Supporting Information for

π-Dimer Formation in an Oligothiophene Tweezer Molecule

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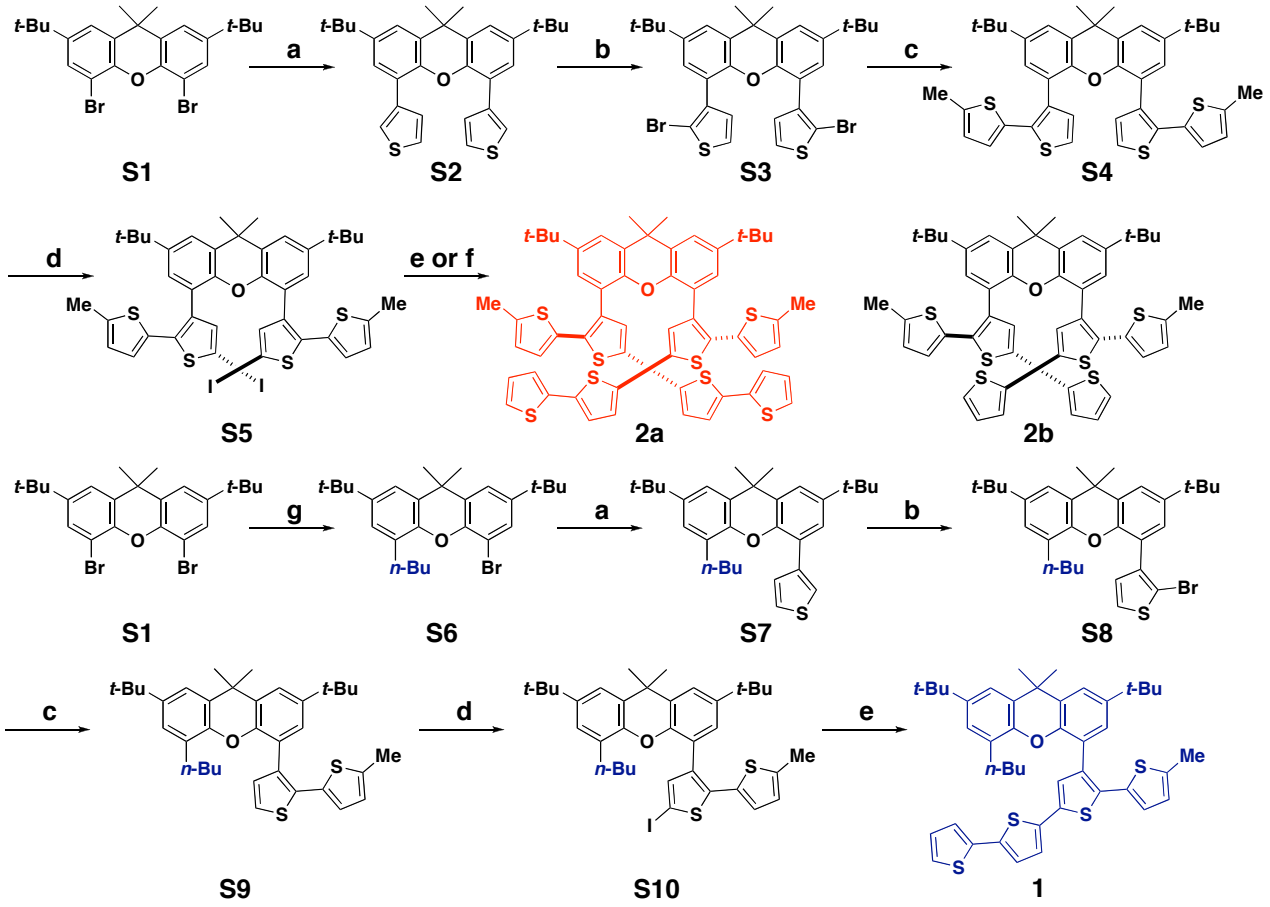
Contents

General: NMR spectra were recorded on a Varian Mercury-300, operating at 300 MHz for ^{1}H NMR and 75.46 MHz for ^{13}C NMR, or Varian Inova-500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to $CHCl_3$ (7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR) or CH_2Cl_2 (5.32 ppm for ^{1}H NMR and 54.00 ppm for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility on a Bruker Daltonics APEX II3 Tesla FT-ICR-MS. IR spectra were obtained on a Nexus 870 ATR-FT-IR spectrometer. Melting point was measured with MEL-TEMP instrument. UV-vis absorption spectra were obtained on an Agilent 8453 diode array spectrophotometer. EPR spectra were obtained on a Bruker EMX EPR spectrometer operating as the X-band with 100kHz modulation at room temperature. Electrochemical measurements were carried out using an Autolab PGSTAT 20 potentionstat (Eco Chemie) in a three-electrode cell configuration consisting of a quasi-internal Ag wire reference electrode (BioAnalytical Systems) submerged in 0.01 $AgNO_3$ / 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in anhydrous CH_2Cl_2, a Pt button (1.6 mm in diameter) electrode as the working electrode, and a Pt coil as the counter electrode. The ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an external reference.

All reactions were performed under an argon atmosphere with dry solvents. Column chromatography was performed with silica gel 60 (230–400 mesh) from Silicycle. Tetrahydrofuran, dichloromethane, and toluene were purified using a solvent purification system (Innovative Technologies, Inc.). $TBAPF_6$ was recystallized from ethanol prior to use. All other chemicals were of reagent grade and used as received.

1. Synthesis of Compounds:



Scheme S1.

[a] Key: (a) 3-thiophene boronic acid, $Pd_2(dba)_3$•$CHCl_3$ (3 mol %), $[(t\text{-}Bu)_3PH]BF_4$ (7.2 mol %), KF, THF, 96% for **S2**, 52% for **S7** (b) NBS, CH_2Cl_2/DMF, 89% for **S3**, 65% for **S8** (c) 2-Methyl-5-tributylstannylthiophene, $Pd(PPh_3)_4$ (5 mol %), toluene/DMF, 91% for **S4**, 96% for **S9** (d) *n*-BuLi, THF, –78 ˚C to r.t.. then I_2, –78 ˚C to r.t., 82% for **S5**, 40% for **S10** (e) tributylstannylbithiophene, $Pd(PPh_3)_4$ (5 mol %), toluene/DMF, 74% for **2a**, 93% for **1** (f) tributylstannyl-2-thiophene, $Pd(PPh_3)_4$ (5 mol %), toluene/DMF, 59%

Synthesis of 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-di(thiophen-3-yl)xanthene (S2): To the mixture of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**S1**, 9.61 g, 20 mmol), 3-thiopheneboronic acid (6.40 g, 50 mmol, 2.5 equiv), $Pd_2(dba)_3$•$CHCl_3$ (621 mg, 0.60 mmol, 3 mol %), $[(t\text{-}Bu)_3PH]BF_4$ (418 mg, 1.44 mmol, 7.2 mol %), KF (7.67 g, 132 mmol, 6.6 equiv) was added THF (80 mL, 0.25 M) at 0 ˚C. After stirring at room temperature for 3 days, the reaction mixture was filtered with Celite® pad and concentrated. The material was purified by flash column chromatography (silica gel, eluent: hexane only - CH_2Cl_2/hexane) and precipitation (CH_2Cl_2/MeOH) to give **S2** (9.30 g, 96% yield) as a white solid: mp 229-230 ˚C; ATR-FTIR (neat) ν 661, 778, 856, 1238, 1279, 1367, 1447, 2869, 2905, 2933, 2966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 18H), 1.71 (s, 6H), 7.14 (dd, J = 2.4, 3.9 Hz, 2H), 7.22 (d, J = 3.9 Hz, 2H), 7.22 (d, J = 2.4 Hz, 2H), 7.30 (d, J = 2.4 Hz, 2H), 7.41 (d, J = 2.4 Hz, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 31.7, 31.8, 34.6, 35.2, 121.5, 123.7, 124.2, 124.5, 125.5, 129.1, 130.6, 138.4, 145.4, 146.2; MS (ESI (+)) *m/z* 487 $[M+H]^+$, 509 $[M+Na]^+$; HRMS (ESI): calcd. for $C_{31}H_{34}OS_2$ 509.1943 $[M+Na]^+$, found 509.1964

Synthesis of 4,5-bis(2-bromothiophen-3-yl)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (S3): After dissolving **S2** (9.30 g, 19.1 mmol) in CH_2Cl_2 (120 mL), DMF (60 mL) was added. To the mixture was added dropwise the solution of *N*-bromosuccinimide (6.80 g, 38.2 mmol) in DMF (60 mL) at 0 ˚C. The

reaction mixture was gradually warmed to room temperature and after stirring for 17 h, diluted with Et_2O, washed with H_2O, extracted with Et_2O, and dried over Na_2SO_4. After the evaporation of solvent, the crude material was purified by flash column chromatography (silica gel, eluent: hexane only - CH_2Cl_2/hexane) and precipitation (CH_2Cl_2/MeOH) to give **S3** (10.94 g, 89% yield) as a white crystalline solid: mp 209-211 ˚C; ATR-FTIR (neat) ν 660, 716, 760, 831, 858, 1239, 1278, 1366, 1447, 2872, 2905, 2965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 18H), 1.72 (s, 6H), 6.74 (d, J = 2.4 Hz, 2H), 7.03 (d, J = 2.4 Hz, 2H), 7.25 (d, J = 2.4 Hz, 2H), 7.44 (d, J = 2.4 Hz, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 31.7, 32.0, 34.7, 35.2, 110.4, 122.2, 122.5, 124.4, 126.7, 130.0, 130.2, 138.3, 145.1, 146.0; MS (ESI (+)) m/z 667 $[M+Na]^+$; HRMS (ESI): calcd. for $C_{31}H_{32}Br_2OS_2$ 667.0139 $[M+Na]^+$, found 667.0093

Synthesis of 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-bis(5'-methyl-2,2'-bithiophen-3-yl)xanthene (S4): To the mixture of **S3** (4.52 g, 7.0 mmol), 2-methyl-5-tributylstannylthiophene[S1] (8.13 g, 21 mmol, 3 equiv), $Pd(PPh_3)_4$ (404 mg, 0.35 mmol, 5 mol %) were added toluene (10 mL) and DMF (7.5 mL). The mixture was heated to 80 ˚C and stirred for 50 h. After cooling and dilution with Et_2O, aq.NaF (*ca*. 20 equiv of the tin reagent) was added and stirred for a while. The organic layer was separated, dried over Na_2SO_4, and concentrated. The material was purified by flash column chromatography (silica gel, eluent: hexane only - CH_2Cl_2/hexane) and precipitation (CH_2Cl_2/MeOH) to give **S4** (4.33 g, 91% yield) as a white solid: mp 154-155 ˚C; ATR-FTIR (neat) ν 664, 717, 788, 860, 1253, 1282, 1449, 2870, 2924 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 18H), 1.68 (s, 6H), 2.29 (dd, J = 0.3, 1.2 Hz, 6H), 6.43 (dd, J = 1.2, 3.3 Hz, 2H), 6.57 (dd, J = 0.3, 3.3 Hz, 2H), 6.72 (d, J = 5.4 Hz, 2H), 6.96 (d, J = 5.4 Hz, 2H), 7.10 (d, J = 2.4 Hz, 2H), 7.38 (d, J = 2.4 Hz, 2 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 15.4, 31.6, 31.9, 34.6, 35.2, 121.6, 122.1, 123.6, 125.1, 125.6, 127.3, 130.0, 131.0, 133.3, 134.3, 134.5, 139.6, 144.9, 146.6; MS (ESI (+)) m/z 701 $[M+Na]^+$; HRMS (ESI): calcd. for $C_{41}H_{42}OS_4$ 701.2011 $[M+Na]^+$, found 702.2002

Synthesis of 2,7-di-*tert*-butyl-4,5-bis(5-iodo-5'-methyl-2,2'-bithiophen-3-yl)-9,9-dimethylxanthene (S5): To the solution of **S4** (1.36 g, 2.0 mmol) in THF (15 mL) was slowly added *n*-BuLi (1.6 M in hexanes, 2.6 mL, 2.0 equiv) at –78 ˚C. After stirring for 20 minutes at the temperature and for 20 minutes at 0 ˚C, the resulting dark blue solution was cooled to –78 ˚C and the solution of iodine (1.12 g, 4.4 mmol, 2.2 equiv) in THF (15 mL) was added via cannula. The reaction mixture was stirred for 1.5 h at the same temperature and for 2 h at room temperature. After diluted with Et_2O, the reaction was quenched with aq. Na_2SO_3, extracted with Et_2O. The organic layer was washed with 1N HCl, then brine, dried over Na_2SO_4, evaporated in *vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, eluent: hexane only - CH_2Cl_2/hexane) and precipitation (CH_2Cl_2/MeOH) to give **S5** (1.52 g, 82% yield) as a white solid: mp 210 ˚C (decomp.) ; ATR-FTIR (neat) ν 790, 834, 883, 1272, 134, 1447, 1480, 2871, 2915, 2966 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 18H), 1.63 (s, 6H), 2.22 (d, J = 1.0 Hz, 6H), 6.34 (dq, J = 1.0 ,3.5 Hz, 2H), 6.50 (d, J = 3.5 Hz, 2H), 6.83 (s, 2H), 7.01 (d, J = 2.5 Hz, 2H), 7.36 (d, J = 2.5 Hz, 2H); ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 15.3, 31.6, 32.2, 34.7, 35.0, 70.6, 122.2, 122.4, 125.0, 125.6, 127.0, 129.8, 133.4, 135.1, 139.8, 140.3, 145.2, 146.2; HRMS (ESI): calcd. for $C_{41}H_{40}OI_2S_4$ 952.9944 $[M+Na]^+$, found 952.9972

Synthesis of 2a: To the mixture of **S5** (465 mg, 0.50 mmol), 5-(tributylstannyl)-2,2-bithiophene[S2] (1.5 mmol, 3.0 equiv), and $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol, 5 mol %) were added toluene (0.6 mL) and

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[S1] Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Aruffo, F.; Cipriani, F.; Ventola, A. *J. Org. Chem.*, **2003**, *68*, 1512.

[S2] Zhu, S. S.; Swager, T. M. *J.Am. Chem. Soc.* **1997**, *119*, 12568.

DMF (0.6 mL). The reaction was heated at 80 ˚C, stirred for 2.5 h, and quenched by the addition of aq. NaF. The product was extracted with CH_2Cl_2, dried over Na_2SO_4, and purified by flash column chromatography (triethylamine-treated silica gel, eluent: hexane only – CH_2Cl_2/hexne) to afford **2a** (375 mg, 74% yield) as an yellow solid: mp 283 ˚C (decomp.) ; ATR-FTIR (neat) ν 679, 782, 832, 1273, 1364, 1449, 2868, 2915, 2966, 3070 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 1.29 (s, 18H), 1.71 (s, 6H), 2.23 (d, J = 1.0 Hz, 6 H), 6.35 (dq, J = 1.0 ,3.5 Hz, 2 H), 6.52 (d, J = 3.5 Hz, 2H), 6.83-6.85 (m, 6H), 6.94 (dd, J = 3.5, 5.0 Hz, 2H), 7.00 (dd, J = 1.0, 3.5 Hz, 2H), 7.12 (d, J = 2.5 Hz, 2H), 7.17 (dd, J = 1.0, 5.0 Hz, 2H), 7.46 (d, J = 2.5 Hz, 2H); ^{13}C NMR (125.65 MHz, CD_2Cl_2) δ 15.4, 31.7, 32.4, 34.9, 35.5, 122.8, 123.8, 124.2, 124.6, 124.7, 125.4, 125.6, 127.2, 127.7, 128.3, 128.7, 130.3, 133.3, 133.5, 134.4, 134.6, 135.9, 136.7, 137.9, 140.0, 145.7, 146.6; HRMS (ESI): calcd. for $C_{57}H_{50}OS_8$ 1029.1520 $[M+Na]^+$, found 1029.1529

Synthesis of 2b: According to a similar procedure of the synthesis of **2a** using 2-(tributylstannyl)-thiophene instead of 5-(tributylstannyl)-2,2-bithiophene, **2b** was obtained in 59% yield as yellow solid: mp 255-256 ˚C (decomp.); ATR-FTIR (neat) ν 683, 783, 811, 833, 1275, 1444, 2871, 2966, 3067 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 1.29 (s, 18H), 1.70 (s, 6H), 2.24 (s, 6H), 6.35 (d, J = 3.5 Hz, 2H), 6.48 (d, J = 3.5 Hz, 2 H), 6.80 (s, 2H), 6.90 (dd, J = 3.5, 5.0 Hz, 2H), 6.96 (d, J = 3.5 Hz, 2H), 7.09-7.11 (m, 4 H), 7.45 (d, J = 2.5 Hz, 2H); ^{13}C NMR (125.65 MHz, CD_2Cl_2) δ 15.4, 31.7, 32.4, 34.9, 35.4, 122.7, 123.7, 123.9, 124.2, 125.4, 125.5, 127.2, 127.7, 128.1, 128.6, 130. 2, 133.0, 133.8, 134.4, 137.9, 139.9, 145.7, 146.6; HRMS (ESI): calcd. for $C_{49}H_{47}OS_6$ 865.1765 $[M+Na]^+$, found 865.1740

Synthesis of 4-bromo-2,7-di-*tert*-butyl-5-butyl-9,9-dimethylxanthene (S6): To the solution of **S1** (1.92 g, 4.0 mmol) in THF (20 mL) was slowly added *n*-BuLi (1.6 M in hexanes, 2.5 mL, 1.0 equiv) at –78 ˚C. The solution was gradually warmed to room temperature and stirred for 14 h before quenched by excess amount of H_2O. After diluted with Et_2O, the organic layer was washed with brine, dried over Na_2SO_4, and evaporated in *vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, eluent: hexane only) to afford **S6** (1.33 g, 73% yield) as a colorless oil: ATR-FTIR (neat) ν 736, 873, 1200, 1276, 1367, 1451, 2874, 2934, 2961 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H), 1.35 (s, 9H), 1.48 (tq, J = 7.2, 8.1 Hz, 2H), 1.64-1.77 (m, 8H), 2.85 (dd, J = 7.8, 8.1 Hz, 2 H), 7.11 (d, J = 2.4 Hz, 1 H), 7.25 (d, J = 2.4 Hz, 1 H), 7.36 (d, J = 2.1 Hz, 1H), 7.46 (d, J = 2.1 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.3, 23.2, 30.8, 31.6, 31.7, 32.0, 32.8, 34.6, 34.7, 35.5, 110.4, 119.8, 121.8, 125.4, 128.1, 129.1, 130.1, 131.7, 145.6, 145.7, 146.4, 146.5; HRMS (ESI): calcd. for $C_{27}H_{37}BrO$ 479.1920 $[M+Na]^+$, found 479.1928

Synthesis of 2,7-di-*tert*-butyl-4-butyl-9,9-dimethyl-5-(thiophen-3-yl)xanthene (S7): According to a similar procedure of the synthesis of **S2**, **S7** was obtained in 52% yield as a white solid: mp 110-112 ˚C; ATR-FTIR (neat) ν 664, 783, 854, 1233, 1277, 1365, 1451, 2871, 2936, 2965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3H), 1.21-1.44 (m, 22H), 1.68 (s, 6H), 2.59 (dd, J = 7.5, 8.1 Hz, 2 H), 7.03 (d, J = 2.4 Hz, 1 H), 7.26 (d, J = 2.4 Hz, 1 H), 7.35 (d, J = 2.4 Hz, 1H), 7.37 (dd, J = 3.0, 5.1 Hz, 1H), 7.41 (d, J = 2.1 Hz, 1H), 7.48 (dd, J = 1.5, 5.1 Hz, 1H), 7.57 (dd, J = 1.5, 3.0 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.3, 23.0, 31.1, 31.7, 32.0, 33.0, 34.5, 34.5, 34.6, 35.1, 119.8, 121.8, 123.2, 124.0, 124.4, 125.2, 129.3, 129.5, 129.6, 130.6, 139.0, 145.1, 146.0, 146.8; HRMS (ESI): calcd. for $C_{31}H_{40}OS$ 483.2692 $[M+Na]^+$, found 483.2700.

Synthesis of 5-(2-bromothiophen-3-yl)-2,7-di-*tert*-butyl-4-butyl-9,9-dimethylxanthene (S8): According to a similar procedure of the synthesis of **S3**, **S8** was obtained in 65% yield as a white solid:

mp 122-123 °C; ATR-FTIR (neat) ν 731, 760, 859, 881, 1240, 1280, 1366, 1450, 2874, 2934, 2964 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3H), 1.14 (tq, J = 7.5, 7.2 Hz, 2H), 1.21-1.44 (m, 20H), 1.67 (s, 6H), 2.45 (dd, J = 7.5, 8.1 Hz, 2 H), 7.00 (d, J = 2.1 Hz, 1 H), 7.15 (d, J = 5.7 Hz, 1 H), 7.24 (d, J = 2.1 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 5.7 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.3, 23.1, 31.0, 31.7, 31.7, 32.0, 32.9, 34.5, 34.7, 35.1, 35.1, 110.7, 119.8, 122.4, 122.4, 124.7, 125.2, 126.5, 129.3, 129.7, 130.3, 130.5, 138.9, 144.7, 145.1, 146.2, 146.6; HRMS (ESI): calcd. for $C_{31}H_{39}BrOS$ 561.1797 $[M+Na]^+$, found 561.1802.

Synthesis of 2,7-di-*tert*-butyl-4-butyl-9,9-dimethyl-5-(5'-methyl-2,2'-bithiophen-3-yl)xanthene (S9): According to a similar procedure of the synthesis of **S4**, **S9** was obtained in 96% yield as a white solid: mp 54-56 °C; ATR-FTIR (neat) ν 670, 795, 856, 1247, 1278, 1366, 1449, 2873, 2934, 2959, 3070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, J = 7.2 Hz, 3H), 1.11-1.30 (m, 22H), 1.66 (s, 6H), 2.31 (d, J = 0.9 Hz, 3H), 2.37 (dd, J = 7.5, 7.8 Hz, 2 H), 6.48 (dq, J = 3.6, 0.9 Hz, 1 H), 6.76 (d, J = 3.6 Hz, 1 H), 6.97 (d, J = 2.4 Hz, 1H), 7.10 (d, J = 5.1 Hz, 1H), 7.17 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.41 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.3, 15.4, 23.2, 31.1, 31.7, 31.8, 32.0, 32.9, 34.6, 34.7, 35.2, 119.8, 122.0, 122.1, 123.7, 125.1, 125.4, 127.0, 129.4, 130.0, 130.2, 131.5, 133.9, 134.5, 134.6, 139.7, 144.9, 144.9, 146.8 (two carbons are missing due to overlap in the aromatic region); HRMS (ESI): calcd. for $C_{36}H_{44}OS_2$ 557.2906 $[M+Na]^+$, found 557.2897.

Synthesis of 2,7-di-*tert*-butyl-4-butyl-5-(5-iodo-5'-methyl-2,2'-bithiophen-3-yl)-9,9-dimethylxanthene (S10): According to a similar procedure of the synthesis of **S5**, **S10** was obtained in 40% yield as a white solid: mp 61-64 °C; ATR-FTIR (neat) ν 793, 877, 1224, 1274, 1366, 1448, 2872, 2931, 2959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3H), 1.16-1.31 (m, 22H), 1.64 (s, 6H), 2.29 (d, J = 0.9 Hz, 3H), 2.43 (dd, J = 7.2, 7.8 Hz, 2 H), 6.47 (dq, J = 3.6, 0.9 Hz, 1 H), 6.72 (d, J = 3.6 Hz, 1 H), 6.99 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 5.1 Hz, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.26 (s, 1H), 7.41 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.5, 15.3, 23.3, 31.1, 31.6, 31.7, 31.9, 32.9, 34.5, 34.6, 35.1, 69.9, 119.7, 122.1, 122.3, 125.2, 125.8, 126.7, 129.3, 129.9, 130.3, 133.2, 136.0, 139.7, 140.4, 140.9, 145.0, 145.0, 146.6, 146.6; HRMS (ESI): calcd. for $C_{36}H_{43}IOS_2$ 705.1692 $[M+Na]^+$, found 705.1707.

Synthesis of 1: According to a similar procedure of the synthesis of **2a**, **1** was obtained in 93% yield as an yellow solid: mp 167 °C; ATR-FTIR (neat) ν 695, 793, 1219, 1275, 1454, 2871, 2931, 2957, 3071 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.69 (t, J = 7.2 Hz, 3H), 1.07-1.15 (m, 2H), 1.23-1.39 (m, 20H), 1.68 (s, 6H), 2.33 (d, J = 0.6 Hz, 3H), 2.43 (dd, J = 7.5, 7.8 Hz, 2 H), 6.51 (dq, J = 3.3, 0.6 Hz, 1 H), 6.80 (d, J = 3.3 Hz, 1 H), 6.99 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 3.6, 5.1 Hz, 1H), 7.09-7.13 (m, 1H), 7.11 (s, 1H), 7.18 (dd, J = 1.2, 3.6 Hz, 1H), 7.20-7.23 (m, 3H), 7.26 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 14.3, 15.4, 23.2, 31.3, 31.7, 31.8, 32.1, 33.0, 34.6, 34.7, 35.1, 119.8, 122.4, 123.2, 123.8, 124.1, 124.6, 125.2, 125.3, 125.4, 126.8, 128.1, 129.3, 130.0, 130.3, 130.3, 133.0, 133.2, 134.2, 135.0, 136.1, 136.4, 137.5, 140.1, 145.0, 145.1, 146.6, 146.7; HRMS (ESI): calcd. for $C_{44}H_{48}OS_4$ 743.2480 $[M+Na]^+$, found 743.2508.

2. X-ray Crystal Structure of S5

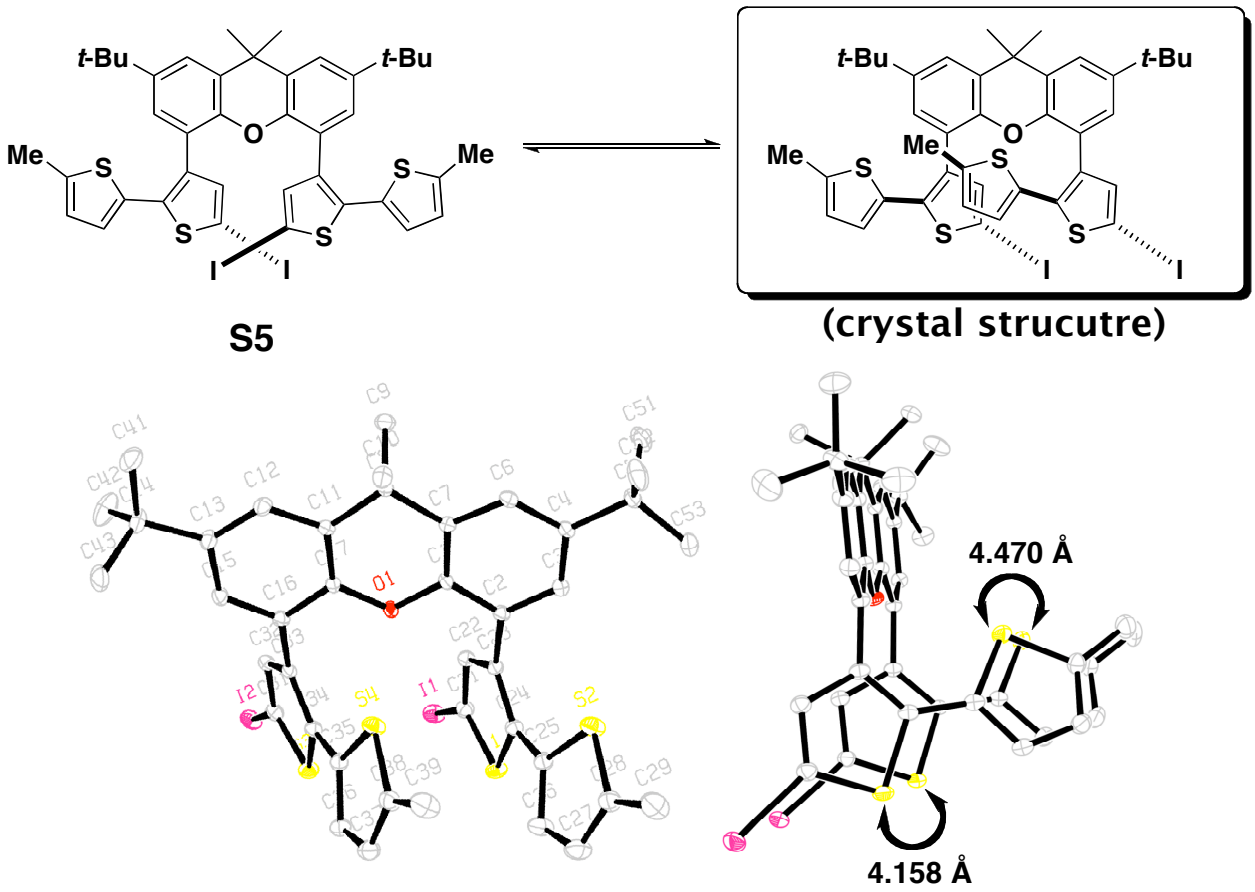


Figure S1. X-ray crystal structure of **S5**. Suitable crystals were grown using CH_2Cl_2/Et_2O solutions stored in fridge for two days. One of the *t*-butyl groups on the xanthene moiety showed disorder in the structure, however, it was omitted for clarity.

Crystallographic Data for S5

Empirical formula (observed): $C_{41}H_{40}I_2OS_4$
a: 11.9286 Å
b: 13.3443 Å
c: 14.1759 Å
alpha: 100.700 °
beta: 107.730 °
gamma: 110.300 °
space group: P-1
calculated density: 1.622 g/cm^3
color: colorless
z: 2
temperature: -173.0 °C
volume: 1905.63 Å^3
formula weight: 930.841 g/mole
R(F): 0.019
$R_w(F^2)$: 0.051
goodness of fit: 1.028

3. Equilibrium between *anti*- and *syn*-Isomers of 2a; VT NMR Experiments

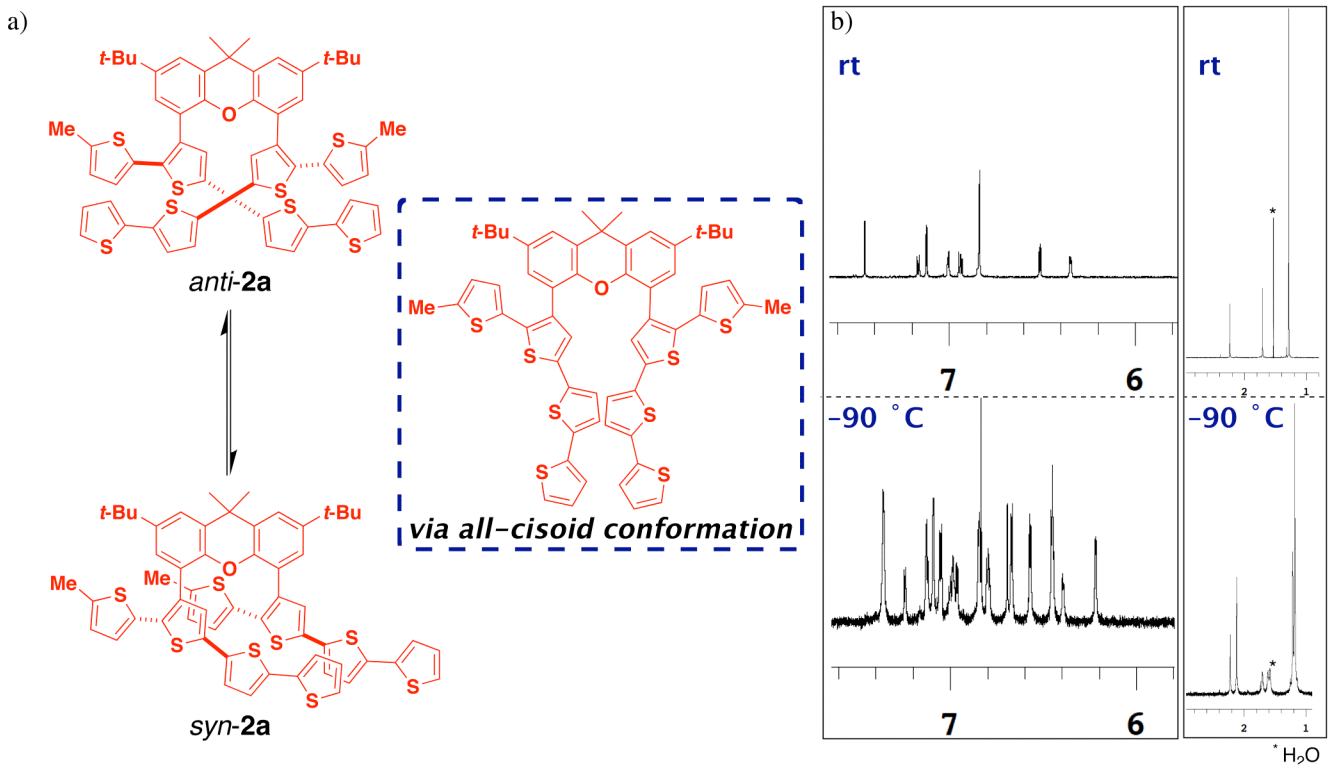


Figure S2. (a) Illustration of the equilibrium between *anti*- and *syn*-isomers via all-cisoid conformation (b) ^{1}H NMR spectra of **2a** obtained in CD_2Cl_2 at room temperature (top) and at –90 ˚C (bottom) (left: aromatic region, right: aliphatic region).

The existence of equilibrium between *anti*- and *syn*-isomers of **2a** was revealed by NMR measurements at low temperature. As shown in Figure S2b, **2a** afforded one set of peaks in its NMR spectrum at room temperature (top). On the other hand, at –90 ˚C, the peaks were separated into two sets of peaks in the ratio of approx. 2:1 (bottom). This result suggests that **2a** can have two conformations at room temperature and those two conformations are in the equilibrium. Probably, the conformational changes between two isomers would occur via all-cisoid conformation as shown in Figure S2a.

4. UV-vis Absorption

50 μL of 1 mM substrate (**1**, **2a**, or **2b**) solution (0.05 μmol) in CH_2Cl_2 was diluted with *ca*. 3.5 mL of CH_2Cl_2 in a cuvette. Absorption spectra of neutral compounds were recorded with this solution. 0.05 M of the oxidant $Et_3O•SbCl_6$ solution in CH_2Cl_2 was prepared. Each time 1 μL (0.05 μmol of the oxidant) of this solution was added and mixed well, and the absorption was recorded. This process was repeated until one-electron oxidation of oligothiophene moieties was completed. The spectral changes for **1**, **2a**, and **2b** are displayed in Figure 2. Superimposed spectra are shown in Figure S3a for **1** and **2a** at neutral state, and in Figure S3b for radical cation $\mathbf{1}^{\bullet+}$ and π-dimer $\mathbf{2a}^{2+}$.

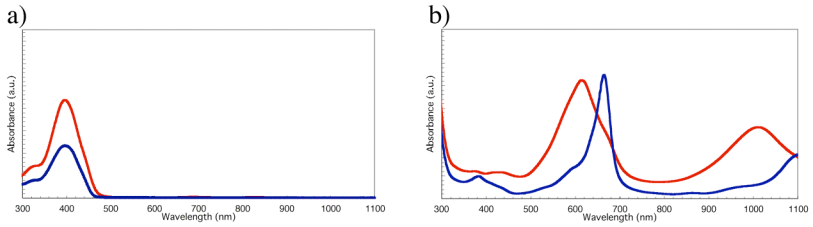


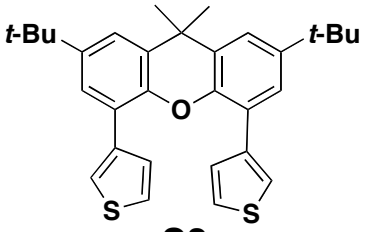
Figure S3. Superimposed UV-vis absorption spectra (a) at neutral state of **1** (blue line) and **2a** (red line) (b) of radical cation $\mathbf{1}^{\bullet+}$ (blue line) and π-dimer $\mathbf{2a}^{2+}$ (red line).

5. EPR Measurement

1.0 mM of **1**, 0.5 mM of **2a**, and 50 mM of the oxidant solutions $Et_3O•SbCl_6$ in CH_2Cl_2 were prepared. 0.5 mL of substrate (**1** or **2a**) solutions were charged in a quartz EPR tube under argon atmosphere and the specified equivalents of oxidant solution were added (for **1**, 1.5 or 5 equivalents; for **2a**, 3 or 10 equivalents). After recording EPR spectra (Figure 4a and 4c), small amount of sample solution was transferred into a cuvette and diluted with some amounts of CH_2Cl_2. Absorption spectra of these samples are shown in Figure 4b and 4d.

6. NMR Spectra

^{1}H NMR and ^{13}C NMR spectra of all compounds are attached from page S-9.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t-Bu
O
S
S

S2

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7.232
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7.220
7.163
7.155
7.151
7.142
1.717
1.365
1.359
1.353
9
8
7
6
5
4
3
2
1
ppm
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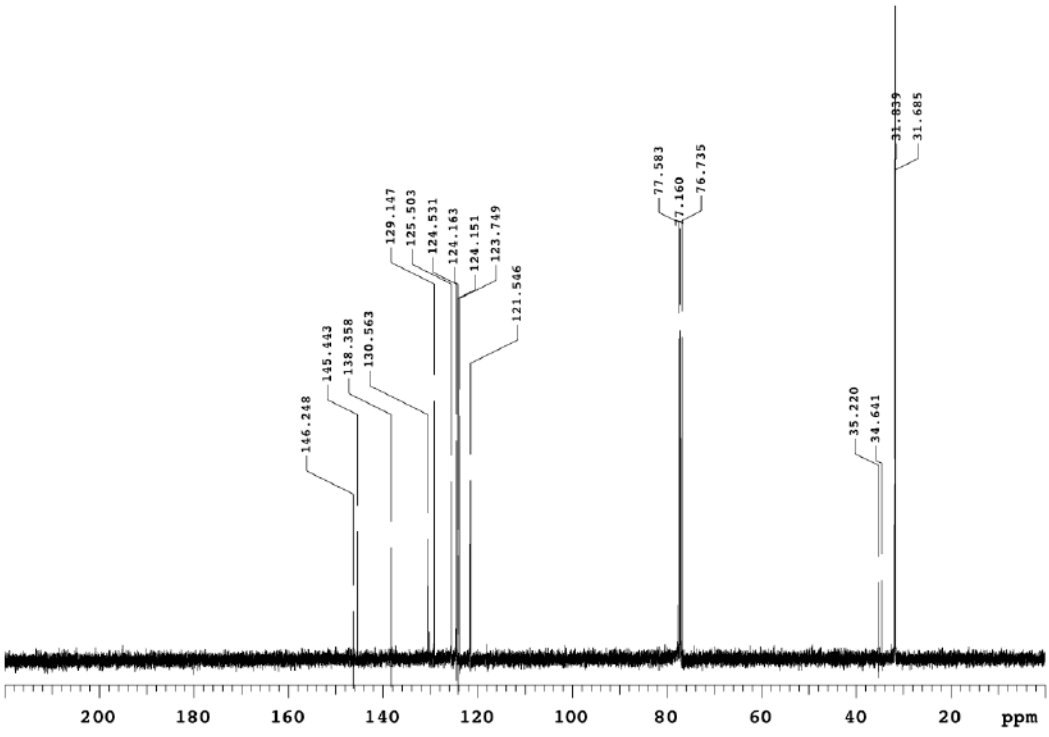
1.99
6.73
19.97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124.531
124.163
124.151
123.749
121.546
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77.160
76.735
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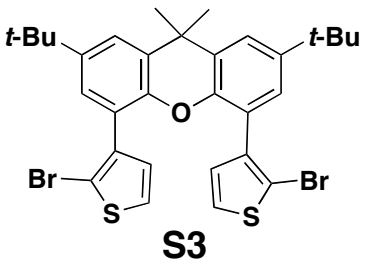
31.839
31.685
200
180
160
140
120
100
80
60
40
20
ppm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t-Bu
O
Br
Br
S
S

S3

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7.244
7.041
7.022
6.750
6.732
1.718
1.550
1.348
0.009
0.002
0.013
9
8
7
6
5
4
3
2
1
ppm
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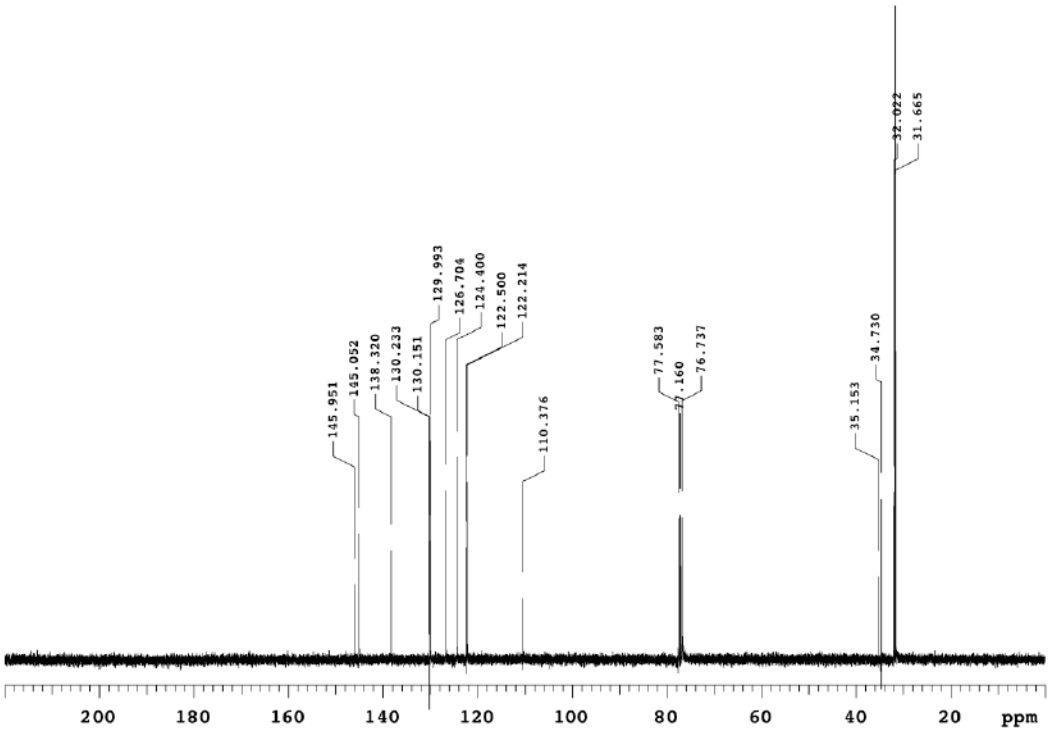
8.53 22.86
2.80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130.151
129.993
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124.400
122.500
122.214
110.376
77.583
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76.737
35.153
34.730
32.022
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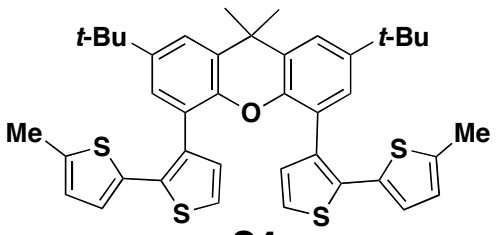
140
120
100
80
60
40
20
ppm


t-Bu
t-Bu
Me
Me
S
S
S
S
O

S4

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6.954
6.733
6.716
6.579
6.578
6.568
6.566
6.438
6.434
6.427
6.423
2.296
2.295
2.292
2.291
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1.550
1.246
0.007
0.006
0.005
0.003
9
8
7
6
5
4
3
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ppm
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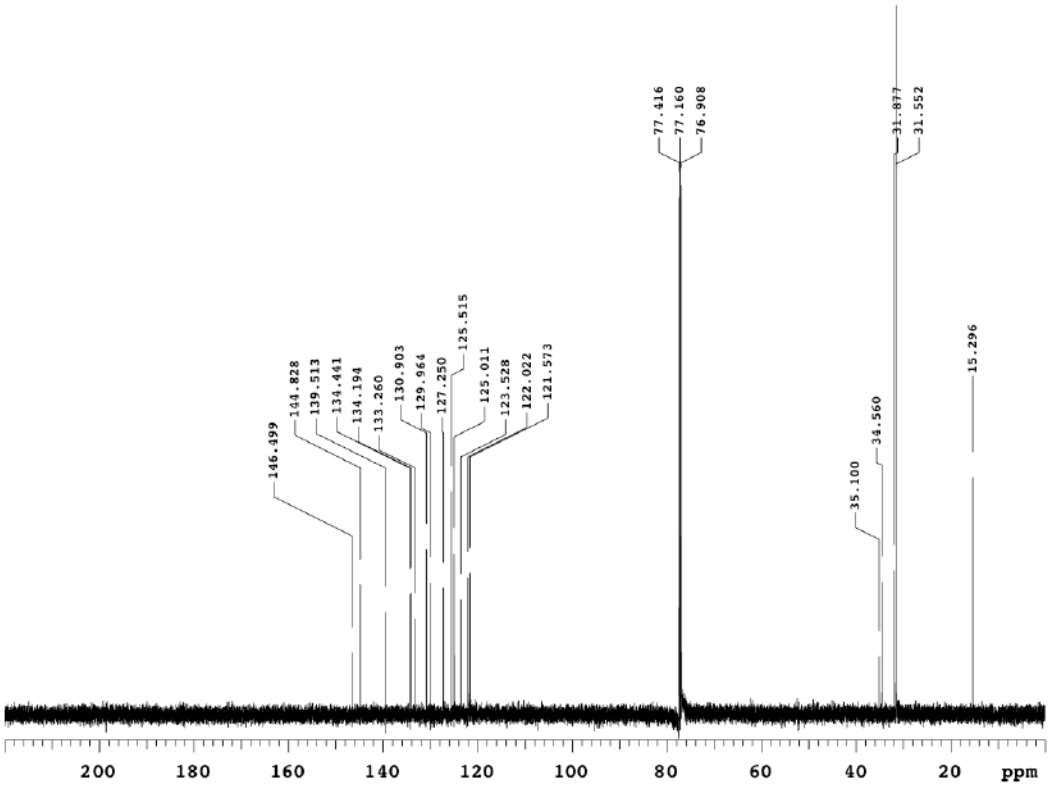
22.51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122.022
121.573
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77.160
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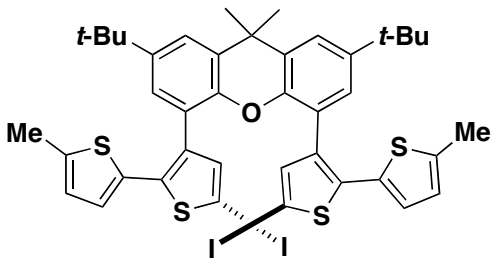
140
120
100
80
60
40
20
ppm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Me
O
S
S
S
S
I
I

S5

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0.001
9
8
7
6
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1
ppm
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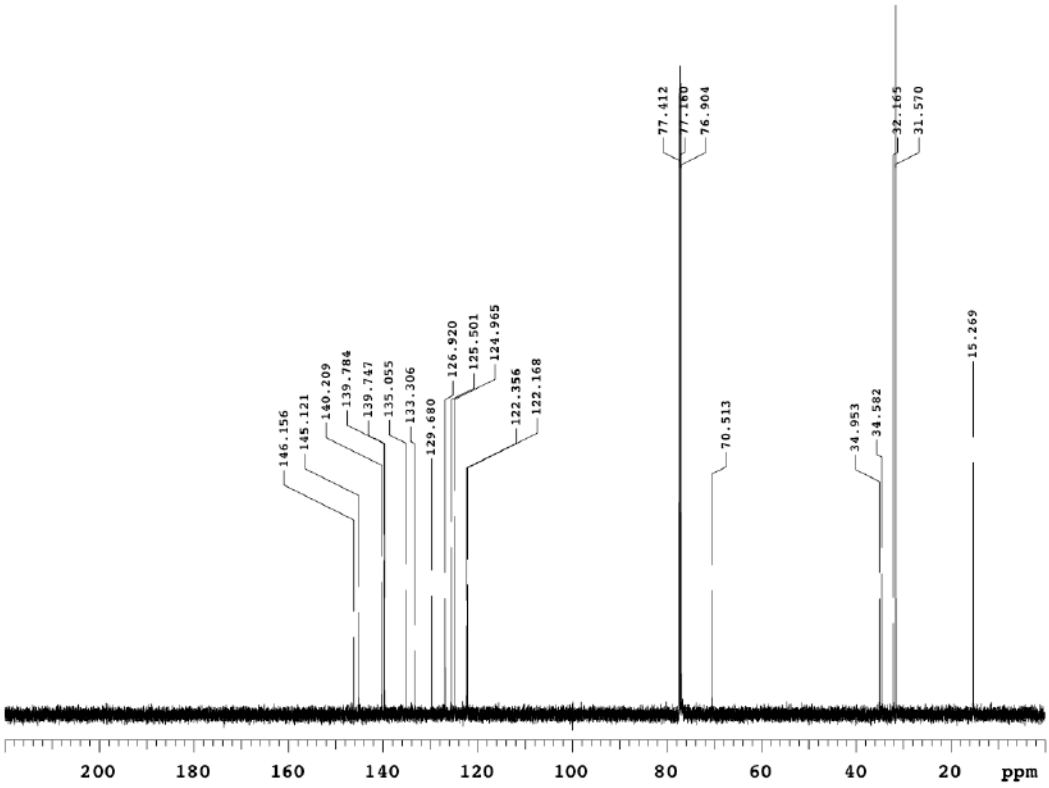
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122.168
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77.160
76.904
70.513
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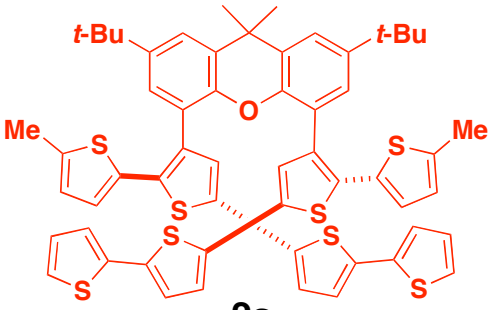
140
120
100
80
60
40
20
ppm


t-Bu
t-Bu
Me
Me
O
S
S
S
S
S
S
S
S

2a

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7.172
7.164
7.162
7.127
7.122
7.013
7.012
7.006
7.004
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6.942
6.935
6.855
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6.841
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6.513
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6.353
6.351
6.348
6.346
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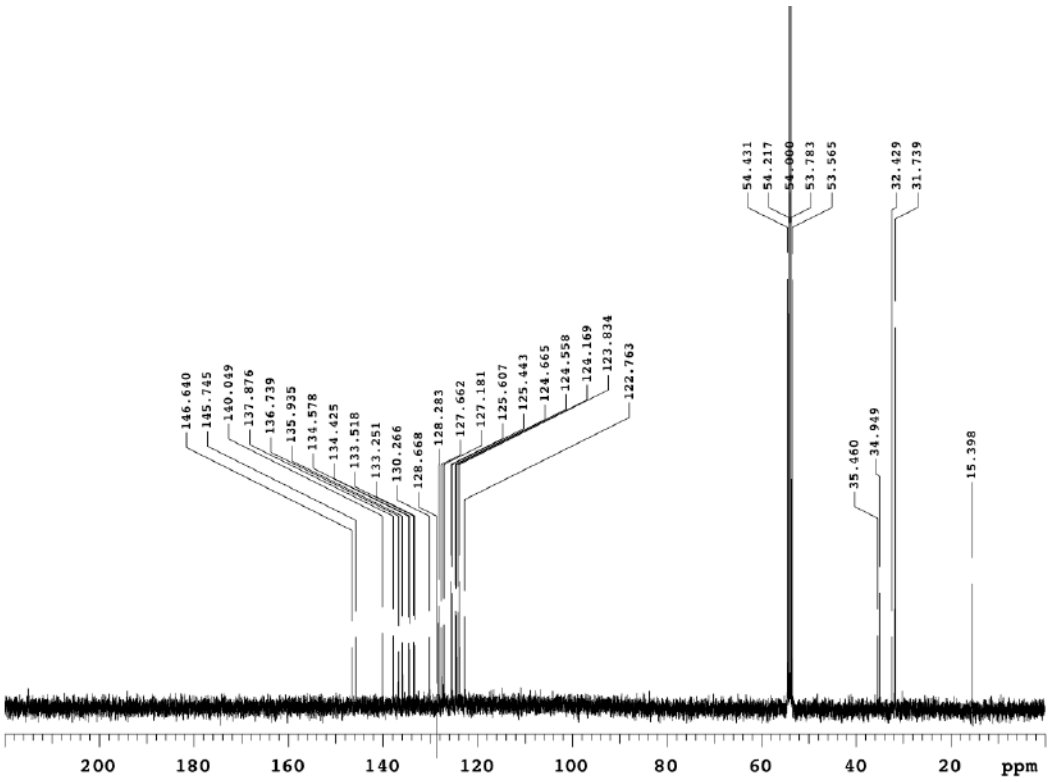
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124.558
124.169
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54.000
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53.565
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20
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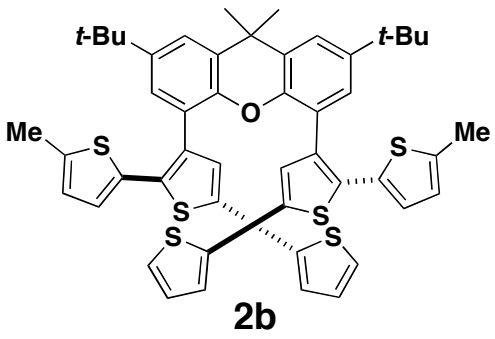
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Me
Me
O
S
S
S
S
S
S

2b

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7.103
7.101
7.093
7.091
6.964
6.957
6.912
6.905
6.902
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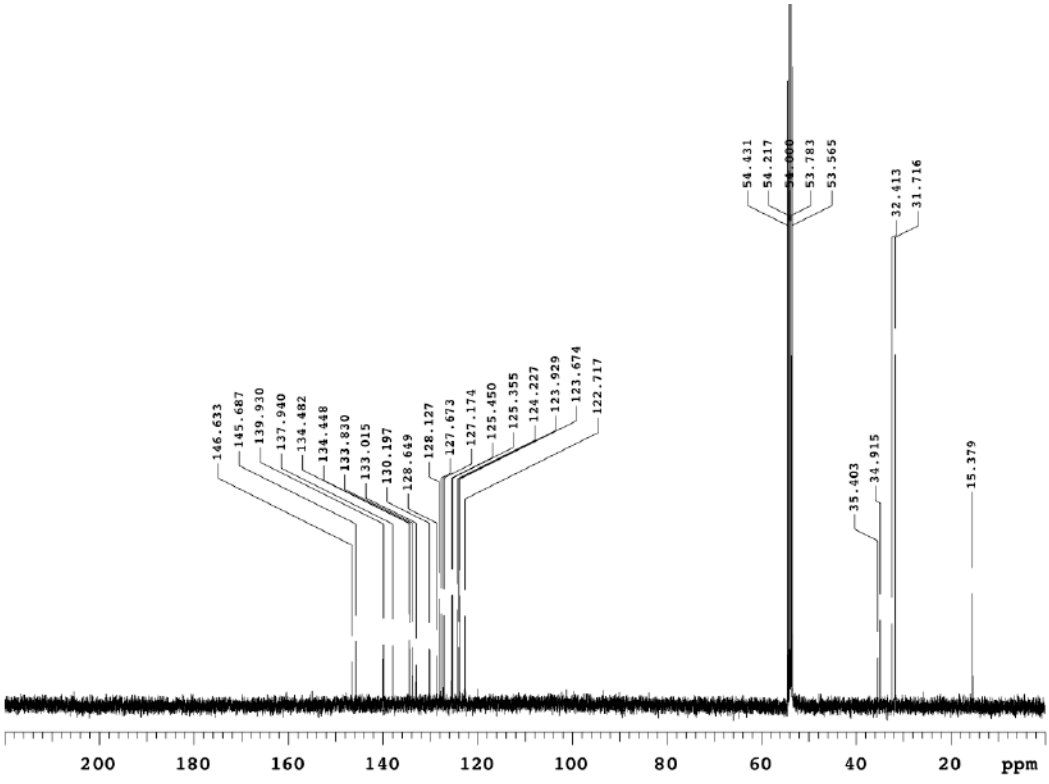
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125.355
124.227
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123.674
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54.217
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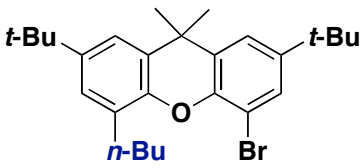
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O
n-Bu
Br

S6

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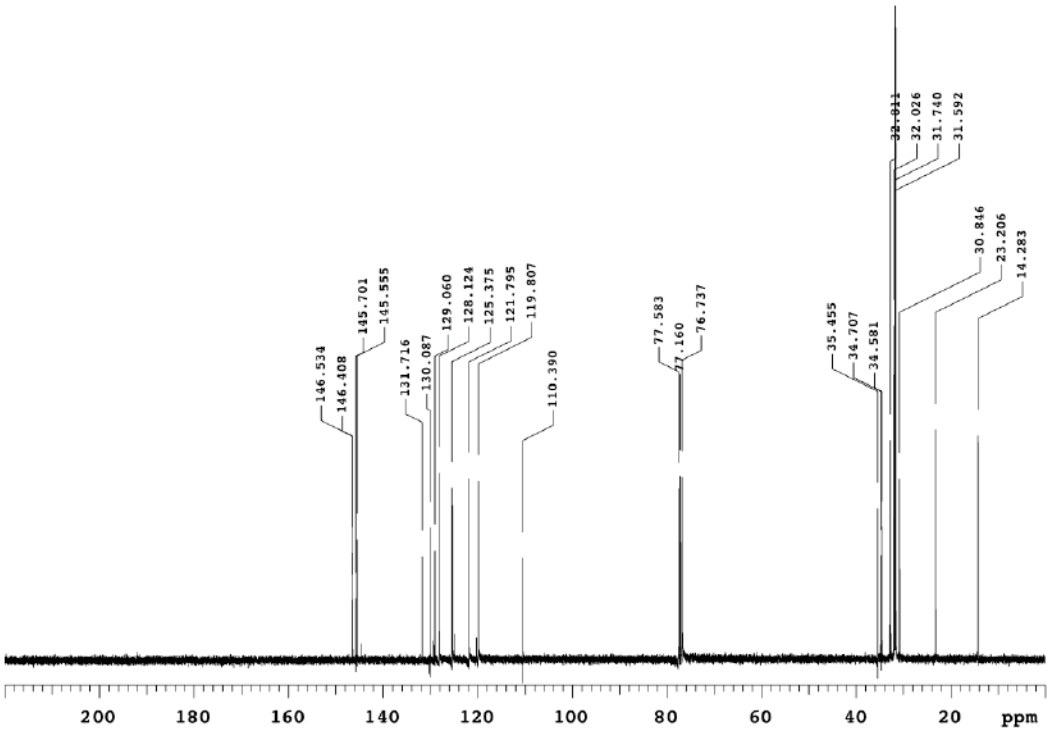
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77.160
76.737
35.455
34.707
34.581
32.011
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140
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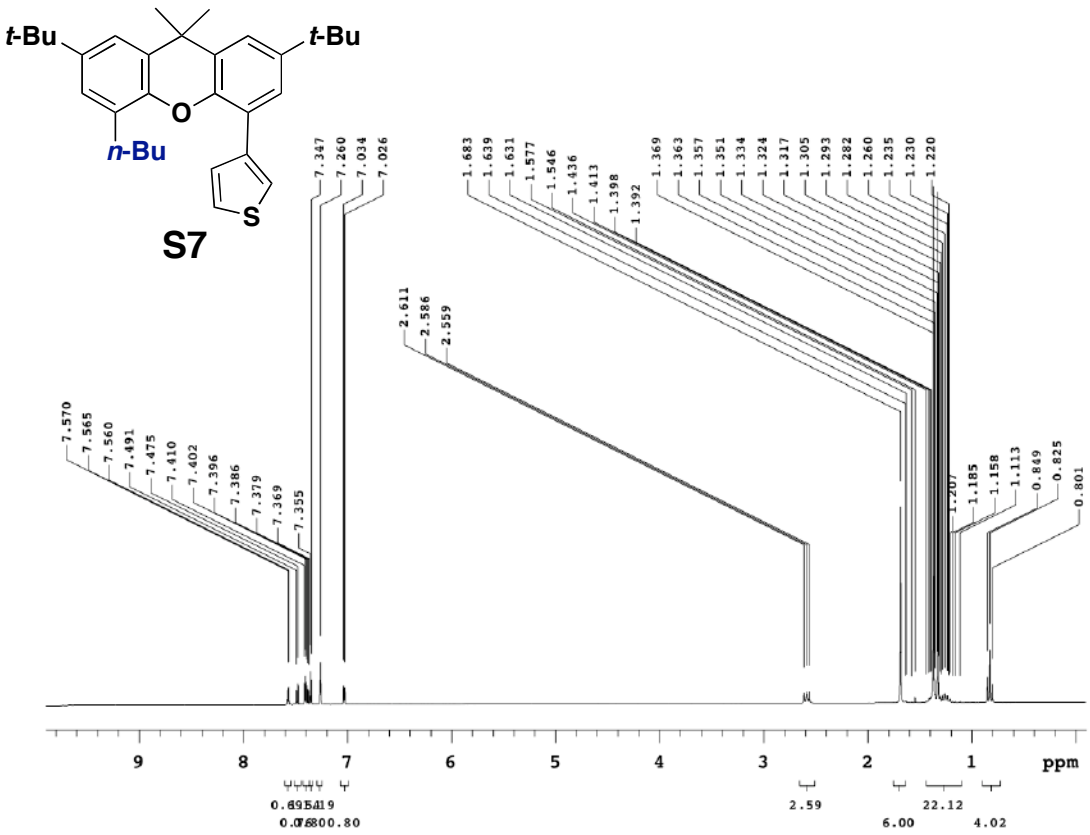
ppm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t-Bu
O
n-Bu
S
S7
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7.386
7.379
7.369
7.355
7.347
7.260
7.034
7.026
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2.559
1.683
1.639
1.631
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1.546
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1.398
1.392
1.369
1.363
1.357
1.351
1.334
1.324
1.317
1.305
1.293
1.282
1.260
1.235
1.230
1.220
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1.158
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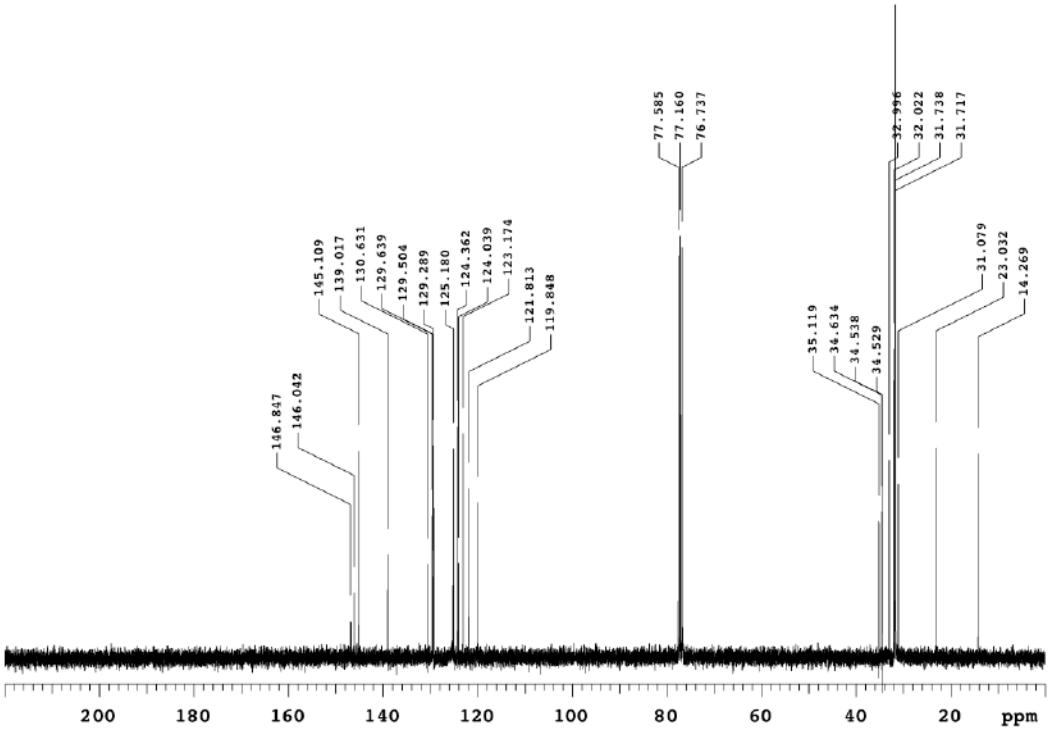
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76.737
35.119
34.634
34.538
34.529
32.396
32.022
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20
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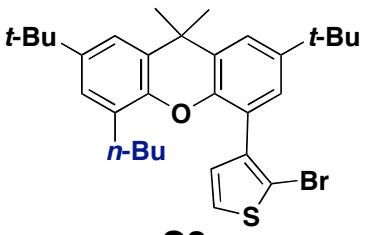
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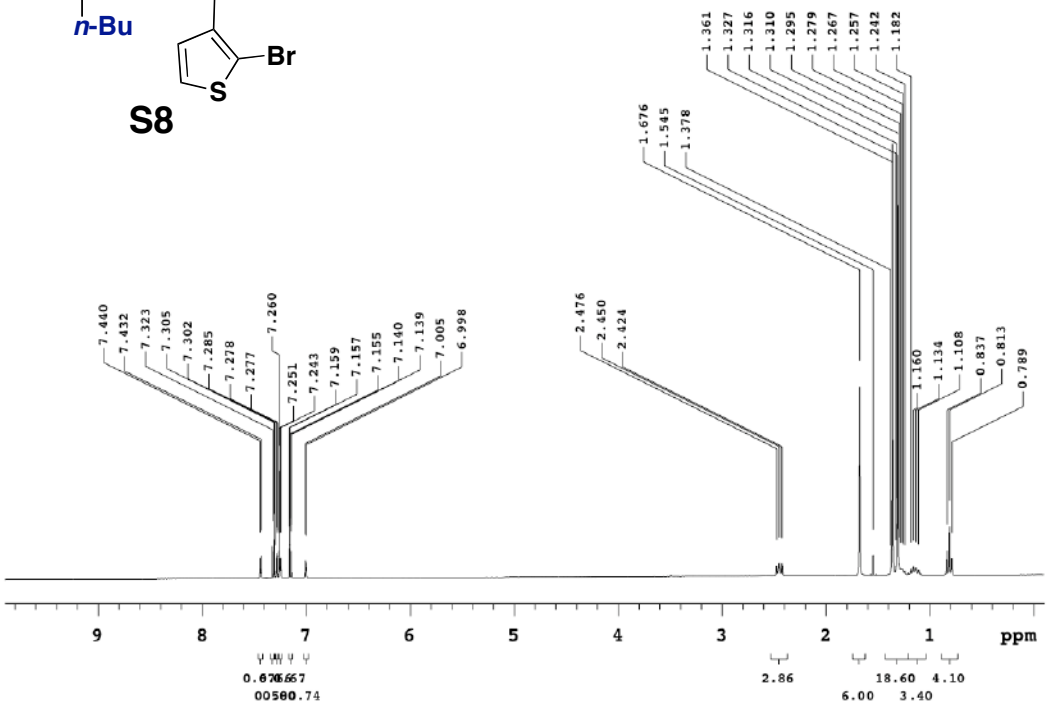
t-Bu
O
n-Bu
Br
S

S8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1.378
7.440
7.432
7.323
7.305
7.302
7.285
7.278
7.277
7.260
7.251
7.243
7.159
7.157
7.155
7.140
7.139
7.005
6.998
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2.424
1.160
1.134
1.108
0.837
0.813
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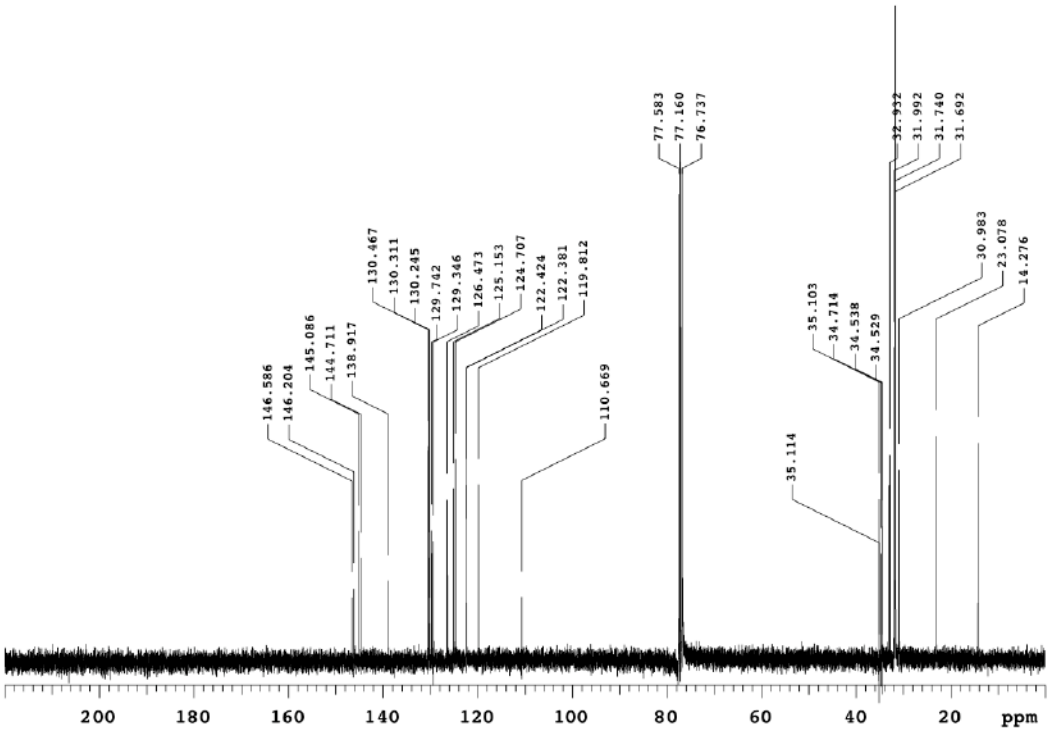
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125.153
124.707
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119.812
146.586
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145.086
144.711
138.917
110.669
35.103
34.714
34.538
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140
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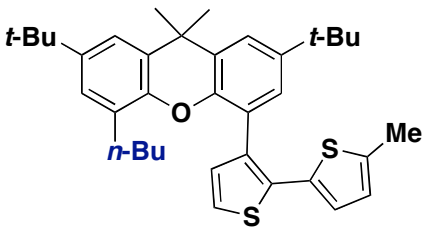
100
80
60
40
20
ppm


t-Bu
t-Bu
n-Bu
O
S
Me
S

S9

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4
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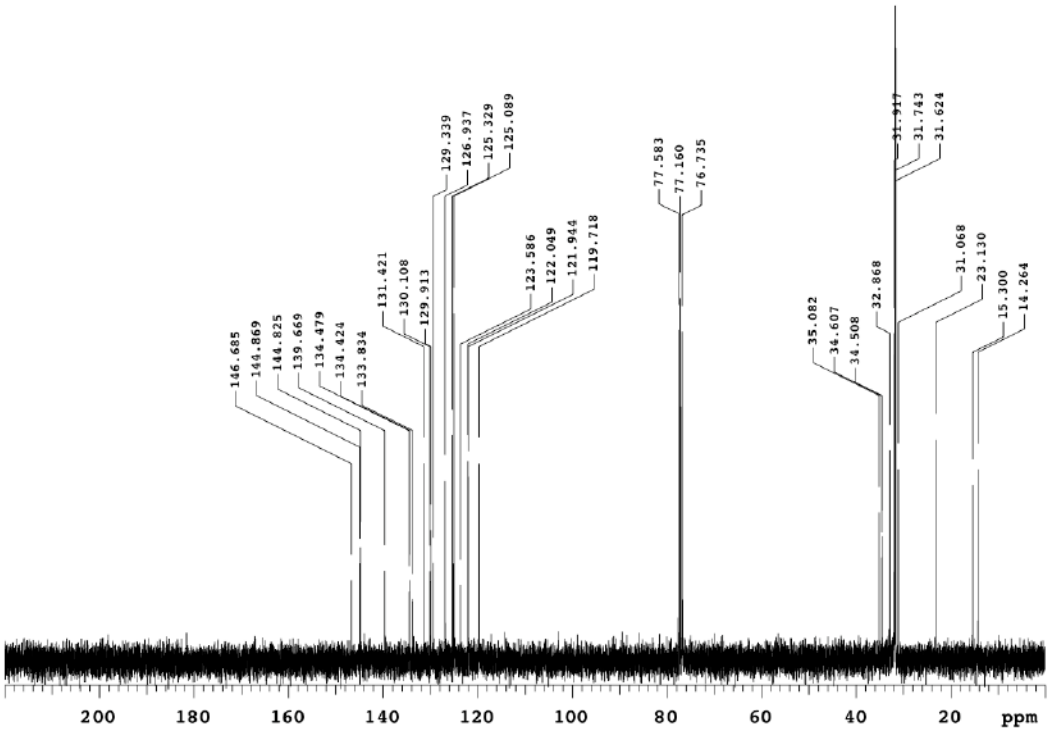
3.17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125.089
123.586
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121.944
119.718
77.583
77.160
76.735
35.082
34.607
34.508
32.868
31.917
31.743
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140
120
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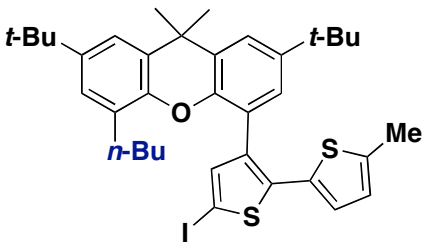
80
60
40
20
ppm


t-Bu
t-Bu
n-Bu
O
S
Me
S
I

S10

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1.291
9
8
7
6
5
4
3
2
1
ppm
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1.00
2.11
3.25
7.16
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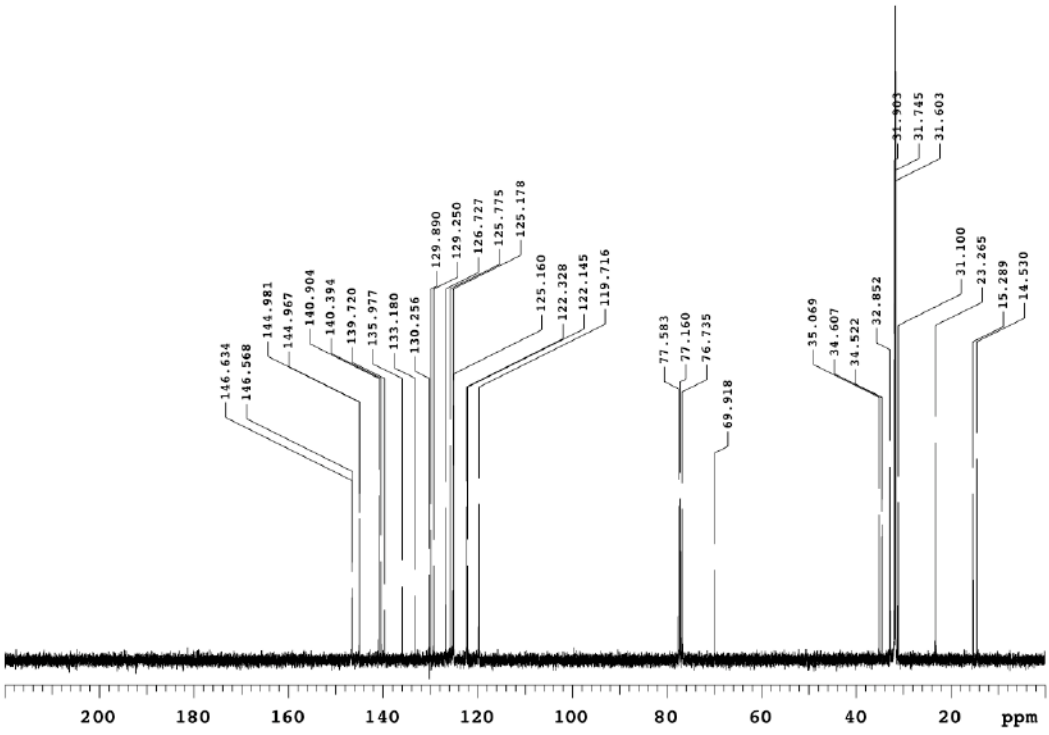
3.70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180
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140
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100
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20
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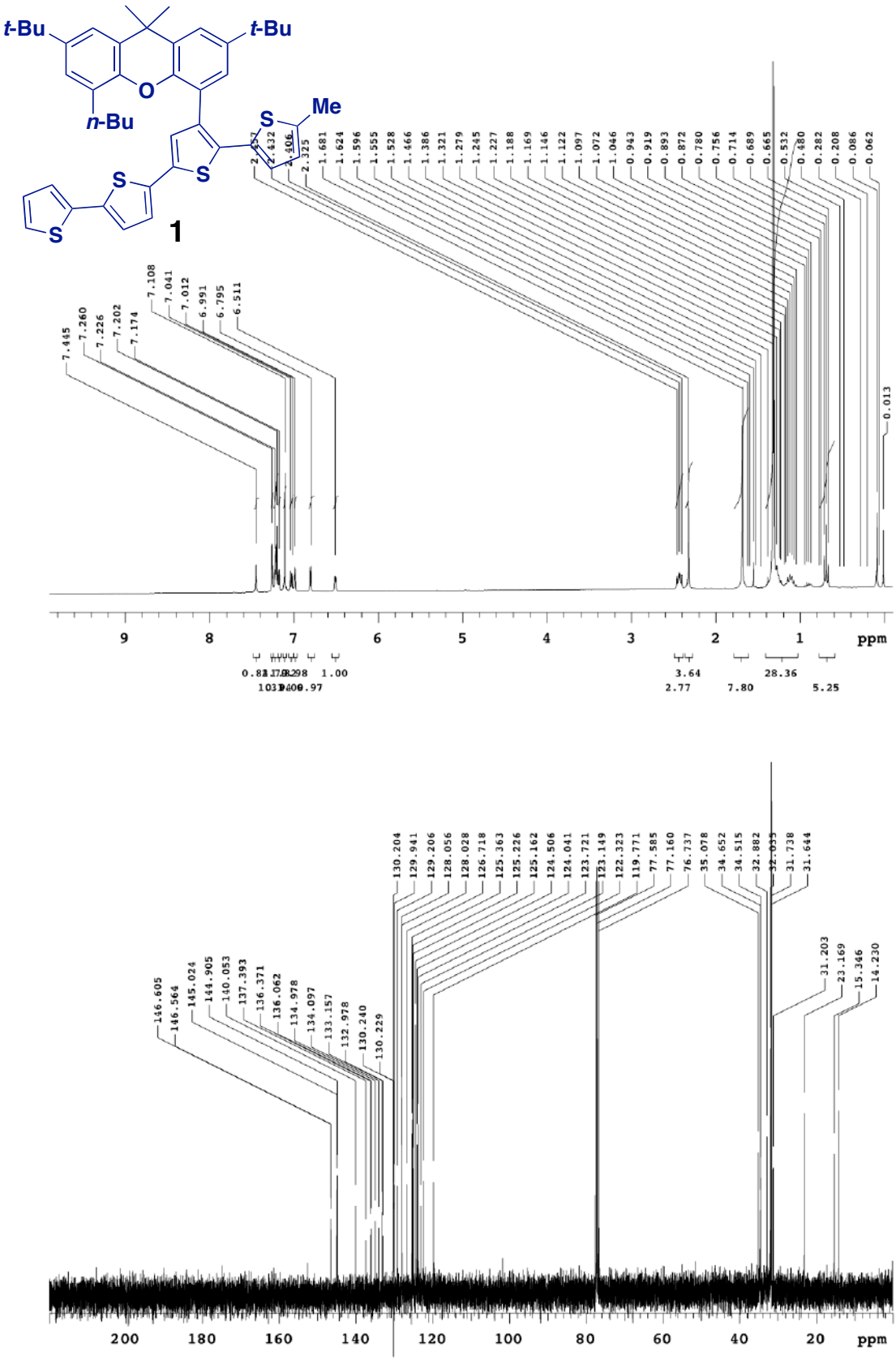
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t-Bu
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1
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ppm