Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Functionalized Anthrathienothiophenes: Synthesis, Properties, and Integration into OFETs

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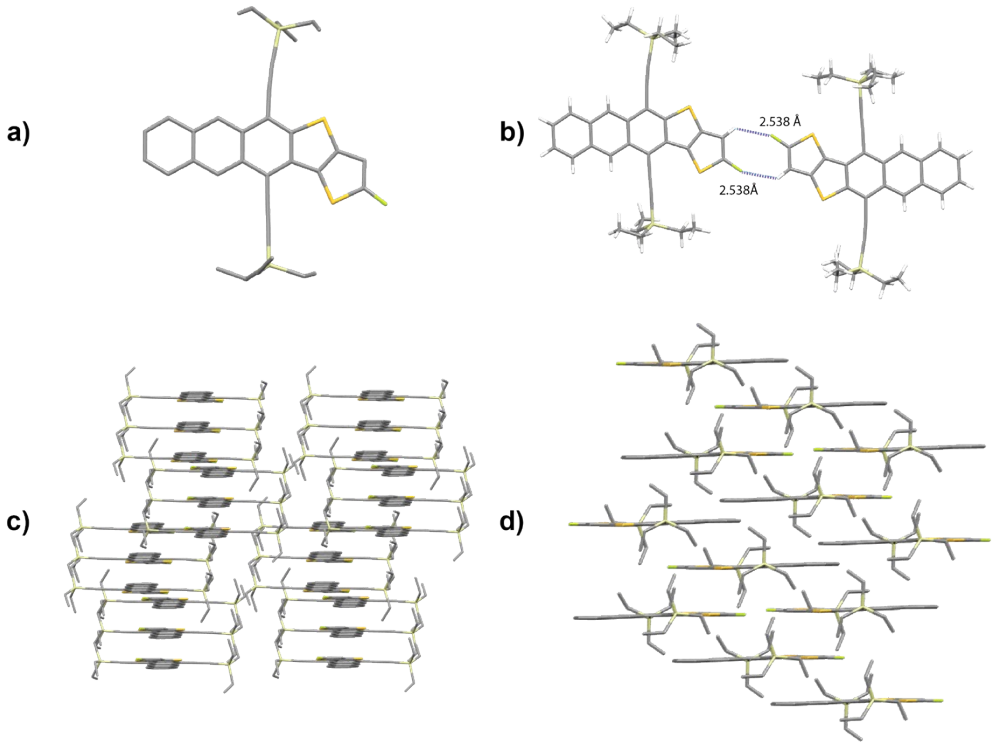


Figure S1: a) Crystal Structure, b) intermolecular close contacts, c) short axis packing, and d) long axis packing for F-TES ATT. Where applicable, hydrogens have been omitted for clarity.

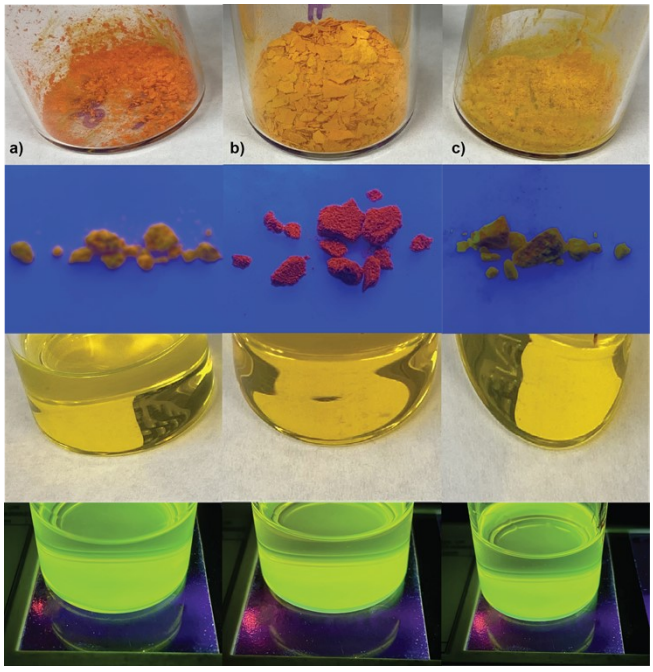


Figure S2: From top to bottom; solid state, solid state fluorescence, solution, solution fluorescence images for a) TiPS ATT, b) F-TiPS ATT, and c) DiF-TiPS ATT. Solutions of each compound were prepared in toluene at a concentration of 50 µM.

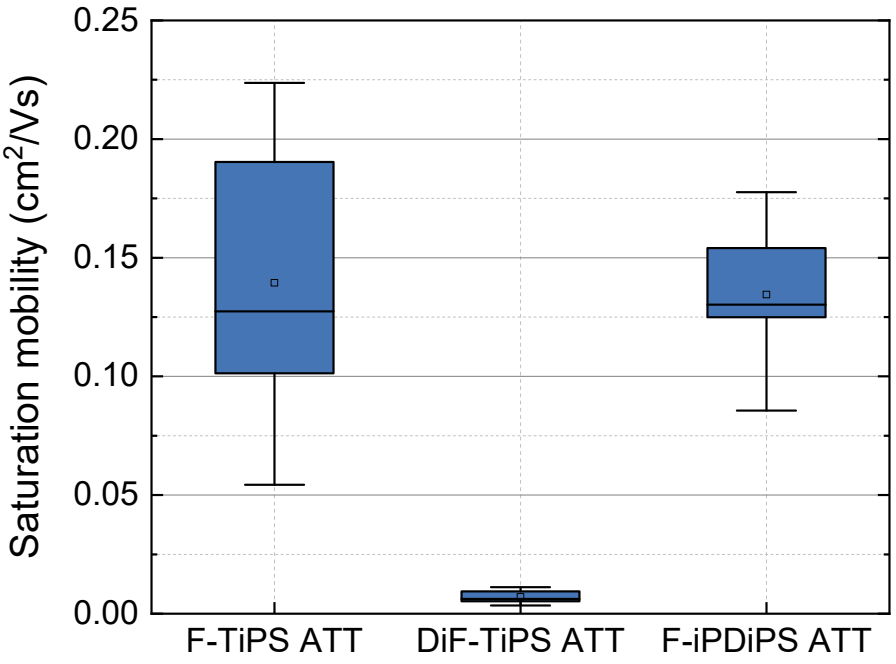


Figure S3: Statistical mobilities for 5 devices fabricated from ATT derivatives exhibiting 2-dimensional crystal packing. Devices fabricated for each material have varying channel lengths between 30-100 μm.

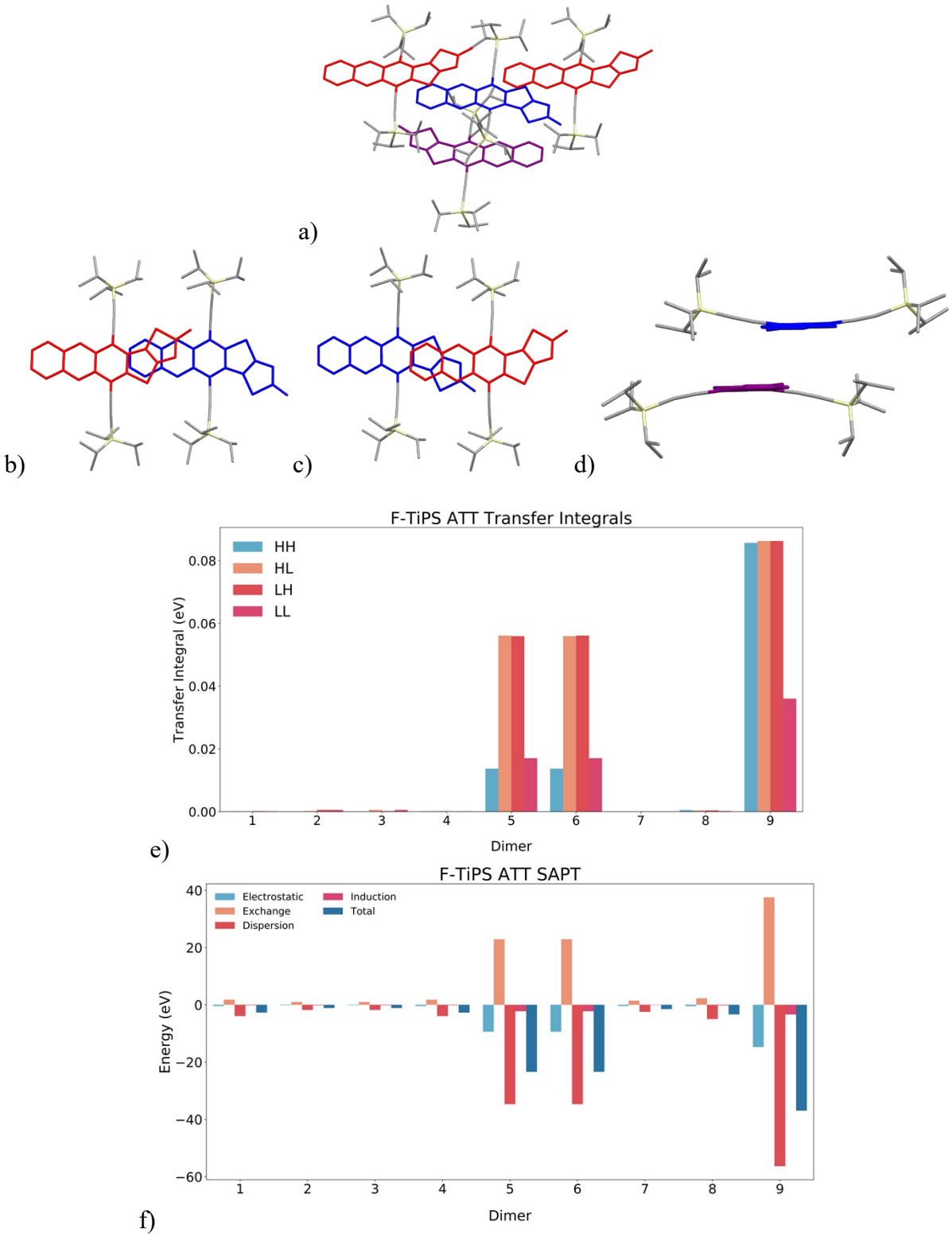


Figure S4: a) Close contact dimeric pairs notated as b) Dimer 5, c) Dimer 6, d) Dimer 9 used for e) coupling and f) SAPT calculations for F-TiPS ATT.

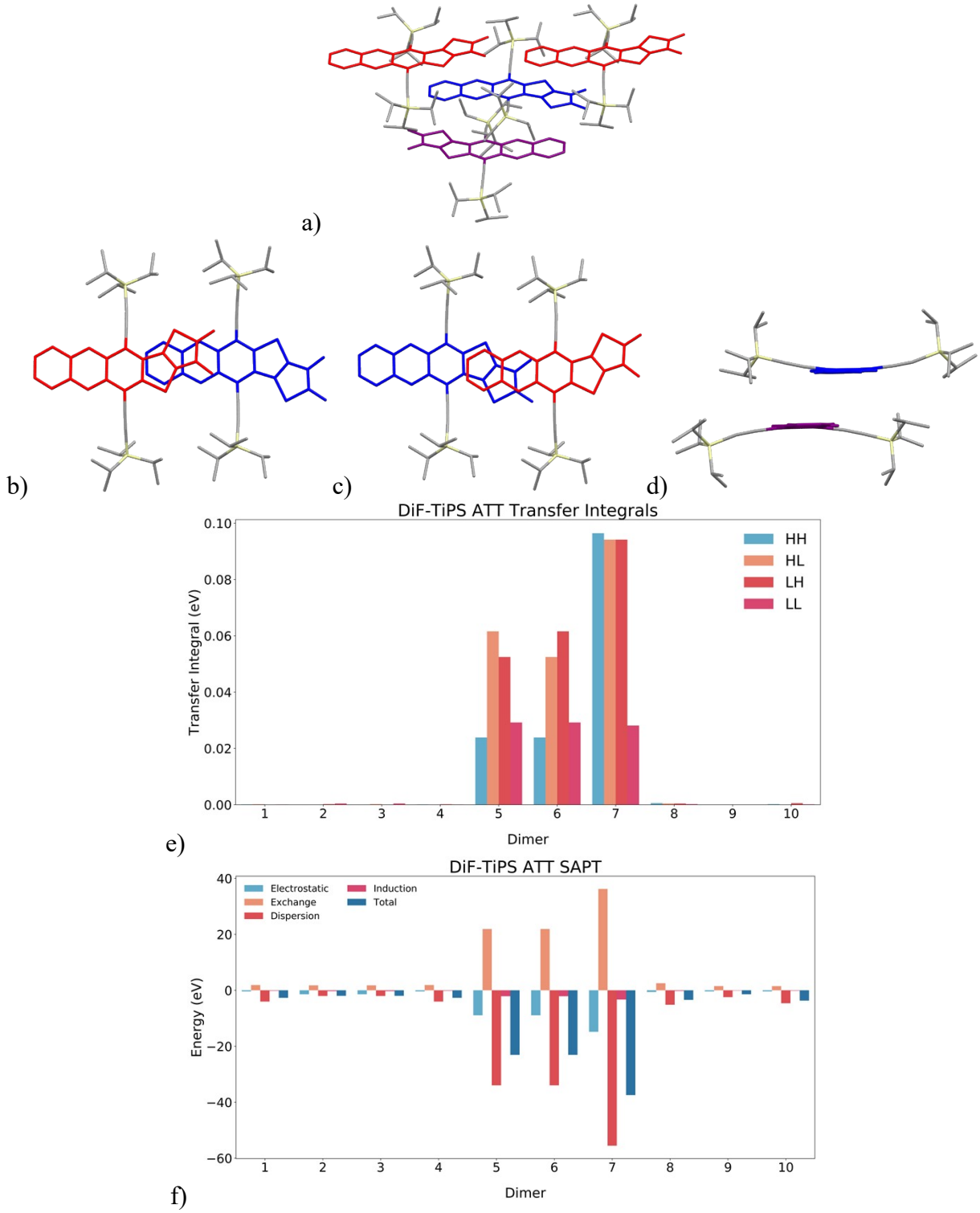


Figure S5: a) Close contact dimeric pairs notated as b) Dimer 5, c) Dimer 6, d) Dimer 7 used for e) coupling and f) SAPT calculations for DiF-TiPS ATT.

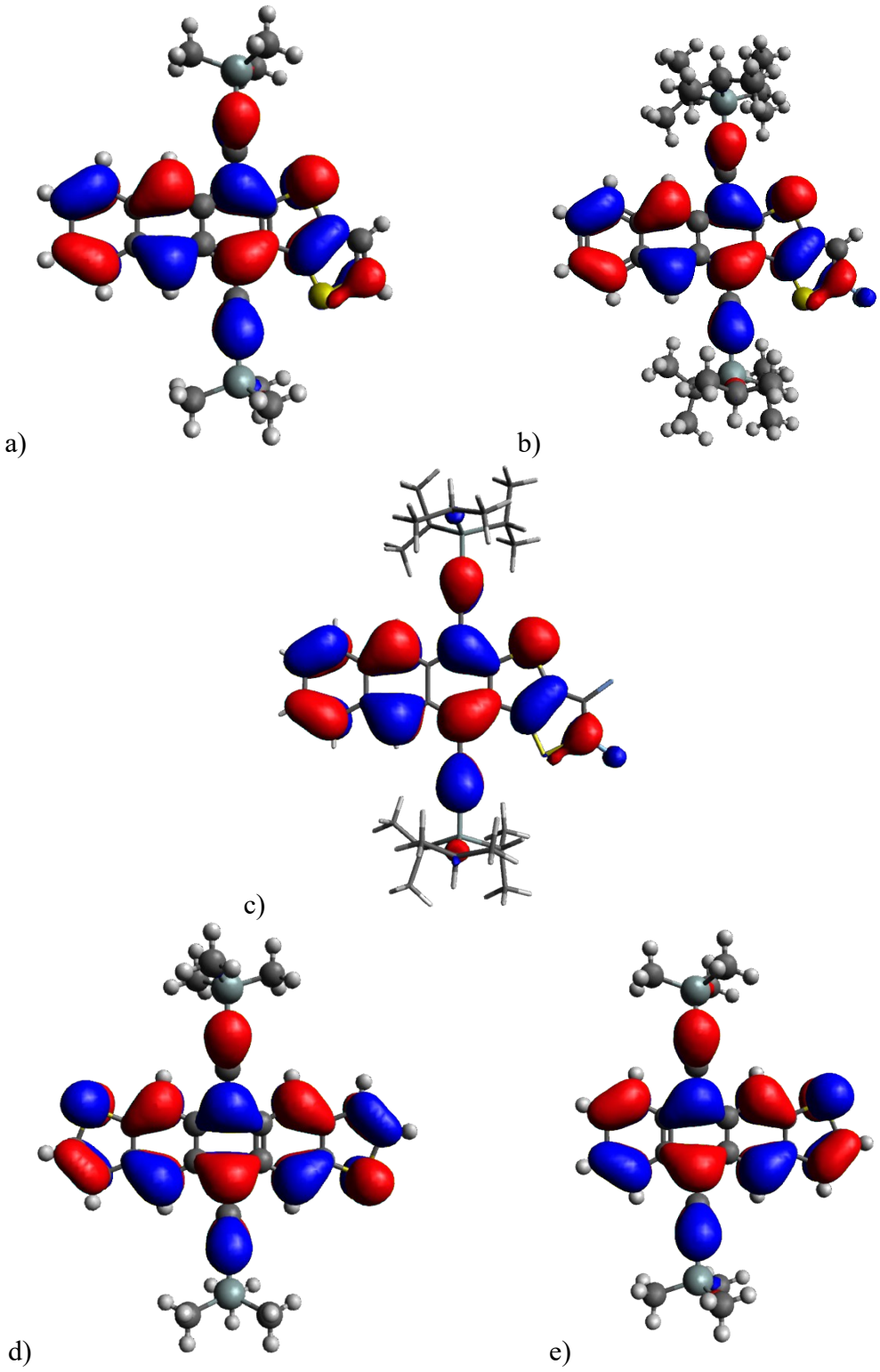


Figure S6: Molecular orbital diagrams for the HOMOs of a) ATT, b) F-ATT, c) DiF-ATT, d) anthradithiophene (ADT), e) thienoanthracene (TA).

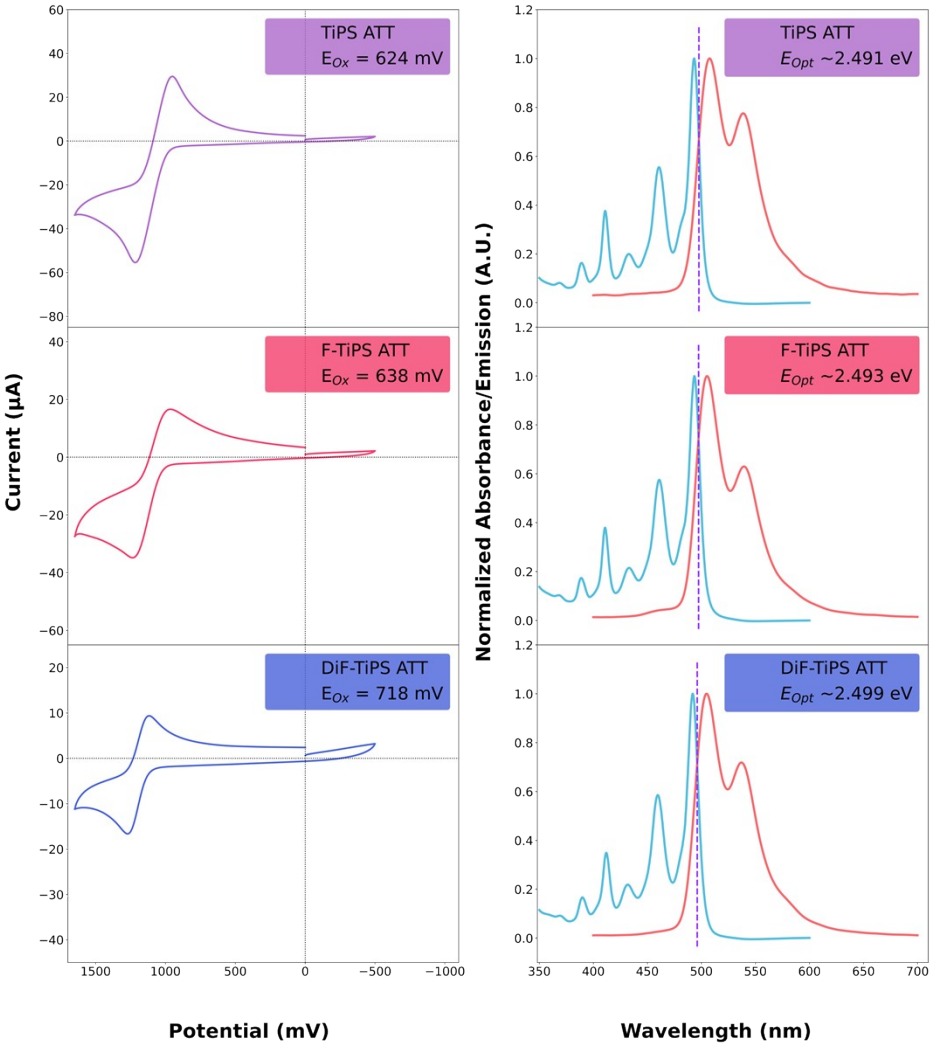


Figure S7: Cyclic voltammetry (left) and absorbance/emission (right) plots for the effect of fluorine on anthrathienothiophene. CV were run in 0.1 M $Bu_4NH_4PF_6$ in DCM with glassy carbon working, aluminum counter, and Ag/AgCl in 3 M NaCl reference electrodes and E_{Ox} is referenced to Fc/Fc^+ for each compound. Absorbance and emission spectra were run in toluene at a concentration of 50 µM, and E_{opt} is estimated from the intersection point of the absorbance and emission traces.

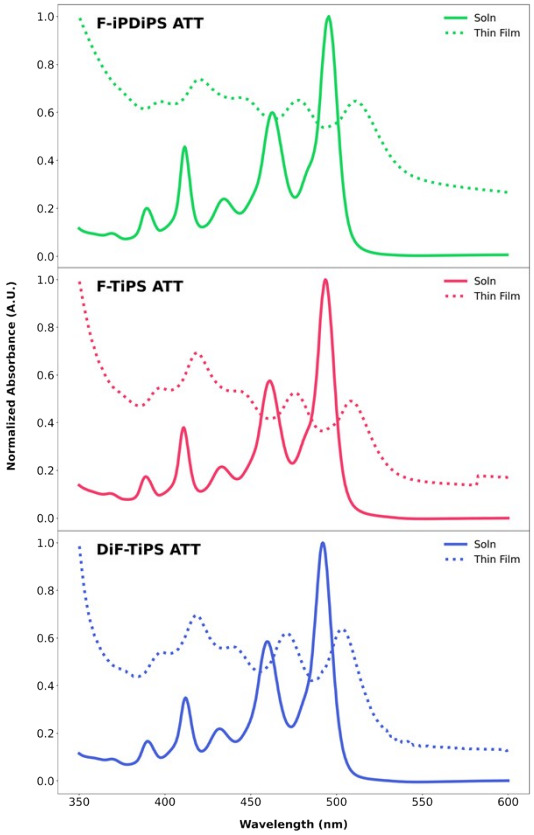
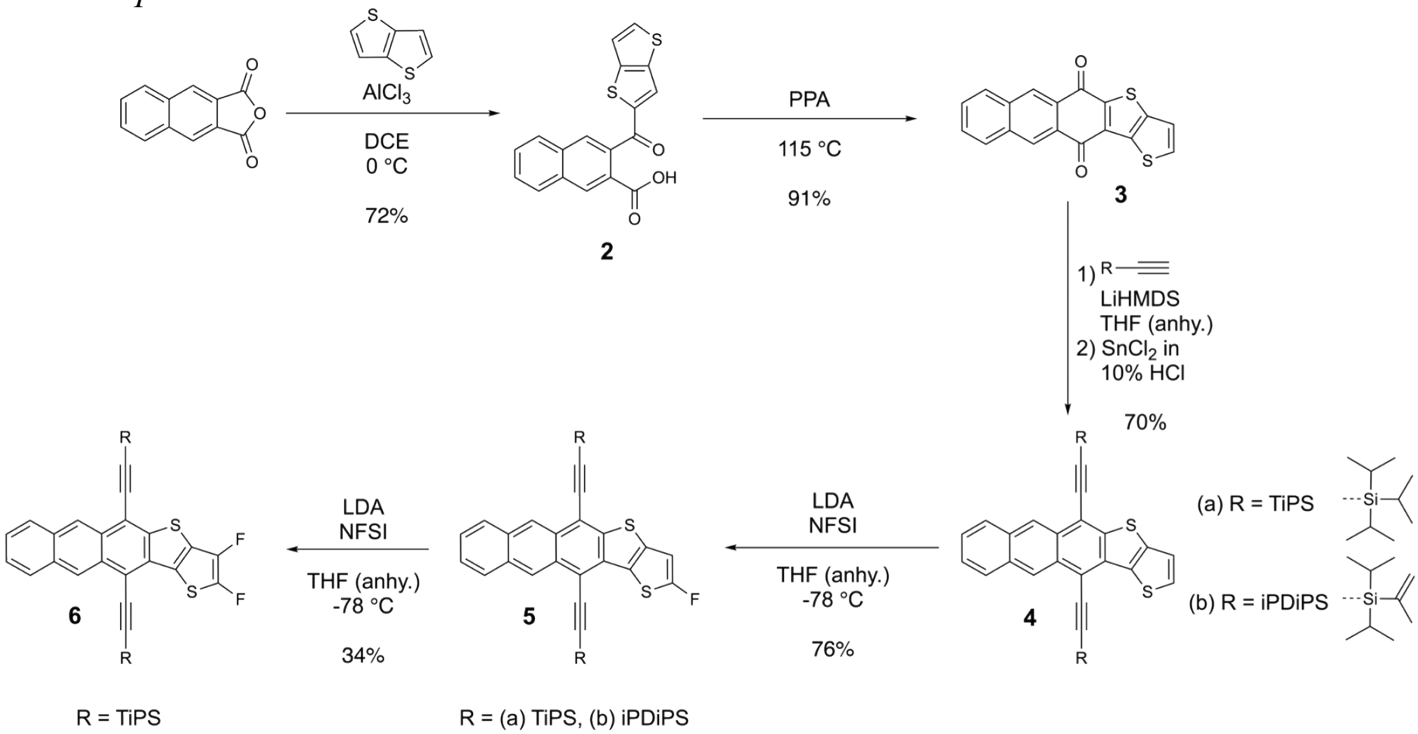
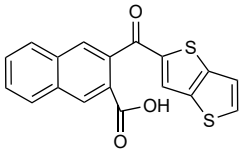


Figure S8: Solution and thin film UV-Vis traces for the ATT series. Thin films were dropcast from toluene and allowed to slowly evaporate under ambient conditions.

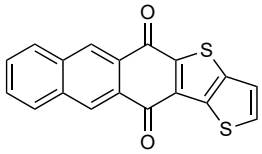
Experimental



All chemicals utilized in the synthesis were purchased from commercial vendors and used without additional purification unless otherwise stated. Bulk solvents were purchased from VWR, while anhydrous, stabilizer free, THF was purchased from Sigma-Aldrich. NMR spectra were measured on either 400 MHz Bruker or 500 MHz JEOL spectrometer, and all chemical shifts are reported in ppm and referenced to their indicated deuterated solvents. UV-Vis absorbance and fluorescence were measured with Agilent Cary 60 UV-vis spectrometer and StellarNet Inc. fluorimeter respectively. Crystal structures were collected and refined by Dr. Sean Parkin at the University of Kentucky-Department of Chemistry using a dual-microsource Bruker D8 Venture κ-axis diffractometer (MoKα and CuKα) with large-area 'Photon-II' CMOS detector.



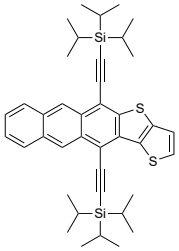
3-{thieno[3,2-b]thiophene-2-carbonyl}naphthalene-2-carboxylic acid (2):
In a 2 neck round bottom flask fitted with an addition funnel, 1.64 g of naphthalic anhydride (8.3mmol, 1 eq) was dissolved in 33 mL of DCE. This solution was then placed under inert atmosphere and cooled to 0 °C. To this solution, 2.43 g $AlCl_3$ (18.3 mmol, 2.2 eq) was added in one portion and allowed to stir at 0 °C for 30 min. In the attached addition funnel, 2 g of thieno[3,2-b]thiophene (8.3 mmol, 1 eq) was dissolved in 40 mL DCE. This solution was then added dropwise while maintaining the solution temperature at 0 °C. After all the thieno[3,2-b]thiophene solution was added, the resulting reaction mixture was allowed to warm to room temperature overnight. The solution was quenched with 10% HCl and the resulting precipitate was collected by vacuum filtration and washed with water followed by MeOH to yield 3.34 g (69%) of a white powder. Characterization matches previously reported data.[1]



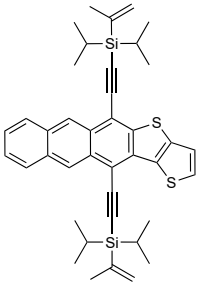
Anthra[2,3-b]thieno[2,3-d]thiophene-5,12-dione (3):
A 100 mL round bottom flask was charged with 2.50 g (7.38 mmol) of 2. In a separate beaker, 50 mL of polyphosphoric acid was preheated until free-flowing and added to the round bottom containing compound 2. The resulting mixture was then heated and swirled until a homogenous deep purple solution was achieved, at which point the flask was loosely stoppered and placed in an aluminum heating mantle and heated to 115 °C for 24 h. The hot acid mixture was then poured over 700 mL ice water and the flask was rinsed with DI water until all of the mixture was transferred and the resulting precipitate was allowed to stir for 2 h while it warmed to RT. The precipitate was then extracted via Soxhlet column extraction with EtOAc as the eluting solvent until extraction produced no more yellow color. The solvent was removed under reduced pressure, and the resulting solid was collected by filtering with MeOH to yield 2.15 g (91%) of a fluffy yellow solid. Due to extremely low solubility of this material, the collected solid was used without further purification.

General Method for ethynylation of quinone 3:
In a flame dried round bottom flask, cooled under N_2, (5 eq) trialkylsilylacetylene was dissolved in anhydrous THF (0.25 M wrt acetylene), and cooled to 0 °C. To this solution, (4.8 eq) of 1 M LiHMDS solution was added slowly. The resulting solution was allowed to stir at 0 °C for 30 min. To this solution, and (1 eq) of anthrathienothiophene quinone (3) was then added in one portion, and the solution was allowed to slowly warm to room temperature. The reaction mixture was then quenched with a saturated solution of $SnCl_2 \bullet 2H_2O$ in 10% HCl. This solution was

allowed to stir at RT overnight. The solution was then extracted into hexanes and washed with brine. The organic layer was dried with $MgSO_4$ and passed through a pad of silica and eluted with Hexanes (R_f = 0.3).

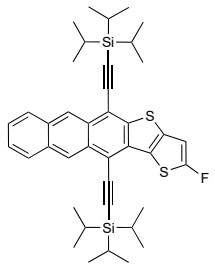


5,12-bis(triisopropylsilylethynyl)anthrathienothiophene (4a):
0.47 g (70%) of a bright orange solid. ^{1}H NMR (400 MHz; CDCl3) δ 9.21 (s, 1H), 9.04 (s, 1H), 8.06 (dd, *J* = 9.7, 6.3, 3.4 Hz, 2H), 7.71 (d, J = 5.1 Hz, 1H), 7.53 (dd, J = 6.6, 3.2 Hz, 2H), 7.38 (d, J = 5.1 Hz, 1H), 1.33 (m, 42H). ^{13}C NMR (101 MHz; CDCl3): δ 146.7, 139.9, 134.1, 133.9, 131.96, 131.88, 131.73, 129.9, 128.9, 128.58, 128.53, 126.10, 126.04, 125.96, 124.6, 120.3, 115.8, 112.4, 106.6, 105.3, 103.7, 102.6, 19.12, 19.04, 11.79, 11.61. ESI-MS calcd for $C_{40}H_{51}S_2Si_2$ ([M+H]$^+$) m/z = 651.2971, found 651.2966. mp: 219.17 °C (DSC). Structure confirmed by XRD.

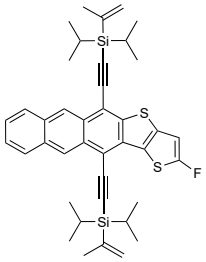


5,12-bis(isopropyldiisopropenylsilylethynyl)anthrathienothiophene (4b):
0.84 g (67%) of a bright orange powder. ^{1}H NMR (400 MHz; $CDCl_3$) *δ* 9.21 (1H), 9.05 (1H), 8.10—8.04 (m, 2H), 7.72 (d, *J* = 5.2 Hz, 1H), 7.54 (dd, *J* = 5.36, 2.4 Hz, 2H), 7.38 (d, *J* = 5.2 Hz, 1H), 5.92 (q, *J* = 1.4 Hz, 1H), 5.89 (q, *J* = 1.4 Hz, 1H), 5.81 (q, *J* = 1.4 Hz, 1H), 5.76 (q, *J* = 1.4 Hz, 1H), 2.09 (t, *J* =1.4 Hz, 3H), 2.07 (t, *J* =1.4 Hz, 3H), 1.38—1.23 (m, 28H). ^{13}C NMR (101 MHz; CDCl3): δ 146.9, 141.09, 141.02, 140.0, 134.11, 133.98, 132.02, 131.93, 131.88, 129.9, 129.64, 129.46, 128.9, 128.57, 128.53, 126.18, 126.12, 125.94, 124.6, 120.3, 115.8, 112.3, 105.2, 104.1, 103.9, 103.1, 77.5, 77.2, 76.8, 24.49, 24.36, 18.44, 18.37, 18.36, 18.28, 11.9, 11.7. ESI-MS calcd for $C_{40}H_{46}S_2Si_2$ (M^+) m/z = 646.2579, found 646.2573. mp: 202.85 °C (DSC).

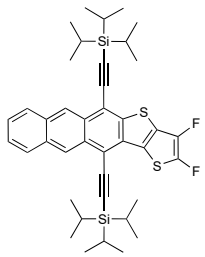
General Method for fluorination of the 2- and 3- positions of ATT:
In a flame dried round bottom flask, cooled under N_2, (1 eq) of compound 4/5 was dissolved in dry THF [0.02 M] and cooled to -78 °C. Once cooled, 1 M LDA solution (4 eq) was added slowly, the resulting crimson solution was allowed to stir at – 78 °C for 30 min before (5 eq) of NFSI was added in one portion. The resulting mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with water, and extracted into hexanes. The organic layer was then washed with water (3 x 100 mL), dried with $MgSO_4$, and the solvent was removed under reduced pressure. The resulting solid was then purified by column chromatography with hexanes as the eluent (R_f = 0.43) for 2-fluoro derivatives, and (Rf = 0.52) for 2,3-difluoro derivatives.



2-fluoro-5,12-bis(triisopropylsilylethynyl)anthrathienothiophene (5a):
0.39 g (76%) of a pale orange-yellow solid. ^{1}H NMR (400 MHz; CDCl3) δ 9.16 (s, 1H), 9.03 (s, 1H), 8.05 (dd, J = 10.4, 6.1 Hz, 2H), 7.53 (dd, J = 5.7, 3.4 Hz, 2H), 6.92 (s, 1H), 1.38—1.29 (m, 42H). ^{13}C NMR (101 MHz; CDCl3): δ 170.7, 167.7, 144.0, 135.12, 135.06, 134.4, 132.1, 131.8, 129.9, 128.66, 128.60, 128.49, 126.16, 126.12, 125.7, 124.8, 121.1, 115.7, 111.25, 111.22, 106.67, 106.66, 105.4, 103.5, 102.66, 102.54, 102.52, 19.0, 11.77, 11.59. ESI-MS calcd for $C_{40}H_{49}FS_2Si_2$ (M^+) m/z = 668.2798, found 668.2790. mp: 295.93 °C (DSC). Structure confirmed by XRD



2-fluoro-5,12-bis(isopropenyldiisopropylsilylethynyl)anthrathienothiophene (5b):
0.28 g (61%) of a pale orange powder. ^{1}H NMR (500 MHz; CDCl3) δ 9.14 (s, 1H), 9.02 (s, 1H), 8.05 (dd, *J* = 2H), 7.53 (dd, *J* = 6.4, 3.0 Hz, 2H), 6.91 (s, 1H), 5.92 (broadened q, *J* =1.4 Hz, 1H), 5.89 (broadened q, *J* =1.4 Hz, 1H), 5.80 (broadened q, *J* =1.4 Hz, 1H), 5.75 (broadened q, *J* =1.4 Hz, 1H), 2.09 (br s), 2.06 (br s), 1.34—1.24 (m, 28H). ^{13}C NMR (101 MHz; CDCl3): δ 170.5, 167.5, 143.8, 140.6, 134.9, 134.2, 131.8, 131.6, 129.53, 129.40, 129.2, 128.30, 128.27, 128.18, 125.92, 125.88, 125.4, 124.5, 115.3, 104.9, 103.8, 102.7, 102.36, 102.22, 77.0, 24.13, 24.02, 18.10, 18.02, 17.94, 17.92, 17.85, 11.6, 11.4. ESI-MS calcd for $C_{40}H_{46}FS_2Si_2$ ($[M+H]^+$) m/z = 665.2563, found 665.2561. mp: 128.54 °C (DSC). Structure confirmed by XRD.

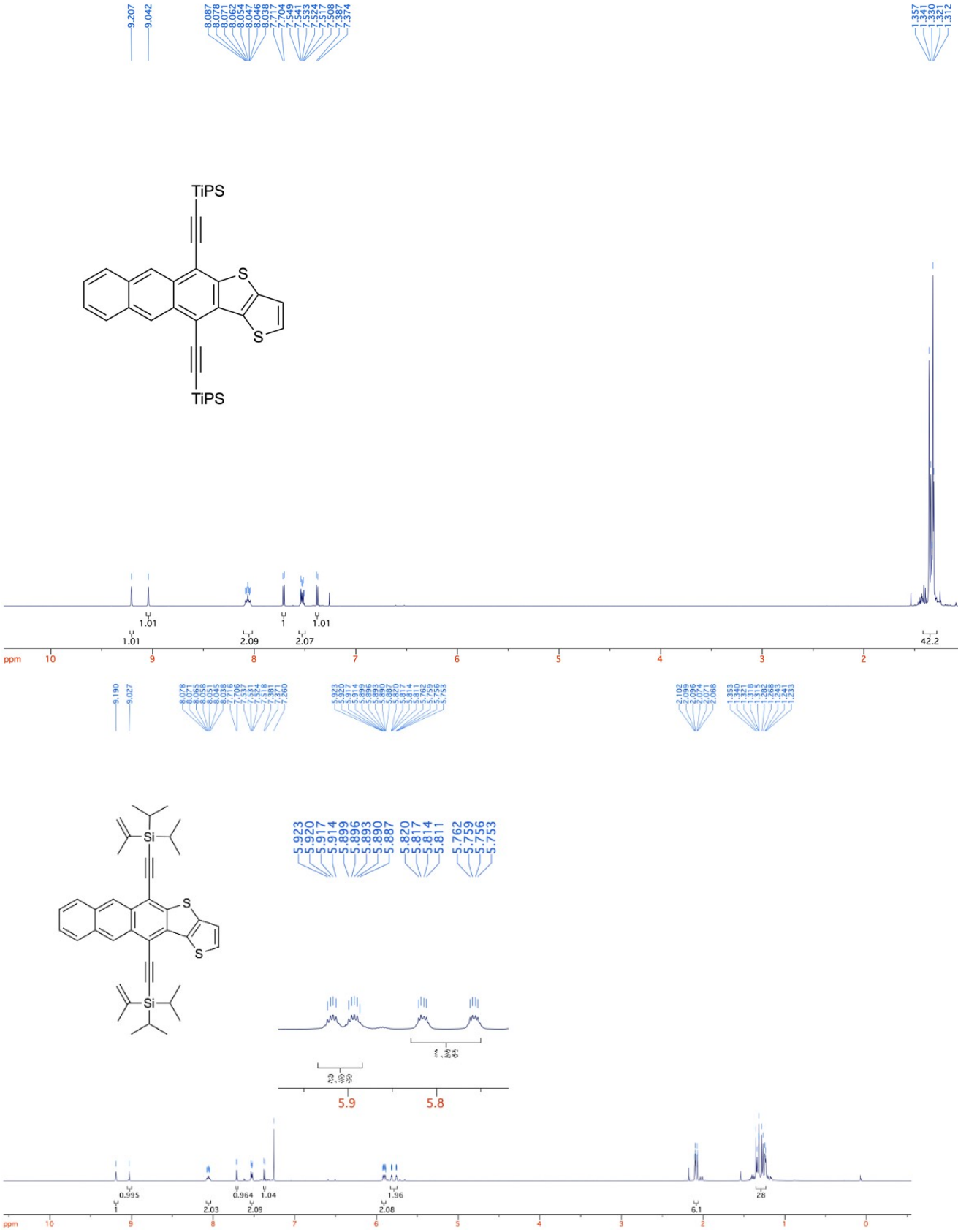


2,3-difluoro-5,12-bis(triisopropylsilylethynyl)anthrathienothiophene (6):
0.165 g (34%) of a dull-yellow solid. ^{1}H NMR (400 MHz; CDCl3) δ 9.14 (s, 1H), 9.03 (s, 1H), 8.05 (m, 2H), 7.54 (dd, J = 6.5, 3.2 Hz, 2H), 1.32 (m, 42H). ^{13}C NMR (101 MHz; CDCl3): δ 132.16, 132.04, 129.8, 128.79, 128.61, 128.50, 126.4, 125.8, 124.9, 116.0, 111.88, 111.85, 107.62, 107.60, 106.2, 103.2, 102.1, 19.09, 19.02, 11.74, 11.57. ESI-MS calcd for $C_{40}H_{48}F_2S_2Si_2$ ($[M+H]^+$) m/z = 687.2782, found 687.2780. Decomposes before melting at 390.39 °C, (DSC). Structure confirmed by XRD.

XRD Methods

X-ray diffraction data were collected at 90.0(2) K on a Bruker D8 Venture kappa-axis diffractometer MoK(α) X-rays. Raw data were integrated, scaled, merged, and corrected for Lorentz/polarization effects using the APEX3 package.[2] Corrections for absorption were applied using SADABS.[3] The structures were solved by dual-space methods (SHELXT)[4] and refined against F^2 by weighted full-matrix least-squares (SHELXL).[5] Hydrogen atoms were found in difference maps, but subsequently placed at calculated positions and refined using riding models. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.[6] Crystal data and relevant details of the structure determinations are summarized in Tables 2181075-2181078 and selected geometrical parameters are given in Tables 2181075-2181078.

[1]H NMR

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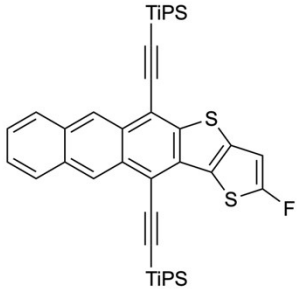
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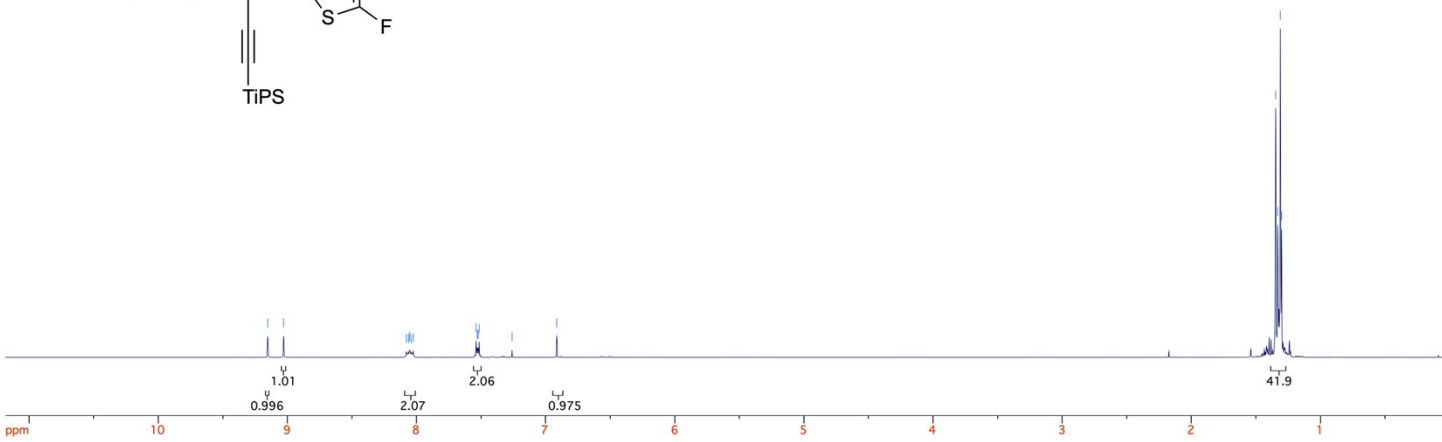
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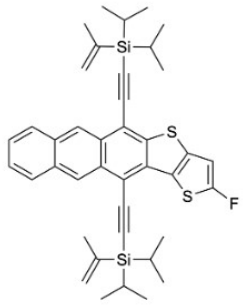
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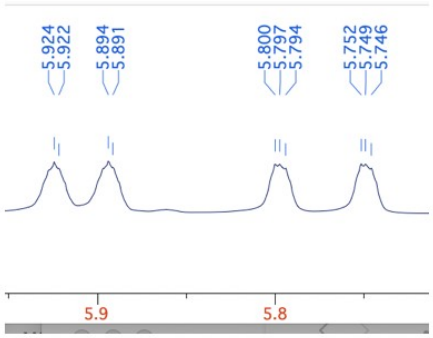
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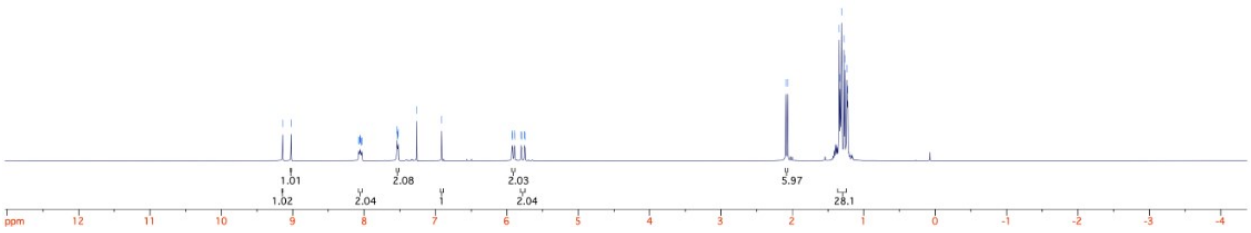
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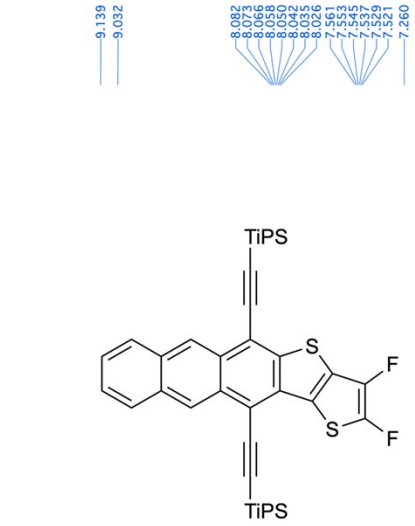
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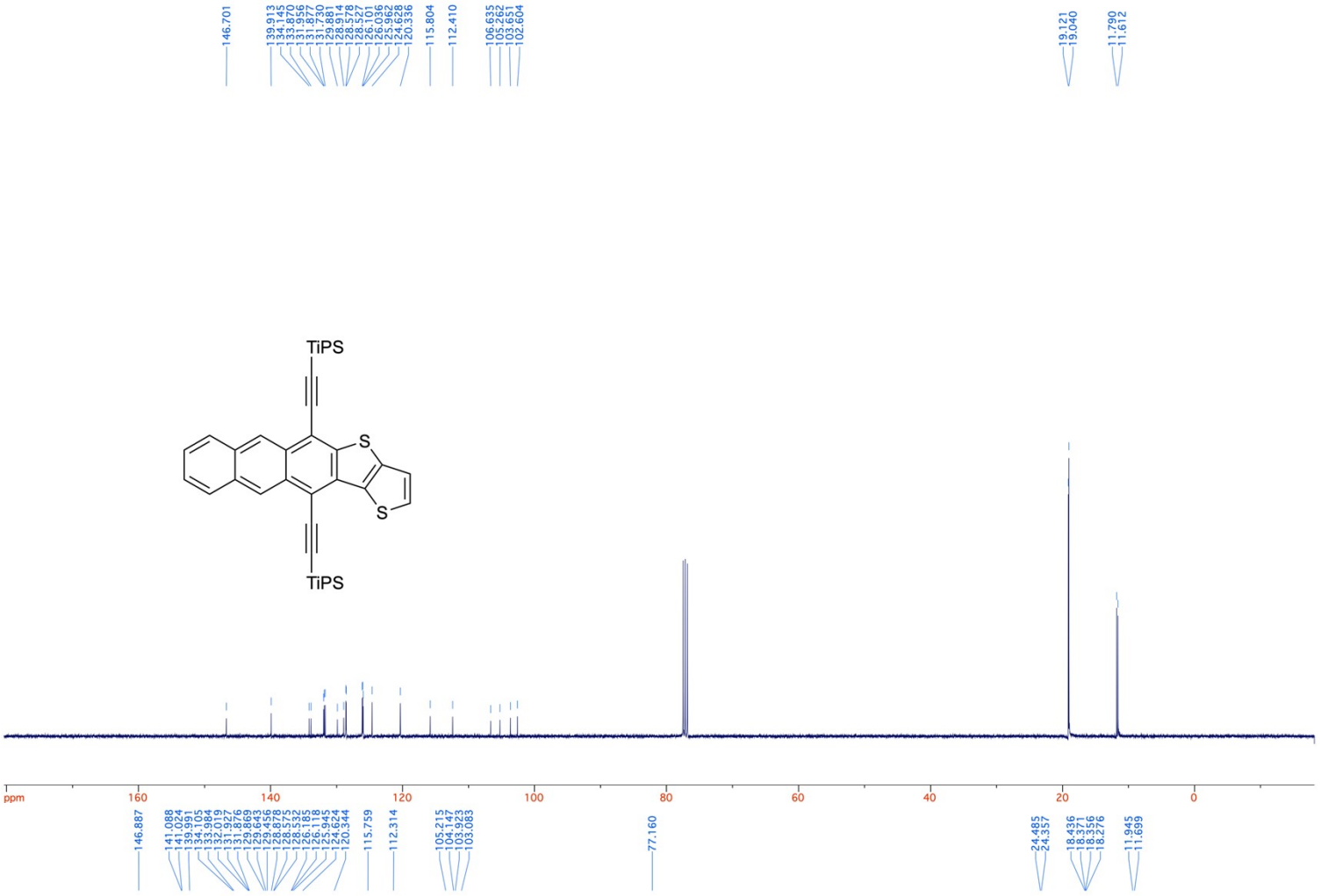
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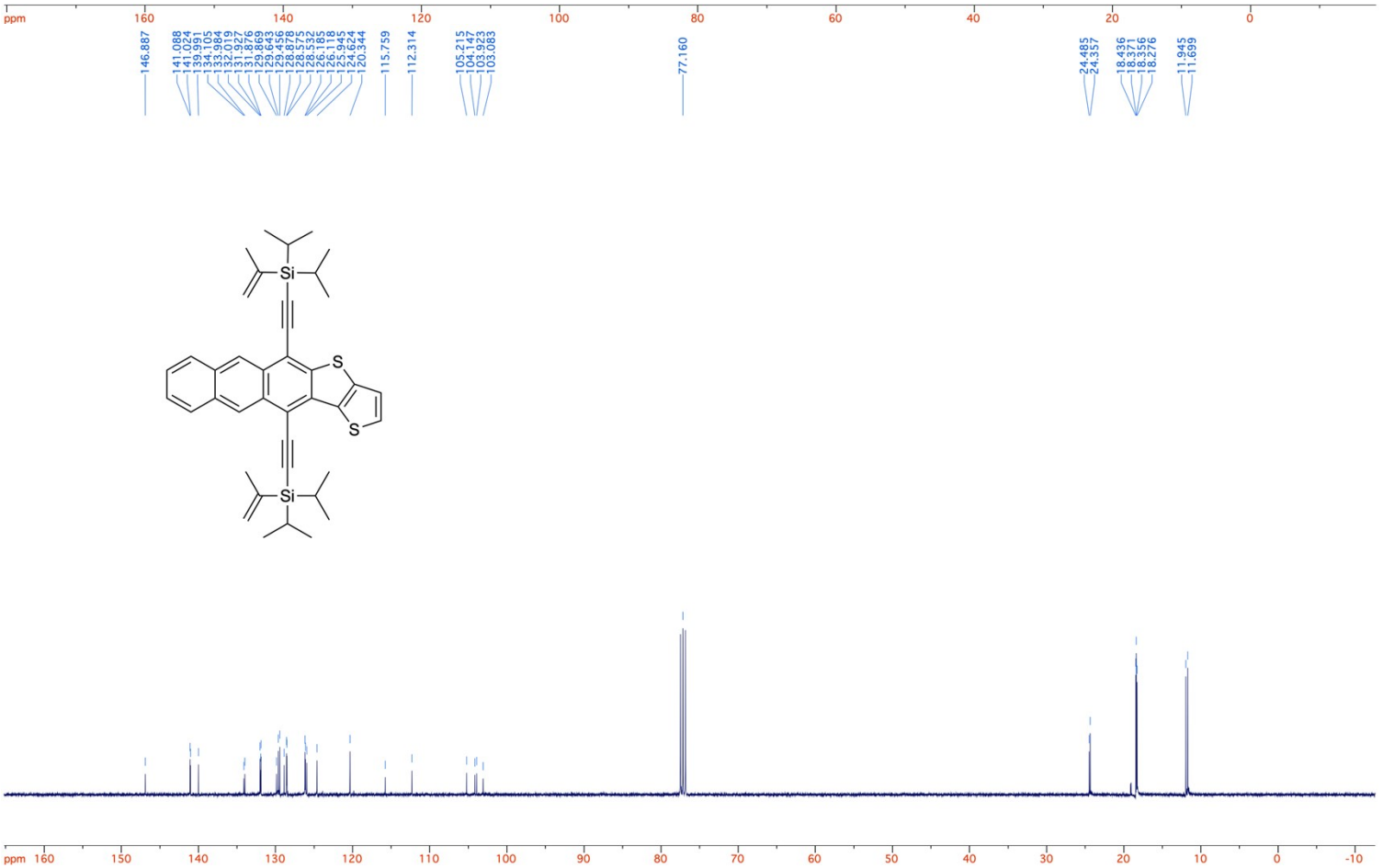
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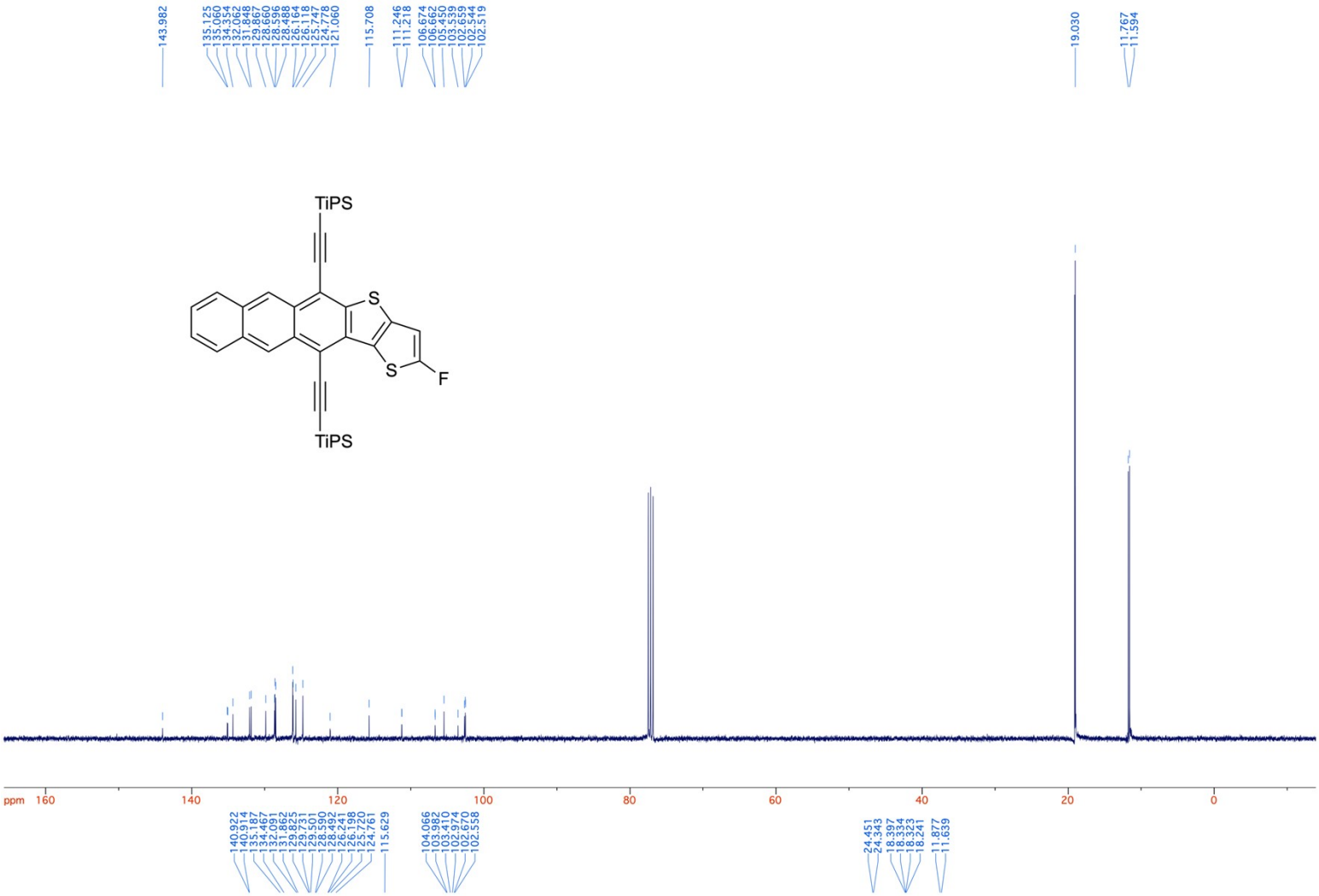
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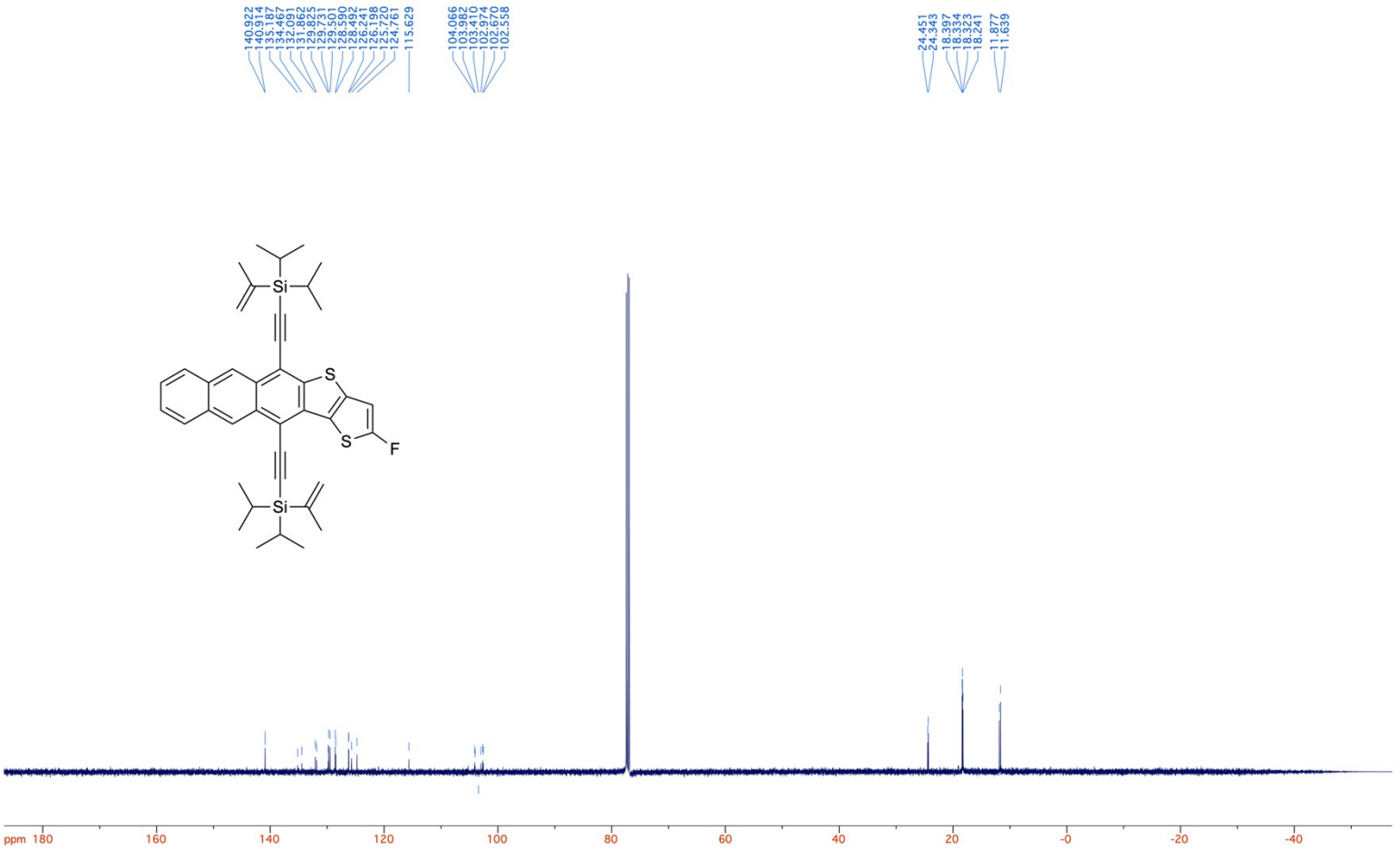
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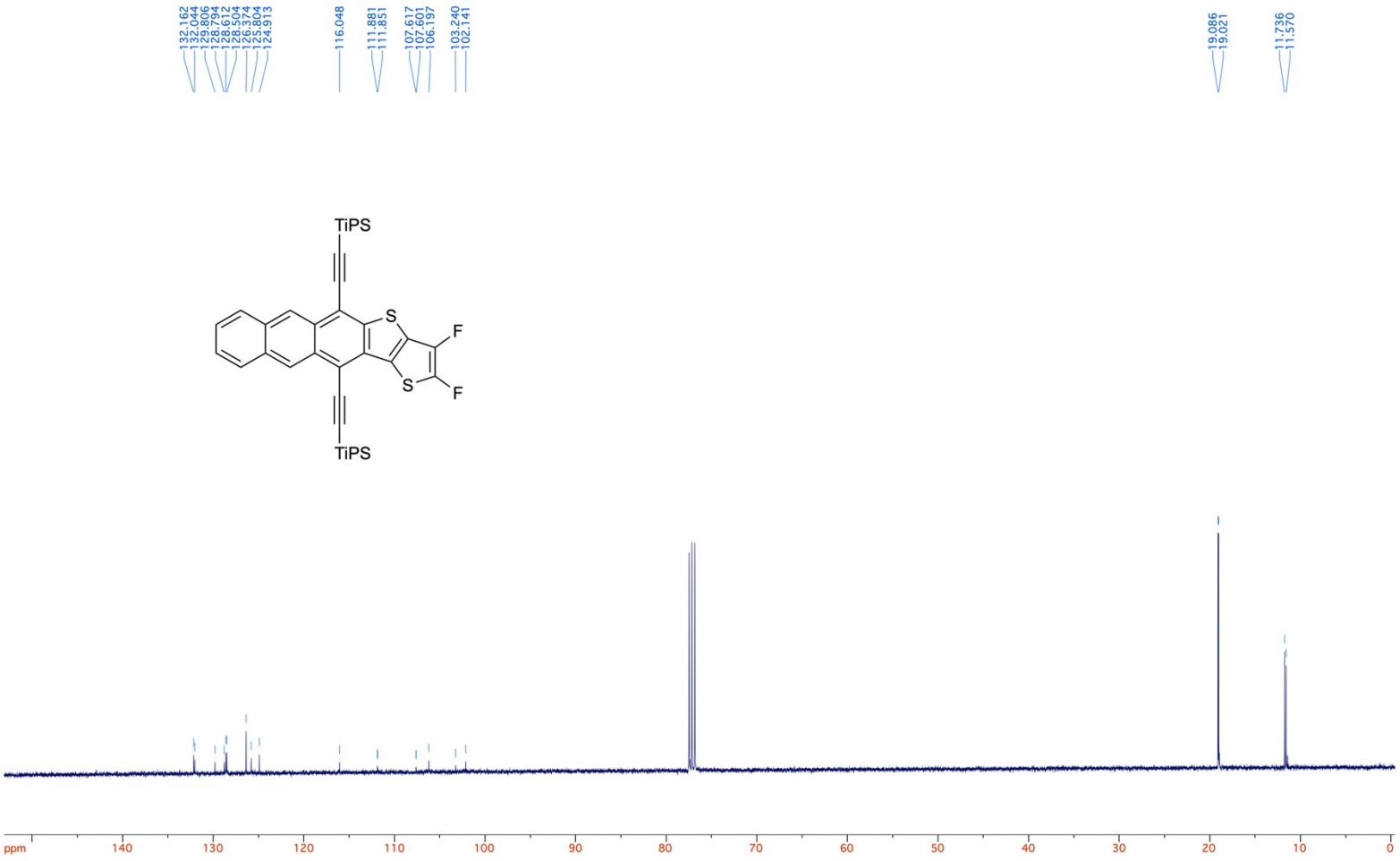
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102.141
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TiPS
S
F
S
F
TiPS
ppm
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130
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90
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0

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