

Electronic Supplementary Material (ESI)

Side Chain Engineering in DTBDT-Based Small Molecules for Efficient Organic Photovoltaics

Jisu Hong,^{a†} Ji Young Choi,^{b†} Kyunghun Kim,^a Nam-Suk Lee,^c Jiqiang Li^b Chan Eon Park,^a
Tae Kyu An ^{*d} Yun-Hi Kim ^{*e} and Soon-Ki Kwon^{*b}

^aDepartment of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

^bDepartment of Materials Engineering and Convergence Technology and ERI, Gyeongsang National University, Jinju 660-701, Republic of Korea

^cNational Institute for Nanomaterials Technology (NINT), Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea

^dDepartment of Polymer Science & Engineering and Department of IT Convergence, Korea National University of Transportation, Chungju, 380-702, Republic of Korea

^eDepartment of Chemistry and RINS, Gyeongsang National University, Jinju 660-701, Republic of Korea

[†]These authors contributed equally to this work.

Experimental section

Materials

All chemicals were purchased from Sigma-Aldrich, and TCI. Pd2(dba)3, P(o-tol)3 were used without further purification. 3,3''-Dioctyl-5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde was synthesized using procedures reported in the literature.^{R1}

Synthesis

Synthesis of 2-((2-ethylhexyl)thio)-3-octylthiophene (1)

n-BuLi (8 mL, 19.9 mmol) was added at -78 °C to a solution of 2-bromo-3-octylthiophene (5 g, 18.1 mmol) in THF (30 mL) with stirring, and then stirring of the reaction mixture was continued for one hour. 1,2-Bis(2-ethylhexyl)disulfane (7.9 g, 27.2 mmol) was added to this mixture and the reaction was allowed to warm to room temperature overnight under N₂. The reaction was terminated by including 50 mL of water extracted in ether (30 mL x 3), washed with brine and dried over anhydrous MgSO₄. The resulting crude oil was then distilled to form a clear oil identified as 2-((2-ethylhexyl)thio)-3-octylthiophene, which was obtained in 70% yield. ¹H NMR (300 MHz, CDCl₃, δ) : 7.16-7.15(J=5.4Hz, d, 1H), 6.82-6.8(J=5.4Hz, d, 1H), 2.66-2.64(J=5.9Hz, d, 2H), 2.63-2.58 (m, 2H), 1.49-1.35(m, 5H), 1.33-1.15(m, 16H), 0.83-0.75(m, 9H). ¹³C NMR (500 MHz, CDCl₃, δ) : 146.89, 129.38, 128.64, 126.96, 77.29, 77.03, 76.78, 43.61, 39.06, 32.11, 31.91, 30.82, 29.48, 29.29, 29, 28.75, 25.33, 22.98, 22.69, 14.10, 10.75, 10.71 HRMS (EI) m/z: 340.2258; found, 340.2258 (M⁺)

Synthesis of 5,10-bis(2-((2-ethylhexyl)thio)-3-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithieno [3,2-b] thiophene (2)

The reaction was carried out by following the methods reported in the literature.^{R1-2} ¹H NMR (300 MHz, CDCl₃, δ) : 7.43-7.42(J=5.2Hz, d, 2H), 7.28-7.27(J=5.2Hz, d, 2H), 7.18(s, 2H), 2.92-2.89(J=6.2Hz, d, 4H), 2.87-2.85(J=7.3Hz, d, 4H), 1.77-1.54(m, 10H), 1.53-1.33(m, 32H), 0.98-0.92(m, 18H) ¹³C NMR (500 MHz, CDCl₃, δ) : 147.54, 143.02, 139.19, 137.88, 133.45,

132.13, 130.35, 129.78, 129.49, 123.53, 119.86, 43.72, 39.15, 32.21, 31.93, 30.72, 29.54, 29.4, 29.37, 29.23, 28.93, 25.37, 23, 22.72, 14.18, 14.14, 10.85. HRMS (FAB) m/z: 978.3556; found, 978.40(M⁺).

Synthesis of 2,7-dibromo-5,10-bis(2-((2-ethylhexyl)thio)-3-octylthiophene-2-yl)benzo[1,2-b:4,5-b'] dithieno[3,2-b]thiophene (3)

The reaction was carried out by following the methods reported in the literature.² ¹H NMR (300 MHz, CDCl₃, δ) : 7.16(s, 2H), 7.04(s, 2H), 2.8-2.78(J=6.2Hz, d, 4H), 2.76-2.73(J=6.2Hz, d, 4H), 1.66-1.48(m, 10H), 1.46-1.22(m, 32H), 0.87-0.8(m, 18H). ¹³C NMR (500 MHz, CDCl₃, δ) : 147.63, 141.92, 138.15, 137.43, 133.5, 132.69, 130.36, 129.78, 123.25, 122.58, 110.37, 43.64, 39.12, 32.16, 31.95, 30.69, 29.56, 29.46, 29.36, 29.22, 28.86, 25.37, 23.05, 22.71, 14.15, 10.89. MS(MALDI-TOF): m/z 1134.1766; found, 1134.0544 (M⁺).

Synthesis of 2,7-bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde)-5,10-bis(2-((2-ethylhexyl)thio)-3-octylthiophene -2-yl)benzo[1,2-b:4,5-b']dithieno[3,2 b]thiophene (4)

Compound (2) (0.6 g, 0.527 mmol) and 3,3''-dioctyl-5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (1.04 g, 1.319 mmol) along with Pd₂(dba)₃ (0.015 g, 0.016 mmol) and tri-*o*-tolylphosphine (0.019 g, 0.063 mmol) were dissolved in dry toluene (25 ml). The resulting mixture was stirred at 110 °C for 24 h under N₂, and then the reaction was terminated using 50 mL of water. The resulting mixture was extracted in CH₂Cl₂ (30 ml x 3), washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated under vacuum, and the crude product was purified using silica gel chromatography with *n*-hexane/THF (6:1), to give a dark-red solid (0.5 g, 48%). ¹H NMR (300 MHz, CDCl₃, δ) : 9.85(s, 2H), 7.62(s, 2H), 7.33(s, 2H), 7.27-7.25(J=3.9Hz, d, 2H), 7.20(s, 2H), 7.13-7.12(J=3.9Hz, d, 2H), 7.00(s, 2H), 2.95-2.92(J=6.3Hz, d, 4H), 2.87-2.75(m, 12H), 1.82-1.62(m, 18H), 1.46-1.30(m, 72H), 0.95-0.86(m, 30H). ¹³C NMR (500 MHz, CDCl₃, δ) : 182.53, 147.52, 130.62, 43.71, 39.26, 32.23, 31.95, 31.91, 31.88, 30.90, 30.65, 30.38, 30.33, 29.70, 29.65, 29.59, 29.55, 29.52, 29.48, 29.43, 29.40, 29.33, 29.26, 28.89, 25.47, 23.05, 22.69, 14.12, 10.97. MS(MALDI-TOF): m/z 1974.7726; found, 1974.6031 (M⁺).

Synthesis of 2,7-bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-(3'-ethylrhodanine)-5,10-bis(2-(2-ethylhexyl)thio)-3-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithienof[3,2 b]thiophene (DTBDT-S-C8-TTR)

Compound (4) (0.3 g, 0.152 mmol) and 3-ethylrhodanine (0.147 g, 0.91 mmol) were dissolved in a dry chloroform (30 mL) solution under the protection of nitrogen, and then five drops of piperidine were added to the mixture. The resulting mixture was stirred at 80 °C for 48 h under N₂, and the reaction was then terminated using 50 mL of water. The resulting organic layer was removed, and the remaining aqueous phase was extracted with CH₂Cl₂ (30 ml x 3) and dried over anhydrous MgSO₄. The solvent was evaporated under vacuum, and the resulting crude product was purified using silica gel chromatography with n-hexane/MC(1:1), to give a dark red solid (0.25 g, 72%). ¹H NMR (300 MHz, CDCl₃, δ) : 7.76(s, 2H), 7.25-7.19(m, 8H), 7.08-7.07(J=3.9Hz, d, 2H), 6.96(s, 2H), 4.21-4.15(m, 4H), 2.96-2.94(J=6.3Hz, d, 4H), 2.91-2.74(m, 12H), 1.83-1.63(m, 18H), 1.45-1.28(m, 78H), 0.99-0.97(J=7.2Hz, d, 6H), 0.95-0.85(m, 24H). ¹³C NMR (500 MHz, CDCl₃, δ): 192.03, 167.30, 147.51, 142.75, 141.10, 139.91, 137.62, 137.44, 137.27, 136.23, 132.42, 130.61, 127.23, 127.10, 126.22, 124.88, 120.60, 116.04, 43.72, 39.92, 39.27, 32.26, 31.96, 31.92, 31.88, 30.92, 30.61, 30.29, 29.72, 29.57, 29.50, 29.44, 29.35, 29.28, 26.90, 25.48, 23.06, 22.71, 14.15, 12.3, 10.99. MS(MALDI-TOF): m/z 2260.7453; found, 2260.6396 (M⁺).

Instruments and measurements

¹H- and ¹³C- nuclear magnetic resonance (NMR) spectra were acquired using Bruker Advance 300 and 500 spectrometers, respectively. Thermogravimetric analysis (TGA) was performed using a TA TGA 2100 analyzer under a purified nitrogen atmosphere with a heating rate of 10 °C min⁻¹. A differential scanning calorimetry (DSC) plot was obtained using a TA Instruments 2100 DSC with a heating rate of 10 °C min⁻¹ from 0 °C to 300 °C. UV-visible-near IR spectra were obtained with a Cary 5000 UV-Vis-near-IR double-beam spectrophotometer. The highest occupied molecular orbital (HOMO) energy level was determined using cyclic voltammetry (CV) performed with a PowerLab/AD instrument model system and with the synthesized

compound in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile as the supporting electrolyte. A glassy carbon disk (ca. 0.05 cm^2) coated with a thin polymer film, an Ag/AgCl electrode, and a platinum wire were used as the working electrode, reference electrode, and counter electrode, respectively. The scan rate was 50 mV s^{-1} . Atomic force microscopy (AFM) images were acquired with an atomic force microscope (Digital Instruments Multimode IIIa) operated in tapping mode. One-dimensional and two-dimensional grazing incidence wide-angle x-ray scattering (GIWAXS) studies were performed at the 5A XRS-MS and 3C SAXS I beamline of the Pohang Accelerator Laboratory (PAL). Thin film samples for AFM and GIWAXS measurements were prepared by sequentially spin coating the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer and the active layer on SiO_2 substrates. The transmission electron microscopy (TEM) measurement was taken with a high-resolution transmission electron microscope (JEOL JEM-2100F) operated at 200 kV. The samples morphologically characterized using TEM and UV-Vis absorption spectroscopy were prepared on PEDOT:PSS-coated glass substrates. For the TEM measurements, the glass/PEDOT:PSS/active layer substrates were submerged in deionized water to make the active layers float on the water surface. The active layers were transferred onto 200-mesh copper grids.

Device fabrication and characterization

Photovoltaic devices were fabricated with a conventional structure of glass/indium tin oxide (ITO)/PEDOT:PSS/active layer (DTBDT-S-C8-TTR:PC₇₁BM)/LiF/Al. The ITO-coated glass substrates were ultrasonically cleaned in detergent, deionized water, acetone and isopropanol. The residual solvents were dried using pressurized nitrogen gas. After the PEDOT:PSS (Clevios P VP AI 4083) layer was deposited using spin coating, the glass/ITO/PEDOT:PSS

substrates were baked at 120 °C for 30 min. The active solutions were prepared by dissolving DTBBDT-S-C8-TTR and PC₇₁BM in chloroform. The ratio of DTBBDT-S-C8-TTR to PC₇₁BM in the blend was 1:0.8 and the total concentration was 30 mg ml⁻¹. The active solutions were filtered with 0.2- μ m polytetrafluoroethylene (PTFE) filters and spin-coated at 1500 rpm. For solvent vapor annealing (SVA), the substrates were placed in a glass Petri dish saturated with chloroform vapor for 60 s. The 0.8-nm-thick LiF interfacial layer and 100-nm-thick Al cathode were deposited sequentially by performing thermal evaporation under 5×10^{-6} torr. The current density-voltage (J - V) characteristics were evaluated using a Keithley Model 2400 source measurement unit, and a 450 W xenon lamp (Oriel) with an AM 1.5 G filter as the solar simulator. The external quantum efficiency (EQE) measurement was performed using a photomodulation spectroscopy setup (model Merlin, Oriel).

Hole mobility measurements

The hole-only devices were fabricated with a glass/ITO/MoO₃/active layer/Au configuration and with the same fabrication procedure used to fabricate the photovoltaic devices except for the evaporation of the Au electrode. The hole mobility was extracted by obtaining J - V curves under dark conditions and fitting the curves with the space-charge-limited current model, described by the equation

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3,$$

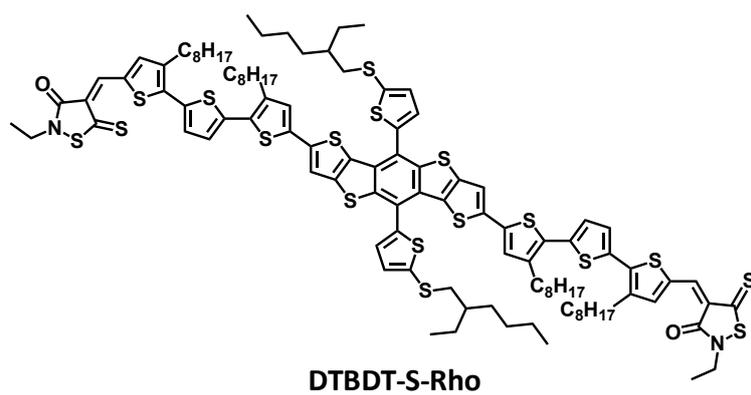
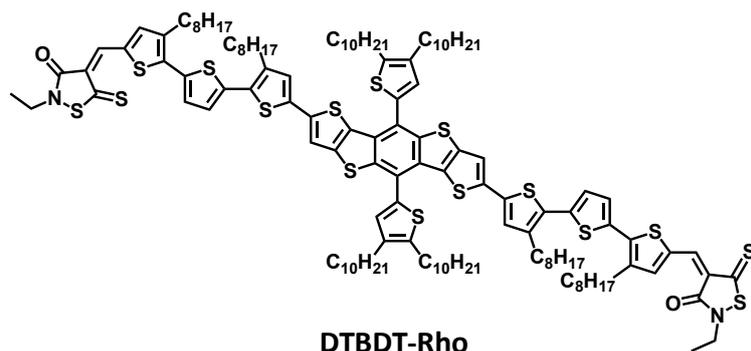
where J is the current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the transport medium, μ is the charge carrier mobility, V is the internal voltage, and L is the thickness of the active layers. The internal voltage was determined using the equation $V=V_{\text{appl}}-V_r-V_{\text{bi}}$, where V_{appl} is the voltage applied to the devices, V_r is the voltage drop due to the contact

resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference across the electrodes.

References

R1 H. G. Song, Y. J. Kim, J. S. Lee, Y.-H. Kim, C. E. Park, and S.-K. Kwon, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34353–34359.

R2 Y. S. Lee, S. Song, Y. J. Yoon, Y.-J.; Lee, S.-K. Kwon, J. Y. Kim, and Y.-H. Kim, *J. Polym. Sci. Part A: Polym. Chem.*, 2016, **54**, 3182–3192.



Scheme S1 Molecular structures of DTBDT-Rho and DTBDT-S-Rho.

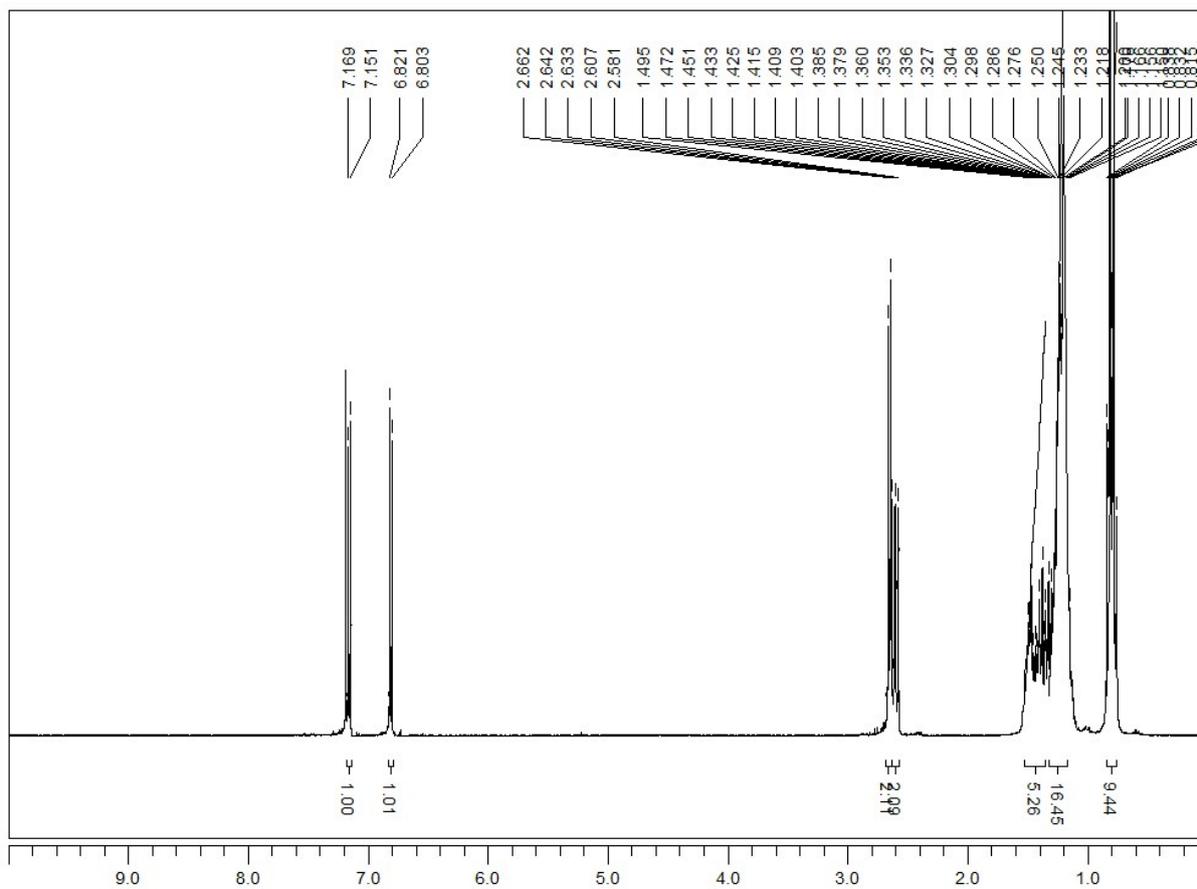


Fig. S1 ^1H NMR spectrum of compound (1) in CDCl_3 .

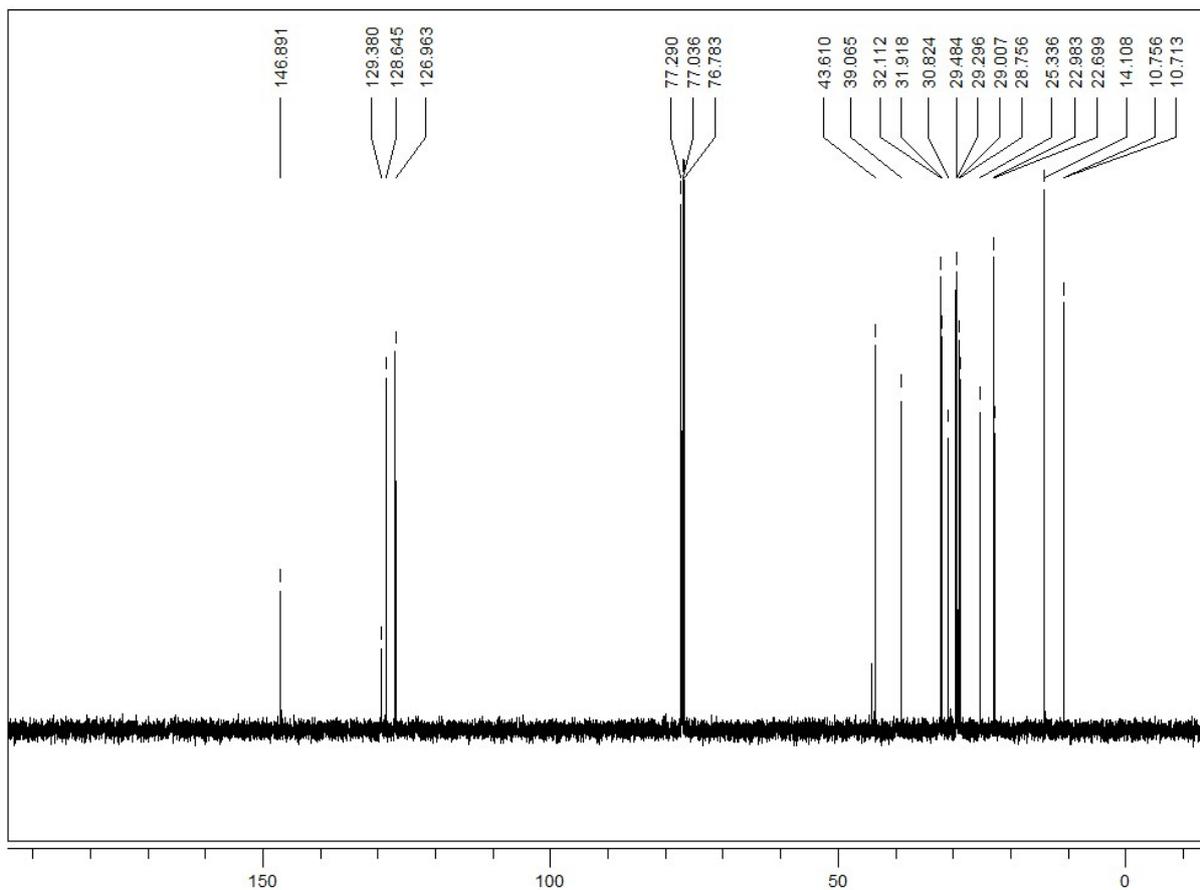


Fig. S2 ^{13}C NMR spectrum of compound (1) in CDCl_3 .

Data : TH-SENCE-HR Date : 17-Jan-2018 16:16
Instrument : MSStation
Sample : -
Note : -
Inlet : Direct Ion Mode : E+
RT : 0.80 min Scan# : 13
Elements : C 100/1, H 100/1, S 5/0
Mass Tolerance : 1000ppm, 5mmu if m/z > 5
Unsaturation (U.S.) : -0.5 - 30.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
1 340.2258	93.36	+9.8 / +3.3	9.0 C23 H32 S
2		-0.1 / -0.0	5.0 C20 H36 S2
3		-10.0 / -3.4	1.0 C17 H40 S3

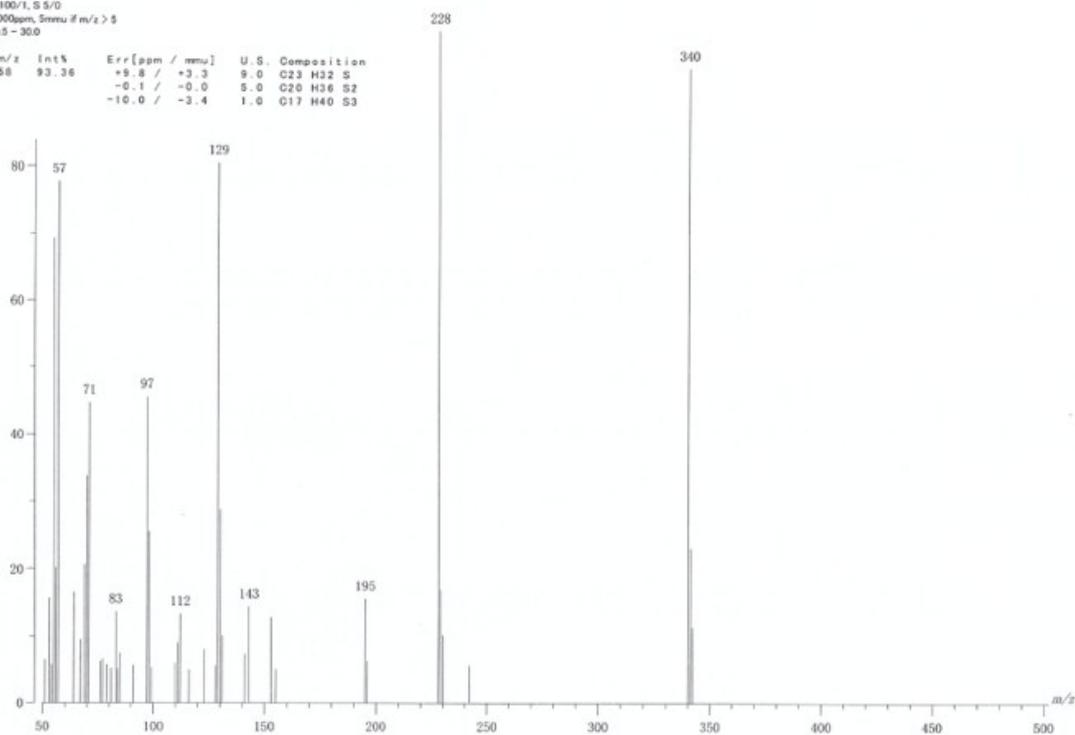


Fig. S3 High-resolution MS spectrum of compound (1).

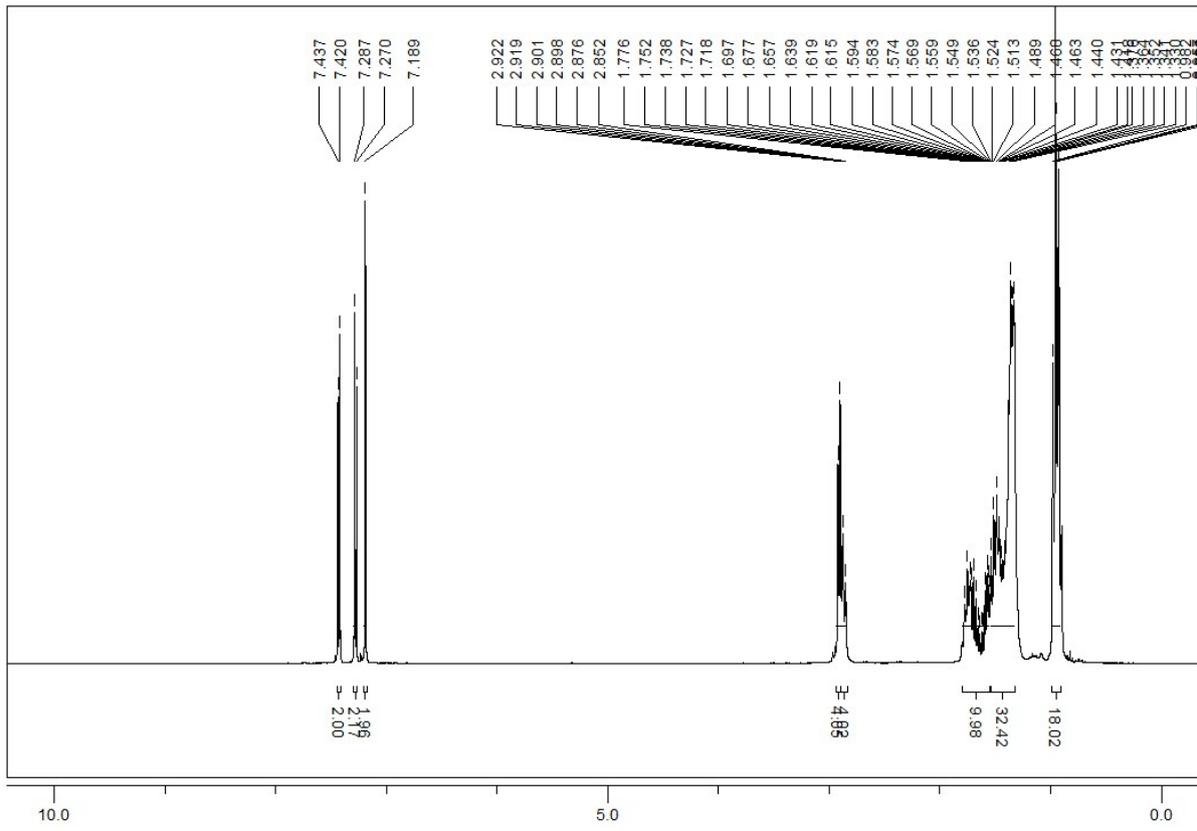


Fig. S4 ^1H NMR spectrum of compound (2) in CDCl_3 .

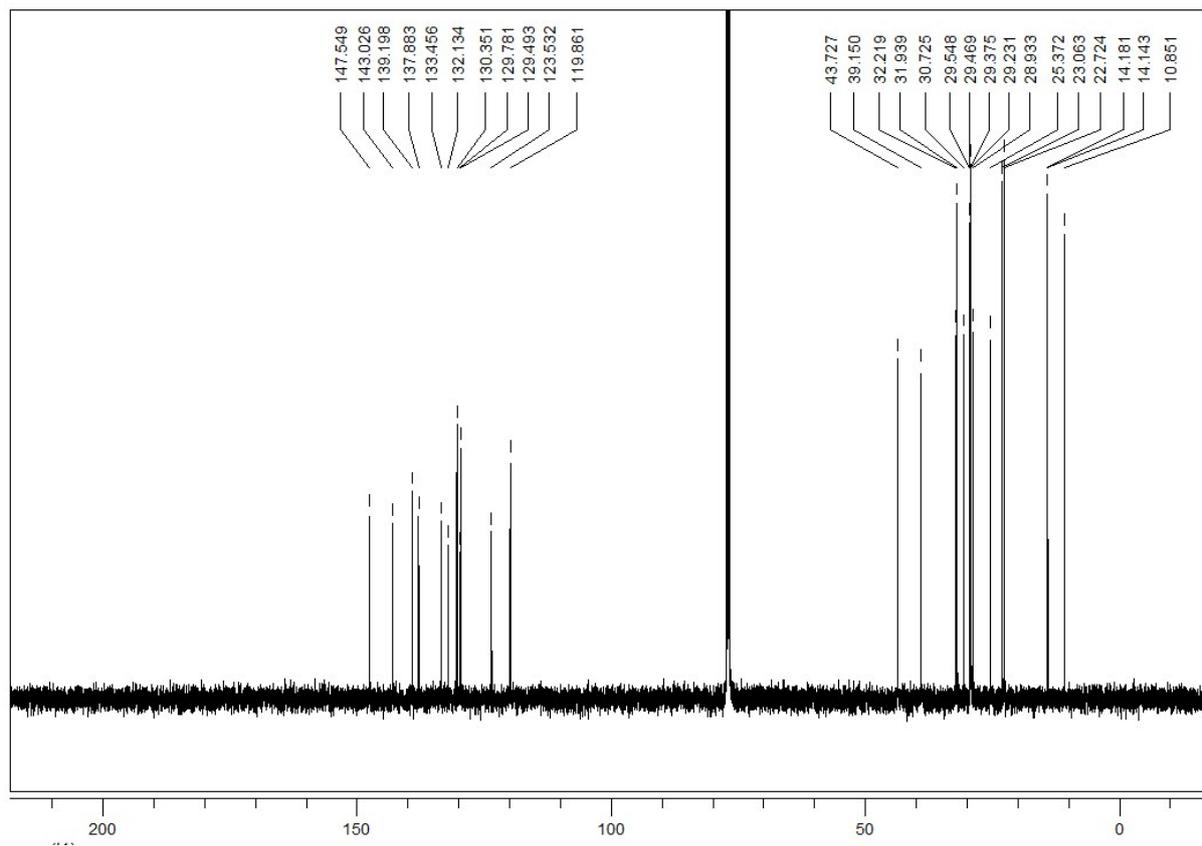


Fig. S5 ^{13}C NMR spectrum of compound (2) in CDCl_3 .

[Elemental Composition]
Data : DTBTD-SEh-C8-HR Date : 27-Sep-2017 15:06
Sample : -
Note : -
Inlet : Direct Ion Mode : FAB+
RT : 2.00 min Scan#: 25
Elements : C 100/1, H 100/1, S 10/1
Mass Tolerance : 100ppm, 3mmu if m/z > 30
Unsaturation (U.S.) : 0.0 - 30.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
978.3539	100.0	+1.7 / +1.7	30.0 C 57 H 70 S 7
		-1.7 / -1.7	26.0 C 54 H 74 S 8

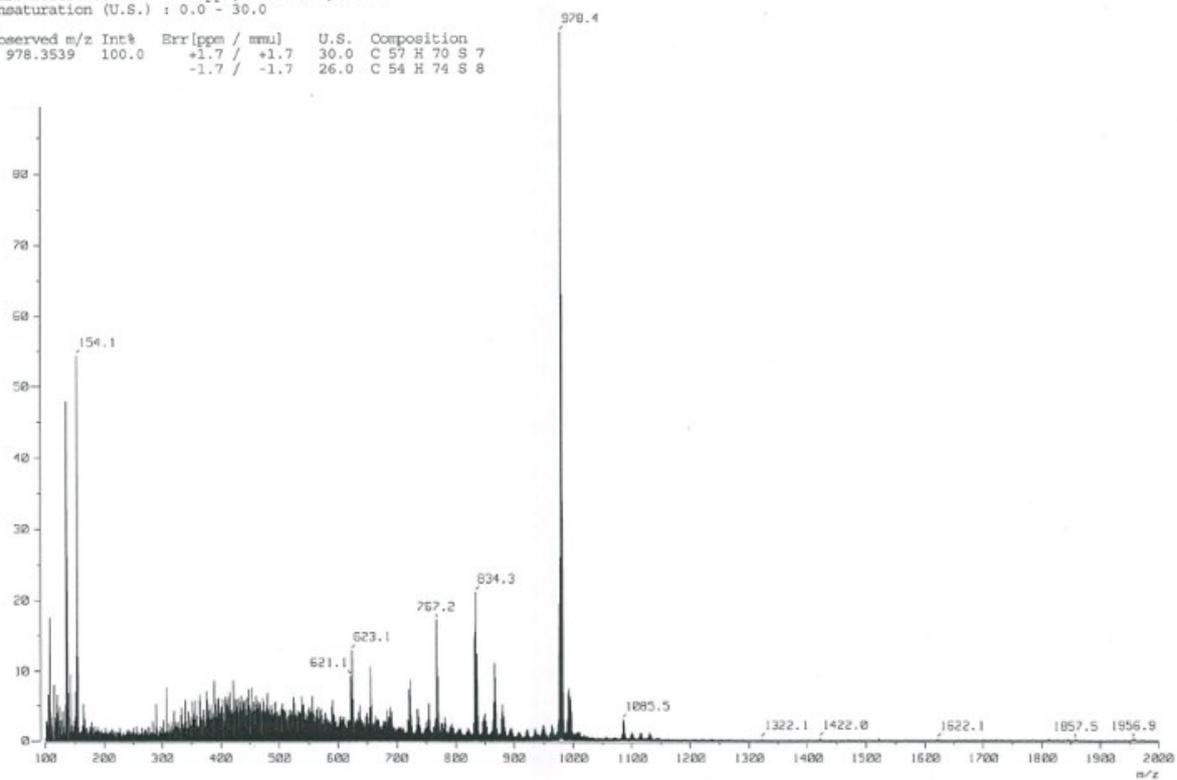


Fig. S6 High-resolution MS spectrum of compound (2).

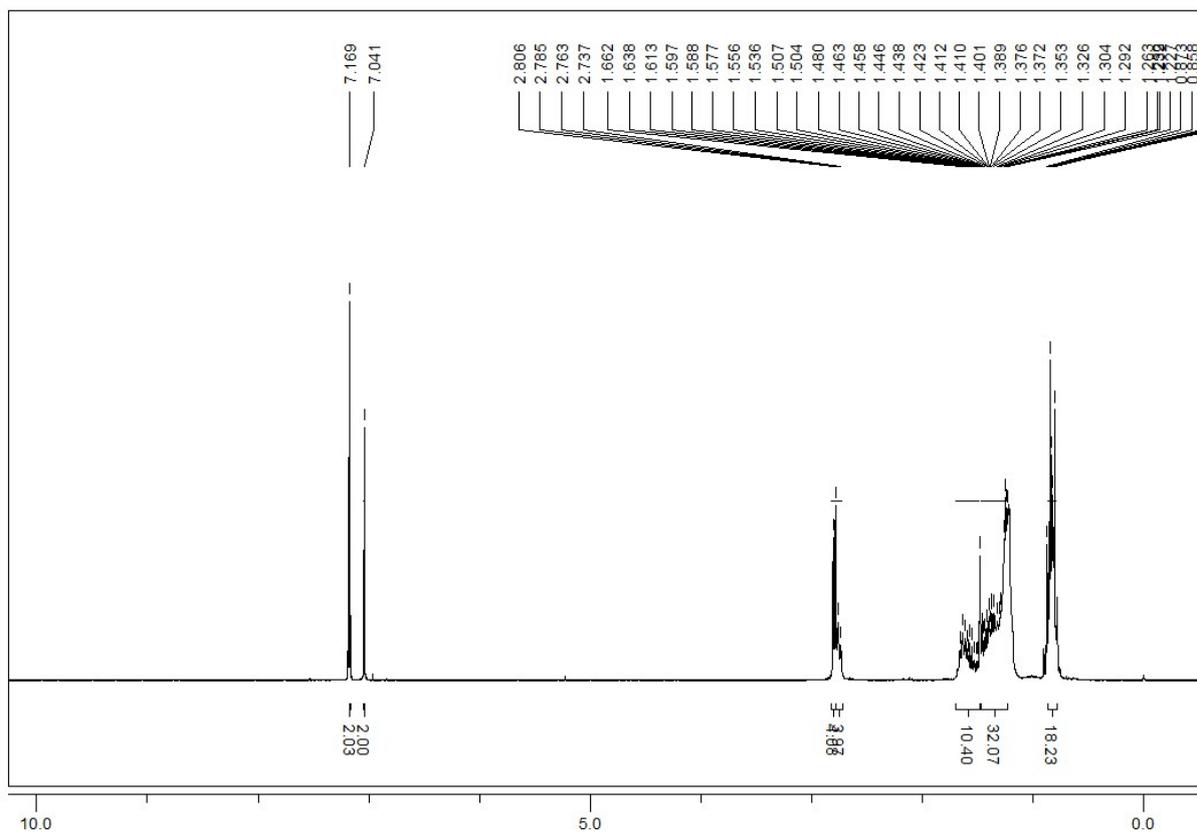


Fig. S7 ^1H NMR spectrum of compound (3) in CDCl_3 .

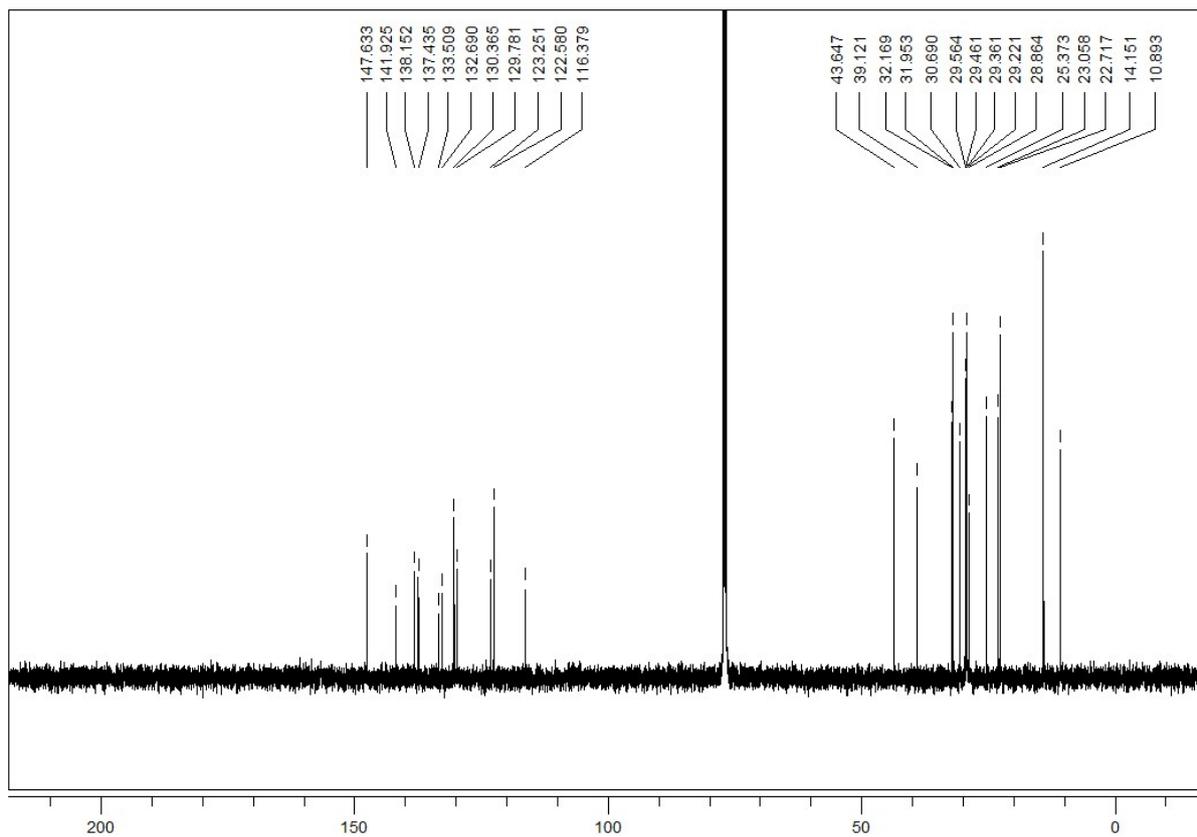


Fig. S8 ^{13}C NMR spectrum of compound (3) in CDCl_3 .

Applied Biosystems 4700 Proteomics Analyzer 901

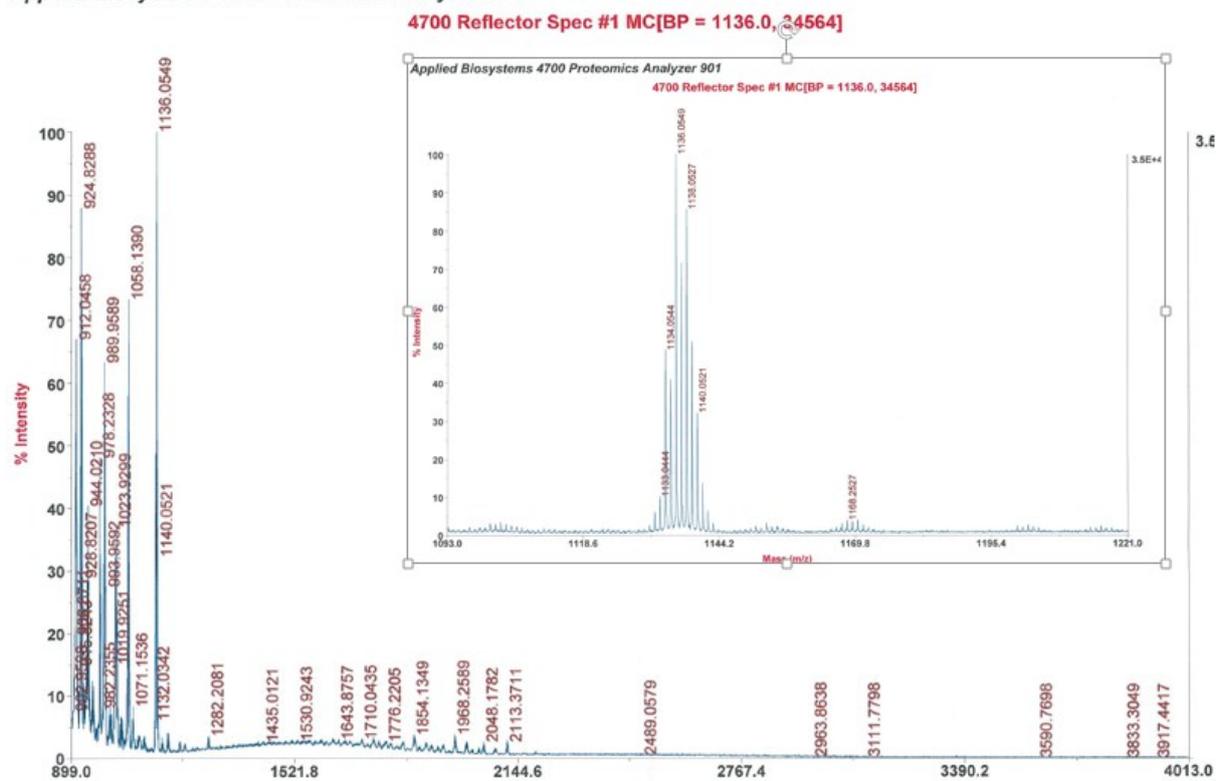


Fig. S9 MALDI-TOF MS plots of compound (3).

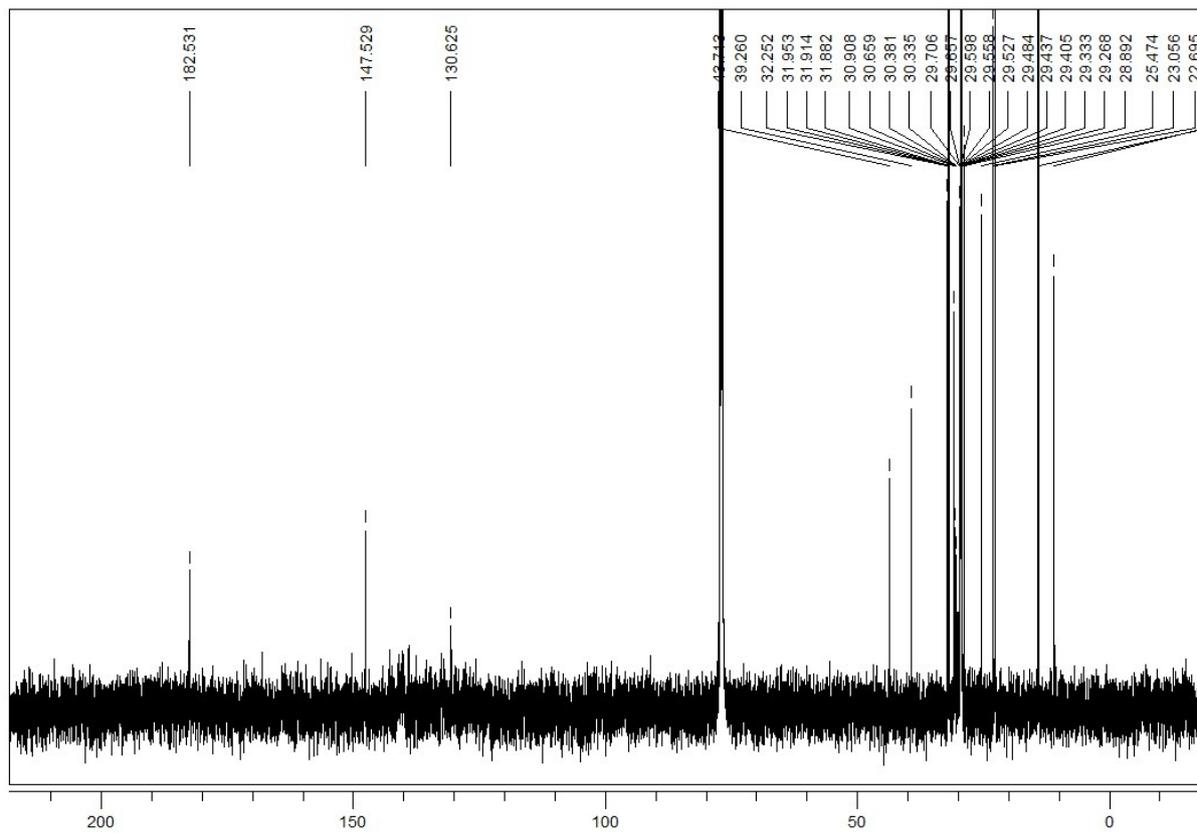


Fig. S11 ^{13}C NMR spectrum of compound (4) in CDCl_3 .

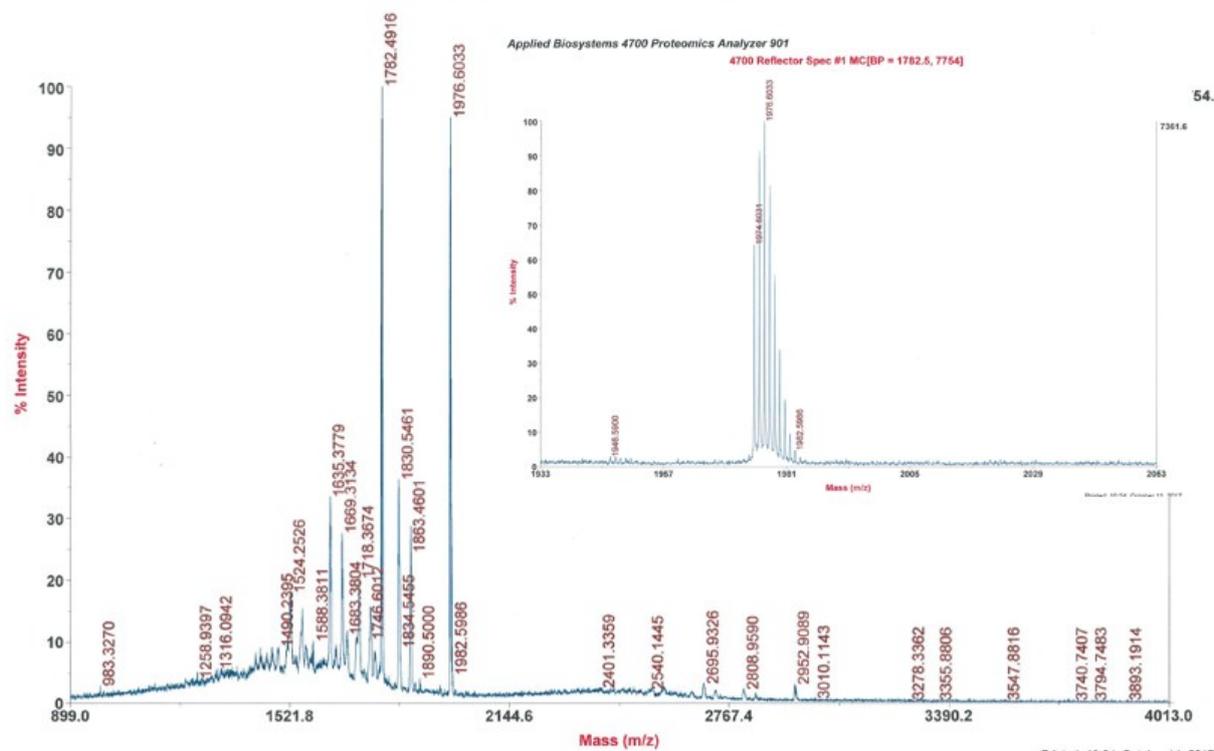


Fig. S12 MALDI-TOF MS plots of compound (4).

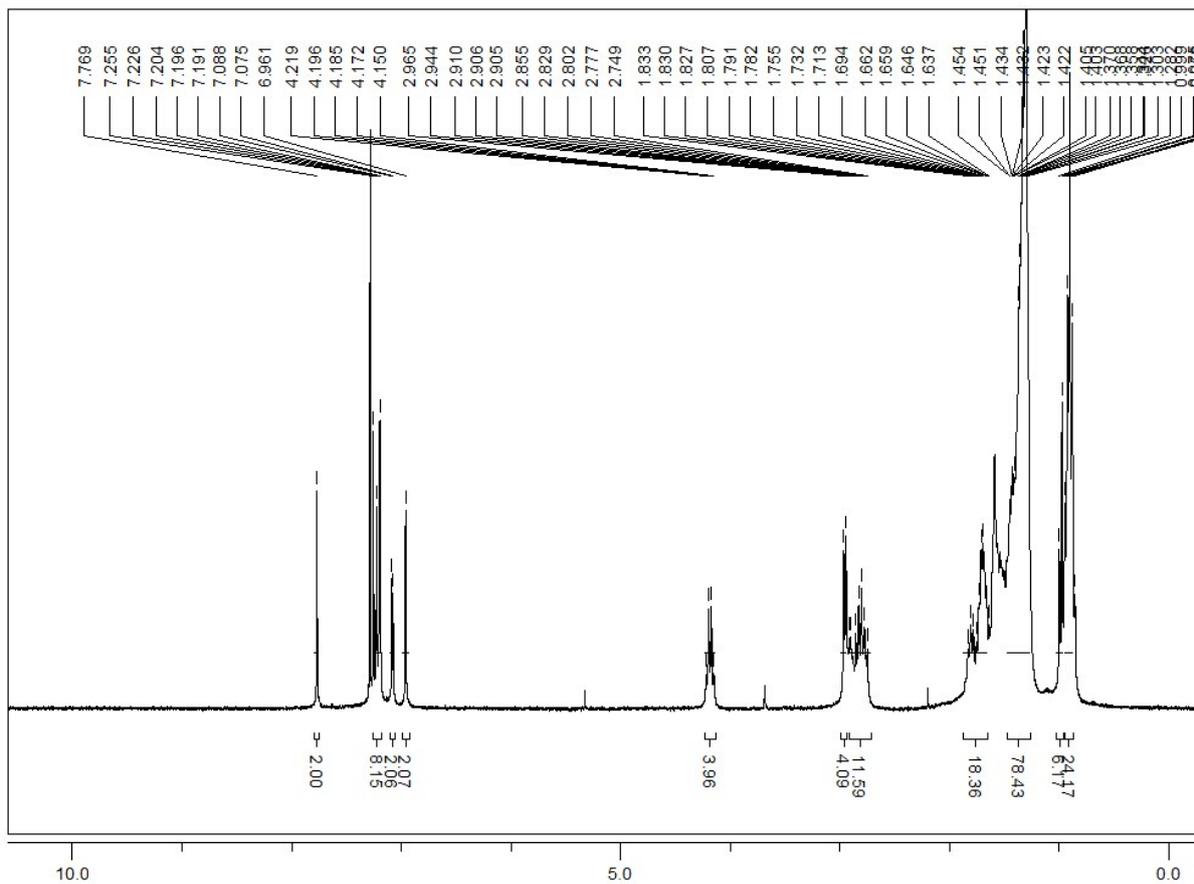


Fig. S13 ¹H NMR spectrum of DTBDT-S-C8-TTR in CDCl₃.

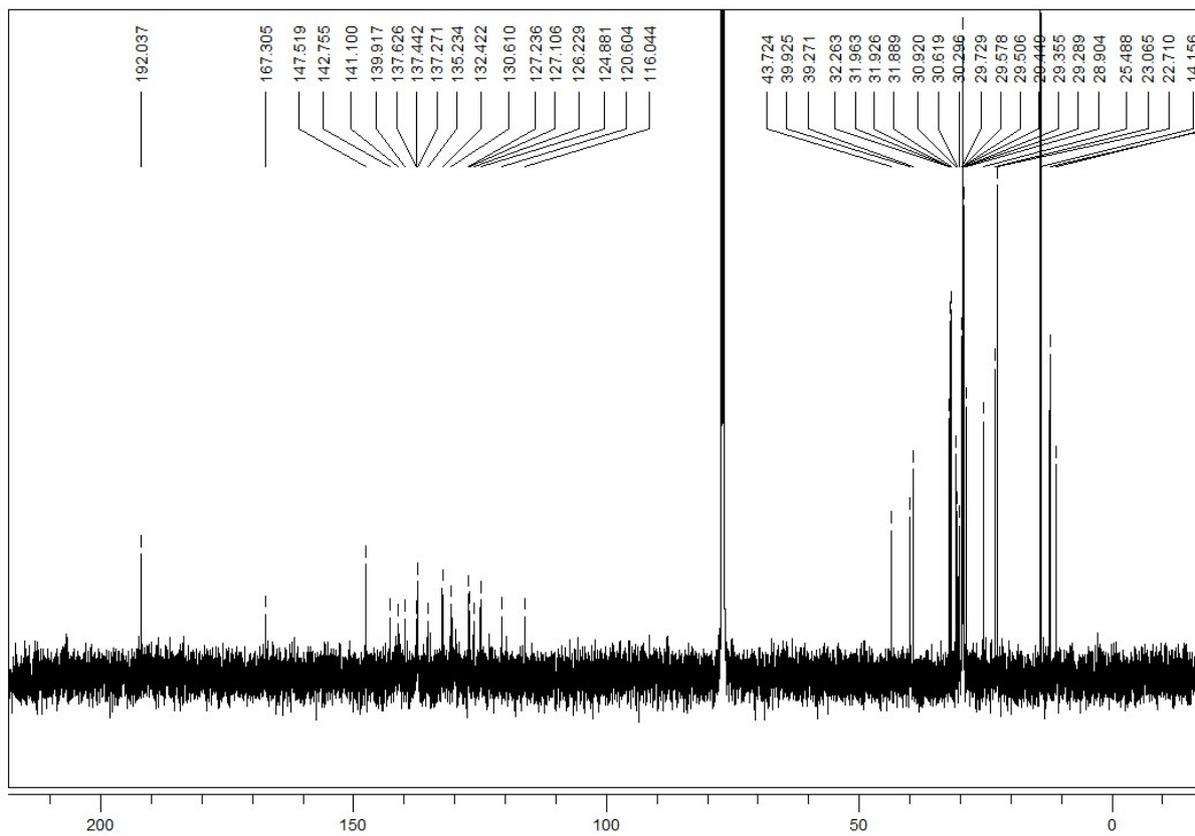


Fig S14 ^{13}C NMR spectrum of DTBBDT-S-C8-TTR in CDCl_3 .

6

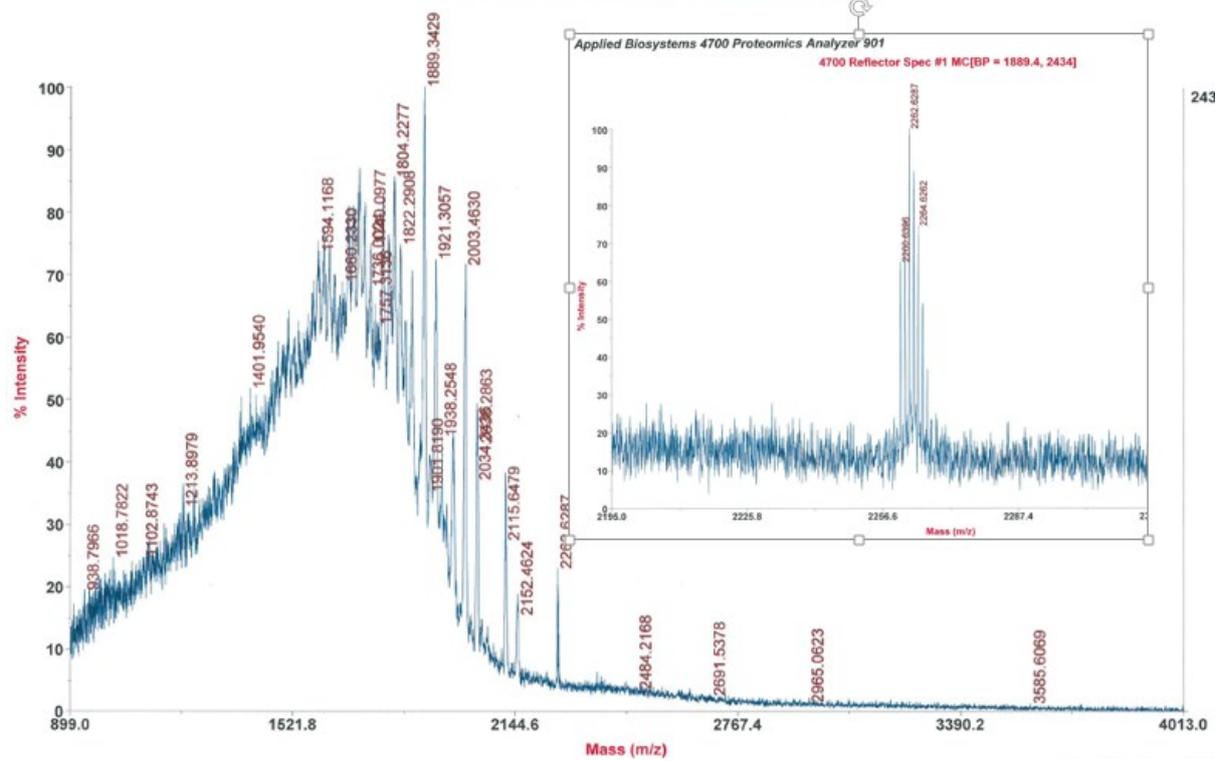


Fig. S15 MALDI-TOF MS plots of DTBDT-S-C8-TTR.

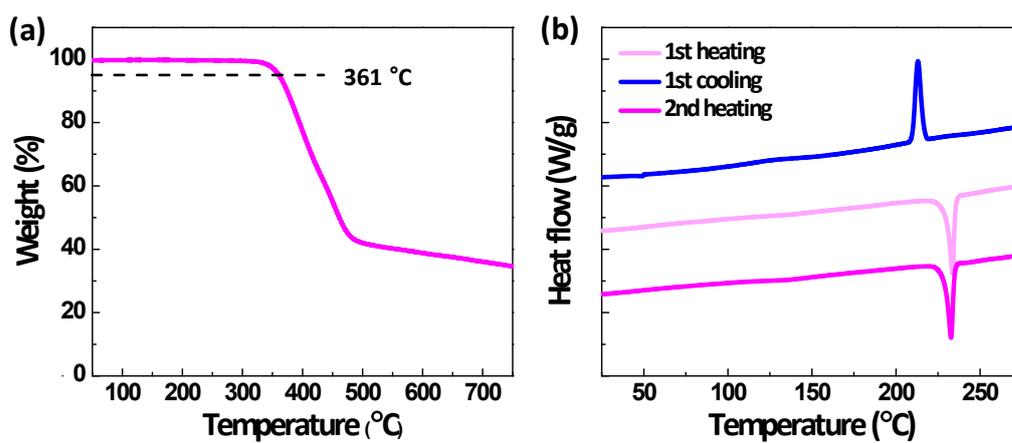


Fig. S16 (a) TGA and (b) DSC plots of DTBBDT-S-C8-TTR with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an inert atmosphere.