

Supporting Information for

Thiophene/Selenophene-Based Windmill-Shaped Triple

[6]Helicenes

Wan Xu, Jichang Wei, Kun Tang, Zhiying Ma, Jianwu Shi, Chunli Li* and Hua Wang*

Engineering Research Center for Nanomaterials, Henan University, Kaifeng, 475004, China

*Corresponding author: Chunli Li (Email: chunli79@126.com); Hua Wang (Email: hwang@henu.edu.cn).

Table of Contents

1. Experimental Section	S3
General procedures and materials.	S3
Synthesis of 3	S4
Synthesis of (TMS) ₂ - DTS	S4
Synthesis of 4b	S4
Synthesis of 5b	S5
Synthesis of 6a	S5
Synthesis of 6b	S6
Synthesis of 6c	S6
Synthesis of 6d	S6
Synthesis of <i>rac</i> - 1a	S7
Synthesis of <i>rac</i> - 1b	S7
Synthesis of <i>rac</i> - 1c	S8
Synthesis of <i>rac</i> - 1d	S8
2. NMR and HRMS Spectra	S8
NMR and HRMS spectra of 3	S8
NMR and HRMS spectra of (TMS) ₂ - DTS	S10
NMR and HRMS spectra of 4b	S11

NMR and HRMS spectra of 5b	S13
NMR and HRMS spectra of 6a	S14
NMR and HRMS spectra of 6b	S16
NMR and HRMS spectra of 6c	S17
NMR and HRMS spectra of 6d	S18
NMR and HRMS spectra of <i>rac-1a</i>	S19
NMR and HRMS spectra of <i>rac-1b</i>	S20
NMR and HRMS spectra of <i>rac-1c</i>	S22
NMR and HRMS spectra of <i>rac-1d</i>	S23
3. Quantum Calculation of <i>rac-1(a)–(d)</i>	S25
UV-vis spectra prediction and transition nature <i>rac-1(a)–(d)</i>	S25
4. Resolution of <i>rac-1c</i>	S27
HPLC trace of (+)- 1c , (–)- 1c , and <i>rac-1c</i>	S27
Racemization of (–)- 1c	S27
5. X-ray Crystallographic Data.....	S30
X-ray crystallographic data of <i>rac-1a</i>	S30
X-ray crystallographic data of <i>rac-1b</i>	S32
X-ray crystallographic data of <i>rac-1c</i>	S34
X-ray crystallographic data of <i>rac-1d</i>	S36
6. References.....	S41

1. Experimental Section

General Procedures and Materials

Ether and tetrahydrofuran (THF) for use on vacuum line were freshly distilled from sodium/benzophenone prior to use. *t*-BuLi (pentane) and *n*-BuLi (hexane) were obtained from Energy Chemical, and their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine.¹ Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of silica gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stopcock, were employed. All starting materials and reagents were commercially available.

¹H NMR and ¹³C NMR spectra were recorded on 300 or 400 or 600 MHz NMR instruments using CDCl₃ (δ H (7.26 ppm) and CDCl₃ δ C (77.00 ppm)) as solvent. IR spectra were obtained using an FT-IR instrument. HRMS analysis was carried out on a mass spectrometer equipped with EI⁺, DART-FTICR and DART-Positive. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. Ultraviolet-visible (UV-vis) absorption spectra were recorded on PE Lambda 950 equipment. The steady-state photoluminescence (PL) spectra and the fluorescence measurements for all samples were recorded on a JY HORIBA FluoroLog-3. CD spectrum was recorded on Aviv Biomedical Inc Model 420SF. Cyclic voltammetry (CV) behaviors were recorded on IM6eX equipment with three electrode cell in the solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in CH₂Cl₂. Platinum electrode (0.6 cm²), Pt wire and Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. The X-ray crystallographic analyses were performed using crystals of compounds *rac*-**1(a)**–**(d)** with sizes of 0.48 × 0.23 × 0.22, 0.17 × 0.09 × 0.04, 0.1611 × 0.1222 × 0.0669 and 0.1525 × 0.0577 × 0.0404 mm³, respectively. The intensity data were collected with the ω scan mode (296, 298, 293, 293 K) on a diffractometer with CCD detector using Cu K α radiation (λ = 1.54178, 1.54184 Å). The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using SADABS program.² The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares.³ Further details were in the deposited CIF files. Slow evaporation of solutions of *rac*-**1(a)**–**(d)** in CHCl₃/CH₃OH (3/1, 2/1, 3/2, 1/1, v/v) were

employed for growing single crystals. The fluorescence quantum yields (Φ_F) of *rac*-**1(a)–(d)** were characterized in dichloromethane with quinine sulfate in 0.1 N H₂SO₄ as the control. The predicted absorption spectra were computed within the TD-DFT/PCM approaches based on B3LYP/6-31G* level. HOMO and LUMO distributions and isomerization barriers of *rac*-**1(a)–(d)** (i.e., the TMS replaced by hydrogen atom) were at the B3LYP/6-31G* level.

Synthesis of 2,7-Bis(trimethylsilyl)-[1,2]diselenino[3,4-b:6,5-b']dithiophene (3)

n-BuLi (2.38 M in hexane, 6.12 mL, 14.56 mmol, 2.05 equiv) was added dropwise into a solution of **2** (3.10 g, 6.62 mmol) in Et₂O (100 mL) at –78 °C, and then the reaction mixture was kept for 2 h. Dry Se (metals basis) (2.61 g, 33.1 mmol, 5.0 equiv) was added at –78 °C; the reaction mixture was kept at –78 °C for 2 h and –55 °C for 2 h, and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at –78 °C, extracted with dichloromethane (3 × 25 mL), and then washed with water (3 × 30 mL). After drying over anhydrous MgSO₄, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) as eluent to yield **3** (1.02 g, 33%) as a red solid. Mp: 137–138 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (s, 2H), 0.35 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 142.2, 132.3, 119.2, –0.1. HRMS (DART-Positive) *m/z* [M + H]⁺ calcd for C₁₄H₂₁S₂Se₂Si₂ 468.8948; found 468.8950. IR (KBr): 3050, 2947, 1252, 986, 830 cm^{–1}.

Synthesis of 2,5-Bis(trimethylsilyl)dithieno[2,3-b:3',2'-d]selenophene((TMS)₂-DTS)

Compound **3** (300 mg, 0.64 mmol) and Cu nanopowder (200 mg, 3.22 mmol, 5.0 equiv) were heated to 145 °C without use of any solvent for 0.5 h. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) as eluent to yield (TMS)₂-**DTS** (120.7 mg, 50%) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.51 (s, 2H), 0.36 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 145.6, 141.6, 141.2, 126.4, 0.0. HRMS (DART-Positive) *m/z* [M + H]⁺ calcd for C₁₄H₂₁SeS₂Si₂ 388.9783; found 388.9785. IR (KBr): 3061, 2978, 1251, 963, 845 cm^{–1}.

Synthesis of 5-Bromo-2-(trimethylsilyl)dithieno[2,3-b:3',2'-d]selenophene (4b)

(TMS)₂-**DTS** (605 mg, 1.56 mmol) was dissolved in CHCl₃ (20 mL), and NBS (333 mg, 1.87 mmol, 1.2 equiv) was dissolved in 16 mL of HOAc/CHCl₃ (v/v = 1/8) and added dropwise under good stirring at 0 °C in an ice-water bath. After stirring for 2 h, the reaction mixture was quenched with H₂O, extracted with dichloromethane (3 × 10 mL), and then washed with saturated NaHCO₃ (20

mL) and water (2 × 20 mL). The organic layer was dried over anhydrous MgSO₄. After the solvent was removed under vacuum, the residue was washed with 3 × 5 mL hexane to yield **4b** (326.2 mg, 53%) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.41 (s, 1H), 0.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 142.0, 140.7, 139.0, 134.7, 126.2, 123.5, 113.2, -0.1. HRMS (EI⁺) *m/z* [M⁺] calcd for C₁₁H₁₁BrS₂⁷⁴SeSi 387.8480; found 387.8478. IR (KBr): 3084, 2963, 1259, 910, 842 cm⁻¹.

Synthesis of 5-(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]selenophene-2-carbaldehyde (5b)

n-BuLi (2.45 M in hexane, 0.98 mL, 2.40 mmol, 1.05 equiv) was added dropwise to **4b** (900 mg, 2.28 mmol) in THF (30 mL) at -78 °C. After 2 h at -78 °C, DMF (0.36 mL, 4.57 mmol, 2.0 equiv) was added at -78 °C and kept 0.5 h, and then the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H₂O and extracted with dichloromethane (3 × 15 mL). The organic layer was washed with saturated NaHCO₃ (20 mL) and water (2 × 20 mL) and then dried over anhydrous MgSO₄. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) Hexane/CH₂Cl₂ (v/v = 2/1) as eluent to yield **5b** (243 mg, 31%) as a brown solid. Mp: 124–125 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 8.01 (s, 1H), 7.54 (s, 1H), 0.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 182.3, 147.7, 147.5, 147.2, 141.9, 141.6, 140.0, 128.7, 126.1, -0.1. HRMS (DART-FTICR) *m/z* [M + H]⁺ calcd for C₁₂H₁₃OS₂SeSi 344.9337; found 344.9337. IR (KBr): 3091, 2938, 1656, 993, 849 cm⁻¹.

1,3,5-tris(2-(5-(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]thiophene-2-yl)vinyl)benzene (6a)

n-BuLi (2.5 M in hexane, 0.29 mL, 0.74 mmol, 3.5 equiv) was added dropwise into the phosphonium salt (241 mg, 0.21 mmol, 1.0 equiv) in THF at -78 °C for 2 h, then a solution of 5-(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]thiophene-2-carbaldehyde **5a** (200 mg, 0.67 mmol, 3.2 equiv) in dry THF (5 mL) was added at -78 °C. After keeping stirring for 2 h, the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction was quenched with water at -78 °C, extracted with dichloromethane (3 × 15 mL), washed with H₂O (3 × 25 mL), and then dried over anhydrous MgSO₄. After the solvent was removed in vacuum, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) Hexane/CH₂Cl₂(v/v = 1/1) as eluent to give 1,3,5-tris(2-(5-(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]thiophene-2-yl)vinyl)-benzene **6a** (100.3 mg, 50%) as a yellow solid. Mp: 157–159 °C. ¹H NMR (400 MHz, CDCl₃) δ

7.45 (s, 6H), 7.32 (t, $J = 8.0$ Hz, 6H), 6.91 (d, $J = 16.0$ Hz, 3H), 0.40 (s, 27H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 144.6, 143.7, 140.6, 138.4, 137.8, 137.5, 127.4, 124.9, 123.5, 123.0, 118.1, -0.1 . HRMS (MALDI MS EI^+) m/z [M^+] calcd for $\text{C}_{45}\text{H}_{42}\text{S}_9\text{Si}_3$ 954.0081; found 954.0075. IR (KBr) 3017, 2955, 1259, 941, 833 cm^{-1} .

1,3,5-tris(2-(5-(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]selenophene-2-yl)vinyl)benzene (6b)

Compound **6b** was synthesized according to the procedure for making **6a**. From the reaction on the 200 mg scale of **5b**, 27.9 mg (14%) of **6b** was obtained as yellow solid. Mp: >300 °C. ^1H NMR (400 MHz, CDCl_3) (for a mixture of *cis* and *trans* isomers of **6b**) δ 7.51 (d, $J = 8.0$ Hz), 7.49 (d, $J = 6.0$ Hz), 7.45 (d, $J = 1.6$ Hz), 7.39 (d, $J = 7.2$ Hz), 7.33(s), 7.27(s), 6.97 (s), 6.93 (t, $J = 8.0$ Hz), 6.83 (d, $J = 8.0$ Hz), 6.63 (d, $J = 12.0$ Hz), 0.39 (s), 0.38 (s), 0.33 (s); the ratio of integral areas of the peaks are 1 : 1 : 0.5 : 1.5 : 0.5 : 0.5 : 0.5 : 1 : 0.3 : 0.3 : 7 : 3 : 1. HRMS (AP-MALDI- Positive) m/z [M^+] calcd for $\text{C}_{45}\text{H}_{42}\text{S}_6^{80}\text{Se}_3\text{Si}_3$ 1097.8409; found 1097.8435. IR (KBr) 3029, 2954, 1259, 941, 834 cm^{-1} .

1,3,5-tris(2-(5-(trimethylsilyl)diseleno[2,3-*b*:3',2'-*d*]thiophene-2-yl)vinyl)benzene (6c)

Compound **6c** was synthesized according to the procedure for making **6a**. From the reaction on the 200 mg scale of **5c**, 21.7 mg (11%) of **6c** was obtained as yellow solid. Mp: 258–260 °C. ^1H NMR (400 MHz, CDCl_3) (for a mixture of *cis* and *trans* isomers of **6c**) δ 7.74 (s), 7.71 (d, $J = 4.4$ Hz), 7.56 (d, $J = 6.0$ Hz), 7.49 (d, $J = 3.6$ Hz), 7.43 (d, $J = 11.2$ Hz), 7.37 (d, $J = 7.2$ Hz), 6.93 (d, $J = 11.6$ Hz), 6.83 (d, $J = 6.0$ Hz), 6.79 (d, $J = 6.0$ Hz), 6.66 (d, $J = 10.8$ Hz), 0.39 (s), 0.38 (s), 0.35 (s); the ratio of integral areas of the peaks are 1 : 0.5 : 1 : 1 : 1 : 1 : 0.15 : 0.85 : 0.85 : 0.15 : 9 : 3 : 3. HRMS (AP-MALDI-Positive) m/z [M^+] calcd for $\text{C}_{45}\text{H}_{42}\text{S}_3^{80}\text{Se}_6\text{Si}_3$ 1241.6742; found 1241.6768. IR (KBr) 3015, 2950, 1245, 908, 833 cm^{-1} .

1,3,5-tris(2-(5-(trimethylsilyl)diseleno[2,3-*b*:3',2'-*d*]selenophene-2-yl)vinyl)benzene (6d)

Compound **6d** was synthesized according to the procedure for making **6a**. From the reaction on the 200 mg scale of **5d**, 19.7 mg (10%) of **6d** was obtained as yellow solid. Mp: 280–282 °C. ^1H NMR (400 MHz, CDCl_3) (for a mixture of *cis* and *trans* isomers of **6d**) δ 7.76 (s), 7.74 (d, $J = 4.0$ Hz), 7.59 (d, $J = 6.0$ Hz), 7.53 (d, $J = 11.6$ Hz), 7.48 (s), 7.43 (d, $J = 10.4$ Hz), 7.38 (d, $J = 4.4$ Hz), 7.33(s), 6.93 (d, $J = 11.6$ Hz), 6.83 (d, $J = 4.8$ Hz), 6.79 (d, $J = 4.4$ Hz), 6.65 (d, $J = 11.6$ Hz), 0.39 (s), 0.37 (s), 0.35 (s); the ratio of integral areas of the peaks are 1 : 1 : 1 : 1 : 1 : 1 : 0.7 : 0.3 : 0.3 :

0.7 : 0.7 : 0.3 : 9 : 6 : 3. HRMS (AP-MALDI-Positive) m/z [M^+] calcd for $C_{45}H_{42}^{80}Se_9Si_3$ 1385.5076; found 1385.5099. IR (KBr) 3010, 2950, 1245, 911, 832 cm^{-1} .

1,3,5-tris(trimethylsilyl)benzo[1,2-b:3,4-b']-tris(dithieno[2,3-b:3',2'-d]thiophene)benzene (rac-1a)

Iodine (22 mg, 0.088 mmol, 3.0 equiv) and 2-methyloxirane (0.1 mL) were added into solution of **6a** (28 mg, 0.029 mmol) in dry toluene (25 mL). The reaction solution was irradiated with a 450 W unfiltered Hg medium pressure lamp. The reaction was monitored by thin layer chromatography every hour, and irradiation was stopped when the **6a** was consumed. The reaction was quenched with saturated $Na_2S_2O_3$ (10 mL). The reaction mixture was extracted with dichloromethane (3×10 mL) and washed with H_2O (3×10 mL) and then dried over anhydrous $MgSO_4$. After the solvent was removed in vacuum, the crude product was purified by PTLC with petroleum ether (60–90 °C) Hexane/ CH_2Cl_2 (v/v = 2/1) as developer to yield **rac-1a** (10.0 mg, 35%) as a light yellow solid. Mp: 258–260 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.8 Hz, 3H), 7.77 (d, J = 8.8 Hz, 3H), 6.53 (s, 3H), 0.10 (s, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 143.0, 142.0, 141.6, 141.6, 135.1, 130.2, 127.6, 127.5, 127.2, 126.6, 119.2, –0.3. HRMS (MALDI MS EI^+) m/z [M^+] calcd for $C_{45}H_{36}S_9Si_3$ 947.9611, found 947.9606. IR (KBr) 3074, 2953, 2920, 1253, 979, 838 cm^{-1} .

1,3,5-tris(trimethylsilyl)benzo[1,2-b:3,4-b']-tris(dithieno[2,3-b:3',2'-d]selenophene)benzene (rac-1b)

Rac-1b was synthesized according to the procedure for making **rac-1a**. From the reaction on the 32.5 mg scale of **6b**, 6.5 mg (20%) of **rac-1b** was obtained as yellow solid. Mp: > 300 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.8 Hz, 3H), 7.72 (d, J = 8.4 Hz, 3H), 6.51 (s, 3H), 0.02 (s, 27H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.5, 142.4, 140.5, 140.2, 136.7, 131.8, 128.3, 127.9, 127.6, 126.9, 118.8, –0.4. HRMS (AP-MALDI-Positive) m/z [M^+] calcd for $C_{45}H_{36}S_6Se_3Si_3$ 1091.7049; found 1091.7936. IR (KBr) 3061, 2963, 1265, 970, 834 cm^{-1} .

1,3,5-tris(trimethylsilyl)benzo[1,2-b:3,4-b']-tris(diseleno[2,3-b:3',2'-d]thiophene)benzene (rac-1c)

Rac-1c was synthesized according to the procedure for making **rac-1a**. From the reaction on the 35.5 mg scale of **6c**, 3.5 mg (10%) of **rac-1c** was obtained as yellow solid. Mp: 290–292 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 3H), 7.69 (d, J = 8.8 Hz, 3H), 6.68 (s, 3H), –0.05

(s, 27H). ^{13}C NMR (150 MHz, CDCl_3) δ 147.2, 145.4, 144.7, 142.8, 139.3, 139.2, 132.7, 129.4, 128.8, 128.7, 126.6, 122.0, -0.2. HRMS (DART-Positive) m/z [M^+] calcd for $\text{C}_{45}\text{H}_{36}\text{S}_3\text{Se}_6\text{Si}_3$ 1235.6278; found 1235.6322. IR (KBr) 3080, 2957, 1251, 944, 833 cm^{-1} .

1,3,5-tris(trimethylsilyl)benzo[1,2-b:3,4-b']-tris(diseleno[2,3-b:3',2'-d]selenophene)benzene
(*rac-1d*)

Rac-1d was synthesized according to the procedure for making *rac-1a*. From the reaction on the 37.3 mg scale of **6d**, 3.0 mg (8%) of *rac-1d* was obtained as yellow solid. Mp: >300 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 3H), 7.65 (d, $J = 8.4$ Hz, 3H), 6.71 (s, 3H), -0.16 (s, 27H). ^{13}C NMR (150 MHz, CDCl_3) δ 148.4, 146.9, 145.8, 141.2, 141.2, 138.6, 133.9, 130.5, 128.9, 128.4, 126.5, 121.6, -0.4. HRMS (DART-Positive) m/z [M^+] calcd for $\text{C}_{45}\text{H}_{36}\text{Se}_9\text{Si}_3$ 1379.4612; found 1379.4645. IR (KBr) 3070, 2950, 1251, 935, 833 cm^{-1} .

2. NMR and HRMS Spectra

NMR and HRMS spectra of **3**

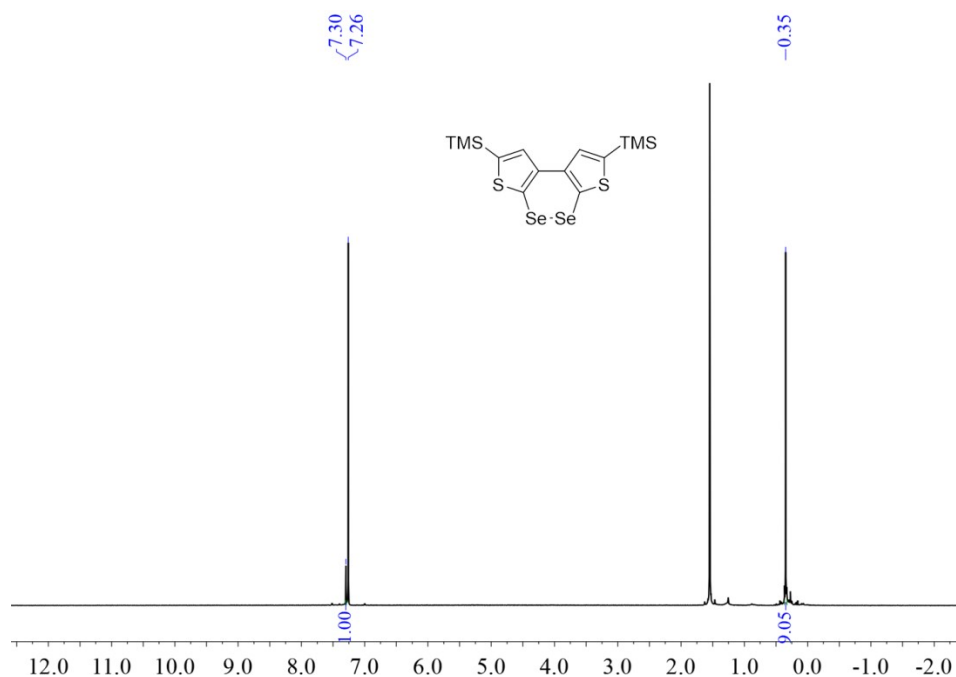


Fig. S1. ^1H NMR (400 MHz, CDCl_3) spectrum of **3**

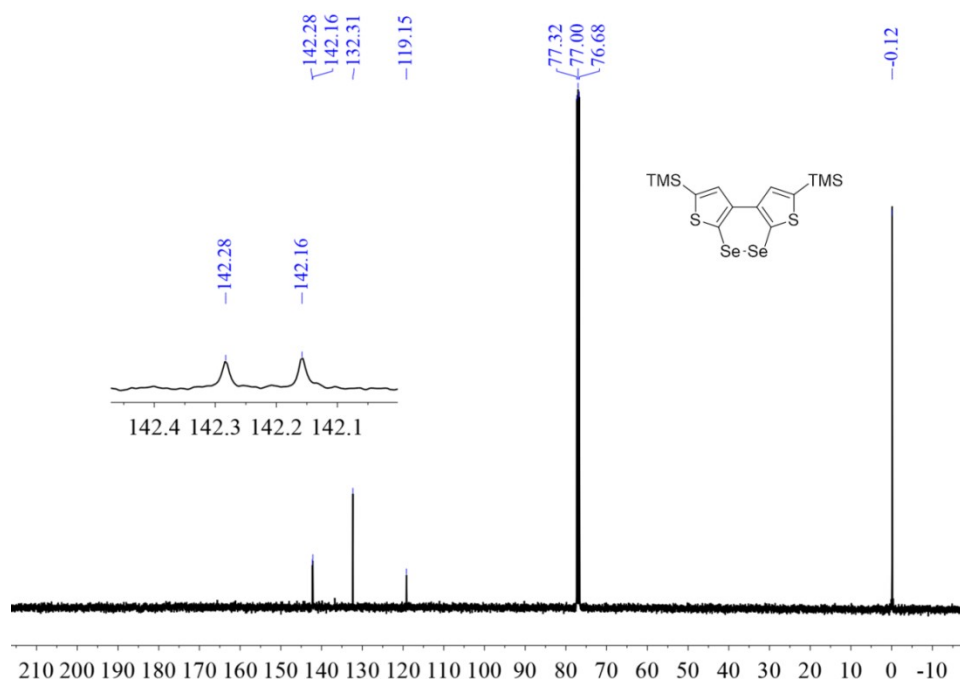


Fig. S2. ^{13}C NMR (100 MHz, CDCl_3) spectra of **3**

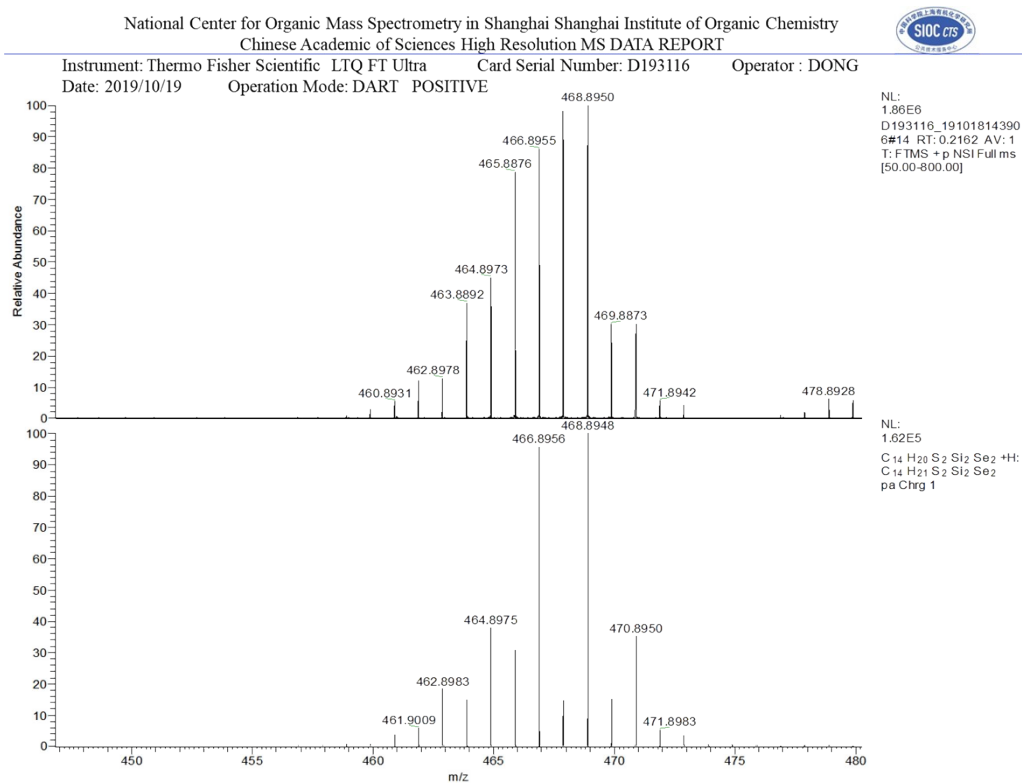


Fig. S3. HRMS spectra of **3**

NMR and HRMS spectra of ((TMS)₂-DTS)

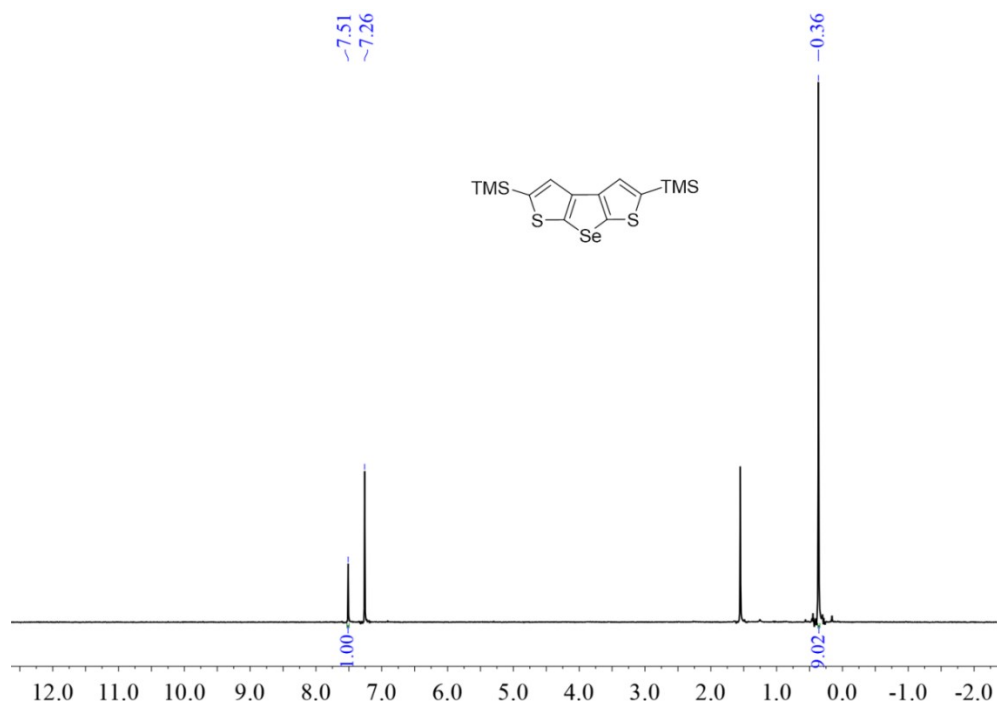


Fig. S4. ¹H NMR (300 MHz, CDCl₃) spectrum of ((TMS)₂-DTS)

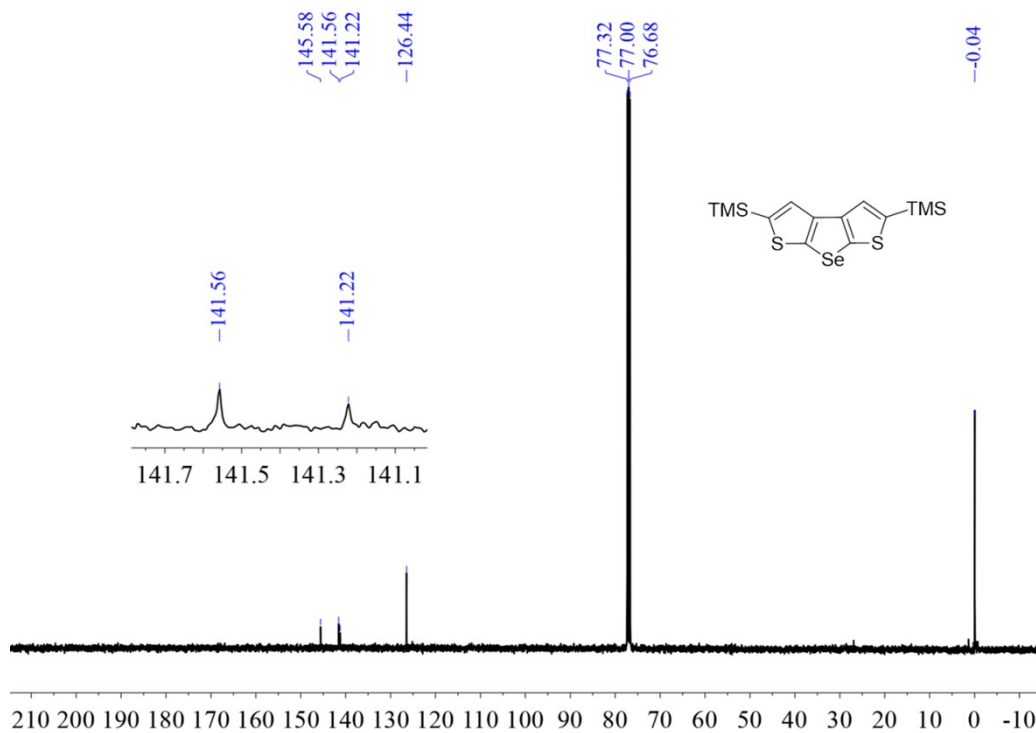


Fig. S5. ¹³C NMR (100 MHz, CDCl₃) spectra of ((TMS)₂-DTS)

Instrument: Thermo Fisher Scientific LTQ FT Ultra Card Serial Number: D193118 Operator: DONG
Date: 2019/10/19 Operation Mode: DART POSITIVE

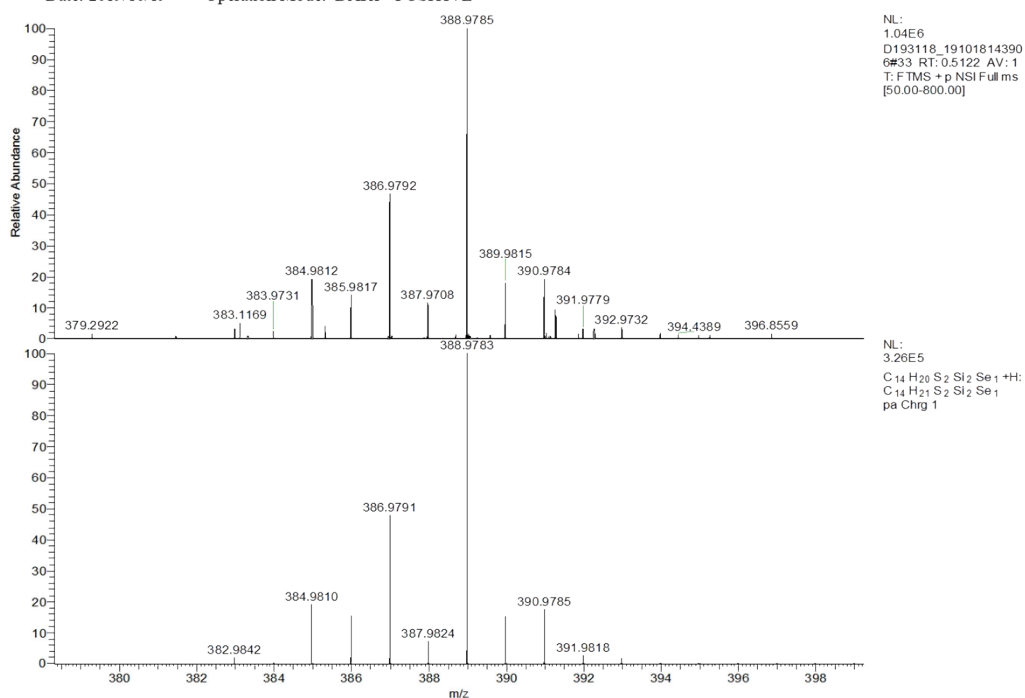


Fig. S6. HRMS spectra of ((TMS)₂-DTS)

NMR and HRMS spectra of 4b

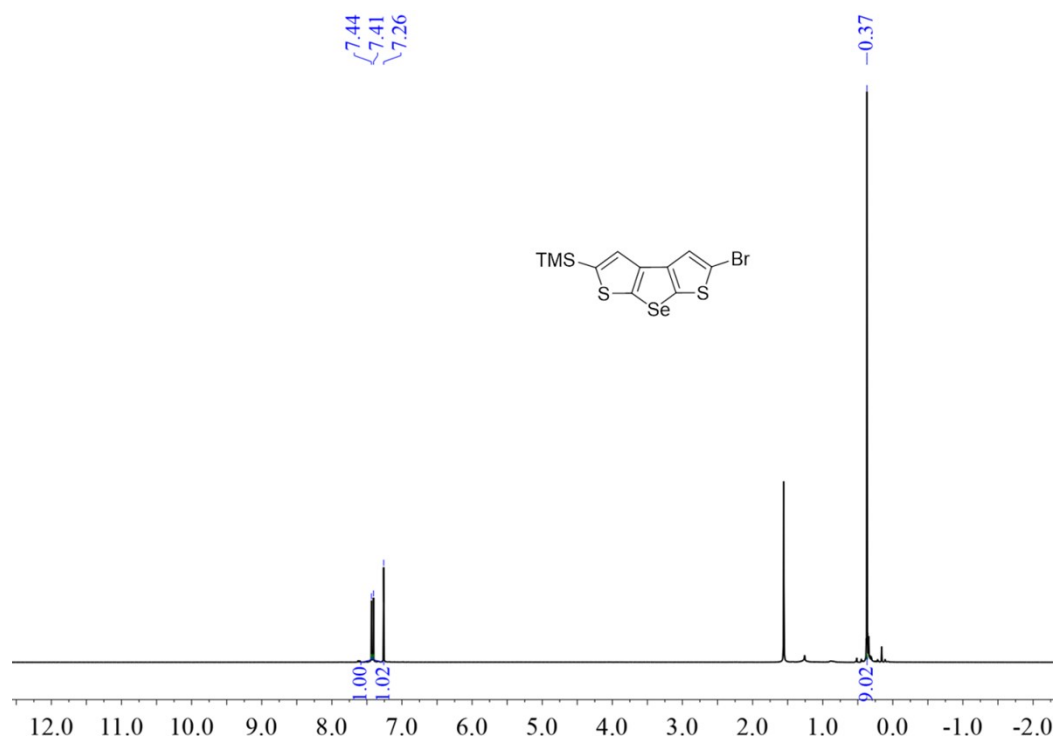


Fig. S7. ¹H NMR (400 MHz, CDCl₃) spectrum of 4b

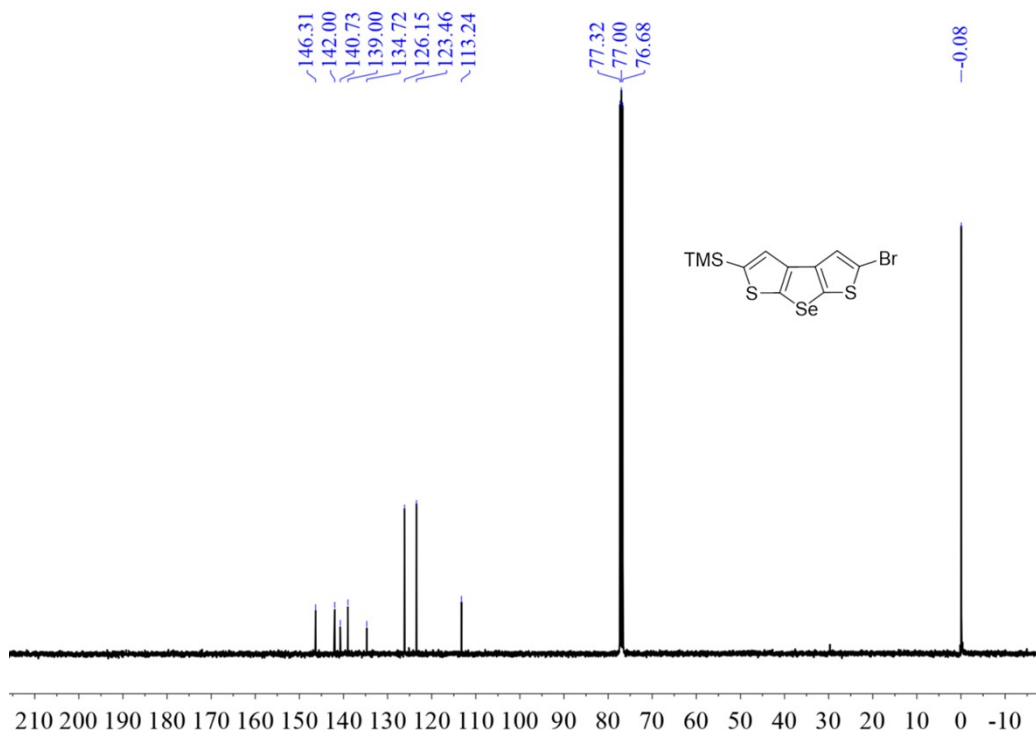


Fig. S8. ^{13}C NMR (100 MHz, CDCl_3) spectrum of **4b**

National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences High Resolution MS Data Report



Instrument: Waters Micromass GCT Premier Ionisation Mode: EI^+
 Electron Energy: 70eV Card Serial Number: GCT-P-T19-OS-866
 Operator: Li Date: 2019/11/18

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
387.8478	387.8480	-0.2	-0.5	8.0	5546026.5	$\text{C}_{11}\text{H}_{11}\text{SiS}_2\text{74SeBr}$
	387.8473	0.5	1.3	9.0	5546026.5	$\text{C}_{11}\text{H}_7\text{O}_4\text{S}_7\text{4SeBr}$
	387.8472	0.6	1.5	19.0	5546025.5	$\text{C}_{18}\text{HSiS}_2\text{Br}$
	387.8466	1.2	3.1	18.5	5546026.5	$\text{C}_{17}\text{HNO}_7\text{4SeBr}$
	387.8498	-2.0	-5.2	13.5	5546026.5	$\text{C}_{13}\text{H}_5\text{NO}_2\text{Si}_7\text{4SeBr}$

Fig. S9. HRMS data of **4b**

NMR and HRMS spectra of **5b**

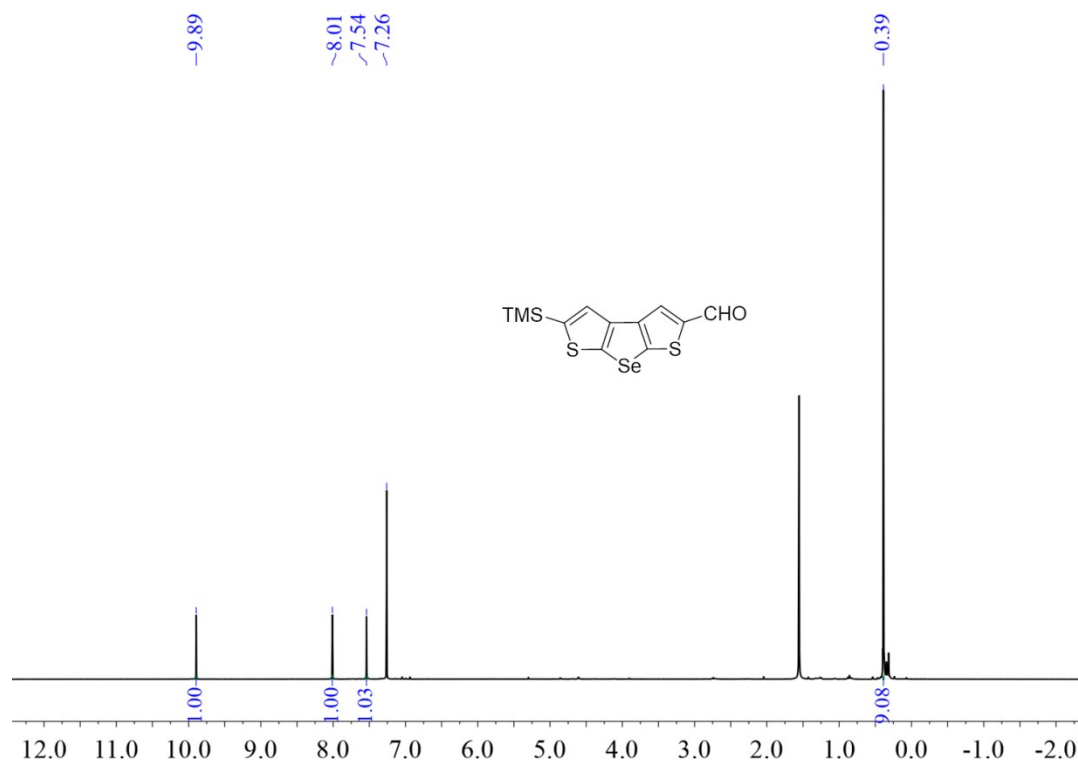


Fig. S10. ¹H NMR (400 MHz, CDCl₃) spectrum of **5b**

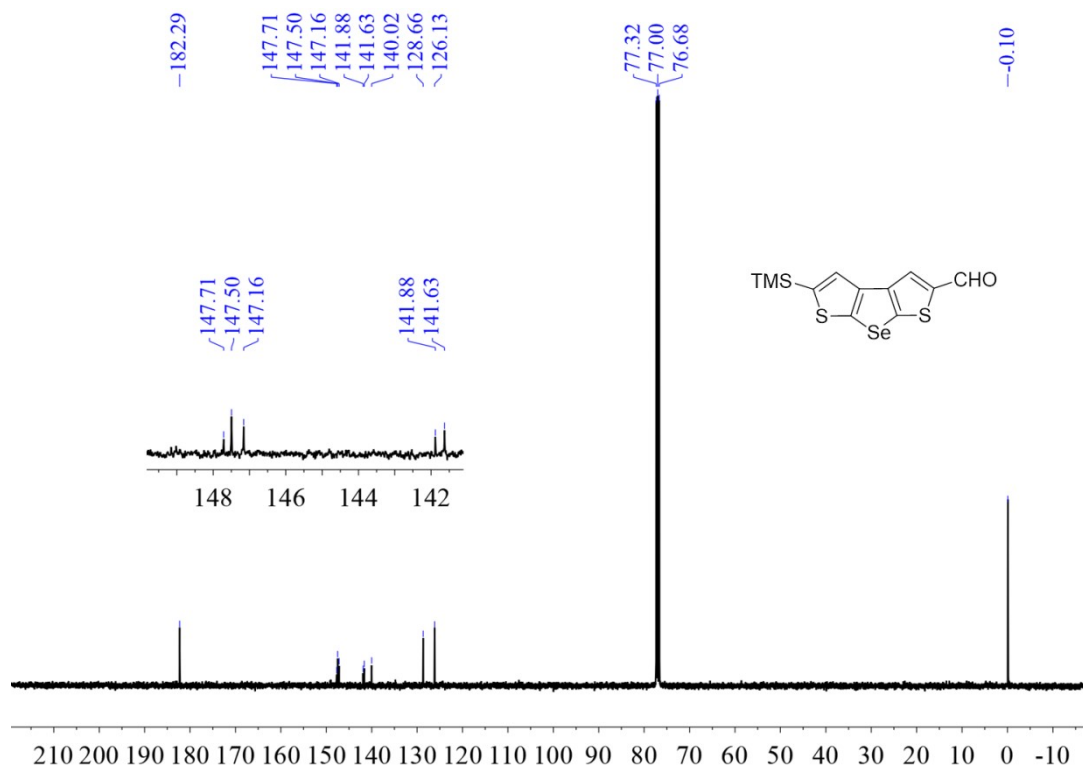


Fig. S11. ¹³C NMR (100 MHz, CDCl₃) spectra of **5b**

Instrument: Thermo Fisher Scientific LTQ FT Ultra Card Serial Number: D193122 Operator: DONG
Date: 2019/10/19 Operation Mode: DART POSITIVE

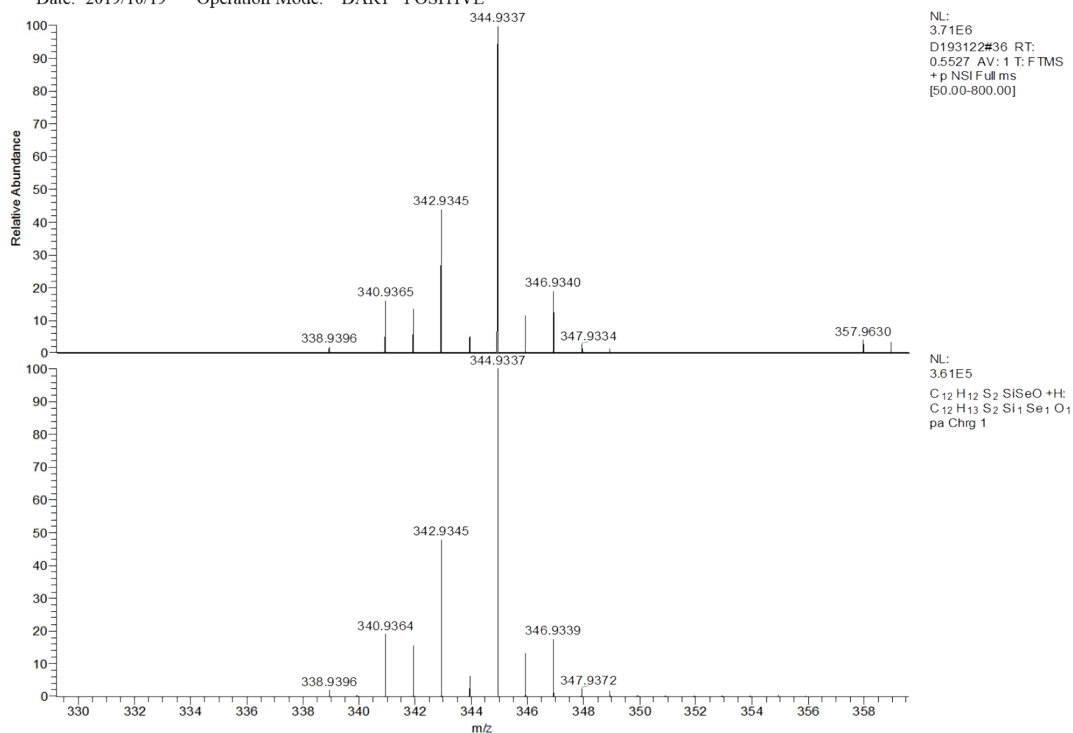


Fig. S12. HRMS spectra of 5b

NMR and HRMS spectra of 6a

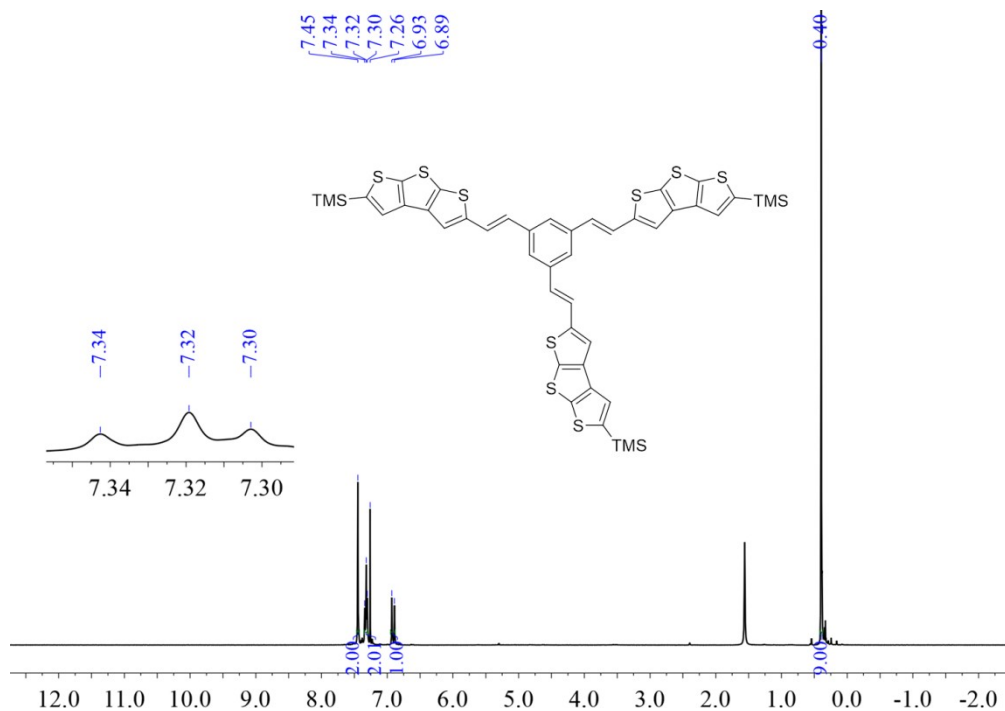


Fig. S13. ¹H NMR (400 MHz, CDCl₃) spectra of 6a

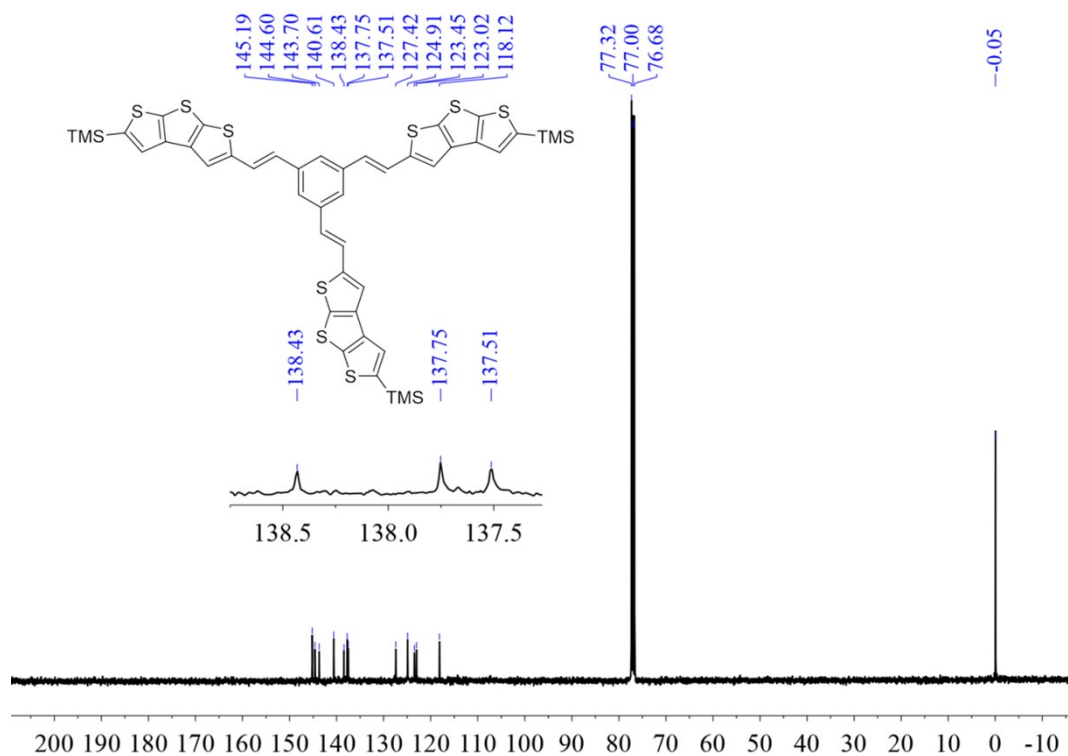


Fig. S14. ^{13}C NMR (100 MHz, CDCl_3) spectra of **6a**

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT



Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI14 426

Sample Serial Number: WJC-4-187-COL

Operator : HuaQin Date: 2014/02/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 954.0075 ± 0.004
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
S	31.972071	0	10
Si	27.976927	0	3

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:

Number of Hits = 5

m/z	Delta m/z	DBE	Formula
954.00752	-0.00002	25.0	$\text{C}_{45}\text{H}_{42}\text{S}_9\text{Si}_3^{+1}$
954.00888	-0.00138	52.0	$\text{C}_{62}\text{H}_{22}\text{S}_9\text{Si}^{+1}$
954.00551	0.00199	57.0	$\text{C}_{65}\text{H}_{18}\text{S}_4\text{Si}^{+1}$
954.00415	0.00335	30.0	$\text{C}_{48}\text{H}_{38}\text{S}_8\text{Si}_3^{+1}$
954.01089	-0.00339	20.0	$\text{C}_{42}\text{H}_{46}\text{S}_{10}\text{Si}_3^{+1}$

Fig. S15. HRMS data of **6a**

NMR and HRMS spectra of 6b

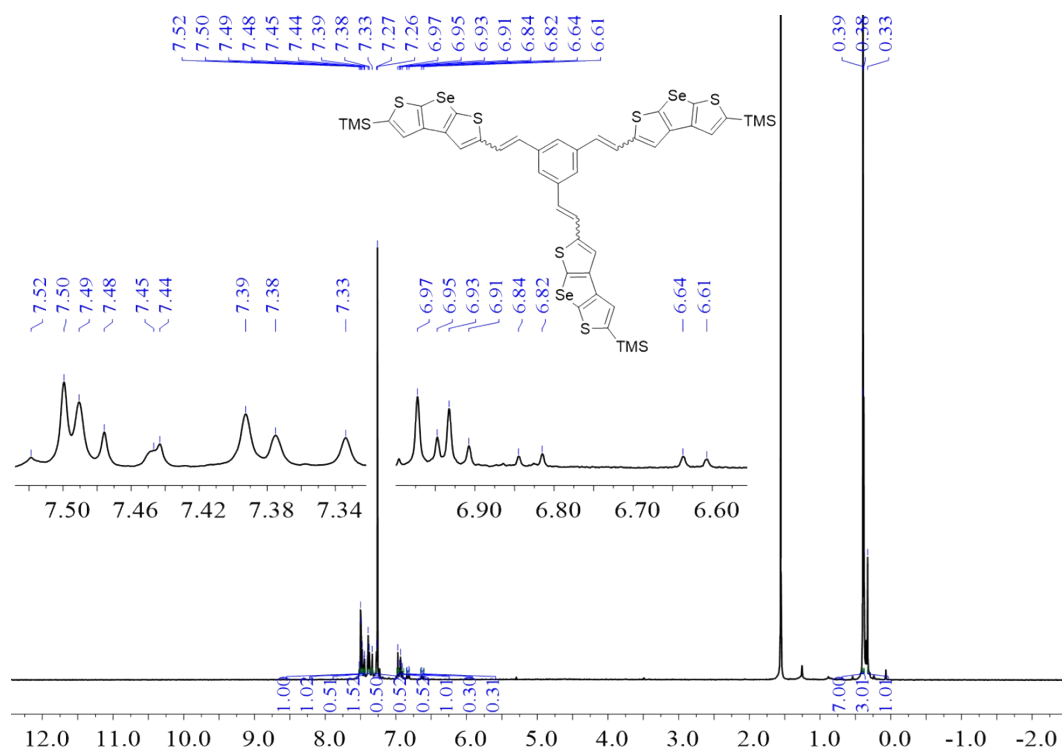


Fig. S16. ¹H NMR (400 MHz, CDCl₃) spectra of **6b**

National Center for Organic Mass Spectrometry in Shanghai Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences High Resolution MS DATA REPORT



Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS Card Serial Number: H-W190996 Operator : QHL
Date: 2019/11/1 Operation Mode: AP- MALDI Positive Ion Mode

Elemental composition search on mass 1097.8435

m/z = 1092.8435-1102.8435

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1097.8435	1097.8409	2.40	28.0	C ₄₅ H ₄₂ S ₆ Se ₃ Si ₃

XV-Se-w-s #267 RT: 1.52 AV: 1 NL: 1.44E4
T: FTMS + p NSI Full ms [400.0000-1500.0000]

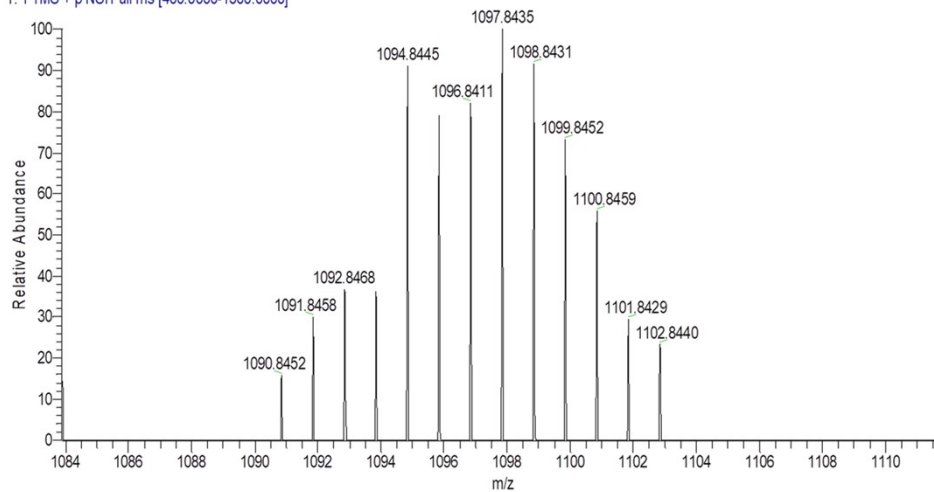


Fig. S17. HRMS spectrum of **6b**

NMR and HRMS spectra of 6c

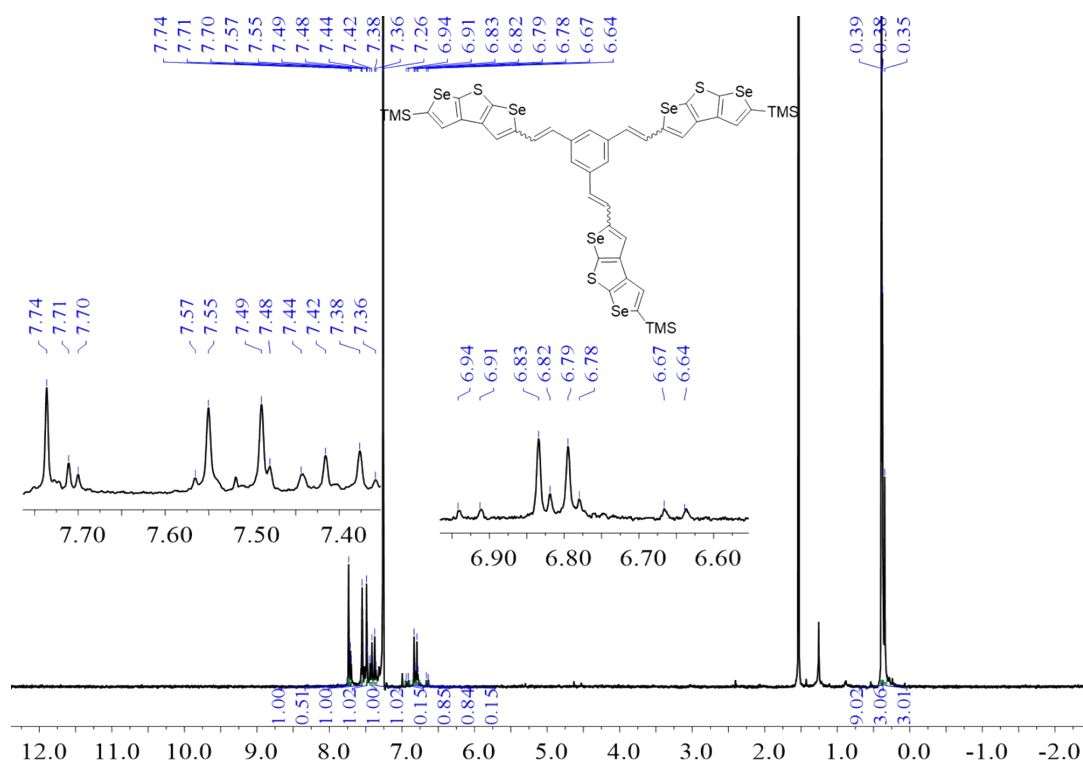


Fig. S18. ^1H NMR (400 MHz, CDCl_3) spectra of **6c**

National Center for Organic Mass Spectrometry in Shanghai Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences High Resolution MS DATA REPORT



Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS Card Serial Number: H-W190994 Operator : QHL
Date: 2019/11/1 Operation Mode: AP- MALDI Positive Ion Mode

Elemental composition search on mass 1241.6768

$m/z = 1236.6768 - 1246.6768$

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1241.6768	1241.6742	2.04	28.0	$\text{C}_{45}\text{H}_{42}\text{S}_3\text{Se}_6\text{Si}_3$

XW-2Se-w-s_20191029163053 #82 RT: 0.50 AV: 1 NL: 9.80E3
T: FTMS + p NSI Full ms [400.0000-1500.0000]

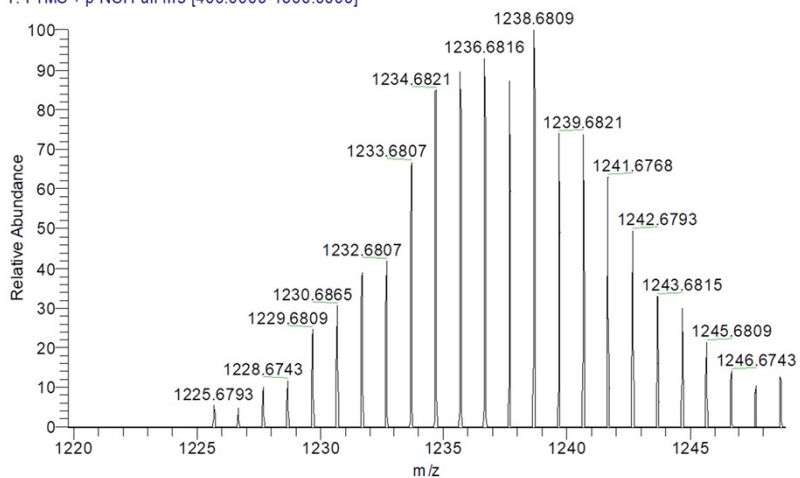


Fig. S19. HRMS spectrum of **6c**

NMR and HRMS spectra of 6d

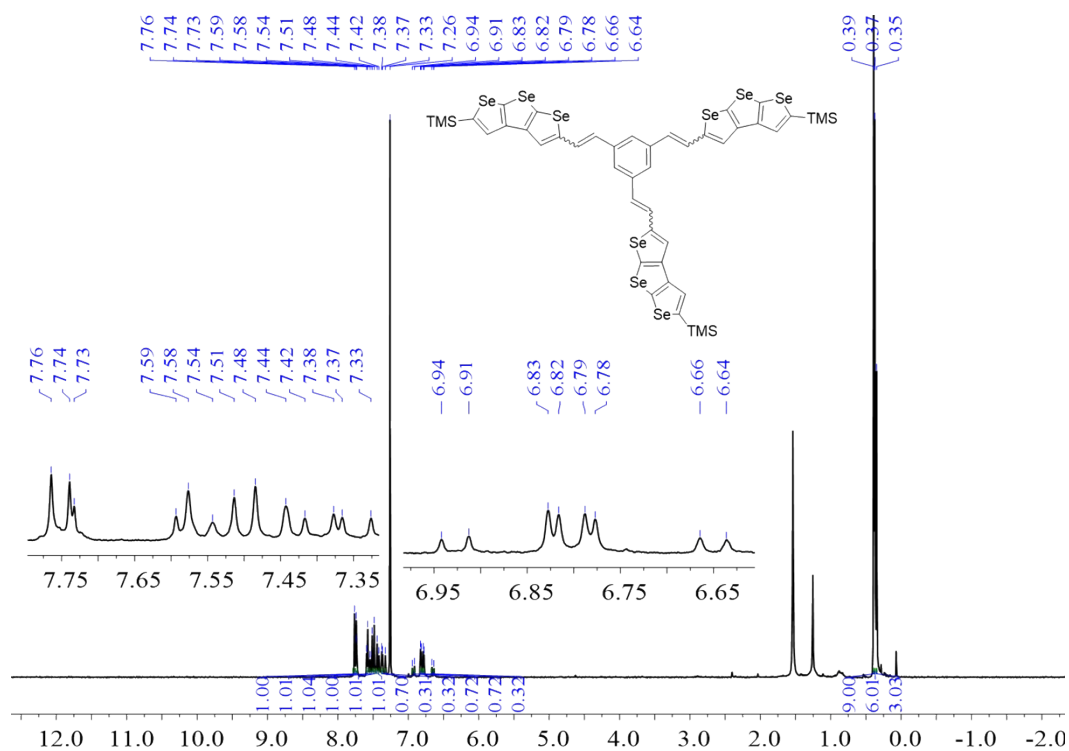


Fig. S20. ¹H NMR (400 MHz, CDCl₃) spectra of **6d**

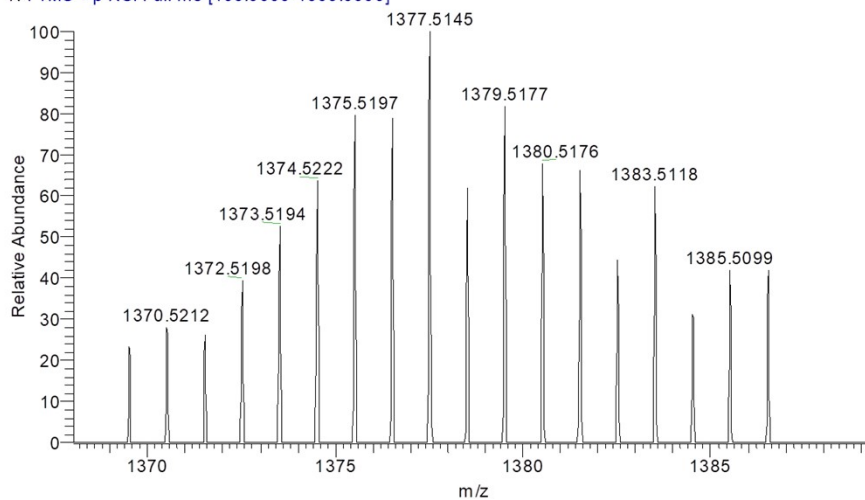
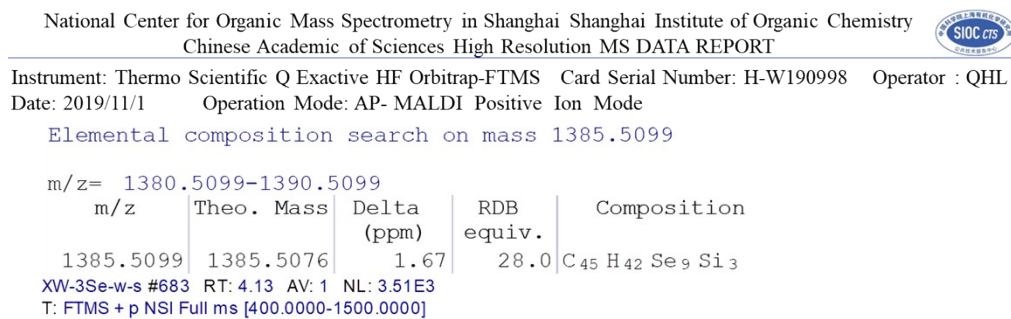


Fig. S21. HRMS spectrum of **6d**

NMR and HRMS spectra of *rac-1a*

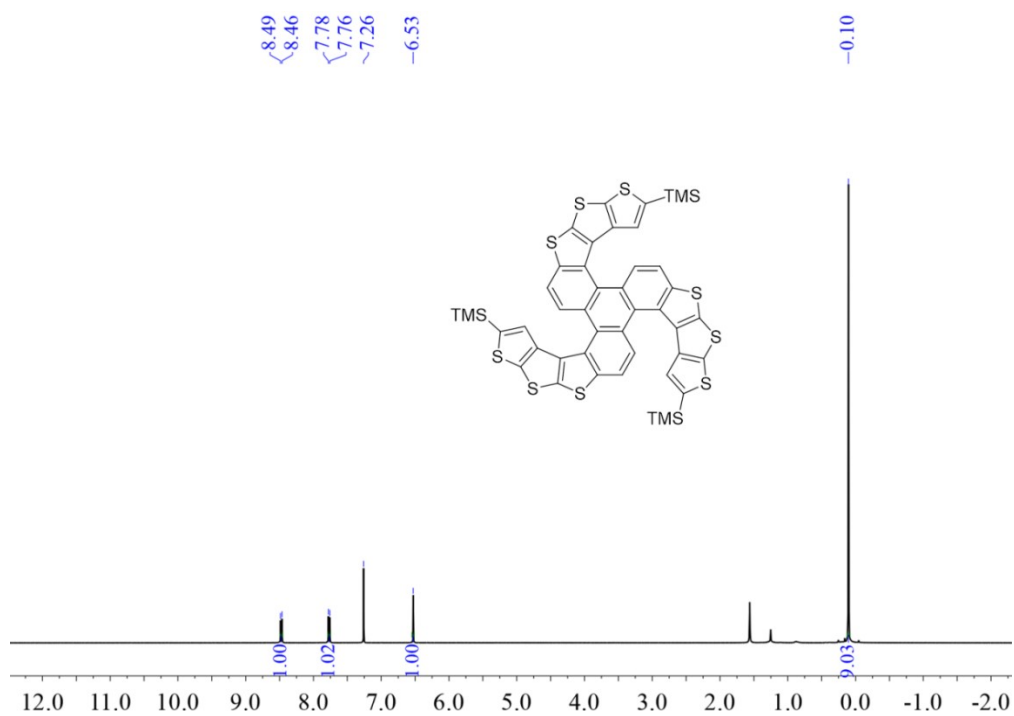


Fig. S22. ¹H NMR (400 MHz, CDCl₃) spectrum of *rac-1a*

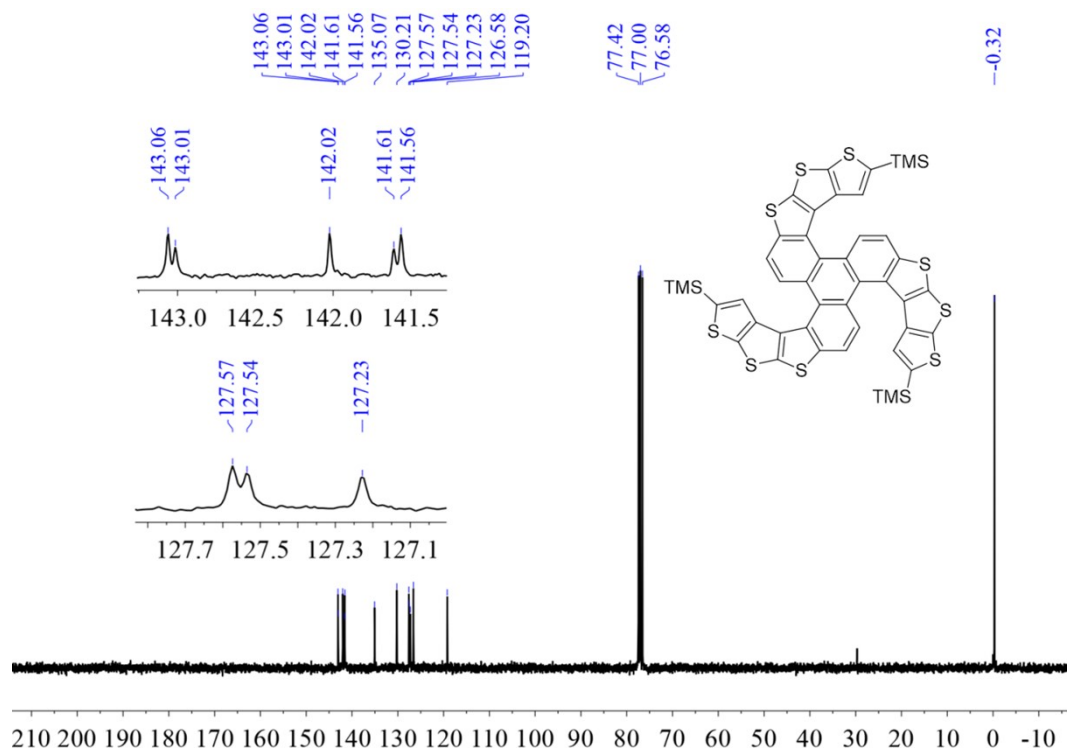


Fig. S23. ¹³C NMR (100 MHz, CDCl₃) spectra of *rac-1a*

Instrument: IonSpec 4.7 Tesla FTMS Card Serial Number: WI132017 Operator: HuaQin
Date: 2013/10/16 Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 947.9608 ± 0.004
Charge = +1

Possible Elements:

Element	Exact Mass	Min	Max
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	4
S	31.972071	0	10

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:

Number of Hits = 5

m/z	Delta m/z	DBE	Formula
947.96057	0.00023	28.0	$C_{45}H_{36}Si_3S_9^{+1}$
947.96193	-0.00113	55.0	$C_{62}H_{16}Si_5^{+1}$
947.95856	0.00224	60.0	$C_{65}H_{12}Si_4^{+1}$
947.96394	-0.00314	23.0	$C_{42}H_{40}Si_3S_{10}^{+1}$
947.95720	0.00360	33.0	$C_{48}H_{32}Si_3S_8^{+1}$

Fig. S24. HRMS data of *rac-1a*

NMR and HRMS spectra of *rac-1b*

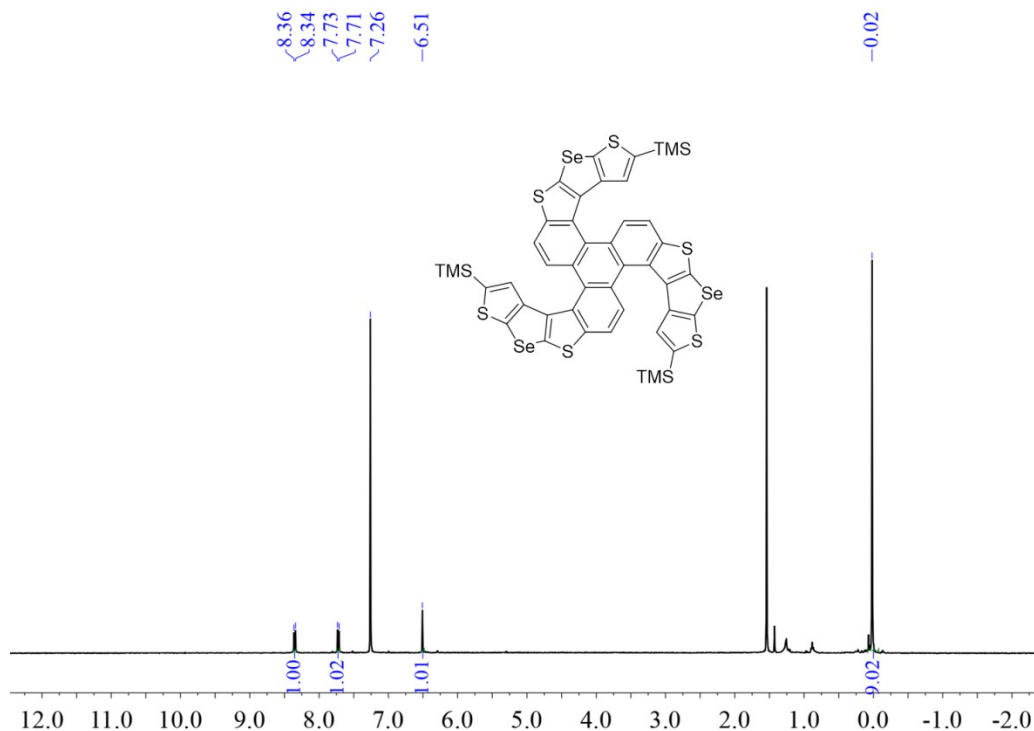


Fig. S25. ¹H NMR (400 MHz, CDCl₃) spectrum of *rac-1b*

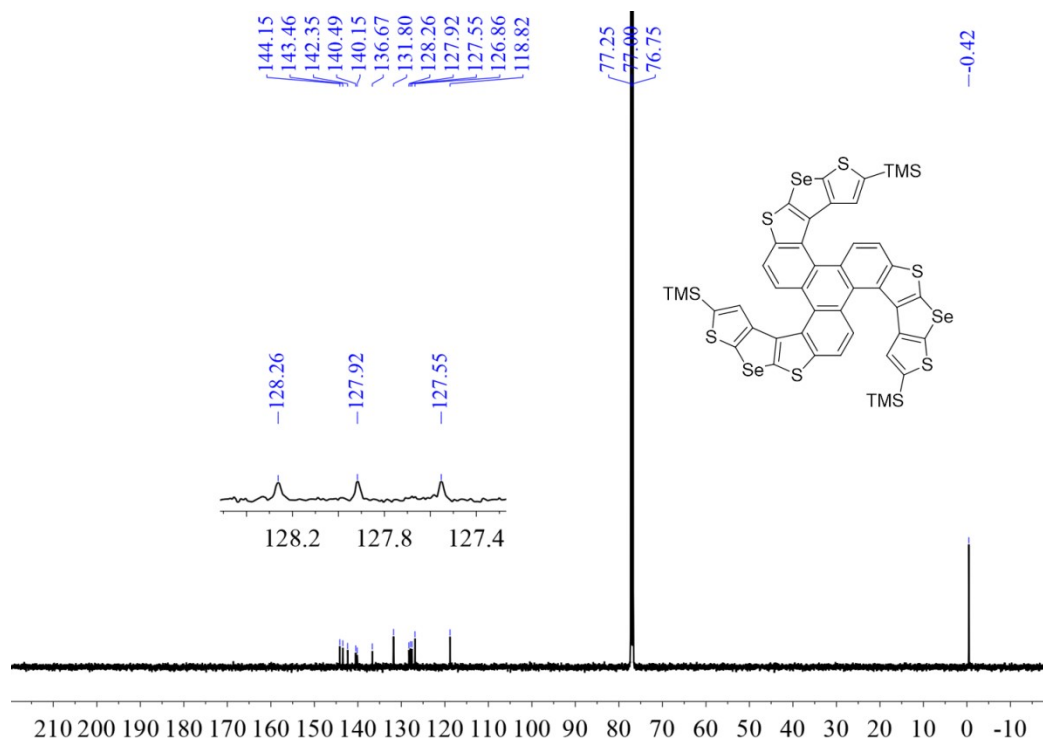


Fig. S26. ¹³C NMR (125 MHz, CDCl₃) spectra of *rac-1b*

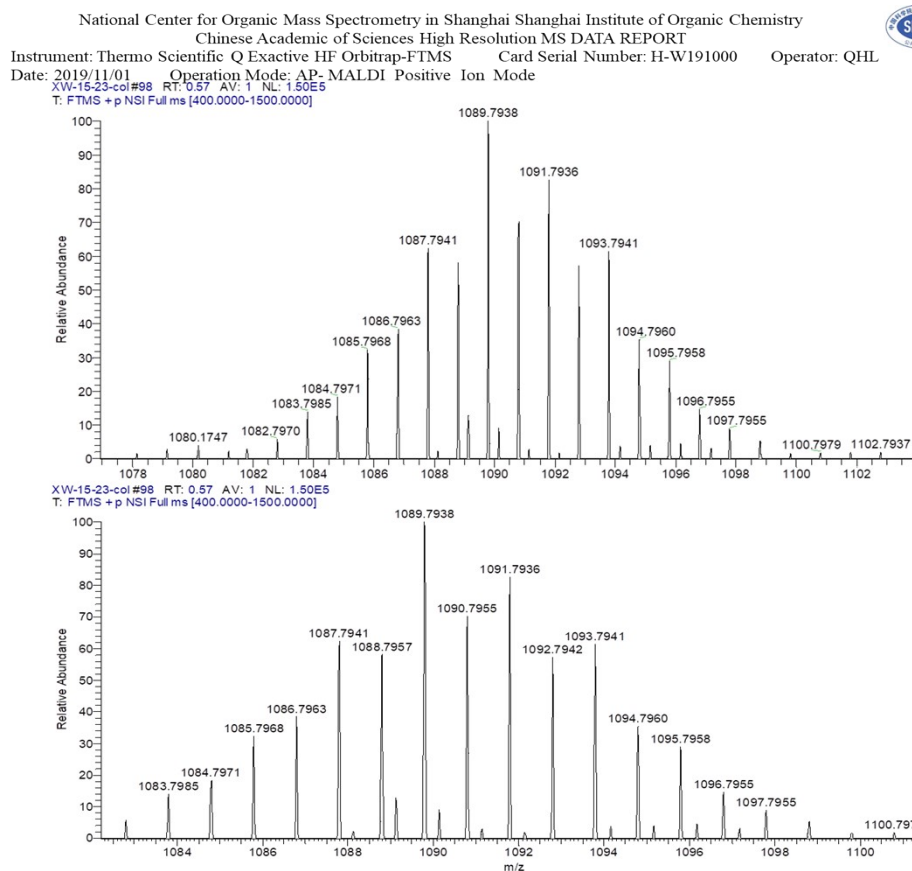


Fig. S27. HRMS spectra of *rac-1b*

NMR and HRMS spectra of *rac-1c*

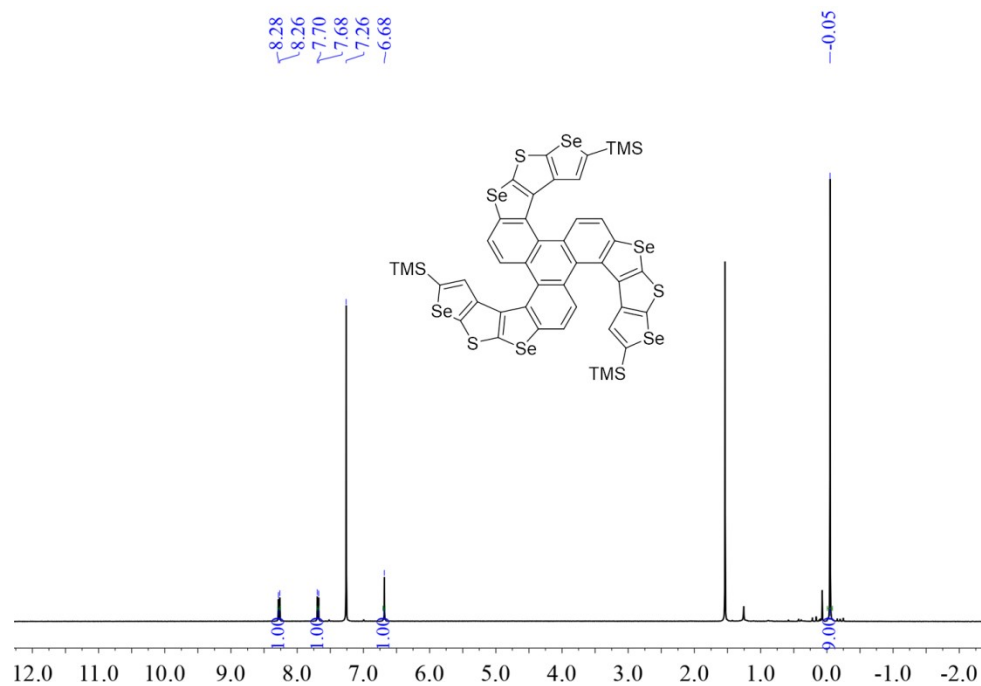


Fig. S28. ¹H NMR (400 MHz, CDCl₃) spectrum of *rac-1c*

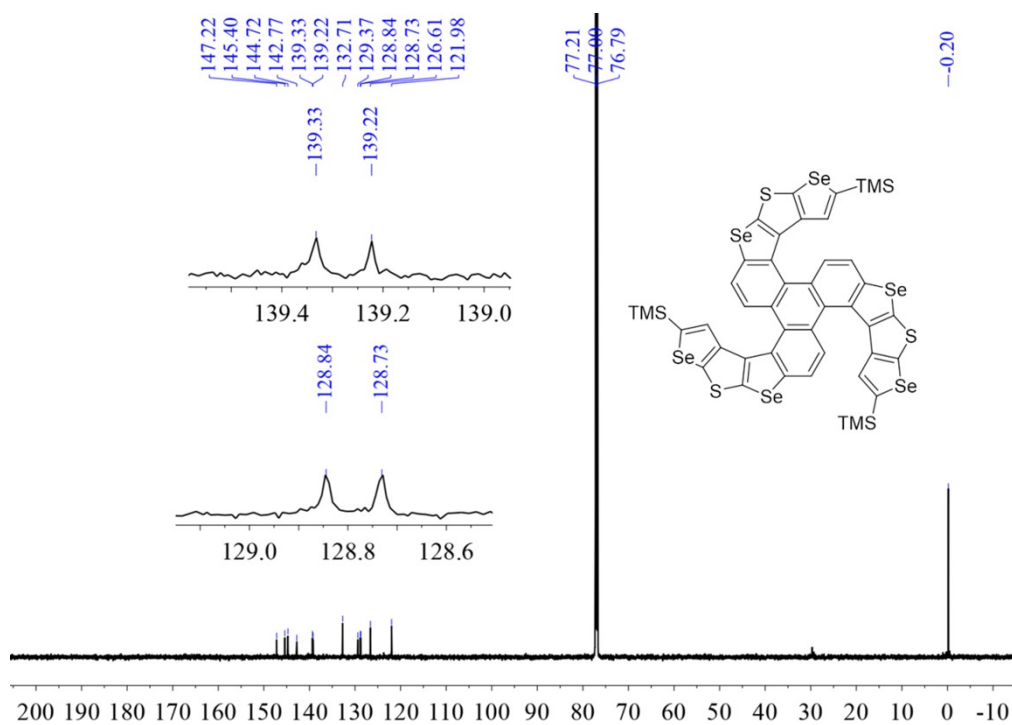


Fig. S29. ¹³C NMR (150 MHz, CDCl₃) spectra of *rac-1c*

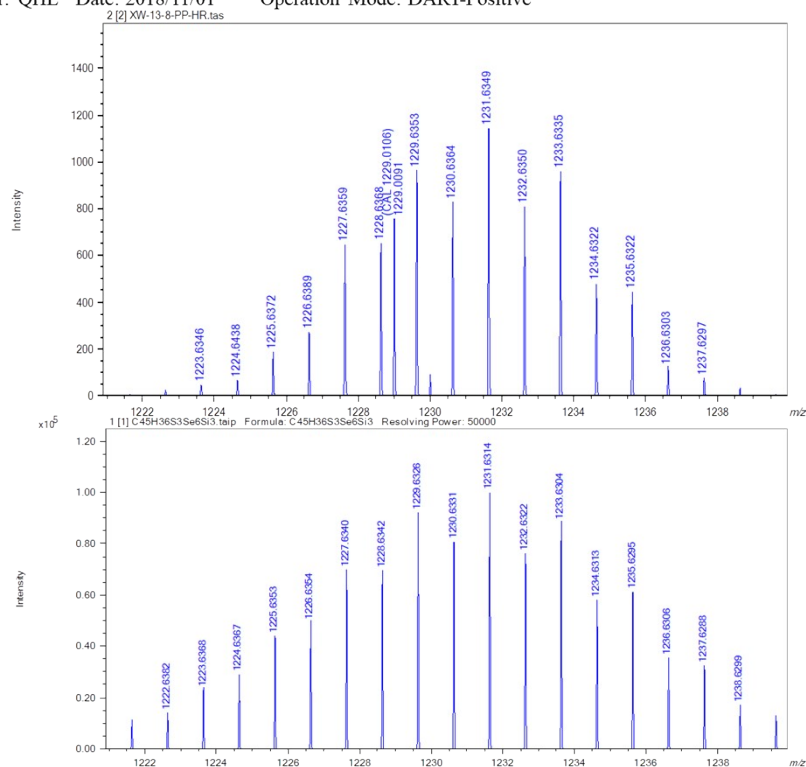


Fig. S30. HRMS spectra of *rac-1c*

NMR and HRMS spectra of *rac-1d*

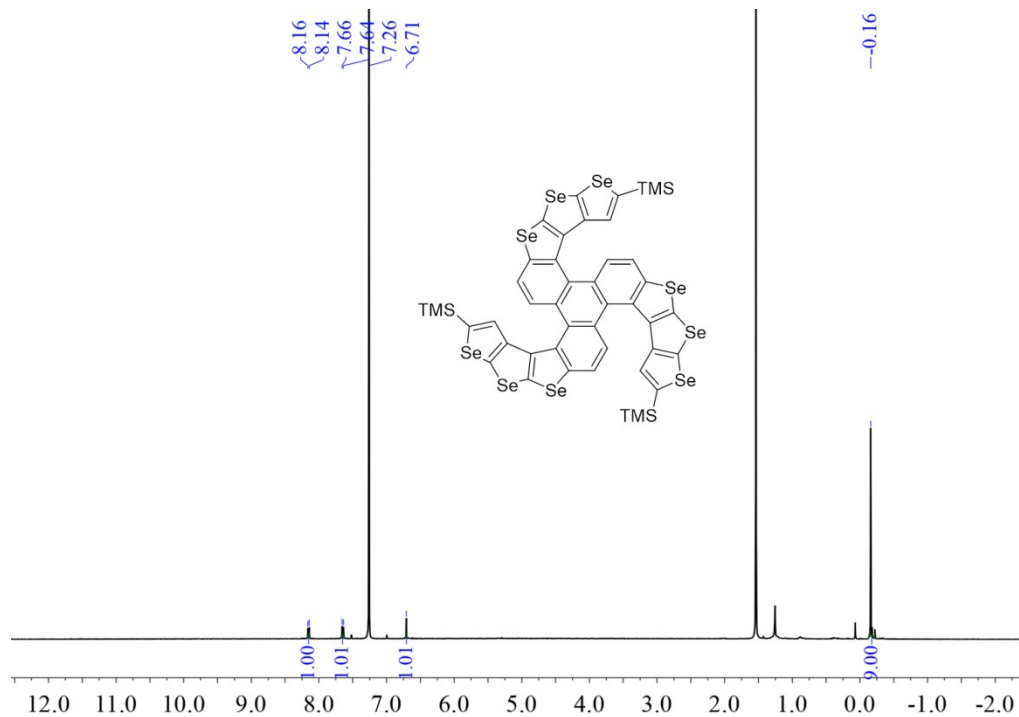


Fig. S31. ¹H NMR (400 MHz, CDCl₃) spectrum of *rac-1d*

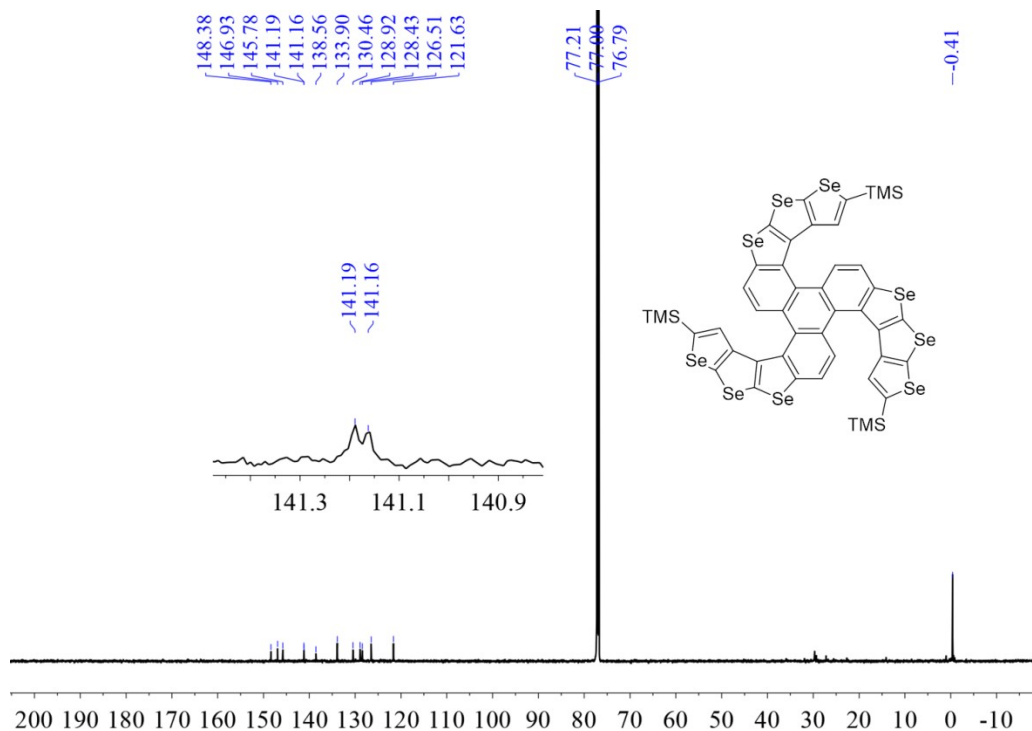


Fig. S32. ¹³C NMR (150 MHz, CDCl₃) spectra of *rac-1d*

National Center for Organic Mass Spectrometry in Shanghai Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences High Resolution MS DATA REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS
Date: 2018/11/01

Card Serial Number: H-W181011

Operator : QHL

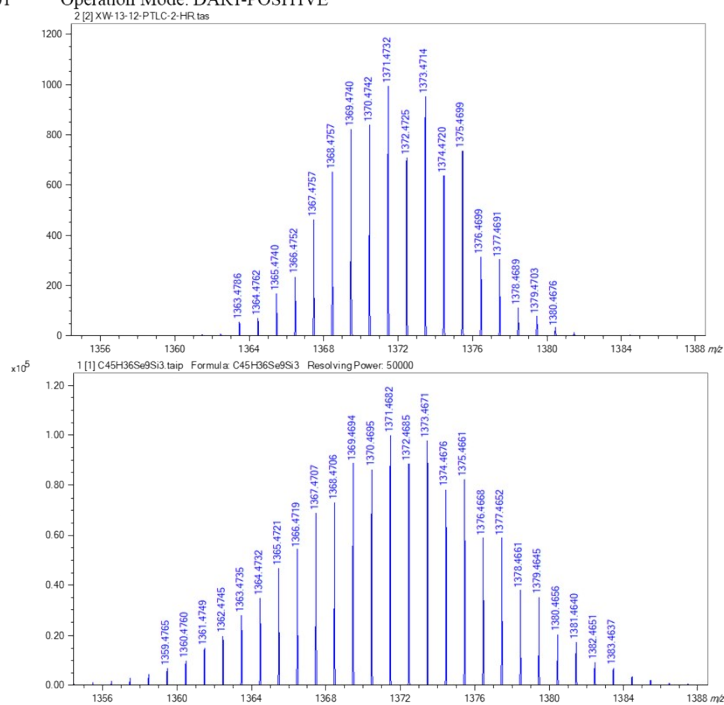


Fig. S33. HRMS spectra of *rac-1d*

3. Quantum Calculation of *rac-1(a)–(d)*

UV-vis spectra prediction and transition nature of *rac-1(a)–(d)*

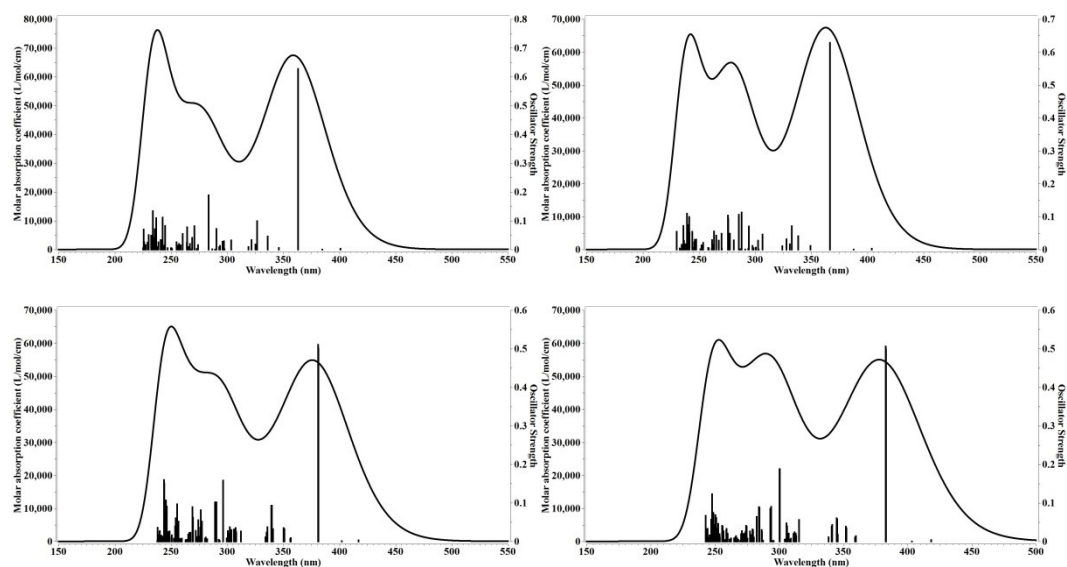


Fig. S34. The simulated UV-vis spectra of compounds *rac-1(a)–(d)* in dichloroethane solvent at the PCM-TD-B3LYP/6-31G* level of theory.

Table S1 Selected computational absorption energies (nm), oscillator strength (*f*), and transition nature in dichloromethane solvent for compounds *rac-1(a)–(d)* at the TD-B3LYP/6-31G* level of theory.

		states	λ	<i>f</i>	Transition Contributions
<i>rac-1a</i>	Band-I	$S_0 \rightarrow S_3$	363.0 (3.42)	0.6268	HOMO-1 \rightarrow LUMO (9%) HOMO-1 \rightarrow LUMO+1 (39%) HOMO \rightarrow LUMO (39%) HOMO \rightarrow LUMO+1(9%)
		$S_0 \rightarrow S_4$	363.0 (3.42)	0.6270	HOMO-1 \rightarrow LUMO (39%) HOMO-1 \rightarrow LUMO+1 (9%) HOMO \rightarrow LUMO (9%) HOMO \rightarrow LUMO+1(39%)
<i>rac-1b</i>	Band-I	$S_0 \rightarrow S_3$	366.7 (3.38)	0.6282	HOMO-1 \rightarrow LUMO (31%) HOMO-1 \rightarrow LUMO+1 (17%) HOMO \rightarrow LUMO (16%) HOMO \rightarrow LUMO+1(31%)
		$S_0 \rightarrow S_4$	366.7 (3.38)	0.6278	HOMO-1 \rightarrow LUMO (16%) HOMO-1 \rightarrow LUMO+1 (31%) HOMO \rightarrow LUMO (31%) HOMO \rightarrow LUMO+1(17%)

<i>rac-1c</i>	Band-I	$S_0 \rightarrow S_3$	381.2 (3.25)	0.5000	HOMO-1 \rightarrow LUMO (9%) HOMO-1 \rightarrow LUMO+1 (40%) HOMO \rightarrow LUMO (36%) HOMO \rightarrow LUMO+1(11%)
		$S_0 \rightarrow S_4$	380.9 (3.26)	0.5101	HOMO-1 \rightarrow LUMO (37%) HOMO-1 \rightarrow LUMO+1 (11%) HOMO \rightarrow LUMO (9%) HOMO \rightarrow LUMO+1(39%)
<i>rac-1d</i>	Band-I	$S_0 \rightarrow S_3$	383.3 (3.24)	0.4985	HOMO-1 \rightarrow LUMO (46%) HOMO \rightarrow LUMO+1(48%)
		$S_0 \rightarrow S_4$	383.0 (3.24)	0.5061	HOMO-1 \rightarrow LUMO (49%) HOMO \rightarrow LUMO+1(45%)

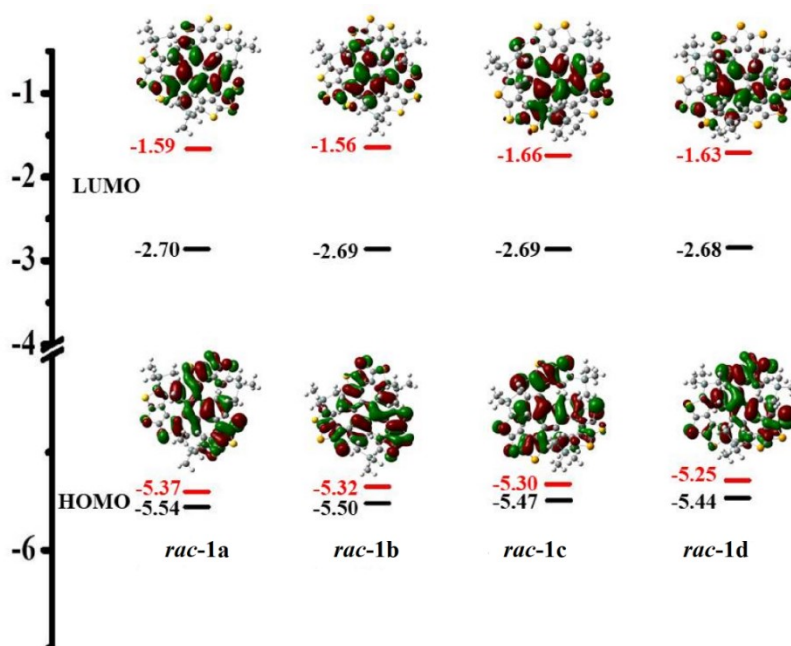


Fig. S35. Visualizations of HOMO and LUMO distributions (B3LYP/6-31G*) for *rac-1(a)–(d)*.

Table S2 Optical and electrochemical data of *rac-1(a)–(d)*.

Compound	λ_{onset} (nm)	Φ_F	Time (ns)	E_{ox} (V)	E_g^{opt} (eV)	HOMO (eV) experimental	HOMO (eV) theory	LUMO (eV) experimental	LUMO (eV) theory
<i>rac-1</i>	437	0.029	3.35	1.18	2.84	-5.54	-5.37	-2.70	-1.59
<i>rac-2</i>	441	0.020	3.10	1.16	2.81	-5.50	-5.32	-2.69	-1.56
<i>rac-3</i>	446	0.011	2.47	1.14	2.78	-5.47	-5.30	-2.69	-1.66
<i>rac-4</i>	449	0.008	2.11	1.10	2.76	-5.44	-5.25	-2.68	-1.63

Measured in anhydrous $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{F}_6\text{NP}$ (0.1 M), $[C] = 1 \times 10^{-3} \text{ mol L}^{-1}$, vs Fc/Fc^+ .

$$E_{\text{HOMO}} = -[E_{\text{ox}}^{\text{onset}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8] \text{ eV}. \quad E_{\text{LUMO}} = E_g^{\text{(opt)}} + E_{\text{HOMO}}.$$

4. Resolution of *rac*-**1c**

The resolution of the *rac*-**1c** was carried out by chiral HPLC with methanol/dichloromethane/diethylamine (80/20/0.1, v/v/v) as eluent. The two enantiomers were obtained on a semipreparative scaled chiral column (ID). From the 15 mg scale of *rac*-**1c**, 0.6 mg (*ee* > 97%) of (+)-**1c** and 1.6 mg (*ee* > 99%) of (-)-**1c** were efficiently obtained.

HPLC trace of (+)-**1c**, (-)-**1c**, and *rac*-**1c**

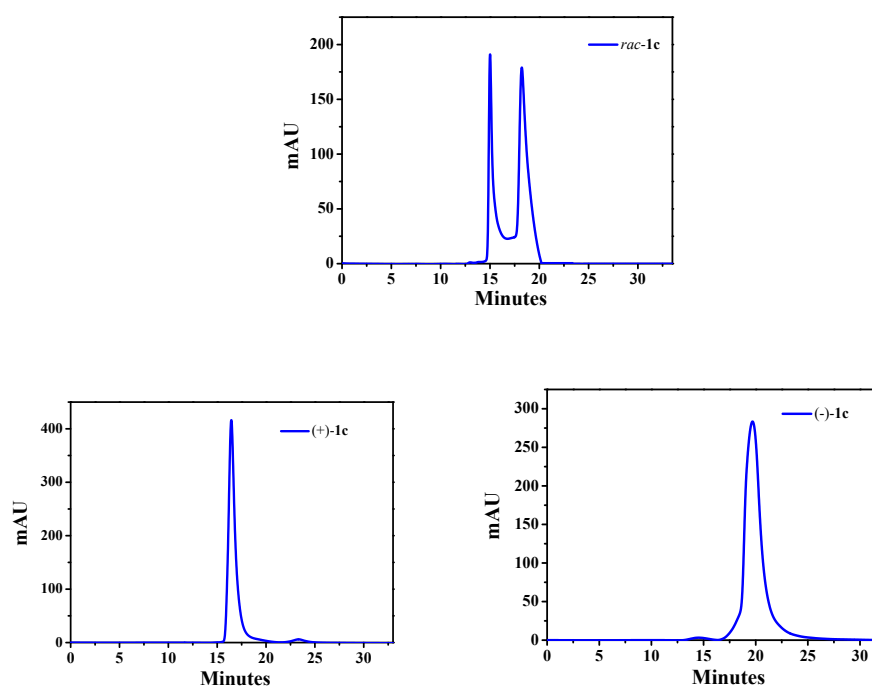


Fig. S36. HPLC trace of *rac*-**1c** (top), (+)-**1c** (bottom left, *ee* > 97%) and (-)-**1c** (bottom right, *ee* > 99%) at room temperature. Conditions: Eluent: methanol/dichloromethane/diethylamine (80/20/0.1, v/v/v), Flow Rate: 1.0 mL/min, Column: CHIRALPAK-ID.

Racemization of (-)-**1c**

Racemization of (-)-**1c** was carried out in CH₂Cl₂ by heating at different temperatures. The process was monitored from time to time by chiral HPLC (CHIRALPAK-ID) with methanol/dichloromethane/diethylamine (80/20/0.1, v/v/v) as eluent. The half-life of racemization of (-)-**1c** is proposed as below:

$$\begin{array}{ccc}
 (+) \text{-1c} & \rightarrow & (-) \text{-1c} \\
 t = 0 & C_0 & 0 \\
 t = t & C_t & C_0 - C_t
 \end{array}$$

The racemization of (-)-1c could be taken as first-order reaction, so

$$\ln C_0 / C_t = kt$$

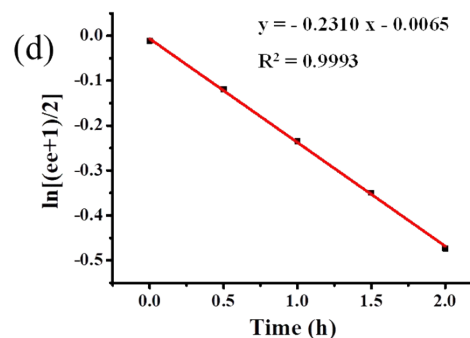
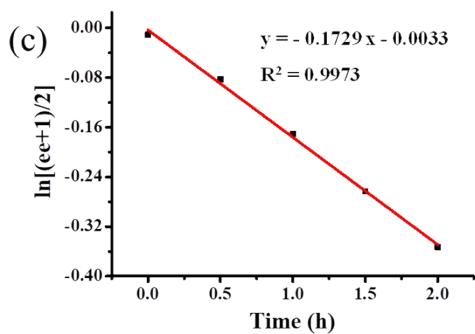
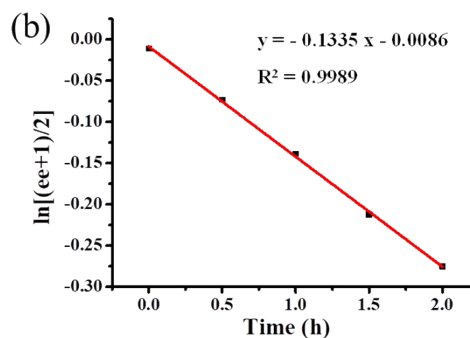
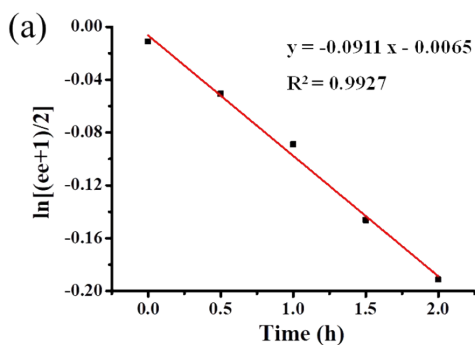
Here, C_0 is the concentration of (-)-1c before heating, and C_t is the concentration of (-)-1c after heating for time of t .

Because

$$\begin{aligned}
 ee &= \frac{C_t - (C_0 - C_t)}{C_t + (C_0 + C_t)} = \frac{2C_t - C_0}{C_0} = 2 \frac{C_t}{C_0} - 1 \\
 &\Rightarrow \frac{C_t}{C_0} = \frac{ee + 1}{2}
 \end{aligned}$$

So, we can obtain the formula as below:

$$\begin{aligned}
 \ln \frac{C_0}{C_t} &= \ln \frac{2}{ee + 1} = kt \\
 \Rightarrow \ln \frac{ee + 1}{2} &= -kt
 \end{aligned}$$



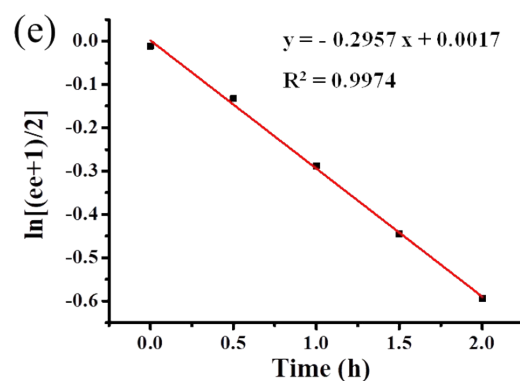


Fig. S37. Time-dependent enantiomeric excess value decay profiles at (a) 70 °C, (b) 75 °C, (c) 80 °C, (d) 85 °C and (e) 90 °C, respectively.

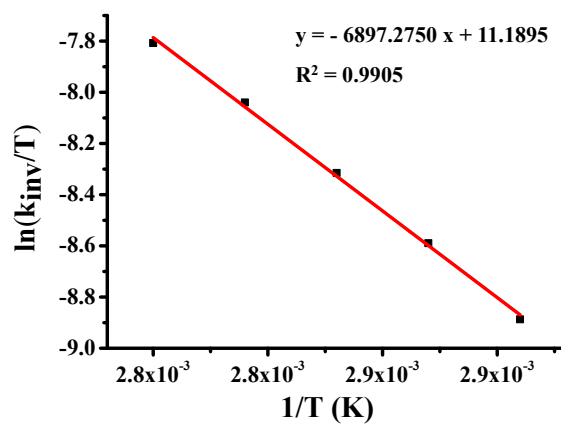


Fig. S38. The half-life of (-)-1c at different temperatures.

Table S3. The half-life of (-)-1c at different temperatures.

T/°C	70	75	80	85	90
$t_{1/2}/h$	7.61	5.19	4.00	3.00	2.34

5. X-ray Crystallographic Data

X-ray crystallographic data of *rac-1a*

Table S4. Crystal data and structure refinement for *rac-1a*

Identification code	<i>rac-1a</i>
Empirical formula	C ₄₅ H ₃₆ OS ₉ Si ₃
Formula weight	965.55
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P2₁/c</i>
Unit cell dimensions	$a = 25.663(6)$ Å $\alpha = 90^\circ$ $b = 18.397(5)$ Å $\beta = 104.320(5)^\circ$ $c = 23.432(6)$ Å $\gamma = 90^\circ$
Volume	10719(5) Å ³
Z	8
Density (Calculated)	1.197 Mg/m ³
Absorption coefficient	0.469 mm ⁻¹
F(000)	4000
Crystal size	0.48 × 0.23 × 0.22 mm ³
Theta range for data collection	1.98 to 25.00°
Limiting indices	-26 ≤ h ≤ 30, -21 ≤ k ≤ 21, -24 ≤ l ≤ 27
Reflections collected / unique	54813 / 18767 [R _{int} = 0.0435]
Completeness to theta = 25.00	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9038 and 0.8060
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	18767 / 84 / 1063
Goodness-of-fit on F ²	1.129
Final R indices [I > 2σ(I)]	R ₁ = 0.0791, wR ₂ = 0.1948
R indices (all data)	R ₁ = 0.1233, wR ₂ = 0.2077
Largest diff. peak and hole	1.291 and -0.564 e. Å ⁻³

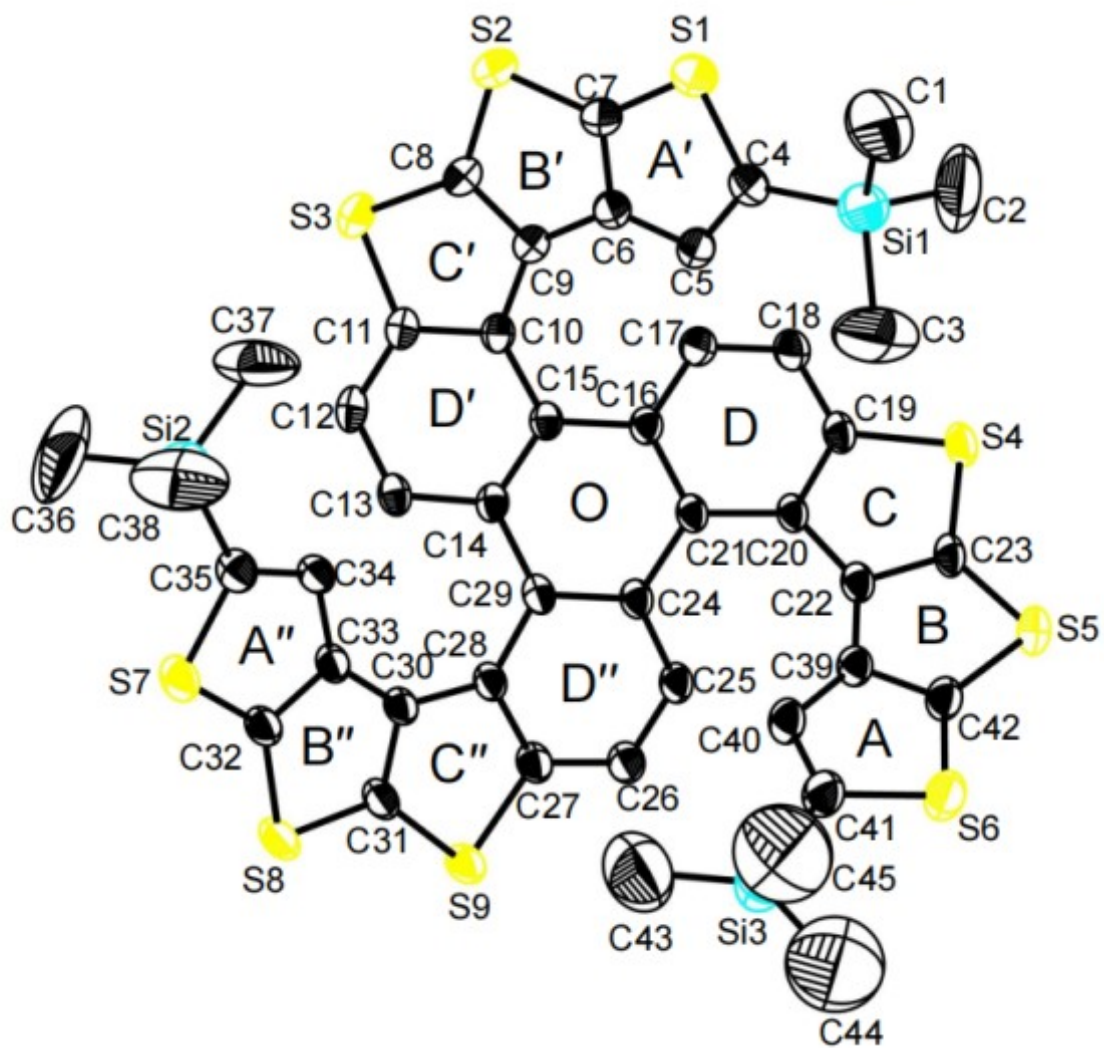


Fig. S39. Molecular structure for *rac*-1a, Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 30% probability level, and all hydrogen atoms are omitted for clarity.

X-ray crystallographic data of *rac-1b*

Table S5. Crystal data and structure refinement for *rac-1b*

Identification code	<i>rac-1b</i>
Empirical formula	C ₄₅ H ₃₆ S ₆ Se ₃ Si ₃
Formula weight	1090.25
Temperature	298.01 K
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	$a = 25.663(3) \text{ \AA}$ $\alpha = 90^\circ$ $b = 18.4115(18) \text{ \AA}$ $\beta = 90^\circ$ $c = 23.619(2) \text{ \AA}$ $\gamma = 90^\circ$
Volume	10803.4(18) \AA^3
Z	8
Density (Calculated)	1.341 Mg/m ³
Absorption coefficient	5.502 mm ⁻¹
F(000)	4368
Crystal size	0.17 × 0.09 × 0.04 mm ³
Radiation	CuK α ($\lambda = 1.54178$)
Theta range for data collection	5.974 to 134.144°
Index ranges	-30 ≤ h ≤ 30, -21 ≤ k ≤ 21, -28 ≤ l ≤ 23
Reflections collected	88921
Independent reflections	19069 [$R_{\text{int}} = 0.1462$, $R_{\text{sigma}} = 0.0953$]
Data / restraints / parameters	19069 / 353 / 1108
Goodness-of-fit on F ²	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0714$, $wR_2 = 0.1780$
R indices (all data)	$R_1 = 0.1219$, $wR_2 = 0.2100$
Largest diff. peak and hole	0.58 and -0.72e. \AA^{-3}

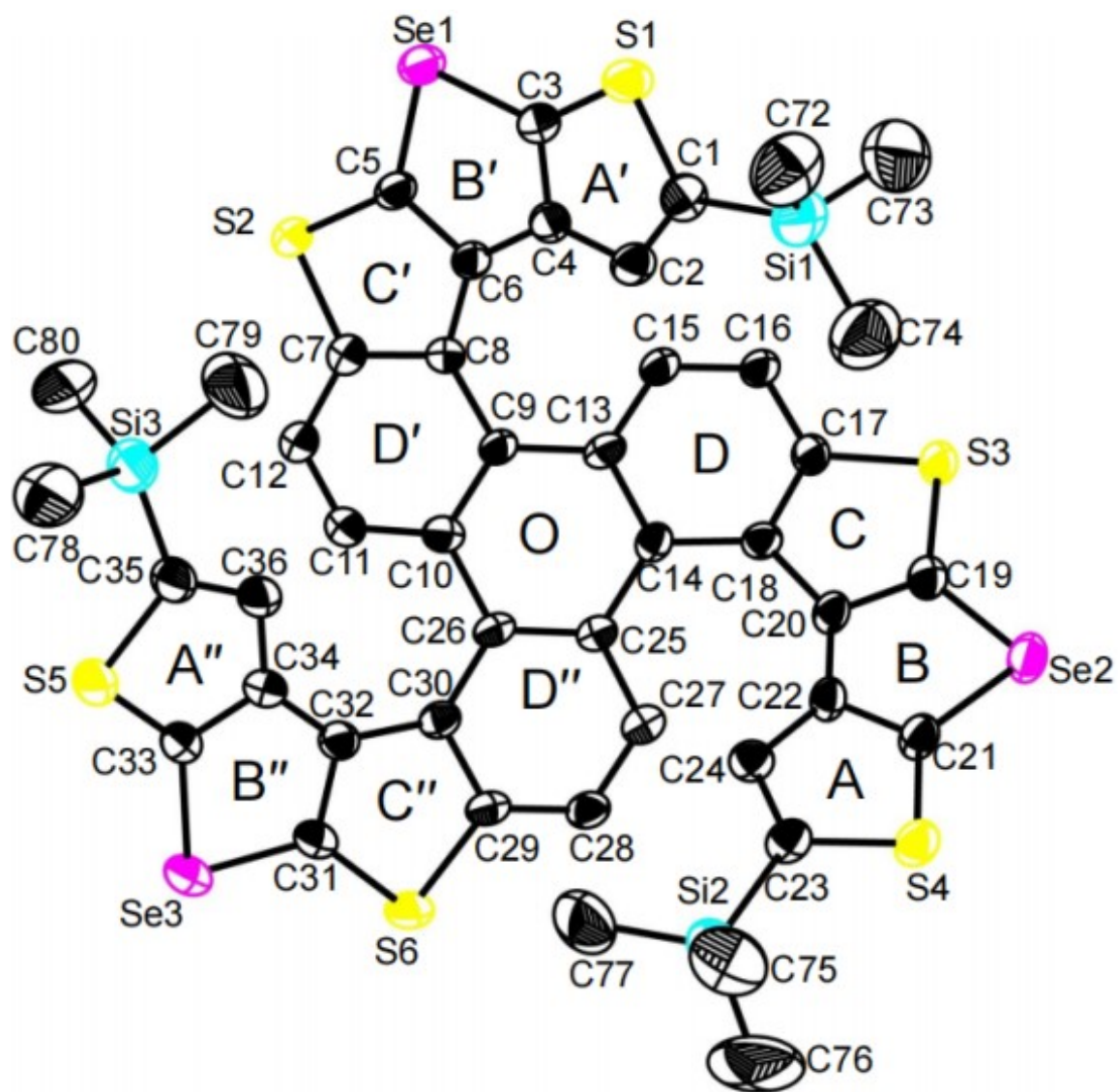


Fig. S40. Molecular structure for *rac-1b*, Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 30% probability level, and all hydrogen atoms are omitted for clarity.

X-ray crystallographic data of *rac-1c*

Table S6. Crystal data and structure refinement for *rac-1c*

Identification code	<i>rac-1c</i>
Empirical formula	C ₄₅ H ₃₆ S ₃ Se ₆ Si ₃
Formula weight	1230.96
Temperature	293(2) K
Crystal system, space group	cubic, <i>Pa</i> -3
Unit cell dimensions	a = 21.30032(10) Å α = 90° b = 21.30032(10) Å β = 90° c = 21.30032(10) Å γ = 90°
Volume	9664.03(13) Å ³
Z	7.99992
Density (Calculated)	1.692 Mg/m ³
Absorption coefficient	7.524 mm ⁻¹
F(000)	4800.0
Crystal size	0.1611 × 0.1222 × 0.0669 mm ³
Radiation	CuKα (λ = 1.54184)
Theta range for data collection	7.188 to 133.822°
Index ranges	-19 ≤ h ≤ 25, -25 ≤ k ≤ 24, -19 ≤ l ≤ 25
Reflections collected	23768
Independent reflections	2879 [R _{int} = 0.0392, R _{sigma} = 0.0202]
Data / restraints / parameters	2879 / 0 / 175
Goodness-of-fit on F ²	1.049
Final R indices [I > 2σ(I)]	R ₁ = 0.0370, wR ₂ = 0.0985
R indices (all data)	R ₁ = 0.0454, wR ₂ = 0.1034
Largest diff. peak and hole	0.63 and -0.26e. Å ⁻³

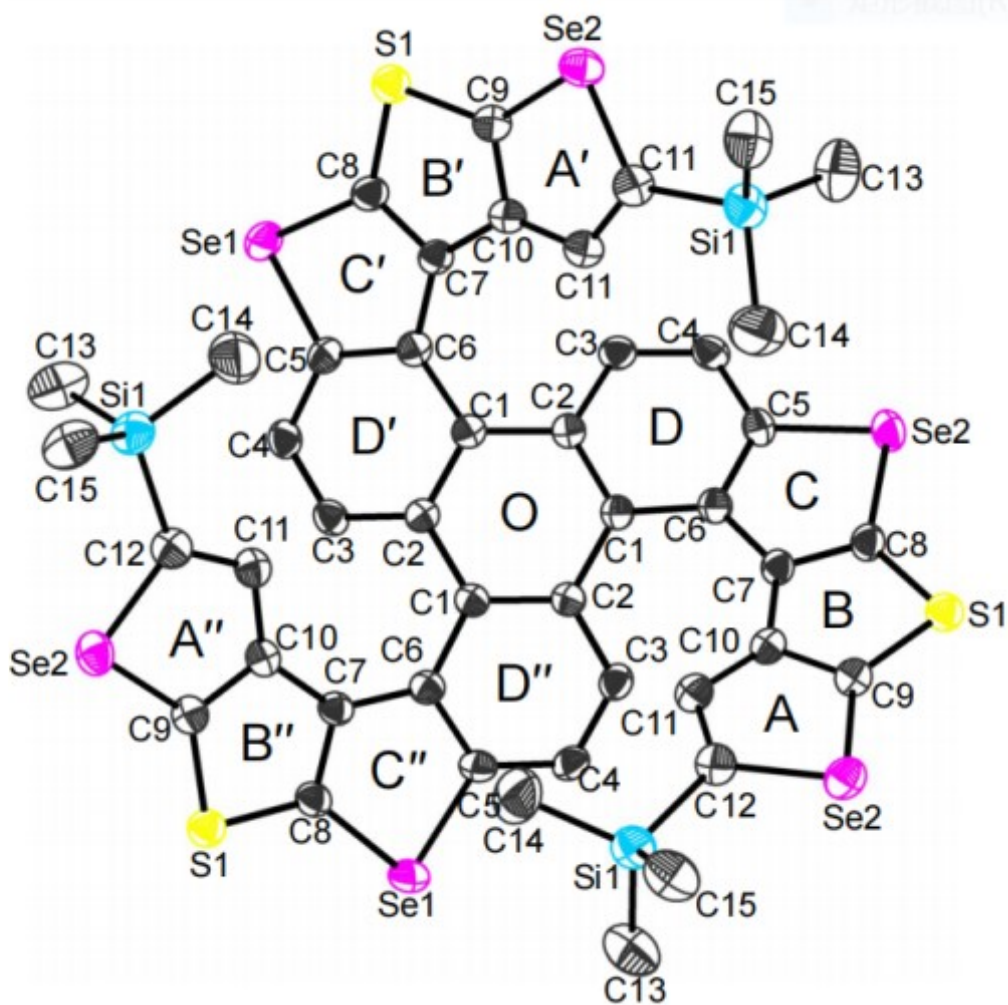


Fig. S41. Molecular structure for *rac*-1c, Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 30% probability level, and all hydrogen atoms are omitted for clarity.

X-ray crystallographic data of *rac-1d*

Table S7. Crystal data and structure refinement for *rac-1d*

Identification code	<i>rac-1d</i>
Empirical formula	C ₉₁ H ₇₄ Cl ₂ Se ₁₈ Si ₆
Formula weight	2828.22
Temperature	293(2) K
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	$a = 15.2593(17) \text{ \AA}$ $\alpha = 90^\circ$ $b = 19.9001(3) \text{ \AA}$ $\beta = 95.0760(10)^\circ$ $c = 16.53532(18) \text{ \AA}$ $\gamma = 90^\circ$
Volume	5001.44(10) \AA^3
Z	2
Density (Calculated)	1.878 Mg/m ³
Absorption coefficient	9.099 mm ⁻¹
F(000)	2700.0
Crystal size	0.1525 × 0.0577 × 0.0404 mm ³
Radiation	CuK α ($\lambda = 1.54184$)
Theta range for data collection	6.966 to 134.16°
Index ranges	-18 ≤ h ≤ 18, -21 ≤ k ≤ 23, -12 ≤ l ≤ 19
Reflections collected	21782
Independent reflections	8906 [$R_{\text{int}} = 0.0297$, $R_{\text{sigma}} = 0.0386$]
Data / restraints / parameters	8906 / 106 / 586
Goodness-of-fit on F ²	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0455$, $wR_2 = 0.1246$
R indices (all data)	$R_1 = 0.0596$, $wR_2 = 0.1354$
Largest diff. peak and hole	0.83 and -0.52e. \AA^{-3}

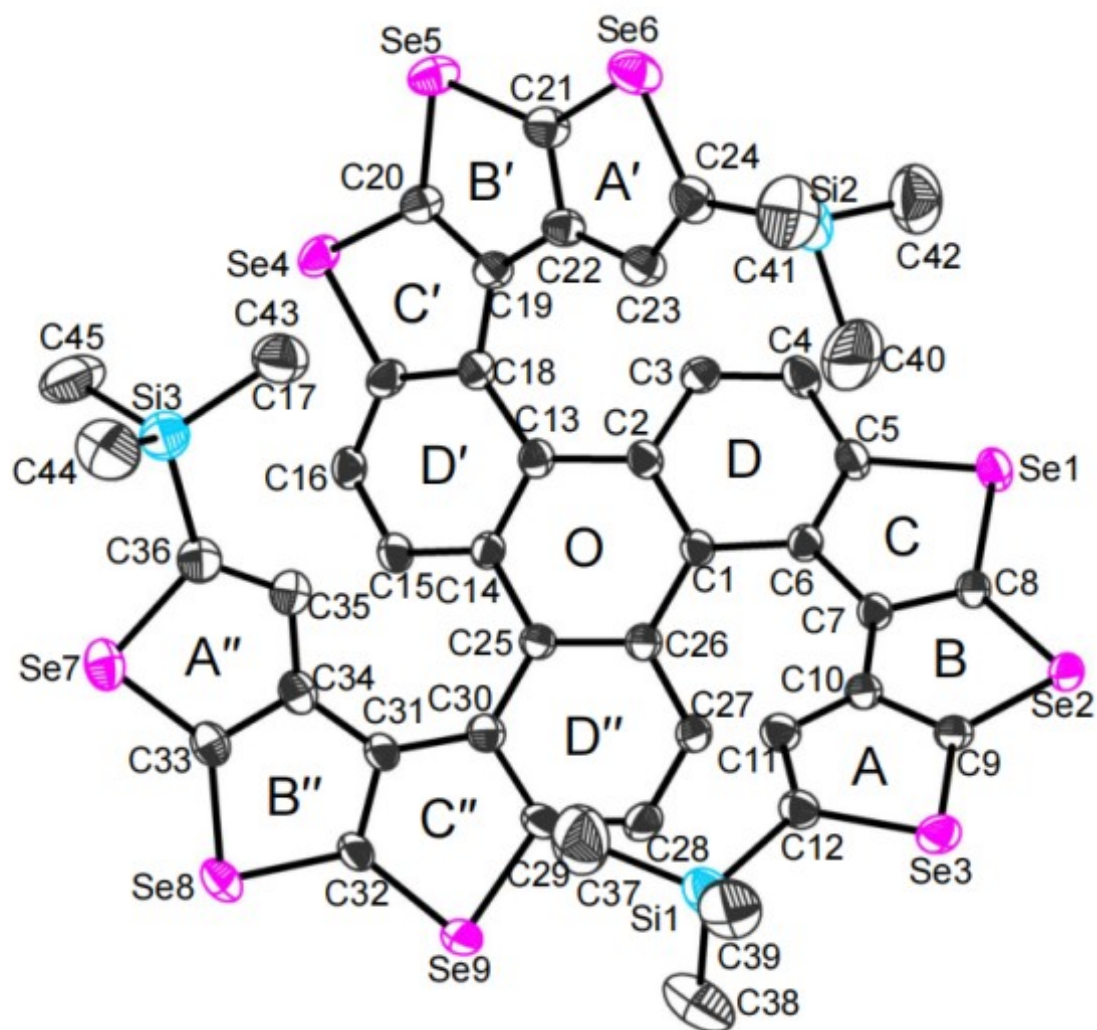


Fig. S42. Molecular structure for *rac*-**1d**, Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 30% probability level, and all hydrogen atoms are omitted for clarity.

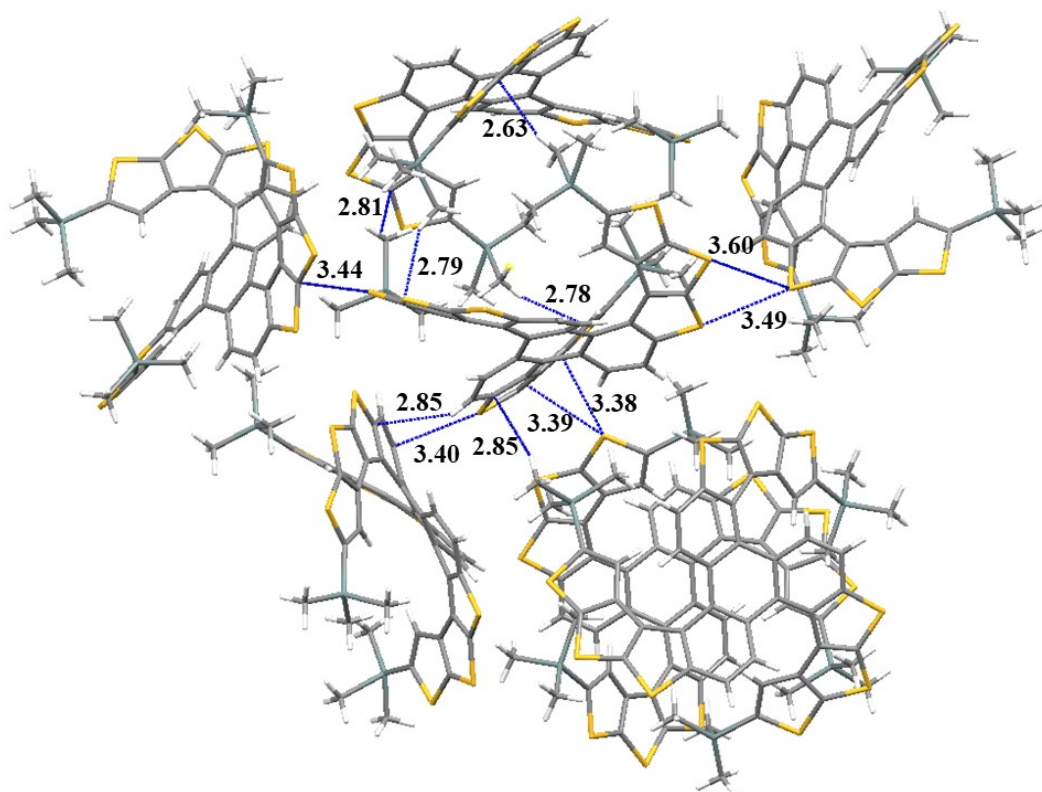


Fig. S43. Multiple interactions in the crystal packings of *rac-1a*.

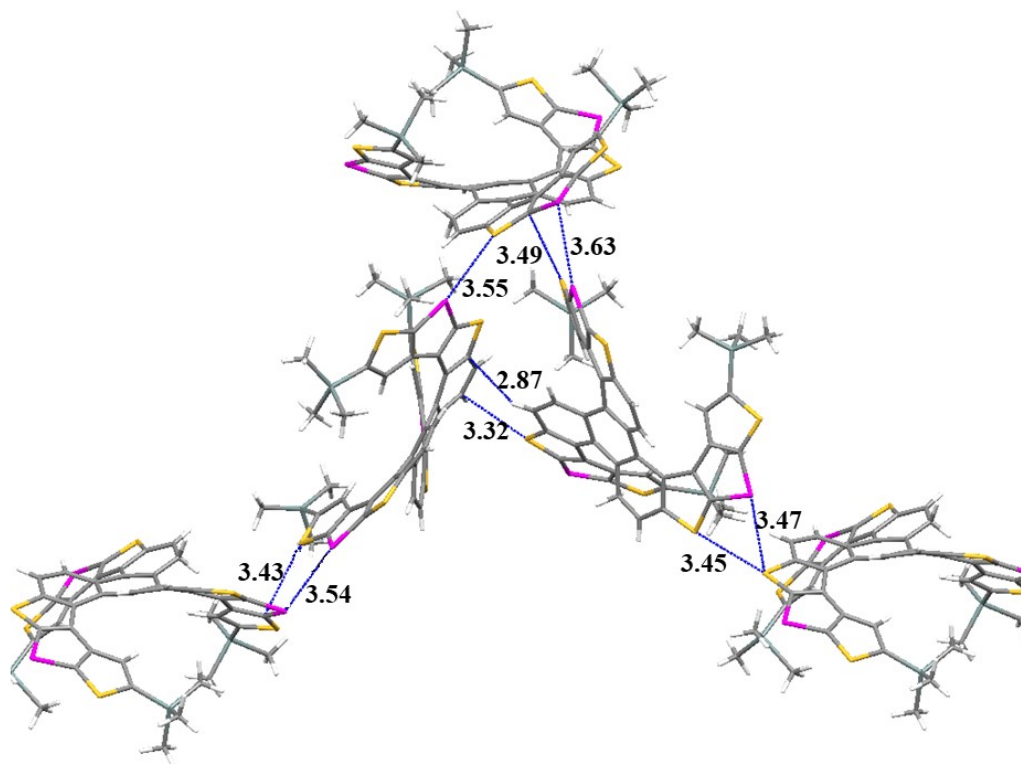


Fig. S44. Multiple interactions in the crystal packings of *rac-1b*.

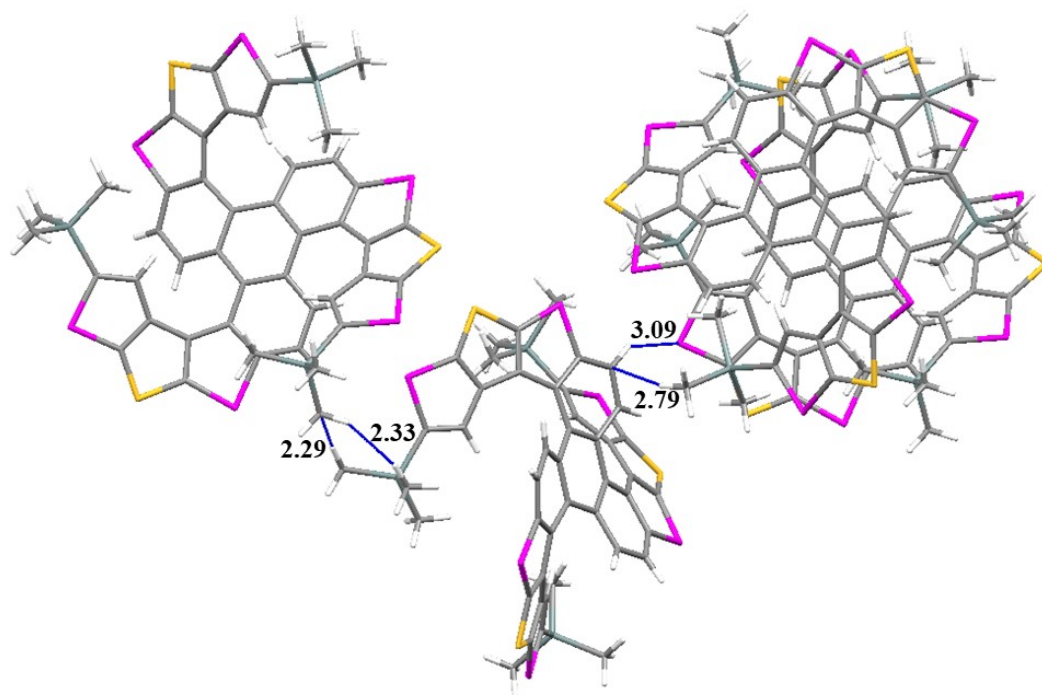


Fig. S45. Multiple interactions in the crystal packings of *rac-1c*.

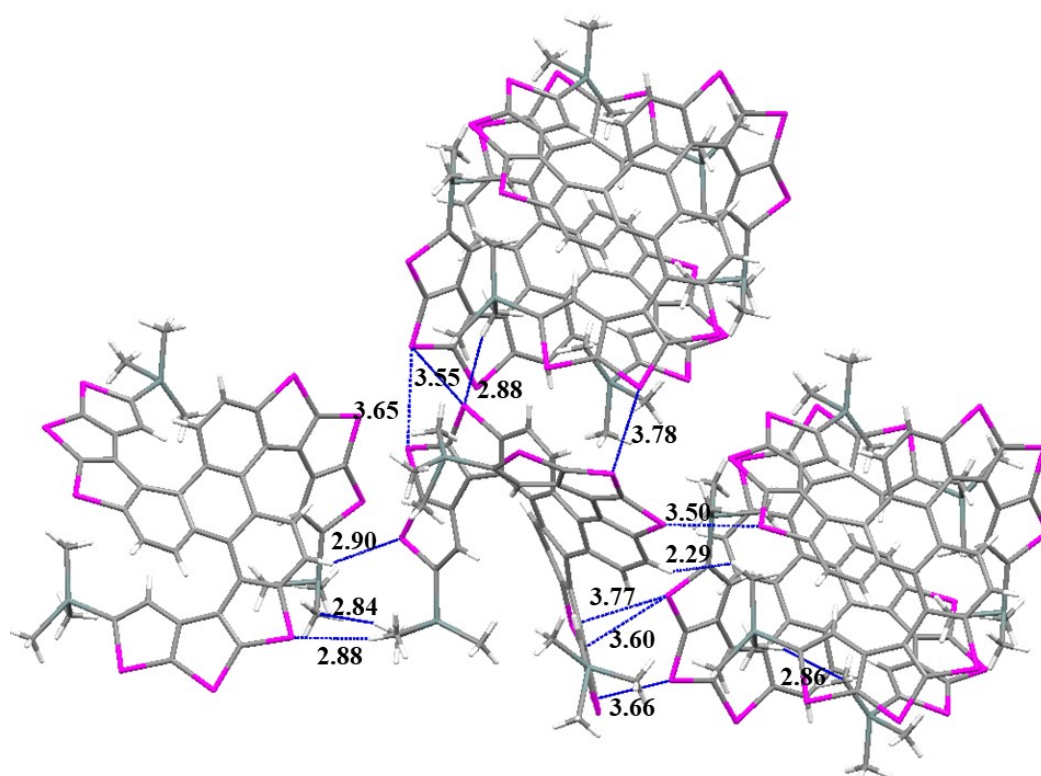


Fig. S46. Multiple interactions in the crystal packings of *rac-1d*.

Table S8. Intermolecular interactions (Å) of *rac-1(a)–(d)*

Compound	Intermolecular interactions (Å)
<i>rac-1a</i>	S6···S17: 3.39, S10···S13: 3.49, S11···S13: 3.60, C13···S16: 3.40, C54···S15: 3.44, C83···S6: 3.38, S18···H46A: 2.78, C11···H78A: 2.85, C52···H71B: 2.81, C66···H89C: 2.79, C79···H36A: 2.85, C83···H46A: 2.63
<i>rac-1b</i>	S2···S3: 3.43, S8···S12: 3.45, C27···S10: 3.32, C67···S7: 3.49, Se6···S8: 3.47, Se4···Se6: 3.63, H13A···H15A: 2.29, H87C···S9: 2.83, H87C···C58: 2.66
<i>rac-1c</i>	Se2···H4: 3.09, C4···H13B: 2.79, H13C···H13C: 2.33, H13A···H15A: 2.29
<i>rac-1d</i>	Se1···Se5: 3.55, Se2···Se4: 3.78, Se2···Se5: 3.65, Se5···Se8: 3.66, Se6···Se9: 3.77, Se9···Se4: 3.50, Se6···C32: 3.60, Se1···H39B: 2.88, Se3···H4: 2.90, C38···H42C: 2.50, C42···H38A: 2.84, C43···H39A: 2.86, H37B···H16: 2.29, H43C···H39A: 2.35, H42C···H38B: 2.36

Table S9. Dihedral angles of fused aromatic rings in *rac-1(a)–(d)*

	Ring plane	Dihedral angles/°	Ring plane	Dihedral angles/°	Ring plane	Dihedral angles/°
<i>rac-1a</i>	AB	6.36	A'B'	2.49	A''B''	5.67
	BC	8.60	B'C'	7.77	B''C''	9.17
	CD	9.73	C'D'	10.63	C''D''	9.25
	DO	14.41	D'O'	16.15	D''O''	16.13
	AD''	46.69	A'D	43.43	A''D'	50.80
<i>rac-1b</i>	AB	4.48	A'B'	5.68	A''B''	6.16
	BC	6.75	B'C'	8.17	B''C''	8.65
	CD	9.84	C'D'	9.34	C''D''	8.70
	DO	17.13	D'O'	18.35	D''O''	15.62
	AD''	44.39	A'D	49.64	A''D'	45.64
<i>rac-1c</i>	AB	5.69	A'B'	5.69	A''B''	5.69
	BC	7.89	B'C'	7.89	B''C''	7.89
	CD	9.23	C'D'	9.23	C''D''	9.23
	DO	15.98	D'O'	15.98	D''O''	15.98
	AD''	44.63	A'D	44.63	A''D'	44.63
<i>rac-1d</i>	AB	4.29	A'B'	7.41	A''B''	4.34
	BC	6.00	B'C'	5.35	B''C''	10.92
	CD	10.45	C'D'	6.31	C''D''	8.74
	DO	21.46	D'O'	14.97	D''O''	17.71
	AD''	52.60	A'D	44.95	A''D'	44.95

Table S10. Torsion angles of the internal helix of *rac-1(a)–(d)*

	Carbon atoms	Torsion angles/°	Carbon atoms	Torsion angles/°	Carbon atoms	Torsion angles/°
<i>rac-1a</i>	C(5-6-9-10)	1.65	C(34-33-30-28)	4.83	C(40-39-22-20)	0.58
	C(6-9-10-15)	14.66	C(33-30-28-29)	11.47	C(39-22-20-21)	12.78
	C(9-10-15-16)	26.06	C(30-28-29-14)	28.08	C(22-20-21-24)	27.61
	C(10-15-16-17)	20.45	C(28-29-14-13)	16.59	C(20-21-24-25)	20.85
<i>rac-1b</i>	C(2-4-6-8)	0.84	C(24-22-20-18)	2.40	C(36-34-32-30)	2.39
	C(4-6-8-9)	11.66	C(22-20-18-14)	10.52	C(34-32-30-26)	15.59
	C(6-8-9-13)	21.58	C(20-18-14-25)	22.65	C(32-30-26-10)	21.78
	C(8-9-13-15)	19.72	C(18-14-25-27)	15.68	C(30-26-10-11)	15.73
<i>rac-1c</i>	C(11-10-7-6)	2.77	C(11-10-7-6)	2.77	C(11-10-7-6)	2.77
	C(10-7-6-1)	12.58	C(10-7-6-1)	12.58	C(10-7-6-1)	12.58
	C(7-6-1-2)	27.15	C(7-6-1-2)	27.15	C(7-6-1-2)	27.15
	C(6-1-2-3)	20.49	C(6-1-2-3)	20.49	C(6-1-2-3)	20.49
<i>rac-1d</i>	C(11-10-7-6)	6.00	C(23-22-19-18)	8.51	C(35-34-31-30)	0.83
	C(10-7-6-1)	13.39	C(22-19-18-13)	21.11	C(34-31-30-25)	9.68
	C(7-6-1-26)	24.12	C(19-18-13-2)	26.01	C(31-30-25-14)	32.80
	C(6-1-26-27)	25.17	C(18-13-2-3)	14.22	C(30-25-14-15)	19.97

6. References

- [1] J. Suffert, Simple Direct Titration of Organolithium Reagents Using N-Pivaloyl-otoluidine and/or N-pivaloyl-*o*-benzylaniline, *J. Org. Chem.*, 1989, **54**, 509–510.
- [2] G. M. Sheldrick, *SADABS*, University of gottingen: Germany, 1996.
- [3] G. M. Sheldrick, *SHELXTL*, version. 5.1; Bruker analytical X-ray systems, Inc.: Madison, WI, 1997.