Supporting information

6,6'-Diaryl-Substituted Biazulene Diimides for Solution-Processable High-Performance n-Type Organic Semiconductors

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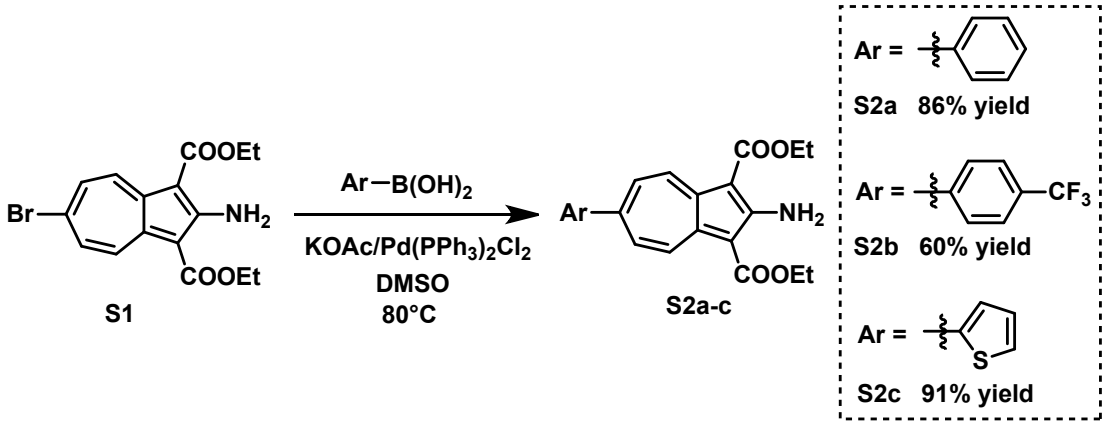
Contents:

1. Materials and General Methods.

Commercially available reagents and solvents were obtained and used as received unless otherwise mentioned. Compounds **S1**[1] and 2-hexyldecan-1-amine[2] were prepared according to the literature methods. ^{1}H NMR (300 MHz or 400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Varian Mercury (300 MHz and 400 MHz) or JEOL NMR (400 MHz) instruments. Elemental analyses were performed on an ElementarVario EL III elemental analyzer. Mass spectra (EI, DART, ESI and MALDI-FT) were carried out on Thermo Fisher Scientific LTQ FT Ultra Mass Spectrometer, Waters Micromass GCT premier or Agilent Technologies 5973N. Single crystal X-ray diffraction analysis was carried out on a D8 VENTURE SC-XRD instrument. Optical absorption spectra were measured on a U-3900 UV-vis spectrophotometer. TGA measurements were conducted on a TGA Q500 instrument under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500 °C. DSC analyses were performed on a DSC Q2000 instrument under a dry nitrogen flow at a heating rate of 5 °C/min. Cyclic voltammetry (CV) was carried out on CHI610D or CHI810D instruments using Bu_4NPF_6 (0.1 M) as supporting electrolyte and ferrocene as an internal reference at a scan rate of 100 mV S^{-1}. The CV cell consisted of a platinum button working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. Melting point were measured on SGW X-4 or WRS-1A microscopic melting point apparatus.

2. Synthesis and characterizations

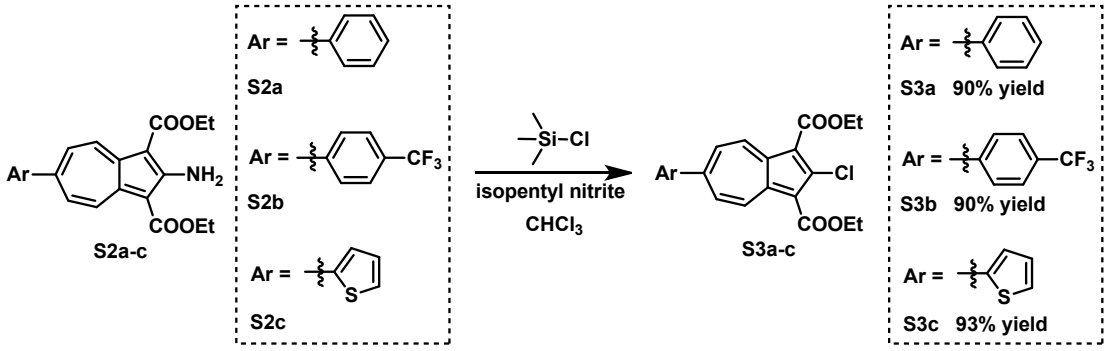


Diethyl 2-amino-6-phenylazulene-1,3-dicarboxylate S2a： A mixture of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate **S1** (367 mg, 1 mmol), phenylboronic acid (183 mg, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) and KOAc (200 mg, 2 mmol) was dissolved in 8 mL DMSO under nitrogen atmosphere. The reaction mixture was heated at 80 °C for 12 h. After cooling down to room temperature, the mixture was poured into water and extracted with dichloromethane. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/hexane (2:1) to give **S2a** as orange crystals (312 mg, 86% yield). M.p. 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.17 (d, *J* = 11.4 Hz, 2H), 7.79 (s, 2H), 7.78 (d, *J* = 11.4 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.48 (dd, *J* = 7.4 Hz, 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 4H), 1.48 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 166.54, 162.38, 146.37, 144.81, 143.81, 132.78, 130.85, 128.83, 128.25, 127.88, 99.92, 59.83, 14.66. FT-IR (KBr, cm^{-1}) ν: 3494.6, 3435.5, 3347.2, 3322.6, 2980.7, 1691.5, 1648.3, 1584.4, 1535.1, 1509.3, 1474.0, 1428.5, 1378.7, 1353.5, 1334.6, 1280.8, 1240.8, 1192.2, 1138.3, 1120.8, 1106.5, 1066.6, 1039.8, 1022.0, 1002.8, 923.9, 860.8, 848.8, 787.5, 754.4, 697.4. MS (MALDI) m/z: 364.1 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd for $C_{22}H_{21}NO_4$ 364.1543; Found, 364.1541.

Diethyl 2-amino-6-(4-(trifluoromethyl)phenyl)azulene-1,3-dicarboxylate S2b: A similar procedure to that used for **S2a** gave **S2b** as a yellow solid (259 mg, 60% yield). M.p. 177-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.12 (d, *J* = 10.6 Hz, 2H), 7.81 (s, 2H), 7.68 (m, 6H), 4.45 (q, *J* = 6.6 Hz, 4H), 1.47 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.50, 162.74, 147.38, 145.09, 144.31, 132.50, 130.66, 128.61, 125.82, 100.39, 60.05, 14.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.49. FT-IR (KBr, cm^{-1}) ν: 3488.6, 3344.6, 2980.2, 2904.7, 1692.1, 1644.8, 1615.1, 1587.7, 1542.5, 1511.4, 1475.3, 1431.6, 1381.9, 1357.3, 1329.3, 1285.3, 1245.3, 1197.0, 1169.7, 1140.8, 1109.8, 1070.8, 1033.9, 1015.7, 998.8, 928.4, 823.5, 788.6. MS (EI) m/z: 431 $(M)^+$. HRMS (EI) (m/z): $(M)^+$ Calcd for $C_{23}H_{20}F_3NO_4$ 431.1344; Found, 431.1338.

Diethyl 2-amino-6-(thiophen-2-yl)azulene-1,3-dicarboxylate S2c: A similar

procedure to that used for **S2a** gave **S2c** as a yellow solid (336 mg, 91% yield). M.p. 127-128 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.08 (d, *J* = 10.7 Hz, 2H), 7.89 (d, *J* = 10.7 Hz, 2H), 7.79 (s, 2H), 7.46 (d, *J* = 3.1 Hz, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.14 (dd, *J* = 5.2 Hz, *J* = 3.1 Hz, 1H), 4.47 (q, *J* = 7.0 Hz, 4H), 1.49 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.40, 162.25, 146.66, 144.37, 138.45, 130.46, 130.27, 128.62, 126.94, 125.29, 100.22, 59.83, 14.67. FT-IR (KBr, cm^{-1}) ν: 3499.3, 3365.2, 2980.1, 2902.2, 1679.9, 1654.9, 1589.5, 1539.2, 1505.5, 1488.1, 1473.9, 1428.8, 1416.8, 1381.7, 1349.1, 1324.9, 1280.5, 1248.2, 1189.6, 1147.4, 1107.1, 1069.8, 1035.2, 967.7, 890.5, 852.9, 843.4, 812.7, 789.1, 747.3, 691.8. MS (MALDI) m/z: 370.1 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd. for $C_{20}H_{20}O_4NS$: 370.1108; Found: 370.1104.

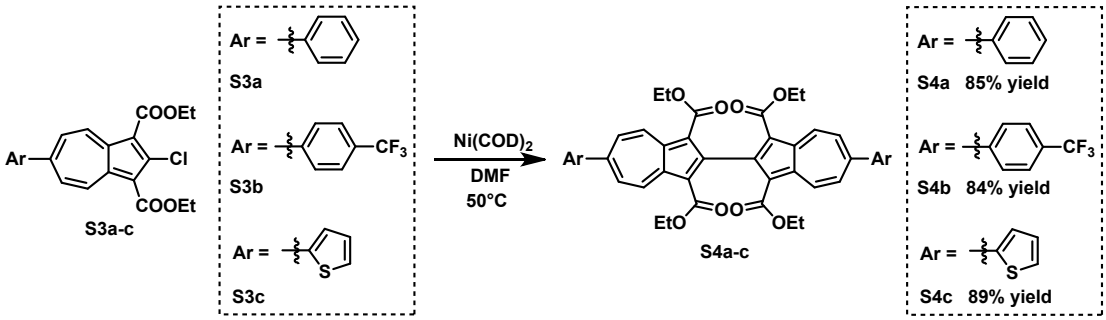


Diethyl 2-chloro-6-phenylazulene-1,3-dicarboxylate S3a: A mixture of chlorotrimethylsilane (2.7 g, 25 mmol) and isopentyl nitrite (2.9 g, 25 mmol) in 30 mL $CHCl_3$ was stirred at room temperature for 10 min. Diethyl 2-amino-6-phenylazulene-1,3-dicarboxylate **S2a** (1.91 g, 5.0 mmol) in 20 mL $CHCl_3$ was then added to the mixture. The reaction mixture was stirred at room temperature for 6 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with dichloromethane/hexane (2:1) to give **S3a** as a red solid (1.72 g, 90% yield). M.p. 123-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.52 (d, *J* = 11.2 Hz, 2H), 7.91 (d, *J* = 11.2 Hz, 2H), 7.65 (d, *J* = 6.8 Hz, 2H), 7.56 – 7.42 (m, 3H), 4.49 (q, *J* = 7.1 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 164.35, 154.02, 143.14, 143.00, 140.41, 137.28, 131.26, 129.10, 129.03, 128.65, 115.44, 60.66, 14.42. FT-IR (KBr, cm^{-1}) ν: 3051.5, 2981.0, 1703.7, 1686.1, 1586.2, 1565.7, 1485.7, 1445.3, 1421.3, 1381.9, 1304.0, 1259.3,

1234.7, 1208.3, 1174.7, 1112.9, 1081.3, 1055.1, 1028.3, 1001.5, 909.0, 867.8, 852.2, 810.4, 776.4, 750.9, 694.4. MS (MALDI) m/z: 383.1 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd for $C_{22}H_{19}ClO_4$ 383.1045; Found, 383.1039.

Diethyl 2-chloro-6-(4-(trifluoromethyl)phenyl)azulene-1,3-dicarboxylate S3b: A similar procedure to that used for **S3a** gave **S3b** as a red solid (2.02 g, 90% yield). M.p. 174-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.51 (d, *J* = 10.8 Hz, 2H), 7.84 (d, *J* = 10.8 Hz, 2H), 7.75 (m, 4H), 4.48 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.28, 152.10, 146.68, 143.88, 140.67, 137.34, 131.06, 129.08, 126.09, 115.96, 60.87, 14.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.68. FT-IR (KBr, cm^{-1}) ν: 3078.8, 2979.3, 2932.5, 2902.4, 1691.0, 1614.6, 1585.5, 1563.9, 1474.3, 1438.0, 1411.4, 1383.1, 1326.1, 1259.4, 1247.1, 1224.5, 1181.8, 1114.3, 1071.5, 1051.1, 1025.3, 1015.7, 928.9, 880.2, 860.7, 844.2, 822.0, 779.0. MS (EI) m/z: 450 $(M)^+$. HRMS (EI) (m/z): $(M)^+$ Calcd for $C_{23}H_{18}ClF_3O_4$ 450.0846; Found, 450.0836.

Diethyl 2-chloro-6-(thiophen-2-yl)azulene-1,3-dicarboxylate S3c: A similar procedure to that used for **S3a** gave **S3c** as a red solid (1.81 g, 93% yield). M.p. 124-125 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.42 (d, *J* = 10.7 Hz, 2H), 8.03 (d, *J* = 10.7 Hz, 2H), 7.63 (d, *J* = 2.7 Hz, 1H), 7.53 (d, *J* = 5.0 Hz, 1H), 7.20 (dd, *J* = 5.0 Hz, *J* = 2.7 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 4H), 1.48 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.18, 145.82, 145.59, 142.56, 139.93, 136.99, 129.60, 129.19, 128.49, 127.74, 115.62, 60.62, 14.45. FT-IR (KBr, cm^{-1}) ν: 3099.8, 3085.9, 2984.5, 2901.3, 1669.5, 1581.2, 1566.5, 1548.0, 1474.9, 1437.4, 1411.1, 1385.2, 1353.3, 1260.0, 1231.4, 1201.2, 1113.5, 1085.7, 1071.4, 1052.3, 1031.4, 948.3, 892.6, 853.9, 837.2, 777.4, 748.4, 720.2, 687.6, 652.1, 636.3. MS (MALDI) m/z: 389.0 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd. for $C_{20}H_{18}O_4ClS$: 389.0609; Found: 389.0607.

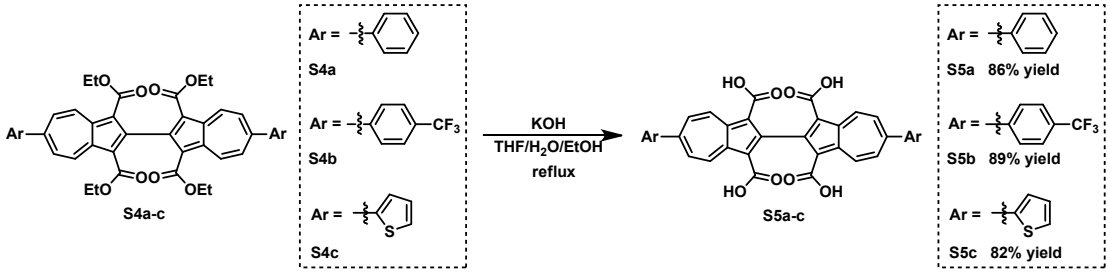


Tetraethyl 6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylate S4a: Under nitrogen atmosphere, a mixture of diethyl 2-chloro-6-phenylazulene-1,3-dicarboxylate **S3a** (382 mg, 1.0 mmol) and $Ni(COD)_2$ (165 mg, 0.6 mmol) was dissolved in DMF (2 mL). The reaction was stirred at 50 °C for 6 h. After cool down to room temperature, the mixture was poured into water and extracted with dichloromethane. The combined organic phase was dried over Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/ hexane (8:1) to give **S4a** as dark red crystals (294 mg, 85% yield). M.p. 333-334 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.84 (d, *J* = 11.1 Hz, 4H), 7.96 (d, *J* = 11.1 Hz, 4H), 7.74 (d, *J* = 7.2 Hz, 4H), 7.58 – 7.46 (m, 6H), 3.94 (q, *J* = 7.1 Hz, 8H), 0.61 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 165.26, 155.11, 153.16, 143.66, 142.02, 137.50, 130.57, 129.02, 128.73, 116.43, 59.34, 13.42. FT-IR (KBr, cm^{-1}) ν: 2979.8, 2901.1, 1678.2, 1580.1, 1564.5, 1642.4, 1478.3, 1423.5, 1388.8, 1345.3, 1241.6, 1210.2, 1184.8, 1113.5, 1096.1, 1075.6, 1044.5, 1031.4, 1001.8, 973.4, 861.6, 760.9, 722.6, 702.6. MS (MALDI) m/z: 695.3 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd for $C_{44}H_{38}O_8$ 695.2639; Found, 695.2623.

Tetraethyl 6,6'-bis(4-(trifluoromethyl)phenyl)-[2,2'-biazulene]-1,1',3,3'-tetracarb- oxylate S4b: A similar procedure to that used for **S4a** gave **S4b** as a dark red solid (348 mg, 84% yield). M.p. 331-332 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.86 (d, *J* = 10.7 Hz, 1H), 7.92 (d, *J* = 10.7 Hz, 1H), 7.82 (s, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 0.62 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ 165.16, 155.63, 151.49, 147.22, 142.25, 137.71, 130.46, 129.17, 126.05, 116.94, 59.59, 13.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.60. FT-IR (KBr, cm^{-1}) ν: 2981.8, 2903.6, 1679.3, 1613.7, 1584.2, 1564.6, 1547.3, 1477.5, 1426.5, 1390.8, 1321.2, 1254.1,

1211.5, 1185.0, 1129.5, 1069.8, 1040.5, 1015.8, 997.7, 976.0, 880.7, 838.7. MS (MALDI) m/z: 853.3 $(M+Na)^+$. HRMS (MALDI-FT) (m/z): $(M+Na)^+$ Calcd for $C_{46}H_{36}F_6O_8Na$ 853.2231; Found, 853.2247.

Tetraethyl 6,6'-di(thiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxylate S4c: A similar procedure to that used for **S4a** gave **S4c** as a dark red solid (314 mg, 89% yield). M.p. 298-299 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.74 (d, *J* = 11.3 Hz, 4H), 8.08 (d, *J* = 11.3 Hz, 4H), 7.66 (d, *J* = 2.9 Hz, 2H), 7.51 (d, *J* = 5.1 Hz, 2H), 7.19 (dd, *J* = 5.1 Hz, *J* = 2.9 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 4H), 0.61 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.19, 154.79, 146.30, 145.19, 141.76, 137.33, 129.09, 129.05, 128.11, 127.35, 116.75, 59.37, 13.41. FT-IR (KBr, cm^{-1}) ν: 3099.7, 2976.5, 2904.4, 1671.7, 1579.7, 1565.6, 1549.4, 1477.8, 1428.9, 1389.2, 1352.0, 1254.0, 1218.9, 1184.6, 1111.0, 1084.7, 1068.0, 1040.4, 993.2, 890.6, 860.9, 832.2, 804.7, 779.8, 723.1, 690.2. MS (MALDI) m/z: 706.2 $(M)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd. for $C_{40}H_{35}O_8S_2$: 707.1768; Found: 707.1764.

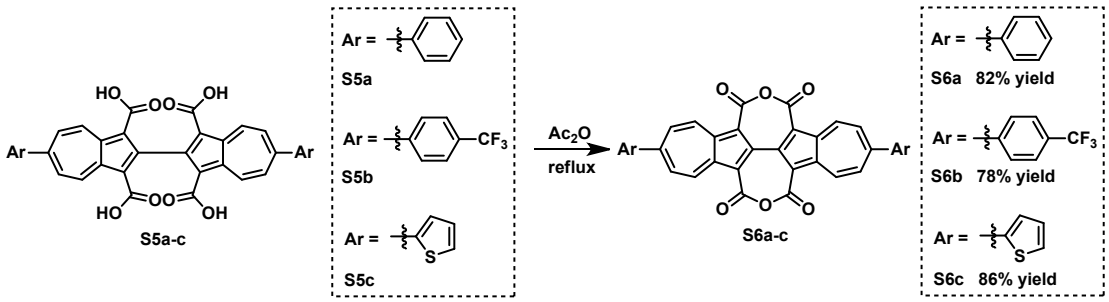


6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic acid S5a: A mixture of tetraethyl 6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylate **S4a** (695 mg, 1.0 mmol), THF (8 mL), EtOH (8 mL) and 12 M KOH aq. (1 mL) was refluxed for 12 h. After cool down to room temperature, the mixture was diluted with water and filtered to remove insoluble materials. The filtrate was then acidified with 2 M HCl and solid separated out was collected by filtration to give **S5a** as a red solid (500 mg, 86% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 3020.4, 1651.8, 1581.2, 1563.4, 1439.6, 1390.7, 1288.4, 1208.6, 1078.9, 1014.6, 975.3, 903.2, 856.7, 758.7, 735.9, 698.6. MS (ESI) m/z: 581.0 $(M-H)^-$. HRMS (ESI Negative) (m/z): $(M-H)^-$ Calcd. for $C_{36}H_{21}O_8$: 581.1242; Found: 581.1246.

6,6'-bis(4-(trifluoromethyl)phenyl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic acid

S5b: A similar procedure to that used for **S5a** gave **S5b** as a red solid (639 mg, 89% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 2929.4, 1697.5, 1616.1, 1584.6, 1564.4, 1436.8, 1324.9, 1248.9, 1167.8, 1125.8, 1069.9, 1014.8, 831.9. MS (ESI) m/z: 716.9 $(M-H)^-$. HRMS (ESI Negative) (m/z): $(M-H)^-$ Calcd. for $C_{38}H_{19}F_6O_8$: 717.0990; Found: 717.0998.

6,6'-di(thiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic acid 5: A similar procedure to that used for **S5a** gave **S5c** as a red solid (489 mg, 82% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 2928.4, 1651.3, 1582.4, 1566.0, 1440.6, 1388.4, 1349.1, 1202.1, 1083.5, 1009.5, 890.7, 850.1, 826.5, 706.2, 615.8. MS (MALDI) m/z: 633.0 $(M+K)^+$. HRMS (MALDI-FT) (m/z): $(M+H)^+$ Calcd. for $C_{32}H_{19}O_8S_2$: 595.0516; Found: 595.0514.

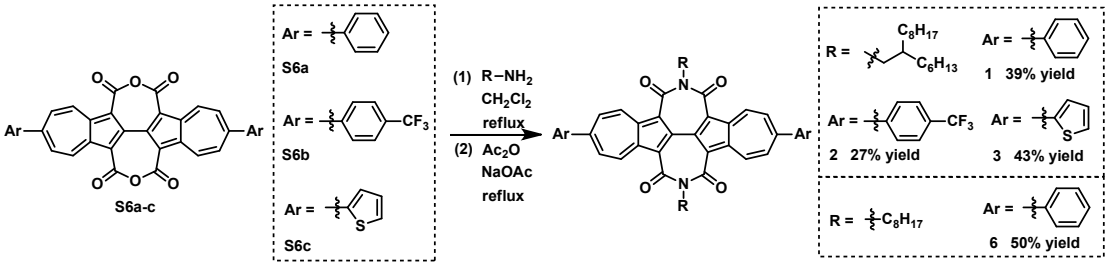


6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic dianhydride S6a: A mixture of 6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic acid **S5a** (581 mg, 1.0 mmol) and acetic anhydride (8 mL) was refluxed for 2 h. Then the mixture was cooled to room temperature and filtrated to give product as a dark red solid (448 mg, 82% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 1705.7, 1580.5, 1438.4, 1407.5, 1378.1, 1307.9, 1268.9, 1172.6, 1141.4, 1098.8, 1023.0, 1000.8, 977.7, 907.9, 856.9, 759.4, 691.6. MS (MALDI) m/z: 547.1 $(M+H)^+$. HRMS (MALDI-FT) (m/z): $(M+H)^+$ Calcd. for $C_{36}H_{19}O_6$: 547.1176; Found: 547.1184.

6,6'-bis(4-(trifluoromethyl)phenyl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic dianhydride S6b: A similar procedure to that used for **S6a** gave **S6b** as a red solid (532 mg, 78% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 1709.3, 1614.1, 1584.0, 1560.3, 1480.8, 1436.3, 1404.0, 1383.9, 1321.0, 1256.9, 1164.8, 1127.9, 1069.8, 1008.4, 977.1, 879.2, 833.5, 780.5, 759.2. MS (MALDI) m/z: 582.1 $(M)^+$. HRMS (MALDI-

FT) (m/z): $(M+H)^+$ Calcd. for $C_{38}H_{17}F_6O_6$: 583.0924; Found: 583.0950.

6,6'-di(thiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic dianhydride S6c: A similar procedure to that used for **S6a** gave **S6c** as a red solid (480 mg, 86% yield). M.p. >350 °C. FT-IR (KBr, cm^{-1}) ν: 3100.5, 1698.0, 1581.4, 1504.9, 1438.2, 1408.9, 1375.1, 1352.6, 1306.9, 1286.1, 1263.4, 1175.2, 1139.1, 1101.4, 1072.8, 1015.1, 890.6, 852.6, 835.9, 760.7, 739.9, 708.1, 651.5. Anal. Calcd. for $C_{32}H_{14}O_6S_2$: C, 68.81; H, 2.53. Found: C, 68.50; H, 2.84.



***N,N'*-bis(2-hexyldecyl)-6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 1:** A solution of 2-hexyldecan-1-amine (460 mg, 2.0 mmol) in 5 mL of dichloromethane was added dropwise to the solution of 6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxylic dianhydride **S6a** (273 mg, 0.5 mmol) in 5 mL of dichloromethane. The reaction was stirred under reflux for 12 h. Upon removal of solvent, the residue was then added 8 mL of acetic anhydride and NaOAc (164 mg, 2.0 mmol). The resulting mixture was reflux for another 6 h. After cool down to room temperature, the reaction mixture was diluted with water and thoroughly extracted with dichloromethane. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography with dichloromethane/hexane (1:3) to give product as green solid (193 mg, 39% yield). M.p. = 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.79 (d, *J* = 11.2 Hz, 4H), 8.02 (d, *J* = 11.2 Hz, 4H), 7.70 (d, *J* = 6.8 Hz, 4H), 7.56 – 7.50 (m, 4H), 4.42 (d, *J* = 7.3 Hz, 4H), 2.07 (s, 2H), 1.37 – 1.16 (m, 48H), 0.81 – 0.75 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.31, 155.79, 143.05, 142.66, 139.74, 136.49, 131.35, 129.34, 129.20, 128.75, 118.86, 50.22, 37.28, 31.85, 31.78, 30.14, 29.79, 29.56, 29.35, 26.45, 22.65, 22.63, 14.06, 14.03. FT-IR (KBr, cm^{-1}) ν: 2954.6, 1924.5, 2853.6, 1651.9, 1619.3, 1581.5, 1559.7, 1492.0, 1428.4, 1393.3, 1303.4,

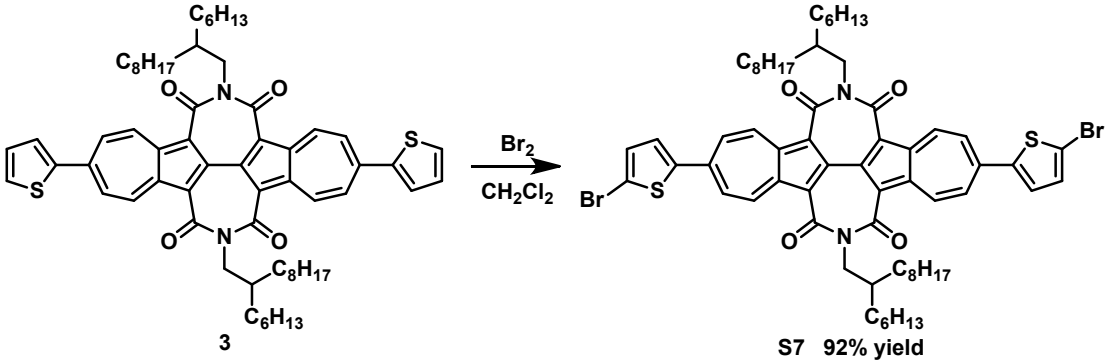
1263.2, 1232.2, 1178.4, 1032.4, 1002.5, 854.4, 782.3, 765.9. MS (MALDI) m/z: 993.6 $(M+H)^+$. HRMS (DART-FT) (m/z): $(M+H)^+$ Calcd. for $C_{68}H_{85}O_4N_2$: 993.6504; Found: 993.6468. Anal. Calcd. for $C_{68}H_{84}O_4N_2$: C, 82.21; H, 8.52; N, 2.82. Found: C, 82.43; H, 8.77; N, 2.71.

***N,N'*-bis(2-hexyldecyl)-6,6'-bis(4-(trifluoromethyl)phenyl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 2:** A similar procedure to that used for **1** gave **2** as a green solid (152 mg, 27% yield). M.p. = 200-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.82 (d, *J* = 11.2 Hz, 4H), 7.99 (d, *J* = 11.2 Hz, 4H), 7.81 (s, 8H), 4.42 (d, *J* = 7.3 Hz, 4H), 2.07 (s, 2H), 1.37 – 1.15 (m, 48H), 0.81 – 0.77 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.99, 153.67, 146.21, 142.65, 139.78, 136.61, 130.94, 128.91, 125.99, 119.10, 50.31, 37.29, 31.85, 31.79, 30.19, 29.82, 29.58, 29.38, 26.42, 22.67, 22.64, 14.03. FT-IR (KBr, cm^{-1}) ν: 2923.1, 2851.8, 2357.3, 1655.3, 1620.4, 1581.6, 1559.3, 1426.4, 1396.5, 1320.3, 1261.6, 1227.8, 1169.1, 1128.8, 1070.4, 1015.1, 869.4, 827.3, 780.7, 760.4, 734.2, 684.9. MS (MALDI) m/z: 1127.6 $(M-H)^-$. HRMS (MALDI) (m/z): $(M-H)^-$ Calcd. for $C_{70}H_{81}F_6O_4N_2$: 1127.6095; Found: 1127.6098. Anal. Calcd. for $C_{68}H_{84}O_4N_2$: C, 74.44; H, 7.32; N, 2.48. Found: C, 74.37; H, 7.30; N, 2.42.

***N,N'*-bis(2-hexyldecyl)-6,6'-di(thiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 3:** A similar procedure to that used for **1** gave **3** as a brown solid (216 mg, 43% yield). M.p. = 231-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.57 (d, *J* = 11.2 Hz, 4H), 8.02 (d, *J* = 11.2 Hz, 4H), 7.60 (d, *J* = 3.3 Hz, 2H), 7.48 (d, *J* = 4.8 Hz, 2H), 7.12 (dd, *J* = 3.3 Hz, *J* = 4.8 Hz,2H), 4.41 (d, *J* = 7.2 Hz, 4H), 2.07 (s, 2H), 1.53 – 1.07 (m, 48H), 0.86 – 0.77 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.09, 147.24, 145.67, 142.21, 139.30, 135.93, 130.16, 129.29, 128.38, 128.14, 118.99, 50.15, 37.26, 31.89, 31.84, 30.22, 29.87, 29.62, 29.41, 26.46, 22.71, 22.68, 14.09. FT-IR (KBr, cm^{-1}) ν: 3073.9, 2954.1, 2922.8, 2851.9, 1643.5, 1607.5, 1578.1, 1508.7, 1430.0, 1386.0, 1351.8, 1301.0, 1281.9, 1253.3, 1239.3, 1180.5, 1084.8, 1066.7, 944.8, 891.7, 849.7, 821.7, 779.6, 698.2. MS (MALDI) m/z: 1005.6 $(M+H)^+$. HRMS (MALDI) (m/z): $(M+H)^+$ Calcd. for $C_{64}H_{81}O_4N_2S_2$: 1005.5632; Found: 1005.5633. Anal. Calcd. for $C_{64}H_{81}O_4N_2S_2$: C, 76.45; H, 8.02; N, 2.79. Found:

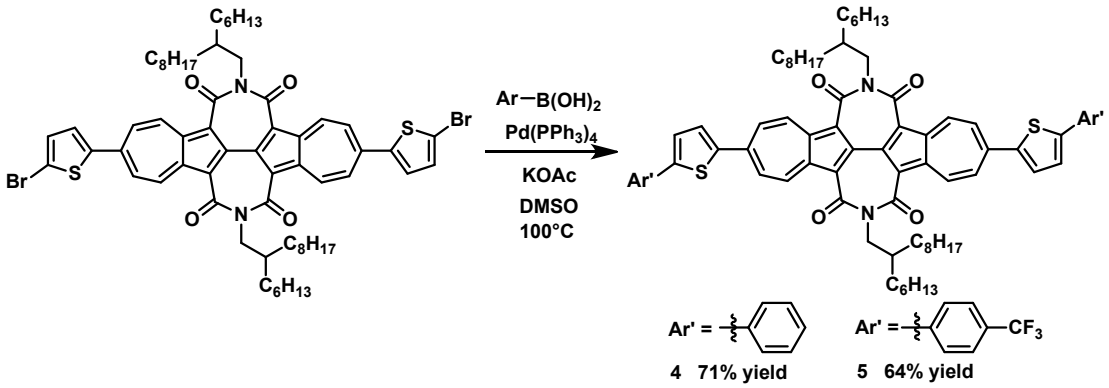
C, 76.27; H, 8.22; N, 2.58.

***N,N'*-dioctyl-6,6'-diphenyl-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 6:** A similar procedure to that used for **1** gave **6** as a green solid (192 mg, 50% yield). M.p. = 279-280 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.82 (d, *J* = 11.1 Hz, 4H), 8.00 (d, *J* = 11.1 Hz, 4H), 7.68 (d, *J* = 6.9 Hz, 4H), 7.58 – 7.41 (m, 4H), 4.42 (t, *J* = 7.3 Hz, 4H), 1.95 – 1.79 (m, 4H), 1.52 – 1.18 (m, 22H), 0.84 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.89, 155.76, 142.95, 142.66, 139.82, 136.46, 131.42, 129.31, 129.18, 128.72, 118.65, 46.44, 31.80, 29.45, 29.33, 29.01, 27.40, 22.66, 14.08. FT-IR (KBr, cm^{-1}) ν: 3056.4, 2920.6, 2851.3, 2352.4, 1650.7, 1615.5, 1580.0, 1426.9, 1390.6, 1300.7, 1262.7, 1229.1, 1167.8, 1136.4, 1014.6, 1001.6, 942.2, 853.1, 765.2, 735.5, 694.1. MS (MALDI) m/z: 769.4 $(M+H)^+$. HRMS (MALDI) (m/z): $(M+H)^+$ Calcd. for $C_{52}H_{53}O_4N_2$: 769.4000; Found: 769.4002. Anal. Calcd. for $C_{52}H_{52}O_4N_2$: C, 81.22; H, 6.82; N, 3.64. Found: C, 81.12; H, 6.88; N, 3.52.



***N,N'*-bis(2-hexyldecyl)-6,6'-di(5-bromothiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide S7:** To a solution of **3** (300 mg, 0.3 mmol) in 12 mL CH_2Cl_2, Br_2 (120 mg, 0.25 mmol) in 1 mL CH_2Cl_2 was added dropwise, and the reaction was stirred for 2 h at room temperature. The mixture was then extracted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography with dichloromethane/hexane (1:3) to give product as brown solid (320 mg, 92% yield). M.p. = 262-263 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.54 (d, *J* = 11.3 Hz, 4H), 7.86 (d, *J* = 11.3 Hz, 4H), 7.36 (d, *J* = 4.0 Hz, 4H), 7.10 (d, *J* = 4.0 Hz, 2H), 4.39 (d, *J* = 7.2 Hz, 2H), 2.05 (s, 2H), 1.47 – 1.01 (m, 48H), 0.88 – 0.68 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.84, 146.65, 145.78, 142.08, 139.28, 135.71, 132.17, 128.21, 127.44, 119.08, 117.69, 50.33, 37.36, 32.02, 31.97,

30.40, 30.03, 29.77, 29.57, 26.53, 22.83, 22.80, 14.20. FT-IR (KBr, cm^{-1}) ν: 2921.8, 2850.8, 1648.6, 1614.2, 1575.5, 1428.5, 1414.4, 1390.5, 1324.9, 1276.1, 1255.2, 1237.2, 1176.9, 1069.1, 977.6, 936.4, 839.4, 785.4. MS (MALDI) m/z: 1161.4 $(M+H)^+$. HRMS (MALDI-FT) (m/z): $(M+H)^+$ Calcd. for $C_{64}H_{79}O_4N_2Br_2S_2$: 1161.3843; Found: 1161.3822.



***N,N'*-bis(2-hexyldecyl)-6,6'-bis(5-phenylthiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 4:** A mixture of phenylboronic acid (74 mg, 0.6 mmol), *N,N'*-bis(2-hexyldecyl)-6,6'-di(5-bromothiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide **S7** (232 mg, 0.2 mmol), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) and KOAc (200 mg, 2 mmol) was dissolved in 2 mL DMSO under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 12 h. After cooling down to room temperature, the mixture was poured into water and extracted with dichloromethane. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/hexane (1:3) to give **4** as brown solid (164 mg, 71% yield). M.p. 227-228 °C. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.31 (d, *J* = 10.8 Hz, 4H), 7.70 (d, *J* = 10.8 Hz, 4H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.35 (d, *J* = 3.3 Hz, 2H), 7.29 – 7.24 (m, 6H), 7.08 (d, *J* = 3.3 Hz, 2H), 4.43 (d, *J* = 6.3 Hz, 4H), 2.11 (s, 2H), 1.47 – 1.21 (m, 48H), 0.91 – 0.74 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 165.81, 148.88, 146.40, 144.09, 141.86, 138.76, 135.29, 133.05, 129.10, 128.94, 128.46, 127.27, 125.62, 124.91, 118.72, 50.09, 37.30, 31.94, 31.81, 30.36, 29.99, 29.71, 29.49, 26.43, 22.76, 22.71, 14.13, 14.10. FT-IR (KBr, cm^{-1}) ν: 2922.5, 2851.5, 1647.1, 1613.1, 1575.7, 1425.3, 1389.2, 1342.7, 1268.5, 1253.3, 1215.3, 1174.8, 1070.4, 934.1, 887.3,

841.4, 780.4, 752.7, 685.1. MS (MALDI) m/z: 1155.8 $(M-H)^-$. HRMS (MALDI) (m/z): $(M-H)^-$ Calcd for $C_{76}H_{87}N_2O_4S_2$ 1155.6077; Found, 1155.6102. Anal. Calcd. for $C_{76}H_{88}N_2O_4S_2$: C, 78.85; H, 7.66; N, 2.42. Found: C, 78.55; H, 7.83; N, 2.28.

***N*,*N*'-bis(2-hexyldecyl)-6,6'-bis(5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-[2,2'-biazulene]-1,1',3,3'-tetracarboxdiimide 5:** A similar procedure to that used for **4** gave **5** as a brown solid (165 mg, 64% yield). M.p. 270-271 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.26 (d, *J* = 10.9 Hz, 4H), 7.62 (d, *J* = 10.9 Hz, 4H), 7.53 – 7.45 (m, 8H), 7.32 (d, *J* = 3.6 Hz, 2H), 7.11 (d, *J* = 3.6 Hz, 2H), 4.43 (d, *J* = 6.3 Hz, 4H), 2.14 (br, 2H), 1.43 – 1.23 (m, 48H), 0.88 – 0.82 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 165.61, 146.32, 145.68, 145.27, 141.85, 138.76, 136.13, 135.27, 128.90, 127.13, 126.03, 125.82, 125.49, 118.77, 37.34, 31.95, 31.80, 30.41, 30.05, 29.74, 29.52, 26.42, 22.79, 22.72, 14.14, 14.10. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.70. FT-IR (KBr, cm^{-1}) ν: 2922.9, 2851.8, 1650.1, 1613.8, 1575.3, 1504.9, 1425.5, 1392.6, 1323.1, 1267.8, 1167.2, 1125.7, 1064.5, 1015.2, 936.1, 887.7, 837.6, 796.5, 780.0, 759.7, 735.4. MS (MALDI) m/z: 1291.8 $(M-H)^-$. HRMS (MALDI) (m/z): $(M-H)^-$ Calcd for $C_{78}H_{85}F_6N_2O_4S_2$ 1291.5850; Found, 1291.5795. Anal. Calcd. for $C_{78}H_{86}F_6N_2O_4S_2$: C, 72.42; H, 6.70; N, 2.17. Found: C, 72.46; H, 6.73; N, 2.11.

3. Thermal properties

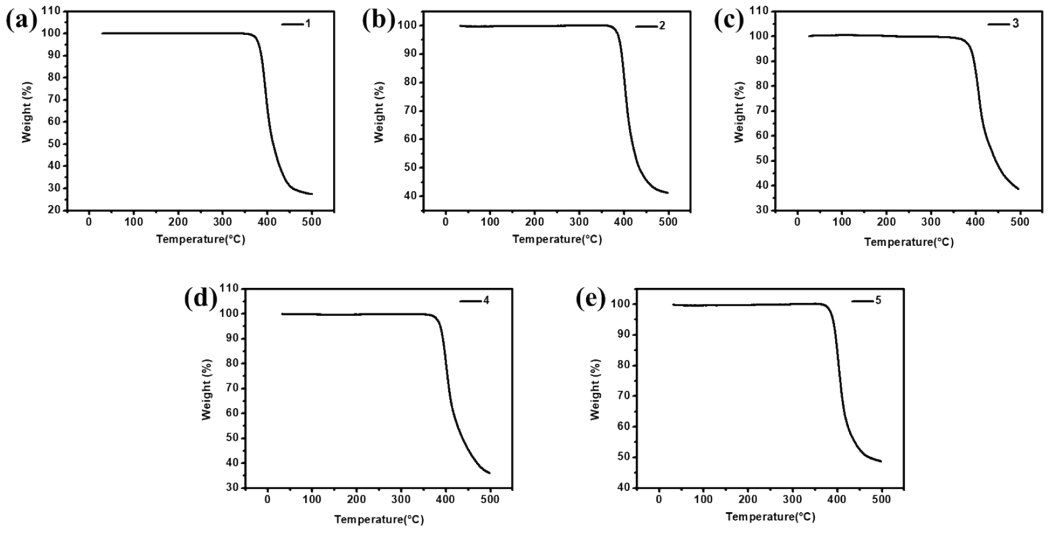


Figure S1. TGA measurements of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5**.

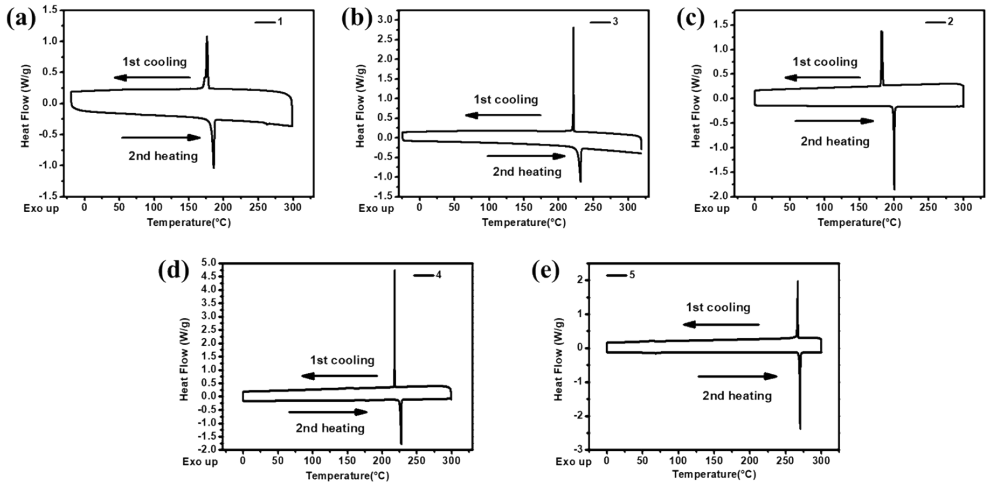


Figure S2. DSC curves of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5**.

4. X-ray Crystallographic data

Table S1. Crystal data and structure refinement for **6**.

Empirical formula	$C_{104}\ H_{102}\ N_4\ O_8$
Formula weight	1535.90
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.3247(7) A alpha = 93.227(3) deg. b = 16.6349(9) A beta = 97.302(3) deg. c = 19.0232(8) A gamma = 103.143(3) deg.
Volume	4057.0(4) A^3
Z, Calculated density	2, 1.257 Mg/m^3
Absorption coefficient	0.618 mm^-1
F(000)	1782
Crystal size	0.05 x 0.04 x 0.03 mm
Theta range for data collection	2.351 to 65.132 deg.
Limiting indices	-15<=h<=15, -19<=k<=19, -19<=l<=22
Reflections collected / unique	35999 / 13185 [R(int) = 0.1232]
Completeness to theta = 65.132	95.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13185 / 1011 / 1049
Goodness-of-fit on F^2	1.347
Final R indices [I>2sigma(I)]	R1 = 0.0976, wR2 = 0.2346
R indices (all data)	R1 = 0.1758, wR2 = 0.2647
Extinction coefficient	n/a
Largest diff. peak and hole	1.133 and -0.600 e.A^-3

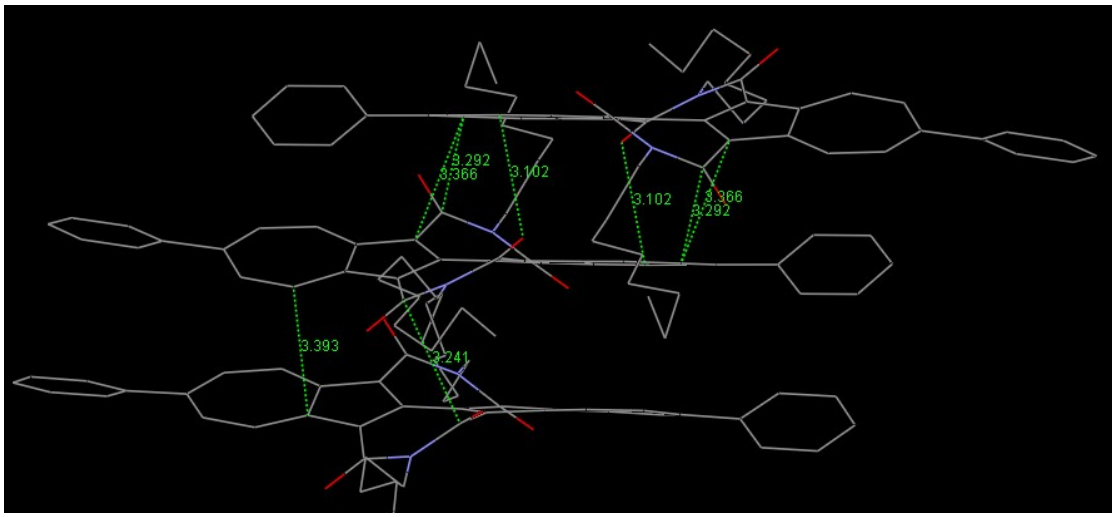


Figure S3. Packing structure of compound **6** with short contact distances.

5. OFET device fabrication and measurement

The Si/SiO_2 substrates with a capacitance of 10 nF cm^{-2} was used as the gate electrode and dielectric layer. Thin films of semiconductors **1**–**5** were deposited on octadecyltrimethoxysilane (OTMS)-treated Si/SiO_2 substrates by spin-coating their respectively chloroform solutions (5 or 10 mg mL^{-1}). Gold, used as source and drain electrode, were deposited on the top of the active layer through a shadow mask under high vacuum, affording a bottom-gate top-contact (BGTC) device configuration. The channel length (L) and width (W) were 31 μm and 273 μm, respectively. The electric characteristics of the OFET devices were measured by using a Keithley 4200-SCS semiconductor parameter analyzer in a glovebox with a nitrogen atmosphere. The field-effect mobility was calculated in the saturation regime according to the equation $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, V_G is the gate voltage, V_T is the threshold voltage, μ is the field-effect mobility, W is the channel width, L is the channel length, and C_i is the capacitance per unit area of the gate dielectric layer.

The performance of the OFET devices were also measured under ambient conditions. Since the LUMO levels of compounds **1-5** are relatively high (3.63-3.73 eV), the devices of these compounds tested in air showed nonstandard transfer and output characteristics with electron mobilities 1-2 orders of magnitude lower than those

measured in nitrogen atmosphere. Further modifications of these compounds such as adding electron-withdrawing group in the 4- and 8-positions of azulene units might lower the LUMO levels and make their OFET devices air stable.

6. All-PSC device fabrication and measurement

PTB7-Th and small molecule acceptor (**2** or **5**) with a weight ratio of 1:1 were co-dissolved in o-dichlorobenzene solution for the blend films, the total material concentration was 20 mg mL^{-1} and the solution was stirred at 100 °C overnight under N_2 atmosphere. The photovoltaic solar cells were fabricated with a structure of ITO / ZnO / active layer / MoO_3 / Ag. A thin layer (~30 nm) of ZnO sol-gel was spin-coated onto ITO glass and annealed at 200 °C in ambient condition for 30 min then transferred into glovebox immediately. Active layers (the as prepared solutions) were then spin-coated in the glovebox. After staying at room temperature for 10-15 min, the film was annealed at 120 °C for 30 min. Finally, MoO_3 (5-6 nm) and Ag (100 nm) anodes were thermal evaporated through a shadow mask in glovebox at a chamber pressure of ~2.0×10^{-6} mbar. The active area of the device was 7 mm^2. Current density-voltage (*J-V*) curves were detected on a Keithley 2420 source meter. Photocurrent was obtained upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W, USA) with AM 1.5 G filter. Light intensity was calibrated to 100 mW cm^{-2} using a NREL-certified standard silicon cell (Oriel reference cell 91150, USA). External quantum efficiency (EQE) was recorded with a 75 W Xe lamp, an Oriel monochromator (74125), an optical chopper, a lock-in amplifier, and a NREL-calibrated crystalline silicon cell.

SCLC mobility evaluations

SCLC method with a device configuration of glass/Al/blend films/Al and ITO/PEDPOT:PSS/blend films/Au to measure the electron and hole mobility, respectively.[3,4] According to Mott–Gurney law, SCLC theory can be described by the equation (1), where J is current density, ε_0 is permittivity of vacuum, ε_r is relative permittivity of the material, μ is mobility, V_a is applied voltage, V_{bi} is built-in voltage, which results from the difference in the work function of the anode and the cathode

(in electron-only device structure, V_{bi} = 0 V, and in hole-only device structure, V_{bi} = 0.4 V), and d is the thickness of the active film.[5]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{(V_a - V_{bi})^2}{d^3} \qquad (1)$$

We tested the I-V curve of the devices and made the ln$V$ versus the ln$J$ curve (Figure S4 and S5, the red line), we also made the curve fitting, where the slope is 2 (Figure S4 and S5, the black line).[6]

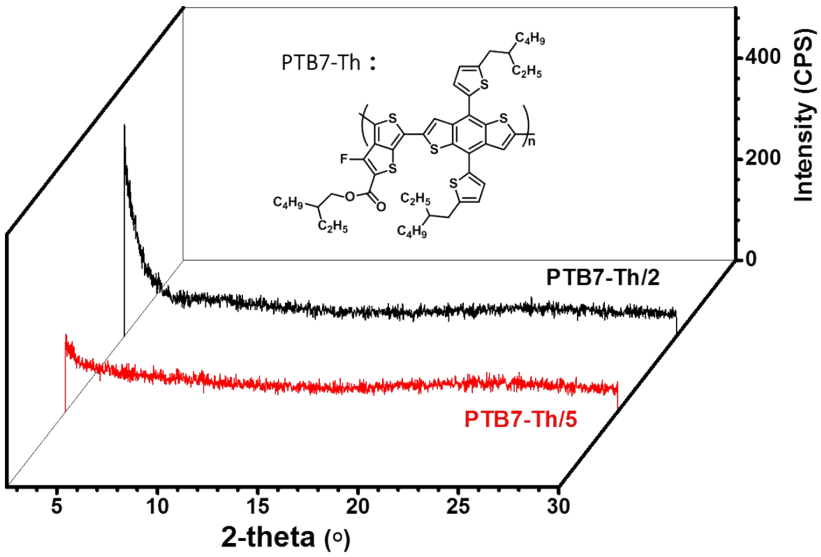


Figure S4. XRD patterns of blend films of PTB7-Th:**2** and PTB7-Th:**5**. Inset is the chemical structure of PTB7-Th.

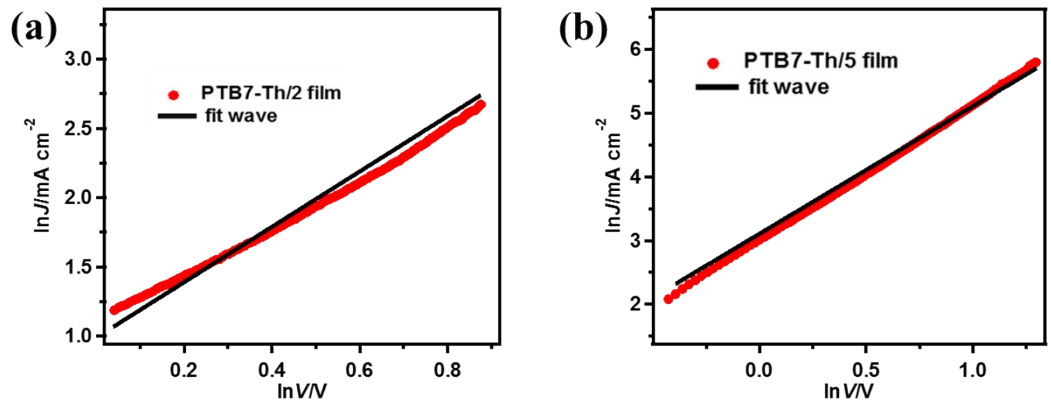


Figure S5. SCLC fittings of the hole-only devices based on the blend films of (a) PTB7-Th:**2** and (b) PTB7-Th:**5**.

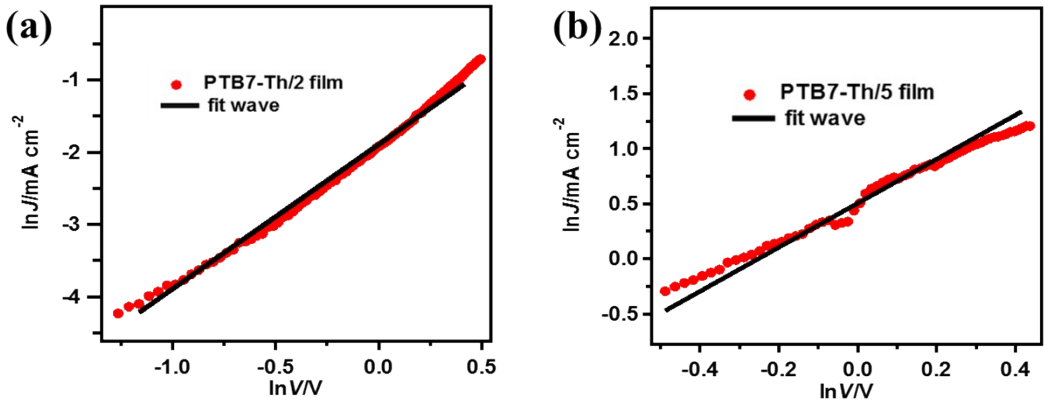


Figure S6. SCLC fittings of the electron-only devices based on the blend films of (a) PTB7-Th:**2** and (b) PTB7-Th:**5**.

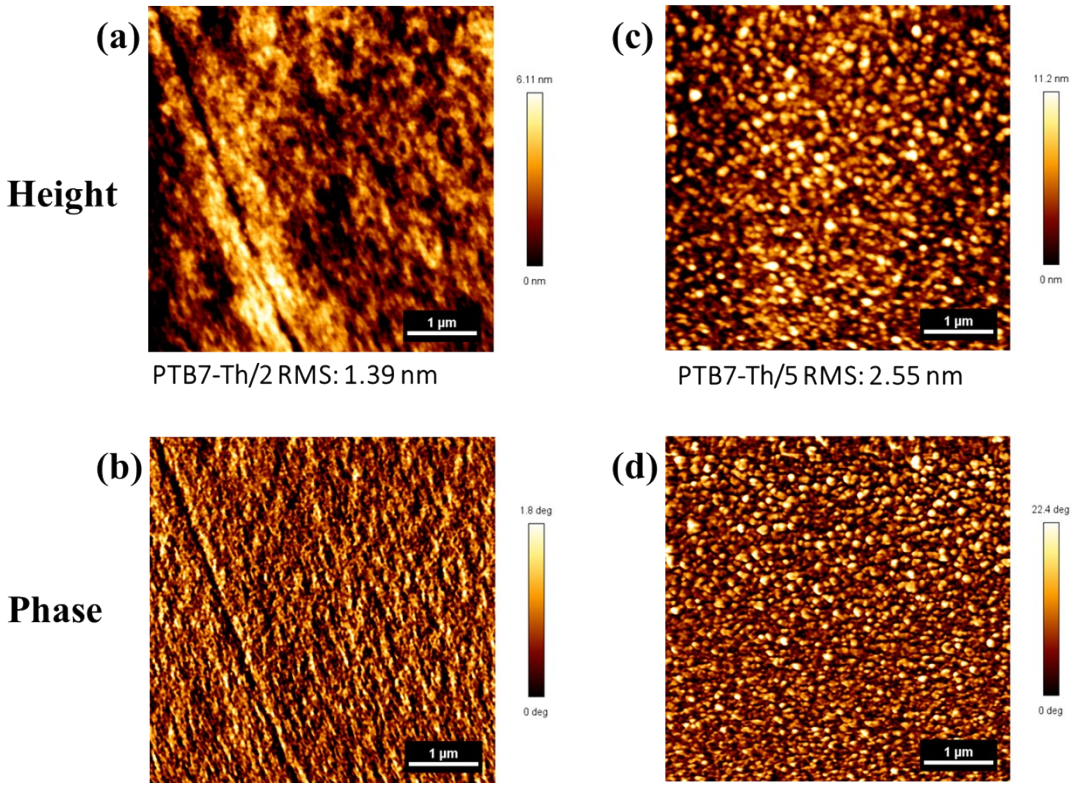


Figure S7. AFM height and phase images of blend films of PTB7-Th:**2** (a, b) and PTB7-Th:**5** (c, d).

7. References

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8. NMR and MS spectra

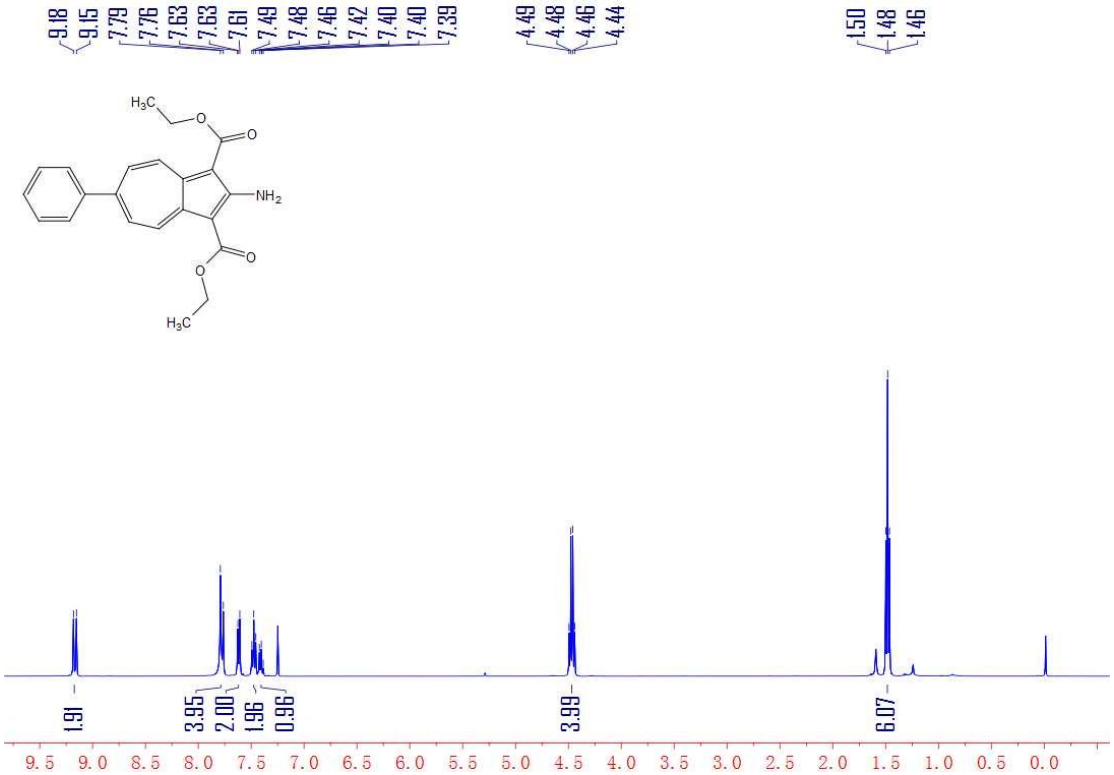


Figure S8. ^{1}H NMR spectrum of **S2a** (400 MHz, $CDCl_3$).

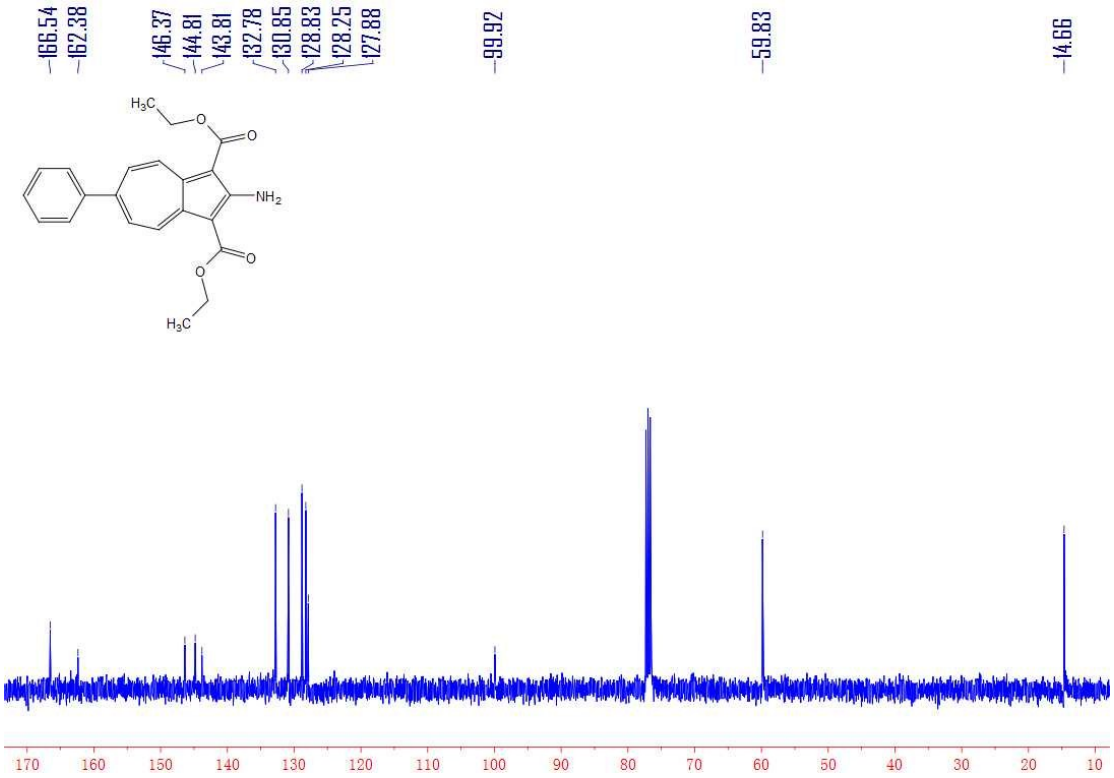


Figure S9. ^{13}C NMR spectrum of **S2a** (100 MHz, $CDCl_3$).

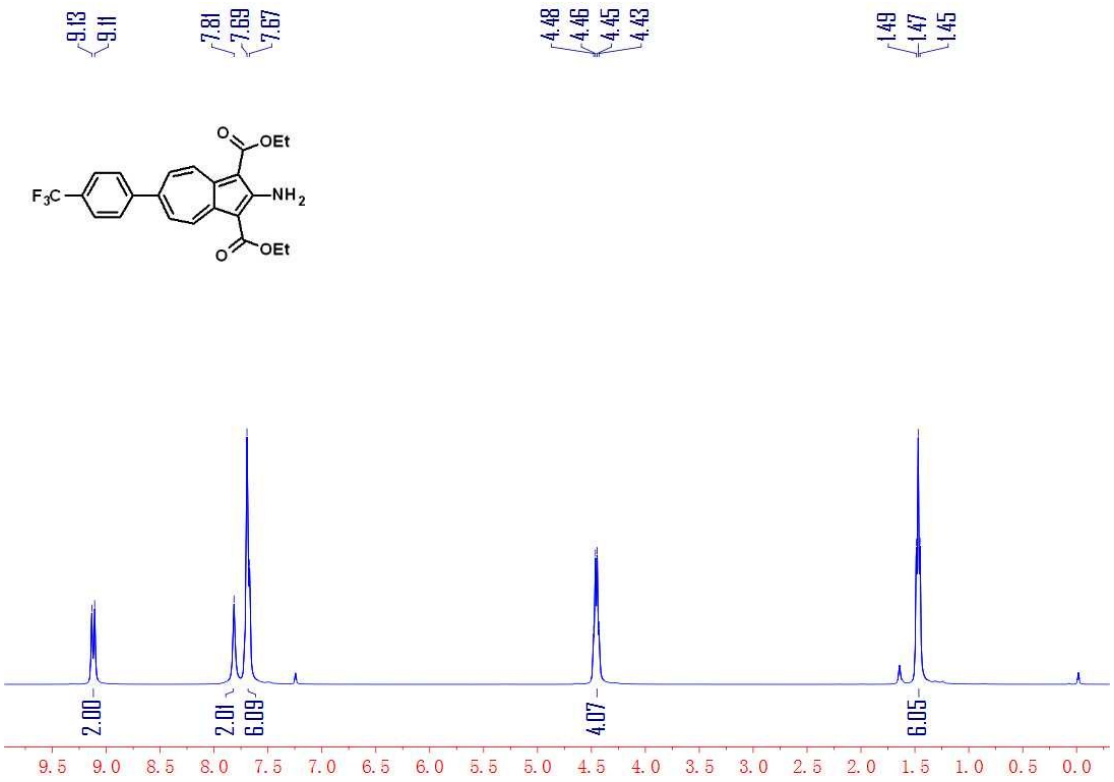


Figure S10. ^{1}H NMR spectrum of **S2b** (400 MHz, $CDCl_3$).

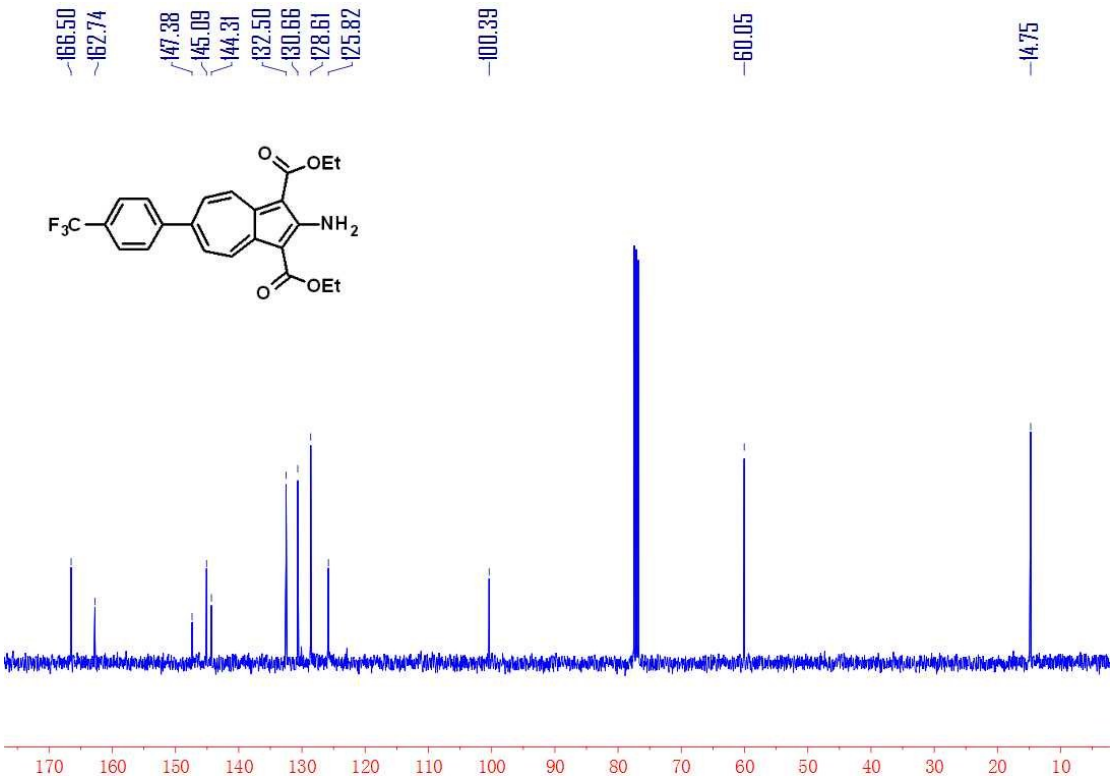


Figure S11. ^{13}C NMR spectrum of **S2b** (100 MHz, $CDCl_3$).

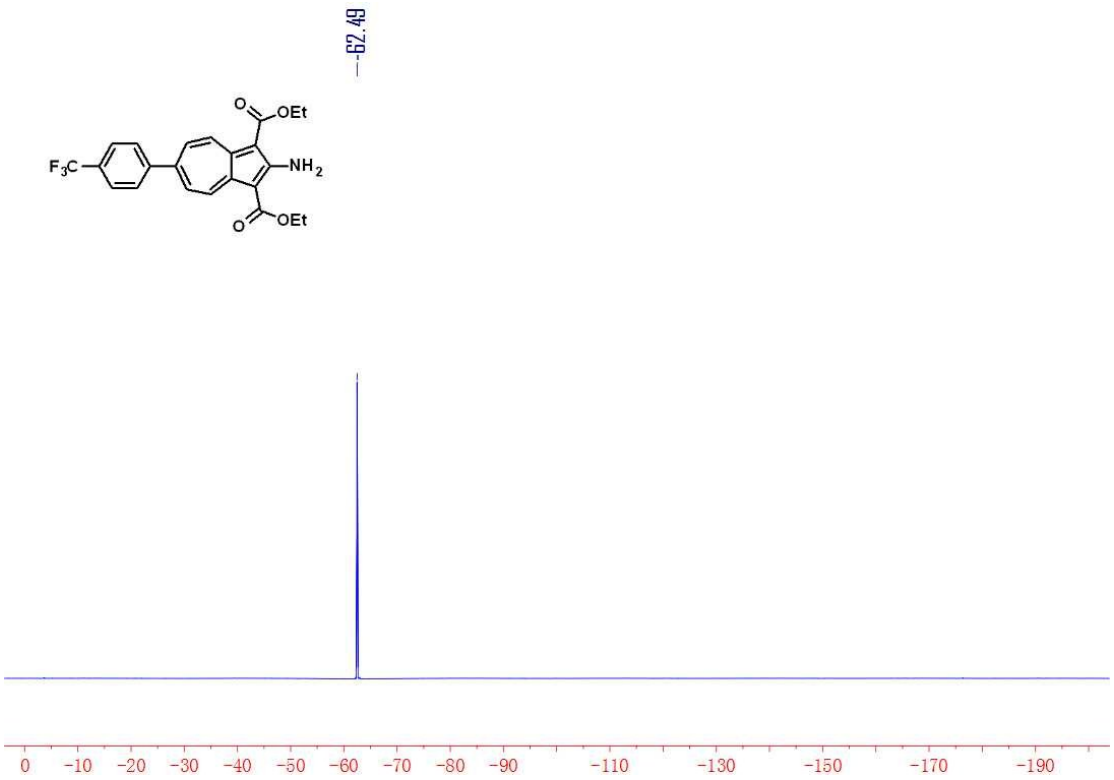


Figure S12. ^{19}F NMR spectrum of **S2b** (376 MHz, $CDCl_3$).

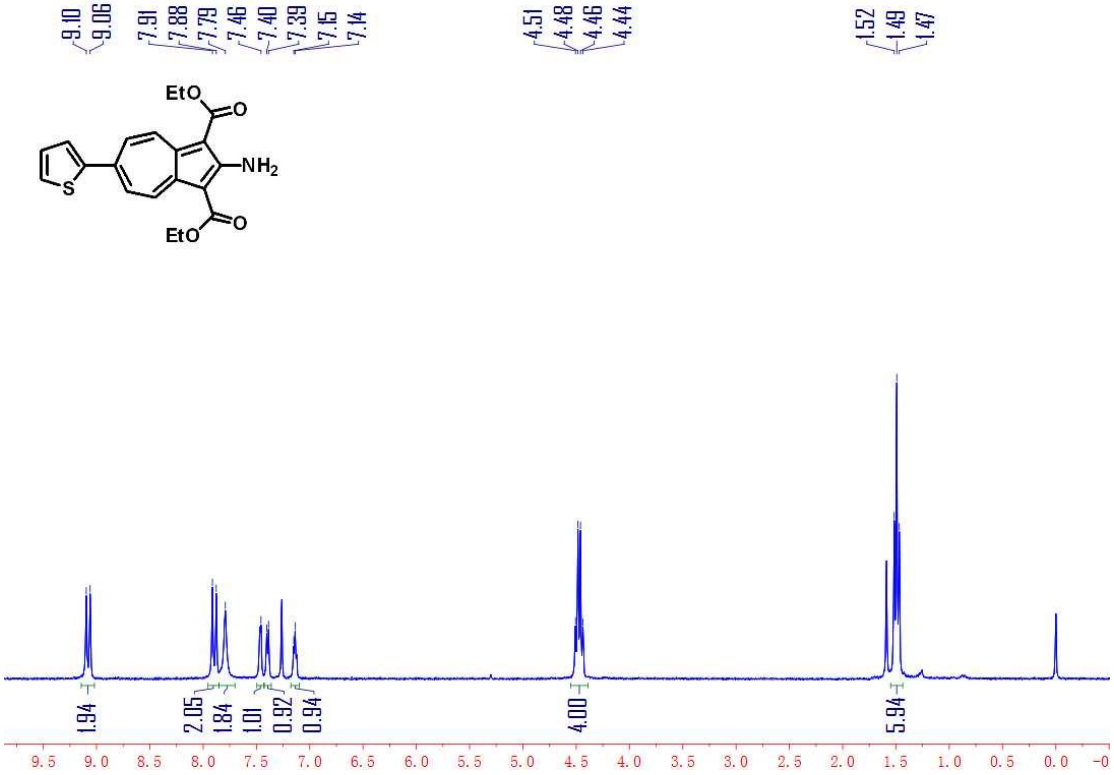


Figure S13. ^{1}H NMR spectrum of **S2c** (300 MHz, $CDCl_3$).

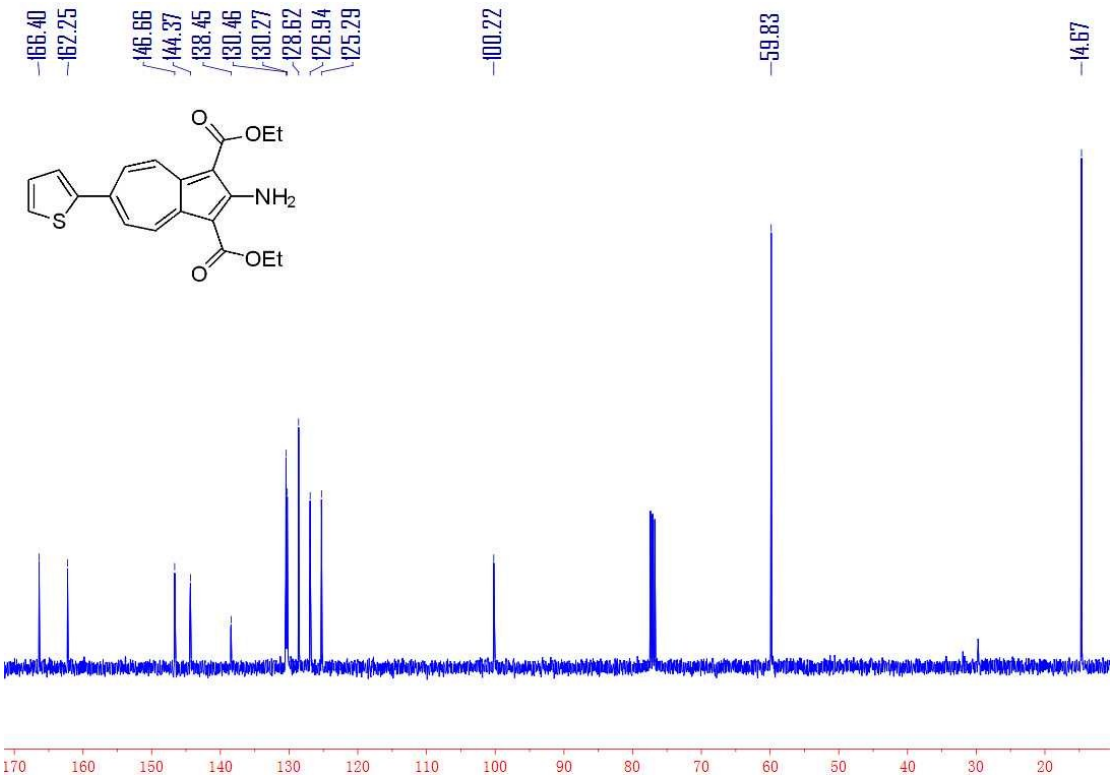


Figure S14. ^{13}C NMR spectrum of **S2c** (100 MHz, $CDCl_3$).

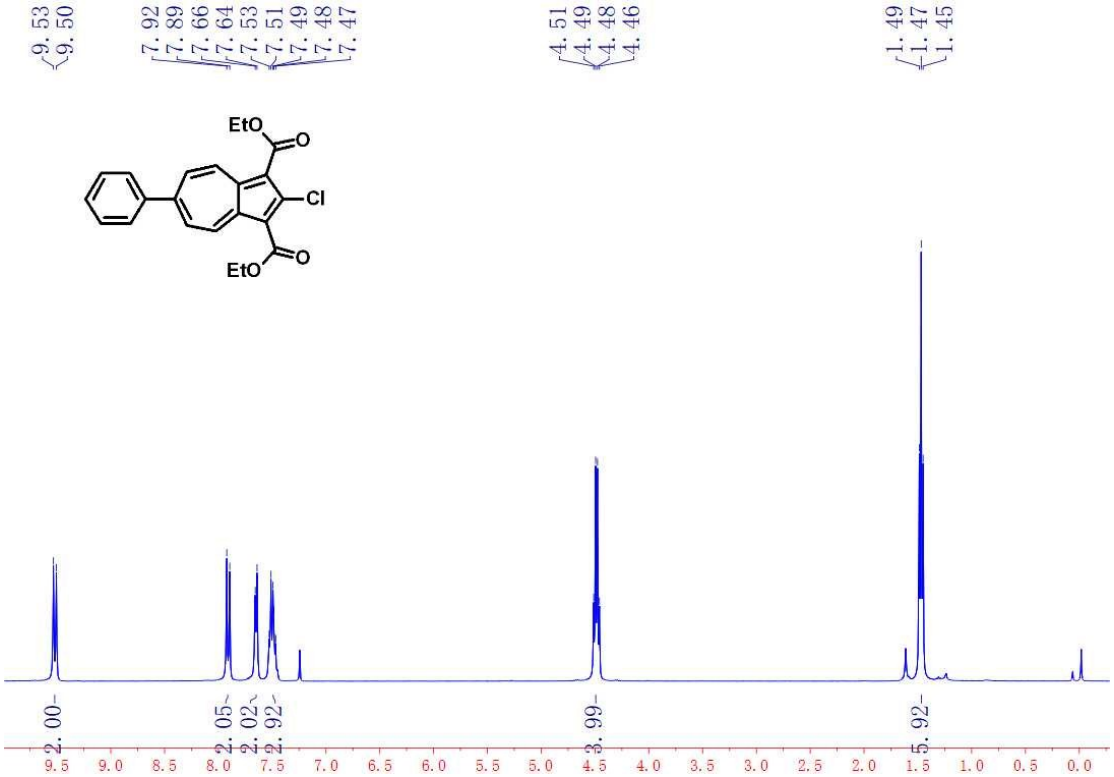


Figure S15. ^{1}H NMR spectrum of **S3a** (400 MHz, $CDCl_3$).

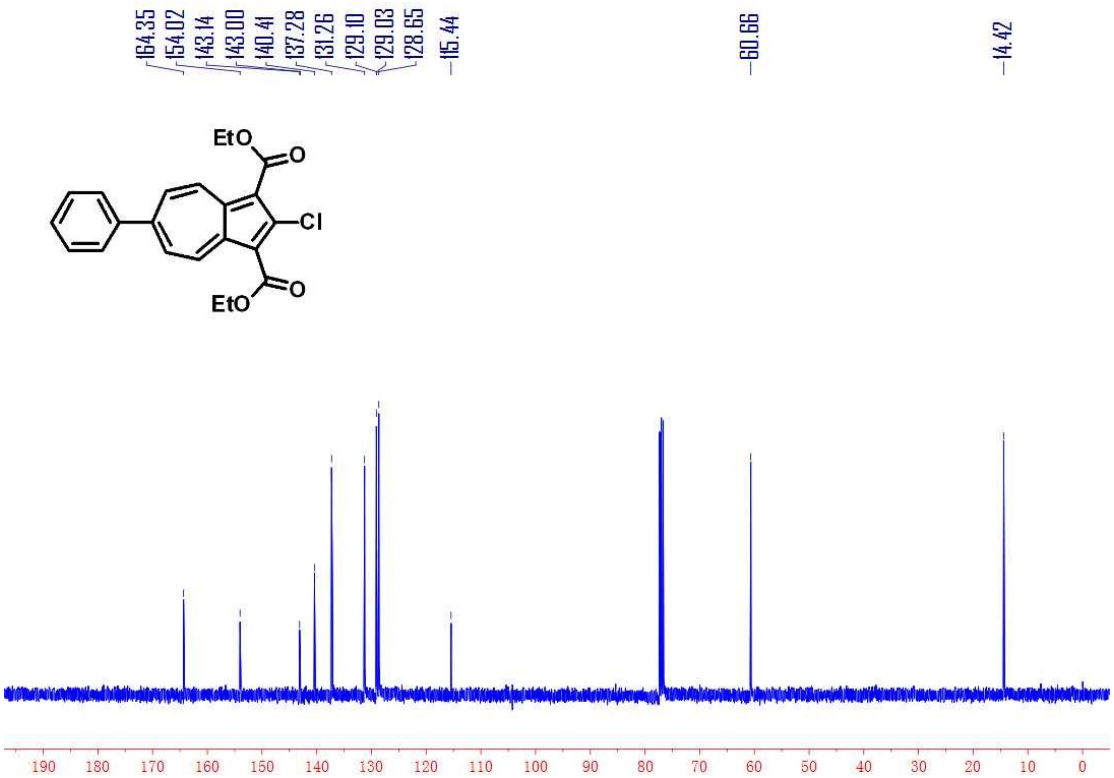


Figure S16. ^{13}C NMR spectrum of **S3a** (100 MHz, $CDCl_3$).

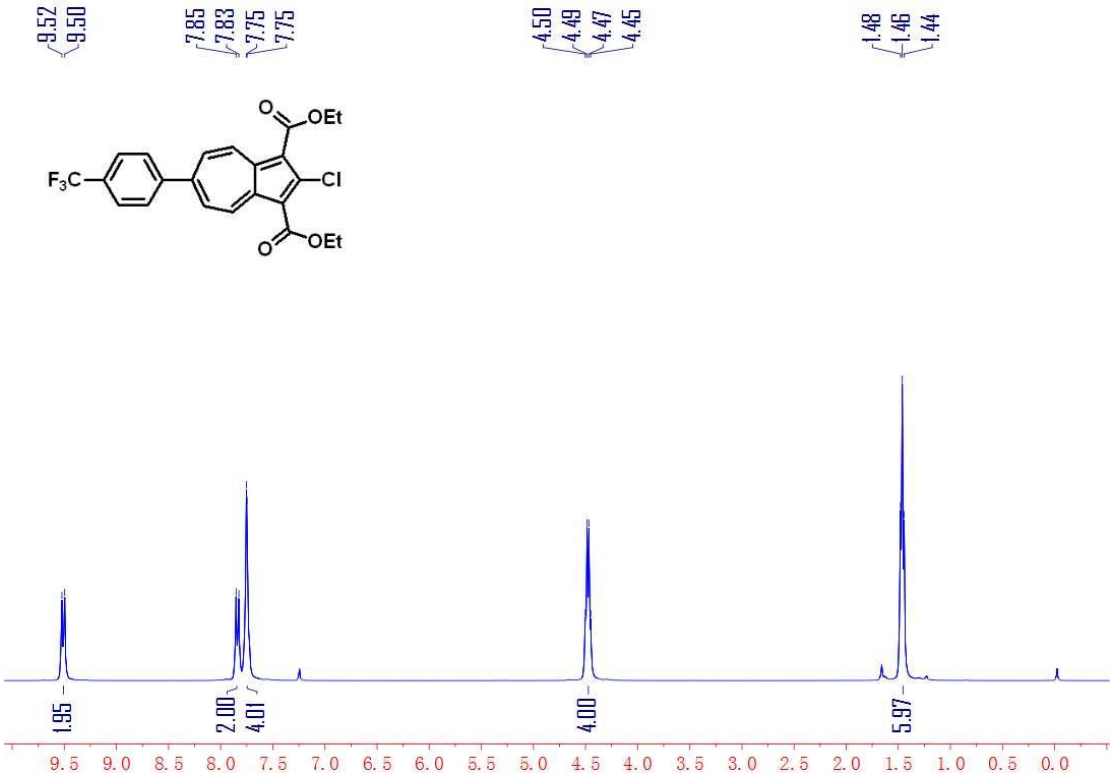


Figure S17. ^{1}H NMR spectrum of **S3b** (400 MHz, $CDCl_3$).

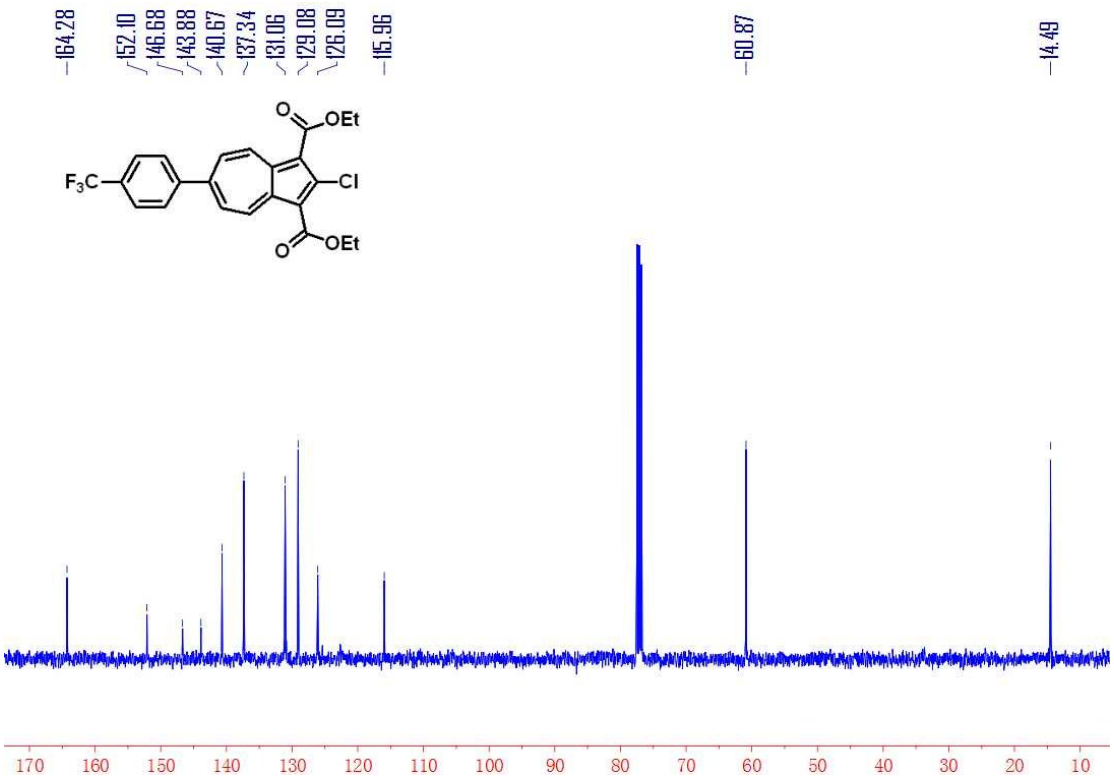


Figure S18. ^{13}C NMR spectrum of **S3b** (100 MHz, $CDCl_3$).

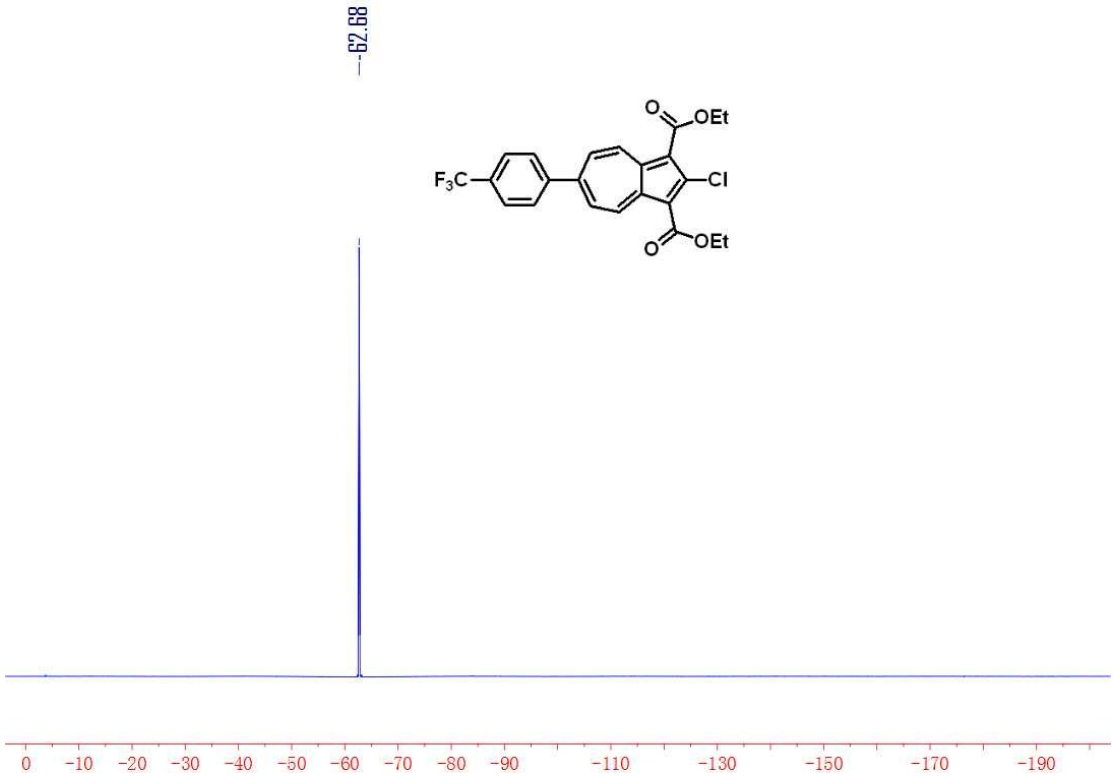


Figure S19. ^{19}F NMR spectrum of **S3b** (376 MHz, $CDCl_3$).

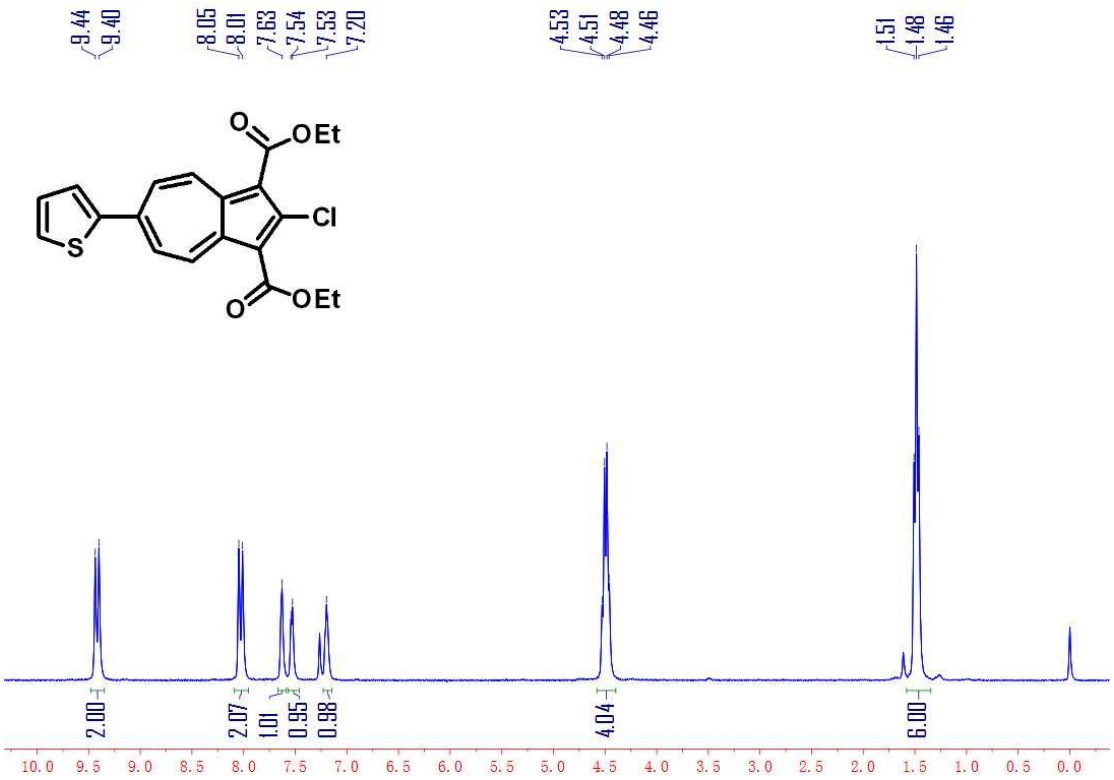


Figure S20. ^{1}H NMR spectrum of **S3c** (300 MHz, DMSO-d_6).

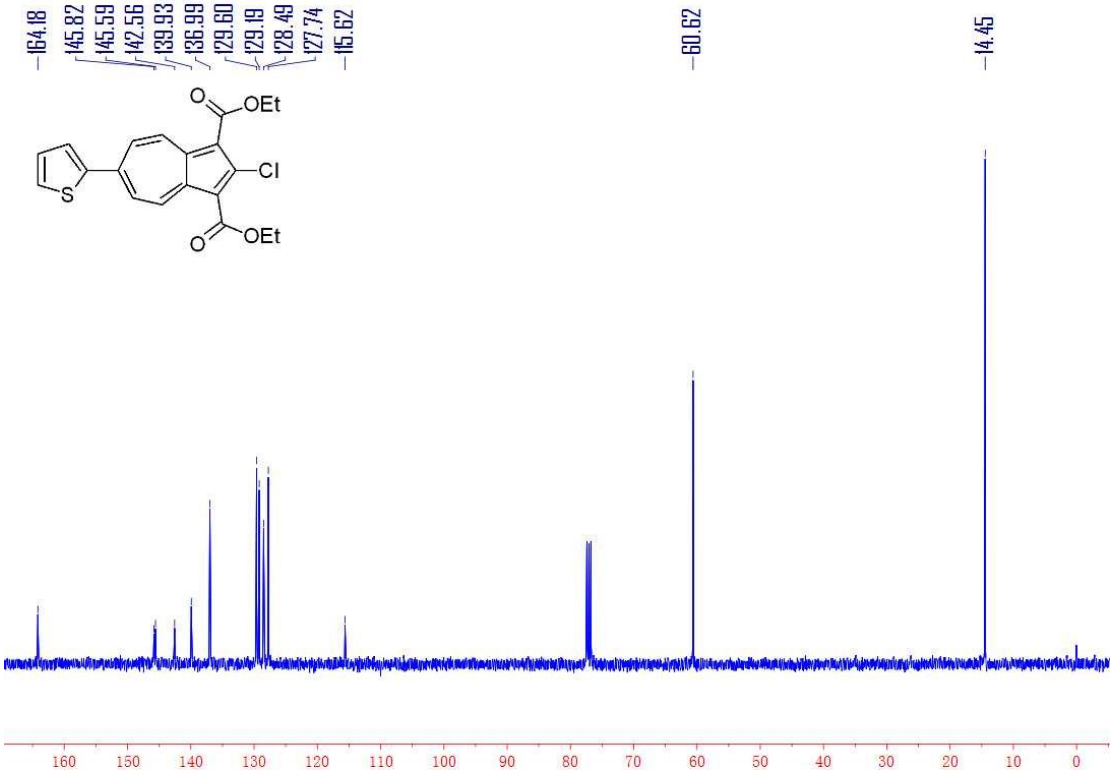


Figure S21. ^{13}C NMR spectrum of **S3c** (100 MHz, $CDCl_3$).

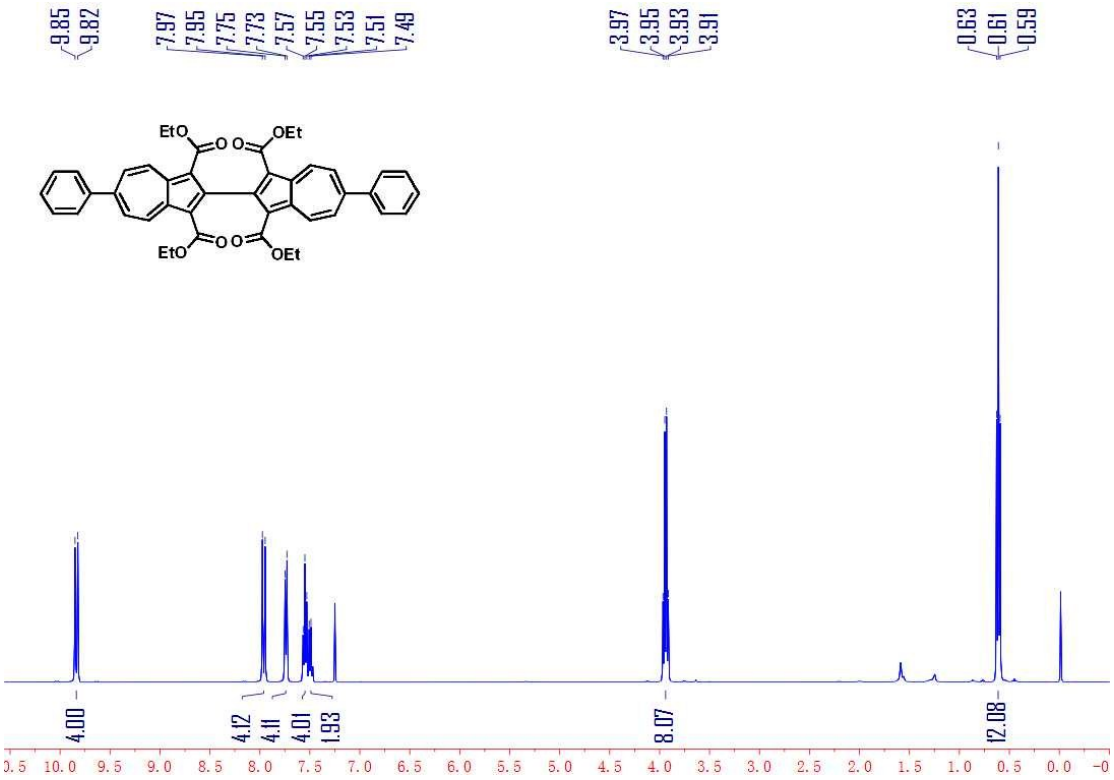


Figure S22. ^{1}H NMR spectrum of **S4a** (400 MHz, $CDCl_3$).

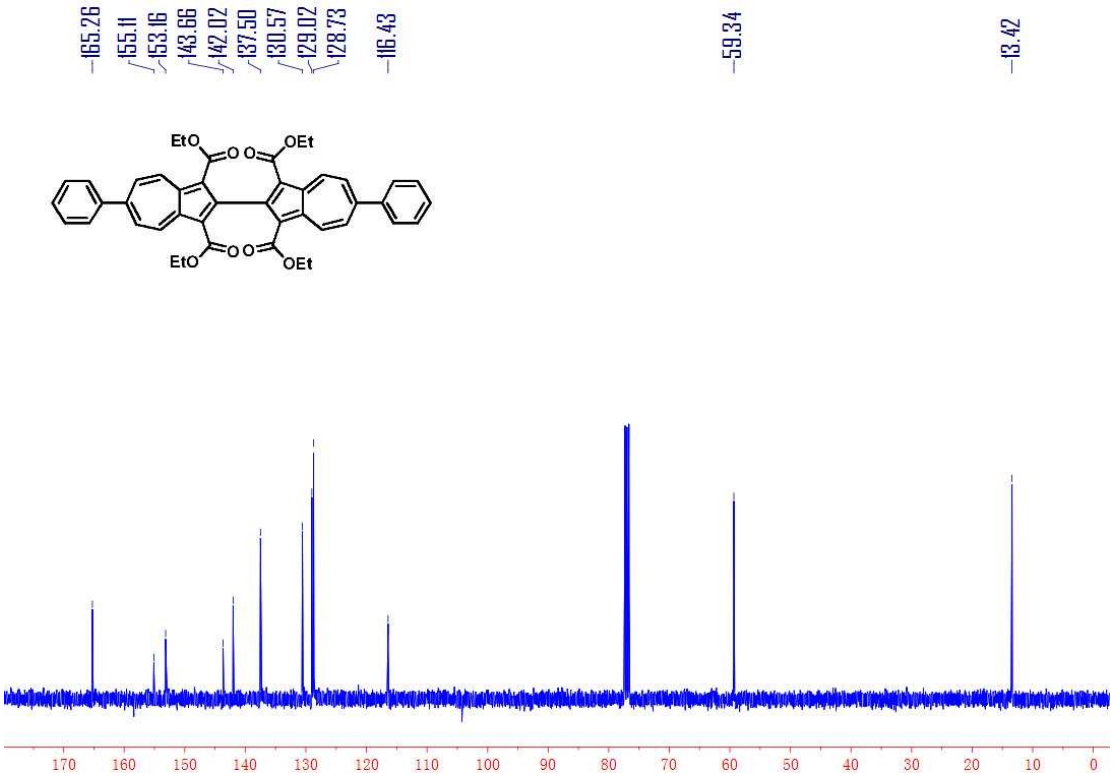


Figure S23. ^{13}C NMR spectrum of **S4a** (100 MHz, $CDCl_3$).

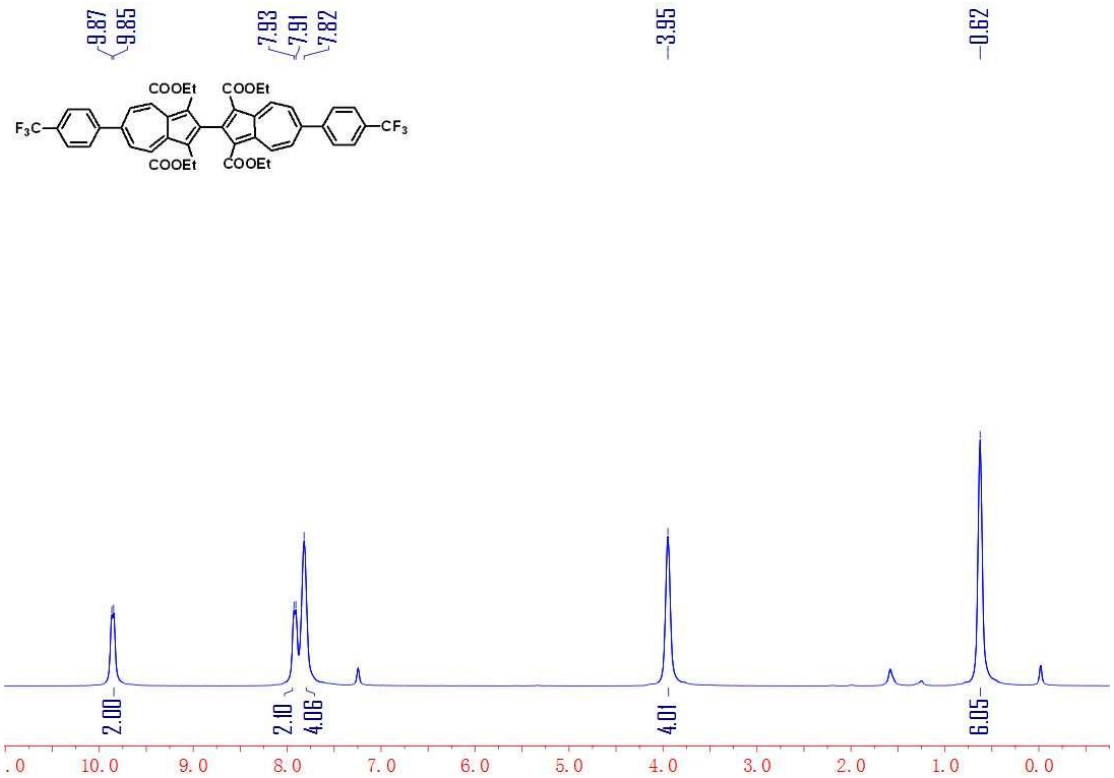


Figure S24. ^{1}H NMR spectrum of **S4b** (400 MHz, $CDCl_3$).

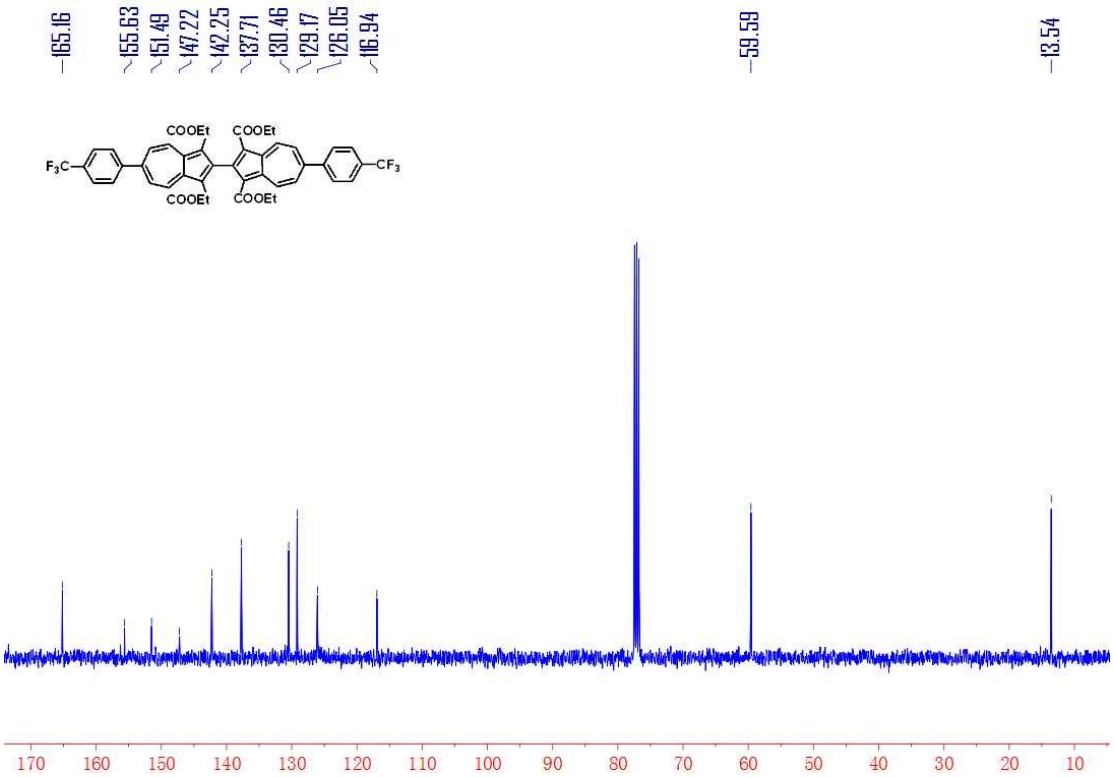


Figure S25. ^{13}C NMR spectrum of **S4b** (100 MHz, $CDCl_3$)

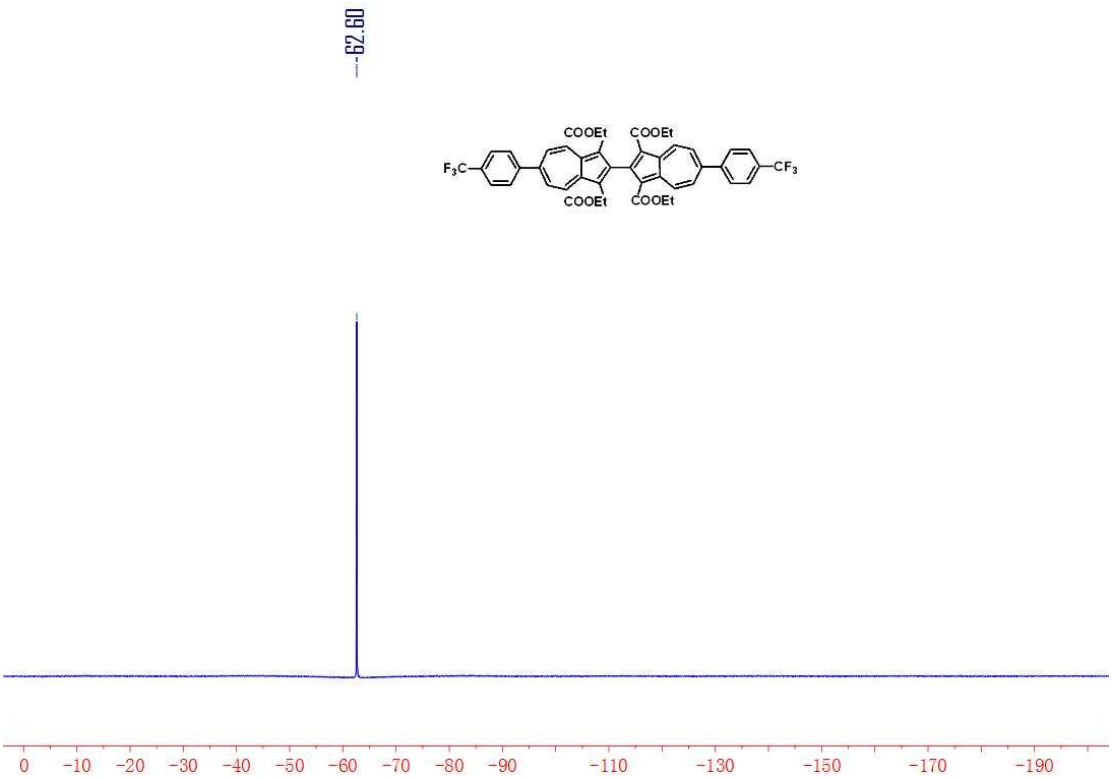


Figure S26. ^{19}F NMR spectrum of **S4b** (376 MHz, $CDCl_3$).

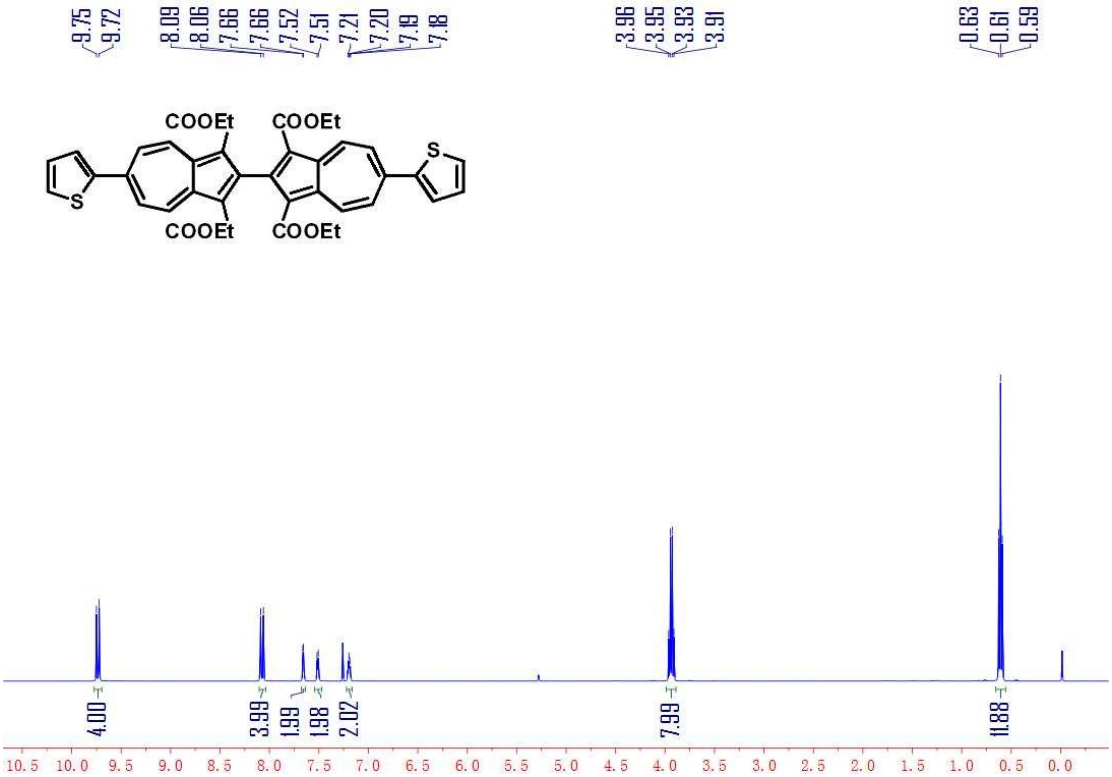


Figure S27. ^{1}H NMR spectrum of **S4c** (400 MHz, $CDCl_3$).

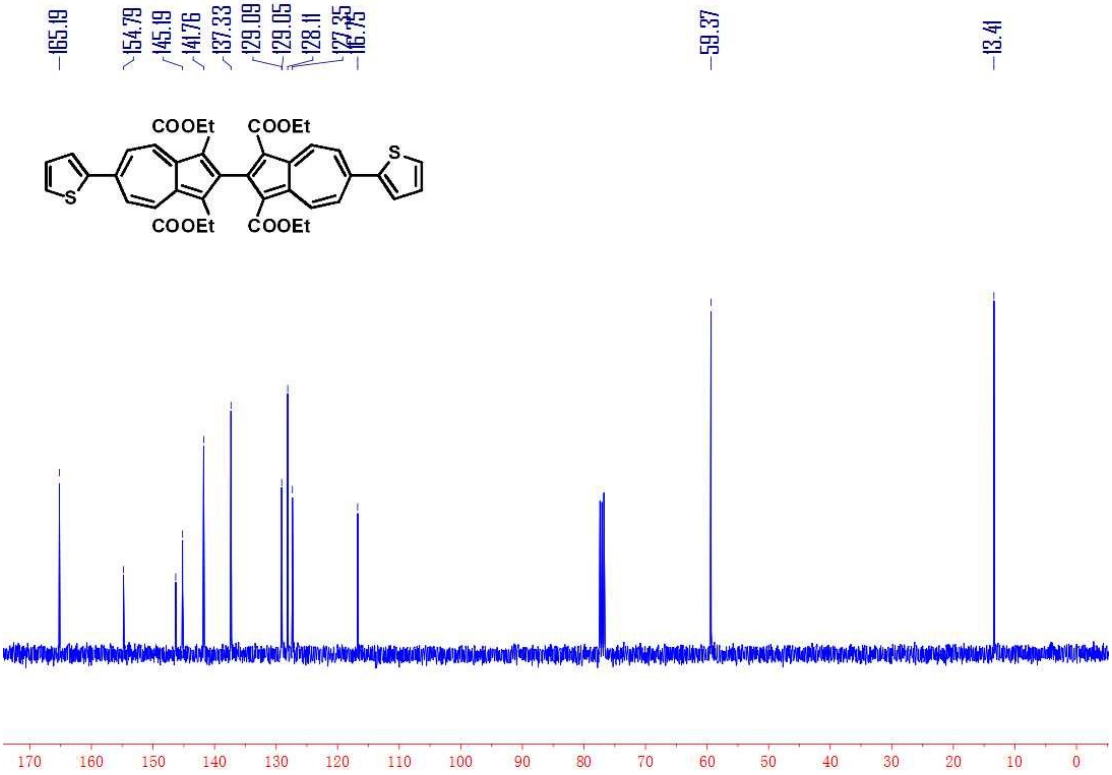


Figure S28. ^{13}C NMR spectrum of **S4c** (100 MHz, $CDCl_3$).

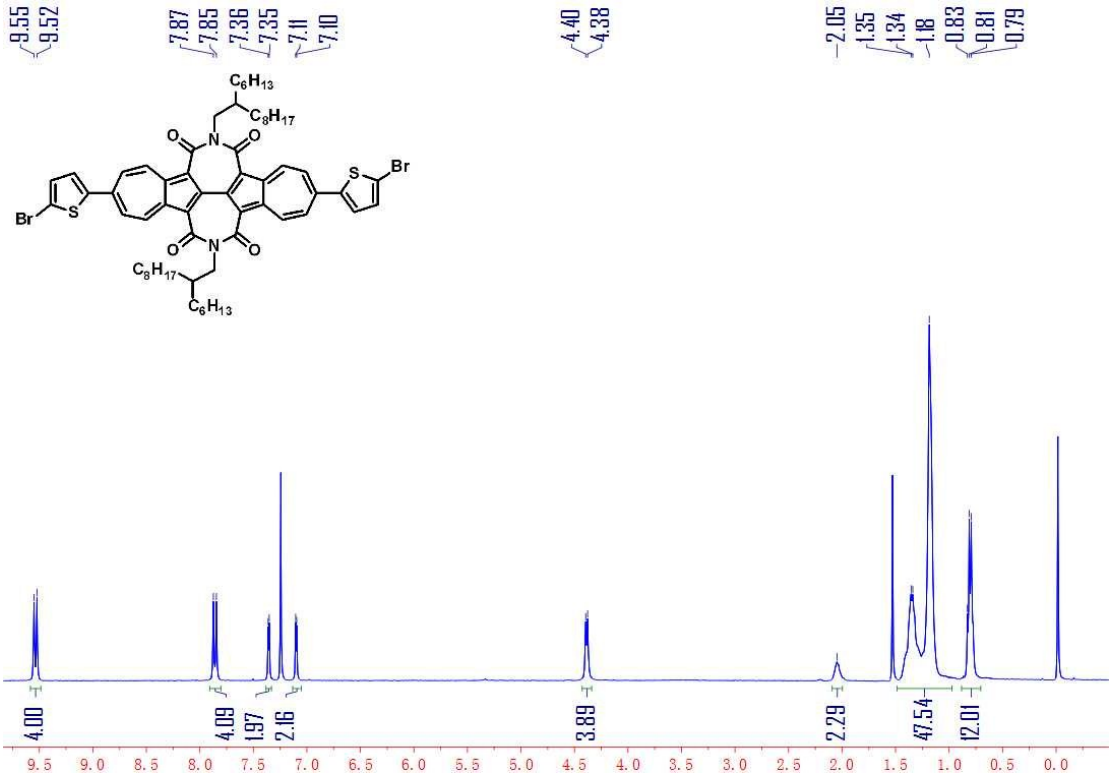


Figure S29. ^{13}C NMR spectrum of **S7** (100 MHz, $CDCl_3$).

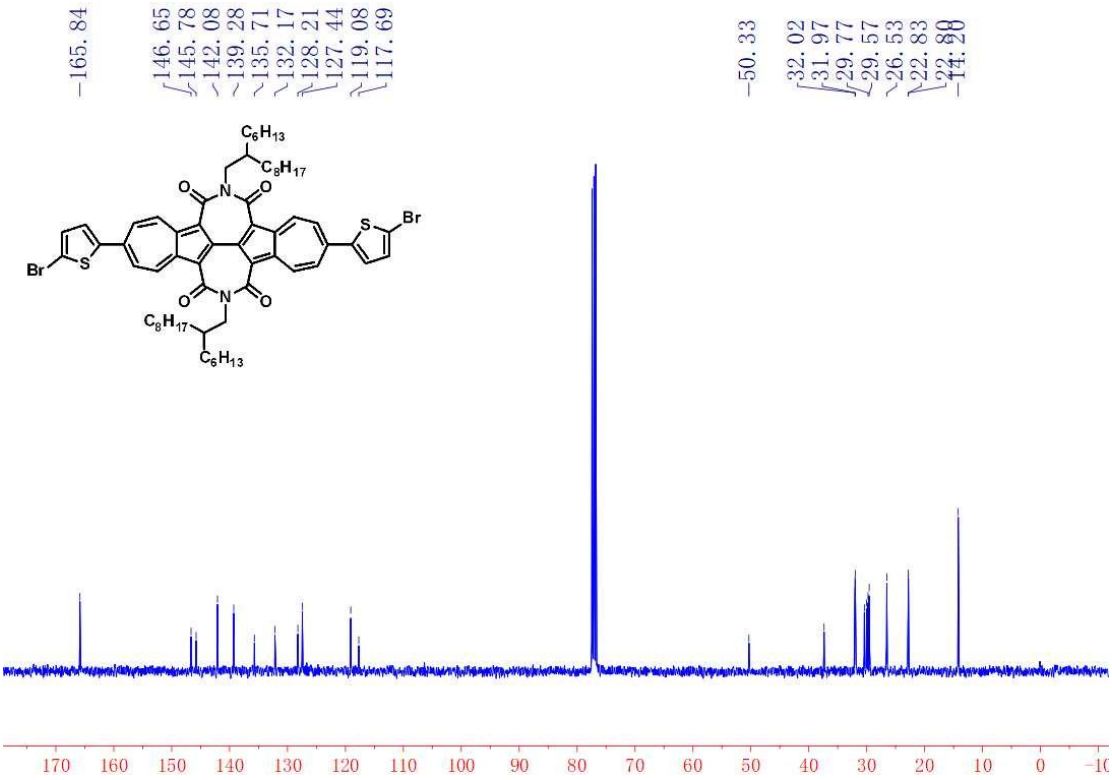


Figure S30. ^{13}C NMR spectrum of **S7** (100 MHz, $CDCl_3$).

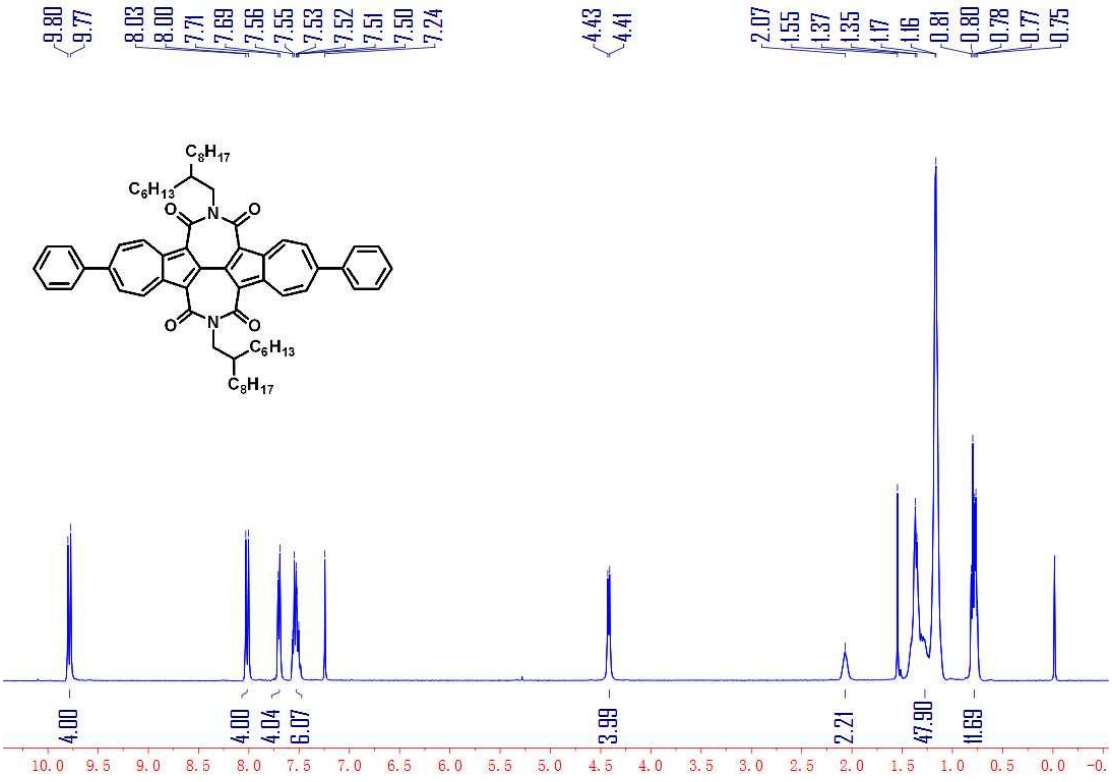


Figure S31. ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$).

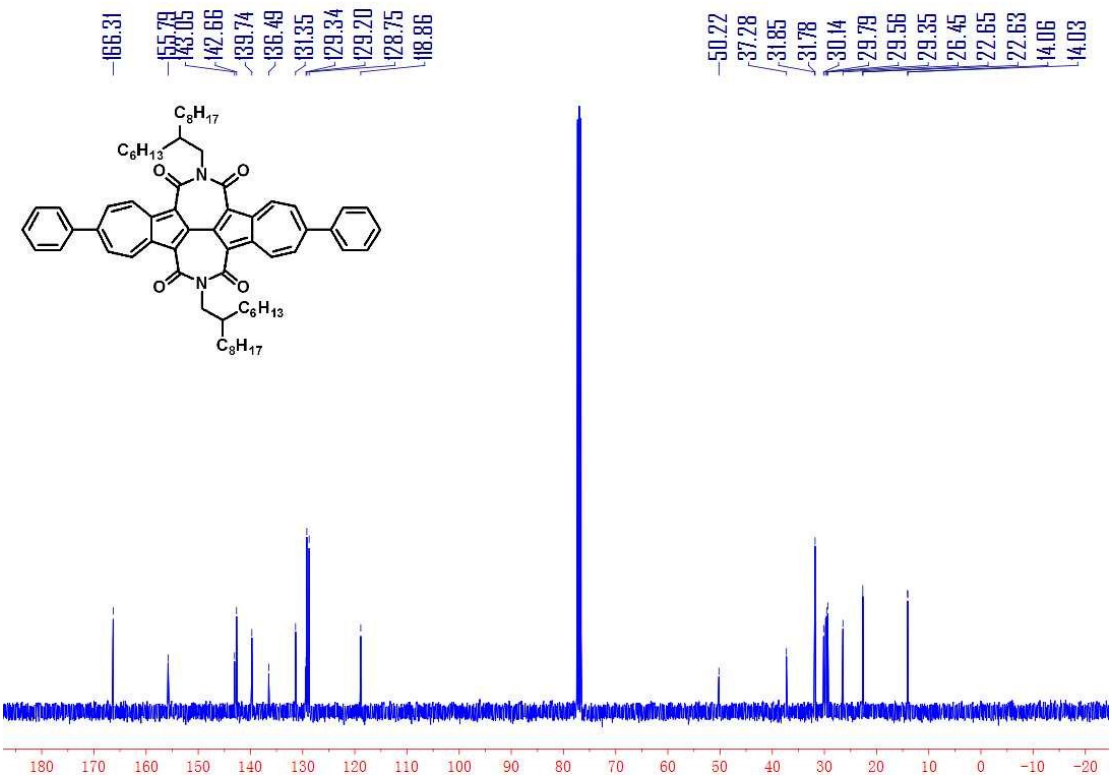


Figure S32. ^{13}C NMR spectrum of **1** (100 MHz, $CDCl_3$).

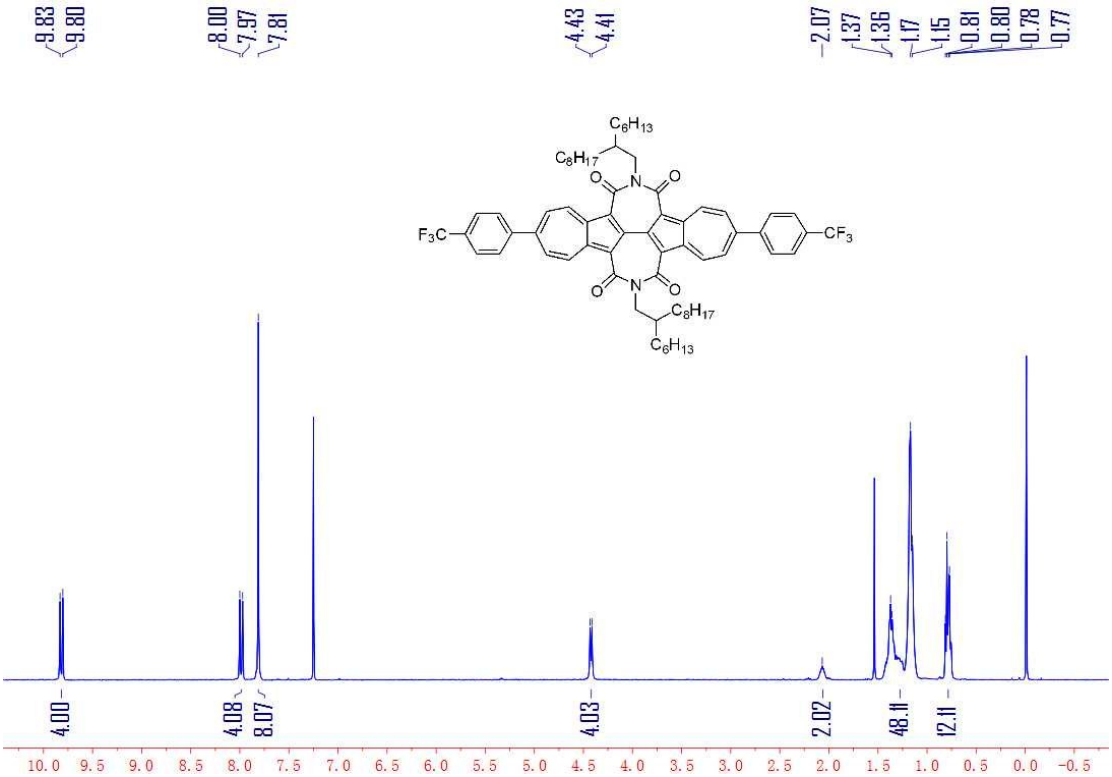


Figure S33. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

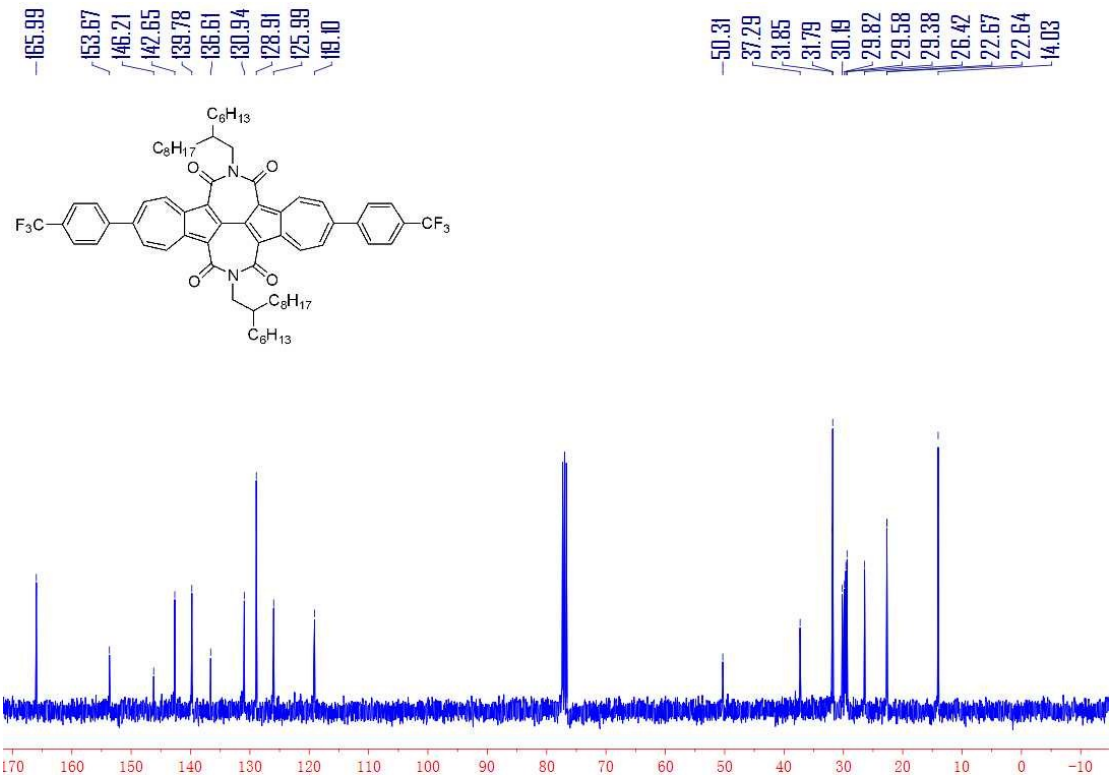


Figure S34. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$).

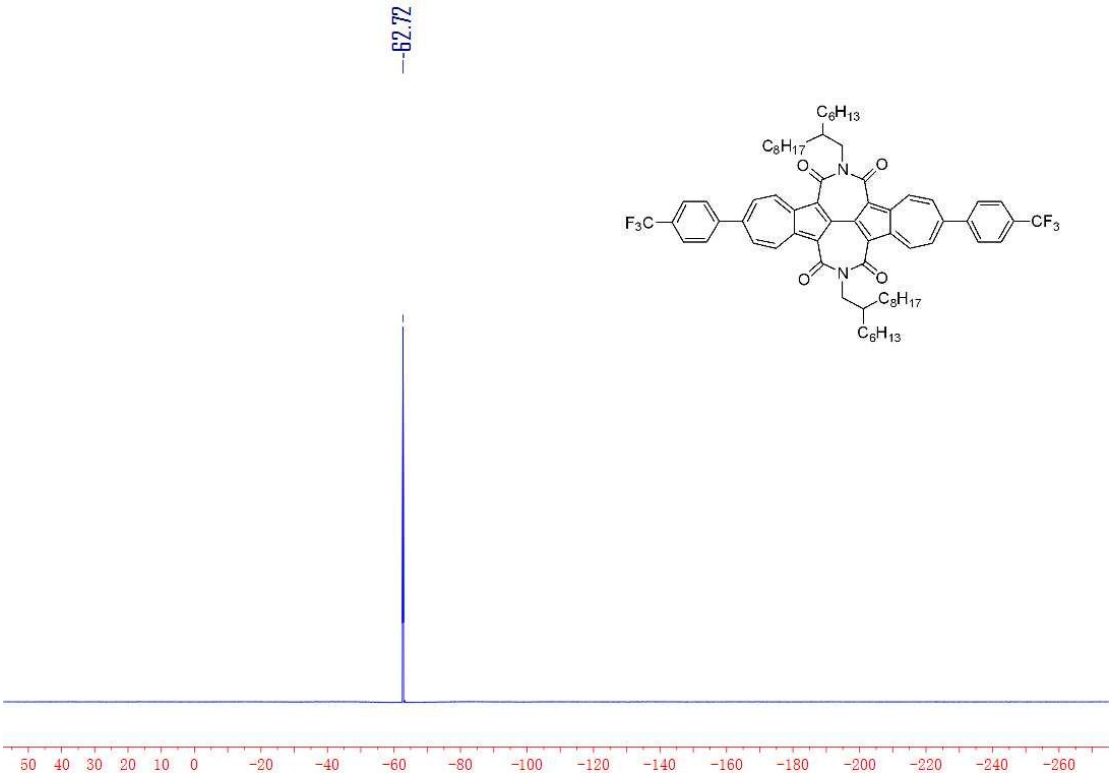


Figure S35. ^{19}F NMR spectrum of **2** (376 MHz, $CDCl_3$).

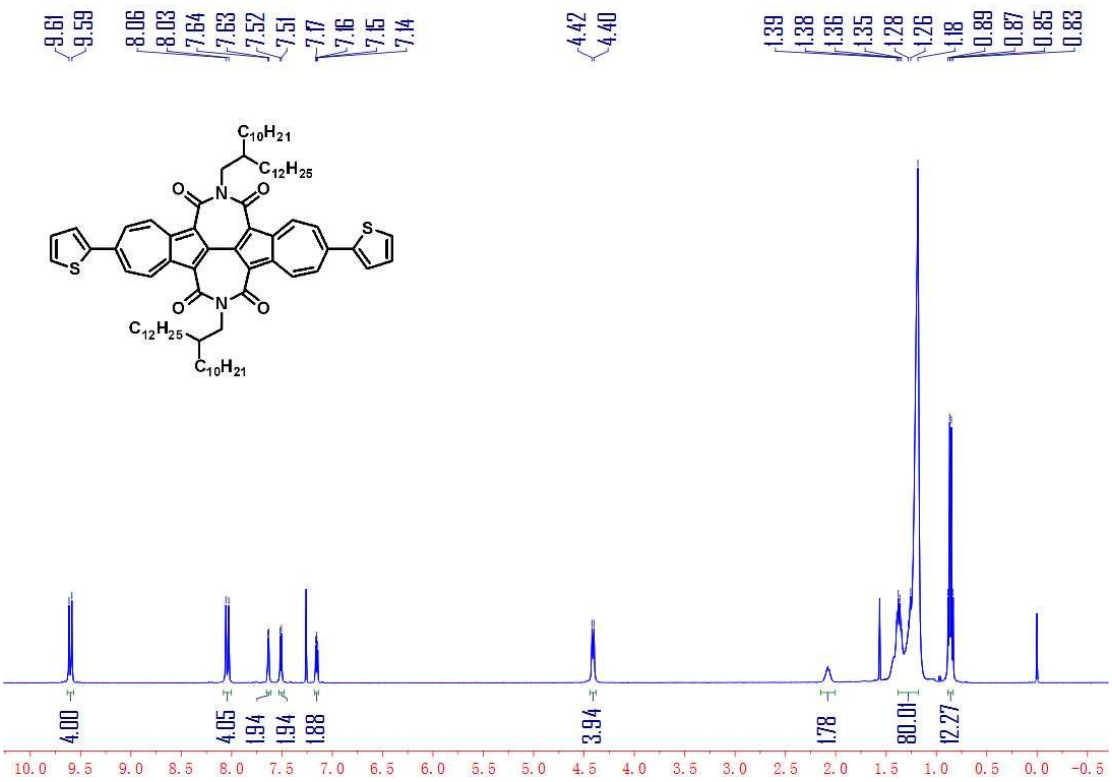


Figure S36. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

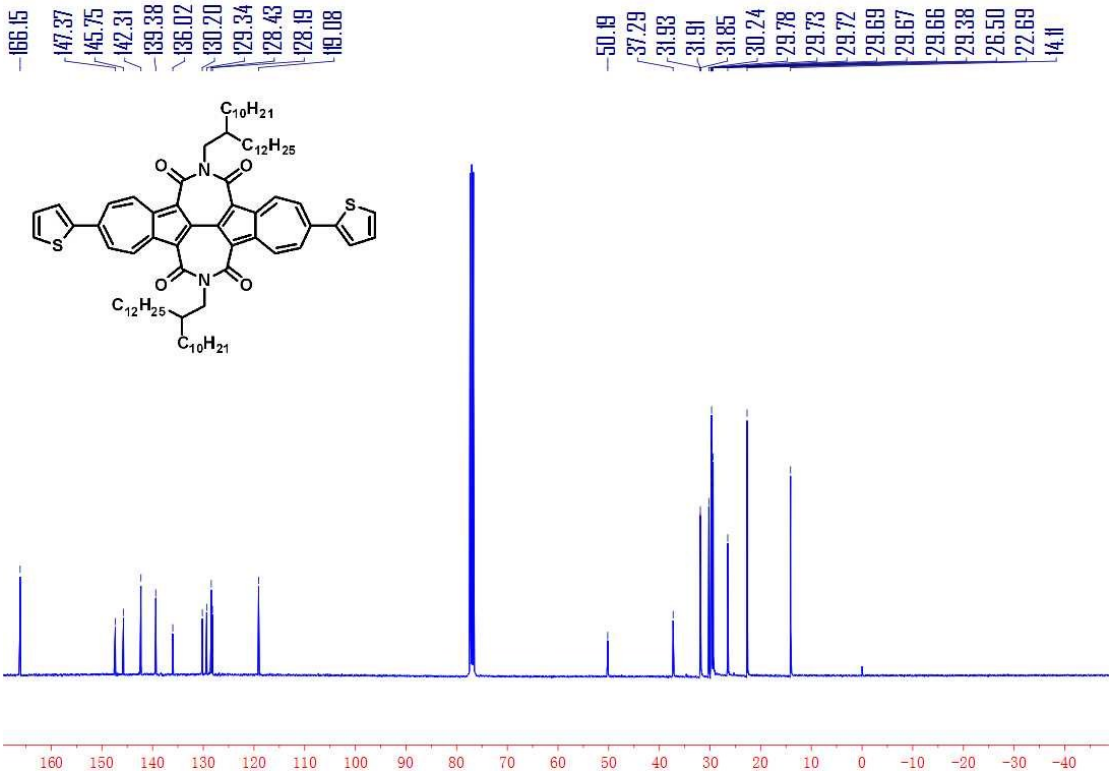


Figure S37. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

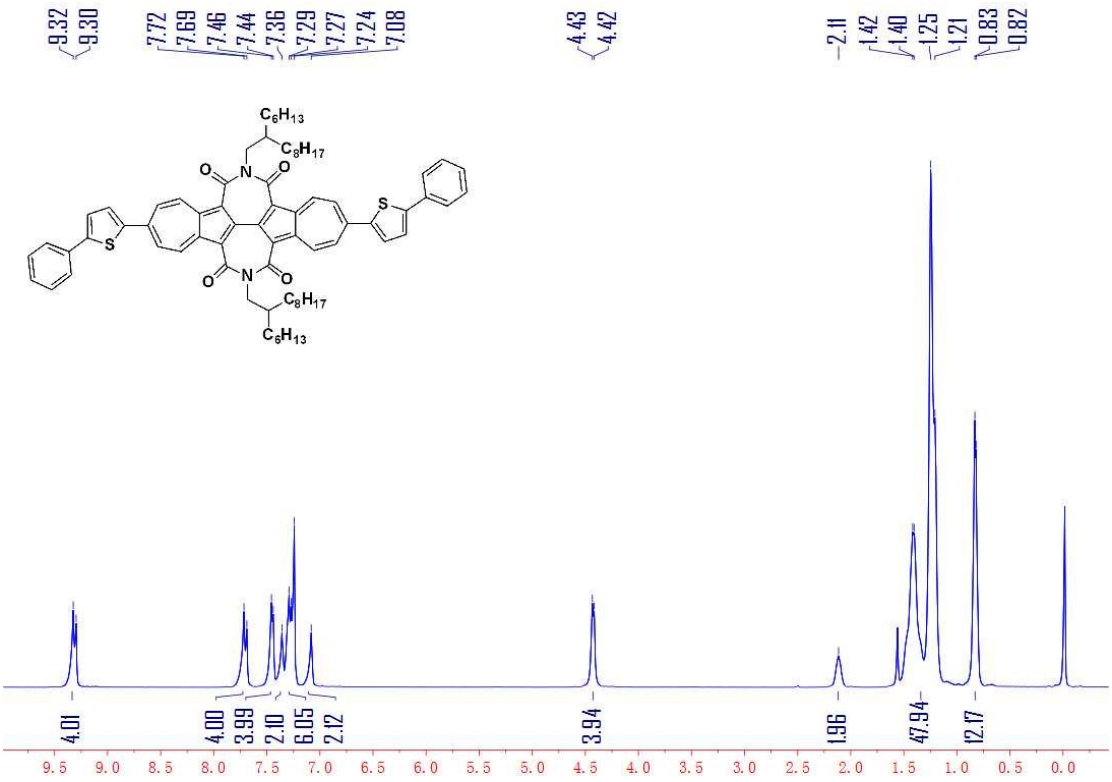


Figure S38. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

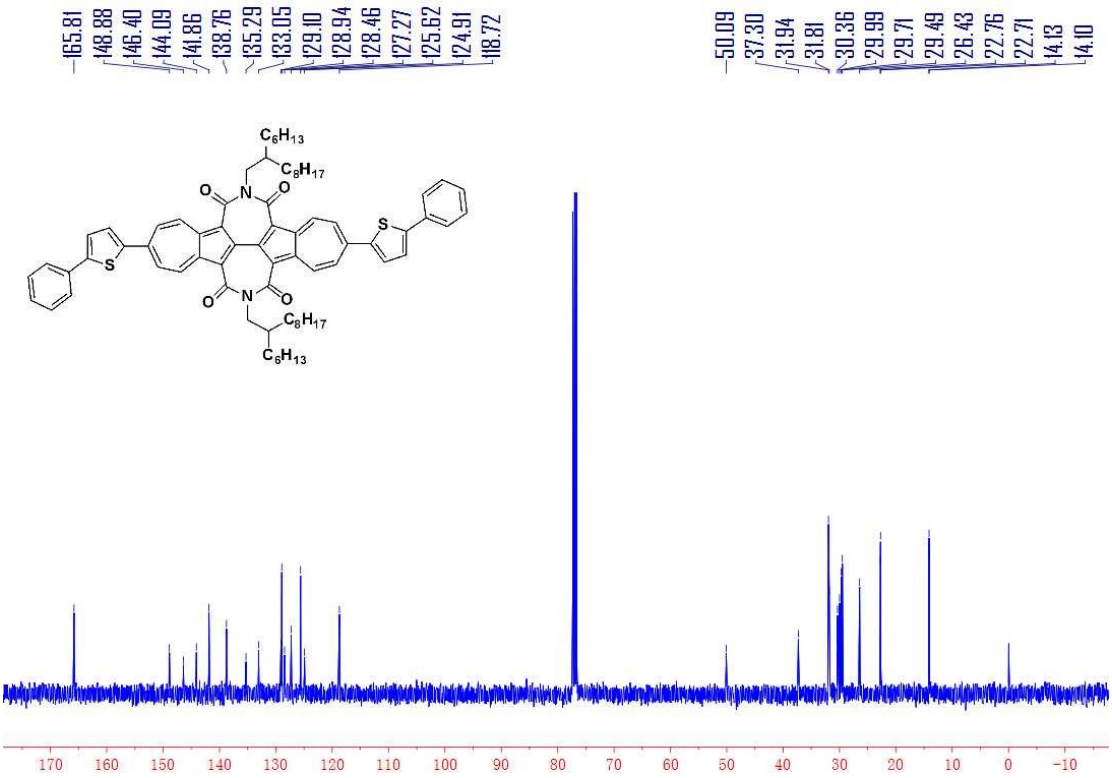


Figure S39. ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

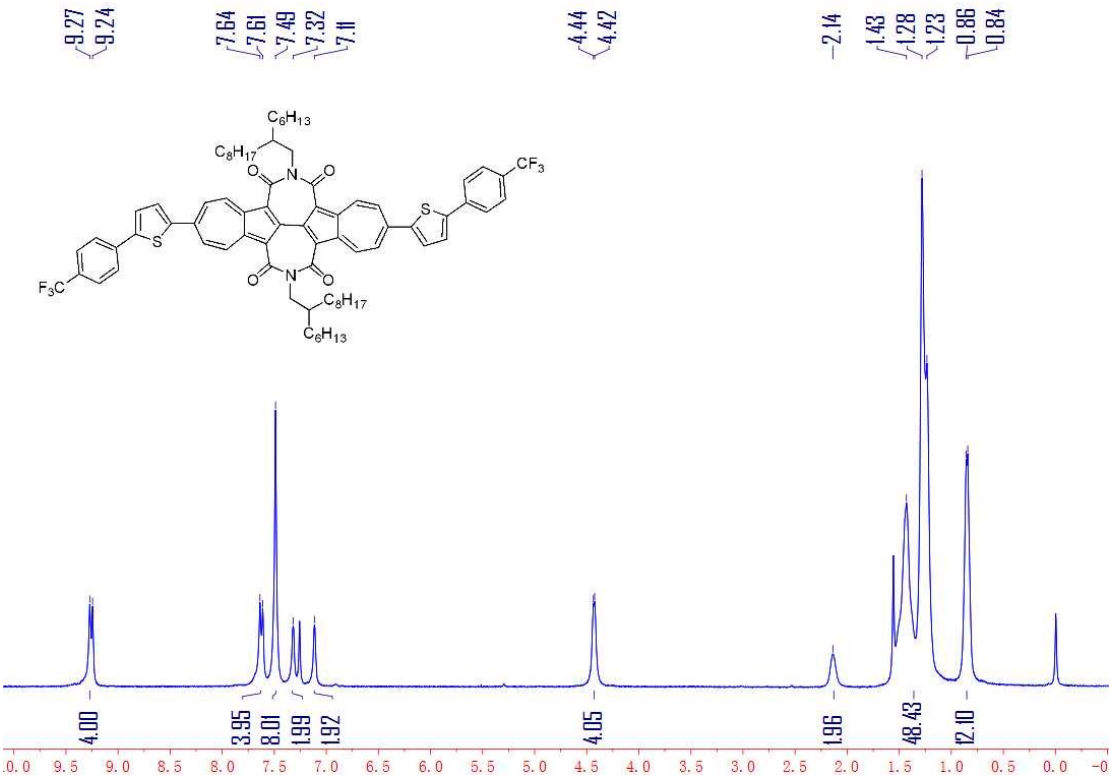


Figure S40. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

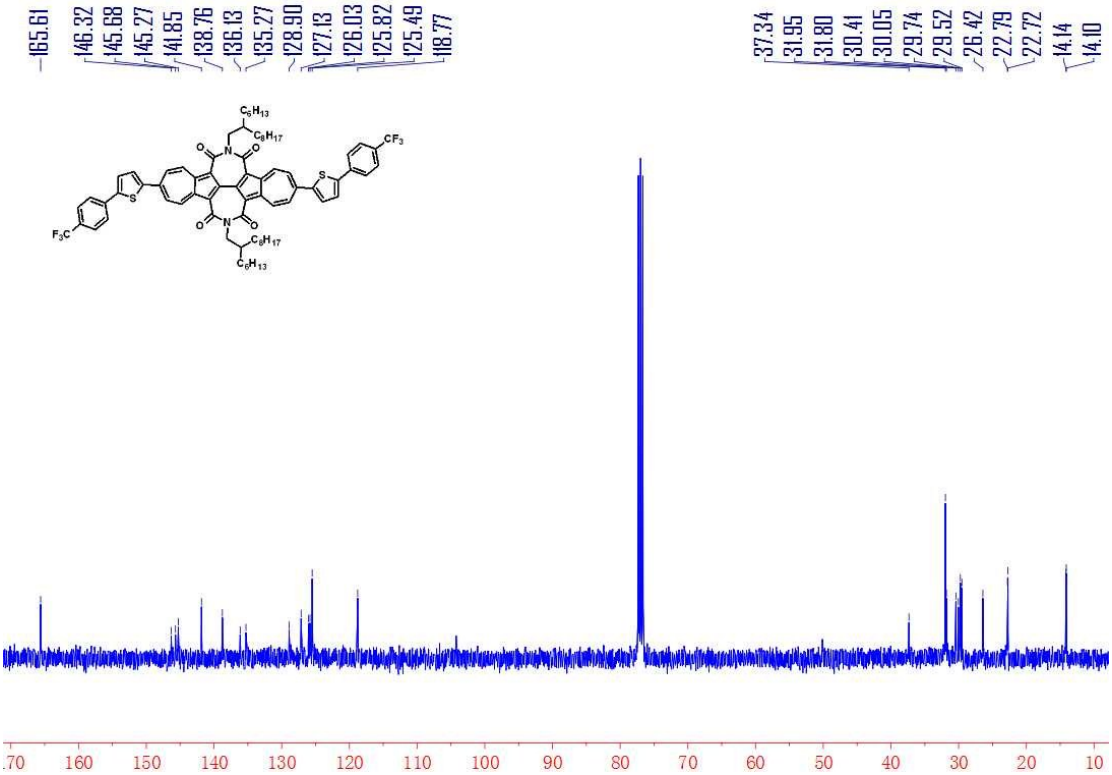


Figure S41. ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

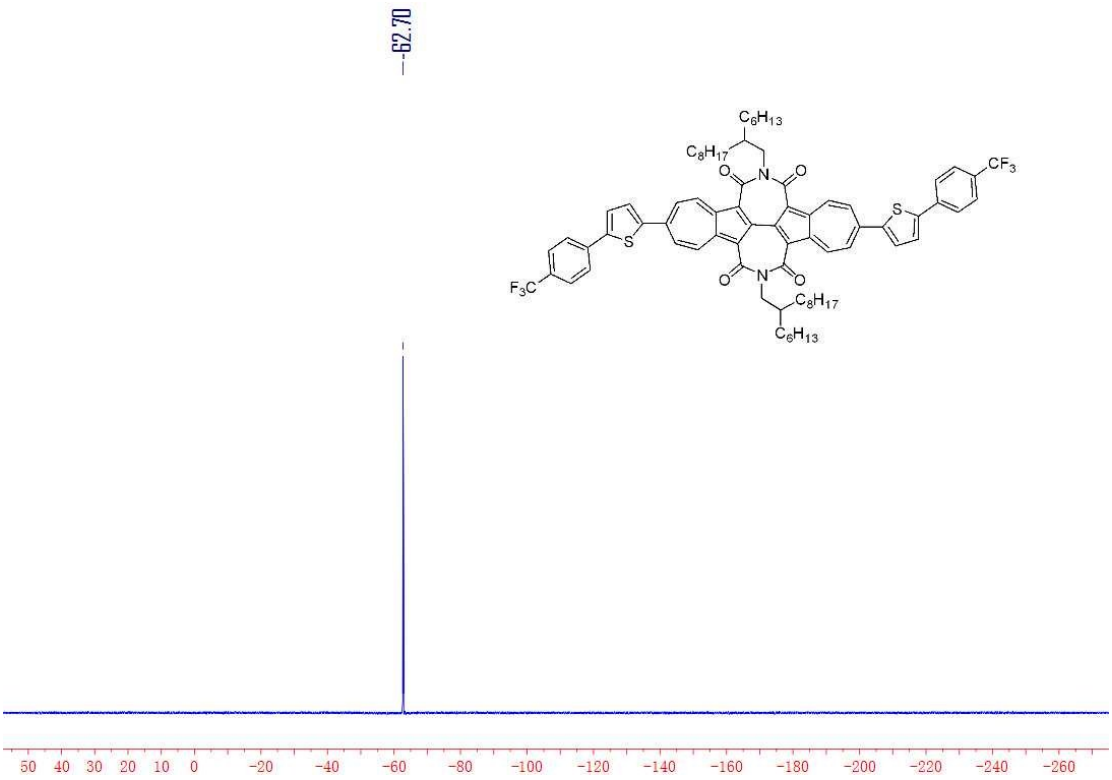


Figure S42. ^{19}F NMR spectrum of **5** (376 MHz, $CDCl_3$).

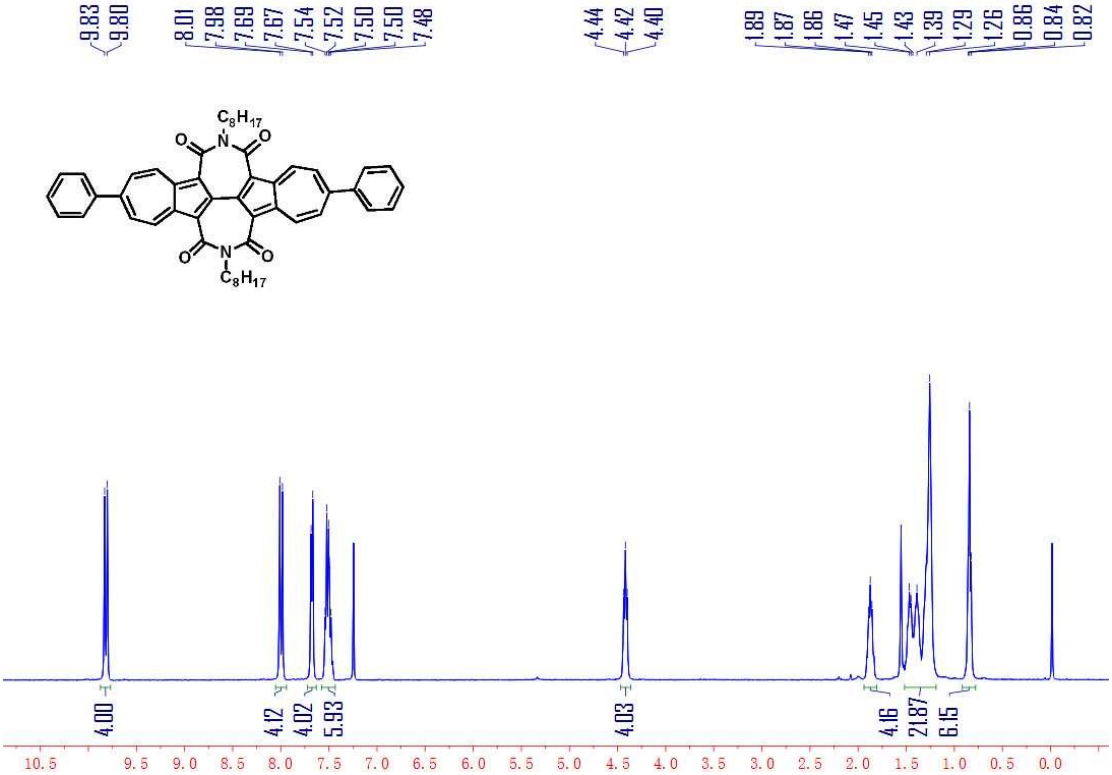


Figure S43. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

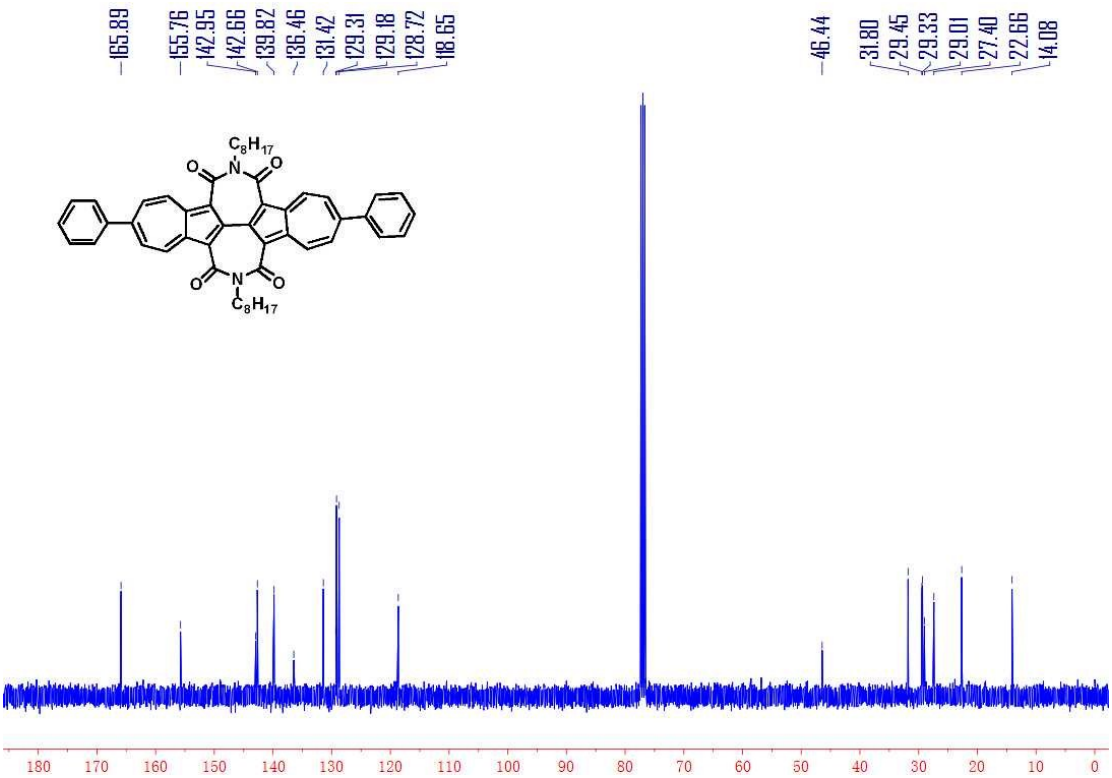


Figure S44. ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

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

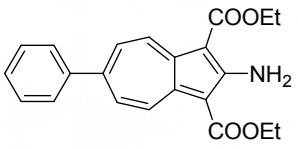
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : E172173

Sample Serial Number: 2013128-7-11

Operator : ZHUFJ Date: 2017/05/26

Operation Mode: DART Positive Ion Mode



Elemental composition search on mass 364.15

m/z= 359.15-369.15

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
364.1541	364.1543	-0.75	12.5	$C_{22}H_{22}O_4N$

Figure S45. HRMS spectrum of **S2a**

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

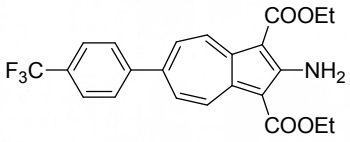
Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-P-T17-09-4263

Sample Serial Number: 2013128-7-15-1

Operator: Li

Date: 2017/09/25



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
313 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-80 N: 0-2 O: 0-4 F: 0-3

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
431.1338	431.1344	-0.6	-1.4	13.0	6.7	C23 H20 N O4 F3
	431.1333	0.5	1.2	17.0	9.5	C26 H19 N O3 F2
	431.1322	1.6	3.7	21.0	13.5	C29 H18 N O2 F

Figure S46. HRMS spectrum of **S2b**

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

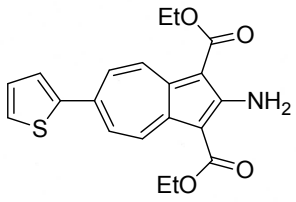
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D160857

Sample Serial Number: 4-61-1

Operator :HUAQIN Date: 2016/03/31

Operation Mode: DART Positive



Elemental composition search on mass 370.11

m/z= 365.11-375.11

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
370.1104	370.1101	0.80	21.0	$C_{26}H_{14}ON_2$
	370.1108	-1.07	11.5	$C_{20}H_{20}O_4NS$
	370.1094	2.56	12.0	$C_{18}H_{18}O_3N_4S$
	370.1087	4.43	21.5	$C_{24}H_{12}N_5$
	370.1121	-4.68	16.5	$C_{21}H_{16}N_5S$

Figure S47. HRMS spectrum of **S2c**

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

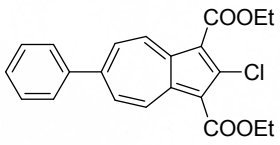
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : E172174

Sample Serial Number: 2013128-7-25

Operator : ZHUFJ Date: 2017/05/26

Operation Mode: DART Positive Ion Mode



Elemental composition search on mass 383.10

m/z= 378.10-388.10

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
383.1039	383.1045	-1.55	12.5	$C_{22}H_{20}O_4Cl$
	383.1026	3.23	17.5	$C_{23}H_{15}O_4N_2$

Figure S48. HRMS spectrum of **S3a**

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

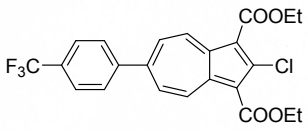
Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-P-T*17-09*-4262

Sample Serial Number: 2013128-7-18-1

Operator: Li

Date: 2017/09/25



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
214 formula(e) evaluated with 5 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-80 O: 0-4 F: 0-3 Cl: 0-1

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
450.0836	450.0846	-1.0	-2.2	13.0	3.6	C23 H18 O4 F3 Cl
	450.0834	0.2	0.4	17.0	13.8	C26 H17 O3 F2 Cl
	450.0823	1.3	2.9	21.0	31.6	C29 H16 O2 F Cl
	450.0856	-2.0	-4.4	26.0	414.0	C32 H12 O F2
	450.0845	-0.9	-2.0	30.0	425.6	C35 H11 F

Figure S49. HRMS spectrum of **S3b**

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

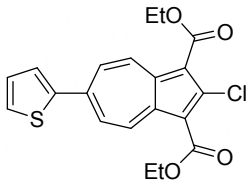
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D160859

Sample Serial Number: 5-2-1

Operator :HUAQIN Date: 2016/03/31

Operation Mode: DART Positive



Elemental composition search on mass 389.06

m/z= 384.06-394.06

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
389.0607	389.0609	-0.45	11.5	$C_{20}H_{18}O_4ClS$
	389.0602	1.33	21.0	$C_{26}H_{12}ONCl$
	389.0597	2.58	25.5	$C_{29}H_9O_2$

Figure S50. HRMS spectrum of **S3c**

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

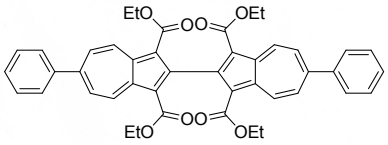
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : E172195

Sample Serial Number: 2013128-7-33

Operator : ZHUFJ Date: 2017/05/26

Operation Mode: DART Positive Ion Mode

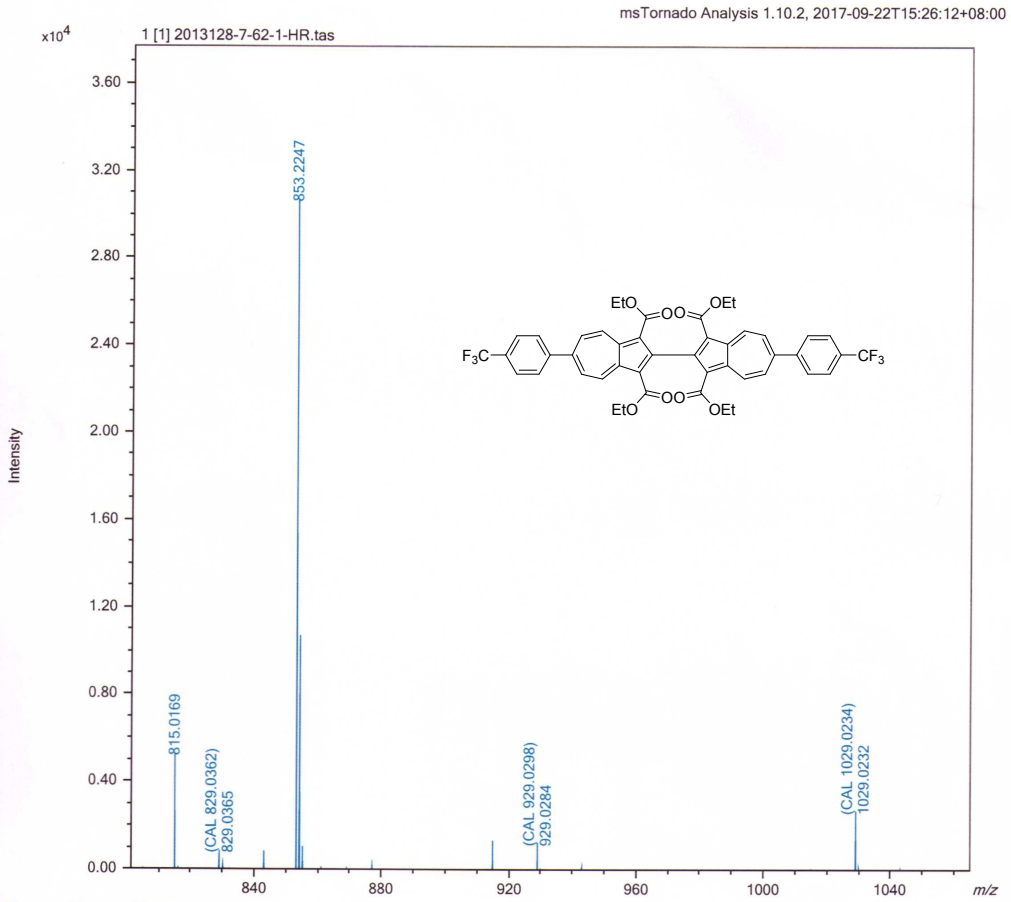


Elemental composition search on mass 695.26

m/z= 690.26-700.26

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
695.2623	695.2639	-2.29	25.5	$C_{44}H_{39}O_8$
	695.2608	2.30	39.0	$C_{54}H_{33}N$

Figure S51. HRMS spectrum of **S4a**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
853.22471 ± 0.00427	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 50 H 0 - 50 F 0 - 6 O 0 - 10 S 0 - 0 Na 0 - 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C50 H36 O10 F3	853.22551	31.5	0.00080	-0.00080	-0.94
2	C48 H37 O10 F3 Na	853.22310	28.5	0.00160	0.00160	1.88
3	C48 H35 O8 F6	853.22306	28.5	0.00164	0.00164	1.92
4	C46 H36 O8 F6 Na	853.22066	25.5	0.00405	0.00405	4.74

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Figure S52. HRMS spectrum of **S4b**

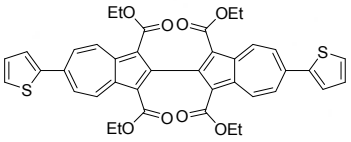
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D160861

Sample Serial Number: 5-15-1

Operator :HUAQIN Date: 2016/03/31



Operation Mode: DART Positive

Elemental composition search on mass 707.18

m/z= 702.18-712.18

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
707.1764	707.1768	-0.49	23.5	$C_{40}H_{35}O_8S_2$

Figure S53. HRMS spectrum of **S4c**

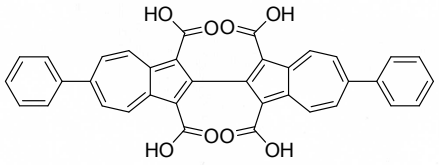
National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : E175056

Sample Serial Number: 2013128-7-37-1

Operator : ZHUFJ Date: 2017/11/13



Operation Mode: ESI Negative Ion Mode

Elemental composition search on mass 581.12

m/z= 576.12-586.12

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
581.1246	581.1242	0.79	26.5	$C_{36}H_{21}O_8$
	581.1262	-2.70	22.0	$C_{31}H_{23}O_7N_3S$
	581.1228	3.10	27.0	$C_{34}H_{19}O_7N_3$

Figure S54. HRMS spectrum of **S5a**

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

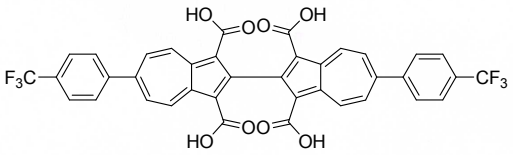
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : E175057

Sample Serial Number: 2013128-7-64-1

Operator : ZHUFJ Date: 2017/11/13

Operation Mode: ESI Negative Ion Mode



Elemental composition search on mass 717.10

m/z= 712.10-722.10

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
717.0998	717.1001	-0.35	30.0	$C_{38}H_{18}O_9N_3F_3$
	717.0990	1.19	26.5	$C_{38}H_{19}O_8F_6$
	717.0989	1.24	34.0	$C_{41}H_{17}O_8N_3F_2$
	717.1016	-2.55	31.0	$C_{41}H_{17}O_5NF_6$
	717.0978	2.78	30.5	$C_{41}H_{18}O_7F_5$
	717.0976	3.06	27.0	$C_{36}H_{17}O_7N_3F_6$
	717.0965	4.65	31.0	$C_{39}H_{16}O_6N_3F_5$

Figure S55. HRMS spectrum of **S5b**

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

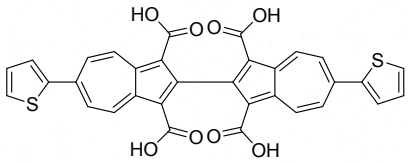
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M160480

Sample Serial Number: 5-24-1

Operator : HUAQIN Date: 2016/01/29

Operation Mode: MALDI-FT_DHB

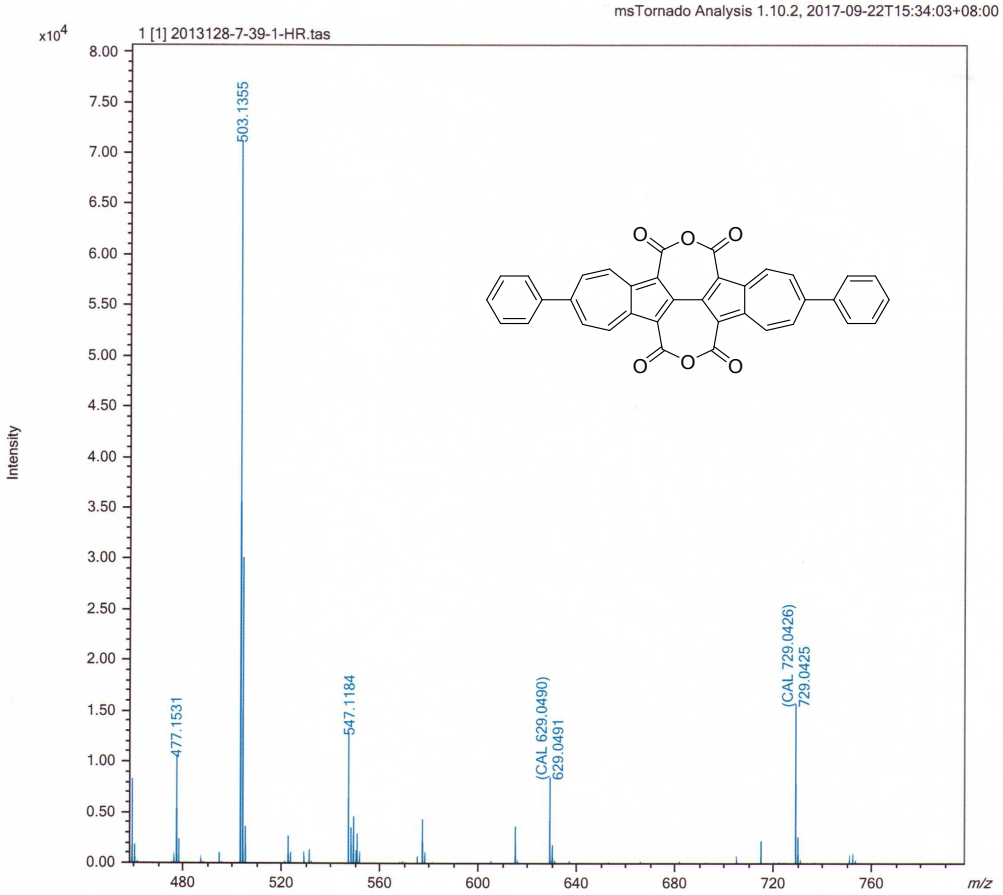


Elemental composition search on mass 595.05

m/z= 590.05-600.05

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
595.0514	595.0516	-0.24	23.5	$C_{32}H_{19}O_8S_2$
	595.0509	0.92	33.0	$C_{38}H_{13}O_5NS$
	595.0534	-3.29	29.0	$C_{34}H_{13}O_{10}N$
	595.0543	-4.75	28.0	$C_{35}H_{17}O_5NS_2$

Figure S56. HRMS spectrum of **S5c**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
547.11840 ± 0.00274	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 60 H 0 - 60 F 0 - 10 O 0 - 8 N 0 - 0 Na 0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C25 H21 O7 F6	547.11860	12.5	0.00020	-0.00020	-0.36
2	C33 H20 O7 F	547.11876	23.5	0.00036	-0.00036	-0.65
3	C36 H19 O6	547.11761	27.5	0.00078	0.00078	1.43
4	C28 H20 O6 F5	547.11746	16.5	0.00094	0.00094	1.73
5	C20 H21 O6 F10	547.11730	5.5	0.00110	0.00110	2.02
6	C22 H22 O8 F7	547.11974	8.5	0.00134	-0.00134	-2.45
7	C30 H21 O8 F2	547.11990	19.5	0.00150	-0.00150	-2.74
8	C31 H19 O5 F4	547.11631	20.5	0.00209	0.00209	3.81
9	C23 H20 O5 F9	547.11615	9.5	0.00225	0.00225	4.10

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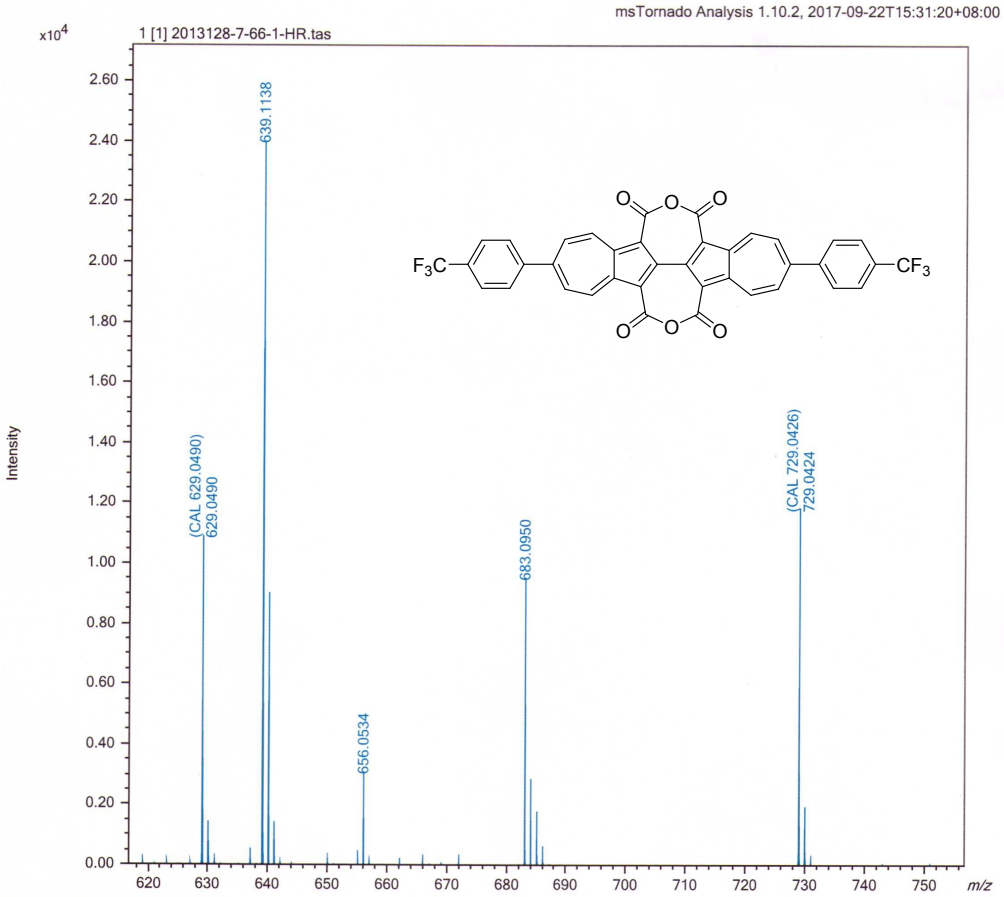
Figure S57. HRMS spectrum of **S6a**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
683.09504 ± 0.00342	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 60 H 0 - 60 F 0 - 10 O 0 - 8 N 0 - 0 Na 0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C40 H18 O8 F3	683.09483	30.5	0.00021	0.00021	0.31
2	C32 H19 O8 F8	683.09467	19.5	0.00037	0.00037	0.54
3	C43 H17 O7 F2	683.09369	34.5	0.00135	0.00135	1.98
4	C35 H18 O7 F7	683.09353	23.5	0.00151	0.00151	2.21
5	C46 H16 O6 F	683.09254	38.5	0.00250	0.00250	3.65
6	C38 H17 O6 F6	683.09238	27.5	0.00265	0.00265	3.89

1/1

Figure S58. HRMS spectrum of **S6b**

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

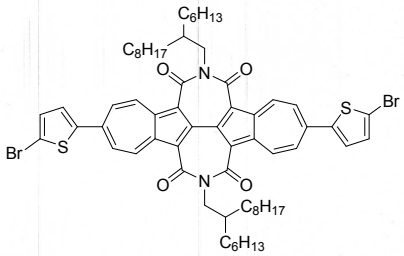
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161094

Sample Serial Number: 5-82-1

Operator : HUAQIN Date: 2016/04/08

Operation Mode: MALDI-FT_DHB



Elemental composition search on mass 1161.38

m/z= 1156.38-1166.38

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1161.3822	1161.3836	-1.14	35.0	$C_{70}H_{73}ONBr_2S$
	1161.3809	1.17	30.5	$C_{67}H_{75}O_4N_2Br_2S$
	1161.3843	-1.73	25.5	$C_{64}H_{79}O_4N_2Br_2S_2$
	1161.3778	3.80	37.0	$C_{69}H_{68}O_5N_3BrS_2$
	1161.3869	-4.04	30.0	$C_{67}H_{77}ON_3Br_2S_2$
	1161.3775	4.07	35.5	$C_{70}H_{71}O_4N_2Br_2$

Figure S59. HRMS spectrum of **S7**

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 FTICR-MS

Card Serial Number : E172198

Sample Serial Number: 2013128-7-40

Operator : ZHUFJ Date: 2017/05/26

Operation Mode: DART Positive Ion Mode

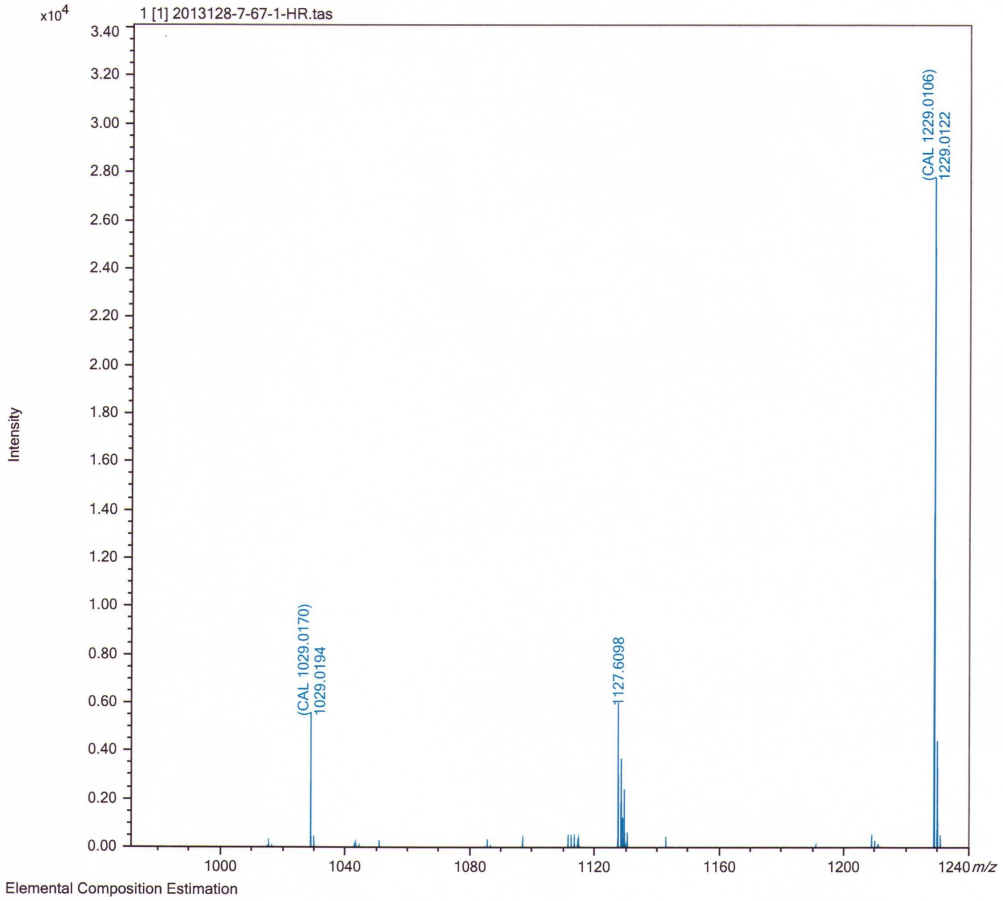
Elemental composition search on mass 993.65

m/z= 988.65-998.65

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
993.6468	993.6477	-0.89	23.0	$C_{65}H_{87}O_7N$
	993.6504	-3.59	27.5	$C_{68}H_{85}O_4N_2$

Figure S60. HRMS spectrum of **1**

msTornado Analysis 1.10.2, 2017-09-22T15:37:45+08:00



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
1127.60984 ± 0.00564	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 75 H 0 - 85 F 0 - 8 O 0 - 4 N 0 - 2 Na 0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C70 H81 N2 O4 F6	1127.60950	28.5	0.00034	0.00034	0.30
2	C73 H80 N2 O3 F5	1127.60836	32.5	0.00148	0.00148	1.31
3	C75 H81 O2 F6	1127.61353	32.5	0.00369	-0.00369	-3.27
4	C71 H79 N2 O F8	1127.60592	29.5	0.00392	0.00392	3.48
5	C72 H82 O3 F7	1127.61467	28.5	0.00483	-0.00483	-4.28
6	C74 H78 N2 F7	1127.60477	33.5	0.00507	0.00507	4.49

1/1

Figure S61. HRMS spectrum of **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 : M160748

Sample Serial Number: 5-51-1

Operator : HUAQIN Date: 2016/3/15

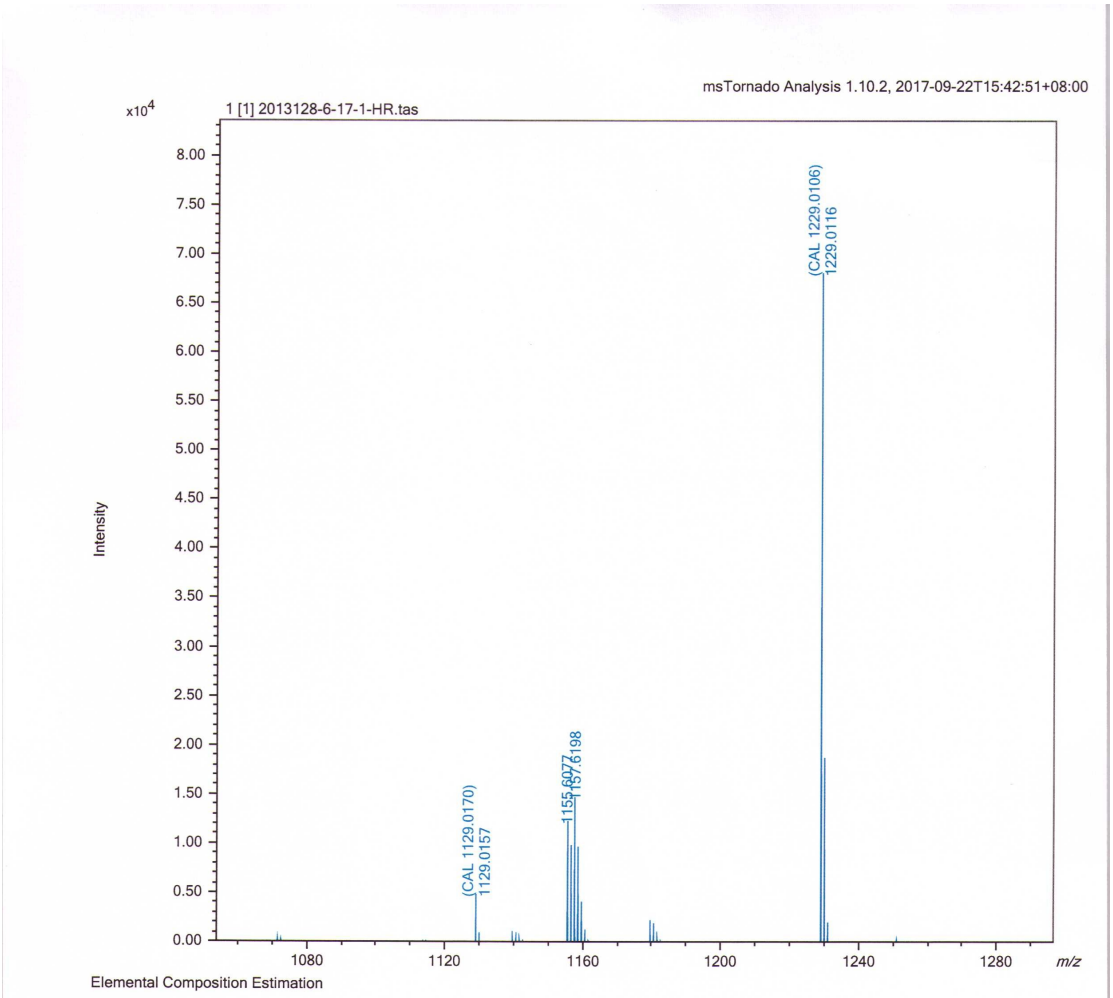
Operation Mode: MALDI-FT_DHB

Elemental composition search on mass 1005.56

m/z= 1000.56-1010.56

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1005.5633	1005.5632	0.03	25.5	$C_{64}H_{81}O_4N_2S_2$
	1005.5625	0.72	35.0	$C_{70}H_{75}ON_3S$
	1005.5619	1.37	26.0	$C_{62}H_{79}O_3N_5S_2$
	1005.5659	-2.63	30.0	$C_{67}H_{79}ON_3S_2$
	1005.5599	3.39	30.5	$C_{67}H_{77}O_4N_2S$
	1005.5672	-3.97	29.5	$C_{69}H_{81}O_2S_2$
	1005.5677	-4.43	35.5	$C_{69}H_{73}O_3N_4$
	1005.5585	4.72	31.0	$C_{65}H_{75}O_3N_5S$

Figure S62. HRMS spectrum of **3**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
1155.60773 ± 0.00578	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 80 H 0 - 90 S 0 - 2 O 0 - 4 N 0 - 2 Na 0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C79 H83 N2 O4 S	1155.60681	39.5	0.00092	0.00092	0.80
2	C76 H87 N2 O4 S2	1155.61018	34.5	0.00245	-0.00245	-2.12

1/1

Figure S63. HRMS spectrum of **4**

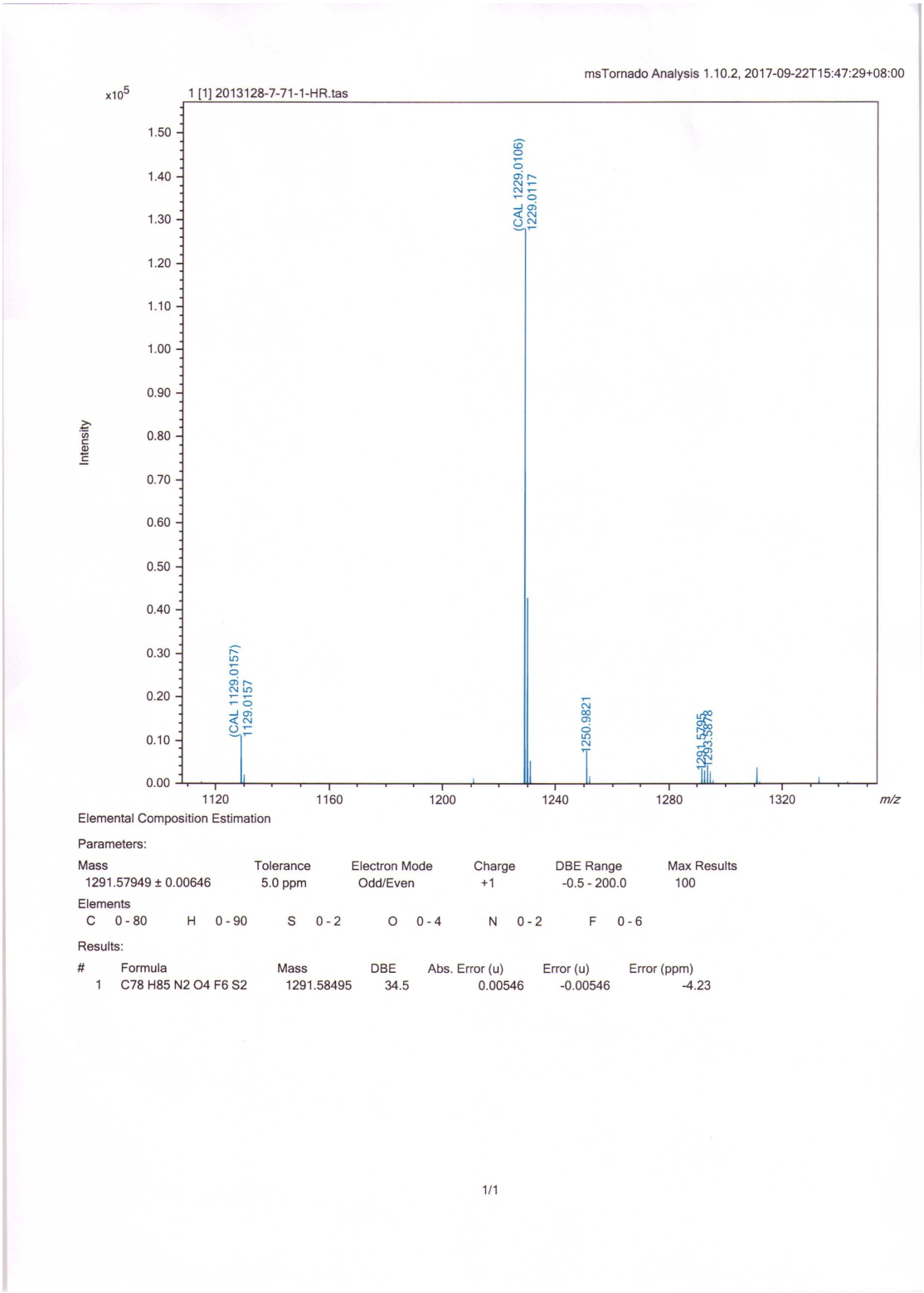
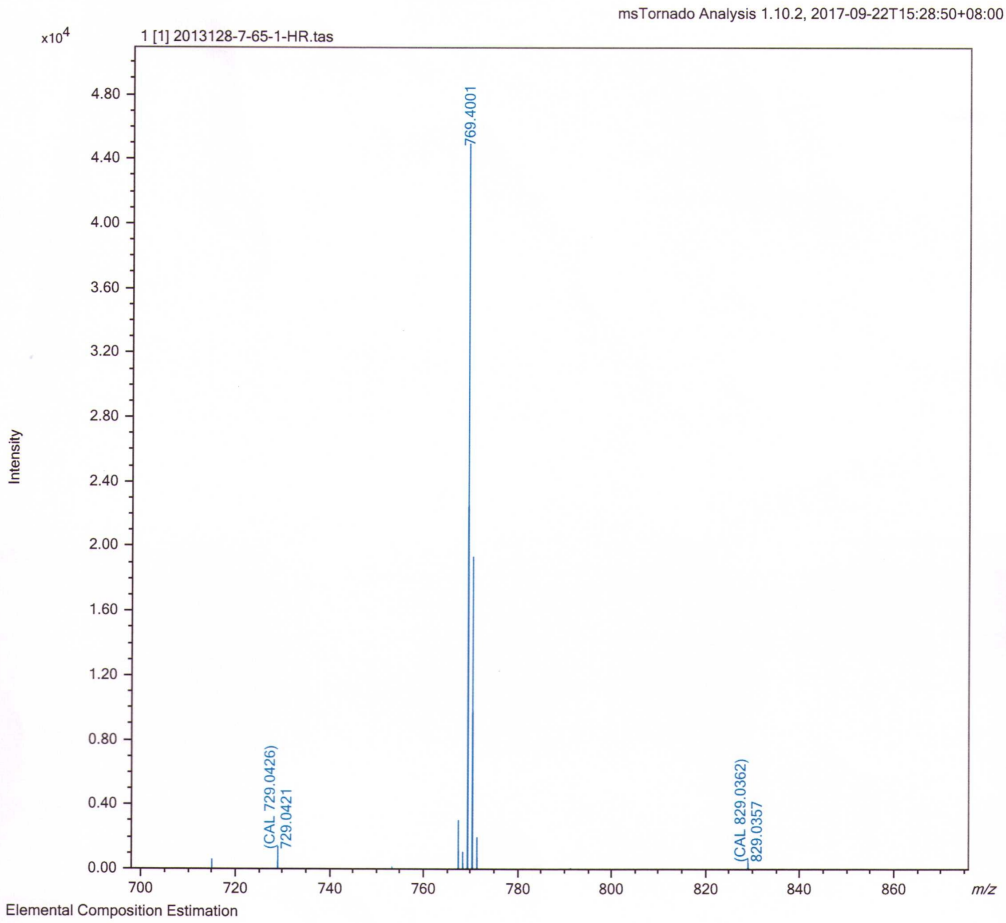


Figure S64. HRMS spectrum of **5**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
769.40015 ± 0.00385	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 60 H 0 - 60 F 0 - 0 O 0 - 5 N 0 - 5 Na 0 - 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C53 H52 N3 O Na	769.40026	29.0	0.00011	-0.00011	-0.15
2	C52 H53 N2 O4	769.39998	27.5	0.00016	0.00016	0.21
3	C55 H54 O2 Na	769.40160	28.5	0.00145	-0.00145	-1.89
4	C50 H51 N5 O3	769.39864	28.0	0.00151	0.00151	1.96
5	C55 H51 N3 O	769.40266	32.0	0.00252	-0.00252	-3.27
6	C50 H54 N2 O4 Na	769.39758	24.5	0.00257	0.00257	3.34

1/1

Figure S65. HRMS spectrum of **6**