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Supporting Information for:

Syntheses and Structures of [7]Helicene and Double Helicene Based on Dithieno[2,3-*b*:2',3'-*d*]thiophene

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1. General Experimental Details

Ether and tetrahydrofuran (THF) for use on vacuum line were freshly distilled from sodium/benzophenone prior to use. Compound **14** was prepared according to our previous research work.[S1] *t*-BuLi (pentane) and *n*-BuLi (hexane) were obtained from Energy Chemical, prior to use, their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine.[S2] Column chromatography was carried out on silica gel (200-300 or 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 stop-cock were employed. All starting materials and reagents were commercially available.

^{1}H NMR and ^{13}C NMR spectra were recorded on 300 or 400 MHz NMR instrument using $CDCl_3$ and benzene-d_6 as solvents. IR spectra were obtained using an FT-IR instrument. HRMS analysis was carried out on a mass spectrometer, operation mode is EI or MALD/DHB. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. The X-ray crystallographic analyses were performed using crystals of compounds **11**, **14**, *rac*-**1** and **4** with the size 0.46 x 0.23 x 0.19, 0.19 x 0.15 x 0.13, 0.39 x 0.32 x 0.27, 0.43 x 0.26 x 0.17 mm^3, respectively. The intensity data were collected with the ω scan mode (296 K) on diffractometer with CCD detector using Mo K_α radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarisation effects and absorption corrections were performed using SADABS program.[S3] The crystal structures were solved using the SHELXTL program and refined using full matrix least squares.[S4] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Further details are in the deposited CIFs. Slow evaporation of solutions of **11**, **14**, *rac*-**1** and **4** in $CHCl_3$-CH_3OH was employed for growing single crystals.

Reference

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2. Experimental Procedures

Synthesis of 2,3-dibromo-5-trimethylsilylthiophene (8)

Me_3SiCl (0.4 mL, 3.1517 mmol, 1.2 equiv) was added dropwise to the LDA (1.05 equiv) solution in Et_2O (30 mL) at -78 °C, after 15 min at -78 °C, 2,3-dibromothiophene (0.6411 g, 2.6499 mmol, 1.0 equiv) was added dropwise to mixture of LDA and Me_3SiCl. After keeping at -78 °C for 15 min, the reaction mixture was warmed slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O (30 mL), extracted with Et_2O (2 × 40 mL), and then washed with H_2O (2 × 40 mL). After drying over $MgSO_4$, the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield **8** (0.8121 g, 97%) as a colorless liquid. From the other reaction on a 10.685 g scale of 2,3-dibromothiophene, 13.3521 g (96%) of **8** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.00 (s, 1H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.0, 136.1, 115.4, 115.2, -0.5. HRMS (EI^+ 70 eV) *m*/*z* calcd for [$C_7H_{10}Br_2SSi$] 311.8639, found 311.8637. IR(liquid): 2956, 2896 cm^{-1}.

Synthesis of 3-bromo-5-trimethylsilanyl-[2,3']bithiophene (9)

Compound **8** (0.5855 g, 1.8639 mmol), thiophen-3-ylboronic acid (0.2623 g, 2.0504 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (86.2 mg, 0.074 mmol, 0.04 equiv) and K_2CO_3 aqueous solution (2 M, 2.3 mL, 4.6 mmol, 2.5 equiv) were added into THF(100 mL) under argon. The reaction mixture was stirred for 48 h at 80 °C. The reaction mixture was

extracted with chloroform (3 × 10 mL) and washed with H_2O (2 × 20 mL). After drying over $MgSO_4$, the solvent was removed in vacuo to obtain the crude. The crude was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield **9** (0.3352 g, 57%) as a colorless liquid. From the other reaction on a 6.7347 g scale of **8**, 4.1620 g (61%) of **9** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.45 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.37 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.12 (s, 1H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.1, 138.04, 138.00, 133.1, 127.6, 125.6, 122.9, 108.3, -0.4. HRMS (EI 70 eV) *m*/*z* calcd for [$C_{11}H_{13}BrS_2Si$] 315.9411, found 315.9410. IR(liquid): 3109, 2954, 2894 cm^{-1}.

Synthesis of 2-trimethylsilanyl-dithieno[2,3-*b*:2',3'-*d*]thiophene (10)

To a solution of **9** (0.3062 g, 0.9649 mmol) in dry ethyl ether (10 mL), *n*-BuLi (2.2935 M in hexane, 0.86 mL, 2.05 equiv) was added dropwise at -78 °C. After keeping at -78 °C for 2 h, dry $(PhSO_2)_2S$ (0.3021 g, 0.9614 mmol, 0.95 equiv) was added. The reaction mixture was kept at -78 °C for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 20 mL). The organic layer was washed with water (3 × 25 mL) and then dried over $MgSO_4$. The colorless liquid **10** (0.1297 g, 50%) was obtained by column chromatography on silica gel with petrol ether (60-90 °C) as eluent. From other reaction on the 2.7969 g scale of **9**, 1.1074 g (47%) of **10** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.38 (d, *J* = 5.2 Hz, 1H), 7.35 (s, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 143.3, 141.2, 139.7, 137.2, 135.8, 127.9, 126.2, 118.6, -0.1. HRMS (EI, 70 eV) *m*/*z* calcd for [$C_{11}H_{12}S_3Si$] 267.9870, found 267.9874. IR (KBr): 3105, 3078, 2954, 2896 cm^{-1}.

Synthesis of 6-bromo-2-trimethylsilanyl-dithieno[2,3-*b*:2',3'-*d*]thiophene (11)

n-BuLi (2.3353 M in hexane, 0.6 mL, 1.4012 mmol, 1.5 equiv) was added dropwise to diisopropylamine (0.24 mL, 1.7029 mmol, 1.8 equiv) in THF (5 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **10** (0.3495 g, 1.3017 mmol) in dry ethyl ether (10 mL) at -78 °C. After keeping at -78

°C for 2 h, $C_2Br_2Cl_4$ (0.4620 g, 1.4187 mmol, 1.1 equiv) was added. The reaction mixture was kept at -78 °C for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 20 mL). The organic layer was washed with water (3 × 25 mL) and then dried over $MgSO_4$. The white product **11** (0.4368 g, 97%) was obtained by column chromatography on silica gel with petrol ether (60-90 °C) as eluent. From other reaction on the 0.5985 g scale of **10**, 0.7588 g (98%) of **11** was obtained. Mp: 85-86 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm):7.332 (s, 1H), 7.330 (s, 1H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 142.5, 142.1, 138.5, 136.5, 135.5, 126.0, 121.7, 113.0, -0.2. HRMS (EI^+, 70 eV) *m*/*z* calcd for [$C_{11}H_{11}BrS_3Si$] 345.8976, found 345.8973. IR: 3095, 2951, 2893, 2854 cm^{-1}.

Synthesis of 7-bromo-2-trimethylsilanyl-dithieno[2,3-*b*:2',3'-*d*]thiophene (12)

n-BuLi (2.3353 M in hexane, 0.2 mL, 0.4671 mmol, 1.5 equiv) was added dropwise to diisopropylamine (0.08 mL, 0.5676 mmol, 1.8 equiv) in THF (5 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **11** (0.1028 g, 0.2959 mmol) in THF (10 mL) at -30 °C. After 10 h at -30 °C, methanol (excess) was added to quench the reaction. The reaction mixture was extracted with $CHCl_3$ (3 × 15 mL) and washed with saturated NaCl (30 mL) and water (30 mL), and then dried over $MgSO_4$. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield colorless ropiness liquid **12** (98.3 mg, 96%). From other reaction on the 0.6374 g scales of **11**, 0.5788 g (91%) of **12** were obtained. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.36 (s, 1H), 7.27 (s, 1H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 143.6, 142.8, 138.7, 137.0, 135.0, 125.8, 124.0, 102.3, -0.2. HRMS (EI, 70 eV) *m*/*z* calcd for [$C_{11}H_{11}BrS_3Si$] 345.8976, found 345.8975. IR: 3106, 2954, 2894 cm^{-1}.

Synthesis of 2,2'-di(trimethylsilanyl)-7,7'-bis-dithieno-[2,3-*b*:2',3'-*d*]thiophene (13)

To the solution of **12** (0.1359 g, 0.3912 mmol) in dry ethyl ether (10 mL), *t*-BuLi (1.7588 M in pentane, 0.46 mL, 0.8090 mmol, 2.1 equiv) was added dropwise at -78 °C. After keeping for 2 h at -78 °C, dry $CuCl_2$ (0.1631 mg, 1.2131 mmol, 3.0 equiv) was added. The reaction mixture then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 20 mL). The organic layer was washed with water (3 × 25 mL) and then dried over $MgSO_4$. The white product **13** (0.0531 g, 51%) was obtained by column chromatography on silica gel with petrol ether (60-90 °C) as eluent. From other reaction on the 0.7492 g scale of **12**, 0.3160 g (55%) of **13** was obtained. Mp: 182-184 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.71 (s, 2H), 7.37 (s, 2H), 0.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 143.8, 141.3, 140.2, 136.6, 135.4, 127.5, 126.1, 124.8, -0.1. HRMS (Tesla FTMS) *m*/*z* calcd for [$C_{22}H_{22}S_6Si_2$] 533.9584, found 533.9563. IR (KBr): 3098, 2951, 2890 cm^{-1}.

Synthesis of [7]helicene (*rac*-1)

n-BuLi (2.2637 M in hexane, 0.26 mL, 0.5885 mmol, 2.2 equiv) was added dropwise to diisopropylamine (0.1 mL, 0.7095 mmol, 2.7 equiv) in Et_2O (15 mL) at 0 °C. After 1.5 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **13** (19.8 mg, 0.0198 mmol) in Et_2O (20 mL) at 0 °C. After 2 h at 0 °C, dry $(PhSO_2)_2S$ (12.6 mg, 0.0401 mmol, 1.0 equiv) was added at 0 °C, then the reaction mixture was kept at 0 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 20 mL) and then washed with water (2× 30 mL). After drying over $MgSO_4$, 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 *rac*-**1** (0.0167 g, 80%) as a white solid. From other reaction on the 0.0442 g scales of **13**, 0.0337 g (72%) of *rac*-**1** were obtained, respectively. Mp: 265-268 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.40 (s, 2H), 0.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 143.2, 141.6, 140.7, 140.2, 135.9, 130.3, 129.1, 125.5, -0.0. HRMS (Tesla FTMS) *m*/*z* calcd for [$C_{22}H_{20}S_7Si_2$] 563.9148, found 563.9131. IR (KBr): 3069, 2952 cm^{-1}.

Synthesis of D_2-Symmetric Dimer (*rac*-2)

LDA (0.83 mmol, 4.05 equiv) solution in Et_2O (5 mL) was added dropwise into the solution of **13** (0.1101 g, 0.21 mmol) in Et_2O (10 mL) at -78 °C. Reaction mixture was warmed up slowly to 0 °C for and kept for 2 h, then dry $CuCl_2$ (0.1407 g, 1.05 mmol, 5.0 equiv) was added at -78 °C. The reaction mixture was warmed up slowly to ambient temperature and kept for 13 h. The reaction mixture was warmed up slowly to 60 °C kept for 6 h. The reaction mixture was quenched with water, extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was washed with water (2 × 20 mL), and then dried over $MgSO_4$, 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 *rac*-**2** (0.0471 g, 43%) as a yellow solid, Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): 7.20 (s, 4 H), 0.13 (s, 36 H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm): 142.8, 142.6, 140.9, 137.3, 136.8, 135.0, 127.4 , 124.6 , -0.13. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{44}H_{40}Si_4S_{12}$] 1063.8856. found 1063.8882. IR (KBr): 3070, 2954, 1373 cm^{-1}.

Synthesis of 6-trimethylsilanyl-dithieno[2,3-*b*:2',3'-*d*]thiophene-2-carbaldehyde (15)

n-BuLi (2.39 M in hexane, 0.24 mL, 0.55 mmol, 1.0 equiv) was added dropwise to **14** (0.19 g, 0.55 mmol) in THF (15 mL) at -78 °C. After 1.5 h at -78 °C, DMF (0.08 mL, 1.03 mmoL, 2.0 equiv) was added at -78 °C, then the reaction mixture warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with $CHCl_3$ (3 × 10 mL). The organic layer was washed with saturated NaCl (20 mL) and water (2 × 20 mL), and then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield **15** (0.14 g, 86%) as a yellow solid. From other reaction on the 0.40 g of **14**, (0.30 g, 90%) of **15** was obtained. Mp: 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, H), 7.93 (s, 1H), 7.47 (s, 1H), 0.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 149.3, 147.1, 143.2, 141.9, 139.4, 137.4, 130.0, 125.0, -0.2. HRMS

(EI$^+$, 70 eV) m/z calcd for [$C_{12}H_{12}OS_3Si$] 295.9820, found 295.9822. IR (KBr): 2800, 2948 cm^{-1}, 1664 cm^{-1}.

Synthesis of 1,2-bis(6-(trimethylsilyl)dithieno[2,3-*b*:2',3'-*d*]thiophen-2-yl)ethene (16)

$TiCl_4$ (0.18 mL, 1.65 mmol, 5.0 equiv) was carefully added into dry THF (10 mL) at 0 °C. After keeping at 0 °C for 30 min, zinc dust (0.21 g, 3.30 mmol, 10.0 equiv) was added, and then the mixture was refluxed at 85 °C for 2 h. After that, pyridine (0.14 mL, 1.65 mmol, 5.0 equiv) was added and the mixture was refluxed for another 1 h. After cooling to ambient temperature, a solution of **15** (0.10 g, 1 mmol) in dry THF (5 mL) was added and the reaction mixture was refluxed at 90 °C for 18 h. The reaction was quenched with water at 0 °C, then extracted with $CHCl_3$ (3 × 15 mL) and washed with saturated NH_4Cl (10 mL) and H_2O (3 × 10 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, the residue was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield **16** (0.08 g, 85%) as a yellow solid. From other reaction on the 0.25 g of **15**, 0.212 g (90%) of **16** was obtained. Mp: 245-247 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.20 (s, 2H), 7.08 (s, 2H), 0.39 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 144.4, 142.4, 142.1, 139.9, 128.8, 124.5, 121.5, 119.4, -0.1. HRMS (MALDI) m/z calcd for [$C_{24}H_{24}Si_2S_6$] 559.9741, found 559.9753. IR (KBr): 2952, 3018, 3067 cm^{-1}.

Synthesis of bull's horn-shaped benzohexathienoacene (4)

To a solution of **16** (0.023 g, 0.04 mmol) in dry toluene (40 mL), iodine (5.3 mg, 0.02 mmol, 0.5 equiv) was added. The reaction solution was irradiated with a 450 W unfiltered Hg medium pressure lamp for 40 minutes. The reaction was quenched with saturated $Na_2S_3O_3$ (5 mL). The reaction mixture was extracted with $CHCl_3$ (3 × 10 mL) and washed with H_2O (3 × 10 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, the crude product was purified by column chromatography on silica gel with petrol ether (60-90 °C) /$CHCl_3$ (4:1, v/v) as eluent to yield **4** (0.017 mg, 72%) as a yellow solid. From other reaction on the 0.032 g of **16**, 0.023 g (70%) of **4**

was obtained. Mp: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.50 (s, 2H), 0.42 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 144.8, 139.9, 138.7, 135.6, 129.4, 126.7, 124.7, 119.7, -0.1. HRMS (MDALI) m/z calcd for [$C_{24}H_{22}$ $Si_2S_6^{+1}$] 557.9584, found 557.9595. IR (KBr): 2953, 2894, 1631, 1555, 1531 cm^{-1}.

Synthesis of 2-bromo-dithieno[2,3-*b*:2',3'-*d*]thiophene (17)

14 (0.30 g, 0.86 mmol) was dissolved in 15 mL $CHCl_3$, TFA (0.12 mL, 1.72 mmol, 2.0 equiv) was added dropwise. The mixture was stirred at room temperature for 2 h, then the reaction mixture was quenched with 10 mL water and extracted with chloroform (3 × 10 mL), then washed with saturated $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried over anhydrous $MgSO_4$. After the solvent was removed under vacuum, the residue was purified by column chromatography on silica gel with PE (60-90 °C) as eluent to yield **17** (0.22 g, 95%) as a white solid. From other reactions on the 0.45 g scale of **14**, 0.35 g (97%) of **17** were obtained, respectively. Mp: 84-86 °C. ^{1}H NMR (400 MHz, benzene-d_6) δ 6.66 (d, J = 5.2 Hz, 1H), 6.60 (d, J = 5.2 Hz, 1H), 6.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.5, 137.5, 131.1, 128.5, 122.9, 118.1, 111.7. HRMS (EI^+, 70 eV): m/z calcd for [$C_8H_3S_3Br$] 273.8580, found 273.8578. IR (KBr): 2895, 2953, 3060 cm^{-1}.

Synthesis of 2-[(5-trimethylsilyl)-2-thienyl]-dithieno[2,3-*b*:2',3'-*d*]thiophen (18)

Compound **17** (0.36 g, 1.31 mmol), trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thio-phen-2-yl)silane (0.4 g, 1.41 mmol 1.05 equiv), K_2CO_3 (0.45 g, 3.28 mmol, 2.5 equiv) and $Pd(PPh_3)_4$ (90.80 mg, 78.61 μmol, 0.06 equiv) were added into a Schlenk vessel under argon, then THF (20 mL) and water (0.85 mL) were added into the mixture. The reaction mixture was stirred for 23 h at 80 °C. The reaction mixture was extracted with chloroform (3 × 30 mL), and finally dried over anhydrous $MgSO_4$. After the solvent was removed in vacuum, the residue was purified by column chromatography on silica gel with petroleum ether (60-90 °C) as eluent to yield **18** (0.37 g, 81%) as a white solid. From other two reactions on the 0.44 g and 0.42 g scales of **17**, 0.46 g (84%) and 0.43 g (82%) of **18** were obtained,

respectively. Mp: 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz 1H), 7.36 (s, 1H), 7.29 (d, *J* = 8.0 Hz 1H), 7.27 (d, *J* = 4.0 Hz 1H), 7.17 (d, *J* = 4.0 Hz 1H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.6, 140.2, 138.7, 137.7, 137.4, 134.8, 129.5, 128.3, 125.0, 118.3, 116.7, -0.1. HRMS (MADLI/DBH) m/z calcd for [$C_{15}H_{14}S_4Si$] 349.9748, found 349.9729. IR (KBr): 2895, 2953, 3060 cm^{-1}.

Synthesis of 2-(5-(trimethylsilyl)thiophen-2-yl)dithieno[2,3-*b*:2',3'-*d*]thiophene-6-carbaldehyde (19)

n-BuLi (2.36 M in hexane, 0.10 mL, 0.25 mmol, 1.2 equiv) was added dropwise to **18** (0.12 g, 0.21 mmol) in THF (12 mL) at -78 °C. After 2 h at -78 °C, DMF (0.04 mL, 0.42 mmoL, 2.0 equiv) was added at -78 °C, then the reaction mixture warmed up slowly to ambient temperature over night. The reaction mixture was quenched with water, extracted with $CHCl_3$ (3 × 10 mL). The organic layer was washed with saturated NaCl (20 mL) and water (2 × 20 mL), and then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel with petrol ether (60-90 °C) as eluent to yield **19** (0.12 g, 90%) as a yellow solid. From other reaction on the 0.265 g of **18**, 0.25 g 88%) of **19** was obtained. Mp: 181-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.94 (s, 1H), 7.37 (s, 1H), 7.30 (d, *J* = 4.0 Hz 1H), 7.18 (d, *J* = 4.0 Hz 1H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5, 148.1, 146.5, 142.2, 141.7, 141.1, 139.3, 137.6, 134.8, 129.3, 127.0, 125.5, 116.4, -0.1. HRMS (EI^+, 70 ev) m/z calcd for [$C_{15}H_{14}S_4Si$] 349.9667, found 349.9701. IR (KBr): 2815, 2959, 3052, 1676 cm^{-1}.

Synthesis of 1,2-bis(2-(5-(trimethylsilyl)thiophen-2-yl)dithieno[2,3-*b*:2',3'-*d*]thiophen-6-yl)ethene (20)

$TiCl_4$ (0.14 mL, 1.25 mmol, 5.0 equiv) was added into dry THF (10 mL) at 0 °C. After keeping at 0 °C for 30 min, zinc dust (0.16 g, 2.50 mmol, 10.0 equiv) was added, and then the mixture was refluxed for 2 h at 85 °C. After that, pyridine (0.10 mL, 1.25 mmol, 5.0 equiv) was added and the mixture was refluxed for another 1 h. After cooling to ambient temperature, a solution of **19** (0.093 g, 0.25 mmol) in dry

THF (5 mL) was added and the reaction mixture was refluxed for 18 h at 90 °C. The reaction was quenched with water at 0 °C, then extracted with $CHCl_3$ (3 × 10 mL) and washed with saturated NH_4Cl (20 mL) and H_2O (3 × 10 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, orange powder centrifugal was washed from hexane, **20** was obtained (0.078 g, 86%). From other reaction on the 0.22 g of **19**, 0.187 g (82%) of **20** was obtained. Mp: >300 °C. NMR spectra were not recorded due to its poor solubility. MS (EI, 70 eV): m/z =724.2 (25) [M^+]. HRMS (MADLI) m/z calcd for [$C_{32}H_{28}Si_2S_8$] 723.9495, found 723.9497. IR (KBr): 3054, 2952, 1619, 986 cm^{-1}.

Synthesis of benzohexathia[7]helicene derivative *rac*-3

To a solution of **20** (0.044 g, 0.06 mmol) in dry toluene (60 mL), iodine (7.7 mg, 0.03 mmol, 0.5 equiv) was added. The reaction solution was irradiated with a 450 W unfiltered Hg medium pressure lamp for 40 minutes. The reaction was quenched with saturated $Na_2S_3O_3$ (5 mL). The reaction mixture was extracted with $CHCl_3$ (3 × 15 mL) and washed with H_2O (3 × 20 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, the crude product was purified by column chromatography on silica gel with petrol ether (60-90 °C) /$CHCl_3$ (4:1, v/v) as eluent to yield *rac*-**3** (0.02 g, 44%) as a yellow solid. From other reaction on the 0.073 g of **20**, 0.031 g (43%) of *rac*-**3** was obtained. Mp: 237-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.34 (s, 2H), 7.05 (d, J = 3.6 Hz 2H), 7.04 (d, J = 3.6 Hz 2H), 0.29 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 142.3, 141.8, 141.2, 140.1, 137.8, 134.7, 132.2, 131.9, 125.6, 125.3, 118.7, 116.0, -0.2. HRMS (MALDI/DBH) m/z calcd for [$C_{32}H_{26}Si_2S_8$] 721.9339, found 721.9346. IR (KBr): 3055, 2953, 1532, 1482, 1430, 840 cm^{-1}.

3. NMR and HRMS Spectra

NMR and HRMS Spectra of 8

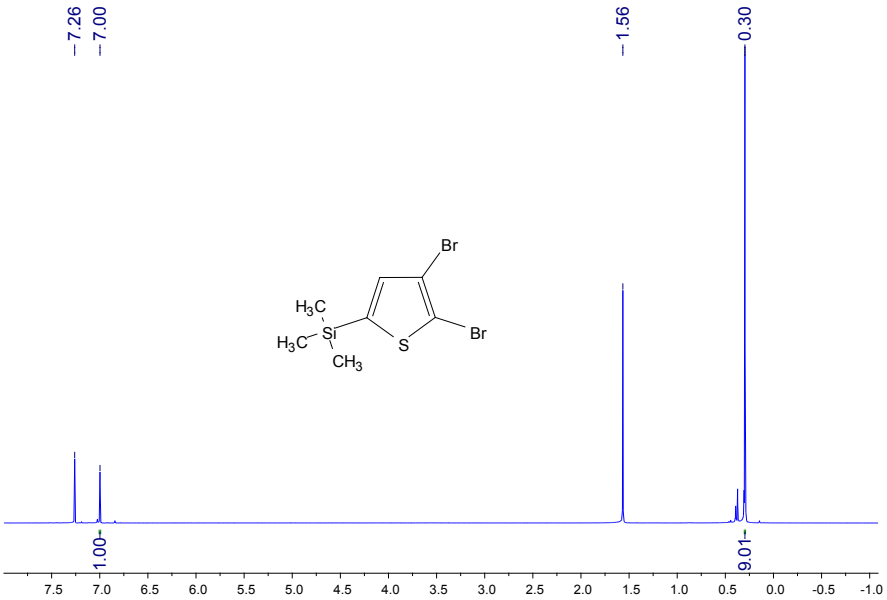

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

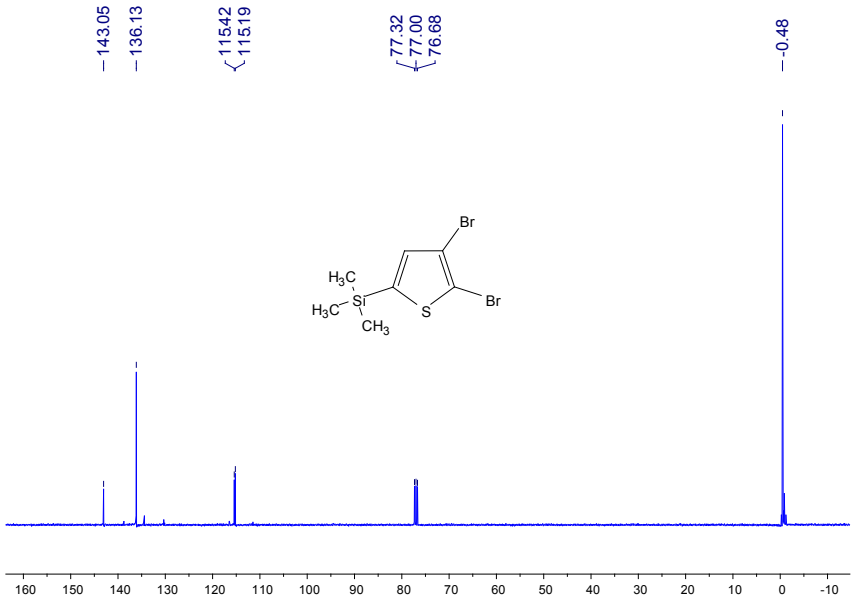

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-P-T13-09-OS0841

Sample Serial Number: WSS-2-60-col

Operator: Li

Date: 2013/10/18

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
949 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-2 O: 0-6 S: 0-2 Br: 0-2 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
311.8637	311.8636	0.1	0.3	5.5	248.1	C6 H3 N O5 S2 Br
	311.8639	-0.2	-0.6	3.0	3.8	C7 H10 S Br2 Si
	311.8634	0.3	1.0	5.5	255.2	C5 H3 N O6 S Br Si
	311.8633	0.4	1.3	4.0	24.2	C7 H6 O4 Br2

Figure S3. HRMS data of **8**

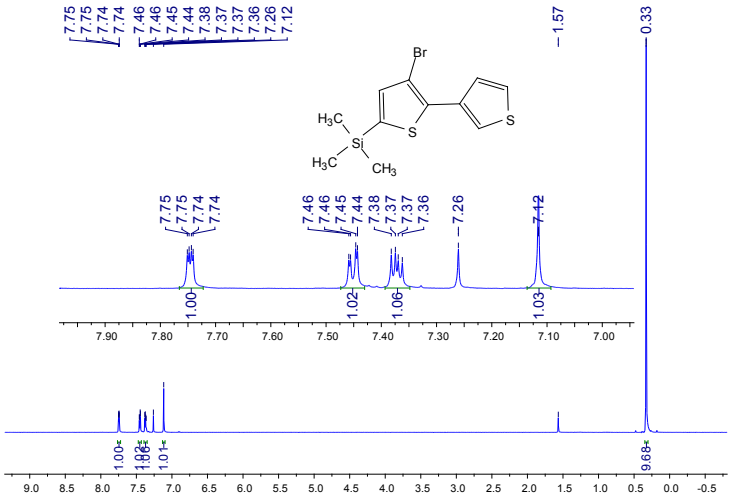

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**

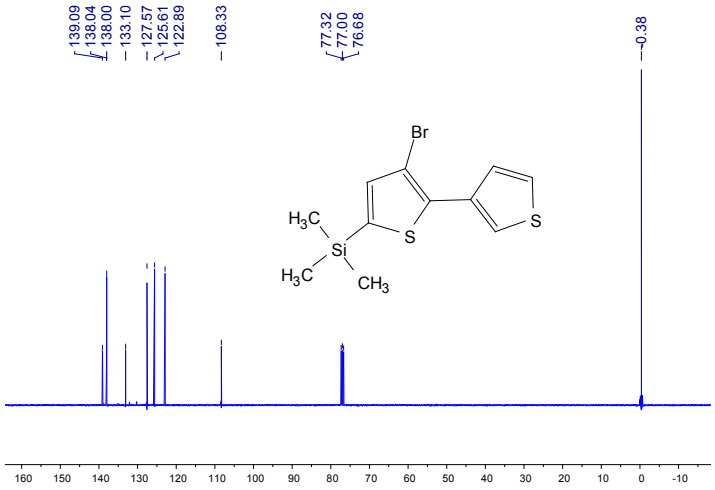

Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**

Shanghai Mass Spectrometry Center
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-T13-05-050332

Sample Serial Number: LXM-3-157col

Operator: Li

Date: 2013/05/08

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
447 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 O: 0-2 Si: 0-3 S: 0-3 Br: 0-1 I: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
315.9410	315.9411	-0.1	-0.3	6.0	3.5	C11 H13 Si S2 Br
	315.9409	0.1	0.3	6.0	32.3	C10 H13 O Si2 S Br
	315.9407	0.3	0.9	6.0	88.3	C9 H13 O2 Si3 Br
	315.9417	-0.7	-2.2	7.0	2962.1	C10 H9 O2 Si I
	315.9419	-0.9	-2.8	7.0	2953.7	C11 H9 O S I

Figure S6. HRMS data of **9**

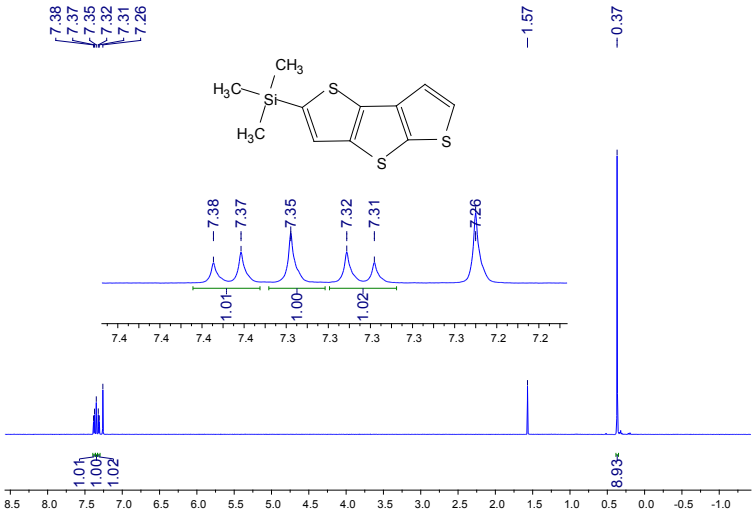

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

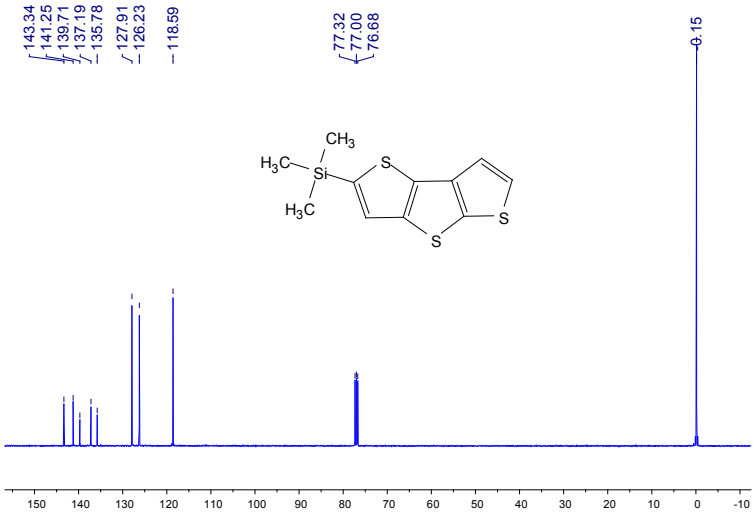

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**

Shanghai Mass Spectrometry Center
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-T13-03-OS0161

Sample Serial Number: LXM-3-168col

Operator: Li

Date: 2013/03/12

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
483 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-2 O: 0-6 S: 0-3 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
267.9874	267.9870	0.4	1.5	7.0	1.3	C11 H12 S3 Si
	267.9882	-0.8	-3.0	13.5	587.1	C13 H2 N O6
	267.9864	1.0	3.7	8.0	185.2	C11 H8 O4 S2
	267.9862	1.2	4.5	8.0	157.5	C10 H8 O5 S Si

Figure S9. HRMS data of **10**

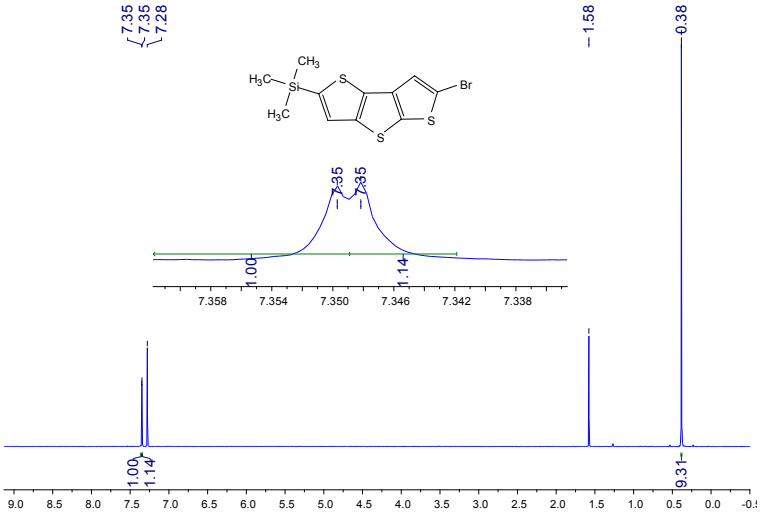

Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

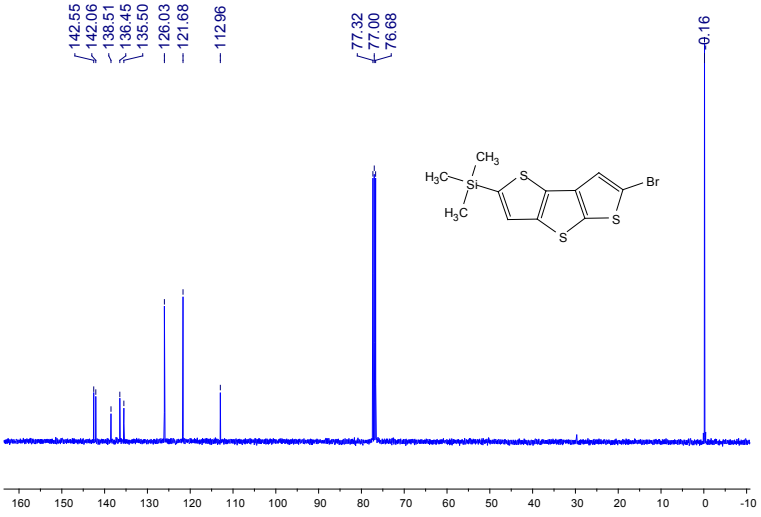

Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**

Shanghai Mass Spectrometry Center
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-T13-03 GS0162

Sample Serial Number: LXM-3-169col

Operator: Li

Date: 2013/03/12

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
840 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-2 O: 0-4 S: 0-3 Br: 0-1 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
345.8973	345.8976	-0.3	-0.9	7.0	2.8	C11 H11 S3 Br Si
	345.8969	0.4	1.2	8.0	6.4	C11 H7 O4 S2 Br
	345.8962	1.1	3.2	17.5	6.3	C17 H N O S Br
	345.8960	1.3	3.8	17.5	7.5	C16 H N O2 Br Si

Figure S12. HRMS data of **11**

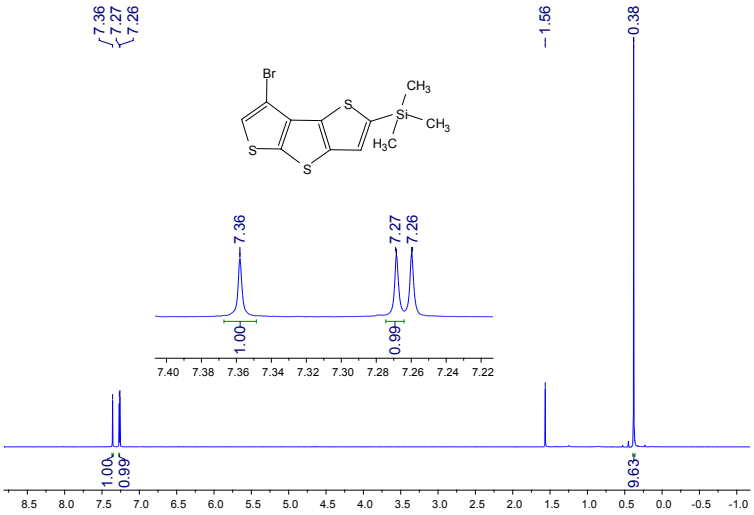

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**

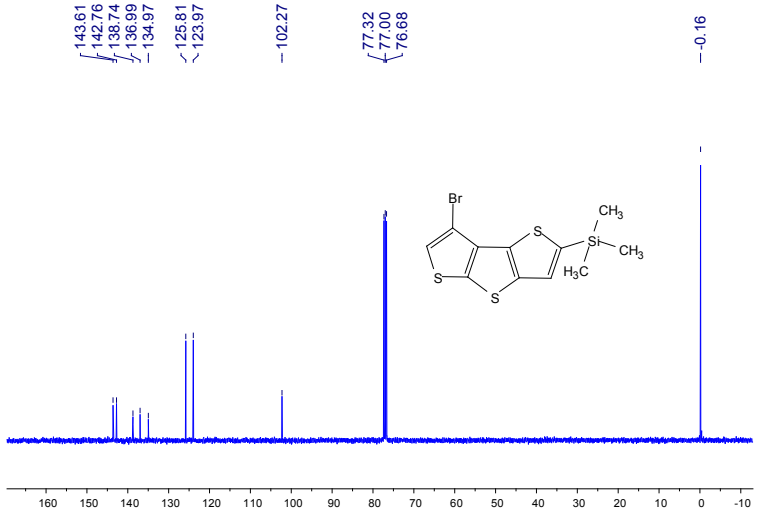

Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12**

Shanghai Mass Spectrometry Center
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-TI3-03-OS0164

Sample Serial Number: LXM-3-175-col

Operator: Li

Date: 2013/03/12

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
840 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-2 O: 0-4 S: 0-3 Br: 0-1 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
345.8975	345.8976	-0.1	-0.3	7.0	1.8	C11 H11 S3 Br Si
	345.8969	0.6	1.7	8.0	0.0	C11 H7 O4 S2 Br
	345.8962	1.3	3.8	17.5	2.6	C17 H N O S Br
	345.8960	1.5	4.3	17.5	5.9	C16 H N O2 Br Si

Figure S15. HRMS data of **12**

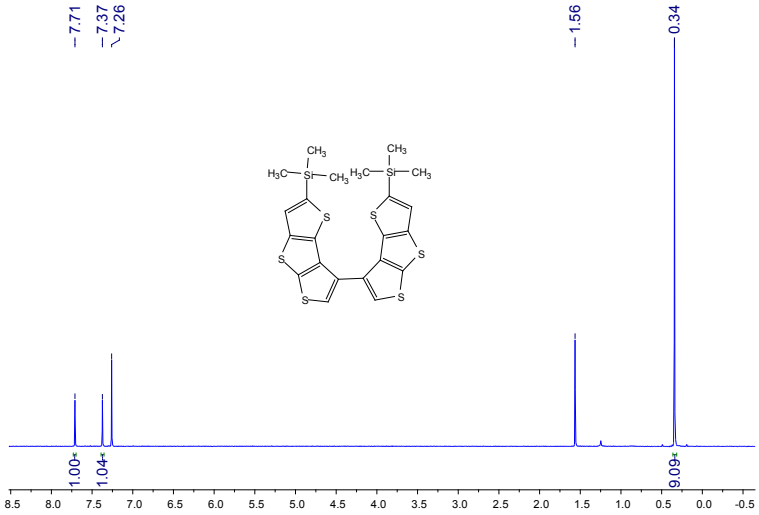

Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**

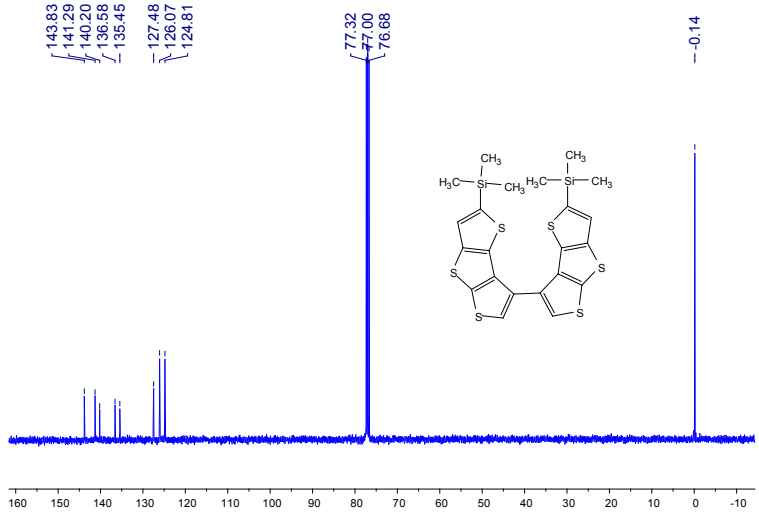

Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13**

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI13 0562

Sample Serial Number: lxm-3-178-col

Operator : HuaQin Date: 2013/03/07

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 533.9563 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	3
S	31.972071	0	7

Additional Search Restrictions:

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

Search Results:

Number of Hits = 3

m/z	Delta m/z	DBE	Formula
533.95788	-0.00158	12.0	$C_{22}H_{22}Si_2S_6^{+1}$
533.95451	0.00179	17.0	$C_{25}H_{18}Si_2S_5^{+1}$
533.95924	-0.00294	39.0	$C_{39}H_2S_2^{+1}$

Figure S18. HRMS data of **13**

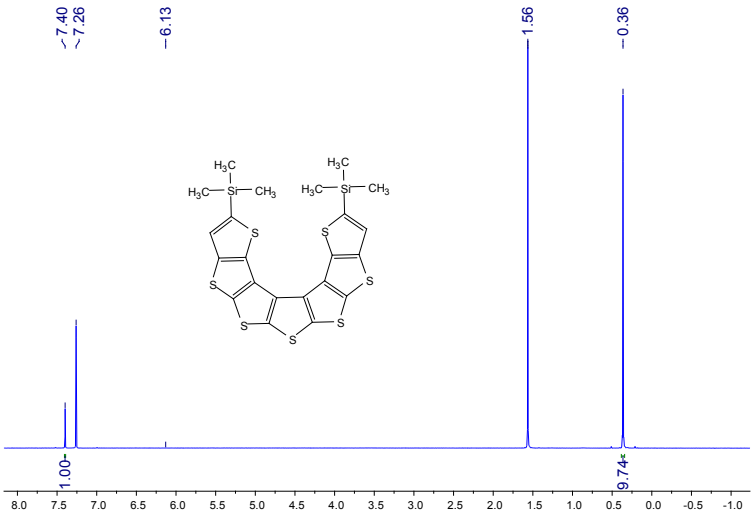

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *rac*-**1**

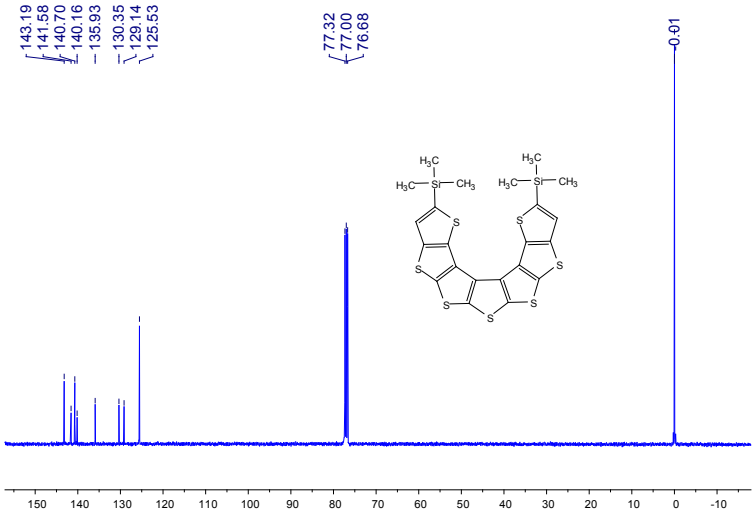

Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *rac*-**1**

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI13 0563

Sample Serial Number: lxm-3-181-col

Operator : HuaQin Date: 2013/03/07

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 563.9131 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	3
S	31.972071	0	7

Additional Search Restrictions:

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

Search Results:

Number of Hits = 3

m/z	Delta m/z	DBE	Formula
563.91430	-0.00120	13.0	$C_{22}H_{20}Si_2S_7^{+1}$
563.91093	0.00217	18.0	$C_{25}H_{16}Si_2S_6^{+1}$
563.91566	-0.00256	40.0	$C_{39}S_3^{+1}$

Figure S21. HRMS data of *rac*-**1**

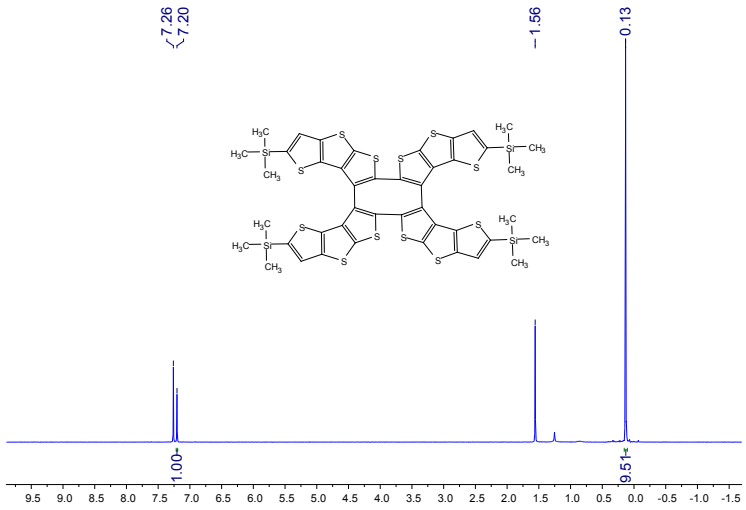

Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *rac*-**2**

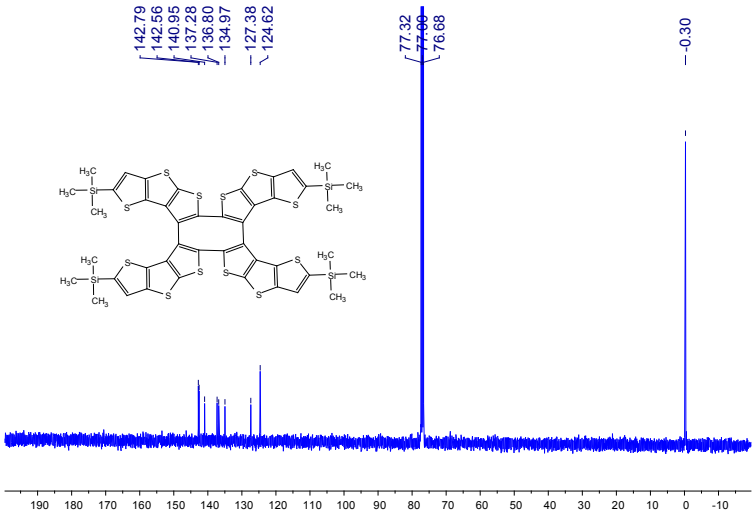

Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *rac*-**2**

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

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M150092

Sample Serial Number: wss-4-cot

Operator : HUAQIN Date: 2015/01/08

Operation Mode: MALDI_DHB

Elemental composition search on mass 1063.89

m/z= 1058.89-1068.89

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1063.8882	1063.8856	2.51	29.0	$C_{44}H_{40}S_{12}Si_4$

Figure S24. HRMS data of *rac*-**2**

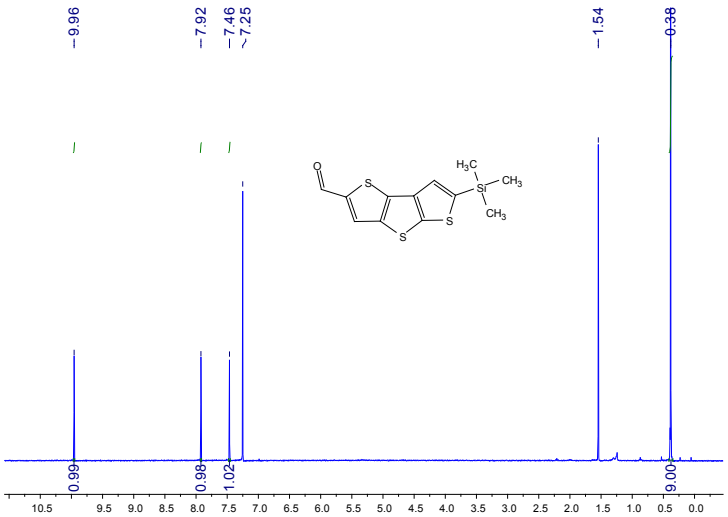

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**

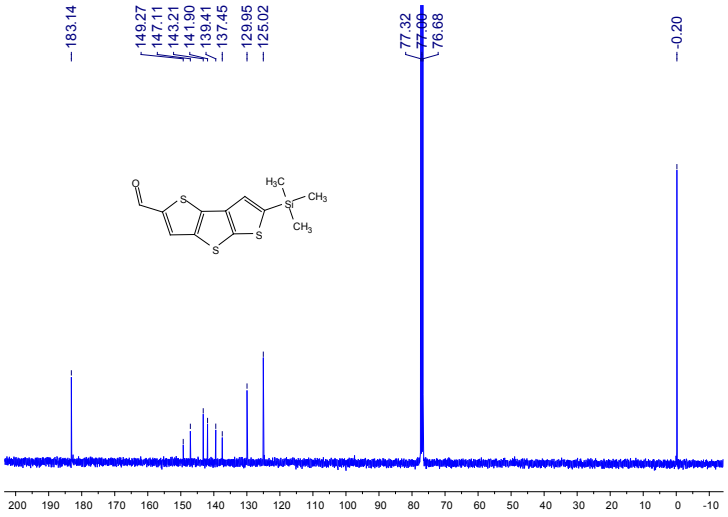

Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **15**

Shanghai Mass Spectrometry Center
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-T12-12-OS0908

Sample Serial Number: SHL-4-82

Operator: Li

Date: 2012/12/11

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
324 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-1 O: 0-4 S: 0-4 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
295.9822	295.9822	0.0	0.0	8.0	3.9	C13 H12 S4
	295.9820	0.2	0.7	8.0	0.1	C12 H12 O S3 Si

Figure S27. HRMS data of **15**

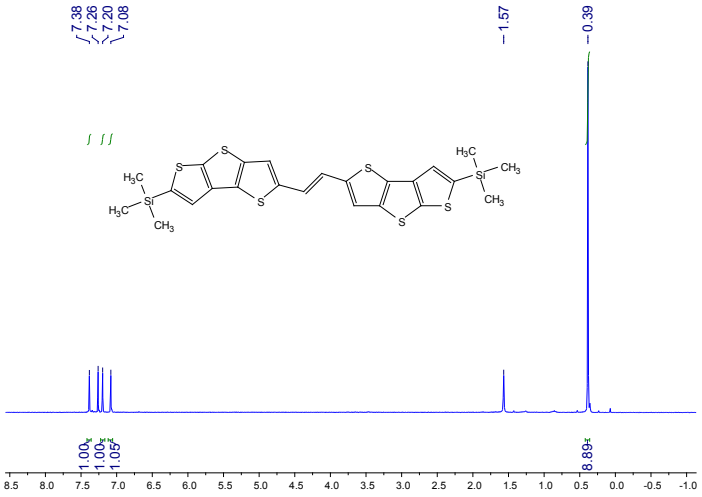

Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16**

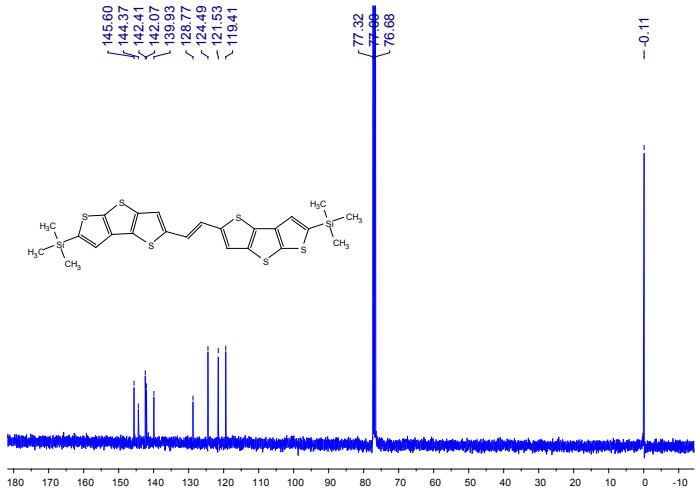

Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16**

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 : WI13 0101

Sample Serial Number: shl-4-87

Operator : HuaQin Date: 2012/12/26

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 559.9753 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	5
S	31.972071	0	9

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
559.97489	0.00041	40.0	$C_{41}H_4S_2^{+1}$
559.97690	-0.00160	8.0	$C_{21}H_{28}Si_2S_7^{+1}$
559.97353	0.00177	13.0	$C_{24}H_{24}Si_2S_6^{+1}$
559.97799	-0.00269	29.0	$C_{34}H_{12}Si_5^{+1}$
559.97826	-0.00296	35.0	$C_{38}H_8S_3^{+1}$

Figure S30. HRMS data of **16**

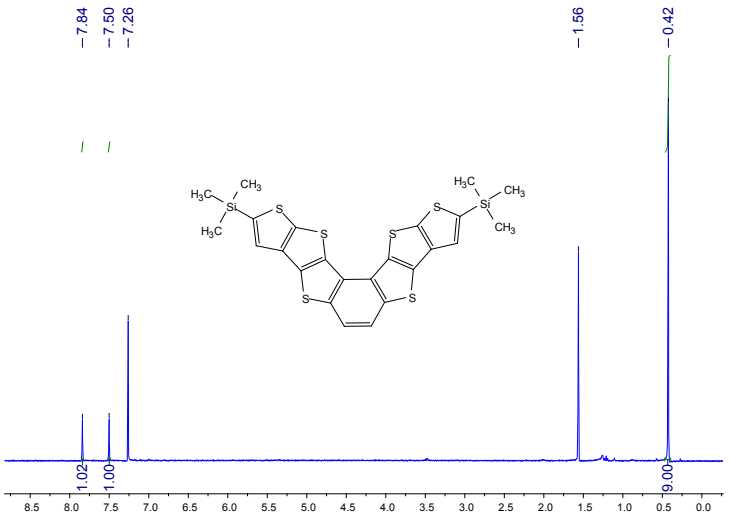

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**

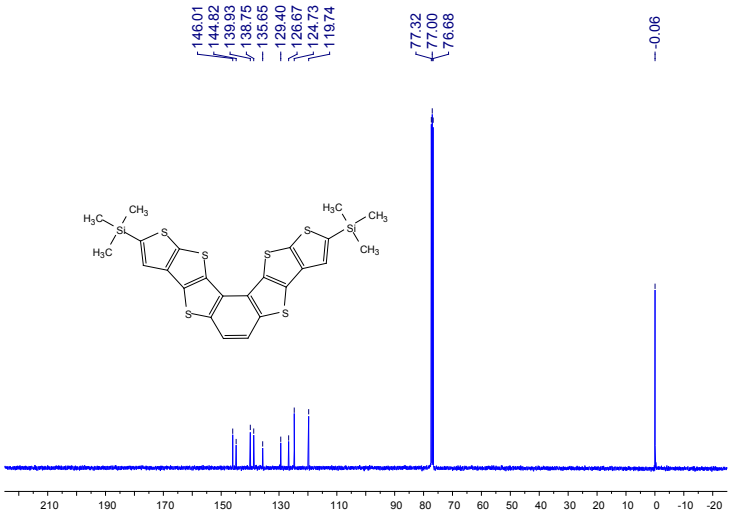

Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**

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 : WI13 0102

Sample Serial Number: shl-4-93

Operator : HuaQin Date: 2012/12/26

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 557.9595 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	5
S	31.972071	0	9

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 4

m/z	Delta m/z	DBE	Formula
557.95924	0.00026	41.0	$C_{41}H_2S_2^{+1}$
557.95788	0.00162	14.0	$C_{24}H_{22}Si_2S_6^{+1}$
557.96125	-0.00175	9.0	$C_{21}H_{26}Si_2S_7^{+1}$
557.96234	-0.00284	30.0	$C_{34}H_{10}Si_5^{+1}$

Figure S33. HRMS data of **4**

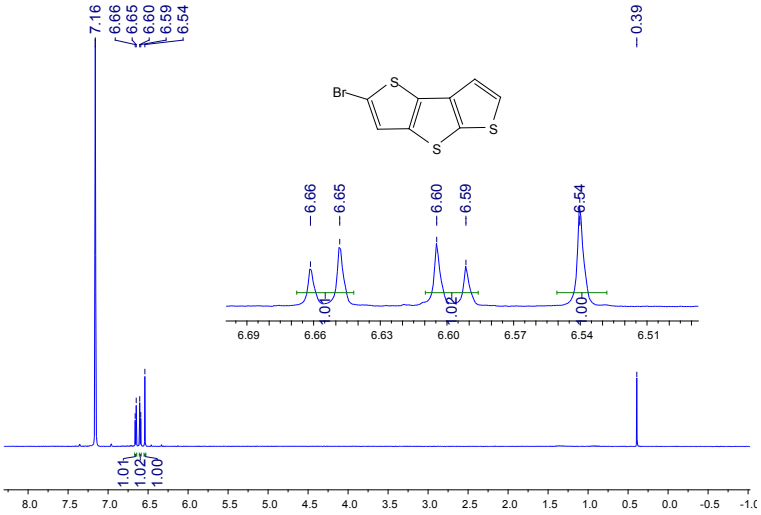

Figure S34. ^{1}H NMR (400 MHz, benzene-d_6) spectrum of **17**

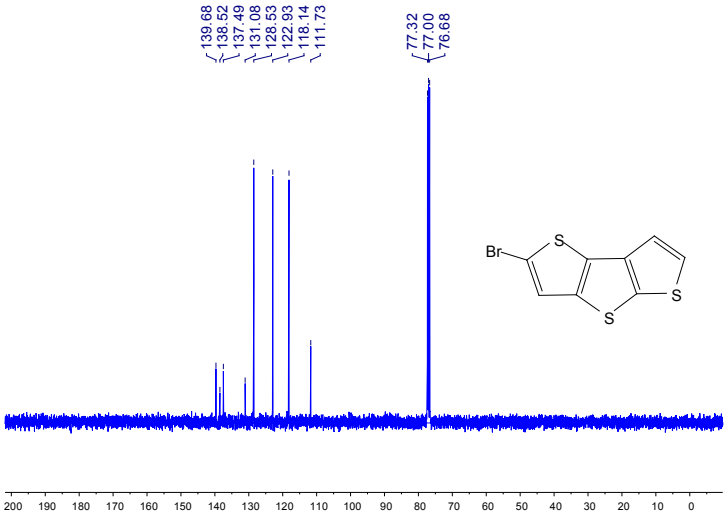

Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **17**

Shanghai Mass Spectrometry Center
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-T12-09-OS0737

Sample Serial Number: SHL-3-176

Operator: Li

Date: 2012/09/19

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
695 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-2 O: 0-4 S: 0-3 Cl: 0-1 Br: 0-2

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
273.8578	273.8580	-0.2	-0.7	7.0	2773014.5	C8 H3 S3 Br
	273.8576	0.2	0.7	3.5	2773012.8	C4 H2 N O4 S Cl Br
	273.8589	-1.1	-4.0	2.0	2773014.3	C3 H4 N2 O3 Br2

Figure S36. HRMS data of **17**

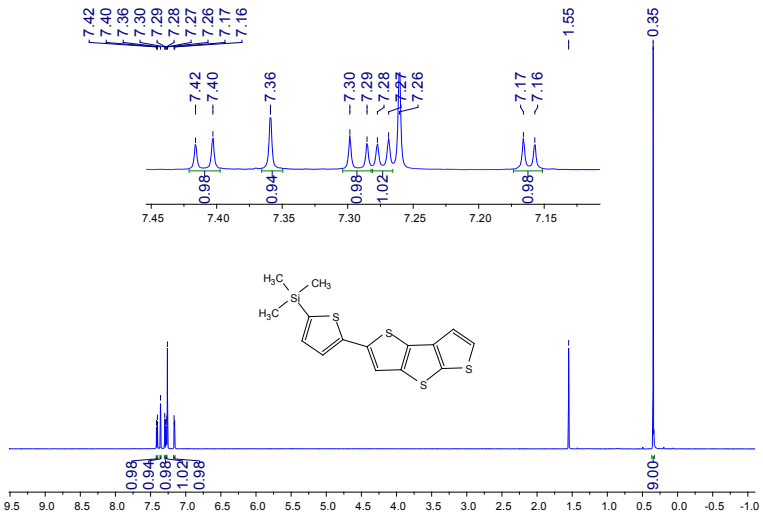

Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**

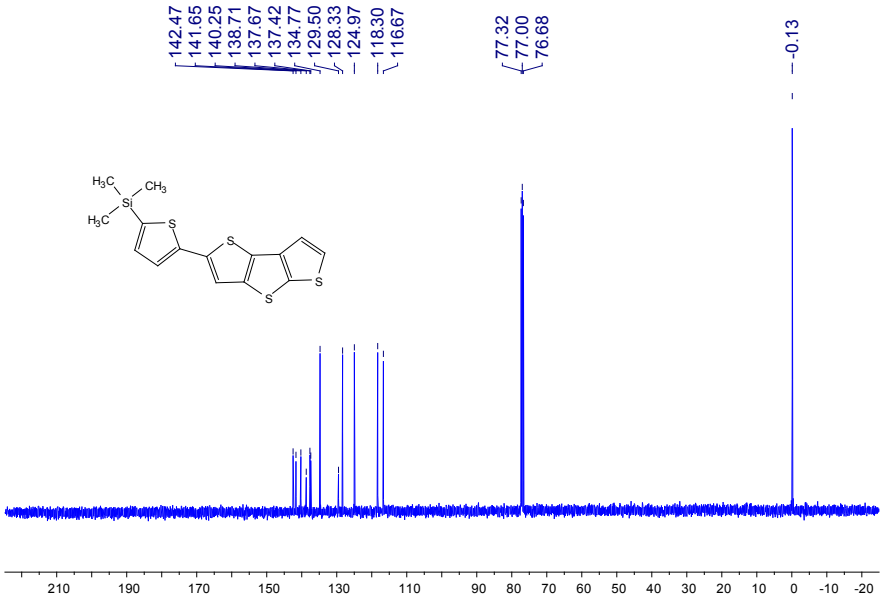

Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **18**

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 : I12 1449

Sample Serial Number: shl-3-160

Operator : HuaQin Date: 2012/09/18

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 349.9729 ± 0.002
Charge = +1

Possible Elements:

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

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 2

m/z	Delta m/z	DBE	Formula
349.97393	-0.00103	3.0	$C_{11}H_{18}SSi_6^{+1}$
349.97421	-0.00131	9.0	$C_{15}H_{14}S_4Si^{+1}$

Figure S39. HRMS data of **18**

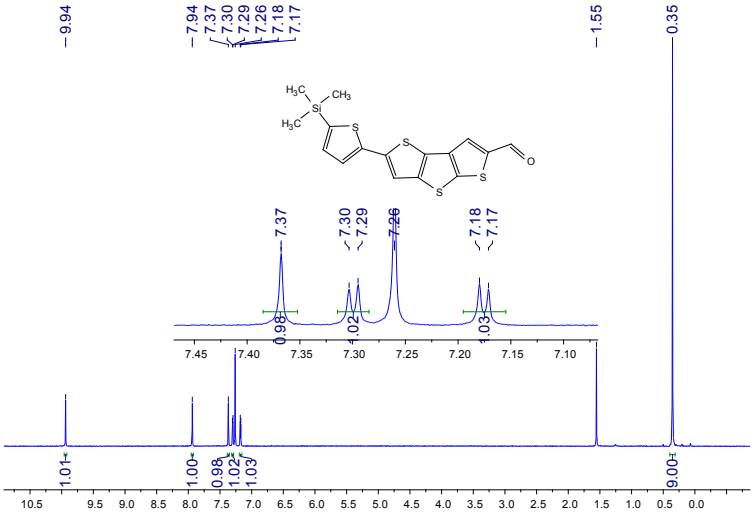

Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**

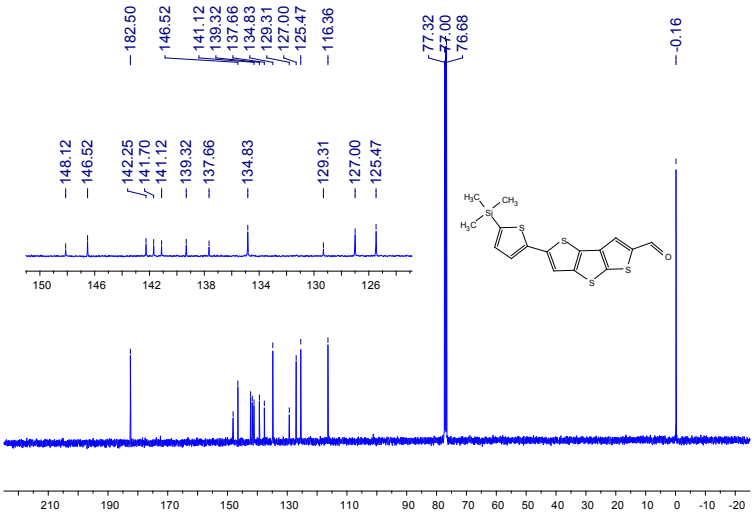

Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **19**

Shanghai Mass Spectrometry Center
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-T12-12-OS0906

Sample Serial Number: SHL-4-37

Operator: Li

Date: 2012/12/11

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
422 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-1 O: 0-4 S: 0-4 Si: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
377.9701	377.9697	0.4	1.1	11.0	3.9	C16 H14 O S4 Si
	377.9715	-1.4	-3.7	16.5	13.0	C18 H8 N O3 S2 Si
	377.9717	-1.6	-4.2	16.5	7.6	C19 H8 N O2 S3
	377.9683	1.8	4.8	21.5	21.7	C22 H4 N O2 S2

Figure S42. HRMS data of **19**

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 : WI13 0099

Sample Serial Number: shl-4-40

Operator : HuaQin Date: 2012/12/26

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 723.9497 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	5
S	31.972071	0	9

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
723.95006	-0.00036	40.0	$C_{45}H_{12}Si_5S^{+1}$
723.95034	-0.00064	46.0	$C_{49}H_8S_4^{+1}$
723.94897	0.00073	19.0	$C_{32}H_{28}Si_2S_8^{+1}$
723.95234	-0.00264	14.0	$C_{29}H_{32}Si_2S_9^{+1}$
723.94696	0.00274	51.0	$C_{52}H_4S_3^{+1}$

Figure S43. HRMS data of **20**

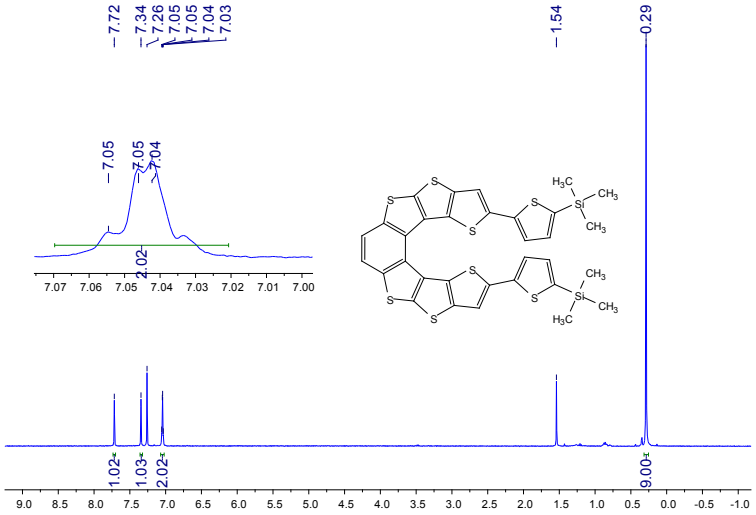

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *rac*-**3**

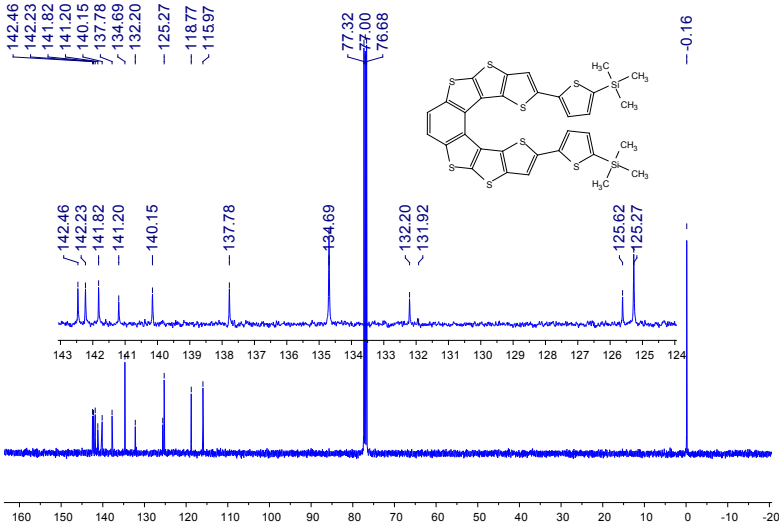

Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *rac*-**3**

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 : WI13 0100

Sample Serial Number: shl-4-60

Operator : HuaQin Date: 2012/12/26

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 721.9346 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
Si	27.976927	0	5
S	31.972071	0	9

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 4

m/z	Delta m/z	DBE	Formula
721.93469	-0.00009	47.0	$C_{49}H_6S_4^{+1}$
721.93441	0.00019	41.0	$C_{45}H_{10}Si_5S^{+1}$
721.93332	0.00128	20.0	$C_{32}H_{26}Si_2S_8^{+1}$
721.93669	-0.00209	15.0	$C_{29}H_{30}Si_2S_9^{+1}$

Figure S46. HRMS data of *rac*-**3**

4. X-ray crystallographic Data

X-ray crystallographic Data of 11

Table 1. Crystal data and structure refinement for **11**

Identification code	**11**
Empirical formula	$C_{11}H_{11}BrS_3Si$
Formula weight	347.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.5286(10) Å α = 90 °. b = 15.8164(13) Å β = 110.1900(10) °.

	c = 8.4588(7) Å γ = 90 °.
Volume	1447.6(2) Å ^{3}
Z, Calculated density	4, 1.594 Mg/m^3
Absorption coefficient	3.327 mm^{-1}
F(000)	696
Crystal size	0.46 x 0.23 x 0.19 mm^3
Theta range for data collection	1.88 to 26.00 °
Limiting indices	-14<=h<=14, -19<=k<=12, -10<=l<=10
Reflections collected / unique	7997 / 2843 [R(int) = 0.0241]
Completeness to theta = 24.99 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5706 and 0.3098
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2843 / 0 / 145
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0691
R indices (all data)	R1 = 0.0442, wR2 = 0.0751
Largest diff. peak and hole	0.266 and -0.345 e. Å $^{-3}$

X-ray crystallographic Data of *rac*-1

Table 2. Crystal data and structure refinement for ***rac*-1**

Identification code	***rac*-1**
Empirical formula	$C_{22}H_{20}S_7Si_2$
Formula weight	564.98
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 19.710(4) Å α = 90 °
	b = 13.215(3) Å β = 103.753(3) °
	c = 10.489(2) Å γ = 90°
Volume	2653.9(9) Å ^{3}
Z, Calculated density	4, 1.414 Mg/m^3
Absorption coefficient	0.695 mm^{-1}
F(000)	1168
Crystal size	0.39 x 0.32 x 0.27 mm^3
Theta range for data collection	1.87 to 26.00 °
Limiting indices	-24<=h<=24, -16<=k<=14, -12<=l<=11
Reflections collected / unique	14534 / 5193 [R(int) = 0.0230]
Completeness to theta = 24.99 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8346 and 0.7733
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5193 / 21 / 280
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0985

R indices (all data)	R1 = 0.0446, wR2 = 0.1037
Largest diff. peak and hole	0.411 and -0.554 e·Å^{-3}

X-ray crystallographic Data of 14

Table 3. Crystal data and structure refinement for **14**

Identification code	**14**
Empirical formula	$C_{11}H_{11}BrS_3Si$
Formula weight	347.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	a = 12.594(5) Å α = 90 ° b = 7.353(3) Å β = 90 ° c = 15.175(6) Å γ = 90 °
Volume	1405.2(9) Å^3
Z, Calculated density	4, 1.642 Mg/m^3
Absorption coefficient	3.427 mm^{-1}
F(000)	696
Crystal size	0.19 x 0.15 x 0.13 mm
Theta range for data collection	2.10 to 25.00 °
Limiting indices	-14<=h<=14, -8<=k<=8, -14<=l<=18
Reflections collected / unique	6936 / 1335 [R(int) = 0.0366]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.6643 and 0.5621
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1335 / 2 / 95
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0795
R indices (all data)	R1 = 0.0414, wR2 = 0.0832
Extinction coefficient	0.0055(7)
Largest diff. peak and hole	0.384 and -0.384 e. $Å^{-3}$

X-ray crystallographic Data of 4

Table 4. Crystal data and structure refinement for **4**

Identification code	**4**
Empirical formula	$C_{24}H_{22}S_6Si_2$
Formula weight	558.96
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 31.277(9) Å α = 90 ° b = 16.691(5) Å β = 93.503(6) ° c = 10.668(3) Å γ = 90 °
Volume	5559(3) $Å^3$
Z, Calculated density	8, 1.336 Mg/m^3
Absorption coefficient	0.590 mm^{-1}
F(000)	2320
Crystal size	0.43 x 0.26 x 0.17 mm
Theta range for data collection	1.38 to 25.00 °
Limiting indices	-29<=h<=37, -19<=k<=19, -12<=l<=12
Reflections collected / unique	13684 / 4896 [R(int) = 0.0661]
Completeness to theta = 25.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9063 and 0.7854

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4896 / 0 / 290
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1494
R indices (all data)	R1 = 0.1099, wR2 = 0.1644
Extinction coefficient	0.00077(17)
Largest diff. peak and hole	0.656 and -0.523 e. $Å^{-3}$

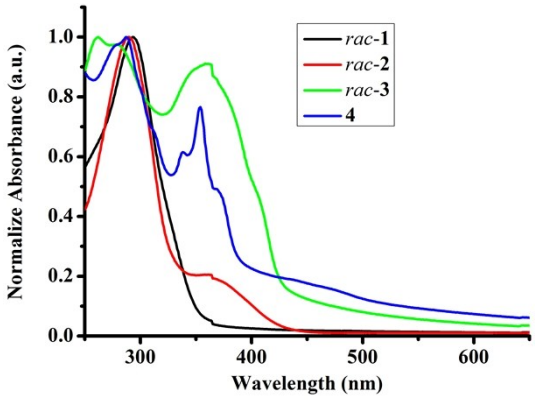

Figure S47. UV-vis absorption spectra of *rac*-**1**, *rac*-**2**, *rac*-**3** and **4** in thin films on quartz substrates.

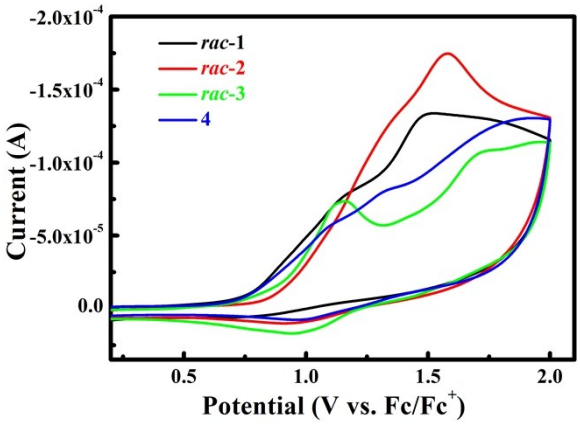

Figure S48. Cyclic voltammograms (left) of *rac*-**1**, *rac*-**2**, *rac*-**3** and **4** films in 0.1 M Bu_4NPF_6-CH_3CN solutions at a scanning rate of 100 mV/s.