100% Atom-economical and highly regio- and stereoselective iodosulfenylation of alkynes: A reagentless and sustainable approach to access (*E*)-β-iodoalkenyl sulfides and (*Z*)-tamoxifen

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Supporting Information

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1. General consideration

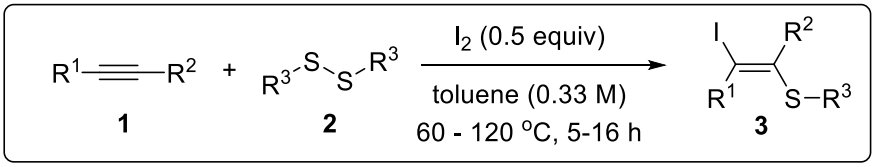
1.1 General reagent information

All reagents were purchased from BLD pharma, TCI chemicals, Sigma-Aldrich, AVRA, and SRL chemicals, solvents were purchased from Finar chemicals. Flash chromatography was performed using silica gel (100-200 mash)

1.2 General analytical information

The products were characterized by ^{1}H, ^{13}C NMR spectra which were recorded on a Bruker 400 MHz instrument (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Copies of ^{1}H, ^{13}C, NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.00 ppm) and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. Reactions were monitored by thin layer chromatography (TLC) and ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. Mass spectral data were obtained on a high resolution mass spectrometer, Agilent MassHunter Qualitative Analysis B.06.00 and also in LCMS-8040 (Shimadzu), HPLC (Shimadzu). Melting points of unknown compounds were recorded on a KRUSS Optronic M3000 apparatus. Single Crystal X-ray data were recorded on Rigaku Oxford Diffraction (XtalLab).

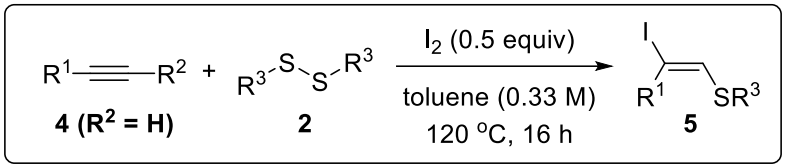
2. Experimental procedure for the synthesis of tetrasubstituted (*E*)-*β*-iodoalkenyl sulfides (3aa – 3da)



Representative experimental procedure for the synthesis of (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane (3aa): 1,2-diphenylethyne **1a** (0.0891 g, 0.5 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (0.0545 g, 0.25 mmol, 0.5 equiv) and I_2 (0.0635 g, 0.25 mmol) were taken in a round-bottomed flask (RBF) and toluene (1.5 mL) was added to it. The reaction mixture was stirred in an oil bath at 60 °C. The progress of the reaction was monitored by TLC. After the

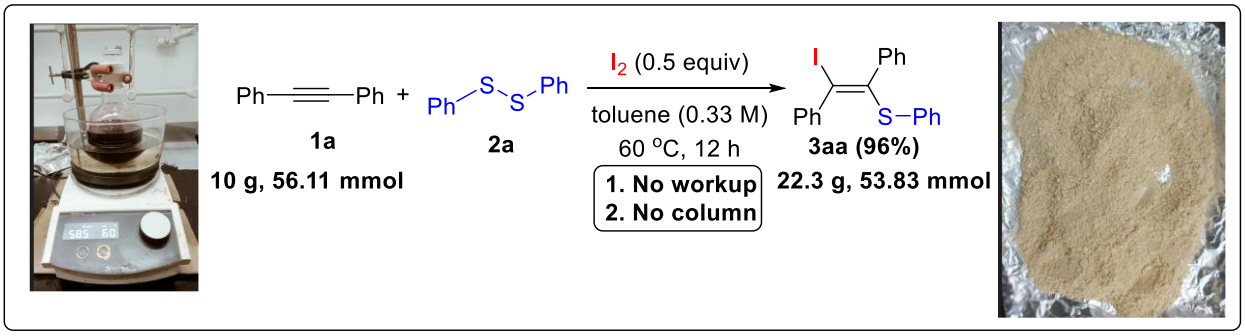
completion of the reaction, the solvent was evaporated under reduced pressure and the crude solid was purified just by washings with ethanol (1 mL X 2) or hexane (5 mL X 2) to afford the pure (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane **3aa** (0.197 g, 0.478 mmol) as an off-white solid in 96% yield. The purity of the **3aa** was found to be 97.5% as evident by HPLC. But to get pure **3ah, 3ca, 3af, 3ag,** and **3da**, we performed flash chromatography (100-200 silica) using 0-5% EtOAc in hexane as an eluent.

3. Experimental procedure for the synthesis of trisubstituted (*E*)-*β*-iodoalkenyl sulfides (5aa – 5eb)



Representative experimental procedure for the synthesis of (*E*)-(2-iodo-2-phenylvinyl)(phenyl)sulfane (5aa): Phenylacetylene **1a** (0.051 g, 0.5 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (0.0545 g, 0.25 mmol, 0.5 equiv) and I_2 (0.0635 g, 0.25 mmol) were taken in a sealed tube and toluene (1.5 mL) was added to it. The reaction mixture was stirred in an oil bath at 120 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated under reduced pressure and crude reaction mixture was purified by flash column chromatography (100-200 silica) using hexane as an eluent to afford the pure (*E*)-(2-iodo-2-phenylvinyl)(phenyl)sulfane **5aa** (0.095 g, 0.28 mmol) as yellow gummy oil in 56% yield.

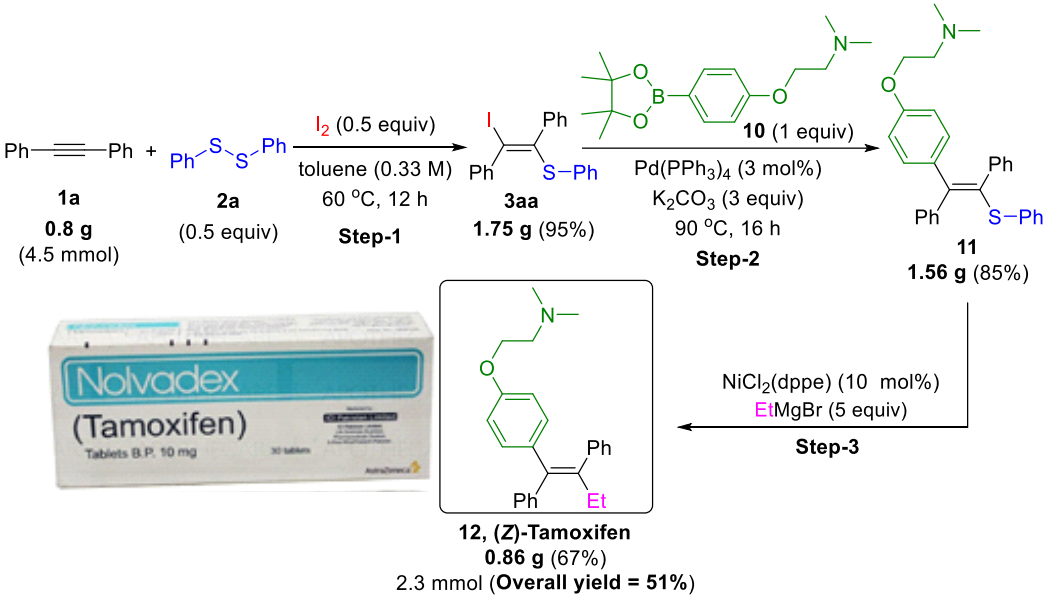
4. Scale up experiment



4.1 Experimental procedure for the synthesis of (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane (3aa)

1,2-diphenylethyne **1a (**10 g, 56.1 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (6.12 g, 28.05 mmol, 0.5 equiv) and I_2 (7.12 g, 28.05 mmol, 0.5 equiv) were taken in a round-bottomed flask (RBF) and toluene (170 mL) was added to it. The reaction mixture was stirred in an oil bath at 60 ^oC. The progress of the reaction was monitored by TLC. The solvent was evaporated under reduced pressure and the crude product was purified by washing with hexane (50 mL X 2) to afford the pure (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane **3aa** (22.3 g, 53.83 mmol) in 96%.

5. Synthesis of (*Z*)-Tamoxifen from 1a and 2a in three steps



Step 1: 1,2-diphenylethyne **1a (**0.8 g, 4.5 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (0.49 g, 2.24 mmol, 0.5 equiv) and I_2 (0.571 g, 2.24 mmol, 0.5 equiv) were taken in a round-bottomed flask (RBF) and toluene (13.5 mL) was added to it. The reaction mixture was stirred in an oil bath at 60 ^oC. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated under reduced pressure and the crude solid was purified by washing with hexane (15 mL X 2) to afford the pure (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane **3aa** (1.75 g, 4.2 mmol) as an off-white solid in 95% yield.

Step 2: (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane **3aa** (1.75 g, 4.22 mmol), *N*,*N*-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)ethan-1-amine (1.23 g, 4.22mmol, 1.0 equiv) and 1,4-dioxane (16 mL) were taken in a RBF. Then, aqueous potassium carbonate (1.75 g dissolved in 4 mL water) solution was added to the RBF. The reaction mixture was purged with nitrogen gas for 15 min, and then $Pd(PPh_3)_4$ (0.146 g, 3 mol%) was added to it. The reaction mixture was heated at 90 ^oC. The progress of the reaction was monitored by TLC. After the completion of the reaction, volatiles were removed under reduced pressure. The crude reaction mixture was extracted with EtOAc (50 mL X 2) and the organic layer was washed with water (30 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford the crude product which was purified by flash column chromatography using 1-2% MeOH in DCM as an eluent to afford (*E*)-2-(4-(1,2-diphenyl-2-(phenylthio)vinyl)phenoxy)-*N*,*N*-dimethylethan-1-amine (**11**) (1.56 g, 3.45 mmol) in 82% yield as a yellow solid.

Step 3: In flame dried RBF, (*E*)-2-(4-(1,2-diphenyl-2-(phenylthio)vinyl)phenoxy)-*N*,*N*-dimethylethan-1-amine (1.56 g, 3.45 mmol, 1 equiv) and $NiCl_2$(dppe) (159 mg, 0.354 mmol, 10 mol%) were taken. EtMgBr (1M in diethyl ether) (17.71 mL, 17.71 mmol, 5 equiv) was added to the RBF under argon atmosphere at room temperature. Then the reaction mixture was refluxed under argon atmosphere. The progress of the reaction was monitored by TLC and LC-MS. After the completion of the reaction, it was quenched with water (50 mL) at 0 ^oC. The reaction mixture was extracted with EtOAc (50 mL X 2) and the combined organic layers was washed with water (30 mL) which was dried over sodium sulfate. The solvent, ethyl acetate was evaporated under reduced pressure to afford the crude reaction mixture which was purified by column chromatography using 0-2% MeOH in DCM as an eluent to afford the marketed drug, (*Z*)-tamoxifen (0.860 g, 2.4 mmol) in 67% yield (51% overall yield) as a brown solid.

6. X-ray crystal structure of 3ai, 3ac, 3aj and 9.

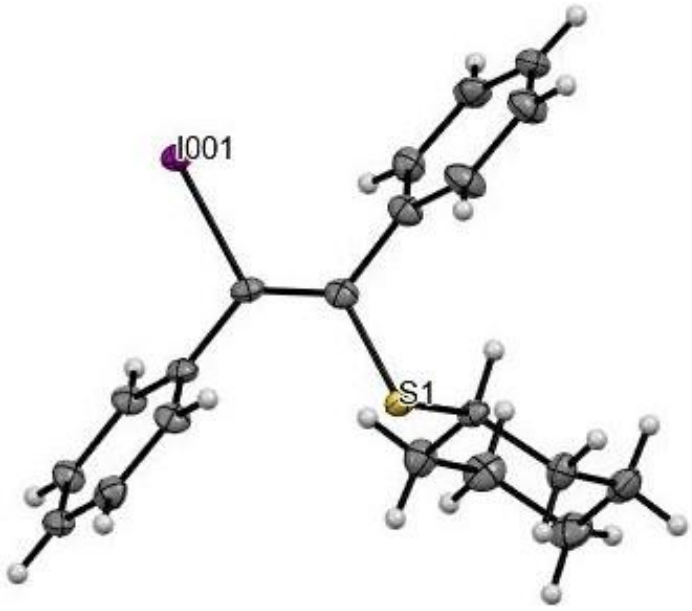


Figure *S1*. X-ray crystal structure of **3ai** (thermal ellipsoids shown at 50% probability) including hetero-atom numbering.

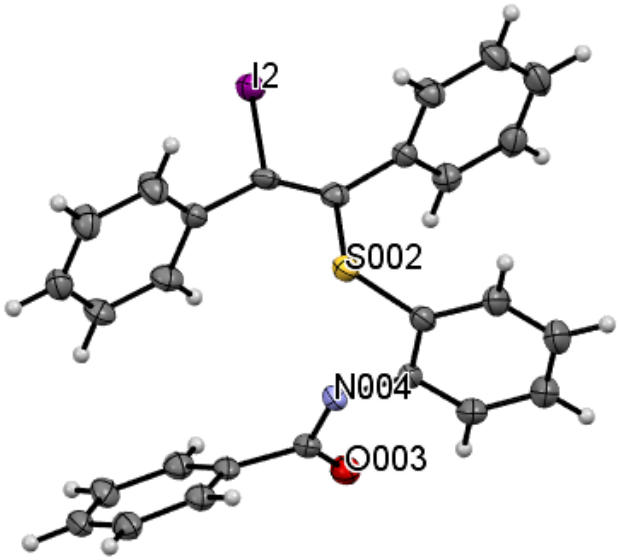


Figure *S2*. X-ray crystal structure of **3ac** (thermal ellipsoids shown at 50% probability) including hetero-atom numbering.

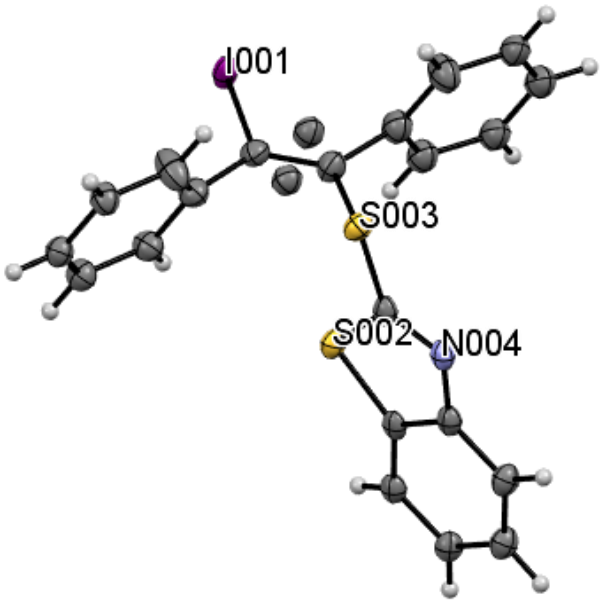


Figure *S3*. X-ray crystal structure of **3aj** (thermal ellipsoids shown at 50% probability) including hetero-atom numbering. (**Disordered structure due to pedal motion)**

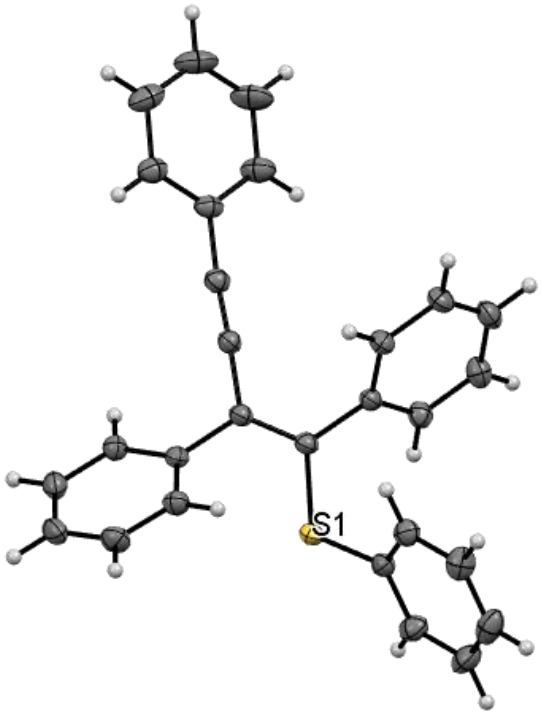


Figure *S4*. X-ray crystal structure of **9** (thermal ellipsoids shown at 50% probability) including hetero-atom numbering.

7. Table-S1. Selected crystal data of 3ai, 3ac, 3aj, 9

Empirical formula	$C_{20}H_{21}IS$	$C_{27}H_{19}INOS$	$C_{21}H_{14}INS_2$	$C_{28}H_{20}S$
Formula weight	420.35	534.39	471.35	388.537
Temperature/K	293	138	220	138
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C 1 2/c 1	P 1 21/c 1	I 1 2/a 1	P 1 21/c 1
a/Å	20.7801(3)	5.52700(10)	17.9022(3)	10.7954(1)
b/Å	5.8767(1)	10.7795(2)	6.05370(10)	8.6148(1)
c/Å	29.2394(4)	37.5935(6)	34.1626(6)	22.6825(2)
α (°)	90	90	90	90
β (°)	96.032(1)	92.4910(10)	91.270(2)	92.306(1)
γ(°)	90	90	90	90
Volume/Å3	3550.90(9)	2237.64(7)	3701.45(11)	2107.77(4)
Z	16	4	8	4
μ/mm-1	15.203	12.275	15.715	1.424
Dx [g cm-3]	1.572	1.586	1.692	1.224
F(000)	1680.0	1064	1856	819.529
2Θ range for data collection (°)	4.9660-79.5390	4.6680-79.5430	5.1930-79.5250	5.4770-79.0720
Index ranges	-25≤ h ≤ 26, -5≤ k ≤ 7, -33 ≤ l ≤ 36	-6≤ h ≤ 6, -13≤ k ≤ 12, -47 ≤ l ≤ 47	-21≤ h ≤ 18, -4≤ k ≤ 7, -31 ≤ l ≤ 41	-13≤ h ≤ 13, -8≤ k ≤ 10, -23 ≤ l ≤ 27
Reflections measured	6956	4709	8441	7730
Unique reflections	3754	4709	3395	4453
Parameters /restraints	199/0	281/0	249/227	262/0
Goodness-of-fit on F2	1.087	1.093	1.182	1.0214
R1 [I ≥ 2σ (I)]	0.0423	0.0432	0.0449	0.0376
wR2 (all data)	0.1204	0.1231	0.1002	0.1020
Largest diff. peak/hole/e Å-3	1.564/ -1.403	1.196/-1.122	1.110/-0.997	0.2453/-0.3728
CCDC	**2167118**	**2223229**	**2209237**	**2223443**

8. Determination of regiochemistry of iodosulfenylation adduct, 5cc.

^{1}H-^{13}C HMBC Spectrum of 5cc.

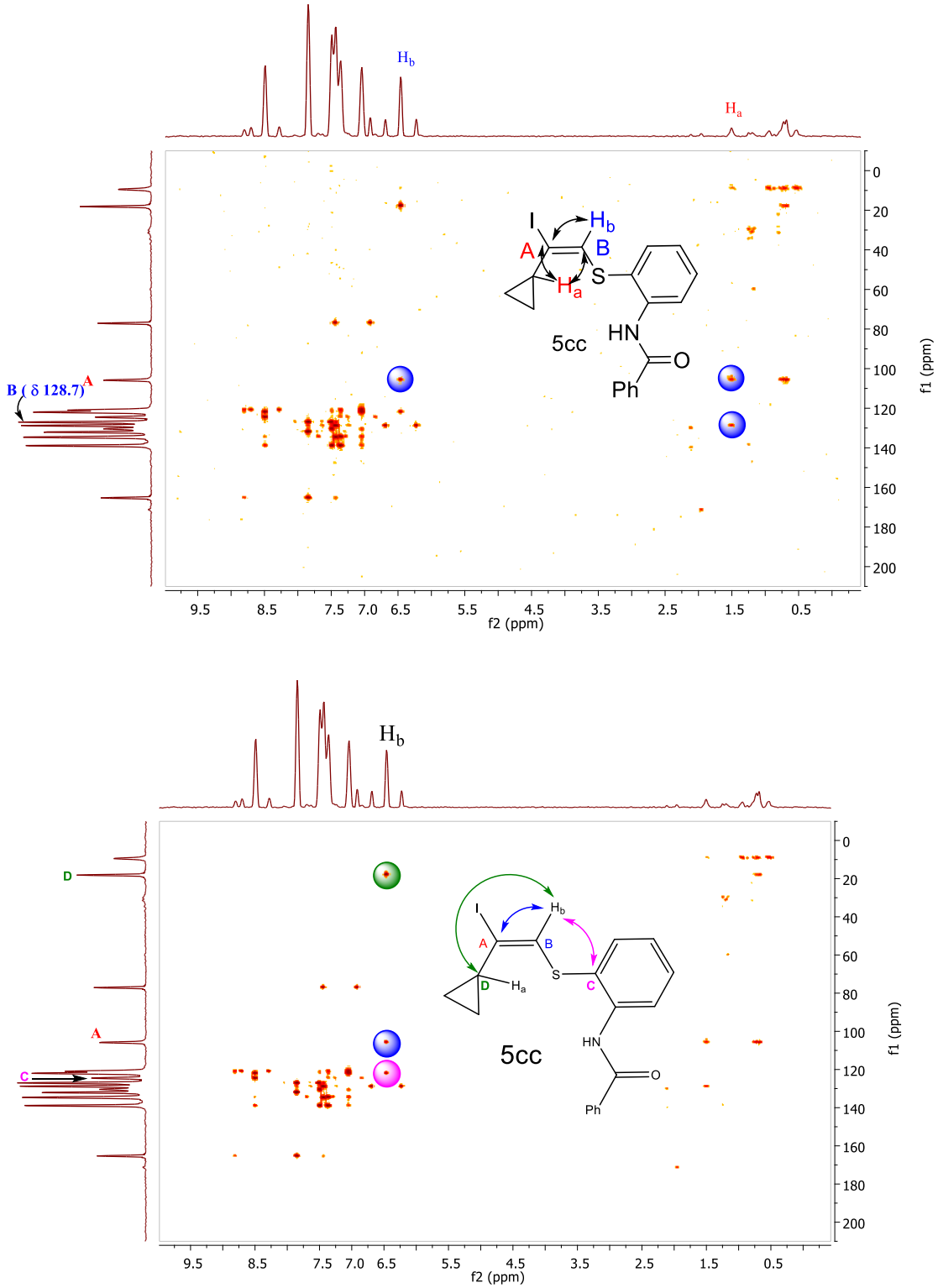


Figure *S5*: ^{1}H-^{13}C HMBC Spectrum of **5cc**.

9. Determination of stereochemistry of iodosulfenylation adduct, 5cf.

NOE Difference Spectrum of 5cf.

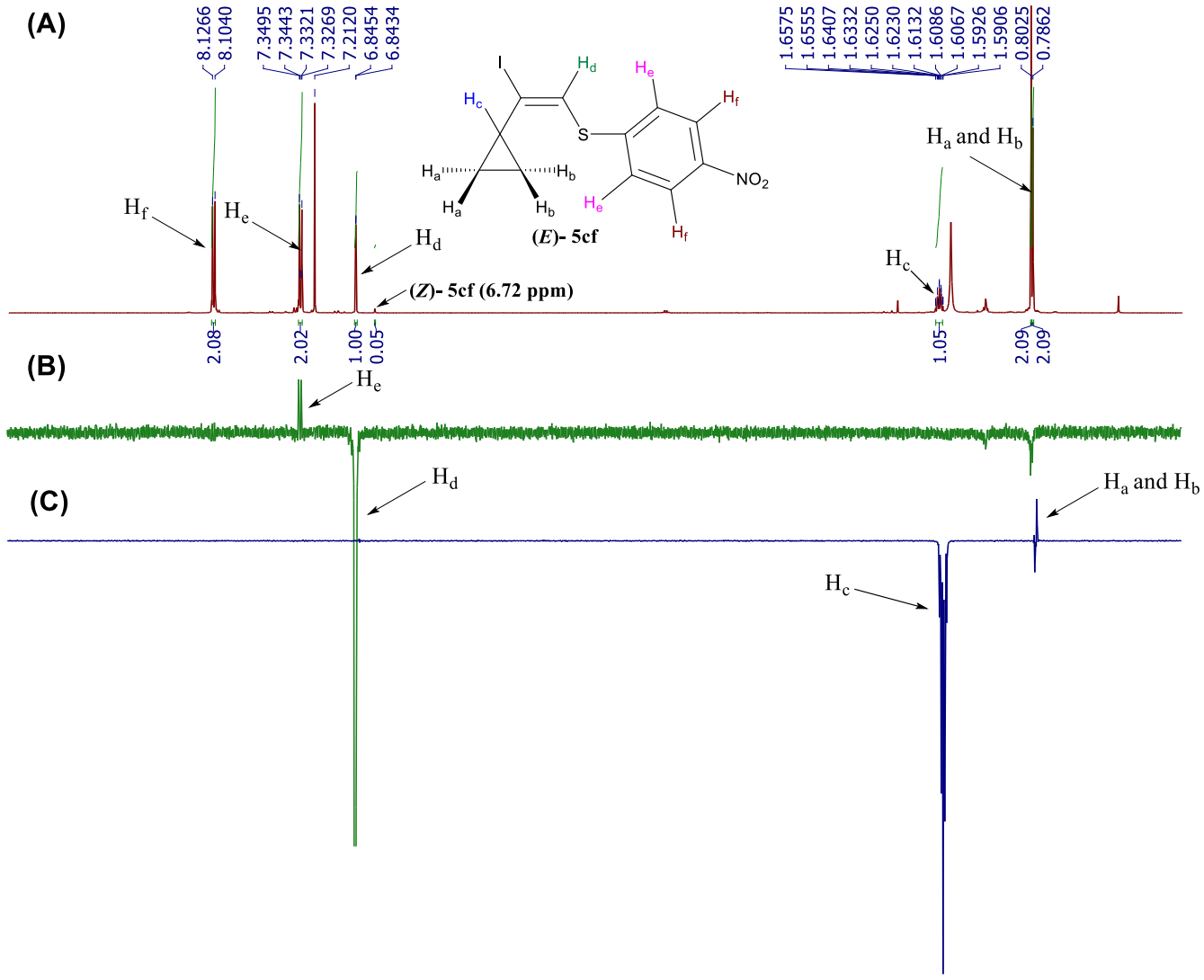
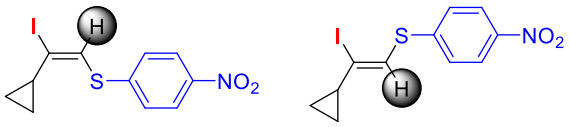


Figure *S6*: (A) ^{1}H-NMR spectrum of **5cf**, (B) NOE difference spectrum, with irradiation at 6.89 ppm, (C) NOE difference spectrum, with irradiation at 1.65 ppm.

The NOE difference spectral analysis clearly revealed that the stereochemistry of the major product is (*E*). The chemical shift of the alkenyl proton in the (*E*) isomer is found deshielded (6.89 ppm) in comparison to that of in the minor isomer, i.e., (Z) isomer (6.72 ppm).

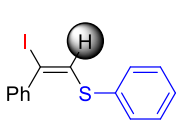
- **The comparison of the chemical shift of the alkenyl proton**

(i) The chemical shift of alkenyl proton has obvious differences by contrasting two different configurations.

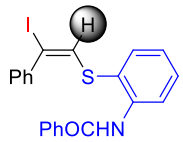


E-5cf (major) v/s Z-5cf (minor) = 6.89 v/s 6.72

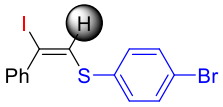
(ii) In all other synthesized trisubstituted alkenes, the alkenyl proton of the major isomer was found deshielded than that of the minor isomer which revealed that the major isomer is (*E*) while the minor isomer is (*Z*) with respect to our above mentioned analogy.



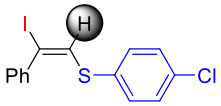
***E*-5aa = δ 7.12 (major)**
***Z*-5aa = δ 7.11 (minor)**



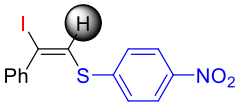
***E*-5ac = δ 6.81 (major)**
***Z*-5ac = δ 6.76 (minor)**



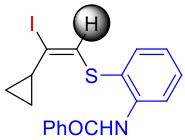
***E*-5ad = δ 7.05 (major)**
***Z*-5ad = δ 7.03 (minor)**



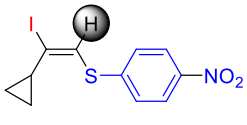
***E*-5ae = δ 7.02 (major)**
***Z*-5ae = δ 7.00 (minor)**



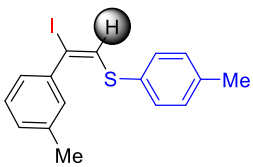
***E*-5af = δ 7.16 (major)**
***Z*-5af = δ 7.13 (minor)**



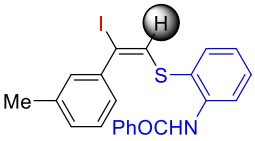
***E*-5cc = δ 6.54 (major)**
***Z*-5cc = δ 6.33 (minor)**



***E*-5cf = δ 6.88 (major)**
***Z*-5cf = δ 6.72 (minor)**



***E*-5db = δ 7.05 (major)**
***Z*-5db = δ 7.04 (minor)**

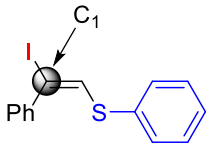


***E*-5dc = δ 6.69 (major)**
***Z*-5dc = δ 6.64 (minor)**

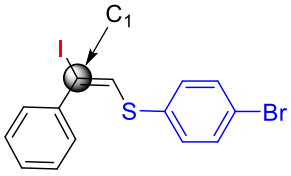
The same trend of chemical shift of the alkenyl proton is found in the same compounds (**3m**, **3n**) or similar compounds (**3b**, **3o** and **3r**) reported previously by Lu and Yi *et al.* (*Org. Lett.*, 2015, **17**, 3310–3313).[1] The authors isolated the (*E*)- and (*Z*)-isomers for a couple of products (**3r** and **4d**), determined the regiochemistry of a couple of products (**3p** and **4d**) by HMBC and also confirmed the configuration of the major isomer of a couple of products (**3a** and **4a**) by the SCXRD analysis of its synthetically diversified product (**5b** and **6a** respectively). They found an obvious difference of the chemical shift of the carbon attached with iodine (C-I) in the isolated (*E*) and (*Z*) isomers of **3r** and **4d** [The C-I carbon is more shielded in the (*E*) isomer compared to the (*Z*) isomer] and correlated the same analogy to rest of the compounds.[1]

- **The comparison of the chemical shift of the carbon which directly links with iodine (C-I)**

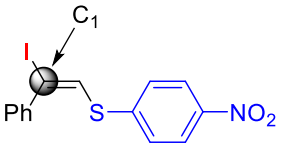
The same trend of chemical shift of C-I carbon was observed in our synthesized products (**5aa**, **5ad**, **5af**, **5dc**, **3ag** and **3da**) as shown below which certainly supported the fact that the major isomer formed in our reaction is having (*E*) configuration. The signal for the C-I quaternary carbon of the Z-isomer was not detected properly in some cases [**5ac**, **5ae**, **5ba**, **5be**, **5cc**, **5cf** and **5db**) as it was present <10%]



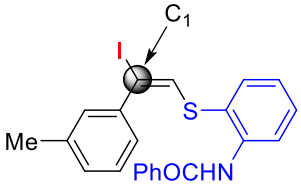
***E*-5aa (C_1 = δ 89.57)**
***Z*-5aa (C_1 = δ 98.41)**



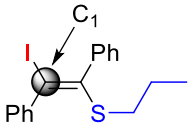
***E*-5ad (C_1 = δ 90.94)**
***Z*-5ad (C_1 = δ 99.52)**



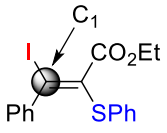
***E*-5af (C_1 = δ 96.82)**
***Z*-5af (C_1 = δ 104.23)**



***E*-5dc (C_1 = δ 91.32)**
***Z*-5dc (C_1 = δ 101.49)**



***E*-3ag (C_1 = δ 94.38)**
***Z*-3ag (C_1 = δ 97.57)**



***E*-3da (C_1 = δ 96.94)**
***Z*-3da (C_1 = δ 105.07)**

10. Table *S2*. Calculation of EcoScale score for the synthesis (*E*)-(2-iodo-2-phenylvinyl)(phenyl)sulfane (3aa) from diphenylacetylene (1a) and diphenyl disulfide (2a)

Eco Scale Calculation:

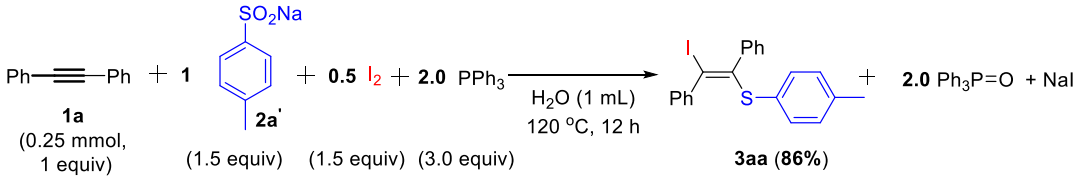
Eco Scale = 100 - Sum of individual penalties
Score on Eco Scale: > 75, Excellent; >50, acceptable; <50, Inadequate

Parameters	Penalty Points
1. Yield: (100 - % of yield)/2 = (100 - 96)/2 =	**2**
2. Price of reaction components (To obtain 10 mmol of end product, **3aa**)	
A. Calculation of Penalty Points :	
a. 1,2-diphenylethyne = 10.55 mmol = 1.88 g = USD 3.76	
b. 1,2-diphenyldisulfide = 5.275 mmol = 1.15 g = USD 0.598	
c. Iodine = 5.275 mmol = 1.34 g = USD 0.71	
Total cost of synthesis of **3aa** = (3.76 + 0.598 + 0.71) = USD 5.068	
Thus expensive, since \$10<(total cost of synthesis of 10 mmol of **3aa**) < \$50:	**0**
3. Safety	
1,2-diphenylethyne	**0**
1,2-diphenyldisulfide (N)	**5**
Iodine (T)	**5**
4. Technical Setup	
Common Setup	**0**
5. Temperature/ Time	
100 ^{o}C, 12 h (Heating, > 1h)	**3**
6. Work up and purification :	
a. Removal of solvent with bp < 150°C	**0**
b. Crystallization and filtration	**1**
c. Adding solvent	**0**
d. Liquid-Liquid extraction	**0**
e. Classical Chromatography	**0**
Total penalty points:	**16**

B. Ecoscale calculation:

EcoScale score: (100 - 16) = 84 (>50; it is an acceptable synthesis)

Table S3. Evaluation of green metrics of the previously reported iodosulfenylation of alkynes using molecular iodine.[1]



Yield of desired product (3aa) = 86%

Atom Economy (%) = $\frac{\text{Mol. wt. of product}}{\text{Mol. wt. of all reactants}} \times 100 = \frac{428.33 \times 100}{178.23+178.18 + (0.5 \times 253.81) + (2 \times 262.69)} =$ **42.46%**

Atom Efficiency (%) = (%yield of product x %atom economy) x 100 = (86% x 42.46%) x 100 = **36.5%**

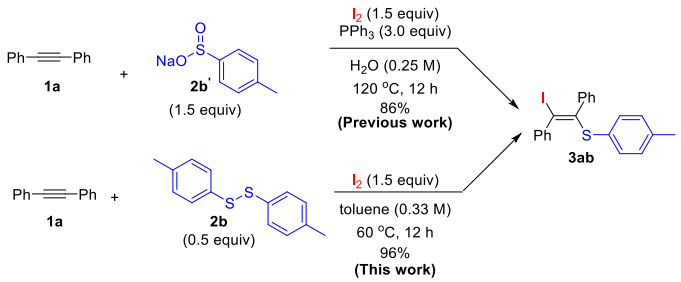
Carbon Efficiency (%) = $\frac{\text{(moles of 3aa x no. of carbons in 3aa) x 100}}{\text{(moles of 1a x carbons in 1a) + (moles of 2a' x carbons in 2a')}} = \frac{(0.215 \times 17) \times 100}{(0.25 \times 14) + (0.375 \times 7)} =$ **59.6%**

Reaction Mass Efficiency (%) = $\frac{\text{mass of isolated product}}{\text{mass of all reactants}} \times 100 = \frac{0.092 \times 100}{0.045 + 0.067 + 0.095 + 0.196} =$ **22.8%**

Reactant 1:	**1,2-diphenylethyne (1a)**	0.045 g	0.25 mmol	FW 178.23
Reactant 2:	**sodium 4-methylbenzenesulfinate ($2a^1$)**	0.067 g	0.375 mmol	FW 178.18
Reagent 1:	**Iodine**	0.095 g	0.375 mmol	FW 253.81
Reagent 2:	**PPh_3**	0.196 g	0.75 mmol	FW 262.29
Solvent:	**Water**	1.0 g	55.51 mmol	FW 18
	Product: (*E*)-(2-iodo-1,2-diphenylvinyl)(p-tolyl)sulfane (3aa)	0.092 g	0.214 mmol	FW 428.33

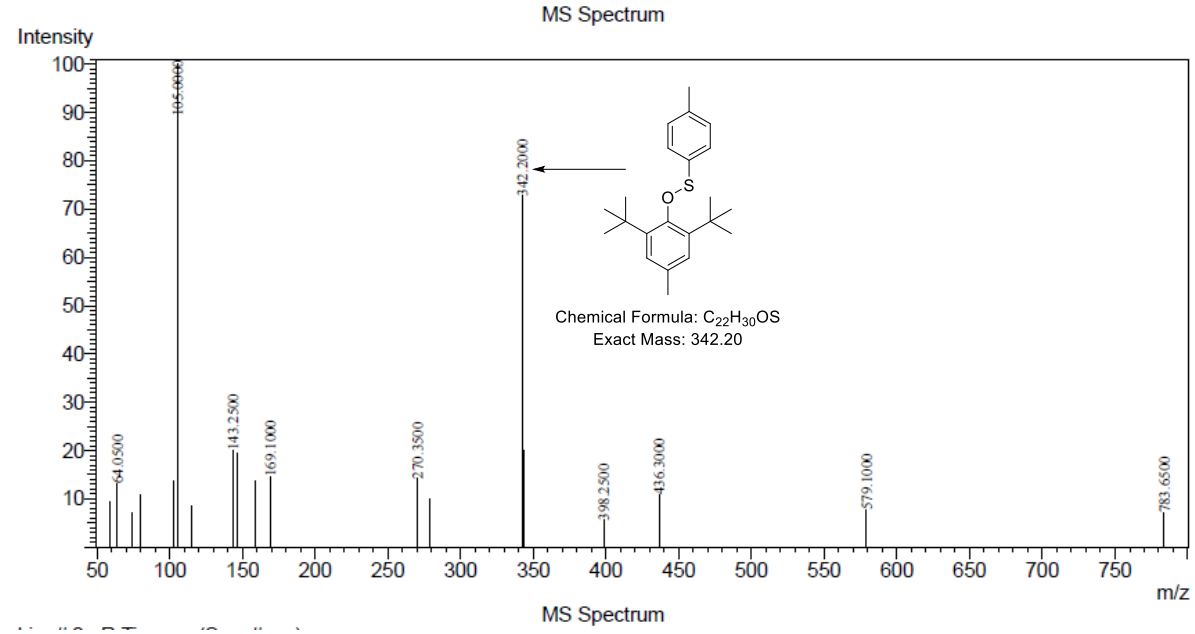
E-factor = $\frac{\text{total waste (g)}}{\text{total product (g)}} = \frac{(0.045 + 0.067 + 0.095 + 0.196 + 1.0) - (0.092)}{0.092} =$ **14.25** g waste/g product

Table *S4*. Comparison of green metrics of the previous work[1] with this work.

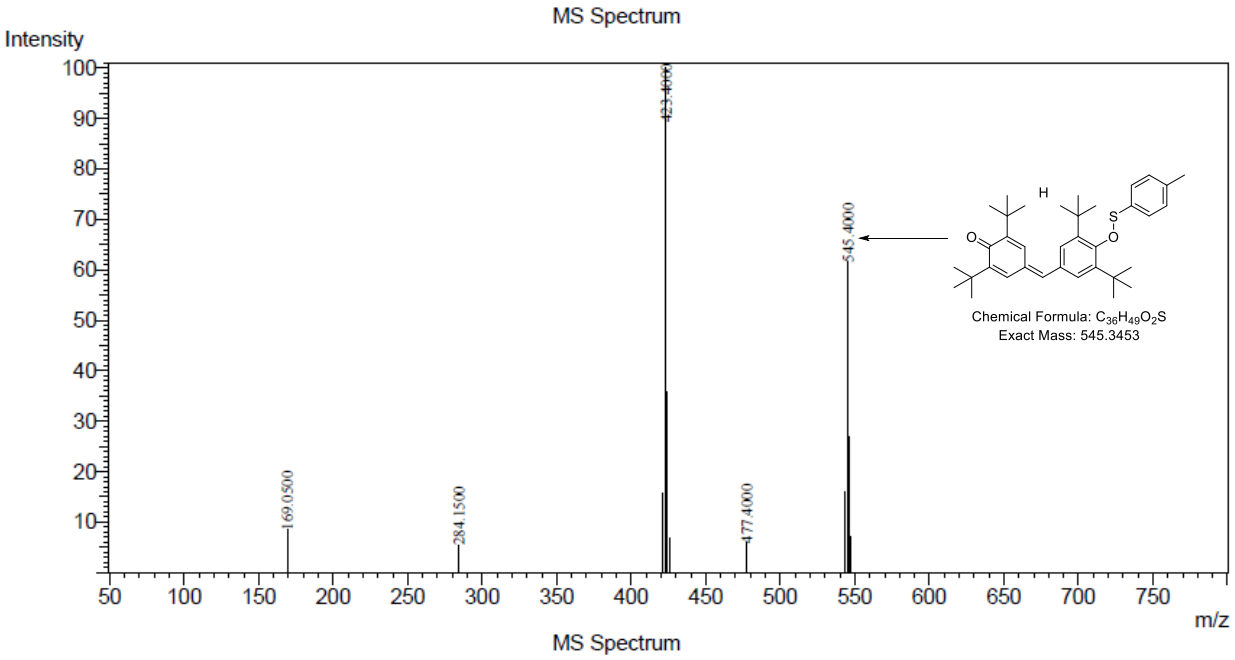


entry	I_2 (equiv)	2b/2b' (equiv)	reagent (equiv)	solvent	temp (°C)	yield (%)	byproduct	% atom economy	%atom efficiency	%reaction-mass efficiency	% carbon efficiency	E-factor (g waste/ g pdt)	purification
1	1.5	**2a'** (1.5)	PPh_3 (3)	H_2O	120 °C	86	O=PPh_3	42.46	36.5	22.8	59.6	14.25	workup and column chromatography
2	**0.5**	**2a (0.5)**	**-**	**toluene**	**60 °C**	**96**	**-**	**100**	**96**	**95.77**	**95.2**	**0.24**	**washing the crude with hexane (column chromatography-free)**

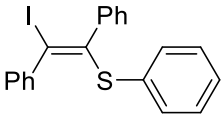
11. Detection of (2,6-di-tert-butyl-4-methylphenoxy)(p-tolyl)sulfane by LCMS



12.Detection of (2,6-di-tert-butyl-4-methylphenoxy)(p-tolyl)sulfane by LCMS

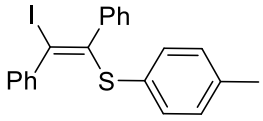


13. Analytical Data of the Synthesized Products

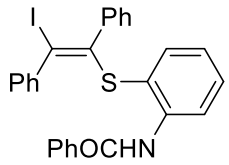


(*E*)-(2-Iodo-2-phenylvinyl)(phenyl)sulfane (3aa)[1] **:** White solid (22.3 g, 96%); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.48 (dd, *J* = 7.3 , 1.1 Hz, 2H), 7.39-

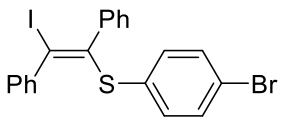
7.35 (m, 2H), 7.30 – 7.28 (m, 3H), 7.21 – 7.18 (m, 2H), 7.16 – 7.12 (m, 1H**)**, 7.1 – 7.07 (m, 2H**)**, 7.05 – 7.02 (m, 3H**)**; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.14, 142.43, 140.93, 133.86, 132.37, 129.68, 128.79, 128.41, 128.27, 127.85, 127.74, 127.33, 98.38. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



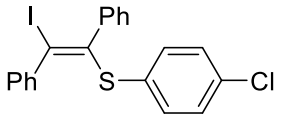
(*E*)-(2-Iodo-1,2-diphenylvinyl)(p-tolyl)sulfane (3ab)[1]**:** Light yellow solid (0.204 g, 96%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.15 (m, 3H), 7.15 – 7.07 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 2.12 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** 144.14, 142.61, 141.48, 137.51, 132.71, 130.10, 129.62, 129.20, 128.87, 128.25, 128.19, 127.75, 127.72, 97.53, 77.32, 77.00, 76.68, 21.03. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



(*E*)-N-(2-((2-Iodo-1,2-diphenylvinyl)thio)phenyl)benzamide (3ac): White solid (0.245 g, 92%); mp = 119−121 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 8.31 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.80 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.31 (m, 5H), 7.25 – 7.19 (m, 1H), 7.17 – 7.09 (m, 4H), 7.01 – 6.93 (m, 2H), 6.82 (td, *J* = 7.6, 1.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.01, 142.89, 141.86, 140.02, 139.72, 136.81, 134.85, 131.97, 130.81, 128.90, 128.81, 128.71, 128.56, 128.45,128.05, 128.02, 127.17, 123.66, 120.64, 120.01, 96.94; HRMS (ESI) m/z calcd for $C_{27}H_{20}INOS$ $[M+H]^+$: 534.089; found: 534.0387.

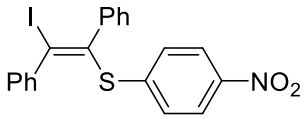


(*E*)-(4-Bromophenyl)(2-iodo-1,2-diphenylvinyl)sulfane (3ad): White solid (0.226 g, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.45 (m, 2H), 7.38 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.02, 142.05, 140.04, 133.57, 133.12, 131.54, 129.66, 128.65, 128.37, 128.32, 128.13, 127.92, 121.60, 99.30.

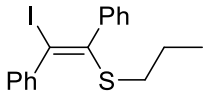


(*E*)-(4-Chlorophenyl)(2-iodo-1,2-diphenylvinyl)sulfane (3ae): White solid (0.192 g, 86%); mp = 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

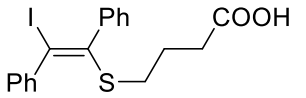
7.38 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (m, 3H), 7.14 (m, 3H), 6.93 (d, *J* = 1.3 Hz, 4H); **^{13}C NMR (100 MHz, $CDCl_3$) merged peaks were present** δ 143.95, 142.04, 140.23 , 133.47, 132.36 , 129.61, 128.65, 128.57, 128.33, 128.29, 128.06, 127.87, 98.90; HRMS (ESI) m/z calcd for $C_{20}H_{14}ClIS$ [M]: 447.9549; found: 447.9545.



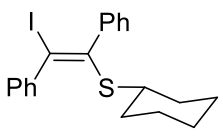
(*E*)-(2-Iodo-1,2-diphenylvinyl)(4-nitrophenyl)sulfane (3af): Yellow solid (0.215 g, 94%); mp = 123−125 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.10 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$) merged peaks were present** δ 145.88, 144.28, 144.06, 141.32, 137.18, 129.85, 129.40, 128.62, 128.35, 128.15, 128.05, 123.47, 104.72; HRMS (ESI) m/z calcd for $C_{20}H_{14}INO2S$ [M]: 458.9790; found: 458.9779.



(*E*)-(2-Iodo-1,2-diphenylvinyl)(propyl)sulfane (3ag): Pale yellow solid (0.142 g,74%); mp = 125−127 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.39 (m, 9H), 7.34 – 7.30 (m, 1H), 2.18 (t, *J* = 8 Hz 2H), 1.42 – 1.33 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.10, 142.42, 141.54, 129.38, 128.94, 128.52, 128.29, 128.16, 127.99, 94.38, 35.94, 23.04, 13.02; HRMS (ESI) m/z calcd for $C_{20}H_{14}INO2S$ [M]: 458.9790; found: 458.9779; HRMS (ESI) m/z calcd for $C_{17}H_{17}IS$ [M+18]: 398.0201; found: 398.1599.

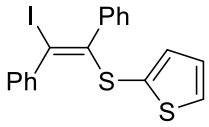


(*E*)-4-((2-Iodo-1,2-diphenylvinyl)thio)butanoic acid (3ah): Pale yellow solid (0.124 g, 59%) mp = 103−105 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.35 (m, 9H), 7.33 – 7.27 (m, 1H), 2.26 (t, *J* = 7.1 Hz, 2H), 2.22 (t, *J* = 7.4 Hz, 2H), 1.66 (p, *J* = 7.3 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.81, 144.04, 141.94, 140.56, 129.40, 128.76, 128.40, 128.32, 128.23, 128.13, 95.72, 32.96, 32.20, 24.52; HRMS (ESI) m/z calcd for $C_{18}H_{17}IO2S$ [M]: 423.9994; found: 423.9994.

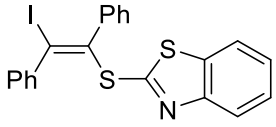


(*E*)-Cyclohexyl(2-iodo-1,2-diphenylvinyl)sulfane (3ai): Off-white solid (0.115 g, 55%); mp = 140−142 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.41 (m, 3H), 7.41 – 7.34 (m, 6H), 7.29 – 7.25 (m, 1H), 2.37 – 2.15 (m, 1H), 1.80 – 1.60 (m, 2H), 1.64 – 1.50 (m, 2H), 1.43 (dd, *J* = 7.8, 3.9 Hz, 1H), 1.31 – 0.91 (m, 5H); **^{13}C NMR**

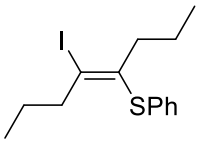
(100 MHz, $CDCl_3$) δ 144.43, 143.04, 141.28, 129.33, 128.98, 128.53, 128.17, 128.10, 127.84, 96.66, 45.84, 33.10, 25.66, 25.42; HRMS (ESI) m/z calcd for $C_{20}H_{21}IS$ [M]: 420.0409; found: 420.0406.



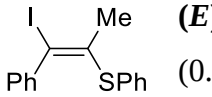
(*E*)-2-((2-Iodo-1,2-diphenylvinyl)thio)thiophene (3aj): Yellow solid (0.202 g, 96%); mp = 130−132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.23 (t, *J* = 7.1 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.14 – 7.10 (m, 1H), 7.09 – 7.05 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) Merged peaks were present** δ 144.14, 142.42, 140.92, 133.85, 132.36, 129.67, 128.79, 128.41, 128.27, 127.84, 127.73, 127.33, 98.38; HRMS (ESI) m/z calcd for $C_{18}H_{13}IS_2$ $[M+H]^+$: 420.9582; found: 420.9581.



(*E*)-2-((2-Iodo-1,2-diphenylvinyl)thio)benzo[d]thiazole (3ak): White solid (0.193 g ,82%); mp = 153−155 °C; **^{1}H NMR (400 MHz, DMSO-d^6)** δ 7.89 (d, 8.0 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.56 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.40 (m, 11H); **^{13}C NMR (100 MHz, DMSO-d^6)** δ 164.52, 153.13, 148.17, 144.67, 142.33, 135.81, 134.27, 131.85, 130.32, 129.25, 129.20, 129.09, 128.92, 128.82, 128.57, 128.18, 126.98, 125.39, 122.28, 122.23, 112.18, 99.70; HRMS (ESI) m/z calcd for $C_{21}H_{14}INS_2$ $[M+H]^+$: 471.9691; found: 471.9691.

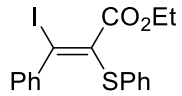


(*E*)-(5-Iodooct-4-en-4-yl)(phenyl)sulfane (3ba)[2]: Yellow liquid (0.164 g, 95%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 2.95 (t, *J* = 8 Hz, 2H), 2.40 (t, *J* = 8 Hz,1H), 1.62 – 1.52 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 135.36, 129.22, 128.95, 126.35, 113.06, 45.39, 43.85, 22.85, 21.24, 13.53, 12.85. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[2]

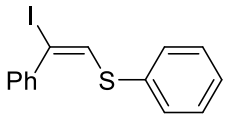


(*E*)-(1-Iodo-1-phenylprop-1-en-2-yl)(phenyl)sulfane (3ca)[1]: Yellow gummy solid (0.122 g, 70%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.29 (m, 4H), 7.25 (dt, *J* = 5.7, 2.3 Hz, 4H), 7.23 – 7.18 (m, 2H), 2.26 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.23, 134.81, 134.62, 130.96, 128.92, 128.64, 128.07, 128.02, 127.10, 99.67, 29.86. The assignment of the

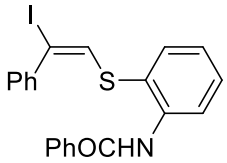
structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



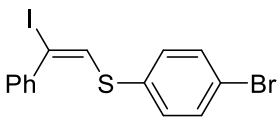
Ethyl (*E*)-3-Iodo-3-phenyl-2-(phenylthio)acrylate (3da): Yellow gummy solid (0.10 g, 49%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.35 (m, 6H), 7.34 – 7.26 (m, 4H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.83, 141.79, 134.34, 133.12, 132.52, 128.98, 128.88, 128.41, 128.34, 128.29, 96.98, 61.96, 13.70; HRMS (ESI) m/z calcd for $C_{17}H_{15}IO_2S$ $[M+H]^+$: 410.9916; found: 410.9913.



(*E*)-(2-Iodo-2-phenylvinyl)(phenyl)sulfane (5aa)[1]: Yellow gummy (0.095 g, 56%)**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.37 (dd, *J* = 8.1, 1.2 Hz, 3H), 7.33 (dd, *J* = 7.2, 0.8 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.12 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.56, 134.85, 133.17, 129.89, 129.21, 129.03, 128.71, 128.22, 127.41, 89.57. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]

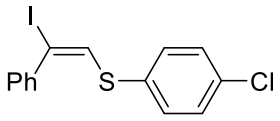


(*E*)-*N*-(2-((2-Iodo-2-phenylvinyl)thio)phenyl)benzamide (5ac): White solid (0.165 g, 72%)**;** mp = 108−110 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (s, 1H), 8.59 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 3H), 7.45 – 7.42 (m, 2H), 7.41 – 7.34 (m, 3H), 7.13 (td, *J* = 7.6, 1.3 Hz, 1H), 6.81 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.13, 140.10, 139.22, 134.90, 134.60, 132.32, 132.00, 130.98, 129.05, 128.86, 128.39, 127.06, 124.48, 121.61, 120.88, 91.05; HRMS (ESI) m/z calcd for $C_{21}H_{16}INOS$ $[M+H]^+$: 458.0076; found: 458.0078.

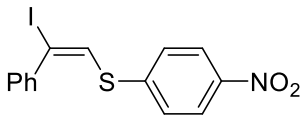


(*E*)-(4-Bromophenyl)(2-iodo-2-phenylvinyl)sulfane[1] (5ad): Yellow solid (0.120 g, 58%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47- 7.43 (m, 4H), 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.50, 137.94, 137.65, 133.90, 131.31, 130.43, 129.94, 129.59,

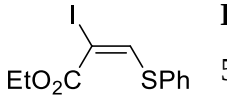
129.47, 128.06, 126.06, 88.52, 21.36, 21.06. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



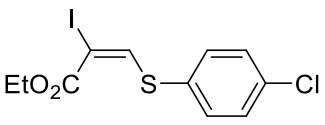
(*E*)-(4-Chlorophenyl)(2-iodo-2-phenylvinyl)sulfane (5ae)[1]: White solid (0.065 g, 35%)**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.28 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.22 (s, 2H), 7.02 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.42, 133.78, 132.28, 131.09, 129.36, 129.21, 128.95, 128.86, 128.26, 90.69.



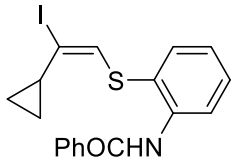
(*E*)-(2-Iodo-2-phenylvinyl)(4-nitrophenyl)sulfane (5af)[1]: Yellow solid (0.102 g, 54%); mp = 125−127 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.44 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.37 – 7.31 (m, 2H), 7.16 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.08, 144.53, 140.16, 129.24, 128.73, 128.32, 128.08, 127.44, 124.17, 96.82. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



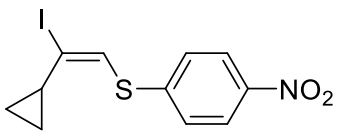
Ethyl (*E*)-2-iodo-3-(phenylthio)acrylate (5ba)[3]: Yellow gummy solid (0.088 g, 53%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 2.1 Hz, 1H), 7.49 (m, *J* = 4.6, 3.8, 1.6 Hz, 2H), 7.40 – 7.36 (m, 3H), 4.30 (dd, *J* = 8.1, 4.5 Hz, 2H), 1.37 (dd, *J* = 7.0, 4.7 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.64, 155.27, 135.54, 131.37, 129.49, 128.73, 86.65, 62.72, 14.20. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[3]



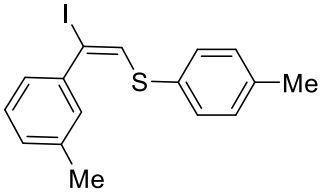
Ethyl (*E*)-3-((4-chlorophenyl)thio)-2-iodoacrylate (5be): White solid (0.088 g, 48%); mp = 79−81 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.30 (d, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.61, 154.29, 135.14, 134.00, 132.71, 129.68, 72.81, 62.83, 14.19; HRMS (ESI) m/z calcd for $C_{18}H_{16}INOS$ $[M+H]^+$: 368.9213; found: 368.9211.



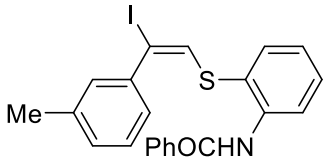
(*E*)-*N*-(2-((2-Cyclopropyl-2-iodovinyl)thio)phenyl)benzamide (5cc): White solid (0.101 g, 48%); mp = 130−132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.88 (s, 1H), 8.57 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.44 (td, *J* = 8.2, 1.5 Hz, 1H), 7.12 (td, *J* = 7.6, 1.4 Hz, 1H), 6.54 (s, 1H), 1.59 (m, 1H), 0.81 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.25, 138.95, 134.79, 134.50, 132.03, 130.49, 128.86, 128.77, 127.10, 124.49, 122.00, 120.92, 105.90, 18.28, 9.58; HRMS (ESI) m/z calcd for $C_{18}H_{16}INOS$ $[M+H]^+$: 422.0076; found: 422.0075.



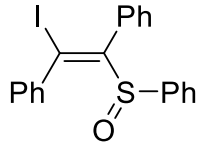
(*E*)-(2-Cyclopropyl-2-iodovinyl)(4-nitrophenyl)sulfane(*E*-5cf): Pale yellow solid (0.107 g, 62%); mp: 121-123 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.1 Hz, 2H), 6.88 (d, *J* = 0.8 Hz, 1H), 1.72 – 1.62 (m, 1H), 0.85 (s, 2H), 0.82 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.78, 145.62, 126.71, 124.18, 123.65, 116.48, 18.43, 9.95. Anal. calcd. for $C_{11}H_{10}INO_2S$: C, 38.06; H, 2.90; N, 4.03; S, 9.23; found: C, 38.26; H, 2.70; N, 4.33; S, 9.48.



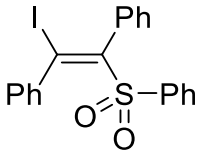
(*E*)-(2-Iodo-2-(*m*-tolyl)vinyl)(p-tolyl)sulfane (5db): Colorless gummy liquid (0.121 g, 66%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29-7.25 (m, 4H), 7.23-7.21 (m, 1H), 7.13-7.08 (m, 3H), 7.05 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.57, 138.00, 137.72, 133.96, 131.38, 130.50, 130.01, 129.65, 129.54, 128.12, 126.12, 88.59, 21.43, 21.12.



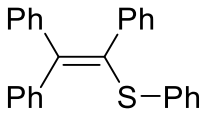
(*E*)-*N*-(2-((2-Iodo-2-(*m*-tolyl)vinyl)thio)phenyl)benzamide (5dc): Yellow gummy liquid (0.119 g, 51%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (s, 1H), 8.49 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 3H), 7.15 (dd, *J* = 7.3, 5.2 Hz, 3H), 7.03 (dd, *J* = 7.6, 6.2 Hz, 2H), 6.69 (s, 1H), 2.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.09, 139.99, 139.16, 138.11, 134.81, 134.57, 131.98, 131.95, 130.88, 129.87, 129.38, 128.80, 128.21, 127.05, 125.85, 124.42, 121.72, 120.87, 91.32, 21.37; HRMS (ESI) m/z calcd for $C_{22}H_{18}INOS$ $[M+H]^+$: 472.0232; found: 472.0236.



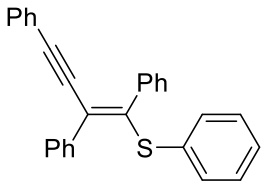
(*E*)-(1-Iodo-2-(phenylsulfinyl)ethene-1,2-diyl)dibenzene (6): White solid (0.198 g, 92%); mp = 151−153 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (dt, *J* = 4.4, 1.8 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.29 (m, 3H), 7.27 (dd, *J* = 4.2, 3.0 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 8.3, 1.3 Hz, 2H), 6.84 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.82, 142.06, 141.43, 134.79, 130.79, 129.87, 129.38, 128.74, 128.71, 128.62, 128.58, 127.61, 124.54, 113.49; HRMS (ESI) m/z calcd for $C_{20}H_{15}IOS$ $[M+H]^+$: 430.9970; found: 430.9967.



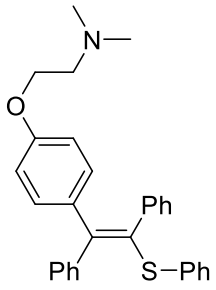
(*E*)-(1-Iodo-2-(phenylsulfonyl)ethene-1,2-diyl)dibenzene (7)[1]: White solid (0.161 g, 72%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.45 (m, 1H), 7.40 – 7.31 (m, 10H), 7.31 – 7.26 (m, 2H), 7.17 (dd, *J* = 7.9, 1.6 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.92, 142.33, 139.70, 139.17, 133.18, 130.24, 129.23, 129.03, 128.52, 128.39, 128.34, 127.87, 127.37, 118.34. The assignment of the structure was verified with the chemical shift values of both the ^{1}H and ^{13}C NMR with that of the literature.[1]



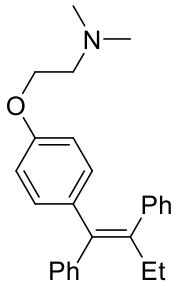
Phenyl(1,2,2-triphenylvinyl)sulfane (8): Yellow solid (0.162 g, 89%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.34 – 7.25 (m, 5H), 7.18 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.11 – 7.03 (m, 5H), 7.02 – 6.94 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.30, 143.75, 142.45, 139.16, 135.69, 133.96, 131.07, 130.75, 129.63, 129.54, 128.41, 128.12, 127.64, 127.55, 127.26, 126.99, 126.67, 125.73.



(*E*)-(2,4-Diphenylbut-1-en-3-yn-1-yl)(phenyl)sulfane (9): Yellow solid (0.167 g, 86%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (t, *J* = 8.3 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 – 7.04 (m, 10H), 7.0-6.9 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.13, 139.19, 138.70, 134.37, 131.26, 131.11, 130.40, 129.10, 128.45, 128.14, 128.13, 128.03, 128.00, 127.86, 127.39, 126.58, 124.86, 123.31, 93.35, 91.09.



(*E*)-2-(4-(1,2-Diphenyl-2-(phenylthio)vinyl)phenoxy)-*N*,*N*-dimethylethan-1-amine (11): Yellow solid (1.56 g, 82%); mp = 112−114 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.33- 7.3 (m, 4H), 7.29 (m, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.11 – 7.03 (m, 3H), 7.03 – 6.96 (m, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.03 (t, *J* = 5.5 Hz, 2H), 2.84 (t, *J* = 5.4 Hz, 2H), 2.41 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.13, 146.13, 144.00, 139.42, 135.96, 135.18, 132.55, 132.11, 131.03, 129.53, 129.35, 128.39, 128.08, 127.65, 127.23, 126.86, 125.58, 113.61, 64.81, 57.25, 44.78.



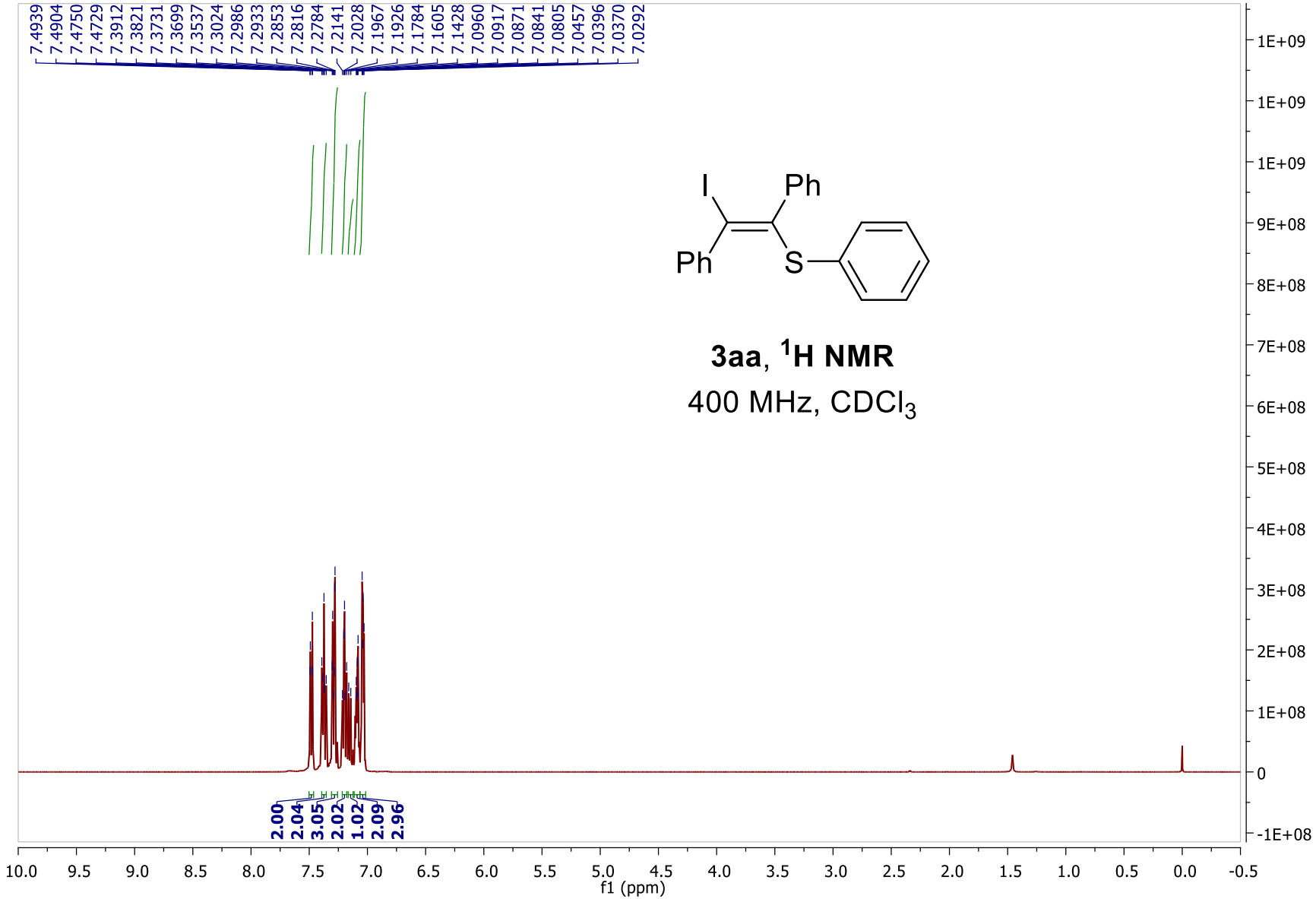
(*Z*)-2-(4-(1,2-Diphenylbut-1-en-1-yl)phenoxy)-*N*,*N*-dimethylethan-1-amine (*Z*-Tomoxifen) (12)[2]**:** Brown solid (0.86 g, 67%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.06 (m, 2H), 7.07 – 7.00 (m, 3H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 8.8 Hz, 2H), 3.89 (t, *J* = 5.6 Hz, 2H), 2.66 (t, *J* = 5.6 Hz, 2H), 2.38 (q, *J* = 7.4 Hz, 2H), 2.26 (s, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.47, 143.73, 142.33, 141.33, 138.14, 135.66, 131.82, 129.63, 129.40, 128.04, 127.82, 126.47, 125.97, 113.31, 65.10, 57.76, 45.29, 28.96, 13.54.

14. Reference:

(1) Lin, Y. M.; Lu, G. P.; Cai, C.; Yi, W. bin. Odorless, One-Pot Regio- and Stereoselective Iodothiolation of Alkynes with Sodium Arenesulfinates under Metal-Free Conditions in Water. *Org Lett* **2015**, *17* (13), 3310–3313.

(2) Taniguchi, N. Copper-Catalyzed Synthesis of β-Haloalkenyl Chalcogenides by Addition of Dichalcogenides to Internal Alkynes and Its Application to Synthesis of (Z)-Tamoxifen. *Tetrahedron* **2009**, *65* (14), 2782–2790.

(3) Lu, L. H.; Ou, G.; Zhao, X.; Wang, Y.; Chen, X.; Liao, W.; Li, S.; Wu, C. Selective Difunctionalization of Electron-Deficient Alkynes: Access to (E)-2-Iodo-3-(Methylthio)Acrylate. *Org Biomol Chem* **2021**, *19* (37), 8128–8132.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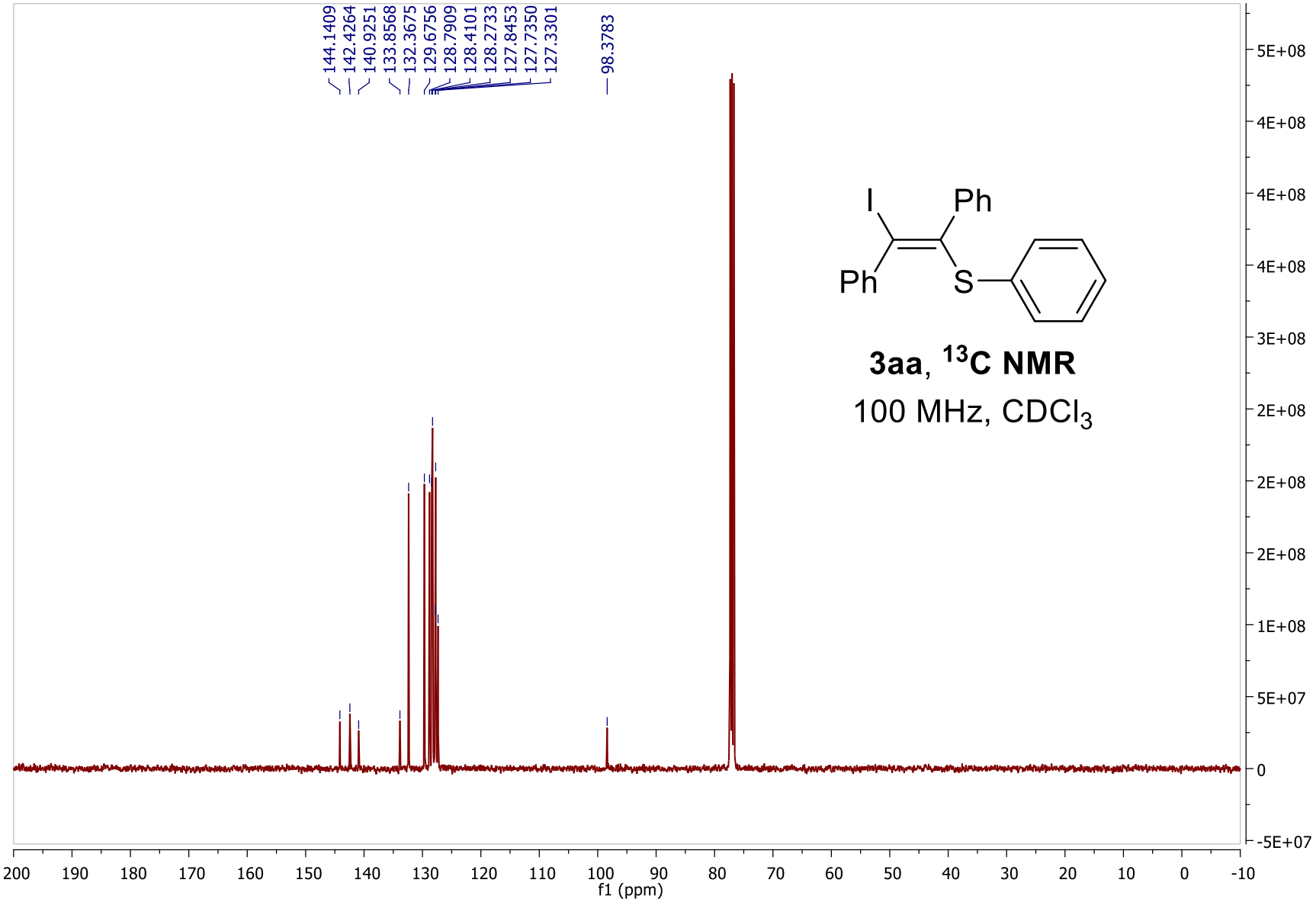
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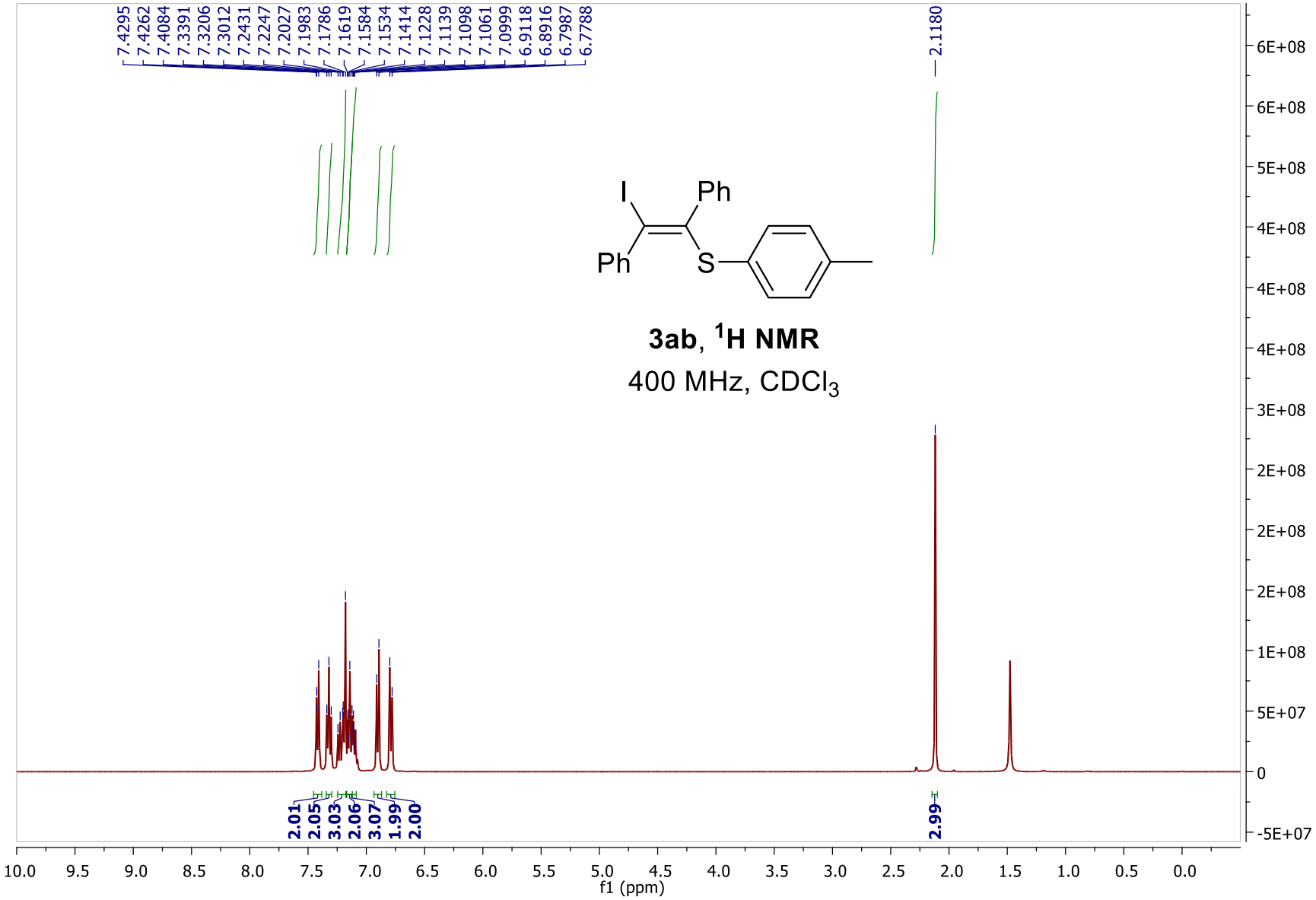
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7.1414
7.1228
7.1139
7.1098
7.1061
7.0999
6.9118
6.8916
6.7987
6.7788
2.1180
I
Ph
Ph
S
3ab, 1H NMR
400 MHz, CDCl3
2.01
2.05
3.03
2.06
3.07
1.99
2.00
2.99
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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1.0
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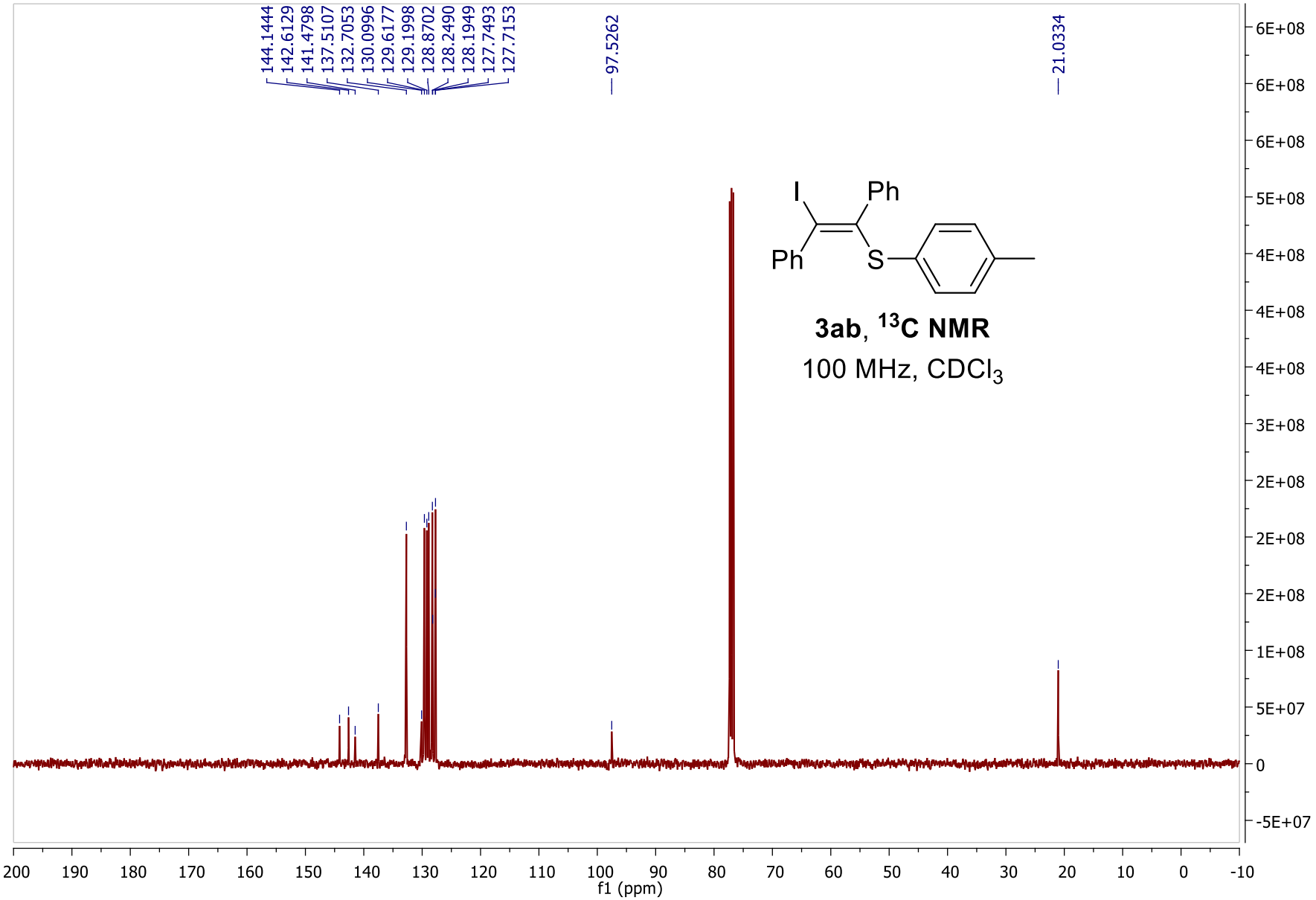
0.0
f1 (ppm)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132.7053
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129.6177
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128.8702
128.2490
128.1949
127.7493
127.7153
97.5262
21.0334
I
Ph
Ph
S
3ab, 13C NMR
100 MHz, CDCl3
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
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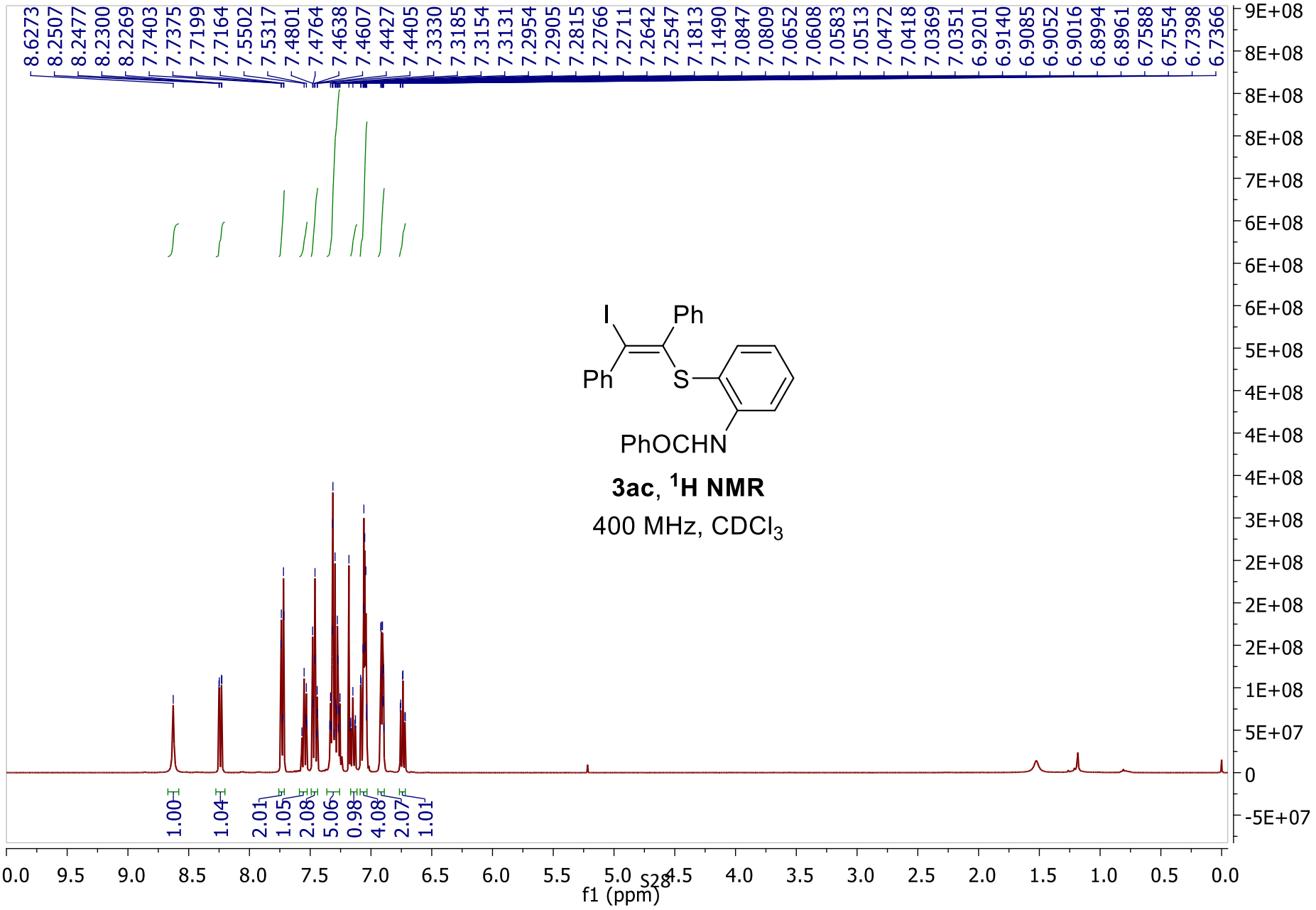
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.2477
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8.2269
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7.7375
7.7199
7.7164
7.5502
7.5317
7.4801
7.4764
7.4638
7.4607
7.4427
7.4405
7.3330
7.3185
7.3154
7.3131
7.2954
7.2905
7.2815
7.2766
7.2711
7.2642
7.2547
7.1813
7.1490
7.0847
7.0809
7.0652
7.0608
7.0583
7.0513
7.0472
7.0418
7.0369
7.0351
6.9201
6.9140
6.9085
6.9052
6.9016
6.8994
6.8961
6.7588
6.7554
6.7398
6.7366
I
Ph
Ph
S
PhOCHN
3ac, 1H NMR
400 MHz, CDCl3
1.00
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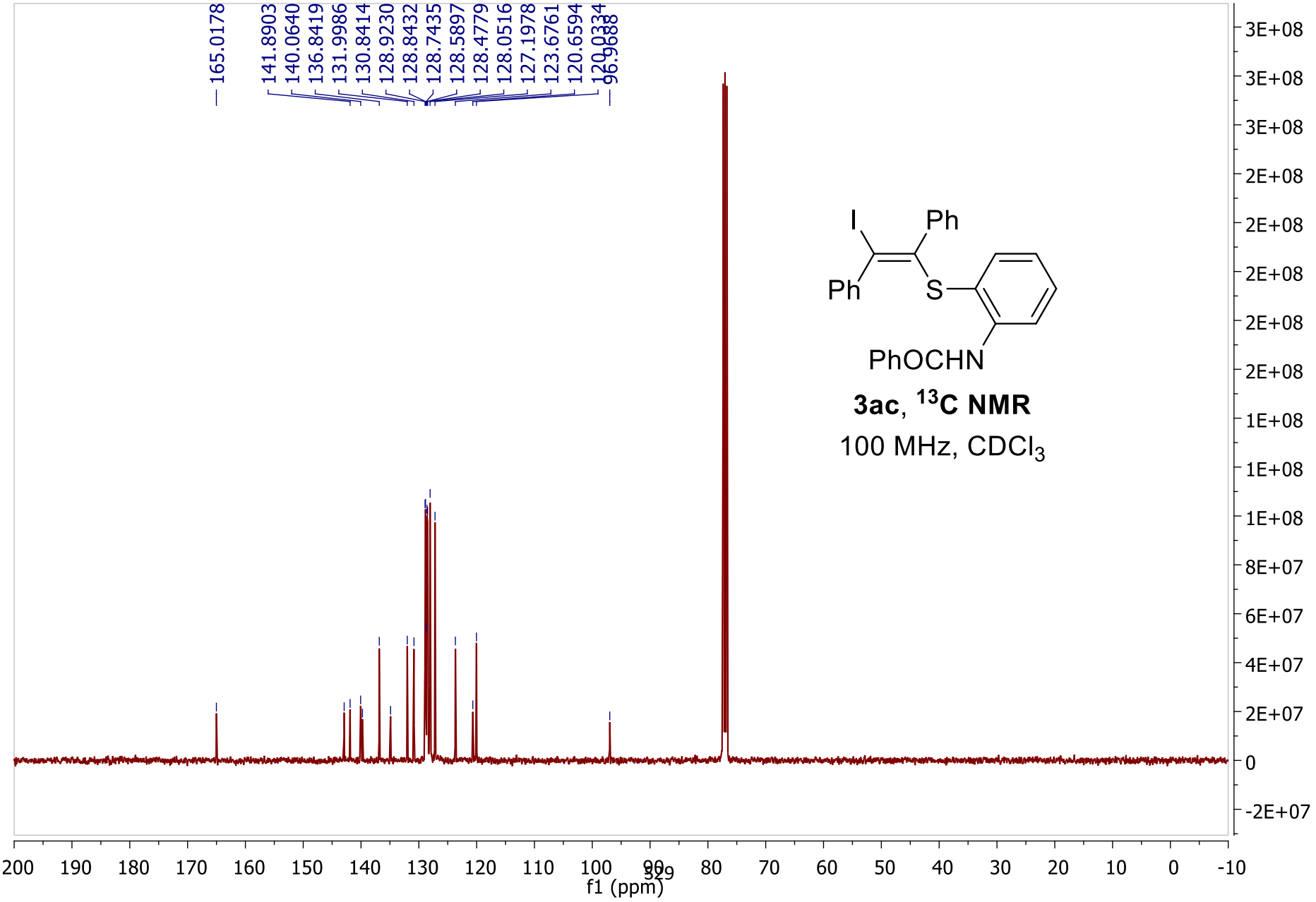
2.01
1.05
2.08
5.06
0.98
4.08
2.07
1.01
f1 (ppm)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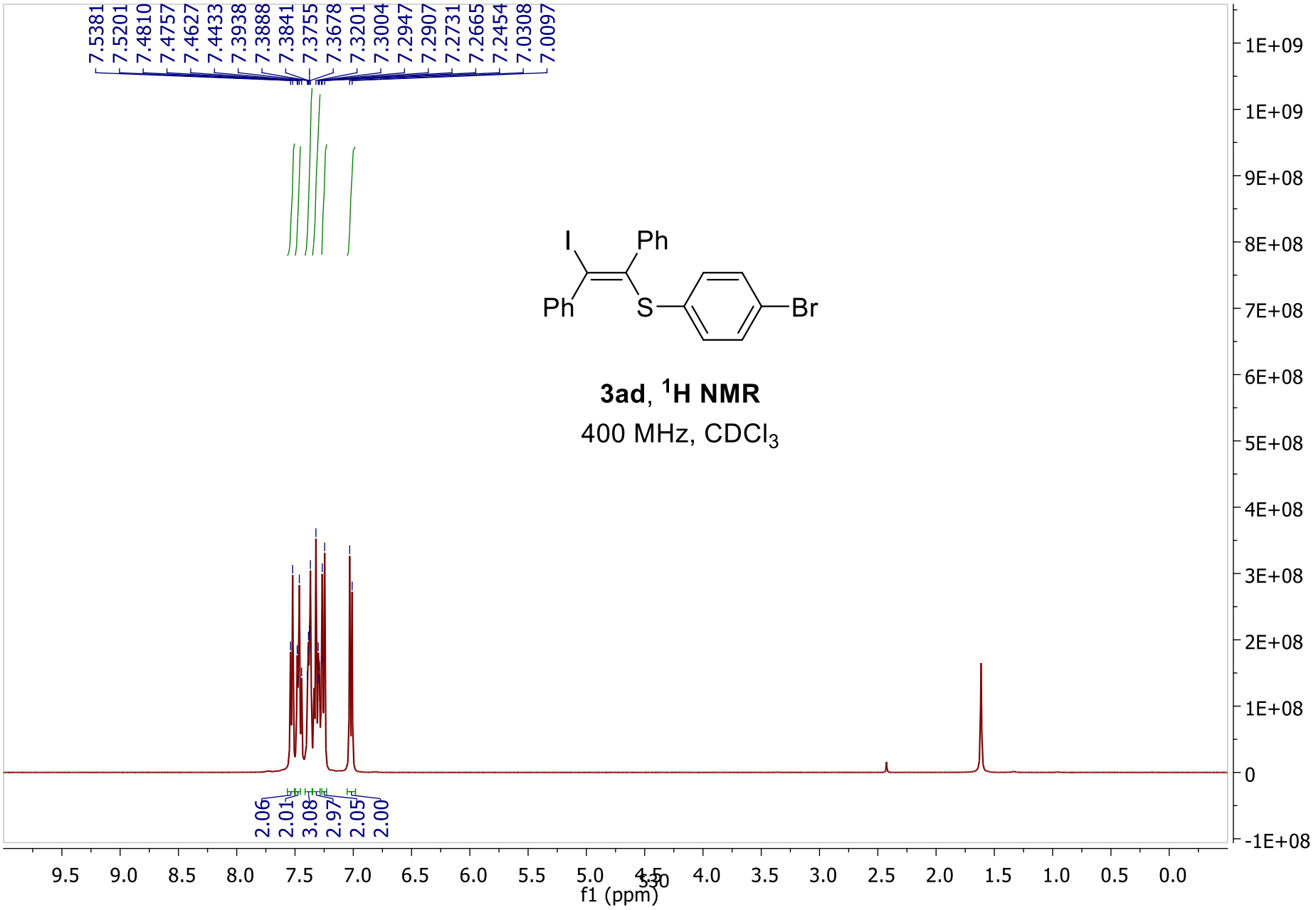
141.8903
140.0640
136.8419
131.9986
130.8414
128.9230
128.8432
128.7435
128.5897
128.4779
128.0516
127.1978
123.6761
120.6594
120.0334
96.9688
I
Ph
Ph
S
PhOCHN
3ac, 13C NMR
100 MHz, CDCl3
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.4810
7.4757
7.4627
7.4433
7.3938
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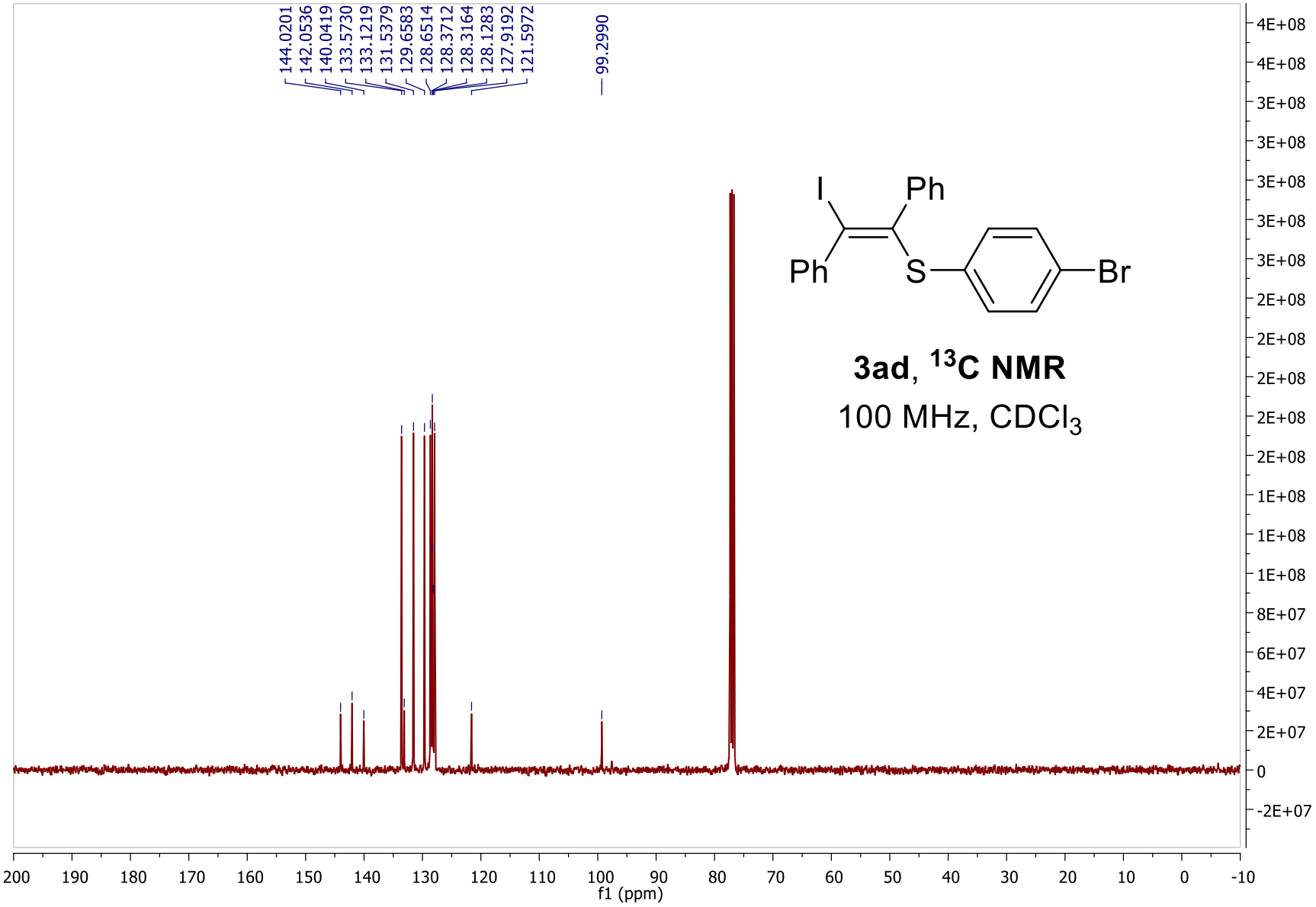
7.3841
7.3755
7.3678
7.3201
7.3004
7.2947
7.2907
7.2731
7.2665
7.2454
7.0308
7.0097
I
Ph
Ph
S
Br
3ad, 1H NMR
400 MHz, CDCl3
2.06
2.01
3.08
2.97
2.05
2.00
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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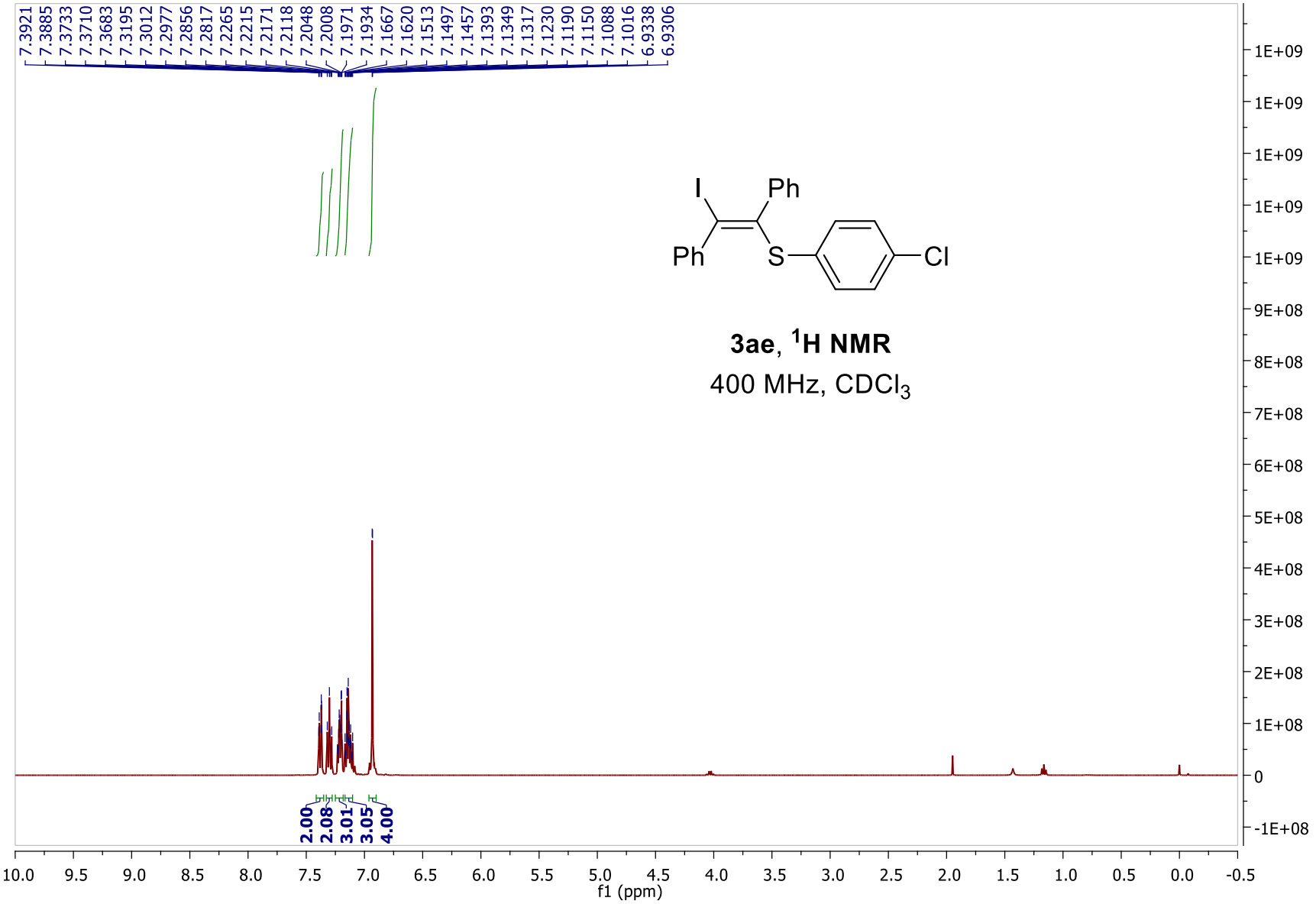
140.0419
133.5730
133.1219
131.5379
129.6583
128.6514
128.3712
128.3164
128.1283
127.9192
121.5972
99.2990
I
Ph
Ph
S
Br
3ad, 13C NMR
100 MHz, CDCl3
4E+08
4E+08
3E+08
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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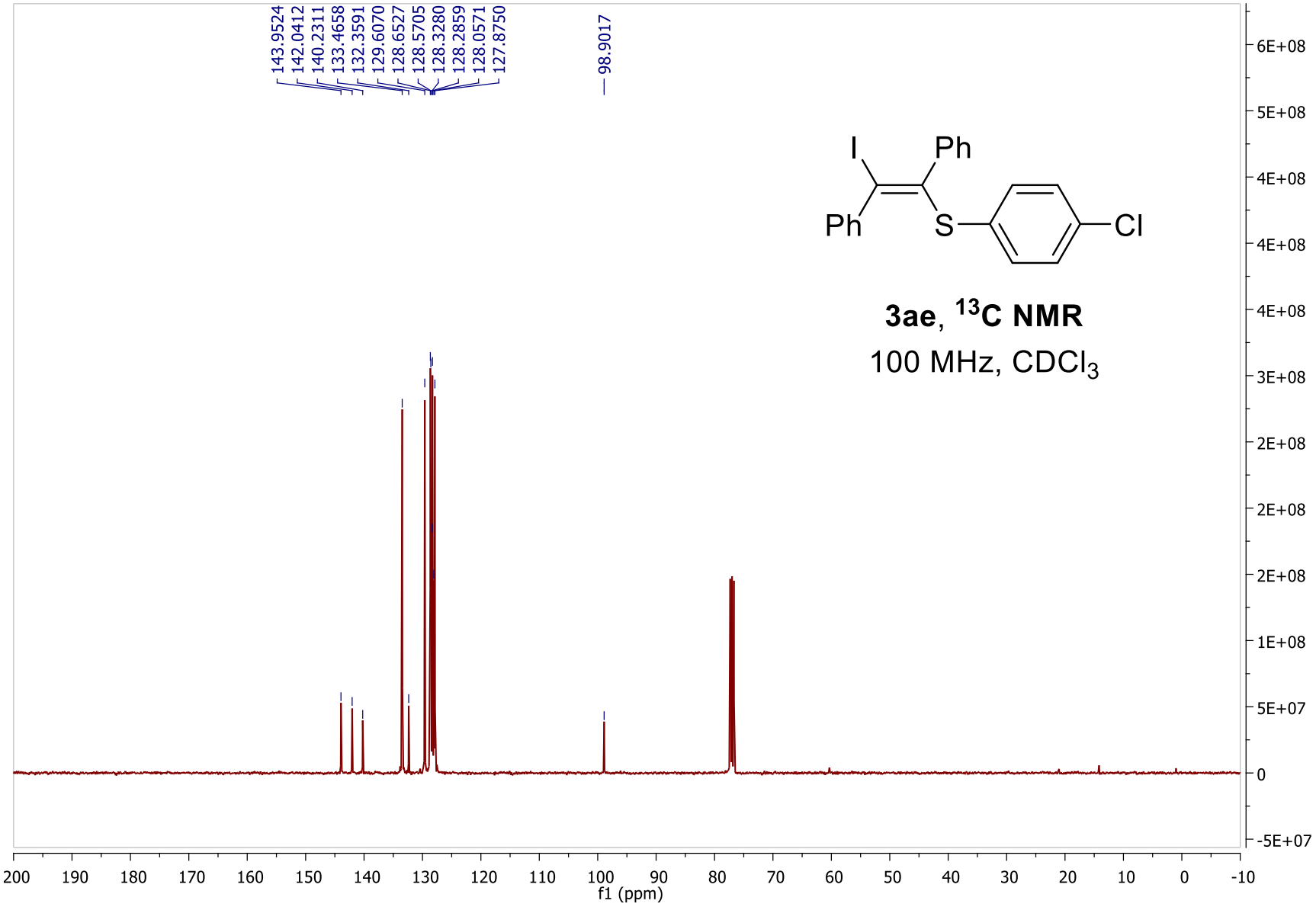
7.3885
7.3733
7.3710
7.3683
7.3195
7.3012
7.2977
7.2856
7.2817
7.2265
7.2215
7.2171
7.2118
7.2048
7.2008
7.1971
7.1934
7.1667
7.1620
7.1513
7.1497
7.1457
7.1393
7.1349
7.1317
7.1230
7.1190
7.1150
7.1088
7.1016
6.9338
6.9306
I
Ph
Ph
S
Cl
3ae, 1H NMR
400 MHz, CDCl3
2.00
2.08
3.01
3.05
4.00
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
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
f1 (ppm)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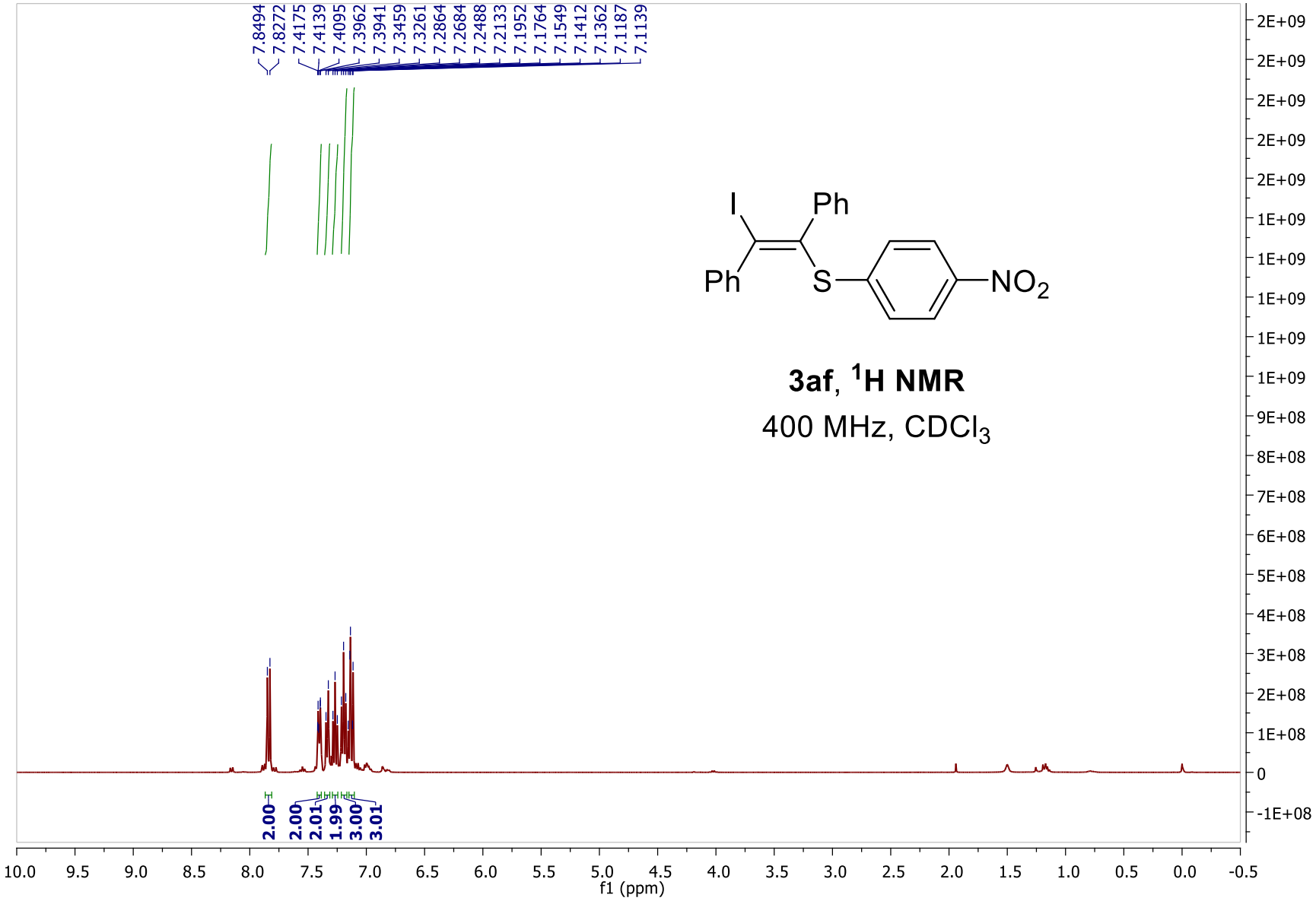
140.2311
133.4658
132.3591
129.6070
128.6527
128.5705
128.3280
128.2859
128.0571
127.8750
98.9017
I
Ph
Ph
S
Cl
3ae, 13C NMR
100 MHz, CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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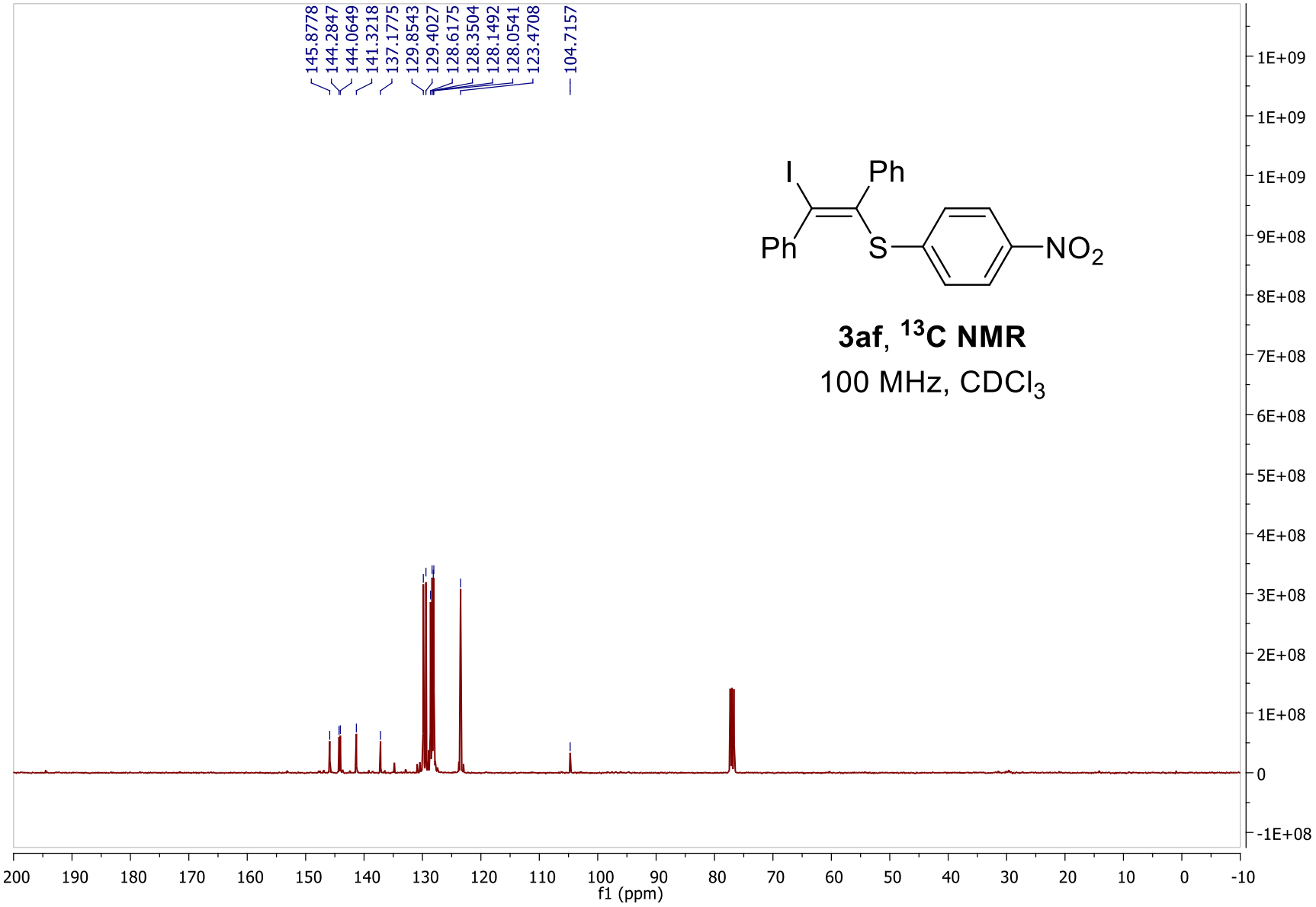
7.4095
7.3962
7.3941
7.3459
7.3261
7.2864
7.2684
7.2488
7.2133
7.1952
7.1764
7.1549
7.1412
7.1362
7.1187
7.1139
I
Ph
Ph
S
NO2
3af, 1H NMR
400 MHz, CDCl3
2.00
2.00
2.01
1.99
3.00
3.01
f1 (ppm)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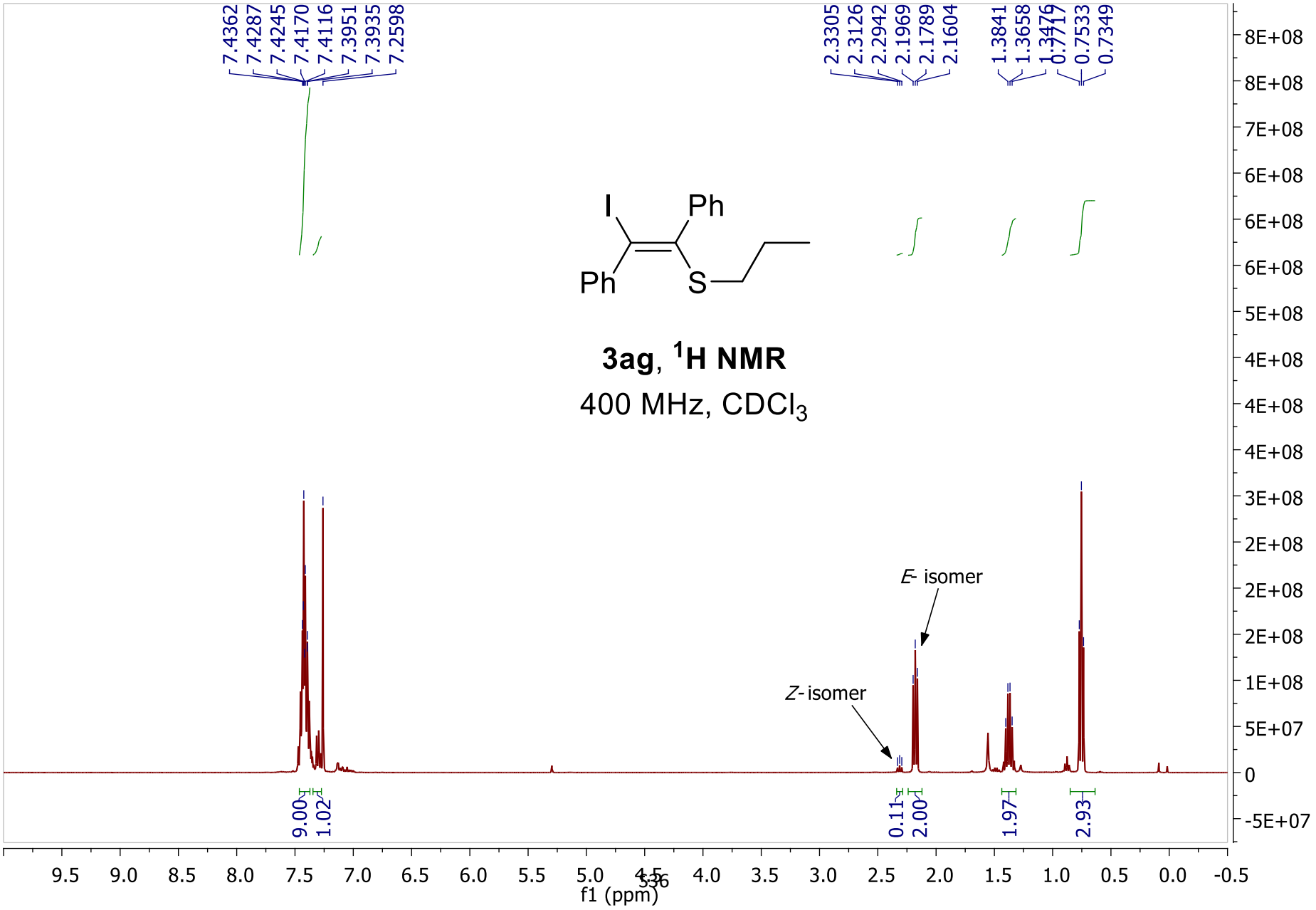
141.3218
137.1775
129.8543
129.4027
128.6175
128.3504
128.1492
128.0541
123.4708
104.7157
I
Ph
Ph
S
NO2
3af, 13C NMR
100 MHz, CDCl3
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4116
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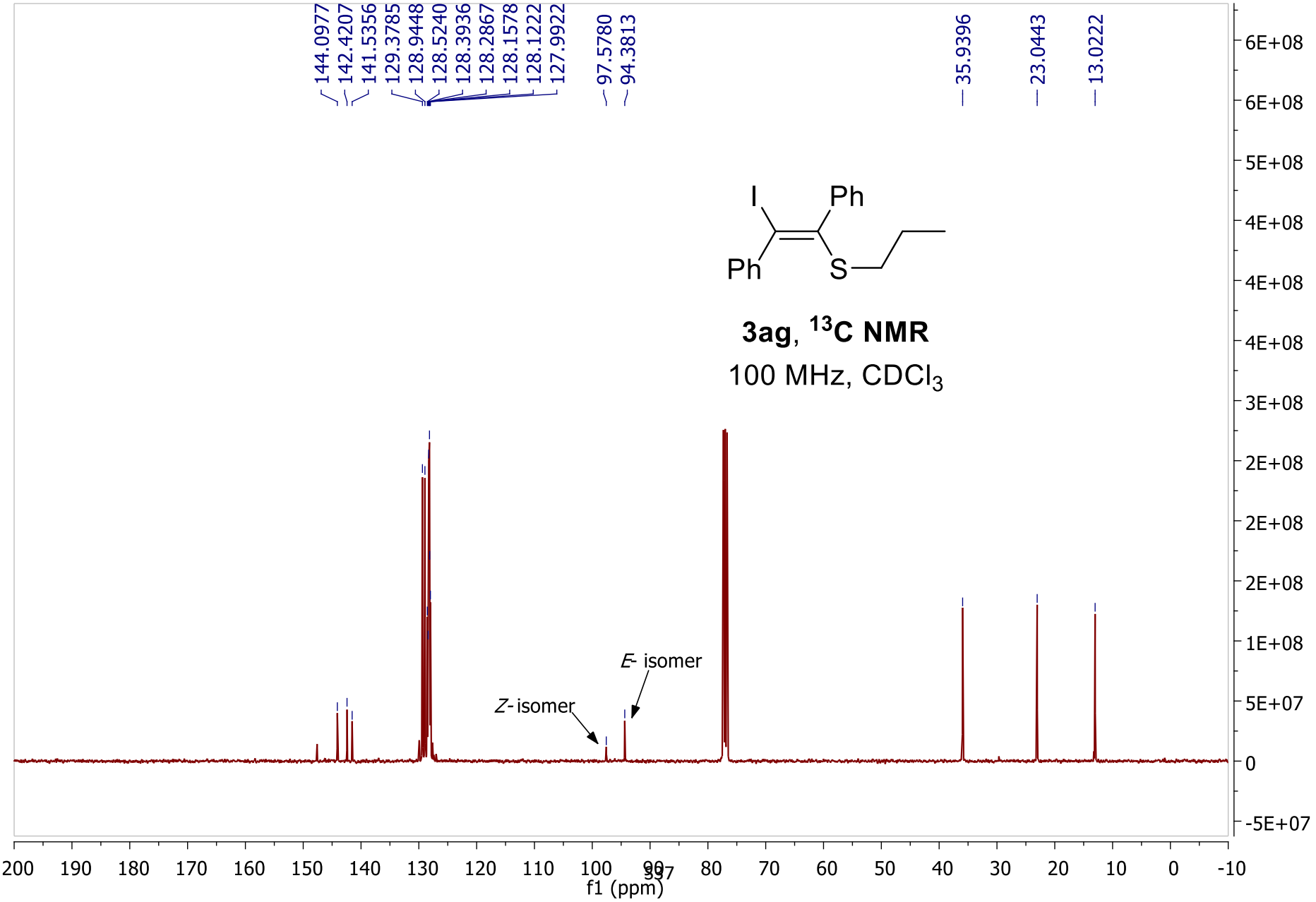
7.3935
7.2598
2.3305
2.3126
2.2942
2.1969
2.1789
2.1604
1.3841
1.3658
1.3476
0.7717
0.7533
0.7349
I
Ph
Ph
S
3ag, 1H NMR
400 MHz, CDCl3
E- isomer
Z- isomer
9.00
1.02
0.11
2.00
1.97
2.93
f1 (ppm)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128.3936
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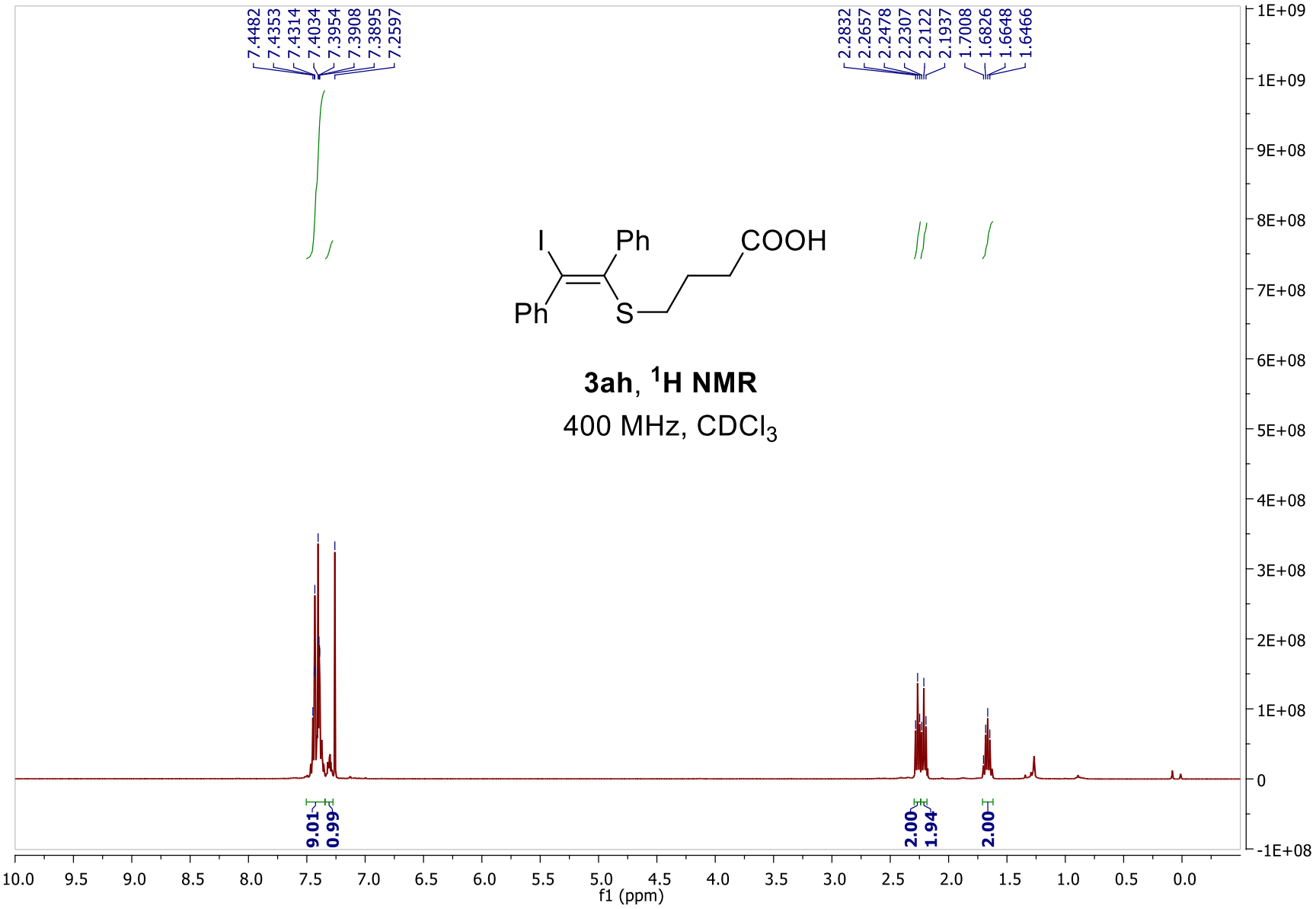
128.1578
128.1222
127.9922
97.5780
94.3813
35.9396
23.0443
13.0222
I
Ph
Ph
S
3ag, 13C NMR
100 MHz, CDCl3
E- isomer
Z- isomer
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.3954
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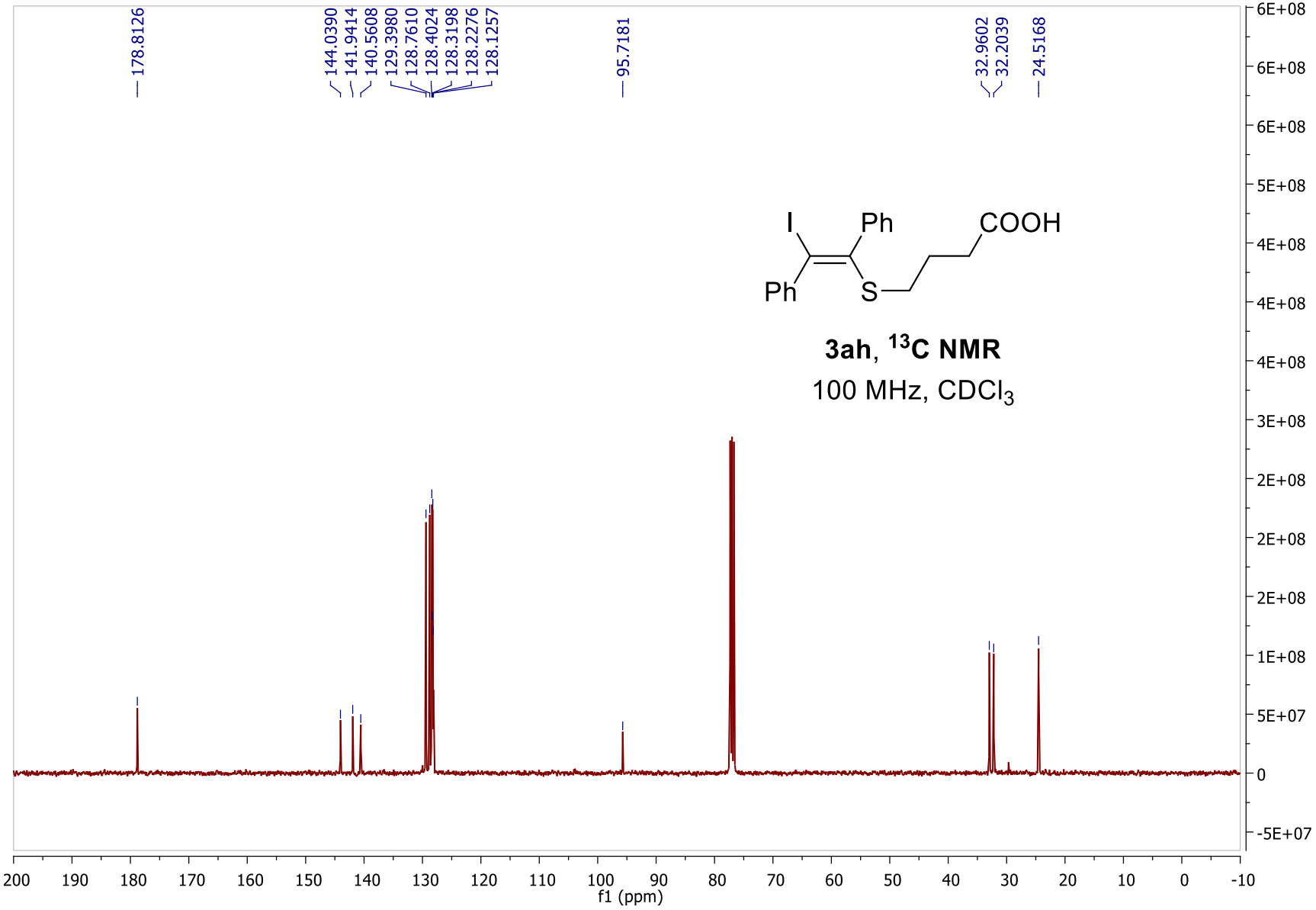
7.3895
7.2597
2.2832
2.2657
2.2478
2.2307
2.2122
2.1937
1.7008
1.6826
1.6648
1.6466
I
Ph
COOH
Ph
S
3ah, 1H NMR
400 MHz, CDCl3
9.01
0.99
2.00
1.94
2.00
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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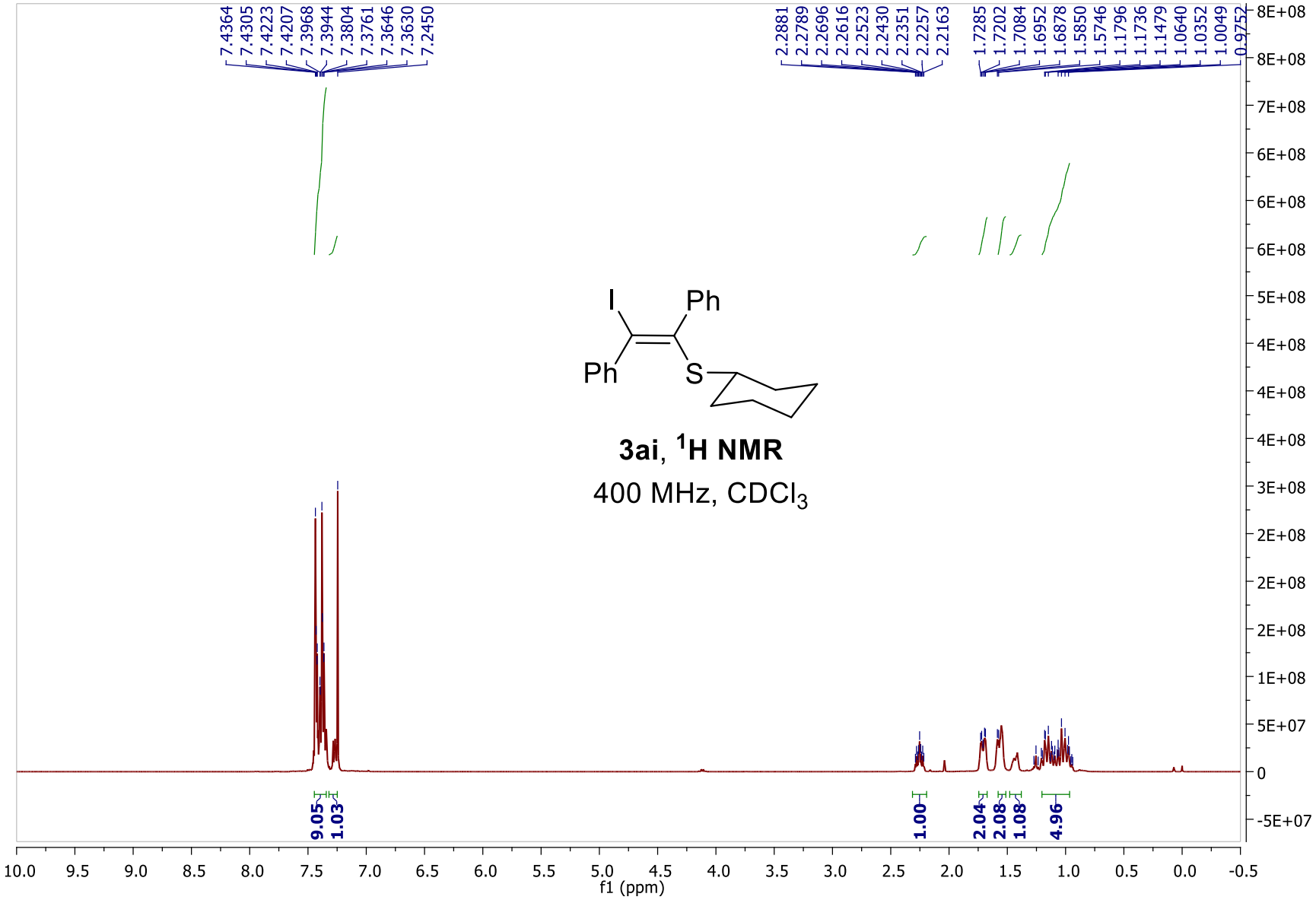
128.1257
95.7181
32.9602
32.2039
24.5168
I
Ph
COOH
Ph
S
3ah, 13C NMR
100 MHz, CDCl3
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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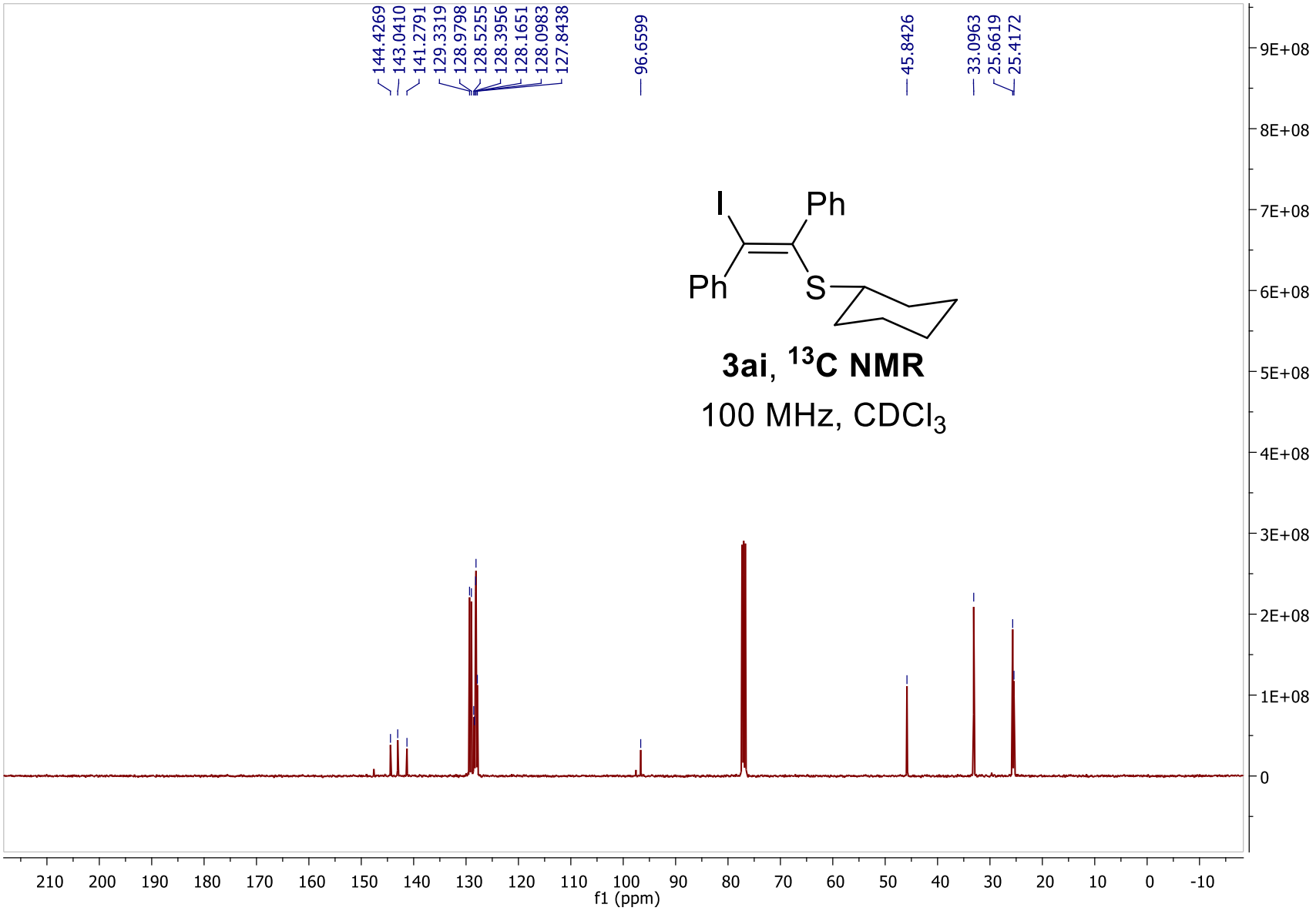
7.3804
7.3761
7.3646
7.3630
7.2450
2.2881
2.2789
2.2696
2.2616
2.2523
2.2430
2.2351
2.2257
2.2163
1.7285
1.7202
1.7084
1.6952
1.6878
1.5850
1.5746
1.1796
1.1736
1.1479
1.0640
1.0352
1.0049
0.9752
I
Ph
Ph
S
3ai, 1H NMR
400 MHz, CDCl3
9.05
1.03
1.00
2.04
2.08
1.08
4.96
f1 (ppm)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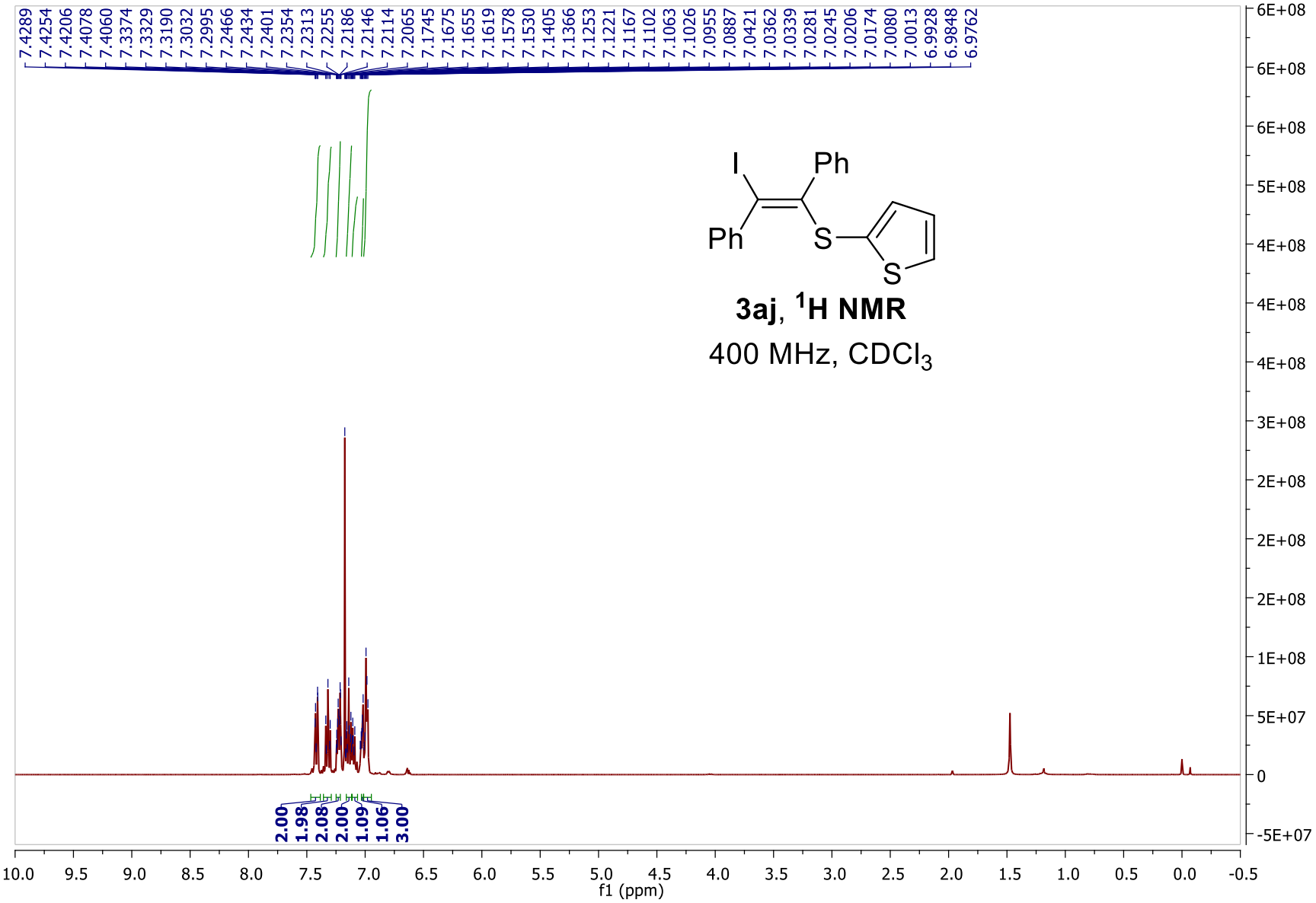
128.5255
128.3956
128.1651
128.0983
127.8438
96.6599
45.8426
33.0963
25.6619
25.4172
I
Ph
Ph
S
3ai, 13C NMR
100 MHz, CDCl3
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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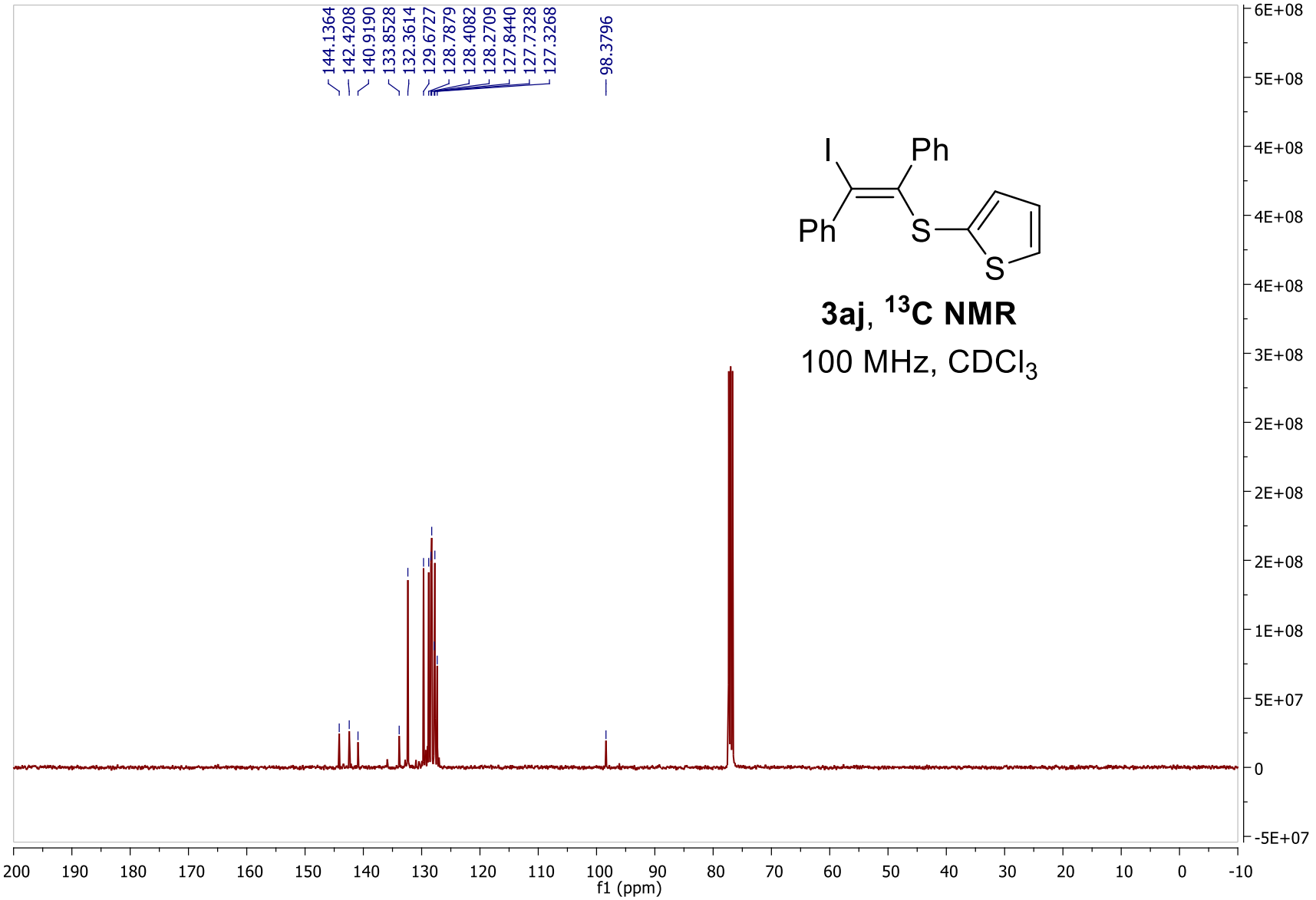
7.3032
7.2995
7.2466
7.2434
7.2401
7.2354
7.2313
7.2255
7.2186
7.2146
7.2114
7.2065
7.1745
7.1675
7.1655
7.1619
7.1578
7.1530
7.1405
7.1366
7.1253
7.1221
7.1167
7.1102
7.1063
7.1026
7.0955
7.0887
7.0421
7.0362
7.0339
7.0281
7.0245
7.0206
7.0174
7.0080
7.0013
6.9928
6.9848
6.9762
I
Ph
Ph
S
S
3aj, 1H NMR
400 MHz, CDCl3
2.00
1.98
2.08
2.00
1.09
1.06
3.00
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
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
f1 (ppm)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128.7879
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128.2709
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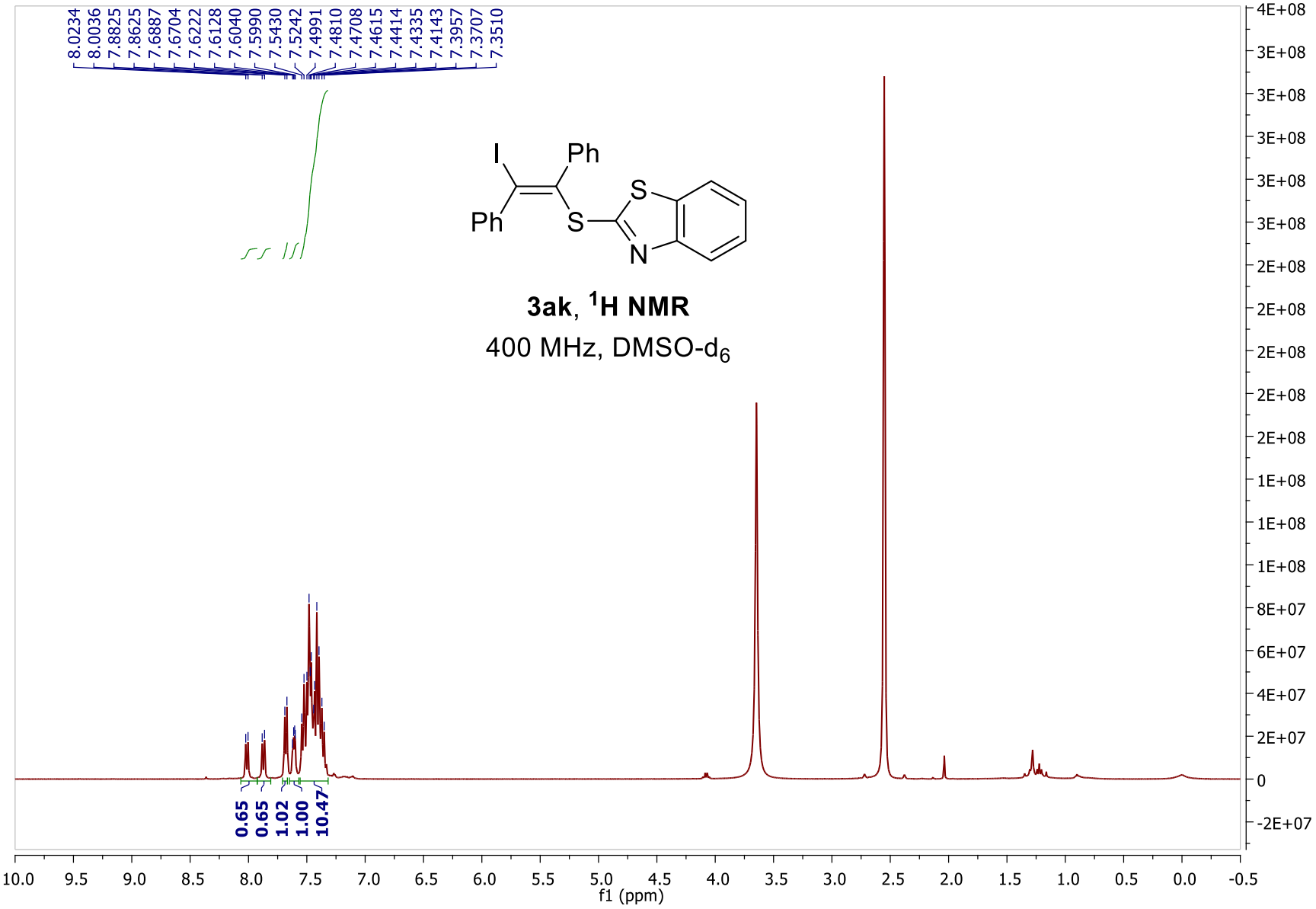
127.7328
127.3268
98.3796
I
Ph
Ph
S
S
3aj, 13C NMR
100 MHz, CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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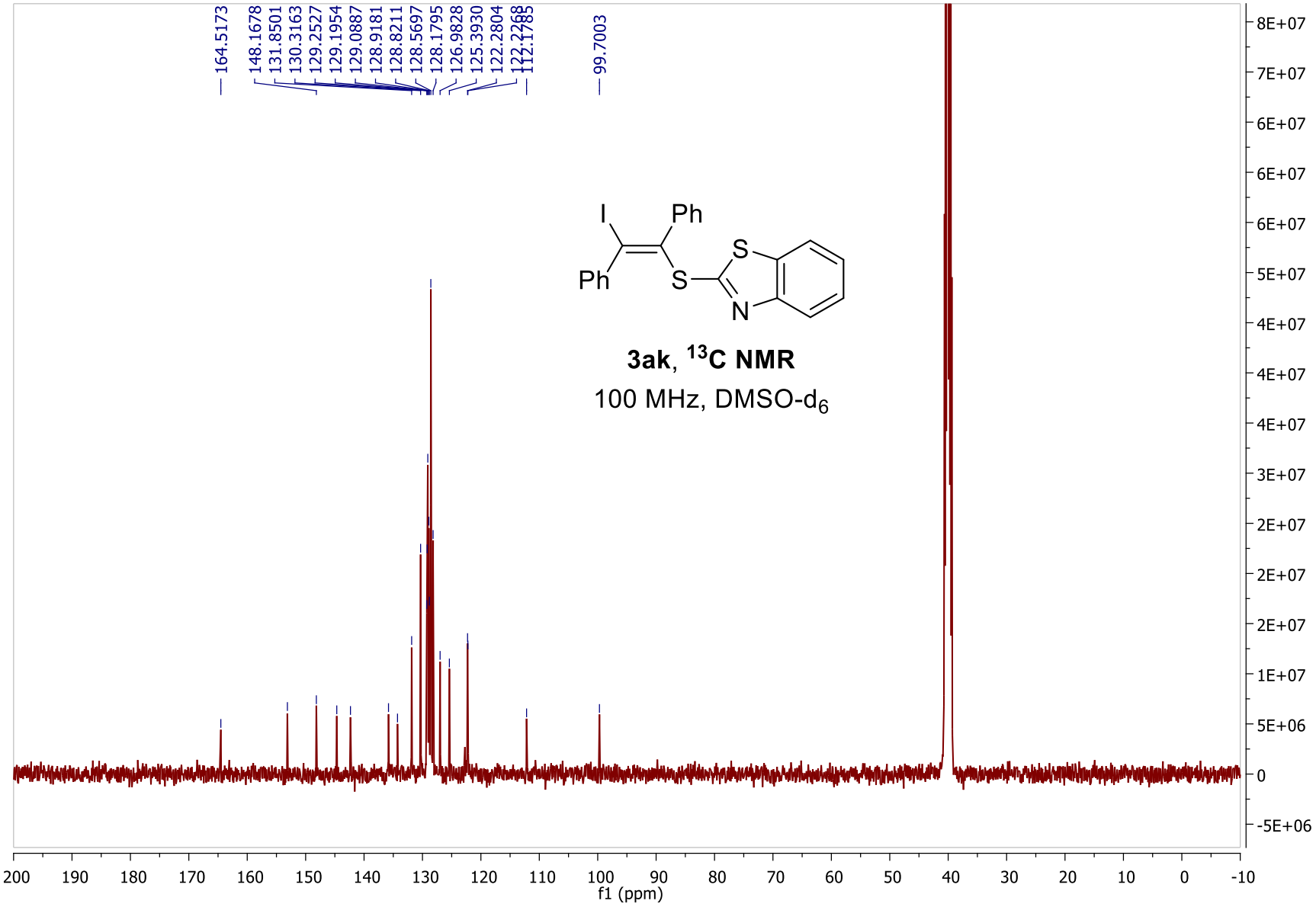
7.6040
7.5990
7.5430
7.5242
7.4991
7.4810
7.4708
7.4615
7.4414
7.4335
7.4143
7.3957
7.3707
7.3510
I
Ph
Ph
S
S
N
3ak, 1H NMR
400 MHz, DMSO-d6
0.65
0.65
1.02
1.00
10.47
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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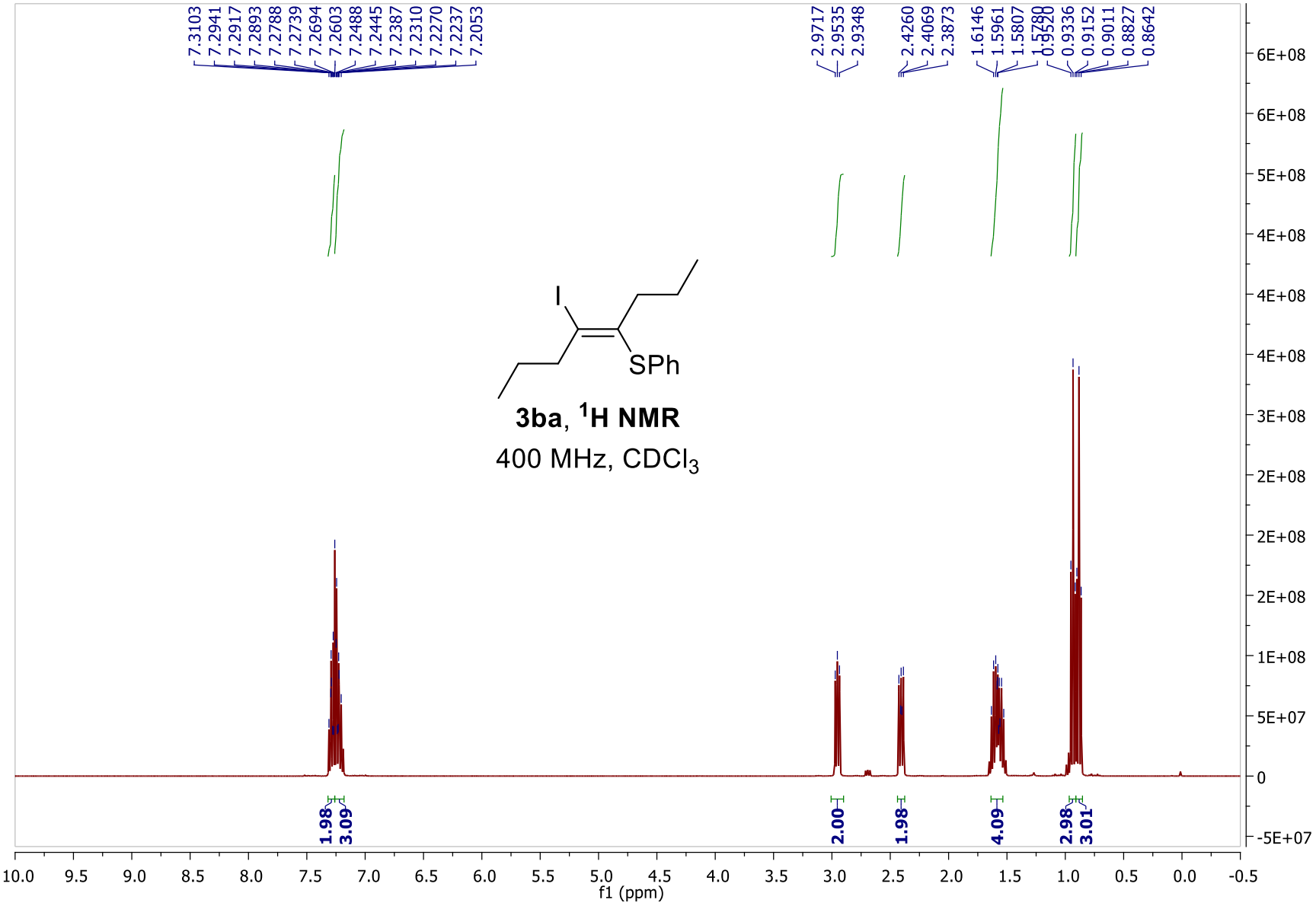
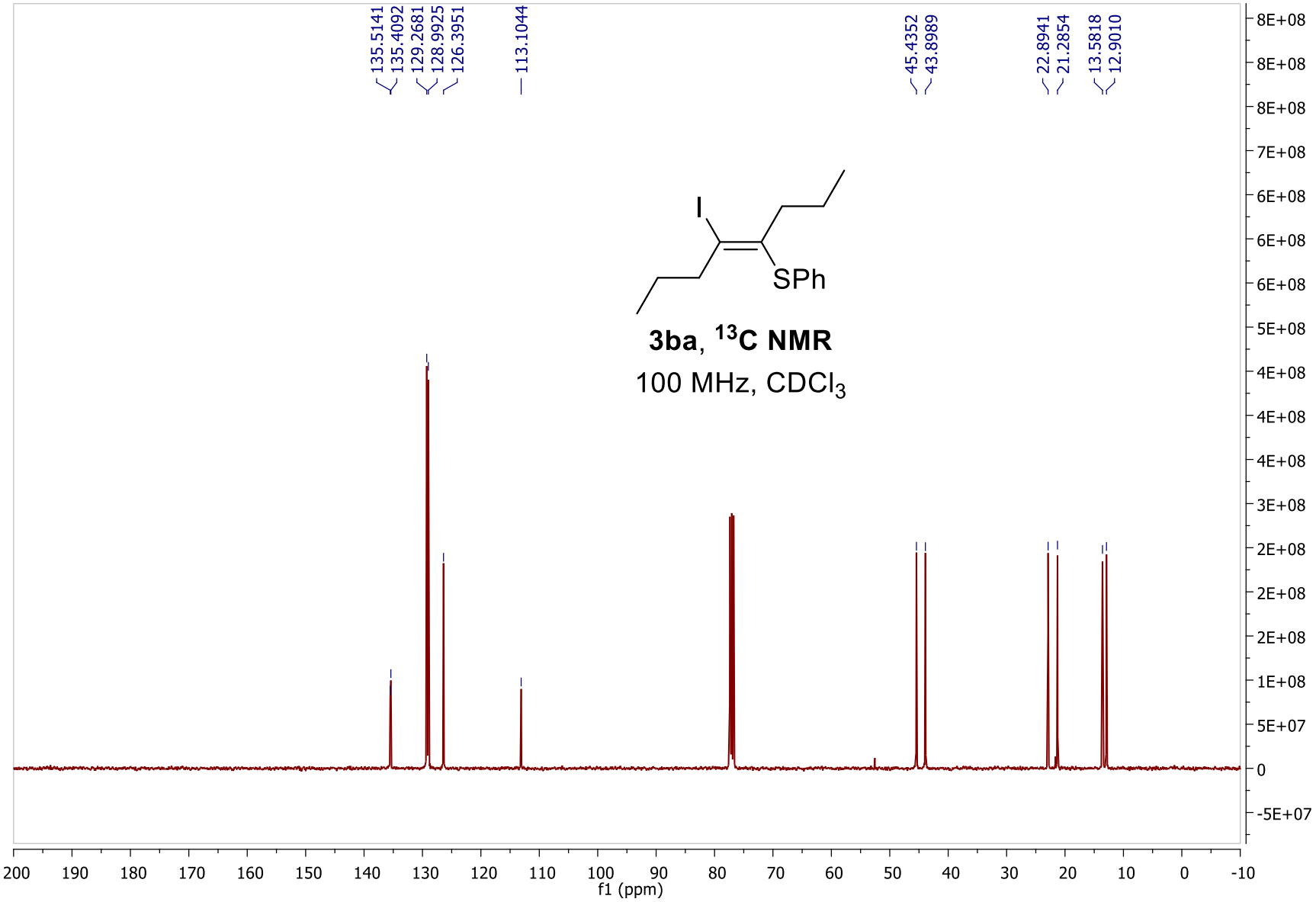
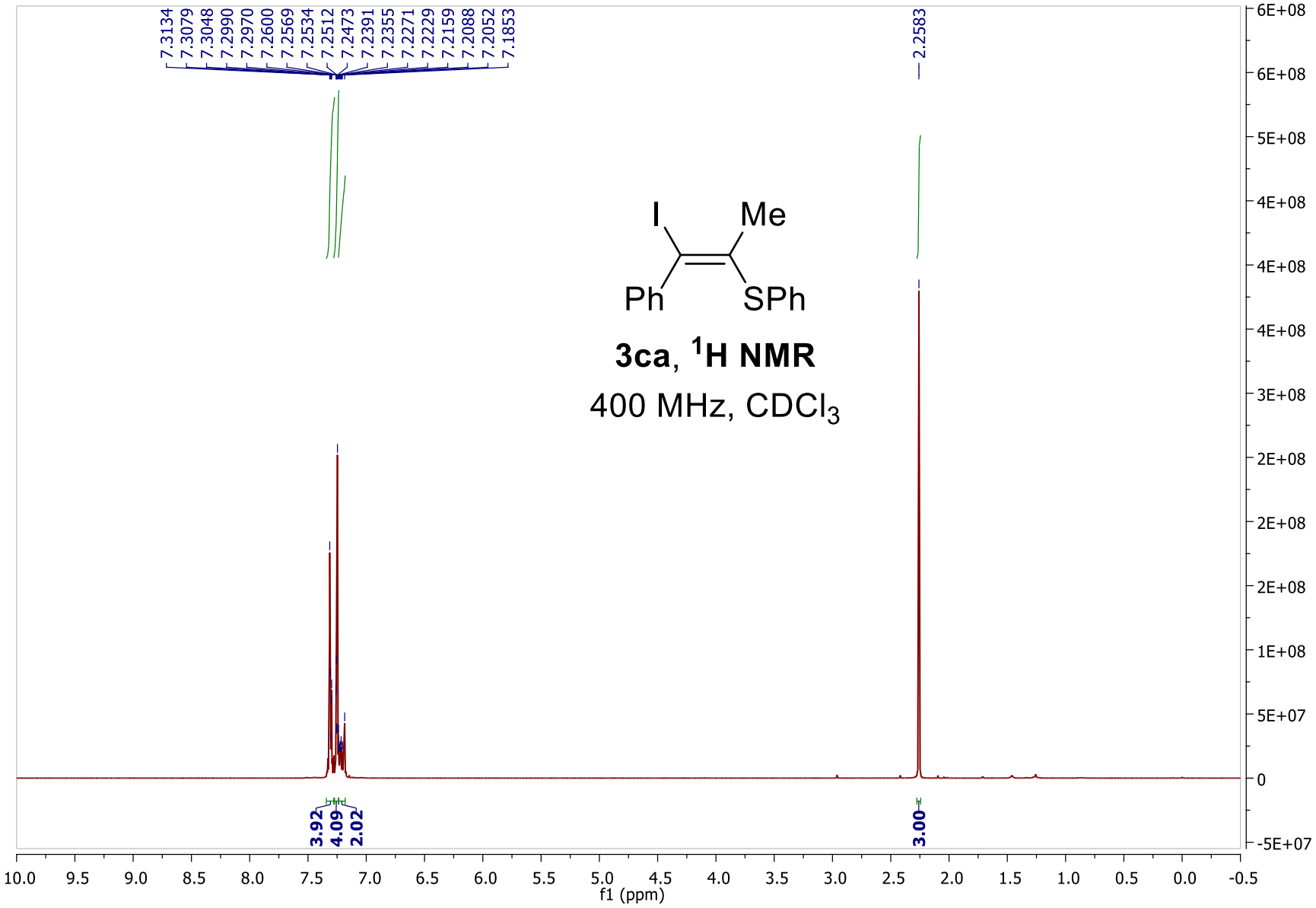
131.8501
130.3163
129.2527
129.1954
129.0887
128.9181
128.8211
128.5697
128.1795
126.9828
125.3930
122.2804
99.7003
I
Ph
Ph
S
S
N
3ak, 13C NMR
100 MHz, DMSO-d6
8E+07
7E+07
6E+07
6E+07
6E+07
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
-5E+06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.3103
7.2941
7.2917
7.2893
7.2788
7.2739
7.2694
7.2603
7.2488
7.2445
7.2387
7.2310
7.2270
7.2237
7.2053
2.9717
2.9535
2.9348
2.4260
2.4069
2.3873
1.6146
1.5961
1.5807
1.5780
1.5520
0.9336
0.9152
0.9011
0.8827
0.8642
I
SPh
3ba, 1H NMR
400 MHz, CDCl3
1.98
3.09
2.00
1.98
4.09
2.98
3.01
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
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
f1 (ppm)


135.5141
135.4092
129.2681
128.9925
126.3951
113.1044
45.4352
43.8989
22.8941
21.2854
13.5818
12.9010
I
SPh
3ba, 13C NMR
100 MHz, CDCl3
f1 (ppm)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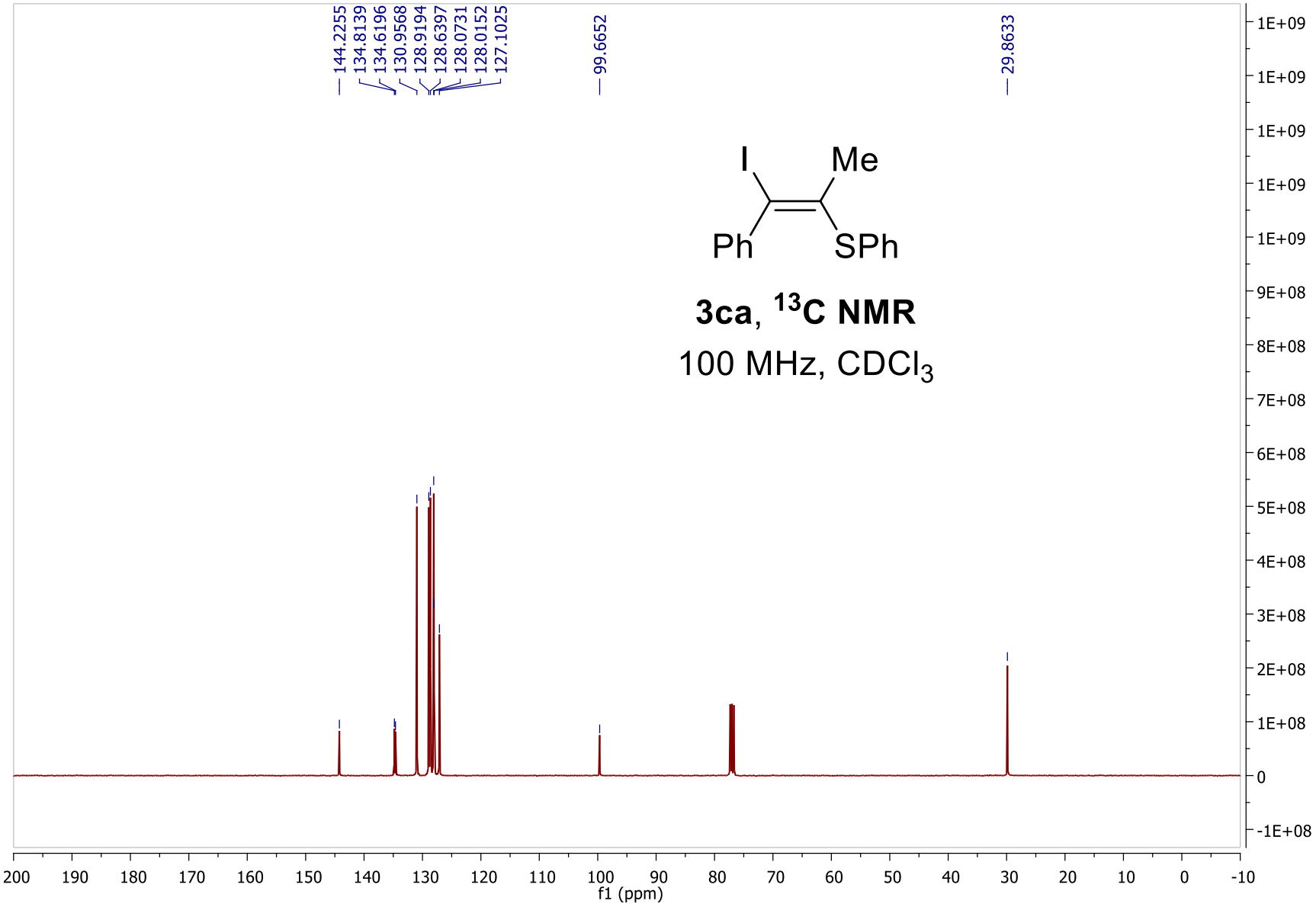
7.3079
7.3048
7.2990
7.2970
7.2600
7.2569
7.2534
7.2512
7.2473
7.2391
7.2355
7.2271
7.2229
7.2159
7.2088
7.2052
7.1853
2.2583
I
Me
Ph
SPh
3ca, 1H NMR
400 MHz, CDCl3
3.92
4.09
2.02
3.00
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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
f1 (ppm)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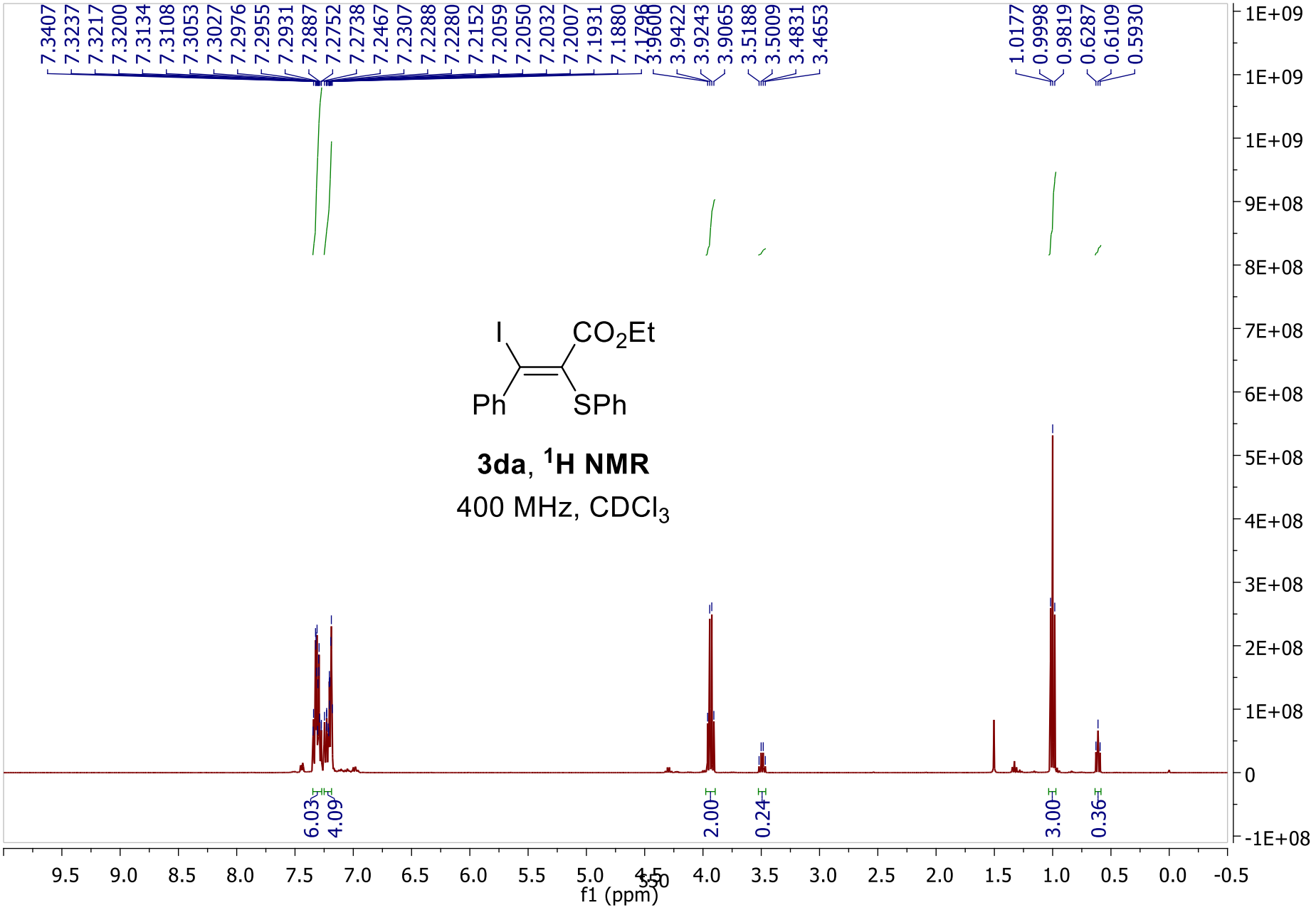
134.8139
134.6196
130.9568
128.9194
128.6397
128.0731
128.0152
127.1025
99.6652
29.8633
I
Me
Ph
SPh
3ca, 13C NMR
100 MHz, CDCl3
1E+09
1E+09
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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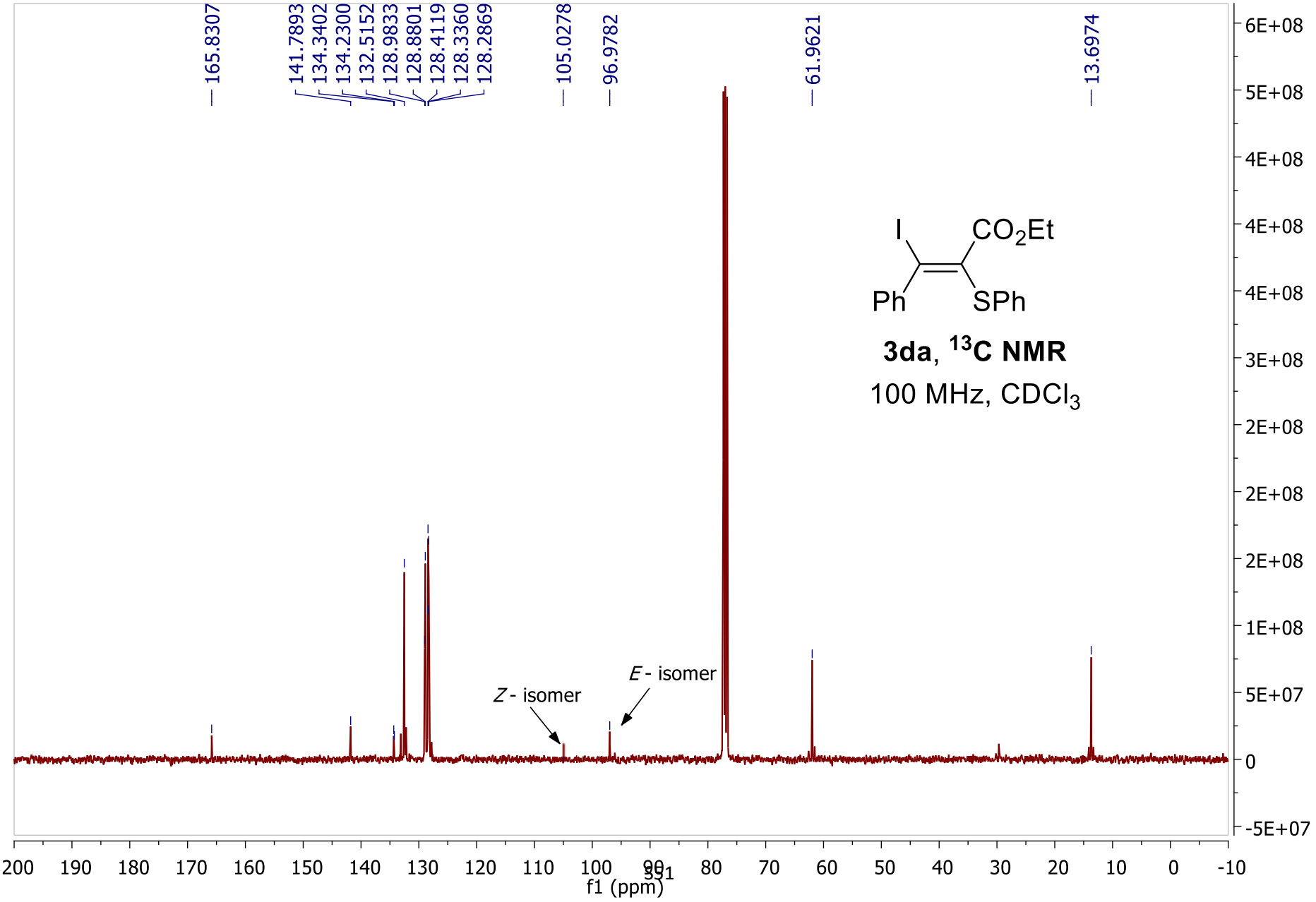
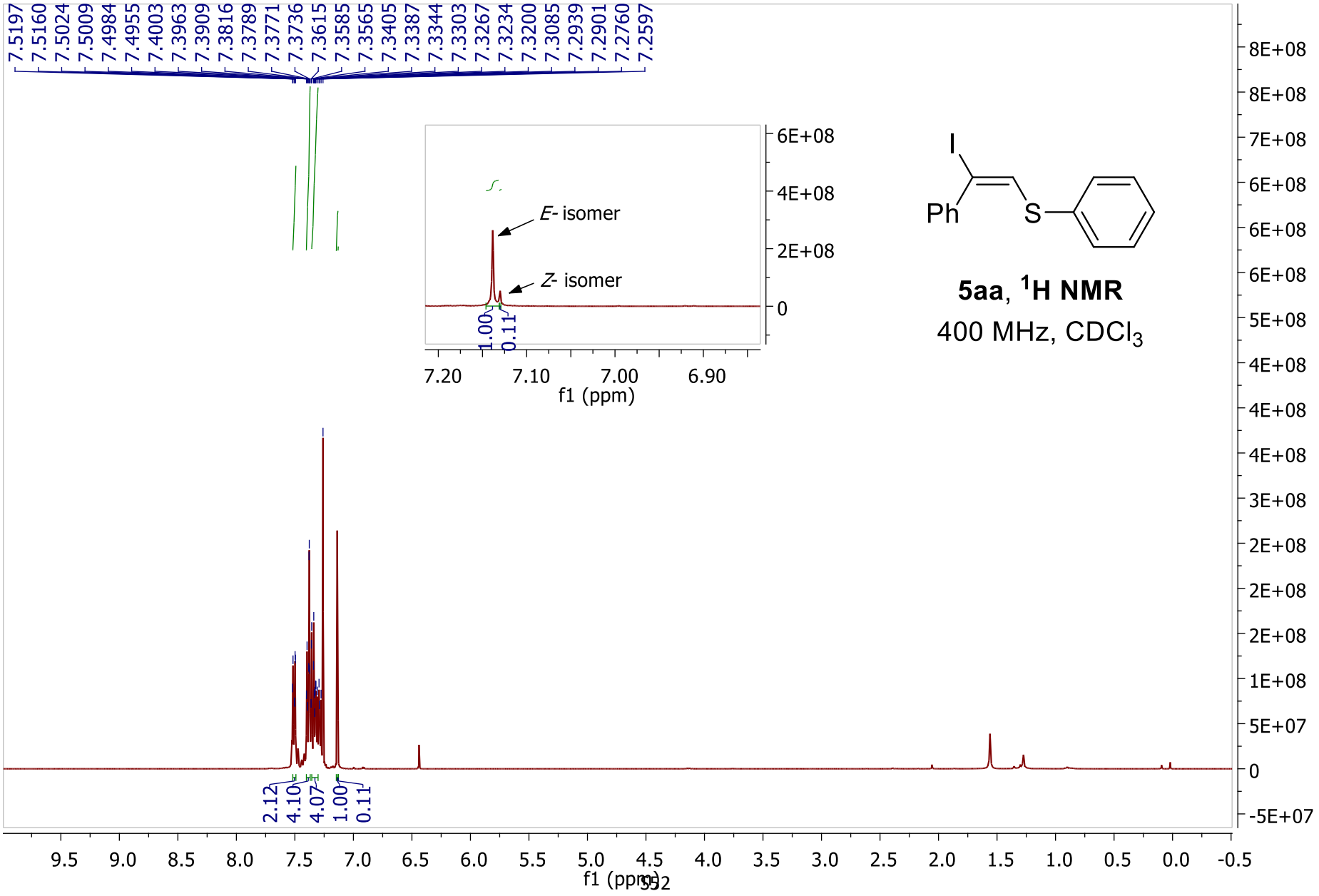
7.3237
7.3217
7.3200
7.3134
7.3108
7.3053
7.3027
7.2976
7.2955
7.2931
7.2887
7.2752
7.2738
7.2467
7.2307
7.2288
7.2280
7.2152
7.2059
7.2050
7.2032
7.2007
7.1931
7.1880
7.1796
3.9600
3.9422
3.9243
3.9065
3.5188
3.5009
3.4831
3.4653
1.0177
0.9998
0.9819
0.6287
0.6109
0.5930
I
CO2Et
Ph
SPh
3da, 1H NMR
400 MHz, CDCl3
6.03
4.09
2.00
0.24
3.00
0.36
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
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
f1 (ppm)


165.8307
141.7893
134.3402
134.2300
132.5152
128.9833
128.8801
128.4119
128.3360
128.2869
105.0278
96.9782
61.9621
13.6974
I
CO2Et
Ph
SPh
3da, 13C NMR
100 MHz, CDCl3
Z - isomer
E - isomer
f1 (ppm)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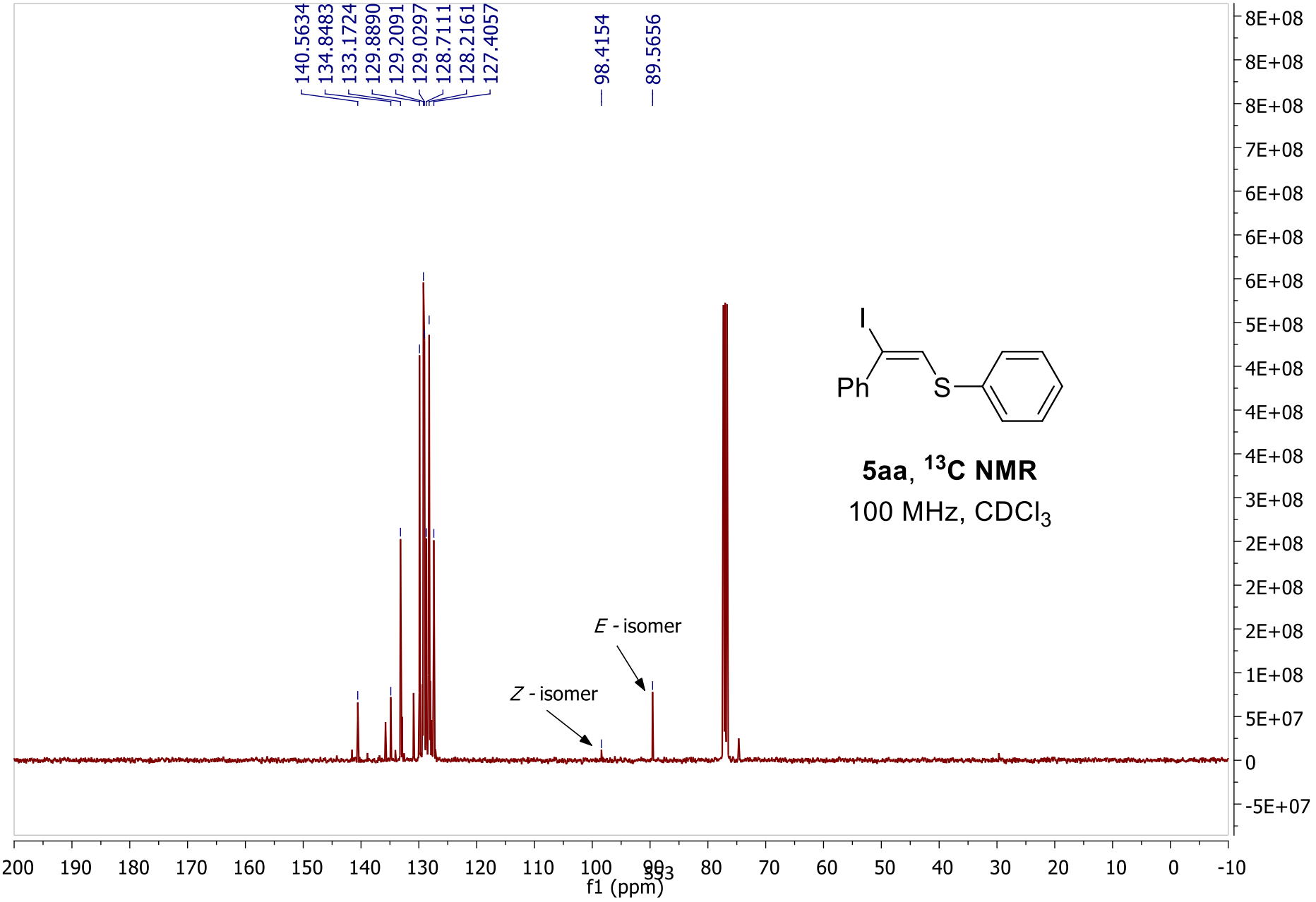
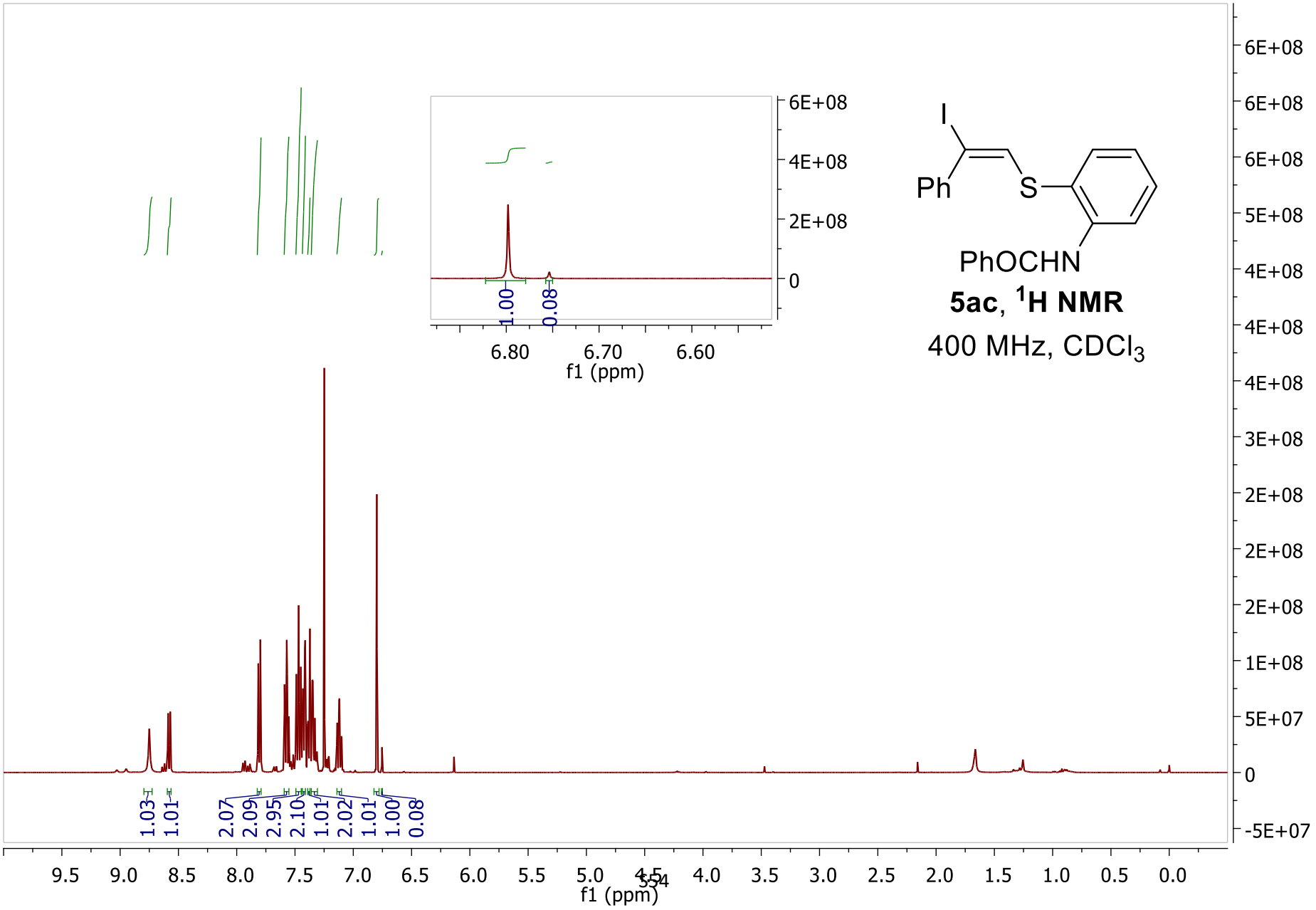
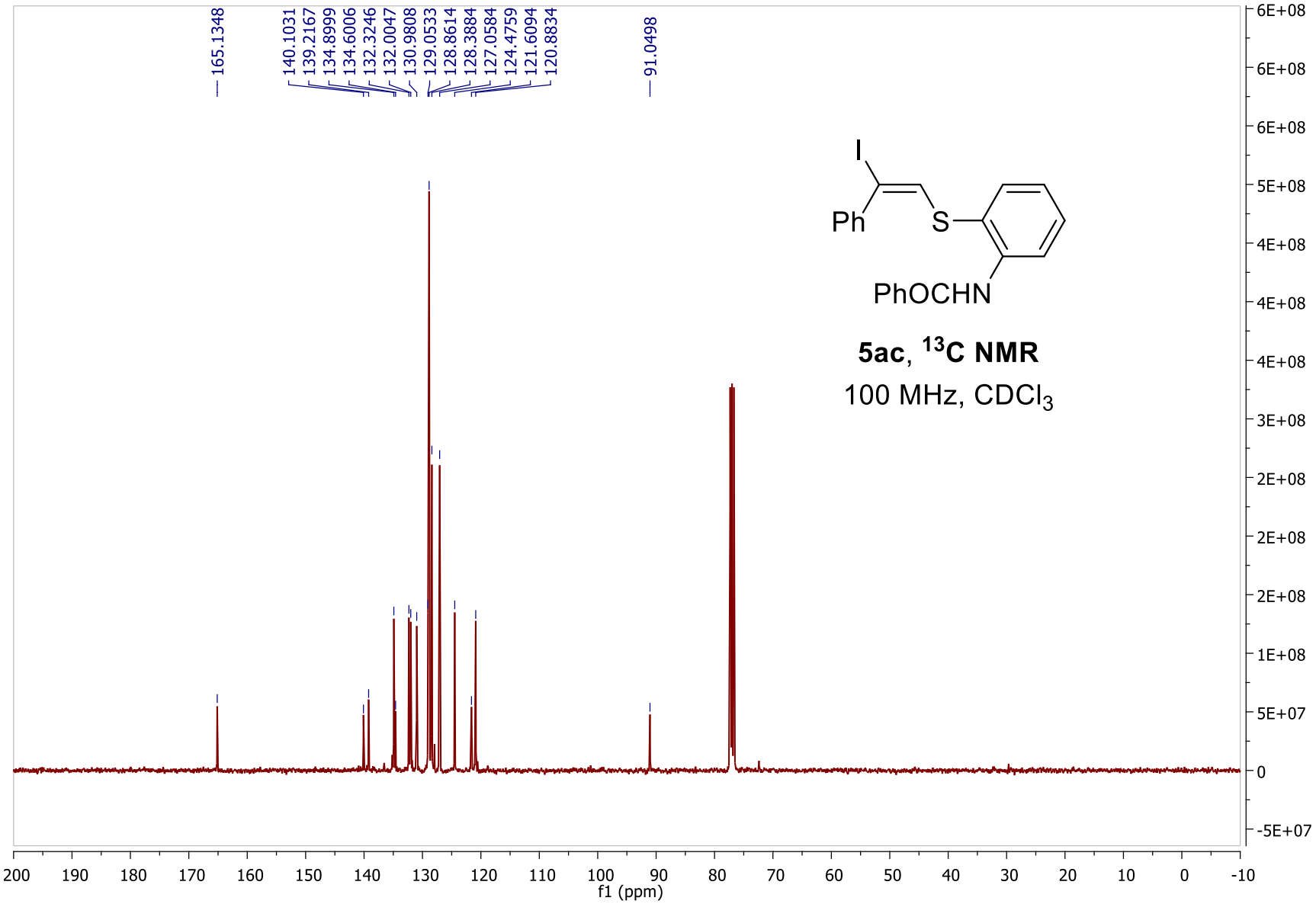
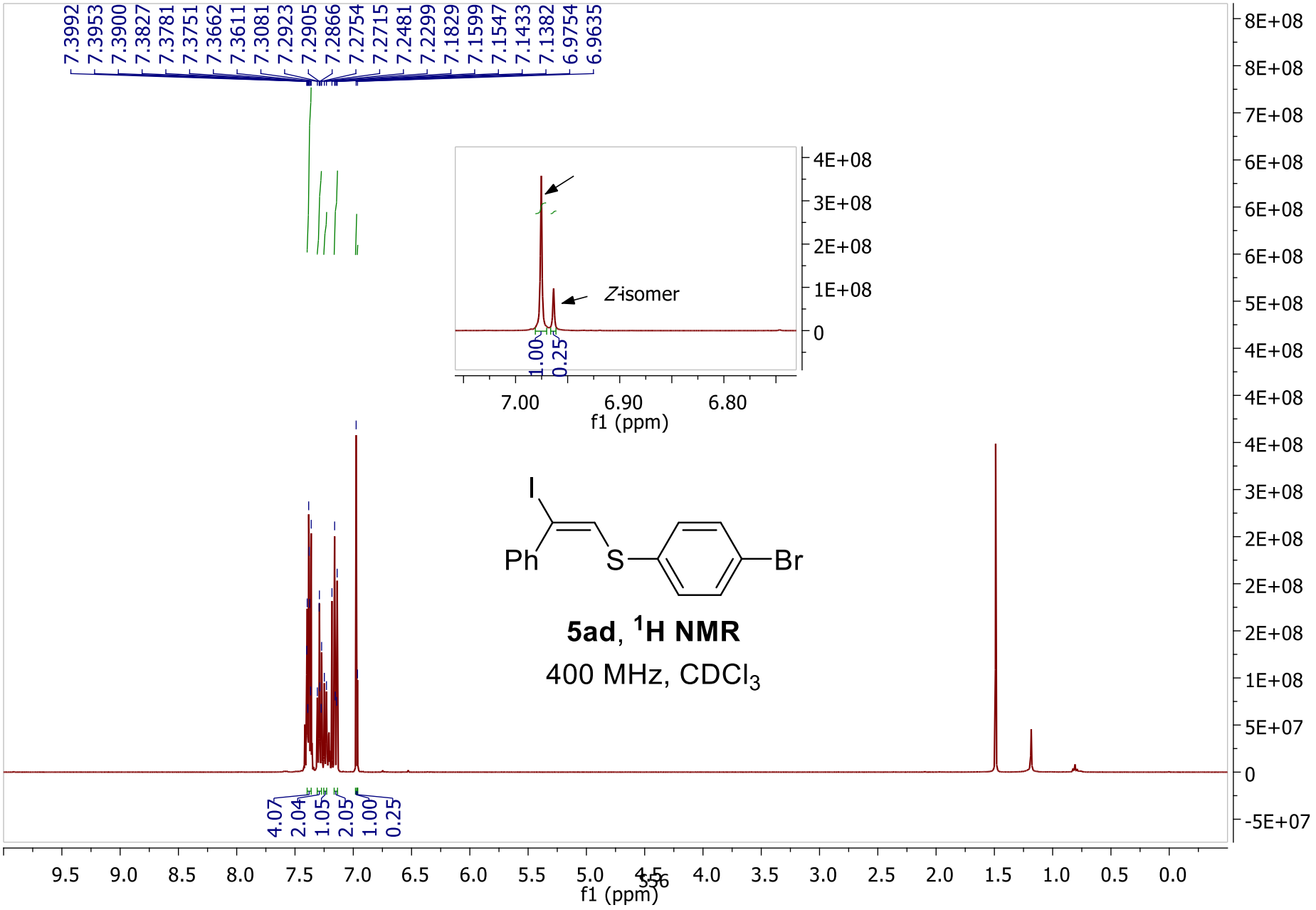
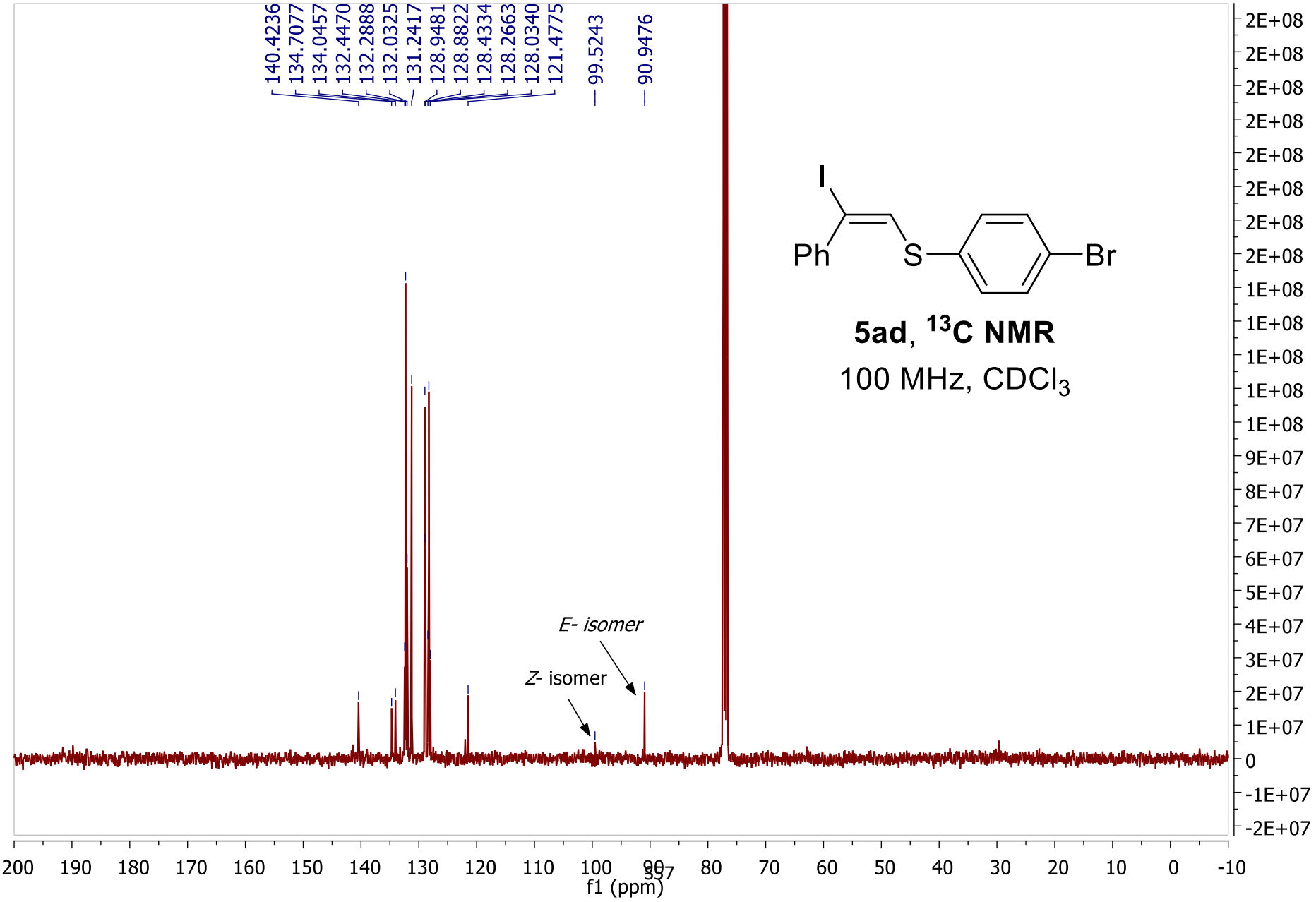
7.5160
7.5024
7.5009
7.4984
7.4955
7.4003
7.3963
7.3909
7.3816
7.3789
7.3771
7.3736
7.3615
7.3585
7.3565
7.3405
7.3387
7.3344
7.3303
7.3267
7.3234
7.3200
7.3085
7.2939
7.2901
7.2760
7.2597
E- isomer
Z- isomer
1.00
0.11
7.20
7.10
7.00
6.90
f1 (ppm)
6E+08
4E+08
2E+08
0
I
Ph
S
5aa, 1H NMR
400 MHz, CDCl3
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
-5E+07
2.12
4.10
4.07
1.00
0.11
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
f1 (ppm)


140.5634
134.8483
133.1724
129.8890
129.2091
129.0297
128.7111
128.2161
127.4057
98.4154
89.5656
I
Ph
S
5aa, 13C NMR
100 MHz, CDCl3
E - isomer
Z - isomer
f1 (ppm)


I
Ph
S
PhOCHN
5ac, 1H NMR
400 MHz, CDCl3
f1 (ppm)
1.00
0.08
1.03
1.01
2.07
2.09
2.95
2.10
1.01
2.02
1.01
1.00
0.08


165.1348
140.1031
139.2167
134.8999
134.6006
132.3246
132.0047
130.9808
129.0533
128.8614
128.3884
127.0584
124.4759
121.6094
120.8834
91.0498
I
Ph
S
PhOCHN
5ac, 13C NMR
100 MHz, CDCl3
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.3992
7.3953
7.3900
7.3827
7.3781
7.3751
7.3662
7.3611
7.3081
7.2923
7.2905
7.2866
7.2754
7.2715
7.2481
7.2299
7.1829
7.1599
7.1547
7.1433
7.1382
6.9754
6.9635
Z-isomer
1.00
0.25
7.00
6.90
6.80
f1 (ppm)
I
Ph
S
Br
5ad, 1H NMR
400 MHz, CDCl3
4.07
2.04
1.05
2.05
1.00
0.25
f1 (ppm)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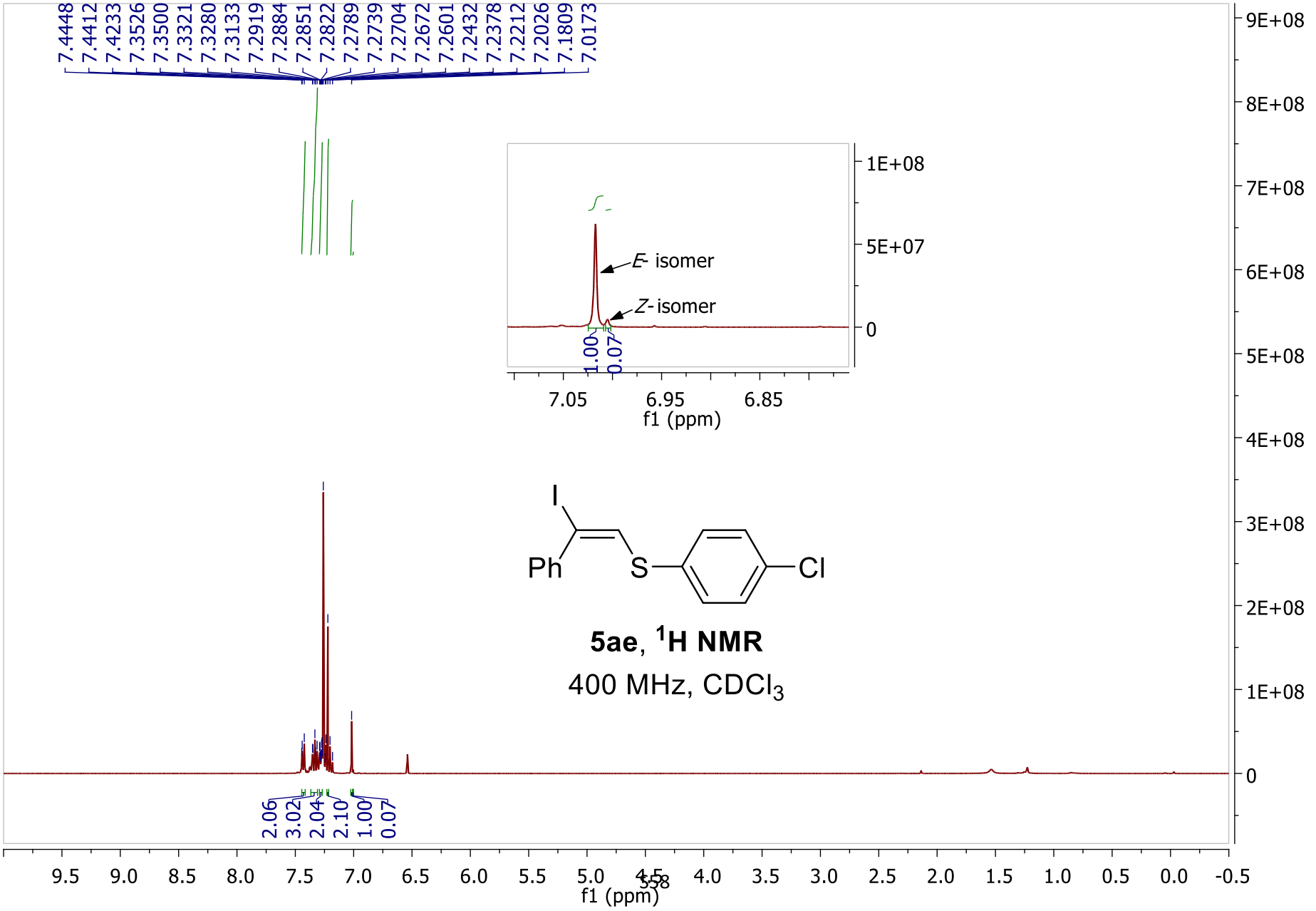
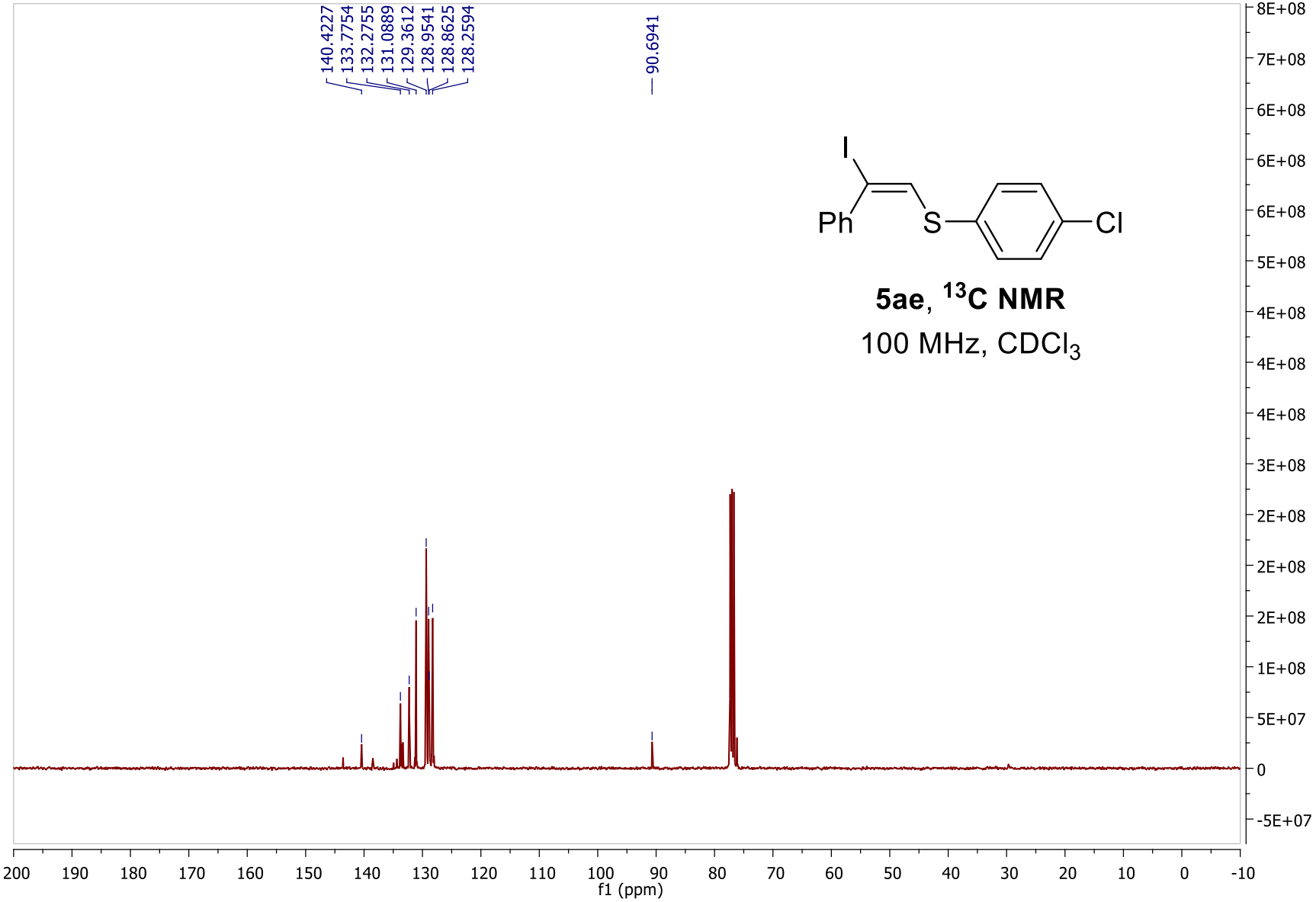
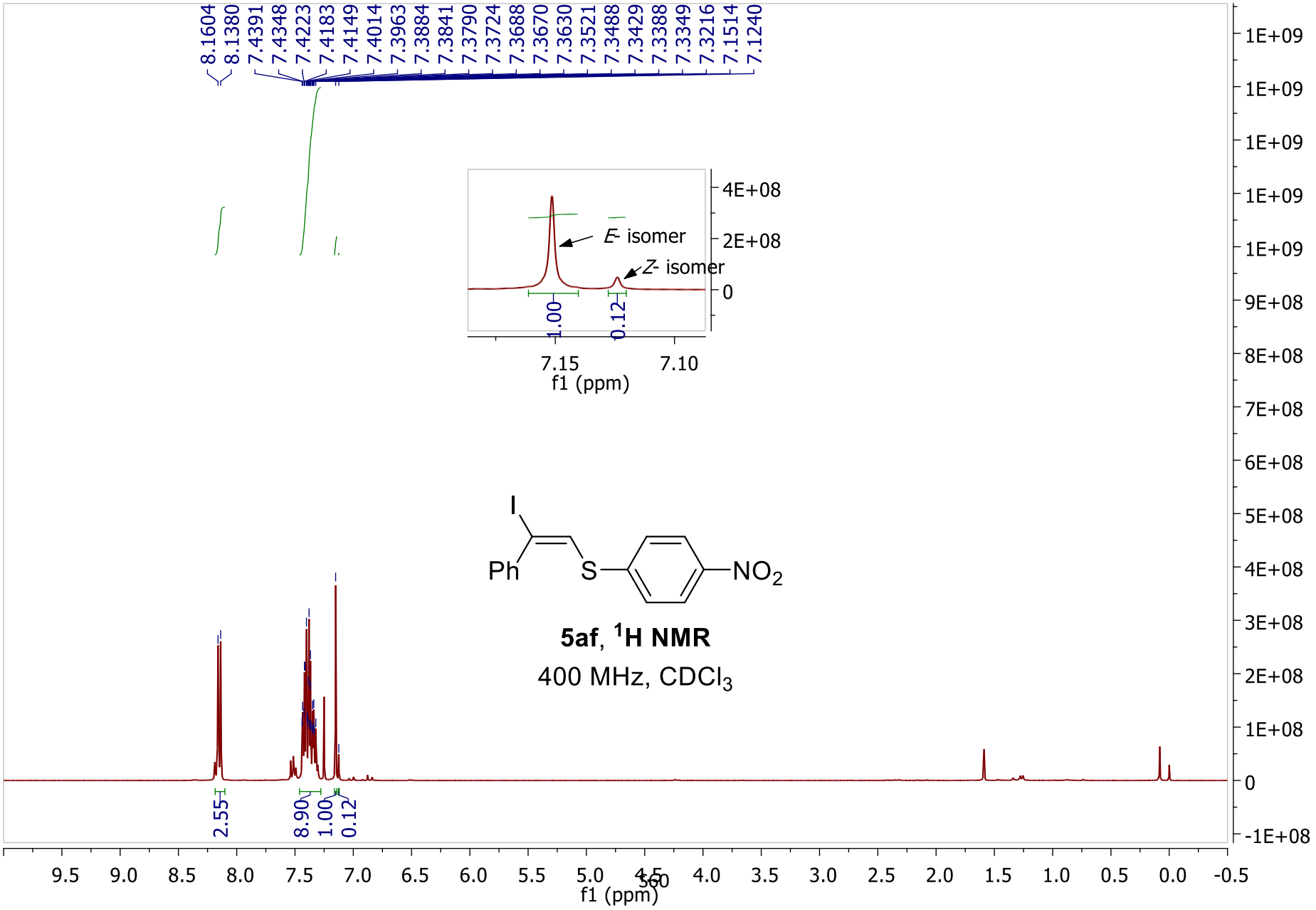
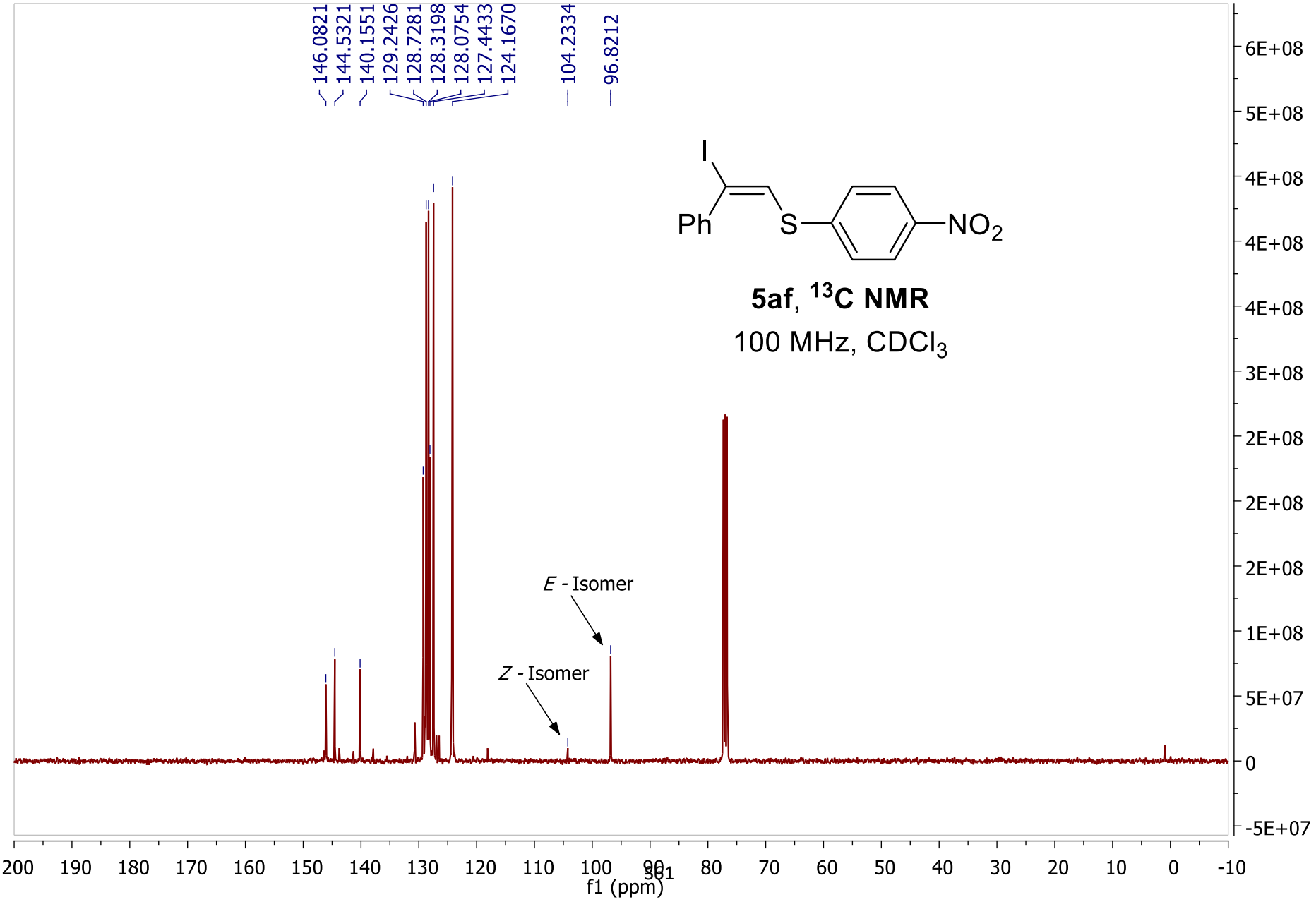
134.7077
134.0457
132.4470
132.2888
132.0325
131.2417
128.9481
128.8822
128.4334
128.2663
128.0340
121.4775
99.5243
90.9476
I
Ph
S
Br
5ad, 13C NMR
100 MHz, CDCl3
E- isomer
Z- isomer
f1 (ppm)


7.4448
7.4412
7.4233
7.3526
7.3500
7.3321
7.3280
7.3133
7.2919
7.2884
7.2851
7.2822
7.2789
7.2739
7.2704
7.2672
7.2601
7.2432
7.2378
7.2212
7.2026
7.1809
7.0173
E- isomer
Z- isomer
1.00
0.07
7.05
6.95
6.85
f1 (ppm)
1E+08
5E+07
0
I
Ph
S
Cl
5ae, 1H NMR
400 MHz, CDCl3
2.06
3.02
2.04
2.10
1.00
0.07
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
f1 (ppm)
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0


140.4227
133.7754
132.2755
131.0889
129.3612
128.9541
128.8625
128.2594
90.6941
I
Ph
S
Cl
5ae, 13C NMR
100 MHz, CDCl3
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.1604
8.1380
7.4391
7.4348
7.4223
7.4183
7.4149
7.4014
7.3963
7.3884
7.3841
7.3790
7.3724
7.3688
7.3670
7.3630
7.3521
7.3488
7.3429
7.3388
7.3349
7.3216
7.1514
7.1240
E- isomer
Z- isomer
1.00
0.12
7.15
7.10
f1 (ppm)
4E+08
2E+08
0
I
Ph
S
NO2
5af, 1H NMR
400 MHz, CDCl3
2.55
8.90
1.00
0.12
f1 (ppm)
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
-1E+08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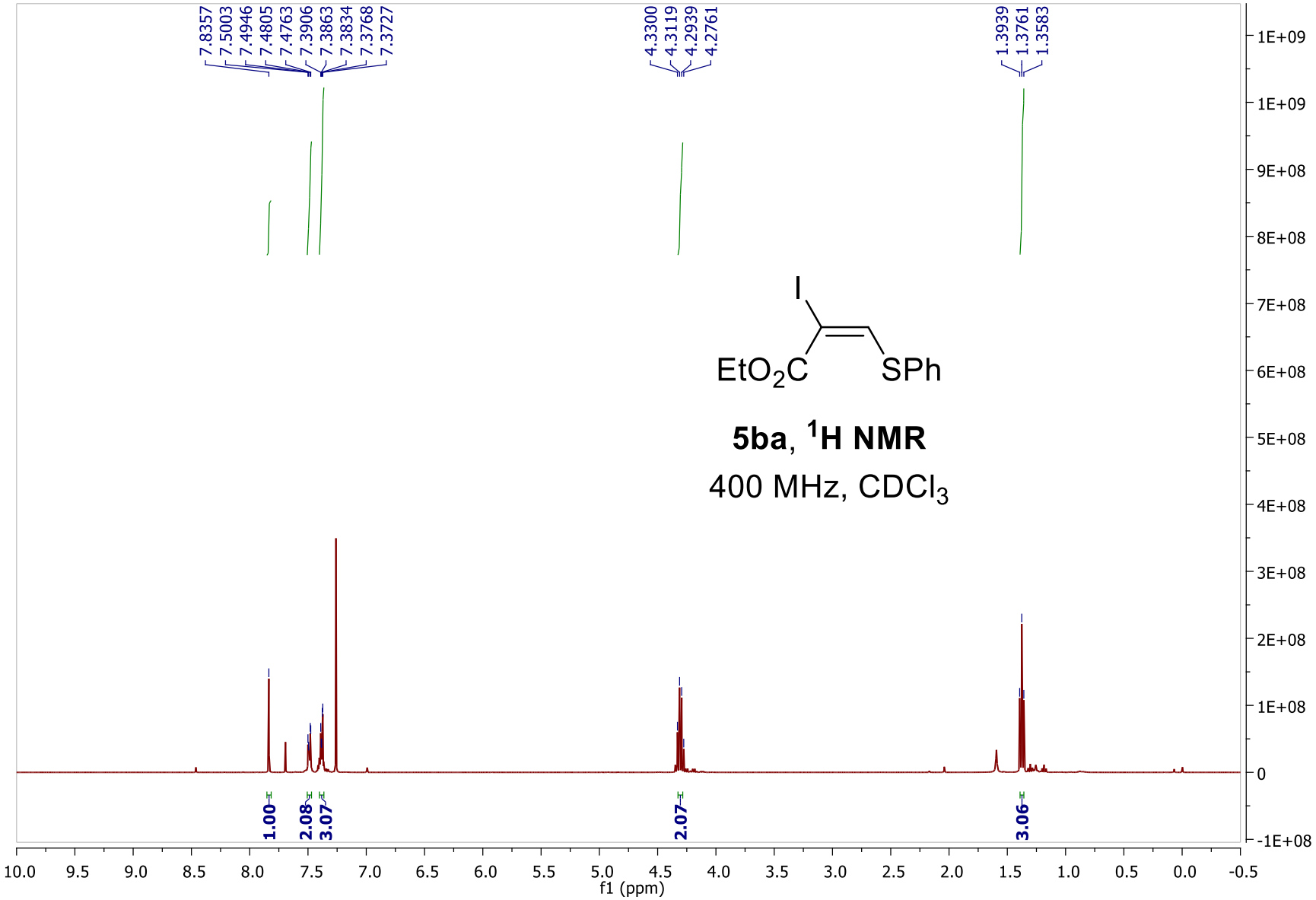
144.5321
140.1551
129.2426
128.7281
128.3198
128.0754
127.4433
124.1670
104.2334
96.8212
I
Ph
S
NO2
5af, 13C NMR
100 MHz, CDCl3
E - Isomer
Z - Isomer
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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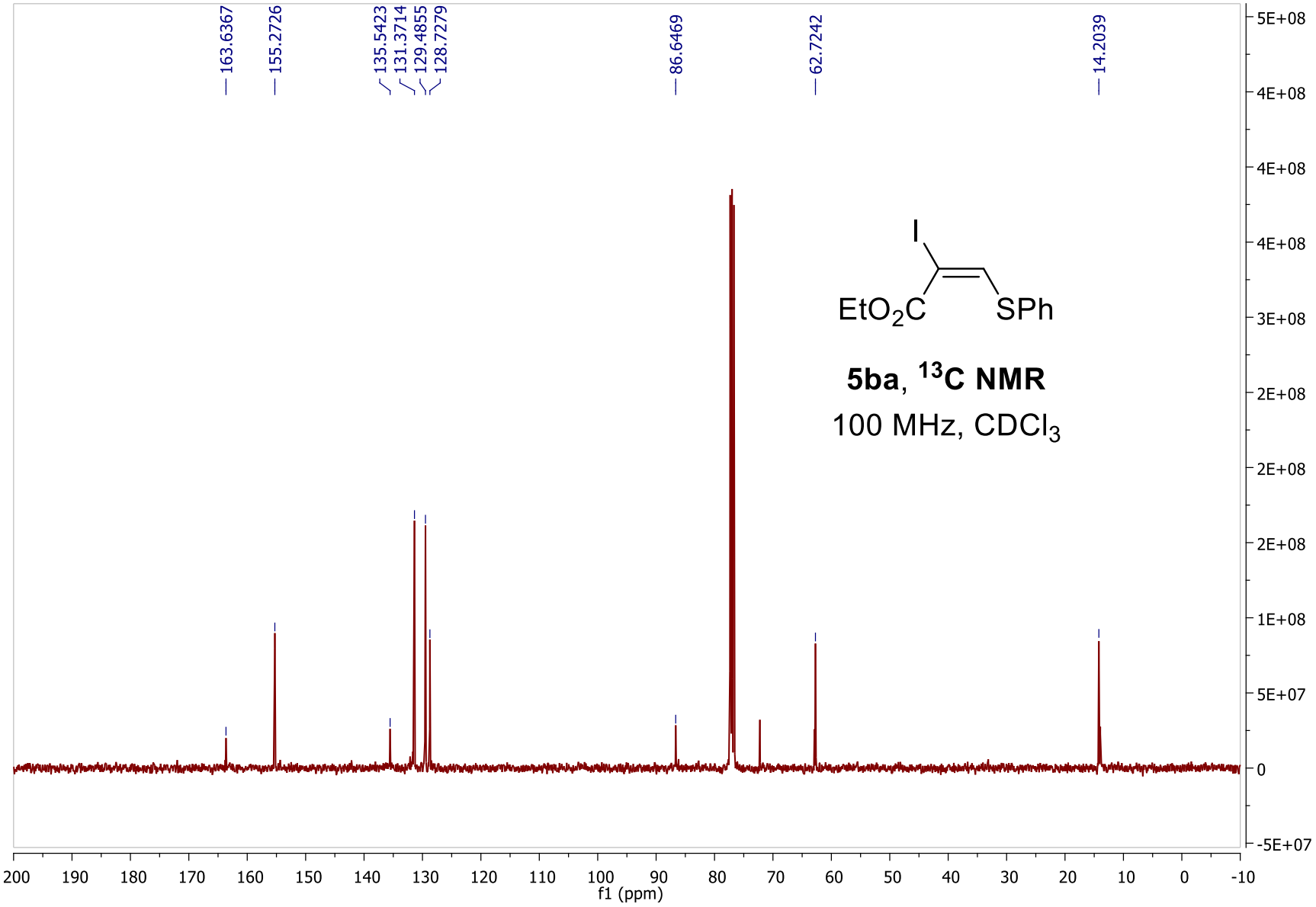
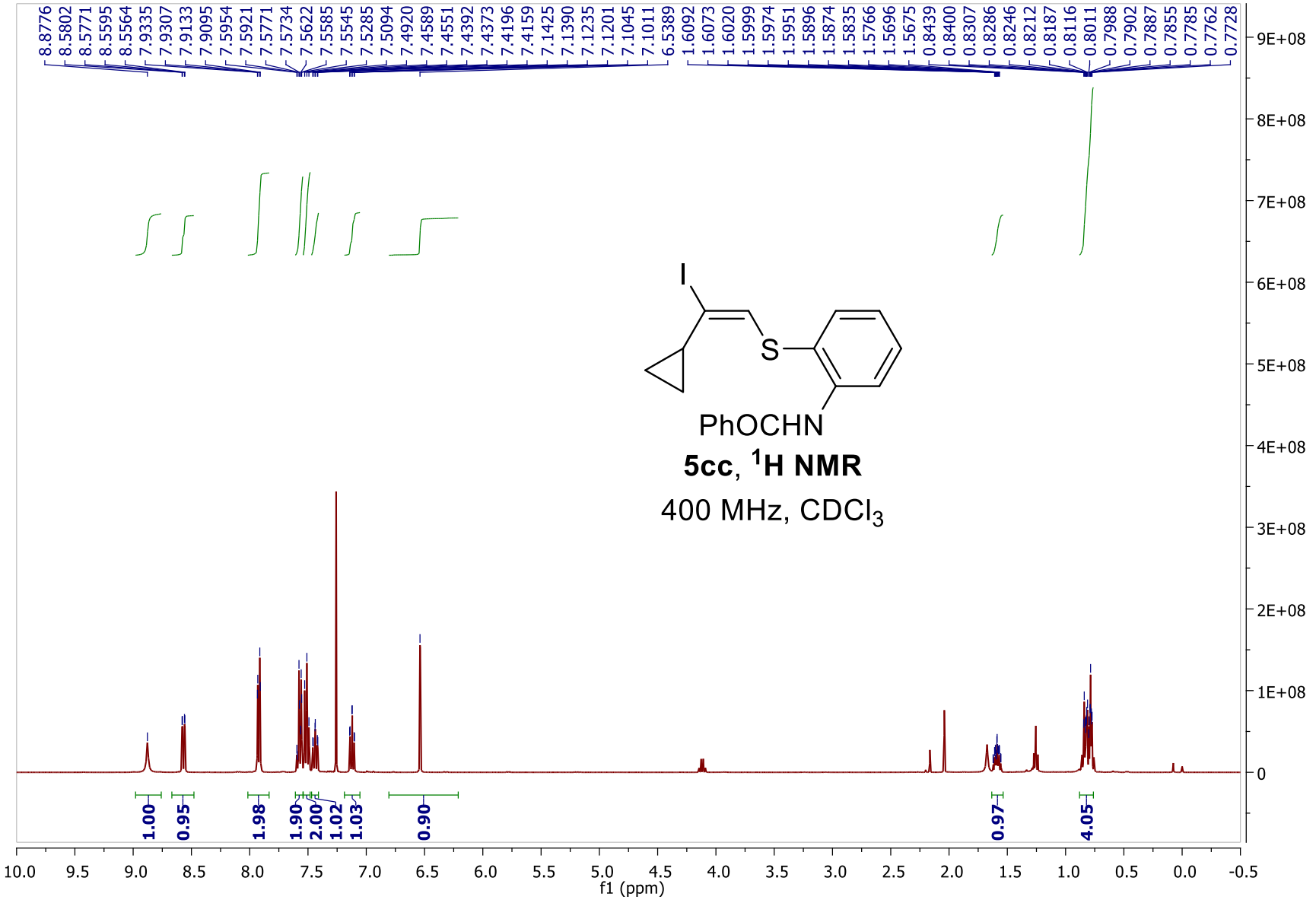
7.5003
7.4946
7.4805
7.4763
7.3906
7.3863
7.3834
7.3768
7.3727
4.3300
4.3119
4.2939
4.2761
1.3939
1.3761
1.3583
I
EtO2C
SPh
5ba, 1H NMR
400 MHz, CDCl3
1.00
2.08
3.07
2.07
3.06
f1 (ppm)


163.6367
155.2726
135.5423
131.3714
129.4855
128.7279
86.6469
62.7242
14.2039
I
EtO2C
SPh
5ba, 13C NMR
100 MHz, CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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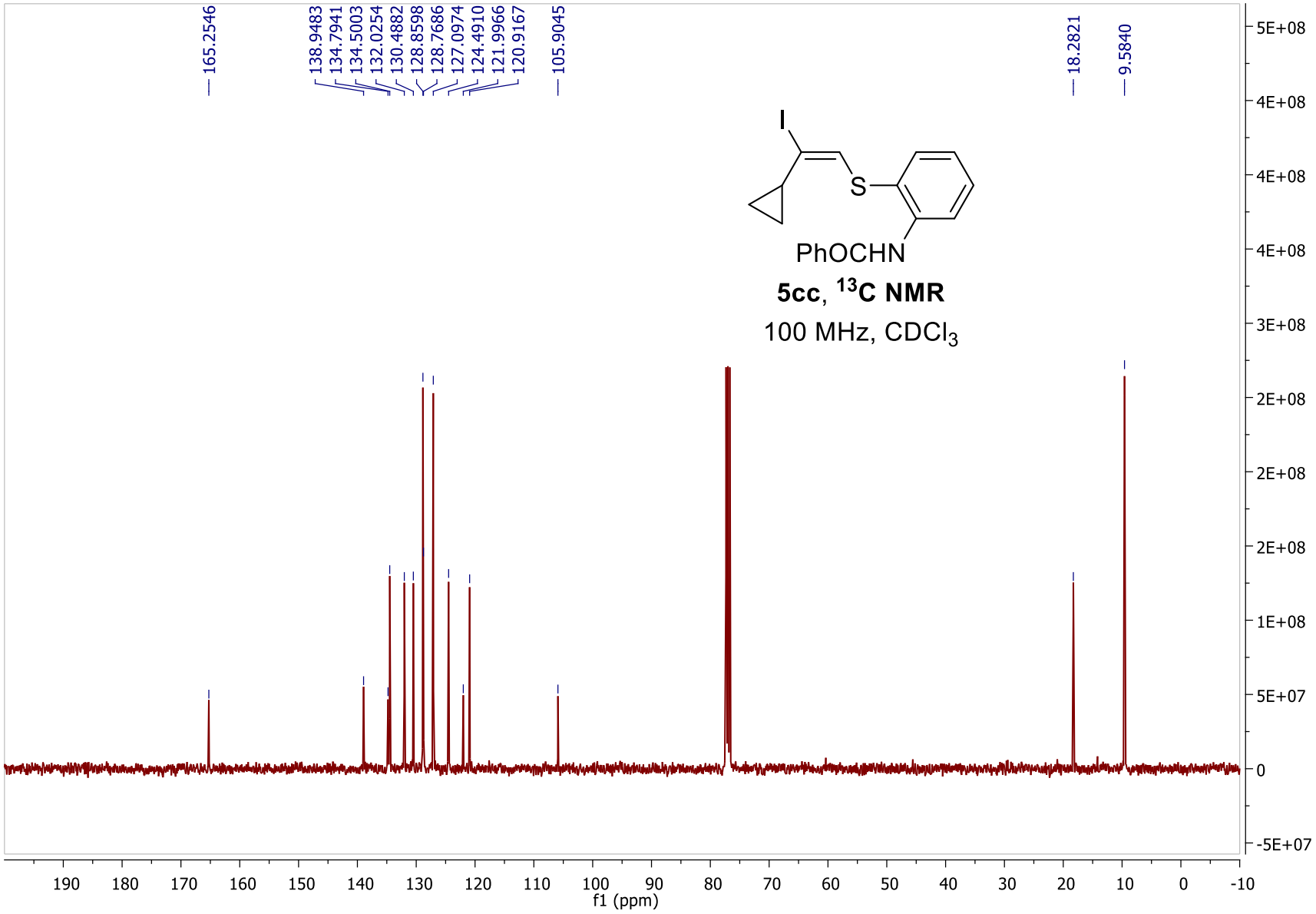
8.5771
8.5595
8.5564
7.9335
7.9307
7.9133
7.9095
7.5954
7.5921
7.5771
7.5734
7.5622
7.5585
7.5545
7.5285
7.5094
7.4920
7.4589
7.4551
7.4392
7.4373
7.4196
7.4159
7.1425
7.1390
7.1235
7.1201
7.1045
7.1011
6.5389
1.6092
1.6073
1.6020
1.5999
1.5974
1.5951
1.5896
1.5874
1.5835
1.5766
1.5696
1.5675
0.8439
0.8400
0.8307
0.8286
0.8246
0.8212
0.8187
0.8116
0.8011
0.7988
0.7902
0.7887
0.7855
0.7785
0.7762
0.7728
I
S
PhOCHN
5cc, 1H NMR
400 MHz, CDCl3
1.00
0.95
1.98
1.90
2.00
1.02
1.03
0.90
0.97
4.05
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
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
f1 (ppm)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134.7941
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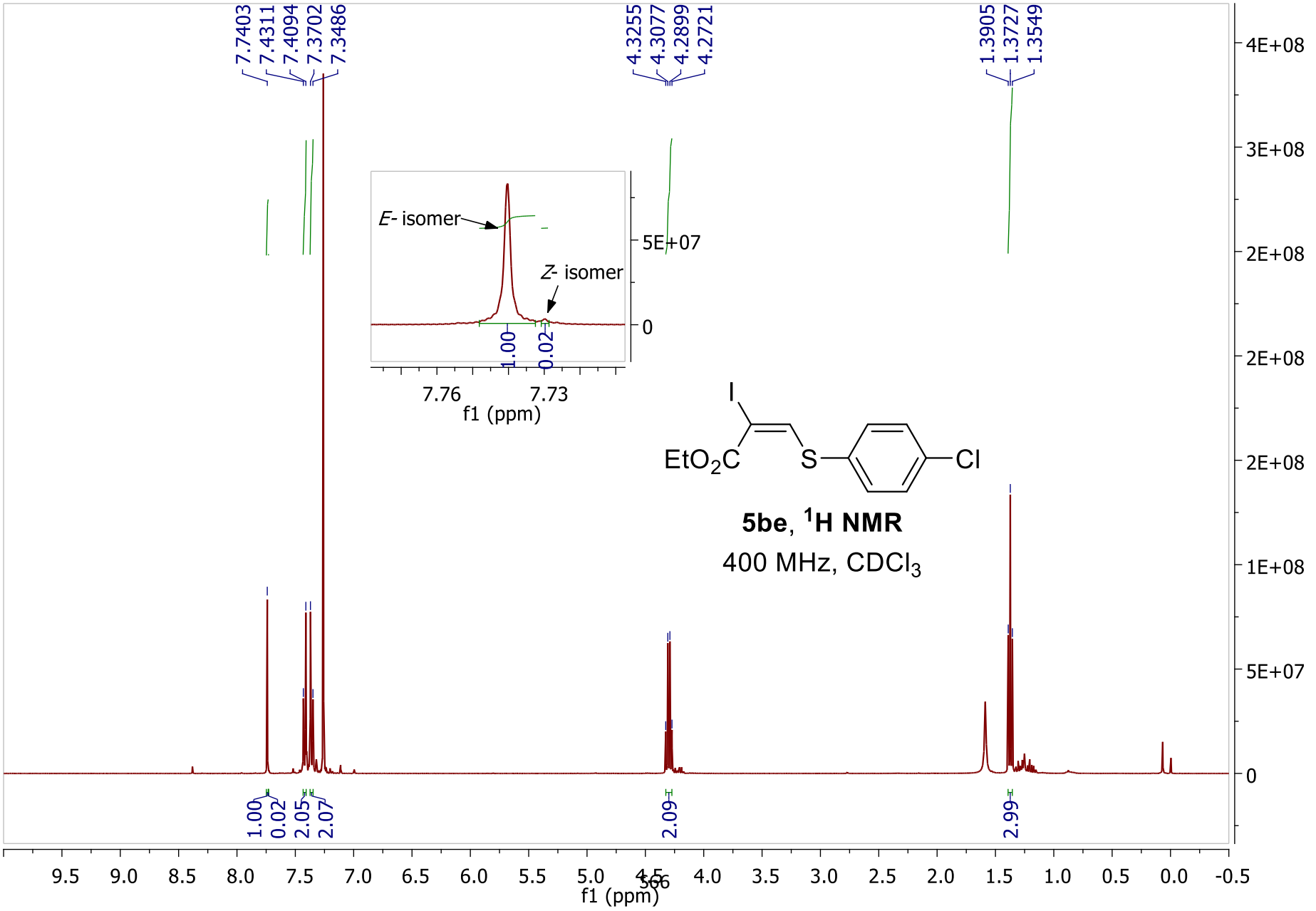
132.0254
130.4882
128.8598
128.7686
127.0974
124.4910
121.9966
120.9167
105.9045
18.2821
9.5840
I
S
PhOCHN
5cc, 13C NMR
100 MHz, CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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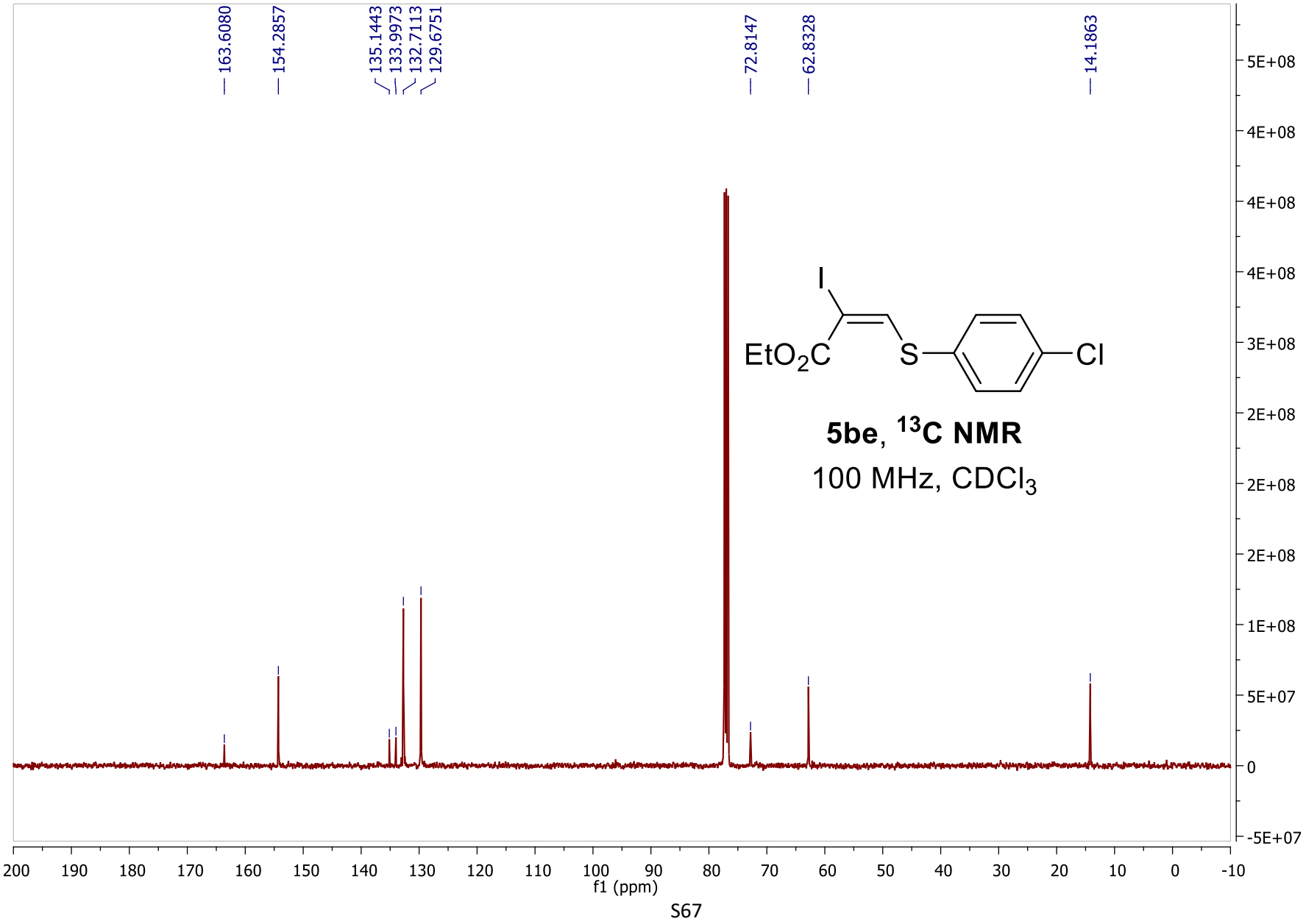
7.4311
7.4094
7.3702
7.3486
4.3255
4.3077
4.2899
4.2721
1.3905
1.3727
1.3549
E- isomer
Z- isomer
5E+07
0
1.00
0.02
7.76
7.73
f1 (ppm)
I
EtO2C
S
Cl
5be, 1H NMR
400 MHz, CDCl3
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
1.00
0.02
2.05
2.07
2.09
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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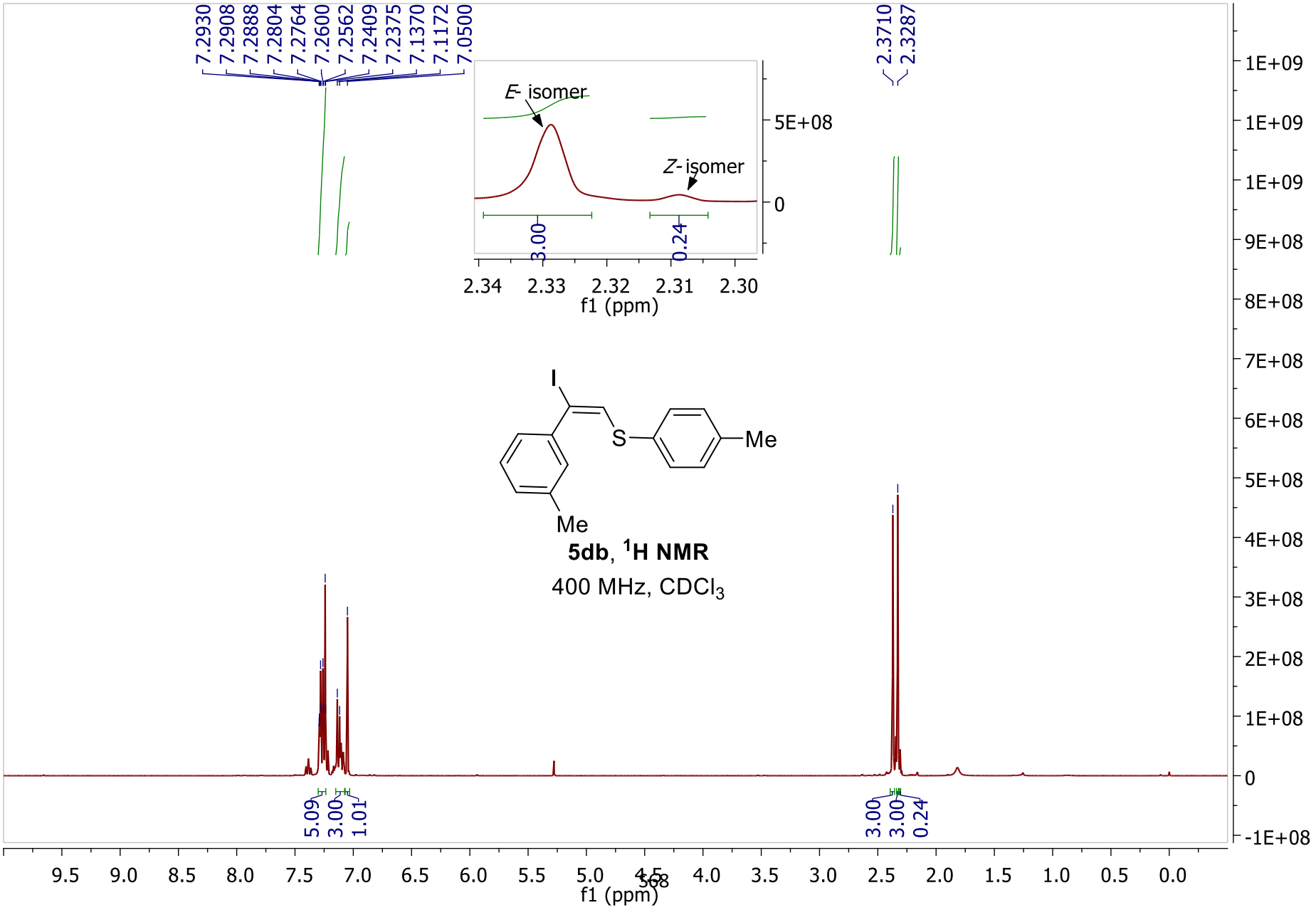
154.2857
135.1443
133.9973
132.7113
129.6751
72.8147
62.8328
14.1863
I
EtO2C
S
Cl
5be, 13C NMR
100 MHz, CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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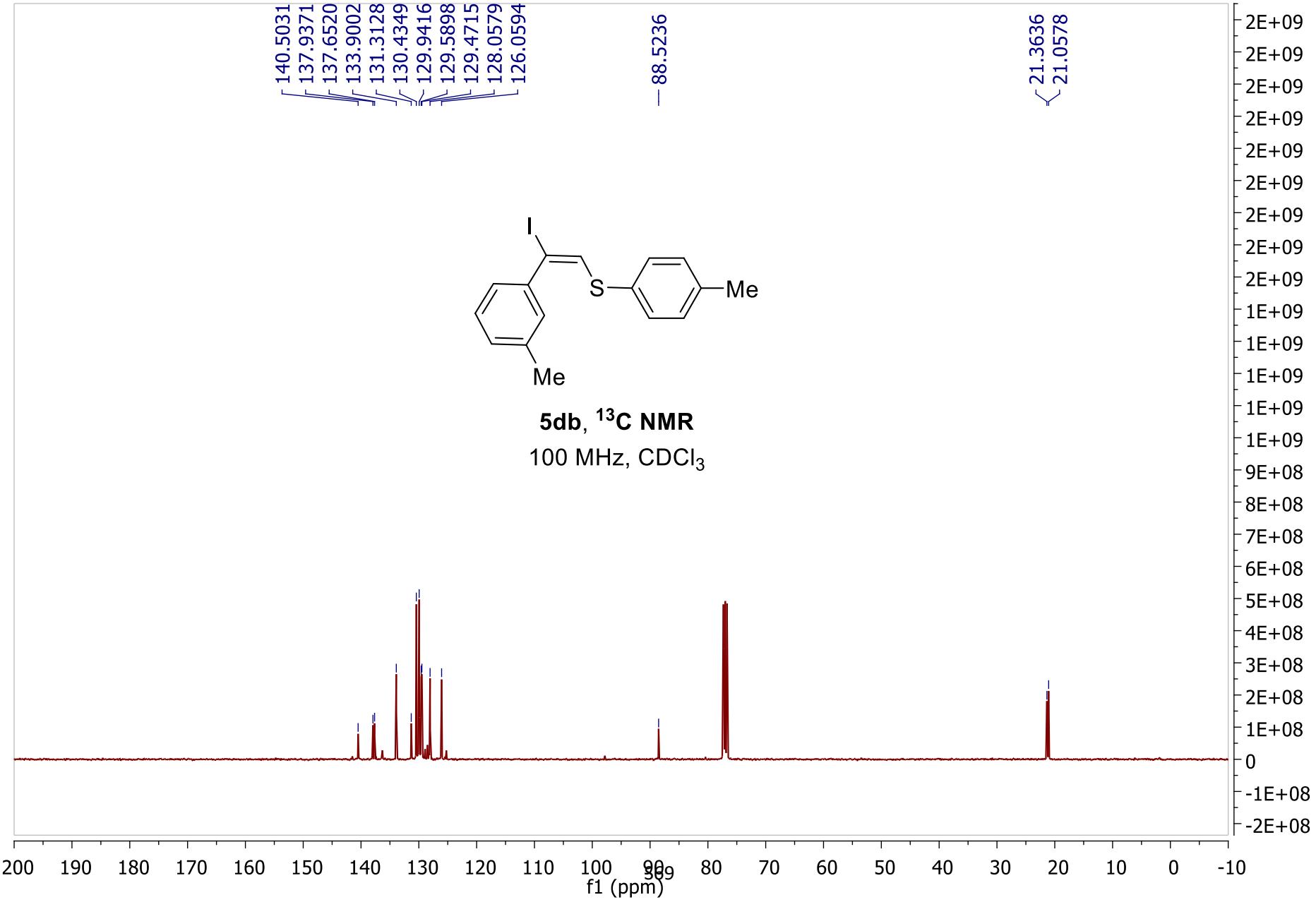
7.2908
7.2888
7.2804
7.2764
7.2600
7.2562
7.2409
7.2375
7.1370
7.1172
7.0500
2.3710
2.3287
E- isomer
Z- isomer
5E+08
0
3.00
0.24
2.34
2.33
2.32
2.31
2.30
f1 (ppm)
I
S
Me
Me
5db, 1H NMR
400 MHz, CDCl3
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
5.09
3.00
1.01
3.00
3.00
0.24
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
f1 (ppm)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137.6520
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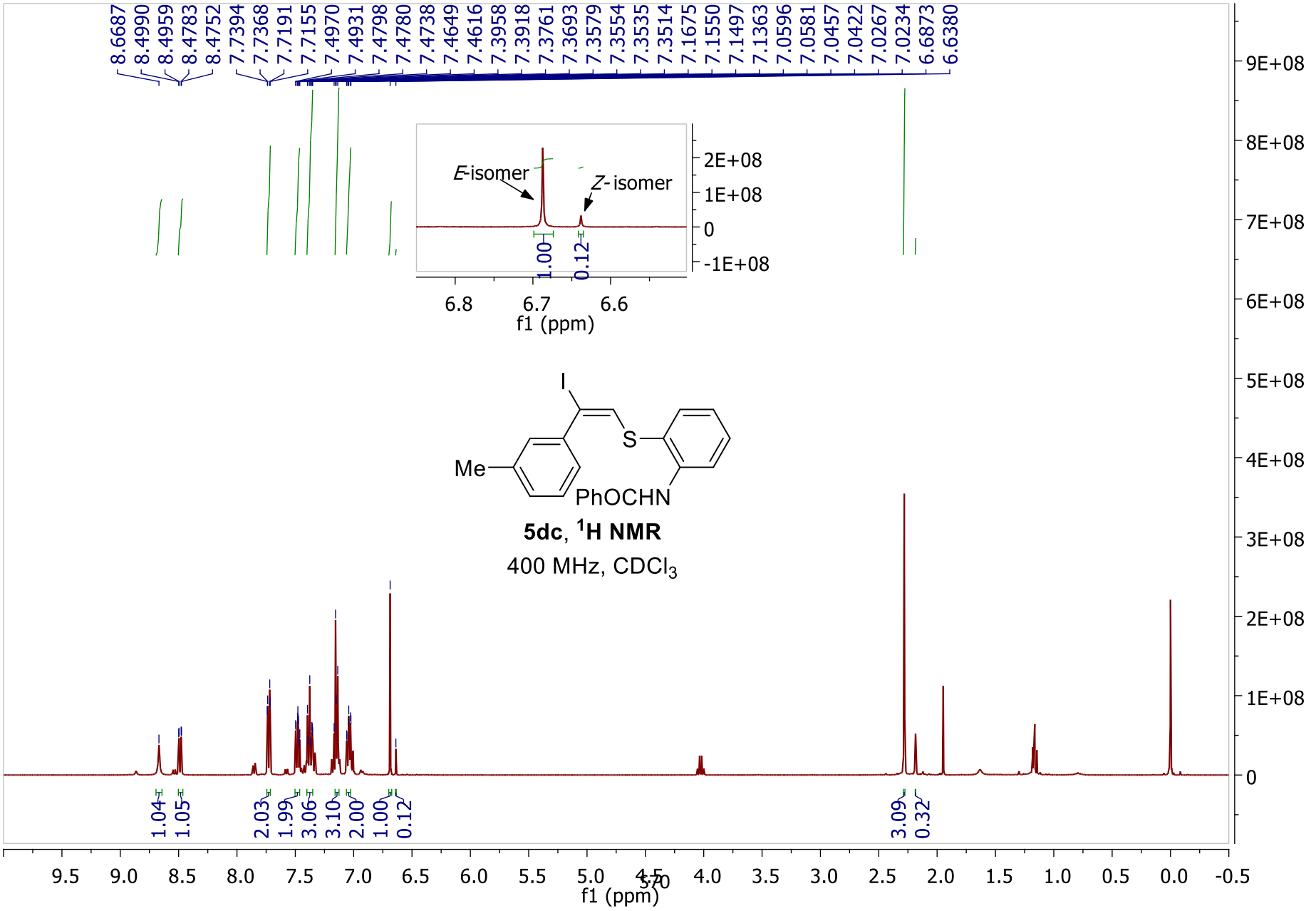
130.4349
129.9416
129.5898
129.4715
128.0579
126.0594
88.5236
21.3636
21.0578
I
S
Me
Me
5db, 13C NMR
100 MHz, CDCl3
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
-2E+08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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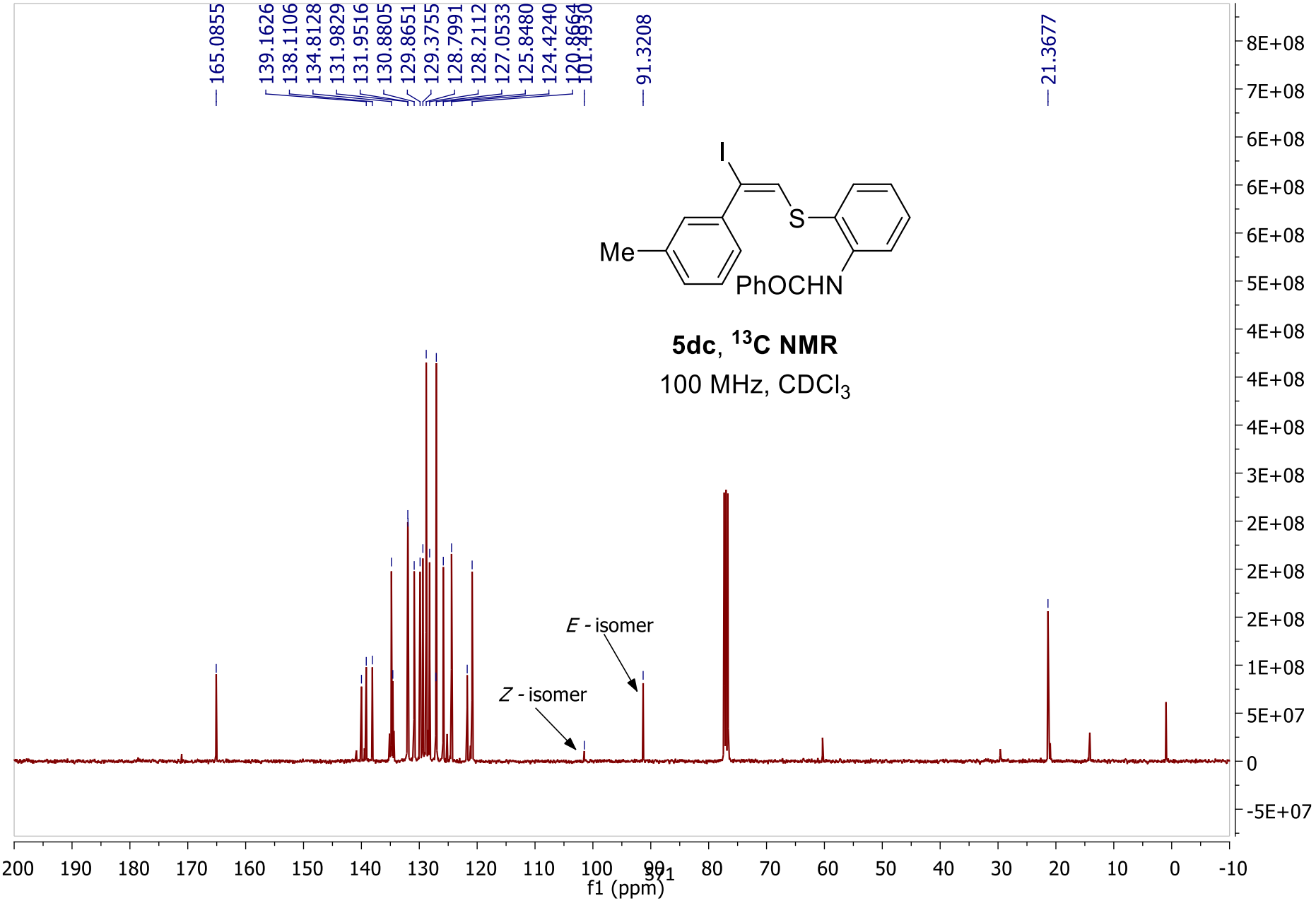
8.4990
8.4959
8.4783
8.4752
7.7394
7.7368
7.7191
7.7155
7.4970
7.4931
7.4798
7.4780
7.4738
7.4649
7.4616
7.3958
7.3918
7.3761
7.3693
7.3579
7.3554
7.3535
7.3514
7.1675
7.1550
7.1497
7.1363
7.0596
7.0581
7.0457
7.0422
7.0267
7.0234
6.6873
6.6380
E-isomer
Z-isomer
1.00
0.12
2E+08
1E+08
0
-1E+08
6.8
6.7
6.6
f1 (ppm)
I
S
Me
PhOCHN
5dc, 1H NMR
400 MHz, CDCl3
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
1.04
1.05
2.03
1.99
3.06
3.10
2.00
1.00
0.12
3.09
0.32
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
f1 (ppm)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138.1106
134.8128
131.9829
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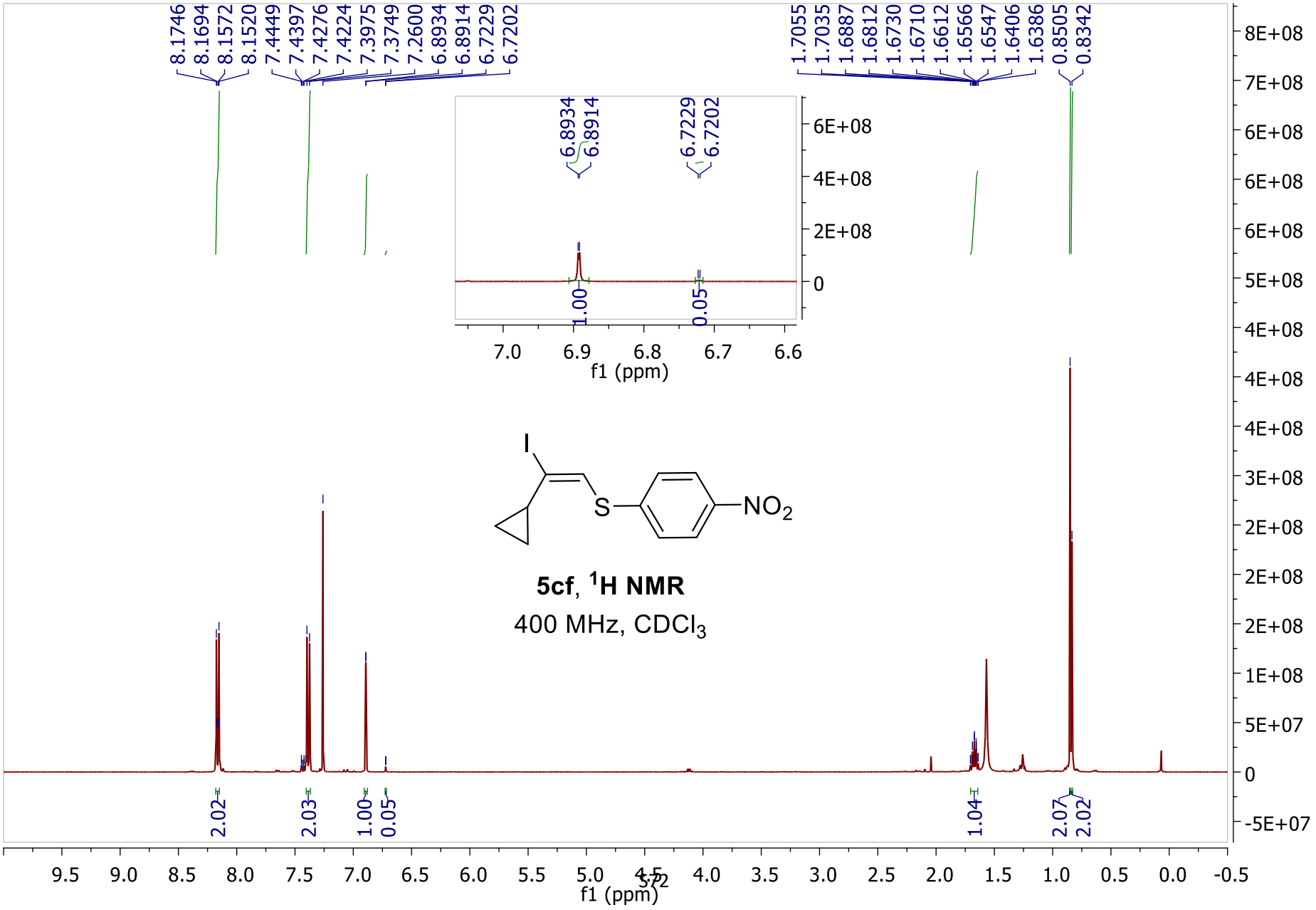
130.8805
129.8651
129.3755
128.7991
128.2112
127.0533
125.8480
124.4240
120.8664
101.4930
91.3208
21.3677
I
S
Me
PhOCHN
5dc, 13C NMR
100 MHz, CDCl3
E - isomer
Z - isomer
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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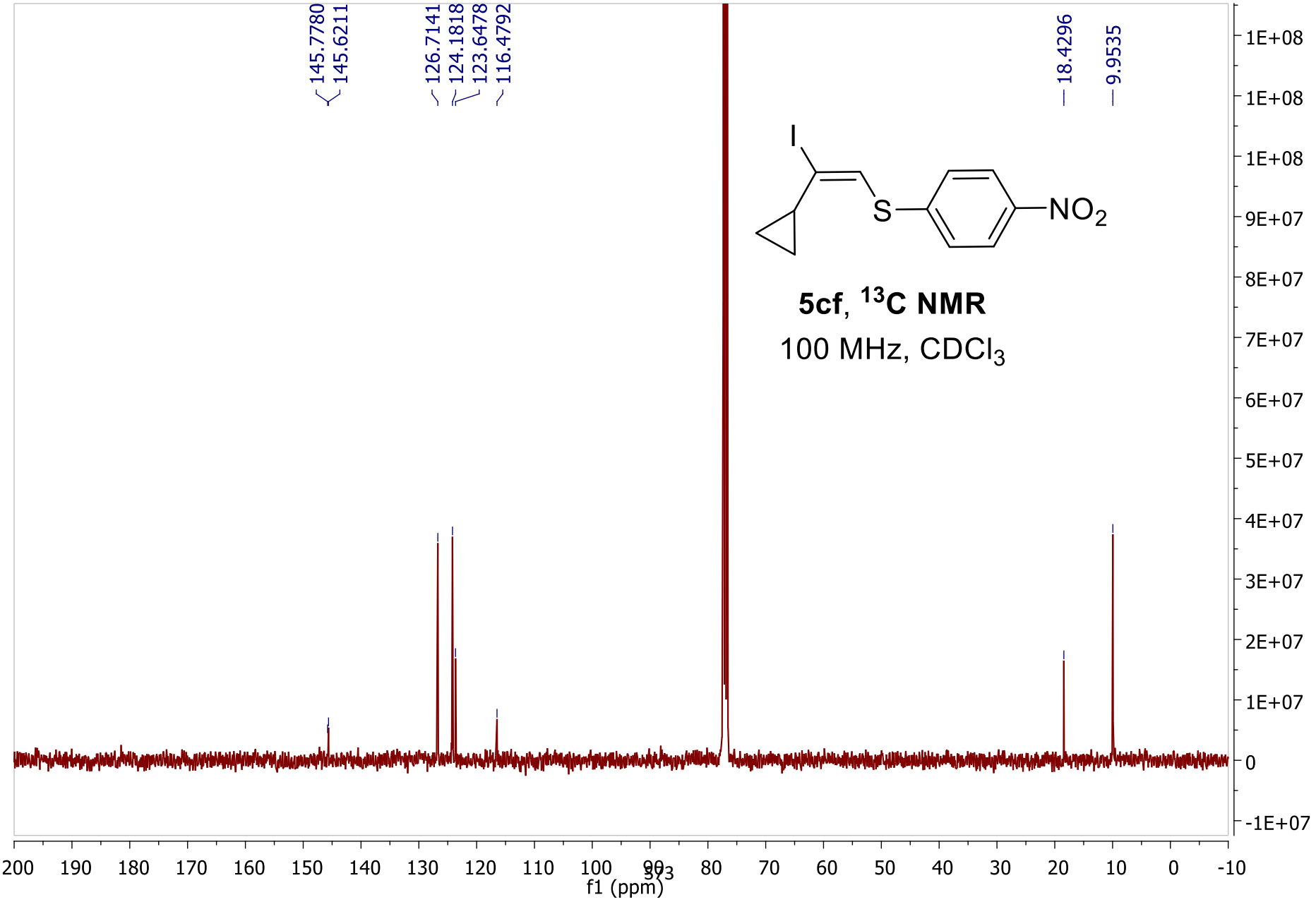
8.1694
8.1572
8.1520
7.4449
7.4397
7.4276
7.4224
7.3975
7.3749
7.2600
6.8934
6.8914
6.7229
6.7202
1.7055
1.7035
1.6887
1.6812
1.6730
1.6710
1.6612
1.6566
1.6547
1.6406
1.6386
0.8505
0.8342
6.8934
6.8914
6.7229
6.7202
1.00
0.05
f1 (ppm)
I
S
NO2
5cf, 1H NMR
400 MHz, CDCl3
2.02
2.03
1.00
0.05
1.04
2.07
2.02
f1 (ppm)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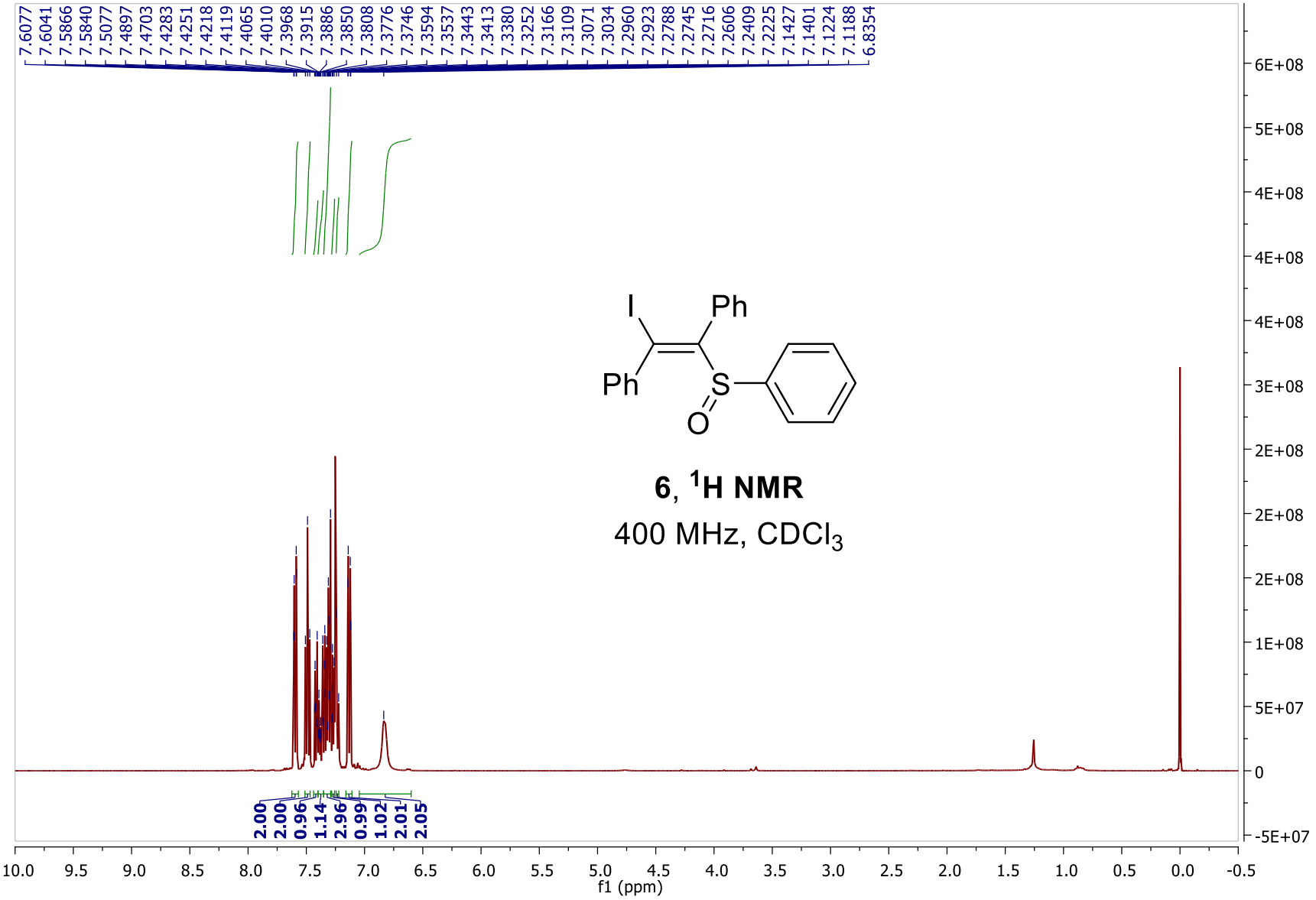
145.6211
126.7141
124.1818
123.6478
116.4792
18.4296
9.9535
I
S
NO2
5cf, 13C NMR
100 MHz, CDCl3
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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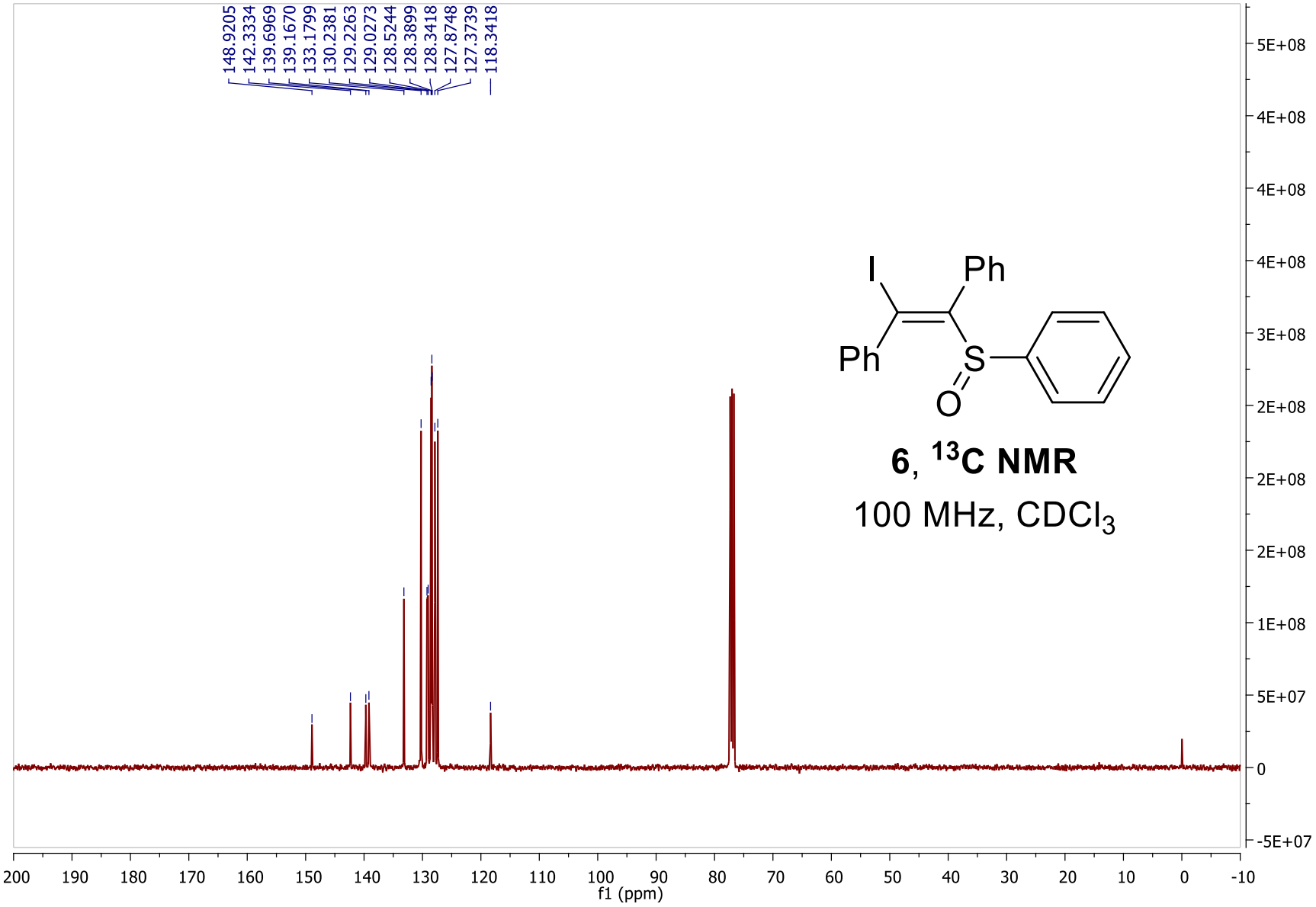
7.4218
7.4119
7.4065
7.4010
7.3968
7.3915
7.3886
7.3850
7.3808
7.3776
7.3746
7.3594
7.3537
7.3443
7.3413
7.3380
7.3252
7.3166
7.3109
7.3071
7.3034
7.2960
7.2923
7.2788
7.2745
7.2716
7.2606
7.2409
7.2225
7.1427
7.1401
7.1224
7.1188
6.8354
I
Ph
Ph
S
O
6, 1H NMR
400 MHz, CDCl3
2.00
2.00
0.96
1.14
2.96
0.99
1.02
2.01
2.05
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
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
f1 (ppm)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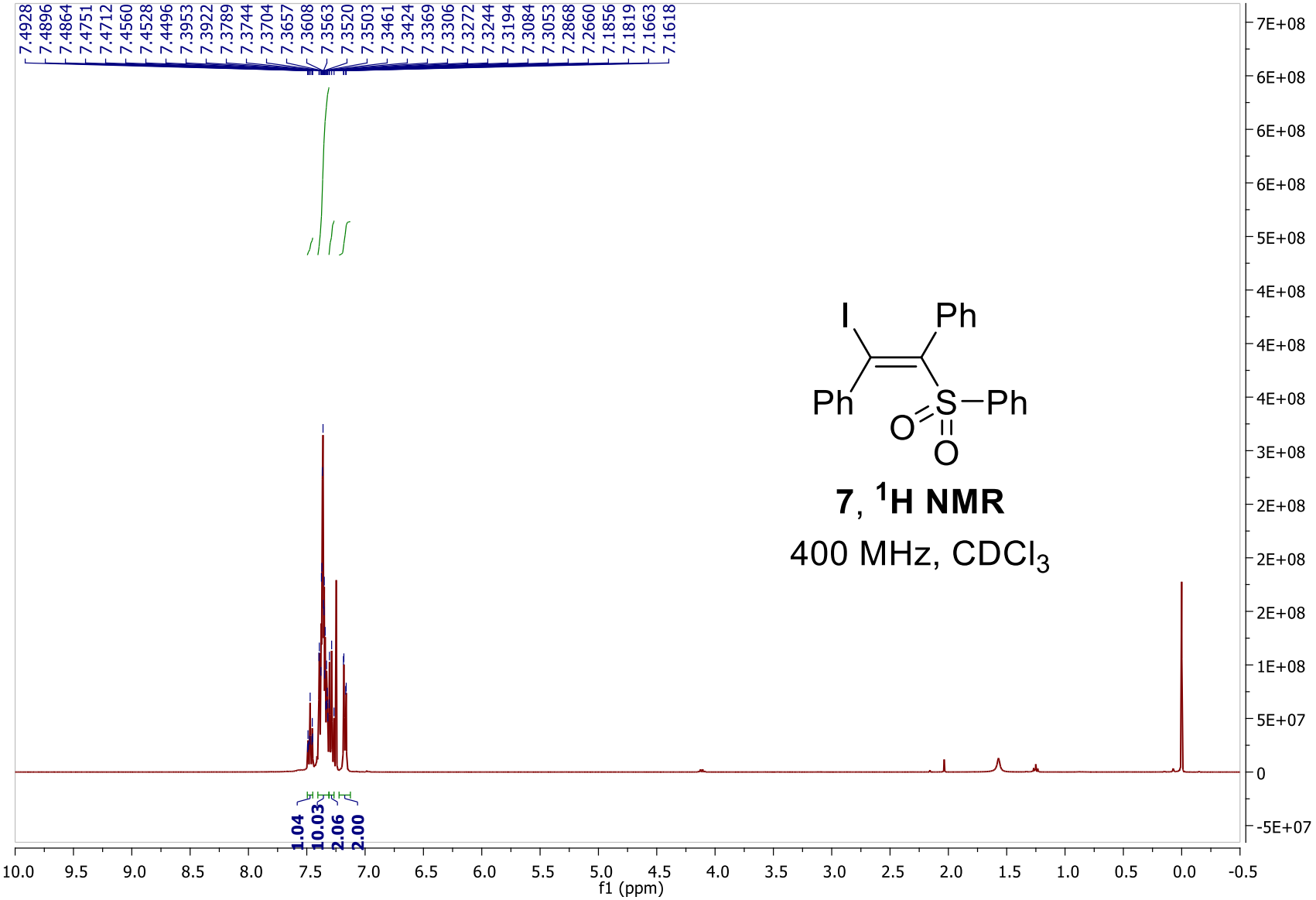
139.6969
139.1670
133.1799
130.2381
129.2263
129.0273
128.5244
128.3899
128.3418
127.8748
127.3739
118.3418
I
Ph
Ph
S
O
6, 13C NMR
100 MHz, CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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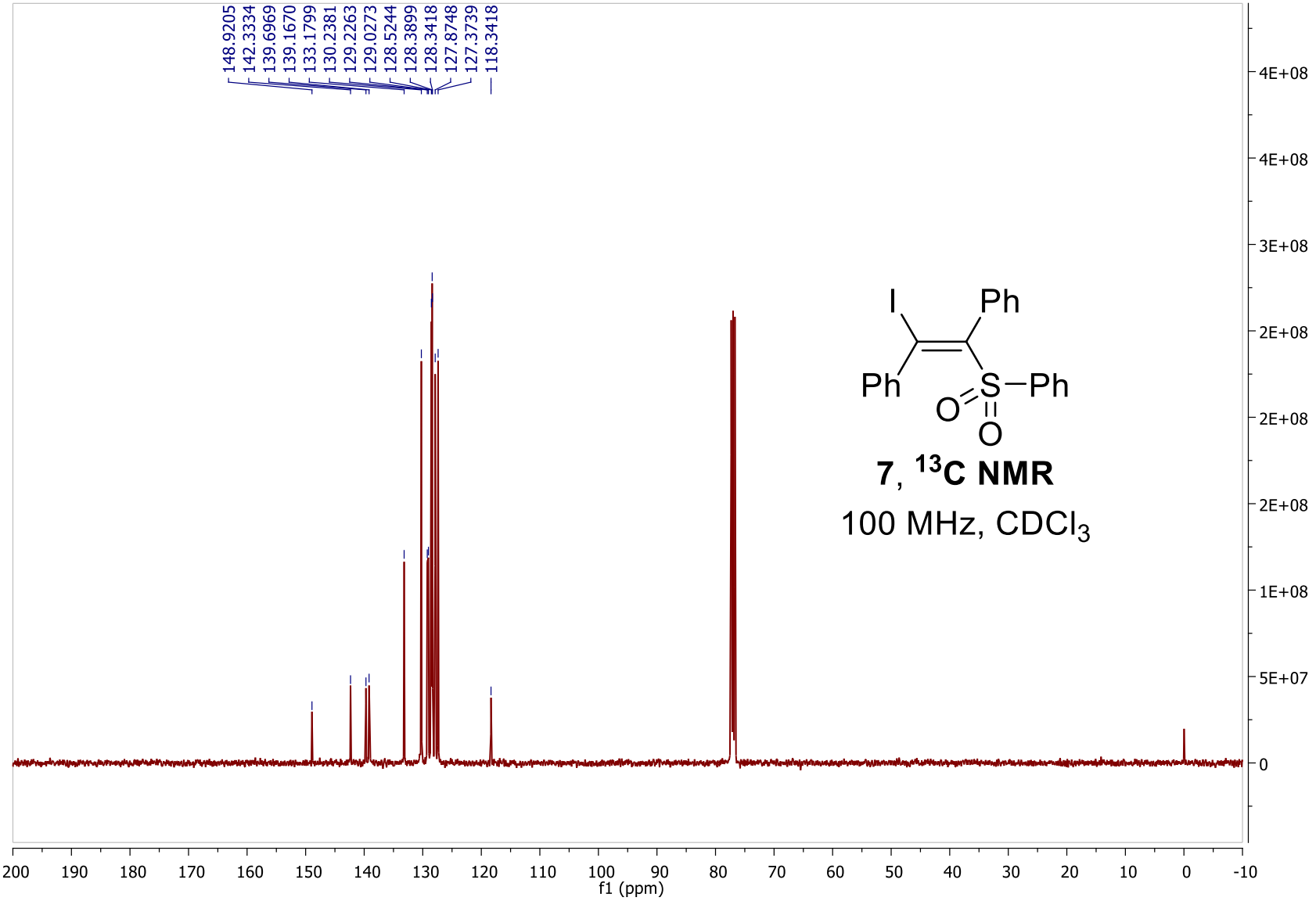
7.4528
7.4496
7.3953
7.3922
7.3789
7.3744
7.3704
7.3657
7.3608
7.3563
7.3520
7.3503
7.3461
7.3424
7.3369
7.3306
7.3272
7.3244
7.3194
7.3084
7.3053
7.2868
7.2660
7.1856
7.1819
7.1663
7.1618
I
Ph
Ph
S
Ph
O
O
7, 1H NMR
400 MHz, CDCl3
1.04
10.03
2.06
2.00
f1 (ppm)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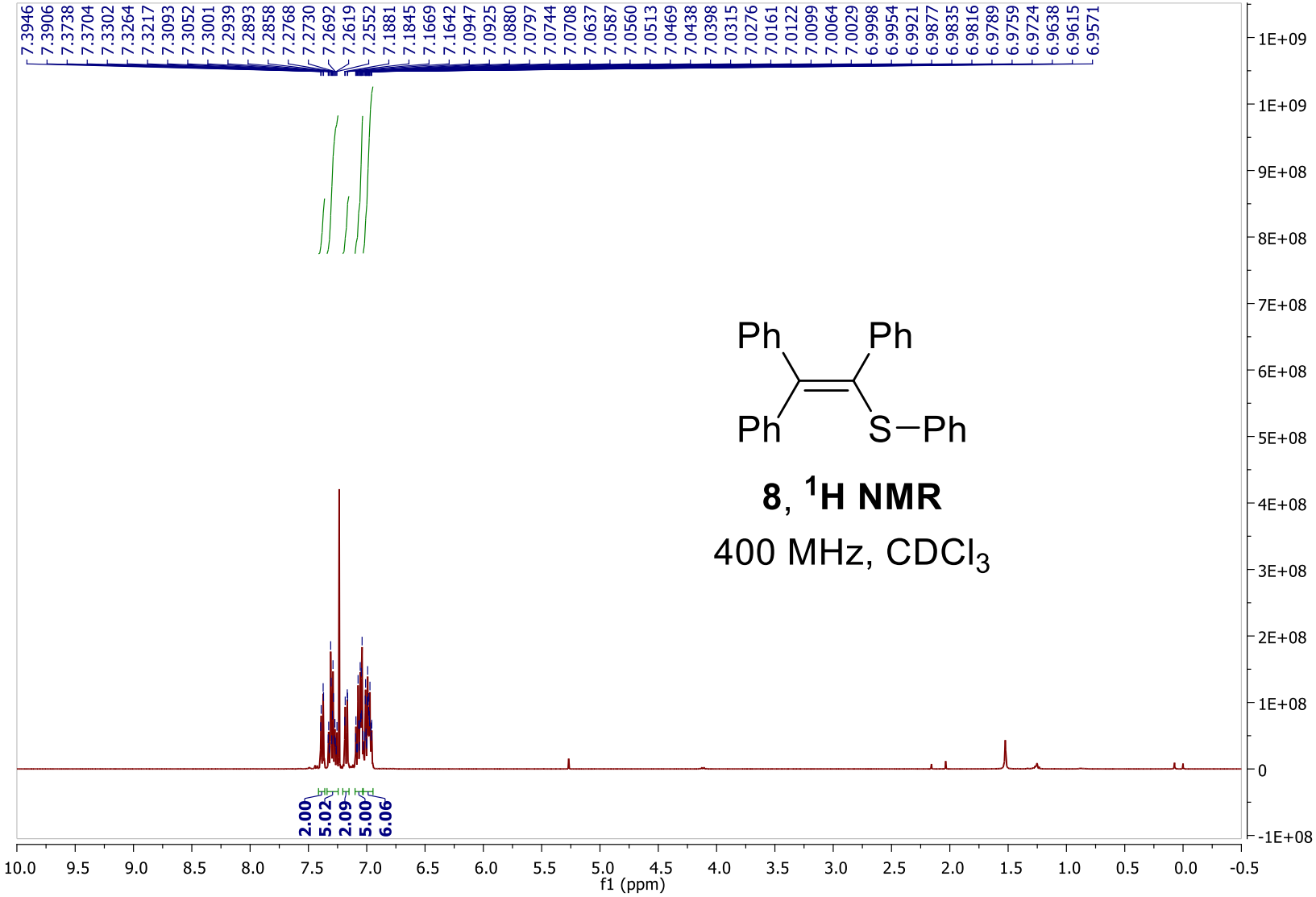
142.3334
139.6969
139.1670
133.1799
130.2381
129.2263
129.0273
128.5244
128.3899
128.3418
127.8748
127.3739
118.3418
I
Ph
Ph
S
Ph
O
O
7, 13C NMR
100 MHz, CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.3217
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7.3052
7.3001
7.2939
7.2893
7.2858
7.2768
7.2730
7.2692
7.2619
7.2552
7.1881
7.1845
7.1669
7.1642
7.0947
7.0925
7.0880
7.0797
7.0744
7.0708
7.0637
7.0587
7.0560
7.0513
7.0469
7.0438
7.0398
7.0315
7.0276
7.0161
7.0122
7.0099
7.0064
7.0029
6.9998
6.9954
6.9921
6.9877
6.9835
6.9816
6.9789
6.9759
6.9724
6.9638
6.9615
6.9571
Ph
Ph
Ph
S—Ph
8, 1H NMR
400 MHz, CDCl3
2.00
5.02
2.09
5.00
6.06
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
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
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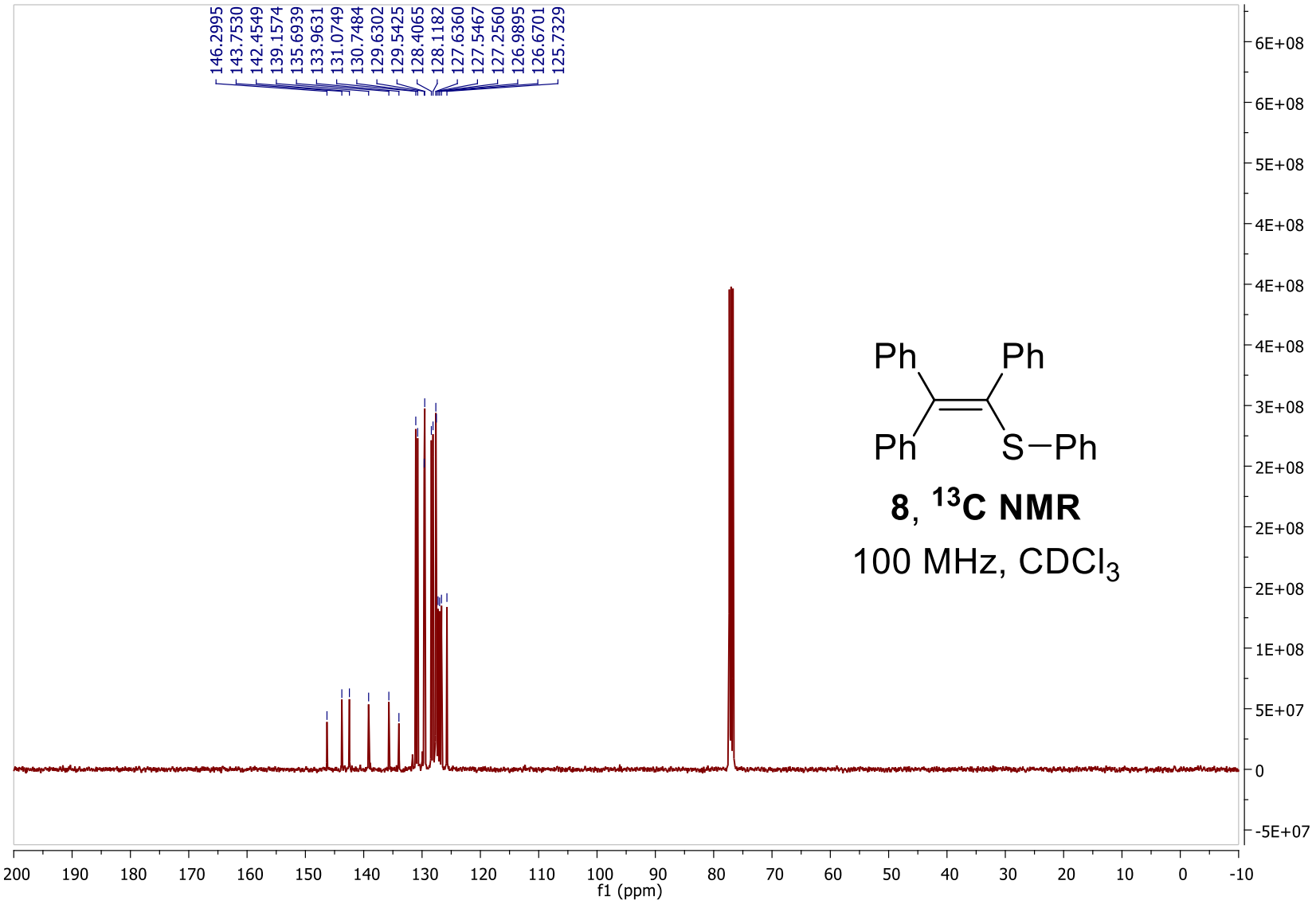
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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131.0749
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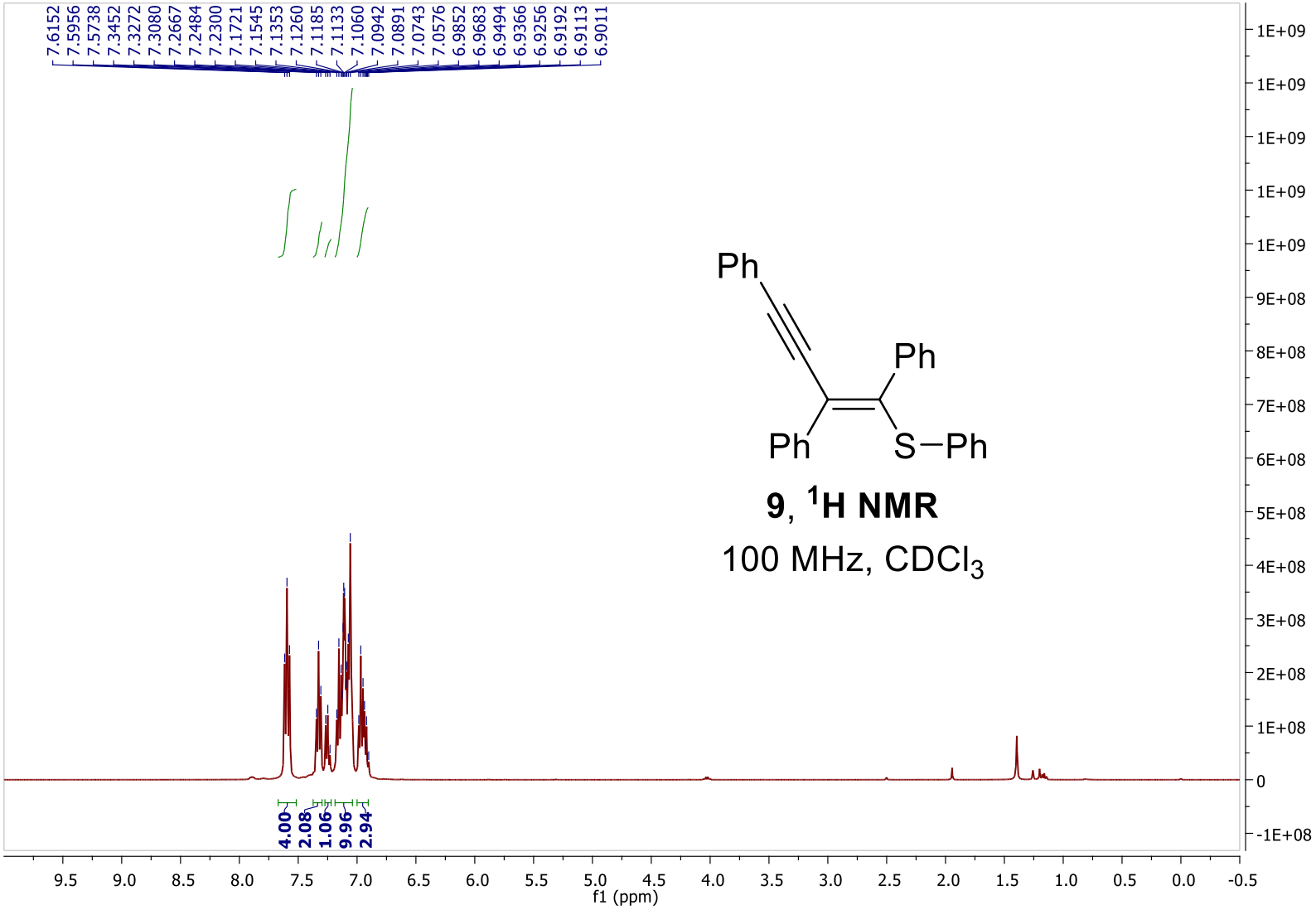
128.4065
128.1182
127.6360
127.5467
127.2560
126.9895
126.6701
125.7329
Ph
Ph
Ph
S—Ph
8, 13C NMR
100 MHz, CDCl3
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.5738
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7.3272
7.3080
7.2667
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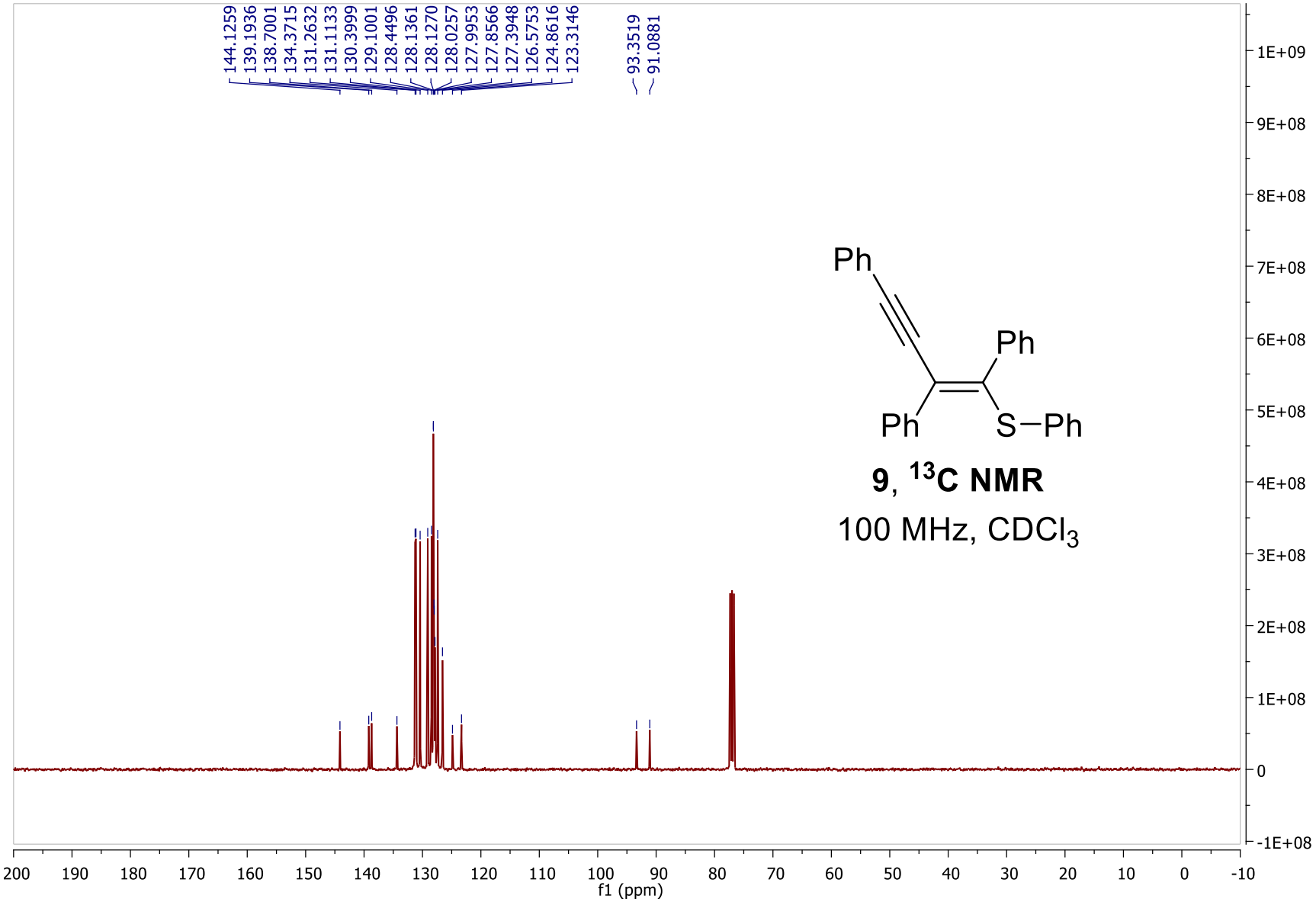
7.2300
7.1721
7.1545
7.1353
7.1260
7.1185
7.1133
7.1060
7.0942
7.0891
7.0743
7.0576
6.9852
6.9683
6.9494
6.9366
6.9256
6.9192
6.9113
6.9011
Ph
Ph
Ph
S—Ph
9, 1H NMR
100 MHz, CDCl3
4.00
2.08
1.06
9.96
2.94
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)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138.7001
134.3715
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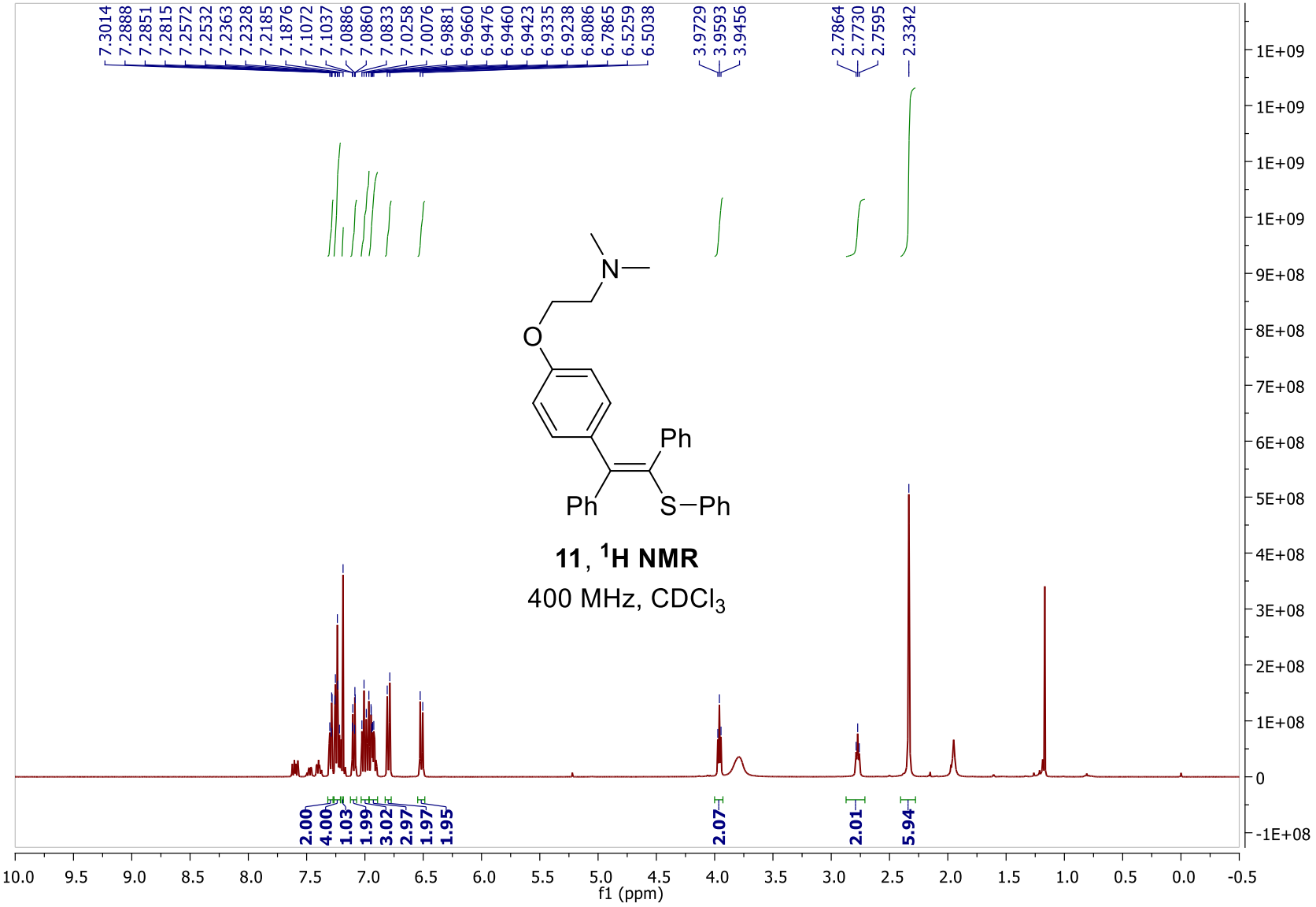
128.1270
128.0257
127.9953
127.8566
127.3948
126.5753
124.8616
123.3146
93.3519
91.0881
Ph
Ph
Ph
S—Ph
9, 13C NMR
100 MHz, CDCl3
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2363
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7.2185
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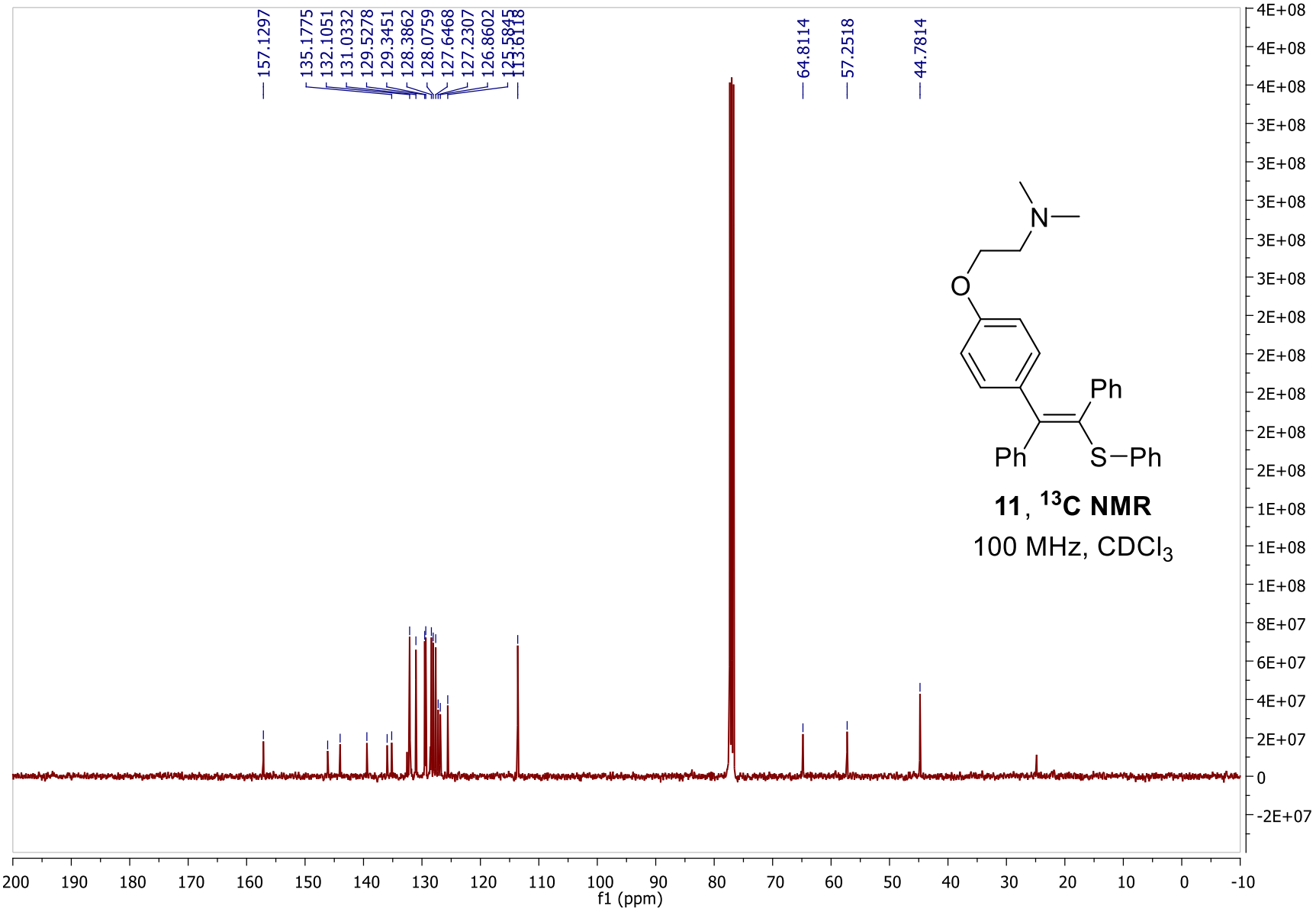
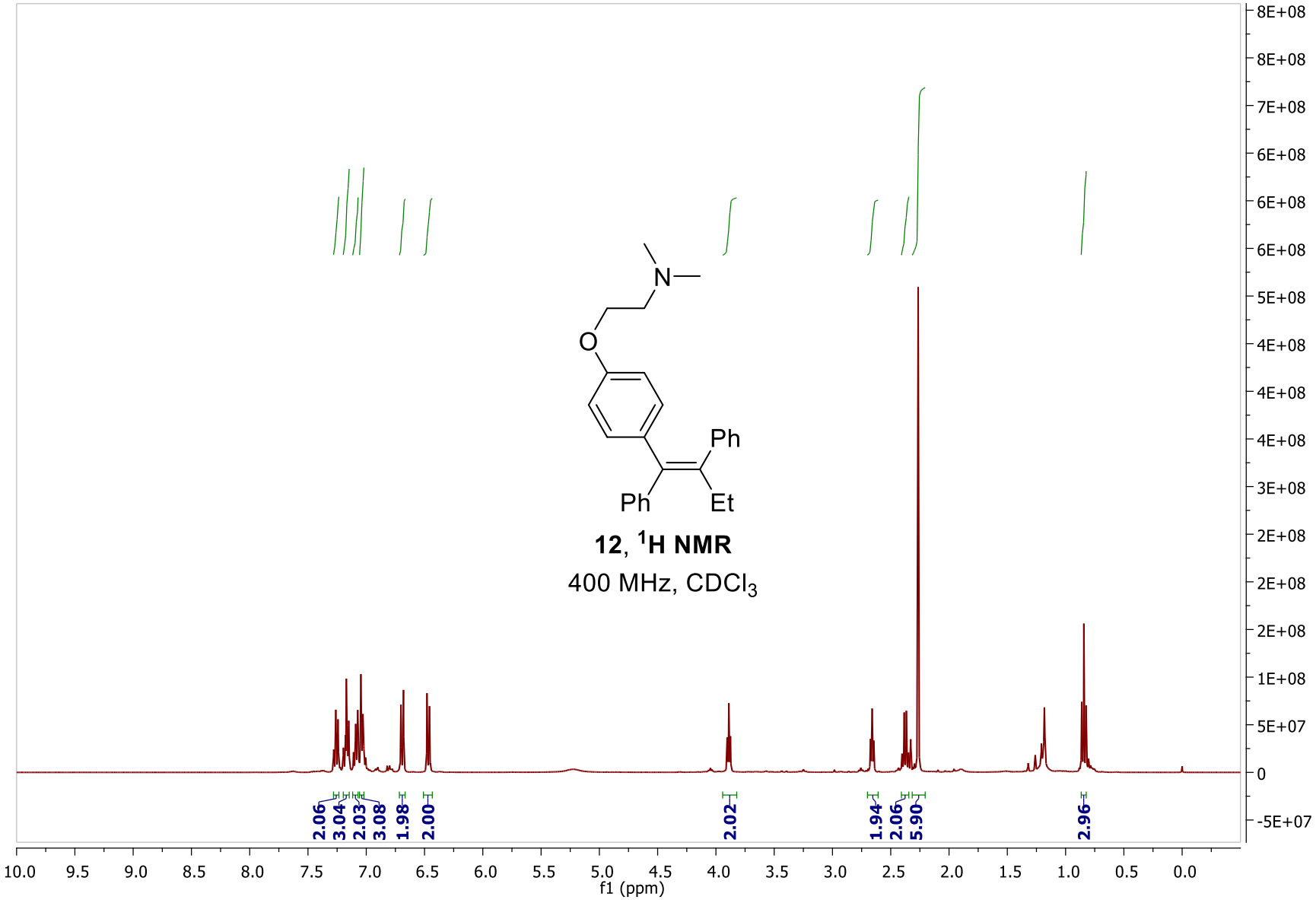
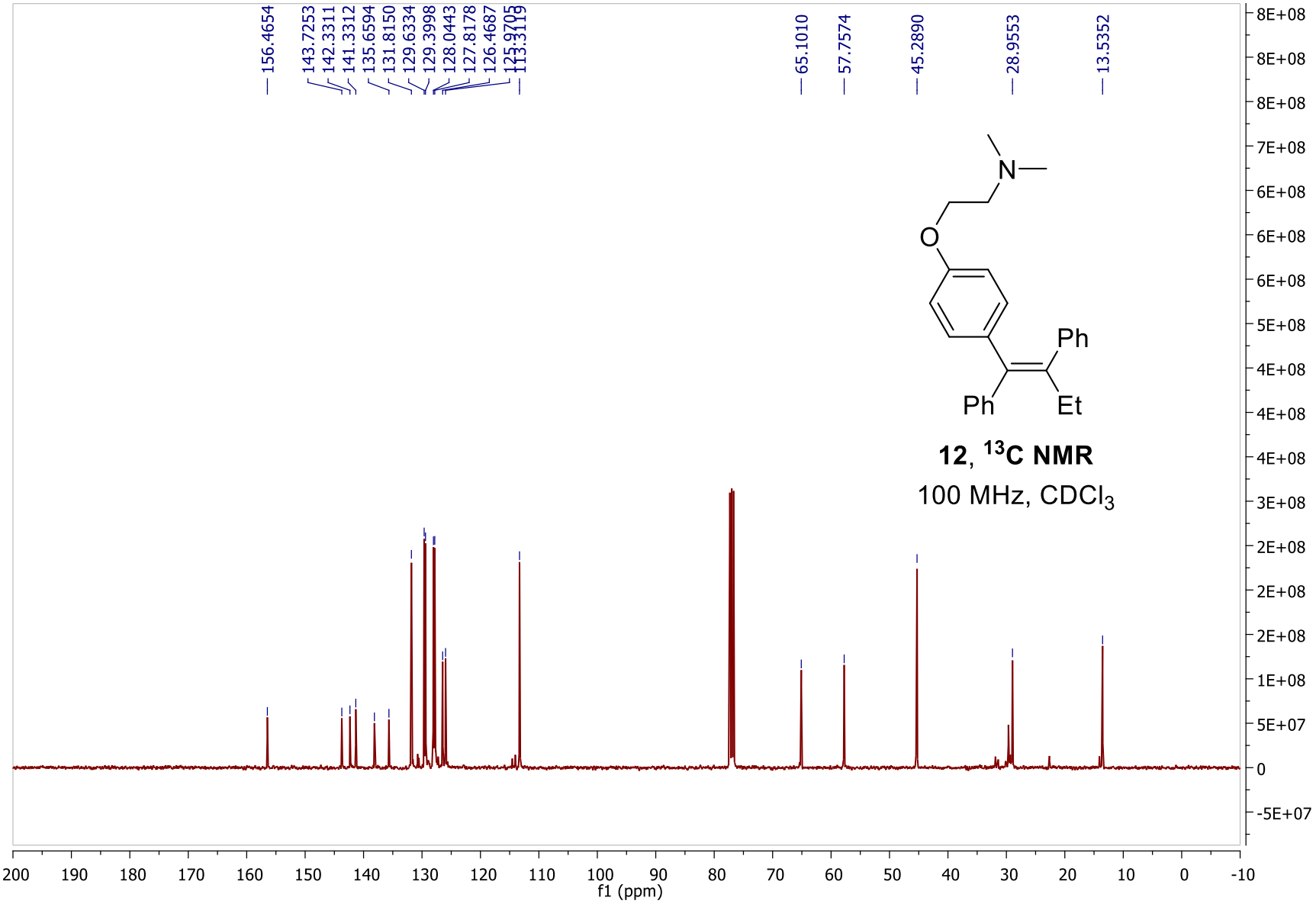
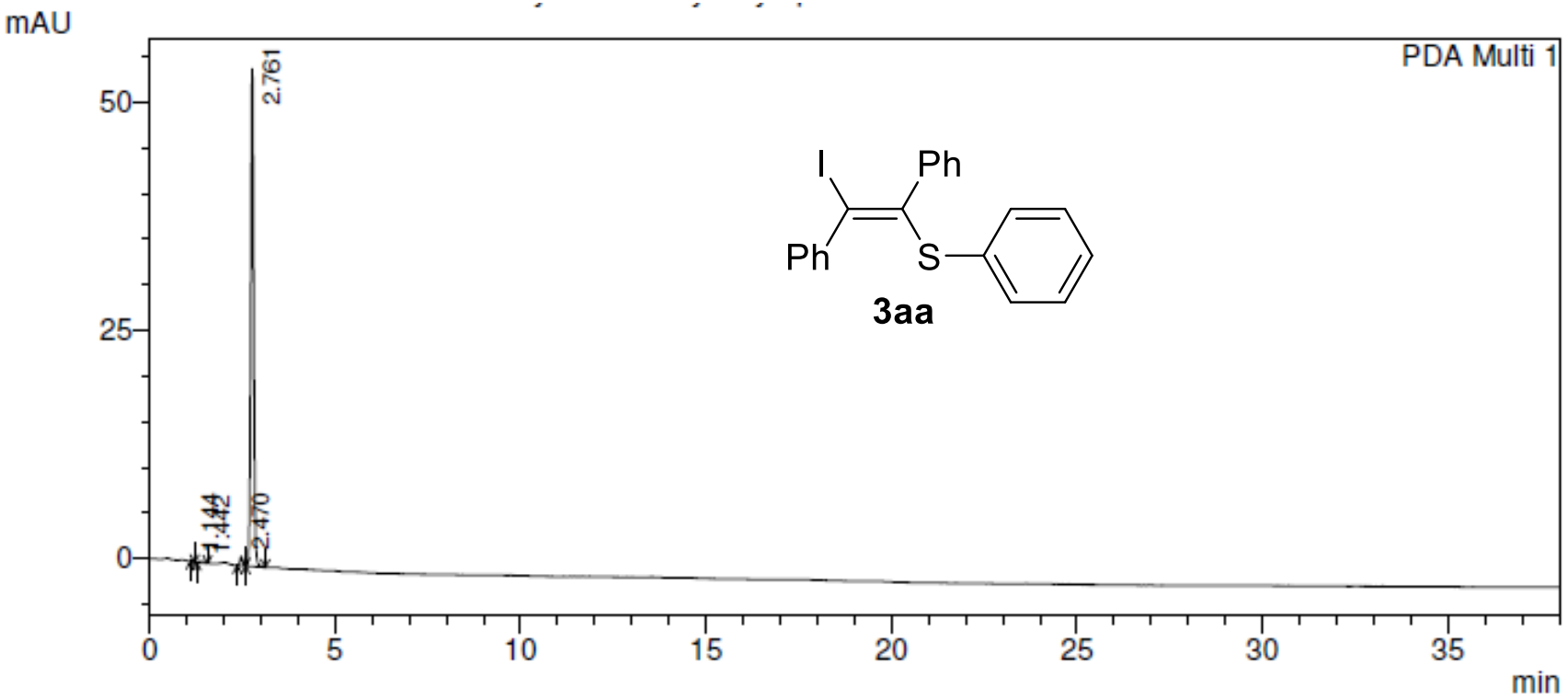
7.1072
7.1037
7.0886
7.0860
7.0833
7.0258
7.0076
6.9881
6.9660
6.9476
6.9460
6.9423
6.9335
6.9238
6.8086
6.7865
6.5259
6.5038
3.9729
3.9593
3.9456
2.7864
2.7730
2.7595
2.3342
N
O
Ph
Ph
S—Ph
11, 1H NMR
400 MHz, CDCl3
2.00
4.00
1.03
1.99
3.02
2.97
1.97
1.95
2.07
2.01
5.94
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
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
f1 (ppm)


157.1297
135.1775
132.1051
131.0332
129.5278
129.3451
128.3862
128.0759
127.6468
127.2307
126.8602
125.5845
113.6118
64.8114
57.2518
44.7814
N
O
Ph
Ph
S—Ph
11, 13C NMR
100 MHz, CDCl3
f1 (ppm)


N
O
Ph
Ph
Et
12, 1H NMR
400 MHz, CDCl3
2.06
3.04
2.03
3.08
1.98
2.00
2.02
1.94
2.06
5.90
2.96
f1 (ppm)


156.4654
143.7253
142.3311
141.3312
135.6594
131.8150
129.6334
129.3998
128.0443
127.8178
126.4687
65.1010
57.7574
45.2890
28.9553
13.5352
N
O
Ph
Ph
Et
12, 13C NMR
100 MHz, CDCl3
f1 (ppm)

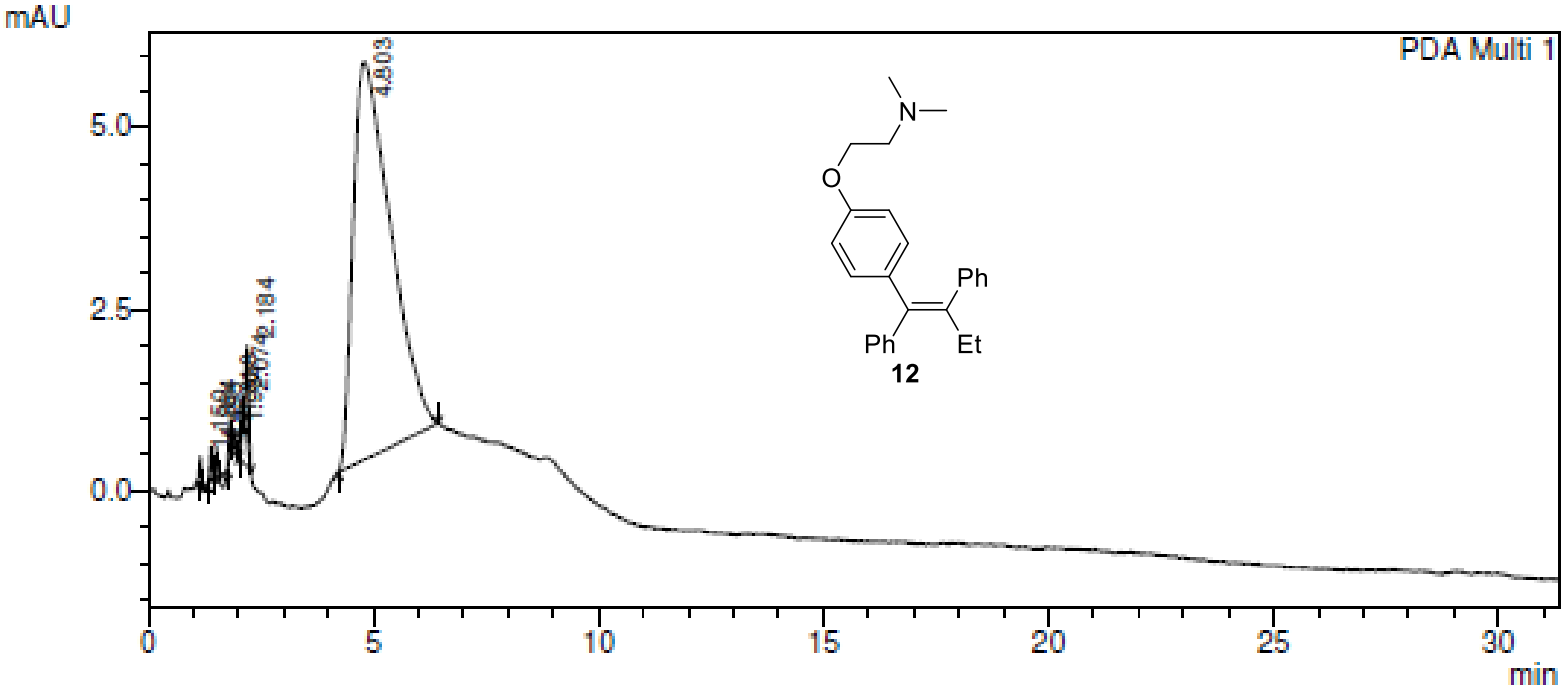


1 PDA Multi 1/307nm 4nm

PeakTable

PDA Ch1 307nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	1.144	720	259	0.236	0.462
2	1.442	1703	177	0.558	0.316
3	2.470	4908	1035	1.608	1.850
4	2.761	297939	54494	97.599	97.372
Total		305269	55964	100.000	100.000

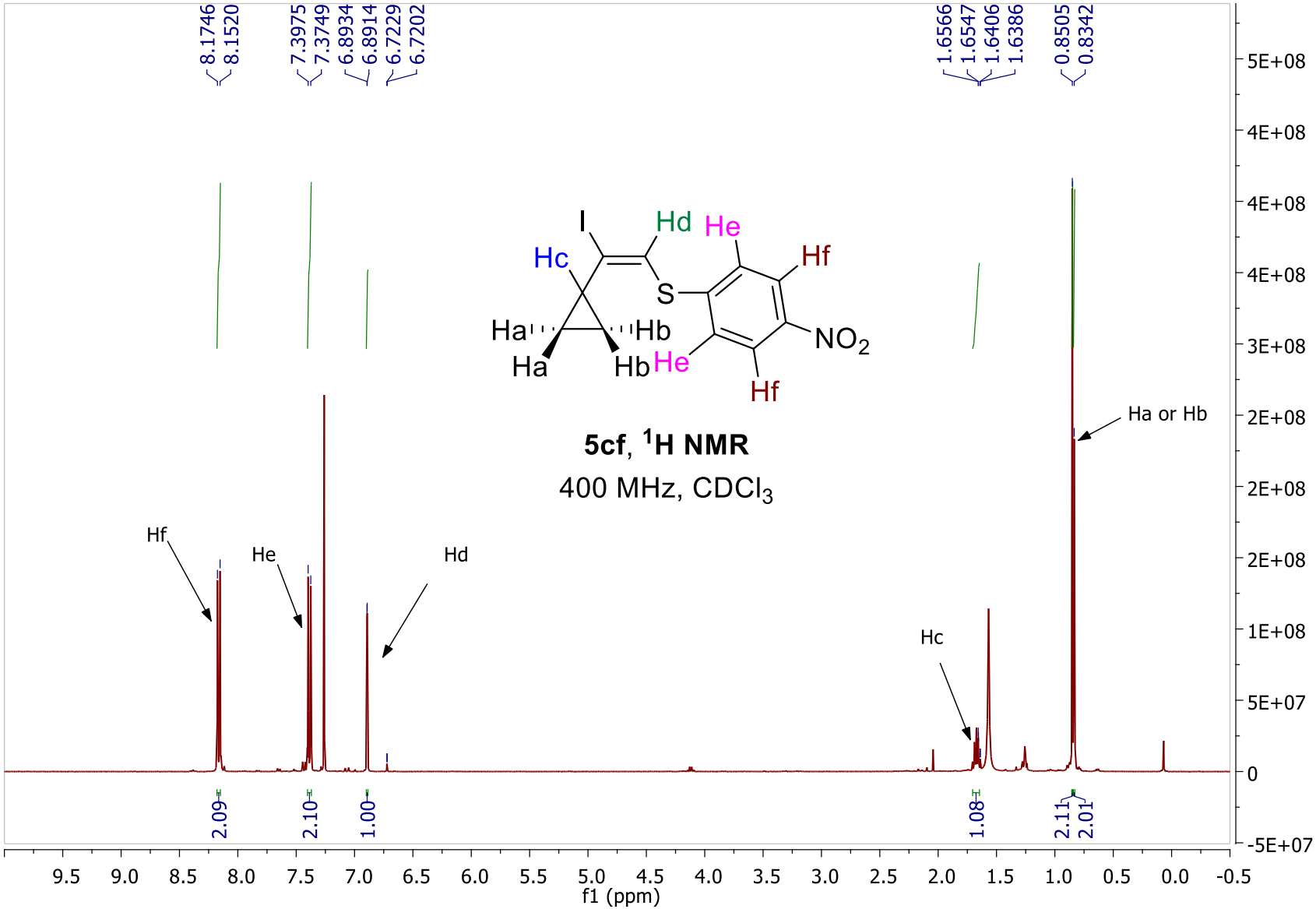


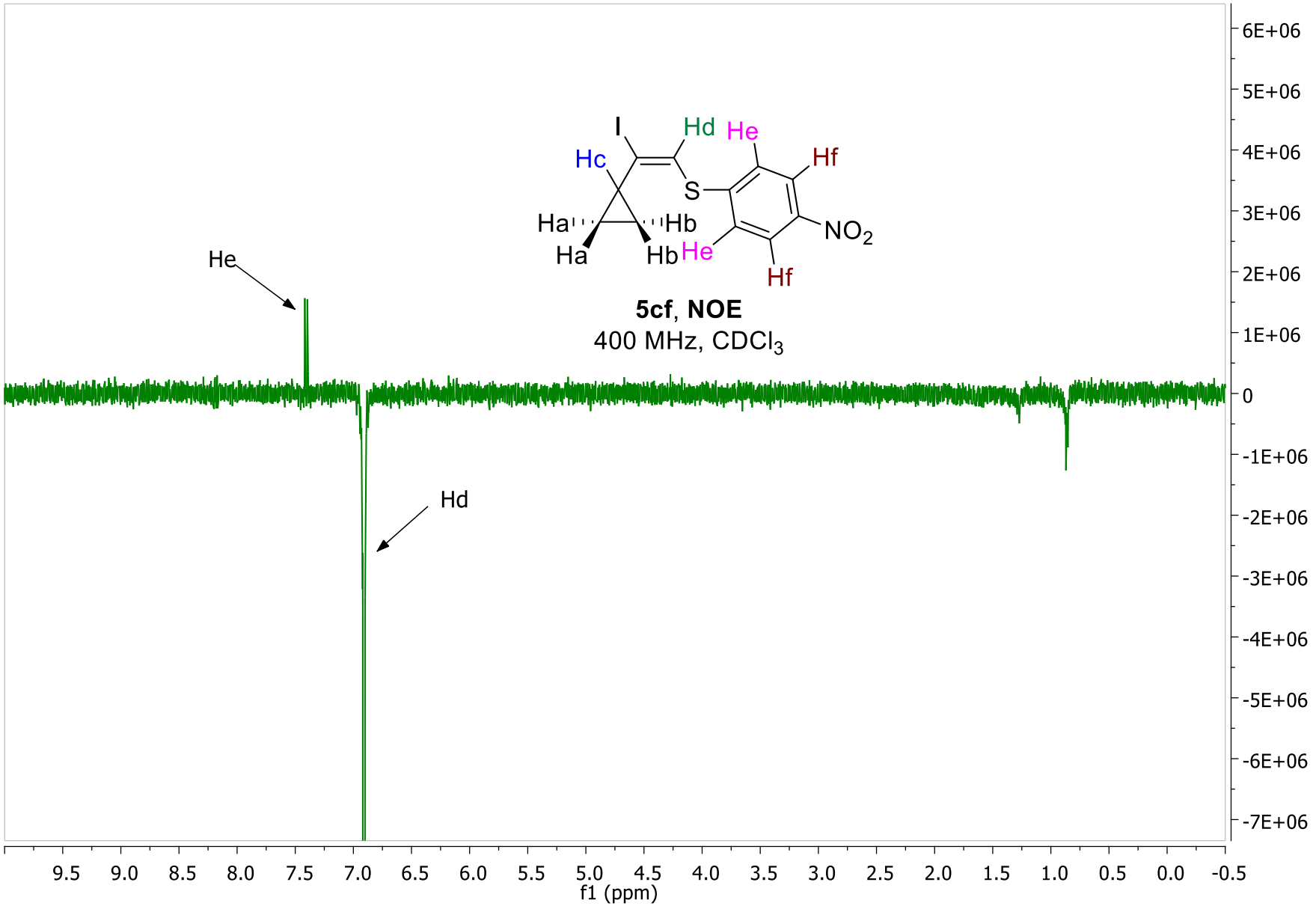
1 PDA Multi 1/236nm 4nm

PeakTable

PDA Ch1 236nm 4nm

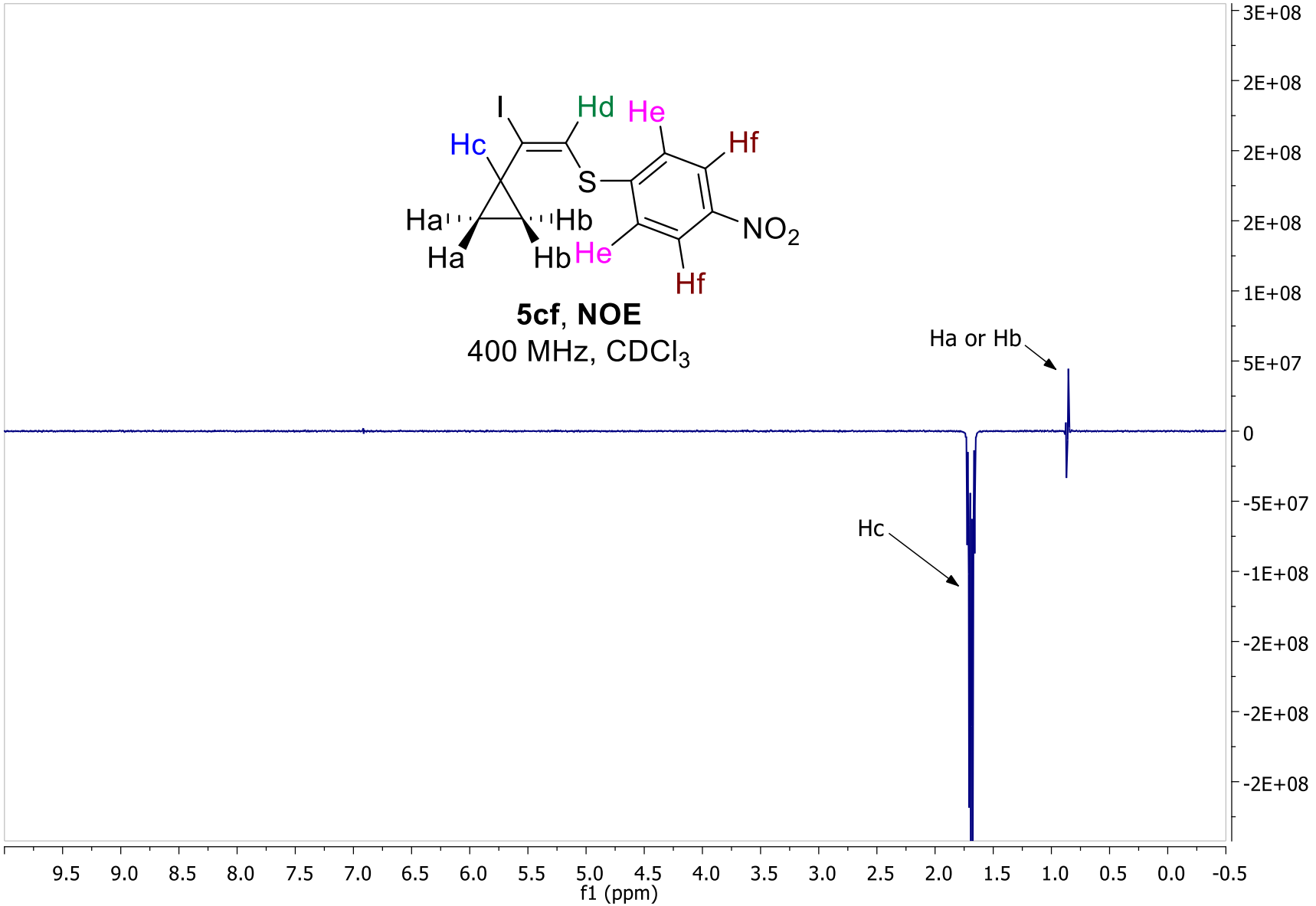
Peak#	Ret. Time	Area	Height	Area %	Height %
1	1.150	1244	390	0.373	4.177
2	1.384	1711	463	0.512	4.954
3	1.498	1506	414	0.451	4.427
4	1.818	2025	504	0.606	5.397
5	1.934	974	276	0.292	2.956
6	2.074	1936	586	0.579	6.268
7	2.184	5145	1247	1.540	13.340
8	4.803	319498	5465	95.647	58.481
Total		334039	9346	100.000	100.000


8.1746
8.1520
7.3975
7.3749
6.8934
6.8914
6.7229
6.7202
1.6566
1.6547
1.6406
1.6386
0.8505
0.8342
I
Hd
He
Hc
Hf
S
Ha
Hb
NO2
Ha
Hb
He
Hf
5cf, 1H NMR
400 MHz, CDCl3
Hf
He
Hd
Hc
Ha or Hb
2.09
2.10
1.00
1.08
2.11
2.01
f1 (ppm)



5cf, **NOE**

400 MHz, $CDCl_3$


I
Hd
He
Hc
Hf
S
Ha
Hb
NO2
Ha
Hb
He
Hf
5cf, NOE
400 MHz, CDCl3
Ha or Hb
Hc
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
-2E+08
-2E+08
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
f1 (ppm)