Supporting Information for:

Cyclopenta[*b*]thiopyran and Cyclopenta[*b*]selenopyran Based Heteroarenes: Electronic Communication Between S- and/or Se-Fused Aromatics

Yanjun Qiao,[†] Yifan Lu,[†] Weinan Chen,[†] Yijing Chen,[†] Martin Baumgarten,[‡] and Gang Zhou[†,*]

[†]Lab of Advanced Materials, State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200438, P. R. China.

[‡]Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.

*Corresponding author: E-mail: zhougang@fudan.edu.cn, Tel./Fax: +86-21-5163-0350.

Contents:

EXPERIMENTAL SECTION

Materials and reagents.

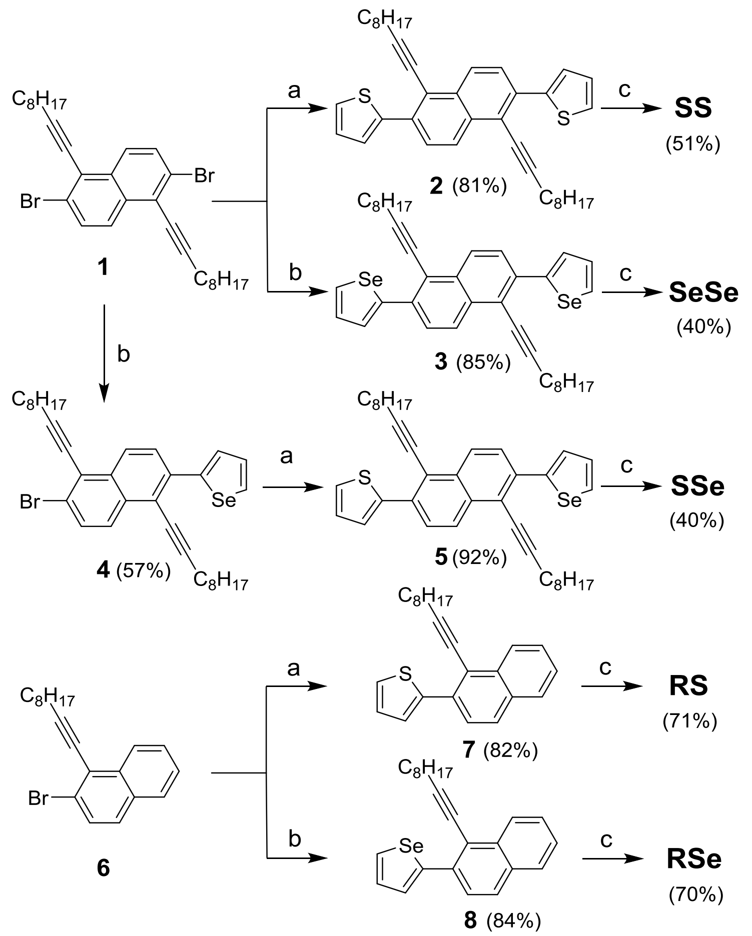
All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. Anhydrous tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Dichloromethane (DCM) and chloroform were distilled from CaH_2. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

Characterizations.

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. 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 recorded on PerkinElmer Lambda 750 spectrophotometer. Cyclic and differential pulse voltammetry measurements were performed on 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. Continuous wave X-band electron spin resonance spectra were obtained with a JEOL (FA200) spectrometer. Time-dependent density functional theory (TD-DFT) calculations were conducted with the Gaussian 03 program using B3LYP method and 6-31G(d) basis set.[S1] The geometries were optimized on basis of their single crystal structures using the default convergence criteria without any constraints.

Synthesis.

Synthesis of 1,5-di(1-decynyl)-2,6-di(2-thienyl)naphthalene (2).



Scheme S1. Synthetic routes for **SS**, **SSe**, **SeSe**, **RS**, and **RSe**.

To a degassed solution of **1**[S2] (1.01 g, 1.8 mmol) in DMF (10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.126 g, 0.18 mmol) and 2-(tri-*n*-butylstannyl)thiophene (2.02 g, 5.4 mmol). Then the mixture was stirred at 90 ^{o}C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow solid (0.82 g, yield: 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 3.3 Hz, 2H), 7.41 (d, J = 4.9 Hz, 2H), 7.15 (t, J = 3.8 Hz, 2H), 2.62 (t, J = 6.9 Hz, 4H), 1.71 (m, 4H), 1.51 (m, 4H), 1.29 (m, 16H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 142.9, 134.3, 133.4, 127.9, 127.4, 127.2, 127.1, 126.3, 118.1, 102.3, 78.4, 32.1, 29.5, 29.4, 29.4, 28.6, 22.9, 20.4, 14.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{38}H_{45}S_2$, 565.2963; found. 565.2935.

Synthesis of 1,5-di(1-decynyl)-2,6-di(2-selenophenyl)naphthalene (3).

To a degassed solution of **1** (1.01 g, 1.8 mmol) in DMF (10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.126 g, 0.18 mmol) and 2-(tri-*n*-butylstannyl)selenophene (1.68 g, 4.5 mmol). Then the mixture was stirred at 90 ^oC overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 10/1) to give a brownish-yellow solid (1.00 g, yield: 85%). ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.43 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 5.6 Hz, 2H), 7.94 (d, J = 3.6 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 4.0 Hz, 2H), 2.71 (t, J = 7.2 Hz, 4H), 1.81 (m, 4H), 1.61 (m, 4H), 1.40 (m, 16H), 0.94 (t, J = 5.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ (ppm): 148.1, 136.3, 133.3, 132.4, 129.6, 129.5, 127.3, 127.0, 117.7, 103.8, 78.4, 32.1, 29.5, 29.4, 29.4, 28.6, 22.9, 20.5, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{38}H_{45}Se_2$, 661.1852; found 661.1822.

Synthesis of 6-bromo-1,5-di(1-decynyl)-2-(2-selenophenyl)naphthalene (4).

To a degassed solution of **1** (0.40 g, 0.716 mmol) in DMF (5 mL) was added $Pd(PPh_3)_2Cl_2$ (0.051 g, 0.072 mmol) and 2-(tri-*n*-butylstannyl)selenophene (0.302 g, 0.716 mmol). Then the mixture was stirred at 90 ^oC overnight under nitrogen atmosphere. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 20/1) to give a brownish-yellow solid (0.25 g, yield: 57%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.26 (t, J = 8.8 Hz, 2H), 8.14 (d, J = 5.6 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.41 (t, J = 5.6 Hz, 1H), 2.65 (m, 4H), 1.79 (m, 4H), 1.62 (m, 2H), 1.54 (m, 2H), 1.43 (m, 16H), 0.90 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 148.1, 136.6, 133.7, 133.1, 132.5, 130.8, 129.7, 129.6, 128.0, 127.8, 126.5, 124.9, 123.4, 118.1, 103.9, 101.7, 78.4, 77.8, 32.1, 29.5, 29.5, 29.4, 29.3, 29.0, 28.6,

23.0, 20.6, 20.2, 14.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{34}H_{42}BrSe$, 609.1635; found. 609.1623.

Synthesis of 1,5-di(1-decynyl)-2-(2-selenophenyl)-6-(2-thienyl)naphthalene (5).

To a degassed solution of **4** (0.49 g, 0.806 mmol) in DMF (10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.057 g, 0.0806 mmol) and 2-(tri-*n*-butylstannyl)thiophene (0.603 g, 1.611 mmol). Then the mixture was stirred at 90 ^oC overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 10/1) to give a brownish-yellow solid (0.45 g, yield: 92%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 5.2 Hz, 1H), 7.87 (t, J = 8.8 Hz, 2H), 7.79 (t, J = 8.8 Hz, 2H), 7.42 (m, 2H), 7.16 (d, J = 3.2 Hz, 1H), 2.66 (m, 4H), 1.77 (m, 4H), 1.51 (s, 4H), 1.30 (s, 16H), 0.89 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 148.4, 145.4, 142.9, 136.3, 134.3, 133.4, 133.4, 132.3, 129.6, 129.5, 128.0, 127.5, 127.3, 127.2, 127.1, 126.4, 118.1, 117.8, 103.5, 102.3, 78.7, 78.4, 32.1, 29.5, 29.4, 29.4, 28.7, 28.6, 23.0, 20.7, 20.5, 14.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{38}H_{45}SSe$, 613.2407; found 613.2403.

Synthesis of 1-(1-decynyl)-2-(2-thienyl)naphthalene (7).

To a degassed solution of **6**[S3] (0.13 g, 0.38 mmol) in DMF (2 mL) was added $Pd(PPh_3)_2Cl_2$ (0.027 g, 0.038 mmol) and 2-(tri-*n*-butylstannyl)thiophene (0.21 g, 0.57 mmol). Then the mixture was stirred at 90 ^oC overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow oil (0.11 g, yield: 82%) ^1H NMR (400 MHz, THF-d_8) δ (ppm): 8.45 (d, J = 8.5 Hz, 1H), 7.85-7.78 (m, 2H), 7.75 (m, 2H), 7.55 (m, 1H), 7.51-7.44 (m, 2H), 7.12 (m, 1H), 2.64 (t, J = 7.1 Hz, 2H), 1.73 (m, 2H), 1.54 (m, 2H), 1.37 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ (ppm): 142.9, 134.5, 134.2, 132.5, 128.0, 127.9, 127.3, 127.0, 126.9, 126.8, 126.6, 126.2, 126.1, 117.8, 101.7, 78.5, 32.1, 29.5, 29.4, 29.3, 28.7, 22.8, 19.9, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{27}S$ 347.1833; found 347.1824.

Synthesis of 1-(1-decynyl)-2-(2-selenophenyl)naphthalene (8).

To a degassed solution of 2-bromo-1-(1-decynyl)naphthalene (0.13 g, 0.38 mmol) in DMF (2 mL) was added $Pd(PPh_3)_2Cl_2$ (0.027 g, 0.038 mmol) and 2-(tri-*n*-butylstannyl)selenophene (0.24 g, 0.57 mmol). Then the mixture was stirred at 90 ^oC overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow oil (0.13 g, yield: 84%) ^1H NMR (400 MHz, THF-d_8) δ (ppm): 8.45 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 5.6 Hz, 1H), 7.90 (d, J = 4.8 Hz, 1H), 7.83 (m, 3H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 6.8 Hz, 1H), 7.36 (m, 1H), 2.68 (t, J = 7.2 Hz, 2H), 1.77 (m, 2H), 1.58 (m, 2H), 1.39 (m, 8H), 0.91 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ (ppm): 148.3, 136.2, 134.5, 132.4, 132.1, 129.3, 129.0, 128.0, 127.9, 127.0, 127.0, 126.2, 126.0, 117.4, 102.9, 78.8, 32.1, 29.5, 29.4, 29.3, 28.6, 22.8, 20.1, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{27}Se$ 395.1278; found 395.1270.

Synthesis of 7,14-dioctylnaphtho[2,1-*f*:6,5-*f*']bis(cyclopenta[*b*]thiopyran) (SS).

To a degassed solution of **2** (0.31 g, 0.55 mmol) in dry toluene (15 mL) was added $PtCl_2$ (0.03 g, 0.11 mmol). The mixture was heated overnight under 110 ℃ and then cooled to room temperature. After removing toluene in vacuum, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give **SS** as dark green crystals (0.16 g, yield: 51%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (d, J = 8.6 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 8.03 (d, J = 7.1 Hz, 2H), 7.57 (d, J = 9.1 Hz, 2H), 7.15 (t, J = 9.1, 2H), 3.38-3.33 (m, 4H), 1.92 (m, 4H), 1.41 (m, 4H), 1.27 (m, 16H), 0.88 (t, J = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 137.4, 130.6, 128.4, 127.3, 126.4, 126.3, 123.3, 122.8, 118.3, 118.1, 117.2, 32.1, 30.1, 29.9, 29.8, 29.6, 29.0, 22.9, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{38}H_{45}S_2$ 565.2963; found 565.2965.

Synthesis of 7,14-dioctylnaphtho[2,1-*f*:6,5-*f*']bis(cyclopenta[*b*]selenopyran) (SeSe).

To a degassed solution of **3** (0.30 g, 0.55 mmol) in dry toluene (30 mL) was added $PtCl_2$ (0.03 g, 0.11 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give **SeSe** as dark green crystals (0.12 g, yield: 40%). ^{1}H NMR (400 MHz, THF-d_8) δ (ppm): 8.44 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), 7.95 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 9.2 Hz, 2H), 3.28 (t, J = 7.6 Hz, 4H), 2.08-1.90 (m, 4H), 1.62 (m, 4H), 1.44-1.30 (m, 16H), 0.90 (t, J = 3.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ (ppm): 137.1, 130.9, 130.5, 129.0, 128.3, 127.7, 122.8, 122.6, 120.45, 120.4, 118.11, 118.07, 32.1, 31.2, 30.1, 29.9, 29.6, 28.6, 22.8, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{38}H_{45}Se_2$, 661.1852; found 661.1850.

Synthesis of 7,14-dioctyl-thiopyran[5'',6'':1',2']indeno[5',4':4,5]indeno[2,1-*b*]seleno-pyran (SSe).

To a degassed solution of **5** (0.30 g, 0.49 mmol) in dry toluene (30 mL) was added $PtCl_2$ (0.03 g, 0.098 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give **SSe** as dark green crystals (0.12 g, yield: 40%). ^{1}H NMR (400 MHz, THF-d_8) δ (ppm): 8.51 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 8.8 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.14 (t, J = 6.4 Hz, 2H), 7.96 (d, J = 8.0 Hz, 1H),7.78 (d, J = 9.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 3.39 (t, J = 7.2 Hz, 2H), 3.29 (t, J = 7.2 Hz, 2H), 2.08-1.90 (m, 4H), 1.63 (m, 4H), 1.46-1.30 (m, 16H), 0.91 (t, J = 5.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ (ppm): 137.3, 137.1, 131.0, 130.6, 130.5, 129.2, 128.6, 128.2, 127.6, 127.3, 127.3, 126.4, 125.5, 123.3, 123.0, 122.7, 122.6, 120.4, 118.3, 118.0, 117.7, 117.2, 54.1, 35.4, 32.1, 31.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.0, 28.6, 27.2, 22.8, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{38}H_{45}SSe$, 613.2407; found 613.2410.

Synthesis of 11-octylbenzo[4,5]indeno[2,1-*b*]thiopyran (RS).

To a degassed solution of **7** (0.35 g, 1.01 mmol) in dry toluene (30 mL) was added $PtCl_2$ (0.05 g, 0.20 mmol). The mixture was heated overnight under 110 ^oC and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE) to give **RS** as blue oil (0.25 g, yield: 71%). ^1H NMR (400 MHz, THF-d_8) δ (ppm): 8.60 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 6.8 Hz, 1H), 7.51 (t, J = 6.8 Hz, 1H), 7.22 (m, 1H), 3.33 (t, J = 7.6 Hz, 2H), 1.93 (m, 2H), 1.59 (m, 2H), 1.40-1.30 (m, 8H), 0.90 (t, J = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ (ppm): 136.5, 134.9, 130.3, 128.8, 127.8, 127.7, 126.7, 125.2, 125.1, 125.0, 124.7, 123.7, 123.2, 121.3, 119.0, 117.1, 32.1, 30.0, 29.8, 29.5, 29.1, 29.0, 22.8, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{27}S$ 347.1833; found 347.1845.

Synthesis of 11-octylbenzo[4,5]indeno[2,1-*b*]selenopyran (RSe)

To a degassed solution of **8** (0.30 g, 0.76 mmol) in dry toluene (30 mL) was added $PtCl_2$ (0.04 g, 0.15 mmol). The mixture was heated overnight under 110 ^oC and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE) to give **RSe** as blue oil (0.21 g, yield: 70%). ^1H NMR (400 MHz, THF-d_8) δ (ppm): 8.53 (d, J = 8.4 Hz, 1H), 8.18 (t, J = 8.4 Hz, 2H), 7.96

(m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 6.8 Hz, 1H), 7.39 (m, 1H), 3.22 (t, J = 7.6 Hz, 2H), 1.92 (m, 2H), 1.60 (m, 2H), 1.42-1.29 (m, 8H), 0.90 (t, J = 6.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8) δ (ppm): 136.3, 135.0, 130.4, 130.2, 129.5, 128.9, 128.2, 127.5, 125.2, 124.9, 124.6, 123.5, 122.5, 121.6, 120.3, 118.9, 32.1, 30.7, 30.0, 29.8, 29.5, 28.6, 22.8, 13.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{27}Se$ 395.1278; found 395.1265.

Table S1 S-C and Se-C bond lengths for heteroarenes **SS**, **SSe**, and **SeSe**.

	S-C bond length (Å)	Se-C bond length (Å)
SS	1.7158(18) / 1.7376(17)	----
SSe	1.695(17) / 1.870(16)	1.791(17) / 1.920(15)
SeSe	----	1.879(4) / 1.876(4)

Table S2 Crystal data and structure refinement details for isomers **SS**, **SSe**, and **SeSe**.

	SS	**SSe**	**SeSe**
formula	$C_{38}H_{44}S_2$	$C_{38}H_{44}SSe$	$C_{38}H_{44}Se_2$
formula wt.	564.85	611.75	658.65
T (K)	173	173	300
wavelength (Å)	1.54178	1.54178	1.54178
crystal size	0.16 x 0.15 x 0.12	0.05 x 0.04 x 0.03	0.24 x 0.22 x 0.18
crystal syst.	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P1$	$P\bar{1}$
a (Å)	4.9037(8)	4.9067(2)	5.0411(3)
b (Å)	9.209(3)	9.2799(3)	9.2861(5)
c (Å)	17.287(5)	17.3392(6)	17.3658(10)
α (deg.)	78.265(16)	78.036(10)	78.341(2)
β (deg.)	87.365(18)	87.305(10)	88.254(2)
γ (deg.)	80.485(15)	80.354 (10)	80.527(2)
V (Å^3)	753.8(3)	761.39(5)	785.30(8)
Z / $D_{calcd.}$ (mg/m^3)	1 / 1.244	1 / 1.334	1 / 1.393
μ (mm^{-1})	1.776	2.484	3.113
F(000)	304	322	340
max / min transmission	0.753/0.698	0.928/0.888	0.753/0.604
final R indices	$R1 = 0.0354$	$R1 = 0.1062$	$R1 = 0.0404$
[$I > 2\theta(I)$]	$wR2 = 0.0800$	$wR2 = 0.3024$	$wR2 = 0.1127$
R indices (all data)	$R = 0.0411$	$R = 0.1207$	$R = 0.0434$
	$wR2 = 0.0824$	$wR2 = 0.3353$	$wR2 = 0.1144$

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

Bond	Length/Å
S1-C1	1.7158(18)
S1-C5	1.7376(17)
C1-C2	1.3480(30)
C2-C3	1.4280(20)
C3-C4	1.3510(20)
C4-C8	1.4400(20)
C4-C5	1.4640(20)
C5-C6	1.3600(20)
C6-C7	1.4720(20)
C6-C12	1.5040(20)
C7-C8	1.4050(20)
C7-C11	1.4280(20)
C9-C10	1.3610(20)
C9-C8	1.4050(20)
C10-C11	1.4200(20)
C11-C7	1.4280(20)
C12-C13	1.5370(20)
C13-C14	1.5200(20)
C14-C15	1.5260(20)
C15-C16	1.5190(20)
C16-C17	1.5190(30)
C17-C18	1.5190(20)
C18-C19	1.5210(30)

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

Bond	Length/Å	Bond	Length/Å
Se1-C18	1.791(17)	C15-C19	1.48(2)
Se1-C22	1.920(15)	C16-C17	1.41(2)
S1-C1	1.695(17)	C17-C18	1.45(2)
S1-C5	1.870(16)	C17-C23	1.46(2)
C1-C2	1.39(2)	C18-C19	1.48(2)
C2-C3	1.44(2)	C19-C20	1.34(2)
C3-C4	1.39(2)	C20-C21	1.41(2)
C4-C8	1.38(2)	C21-C22	1.34(2)
C4-C5	1.46(2)	C23-C24	1.588(19)
C5-C6	1.31(2)	C24-C25	1.50(2)
C6-C7	1.53(2)	C25-C26	1.62(2)
C6-C31	1.538(19)	C26-C27	1.49(2)
C7-C12	1.40(2)	C27-C28	1.505(19)
C7-C8	1.43(2)	C28-C29	1.56(2)
C9-C10	1.39(2)	C29-C30	1.55(2)
C9-C8	1.44(2)	C31-C32	1.48(2)
C10-C11	1.45(2)	C32-C33	1.56(2)
C11-C12	1.457(15)	C33-C34	1.48(2)
C11-C16	1.47(2)	C34-C35	1.52(3)
C13-C14	1.37(2)	C35-C36	1.60(3)
C13-C12	1.38(2)	C36-C37	1.49(3)
C14-C15	1.36(2)	C37-C38	1.46(3)
C15-C16	1.38(2)		

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

Bond	Length/Å
Se1-C1	1.879(4)
Se1-C5	1.876(4)
C1-C2	1.328(6)
C2-C3	1.425(6)
C3-C4	1.355(5)
C4-C8	1.450(5)
C4-C5	1.465(5)
C5-C6	1.356(5)
C6-C7	1.478(5)
C6-C12	1.507(5)
C7-C8	1.399(5)
C7-C11	1.432(5)
C9-C10	1.367(5)
C9-C8	1.402(5)
C10-C11	1.416(5)
C12-C13	1.544(5)
C13-C14	1.504(6)
C14-C15	1.522(6)
C15-C16	1.520(6)
C16-C17	1.510(6)
C17-C18	1.508(7)
C18-C19	1.515(9)

Table S6 Calculated energies, oscillator strength and compositions of major electronic transitions for **SS**.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
657.14	0.0780	H→L (97%)
425.74	0.5051	H-2→L (89%)
409.36	0.1037	H-1→L+1 (92%)
353.10	1.2313	H→L+2 (88%)
319.85	0.1013	H-3→L (83%), H-2→L+2 (10%)

Table S7 Calculated energies, oscillator strength and compositions of major electronic transitions for **SeSe**.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
652.99	0.1006	H→L (98%)
428.52	0.4641	H-2→L (89%)
414.27	0.1284	H-1→L+1 (92%)
354.59	1.0959	H→L+2 (88%)
321.67	0.1287	H-3→L (83%)

Table S8 Calculated energies, oscillator strength and compositions of major electronic transitions for **SSe**.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
649.26	0.0926	H→L (97%)
425.29	0.456	H-2→L (88%)
410.30	0.1195	H-1→L+1 (91%)
364.74	0.0038	H-2→L+1 (92%)
353.70	1.1532	H→L+2 (87%)
319.46	0.1018	H-3→L (82%)

Table S9 Calculated energies, oscillator strength and compositions of major electronic transitions for **RS**.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
561.11	0.0459	H→L (98%)
373.31	0.2074	H-1→L (87%)
335.67	0.3279	H-2→L (18%), H→L+1 (72%)
317.82	0.1877	H-2→L (71%)
287.97	0.2533	H-1→L+1 (32%), H→L+2 (51%)
272.99	0.106	H-1→L+1 (52%)
259.68	0.062	H-3→L (60%), H→L+3 (30%)
257.43	0.2262	H→L+3 (55%)
251.33	0.009	H→L+4 (95%)

Table S10 Calculated energies, oscillator strength and compositions of major electronic transitions for **RSe**.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
567.77	0.0549	H→L (98%)
379.24	0.226	H-1→L (90%)
338.68	0.256	H-2→L (22%), H→L+1 (72%)
320.89	0.2076	H-2→L (69%)
289.61	0.2493	H→L+2 (57%)
275.07	0.0212	H→L+4 (72%)
273.77	0.0665	H-1→L+1 (42%), H→L+2 (28%)
262.3	0.0045	H-3→L (90%)
258.80	0.2121	H→L+3 (82%)

Fig. S1 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of **SS**.

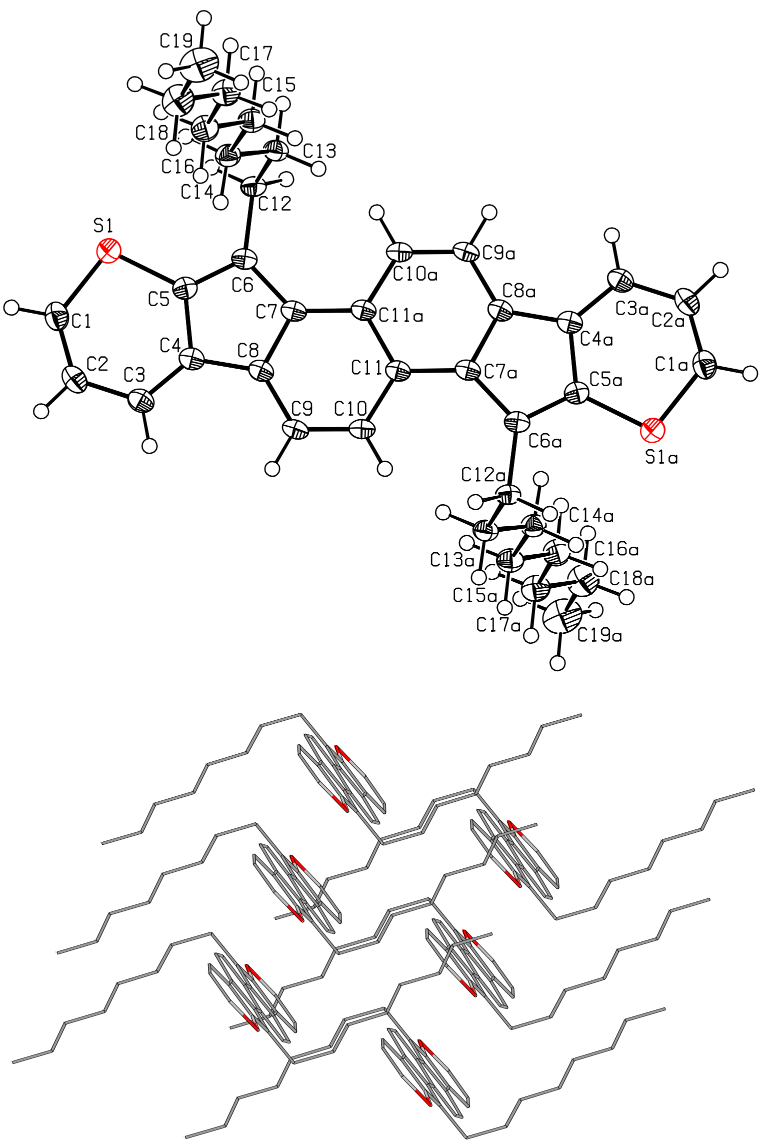


Fig. S2 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of **SSe**.

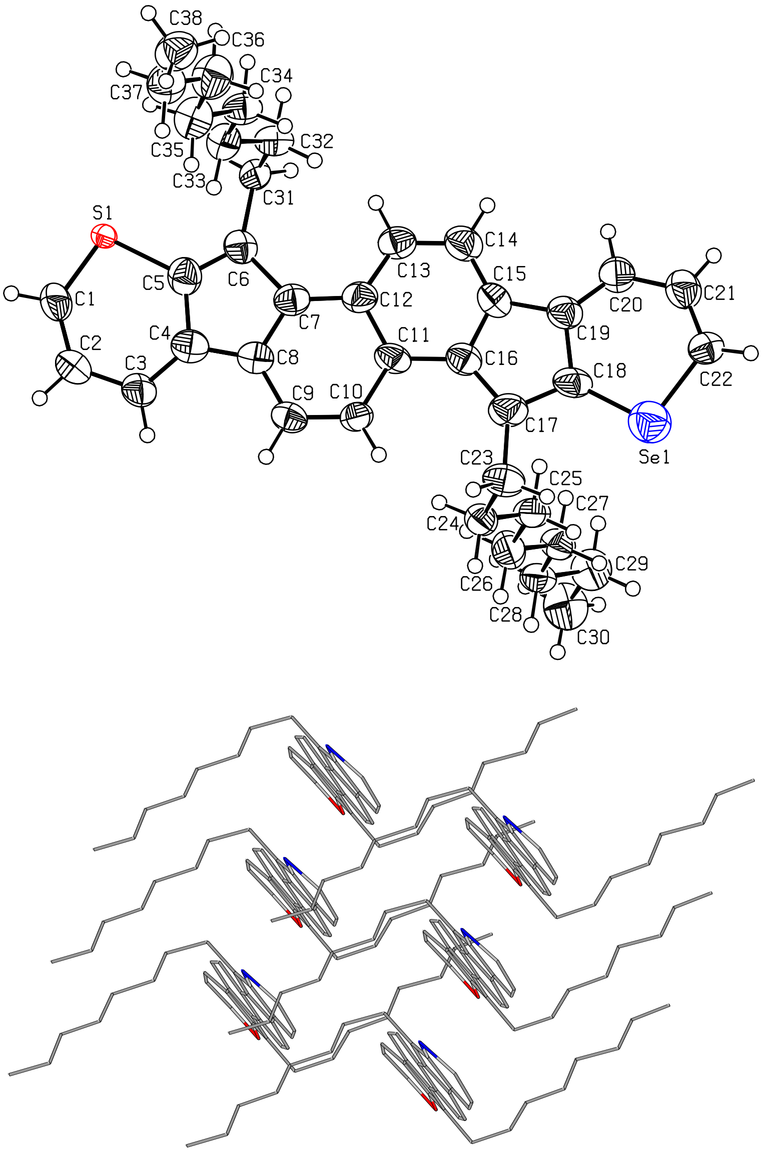


Fig. S3 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of **SeSe**.

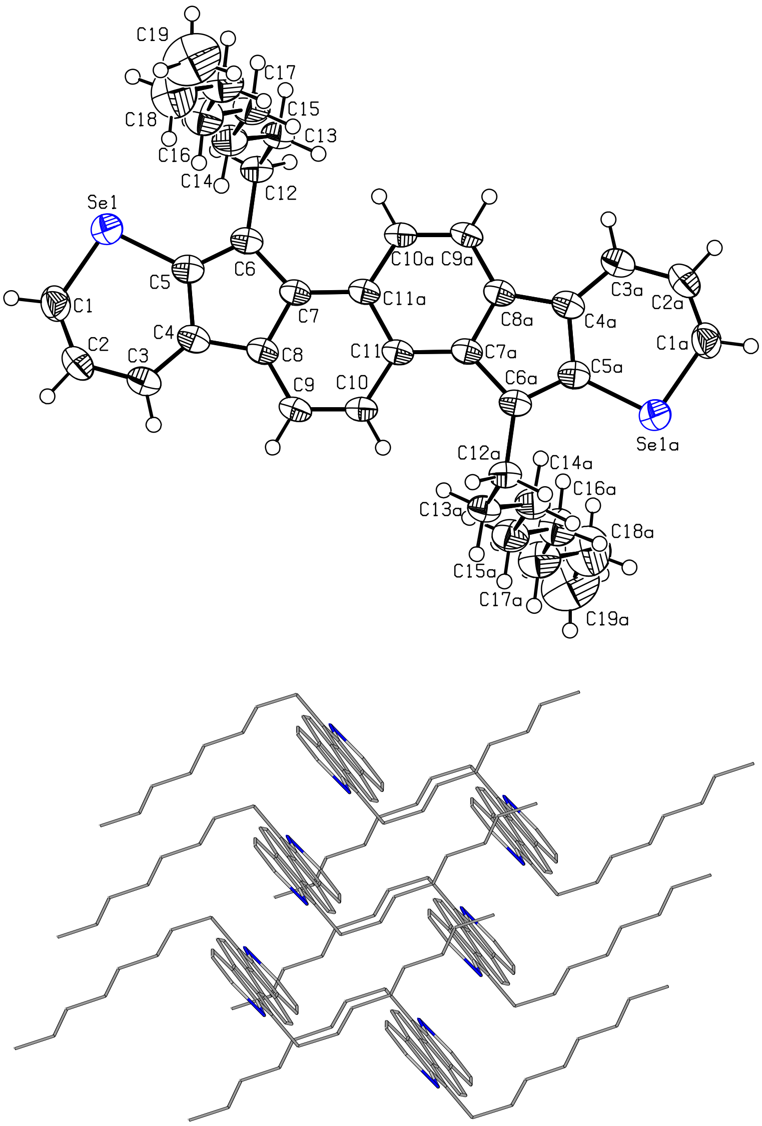


Fig. S4 Calculated frontier orbitals of the S- and Se-fused heteroarenes.

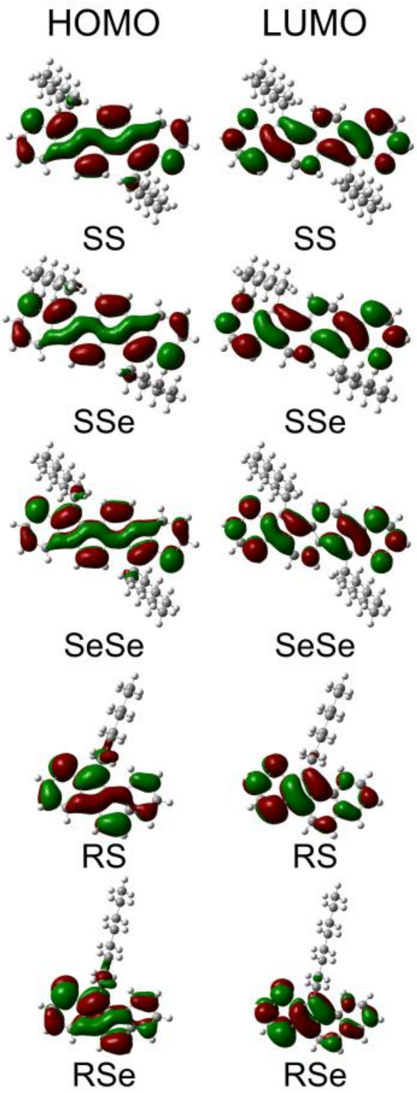


Fig. S5 Differential pulse voltammograms of heteroarenes **SS**, **SSe**, **SeSe**, **RS**, and **RSe** in DCM solutions (0.1 mM).

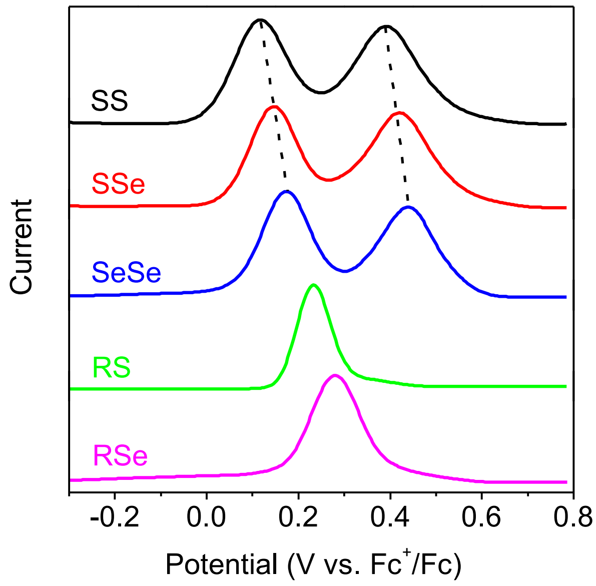


Fig. S6 UV-vis-NIR absorption spectra of heteroarenes (a) **SS**, (b) **SSe**, (c) **SeSe**, and (d) **RS** and **RSe** in DCM solutions upon titration of $SbCl_5$.

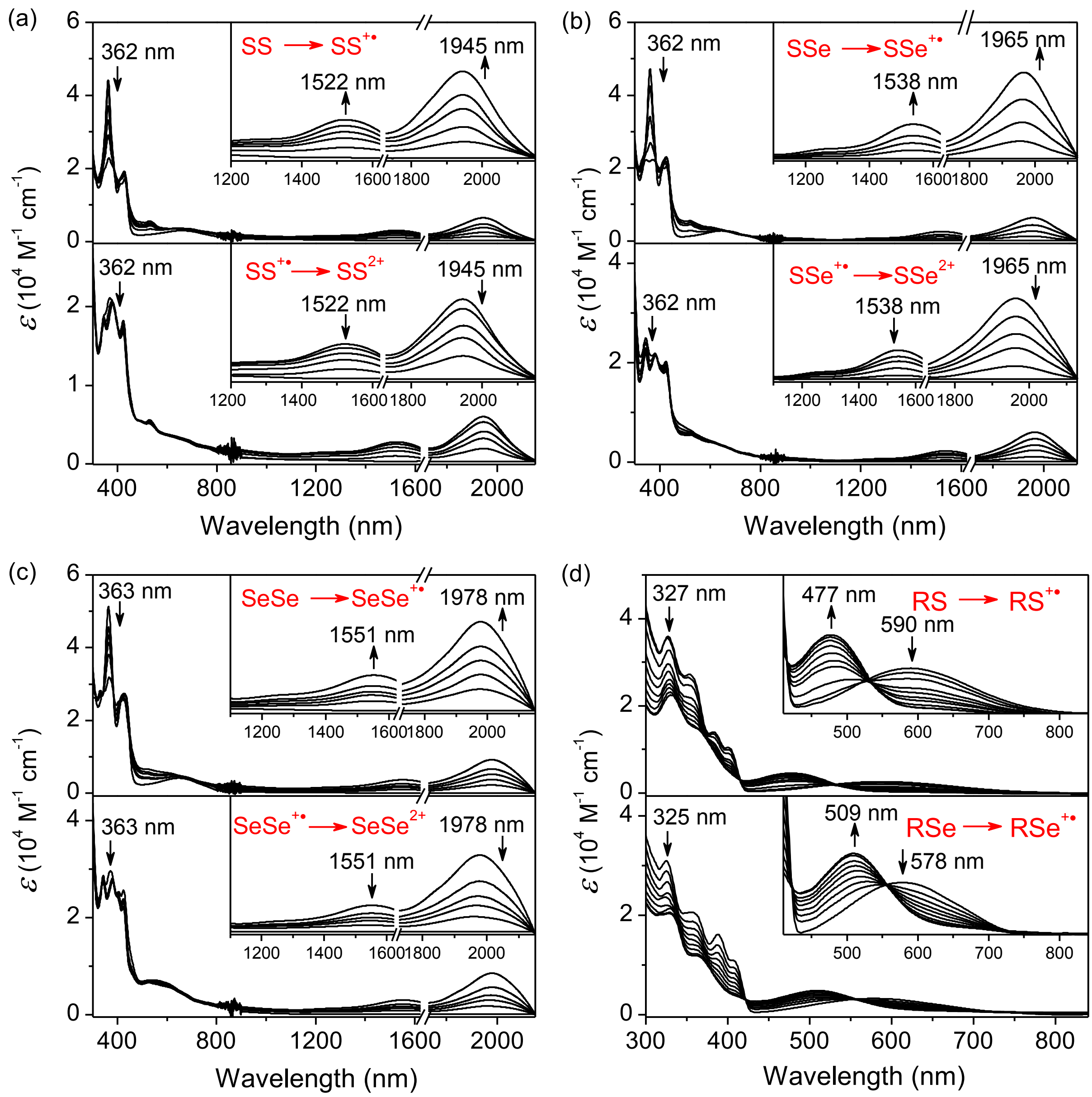


Fig. S7 ESR spectra of **SS**$^{+\bullet}$, **SSe**$^{+\bullet}$, **SeSe**$^{+\bullet}$, **RS**$^{+\bullet}$, and **RSe**$^{+\bullet}$ recorded in DCM at room temperature.

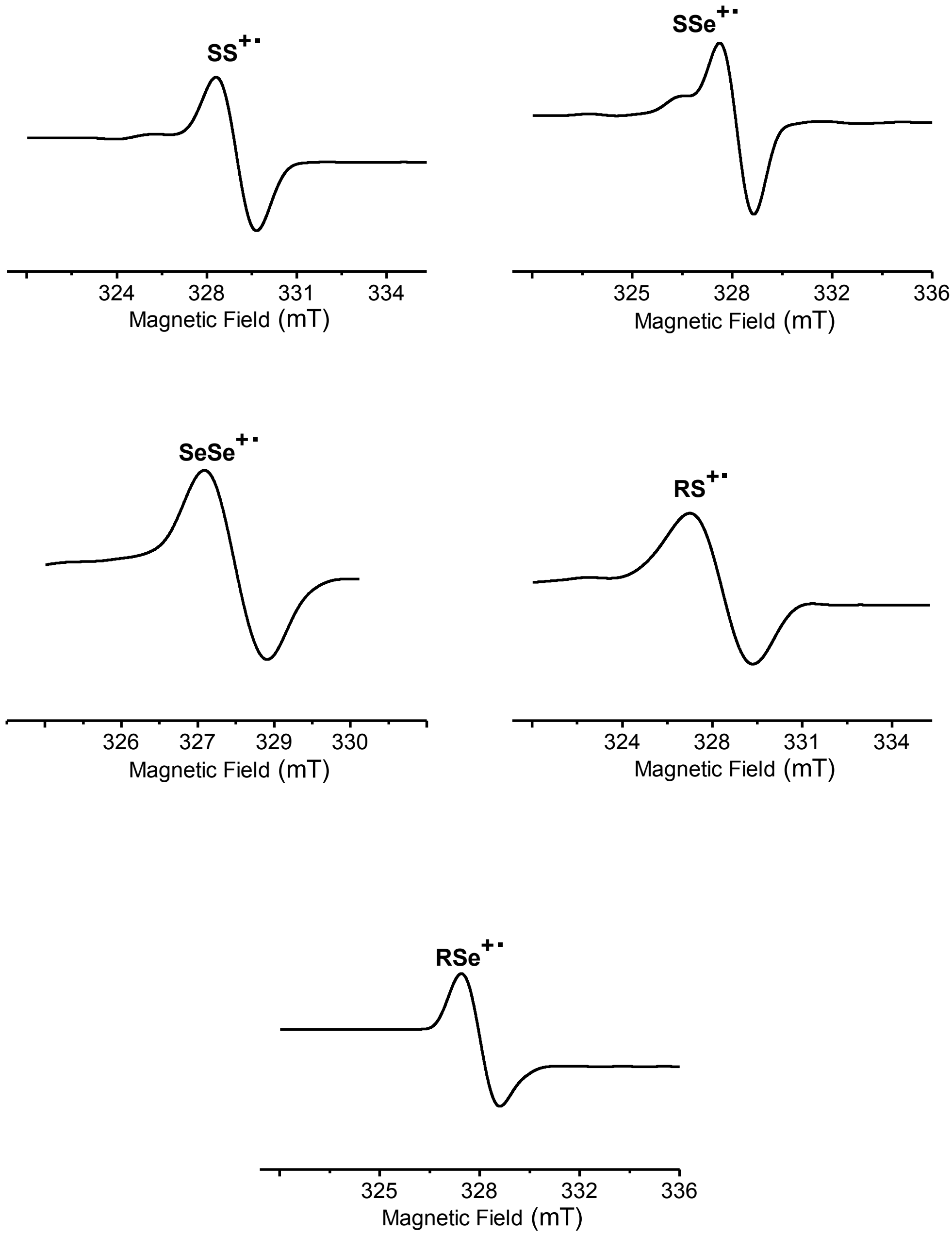


Fig. S8 ^{1}H NMR spectrum of **2** in $CDCl_3$.

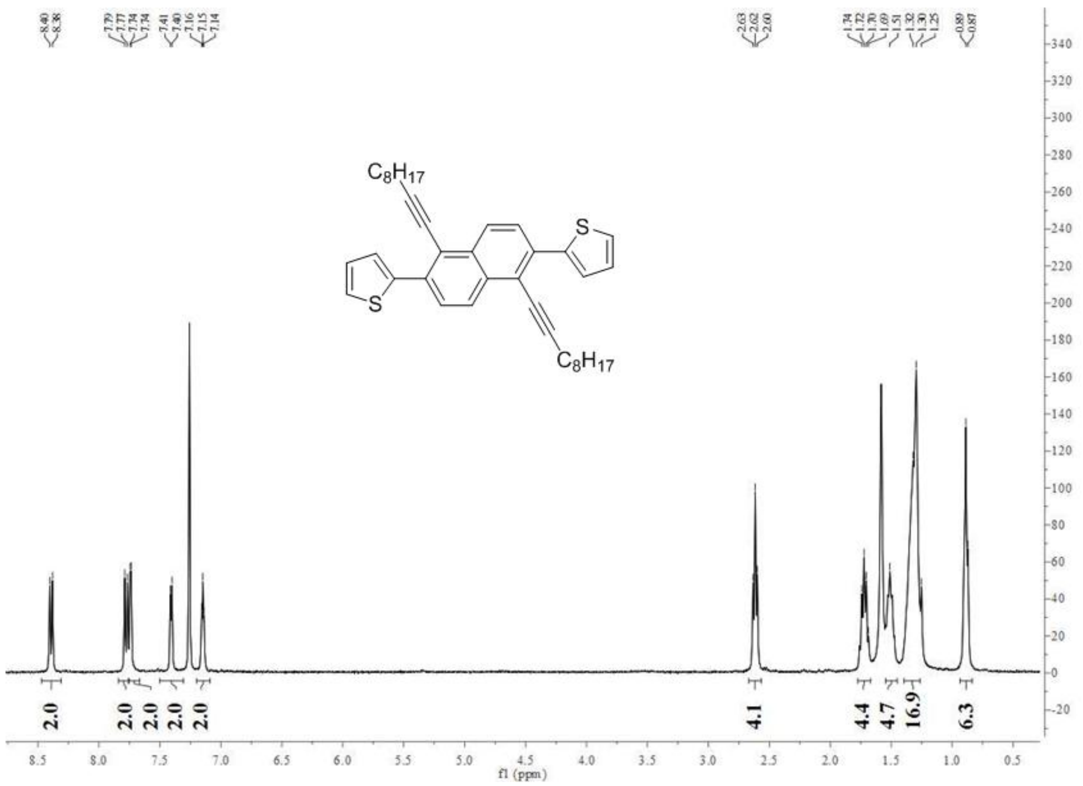


Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

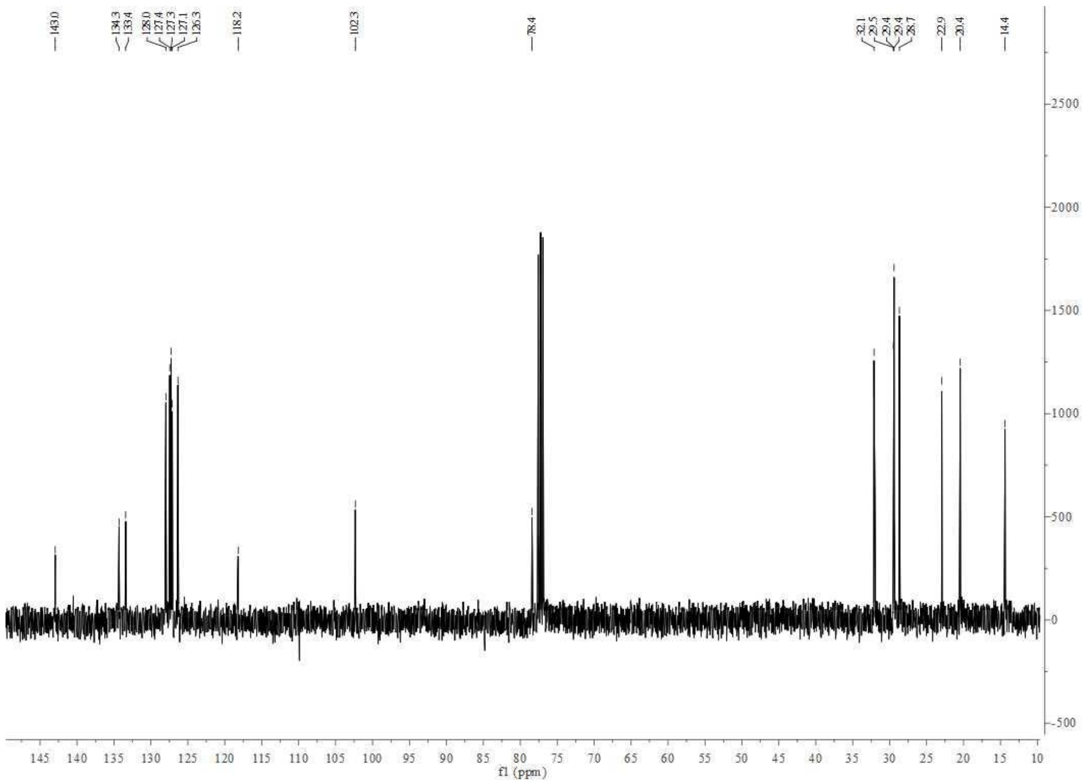


Fig. S10 ^{1}H NMR spectrum of **3** in CD_2Cl_2.

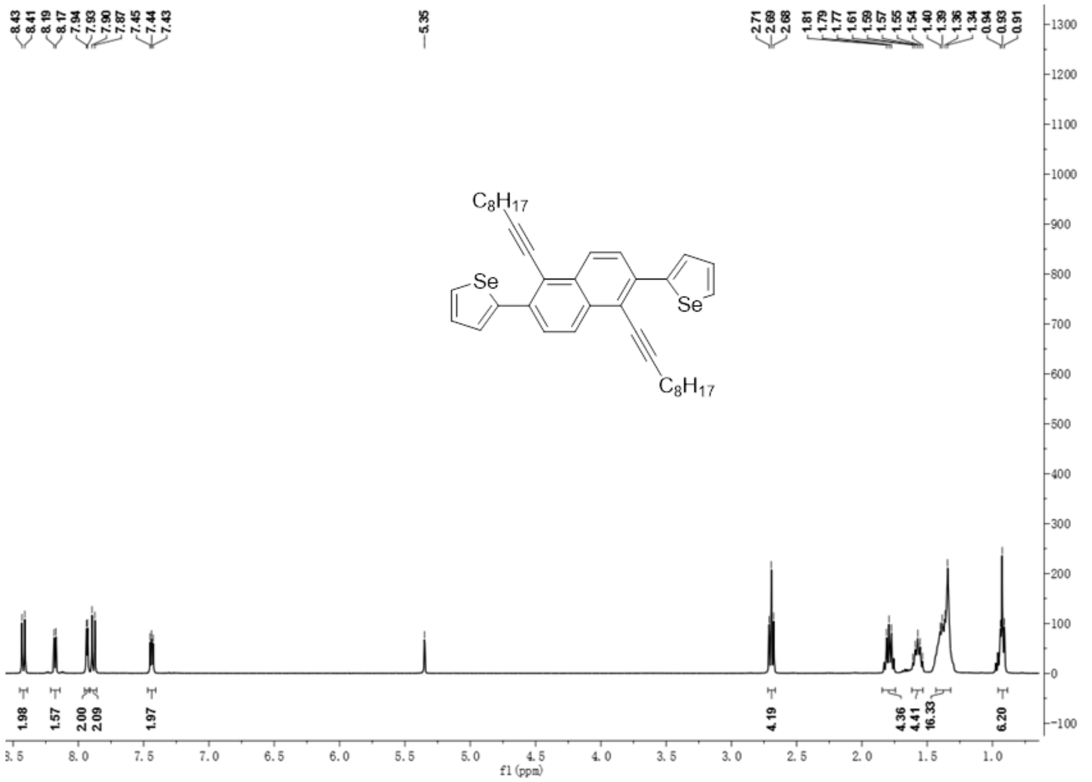


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in CD_2Cl_2.

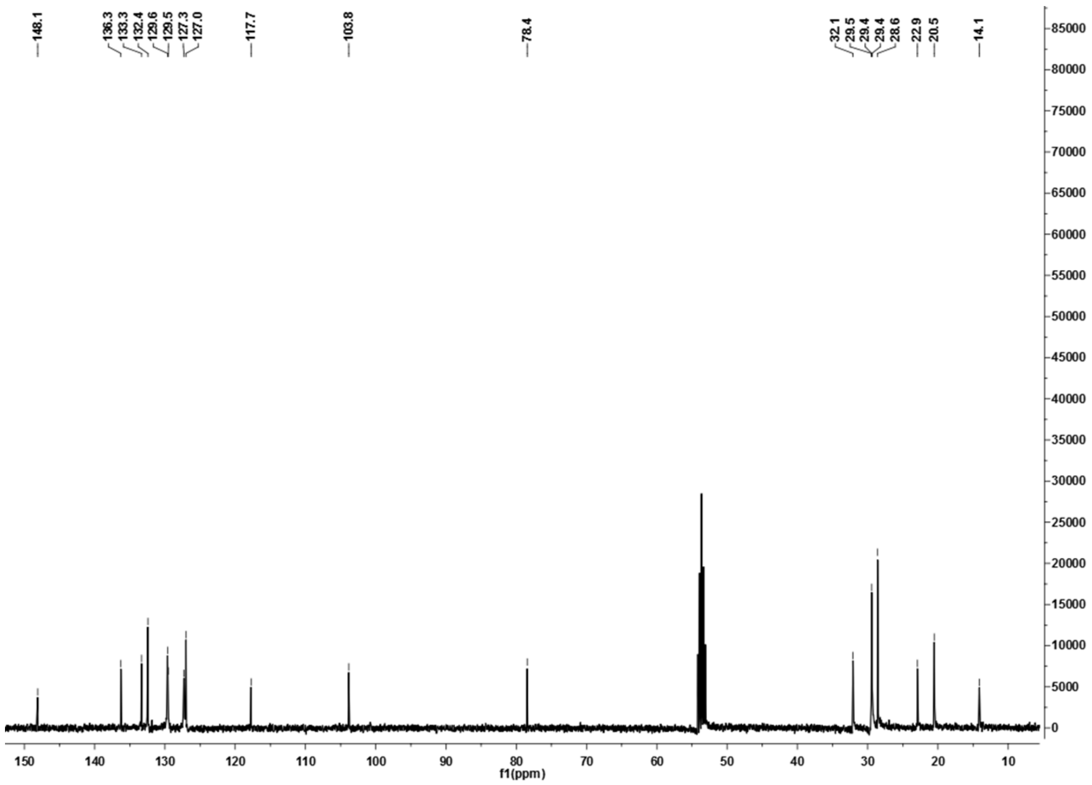


Fig. S12 ^{1}H NMR spectrum of **4** in $CDCl_3$.

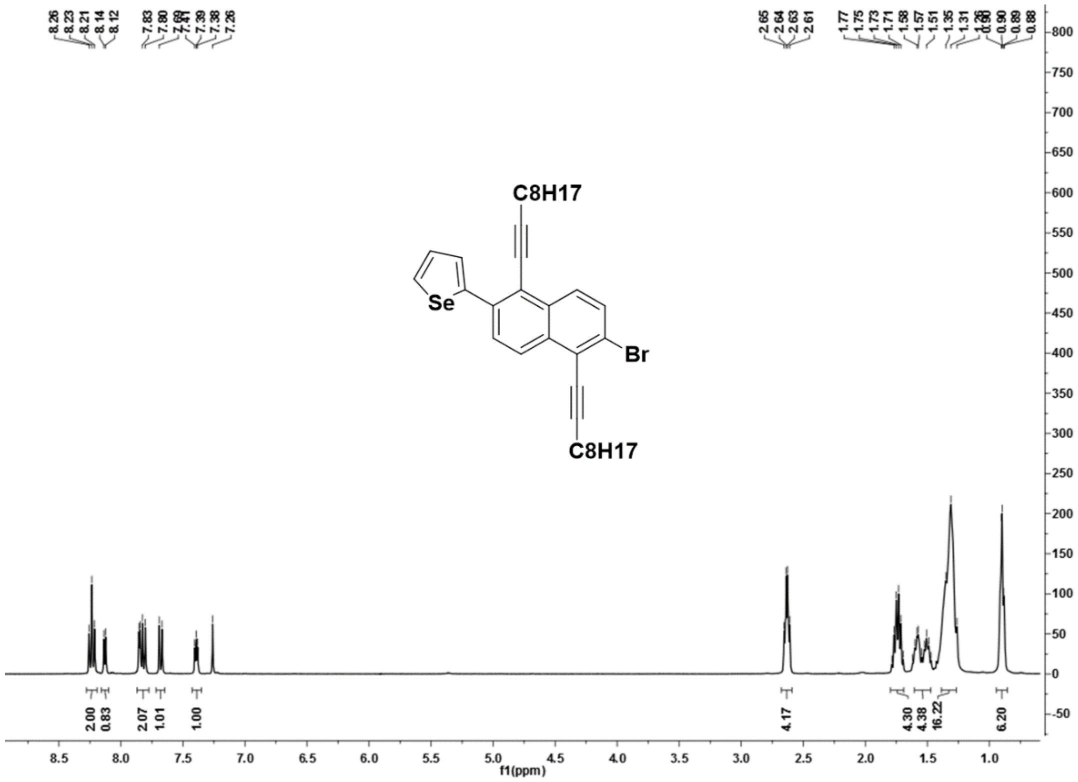


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

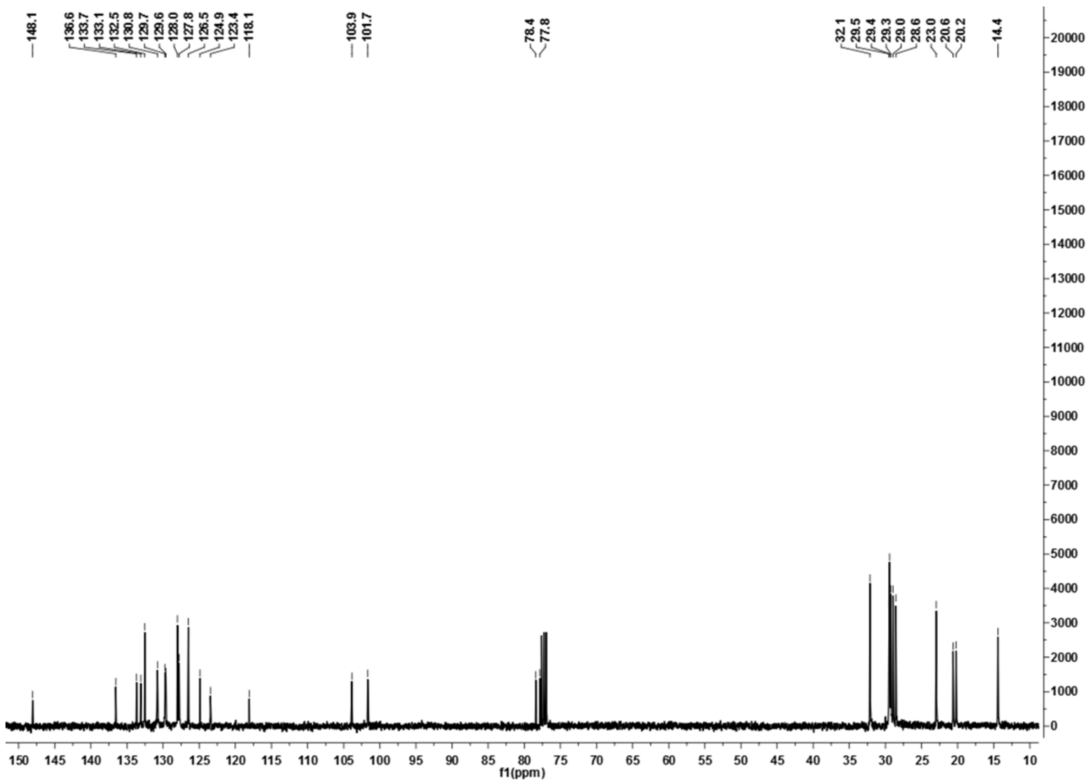


Fig. S14 ^{1}H NMR spectrum of **5** in $CDCl_3$.

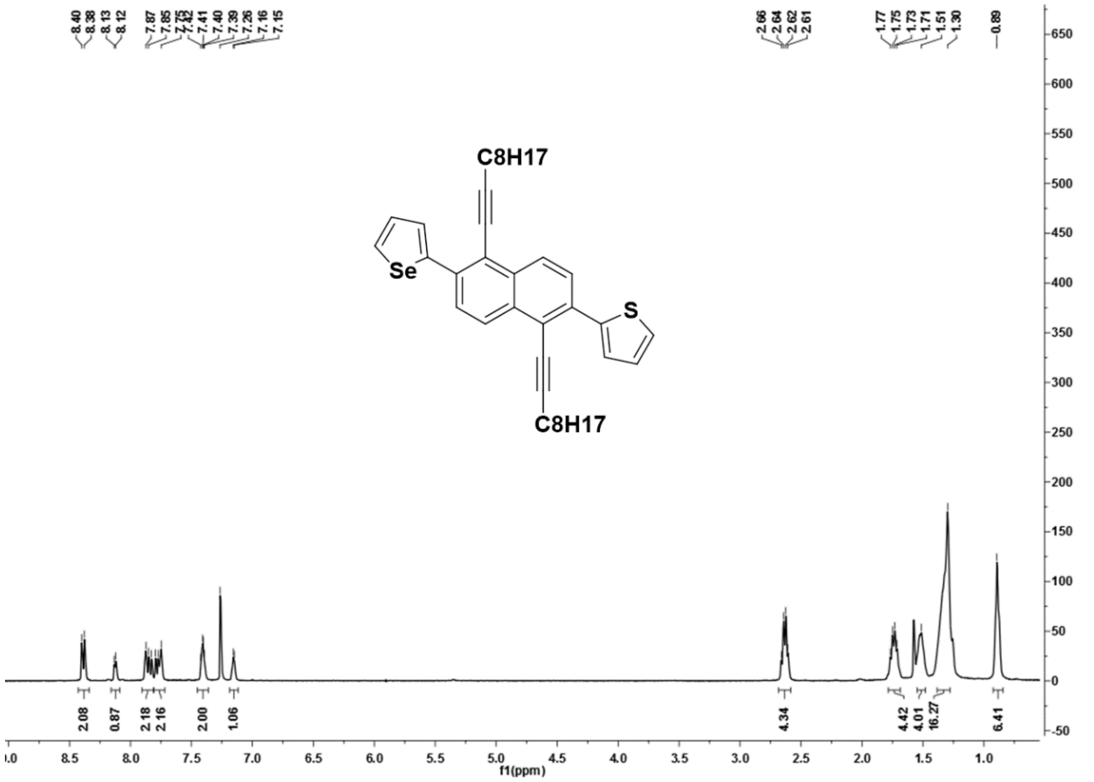


Fig. S15 $^{13}C\{^1H\}$ NMR spectrum of **5** in $CDCl_3$

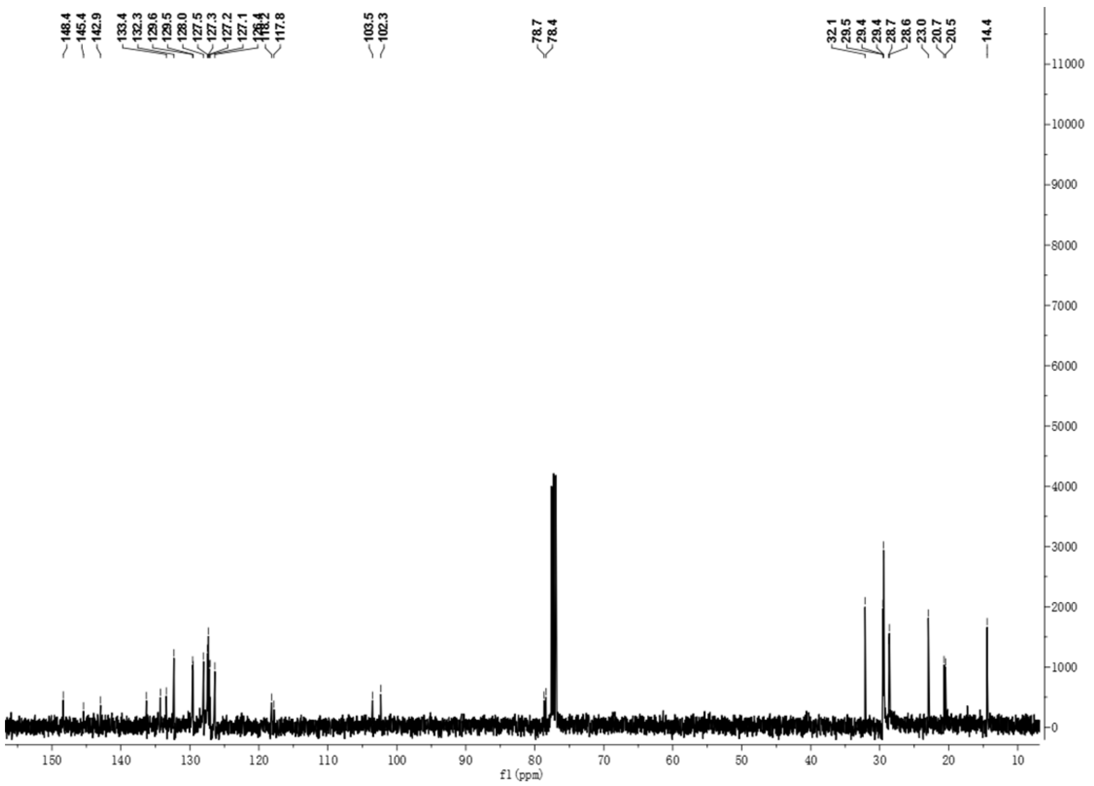


Fig. S16 ^{1}H NMR spectrum of **7** in THF-d_8.

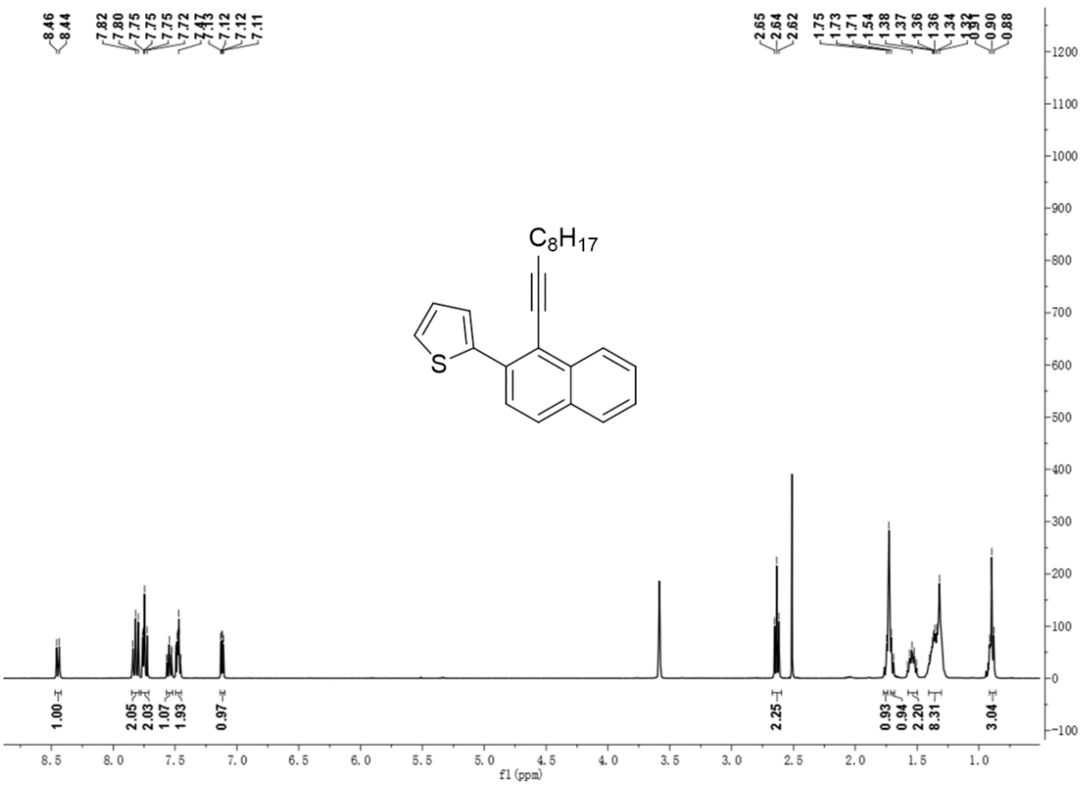


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in THF-d_8.

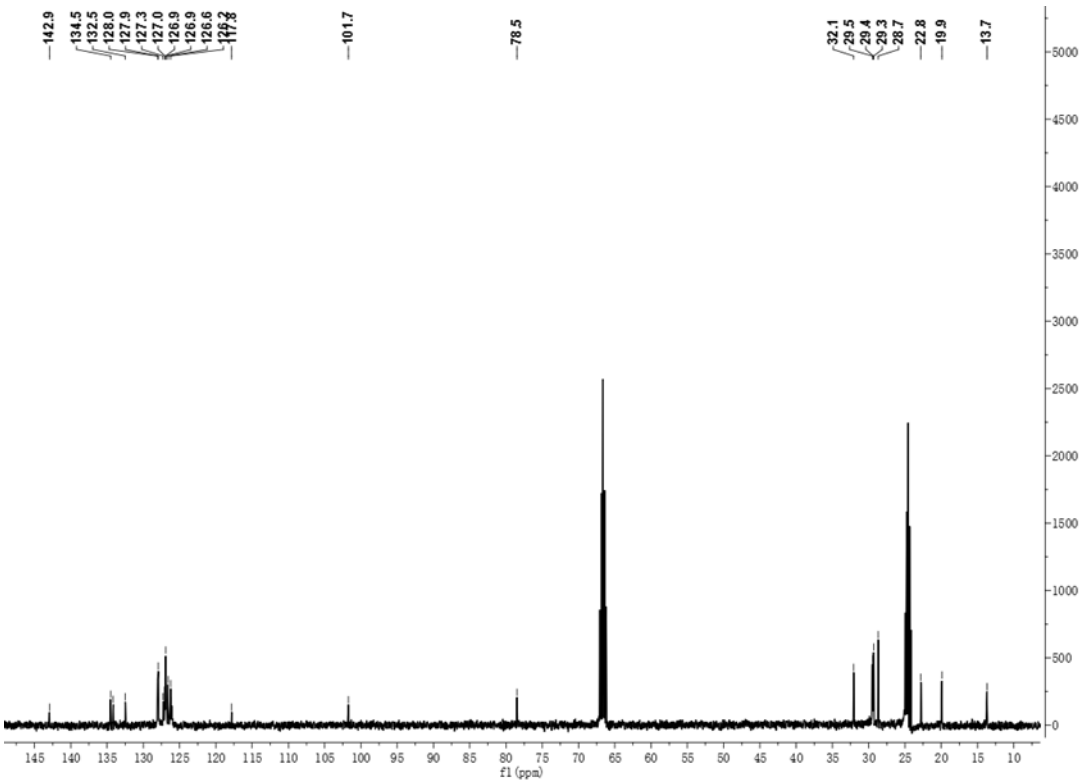


Fig. S18 ^{1}H NMR spectrum of **8** in THF-d_8.

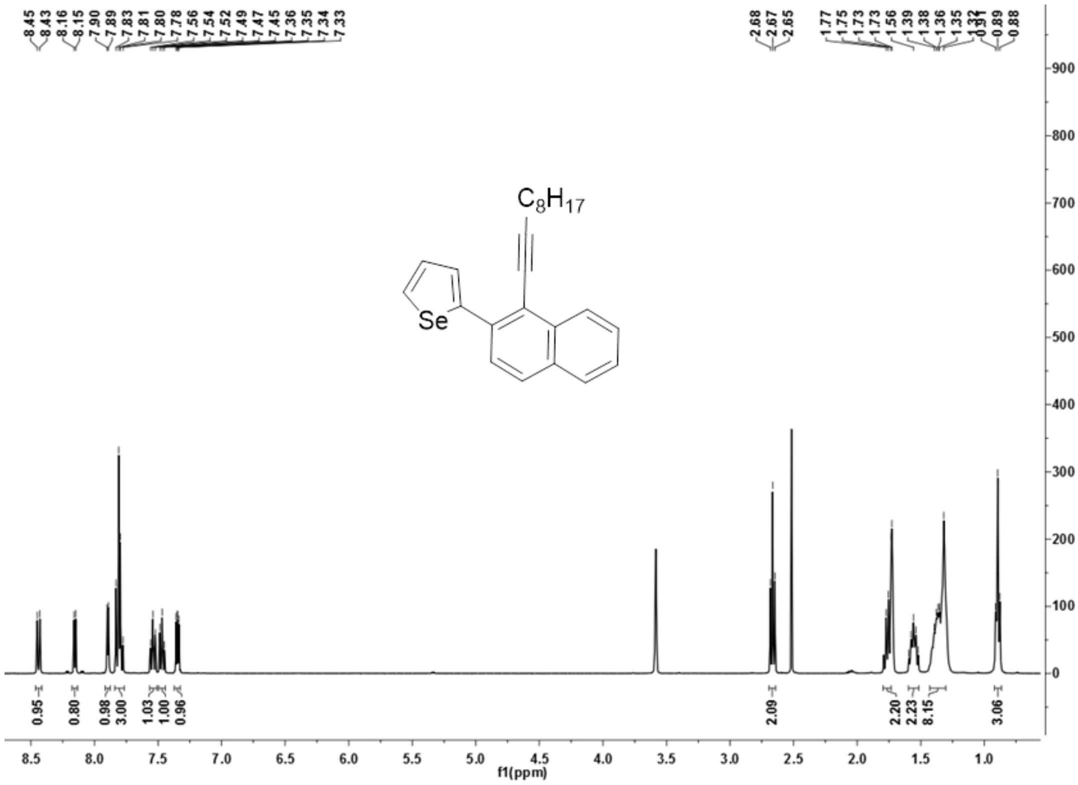


Fig. S19 ^{13}C{^{1}H} NMR spectrum of **8** in THF-d_8.

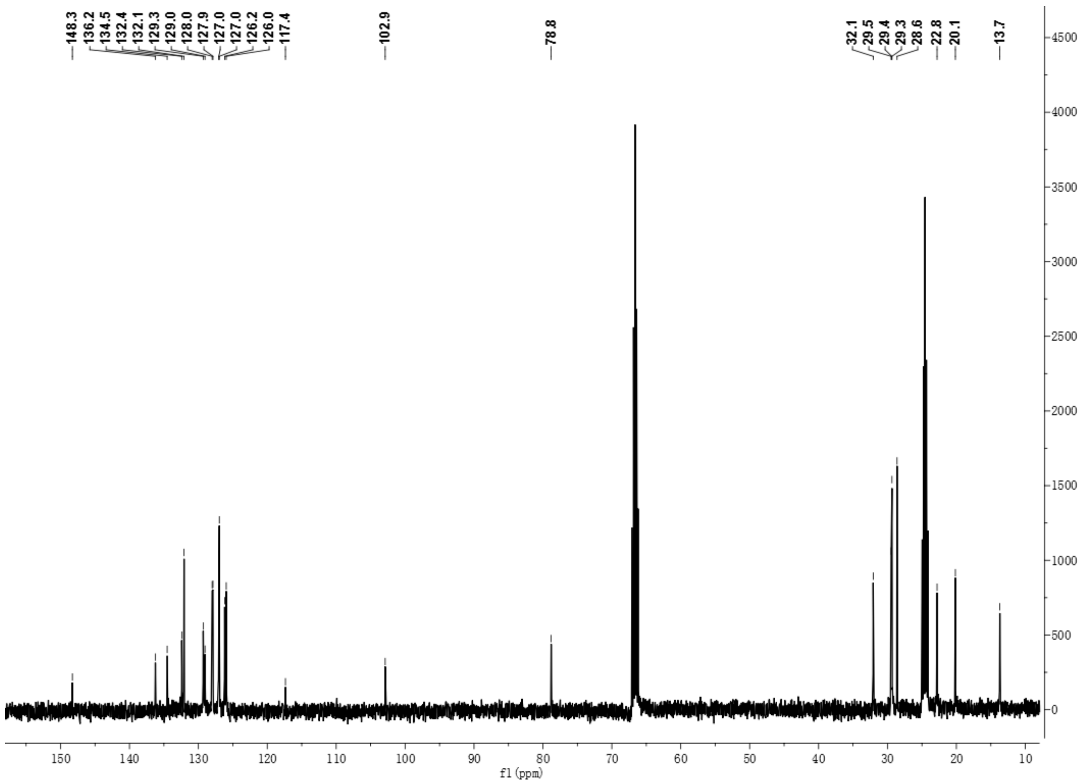


Fig. S20 ^{1}H NMR spectrum of **SS** in $CDCl_3$.

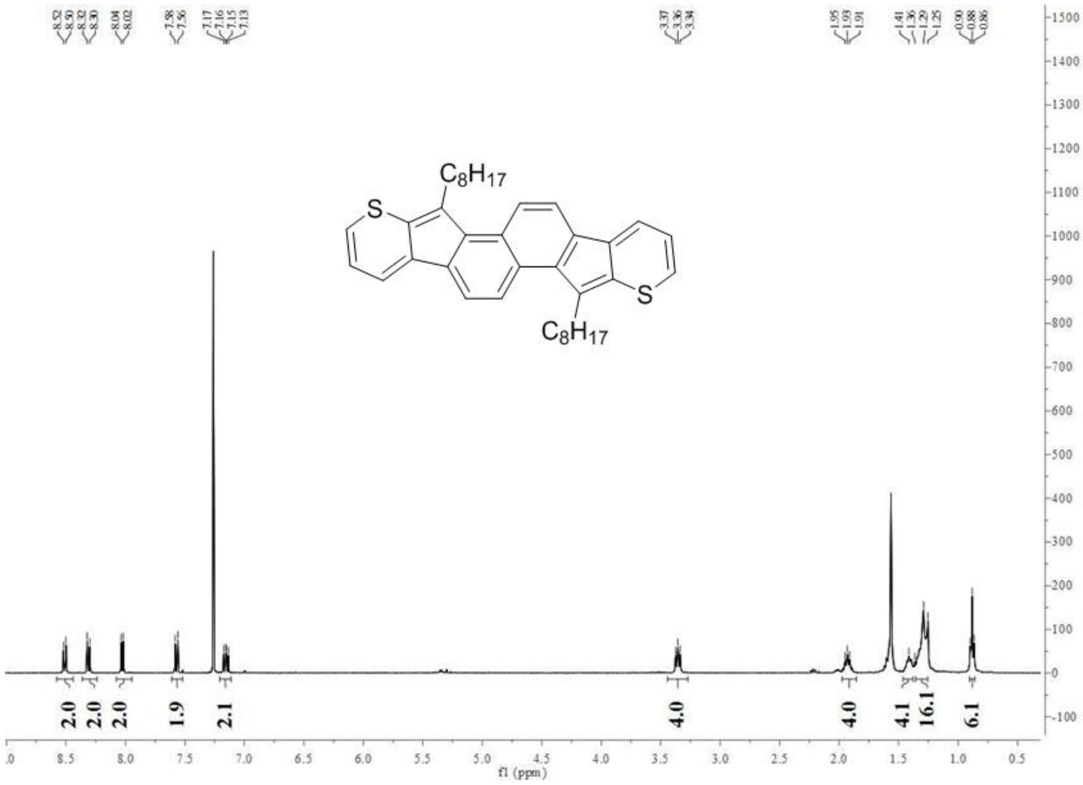


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of **SS** in $CDCl_3$.

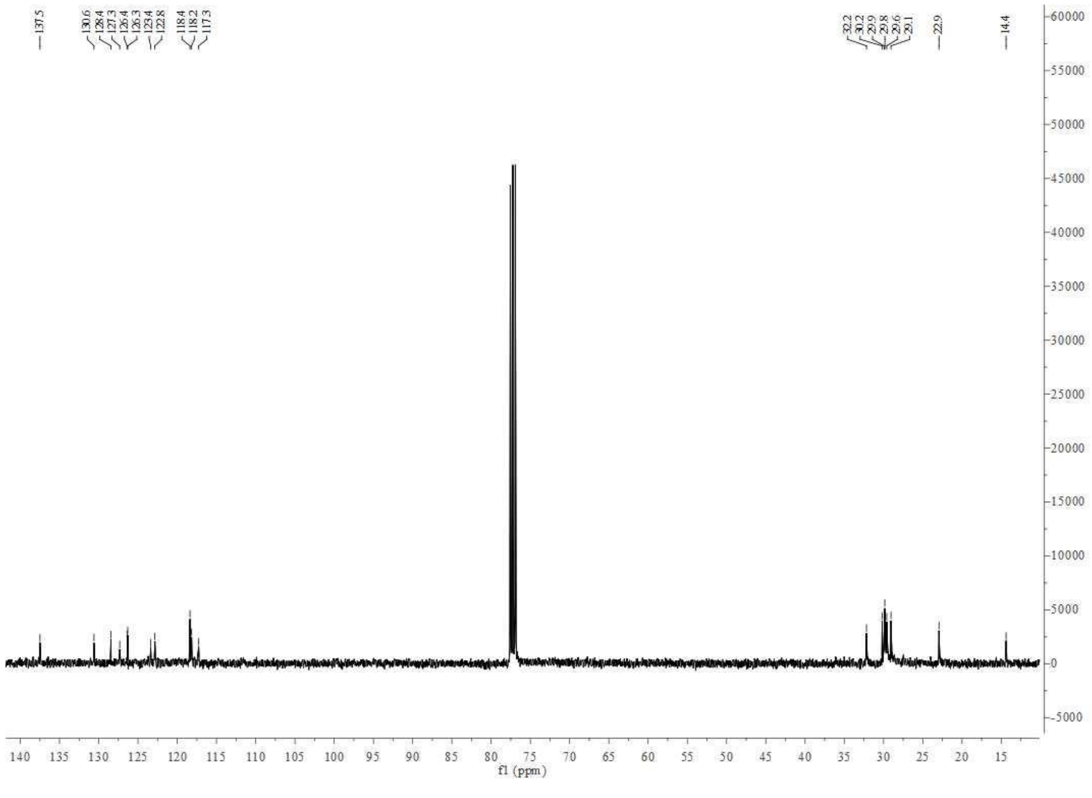


Fig. S22 ^{1}H NMR spectrum of **SeSe** in THF-d_8.

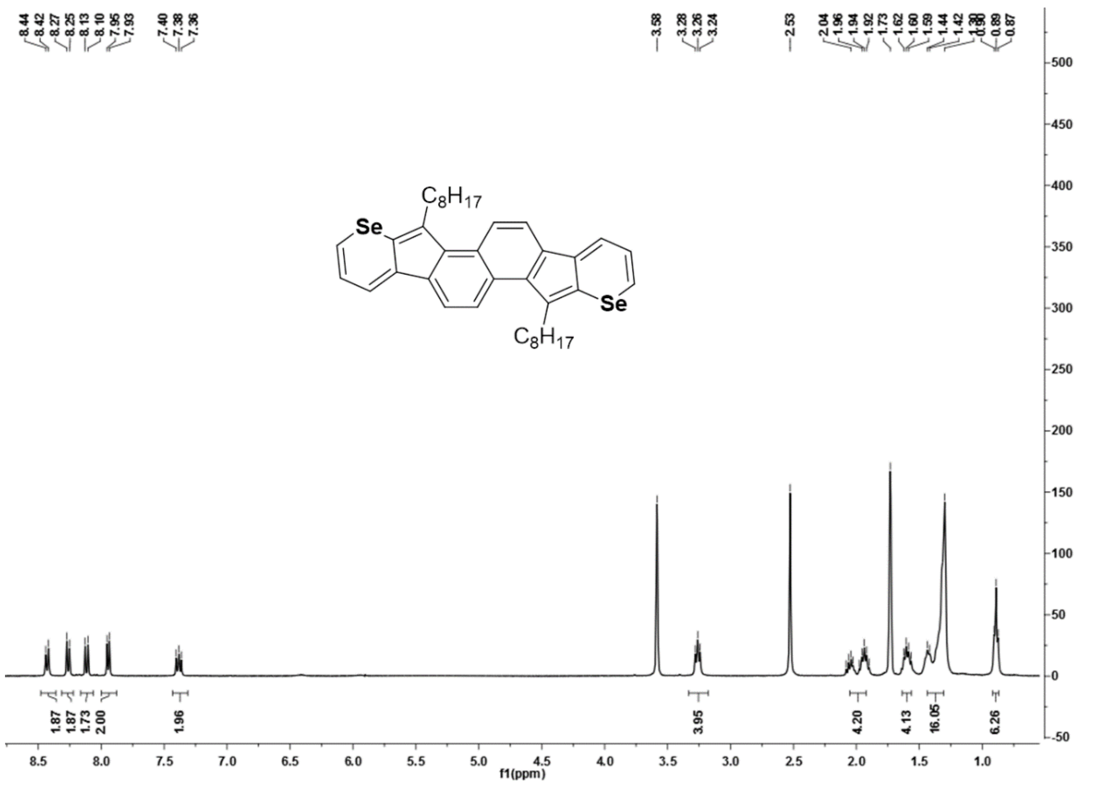


Fig. S23 $^{13}C\{^{1}H\}$ NMR spectrum of **SeSe** in THF-d_8.

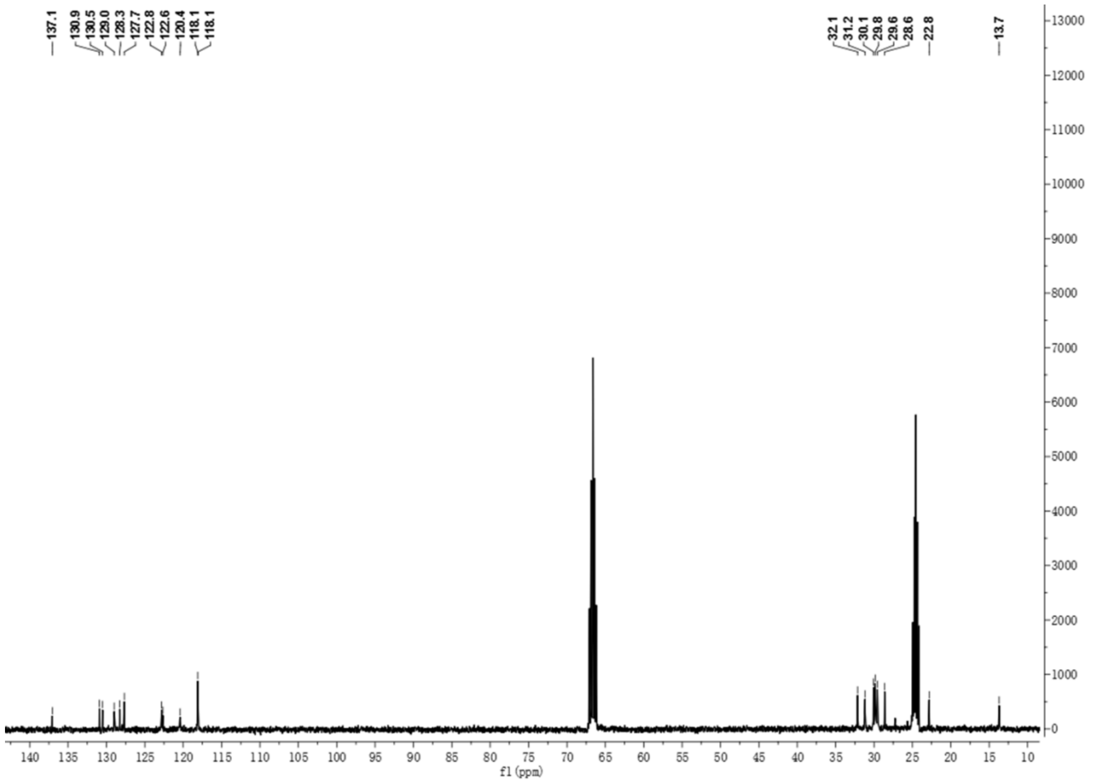


Fig. S24 ^{1}H NMR spectrum of **SSe** in THF-d_8.

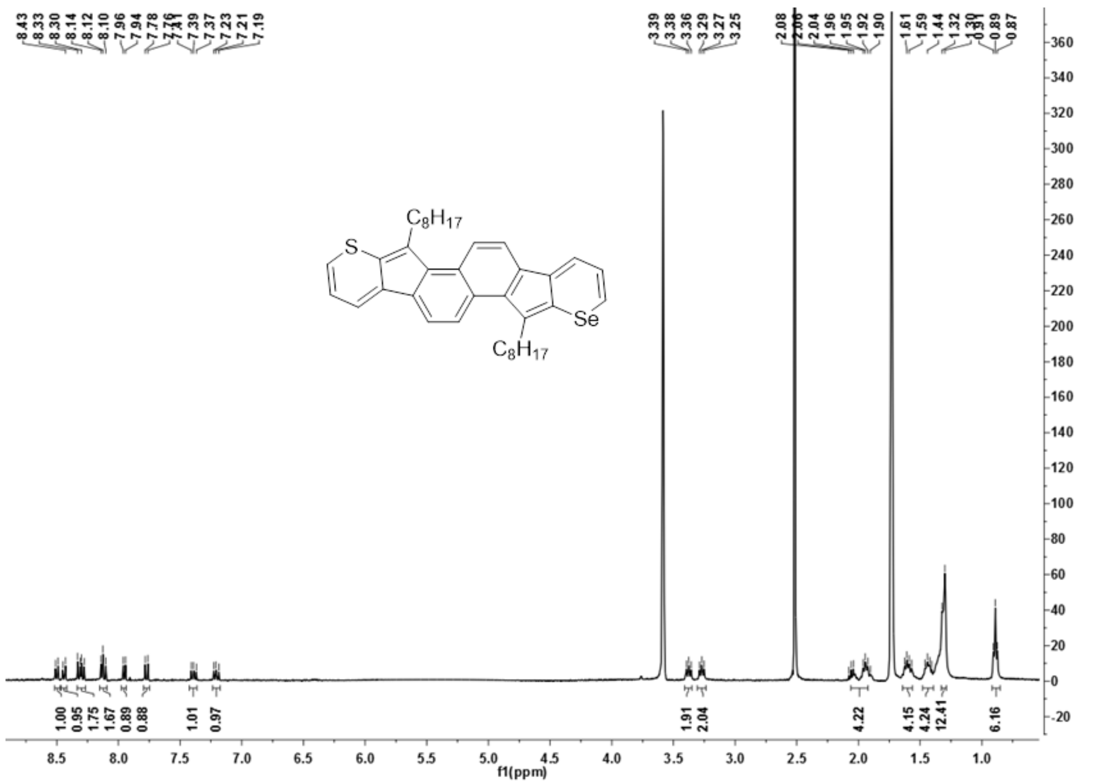


Fig. S25 ^{13}C{^{1}H} NMR spectrum of **SSe** in THF-d_8.

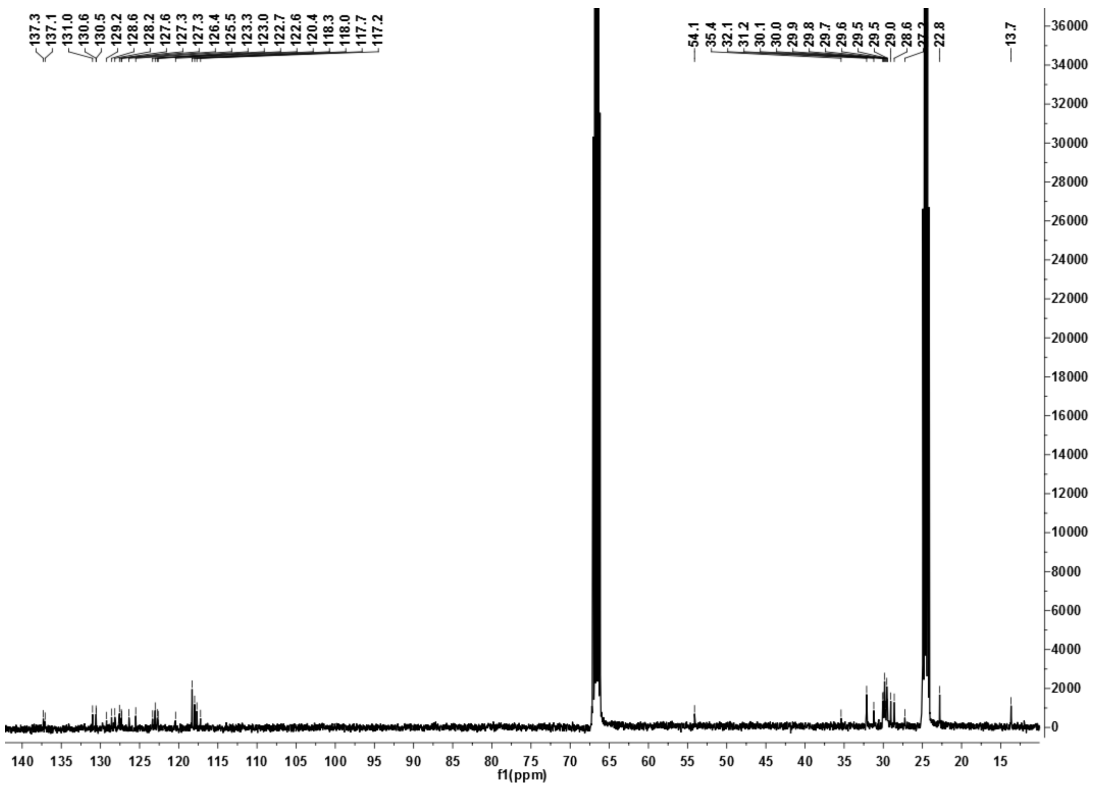


Fig. S26 ^{1}H NMR spectrum of **RS** in THF-d_8.

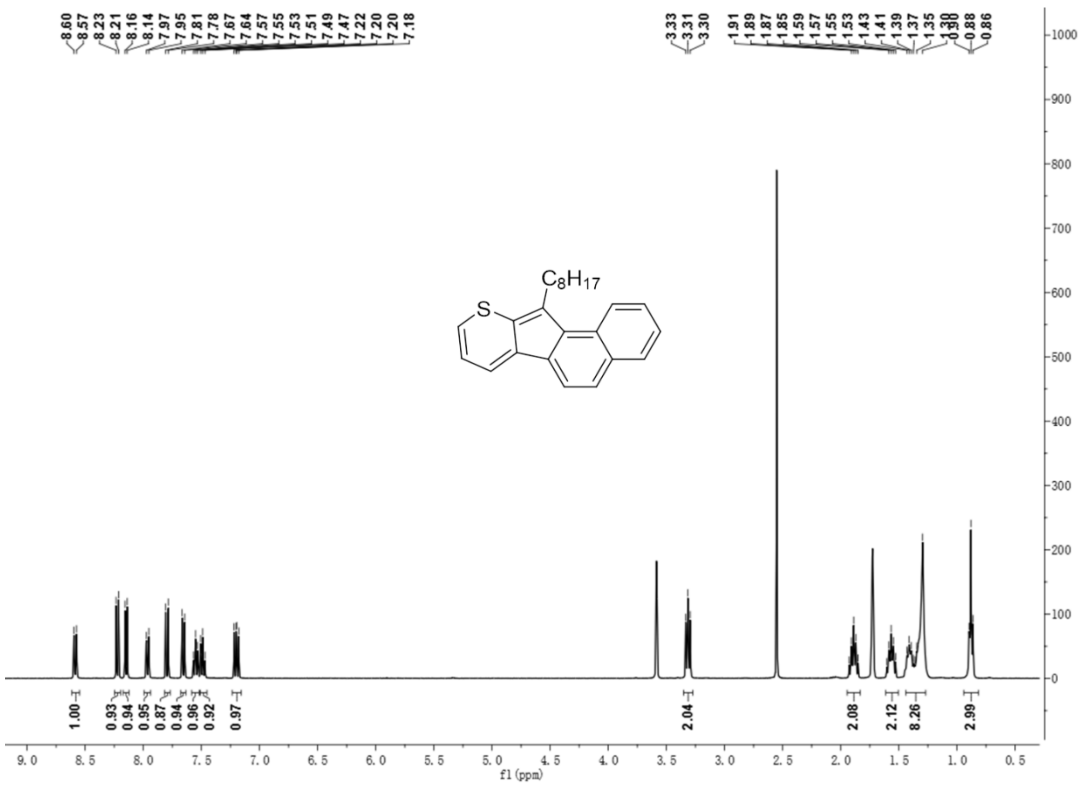


Fig. S27 $^{13}C\{^{1}H\}$ NMR spectrum of **RS** in THF-d_8.

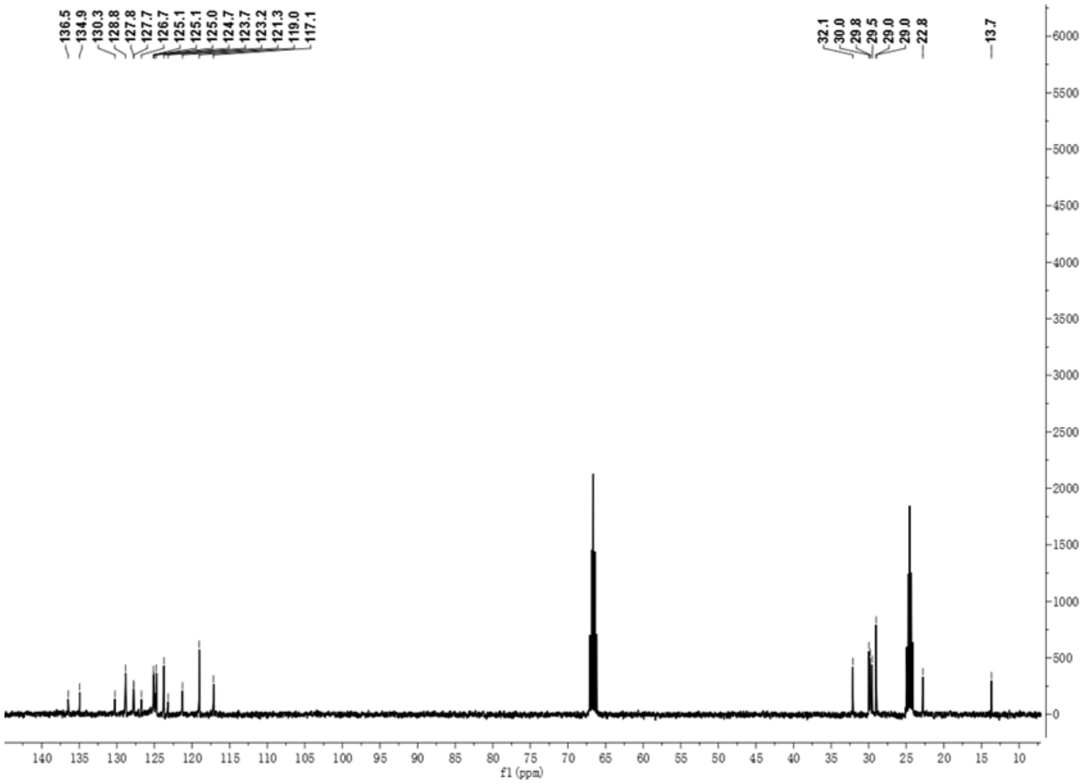


Fig. S28 ^{1}H NMR spectrum of **RSe** in THF-d_8.

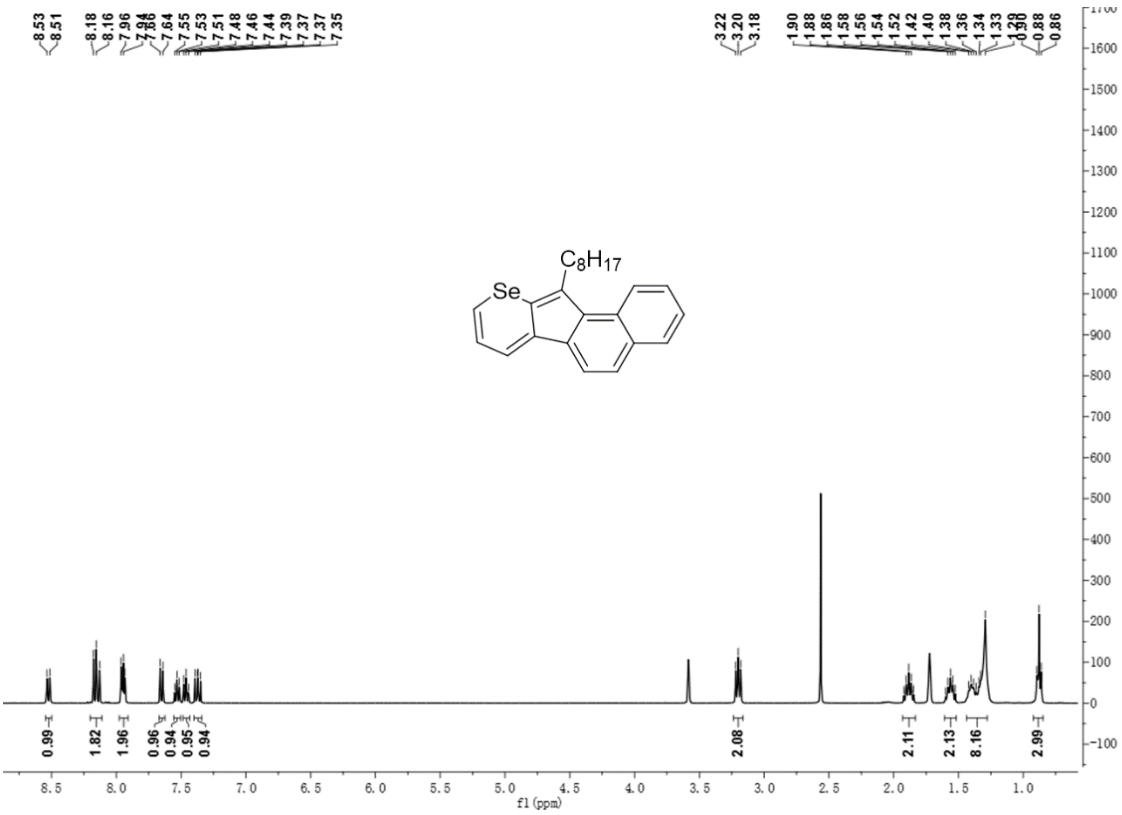
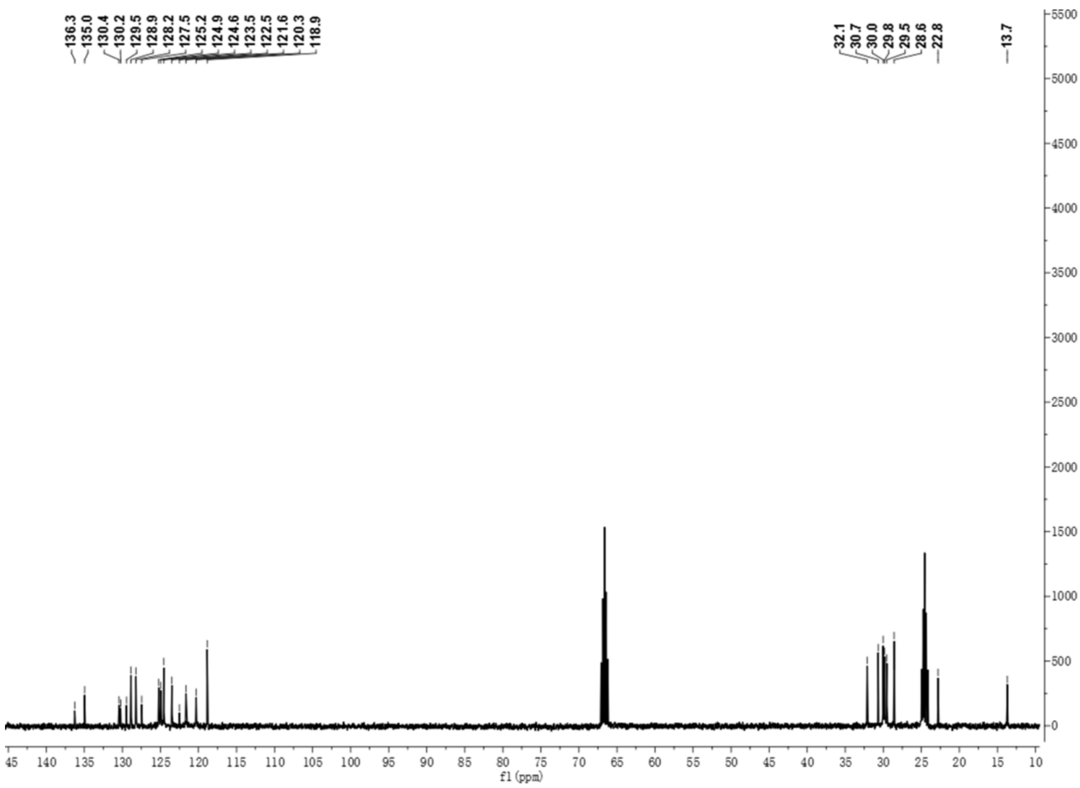


Fig. S29 ^{13}C{^{1}H} NMR spectrum of **RSe** in THF-d_8.



References.

S1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Al M. A. Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople. Gaussian 03, revision c.02. Gaussian, Inc., Wallingford, CT **2004**.

S2. S. Shinamura, I. Osaka, E. Miyazaki, A. Nakao, M. Yamagishi, J. Takeya and K. Takimiya, *J. Am. Chem. Soc.*, 2011, **133**, 5024.

S3. M. Weimar, R. C. da Costa, F. -H. Lee and M. J. Fuchter, *Org. Lett.*, 2013, **15**, 1706.