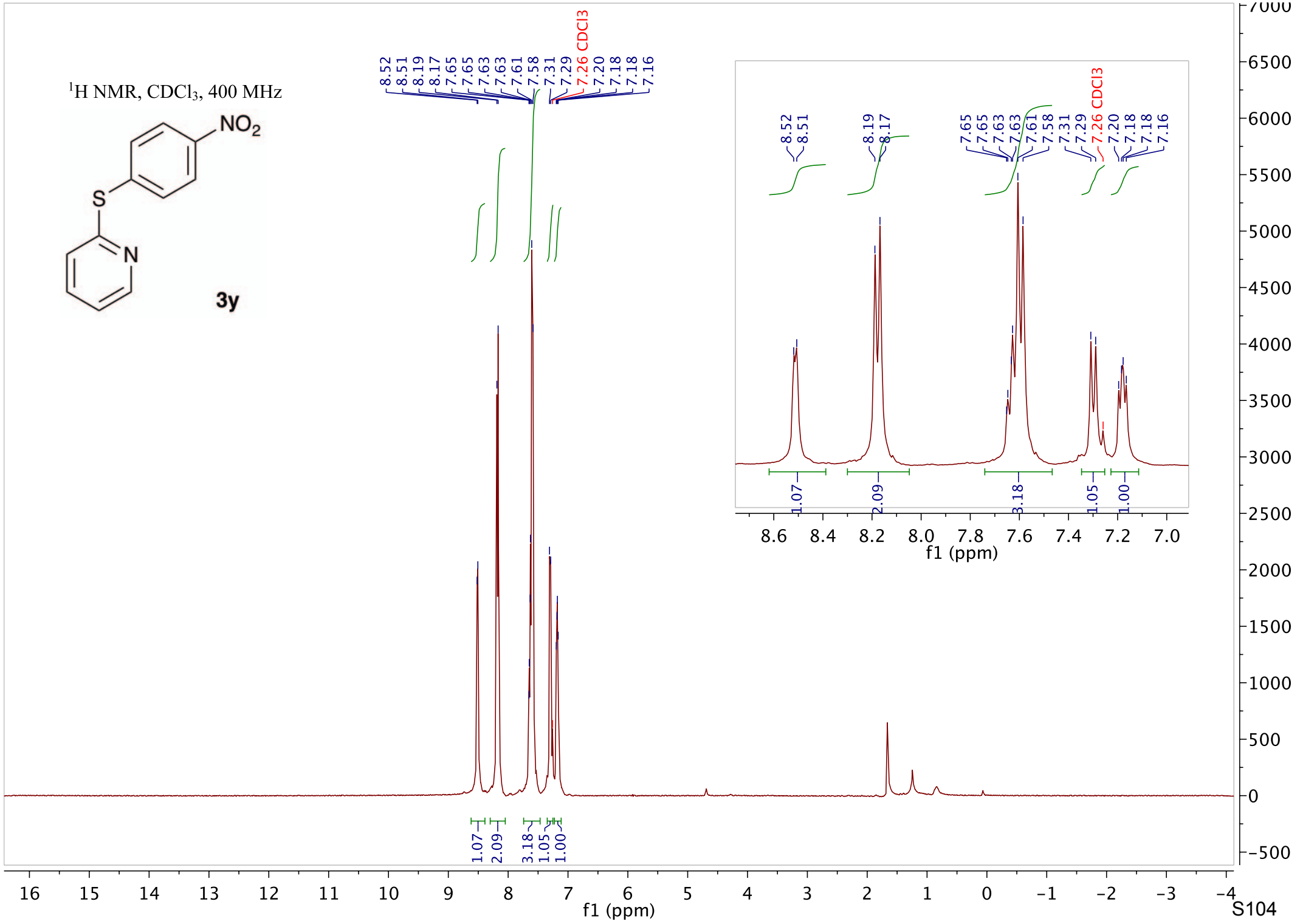

170.14
159.77
136.18
134.28
131.11
130.02
129.26
129.06
128.48
128.31
82.42
28.03
27.95
27.33
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
3w
S100


^{1}H NMR, $CDCl_3$, 400 MHz
3w
f1 (ppm)

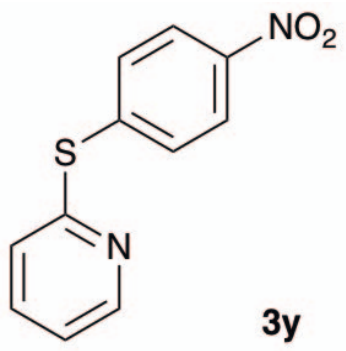

7.68 7.68 7.67 7.67 7.66 7.66 7.51 7.49 7.46 7.46 7.45 7.45 7.44 7.43 7.42 7.42 7.42 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.22 7.21 7.19 7.19
1.91 1.02 2.08 2.13 1.03
7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)
1.41
0.34 9.00
1.7 1.6 1.5 1.4 1.3 1.2
f1 (ppm)
^{13}C NMR, $CDCl_3$, 101 MHz
Cl
Cl
S
N
Boc
3x
70000 60000 50000 40000 30000 20000 10000 0
1.91 1.02 2.08 2.13 1.03
0.34 9.00
f1 (ppm)


168.27
159.37
138.96
137.41
136.34
135.80
131.51
130.24
128.48
128.36
127.83
168
166
164
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
f1 (ppm)


^{13}C NMR, CDCl$_3$, 101 MHz
Cl
Cl
S
N
Boc
3x
168.27
159.37
138.96
137.41
136.34
135.80
131.51
130.24
128.48
128.36
127.83
82.67
28.03
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


^{1}H NMR, $CDCl_3$, 400 MHz
NO_2
S
N
3y
8.52
8.51
8.19
8.17
7.65
7.65
7.63
7.63
7.61
7.58
7.31
7.29
7.26 CDCl3
7.20
7.18
7.18
7.16
1.07
2.09
3.18
1.05
1.00
f1 (ppm)
S104

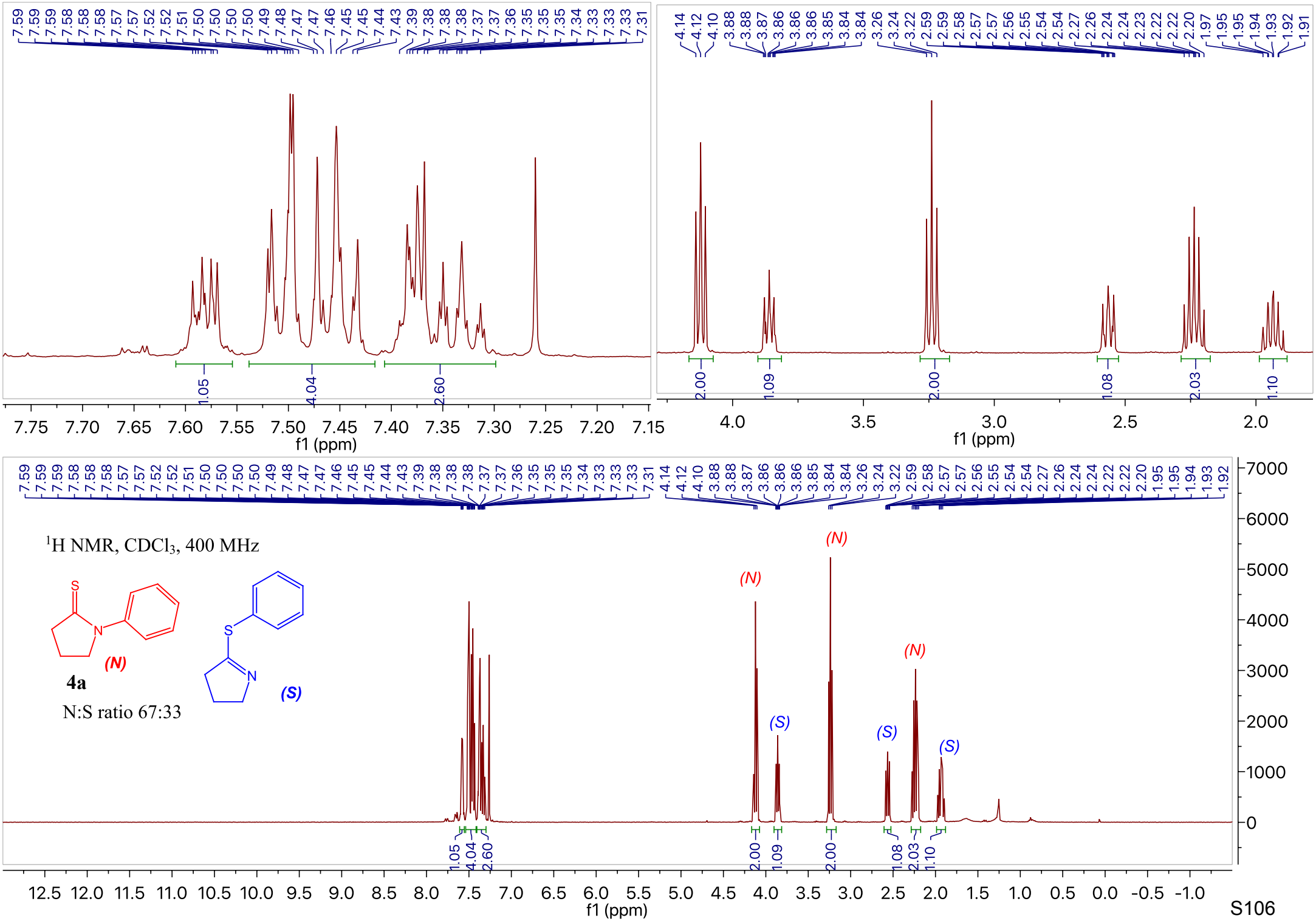
^{13}C NMR, $CDCl_3$, 101 MHz

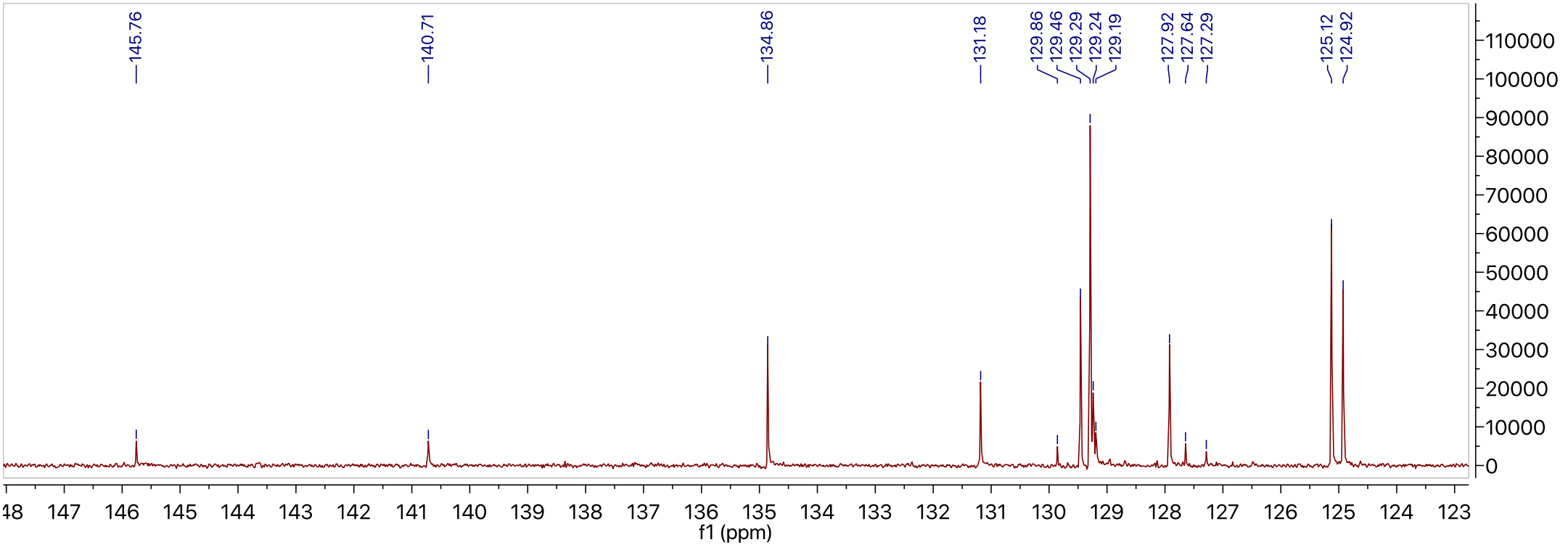


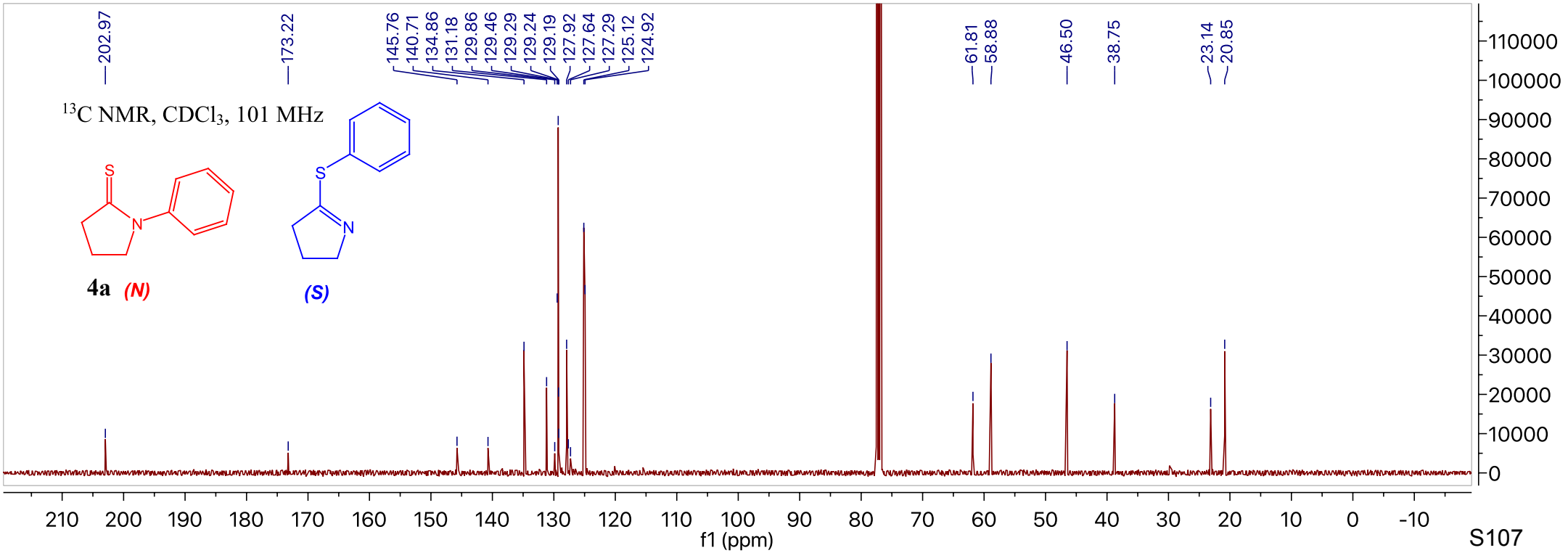
3y

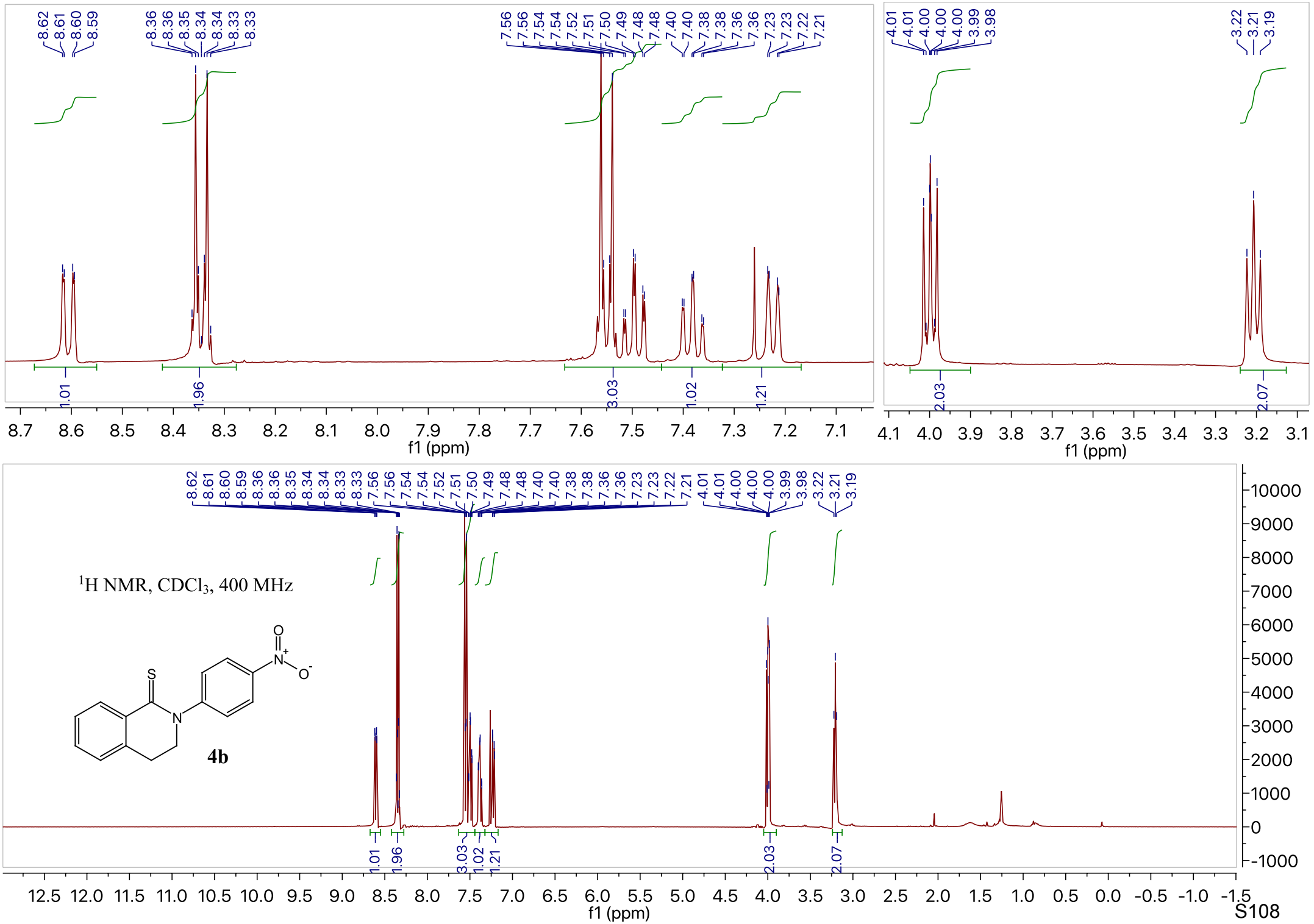
156.55
150.40
146.94
142.34
137.31
131.84
124.82
124.09
121.96
77.32 CDCl3
77.20
77.00 CDCl3
76.68 CDCl3

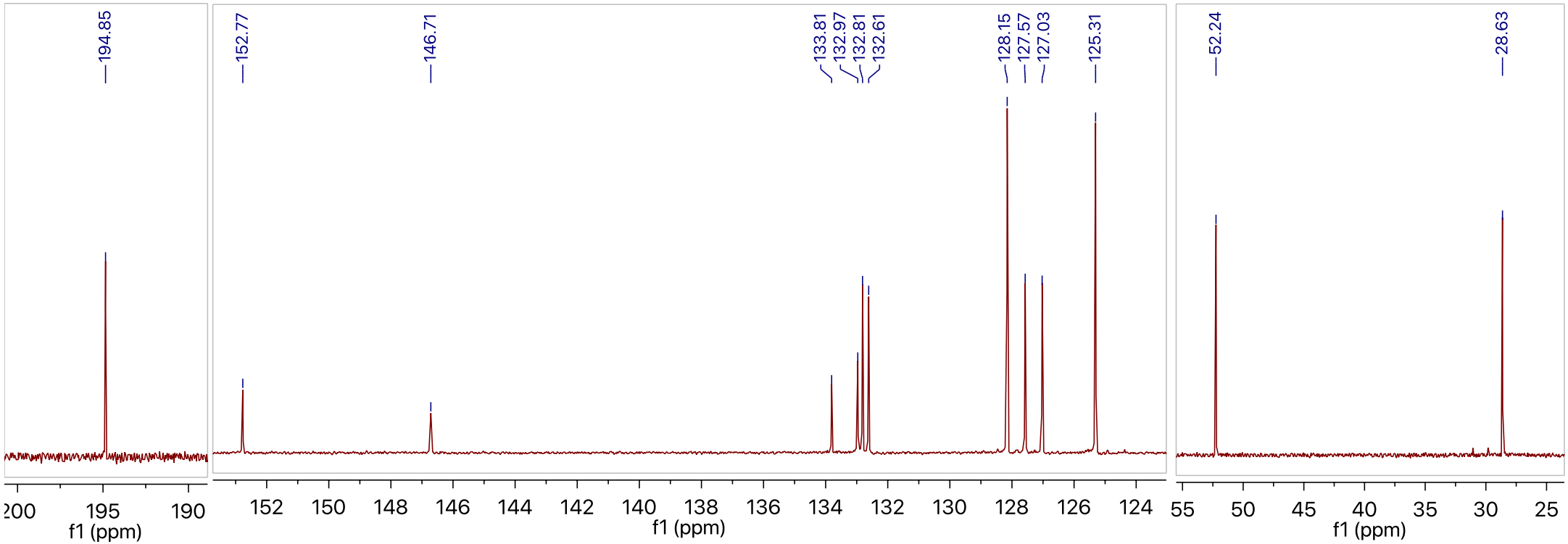
f1 (ppm)

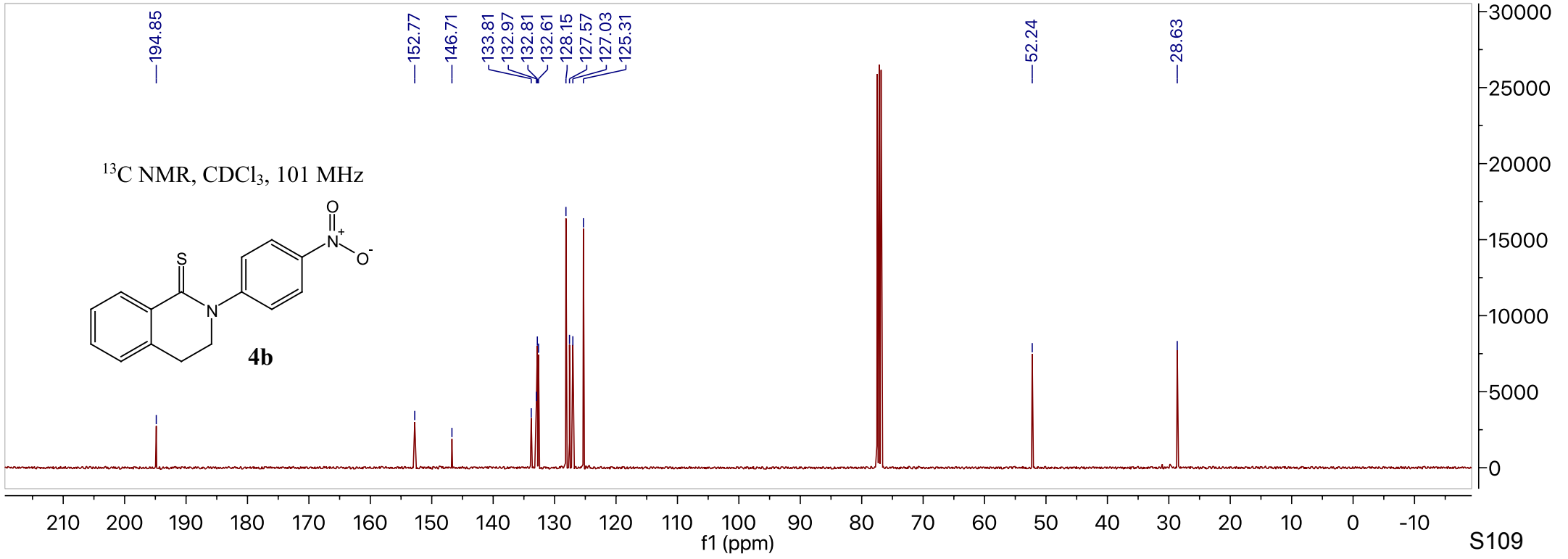

^{1}H NMR, $CDCl_3$, 400 MHz
(N)
4a
N:S ratio 67:33
(S)
f1 (ppm)


145.76
140.71
134.86
131.18
129.86
129.46
129.29
129.24
129.19
127.92
127.64
127.29
125.12
124.92
f1 (ppm)


202.97
173.22
145.76
140.71
134.86
131.18
129.86
129.46
129.29
129.24
129.19
127.92
127.64
127.29
125.12
124.92
61.81
58.88
46.50
38.75
23.14
20.85
13C NMR, CDCl3, 101 MHz
4a (N)
(S)
f1 (ppm)


8.62 8.61 8.60 8.59 8.36 8.36 8.35 8.34 8.34 8.33 8.33 7.56 7.56 7.54 7.54 7.52 7.51 7.50 7.49 7.48 7.48 7.40 7.40 7.38 7.38 7.36 7.36 7.23 7.23 7.22 7.21
4.01 4.01 4.00 4.00 4.00 3.99 3.98 3.22 3.21 3.19
1.01 1.96 3.03 1.02 1.21 2.03 2.07
f1 (ppm)
^{1}H NMR, $CDCl_3$, 400 MHz
4b
S108


194.85
152.77
146.71
133.81
132.97
132.81
132.61
128.15
127.57
127.03
125.31
52.24
28.63
f1 (ppm)


194.85
152.77
146.71
133.81
132.97
132.81
132.61
128.15
127.57
127.03
125.31
52.24
28.63
^{13}C NMR, $CDCl_3$, 101 MHz
4b
f1 (ppm)