Supporting Information for

Trisulfur Radical Anion-Triggered Stitching Thienannulation: Rapid Access to Largely π-Extended Thienoacenes

Feng Su, Shuqi Chen, Xiaogang Mo, Kongchuan Wu, Jiajun Wu, Weidong Lin, Zhiwei Lin, Jianbin Lin, Hui-Jun Zhang* and Ting-Bin Wen

Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, P. R. China.

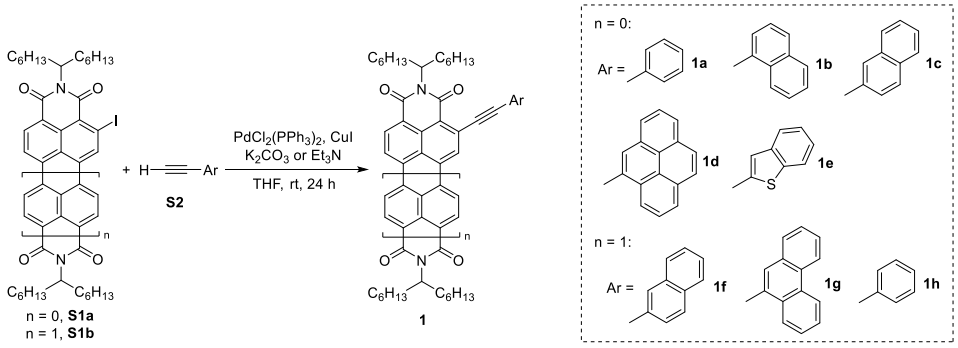
**E-mail: meghjzhang@xmu.edu.cn*

Contents:

1. General Information

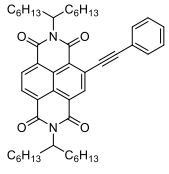
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Potassium sulfide crystal 99%+ was purchased from Adams-beta® (CAS: 1312-73-8), which was grinded and stored in the glove box before use. Super dehydrated *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Energy Chemical. Unless otherwise noted, all reactions were carried out under argon atmosphere using standard Schlenk technique. TLC was performed on glass-backed silica plates. Column chromatography was performed on 200-300 mesh silica gel, eluting with *n*-hexane and CH_2Cl_2. NMR data of **1a-p** were obtained on a Bruker AV-400 spectrometer or a Bruker AV-500 spectrometer in $CDCl_3$ or toluene-d_8 at 298 K. ^{1}H NMR spectra of **2a, 3a-3h**, **3j-3q**, **3a'**, **3k'** and **3o'** were recorded at 400 MHz in $C_2D_2Cl_4$ solutions at 333 K or 353 K. ^{13}C NMR spectra of **2a, 3a-3h**, **3j-3q**, **3a'**, **3k'** and **3o'** were recorded at 400 MHz or 500 MHz in $CDCl_3$ at 298 K. Chemical shifts are given in ppm with reference to the residual solvent resonance of the deuterated solvents. High-resolution mass spectra (HRMS) were obtained on a MALDI-TOF instrument or a FT-MS instrument using ESI, APCI or APPI technique. UV-Vis absorption spectra were obtained on a Hitachi U-3900 or SHIMADZU UV-2700 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a Bio-Logic-Science Instrument (EC-LAB SP-200).

2. Preparation of Substrates

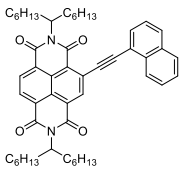


Compounds **S1a** and **S1b** were prepared according to the literature.[1]

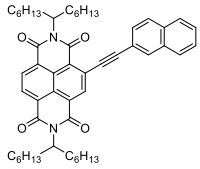
Synthesis of 1a-h: To the solution of **S1** (0.2 mmol), **S2** (0.24 mmol), $PdCl_2(PPh_3)_2$ (7.1 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) in THF (4 mL) was added K_2CO_3 (0.14 g, 1 mmol, for the reactions with **S1a**) or Et_3N (4 mL, for the reactions with **S1b**). The resulting mixture was stirred under Ar atmosphere at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent for **1a-e**: *n*-hexane/CH_2Cl_2 = 4:1; eluent for **1f-g** and **1h**: *n*-hexane/CH_2Cl_2 = 2:1, v/v) to afford compound **1**.



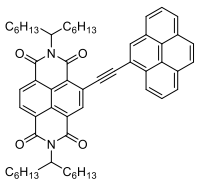
1a: yellow solid (138.9 mg, 95%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.79 – 8.64 (m, 2H), 7.78 – 7.72 (m, 2H), 7.48 – 7.38 (m, 3H), 5.25 – 5.11 (m, 2H), 2.30 – 2.17 (m, 4H), 1.93 – 1.80 (m, 4H), 1.34 – 1.18 (m, 32H), 0.85 – 0.78 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 163.7, 162.9, 162.5, 137.3, 136.7, 132.6, 130.9, 130.2, 129.8, 128.5, 127.6, 126.8, 126.1, 125.7, 125.1, 122.6, 102.5, 89.7, 55.2, 32.3, 31.71, 31.69, 29.2, 29.1, 26.9, 26.8, 22.6, 22.5, 14.0.



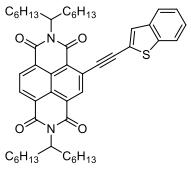
1b: orange yellow solid (140.6 mg, 90%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 – 8.81 (m, 2H), 8.78 – 8.64 (m, 2H), 7.98 (d, *J* = 6.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 5.36 – 5.12 (m, 2H), 2.40 – 2.19 (m, 4H), 1.99 – 1.84 (m, 4H), 1.39 – 1.29 (m, 14H), 1.27 – 1.21 (m, 18H), 0.86 – 0.80 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 163.7, 162.9, 162.6, 137.3, 136.6, 133.8, 133.1, 132.4, 131.6, 131.3, 130.8, 130.6, 130.1, 128.2, 127.6, 127.4, 126.8, 126.7, 126.0, 125.8, 125.7, 125.3, 125.1, 120.3, 101.0, 94.5, 55.2, 55.1, 32.4, 32.3, 31.72, 31.70, 31.68, 29.2, 29.14, 29.11, 26.9, 26.9, 26.8, 22.54, 22.53, 22.51, 14.0.



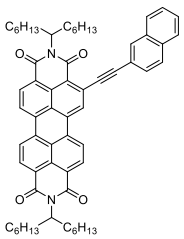
1c: orange yellow solid (114.1 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 – 8.53 (m, 3H), 8.13 (s, 1H), 7.78 – 7.67 (m, 4H), 7.46 – 7.40 (m, 2H), 5.37 – 5.10 (m, 2H), 2.37 – 2.16 (m, 4H), 1.97 – 1.88 (m, 4H), 1.38 – 1.22 (m, 32H), 0.85 – 0.80 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 163.6, 162.8, 162.4, 161.5, 137.2, 136.6, 133.2, 132.9, 132.6, 131.4, 130.6, 129.9, 128.5, 128.0, 127.9, 127.6, 127.3, 127.2, 126.7, 126.6, 125.8, 125.6, 125.4, 125.2, 124.9, 119.9, 102.8, 90.4, 55.04, 55.00, 32.3, 32.2, 31.7, 31.7, 29.2, 29.1, 26.9, 26.8, 22.52, 22.49, 13.96, 13.95.



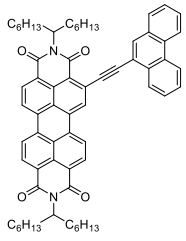
1d: red orange solid (150.5 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 – 9.15 (m, 1H), 8.69 (brs, 1H), 8.51 (s, 1H), 8.41 – 8.27 (m, 2H), 8.22 – 8.14 (m, 3H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.95 (d, *J* = 8.9 Hz, 1H), 5.43 – 5.10 (m, 2H), 2.54 – 2.20 (m, 4H), 2.18 – 1.90 (m, 4H), 1.48 – 1.27 (m, 32H), 0.92 – 0.89 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 163.4, 162.8, 162.3, 136.9, 136.3, 134.5, 130.8, 130.7, 130.1, 129.9, 129.5, 127.6, 127.0, 126.9, 126.6, 126.2, 125.9, 125.8, 125.5, 125.1, 124.9, 124.4, 124.0, 120.1, 100.7, 94.5, 55.1, 32.5, 32.3, 31.81, 31.76, 29.3, 29.2, 27.2, 27.0, 22.6, 22.58, 14.03, 14.01.



1e: yellow solid (126.2 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 – 8.60 (m, 3H), 7.83 – 7.78 (m, 2H), 7.76 (s, 1H), 7.43 – 7.35 (m, 2H), 5.30 – 5.08 (m, 2H), 2.34 – 2.13 (m, 4H), 1.95 – 1.80 (m, 4H), 1.37 – 1.20 (m, 32H), 0.90 – 0.78 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 163.7, 162.8, 162.5, 141.5, 134.0, 136.8, 136.2, 131.5, 131.0, 130.3, 127.5, 126.7, 126.2, 126.1, 125.9, 125.8, 125.2, 124.9, 124.3, 124.1, 122.5, 122.1, 95.8, 95.3, 55.2, 32.3, 32.3, 31.73, 31.70, 29.2, 29.1, 26.9, 26.8, 22.6, 22.5, 14.02, 14.00.

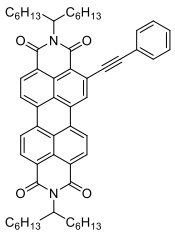


1f: red solid (166.0 mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 – 8.58 (m, 5H), 8.49 (d, *J* = 7.9 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.17 (s, 1H), 7.75 – 7.71 (m, 4H), 7.70 – 7.40 (m, 2H), 5.33 – 5.15 (m, 2H), 2.42 – 2.21 (m, 4H), 2.02 – 1.86 (m, 4H), 1.38 – 1.23 (m, 32H), 0.86 – 0.80 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 163.5, 163.0, 162.1, 134.3, 133.9, 133.7, 133.2, 133.1, 132.8, 132.7, 131.8, 131.7, 131.3, 131.1, 130.1, 129.4, 129.1, 128.5, 127.9, 127.9, 127.7, 127.1, 126.5, 126.2, 125.4, 123.1, 122.9, 122.8, 120.1, 100.7, 90.7, 54.8, 32.4, 31.77, 31.75, 29.3, 29.2, 27.04, 26.95, 22.59, 22.57, 14.0.

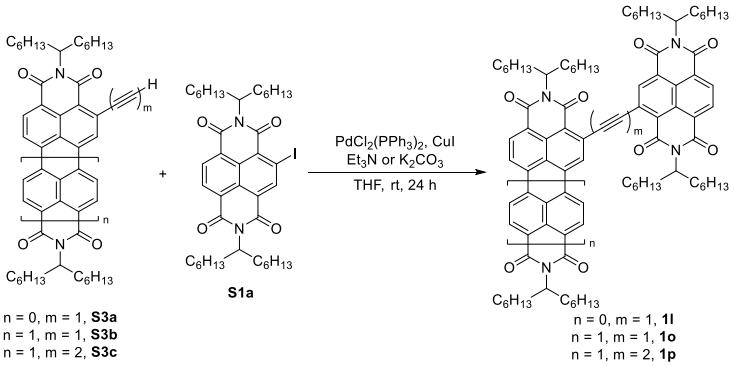


1g: red solid (191.1 mg, 99%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.1 Hz, 1H), 8.73 (brs, 1H), 8.63 (brs, 3H), 8.45 (d, *J* = 7.7 Hz, 1H), 8.35 (d, *J* = 6.9 Hz, 1H), 8.27 (brs, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 7.88 – 7.38 (m, 6H), 5.50 – 5.32 (m, 1H), 5.25 – 5.20 (m, 1H), 2.62 – 2.26 (m, 4H), 2.17 – 1.89 (m, 4H), 1.60 – 1.28 (m, 32H), 0.87 – 0.78 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 164.2,

163.7, 163.3, 134.2, 133.7, 133.5, 133.2, 133.0, 132.13, 132.06, 131.9, 131.6, 130.9, 130.6, 130.4, 130.0, 129.4, 129.2, 128.5, 127.8, 127.5, 127.0, 126.7, 126.7, 126.0, 125.1, 123.4, 122.5, 122.4, 122.1, 121.9, 121.84, 121.80, 119.4, 100.0, 95.1, 54.7, 32.6, 32.4, 31.9, 31.8, 29.3, 29.3, 27.2, 27.0, 22.6, 14.1.

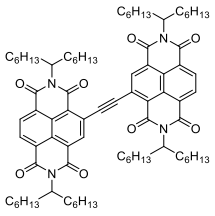


1h: red solid (147 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.48 (m, 7H), 7.81 – 7.78 (m, 2H), 7.46 – 7.40 (m, 3H), 5.26 – 5.07 (m, 2H), 2.31 – 2.17 (m, 4H), 1.96 – 1.83 (m, 4H), 1.37 – 1.20 (m, 32H), 0.87 – 0.76 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.60, 163.59, 134.5, 134.1, 133.8, 133.2, 132.6, 132.0, 131.8, 131.3, 131.1, 130.3, 129.6, 129.0, 128.6, 126.4, 125.6, 123.2, 123.1, 100.5, 90.3, 54.9, 32.51, 32.46, 31.91, 31.90, 29.41, 29.36, 27.2, 27.1, 22.74, 22.72, 14.2.

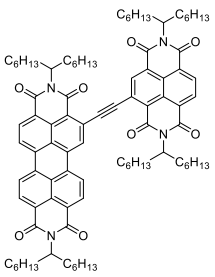


Compounds **S3a-3c** were prepared according to the literature.[1,2]

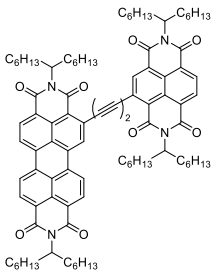
Synthesis of 1l, 1o and 1p: To the solution of **S1a** (151.4 mg, 0.2 mmol), **S3** (0.24 mmol), $PdCl_2(PPh_3)_2$ (7.1 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) in THF (5 mL) was added K_2CO_3 (138 mg, 1 mmol, for the reaction with **S3a**) or Et_3N (5 mL, for the reactions with **S3b** and **S3c**). The resulting mixture was stirred under Ar atmosphere at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent for **1l**: *n*-hexane/CH_2Cl_2 = 3:1; eluent for **1o**: *n*-hexane/CH_2Cl_2 = 2:1; eluent for **1p**: *n*-hexane/CH_2Cl_2 = 2:1, v/v) to afford compound **1l**, **1o** or **1p**.



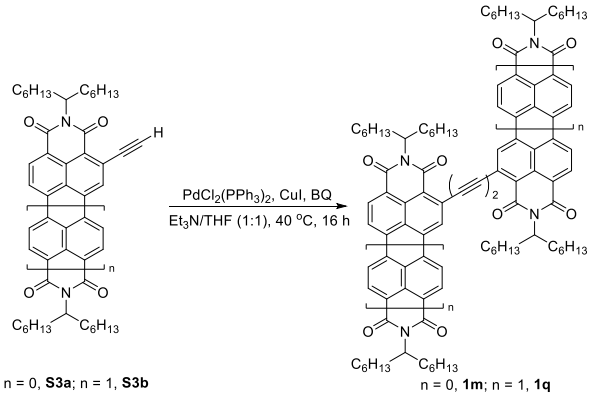
1l: yellow solid (192.8 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 – 8.63 (m, 6H), 5.26 – 5.11 (m, 4H), 2.35 – 2.13 (m, 8H), 1.94 – 1.80 (m, 8H), 1.35 – 1.18 (m, 64H), 0.85 – 0.76 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 163.5, 162.7, 162.4, 137.3, 136.6, 131.8, 131.6, 131.1, 130.9, 127.40, 127.36, 126.9, 126.2, 126.1, 125.4, 100.4, 55.3, 32.2, 31.7, 31.7, 29.2, 29.1, 26.9, 26.8, 22.5, 22.5, 13.97, 13.96.



1o: yellow solid (135.2 mg, yield 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 – 8.97 (m, 2H), 8.85 – 8.61 (m, 8H), 5.37 – 5.10 (m, 4H), 2.46 – 2.18 (m, 8H), 2.03 – 1.81 (m, 8H), 1.40 – 1.20 (m, 64H), 0.87 – 0.75 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.52, 163.49, 163.0, 161.9, 137.3, 136.6, 134.4, 134.2, 133.8, 133.4, 132.0, 131.5, 131.3, 130.1, 129.5, 127.5, 127.0, 126.4, 126.2, 126.2, 124.2, 124.0, 123.5, 123.22, 123.15, 101.5, 99.0, 55.4, 55.3, 55.1, 54.8, 32.43, 32.36, 32.3, 31.8, 31.7, 31.7, 29.21, 29.19, 29.1, 27.0, 26.91, 26.85, 22.58, 22.55, 22.5, 14.01, 13.99, 13.97.

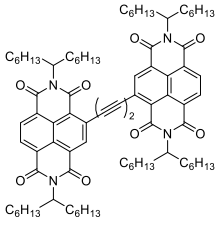


1p: yellow solid (114.6 mg, yield 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 – 8.52 (m, 10H), 5.28 – 5.07 (m, 4H), 2.35 – 2.11 (m, 8H), 1.96 – 1.79 (m, 8H), 1.31 – 1.29 (m, 64H), 0.89 – 0.76 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 163.9, 163.4, 162.7, 137.4, 136.9, 134.3, 134.2, 133.5, 133.4, 131.8, 131.2, 130.1, 129.5, 129.3, 127.4, 126.3, 126.1, 125.5, 123.6, 123.3, 123.2, 87.0, 86.5, 85.0, 84.3, 55.5, 55.3, 55.2, 54.8, 32.4, 32.3, 32.2, 31.8, 31.72, 31.69, 29.2, 29.1, 27.01, 26.95, 26.9, 26.8, 22.6, 22.5, 14.0.

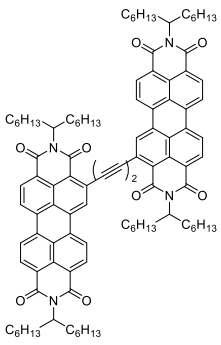


n = 0, **S3a**; n = 1, **S3b** n = 0, **1m**; n = 1, **1q**

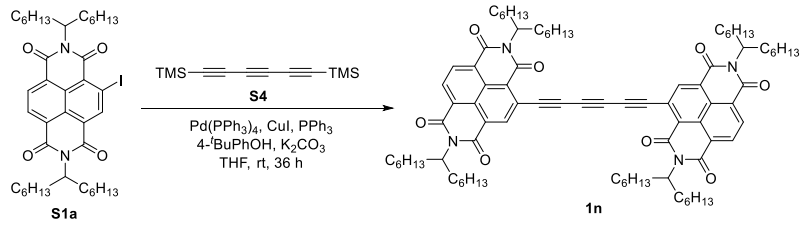
Synthesis of 1m and 1q: To the solution of **S3** (0.5 mmol), $PdCl_2(PPh_3)_2$ (17.6 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and 1,4-benzoquinone (64.9 mg, 1.2 mmol) in THF (10 mL) was added K_2CO_3 (0.21 g, 1.5 mmol, for the reaction with **S3a**) or Et_3N (10 mL, for the reaction with **S3b**). The resulting mixture was stirred under Ar atmosphere at 40 °C for 16 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent for **1m**: *n*-hexane/CH_2Cl_2 = 1:1; eluent for **1q**: *n*-hexane/CH_2Cl_2 = 1:3, v/v) to afford compound **1m** or **1q**.



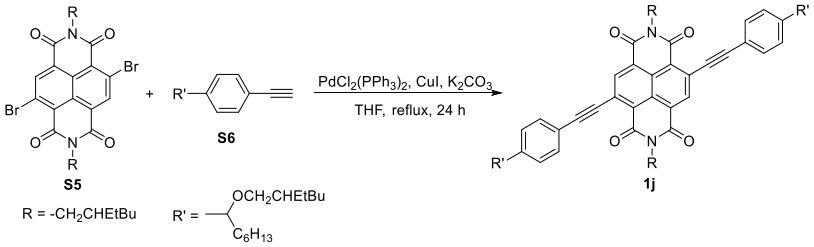
1m: yellow solid (327.1 mg, yield 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 – 8.58 (m, 6H), 5.27 – 5.04 (m, 4H), 2.32 – 2.09 (m, 8H), 1.92 – 1.78 (m, 8H), 1.33 – 1.16 (m, 64H), 0.84 – 0.75 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 162.5, 162.2, 161.2, 137.3, 136.6, 132.0, 131.7, 131.3, 131.0, 128.3, 127.6, 127.3, 126.9, 126.7, 126.1, 125.7, 125.4, 125.1, 86.1, 85.8, 55.5, 55.3, 32.2, 31.7, 31.7, 29.1, 29.0, 26.9, 26.8, 22.50, 22.49, 14.1, 14.04, 13.97, 13.95, 13.8.



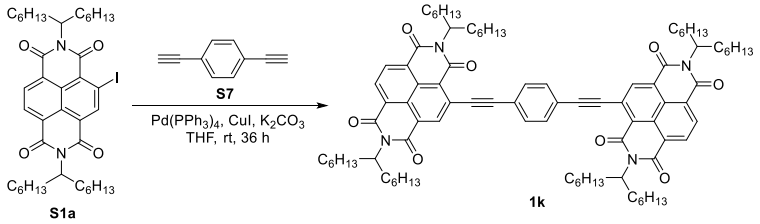
1q: red solid (576.0 mg, yield 74%); ^{1}H NMR (400 MHz, toluene-d_8, 353 K) δ 8.50 (d, *J* = 7.9 Hz, 2H), 8.45 (d, *J* = 8.0 Hz, 2H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.27 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.0 Hz, 4H), 5.50 – 5.38 (m, 4H), 2.58 – 2.46 (m, 8H), 2.08 – 1.99 (m, 8H), 1.59 – 1.39 (m, 40H), 1.35 – 1.26 (m, 24H), 0.85 – 0.76 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 163.6, 163.0, 162.6, 134.1, 133.4, 133.3, 131.9, 131.6, 131.3, 130.0, 129.5, 129.5, 126.3, 125.9, 123.7, 123.4, 123.3, 123.2, 86.1, 85.1, 55.4, 55.1, 32.6, 32.5, 312.0, 31.9, 29.8, 29.4, 29.4, 27.3, 27.1, 22.8, 22.7, 14.17, 14.15.



Synthesis of 1n: To the solution of **S1a** (151.4 mg, 0.2 mmol), **S4** (21.8mg, 0.1 mmol), $Pd(PPh_3)_4$ (13.9 mg, 0.024 mmol), PPh_3 (6.3 mg, 0.024 mmol) and 4-(*tert*-butyl)phenol (45.1 mg, 0.6 mmol), K_2CO_3 (82.9 mg, 1.2 mmol) in THF (4 mL) was added CuI (2.3 mg, 0.024 mmol). The resulting mixture was stirred under Ar atmosphere at room temperature for 36 h. The reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 1:1, v/v) to afford compound **1n** as yellow solid (146.5 mg, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 – 8.63 (m, 6H), 5.26 – 5.05 (m, 4H), 2.29 – 2.11 (m, 8H), 1.92 – 1.79 (m, 8H), 1.33 – 1.17 (m, 64H), 0.88 – 0.77 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 163.3, 162.5, 162.2, 137.4, 136.8, 131.9, 131.4, 129.3, 128.6, 127.3, 126.9, 126.7, 126.6, 126.2, 125.5, 125.1, 124.6, 86.0, 79.7, 72.0, 55.5, 55.4, 32.2, 31.70, 31.68, 29.1, 26.9, 26.8, 22.52, 22.51, 13.99, 13.97.

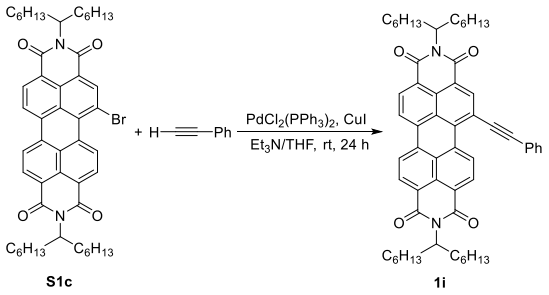


Synthesis of 1j: To the solution of **S5** (129.7 mg, 0.2 mmol), **S6** (132.1 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (7.1 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) in THF (4 mL) was added K_2CO_3 (276.4 mg, 2 mmol). The resulting mixture was stirred under Ar atmosphere at reflux for 24 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 3:1, v/v) to afford compound **1j** as yellow solid (212.7 mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 2H), 7.75 (d, J = 8.1 Hz, 4H), 7.38 (d, J = 8.1 Hz, 4H), 4.26 – 4.15 (m, 6H), 3.26 – 3.22 (m, 2H), 3.18 – 3.14 (m, 2H), 2.08 – 1.94 (m, 2H), 1.92 – 1.74 (m, 2H), 1.47 – 1.25 (m, 52H), 0.99 – 0.86 (m, 30H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 161.7, 146.1, 146.0, 137.2, 132.6, 127.1, 126.83, 126.81, 126.4, 125.2, 125.0, 121.2, 103.2, 89.5, 82.26, 82.25, 71.8, 71.7, 44.5, 40.0, 39.9, 38.4, 37.8, 31.8, 30.6, 30.6, 30.5, 29.7, 29.2, 29.1, 29.0, 28.5, 25.8, 24.0, 23.94, 23.87, 23.1, 23.0, 22.6, 14.08, 14.05, 11.1, 11.0, 10.6.



Synthesis of 1k: To the solution of **S1a** (151.4 mg, 0.2 mmol), **S7** (12.6 mg, 0.1 mmol), $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) and CuI (7.6 mg, 0.04 mmol) in THF (10 mL) was added K_2CO_3 (0.55 g, 4

mmol). The resulting mixture was stirred under Ar atmosphere at room temperature for 36 h. The reaction mixture was diluted with CH_2Cl_2, washed with *sat.* NH_4Cl, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 1:2, v/v) to afford compound **1k** as yellow solid (138.4 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.63 (m, 6H), 7.82 (s, 4H), 5.27 – 5.08 (m, 4H), 2.32 – 2.15 (m, 8H), 1.95 – 1.81 (m, 8H), 1.33 – 1.19 (m, 64H), 0.88 – 0.79 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.7, 162.8, 162.5, 137.2, 136.5, 132.6, 131.7, 131.1, 130.5, 127.6, 127.2, 126.8, 126.1, 125.9, 125.3, 123.9, 101.5, 92.1, 55.2, 32.27, 32.25, 31.71, 31.69, 29.2, 29.1, 26.9, 26.8, 22.54, 22.52, 13.99, 13.98.

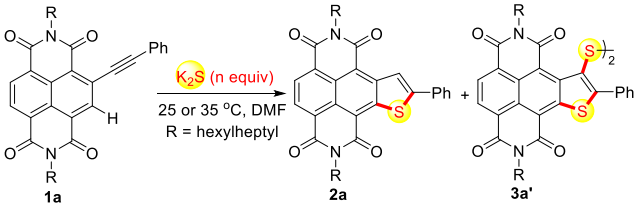


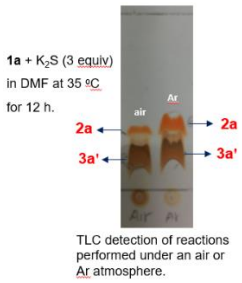
1i was synthesized according to previous literature.[3]

3. Optimization of Reaction Parameters

3.1 Thienannulation of 1a at 25 and 35 °C

Table S1 Optimization of reaction conditions





TLC detection of reactions performed under an air or Ar atmosphere.

entry	reaction conditions[a]	% yield of **2a**[b]	% yield of **3a'**[b]
1	K_2S (3 equiv), 25 °C, Ar, 10 min	14	41
2	K_2S (3 equiv), 35 °C, Ar, 10 min	7	36
3	K_2S (3 equiv), 35 °C, Ar, 24 h	73	0
4	**K_2S (6 equiv), 25 °C, Ar, 10 min**	**13**	**60**
5	K_2S (6 equiv), 25 °C, Ar, 12 h	12	43
6	K_2S (6 equiv), 25 °C, air, 10 min	9	57
7	K_2S (3 equiv), 35 °C, air, 12 h	16	58
8	1/8 S_8 (6 equiv), NaOH (12 equiv), Ar, 25 °C, 10 min	15	36
9	$Na_2S·9H_2O$ (6 equiv), Ar, 25 °C, 10 min	22	0

[a]Reactions run in 0.03 mmol scale. [b]Isolated yields of **2a** and **3a'**.

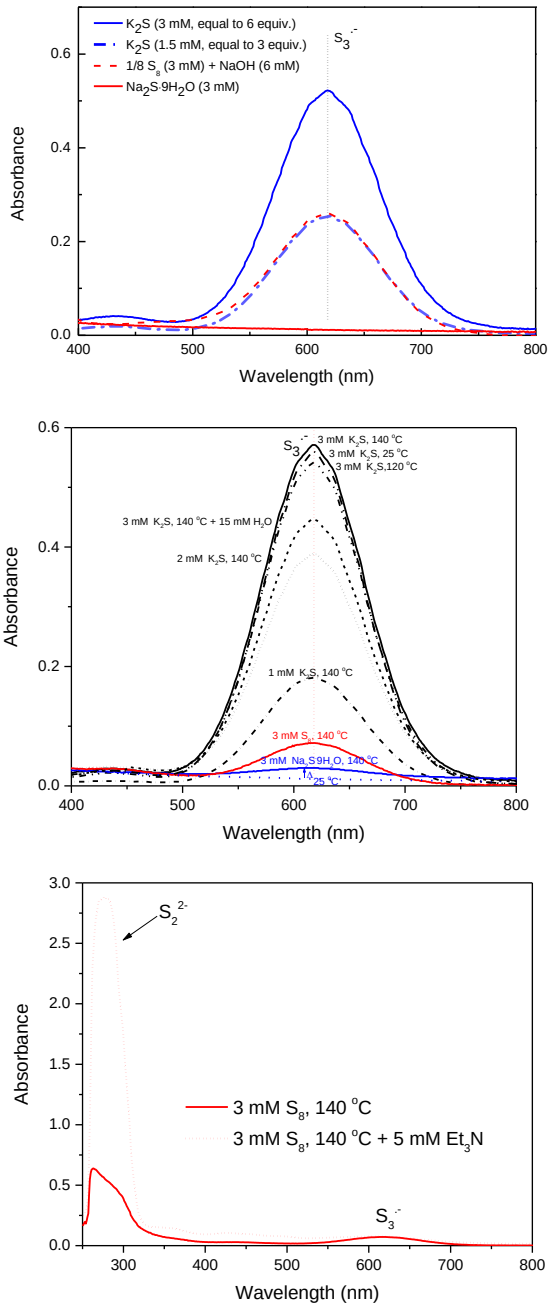
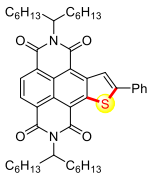
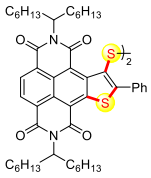


Figure S1 UV-visible spectra studies of several sulfur reagents in DMF
(For the feature peak of S_2^{2-}, see: *J. Power Sources*, **2014**, *255*, 204-218)

Synthesis of 2a and 3a': To a 25 mL tube, **1a** (21.9 mg, 0.03 mmol), K_2S (19.8 mg, 6 equiv, 0.18 mmol) and DMF (2.0 mL) were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at room temperature for 10 min. After opening the cap, the reaction mixture was stirred in air for 1 h. The resulting solution was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **2a** (*n*-hexane/CH_2Cl_2 = 4:1) and **3a'** (*n*-hexane/CH_2Cl_2 = 3:2).



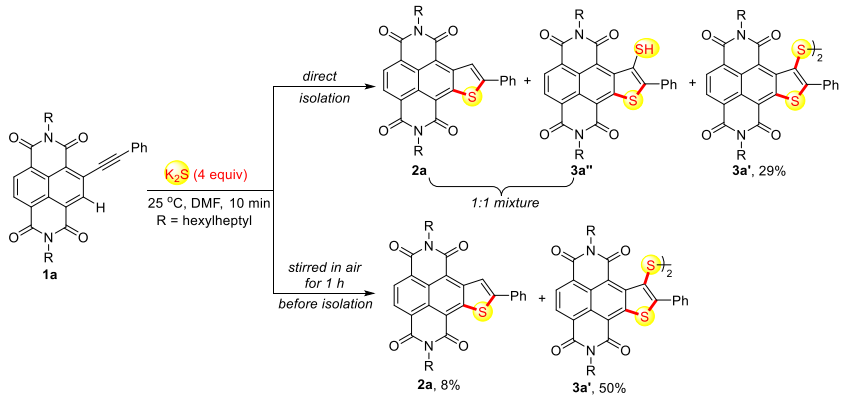
2a: orange-yellow solid (16.7 mg, yield 73%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 9.26 (s, 1H), 8.83 (d, *J* = 7.6 Hz, 1H), 8.81 (d, *J* = 7.6 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.63 – 7.53 (m, 3H), 5.35 – 5.23 (m, 2H), 2.41 – 2.28 (m, 4H), 2.07 – 1.96 (m, 5.2 Hz, 4H), 1.46 – 1.28 (m, 32H), 0.90 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 164.1, 163.7, 163.0, 156.9, 145.7, 145.0, 144.6, 144.3, 133.0, 130.4, 129.9, 129.7, 129.2, 127.2, 126.94 126.1, 125.6, 125.3, 123.9, 119.0, 118.2, 117.5, 55.4, 55.2, 32.4, 32.3, 31.7, 31.7, 29.19, 29.17, 27.0, 26.97, 26.9, 22.5, 14.0; HRMS m/z (APCI) calcd for $C_{48}H_{61}N_2O_4S_2^+$ $[M + H]^+$ 793.4067, found 793.4050.



3a': red-brown solid (14.3 mg, yield 60%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.86 (d, *J* = 7.5 Hz, 2H), 8.78 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.0 Hz, 4H), 6.71 (t, *J* = 7.0 Hz, 4H), 6.57 (t, *J* = 6.9 Hz, 2H), 5.36 – 5.28 (m, 2H), 5.22 – 5.12 (m, 2H), 2.41 – 2.30 (m, 8H), 2.09 – 1.99 (m, 8H), 1.52 – 1.44 (m, 32H), 1.39 – 1.33 (m, 32H), 0.98 – 0.88 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 164.0, 163.7, 162.9, 143.9, 143.2, 140.8, 131.3, 131.0, 130.3, 129.6, 129.1, 128.9, 127.2, 126.8, 125.4, 124.8, 124.6, 123.9, 122.6, 121.9, 117.8, 117.2, 55.9, 55.4, 33.6, 32.6, 32.1, 31.9, 31.8, 29.7, 29.3, 29.1, 27.3, 26.9, 22.7, 22.6, 14.1.

*Note: The reaction mixture should be stirred in air for 1 h before product isolation. Otherwise, three thienannulation products (**2a**, **3a'** and thiol **3a''**, see below) could be formed. Separation of **2a** and **3a''** is impossible due to their similar polarities. One ^{1}H NMR spectrum for the mixture (**2a/3a''**) was shown in Fig. S2. When a DMF solution of the mixture (**2a/3a''**) was stirred in air at room temperature for 1 h, thiol **3a''** could be oxidized by air to give **3a'**.*

Scheme S1 Observation of thiol 3a''



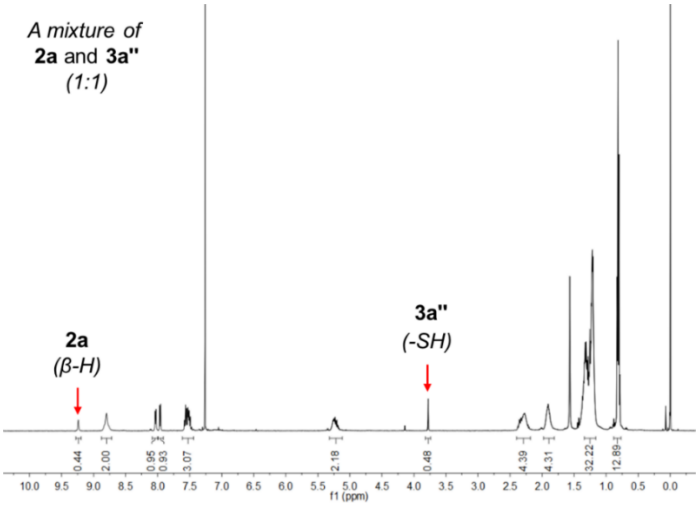
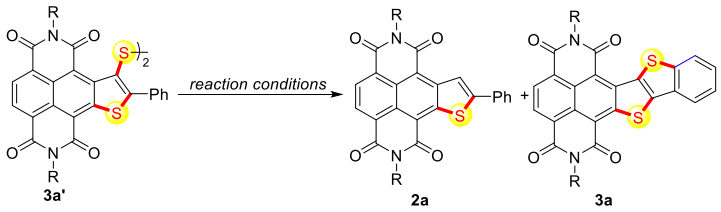


Figure S2 ^{1}H NMR spectrum of **2a**/**3a''** (molar ratio: ~1/1)

3.2 Thienannulation of 3a'

Table S2 Optimization of reaction conditions



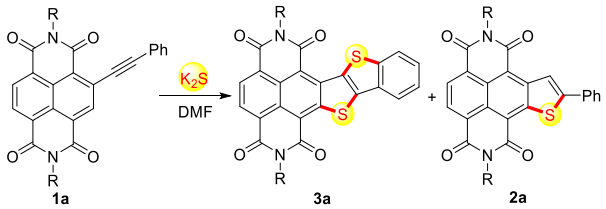
entry	reaction conditions[a]	% yield of **2a**[b]	% yield of **3a**[b]	% recovery yield of **3a'**[c]
1	Ar, 80 °C,	0	0	> 90
2	Ar, 100 °C	0	0	> 90
3	**Ar, 120 °C**	**19**	**78**	**0**
4	Ar, 140 °C	20	71	0
5	air, 120 °C	trace	trace	70
6	TEMPO (3 equiv), Ar, 140 °C	0	0	99
7	TEMPO (5 equiv), Ar, 140 °C	0	0	96

[a]Reactions run in 0.015 mmol scale in DMF for 24 h. [b]Isolated yields of **2a** and **3a**. [c]Recovery yields of **3a'**.

Synthesis of 3a: To a 25 mL tube, **3a'** (23.8 mg, 0.015 mmol) and DMF (2 mL) were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 120 °C for 24 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 2:1, v/v) to afford compound **3a** as pale brown solid (18.5 mg, 78%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.73 (d, *J* = 7.6 Hz, 1H), 8.67 (d, *J* = 7.6 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.63 – 7.54 (m, 2H), 5.43 – 5.28 (m, 2H), 2.50 – 2.37 (m, 4H), 2.14 – 2.03 (m, 4H), 1.59 – 1.35 (m, 16H), 1.38 – 1.31 (m, 16H), 0.92 – 0.88 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 163.8, 163.3, 162.8, 148.1, 147.3, 145.8, 144.0, 136.4, 135.9, 131.2, 131.1, 130.8, 129.9, 129.2, 128.5, 127.3, 125.8, 125.4, 124.8, 124.5, 124.2, 122.8, 122.6, 121.9, 119.2, 118.6, 116.5, 55.9, 55.5, 32.6, 32.4, 31.94, 31.88, 29.4, 27.5, 27.4, 22.7, 14.0; HRMS m/z (APCI) calcd for $C_{48}H_{61}N_2O_4S_2^+$ $[M + H]^+$ 793.4067, found 793.4050.

3.3 Stitching thienannulation of 1a

Table S3 Optimization of reaction conditions[a]

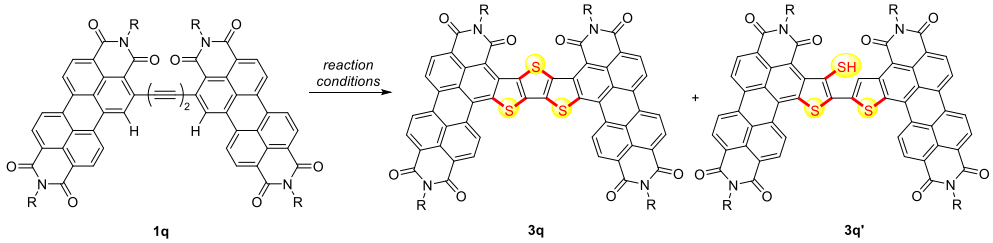


entry	reaction conditions	% yield of **3a**[b]	% yield of **2a**[b]
1	K_2S (6 equiv), 140 °C	66	16
2	K_2S (6 equiv), 120 °C	51	19
3	K_2S (6 equiv), 100 °C	trace	--
4	K_2S (8 equiv), 140 °C	64	20
5	K_2S (4 equiv), 140 °C	42	44
6	K_2S (2 equiv), 140 °C	10	64
7[c]	K_2S (6 equiv), H_2O (30), 140 °C	60	19
8	S_8 (6 equiv), 140 °C	10	71
9	**S_8 (6 equiv), Et_3N (10 equiv), 140 °C**	**trace**	**98**
10	S_8 (6 equiv), NaO^{t}Bu (12 equiv), 140 °C	35	17
11	$Na_2S{\cdot}9H_2O$ (6 equiv), 140 °C	20	15
12[d]	**K_2S (6 equiv), 140 °C**	**83**	**16**

[a]Reactions run in 0.03 mmol scale for 24 h in Ar (R = hexylheptyl). [b]Isolated yields of **2a** and **3a**. [c]40 h. [d]Before heating at 140 °C, the reaction mixture was stirred at 25 °C for 10 min.

3.4 Consecutive thienannulations of PDI dimer 1q and NDI dimer 1m

Table S4 Optimization of reaction conditions



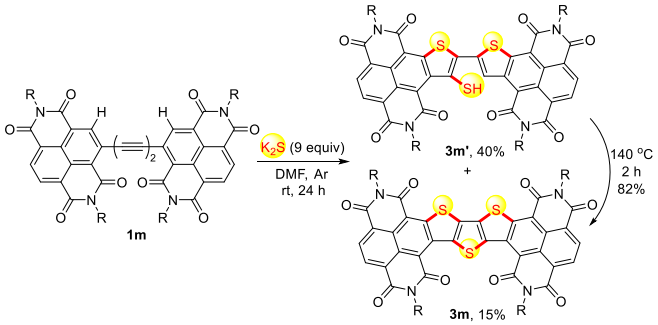
entry	reaction conditions[a]	% yield of **3q**[b]	% yield of **3q'**[b]
1	K_2S (9 equiv), 40 °C, 15 h	0	78
2	K_2S (9 equiv), TEMPO (9 equiv), 40 °C, 15 h	0	0
3	K_2S (9 equiv), 140 °C, 48 h	73	0
4	K_2S (12 equiv), 140 °C, 48 h	74	0
5	S_8 (6 equiv), 140 °C, 48 h	50	0
6[c]	K_2S (9 equiv), 140 °C, 48 h	79	0

[a]Reactions run in 0.02 mmol scale in Ar (R = hexylheptyl). [b]Isolated yields of **3q** and **3q'**. [c]Before heating at 140 °C, the reaction mixture was stirred at 25 °C for 15 h.

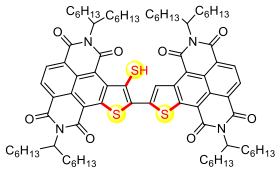
Synthesis of 3q': To a 25 mL tube, **1q** (31.1 mg, 0.02 mmol), K_2S (19.8 mg, 9 equiv, 0.18 mmol) and DMF (0.5 mL) were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 40 °C for 15 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL) and dried over Na_2SO_4.

After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 1:3, v/v) to afford compound **3q'** as brown solid (25.8 mg, 78%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 10.12 (s, 1H), 8.95 (d, *J* = 7.9 Hz, 1H), 8.56 (t, *J* = 8.3 Hz, 2H), 8.49 (s, 2H), 8.40 – 8.31 (m, 2H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.05 (brs, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.55 (brs, 1H), 5.51 – 5.26 (m, 4H), 2.72 – 2.35 (m, 10H), 2.25 – 2.08 (m, 8H), 1.89 – 1.56 (m, 38H), 1.49 – 1.34 (m, 24H), 1.08 – 0.94 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 163.0, 162.2, 151.5, 144.5, 140.5, 139.1, 135.4, 134.1, 132.9, 132.4, 132.3, 131.6, 130.9, 130.0, 129.3, 128.7, 128.4, 128.3, 127.7, 127.2, 127.0, 126.7, 126.0, 124.6, 124.5, 124.0, 123.4, 122.9, 122.5, 121.9, 121.6, 121.3, 55.9, 55.4, 55.2, 55.10 34.4, 33.3, 33.1, 32.8, 32.6, 32.1, 32.0, 31.9, 29.6, 29.5, 29.4, 27.34, 27.27, 27.1, 27.0, 22.8, 22.7, 14.21, 14.16

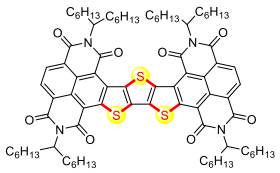
Synthesis of 3q: To a 25 mL tube, **1q** (31.1 mg, 0.02 mmol), K_2S (19.8 mg, 9 equiv, 0.18 mmol) and DMF (0.5 mL) were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at room temperature for 15 h and then 140 °C for 48 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 1:5, v/v) to afford compound **3q** as purple solid (26.2 mg, 79%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.85 – 8.81 (m, 4H), 8.73 (d, *J* = 8.0 Hz, 2H), 8.56 (d, *J* = 8.0 Hz, 2H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.32 (d, *J* = 7.8 Hz, 2H), 5.46 – 5.38 (m, 2H), 5.35 – 5.27 (m, 2H), 2.59 – 2.50 (m, 4H), 2.46 – 2.38 (m, 4H), 2.27 – 2.23, (m, 4H), 2.10 – 2.06 (m, 4H), 1.52 – 1.42 (m, 62H), 1.01 – 0.92 (m, 26H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.75, 163.77, 163.5, 162.3, 143.6, 142.0, 137.7, 133.4, 133.3, 132.5, 132.38, 132.35, 131.5, 131.3, 131.2, 130.7, 130.62, 130.57, 130.5, 130.1, 130.0, 129.5, 129.4, 129.0, 128.8, 126.8, 126.4, 126.0, 123.6, 123.4, 123.3, 122.9, 122.1, 121.8, 116.2, 77.4, 77.2, 76.9, 55.7, 55.4, 32.7, 32.3, 32.1, 29.6, 29.5, 27.7, 27.4, 22.9, 14.4, 14.3; MALDI-TOF-MS m/z (DCTB as matrix) calc for $C_{104}H_{120}N_4O_8S_3Na^+$ $[M + Na]^+$: 1671.816, obtained = 1671.764.



Synthesis of 3m and 3m': To a 25 mL tube, **1m** (52.4 mg, 0.04 mmol), K_2S (39.6 mg, 9 equiv, 0.36 mmol) and DMF (2.0 mL) were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at room temperature for 5 h. The resulting solution was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 2:1, v/v) to afford **3m'** and **3m**.



3m': brown solid (22.4 mg, yield 40%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 9.04 – 8.90 (m, 2H), 8.76 (brs, 1H), 7.75 (brs, 1H), 6.94 (brs, 1H), 5.46 – 5.22 (m, 4H), 5.19 (brs, 1H), 2.60 – 2.00 (m, 18H), 1.80 – 1.25 (m, 62H), 1.12 –0.88 (m, 24H).



3m: dull red solid (8.2 mg, yield 15%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.92 (brs, 4H), 5.53 – 5.42 (m, 2H), 5.39 – 5.31 (m, 2H), 2.54 – 2.35 (m, 8H), 2.17 – 2.02 (m, 8H), 1.52 – 1.41 (m, 32H), 1.37 – 1.30 (m, 32H), 0.94 – 0.85 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 164.6, 163.8, 162.7, 142.7, 139.8, 130.8, 130.2, 126.9, 125.1, 124.3, 119.5, 118.9, 117.7, 55.7, 32.3, 31.8, 29.2, 27.0, 22.6, 14.0; HRMS m/z (ESI) calcd for $C_{84}H_{113}N_4O_8S_3^+$ $[M + H]^+$ 1401.7715, found 1401.7725.

Preliminary results of single-crystal X-ray diffraction analysis confirmed the solid-state structure of of **3m'** (Fig S3). A dimer having the symmetry of an inversion center was formed through π-π interactions between two adjacent **3m'** molecules.

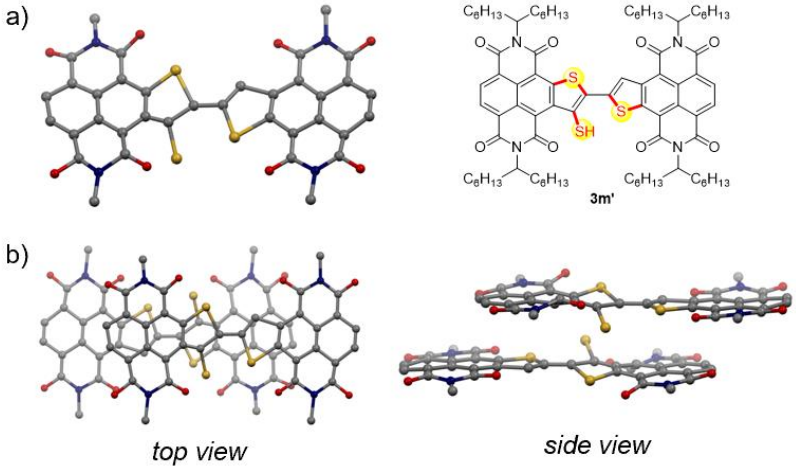
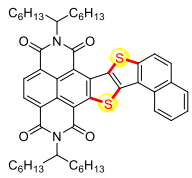


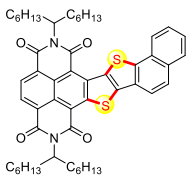
Figure S3 a) X-ray crystal structure of **3m'**; b) Packing mode of two adjacent **3m'** molecules (for clarity, alkyl chains on nitrogen atoms are omitted)

4. Typical Procedures for Stitching Thienannulations

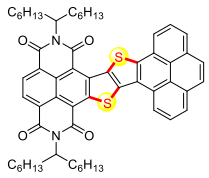
General procedure: To a 25 mL tube, acetylenic RDI **1** (0.03 mmol), K_2S (6-12 equiv) and DMF (2 mL) were added under an argon atmosphere. Then the tube was sealed with a Teflon lined cap, and the reaction mixture was stirred under Ar atmosphere at a certain reaction temperature for 24 or 48 h. After cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with water (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane:CH_2Cl_2 = 4:1~1:5) to afford the corresponding multiple thienannulation product **3**.



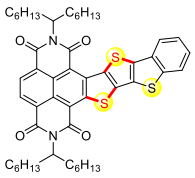
Compound **3b** was prepared from **1b** (35.6 mg, 0.046 mmol) and K_2S (30.2 mg, 6 equiv). The reaction was performed at 25 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 3:1, v/v) yielded pure **3b** as purple solid (25.1 mg, 65%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.32 – 8.18 (m, 2H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.96 (s, 2H), 7.88 (t, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 5.46 – 5.32 (m, 2H), 2.61 – 2.44 (m, 4H), 2.21 – 2.08 (m, 4H), 1.61 – 1.50 (m, 16H), 1.45 – 1.36 (m, 16H), 0.96 – 0.90 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 163.7, 163.3, 162.7, 147.6, 145.4, 145.3, 145.2, 143.1, 142.9, 134.9, 131.1, 131.0, 130.9, 129.2, 128.8, 128.4, 128.0, 127.8, 126.8, 126.0, 124.9, 124.2, 123.6, 122.3, 120.6, 118.7, 116.0, 55.7, 55.6, 32.6, 32.6, 31.9, 29.5, 27.5, 22.7, 14.1; HRMS m/z (ESI) calcd for $C_{52}H_{63}N_2O_4S_2^+$ $[M + H]^+$ 843.4224, found 843.4237.



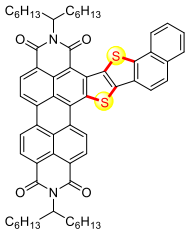
Compound **3c** was prepared from **1c** (23.4 mg, 0.03 mmol) and K_2S (19.8 mg, 6 equiv). The reaction was performed at 25 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 2:1, v/v) yielded pure **3c** as purple solid (19.4 mg, 77%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.48 (d, *J* = 7.5 Hz, 1H), 8.41 (d, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 5.50 – 5.42 (m, 1H), 5.31 – 5.38 (m, 1H), 2.63 – 2.51 (m, 2H), 2.50 – 2.38 (m, 2H), 2.23 – 2.10 (m, 4H), 1.62 – 1.49 (m, 16H), 1.45 – 1.36 (m, 16H), 0.97 – 0.89 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 164.0, 163.5, 162.7, 148.5, 147.8, 145.0, 144.4, 136.6, 136.2, 131.1, 130.4, 129.8, 129.3, 129.1, 128.6, 128.3, 127.2, 126.9, 125.8, 125.2, 124.2, 123.4, 122.7, 119.3, 118.6, 117.9, 116.2, 115.5, 55.6, 55.4, 32.5, 32.0, 31.9, 29.7, 29.4, 27.4, 27.3, 22.70, 22.66, 14.08, 14.06; HRMS m/z (ESI) calcd for $C_{52}H_{63}N_2O_4S_2^+$ $[M + H]^+$ 843.4224, found 843.4236.



Compound **3d** was prepared from **1d** (46.2 mg, 0.054 mmol) and K_2S (35.7 mg, 6 equiv). The reaction was performed at 25 °C for 40 h. Purification by flash column chromatography (silica gel, *n*-hexane:$CHCl_3$ = 3:2, v/v) yielded pure **3d** as purple solid (43.1 mg, 87%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.82 (d, *J* = 7.3 Hz, 1H), 8.70 (d, *J* = 7.6 Hz, 1H), 8.33 – 8.23 (m, 3H), 8.22 – 8.17 (m, 1H), 8.15 – 8.07 (m, 3H), 8.04 (d, *J* = 8.9 Hz, 1H), 5.48 – 5.38 (m, 1H), 5.36 – 5.26 (m, 1H), 2.61 – 2.40 (m, 4H), 2.29 – 2.12 (m, 4H), 1.51 – 1.63 (m, 16H), 1.47 – 1.36 (m, 16H), 0.92 – 0.90 (m, 12H); HRMS m/z (ESI) calcd for $C_{58}H_{65}N_2O_4S_2^+$ $[M + H]^+$ 917.4380, found 917.4361.

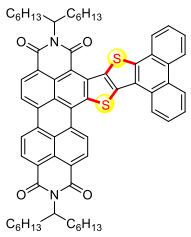


Compound **3e** was prepared from **1e** (31.1 mg, 0.04 mmol) and K_2S (26.1 mg, 6 equiv). The reaction was performed at 140 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 3:1, v/v) yielded pure **3e** as purple solid (10.5 mg, 31%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.73 (d, *J* = 7.6 Hz, 1H), 8.63 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 2H), 5.47 – 5.39 (m, 1H), 5.37 – 5.29 (m, 1H), 2.54 – 2.36 (m, 4H), 2.16 – 2.02 (m, 4H), 1.53 – 1.46 (m, 16H), 1.39 – 1.33 (m, 16H), 0.96 – 0.90 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 164.3, 163.8, 162.9, 149.0, 148.2, 145.1, 142.9, 140.4, 136.3, 134.4, 132.4, 130.0, 129.4, 129.3, 129.2, 128.6, 126.3, 125.9, 125.3, 124.4, 123.6, 122.7, 121.65, 118.8, 55.8, 55.5, 32.5, 32.0, 31.9, 29.6, 29.3, 27.5, 27.3, 22.7, 22.7, 14.1; HRMS m/z (ESI) calcd for $C_{50}H_{60}N_2O_4S_3Na^+$ $[M + Na]^+$ 871.3607, found 871.3622.

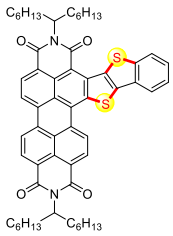


Compound **3f** was prepared from **1f** (46.3 mg, 0.05 mmol) and K_2S (34 mg, 6 equiv). The reaction was performed at 140 °C for 48 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 1:2, v/v) yielded pure **3f** as yellow solid (30.7 mg, 62%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 333 K) δ 9.24 (d, *J* = 8.1 Hz, 1H), 8.89 (d, *J* = 8.1 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.52 – 5.41 (m, 1H), 5.32 – 5.22 (m, 1H), 2.58 – 2.47 (m, 2H), 2.40 – 2.30 (m, 2H), 2.20 – 2.11 (m, 2H), 2.06 – 1.97 (m, 2H), 1.66 – 1.56 (m, 4H), 1.50 – 1.29 (m, 28H), 0.94 – 0.91 (m, 12H); ^{13}C NMR (214 MHz, $CDCl_3$) δ 165.0, 164.6, 164.0, 163.50, 143.47, 141.5, 139.7, 134.3, 134.2, 134.0, 132.4, 131.8, 131.0, 130.8, 130.1, 130.0, 129.5, 129.1, 128.6, 128.2, 127.8, 127.5, 127.1, 126.8, 126.6, 126.2, 125.6, 123.3, 122.9, 122.7,

122.6, 122.0, 118.5, 55.2, 55.0, 32.7, 32.6, 32.2, 32.0, 29.5, 27.6, 27.2, 22.9, 22.8, 14.29, 14.26; MALDI-TOF-MS m/z (DCTB as matrix) calc for $C_{62}H_{67}N_2O_4S_2$ $[M + H]^+$ 967.454, found 967.379.

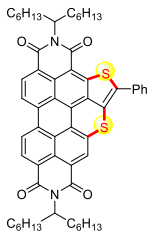


Compound **3g** was prepared from **1g** (47.8 mg, 0.05 mmol) and K_2S (33.1 mg, 6 equiv). The reaction was performed at 140 °C for 48 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 1:5, v/v) yielded pure **3g** as yellow solid (36.6 mg, 72%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ + $CDCl_3$ + TFA-d, 333 K) δ 9.05 (d, *J* = 8.1 Hz, 1H), 8.89 (d, *J* = 8.1 Hz, 1H), 8.79 (d, *J* = 8.0 Hz, 1H), 8.56 – 8.44 (m, 2H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.01 (t, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 5.60 – 5.49 (m, 1H), 5.44 – 5.34 (m, 1H), 2.62 – 2.55 (m, 2H), 2.48 – 2.39 (m, 2H), 2.33 – 2.22 (m, 2H), 2.18 – 2.09 (m, 2H), 1.55 – 1.45 (m, 14H), 1.44 – 1.40 (m, 8H), 1.36 – 1.33 (m, 8H), 1.00 – 0.90 (m, 14H); ^{13}C NMR (126 MHz, $C_2D_2Cl_4$ + $CDCl_3$ + TFA-d) δ 165.4, 164.8, 143.9, 141.8, 138.4, 136.1, 134.5, 134.4, 132.4, 131.9, 131.4, 128.8, 128.5, 128.2, 127.9, 127.7, 127.6, 126.9, 126.8, 126.7, 126.5, 126.1, 125.7, 125.4, 125.2, 124.8, 123.2, 123.1, 122.8, 122.7, 122.6, 122.5, 122.4, 56.1, 32.6, 32.4, 32.0, 31.9, 29.8, 29.2, 27.5, 27.1, 22.8, 22.7, 14.10, 14.05, 0.8, 0.7; MALDI-TOF-MS m/z (DCTB as matrix) calc for $C_{66}H_{69}N_2O_4S_2$ $[M + H]^+$ 1017.469, obtained = 1017.458.

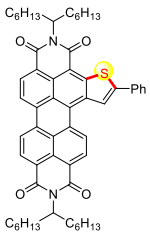


Compound **3h** was prepared from **1h** (25.7 mg, 0.03 mmol) and K_2S (19.8 mg, 6 equiv). The reaction was performed at 170 °C for 12 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 1:3, v/v) yielded pure **3h** as purple solid (16.5 mg, 60%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 9.27 (d, *J* = 8.1 Hz, 1H), 8.87 (d, *J* = 8.2 Hz, 1H), 8.86 (d, *J* = 7.9 Hz, 1H), 8.77 – 8.69 (m, 3H), 8.13 – 8.04 (m, 2H), 7.65 – 7.57 (m, 2H), 5.43 – 5.35 (m, 1H), 5.29 – 5.19 (m, 1H), 2.49 – 2.39 (m, 2H), 2.37 – 2.26 (m, 2H), 2.12 – 2.03 (m, 2H), 2.03 – 1.94 (m, 2H), 1.49 – 1.39 (m, 14H), 1.38 – 1.28 (m, 18H), 0.95 – 0.88 (m, 12H); ^{13}C NMR (126 MHz, $C_2D_2Cl_4$) δ 164.8, 164.4, 163.7, 163.3, 145.5, 142.1, 139.9, 134.5, 134.1, 133.5, 133.4, 131.6, 131.2, 131.0, 130.4, 129.2, 127.6, 127.4, 126.9, 125.1, 124.2, 123.7, 123.6, 123.3, 123.2, 122.9, 122.8, 122.2, 54.9, 32.5, 31.93, 31.90, 29.43, 29.40, 27.2, 27.1, 22.8, 22.8, 14.3; HRMS m/z (ESI) calcd for $C_{58}H_{64}N_2O_4S_2Na^+$ $(M + Na)^+$ 939.4200, found 939.4193.

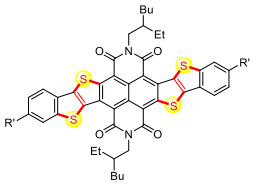
Compound **4** was prepared from **1i** (25.7 mg, 0.03 mmol) and K_2S (19.8 mg, 6 equiv). The reaction was performed at 40 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 1:2, v/v) yielded pure **4** and **2i**.



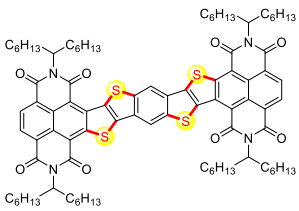
4: green solid (17.3 mg, 63%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.40 (d, *J* = 7.9 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 8.03 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 5.27 – 5.19 (m, 1H), 5.18 – 5.11 (m, 1H), 2.35 – 2.20 (m, 4H), 2.12 – 1.96 (m, 4H), 1.48 – 1.36 (m, 32H), 0.97 – 0.91 (m, 12H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ 162.8, 162.3, 134.4, 133.9, 133.6, 132.4, 132.3, 131.9, 131.2, 129.1, 128.7, 127.6, 127.4, 127.3, 127.0, 126.7, 125.2, 125.0, 123.2, 122.1, 120.2, 116.1, 54.8, 54.7, 32.0, 31.7, 31.7, 29.2, 27.1, 27.0, 22.6, 22.6, 14.1; HR-MS (ESI) m/z calcd for $C_{58}H_{64}N_2O_4S_2Na^+$ $[M+H]^+$ 939.4200; found 939.4198.



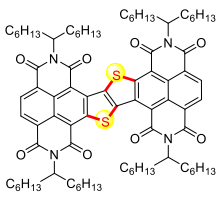
2i: purple solid (6.1 mg, 23%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 333 K) δ 8.85 (d, *J* = 8.1 Hz, 1H), 8.80 – 8.71 (m, 3H), 8.72 – 8.60 (m, 2H), 8.54 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.51 (m, 3H), 5.34 – 5.20 (m, 2H), 2.38 – 2.26 (m, 4H), 2.05 – 1.92 (m, 4H), 1.43 – 1.30 (m, 32H), 0.94 – 0.88 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.59, 163.63, 154.19, 139.64, 135.54, 134.43, 134.37, 133.41, 131.63, 130.94, 130.09, 129.48, 129.36, 129.23, 128.47, 128.10, 127.10, 127.05, 126.38, 125.05, 122.95, 122.48, 118.13, 55.19, 54.90, 32.56, 32.51, 31.93, 31.92, 29.40, 29.36, 27.22, 27.12, 22.74, 22.72, 14.17. HR-MS (ESI) m/z $[M+Na]^+$ calcd for $C_{58}H_{66}N_2O_4SNa^+$ 909.4641; Found 909.4633.



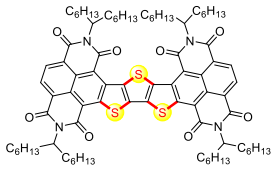
Compound **3j** (R′ = -CH(C_6H_{13})($OCH_2CHEtBu$)) was prepared from **1j** (48.0 mg, 0.042 mmol) and K_2S (55.5 mg, 12 equiv). The reaction was performed at 140 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 3:1, v/v) yielded pure **3j** as purple solid (28.6 mg, 50%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 7.98 (s, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 4.47 – 4.34 (m, 6H), 3.46 – 3.37 (m, 2H), 3.34 – 3.28 (m, 2H), 2.26 – 2.17 (m, 2H), 2.00 – 1.88 (m, 2H), 1.84 – 1.74 (m, 2H), 1.64 – 1.52 (m, 16H), 1.49 – 1.31 (m, 34H), 1.13 – 1.05 (m, 6H), 0.92 – 0.90 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 162.9, 148.1, 146.4, 144.8, 143.7, 136.0, 131.5, 130.6, 123.6, 121.8, 121.4, 120.6, 117.7, 114.6, 82.3, 72.0, 71.9, 45.0, 40.2, 38.4, 37.8, 32.0, 30.8, 30.7, 30.6, 29.3, 29.19, 29.15, 28.5, 25.9, 24.1, 24.04, 23.97, 23.3, 23.2, 22.7, 14.2, 14.1, 11.2, 10.7; HRMS m/z (APPI) calcd for $C_{76}H_{103}N_2O_6S_4^+$ $[M + H]^+$ 1267.6693, found 1267.6693.



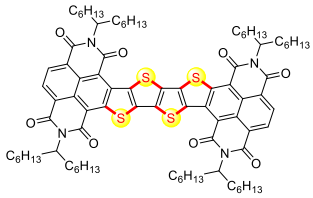
Compound **3k** was prepared from **1k** (20.2 mg, 0.015 mmol) and K_2S (19.8 mg, 12 equiv). The reaction was performed at at room temperature for 10 min and then 140 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 2:1, v/v) yielded pure **3k** as brown solid (20.5 mg, 90%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.47 (brs, 4H), 7.92 (s, 2H), 5.57 – 5.47 (m, 2H), 5.46 – 5.35 (m, 2H), 2.69 – 2.45 (m, 8H), 2.27 – 2.11 (m, 8H), 1.75 – 1.51 (m, 32H), 1.46 – 1.35 (m, 32H), 0.98 – 0.90 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 164.1, 163.5, 162.8, 159.5, 145.4, 140.4, 136.6, 129.9, 129.8, 126.8, 125.1, 117.2, 116.4, 56.2, 55.8, 32.5, 31.9, 29.7, 29.4, 27.5, 27.2, 22.7, 14.1; HRMS m/z (APPI) calcd for $C_{90}H_{115}N_4O_8S_4^+$ $[M + H]^+$ 1507.7592, found 1507.7592.



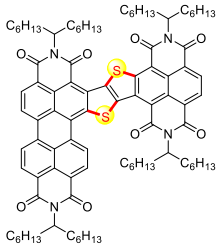
Compound **3l** was prepared from **1l** (30.3 mg, 0.024 mmol) and K_2S (15.6 mg, 6 equiv). The reaction was performed at 120 °C for 48 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 2:1, v/v) yielded pure **3l** as green solid (11.1 mg, 35%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.76 (brs, 4H), 5.50 – 5.43 (m, 2H), 5.40 – 5.34 (m, 2H), 2.56 – 2.42 (m, 8H), 2.21 – 2.09 (m, 8H), 1.55 – 1.49 (m, 24H), 1.41 – 1.32 (m, 40H), 0.94 – 0.88 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 164.0, 163.1, 162.7, 151.3, 150.5, 150.4, 142.9, 135.5, 130.9, 128.4, 126.3, 124.7, 120.2, 119.4, 118.5, 56.2, 32.6, 31.8, 29.3, 27.1, 22.7, 22.6, 14.0; HRMS m/z (ESI) calcd for $C_{82}H_{113}N_4O_8S_2^+$ $[M + H]^+$ 1345.7994, found 1345.8002.



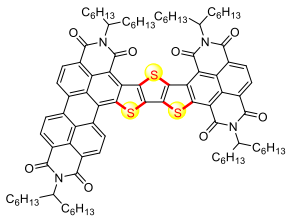
Compound **3m** was prepared from **1m** (32.3 mg, 0.025 mmol) and K_2S (24.5 mg, 9 equiv). The reaction was performed at 80 °C for 22 h and then 140 °C for 3 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 3:1, v/v) yielded pure **3m** as dull red solid (25.1 mg, 73%); for NMR data, see section 3.4.



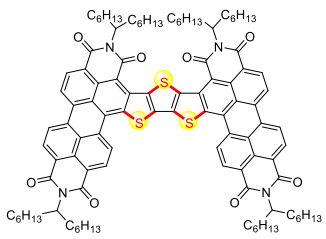
Compound **3n** was prepared from **1n** (32.5 mg, 0.024 mmol) and K_2S (32.3 mg, 12 equiv). The reaction was performed at 40 °C for 24 h and then 140 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 3:2, v/v) yielded pure **3n** as purple solid (15.6 mg, 44%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 8.81 (d, *J* = 6.7 Hz, 2H), 8.72 (d, *J* = 6.7 Hz, 2H), 5.47 – 5.41 (m, 2H), 5.38 – 5.32 (m, 2H), 2.52 – 2.40 (m, 8H), 2.16 – 2.05 (m, 8H), 1.54 – 1.44 (m, 32H), 1.39 – 1.34 (m, 32H), 0.96 – 0.90 (m, 24H); MALDI-TOF-MS m/z (DCTB as matrix) calc for $C_{86}H_{113}N_4O_8S_4^+$ $[M + H]^+$ 1457.743, found 1457.858.



Compound **3o** was prepared from **1o** (31.2 mg, 0.022 mmol) and K_2S (14.7 mg, 6 equiv). The reaction was performed at 60 °C for 48 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 2:1, v/v) yielded pure **3o** as dull-green solid (13.4 mg, 41%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 9.65 (d, *J* = 8.2 Hz, 1H), 9.00 (d, *J* = 8.2 Hz, 1H), 8.96 – 8.90 (m, 3H), 8.83 (d, *J* = 8.1 Hz, 1H), 8.82 – 8.78 (m, 2H), 5.52 – 5.43 (m, 2H), 5.40 – 5.33 (m, 1H), 5.30 – 5.23 (m, 1H), 2.55 – 2.46 (m, 4H), 2.43 – 2.31 (m, 4H), 2.16 – 1.99 (m, 8H), 1.50 – 1.32 (m, 64H), 0.95 – 0.86 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.49, 164.52, 163.71, 162.67, 145.2, 134.7, 134.2, 133.6, 131.0, 129.3, 128.6, 127.7, 127.2, 125.3, 124.9, 123.7, 123.2, 55.6, 54.9, 32.4, 32.3, 31.82, 31.80, 29.33, 29.28, 27.1, 27.0, 22.61, 22.59, 14.1, 14.04, 14.02; HRMS m/z (ESI) calcd for $C_{92}H_{117}N_4O_8S_2^+$ $[M + H]^+$ 1469.8307, found 1469.8310.



Compound **3p** was prepared from **1p** (45.8 mg, 0.032 mmol) and K_2S (31.7 mg, 9 equiv). The reaction was performed at room temperature for 10 min and then 140 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 2:1, v/v) yielded pure **3p** as purple solid (29.8 mg, 61%); ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K) δ 9.34 (d, *J* = 8.1 Hz, 1H), 8.94 (d, *J* = 8.0 Hz, 1H), 8.95 (d, *J* = 8.1 Hz, 1H), 8.92 – 8.88 (m, 2H), 8.81 (d, *J* = 8.1 Hz, 1H), 8.80 (d, *J* = 8.1 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 5.51 – 5.42 (m, 2H), 5.39 – 5.31 (m, 1H), 5.29 – 5.22 (m, 1H), 2.57 – 2.45 (m, 4H), 2.42 – 2.31 (m, 4H), 2.18 – 2.00 (m, 8H), 1.50 – 1.30 (m, 64H), 0.95 – 0.87 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 164.3, 163.5, 163.2, 144.1, 142.6, 141.8, 138.7, 137.9, 137.3, 134.1, 133.9, 133.1, 131.4, 131.0, 130.1, 129.1, 127.6, 126.8, 124.9, 124.6, 123.9, 123.0, 122.8, 55.7, 55.32, 55.27, 54.9, 32.5, 32.4, 32.3, 31.9, 31.8, 29.5, 29.3, 27.2, 27.0, 22.6, 14.07, 14.05; MALDI-TOF-MS m/z (DCTB as matrix) calc for $C_{94}H_{117}N_4O_8S_3^+$ $[M + H]^+$ 1525.803, found 1525.791.



Compound **3q** was prepared from **1q** (31.1 mg, 0.02 mmol) and K_2S (19.8 mg, 9 equiv). The reaction was performed at room temperature for 15 h and then 140 °C for 48 h. Purification by flash column chromatography (silica gel, *n*-hexane:CH_2Cl_2 = 1:3, v/v) yielded pure **3q** as purple solid (26.2 mg, 79%); for NMR data, see section 3.4.

5. Mechanistic Study

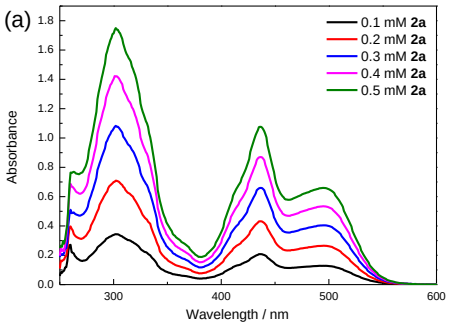
5.1 Observed kinetics of the thienannulation of 1a

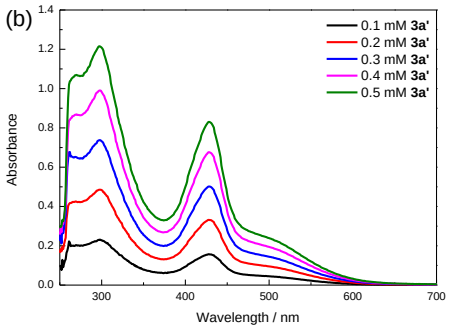
The thienannulation of **1a** with K_2S in DMF at room temperature was fast, reproducible, and relatively clean. During the reaction, the starting compound **1a** could be entirely consumed in 10 min. Therefore, the progress of the reaction could be monitored by UV−vis spectroscopy.

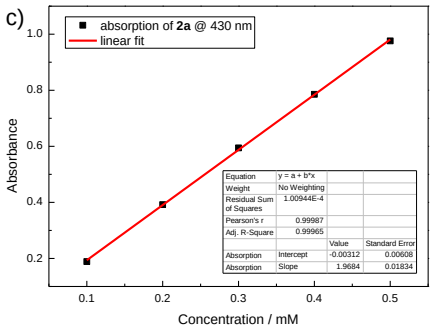
1) Concentration-dependent UV-vis absorption spectra of **2a** and **3a'** in DMF were recorded (Fig. S4, a and b). According to the Beer-Lambert law, the absorption of the solution is proportional to the path length and the concentration of the material. Therefore, measurements of the absorptions of **2a** or **3a'** in DMF at 430 and 500 nm gave four equations as shown in Fig. S4, c-f. Supposing the reaction mixture (DMF solution) contained only two species (**2a** and **3a'**), absorptions of the reaction mixture would be related to the concentrations of **2a** and **3a'** ([**2a**] and [**3a'**]) as shown in the following two equations.

430 nm: 1.9684×[**2a**]+1.7556×[**3a'**] = Absorbance+0.01126

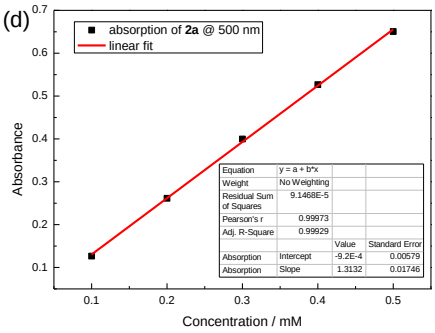
500 nm: 1.3132×[**2a**]+0.5081×[**3a'**] = Absorbance+0.00378



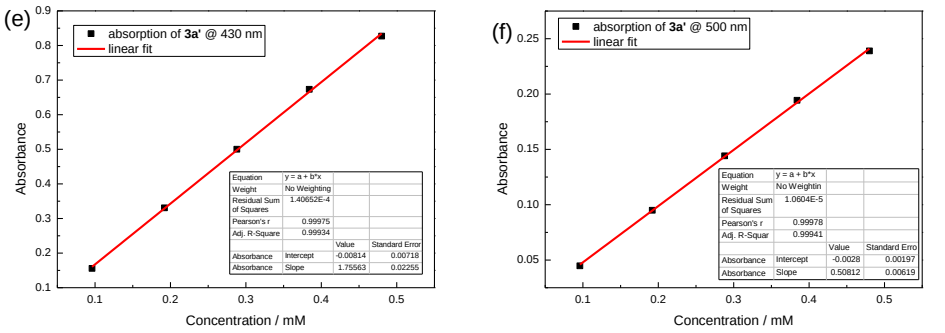




430 nm: Absorbance = -0.00312+1.9684×[**2a**]



500 nm: Absorbance = -0.00092+1.3132×[**2a**]

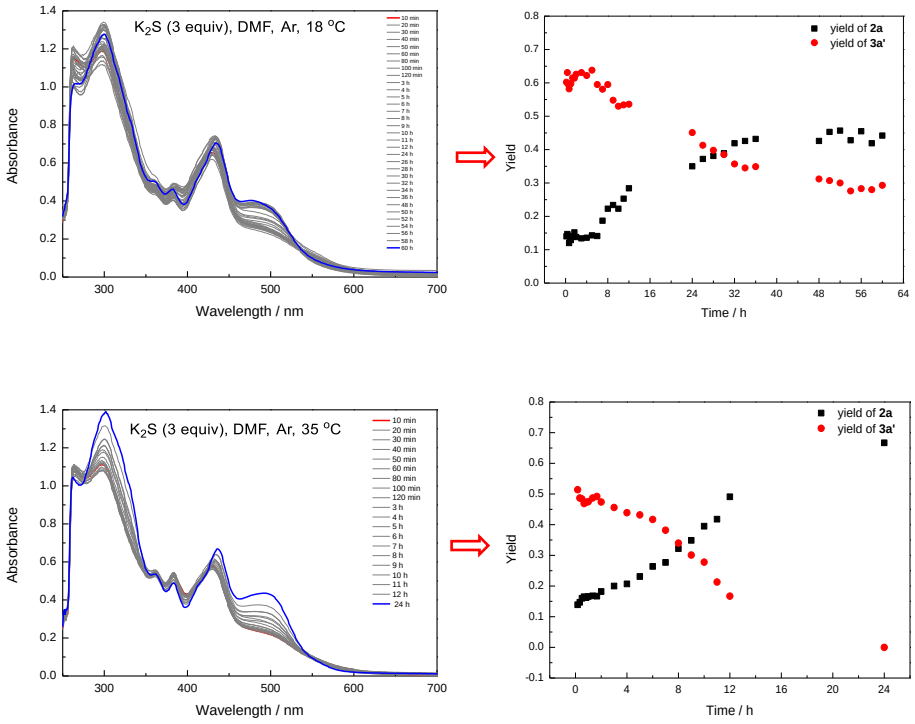


430 nm: Absorbance = -0.00814+1.7556×[**3a'**]

500 nm: Absorbance = -0.00286+0.5081×[**3a'**]

Figure S4 (a), (b) Concentration-dependent UV-vis absorption spectra of **2a** and **3a'** in DMF at 298 K; (c), (d), (e), (f) linear fit

2) To the solution of **1a** (21.9 mg, 0.03 mmol) in DMF (2 mL) was added K_2S (0.09 mmol or 0.18 mmol). The resulting mixture was stirred under Ar atmosphere (in a glove box) at 18, 25 or 35 °C. After a certain reaction time, 33 μL of reaction solution was took out of the glove box and diluted with 957 μL of DMF under air. Then the resulting solution was measured by UV-vis spectroscopy. The values of absorption at 430 and 500 nm would suffice to determine the concentrations of **2a** and **3a'** in the original reaction mixture. Accordingly, the yields of **2a** and **3a'** after a certain reaction time could be caculated without difficulty (Figure S5).



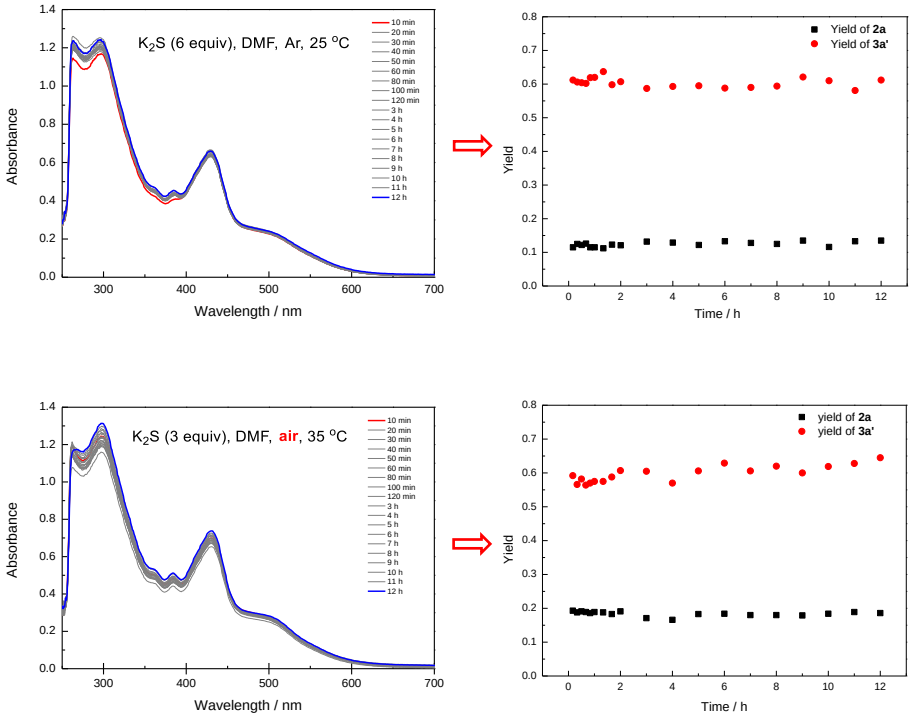


Figure S5 Reaction progresses between **1a** and K_2S monitored by UV−vis spectroscopy

5.2 UV-Vis absorption spectra of NDI and PDI

UV-vis absorption spectra of the DMF solutions of core-unsubstituted NDI and PDI in the presence of 6 equiv. of K_2S were measured (see below). Featured absorptions of $NDI^{\bullet-}$ (λ_{max} = 473 nm) and $PDI^{\bullet-}$ (λ_{max} = 702 nm) in the spectra indicated the formation of reactive NDI and PDI radical anions during the annulations.[4]

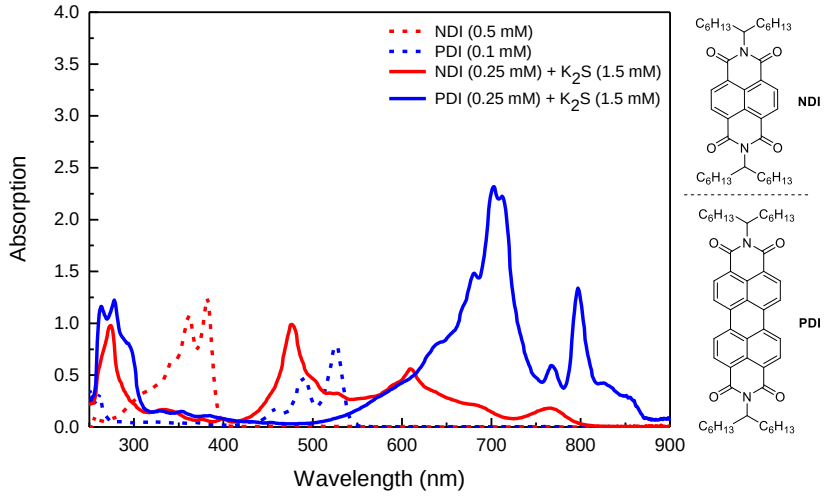
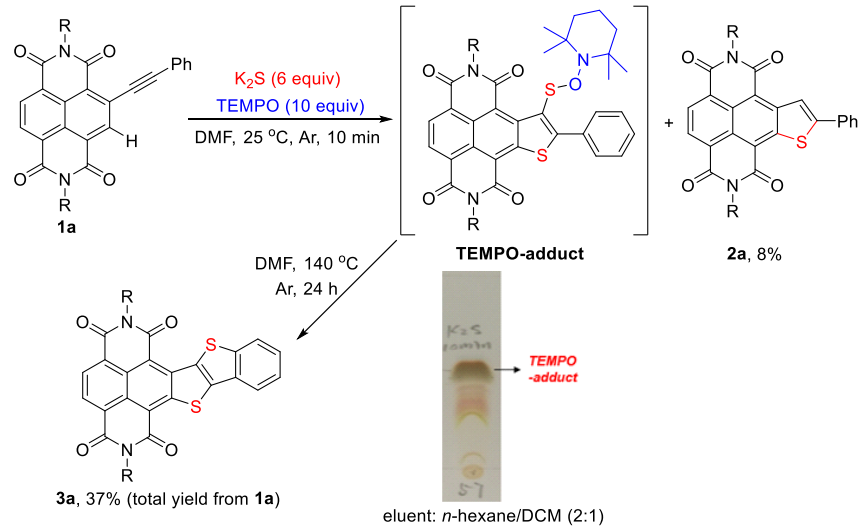


Figure S6 UV-vis absorption spectral changes of NDI and PDI in DMF up on the addition of 6 equiv K_2S

5.3 Radical-trapping experiments

Scheme S2 Radical-trapping experiments



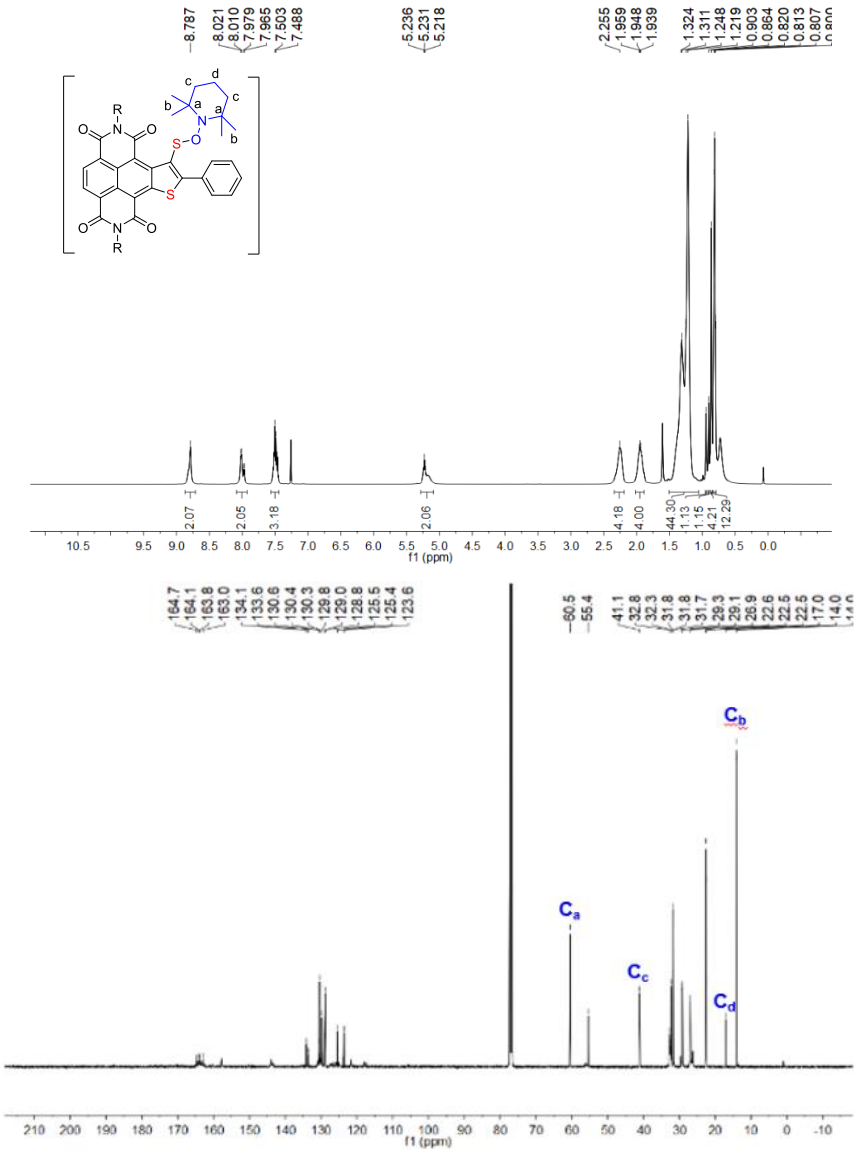
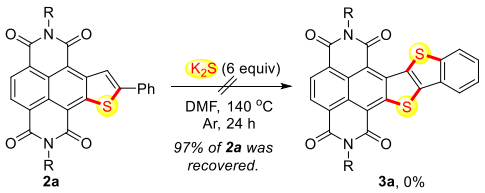
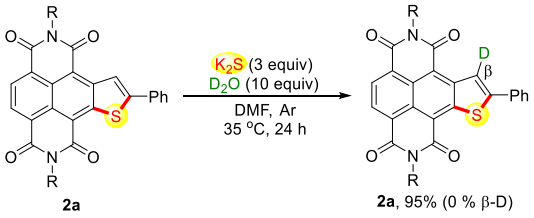


Figure S7 ^{1}H and ^{13}C NMR spectra for the TEMPO-adduct in $CDCl_3$

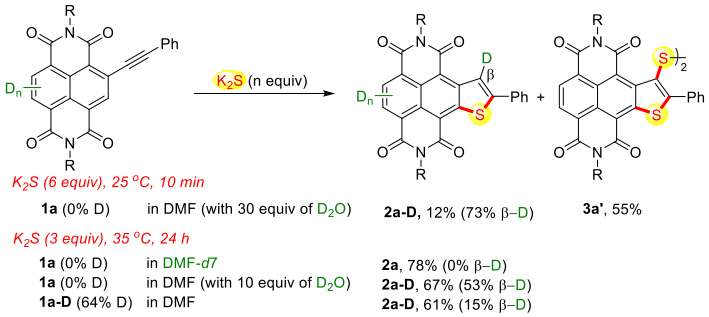
5.4 Several other experiments



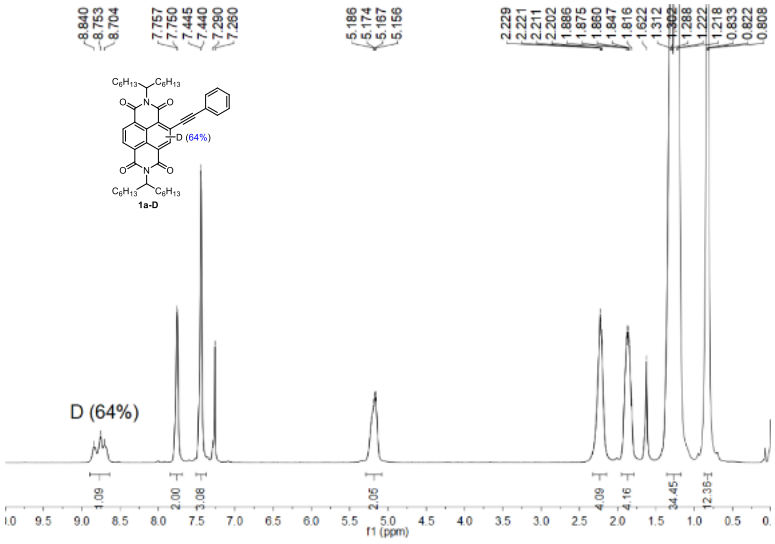
Direct treatment of **2a** with 6 equiv of K_2S in DMF at 140 °C for 24 h could not yield **3a**, indicating that **2a** is not the key intermediate for the double thienannulation process.



Treatment of **2a** with 3 equiv of K_2S in the presence of 10 equiv of D_2O in DMF at 35 °C for 24 h did not yield the β-deuterated **2a-D**.



Procedures for deuteration experiments: To a 25 mL tube, **1a** or **1a-D** (0.03 mmol), K_2S (3 or 6 equiv), D_2O (10 or 30 equiv) and DMF were added under Ar atmosphere. The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 25 °C for 10 min or at 35 °C for 24 h. After opening the cap, the reaction mixture was stirred in air for 1 h. The resulting solution was diluted with CH_2Cl_2 (20 mL), washed with water (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **2a** (*n*-hexane/CH_2Cl_2 = 4:1) and **3a'** (*n*-hexane/CH_2Cl_2 = 3:2).



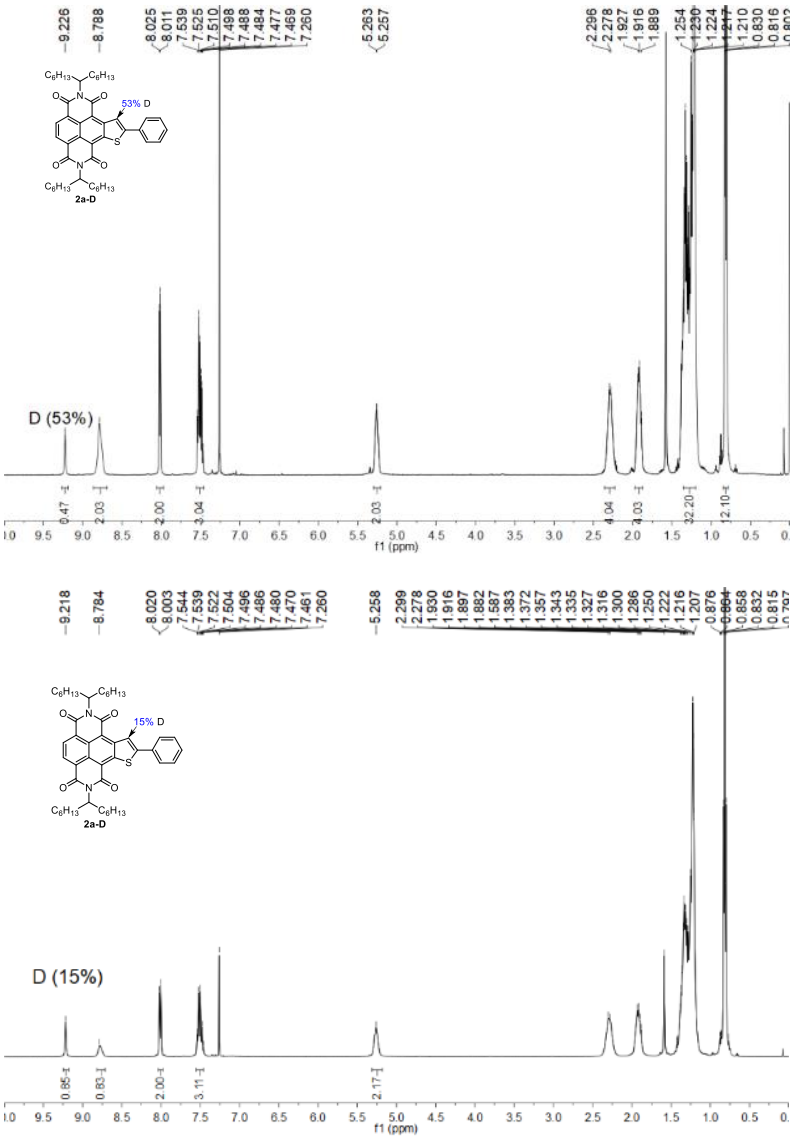
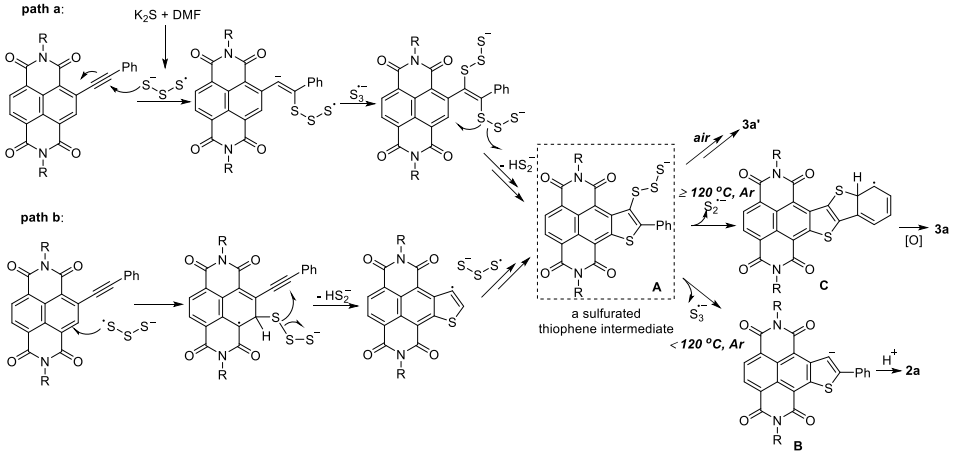


Figure S8 ^{1}H NMR spectra of **1a-D** and **2a-D** in $CDCl_3$

5.5 Proposed mechanism

Scheme S3 Plausible reaction pathways of stitching thienannulation



Based on the substrate scope and the results of the mechanistic studies, we proposed a possible

reaction mechanism for the stitching thienannulation of **1a**. Initially, K_2S was activated by DMF to yield $S_3^{\bullet-}$. Then one **1a** molecule interacted with two $S_3^{\bullet-}$ rapidly, producing a sulfurated thiophene intermediate **A**. In air, intermediate **A** can be oxidized to yield **3a'**. In Ar, intermediate **A** can either slowly decompose below 120 °C to give a thiophene anion intermediate **B** or undergo radical cyclization at above 120 °C to furnish intermediate **C**. Protonation of **B** leads to the formation of **2a**. Oxidative aromatization of **C** affords the final stitching thienannulation product **3a**.

6. X-ray Crystal Structures of 3l and 3m

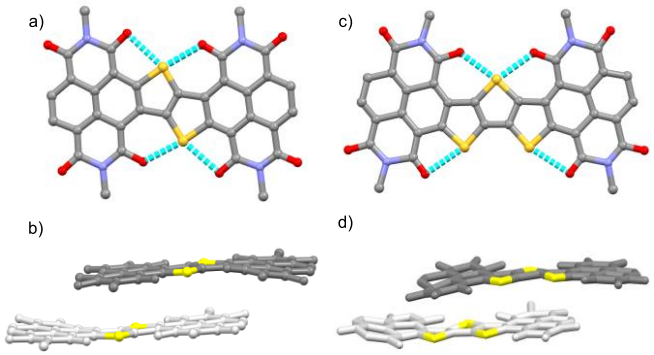
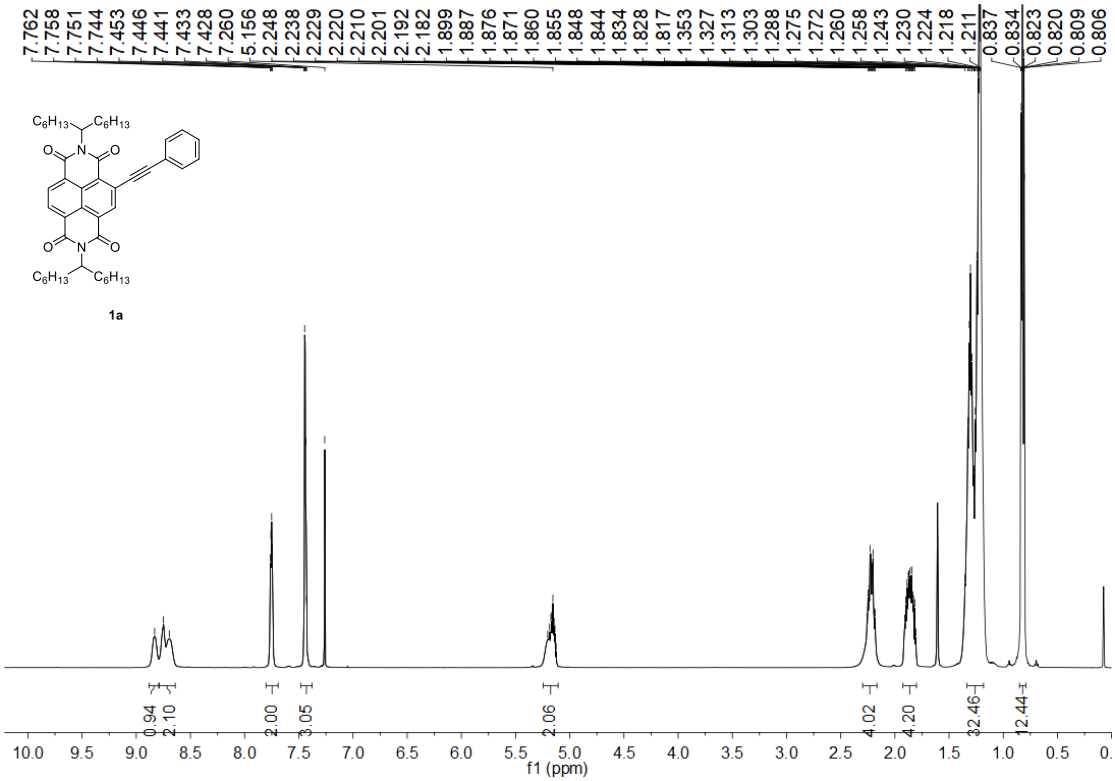
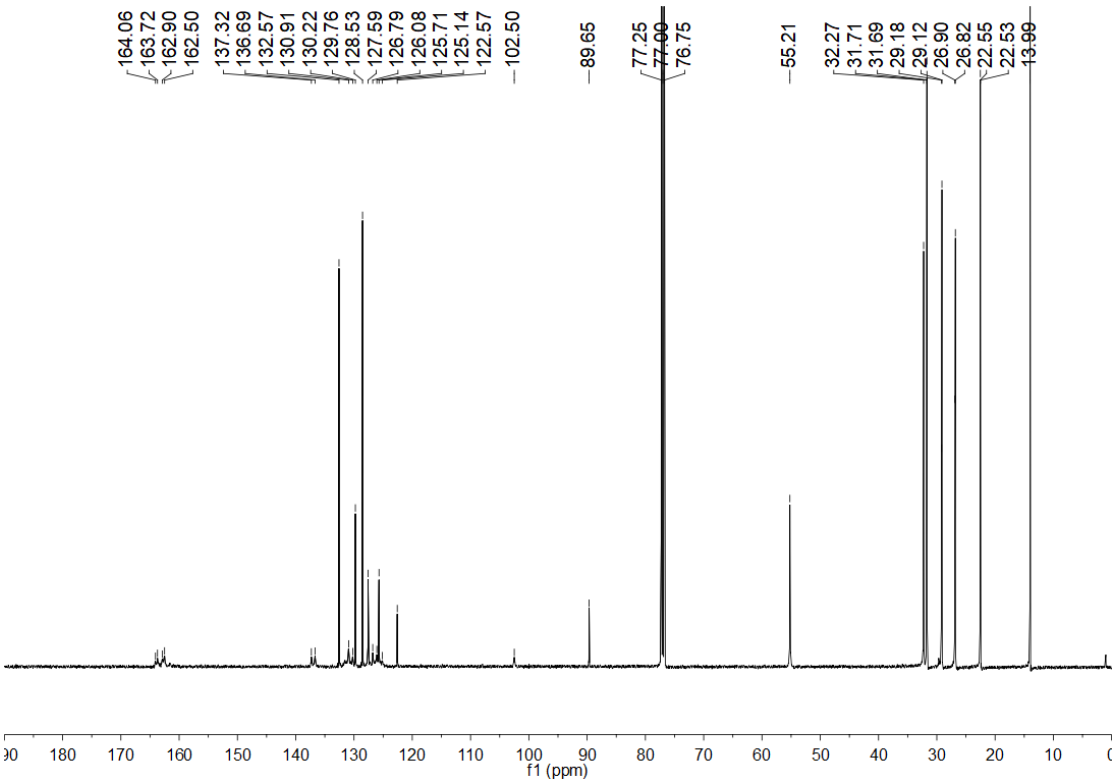


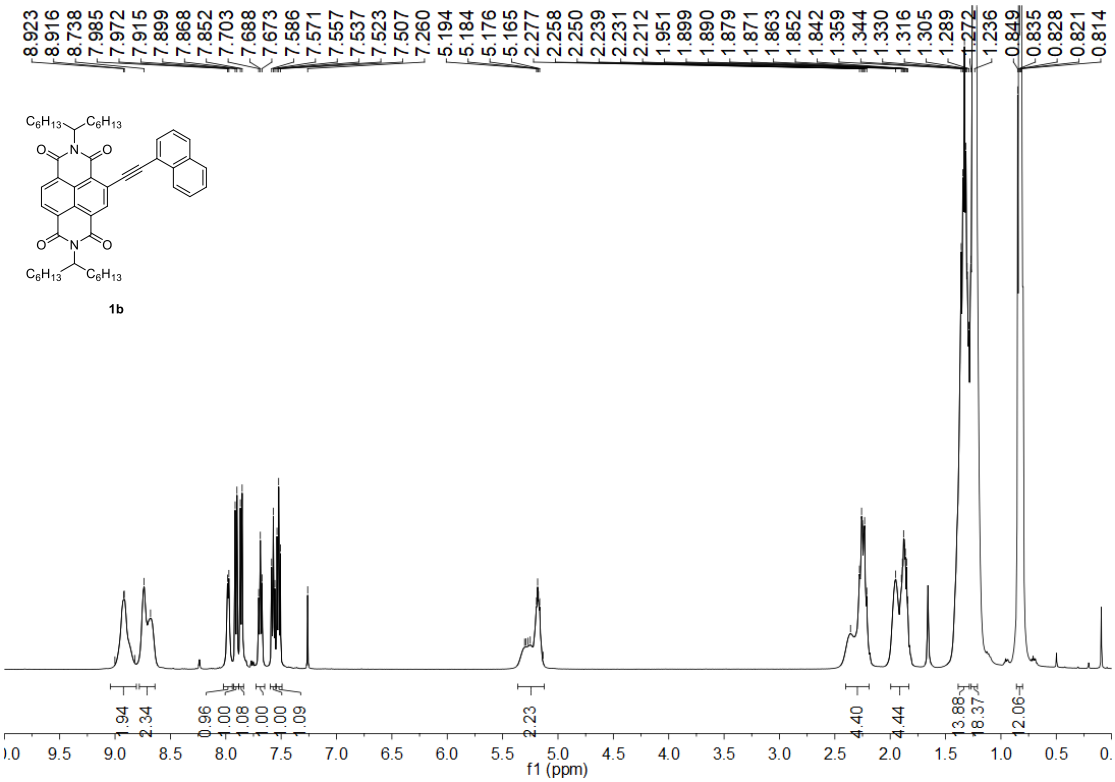
Figure S9. a,c) X-ray crystal structures of **3l** and **3m**. b,d) side views of the slip-stacked dimers (hexylheptyl groups and minor parts of disordered atoms are omitted for clarity).

Preliminary results of single-crystal X-ray diffraction analysis confirmed the solid-state structures of **3l** (CCDC 1960794) and **3m** (CCDC 1960809). Intramolecular sulfur-oxygen interactions [5] led to **3l** and **3m** both having highly planar molecular backbones, which is beneficial for close π-stackings (~3.30 Å) between two identical molecules. In addition, D-A interactions between π-rich thiophene rings and π-poor NDI unit as well as the steric hindrance between swallow-tailed hexylheptyl substituents at imide positions promoted the formation of slip-stacked dimers, which further crystalized in a "face-to-edge" manner to form a four-membered ring.

7. ^{1}H and ^{13}C NMR Spectra for New Compounds



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7.537
7.523
7.507
7.260
5.194
5.184
5.176
5.165
2.277
2.258
2.250
2.239
2.231
2.212
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1.899
1.890
1.879
1.871
1.863
1.852
1.842
1.359
1.344
1.330
1.316
1.305
1.289
1.272
1.236
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0.835
0.828
0.821
0.814
1.94
2.34
0.96
1.00
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1.00
1.00
1.09
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12.06
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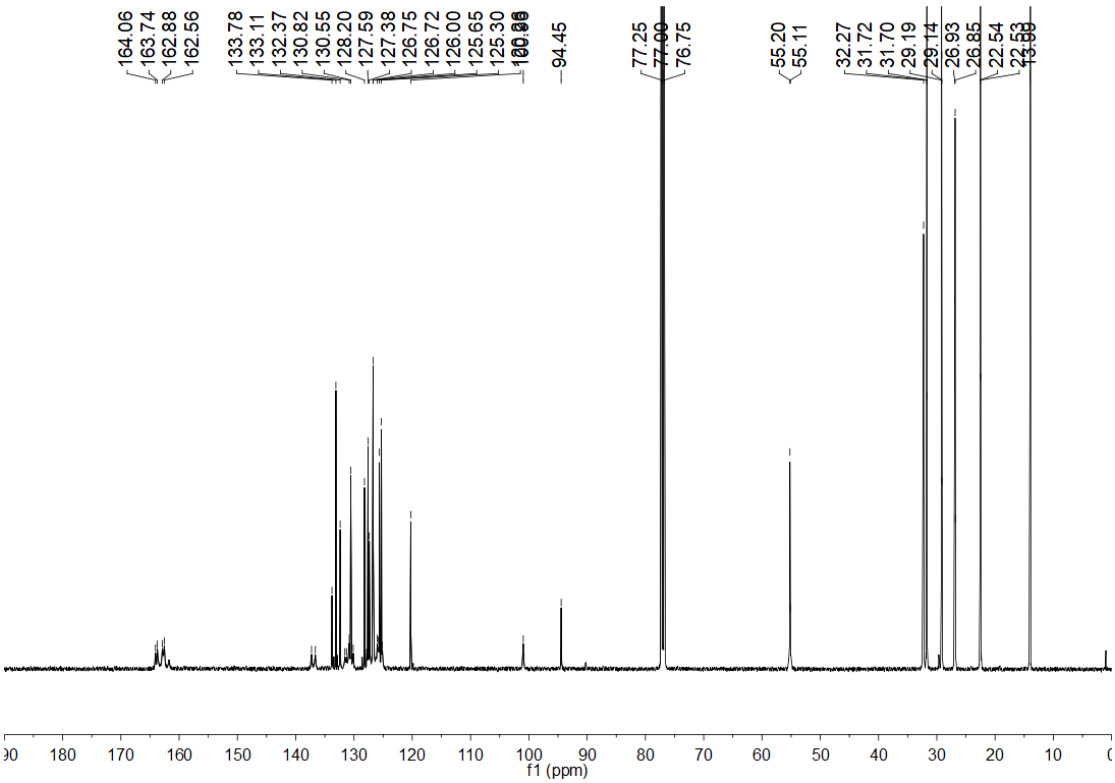
1b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77.00
76.75
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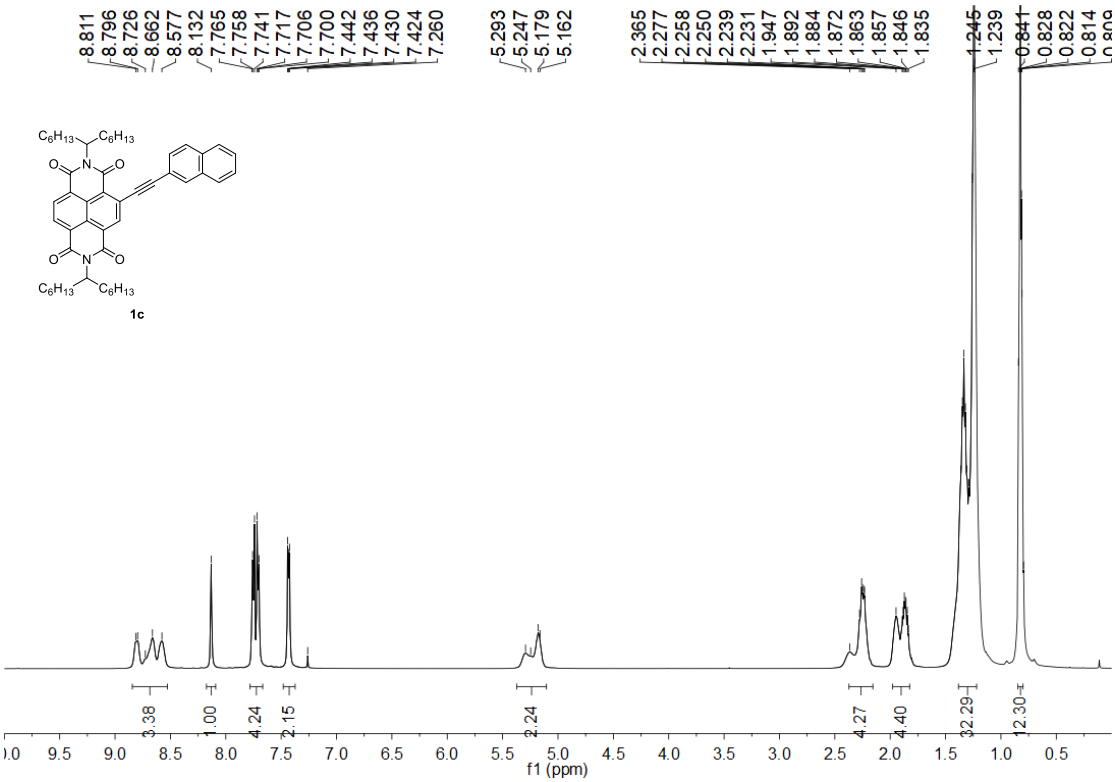
f1 (ppm)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1.872
1.863
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1.835
1.245
1.239
0.841
0.828
0.822
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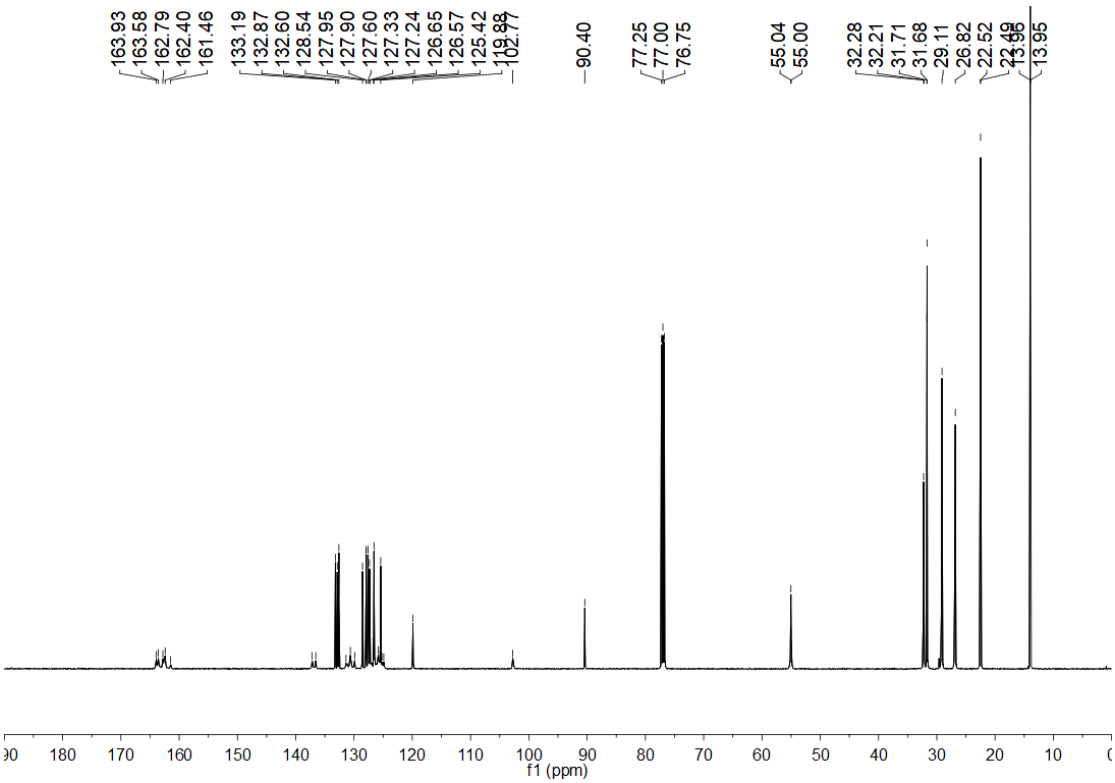
f1 (ppm)

1c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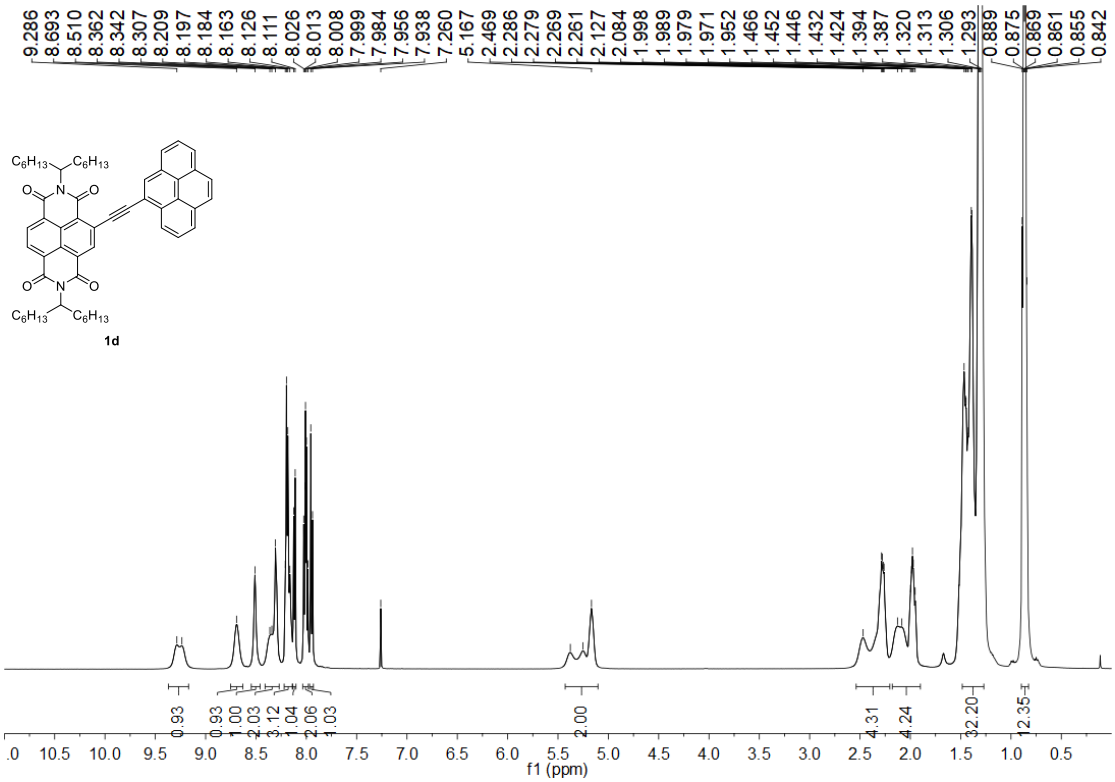
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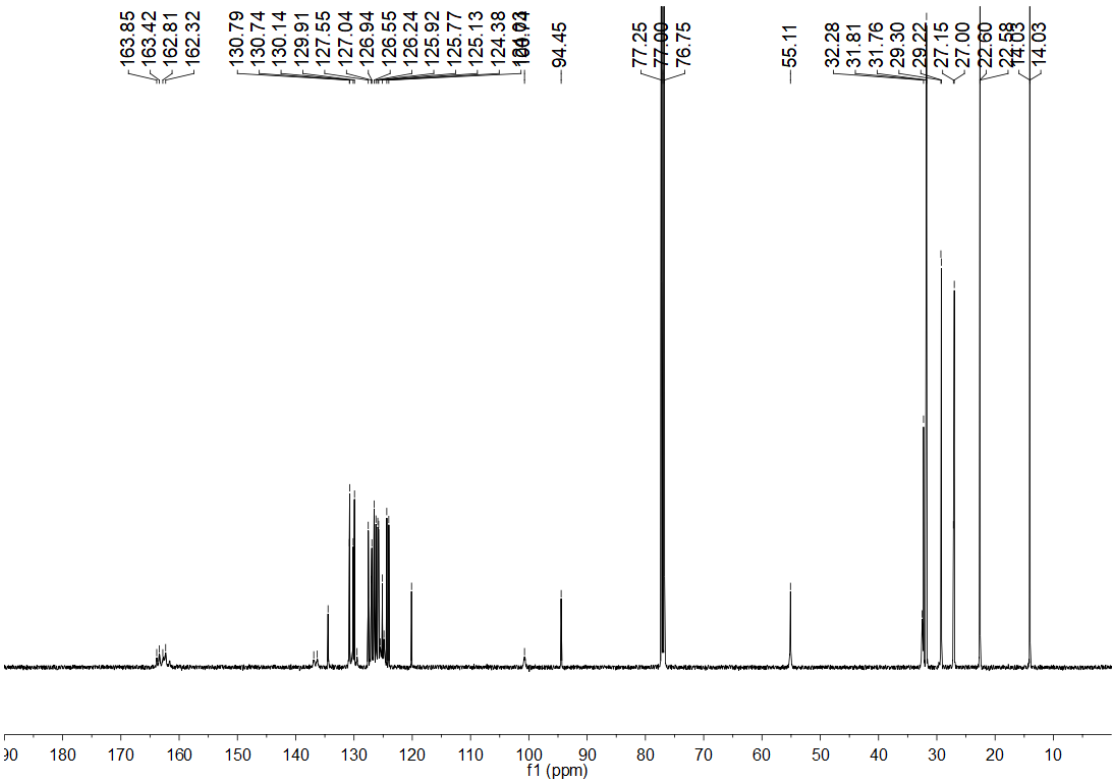
1d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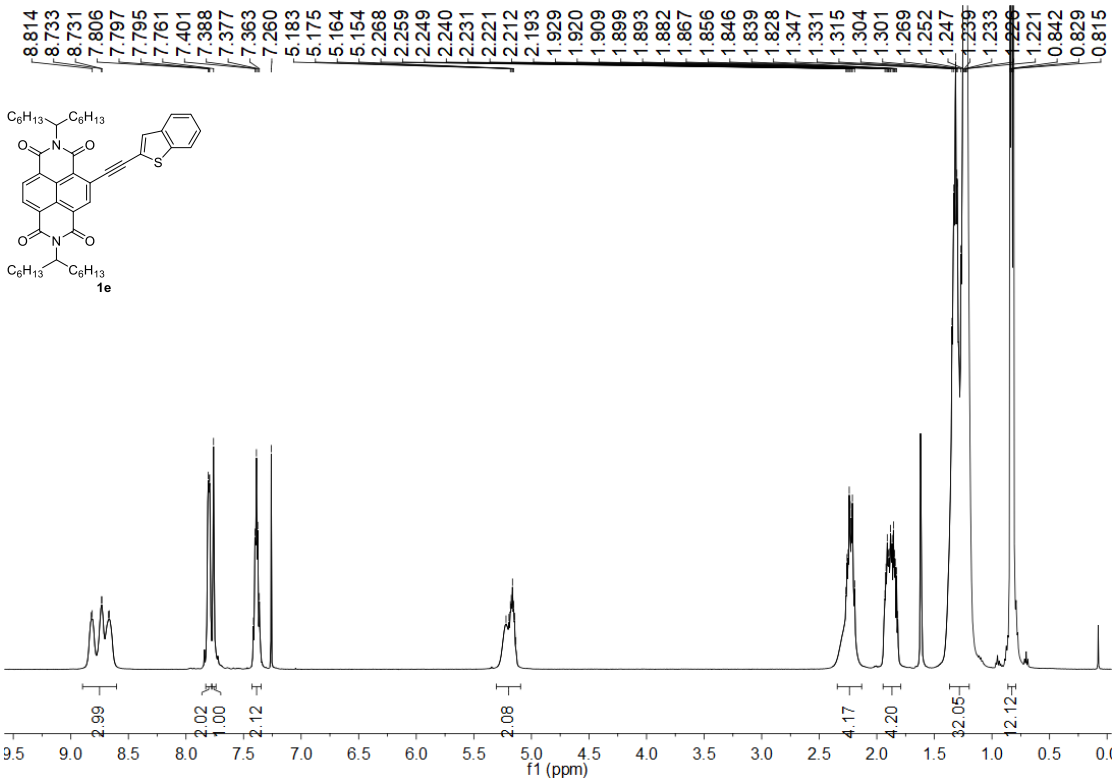
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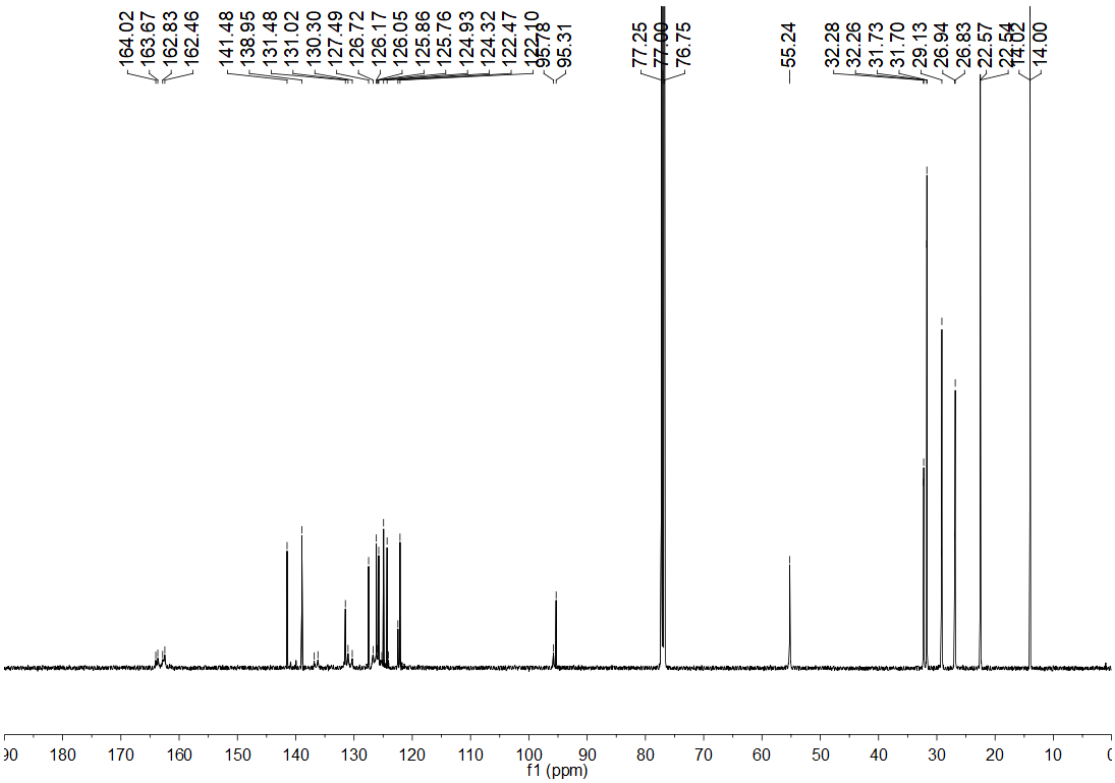
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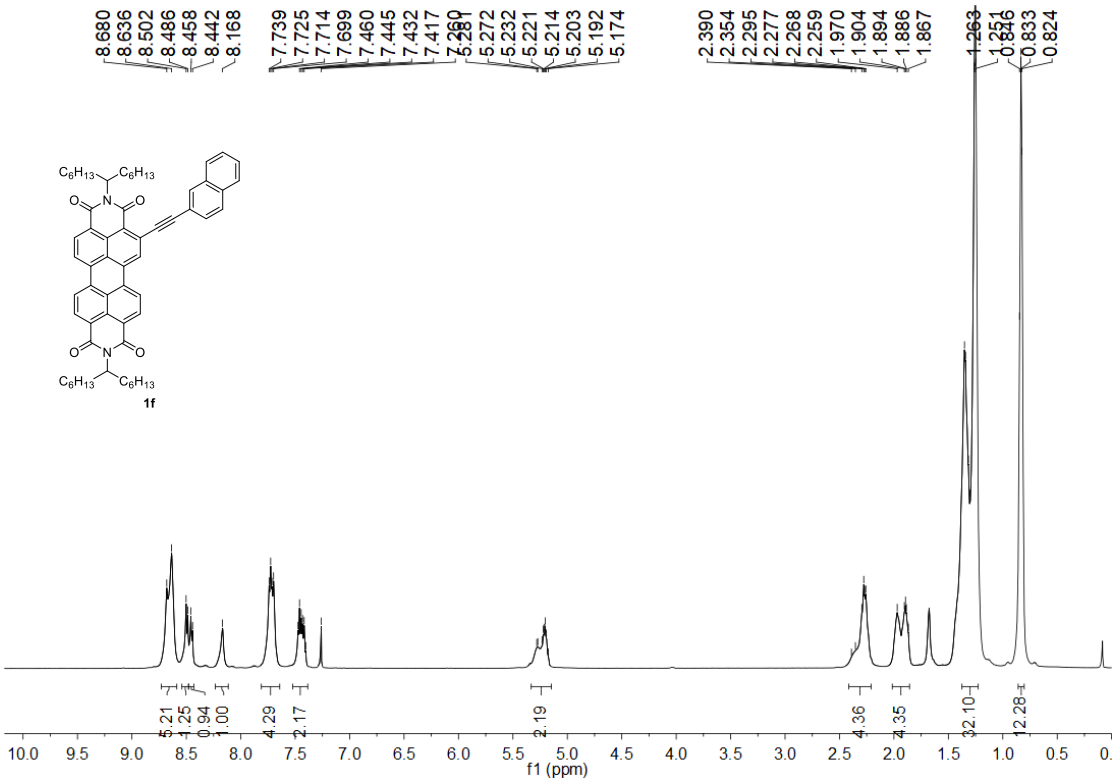
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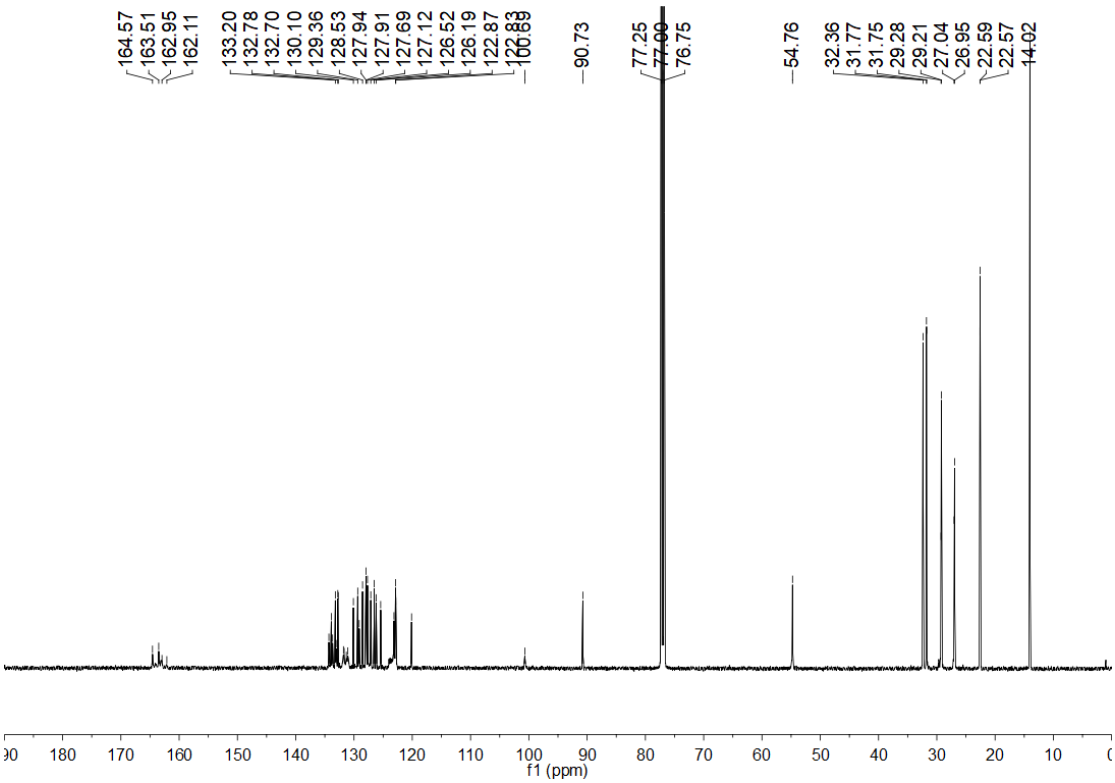
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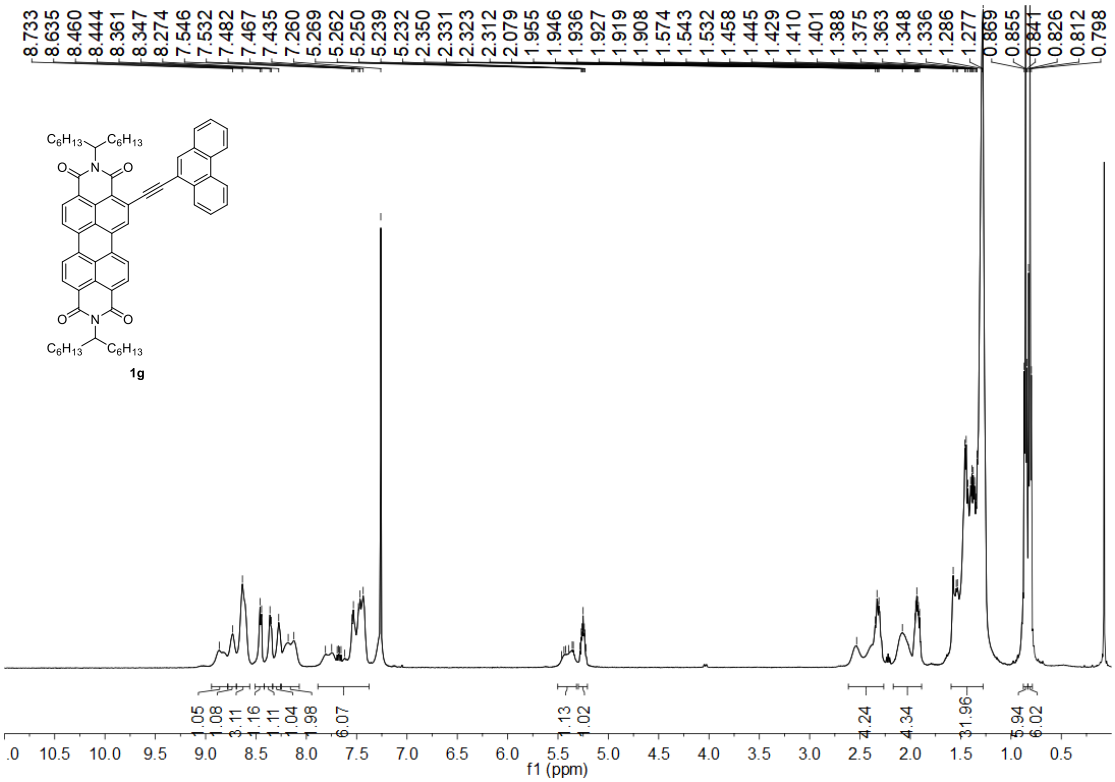
f1 (ppm)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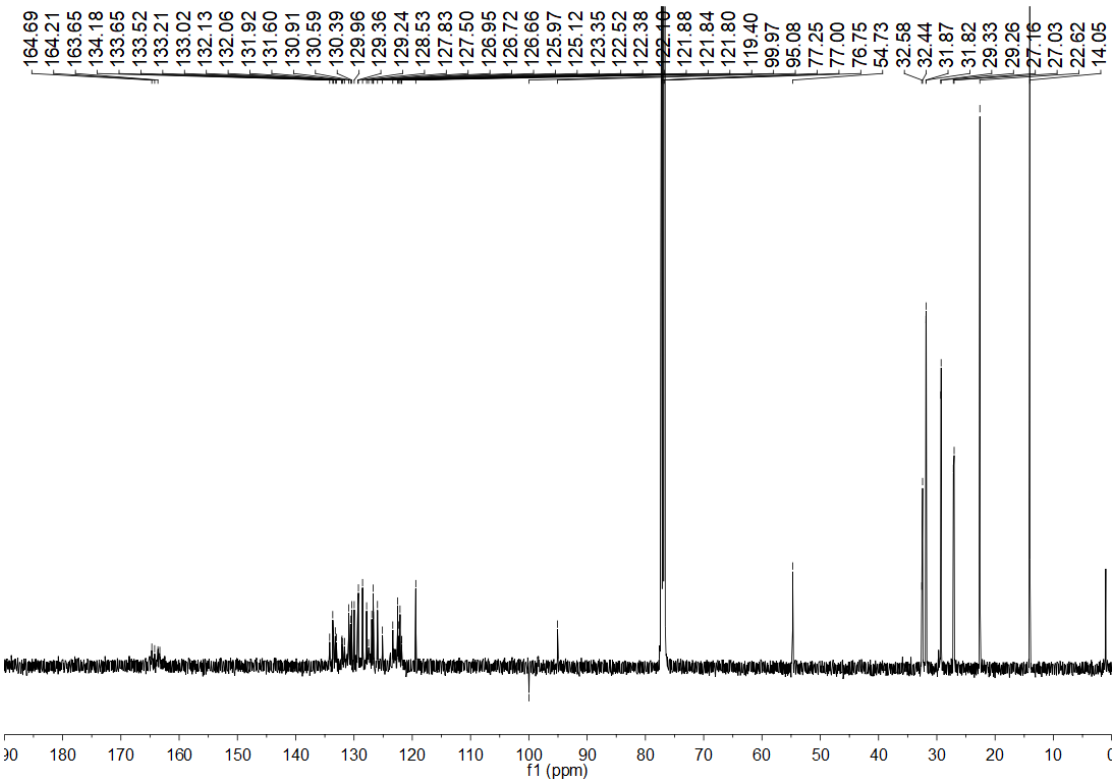
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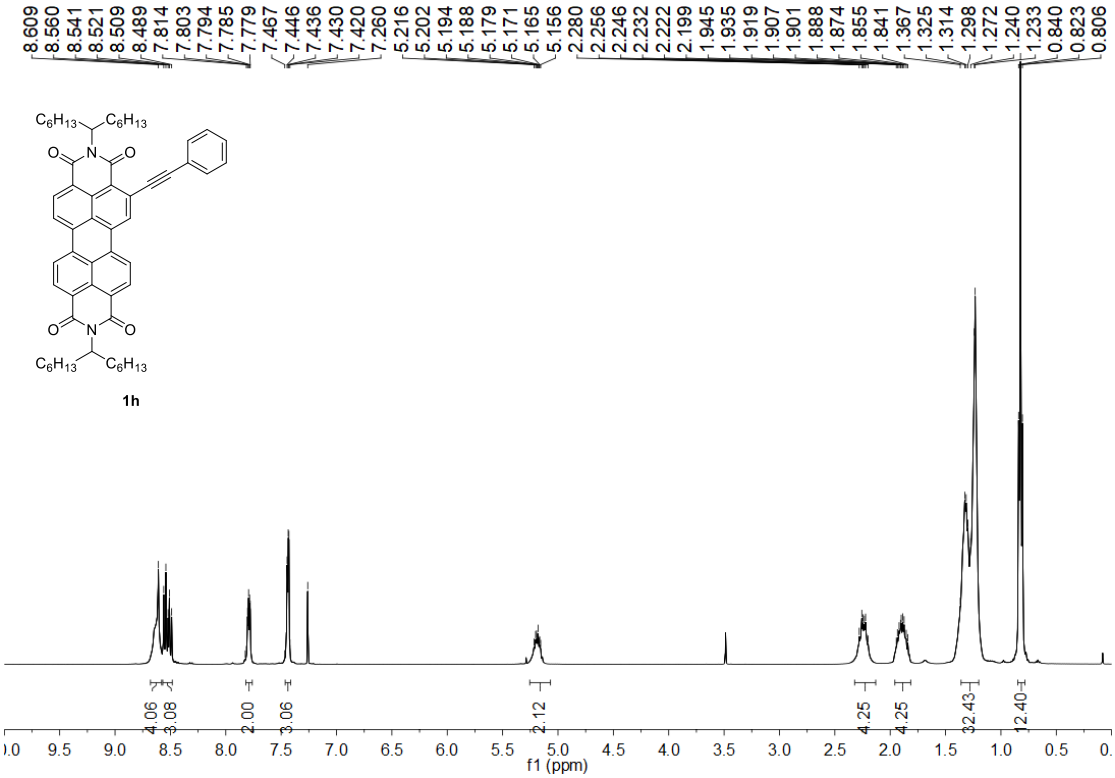
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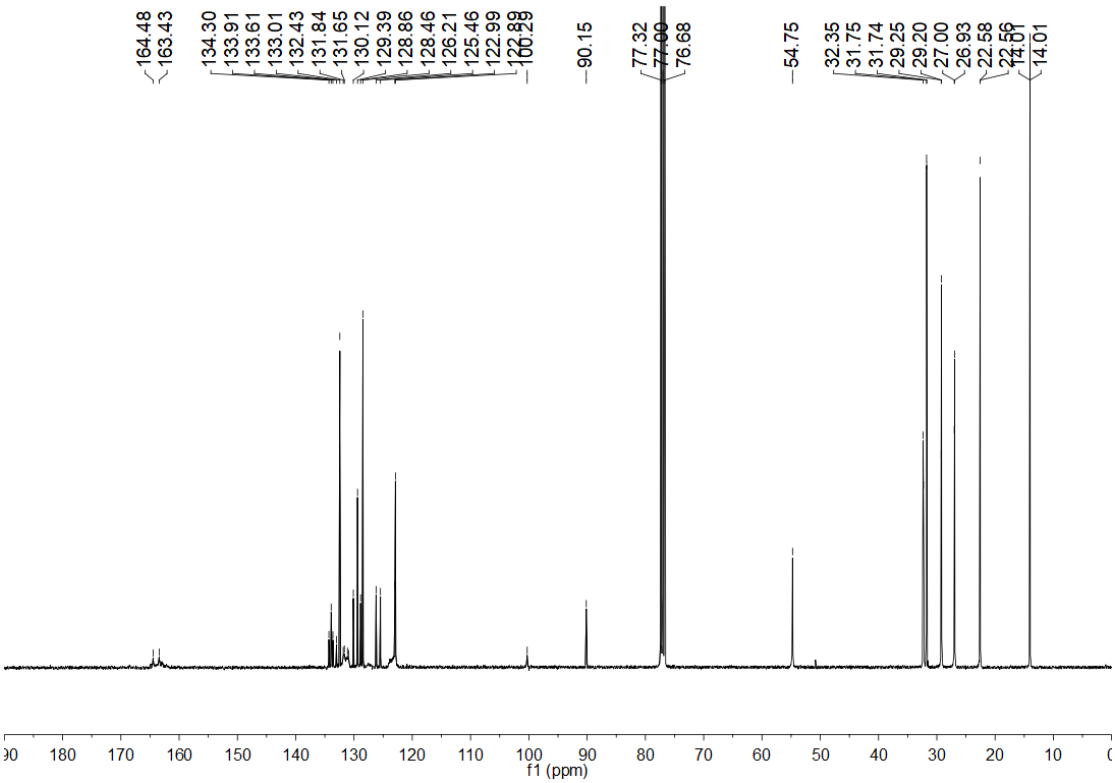
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f1 (ppm)


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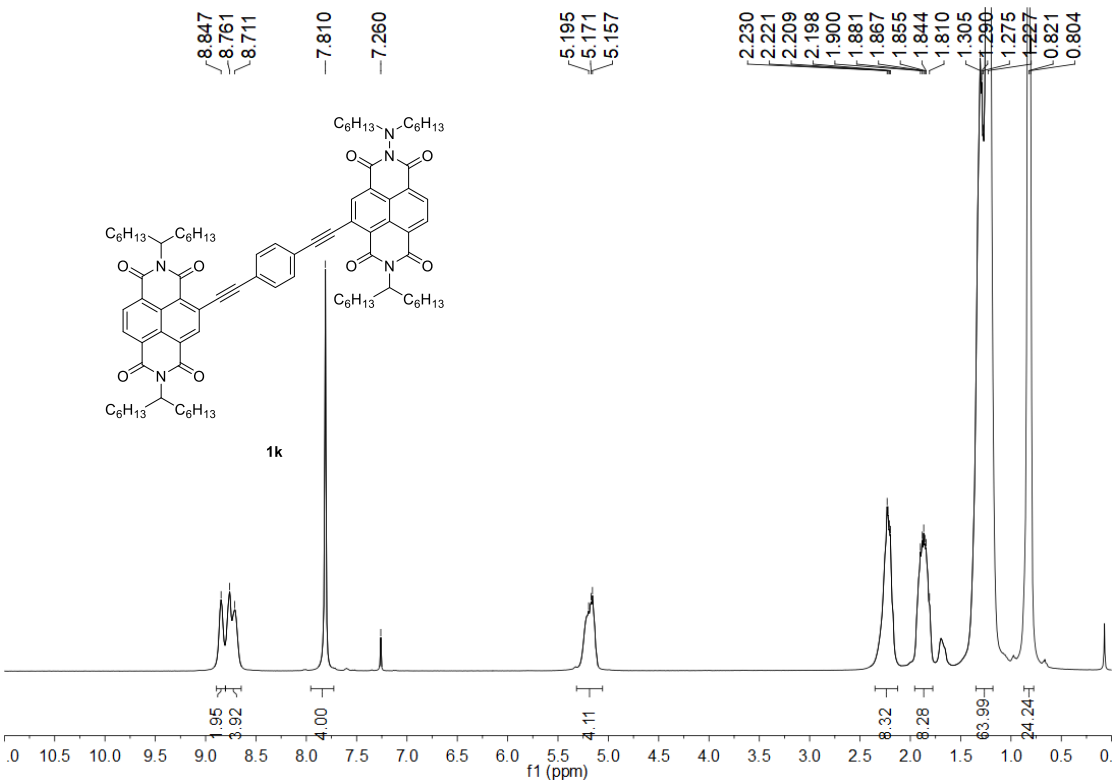
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8.28
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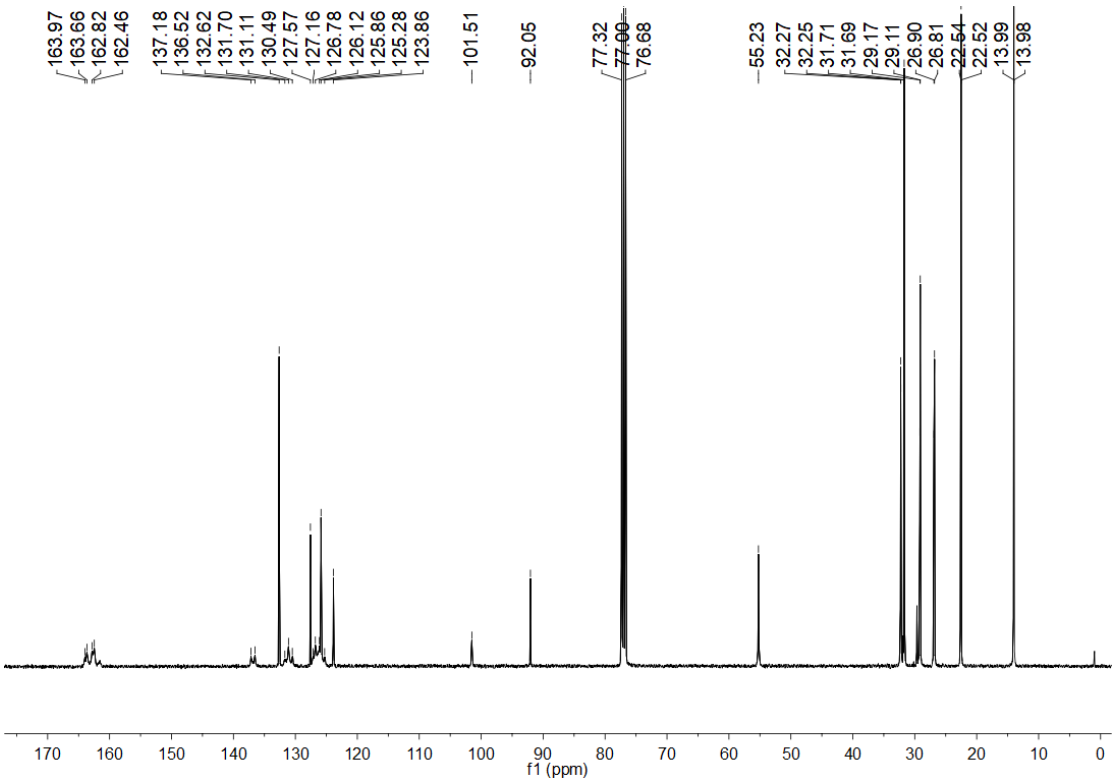
24.24
f1 (ppm)

1k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130.49
127.57
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126.78
126.12
125.86
125.28
123.86
101.51
92.05
77.32
77.00
76.68
55.23
32.27
32.25
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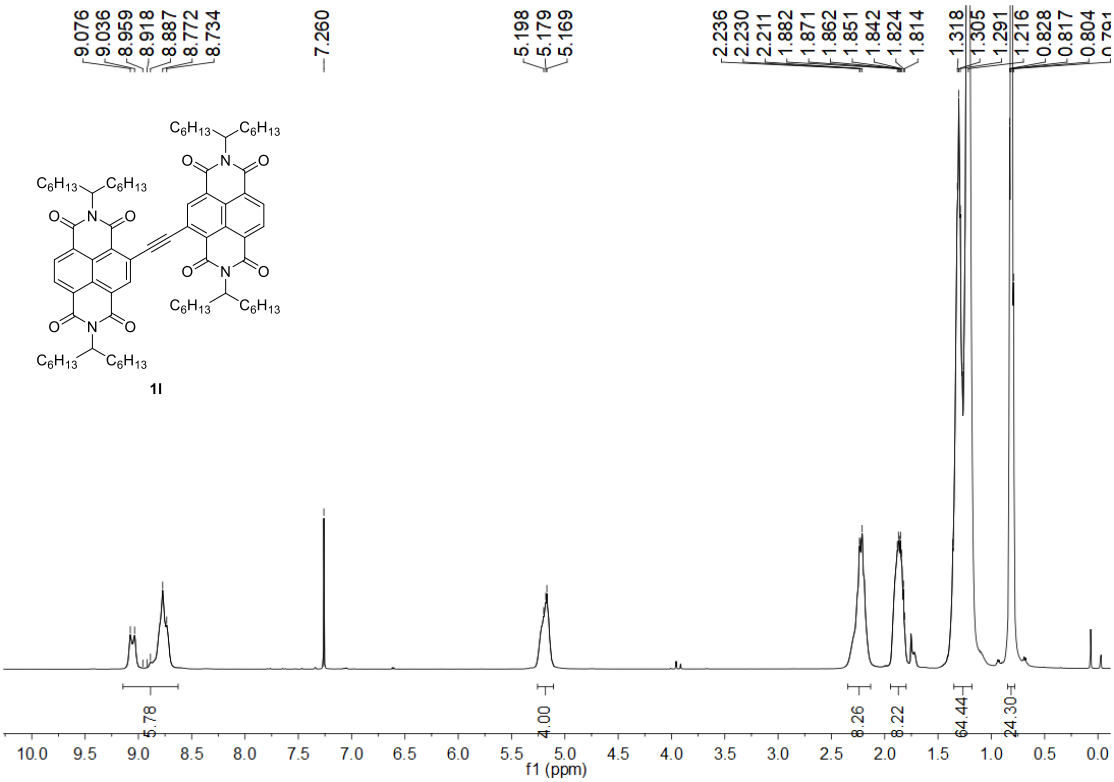
29.11
26.90
26.81
22.64
22.52
13.99
13.98
f1 (ppm)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7.260
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5.179
5.169
2.236
2.230
2.211
1.882
1.871
1.862
1.851
1.842
1.824
1.814
1.318
1.305
1.291
1.216
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0.804
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4.00
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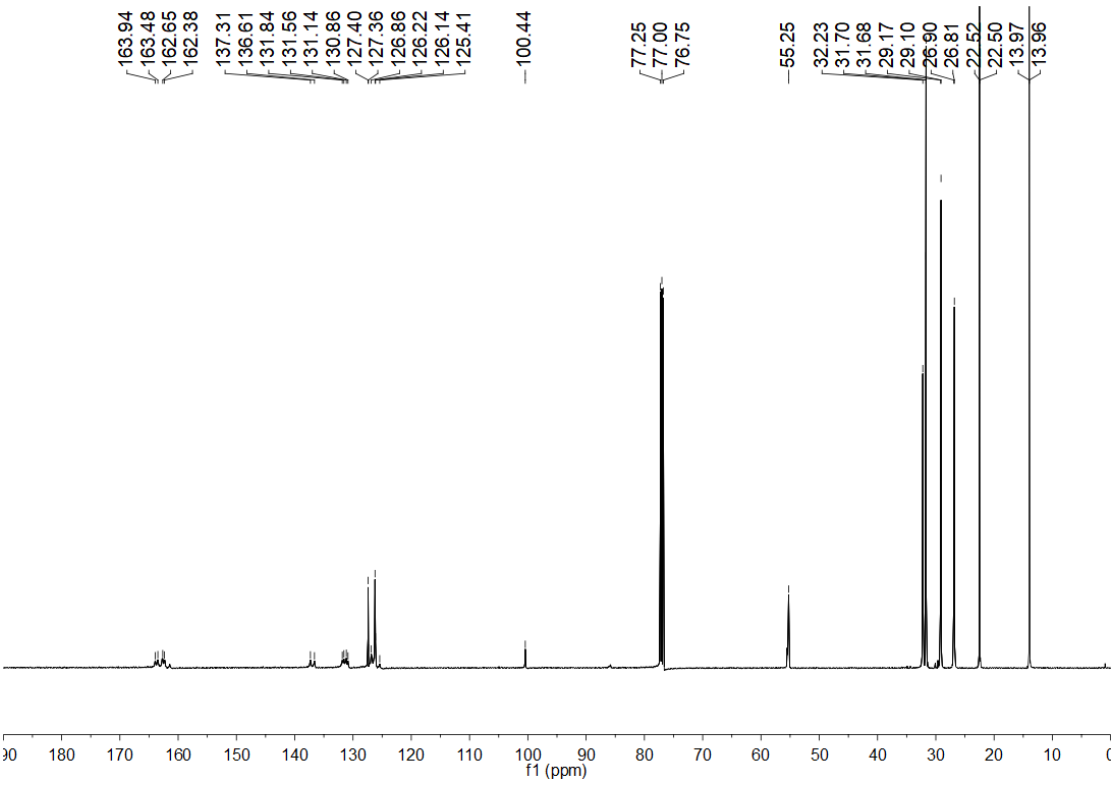
8.22
64.44
24.30
f1 (ppm)

1l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131.14
130.86
127.40
127.36
126.86
126.22
126.14
125.41
100.44
77.25
77.00
76.75
55.25
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26.90
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22.50
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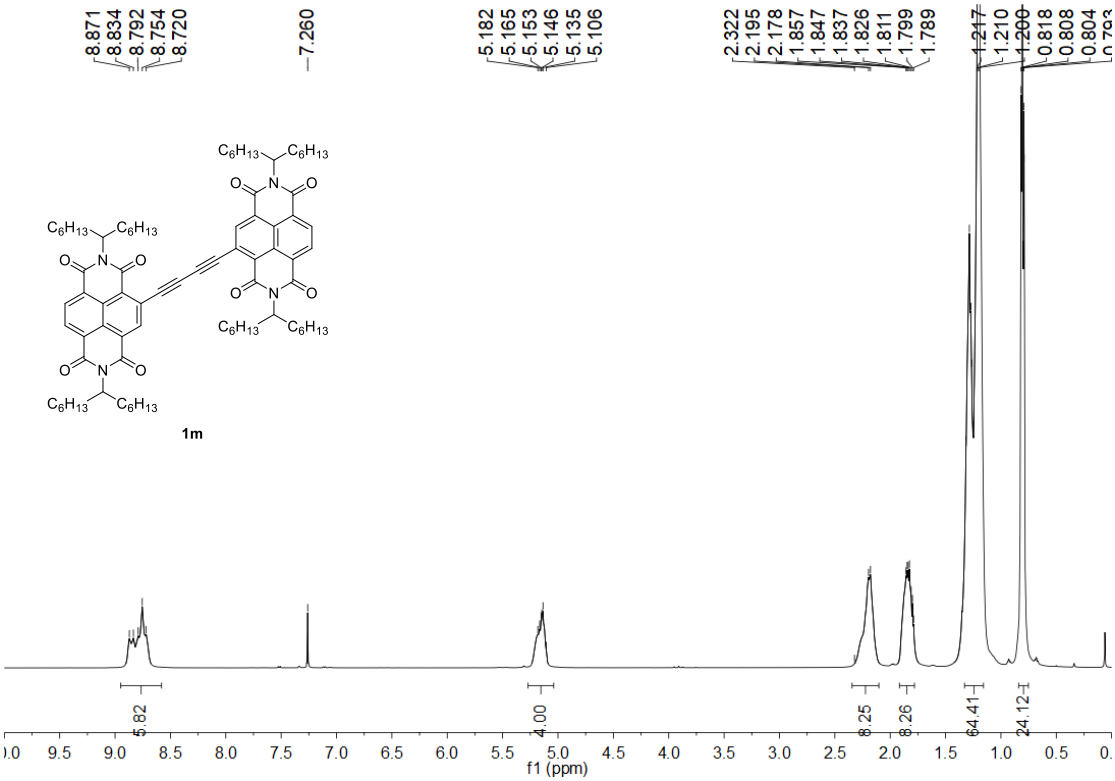
13.96
f1 (ppm)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5.165
5.153
5.146
5.135
5.106
2.322
2.195
2.178
1.857
1.847
1.837
1.826
1.811
1.799
1.789
1.217
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5.82
4.00
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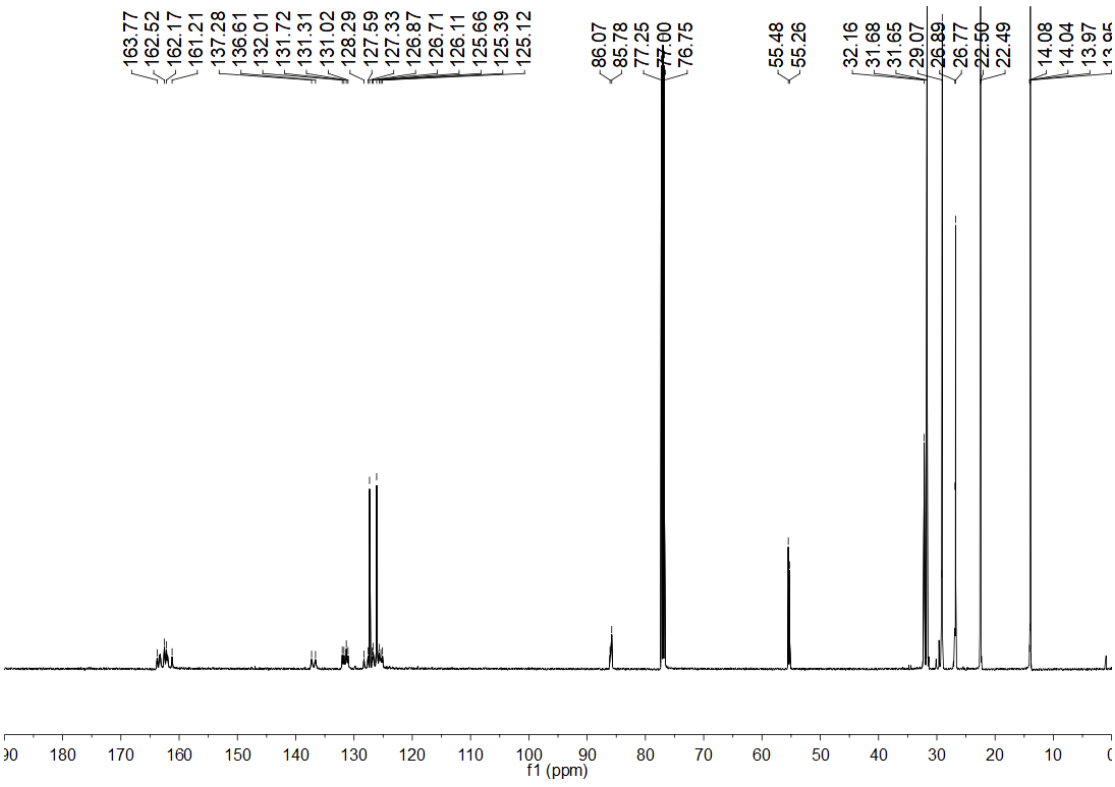
64.41
24.12
f1 (ppm)

1m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126.71
126.11
125.66
125.39
125.12
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85.78
77.25
77.00
76.75
55.48
55.26
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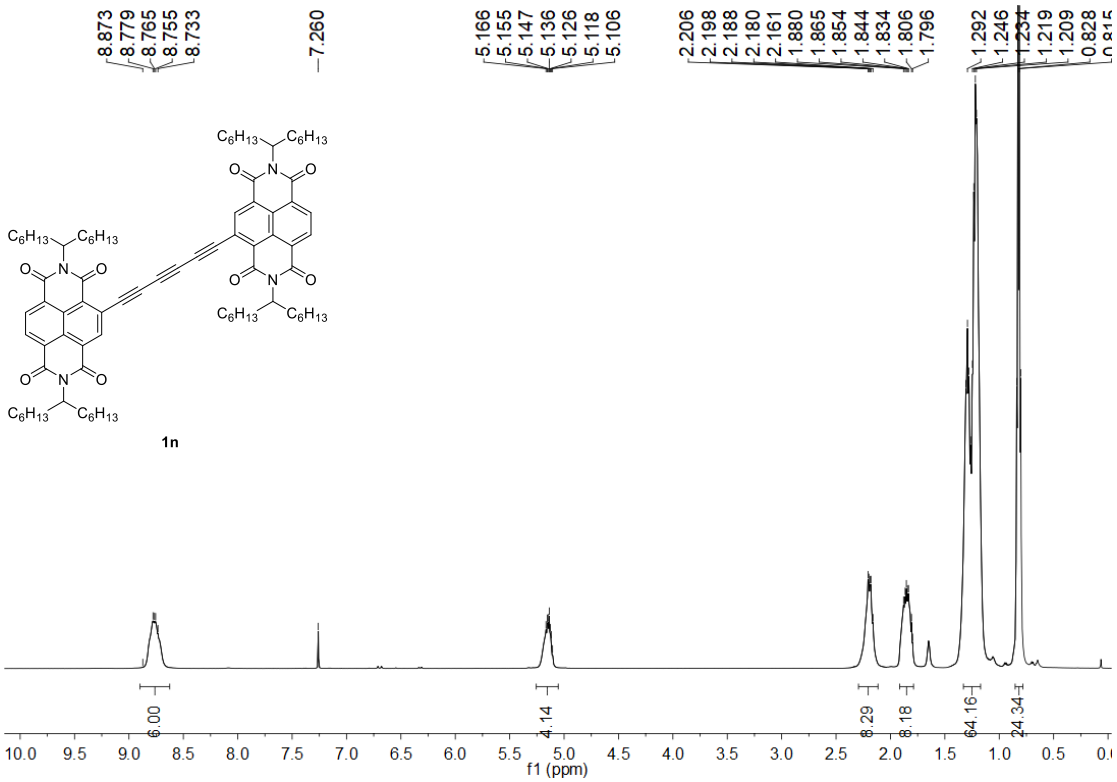
13.97
f1 (ppm)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5.147
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5.126
5.118
5.106
2.206
2.198
2.188
2.180
2.161
1.880
1.865
1.854
1.844
1.834
1.806
1.796
1.292
1.246
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4.14
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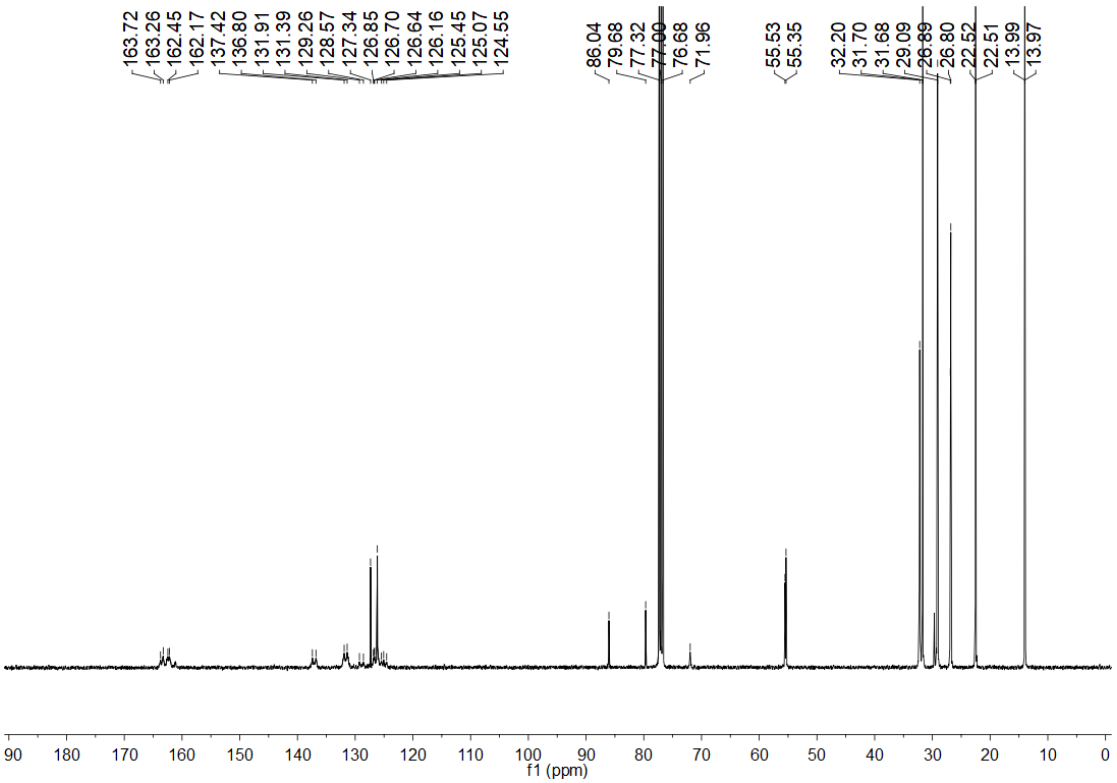
8.18
64.16
24.34
f1 (ppm)

1n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131.91
131.39
129.26
128.57
127.34
126.85
126.70
126.64
126.16
125.45
125.07
124.55
86.04
79.68
77.32
77.00
76.68
71.96
55.53
55.35
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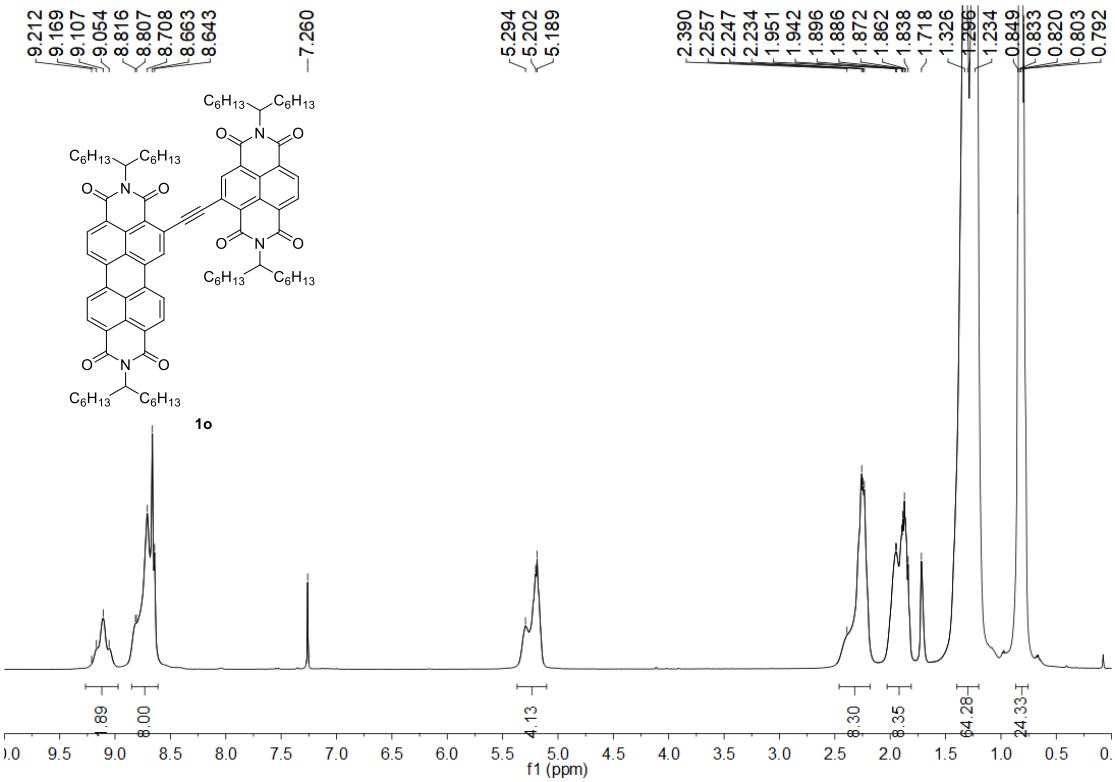
31.68
29.09
26.89
26.80
22.52
22.51
13.99
13.97
f1 (ppm)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9.169
9.107
9.054
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8.807
8.708
8.663
8.643
7.260
5.294
5.202
5.189
2.390
2.257
2.247
2.234
1.951
1.942
1.896
1.886
1.872
1.862
1.838
1.718
1.326
1.296
1.234
0.849
0.833
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0.803
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1.89
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4.13
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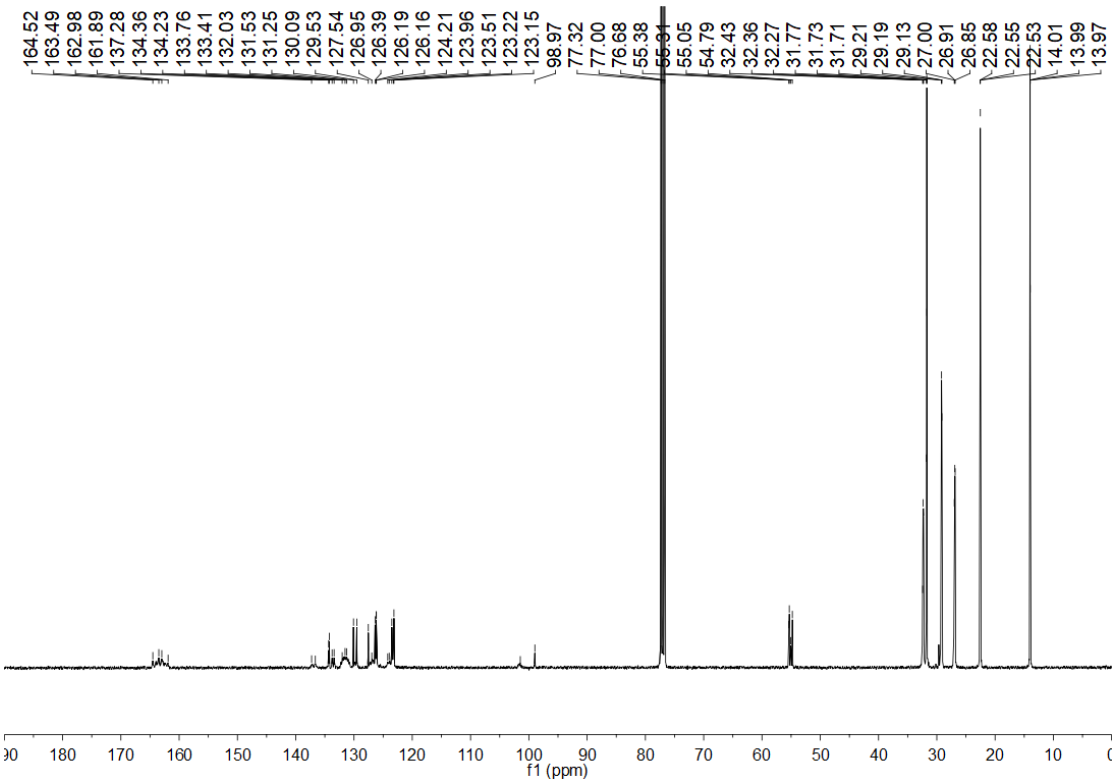
8.35
64.28
24.33
f1 (ppm)

1o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129.53
127.54
126.95
126.39
126.19
126.16
124.21
123.96
123.51
123.22
123.15
98.97
77.32
77.00
76.68
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55.31
55.05
54.79
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32.36
32.27
31.77
31.73
31.71
29.21
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29.13
27.00
26.91
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22.58
22.55
22.53
14.01
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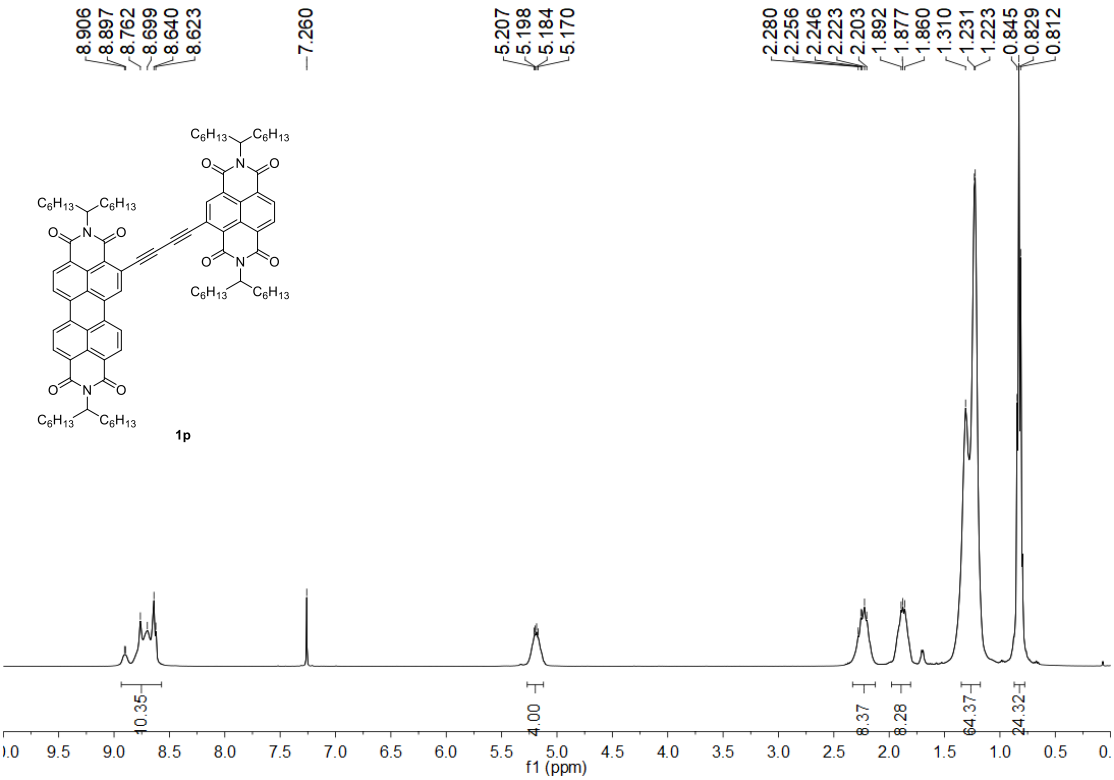
13.97
f1 (ppm)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5.184
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2.280
2.256
2.246
2.223
2.203
1.892
1.877
1.860
1.310
1.231
1.223
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0.812
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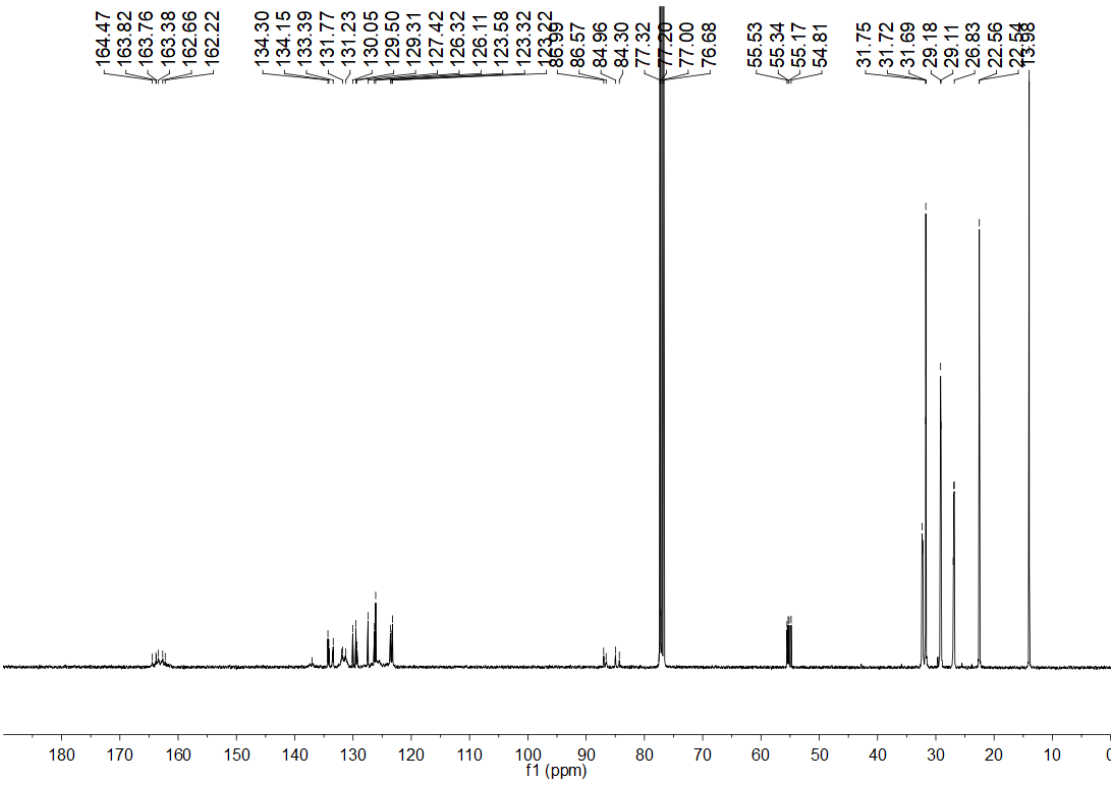
10.35
4.00
8.37
8.28
64.37
24.32
f1 (ppm)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131.77
131.23
130.05
129.50
129.31
127.42
126.32
126.11
123.58
123.32
123.22
86.99
86.57
84.96
84.30
77.32
77.20
77.00
76.68
55.53
55.34
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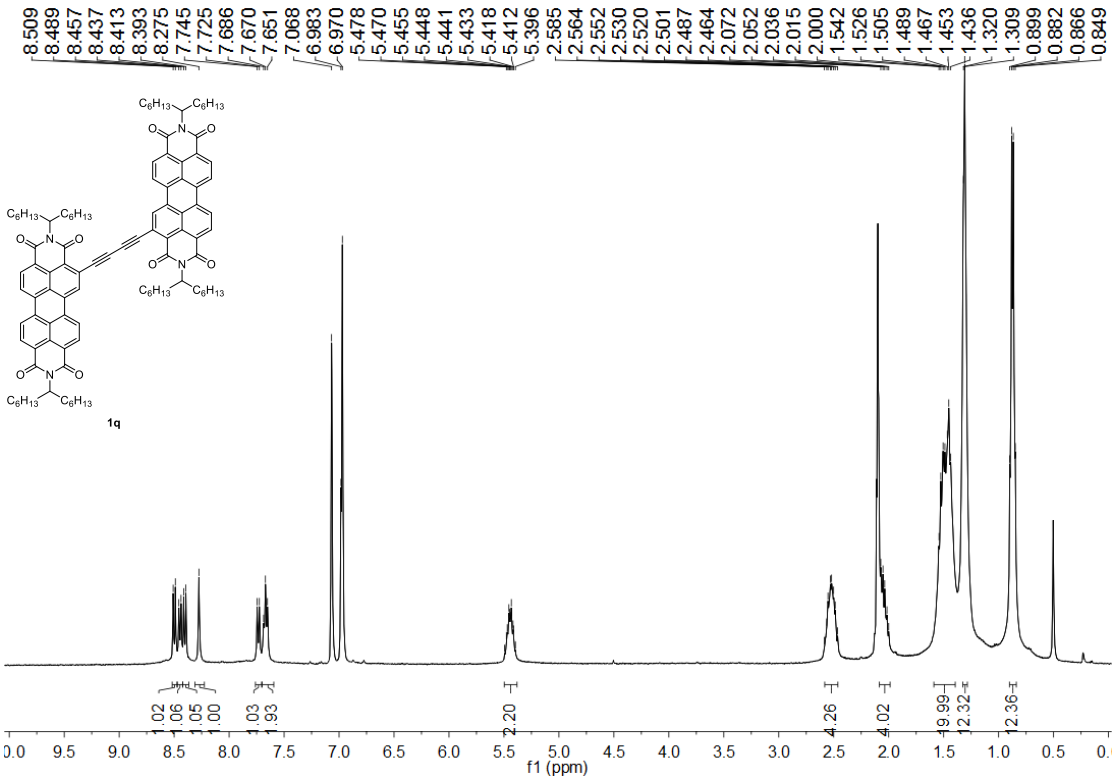
29.18
29.11
26.83
22.56
22.54
13.98
f1 (ppm)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7.068
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6.970
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5.470
5.455
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5.441
5.433
5.418
5.412
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2.564
2.552
2.530
2.520
2.501
2.487
2.464
2.072
2.052
2.036
2.015
2.000
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1.526
1.505
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1.467
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1.436
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1.309
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0.866
0.849
1.02
1.06
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1.93
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4.02
9.99
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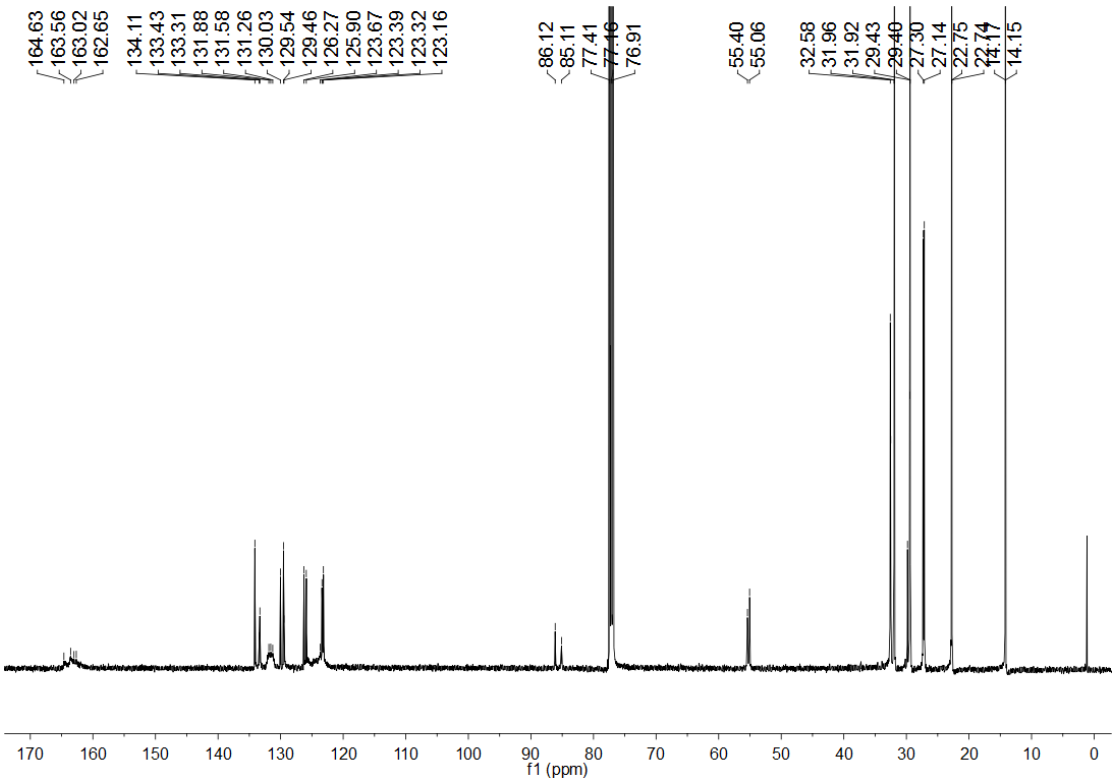
12.36
f1 (ppm)
1q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131.26
130.03
129.54
129.46
126.27
125.90
123.67
123.39
123.32
123.16
86.12
85.11
77.41
77.16
76.91
55.40
55.06
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22.74
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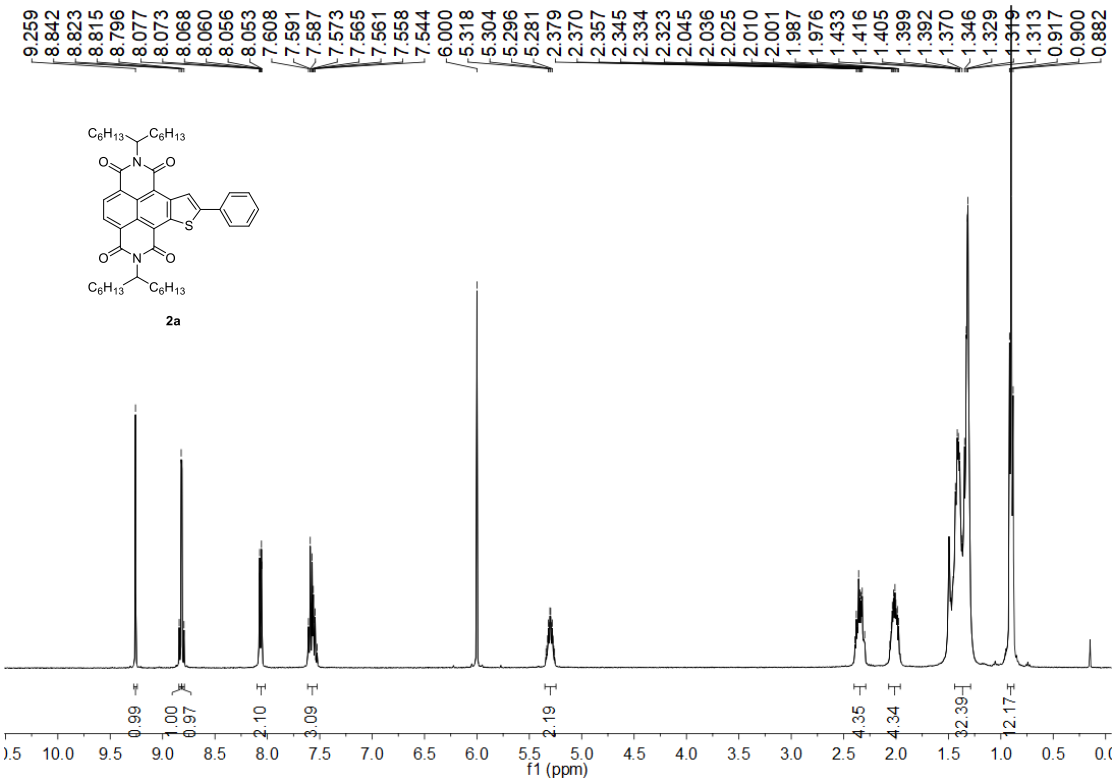
14.15
f1 (ppm)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7.591
7.587
7.573
7.565
7.561
7.558
7.544
6.000
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5.281
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2.370
2.357
2.345
2.334
2.323
2.045
2.036
2.025
2.010
2.001
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1.392
1.370
1.346
1.329
1.319
1.313
0.917
0.900
0.882
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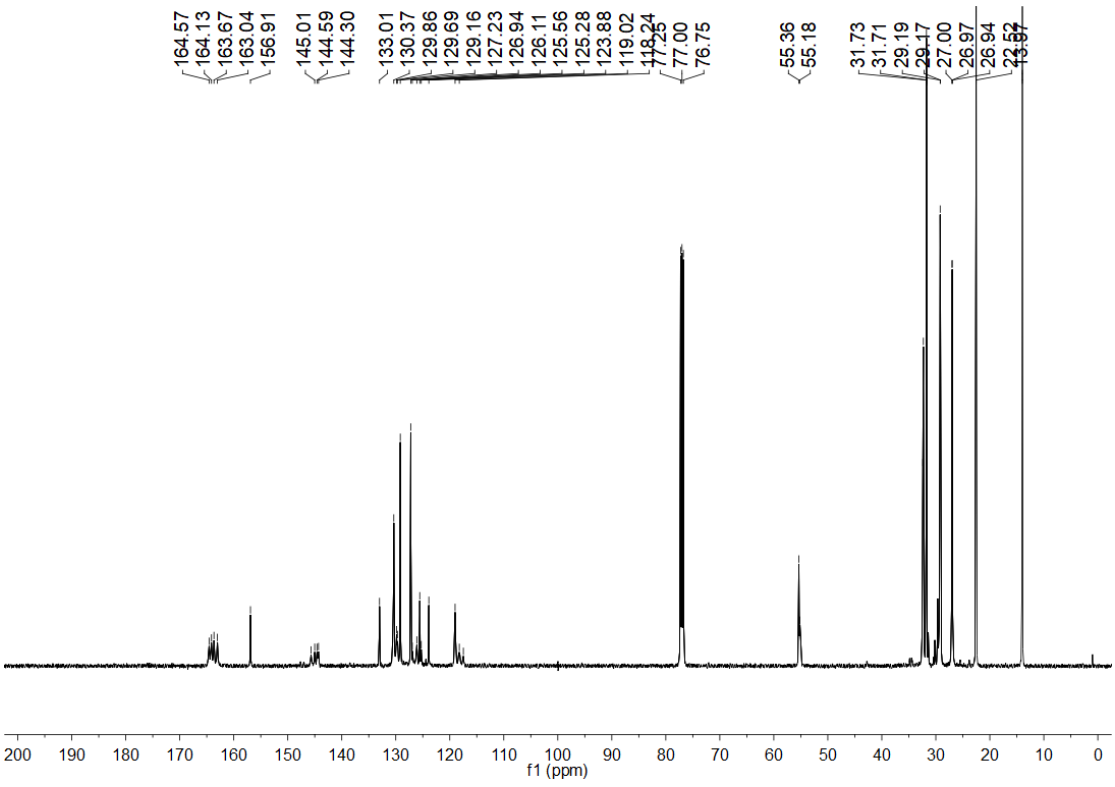
f1 (ppm)

2a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126.94
126.11
125.56
125.28
123.88
119.02
118.24
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77.00
76.75
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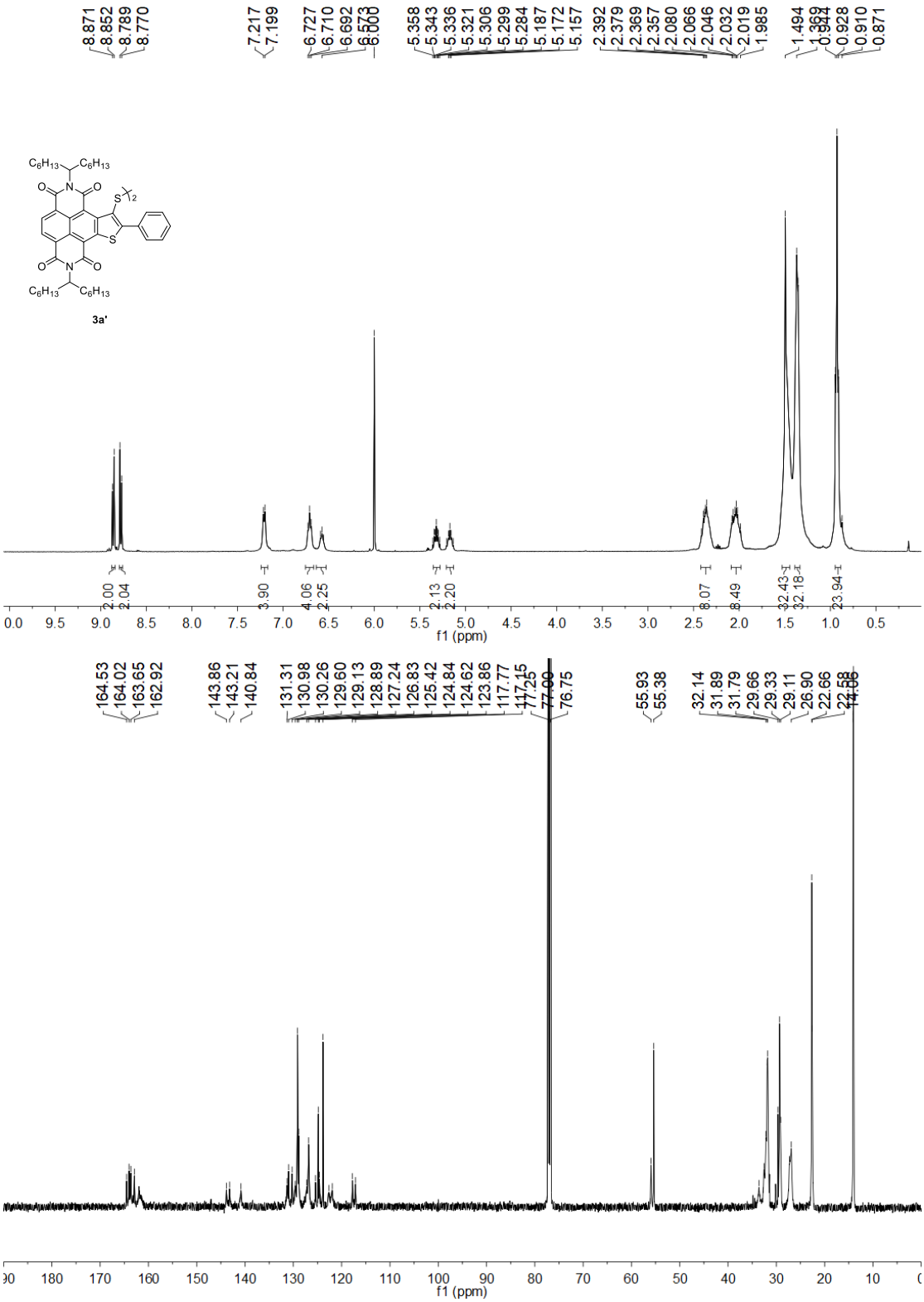
13.97
f1 (ppm)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5.187
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2.369
2.357
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2.046
2.032
2.019
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1.494
1.369
0.928
0.910
0.871
3a'
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2.04
3.90
4.06
2.25
2.13
2.20
8.07
8.49
32.43
32.18
23.94
f1 (ppm)
164.53
164.02
163.65
162.92
143.86
143.21
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129.60
129.13
128.89
127.24
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125.42
124.84
124.62
123.86
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117.15
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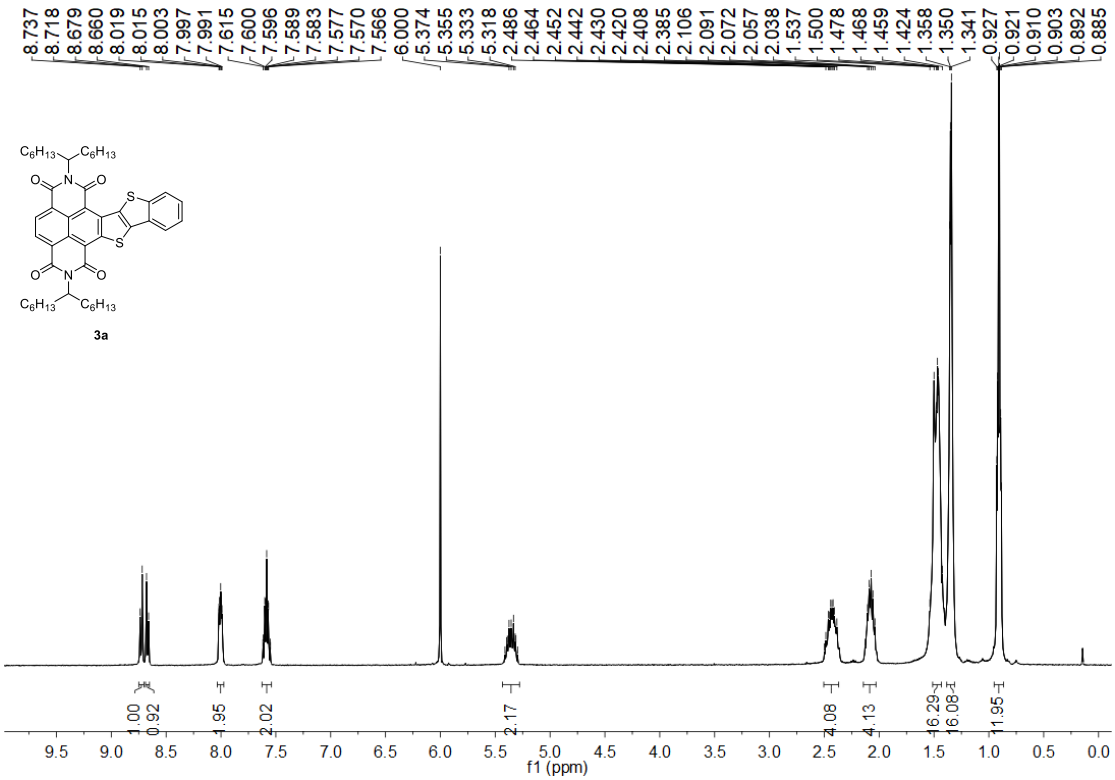
14.06
f1 (ppm)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7.570
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5.355
5.333
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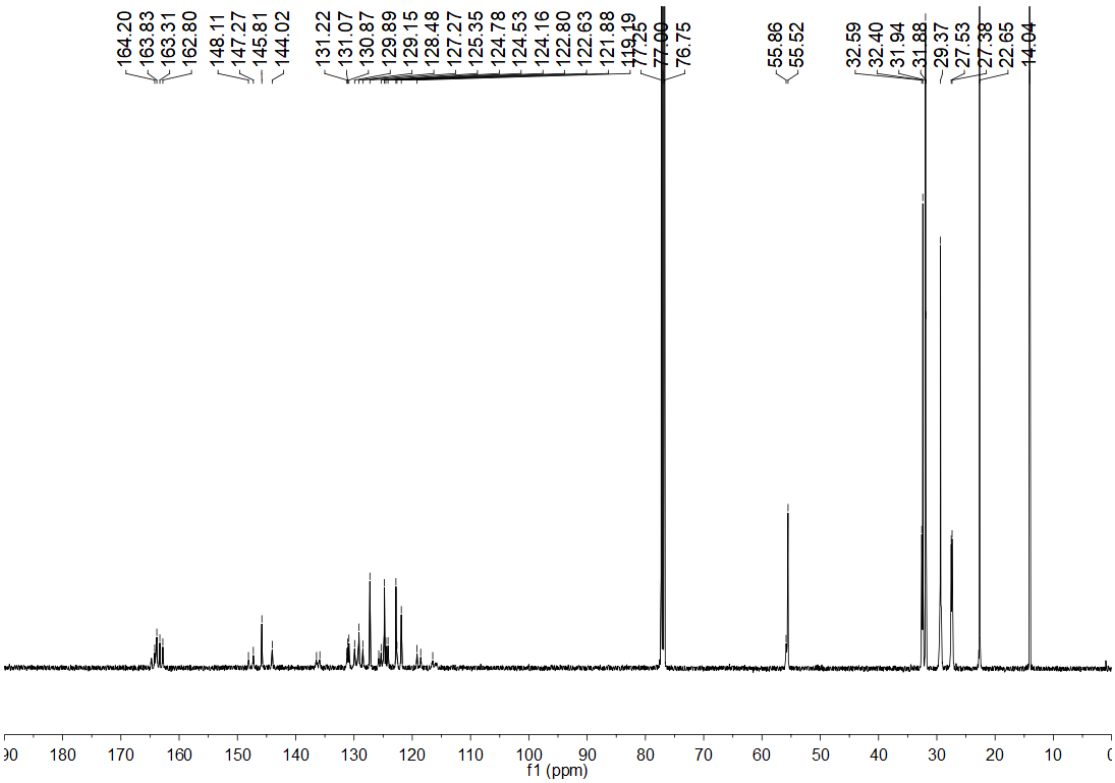
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129.15
128.48
127.27
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124.78
124.53
124.16
122.80
122.63
121.88
119.19
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77.00
76.75
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32.40
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27.38
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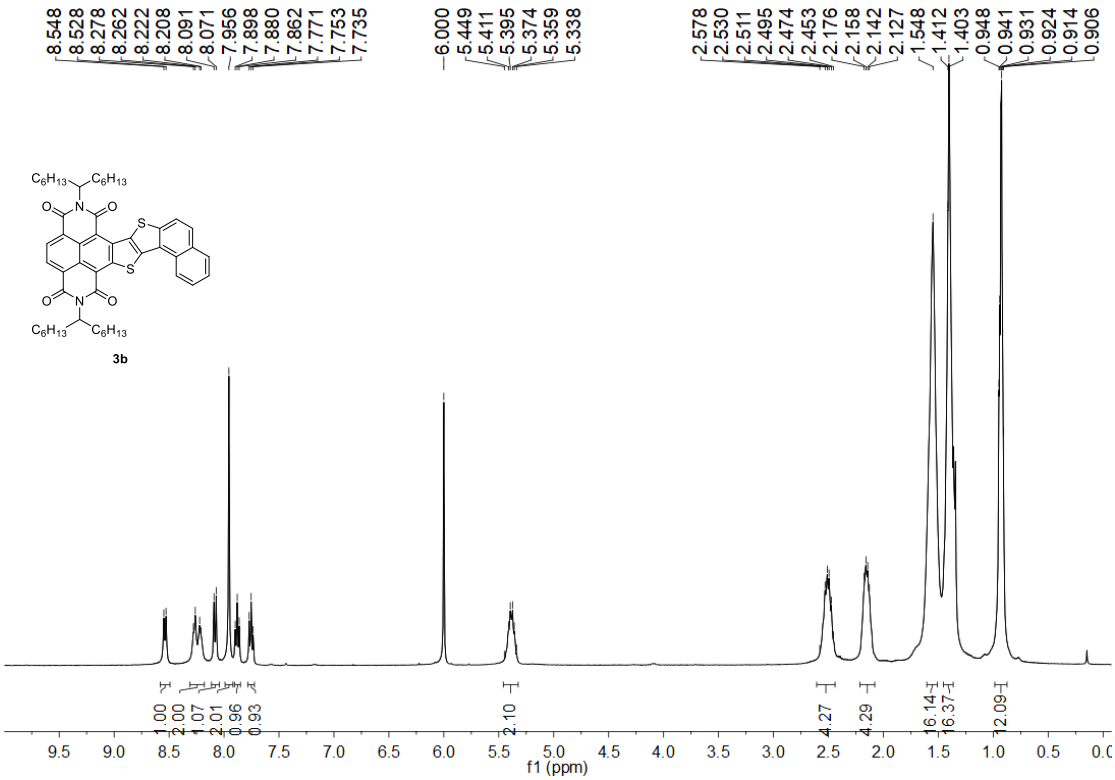
14.04
f1 (ppm)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7.753
7.735
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5.395
5.374
5.359
5.338
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2.530
2.511
2.495
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2.453
2.176
2.158
2.142
2.127
1.548
1.412
1.403
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0.941
0.931
0.924
0.914
0.906
3b
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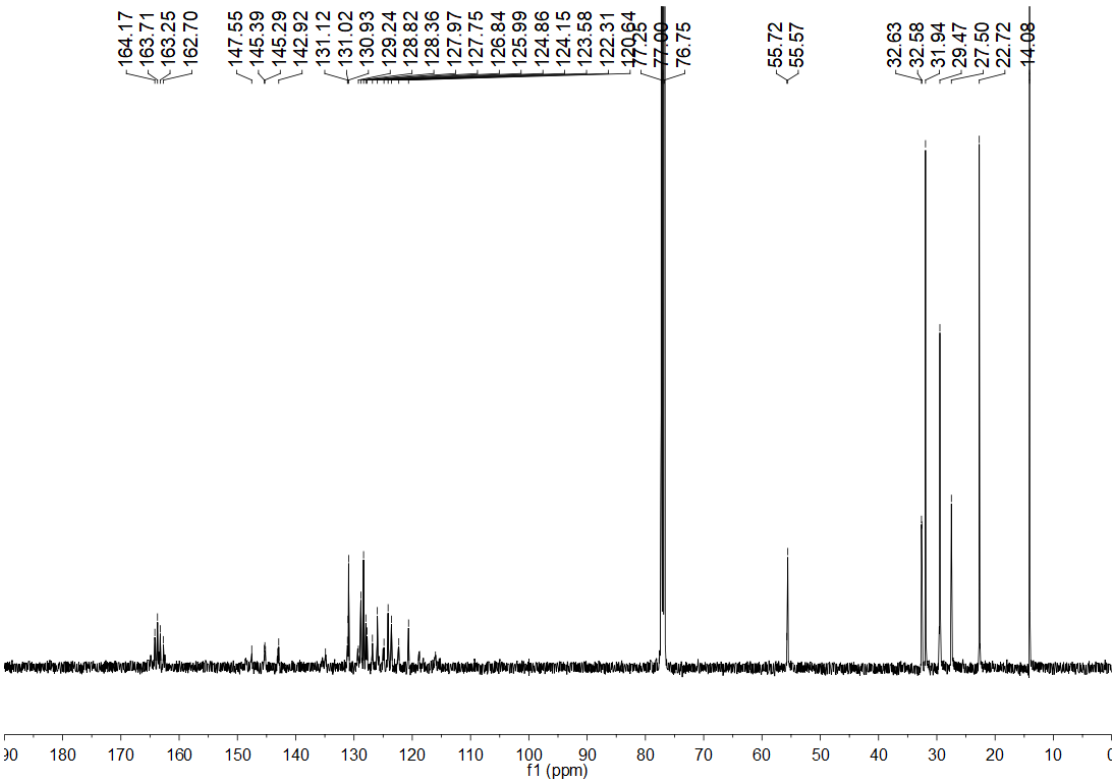
f1 (ppm)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125.99
124.86
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123.58
122.31
120.64
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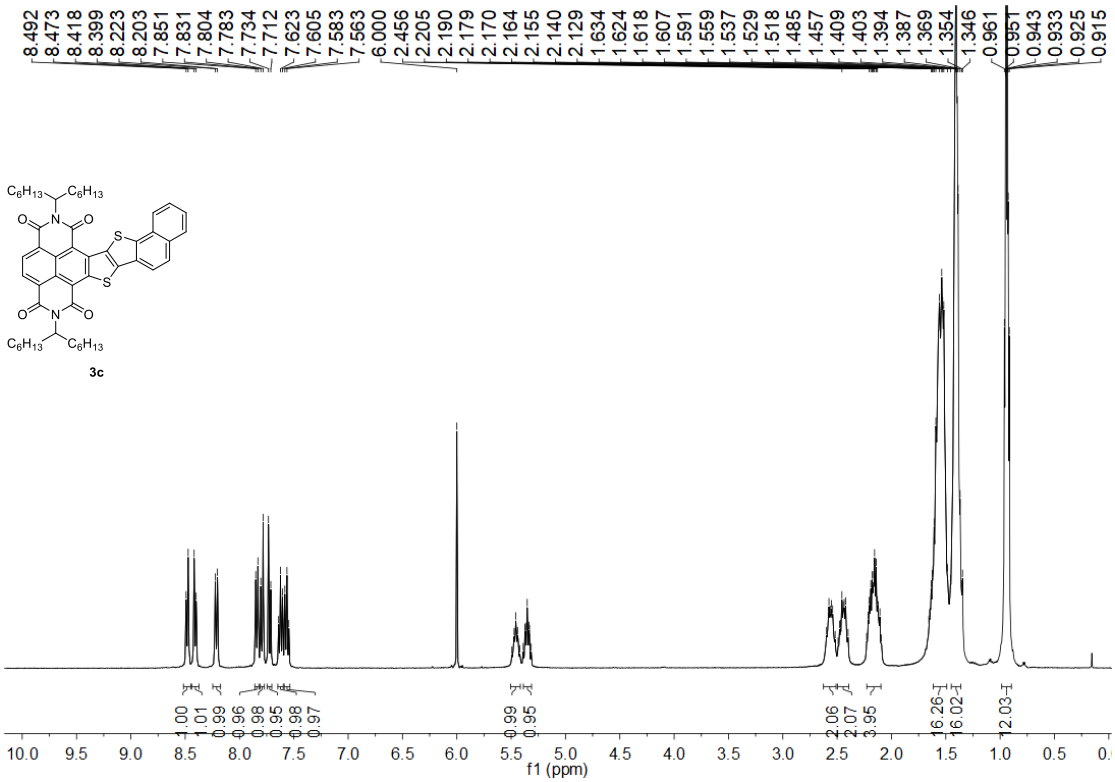
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2.140
2.129
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1.618
1.607
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1.537
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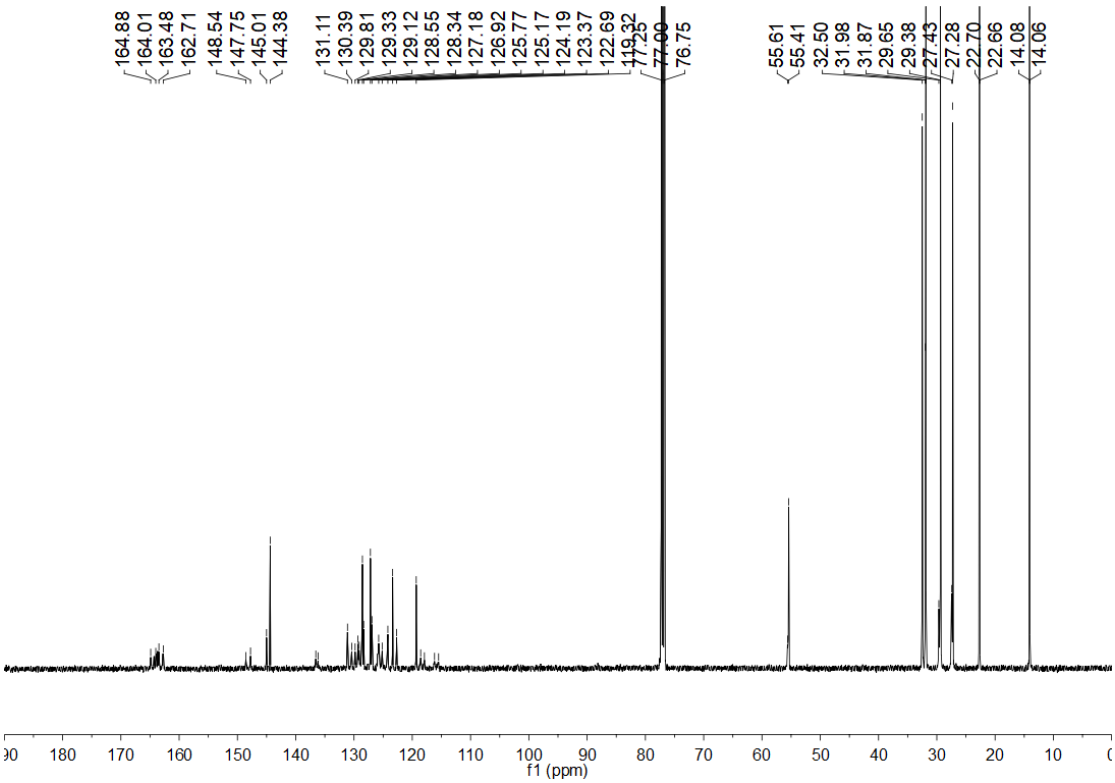
0.98
0.95
0.98
0.97
0.99
0.95
2.06
2.07
3.95
16.26
16.02
12.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

C6H13
C6H13
O
N
O
S
S
O
N
O
C6H13
C6H13

3c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163.48
162.71
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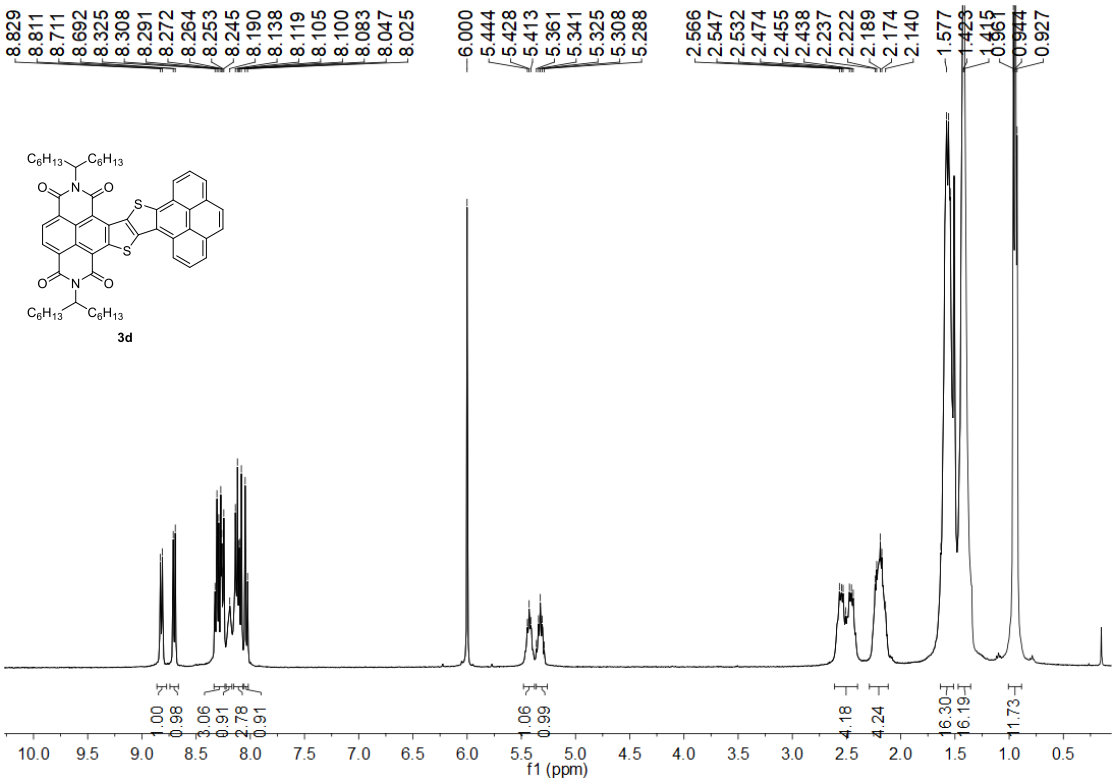
147.75
145.01
144.38
131.11
130.39
129.81
129.33
129.12
128.55
128.34
127.18
126.92
125.77
125.17
124.19
123.37
122.69
119.32
77.25
77.00
76.75
55.61
55.41
32.50
31.98
31.87
29.65
29.38
27.43
27.28
22.70
22.66
14.08
14.06
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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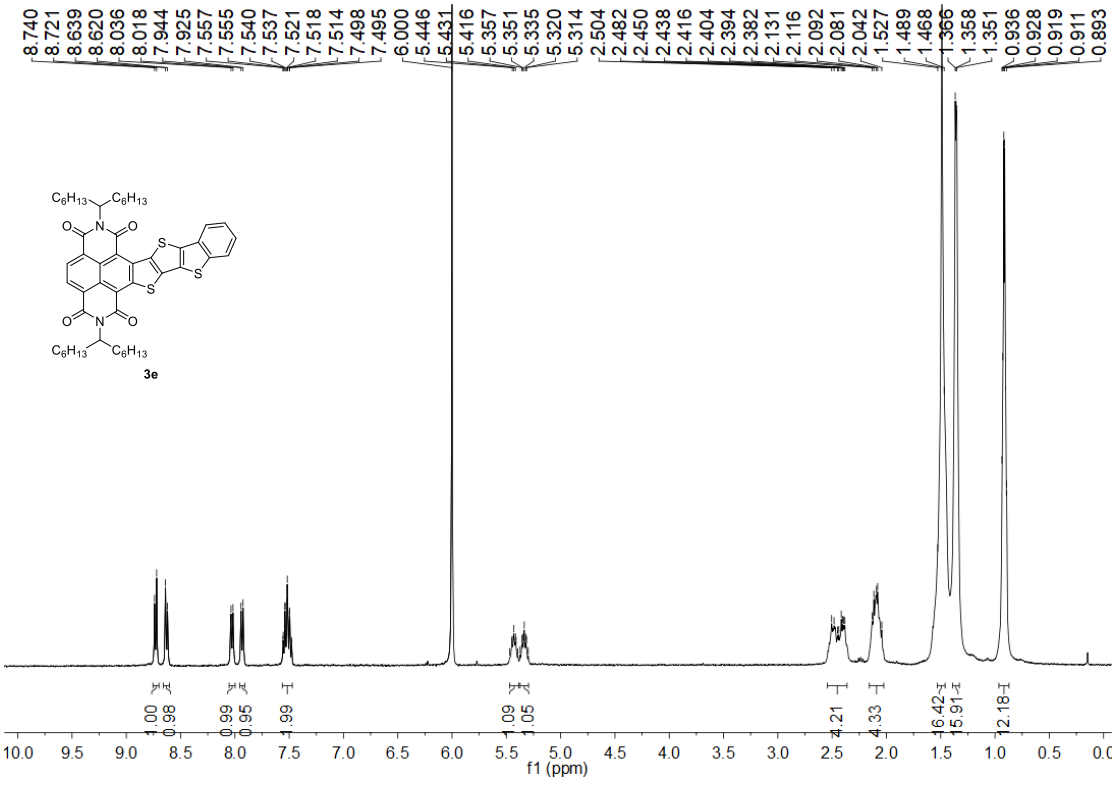
8.811
8.711
8.692
8.325
8.308
8.291
8.272
8.264
8.253
8.245
8.190
8.138
8.119
8.105
8.100
8.083
8.047
8.025
6.000
5.444
5.428
5.413
5.361
5.341
5.325
5.308
5.288
2.566
2.547
2.532
2.474
2.455
2.438
2.237
2.222
2.189
2.174
2.140
1.577
1.423
1.415
0.961
0.944
0.927
1.00
0.98
3.06
0.91
2.78
0.91
1.06
0.99
4.18
4.24
16.30
16.19
11.73
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
3d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8.036
8.018
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7.925
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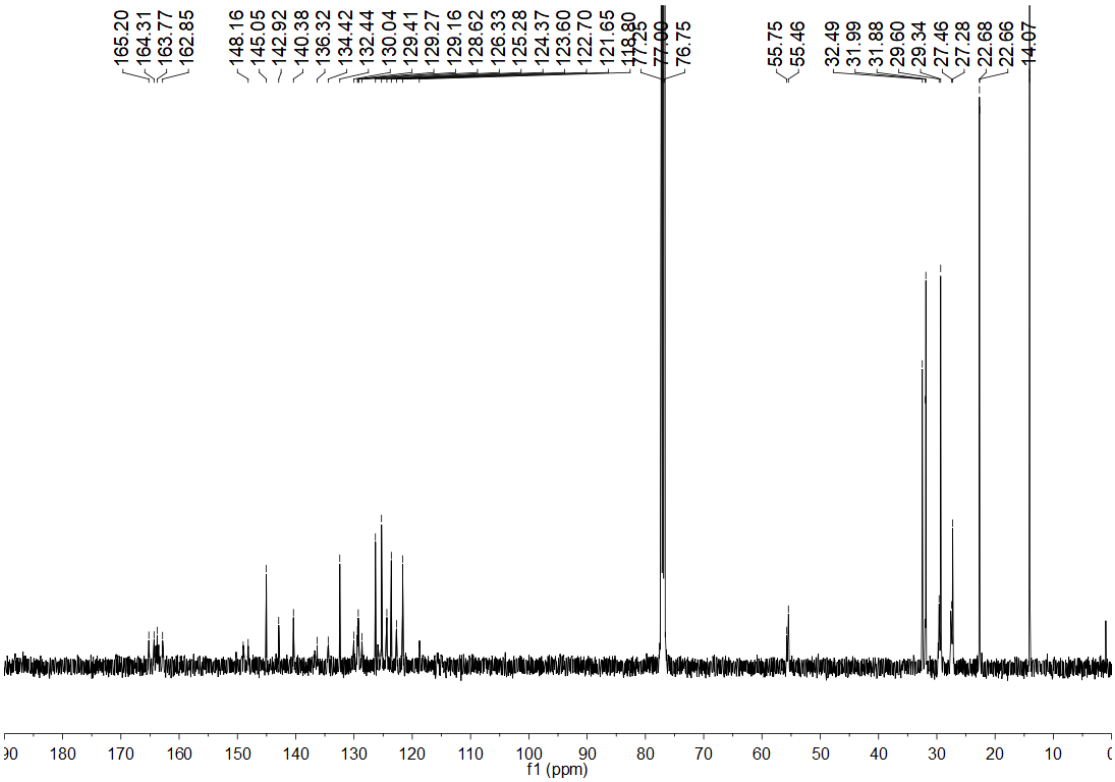
7.555
7.540
7.537
7.521
7.518
7.514
7.498
7.495
6.000
5.446
5.431
5.416
5.357
5.351
5.335
5.320
5.314
2.504
2.482
2.450
2.438
2.416
2.404
2.394
2.382
2.131
2.116
2.092
2.081
2.042
1.527
1.489
1.468
1.366
1.358
1.351
0.936
0.928
0.919
0.911
0.893
1.00
0.98
0.99
0.95
1.99
1.09
1.05
4.21
4.33
16.42
15.91
12.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3e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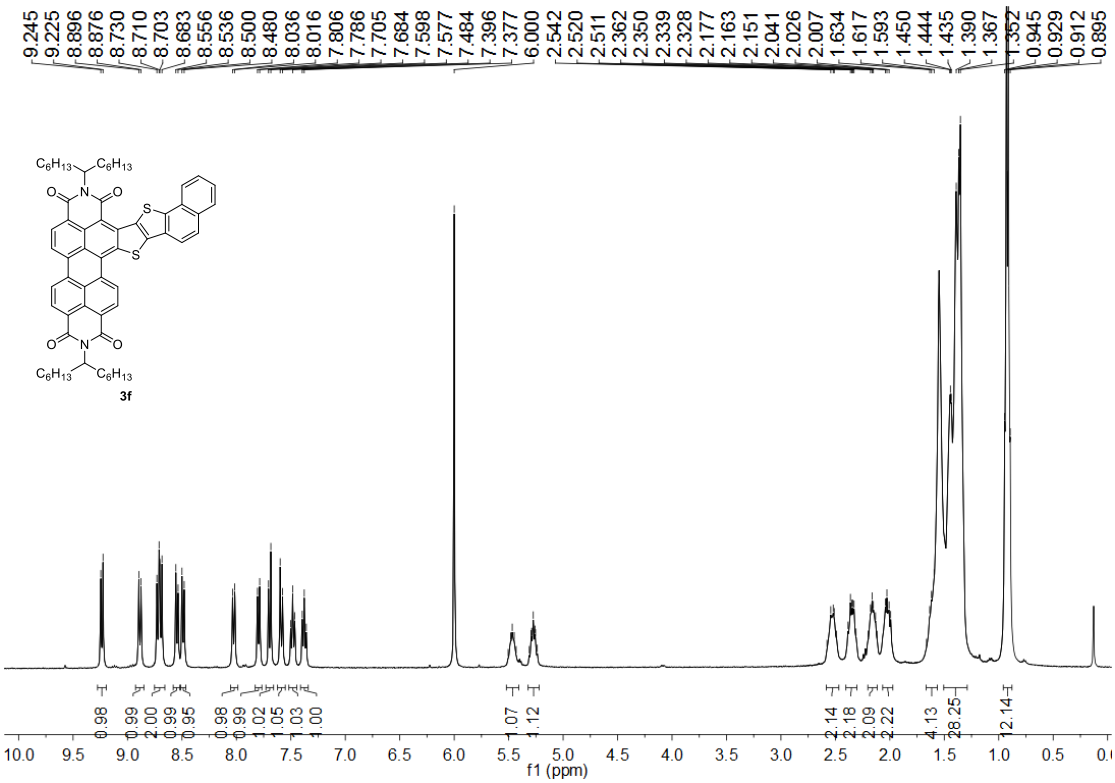
164.31
163.77
162.85
148.16
145.05
142.92
140.38
136.32
134.42
132.44
130.04
129.41
129.27
129.16
128.62
126.33
125.28
124.37
123.60
122.70
121.65
118.80
77.25
77.00
76.75
55.75
55.46
32.49
31.99
31.88
29.60
29.34
27.46
27.28
22.68
22.66
14.07
f1 (ppm)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9.225
8.896
8.876
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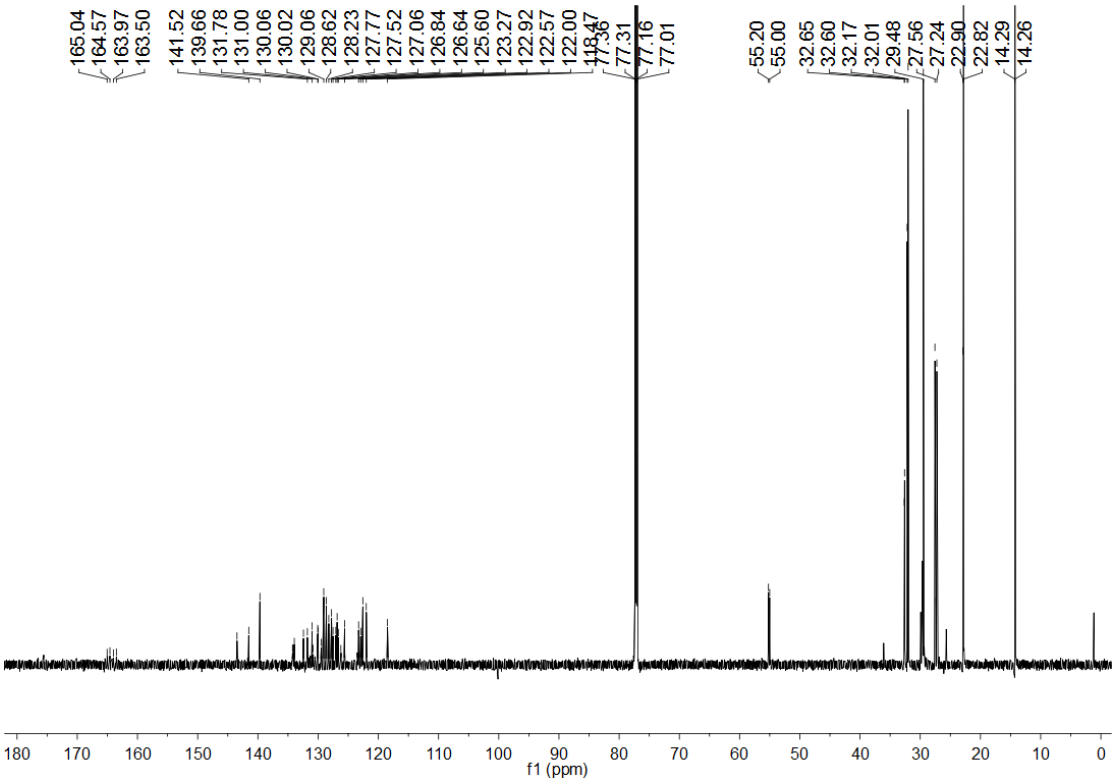
8.683
8.556
8.536
8.500
8.480
8.036
8.016
7.806
7.786
7.705
7.684
7.598
7.577
7.484
7.396
7.377
6.000
2.542
2.520
2.511
2.362
2.350
2.339
2.328
2.177
2.163
2.151
2.041
2.026
2.007
1.634
1.617
1.593
1.450
1.444
1.435
1.390
1.367
1.352
0.945
0.929
0.912
0.895
0.98
0.99
2.00
0.99
0.95
0.98
0.99
1.02
1.05
1.03
1.00
1.07
1.12
2.14
2.18
2.09
2.22
4.13
28.25
12.14
f1 (ppm)

C6H13
C6H13
O
N
O
S
S
O
N
O
C6H13
C6H13

3f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164.57
163.97
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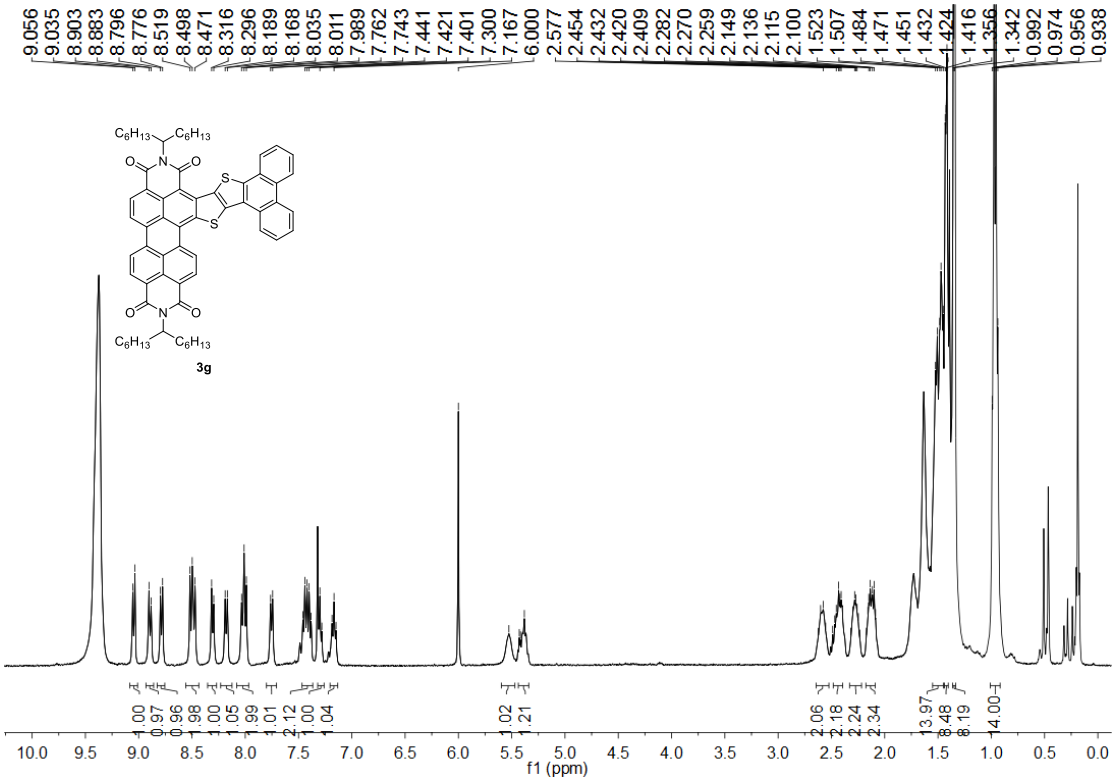
141.52
139.66
131.78
131.00
130.06
130.02
129.06
128.62
128.23
127.77
127.52
127.06
126.84
126.64
125.60
123.27
122.92
122.57
122.00
77.36
77.31
77.16
77.01
55.20
55.00
32.65
32.60
32.17
32.01
29.48
27.56
27.24
22.90
22.82
14.29
14.26
f1 (ppm)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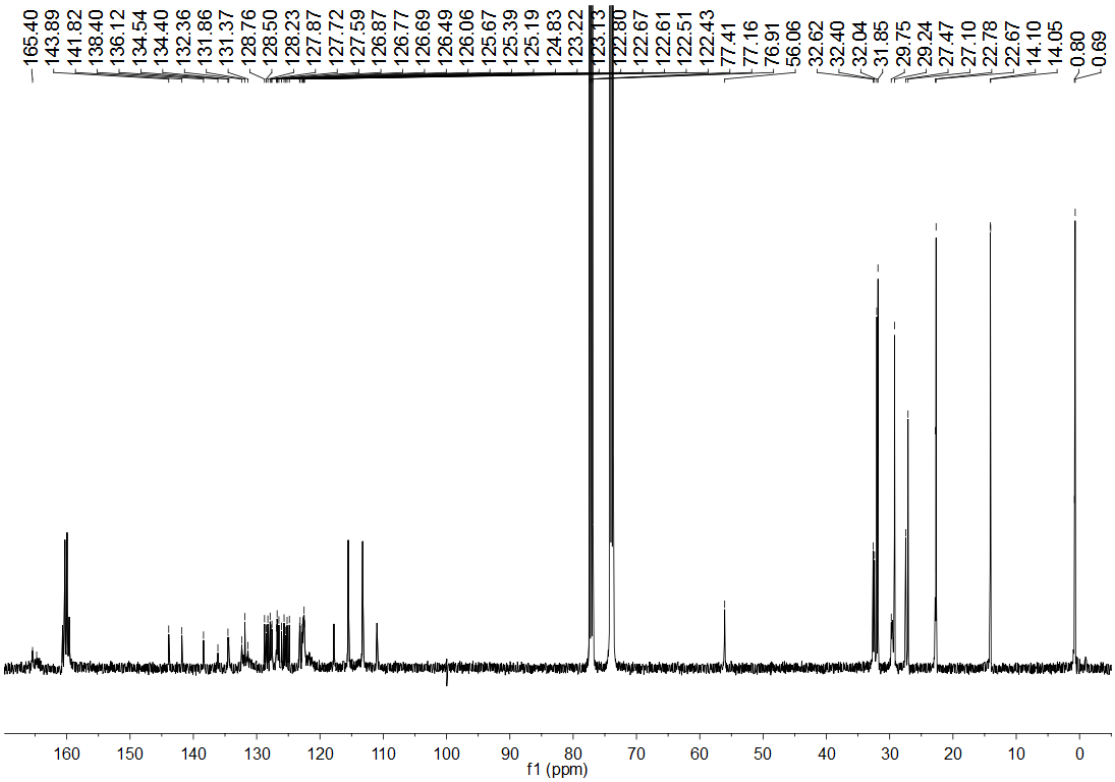
9.035
8.903
8.883
8.796
8.776
8.519
8.498
8.471
8.316
8.296
8.189
8.168
8.035
8.011
7.989
7.762
7.743
7.441
7.421
7.401
7.300
7.167
6.000
2.577
2.454
2.432
2.420
2.409
2.282
2.270
2.259
2.149
2.136
2.115
2.100
1.523
1.507
1.484
1.471
1.451
1.432
1.424
1.416
1.356
1.342
0.992
0.974
0.956
0.938
3g
f1 (ppm)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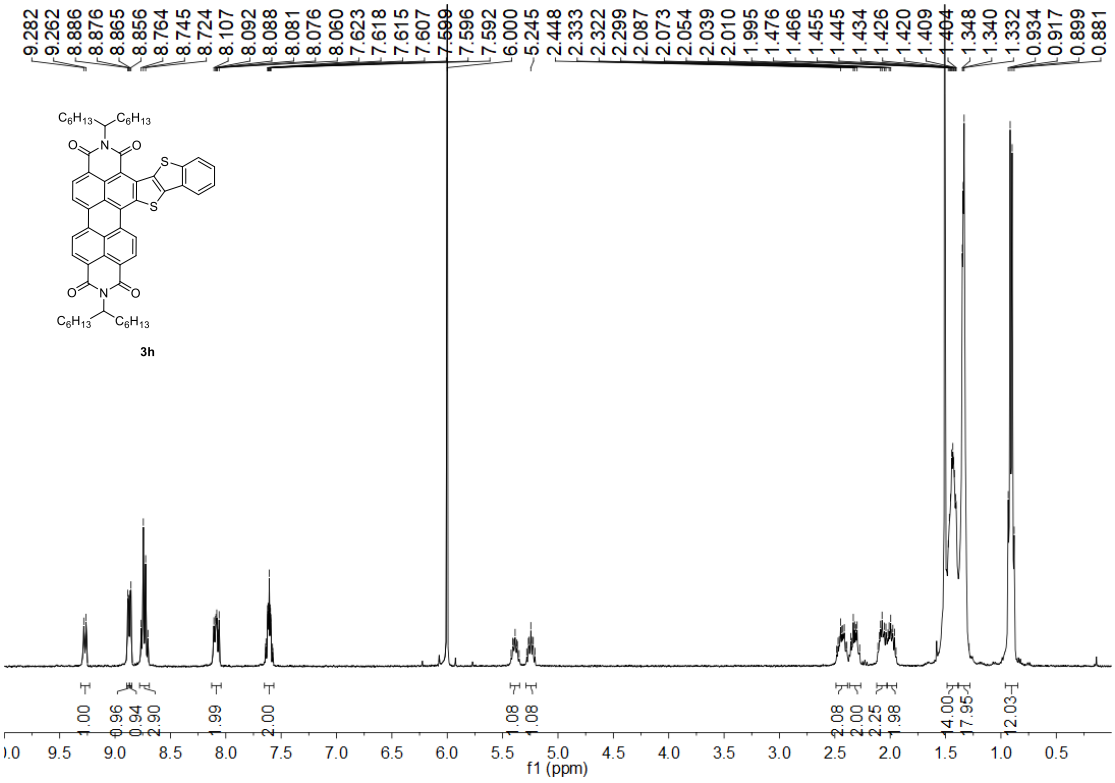
143.89
141.82
138.40
136.12
134.54
134.40
132.36
131.86
131.37
128.76
128.50
128.23
127.87
127.72
127.59
126.87
126.77
126.69
126.49
126.06
125.67
125.39
125.19
124.83
123.22
123.13
122.80
122.67
122.61
122.51
122.43
77.41
77.16
76.91
56.06
32.62
32.40
32.04
31.85
29.75
29.24
27.47
27.10
22.78
22.67
14.10
14.05
0.80
0.69
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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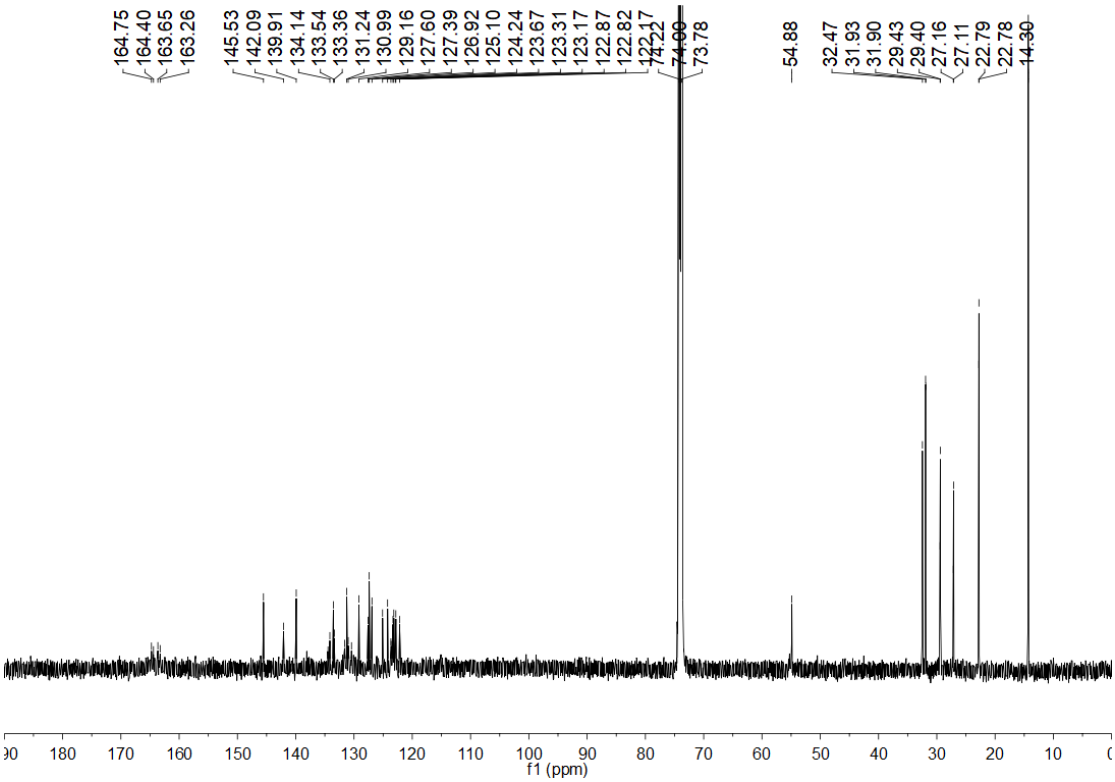
8.876
8.865
8.856
8.764
8.745
8.724
8.107
8.092
8.088
8.081
8.076
8.060
7.623
7.618
7.615
7.607
7.599
7.596
7.592
6.000
5.245
2.448
2.333
2.322
2.299
2.087
2.073
2.054
2.039
2.010
1.995
1.476
1.466
1.455
1.445
1.434
1.426
1.420
1.409
1.404
1.348
1.340
1.332
0.934
0.917
0.899
0.881
1.00
0.96
0.94
2.90
1.99
2.00
1.08
1.08
2.08
2.00
2.25
1.98
14.00
17.95
12.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

3h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163.65
163.26
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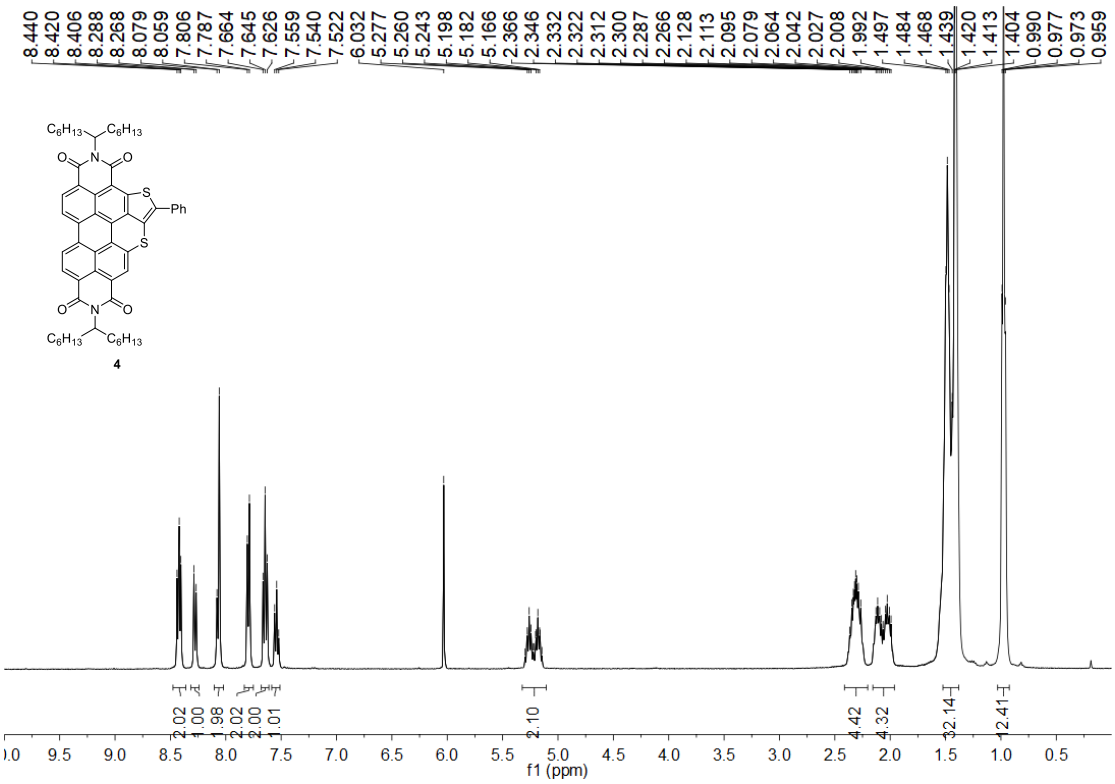
142.09
139.91
134.14
133.54
133.36
131.24
130.99
129.16
127.60
127.39
126.92
125.10
124.24
123.67
123.31
123.17
122.87
122.82
122.17
74.22
74.00
73.78
54.88
32.47
31.93
31.90
29.43
29.40
27.16
27.11
22.79
22.78
14.30
f1 (ppm)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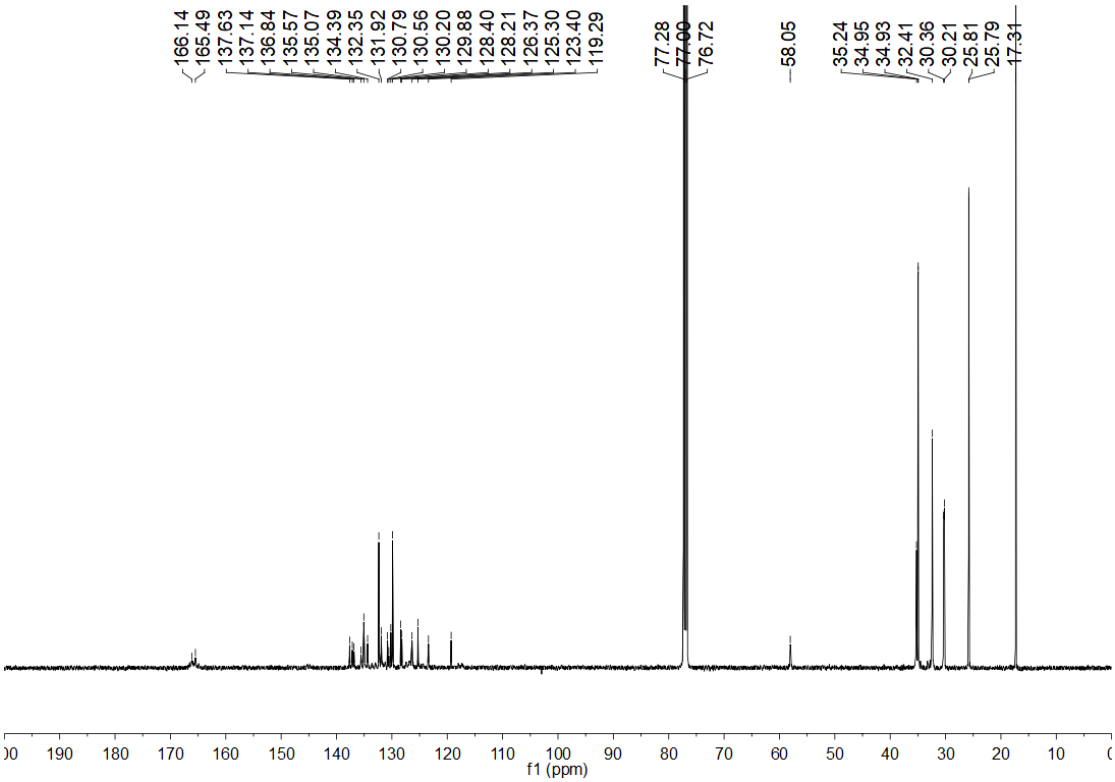
8.268
8.079
8.059
7.806
7.787
7.664
7.645
7.626
7.559
7.540
7.522
6.032
5.277
5.260
5.243
5.198
5.182
5.166
2.366
2.346
2.332
2.322
2.312
2.300
2.287
2.266
2.128
2.113
2.095
2.079
2.064
2.042
2.027
2.008
1.992
1.497
1.484
1.468
1.439
1.420
1.413
1.404
0.990
0.977
0.973
0.959
Ph
4
2.02
1.00
1.98
2.02
2.00
1.01
2.10
4.42
4.32
32.14
12.41
f1 (ppm)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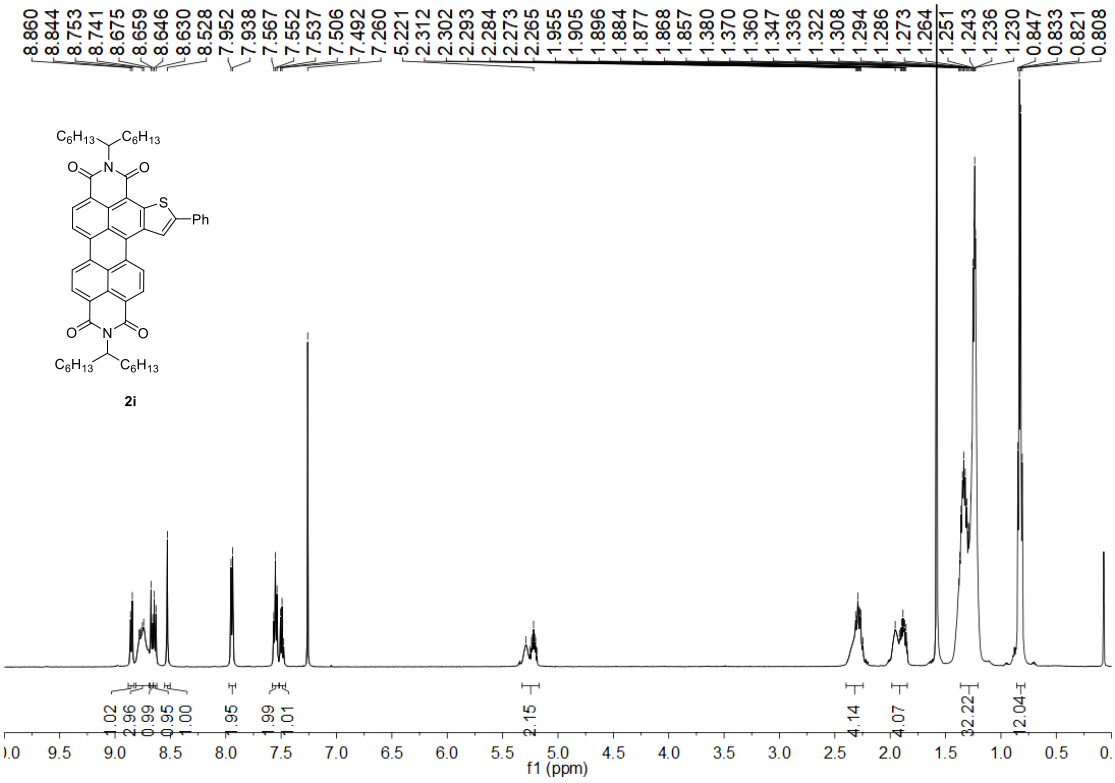
137.63
137.14
136.84
135.57
135.07
134.39
132.35
131.92
130.79
130.56
130.20
129.88
128.40
128.21
126.37
125.30
123.40
119.29
77.28
77.00
76.72
58.05
35.24
34.95
34.93
32.41
30.36
30.21
25.81
25.79
17.31
f1 (ppm)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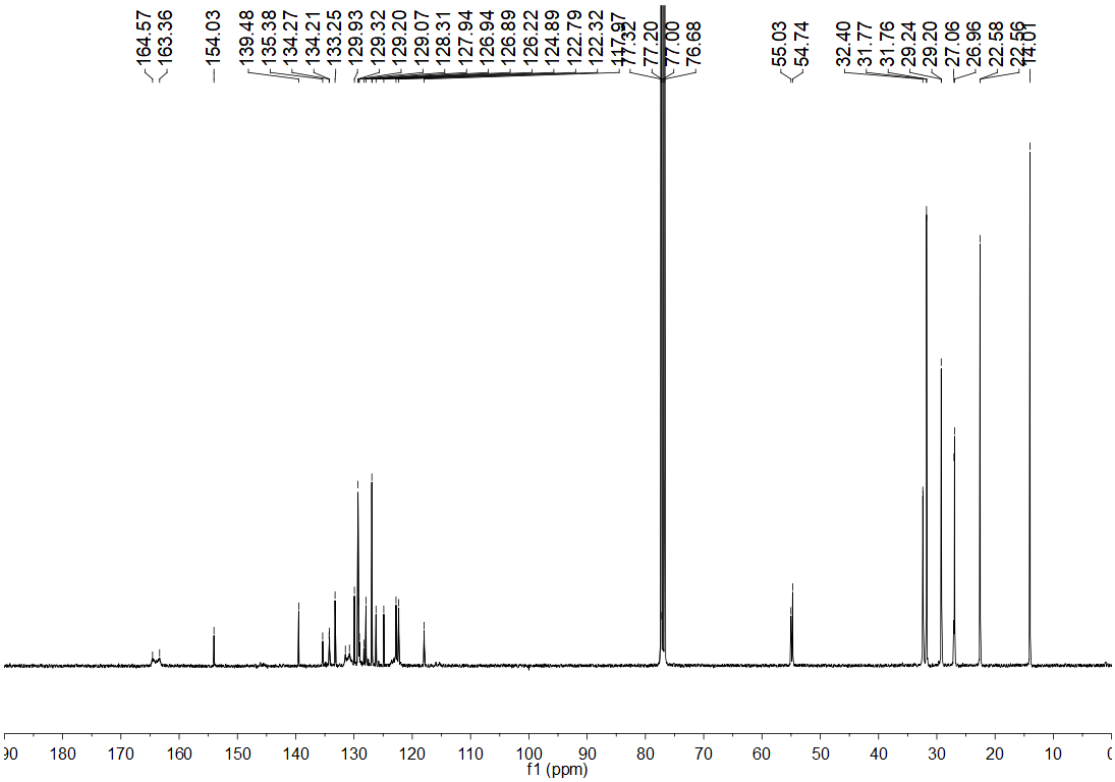
8.741
8.675
8.659
8.646
8.630
8.528
7.952
7.938
7.567
7.552
7.537
7.506
7.492
7.260
5.221
2.312
2.302
2.293
2.284
2.273
2.265
1.955
1.905
1.896
1.884
1.877
1.868
1.857
1.380
1.370
1.360
1.347
1.336
1.322
1.308
1.294
1.286
1.273
1.264
1.251
1.243
1.236
1.230
0.847
0.833
0.821
0.808
1.02
2.96
0.99
0.95
1.00
1.95
1.99
1.01
2.15
4.14
4.07
12.22
12.04
f1 (ppm)

2i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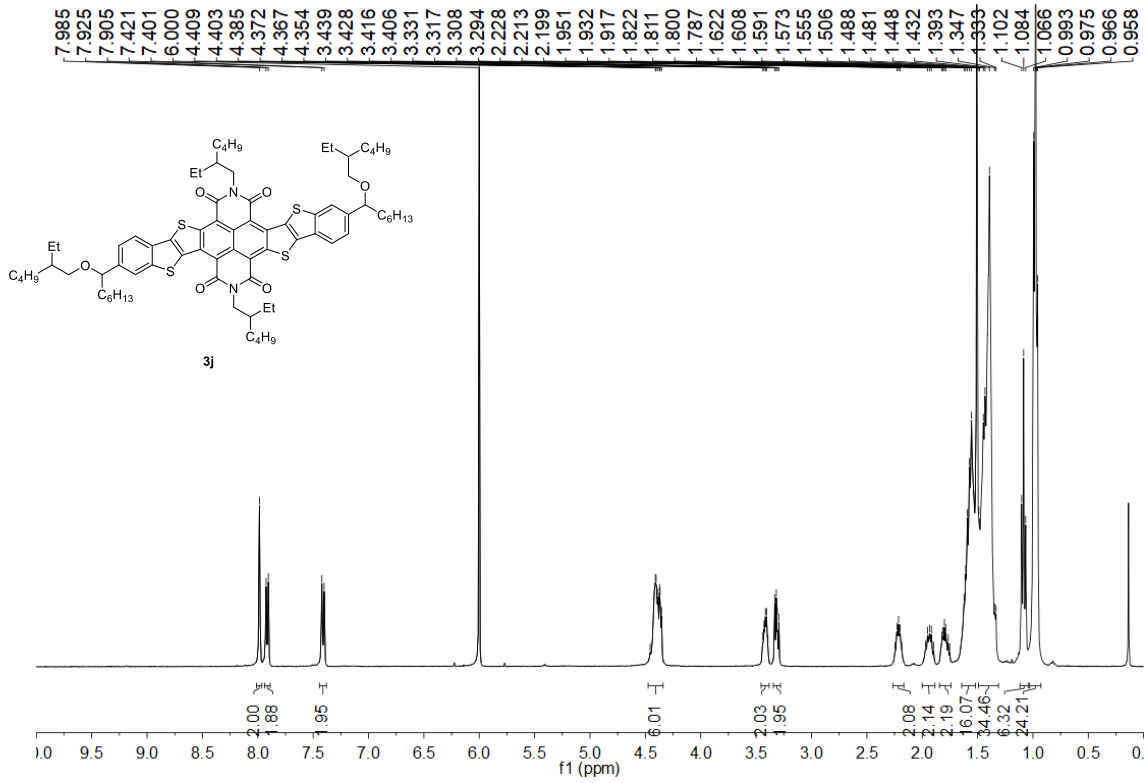
163.36
154.03
139.48
135.38
134.27
134.21
133.25
129.93
129.32
129.20
129.07
128.31
127.94
126.94
126.89
126.22
124.89
122.79
122.32
77.20
77.00
76.68
55.03
54.74
32.40
31.77
31.76
29.24
29.20
27.06
26.96
22.58
14.01
f1 (ppm)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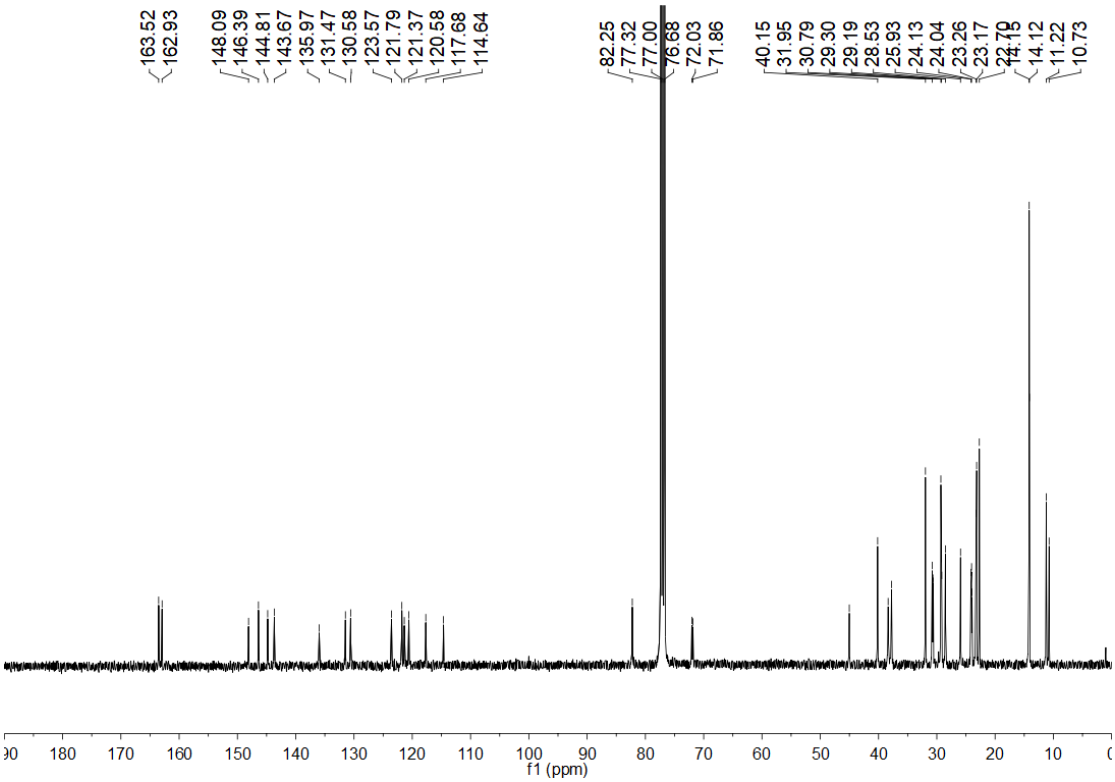
7.905
7.421
7.401
6.000
4.409
4.403
4.385
4.372
4.367
4.354
3.439
3.428
3.416
3.406
3.331
3.317
3.308
3.294
2.228
2.213
2.199
1.951
1.932
1.917
1.822
1.811
1.800
1.787
1.622
1.608
1.591
1.573
1.555
1.506
1.488
1.481
1.448
1.432
1.393
1.347
1.333
1.102
1.084
1.066
0.993
0.975
0.966
0.958
2.00
1.88
1.95
6.01
2.03
1.95
2.08
2.14
2.19
16.07
34.46
6.32
24.21
f1 (ppm)

3j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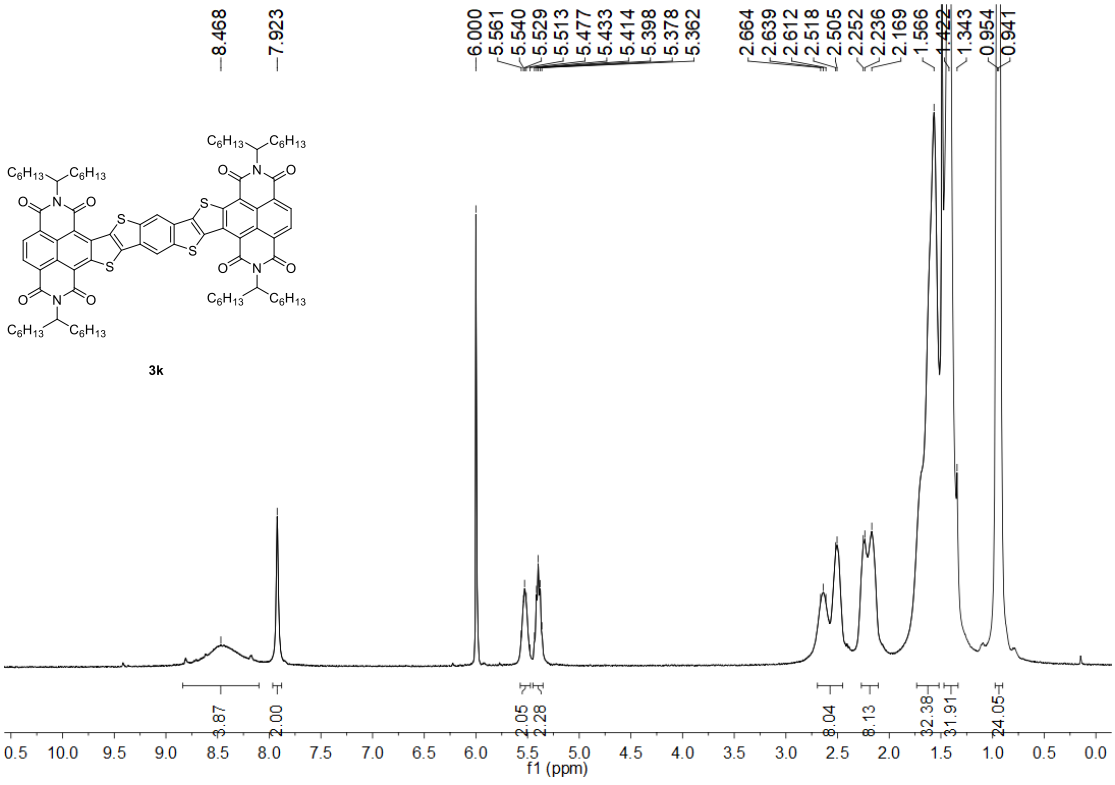
162.93
148.09
146.39
144.81
143.67
135.97
131.47
130.58
123.57
121.79
121.37
120.58
117.68
114.64
82.25
77.32
77.00
76.68
72.03
71.86
40.15
31.95
30.79
29.30
29.19
28.53
25.93
24.13
24.04
23.26
23.17
14.12
11.22
10.73
f1 (ppm)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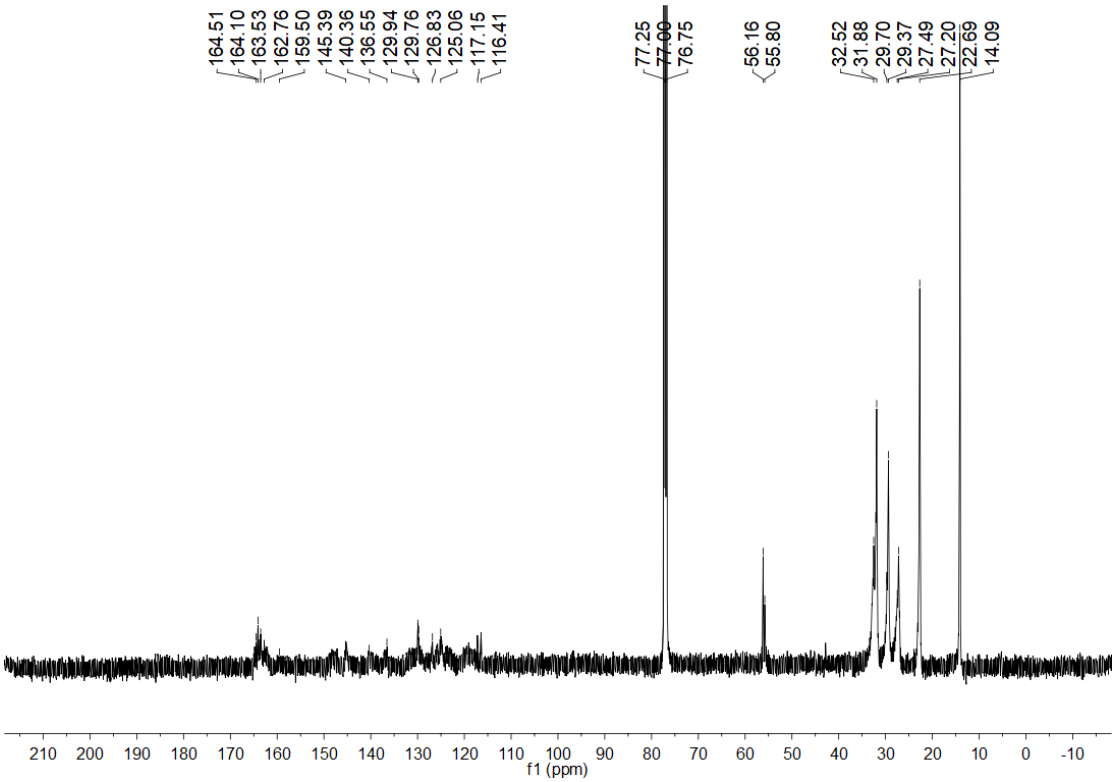
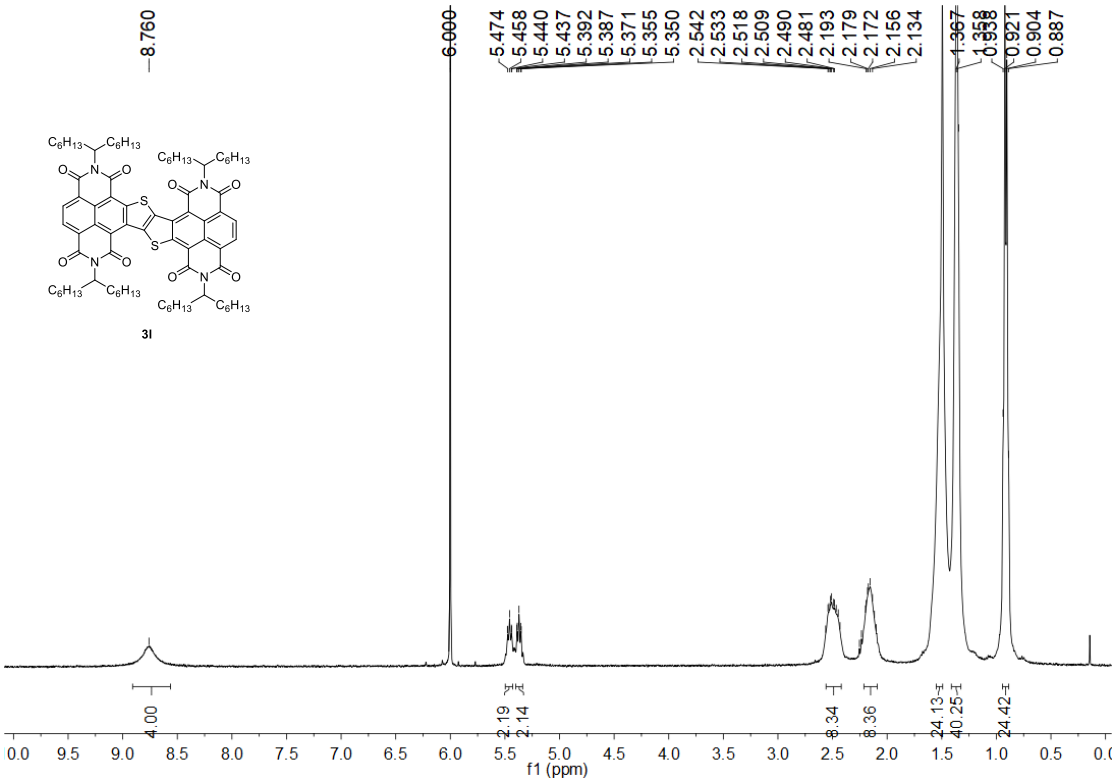
5.540
5.529
5.513
5.477
5.433
5.414
5.398
5.378
5.362
2.664
2.639
2.612
2.518
2.505
2.252
2.236
2.169
1.566
1.422
1.343
0.954
0.941
3.87
2.00
2.05
2.28
8.04
8.13
32.38
31.91
24.05
f1 (ppm)

3k


164.51
164.10
163.53
162.76
159.50
145.39
140.36
136.55
129.94
129.76
126.83
125.06
117.15
116.41
77.25
77.00
76.75
56.16
55.80
32.52
31.88
29.70
29.37
27.49
27.20
22.69
14.09
f1 (ppm)


8.760
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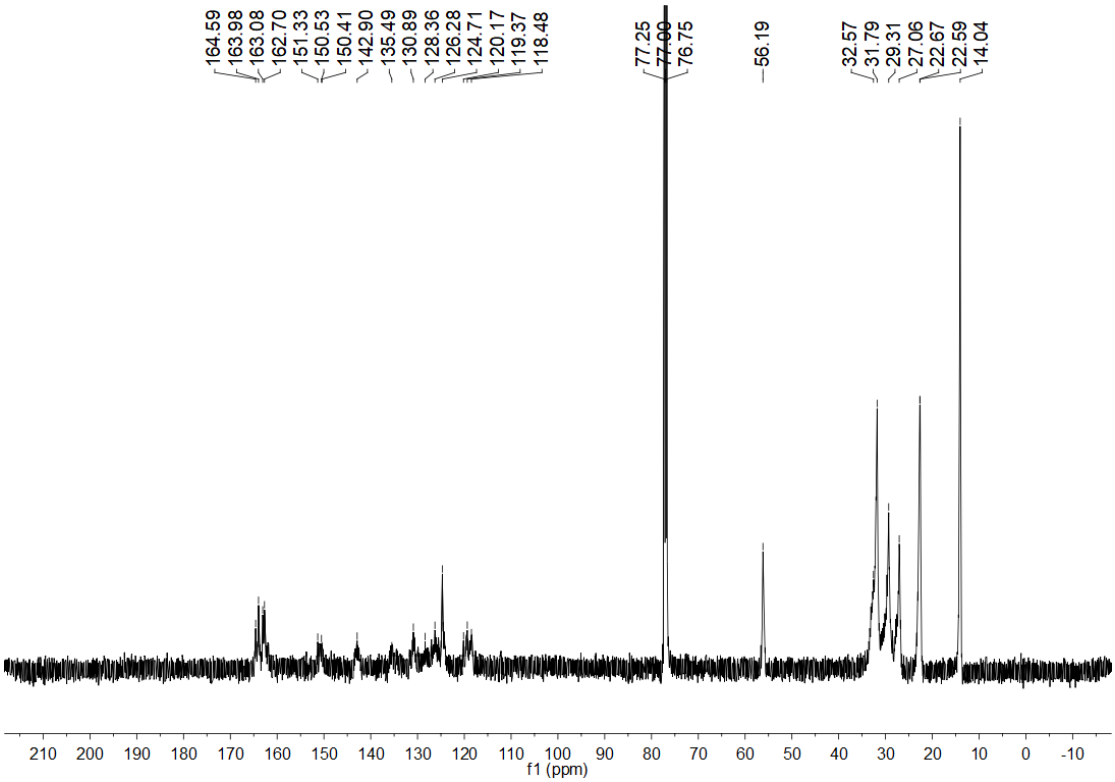
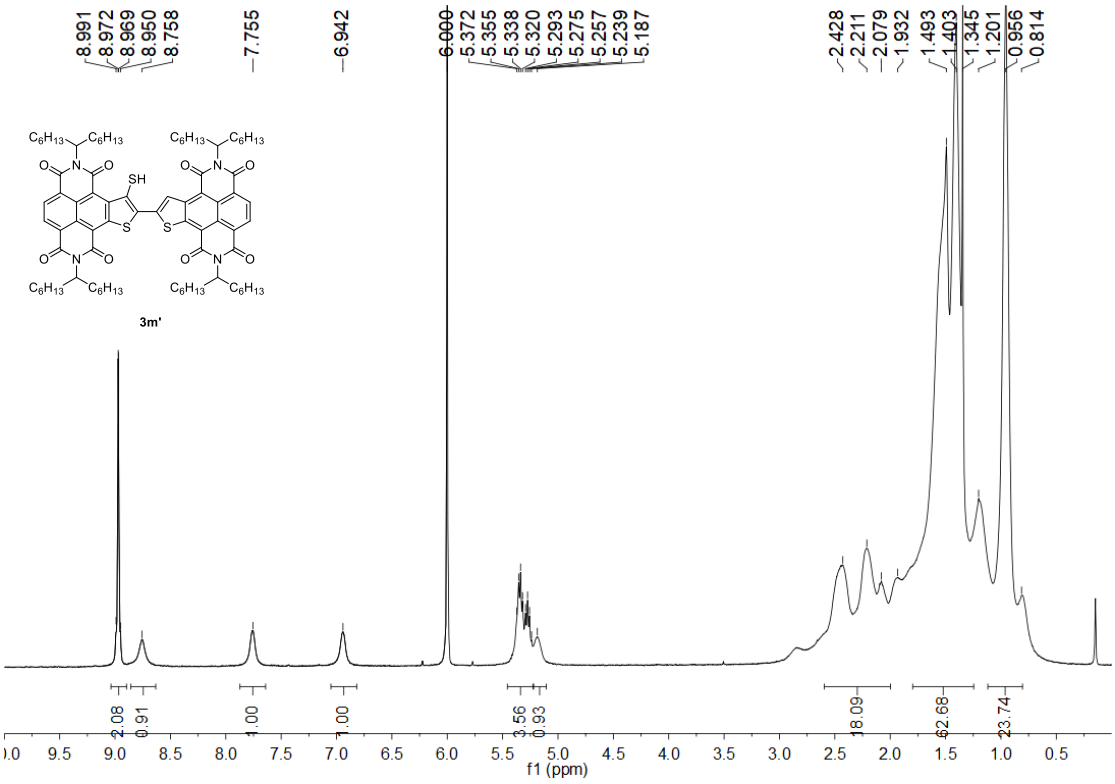
5.474
5.458
5.440
5.437
5.392
5.387
5.371
5.355
5.350
2.542
2.533
2.518
2.509
2.490
2.481
2.193
2.179
2.172
2.156
2.134
1.367
1.358
0.938
0.921
0.904
0.887
4.00
2.19
2.14
8.34
8.36
24.13
40.25
24.42
f1 (ppm)

3l


164.59
163.98
163.08
162.70
151.33
150.53
150.41
142.90
135.49
130.89
128.36
126.28
124.71
120.17
119.37
118.48
77.25
77.00
76.75
56.19
32.57
31.79
29.31
27.06
22.67
22.59
14.04
f1 (ppm)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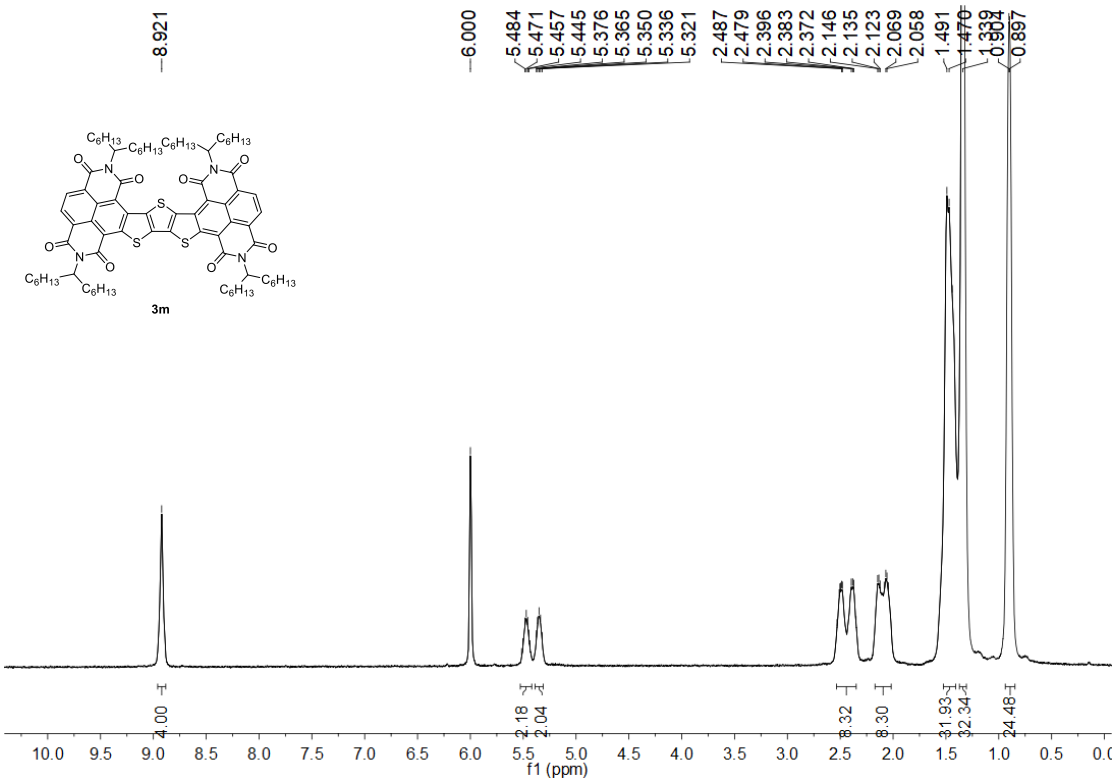
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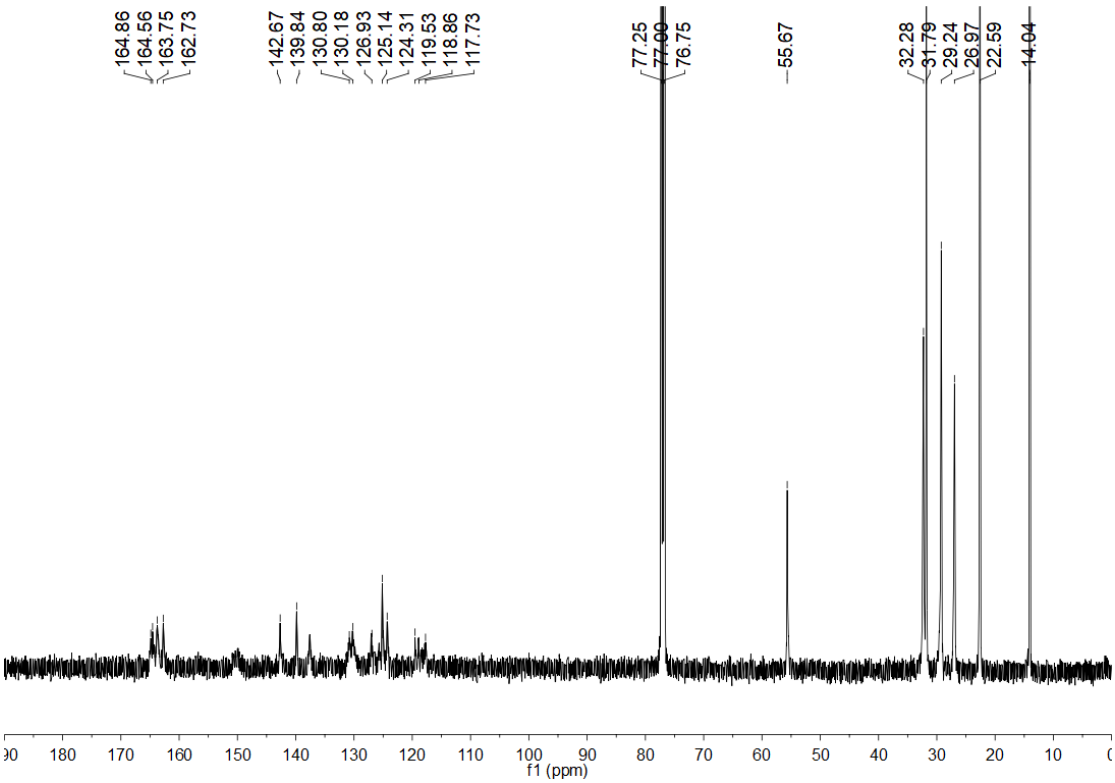
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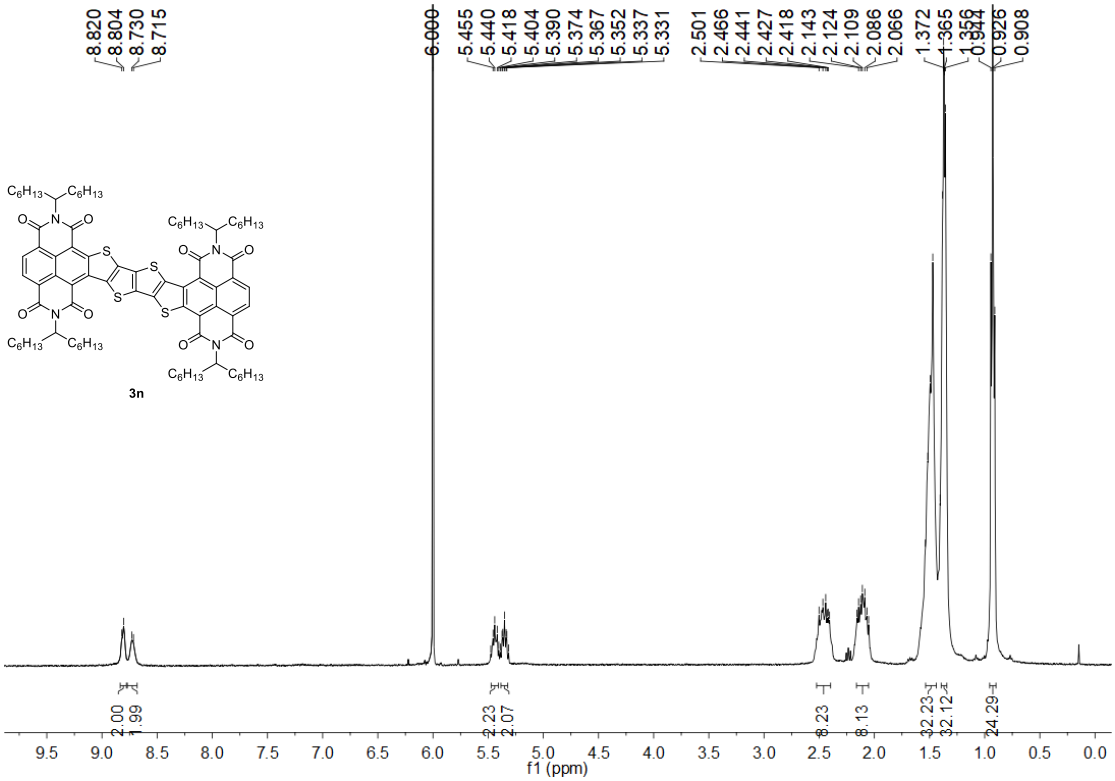
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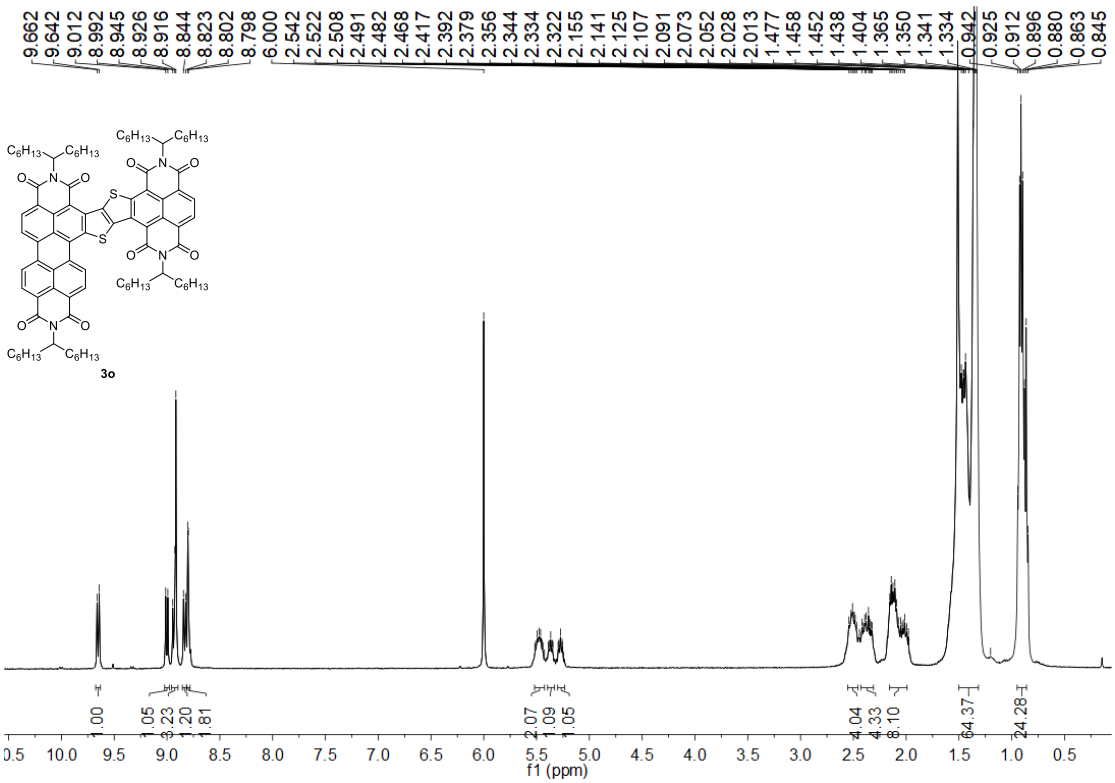
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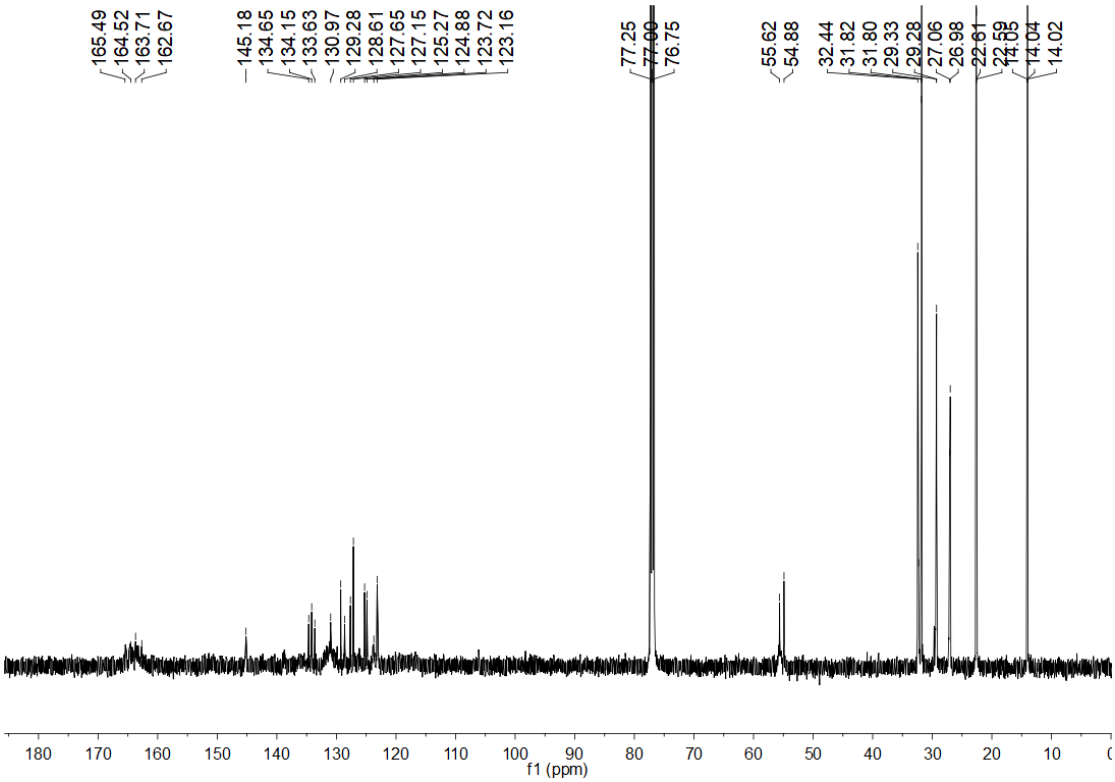
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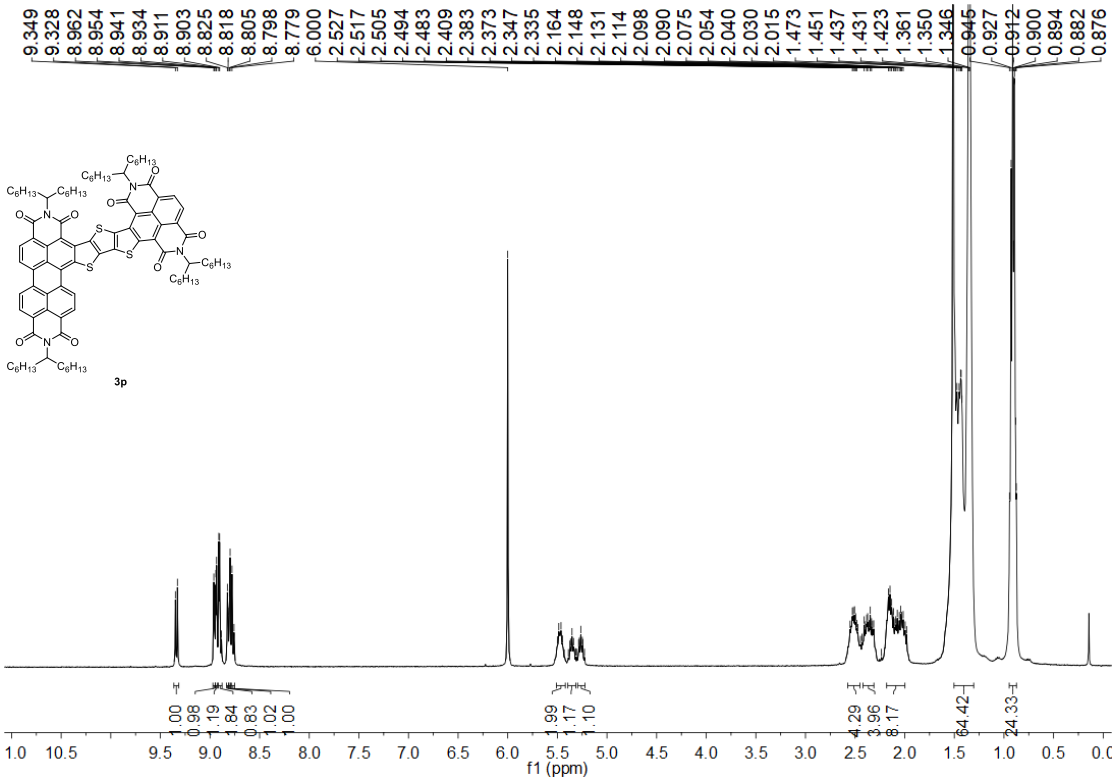
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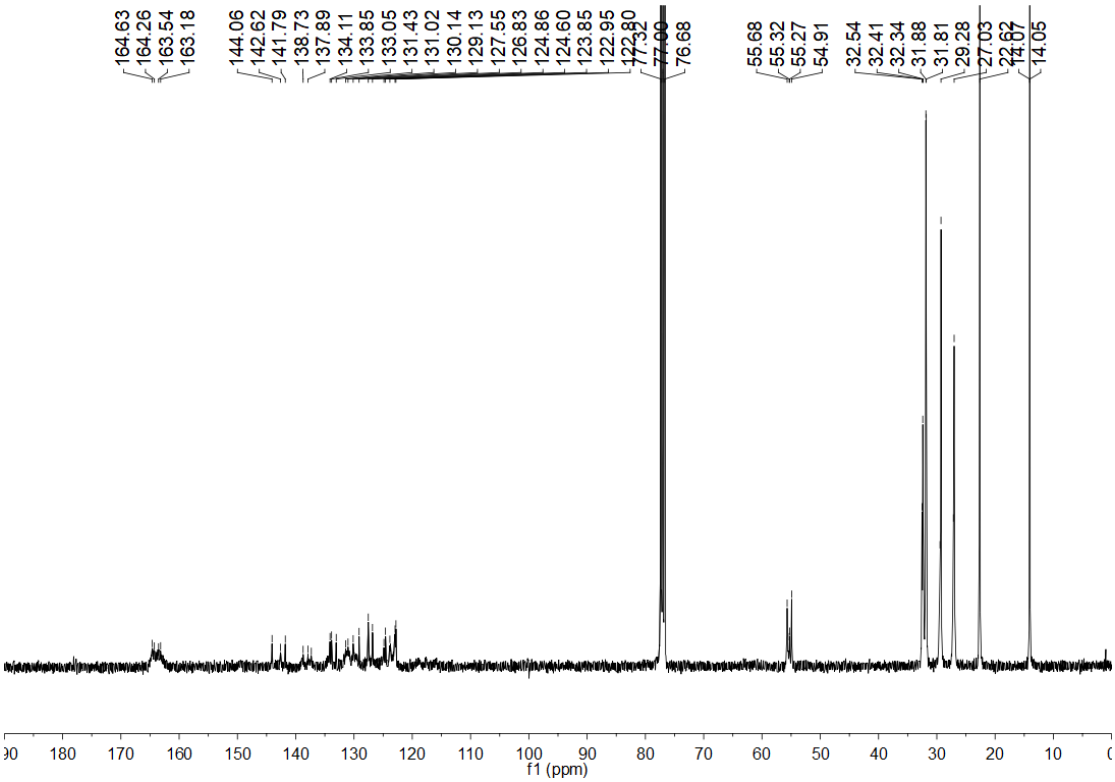
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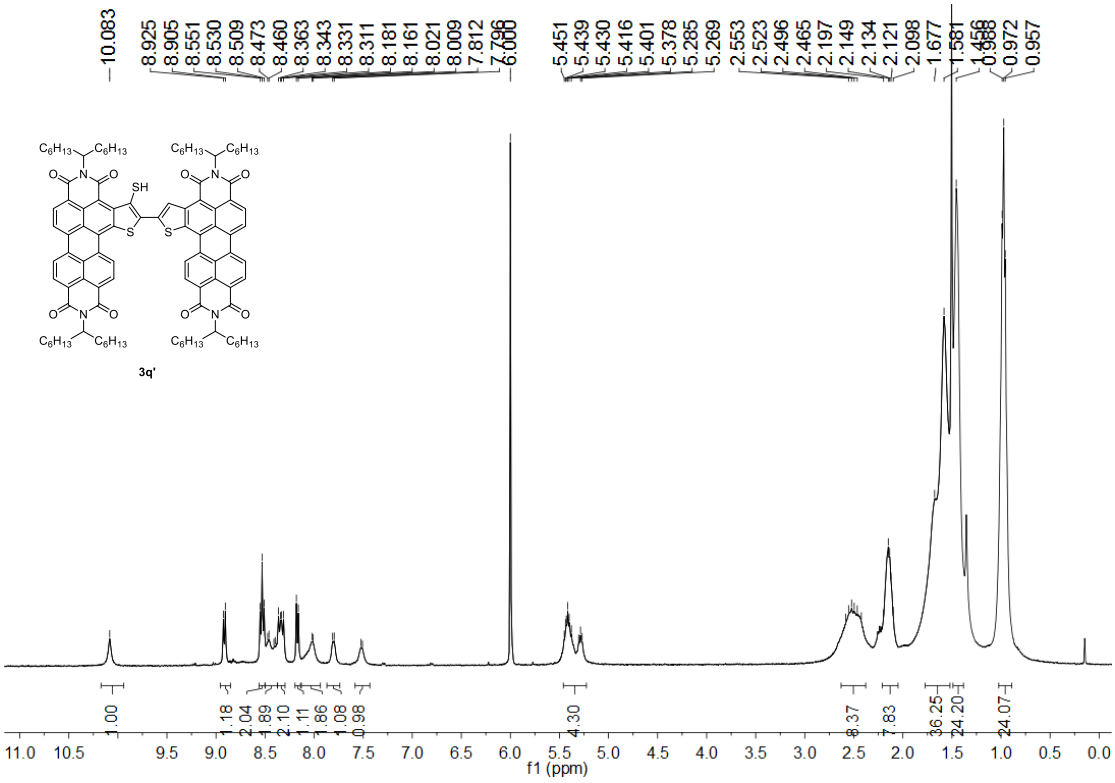
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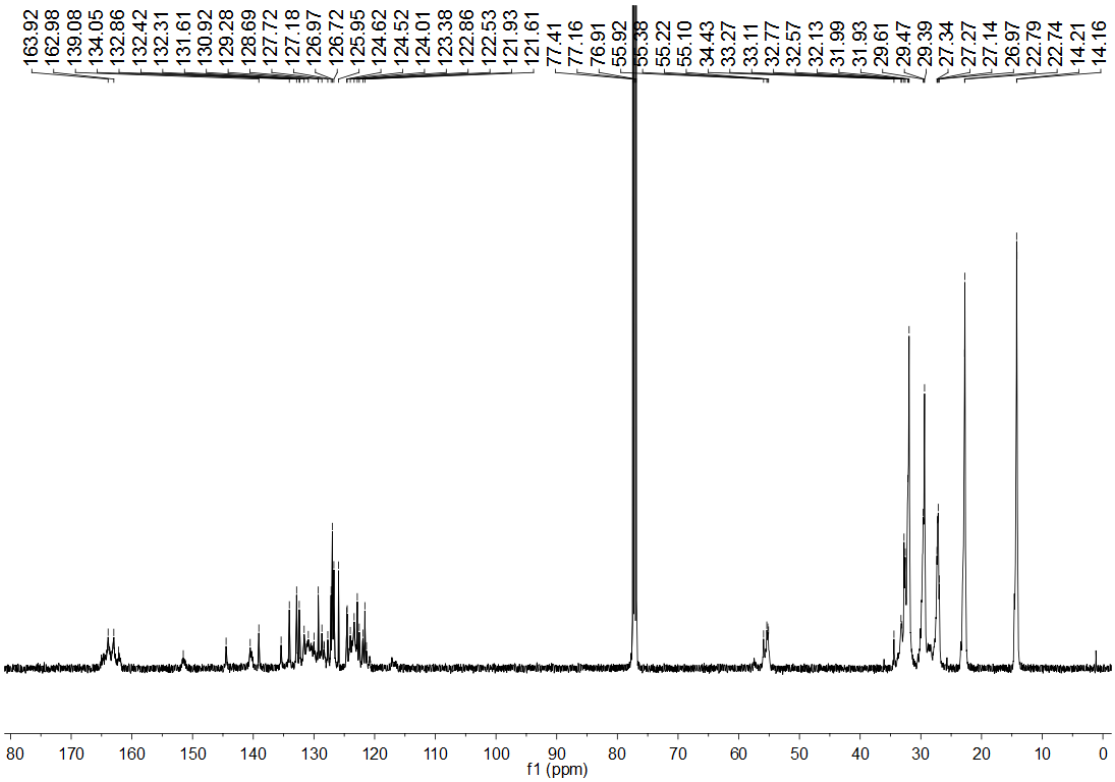
3q'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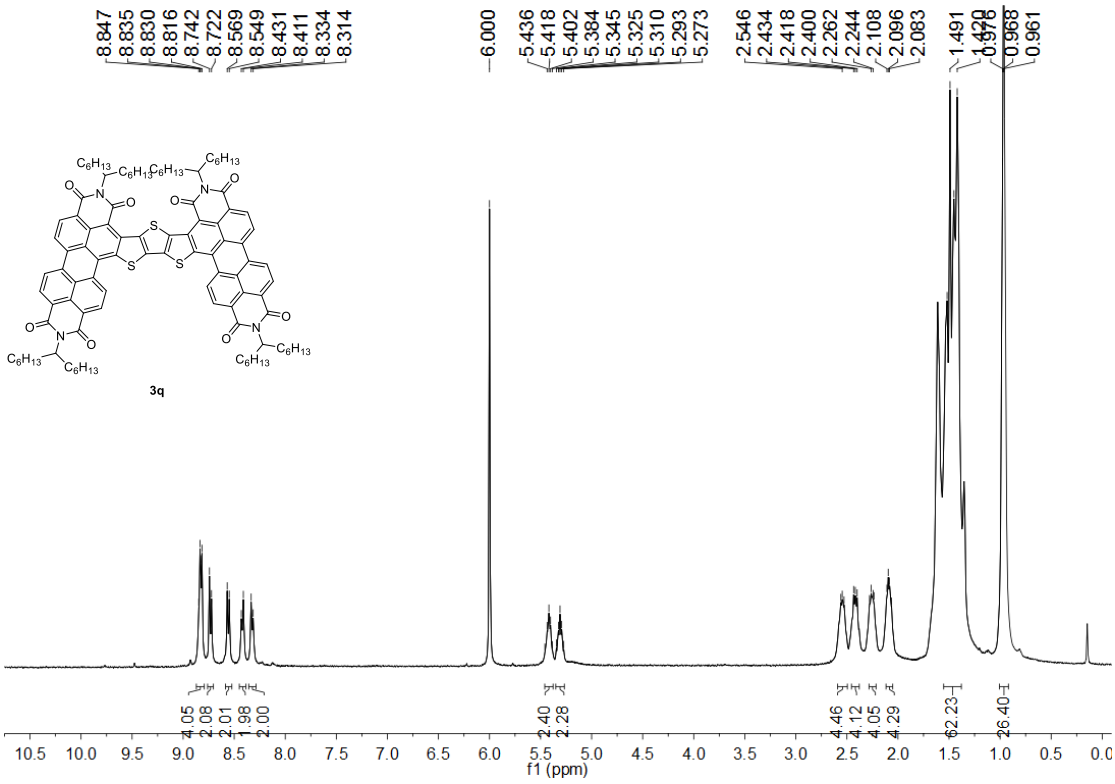
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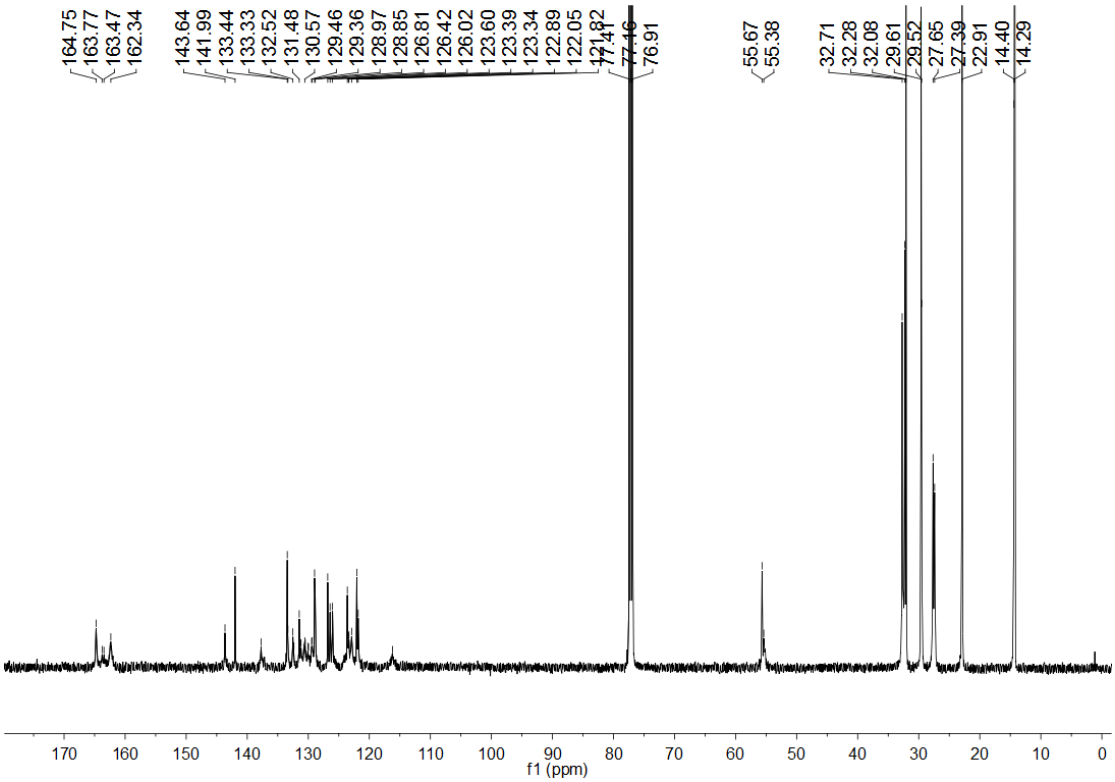
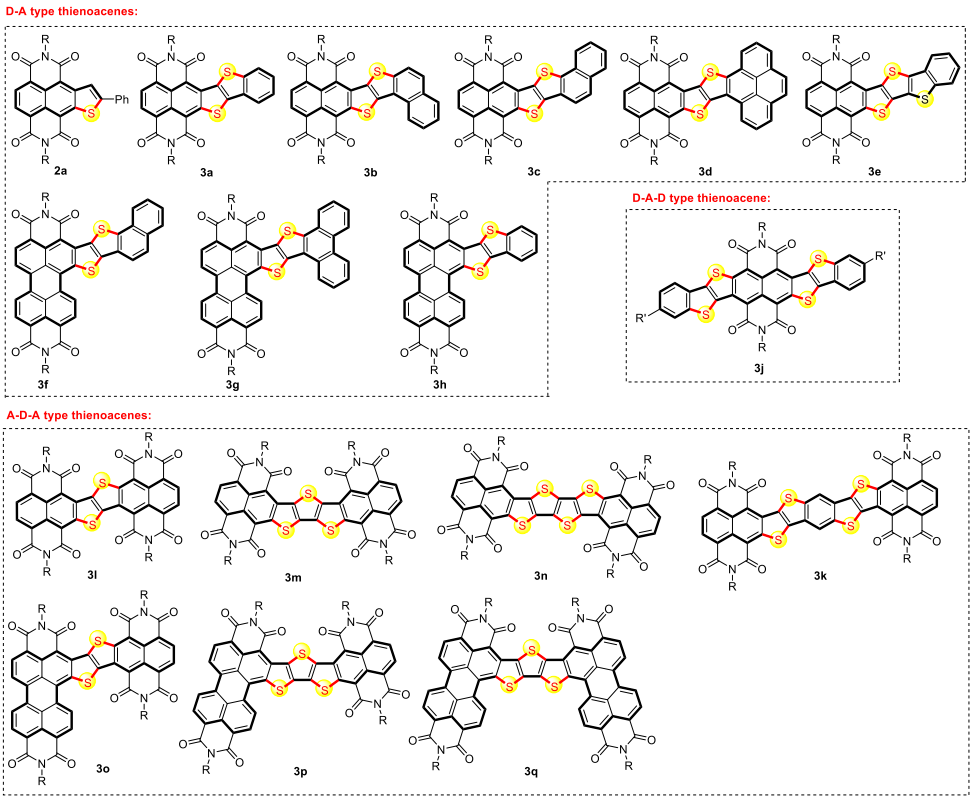
3q



8. Optical and Redox Properties of 2a and 3a-3h, 3j-3q

Scheme S4 Summary of the D-A, D-A-D, and A-D-A type thienoacenes



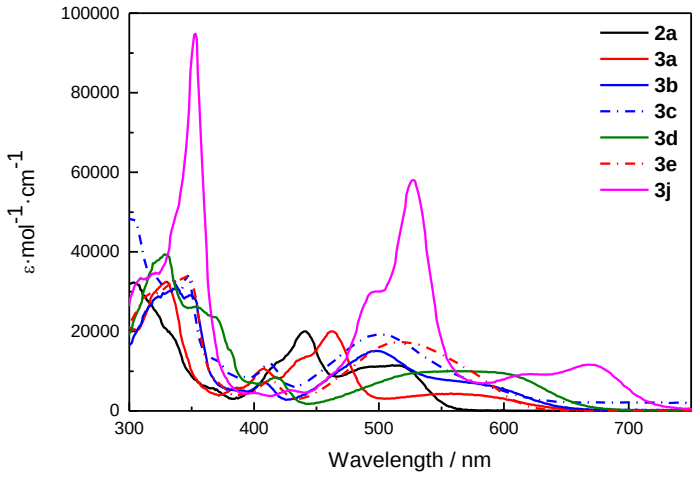


Figure S10 UV-vis absorption spectra of NDI-fused D-A (**2a** and **3a-e)** and D-A-D type (**3j**) thienoacenes in $CHCl_3$ solution (10 μM)

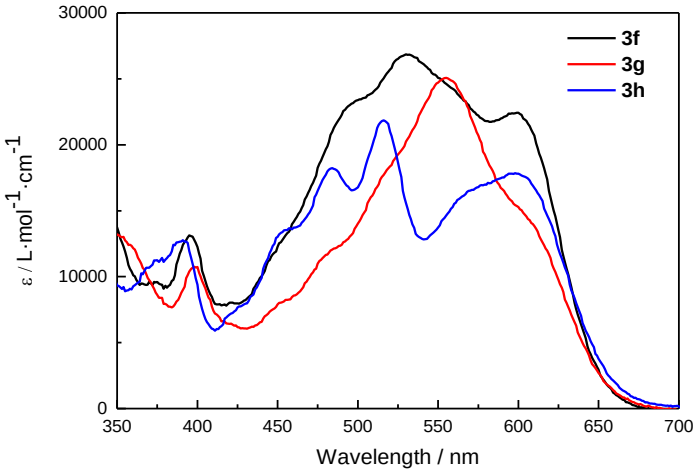


Figure S11 UV-vis absorption spectra of PDI-fused D-A type thienoacenes (**3f-h**) in $CHCl_3$ solution (10 μM)

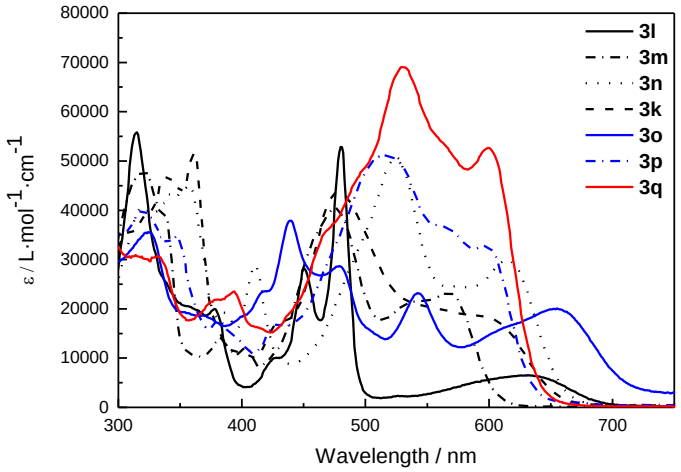


Figure S12 UV-vis absorption spectra of A-D-A type thienoacenes (**3l-n** and **3k-3q**) in $CHCl_3$ solution (10 μM)

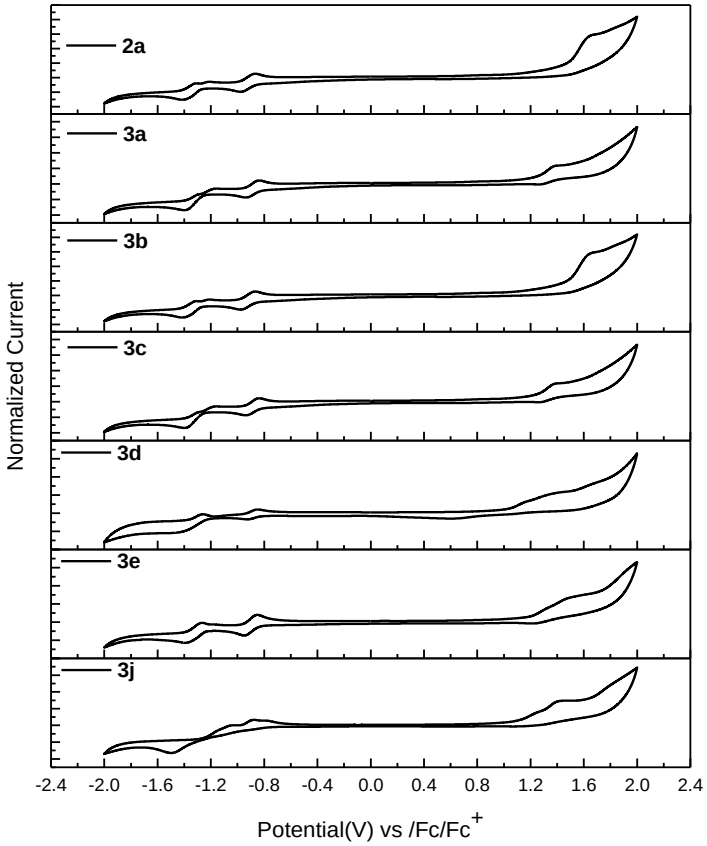


Figure S13 Cyclic voltammograms of NDI-fused D-A and D-A-D type thienoacenes (Measured in CH_2Cl_2 solution (1 mM) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte with a scan rate of 50 $mV \cdot s^{-1}$. Potentials are reported vs the Fc/Fc+ redox couple as an standard. Counter electrode: Pt, Reference electrode: Ag/ $AgNO_3$.)

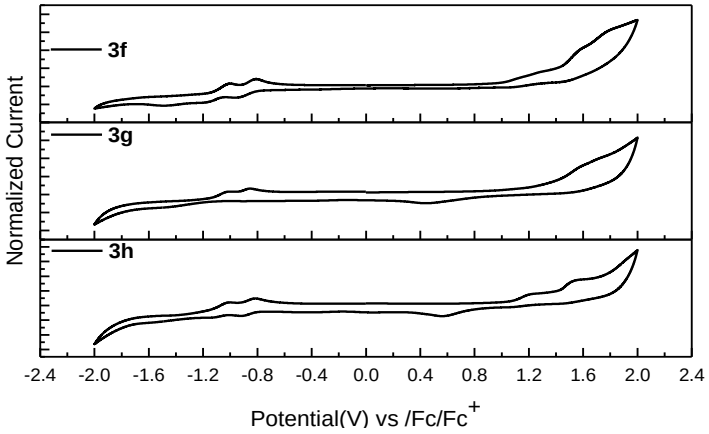


Figure S14 Cyclic voltammograms of PDI-fused D-A type thienoacenes (**3f-h**) in CH_2Cl_2 solution (1 mM)

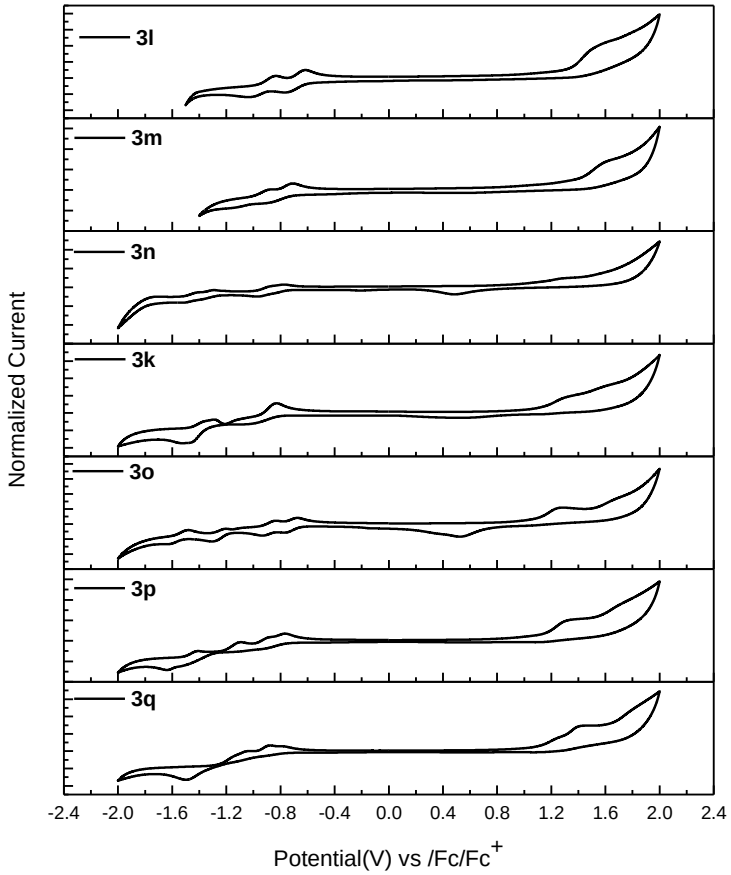


Figure S15 Cyclic voltammograms of A-D-A type thienoacenes (**3l-n** and **3k-3q**) in CH_2Cl_2 solution (1 mM)

Table S5 Optical and Redox properties of compounds **2a, 3a-3h**, **3j-3q**

	λ_{abs} nm	ε_{max} $M^{-1}\cdot cm^{-1}$	λ_{em} nm	λ_{onset} nm	E_{red1} [a] V	E_{red2} [a] V	$E_{g,opt}$ [b] eV	LUMO [c] eV	HOMO [d] eV
2a	441	20030	566	576	-1.12	-1.55	2.15	-3.68	-5.83
3a	463	20010	681	675	-1.09	-1.53	1.84	-3.71	-5.55
3b	498	15090	670	673	-1.09	-1.53	1.84	-3.71	-5.55
3c	500	19300	658	649	-1.09	-1.54	1.91	-3.71	-5.62
3d	560	10040	704	710	-1.07	-1.53	1.75	-3.73	-5.48
3e	518	17290	642	640	-1.08	-1.52	1.94	-3.72	-5.66
3f	530	26850	664	675	-1.07	-1.33	1.84	-3.73	-5.57
3g	555	25070	667	684	-1.11	-1.28	1.81	-3.69	-5.50
3h	516	21850	677	694	-1.05	-1.28	1.79	-3.75	-5.54
3j	527	58050	722	744	-1	-1.6	1.67	-3.8	-5.47
3k	478	43820	666	692	-1.13	-1.59	1.79	-3.67	-5.46
3l	480	52870	534	718	-0.88	-1.16	1.73	-3.92	-5.65
3m	476	40510	615	636	-1	-1.29	1.95	-3.8	-5.75
3n	524	50740	666	705	-1.06	-1.59	1.76	-3.74	-5.50
3o	440	37900	715	731	-0.91	-1.09	1.70	-3.89	-5.59

3p	517	51200	635	695	-1.01	-1.16	1.78	-3.79	-5.57
3q	530	69070	640	678	-1.14	-1.36	1.83	-3.66	-5.49

[a] Half-wave reduction potentials (vs. Fc/Fc+) measured in $CHCl_2$ with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte with a scan rate of 50 $mV \cdot s^{-1}$. [b] Optical band gap ($E_{g,opt}$) calculated from the onset of the absorption peak (λ_{onset}): $E_{g,opt}$ = 1240 / λ_{onset}. [c] LUMO values was calculated from the first reduction potentials (E_{red1}): LUMO = - 4.80 eV - E_{red1}. [d] HOMO values was calculated from HOMO = LUMO - $E_{g,opt}$.

9. Reference

[1] a) Wu, J.; He, D.; Zhang, L.; Liu, Y.; Mo, X.; Lin, J.; Zhang, H.-J., Direct synthesis of large-scale *ortho*-iodinated perylene diimides: key precursors for functional dyes. *Org. Lett.* **2017**, *19*, 5438-5441. b) Wu, J.; He, D.; Wang, Y.; Su, F.; Guo, Z.; Lin, J.; Zhang, H.-J., Selective ortho-π-extension of perylene diimides for rylene dyes. *Org. Lett.* **2018**, *20*, 6117-6120.

[2] Su, F.; Chen, G.; Korevaar, P. A.; Pan, F.; Liu, H. Guo, Z.; Schenning, A. P. H. J.; Zhang, H.-J.; Lin, J.; Jiang, Y.-B., Discrete π-stacks from self-assembled perylenediimide analogues. *Angew. Chem. Int. Ed.* **2019**, *58*, 15273-15277.

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