



Supporting Information

Peptide Functionalization Through the Generation of Selenocysteine Electrophile

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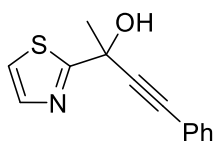
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Thin layer chromatography (TLC) was performed using MERCK Silica gel 60 F254 plates and visualized by UV (254 nm) fluorescence. ZEOCHEM silica gel (ZEOprep 60/35-70 microns – SI23501) was used for column chromatography. ^1H , ^{13}C , ^{77}Se , ^{125}Te NMR spectra were recorded on a Bruker Avance Neo spectrometer at 400, 101, 76, and 126 MHz correspondingly at 298 K in CD_3OD or CDCl_3 . Infrared (IR) spectra were recorded with a Prestige-21 FTIR spectrometer (Shimadzu, Kyoto, Japan). Single crystals of **3b** and **5b-R,S** were investigated on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 140.0(1) K during data collection. Using Olex2,^{1a} the structure was solved with the olex2.solve.^{1b} structure solution program using Charge Flipping and refined with the ShelXL² refinement package using Least Squares minimisation. Optical density was studied on a Tecan Infinite1000 microplate reader.

Propargylpyridines **1a**,³ **1b**,⁴ Boc-L-selenocystine **4**⁵, arene-alkynes **12a-c**,⁶ **12d**⁷ are known compounds which were prepared according to literature procedures.

2. Experimental section with HRMS spectra

4-Phenyl-2-(thiazol-2-yl)but-3-yn-2-ol (**1c**)



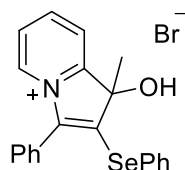
To the solution of phenylacetylene (2.73 g, 26.77 mmol) and 18-crown-6 (0.83 g, 3.15 mmol) in dry toluene freshly dried CsF (0.5 g, 3.15 mmol) and trimethylsilylacetylene (2.62 g, 26.77 mmol) were added. Then reaction mixture was stirred at 50 °C for 3 hours. After cooling to room temperature solution of 2-acetylthiazole (2 g, 15.75 mmol) in dry toluene was added and the mixture was stirred overnight. Toluene was then evaporated and to the crude residue methanol (100 mL) and an excess of K_2CO_3 were added. After stirring for 12 hours, solvent was evaporated and crude residue was

purified by column chromatography on silica gel (eluent: CH₂Cl₂/EtOAc 3:1) to yield the product as white solid (g, 44%). M.p. = 114-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 3.4 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.35 – 7.26 (m, 3H), 4.02 (d, *J* = 0.9 Hz, 1H), 2.05 (d, *J* = 0.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.1, 142.6, 132.0, 128.9, 128.4, 122.1, 120.0, 90.7, 85.2, 69.1, 31.9.

General method for the preparation of 3a,b

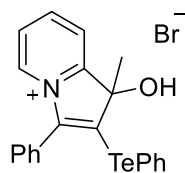
A vial charged with diphenyl diselenide **2a** or diphenyl ditelluride **2b** (1 mmol), copper(II) bromide (0.27 g, 1.2 mmol) and 25 ml of acetonitrile was stirred for 30 min. Then solution of 4-phenyl-2-(pyridin-2-yl)but-3-yn-2-ol (**1a**) in 10 ml of acetonitrile was added in one portion. Resulting mixture continued stirring for 30 min. Then 1 ml of water was added and volatiles were evaporated under reduced pressure. Crude product was purified by flash chromatography yielding **3a** or **3b** in 90% and 76%, correspondingly. It should be noted that this reaction could be performed in ethanol and dichloromethane as well.

1-Hydroxy-1-methyl-3-phenyl-2-(phenylselanyl)-1*H*-indolizin-4-ium bromide (**3a**)



Yellowish solid. ¹H NMR (400 MHz, CD₃OD) δ 8.57 (td, *J* = 7.8, 1.2 Hz, 1H), 8.40 (dt, *J* = 6.2, 1.1 Hz, 1H), 8.36 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.96 (ddd, *J* = 7.6, 6.2, 1.2 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.36 (m, 7H), 7.26 – 7.19 (m, 1H), 7.15 – 7.08 (m, 2H), 1.86 (s, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 161.9, 145.8, 142.8, 141.0, 136.3, 136.0, 132.2, 131.9, 130.6, 130.4, 129.9, 128.5, 126.3, 126.0, 123.9, 83.6, 25.1. ⁷⁷Se NMR (76 MHz, CD₃OD) δ 303.78. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₂₁H₁₈NOSe]⁺ 380.0548; found 380.0562.

1-Hydroxy-1-methyl-3-phenyl-2-(phenyltellanyl)-1*H*-indolizin-4-ium bromide (**3b**)

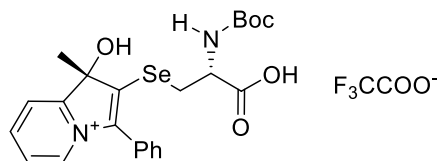


Reddish solid. ^1H NMR (400 MHz, CD_3OD) δ 8.53 (td, $J = 7.6, 1.2$ Hz, 1H), 8.41 – 8.34 (m, 2H), 7.92 (ddd, $J = 7.6, 6.2, 1.2$ Hz, 1H), 7.64 – 7.59 (m, 2H), 7.54 (tt, $J = 7.6, 1.4$ Hz, 1H), 7.30 – 7.24 (m, 1H), 7.12 – 7.04 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.3, 141.7, 131.9, 129.0, 128.7, 128.7, 128.5, 126.9, 125.9, 123.6, 122.3, 87.8 (d, $J_{(\text{Te-C})} = 21.2$ Hz), 70.2, 34.1. ^{125}Te NMR (126 MHz, CD_3OD) δ 502.3. HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{21}\text{H}_{18}\text{NOTe}]^+$ 430.0445; found 430.0457.

General method for the preparation of 5a-c

Compound **4** (0.5 mmol, 269 mg) and copper(II) bromide (1 mmol, 224 mg) were dissolved in acetonitrile and stirred for 30 minutes. Then propargyl *N*-heterocycle (**1a-c**) (1.2 mmol) in acetonitrile was added and the stirring was continued for 4-16 hours. After consumption of the initial compound volatiles were removed and crude product was purified by reverse phase chromatography [MeCN/water (1% AcOH)] giving a mixture of the corresponding diastereomers **5a-c**. Separation of diastereomers was performed on preparative HPLC Shimadzu prominence apparatus, equipped with XBridge® peptide BEH C18 OBD™ prep column, 130Å, 10 μm , 19 mm x 250 mm as eluents were used MeCN:H₂O (28:72 to 100:0%) at flow rate 4mL/min.

(*S*)-2-(((*R*)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selenanyl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indolizin-4-ium trifluoroacetate (**5a-S,R**)

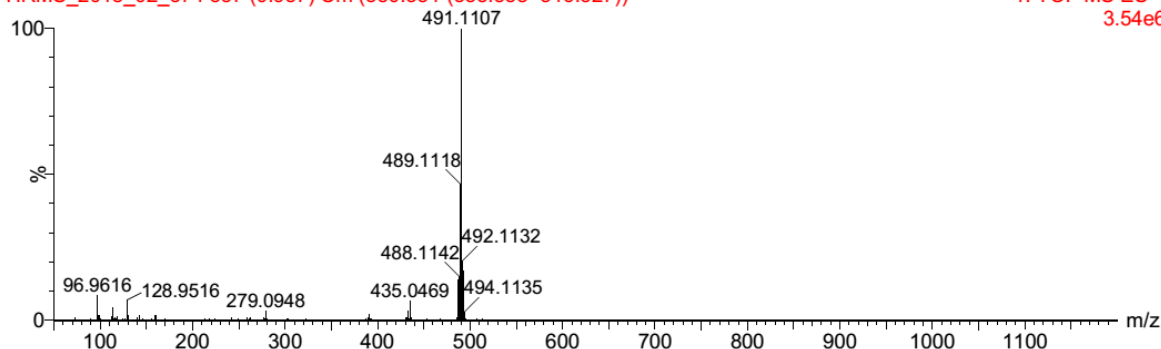


Foam (53 mg, 35%). ^1H NMR (400 MHz, CD_3OD) δ 8.55 (td, $J = 7.8, 1.0$ Hz, 1H), 8.50 (d, $J = 6.1$ Hz, 1H), 8.36 (d, $J = 7.8$ Hz, 1H), 7.95 (td, $J = 6.9, 6.3, 1.1$ Hz, 1H), 7.67 (m,

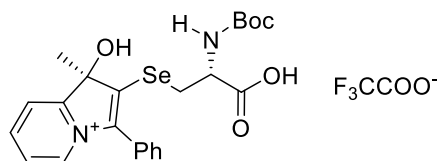
5H), 4.12 (t, $J = 5.2$ Hz, 1H), 3.39 (dd, $J = 12.0, 5.6$ Hz, 1H), 3.12 (dd, $J = 11.7, 5.9$ Hz, 1H), 1.83 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 176.4, 162.7, 140.9, 135.8, 132.6, 132.1, 130.9, 128.3, 126.7, 123.8, 84.2, 49.0, 30.4, 28.7, 25.4. HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_5\text{Se}]^+$ 491.1080; found 491.1107.

HRMS_2018_02_374 337 (0.957) Cm (330:354-(355:358+316:327))

1: TOF MS ES+
3.54e6



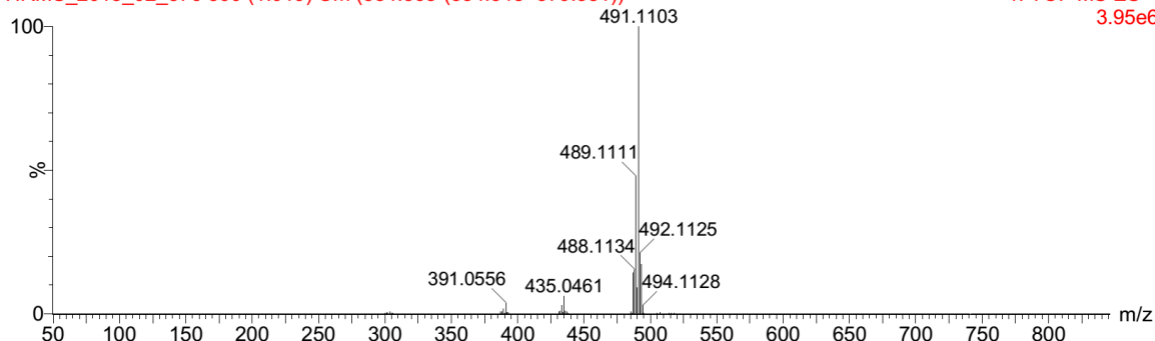
(*R*)-2-(((*R*)-2-((*tert*-butoxycarbonyl)amino)-2-carboxyethyl)selenyl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indolizin-4-ium trifluoroacetate (5a-*R,R*)



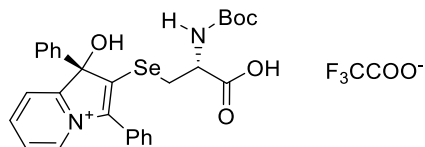
Foam (50 mg, 33%). ^1H NMR (400 MHz, CD_3OD) δ 8.54 (td, $J = 7.8, 1.2$ Hz, 1H), 8.49 – 8.43 (m, 1H), 8.37 – 8.30 (m, 1H), 7.94 (ddd, $J = 7.6, 6.2, 1.3$ Hz, 1H), 7.73 (s, 5H), 4.23 (t, $J = 4.2$ Hz, 1H), 3.93 (dd, $J = 12.7, 4.3$ Hz, 1H), 3.16 (dd, $J = 12.6, 4.6$ Hz, 1H), 1.84 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 175.4, 163.1, 145.3, 140.8, 140.8, 135.8, 132.5, 132.2, 130.7, 128.1, 126.8, 123.7, 84.6, 49.0, 48.8, 29.4, 28.7, 26.2. HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_5\text{Se}]^+$ 491.1080; found 491.1103.

HRMS_2018_02_376 360 (1.019) Cm (354:368-(334:348+379:381))

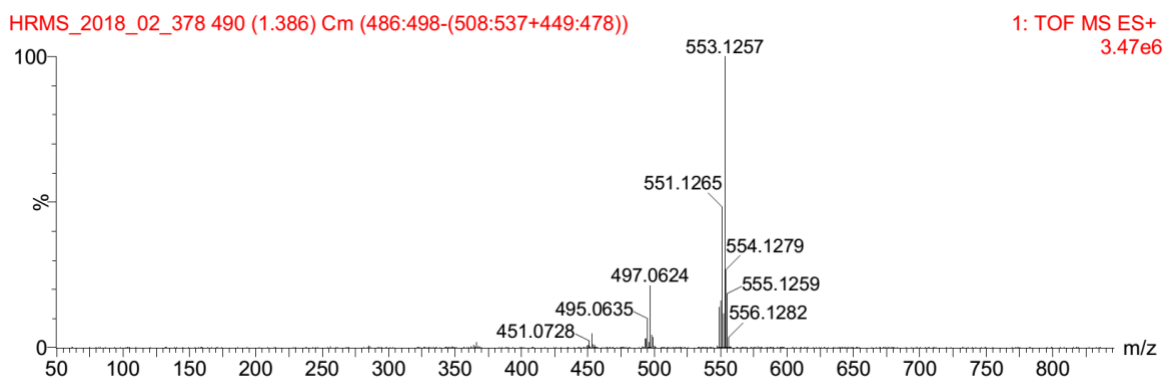
1: TOF MS ES+
3.95e6



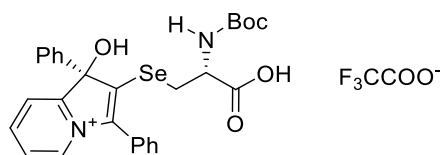
(S)-2-(((R)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selanyl)-1-hydroxy-1,3-diphenyl-1H-indolizin-4-ium trifluoroacetate (5b-S,R)



Foam. (63 mg, 38%). ¹H NMR (400 MHz, CD₃OD) δ 8.57 (d, *J* = 6.1 Hz, 1H), 8.44 (td, *J* = 7.8, 1.0 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.67 (m, 3H), 7.65 – 7.59 (m, 2H), 7.50 – 7.34 (m, 3H), 4.13 (s, 1H), 3.19 (s, 1H), 2.81 (d, *J* = 47.4 Hz, 1H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CD₃OD) δ 162.6, 145.6, 142.8, 140.7, 137.5, 136.0, 132.8, 132.0, 131.0, 130.5, 130.4, 128.4, 126.6, 126.4, 124.8, 87.4, 49.6, 30.0, 28.7. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₂₈H₂₉N₂O₅Se]⁺ 553.1236; found 553.1257.



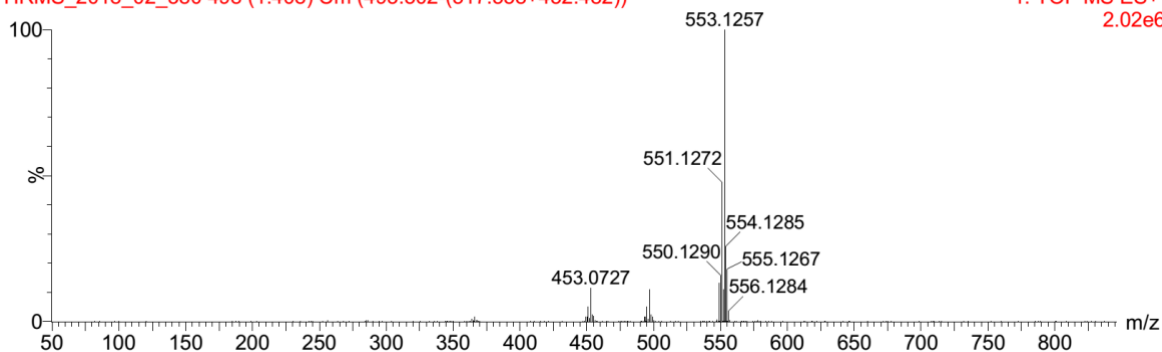
(R)-2-(((R)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selanyl)-1-hydroxy-1,3-diphenyl-1H-indolizin-4-ium trifluoroacetate (5b-R,R)



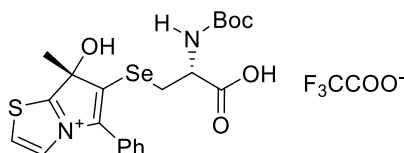
Foam (56 mg, 34%). ¹H NMR (400 MHz, CD₃OD) δ 8.54 (d, *J* = 6.1 Hz, 1H), 8.44 (t, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.93 (t, *J* = 6.6 Hz, 1H), 7.81 – 7.69 (m, 5H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.48 – 7.38 (m, 3H), 4.21 – 4.05 (m, 1H), 3.80 – 3.71 (m, 1H), 2.92 – 2.84 (m, 1H), 1.39 (s, 8H). ¹³C NMR (101 MHz, CD₃OD) δ 145.60, 141.97, 141.12, 138.12, 136.05, 132.68, 132.09, 130.92, 130.37, 128.33, 126.60, 126.35, 124.66, 87.94, 80.52, 28.68. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₂₈H₂₉N₂O₅Se]⁺ 553.1236; found 553.1257.

HRMS_2018_02_380 498 (1.408) Cm (493:502-(517:558+452:482))

1: TOF MS ES+
2.02e6

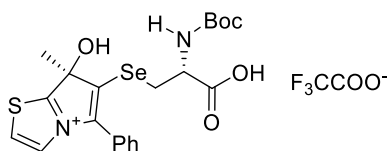


(S)-6-(((R)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selanyl)-7-hydroxy-7-methyl-5-phenyl-7H-pyrrolo[2,1-b]thiazol-4-ium trifluoroacetate (5c-R,S)



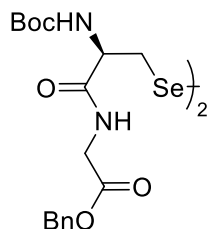
Foam (42 mg, 28%). Compound is not stable. ^1H NMR (400 MHz, CD_3OD) δ 8.34 (d, J = 3.6 Hz, 1H), 8.17 (d, J = 3.6 Hz, 1H), 7.75 (m, 2H), 7.63 (m, 3H), 4.16 (d, J = 6.8 Hz, 1H), 3.42 (dd, J = 12.3, 5.2 Hz, 1H), 3.05 (dd, J = 12.3, 7.0 Hz, 1H), 1.90 (s, 3H), 1.41 (s, 10H). HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_5\text{SSe}]^+$ 497.0644; found 497.0648.

(R)-6-(((R)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selanyl)-7-hydroxy-7-methyl-5-phenyl-7H-pyrrolo[2,1-b]thiazol-4-ium trifluoroacetate (5c-R,R)

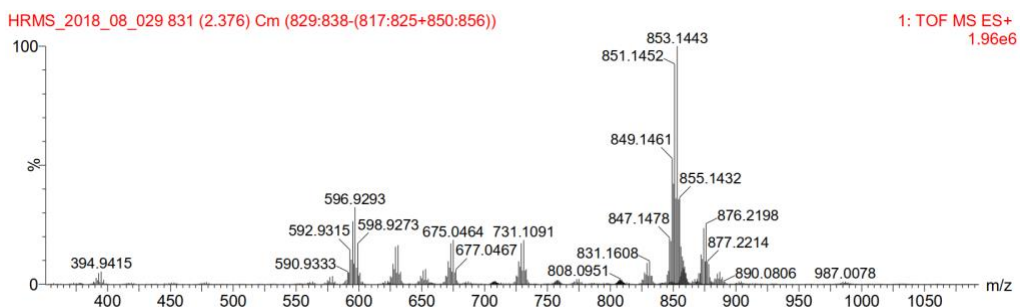


Foam (39 mg, 25%). Compound is not stable. ^1H NMR (400 MHz, CD_3OD) δ 8.31 (d, J = 3.7 Hz, 1H), 8.14 (d, J = 3.7 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.63 – 7.61 (m, 3H), 4.27 (m, 2H), 3.77 (dd, J = 12.8, 4.7 Hz, 1H), 3.15 (dd, J = 12.8, 4.7 Hz, 1H), 1.91 (s, 3H), 1.41 (s, 9H). HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_5\text{SSe}]^+$ 497.0644; found 497.0650.

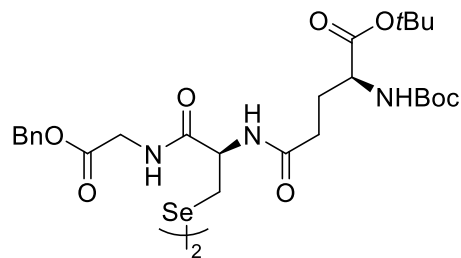
Benzyl (6*R*,11*R*)-6-((2-(benzyloxy)-2-oxoethyl)carbamoyl)-11-((*tert*-butoxycarbonyl)amino)-2,2-dimethyl-4,12-dioxo-3-oxa-8,9-diselena-5,13-diazapentadecan-15-oate (6)



To a solution of benzyl glycinate (3.17 g, 15.72 mmol, 5 equiv) in DMF (30 ml) NMM (2.07 ml, 18.87 mmol, 6 equiv) was added at 0 °C and the mixture was stirred for 5 minutes. Then HOBt (0.48 g, 3.14 mmol, 1 equiv) was added to the reaction mixture followed by the addition of **4** (1.68 g, 3.14 mmol, 1 equiv) in DMF (8+2 ml) and EDC (3.62 g, 18.87 mmol, 6 equiv). The reaction mixture was stirred at 0 °C for 10 minutes and then at rt for 2 h then it was evaporated and the residue was purified by reverse phase chromatography (MeCN/H₂O) to yield **6** as yellow solid (2.1 g, 80%). ¹H NMR (400 MHz, CD₃OD) δ 7.40-7.27 (m, 10H), 5.17 (s, 4H), 4.54-4.46 (m, 2H), 4.08-3.93 (m, 4H), 3.40-3.33 (m, 1H), 3.16-3.07 (m, 2H), 1.43 (s, 18H). ¹³C NMR (101 MHz, CD₃OD) δ 173.9, 170.8, 157.7, 137.1, 129.6, 129.3, 80.9, 67.9, 56.6, 42.2, 28.7. ⁷⁷Se NMR (76 MHz, CD₃OD) δ 310.9. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ calcd for [C₃₄H₄₇N₄O₁₀Se₂]⁺ 831.1623; found 831.1608.

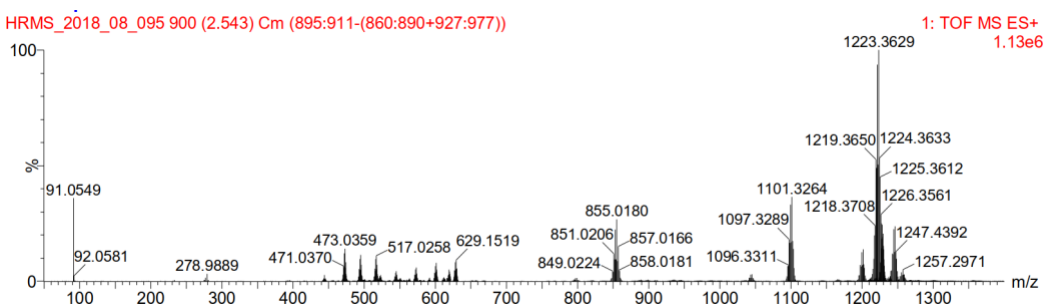


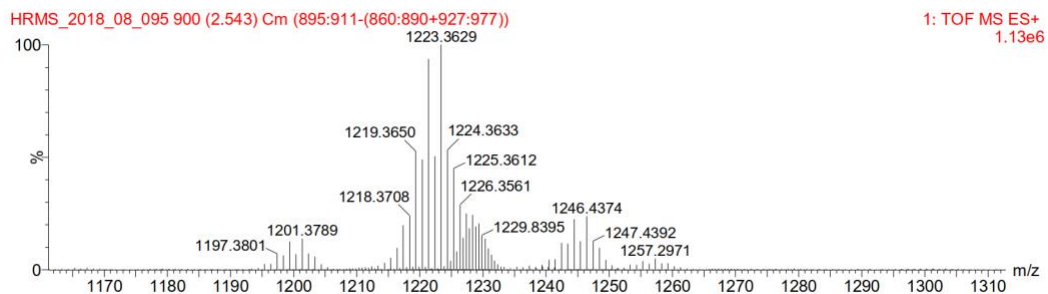
Dibenzyl 11,11'-(diselenediylbis(methylene))(6*S*,6'*S*,11*R*,11'*R*)-bis(6-((*tert*-butoxycarbonyl)-2,2-dimethyl-4,9,12-trioxo-3-oxa-5,10,13-triazapentadecan-15-oate) (7)



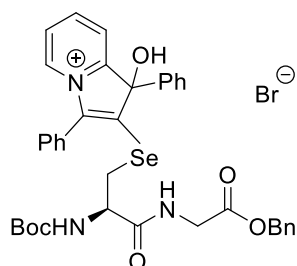
To a solution of **6** (1 g, 1.21 mmol, 1 equiv) in CH₂Cl₂ (18 ml) TFA (12 ml) was added at 0 °C and the reaction mixture was stirred for 2 h at rt. Then it was evaporated and dissolved in DMF (30 ml) and NMM (0.80 ml, 7.24 mmol, 6 equiv) was added at 0 °C and the mixture was stirred for 5 minutes. Then HOBt (0.37 g, 2.41 mmol, 1 equiv), a solution of compound (Boc)Glu-OtBu (1.55 g, 4.83 mmol, 4 equiv) in DMF (8+2 ml) and EDC (1.39 g, 7.24 mmol, 6 equiv) was added and the reaction mixture was stirred at 0 °C for 10 minutes and then at rt for 2 hours. The reaction mixture was evaporated and the residue was purified by reverse phase chromatography (MeCN/H₂O) to give the title compound as yellow solid (1.2 g, 80%). ¹H NMR (400 MHz, CD₃OD) δ 7.40-7.26 (m, 10H), 5.16 (s, 4H), 4.94-4.86 (m, 2H), 4.09-3.94 (m, 6H), 3.38-3.32 (m, 1H), 3.19-09 (m, 2H), 2.36 (t, *J* = 7.6 Hz, 4H), 2.17-2.01 (m, 3H), 1.95-1.79 (m, 3H), 1.46 (s, 18H), 1.43 (s, 18H). ¹³C NMR (101 MHz, CD₃OD) δ 174.8, 173.3, 173.2, 170.9, 158.1, 137.1, 129.6, 129.4, 82.8, 80.5, 68.0, 55.4, 55.1, 42.3, 33.1, 33.0, 28.8, 28.5, 28.3. ⁷⁷Se NMR (76 MHz, CD₃OD) δ 312.6. HRMS (ESI/Q-TOF) *m/z*: [M+H]⁺ calcd for [C₅₂H₇₆N₆O₁₆Se₂]⁺ 1201.3724; found 1201.3789.

HRMS_2018_08_095 900 (2.543) Cm (895:911-(860:890+927:977))





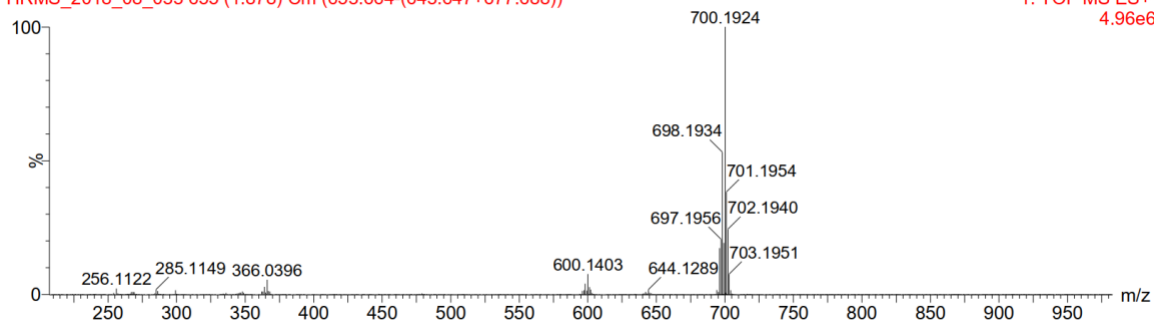
2-(((*R*)-3-((2-(benzyloxy)-2-oxoethyl)amino)-2-((*tert*-butoxycarbonyl)amino)-3-oxopropyl)selanyl)-1-hydroxy-1,3-diphenyl-1*H*-indolizin-4-ium bromide (8a**)**



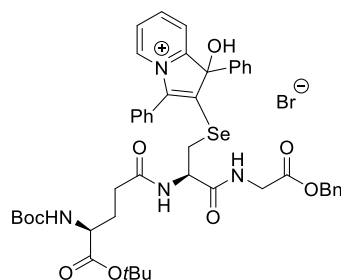
To a solution of **6** (100 mg, 0.12 mmol, 1 equiv) in CH₂Cl₂ (5 ml) was added CuBr₂ (67 mg, 0.3 mmol, 2.5 equiv) at rt and the mixture was stirred for 30 min. Then a solution of **1b** (103 mg, 0.36 mmol, 3 equiv) in CH₂Cl₂ (3+1 ml) was added. Reaction mixture was stirred for 16 h, then it was evaporated and purified by reverse phase chromatography (MeCN/H₂O+AcOH) to give **8a** as yellow oil (80 mg, 85%). ¹H NMR (400 MHz, CD₃OD) δ 8.61-8.54 (m, 1H), 8.45 (t, *J* = 7.8 Hz, 1H), 8.02 – 7.93 (m, 2H), 7.83 – 7.73 (m, 2H), 7.74 – 7.63 (m, 5H), 7.51 – 7.39 (m, 3H), 7.38 – 7.28 (m, 5H), 5.15-5.11 (m, 2H), 4.22-4.19 (m, 0.5H). ¹³C NMR (101 MHz, CD₃OD) δ 173.2, 173.0, 170.7, 161.9, 157.4, 145.8, 145.7, 142.1, 141.8, 140.2, 140.1, 137.3, 137.1, 136.1, 132.9, 131.8, 131.1, 131.1, 130.7, 130.6, 129.6, 129.4, 129.3, 129.2, 128.7, 126.4, 126.4, 124.8, 124.7, 87.5, 87.4, 81.0, 67.8, 55.9, 55.6, 42.1, 42.1, 40.1, 28.7, 27.2, 27.1. ⁷⁷Se NMR (76 MHz, CD₃OD) δ 215.0, 206.2. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₃₇H₃₇N₃O₆Se]⁺ 700.1920; found 700.1924.

HRMS_2018_08_033 655 (1.878) Cm (653:664-(643:647+677:688))

1: TOF MS ES+
4.96e6

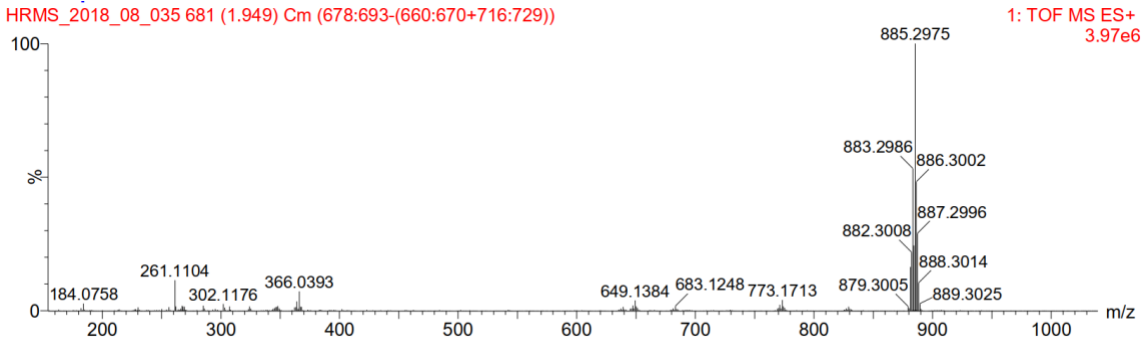


2-(((*R*)-3-((2-(benzyloxy)-2-oxoethyl)amino)-2-(((*S*)-5-(*tert*-butoxy)-4-(((*tert*-butoxycarbonyl)amino)-5-oxopentanamido)-3-oxopropyl)selenyl)-1-hydroxy-1,3-diphenyl-1*H*-indolizin-4-ium bromide (8b**)**

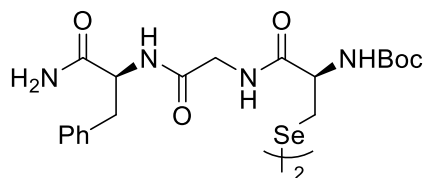


To a solution of **7** (100 mg, 0.083 mmol, 1 equiv) in CH₂Cl₂ (5 ml) was added CuBr₂ (47 mg, 0.208 mmol, 2.5 equiv) at rt and the mixture was stirred for 30 min. Then a solution of **1b** (71 mg, 0.25 mmol, 3 eq.) in CH₂Cl₂ (3+1 ml) was added. Reaction mixture was stirred for 16 h and then it was evaporated and purified by reverse phase chromatography (MeCN/H₂O+AcOH) to give product as yellow oil (70 mg, 88%). ¹H NMR (400 MHz, CD₃OD) δ 8.57 (t, *J* = 5.0 Hz, 1H), 8.45 (t, *J* = 7.7 Hz, 1H), 8.04 – 7.92 (m, 2H), 7.79 – 7.69 (m, 4H), 7.68-7.62 (m, 2H), 7.50-7.41 (m, 3H), 7.38 – 7.27 (m, 5H), 5.14 and 5.13 (2 s, 2H), 4.44 (dd, *J* = 8.5, 5.8 Hz, 0.5H), 4.34 (t, *J* = 7.1 Hz, 0.5H), 4.00 – 3.86 (m, 3H), 3.52 – 3.42 (m, 1H), 3.09-3.01 (m, 1H), 2.76 – 2.65 (m, 1H), 2.32-2.19 (m, 2H), 2.07 – 1.97 (m, 1H), 1.87-1.75 (m, 2H), 1.47 and 1.43 (2 s, 18H). ¹³C NMR (101 MHz, CD₃OD) δ 174.8, 173.2, 172.7, 172.52, 170.8, 162.1, 158.1, 145.8, 137.5, 137.14, 136.2, 132.90, 131.8, 131.1, 130.7, 130.6, 129.6, 129.3, 129.2, 128.6, 128.0, 126.4, 124.8, 87.6, 87.4, 82.8, 80.5, 67.9, 55.4, 54.7, 54.3, 42.2, 32.9, 28.8, 28.3, 26.5. ⁷⁷Se NMR (76 MHz, CD₃OD) δ 213.9, 207.2. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₄₆H₅₂N₄O₉Se]⁺ 885.2972; found 885.2972.

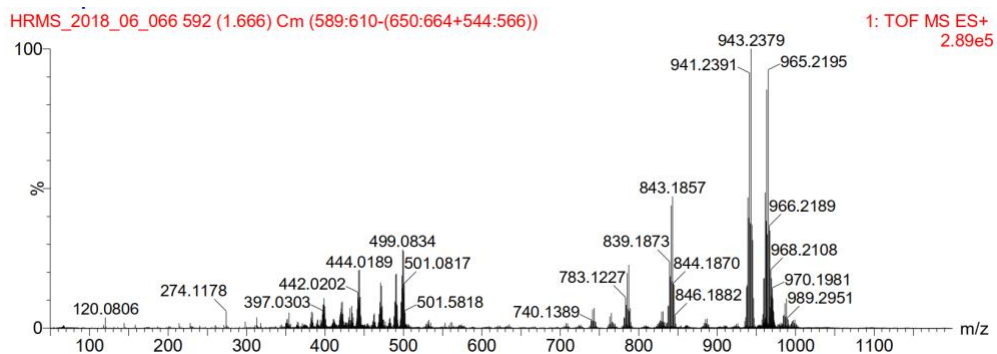
HRMS_2018_08_035 681 (1.949) Cm (678:693-(660:670+716:729))



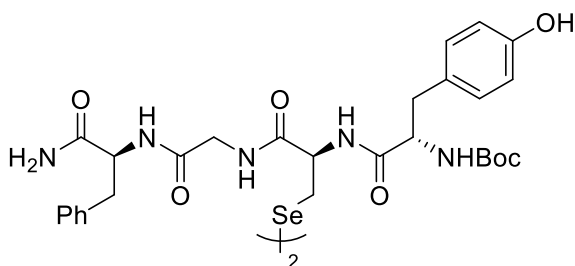
Di-*tert*-butyl ((2*S*,8*R*,13*R*,19*S*)-1,20-diamino-2,19-dibenzyl-1,4,7,14,17,20-hexaoxo-10,11-diselena-3,6,15,18-tetrazaicosane-8,13-diyl)dicarbamate (9)



To a solution of (*S*)-2-(2-aminoacetamido)-3-phenylpropanamide (245 mg, 0.730 mmol, 3 equiv) in DMF (5 ml) at 0 °C was added NMM (0.11 ml, 0.973 mmol, 4 equiv) and the mixture was stirred for 5 minutes. Then to the reaction mixture was added HOBt (37 mg, 0.243 mmol, 1 equiv), a solution of compound **4** (130 mg, 0.243 mmol, 1 equiv) in DMF (3+1 ml) and EDC (187 mg, 0.973 mmol, 4 equiv). The reaction mixture was stirred at 0 °C for 10 minutes and at rt for 3 hours, then it was evaporated and the residue was purified by reverse phase chromatography (MeCN/H₂O) to give the product as light yellow solid (101 mg, 44%). ¹H NMR (400 MHz, CD₃OD) δ 7.30 – 7.16 (m, 10H), 4.65 – 4.57 (m, 2H), 4.42 – 4.35 (m, 2H), 3.88 (d, *J* = 16.7 Hz, 2H), 3.74 (d, *J* = 16.7 Hz, 2H), 3.38 (dd, *J* = 12.7, 5.3, 2H), 3.23 – 3.08 (m, 4H), 2.92 (dd, *J* = 13.9, 9.1 Hz, 2H), 1.44 (s, 18H). ¹³C NMR (101MHz, CD₃OD) δ 175.9, 173.9, 171.2, 157.8, 138.3, 129.5, 127.7, 81.0, 56.8, 55.9, 43.7, 38.7, 32.7, 28.8. HRMS (ESI/Q-TOF) *m/z*: [M+H]⁺ calcd for [C₃₈H₅₅N₈O₁₀Se₂]⁺ 943.2372; found 943.2379.

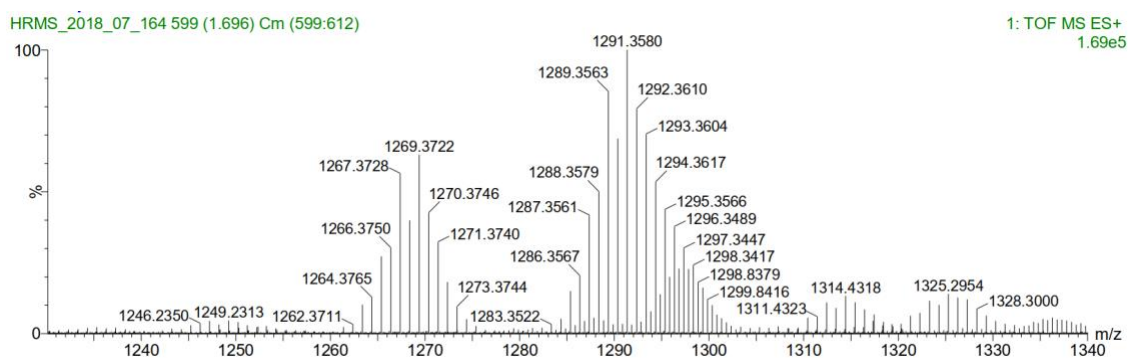
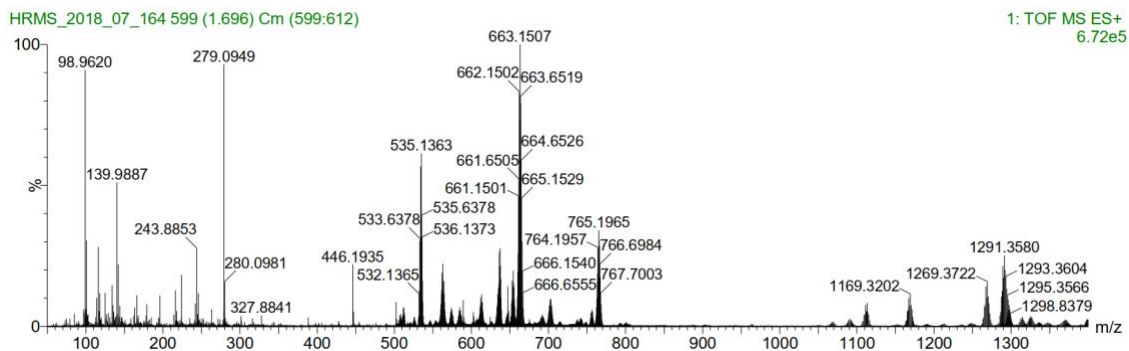


***Tert*-butyl ((6*R*,9*R*,14*R*,17*R*)-9,14-bis((2-(((*S*)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)carbamoyl)-6-(4-hydroxybenzyl)-18-(4-hydroxyphenyl)-2,2-dimethyl-4,7,16-trioxo-3-oxa-11,12-diselena-5,8,15-triazaoctadecan-17-yl)carbamate (10)**

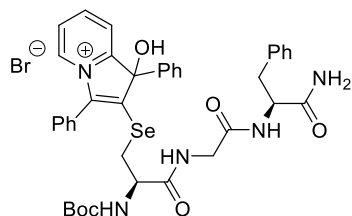


To a solution of compound **9** (270 mg, 0.287 mmol, 1 equiv) in CH₂Cl₂ (5 ml) was added TFA (2 ml) at 0 °C and reaction mixture was stirred for 2 hours at room temperature, then it was evaporated, dissolved in DMF (5 ml) and to this was added NMM (0.19 ml, 1.72 mmol, 6 equiv) at 0 °C and the mixture was stirred for 5 minutes. Then HOBT was added (88 mg, 0.574 mmol, 2 equiv) and a solution of Boc-L-tyrosine (323 mg, 1.15 mmol, 4 equiv) in DMF (3+1 ml) was added. Then EDC (330 mg, 1.72 mmol, 6 equiv) was added and the reaction mixture was stirred at 0 °C for 5 minutes and then at rt for 3 hours. The reaction mixture was evaporated and the residue was purified by reverse phase chromatography (MeCN/H₂O) to give product as white solid (185 mg, 51%). ¹H NMR (400 MHz, CD₃OD) δ 7.30 – 7.11 (m, 10H), 7.04 (d, *J* = 8.6 Hz, 4H), 6.69 (d, *J* = 8.5 Hz, 4H), 4.69 – 4.57 (m, 2H), 4.31 – 4.23 (m, 2H), 3.87 (d, *J* = 16.7 Hz, 2H), 3.74 (d, *J* = 16.7 Hz, 2H), 3.41-3.34 (m, 2H), 3.24 – 3.11 (m, 4H), 3.03-2.92 (m, 4H), 2.84-2.75 (m, 2H), 1.36 (s, 9H). ¹³C NMR spectra was not recorded due to lack of solubility.

HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $[C_{56}H_{73}N_{10}O_{14}Se_2]^+$ 1269.3638; found 1269.3722.

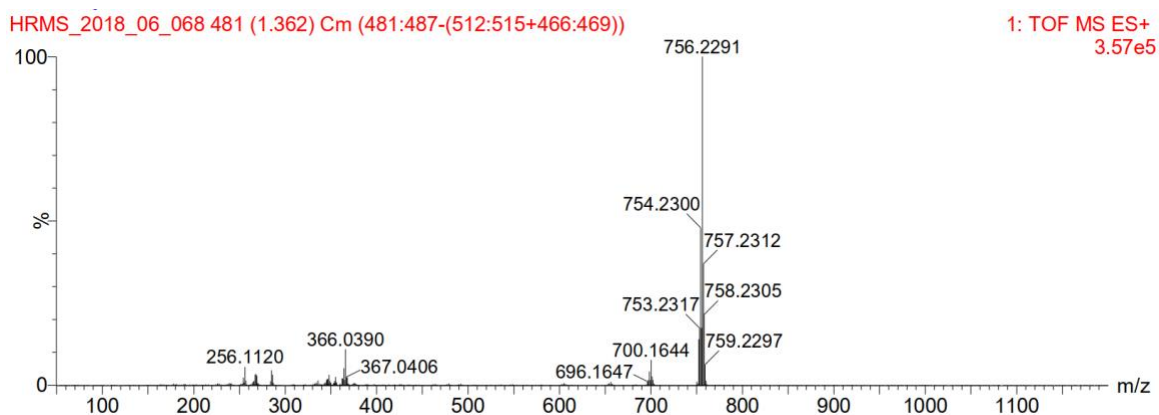


2-(((R)-3-((2-(((S)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)amino)-2-((tert-butoxycarbonyl)amino)-3-oxopropyl)selanyl)-1-hydroxy-1,3-diphenyl-1H-indolizin-4-ium bromide (11a)

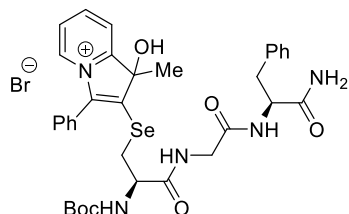


To a solution of **9** (100 mg, 0.11 mmol, 1 equiv) in CH_2Cl_2 (3 ml) and MeOH (1 ml) was added $CuBr_2$ (59 mg, 0.27 mmol, 2.5 equiv) at rt and the mixture was stirred for 30 min. Then a solution of **1b** (91 mg, 0.32 mmol, 3 equiv) in CH_2Cl_2 (3+1 ml) was added. Reaction mixture was stirred for 16 h, then it was evaporated and the product was purified by reverse phase chromatography (MeCN/ H_2O) to give product in 98% yield. 1H NMR (400 MHz, CD_3OD) δ 8.57 (t, $J = 6.5$ Hz, 1H), 8.46 (t, $J = 7.8$ Hz, 1H), 8.03-7.94 (m, 2H), 7.79-7.64 (m, 7H), 7.49-7.40 (m, 3H), 7.28-7.15 (m, 5H), 4.56-4.45 (m, 1H),

4.12 (t, $J = 7$ Hz, 0.5H), 4.03 (t, $J = 6.8$ Hz, 0.5H), 3.86-3.75 (m, 1H), 3.62 (d, $J = 16.1$ Hz, 1H), 3.40 (dd, $J = 12.6, 5.9$ Hz, 0.5), 3.22-3.11 (m, 1H), 3.01 (dd, $J = 12.4, 6.1$ Hz, 0.5H), 2.88 (ddd, $J = 13.5, 9.2, 3.6$ Hz, 1H), 2.70 (dd, $J = 12.4, 8.2$ Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 175.88, 173.11, 172.93, 171.14, 171.03, 162.11, 162.03, 157.50, 145.73, 142.19, 142.01, 140.19, 138.52, 137.36, 137.26, 136.14, 132.89, 131.82, 131.11, 130.70, 130.56, 130.24, 129.47, 128.68, 127.74, 126.43, 126.38, 124.76, 87.51, 81.18, 55.98, 55.74, 43.51, 38.70, 38.62, 28.72, 27.00, 26.87. ^{77}Se NMR (76 MHz, CDCl_3) δ 212.3, 206.1. HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{39}\text{H}_{41}\text{N}_5\text{O}_6\text{Se}]^+$ 756.2295; found 756.2291.

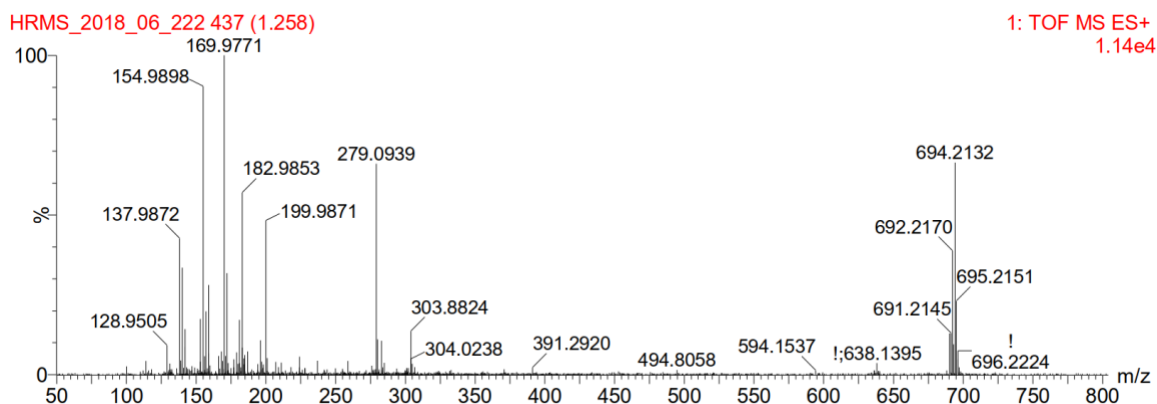


2-(((*R*)-3-(((*S*)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)amino)-2-((*tert*-butoxycarbonyl)amino)-3-oxopropyl)selanyl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indolizin-4-ium bromide (11b)

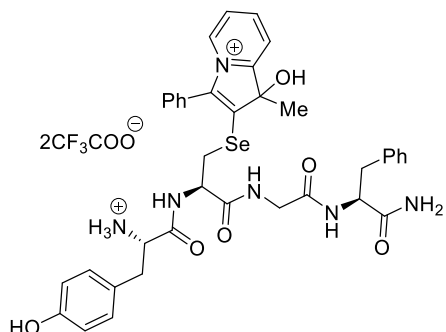


To a solution of compound **9** (100 mg, 0.11 mmol, 1 equiv) in CH_2Cl_2 (4 ml) and MeOH (1 ml) was added CuBr_2 (59 mg, 0.27 mmol, 2.5 equiv) at rt and the mixture was stirred for 30 min. Then a solution of alkyne (71 mg, 0.32 mmol, 3 equiv) in CH_2Cl_2 (2+1 ml) was added. Reaction mixture was stirred for 16 h, then it was evaporated and the product was purified by reverse phase chromatography ($\text{MeCN}/\text{H}_2\text{O}$) to give product as yellow oil in 98% yield. ^1H NMR (400 MHz, CD_3OD): 8.58 (t, $J = 7.7$ Hz, 1H), 8.50 (t, $J =$

7.0 Hz, 1H), 8.41-8.35 (m, 1H), 7.98 (t, $J = 7$ Hz, 1H), 7.70-7.62 (m, 5H), 7.29-7.16 (m, 5H), 4.53 (dd, $J = 9.4, 5$ Hz, 0.5H), 4.45 (dd, $J = 9.3, 5$ Hz, 0.5H), 4.34 (t, $J = 6.6$ Hz, 0.5H), 4.20 (dd, $J = 9.0, 5.3$ Hz, 0.5H), 3.89-3.78 (m, 1H), 3.74-3.63 (m, 1H), 3.55 (dd, $J = 12.6, 5.2$ Hz, 0.5), 3.42-3.34 (m, 0.5H), 3.26 (dd, $J = 12.5, 5.9$ Hz, 0.5H), 3.17 (ddd, $J = 14.0, 11.1, 5.0$ Hz, 1H), 2.99-2.84 (m, 1.5H), 1.89 un 1.88 (2 signals, s, 3H), 1.42 and 1.41 (2 signals, s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 175.9, 175.9, 173.4, 173.1, 171.2, 171.1, 162.2, 157.7, 145.7, 141.2, 140.8, 140.1, 138.6, 135.9, 132.7, 131.9, 130.9, 130.2, 129.5, 128.5, 127.7, 126.5, 126.5, 123.9, 84.3, 81.3, 56.3, 56.0, 43.5, 38.7, 38.6, 28.7, 27.7, 25.4. ^{77}Se NMR (76 MHz, CDCl_3) δ 184.1, 177.8. HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ calcd for $[\text{C}_{34}\text{H}_{39}\text{N}_5\text{O}_6\text{Se}]^+$ 694.2138; found 694.2132.

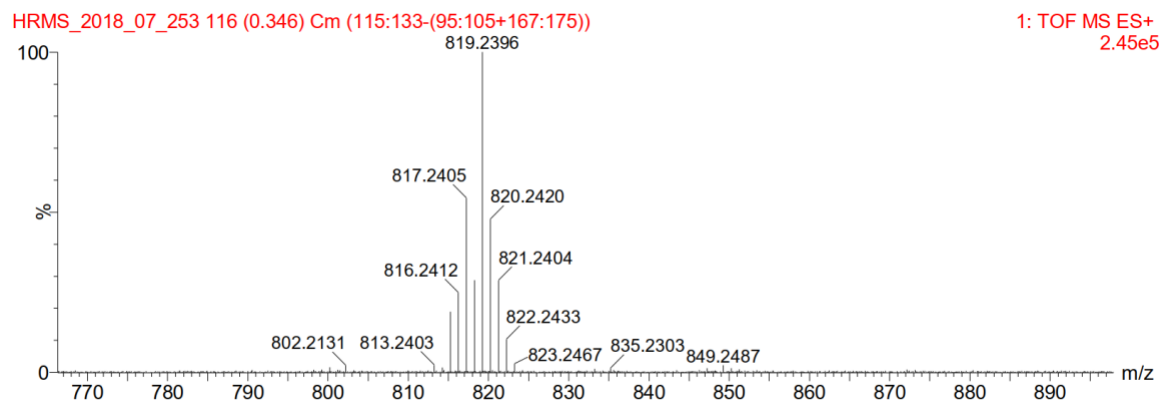
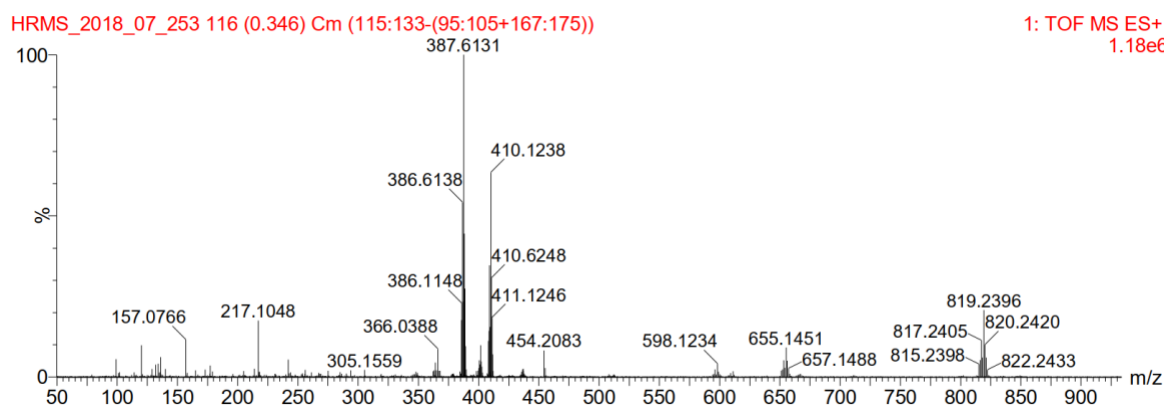


2-(((*R*)-3-((2-(((*S*)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)amino)-2-(((*S*)-2-amino-3-(4-hydroxyphenyl)propanamido)-3-oxopropyl)selanyl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indolizin-4-ium trifluoroacetate (11c)



To a solution of compound **10** (84 mg, 0.07 mmol, 1 equiv) in CH_2Cl_2 (10 ml) and MeOH (4 ml) was added CuBr_2 (37 mg, 0.17 mmol, 2.5 equiv) at rt and the mixture was stirred for 30 min. Then a solution of alkyne (57 mg, 0.20 mmol, 3 equiv) in CH_2Cl_2 (3+1 ml)

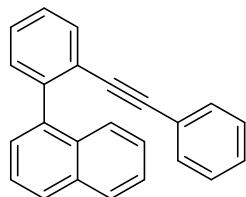
was added. Reaction mixture was stirred for 16 h and then it was evaporated. The product was dissolved in CH₂Cl₂ (3 ml) and TFA (3 ml) was added at 0 °C. The reaction mixture was stirred for 2 hours, then it was evaporated and purified by reverse phase chromatography (MeCN/H₂O+HCl) to give product as yellow oil (50 mg, 81%). ¹H NMR (400 MHz, CD₃OD) δ 8.56 (t, *J* = 6.4 Hz, 1H), 8.45 (t, *J* = 7.8 Hz, 1H), 8.04 – 7.93 (m, 2H), 7.81 – 7.74 (m, 2H), 7.72-7.63 (m, 6H), 7.51-7.40 (m, 3H), 7.28 – 7.21 (m, 5H), 7.21 – 7.15 (m, 1H), 7.13 – 7.07 (m, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 4.55 (dd, *J* = 9.4, 5.3 Hz, 0.5H), 4.49 (dd, *J* = 9.4, 5.2 Hz, 0.5H), 4.23 (t, *J* = 7.0 Hz, 0.5H), 4.13 – 4.06 (m, 1.5H), 3.95-3.83 (m, 1H), 3.63 – 3.53 (m, 1H), 3.22 – 3.07 (m, 3H), 2.99 – 2.79 (m, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 176.0, 171.4, 171.0, 170.4, 162.0, 158.3, 145.7, 141.9, 140.2, 138.4, 137.3, 136.1, 132.9, 131.8, 131.7, 131.2, 130.7, 130.6, 130.4, 129.5, 128.6, 127.7, 126.5, 126.4, 125.8, 124.8, 116.9, 87.5, 55.9, 55.5, 43.4, 39.0, 37.7, 25.4. ⁷⁷Se NMR (76 MHz, CDCl₃) δ 216.2, 211.0. HRMS (ESI/Q-TOF) *m/z*: [M]⁺ calcd for [C₄₃H₄₂N₆O₆Se]⁺ 819.2404; found 819.2396.



General procedure for the synthesis of arene-alkynes **12e-h**

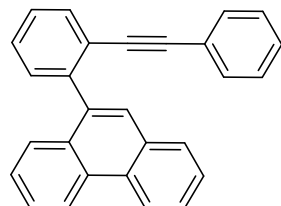
1-bromo-2-substituted ethynyl)benzene (1 equiv), arylboronic acid (2 equiv), Pd(PPh₃)₄ (0.05 equiv), Na₂CO₃ (6 equiv), and mixture of solvents (60 mL, EtOH/H₂O/toluene = 1:1:4) were added subsequently into a high pressure vial. The resulting mixture was stirred at 70-80 °C for 8 h. After that the mixture was cooled to rt and extracted with ethyl acetate (40 mL x 3 times). The combined organic layers were dried over MgSO₄. Then it was filtrated, volatiles were evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford **12e-h** majorly as an oils.

1-(2-(phenylethynyl)phenyl)naphthalene (**12e**)



Yellowish oil which solidified in a fridge (0.8 g, 84%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (t, *J* = 8.1 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.60 – 7.54 (m, 1H), 7.53 – 7.39 (m, 6H), 7.18 – 7.08 (m, 3H), 6.82 – 6.77 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 139.0, 133.7, 132.1, 132.0, 131.3, 130.8, 128.2, 128.1, 128.1, 128.0, 127.6, 127.5, 126.6, 126.0, 125.8, 125.3, 123.8, 123.2, 93.1, 89.2. GC-MS (*m/z*): 303.1.1(100) [M]⁺, 151.1(11).

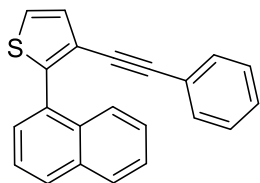
9-(2-(phenylethynyl)phenyl)phenanthrene (**12f**)



White solid (0.62 g, 31%). ¹H NMR (400 MHz, CDCl₃) δ 8.85 – 8.80 (m, 4H), 7.93 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.87 (s, 2H), 7.74 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 2H), 7.70 – 7.63 (m, 4H), 7.51 (ddd, *J* = 8.2, 1.5, 0.7 Hz, 2H), 7.38 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H). ¹³C NMR

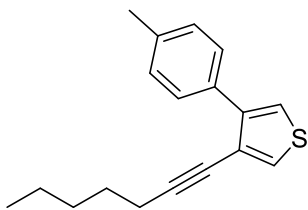
(101 MHz, CDCl₃) δ 137.3, 132.3, 131.8, 130.5, 128.9, 128.6, 127.7, 127.1, 126.9, 126.8, 126.7, 123.0, 122.8. GC-MS (m/z): 353.1(100) [M-1]⁺, 175.0(40).

2-(naphthalen-1-yl)-3-(phenylethynyl)thiophene (12g)



Yellowish solid (0.84 g, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 1H), 7.81 (ddt, *J* = 10.6, 8.1, 1.5 Hz, 2H), 7.56 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.46 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.29 (d, *J* = 5.1 Hz, 1H), 7.14 – 7.08 (m, 3H), 7.08 – 7.02 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 134.0, 133.6, 131.8, 131.3, 130.3, 128.4, 128.4, 128.3, 128.1, 126.4, 126.1, 126.0, 125.9, 125.4, 123.1, 120.8, 95.4, 83.0. GC-MS (m/z): 309.1(100) [M]⁺, 175.0(34).

4-(hept-1-yn-1-yl)-3-(*p*-tolyl)thiophene (12h)



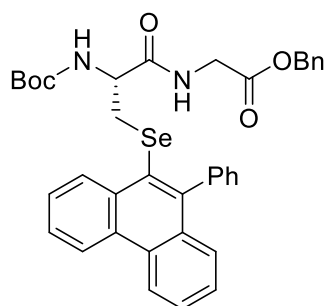
Yellowish oil (0.4 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.43 (d, *J* = 3.3 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.20 (s, 1H), 2.39 (s, 3H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.62 – 1.50 (m, 2H), 1.44 – 1.24 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.4, 137.2, 132.9, 129.2, 129.0, 128.2, 122.6, 121.5, 92.2, 75.9, 31.2, 28.4, 22.4, 21.4, 19.6, 14.1. GC-MS (m/z): 268.0(80) [M]⁺, 210.9(100).

General procedure for the synthesis of aryl fused peptides via 6-endo-dig cyclization

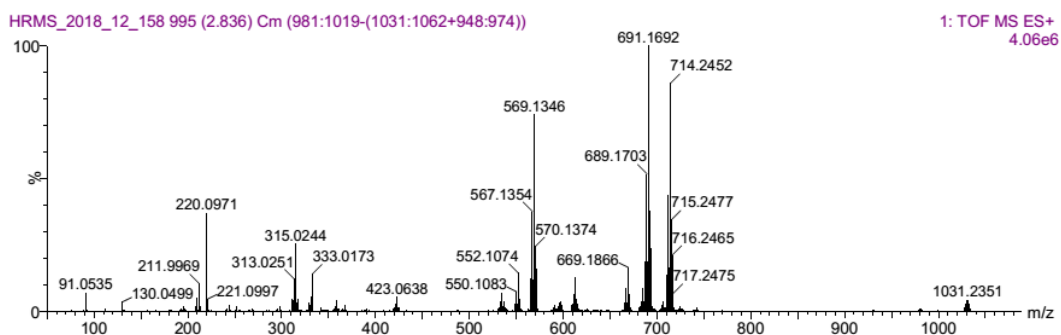
A vial loaded with selenocystine-based peptide (1 equiv) and CuBr₂ (1 equiv) dissolved in dry CH₂Cl₂ (2 ml) was stirred for 4 h at rt (*Note*: if the mixture is not transparent, a few

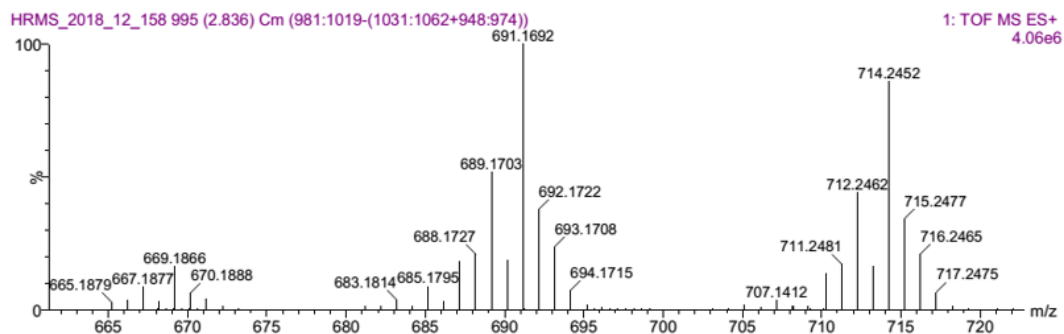
drops of acetonitrile can be added). Then dry CH₂Cl₂ (1 ml) solution of 2-ethynyl biphenyl (2 equiv) was added dropwise, and the mixture was stirred at rt overnight. After this period, the solvents were evaporated, and the products (**13a-h**) was isolated by reverse-phase flash chromatography on silica gel C-18 using the mixture of water/acetonitrile as eluent.

Benzyl (*R*)-(2-((*tert*-butoxycarbonyl)amino)-3-((10-phenylphenanthren-9-yl)selenyl)propanoyl)glycinate (13a**)**

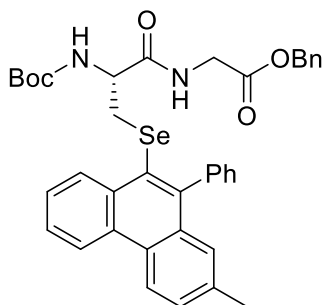


Foam (51 mg, 85%). Synthesised from 2-(phenylethynyl)-1,1'-biphenyl (**12a**) (0.181 mmol, 0.046 g) and **6** (0.09 mmol, 0.075 g). ¹H NMR (400 MHz, CD₃OD) δ 8.89 – 8.81 (m, 3H), 7.76 – 7.65 (m, 3H), 7.55 – 7.42 (m, 4H), 7.38 (dd, J = 8.3, 1.0 Hz, 1H), 7.35 – 7.21 (m, 7H), 5.11 (s, 2H), 4.13 – 4.06 (m, 1H), 3.89 – 3.75 (m, 2H), 2.97 (dd, J = 12.6, 4.8 Hz, 1H), 2.92 – 2.83 (m, 1H), 1.29 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 169.3, 142.2, 135.3, 132.5, 131.9, 130.9, 130.3, 129.5, 129.1, 128.8, 128.7, 128.7, 128.5, 128.5, 128.2, 128.1, 127.8, 127.7, 127.6, 127.4, 127.2, 126.9, 123.2, 122.7, 80.5, 67.3, 41.3, 31.0, 28.3. ⁷⁷Se NMR (76 MHz, CDCl₃) δ 167.6. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ calcd for [C₃₇H₃₆N₂O₅Se]⁺ 669.1868; found 669.1866.

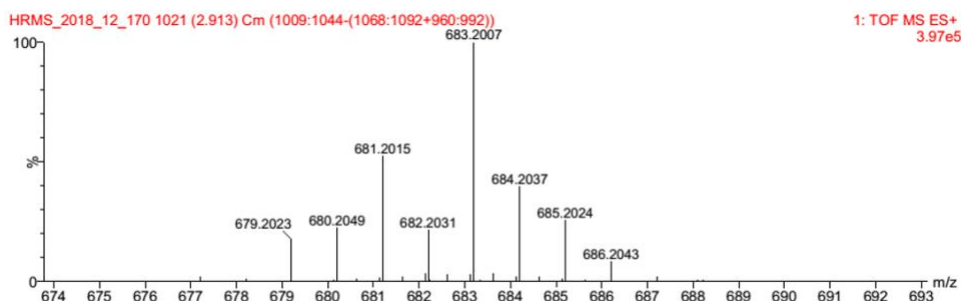
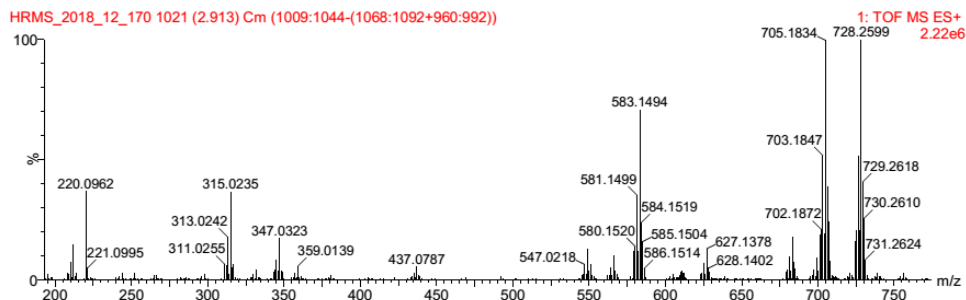




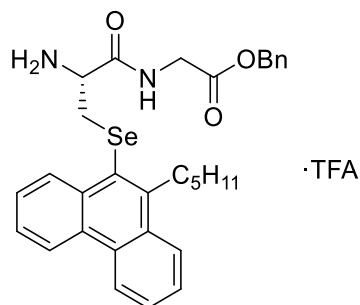
Benzyl (*R*)-(2-((*tert*-butoxycarbonyl)amino)-3-((2-methyl-10-phenylphenanthren-9-yl)selanyl)propanoyl)glycinate (13b**)**



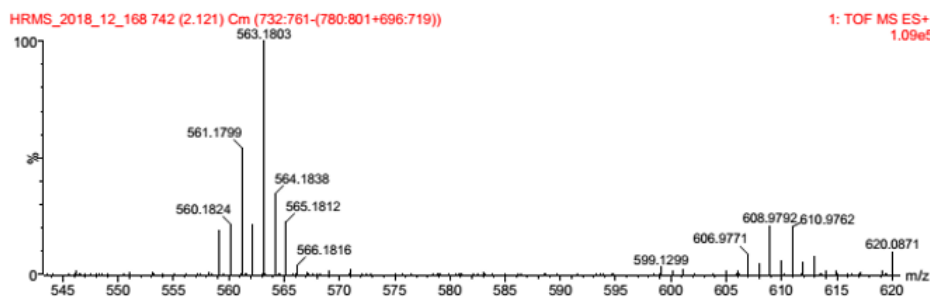
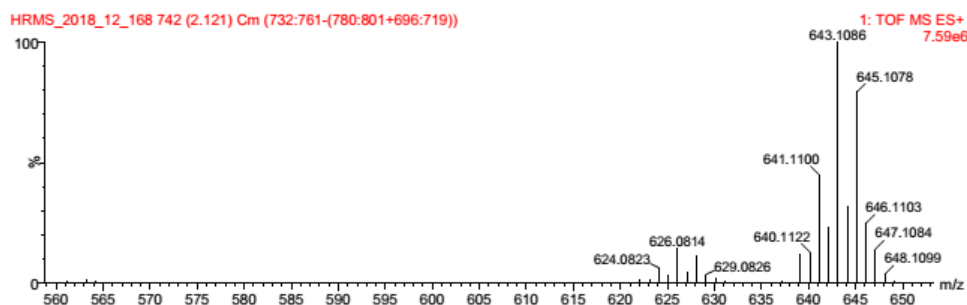
Foam (38 mg, 94%). Synthesised from 4'-methyl-2-(phenylethynyl)-1,1'-biphenyl (**12b**) (0.121 mmol, 0.032 g) and **6** (0.06 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 8.82 – 8.74 (m, 2H), 8.69 (d, $J = 8.5$ Hz, 1H), 7.72 – 7.62 (m, 2H), 7.54 – 7.42 (m, 4H), 7.33 – 7.20 (m, 7H), 7.15 (s, 1H), 5.09 (s, 2H), 4.09 (dd, $J = 8.3, 4.8$ Hz, 1H), 3.87 – 3.74 (m, 2H), 2.95 (dd, $J = 12.5, 4.8$ Hz, 1H), 2.86 (dd, $J = 12.5, 8.3$ Hz, 1H), 2.34 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 173.7, 170.7, 157.1, 147.2, 143.4, 137.7, 137.1, 133.6, 133.4, 132.0, 131.5, 131.4, 131.3, 130.1, 130.1, 129.5, 129.3, 129.3, 129.2, 129.0, 128.4, 128.2, 128.1, 123.9, 123.7, 80.8, 67.9, 56.2, 42.1, 31.8, 28.5, 21.6. ^{77}Se NMR (76 MHz, CD_3OD) δ 178.3. IR ν_{max} (film): 3327, 3061, 3026, 2977, 2932, 1751, 1685, 1497, 1367, 1246, 1171, 1029, 758, 701. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{38}\text{H}_{38}\text{N}_2\text{O}_5\text{Se}]^+$ 683.2024; found 683.2007.



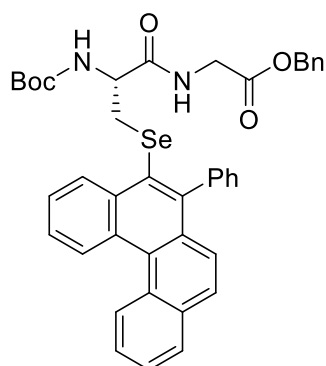
Benzyl (R)-(2-amino-3-((10-pentylphenanthren-9-yl)selenyl)propanoyl)glycinate trifluoroacetate (13d)



Foam (40 mg, 94%). Synthesised from 2-(hept-1-yn-1-yl)-1,1'-biphenyl (**12d**) (0.121 mmol, 0.032 g) and **6** (0.060 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.26 (m, 11H), 5.24 – 5.16 (m, 2H), 4.04 (s, 1H), 3.98 (d, $J = 2.1$ Hz, 1H), 3.88 (q, $J = 5.9, 5.3$ Hz, 1H), 3.02 – 2.73 (m, 3H), 2.38 – 2.26 (m, 1H), 1.39 – 1.23 (m, 5H), 1.20 – 1.11 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 170.5, 143.0, 142.9, 141.9, 141.1, 137.1, 132.1, 131.3, 130.9, 130.4, 130.2, 129.6, 129.5, 129.4, 129.0, 128.6, 128.5, 121.8, 68.2, 42.2, 38.3, 38.0, 32.1, 28.1, 23.6, 14.3. ^{77}Se NMR (76 MHz, CDCl_3) δ 270.8. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_3\text{Se}]^+$ 563.1813; found 563.1803.

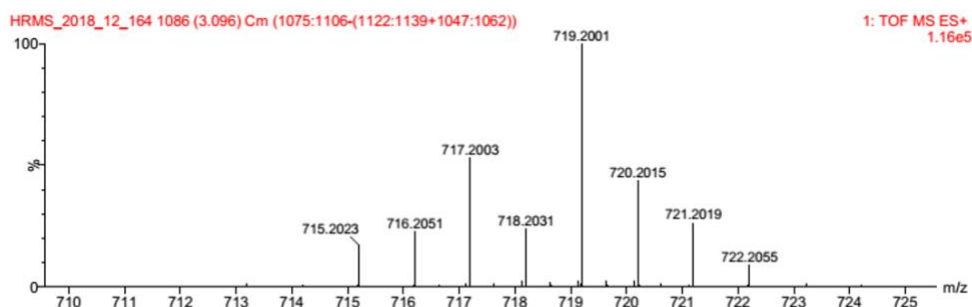
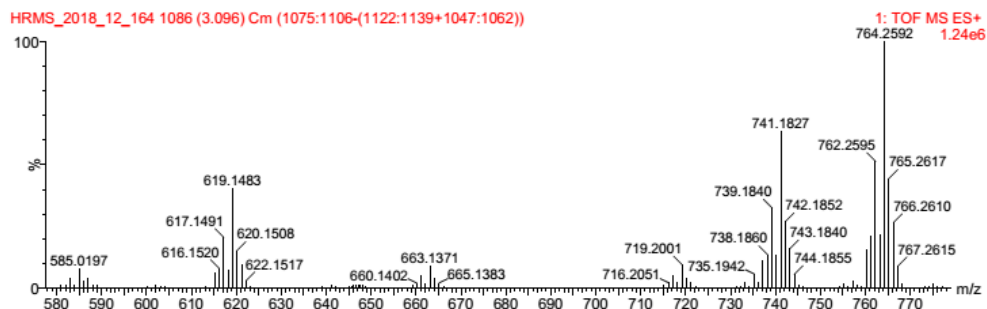


Benzyl (R)-2-((*tert*-butoxycarbonyl)amino)-3-((6-phenylbenzo[*c*]phenanthren-5-yl)selanyl)propanoyl)glycinate (13e**)**



Foam (39 mg, 92%). Synthesised from compounds **12e** (0.121 mmol, 0.037 g) and **6** (0.06 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 9.03 – 8.96 (m, 2H), 8.91 – 8.84 (m, 1H), 7.97 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.74 – 7.59 (m, 5H), 7.53 – 7.43 (m, 3H), 7.34 – 7.19 (m, 8H), 5.06 (s, 2H), 4.08 (dd, $J = 7.6, 4.8$ Hz, 1H), 3.82 – 3.69 (m, 2H), 3.03 – 2.88 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 173.7, 170.6, 157.1, 146.6, 143.2, 137.1, 135.1, 134.9, 131.8, 131.7, 131.6, 131.2, 130.9, 130.7, 129.8, 129.7, 129.7, 129.5, 129.4, 129.3, 129.3, 128.6, 128.2, 128.2, 127.6, 127.4, 127.3, 126.3, 80.8, 67.8, 56.2, 54.8, 42.0, 31.9, 28.5. ^{77}Se NMR (76 MHz, CD_3OD) δ 178.0. IR ν_{max} (film): 3396, 3332, 3061, 2977, 2932, 1747, 1691, 1508, 1367, 1237, 1168, 1024, 826, 753, 699.

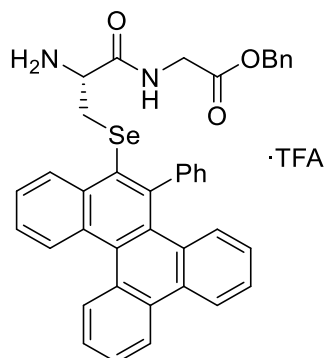
HRMS (ESI/Q-TOF) m/z : $[M+H]^+$ calcd for [for $C_{41}H_{39}N_2O_5Se$] $^+$ 719.2024; found 719.2001.



Benzyl

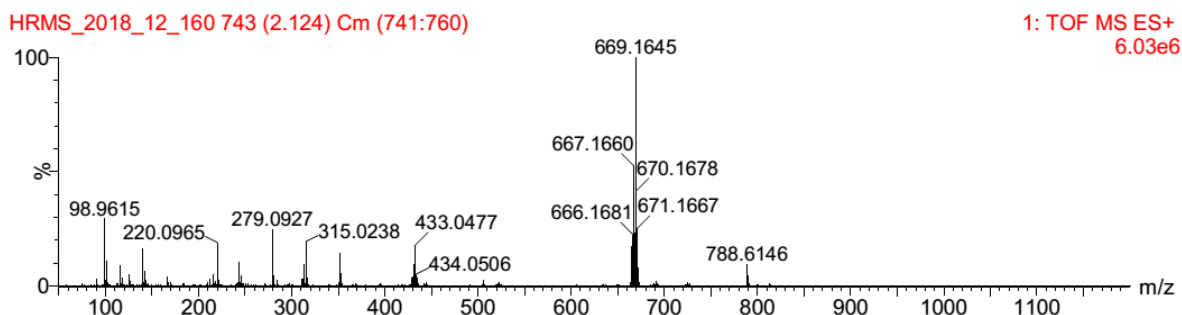
(R)-(2-amino-3-((5-phenylbenzo[g]chrysen-6-

yl)selenanyl)propanoyl)glycinate (13f)

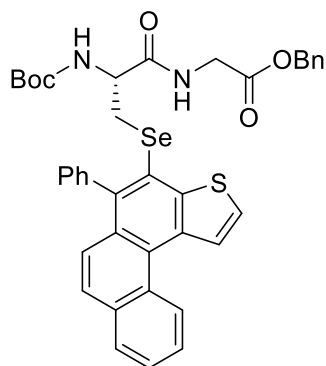


Foam (47 mg, 62%). Synthesised from compounds **12f** (0.121 mmol, 0.041 g) and **6** (0.06 mmol, 0.05 g) followed by removing of Boc protecting group with TFA (0.5 ml) in DCM (1 ml), at rt for 3 h. The product was isolated by reverse-phase flash chromatography. 1H NMR (400 MHz, CD_3OD) δ 8.79 – 8.67 (m, 4H), 8.63 (dt, $J = 8.2$, 0.8 Hz, 1H), 7.79 – 7.67 (m, 3H), 7.62 (ddd, $J = 8.3$, 7.1, 1.3 Hz, 1H), 7.51 – 7.38 (m, 6H), 7.35 – 7.25 (m, 6H), 7.02 (ddd, $J = 8.4$, 7.0, 1.3 Hz, 1H), 5.03 (d, $J = 2.3$ Hz, 2H), 3.64 (dd, $J = 6.8$, 6.0 Hz, 1H), 3.64 – 3.40 (m, 3H), 3.00 (dd, $J = 6.4$, 3.8 Hz, 2H), 1.29 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.7, 142.7, 135.3, 133.4, 132.5, 131.7,

131.5, 131.0, 130.9, 130.2, 130.0, 129.8, 129.5, 129.4, 129.2, 129.1, 128.7, 128.6, 128.5, 128.3, 127.8, 127.5, 127.4, 126.8, 126.4, 125.7, 123.6, 123.2, 67.1, 41.0, 35.3. ^{77}Se NMR (76 MHz, CDCl_3) δ 163.9. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{40}\text{H}_{33}\text{N}_2\text{O}_3\text{Se}]^+$ 669.1656; found 669.1645.

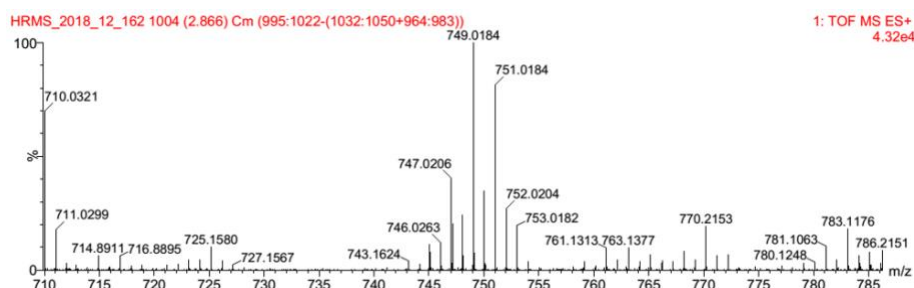
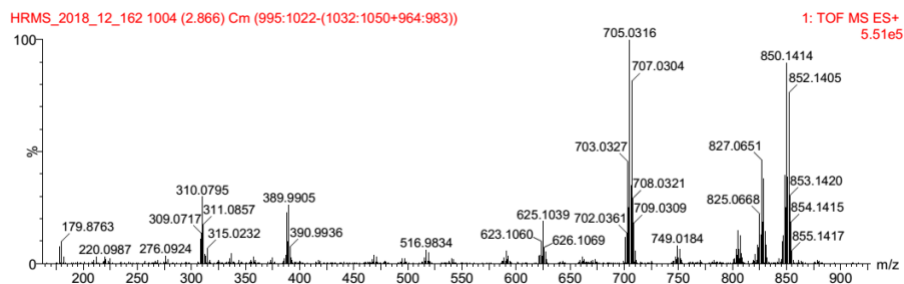


Benzyl (R)-2-((tert-butoxycarbonyl)amino)-3-((5-phenylphenanthro[3,4-b]thiophen-4-yl)selanyl)propanoyl)glycinate (13g)

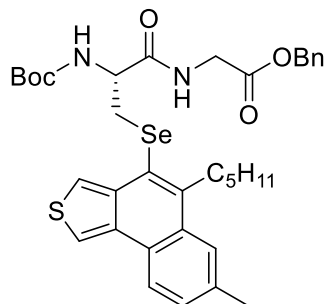


Foam (24 mg, 84%). Synthesised from compounds **12g** (0.121 mmol, 0.037 g) and **6** (0.06 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 7.95 (d, $J = 8.2$ Hz, 1H), 7.93 – 7.88 (m, 1H), 7.84 (t, 1H), 7.67 – 7.61 (m, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.39 (m, 3H), 7.35 – 7.14 (m, 9H), 6.95 – 6.90 (m, 1H), 6.88 – 6.81 (m, 1H), 6.79 (d, $J = 5.2$ Hz, 1H), 6.69 (t, $J = 7.6$ Hz, 1H), 6.38 (d, $J = 7.0$ Hz, 1H), 5.11 (d, $J = 9.6$ Hz, 2H), 3.97 – 3.81 (m, 3H), 2.39 – 2.27 (m, 1H), 2.27 – 2.16 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 173.4, 170.6, 137.1, 137.1, 135.4, 135.3, 134.9, 131.4, 130.8, 130.1, 129.9, 129.6, 129.5, 129.4, 129.3, 129.3, 129.0, 128.9, 128.9, 128.8, 128.3, 127.7, 127.4, 127.2, 127.0, 126.9, 126.6, 126.3, 80.9, 67.9, 55.5, 42.1, 28.7. ^{77}Se NMR (76 MHz,

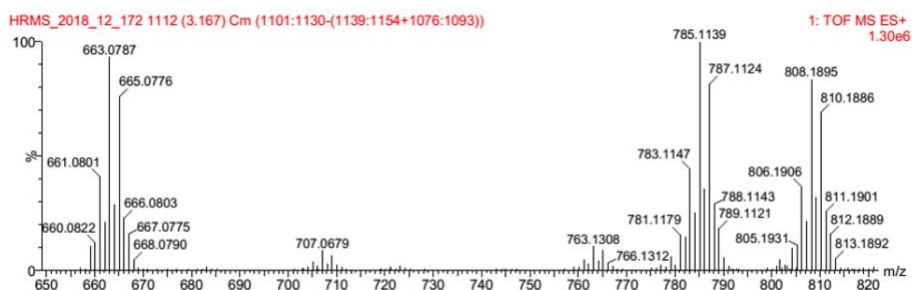
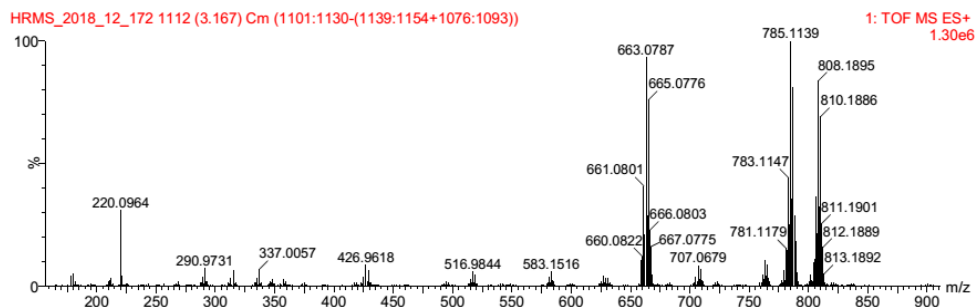
CD₃OD) δ 392.1. IR ν_{\max} (film): 3410, 3340, 2978, 2932, 1748, 1682, 1514, 1367, 1170, 1046, 1024, 756, 699. HRMS (ESI/Q-TOF) m/z : $[M+H]^+$ calcd for $[C_{39}H_{37}N_2O_5SSe]^+$ 725.1588; found 725.1580.



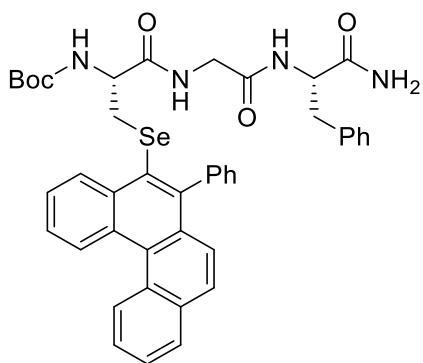
Benzyl (R)-2-((*tert*-butoxycarbonyl)amino)-3-((7-methyl-5-pentyl-naphtho[1,2-*c*]thiophen-4-yl)selanyl)propanoyl)glycinate (13h)



Foam (36 mg, 89%). Synthesised from compounds **12h** (0.121 mmol, 0.032 g) and **6** (0.06 mmol, 0.05 g). ¹H NMR (400 MHz, CD₃OD) δ 7.38 – 7.30 (m, 7H), 7.28 (d, $J = 3.3$ Hz, 1H), 7.16 – 7.11 (m, 2H), 5.15 (s, 2H), 4.14 (broad s, 1H), 4.01 – 3.88 (m, 2H), 3.03 – 2.43 (m, 4H), 2.33 (s, 3H), 1.61 – 1.23 (m, 15H), 0.92 (t, $J = 7.0$ Hz, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 173.7, 170.8, 157.4, 143.1, 142.1, 138.1, 137.1, 135.5, 134.4, 129.9, 129.6, 129.4, 129.3, 129.3, 127.6, 123.4, 81.0, 67.9, 56.1, 49.6, 42.2, 37.8, 32.3, 28.7, 28.4, 23.6, 21.3, 14.4. IR ν_{\max} (film): 3316, 2955, 2929, 2858, 1752, 1674, 1507, 1456, 1367, 1249, 1188, 1046, 1023, 755, 698. HRMS (ESI/Q-TOF) m/z : $[M+H]^+$ calcd for $[C_{35}H_{43}N_2O_5SSe]^+$ 683.2058; found 683.2047.



***Tert*-butyl ((*R*)-1-((2-(((*S*)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)amino)-1-oxo-3-((6-phenylbenzo[*c*]phenanthren-5-yl) selanyl) propan-2-yl)carbamate (**13i**)**

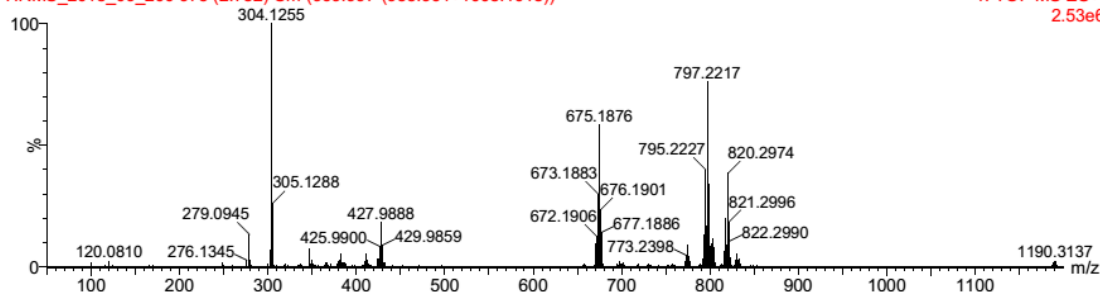


Foam (39 mg, 95%). Synthesised from compounds **12e** (0.106 mmol, 0.032 g) and **9** (0.053 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 9.06 – 8.97 (m, 2H), 8.94 – 8.86 (m, 1H), 7.98 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.77 – 7.59 (m, 5H), 7.56 – 7.45 (m, 3H), 7.35 – 7.28 (m, 3H), 7.23 – 7.13 (m, 4H), 7.15 – 7.06 (m, 1H), 4.53 (dd, $J = 8.9, 5.2$ Hz, 1H), 3.98 (dd, $J = 8.9, 4.8$ Hz, 1H), 3.71 (d, $J = 16.7$ Hz, 1H), 3.51 (d, $J = 16.7$ Hz, 1H), 3.14 (dd, $J = 13.3, 5.2$ Hz, 1H), 3.03 (dd, $J = 13.3, 4.8$ Hz, 1H), 2.98 – 2.80 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 174.5, 172.4, 169.6, 156.0, 145.3, 141.9, 137.0, 133.6, 133.5, 130.4, 130.3, 130.2, 129.8, 129.5, 129.3, 128.8, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.2, 126.8, 126.8, 126.3, 126.3, 126.0, 124.9, 79.6, 55.2, 54.4,

42.2, 37.3, 30.2, 27.2. ^{77}Se NMR (76 MHz, CD_3OD) δ 178.2. IR ν_{max} (film): 3302, 1640, 1527, 1428, 1251, 1167, 1047, 1030, 826, 754, 699. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{43}\text{H}_{43}\text{N}_4\text{O}_5\text{Se}]^+$ 775.2399; found 775.2390.

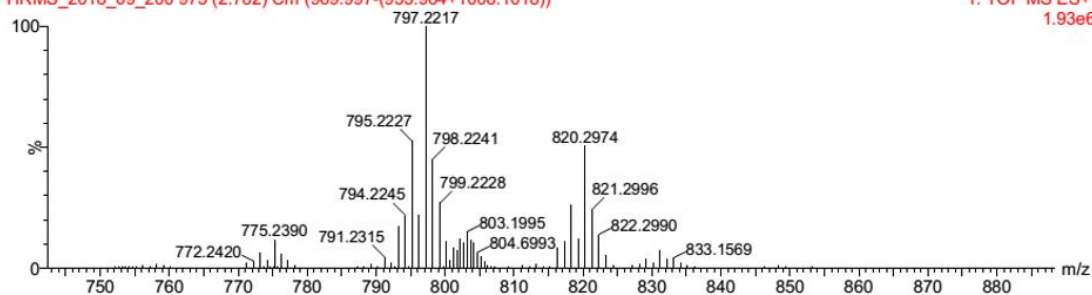
HRMS_2018_09_200_975 (2.782) Cm (969:997-(953:964+1008:1018))

1: TOF MS ES+
2.53e6

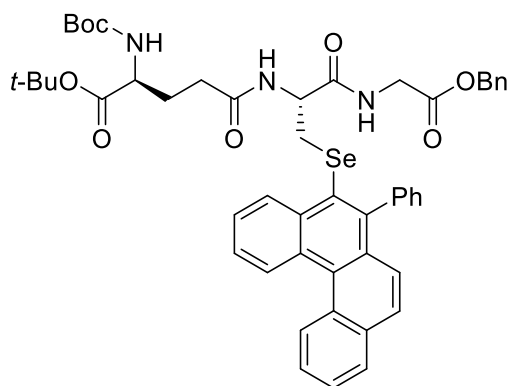


HRMS_2018_09_200_975 (2.782) Cm (969:997-(953:964+1008:1018))

1: TOF MS ES+
1.93e6

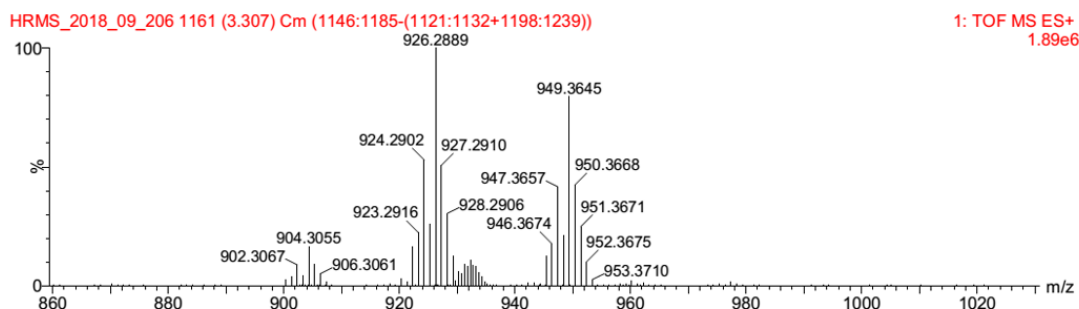
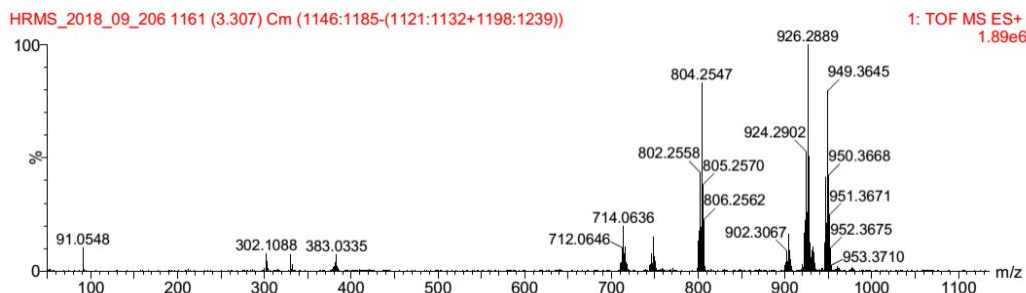


***Tert*-butyl N^6 -((*R*)-1-((2-(benzyloxy)-2-oxoethyl)amino)-1-oxo-3-((6-phenylbenzo[*c*]phenanthren-5-yl)selenyl)propan-2-yl)- N^2 -(*tert*-butoxycarbonyl)-L-glutamate (**13**)**

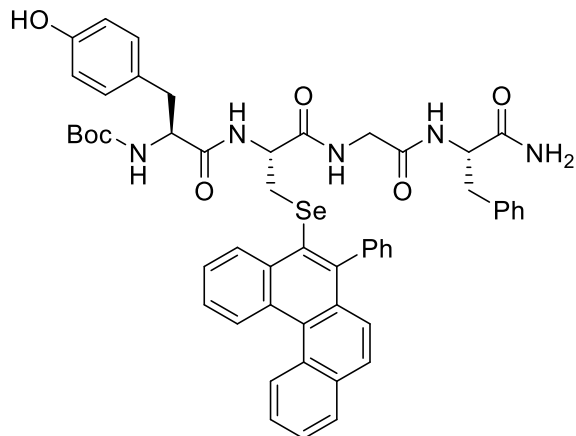


Foam (28 mg, 80%). Synthesised from compounds **12e** (0.085 mmol, 0.026 g) and **7** (0.043 mmol, 0.05 g). ^1H NMR (400 MHz, CD_3OD) δ 9.04 – 8.98 (m, 2H), 8.93 – 8.88 (m, 1H), 7.98 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.76 – 7.61 (m, 5H), 7.54 – 7.44 (m, 3H), 7.34 – 7.20 (m, 8H), 5.06 (s, 2H), 4.27 (dd, $J = 9.0, 5.0$ Hz, 1H), 3.91 (dd, $J = 9.0, 5.0$ Hz, 1H), 3.76 (s, 2H), 3.06 (dd, $J = 12.7, 5.0$ Hz, 1H), 2.89 – 2.81 (m, 1H), 2.20 – 2.02 (m, 2H), 1.99 –

1.88 (m, 1H), 1.79 – 1.67 (m, 1H), 1.44 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 174.5, 173.2, 173.2, 170.6, 158.0, 146.9, 143.2, 137.0, 135.2, 134.9, 131.8, 131.5, 131.3, 130.9, 130.7, 129.7, 129.6, 129.5, 129.3, 129.3, 129.2, 129.1, 128.6, 128.2, 128.0, 127.7, 127.4, 127.4, 126.4, 82.7, 80.5, 67.8, 55.4, 54.9, 42.0, 32.9, 31.3, 28.7, 28.3. ^{77}Se NMR (76 MHz, CD_3OD) δ 179.8. IR ν_{max} (film): 3311, 3061, 2978, 2932, 1742, 1652, 1524, 1367, 1154, 1055, 1030, 826, 754, 701. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{54}\text{H}_{54}\text{N}_3\text{O}_8\text{Se}]^+$ 904.3076; found 904.3055.

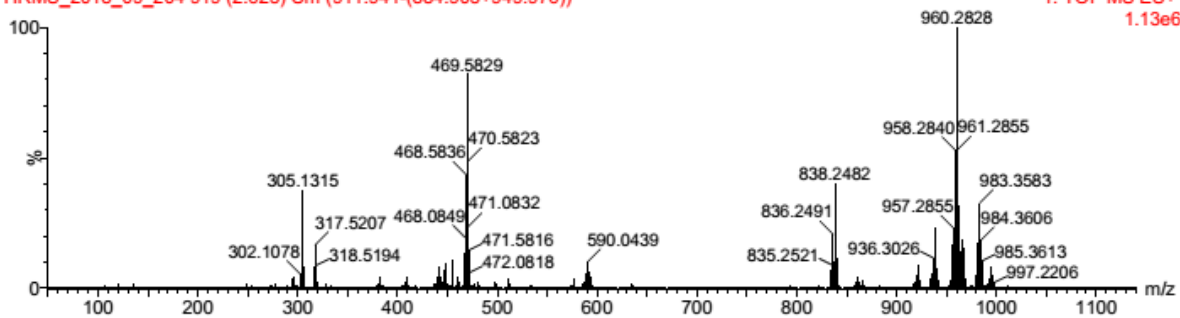


***Tert*-butyl ((*S*)-1-(((*R*)-1-((2-(((*S*)-1-amino-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)amino)-1-oxo-3-((6-phenylbenzo[*c*]phenanthren-5-yl)selanyl)propan-2-yl)amino)-3-(4-hydroxyphenyl)-1-oxopropan-2-yl)carbamate (13k)**

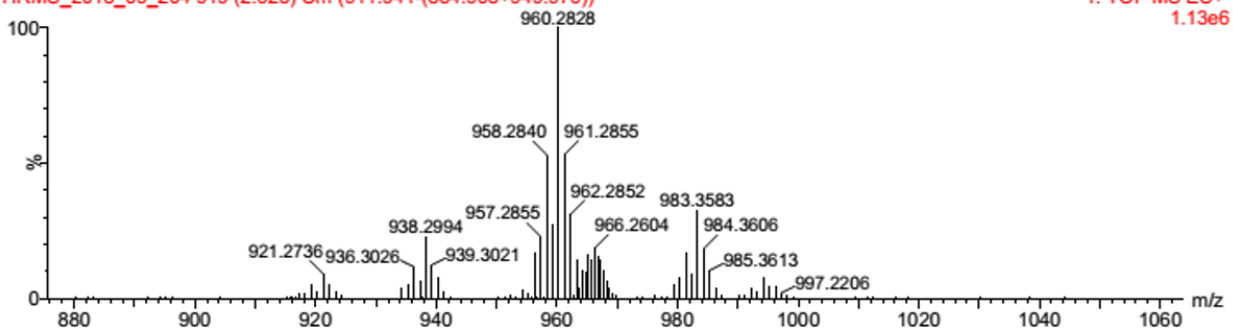


Foam (23 mg, 92%). Synthesised from compounds **12e** (0.055 mmol, 0.017 g) and **10** (0.028 mmol, 0.035 g). ^1H NMR (400 MHz, CD_3OD) δ 8.97 – 8.88 (m, 2H), 8.81 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.89 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.69 – 7.50 (m, 5H), 7.45 – 7.31 (m, 3H), 7.26 – 7.16 (m, 3H), 7.14 – 7.05 (m, 4H), 7.06 – 6.96 (m, 1H), 6.78 (d, $J = 8.2$ Hz, 2H), 6.51 (d, $J = 8.2$ Hz, 2H), 4.42 (dd, $J = 8.7, 5.6$ Hz, 1H), 4.07 (dd, $J = 8.2, 5.6$ Hz, 1H), 3.96 (dd, $J = 8.7, 5.6$ Hz, 1H), 3.62 (d, $J = 16.9$ Hz, 1H), 3.34 (d, $J = 16.9$ Hz, 1H), 3.06 – 2.95 (m, 2H), 2.87 – 2.69 (m, 3H), 2.48 (dd, $J = 14.0, 8.7$ Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 176.0, 174.5, 172.8, 171.0, 157.8, 157.3, 146.8, 143.2, 138.5, 135.1, 134.9, 131.8, 131.8, 131.6, 131.4, 131.3, 130.9, 130.7, 130.3, 129.8, 129.7, 129.4, 129.4, 129.3, 129.3, 128.6, 128.3, 128.2, 127.7, 127.4, 126.4, 116.2, 81.0, 57.6, 56.0, 55.7, 43.6, 38.7, 30.8, 28.7. ^{77}Se NMR (76 MHz, CD_3OD) δ 180.9. IR ν_{max} (film): 3230, 1682, 1638, 1516, 1436, 1247, 1167, 825, 754, 699. HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{52}\text{H}_{52}\text{N}_5\text{O}_7\text{Se}]^+$ 938.3032; found 938.2994.

HRMS_2018_09_204 919 (2.623) Cm (911:941-(884:903+949:976))



HRMS_2018_09_204 919 (2.623) Cm (911:941-(884:903+949:976))



3. X-Ray

1-Hydroxy-1-methyl-3-phenyl-2-(phenyltellanyl)-1*H*-indolizin-4-ium bromide (**3b**)

CCDC 1901311

Single crystals of C₂₁H₁₈BrNOTe [**3b**] were investigated on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 130.0(1) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation. **Crystal Data** for C₂₁H₁₈BrNOTe (*M* = 507.89 g/mol): triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 7.3244(2) Å, *b* = 8.05570(10) Å, *c* = 17.7657(3) Å, α = 86.1550(10)°, β = 89.988(2)°, γ = 64.242(2)°, *V* = 941.46(4) Å³, *Z* = 2, *T* = 130.0(1) K, μ (Mo K α) = 3.710 mm⁻¹, *D*_{calc} = 1.7915 g/cm³, 15841 reflections measured (2 θ \leq 63.5°), 5236 unique (*R*_{int} = 0.0252, *R*_{sigma} = 0.0248) which were used in all calculations. The final *R*₁ was 0.0212 (*I* \geq 2*u*(*I*)) and *wR*₂ was 0.0508 (all data).

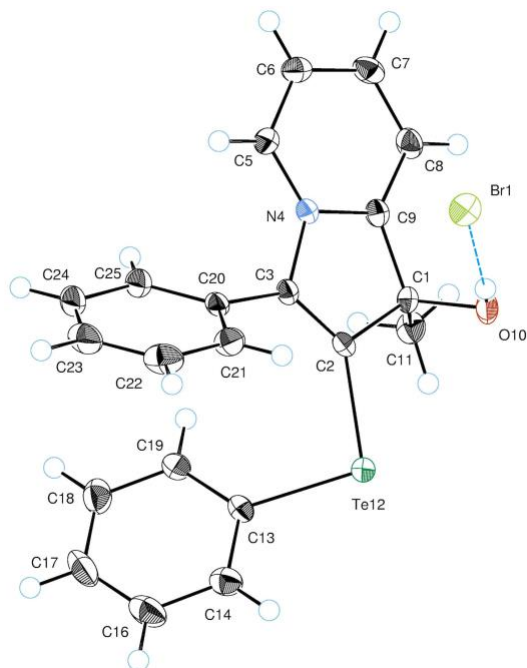


Table S1. Crystal data and structure refinement for **3b**.

Identification code	p2606_Mo
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Empirical formula	C ₂₁ H ₁₈ BrNOTe
Formula weight	507.89
Temperature/K	130.0(1)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.3244(2)
<i>b</i> /Å	8.0557(1)
<i>c</i> /Å	17.7657(3)
α /°	86.155(1)
β /°	89.988(2)
γ /°	64.242(2)
Volume/Å ³	941.46(4)
<i>Z</i>	2
ρ_{calc} /cm ³	1.7915
μ /mm ⁻¹	3.710
<i>F</i> (000)	490.8
Crystal size/mm ³	0.04 × 0.06 × 0.11
Radiation	Mo K α (λ = 0.71073)
2 θ max. for data collection/°	63.5
Index ranges	-10 ≤ <i>h</i> ≤ 9, -11 ≤ <i>k</i> ≤ 10, -25 ≤ <i>l</i> ≤ 24
Reflections collected	15841
Independent reflections	5236 [<i>R</i> _{int} = 0.0252, <i>R</i> _{sigma} = 0.0248]
Data/restraints/parameters	5236/0/231
Goodness-of-fit on <i>F</i> ²	1.027
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)	<i>R</i> ₁ = 0.0212, <i>wR</i> ₂ = 0.0496
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0508
Largest diff. peak/hole / e Å ⁻³	0.97/-0.47

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3b**. *U*_{eq} is defined as 1/3 of the trace of the orthogonalised *U*_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Te12	5704.32(17)	3692.87(15)	1960.33(6)	17.70(4)
Br1	-1630.9(3)	8728.8(3)	1727.34(1)	21.84(5)

			0)		
O10	2233(2)	6720.1(18)	678.4(7)	19.1(3)	
N4	2776(2)	9718.9(19)	1784.0(8)	12.8(3)	
C2	4282(2)	6587(2)	1785.4(9)	13.9(3)	
C13	7622(3)	3411(2)	2900.0(10)	16.5(3)	
C1	3621(3)	7347(2)	970.1(9)	15.4(3)	
C14	8259(3)	1802(3)	3378.7(11)	22.3(4)	
C5	2006(3)	11445(2)	2022.0(10)	15.6(3)	
C3	3759(2)	7976(2)	2240.7(9)	13.2(3)	
C19	8334(3)	4716(2)	3031.1(10)	18.7(3)	
C11	5379(3)	6859(3)	439.7(10)	20.5(4)	
C20	3966(3)	7959(2)	3064.7(9)	14.8(3)	
C9	2625(2)	9407(2)	1051.0(9)	14.8(3)	
C21	3210(3)	6945(2)	3518.1(10)	20.4(3)	
C18	9618(3)	4426(3)	3655.0(11)	25.0(4)	
C6	1058(3)	12929(2)	1502.9(10)	18.6(3)	
C8	1683(3)	10849(3)	519.1(10)	19.1(3)	
C25	4997(3)	8850(2)	3393.7(10)	18.7(3)	
C16	9564(3)	1512(3)	3987.7(11)	28.3(4)	
C22	3492(3)	6800(3)	4298.4(11)	27.2(4)	
C7	878(3)	12642(2)	749.5(10)	19.8(3)	
C24	5282(3)	8689(3)	4175.1(10)	24.0(4)	
C23	4540(3)	7676(3)	4622.5(11)	28.4(4)	
C17	10228(3)	2834(3)	4134.2(11)	28.9(4)	

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te12	18.80(6)	13.73(6)	19.69(6)	-6.30(4)	-5.52(4)	-0.99(4)
Br1	22.26(10)	23.52(9)	22.21(9)	-12.18(7)	4.06(7)	-2.34(7)
O10	18.2(6)	23.1(6)	17.7(6)	-10.0(5)	-3.2(5)	-4.8(5)
N4	12.6(6)	14.5(6)	11.4(6)	-6.4(5)	-0.9(5)	0.5(5)
C2	12.2(7)	15.1(7)	13.3(7)	-5.2(6)	-2.5(6)	0.9(6)
C13	12.9(8)	18.4(8)	16.4(8)	-5.5(6)	-1.6(6)	0.1(6)
C1	18.0(8)	15.7(8)	12.8(7)	-7.3(6)	-2.6(6)	-2.6(6)
C14	23.5(9)	19.2(8)	21.6(9)	-7.4(7)	-0.4(7)	1.9(7)
C5	16.5(8)	15.7(8)	15.2(8)	-7.2(6)	1.0(6)	-2.6(6)

C3	14.1(7)	15.3(7)	11.2(7)	-7.5(6)	-1.4(6)	0.5(6)
C19	14.8(8)	17.8(8)	21.0(8)	-5.0(6)	-0.7(6)	-1.1(7)
C11	20.8(9)	24.2(9)	16.0(8)	-8.8(7)	3.5(7)	-5.4(7)
C20	15.7(8)	14.5(7)	10.7(7)	-3.3(6)	-1.8(6)	-0.8(6)
C9	14.9(8)	18.0(8)	12.5(7)	-8.1(6)	0.1(6)	-0.9(6)
C21	25.2(9)	18.3(8)	16.6(8)	-8.5(7)	1.7(7)	-0.9(7)
C18	19.4(9)	29.5(10)	26.6(10)	-10.3(8)	-1.0(7)	-7.2(8)
C6	16.7(8)	15.0(8)	22.7(9)	-5.6(6)	1.5(7)	-1.0(7)
C8	22.7(9)	22.0(8)	13.1(8)	-10.6(7)	-2.3(6)	1.6(6)
C25	19.8(8)	19.2(8)	16.0(8)	-7.4(7)	-0.7(6)	-2.7(7)
C16	28.5(10)	27.5(10)	19.7(9)	-4.5(8)	-2.9(8)	5.4(8)
C22	35.7(11)	22.3(9)	17.5(9)	-7.7(8)	4.7(8)	3.7(7)
C7	19.9(8)	18.2(8)	20.1(9)	-8.2(7)	-2.1(7)	6.3(7)
C24	26.3(10)	22.9(9)	17.5(9)	-5.1(7)	-5.9(7)	-6.1(7)
C23	36.4(11)	25.1(10)	12.0(8)	-2.3(8)	-2.9(7)	-1.4(7)
C17	20.6(9)	36.8(11)	19.7(9)	-3.6(8)	-6.9(7)	-2.3(8)

Table S4. Bond Lengths for **3b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Te12	C2	2.1001(16)	C3	C20	1.470(2)
Te12	C13	2.1176(17)	C19	C18	1.394(3)
O10	C1	1.428(2)	C20	C21	1.389(2)
N4	C5	1.352(2)	C20	C25	1.398(2)
N4	C3	1.455(2)	C9	C8	1.369(2)
N4	C9	1.356(2)	C21	C22	1.391(3)
C2	C1	1.527(2)	C18	C17	1.387(3)
C2	C3	1.342(2)	C6	C7	1.389(3)
C13	C14	1.395(3)	C8	C7	1.393(3)
C13	C19	1.393(2)	C25	C24	1.393(3)
C1	C11	1.519(2)	C16	C17	1.387(3)
C1	C9	1.512(2)	C22	C23	1.394(3)
C14	C16	1.383(3)	C24	C23	1.376(3)
C5	C6	1.376(3)			

Table S5. Bond Angles for **3b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	Te12	C2	99.33(6)	C20	C3	C2	131.05(16)
C3	N4	C5	127.60(14)	C18	C19	C13	119.44(17)
C9	N4	C5	121.98(15)	C21	C20	C3	118.50(15)
C9	N4	C3	110.36(13)	C25	C20	C3	121.49(16)
C1	C2	Te12	115.40(11)	C25	C20	C21	119.91(16)
C3	C2	Te12	134.18(13)	C1	C9	N4	109.07(14)
C3	C2	C1	110.40(14)	C8	C9	N4	120.76(15)
C14	C13	Te12	117.73(13)	C8	C9	C1	130.16(15)
C19	C13	Te12	122.54(13)	C22	C21	C20	120.13(17)
C19	C13	C14	119.65(16)	C17	C18	C19	120.65(18)
C2	C1	O10	111.45(14)	C7	C6	C5	120.07(16)
C11	C1	O10	108.40(13)	C7	C8	C9	118.41(16)
C11	C1	C2	113.53(14)	C24	C25	C20	119.57(18)
C9	C1	O10	111.92(14)	C17	C16	C14	120.17(19)
C9	C1	C2	101.55(13)	C23	C22	C21	119.68(19)
C9	C1	C11	109.93(14)	C8	C7	C6	119.86(16)
C16	C14	C13	120.40(18)	C23	C24	C25	120.37(18)
C6	C5	N4	118.92(16)	C24	C23	C22	120.33(17)
C2	C3	N4	108.56(14)	C16	C17	C18	119.65(18)
C20	C3	N4	120.35(14)				

Table S6. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **3b**.

Atom	x	y	z	U(eq)
H10	1290(40)	7090(30)	929(13)	22(6)
H14	7803(3)	920(3)	3287.5(11)	26.8(4)
H5	2115(3)	11626(2)	2528.4(10)	18.8(4)
H19	7955(3)	5772(2)	2705.1(10)	22.4(4)
H11a	6036(14)	5544(3)	406(6)	30.8(5)
H11b	4878(4)	7460(16)	-52(2)	30.8(5)
H11c	6333(11)	7263(18)	630(4)	30.8(5)
H21	2514(3)	6361(2)	3299.6(10)	24.5(4)
H18	10071(3)	5308(3)	3750.9(11)	30.0(5)
H6	537(3)	14126(2)	1656.4(10)	22.3(4)
H8	1583(3)	10636(3)	16.1(10)	22.9(4)
H25	5490(3)	9545(2)	3092.7(10)	22.4(4)
H16	9999(3)	429(3)	4299.9(11)	34.0(5)
H22	2985(3)	6122(3)	4602.3(11)	32.6(5)

H7	221(3)	13645(2)	399.8(10)	23.8(4)
H24	5979(3)	9271(3)	4395.7(10)	28.8(5)
H23	4738(3)	7575(3)	5143.8(11)	34.1(5)
H17	11077(3)	2654(3)	4551.5(11)	34.7(5)

(S)-2-(((R)-2-((tert-butoxycarbonyl)amino)-2-carboxyethyl)selenanyl)-1-hydroxy-1,3-diphenyl-1*H*-indolizin-4-ium (5b-*R,S*):

(CCDC 1889565)

Single crystals of $C_{84}H_{79}N_6O_{17}Se_3$ [**5b-*R,S***] were investigated on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 130.0(1) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the help of ShelXL [2] refinement package using Least Squares minimisation. **Crystal Data** for $C_{84}H_{79}N_6O_{17}Se_3$ ($M=1681.41$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 17.8073(2)$ Å, $b = 12.2429(1)$ Å, $c = 19.8681(1)$ Å, $\beta = 99.527(1)^\circ$, $V = 4271.76(6)$ Å³, $Z = 2$, $T = 130.0(1)$ K, $\mu(CuK\alpha) = 2.121$ mm⁻¹, $D_{calc} = 1.307$ g/cm³, 61372 reflections measured ($7.294^\circ \leq 2\theta \leq 154.506^\circ$), 16681 unique ($R_{int} = 0.0705$, $R_{sigma} = 0.0386$) which were used in all calculations. The final R_1 was 0.0544 ($I > 2\sigma(I)$) and wR_2 was 0.1446 (all data).

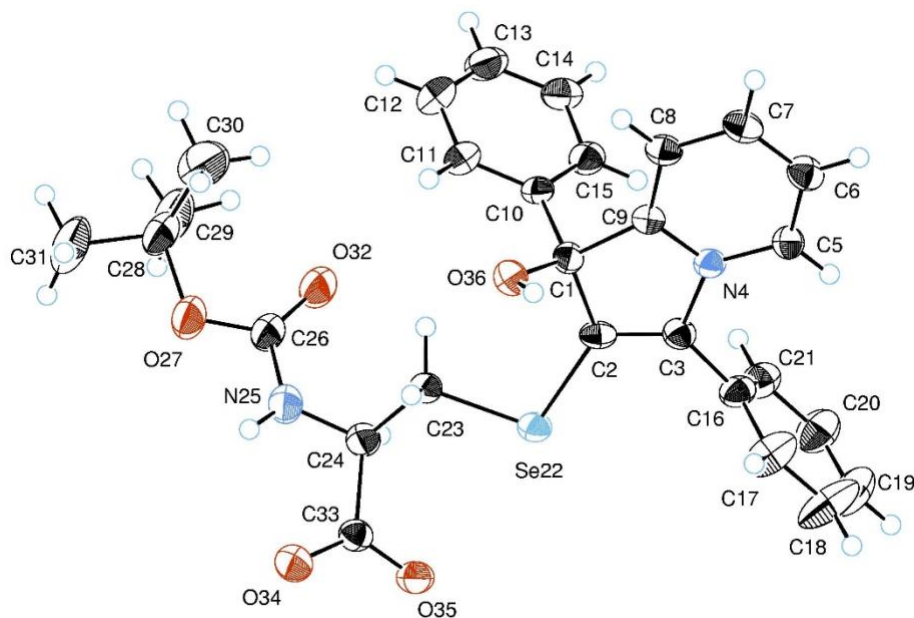


Table S7. Crystal data and structure refinement for **5b-*R,S***.

Identification code	P-2311
Empirical formula	C ₈₄ H ₇₉ N ₆ O ₁₇ Se ₃
Formula weight	1681.41
Temperature/K	130.0(1)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> /Å	17.8073(2)
<i>b</i> /Å	12.2429(1)
<i>c</i> /Å	19.8681(1)
α /°	90
β /°	99.527(1)
γ /°	90
Volume/Å ³	4271.76(6)
<i>Z</i>	2
ρ_{calc} /cm ³	1.307
μ /mm ⁻¹	2.121
<i>F</i> (000)	1726.0
Crystal size/mm ³	0.24 × 0.10 × 0.01
Radiation	CuK α (λ = 1.54184)
2 Θ max. for data collection/°	155.0
Index ranges	-22 ≤ <i>h</i> ≤ 22, -15 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 25
Reflections collected	61372
Independent reflections	16681 [<i>R</i> _{int} = 0.0705, <i>R</i> _{sigma} = 0.0386]
Data/restraints/parameters	16681/1/1006
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indexes [$\geq 2\sigma(I)$]	<i>R</i> ₁ = 0.0544, <i>wR</i> ₂ = 0.1429
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0563, <i>wR</i> ₂ = 0.1446
Largest diff. peak/hole / e Å ⁻³	2.42/-1.01
Flack's <i>x</i> parameter	0.032(8)

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5b-R,S**. *U*_{eq} is defined as 1/3 of the trace of the orthogonalised *U*_{*ij*} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Se22	4372.4(3)	9677.6(4)	9159.5(2)	29.42(13)
Se58	2604.7(3)	4771.1(4)	7160.4(2)	30.31(13)

Se94	1010.7(3)	-174.8(4)	5851.6(2)	32.70(13)
O72	2805(2)	6915(3)	8318.7(16)	30.9(7)
O35	4238(2)	7420(3)	8584.2(18)	34.2(8)
O108	710(2)	2037(3)	4753.8(17)	31.8(7)
O106	726(2)	-2381(3)	5323.8(18)	32.5(7)
O99	3098(2)	-1438(4)	3796.9(18)	41.4(9)
O104	3207(2)	-695(4)	4867.4(18)	40.6(9)
O36	4438(2)	11989(3)	8155.7(18)	32.8(8)
O70	3009(2)	2642(3)	7692.3(18)	35.1(8)
O34	4540(2)	7305(4)	7530.7(18)	39.3(8)
O68	493(2)	4265(4)	8251(2)	44.7(9)
N79	642(2)	2998(3)	6334(2)	28.3(8)
O71	2651(2)	1898(3)	8621(2)	41.0(9)
O63	613(3)	3355(4)	9265(2)	48.6(10)
O27	6928(2)	8567(4)	7530(2)	46.3(10)
O107	923(2)	-2771(4)	4263(2)	44.8(10)
O32	6783(2)	9218(4)	8580(2)	47.4(10)
N4	3914(2)	12815(3)	9642(2)	26.4(8)
O109	4625(2)	5036(4)	7439(2)	46.3(10)
N40	3003(2)	7974(3)	6774.5(19)	26.6(8)
C23	4992(3)	9609(4)	8430(2)	31.2(9)
N61	1556(3)	3301(4)	8662(2)	38.3(10)
C59	2198(3)	4582(5)	8017(2)	31.1(10)
C95	1452(2)	-286(5)	5010(2)	31.0(9)
C33	4637(3)	7646(4)	8133(2)	29.1(10)
N97	2123(2)	-1515(4)	4349(2)	34.4(9)
C43	3120(3)	10046(4)	7277(3)	36.0(11)
C50	367(3)	7635(5)	6962(3)	34.9(11)
C41	3276(3)	8757(4)	6400(2)	30.6(9)
C78	391(3)	3768(4)	6733(3)	32.7(10)
N25	5805(3)	8439(4)	7872(2)	38.9(10)
C73	1119(3)	2217(4)	5410(2)	28.1(9)
C7	3949(3)	14958(4)	9282(2)	34.5(11)
C105	1066(3)	-2278(4)	4827(3)	30.4(10)
C15	5831(3)	12353(4)	9739(3)	32.6(10)
C44	2836(3)	9221(4)	7646(3)	31.8(10)
C60	1928(3)	3404(4)	8078(2)	30.4(9)
C98	2851(3)	-1173(5)	4382(3)	34.9(10)

C45	2777(3)	8179(4)	7376(2)	27.9(9)
C13	7069(3)	12479(5)	9428(3)	43.8(12)
C74	856(3)	3245(4)	5730(2)	27.8(9)
C5	3555(3)	13551(4)	9990(2)	29.0(9)
C69	2587(3)	2573(4)	8143(2)	31.0(10)
C96	1727(3)	-1463(4)	4926(2)	28.1(9)
C82	1967(3)	2317(4)	5377(2)	30.7(9)
C88	535(3)	1382(4)	7107(3)	32.9(10)
C62	853(3)	3686(5)	8685(3)	38.8(11)
C16	3563(3)	11160(4)	10278(3)	31.5(10)
C9	4280(3)	13104(4)	9130(2)	28.3(9)
C49	45(3)	7540(5)	7542(3)	42.5(12)
C52	3155(3)	6398(4)	5984(2)	30.3(10)
C6	3572(3)	14638(5)	9810(2)	32.7(9)
C8	4307(3)	14181(4)	8941(2)	30.2(10)
C14	6612(3)	12509(5)	9923(3)	36.9(11)
C51	1145(3)	7486(4)	6996(2)	31.4(10)
C37	2472(3)	7131(4)	7647(2)	26.3(9)
C81	970(3)	1358(4)	5936(2)	27.5(9)
C80	709(3)	1840(4)	6464(3)	30.6(10)
C76	588(3)	5115(4)	5910(3)	37.0(12)
C11	5973(3)	12188(5)	8566(3)	37.6(11)
C47	1281(3)	7187(5)	8199(3)	36.3(11)
C46	1608(3)	7264(4)	7614(2)	28.5(9)
C57	3915(3)	6427(5)	5884(3)	37.3(11)
C48	504(3)	7315(5)	8165(3)	43.9(13)
C3	3948(3)	11650(4)	9742(2)	27.6(9)
C83	2226(3)	2322(5)	4760(3)	36.5(10)
C38	2647(3)	6310(4)	7116(2)	26.8(9)
C26	6533(3)	8776(5)	8041(3)	37.0(11)
C100	3825(3)	-1030(5)	3659(3)	41.0(13)
C42	3330(3)	9812(5)	6649(2)	36.6(10)
C39	2928(3)	6823(4)	6611(2)	27.5(9)
C12	6754(3)	12316(6)	8752(3)	46.9(13)
C86	3259(3)	2567(5)	5956(3)	42.9(13)
C85	3517(3)	2553(5)	5328(4)	49.4(15)
C24	5289(3)	8450(4)	8357(2)	32.0(10)
C91	254(4)	514(6)	8337(3)	47.4(14)

C77	367(3)	4843(5)	6521(3)	37.4(10)
C21	3989(3)	10864(5)	10904(3)	37.5(11)
C84	2995(4)	2430(5)	4734(3)	46.8(13)
C55	3557(4)	5564(6)	4791(3)	51.0(15)
C10	5506(3)	12202(4)	9057(2)	28.1(9)
C75	837(3)	4307(4)	5500(3)	32.9(10)
C87	2493(3)	2432(4)	5982(3)	35.0(10)
C89	-181(3)	1495(5)	7295(3)	41.0(12)
C2	4329(3)	11204(4)	9280(2)	27.6(9)
C28	7668(3)	9084(7)	7533(3)	49.0(16)
C1	4635(3)	12091(4)	8857(2)	27.0(9)
C93	1099(3)	823(5)	7538(3)	37.8(11)
C92	956(4)	396(6)	8148(3)	48.3(14)
C53	2607(3)	5952(5)	5481(3)	39.8(11)
C20	3631(4)	10458(6)	11416(3)	47.9(14)
C56	4114(4)	6010(6)	5286(3)	46.3(13)
C64	-79(4)	3818(6)	9456(4)	53.5(16)
C17	2785(3)	11022(7)	10173(3)	54.6(17)
C90	-313(4)	1065(6)	7914(3)	45.5(13)
C54	2808(4)	5546(6)	4880(3)	50.1(14)
C103	3858(4)	-1523(6)	2958(3)	53.8(15)
C18	2432(4)	10625(8)	10696(4)	70(2)
C101	3814(4)	210(6)	3612(4)	50.3(15)
C19	2863(4)	10346(7)	11318(4)	58.1(17)
C67	2(5)	5046(6)	9550(4)	61.3(18)
C31	7899(4)	8637(9)	6880(4)	67(2)
C65	-86(6)	3290(7)	10150(5)	76(2)
C102	4482(3)	-1430(7)	4173(4)	55.9(17)
C29	8235(4)	8741(8)	8153(3)	60.3(19)
C30	7553(5)	10320(8)	7487(5)	69(2)
C66	-779(5)	3495(10)	8940(5)	79(3)
O110	958(8)	-4939(10)	3989(6)	159(5)

Table S9. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5b-R,S**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se22	30.7(2)	19.6(2)	37.5(2)	0.8(2)	4.21(16)	-1.9(2)
Se58	35.5(2)	18.4(2)	37.7(2)	-0.4(2)	8.02(17)	-0.5(2)

Se94	39.9(3)	18.0(2)	42.4(2)	0.4(2)	13.34(19)	-0.1(2)
O72	30.7(17)	31.7(19)	28.0(14)	1.1(13)	-1.6(12)	-4.4(15)
O35	33.1(17)	29.3(19)	38.5(17)	-0.1(14)	0.5(14)	-4.7(15)
O108	28.1(16)	30.3(19)	35.1(16)	-1.9(14)	-0.8(13)	0.7(15)
O106	34.7(18)	22.4(17)	39.4(17)	0.7(14)	2.8(14)	-5.6(15)
O99	36.8(19)	52(2)	37.4(17)	-4.6(17)	11.9(14)	-5.1(18)
O104	33.3(18)	52(2)	36.0(17)	-5.2(16)	4.7(14)	-9.3(17)
O36	33.8(18)	28.1(19)	34.8(17)	-1.9(14)	1.2(13)	2.2(15)
O70	41.1(19)	22.3(17)	40.2(17)	-0.1(14)	2.1(14)	4.4(15)
O34	37.6(19)	39(2)	38.5(17)	-6.2(16)	-0.3(14)	-3.9(16)
O68	45(2)	49(2)	41.3(18)	4.8(17)	10.2(16)	9.3(19)
N79	25.3(18)	20.8(19)	37.0(19)	-0.5(15)	-0.2(14)	3.8(15)
O71	38.2(19)	32(2)	49(2)	13.4(16)	-3.1(15)	2.1(16)
O63	63(3)	36(2)	52(2)	4.8(18)	23.2(19)	3(2)
O27	32.1(19)	62(3)	46.1(19)	-14(2)	9.2(15)	-2.4(19)
O107	31.4(18)	51(3)	50(2)	-20.9(19)	3.8(15)	-9.9(18)
O32	31.7(19)	62(3)	49(2)	-12.3(19)	7.9(15)	-7.6(18)
N4	24.9(17)	20.6(19)	33.1(18)	0.1(14)	2.8(14)	-0.7(15)
O109	42(2)	47(3)	49.2(19)	4.2(17)	4.9(16)	1.9(17)
N40	27.0(18)	21.6(19)	29.0(17)	-0.1(14)	-1.8(13)	-0.9(15)
C23	31(2)	22(2)	41(2)	-2.4(19)	8.6(16)	-2(2)
N61	44(2)	33(2)	39(2)	6.4(18)	6.5(18)	1(2)
C59	33(2)	29(3)	30.3(18)	0.5(19)	3.7(15)	-1(2)
C95	32(2)	26(2)	35.9(19)	-1(2)	8.3(15)	1(2)
C33	26(2)	26(2)	33(2)	-0.8(18)	-1.8(17)	0.1(19)
N97	27.8(19)	38(2)	37.0(19)	-6.5(18)	3.2(15)	-3.7(18)
C43	28(2)	20(2)	57(3)	-3(2)	-1(2)	-3.1(17)
C50	30(2)	26(3)	47(3)	1(2)	1(2)	1(2)
C41	29(2)	24(2)	37(2)	5.6(18)	1.3(17)	-0.8(18)
C78	31(2)	26(2)	40(2)	-5.2(19)	1.1(18)	3.3(19)
N25	33(2)	45(3)	38(2)	-9.6(19)	4.2(16)	-2(2)
C73	30(2)	20(2)	34(2)	2.3(17)	2.4(17)	-0.3(18)
C7	38(2)	23(3)	39(2)	2.8(19)	-4.9(18)	-1(2)
C105	27(2)	24(2)	37(2)	-0.5(19)	-2.7(18)	0.0(19)
C15	34(2)	24(2)	39(2)	5.1(19)	5.1(18)	0.2(19)
C44	29(2)	27(2)	37(2)	-3.3(19)	-2.8(18)	5(2)
C60	32(2)	23(2)	35(2)	4.3(18)	1.7(17)	0.9(19)
C98	34(2)	37(3)	34(2)	1.1(19)	6.8(19)	1(2)

C45	24(2)	23(2)	34(2)	-0.5(18)	-4.1(16)	-1.4(17)
C13	30(2)	37(3)	63(3)	2(3)	6(2)	-7(2)
C74	26(2)	19(2)	36(2)	0.9(17)	-3.1(17)	0.7(17)
C5	26(2)	27(2)	34(2)	-2.7(18)	2.6(16)	1.5(18)
C69	38(3)	22(2)	29(2)	0.7(18)	-3.7(18)	-1(2)
C96	26(2)	24(2)	34(2)	-1.4(18)	4.3(16)	0.9(18)
C82	29(2)	18(2)	42(2)	2.8(18)	-0.7(18)	-0.3(18)
C88	33(2)	22(2)	41(2)	-0.5(19)	0.3(19)	0(2)
C62	47(3)	30(3)	40(2)	-3(2)	11(2)	-4(2)
C16	29(2)	23(2)	43(2)	5.4(19)	4.8(18)	0.5(18)
C9	28(2)	25(2)	31(2)	-2.0(17)	1.5(16)	-4.4(18)
C49	36(3)	32(3)	60(3)	-5(2)	8(2)	6(2)
C52	35(2)	20(2)	35(2)	1.2(18)	2.3(18)	2.5(19)
C6	33(2)	24(2)	39(2)	0(2)	-2.3(16)	4(2)
C8	34(2)	23(2)	32(2)	3.6(18)	-1.7(17)	-2.4(19)
C14	33(2)	28(3)	47(3)	2(2)	-2(2)	-4(2)
C51	32(2)	25(2)	36(2)	-0.8(18)	1.6(17)	0.1(19)
C37	27(2)	17(2)	34(2)	-2.8(17)	1.5(16)	-1.2(18)
C81	28(2)	16(2)	38(2)	4.4(17)	2.7(17)	1.3(17)
C80	25(2)	25(2)	39(2)	-0.1(19)	-1.2(17)	3.7(19)
C76	30(2)	16(2)	61(3)	4(2)	-4(2)	1.6(18)
C11	39(3)	37(3)	39(2)	1(2)	11(2)	-9(2)
C47	36(3)	32(3)	41(2)	-1(2)	5.7(19)	5(2)
C46	33(2)	17(2)	35(2)	-1.3(16)	3.9(17)	0.4(17)
C57	38(3)	37(3)	36(2)	3(2)	3.5(19)	1(2)
C48	39(3)	42(3)	54(3)	-2(2)	19(2)	10(2)
C3	27(2)	21(2)	34(2)	1.0(17)	1.1(17)	1.8(18)
C83	34(2)	30(3)	45(2)	0(2)	5.6(19)	-3(2)
C38	29(2)	19(2)	31(2)	-3.8(16)	1.2(17)	1.5(17)
C26	29(2)	43(3)	39(2)	-5(2)	5.9(19)	-3(2)
C100	37(3)	43(3)	45(3)	5(2)	14(2)	1(2)
C42	33(2)	24(2)	50(2)	7(2)	-0.7(18)	-3(2)
C39	27(2)	23(2)	31(2)	-0.2(17)	-0.5(16)	-4.0(18)
C12	41(3)	50(4)	53(3)	-1(3)	18(2)	-11(3)
C86	31(3)	29(3)	65(3)	-2(3)	-4(2)	0(2)
C85	26(2)	35(3)	84(4)	4(3)	1(2)	-4(2)
C24	27(2)	32(3)	36(2)	-4.0(19)	0.2(17)	-2(2)
C91	62(4)	43(3)	38(2)	5(2)	12(2)	-9(3)

C77	31(2)	25(3)	53(2)	-4(2)	-1.8(18)	3(2)
C21	34(2)	34(3)	44(3)	7(2)	4(2)	-1(2)
C84	41(3)	37(3)	64(3)	2(3)	16(2)	-3(2)
C55	72(4)	44(3)	40(3)	-5(2)	17(3)	4(3)
C10	28(2)	20(2)	37(2)	-0.2(17)	6.6(17)	-4.5(17)
C75	28(2)	19(2)	49(3)	2(2)	-0.9(18)	0.2(18)
C87	32(2)	24(2)	47(3)	-2(2)	0(2)	-0.5(19)
C89	41(3)	37(3)	45(3)	2(2)	9(2)	1(2)
C2	29(2)	19(2)	32.5(19)	5.8(17)	-1.8(16)	-3.0(17)
C28	33(3)	64(4)	53(3)	-6(3)	16(2)	-5(3)
C1	33(2)	19(2)	30(2)	2.4(16)	6.9(16)	1.8(18)
C93	38(3)	32(3)	43(2)	5(2)	3(2)	6(2)
C92	56(4)	41(3)	45(3)	13(2)	2(2)	7(3)
C53	45(3)	36(3)	38(2)	-7(2)	5(2)	-6(2)
C20	51(3)	51(4)	42(3)	15(3)	7(2)	-2(3)
C56	44(3)	52(4)	46(3)	4(3)	16(2)	7(3)
C64	67(4)	40(3)	61(4)	-8(3)	33(3)	-3(3)
C17	35(3)	69(5)	58(3)	26(3)	1(2)	-4(3)
C90	45(3)	47(3)	48(3)	1(2)	16(2)	-7(3)
C54	52(3)	52(4)	45(3)	-16(3)	4(2)	-2(3)
C103	61(4)	52(4)	55(3)	-4(3)	29(3)	-8(3)
C18	30(3)	95(7)	84(5)	42(5)	6(3)	-9(3)
C101	52(4)	44(3)	57(3)	5(3)	17(3)	-1(3)
C19	57(4)	63(4)	59(3)	23(3)	23(3)	1(3)
C67	83(5)	37(4)	72(4)	-5(3)	36(4)	-2(3)
C31	44(3)	103(7)	57(4)	-6(4)	20(3)	2(4)
C65	108(7)	54(4)	80(5)	9(4)	58(5)	6(5)
C102	30(3)	68(5)	72(4)	21(4)	13(3)	10(3)
C29	36(3)	93(6)	53(3)	-7(4)	9(3)	2(3)
C30	58(4)	67(5)	84(6)	3(4)	14(4)	-9(4)
C66	61(4)	87(7)	96(6)	-37(5)	37(4)	-15(4)
O110	202(12)	124(9)	142(8)	6(7)	2(8)	12(9)

Table S10. Bond Lengths for **5b-R,S**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se22	C23	1.962(5)	C45	C37	1.526(7)
Se22	C2	1.887(5)	C13	C14	1.377(9)

Se58	C59	1.970(5)	C13	C12	1.382(9)
Se58	C38	1.888(5)	C74	C75	1.376(7)
Se94	C95	1.965(4)	C5	C6	1.381(8)
Se94	C81	1.887(5)	C82	C83	1.379(8)
O72	C37	1.393(5)	C82	C87	1.403(7)
O35	C33	1.263(7)	C88	C80	1.475(8)
O108	C73	1.401(5)	C88	C89	1.393(8)
O106	C105	1.247(7)	C88	C93	1.387(7)
O99	C98	1.350(6)	C16	C3	1.484(7)
O99	C100	1.455(7)	C16	C21	1.394(7)
O104	C98	1.213(7)	C16	C17	1.376(8)
O36	C1	1.386(6)	C9	C8	1.374(7)
O70	C69	1.263(7)	C9	C1	1.530(7)
O34	C33	1.252(6)	C49	C48	1.393(9)
O68	C62	1.214(7)	C52	C57	1.401(8)
N79	C78	1.355(6)	C52	C39	1.466(7)
N79	C74	1.351(7)	C52	C53	1.389(7)
N79	C80	1.442(7)	C51	C46	1.387(6)
O71	C69	1.250(6)	C37	C46	1.538(7)
O63	C62	1.356(7)	C37	C38	1.527(6)
O63	C64	1.461(8)	C81	C80	1.351(7)
O27	C26	1.352(7)	C76	C77	1.377(8)
O27	C28	1.460(8)	C76	C75	1.400(8)
O107	C105	1.261(6)	C11	C12	1.388(8)
O32	C26	1.218(7)	C11	C10	1.384(7)
N4	C5	1.358(6)	C47	C46	1.386(7)
N4	C9	1.345(6)	C47	C48	1.382(8)
N4	C3	1.440(6)	C57	C56	1.392(8)
N40	C41	1.353(6)	C3	C2	1.344(7)
N40	C45	1.346(7)	C83	C84	1.385(8)
N40	C39	1.446(6)	C38	C39	1.349(7)
C23	C24	1.531(7)	C100	C103	1.529(8)
N61	C60	1.434(7)	C100	C101	1.521(9)
N61	C62	1.345(8)	C100	C102	1.502(9)
C59	C60	1.532(7)	C86	C85	1.399(10)
C95	C96	1.540(7)	C86	C87	1.384(8)
C33	C24	1.531(7)	C85	C84	1.385(9)
N97	C98	1.353(7)	C91	C92	1.371(10)

N97	C96	1.443(6)	C91	C90	1.379(9)
C43	C44	1.391(8)	C21	C20	1.381(8)
C43	C42	1.389(8)	C55	C56	1.388(9)
C50	C49	1.375(9)	C55	C54	1.373(10)
C50	C51	1.388(7)	C10	C1	1.542(7)
C41	C42	1.380(8)	C89	C90	1.393(8)
C78	C77	1.380(8)	C2	C1	1.527(6)
N25	C26	1.348(7)	C28	C31	1.526(9)
N25	C24	1.437(7)	C28	C29	1.516(9)
C73	C74	1.519(7)	C28	C30	1.528(11)
C73	C82	1.527(7)	C93	C92	1.381(8)
C73	C81	1.536(6)	C53	C54	1.394(8)
C7	C6	1.393(8)	C20	C19	1.357(10)
C7	C8	1.383(7)	C64	C67	1.520(10)
C105	C96	1.532(7)	C64	C65	1.525(11)
C15	C14	1.391(7)	C64	C66	1.528(12)
C15	C10	1.395(7)	C17	C18	1.388(10)
C44	C45	1.382(7)	C18	C19	1.384(10)
C60	C69	1.543(7)			

Table S11: Bond Angles for **5b-R,S**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	Se22	C23	100.1(2)	C45	C37	C46	107.9(4)
C38	Se58	C59	100.4(2)	C45	C37	C38	100.6(4)
C81	Se94	C95	99.8(2)	C38	C37	C46	111.0(4)
C98	O99	C100	120.5(4)	C73	C81	Se94	127.3(4)
C78	N79	C80	127.2(5)	C80	C81	Se94	121.8(4)
C74	N79	C78	122.1(4)	C80	C81	C73	110.5(4)
C74	N79	C80	110.7(4)	N79	C80	C88	120.4(5)
C62	O63	C64	120.2(5)	C81	C80	N79	108.5(4)
C26	O27	C28	119.7(5)	C81	C80	C88	131.0(5)
C5	N4	C3	126.9(4)	C77	C76	C75	120.4(5)
C9	N4	C5	122.6(4)	C10	C11	C12	120.2(5)
C9	N4	C3	110.5(4)	C48	C47	C46	120.5(5)
C41	N40	C39	126.5(4)	C51	C46	C37	120.1(4)
C45	N40	C41	122.9(4)	C47	C46	C51	119.0(5)
C45	N40	C39	110.6(4)	C47	C46	C37	120.9(4)

C24	C23	Se22	110.8(3)	C56	C57	C52	120.0(5)
C62	N61	C60	123.6(4)	C47	C48	C49	120.1(5)
C60	C59	Se58	110.2(3)	N4	C3	C16	119.0(4)
C96	C95	Se94	109.7(3)	C2	C3	N4	108.8(4)
O35	C33	C24	115.0(4)	C2	C3	C16	132.2(5)
O34	C33	O35	126.9(5)	C82	C83	C84	120.7(5)
O34	C33	C24	118.1(5)	C37	C38	Se58	127.6(3)
C98	N97	C96	122.5(4)	C39	C38	Se58	121.5(4)
C42	C43	C44	119.9(5)	C39	C38	C37	110.5(4)
C49	C50	C51	120.0(5)	O32	C26	O27	125.9(5)
N40	C41	C42	118.5(5)	O32	C26	N25	123.4(5)
N79	C78	C77	118.8(5)	N25	C26	O27	110.7(4)
C26	N25	C24	121.7(4)	O99	C100	C103	101.9(5)
O108	C73	C74	111.8(4)	O99	C100	C101	110.6(6)
O108	C73	C82	109.8(4)	O99	C100	C102	112.1(5)
O108	C73	C81	113.8(4)	C101	C100	C103	109.9(6)
C74	C73	C82	109.1(4)	C102	C100	C103	110.3(6)
C74	C73	C81	100.5(4)	C102	C100	C101	111.6(6)
C82	C73	C81	111.6(4)	C41	C42	C43	120.1(5)
C8	C7	C6	119.7(5)	N40	C39	C52	120.6(4)
O106	C105	O107	127.0(5)	C38	C39	N40	108.6(4)
O106	C105	C96	115.3(4)	C38	C39	C52	130.8(5)
O107	C105	C96	117.6(5)	C13	C12	C11	120.1(5)
C14	C15	C10	120.7(5)	C87	C86	C85	120.2(5)
C45	C44	C43	118.5(5)	C84	C85	C86	119.2(5)
N61	C60	C59	109.9(4)	C23	C24	C33	111.5(4)
N61	C60	C69	108.8(4)	N25	C24	C23	110.0(4)
C59	C60	C69	112.5(4)	N25	C24	C33	109.7(4)
O99	C98	N97	109.3(4)	C92	C91	C90	119.6(5)
O104	C98	O99	126.8(5)	C76	C77	C78	120.0(5)
O104	C98	N97	123.9(5)	C20	C21	C16	120.1(5)
N40	C45	C44	120.2(5)	C85	C84	C83	120.5(6)
N40	C45	C37	109.5(4)	C54	C55	C56	120.8(6)
C44	C45	C37	130.4(5)	C15	C10	C1	120.0(4)
C14	C13	C12	120.4(5)	C11	C10	C15	119.1(5)
N79	C74	C73	109.7(4)	C11	C10	C1	120.9(4)
N79	C74	C75	120.7(5)	C74	C75	C76	117.9(5)
C75	C74	C73	129.5(5)	C86	C87	C82	120.1(6)

N4	C5	C6	118.4(4)	C90	C89	C88	119.7(5)
O70	C69	C60	115.5(4)	C3	C2	Se22	121.6(4)
O71	C69	O70	126.4(5)	C3	C2	C1	110.7(4)
O71	C69	C60	118.1(5)	C1	C2	Se22	127.5(4)
N97	C96	C95	109.5(4)	O27	C28	C31	102.1(5)
N97	C96	C105	109.6(4)	O27	C28	C29	111.3(6)
C105	C96	C95	111.8(4)	O27	C28	C30	108.5(6)
C83	C82	C73	121.0(4)	C31	C28	C30	110.9(8)
C83	C82	C87	119.2(5)	C29	C28	C31	110.8(6)
C87	C82	C73	119.7(5)	C29	C28	C30	112.8(7)
C89	C88	C80	121.8(5)	O36	C1	C9	112.2(4)
C93	C88	C80	119.2(5)	O36	C1	C10	110.1(4)
C93	C88	C89	119.0(5)	O36	C1	C2	115.8(4)
O68	C62	O63	125.1(6)	C9	C1	C10	107.1(4)
O68	C62	N61	124.5(5)	C2	C1	C9	100.1(4)
N61	C62	O63	110.4(5)	C2	C1	C10	110.9(4)
C21	C16	C3	119.7(5)	C92	C93	C88	120.6(6)
C17	C16	C3	121.0(5)	C91	C92	C93	120.6(5)
C17	C16	C21	119.2(5)	C52	C53	C54	120.5(6)
N4	C9	C8	120.2(5)	C19	C20	C21	120.6(5)
N4	C9	C1	109.6(4)	C55	C56	C57	119.7(6)
C8	C9	C1	130.2(5)	O63	C64	C67	110.5(6)
C50	C49	C48	119.7(5)	O63	C64	C65	101.8(6)
C57	C52	C39	121.3(4)	O63	C64	C66	110.8(6)
C53	C52	C57	119.2(5)	C67	C64	C65	108.8(6)
C53	C52	C39	119.5(5)	C67	C64	C66	112.8(8)
C5	C6	C7	120.0(5)	C65	C64	C66	111.6(8)
C9	C8	C7	119.1(5)	C16	C17	C18	120.0(6)
C13	C14	C15	119.4(5)	C91	C90	C89	120.6(6)
C46	C51	C50	120.7(5)	C55	C54	C53	119.8(6)
O72	C37	C45	112.2(4)	C19	C18	C17	120.1(6)
O72	C37	C46	109.0(4)	C20	C19	C18	120.0(6)
O72	C37	C38	115.7(4)				

Table S12: Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5b-R,S**.

Atom	x	y	z	U(eq)
H72	3258.67	7069.81	8371.58	46

H108	260.59	2188.88	4748.08	48
H36	4007.72	12232.87	8033.59	49
H10J	4217.95	4660.85	7386.35	69
H10K	4681.6	5319.4	7060.1	69
H23A	4686.93	9835.41	8002.68	37
H23B	5418.19	10108.51	8533.5	37
H61	1794.75	2974.98	9017.65	46
H59A	2590.64	4753.52	8401.82	37
H59B	1775.72	5079.51	8024.12	37
H95A	1072.07	-89.02	4620.83	37
H95B	1876.28	216.46	5031.6	37
H97	1887.31	-1772.86	3969.89	41
H43	3169.86	10752.5	7450.08	43
H50	63.68	7798.81	6546.67	42
H41	3422.93	8589.89	5984.31	37
H78	237.16	3576.23	7141.81	39
H25	5646.09	8211.09	7464.09	47
H7	3960.38	15690.41	9158.79	41
H15	5522.73	12349.3	10074.24	39
H44	2689.33	9368.12	8064.66	38
H60	1560.79	3226.62	7668.98	36
H13	7592.2	12567.78	9549.8	53
H5	3303.09	13326.99	10341.08	35
H96	2082.54	-1665.17	5337.93	34
H49	-478.07	7625.44	7518.78	51
H6	3332.06	15158.06	10042.34	39
H8	4563.27	14385.1	8588.57	36
H14	6823.22	12632.58	10377.11	44
H51	1358.8	7534.76	6600.85	38
H76	570.74	5840.5	5768.89	44
H11	5762.4	12092.6	8108.85	45
H47	1585.74	7047.8	8616.9	44
H57	4287.11	6725.67	6217.52	45
H48	287.9	7251.69	8558.22	53
H83	1879.88	2251.96	4356.45	44
H42	3508.15	10366.26	6397.19	44
H12	7066.7	12293.34	8420.36	56
H86	3603.47	2666.73	6357.06	52

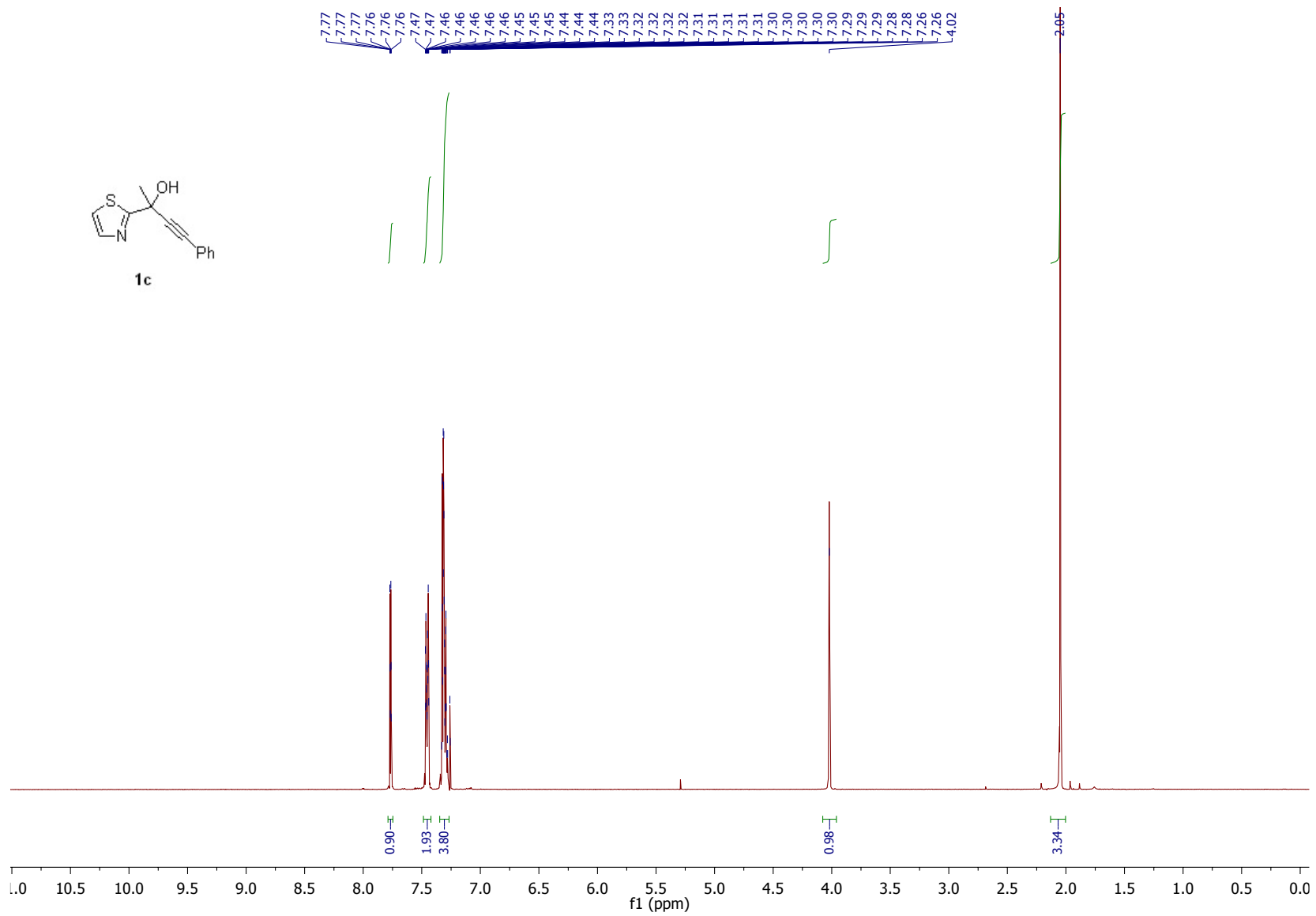
H85	4033.09	2626.03	5310.02	59
H24	5566.21	8214.16	8800.83	38
H91	160.99	223.84	8748.01	57
H77	201.42	5384.1	6790.75	45
H21	4516.18	10940.62	10976.16	45
H84	3161.69	2420.59	4314.58	56
H55	3691.64	5275.12	4395.33	61
H75	986.07	4482.05	5086.26	39
H87	2325.75	2416.82	6401.65	42
H89	-568.6	1854.16	7008.14	49
H93	1577.05	734.89	7415.46	45
H92	1339.45	24.33	8432.9	58
H53	2101.33	5923.37	5544.8	48
H20	3919.01	10258.51	11832.1	58
H56	4618.55	6029.54	5218.53	56
H17	2496.25	11194.3	9752.91	66
H90	-788.22	1151.7	8043.05	55
H54	2436.92	5263.46	4539.68	60
H10A	3855.61	-2305.7	2989.51	81
H10B	4315.7	-1288.19	2804.64	81
H10C	3423.84	-1286.02	2638.9	81
H18	1905.42	10546.87	10629.24	84
H10D	3385.23	439.13	3284.25	75
H10E	4275.48	460.57	3472.91	75
H10F	3774.24	513.89	4050.64	75
H19	2625.42	10081.88	11668.34	70
H67A	461.6	5205.91	9860.22	92
H67B	-427.22	5324.4	9732.52	92
H67C	20.91	5385.16	9117.61	92
H31A	7883.97	7853.42	6887.24	100
H31B	8405.76	8875.43	6849.51	100
H31C	7552.16	8901.65	6492.56	100
H65A	-89.91	2510	10102.34	114
H65B	-532.1	3519.97	10323.97	114
H65C	360.53	3509.33	10460.46	114
H10G	4456.39	-1110.07	4609.93	84
H10H	4951.88	-1225.11	4030.94	84
H10I	4457.26	-2211.07	4207.19	84

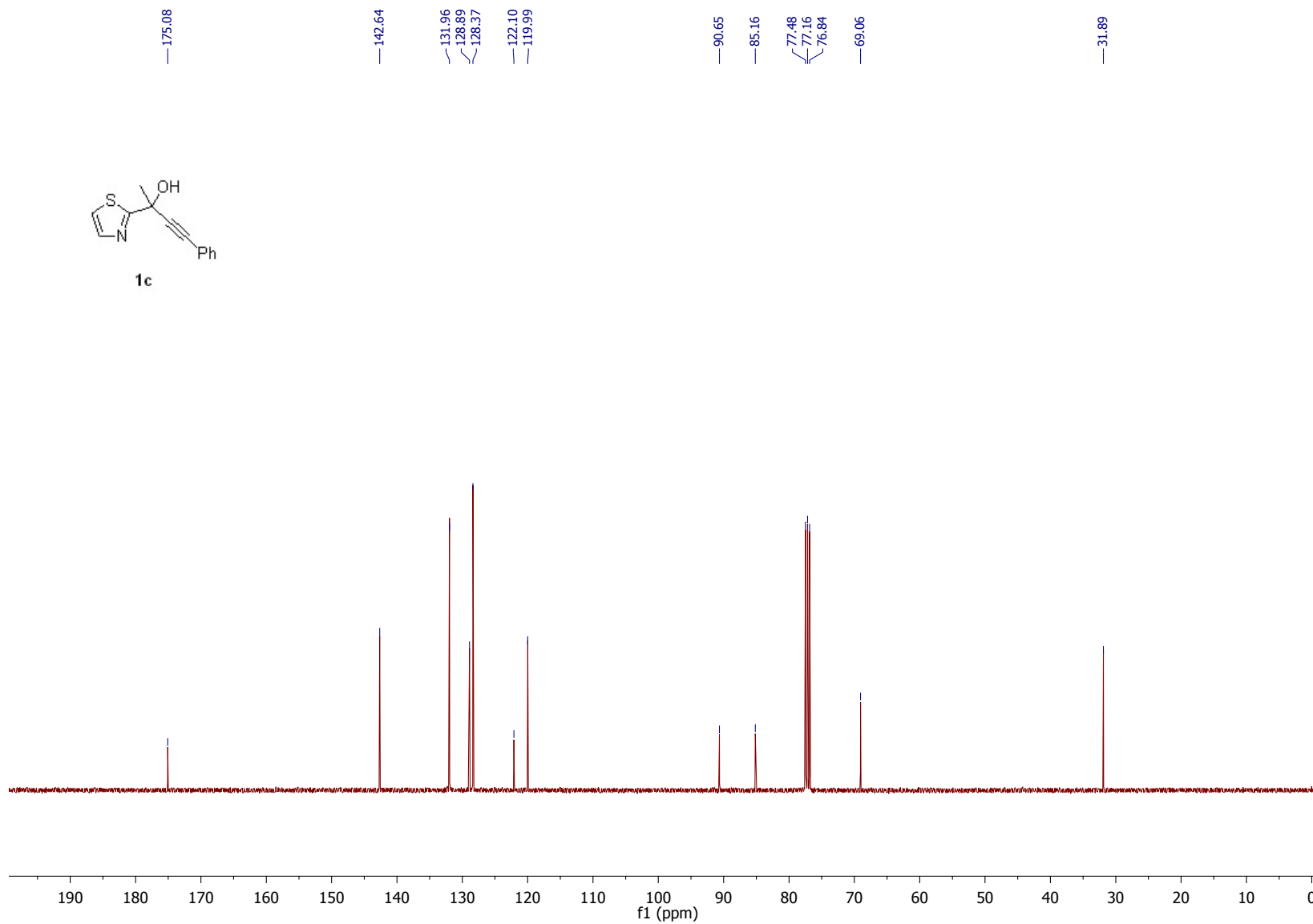
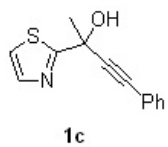
H29A	8122.9	9114.82	8549.51	90
H29B	8740.75	8923.6	8083.99	90
H29C	8199.68	7966.57	8218.37	90
H30A	7142.75	10486.59	7124.58	104
H30B	8011.89	10661.47	7397.67	104
H30C	7433.43	10587.99	7911.11	104
H66A	-750.84	3827.05	8507.49	118
H66B	-1230.26	3740.48	9099.81	118
H66C	-794.63	2715.13	8890.39	118

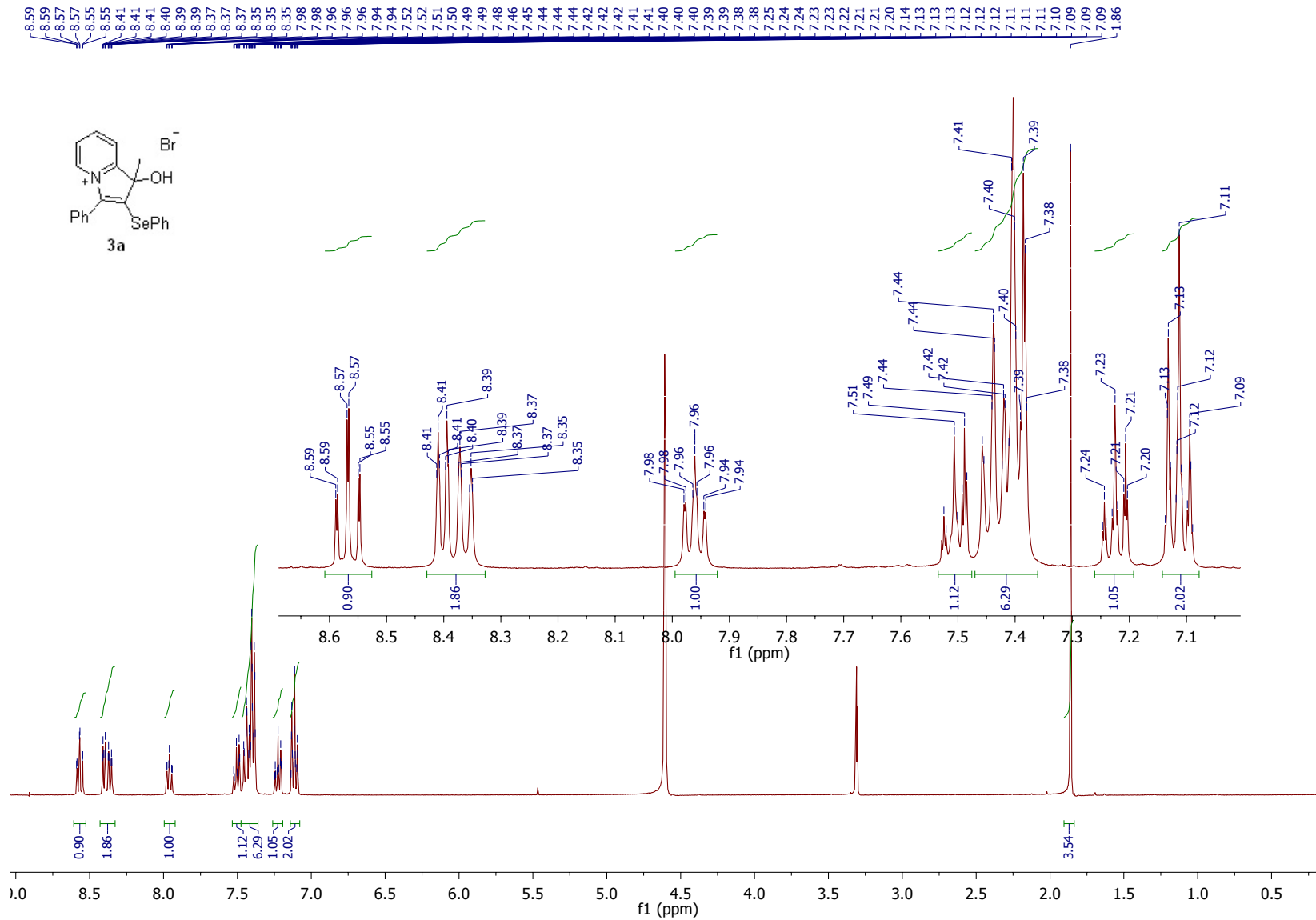
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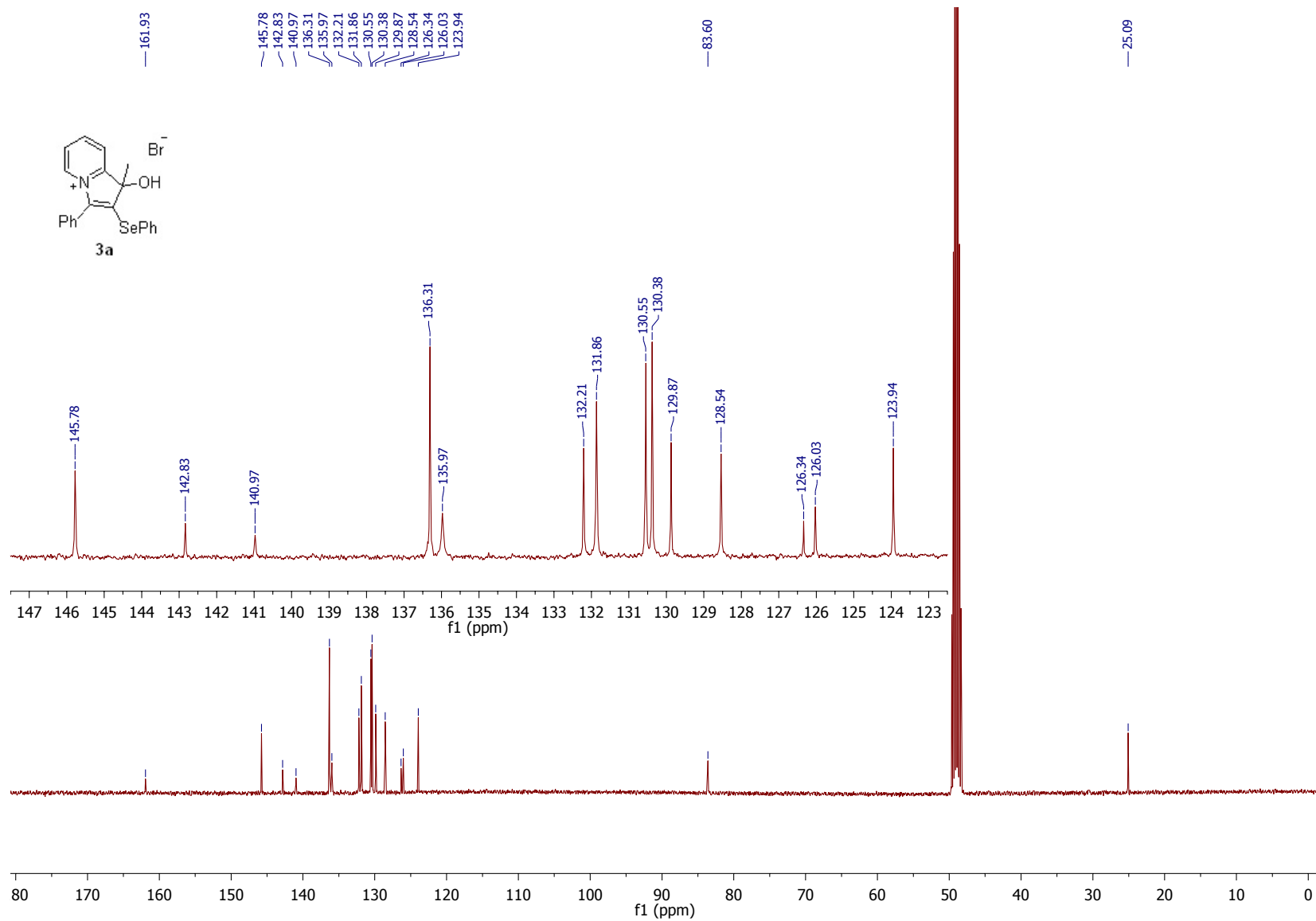
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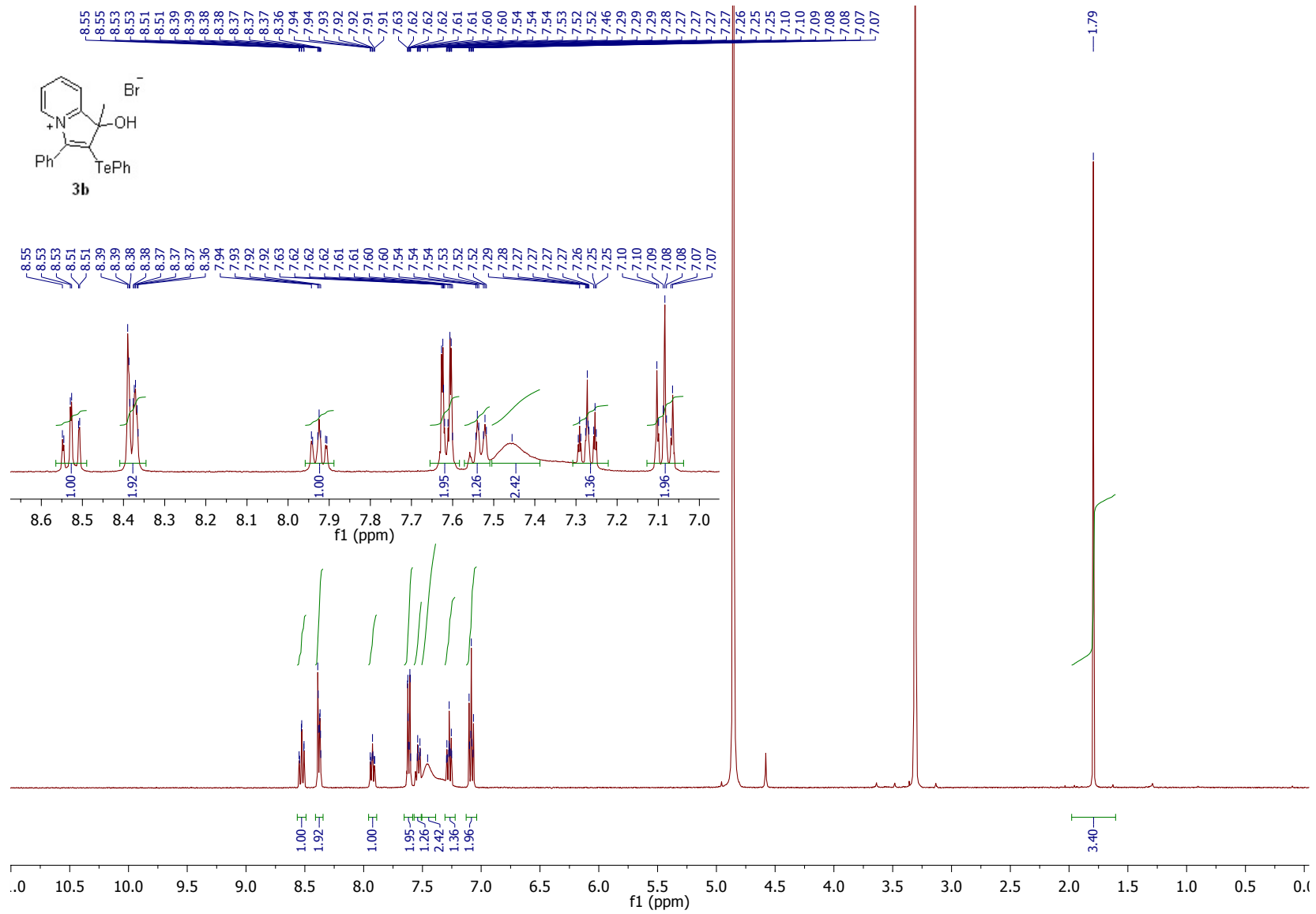
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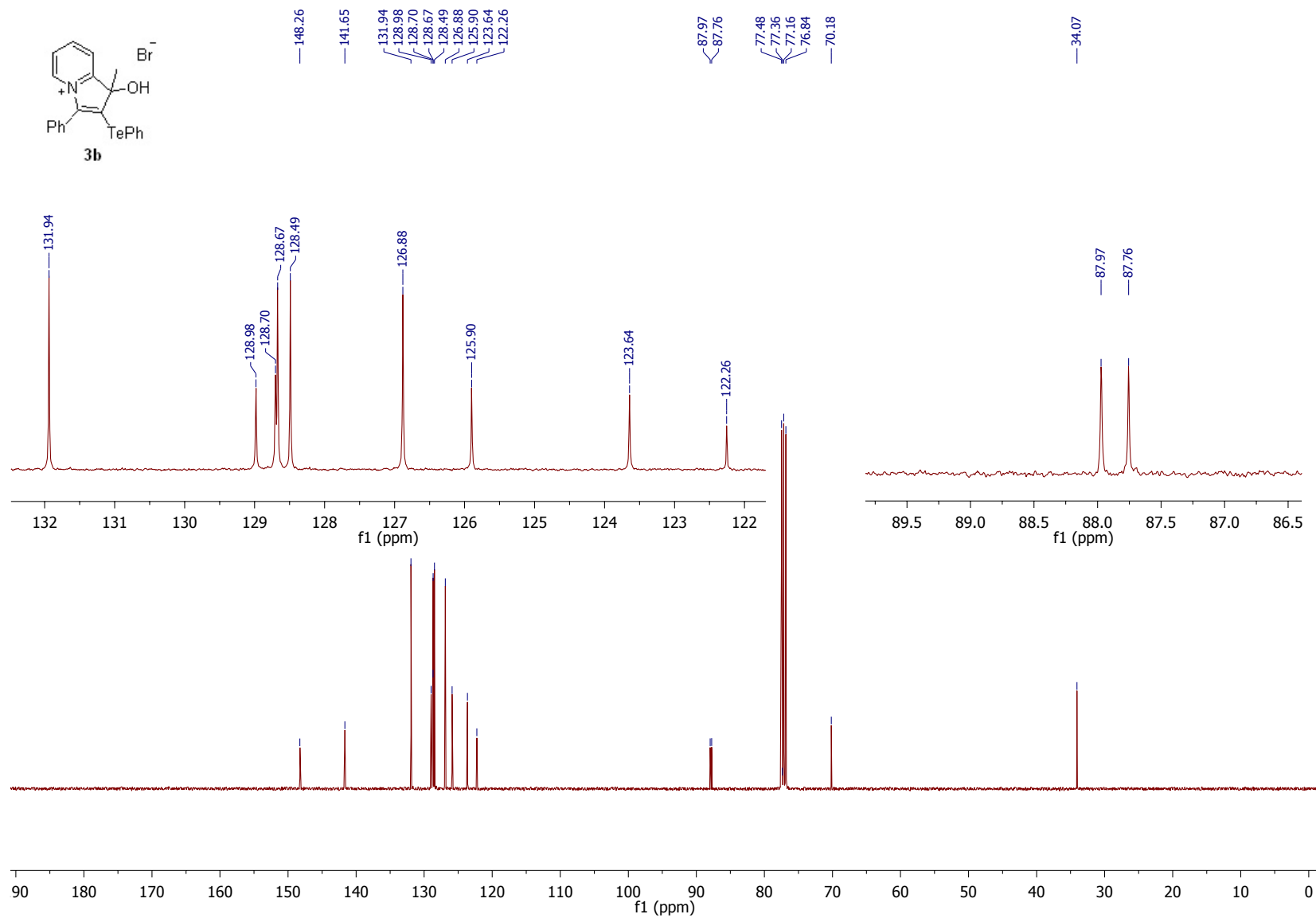
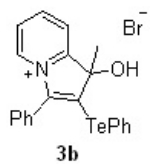


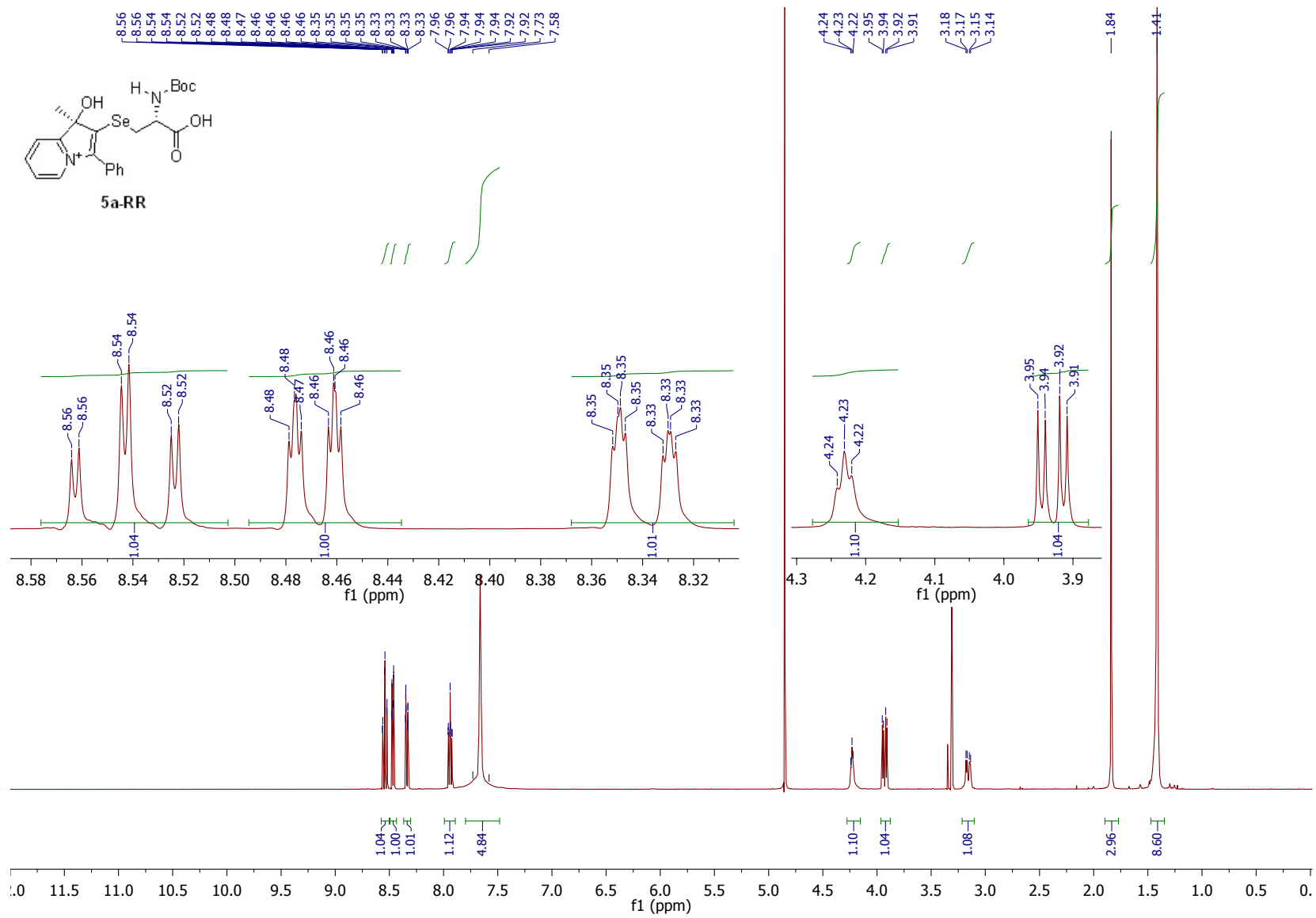


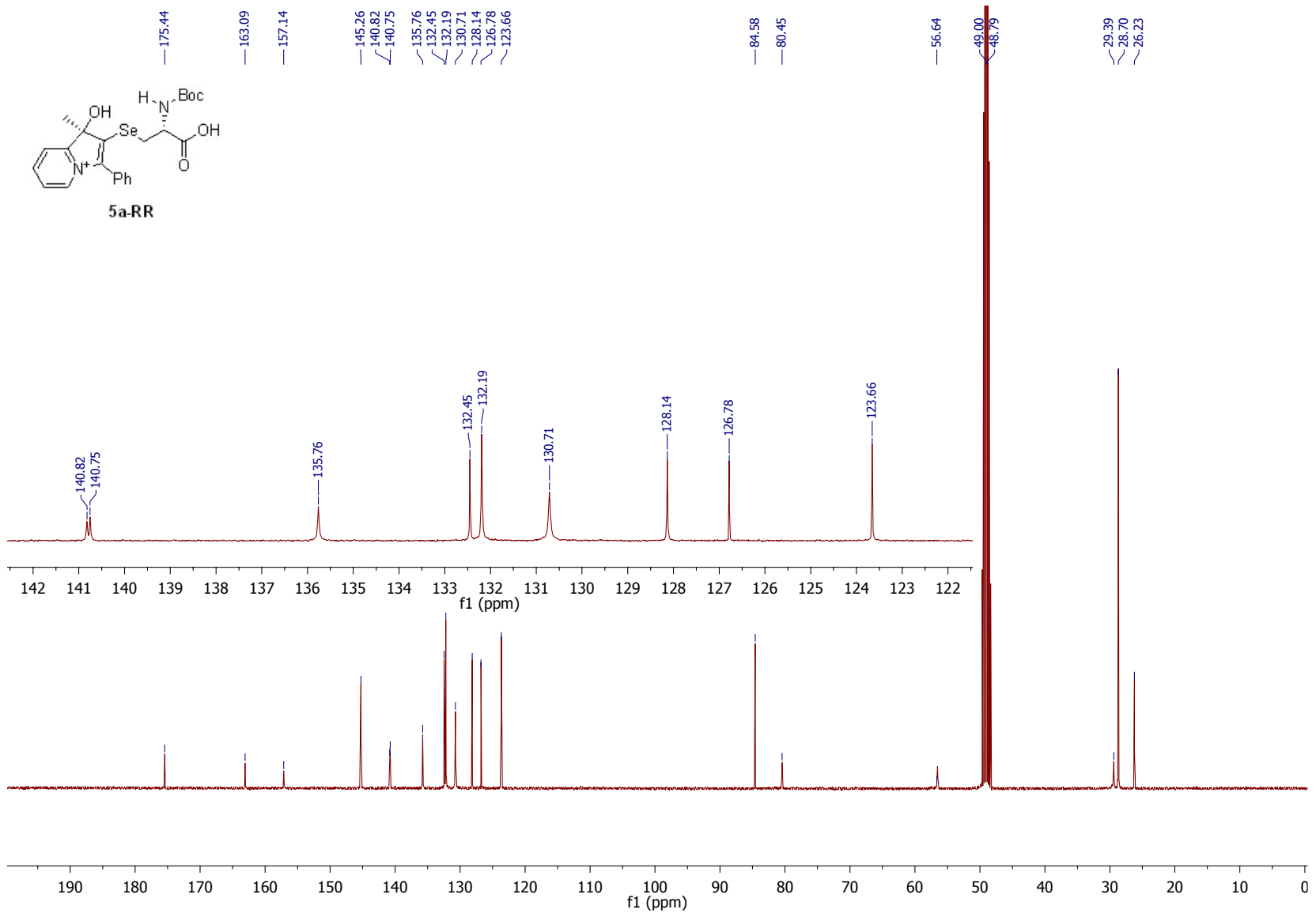
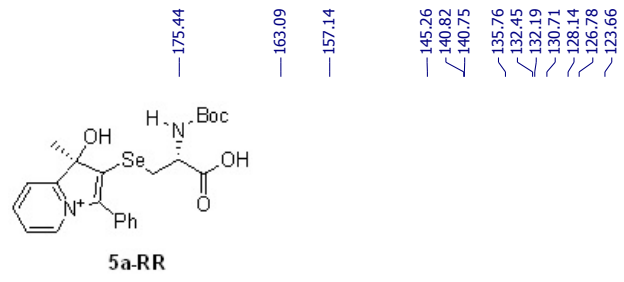


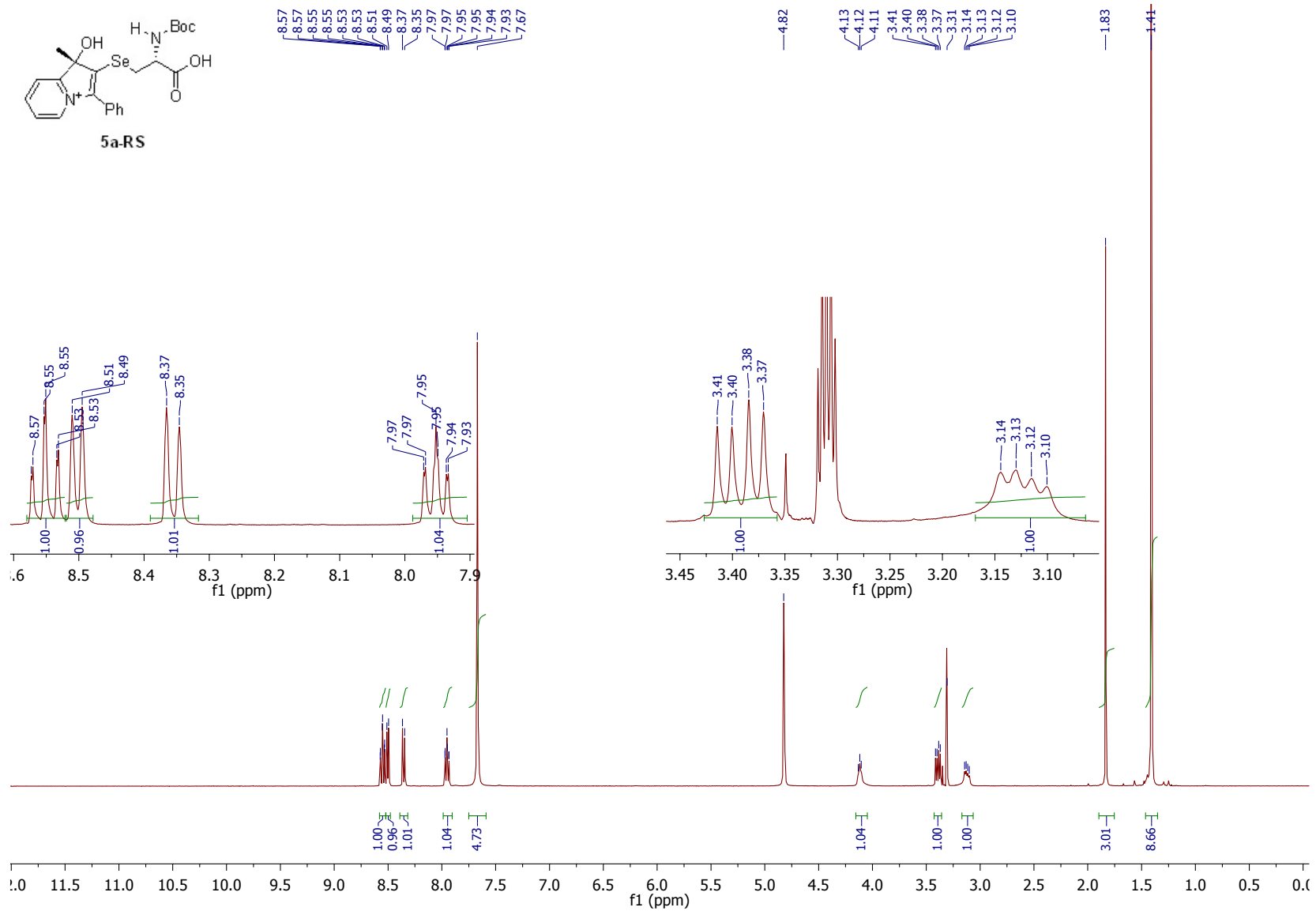
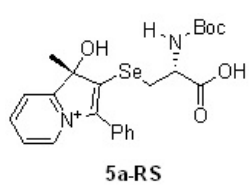


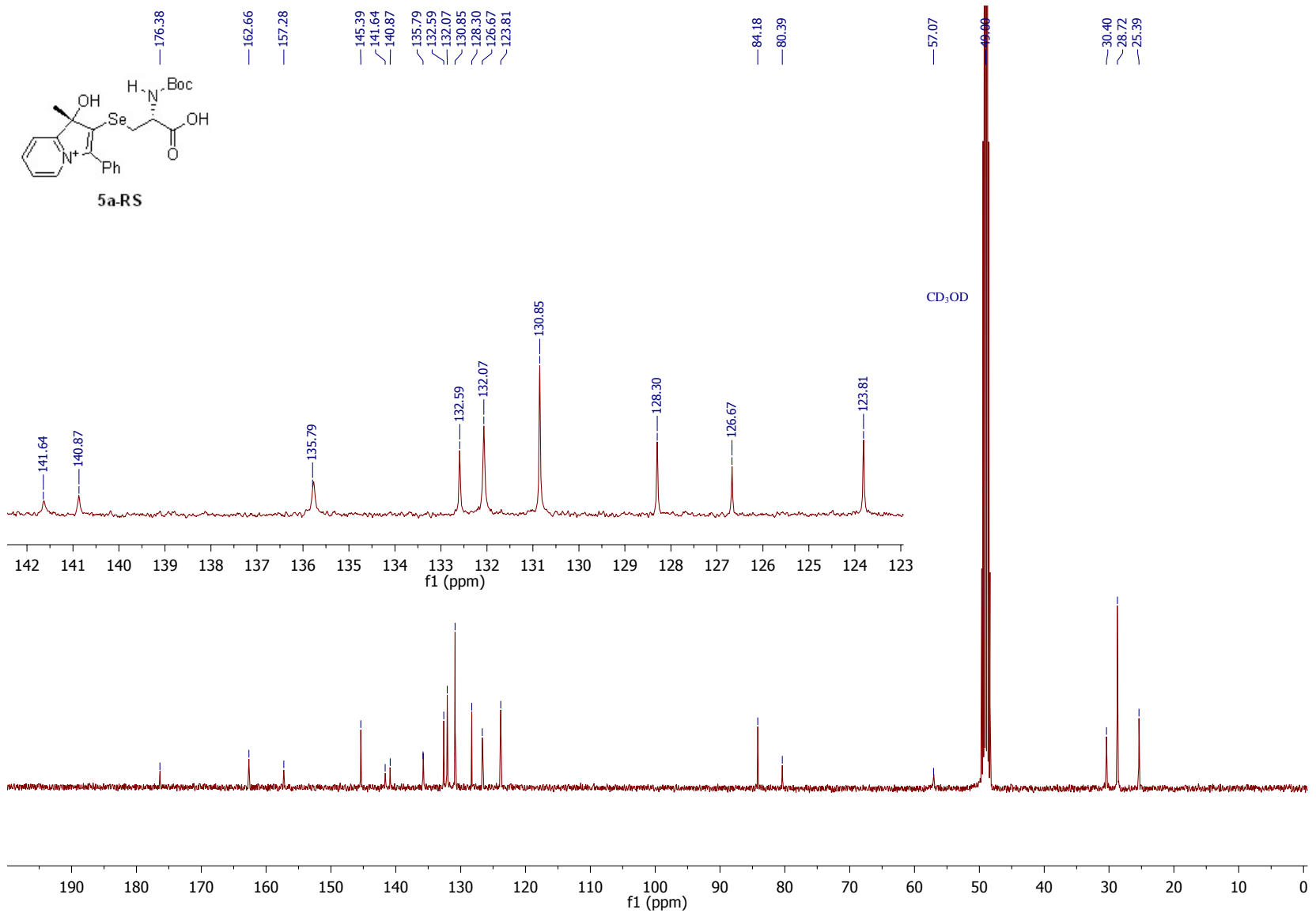
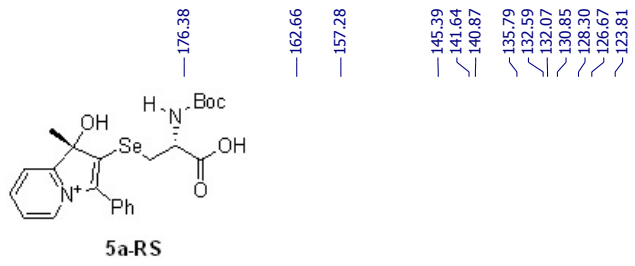


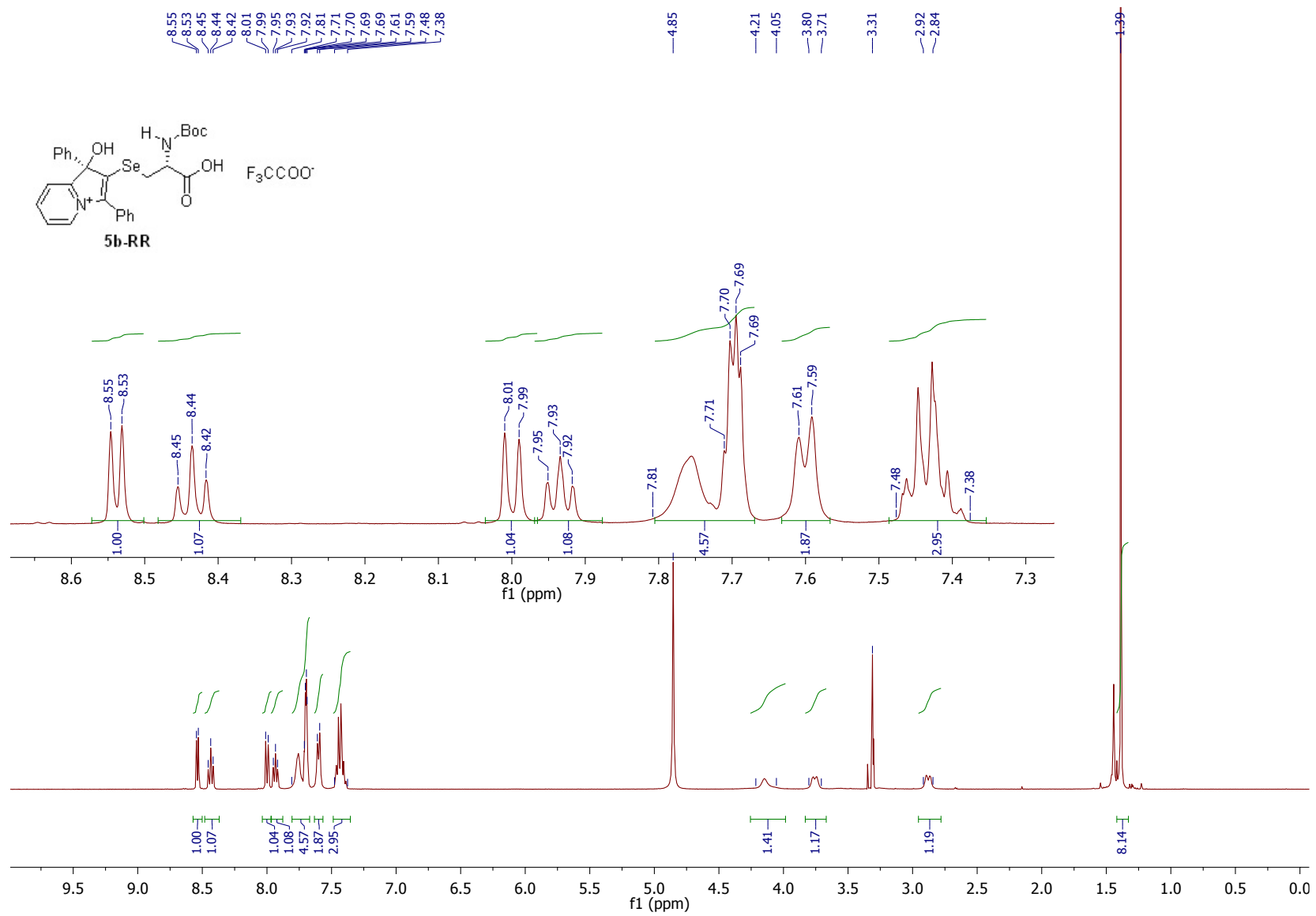


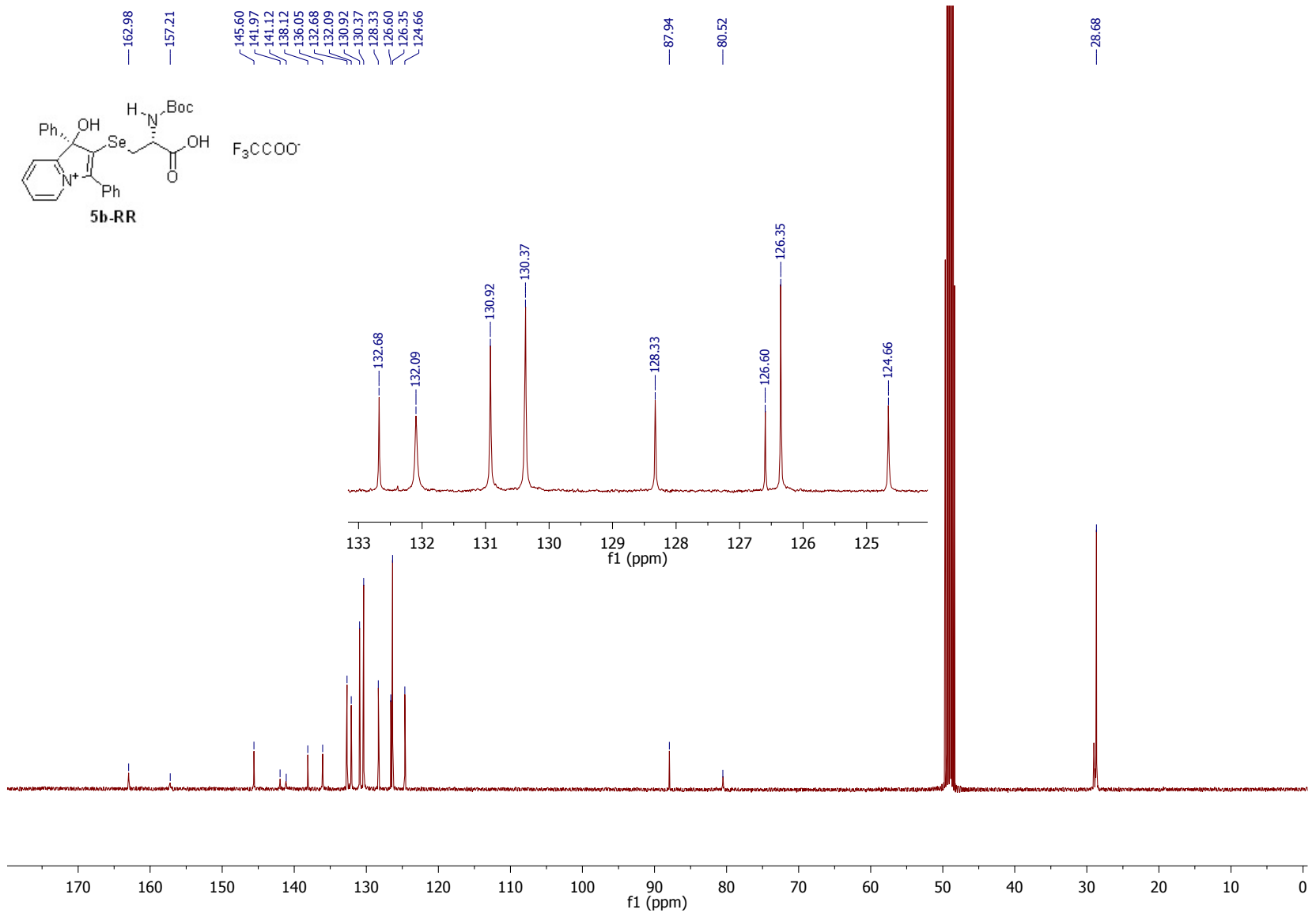


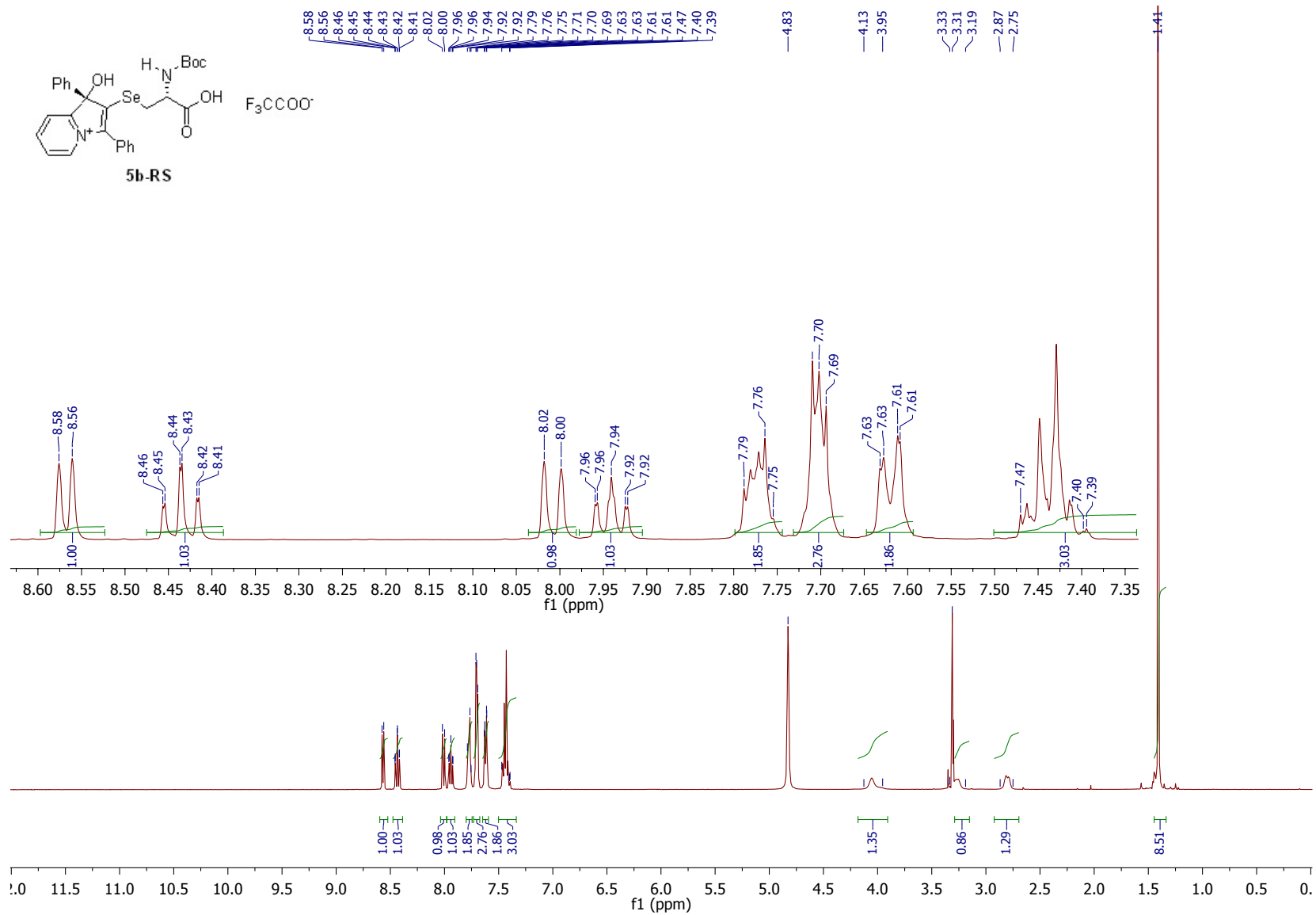


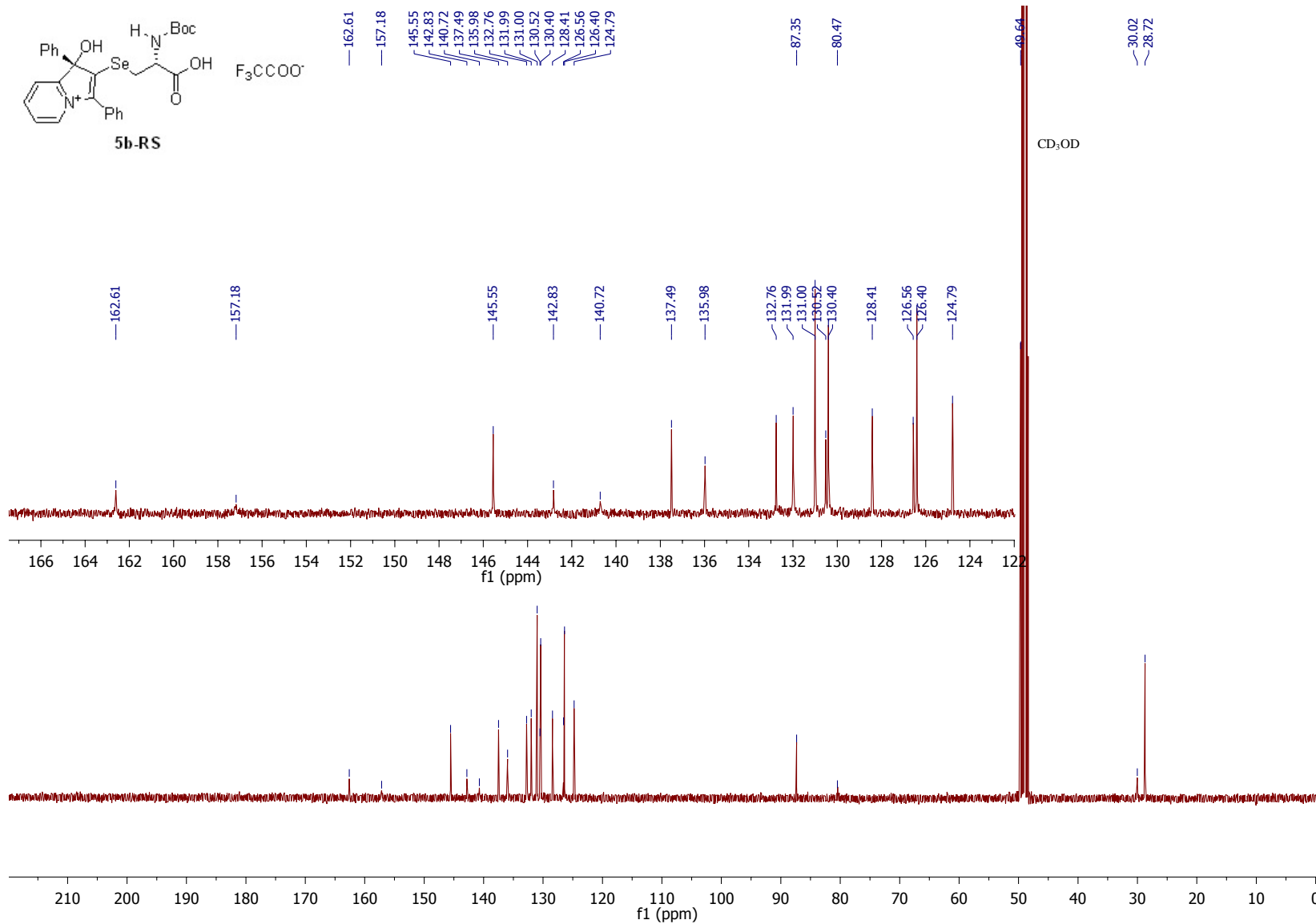
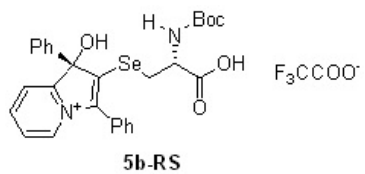


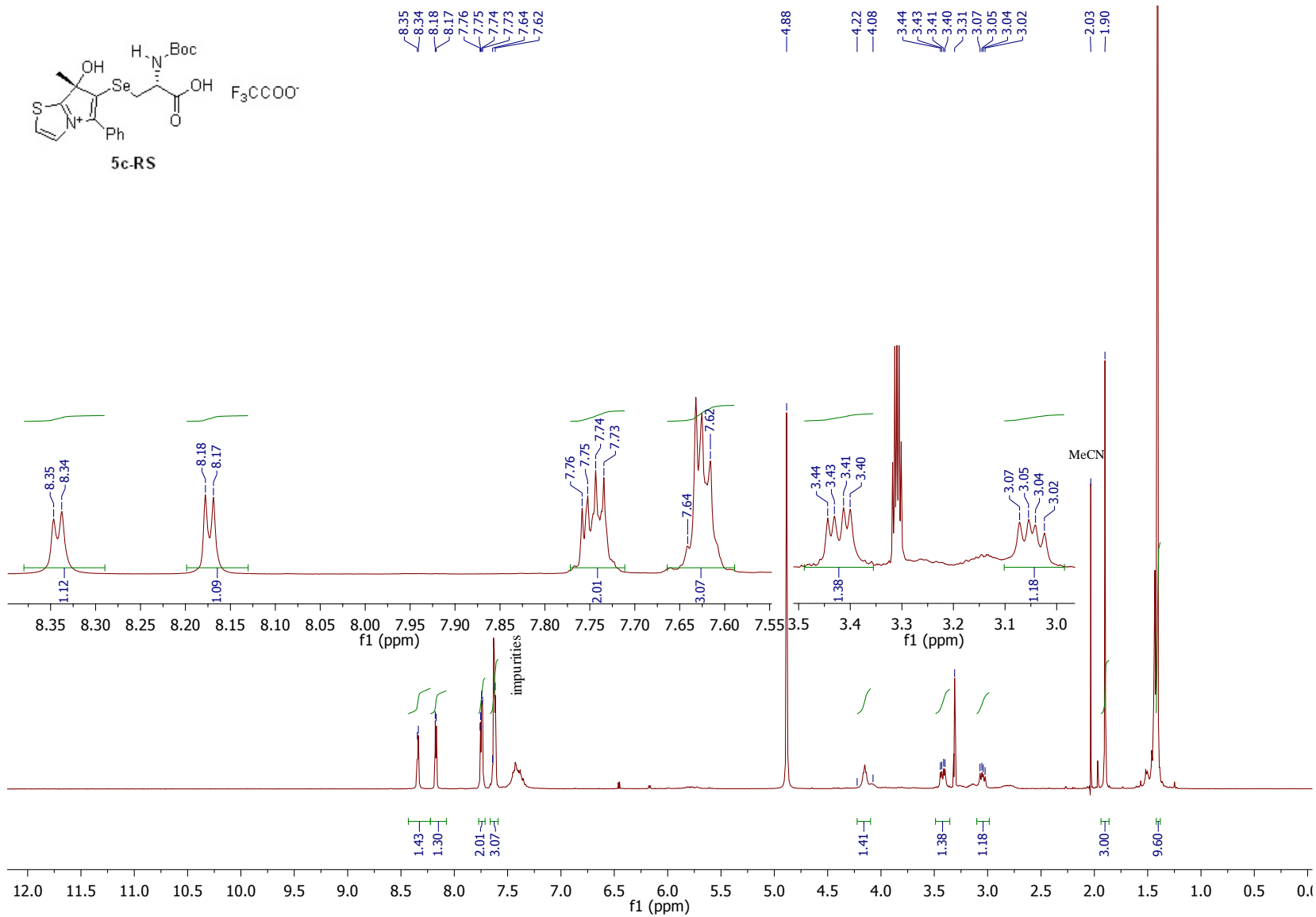
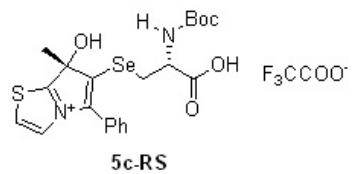


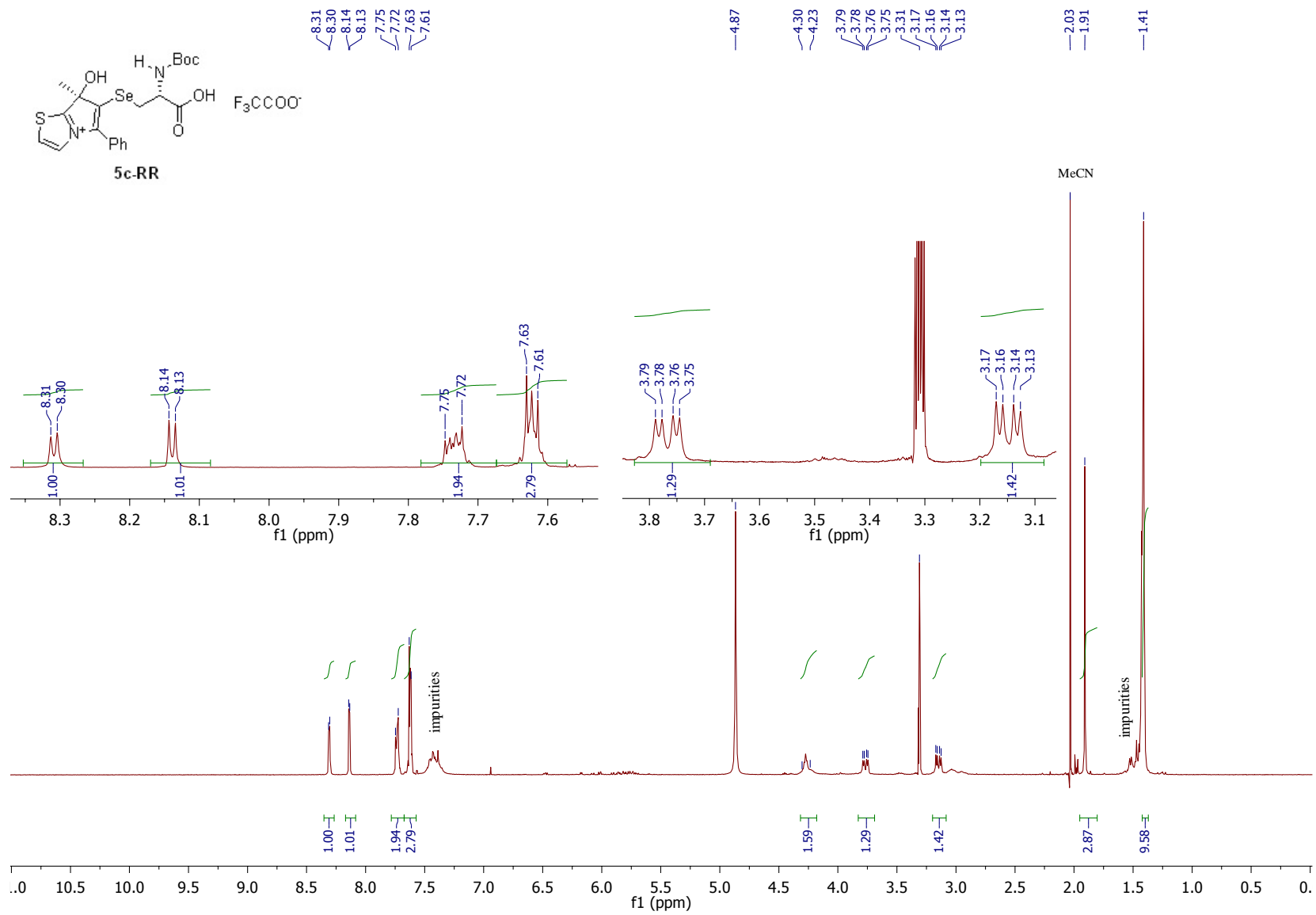


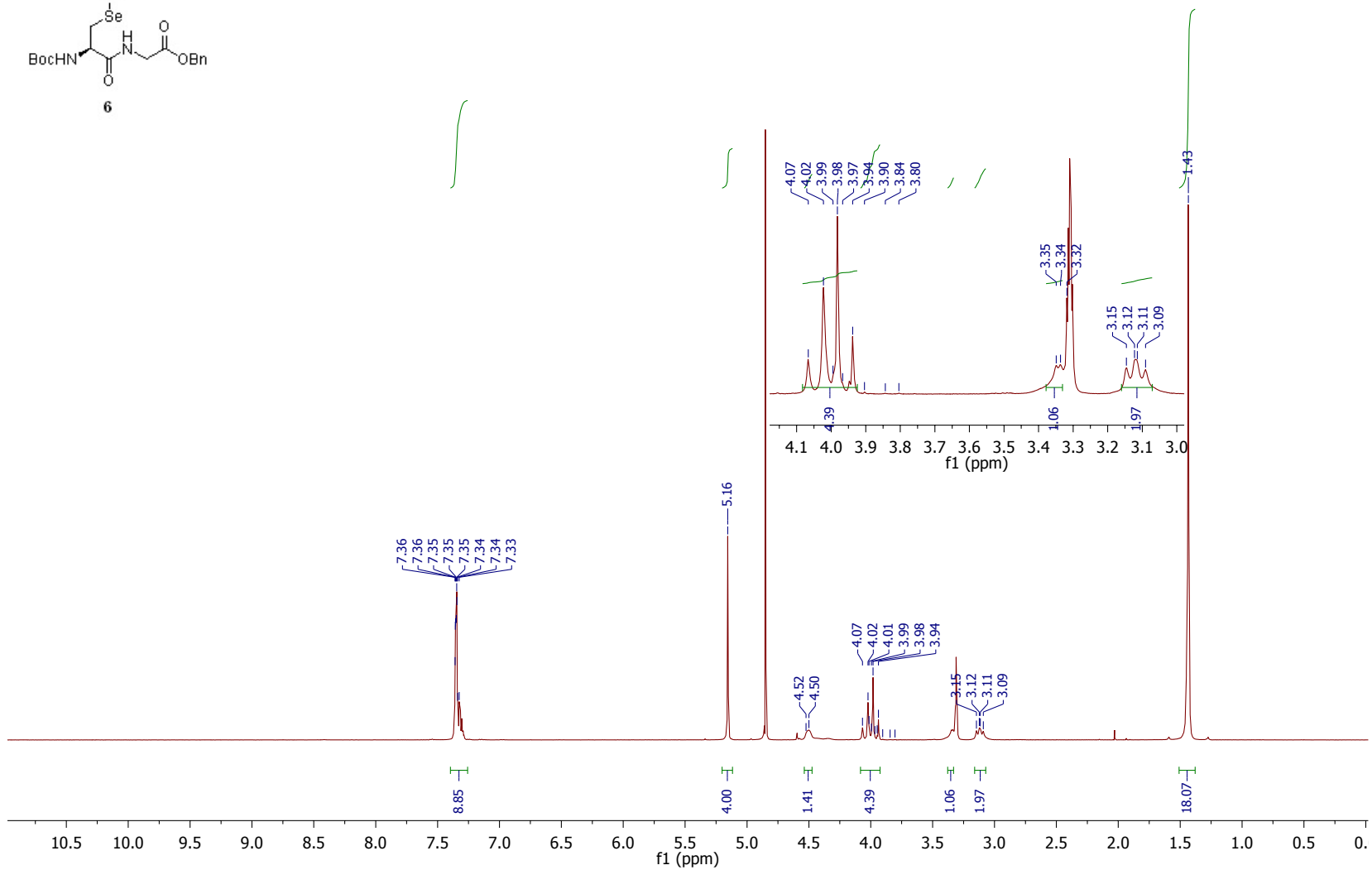
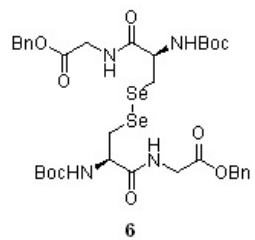


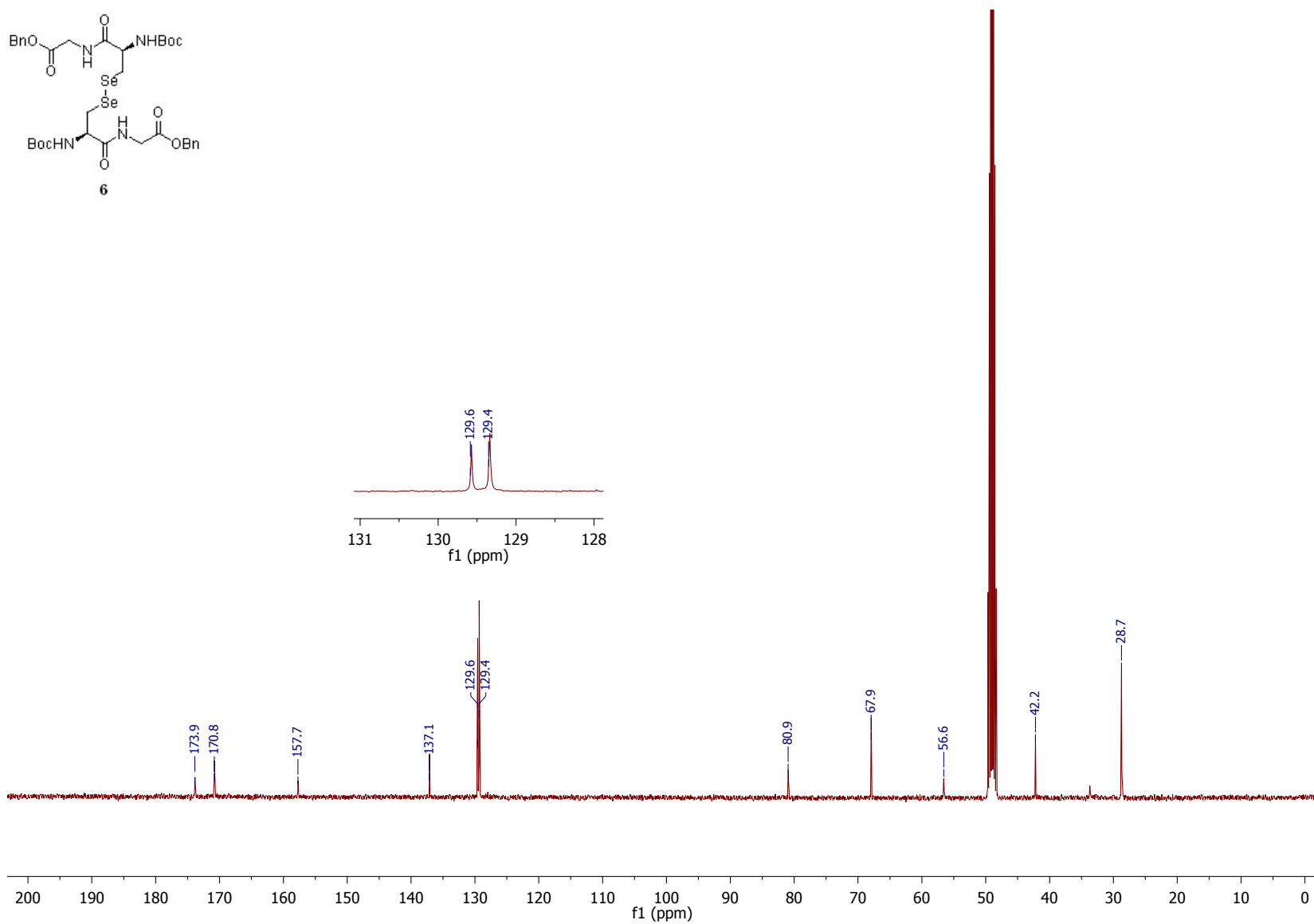
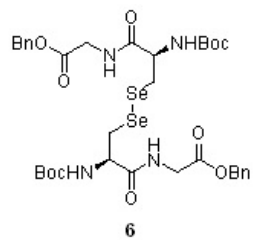


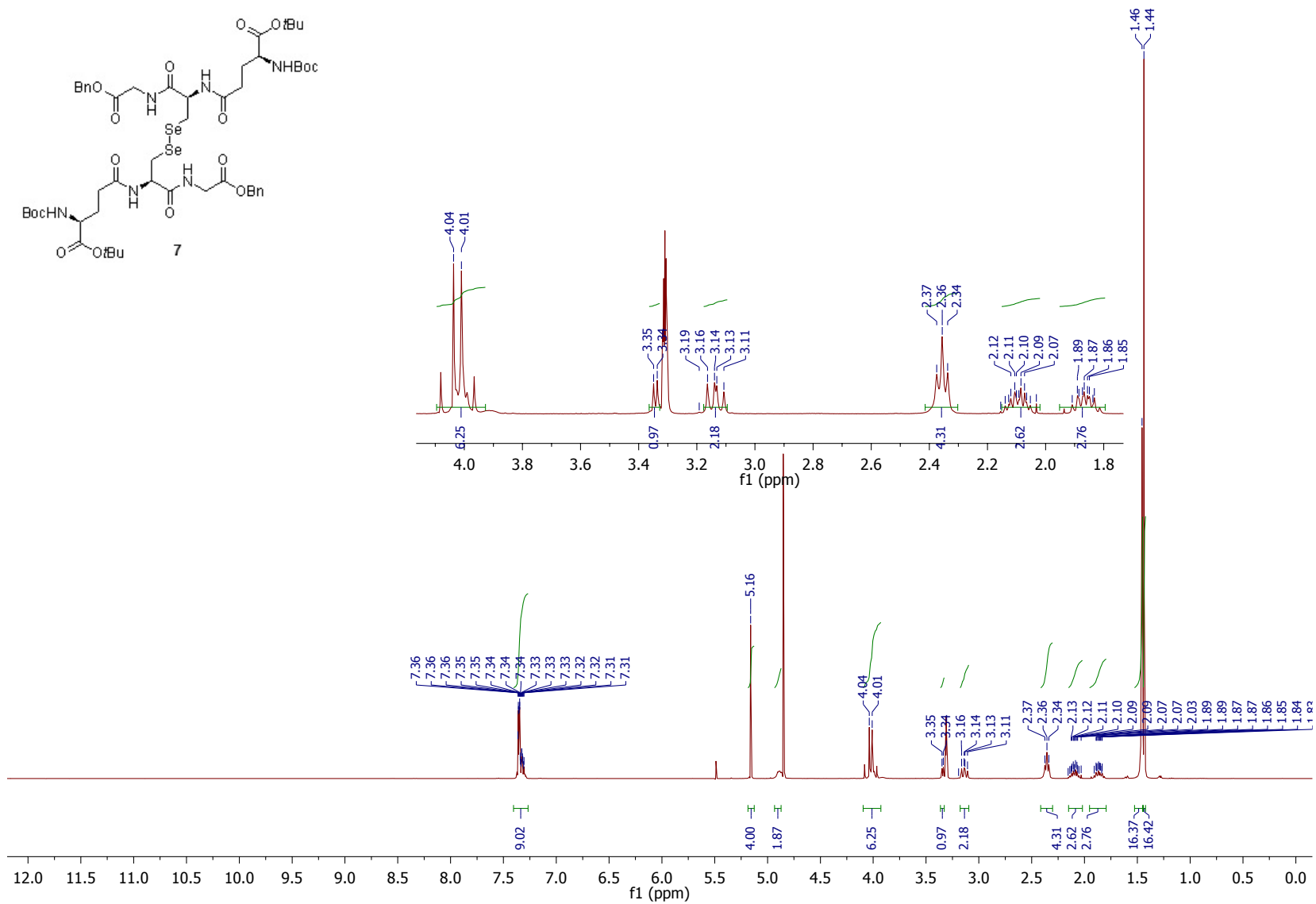
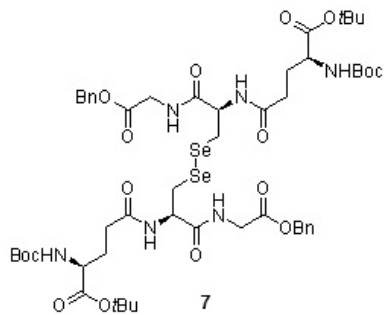


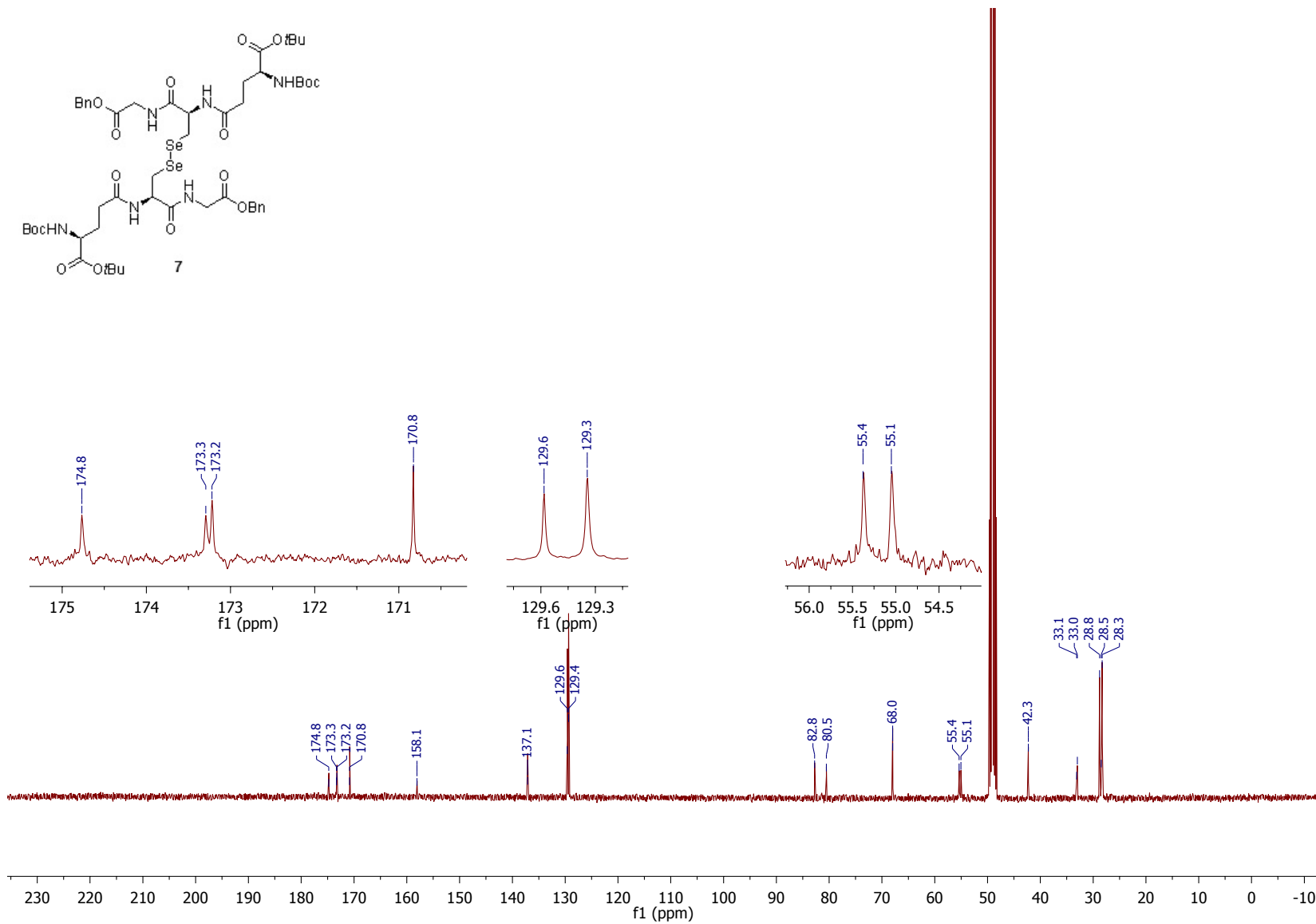
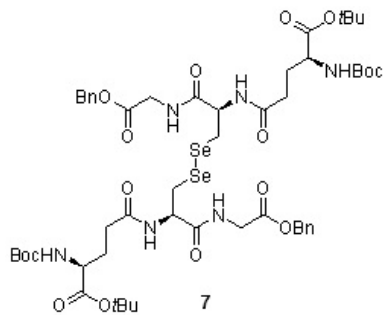


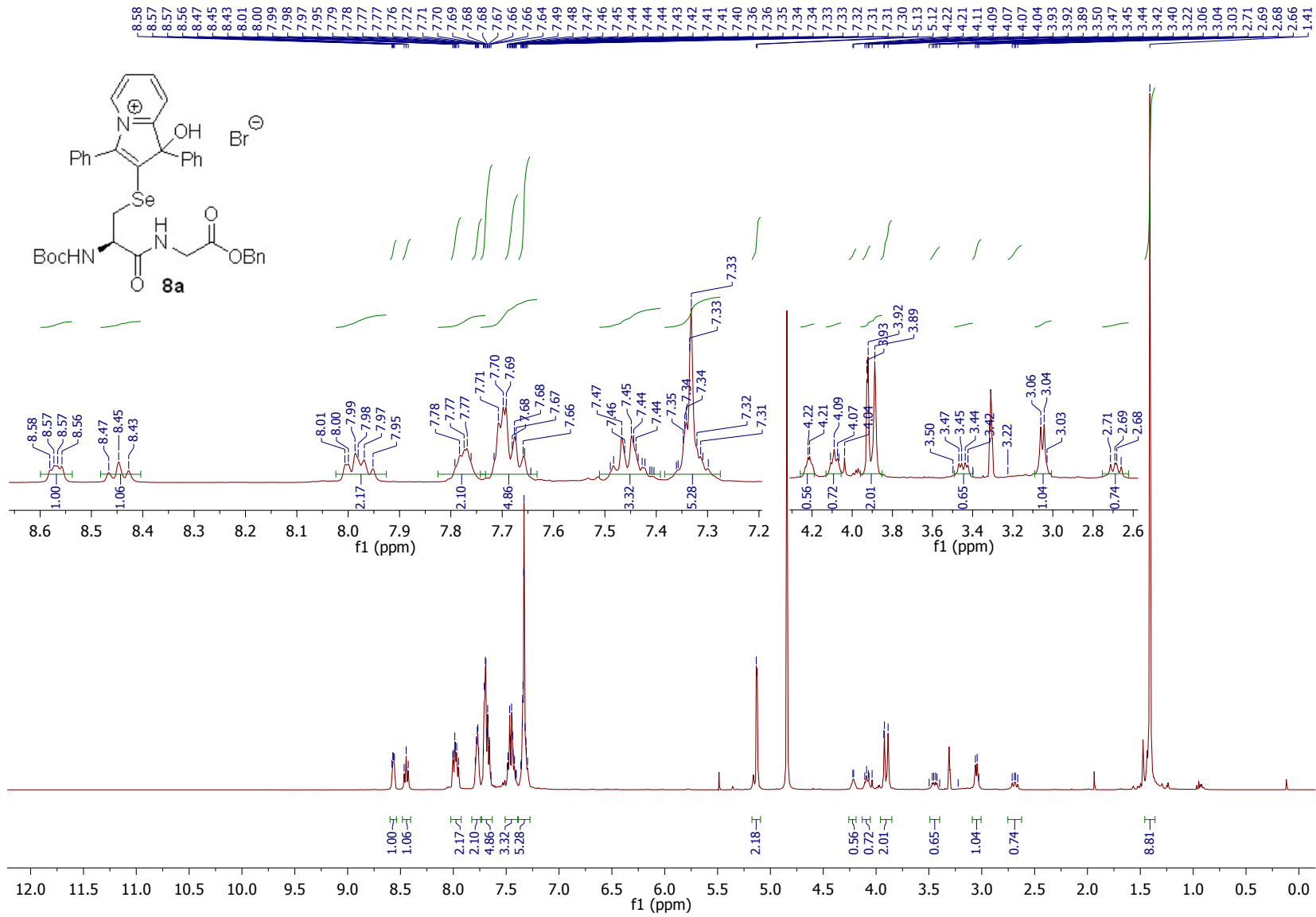


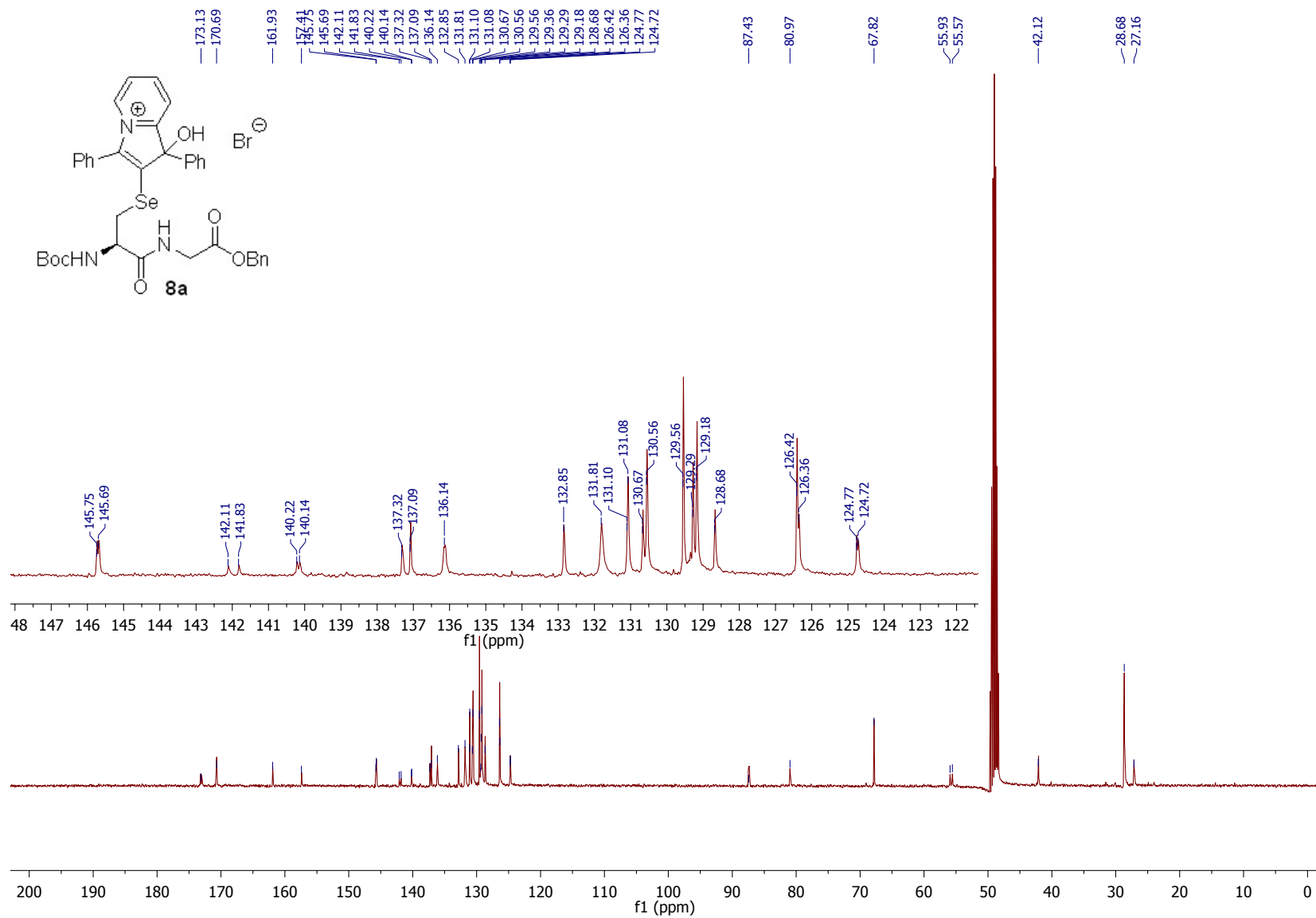


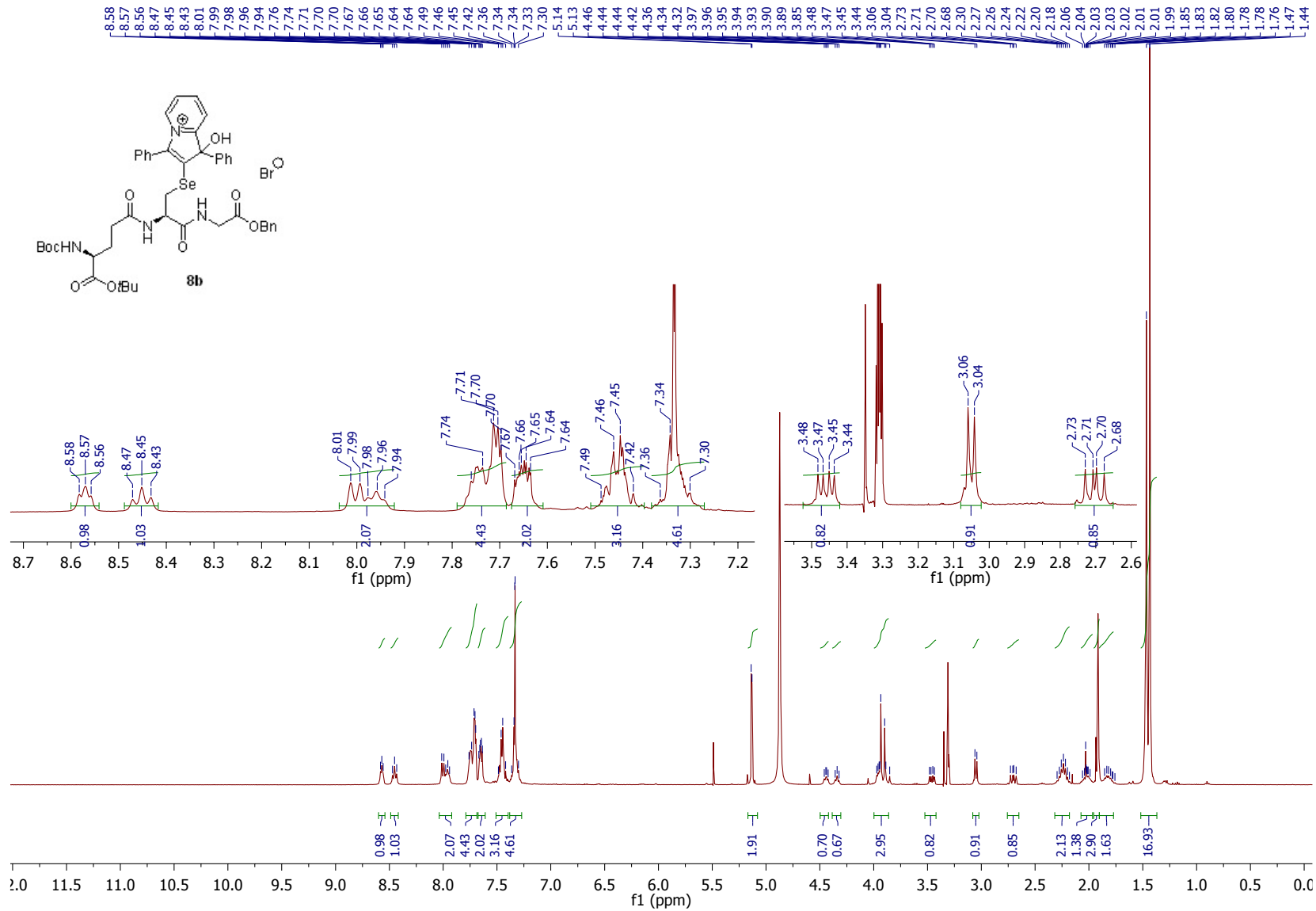


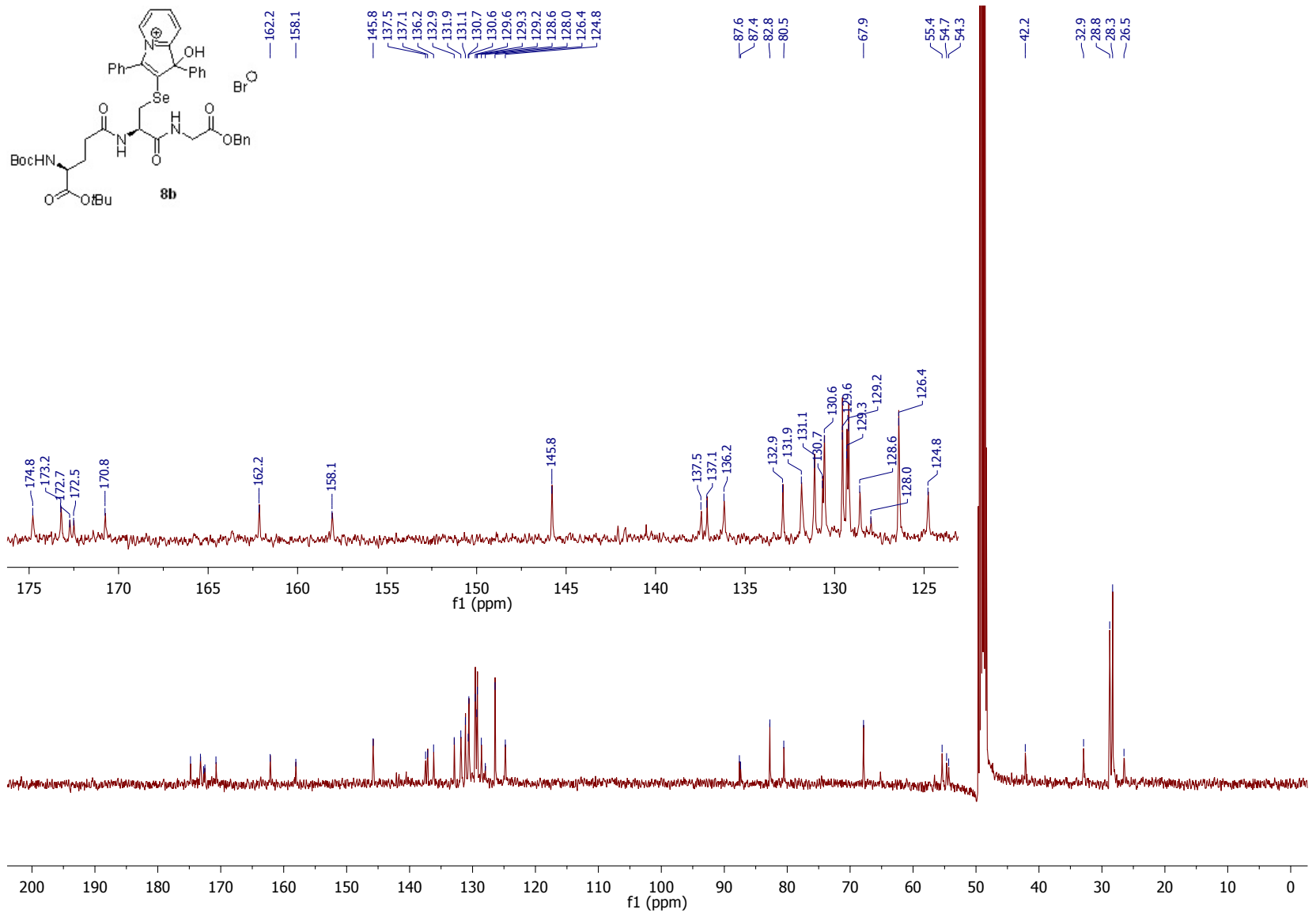


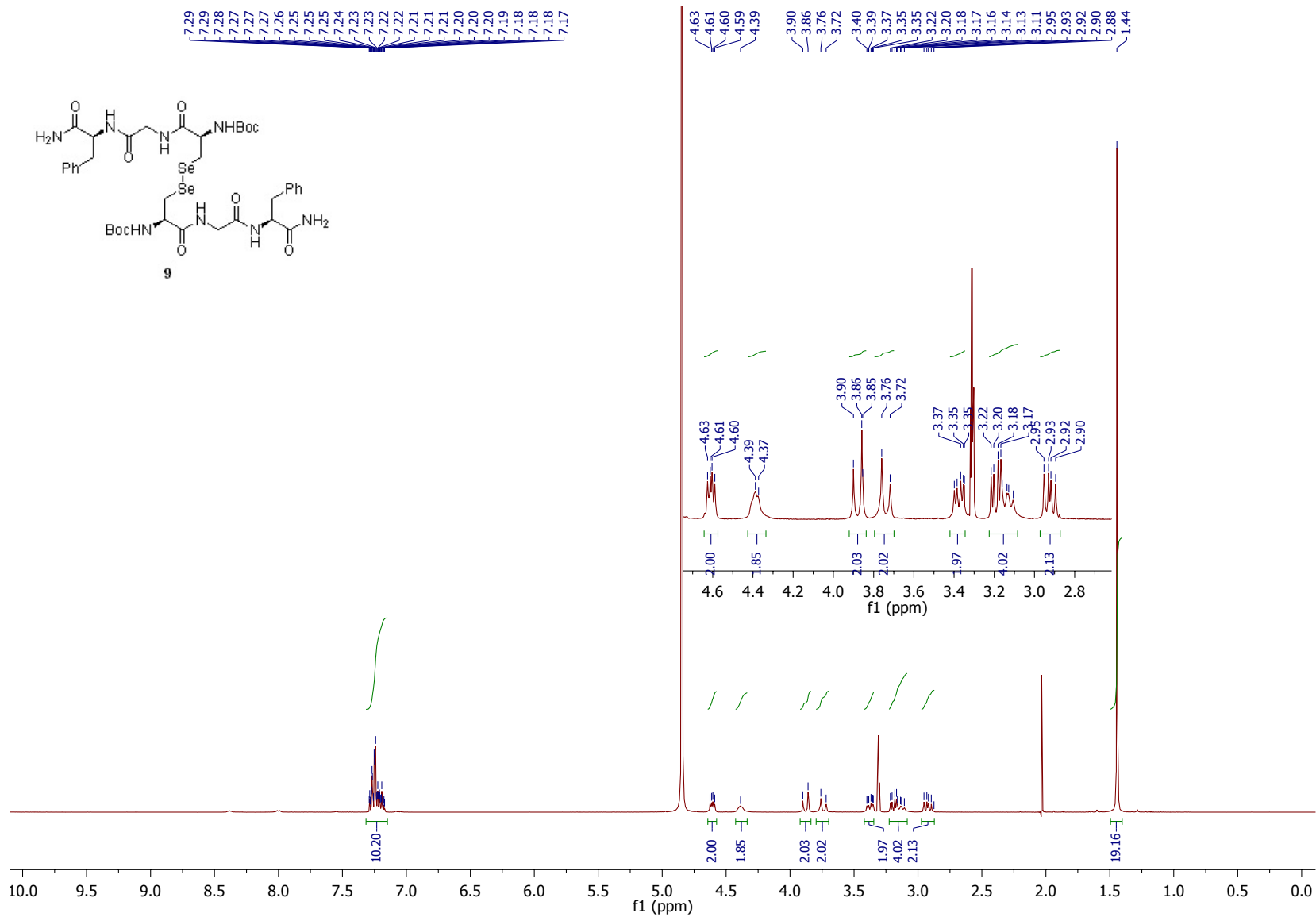


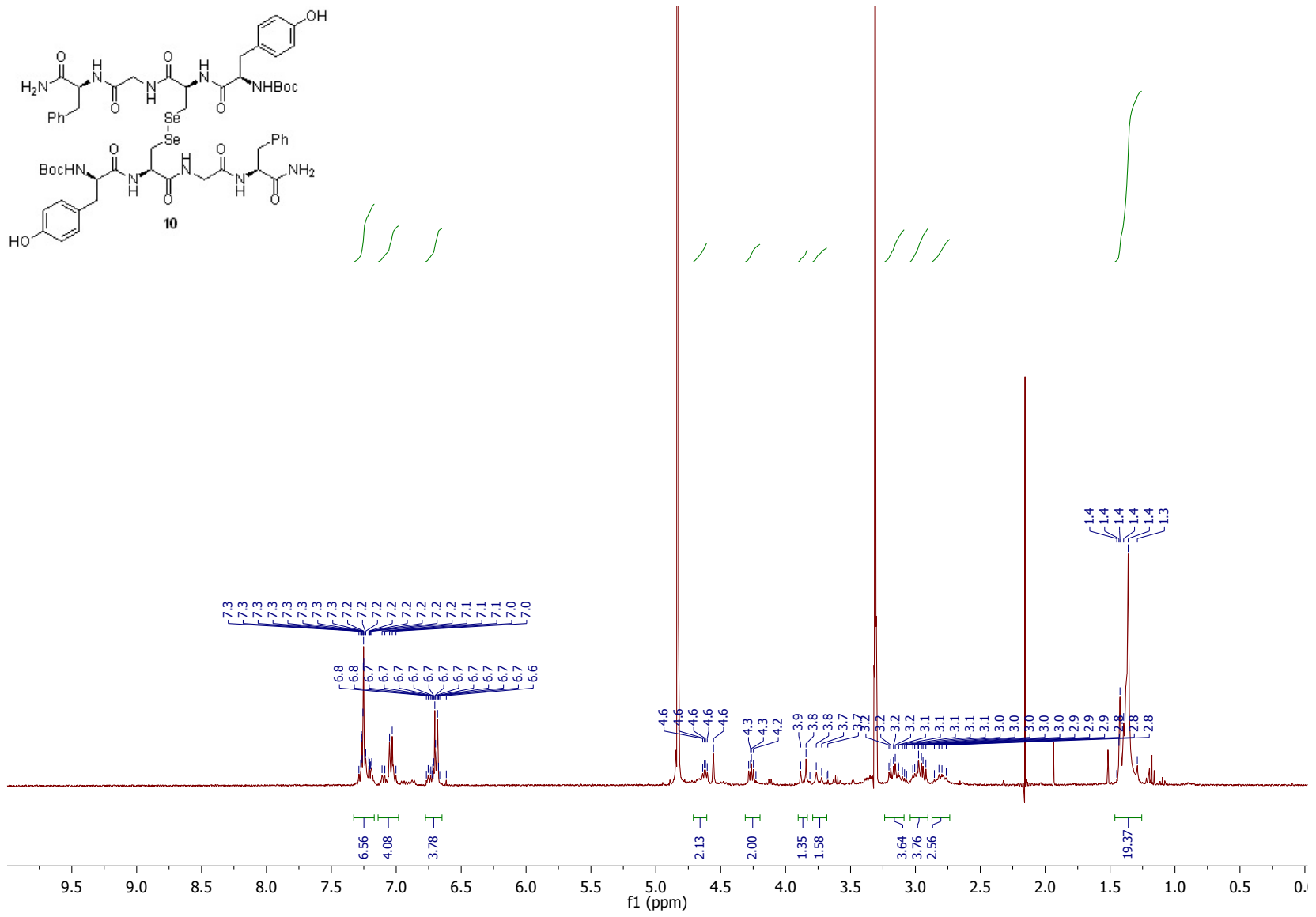
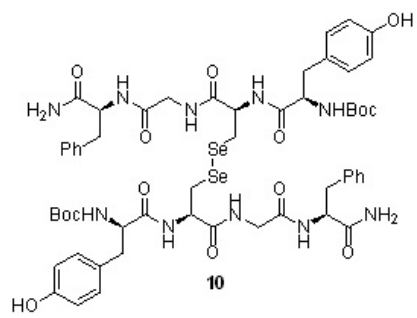


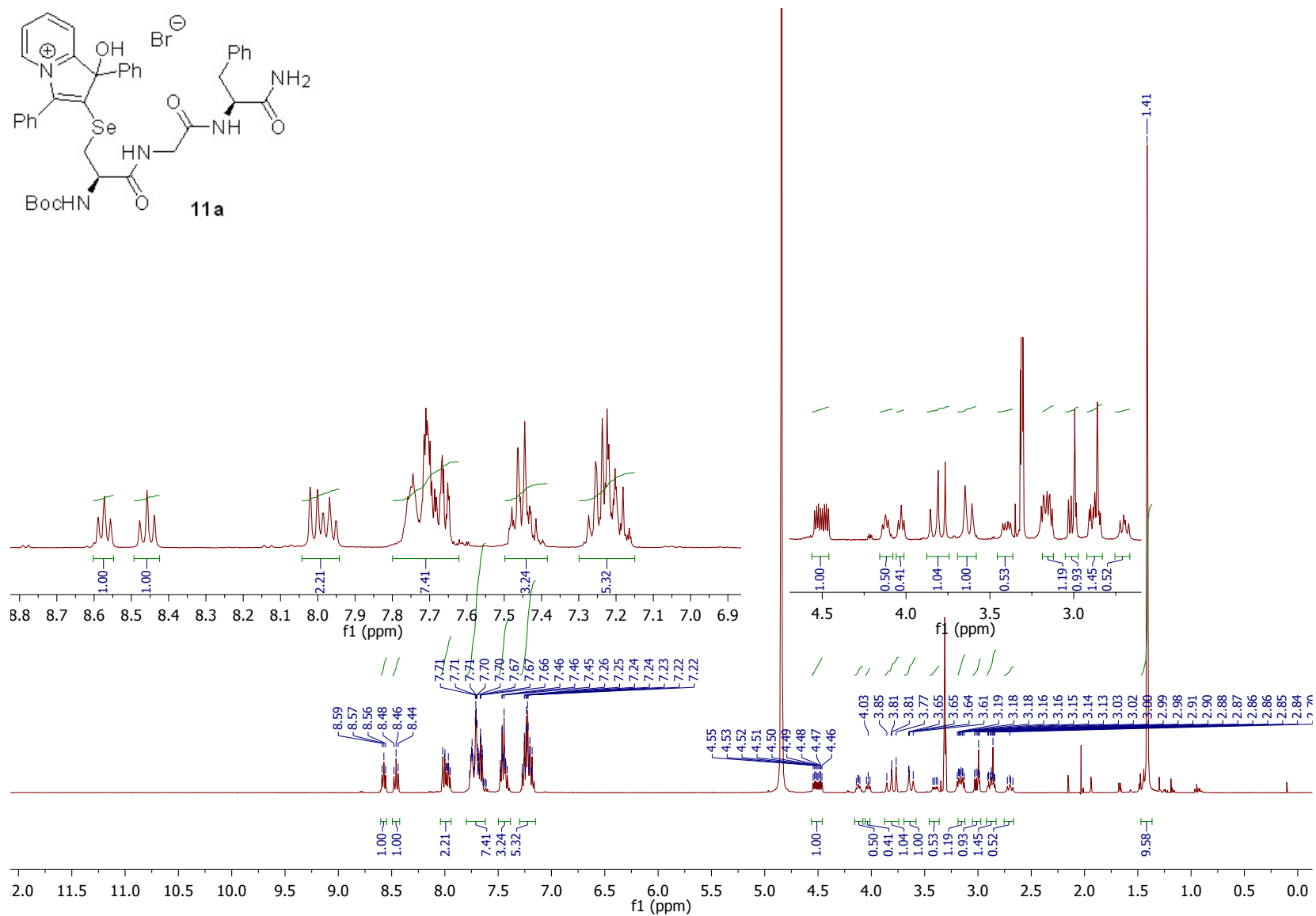
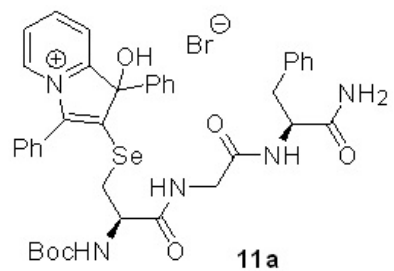


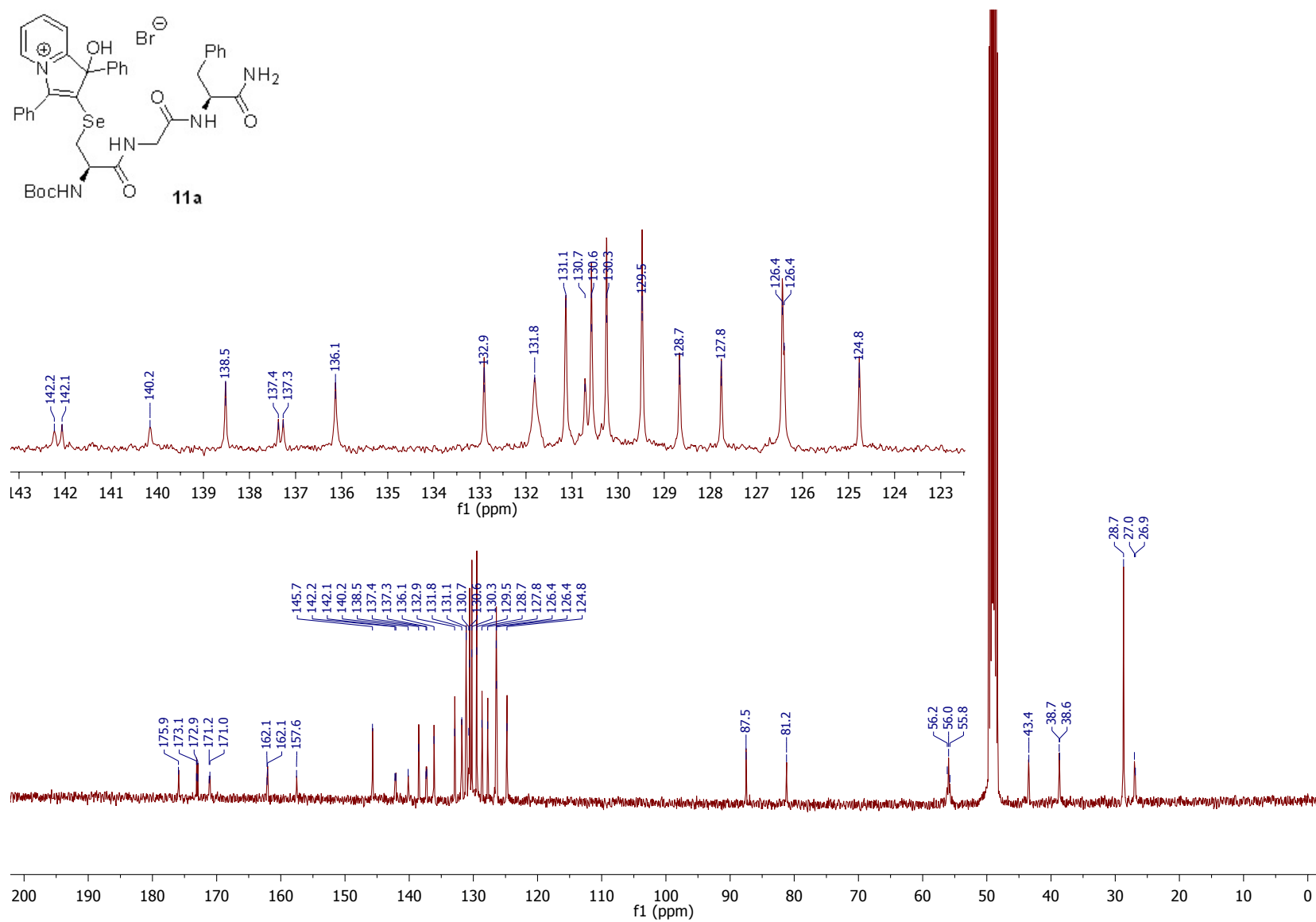
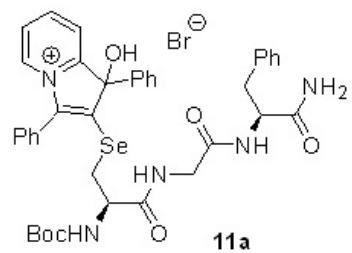


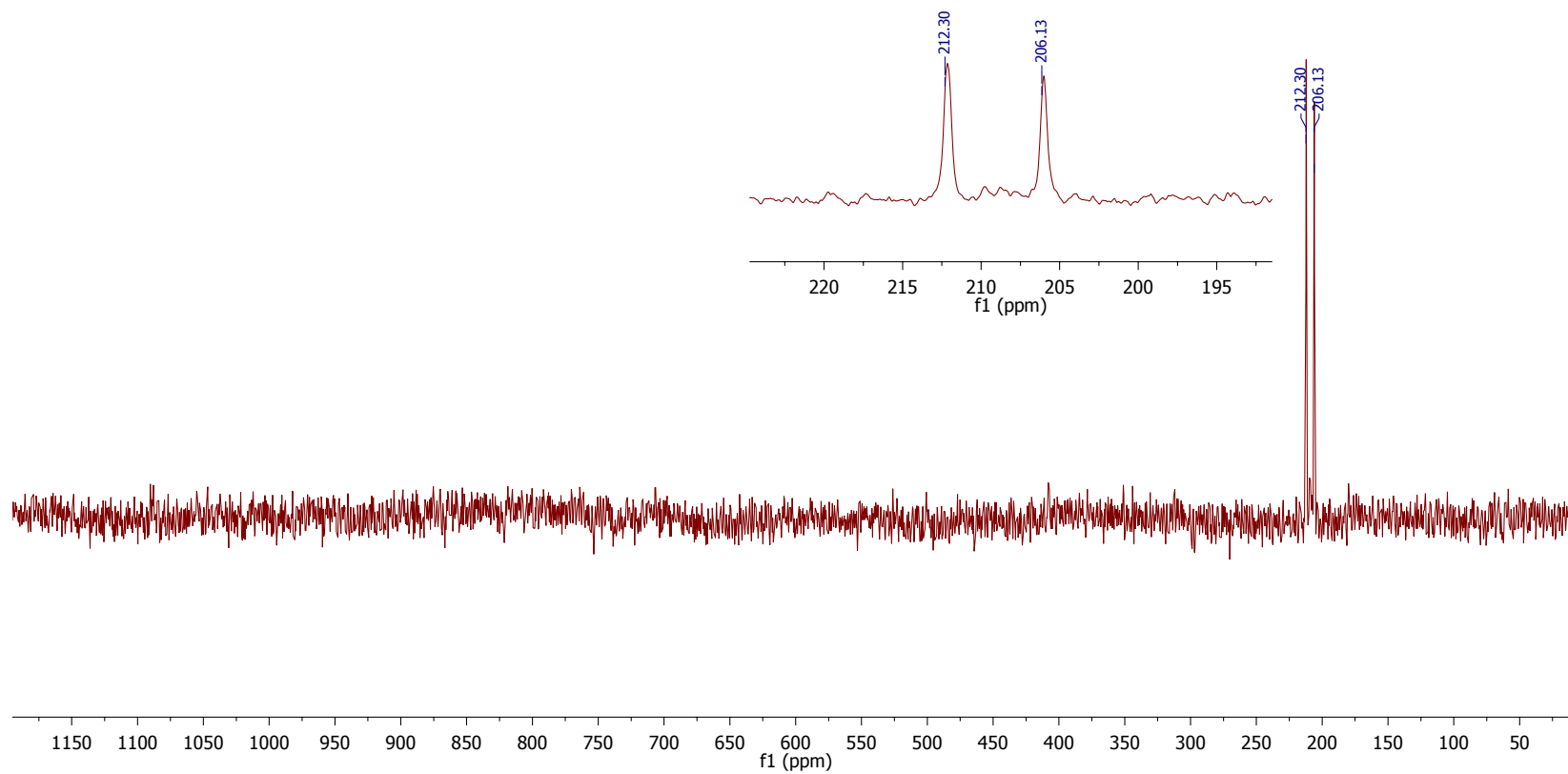
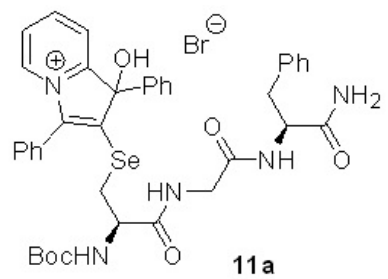


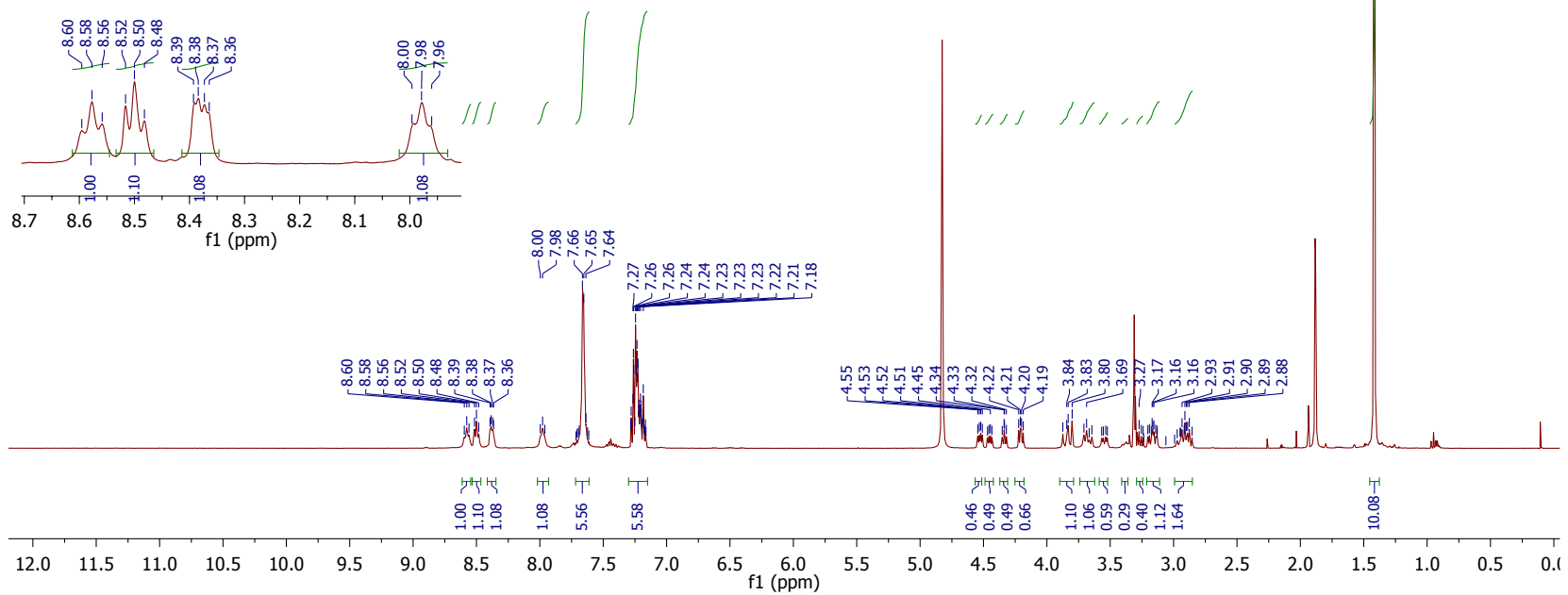
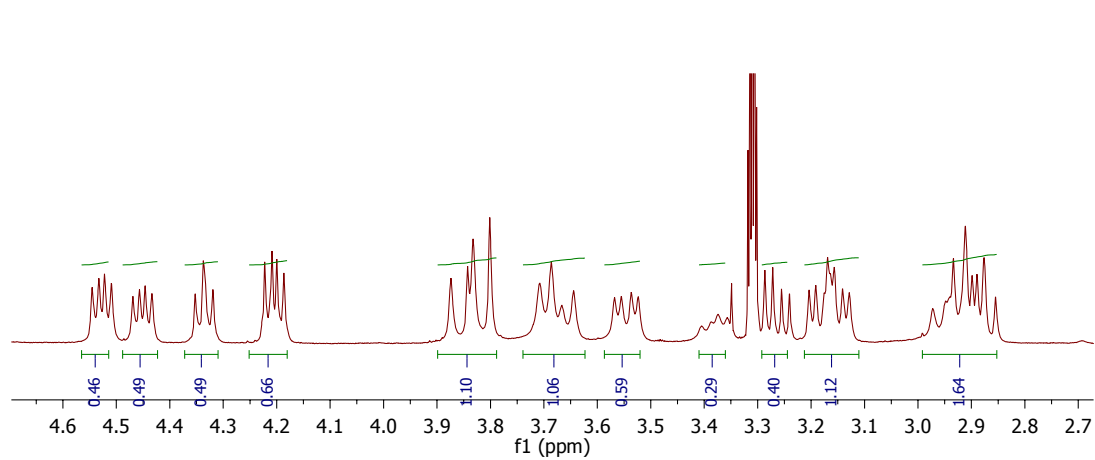
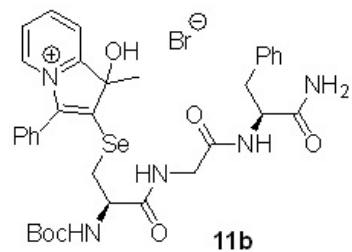


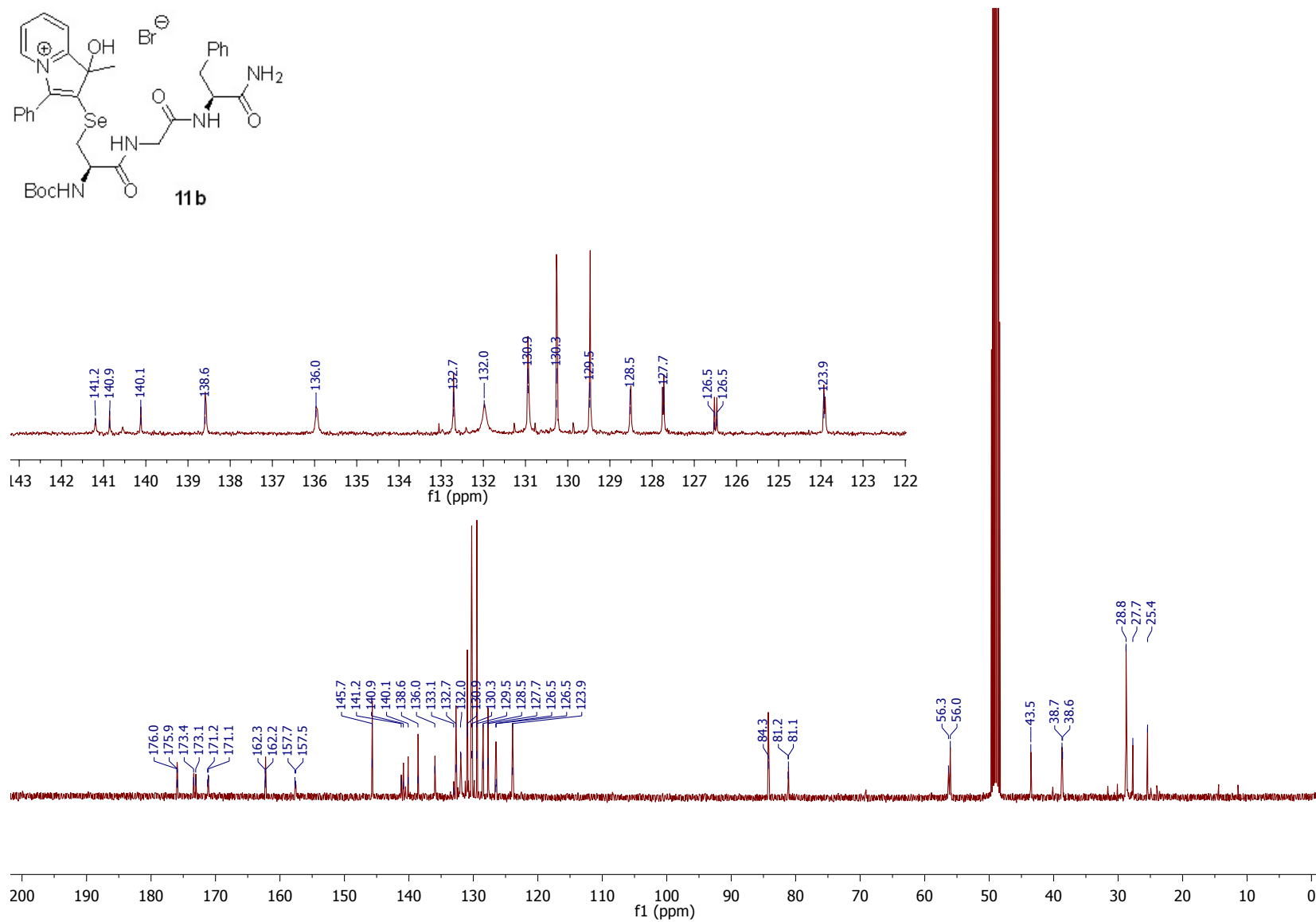
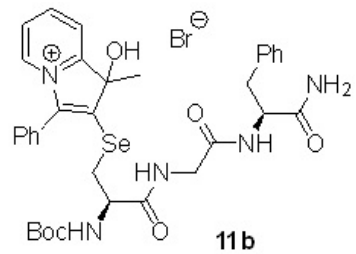


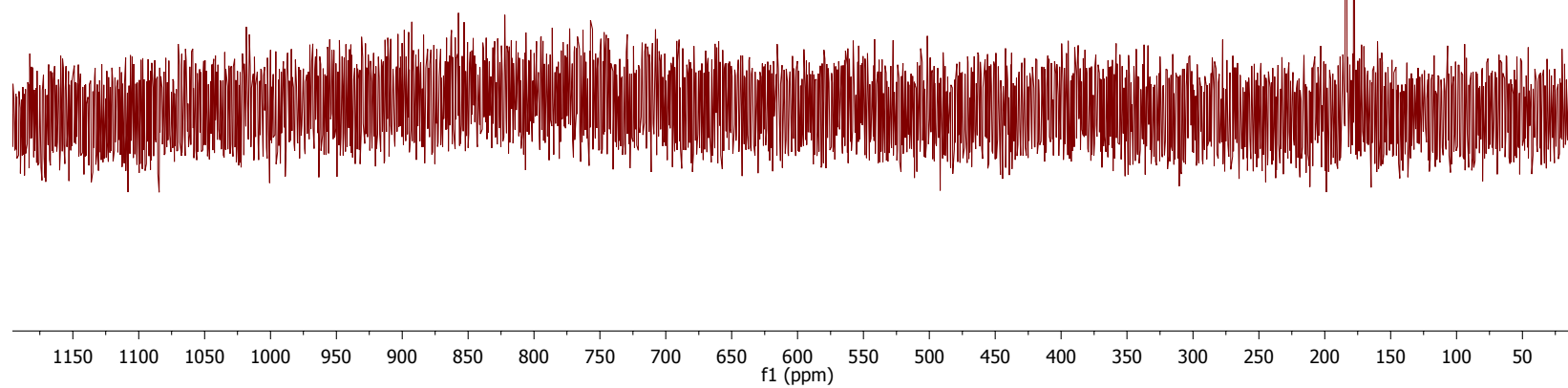
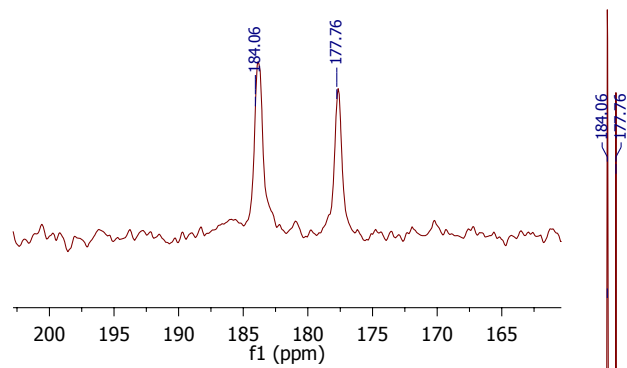
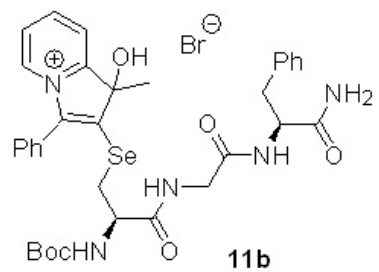


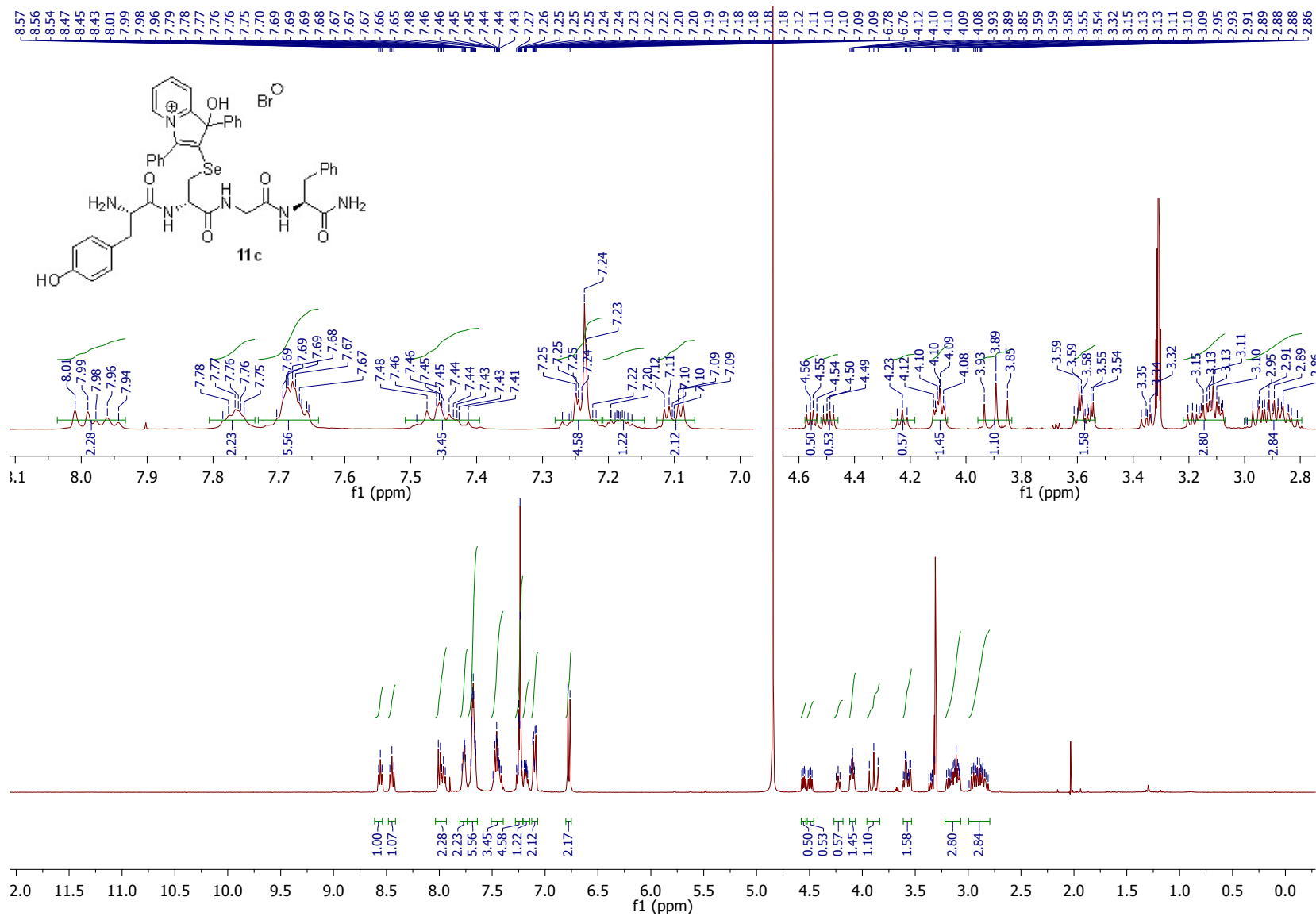


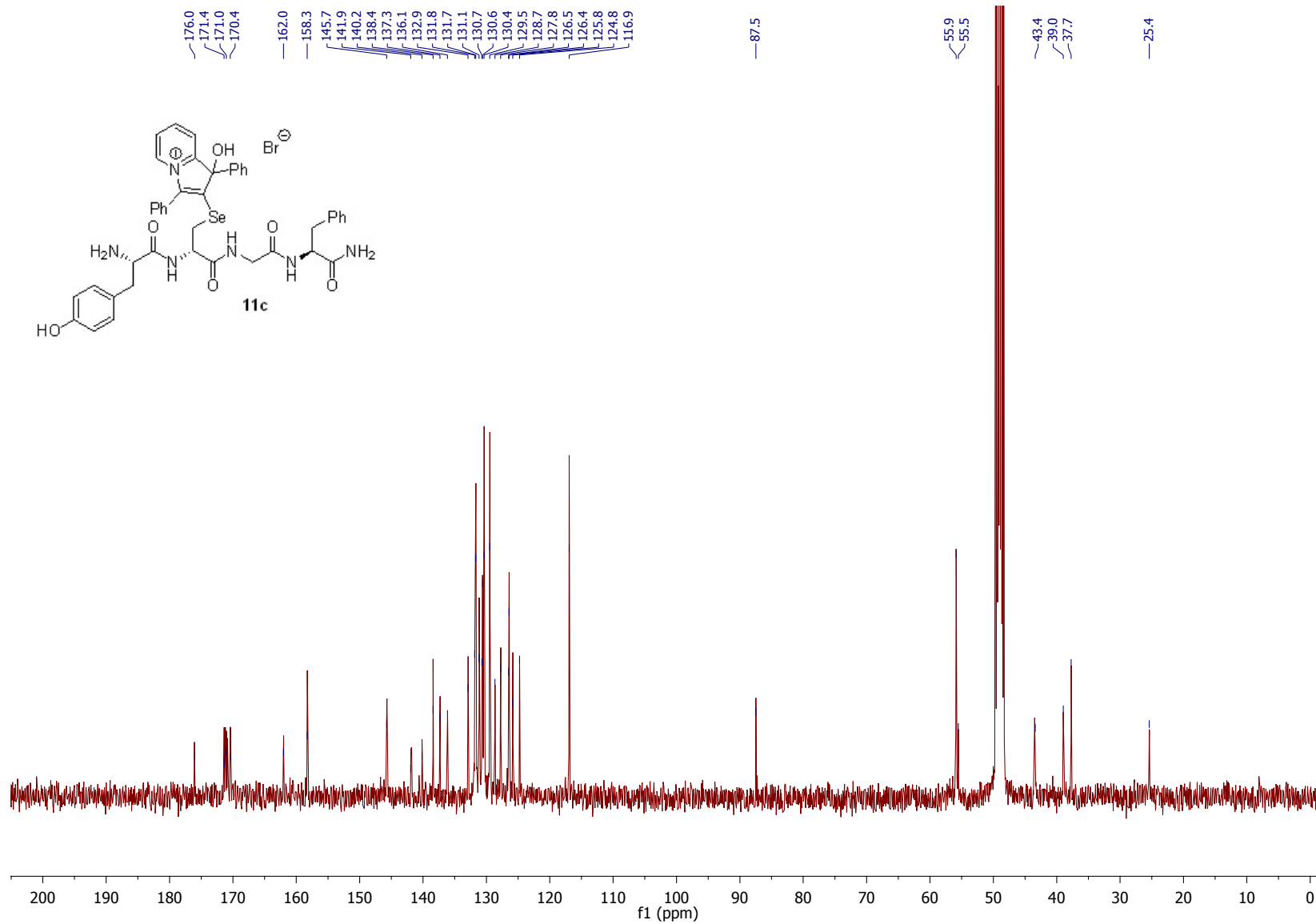


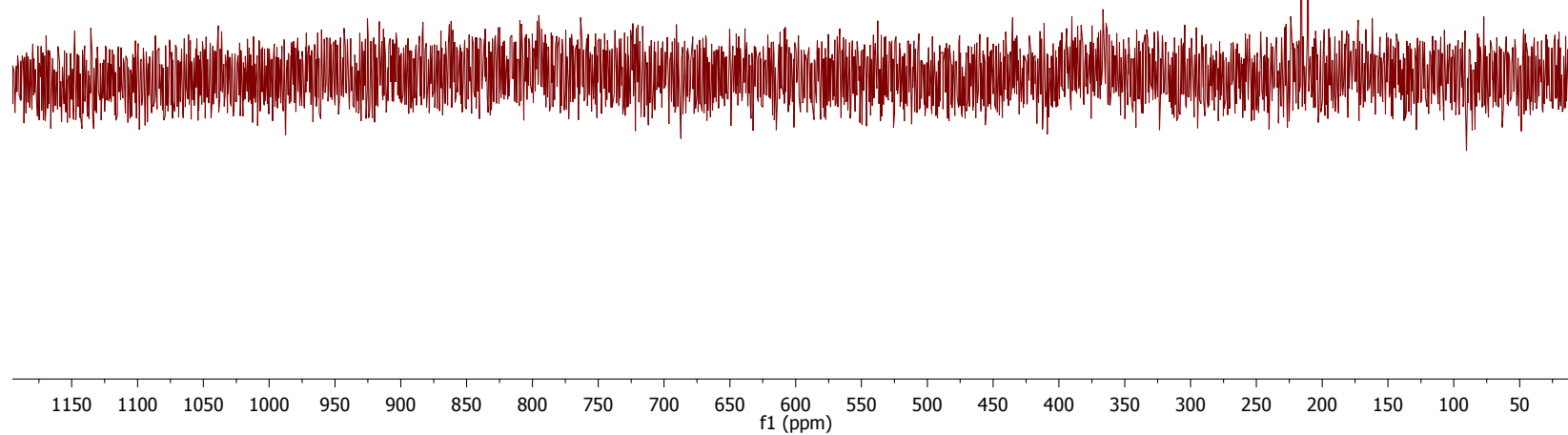
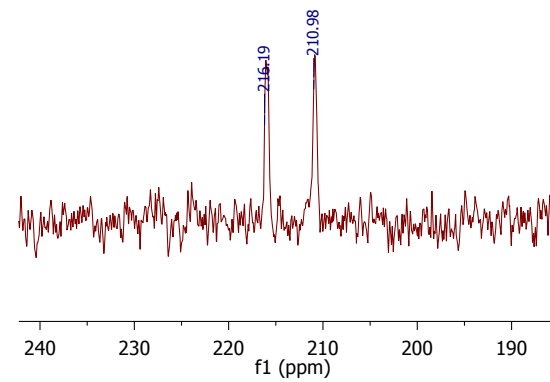
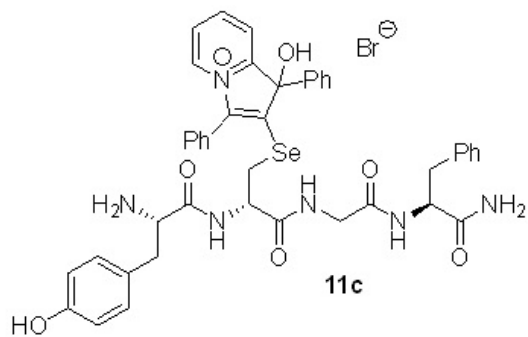


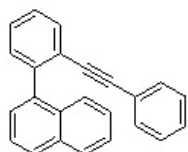




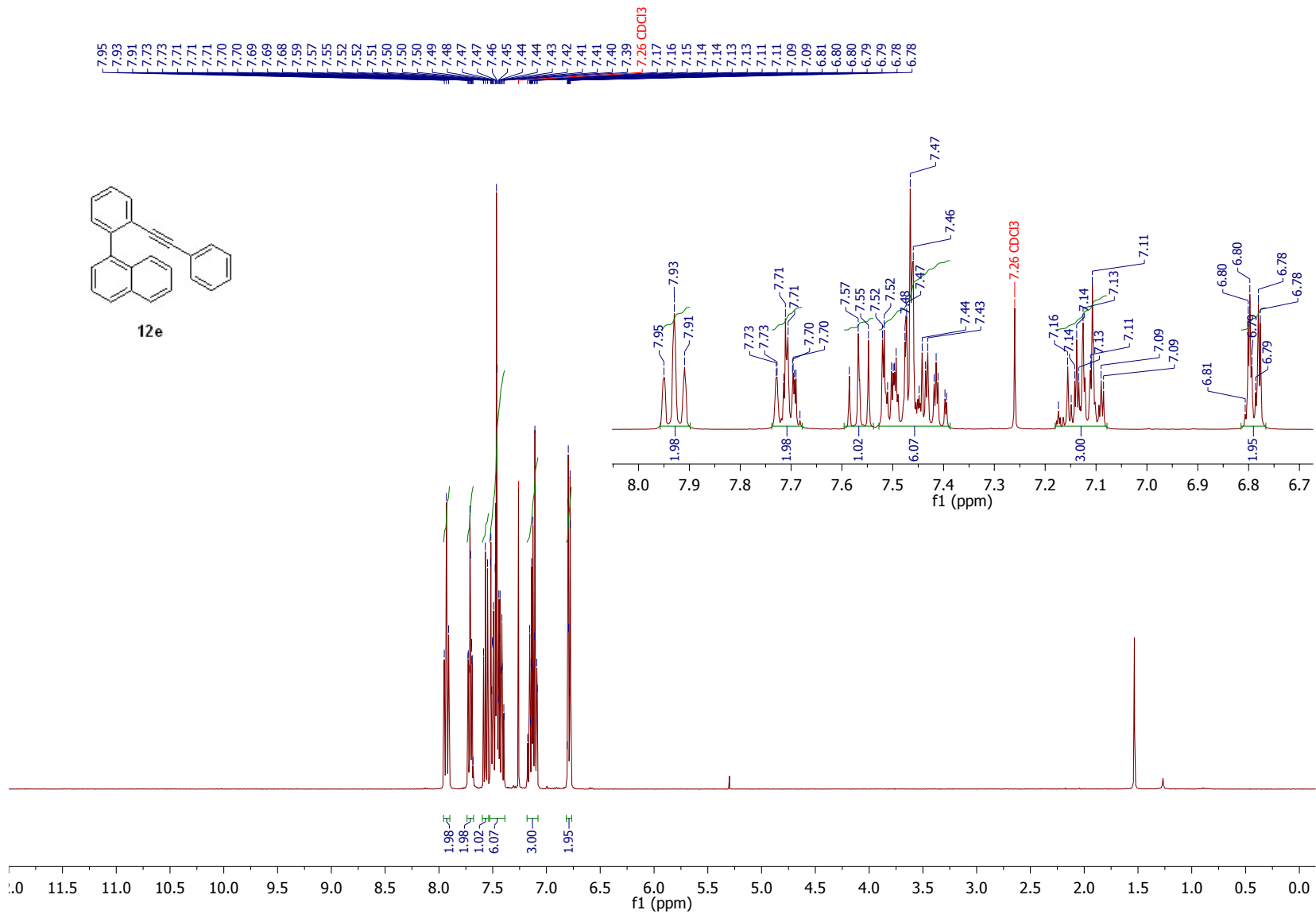


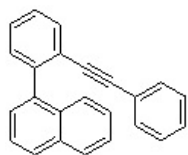




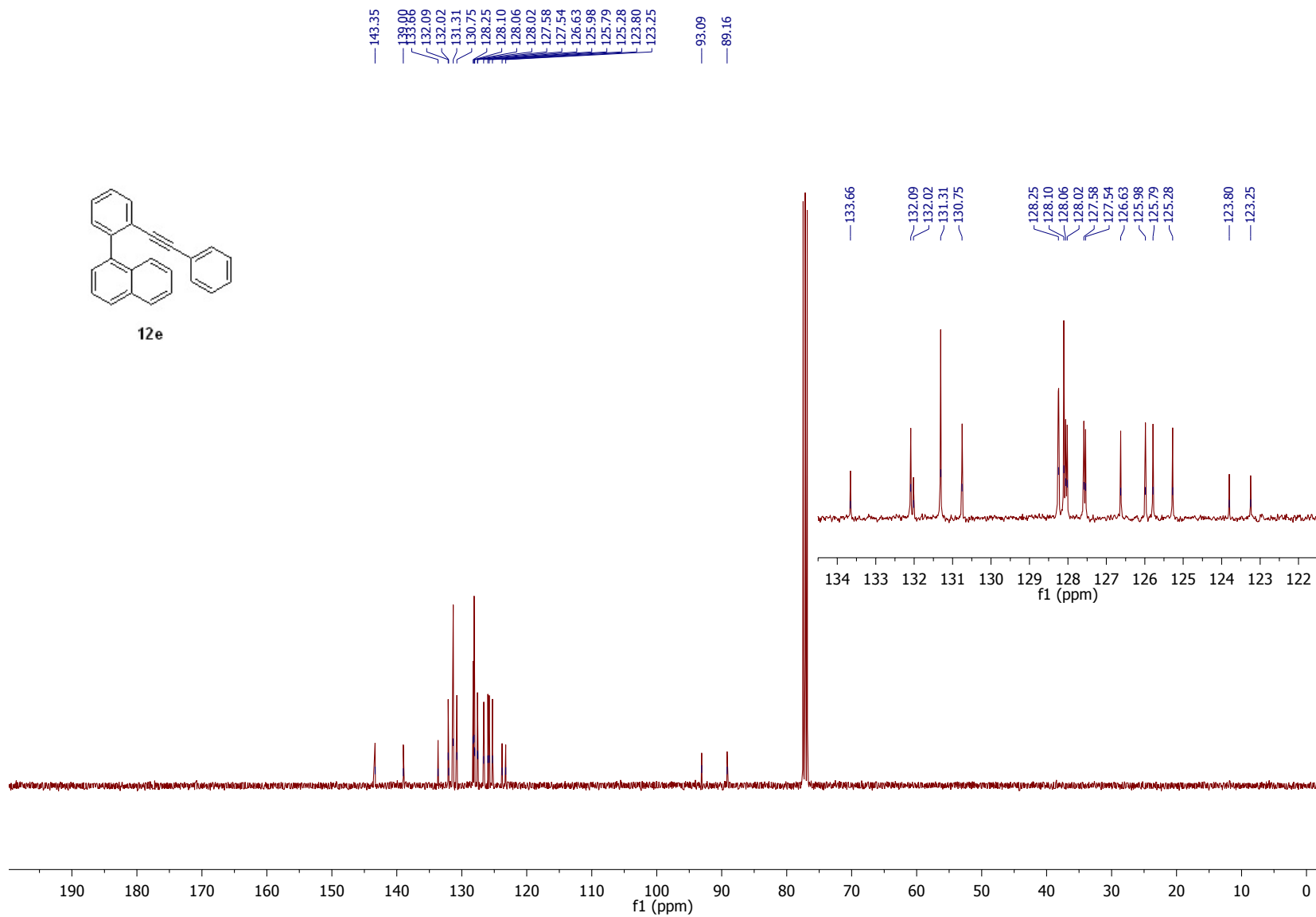


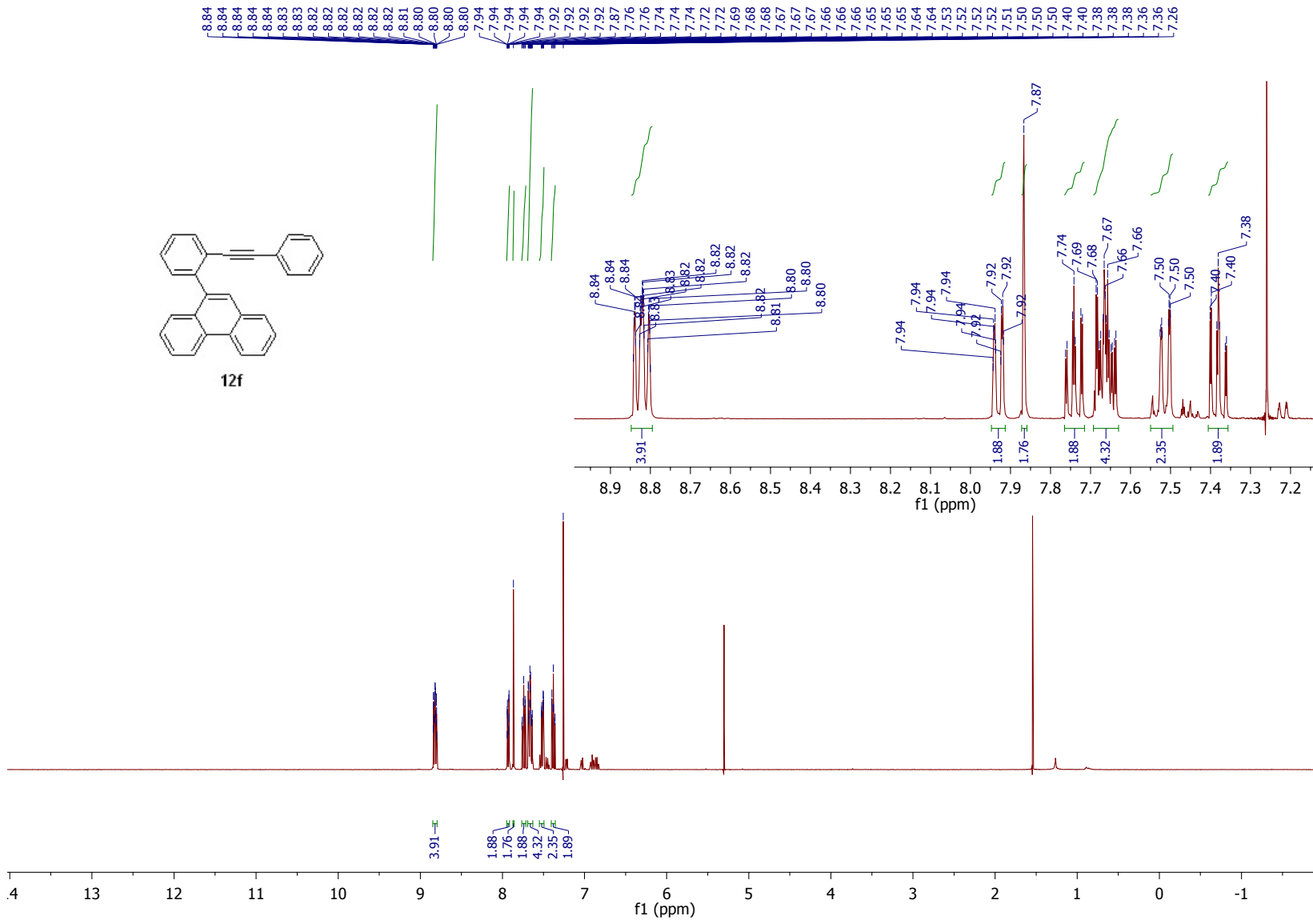
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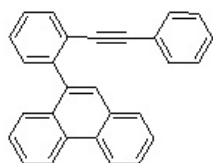




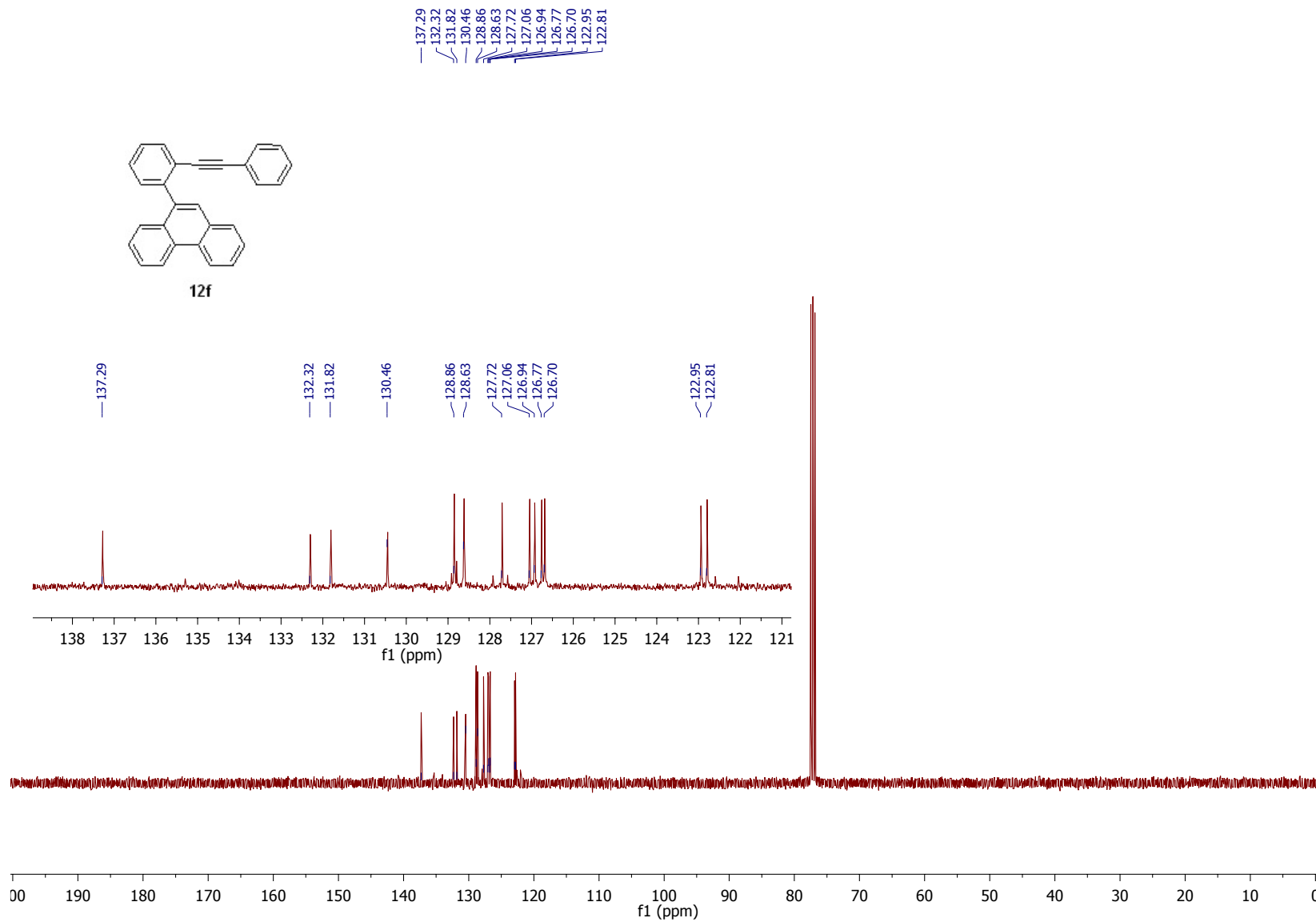
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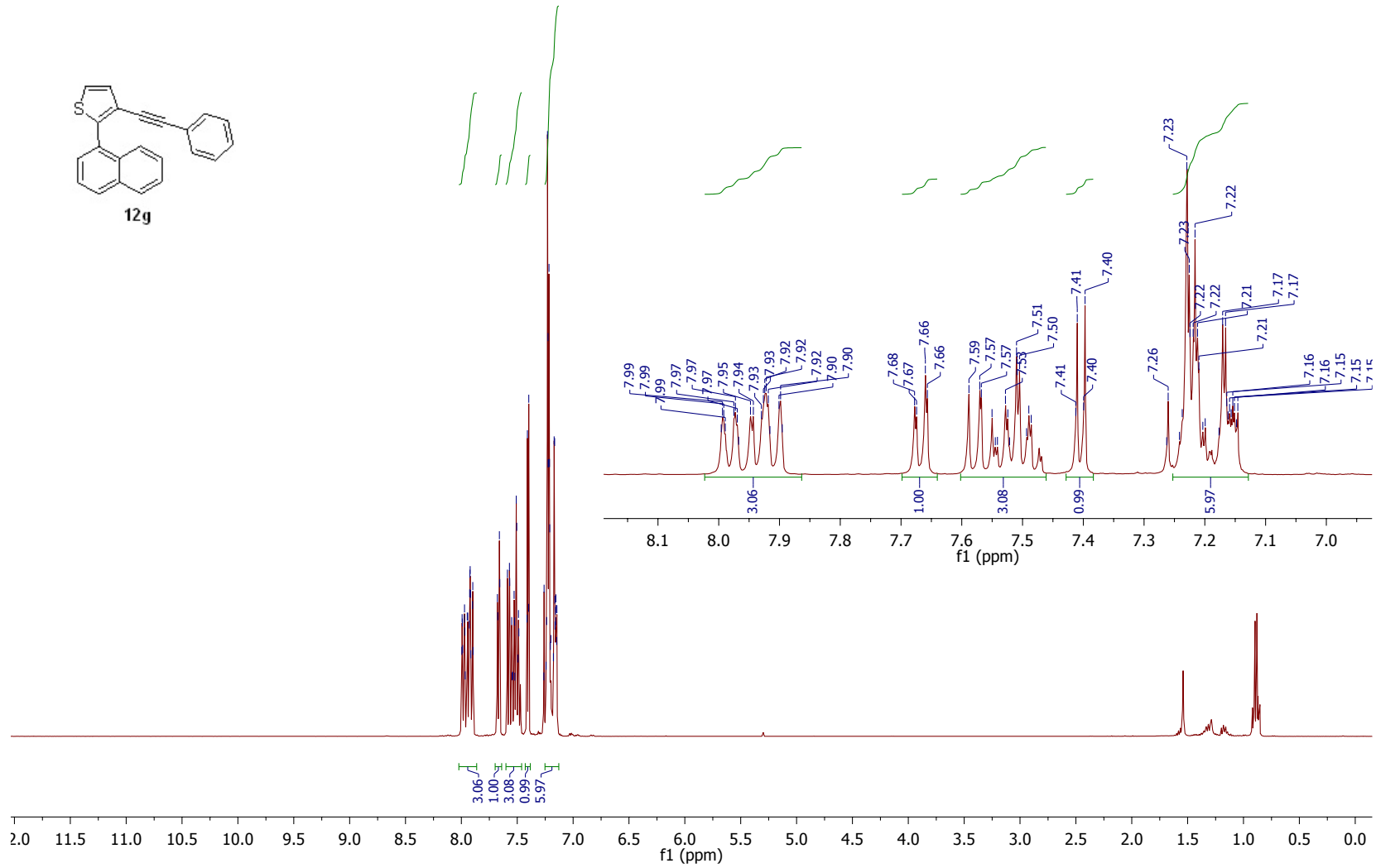
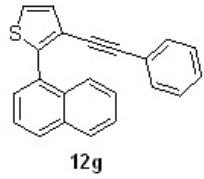


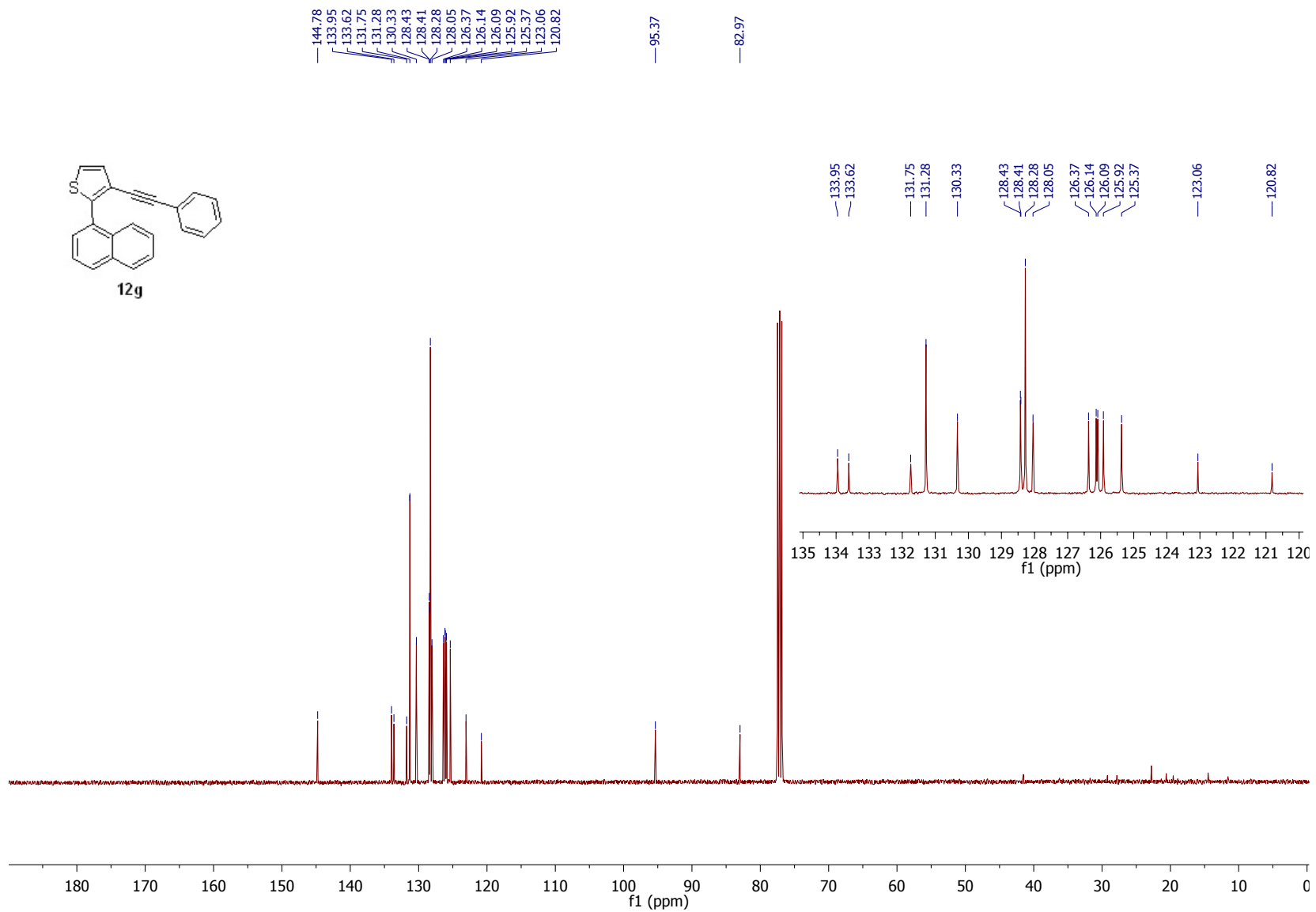
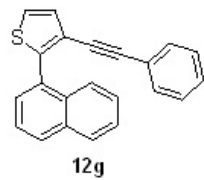


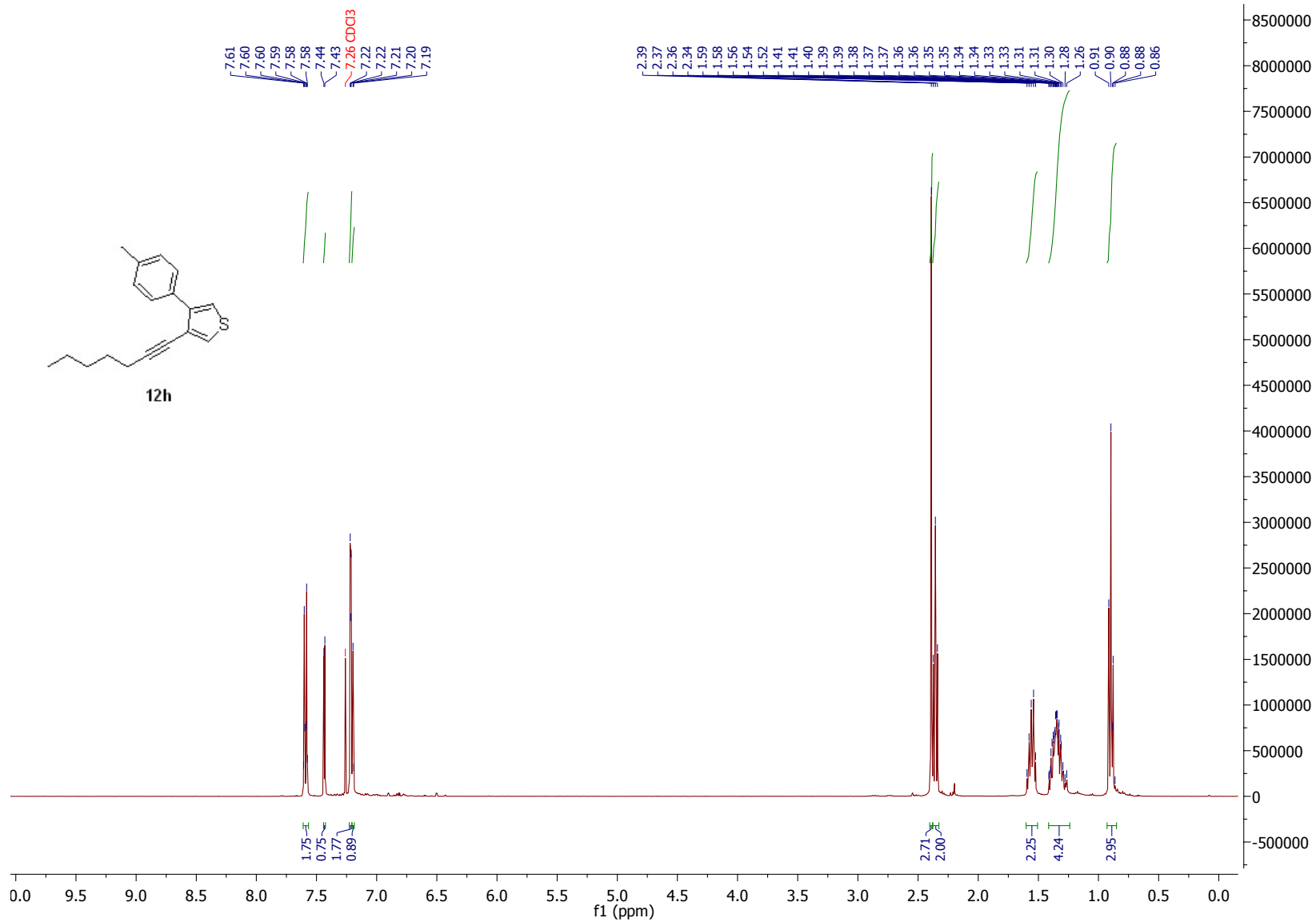
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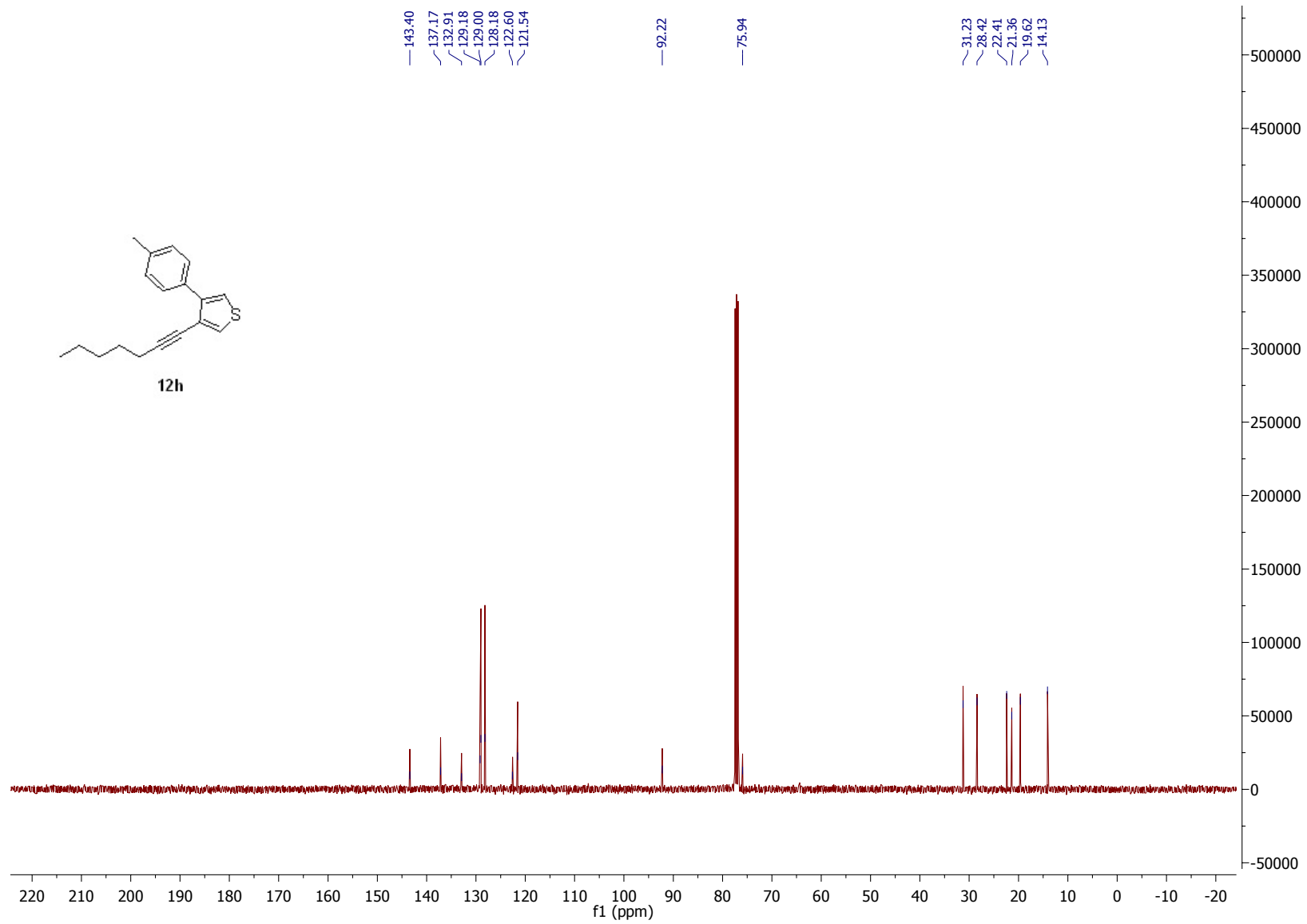


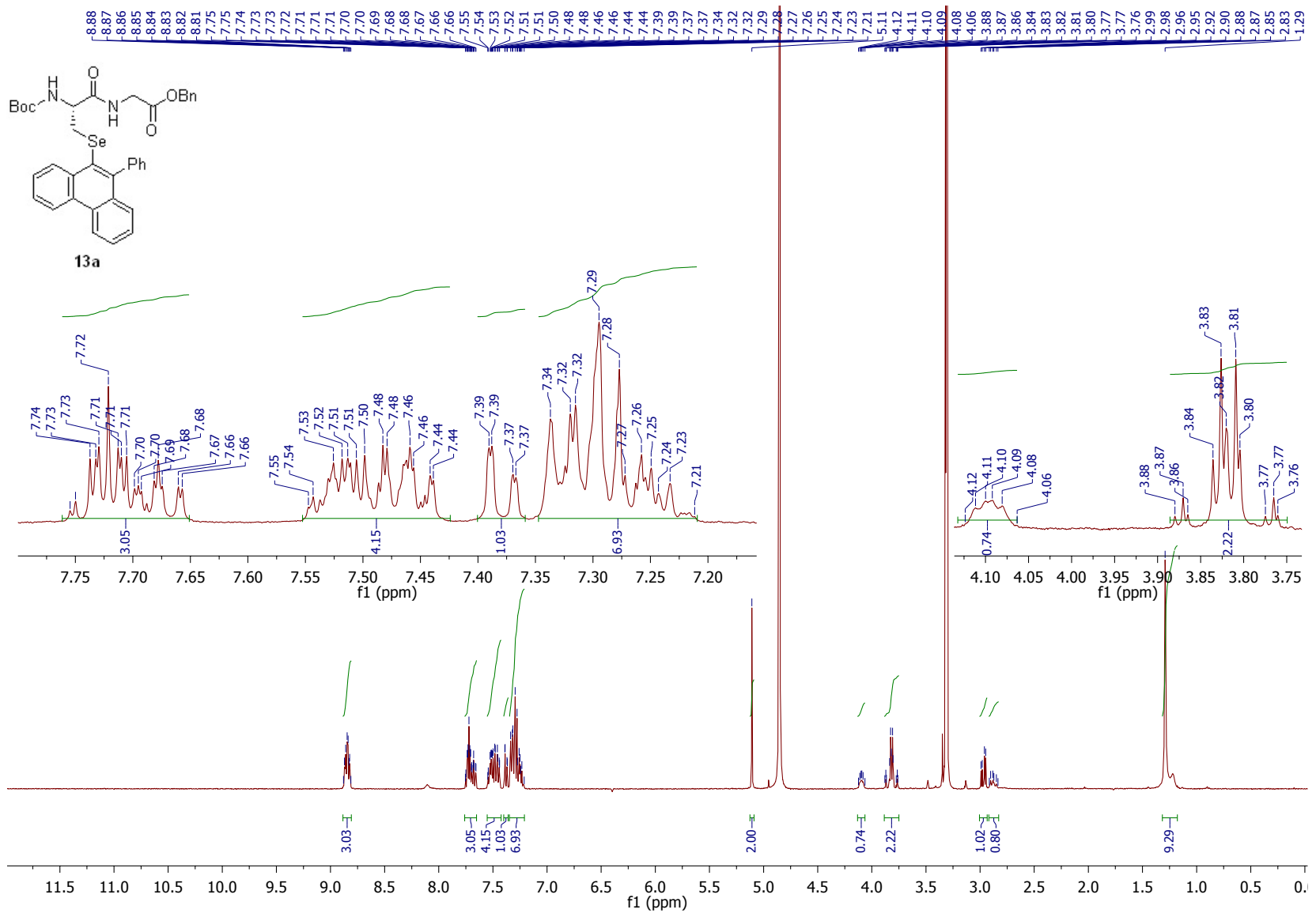
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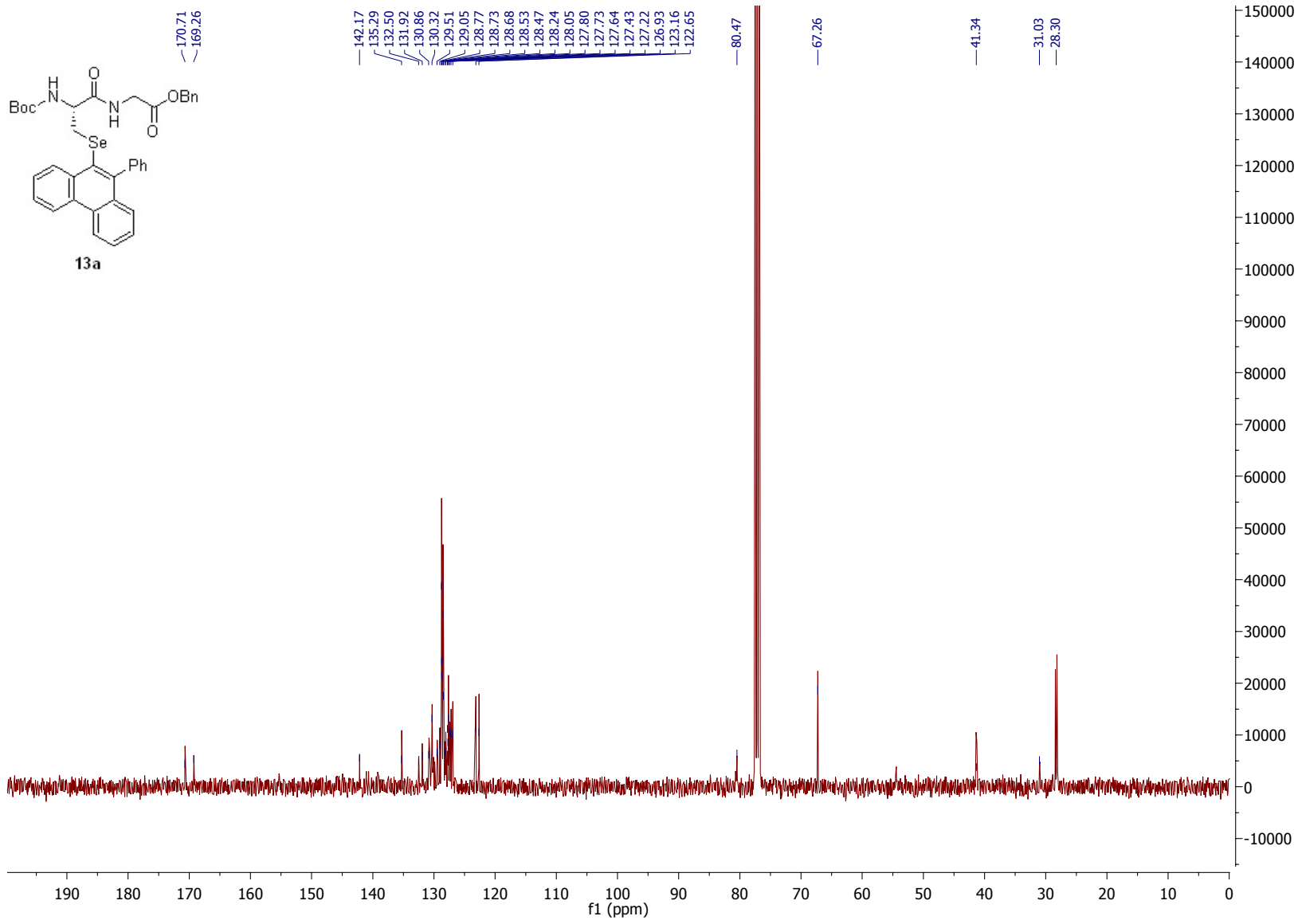


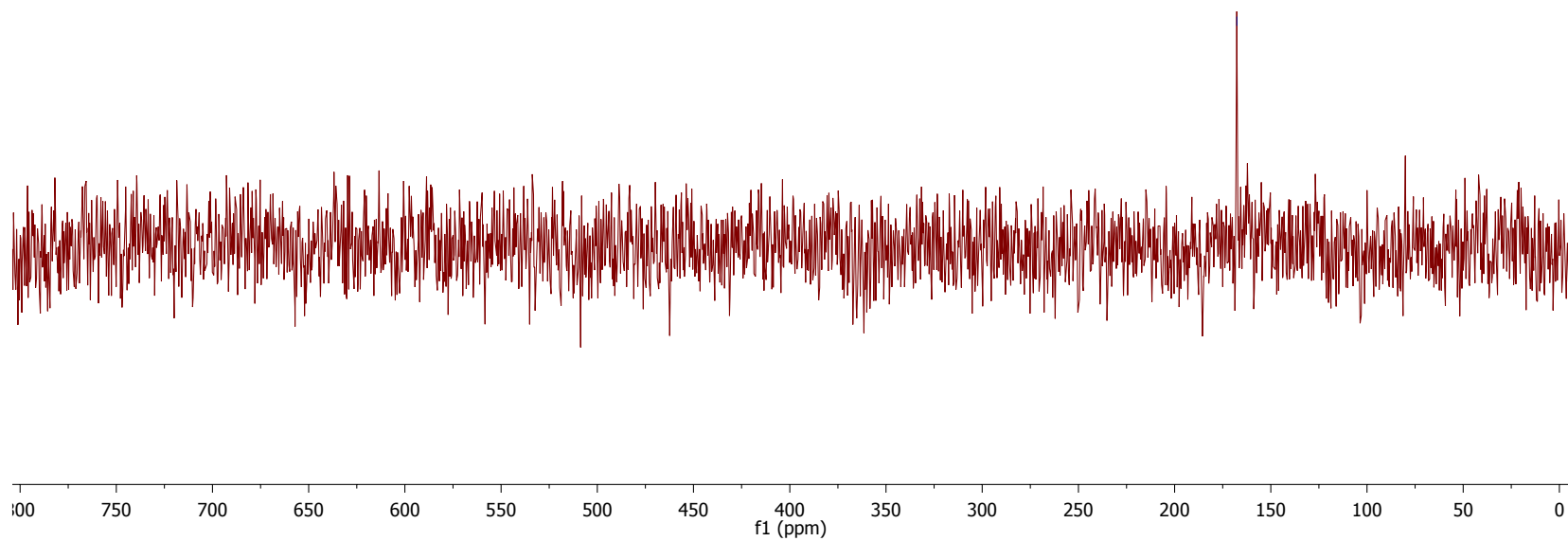
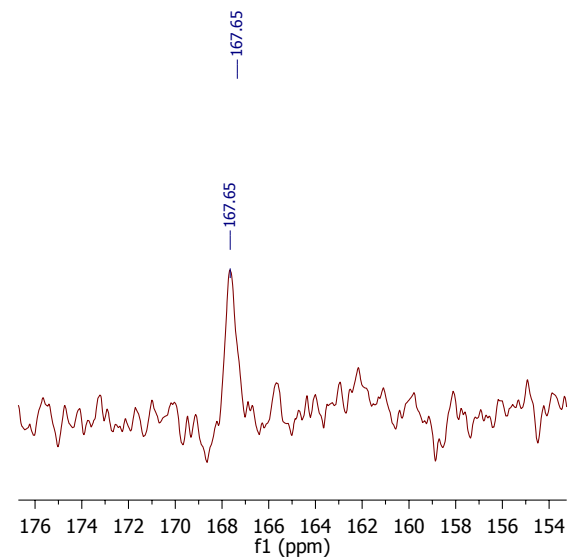
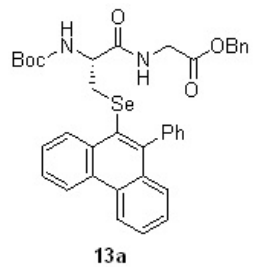


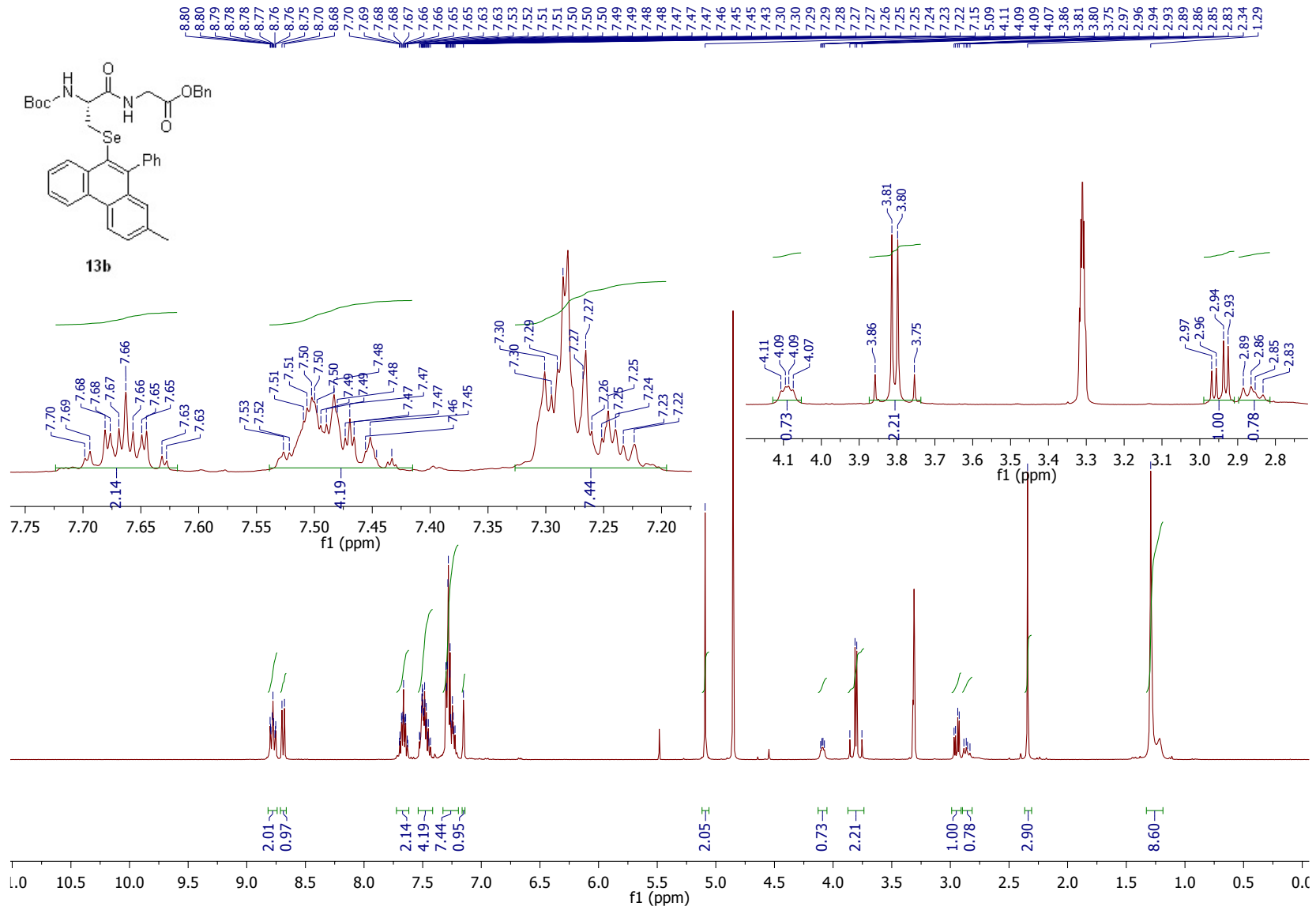


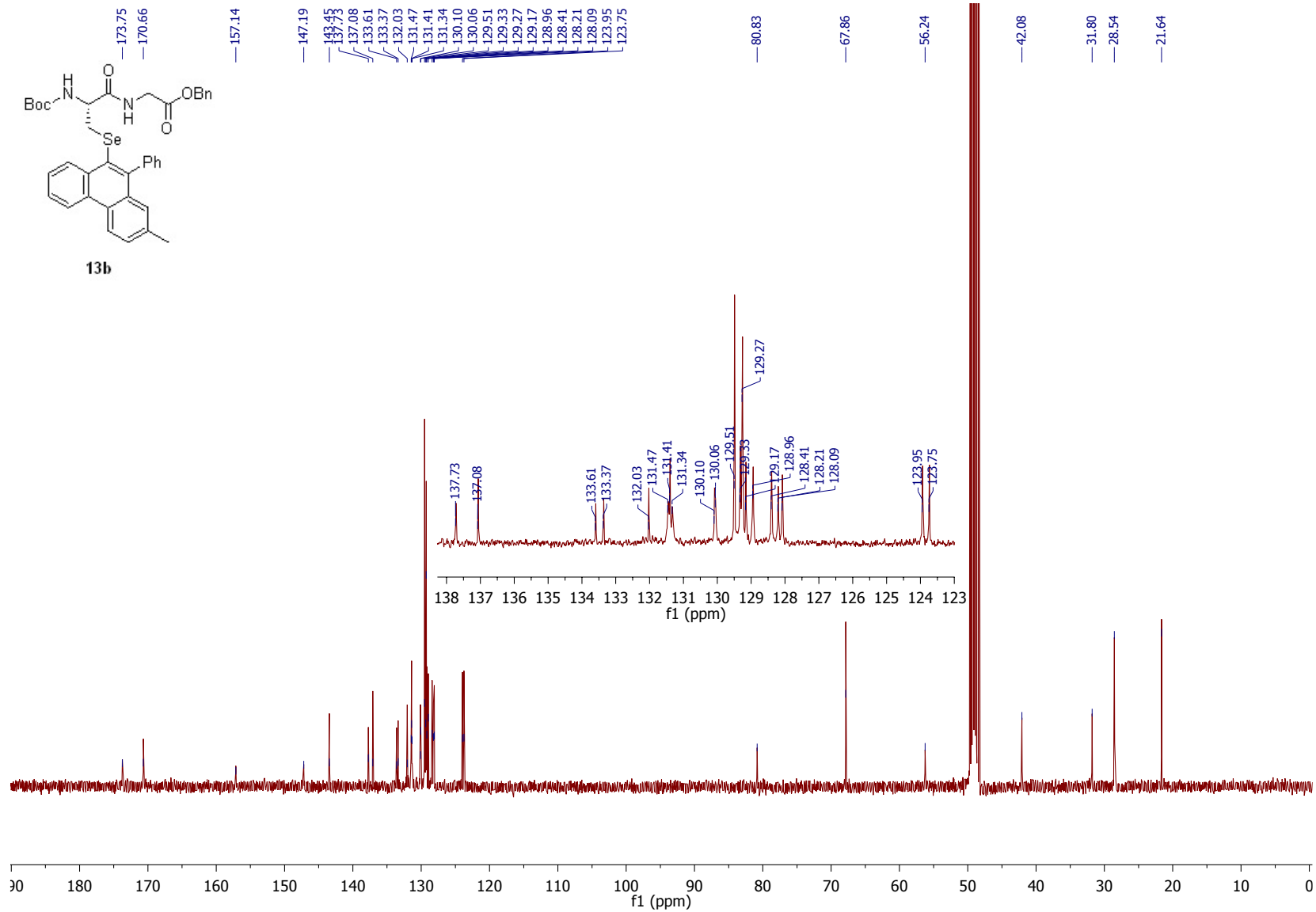
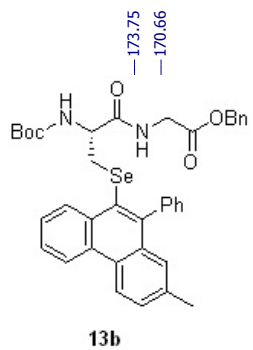


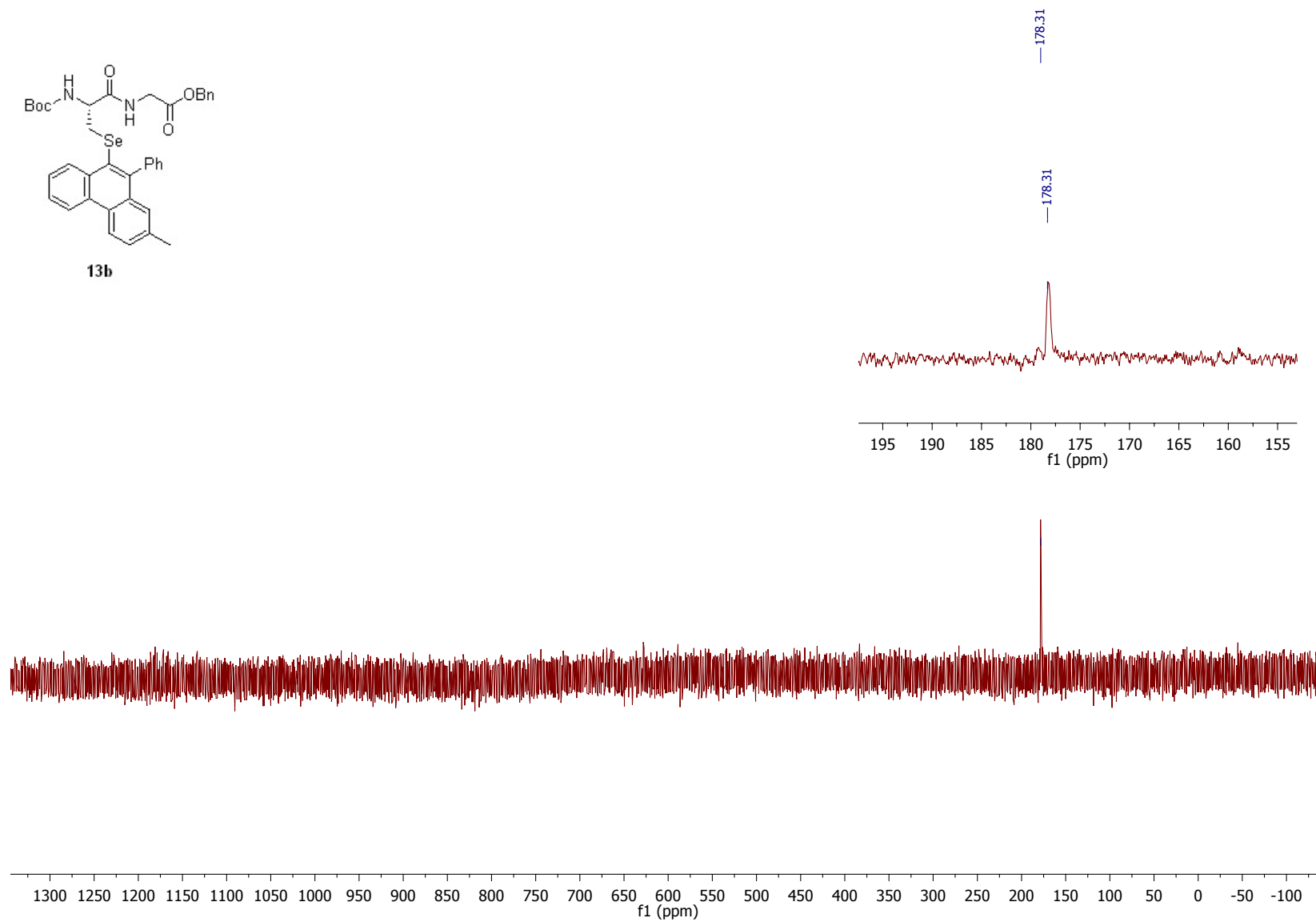
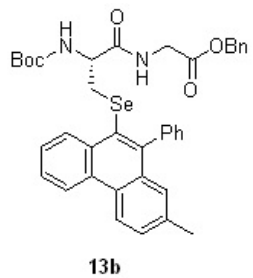


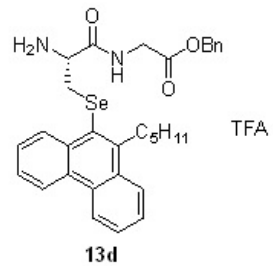




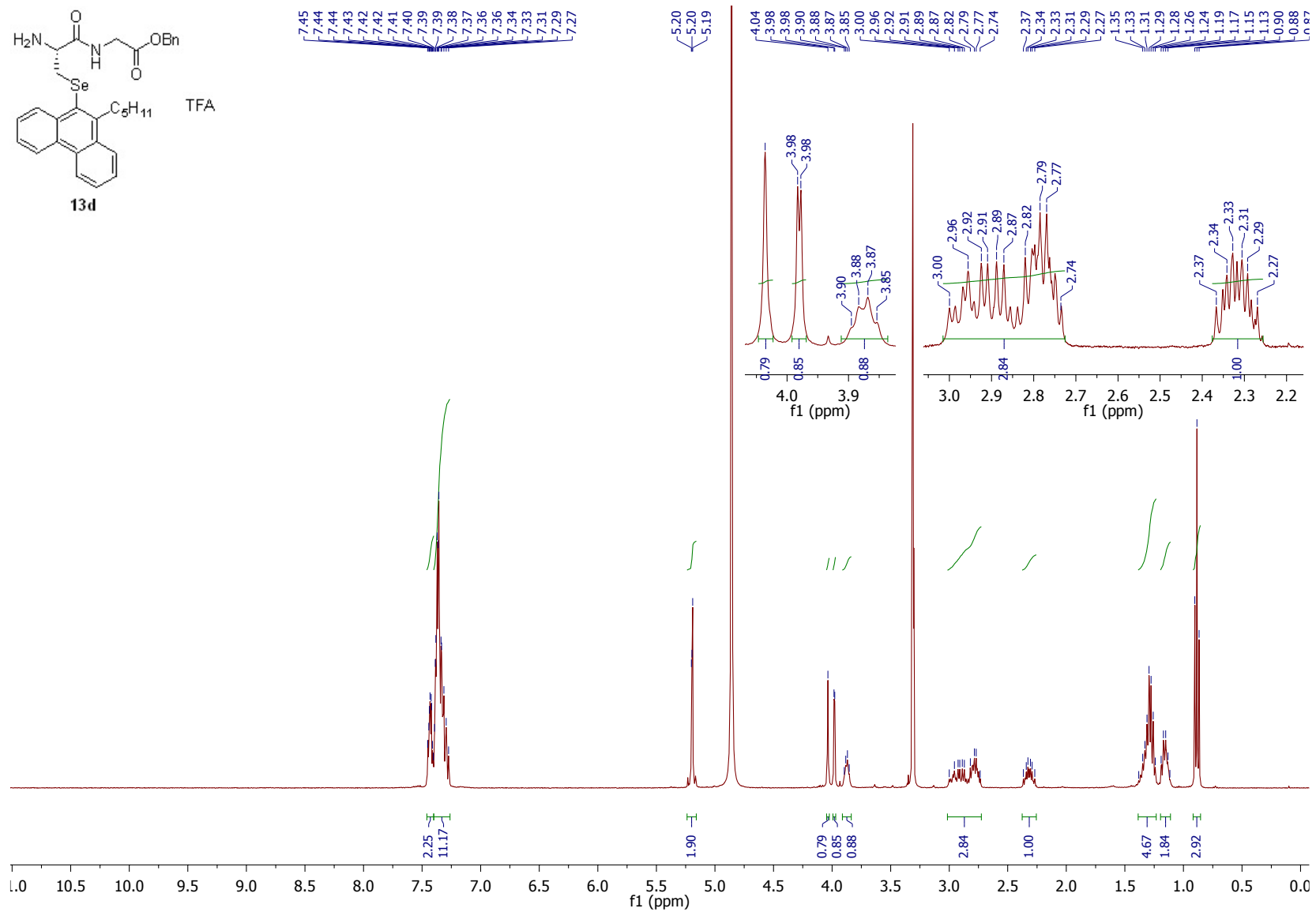


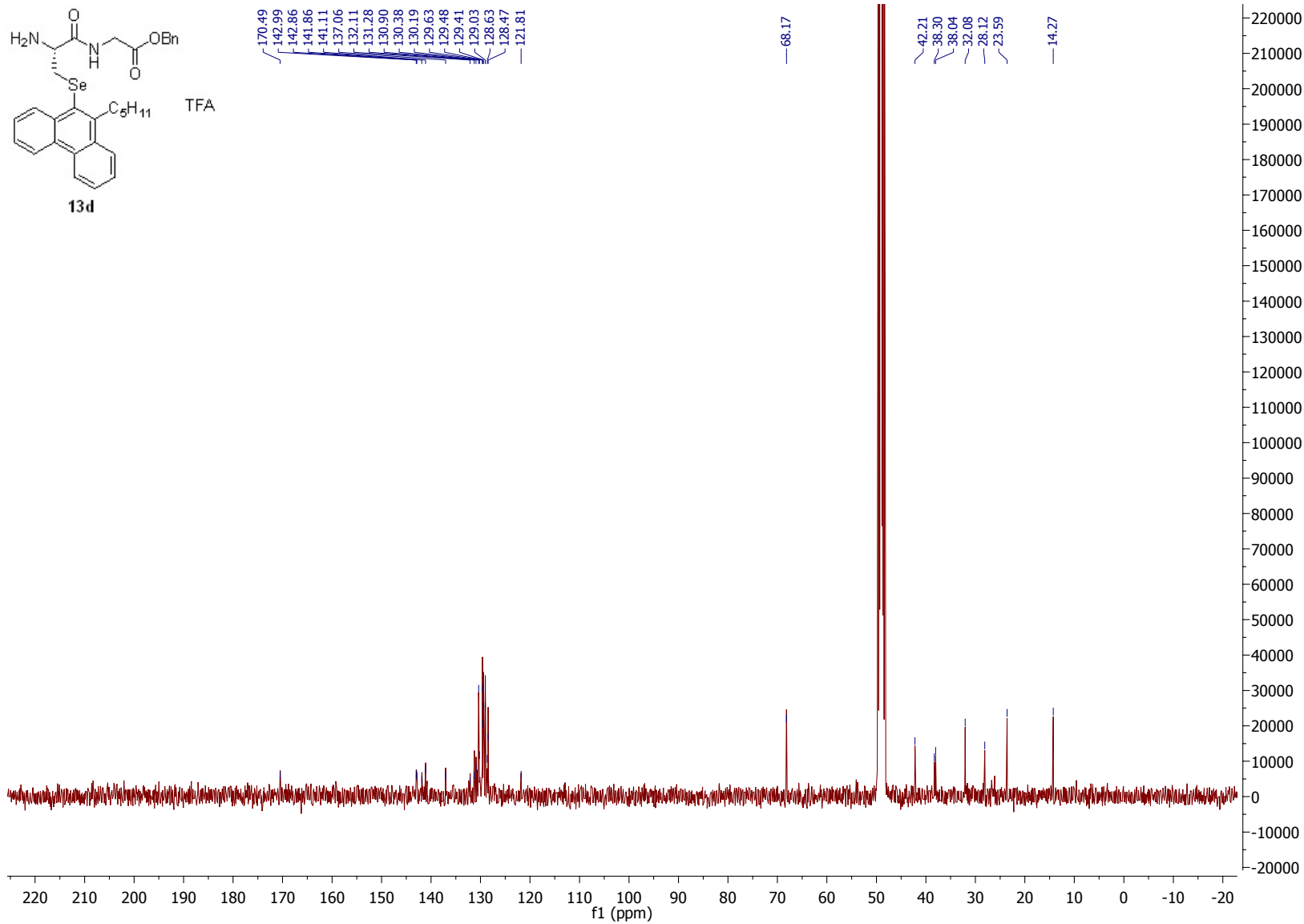


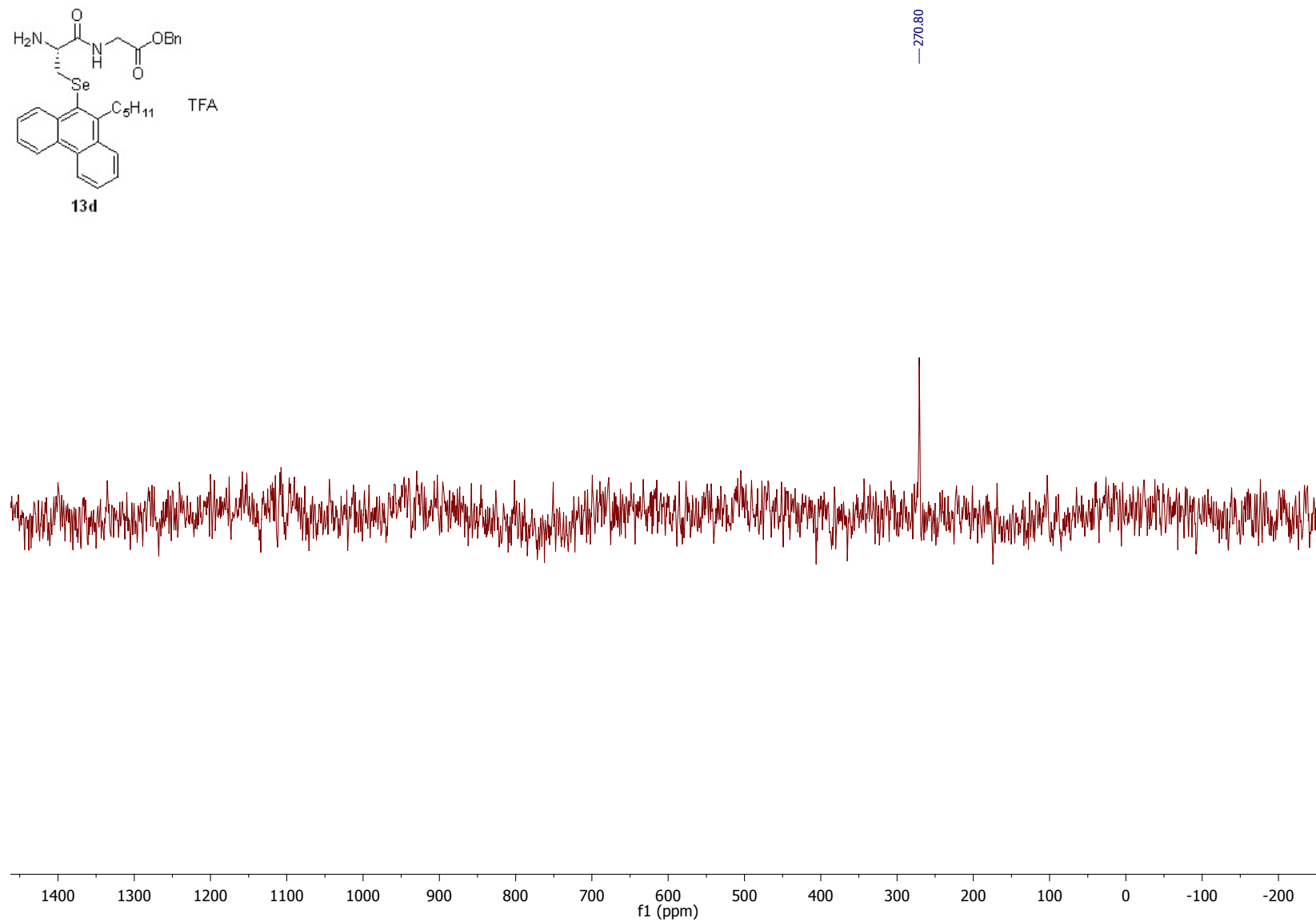
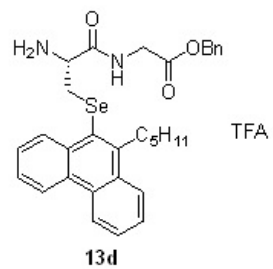


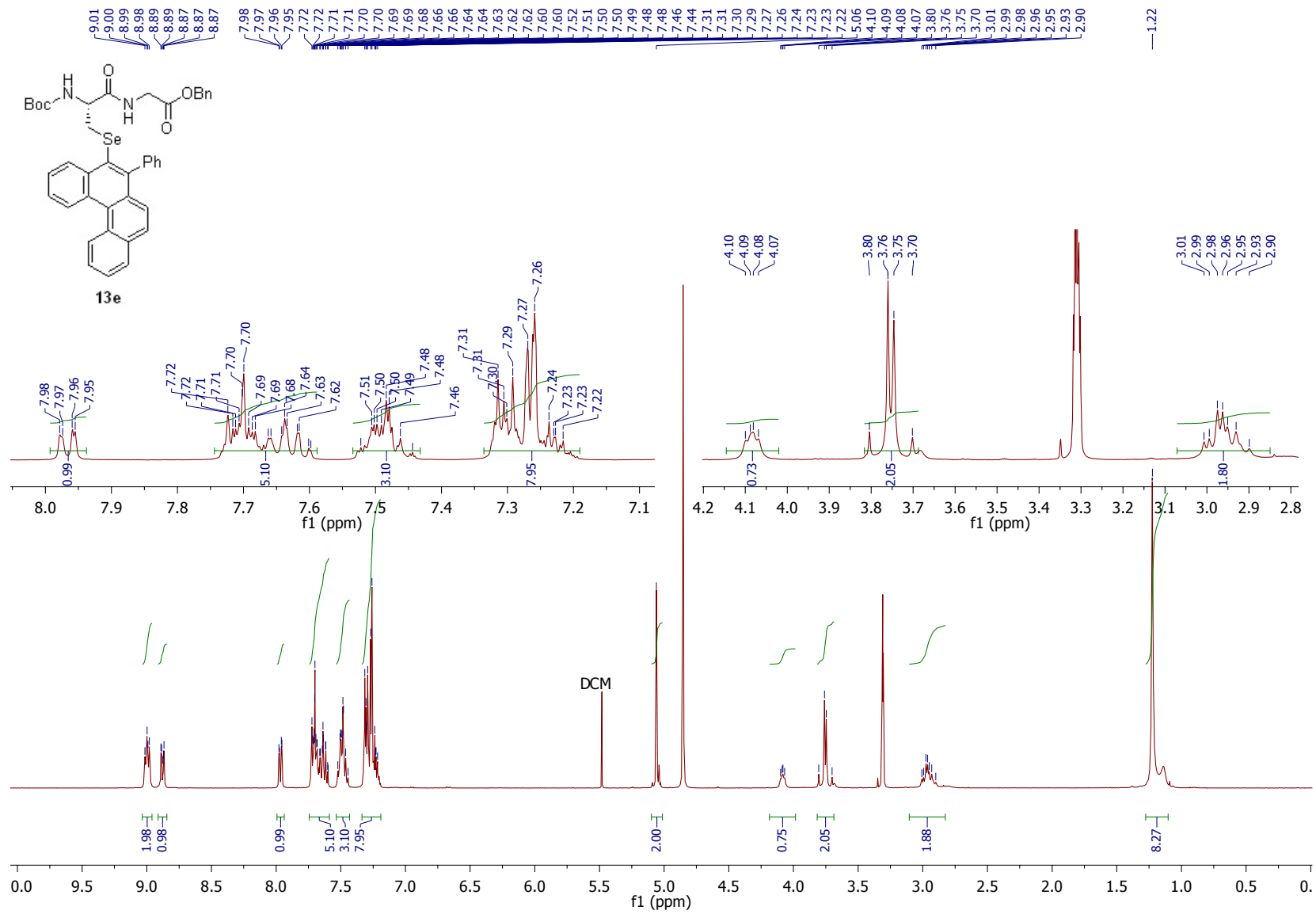


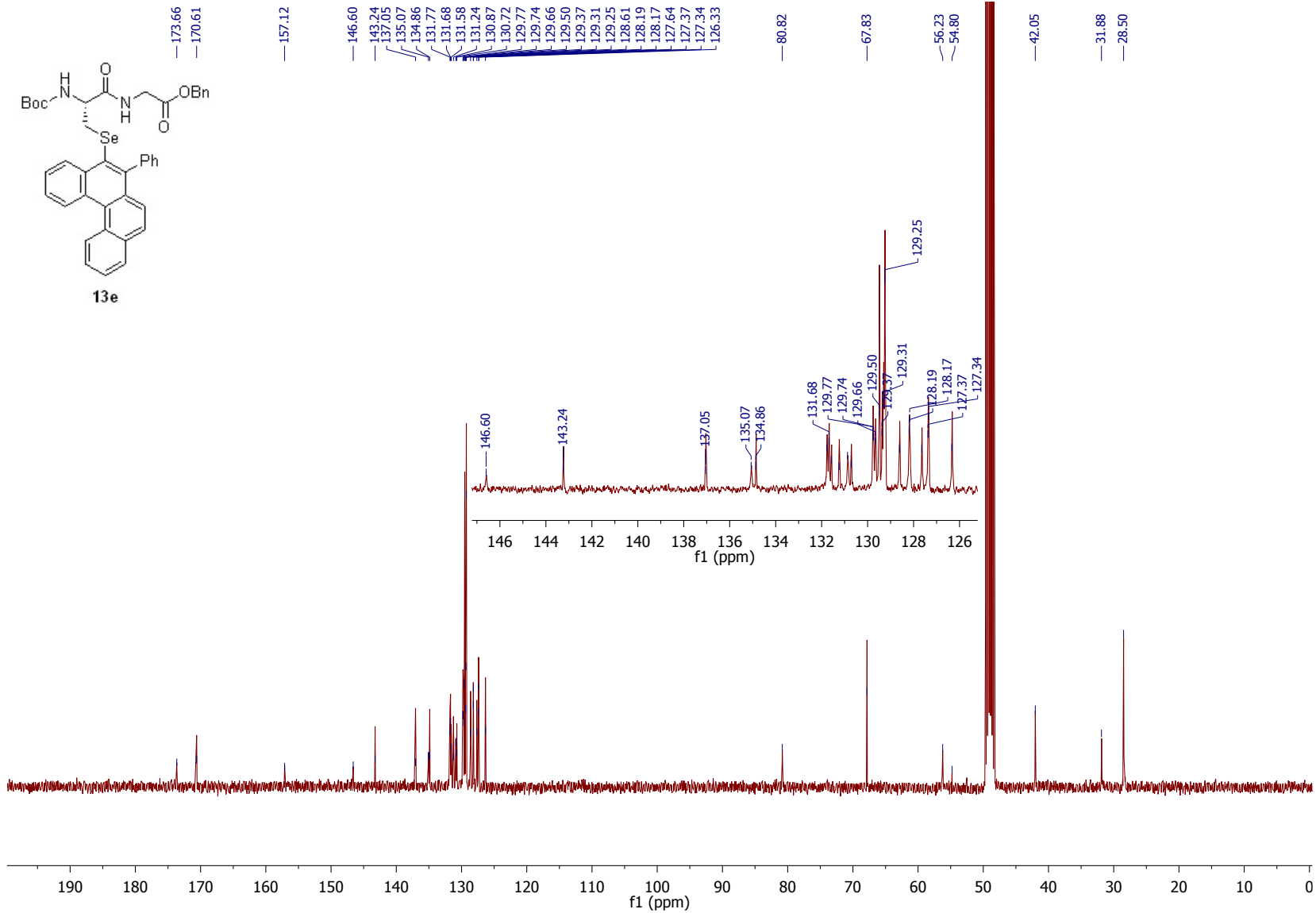
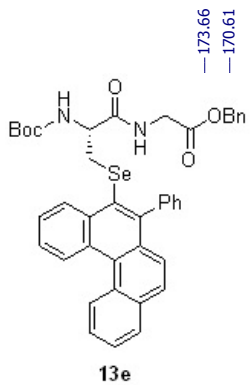
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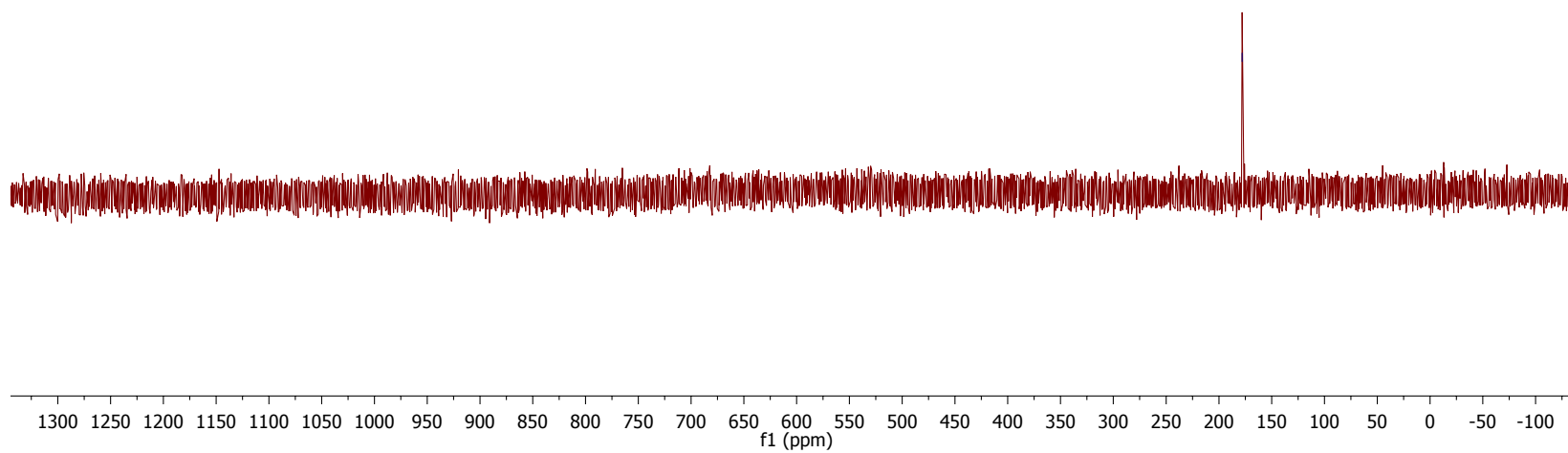
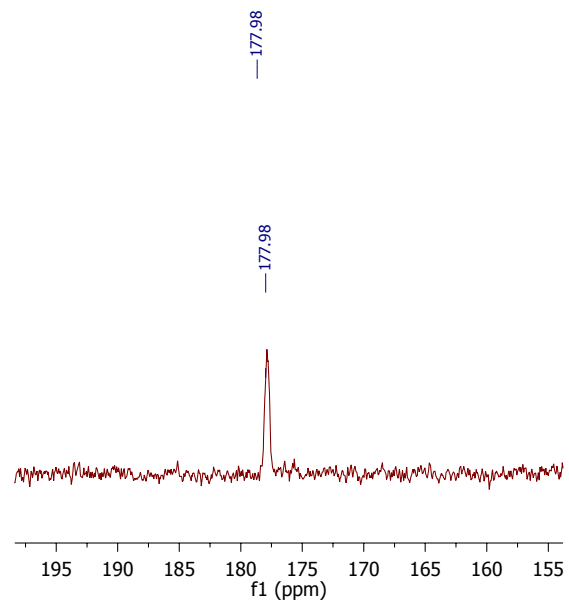
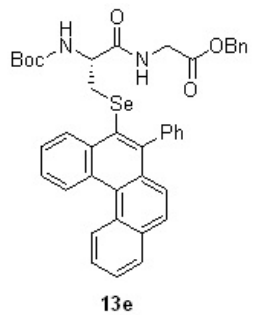


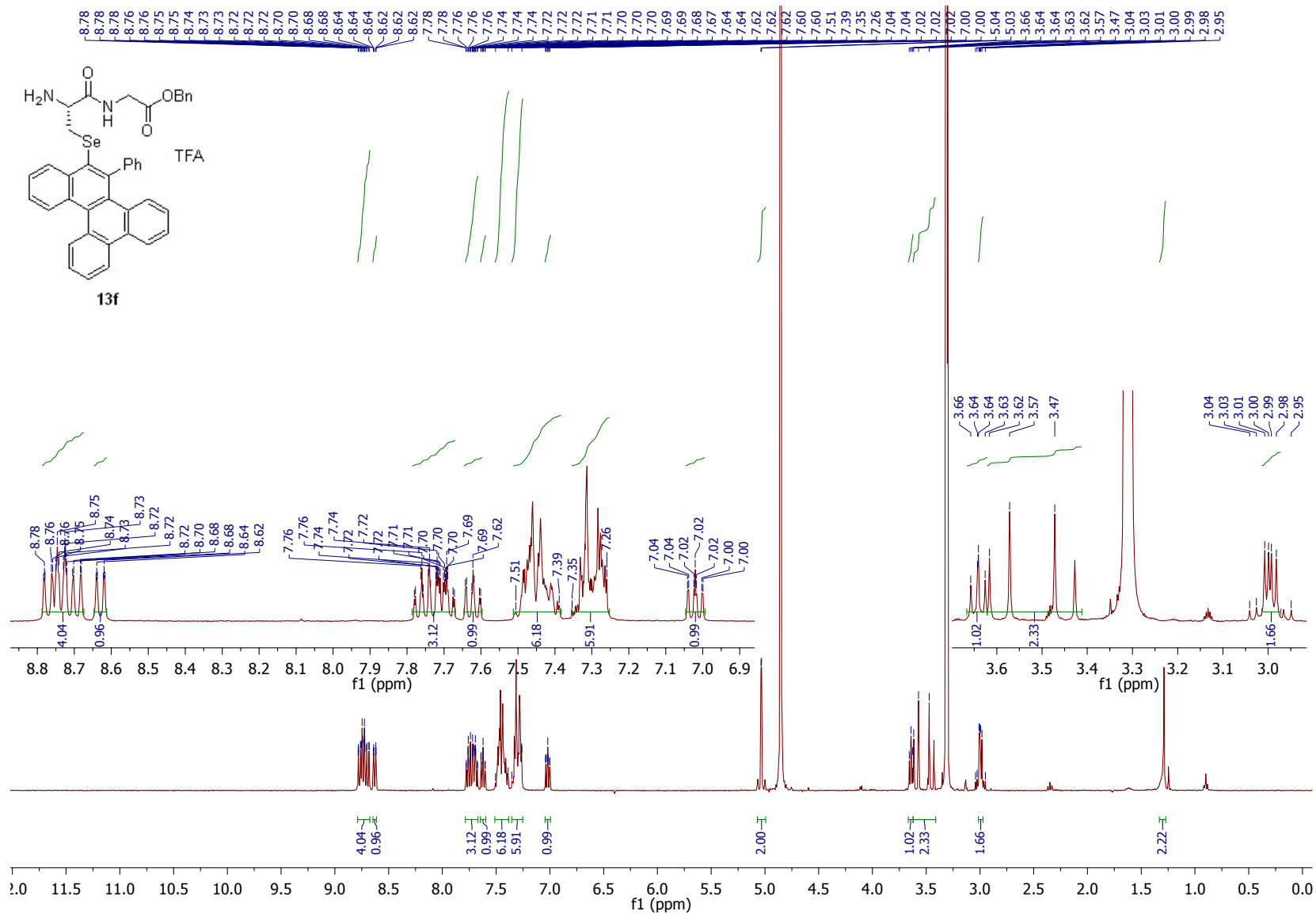


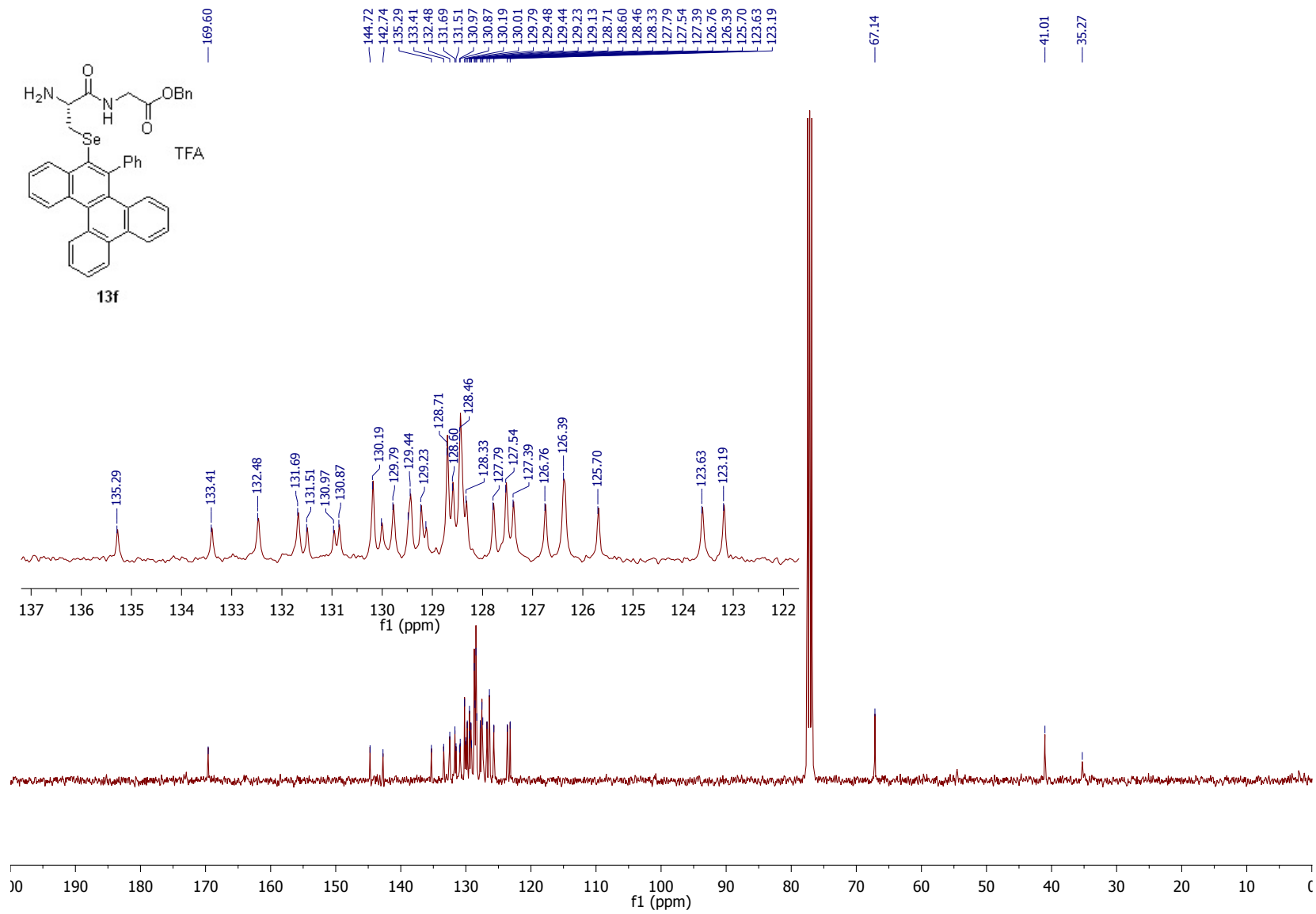


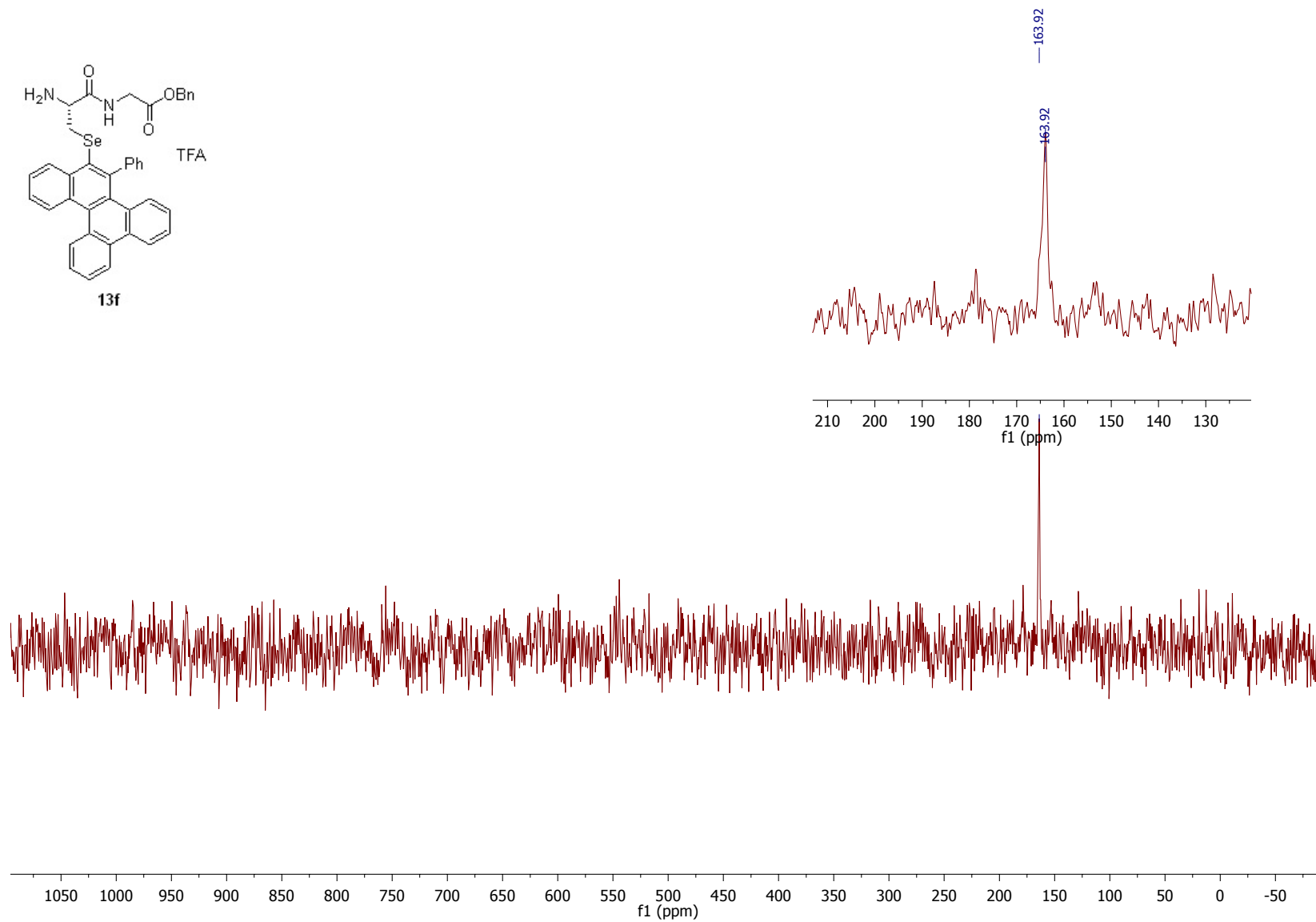
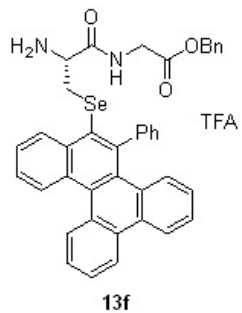


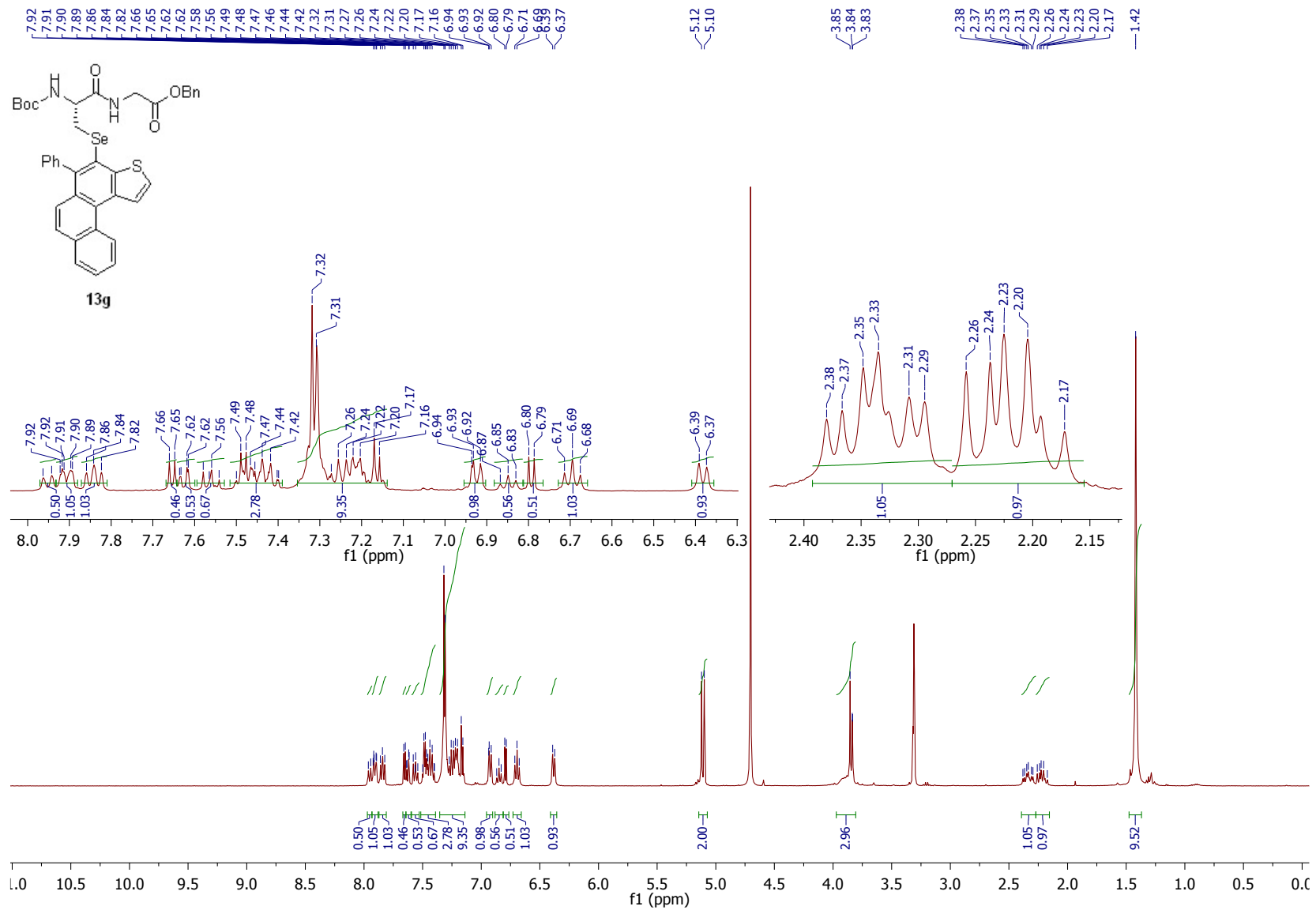


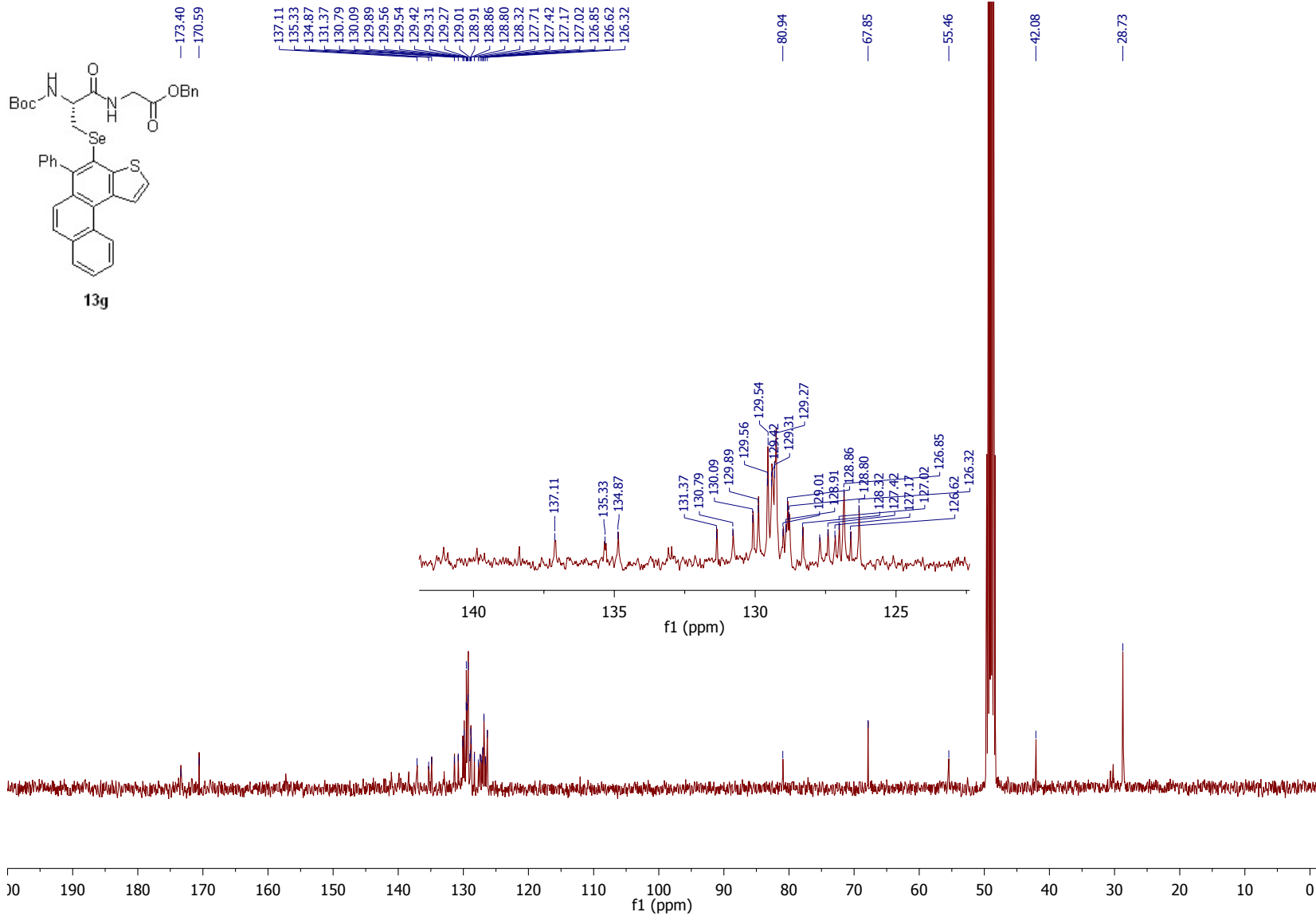


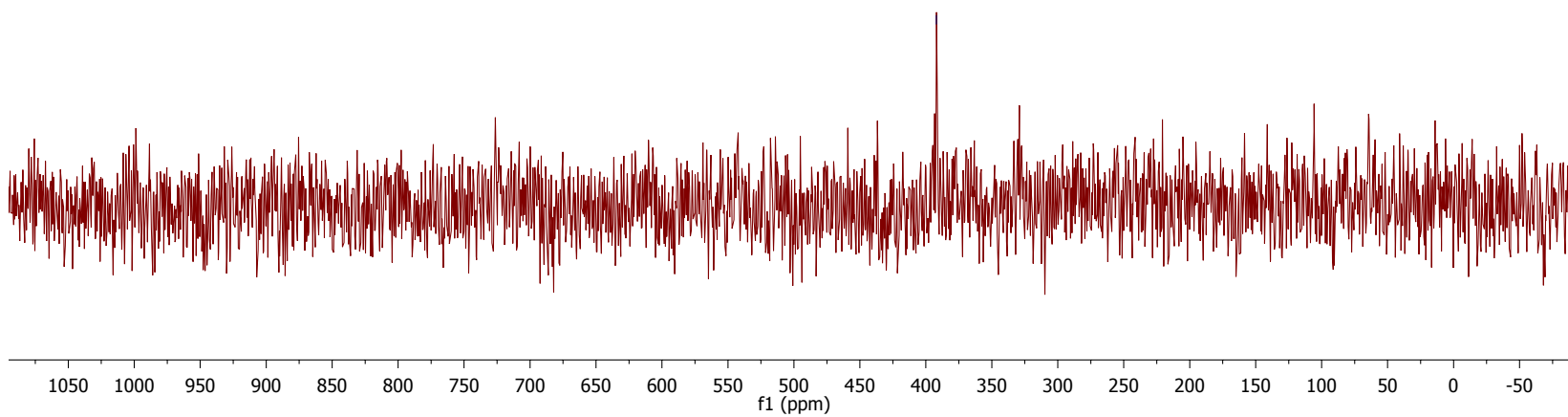
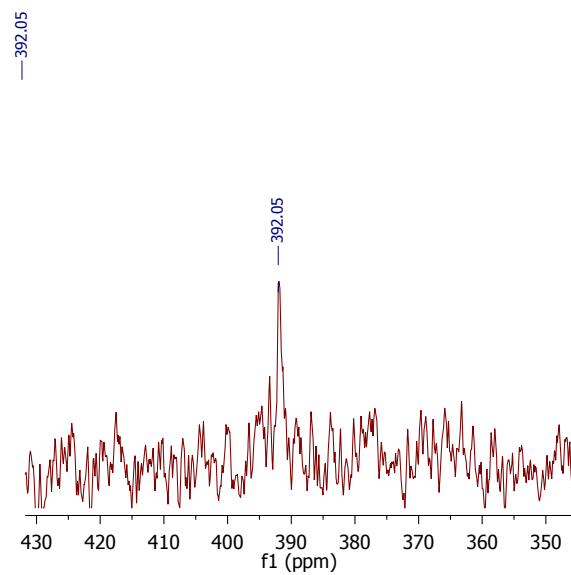
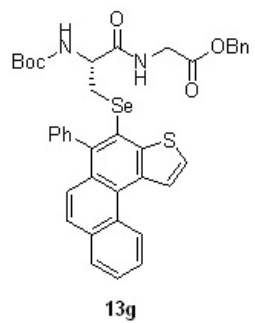


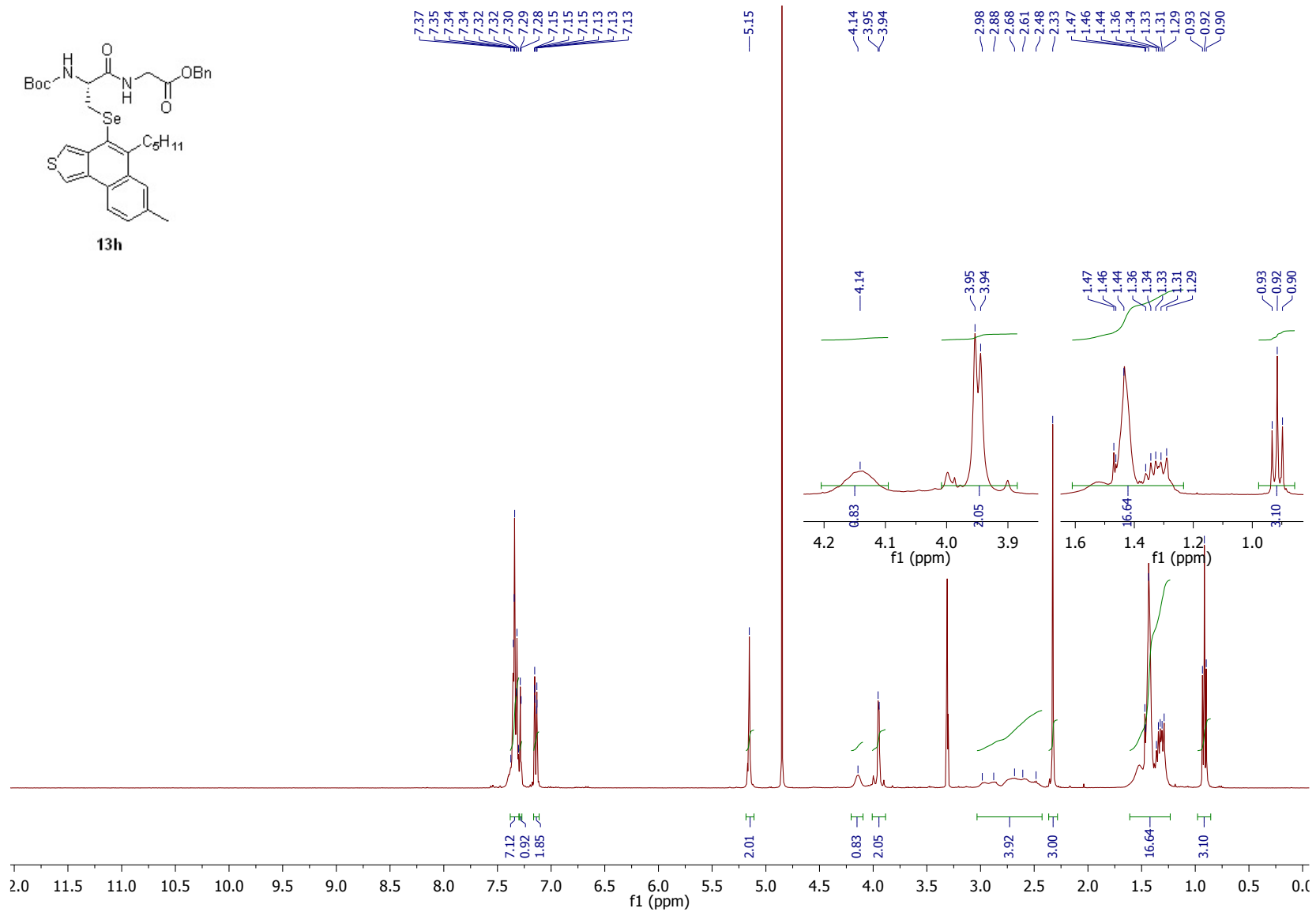
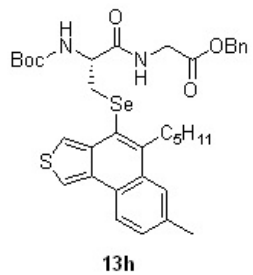


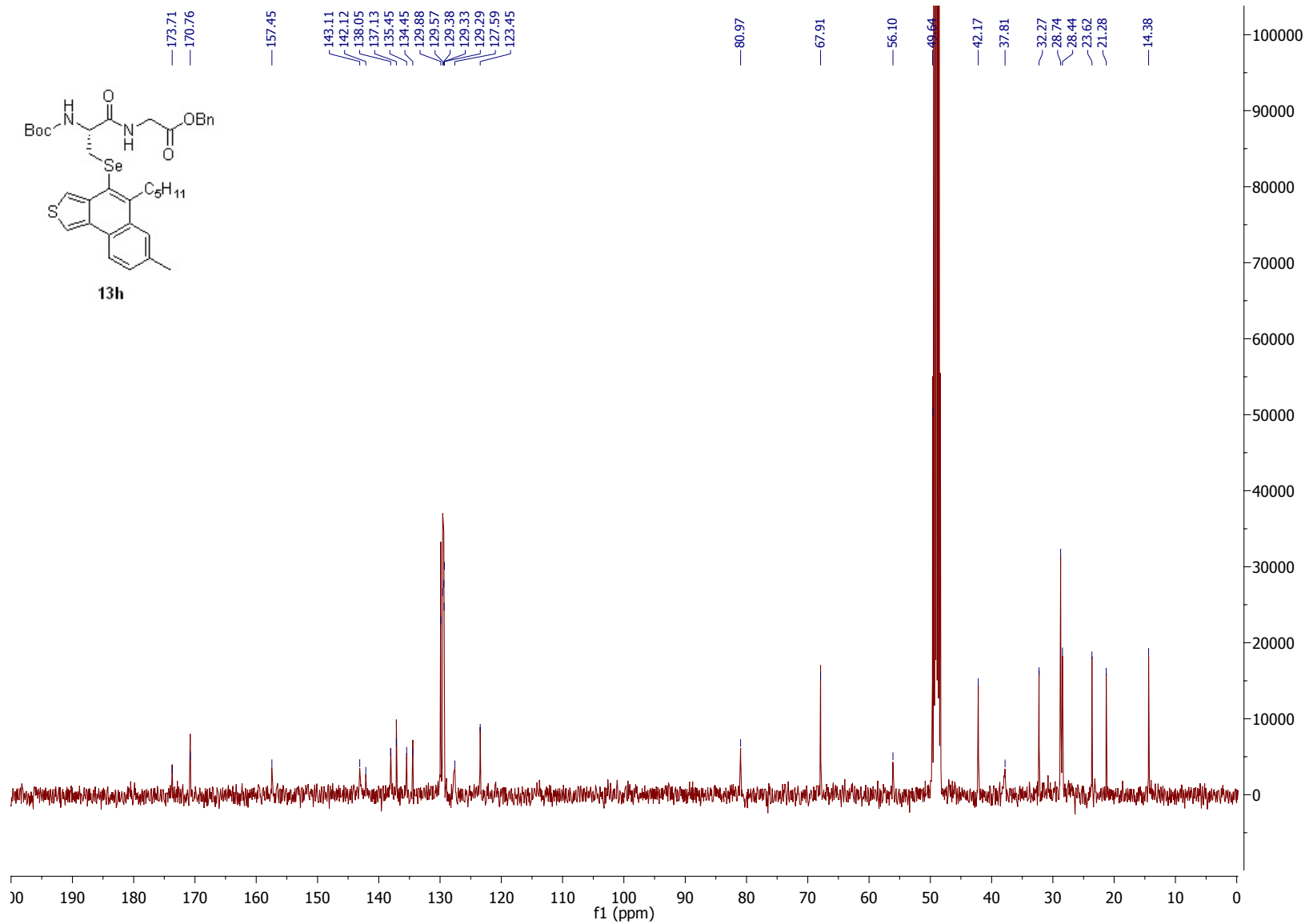


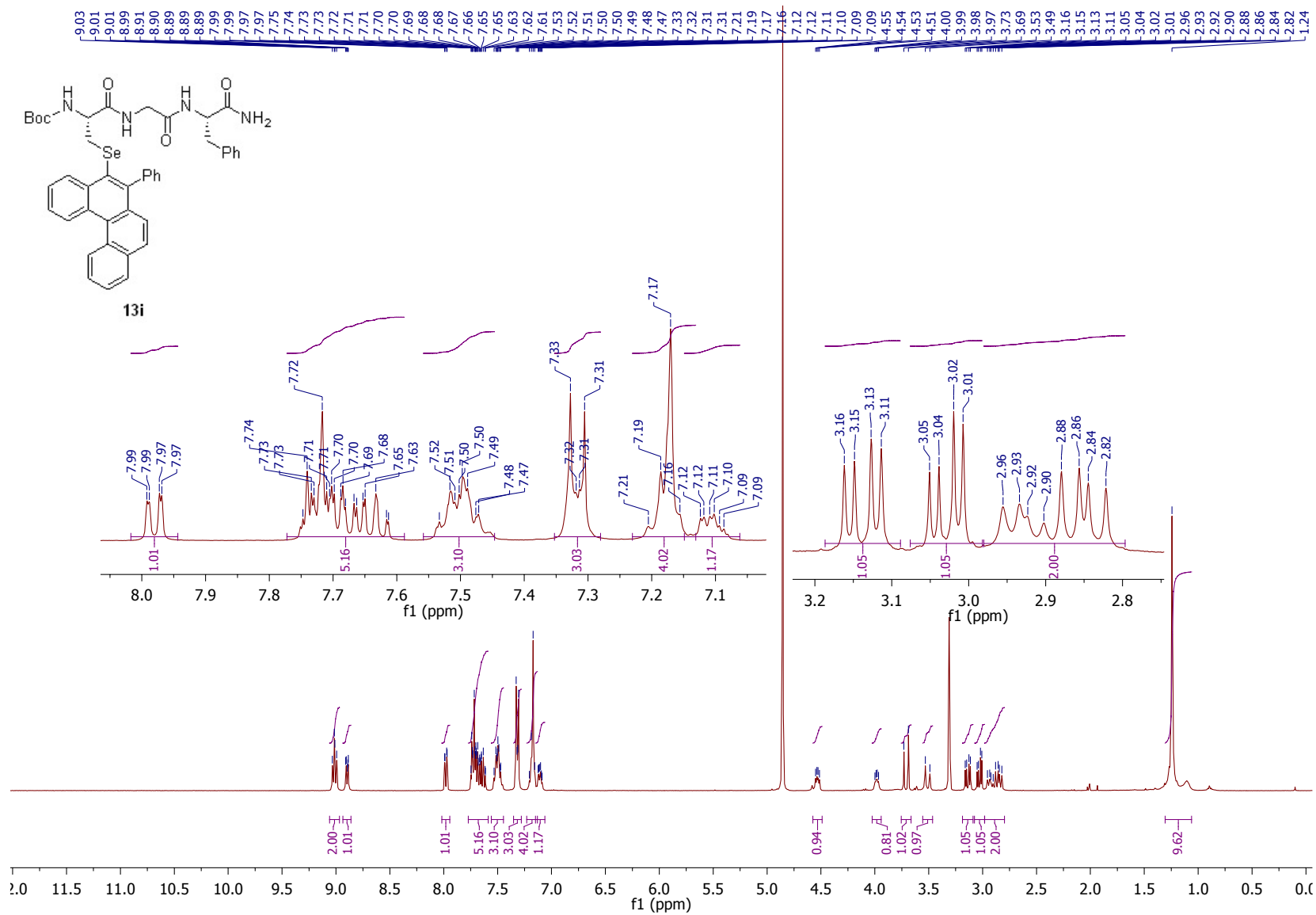


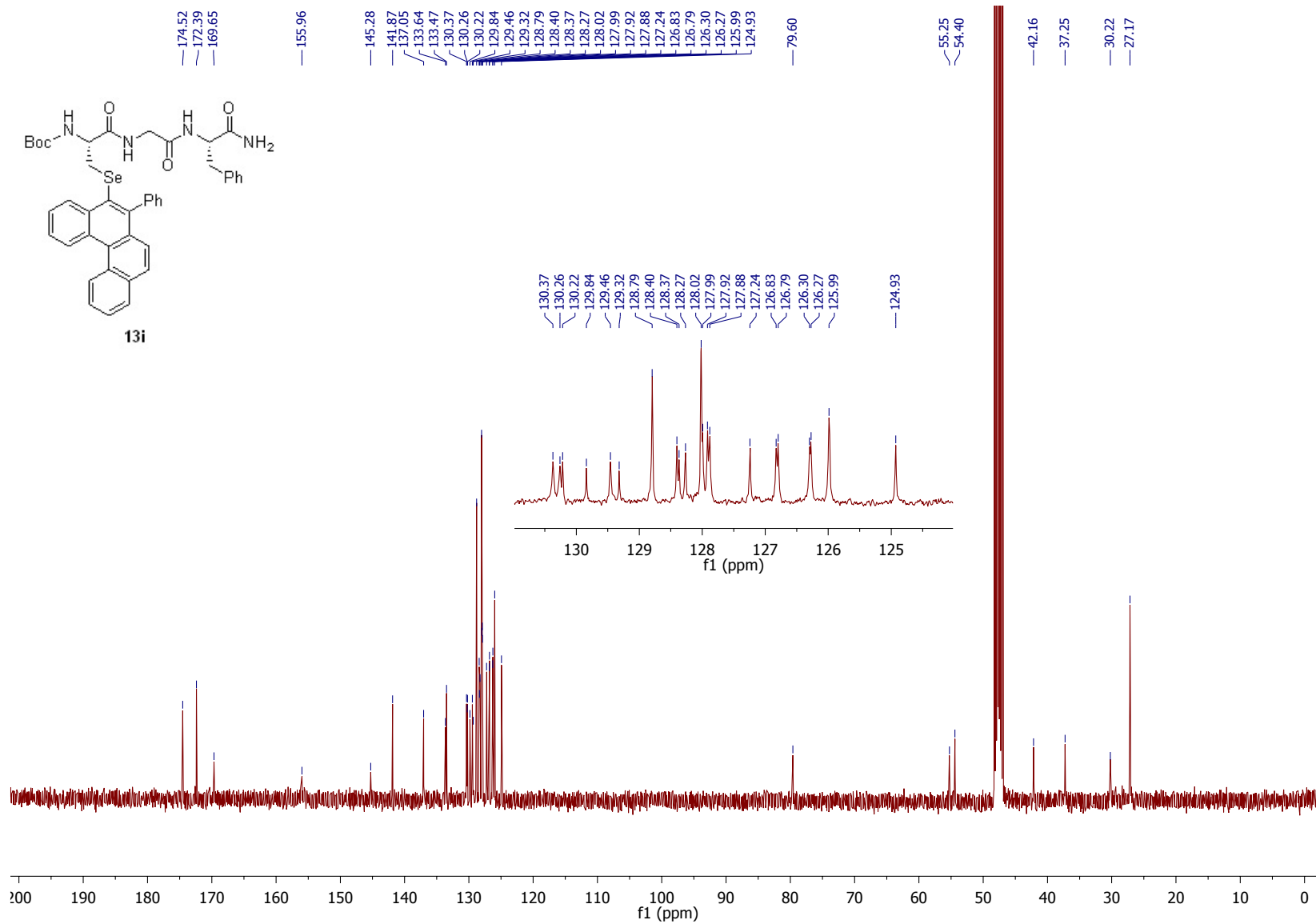


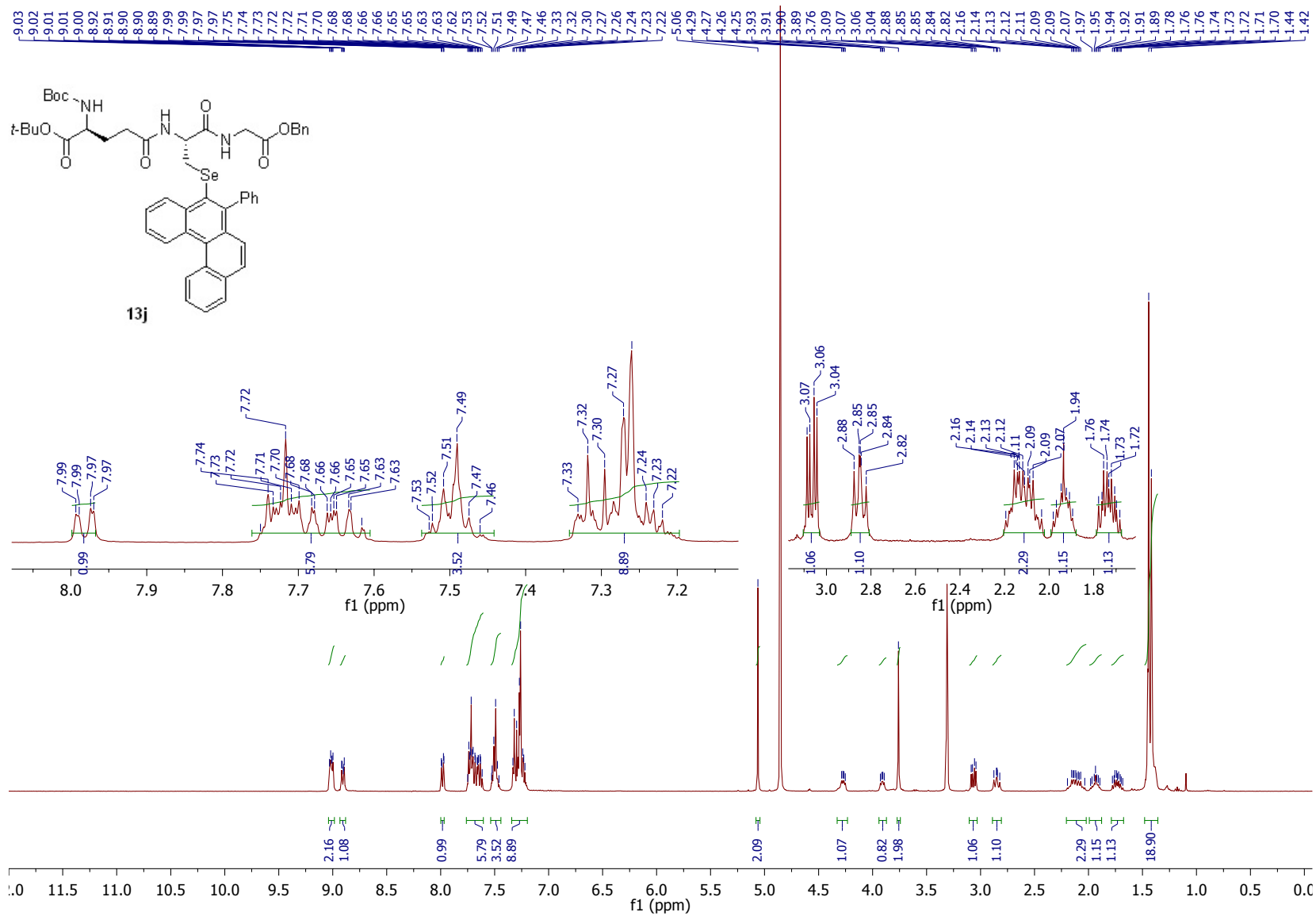


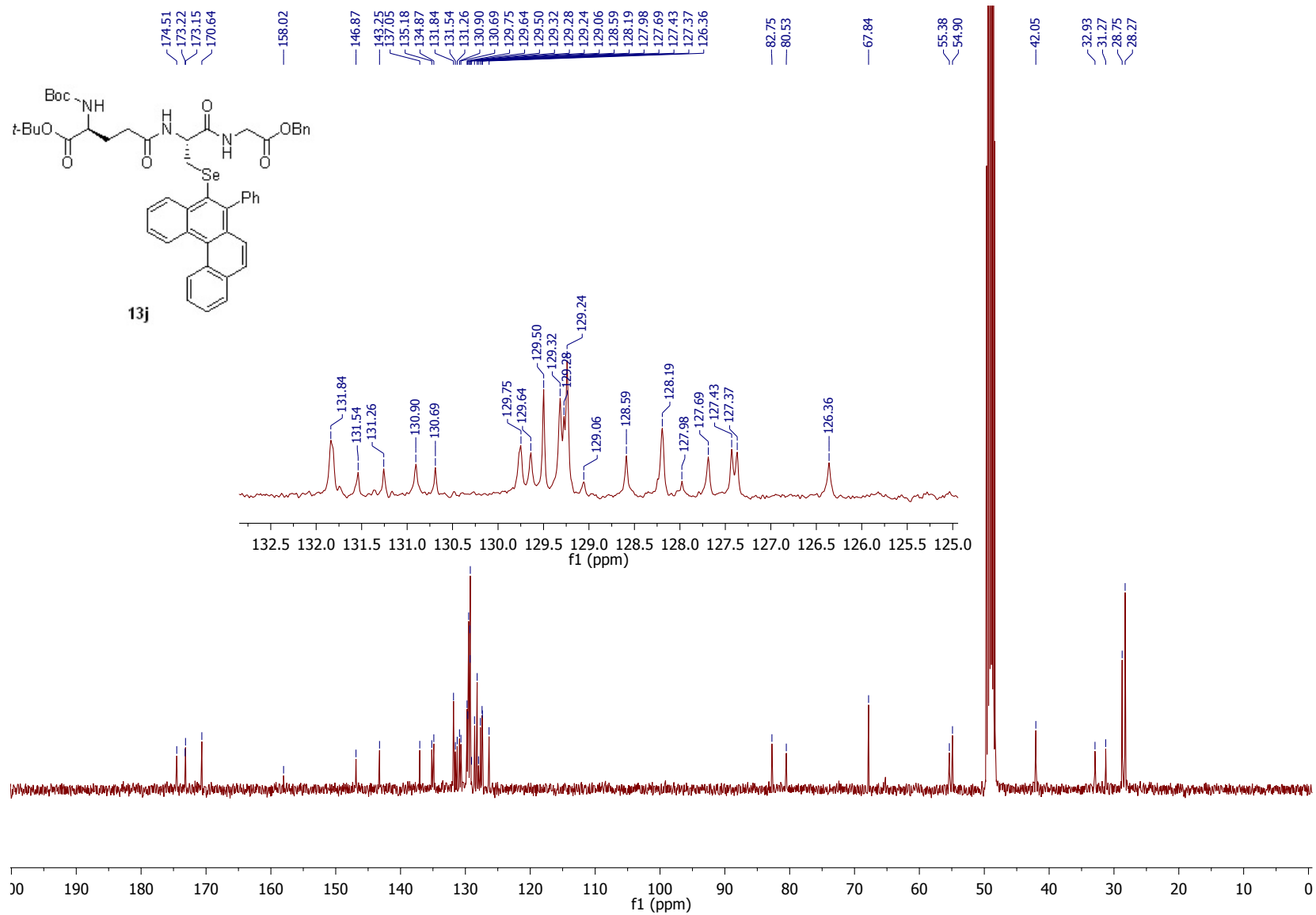


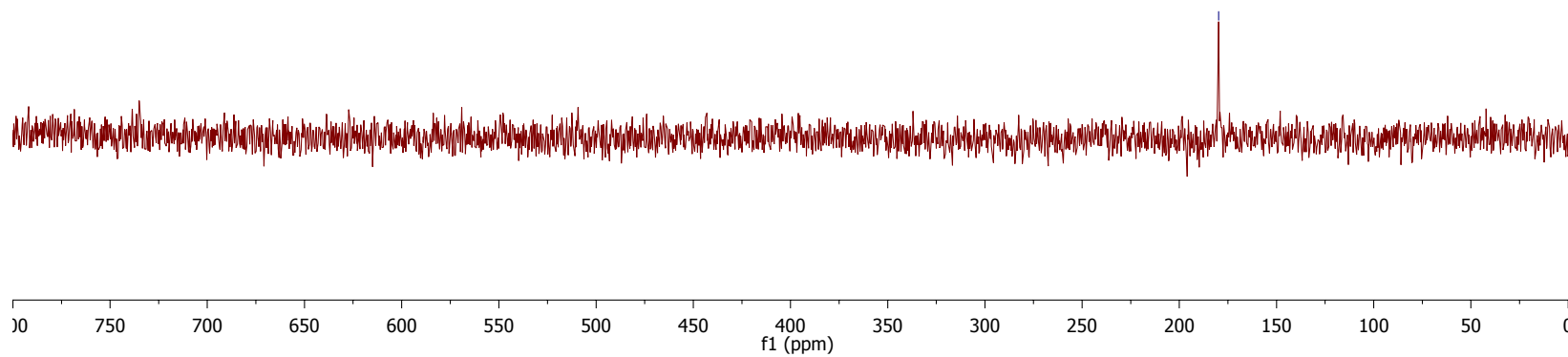
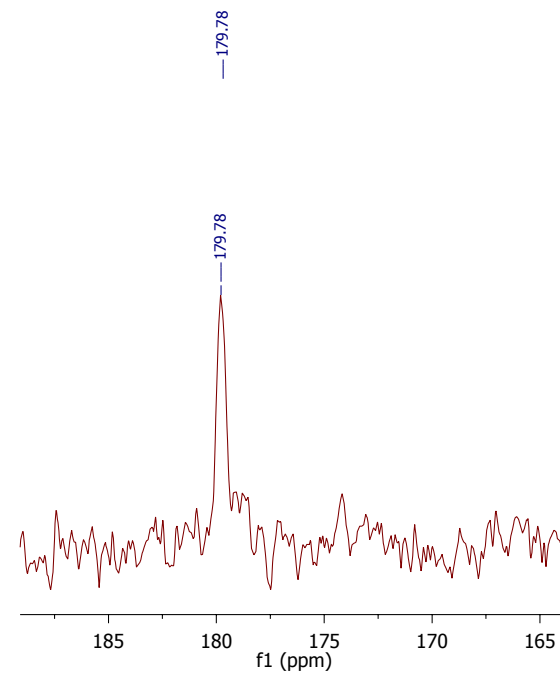
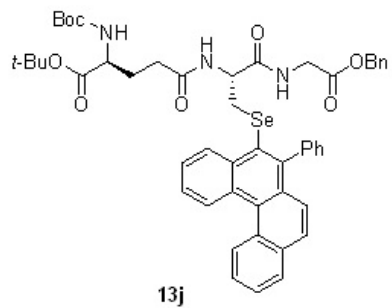


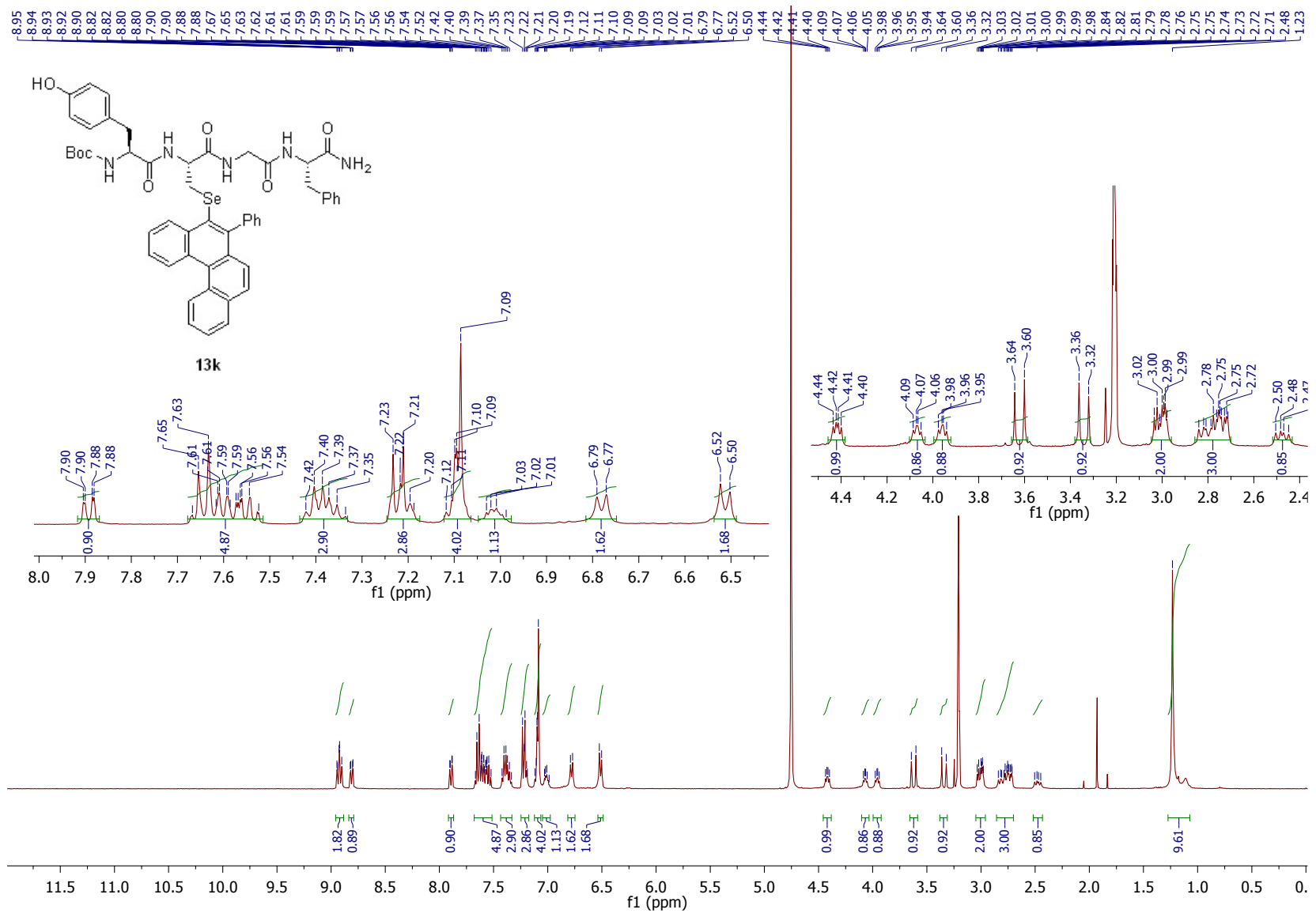


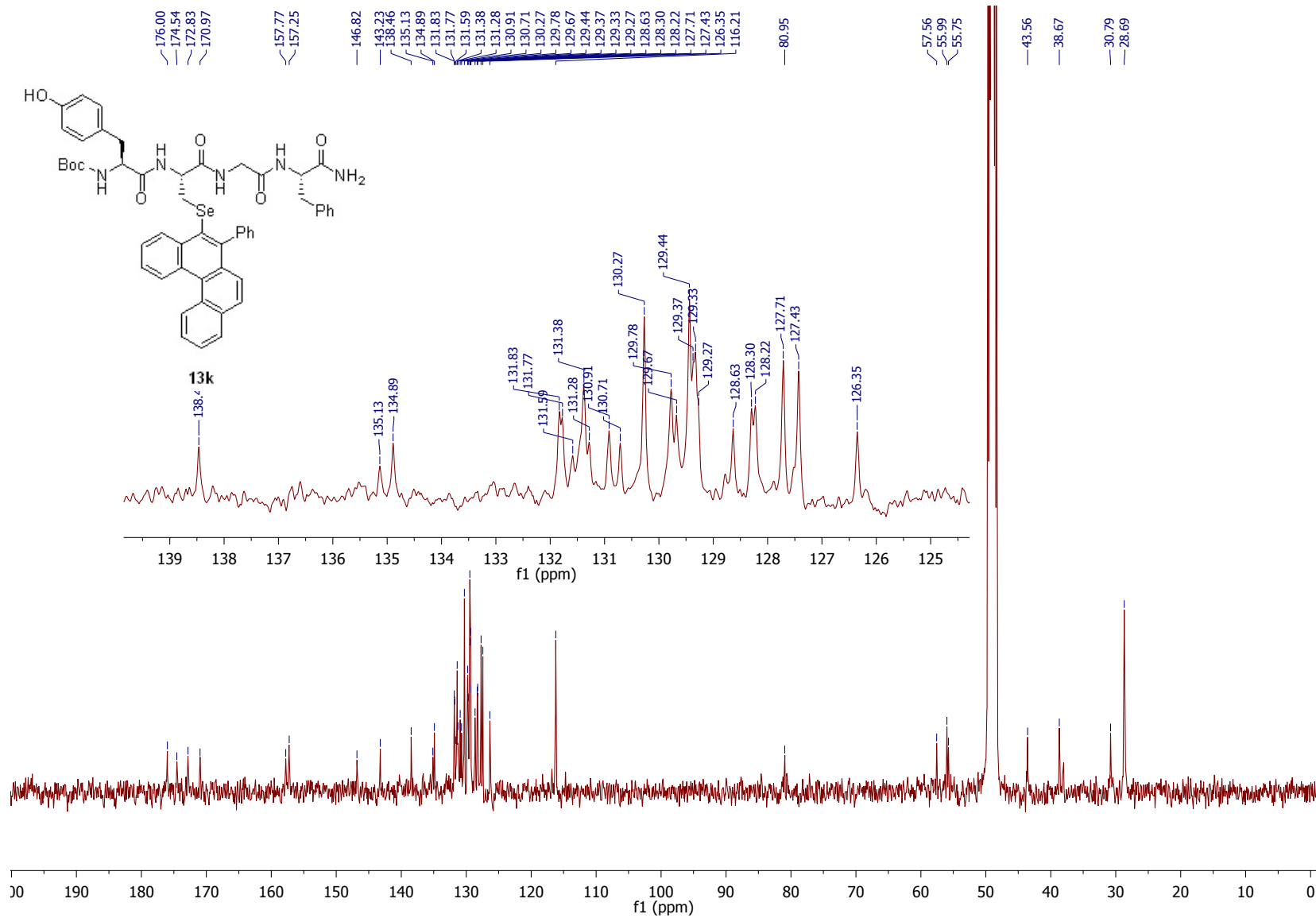


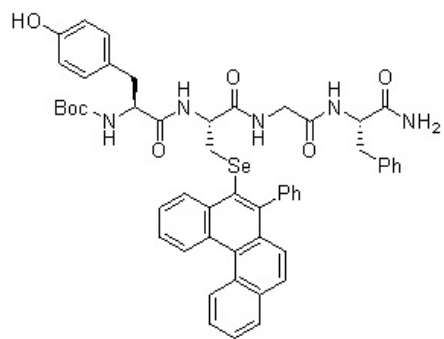












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