Supporting Information

Iodine-catalyzed, highly atom-economic synthesis of 9-sulfenylphenanthrenes and polycyclic heteroaromatics in water

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1. General considerations

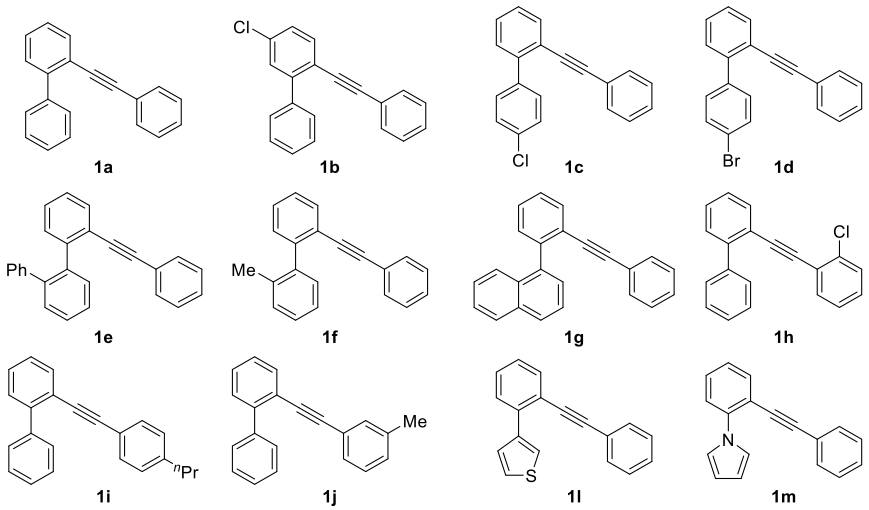
General reagent information

All reagents and solvents were purchased from Sigma-Aldrich, TCI and AVRA chemical companies. Flash column chromatography was performed using silica gel (100-200 mesh).

General analytical information

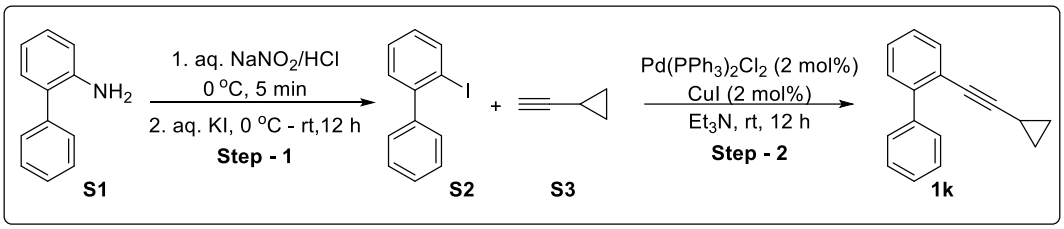
The starting materials such as 2-(phenylethynyl)-1,1'-biaryls and products such as 9-sulphenyl phenanthrenes and polycyclic heteroaromatics were characterized by ^{1}H and ^{13}C NMR. NMR spectra were recorded on a Bruker 400 MHz instrument (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Copies of ^{1}H and ^{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 are 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 of unknown compounds were obtained from BITS-Pilani, Pilani Campus, India on a high resolution mass spectrometer, HRMS (6545 Q-TOF LC/MS, Agilent). Melting points of unknown compounds were recorded on a KRUSS Optronic M3000 apparatus.

2. Experimental procedure for the synthesis of 2-alkynyl biaryls (1a-1m).



All starting materials except **1k** (**1a**,[1] **1b**,[1] **1c**,[1] **1d**,[1] **1e**,[1] **1f**,[1] **1g**,[1] **1h**,[1] **1i**,[1] **1j**,[1]**1l**,[1] **1m**[2]) were synthesized by following a literature protocol and characterized by ^{1}H and ^{13}C-NMR.[1,2]

3. Experimental procedure for the synthesis of 2-(cyclopropylethynyl)-1,1'-biphenyl (1k).



Step-1: 2-Iodo-1,1'-biphenyl **S2** was synthesized from [1,1'-biphenyl]-2-amine **S1** by following a reported protocol.[1]

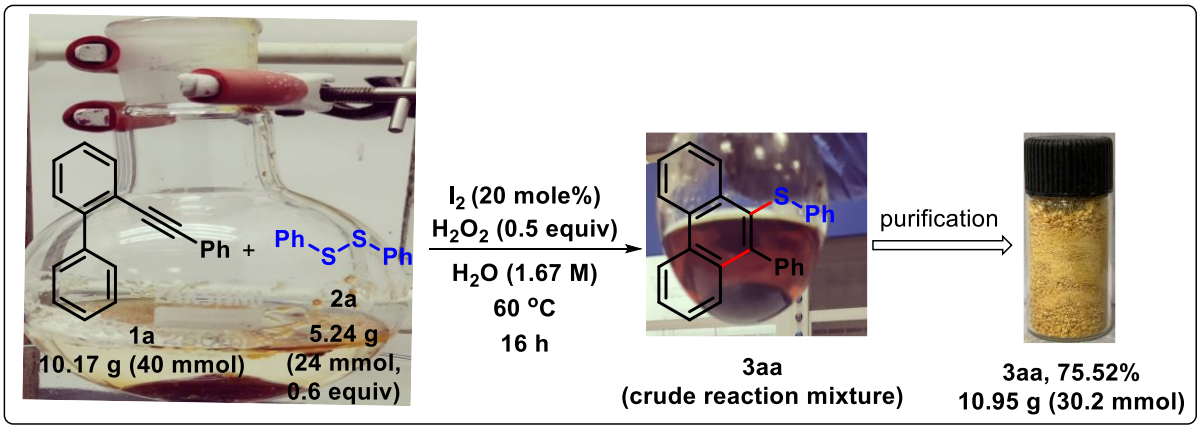
Step-2: 2-iodo-1,1'-biphenyl **S2** (1.4 g, 5 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol), CuI (0.019 g, 0.1 mmol) and Et_3N (13 mL) were added in a flame-dried two neck round bottomed flask (RBF) under N_2 atmosphere in a standard Schlenk-line process and stirred for 5 min at room temperature. Cyclopropylacetylene **S3** (508 μL, 6 mmol, 1.2 equiv) was then added to the reaction mixture under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature. After the completion of the reaction, Et_3N was evaporated under reduced pressure. The crude reaction mixture was diluted with ethyl acetate (30 mL) and washed with water three times (3 x 10 mL). The solvent was evaporated under reduced pressure and the crude product was purified through silica gel column chromatography to provide 2-(cyclopropylethynyl)-1,1'-biphenyl **1k** (0.436 g, 2 mmol) in 40% yield.

4. General experimental procedure for the synthesis of 9-sulfenylphenanthrenes and polycyclic Heteroaromatics (3aa-3al and 3ba−3ma). Representative experimental procedure for the synthesis of phenyl(10-phenylphenanthren-9-yl)sulfane (3aa):

Phenyl(10-phenylphenanthren-9-yl)sulfane **1a** (0.127 g, 0.5 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (0.065 g, 0.3 mmol, 0.6 equiv) and I_2 (0.0254 g, 0.1 mmol) were taken in a RBF and H_2O (0.3 mL, 1.6 M) was added to it. Then H_2O_2 (0.02 mL, 0.25 mmol, 0.5 equiv) was added to the RBF and the reaction mixture was stirred in an oil bath at 60 °C under aerobic atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, iodine was quenched with

saturated sodium thiosulfate solution and ethyl acetate (30 mL) was added to the reaction mixture. The whole solution was then transferred to a separating funnel for extraction. The reaction mixture was extracted with ethyl acetate twice (2 X 10 mL) and the combined organic layer was washed with water (3 X 10 mL). The solvent was evaporated under reduced pressure to afford the crude product which was purified by flash column chromatography through silica gel to afford the pure product, phenyl(10-phenylphenanthren-9-yl)sulfane **3aa** (0.167 g, 0.46 mmol) in 92% yield.

4.1. Multigram-scale synthesis of phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) : Phenyl(10-phenylphenanthren-9-yl)sulfane **1a** (10.17 g, 40 mmol, 1 equiv), 1,2-diphenyldisulfane **2a** (5.24 g, 24 mmol, 0.6 equiv) and I_2 (2.03 g, 8 mmol) were taken in a RBF and H_2O (24.4 mL, 1.6 M) was added to it. Then H_2O_2 (1.6 mL, 20 mmol, 0.5 equiv) was added to the RBF and the reaction mixture was stirred in an oil bath at 60 ^oC under aerobic atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, iodine was quenched with saturated sodium thiosulfate solution and ethyl acetate was added to the reaction mixture. The whole solution was then transferred to a separating funnel for extraction. The reaction mixture was extracted with ethyl acetate twice and the combined organic layer was washed with water. The solvent was evaporated under reduced pressure to afford the crude product which was purified by flash column chromatography through silica gel to afford the pure product, phenyl(10-phenylphenanthren-9-yl)sulfane **3aa** (10.95 g, 30.2 mmol) in 75.52% yield.



5. Table S1. Calculation of EcoScale score for the I_2 catalyzed synthetic process in water to synthesize phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) from 2-(phenylethynyl)-1,1'-biphenyl (1a) and diphenyl diselenide (2a) (this work)

EcoScale Calculation:

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

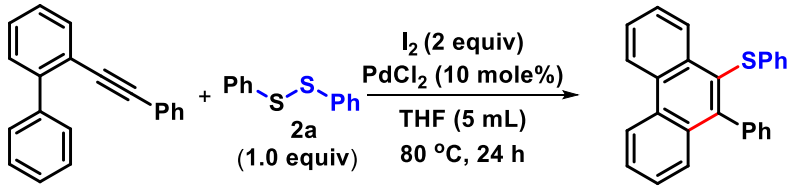
A. Calculation of Penalty Points :

Parameters		Penalty Points
1. Yield:	(100 - % of yield)/2 = (100 - 92)/2	4
2. Price of reaction components (To obtain 10 mmol of end product, **3aa**)		
a. 2-(Phenylethynyl)-1,1'-biphenyl = 10.87 mmole		
[Synthesis cost : Required Chemicals :		
i) [1,1'-biphenyl]-2-amine = 2.74 g = USD 7.85		
ii) HCl = 8.32 mL= USD 0.264		
iii) $NaNO_2$ = 1.344 g = USD 0.0062		
iv) KI = 4 g = USD 1.272		
v) Bis(triphenyl phosphine)Pd(II) dichloride= 0.095 g = USD 1.81		
vi) CuI = 0.025 g = USD 0.0083		
vii) Phenyl acetylene = 1.79 mL = USD 0.765		
viii) Triethylamine = 35.36 mL = USD 0.375		
b. 1,2-Diphenyldisulfane = 6.5 mmole = 1.423 g = USD 0.911		
c. Iodine (As catalyst) = 2.17 mmole = 0.552 g = USD 0.163		
d. Hydrogen Peroxide (30% aqueous solution) = 0.42 mL = USD 0.11		
Total cost of synthesis of **3aa** = (13.84 + 0.911 + 0.163 + 0.11) = USD 15.024 Thus expensive, since \$10<(total cost of synthesis of 10 mmol of **3aa**) < \$50:		**3**
3. Safety		
1,2-Diphenyldisulfane (T)		**5**
Iodine (T)		**5**
4. Technical Setup Common Setup		**0**
5. Temperature/ Time 60 ^oC, 14 h (Heating, > 1h)		**3**
6. Work up and purification :		
a. Adding solvent		**0**
b. Liquid-Liquid extraction		**3**
c. Classical Chromatography		**10**
	Total penalty points:	**33**

B. Ecoscale calculation:

EcoScale score: (100 - 33) = 67 (>50; it is an acceptable synthesis)

6. Table S2. Calculation of green metrics for the Pd-catalyzed synthetic process to synthesize phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) from 2-(phenylethynyl)-1,1'-biphenyl (1a) and diphenyl diselenide (2a)[3]



1a (0.5 mmol) 3aa (92%)

Yield of desired product (3aa) = 95%

$$\text{Atom Economy (\%)} = \frac{\text{mass of desired product}}{\text{total mass of all reactants}} \times 100 = \frac{362.49}{254.33 + 218.33 + (2 \times 253.81)} \times 100 = 36.98\%$$

$$\text{Atom Efficiency (\%)} = (\%\text{yield of product} \times \%\text{atom economy}) \times 100 = (95\% \times 36.98\%) \times 100 = 35.13\%$$

$$\text{Carbon Efficiency (\%)} = \frac{\text{amount of carbon in desired product}}{\text{total amount of carbon presented in all reactants}} \times 100 = \frac{26}{20 + 12} \times 100 = 81.3\%$$

$$\text{Reaction Mass Efficiency (\%)} = \frac{\text{mass of isolated product}}{\text{mass of all reactants}} \times 100 = \frac{0.172}{0.127 + 0.109 + 0.253} \times 100 = 35.17\%$$

Reactant 1:	2-(Phenylethynyl) 1,1'-biphenyl (1a)	0.127 g	0.5 mmol	FW 254.332
Reactant 2:	1,2-Diphenyldisulfane (2a)	0.109 g	0.5 mmol	FW 218.332
Catalyst 1:	Iodine	0.253 g	1.0 mmol	FW 253.8089
Catalyst 2:	palladium(II) chloride	0.008 g	0.05 mmol	FW 177.32
Solvent:	THF	4.44 g	61.57 mmol	FW 72.11
Product:	Phenyl(10-phenylphenanthren-9-yl)sulfane	0.172 g	0.47 mmol	FW 362.49

$$\text{E-factor} = \frac{\text{total waste (Kg)}}{\text{total product (Kg)}} = \frac{(0.127 + 0.109 + 0.253 + 0.008 + 4.44) - 0.172}{0.172} = 27.7 \text{ Kg waste/Kg pdt}$$

7. Table S3. Calculation of EcoScale score for the Pd-catalyzed synthetic process to synthesize phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) from 2-(phenylethynyl)-1,1'-biphenyl (1a) and diphenyl diselenide (2a)[3]

Eco Scale Calculation:

Eco Scale = 100 - Sum of individual penalties

Score on Eco Scale: > 75, Excellent; >50, acceptable; <50, Inadequate

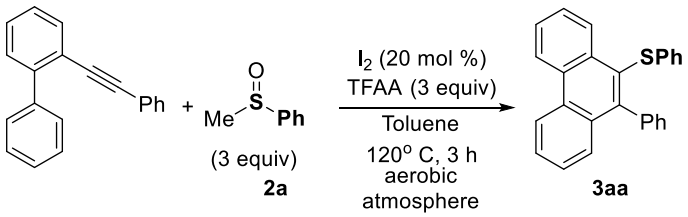
A. Calculation of Penalty Points :

Parameters		Penalty Points
1. Yield:	(100 - % of yield)/2 = (100 - 95)/2 = 2.5	**2.5**
2. Price of reaction components (To obtain 10 mmol of end product, **3aa**)		
a. 2-(Phenylethynyl)-1,1'-biphenyl = 10.64 mmole = 2.94 g = USD 13.55		
[Synthesis cost : Required Chemicals :		
i) [1,1'-biphenyl]-2-amine = 2.65 g = USD 7.71		
ii) HCl = 8.13 mL= USD 0.26		
iii) $NaNO_2$ = 1.31 g = USD 0.059		
i**v)** KI = 3.91 g = USD 1.24		
v) Bis(triphenyl phosphine)Pd(II) dichloride= 0.093 g = USD 1.77		
vi) CuI = 0.025 g = USD 0.0083		
vii) Phenyl acetylene = 1.75 mL = USD 2.19		
viii) Triethylamine = 31.90 mL = USD 0.316		
b. 1,2-Diphenyldisulfane = 10.64 mmole = 2.32 g = USD 1.49		
c. Iodine = 21.28 mmole = 5.40 g = USD 1.60		
d. Palladium(II) chloride (As catalyst) = 0.188 g = USD 13.35		
e. THF = 106.4 mL = USD 8.34		
Total cost of synthesis of **3aa** = (13.55 + 1.49 + 1.60 + 13.35 + 8.34) = USD 38.33 Thus expensive, since \$10<(total cost of synthesis of 10 mmol of **3aa**) < \$50:		**3**
3. Safety		
1,2-Diphenyldisulfane (T)		**5**
Iodine (T)		**5**
Palladium(II) chloride (T)		**5**
THF (T, F)		**10**
4. Technical Setup		
Common Setup		**0**
Inert gas atmosphere		**1**
5. Temperature/ Time		
80 ^{o}C, 14 h (Heating, > 1h)		**3**
6. Work up and purification :		
a. Adding solvent		**0**
b. Liquid-Liquid extraction		**3**
c. Classical Chromatography		**10**
	Total penalty points:	**47.5**

B. Ecoscale calculation:

Eco-scale Score: (100 - 47.5) = 52.5 (>50; it is an acceptable synthesis)

8. Table S4. Calculation of green metrics for the I_2-catalyzed synthetic process to synthesize phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) from 2-(phenylethynyl)-1,1'-biphenyl (1a) and (methylsulfinyl)benzene (2a′)[1]



Yield of desired product (3aa) = 81%

$$\text{Atom Economy (\%)} = \frac{\text{mass of desired product}}{\text{total mass of all reactants}} \times 100 = \frac{362.49}{254.33 + [(3 \times 140.2) + (3 \times 210.3)]} \times 100 = \mathbf{27.76\%}$$

$$\text{Atom Efficiency (\%)} = (\%\text{yield of product} \times \%\text{atom economy}) \times 100 = (81\% \times 27.76\%) \times 100 = \mathbf{22.48\%}$$

$$\text{Carbon Efficiency (\%)} = \frac{\text{amount of carbon in desired product}}{\text{total amount of carbon presented in all reactants}} \times 100 = \frac{24}{20 + (3 \times 7) + (3 \times 4)} \times 100 = \mathbf{45.28\%}$$

$$\text{Reaction Mass Efficiency (\%)} = \frac{\text{mass of isolated product}}{\text{total mass of all reactants}} \times 100 = \frac{0.147}{0.127 + 0.210 + 0.315} \times 100 = \mathbf{22.55\%}$$

Reactant 1:	**2-(Phenylethynyl) 1,1'-biphenyl (1a)**	0.127 g	0.5 mmol	FW 254.332
Reactant 2:	**Methyl Phenyl Sulfoxide**	0.210 g	1.5 mmol	FW 140.2
Catalyst:	**Iodine**	0.025 g	0.1 mmol	FW 253.8089
Reagent :	**TFAA**	0.315 g	1.5 mmol	FW 210.3
Solvent:	**Toluene**	1.083 g	11.75 mmol	FW 92.14
Product:	**phenyl(10-phenylphenanthren-9-yl)sulfane (3aa)**	0.147 g	0.405 mmol	FW 362.49

$$\text{E-factor} = \frac{\text{total waste (Kg)}}{\text{total product (Kg)}} = \frac{(0.127 + 0.210 + 0.025 + 0.315 + 1.083) - 0.147}{0.147} = \mathbf{10.97}\ \text{Kg waste/Kg pdt}$$

9. Table S5. Calculation of EcoScale score for the I_2-catalyzed synthetic process to synthesize phenyl(10-phenylphenanthren-9-yl)sulfane (3aa) from 2-(phenylethynyl)-1,1'-biphenyl (1a) and (methylsulfinyl)benzene (2a′)[1]

Eco Scale Calculation:

Eco Scale = 100 - Sum of individual penalties

Score on Eco Scale: > 75, Excellent; >50, acceptable; <50, Inadequate

A. Calculation of Penalty Points :

Parameters		Penalty Points
1. Yield:	(100 - % of yield)/2 = (100 - 81)/2	**9.5**
2. Price of reaction components (To obtain 10 mmol of end product, **3aa**)		
a. 2-(Phenylethynyl)-1,1'-biphenyl = 12.35 mmol = 3.14 g = USD 15.72		
[Synthesis cost : Required Chemicals :		
i) [1,1'-biphenyl]-2-amine = 3.07 g = USD 8.93		
ii) HCl = 9.44 mL= USD 0.30		
iii) $NaNO_2$ = 1.53 g = USD 0.07		
i**v)** KI = 4.54 g = USD 1.44		
v) Bis(triphenyl phosphine)Pd(II) dichloride= 0.108 g = USD 2.06		
vi) CuI = 0.029 g = USD 0.0097		
vii) Phenyl acetylene = 2.034 mL = USD 2.54		
viii) Triethylamine = 37.06 mL = USD 0.37		
b. Methyl Phenyl Sulfoxide = 37.05 mmol = 5.19 g = USD 28.65		
c. Iodine (As catalyst) = 2.47 mmol = 0.627 g = USD 0.19		
d. TFAA = 5.16 mL = USD 0.97		
e. Toluene = 30.88 mL = USD 1.13		
Total cost of synthesis of **3aa** = (13.67 + 28.74 + 0.186 + 0.967 + 1.136) = USD 46.66 Thus expensive, since \$10<(total cost of synthesis of 10 mmol of **3aa**) < \$50:		**3**
3. Safety		
Methyl Phenyl Sulfoxide (T)		**5**
Iodine (T)		**5**
TFAA		**5**
Toluene (F,T)		**10**
4. Technical Setup Common Setup		**0**
5. Temperature/time: 120 ^oC, 3 h (Heating, > 1h)		**3**
6. Work-up and purification:		
Adding of solvents		**0**
Liquid-liquid Extraction		**3**
Column Chromatography		**10**
Total penalty points:		**53.5**

B. Ecoscale calculation:

Eco-scale Score: (100 - 53.5) = 46.5 (<50, it is an inadequate synthesis)

10.

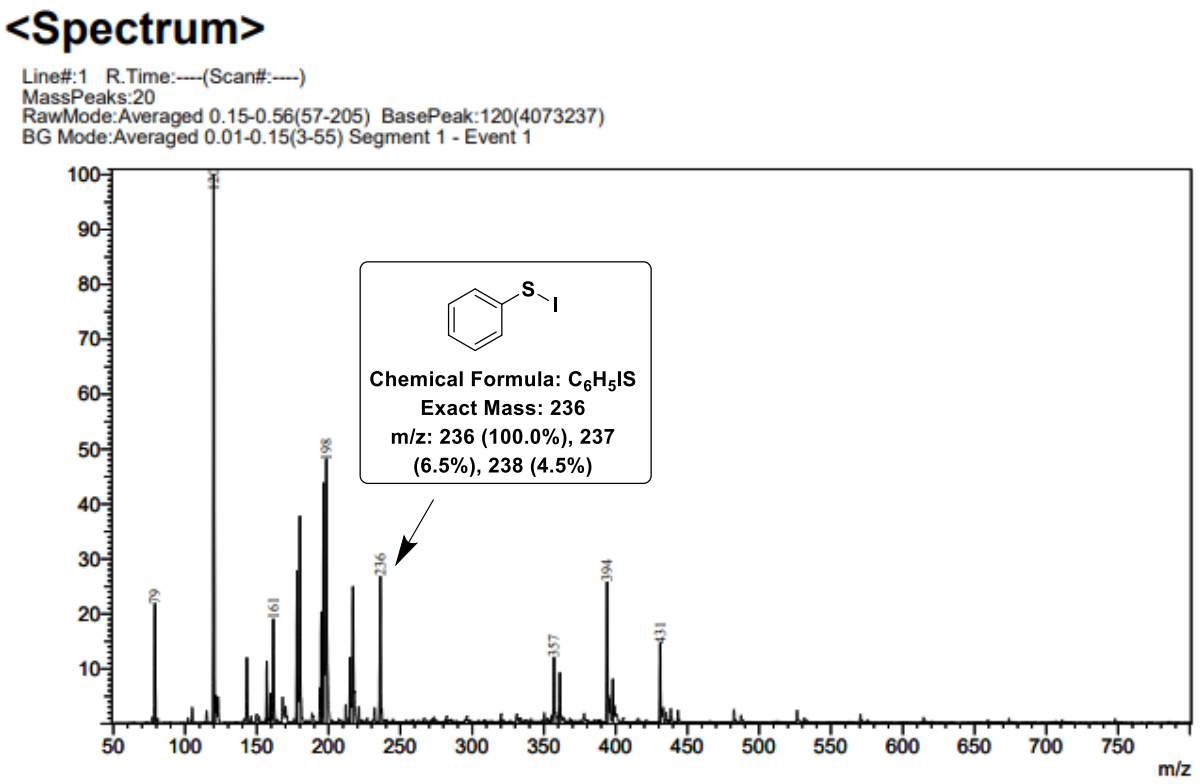
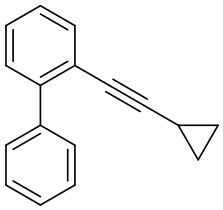


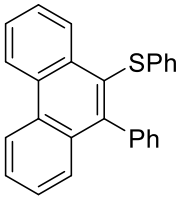
Figure 1 Mass spectrum of the reaction mixture of diphenyl disulfide and I_2

11. Analytical data of starting material (1k)

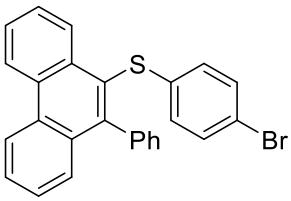


2-(cyclopropylethynyl)-1,1'-biphenyl (1k). Pale yellow liquid (0.436 g, 40%); eluent hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.53 – 7.48 (m, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 1.33 (ddd, *J* = 10.0, 6.6, 4.1 Hz, 1H), 0.81 – 0.74 (m, 2H), 0.68 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 140.74, 132.84, 129.28, 129.21, 127.69, 127.59, 127.19, 126.87, 122.20, 96.44, 75.20, 8.32, 0.30. HRMS (ESI), m/ z calcd for $C_{17}H_{15}$ $[M + H]^+$: 219.1168; found: 219.1158.

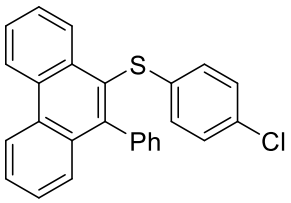
12. Analytical data of all synthesized products (3aa-3al and 3ba -3ma)



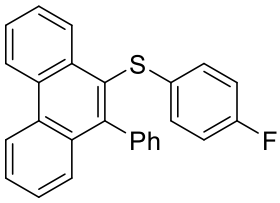
Phenyl(10-phenylphenanthren-9-yl)sulfane (3aa).[3] Yellow solid (0.167 g, 92%); eluent hexane; mp = 125–127 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (dd, *J* = 8.2, 3.1 Hz, 2H), 8.72 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.64 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.46 (m, 3H), 7.36 – 7.32 (m, 2H), 7.13 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.09 – 7.03 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.82, 140.15, 138.97, 132.21, 132.04, 131.08, 130.87, 129.48, 128.70, 128.63, 128.02, 127.93, 127.61, 127.57, 127.34, 127.09, 127.05, 126.71, 126.33, 124.63, 122.74, 122.55.



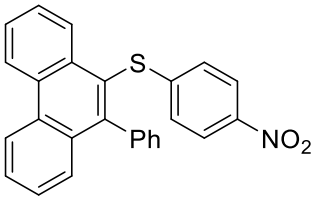
(4-Bromophenyl)(10-phenylphenanthren-9-yl)sulfane (3ab) : White solid (0.185 g, 84%); eluent hexane; mp = 166–168 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (dd, *J* = 18.2, 8.2 Hz, 2H), 8.63 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.73 – 7.59 (m, 3H), 7.50 – 7.44 (m, 3H), 7.28 – 7.24 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.93 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.63, 139.34, 138.61, 133.68, 132.02, 130.76, 130.70, 130.41, 129.74, 129.46, 128.88, 128.71, 128.23, 128.16, 127.94, 127.70, 127.44, 126.51, 124.86, 124.38, 122.64, 121.06. Anal calcd for $C_{26}H_{17}BrS$: C, 70.75; H, 3.88; S, 7.26; found C, 70.91; H, 3.56; S, 7.41.



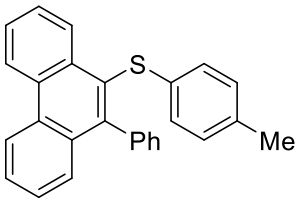
(4-Chlorophenyl)(10-phenylphenanthren-9-yl)sulfane (3ac) :[3] White solid (0.131 g, 66%); eluent hexane; mp = 115–117 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81 – 8.78 (m, 2H), 8.58 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.71 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.48 (m, 2H), 7.44 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.24 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR (100 MHz, CDCl3)** δ 147.04, 140.01, 137.54, 132.17, 131.80, 131.17, 130.97, 130.47, 129.43, 128.78, 128.03, 127.82, 127.79, 127.71, 127.55, 127.50, 127.21, 126.84, 126.66, 122.87, 122.60.



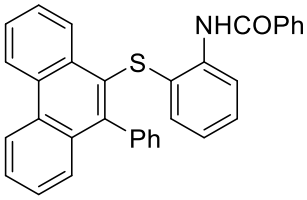
(4-Fluorophenyl)(10-phenylphenanthren-9-yl)sulfane (3ad) :[3] Fluoroscent Blue solid (0.144 g, 70%); eluent hexane; mp = 118−120 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (d, *J* = 8.2 Hz, 2H), 8.76 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.75 (ddt, *J* = 8.4, 6.8, 1.8 Hz, 2H), 7.69 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.61 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.54 – 7.51 (m, 3H), 7.34 (ddd, *J* = 4.0, 2.9, 1.5 Hz, 2H), 6.97 (dd, *J* = 9.0, 5.1 Hz, 2H), 6.86 (t, *J* = 8.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.89, 159.46, 146.67, 140.02, 133.86, 133.84, 132.14, 131.91, 131.03, 130.91, 129.54, 128.64, 128.32, 128.25, 127.96, 127.85, 127.67, 127.58, 127.53, 127.38, 127.10, 126.76, 122.80, 122.54, 115.83, 115.61.



(4-Nitrophenyl)(10-phenylphenanthren-9-yl)sulfane (3ae) :[3] Yellow crystalline solid (0.082 g, 36%); eluent hexane/EtOAc (10:1); mp = 188−190 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (d, *J* = 8.4 Hz, 2H), 8.46 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 2H), 7.79 – 7.72 (m, 2H), 7.67 – 7.45 (m, 4H), 7.43 (dd, *J* = 4.7, 2.4 Hz, 2H), 7.24 – 7.21 (m, 2H), 6.96 (d, *J* = 9.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.95, 147.78, 144.81, 139.61, 132.05, 131.41, 131.33, 131.07, 129.14, 128.96, 128.32, 128.16, 128.00, 127.80, 127.56, 127.18, 127.06, 125.60, 124.69, 123.89, 123.12, 122.71.

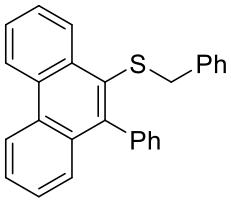


(10-Phenylphenanthren-9-yl)(p-tolyl)sulfane (3af) :[3] Yellow solid (0.170 g, 90%); eluent hexane; mp = 105–107 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (dd, *J* = 8.2, 4.4 Hz, 2H), 8.72 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.66 – 7.61 (m, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.48 (m, 3H), 7.37 – 7.31 (m, 2H), 6.92 (dd, *J* = 21.3, 8.3 Hz, 4H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.63, 140.25, 135.34, 134.38, 132.23, 132.07, 131.04, 130.88, 129.55, 129.44, 128.68, 128.12, 127.94, 127.52, 127.30, 126.98, 126.68, 126.47, 122.71, 122.54, 20.82.

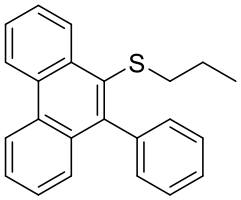


N-(2-(10-Phenylphenanthren-9-yl)phenyl)benzamide (3ag) : Off White solid (0.145 g, 60%); eluent hexane/EtOAc (20:1); mp = 155−157 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.36 – 8.27 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H),

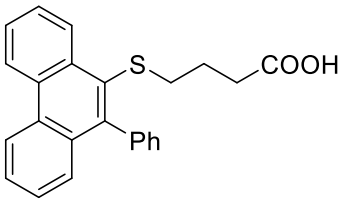
7.28 (s, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.21 (ddd, *J* = 8.3, 5.1, 1.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.00 – 6.94 (m, 3H), 6.88 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.78 (dd, *J* = 5.3, 2.1 Hz, 3H), 6.72 – 6.66 (m, 1H), 6.58 – 6.53 (m, 2H), 6.43 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.31 (m, 1H**). ^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.93, 146.03, 139.65, 136.45, 134.60, 132.76, 132.20, 131.64, 130.78, 130.71, 130.57, 129.41, 128.63, 128.50, 128.22, 128.16, 128.08, 127.83, 127.70, 127.45, 127.38, 127.27, 127.16, 127.11, 126.80, 124.65, 122.85, 122.53, 121.10. HRMS (ESI), m/z calcd for $C_{33}H_{24}NOS$ $[M + H]^+$: 482.1573; found: 482.1553.



Benzyl(10-phenylphenanthren-9-yl)sulfane (3ah) : White crystalline solid (0.143 g, 76%); eluent hexane; mp = 185−187 ºC; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.90 (dd, *J* = 6.2, 3.3 Hz, 1H), 8.82 – 8.73 (m, 2H), 7.74 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.42 (d, *J* = 6.9 Hz, 3H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 3H), 6.97 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.82 (d, *J* = 6.4 Hz, 2H), 3.83 (s, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 146.22, 140.35, 137.72, 132.22, 132.10, 130.70, 130.60, 130.11, 128.95, 128.53, 128.19, 127.80, 127.40, 127.17, 127.03, 126.84, 126.57, 122.98, 122.45, 40.84. HRMS (ESI), m/z calcd for $C_{27}H_{20}S$ $[M + H]^+$: 377.1358; found: 377.1285.

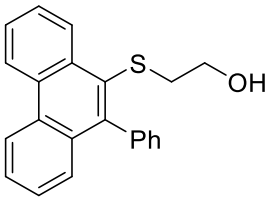


(10-Phenylphenanthren-9-yl)(propyl)sulfane (3ai) : White crystalline solid (0.115 g, 70%); eluent hexane; mp = 100−102 ºC; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.97 (d, *J* = 7.6 Hz, 1H), 8.79 (dd, *J* = 12.8, 8.0 Hz, 2H), 7.80 – 7.72 (m, 2H), 7.67 (ddd, *J* = 8.3, 5.8, 2.4 Hz, 1H), 7.60 – 7.49 (m, 5H), 7.40 (dd, *J* = 7.8, 1.3 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.45 (dd, *J* = 14.7, 7.3 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 145.39, 140.64, 132.53, 132.10, 130.65, 130.45, 130.35, 128.32, 127.93, 127.87, 127.20, 127.11, 126.98, 126.74, 126.56, 122.85, 122.41, 38.67, 22.87, 13.41 (Overlapping peaks present). HRMS (ESI), m/z calcd for $C_{23}H_{21}S$ $[M + H]^+$: 329.1358; found: 329.1292.

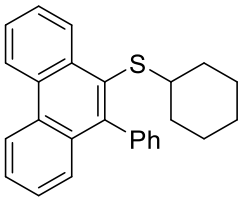


4-((10-Phenylphenanthren-9-yl)thio)butanoic acid (3aj) : Yellow crystalline solid (0.104 g, 56%); eluent hexane/EtOAc (20:1); mp = 130−132 ºC; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.90 (dd, *J* = 6.9, 2.6 Hz, 1H), 8.77 (dd, *J* = 12.4, 7.9 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.67 (ddd, *J* = 8.3, 5.9, 2.4 Hz, 1H), 7.56 – 7.48 (m, 5H), 7.37 (dd, *J* = 7.8, 1.5

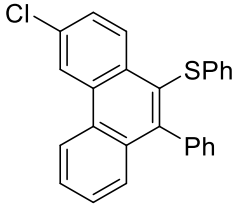
Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 2.24 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.65 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.33, 145.69, 140.38, 132.23, 131.97, 130.71, 130.53, 130.40, 129.42, 128.38, 127.94, 127.69, 127.32, 127.26, 127.15, 126.83, 126.63, 122.94, 122.42, 77.00, 35.54, 32.55, 24.04. HRMS (ESI), m/z calcd for $C_{24}H_{21}O_2S$ [M]: 373.1257; found: 373.1180.



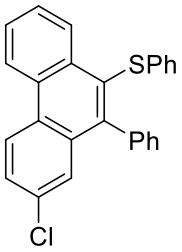
2-(10-Phenylphenanthren-9-yl)ethan-1-ol (3ak) : Yellow solid (0.066g, 40%); eluent hexane/EtOAc (25:1); mp = 123−125 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (dd, *J* = 7.5, 2.1 Hz, 1H), 8.79 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.67 (ddd, *J* = 8.3, 5.0, 3.3 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.53 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 3.38 (t, *J* = 5.6 Hz, 2H), 2.87 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.03, 140.35, 131.80, 130.89, 130.63, 130.38, 128.50, 128.28, 127.60, 127.50, 127.37, 126.99, 126.80, 123.13, 122.48, 59.78, 39.77. Anal calcd for $C_{22}H_{18}OS$: C, 79.97; H, 5.49; S, 9.70; found C, 79.81; H, 5.61; S, 9.86.



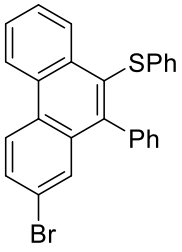
Cyclohexyl(10-phenylphenanthren-9-yl)sulfane (3al) :[3] Off White solid (,0.074 g, 38%); eluent hexane; mp = 129−131 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (dd, *J* = 7.2, 2.5 Hz, 1H), 8.76 (dd, *J* = 10.5, 7.8 Hz, 2H), 7.72 (ddd, *J* = 4.6, 2.4, 0.6 Hz, 2H), 7.65 (m, 1H), 7.55 – 7.52 (m, 1H), 7.52 – 7.46 (m, 2H), 7.45 (d, *J* = 3.6 Hz, 2H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 1.4 Hz, 1H), 2.83 (tt, *J* = 10.7, 3.7 Hz, 1H), 1.69 (dd, *J* = 13.3, 3.0 Hz, 2H), 1.51 – 1.45 (m, 1H), 1.33 – 1.18 (m, 4H), 1.09 (ddd, *J* = 16.7, 10.3, 3.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.47, 140.62, 133.16, 132.17, 130.69, 130.56, 130.44, 129.85, 128.36, 128.25, 127.78, 127.10, 127.05, 126.94, 126.70, 126.57, 122.77, 122.42, 48.55, 33.46, 26.03, 25.63.



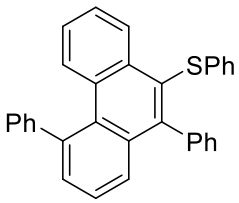
(6-Chloro-10-phenylphenanthren-9-yl)(phenyl)sulfane (3ba) : Yellow crystalline solid (0.133 g, 67%); eluent hexane; mp = 155−157 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 2.1 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.9 Hz, 1H), 7.71 (ddd, *J* = 8.3, 6.2, 2.1 Hz, 1H), 7.51 (dd, *J* = 3.0, 1.6 Hz, 1H), 7.49 (dd, *J* = 1.9, 1.0 Hz, 2H), 7.45 (d, *J* = 2.0 Hz, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.06 (ddd, *J* = 4.9, 3.3, 1.9 Hz, 3H), 7.04 – 7.01 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.04, 141.63, 133.87, 133.28, 132.45, 132.36, 131.80, 130.86, 130.09, 129.61, 129.20, 129.03, 128.03, 127.93, 127.72, 127.47, 127.39, 127.14, 125.72, 122.63, 122.32. HRMS (ESI), m/z calcd for $C_{26}H_{17}ClS$ [M]: 396.0739; found: 396.0717.



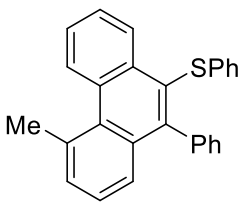
(2-Chloro-10-phenylphenanthren-9-yl)(phenyl)sulfane (3ca):[3] White crystalline solid (0.129 g, 62%); eluent hexane; mp = 145−147 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 – 8.72 (m, 3H), 7.60 – 7.73 (m, 1H), 7.67 – 7.59 (m, 2H), 7.52 – 7.43 (m, 4H), 7.28 (d, *J* = 2.2 Hz, 2H), 7.15 – 7.07 (m, 2H), 7.07 – 7.01 (m, 1H), 6.99 – 6.89 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.69, 139.37, 138.60, 133.31, 132.76, 131.96, 130.36, 129.44, 128.87, 128.70, 128.20, 128.15, 128.00, 127.83, 127.67, 127.61, 127.42, 126.49, 124.85, 124.24, 122.68.



(2-Bromo-10-phenylphenanthren-9-yl)(phenyl)sulfane (3da) : White solid (0.155 g, 67%); eluent hexane; mp = 166−168 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 8.1 Hz, 1H), 8.69 – 8.59 (m, 2H), 7.78 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.67 – 7.57 (m, 2H), 7.46 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.24 (dd, *J* = 5.4, 2.1 Hz, 2H), 7.13 – 7.06 (m, 2H), 7.06 – 6.99 (m, 1H), 6.92 (dd, *J* = 5.3, 3.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.63, 139.34, 138.61, 133.68, 132.02, 130.76, 130.70, 130.41, 129.74, 129.46, 128.88, 128.71, 128.23, 128.16, 127.94, 127.70, 127.44, 126.51, 126.37, 124.86, 124.38, 122.64, 121.06. Anal calcd for $C_{26}H_{17}BrS$: C, 70.75; H, 3.88; S, 7.26 found C, 70.96; H, 3.61; S, 7.10.

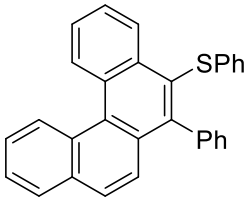


(4,10-Diphenylphenanthren-9-yl)(phenyl)sulfane (3ea) :White crystalline solid (0.154 g, 70%); eluent hexane; mp = 200−202 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 14.7 Hz, 12H), 7.31 (d, *J* = 3.0 Hz, 2H), 7.12 (dd, *J* = 11.6, 7.3 Hz, 3H), 7.00 (dd, *J* = 31.2, 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.71, 145.25, 140.62, 140.23, 138.90, 133.74, 133.06, 131.89, 130.89, 129.60, 129.09, 129.03, 128.89, 128.66, 128.28, 128.00, 127.77, 127.47, 127.35, 127.12, 126.94, 126.53, 125.68, 124.97, 124.71. Anal calcd for $C_{32}H_{22}S$: C, 87.63; H, 5.06; S, 7.31; found C, 87.76; H, 5.18; S, 7.18.

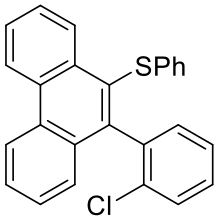


(4-Methyl-10-phenylphenanthren-9-yl)(phenyl)sulfane (3fa) : Yellow solid (0.135 g, 72%); eluent hexane; mp = 188−190 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (d, *J* = 8.2 Hz, 1H), 8.77 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.46 (dd, *J*

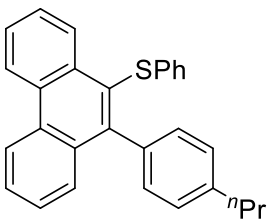
= 4.1, 2.4 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 7.14 – 7.09 (m, 2H), 7.06 – 7.02 (m, 1H), 6.98 (d, *J* = 1.4 Hz, 1H), 6.96 (s, 1H), 3.23 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.23, 140.88, 138.94, 134.98, 133.71, 132.94, 132.23, 132.03, 131.33, 129.50, 128.62, 127.92, 127.71, 127.23, 127.11, 126.84, 126.39, 125.75, 125.64, 124.61, 27.29. HRMS (ESI) m/z calcd for $C_{27}H_{21}S$ $[M + H]^+$: 377.1358; found: 377.1286.



Phenyl(6-phenylbenzo[c]phenanthren-5-yl)sulfane (3ga) : Yellow solid (0.083 g, 38%); eluent hexane; mp = 145−147 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.15 (d, *J* = 8.0 Hz, 2H), 8.83 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.67 (m, 5H), 7.49 (dd, *J* = 5.5, 3.4 Hz, 4H), 7.37 – 7.29 (m, 2H), 7.12 (dd, *J* = 11.4, 4.3 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 1H), 7.00 – 6.94 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.03, 140.21, 138.98, 133.52, 133.31, 130.64, 130.40, 129.84, 129.53, 129.15, 128.83, 128.65, 128.58, 128.21, 127.95, 127.46, 127.40, 127.12, 127.04, 126.64, 126.25, 126.22, 125.47, 124.74. HRMS (ESI), m/z calcd for $C_{30}H_{21}S$ $[M + H]^+$: 413.1358; found: 413.1327.

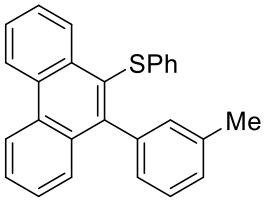


(10-(2-Chlorophenyl)phenanthren-9-yl)(phenyl)sulfane (3ha) : White crystalline solid (0.188g, 95%); eluent hexane; mp = 130−132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (d, *J* = 2.0 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.9 Hz, 1H), 7.72 (ddd, *J* = 8.3, 5.2, 3.1 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.45 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.30 – 7.26 (m, 2H), 7.14 – 7.09 (m, 2H), 7.04 (ddd, *J* = 7.3, 3.6, 1.2 Hz, 1H), 6.94 – 6.90 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.03, 139.80, 138.57, 133.31, 132.59, 132.05, 130.47, 130.08, 129.78, 129.45, 128.82, 128.75, 128.01, 127.97, 127.89, 127.50, 127.37, 126.80, 126.40, 124.89, 122.63, 122.42. Anal calcd for $C_{26}H_{17}ClS$: C, 78.67; H, 4.32; S, 8.08; found C, 78.56; H, 4.48; S, 8.21.

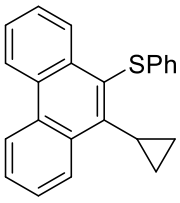


Phenyl(10-(4-propylphenyl)phenanthren-9-yl)sulfane (3ia) : Off White crystalline solid (0.142 g, 70%); eluent hexane; mp = 150−152 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81 (dd, *J* = 8.2, 3.4 Hz, 2H), 8.67 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.72 (dtd, *J* = 8.3, 6.7, 1.5 Hz, 2H), 7.62 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.28 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.08 (m, 2H), 7.06 – 7.01 (m, 1H), 6.99 – 6.94 (m, 2H), 2.75 – 2.70 (m, 2H), 1.78 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C**

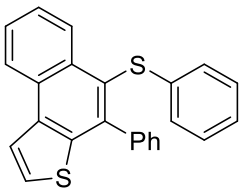
NMR (100 MHz, $CDCl_3$) δ 146.96, 141.68, 139.11, 137.36, 132.44, 132.12, 131.09, 130.86, 129.35, 128.82, 128.61, 128.06, 127.99, 127.55, 127.52, 127.24, 126.95, 126.67, 126.49, 124.62, 122.73, 122.52, 37.91, 24.40, 13.96. Anal calcd for $C_{29}H_{24}S$: C, 86.10; H, 5.98; S, 7.92; found C, 86.46; H, 5.66; S, 7.82.



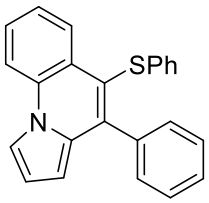
Phenyl(10-(m-tolyl)phenanthren-9-yl)sulfane (3ja) : Yellow crystalline solid (0.132 g, 65%); eluent hexane; mp = 165−167 °C**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81 – 8.78 (m, 2H), 8.67 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.68 – 7.74 (m, 2H), 7.59 – 7.63 (m, 1H), 7.55 – 7.49 (m, 2H), 7.32 – 7.36 (m, 1H), 7.26 – 7.25 (m, 1H), 7.12 – 7.08 (m, 3H), 7.04 (dd, *J* = 9.6, 4.0 Hz, 2H), 6.97 – 6.93 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.93, 140.05, 139.11, 137.39, 132.28, 132.15, 131.05, 130.83, 130.26, 128.76, 128.58, 128.07, 128.03, 127.81, 127.53, 127.15, 126.96, 126.66, 126.53, 124.65, 122.72, 122.51, 21.48. HRMS (ESI) m/z calcd for $C_{27}H_{21}S$ $[M + H]^+$: 377.1358; found: 377.1324.



(10-Cyclopropylphenanthren-9-yl)(phenyl)sulfane (3ka) : Yellow liquid (0.083 g, 51%); eluent hexane; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.42 (m, 2H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.25 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 6.94 (dd, *J* = 8.3, 1.2 Hz, 2H), 1.85 (tt, *J* = 8.2, 5.2 Hz, 1H), 0.76 – 0.64 (m, 2H), 0.64 – 0.56 (m, 1H), 0.44 – 0.32 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.56, 140.88, 140.51, 138.79, 136.39, 130.03, 129.37, 128.95, 128.55, 128.35, 127.79, 127.11, 127.00, 125.53, 107.14, 22.63, 9.54, 8.62. Anal calcd for $C_{26}H_{17}ClS$: C, 84.62; H, 5.56; S, 9.82; found C, 84.71; H, 5.36; S, 9.92.



4-Phenyl-5-(phenylthio)naphtho[2,1-b]thiophene (3la) : Yellow solid (0.103 g, 56%); eluent hexane; mp =80−82 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.47 – 8.38 (m, 1H), 8.09 (d, *J* = 5.5 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.58 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.52 – 7.38 (m, 5H), 7.14 – 7.08 (m, 2H), 7.07 – 7.01 (m, 1H), 6.95 (dd, *J* = 7.2, 1.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.35, 140.14, 139.92, 139.21, 137.14, 132.50, 129.45, 128.96, 128.76, 128.66, 128.15, 128.00, 126.74, 126.60, 126.31, 124.70, 123.98, 123.73, 122.35. HRMS (ESI) m/z calcd for $C_{24}H_{17}S_2$ [M]: 369.0766; found: 369.0732.



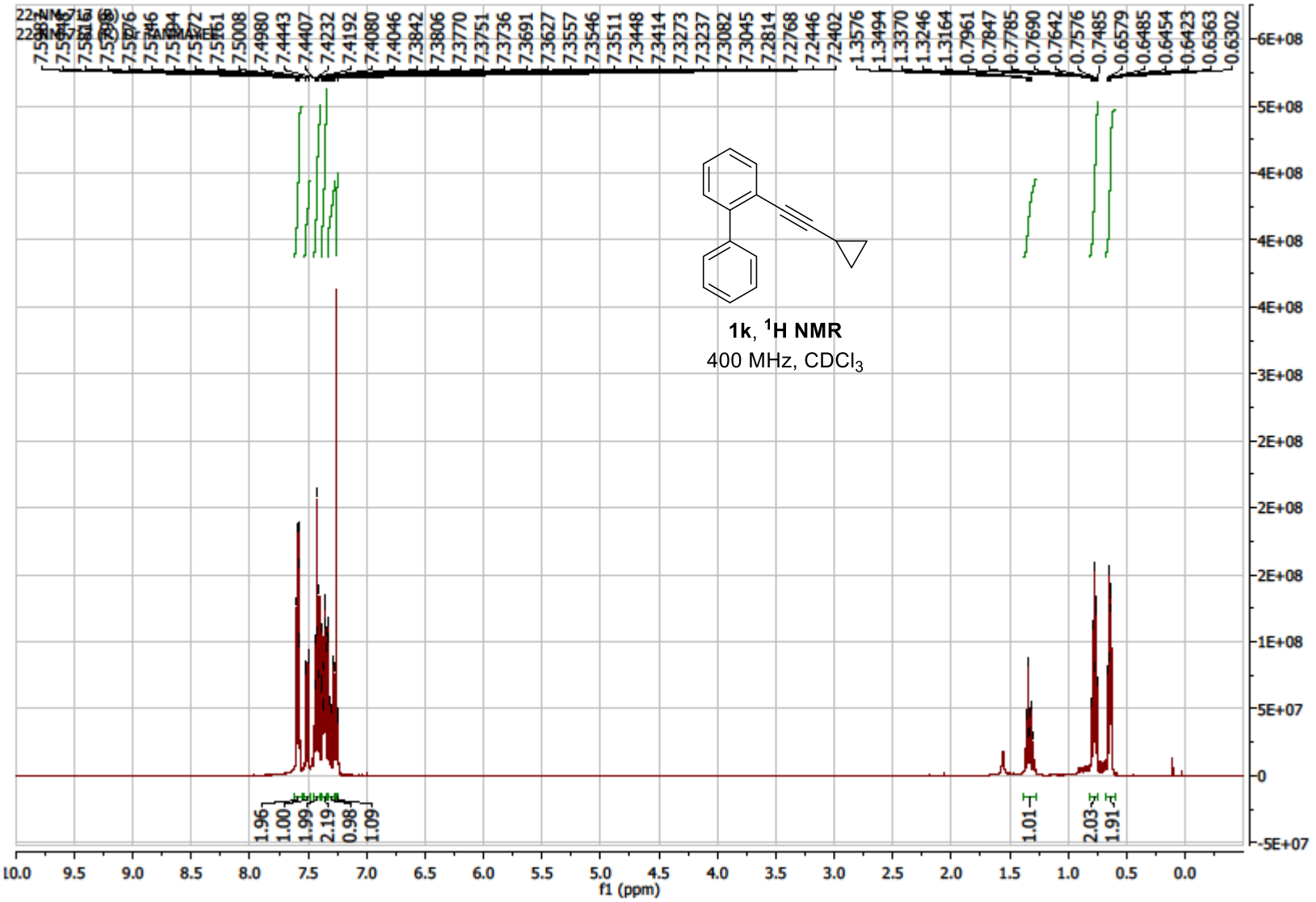
4-Phenyl-5-(phenylthio)pyrrolo[1,2-a]quinoline (3ma) : Yellow solid (0.127 g, 66%); eluent hexane; mp = 56−58 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.12 (m, 1H), 7.58 (s, 1H), 7.51 – 7.49 (m, 1H), 7.48 (t, *J* = 2.4 Hz, 2H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 4.9, 3.6 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.14 (s, 1H), 6.95 – 6.89 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.34, 138.89, 137.34, 136.09, 136.00, 130.24, 130.06, 129.96, 128.80, 128.65, 128.53, 127.74, 126.51, 126.27, 126.16, 125.95, 123.92, 119.98, 101.10, 100.77. Anal calcd for $C_{24}H_{17}NS$: C, 82.02; H, 4.88; N, 3.99; S, 9.12; found C, 82.26; H, 4.36; N, 4.07; S, 9.31.

13. References:

1 N. Mukherjee and T. Chatterjee, *J. Org. Chem.*, 2021, **86**, 7881−7890.

2 S. K. Shukla, J. Singh V. Rustogi and A. K. Verma, *J. Org. Chem.*, 2011, **76,** 5670–5684

3 B. L. Hu, S. S. Pi, P. C. Qian, J. H. Li and X. G. Zhang, *J. Org. Chem.*, 2013, **78**, 1300−1305.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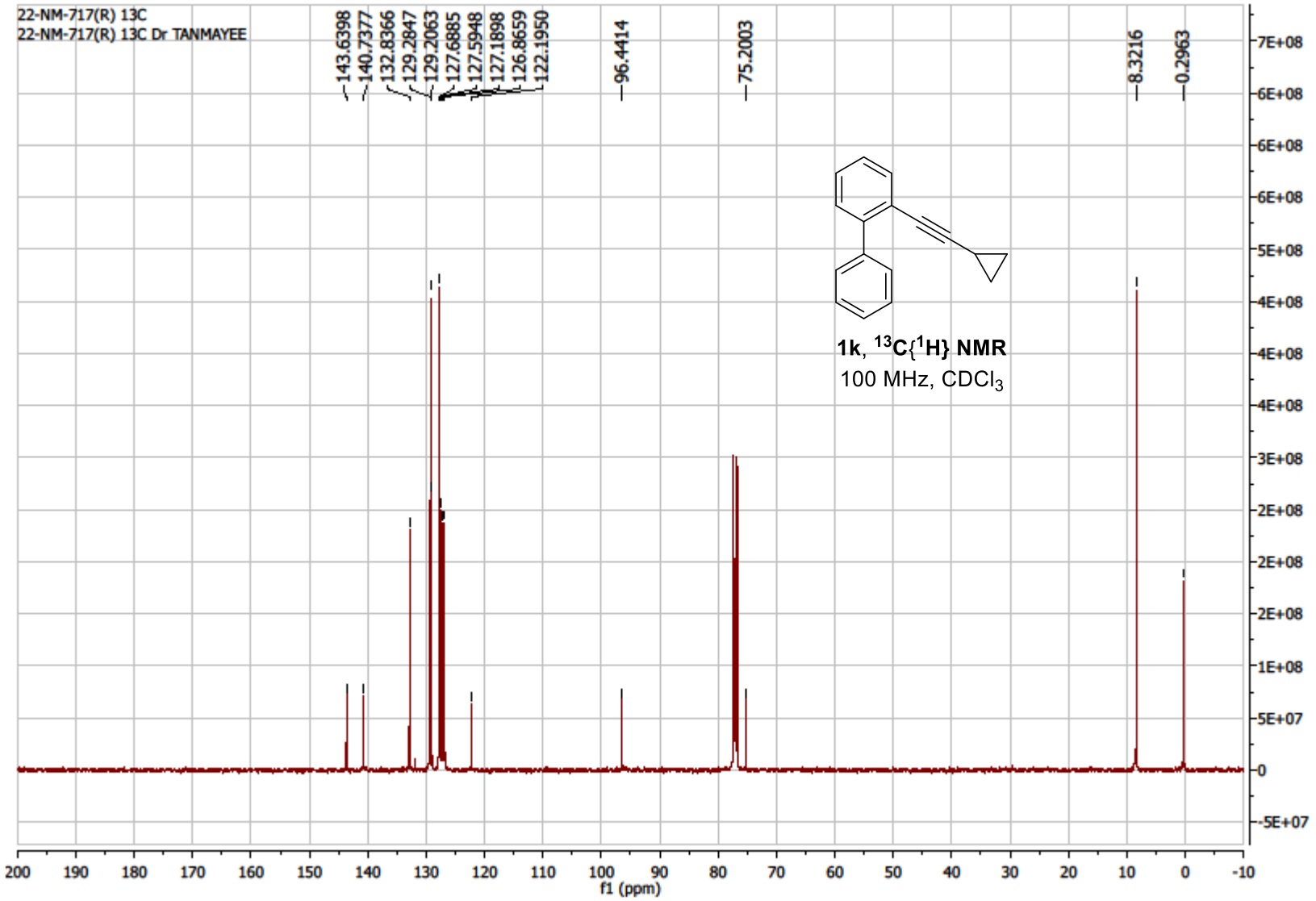
f1 (ppm)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22-NM-717(R) 13C Dr TANMAYEE
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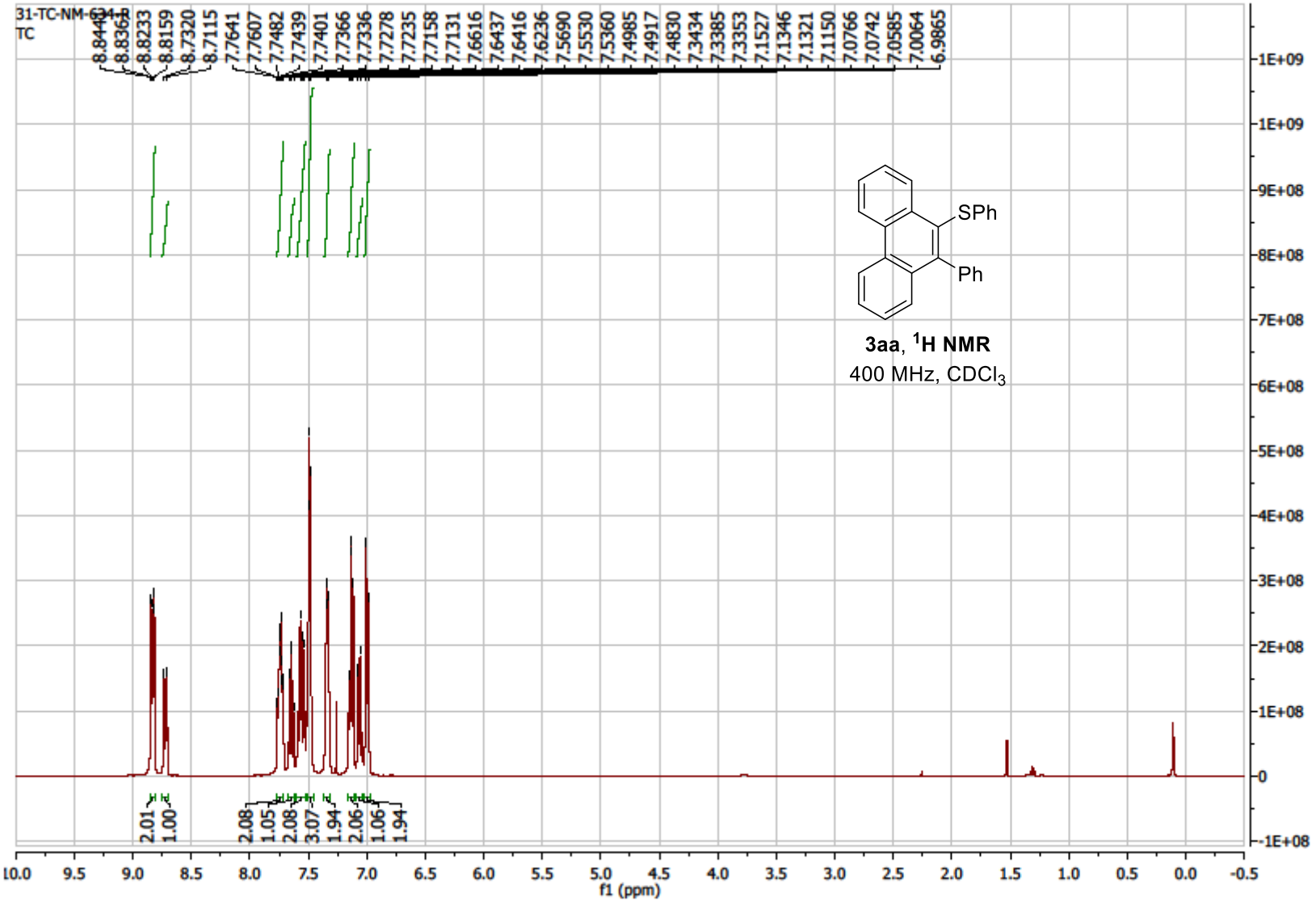
1k, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)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Ph
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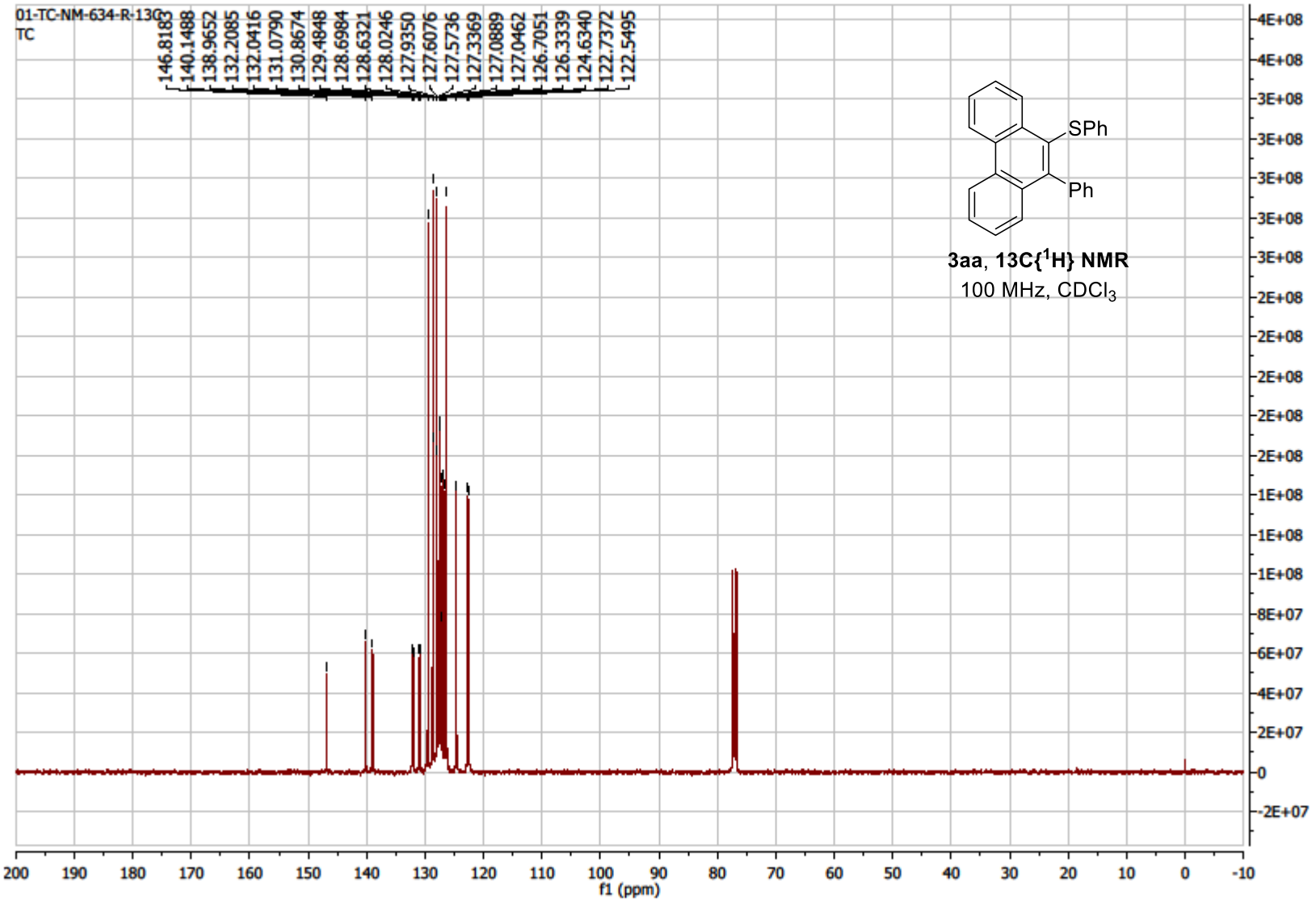
400 MHz, CDCl3
f1 (ppm)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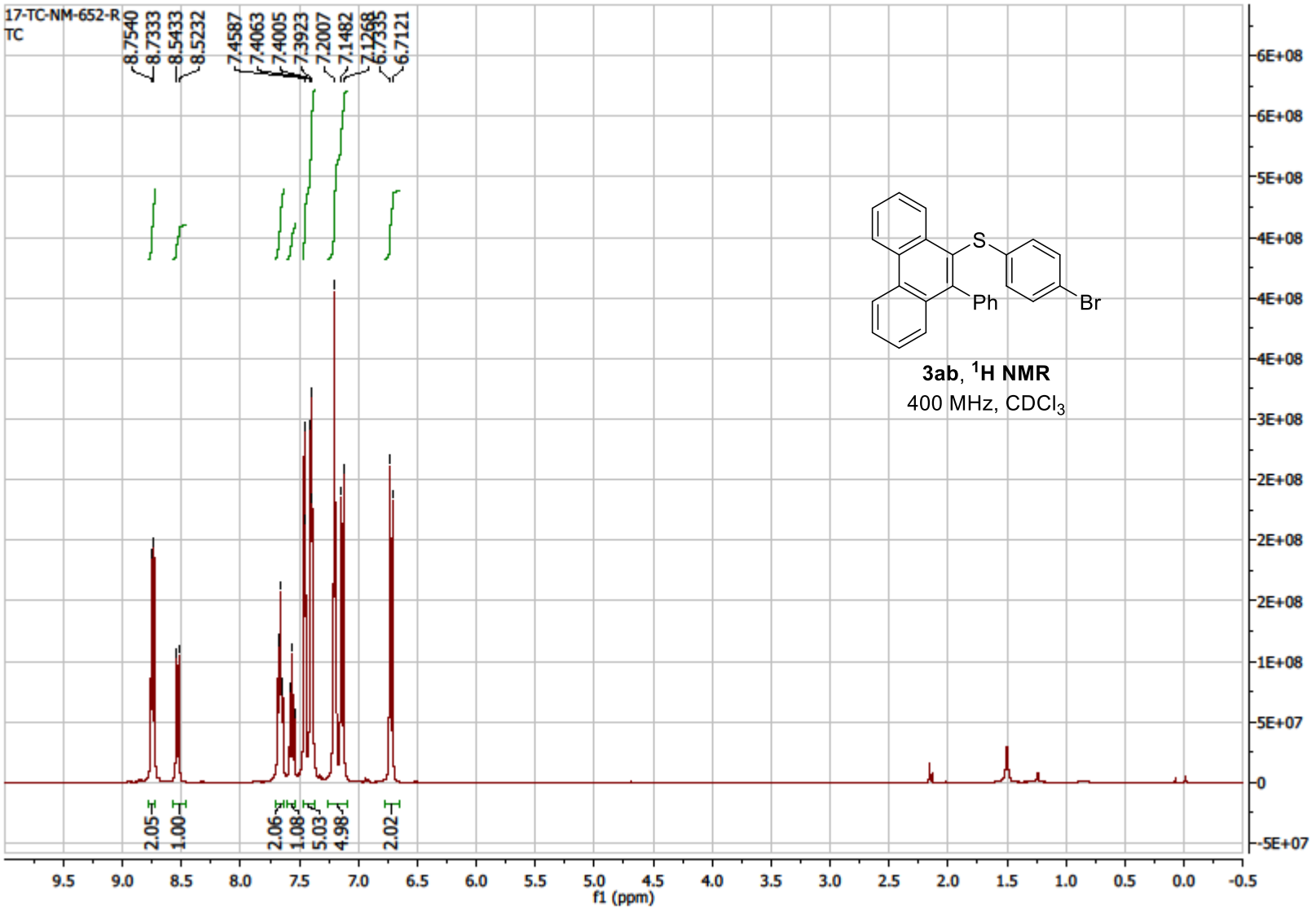
100 MHz, CDCl3
f1 (ppm)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S
Ph
Br
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400 MHz, CDCl3
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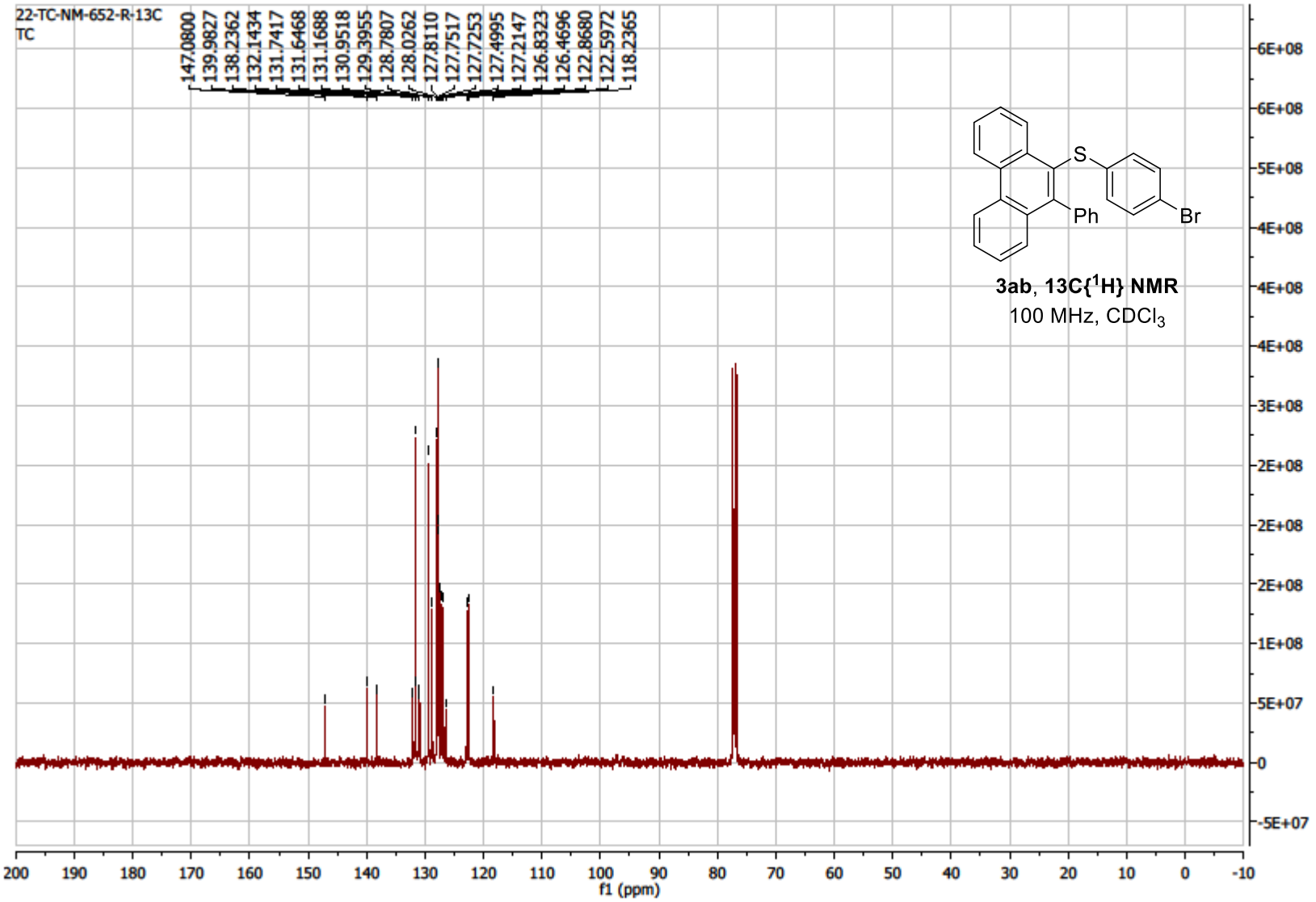
2.02
f1 (ppm)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126.8323
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S
Ph
Br
3ab, 13C{1H} NMR
100 MHz, CDCl3
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
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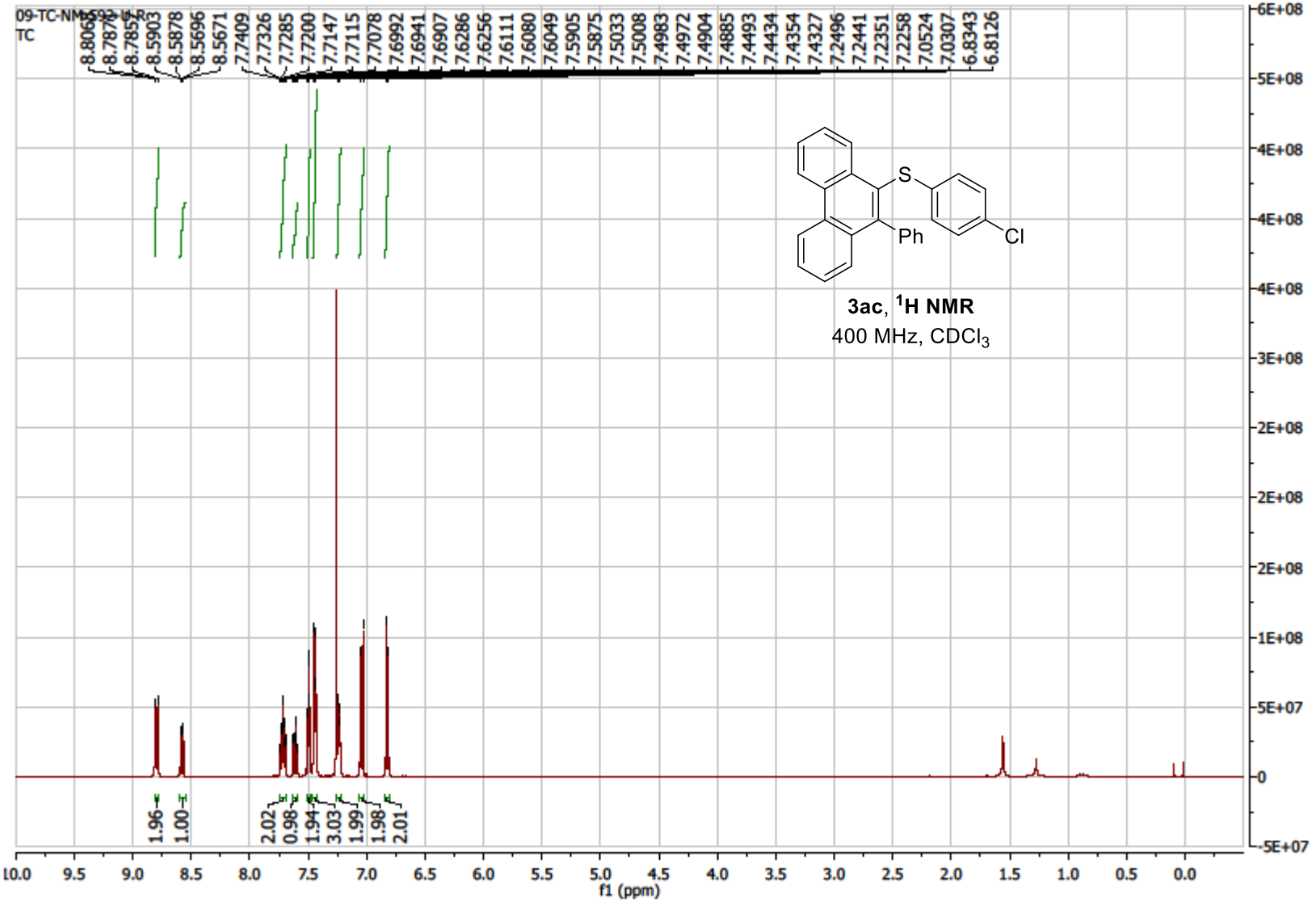
f1 (ppm)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Ph
Cl
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3.03
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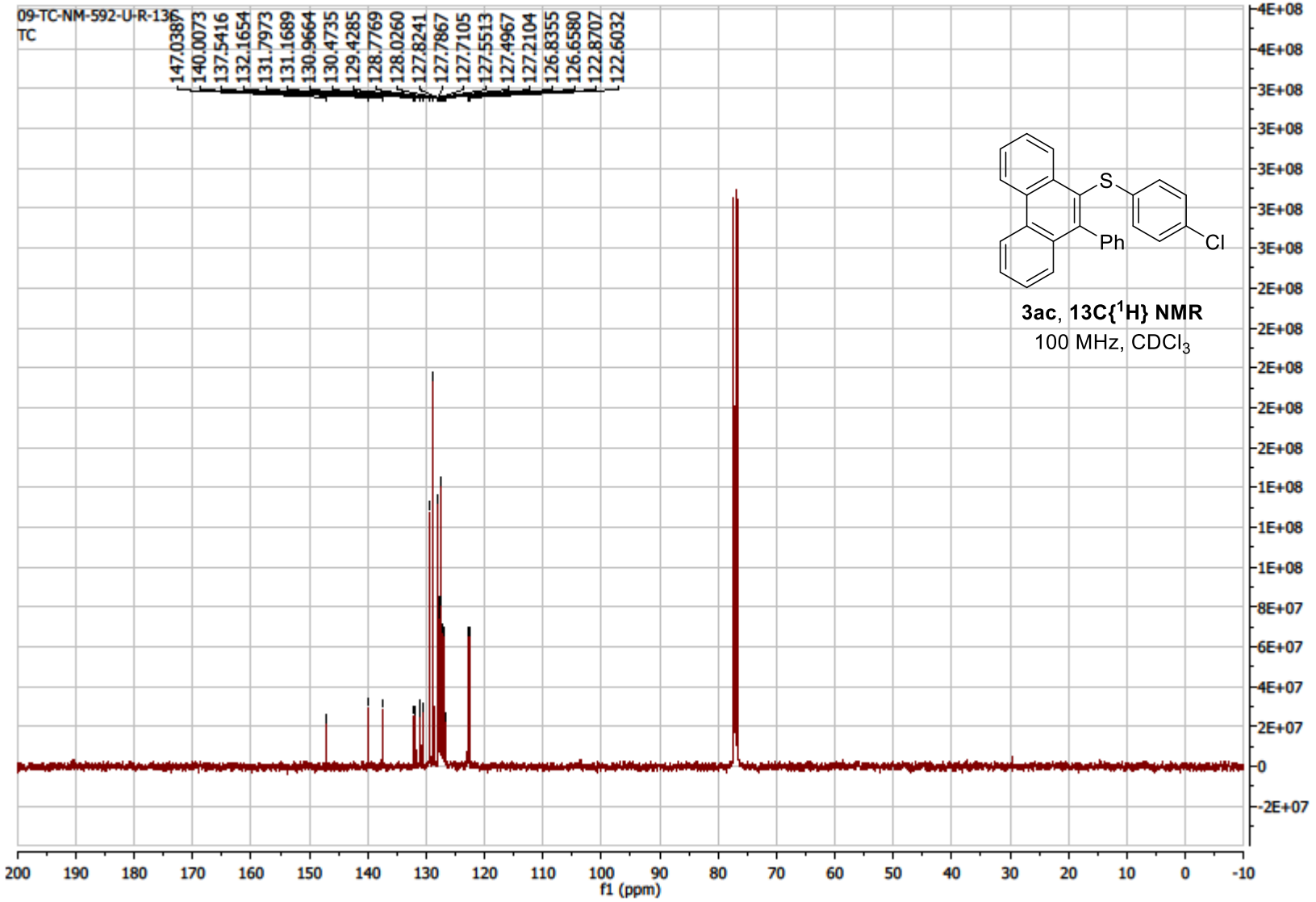
1.98
2.01
f1 (ppm)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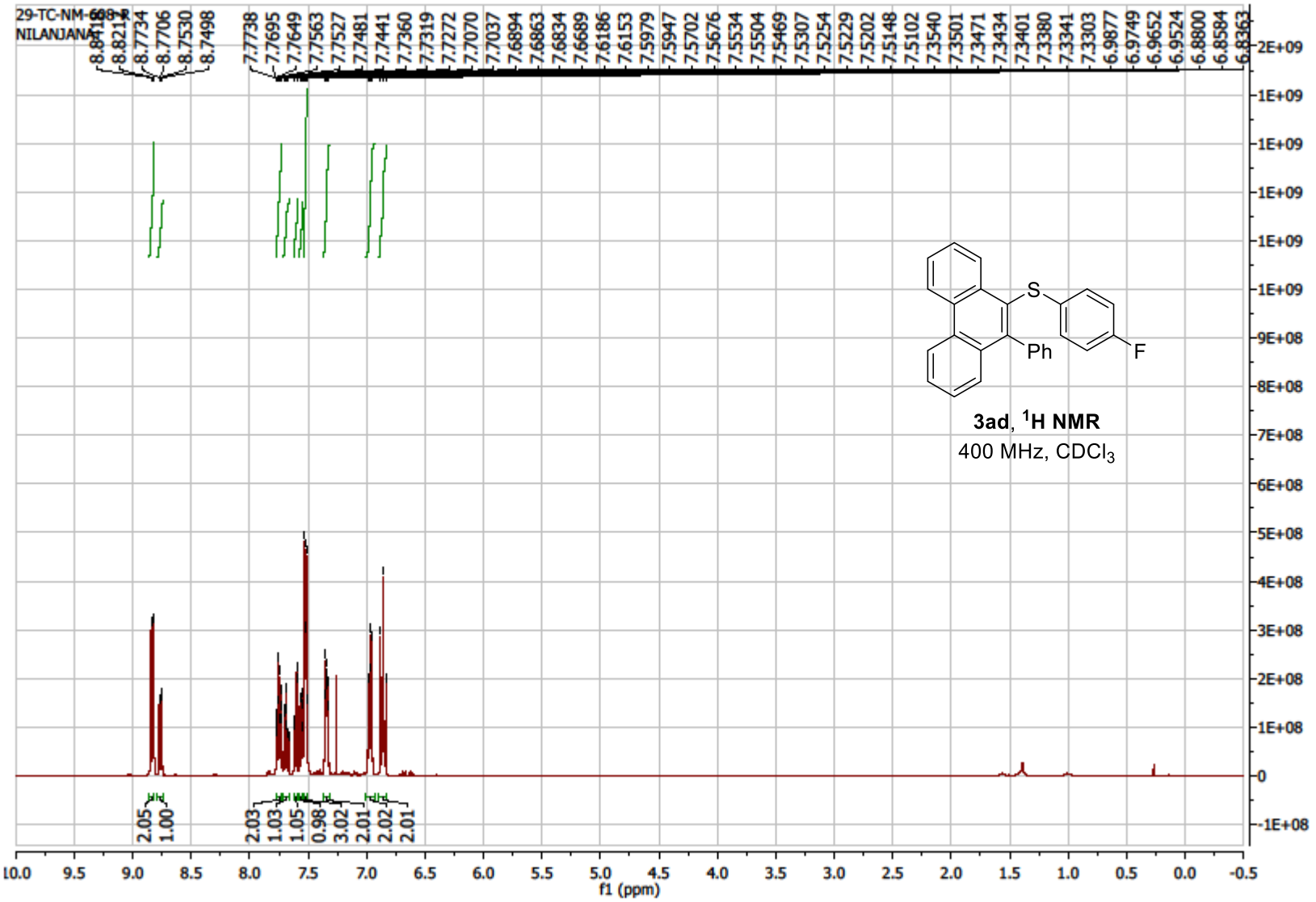
100 MHz, CDCl3
f1 (ppm)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3ad, 1H NMR
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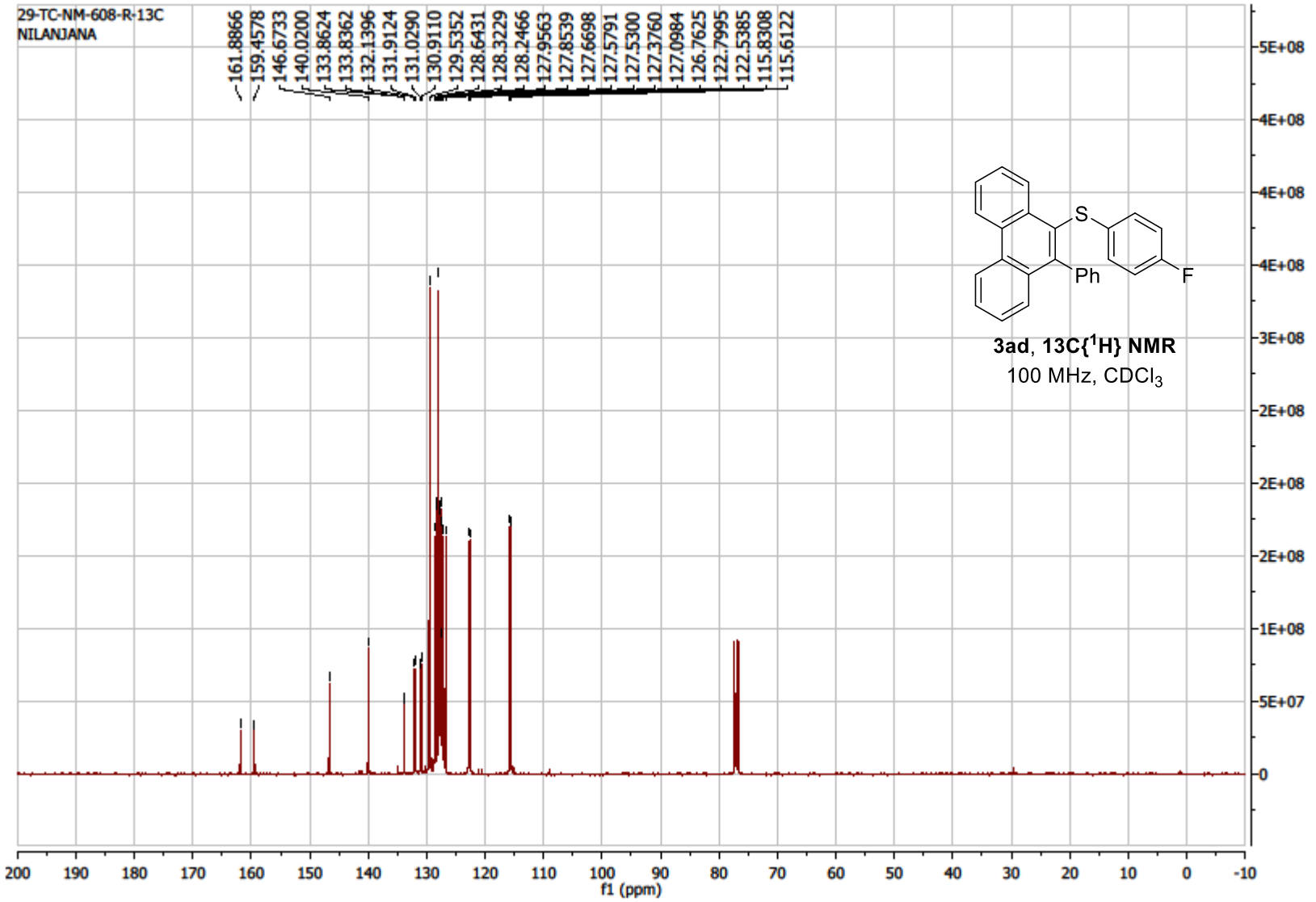
f1 (ppm)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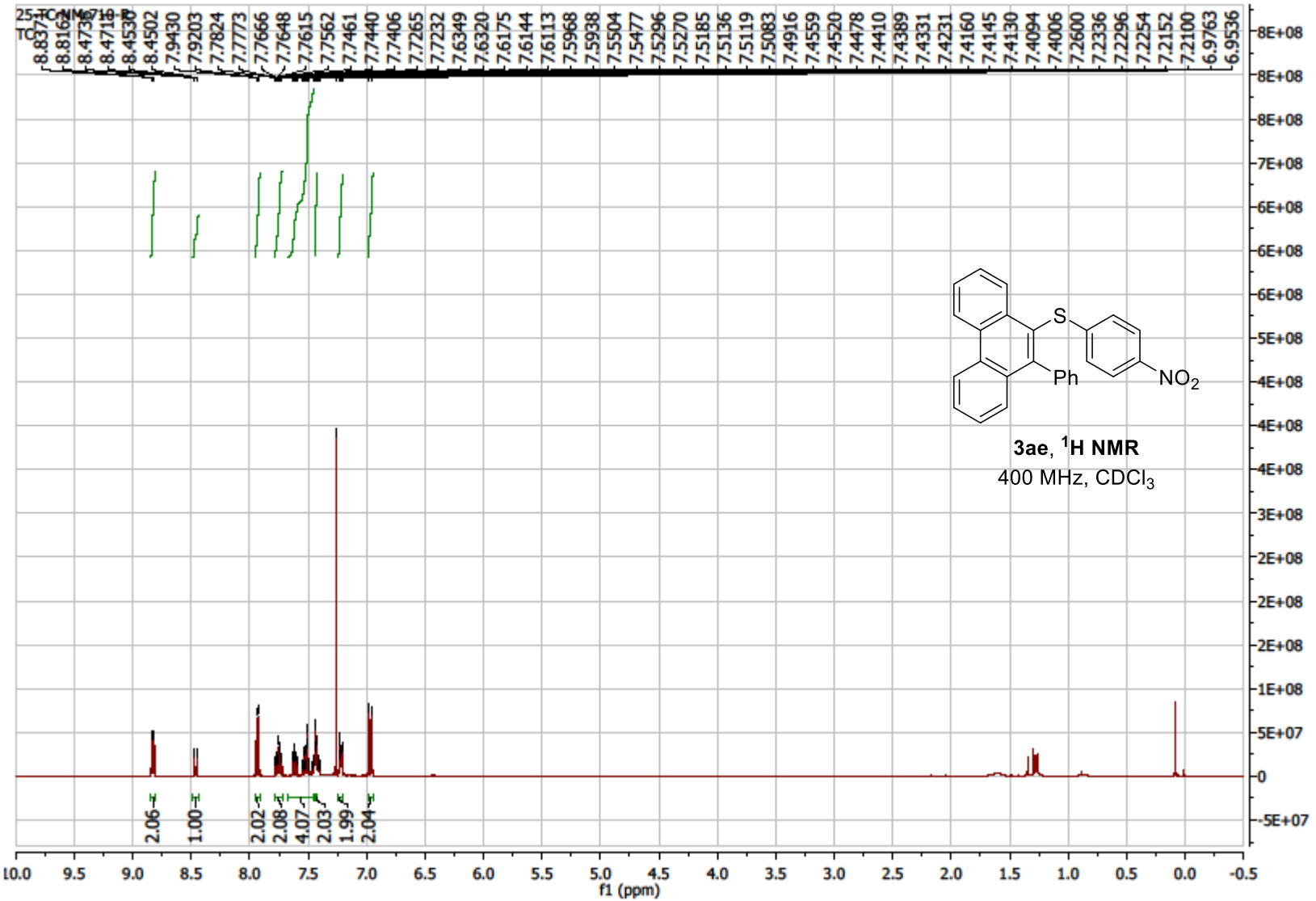
f1 (ppm)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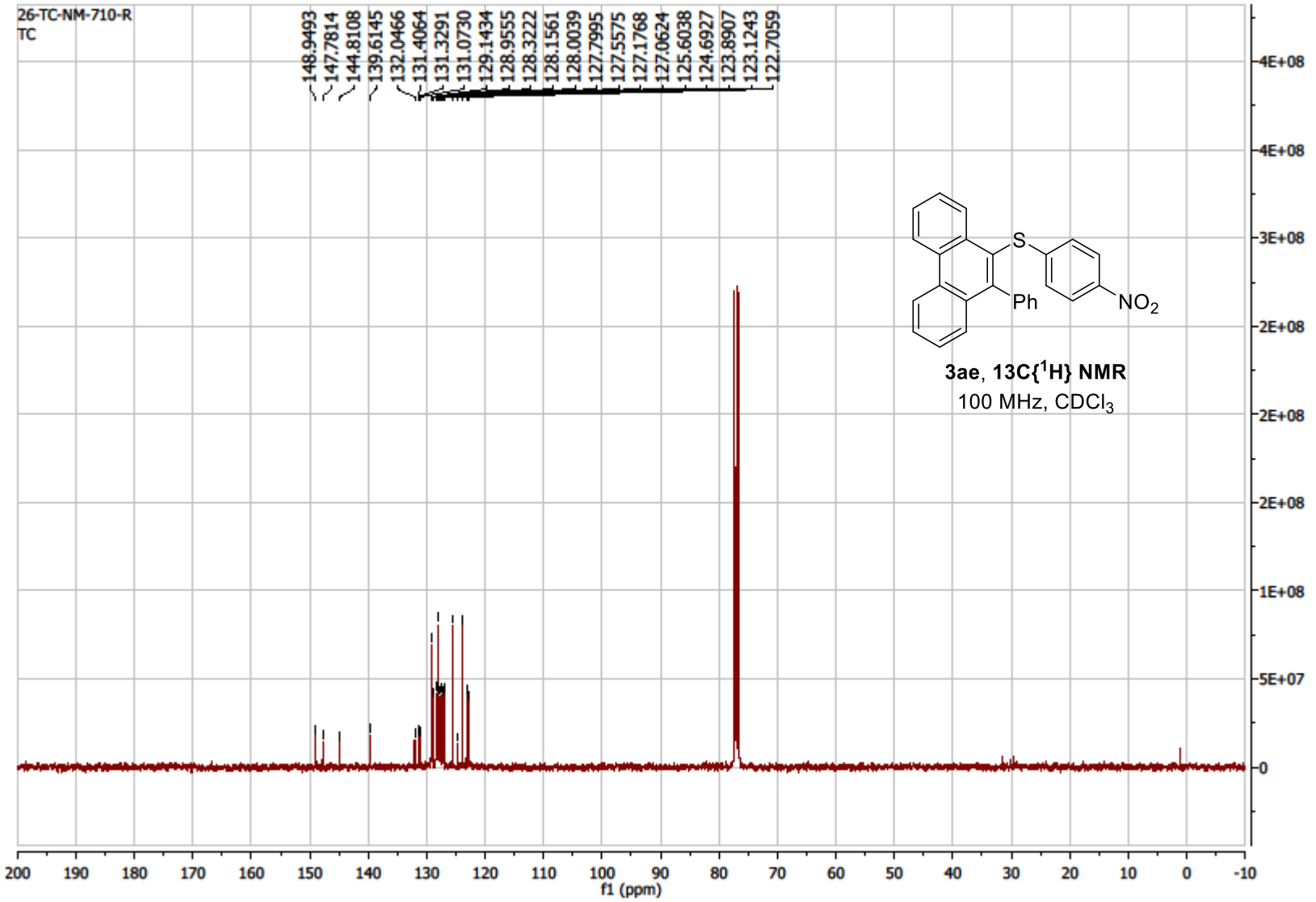
f1 (ppm)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127.0624
125.6038
124.6927
123.8907
123.1243
122.7059
S
Ph
NO2
3ae, 13C{1H} NMR
100 MHz, CDCl3
4E+08
4E+08
3E+08
2E+08
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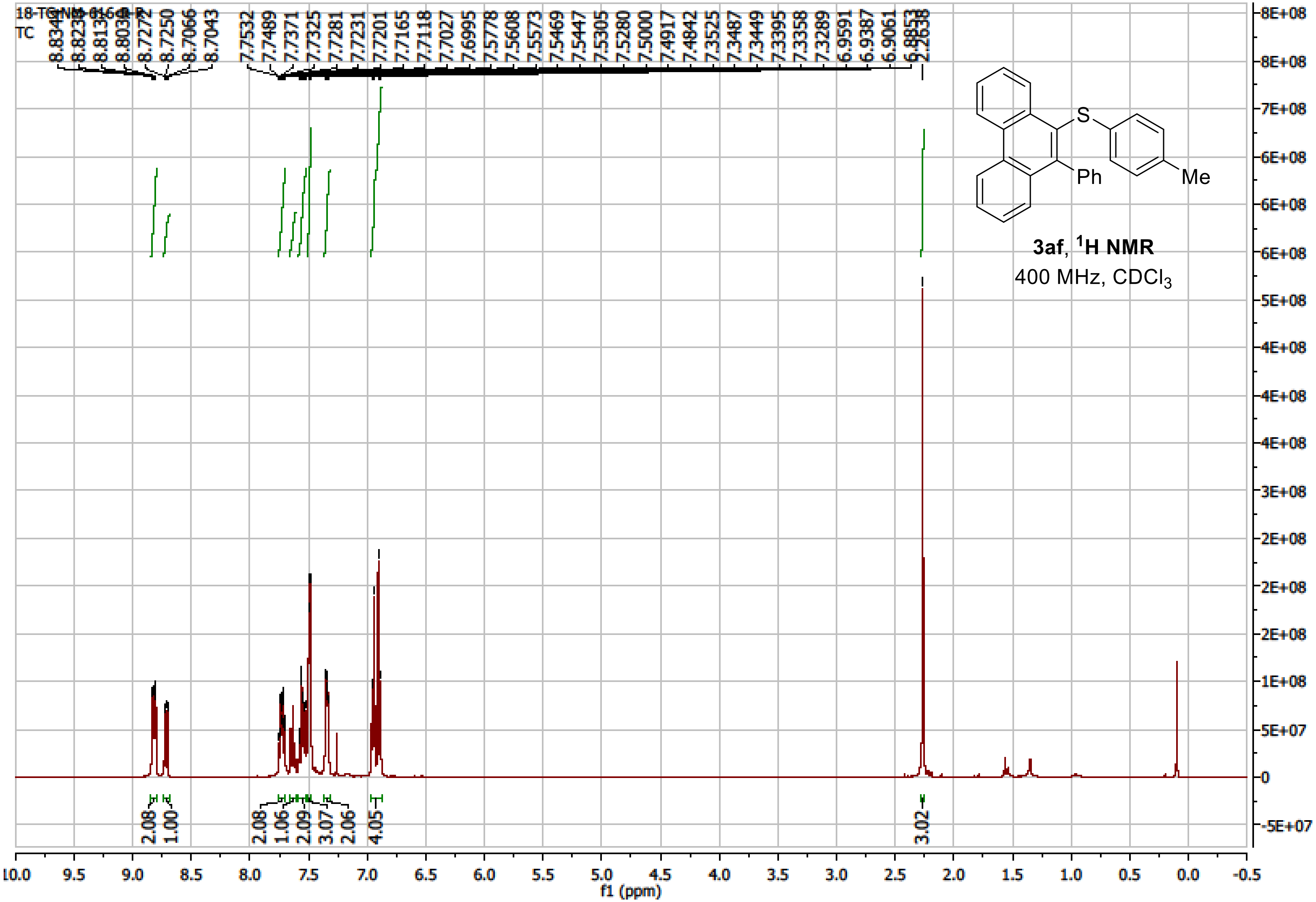
f1 (ppm)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Ph
Me
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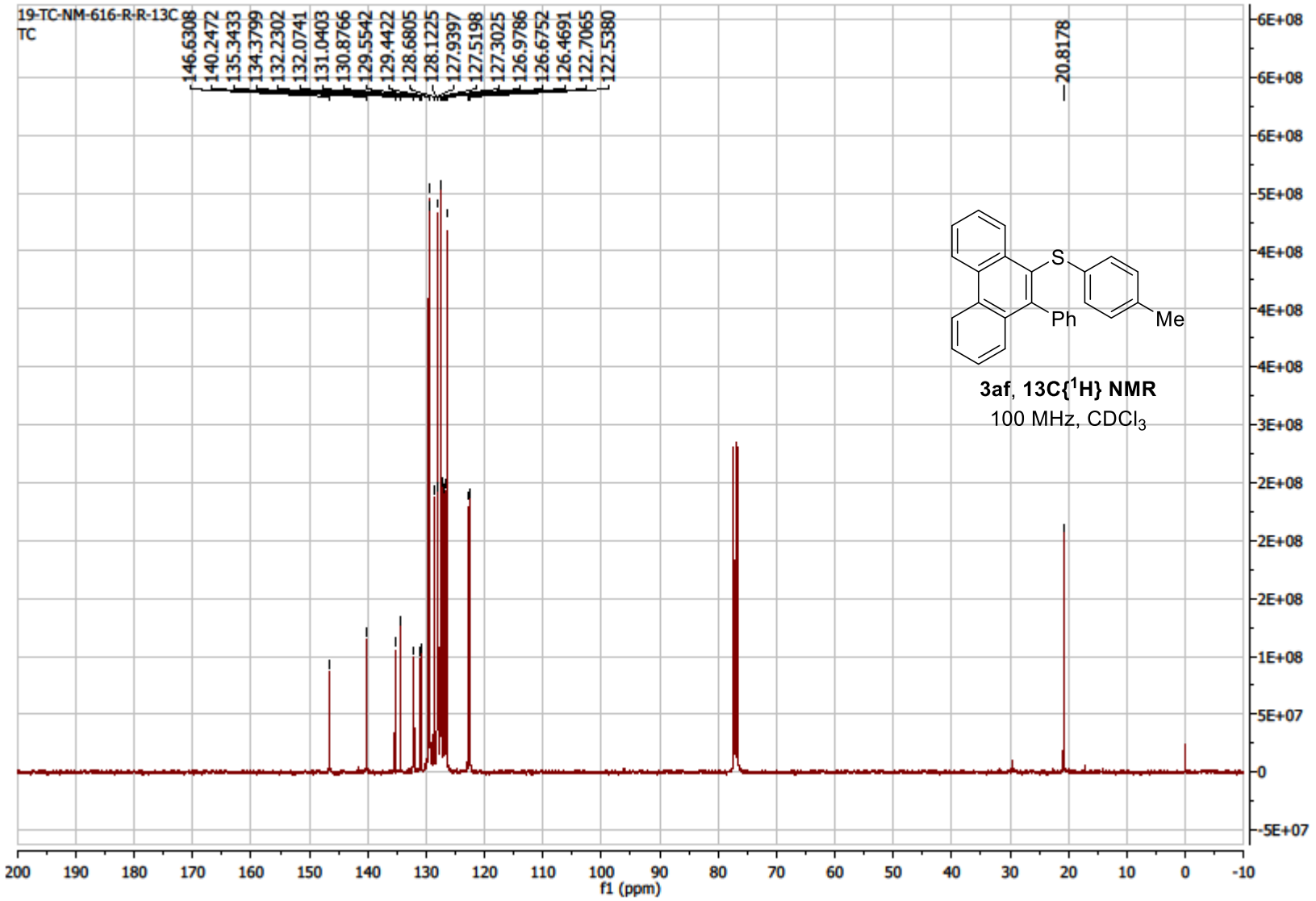
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126.9786
126.6752
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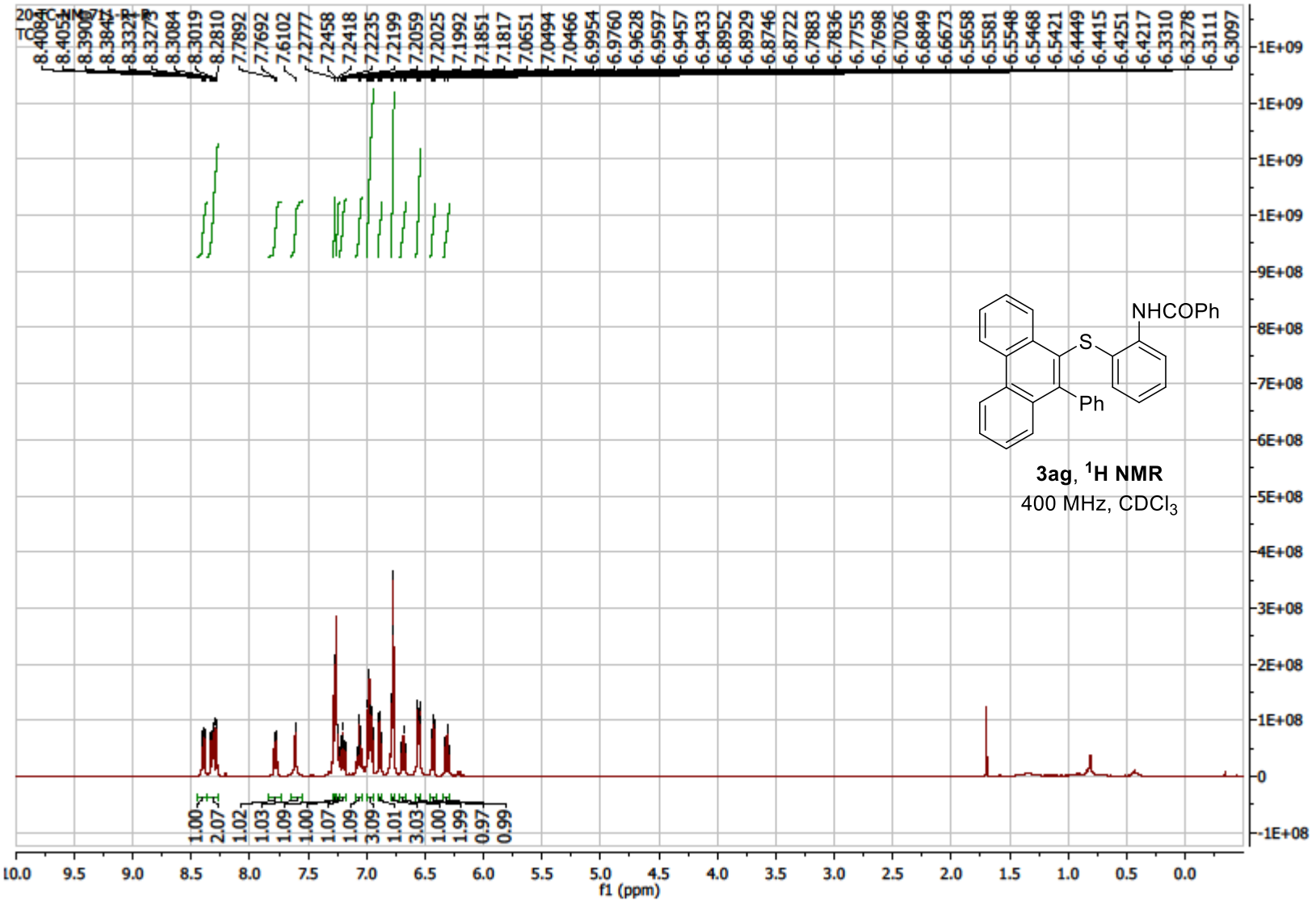
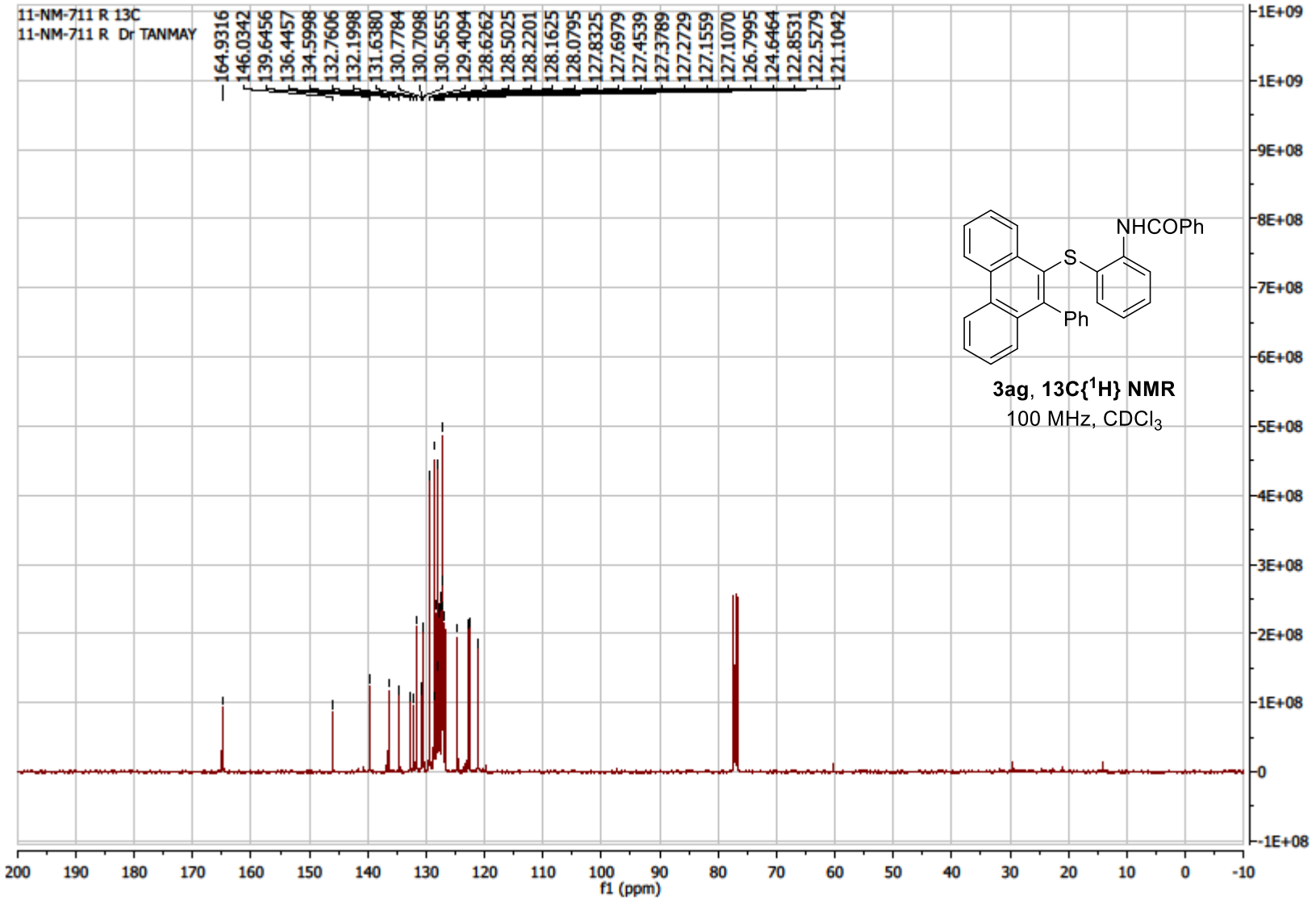
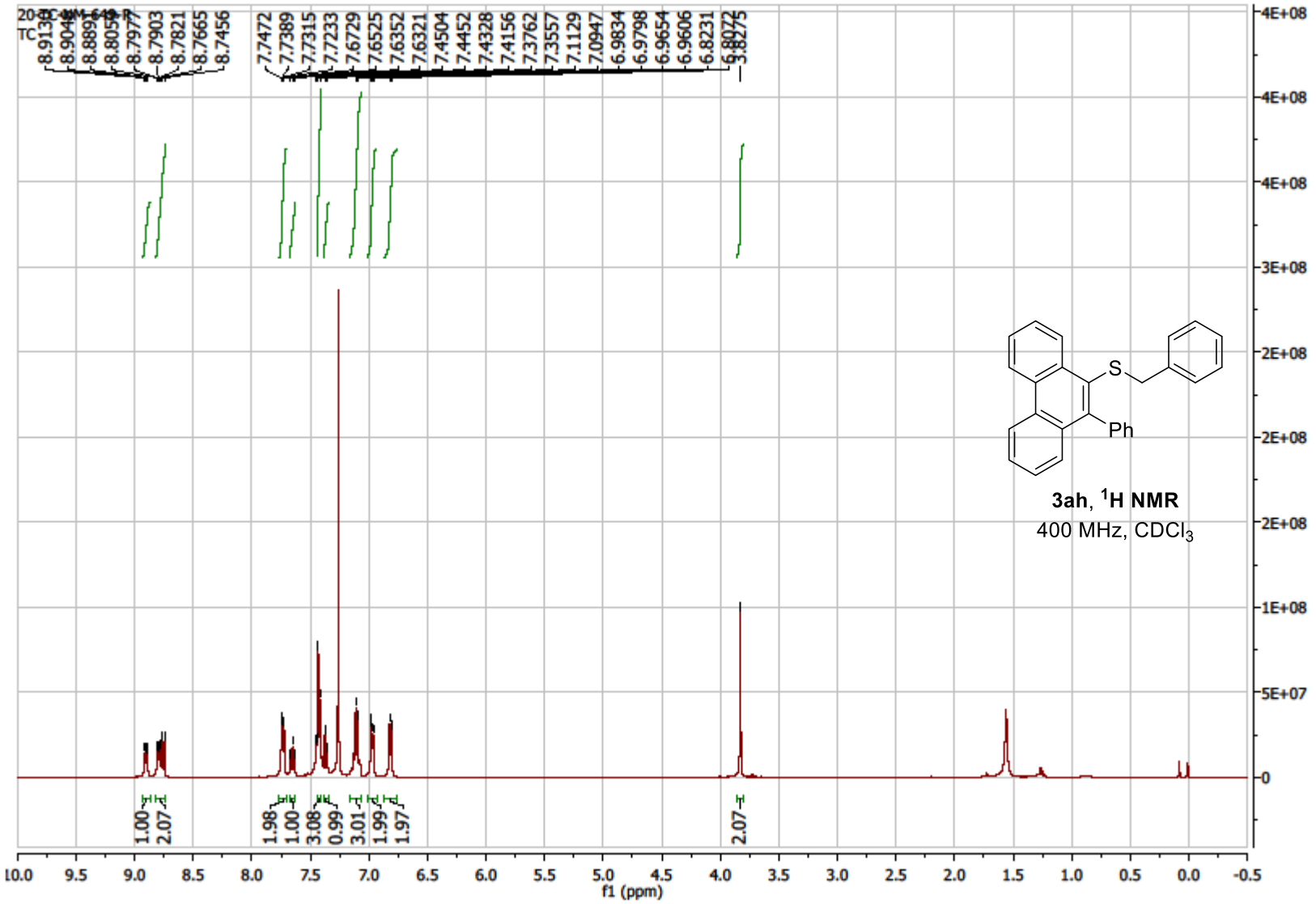
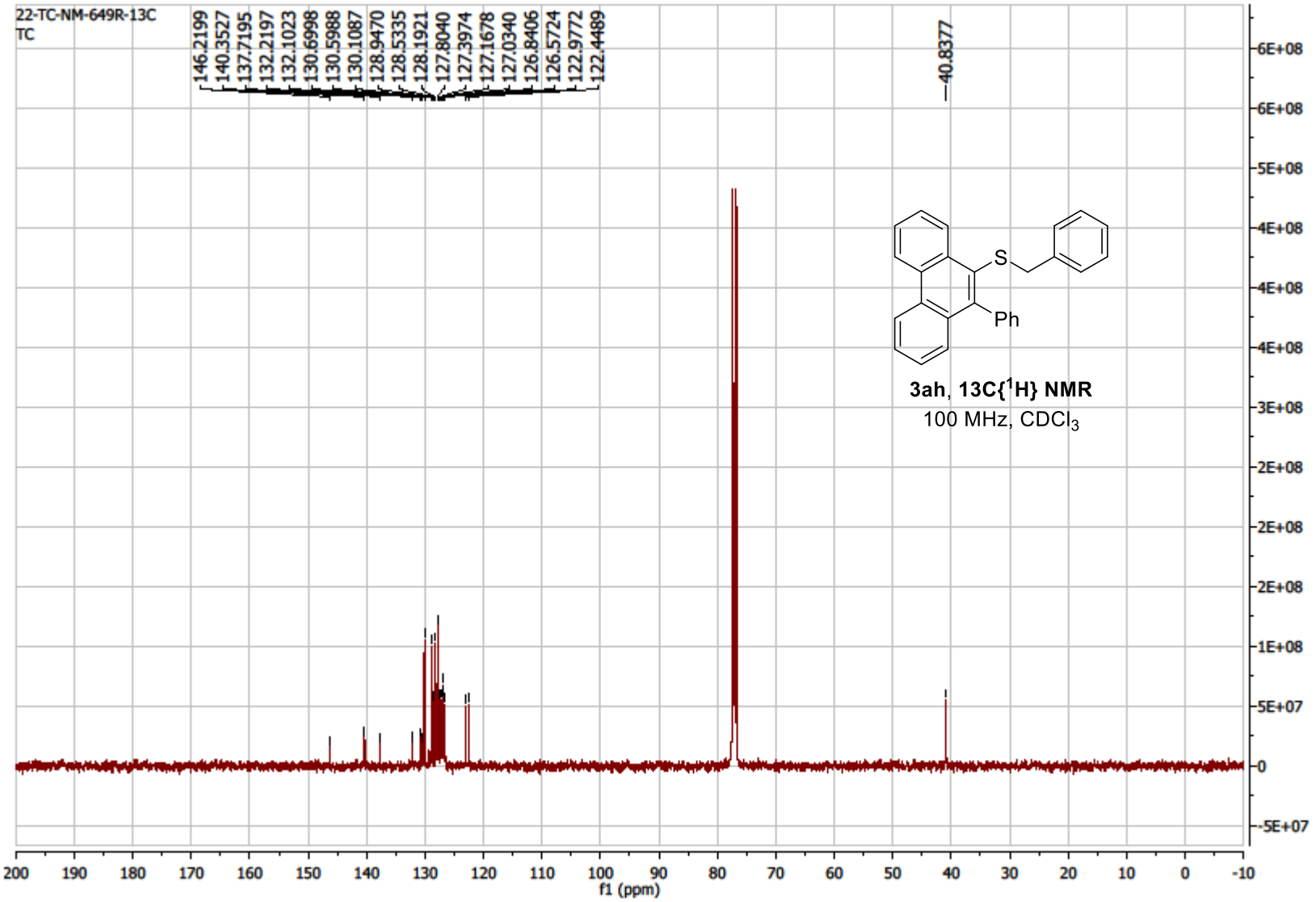
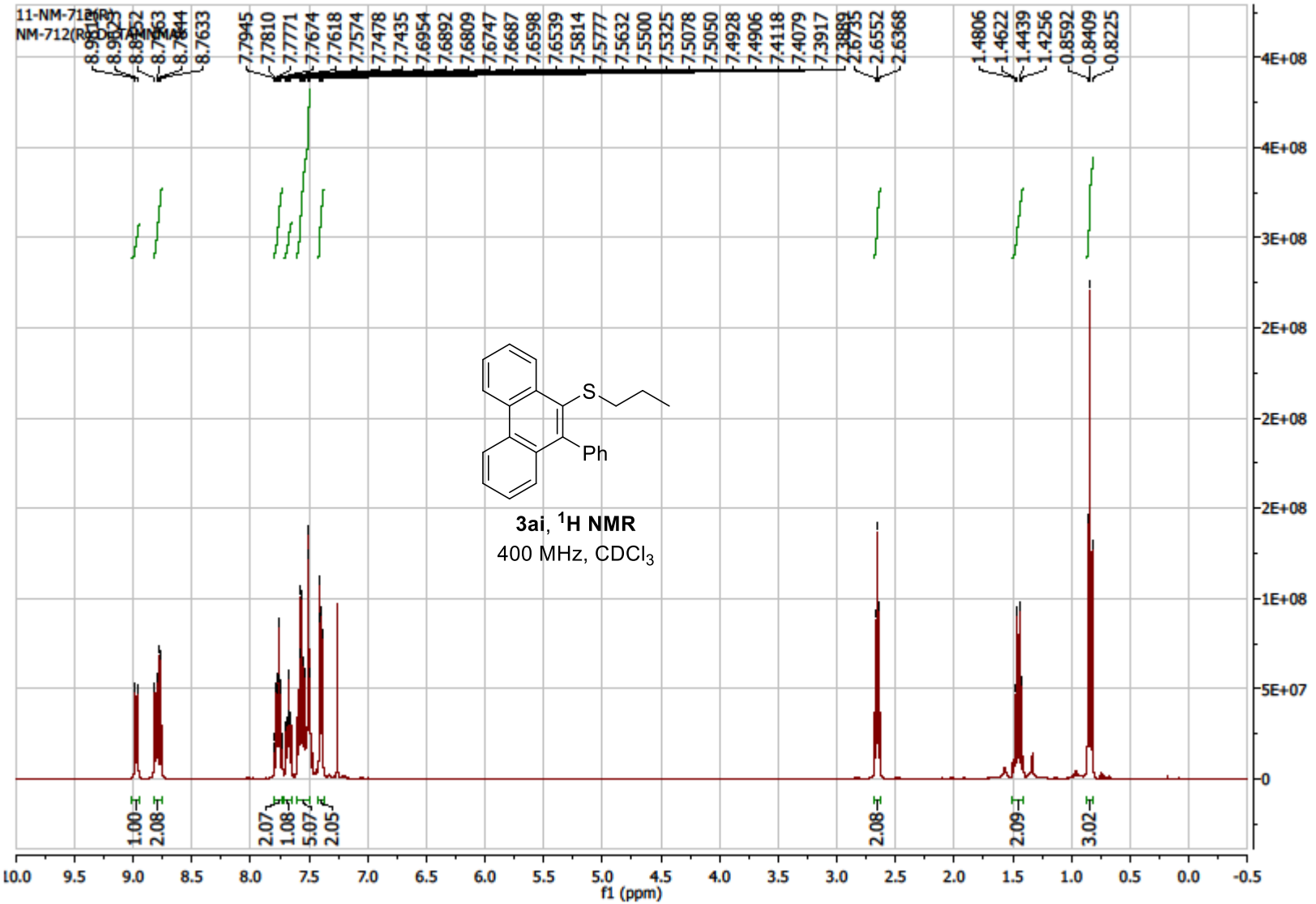
122.5380
20.8178
S
Ph
Me
3af, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

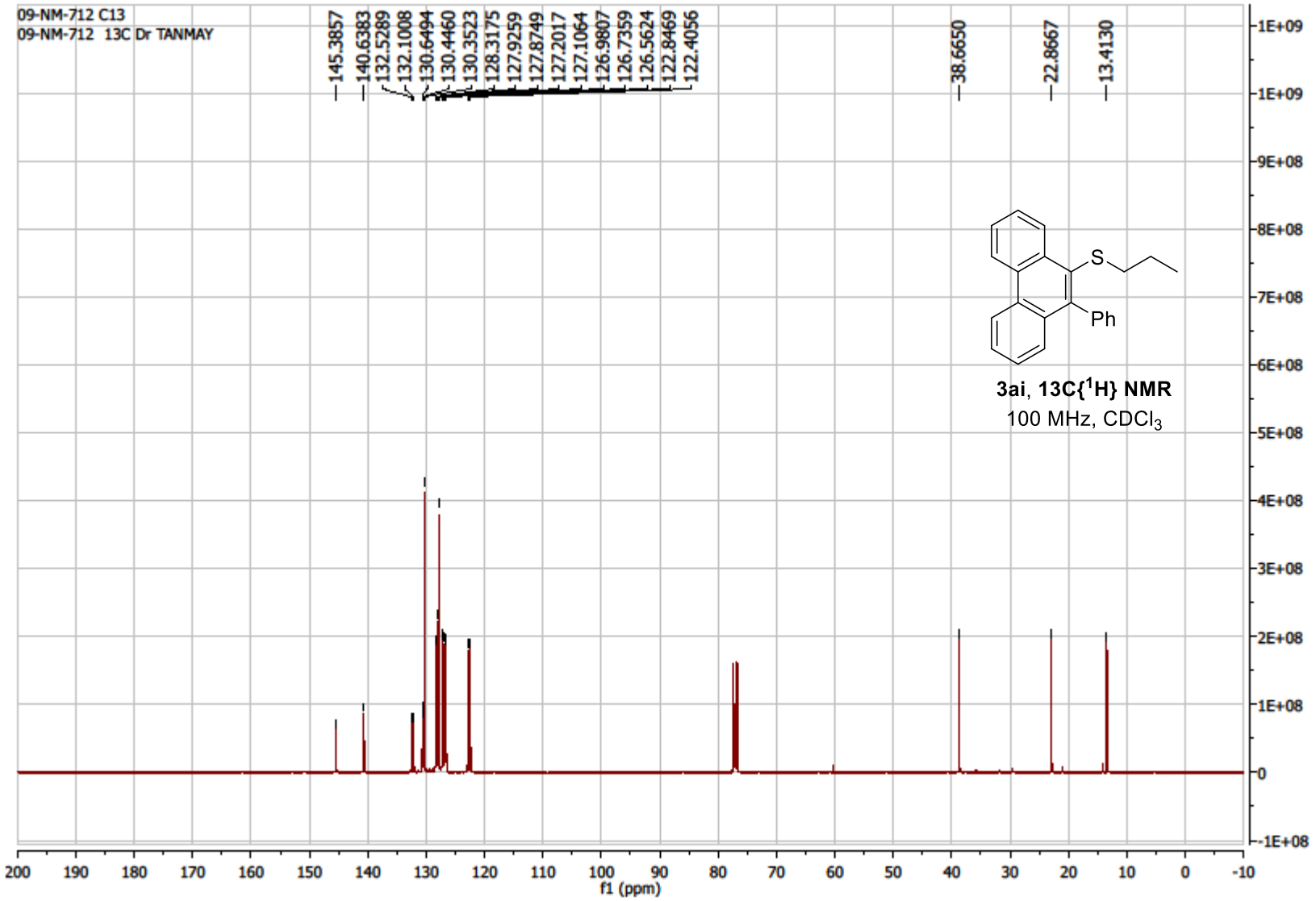

NHCOPh
S
Ph
3ag, ^{1}H NMR
400 MHz, $CDCl_3$
f1 (ppm)

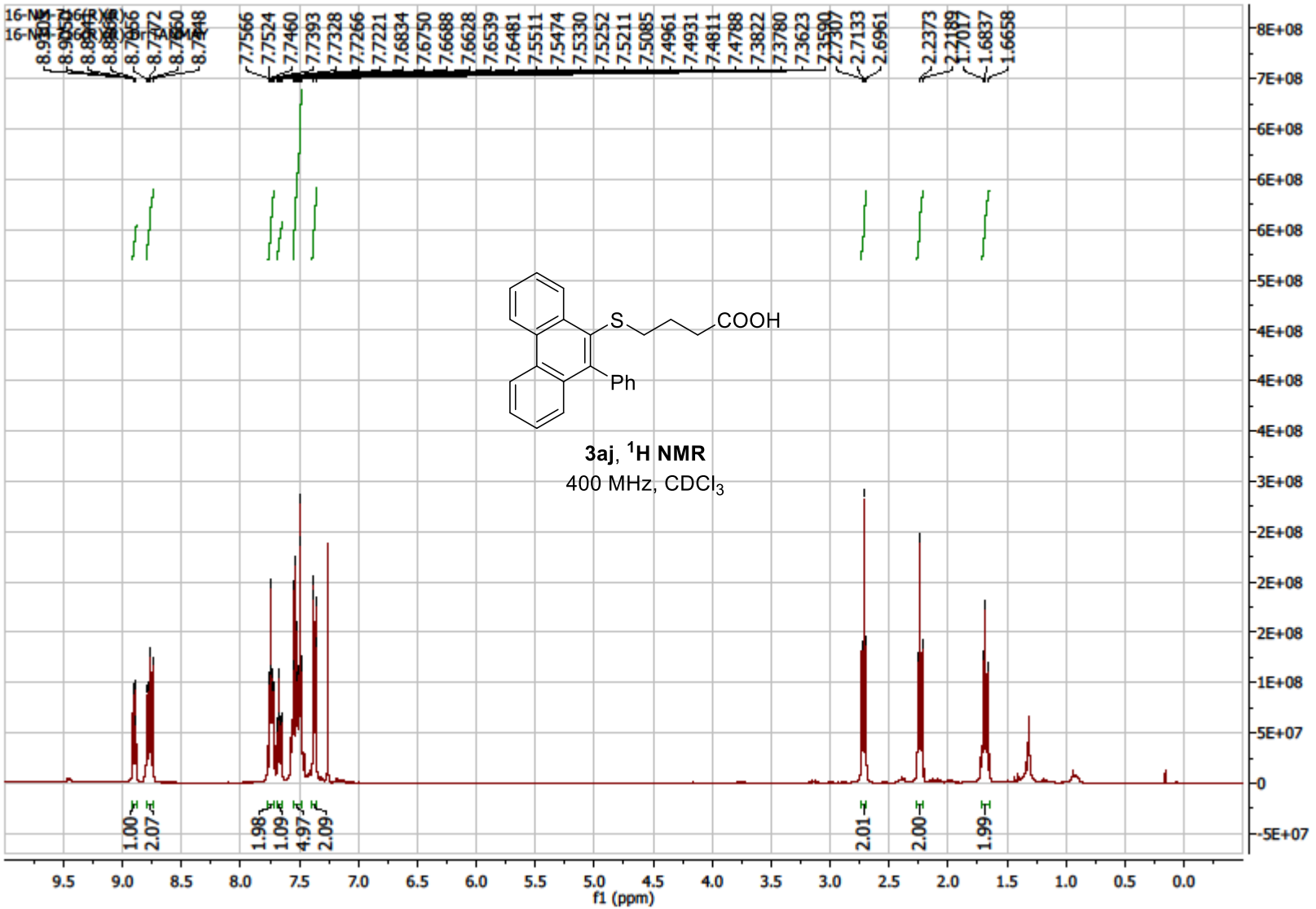

11-NM-711 R 13C
11-NM-711 R Dr TANMAY
164.9316
146.0342
139.6456
136.4457
134.5998
132.7606
132.1998
131.6380
130.7784
130.7098
130.5655
129.4094
128.6262
128.5025
128.2201
128.1625
128.0795
127.8325
127.6979
127.4539
127.3789
127.2729
127.1559
127.1070
126.7995
124.6464
122.8531
122.5279
121.1042
NHCOPh
S
Ph
3ag, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

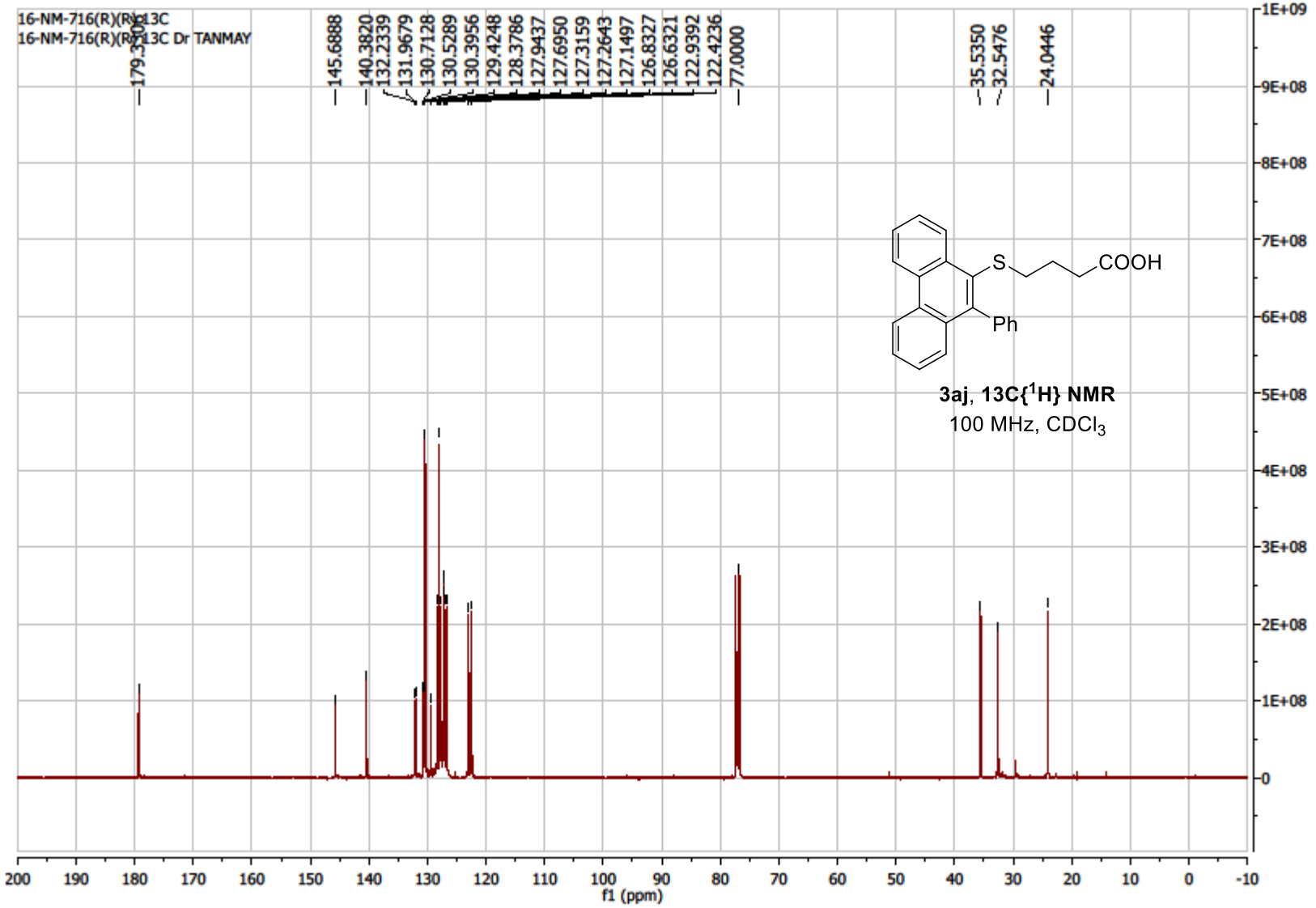

8.9138
8.9044
8.8896
8.8059
8.7977
8.7903
8.7821
8.7665
8.7456
7.7472
7.7389
7.7315
7.7233
7.6729
7.6525
7.6352
7.6321
7.4504
7.4452
7.4328
7.4156
7.3762
7.3557
7.1129
7.0947
6.9834
6.9798
6.9654
6.9606
6.8231
6.8072
3.8275
1.00
2.07
1.98
1.00
3.08
0.99
3.01
1.99
1.97
2.07
f1 (ppm)
S
Ph
3ah, ^{1}H NMR
400 MHz, $CDCl_3$

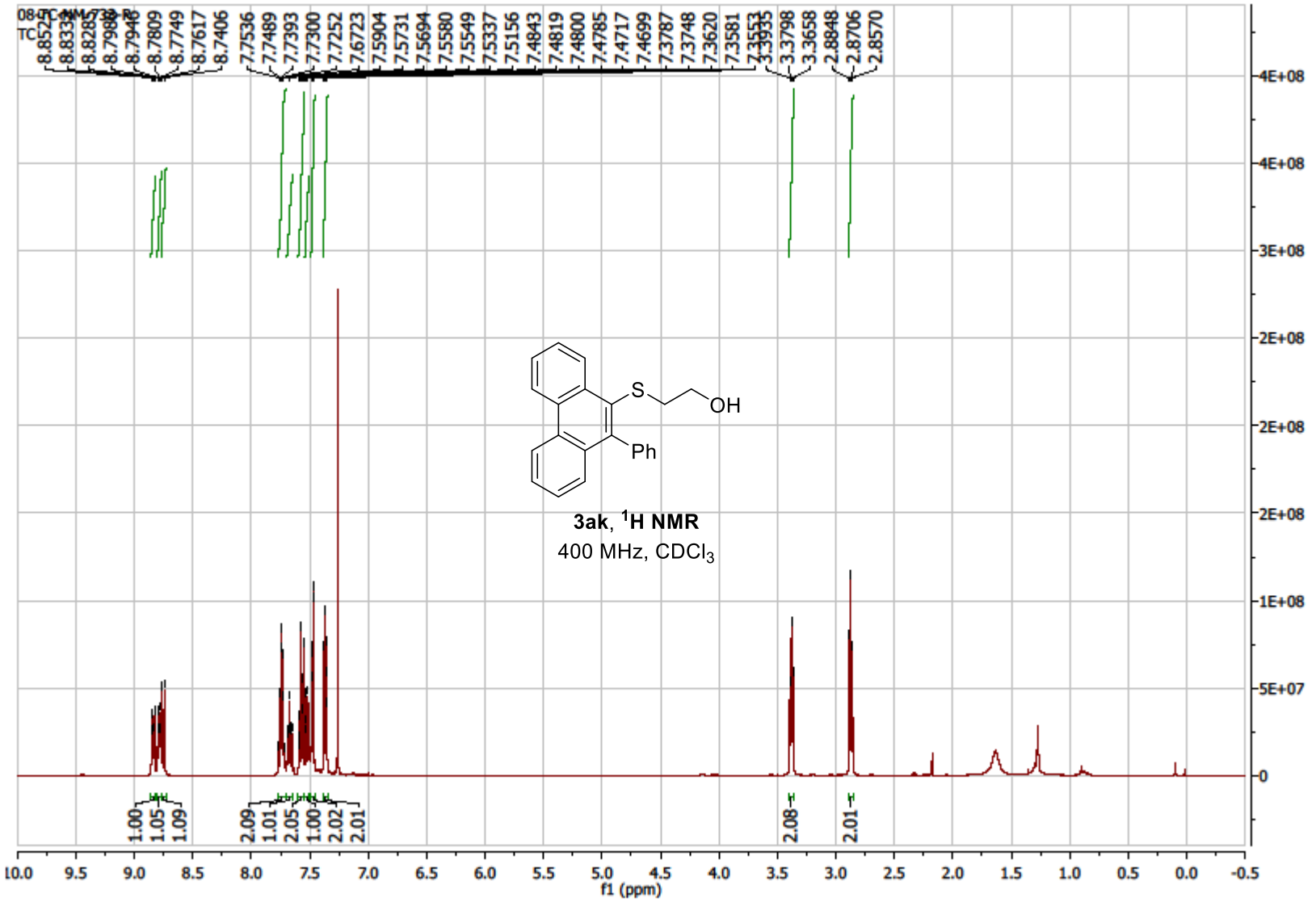

22-TC-NM-649R-13C
TC
146.2199
140.3527
137.7195
132.2197
132.1023
130.6998
130.5988
130.1087
128.9470
128.5335
128.1921
127.8040
127.3974
127.1678
127.0340
126.8406
126.5724
122.9772
122.4489
40.8377
S
Ph
3ah, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

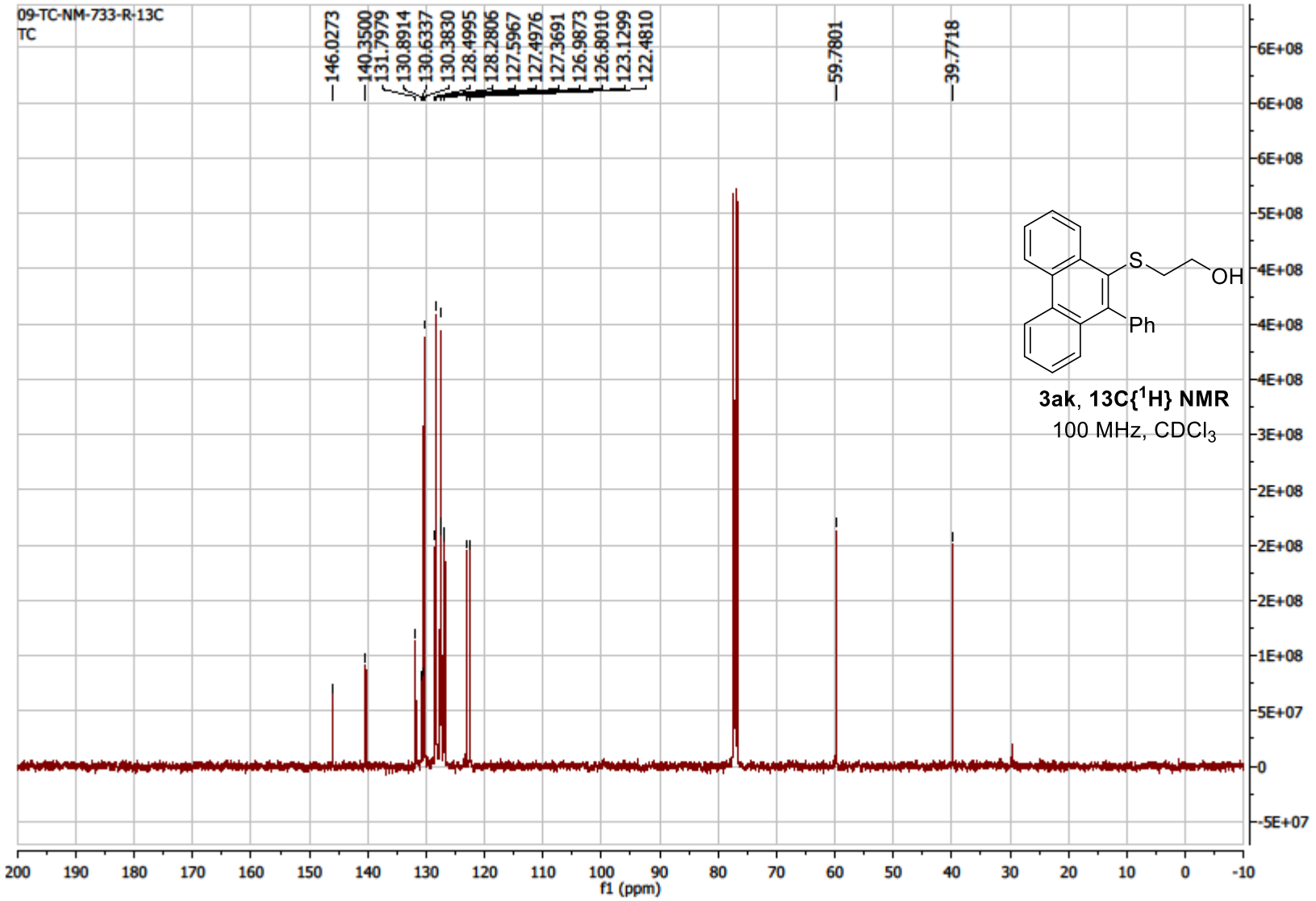

11-NM-712(R)
NM-712(R)-DATANMA8
8.9015
8.8952
8.8852
8.7763
8.7744
8.7633
7.7945
7.7810
7.7771
7.7674
7.7618
7.7574
7.7478
7.7435
7.6954
7.6892
7.6809
7.6747
7.6687
7.6598
7.6539
7.5814
7.5777
7.5632
7.5500
7.5325
7.5078
7.5050
7.4928
7.4906
7.4118
7.4079
7.3917
2.6552
2.6368
1.4806
1.4622
1.4439
1.4256
0.8592
0.8409
0.8225
S
Ph
3ai, 1H NMR
400 MHz, CDCl3
1.00
2.08
2.07
1.08
5.07
2.05
2.08
2.09
3.02
4E+08
3E+08
2E+08
1E+08
5E+07
0
f1 (ppm)

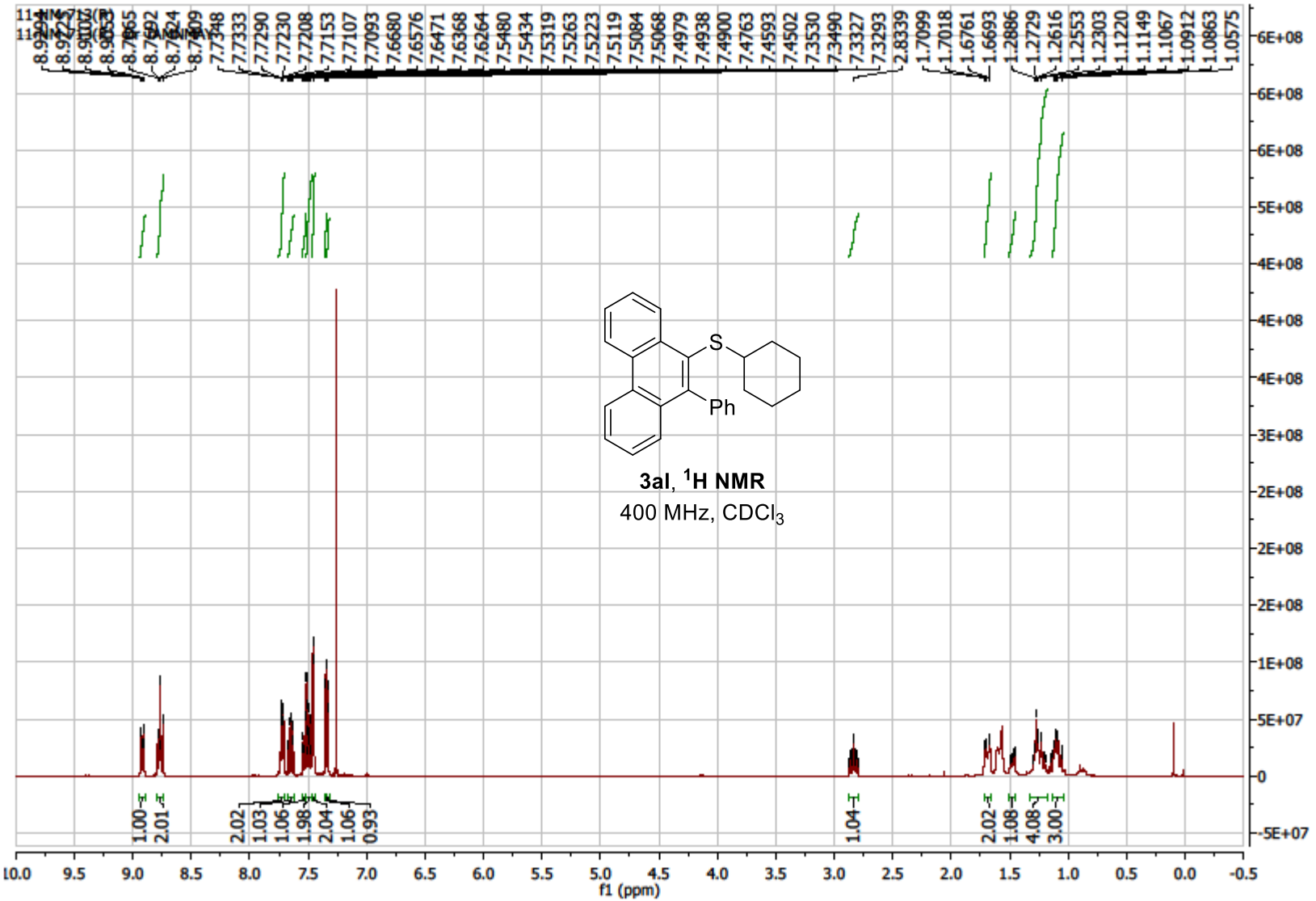

09-NM-712 C13
09-NM-712 13C Dr TANMAY
145.3857
140.6383
132.5289
132.1008
130.6494
130.4460
130.3523
128.3175
127.9259
127.8749
127.2017
127.1064
126.9807
126.7359
126.5624
122.8469
122.4056
38.6650
22.8667
13.4130
S
Ph
3ai, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

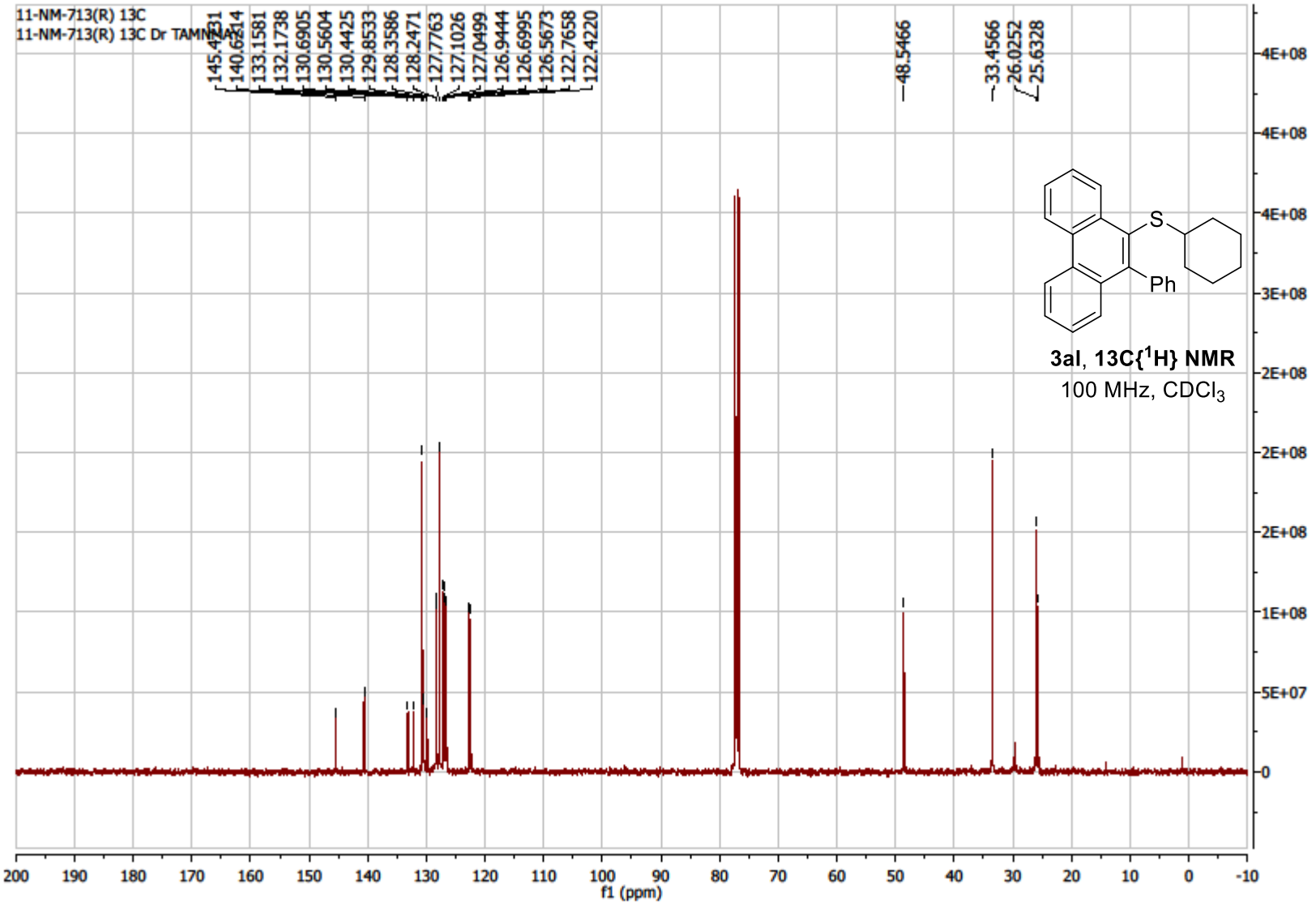

S
COOH
Ph
3aj, 1H NMR
400 MHz, CDCl3
f1 (ppm)

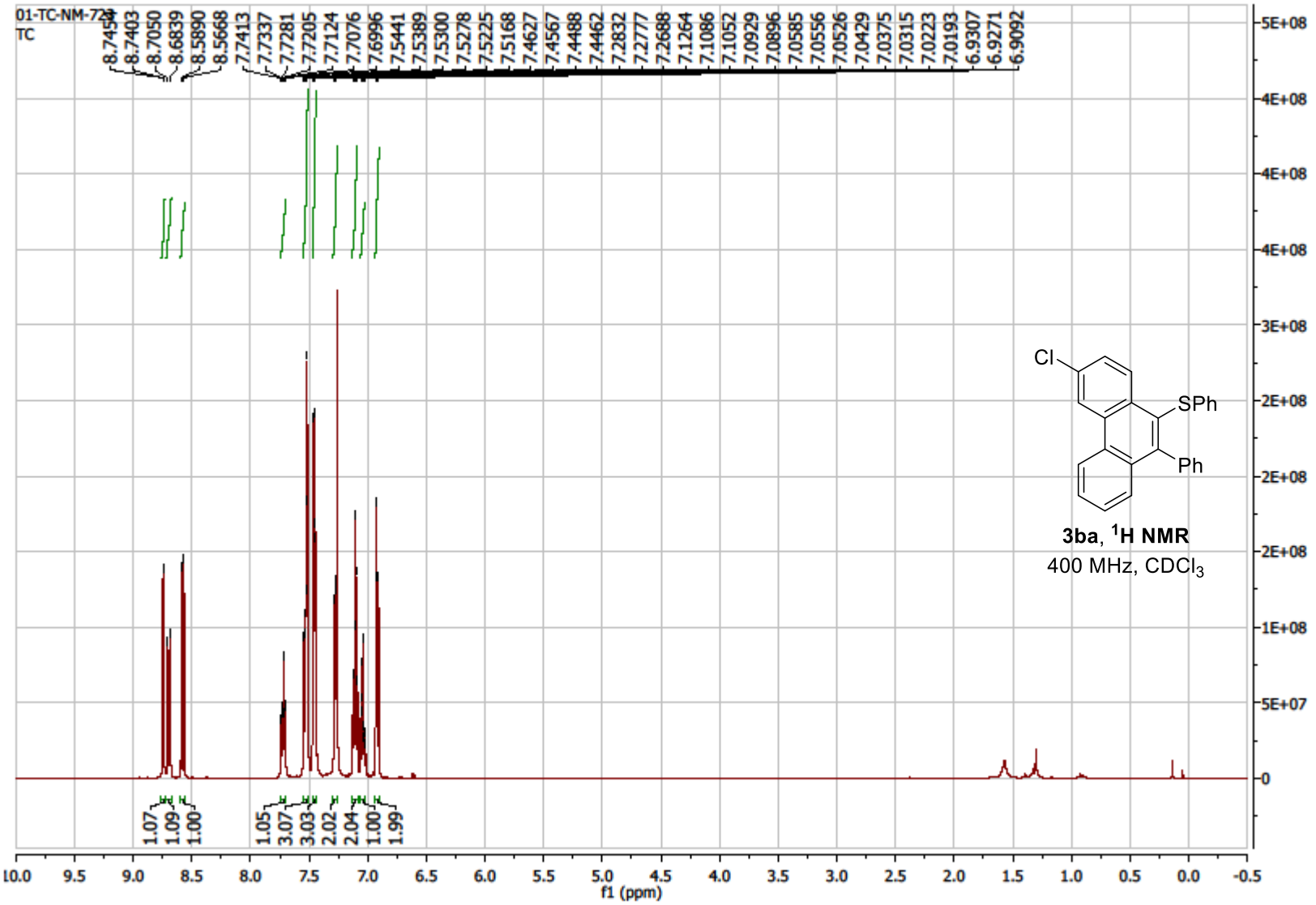

16-NM-716(R)(R)13C
16-NM-716(R)(R)13C Dr TANMAY
179.3300
145.6888
140.3820
132.2339
131.9679
130.7128
130.5289
130.3956
129.4248
128.3786
127.9437
127.6950
127.3159
127.2643
127.1497
126.8327
126.6321
122.9392
122.4236
77.0000
35.5350
32.5476
24.0446
S
COOH
Ph
3aj, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

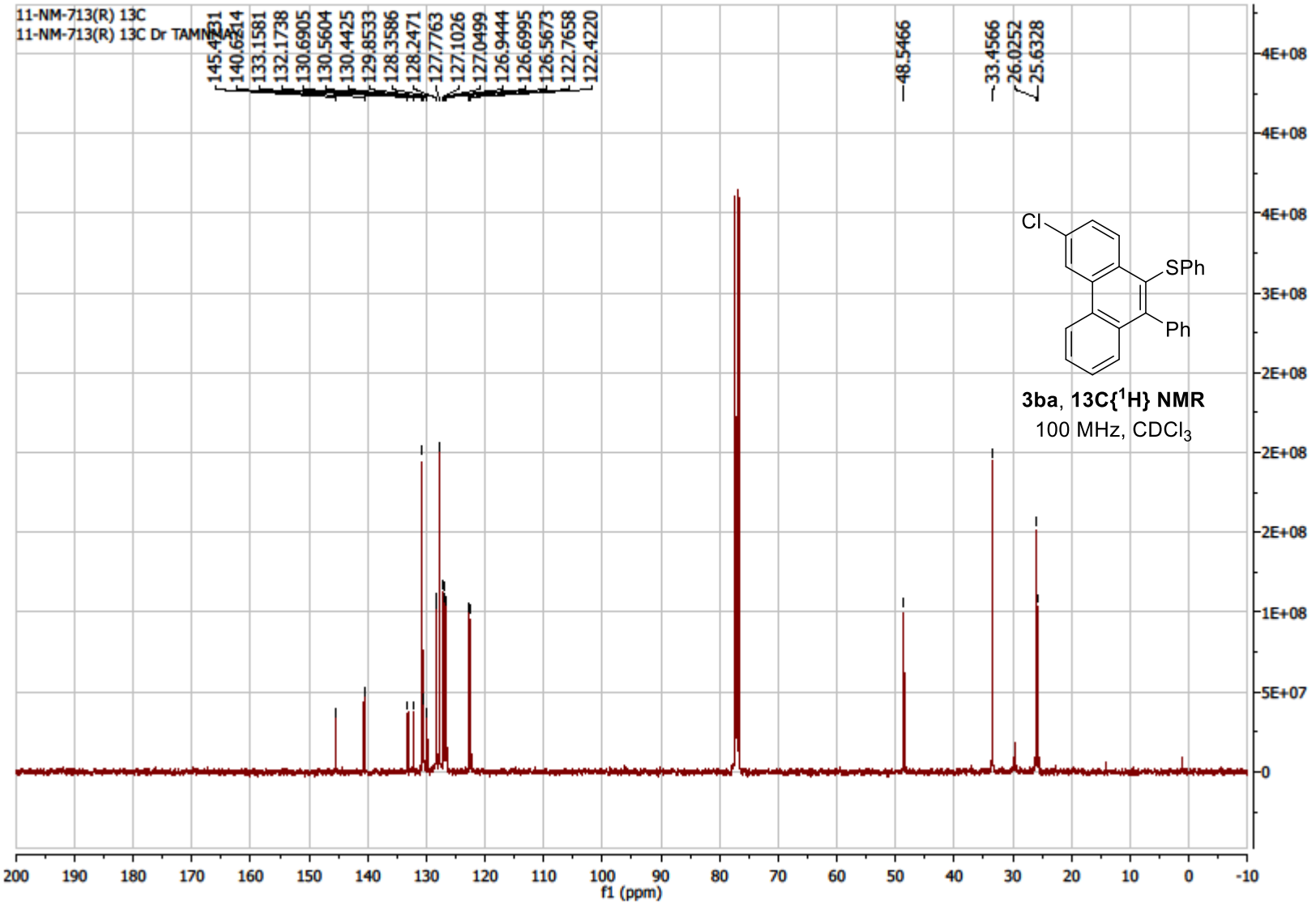

S
OH
Ph
3ak, 1H NMR
400 MHz, CDCl3
f1 (ppm)

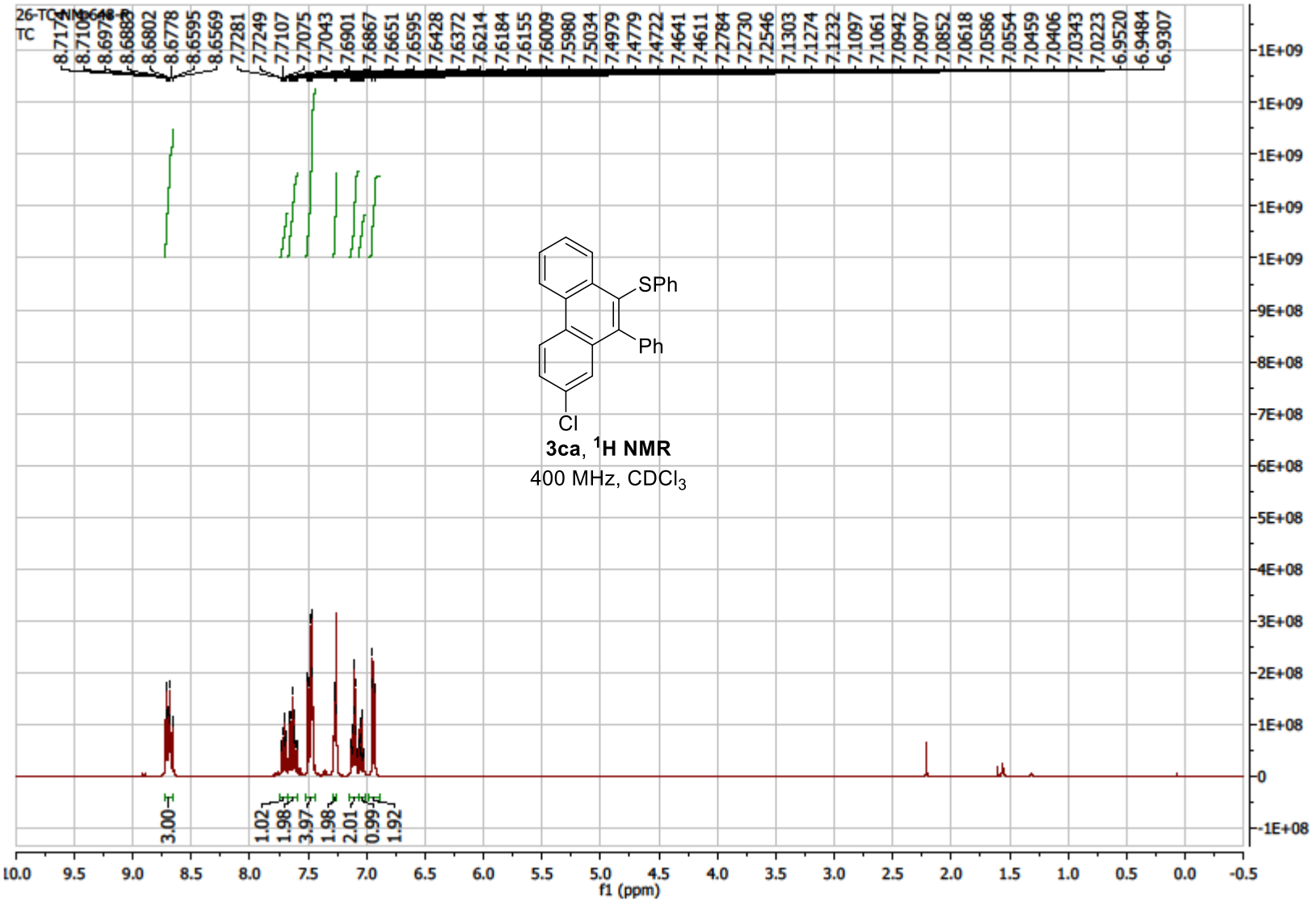

09-TC-NM-733-R-13C
TC
146.0273
140.3500
131.7979
130.8914
130.6337
130.3830
128.4995
128.2806
127.5967
127.4976
127.3691
126.9873
126.8010
123.1299
122.4810
59.7801
39.7718
S
OH
Ph
3ak, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

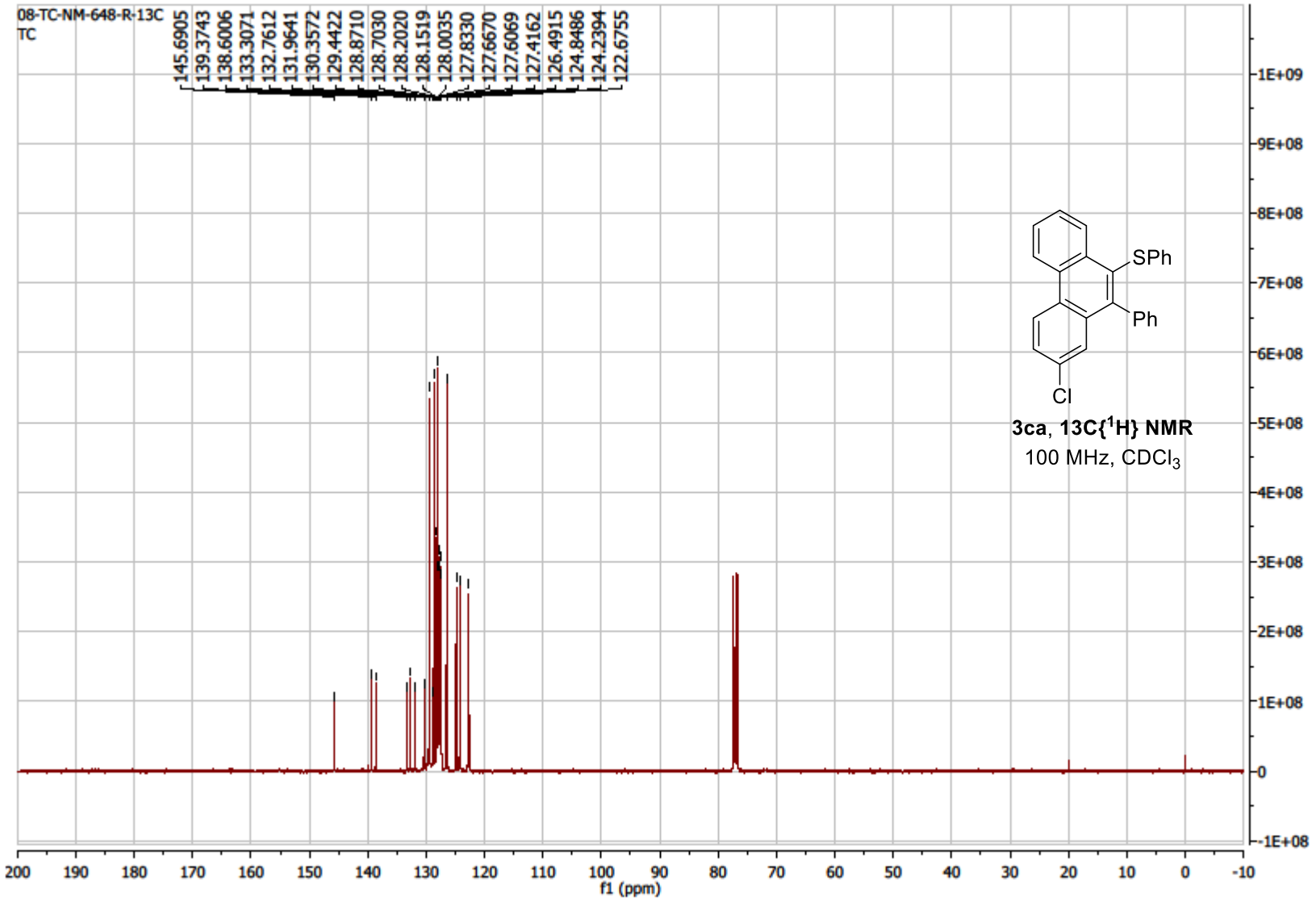

S
Ph
3al, 1H NMR
400 MHz, CDCl3
f1 (ppm)


11-NM-713(R) 13C
11-NM-713(R) 13C Dr TAMINNA
145.4731
140.6214
133.1581
132.1738
130.6905
130.5604
130.4425
129.8533
128.3586
128.2471
127.7763
127.1026
127.0499
126.9444
126.6995
126.5673
122.7658
122.4220
48.5466
33.4566
26.0252
25.6328
S
Ph
3al, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

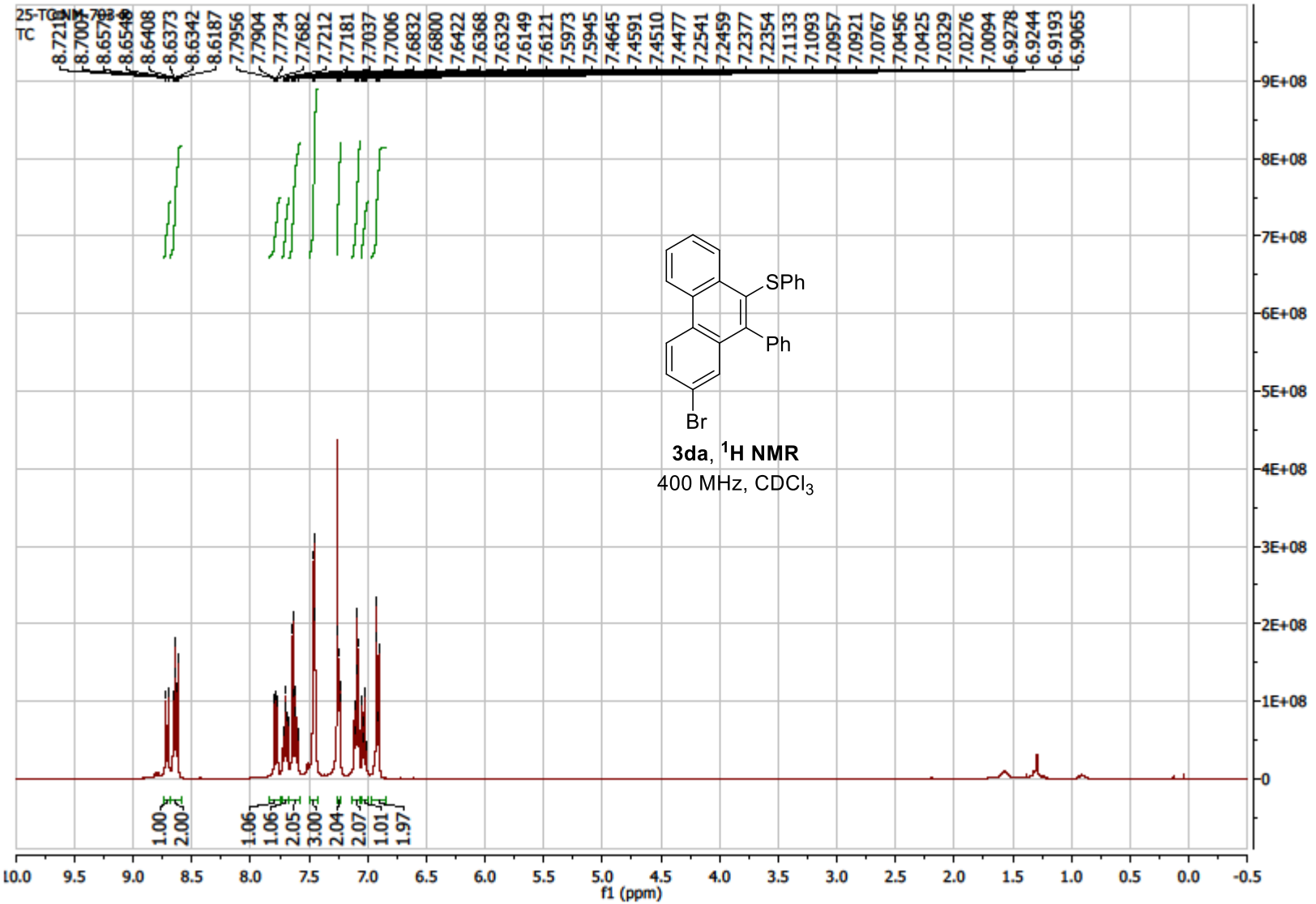

01-TC-NM-724
TC
8.7454
8.7403
8.7050
8.6839
8.5890
8.5668
7.7413
7.7337
7.7281
7.7205
7.7124
7.7076
7.6996
7.5441
7.5389
7.5300
7.5278
7.5225
7.5168
7.4627
7.4567
7.4488
7.4462
7.2832
7.2777
7.2688
7.1264
7.1086
7.1052
7.0929
7.0896
7.0585
7.0556
7.0526
7.0429
7.0375
7.0315
7.0223
7.0193
6.9307
6.9271
6.9092
1.07
1.09
1.00
1.05
3.07
3.03
2.02
2.04
1.00
1.99
f1 (ppm)
Cl
SPh
Ph
3ba, 1H NMR
400 MHz, CDCl3

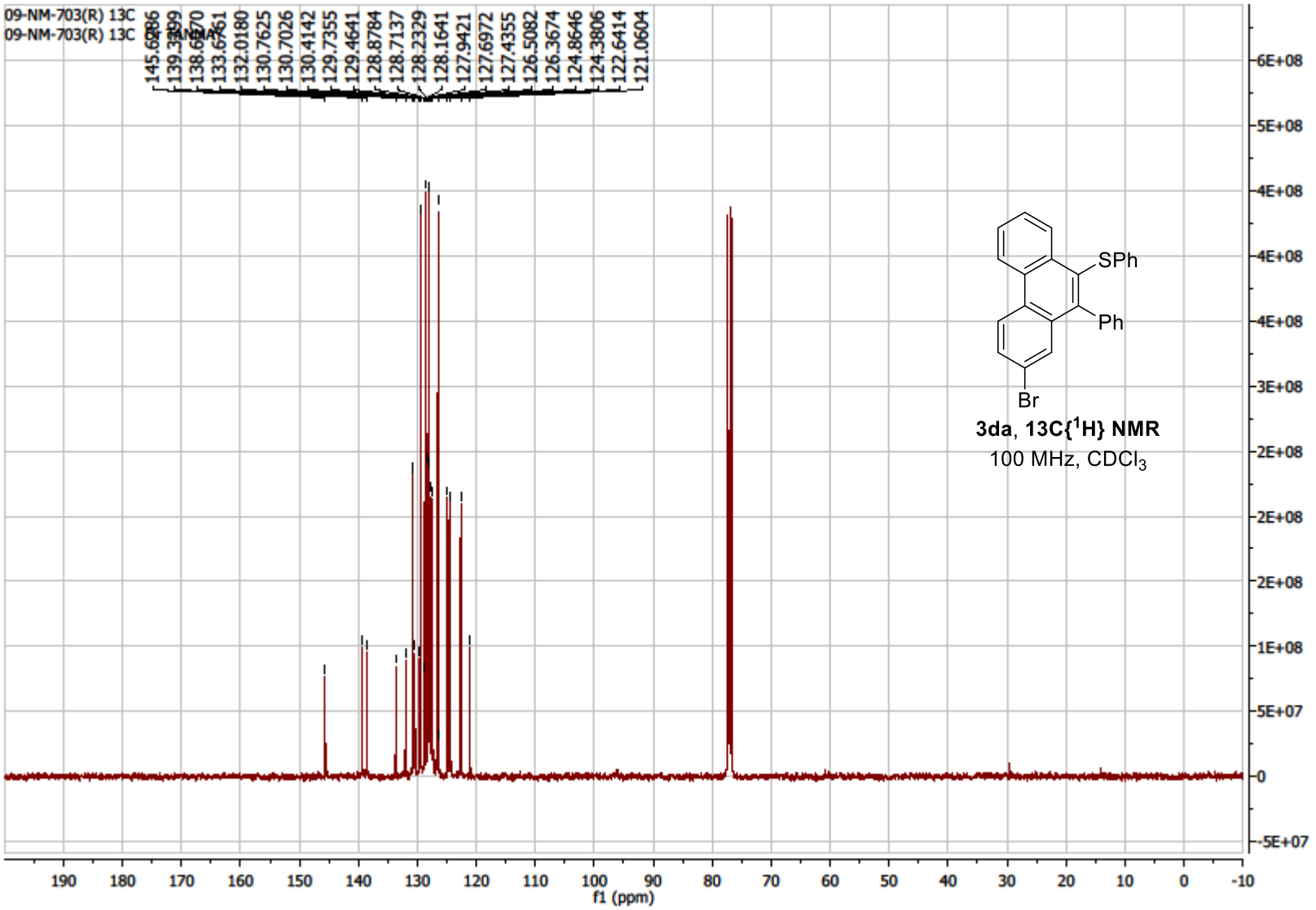

11-NM-713(R) 13C
11-NM-713(R) 13C Dr TAMINNA
145.4731
140.6214
133.1581
132.1738
130.6905
130.5604
130.4425
129.8533
128.3586
128.2471
127.7763
127.1026
127.0499
126.9444
126.6995
126.5673
122.7658
122.4220
48.5466
33.4566
26.0252
25.6328
Cl
SPh
Ph
3ba, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

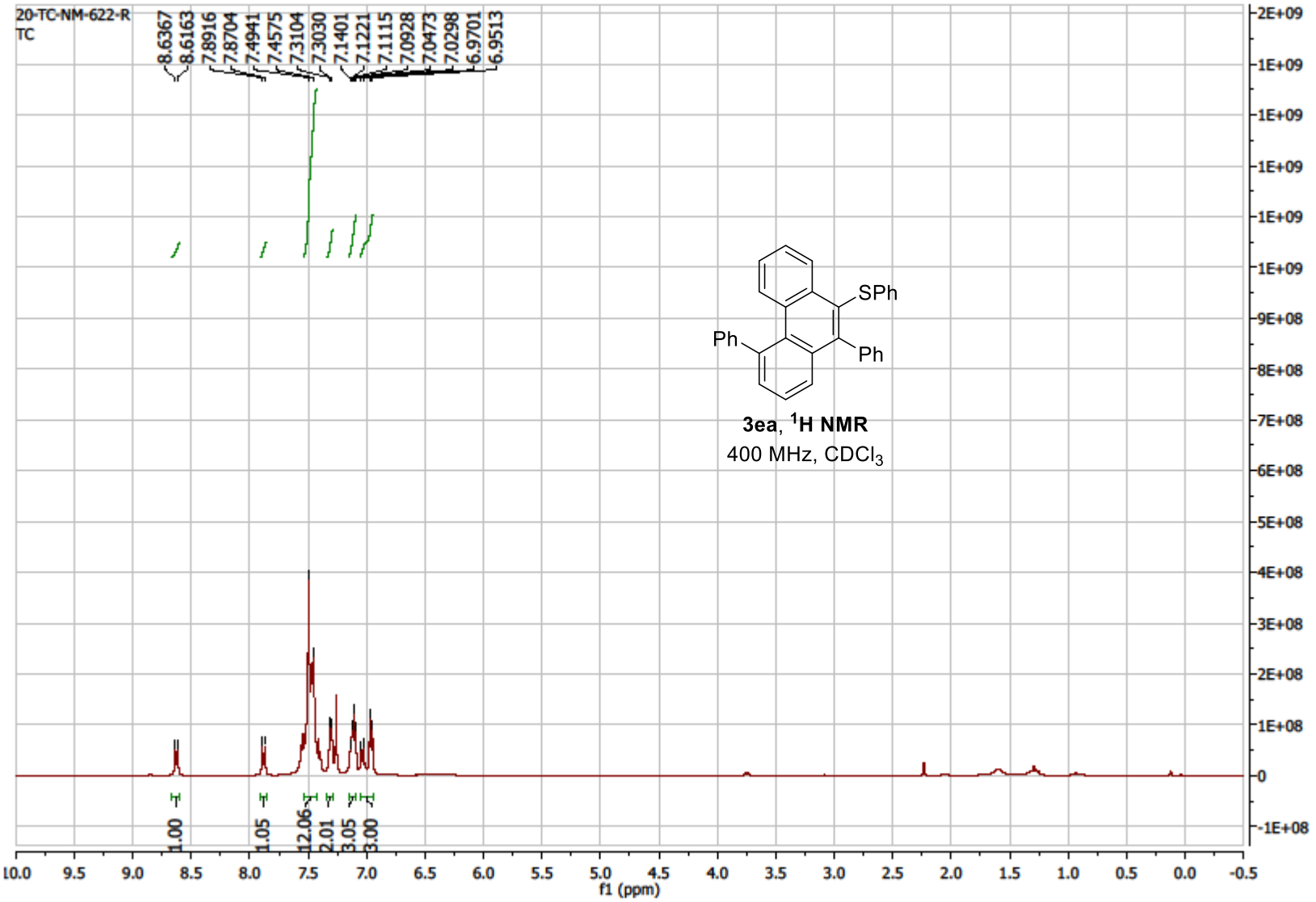

SPh
Ph
Cl
3ca, 1H NMR
400 MHz, CDCl3
f1 (ppm)

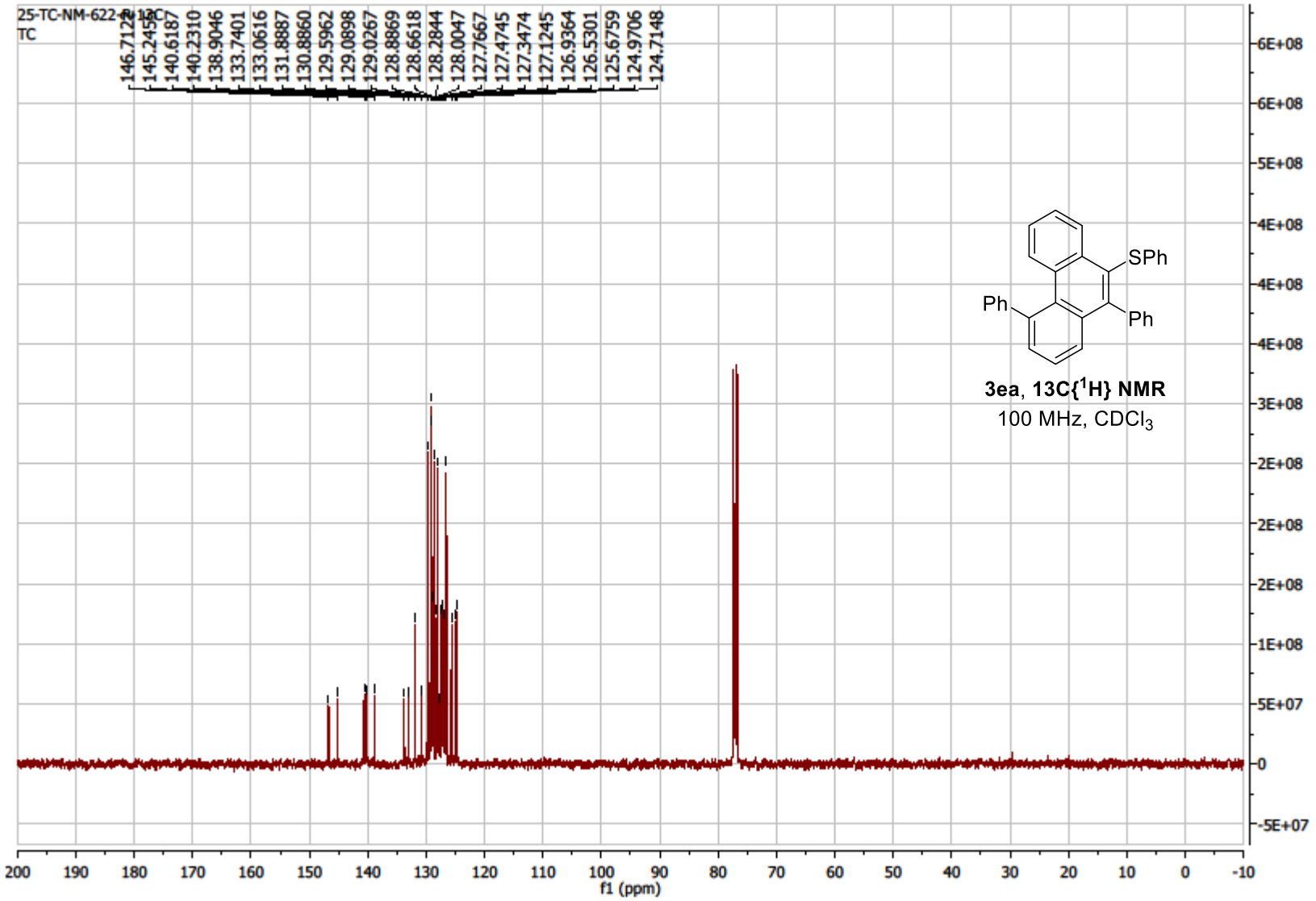


3ca, **13C{^{1}H} NMR**
100 MHz, $CDCl_3$


SPh
Ph
Br
3da, 1H NMR
400 MHz, CDCl3
f1 (ppm)


09-NM-703(R) 13C
09-NM-703(R) 13C
145.6286
139.3399
138.6970
133.6761
132.0180
130.7625
130.7026
130.4142
129.7355
129.4641
128.8784
128.7137
128.2329
128.1641
127.9421
127.6972
127.4355
126.5082
126.3674
124.8646
124.3806
122.6414
121.0604
SPh
Ph
Br
3da, 13C{1H} 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
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


20-TC-NM-622-R
TC
8.6367
8.6163
7.8916
7.8704
7.4941
7.4575
7.3104
7.3030
7.1401
7.1221
7.1115
7.0928
7.0473
7.0298
6.9701
6.9513
SPh
Ph
Ph
3ea, 1H NMR
400 MHz, CDCl3
1.00
1.05
12.06
2.01
3.05
3.00
f1 (ppm)


25-TC-NM-622-R 13C
TC
146.7124
145.2456
140.6187
140.2310
138.9046
133.7401
133.0616
131.8887
130.8860
129.5962
129.0898
129.0267
128.8869
128.6618
128.2844
128.0047
127.7667
127.4745
127.3474
127.1245
126.9364
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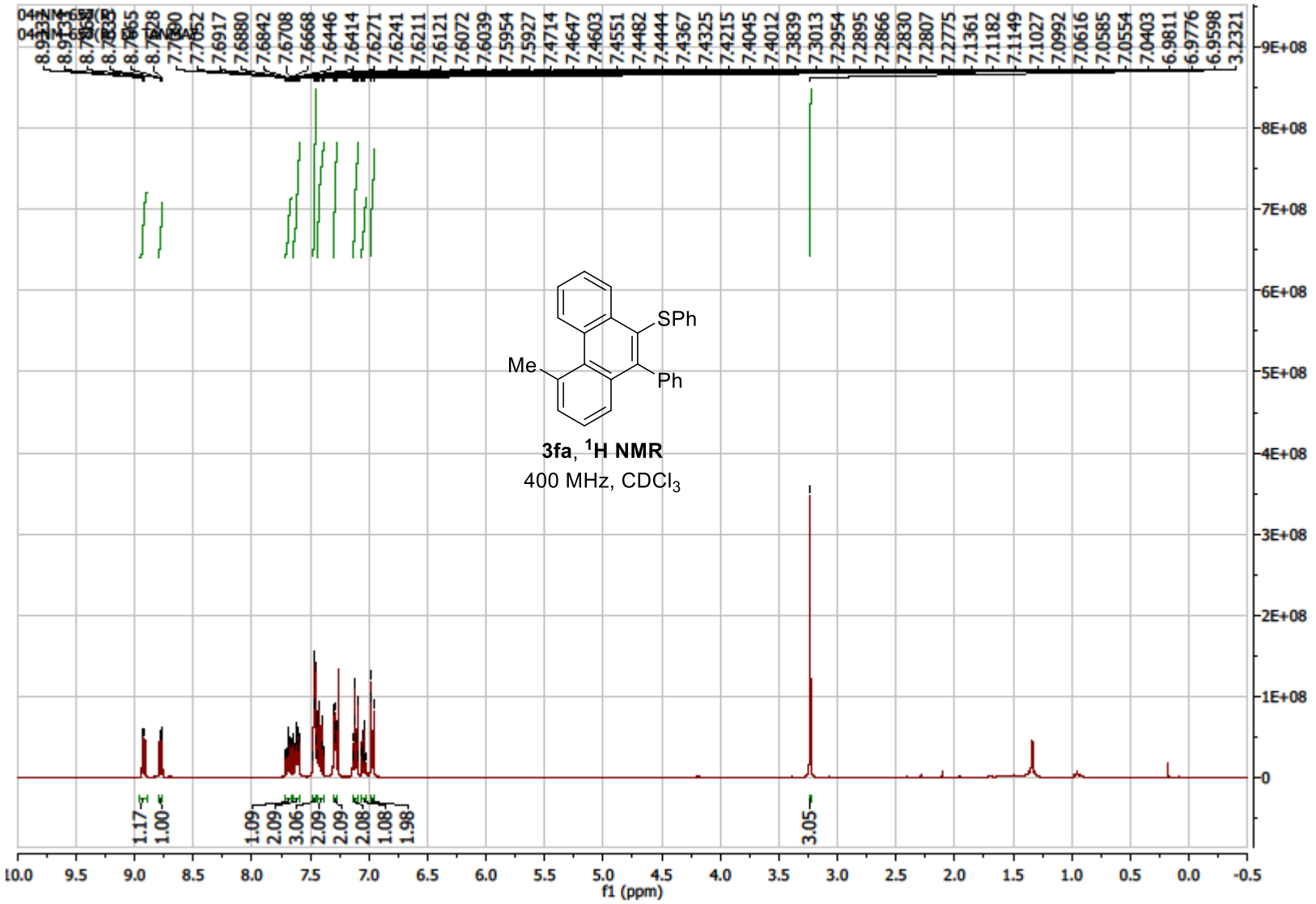
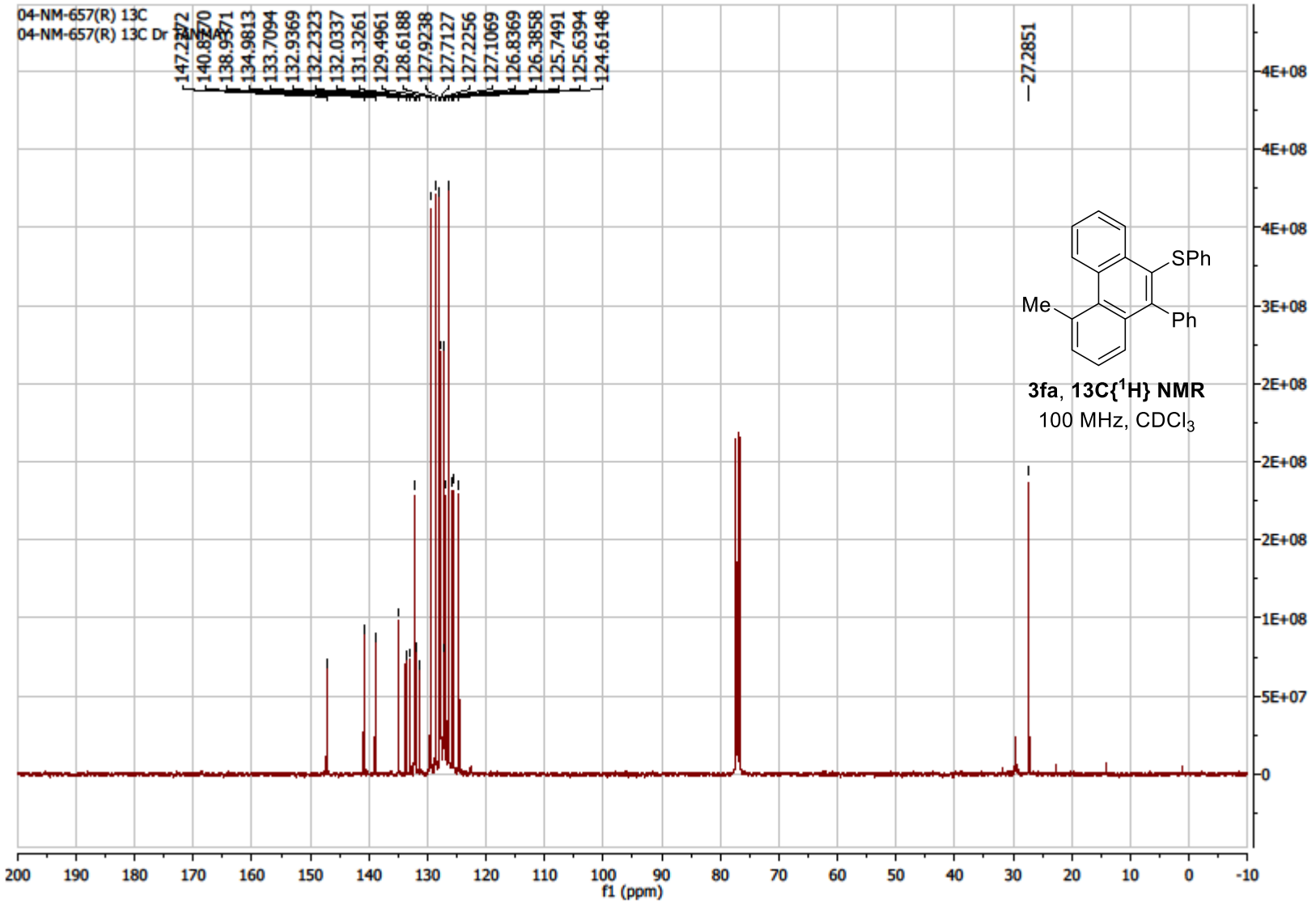
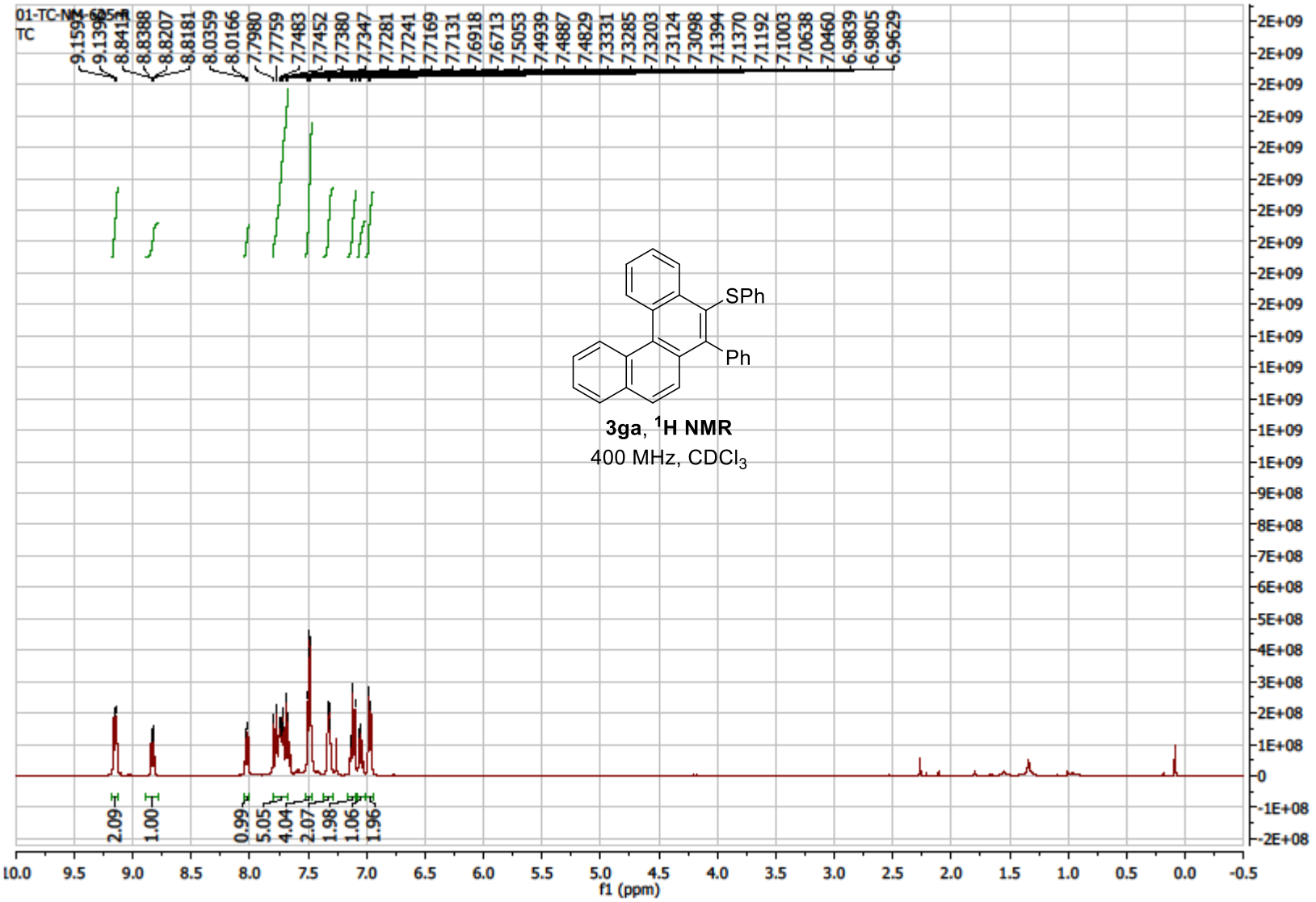
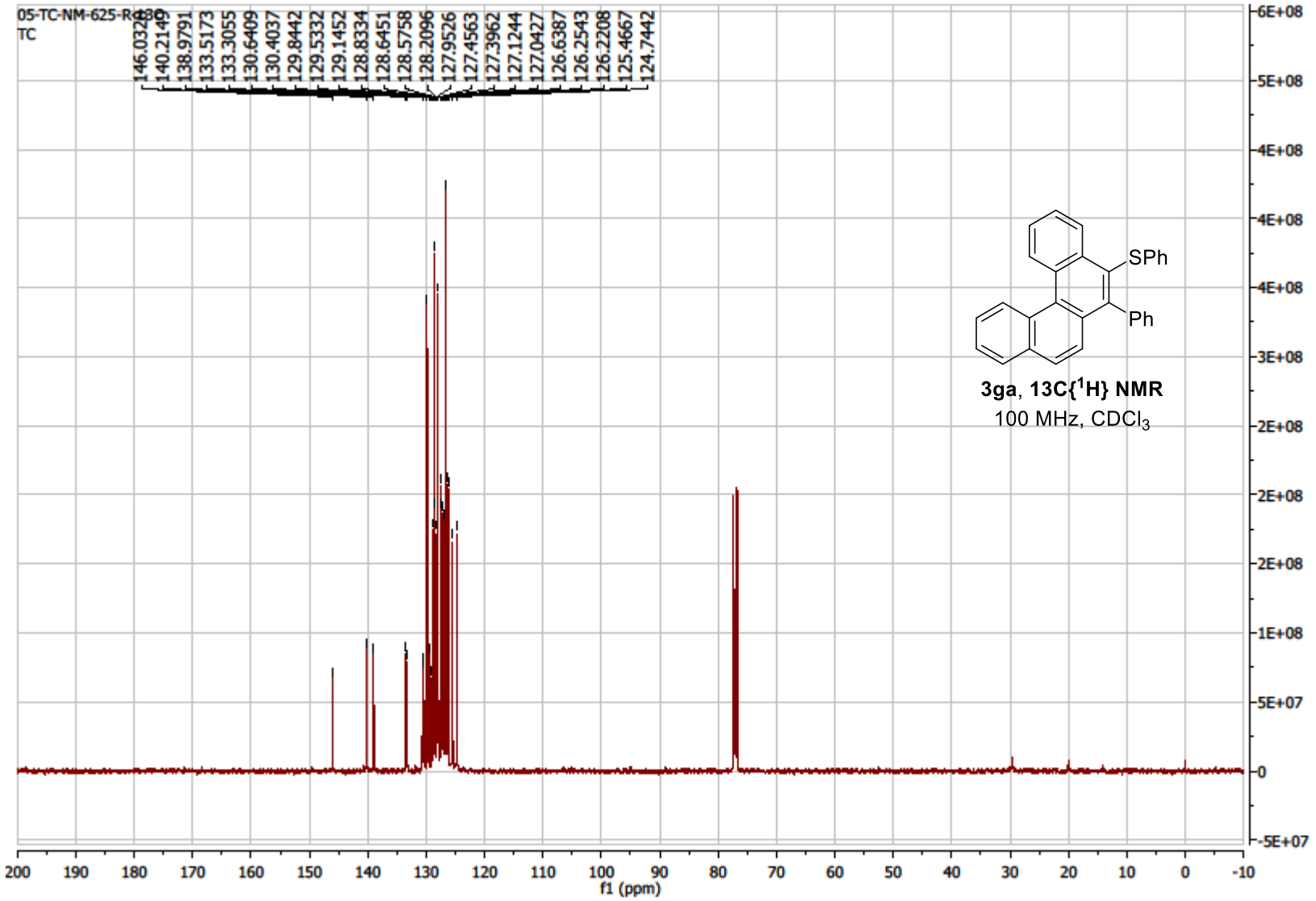
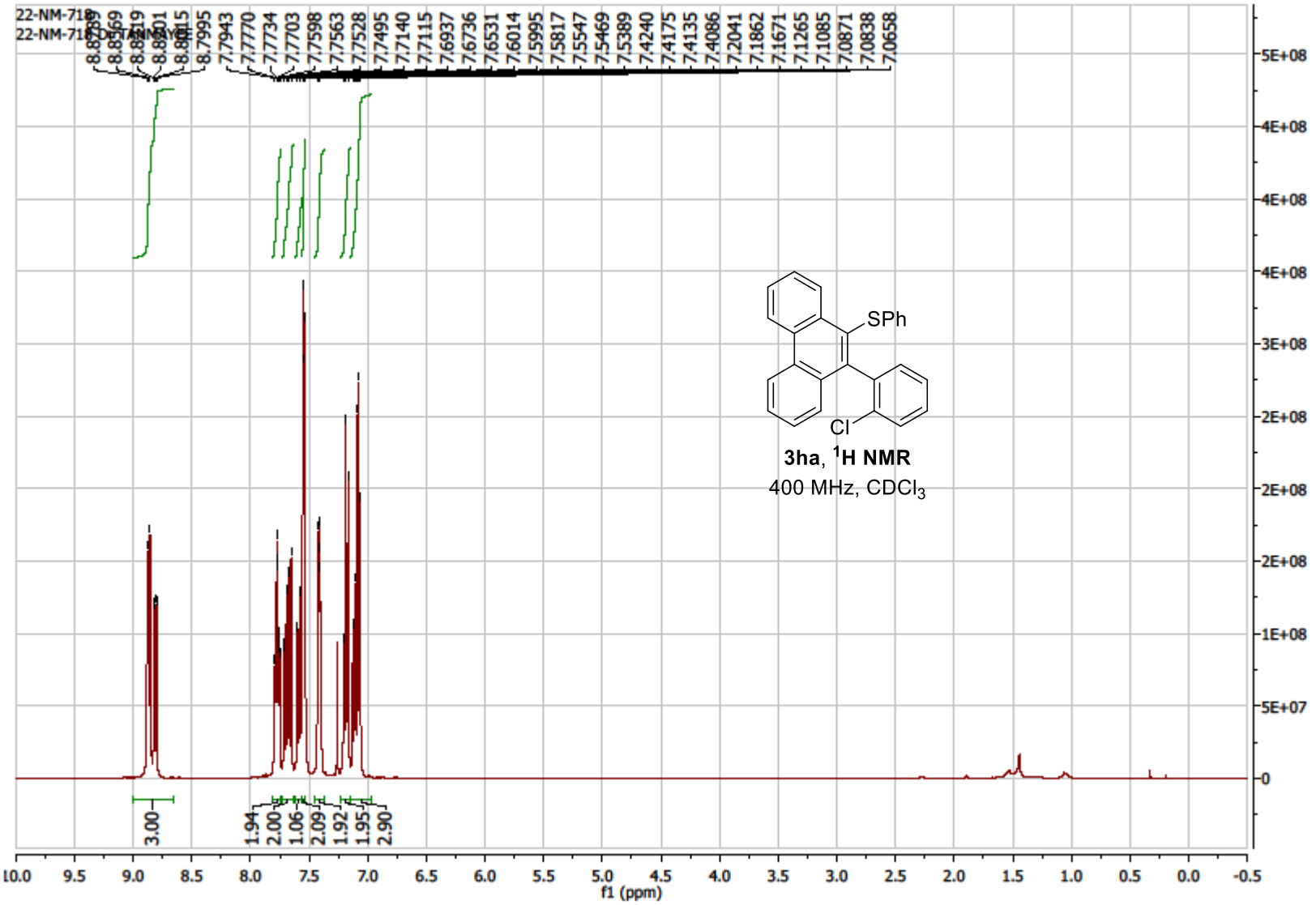
SPh
Ph
Ph
3ea, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

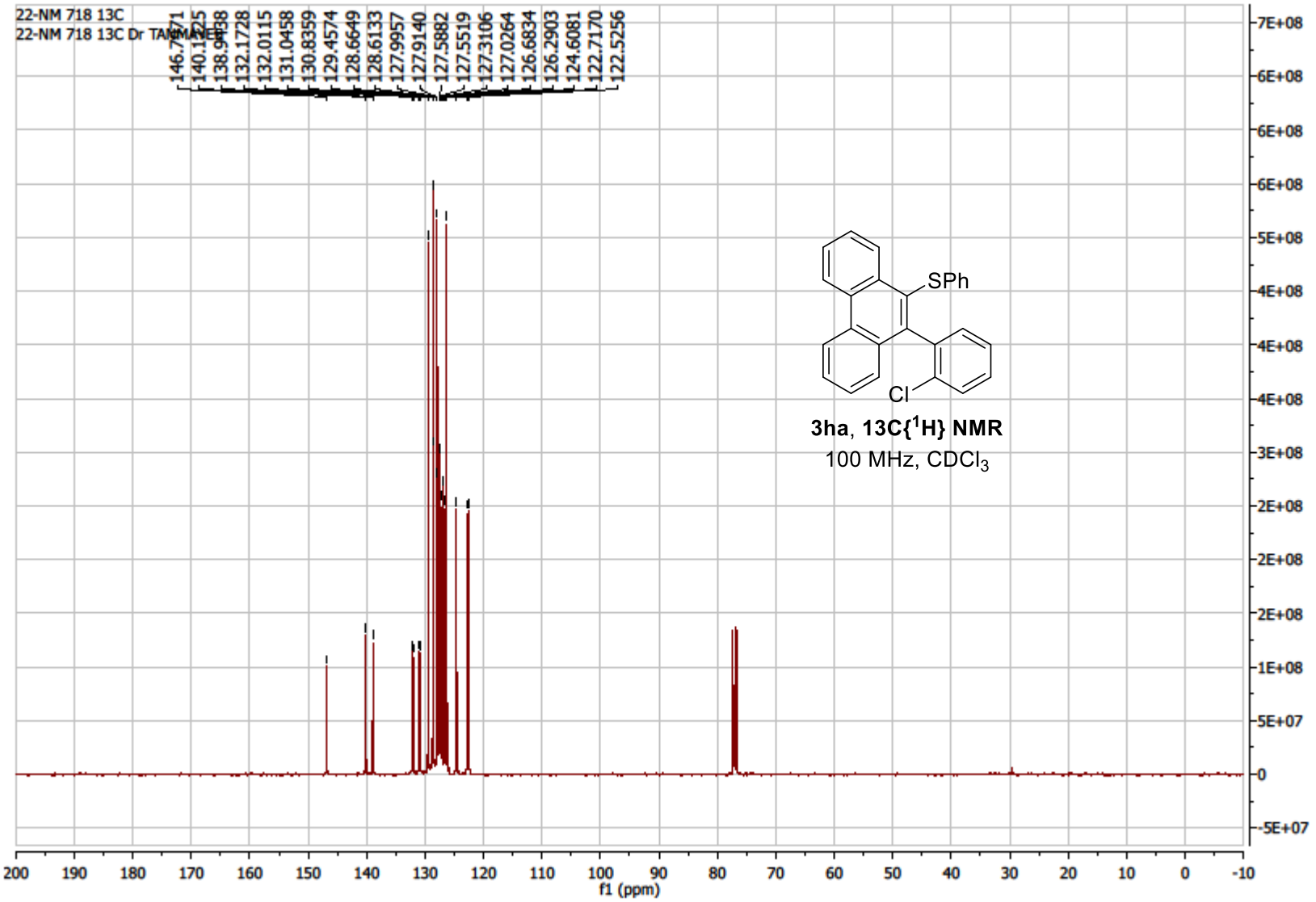

SPh
Me
Ph
3fa, 1H NMR
400 MHz, CDCl3
f1 (ppm)

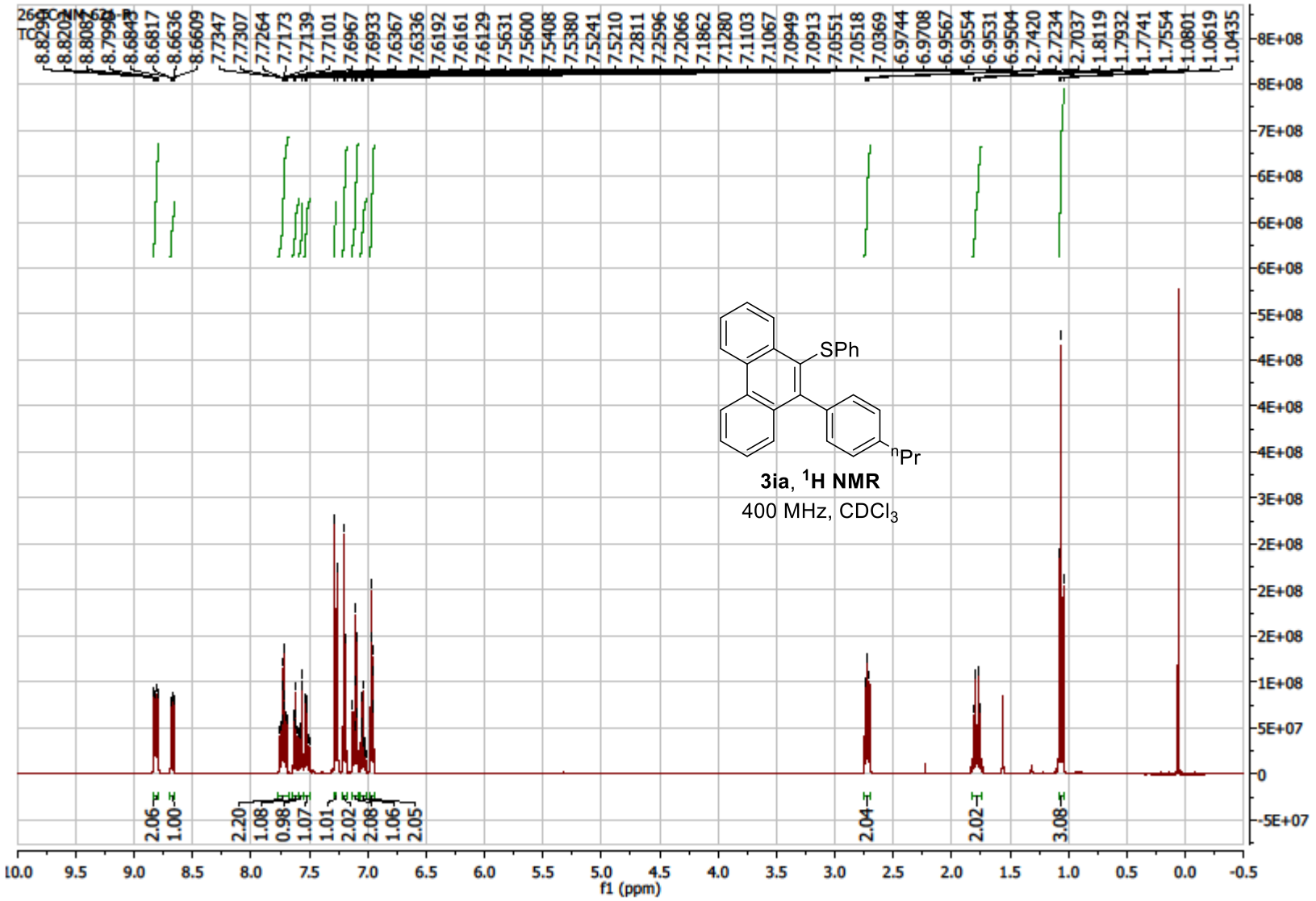

04-NM-657(R) 13C
04-NM-657(R) 13C Dr TANMAY
147.2272
140.8570
138.9371
134.9813
133.7094
132.9369
132.2323
132.0337
131.3261
129.4961
128.6188
127.9238
127.7127
127.2256
127.1069
126.8369
126.3858
125.7491
125.6394
124.6148
27.2851
SPh
Me
Ph
3fa, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

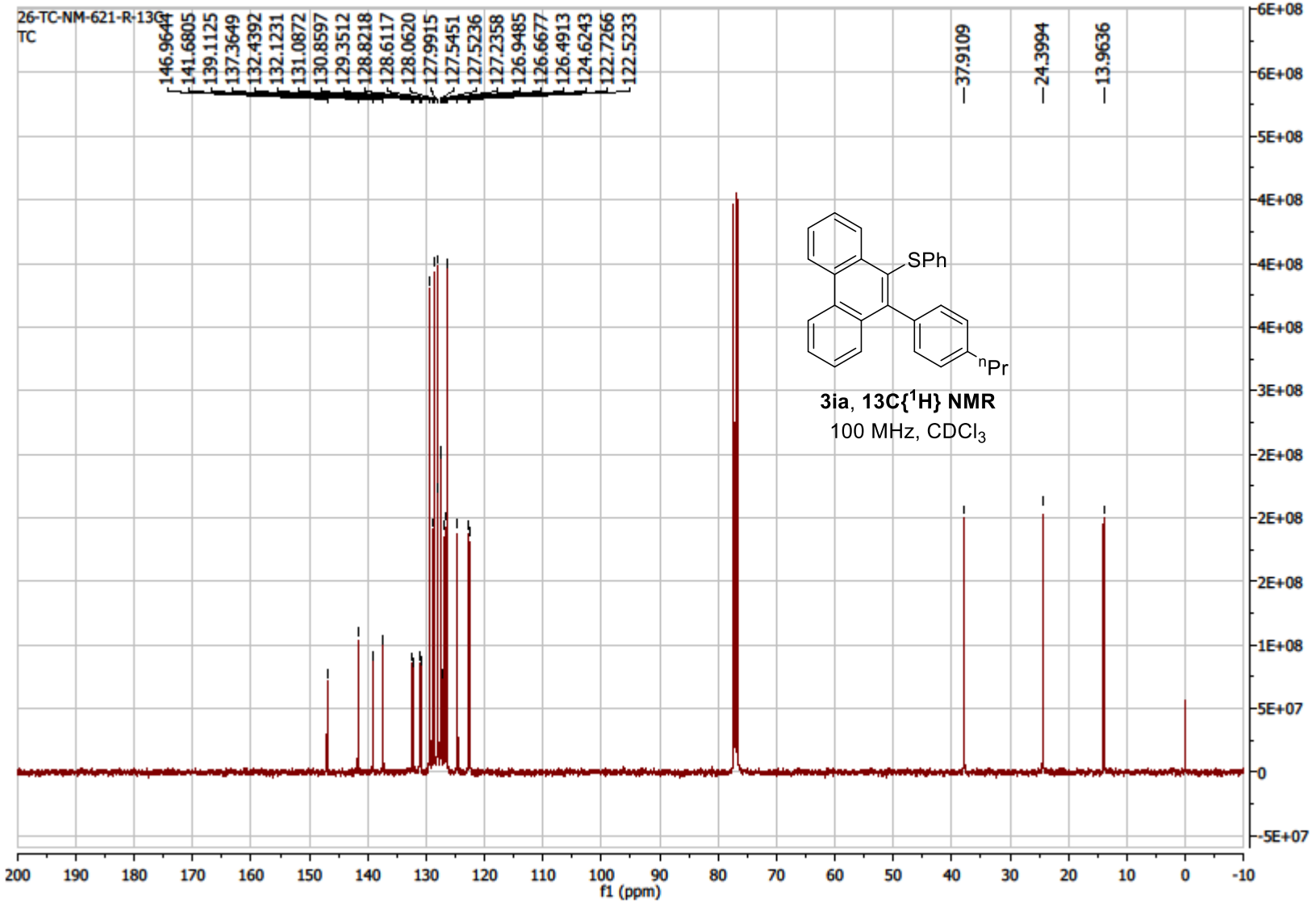

01-TC-NM-605-r
TC
9.1594
9.1396
8.8413
8.8388
8.8207
8.8181
8.0359
8.0166
7.7980
7.7759
7.7483
7.7452
7.7380
7.7347
7.7281
7.7241
7.7169
7.7131
7.6918
7.6713
7.5053
7.4939
7.4887
7.4829
7.3331
7.3285
7.3203
7.3124
7.3098
7.1394
7.1370
7.1192
7.1003
7.0638
7.0460
6.9839
6.9805
6.9629
SPh
Ph
3ga, 1H NMR
400 MHz, CDCl3
2.09
1.00
0.99
5.05
4.04
2.07
1.98
1.06
1.96
f1 (ppm)

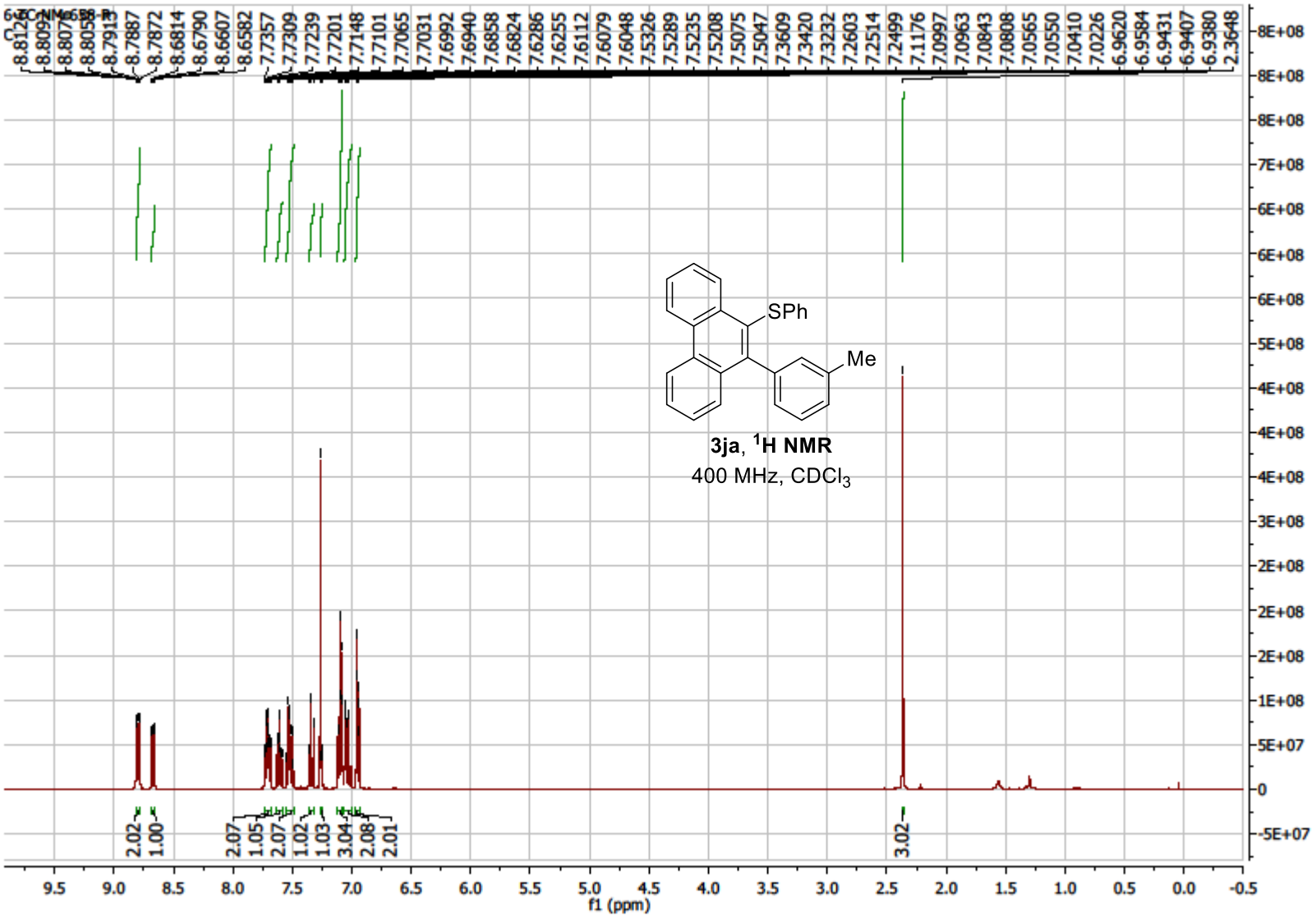

05-TC-NM-625-R
TC
146.0328
140.2149
138.9791
133.5173
133.3055
130.6409
130.4037
129.8442
129.5332
129.1452
128.8334
128.6451
128.5758
128.2096
127.9526
127.4563
127.3962
127.1244
127.0427
126.6387
126.2543
126.2208
125.4667
124.7442
SPh
Ph
3ga, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

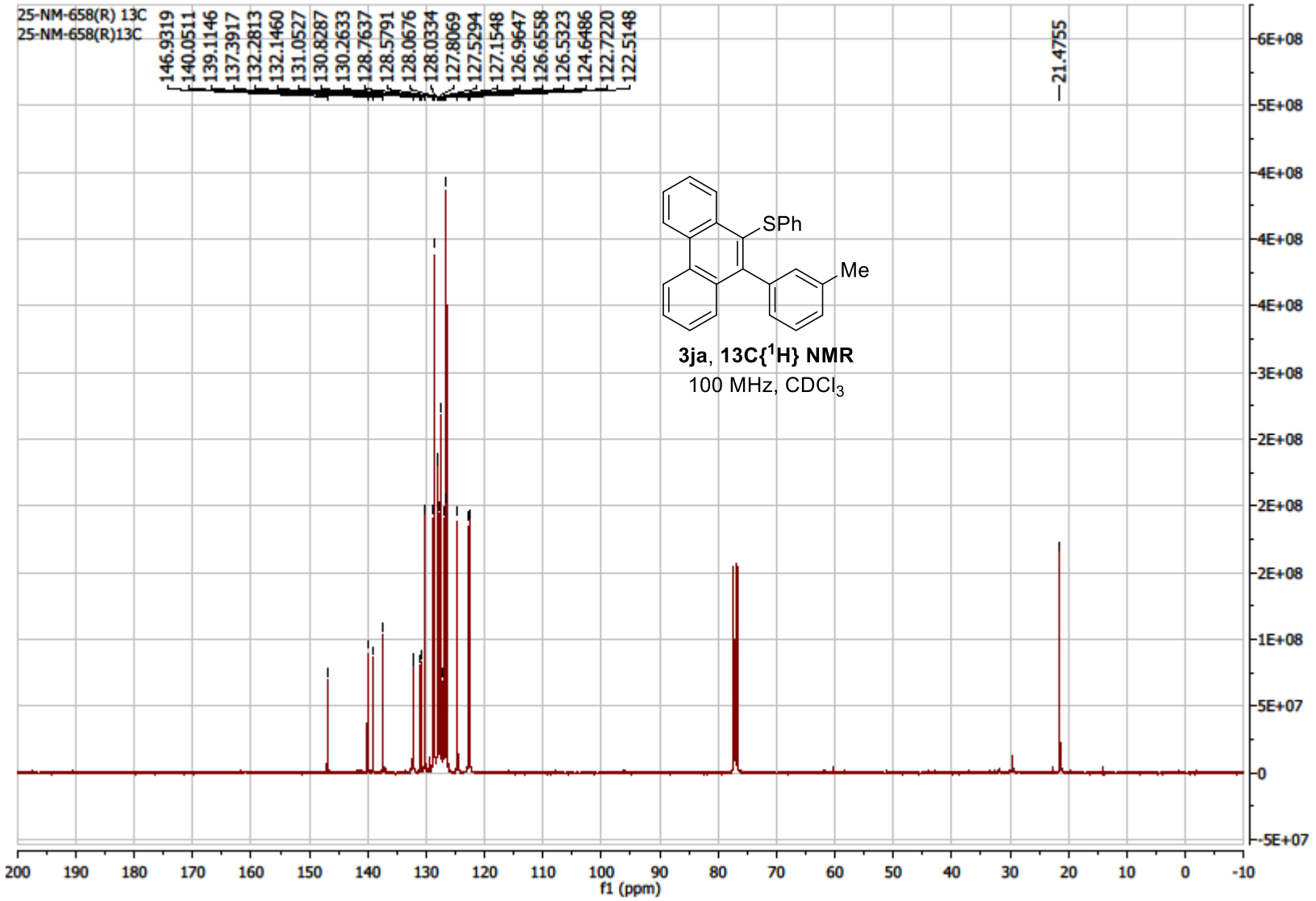

22-NM-718
22-NM-718-DS-TANMAY-1H
8.8789
8.8569
8.8419
8.8301
8.8015
8.7995
7.7943
7.7770
7.7734
7.7703
7.7598
7.7563
7.7528
7.7495
7.7140
7.7115
7.6937
7.6736
7.6531
7.6014
7.5995
7.5817
7.5547
7.5469
7.5389
7.4240
7.4175
7.4135
7.4086
7.2041
7.1862
7.1671
7.1265
7.1085
7.0871
7.0838
7.0658
SPh
Cl
3ha, 1H NMR
400 MHz, CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
3.00
1.94
2.00
1.06
2.09
1.92
1.95
2.90
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)

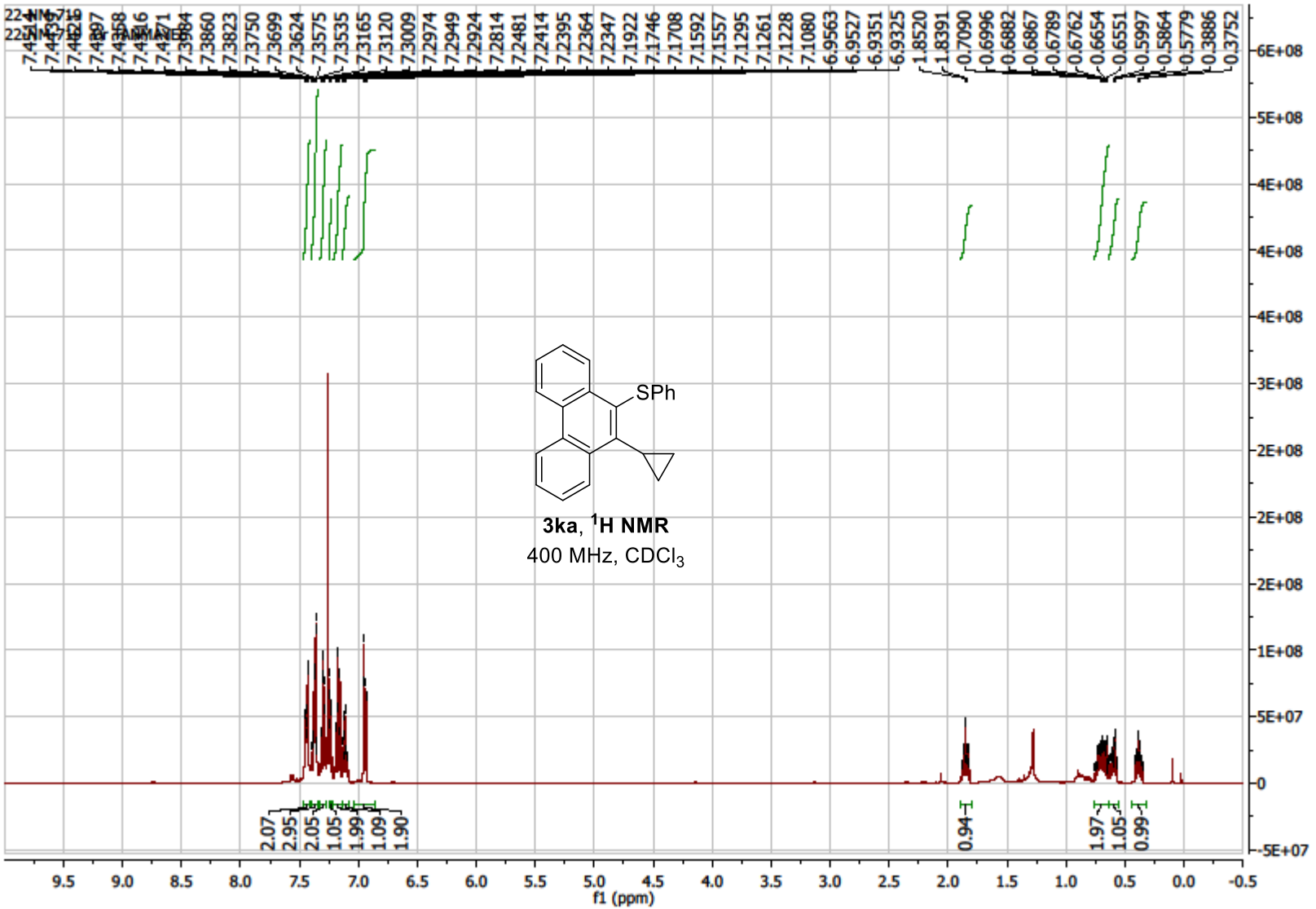

22-NM 718 13C
22-NM 718 13C Dr TANMAY
146.7671
140.1225
138.9438
132.1728
132.0115
131.0458
130.8359
129.4574
128.6649
128.6133
127.9957
127.9140
127.5882
127.5519
127.3106
127.0264
126.6834
126.2903
124.6081
122.7170
122.5256
SPh
Cl
3ha, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

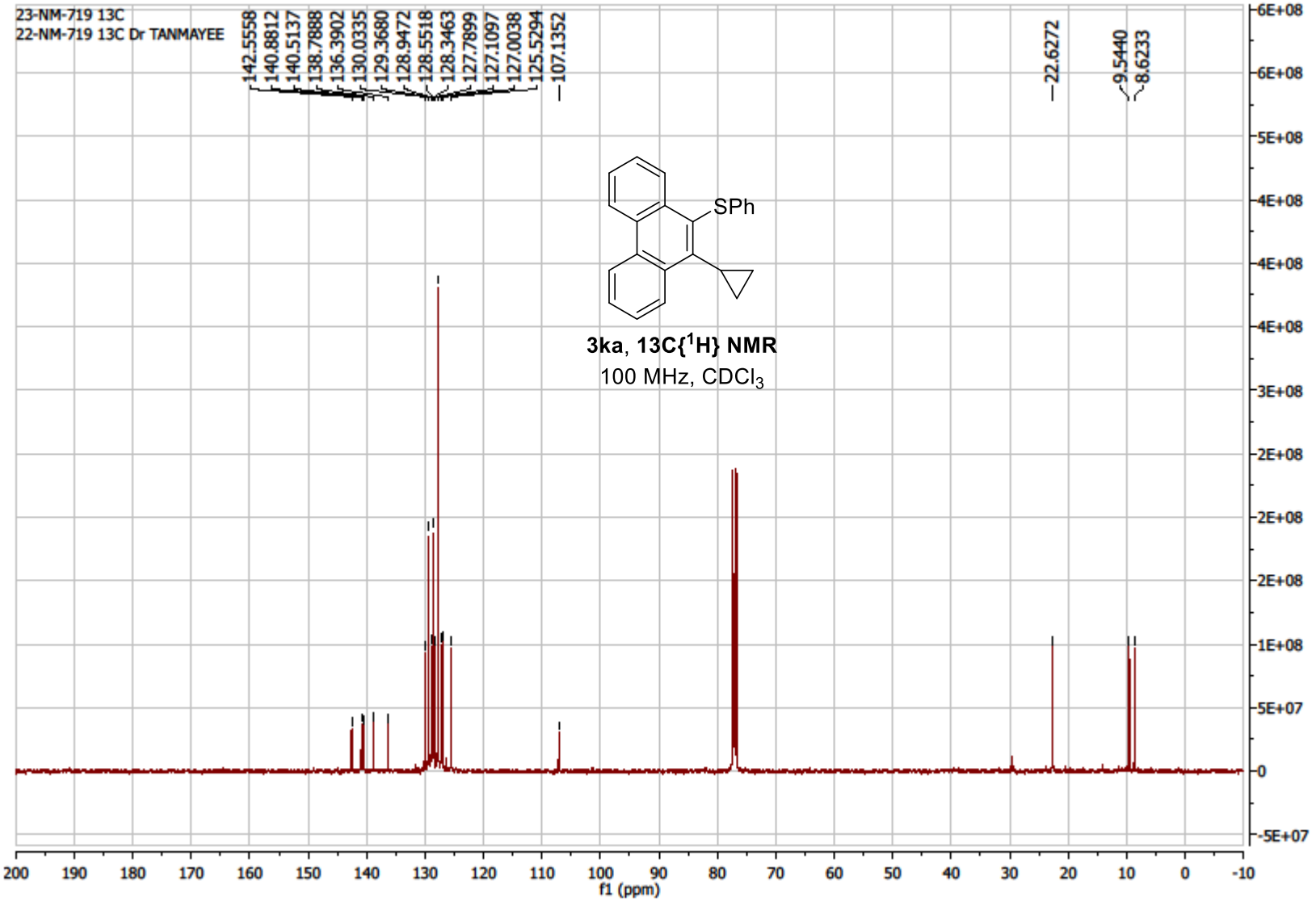

SPh
nPr
3ia, 1H NMR
400 MHz, CDCl3
f1 (ppm)

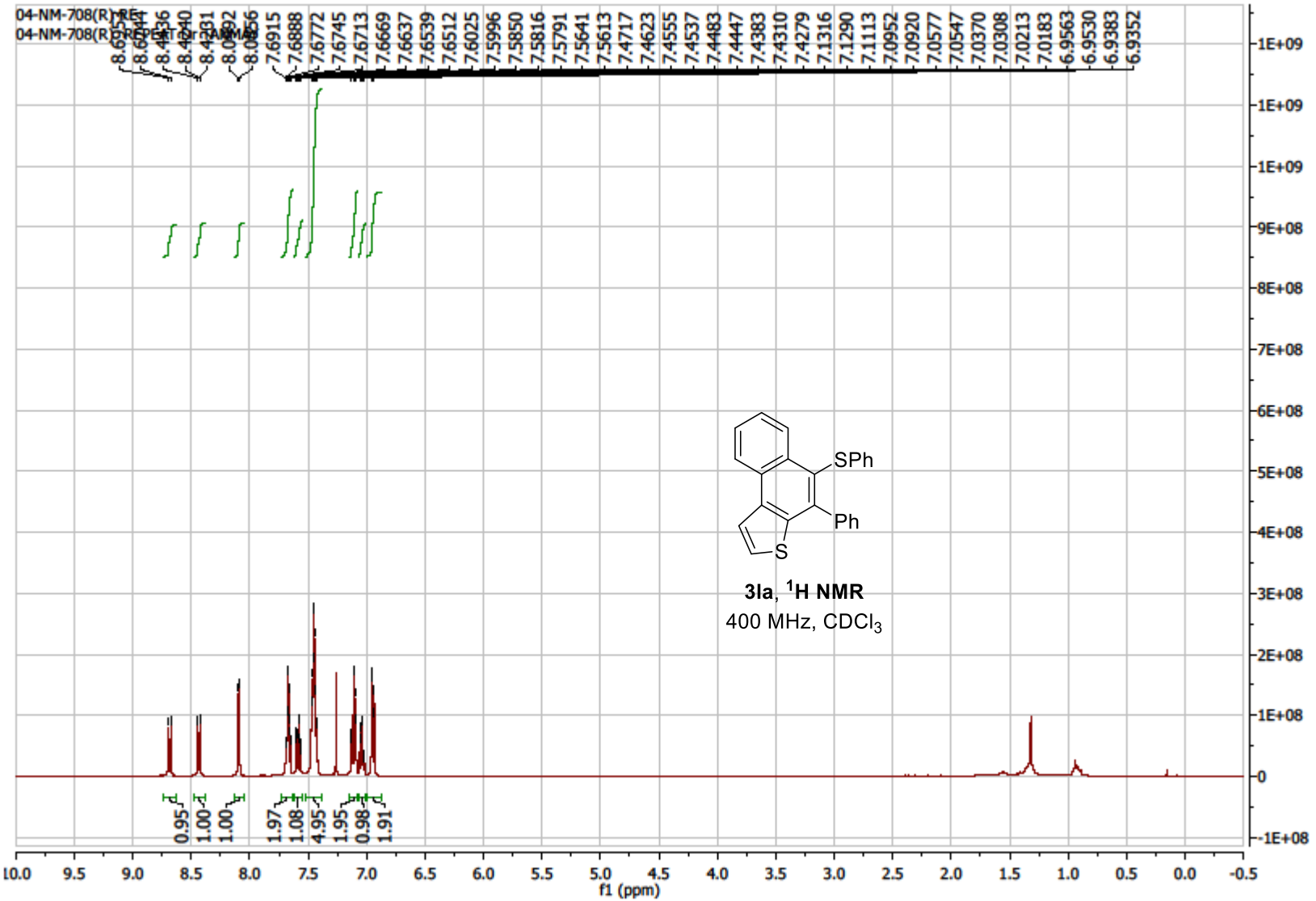

26-TC-NM-621-R-13C
TC
146.9644
141.6805
139.1125
137.3649
132.4392
132.1231
131.0872
130.8597
129.3512
128.8218
128.6117
128.0620
127.9915
127.5451
127.5236
127.2358
126.9485
126.6677
126.4913
124.6243
122.7266
122.5233
37.9109
24.3994
13.9636
SPh
nPr
3ia, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)


SPh
Me
3ja, 1H NMR
400 MHz, CDCl3
f1 (ppm)

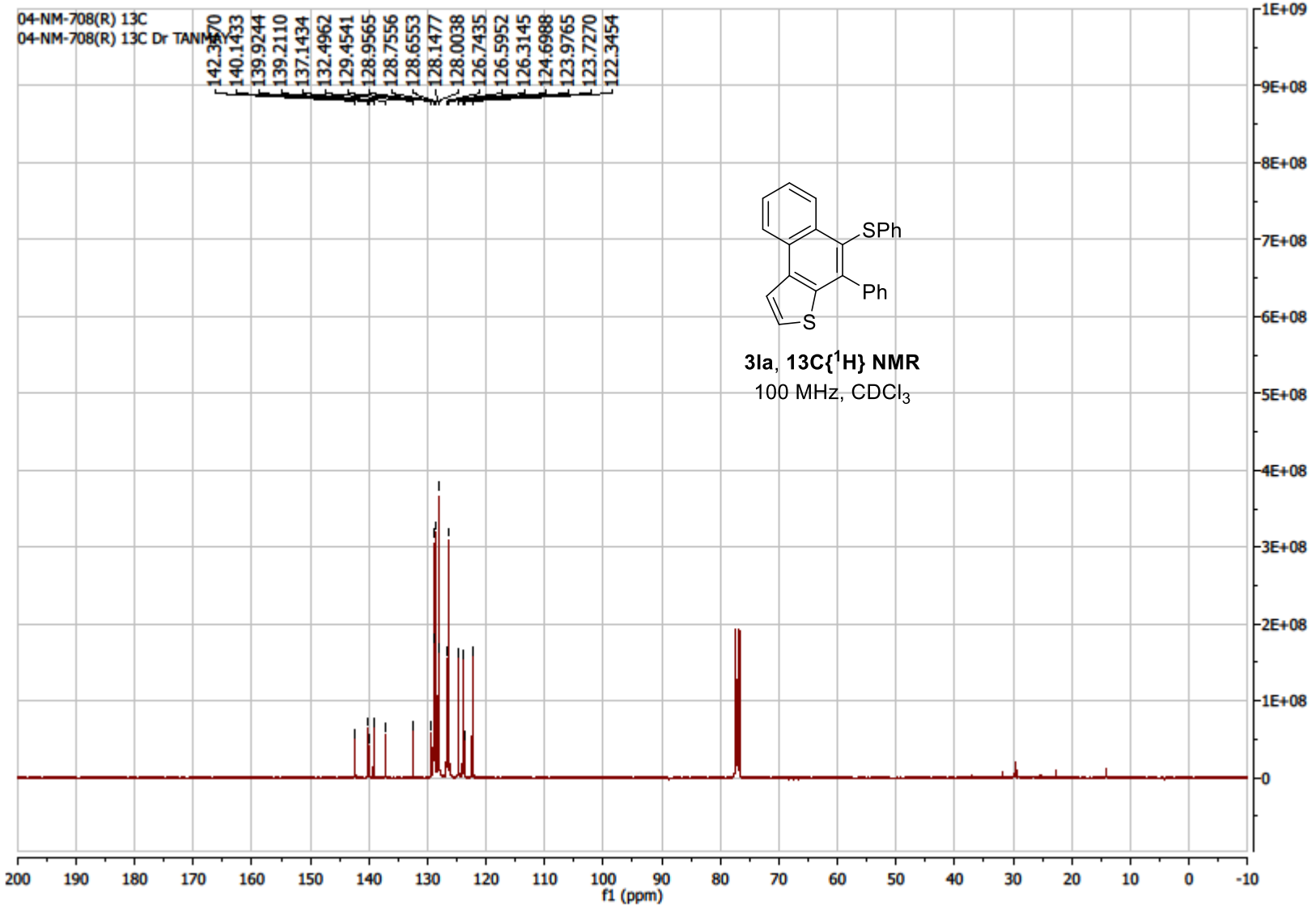

25-NM-658(R) 13C
25-NM-658(R)13C
146.9319
140.0511
139.1146
137.3917
132.2813
132.1460
131.0527
130.8287
130.2633
128.7637
128.5791
128.0676
128.0334
127.8069
127.5294
127.1548
126.9647
126.6558
126.5323
124.6486
122.7220
122.5148
21.4755
SPh
Me
3ja, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

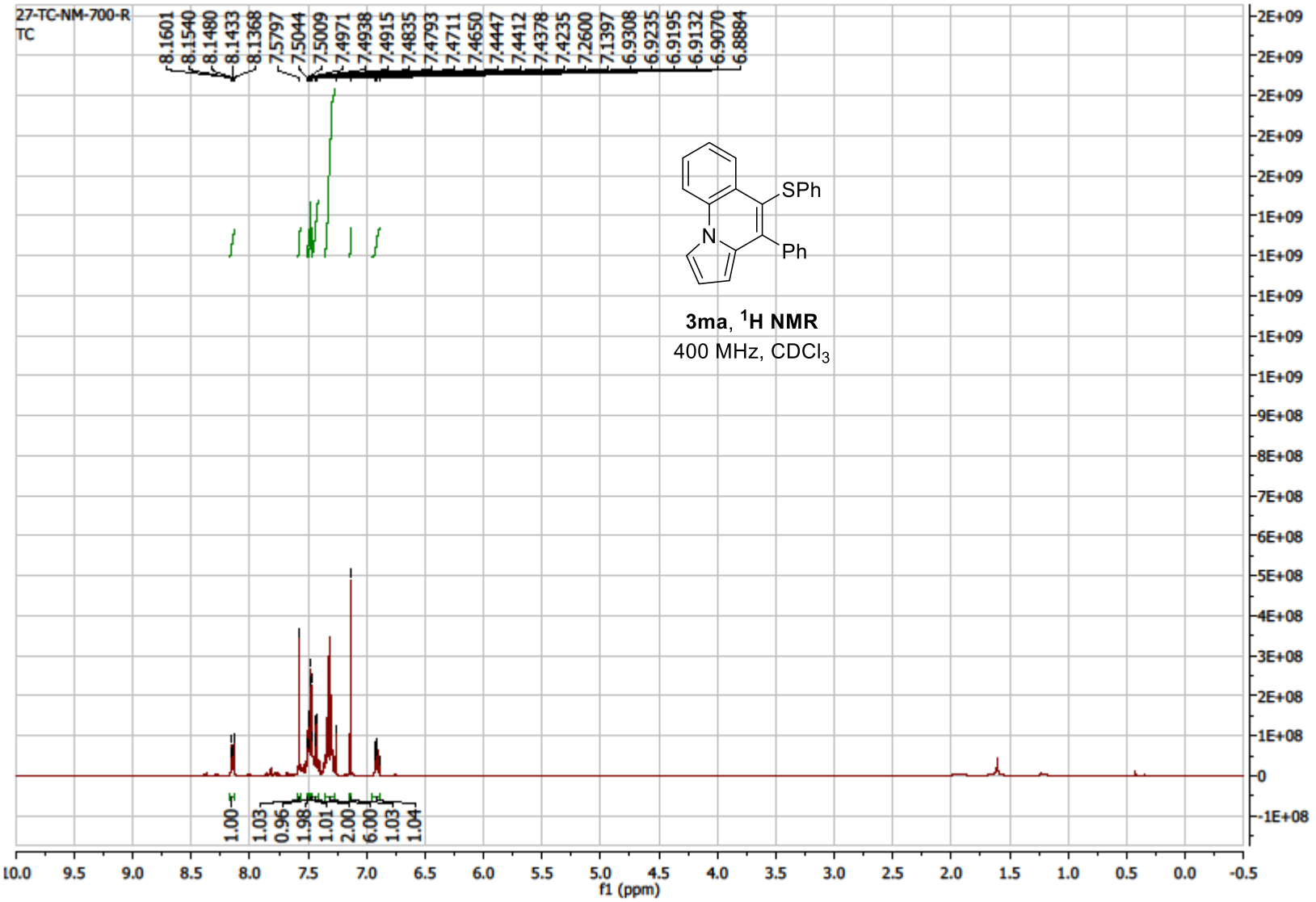

SPh
3ka, 1H NMR
400 MHz, CDCl3
f1 (ppm)


23-NM-719 13C
22-NM-719 13C Dr TANMAYEE
142.5558
140.8812
140.5137
138.7888
136.3902
130.0335
129.3680
128.9472
128.5518
128.3463
127.7899
127.1097
127.0038
125.5294
107.1352
22.6272
9.5440
8.6233
SPh
3ka, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

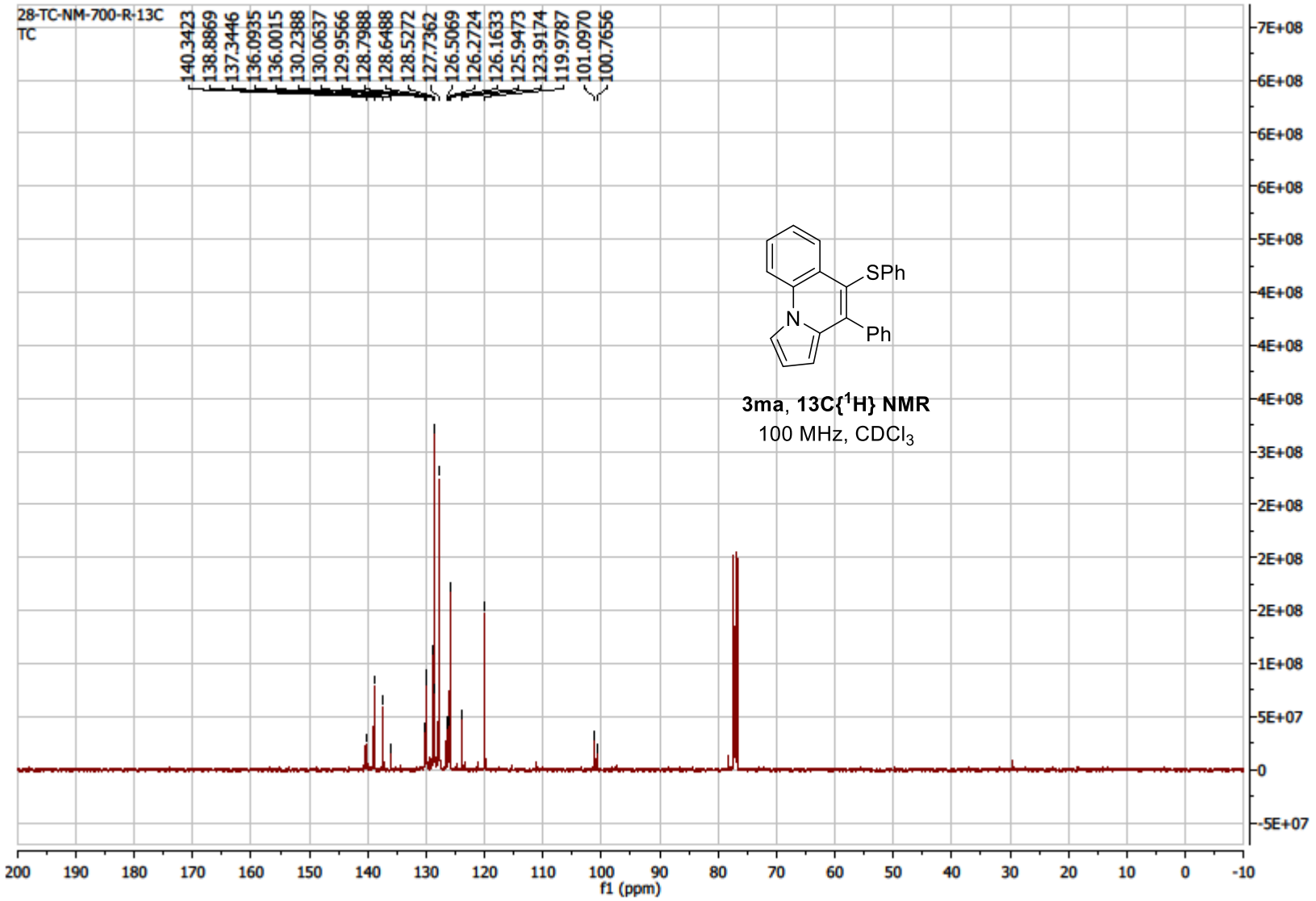


3la, **^{1}H NMR**
400 MHz, $CDCl_3$


04-NM-708(R) 13C
04-NM-708(R) 13C Dr TANMAY
142.3370
140.1433
139.9244
139.2110
137.1434
132.4962
129.4541
128.9565
128.7556
128.6553
128.1477
128.0038
126.7435
126.5952
126.3145
124.6988
123.9765
123.7270
122.3454
SPh
Ph
S
3la, 13C{1H} 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
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3ma, **^{1}H NMR**
400 MHz, $CDCl_3$


28-TC-NM-700-R-13C
TC
140.3423
138.8869
137.3446
136.0935
136.0015
130.2388
130.0637
129.9566
128.7988
128.6488
128.5272
127.7362
126.5069
126.2724
126.1633
125.9473
123.9174
119.9787
101.0970
100.7656
SPh
N
Ph
3ma, 13C{1H} NMR
100 MHz, CDCl3
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)