Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information for

Chalcogen-Doped, (Seco)-Hexabenzocoronene-Based Nanographenes: Synthesis, Properties, and Chalcogen Extrusion Conversion

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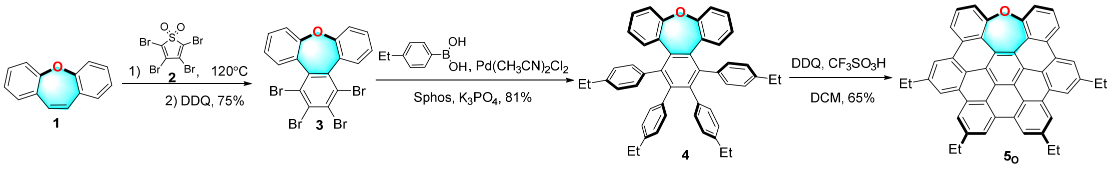
Supplementary Figures and Tables

General Information

Solvents and chemicals were purchased from commercial sources and used directly without further purification. Molecular sieves were activated in an oven and solvents for reaction was stored with molecular sieves. Petroleum ether (PE) used had a boiling range of 60−90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was generally performed through silica gel (200−300 mesh). All reactions were run open to air unless specifically described. NMR spectra were recorded with Bruker-400, 500 or 600 MHz spectrometers. Unless specified otherwise, the NMR spectra were recorded at 22 °C; they were calibrated using the residual solvent signal(^{1}H) or solvent signal (^{13}C). Chemical shifts were reported in parts per million (ppm). Chemical shifts were reported in ppm using TMS or deuterated solvents as internal standards (for ^{1}H NMR: $CDCl_3$, 7.26; for ^{13}C NMR: $CDCl_3$, 77.0). Multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad. Coupling constants (J) are reported in Hertz (Hz). UV-Vis absorption spectra were recorded using a 1-cm quartz cuvette on a Shimadzu-UV-2600 spectrometer. Fluorescence spectra were recorded using a 1-cm quartz cuvette or powder form on a Gangdong F-320 spectrofluorometer at 25 ºC. High-resolution mass spectrometry was performed on a Thermo LTQ-Orbitrap XL mass spectrometer equipped with collision cells for collision-induced dissociation or Bruker MALDI-TOF MS RapifleX. Fluorescent decay was recorded in the HORIBA FL-3 instrument. Crystallographic data were collected on a Bruker D8 Venture diffractometer.

Syntheses

Scheme S1. Synthesis of nanographene $\mathbf{5_O}$.



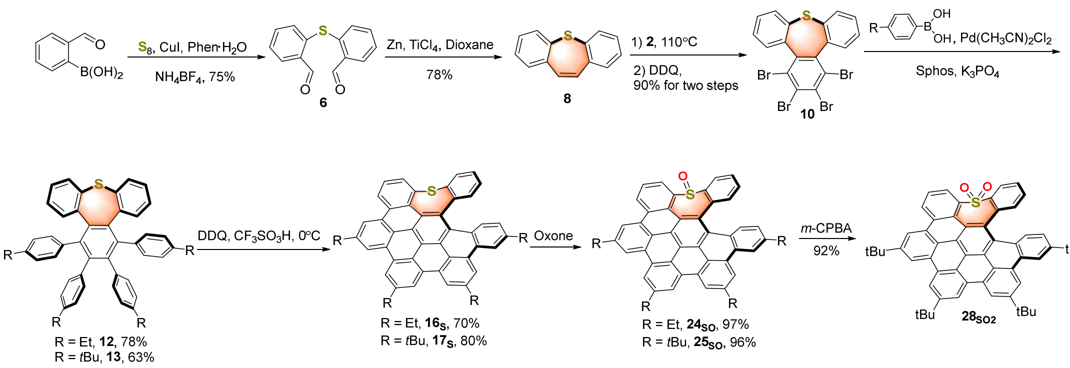
1,2,3,4-Tetrabromotribenzo[b,d,f]oxepine (**3**): A mixture of dibenzo[b,f]oxepine **1** (194 mg, 1.0 mmol, 1.0 equiv), tetrabromothiophene-S,S-dioxide **2**[S1] (647 mg, 1.5 mmol, 1.5 equiv) in toluene (5 mL) in the sealed tube was heated to 110–120 °C until no dibenzo[b,f]oxepine **1** left (around 12 hours, checked by TLC: silica, PE: DCM = 4:1, UV). Then the solvent was removed under reduced pressure, after the residue was dissolved in dichloromethane (15 mL), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (340 mg, 1.5 mmol, 1.5 equiv) was added and the mixture was stirred at room temperature for around 30 minutes. The reaction mixture was concentrated under reduced pressure and purified by silica gel flash chromatography (10-20% DCM in PE) to give the compound **3** (420 mg, 75% for two steps) as a faint yellow solid: mp: 189–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.0, 2.0 Hz, 2H), 7.33 (td, J = 8.0 Hz, 2.0 Hz, 2H), 7.26 (dd, J = 8.0, 2.0 Hz, 2H), 7.15 (td, J = 8.0, 2.0 Hz, 2H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 161.9, 138.3, 133.4, 130.8, 130.6, 130.4, 126.5, 123.8, 120.2; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_8Br_4O$ 555.7304; Found 555.7318.

1,2,3,4-Tetrakis(4-ethyl phenyl)tribenzo[b,d,f]oxepine (**4**): To a solution of oxepine **3** (334mg, 0.6 mmol, 1.0 equiv) in toluene (10 mL) was quickly added (4-ethyl phenyl) boronic acid (720 mg, 4.8 mmol, 8.0 equiv), palladium (II) chloride diacetonitrile complex (23 mg, 0.09 mmol, 0.15 equiv), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos, 74 mg, 0.18 mmol, 0.3 equiv) and potassium phosphate tribasic (2.04 g, 9.6 mmol, 16.0equiv) under argon atmosphere. Then the mixture was carefully gas exchanged to keep stirring under argon at 110°C for around 12 hours. The mixture was filtered over a silica pad and washed the filter cake with dichloromethane, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the compound **4** (320 mg, 81%) as a white solid: mp: 240–241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.19 (m, 4H), 7.04–6.99 (m, 4H), 6.85–6.82 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 6.55 (t, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 8.0 Hz, 2H), 2.43–2.32 (m, 8H), 1.05 (t, *J* = 8.0 Hz, 6H), 0.97 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 142.6, 141.3, 140.9, 140.6, 138.0, 137.9, 135.1, 133.9, 132.6, 131.7, 131.3, 130.8, 130.3, 128.0, 126.5, 126.2, 125.9, 125.2, 123.1, 119.4, 28.4, 28.4, 15.7, 15.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{50}H_{45}O$ 661.3465; found 661.3465.

5,8,11,14-Tetraethyl-19-oxabenzo[5',6']tetraceno [1',12',11',10':5,6,7,8,9] tetrapheno [10,11,12,1-nopqab]pleiadene (5$_O$): To a solution of compound **4** (66 mg, 0.1 mmol, 1.0 equiv) in anhydrous dichloromethane (20 mL) in an oven-dried flask with a magnetic stirring bar was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1 mmol, 10.0 equiv). The mixture was carefully exchanged into an argon atmosphere and stirred in an ice-water bath. Then trifluoromethanesulfonic acid (0.1 mL, 1.3 mmol, 13 equiv) was added dropwise to the above reaction mixture and the mixture was stirred at 0 °C for around 5 minutes. Triethyl amine (1.0 mL, 7.2 mmol, 72 equiv) was added, followed by methanol (1.0 mL, 24.7 mmol, 247 equiv) to quench the reaction and the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the titled compound **5$_O$** (43 mg, 65%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.52 (d, *J* = 6.0 Hz, 2H), 8.47 (s, 2H), 8.42 (s, 4H), 7.73 (t, *J* = 6.0 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 2H), 3.10 (q, *J* = 8.0 Hz, 4H), 3.00 (q, *J* = 8.0 Hz, 4H), 1.57 (t, *J* = 8.0 Hz, 6H), 1.49 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 142.3, 142.3, 132.5, 129.9, 129.9, 129.7, 128.2, 128.1, 126.2, 123.3, 122.9, 122.8, 122.4, 122.2, 121.3, 120.8, 120.4, 120.3, 119.4, 118.2, 29.9, 29.6, 16.2, 16.0 ; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{50}H_{34}O$ 650.2605; Found 650.2614.

Scheme S2. Synthesis of sulfur-doped nanographenes.



2,2'-Thiodibenzaldehyde (**6**): A mixture of sulfur S_8 (192 mg, 0.75 mmol, 1.0 equiv), (2-formyl phenyl) boronic acid (2.25 g, 15.0 mmol, 20.0 equiv), CuI (114 mg, 0.6 mmol, 0.8 equiv), 1,10-phenanthroline monohydrate (120 mg, 0.6 mmol, 0.8 equiv), and NH_4BF_4 (156 mg, 1.5 mmol, 2.0 equiv), in DMSO (5 mL) and H_2O (2.5 mL) was stirred at 100 °C for 18 hours. After the residue was cooled to room temperature and dissolved in EtOAc, the solution was washed with H_2O and brine and dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure and purified by silica gel flash chromatography (10-20% EtOAc in PE) to give title compound **6** (1.089 g, 75%) as colorless solid. The NMR data were identical with the reported results[S2].

Dibenzo[b,f]thiepine (**8**): To a mixture of zinc powder (1.3 g, 20 mmol, 8.0 equiv) in anhydrous THF, $TiCl_4$ (1.1ml, 10 mmol, 4.0 equiv) was added cautiously during 10 min at 0°C under argon atmosphere, The resulting suspension was heated at reflux for 2.5 hours. Then the mixture cooled to room temperature and 2,2'-Thiodibenzaldehyde **6** (612 mg, 2.5 mmol, 1.0 equiv) was added slowly as a dilute solution in THF over 10 minutes. After the addition was complete, the reaction mixture was heated at reflux for an additional period of 4 hours. After the mixture was cooled to room temperature, The resulting mixture was filtered over a silica pad, the filter cake was washed with EtOAc. The combined organic layers were washed with water and brine and dried with Na_2SO_4, Evaporation of the solvents in vacuo, the residue was purified by silica gel flash chromatography (PE) to give title compound **8** (410 mg, 78%) as faint yellow solid. The NMR data were identical with the reported results[S3].

1,2,3,4-Tetrabromotribenzo[b,d,f]thiepine (**10**): A mixture of dibenzo[b,f]thiepine **8** (210 mg, 1.0 mmol, 1.0 equiv), tetrabromothiophene-S,S-dioxide **2**[S1] (647 mg, 1.5 mmol, 1.5 equiv) in toluene (5 mL) in the sealed tube was heated to 110–120 °C until no dibenzo[b,f]thiepine **8** left (around 12 hours, checked by TLC: silica, PE: DCM = 5:1, UV). Then the solvent was removed in vacuo and the residue was dissolved in dichloromethane (15 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (340 mg, 1.5 mmol, 1.5 equiv) was added, the mixture was stirred at room temperature for around 30 minutes. The reaction mixture was concentrated under reduced pressure and purified by silica gel flash chromatography (10-20% DCM in PE) to give the compound **10** (519 mg, 90% for two steps) as a colorless solid: mp: 198–199 °C; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 6.0, 1.5 Hz, 2H), 7.50 (dd, J = 6.0, 1.5 Hz, 2H), 7.26–7.19 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.4, 140.7, 132.9, 132.3, 129.6, 128.9, 127.3, 126.3; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_9Br_4S$ 572.7153; Found 572.7176.

1,2,3,4-Tetrakis(4-ethyl phenyl)tribenzo[b,d,f]thiepine (12): To a solution of thiepine **10** (460 mg, 0.8 mmol, 1.0 equiv) in toluene (15 mL) was quickly added (4-ethyl phenyl)boronic acid (980 mg, 6.4 mmol, 8.0 equiv), palladium(II) chloride diacetonitrile complex (31 mg, 0.12 mmol, 0.15 equiv), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos, 123 mg, 0.24 mmol, 0.3 equiv) and potassium phosphate tribasic (2.71 g, 12.8 mmol, 16.0equiv) under argon atmosphere. Then the mixture was carefully gas exchanged to keep stirring under argon at 110°C for around 12 hours. The mixture was filtered through a silica pad and washed the filter cake with dichloromethane, the filtrate was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the compound **12** (422 mg, 78%) as a white solid: mp: 300–301 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.91–6.88 (m, 6H), 6.73 (d, J = 8.0 Hz, 2H), 6.67 (t, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.0 Hz, 2H), 6.46 (d, J = 8.0 Hz, 2H), 6.40 (d, J = 8.0 Hz, 2H), 2.42–2.34 (m, 8H), 1.04–0.98 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.9, 141.4, 141.0, 140.9, 140.1, 139.1, 138.1, 137.9, 133.8, 132.3, 131.9, 131.2, 130.9, 130.4, 126.5, 126.3, 126.3, 125.7, 125.3, 28.4, 15.6, 15.6; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{50}H_{44}S$ 676.3159; Found 676.3140.

1,2,3,4-Tetrakis(4-(*tert*-butyl)phenyl)tribenzo[b,d,f]thiepine (13): To a solution of thiepine **10** (460mg, 0.8 mmol, 1.0 equiv) in xylene (15 mL) was quickly added (4-(tert-butyl)phenyl)boronic acid (1140 mg, 6.4 mmol, 8.0 equiv), palladium (II) chloride diacetonitrile complex (31 mg, 0.12 mmol, 0.15 equiv), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos, 99 mg, 0.24 mmol, 0.3 equiv) and potassium phosphate tribasic (2.71 g, 12.8 mmol, 16.0equiv) under argon atmosphere. Then the mixture was carefully gas exchanged to keep stirring under argon at 140°C for around 24 hours. The mixture was filtered through a silica pad and washed the filter cake with dichloromethane, the filtrate was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the compound **13** (397 mg, 63%) as a white solid: mp: 276–277 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.02–7.00 (br, 4H), 6.91–6.85 (m, 6H), 6.76 (d, J = 8.0 Hz, 2H), 6.66–6.62 (m, 4H), 6.45 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 8.0 Hz, 2H), 1.10 (s, 18H), 1.07 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.6, 141.9, 141.8, 141.4, 140.1, 139.0, 137.8, 137.6, 133.8, 132.1, 131.6, 131.2, 130.4, 130.2, 126.4, 126.3, 123.4, 123.1, 122.4, 34.1, 34.0, 31.2, 31.1; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{58}H_{60}S$ 788.4411; Found 788.4423.

3,6,9,12-Tetraethylbenzo[f]naphtho[1',2',3',4':12,13] phenanthro[1',10',9',8':5,6,7,8] piceno[1,14-bcd]thiepine (16$_S$): To a solution of compound **12** (68 mg, 0.1 mmol, 1.0 equiv) in anhydrous dichloromethane (15 mL) in an oven-dried flask with a magnetic stirring bar was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1 mmol, 10.0 equiv). The mixture was carefully exchanged into an argon atmosphere and stirred in an ice-water bath. Then trifluoromethanesulfonic acid (0.1 mL, 1.3 mmol, 13 equiv) was added dropwise to the above reaction mixture and the mixture was stirred at 0 °C for around 3 minutes. Triethyl amine (1.0 mL, 7.2 mmol, 72 equiv) was added, followed by methanol (1.0 mL, 24.7 mmol, 247 equiv) to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the title compound **16$_S$** (48 mg, 70%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.91 (s, 2H), 8.84 (s, 1H), 8.82 (s, 1H), 8.79 (d, J = 6.0 Hz, 1H), 8.78 (s, 1H), 8.65 (s, 1H), 8.57 (s, 1H), 8.16 (d, J = 6.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 6.0 Hz, 1H), 7.68 (t, J = 6.0 Hz, 1H), 7.29 (t, J = 6.0 Hz, 1H), 7.12 (d, J = 6.0 Hz, 1H), 6.88 (t, J = 6.0 Hz, 1H), 6.27 (d, J = 6.0 Hz, 1H), 3.27–3.14 (m, 6H), 2.87 (q, J = 8.0 Hz, 2H), 1.62 (t, J = 8.0 Hz, 6H), 1.55 (t, J = 8.0 Hz, 3H), 1.40 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.3, 142.5, 142.3, 142.2, 142.2, 137.9, 137.5, 134.7, 133.4, 133.2, 132.8, 132.3, 131.5, 131.4, 130.7, 130.4, 130.3, 130.2, 130.1, 129.8, 129.8, 129.1, 128.3, 128.1, 127.8, 127.1, 126.7, 126.3, 124.6, 123.3, 123.0, 123.0, 122.9, 122.7, 122.5, 121.9, 121.7, 121.4, 121.2, 121.1, 120.8, 30.0, 29.8, 29.8, 29.1, 16.5, 16.3, 15.6; HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for $C_{50}H_{36}S$ 668.2533; Found 668.2552.

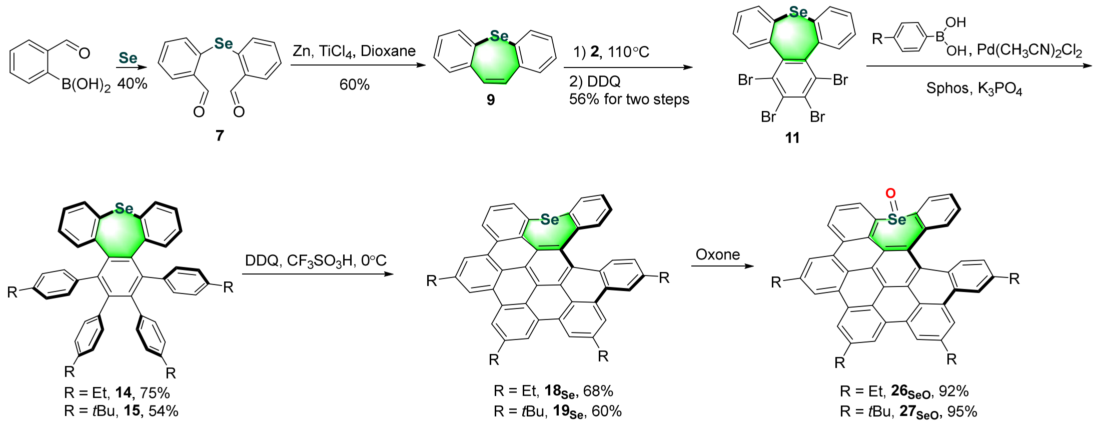
3,6,9,12-tetra-*tert*-butylbenzo[f]naphtha [1',2',3',4':12,13]phenanthro [1',10',9',8':5,6,7,8] piceno[1,14-bcd]thiepine (17$_S$): To a solution of compound **13** (80 mg, 0.1 mmol, 1.0 equiv) in anhydrous dichloromethane (10 mL) in an oven-dried flask with a magnetic stirring bar was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1.0 mmol, 10.0 equiv). The mixture was carefully exchanged into an argon atmosphere and stirred in an ice-water bath. Then trifluoromethanesulfonic acid (0.1 mL, 1.3 mmol, 13 equiv) was added dropwise to the above reaction mixture and the mixture was stirred at 0 °C for around 2 minutes. Triethyl amine (1.0 mL, 7.2 mmol, 72 equiv) was added, followed by methanol (1.0 mL, 24.7 mmol, 247 equiv) to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the title compound **17$_S$** (63 mg, 80%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.22 (s, 1H), 9.18 (s, 1H), 9.13 (s, 1H), 9.09 (s, 1H), 9.03 (s, 1H), 8.91 (s, 1H), 8.83 (d, J = 6.0 Hz, 1H), 8.78 (s, 1H), 8.19 (d, J = 6.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 6.0 Hz, 1H), 7.72 (t, J = 6.0 Hz, 1H), 7.33–7.29 (m, 2H), 6.90 (t, J = 6.0 Hz, 1H), 6.31 (d, J = 6.0 Hz, 1H), 1.79 (s, 9H), 1.77 (s, 9H), 1.71 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.3, 149.2, 149.1, 149.1, 137.8, 135.1, 133.6, 133.5, 132.8, 132.6, 131.3, 131.1, 130.8, 130.5, 130.4, 130.4, 130.2, 130.1, 129.9, 128.9, 128.5, 128.3, 127.9, 127.3, 127.0, 124.8, 124.2, 123.6, 123.2, 123.1, 123.0, 122.7, 121.3, 119.9, 119.1, 119.0, 118.3, 35.7, 35.7, 35.60, 35.0, 32.0, 31.9, 31.9, 31.4; HRMS (MALDI-TOF) m/z: [M+H]$^+$ Calcd for $C_{58}H_{53}S$ 781.3862; Found 781.3881.

(17R)-3,6,9,12-Tetraethylbenzo[f]naphtha [1',2',3',4':12,13]phenanthro [1',10',9',8':5,6,7,8] piceno[1,14-bcd]thiepine 17-oxide (24$_{SO}$): To a solution of compound **16$_S$** (34 mg, 0.05 mmol, 1.0 equiv) in anhydrous dichloromethane (5 mL) in an oven-dried flask with a magnetic stirring bar was added $2KHSO_5.KHSO_4.K_2SO_4$, (Oxone, 307 mg, 0.5 mmol, 10.0 equiv). The mixture was stirred for 2 hours in room temperature. 10% aqueous sodium sulfite solution (1.4 mL, 1.0 mmol, 20 equiv) was added to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 30-50 % PE in DCM, UV) to give the title compound **24$_{SO}$** (33 mg, 97%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 6.0 Hz, 1H), 8.78 (s, 1H), 8.76 (s, 1H), 8.70 (s, 1H), 8.68 (s, 1H), 8.61 (s, 1H), 8.58 (s, 2H), 8.43 (d, J = 6.0 Hz, 1H), 8.04 (d, J = 6.0 Hz, 1H), 8.01 (d, J = 6.0 Hz, 1H), 7.95 (t, J = 6.0 Hz, 1H), 7.52–7.48 (m, 1H), 7.14 (d, J = 6.0 Hz, 1H), 6.93 (t, J = 6.0 Hz, 1H), 6.19 (d, J = 6.0 Hz, 1H), 3.22 (q, J = 8.0 Hz, 2H), 3.15 (q, J = 8.0 Hz, 2H), 2.98 (q, J = 8.0 Hz, 2H), 2.92 (q, J = 8.0 Hz, 6H), 1.62 (t, J = 8.0 Hz, 3H), 1.52 (t, J = 8.0 Hz, 6H), 1.44 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 144.6, 143.1, 143.0, 142.8, 136.3, 133.2, 132.4, 131.6, 131.1, 130.6, 130.4, 130.2, 130.0, 129.5, 129.2, 128.6, 128.4, 127.8, 126.5, 125.0, 124.9, 124.7, 123.2, 122.6, 122.3, 122.2, 122.1, 121.9, 121.5, 121.4, 121.1, 118.9, 118.5, 30.1, 29.9, 29.7, 29.1, 16.4, 16.2, 16.2, 15.6; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{50}H_{37}OS$ 685.2560; Found 685.2543.

(17R)-3,6,9,12-Tetra-*tert*-butylbenzo[f]naphtha [1',2',3',4':12,13]phenanthro [1',10',9',8':5,6,7,8] piceno [1,14-bcd]thiepine 17-oxide (25$_{SO}$): To a solution of compound **17**$_S$ (38 mg, 0.05 mmol, 1.0 equiv) in anhydrous dichloromethane (5 mL) in an oven-dried flask with a magnetic stirring bar was added $2KHSO_5.KHSO_4.K_2SO_4$, (Oxone, 307 mg, 0.5 mmol, 10.0 equiv).The mixture was stirred for 2 hours in room temperature. 10% aqueous sodium sulfite solution (1.4 mL, 1.0 mmol, 20 equiv) was added to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 30-50 % PE in DCM, UV) to give the title compound **25$_{SO}$** (38 mg, 96%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 9.21 (s, 1H), 9.17 (s, 1H), 9.15 (s, 1H), 9.07 (s, 1H), 8.99 (s, 1H), 8.98 (d, J = 6.0 Hz, 1H), 8.82 (s, 1H), 8.49 (d, J = 6.0 Hz, 1H), 8.11–8.08 (m, 2H), 8.03 (t, J = 8.0 Hz, 1H), 7.57 (t, J = 6.0 Hz, 1H), 7.35 (d, J = 6.0 Hz, 1H), 7.02 (t, J = 6.0 Hz, 1H), 6.38 (d, J = 6.0 Hz, 1H), 1.80 (s, 9H), 1.77 (s, 9H), 1.72 (s, 9H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.7, 145.5, 145.0, 136.2, 133.2, 132.9, 131.5, 130.7, 130.7, 130.6, 130.5, 130.4, 130.2, 129.9, 129.6, 129.2, 128.8, 128.6, 128.2, 128.0, 125.3, 125.0, 124.5, 123.5, 123.3, 122.8, 122.4, 122.3, 120.4, 119.4, 119.3, 119.2, 119.2, 119.1, 119.0, 118.7, 118.6, 35.7, 35.7, 35.7, 35.0, 31.9, 31.9, 31.8, 31.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{58}H_{53}OS$ 797.3812; found 797.3833.

3,6,9,12-Tetra-*tert*-butylbenzo[f]naphtha [1',2',3',4':12,13]phenanthro [1',10',9',8':5,6,7,8] piceno[1,14-bcd]thiepine 17,17-dioxide (**28$_{SO2}$**): To a solution of compound **25$_{SO}$** (40 mg, 0.05 mmol, 1.0 equiv) in anhydrous dichloromethane (5 mL) in an oven-dried flask with a magnetic stirring bar was added *m*-chloroperbenzoic acid (*m*-CPBA, 34 mg, 0.2 mmol, 4.0 equiv). The mixture was stirred for 24 hours in room temperature. 10% aqueous sodium sulfite solution (0.6 mL, 0.4 mmol, 8.0 equiv) was added to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 30-50 % PE in DCM, UV) to give the title compound **28**$_{\mathrm{SO_2}}$ (37 mg, 92%) as a yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.19 (d, J = 6.0 Hz, 1H), 9.17 (s, 2H), 9.15 (s, 1H), 9.03 (s, 1H), 8.96 (s, 1H), 8.76 (d, J = 6.0 Hz, 1H), 8.74 (s, 1H), 8.37 (d, J = 6.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 6.0 Hz, 1H), 7.17 (d, J = 6.0 Hz, 1H), 6.63 (d, J = 6.0 Hz, 1H), 1.80 (s, 9H), 1.76 (s, 9H), 1.72 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 149.7, 149.5, 149.5, 141.7, 141.3, 140.2, 135.7, 134.6, 133.6, 132.4, 132.0, 131.5, 131.0, 130.5, 130.4, 130.2, 130.0, 129.3, 128.8, 128.7, 128.6, 128.1, 127.2, 126.9, 126.2, 124.3, 124.3, 124.1, 123.8, 123.3, 123.0, 122.2, 121.8, 120.9, 119.4, 119.2, 119.2, 119.1, 119.0, 118.4, 35.7, 35.7, 35.6, 34.9, 31.9, 31.9, 31.8, 31.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{58}H_{53}O_2S$ 813.3761; found 813.3762.

Scheme S3. Synthesis of selenium-doped nanographenes.



2,2'-Selenodibenzaldehyde (**7**): A mixture of selenium Se (474 mg, 6.0 mmol, 1.0 equiv), (2-2-formyl phenylronic acid (2.25 g, 15.0 mmol, 2.5 equiv), CuI (114 mg, 0.6 mmol, 0.1 equiv), 1,10-phenanthroline monohydrate (120 mg, 0.6 mmol, 0.1 equiv), and NH_4BF_4 (156 mg, 1.5 mmol, 0.25 equiv), in DMSO (0.2 mL) and H_2O (0.1 mL) was stirred at 100 °C for 18 hours. After the residue was dissolved in EtOAc, the solution was washed with H_2O and brine and dried over $MgSO_4$. The solution was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (10-20% EtOAc in PE) to give the title compound **7** (693 mg, 40%) as colorless solid. The NMR data were identical with the reported results[S2].

Dibenzo[b,f]selenepine (**9**): To a mixture of zinc powder (1.30 g, 20 mmol, 8.0 equiv) in anhydrous THF, $TiCl_4$ (1.1 ml, 10.0 mmol, 4.0 equiv) was added cautiously during 10 min at 0°C under argon atmosphere, The resulting suspension was heated at reflux for 2.5 h. Then the mixture cooled to room temperature and 2,2'-selenodibenzaldehyde **7** (723 mg, 2.5 mmol, 1.0 equiv) was added slowly as a dilute solution in THF over 10 minutes. After the addition was completed, the reaction mixture was heated at reflux for an additional period of 4 h. After the mixture was cooled to room temperature, The resulting mixture was filtered over a silica pad and washed filter cake with EtOAc. The combined organic layers were washed with water and brine and dried over Na_2SO_4. Evaporation of the solvents in vacuo, the residue was purified by silica gel flash chromatography (PE) to give title compound **9** (385 mg, 60%) as a faint yellow solid. The NMR data were identical with the reported results[S4].

1,2,3,4-Tetrabromotribenzo[b,d,f]selenepine (**11**): A mixture of dibenzo[b,f]selenepine **9** (257 mg, 1.0 mmol, 1.0 equiv), tetrabromothiophene-S,S-dioxide **2**[S1] (647 mg, 1.5 mmol, 1.5 equiv) in xylene (5 mL) in the sealed tube was heated to 140 °C until no dibenzo[b,f]selenepine **9** left (around 12 hours, checked by TLC: silica, PE: DCM = 5:1, UV). Then the mixture was cooled to room temperature and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (340 mg, 1.5 mmol, 1.5 equiv) was added, the mixture was heated to 90 °C and stirred for around 30 minutes. The reaction mixture was concentrated under reduced pressure and purified by silica gel flash chromatography (10-20% DCM in PE) to give the compound **11** (348 mg, 56% for two steps) as a colorless solid: mp: 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 6.0 Hz, 2H), 7.43 (d, J = 6.0 Hz, 2H), 7.24 (t, J = 6.0 Hz, 2H), 7.15 (t, J = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.3, 137.3, 134.0, 132.5, 129.4, 128.5, 127.5, 126.4; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_9Br_4Se$ 620.6597; Found 620.6584.

1,2,3,4-Tetrakis(4-ethylphenyl)tribenzo[b,d,f]selenepine (**14**): To a solution of selenepine **11** (498mg, 0.8 mmol, 1.0 equiv) in toluene (15 mL) was quickly added (4-ethyl phenyl)boronic acid (980 mg, 6.4 mmol, 8.0 equiv), palladium(II) chloride diacetonitrile complex (31 mg, 0.12 mmol, 0.15 equiv), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos, 99 mg, 0.24 mmol, 0.3 equiv) and potassium phosphate tribasic (2.71 g, 12.8 mmol, 16.0equiv) under argon atmosphere. Then the mixture was carefully gas exchanged to keep stirring under argon at 110°C for around 12 hours. The mixture was filtered through a silica pad and washed the filter cake with dichloromethane, the filtrate was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the compound **14** (434 mg, 75%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.72 (t, J = 8.0 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 6.58 (t, J = 8.0 Hz, 2H), 6.49 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 8.0 Hz, 2H), 6.32 (d, J = 8.0 Hz, 2H), 2.30–2.25 (m, 8H), 0.93–0.89 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 141.6, 140.8, 140.8, 140.2, 139.9, 138.1, 138.0, 137.9, 133.6, 132.8, 132.2, 131.8, 130.8, 130.4, 126.6, 126.2, 126.2, 126.0, 125.6, 125.3, 28.33, 15.56, 15.51; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{50}H_{44}Se$ 724.2603; Found 724.2570.

1,2,3,4-Tetrakis(4-(tert-butyl)phenyl)tribenzo[b,d,f]selenepine (**15**): To a solution of selenepine **11** (498 mg, 0.8 mmol, 1.0 equiv) in xylene (15 mL) was quickly added (4-(tert-butyl)phenyl)boronic acid (1.14 g, 6.4 mmol, 8.0 equiv), palladium(II) chloride diacetonitrile complex (31 mg, 0.12 mmol, 0.15 equiv), 2-dicyclohexylphosphino-2,6-dimethoxy-1,1-biphenyl (SPhos, 99 mg, 0.24 mmol, 0.3 equiv) and potassium phosphate tribasic (2.71 g, 12.8 mmol, 16.0 equiv) under argon atmosphere. Then the mixture was carefully gas exchanged to keep stirring under argon at 140°C for around 24 hours. The mixture was filtered through a silica pad and washed the filter cake with dichloromethane, the filtrate was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the compound **15** (361mg, 54%) as a white solid: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 4H), 6.90 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.78 (t, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.67–6.63 (m, 4H), 6.44 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 8.0 Hz, 2H), 1.09 (s, 18H), 1.07 (s, 18H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.7, 147.6, 141.7, 141.6, 140.1, 140.0, 138.0, 137.7, 137.6, 133.7, 132.8, 132.0, 131.6, 130.3, 130.2, 126.5, 126.0, 123.4, 123.3, 123.0, 122.4, 34.0, 34.0, 31.2, 31.1; HRMS (MALDI-TOF) m/z: [M]+ Calcd for $C_{58}H_{60}Se$ 836.3855 Found 836.3827.

3,6,9,12-Tetraethylbenzo[f]naphtha [1',2',3',4':12,13] phenanthro [1',10',9',8':5,6,7,8] piceno [1,14-bcd]selenepine (**18$_{Se}$**): To a solution of compound **14** (73 mg, 0.1 mmol, 1.0 equiv) in anhydrous dichloromethane (15 mL) in an oven-dried flask with a magnetic stirring bar was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1.0 mmol, 10.0 equiv).The mixture was carefully exchanged into an argon atmosphere and stirred in an ice-water bath. Then trifluoromethanesulfonic acid (0.1 mL, 1.3 mmol, 13 equiv) was added dropwise to the above reaction mixture and the mixture was stirred at 0 °C for around 3 minutes. Triethyl amine (1.0 mL, 7.2 mmol, 72 equiv) was added, followed by methanol (1.0 mL, 24.7 mmol, 247 equiv) to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the title compound **18$_{Se}$** (48 mg, 68%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.80 (s, 1H), 8.75 (s, 1H), 8.73 (s, 1H), 8.66 (d, J = 6.0 Hz, 1H), 8.65 (s, 2H), 8.55 (s, 1H), 8.49 (s, 1H), 8.23 (d, J = 6.0 Hz, 1H), 8.17 (d, J = 6.0 Hz, 1H), 7.94 (d, J = 6.0 Hz, 1H), 7.51 (t, J = 6.0 Hz, 1H), 7.19 (t, J = 6.0 Hz, 1H), 7.11 (dd, J = 6.0, 1.5 Hz, 1H), 6.81 (t, J = 6.0 Hz, 1H), 6.12 (d, J = 6.0 Hz, 1H), 3.21 (q, J = 8.0 Hz, 2H), 3.11–3.03 (m, 4H), 2.88 (q, J = 8.0 Hz, 2H), 1.60 (t, J = 8.0 Hz, 3H), 1.54 (t, J = 8.0 Hz, 3H), 1.49 (t, J = 8.0 Hz, 3H), 1.41 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.1, 142.5, 142.3, 142.3, 142.2, 135.4, 134.7, 134.6, 134.0, 133.3, 133.2, 132.5, 131.5, 131.4, 131.3, 130.7, 130.5, 130.4, 130.1, 129.9, 129.8, 129.1, 128.1, 128.0, 127.8, 127.7, 127.1, 126.3, 124.6, 123.4, 123.0, 123.0, 122.8, 122.6, 121.9, 121.7, 121.5, 121.4, 121.1, 120.9, 120.8, 30.0, 29.8, 29.8, 29.1, 16.5, 16.3, 15.6; HRMS (MALDI-TOF) m/z: [M+H]$^+$ Calcd for $C_{50}H_{37}Se$ 717.2055 Found 717.2069.

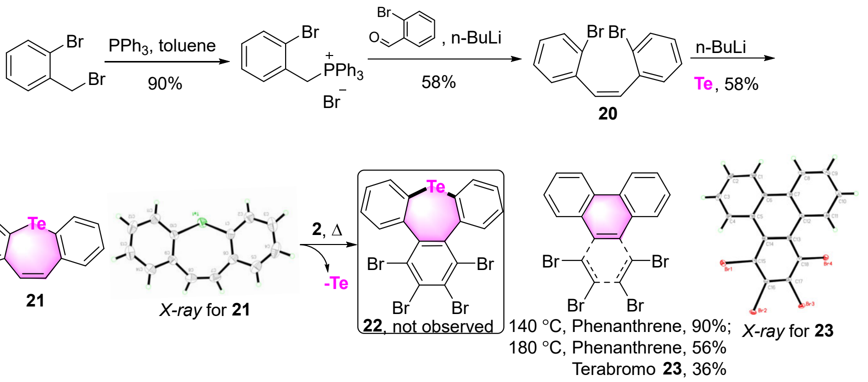
3,6,9,12-tetra-*tert*-butylbenzo[f]naphtho[1',2',3',4':12,13] phenanthro[1',10',9',8':5,6,7,8] piceno[1,14-bcd]selenepine (**19$_{Se}$**): To a solution of compound **15** (84 mg, 0.1 mmol, 1.0 equiv) in anhydrous dichloromethane (10 mL) in an oven-dried flask with a magnetic stirring bar was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1 mmol, 10.0 equiv).The mixture was carefully exchanged into an argon atmosphere and stirred in an ice-water bath. Then trifluoromethanesulfonic acid (0.1 mL, 1.3 mmol, 13.0 equiv) was added dropwise to the above reaction mixture and the mixture was stirred at 0 °C for around 2 minutes. Triethyl amine (1.0 mL, 7.2 mmol, 72 equiv) was added, followed by methanol (1.0 mL, 24.7 mmol, 247 equiv) to quench the reaction and the mixture was concentrated under reduced pressure and purified by flash chromatography (silica, 10–20 % DCM in PE, UV) to give the title compound **16$_S$** (50 mg, 60%) as yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.22 (s, 1H), 9.18 (s, 1H), 9.12 (s, 1H), 9.07 (s, 1H), 9.04 (s, 1H), 8.91 (s, 1H), 8.83 (d, J = 6.0 Hz, 1H), 8.80 (s, 1H), 8.34 (d, J = 6.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 6.0 Hz, 1H), 7.65 (t, J = 6.0 Hz, 1H), 7.33 (d, J = 6.0 Hz, 1H), 7.26 (t, J = 6.0 Hz, 1H), 6.88 (t, J = 6.0 Hz, 1H), 6.24 (d, J = 6.0 Hz, 1H), 1.80 (s, 9H), 1.77 (s, 9H), 1.71 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.9, 149.2, 149.1, 149.1, 135.7, 134.8, 134.4, 133.7, 133.3, 132.9, 131.6, 131.4, 130.9, 130.8, 130.5, 130.3, 130.1, 129.9, 129.0, 128.3, 128.2, 127.8, 127.3, 124.9, 124.2, 123.6, 123.2, 123.1, 122.8, 121.1, 120.0, 119.1, 119.0, 119.0, 118.9, 118.3, 35.7, 35.7, 35.6, 34.9, 32.0, 31.9, 31.9, 31.4; HRMS (MALDI-TOF) m/z: [M+H]$^+$ Calcd for C$_{58}$H$_{53}$Se 829.3307 Found 829.3304.

3,6,9,12-Tetraethylbenzo[f]naphtho[1',2',3',4':12,13]phenanthro[1',10',9',8':5,6,7,8]piceno[1,14-bcd]selenepine 17-oxide (**26**$_{\mathbf{SeO}}$): To a solution of compound **18**$_{\mathbf{Se}}$ (36 mg, 0.05 mmol, 1.0 equiv) in anhydrous dichloromethane (10 mL) in an oven-dried flask with a magnetic stirring bar was added 2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$, (Oxone, 307 mg, 0.5 mmol, 10.0 equiv).The mixture was stirred for 2 hours in room temperature. 10% aqueous sodium sulfite solution (1.4 mL, 1.0 mmol, 20 equiv) was added to quench the reaction and the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (silica, 30-50 % PE in EA, UV) to give the title compound **26**$_{\mathbf{SeO}}$ (34 mg, 92%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.73 (s, 1H), 8.66 (d, J = 6.0 Hz, 1H), 8.60 (s, 2H), 8.44 (s, 1H), 8.40 (s, 2H), 8.35 (s, 1H), 8.25 (s, 1H), 7.99 (d, J = 6.0 Hz, 1H), 7.84 (d, J = 6.0 Hz, 2H), 7.43 (t, J = 6.0 Hz, 1H), 7.08 (d, J = 6.0 Hz, 1H), 6.83 (t, J = 6.0 Hz, 1H), 5.93 (d, J = 6.0 Hz, 1H), 3.29–3.23 (m, 2H), 3.13 (br, 2H), 2.95 (q, J = 8.0 Hz, 2H), 2.78 (q, J = 8.0 Hz, 2H), 1.63 (t, J = 8.0 Hz, 3H), 1.51–1.41 (m, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.1, 142.9, 142.7, 142.5, 133.3, 131.6, 130.5, 130.3, 130.2, 129.8, 129.8, 129.5, 128.8, 128.1, 127.7, 126.6, 126.2, 125.3, 123.0, 122.9, 122.3, 122.2, 122.1, 122.0, 122.0, 121.9, 121.2, 121.1, 121.0, 120.3, 30.0, 29.8, 29.5, 29.1, 16.4, 16.1, 16.0, 15.6; HRMS (MALDI-TOF) m/z: [M+H]$^+$ Calcd for C$_{50}$H$_{37}$OSe 733.2004 Found 733.2020.

3,6,9,12-Tetra-*tert*-butylbenzo[f]naphtho[1',2',3',4':12,13]phenanthro[1',10',9',8':5,6,7,8]piceno[1,14-bcd]selenepine 17-oxide (**27**$_{\mathbf{SeO}}$): To a solution of compound **19**$_{\mathbf{Se}}$ (41 mg, 0.05 mmol, 1.0 equiv) in anhydrous dichloromethane (10 mL) in an oven-dried flask with a magnetic stirring bar was added 2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$ (Oxone, 307 mg, 0.5 mmol, 10.0 equiv). The mixture was stirred for 2 hours at room temperature. 10% aqueous sodium sulfite solution (1.4 mL, 1.0 mmol, 20 equiv) was added to quench the reaction and the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (silica, 30-50 % PE in EA, UV) to give the title compound **27**$_{\mathbf{SeO}}$ (40 mg, 95%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.24 (s, 1H), 9.21 (s, 1H), 9.15 (s, 1H), 9.12 (s, 1H), 9.06 (s, 1H), 8.96 (s, 1H), 8.94 (d, J = 6.0 Hz, 1H), 8.83 (s, 1H), 8.56 (d, J = 6.0 Hz, 1H), 8.13 (d, J = 6.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.00 (t, J = 6.0 Hz, 1H), 7.58 (t, J = 6.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 6.0

Hz, 1H), 6.33 (d, J = 6.0 Hz, 1H), 1.80 (s, 9H), 1.77 (s, 9H), 1.72 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 149.9, 149.9, 149.8, 144.1, 143.4, 139.7, 133.6, 133.5, 131.7, 130.6, 130.6, 130.5, 130.4, 130.2, 130.2, 130.1, 129.7, 129.3, 129.2, 128.8, 128.2, 128.1, 126.9, 125.7, 125.6, 124.6, 123.6, 123.1, 122.8, 122.7, 122.3, 120.6, 120.5, 119.6, 119.4, 119.2, 119.2, 118.7, 35.7, 35.7, 35.7, 35.0, 31.9, 31.9, 31.8, 31.3; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{58}H_{53}OSe$ 845.3256; found 845.3260.

Scheme S4. Attempts to synthesize tellurium-doped nanographene.

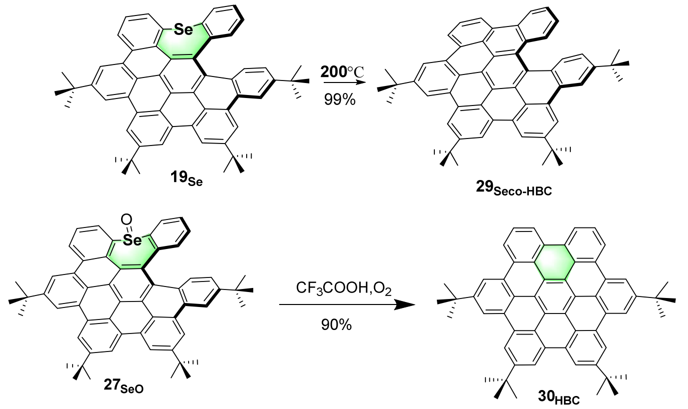


(Z)-1,2-bis(2-bromophenyl)ethane (**20**): To obtain compound **20**, we use the synthetic methodology as reported[S5].

Dibenzo[b,f]tellurepine (**21**): . A solution of (Z)-1,2-bis(2-bromophenyl)ethene **20** (618 mg, 1.83 mmol, 1.0 equiv) in 9 mL of anhydrous THF was added dropwise to a solution of *n*-BuLi (4.58 mL of 1.6 M solution in pentane, 7.32 mmol, 4.0 equiv) in 9 mL of anhydrous THF at −78 °C, and the mixture was stirred for 1 hour under argon at this temperature. Then tellurium (1.83 mmol, 328 mg, 1.0 equiv) was added as s suspension in THF under argon atmosphere, and the reaction mixture was warmed to room temperature. After the mixture was stirred at room temperature for 3 hour, The reaction mixture was quenched with aqueous NH_4Cl solution, and then extracted with EtOAc, dried over anhydrous Na_2SO_4. The organic phase was concentrated and purified by silica gel column chromatography (silica, PE, UV) to give the title product as a colorless solid (325 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.29–7.23 (m, 4H), 7.14 (t, J = 8.0 Hz, 2H), 7.02 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 138.6, 136.3, 129.1, 129.1, 128.4, 115.1; HRMS (ESI) m/z: [M=O + H]$^+$ Calcd for $C_{14}H_{11}OTe$ 324.9867; found 324.9872.

1,2,3,4-Tetrabromotriphenylene (**23**): A mixture of dibenzo[b,f]tellurepine **21** (306 mg, 1.0 mmol, 1.0 equiv), tetrabromothiophene-S,S-dioxide 2[S1] (647 mg, 1.5 mmol, 1.5 equiv) in *ortho*-dichlorobenzene (5 mL) in the sealed tube was heated to140 or 180 °C around 12 hours. Then the mixture was cooled to room temperature and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (340 mg, 1.5 mmol, 1.5 equiv) was added, the mixture was heated to 90 °C and stirred for around 30 minutes. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE) to give anthracene (99 mg, 56% for two steps) at 180 °C or give the title compound **23** (195 mg, 36% for two steps) as colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 8.0 Hz, 2H), 8.41 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 131.0, 129.1, 129.0, 128.8, 128.0, 126.12, 123.4, 119.9; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_9Br_4$ 540.7432 Found 540.7447.

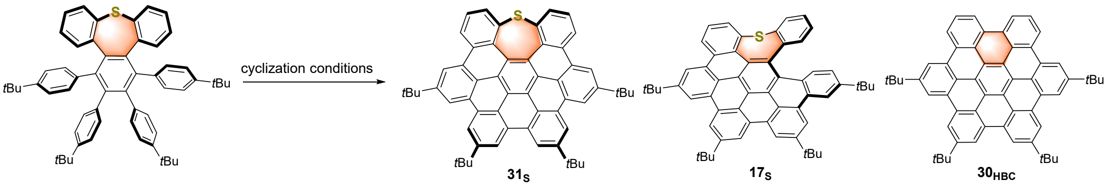
Scheme S5. Synthesis of nanographene **29**$_{\mathbf{Seco\text{-}HBC}}$ and **30**$_{\mathbf{HBC}}$.



2,5,8,19-tetra-*tert*-butyldibenzo[fg,ij]dibenzo[3,4:5,6]phenanthro[2,1,10,9,8,7-pqrstuv]pentaphene (**29**$_{\mathbf{Seco\text{-}HBC}}$): The powder of **19**$_{\mathbf{Se}}$ (41 mg, 0.05 mmol, 1.0 equiv) in a tube was heated to 200 °C for 5 minutes. After the mixture was cooled to room temperature, dichloromethane was added to dissolve the product to check by TLC (PE: DCM = 5:1, UV), all the reactant was converted to the product. Remove the solvent under reduced pressure to give the compound **29**$_{\mathbf{Seco\text{-}HBC}}$ (41 mg, 90%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 2H), 9.22 (s, 2H), 9.20 (s, 1H), 9.16 (d, J = 8.0 Hz, 1H), 9.07 (s, 1H), 8.97 (d, J = 8.0 Hz, 1H), 8.74 (s, 1H), 8.73 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.17 (t, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 1.80 (s, 18H), 1.79 (s, 9H), 1.55 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.4, 149.2, 131.9, 131.7, 131.4, 130.6, 130.5, 130.5, 130.5, 130.3, 130.2, 130.1, 130.1, 129.9, 129.2, 127.0, 126.6, 125.3, 125.1, 124.0, 123.5, 123.4, 123.1, 123.1, 123.0, 122.7, 122.6, 121.9, 121.2, 120.6, 120.5, 119.7, 119.3, 119.0, 119.0, 118.9, 118.8, 118.4, 35.8, 35.7, 35.7, 35.1, 32.0, 31.4; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{58}H_{52}$ 748.4069 Found 748.4090.

2,5,8,11-Tetra-*tert*-butylhexabenzo[bc,ef,hi,kl,no,qr]coronene (**30**$_{\mathbf{HBC}}$): To a solution of compound **27**$_{\mathbf{SeO}}$ (42 mg, 0.05 mmol, 1.0 equiv) in dichloromethane (10 mL) in an oven-dried flask with a magnetic stirring bar was added CF_3COOH (5 ml). The mixture was roughly stirred in room temperature until no compound **27**$_{\mathbf{SeO}}$ left (around 24 hours, checked by TLC, silica, PE: EtOAc = 1:1, UV). The mixture was washed with water, and the organic phase was dried over anhydrous Na_2SO_4. The organic phase was concentrated and purified by silica gel column chromatography (silica, 10-20 % PE in DCM, UV) to give the titled compound **30**$_{\mathbf{HBC}}$ (33 mg, 90%) as yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.30 (s, 2H), 9.25 (s, 2H), 9.18 (s, 2H), 9.03 (s, 2H), 8.88 (d, J = 8.0 Hz, 2H), 8.73 (d, J = 8.0 Hz, 2H), 7.88 (t, J = 8.0 Hz, 2H), 1.89 (s, 18H), 1.80 (s, 18H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 148.7, 148.5, 130.4, 130.3, 130.0, 130.0, 129.8, 129.8, 126.0, 124.9, 123.7, 123.3, 121.3, 121.3, 120.2, 120.2, 120.1, 118.8, 118.7, 118.7, 118.6, 35.7, 35.6, 32.1, 32.0. The NMR data were identical with the reported results.[S7]

Scheme S6. Attempts to Synthesize fully cyclized product **31$_S$**.



	Reagents	Solvents	Temp (°C)	time	Products (%)		
					31$_S$	**17$_S$**	**30$_{HBC}$**
1	DDQ (10.0 eq), CF$_3$SO$_3$H (13.0 eq.)	DCM	0	2 mins	0	80	0
2	DDQ (10.0 eq), CF$_3$SO$_3$H (13.0 eq.)	DCM	0	10 mins	0	61	16
3	DDQ (10.0 eq), CF$_3$SO$_3$H (13.0 eq.)	DCM	30	10 mins	0	40	15
4	DDQ (10.0 eq), CF$_3$SO$_3$H (30.0 eq.)	DCM	30	10 mins	0	26	8
5	FeCl$_3$(20)	CH$_3$NO$_2$-DCM	0	3 hours	0	42	0
6	FeCl$_3$(20)	CH$_3$NO$_2$-DCM	30	3 hours	0	50	0
7	FeCl$_3$(20)	CH$_3$NO$_2$-DCM	30	18 hours	0	82	trace
8	Cu(OAc)$_2$	THF	30	18 hours	0	0	0
9	Cu(OTf)$_2$	THF	30	18 hours	0	0	0

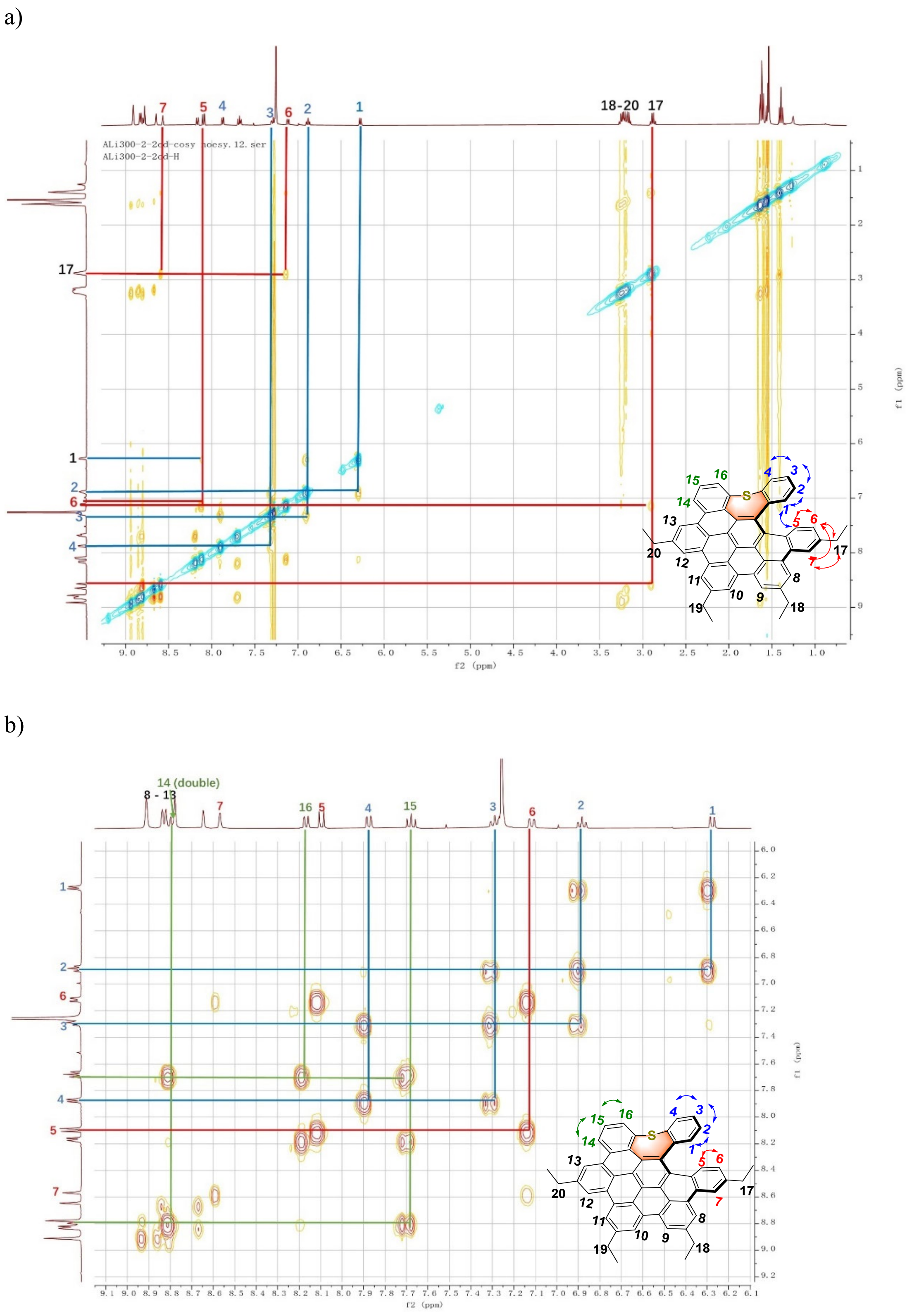


Figure S1. (a) 2D ROESY spectrum of compound **16$_S$** with structure depiction of representative NOEs by arrows. Compared to 18–20, only protons of methylene 17 shows the NOEs with one singlet peak (proton 7) and one doublet peak (proton 6). (b) 2D H-H COSY spectrum of compound **16$_S$** with different spin systems of protons.

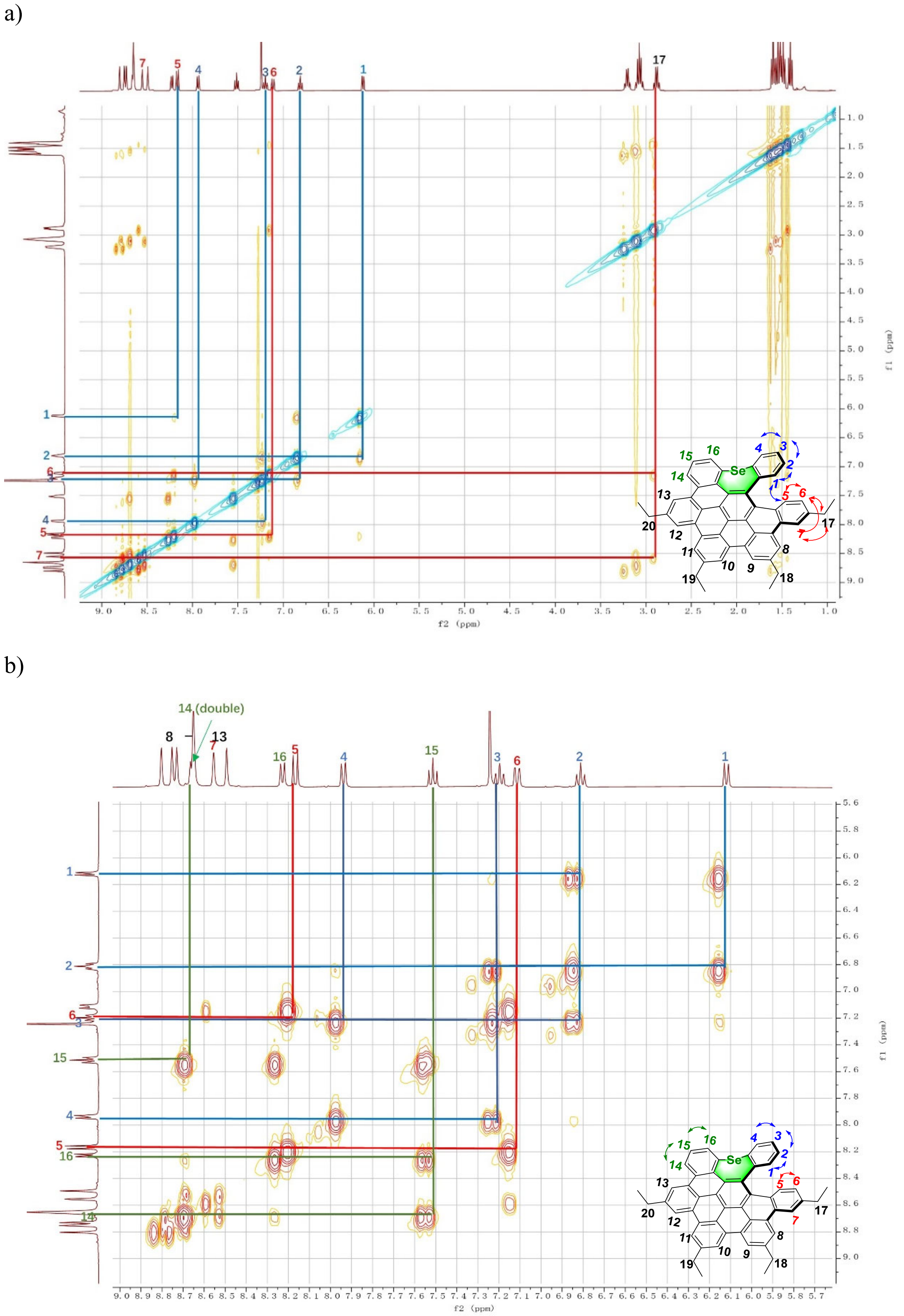


Figure S2. (a) 2D ROESY spectrum of compound **18_{Se}** with structure depiction of representative NOEs by arrows. Compared to 18–20, only protons of methylene 17 shows the NOEs with one singlet peak (proton 7) and one doublet peak (proton 6). (b) 2D H-H COSY spectrum of compound **18_{Se}** with different spin systems of protons.

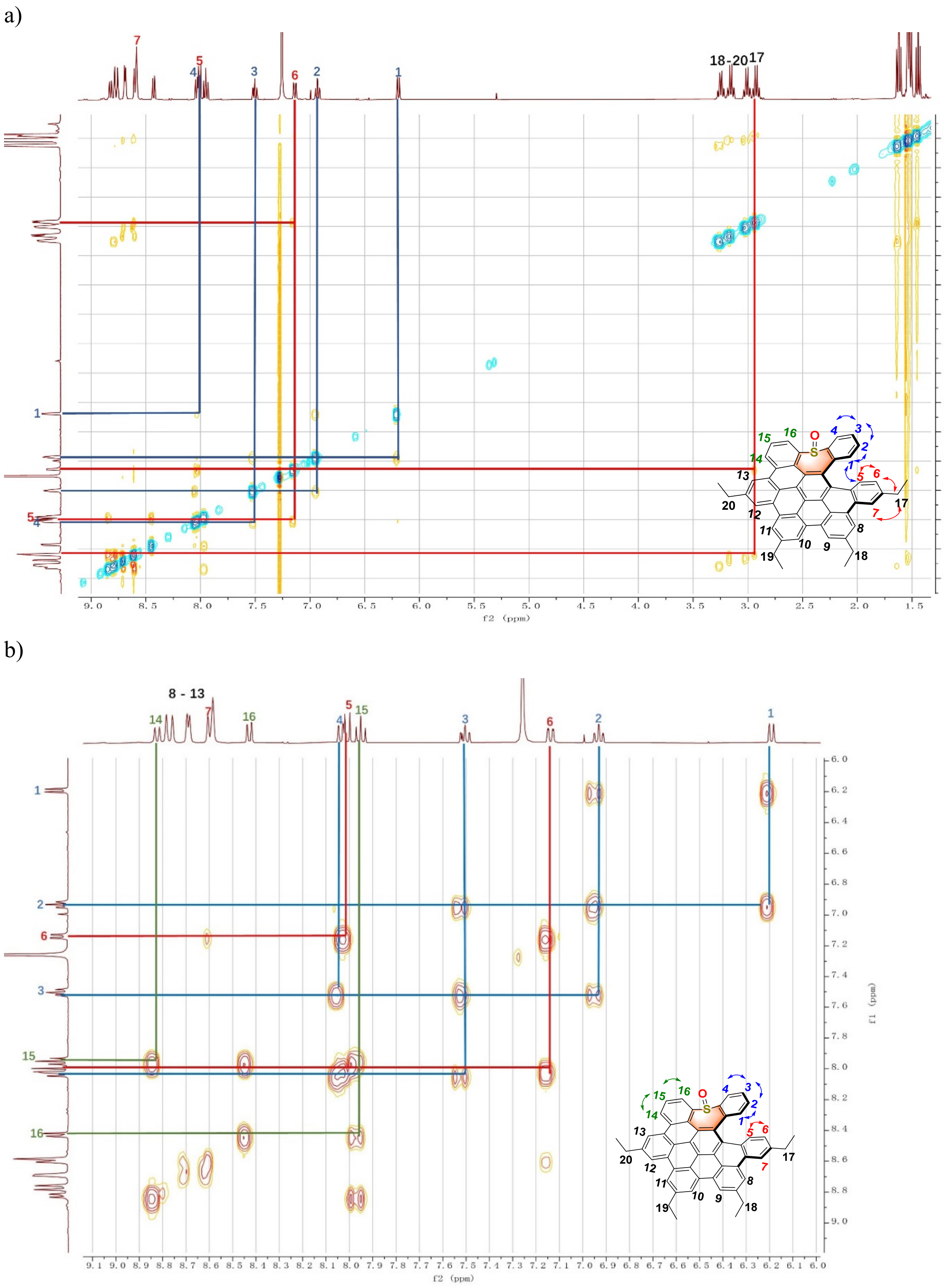


Figure S3. (a) 2D ROESY spectrum of compound **24**$_{\mathbf{SO}}$ with structure depiction of representative NOEs by arrows. Compared to 18–20, only protons of methylene 17 shows the NOEs with one singlet peak (proton 7) and one doublet peak (proton 6). (b) 2D H-H COSY spectrum of compound **24**$_{\mathbf{SO}}$ with different spin systems of protons.

Table S1. Details of the Crystal Structure Analyses of Compounds **5_O**, **17_S** and **18_{Se}**.

	5_O	**17_S**	**18_{Se}**
CCDC No.	2238626	2238630	2238631
empirical formula	$C_{50}H_{34}O$	$C_{58}H_{52}S$	$C_{50}H_{36}Se$
formula wt	650.77	781.05	715.75
crystal description	yellow block	yellow block	yellow block
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2	P 1 21/n 1	P 1 21/c 1
T (K)	296(2)	100.00	150.00
a (Å)	30.193(3)	20.8041(6)	13.038(4)
b (Å)	5.0770(4)	7.5111(2)	12.335(3)
c (Å)	22.061(2)	27.2964(7) A	21.069(6)
α (°)	90	90	90
β (°)	109.639(4)	90.9110(10)	102.674(12)
γ (°)	90	90	90
V (Å^3)	3185.0(5)	4264.8(2)	3305.7(17)
Z	4	4	4
ρ_{calcd} (mg/m^3)	1.357	1.216	1.438
μ (mm^{-1})	0.079	0.958	1.175
θ range (°)	2.699–25.144	2.691–68.401	1.925–25.150
F (000)	1368	1664	1480
collected reflcns no.	9766	34271	37341
unique reflcns no.	5091	7760	5927
R [$I > 2\sigma(I)$]	0.0677	0.0414	0.0560
R (ref)	0.1325	0.0480	0.0720
$wR2$ [$I > 2\sigma(I)$]	0.1465	0.1115	0.1629
wR2 (ref)	0.1921	0.1164	0.1758

Table S2. Details of the Crystal Structure Analyses of Compounds **21**, **23**, **24S$_{\mathbf{O}}$** and **30$_{\mathbf{HBC}}$**.

	21	**23**	**24S$_{\mathbf{O}}$**	**30$_{\mathbf{HBC}}$**
CCDC No.	2238627	2238628	2238629	2238632
empirical formula	$C_{14}H_{10}Te$	$C_{18}H_{8}Br_{4}$	$C_{51}H_{38}Cl_{2}O$ S	$C_{116}H_{100}S_{0.28}$
formula wt	305.82	543.88	769.77	1503.01
crystal description	Colorless block	Colorless block	Yellow block	Yellow block
crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
space group	Pca2(1)	P-1	P 1 21 1	P 1 21/c 1
T (K)	298(2)	150.00	150.00	100.00
a (Å)	11.7118(7)	7.7791(14)	9.2713(2)	14.5888(8)
b (Å)	12.2711(6)	9.3866(15)	28.4806(6)	39.4014(19)
c (Å)	7.8403(4)	11.1959(19)	13.7600(3)	15.8848(8)
α (°)	90	105.367(6)	90	90
β (°)	90	93.035(7)	93.2120(10)	96.813(3)
γ (°)	90	99.210(7)	90	90
V (Å^3)	1126.78(10)	774.2(2)	3627.65(14)	9066.4(8)
Z	4	2	4	4
ρ_{calcd} (mg/m^3)	1.803	2.333	1.409	1.101
μ (mm^{-1})	2.601	10.388	0.279	0.525
θ range (°)	2.404–28.341	2.288–28.285	2.060–24.999	3.018–65.366
F (000)	584	512	1608	3202
collected reflcns no.	14089	23328	22808	91185
unique reflcns no.	2803	3828	12164	15463
R [$I > 2\sigma(I)$]	0.0295	0.0313	0.0792	0.1343
R (ref)	0.0480	0.0417	0.1323	0.1655
$wR2$ [$I > 2\sigma(I)$]	0.0636	0.0698	0.1952	0.3653
$wR2$ (ref)	0.0743	0.0742	0.2349	0.3877

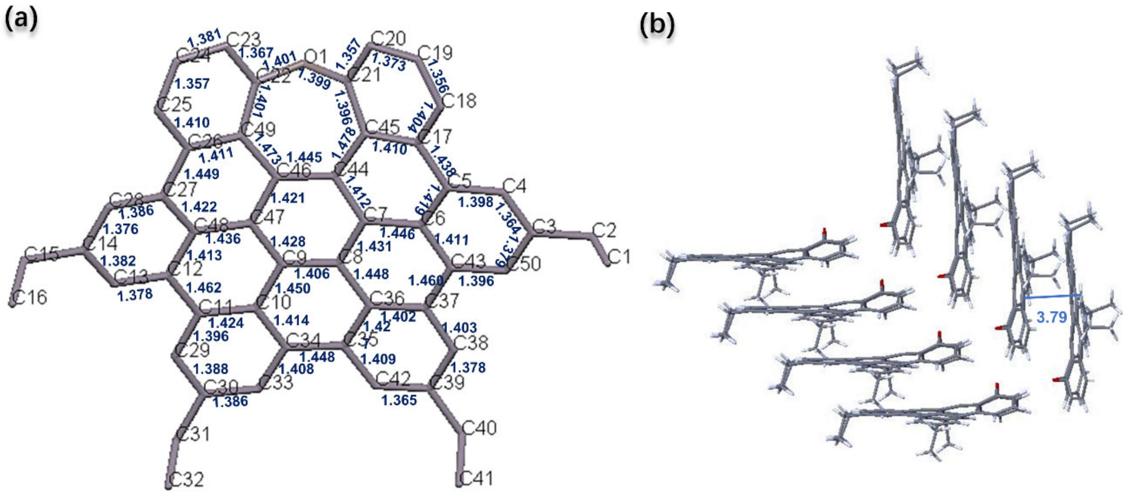


Figure S4. Single crystals suitable for X-ray diffraction analysis were obtained from solutions of **5$_{O}$** in dichloromethane and hexane at room temperature. (a) Crystal structure of compound **5$_{O}$** with atom labels and bond lengths [Å], and (b) molecular packing of compound **5$_{O}$** labeled with π-π stacking distance.

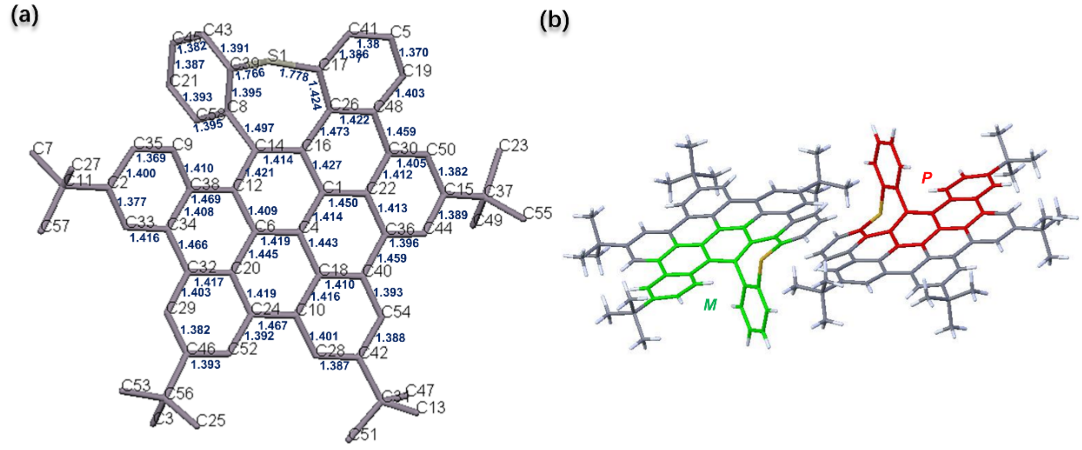


Figure S5. Single crystals suitable for X-ray diffraction analysis were obtained from solutions of **17$_{S}$** in dichloromethane and hexane at room temperature. (a) Crystal structure of compound **17$_{S}$** with atom labels and bond lengths [Å], and (b) molecular packing of compound **17$_{S}$.** The *P*/*M* enantiomers were identified.

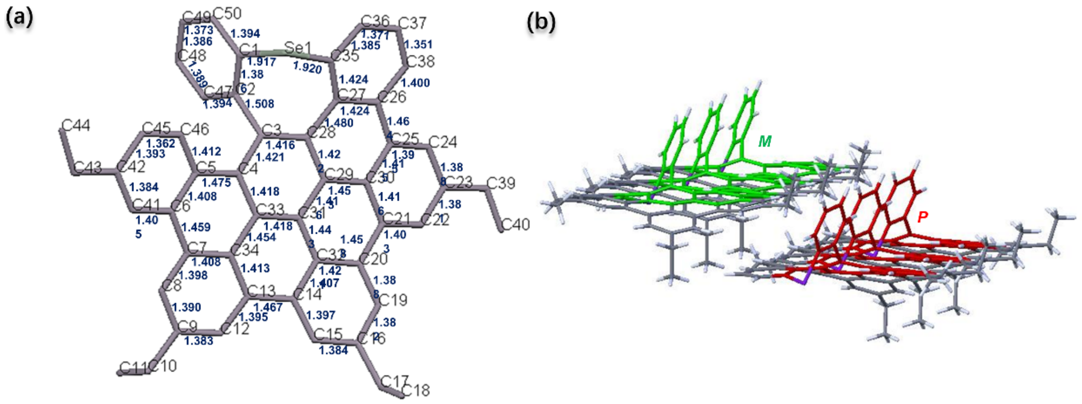


Figure S6. Single crystals suitable for X-ray diffraction analysis were obtained from solutions of **18_{Se}** in dichloromethane and hexane at room temperature. (a) Crystal structure of compound **18_{Se}** with atom labels and bond lengths [Å], and (b) molecular packing of compound **18_{Se}**. The *P*/*M* enantiomers were identified.

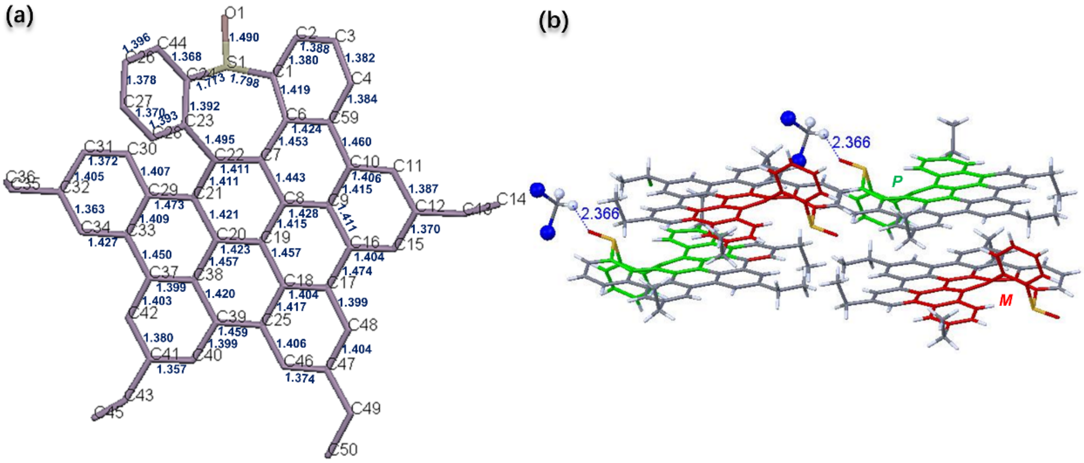


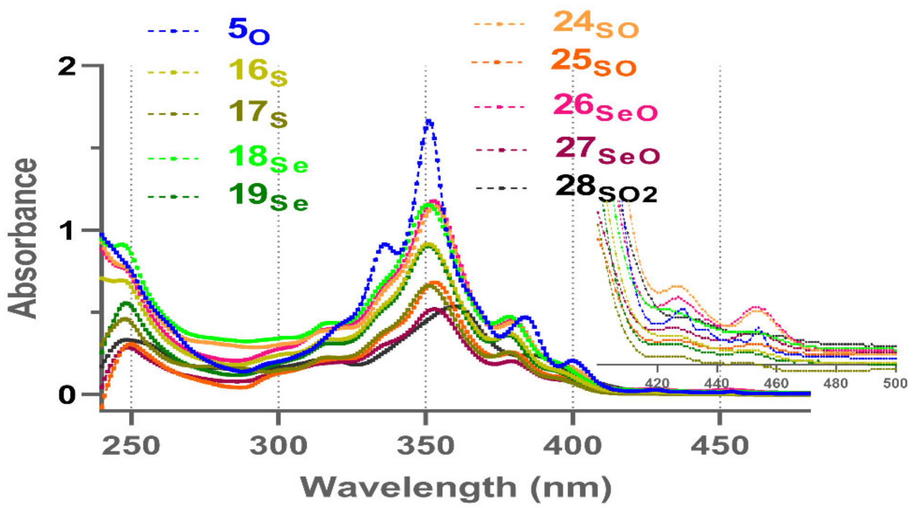
Figure S7. Single crystals suitable for X-ray diffraction analysis were obtained from solutions of **24_{SO}** in dichloromethane and hexane at room temperature. (a) Crystal structure of compound **24_{SO}** with atom labels and bond lengths [Å], and (b) molecular packing of compound **24_{SO}**. The *P*/*M* enantiomers were identified. The hydrogen bond between the oxide and dichloromethane was shown.

Table S3. Photophysical Properties of different NGs.

	λ_{max} (nm) [a]	ε_{max} (M^{-1} cm^{-1})	λ_{em} (nm) [b]	Stokes shift (cm^{-1})	Φ_F [c]
$\mathbf{5_{O}}$	351	3.3 ×10^5	486/459	7913/6704	0.05
$\mathbf{16_{S}}$	351	1.8 ×10^5	477	7526	0.12
$\mathbf{17_{S}}$	351	1.3 ×10^5	475	7437	0.18
$\mathbf{18_{Se}}$	351	2.3×10^5	477	7526	0.0096
$\mathbf{19_{Se}}$	351	1.8×10^5	476	7482	0.0097
$\mathbf{24_{SO}}$	353	2.3×10^5	475	7276	0.20
$\mathbf{25_{SO}}$	353	1.4×10^5	473	7187	0.30
$\mathbf{26_{SeO}}$	353	2.4 ×10^5	477	7364	0.05
$\mathbf{27_{SeO}}$	353	1.0 ×10^5	476	7320	0.12
$\mathbf{28_{SO2}}$	360	1.1×10^5	489	7328	0.19
$\mathbf{29_{Seco\text{-}HBC}}$	359	1.1×10^5	497/474	7734/6758	0.20
$\mathbf{30_{HBC}}$	358	2.4×10^5	494	7690	0.04

[a] Measured in dichloromethane (5 µM). [b] λex = 350 nm. [c] Quinine sulfate (Φ_F = 0.54 in 0.1 M H_2SO_4) as a reference.

a)



b)

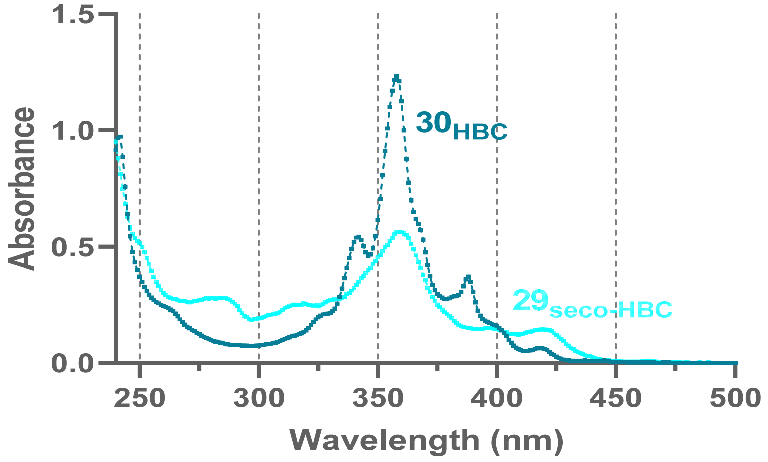


Figure S8. a) UV-vis spectra of compound **5_{O}**, **16_{S}**, **17_{S}**, **18_{Se}**, **19_{Se}**, **24_{SO}**, **25_{SO}**, **26_{SeO}**, **27_{SeO}**, and **28_{SO2}** (5 µM in DCM); b) UV-vis spectra of compounds **$29_{Seco\text{-}HBC}$** and **30_{HBC}** (5 µM in DCM).

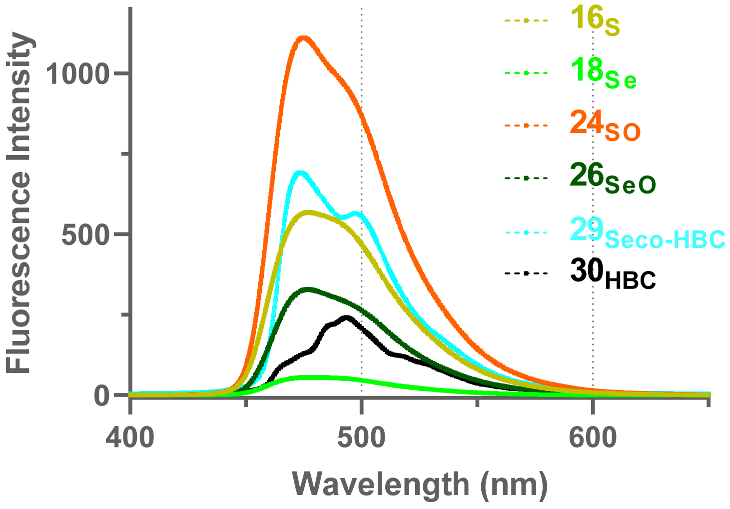


Figure S9. Fluorescent spectrum of compound **16_{S}**, **18_{Se}**, **24_{SO}**, **26_{SeO}**, **$29_{Seco\text{-}HBC}$**, and **30_{HBC}** (5 µM in DCM).

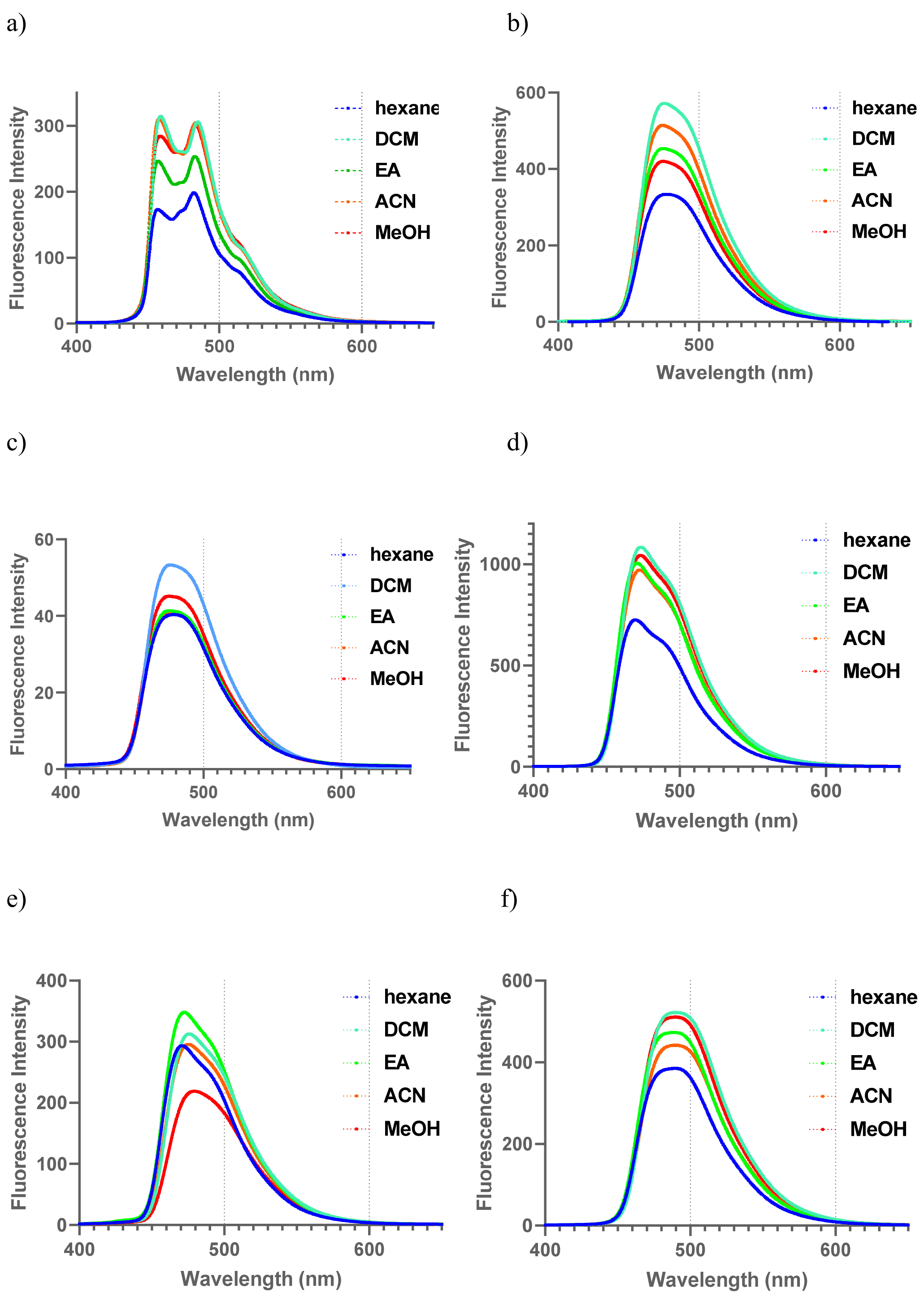
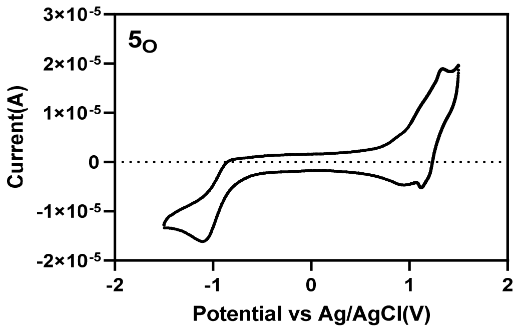


Figure S10. Fluorescence intensity of compounds **5**$_{\mathrm{O}}$ (a), **17**$_{\mathrm{S}}$ (b), **19**$_{\mathrm{Se}}$ (c), **25**$_{\mathrm{SO}}$ (d), **27**$_{\mathrm{SeO}}$ (e), **28**$_{\mathrm{SO2}}$ (f) at 5 µM concentration in different solvents.


5_{O}
3×10^{-5}
2×10^{-5}
1×10^{-5}
0
-1×10^{-5}
-2×10^{-5}
Current(A)
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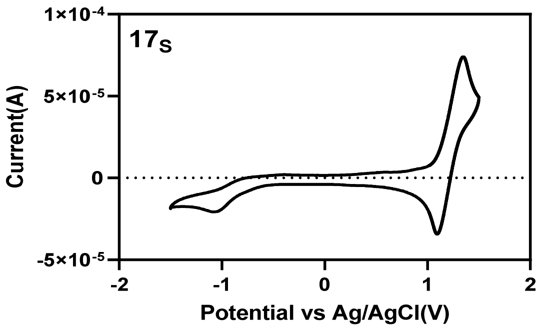
-1
0
1
2
Potential vs Ag/AgCl(V)


17_{S}
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5×10^{-5}
0
-5×10^{-5}
Current(A)
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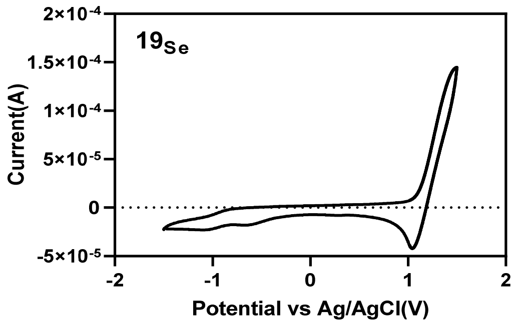
-1
0
1
2
Potential vs Ag/AgCl(V)


19_{Se}
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5×10^{-5}
0
-5×10^{-5}
Current(A)
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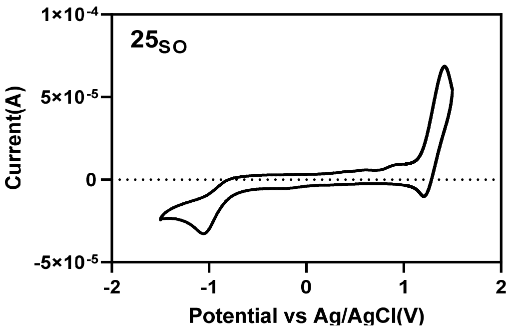
0
1
2
Potential vs Ag/AgCl(V)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-5×10^{-5}
Current(A)
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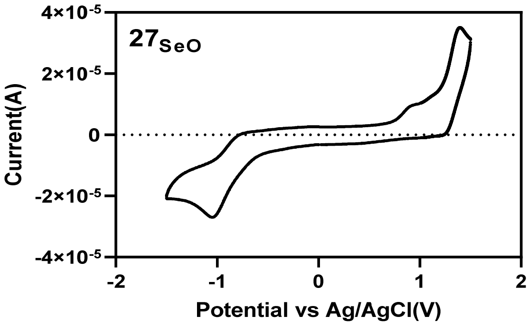
-1
0
1
2
Potential vs Ag/AgCl(V)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-2×10^{-5}
-4×10^{-5}
Current(A)
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-1
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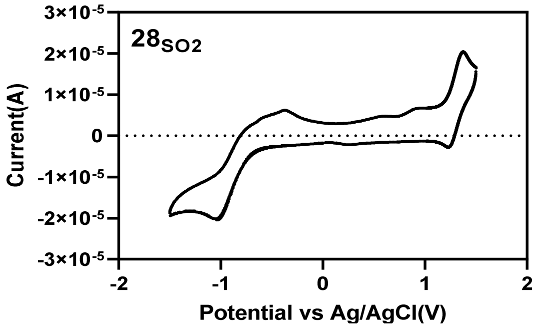
2
Potential vs Ag/AgCl(V)


28_{SO2}
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0
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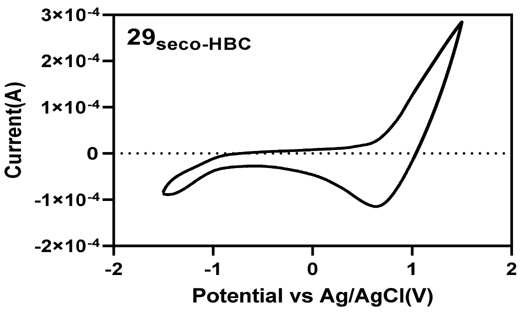
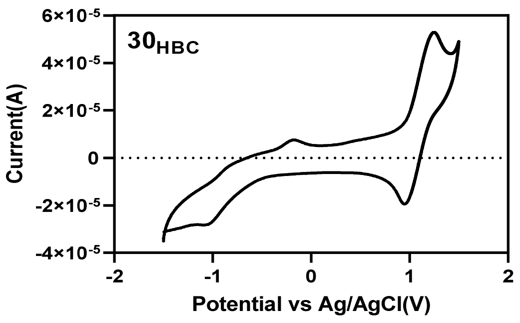
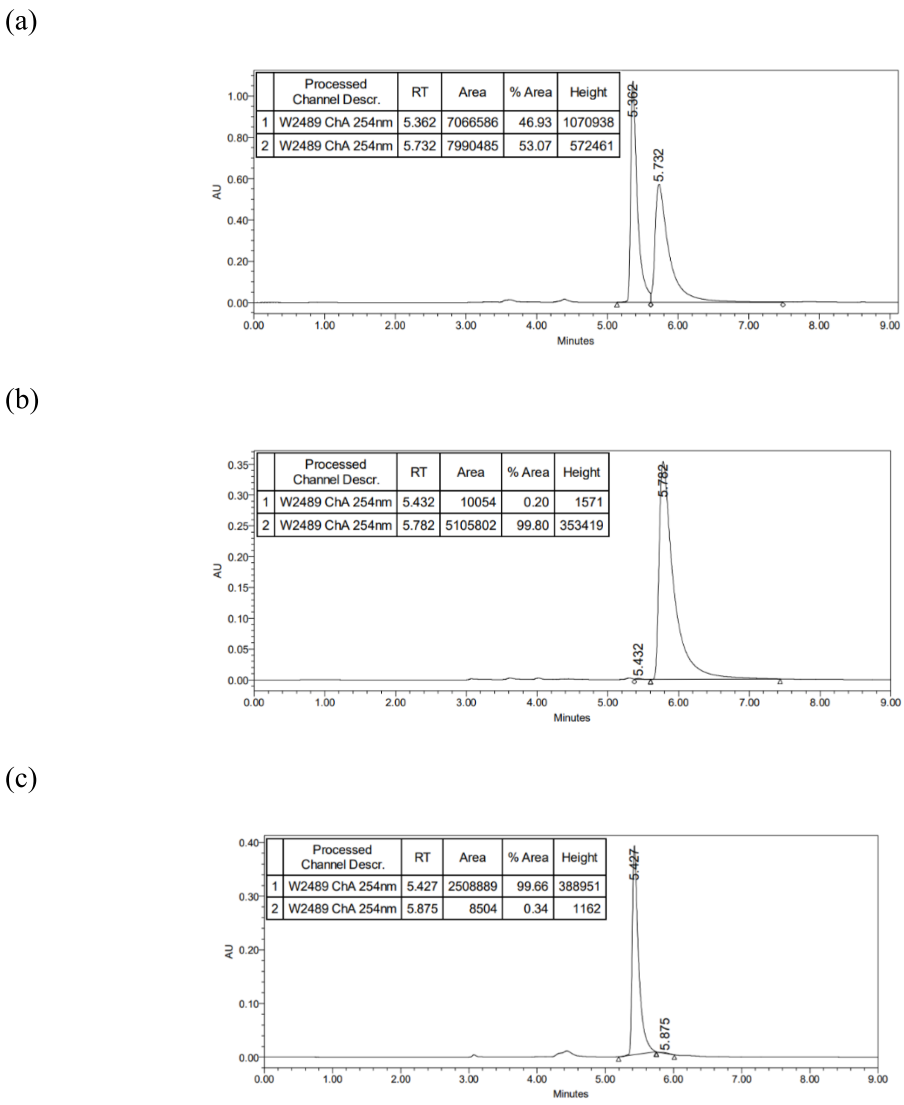
-2×10^{-5}
-3×10^{-5}
Current(A)
-2
-1
0
1
2
Potential vs Ag/AgCl(V)


$29_{seco\text{-}HBC}$
3×10^{-4}
2×10^{-4}
1×10^{-4}
0
-1×10^{-4}
-2×10^{-4}
Current(A)
-2
-1
0
1
2
Potential vs Ag/AgCl(V)


30_{HBC}
6×10^{-5}
4×10^{-5}
2×10^{-5}
0
-2×10^{-5}
-4×10^{-5}
Current(A)
-2
-1
0
1
2
Potential vs Ag/AgCl(V)

	5$_{\mathbf{O}}$	**17**$_{\mathbf{S}}$	**19**$_{\mathbf{Se}}$	**25**$_{\mathbf{SO}}$	**27**$_{\mathbf{SeO}}$	**28**$_{\mathbf{SO2}}$	**29**$_{\mathbf{seco\text{-}HBC}}$	**30**$_{\mathbf{HBC}}$
Ep$_{c}$	1.32 V; -0.88 V	1.36 V; -0.78 V	-0.84 V	1.40 V; 0.92 V; -0.82 V	1.38 V; 0.92 V; -0.81 V	1.36 V; 0.91 V; 0.56 V; -0.40 V		1.23 V; -0.22 V
Ep$_{a}$	1.13 V; -1.12V	1.08 V; -1.08 V	1.059 V; -0.62 V; -1.05 V	1.22 V; -1.08 V	1.23 V; -1.03 V	1.24 V; -1.04 V	0.59 V	0.92 V; -1.05 V

Figure S11 Cyclic Voltammetry of **5**$_{\mathbf{O}}$**,** **17**$_{\mathbf{S}}$**,** **19**$_{\mathbf{Se}}$**,** **25**$_{\mathbf{SO}}$**,** **27**$_{\mathbf{SeO}}$**,** **28**$_{\mathbf{SO2}}$**,** **29**$_{\mathbf{seco\text{-}HBC}}$ and **30**$_{\mathbf{HBC}}$ (Scan rate: 250 mV s^{-1}, supporting electrolyte: 0.1 M nBu$_4$NPF$_6$ in DCM) with summarized oxidation/reduction waves.



(a)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.362	7066586	46.93	1070938
2	W2489 ChA 254nm	5.732	7990485	53.07	572461

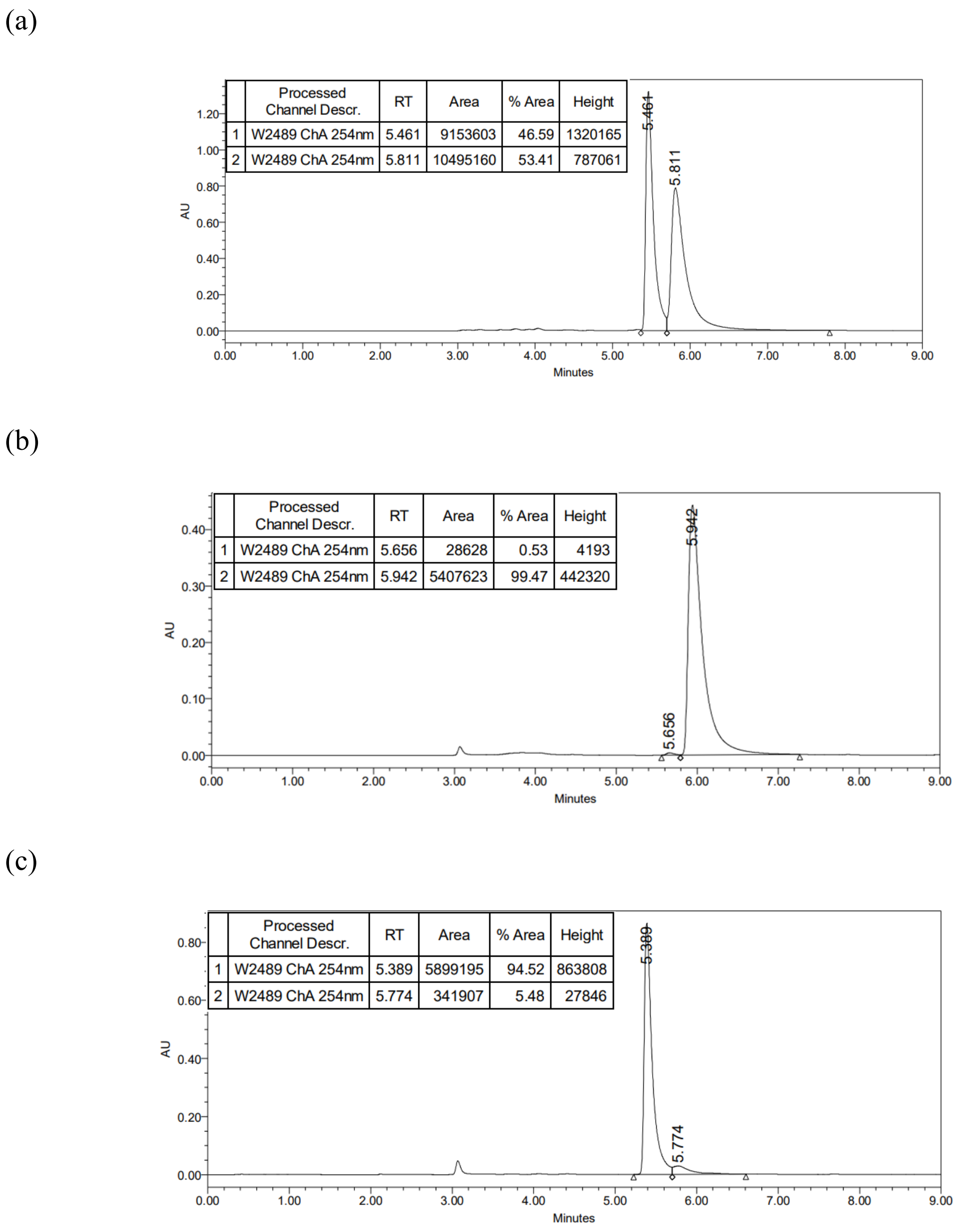
(b)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.432	10054	0.20	1571
2	W2489 ChA 254nm	5.782	5105802	99.80	353419

(c)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.427	2508889	99.66	388951
2	W2489 ChA 254nm	5.875	8504	0.34	1162

Figure S12. Racemic mixtures of **17**$_{\text{S}}$ were separated by preparative chiral HPLC and the purities were tested by analytic chiral HPLC (analytic IE-3 column, n-hexane/isopropanol = 98:2, v/v; 1.0 mL/min; 254 nm); a) Chromatography of racemic sample; b) Chromatography of enantiopure compound **17**$_{\text{S}}$-*P*; c) Chromatography of enantiopure compound **17**$_{\text{S}}$-*M*.



(a)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.461	9153603	46.59	1320165
2	W2489 ChA 254nm	5.811	10495160	53.41	787061

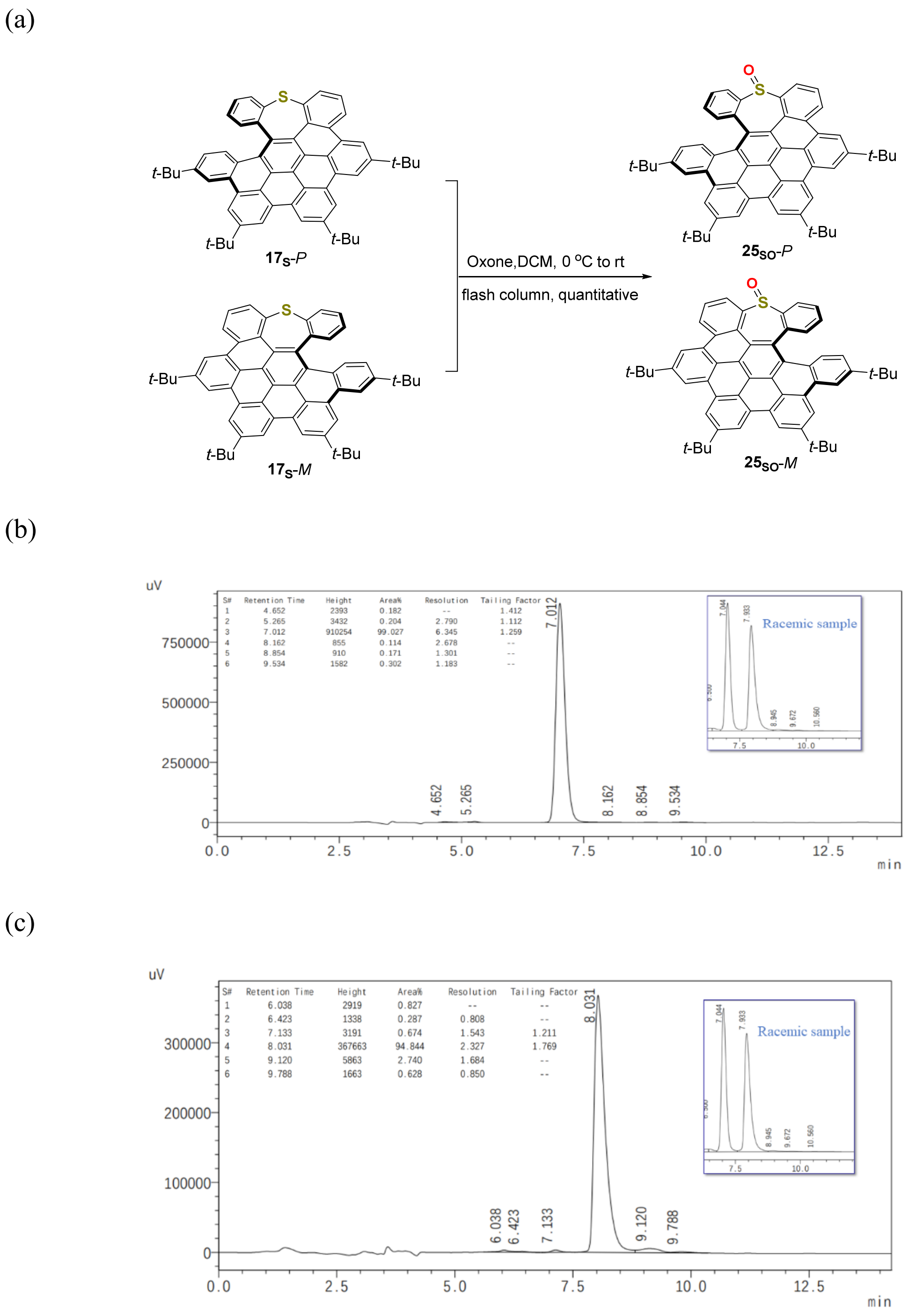
(b)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.656	28628	0.53	4193
2	W2489 ChA 254nm	5.942	5407623	99.47	442320

(c)

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.389	5899195	94.52	863808
2	W2489 ChA 254nm	5.774	341907	5.48	27846

Figure S13. Racemic mixtures of $\mathbf{19_{Se}}$ were separated by preparative chiral HPLC and the purities were tested by analytic chiral HPLC (analytic IE-3 column, n-hexane/isopropanol = 98:2, v/v; 1.0 mL/min; 254 nm); a) Chromatography of racemic sample; b) Chromatography of enantiopure compound $\mathbf{19_{Se}}$ -***P***; c) Chromatography of enantiopure compound $\mathbf{19_{Se}}$ -***M***.



(b)

S#	Retention Time	Height	Area%	Resolution	Tailing Factor
1	4.652	2393	0.182	--	1.412
2	5.265	3432	0.204	2.790	1.112
3	7.012	910254	99.027	6.345	1.259
4	8.162	855	0.114	2.678	--
5	8.854	910	0.171	1.301	--
6	9.534	1582	0.302	1.183	--

(c)

S#	Retention Time	Height	Area%	Resolution	Tailing Factor
1	6.038	2919	0.827	--	--
2	6.423	1338	0.287	0.808	--
3	7.133	3191	0.674	1.543	1.211
4	8.031	367663	94.844	2.327	1.769
5	9.120	5863	2.740	1.684	--
6	9.788	1663	0.628	0.850	--

Figure S14. Preparation of optical pure enantiomers **25_{SO}-*P*** and **25_{SO}-*M*.** (a) Enantiomers **25_{SO}-*P*** and **25_{SO}-*M*** were obtained by following the synthetic procedure as racemic **25_{SO}** in scheme S2 using optical pure compounds **17_S-*P*** and **17_S-*M*.** (b) Chiral chromatography of enantiopure compound **25_{SO}-*P***; (c) Chromatography of enantiopure compound **25_{SO}-*M*.** (Unichiral CND-5H column, 95%n-Hexane/5%Ethanol, 1mL/min, 254 nm);

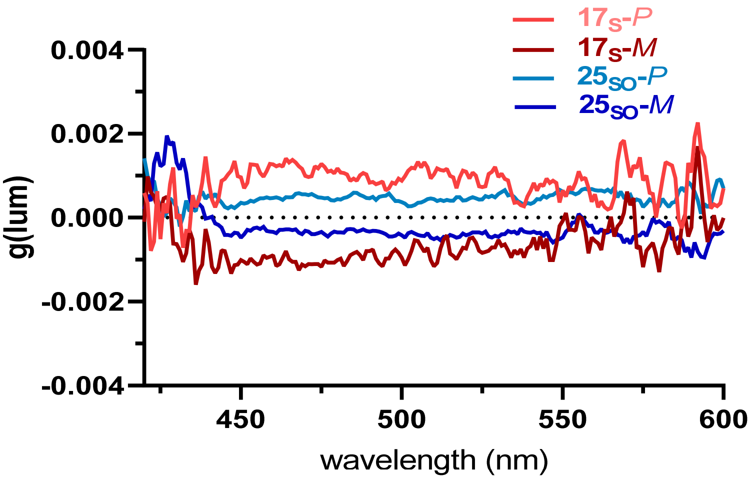
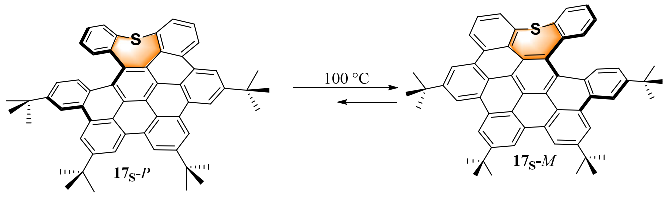


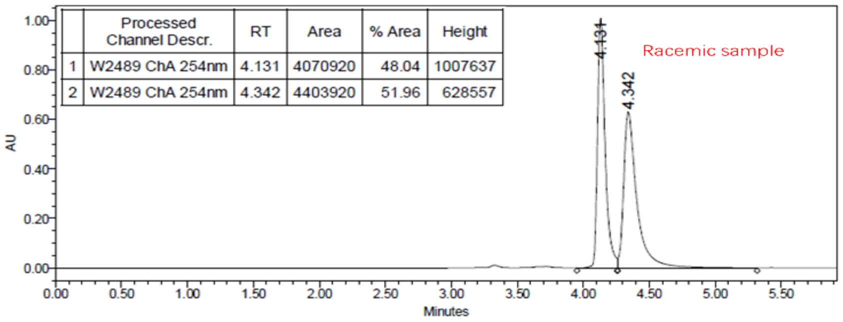
Figure S15. CPL dissymmetry factor g(lum) versus wavelength spectra of **17**$_{\mathrm{S}}$-*P*/**17**$_{\mathrm{S}}$-*M*, and **25**$_{\mathrm{SO}}$-*P*/**25**$_{\mathrm{SO}}$-*M* in dichlomethane..

Thermal enantiomerization of 17_S-*P*.

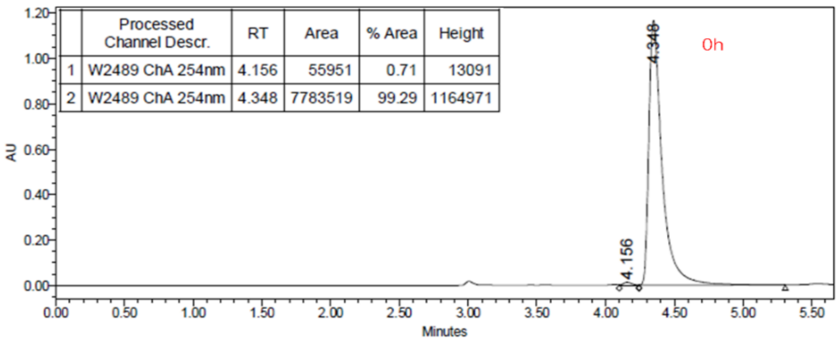
(a)



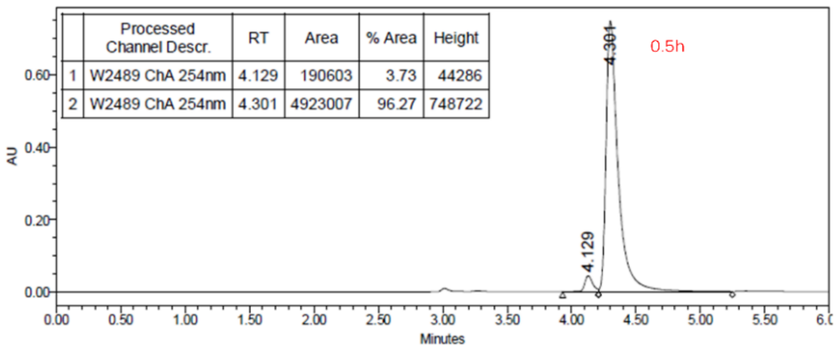
(b)



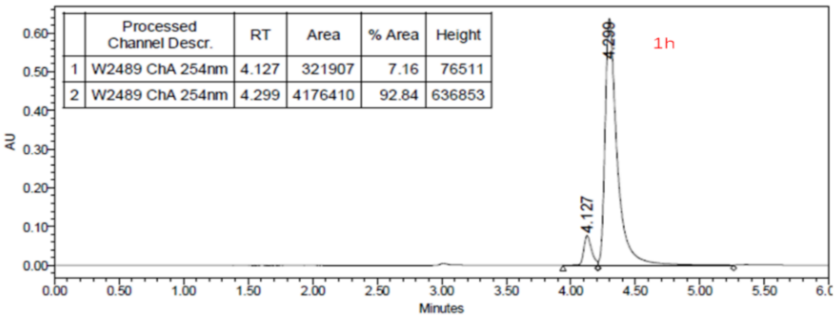
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.131	4070920	48.04	1007637
2	W2489 ChA 254nm	4.342	4403920	51.96	628557



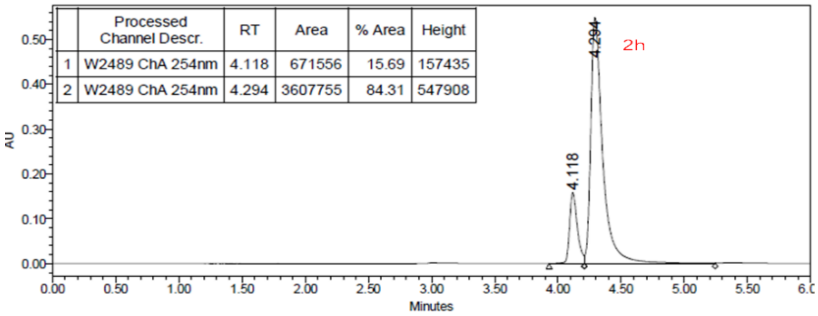
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.156	55951	0.71	13091
2	W2489 ChA 254nm	4.348	7783519	99.29	1164971



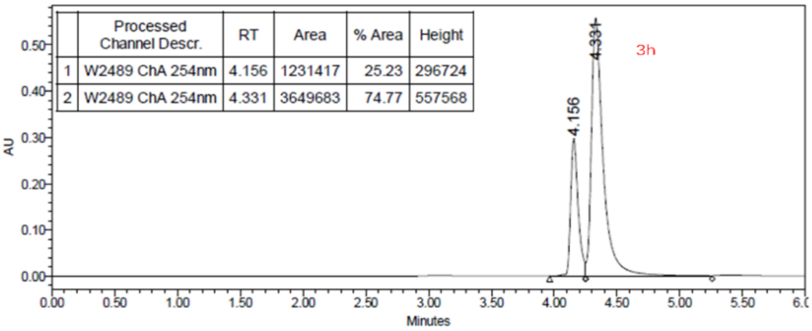
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.129	190603	3.73	44286
2	W2489 ChA 254nm	4.301	4923007	96.27	748722



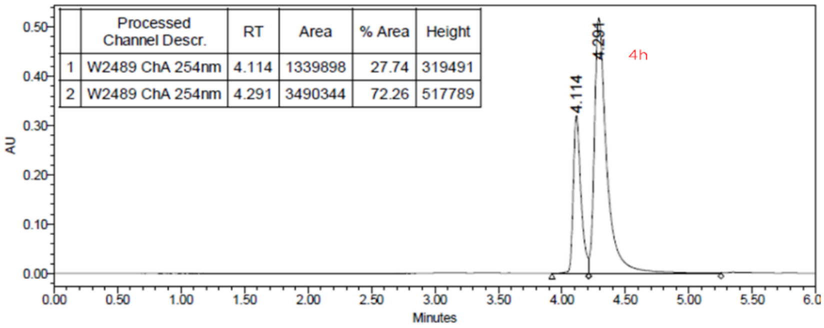
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.127	321907	7.16	76511
2	W2489 ChA 254nm	4.299	4176410	92.84	636853



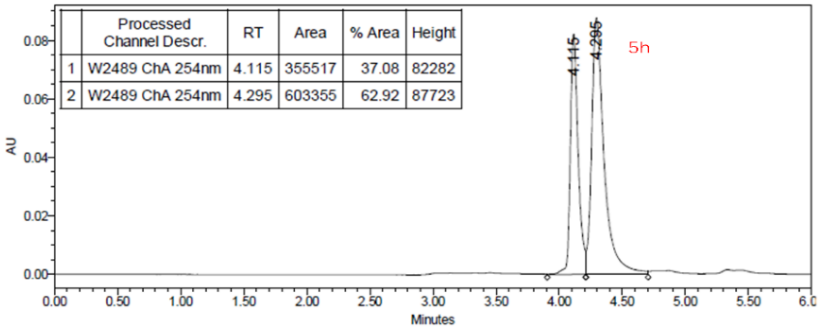
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.118	671556	15.69	157435
2	W2489 ChA 254nm	4.294	3607755	84.31	547908



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.156	1231417	25.23	296724
2	W2489 ChA 254nm	4.331	3649683	74.77	557568

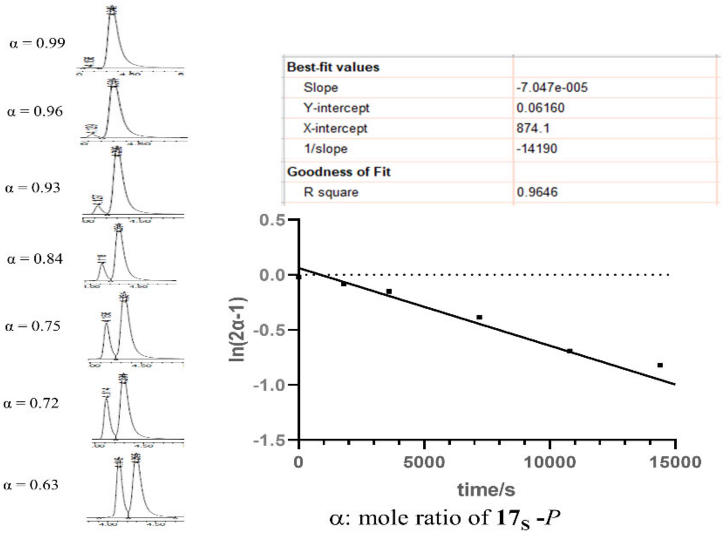


	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.114	1339898	27.74	319491
2	W2489 ChA 254nm	4.291	3490344	72.26	517789



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.115	355517	37.08	82282
2	W2489 ChA 254nm	4.295	603355	62.92	87723

(c)



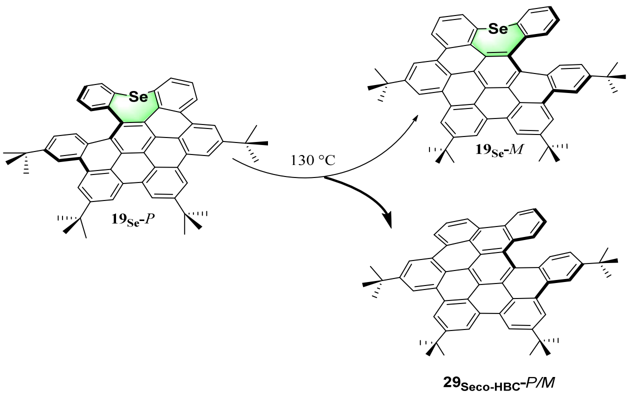
Best-fit values	
Slope	-7.047e-005
Y-intercept	0.06160
X-intercept	874.1
1/slope	-14190
Goodness of Fit	
R square	0.9646

α: mole ratio of $\mathbf{17}_{S}$ -*P*

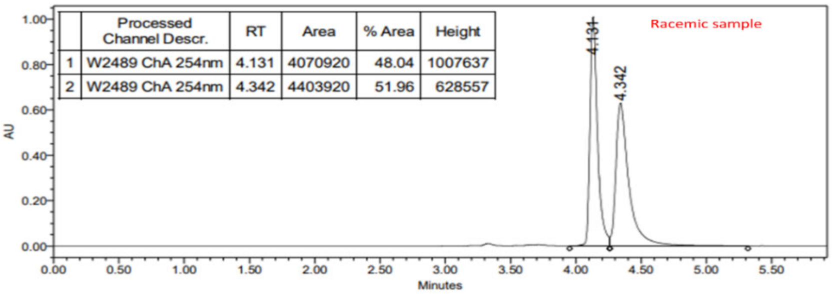
Figure S16. Thermal enantiomerization of $\mathbf{17}_{S}$-*P* at 100 °C followed by chiral HPLC analyses. (a) Scheme for thermal enantiomerization of $\mathbf{17}_{S}$-*P*. (b) Chiral HPLC traces with analytic IE-3 column after specific reaction time at 100 °C in 1,2-dichlorobenzene. The solvent was removed under reduced pressure before analyzing with eluent: n-hexane/isopropanol = 98:2, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. (c) The plot of HPLC-based conversion ratio of $\mathbf{17}_{S}$-*P* (α) at time t. It switches between the *P* and *M* enantiomers following a reversible first-order reaction[S6], with a rate constant (k), which could be obtained by fitting the experimental data using the following equation: ln (2α − 1) = −2kt and k was determined as $3.52 \cdot 10^{-5}$ s^{-1}. Then the enantiomerization barrier (ΔG‡) was calculated from the Eyring equation: k = κkBThK‡ and ΔG‡ = −RTlnK‡. K‡ is the thermodynamic equilibrium constant. The Gibbs activation energy can be determined as ΔG‡(T) = −RTln (kh/κkBT). R is the gas constant (R = 8.314 J K^{-1}); h is the Planck constant (h = 6.626 × 10-34 J s); kB is the Boltzmann constant (kB = 1.38 × 10^{-23} J K^{-1}); κ is the transmission coefficient (κ = 1). As a result, the enantiomerization energy was determined as ΔG‡ = 123845.82 J/mol = 29.59 kcal/mol. $t_{1/2}$ = ln2/k= 19691.7 s =5.5 h.

Thermal enantiomerization of 19_{Se} -*P*.

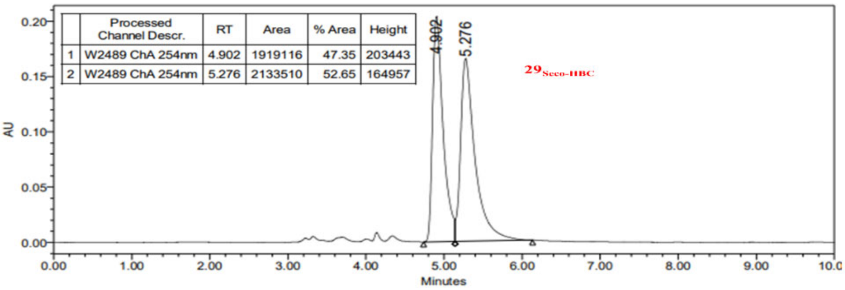
(a)



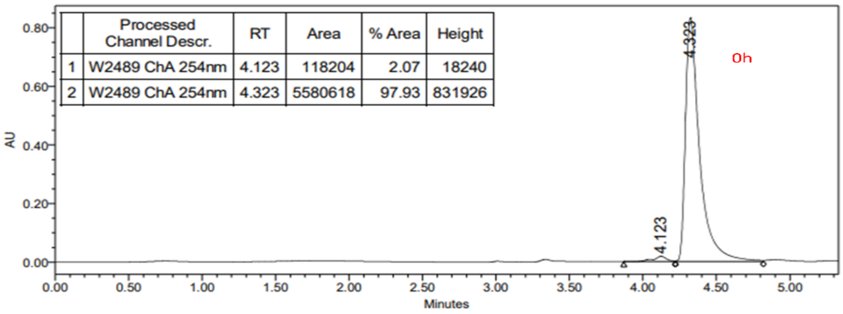
(b)



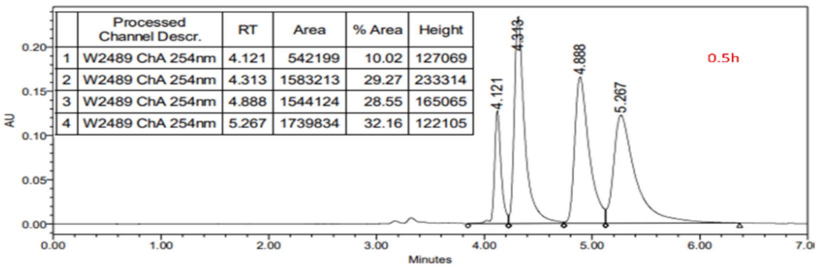
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.131	4070920	48.04	1007637
2	W2489 ChA 254nm	4.342	4403920	51.96	628557



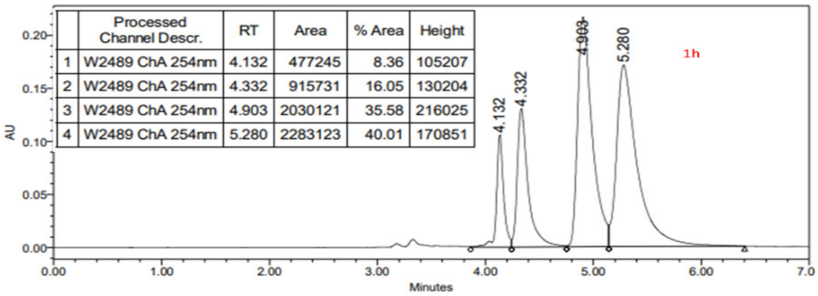
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.902	1919116	47.35	203443
2	W2489 ChA 254nm	5.276	2133510	52.65	164957



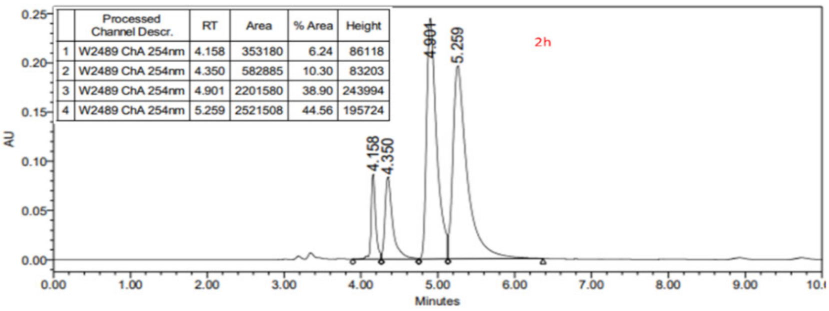
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.123	118204	2.07	18240
2	W2489 ChA 254nm	4.323	5580618	97.93	831926



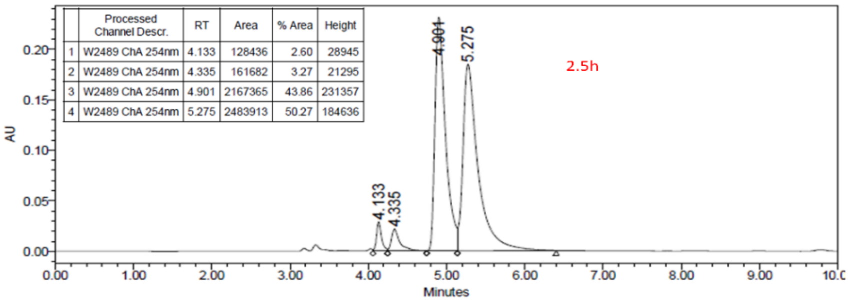
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.121	542199	10.02	127069
2	W2489 ChA 254nm	4.313	1583213	29.27	233314
3	W2489 ChA 254nm	4.888	1544124	28.55	165065
4	W2489 ChA 254nm	5.267	1739834	32.16	122105



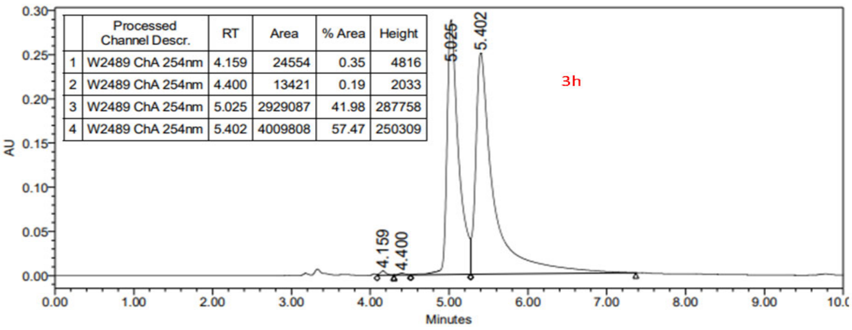
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.132	477245	8.36	105207
2	W2489 ChA 254nm	4.332	915731	16.05	130204
3	W2489 ChA 254nm	4.903	2030121	35.58	216025
4	W2489 ChA 254nm	5.280	2283123	40.01	170851



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.158	353180	6.24	86118
2	W2489 ChA 254nm	4.350	582885	10.30	83203
3	W2489 ChA 254nm	4.901	2201580	38.90	243994
4	W2489 ChA 254nm	5.259	2521508	44.56	195724

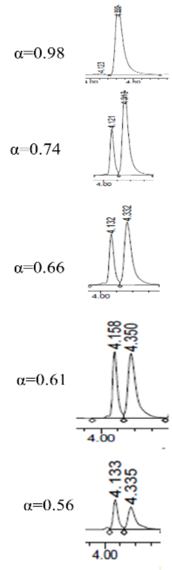


	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.133	128436	2.60	28945
2	W2489 ChA 254nm	4.335	161682	3.27	21295
3	W2489 ChA 254nm	4.901	2167365	43.86	231357
4	W2489 ChA 254nm	5.275	2483913	50.27	184636

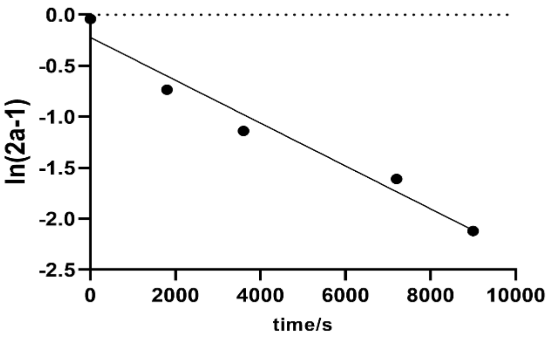


	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.159	24554	0.35	4816
2	W2489 ChA 254nm	4.400	13421	0.19	2033
3	W2489 ChA 254nm	5.025	2929087	41.98	287758
4	W2489 ChA 254nm	5.402	4009808	57.47	250309

(c)



Best-fit values	
Slope	-0.0002102
Y-intercept	-0.2209
X-intercept	-1051
1/slope	-4758
Goodness of Fit	
R square	0.9638



α: mole ratio of $\mathbf{19}_{\mathbf{Se}}$-*P*

Figure S17. Thermal enantiomerization of $\mathbf{19}_{\mathbf{Se}}$-*P* at 130 °C followed by chiral HPLC. (a) Scheme for thermal enantiomerization of $\mathbf{19}_{\mathbf{Se}}$-*P* and selenium-extrusion of $\mathbf{19}_{\mathbf{Se}}$ (b) Chiral HPLC trace for conversion, after specific reaction time at 130 °C in 1,2-dichlorobenzene. The solvent was removed under reduced pressure before analyzing with analytic IE-3 column, eluent: *n*-hexane/isopropanol = 98:2, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. Selenium-extrusion of $\mathbf{19}_{\mathbf{Se}}$-*P* occurs prior to enantiomerization of it at 130°C according to the HPLC spectra; (c) The plot of HPLC-based conversion ratio of $\mathbf{19}_{\mathbf{Se}}$ -*P* (α) at time t (remove the data of 3h). It switches between the - (*P*) and - (*M*) form isomers following a reversible first-order reaction[S6], with a rate constant (k), which could be obtained by fitting the experimental data using the following equation: ln (2α − 1) = −2kt and k was determined as $1.05 \cdot 10^{-4}$ s^{-1}. Then use the same calculation as $\mathbf{17}_{\mathrm{S}}$-*P* above, the enantiomerization energy of $\mathbf{19}_{\mathbf{Se}}$ -*P* was determined as $\Delta G^{\ddagger}$ = 130451.63 J/mol = 31.16 kcal/mol. $t_{1/2}$ = ln2/k= 6601 s =1.83 h.

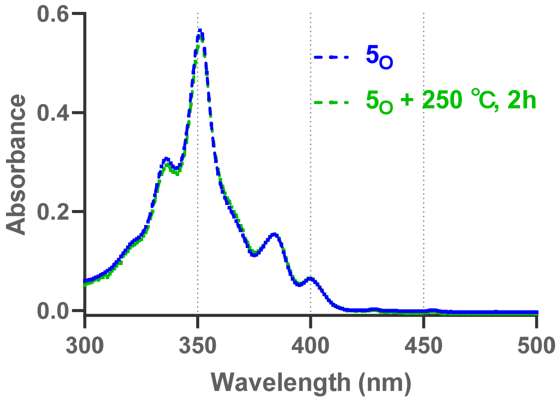
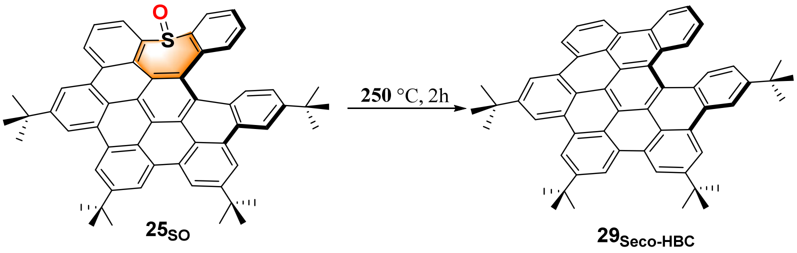
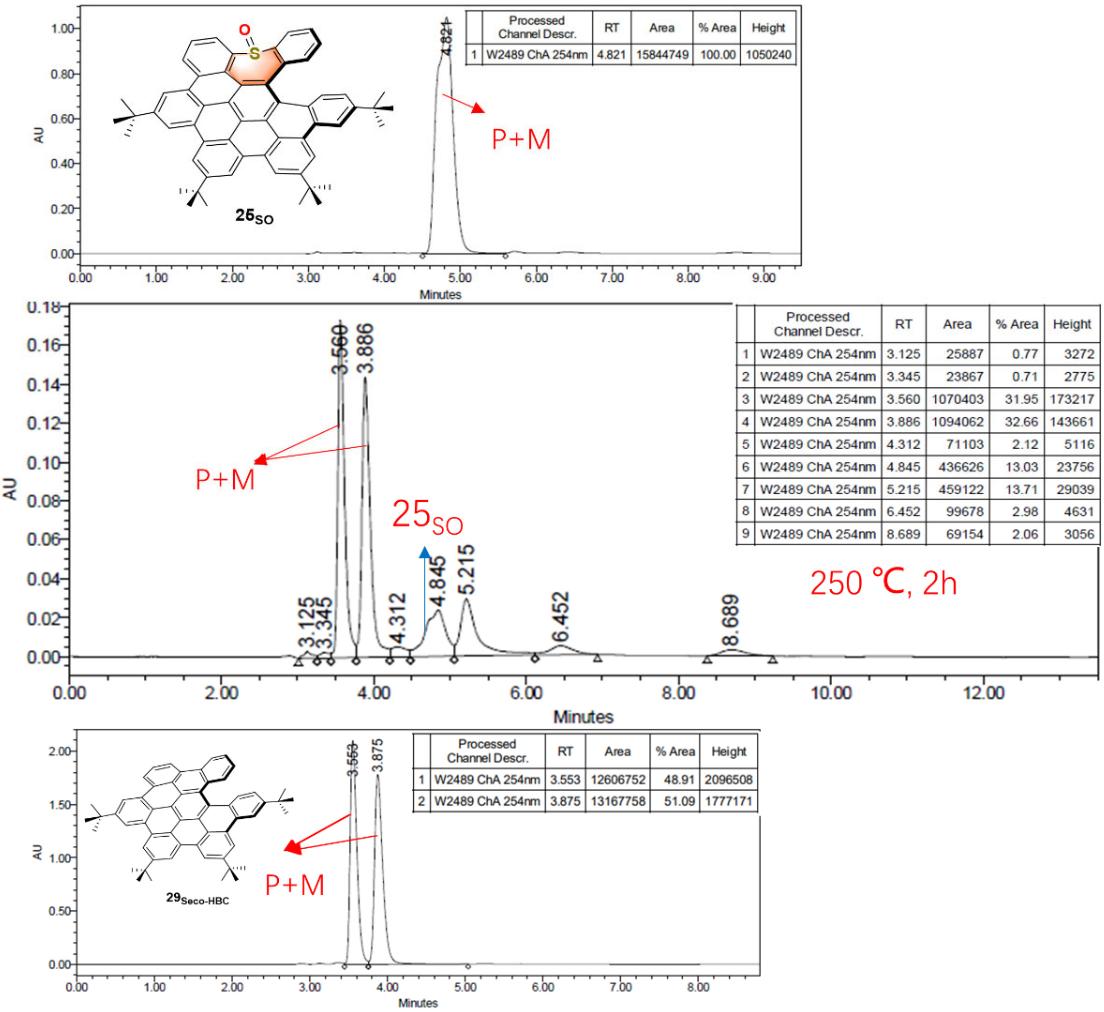


Figure S18. Changes in the UV/vis absorption spectra of **5_O** upon heating. Heating was performed in the solid state and monitored by dissolving in DCM at 5 μM concentration.

(a)



(b)



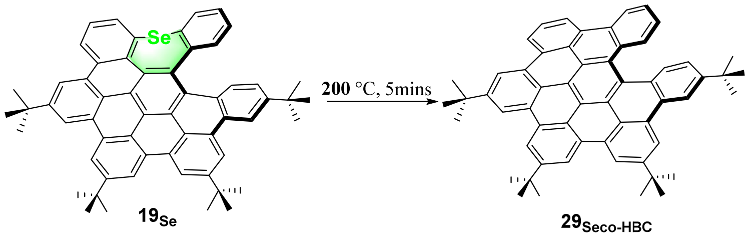
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.821	15844749	100.00	1050240

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	3.125	25887	0.77	3272
2	W2489 ChA 254nm	3.345	23867	0.71	2775
3	W2489 ChA 254nm	3.560	1070403	31.95	173217
4	W2489 ChA 254nm	3.886	1094062	32.66	143661
5	W2489 ChA 254nm	4.312	71103	2.12	5116
6	W2489 ChA 254nm	4.845	436626	13.03	23756
7	W2489 ChA 254nm	5.215	459122	13.71	29039
8	W2489 ChA 254nm	6.452	99678	2.98	4631
9	W2489 ChA 254nm	8.689	69154	2.06	3056

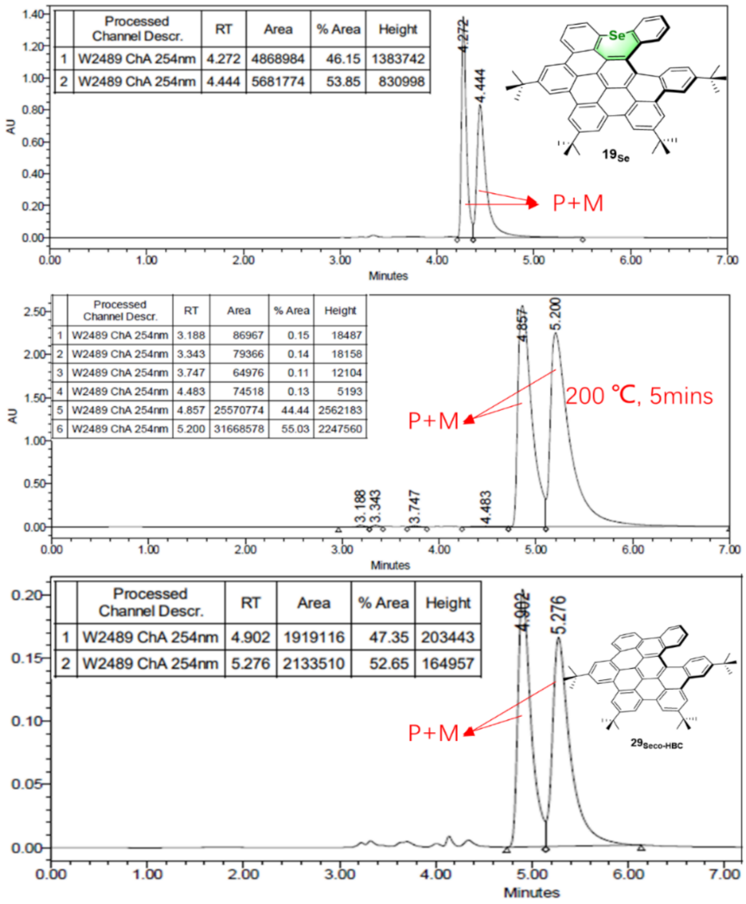
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	3.553	12606752	48.91	2096508
2	W2489 ChA 254nm	3.875	13167758	51.09	1777171

Figure S19. Thermal sulfur-extrusion of **25_{SO}** at 250 °C was analyzed by chiral HPLC. (a) Scheme for thermal sulfur-extrusion of **25_{SO}**. (b) Chiral HPLC trace for the conversion of **25_{SO}** powder reacted at 250 °C for 2 hours, dissolve the powder with *n*-hexane and analyze with analytic OD-3 column, eluent: *n*-hexane/isopropanol = 90:10, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. The sulfur-extrusion did not react completely with the unreacted **25_{SO}** left.

(a)



(b)

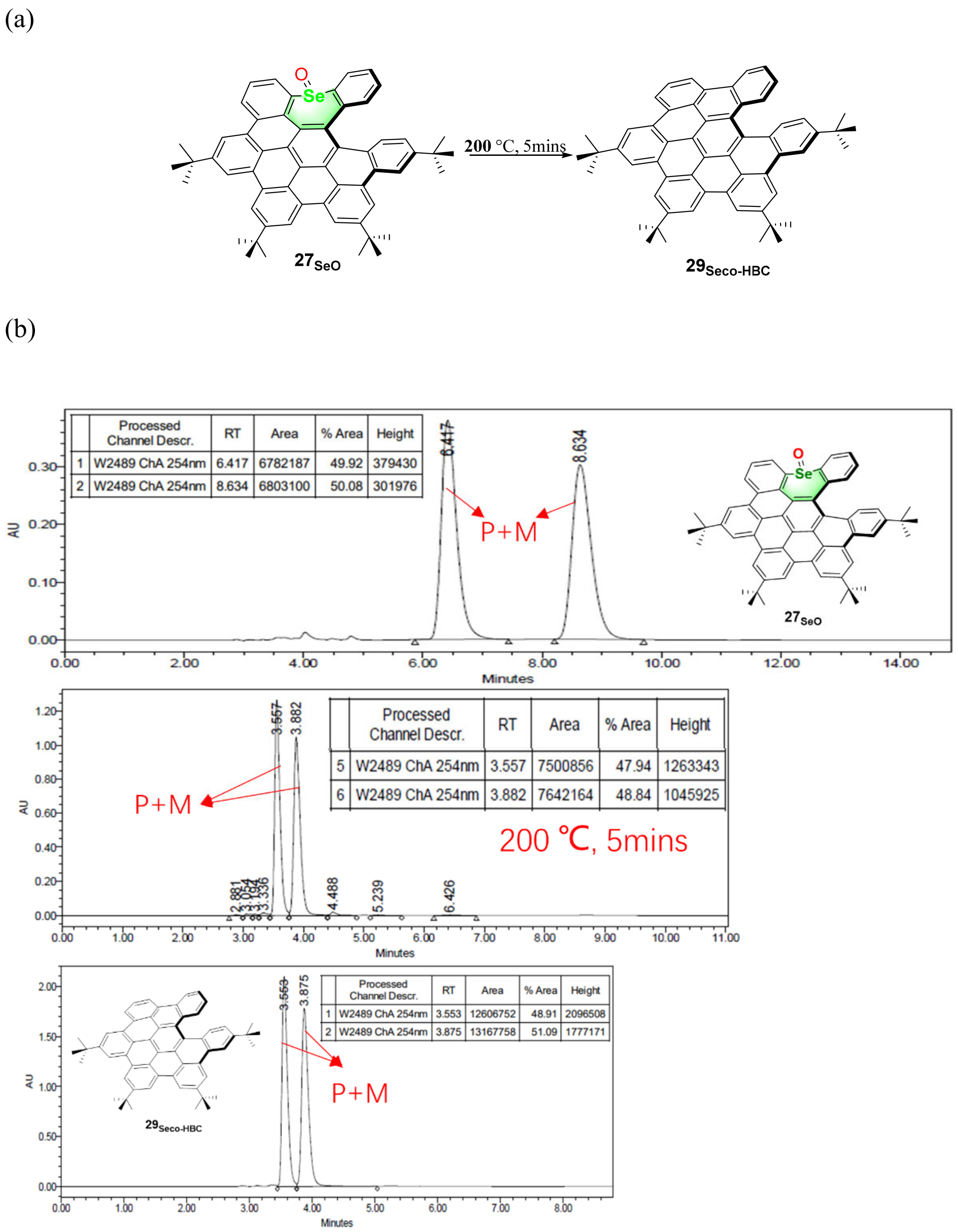


	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.272	4868984	46.15	1383742
2	W2489 ChA 254nm	4.444	5681774	53.85	830998

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	3.188	86967	0.15	18487
2	W2489 ChA 254nm	3.343	79366	0.14	18158
3	W2489 ChA 254nm	3.747	64976	0.11	12104
4	W2489 ChA 254nm	4.483	74518	0.13	5193
5	W2489 ChA 254nm	4.857	25570774	44.44	2562183
6	W2489 ChA 254nm	5.200	31668578	55.03	2247560

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.902	1919116	47.35	203443
2	W2489 ChA 254nm	5.276	2133510	52.65	164957

Figure S20. Thermal sulfur-extrusion of **19**$_{\mathbf{Se}}$ at 200 °C was analyzed by chiral HPLC. (a) Scheme for thermal sulfur-extrusion of **19**$_{\mathbf{Se}}$. (b) Chiral HPLC trace for the conversion of **19**$_{\mathbf{Se}}$ powder reacted at 200 °C for 5 mins, dissolve the powder with *n*-hexane and analyze with analytic IE-3 column, eluent: *n*-hexane/isopropanol = 98:2, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. The **19**$_{\mathbf{Se}}$ completely and quantitatively convert to **29**$_{\mathbf{Seco\text{-}HBC}}$ through sulfur-extrusion reaction according to the HPLC chromatography.



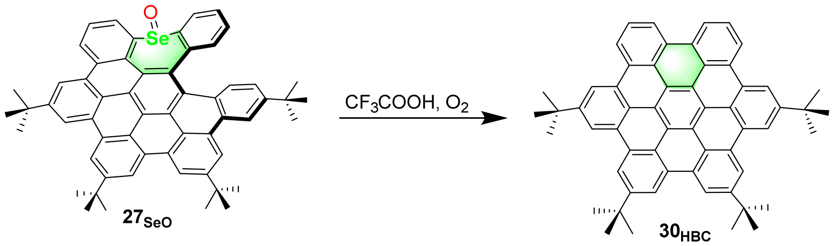
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.417	6782187	49.92	379430
2	W2489 ChA 254nm	8.634	6803100	50.08	301976

	Processed Channel Descr.	RT	Area	% Area	Height
5	W2489 ChA 254nm	3.557	7500856	47.94	1263343
6	W2489 ChA 254nm	3.882	7642164	48.84	1045925

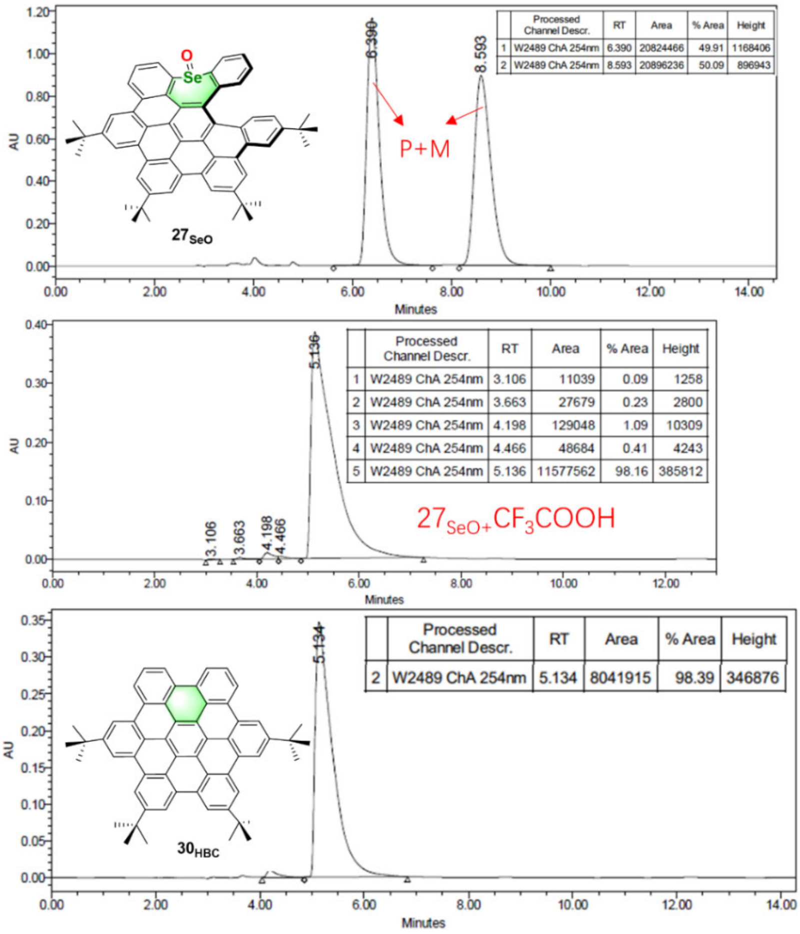
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	3.553	12606752	48.91	2096508
2	W2489 ChA 254nm	3.875	13167758	51.09	1777171

Figure S21. Thermal sulfur-extrusion of **27**$_{\mathbf{SeO}}$ at 200 °C was analyzed by chiral HPLC. (a) Scheme for thermal sulfur-extrusion of **27**$_{\mathbf{SeO}}$. (b) Chiral HPLC trace for the conversion of **27**$_{\mathbf{SeO}}$ powder reacted at 200 °C for 5mins. Dissolve the powder with *n*-hexane and analyze with analytic OD-3 column, eluent: *n*-hexane/isopropanol = 90:10, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. The sulfur-extrusion reacted completely and quantitatively convert to **29**$_{\mathbf{Seco\text{-}HBC}}$ according to the HPLC chromatogram.

(a)



(b)



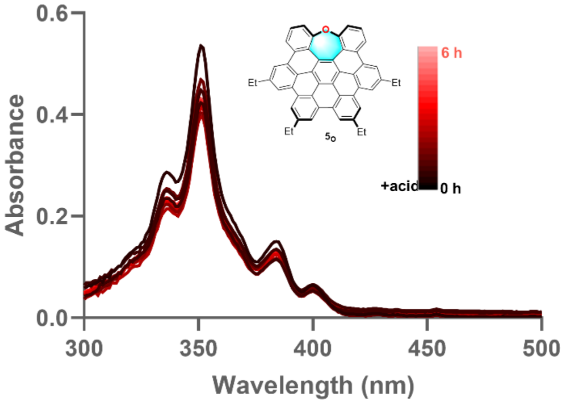
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.390	20824466	49.91	1168406
2	W2489 ChA 254nm	8.593	20896236	50.09	896943

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	3.106	11039	0.09	1258
2	W2489 ChA 254nm	3.663	27679	0.23	2800
3	W2489 ChA 254nm	4.198	129048	1.09	10309
4	W2489 ChA 254nm	4.466	48684	0.41	4243
5	W2489 ChA 254nm	5.136	11577562	98.16	385812

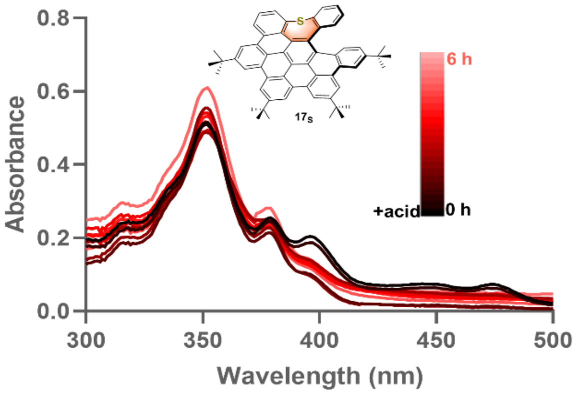
	Processed Channel Descr.	RT	Area	% Area	Height
2	W2489 ChA 254nm	5.134	8041915	98.39	346876

Figure S22. Sulfur-extrusion and cyclization reaction of **27_{SeO}** in acid was analyzed by chiral HPLC. (a) Scheme for thermal sulfur-extrusion of **27_{SeO}**. (b) Chiral HPLC trace for the conversion of **27_{SeO}** in CF_3COOH /DCM (1/2, v/v) reacted at room temperature for 20 hours. Solvent was removed under reduced pressure before analyzing with analytic OD-3 column, eluent before analyzing with eluent: *n*-hexane/isopropanol = 90:10, v/v; flow rate: 1.0 mL/min; detected by absorption at 254 nm. **27_{SeO}** quantitatively converted to **30_{HBC}** according to the HPLC spectra.

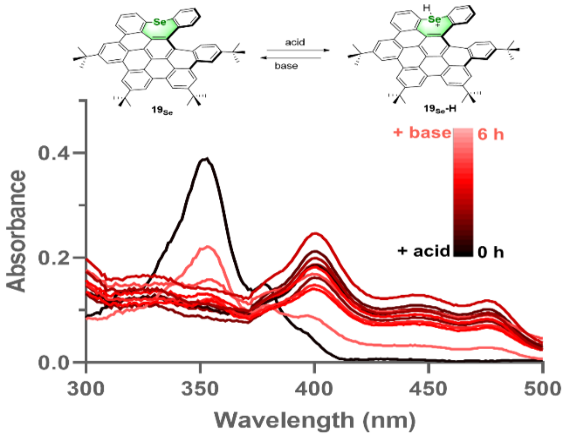
a)


0.6
0.4
0.2
0.0
Absorbance
300
350
400
450
500
Wavelength (nm)
Et
Et
Et
Et
O
5_O
6 h
+acid
0 h

b)


0.8
0.6
0.4
0.2
0.0
Absorbance
300
350
400
450
500
Wavelength (nm)
S
17_S
6 h
+acid
0 h

c)


Se
19_{Se}
acid
base
H
Se
+
19_{Se}-H
0.4
0.2
0.0
Absorbance
300
350
400
450
500
Wavelength (nm)
+ base
6 h
+ acid
0 h

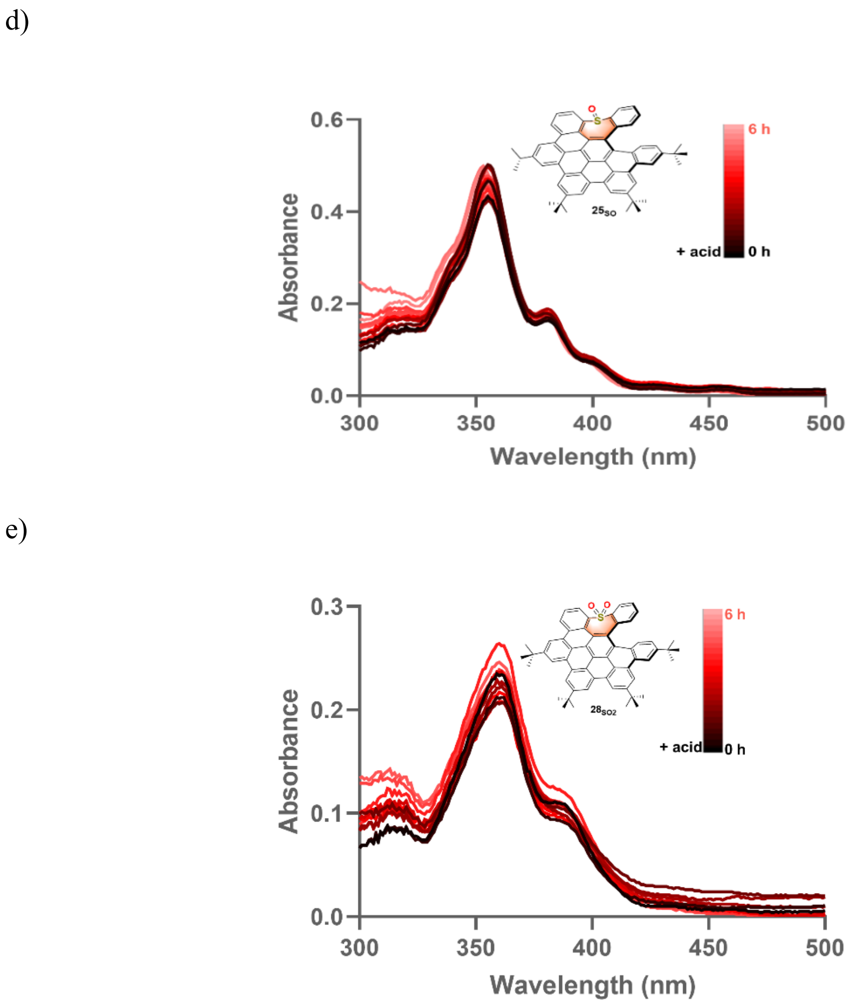


Figure S23. Changes in the UV/vis absorption spectra of **5**$_{\mathbf{O}}$ (a), **17**$_{\mathbf{S}}$ (b), **19**$_{\mathbf{Se}}$ (c), **25**$_{\mathbf{SO}}$ (d), and **28**$_{\mathbf{SO2}}$ (e) upon the addition of trifluoroacetic acid (TFA) in dichloromethane (1:2, v/v).

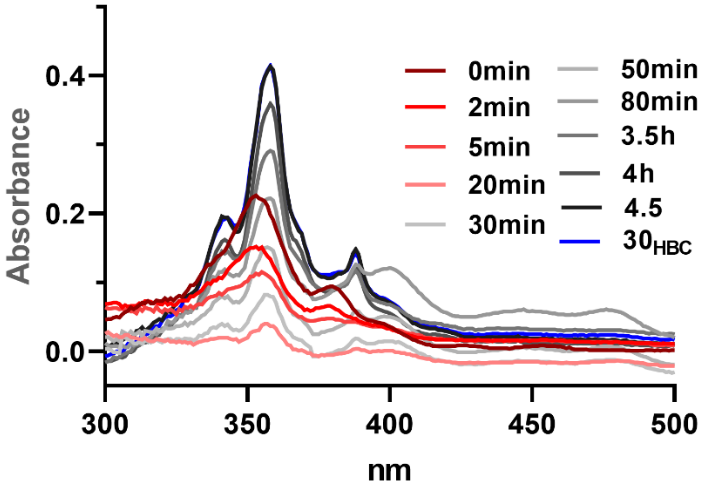
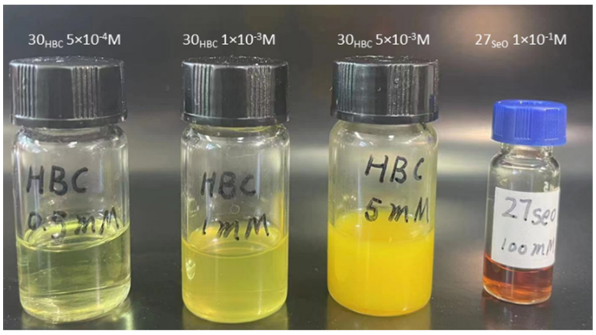
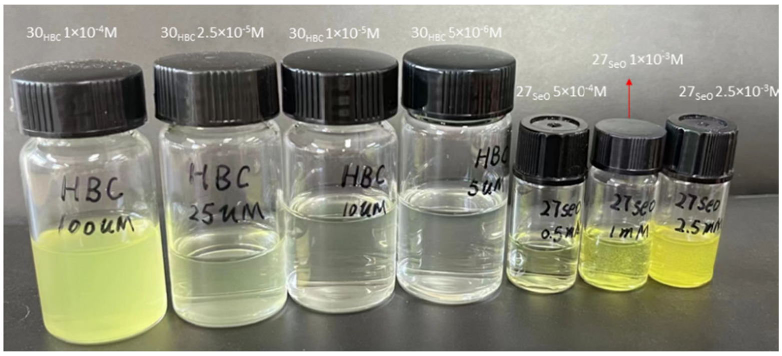


Figure S24. (c) Changes in the UV-vis absorption spectra of **27**$_{\mathbf{SeO}}$ upon dissolving it in methanesulfonic acid /DCM (1/2, v/v) with 3.3 µM concentration under ambient conditions.

a)



b)



c)

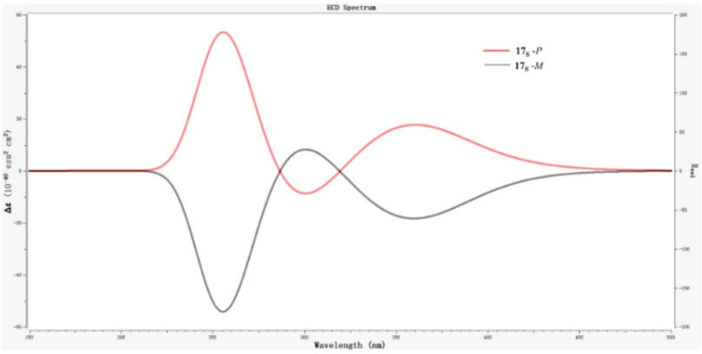
Compound	Solubility in DCM	Solubility in EtOH
27_{SeO}	>1×10^{-1}M	5×10^{-4}M~1×10^{-3}M
30_{HBC}	5×10^{-4}M~1×10^{-3}M	<5×10^{-6}M

Figure S25 Solubility of **27_{SeO}** and **30_{HBC}** in DCM (a） and EtOH (b) at different concentration at room temperature. And the results were summarized in a table (c). Based on the measurement, the solubility of **27_{SeO}** is more than 100-fold higher than that of **30_{HBC}** in both DCM and EtOH.

Computational Details

Geometry calculations of the compounds were carried out by DFT methods using the Gaussian 16 program package.[S8] Different alkyl chains were replaced by methyl group. The optimizations of structures were carried out at the CAM-B3LYP/6-31+G(d,p) level of theory in gas phase. The nucleus independent chemical shift NICS (0) calculations were performed at the B3LYP-GIAO/6-311++G(d,p) level. Electronic transitions of the *M* and *P* enantiomers for calculated ECD spectra of **16**$_{\mathrm{S}}$ and **18**$_{\mathrm{Se}}$ were calculated by means of TD-DFT methods at B3LYP/6-31G(d,p) theory level and the first 40 excited states were considered in the gas phase. The atomic coordinates of the calculated structures are shown in Tables S4–S9. TD-DFT calculated molecular orbits and transitions in the excited states were performed at PBE0/6-311G(d,p). The major transitions of 9 excited states calculated by TD-DFT are shown in Tables S10-S15

(a)



(b)

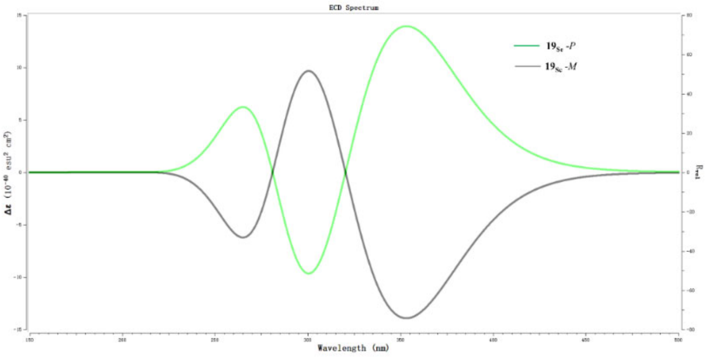


Figure S26. Calculated ECD spectra of **17**$_{\mathrm{S}}$ -*P* and **17**$_{\mathrm{S}}$ -*M* (a); Calculated ECD spectra of **19**$_{\mathrm{Se}}$ -*P* and **19**$_{\mathrm{Se}}$ -*M* (b)

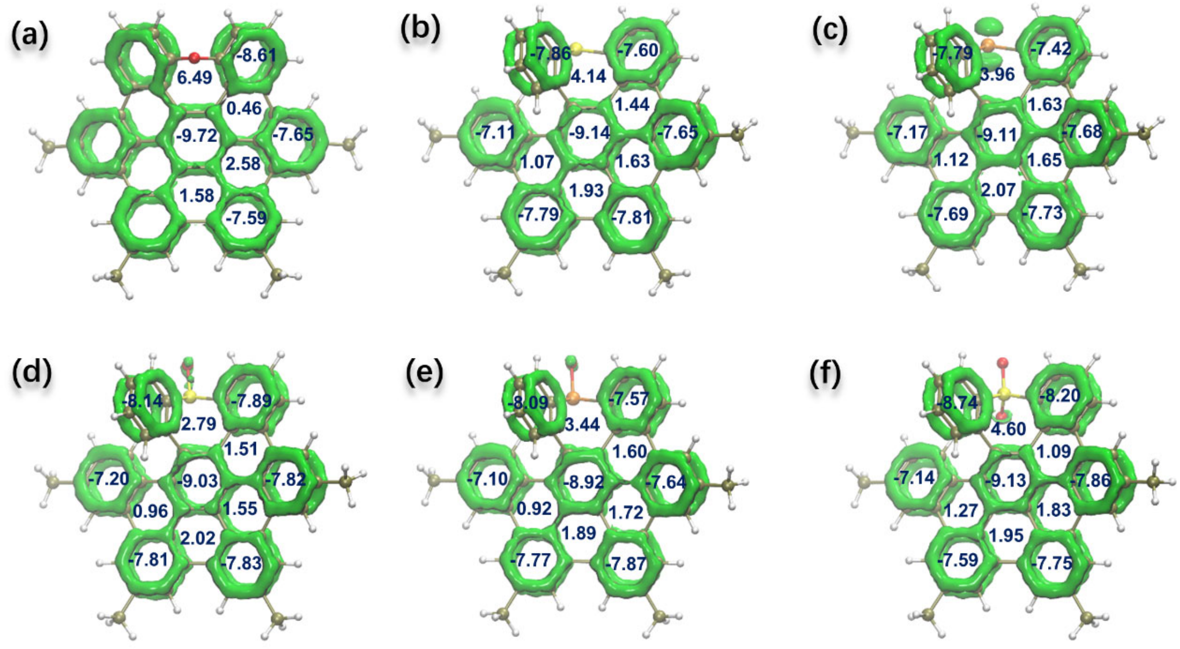


Figure S27. Isosurface of LOL-π of backbones $\mathbf{5_O}$ (a), $\mathbf{16_S}$ (b), $\mathbf{18_{Se}}$ (c), $\mathbf{24_{SO}}$ (d), $\mathbf{26_{SeO}}$ (e), and $\mathbf{28_{SO2}}$ (f) with calculated NICS(0)values..

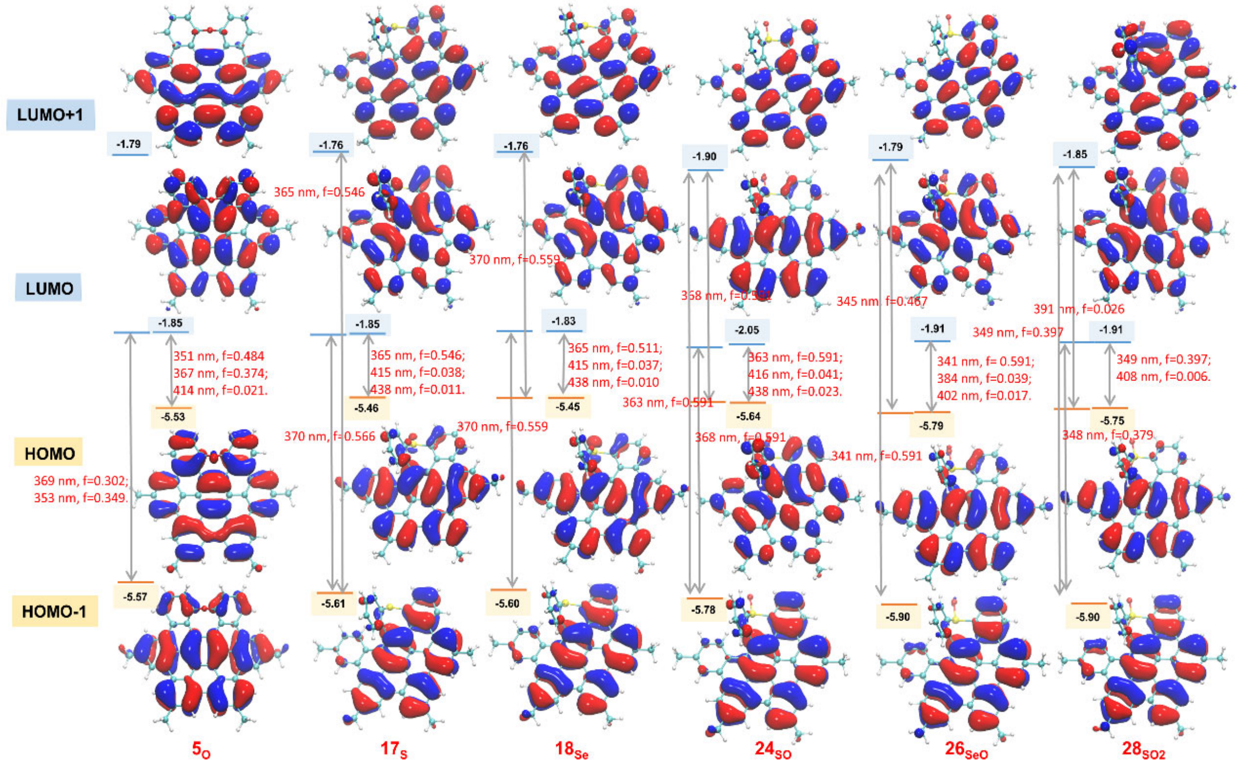
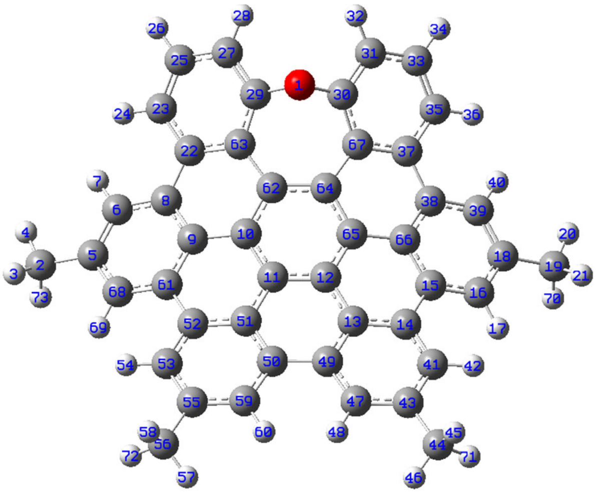


Figure. S28 Molecular orbitals (HOMO-1–LUMO+1) with major transitions of $\mathbf{5_O}$, $\mathbf{17_S}$, $\mathbf{18_{Se}}$, $\mathbf{24_{SO}}$, $\mathbf{26_{SeO}}$, and $\mathbf{28_{SO2}}$ calculated by DFT at the PBE0/6-311G+G(d,p) level of theory.

Table S4. Atomic coordinates for the DFT calculated structure of $\mathbf{5_O}$:



Zero-point correction= 0.579055 (Hartree/Particle)
Thermal correction to Energy= 0.610567
Thermal correction to Enthalpy= 0.611511
Thermal correction to Gibbs Free Energy= 0.517870
Sum of electronic and zero-point Energies= -1842.383087
Sum of electronic and thermal Energies= -1842.351576
Sum of electronic and thermal Enthalpies= -1842.350632
Sum of electronic and thermal Free Energies= -1842.444273

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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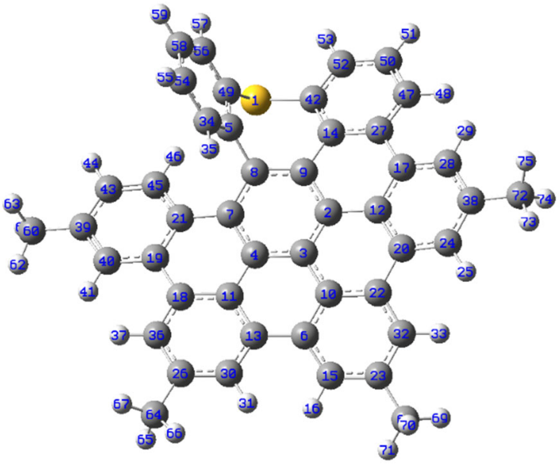
2	6	0	-6.794474	-0.112972	1.905195
3	1	0	-7.511477	0.375827	1.238599
4	1	0	-7.173150	-1.112534	2.128541
5	6	0	-5.423705	-0.170333	1.285089
6	6	0	-4.775798	-1.378034	1.082398
7	1	0	-5.289289	-2.286674	1.370872
8	6	0	-3.493589	-1.444216	0.530943
9	6	0	-2.808948	-0.251371	0.226566
10	6	0	-1.399561	-0.282423	-0.113202
11	6	0	-0.699342	0.948038	-0.158125
12	6	0	0.699397	0.948005	-0.158130
13	6	0	1.417018	2.200540	-0.196746
14	6	0	2.818005	2.218824	-0.029290
15	6	0	3.490832	0.980857	0.362266
16	6	0	4.776843	0.996732	0.893377
17	1	0	5.280124	1.944152	1.049431
18	6	0	5.423738	-0.170555	1.285016

19	6	0	6.794451	-0.113232	1.905249
20	1	0	7.174001	-1.112904	2.126607
21	1	0	7.511028	0.377564	1.239675
22	6	0	-2.873687	-2.711536	0.154319
23	6	0	-3.620142	-3.901061	0.167417
24	1	0	-4.622809	-3.900629	0.572371
25	6	0	-3.134201	-5.065790	-0.384952
26	1	0	-3.734921	-5.968850	-0.375518
27	6	0	-1.893913	-5.052317	-1.012042
28	1	0	-1.502082	-5.916333	-1.535450
29	6	0	-1.150932	-3.891358	-1.009351
30	6	0	1.150761	-3.891433	-1.009241
31	6	0	1.893638	-5.052458	-1.011800
32	1	0	1.501779	-5.916473	-1.535189
33	6	0	3.133871	-5.066000	-0.384601
34	1	0	3.734504	-5.969116	-0.375045
35	6	0	3.619879	-3.901273	0.167716
36	1	0	4.622508	-3.900913	0.572762
37	6	0	2.873537	-2.711678	0.154468
38	6	0	3.493523	-1.444371	0.531006
39	6	0	4.775761	-1.378232	1.082395
40	1	0	5.289235	-2.286885	1.370854
41	6	0	3.513388	3.410214	-0.210906
42	1	0	4.594848	3.420151	-0.135640
43	6	0	2.857150	4.598363	-0.515059
44	6	0	3.636451	5.863590	-0.757923
45	1	0	4.043463	5.885395	-1.774466
46	1	0	3.007899	6.748693	-0.636833
47	6	0	1.472707	4.586170	-0.594142
48	1	0	0.966872	5.523429	-0.790837
49	6	0	0.731265	3.413518	-0.428316
50	6	0	-0.731095	3.413555	-0.428273
51	6	0	-1.416899	2.200612	-0.196703
52	6	0	-2.817884	2.218966	-0.029195
53	6	0	-3.513209	3.410393	-0.210747
54	1	0	-4.594667	3.420383	-0.135443
55	6	0	-2.856916	4.598525	-0.514877
56	6	0	-3.636188	5.863799	-0.757588
57	1	0	-3.007246	6.748813	-0.637888
58	1	0	-4.044517	5.885030	-1.773613
59	6	0	-1.472484	4.586257	-0.594028
60	1	0	-0.966606	5.523493	-0.790717
61	6	0	-3.490766	0.981017	0.362325

62	6	0	-0.716938	-1.505857	-0.303732
63	6	0	-1.559465	-2.712059	-0.368277
64	6	0	0.716878	-1.505890	-0.303715
65	6	0	1.399557	-0.282488	-0.113187
66	6	0	2.808943	-0.251500	0.226584
67	6	0	1.559343	-2.712138	-0.368194
68	6	0	-4.776754	0.996938	0.893489
69	1	0	-5.279965	1.944381	1.049630
70	1	0	6.781337	0.454122	2.841003
71	1	0	4.480412	5.950987	-0.068704
72	1	0	-4.479240	5.951883	-0.067337
73	1	0	-6.781897	0.456295	2.839785

Table S5. Atomic coordinates for the DFT calculated structure of **16$_{\text{S}}$**:



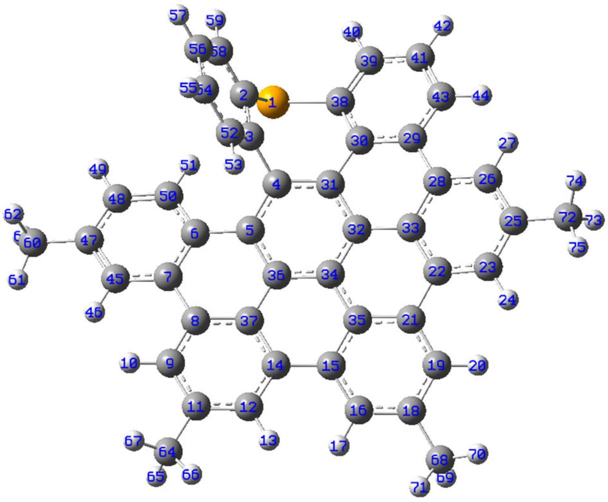
Zero-point correction= 0.598352 (Hartree/Particle)
Thermal correction to Energy= 0.633281
Thermal correction to Enthalpy= 0.634225
Thermal correction to Gibbs Free Energy= 0.531057
Sum of electronic and zero-point Energies= -2166.515673
Sum of electronic and thermal Energies= -2166.480744
Sum of electronic and thermal Enthalpies= -2166.479799
Sum of electronic and thermal Free Energies= -2166.582968

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	0.669339	-4.045513	-1.421178
2	6	0	-1.440156	-0.150681	-0.165856
3	6	0	-0.709947	1.057742	-0.122804
4	6	0	0.703436	1.030618	-0.141835

5	6	0	1.281512	-2.559282	0.748222
6	6	0	-0.681783	3.540380	-0.159285
7	6	0	1.378112	-0.207632	-0.091772
8	6	0	0.630681	-1.400817	0.060669
9	6	0	-0.763163	-1.400719	-0.169305
10	6	0	-1.403855	2.325842	-0.118025
11	6	0	1.450790	2.269615	-0.068563
12	6	0	-2.880865	-0.106654	-0.028421
13	6	0	0.774654	3.510072	-0.030733
14	6	0	-1.560624	-2.622049	-0.402777
15	6	0	-1.376930	4.740082	-0.306602
16	1	0	-0.831080	5.670746	-0.404055
17	6	0	-3.617865	-1.302945	0.104101
18	6	0	2.860872	2.251904	0.046018
19	6	0	3.571786	0.985593	-0.131021
20	6	0	-3.557243	1.127556	0.084969
21	6	0	2.842453	-0.212415	-0.243133
22	6	0	-2.814843	2.370013	-0.099838
23	6	0	-2.763507	4.785268	-0.369222
24	6	0	-4.911844	1.138122	0.422853
25	1	0	-5.419826	2.083270	0.572237
26	6	0	2.881435	4.667002	0.345930
27	6	0	-2.964442	-2.571218	-0.223500
28	6	0	-4.961696	-1.242361	0.467063
29	1	0	-5.516161	-2.155981	0.644455
30	6	0	1.504124	4.680026	0.182513
31	1	0	0.988996	5.629049	0.266622
32	6	0	-3.465559	3.595220	-0.245796
33	1	0	-4.547400	3.627209	-0.298166
34	6	0	1.803731	-2.361094	2.029539
35	1	0	1.726266	-1.379507	2.484288
36	6	0	3.541000	3.448202	0.270465
37	1	0	4.615124	3.441048	0.408775
38	6	0	-5.622110	-0.032217	0.639832
39	6	0	5.661863	-0.199505	-0.584724
40	6	0	4.969424	0.956576	-0.287627
41	1	0	5.533866	1.877750	-0.212776
42	6	0	-1.031227	-3.830497	-0.931008
43	6	0	4.917598	-1.370109	-0.778614
44	1	0	5.419963	-2.285835	-1.076862
45	6	0	3.551457	-1.369057	-0.622018
46	1	0	3.012322	-2.279177	-0.828996
47	6	0	-3.754020	-3.700423	-0.482824

48	1	0	-4.828149	-3.637107	-0.373822
49	6	0	1.378366	-3.831128	0.189726
50	6	0	-3.204238	-4.877679	-0.935158
51	1	0	-3.832677	-5.738700	-1.135876
52	6	0	-1.838154	-4.933098	-1.171668
53	1	0	-1.382955	-5.835656	-1.561840
54	6	0	2.432045	-3.395578	2.709140
55	1	0	2.838038	-3.218109	3.699591
56	6	0	2.005009	-4.873767	0.863855
57	1	0	2.063431	-5.850946	0.397095
58	6	0	2.543596	-4.652352	2.124581
59	1	0	3.037899	-5.460815	2.653004
60	6	0	7.158588	-0.205014	-0.736629
61	1	0	7.458748	-0.642789	-1.693372
62	1	0	7.570017	0.805344	-0.684338
63	1	0	7.632327	-0.799283	0.051554
64	6	0	3.644930	5.943901	0.577468
65	1	0	3.988484	6.374540	-0.369289
66	1	0	3.024699	6.695273	1.071972
67	1	0	4.528596	5.772927	1.197154
68	6	0	-3.484709	6.096592	-0.535115
69	1	0	-4.464445	5.956526	-0.997731
70	1	0	-3.645681	6.583539	0.432790
71	1	0	-2.912784	6.789653	-1.157031
72	6	0	-7.076145	0.001301	1.028971
73	1	0	-7.344084	0.955986	1.487189
74	1	0	-7.721764	-0.136587	0.154981
75	1	0	-7.316427	-0.794163	1.739041

Table S6. Atomic coordinates for the DFT calculated structure of **18**$_{\text{Se}}$:



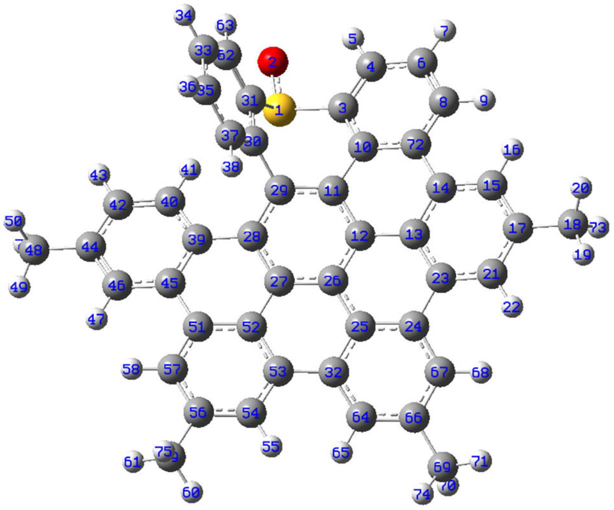
Zero-point correction= 0.597789 (Hartree/Particle)
Thermal correction to Energy= 0.633053
Thermal correction to Enthalpy= 0.633997
Thermal correction to Gibbs Free Energy= 0.530163
Sum of electronic and zero-point Energies= -4167.807097
Sum of electronic and thermal Energies= -4167.771833
Sum of electronic and thermal Enthalpies= -4167.770889
Sum of electronic and thermal Free Energies= -4167.874723

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	34	0	3.002881	-2.519553	-1.346554
2	6	0	3.355969	-1.898885	0.404339
3	6	0	2.420369	-1.003146	0.912493
4	6	0	1.204582	-0.543493	0.161826
5	6	0	1.026271	0.848216	-0.023061
6	6	0	2.163779	1.767806	-0.167837
7	6	0	1.973960	3.156829	-0.055739
8	6	0	0.618747	3.689740	0.090428
9	6	0	0.383557	5.047385	0.301639
10	1	0	1.216794	5.722149	0.455544
11	6	0	-0.900221	5.574459	0.341821
12	6	0	-1.971299	4.713111	0.155148
13	1	0	-2.972337	5.123043	0.211032
14	6	0	-1.791455	3.344098	-0.046065
15	6	0	-2.934380	2.444391	-0.201199
16	6	0	-4.227320	2.930913	-0.390718
17	1	0	-4.391961	3.996259	-0.498499
18	6	0	-5.325895	2.086087	-0.480887
19	6	0	-5.120944	0.722361	-0.327423

20	1	0	-5.978435	0.062618	-0.387779
21	6	0	-3.846686	0.187922	-0.137315
22	6	0	-3.639498	-1.239842	0.086285
23	6	0	-4.704470	-2.081003	0.412629
24	1	0	-5.700728	-1.668745	0.518399
25	6	0	-4.519734	-3.430060	0.672608
26	6	0	-3.236846	-3.950807	0.560716
27	1	0	-3.095857	-5.003639	0.772375
28	6	0	-2.145856	-3.156826	0.212029
29	6	0	-0.824687	-3.732912	-0.048171
30	6	0	0.288246	-2.884869	-0.265253
31	6	0	0.128537	-1.429911	-0.075589
32	6	0	-1.186318	-0.892693	-0.106444
33	6	0	-2.331311	-1.769376	0.026116
34	6	0	-1.388295	0.505389	-0.096321
35	6	0	-2.726827	1.047529	-0.136788
36	6	0	-0.277737	1.378706	-0.104459
37	6	0	-0.482654	2.811565	-0.047922
38	6	0	1.468185	-3.496267	-0.759571
39	6	0	1.573857	-4.871253	-0.891905
40	1	0	2.508760	-5.291587	-1.242745
41	6	0	0.495064	-5.693928	-0.597766
42	1	0	0.576414	-6.769648	-0.711334
43	6	0	-0.693283	-5.119814	-0.207731
44	1	0	-1.553108	-5.759196	-0.061380
45	6	0	3.082267	4.011822	-0.191638
46	1	0	2.943613	5.083052	-0.111822
47	6	0	4.350579	3.545966	-0.475038
48	6	0	4.507320	2.169484	-0.683725
49	1	0	5.474902	1.775935	-0.981684
50	6	0	3.441421	1.311859	-0.544347
51	1	0	3.579365	0.268370	-0.777990
52	6	0	2.612081	-0.527402	2.212311
53	1	0	1.891525	0.164337	2.635275
54	6	0	3.718713	-0.918143	2.955724
55	1	0	3.852550	-0.530719	3.960408
56	6	0	4.650561	-1.800194	2.419877
57	1	0	5.515008	-2.104296	3.000909
58	6	0	4.463636	-2.299265	1.137070
59	1	0	5.163603	-3.003313	0.701041
60	6	0	5.522533	4.480935	-0.601349
61	1	0	5.207183	5.525847	-0.561613
62	1	0	6.243737	4.319662	0.206600

63	1	0	6.055603	4.324487	-1.543872
64	6	0	-1.121256	7.047808	0.559907
65	1	0	-1.081511	7.596570	-0.387249
66	1	0	-2.097831	7.242262	1.009531
67	1	0	-0.356340	7.472740	1.214563
68	6	0	-6.699924	2.635779	-0.758108
69	1	0	-6.876418	2.728202	-1.835155
70	1	0	-7.478984	1.984974	-0.354110
71	1	0	-6.827897	3.629068	-0.320834
72	6	0	-5.679761	-4.315350	1.043372
73	1	0	-6.086058	-4.822962	0.161879
74	1	0	-5.378876	-5.088981	1.754307
75	1	0	-6.492170	-3.740015	1.493214

Table S7. Atomic coordinates for the DFT calculated structure of $\mathbf{24}_{\mathrm{SO}}$:



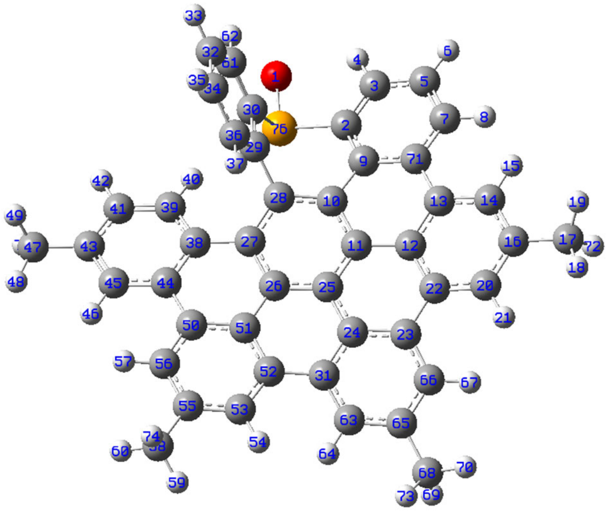
Zero-point correction= 0.602334 (Hartree/Particle)
Thermal correction to Energy= 0.638225
Thermal correction to Enthalpy= 0.639169
Thermal correction to Gibbs Free Energy= 0.534100
Sum of electronic and zero-point Energies= -2241.667325
Sum of electronic and thermal Energies= -2241.631434
Sum of electronic and thermal Enthalpies= -2241.630490
Sum of electronic and thermal Free Energies= -2241.735559

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	16	0	2.381576	-3.127881	-1.358143
2	8	0	3.207148	-4.316460	-1.775142
3	6	0	0.798723	-3.767214	-0.753104

4	6	0	0.664203	-5.131913	-0.894031
5	1	0	1.510884	-5.692988	-1.275449
6	6	0	-0.548131	-5.733715	-0.578569
7	1	0	-0.671703	-6.806515	-0.680972
8	6	0	-1.611419	-4.944976	-0.198818
9	1	0	-2.573560	-5.415262	-0.047298
10	6	0	-0.236864	-2.934168	-0.272303
11	6	0	-0.102601	-1.477827	-0.095521
12	6	0	-1.285171	-0.693060	-0.117333
13	6	0	-2.579740	-1.329622	0.009127
14	6	0	-2.674606	-2.728988	0.183292
15	6	0	-3.905367	-3.294335	0.510161
16	1	0	-3.979174	-4.357188	0.704843
17	6	0	-5.060461	-2.530351	0.618782
18	6	0	-6.377047	-3.172457	0.966330
19	1	0	-7.070531	-2.449240	1.401335
20	1	0	-6.245603	-3.988164	1.681709
21	6	0	-4.970633	-1.168376	0.377224
22	1	0	-5.866449	-0.568331	0.481367
23	6	0	-3.757122	-0.551909	0.067692
24	6	0	-3.675093	0.890365	-0.143694
25	6	0	-2.407236	1.512218	-0.138358
26	6	0	-1.201666	0.716377	-0.101800
27	6	0	0.062283	1.352130	-0.111256
28	6	0	1.238811	0.575213	-0.043280
29	6	0	1.133696	-0.827524	0.121544
30	6	0	2.245855	-1.551732	0.817611
31	6	0	2.904706	-2.648483	0.280823
32	6	0	-2.334980	2.922564	-0.196456
33	6	0	4.298847	-2.888848	2.197029
34	1	0	5.094544	-3.396507	2.731979
35	6	0	3.651023	-1.800076	2.773381
36	1	0	3.939731	-1.460078	3.762480
37	6	0	2.636034	-1.137743	2.093706
38	1	0	2.139760	-0.286805	2.547616
39	6	0	2.536302	1.255394	-0.187633
40	6	0	3.709945	0.563356	-0.545460
41	1	0	3.667637	-0.496239	-0.738272
42	6	0	4.918293	1.201503	-0.696704
43	1	0	5.794278	0.625110	-0.979468
44	6	0	5.023730	2.586551	-0.516238
45	6	0	2.617352	2.656564	-0.087094
46	6	0	3.866879	3.284975	-0.236700

47	1	0	3.932532	4.363815	-0.170659
48	6	0	6.349192	3.282550	-0.662907
49	1	0	6.238798	4.368065	-0.616556
50	1	0	7.040839	2.982922	0.131108
51	6	0	1.394286	3.443125	0.073466
52	6	0	0.141551	2.797295	-0.050783
53	6	0	-1.036723	3.577348	-0.040397
54	6	0	-0.942904	4.954634	0.161275
55	1	0	-1.843115	5.554161	0.217618
56	6	0	0.277158	5.588147	0.344694
57	6	0	1.432121	4.820435	0.285777
58	1	0	2.382967	5.319715	0.425203
59	6	0	0.347564	7.065037	0.628848
60	1	0	-0.522869	7.590063	0.228731
61	1	0	1.243463	7.512764	0.191690
62	6	0	3.922495	-3.322201	0.932004
63	1	0	4.394977	-4.162045	0.433176
64	6	0	-3.505994	3.656288	-0.381346
65	1	0	-3.457086	4.733597	-0.483406
66	6	0	-4.749780	3.045782	-0.474812
67	6	0	-4.818213	1.667685	-0.329698
68	1	0	-5.789230	1.191381	-0.393672
69	6	0	-5.988026	3.857738	-0.746848
70	1	0	-6.140294	3.992596	-1.823053
71	1	0	-6.880712	3.369465	-0.349058
72	6	0	-1.489957	-3.553456	-0.061086
73	1	0	-6.856878	-3.593607	0.076385
74	1	0	-5.918570	4.852759	-0.300514
75	1	0	0.379725	7.256931	1.706719
76	1	0	6.825364	3.031580	-1.615389

Table S8. Atomic coordinates for the DFT calculated structure of **26_{SeO}**:



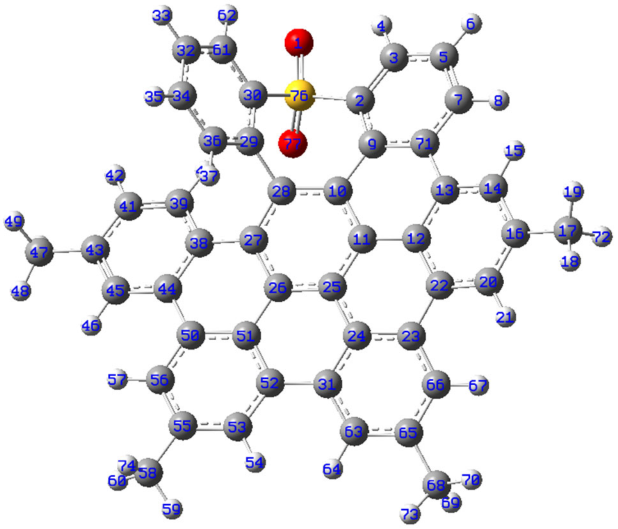
Zero-point correction= 0.601066 (Hartree/Particle)
Thermal correction to Energy= 0.637415
Thermal correction to Enthalpy= 0.638359
Thermal correction to Gibbs Free Energy= 0.532158
Sum of electronic and zero-point Energies= -4242.954330
Sum of electronic and thermal Energies= -4242.917982
Sum of electronic and thermal Enthalpies= -4242.917037
Sum of electronic and thermal Free Energies= -4243.023238

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.275177	-1.077329	-1.583300
2	6	0	2.893679	-2.265236	-0.603436
3	6	0	3.729063	-3.356948	-0.653016
4	1	0	4.748016	-3.206271	-0.998947
5	6	0	3.228022	-4.603968	-0.293741
6	1	0	3.865594	-5.481311	-0.320989
7	6	0	1.893879	-4.726529	0.032060
8	1	0	1.498853	-5.716572	0.216661
9	6	0	1.560252	-2.325561	-0.153972
10	6	0	0.695280	-1.142902	-0.011358
11	6	0	-0.708334	-1.339506	-0.063918
12	6	0	-1.256898	-2.675079	0.055892
13	6	0	-0.405515	-3.784224	0.271183
14	6	0	-0.964168	-5.023390	0.576014
15	1	0	-0.322609	-5.869277	0.790245
16	6	0	-2.338600	-5.217822	0.632254

17	6	0	-2.910406	-6.572456	0.955544
18	1	0	-3.927252	-6.492738	1.346498
19	1	0	-2.302001	-7.094543	1.698315
20	6	0	-3.165356	-4.138517	0.362360
21	1	0	-4.236703	-4.283642	0.429407
22	6	0	-2.655350	-2.872619	0.068726
23	6	0	-3.543866	-1.738023	-0.170375
24	6	0	-3.008050	-0.431458	-0.149932
25	6	0	-1.579918	-0.228709	-0.076599
26	6	0	-1.054115	1.084507	-0.078641
27	6	0	0.339648	1.281927	0.019840
28	6	0	1.187415	0.165208	0.217027
29	6	0	2.469914	0.369905	0.976219
30	6	0	3.720379	0.033110	0.483011
31	6	0	-3.885739	0.673440	-0.232633
32	6	0	4.826911	0.700893	2.474876
33	1	0	5.730911	0.834392	3.059887
34	6	0	3.589434	1.047730	3.010503
35	1	0	3.531084	1.449614	4.016749
36	6	0	2.420924	0.883564	2.274118
37	1	0	1.463170	1.156661	2.704144
38	6	0	0.864927	2.648807	-0.116495
39	6	0	2.207154	2.901547	-0.460949
40	1	0	2.867912	2.075736	-0.668953
41	6	0	2.697396	4.178994	-0.594305
42	1	0	3.738255	4.325452	-0.867410
43	6	0	1.862318	5.288612	-0.409510
44	6	0	-0.001115	3.753454	-0.023105
45	6	0	0.527282	5.050465	-0.152315
46	1	0	-0.134294	5.905364	-0.087496
47	6	0	2.404192	6.686602	-0.531178
48	1	0	1.604726	7.429985	-0.501350
49	1	0	3.099308	6.911047	0.284353
50	6	0	-1.442490	3.533221	0.103196
51	6	0	-1.951677	2.220361	-0.038231
52	6	0	-3.350837	2.024163	-0.061962
53	6	0	-4.196908	3.118313	0.121122
54	1	0	-5.269628	2.971645	0.150873
55	6	0	-3.706179	4.400442	0.319088
56	6	0	-2.331048	4.589963	0.295301
57	1	0	-1.952727	5.593648	0.445204
58	6	0	-4.637936	5.553600	0.581810
59	1	0	-5.626575	5.373048	0.153573

60	1	0	-4.250377	6.483581	0.158595
61	6	0	4.897644	0.185933	1.186016
62	1	0	5.828981	-0.105084	0.710363
63	6	0	-5.243312	0.446981	-0.454888
64	1	0	-5.917654	1.286196	-0.575291
65	6	0	-5.766874	-0.834768	-0.563247
66	6	0	-4.909392	-1.912667	-0.394757
67	1	0	-5.319833	-2.912499	-0.470116
68	6	0	-7.224167	-1.047473	-0.875706
69	1	0	-7.396952	-1.051934	-1.957242
70	1	0	-7.581002	-2.002774	-0.483784
71	6	0	1.037278	-3.615246	0.087468
72	1	0	-2.950080	-7.206195	0.063142
73	1	0	-7.843295	-0.253968	-0.450168
74	1	0	-4.770512	5.714811	1.657025
75	1	0	2.954103	6.818664	-1.467652
76	34	0	3.699432	-0.642537	-1.294276

Table S9. Atomic coordinates for the DFT calculated structure of **28**$_{SO_2}$:



Zero-point correction= 0.607990 (Hartree/Particle)
Thermal correction to Energy= 0.644501
Thermal correction to Enthalpy= 0.645446
Thermal correction to Gibbs Free Energy= 0.539032
Sum of electronic and zero-point Energies= -2316.847042
Sum of electronic and thermal Energies= -2316.810530
Sum of electronic and thermal Enthalpies= -2316.809586
Sum of electronic and thermal Free Energies= -2316.916000

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	8	0	4.416850	-3.220870	-1.333528
2	6	0	1.875010	-3.363520	-0.629587
3	6	0	2.127170	-4.714517	-0.780846
4	1	0	3.112899	-5.024514	-1.104047
5	6	0	1.118096	-5.637611	-0.545959
6	1	0	1.301536	-6.698580	-0.673157
7	6	0	-0.130257	-5.178207	-0.201610
8	1	0	-0.931805	-5.896232	-0.097479
9	6	0	0.619794	-2.849211	-0.201941
10	6	0	0.295171	-1.416649	-0.035130
11	6	0	-1.074100	-1.032898	-0.089783
12	6	0	-2.118009	-2.029451	0.024589
13	6	0	-1.785184	-3.388182	0.203565
14	6	0	-2.784728	-4.302081	0.536237
15	1	0	-2.530544	-5.332803	0.749753
16	6	0	-4.117841	-3.928678	0.633927
17	6	0	-5.178526	-4.937117	0.986378
18	1	0	-6.022555	-4.465969	1.495500
19	1	0	-4.783423	-5.719517	1.638812
20	6	0	-4.446993	-2.606470	0.376175
21	1	0	-5.484115	-2.307991	0.469745
22	6	0	-3.479187	-1.650464	0.067808
23	6	0	-3.843997	-0.254953	-0.152938
24	6	0	-2.827334	0.723418	-0.138630
25	6	0	-1.436277	0.334434	-0.088857
26	6	0	-0.435446	1.330089	-0.101060
27	6	0	0.921213	0.954761	-0.029735
28	6	0	1.256694	-0.401613	0.180784
29	6	0	2.534685	-0.684547	0.906439
30	6	0	3.542113	-1.538157	0.469598
31	6	0	-3.190841	2.088521	-0.198913
32	6	0	4.877574	-1.142317	2.410462
33	1	0	5.778329	-1.311709	2.990129
34	6	0	3.883306	-0.291669	2.884939
35	1	0	4.005634	0.202286	3.843263
36	6	0	2.730507	-0.066329	2.146429
37	1	0	1.965238	0.601467	2.525230
38	6	0	1.944404	1.996236	-0.204575
39	6	0	3.253283	1.686254	-0.620693
40	1	0	3.500758	0.668782	-0.880483
41	6	0	4.209952	2.661357	-0.781865
42	1	0	5.205418	2.381973	-1.114456

43	6	0	3.904926	4.010259	-0.557368
44	6	0	1.600329	3.353867	-0.080617
45	6	0	2.600166	4.329750	-0.237565
46	1	0	2.342938	5.378138	-0.148521
47	6	0	4.959700	5.071947	-0.710895
48	1	0	4.532161	6.074617	-0.642365
49	1	0	5.725183	4.981669	0.066741
50	6	0	0.196009	3.727480	0.095383
51	6	0	-0.800340	2.730358	-0.039567
52	6	0	-2.159502	3.110709	-0.030036
53	6	0	-2.493514	4.449367	0.183814
54	1	0	-3.534369	4.743255	0.241096
55	6	0	-1.526428	5.423148	0.379093
56	6	0	-0.190143	5.046801	0.319725
57	1	0	0.562692	5.812090	0.464961
58	6	0	-1.908310	6.850163	0.670337
59	1	0	-2.945256	7.050365	0.391930
60	1	0	-1.270688	7.551721	0.125943
61	6	0	4.703814	-1.778210	1.190900
62	1	0	5.444382	-2.455490	0.781536
63	6	0	-4.528520	2.427895	-0.397977
64	1	0	-4.809849	3.468783	-0.502703
65	6	0	-5.524273	1.465934	-0.503893
66	6	0	-5.168344	0.133198	-0.354216
67	1	0	-5.945516	-0.618237	-0.427114
68	6	0	-6.948405	1.858754	-0.793694
69	1	0	-7.125212	1.925536	-1.872516
70	1	0	-7.653767	1.127659	-0.391664
71	6	0	-0.405537	-3.811311	-0.034443
72	1	0	-5.569962	-5.426920	0.088304
73	1	0	-7.188693	2.833906	-0.363162
74	1	0	-1.803157	7.076058	1.736763
75	1	0	5.469747	4.986924	-1.674977
76	16	0	3.273412	-2.344533	-1.072048
77	8	0	2.878917	-1.361375	-2.080150

Table S10. Major transitions of **5**$_{\mathbf{O}}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	2.8601	433.49	0.0018	H-1 -> L -0.54035 H -> L+1 -0.47395 H -> L+2 0.11288	50.8738 44.9257 2.5484
2	2.9920	414.39	0.0206	H -> L -0.55660 H-1 -> L+1 0.41803	61.9607 34.9498
3	3.3572	369.31	0.3023	H-2 -> L -0.13759 H-1 -> L 0.33626 H -> L+1 -0.45290 H -> L+2 -0.38485	3.7862 22.6142 41.0237 29.6219
4	3.3732	367.56	0.3737	H-2 -> L+1 0.13238 H-> L+1 -0.49786 H-1 -> L+2 -0.34070 H -> L -0.32072	3.5049 49.5729 23.2153 20.5723
5	3.5160	352.63	0.3485	H-2 -> L -0.30762 H-1 -> L -0.34011 H -> L+1 0.23953 H -> L+2 -0.45993	18.9260 23.1350 11.4749 42.3071
6	3.5239	351.83	0.4839	H-3 -> L 0.12357 H-2 -> L+1 0.24695 H-1 -> L+1 0.25265 H-1 -> L+2 -0.51700 H -> L 0.27005	3.0539 12.1969 12.7664 53.4578 14.5854
7	3.7588	329.85	0.0966	H-2 -> L 0.59328 H -> L+2 -0.32259	70.3962 20.8129
8	3.8022	326.08	0.1012	H-2 -> L+1 0.59372 H-2 -> L+2 -0.12800 H-1 -> L+2 0.28700 H -> L+3 0.11469	70.5007 3.2768 16.4738 2.6308
9	3.8777	319.73	0.0035	H-3 -> L 0.54709 H-2 -> L+1 -0.14570 H-1 -> L+4 0.11823 H -> L+3 0.36976	59.8615 4.2457 2.7957 27.3445

Table S11. Major transitions of **17**$_{\mathrm{S}}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	2.8297	438.16	0.0106	H -> L 0.43418 H -> L+1 0.34076 H-1 -> L -0.31238 H-1 -> L+1 0.28615	37.7025 23.2235 19.5163 16.3764
2	2.9836	415.55	0.0376	H -> L -0.41951 H -> L+1 0.37731 H-1 -> L -0.35677 H-1 -> L+1 -0.20895	35.1977 28.4726 25.4570 8.7320
3	3.3493	370.18	0.5659	H-1 -> L 0.46494 H -> L+1 0.46410 H -> L+2 -0.20888	43.2338 43.0778 8.7262
4	3.4011	364.54	0.5460	H-1 -> L+1 -0.58555 H -> L 0.33869	68.5738 22.9422
5	3.5333	350.90	0.1367	H -> L+2 -0.57740 H-2 -> L -0.22717 H -1-> L -0.20237 H-2 -> L+1 0.16078	66.6782 10.3212 8.1907 5.1700
6	3.6053	343.90	0.0264	H-1 -> L+2 0.44861 H-2 -> L 0.34755 H-3 -> L 0.27993 H-2 -> L+1 0.24642	40.2502 24.1582 15.6722 12.1446
7	3.6992	335.17	0.0410	H-3 -> L 0.47551 H-1 -> L+2 -0.38637 H-2->L 0.23354 H-2->L+1 -0.14617	45.2220 29.8564 10.9082 4.2731
8	3.7862	327.46	0.0573	H-2 -> L 0.46450 H-3 -> L -0.36344 H -> L+2 -0.24211 H -> L+3 -0.20780 H-1->L+2 -0.11944 H-2->L+1 -0.11550	43.1521 26.4177 11.7235 8.6362 2.8532 2.6681
9	3.8823	319.36	0.0103	H -> L+3 -0.42474 H-2 -> L+1 -0.35859 H-3 -> L+1 0.21539 H-1-> L+2 0.20796 H-2->L -0.16386 H-3->L 0.16016	36.0808 25.7174 9.2786 8.6495 5.3700 5.1302

Table S12. Major transitions of **18**$_{\text{Se}}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	2.8322	437.77	0.0101	H -> L 0.43764	38.3058
				H -> L+1 0.34064	23.2071
				H-1 -> L -0.30468	18.5660
				H-1 -> L+1 0.28841	16.6361
2	2.9864	415.16	0.0368	H -> L 0.41533	34.4998
				H -> L+1 -0.38914	30.2860
				H-1 -> L 0.35080	24.6121
				H-1 -> L+1 0.20597	8.4847
3	3.3510	369.99	0.5585	H-1 -> L 0.47176	44.5115
				H -> L+1 0.45741	41.8448
				H -> L+2 -0.21970	9.6536
4	3.3980	364.88	0.5108	H-1 -> L+1 0.57424	65.9503
				H -> L -0.32838	21.5667
				H-2->L -0.14321	4.1018
5	3.5061	353.62	0.0847	H-2 -> L 0.54240	58.8396
				H -> L+2 0.36796	27.0789
				H-1 -> L 0.14660	4.2983
6	3.5478	349.47	0.0986	H -> L+2 0.46202	42.6925
				H-2 -> L -0.31776	20.1943
				H-3 -> L -0.26933	14.5077
				H-1 -> L 0.15122	4.5735
				H-3->L+1 0.13545	3.6693
				H-1->L+1 -0.13478	3.6331
				H-2->L+1 -0.12501	3.1255
7	3.6361	340.98	0.0385	H-1 -> L+2 0.56351	63.5087
				H-2 -> L+1 0.25518	13.0234
				H-3->L -0.22946	10.5304
				H-3->L+1 -0.14411	4.1535
8	3.7745	328.48	0.0204	H-2 -> L+1 0.50610	51.2274
				H-3 -> L 0.31648	20.0319
				H -> L+2 0.17963	6.4534
				H-3 -> L+1 0.16233	5.2702
				H-2->L -0.15193	4.6165
				H-2->L+2 0.14041	3.9430

				H -> L+3 0.13666	3.7352
9	3.7964	326.58	0.0619	H-3 -> L 0.43725	38.2375
				H-2 -> L+1 -0.28803	16.5923
				H-3 -> L+1 -0.27402	15.0174
				H-1-> L+2 0.21483	9.2304
				H->L+2 -0.17589	6.1875
				H->L+2 0.15450	4.7740
				H->L+3 0.14336	4.1104

Table S13. Major transitions of **24**$_{\mathbf{SO}}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	2.8313	437.91	0.0227	H -> L 0.46731	43.6757
				H -> L+1 -0.30437	18.5282
				H-1 -> L 0.30282	18.3400
				H-1 -> L+1 0.28743	16.5232
2	2.9830	415.63	0.0412	H-1-> L 0.40234	32.3755
				H -> L -0.39600	31.3632
				H -> L+1 -0.37105	27.5356
				H-1 -> L+1 -0.18040	6.5088
3	3.3705	367.85	0.5913	H -> L+1 0.48892	47.8086
				H-1-> L 0.44924	40.3633
				H -> L+2 -0.16407	5.3838
4	3.4179	362.75	0.5908	H-1 -> L+1 0.59154	69.9839
				H -> L -0.32355	20.9369
				H->L+1 0.10803	2.3341
5	3.5452	349.72	0.0634	H -> L+2 0.53428	57.0910
				H-2 -> L 0.34485	23.7843
				H-2-> L+1 0.16929	5.7318
				H-1 -> L 0.15720	4.9424
6	3.6360	340.99	0.0199	H-2 -> L+2 0.48352	46.7583
				H-2 -> L -0.31204	19.4738
				H-2 -> L+1 0.28773	16.5577
				H-3 ->L -0.16867	5.6899
				H-1 ->L+2 0.15240	4.6452
7	3.7389	331.60	0.0307	H-3 -> L 0.63994	81.9046
				H-2 -> L -0.18368	6.7477
				H->L+2 0.15599	4.8666

8	3.7667	329.15	0.0790	H-2 -> L 0.46068 H-1 -> L+2 0.36643 H -> L+2 -0.26065 H-3 -> L 0.18400 H-2->L+1 0.11019	42.4452 26.8542 13.5877 6.7712 2.4284
9	3.8859	319.06	0.0135	H-2 -> L+1 0.41712 H -> L+3 0.41710 H-1 -> L+2 -0.23121 H-3-> L+1 -0.15263 H->L+2 -0.13612 H-2->L -0.10677	34.7978 34.7945 10.6916 4.6592 3.7057 2.2800

Table S14. Major transitions of **26$_{SeO}$** calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	3.0872	401.60	0.0174	H -> L 0.40827 H-1 -> L 0.35754 H -> L+1 0.34431 H-1 -> L+1 -0.26164	33.3369 25.5670 23.7099 13.6911
2	3.2257	384.36	0.0392	H-> L 0.44343 H-1 -> L -0.36473 H -> L+1 -0.31913 H-1 -> L+1 -0.23452	39.3260 26.6056 20.3688 10.9999
3	3.5945	344.93	0.4666	H -> L+1 0.48325 H-1-> L -0.40153 H -> L+2 -0.25713	46.7061 32.2453 13.2232
4	3.6372	340.88	0.5908	H-1 -> L+1 0.57746 H -> L 0.32958 H->L+2 -0.12567	66.6920 21.7246 3.1586
5	3.6986	335.22	0.1385	H -> L+2 0.48054 H-2 -> L -0.35754 H-1-> L -0.23385 H -> L+1 0.14890 H-2 -> L+1 0.12405 H-1 -> L+2 -0.10935 H-1 -> L+1 0.10083	46.1837 25.5670 10.9372 4.4342 3.0777 2.3915 2.0333

6	3.7754	328.40	0.0675	H-1 -> L+2 0.50997	52.0139
				H-2 -> L+1 0.31345	19.6502
				H-2 -> L 0.24881	12.3813
				H ->L+2 0.14260	4.0670
7	3.8968	318.17	0.0859	H-2 -> L 0.50890	51.7958
				H -> L+2 0.30815	18.9913
				H-1->L+2 -0.30295	18.3557
				H-3->L -0.13373	3.5767
8	3.9601	313.09	0.0155	H-3 -> L 0.66651	88.8471
				H-1 -> L+2 -0.10569	2.2341
				H-2 -> L 0.10284	2.1152
9	4.0232	308.18	0.0164	H-2 -> L+1 0.45155	40.7795
				H -> L+3 0.38027	28.9211
				H-1 -> L+2 -0.23053	10.6288
				H->L+2 -0.15322	4.6953
				H-4->L -0.10159	2.0641

Table S15. Major transitions of **28**$_{\mathbf{SO2}}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description	Absolute contributions (%)
1	3.0411	407.70	0.0060	H -> L 0.46858	43.9134
				H-1 -> L+1 -0.32377	20.9654
				H -> L+1 0.31246	19.5263
				H-1 -> L 0.24932	12.4321
2	3.1739	390.63	0.0256	H-> L+1 0.44572	39.7333
				H-1 -> L 0.35724	25.5241
				H -> L -0.35364	25.0122
				H-1 -> L+1 0.19947	7.9577
3	3.4998	354.26	0.3356	H -> L+2 0.42619	36.3276
				H-1-> L 0.35168	24.7358
				H-1 -> L+1 0.25548	13.0540
				H -> L+1 -0.24947	12.4471
				H -> L 0.16998	5.7786
				H-1 -> L+2 -0.10759	2.3151
4	3.5478	349.47	0.3965	H-1 -> L+1 0.46203	42.6943
				H -> L 0.29519	17.4274
				H-1->L -0.26081	13.6044
				H->L+1 0.23369	10.9222
				H-1->L+2 -0.19133	7.3214

5	3.5636	347.92	0.3792	H-1 -> L+2	0.51983	54.0446
				H-1 -> L	-0.30288	18.3473
				H -> L+1	0.26901	14.4733
				H-1 -> L+1	-0.13227	3.4991
6	3.6649	338.30	0.0846	H-1 -> L+2	0.59949	71.8777
				H-1 -> L+1	0.18537	6.8724
				H-2 -> L+1	-0.16081	5.1720
				H-2 ->L	-0.15218	4.6318
				H ->L	0.13725	3.7675
7	3.8100	325.42	0.0134	H-2 -> L	0.57288	65.6383
				H-2 -> L+1	-0.25548	13.0540
				H->L+3	-0.23035	10.6122
				H->L+2	-0.12609	3.1797
8	3.8644	320.84	0.0046	H-2 -> L+1	0.51163	52.3531
				H-2 -> L	0.30149	18.1792
				H-1 -> L+2	0.23052	10.6279
				H -> L+3	0.22085	9.7549
				H-1 -> L+3	0.11247	2.5299
9	4.0916	303.02	0.1773	H -> L+3	0.50956	51.9303
				H -> L+4	-0.24641	12.1436
				H-2 -> L+1	-0.23504	11.0488
				H-1->L+3	-0.20455	8.3681
				H-3->L	0.11872	2.8189
				H-2->L	0.10940	2.3937
				H-1->L+4	0.10241	2.0976

Reference:

[S1] Jia, X. et al, Design and Applications of a SO_2 Surrogate in Palladium-Catalyzed Direct Aminosulfonylation between Aryl Iodides and Amines. *Angew. Chem. Int. Ed.* **2021**, *60*, 7353.

[S2] Taniguchi, N., Diarylation of Chalcogen Elements using Arylboronic acids via Copper- or Palladium-catalyzed Oxidative Coupling. *Tetrahedron* **2016**, *72*, 5818.

[S3] Janosik, T. et al, A New Concise Strategy for Synthesis of Dibenzo[b,f]thiepins and Related Fused Symmetrical Thiepin Derivatives. *J. Org. Chem.* **2007**, *72*, 8984.

[S4] Bertozzi, C. R. et al, Synthesis and Reactivity of Dibenzoselenacycloheptynes. *Org. Lett.* **2013**, *15*, 3038.

[S5] Gilheany, D. G. et al, Co-operative ortho-effects on the Wittig reaction. Interpretation of Stereoselectivity in the Reaction of Ortho-halo-substituted Benzaldehydes and Benzylidenetriphenylphosphoranes. *Tetrahedron Lett.* **2002**, *43*, 2449.

[S6] R. H. Martin et al, Thermal Racemisation of Hepta-, Octa-, and Nonahelicene: Kinetic Results, Reaction Path and Experimental Proofs that the Racemisation of Hexa- and Heptahelicene Does not Involve an Intramolecular Double Diels-Alder Reaction. *Tetrahedron* **1974**, *30*, 347.

[S7] T. B. J. Hall, B. R. Hoggard, C. B. Larsen, N. T. Lucas, *Chem.-Asian J.* **2019**, *14*, 1106

[S8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci , G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16, Gaussian, Inc., Wallingford CT, **2016**

Spectra (^{1}H NMR and ^{13}C NMR)

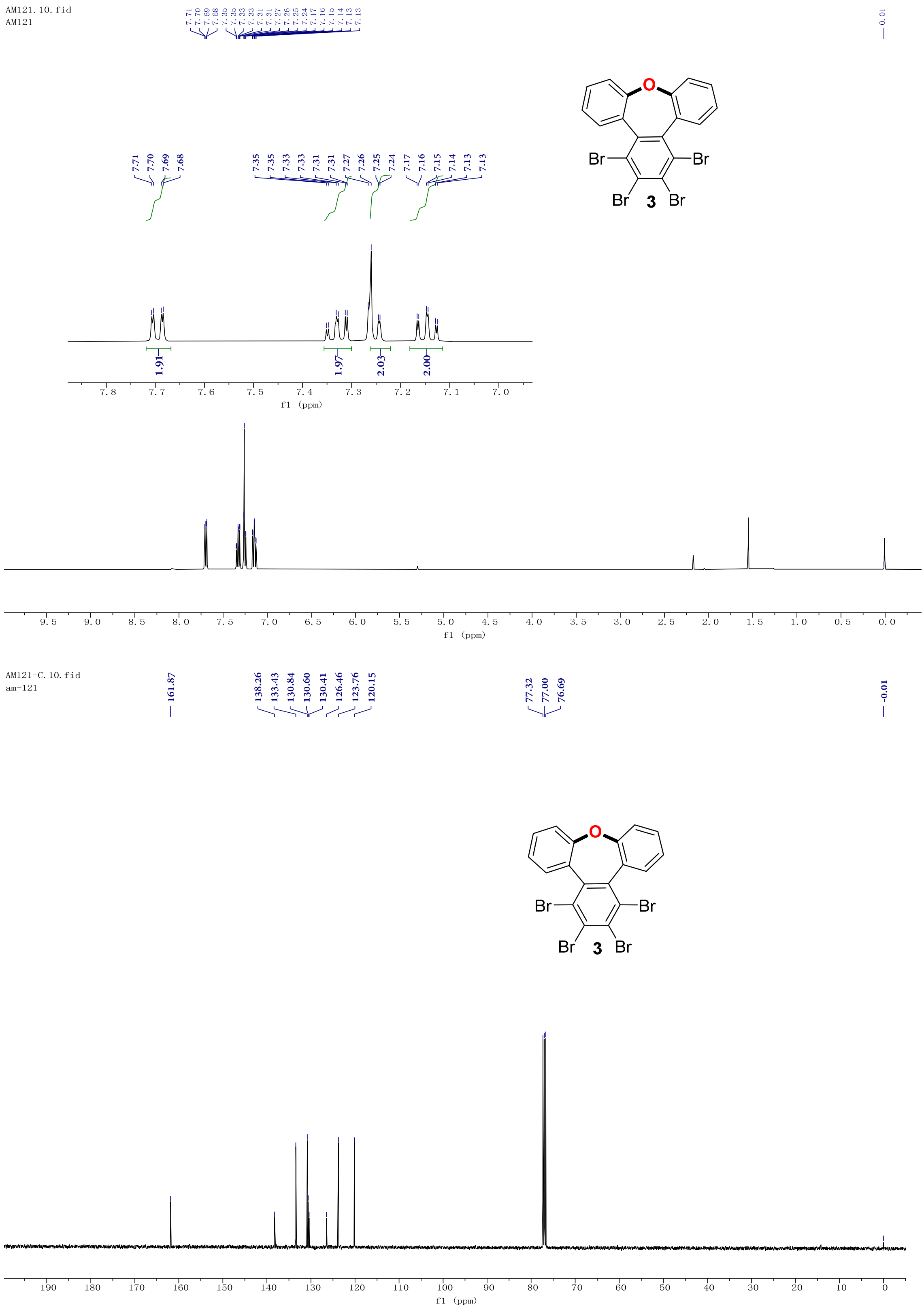


Figure S29. ^{1}H NMR (up) and ^{13}C NMR (down) of **3** in $CDCl_3$.

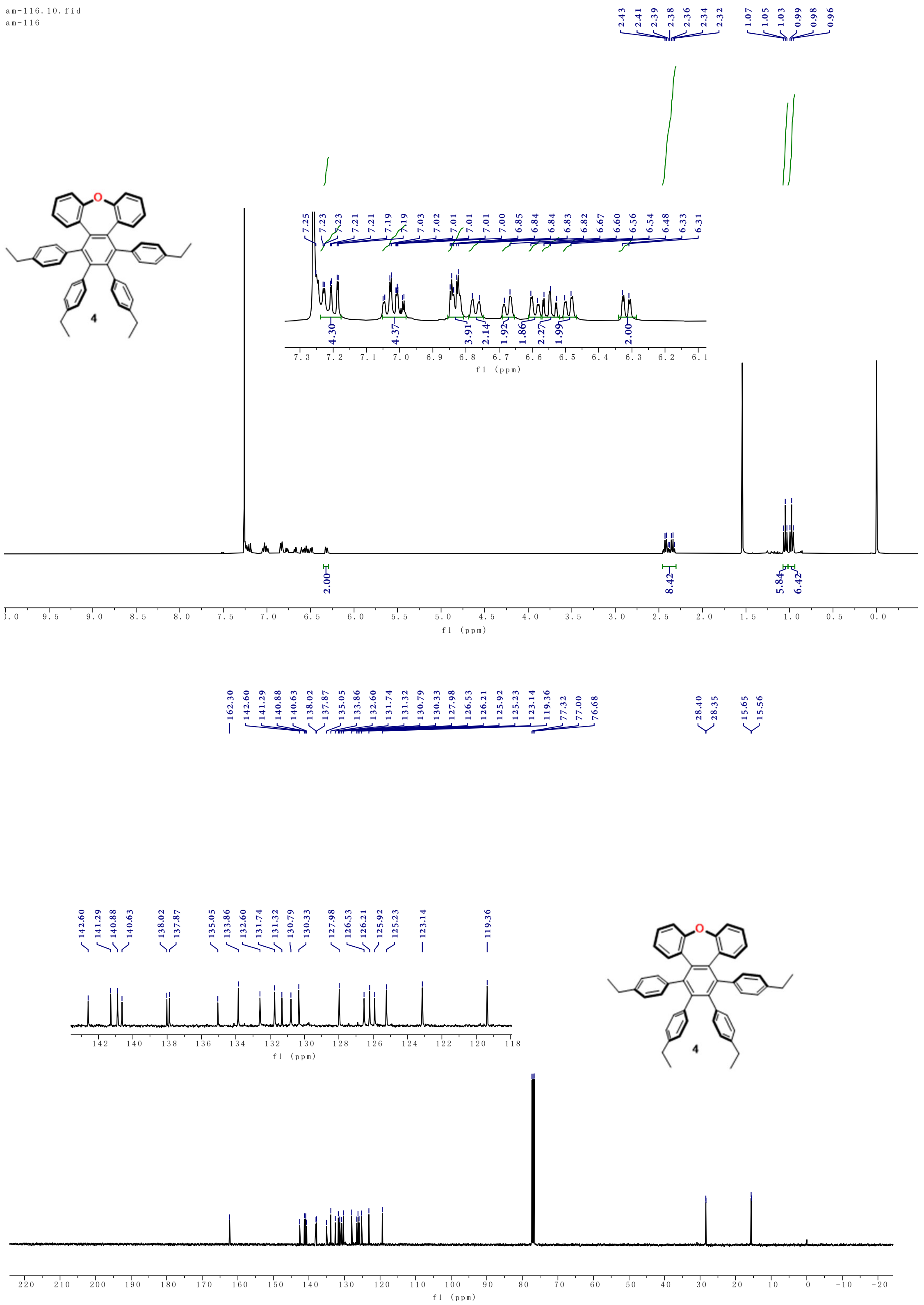


Figure S30. ^{1}H NMR (up) and ^{13}C NMR (down) of **4** in CDCl$_3$.

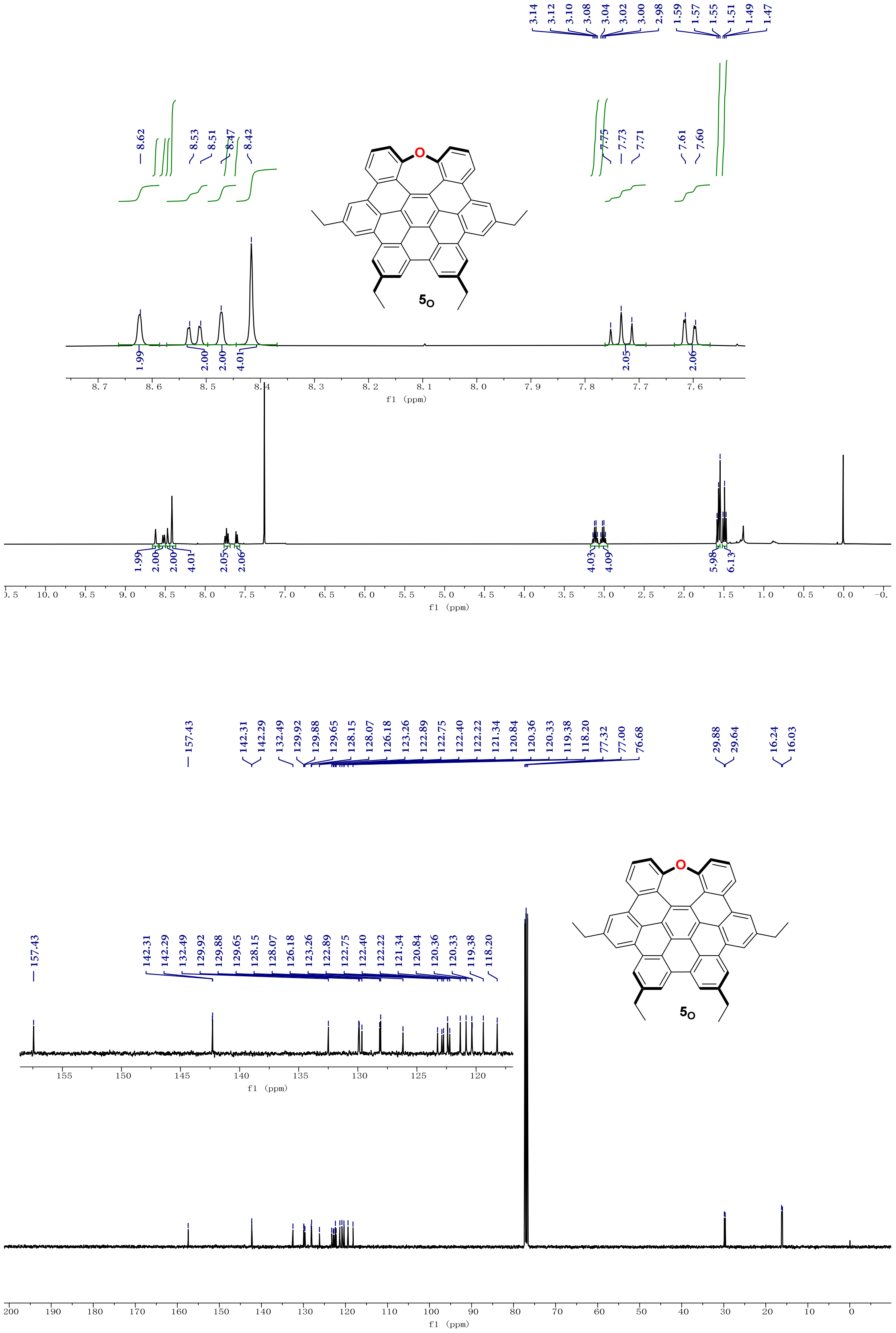
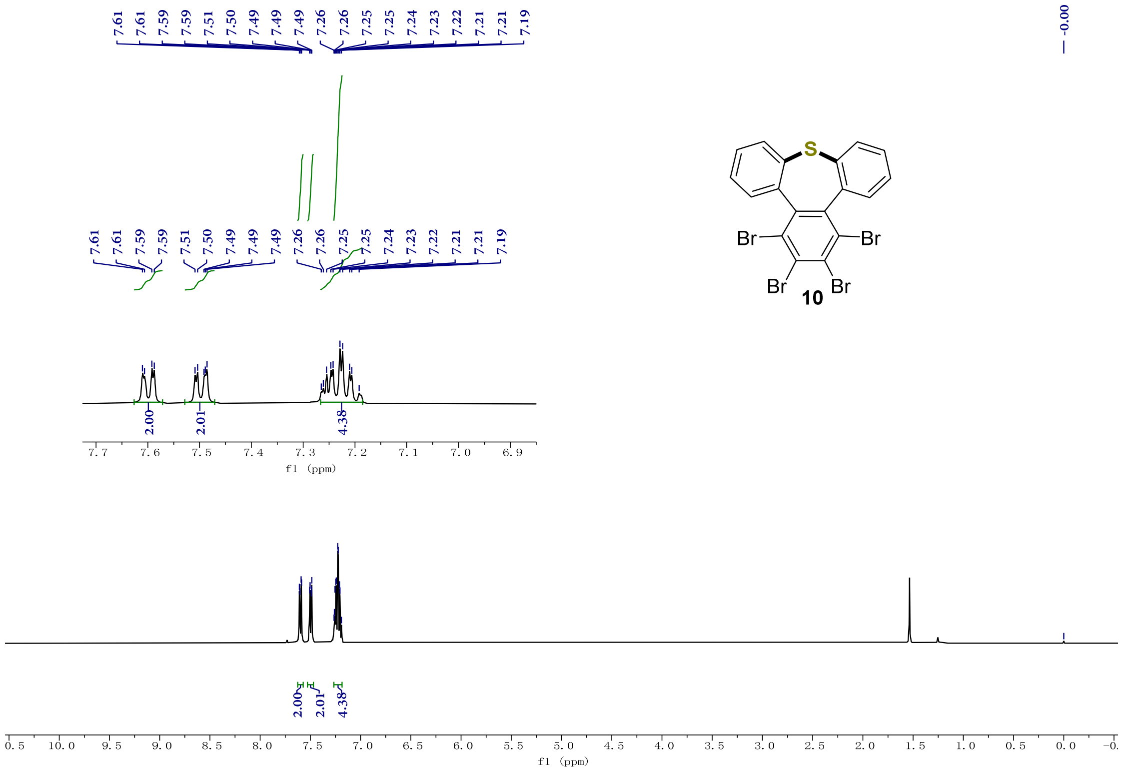


Figure S31. ^{1}H NMR (up) and ^{13}C NMR (down) of **5$_\mathrm{O}$** in CDCl$_3$.



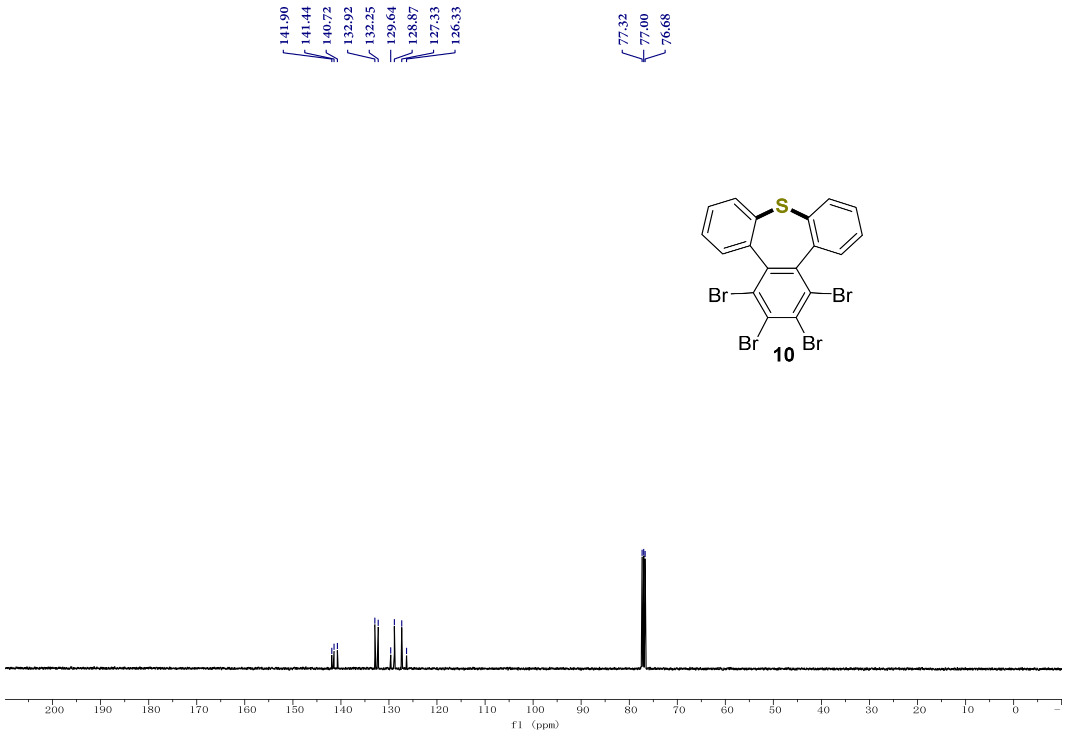


Figure S32. ^{1}H NMR (up) and ^{13}C NMR (down) of **10** in $CDCl_3$.

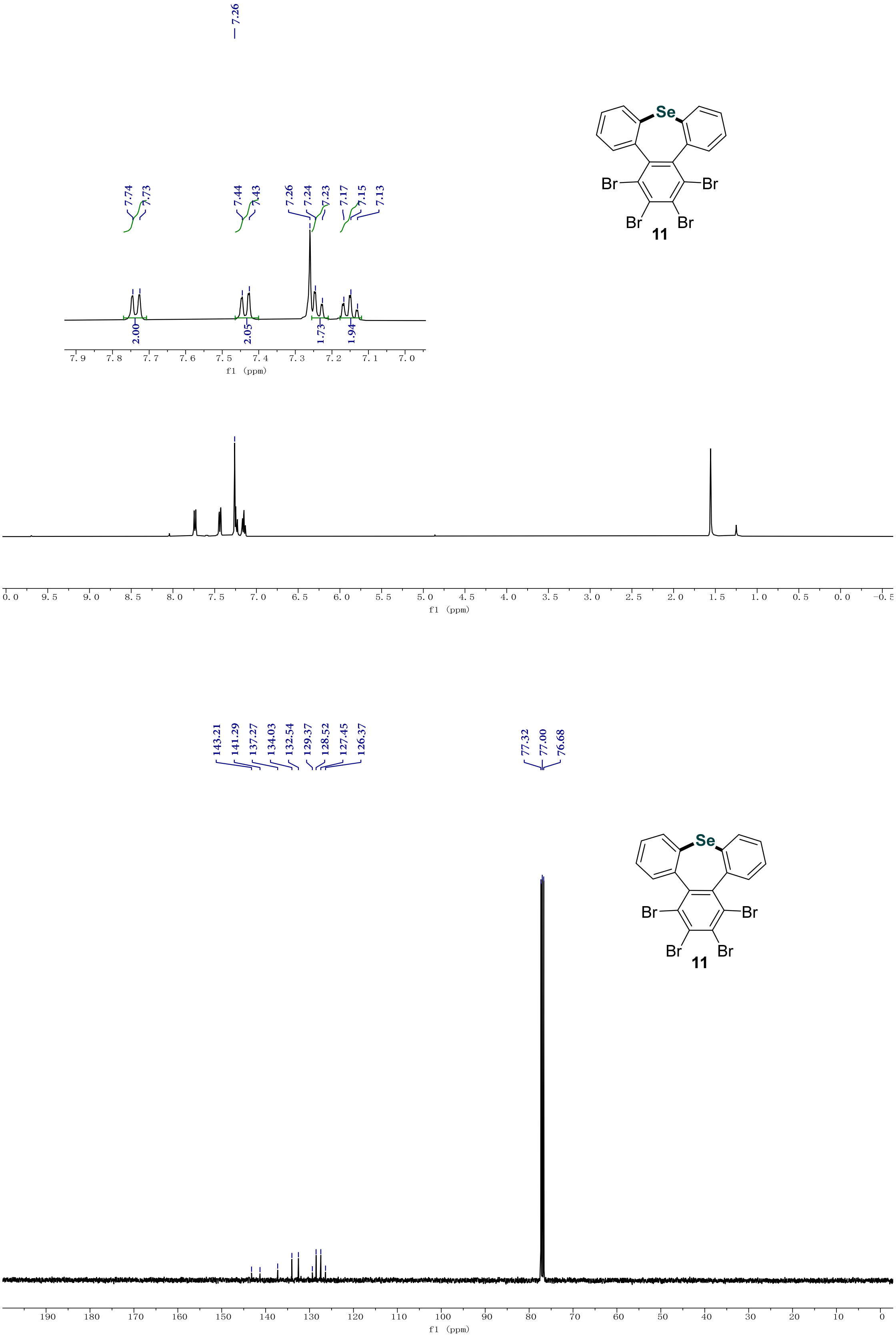


Figure S33. ^{1}H NMR (up) and ^{13}C NMR (down) of **11** in $CDCl_3$.

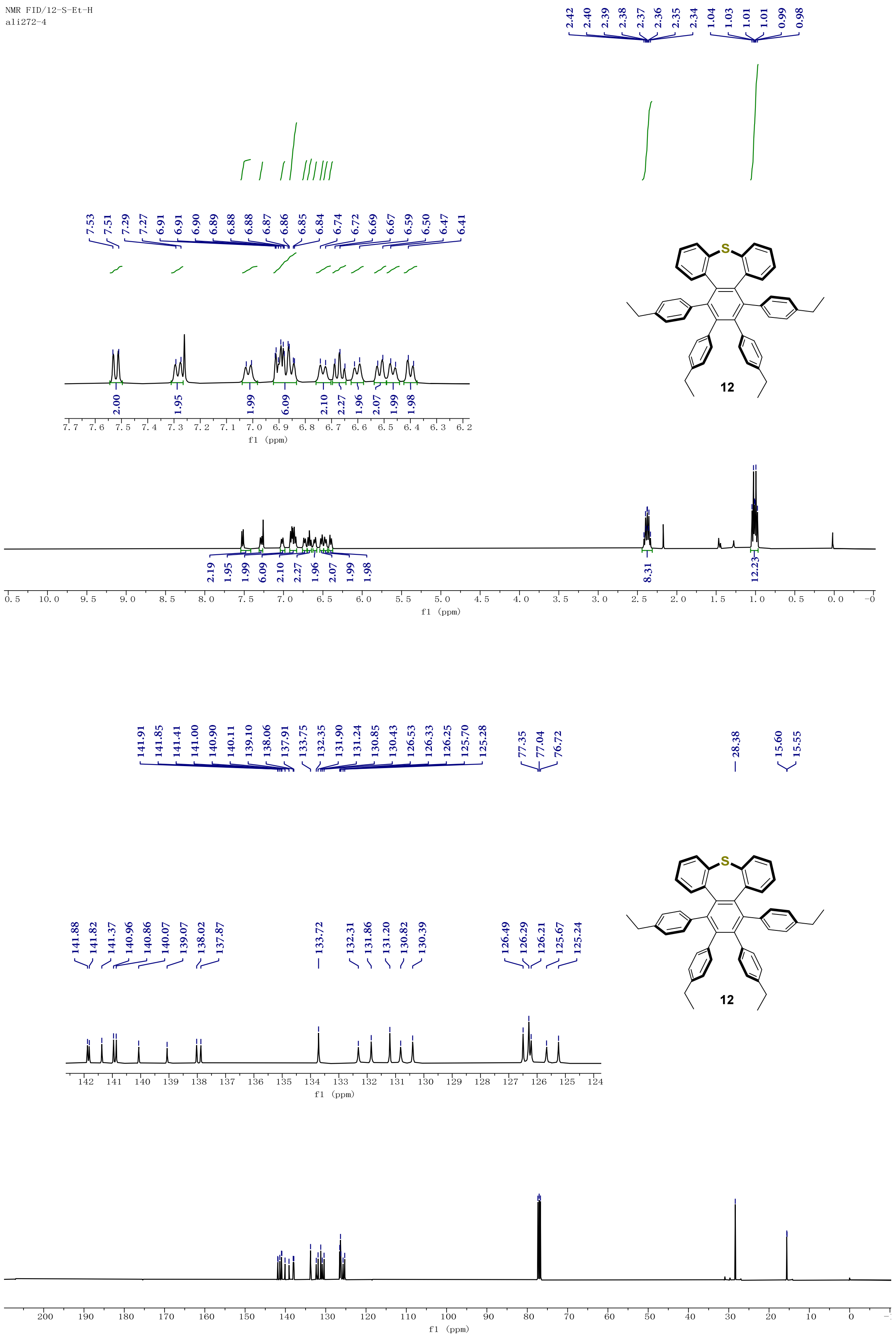


Figure S34. ^{1}H NMR (up) and ^{13}C NMR (down) of **12** in $CDCl_3$.

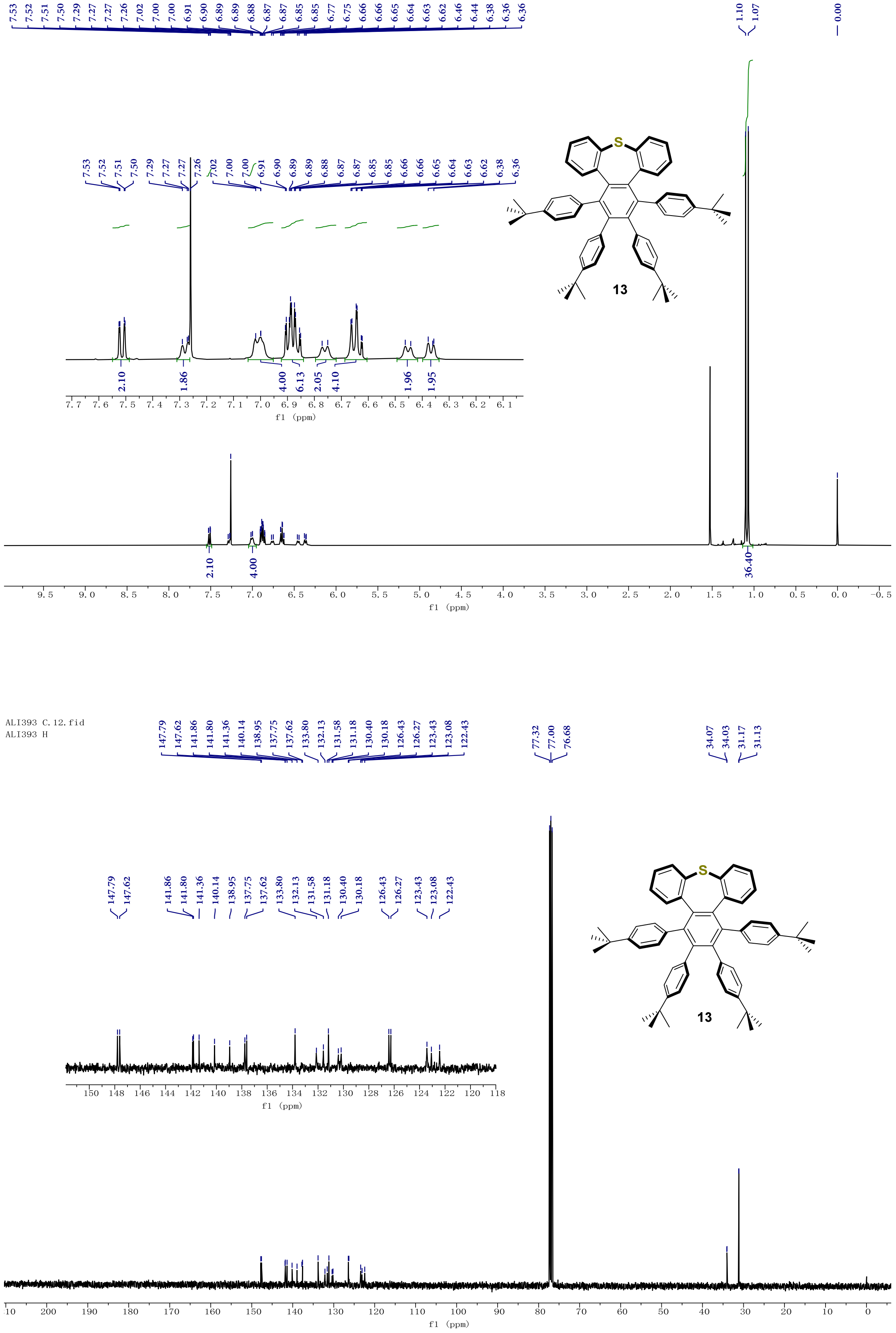
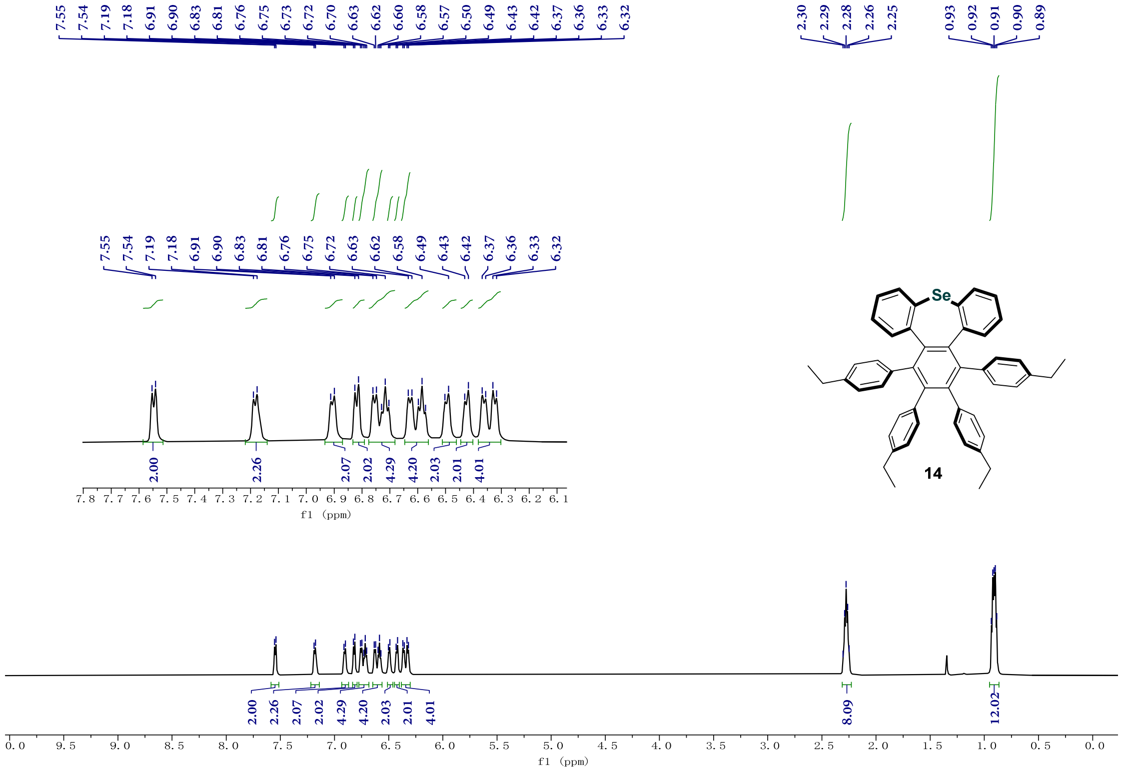


Figure S35. ^{1}H NMR (up) and ^{13}C NMR (down) of **13** in $CDCl_3$.



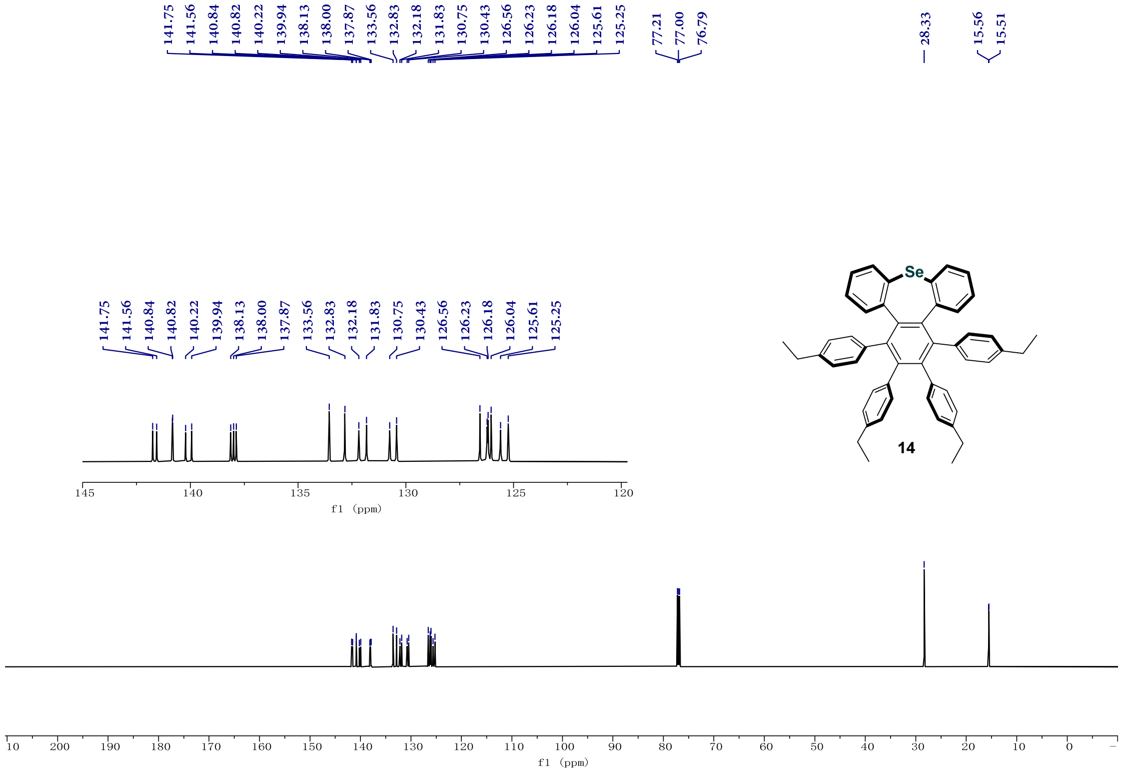


Figure S36. ^{1}H NMR (up) and ^{13}C NMR (down) of **14** in $CDCl_3$.

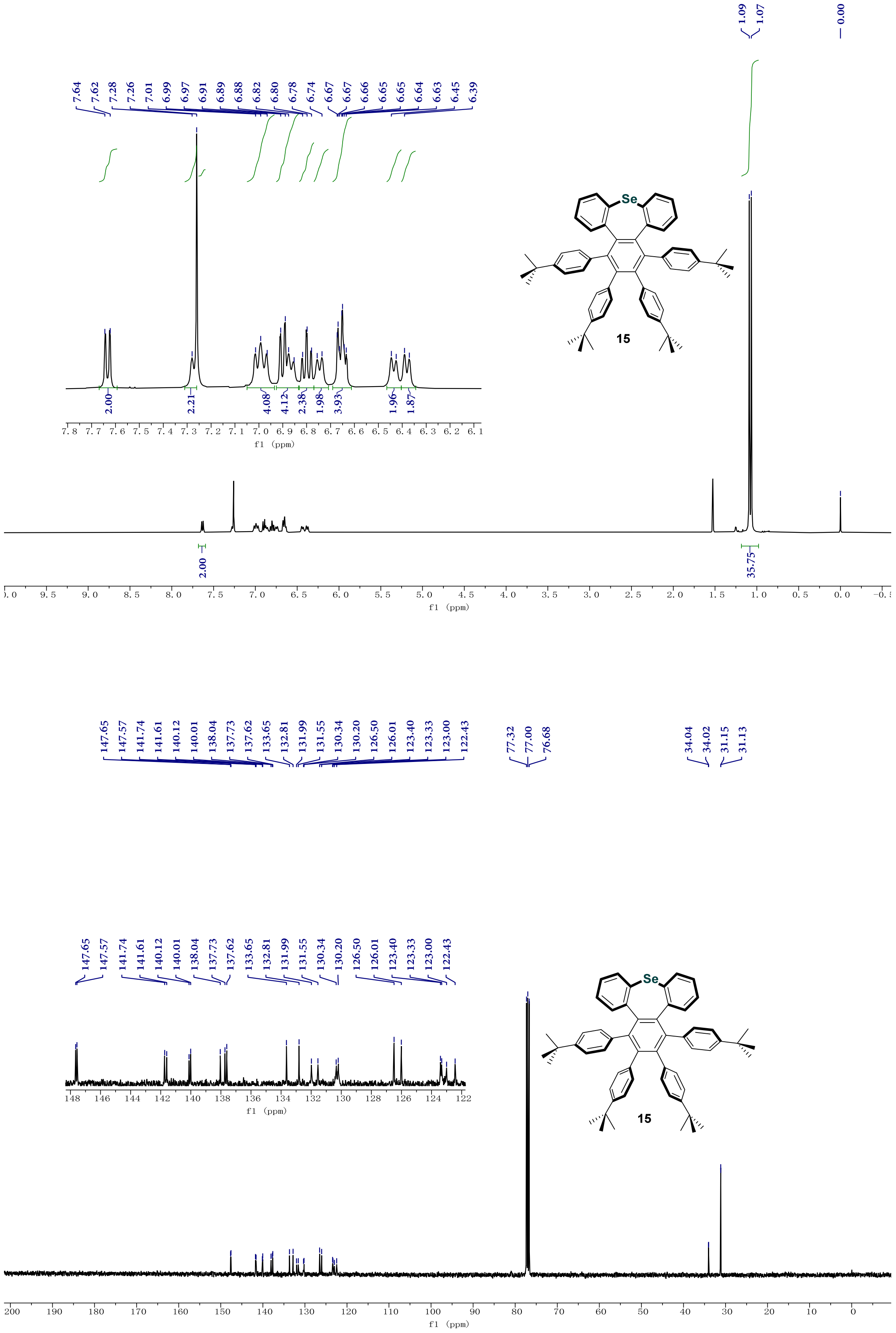


Figure S37. ^{1}H NMR (up) and ^{13}C NMR (down) of **15** in $CDCl_3$.

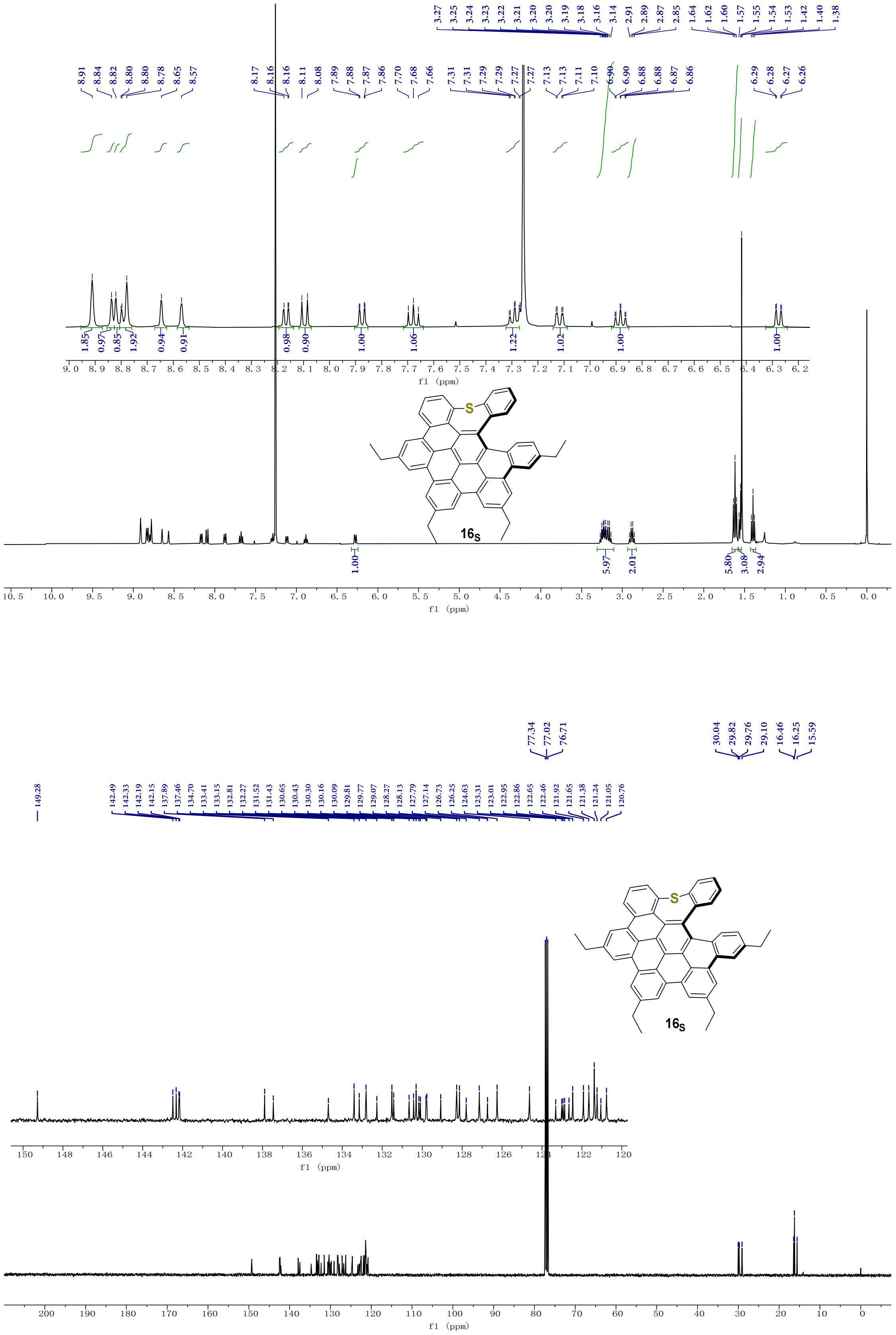


Figure S38. ^{1}H NMR (up) and ^{13}C NMR (down) of **16_S** in $CDCl_3$.

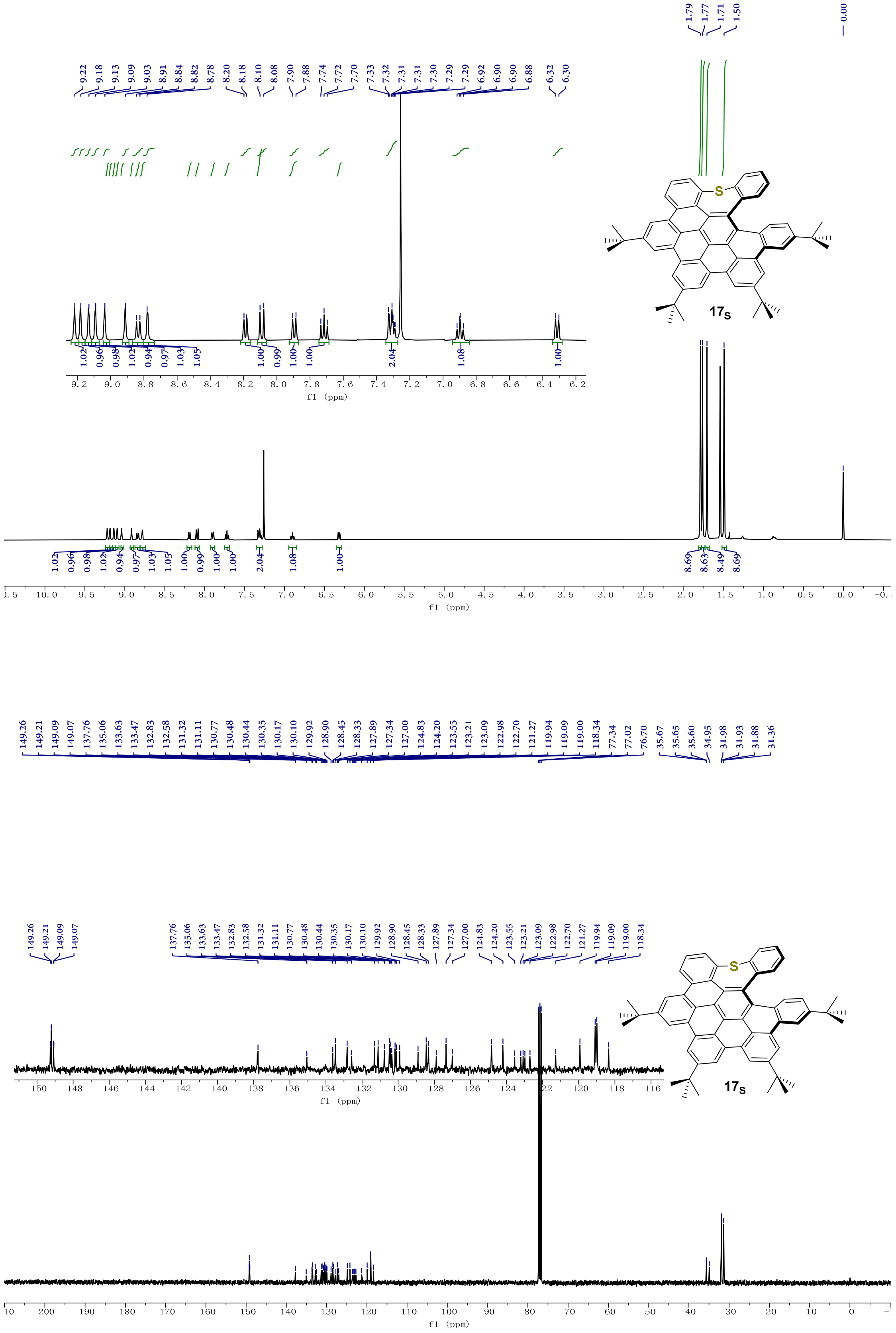


Figure S39. ^{1}H NMR (up) and ^{13}C NMR (down) of **17$_{S}$** in CDCl$_3$.

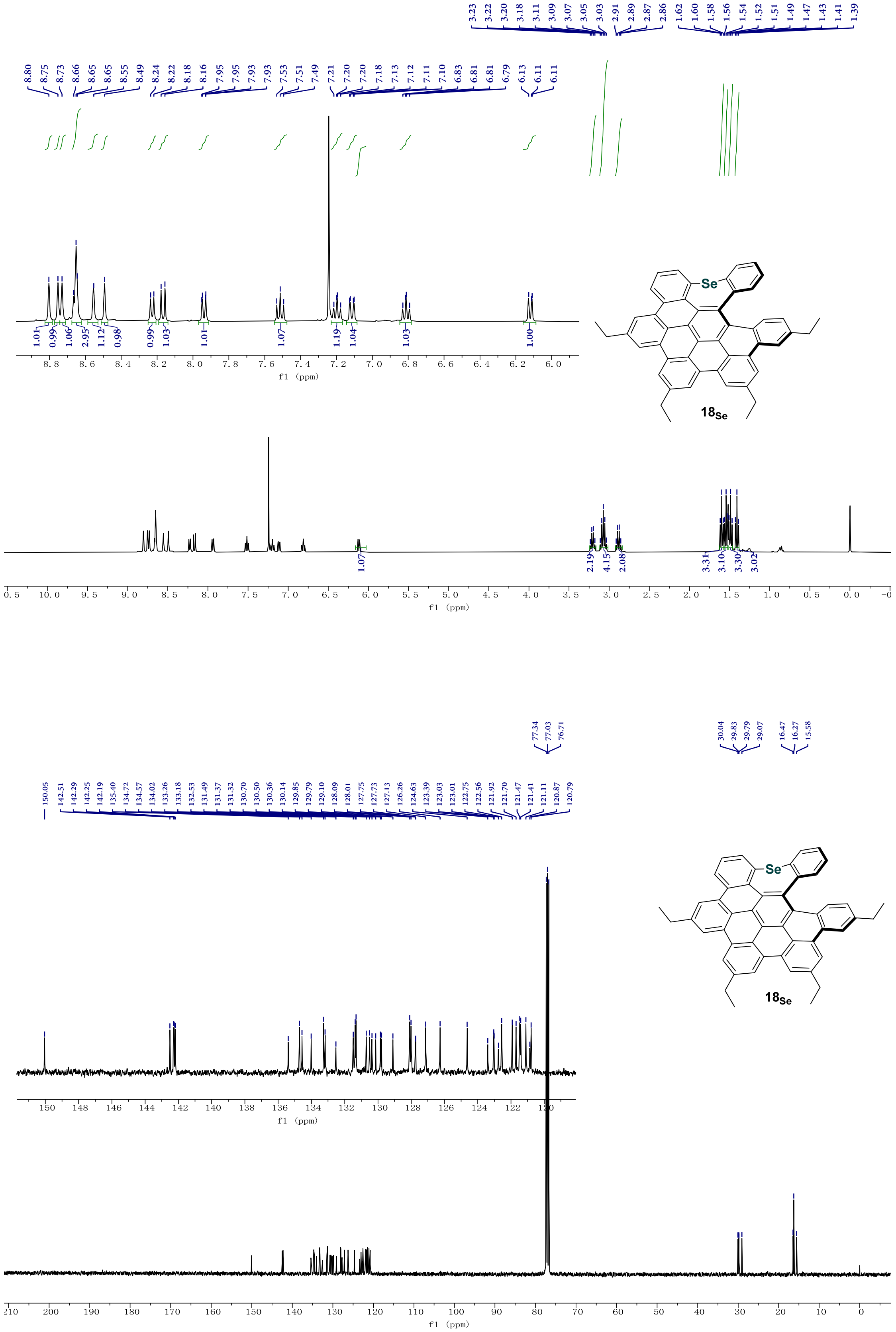


Figure S40. ^{1}H NMR (up) and ^{13}C NMR (down) of **18_{Se}** in CDCl$_3$.

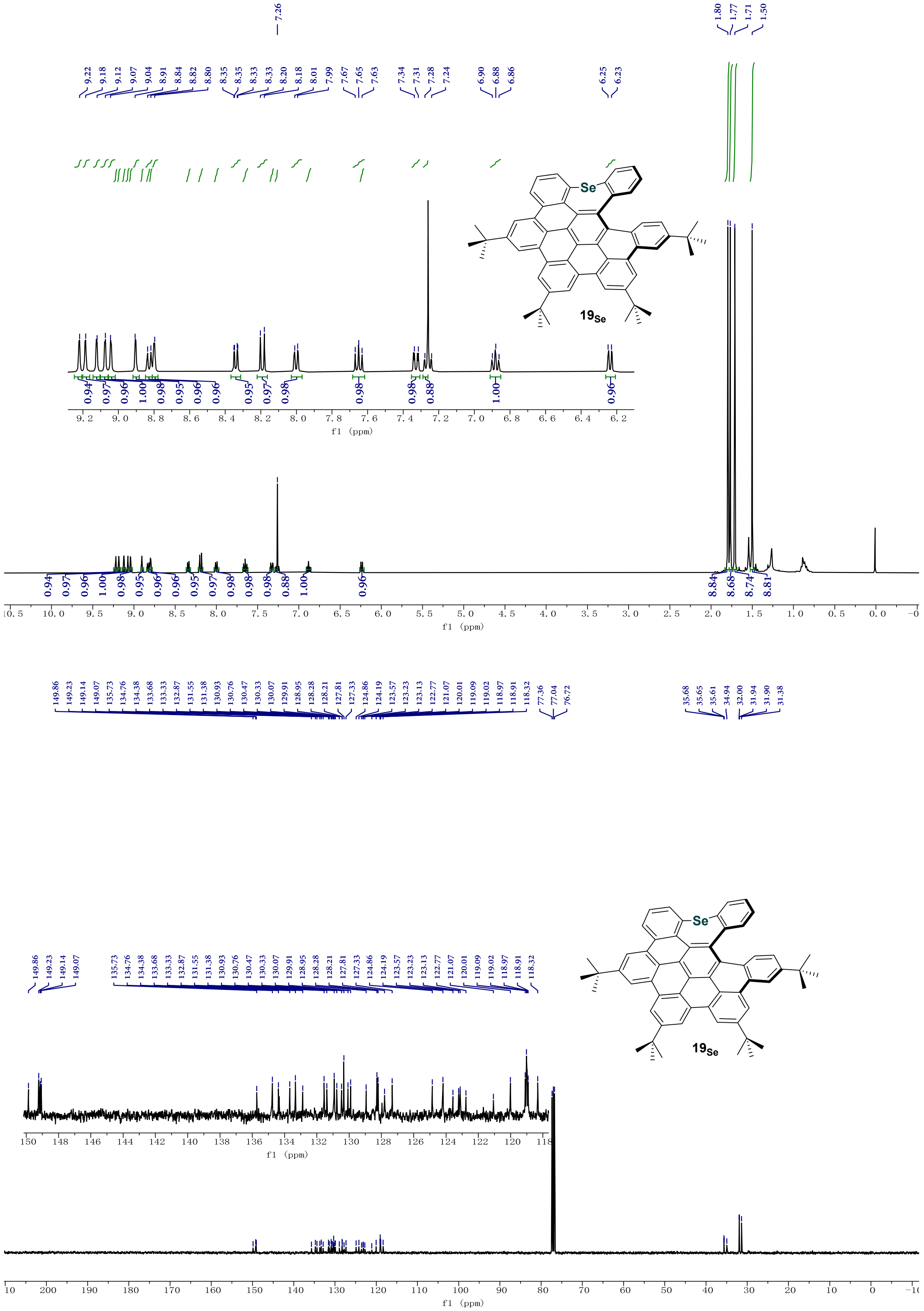


Figure S41. ^{1}H NMR (up) and ^{13}C NMR (down) of **19$_{Se}$** in CDCl$_3$.

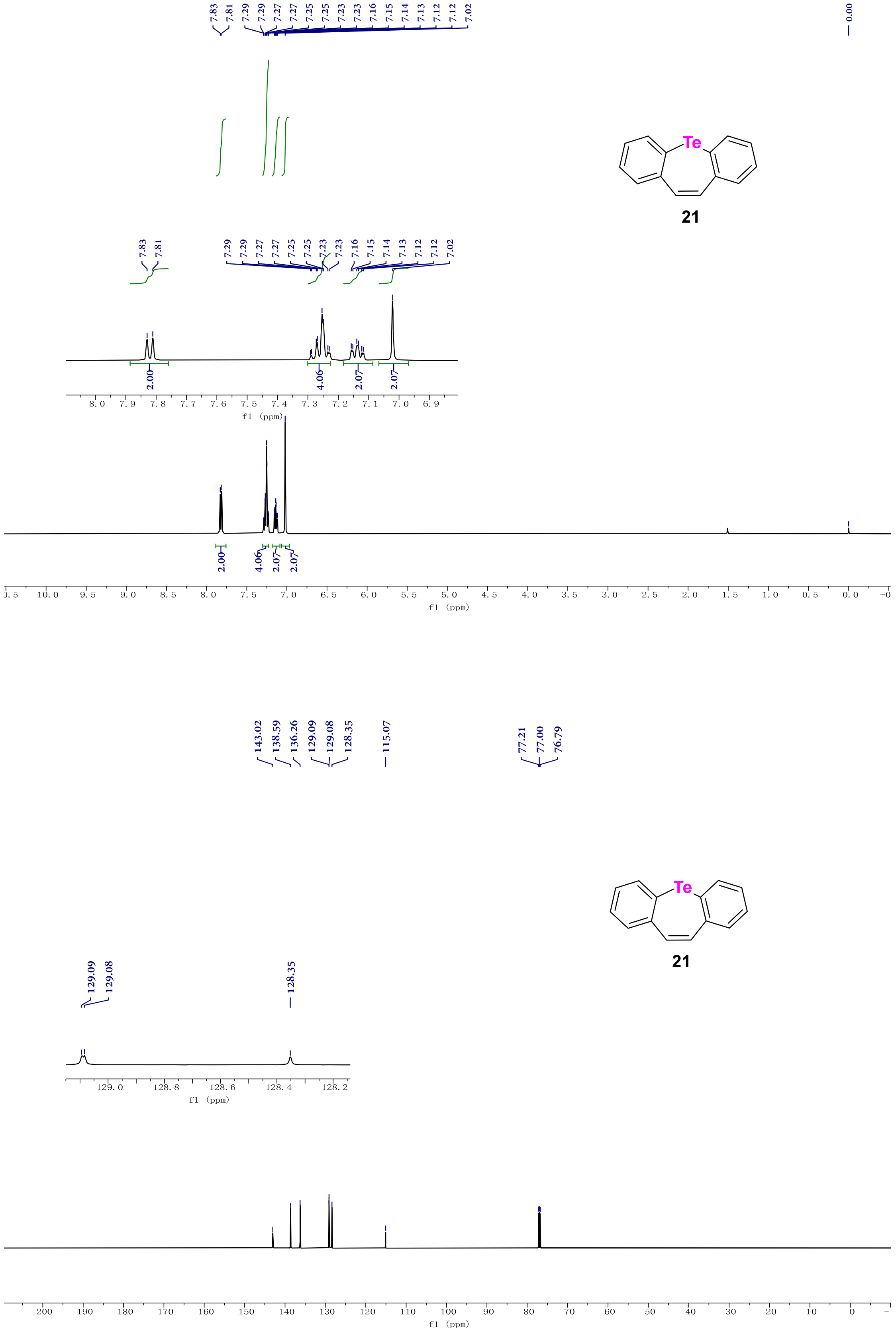


Figure S42. ^{1}H NMR (up) and ^{13}C NMR (down) of **21** in $CDCl_3$.

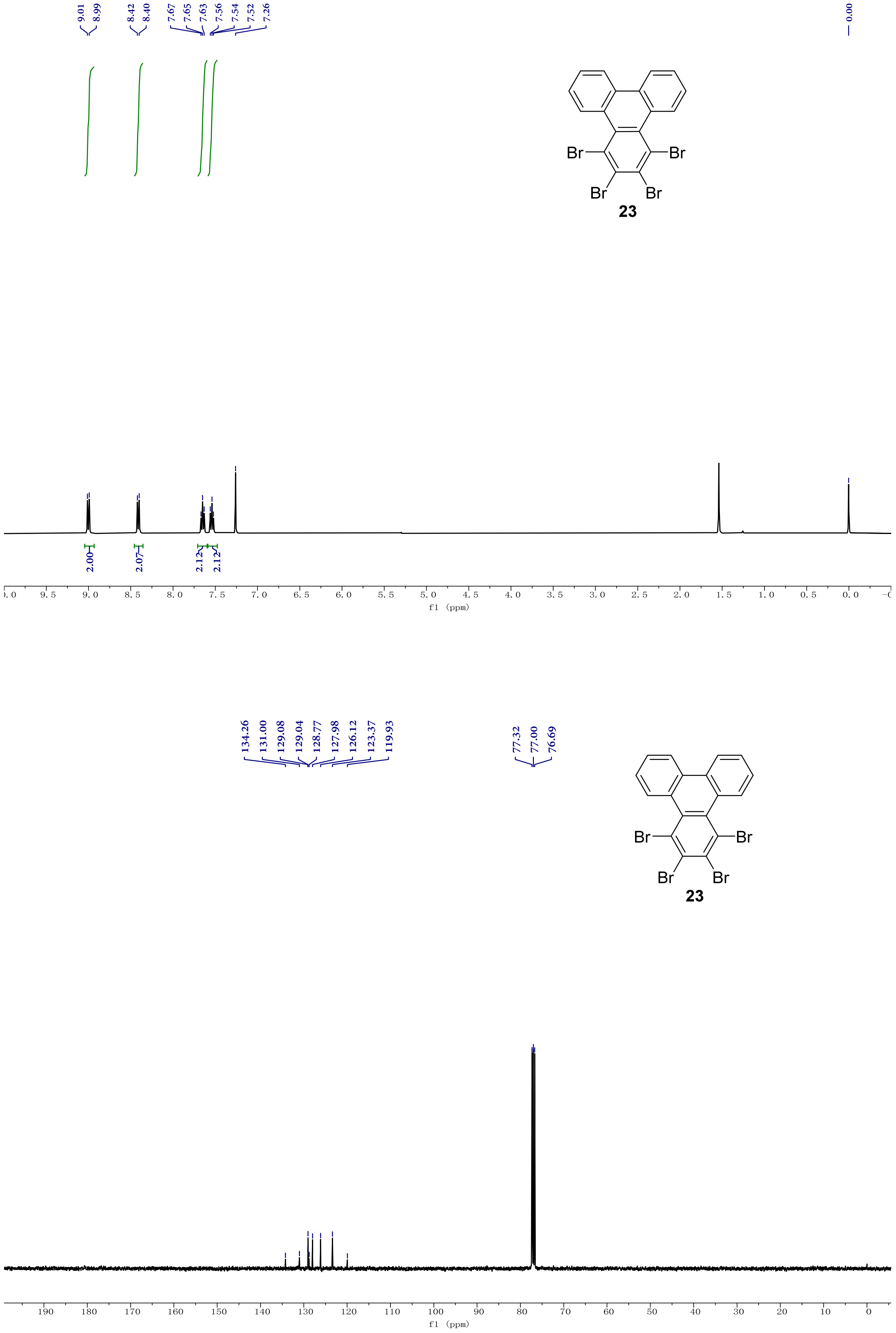


Figure S43. ^{1}H NMR (up) and ^{13}C NMR (down) of **23** in $CDCl_3$.

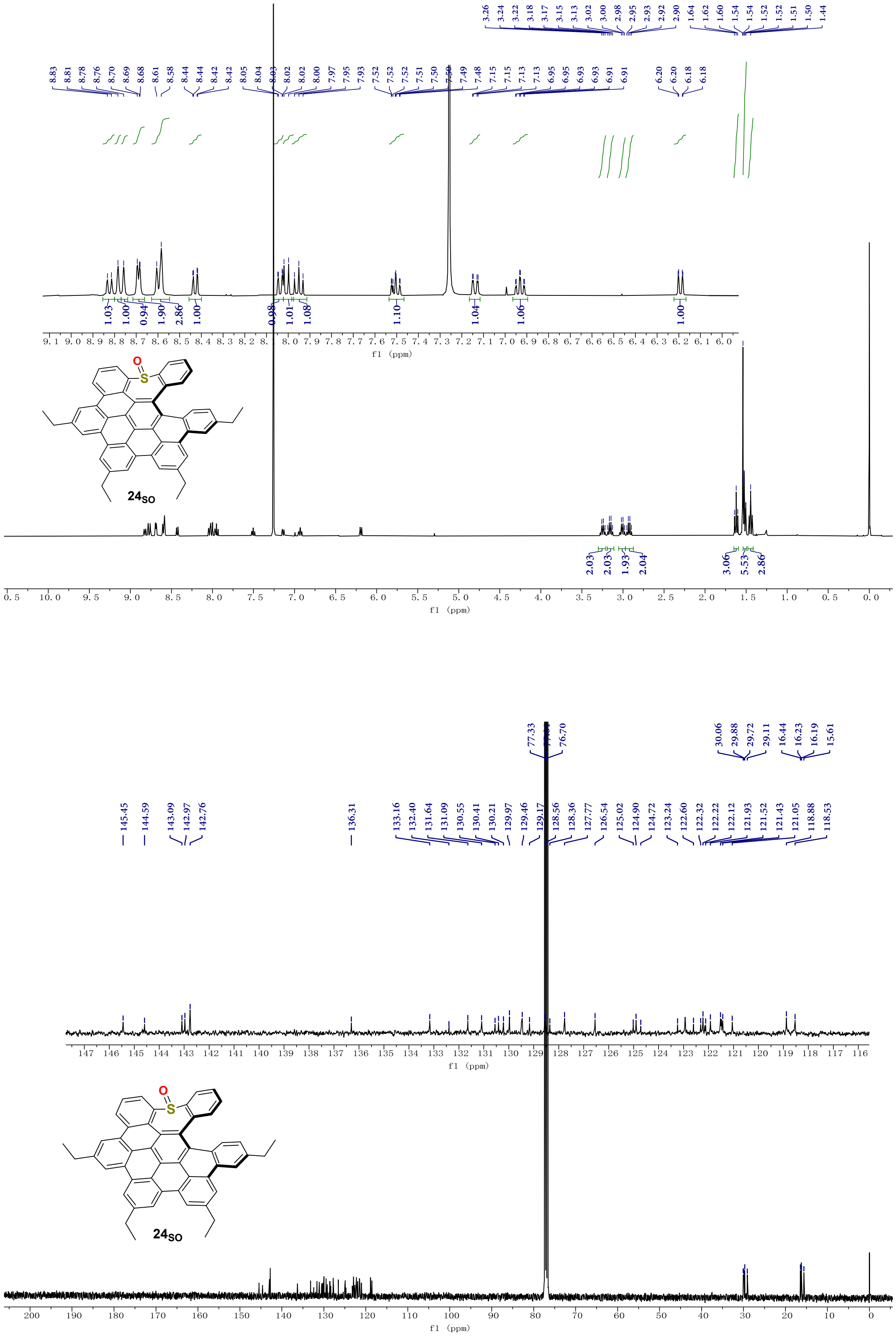


Figure S44. ^{1}H NMR (up) and ^{13}C NMR (down) of **24_{SO}** in $CDCl_3$.

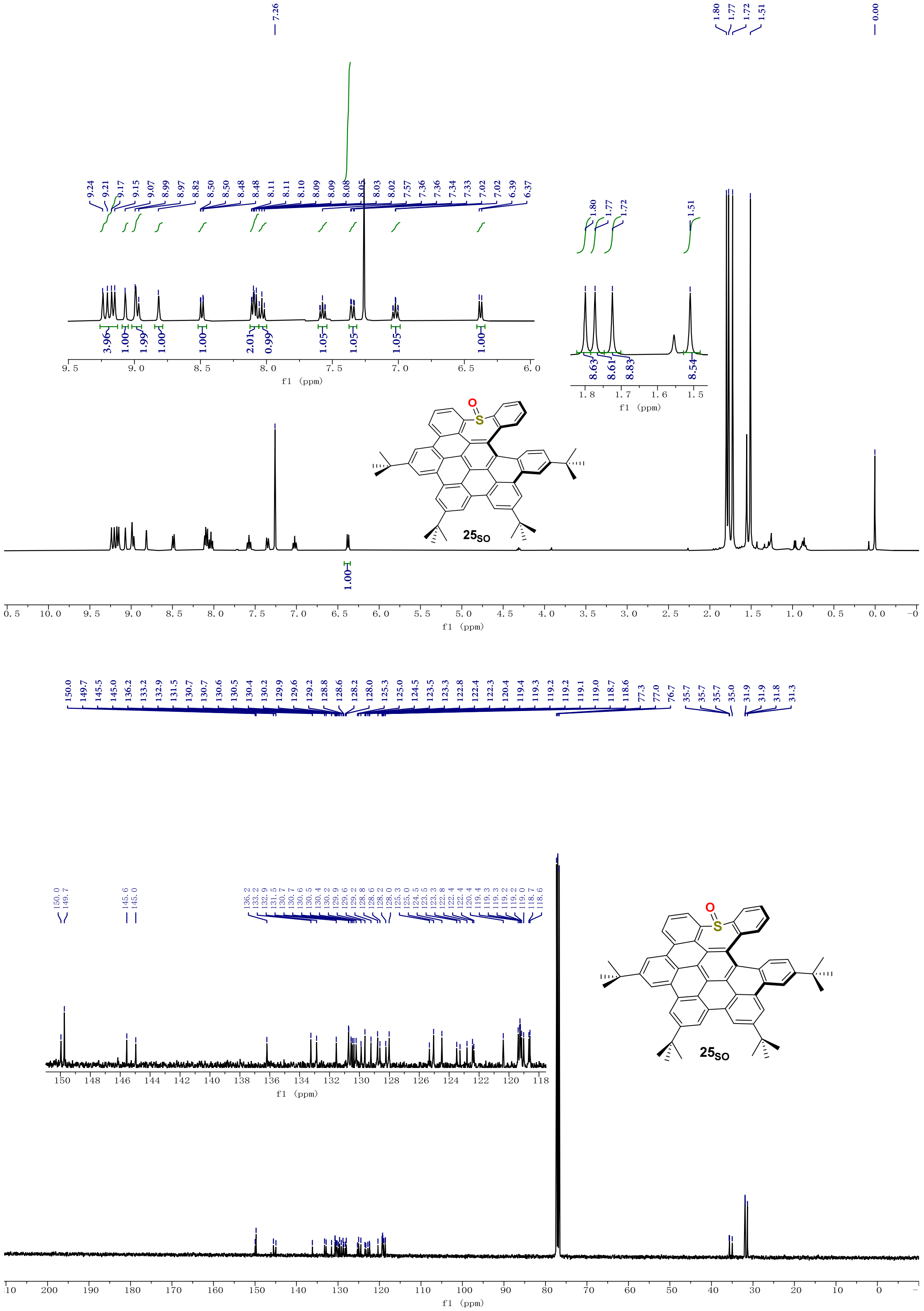


Figure S45. ^{1}H NMR (up) and ^{13}C NMR (down) of **25_{SO}** in CDCl$_3$.

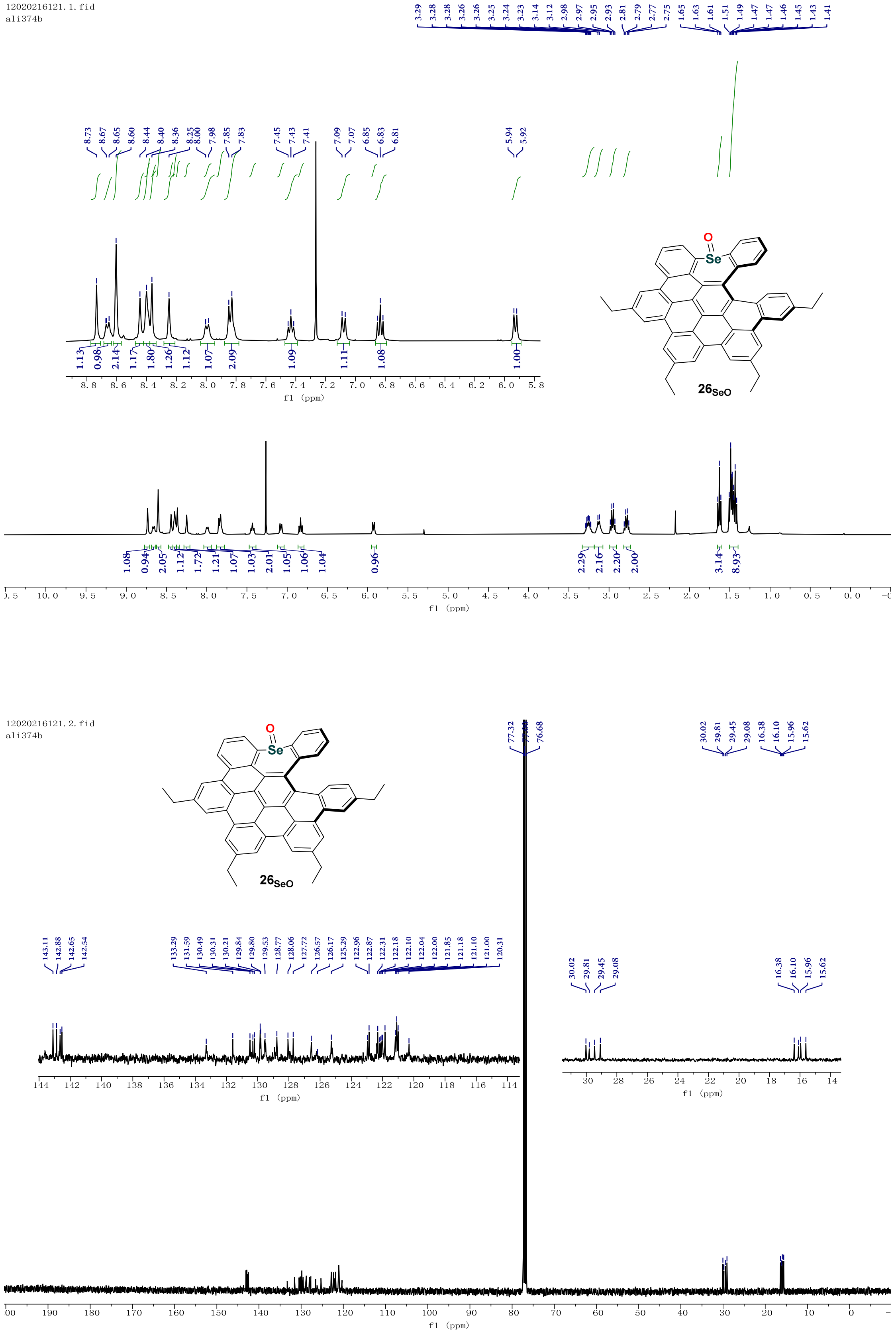


Figure S46. ^{1}H NMR (up) and ^{13}C NMR (down) of **26_{SeO}** in $CDCl_3$.

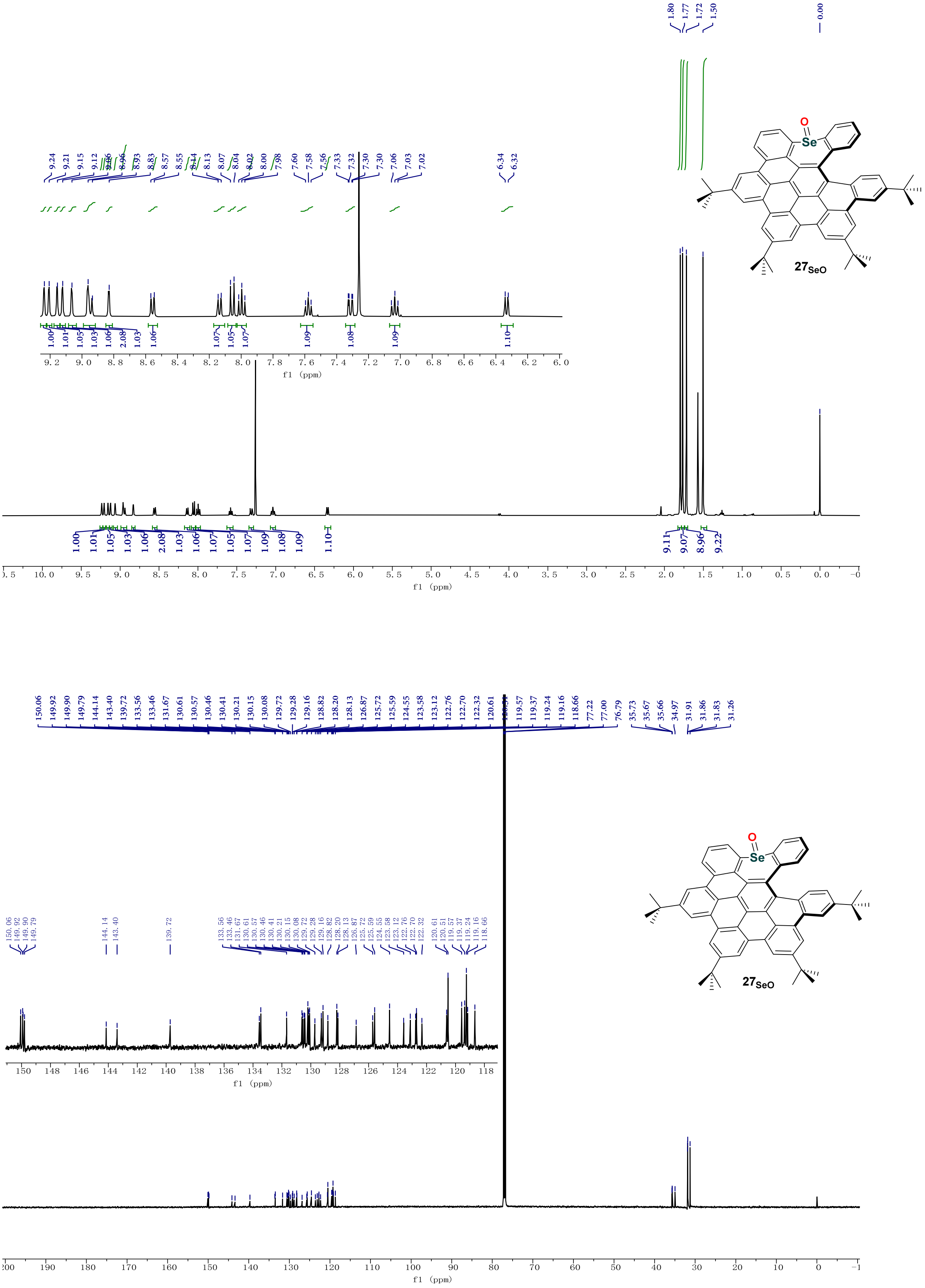


Figure S47. ^{1}H NMR (up) and ^{13}C NMR (down) of **27_{SeO}** in CDCl$_3$.

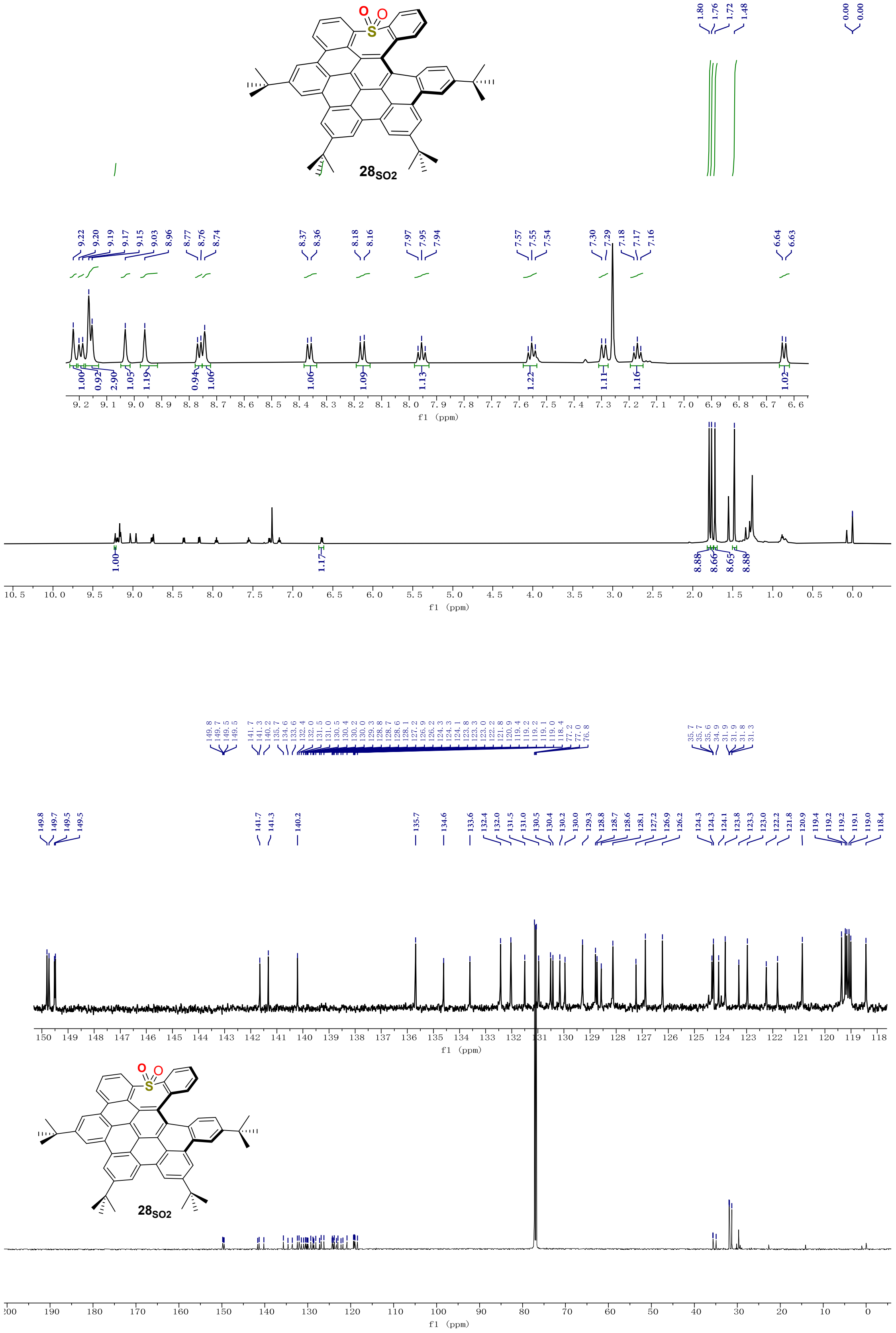


Figure S48. ^{1}H NMR (up) and ^{13}C NMR (down) of **28_{SO2}** in CDCl$_3$.

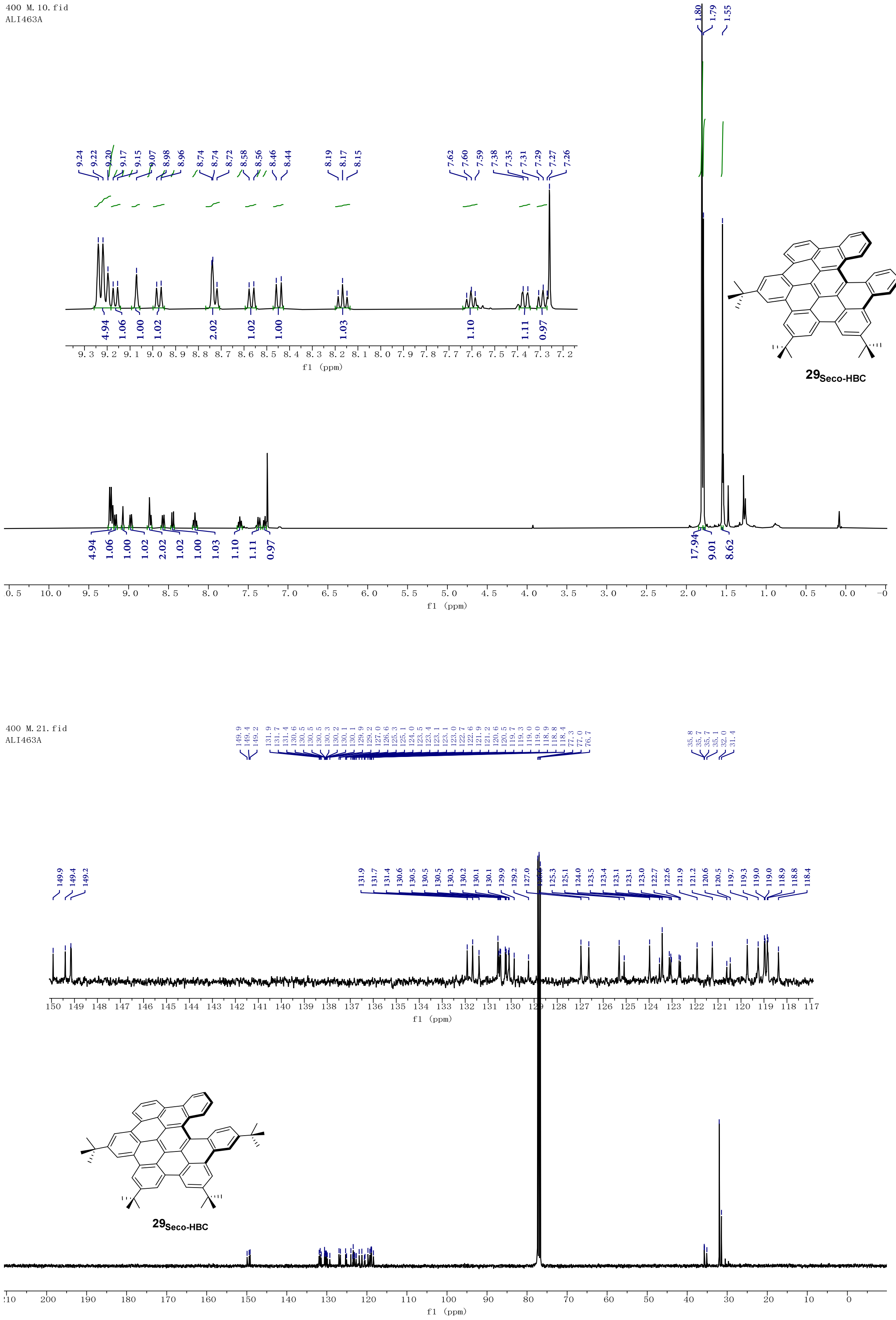


Figure S49. ^{1}H NMR (up) and ^{13}C NMR (down) of **$29_{\text{Seco-HBC}}$** in $CDCl_3$.

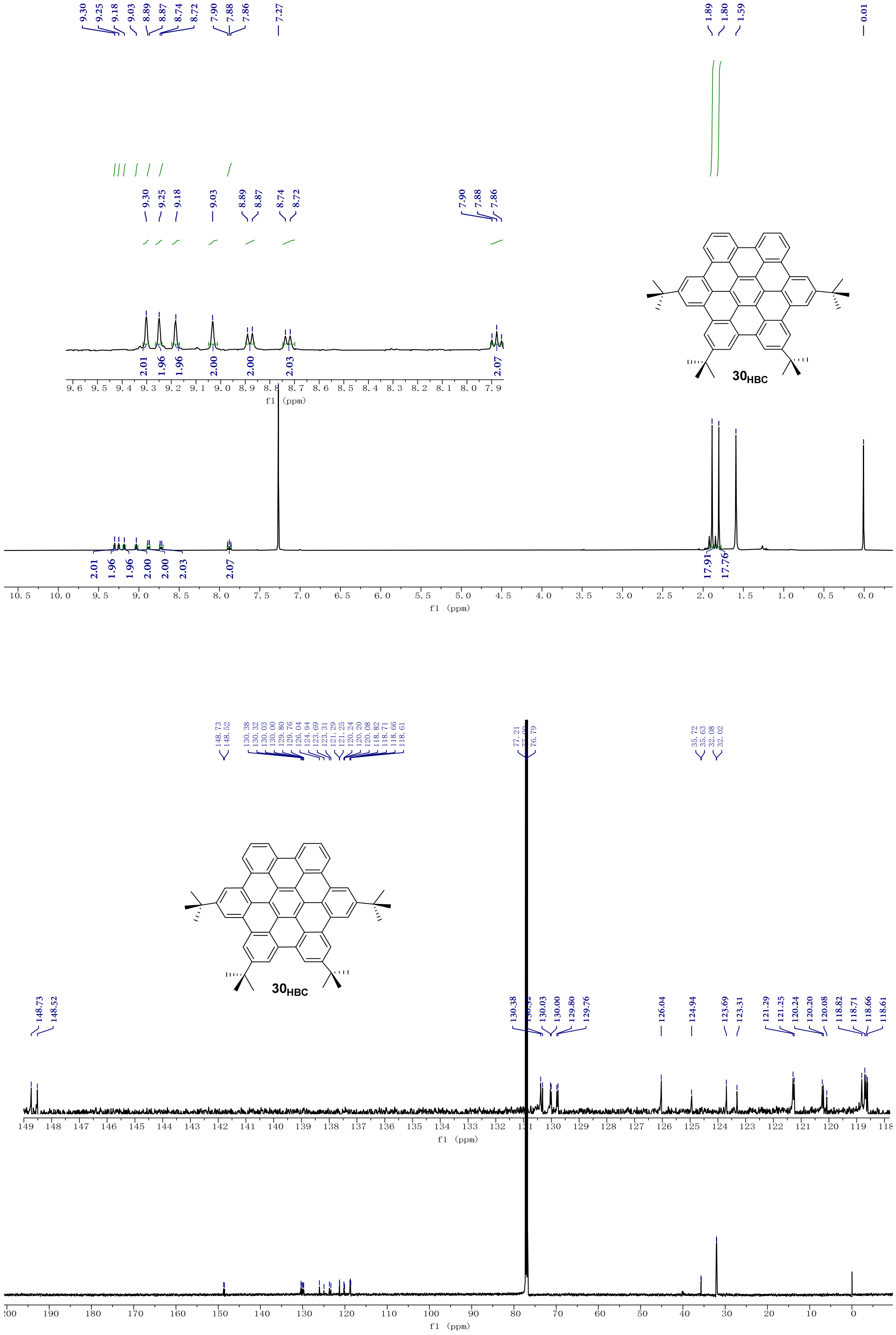


Figure S50. ^{1}H NMR (up) and ^{13}C NMR (down) of **30$_{\text{HBC}}$** in CDCl$_3$.