Tailoring Helical Ends of π-Extended [6]Heterohelicenes to Control Optical, and Electrochemical Features

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General Information

Materials

All chemicals, 3-Bromo-1,2-benzenediamine, 4-tertbutyl Phenylacetylene, 4-tert-butyliodobenzene (TCI), potassium hydroxide (Loba Chemie), Lithium aluminium hydride, Selenium dioxide (Chempure) and copper Iodide (Spectrochem) were used as received. The solvents such as dichloromethane (CH_2Cl_2), N, N-dimethylformamide (DMF), toluene, Disopropylamine, dimethyl sulfoxide (DMSO), Thionyl chloride (Finar), were used after distillation in calcium hydride as further purification.

Thin layer chromatography was carried out using Aluchrosep Silica Gel 60/UV254 purchased from Merck Specialities Pvt Ltd and visualized either by UV Fluorescence or by iodine chamber. Column chromatography was performed using silica gel (100-200 mesh), bed was made by using 60-120 mesh silica purchased from Spectrochem Pvt. Ltd. India, and mixtures of Dichloromethane-Petroleum ether used for elution were distilled before use.

General

All the reactions were carried out in oven-dried round bottom flasks under an argon atmosphere unless otherwise mentioned. The ^{1}H, ^{13}C NMR spectra were recorded at Bruker-400 and 500 MHz NMR spectrometer instruments. The chemical shift values for ^{1}H (TMS as internal standard) and ^{13}C NMR are recorded in $CDCl_3$. The value of the coupling constant (*J*) is stated in Hertz (Hz). UV-Vis absorption spectra were recorded with a Shimadzu 1800 spectrophotometer, while all emission spectra were performed using PTI Quanta Master™ Steady State Spectrofluorometer. The mass spectrometry experiments were conducted on Bruker ultraflex MALDI-TOF MS. The mass spectrum was recorded using 2, 5-Dihydroxybenzoic acid (DHB) as a matrix material. Steady State Spectrofluorometer. HPLC analysis was performed on Agilent 1260, Infinity Series using normal (CHIRALPAK SA, 5 mm, 4.6 mm x 250 mm) columns. Chiral molecule **SNG** and **SeNG** were separated using n-hexane: isopropanol (90:10) by monitoring at 254 nm. CD spectra were recorded on a Jasco J-815 CD spectrometer equipped with a Jasco PTC-424S/15 Peltier system. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo Kα = 0.71073 Å) radiation at ambient temperature.

X-ray Single Crystallography

Single crystal of **SNG** and **SeNG**, suitable for X-ray crystallography analysis was obtained by slow evaporation of methanol and $CHCl_3/CDCl_3$ solution for 3 weeks. The crystal structure was deposited at the Cambridge Crystallographic Data Centre (CCDC) and the data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

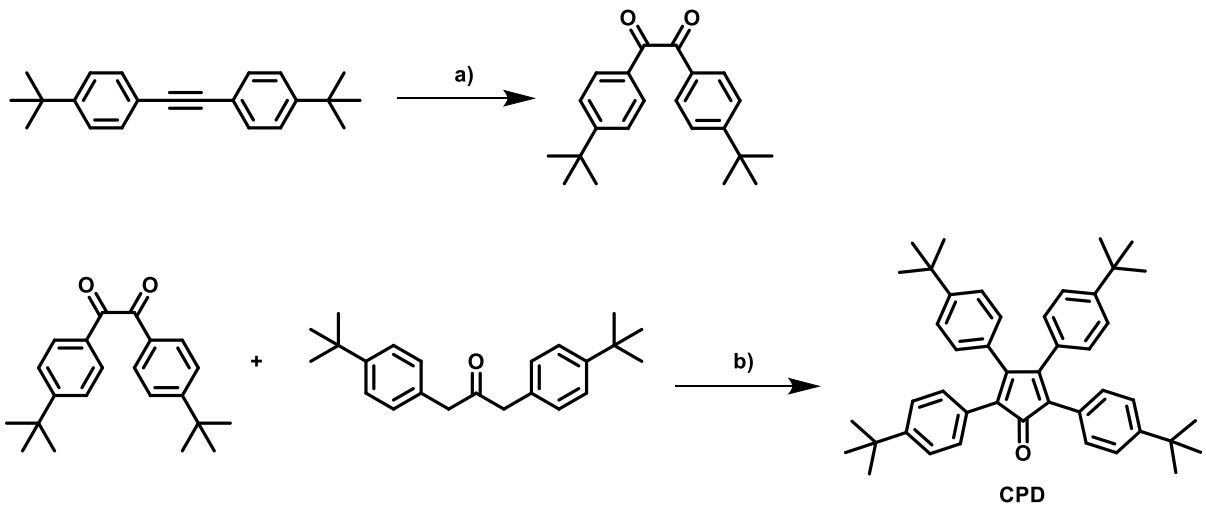
X-ray intensity data measurements

X-ray intensity data measurements of all the samples were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with a micro-focus sealed tube diffraction source (MoK_α= 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω and φ scan width of 0.5° at different settings of φ, ω and 2θ keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by the APEX3 program (Bruker, 2016). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008) structure solution program, using direct methods. The model was refined with a version of ShelXL-2013 (Sheldrick, 2015) using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP* III view of the compound was drawn with 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii.

Experimental Procedures:

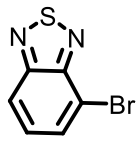
Synthesis:

Heterohelicene synthesis is shown in Scheme S1.[S1]



Scheme S1. Synthesis of π-extended SNG and SeNG helicenes. Conditions: a) I_2, DMSO, 150 ^{o}C, 10 h, 91%, b) KOH, EtOH, reflux, 1 h, 85%.

Synthesis of 4- Bromobenzo[c][1,2,5]thiadiazole (2):



In an oven-dried round bottom flask, 3-bromo-1,2-benzenediamine **1** (5g, 1 mmol) was taken and dissolved in CH_2Cl_2 (20 mL) followed by the addition of triethylamine (16 mL, 5 mmol). In an addition funnel, $SOCl_2$ (5 mL, 3 mmol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to the reaction mixture, the reaction mixture was stirred at reflux temperature. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed under vacuum, and the combined organic layer was washed with water and concentrated under vacuum. The 4-bromobenzo[c][1,2,5]thiadiazole **2** was isolated by column chromatography (4.23g, 75%).

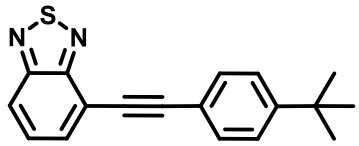
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.94 (d, *J* = 8.8 Hz, 1 H), 7.81 (d, *J* = 7.1 Hz, 1 H), 7.45 ppm (t, *J* = 7.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 154.6, 153.3, 131.9, 129.9, 120.9, 114.4.

HRMS-ESI: m/z calculated for $C_6H_4N_2BrS$ $[M+H]^+$: 214.9279, found: 214.9273.

Melting point: 78 ^oC.

Procedure for synthesis of 4-((4-(tert-butyl)phenyl)ethynyl)benzo[c][1,2,5]thiadiazole (3):



To a mixture of 4-bromo-2,1,3-benzothiadiazole **2** (500 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (37.2 mg, 0.01 mmol), and CuI (11.56 mg, 0.03 mmol) in diisopropylamine (5 mL) was added 4-*tert*-butylphenylacetylene (0.4 mL, 352 mg, 1.1 mmol). The mixture was stirred at rt for 30 mins under nitrogen, then the temperature was raised and kept at 70 ºC for 24 h. After cooling, CH_2Cl_2 (50 mL) was added. Then, the solution was washed with water (30 mL × 2) and brine (30 mL). The obtained organic solution was dried over Na_2SO_4. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using CH_2Cl_2/*n*-hexane (1:10, v/v) as eluent to afford **3** as a greenish-yellow powder (557 mg, 85%).

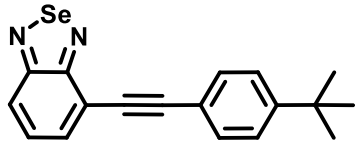
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.99 (dd, *J* = 8.8, 0.9 Hz, 1 H), 7.80 (dd, *J* = 6.9, 0.9 Hz, 1 H), 7.57 - 7.64 (m, 3 H, merged triplet and doublet), 7.42 (d, *J* = 8.5 Hz, 2 H), 1.35 ppm (s, 9 H)

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 154.6, 154.6, 152.3, 132.5, 131.7, 129.2, 125.4, 121.5, 119.6, 117.5, 96.1, 84.5, 34.9, 31.1.

HRMS-ESI: m/z calculated for $C_{18}H_{17}N_2S$ $[M+H]^+$: 293.1112, found: 293.1109.

Melting point: 112 ^oC.

Procedure for synthesis of 4-((4-(tert-butyl)phenyl)ethynyl)benzo[c][1,2,5] selendiazole (4):



The 4-((4-(tert-butyl)phenyl)ethynyl)benzo[c][1,2,5]thiadiazole **3** (100 mg, 1.00 equiv.) was dissolved in THF (5 mL) in a heatgun-dried Schlenk-tube under nitrogen. $LiAlH_4$ (65 mg, 5 equiv.) was added slowly over 10 min at 0°C. After stirring for 2h at room temperature until the starting material was completely consumed. After that, the mixture was cooled down to 0 °C again and added a saturated NH_4Cl solution. The mixture was diluted with water (30 mL) and extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was directly used for the next reaction for which the solution of the diamine (1 equiv.) in EtOH (8 mL per 50 mg diamin) at 60 °C was added a solution of selenium dioxide (5 equiv.) in hot water (100 mg SeO_2 in 1 mL). After heating the mixture overnight it was diluted with water and extracted three times with DCM. Purification by flash column chromatography gives 4-((4-(tert-butyl)phenyl)ethynyl)benzo[c][1,2,5] selendiazole 75 mg, 65% in two steps.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.83 (dd, *J* = 9.1, 0.9 Hz, 1 H), 7.69 (dd, *J* = 6.8, 0.9 Hz, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.48 (t, 1 H), 7.41 (d, *J* = 8.5 Hz, 2 H), 1.35 ppm (s, 9 H)

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 160.1, 159.7, 152.2, 132.7, 131.7, 129.4, 125.4, 123.6, 119.6, 119.0, 96.0, 85.0, 34.9, 31.1

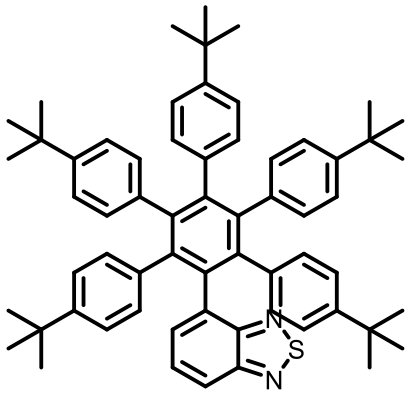
HRMS-ESI: m/z calculated for $C_{18}H_{17}N_2Se$ $[M+H]^+$: 341.0557, found: 341.0536.

Melting point: 115 ^oC.

General procedure for the synthesis of 5 and 6:

A sealing tube (20 mL) equipped with a magnetic stirring bar was charged with **3** or **4** (1 eq.) and 2,3,4,5 tetrakis(4(tertbutyl)phenyl)cyclopenta-2,4-diene-1-one **CPD** (1.1 eq) and toluene (1.5 mL for 200 mg reaction). The flask was purged with N2 and closed. The reaction mixture was stirred for 48 h at 230 °C. After cooling to RT, 20 mL methanol was added and filtered off the white solid precipitate and was washed with an excess of cold methanol until the filtrate remained colorless. The remaining solid was dried under vacuum. The product was obtained as an off-white solid.

Synthesis of 5:



Compound **3** (100 mg, 1eq.) and 2,3,4,5 tetrakis(4(tertbutyl)phenyl)cyclopenta-2,4-diene-1-one **CPD** (206.4 mg, 1.1 eq) were reacted according to the general procedure. An off-white solid was isolated after precipitation and further purification was done by column (silica gel, *n*-hexane/CH_2Cl_2, 9:1, 237 mg, 85%).

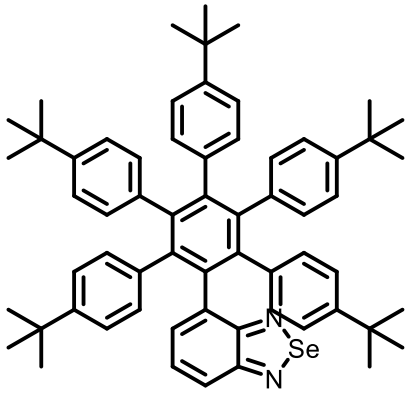
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.55 (d, *J* = 8.6 Hz, 1 H), 7.21 (t, *J* = 7.8 Hz, 1 H), 7.13 (d, *J* = 6.8 Hz, 1 H), 6.78 - 6.87 (m, 6 H), 6.72 (br. s., 10 H), 6.63 (d, *J* = 8.1 Hz, 2 H), 6.58 (d, *J* = 8.1 Hz, 2 H), 1.07 - 1.13 (m, 27 H), 1.00 ppm (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): **δ [ppm]** = 154.5, 154.2, 147.8, 147.5, 147.4, 141.5, 140.7, 140.6, 137.8, 137.6, 137.5, 135.4, 131.7, 131.1, 130.9, 131.0, 130.3, 128.7, 123.1, 123.0, 123.0, 122.6, 119.1, 34.1, 34.0, 33.9, 31.2, 31.0 .

HR MS-ESI: m/z calculated for $C_{62}H_{69}N_2S$ $[M+H]^+$: 873.5181, found: 873.5135.

Melting point: 310 ^oC.

Synthesis of 6:



Compound **4** (50 mg, 1eq.) and 2,3,4,5 tetrakis(4(tertbutyl)phenyl)cyclopenta-2,4-diene-1-one **CPD** (90 mg, 1.1 eq) were reacted according to the general procedure. An off-white solid was isolated after precipitation and further purification was done by column (silica gel, *n*-hexane/ CH_2Cl_2, 9:1, 102 mg, 80%).

^{1}H NMR (400MHz, $CDCl_3$): δ [ppm] = 7.38 (d, *J* = 8.8 Hz, 1 H), 7.11 (t, 1 H), 6.99 (d, *J* = 5.9 Hz, 1 H), 6.82 (m, 6 H), 6.69 - 6.75 (m, 10 H), 6.64 (d, *J* = 8.1 Hz, 2 H), 6.58 (d, *J* = 7.9 Hz, 2 H), 1.11 (s, 9 H), 1.09 (s, 18 H), 1.00 (s, 18 H)

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 160.1, 160.0, 147.8, 147.5, 147.4, 141.4, 140.6, 140.5, 137.8, 137.6, 136.8, 135.8, 131.7, 131.1, 130.9, 131.0, 130.3, 130.2, 129.1, 123.1, 123.1, 124.9, 122.6, 121.2, 34.0, 34.0, 31.2, 31.0.

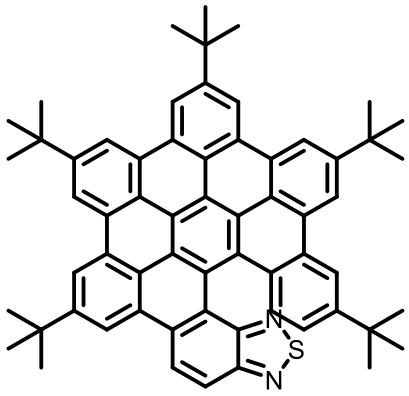
HRMS-ESI: m/z calculated for $C_{62}H_{69}N_2Se$ $[M+H]^+$: 921.4626, found: 921.4658.

Melting point: 312 ^oC.

General procedure for the synthesis of SNG and SeNG:

Round bottom flask (100 mL) equipped with a magnetic stirring bar was charged with **5** or **6** 1 eq., 6 eq. DDQ and CH_2Cl_2 (40 mL for 100 mg reaction). The mixture was degassed via N_2-bubbling for 20 min and meanwhile cooled to 0 °C. Later, 0.15 mL of triflic acid was added in one portion and the flask was closed with a rubber septum under N_2. The reaction mixture was stirred for 2h at 0 °C and after that, MeOH (30 mL) and NEt_3 (10 mL) were added. All solvents were evaporated and the crude was filtered over a pad of silica gel with *n*-hexane/CH_2Cl_2 (1:1). Final purification was achieved by column chromatography over silica gel with *n*-hexane/CH_2Cl_2.

Procedure for synthesis of SNG:



5 (100 mg) was reacted according to the general procedure. An orange crystalline solid was isolated after column chromatography (silica gel, *n*-hexane/CH_2Cl_2, 9:1, 79 mg, 80%).

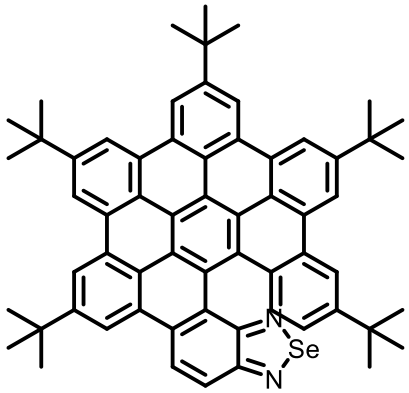
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.34 (s, 1 H), 9.31 (s, 1 H), 9.28 (s, 1 H), 9.27 (s, 1 H), 9.25 (s, 2 H), 9.19-9.17 (m, 3 H), 8.79 (s, 1 H), 8.26 (d, *J* = 9.2 Hz, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 6.89 (dd, *J* = 8.5, 1.8 Hz, 1 H), 1.82 - 1.85 (m, 36 H), 1.46 (s, 9 H)

^{13}C NMR (125 MHz, $CDCl_3$): **δ [ppm]** = 154.4, 153.5, 149.6, 149.4, 149.4, 149.1, 148.9, 130.7, 130.6, 130.4, 130.0, 129.9, 129.8, 129.3, 129.1, 128.8, 127.5, 124.8, 124.8, 124.0, 123.7, 123.6, 123.2, 123.0, 122.6, 121.6, 120.3, 120.0, 119.6, 119.3, 119.2, 119.1, 118.9, 118.8, 117.9, 35.9, 35.8, 35.7, 34.9, 32.0, 31.4.

MALDI-TOF: m/z calculated for $C_{62}H_{58}N_2S$ $[M+H]^+$: 862.4321, found: 862.8814.

Melting point: Stable up to ~320 ^oC, after that slowly decomposes.

Procedure for synthesis of SeNG:



6 (50 mg) was reacted according to the general procedure. A reddish crystalline solid was isolated after column chromatography (silica gel, *n*-hexane/CH_2Cl_2, 9:1, 40.5 mg, 82%).

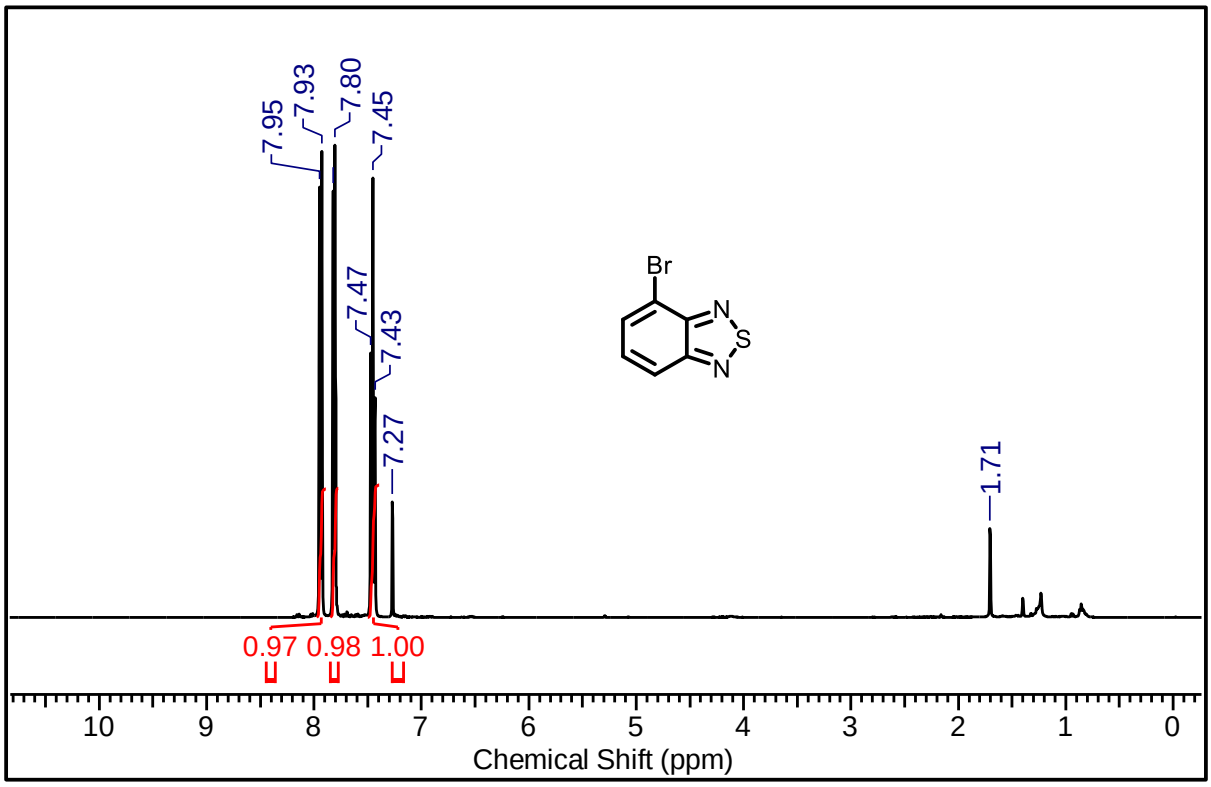
^{1}H NMR (500MHz, $CDCl_3$): δ [ppm] = 9.34 (s, 1 H), 9.28 (s, 1 H), 9.30 (s, 1 H), 9.21-9.27 (m, 3 H), 9.14 (s, 2 H), 9.09 (d, *J* = 9.8 Hz, 1 H), 8.75 (s, 1 H), 8.10 (d, *J* = 9.5 Hz, 1 H), 7.91 (d, *J* = 8.5 Hz, 1 H), 6.90 (dd, *J* = 8.7, 1.7 Hz, 1 H), 1.81 - 1.84 (m, 36 H), 1.45 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): **δ [ppm]** = 159.8, 158.4, 149.6, 149.4, 149.0, 148.7, 130.7, 130.5, 130.4, 129.9, 129.8, 129.6, 129.2, 128.9, 128.7, 127.8, 126.3, 125.0, 124.1, 123.7, 123.6, 123.3, 123.1, 122.4, 122.1, 121.5, 120.3, 119.5, 119.3, 119.2, 119.1, 118.9, 118.8, 118.8, 118.3, 35.8, 35.7, 34.8, 32.0, 31.4.

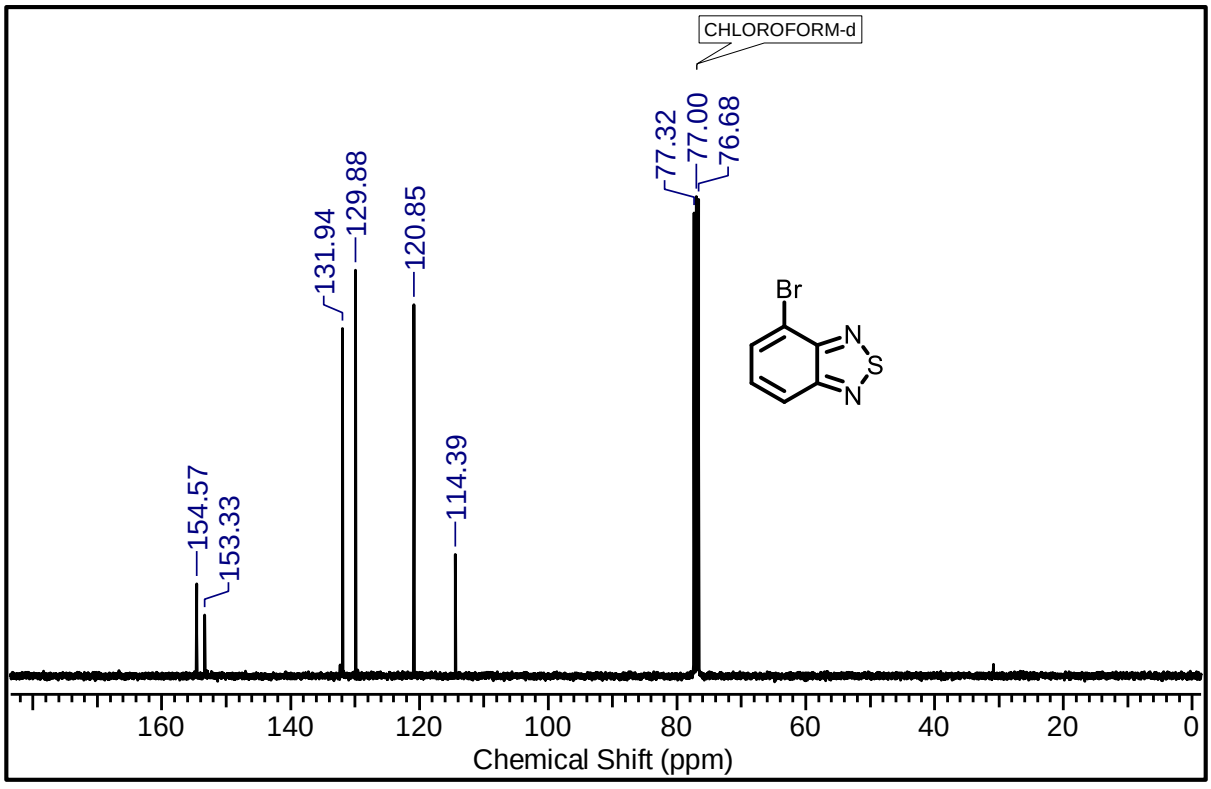
MALDI-TOF: m/z calculated for $C_{62}H_{58}N_2Se$ $[M+H]^+$: 910.3765, found: 910.9074.

Melting point: Stable up to ~320 ^oC, after that slowly decomposes.

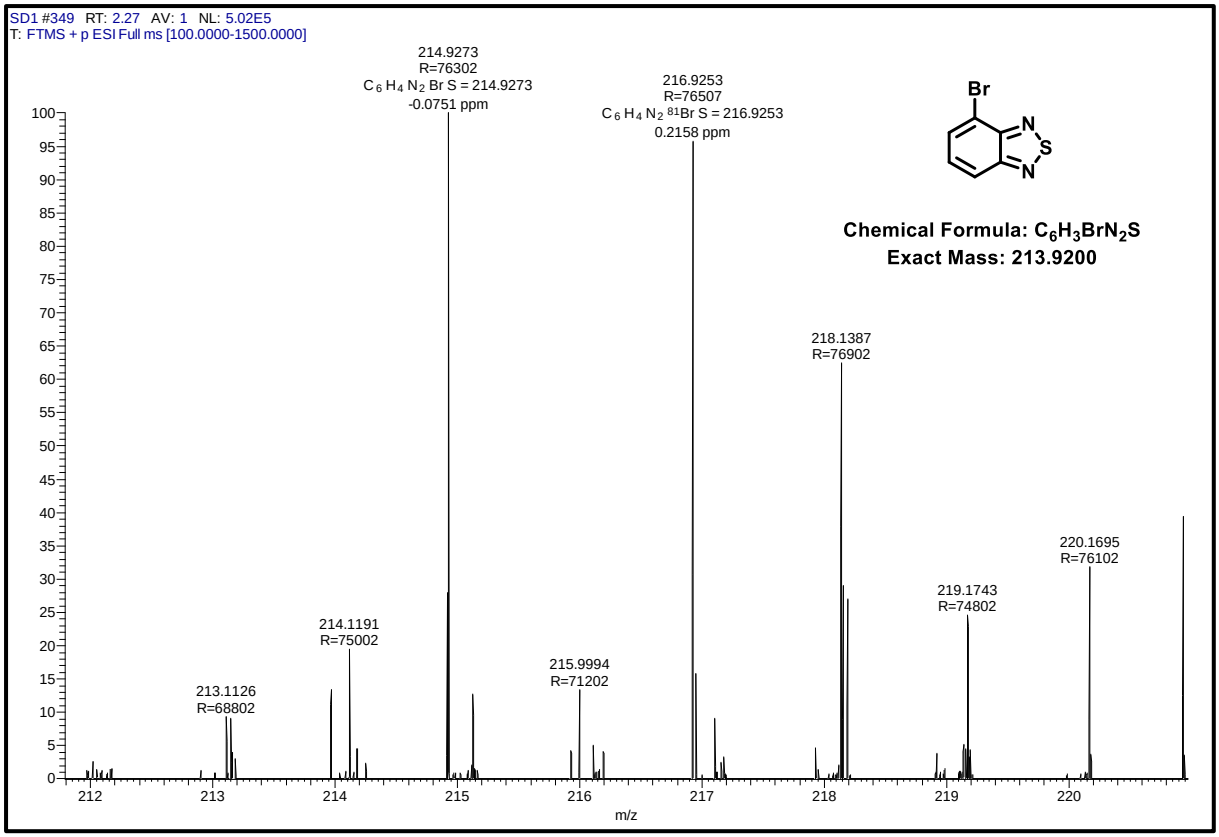
^{1}H, ^{13}C NMR, and Mass Spectra



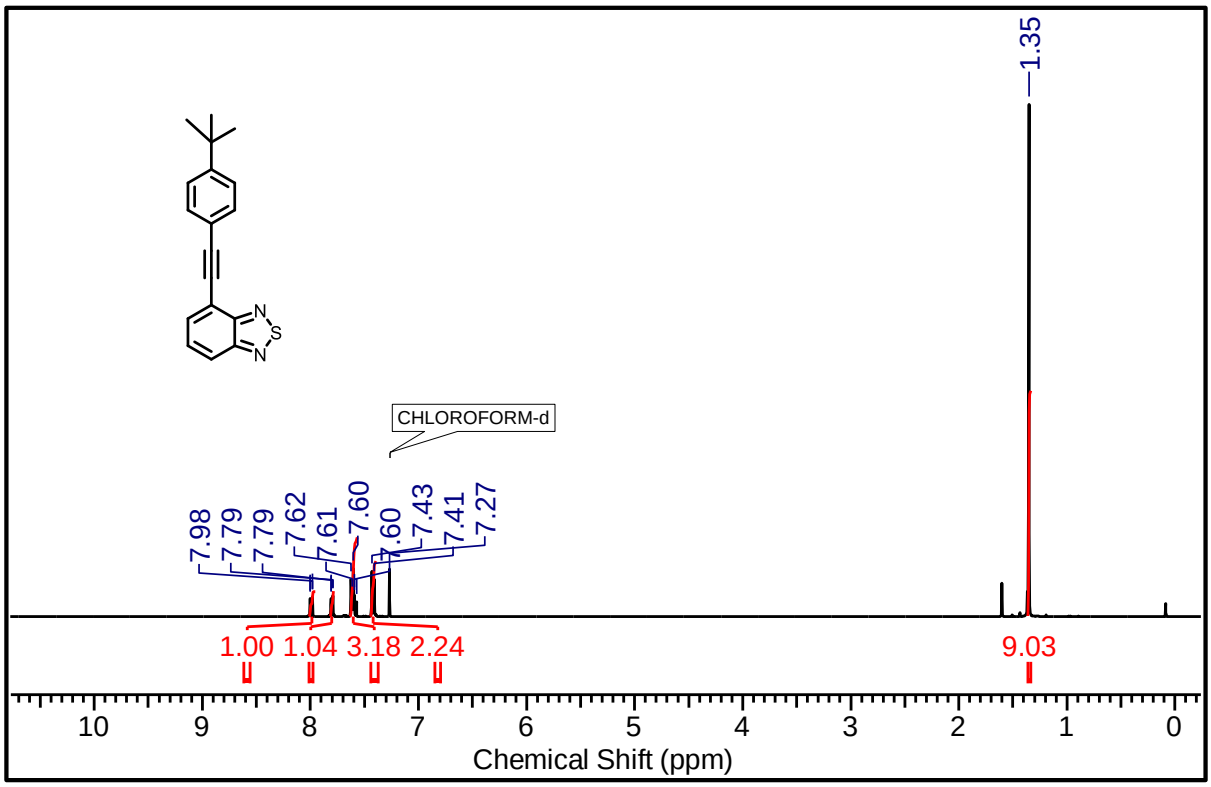
^{1}H NMR (400 MHz) spectrum of 2 in $CDCl_3$ at 298 K



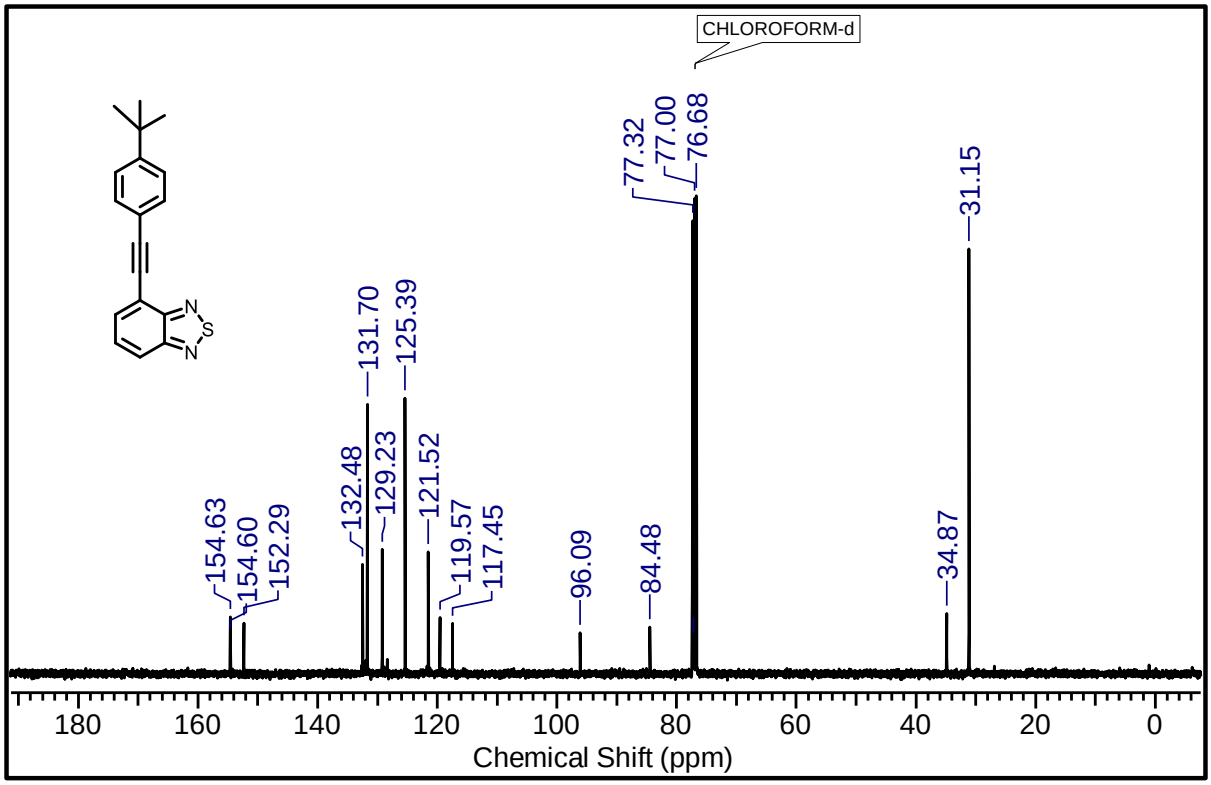
^{13}C NMR (100 MHz) spectrum of 2 in $CDCl_3$ at 298 K



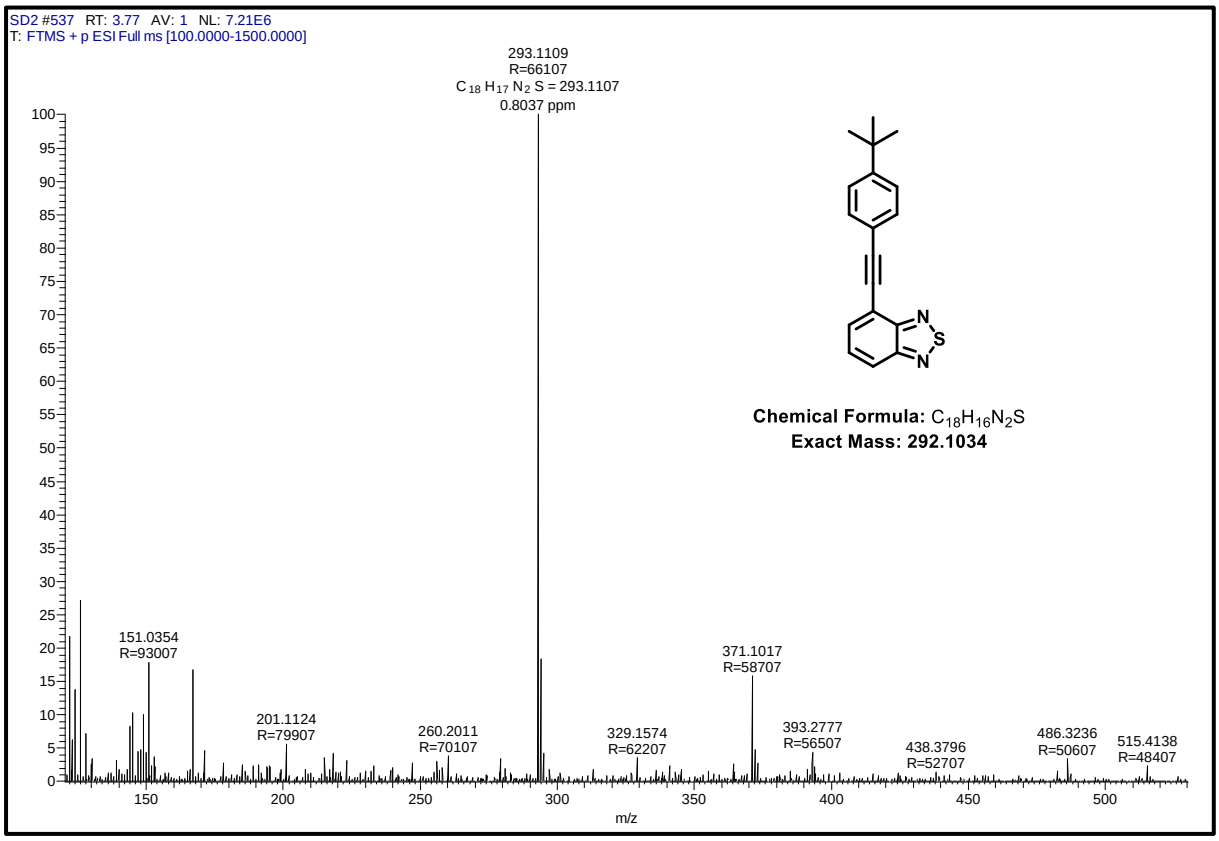
HR MS-ESI spectrum of 2



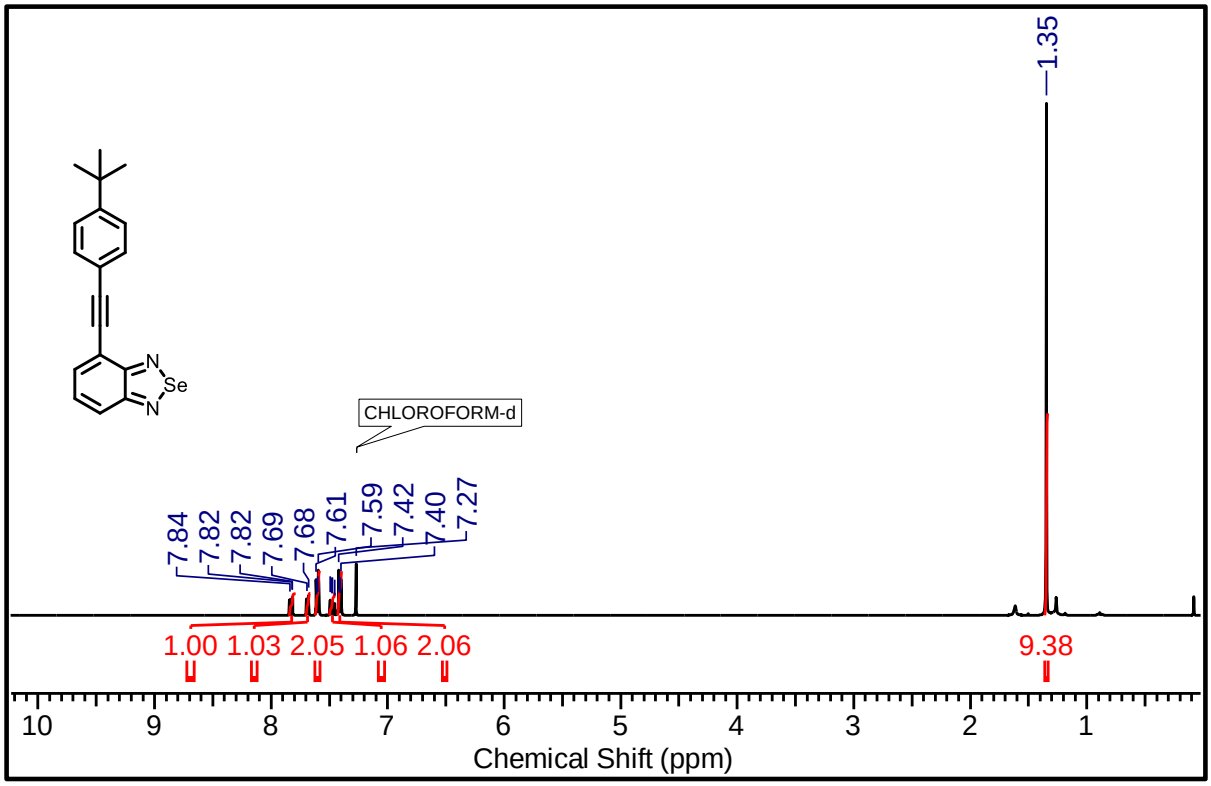
^{1}H NMR (400 MHz) spectrum of 3 in $CDCl_3$ at 298 K



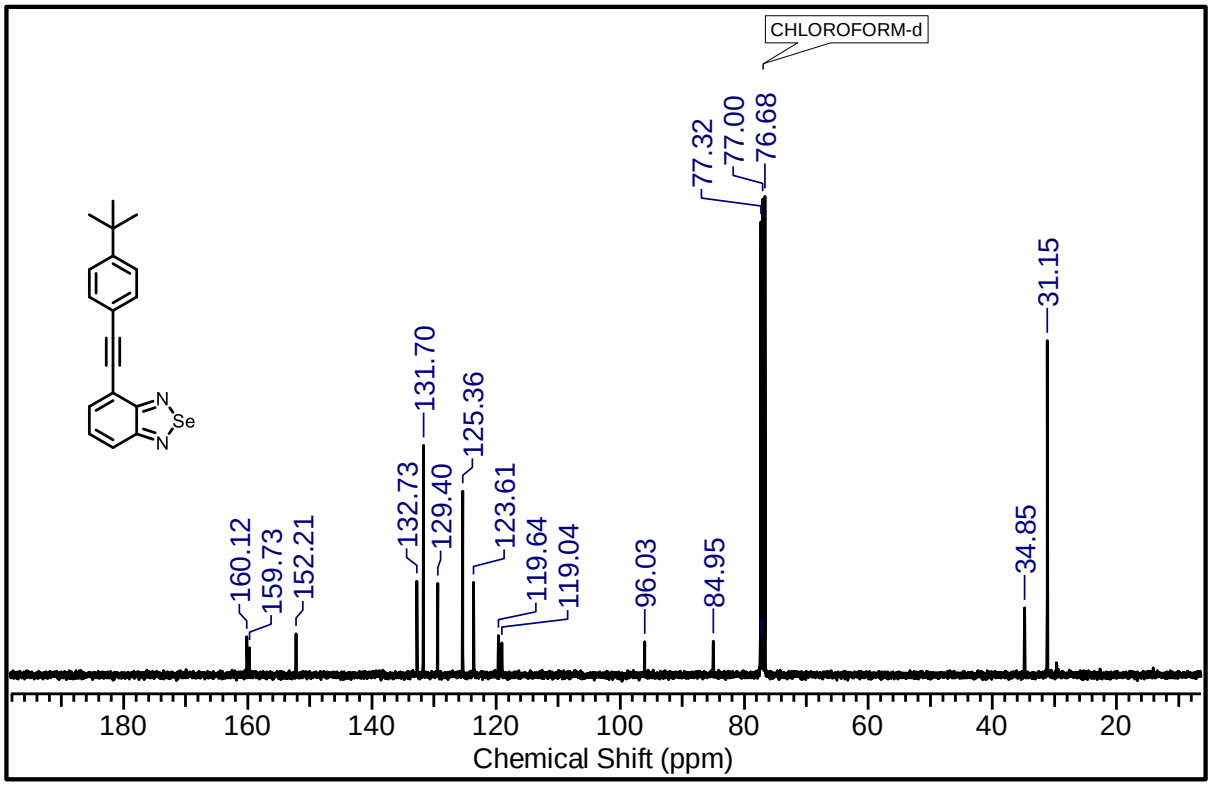
^{13}C NMR (100 MHz) spectrum of 3 in $CDCl_3$ at 298 K



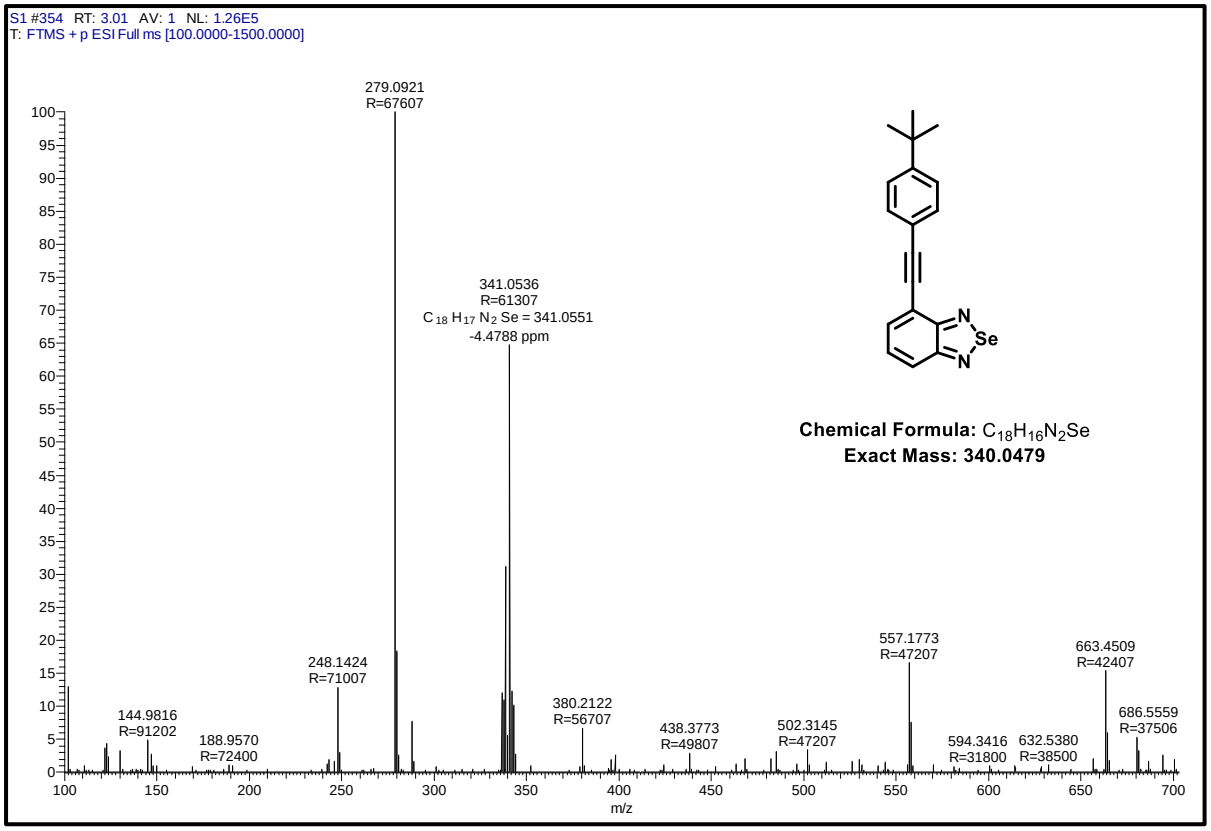
HR MS-ESI spectrum of 3



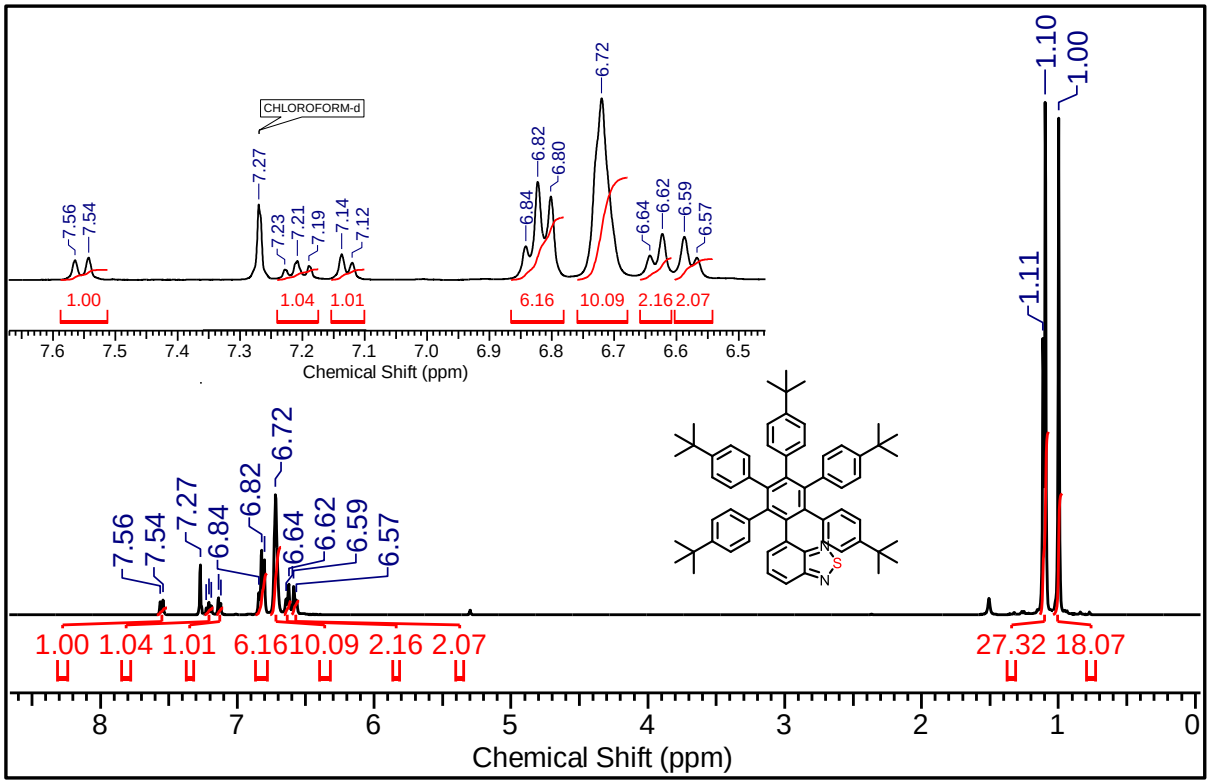
^{1}H NMR (400 MHz) spectrum of 4 in $CDCl_3$ at 298 K



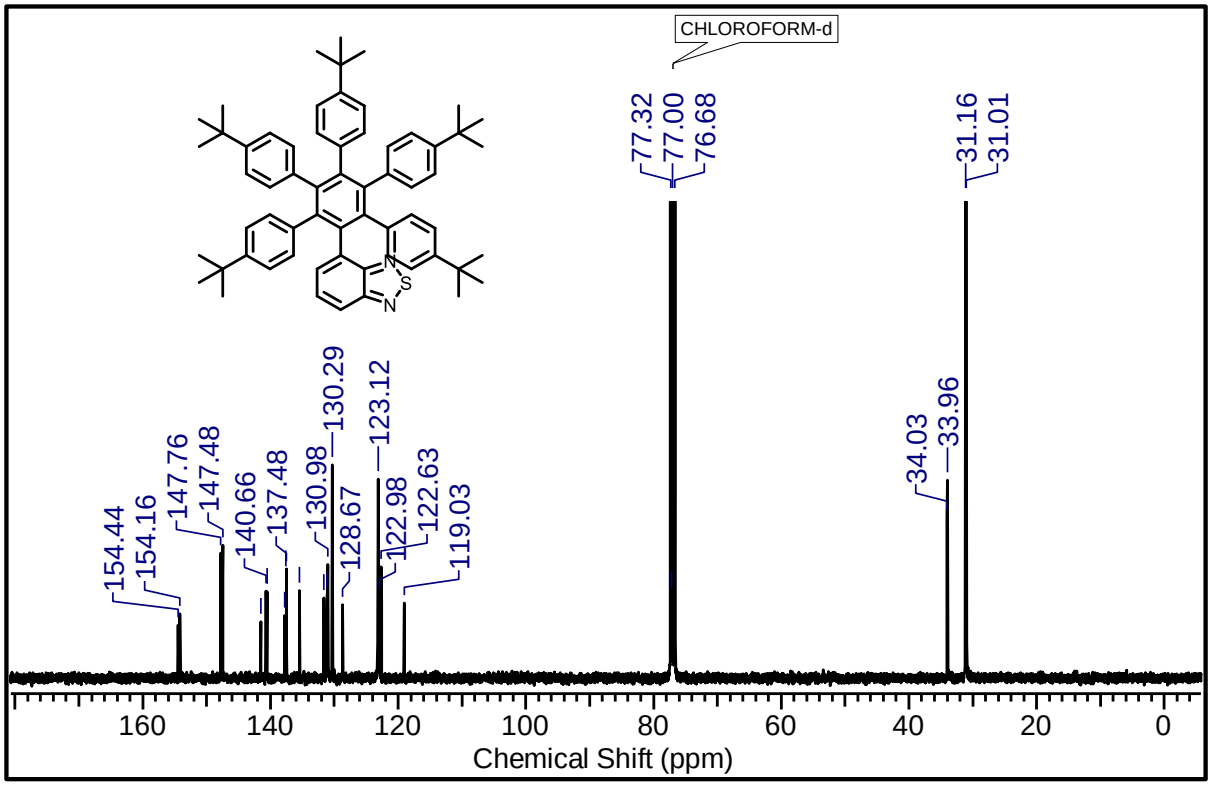
^{13}C NMR (100 MHz) spectrum of 4 in $CDCl_3$ at 298 K



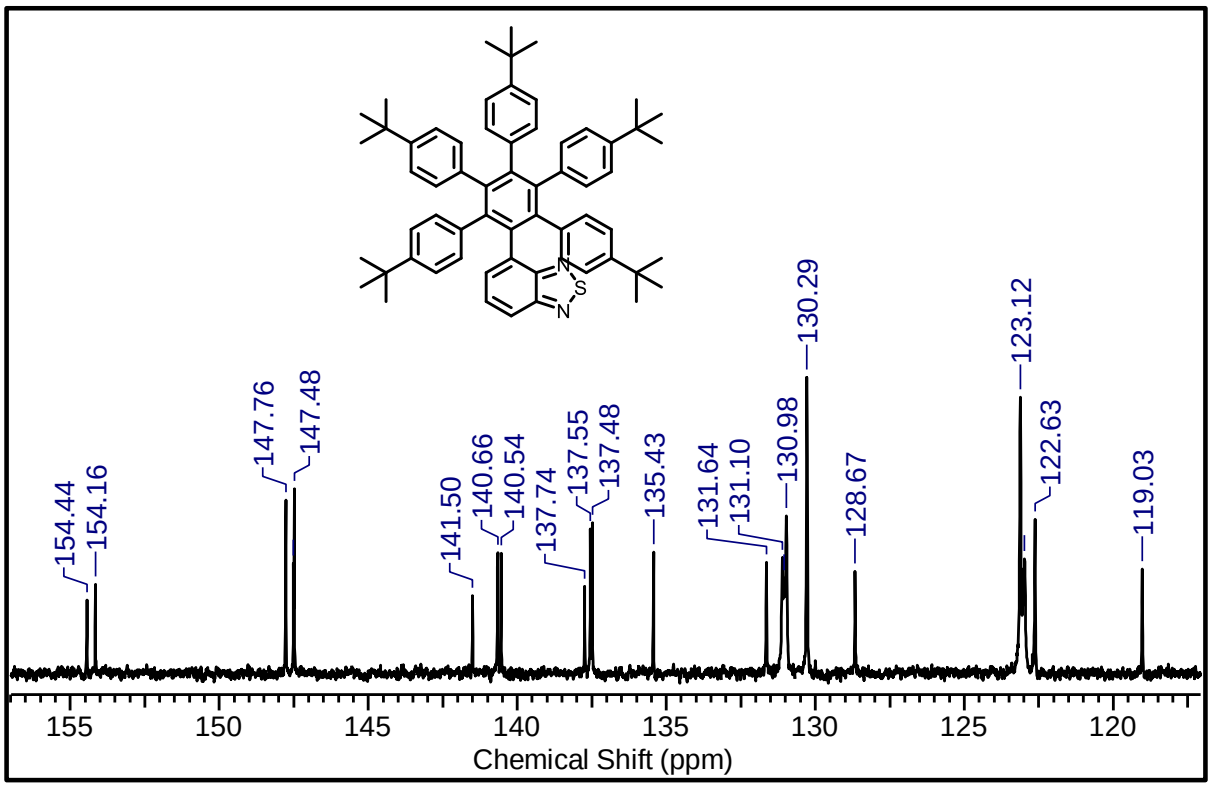
HR MS-ESI spectrum of 4



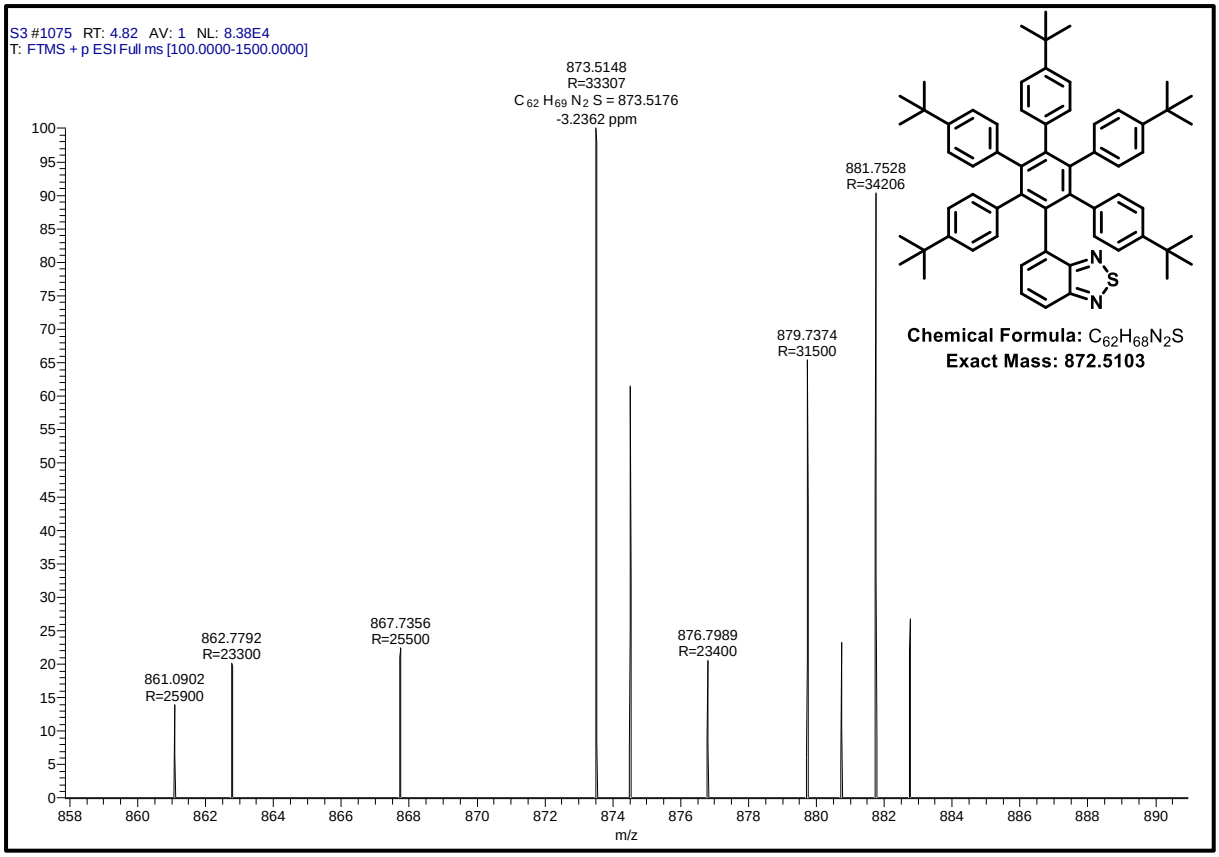
^{1}H NMR (400 MHz) spectrum of 5 in $CDCl_3$ at 298 K



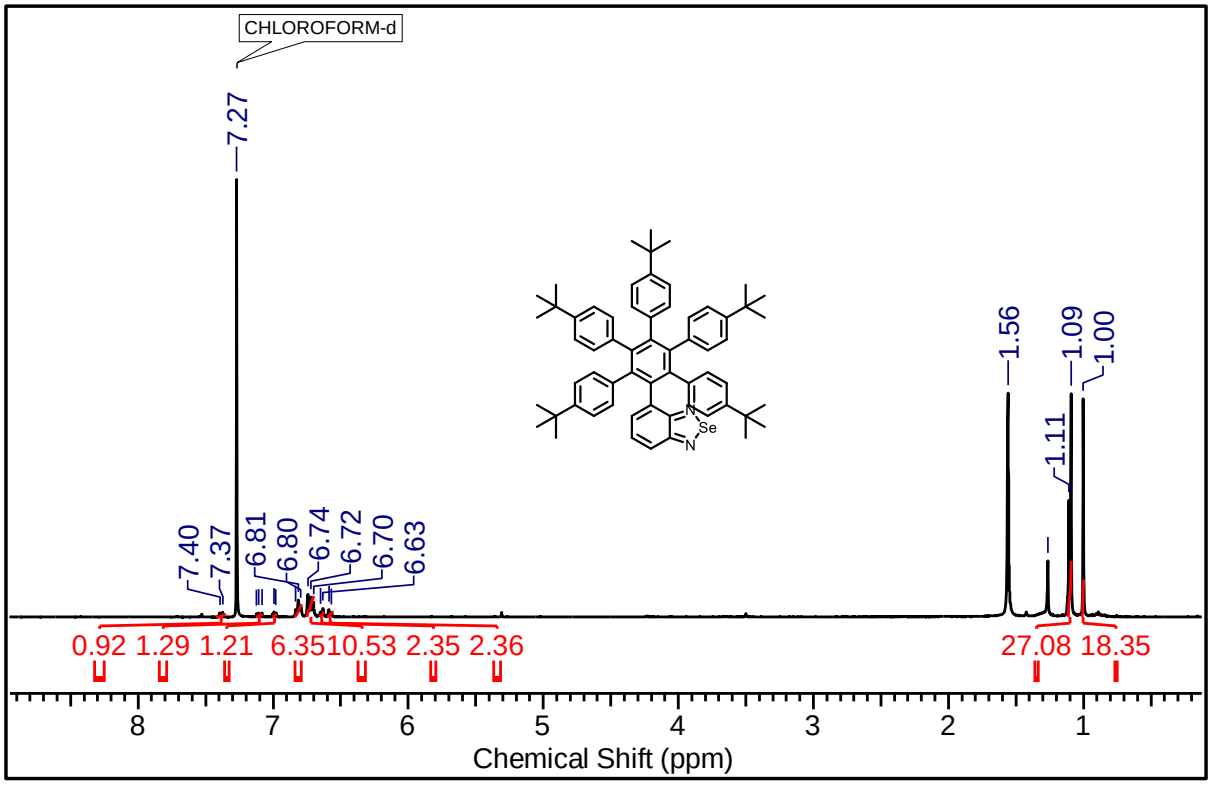
^{13}C NMR (101 MHz) spectrum of 5 in $CDCl_3$ at 298 K



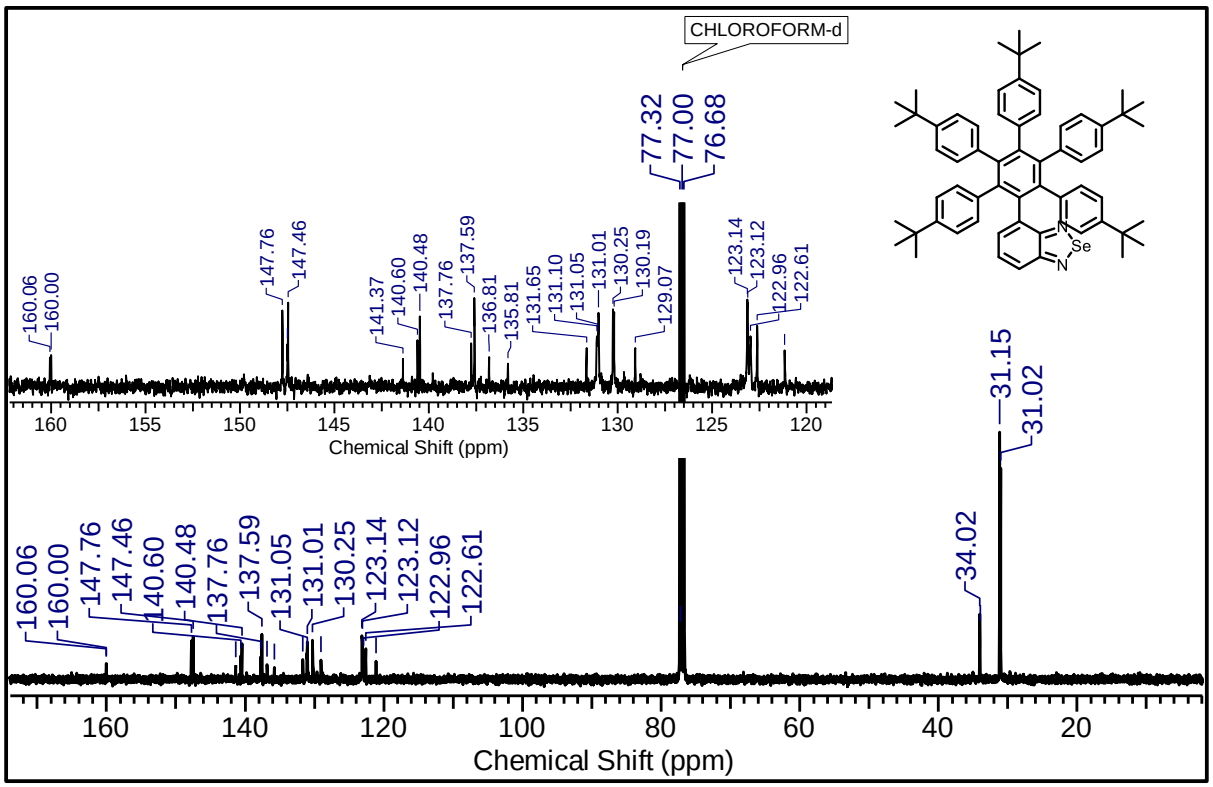
^{13}C NMR (100 MHz) cutout (aromatic region) spectrum of 5



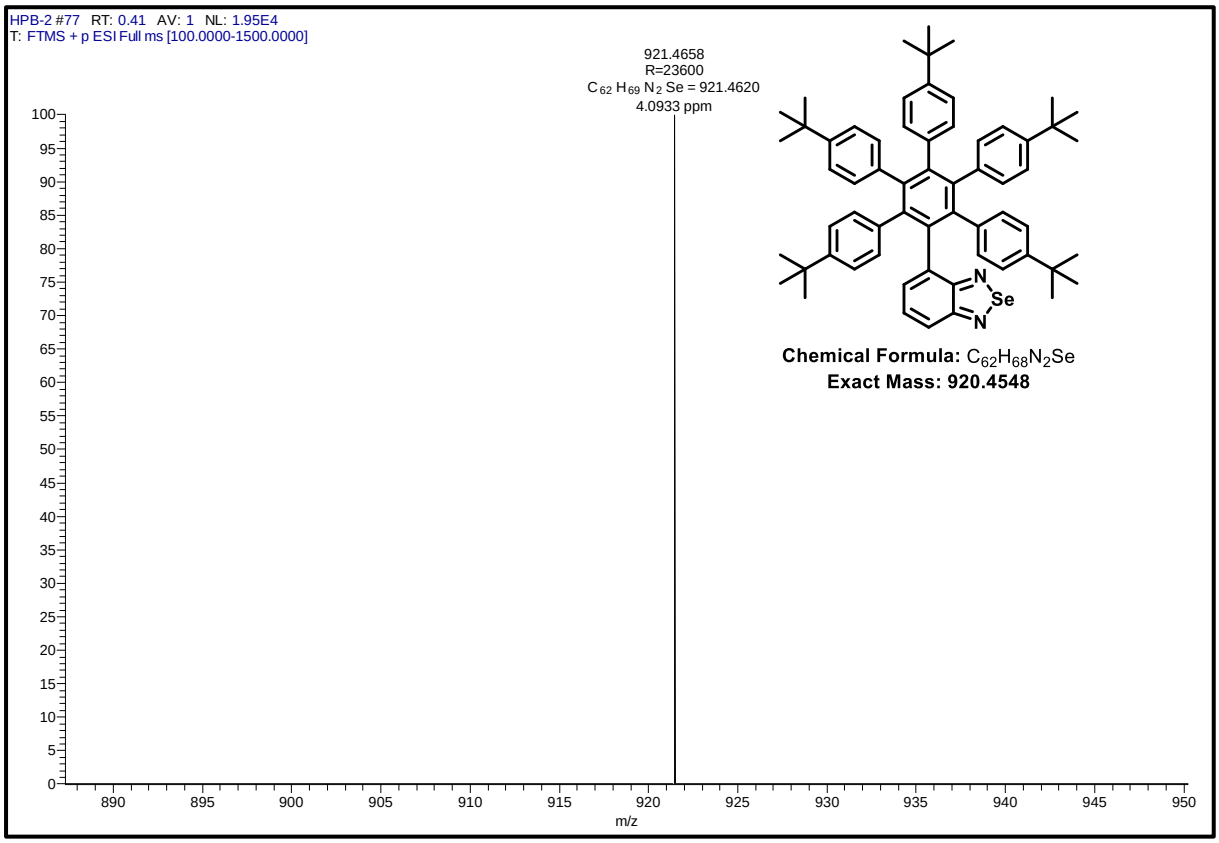
HR MS-ESI spectrum of 5



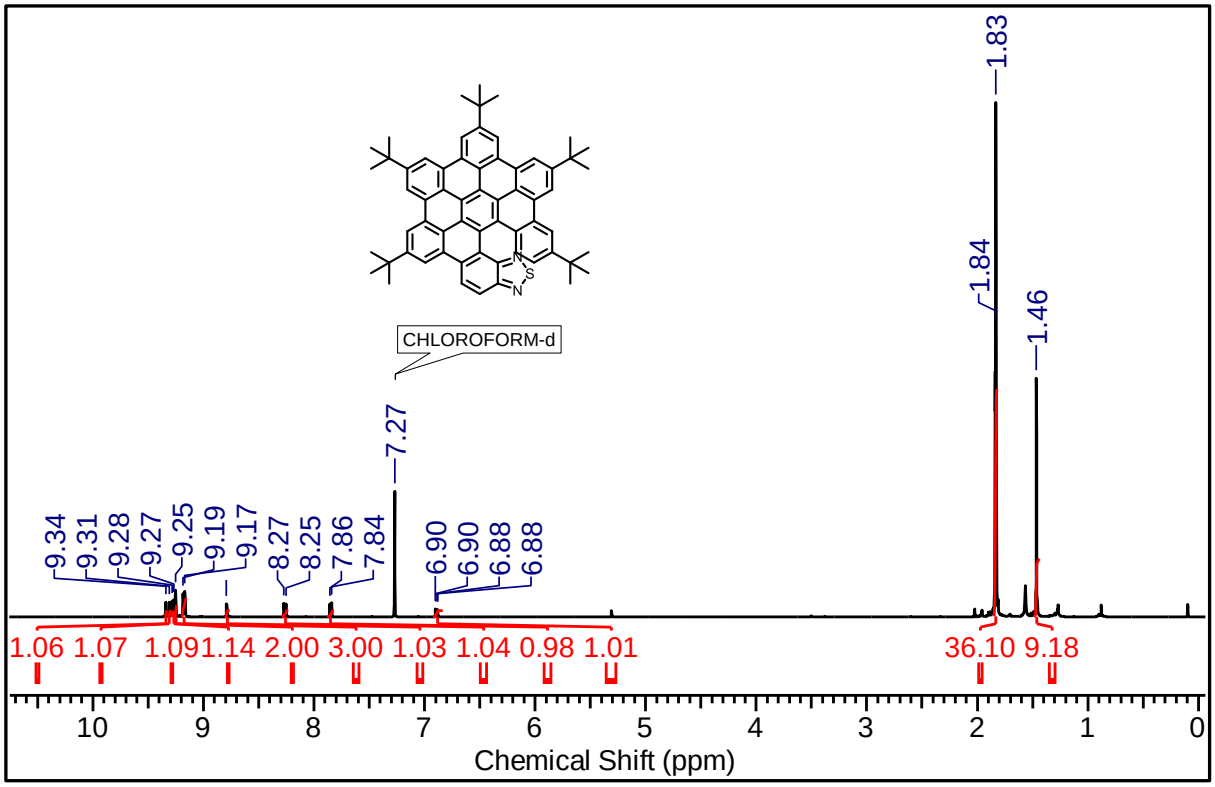
^{1}H NMR (400 MHz) spectrum of 6 in $CDCl_3$ at 298 K



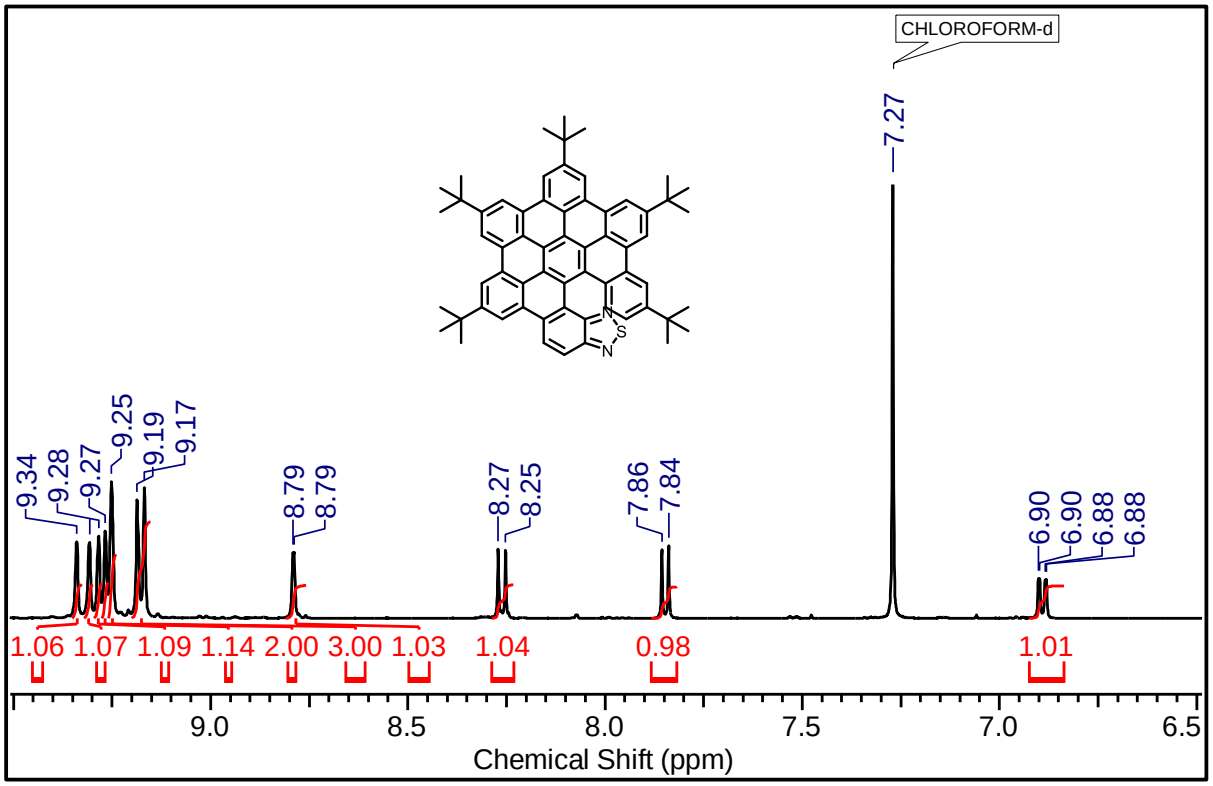
^{13}C NMR (100 MHz) spectrum of 6 in $CDCl_3$ at 298 K



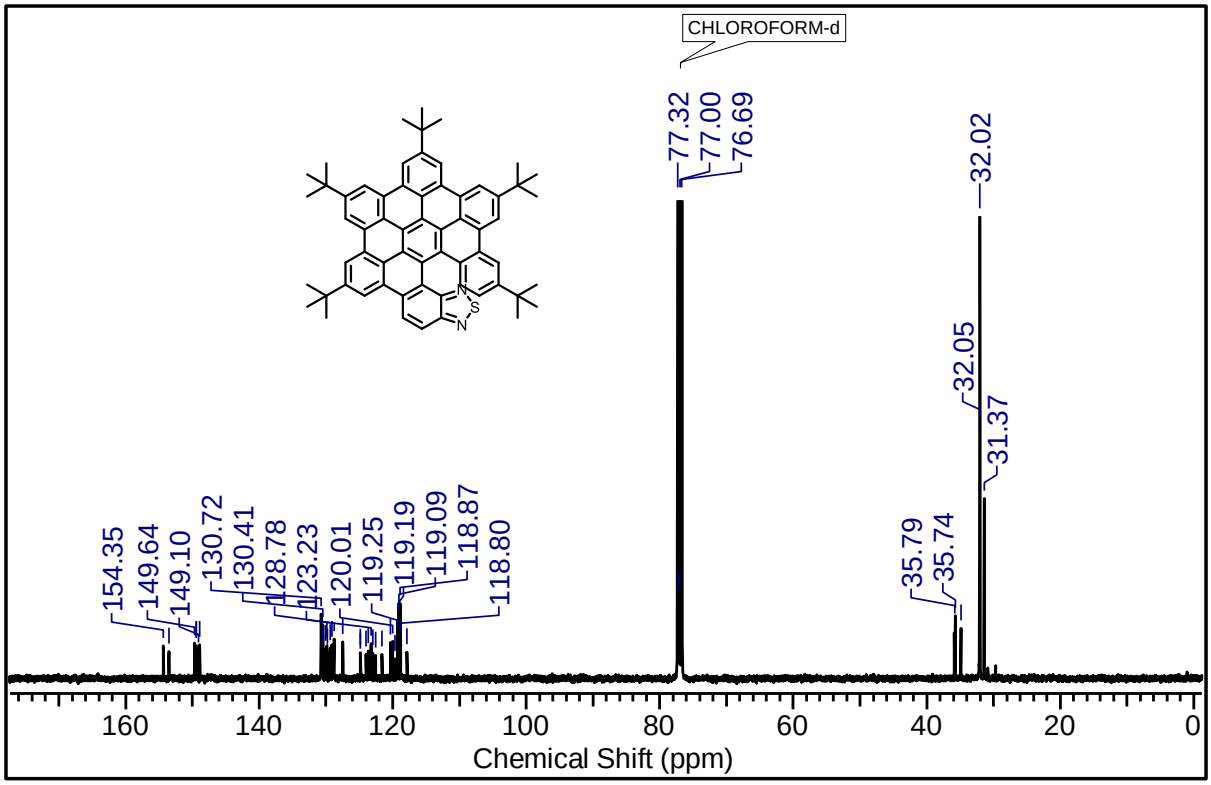
HR MS-ESI spectrum of 6



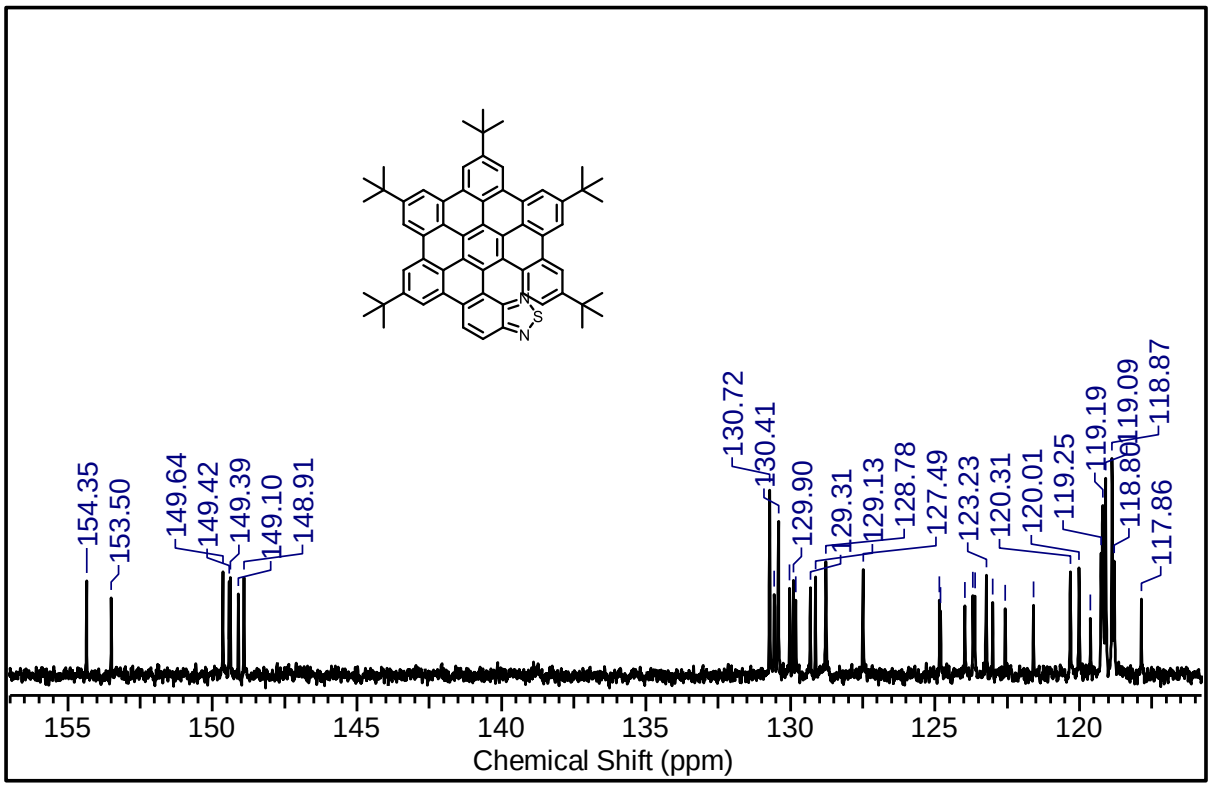
^{1}H NMR (500 MHz) spectrum of SNG in $CDCl_3$ at 298 K



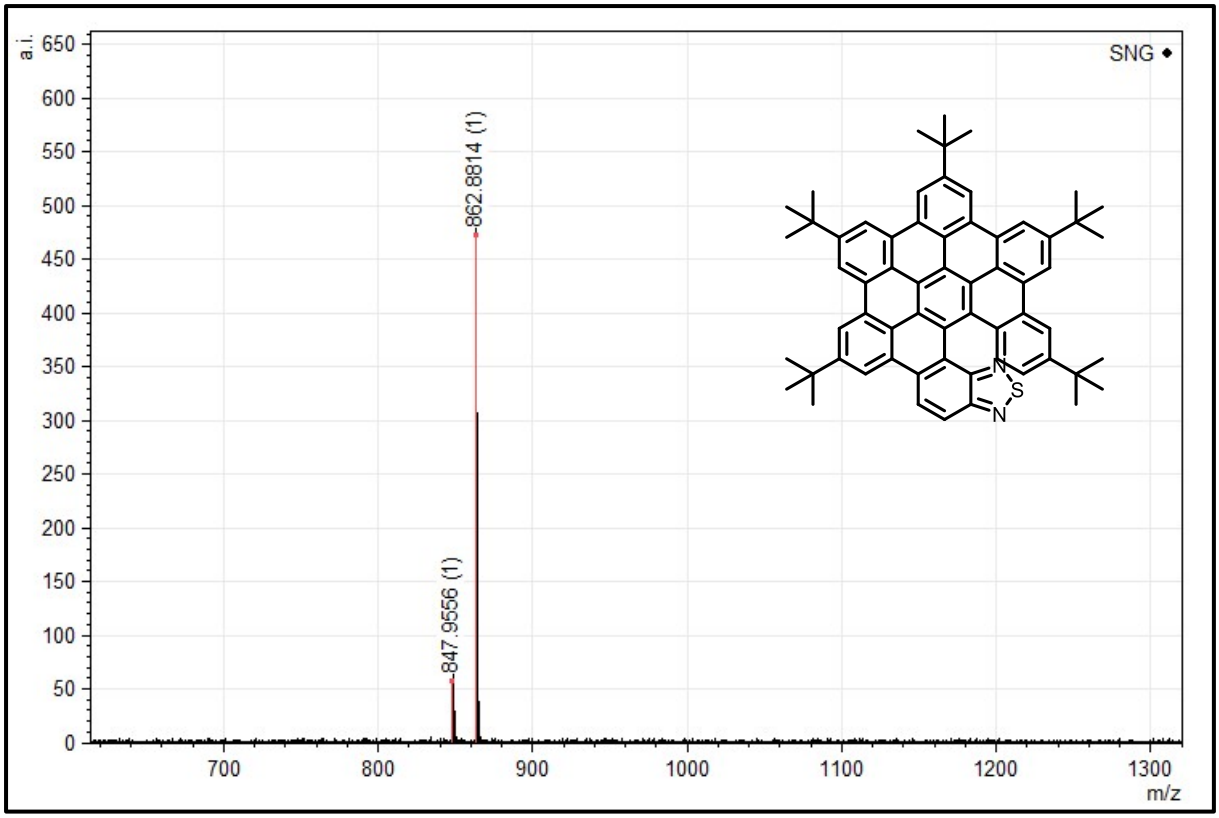
^{1}H NMR (500 MHz) cutout (aromatic region) spectrum of SNG



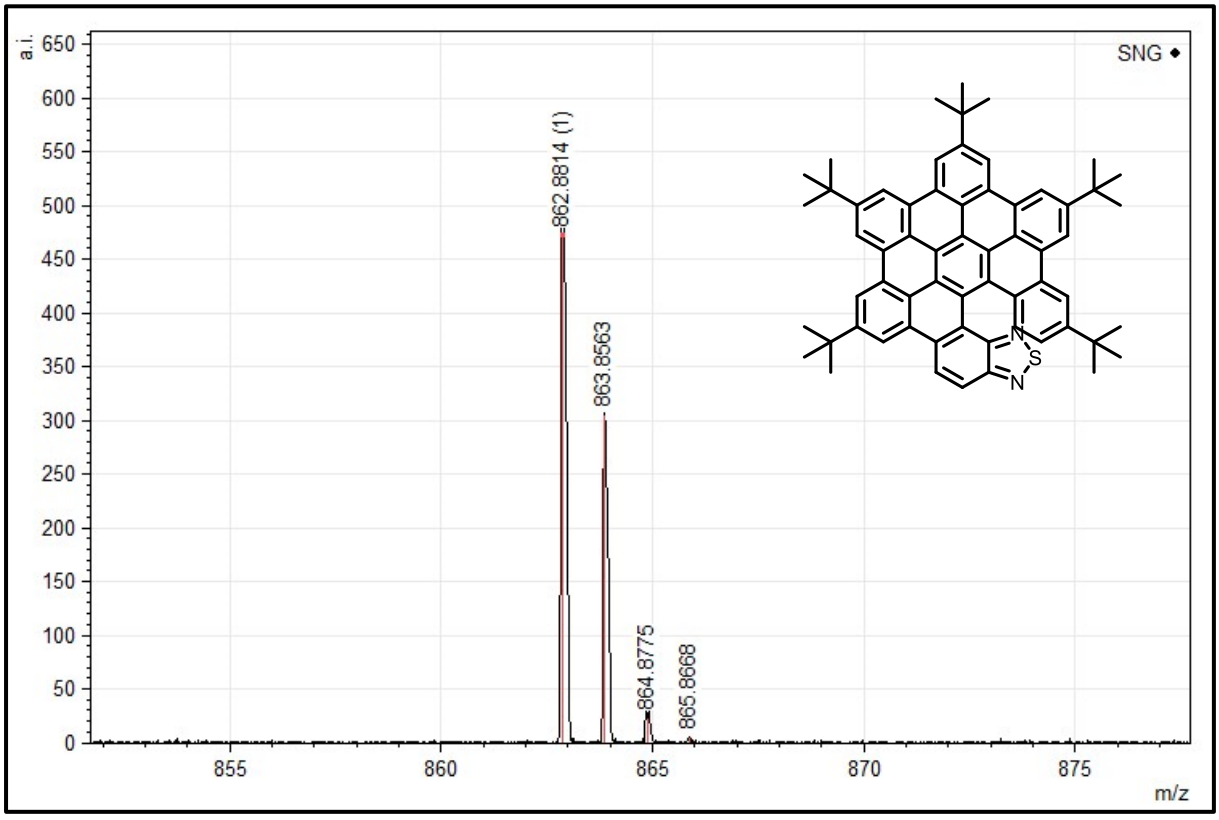
^{13}C NMR (125 MHz) spectrum of SNG in $CDCl_3$ at 298 K



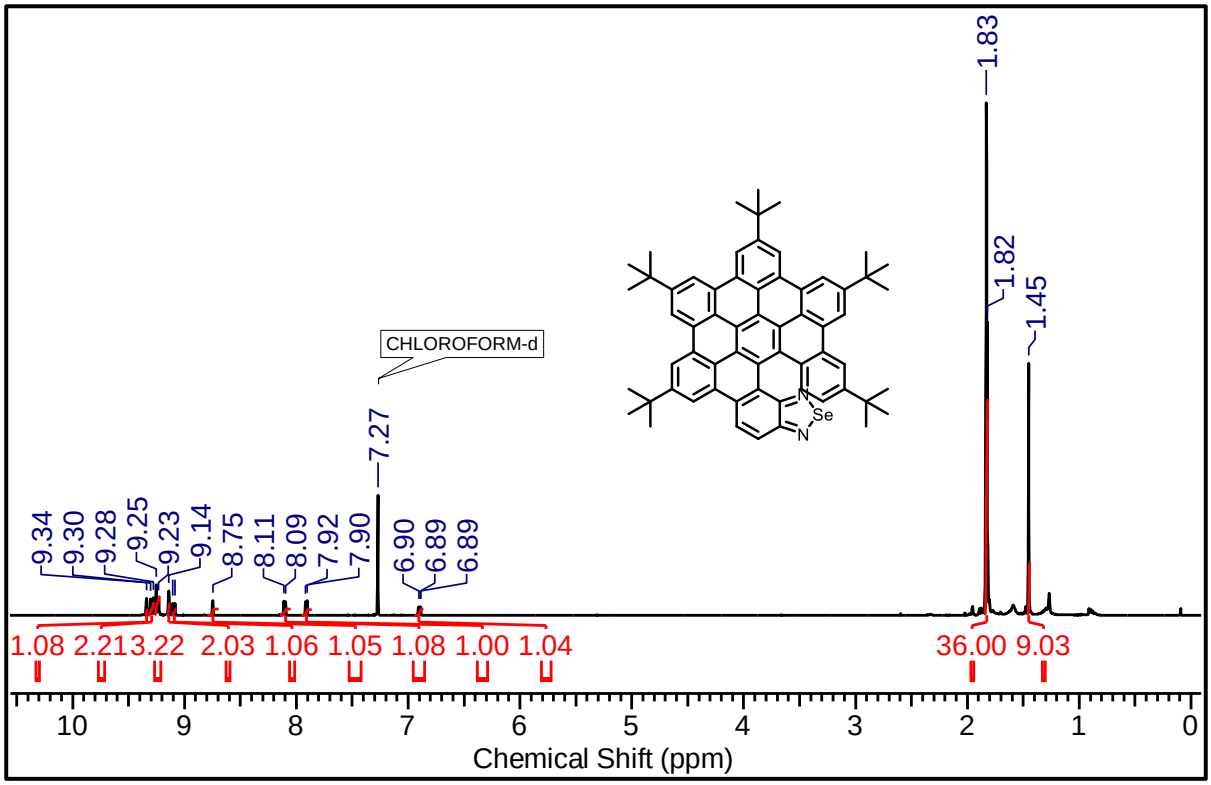
^{13}C NMR (125 MHz) aromatic region cutout of SNG in $CDCl_3$ at 298 K



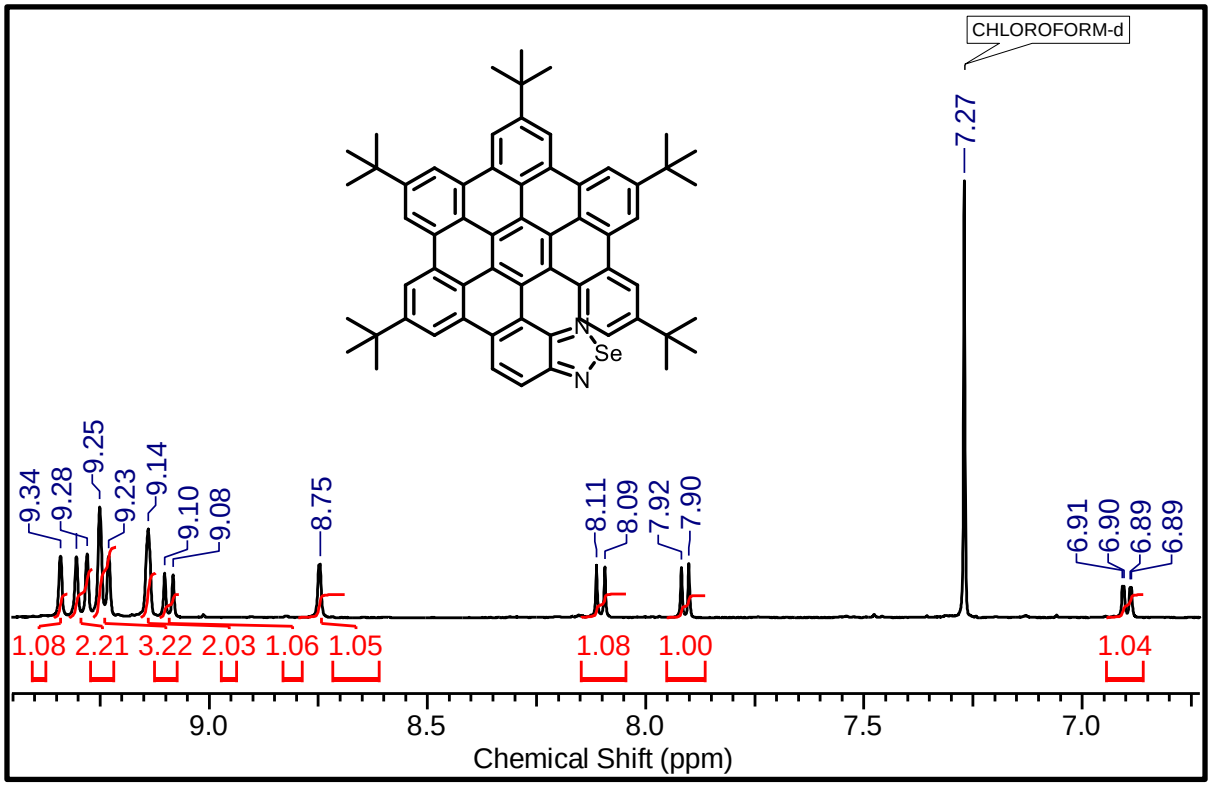
MALDI-TOF MS spectra of SNG



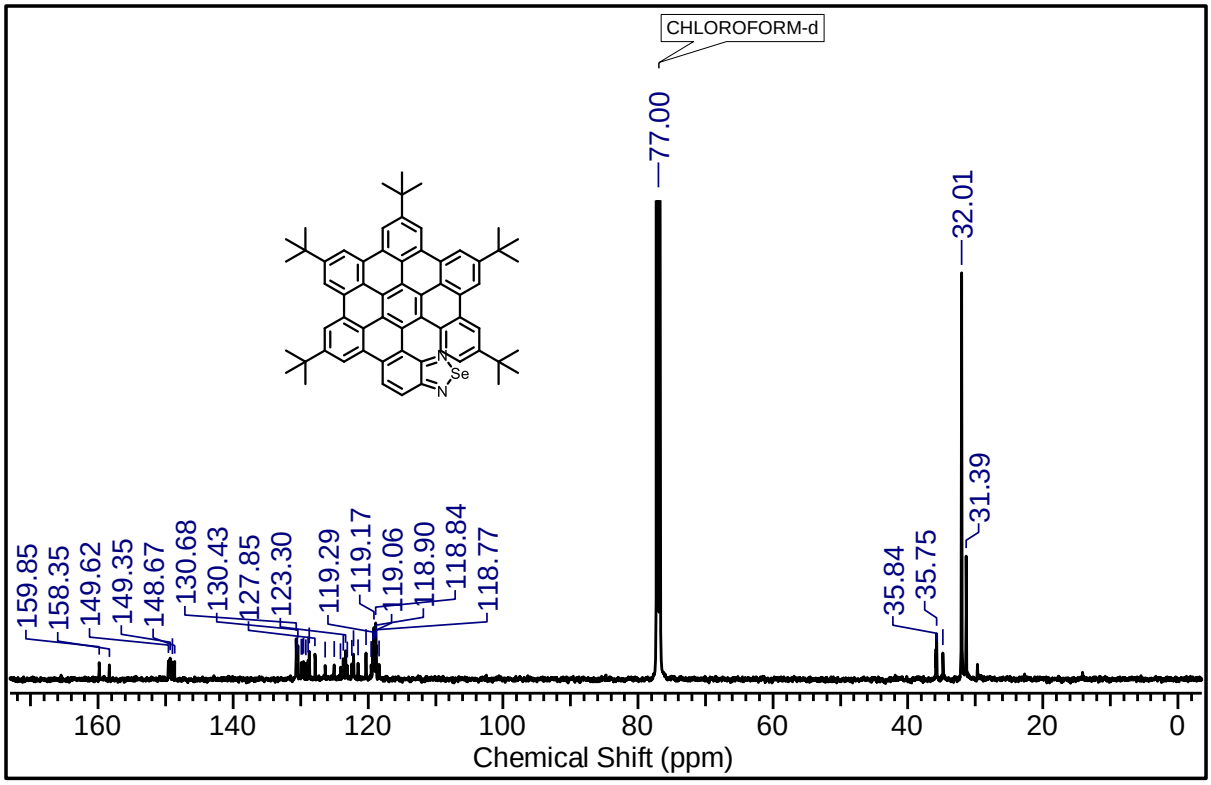
MALDI-TOF MS Zoomed spectra of SNG



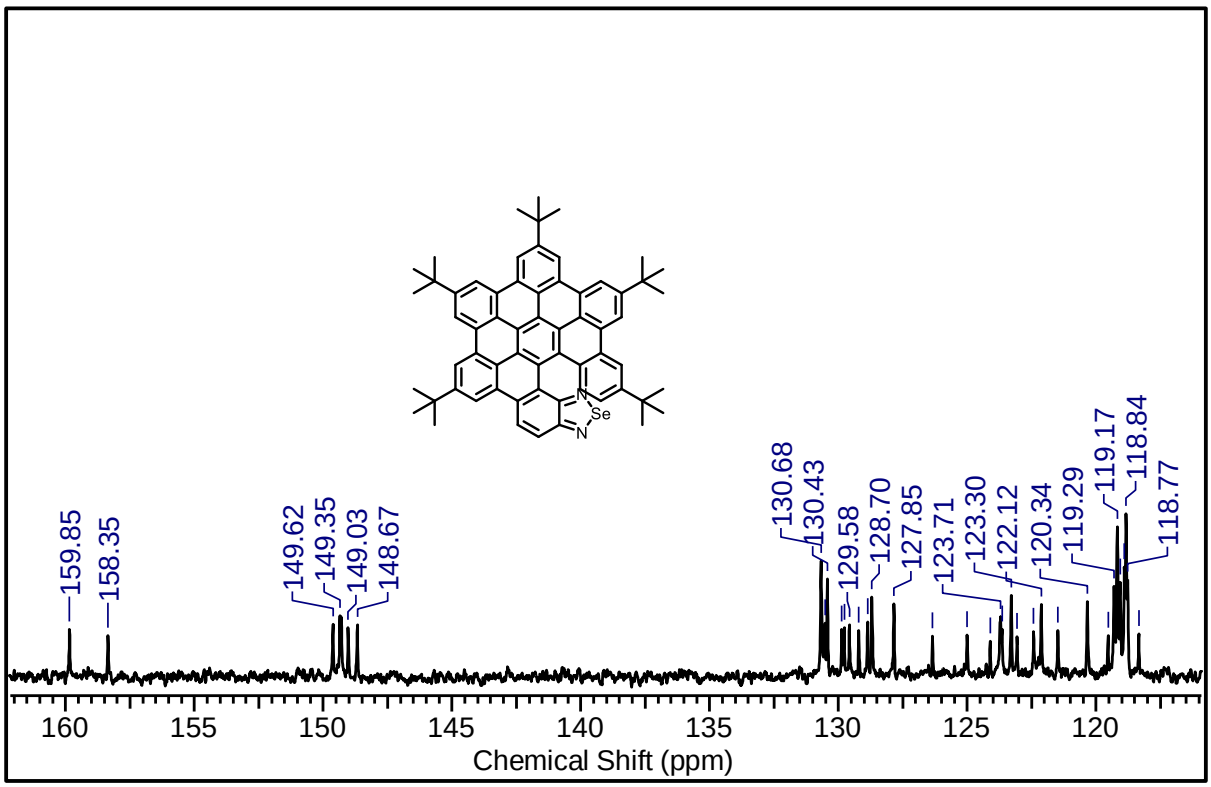
^{1}H NMR (500 MHz) spectrum of SeNG in $CDCl_3$ at 298 K



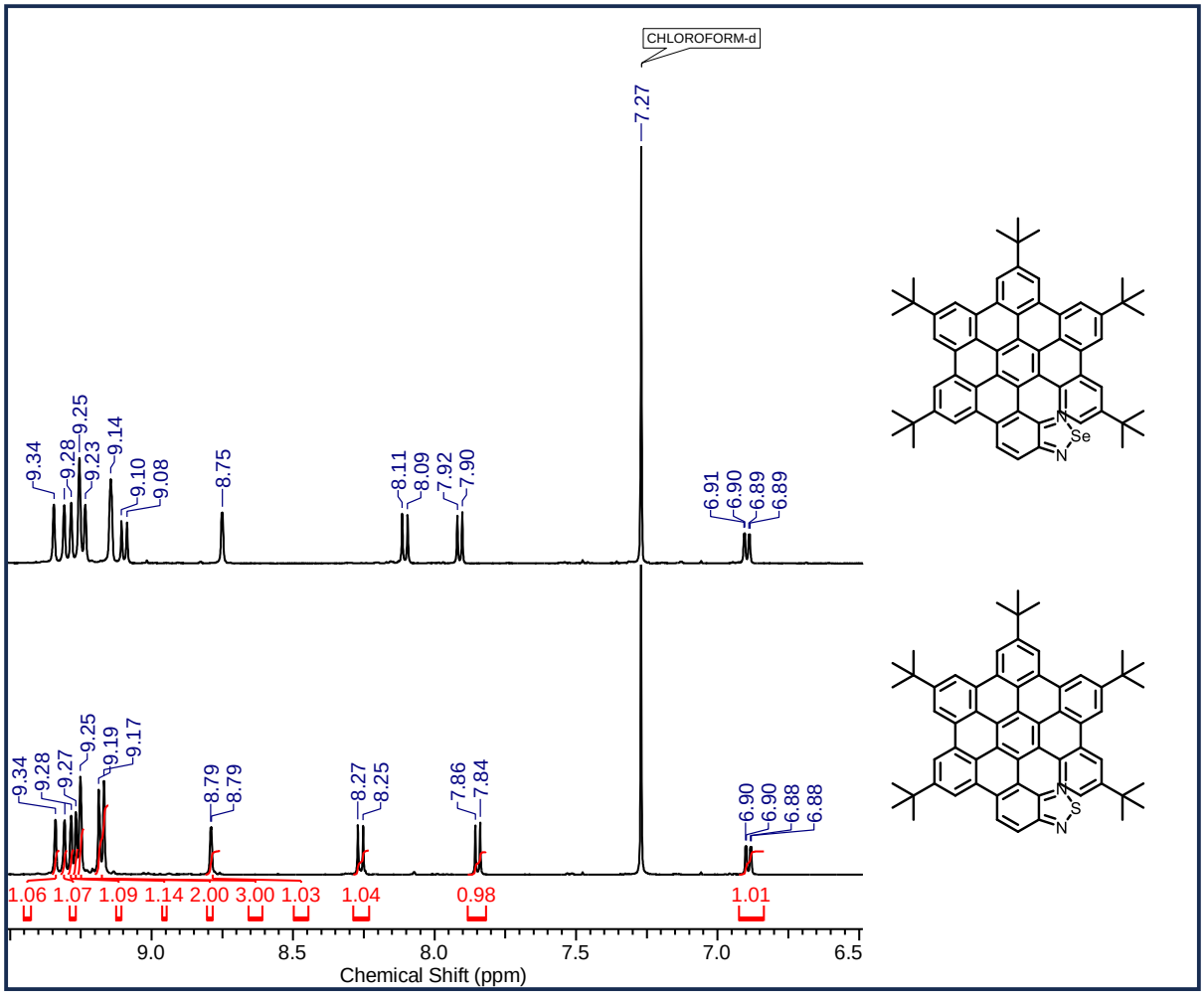
^{1}H NMR (500 MHz) cutout (aromatic region) spectrum of SeNG



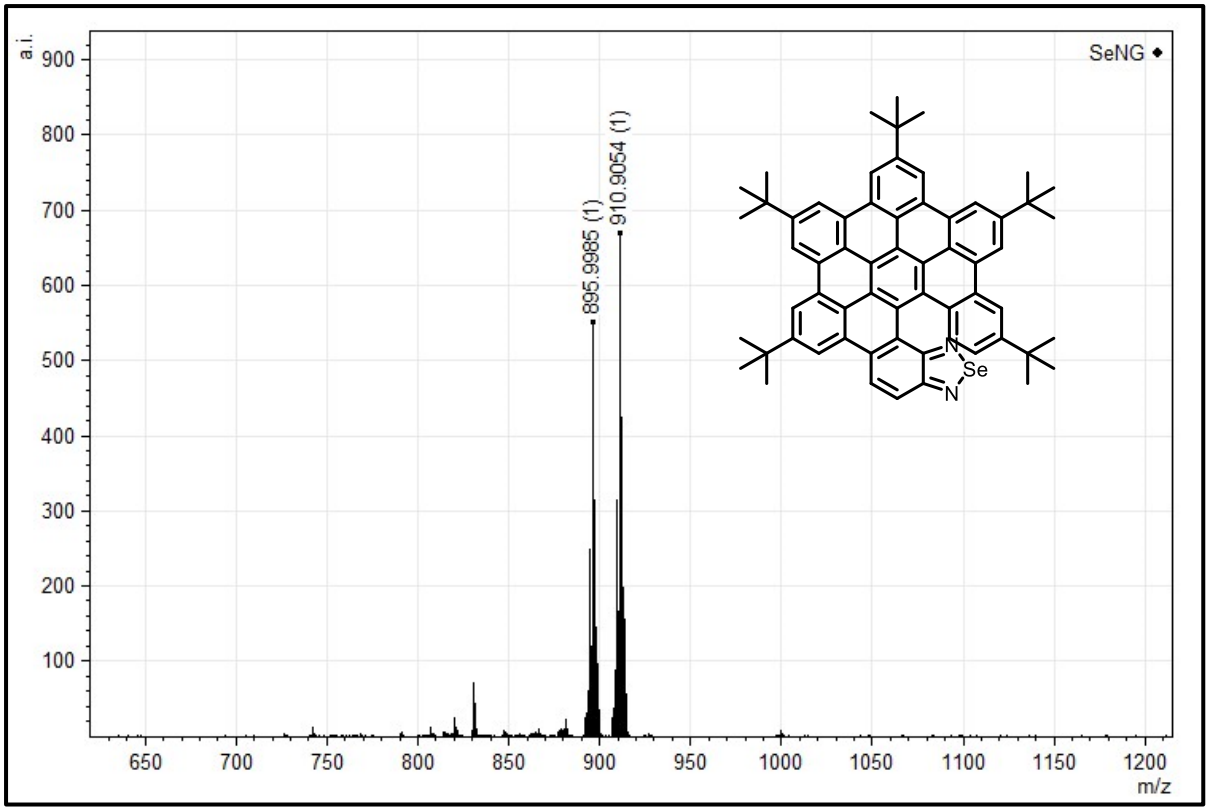
^{13}C NMR (125 MHz) spectrum of SeNG in $CDCl_3$ at 298 K



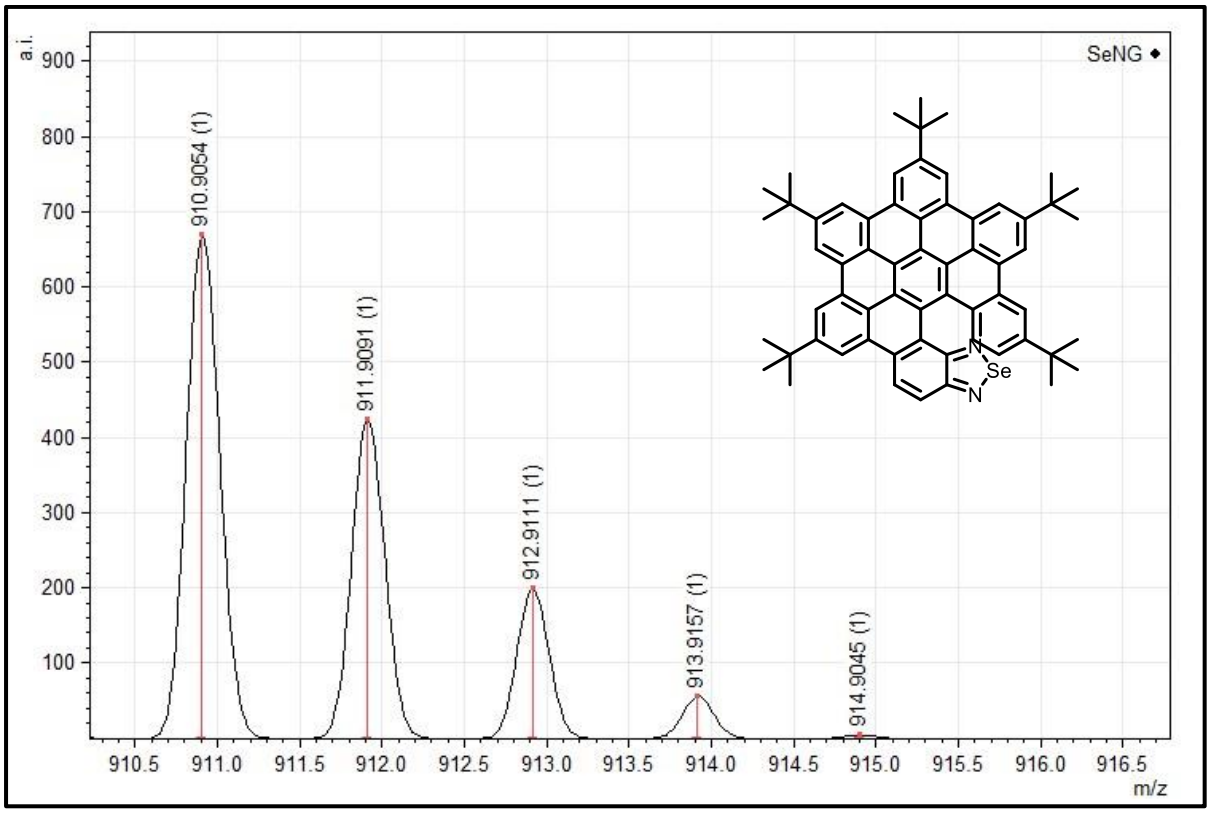
^{13}C NMR (125 MHz) aromatic region cutout of SeNG in $CDCl_3$ at 298 K



Comparison of ^{1}H NMR spectrum (aromatic region) of SNG and SeNG



MALDI-TOF MS spectra of SeNG



MALDI-TOF MS Zoomed spectra of SeNG

Figures

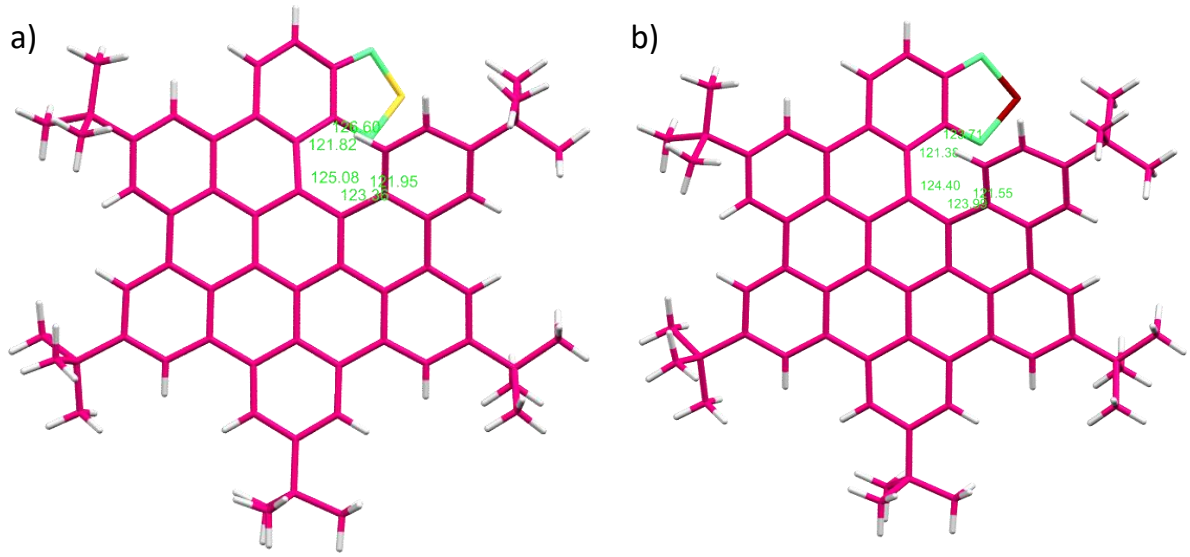


Figure S1. The inner torsion angles of a) **SNG** and b) **SeNG**.

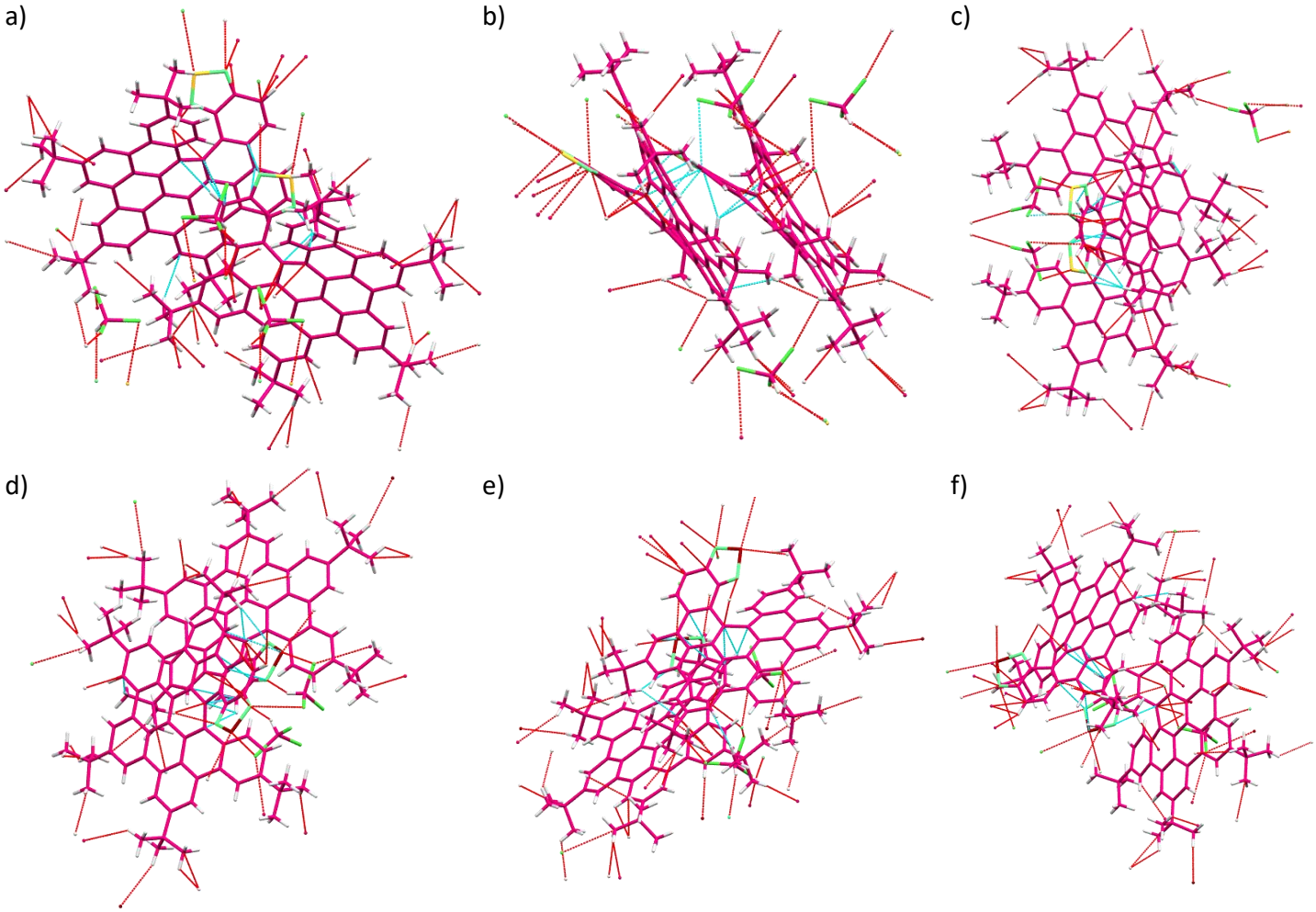


Figure S2. Extended molecular packing of a-c) **SNG** and d-f) **SeNG** along a, b, and c axes, respectively.

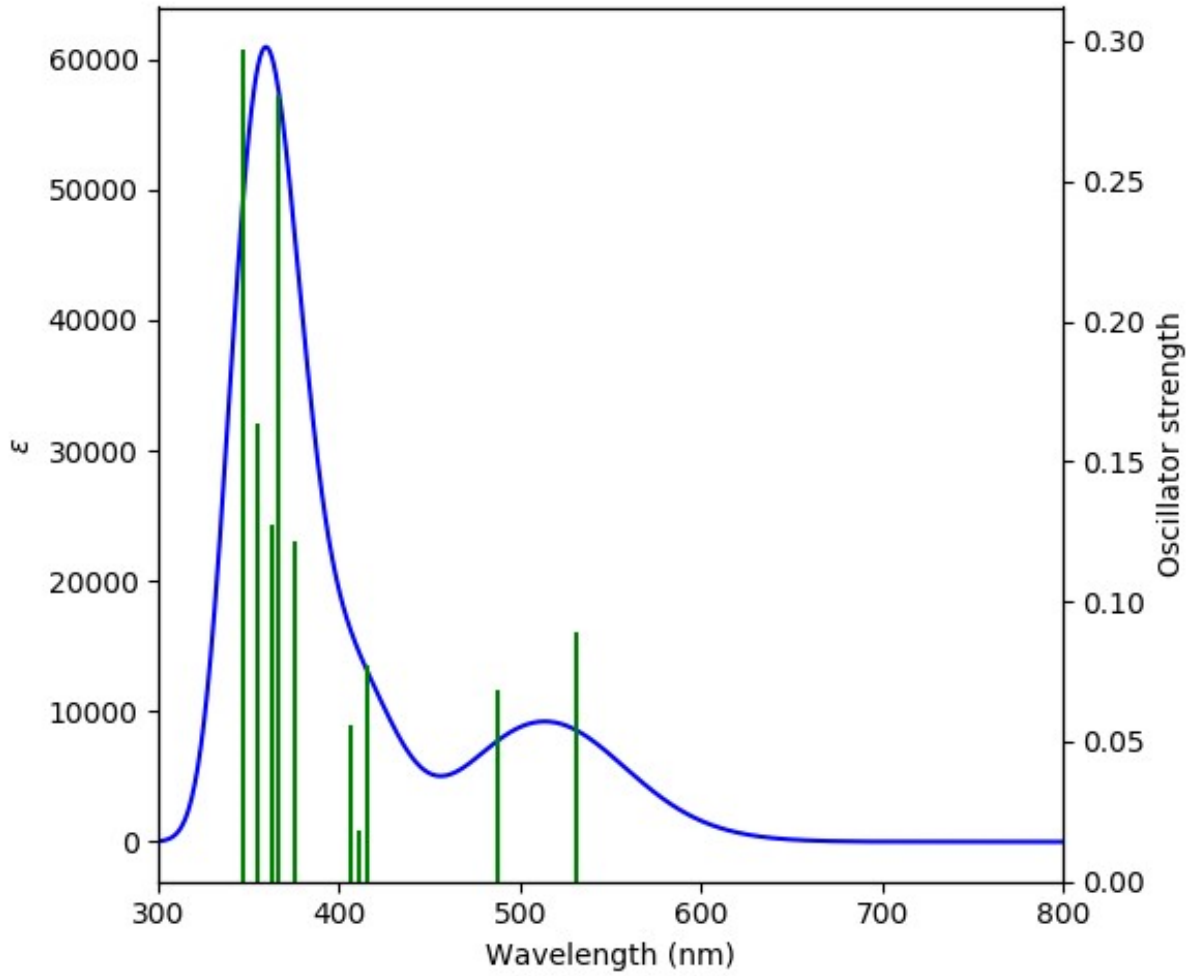


Figure S3. Simulated absorption spectrum (blue line) of **SNG** and calculated oscillator strength (Green bar) of **SNG** at the B3LYP/6-311G (d, p) level.

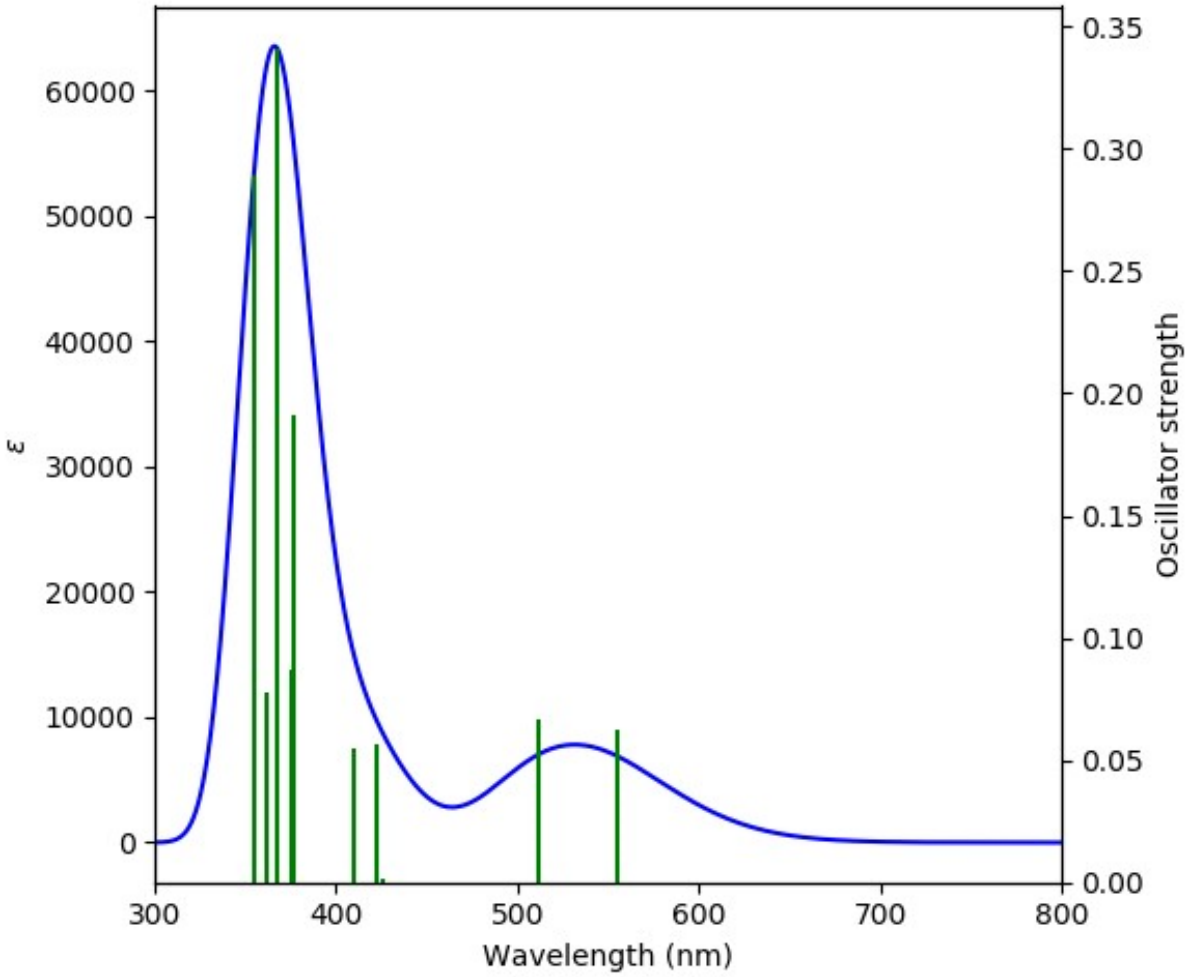


Figure S4. Simulated absorption spectrum (blue line) of **SeNG** and calculated oscillator strength (Green bar) of **SNG** at the B3LYP/6-311G (d, p) level.

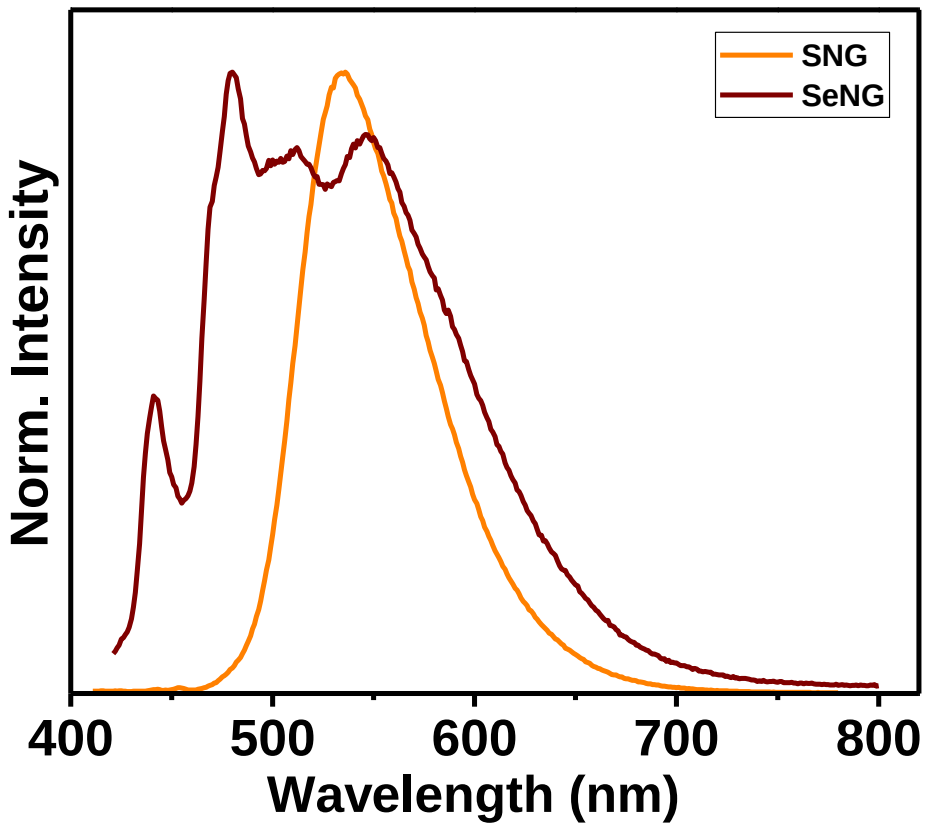


Figure S5. Normalized fluorescence spectra of **SNG** and **SeNG** in CH_2Cl_2.

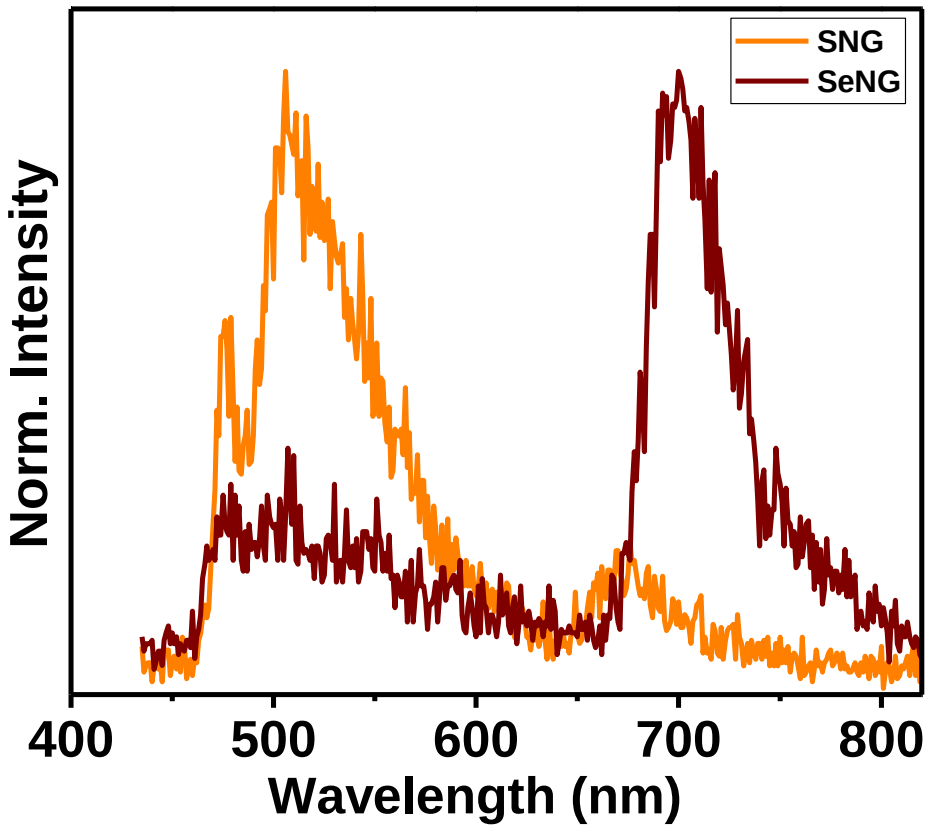


Figure S6. Normalized phosphorescence spectra of **SNG** and **SeNG** in MTHF.

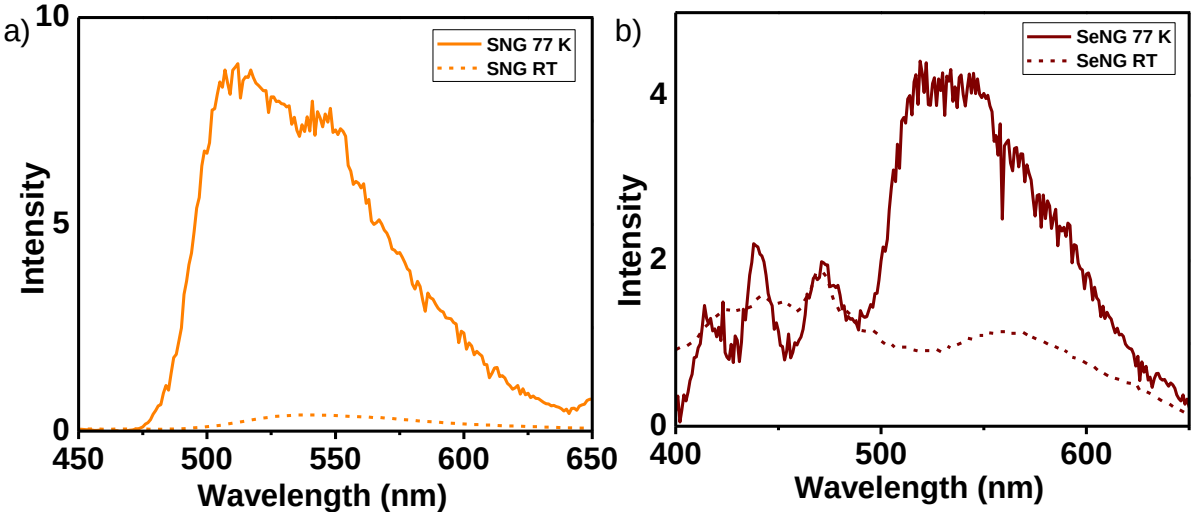


Figure S7. Fluorescence spectra of **SNG** and **SeNG** in MTHF at RT and 77K.

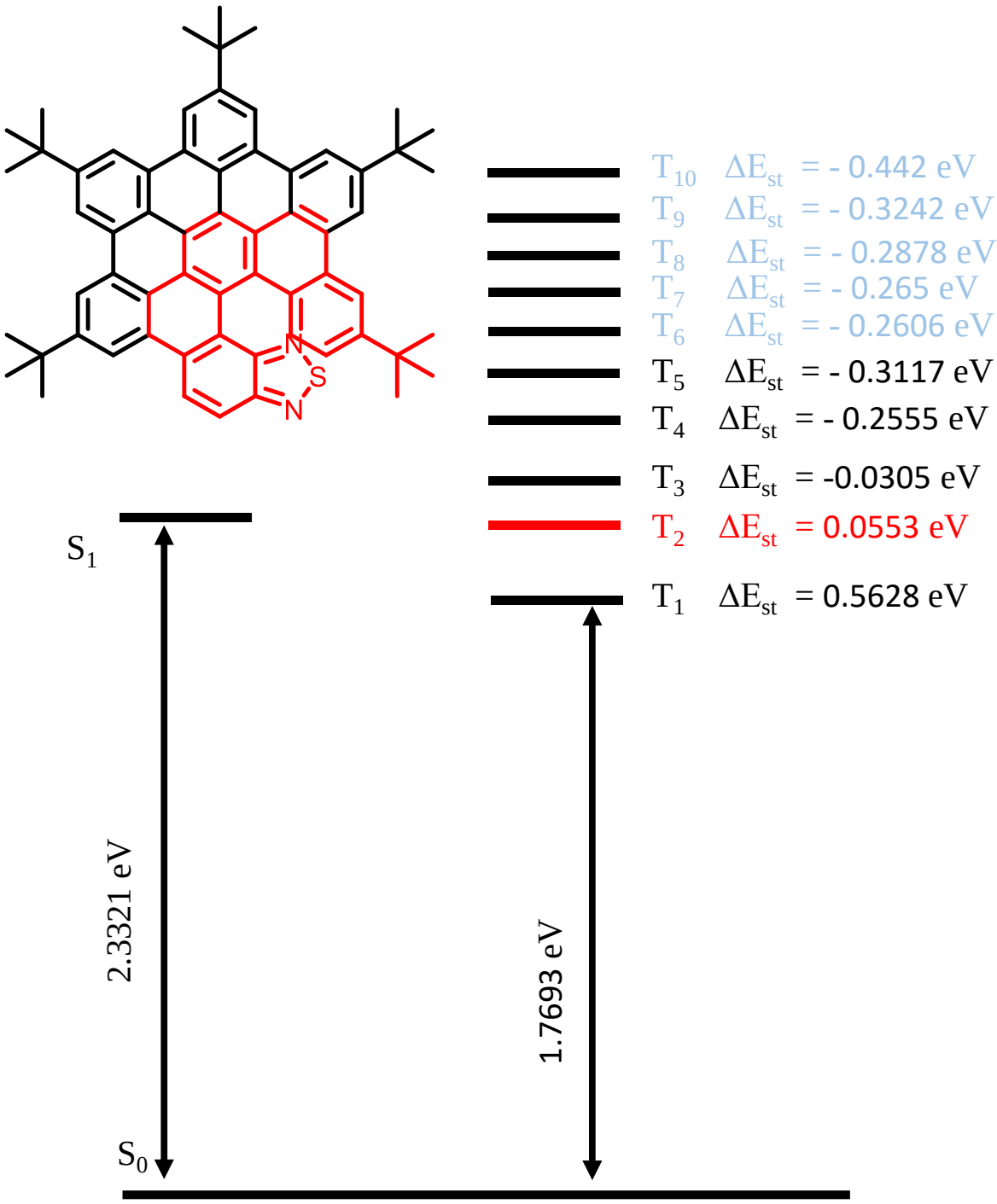


Figure S8. Calculated energy level diagram of **SNG**.

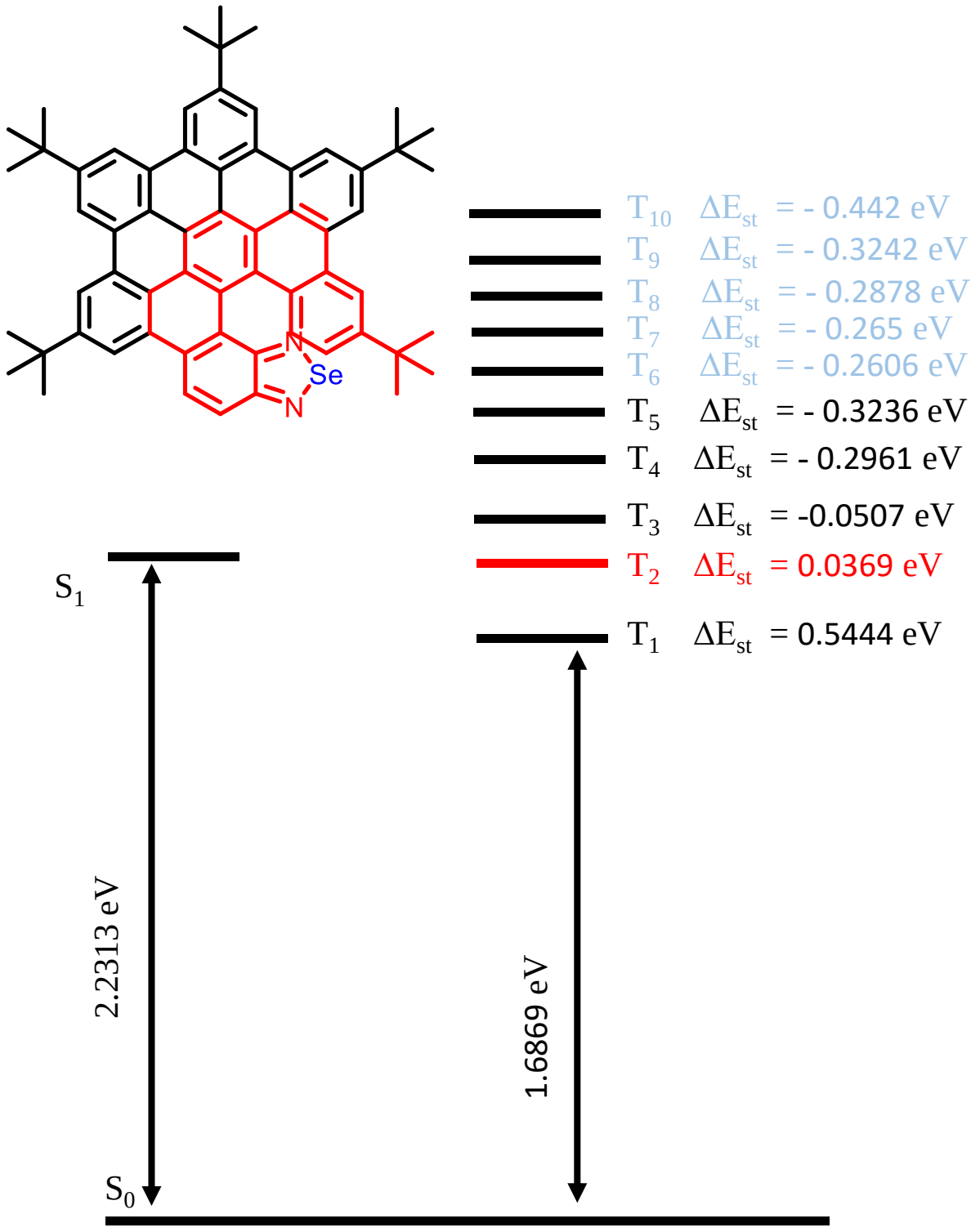


Figure S9. Calculated energy level diagram of **SeNG**.

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Date Processed : 7/21/2023 3:54:41 PM Processed by : System Administrator

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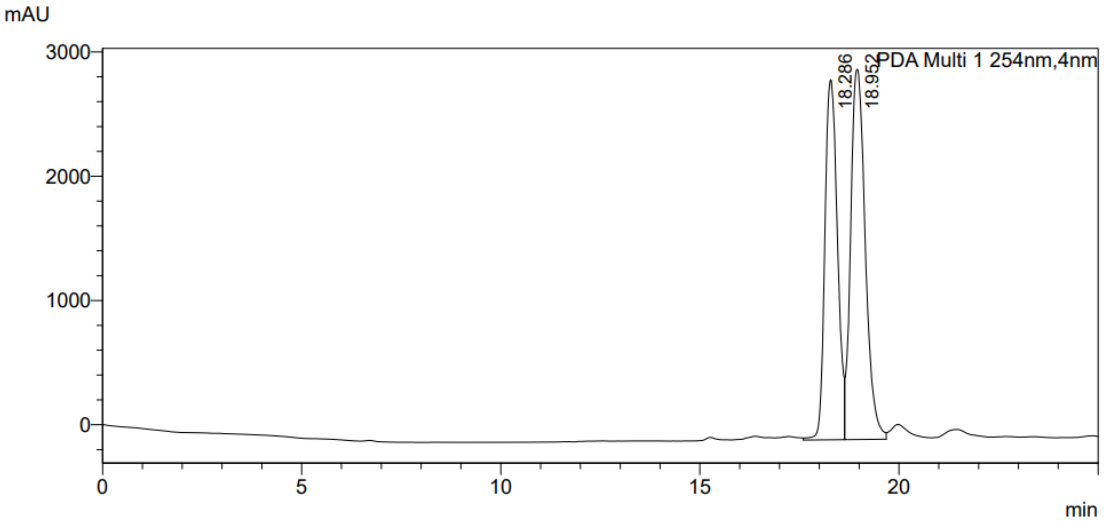

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
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2	18.952	76141598	2980369	54.488
Total		139739600	5878467	100.000

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S10. HPLC profile of **SNG** in *n*-hexane:isopropanol (90:10) by monitoring at 254 nm.

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Date Processed	: 7/21/2023 4:03:35 PM	Processed by	: System Administrator

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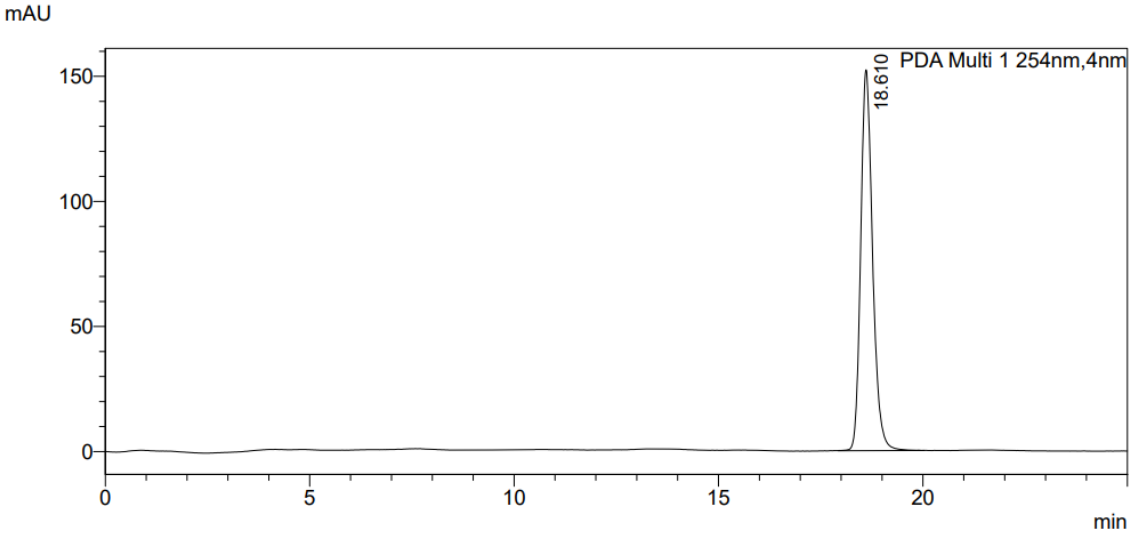

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.610	3081126	152269	100.000
Total		3081126	152269	100.000

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S11. HPLC trace for (*M*)-**SNG**.

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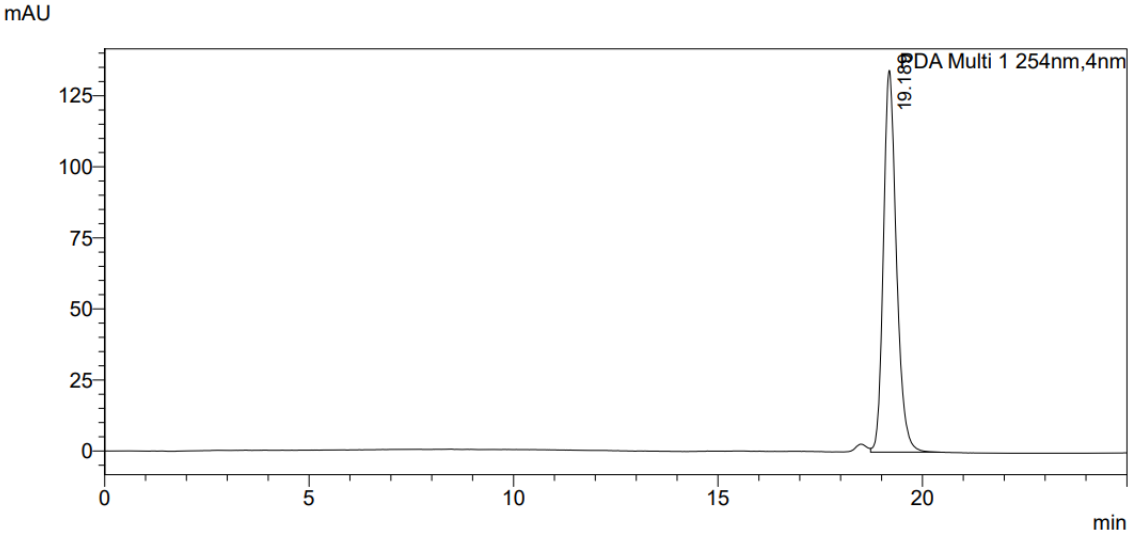

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.189	2975712	134369	100.000
Total		2975712	134369	100.000

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S12. HPLC trace for (*P*)-**SNG**

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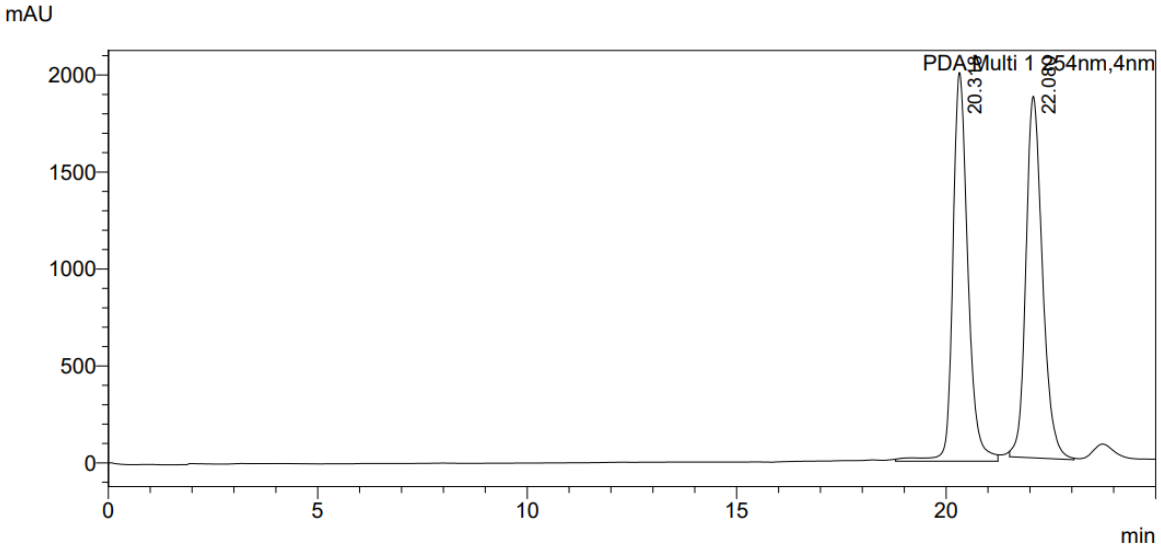

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.318	50200051	2004798	49.444
2	22.080	51328594	1864855	50.556
Total		101528646	3869652	100.000

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S13. HPLC profile of **SeNG** in *n*-hexane:isopropanol (90:10) by monitoring at 254 nm.

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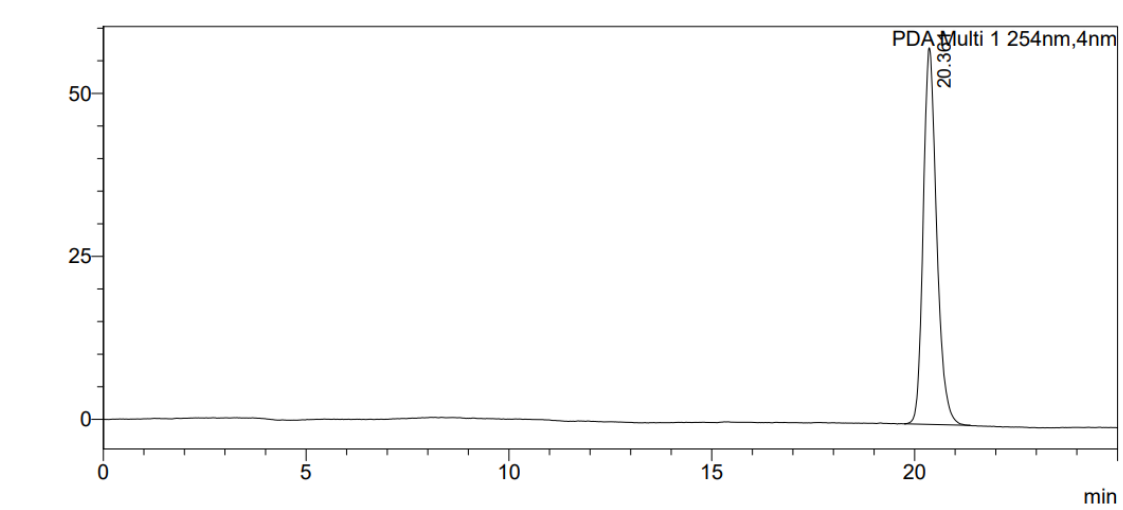

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
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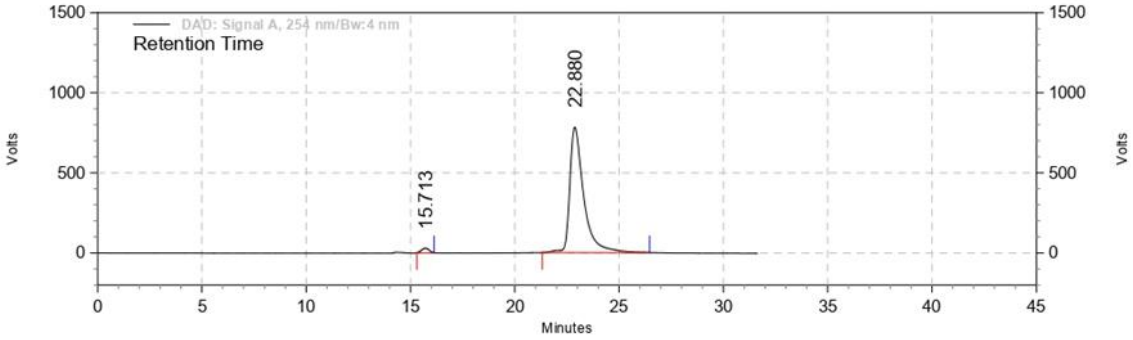
Total		1333804	57785	100.000

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S14. HPLC trace for (*M*)-**SeNG**



DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %
15.713	1484493	1.91
22.880	76254499	98.09
Totals	77738992	100.00

Column: CHIRALPAK SA
Eluent System: 90 : 10 (HEXANE:IPA)
Flow rate: 1 ml/min Injection
vol.: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0mg/ml

Figure S15. HPLC trace for (*P*)-**SeNG**

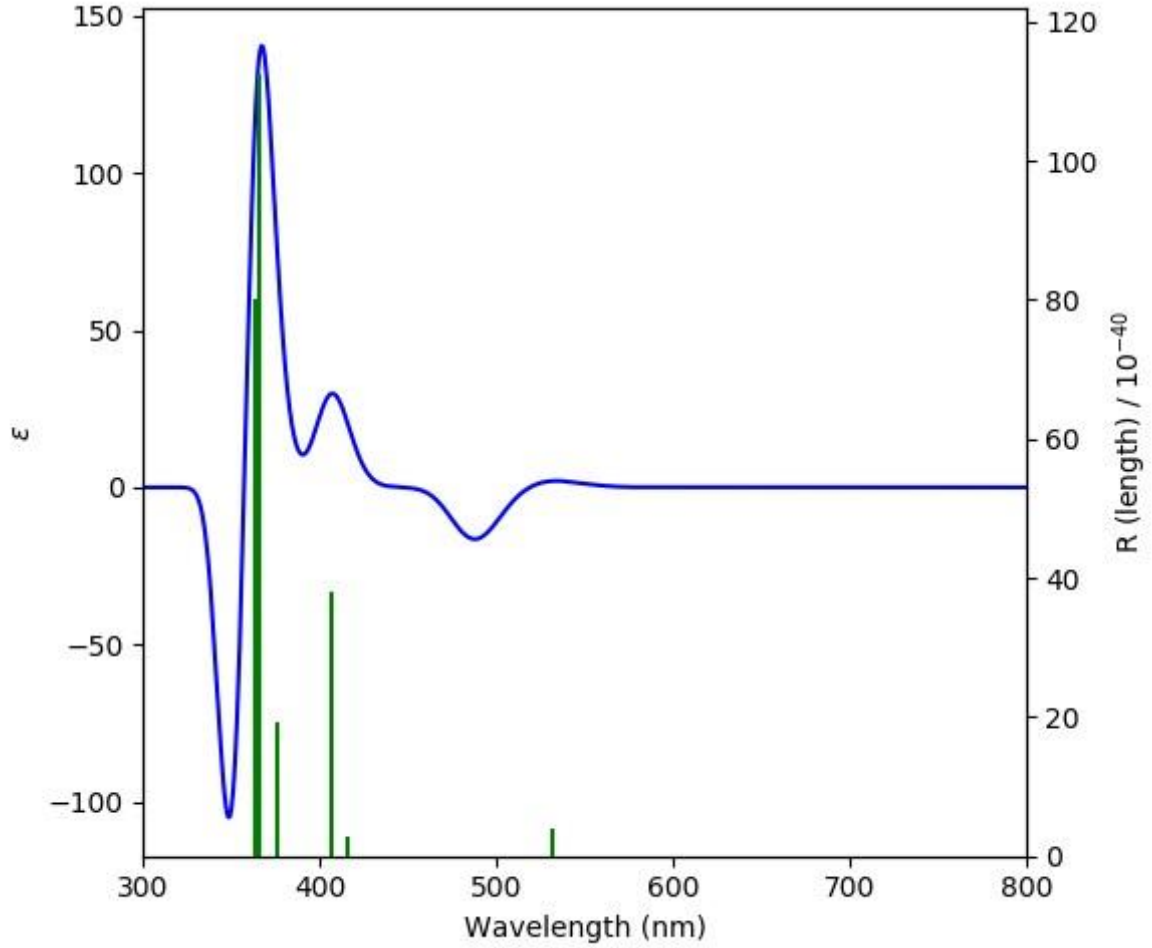


Figure S16. Simulated CD spectra and calculated rotatory strength (Green verticle bar) for assigning absolute configuration of isomer (*P*)-**SNG** at the B3LYP/6-311G (d, p) level.

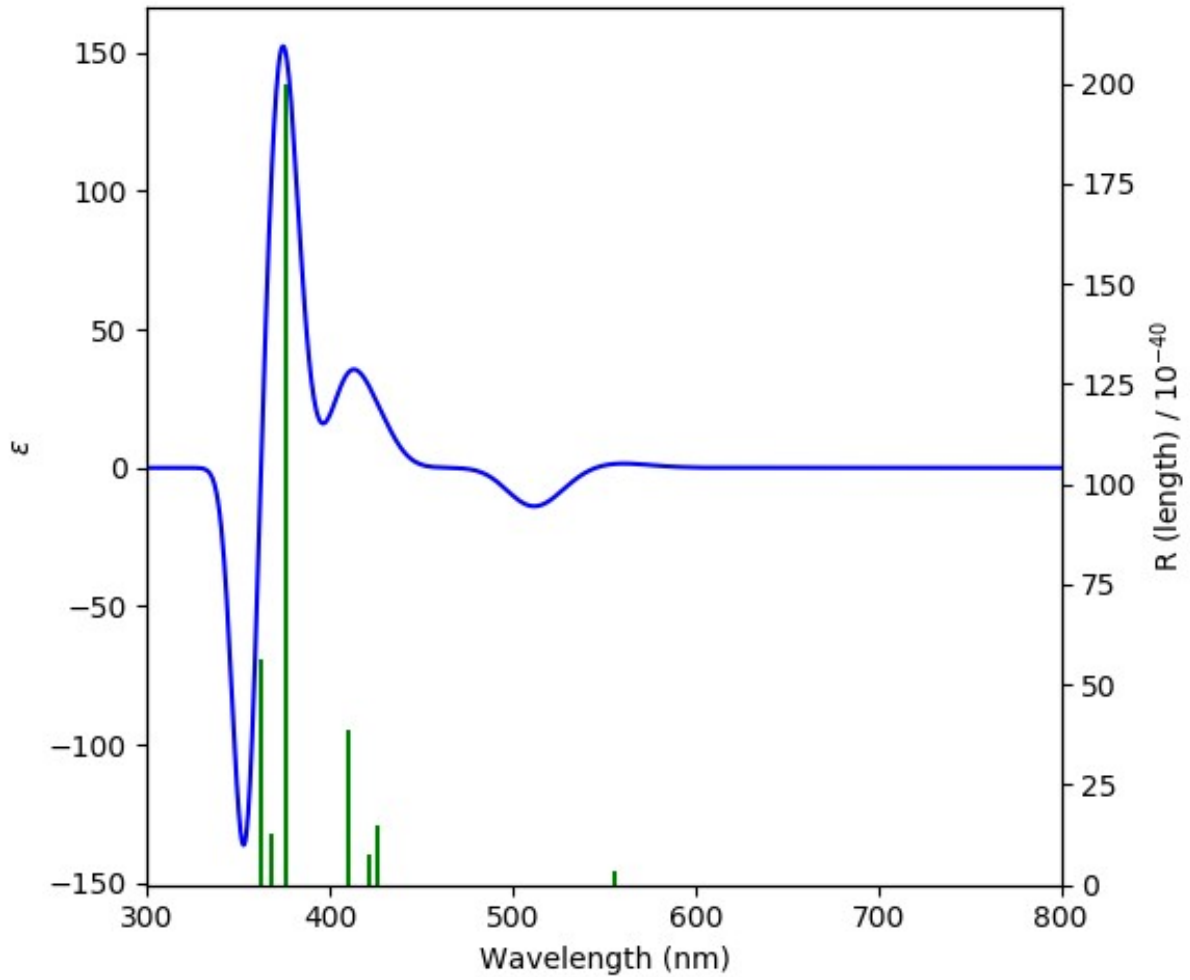


Figure S17. Simulated CD spectra and calculated rotatory strength (Green verticle bar) for assigning absolute configuration of isomer (*P*)-**SeNG** at the B3LYP/6-311G (d, p) level.

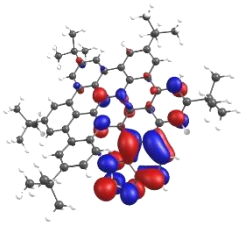
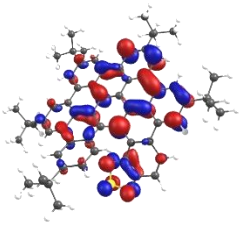
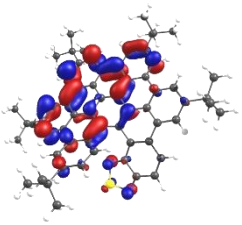
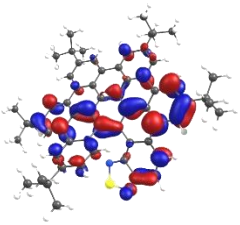
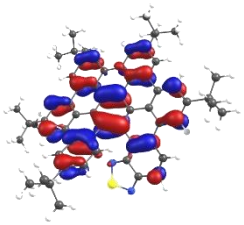
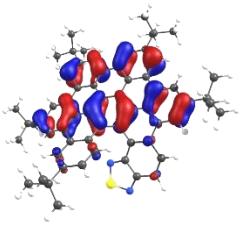
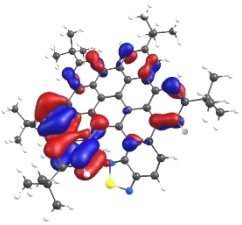
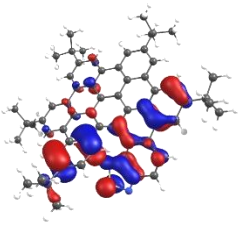
			
LUMO	**LUMO+1**	**LUMO+2**	**LUMO+3**
			
HOMO	**HOMO-1**	**HOMO-2**	**HOMO-3**

Figure S18. Involved frontier orbitals of **SNG**.

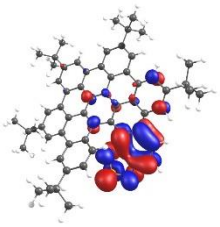
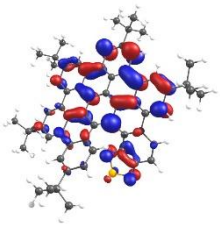
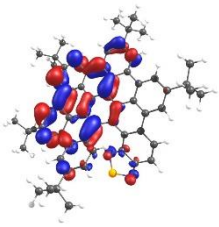
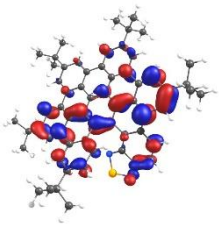
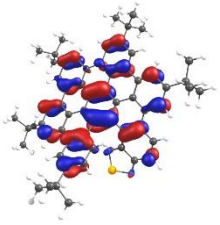
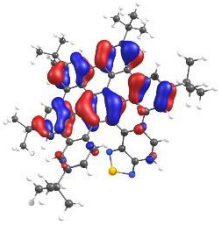
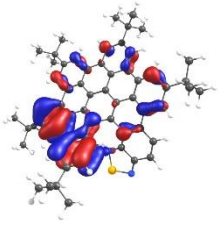
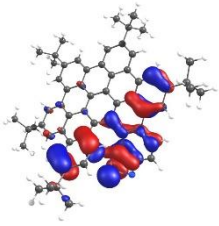
			
LUMO	**LUMO+1**	**LUMO+2**	**LUMO+3**
			
HOMO	**HOMO-1**	**HOMO-2**	**HOMO-3**

Figure S19. Involved frontier orbitals of **SeNG**.

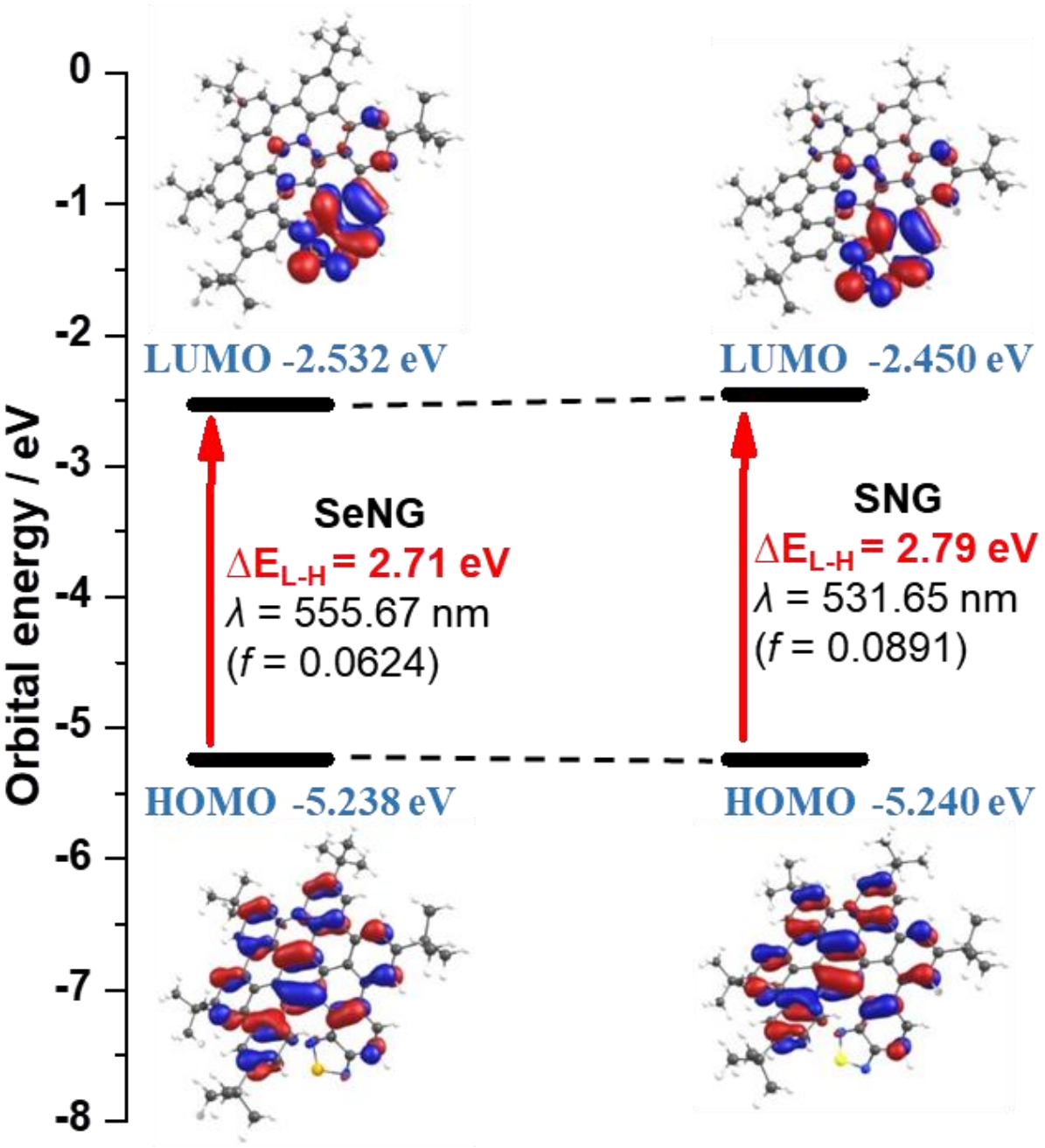


Figure S20. HOMO-LUMO energy gap of **SNG** and **SeNG** obtained by DFT calculation.

Tables

Table S1. Excitation properties of SNG calculated at the TD-B3LYP/6-311G(d,p) level

	Δ*E* (eV)	**λ (nm)**	***f***	**Configuration(orbital symmetry)**	**Coefficient**
S0 _ S1	2.3321	531.65	0.0891	HOMO (230) _ LUMO (231)	0.69583
S0 _ S2	2.5410	487.94	0.0682	HOMO-1 (229) _ LUMO (231)	0.67663
S0 _ S3	2.9827	415.68	0.0775	HOMO (230) _ LUMO+1 (232)	0.50822
S0 _ S4	3.0137	411.41	0.0183	HOMO -2(228) _ LUMO (231)	0.64198
S0 _ S5	3.0477	406.81	0.0560	HOMO (230) _ LUMO+2(233)	0.50825
S0 _ S6	3.2985	375.88	0.1212	HOMO (230) _ LUMO+3 (234)	0.43038
S0 _ S7	3.3859	366.17	0.2805	HOMO-3 (227) _ LUMO (231)	0.38486
S0 _ S8	3.4135	363.22	0.1275	HOMO-3(227) _ LUMO (231)	0.39493
S0 _ S9	3.4947	354.78	0.1635	HOMO-4(226) _ LUMO (231)	0.36789
S0 _ S10	3.5712	347.18	0.2973	HOMO-4(226) _ LUMO (231)	0.45816

	Δ*E* (eV)	**λ (nm)**	***f***	**Configuration (orbital symmetry)**	**Coefficient**
S0 _ T1	1.7693	700.74	0.0000	HOMO (230) _ LUMO (231)	0.60259
S0 _ T2	2.2768	544.55	0.0000	HOMO-1 (229) _ LUMO (231)	0.48939
S0 _ T3	2.3626	524.77	0.0000	HOMO-1 (229) _ LUMO	0.41450

				(231)	
S0 _ T4	2.5876	479.16	0.0000	HOMO (230) _ LUMO+2 (233)	0.36868
S0 _ T5	2.6438	468.97	0.0000	HOMO (230) _ LUMO+1 (232)	0.35992
S0 _ T6	2.7611	449.03	0.0000	HOMO (230) _ LUMO+1 (232)	0.37138
S0 _ T7	2.8302	438.08	0.0000	HOMO (230) _ LUMO+2 (233)	0.35785
S0 _ T8	2.9245	423.94	0.0000	HOMO-3 (227) _ LUMO (231)	0.34216
S0 _ T9	2.9580	419.15	0.0000	HOMO-1 (229) _ LUMO+1 (232)	0.42118
S0 _ T10	3.0988	400.10	0.0000	HOMO-2 (228) _ LUMO (231)	0.39639

Table S2. Excitation properties of SeNG calculated at the TD-B3LYP/6-311G(d,p) level

	Δ*E* (eV)	**λ (nm)**	***f***	**Configuration (orbital symmetry)**	**Coefficient**
S0 _ S1	2.2313	555.67	0.0624	HOMO (239) _ LUMO (240)	0.69809
S0 _ S2	2.4222	511.87	0.0669	HOMO-1 (238) _ LUMO (240)	0.68947
S0 _ S3	2.9111	425.90	0.0013	HOMO-2 (237) _ LUMO (240)	0.68367
S0 _ S4	2.9393	421.81	0.0563	HOMO (239) _ LUMO+1 (241)	0.51130
S0 _ S5	3.0258	409.75	0.0548	HOMO (239) _ LUMO +2(242)	0.52925
S0 _ S6	3.2885	377.03	0.1913	HOMO (239) _ LUMO+3 (243)	0.38899
S0 _ S7	3.3034	375.32	0.0866	HOMO-3 (236) _ LUMO (240)	0.56435
S0 _ S8	3.3739	367.48	0.3412	HOMO -1(238) _ LUMO +2(242)	0.47316
S0 _ S9	3.4286	361.62	0.0777	HOMO-4 (235) _ LUMO (240)	0.57907
S0 _ S10	3.5002	354.22	0.2895	HOMO (239) _ LUMO+3 (243)	0.35022

	Δ*E* (eV)	**λ (nm)**	***f***	**Configuration (orbital symmetry)**	**Coefficient**
S0 _ T1	1.6869	735.00	0.0000	HOMO (239) _ LUMO (240)	0.58927
S0 _ T2	2.1944	565.00	0.0000	HOMO-1(238) _ LUMO (240)	0.51885
S0 _ T3	2.2820	543.30	0.0000	HOMO-1 (238) _ LUMO (240)	0.36959

S0 _ T4	2.5274	490.56	0.0000	HOMO-2 (237) _ LUMO (240)	0.41058
S0 _ T5	2.5549	485.29	0.0000	HOMO-4 (235) _ LUMO (240)	0.33923
S0 _ T6	2.6838	461.98	0.0000	HOMO (239) _ LUMO+1 (241)	0.48055
S0 _ T7	2.7200	455.82	0.0000	HOMO (239) _ LUMO (240)	33920
S0 _ T8	2.8614	433.29	0.0000	HOMO (239) _ LUMO (240)	0.34093
S0 _ T9	2.9101	426.05	0.0000	HOMO-1 (238) _ LUMO+2 (242)	0.42612
S0 _ T10	3.0312	409.02	0.0000	HOMO-2 (237) _ LUMO (240)	0.37869

Table S3. Photophysical parameters of **SNG** and **SeNG**.

Sample	λ_{max}, abs (nm)	λ_{max}, ems (nm)	ϕ_{Fl} **[%]**	t_{Fl} **[ns]**	$K_{nr,\,fl}$ **[10^9 s^{-1}]**	$K_{r,\,fl}$ **[10^9 s^{-1}]**
SNG	340	560	7.35	16.05	0.0577	0.0045
SeNG	349	590	0.9	3.88	0.255	0.0023

Table S4. Fluorescence lifetime of **SNG** and **SeNG**.

Sample	**Fluorescence lifetime (ns)**	**CHISQ.**
SNG@560 nm	16.05 (47.79 %) 4.98 (49.01 %) 0.50 (3.20 %)	1.14
SeNG@590 nm	1.37 (91.47 %) 3.88 (8.53 %)	1.09

Table S5. Phosphorescence lifetime of **SNG** and **SeNG** at 77 K.

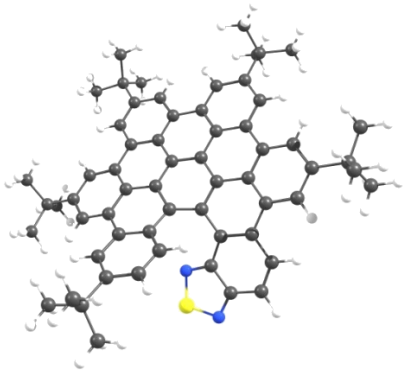
Sample	**Phosphorescence lifetime (ms)**	**CHISQ.**
SNG@540 nm	216 (79.18 %) 103 (20.82%)	1.01
SeNG@550 nm	2600 (90.46 %) 1200 (9.54 %)	1.07

Details of DFT calculations

Ground (S0) state calculations were performed using restricted density functional theory (DFT). Singlet and triplet excited states were investigated using time-dependent density functional theory (TDDFT). The ground state singlet (S_0) state was calculated using rB3LYP/6-311G(d,p) level of theory. Also the TD-DFT calculations were done with same level of theory. All the geometries of the complexes in the S_0 state were optimized. The optimized Cartesian coordinates and total energies are listed below. On the basis of the Frank-Condon principle, the absorption properties were evaluated using the optimized S_0 state structure. The Gaussian05 software was used in all the DFT and TD-DFT calculations.[S2]

Optimized Cartesian coordinates of different complexes (S_0 state) at the B3LYP/6-311G(d,p) level of theory.

SNG



Coordinates of Optimized Structure SNG

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C	-0.791959717	-5.279983596	1.267068487	C	-0.278055973	1.085655488	0.025105843
C	0.312586350	-5.755500938	1.900754041	C	-1.404899079	0.238763236	0.025510729
C	1.384461290	-4.850197936	2.137397826	C	-2.728974667	0.788265737	-0.074924620
C	1.312967242	-3.494756023	1.632247187	C	-0.446406716	2.513633484	0.047106311
C	0.179537701	-3.049746987	0.848700113	C	2.177479960	1.378842745	-0.087678461
N	2.471320360	-5.103655423	2.864387103	C	2.464503006	-1.414775897	-0.537207974
S	3.324110674	-3.699050684	2.922892596	C	0.686002811	3.366630177	0.111942615
N	2.341335599	-2.744741630	2.023696088	C	0.487717149	4.752415532	0.162534339
C	0.079540941	-1.702970975	0.306145206	C	-0.781000330	5.327331561	0.160662972
C	-1.224438614	-1.161049942	0.177294210	C	-1.880457273	4.470120648	0.087571167
C	-2.361778664	-2.037496925	0.130520692	C	-1.751004257	3.080336115	0.019210827
C	-3.654069252	-1.521662933	-0.143554189	C	-2.918318351	2.197284879	-0.089440349
C	-4.698356790	-2.421138799	-0.399383472	C	-4.218525124	2.697197652	-0.203413046
C	-4.526256199	-3.804101263	-0.359867390	C	-5.342051155	1.871511818	-0.282401173
C	-3.267010168	-4.290217306	-0.002462724	C	-5.134565386	0.494739414	-0.256344063
C	-2.186338197	-3.443663520	0.266114953	C	-3.855463535	-0.069965238	-0.165978736
C	-5.662154865	-4.792798334	-0.684645408	C	3.476974948	0.827613622	-0.220326981
C	-6.973012796	-4.078780716	-1.061171007	C	4.592555578	1.657039486	-0.047453609
C	-5.242235975	-5.682438970	-1.878020899	C	4.471300888	3.019959023	0.212090214
C	-5.939779295	-5.685082157	0.547701125	C	3.182293992	3.558082363	0.256566876
C	1.191265900	-0.886662225	-0.055592145	C	2.031567652	2.780075790	0.096668509

C	2.577742376	-2.713120172	-1.075710210
C	3.770977852	-3.194379956	-1.567765596
C	4.936882514	-2.401433333	-1.568128114
C	4.813374137	-1.103675809	-1.096331782
C	3.601847544	-0.580100404	-0.596432412
C	-6.743945724	2.500346436	-0.391515608
C	-7.002373191	3.405762766	0.835318056
C	-6.826303696	3.347823334	-1.682494340
C	-7.861287769	1.442017846	-0.443219563
C	-1.004691184	6.850046450	0.223957996
C	0.316274090	7.635320299	0.320620970
C	-1.745544603	7.314731757	-1.051424536
C	-1.857242717	7.194727745	1.467522375
C	5.688904722	3.933667688	0.445428082
C	5.702405515	5.062272630	-0.611656762
C	5.598995391	4.554761670	1.858954971
C	7.022759480	3.170931720	0.343881621
C	6.254625629	-2.975565222	-2.114326058
C	6.072700418	-3.362502891	-3.600856786
C	7.418157862	-1.972032725	-2.018566302
C	6.637333495	-4.233997409	-1.300886628
H	-1.638827930	-5.942332998	1.155003997
H	0.373316747	-6.769870594	2.272992432
H	-5.666690549	-2.026476009	-0.663953461
H	-3.122296489	-5.359859451	0.052738486
H	-7.741628145	-4.822097942	-1.288335608
H	-7.348698850	-3.457717791	-0.243413754
H	-6.853142137	-3.448438191	-1.946441221
H	-6.039008337	-6.392485245	-2.119863099
H	-4.339579949	-6.257830803	-1.660375287
H	-5.045570896	-5.075888165	-2.766088444
H	-5.059894925	-6.263128872	0.839111458
H	-6.241973266	-5.080981464	1.407402320
H	-6.744994236	-6.392920441	0.328618669
H	1.349701356	5.399635377	0.191473141
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H	-4.367809116	3.766946093	-0.231352538
H	-5.989853750	-0.161306655	-0.290672942
H	5.576092176	1.216136273	-0.099700851
H	3.075300406	4.617108312	0.443740230
H	1.700852282	-3.344436420	-1.125874070
H	3.795388153	-4.198206892	-1.975845611
H	5.668644695	-0.447299641	-1.149120800
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H	-6.947024478	2.830242063	1.763263150
H	-6.275830820	4.218703213	0.903945747
H	-7.816017078	3.805859952	-1.773418501
H	-6.655045057	2.728102413	-2.566772775
H	-6.085353786	4.150473977	-1.690495770
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H	-7.762188216	0.785548952	-1.312051824
H	0.102208883	8.706311073	0.367900716
H	0.881814141	7.373072490	1.219040440
H	0.954868690	7.466806820	-0.550705031
H	-1.916538975	8.395214066	-1.019346181
H	-2.717138543	6.826788634	-1.157807747
H	-1.159361645	7.089227105	-1.946318547
H	-1.356380753	6.874538096	2.385085006
H	-2.020181033	8.275227041	1.527190501
H	-2.836790298	6.712477511	1.437284223
H	6.564897279	5.717399647	-0.455299131
H	5.767191151	4.649638425	-1.622104167
H	4.802816834	5.679829385	-0.561022496
H	6.456327941	5.210121086	2.041373127
H	5.595833610	3.776225581	2.626523872
H	4.691531293	5.149691971	1.984586947
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H	8.332836186	-2.433313532	-2.400647505
H	7.607723388	-1.669329463	-0.985060406
H	7.231061002	-1.073056529	-2.612113772
H	6.779056423	-3.987426773	-0.245154170
H	5.867807167	-5.006595669	-1.362084125
H	7.570889688	-4.661366105	-1.679715667

Optimized Cartesian coordinates of different complexes (S_0 state) at the B3LYP/6-311G(d,p) level of theory.

SeNG

Coordinates of Optimized Structure SeNG

C	0.589771000	-3.900967000	-0.526111000
C	0.301413000	-5.254656000	-0.941469000
C	-0.862536000	-5.624183000	-1.530670000
C	-1.832269000	-4.615208000	-1.824733000
C	-1.585791000	-3.236951000	-1.394537000
C	-0.387236000	-2.906587000	-0.633073000
N	-2.926675000	-4.839784000	-2.529575000
Se	-3.734290000	-3.234099000	-2.733195000
N	-2.473084000	-2.347391000	-1.798180000
C	-0.123040000	-1.560549000	-0.146675000
C	1.235188000	-1.165967000	-0.059428000
C	2.266795000	-2.163909000	-0.002016000
C	3.616440000	-1.790135000	0.218387000
C	4.557789000	-2.791457000	0.489617000
C	4.228356000	-4.146633000	0.514456000
C	2.912948000	-4.498732000	0.208922000
C	1.927662000	-3.544829000	-0.071081000
C	5.253479000	-5.245102000	0.853975000
C	6.648361000	-4.671505000	1.164530000
C	4.771029000	-6.030936000	2.095578000
C	5.390044000	-6.212642000	-0.344890000
C	-1.127514000	-0.610229000	0.208245000
C	-0.801216000	0.763509000	0.160040000
C	0.552938000	1.178596000	0.031807000
C	1.576196000	0.210015000	0.037185000
C	2.955037000	0.609648000	0.083919000
C	0.882416000	2.576335000	-0.032853000
C	-1.852313000	1.751339000	0.188430000
C	-2.439522000	-0.975965000	0.734569000
C	-0.150587000	3.553127000	-0.088692000
C	0.203015000	4.900530000	-0.163235000
C	1.532830000	5.331721000	-0.194439000
C	2.527845000	4.362196000	-0.136187000
C	2.240338000	2.990996000	-0.048241000
C	3.301748000	1.985078000	0.041334000
C	4.659102000	2.340740000	0.081703000
C	5.678941000	1.397132000	0.151904000
C	5.313309000	0.048247000	0.194246000
C	3.982378000	-0.370443000	0.172445000
C	-3.202434000	1.354839000	0.362616000
C	-4.221329000	2.300921000	0.186991000
C	-3.952241000	3.634127000	-0.111616000
C	-2.611470000	4.020812000	-0.193821000
C	-1.553798000	3.121646000	-0.035031000
C	-2.683250000	-2.234700000	1.322042000
C	-3.908917000	-2.561436000	1.859192000
C	-4.978681000	-1.642770000	1.856157000
C	-4.724544000	-0.384813000	1.331836000
C	-3.475162000	-0.017453000	0.787459000
C	7.170161000	1.782350000	0.178244000
C	7.385795000	3.305451000	0.117902000
C	7.813663000	1.258997000	1.483611000
C	7.886919000	1.149023000	-1.037148000
C	1.840552000	6.838443000	-0.278707000
C	1.208501000	7.422106000	-1.563963000
C	1.245840000	7.553699000	0.956938000
C	3.351917000	7.130334000	-0.317101000
C	-5.061677000	4.677405000	-0.340881000
C	-6.472088000	4.072622000	-0.216192000
C	-4.931112000	5.807805000	0.706443000
C	-4.920848000	5.274228000	-1.760755000
C	-6.334926000	-2.043146000	2.459828000
C	-6.151776000	-2.381470000	3.957939000
C	-7.383798000	-0.922389000	2.346228000

C	-6.878405000	-3.286078000	1.716871000
H	1.060089000	-6.010741000	-0.794742000
H	-1.054870000	-6.644041000	-1.837915000
H	5.571294000	-2.499748000	0.715838000
H	2.646760000	-5.546035000	0.202692000
H	7.334667000	-5.488037000	1.403520000
H	7.066133000	-4.131442000	0.310433000
H	6.629170000	-3.995841000	2.023976000
H	5.491843000	-6.813038000	2.352857000
H	3.805563000	-6.512066000	1.923322000
H	4.664046000	-5.368921000	2.958995000
H	5.730422000	-5.681794000	-1.238006000
H	6.117155000	-6.998308000	-0.117895000
H	4.441974000	-6.698313000	-0.586880000
H	-0.578173000	5.647032000	-0.183026000
H	3.558440000	4.678337000	-0.156783000
H	4.923771000	3.385579000	0.053907000
H	6.095905000	-0.696707000	0.226893000
H	-5.247231000	1.976394000	0.269780000
H	-2.388757000	5.055880000	-0.410223000
H	-1.881457000	-2.958718000	1.375721000
H	-4.034345000	-3.540753000	2.306433000
H	-5.499972000	0.364726000	1.378727000
H	8.456524000	3.524786000	0.140297000
H	6.981265000	3.737805000	-0.801327000
H	6.928515000	3.816038000	0.969869000
H	8.875468000	1.521936000	1.515862000
H	7.737460000	0.172511000	1.567547000
H	7.327679000	1.696199000	2.360023000
H	7.455168000	1.508303000	-1.975111000
H	8.949760000	1.409622000	-1.028911000
H	7.811993000	0.059280000	-1.032299000
H	1.416430000	8.494021000	-1.635733000
H	1.615782000	6.935684000	-2.454366000
H	0.124139000	7.292140000	-1.580352000
H	1.452191000	8.627456000	0.910292000
H	1.681696000	7.162959000	1.880341000
H	0.162969000	7.425259000	1.019979000
H	3.833860000	6.670488000	-1.184226000
H	3.513976000	8.209294000	-0.385029000
H	3.858159000	6.778544000	0.585967000
H	-7.220135000	4.849496000	-0.395265000
H	-6.640589000	3.278268000	-0.948370000
H	-6.654477000	3.665153000	0.781965000
H	-5.715692000	6.556384000	0.558398000
H	-3.967891000	6.318141000	0.636328000
H	-5.025560000	5.411536000	1.721032000
H	-5.006825000	4.494167000	-2.521883000
H	-5.706244000	6.014763000	-1.941096000
H	-3.957680000	5.770370000	-1.900175000
H	-7.108181000	-2.676028000	4.401158000
H	-5.449111000	-3.204610000	4.105227000
H	-5.773258000	-1.516149000	4.508747000
H	-8.331865000	-1.262981000	2.770898000
H	-7.568976000	-0.644305000	1.304992000
H	-7.082345000	-0.025305000	2.893805000
H	-7.021356000	-3.072877000	0.654049000
H	-6.199437000	-4.137828000	1.797536000
H	-7.843081000	-3.587430000	2.136861000

References

S1. Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A. and Mullen, K. *Angew. Chem Int. Ed.* Engi. **1997**, *36*, 1603-1607.

S2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O., Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09 (Revision A.02), Gaussian, Inc., Wallingford CT, 2009.