Supporting Information for:

Polycyclic Aromatic Hydrocarbons Containing Antiaromatic Chalcogenopyrano[3,2-*b*]chalcogenopyrans

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EXPERIMENTAL SECTION

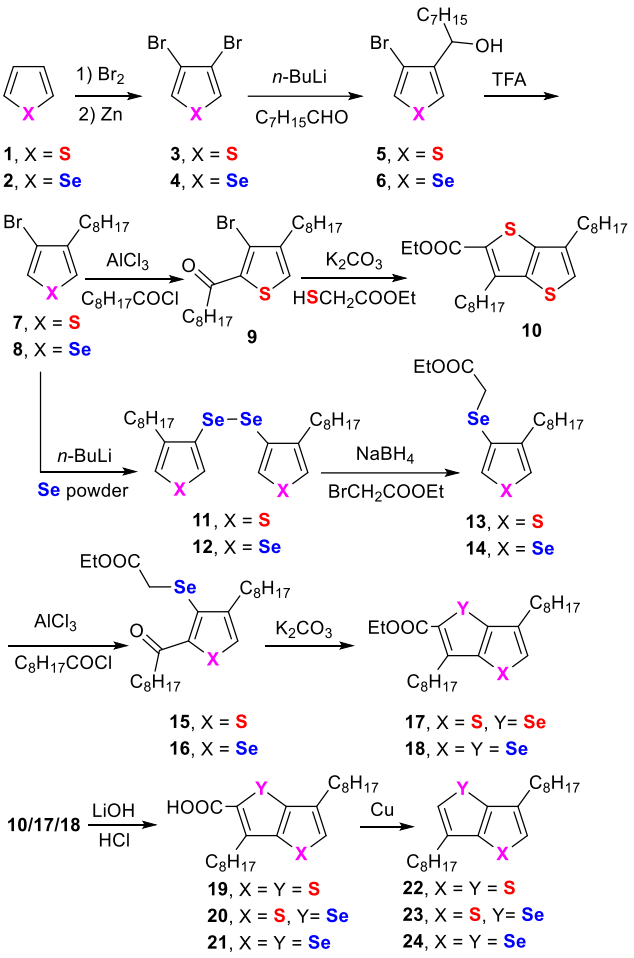
1 Materials and reagents.

All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. The applied solvents anhydrous diethyl ether (E_2O), tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), and chloroform ($CHCl_3$) were distilled from CaH_2. Selenophene, 3-bromothiophene, 3-octylthiophene, 3,4-dibromothiophene, and thieno[2,3-*b*]thiophene were obtained through commercial sources and used without further purification. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

2. Characterizations.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The analyzed chemical shifts δ are referenced to residual solvent signals of the deuterated solvents $CDCl_3$ (δ = 7.26/77.0 ppm). The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were acquired from PerkinElmer Lambda 750 spectrophotometer. Cyclic and differential pulse voltammetry measurements were performed using a CHI660E electrochemical workstation in a three-electrode electrochemical cell. A carbon glass coated electrode was used as the working electrode and an Ag/Ag^+ electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane was the electrolyte, and ferrocene was used as internal standard to estimate frontier orbital energy levels of S/Se-fused heteroarenes. The potential is given vs. Fc/Fc^+. Single crystal analysis was measured at 173 K using Bruker D8 Venture diffractometer equipped with a Cu Kα1 light source (λ = 1.5406 Å). Structures and refinements were completed using program SHELXL-97.

3. Synthesis



Scheme S1. Synthetic routes of 3,6-dioctyl-substituted chalcogenopheno[3,2-*b*]chalcogenophenes.

Synthesis of 3,4-dibromoselenophene (4).

Bromine (31.4 g) in $CHCl_3$ (20 mL) was added dropwise to a stirred solution of selenophene (5.0 g) in $CHCl_3$ (20 mL) and AcOH (3.5 mL) at 0 °C over the course of 1 hour. The reaction mixture was warmed to r.t. and stirred for 12 hours, and then heated to 70 °C for 5 hours. Upon completion of the reaction, the mixture was allowed to cool to r.t. and transferred to a large beaker. Excess bromine was evaporated at r.t. and the resulting mixture was diluted with $CHCl_3$ (200 mL). The organic phase was successively washed with water (80 mL), dilute NaOH solution (50 mL), and brine (60 mL), and then concentrated. The crude crystalline product was further purified by column chromatography on silica gel using hexane as an eluent

to give 2,3,4,5-tetrabromoselenophene as a white crystalline solid (15.5 g, 91%). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 118.12, 112.44. MALDI-TOF MS (m/z): [M-Br$^+$] calcd for C_4Br_4Se-Br, 368.6671; found 368.6704. *n*-BuLi (1.6 M in hexanes, 14.7 mL, 23.5 mmol) was added dropwise to a stirred solution of 2,3,4,5-tetrabromoselenophene (5.0 g, 11.2 mmol) in anhydrous ether (60 mL) under a nitrogen atmosphere at -78 °C over the course of 30 minutes, and the mixture was stirred for another 1.5 hours at that temperature. H_2O (5 mL) was added slowly to the reaction mixture, which was then allowed to warm to r.t. The mixture was then diluted with water (100 mL), extracted with ether (3 × 50 mL), and the combined organic phases were washed with water (50 mL), brine, dried over anhydrous $MgSO_4$, and concentrated. The resulting colorless oil was purified by column chromatography on silica gel using hexane as an eluent to give compound **4** (2.8 g, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 127.73, 114.62. MALDI-TOF MS (m/z): [M$^+$] calcd for C_4Br_2Se, 287.7505; found 287.7489.

Synthesis of 1-(4-bromo-3-thienyl)octan-1-ol (5).

Compound **5** was synthesized according to reported method.[S1]

Synthesis of 1-(4-bromoselenophen-3-yl)octan-1-ol (6).

To a mixture of compound **4** (1.0 eq.) in dry diethyl ether, *n*-BuLi (1.6 M in hexane, 1.1 eq.) was added dropwise at -78 ºC. After the addition was finished, the resulting mixture was stirred another 2 hours and then octanal (1.2 eq.) was added quickly. The final mixture was allowed to warm to r.t. and stirred for 2 hours. This reaction was then quenched with water and extracted with ethyl acetate. The combined extracts were dried over anhydrous $MgSO_4$, filtered and distillation of solvent under reduced pressure gives the crude products. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **6** as a colorless oil (2.53 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (s, 2H), 4.79 (d, J = 8.1 Hz, 1H), 1.33 – 1.26 (m, 12H), 0.90 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.06, 127.36, 126.46, 111.20, 71.61, 37.42, 32.07, 29.63, 29.49, 26.01, 22.92, 14.38. MALDI-TOF MS (m/z): [M$^+$] calcd for $C_{12}H_{19}BrOSe$, 337.9776; found 337.9809.

Synthesis of 3-bromo-4-octylthiophene (7).

Compound **7** was synthesized according to reported method.[S2]

Synthesis of 3-bromo-4-octylselenophene (8).

A round bottom flask containing compound **6** (1.0 eq.) and triethylsilane (4.0 eq.) in anhydrous CH_2Cl_2 were cooled to 0 °C, and then TFA (6.0 eq.) was added via syringe. The solution was stirred at r.t. for a period of 2 hours and quenched with saturated $NaHCO_3$. The mixture was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **8** as a colorless oil (1.90 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, J = 2.9 Hz, 1H), 7.55 – 7.54 (m, 1H), 2.58 – 2.54 (m, 2H), 1.65 – 1.59 (m, 2H), 1.37 – 1.28 (m, 10H), 0.90 – 0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.51, 126.29, 124.77, 124.69, 114.14, 77.58, 77.27, 76.95, 32.31, 32.13, 29.65, 29.54, 29.45, 22.94, 14.39. MALDI-TOF MS (m/z): [M^+] calcd for $C_{12}H_{19}BrSe$, 321.9826; found 321.9840.

Synthesis of 1-(3-bromo-4-octylthien-2-yl)nonan-1-one (9).

Compound **9** was synthesized according to reported method.[S2]

Synthesis of ethyl 3,6-dioctylthieno[3,2-*b*]thiophene-2-carboxylate (10).

Compound **10** was synthesized according to reported method.[S2]

Synthesis of 1,2-bis(4-octylthien-3-yl)diselane (11).

A stirred solution of compounds **7** (1.0 eq.) in Et_2O were cooled to −78 °C and *n*-BuLi (1.6 M solution in hexane, 1.1 eq.) was added dropwise over 60 minutes. After stirring for 2 hours, selenium powder (1.2 eq.) was added in portions. The solution stirred for another an hour at −78 °C and then warmed to r.t. for 4 hours. The resulting solution was poured into HCl (10 %) and was stirred overnight at r.t. After filtration, the aqueous layer was extracted twice with ether, and the combined organic layers were dried with anhydrous magnesium sulfate and the solvents evaporated under vacuum. The residue was purified by

chromatography (eluent: petroleum ether) on silica gel to afford the target compound **11** as a yellow oil (1.40 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (d, J = 3.2 Hz, 1H), 6.96 (d, J = 3.3 Hz, 1H), 2.57 – 2.52 (m, 2H), 1.61 – 1.57 (m, 2H), 1.30 – 1.26 (m, 10H), 0.89 (d, J = 2.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.92, 123.82, 121.78, 114.03, 33.11, 31.12, 30.62, 30.55, 30.53, 30.50, 23.92, 15.36. MALDI-TOF MS (m/z): [M^+] calcd for $C_{24}H_{38}S_2Se_2$, 550.0742; found 550.0771.

Synthesis of 1,2-bis(4-octylselenophen-3-yl)diselane (12).

A stirred solution of compound **8** (1.0 eq.) in anhydrous Et_2O was cooled to −78 °C and *n*-BuLi (1.6 M solution in hexane, 1.1 eq.) was added dropwise over an hour. After stirring for 2 hours, selenium powder (1.2 eq.) was added in portions. The solution stirred for another an hour at −78 °C and then warmed to r.t. for 4 hours. The resulting solution was poured into HCl (10 %) and was stirred overnight at r.t. After filtration, the aqueous layer was extracted twice with ether, and the combined organic layers were dried with anhydrous magnesium sulfate and the solvents evaporated under vacuum. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **12** as a yellow oil (3.35 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, J = 2.7 Hz, 1H), 7.57 (d, J = 2.7 Hz, 1H), 2.55 (s, 2H), 1.62 – 1.58 (m, 2H), 1.29 (d, J = 8.4 Hz, 10H), 0.89 (d, J = 2.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.30, 136.42, 127.32, 124.66, 32.22, 32.19, 31.85, 29.91, 29.40, 29.25, 22.65, 14.09. MALDI-TOF MS (m/z): [M^+] calcd for $C_{24}H_{38}Se_4$, 643.9649; found 643.9675.

Synthesis of ethyl 2-((4-octylthien-3-yl)selanyl)acetate (13).

To a suspension of $NaBH_4$ (2.0 eq.) in anhydrous EtOH was added a solution of diselenide **11** (1.0 eq.) in anhydrous THF dropwise under a nitrogen atmosphere. The reaction mixture was kept under agitation at 0 °C and ethyl bromoacetate (2.0 eq.) in anhydrous THF was added. After 25 minutes, the reaction mixture was quenched with water and organic phase was extracted with dichloromethane. The organic layers were combined, dried over anhydrous magnesium sulfate, and concentrated under vacuum. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **13** as a yellow oil (1.40 g, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (s, 1H), 6.98 (s, 1H), 4.13 – 4.07 (m, 2H), 3.37 (s, 2H), 2.66 – 2.61 (m, 2H), 1.65 – 1.58 (m, 2H), 1.40 – 1.32 (m, 4H), 1.30 – 1.26 (m, 6H),

1.23 – 1.19 (m, 3H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.96, 144.93, 129.71, 123.86, 120.77, 61.54, 32.12, 30.39, 29.68, 29.51, 28.10, 22.92, 14.37, 14.28. MALDI-TOF MS (m/z): [M^+] calcd for $C_{16}H_{26}O_2SSe$, 362.0813; found 362.0845.

Synthesis of ethyl 2-((4-octylselenophen-3-yl)selanyl)acetate (14).

To a suspension of $NaBH_4$ (2.0 eq.) in anhydrous EtOH was added a solution of diselenide compound **12** (1.0 eq.) in anhydrous THF dropwise under a nitrogen atmosphere. The reaction mixture was kept under agitation at 0 °C and ethyl bromoacetate (2.0 eq.) in anhydrous THF was added. After 25 minutes, the reaction mixture was quenched with water and organic phase was extracted with dichloromethane. The organic layers were combined, dried over anhydrous magnesium sulfate, and concentrated under vacuum. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **14** as a yellow oil (3.35 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 2.7 Hz, 1H), 7.59 – 7.58 (m, 1H), 4.13 – 4.08 (m, 2H), 3.40 (s, 2H), 2.63 – 2.59 (m, 2H), 1.64 – 1.59 (m, 2H), 1.34 – 1.26 (m, 10H), 1.20 (d, J = 7.1 Hz, 3H), 0.87 (d, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.97, 146.27, 133.34, 124.93, 61.56, 32.35, 32.12, 30.25, 29.69, 29.52, 28.00, 22.93, 14.37, 14.29. MALDI-TOF MS (m/z): [M^+] calcd for $C_{16}H_{26}O_2Se_2$, 410.0261; found 410.0294.

Synthesis of ethyl 2-((2-nonanoyl-4-octylthien-3-yl)selanyl)acetate (15).

Into a 50 mL flask was placed dichloromethane under a nitrogen atmosphere, and the flask was cooled using an ice bath before $AlCl_3$ (1.5 eq.) was added. A dropping funnel was charged with nonanoyl chloride (1.4 eq.) in dichloromethane, and this solution was added to the $AlCl_3$ suspension over a period of 10 minutes. After about 30 minutes of stirring at 0 °C, most of the $AlCl_3$ had dissolved. Another dropping funnel was charged with compound **13** (1.0 eq.) in dichloromethane, and this mixture was added to the reaction mixture over a 10 minutes period. The reaction was left to proceed at 0 °C for 30 minutes, and then the reaction mixture was warmed slowly to r.t. for 12 hours. Then the reaction mixture was cooled to 0 °C once again, and dilute solution of HCl was added carefully to consume excess $AlCl_3$. The reaction mixture was diluted with dichloromethane, and water was added. The inorganic phase was extracted twice

with dichloromethane, washed with saturated $NaHCO_3$ and brine, and finally dried over anhydrous magnesium sulfate. The combined extracts were dried over anhydrous $MgSO_4$, filtered and distillation of solvent under reduced pressure gives the crude products. The residue was purified by chromatography (eluent: petroleum ether/DCM = 4/1) on silica gel to afford the target compound **15** as a yellow liquid (1.04 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (s, 1H), 4.03 – 3.97 (m, 2H), 3.55 (s, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.74 – 2.68 (m, 2H), 1.76 – 1.69 (m, 2H), 1.61 – 1.54 (m, 2H), 1.40 – 1.30 (m, 8H), 1.30 – 1.24 (m, 12H), 1.11 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.40, 170.75, 149.22, 143.02, 128.64, 125.27, 61.36, 42.38, 32.09, 32.07, 31.13, 30.62, 29.66, 29.64, 29.59, 29.49, 29.39, 28.85, 24.92, 22.90, 14.35, 14.16. MALDI-TOF MS (m/z): [M^+] calcd for $C_{25}H_{42}O_3SSe$, 502.2015; found 502.2019.

Synthesis of ethyl 2-((2-nonanoyl-4-octylselenophen-3-yl)selanyl)acetate (16).

Into a 50 mL flask was placed dichloromethane under a nitrogen atmosphere, and the flask was cooled using an ice bath before $AlCl_3$ (1.5 eq.) was added. A dropping funnel was charged with nonanoyl chloride (1.4 eq.) in dichloromethane, and this solution was added to the $AlCl_3$ suspension over a period of 10 minutes. After about 30 minutes of stirring at 0 °C, most of the $AlCl_3$ had dissolved. Another dropping funnel was charged with compounds **14** (1.0 eq.) in dichloromethane, and this mixture was added to the reaction mixture over a 10 minutes period. The reaction was left to proceed at 0 °C for 30 minutes, and then the reaction mixture was warmed slowly to r.t. for 12 hours. Then the reaction mixture was cooled to 0 °C again, and dilute solution of HCl was added carefully to consume excess $AlCl_3$. The reaction mixture was diluted with dichloromethane, and water was added. The inorganic phase was extracted twice with dichloromethane, washed with saturated $NaHCO_3$ and brine, and finally dried over anhydrous magnesium sulfate. The combined extracts were dried over anhydrous $MgSO_4$, filtered and distillation of solvent under reduced pressure gives the crude products. The residue was purified by chromatography (eluent: petroleum ether/DCM = 4/1) on silica gel to afford the target compound **16** as a yellow oil (2.45 g, 55%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 3.01 (t, J = 7.4 Hz, 2H), 2.79 – 2.73 (m, 2H), 1.79 –1.76 (m, 2H), 1.63 (d, J = 7.8 Hz, 2H), 1.45 – 1.35 (m, 8H),

1.34 – 1.29 (m, 12H), 1.16 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):193.68, 171.02, 149.50, 125.55, 61.63, 42.66, 32.37, 32.35, 31.41, 30.90, 29.93, 29.92, 29.87, 29.77, 29.66, 29.13, 25.19, 23.18, 14.63, 14.44. MALDI-TOF MS (m/z): [M^+] calcd for $C_{25}H_{42}O_3Se_2$, 550.1464; found 508. 550.1498.

Synthesis of ethyl 3,6-dioctylselenopheno[3,2-*b*]thiophene-5-carboxylate (17).

In a 50 mL round bottom flask, precursor compound **15** (1.0 eq.) was taken with anhydrous DMF and K_2CO_3 (3.0 eq.) was added. The mixture was stirred at 70 °C for 24 hours under a nitrogen atmosphere. It was quenched by adding H_2O and the compound extracted with dichloromethane. The organic phase was washed several times with H_2O, dried over anhydrous magnesium sulfate and evaporated in vacuum. The residue was purified by chromatography (eluent: hexane/DCM = 4/1) on silica gel to afford the target compound **17** as a yellow oil (0.94 g, 94%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.12 (s, 1H), 4.36 – 4.31 (m, 2H), 3.20 – 3.06 (m, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.76 – 1.67 (m, 4H), 1.42 – 1.36 (m, 7H), 1.32 (d, J = 6.1 Hz, 4H), 1.30 – 1.25 (m, 12H), 0.90 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.27, 146.51, 142.98, 141.57, 138.76, 129.61, 124.28, 77.58, 77.26, 76.94, 61.16, 32.12, 32.10, 30.78, 30.75, 30.05, 29.67, 29.64, 29.58, 29.48, 29.46, 28.99, 22.91, 14.60, 14.36. MALDI-TOF MS (m/z): [M^+] calcd for $C_{25}H_{40}O_2SSe$, 484.1910; found 484.1942.

Synthesis of ethyl 3,6-dioctylselenopheno[3,2-*b*]selenophene-2-carboxylate (18).

In a 50 mL round bottom flask, precursor compound **16** (1.0 eq.) was taken with anhydrous DMF and K_2CO_3 (3.0 eq.) was added. The mixture was stirred at 70 °C for 24 hours under a nitrogen atmosphere. It was quenched by adding H_2O and the compound extracted with dichloromethane. The organic phase was washed several times with H_2O, dried over anhydrous magnesium sulfate and evaporated in vacuum. The residue was purified by chromatography (eluent: hexane/DCM = 4/1) on silica gel to afford the target compound **18** as a yellow oil (1.30 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.13 – 3.08 (m, 2H), 2.67 (t, J = 7.7 Hz, 2H), 1.75 – 1.69 (m, 4H), 1.38 (s, 3H), 1.36 – 1.21 (m, 20H), 0.89 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.12, 148.94, 144.08, 143.06,

140.83, 128.95, 127.06, 126.99, 77.58, 77.26, 76.94, 61.17, 32.40, 32.11, 31.92, 30.08, 29.82, 29.59, 29.47, 28.87, 22.91, 14.62, 14.36. MALDI-TOF MS (m/z): [M^+] calcd for $C_{25}H_{40}O_2Se_2$, 532.1358; found 532.1377.

General procedure for the synthesis of compounds 19-21.

A mixture of precursor compounds **10**/**17**/**18** (1.0 eq.), LiOH (0.5 eq. 10 wt%), tetrabutylammonium iodide (5 mmol%), and MeOH in THF (1/4, v/v) was heated under reflux at 85 °C for 5 hours. After evaporating the solvent under reduced pressure, the mixture was acidified with concentrated HCl and then extracted with EtOAc. The combined organic phases were dried and the solvent evaporated under reduced pressure. The crude product was directly used in the next reaction without further purification.

Synthesis of 3,6-dioctylthieno[3,2-*b*]thiophene (22).

Compound **22** was synthesized according to reported method.[S2]

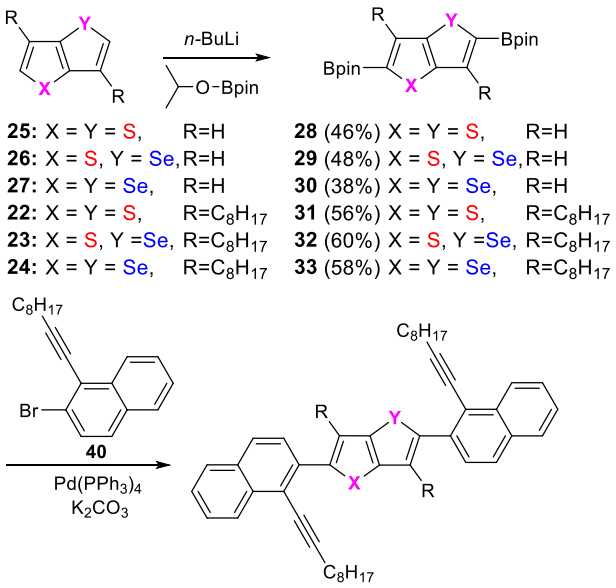
Synthesis of 3,6-dioctylselenopheno[3,2-*b*]thiophene (23).

A mixture of crude precursor compound **20** and Cu powder (0.65 eq.) in quinoline was stirred at 250 °C for 4 hours. After cooling to r.t., the mixture was added to hexane and then washed with 2 M HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **23** as a colorless solid (0.69 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (s, 1H), 6.94 (s, 1H), 2.72 (t, J = 6.4 Hz, 2H), 2.70 – 2.66 (m, 2H), 1.78 – 1.72 (m, 4H), 1.39 – 1.33 (m, 8H), 1.31 – 1.26 (m, 12H), 0.89 (d, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.22, 138.92, 138.48, 137.78, 123.26, 120.38, 77.58, 77.27, 76.95, 32.14, 31.56, 30.82, 29.67, 29.65, 29.63, 29.50, 29.11, 28.81, 22.93, 14.38. MALDI-TOF MS (m/z): [M^+] calcd for $C_{22}H_{36}SSe$, 412.1698; found 412.1730.

Synthesis of 3,6-dioctylselenopheno[3,2-*b*]selenophene (24).

A mixture of crude precursor compound **21** and Cu powder (0.65 eq.) in quinoline was stirred at 250 °C

for 4 hours. After cooling to r.t., the mixture was added to hexane and then washed with 2 M HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by chromatography (eluent: petroleum ether) on silica gel to afford the target compound **24** as a colorless solid (0.86 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (s, 1H), 2.68 (t, J = 7.7 Hz, 2H), 1.74 (t, J = 7.1 Hz, 2H), 1.38 – 1.27 (m, 10H), 0.88 (d, J = 2.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.02, 140.49, 122.82, 77.57, 77.25, 76.93, 32.45, 32.12, 29.65, 29.62, 29.48, 28.97, 22.92, 14.36. MALDI-TOF MS (m/z): [M^+] calcd for $C_{22}H_{36}Se_2$, 460.1146; found 460.1178.



25: X = Y = S, R=H
26: X = S, Y = Se, R=H
27: X = Y = Se, R=H
22: X = Y = S, R=C_8H_{17}
23: X = S, Y =Se, R=C_8H_{17}
24: X = Y = Se, R=C_8H_{17}

28 (46%) X = Y = S, R=H
29 (48%) X = S, Y = Se, R=H
30 (38%) X = Y = Se, R=H
31 (56%) X = Y = S, R=C_8H_{17}
32 (60%) X = S, Y =Se, R=C_8H_{17}
33 (58%) X = Y = Se, R=C_8H_{17}

34 (62%) X = Y = S, R=H
35 (54%) X = S, Y = Se, R=H
36 (59%) X = Y = Se, R=H
37 (52%) X = Y = S, R=C_8H_{17}
38 (45%) X = S, Y =Se, R=C_8H_{17}
39 (59%) X = Y = Se, R=C_8H_{17}

SS2 (38%) X = Y = S, R=H
SSe2 (47%) X = S, Y =Se, R=H
SeSe2 (42%) X = Y = Se, R=H
SS4 (87%) X = Y = S, R=C_8H_{17}
SSe4 (75%) X = S, Y = Se, R=C_8H_{17}
SeSe4 (72%) X = Y = Se, R=C_8H_{17}

Scheme S2. Synthetic routes of the PAHs containing chalcogenopyrano[3,2-*b*]chalcogenopyrans moieties.

Synthesis of selenopheno[3,2-*b*]thiophene (26).

Compound **26** was synthesized according to reported method.[S3]

Synthesis of selenopheno[3,2-b]selenophene (27).

A mixture of crude precursor compound (1.0 eq.) and Cu powder (0.65 eq.) in quinoline was stirred at 250 °C for 4 hours. After cooling to r.t., the mixture was added to hexane and then washed with 2 M HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by chromatography (eluent: petroleum ether/DCM = 8/1) on silica gel to afford the target compound **27** as a colorless solid (1.24 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 – 7.96 (m, 2H), 7.59 – 7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.66, 130.76, 125.29. MALDI-TOF MS (m/z): [M^+] calcd for $C_6H_4Se_2$, 235.8640; found 235.8593.

Synthesis of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-*b*]thiophene (28).

To a solution of compound **25** (1.0 eq.) in dry THF, a 1.6 M solution of *n*-BuLi (2.5 eq.) in hexanes was added at –70 °C. The solution was stirred for 30 minutes at –70 °C, and then 2-isopropoxy-1,3,2-dioxaboralane (3.0 eq.) was added. The mixture was allowed to reach r.t. and stirred overnight. The reaction mixture was poured in water and DCM, and the organic layer was washed with brine. The solvents were evaporated from the organic layer to obtain the mixture. The residue was purified by chromatography (eluent: petroleum ether/DCM = 2/1) on silica gel to afford the target compound **28** as a colorless solid (5.2 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (s, 2H), 1.35 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.88, 129.13, 84.59, 25.02. MALDI-TOF MS (m/z): [M^+] calcd for $C_{18}H_{26}B_2O_4S_2$, 392.1460; found 392.1482.

Synthesis of 2,2'-(selenopheno[3,2-*b*]thiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (29).

To a solution of compound **26** (1.0 eq.) in dry THF, a 1.6 M solution of *n*-BuLi (2.5 eq.) in hexanes were added at –70 °C. The solution was stirred for 30 minutes at –70 °C, and then 2-isopropoxy-1,3,2-

dioxaboralane (3.0 eq.) was added. The mixture was allowed to reach r.t. and stirred overnight. The reaction mixture was poured in water and DCM, and the organic layer was washed with brine. The solvents were evaporated from the organic layer to obtain the mixture. The residue was purified by chromatography (eluent: petroleum ether/DCM = 2/1) on silica gel to afford the target compound **29** as a colorless solid (1.5 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (s, 1H), 7.80 (s, 1H), 1.35 – 1.35 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.81, 145.81, 132.43, 131.85, 84.61, 84.58, 25.03. MALDI-TOF MS (m/z): [M^+] calcd for $C_{18}H_{26}B_2O_4SSe$, 440.0905; found 440.0929.

Synthesis of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)selenopheno[3,2-*b*]selenophene (30).

To a solution of compound **27** (1.0 eq.) in dry THF, a 1.6 M solution of *n*-BuLi (2.5 eq.) in hexanes was added at –70 °C. The solution was stirred for 30 minutes at –70 °C, and then 2-isopropoxy-1,3,2-dioxaboralane (3.0 eq.) was added. The mixture was allowed to reach r.t. and stirred overnight. The reaction mixture was poured in water and DCM, and the organic layer was washed with brine. The solvents were evaporated from the organic layer to obtain the mixture. The residue was purified by chromatography (eluent: petroleum ether/DCM = 2/1) on silica gel to afford the target compound **30** as a colorless solid (1.2 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (s, 2H), 1.35 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.00, 135.02, 84.59, 25.03. MALDI-TOF MS (m/z): [M^+] calcd for $C_{18}H_{26}B_2O_4Se_2$, 488.0354; found 488.0384.

General synthetic procedure of 2,2'-(3,6-dioctylthieno[3,2-*b*]thien-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (31), 2,2'-(3,6-dioctylselenopheno[3,2-*b*]thien-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (32), and 2,2'-(3,6-dioctylselenopheno[3,2-*b*]selenophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (33).

To a solution of compounds **22-24** (1.0 eq.) in dry THF, a 1.6 M solution of *n*-BuLi (2.5 eq.) in hexanes were added at –78 °C. The solution was stirred for 30 minutes at –78 °C, and then 2-isopropoxy-1,3,2-dioxaboralane (2.6 eq.) was added at –78 °C. The mixture was allowed to reach r.t. and stirred overnight.

The reaction mixture was poured in water and DCM, and the organic layer was washed with brine. The solvents were evaporated from the organic layer to obtain the mixture. The crude products **31-33** were directly used in the next reaction without further purification due to their decomposition in the chromatography separation.

Synthesis of 2-bromo-1-(dec-1-yn-1-yl)naphthalene (40).

Compound **40** was synthesized according to reported method.[S2]

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)thieno[3,2-*b*]thiophene (34).

Under the protection of nitrogen, to a degassed mixture solution of toluene and K_2CO_3 (4.0 eq.) was added compound **28** (1.0 eq.), compound **40** (2.3 eq.) and $Pd(PPh_3)_4$ (0.05 eq.). The mixture was heated overnight under nitrogen at 100 °C. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (eluent: petroleum ether/DCM = 6/1) on silica gel to afford the target compound **34** as a colorless solid (0.82 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.50 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 1.2 Hz, 2H), 7.84 – 7.79 (m, 4H), 7.75 – 7.72 (m, 2H), 7.63 – 7.58 (m, 2H), 7.54 – 7.49 (m, 2H), 2.68 – 2.64 (m, 4H), 1.82 – 1.71 (m, 4H), 1.57 – 1.50 (m, 4H), 1.39 – 1.25 (m, 16H), 0.8 – 0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.11, 140.20, 134.60, 134.39, 132.51, 128.23, 128.19, 127.41, 127.34, 126.88, 126.65, 119.84, 118.42, 102.29, 32.13, 29.53, 29.50, 29.46, 28.80, 22.94, 20.52, 14.35. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}S_2$, 664.3192; found 664.3215.

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)selenopheno[3,2-*b*]thiophene (35).

Under the protection of nitrogen, to a degassed mixture solution of toluene and K_2CO_3 (4.0 eq.) was added compound **29** (1.0 eq.), compound **40** (2.3 eq.) and $Pd(PPh_3)_4$ (0.05 eq.). The mixture was heated overnight under nitrogen at 100 °C. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (eluent: petroleum ether/DCM = 6/1) on silica gel to afford the target compound **35** as a

colorless solid (0.65 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 – 8.47 (m, 2H), 8.10 (s, 1H), 8.02 (s, 1H), 7.84 – 7.80 (m, 2H), 7.78 – 7.72 (m, 4H), 7.64 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 2.72 – 2.68 (m, 2H), 2.66 (t, J = 5.8 Hz, 2H), 1.78 – 1.73 (m, 4H), 1.58 – 1.53 (m, 4H), 1.40 – 1.35 (m, 4H), 1.32 – 1.27 (m, 8H), 0.86 (t, J = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.60, 134.27, 132.50, 132.44, 128.24, 128.21, 128.18, 127.45, 127.41, 127.35, 126.86, 126.63, 126.29, 122.96, 121.89, 117.81, 78.60, 32.15, 29.57, 29.54, 29.52, 29.50, 29.48, 28.81, 28.73, 22.97, 20.75, 20.56, 14.39. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}SSe$, 712.2641; found 712.2675.

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)selenopheno[3,2-*b*]selenophene (36).

Under the protection of nitrogen, to a degassed mixture solution of toluene and K_2CO_3 (4.0 eq.) was added compound **30** (1.0 eq.), compound **40** (2.3 eq.) and $Pd(PPh_3)_4$ (0.05 eq.). The mixture was heated overnight under nitrogen at 100 °C. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (eluent: petroleum ether/DCM = 6/1) on silica gel to afford the target compound **36** as a colorless solid (0.32 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.49 – 8.47 (m, 2H), 8.12 (s, 2H), 7.82 – 7.75 (m, 6H), 7.61 – 7.57 (m, 2H), 7.51 – 7.49 (m, 2H), 2.69 (t, J = 7.1 Hz, 4H), 1.83 – 1.76 (m, 4H), 1.60 – 1.53 (m, 4H), 1.40 – 1.36 (m, 4H), 1.32 – 1.27 (m, 12H), 0.95 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.97, 142.12, 136.14, 134.62, 132.43, 128.20, 128.14, 127.43, 127.35, 126.60, 126.19, 124.92, 117.79, 103.66, 32.14, 29.54, 29.51, 29.49, 28.71, 22.95, 20.76, 14.37. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}Se_2$, 760.2092; found 760.2120.

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)-3,6-dioctylthieno[3,2-*b*]thiophene (37).

Compound **37** was synthesized according to reported method.[S2]

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)-3,6-dioctylselenopheno[3,2-*b*]thiophene (38).

Under the protection of nitrogen, to a degassed mixture solution of toluene and K_2CO_3 (4.0 eq.) was added compound **32** (1.0 eq.), compound **40** (2.3 eq.) and $Pd(PPh_3)_4$ (0.05 eq.). The mixture was heated overnight under nitrogen at 100 °C. The resulting mixture was extracted with dichloromethane, and the combined

organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (eluent: petroleum ether/DCM = 8/1) on silica gel to afford the target compound **38** as a colorless solid (0.25 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.52 – 8.44 (m, 2H), 7.89 – 7.86 (m, 2H), 7.82 – 7.78 (m, 2H), 7.64 – 7.59 (m, 2H), 7.57 – 7.53 (m, 4H), 2.73 – 2.65 (m, 4H), 2.48 (t, J = 7.0 Hz, 4H), 1.75 – 1.65 (m, 4H), 1.60 – 1.53 (m, 4H), 1.39 – 1.32 m, 4H), 1.30 – 1.21 (m, 20H), 1.19 – 1.12 (m, 16H), 0.89 – 0.86 (m, 6H), 0.84 – 0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.05, 140.38, 138.49, 137.43, 136.63, 135.77, 135.48, 134.79, 133.99, 133.97, 132.80, 132.72, 129.16, 128.95, 128.28, 127.24, 127.20, 127.14, 126.75, 122.55, 101.16, 100.62, 78.07, 78.01, 32.20, 32.10, 29.99, 29.67, 29.65, 29.53, 29.50, 29.47, 29.39, 29.08, 28.97, 28.91, 28.84, 22.96, 22.88, 20.25, 20.23, 14.39, 14.34. MALDI-TOF MS (m/z): [M^+] calcd for $C_{62}H_{80}SSe$, 936.5148; found 936.5176.

Synthesis of 2,5-bis(1-(dec-1-yn-1-yl)naphthalen-2-yl)-3,6-dioctylselenopheno[3,2-*b*]selenophene (39).

Under the protection of nitrogen, to a degassed mixture solution of toluene and K_2CO_3 (4.0 eq.) was added compound **33** (1.0 eq.), compound **40** (2.3 eq.) and $Pd(PPh_3)_4$ (0.05 eq.). The mixture was heated overnight under nitrogen at 100 °C. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (eluent: petroleum ether/DCM = 8/1) on silica gel to afford the target compound **39** as a colorless solid (0.34 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.48 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.57 – 7.53 (m, 4H), 2.71 – 2.64 (m, 4H), 2.48 (t, J = 7.0 Hz, 4H), 1.72 – 1.65 (m, 4H), 1.64 – 1.51 (m, 4H), 1.39 – 1.35 (m, 4H), 1.27 (d, J = 2.9 Hz, 20H), 1.20 – 1.10 (m, 16H), 0.90 – 0.86 (m, 6H), 0.82 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.65, 137.48, 137.37, 133.97, 132.72, 128.93, 128.27, 127.19, 127.17, 127.14, 126.71, 122.04, 101.19, 78.08, 77.59, 77.27, 76.95, 32.22, 32.10, 30.81, 29.63, 29.51, 29.46, 29.40, 29.18, 29.10, 28.85, 22.97, 22.88, 20.26, 14.40, 14.35. MALDI-TOF MS (m/z): [M^+] calcd for $C_{62}H_{80}Se_2$, 984.4602; found 984.4626.

Synthesis of 9,18-dioctylbenzo[4',5']indeno[1',2':5,6]thiopyrano[3,2-*b*]benzo[4,5]indeno[1,2-

***e*]thiopyran (SS2).**

Under the protection of nitrogen, to a degassed solution of compound **34** (1.0 eq.) in dry toluene were added $PtCl_2$ (0.1 eq.), The mixture was heated overnight at 110 °C and then cooled to r.t. After removing toluene with a rotary evaporator, the product was separated and purified through column chromatography (eluent: petroleum ether/DCM = 4/1) on silica gel to provide the product **SS2** as a yellow solid (68 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.46 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.2 Hz, 2H), 7.98 (s, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.57 – 7.49 (m, 4H), 3.21 (t, J = 7.6 Hz, 4H), 1.98 – 1.80 (m, 4H), 1.64 – 1.53 (m, 4H), 1.45 – 1.38 (m, 4H), 1.33 – 1.21 (m, 12H), 0.89 (t, J = 5.2 Hz, 6H). ^{13}C NMR peaks were barely detected because of the low solubility of **SS2** in deuterated solvent. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}S_2$, 664.3192; found 664.3215.

Synthesis of 9,18-dioctylbenzo[4',5']indeno[1',2':5,6]selenopyrano[3,2-*b*]benzo[4,5]indeno[1,2-*e*]thiopyran (SSe2).

Under the protection of nitrogen, to a degassed solution of compound **35** (1.0 eq.) in dry toluene were added $PtCl_2$ (0.1 eq.), The mixture was heated overnight at 110 °C and then cooled to r.t. After removing toluene with a rotary evaporator, the product was separated and purified through column chromatography (eluent: petroleum ether/DCM = 4/1) on silica gel to provide the product **SSe2** as a yellow solid (84 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (d, J = 8.2 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.95 (s, 1H), 7.89 (t, J = 7.4 Hz, 2H), 7.74 (s, 1H), 7.63 (t, J = 7.3 Hz, 2H), 7.54 – 7.43 (m, 4H), 3.16 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.7 Hz, 2H), 1.88 – 1.86 (m, 4H), 1.56 (t, J = 7.4 Hz, 4H), 1.41 (d, J = 7.3 Hz, 4H), 1.34 – 1.30 (m, 12H), 1.00 – 0.75 (m, 6H). ^{13}C NMR peaks were barely detected because of the low solubility of **SSe2** in deuterated solvent. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}SSe$, 712.2641; found 712.2672.

Synthesis of 9,18-dioctylbenzo[4',5']indeno[1',2':5,6]selenopyrano[3,2-*b*]benzo[4,5]indeno[1,2-*e*]selenopyran (SeSe2).

Under the protection of nitrogen, to a degassed solution of compound **36** (1.0 eq.) in dry toluene were

added $PtCl_2$ (0.1 eq.), The mixture was heated overnight at 110 °C and then cooled to r.t. After removing toluene with a rotary evaporator, the product was separated and purified through column chromatography (eluent: petroleum ether/DCM = 4/1) on silica gel to provide the product **SeSe2** as a yellow solid (92 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (d, J = 8.3 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H), 7.94 – 7.87 (m, 2H), 7.82 (d, J = 1.6 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.56 – 7.43 (m, 4H), 3.07 (t, J = 7.7 Hz, 4H), 1.89 – 1.87 (m, 4H), 1.58 – 1.56 (m, 4H), 1.40 – 1.37 (m, 4H), 1.38 – 1.27 (m, 12H), 0.97 – 0.78 (m, 6H). ^{13}C NMR peaks were barely detected because of the low solubility of **SeSe2** in deuterated solvent. MALDI-TOF MS (m/z): [M^+] calcd for $C_{46}H_{48}Se_2$, 760.2092; found 760.2150.

Synthesis of 7,9,16,18-tetraoctylbenzo[4',5']indeno[1',2':5,6]thiopyrano[3,2-*b*]benzo[4,5]indeno[1,2-*e*]thiopyran (SS4).

Compound **SS4** was synthesized according to reported method.[S2]

Synthesis of 7,9,16,18-tetraoctylbenzo[4',5']indeno[1',2':5,6]selenopyrano[3,2-*b*]benzo[4,5]indeno[1,2-*e*]thiopyran (SSe4).

Under the protection of nitrogen, to a degassed solution of compound **38** (1.0 eq.) in dry toluene was added $PtCl_2$ (0.1 eq.), The mixture was heated overnight at 110 °C and then cooled to r.t. After removing toluene with a rotary evaporator, the product was separated and purified through column chromatography (eluent: petroleum ether/DCM = 6/1) on silica gel to provide the product **SSe4** as a yellow solid (63 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 – 8.46 (m, 2H), 8.22 – 8.18 (m, 2H), 7.96 – 7.61 (m, 2H), 7.70 – 7.67 (m, 2H), 7.58 – 7.49 (m, 4H), 3.83 – 3.73 (m, 4H), 3.35 (t, J = 7.8 Hz, 2H), 3.22 (t, J = 7.9 Hz, 2H), 2.09 (s, 4H), 1.91 (d, J = 8.2 Hz, 4H), 1.80 (m, 4H), 1.66 – 1.55 (m, 8H), 1.50 – 1.43 (m, 8H), 1.41 – 1.37 (m, 10H), 1.34 – 1.30 (m, 10H), 0.99 – 0.94 (m, 6H), 0.93 – 0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.89, 142.42, 139.64, 134.28, 134.27, 130.93, 129.34, 129.04, 129.01, 128.74, 127.73, 127.44, 126.14, 126.07, 125.80, 125.76, 125.64, 125.35, 125.30, 125.10, 124.40, 123.83, 123.29, 122.96, 122.67, 122.11, 34.01, 32.43, 32.32, 31.53, 30.57, 30.52, 30.51, 30.46, 30.14, 30.09, 29.92, 29.89, 29.86, 29.84, 29.81, 29.56, 29.02, 28.48, 23.30, 23.27, 14.66, 14.62. MALDI-TOF MS (m/z): [M^+]

calcd for $C_{62}H_{80}SSe$, 936.5148; found 936.4621.

Synthesis of 7,9,16,18-tetraoctylbenzo[4',5']indeno[1',2':5,6]selenopyrano[3,2-*b*]benzo[4,5]indeno[1,2-*e*]selenopyran (SeSe4).

Under the protection of nitrogen, to a degassed solution of compound **39** (1.0 eq.) in dry toluene was added $PtCl_2$ (0.1 eq.), The mixture was heated overnight at 110 °C and then cooled to r.t. After removing toluene with a rotary evaporator, the product was separated and purified through column chromatography (eluent: petroleum ether/DCM = 6/1) on silica gel to provide the product **SeSe4** as a yellow solid (72 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (d, J = 8.2 Hz, 2H), 8.20 (d, J = 8.7 Hz, 2H), 7.95 – 7.91 (m, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.55 – 7.50 (m, 4H), 3.26 (t, J = 7.9 Hz, 4H), 2.15 – 2.11 (m, 4H), 1.95 – 1.87 (m, 4H), 1.84 – 1.77 (m, 4H), 1.65 – 1.55 (m, 10H), 1.39 – 1.27 (m, 30H), 0.97 – 0.94 (m, 6H), 0.91 – 0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.31, 130.59, 128.82, 128.76, 128.65, 127.51, 126.10, 125.80, 125.16, 123.33, 122.62, 110.21, 34.61, 34.60, 32.43, 32.33, 31.48, 30.54, 30.43, 30.34, 30.21, 30.12, 29.94, 29.90, 29.88, 29.86, 28.58, 23.28, 14.66, 14.63. MALDI-TOF MS (m/z): [M^+] calcd for $C_{62}H_{80}Se_2$, 984.4602; found 984.4074.

4. X-ray crystallographic data.

Table S1. Crystal data and structure refinement details for the PAHs containing chalcogenopyrano[3,2-*b*]chalcogenopyrans moieties.

Compounds	**SS2**	**SSe2**	**SeSe2**	**SS4**	**SSe4**	**SeSe4**
CCDC No.	2294520	2294524	2294527	2204211	2294534	2294533
formula	$C_{46}H_{48}S_2$	$C_{46}H_{48}SSe$	$C_{46}H_{48}Se_2$	$C_{62}H_{80}S_2$	$C_{62}H_{80}SSe$	$C_{62}H_{80}Se_2$
M	664.96	711.86	758.76	891.15	936.28	983.18
T (K)	100	173	173	194	123	293
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178	1.54178
crystal system	Monoclinic	Monoclinic	Monoclinic	Trigonal	Trigonal	Trigonal
space group	*C*2/c	*C*2/c	*C*2/c	*R*3	*R*3	*R*3
a (Å)	20.1191(8)	20.3594(5)	20.4997(5)	53.3488(8)	53.004(11)	53.438(3)
b (Å)	4.7123(2)	4.7400(10)	4.7373(10)	53.3488(8)	53.004(11)	53.438(3)
c (Å)	37.0051(15)	37.0751(9)	37.0859(9)	5.0913(11)	5.077(2)	5.104(3)
α (deg.)	90	90	90	90	90.00(3)	90
β (deg.)	90.592(2)	90.515(10)	90.479(10)	90	90.00(3)	90
γ (deg.)	90	90	90	120	120.00(3)	120
V (Å^3)	3508.2(2)	3577.73(15)	3601.41(15)	12549(3)	12352(7)	12622(8)
Z / D_{calcd} (mg/m^3)	4 / 1.259	4 / 1.322	4 / 1.399	9 / 1.061	9 / 1.133	9 / 1.164
μ (mm^{-1})	1.608	2.195	2.795	1.119	1.537	1.898
F (000)	1424.0	1496.0	1568.0	4364	4518	4680
max/min transmission	0.753 / 0.718	0.167 / 0.064	0.753 / 0.717	0.753 / 0.641	0.837 / 0.791	0.796 / 0.675
final *R* indices [$I > 2\theta(I)$]	*R*1 = 0.0343 *wR*2 = 0.0969	*R*1 = 0.0330 *wR*2 = 0.0890	*R*1 = 0.0240 *wR*2 = 0.0649	*R*1 = 0.0585 *wR*2 = 0.1936	*R*1 = 0.0931 *wR*2 = 0.2503	*R*1 = 0.1205 *wR*2 = 0.2438
R indices (all data)	*R*1 = 0.0381 *wR*2 = 0.1005	*R*1 = 0.0380 *wR*2 = 0.0931	*R*1 = 0.0254 *wR*2 = 0.0660	*R*1 = 0.0747 *wR*2 = 0.2062	*R*1 = 0.1254 *wR*2 = 0.3008	*R*1 = 0.1351 *wR*2 = 0.2516

Fig. S1. ORTEP diagram for the crystal structure of **SS2** with an ellipsoid contour probability level of 50%.

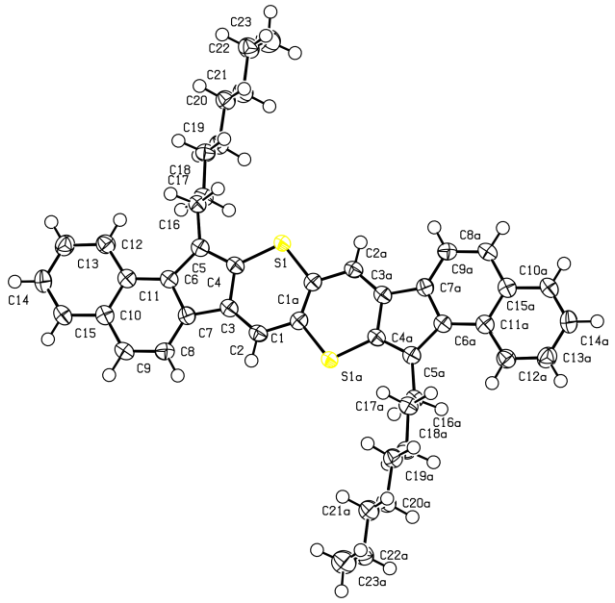


Fig. S2. ORTEP diagram for the crystal structure of **SSe2** with an ellipsoid contour probability level of 50%.

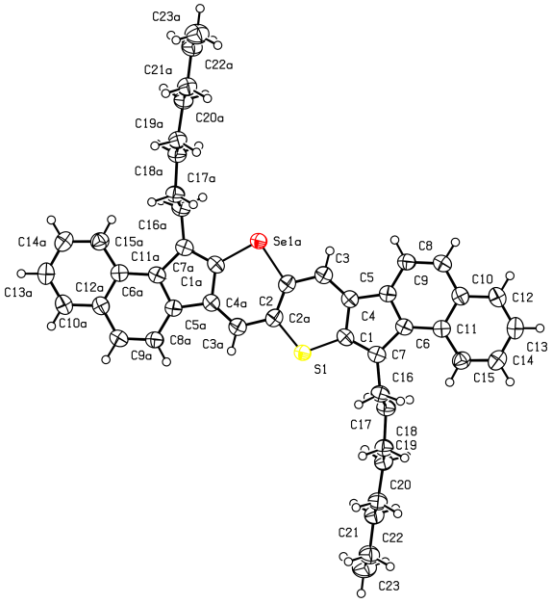


Fig. S3. ORTEP diagram for the crystal structure of **SeSe2** with an ellipsoid contour probability level of 50%.

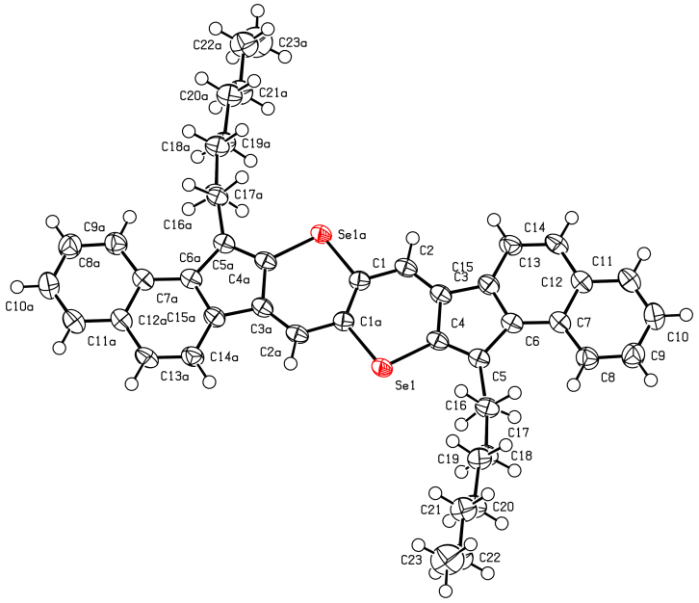


Fig. S4. ORTEP diagram for the crystal structure of **SS4** with an ellipsoid contour probability level of 50%.

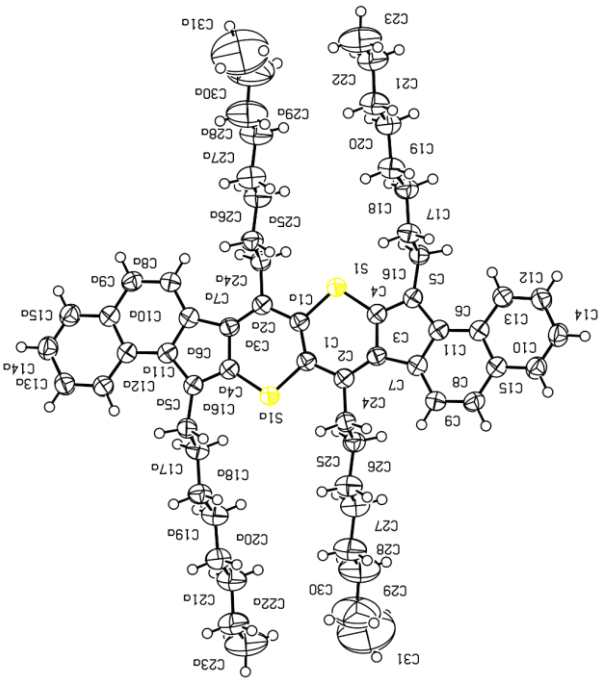


Fig. S5. ORTEP diagram for the crystal structure of **SSe4** with an ellipsoid contour probability level of 50%.

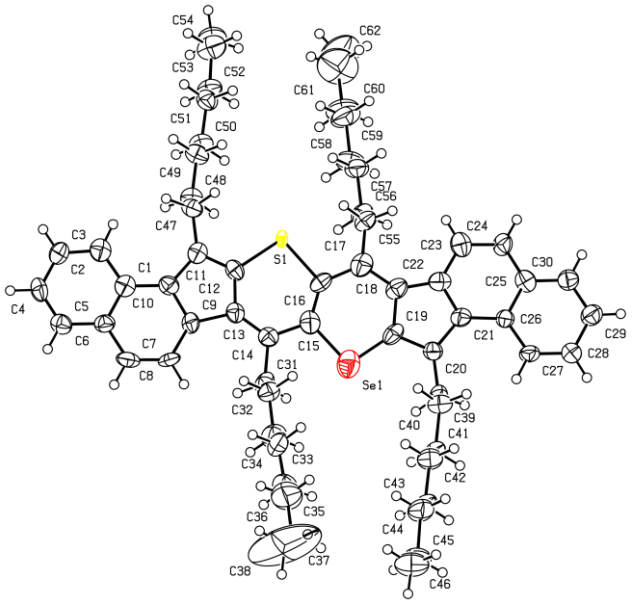


Fig. S6. ORTEP diagram for the crystal structure of **SeSe4** with an ellipsoid contour probability level of 50%.

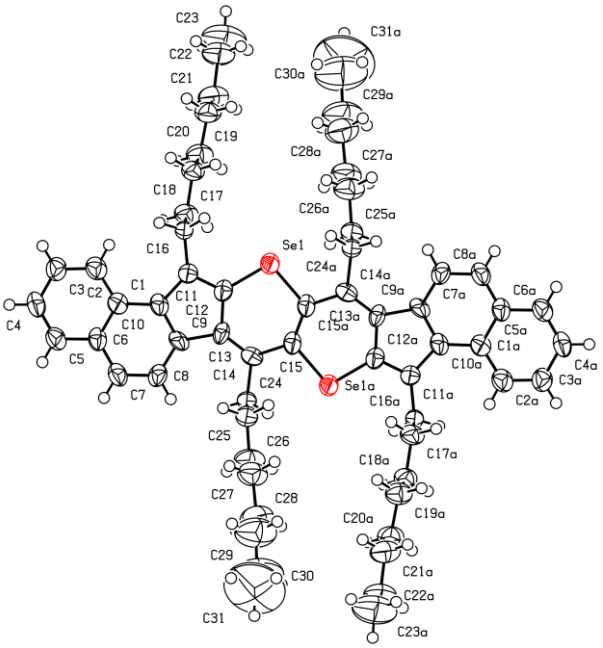


Fig. S7. Crystal packing structures of **SSe2.**

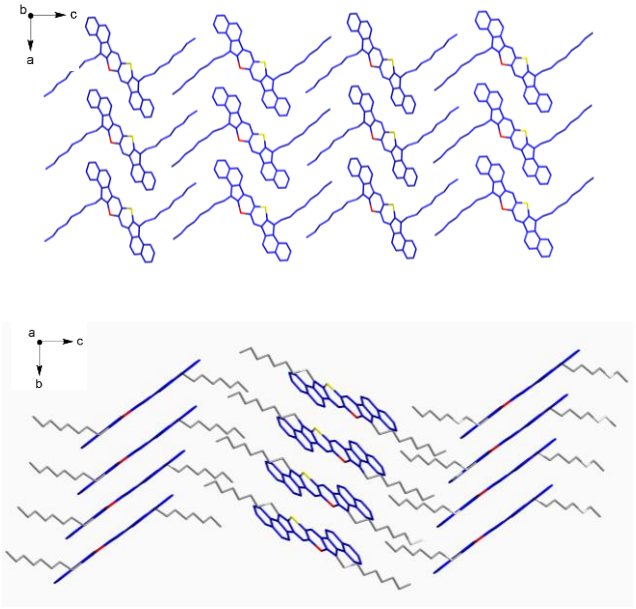


Fig. S8. Crystal packing structures of **SeSe2.**

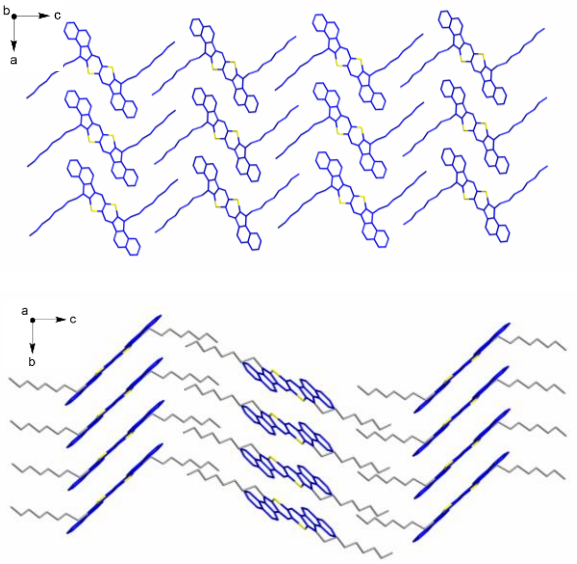


Fig. S9. Crystal packing structures of **SSe4.**

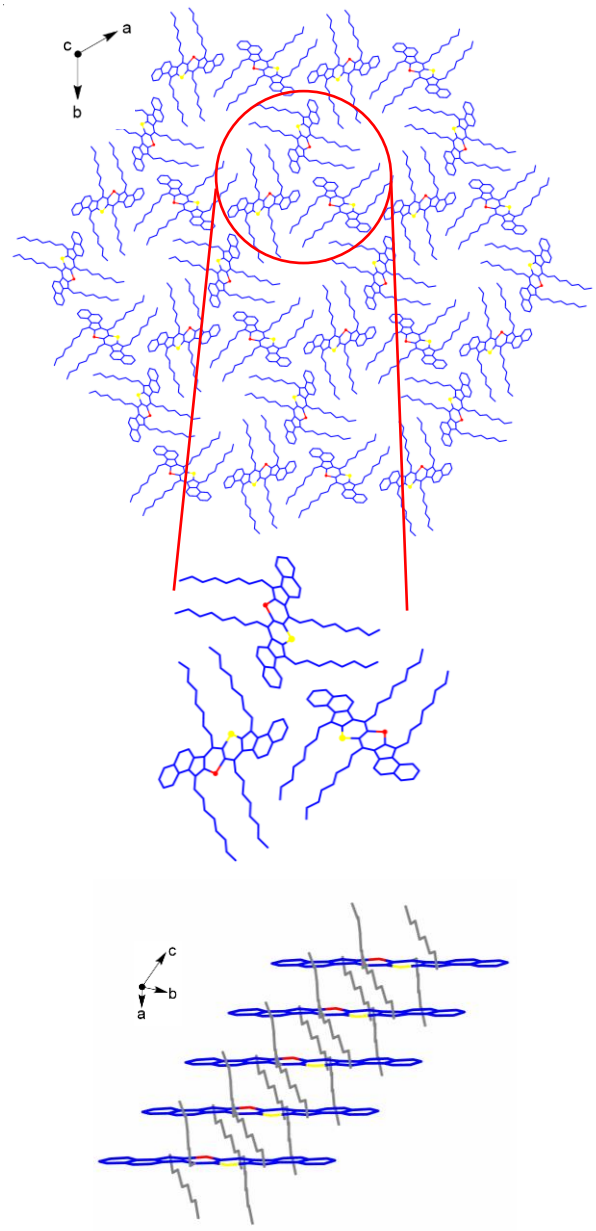


Fig. S10. Crystal packing structures of **SeSe4.**

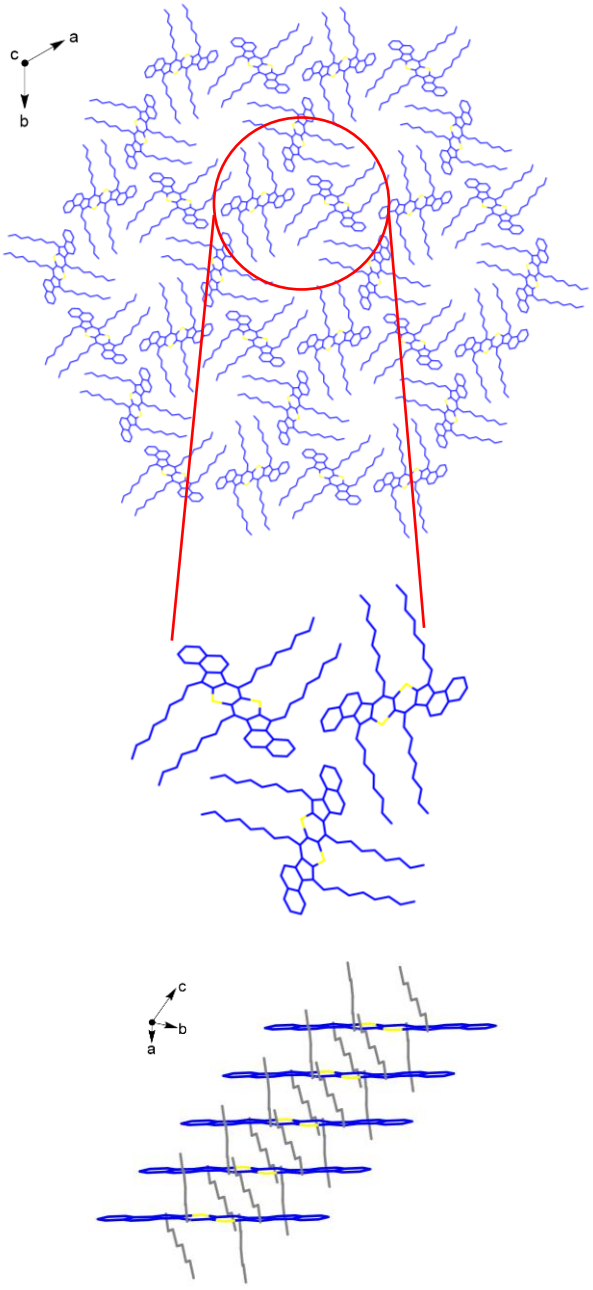


Table S2. Selected bond lengths for **SS2**.

Bond	Length (Å)	Bond	Length (Å)
S1-C4	1.7313(14)	C9-C10	1.422(2)
S1-C1	1.7516(14)	C10-C15	1.415(2)
C1-C1	1.386(3)	C10-C11	1.436(2)
C1-C2	1.4331(19)	C11-C12	1.417(2)
C2-C3	1.356(2)	C12-C13	1.373(2)
C3-C7	1.4500(19)	C13-C14	1.409(2)
C3-C4	1.4631(19)	C14-C15	1.367(2)
C4-C5	1.3685(19)	C16-C17	1.5387(18)
C5-C6	1.4711(19)	C17-C18	1.5227(19)
C5-C16	1.5028(19)	C18-C19	1.5268(19)
C7-C8	1.407(2)	C19-C20	1.5277(19)
C7-C6	1.4100(19)	C20-C21	1.5255(19)
C6-C11	1.4333(19)	C21-C22	1.524(2)
C9-C8	1.366(2)	C22-C23	1.524(2)

Table S3. Selected bond lengths for **SSe2**.

Bond	Length (Å)	Bond	Length (Å)
Se1-C1	1.871(2)	C8-C9	1.366(3)
Se1-C2	1.952(2)	C9-C10	1.414(3)
S1-C2	1.705(4)	C10-C12	1.417(3)
S1-C1	1.743(5)	C10-C11	1.436(2)
C1-C7	1.361(2)	C11-C15	1.413(3)
C1-C4	1.458(2)	C12-C13	1.358(3)
C2-C2	1.382(4)	C13-C14	1.406(3)
C2-C3	1.434(3)	C14-C15	1.372(3)
C3-C4	1.353(3)	C16-C17	1.536(2)
C4-C5	1.455(2)	C17-C18	1.524(2)
C5-C6	1.403(2)	C18-C19	1.519(2)
C5-C8	1.407(3)	C19-C20	1.522(2)
C6-C11	1.432(2)	C20-C21	1.520(3)
C6-C7	1.477(2)	C21-C22	1.519(3)
C7-C16	1.499(2)	C22-C23	1.518(3)

Table S4. Selected bond lengths for **SeSe2**.

Bond	Length (Å)	Bond	Length (Å)
Se1-C4	1.8697(17)	C9-C8	1.372(3)
Se1-C1	1.9010(16)	C9-C10	1.406(3)
C1-C1	1.373(3)	C10-C11	1.365(3)
C1-C2	1.438(2)	C11-C12	1.418(2)
C2-C3	1.352(2)	C12-C13	1.418(2)
C4-C5	1.363(2)	C13-C14	1.369(2)
C4-C3	1.461(2)	C14-C15	1.406(2)
C3-C15	1.457(2)	C16-C17	1.536(2)
C7-C8	1.415(2)	C17-C18	1.521(2)
C7-C6	1.429(2)	C18-C19	1.526(2)
C7-C12	1.438(2)	C19-C20	1.520(2)
C6-C15	1.405(2)	C20-C21	1.525(2)
C6-C5	1.478(2)	C21-C22	1.519(3)
C5-C16	1.500(2)	C22-C23	1.520(3)

Table S5. Selected bond lengths for **SS4**.

Bond	Length (Å)
C1–C1	1.398(6)
C1-C2	1.458(4)
C1-S1	1.745(3)
S1-C4	1.717(3)
C2-C3	1.369(4)
C3-C4	1.458(4)
C3-C7	1.468(4)
C5-C4	1.368(4)
C5-C6	1.460(4)
C6-C7	1.420(4)
C6-C11	1.431(4)
C7-C8	1.408(4)
C9-C8	1.364(4)
C9-C10	1.424(4)
C10-C15	1.411(4)
C10-C11	1.429(4)
C11-C12	1.415(4)
C12-C13	1.367(4)
C13-C14	1.401(5)
C14-C15	1.364(5)

Table S6. Selected bond lengths for **SSe4**.

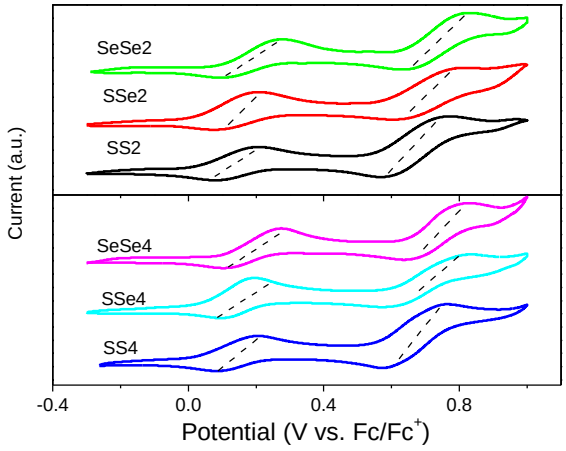
Bond	Length (Å)	Bond	Length (Å)
Se1-C19	1.876(7)	C14-C15	1.454(11)
Se1-C15	1.915(7)	C15-C16	1.374(9)
C1-C6	1.42(1)	C16-C17	1.462(12)
C1-C2	1.428(10)	C17-C18	1.383(11)
C1-C10	1.428(11)	C18-C22	1.442(12)
S1-C12	1.780(8)	C18-C19	1.513(10)
S1-C16	1.865(8)	C19-C20	1.407(10)
C3-C2	1.356(12)	C20-C21	1.461(10)
C3-C4	1.38(1)	C21-C22	1.379(9)
C4-C5	1.348(10)	C21-C26	1.439(10)
C5-C6	1.416(11)	C22-C23	1.417(11)
C6-C7	1.425(10)	C23-C24	1.366(12)
C8-C7	1.344(12)	C24-C25	1.423(10)
C8-C9	1.421(9)	C25-C30	1.394(11)
C9-C10	1.432(9)	C25-C26	1.426(9)
C9-C13	1.499(10)	C26-C27	1.407(9)
C10-C11	1.434(10)	C27-C28	1.376(11)
C11-C12	1.334(10)	C28-C29	1.417(11)
C12-C13	1.421(9)	C29-C30	1.391(10)
C14-C13	1.342(10)		

Table S7. Selected bond lengths for **SeSe4**.

Bond	Length (Å)	Bond	Length (Å)
Se1-C12	1.857(8)	C13-C14	1.330(11)
Se1-C15	1.919(8)	C14-C5	1.466(11)
C1-C2	1.420(12)	C14-C24	1.535(11)
C1-C6	1.421(11)	C15-C15	1.380(16)
C1-C10	1.431(11)	C16-C17	1.542(12)
C2-C3	1.376(12)	C17-C18	1.513(11)
C3-C4	1.405(12)	C18-C19	1.524(13)
C4-C5	1.365(13)	C19-C20	1.508(12)
C5-C6	1.433(11)	C20-C21	1.535(15)
C6-C7	1.412(12)	C21-C22	1.509(14)
C7-C8	1.378(11)	C22-C23	1.523(17)
C8-C9	1.402(11)	C24-C25	1.547(12)
C9-C10	1.414(11)	C25-C26	1.512(13)
C9-C13	1.491(11)	C26-C27	1.507(15)
C10-C11	1.468(11)	C27-C28	1.532(15)
C11-C12	1.353(11)	C28-C29	1.547(19)
C11-C16	1.504(11)	C29-C30	1.48(2)
C12-C13	1.470(11)	C30-C31	1.52(3)

5. Electrochemical properties

Fig. S11. Cyclic voltammograms of the chalcogen-fused PAHs in DCM solutions (*ca*. 10^{-4} M).



6. Theoretical calculations.

All the theoretical calculations were conducted with the Gaussian 16 program.[S4] The geometry optimization, the frontier orbitals, and the reorganization energy calculation were carried out using the B3LYP method and the 6-311G(d, p) basis set. The nucleus-independent chemical shift (NICS)[S5] was calculated at the same level using the standard GIAO procedure[S6] with the assistance of Multiwfn.[S7] Anisotropy of the induced current density (AICD) plots were calculated by Herges's method based on the optimized structure geometry with π orbitals only.[S8] The iso-chemical shielding surface (ICSS) calculations were carried out to analyze two-dimensional nucleus induced chemical shifts (2D-NICS) along the XY planes.[S7,S9] The octyl groups were omitted for simplification. The transfer integrals between the HOMOs of adjacent molecules were calculated based on the crystal geometries using PW91 exchange and PW91 correlation functionals with the 6-31G* basis set.[S10,S11] The transfer integrals, reorganization energies, and the charge hopping mobilities of the chalcogenopyran-fused PAHs were calculated according to the reported method.[S12]

Fig. S12. Calculated HOMO distributions of (a) azulene, cyclopenta[*b*]chalcogenopyran, and (b) chalcogenopyran-fused PAHs

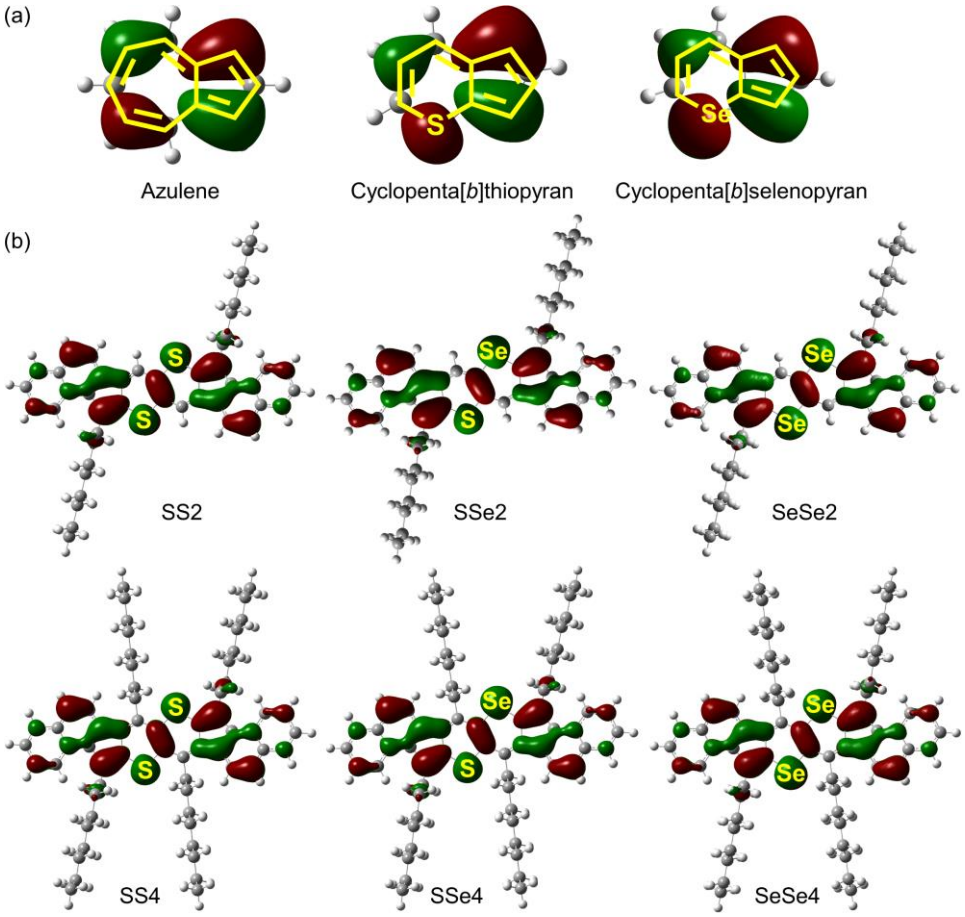


Fig. S13. Calculated (a) NICS(1)$_{zz}$ values and (b) AICD plots of the cyclopenta[5,6]chalcogenopyrano-[3,2-*b*]cyclopenta[e]chalcogenopyran with 18 π-electrons.

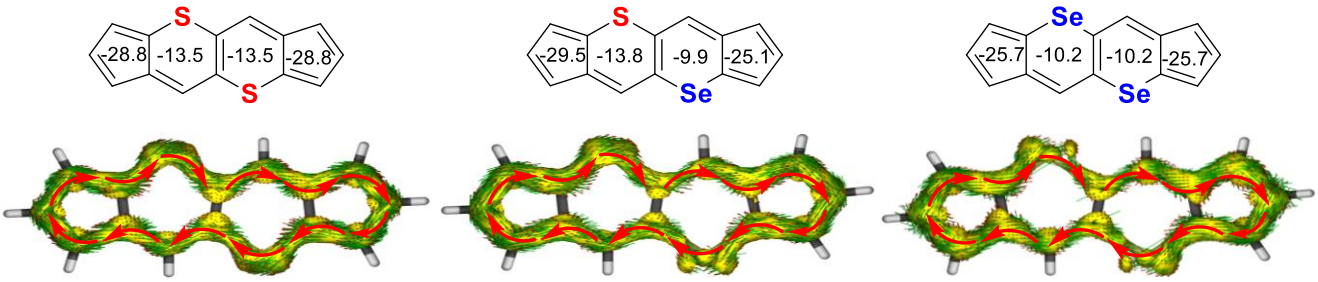


Fig. S14. Correlation between the crystal structures and the calculated transfer integrals of the chalcogenopyran-fused PAHs.

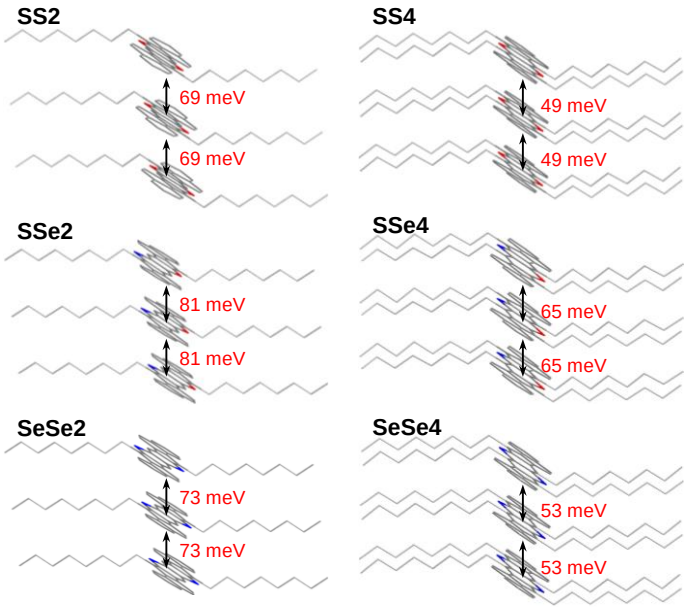


Table S8. Calculated orientation for **SS**.

Center Number	Atomic Name	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	-8.364017	1.438292	0.001007
2	C	0	-6.992311	1.536718	0.000741
3	C	0	-6.177784	0.376819	0.000316
4	C	0	-6.806551	-0.913198	0.000160
5	C	0	-8.222260	-0.974770	0.000440
6	C	0	-8.984737	0.170055	0.000854
7	C	0	-4.755269	0.419325	0.000030
8	C	0	-4.008062	-0.773674	-0.000374
9	C	0	-4.639906	-2.034811	-0.000508
10	C	0	-6.010748	-2.097057	-0.000254
11	C	0	-3.845565	1.552639	0.000172
12	C	0	-2.572516	1.063146	-0.000148
13	C	0	-2.605380	-0.408734	-0.000455
14	S	0	-1.072159	1.943407	-0.000446
15	C	0	0.157555	0.674829	-0.000479
16	C	0	-0.157555	-0.674830	-0.000484
17	C	0	-1.492426	-1.189122	-0.000537
18	C	0	1.492426	1.189121	-0.000554
19	C	0	2.605380	0.408733	-0.000492
20	C	0	2.572517	-1.063146	-0.000166
21	S	0	1.072159	-1.943407	-0.000508
22	C	0	4.008062	0.773674	-0.000414
23	C	0	4.755269	-0.419325	0.000012
24	C	0	3.845565	-1.552639	0.000165
25	C	0	4.639906	2.034811	-0.000549
26	C	0	6.010747	2.097058	-0.000278
27	C	0	6.806550	0.913199	0.000157
28	C	0	6.177784	-0.376819	0.000317
29	C	0	8.222260	0.974771	0.000452
30	C	0	8.984737	-0.170055	0.000887
31	C	0	8.364017	-1.438291	0.001044
32	C	0	6.992311	-1.536717	0.000762
33	H	0	-8.973243	2.335010	0.001334
34	H	0	-6.521877	2.513217	0.000854
35	H	0	-8.700321	-1.948897	0.000317
36	H	0	-10.066840	0.101897	0.001065
37	H	0	-4.052635	-2.946949	-0.000832

38	H	0	-6.514574	-3.057295	-0.000375
39	H	0	-4.130385	2.594008	0.000439
40	H	0	-1.608066	-2.268652	-0.000652
41	H	0	1.608067	2.268651	-0.000677
42	H	0	4.130386	-2.594008	0.000446
43	H	0	4.052635	2.946949	-0.000889
44	H	0	6.514573	3.057295	-0.000400
45	H	0	8.700321	1.948897	0.000326
46	H	0	10.066840	-0.101896	0.001109
47	H	0	8.973244	-2.335009	0.001386
48	H	0	6.521878	-2.513217	0.000879

Table S9. Calculated orientation for **SSe**.

Center Number	Atomic Name	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	-8.397604	-1.047375	0.000827
2	C	0	-7.033956	-1.222807	0.000655
3	C	0	-6.155478	-0.109992	0.000269
4	C	0	-6.711626	1.213364	0.000057
5	C	0	-8.122060	1.354129	0.000241
6	C	0	-8.946928	0.253899	0.000617
7	C	0	-4.738516	-0.230170	0.000076
8	C	0	-3.925116	0.915835	-0.000290
9	C	0	-4.484506	2.209886	-0.000487
10	C	0	-5.850536	2.349324	-0.000322
11	C	0	-3.889329	-1.413070	0.000246
12	C	0	-2.592464	-0.997816	-0.000008
13	C	0	-2.539420	0.471861	-0.000323
14	Se	0	-1.017363	-2.027387	-0.000172
15	C	0	0.285527	-0.627036	-0.000299
16	C	0	-0.065300	0.710539	-0.000334
17	C	0	-1.404942	1.220582	-0.000404
18	C	0	1.629145	-1.111936	-0.000406
19	C	0	2.726588	-0.307834	-0.000364
20	C	0	2.659973	1.162832	-0.000088
21	S	0	1.139925	2.007010	-0.000415
22	C	0	4.136291	-0.640677	-0.000329
23	C	0	4.856368	0.569514	0.000004
24	C	0	3.921716	1.681644	0.000140
25	C	0	4.797165	-1.887169	-0.000423
26	C	0	6.168844	-1.918196	-0.000225
27	C	0	6.937585	-0.716282	0.000105
28	C	0	6.279714	0.559038	0.000239
29	C	0	8.354219	-0.745693	0.000324
30	C	0	9.090615	0.416191	0.000667
31	C	0	8.441325	1.669927	0.000806
32	C	0	7.067655	1.737064	0.000594
33	H	0	-9.056198	-1.908509	0.001123
34	H	0	-6.619163	-2.224226	0.000817
35	H	0	-8.544776	2.353517	0.000078
36	H	0	-10.023560	0.382032	0.000753
37	H	0	-3.847713	3.088140	-0.000785

38	H	0	-6.298939	3.336705	-0.000488
39	H	0	-4.234699	-2.436300	0.000495
40	H	0	-1.508667	2.301673	-0.000538
41	H	0	1.774080	-2.188186	-0.000544
42	H	0	4.182720	2.729218	0.000346
43	H	0	4.230929	-2.812557	-0.000671
44	H	0	6.694581	-2.866629	-0.000322
45	H	0	8.854264	-1.708733	0.000217
46	H	0	10.173993	0.372556	0.000832
47	H	0	9.029996	2.580273	0.001079
48	H	0	6.575031	2.702562	0.000698

Table S10. Calculated orientation for **SeSe**.

Center Number	Atomic Name	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	8.483684	1.278890	0.001962
2	C	0	7.116403	1.423814	0.001542
3	C	0	6.262941	0.291774	0.000687
4	C	0	6.848399	-1.018820	0.000272
5	C	0	8.261517	-1.128115	0.000714
6	C	0	9.061775	-0.009768	0.001538
7	C	0	4.843500	0.380689	0.000209
8	C	0	4.055602	-0.783583	-0.000594
9	C	0	4.644162	-2.064887	-0.000944
10	C	0	6.012751	-2.173882	-0.000544
11	C	0	3.968671	1.544209	0.000529
12	C	0	2.681261	1.099730	-0.000033
13	C	0	2.661208	-0.370637	-0.000700
14	Se	0	1.083111	2.091872	-0.000638
15	C	0	-0.193372	0.661926	-0.000721
16	C	0	0.193371	-0.661926	-0.000714
17	C	0	1.541354	-1.143266	-0.000899
18	C	0	-1.541354	1.143267	-0.000931
19	C	0	-2.661208	0.370637	-0.000725
20	C	0	-2.681260	-1.099730	-0.000036
21	Se	0	-1.083111	-2.091872	-0.000656
22	C	0	-4.055602	0.783582	-0.000631
23	C	0	-4.843500	-0.380689	0.000188
24	C	0	-3.968671	-1.544209	0.000525
25	C	0	-4.644161	2.064887	-0.000972
26	C	0	-6.012751	2.173883	-0.000555
27	C	0	-6.848399	1.018819	0.000271
28	C	0	-6.262941	-0.291774	0.000683
29	C	0	-8.261517	1.128115	0.000729
30	C	0	-9.061774	0.009768	0.001566
31	C	0	-8.483684	-1.278890	0.001985
32	C	0	-7.116403	-1.423814	0.001550
33	H	0	9.122908	2.154499	0.002619
34	H	0	6.679237	2.415668	0.001871
35	H	0	8.706359	-2.117868	0.000388
36	H	0	10.140992	-0.113974	0.001869
37	H	0	4.027246	-2.957249	-0.001570

38	H	0	6.483239	-3.150941	-0.000856
39	H	0	4.291120	2.574871	0.001056
40	H	0	1.674268	-2.221409	-0.001220
41	H	0	-1.674267	2.221409	-0.001281
42	H	0	-4.291120	-2.574871	0.001057
43	H	0	-4.027247	2.957250	-0.001605
44	H	0	-6.483239	3.150941	-0.000860
45	H	0	-8.706359	2.117867	0.000407
46	H	0	-10.140992	0.113974	0.001909
47	H	0	-9.122908	-2.154499	0.002651
48	H	0	-6.679236	-2.415668	0.001873

7. Fabrication and characterization of the OFETs.

The Si/SiO_2 wafer was initially ultrasonically cleaned in acetone, ethanol, and isopropanol for 15 minutes each to remove surface impurities. After drying, a uniformly dense octadecyltrichlorosilane (OTS) monolayer was formed on the surface by maintaining the wafer at 90 ℃ in a vacuum oven for 90 min. After cooling to room temperature, the silicon wafer was cleaned and dried again. Then 20 μL toluene solution of PAH (1 mg/mL) was drop-cast onto the treated silicon wafer. After the solvent evaporated, single crystals successfully grew on the surface. By using the "Au strips" method, a simple single crystal OFET device was successfully fabricated. The current-voltage (*I–V*) characteristics of the device were measured on the micromanipulator probe station using a Keysight B1500A source meter under vacuum conditions.

Fig. S15. (a) Transfer and (b) output characteristics for the OFET based on **SS2**.

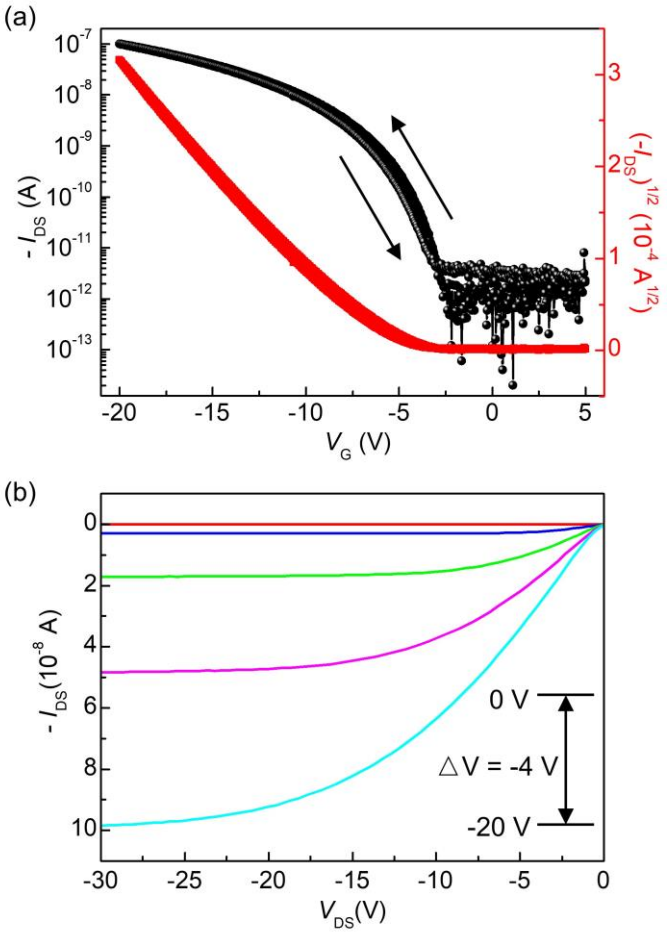


Fig. S16. (a) Transfer and (b) output characteristics for the OFET based on **SeSe2**.

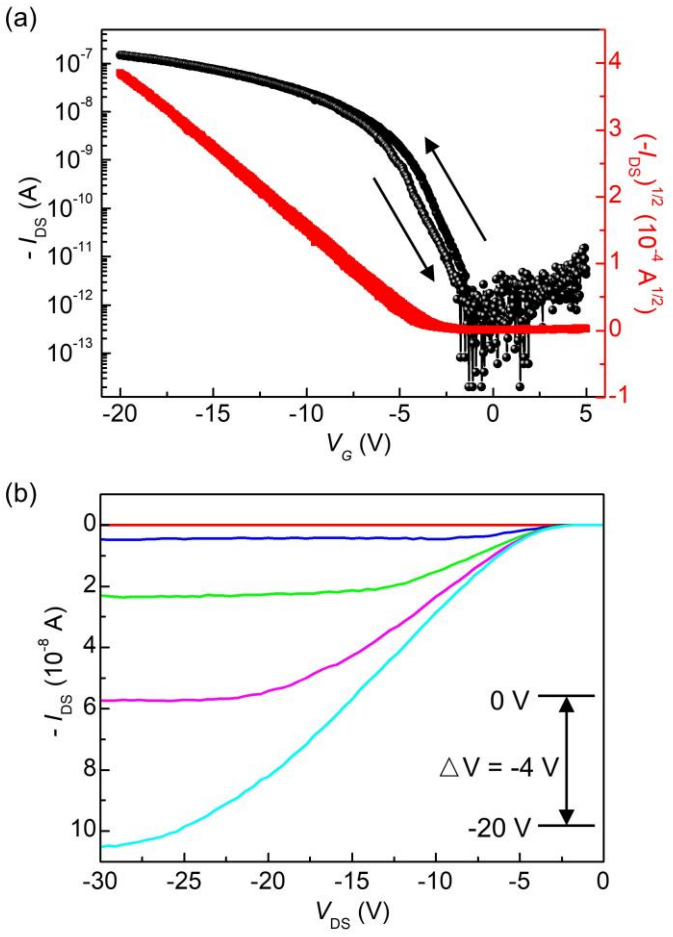


Fig. S17. (a) Transfer and (b) output characteristics for the OFET based on **SS4**.

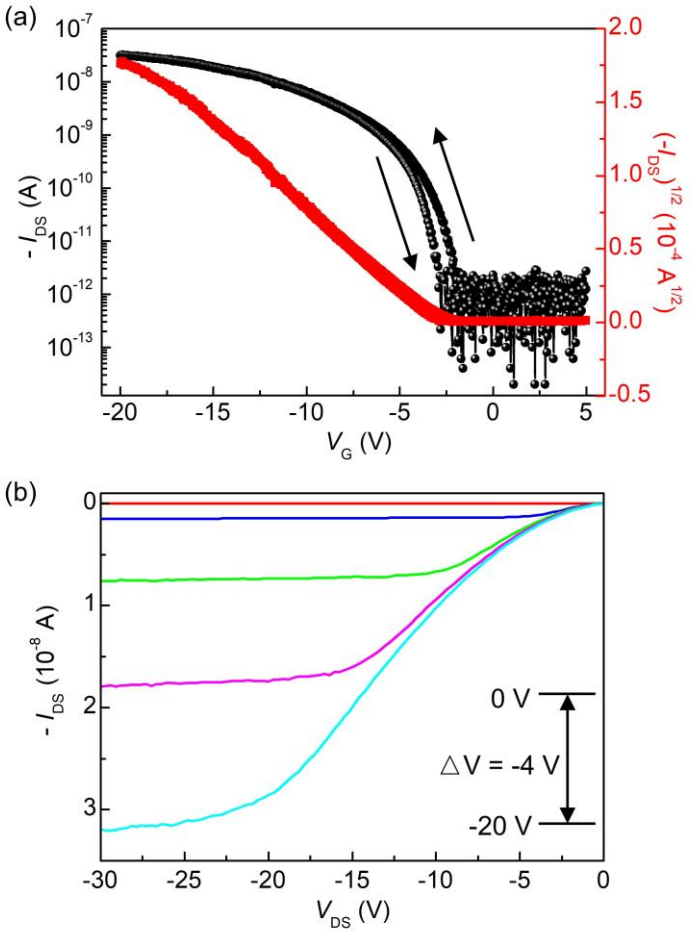


Fig S18. (a) Transfer and (b) output characteristics for the OFET based on **SSe4**.

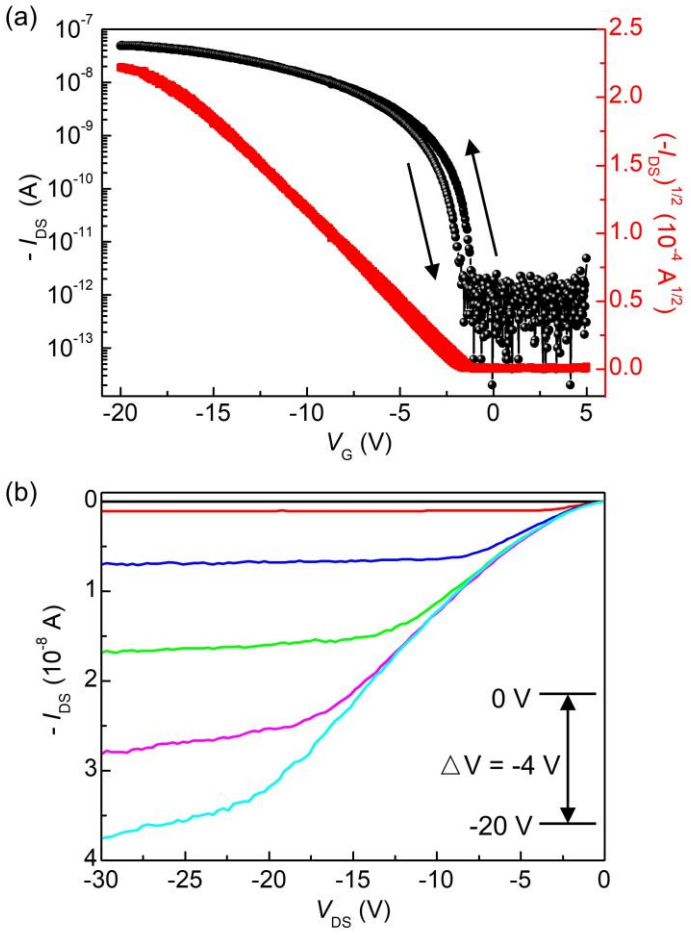
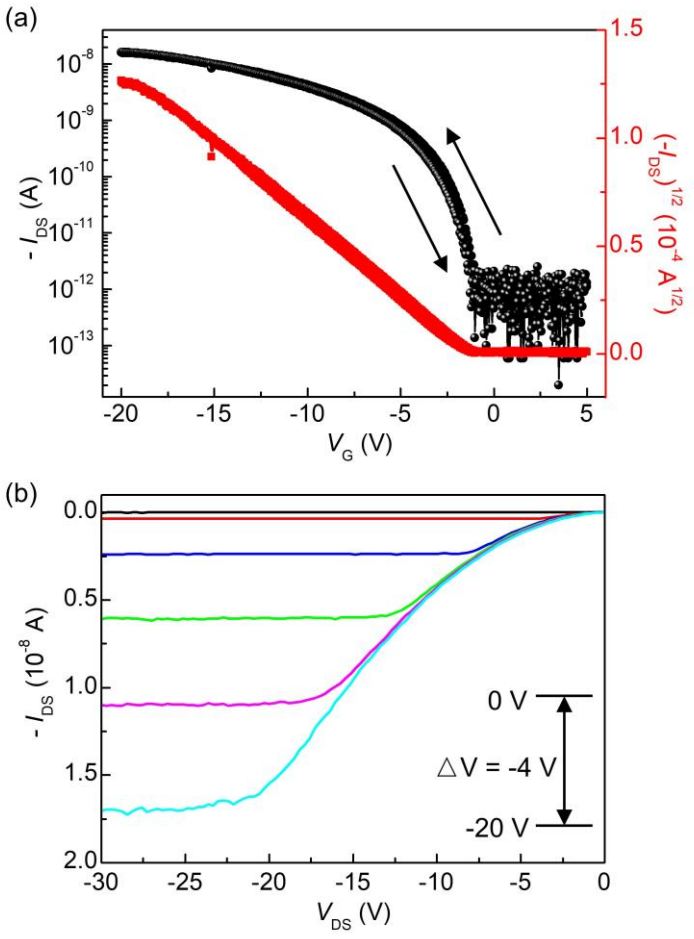


Fig. S19. (a) Transfer and (b) output characteristics for the OFET based on **SeSe4**.



8. ^{1}H and ^{13}C NMR spectra.

Fig. S20. ^{1}H NMR spectrum of **2,3,4,5-tetrabromoselenophene** in $CDCl_3$.

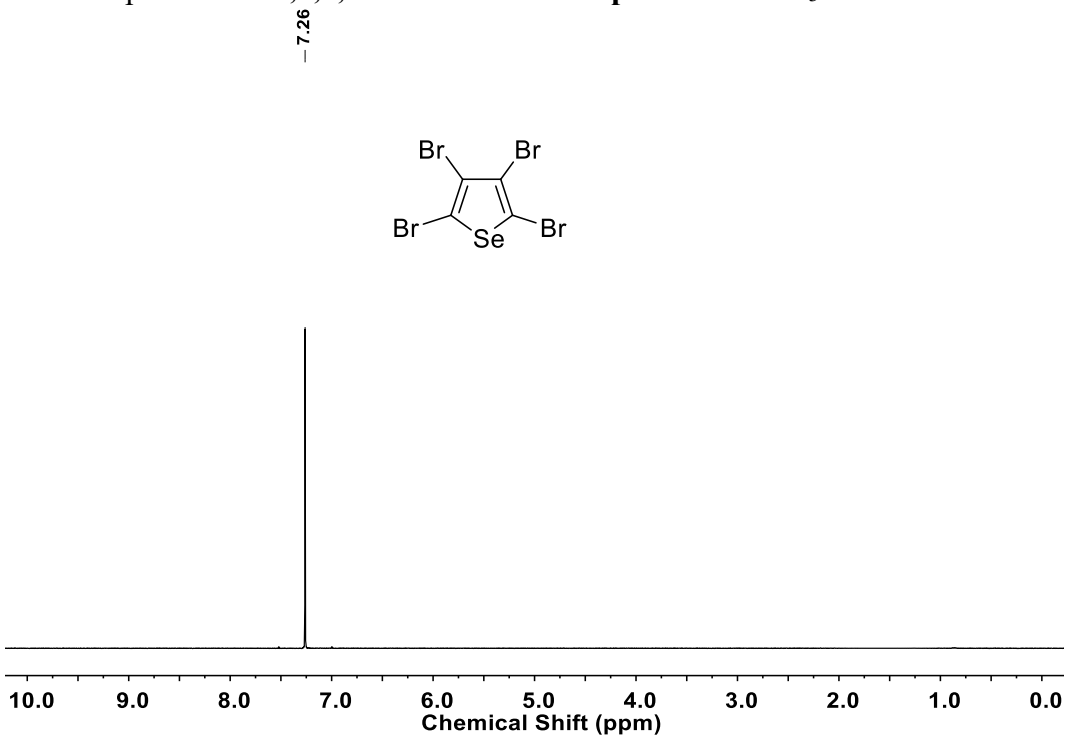


Fig. S21. ^{13}C NMR spectrum of **2,3,4,5-tetrabromoselenophene** in $CDCl_3$.

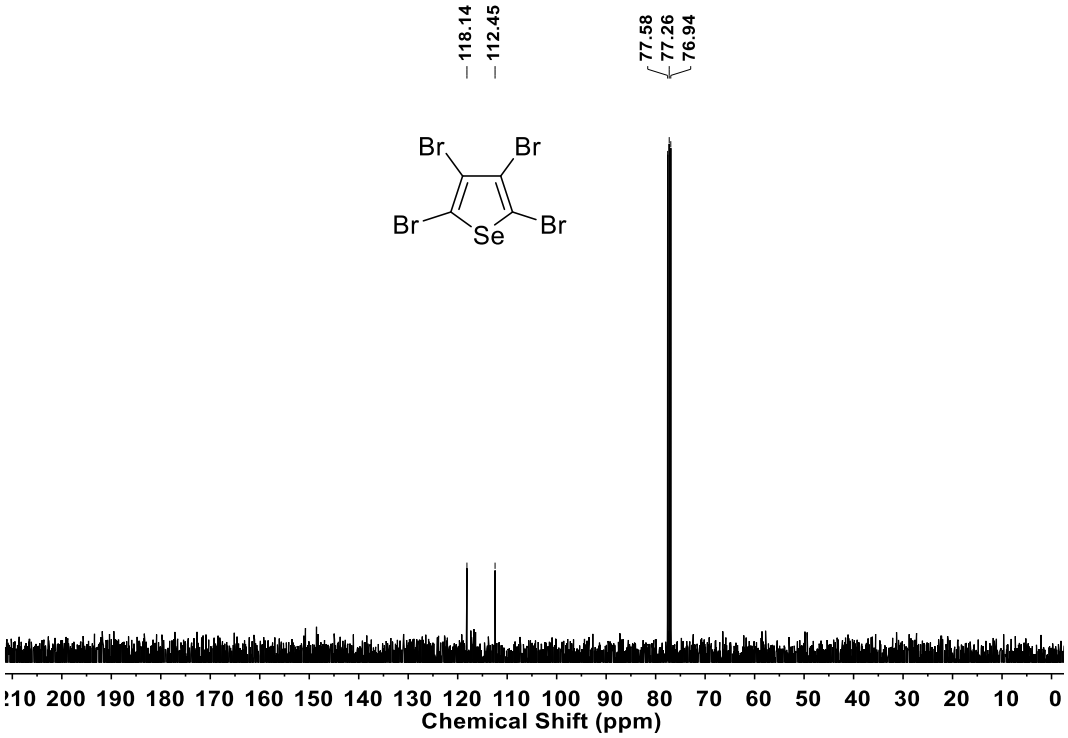


Fig. S22. ^{1}H NMR spectrum of **4** in $CDCl_3$.

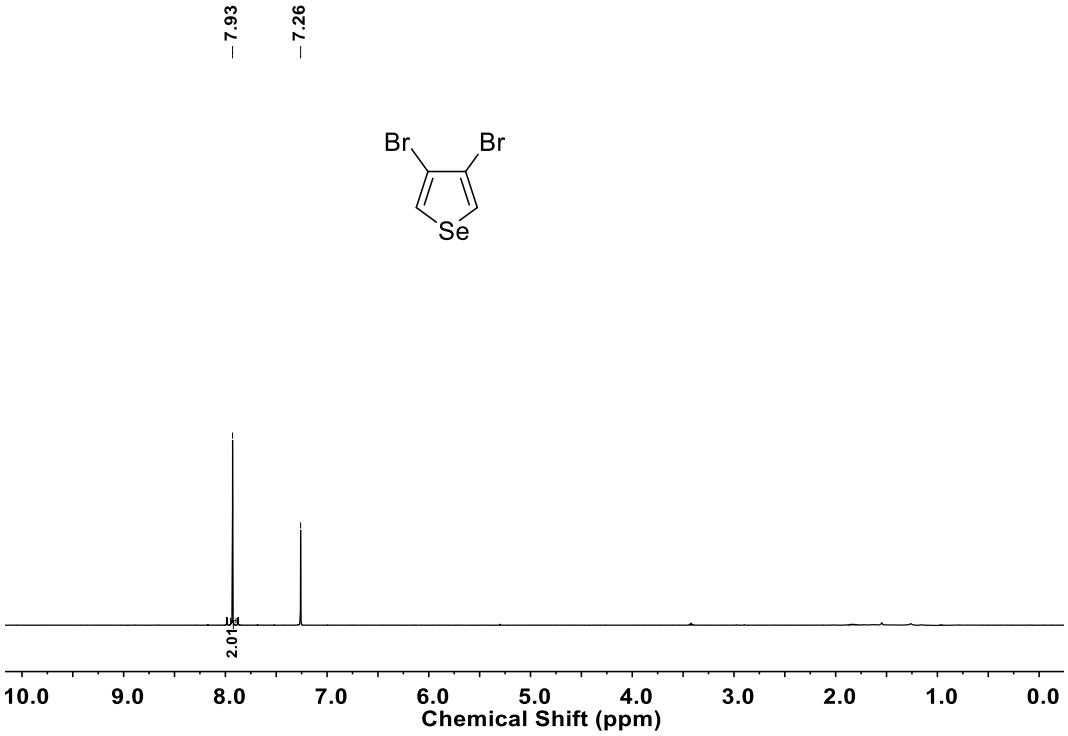


Fig. S23. ^{13}C NMR spectrum of **4** in $CDCl_3$.

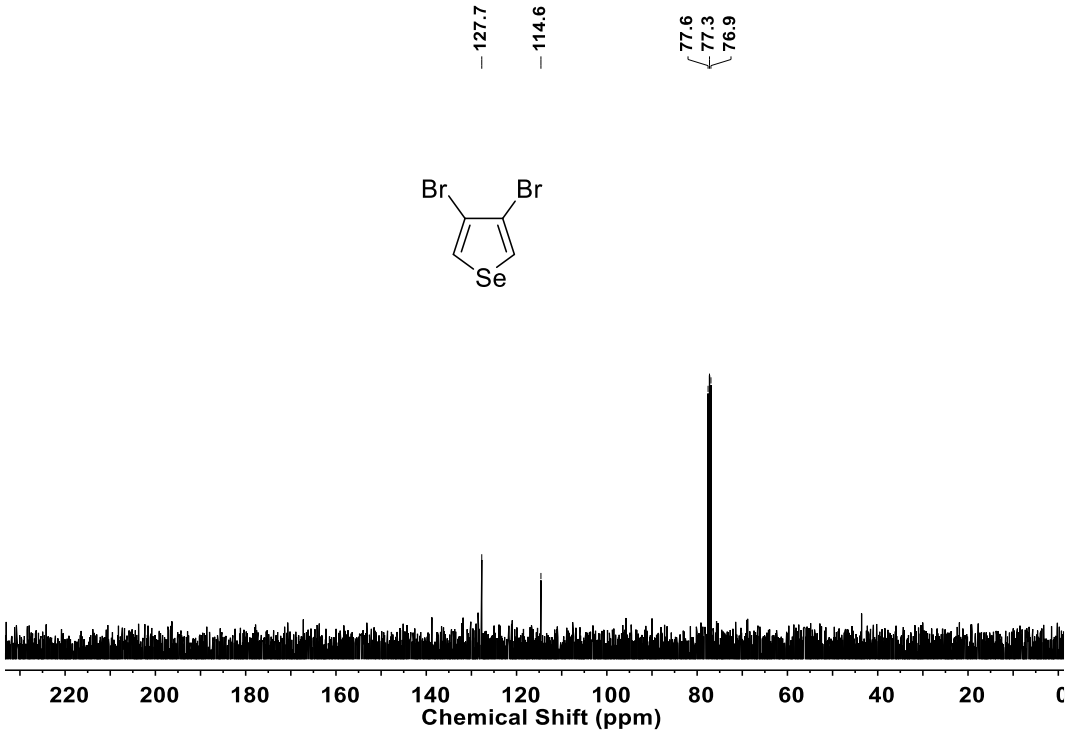


Fig. S24. ^{1}H NMR spectrum of **6** in $CDCl_3$.

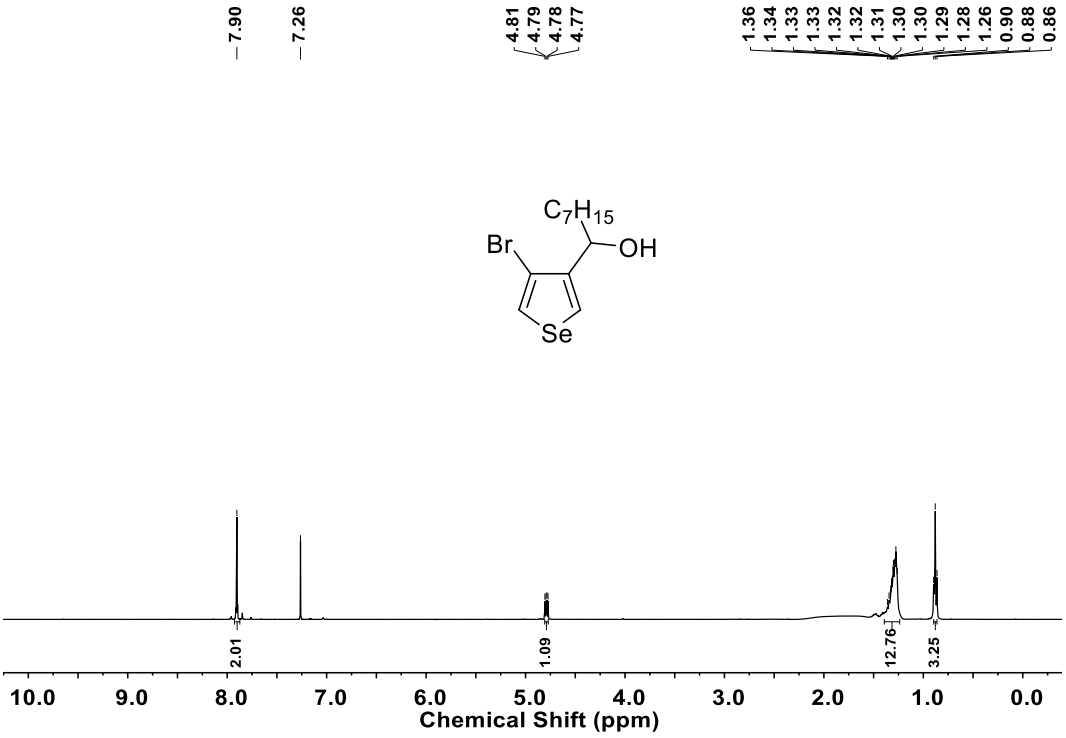


Fig. S25. ^{13}C NMR spectrum of **6** in $CDCl_3$.

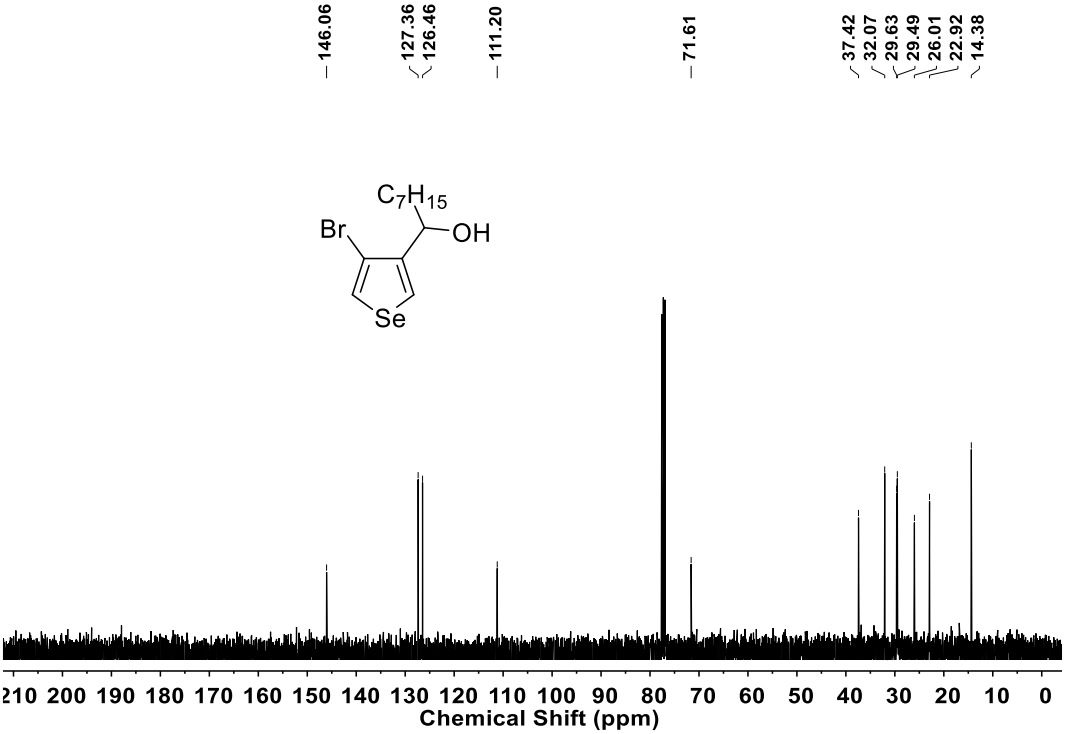


Fig. S26. ^{1}H NMR spectrum of **7** in $CDCl_3$.

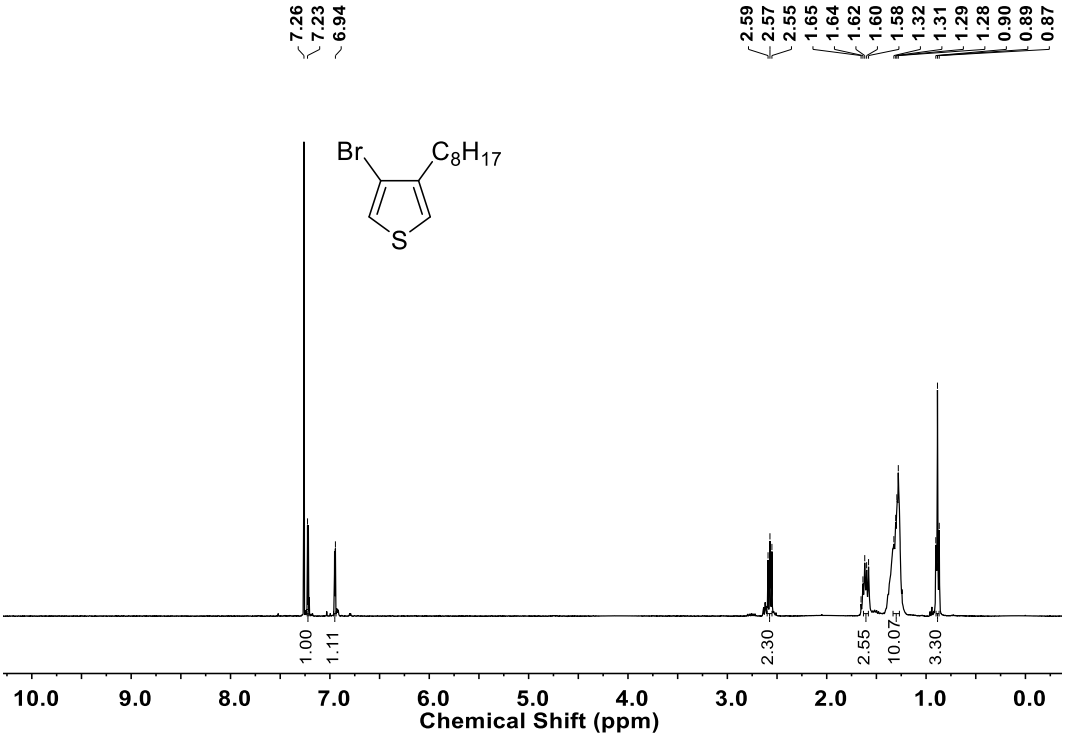


Fig. S27. ^{13}C NMR spectrum of **7** in $CDCl_3$.

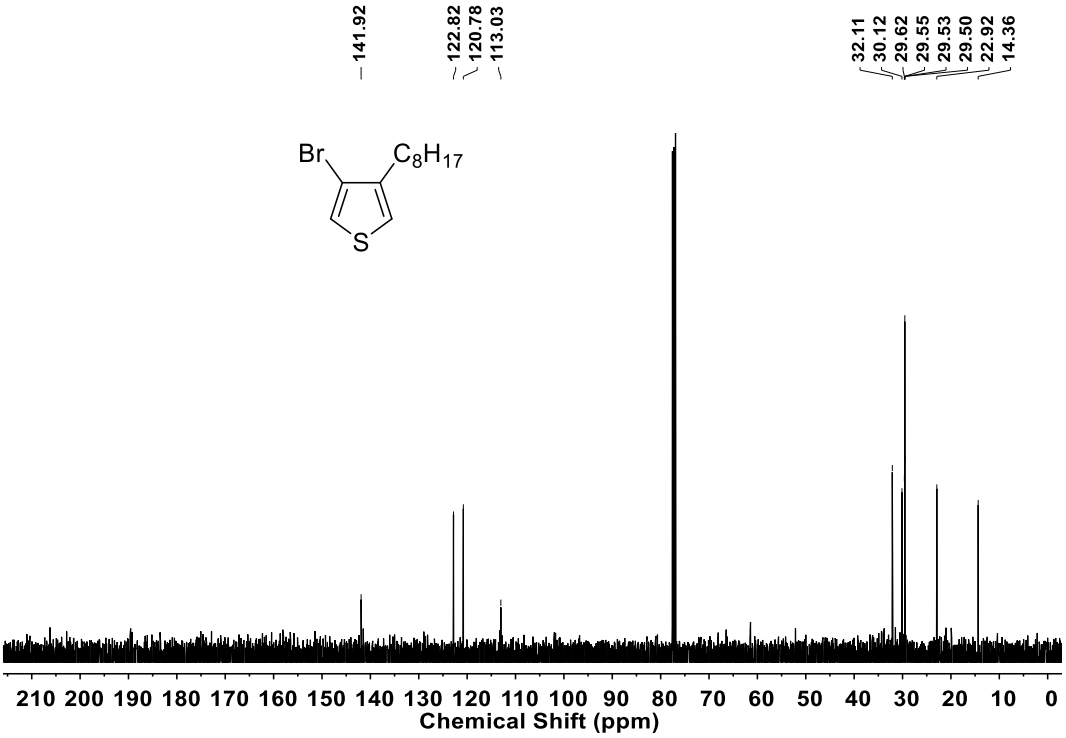


Fig. S28. ^{1}H NMR spectrum of **8** in $CDCl_3$.

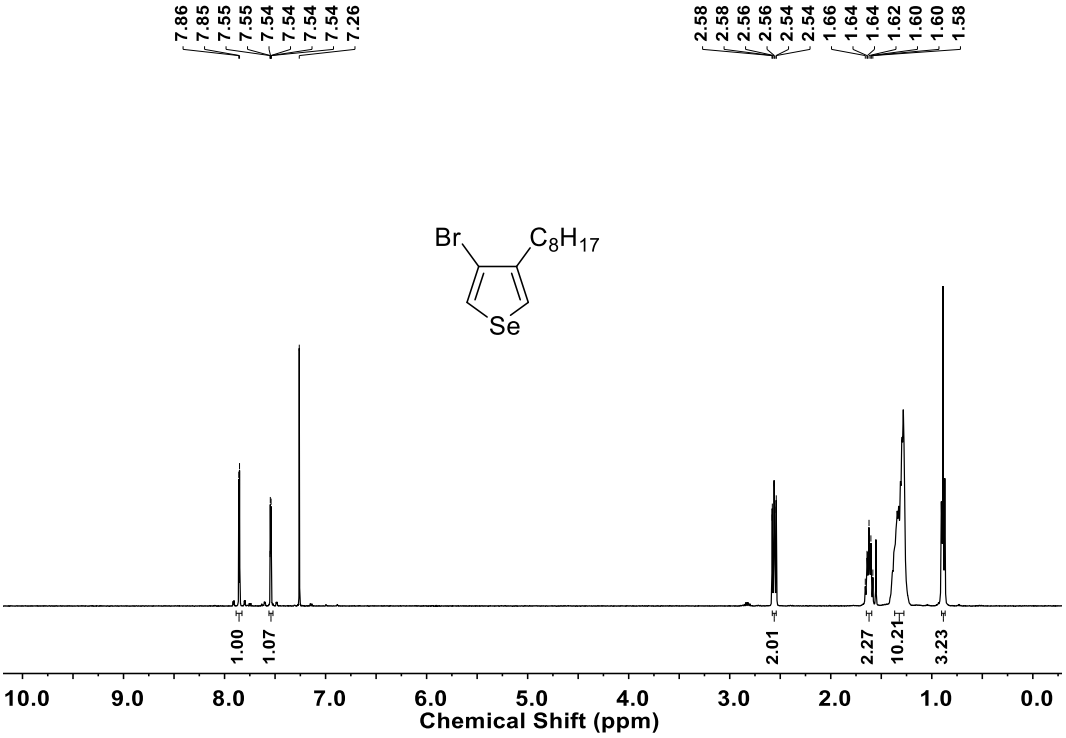


Fig. S29. ^{13}C NMR spectrum of **8** in $CDCl_3$.

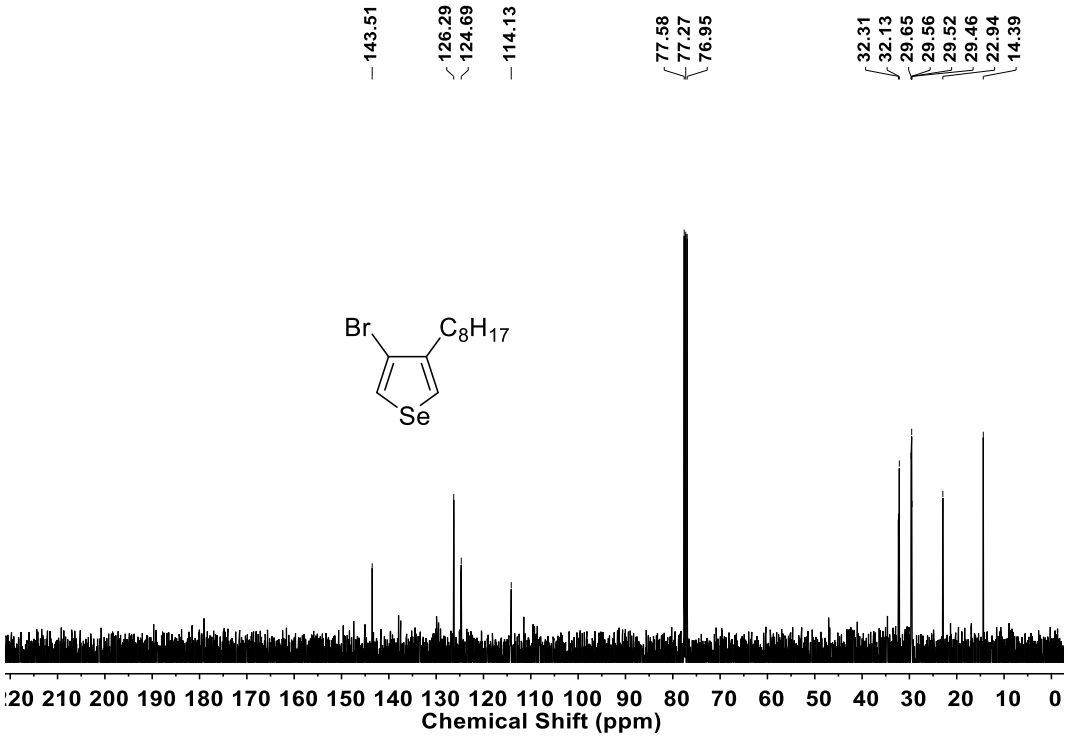


Fig. S30. ^{1}H NMR spectrum of **11** in $CDCl_3$.

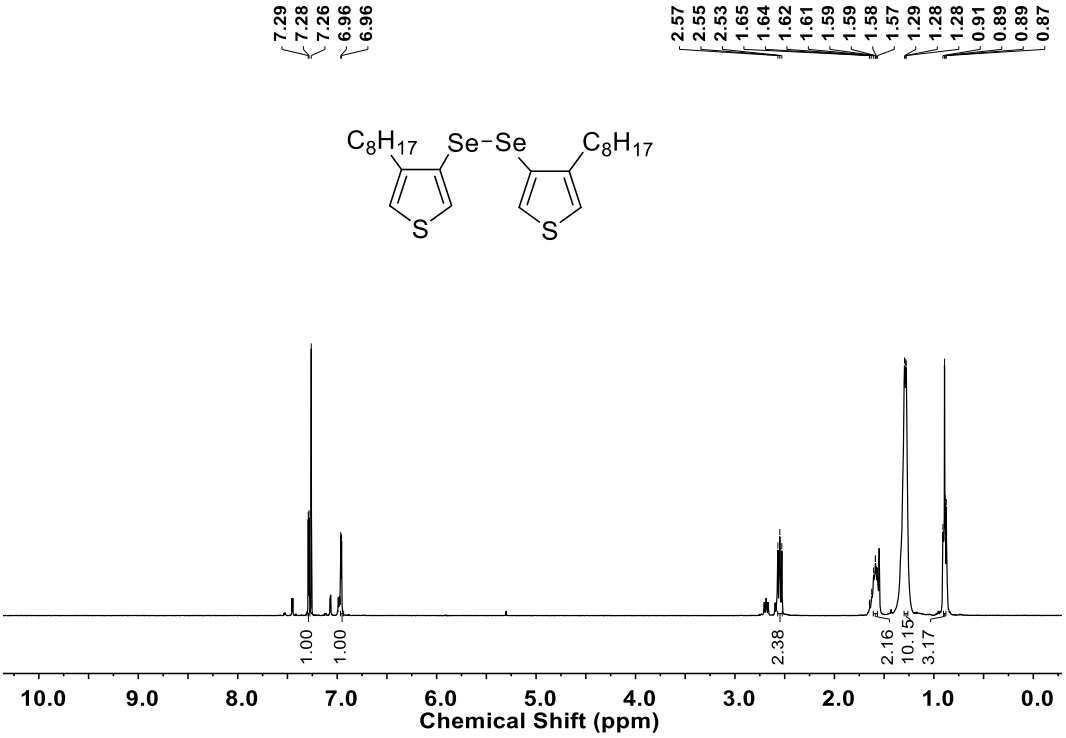


Fig. S31. ^{13}C NMR spectrum of **11** in $CDCl_3$.

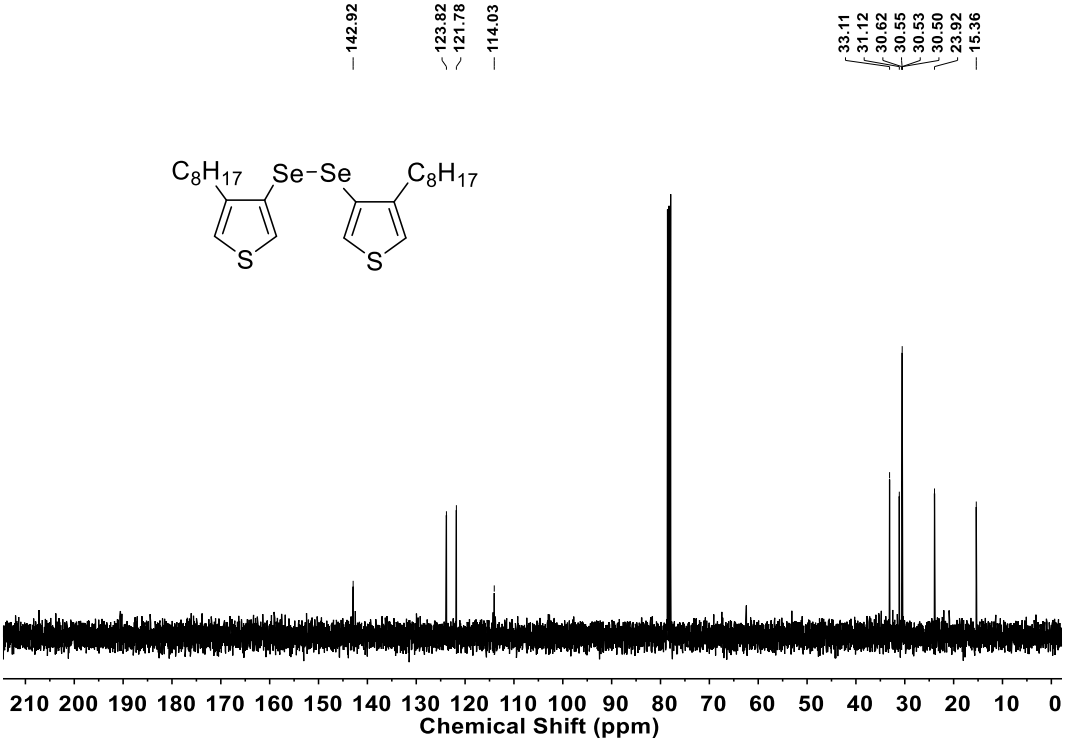


Fig. S32. ^{1}H NMR spectrum of **12** in $CDCl_3$.

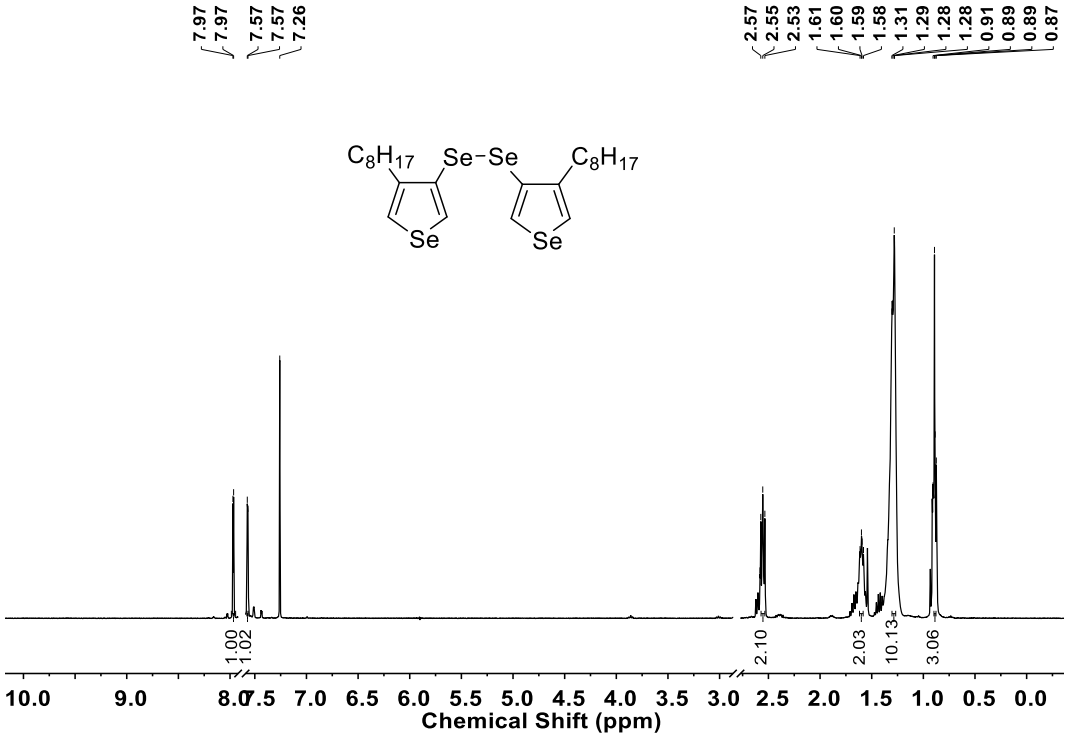


Fig. S33. ^{13}C NMR spectrum of **12** in $CDCl_3$.

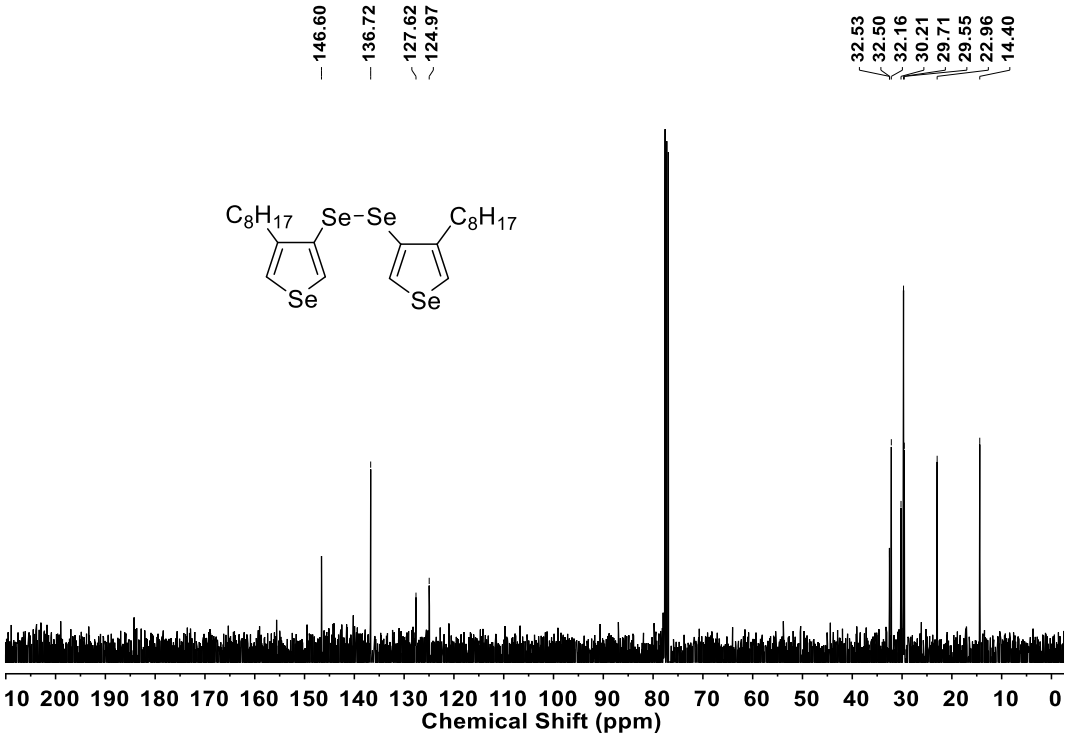


Fig. S34. ^{1}H NMR spectrum of **13** in $CDCl_3$.

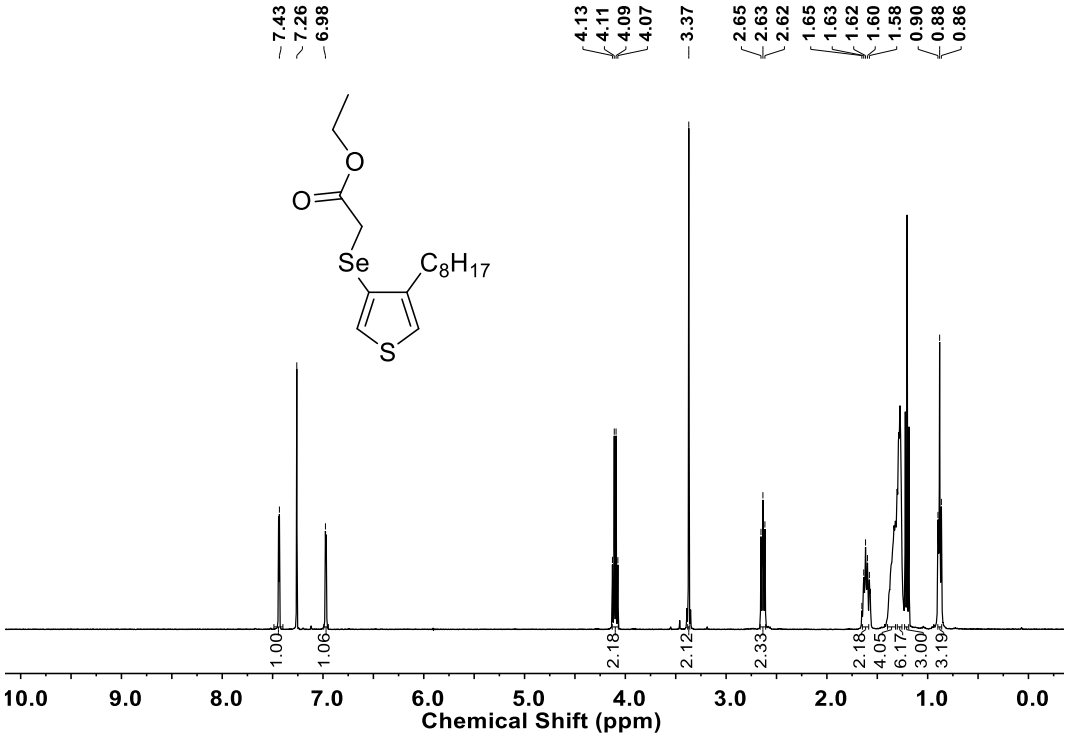


Fig. S35. ^{13}C NMR spectrum of **13** in $CDCl_3$.

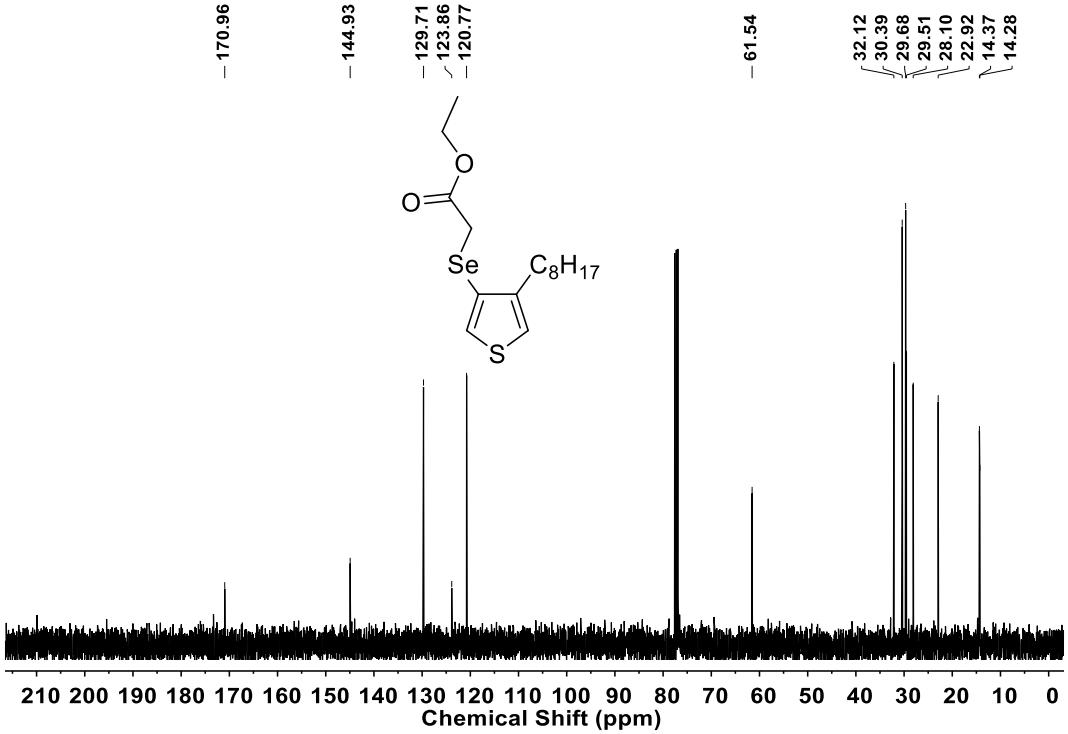


Fig. S36. ^{1}H NMR spectrum of **14** in $CDCl_3$.

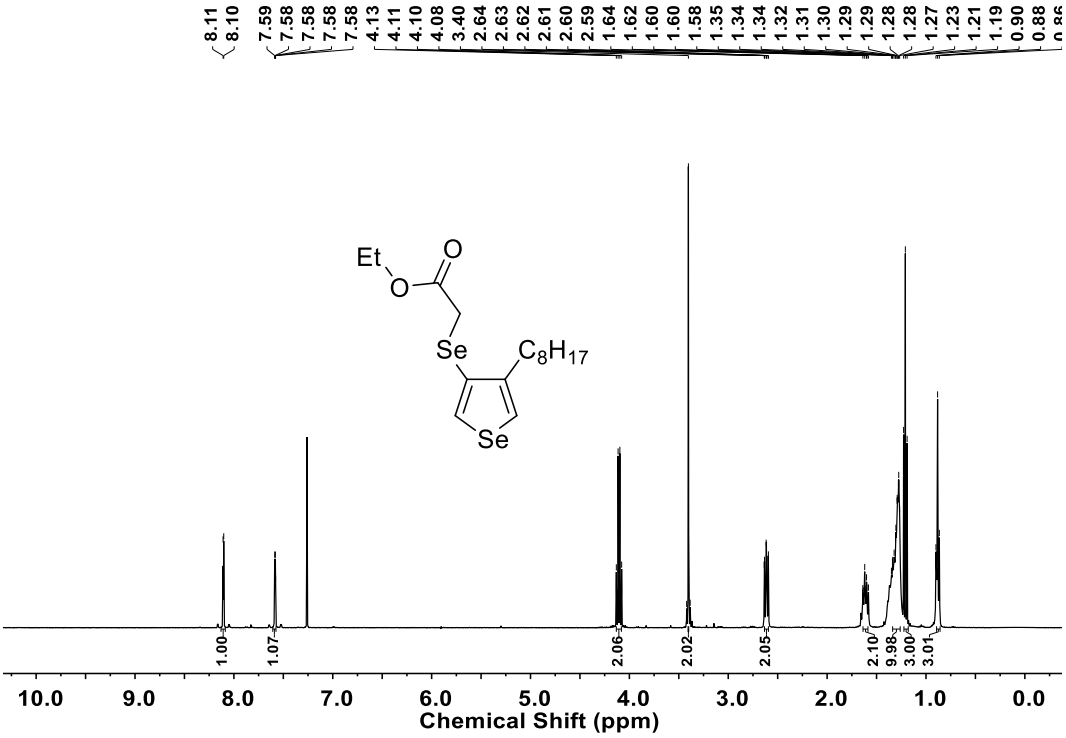


Fig. S37. ^{13}C NMR spectrum of **14** in $CDCl_3$.

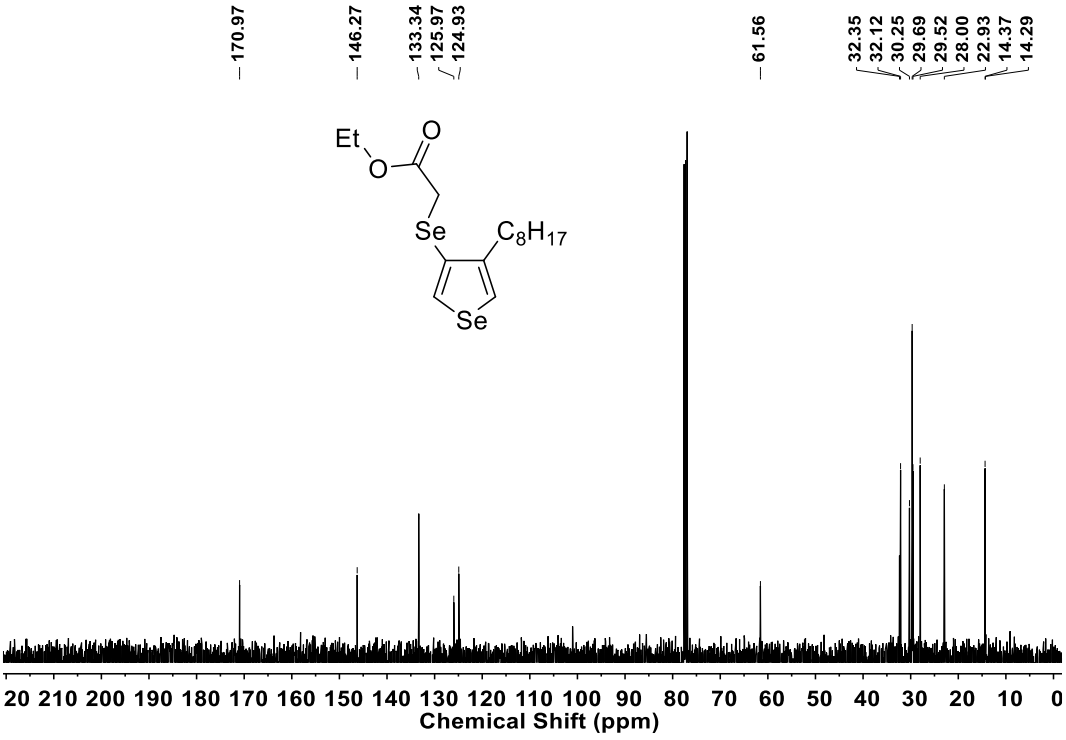


Fig. S38. ^{1}H NMR spectrum of **15** in $CDCl_3$.

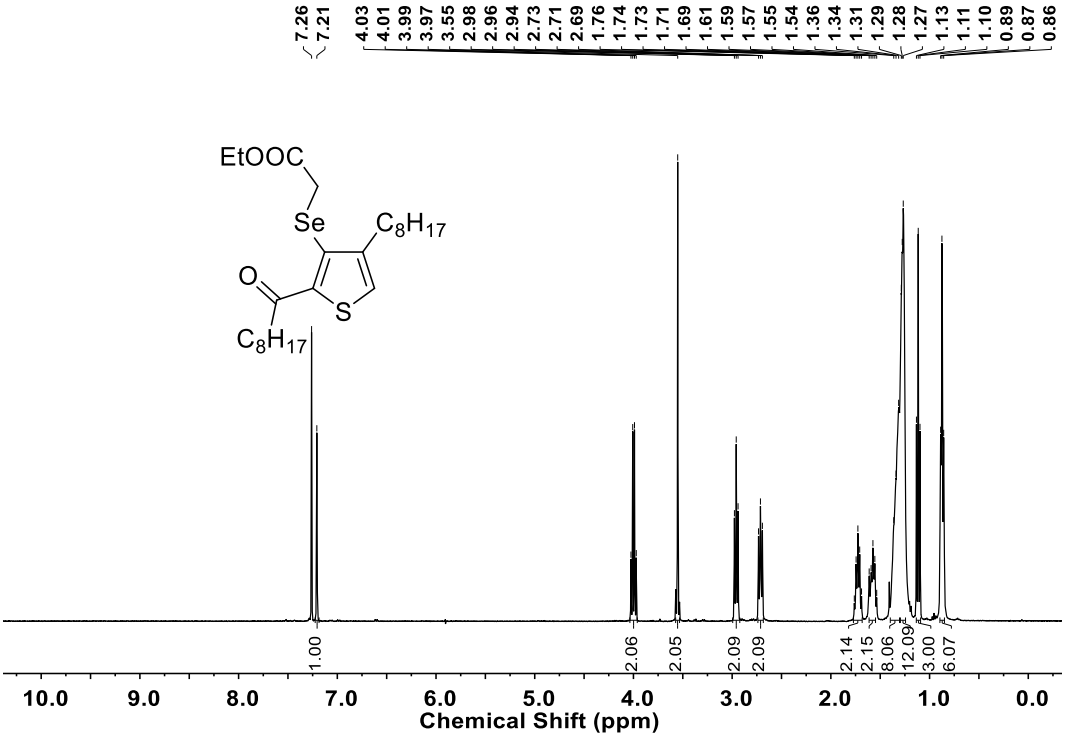


Fig. S39. ^{13}C NMR spectrum of **15** in $CDCl_3$.

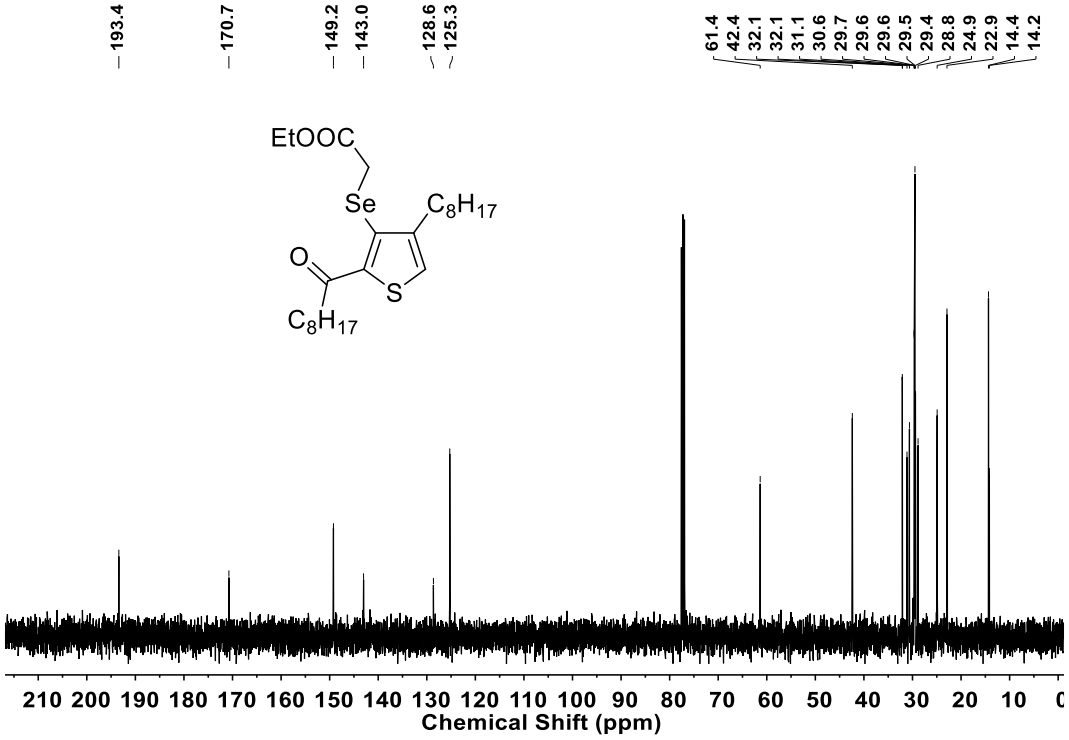


Fig. S40. ^{1}H NMR spectrum of **16** in $CDCl_3$.

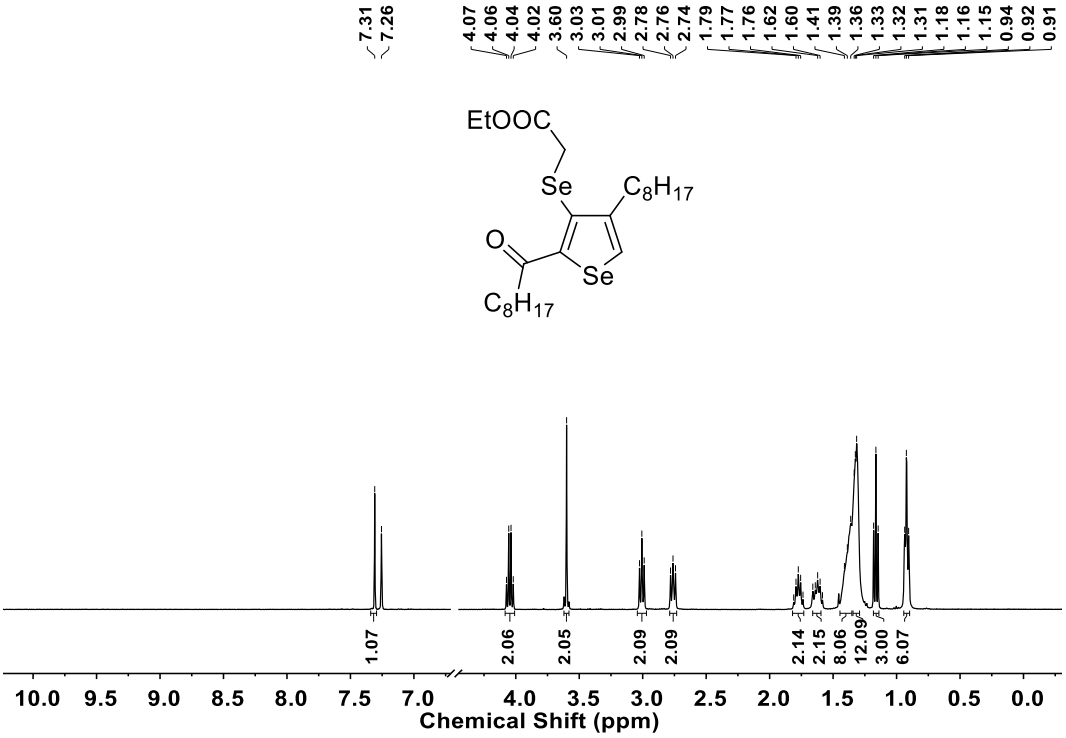


Fig. S41. ^{13}C NMR spectrum of **16** in $CDCl_3$.

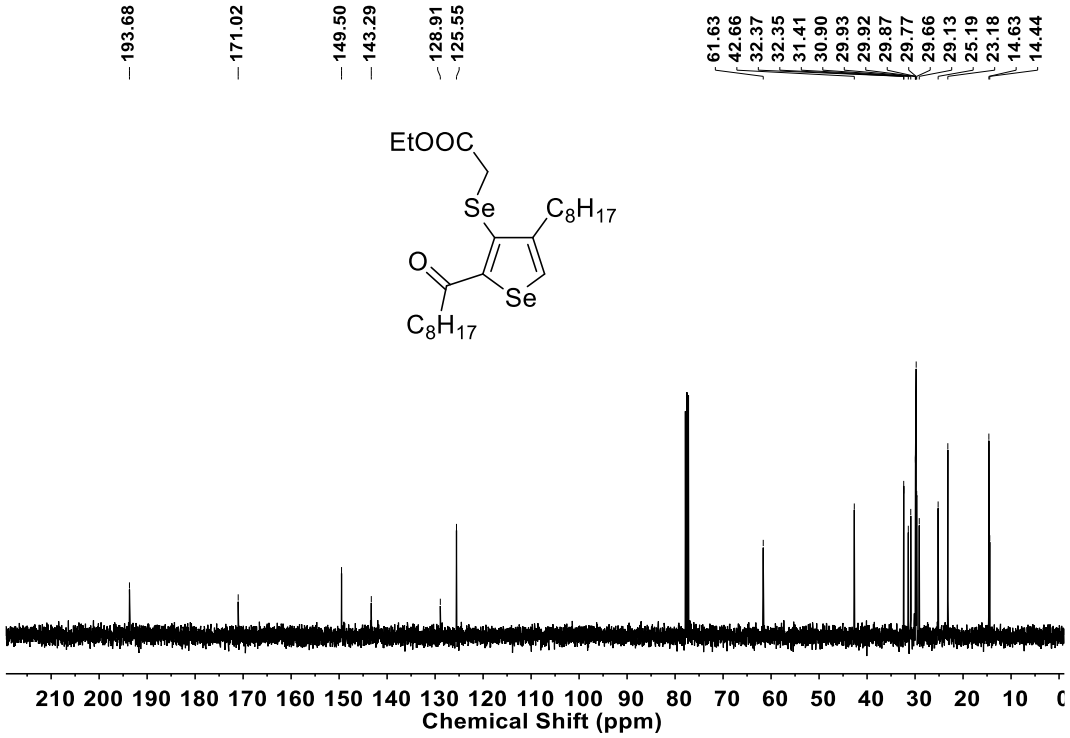


Fig. S42. ^{1}H NMR spectrum of **17** in $CDCl_3$.

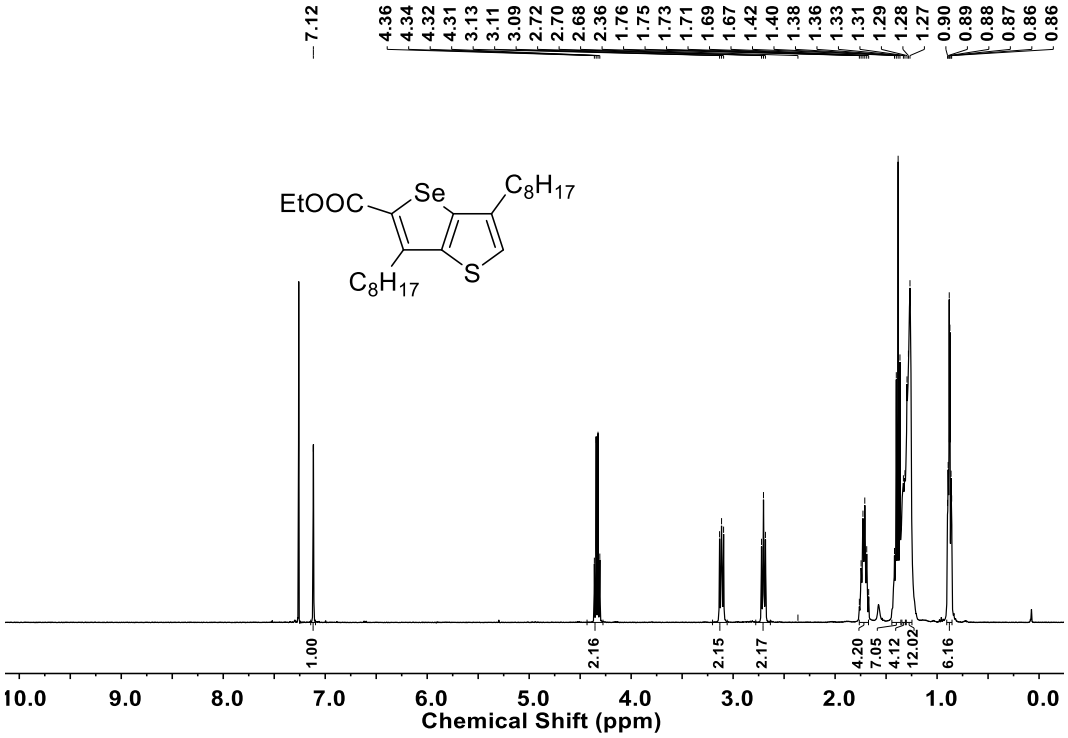


Fig. S43. ^{13}C NMR spectrum of **17** in $CDCl_3$.

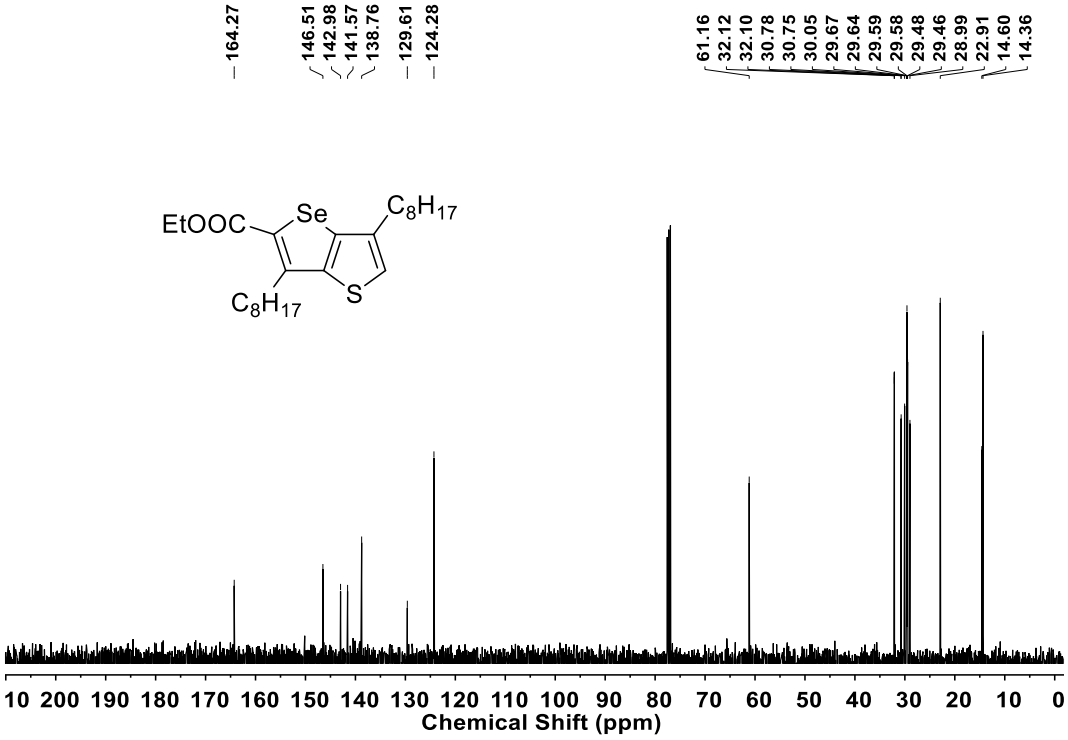


Fig. S44. ^{1}H NMR spectrum of **18** in $CDCl_3$.

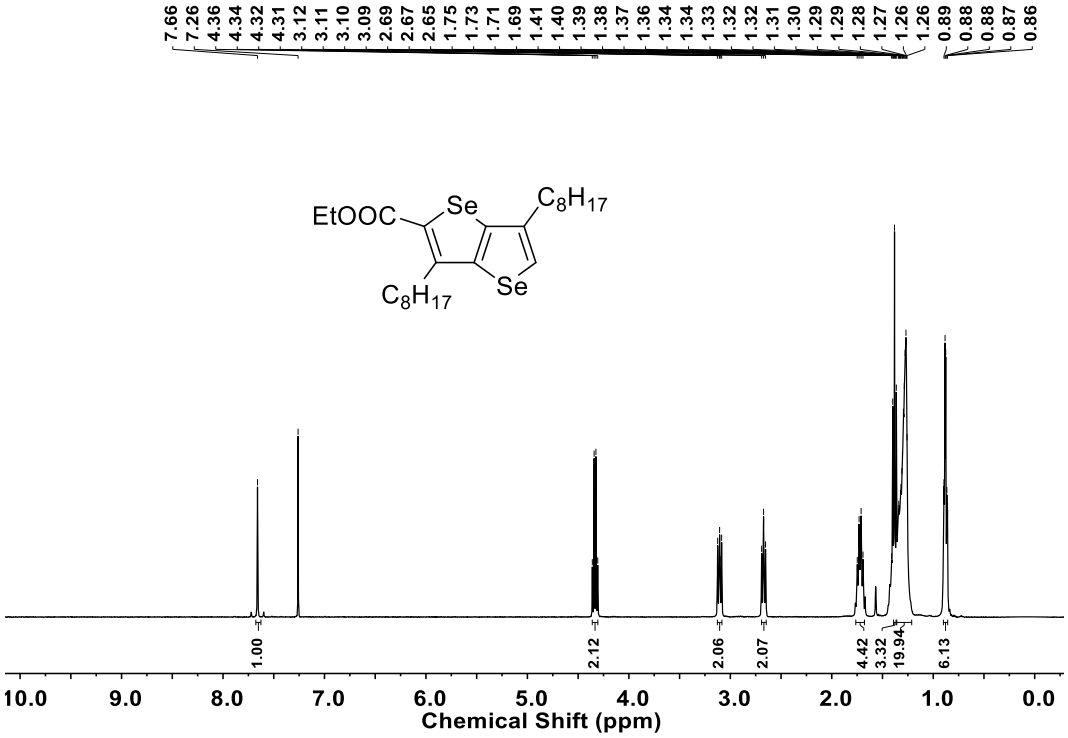


Fig. S45. ^{13}C NMR spectrum of **18** in $CDCl_3$.

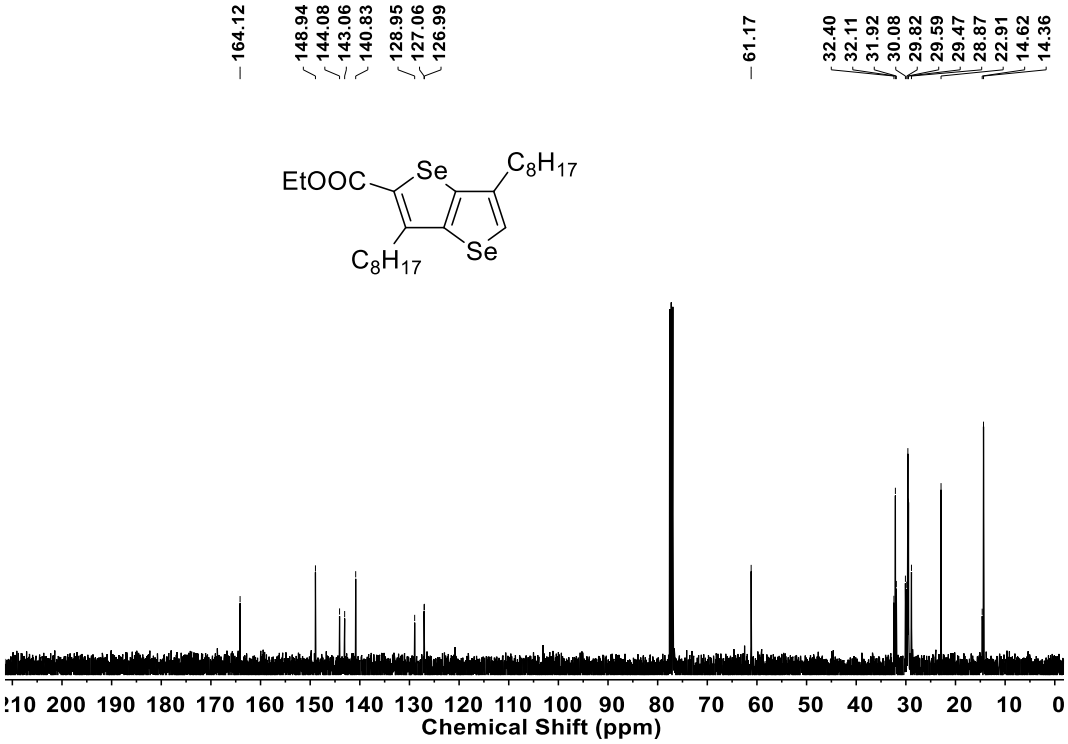


Fig. S46. ^{1}H NMR spectrum of **23** in $CDCl_3$.

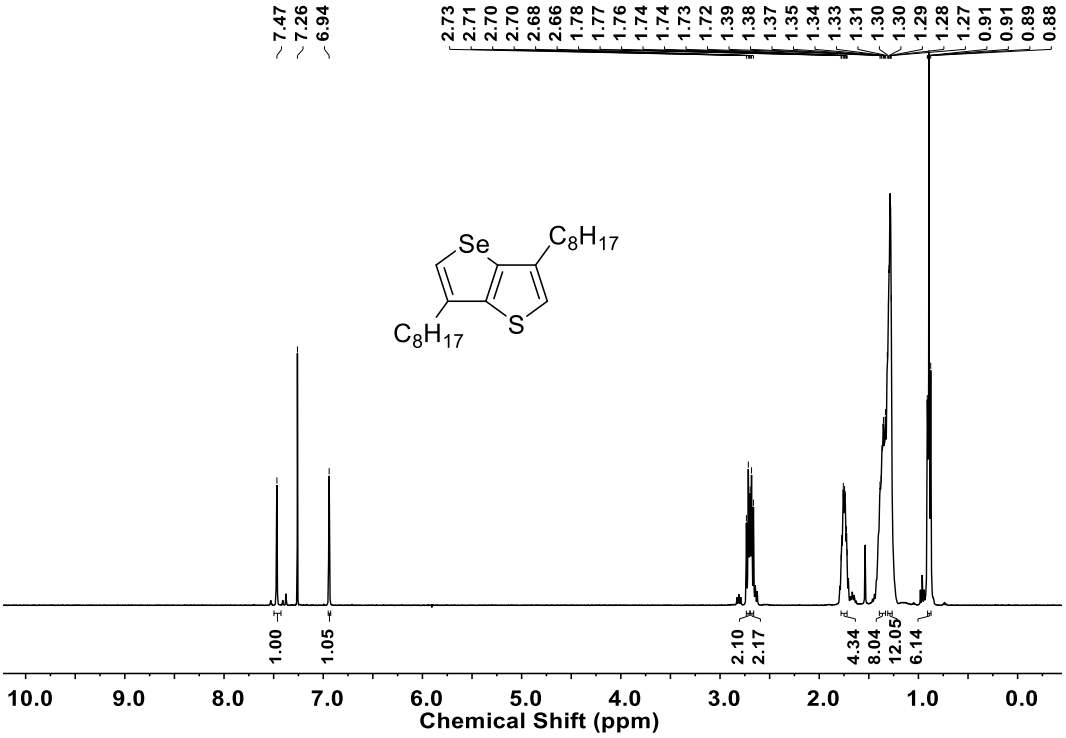


Fig. S47. ^{13}C NMR spectrum of **23** in $CDCl_3$.

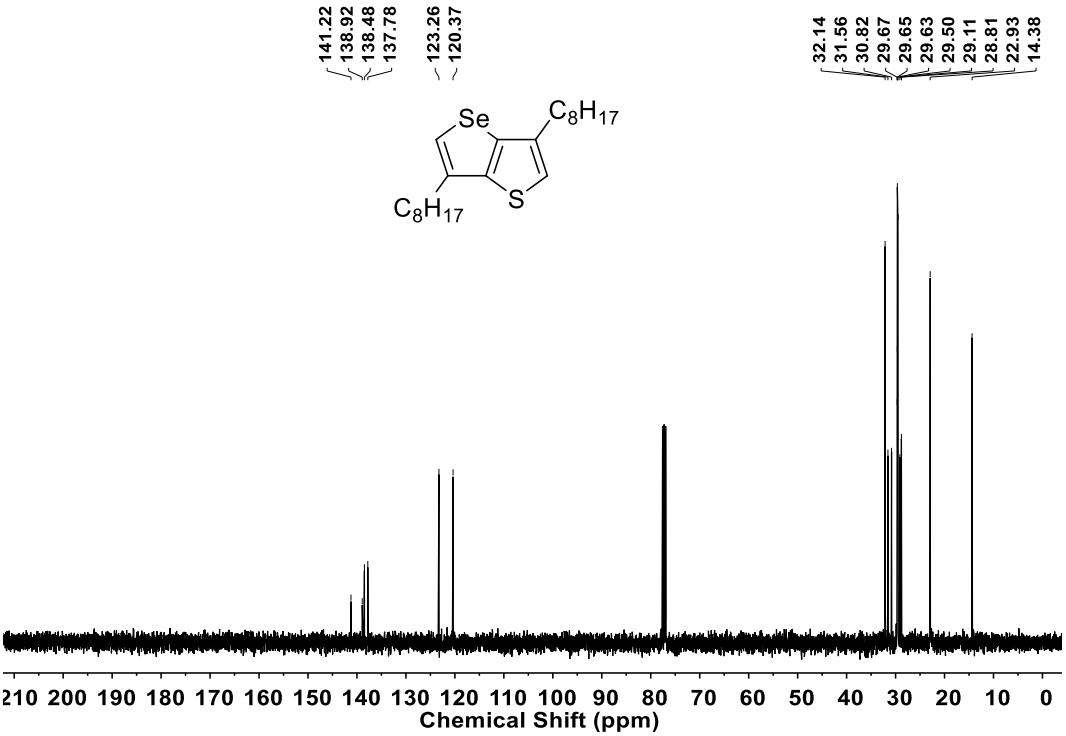


Fig. S48. ^{1}H NMR spectrum of **24** in $CDCl_3$.

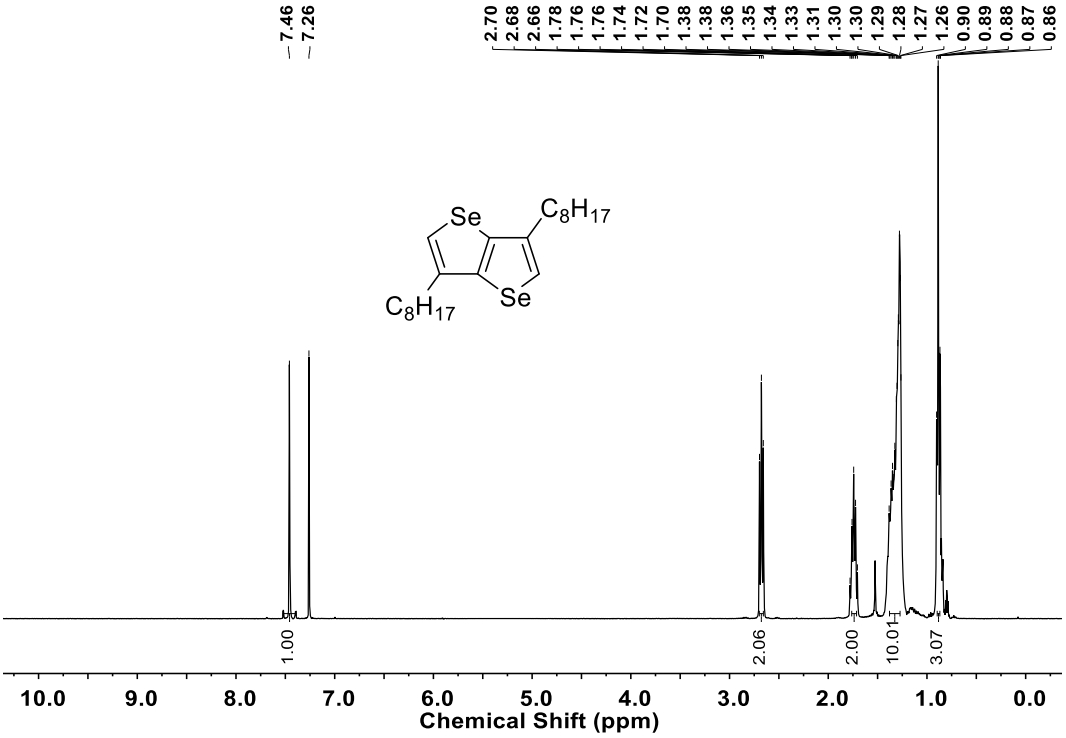


Fig. S49. ^{13}C NMR spectrum of **24** in $CDCl_3$.

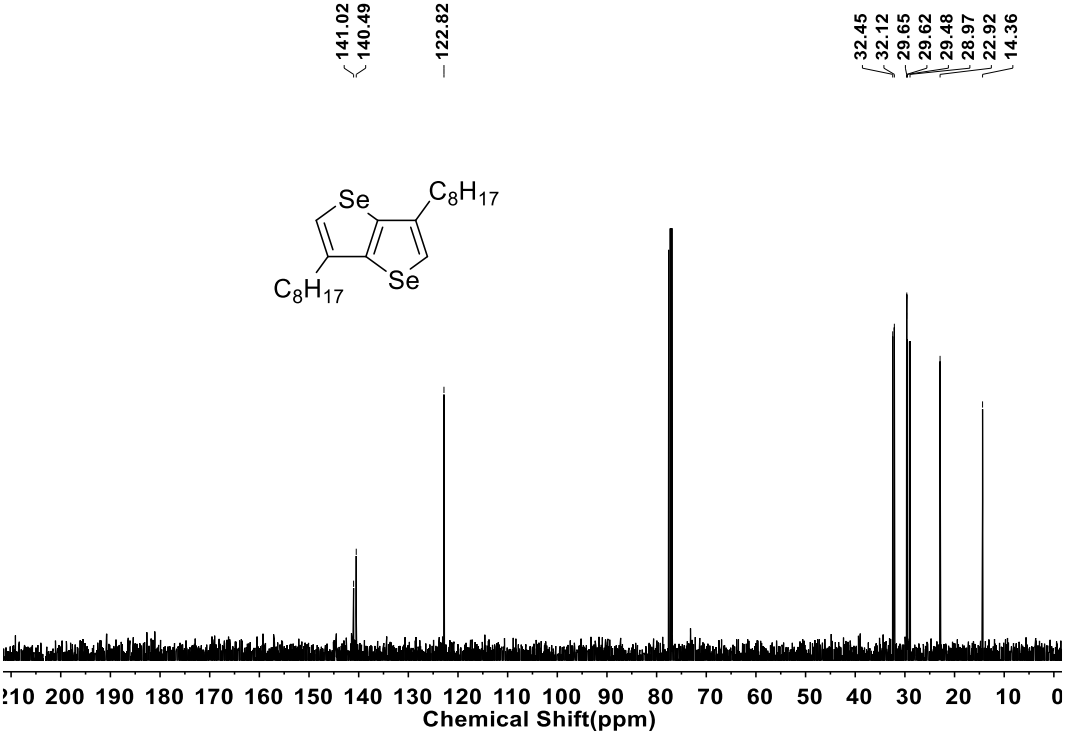


Fig. S50. ^{1}H NMR spectrum of **26** in $CDCl_3$.

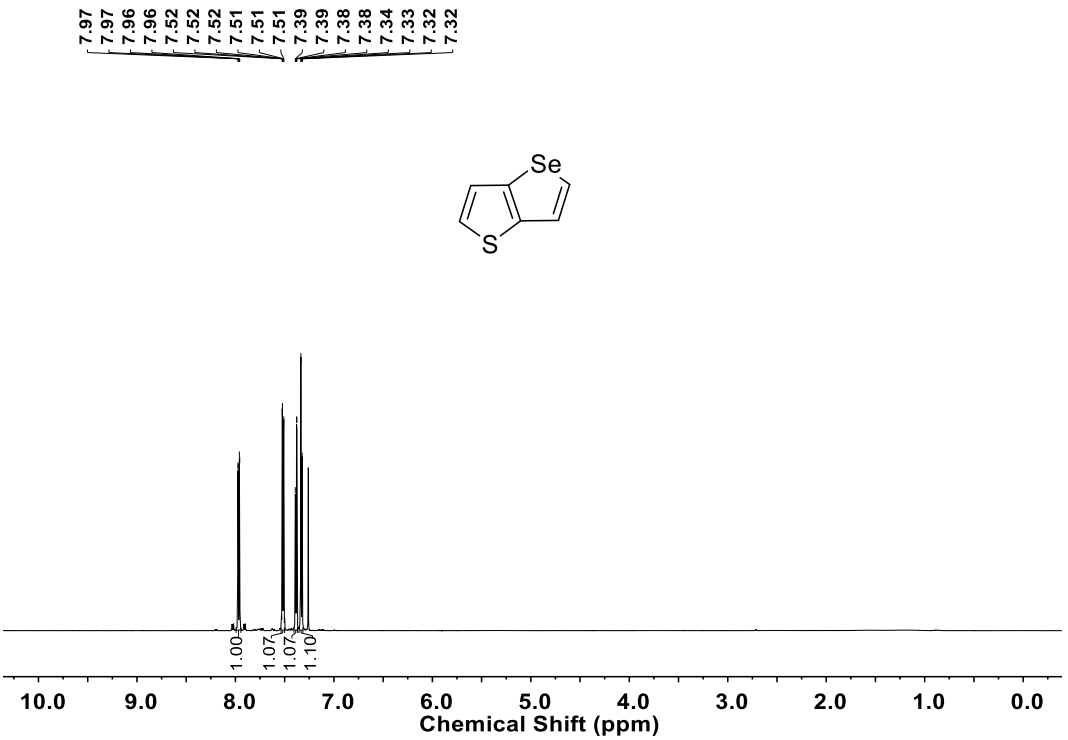


Fig. S51. ^{13}C NMR spectrum of **26** in $CDCl_3$.

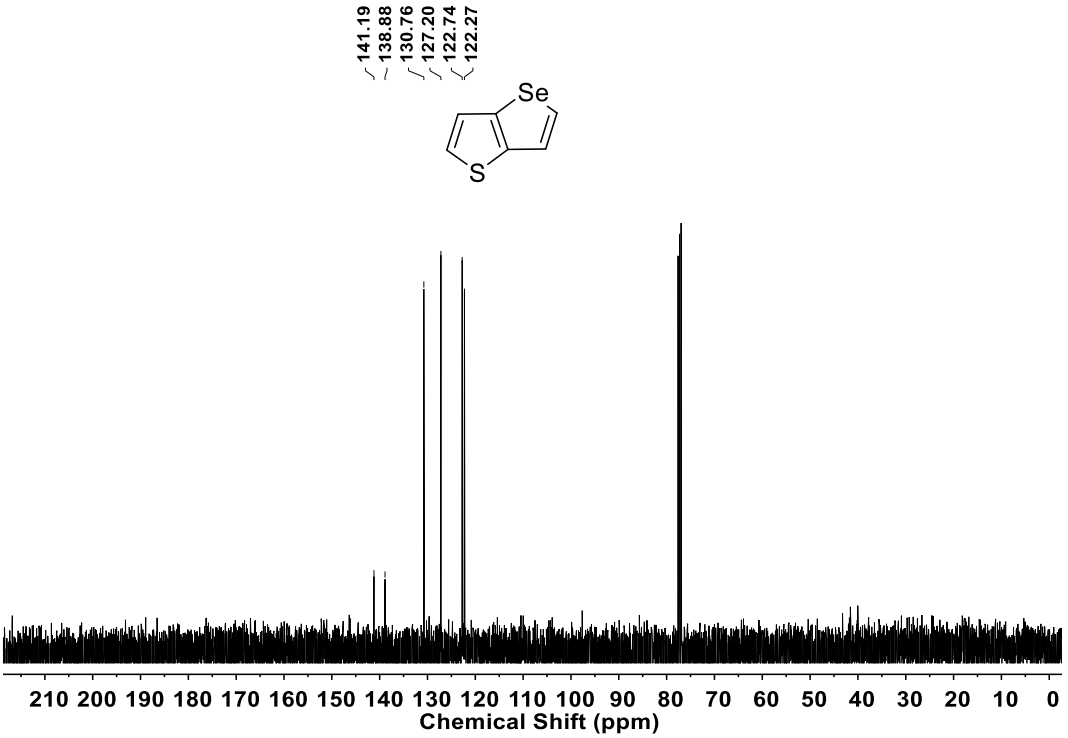


Fig. S52. ^{1}H NMR spectrum of **27** in $CDCl_3$.

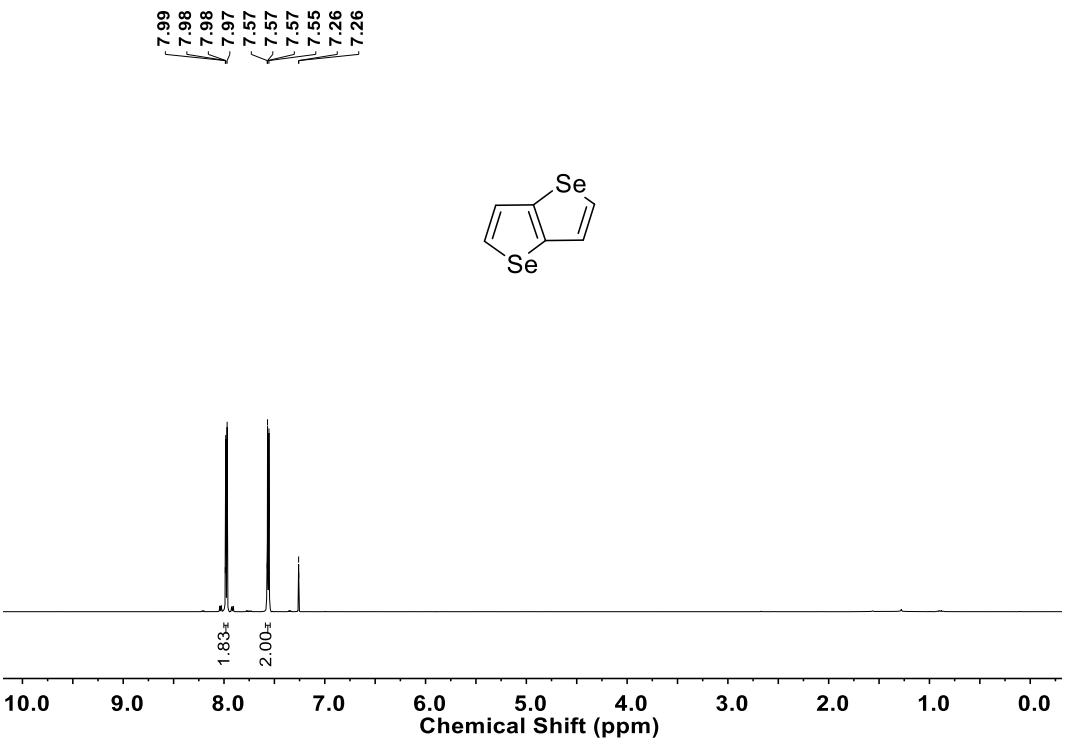


Fig. S53. ^{13}C NMR spectrum of **27** in $CDCl_3$.

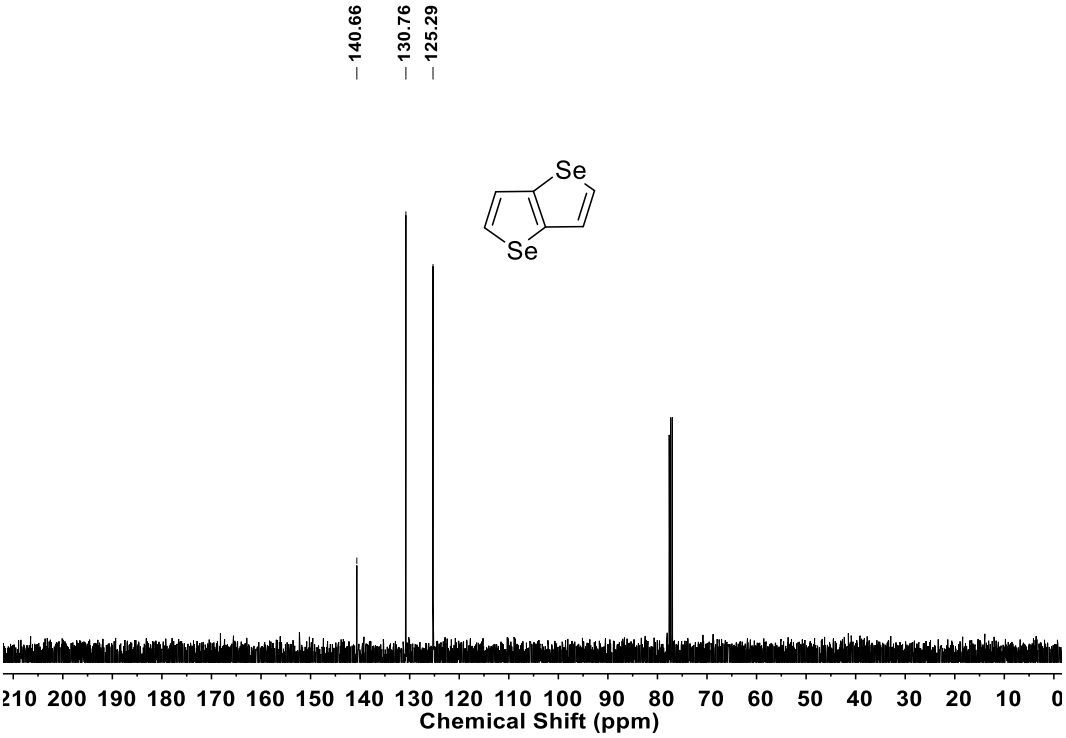


Fig. S54. ^{1}H NMR spectrum of **28** in $CDCl_3$.

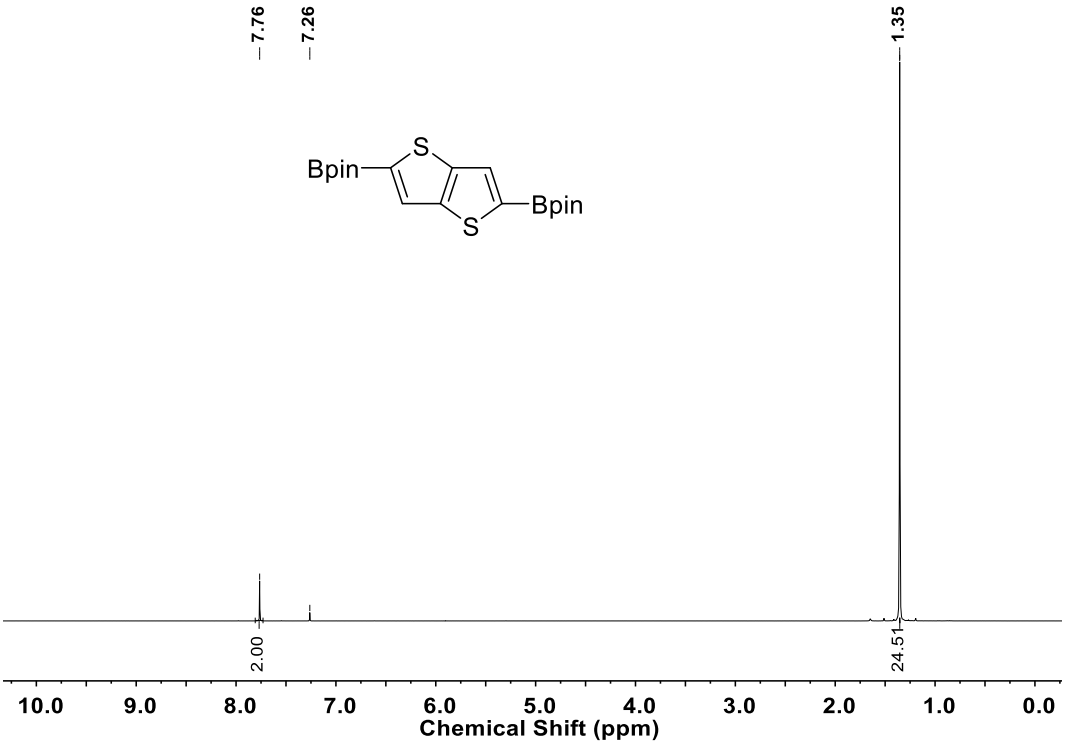


Fig. S55. ^{13}C NMR spectrum of **28** in $CDCl_3$.

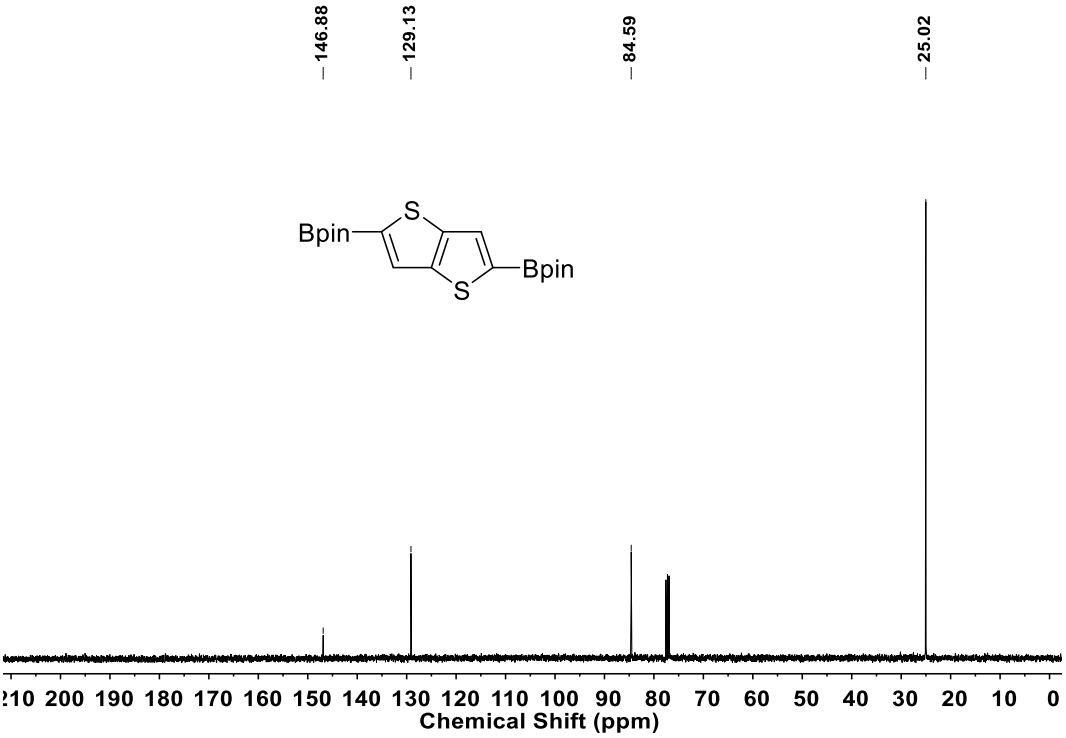


Fig. S56. ^{1}H NMR spectrum of **29** in $CDCl_3$.

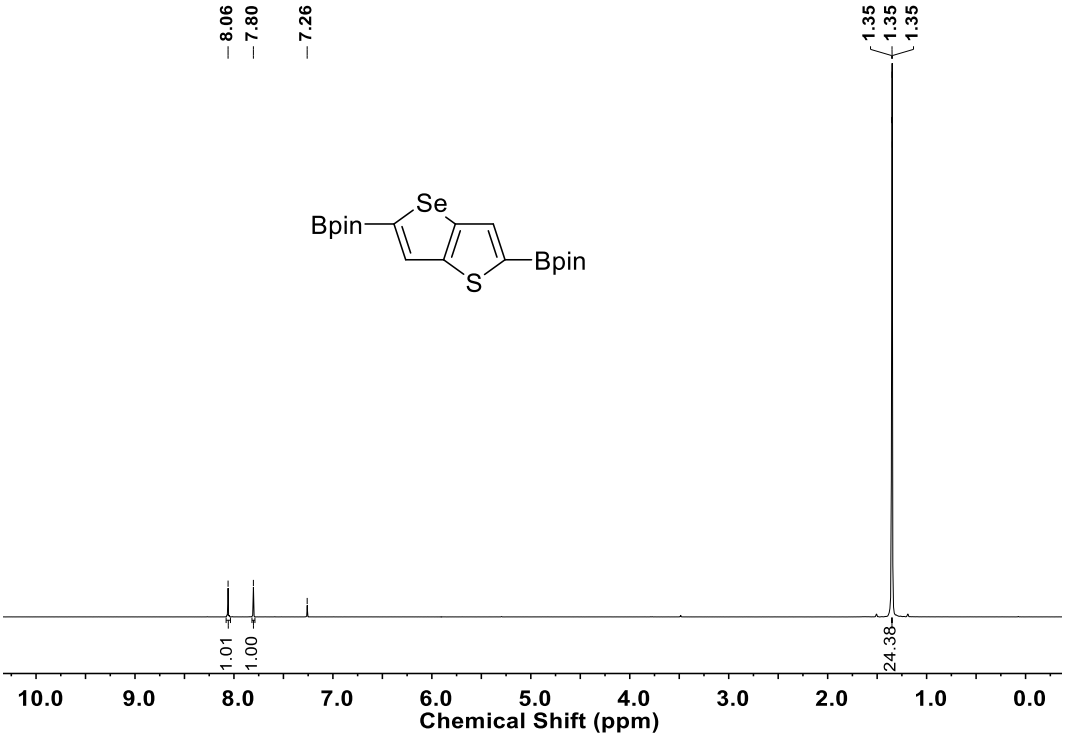


Fig. S57. ^{13}C NMR spectrum of **29** in $CDCl_3$.

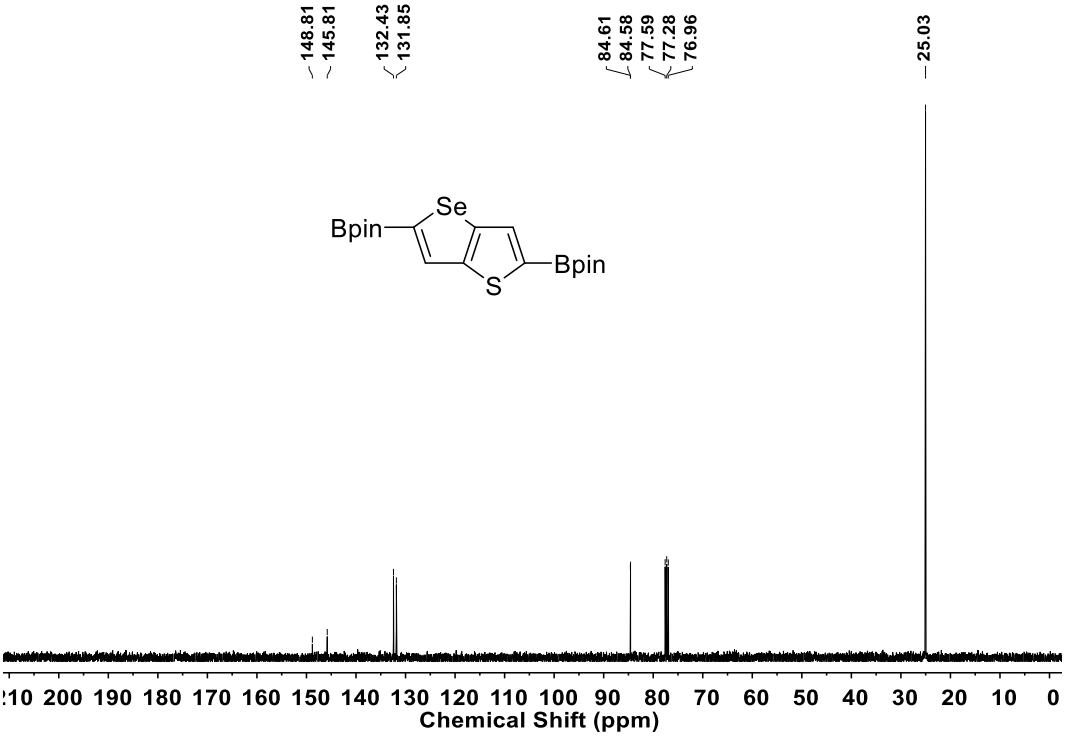


Fig. S58. ^{1}H NMR spectrum of **30** in $CDCl_3$.

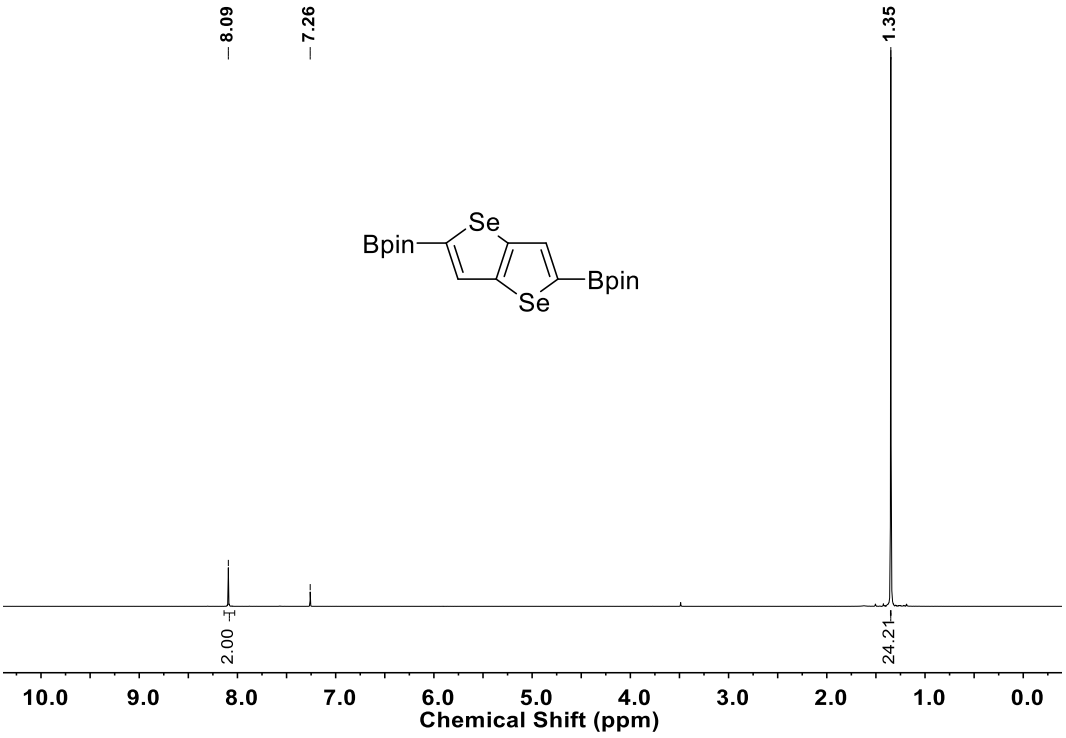


Fig. S59. ^{13}C NMR spectrum of **30** in $CDCl_3$.

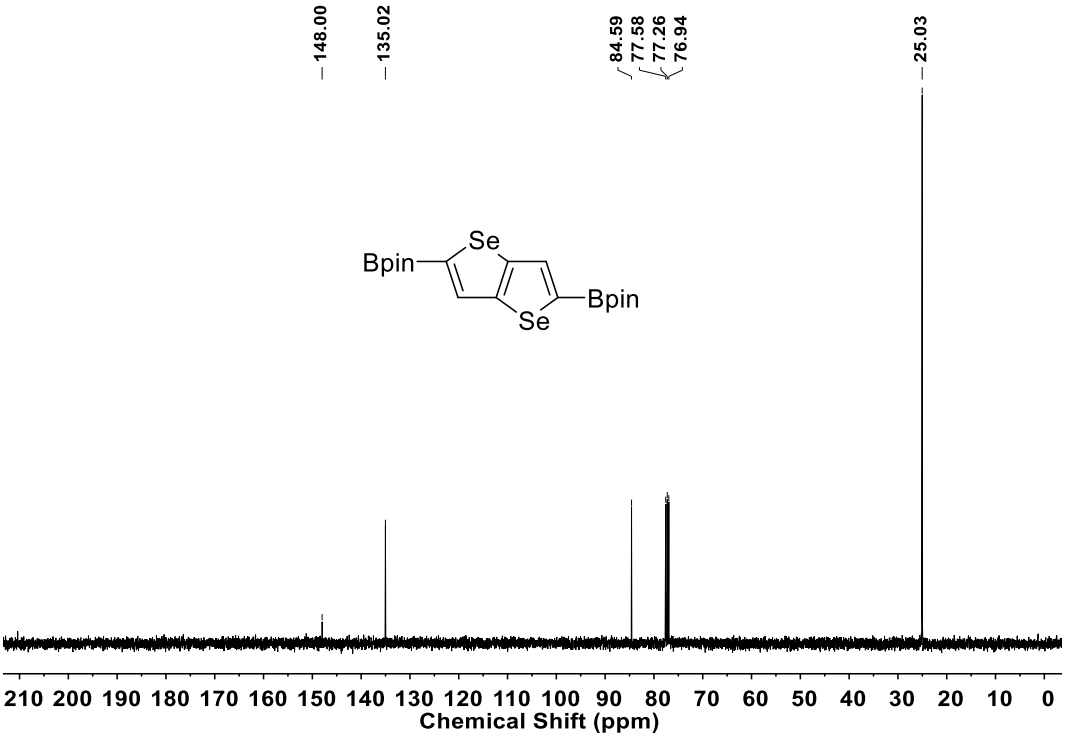


Fig. S60. ^{1}H NMR spectrum of **34** in $CDCl_3$.

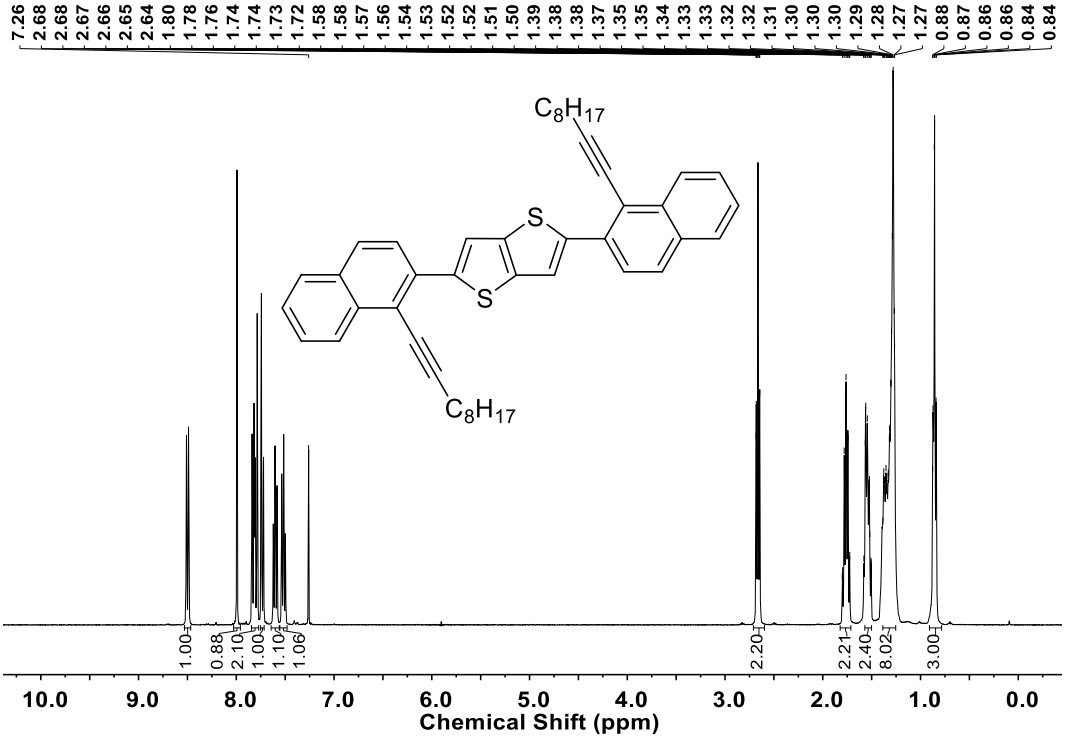


Fig. S61. ^{13}C NMR spectrum of **34** in $CDCl_3$.

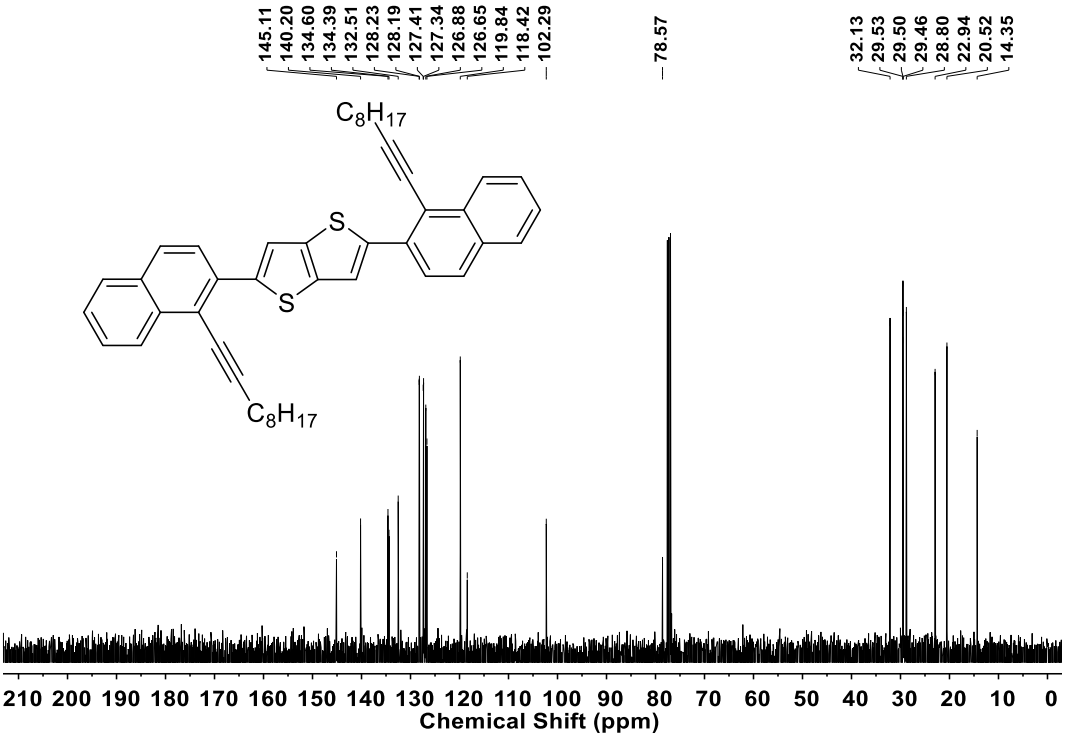


Fig. S62. ^{1}H NMR spectrum of **35** in $CDCl_3$.

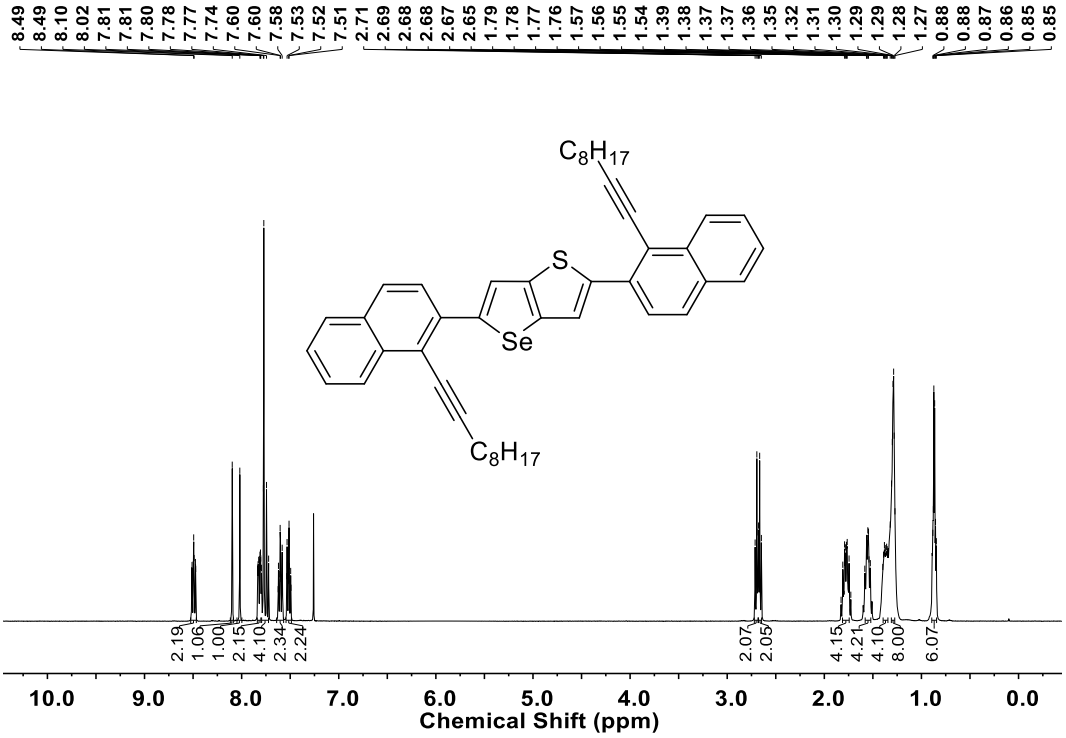


Fig. S63. ^{13}C NMR spectrum of **35** in $CDCl_3$.

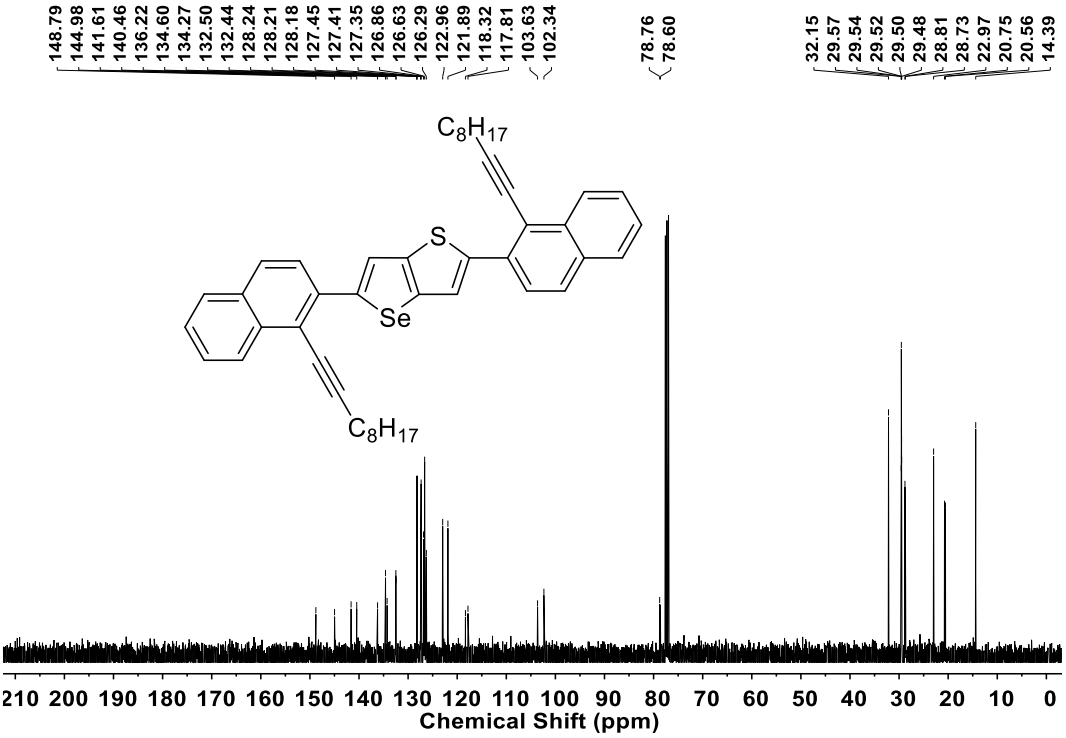


Fig. S64. ^{1}H NMR spectrum of **36** in $CDCl_3$.

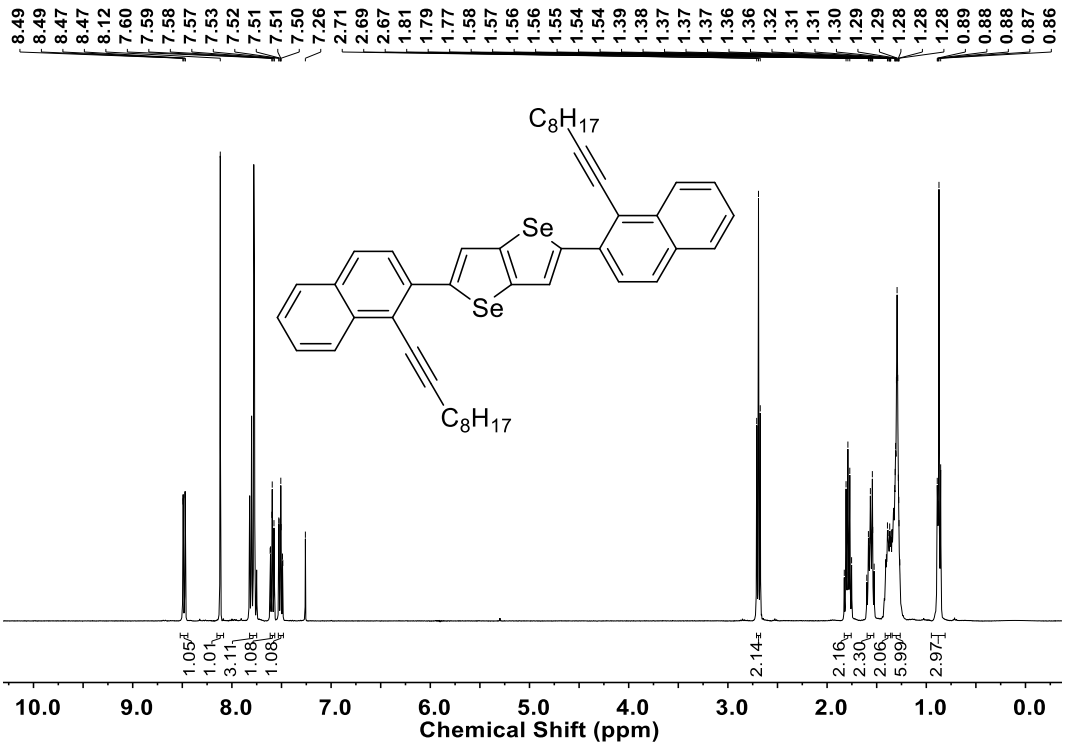


Fig. S65. ^{13}C NMR spectrum of **36** in $CDCl_3$.

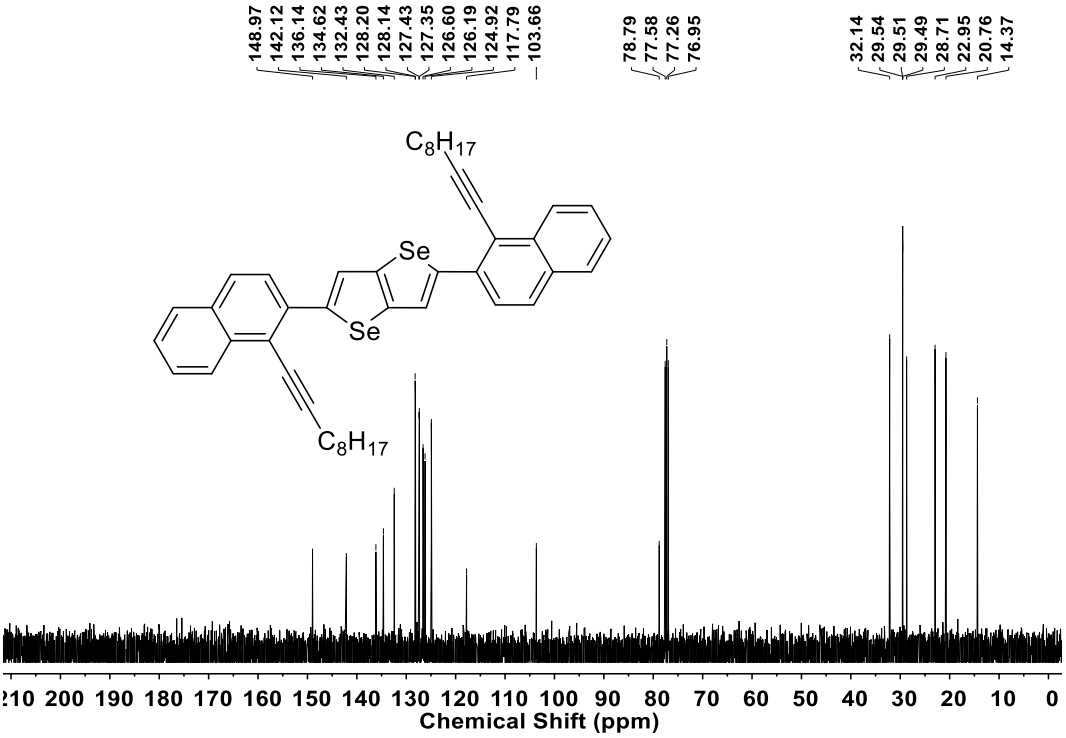


Fig. S66. ^{1}H NMR spectrum of **38** in $CDCl_3$.

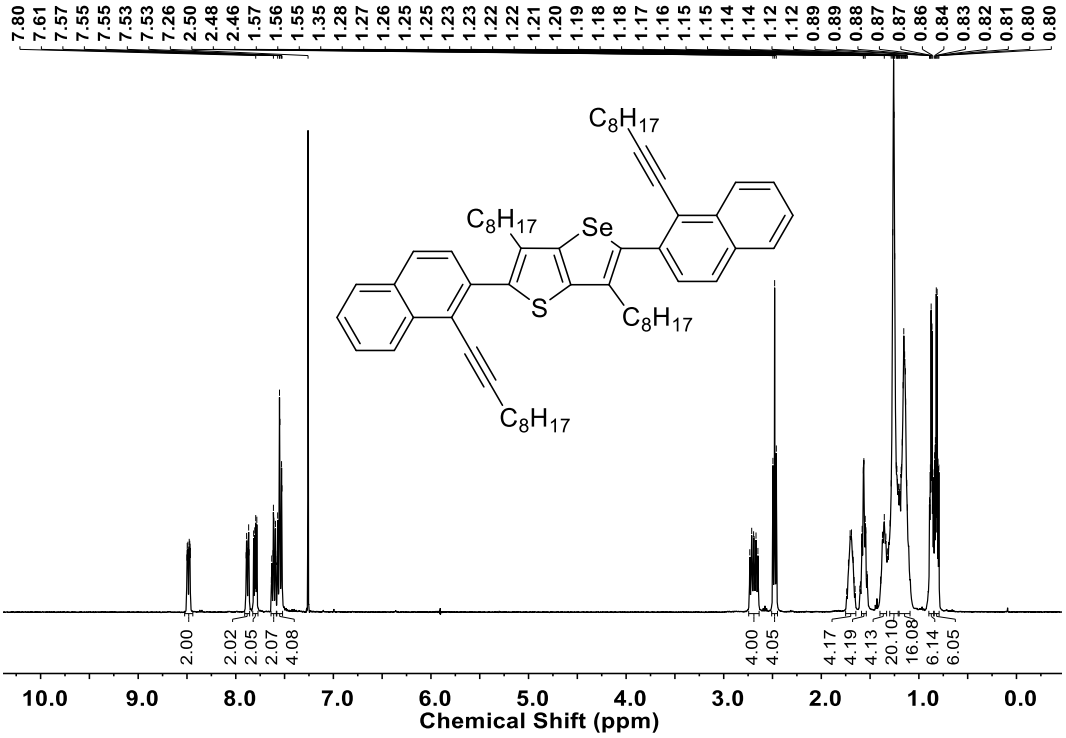


Fig. S67. ^{13}C NMR spectrum of **38** in $CDCl_3$.

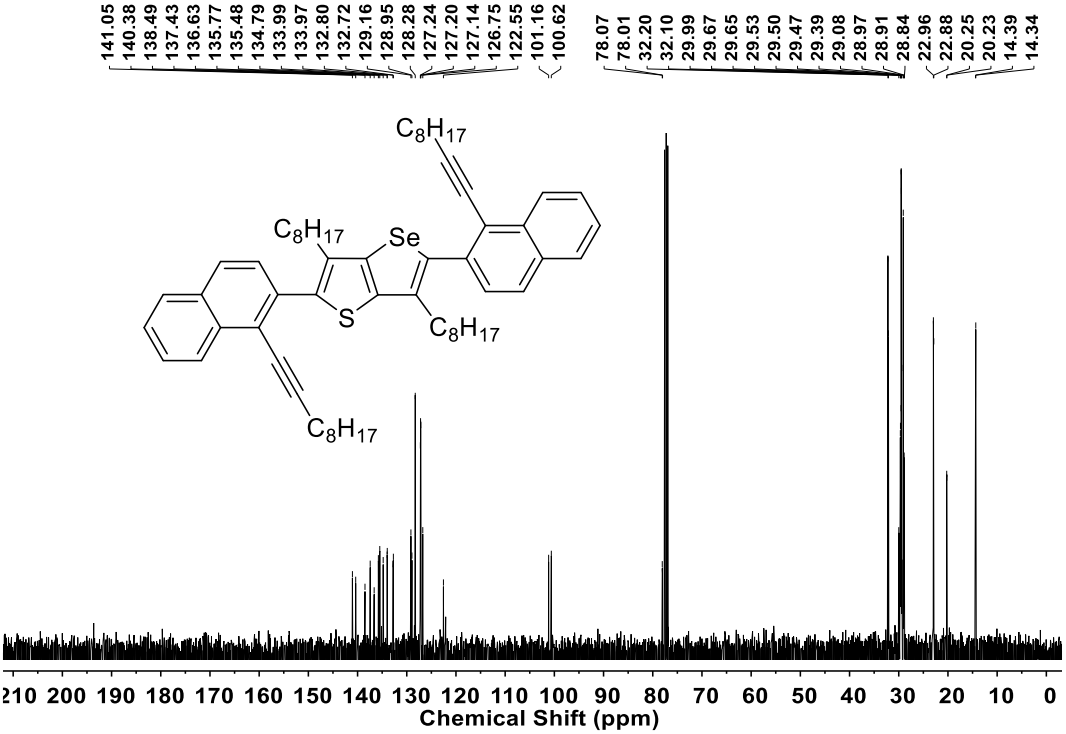


Fig. S68. ^{1}H NMR spectrum of **39** in $CDCl_3$.

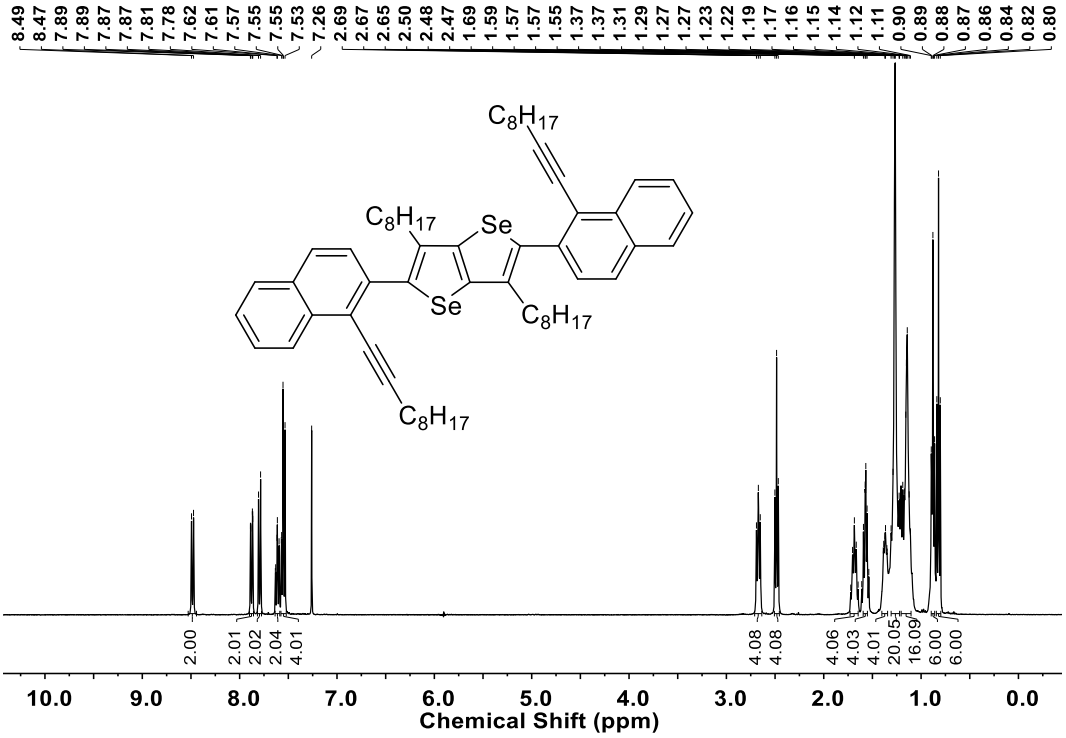


Fig. S69. ^{13}C NMR spectrum of **39** in $CDCl_3$.

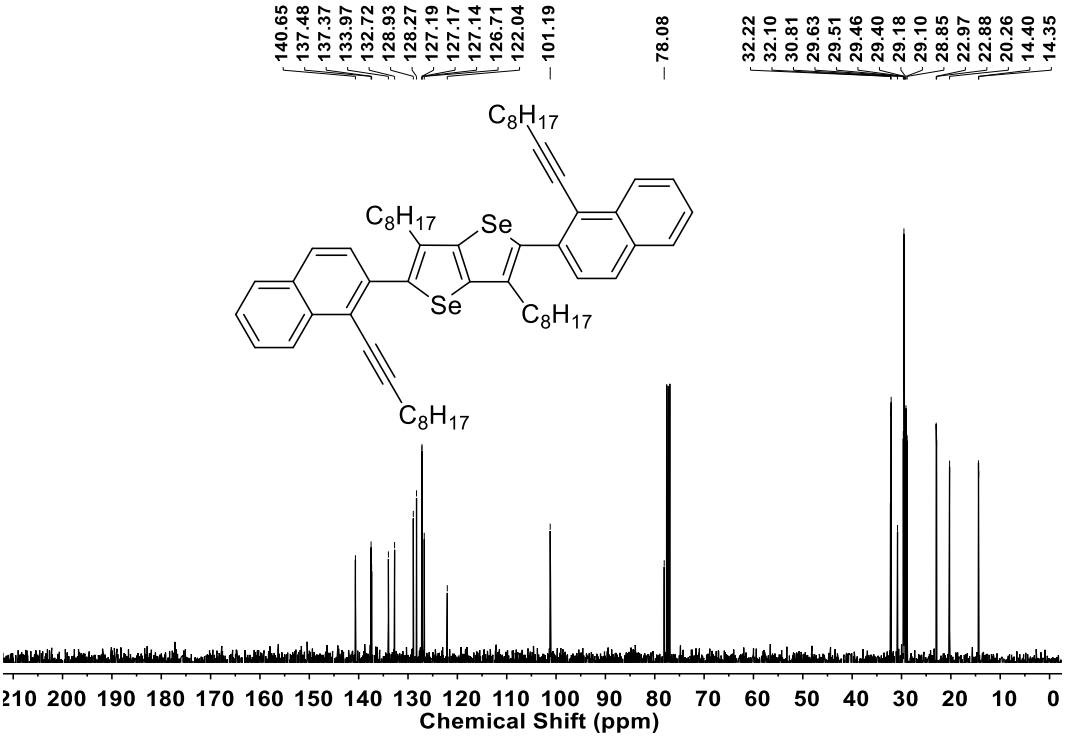


Fig. S70. ^{1}H NMR spectrum of **SS2** in $CDCl_3$.

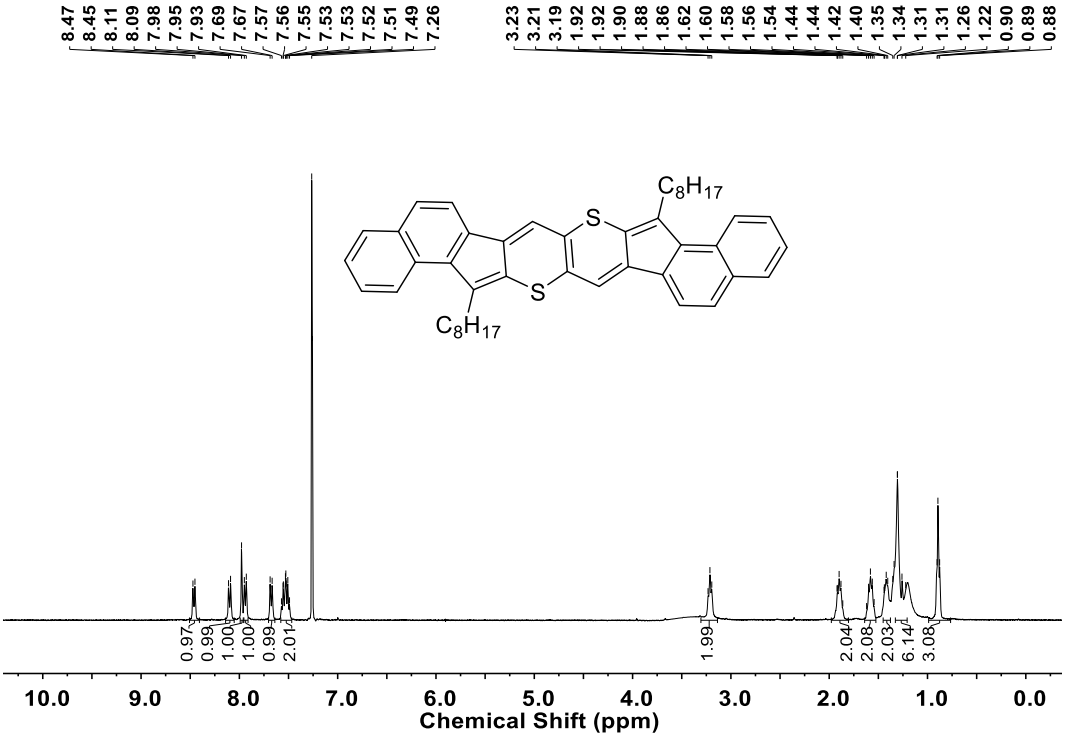


Fig. S71. ^{1}H NMR spectrum of **SSe2** in $CDCl_3$.

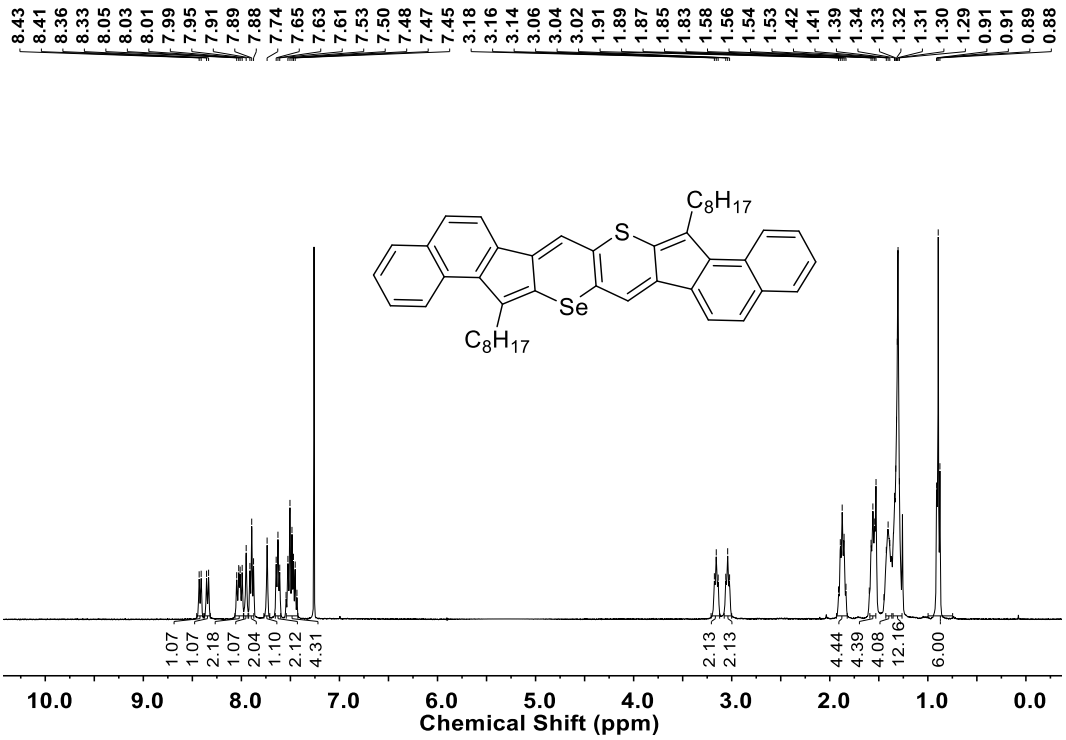


Fig. S72. ^{1}H NMR spectrum of **SeSe2** in $CDCl_3$.

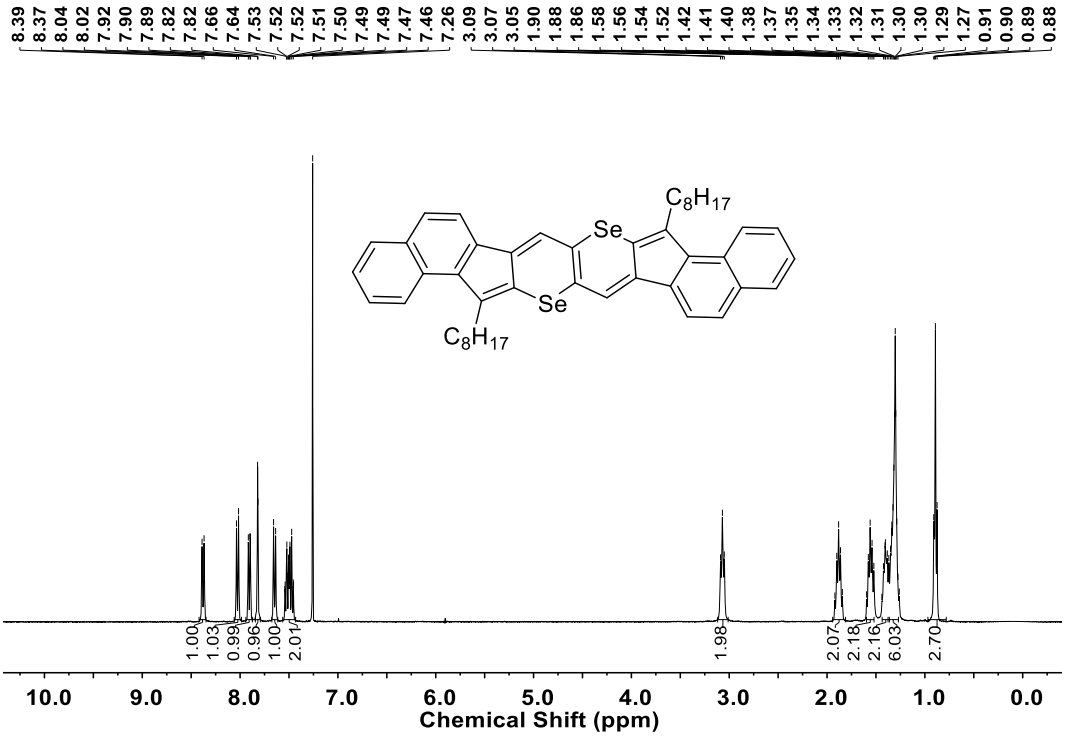


Fig. S73. ^{1}H NMR spectrum of **SSe4** in $CDCl_3$.

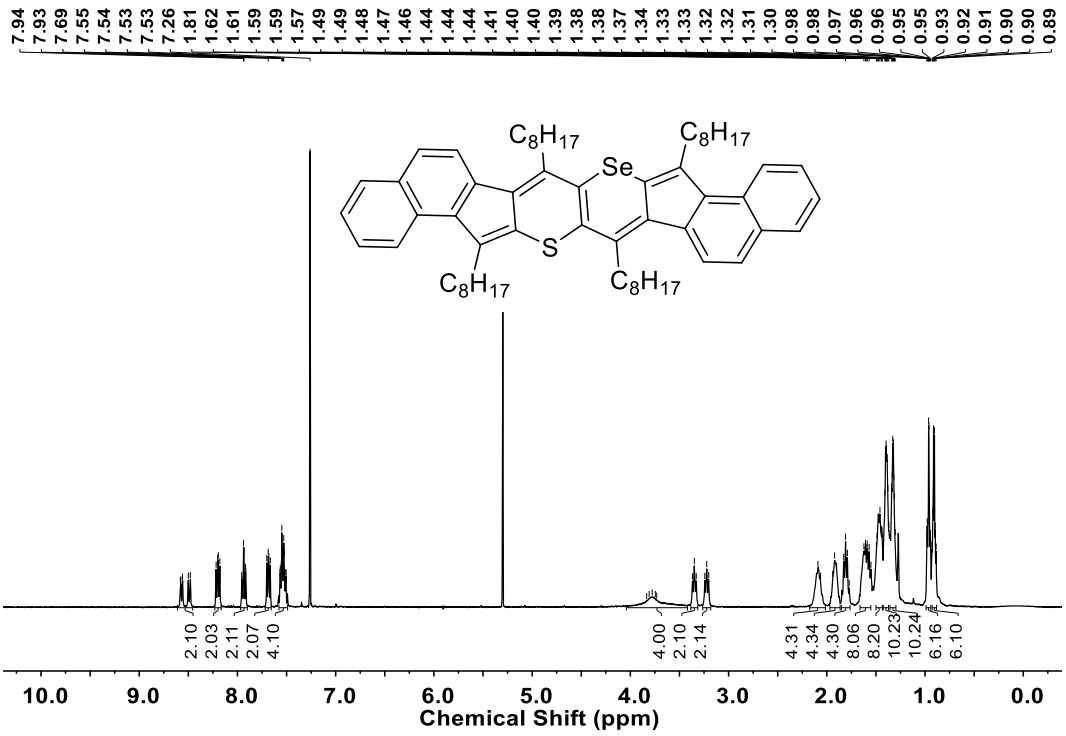


Fig. S74. ^{13}C NMR spectrum of **SSe4** in $CDCl_3$.

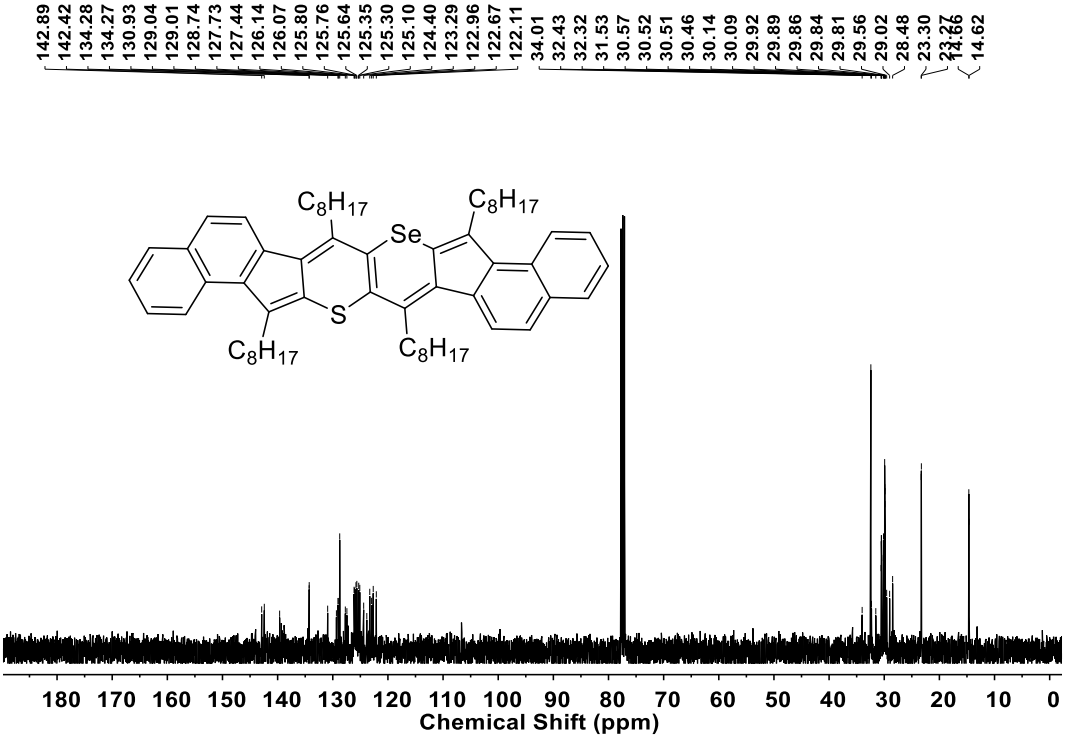


Fig. S75. ^{1}H NMR spectrum of **SeSe4** in $CDCl_3$.

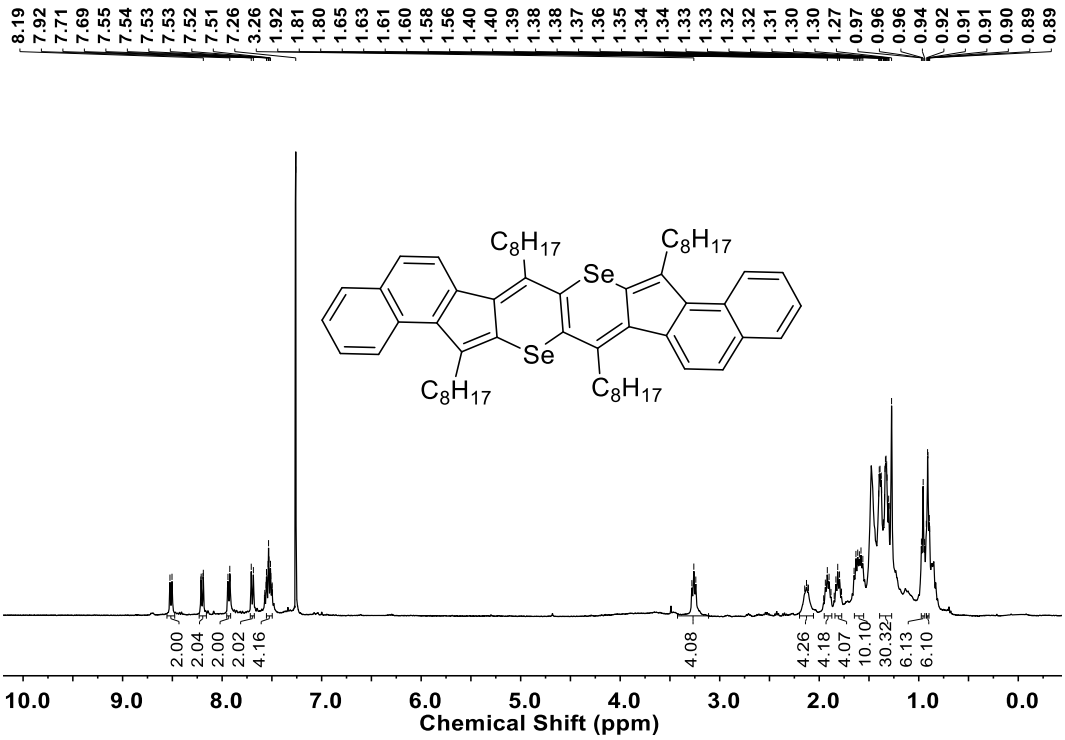
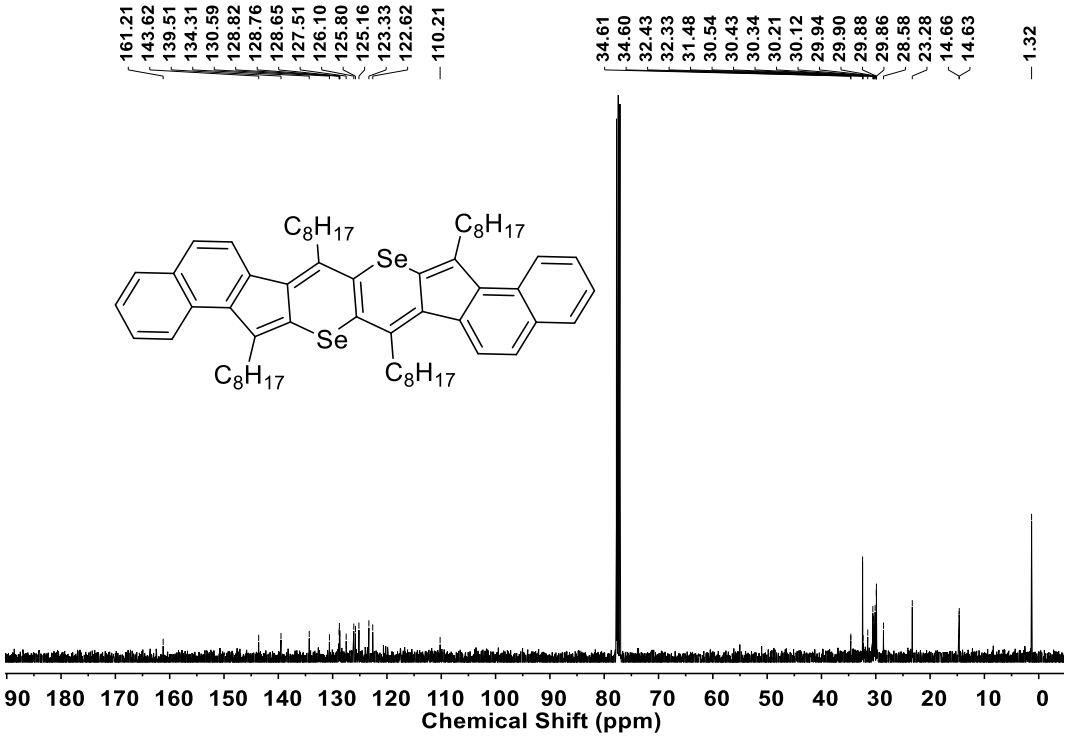


Fig. S76. ^{13}C NMR spectrum of **SeSe4** in $CDCl_3$.



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