

Electronic Supplementary Information for:

Quinoidal Diindenothienoacenes: Synthesis and Properties of New Functional Organic Materials

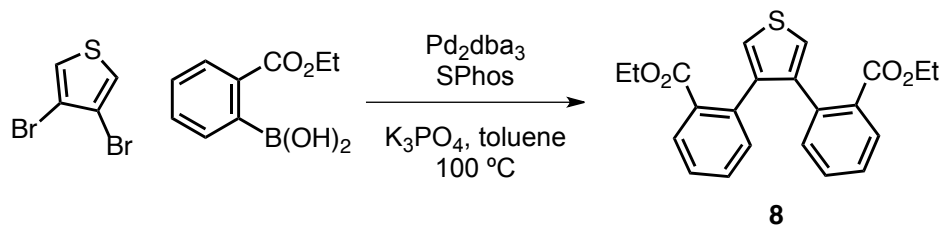
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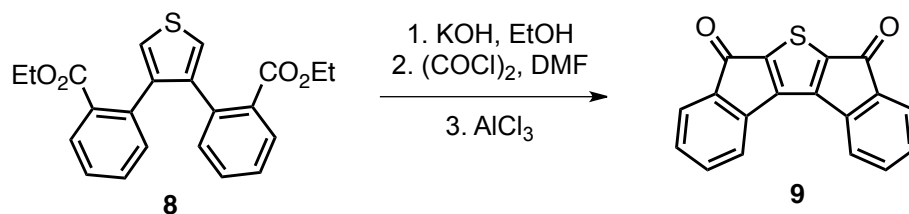
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Experimental details

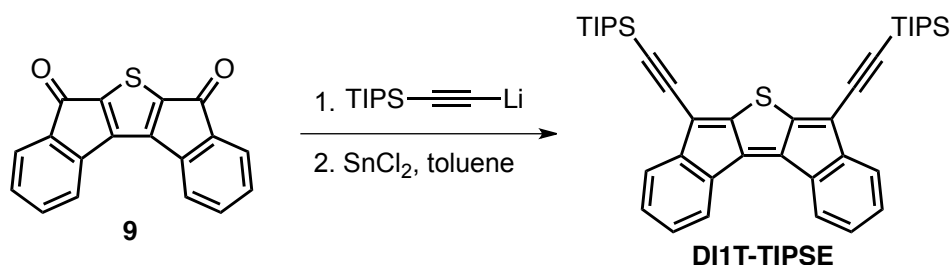
General information. Air sensitive manipulations were performed by standard Schlenk line technique. THF and toluene were refluxed with sodium benzophenone ketyl for 24 h prior to distillation and use. CH_2Cl_2 was distilled from calcium hydride. All other reagents were used without prior purification. 2-Ethoxycarbonylbenzeneboronic acid was purchased from Synthonix, Inc. (Trialkylsilyl)acetylenes were purchased from GFS Chemicals. Chromatography was performed on 230-400 mesh silica gel purchased from Aldrich. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 using a Varian Inova 500 (^1H : 500.11 MHz, ^{13}C : 125.75 MHz) or Bruker Avance-III-HD 600 (^1H : 599.98 MHz, ^{13}C : 150.87 MHz) NMR spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual chloroform (^1H : 7.26 ppm, ^{13}C : 77.16 ppm) reference. UV-Vis spectra were recorded on a HP 8453 UV-Vis spectrometer. High resolution mass spectra were recorded on a JEOL MS-Route mass spectrometer.



Diethyl 2,2'-(thiophene-3,4-diyl)dibenzoate (8) In a dry glass pressure vessel, 2-ethoxycarbonyl-benzeneboronic acid (6.0 g, 31 mmol), Pd_2dba_3 (120 mg, 0.124 mmol), SPhos (100 mg, 0.248 mmol), anhydrous K_3PO_4 (10.5 g, 49.6 mmol) and toluene (35 mL) were combined. The mixture was sparged with nitrogen (10 min) then 3,4-dibromothiophene (3.0 g, 12.4 mmol) was added via syringe. The vessel was sealed and heated at 100 °C for 16 h. Upon cooling to rt, the reaction was diluted with CH_2Cl_2 then filtered. The organics were washed with brine then dried over MgSO_4 . Volatiles were removed under reduced pressure to give an orange oil in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v). ^1H NMR (500 MHz, CDCl_3) δ 7.70 (dd, J = 7.7, 1.5 Hz, 2H), 7.35 (td, J = 7.5, 1.5 Hz, 2H), 7.30 (td, J = 7.6, 1.5 Hz, 2H), 7.26 (dd, J = 7.5, 1.4 Hz, 2H), 7.20 (s, 2H), 4.08 (q, J = 7.2 Hz, 4H), 1.12 (t, J = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.92, 141.38, 136.60, 131.98, 131.74, 130.87, 129.40, 127.11, 122.62, 60.84, 13.84. HRMS (ES+) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 381.1161, found 381.1168.

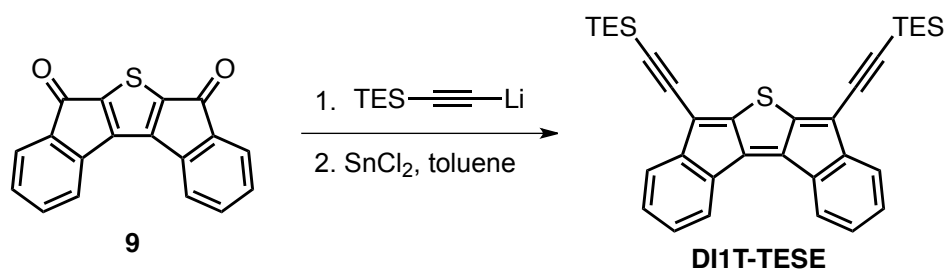


Diindeno[2,1-*b*:1',2'-*d*]thiophene-5,7-dione (9). To a solution of the crude diester **8** (4.4 g) in ethanol (100 mL) was added aqueous KOH (115 mmol, 5 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced *in vacuo* (30 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH₂Cl₂ (100 mL) was added 5 drops DMF. Oxalyl chloride (4.0 mL, 46 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed *in vacuo*. CH₂Cl₂ (100 mL) was added and the flask was cooled to 0 °C. AlCl₃ (9.25 g, 69 mmol) was added and the reaction was stirred at 0 °C for 16 h. The dark solution was poured onto ice and the precipitate was collected by filtration then washed with water. Recrystallization from CHCl₃ (1.5 L) provided the title compound as orange needles (1.71 g, 46% from 3,4-dibromothiophene). ¹H NMR (600 MHz, CDCl₃) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H); limited solubility of the title compound hindered acquisition of ¹³C NMR spectra; UV-Vis (CHCl₃) λ_{max}: 313, 440 (br) nm; HRMS (EI+) calcd for C₁₈H₈O₂S (M⁺) 289.0245, found 288.0240.

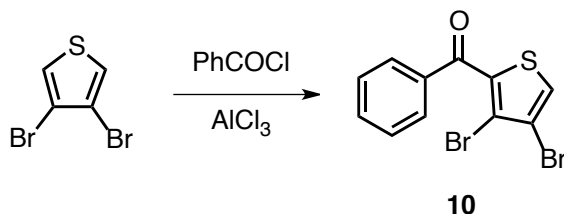


DI1T-TIPSE. In a dry two-neck flask, (triisopropylsilyl)acetylene (0.8 mL, 3.45 mmol) was added to THF (5 mL) and cooled to 0 °C. A solution of *n*-butyllithium (3.1 mmol, 1.6 M) was added dropwise then stirred for 5 min. In a second flask, dione **9** (200 mg, 0.69 mmol) was suspended in THF (25 mL) at 0 °C. The (triisopropylsilyl)ethynyllithium solution was transferred via syringe to the dione suspension and stirred for 30 min. The reaction was quenched with

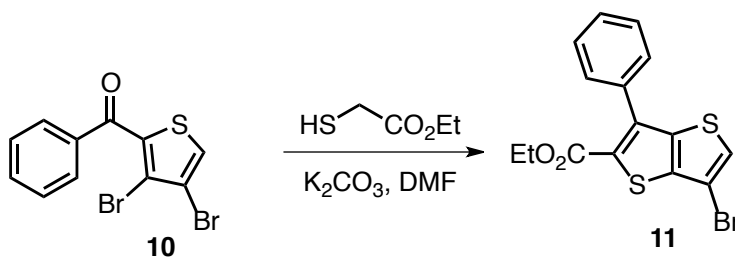
saturated NH_4Cl soln (50 mL). The organics were extracted with EtOAc (2 x 50 mL), washed with brine and dried over MgSO_4 . The volatiles were removed under reduced pressure, then the crude material was passed through a short plug of silica, eluting first with hexanes then EtOAc. The polar fractions were combined and reduced *in vacuo*. Toluene (15 mL) was added and the solution was degassed thoroughly under dynamic vacuum. Finely ground SnCl_2 (400 mg, 10.4 mmol) was added then further degassed under dynamic vacuum. The slurry was stirred for 3 h at rt, then poured onto a plug of silica and eluted with 1:1 CH_2Cl_2 /hexanes. Removal of the volatiles under reduced pressure provided the title compound (270 mg, 63%) as a green solid. ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 7.3$ Hz, 2H), 7.20 (td, $J = 7.5, 1.0$ Hz, 2H), 7.13 (d, $J = 7.3$ Hz, 2H), 7.07 (td, $J = 7.5, 1.2$ Hz, 2H), 1.17 (s, 42H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.77, 148.89, 144.03, 130.77, 130.19, 125.78, 124.37, 120.68, 116.32, 105.90, 99.70, 18.73, 11.28; UV-Vis (CH_2Cl_2) λ_{max} (ϵ): 266 (36000), 303 (30000), 311 (30300), 416 (31600), 443 (38400), 655 (br, 6400), 765 (sh, 6000) nm; HRMS (ES+) calcd for $\text{C}_{40}\text{H}_{51}\text{SSi}_2$ ($\text{M}+\text{H}$) $^+$ 619.3250, found 619.3243.



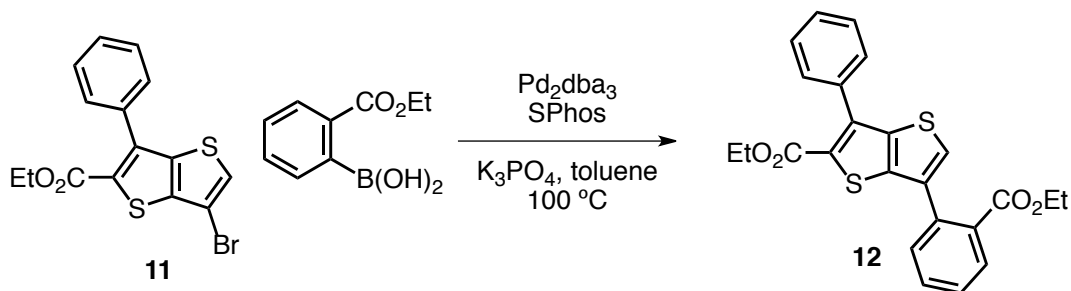
DI1T-TESE. The procedure for **DI1T-TIPSE** was adapted with (triethylsilyl)acetylene (521 mg, 3.71 mmol), n-butyllithium (3.34 mmol, 1.6 M) and **9** (214 mg, 0.74 mmol) to provide the title compound (147 mg, 37%) as a green solid. ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 7.3$ Hz, 2H), 7.19 (td, $J = 7.5, 1.0$ Hz, 2H), 7.11 (d, $J = 7.4$ Hz, 2H), 7.06 (td, $J = 7.5, 1.1$ Hz, 2H), 1.14 (t, $J = 7.9$ Hz, 18H), 0.77 (q, $J = 7.9$ Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.79, 148.73, 144.01, 130.66, 130.11, 125.80, 124.35, 120.62, 116.17, 106.53, 99.06, 7.63, 4.48; HRMS (ES+) calcd for $\text{C}_{34}\text{H}_{38}\text{SSi}_2$ (M^+) 534.2233, found 534.2208.



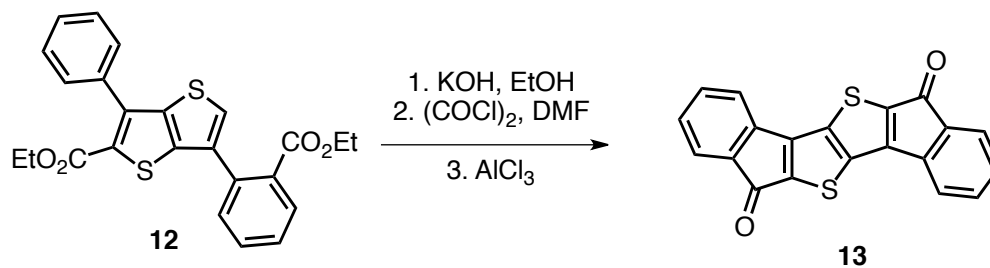
2-Benzoyl-3,4-dibromothiophene (10). AlCl₃ (15 g, 125 mmol) was added in three portions to a stirred solution of 3,4-dibromothiophene (10.0 g, 41.3 mmol) and benzoyl chloride (8.7 g, 62 mmol) in CH₂Cl₂ (100 mL) at 0 °C. The cooling bath was removed and the reaction was stirred for 16 h. The dark solution was poured onto ice, diluted with CH₂Cl₂ (100 mL) and washed successively with aqueous NaOH (1 M) and brine. The organic phases were combined and dried over MgSO₄. Removal of volatiles by reduced pressure provided the title compound (13.13 g, 92%) as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.88–7.84 (m, 2H), 7.67 (s, 1H), 7.67–7.63 (m, 1H), 7.52 (dd, *J* = 8.5, 7.1 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 187.38, 136.87, 136.82, 133.42, 129.86, 128.56, 128.08, 118.19, 116.67; HRMS (ES⁺) calcd for C₁₁H₆SBr₂ (M⁺), 343.8506 found 343.8521.



Ethyl 6-bromo-3-phenylthieno[3,2-*b*]thiophene-2-carboxylate (11). To a solution of **10** (13.13 g, 37.9 mmol) in DMF (50 mL) was added K₂CO₃ (15.7 g, 113.8 mmol) and the reaction was rigorously degassed under dynamic vacuum. With stirring, ethyl thiolglycolate (4.79 g, 39.8 mmol) was added dropwise via syringe and then the reaction was heated at 60 °C for 1 d. After cooling, the mixture was poured into water (100 mL). The solids were collected and washed with water. Recrystallization from ethanol (500 mL) provided **11** (11.2 g, 80%) as tan needles. ¹H NMR (500 MHz, CDCl₃) δ 7.60–7.55 (m, 2H), 7.53–7.45 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.08, 141.75, 141.14, 140.77, 133.72, 129.21, 129.05, 128.82, 128.30, 128.17, 103.14, 61.36, 14.08; HRMS (ES⁺) calcd for C₁₅H₁₂S₂O₂Br (M+H)⁺ 366.9462, found 366.9454.

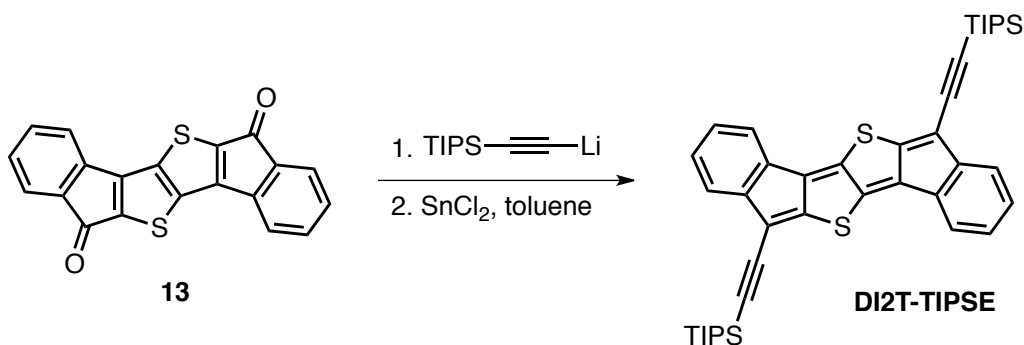


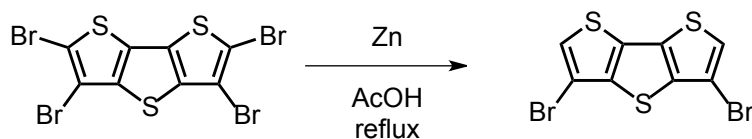
Diester 12. In a dry glass pressure vessel, 2-ethoxycarbonylbenzeneboronic acid (581 mg, 2.99 mmol), Pd_2dba_3 (25 mg, 0.027 mmol), SPhos (22 mg, 0.054 mmol), anhydrous K_3PO_4 (1.15 g, 5.44 mmol), **11** (1.00 g, 2.72 mmol) and toluene (10 mL) were combined. The mixture was sparged with nitrogen (10 min). The vessel was sealed and brought to 100 °C for 16 h. Upon cooling to rt the reaction was diluted with CH_2Cl_2 then filtered. The organics were washed with brine and dried over MgSO_4 . Removal of volatiles under reduced pressure provides the title compound in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v) to give a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.66–7.63 (m, 2H), 7.61 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.57 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.55–7.47 (m, 4H), 7.45 (s, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.06 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.58, 162.35, 141.73, 141.01, 140.94, 134.82, 134.78, 134.28, 131.91, 131.07, 130.61, 130.55, 129.17, 128.61, 128.44, 128.21, 127.88, 127.84, 61.23, 61.09, 14.10, 13.71; HRMS (ES⁺) calcd for $\text{C}_{24}\text{H}_{21}\text{S}_2\text{O}_4$ (M+H)⁺ 437.0881, found 437.0875.



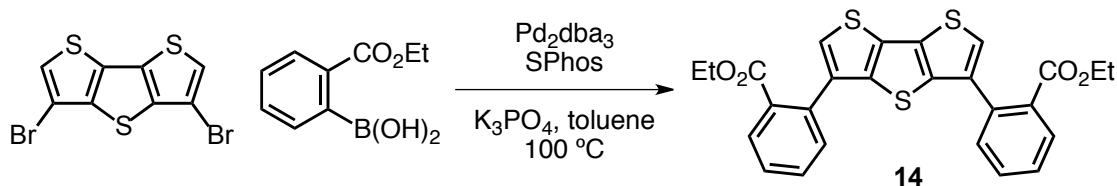
Indeno[2,1-*b*]indeno[1',2':4,5]thieno[2,3-*d*]thiophene-6,12-dione (13). To a solution of **12** (0.98 g, 2.25 mmol) in ethanol (100 mL) was added aqueous KOH (12 mmol, 1.5 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced *in vacuo* (to 20 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH_2Cl_2 (100 mL) was added DMF (5 drops). Oxalyl chloride (1.0

mL, 11.2 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed *in vacuo*. CH₂Cl₂ (50 mL) was added and the flask was cooled to 0 °C. AlCl₃ (3.0 g, 22.3 mmol) was added as a solid. The reaction was allowed to warm to rt and stir for 16 h. The dark solution was poured onto ice and the precipitate was collected by filtration. Successive washes with water and acetone gave the title compound (630 mg, 79%) as a magenta solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis (CHCl₃) λ_{max} : 370, 490, 522 (sh) nm; HRMS (EI+) calcd for C₂₀H₈O₂S₂ (M⁺) 343.9966, found 343.9959.

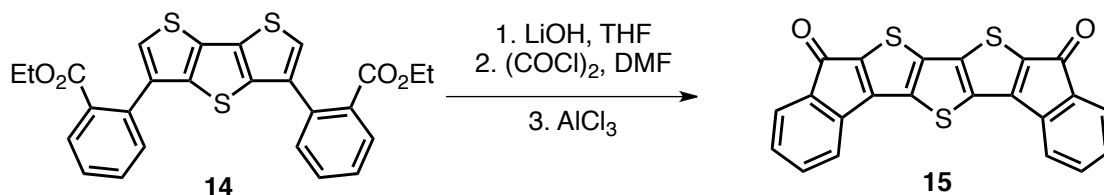




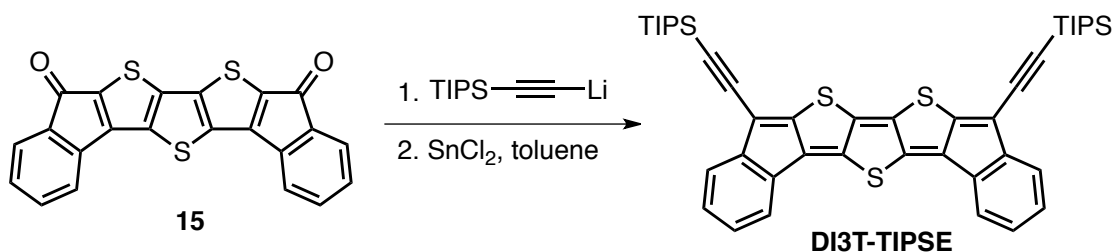
3,5-Dibromodithieno[3,2-*b*:2',3'-*d*]thiophene. In a 3-neck flask, tetrabromodithieno[3,2-*b*:2',3'-*d*]thiophene¹ (2.7 g, 5.3 mmol) in glacial AcOH (150 mL) was brought to reflux. Zn powder (3.44 g, 53 mmol) was added to the suspension. The reaction was refluxed for a further 30 min and then hot filtered through a fritted funnel. The solution was allowed to cool to rt, then the crude product was precipitated by the addition of water. The solids were collected by filtration. Recrystallization from chloroform provided the title compound as colorless needles (450 mg, 24%). ¹H NMR (500 MHz, CDCl₃/CS₂) δ 7.31 (s); ¹³C NMR (126 MHz, CDCl₃/CS₂) δ 142.74, 130.84, 123.16, 103.90. These spectroscopic data correspond to previously reported data.²



Diester 14. In a dry glass pressure vessel, 3,5-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (450 mg, 1.27 mmol), 2-ethoxycarbonylbenzeneboronic acid (754 mg, 3.18 mmol), Pd₂dba₃ (12 mg, 0.013 mmol), SPhos (24 mg, 0.05 mmol), anhydrous K₃PO₄ (1.0 g, 5.1 mmol) and toluene (15 mL) were combined and sparged with nitrogen (10 min). The vessel was sealed and brought to 100 °C for 24 h. Upon cooling to rt the reaction was diluted with CH₂Cl₂ then filtered. The organics were washed with brine and dried over MgSO₄. Removal of volatiles under reduced pressure provided the title compound in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v) to give a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.58-7.54 (m, 4H), 7.50-7.42 (m, 2H), 7.23 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.01 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 167.76, 142.24, 135.53, 135.00, 131.73, 131.27, 130.42, 130.40, 130.18, 128.25, 122.45, 61.13, 13.75; HRMS (ES⁺) calcd for C₂₆H₂₁S₃O₄ (M+H)⁺ 493.0602, found 493.0601.



Diindenodithieno[3,2-*b*:2',3'-*d*]thiophene-3,13-dione (15). To a solution of **14** (0.50 g, 2.25 mmol) in ethanol (100 mL) was added aqueous KOH (14.3 mmol, 1.4 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced *in vacuo* (to 15 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH₂Cl₂ (100 mL) was added DMF (5 drops). Oxalyl chloride (0.35 mL, 11.2 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed *in vacuo*. CH₂Cl₂ (50 mL) was added and the flask was cooled to 0 °C. AlCl₃ (1.0 g, 22.3 mmol) was added as a solid and the reaction was stirred for 1 h. The dark solution was poured onto ice and the precipitate was collected by filtration. Successive washes with water and acetone gave the title compound (328 mg, 81%) as a red solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis (CHCl₃) λ_{max}: 296, 481, 514 nm; HRMS (EI+) calcd for C₂₂H₈O₂S₃ (M⁺) 399.9686, found 399.9700.



DI3T-TIPSE. To a solution of (triisopropylsilyl)acetylene (227 mg, 1.25 mmol) in THF (5 mL) at 0 °C was added *n*-butyllithium (1.12 mmol, 1.5 M in hexanes) dropwise. In a separate flask, **15** (100 mg, 0.25 mmol) was suspended in THF (25 mL) and cooled to 0 °C. The (triisopropylsilyl)ethynyllithium solution was transferred to the dione suspension via syringe then sonicated for 10 min. After quenching with a saturated NH₄Cl solution, the organics were extracted with Et₂O and dried over MgSO₄. The volume was reduced *in vacuo* and passed through a short plug of silica, eluting with EtOAc. Volatiles were removed under reduced pressure. Toluene (15 mL) was added and the flask was rigorously degassed under dynamic vacuum. Finely ground SnCl₂ (250 mg, 1.25 mmol) was added and the reaction was stirred for 10

min. The mixture was passed through a plug of silica (CH_2Cl_2 /hexanes). Evaporation of the volatiles provided the title compound (131 mg, 72%) as a deep purple solid. ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, J = 7.3 Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.07 (t, J = 7.5 Hz, 2H), 1.21 (s, 42H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.91, 146.56, 143.92, 142.96, 138.51, 129.20, 128.52, 125.08, 122.04, 120.72, 113.17, 105.36, 100.45, 18.78, 11.34; UV-Vis (CH_2Cl_2) λ_{max} (ϵ): 256 (32300), 320 (8000), 513 (27600), 553 (39400), 683 (19600), 740 (sh, 16600) nm; HRMS (ES+) calcd for $\text{C}_{44}\text{H}_{51}\text{S}_3\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 731.2691, found 731.2711.

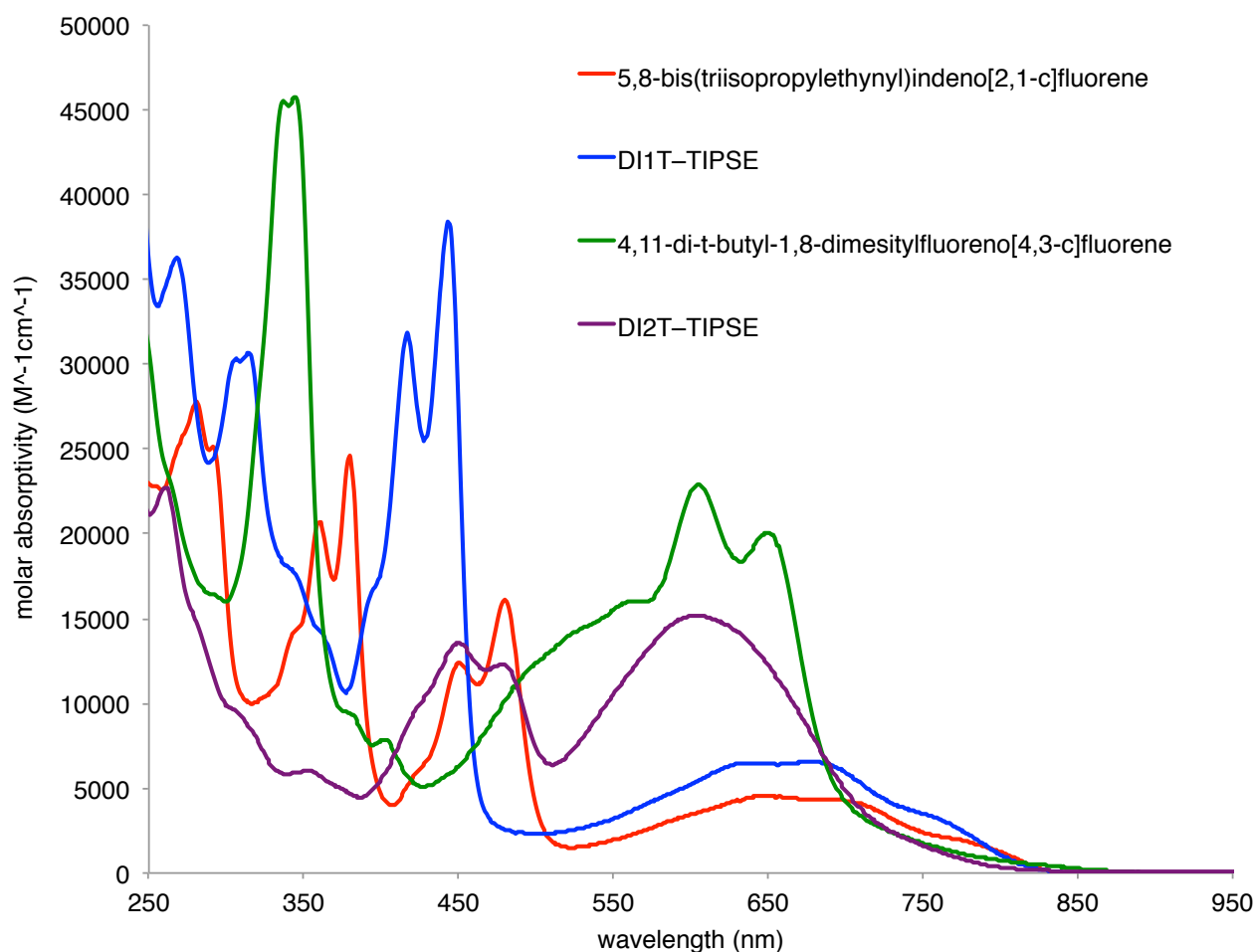


Fig. S1 Comparison of the electronic absorption spectra of **DI1T-TIPSE** and **DI2T-TIPSE** with the analogous indeno[2,1-*c*]fluorene and fluoreno[3,4-*c*]fluorene cores.

X-ray Crystallography

General. Diffraction intensities for **DI1T-TIPSE**, **DI2T**, **DI1T-TESE**, **9** and **13** were collected at 100(2) K and for **DI3T** at 150(2) K on a Bruker Apex2 CCD diffractometer with a micro-focus *I μ S* source using CuK α radiation λ = 1.54178 Å or a sealed X-ray tube with a triumph monochromator, MoK α radiation λ = 0.71073 Å (**9** only). Absorption corrections were applied by SADABS.³ Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were refined in calculated positions in a rigid group model. The Flack parameter for non-centrosymmetrical structure of **9** is 0.00(15). The structures of **DI2T** and **DI1T-TESE** have two symmetrically independent molecules. One of terminal *-i*-Pr groups in **DI3T** is disordered over two positions in ratio 42/58. X-ray diffraction from crystals of **DI2T**, **DI1T-TESE** and **13** at high angles were very weak; even with a strong Incoatec *I μ S* Cu source we could collected data only up to $2\theta_{\text{max}}$ = 114.98°, 120.0° and 132.0°, respectively. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.⁴

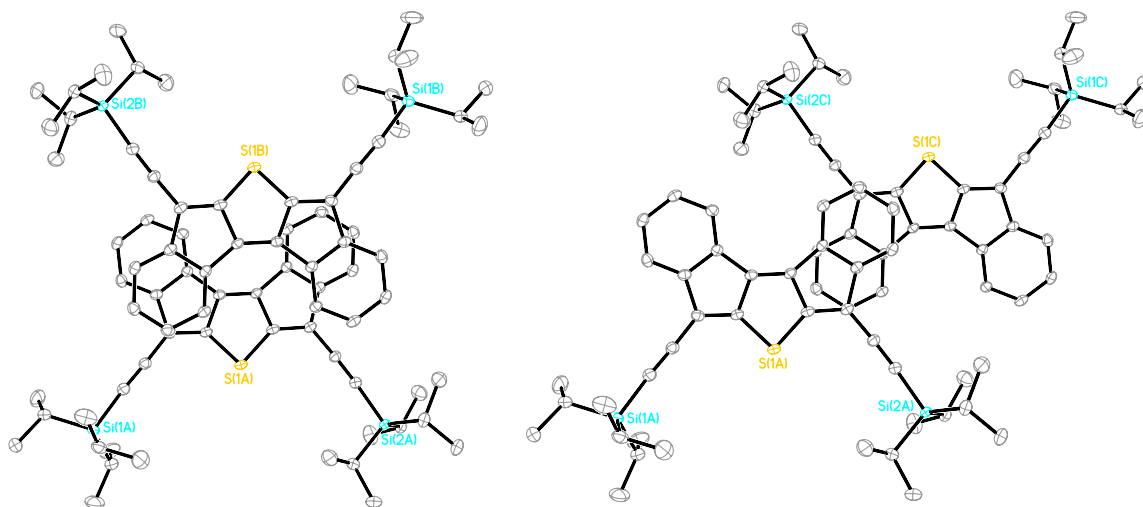


Fig. S2 Additional views of the pairwise arrangement for **DI1T-TIPSE**.

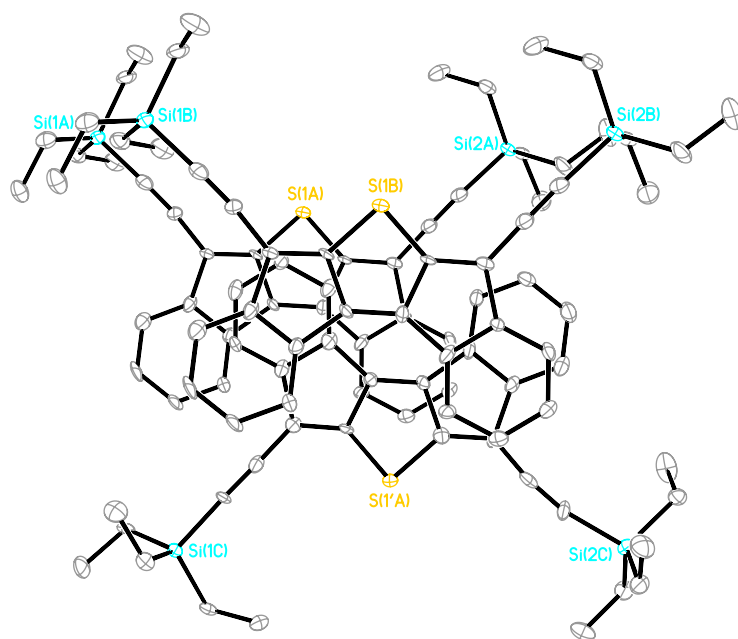


Fig. S3 Pairwise slipped stack of **DI1T-TESE**.

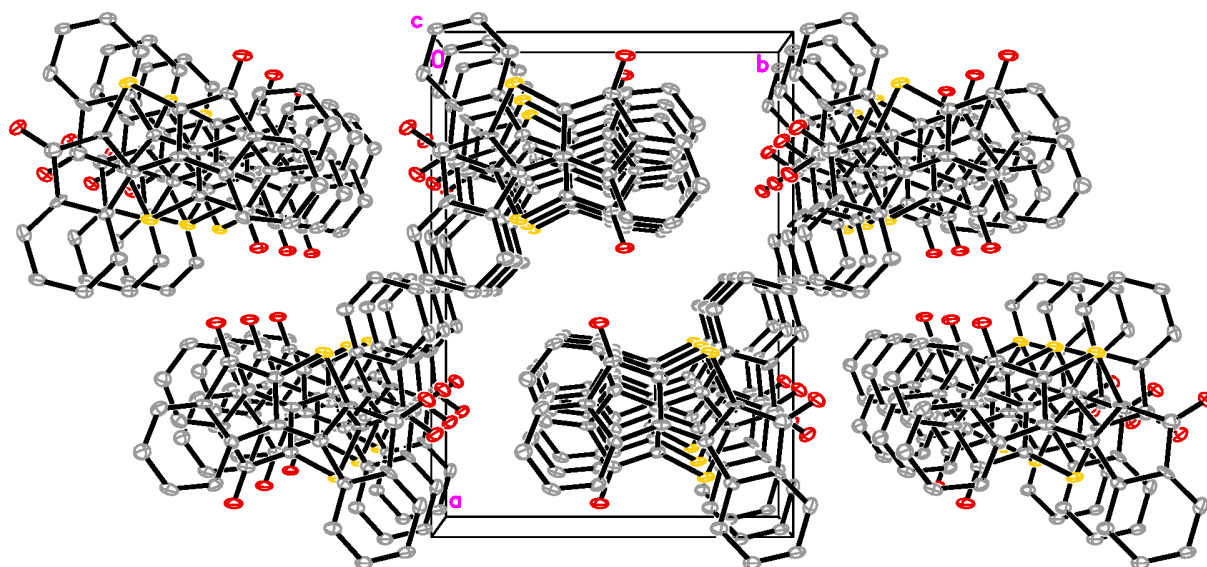


Fig. S4 Expanded packing view of dione **9**.

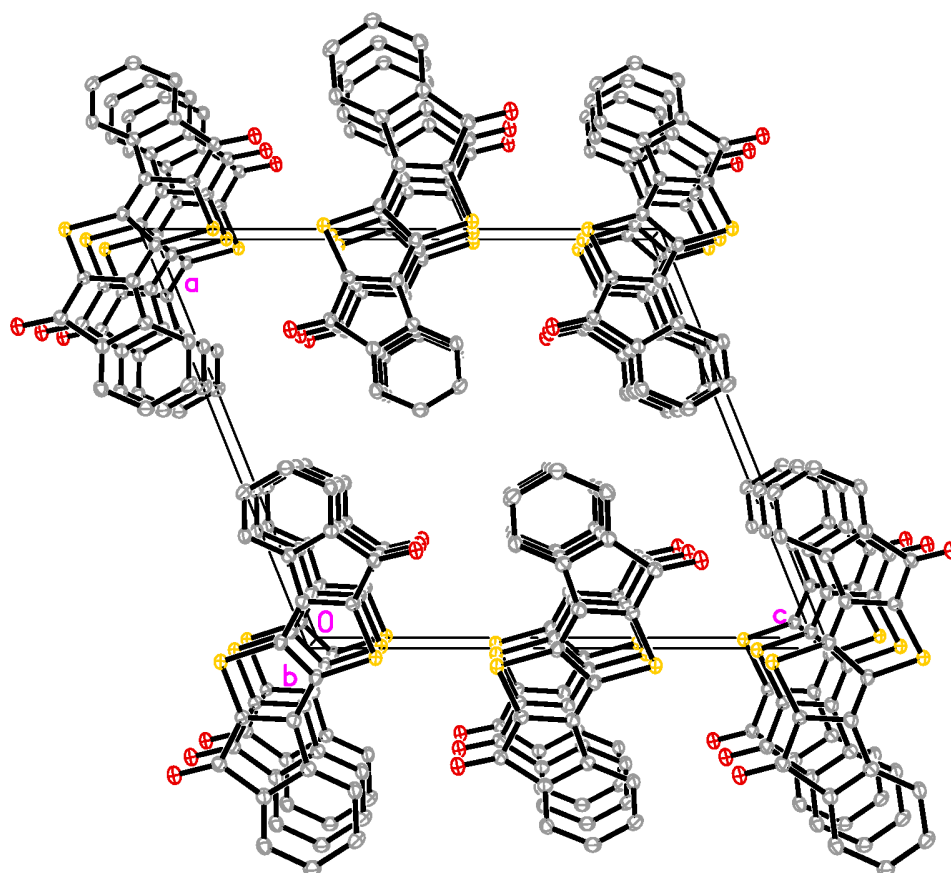


Fig. S5 Expanded packing view of dione **13**.

Cyclic Voltammetry

All electrochemical experiments were conducted in a traditional 3-electrode geometry using a Solartron 1287 potentiostat. Electrolyte solutions (0.1 M) were prepared from HPLC-grade CH_2Cl_2 and anhydrous Bu_4NBF_4 , and the solutions were freeze-pump-thaw degassed (3x) prior to analysis. Cyclic voltammetry was conducted under a nitrogen atmosphere. The working electrode was a glassy carbon electrode (3-mm diameter), with a Pt-coil counter electrode and Ag wire pseudo reference. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as an internal standard following each experiment. Potential values were re-referenced to SCE using a value of 0.46 (V vs. SCE) for the Fc/Fc^+ couple in CH_2Cl_2 . When necessary, potentials were re-referenced to NHE using $\text{SCE} = -0.24$ (V vs. NHE). LUMO and HOMO levels were approximated using $\text{SCE} = -4.68$ eV vs. vacuum.⁵ Cyclic voltammetry experiments were conducted at sweep rates of 50 (reported), 75, 100 and 125 mV s^{-1} . All scan rates show quasi-reversible kinetics with no alteration of peak splitting with scan rate. $E_{1/2}$ values were calculated assuming $E_{1/2} \approx E^{\circ'} = (E_{\text{anodic}} + E_{\text{cathodic}})/2$ based on these observations for reversible couples; for irreversible couples the $E^{\circ'}$ value is estimated as the potential at peak current. The $E_{\text{a,c}}$ peak splitting of the Fc/Fc^+ couple was similar to that of the analyte (~ 100 mV). The anodic peak current increases linearly with the square root of the scan rate in the range 50 to 125 mV s^{-1} , indicating a diffusion-controlled process. Analyte concentrations were ca. 1-5 mM.

Electronic Paramagnetic Resonance

Experimental details. An apparatus (Fig. S6) was constructed from borosilicate glass and dried in a 100 °C oven. The apparatus was then cooled to rt under nitrogen and approximately 0.05 mg of **DI[n]T** was collected on a melting point capillary that was open on both ends and deposited at point A. Potassium metal was added at point B and then opening C was sealed with an oxygen/natural gas torch. Vacuum was pulled (ca. 10^{-6} torr) and K metal was sublimed with a Bunsen burner, resulting in a metal mirror inside D. The apparatus was then sealed at point E. Dry THF (approx. 1 mL) from a NaK still was directly distilled through the vacuum system to A and the apparatus was sealed at point F. Controlled exposure to the potassium mirror resulted in formation of **DI[n]T** radical anion, from which the EPR spectra in Figs. S5-S7 were obtained. The EPR spectra were collected on a Bruker EMX-080 spectrometer.

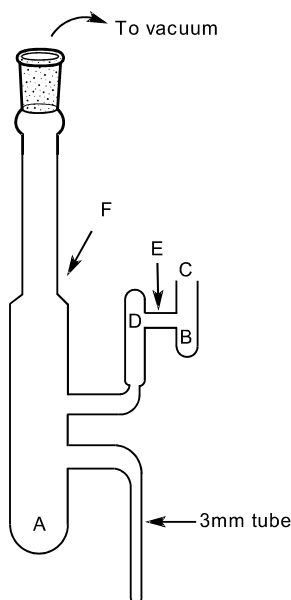


Fig. S6 Apparatus used for generation of anion radical.

EPR Computational Details. To determine the hyperfine coupling constants for the hydrogen and silicon nuclei coupled with the anion radical, the EPR spectra were simulated with the EasySpin⁶ package utilizing MATLAB code.⁷ DFT calculations were performed for the gas phase molecules using Gaussian09 Revision C.01⁸ and the results were used to assign the HFCC and carbon spin density locations (Table S1). These computations were carried out at the UB3W91/6-311++G(2df,2pd)//UCAM-B3LYP/6-31++G(d,p) level of theory.

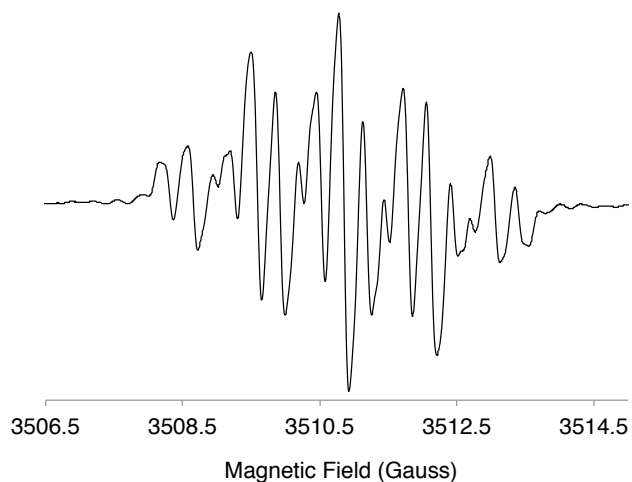


Fig. S7 EPR spectrum of **DI1T^{•-}**.

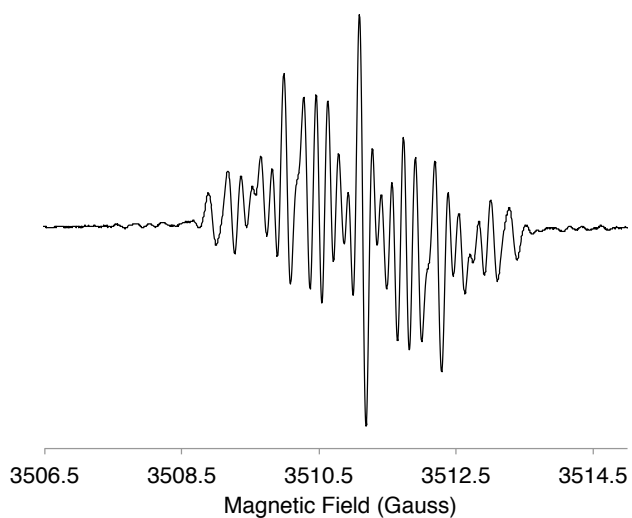


Fig. S8 EPR spectrum of **DI2T^{•-}**.

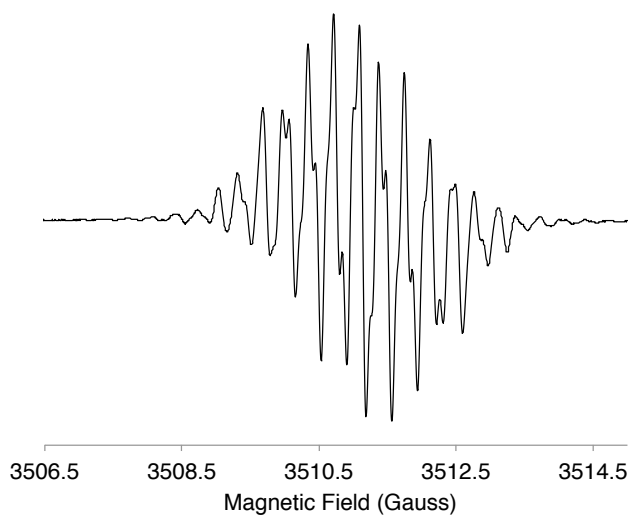


Fig. S9 EPR spectrum of **DI3T^{•-}**.

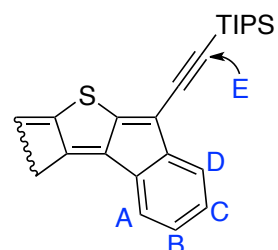


Table S1 Hyperfine Coupling Constants and Carbon spin densities (ρ_c).

	DI1T	DI2T	DI3T
C(A)	0.034	0.022	0.024
C(B)	0.012	0.016	0.014
C(C)	0.044	0.029	0.028
C(D)	0.004	0.010	0.010
C(E)	0.112	0.103	0.094
H(A)	0.95	0.63	0.63
H(B)	0.35	0.46	0.38
H(C)	1.25	0.82	0.77
H(D)	0.11	0.28	0.27
Si	2.00	1.92	1.88
Q_H	28.1	28.2	26.6
Q_{Si}	17.9	18.6	20

Geometry Calculations

DFT calculations were performed for gas phase molecules using the Gaussian09 Revision C.01.⁸ Harmonic frequency analyses, performed at the same level of theory as the minimization, were used to confirm minimized structures.

Cartesian Coordinates

DI1T Neutral

UCAM-B3LYP/6-31G(d,p)

Zero-point correction=	0.448804 (Hartree/Particle)
Thermal correction to Energy=	0.481967
Thermal correction to Enthalpy=	0.482911
Thermal correction to Gibbs Free Energy=	0.379259
Sum of electronic and zero-point Energies=	-2058.703728
Sum of electronic and thermal Energies=	-2058.670565
Sum of electronic and thermal Enthalpies=	-2058.669621
Sum of electronic and thermal Free Energies=	-2058.773273
NIMAG = 0	

C	1.93558	4.11556	-0.00060
C	1.82260	2.73673	0.00025
C	3.21007	4.68787	-0.00134
C	2.98224	1.92787	0.00039
C	4.24123	2.49387	-0.00043
C	4.34546	3.88761	-0.00129
H	5.12629	1.86635	-0.00056
H	5.32724	4.34978	-0.00197
H	1.05689	4.74990	-0.00074
H	3.31141	5.76782	-0.00203
C	2.58279	0.49782	0.00128
C	0.67455	1.82696	0.00094
C	1.22605	0.46961	0.00151
C	3.48230	-0.59110	0.00156
S	-0.00314	-0.78434	0.00212
C	-1.23106	0.47082	0.00153
C	-0.67827	1.82761	0.00099
C	-1.82548	2.73845	0.00041
C	-2.58779	0.50027	0.00113
C	-2.98589	1.93067	0.00049

C	-1.93713	4.11738	-0.00020
C	-4.24428	2.49795	-0.00002
C	-3.21106	4.69094	-0.00073
C	-4.34721	3.89178	-0.00064
H	-1.05782	4.75087	-0.00025
H	-3.31135	5.77098	-0.00121
H	-5.12994	1.87126	0.00010
H	-5.32855	4.35489	-0.00105
C	-3.48759	-0.5882	0.00093
C	4.26800	1.51855	0.00153
Si	5.44268	2.93551	-0.00042
C	-4.27192	-1.51704	0.00060
Si	-5.43894	-2.94056	-0.00053
C	-6.63740	-2.73204	1.43019
C	-4.44445	-4.51988	0.20022
C	-6.36728	-2.95221	-1.63294
C	4.87476	-4.17921	-1.28695
C	5.44532	-3.71522	1.70780
C	7.15304	-2.28615	-0.42501
H	-3.88452	-4.51898	1.13918
H	-3.72743	-4.64272	-0.61587
H	-5.10247	-5.39445	0.20288
H	-6.11060	-2.70409	2.38770
H	-7.34853	-3.56343	1.46294
H	-7.21065	-1.80570	1.33711
H	3.86916	-4.54664	-1.06559
H	5.54809	-5.04165	-1.31499
H	4.85564	-3.73611	-2.28617
H	4.45105	-4.08030	1.97859
H	5.75677	-2.99762	2.47150
H	6.13549	-4.56399	1.74364
H	7.16412	-1.81134	-1.40976
H	7.88358	-3.10100	-0.43824
H	7.49054	-1.54744	0.30704
H	-6.93524	-2.02873	-1.77418
H	-7.07292	-3.78810	-1.67030
H	-5.68142	-3.05482	-2.47804

DI1T Radical Anion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.444806 (Hartree/Particle)

Thermal correction to Energy= 0.478102

Thermal correction to Enthalpy= 0.479046

Thermal correction to Gibbs Free Energy= 0.375054

Sum of electronic and zero-point Energies= -2058.828161

Sum of electronic and thermal Energies= -2058.794866

Sum of electronic and thermal Enthalpies= -2058.793921

Sum of electronic and thermal Free Energies= -2058.897913

NIMAG = 0

C	1.94799	4.11942	0.00310
C	1.83308	2.73021	0.00100
C	3.21242	4.70462	0.00361
C	3.01300	1.92490	-0.00045
C	4.27089	2.52068	-0.00017
C	4.36507	3.91079	0.00198
H	5.16532	1.90406	-0.00199
H	5.34346	4.38340	0.00221
H	1.06232	4.74584	0.00427
H	3.30306	5.78712	0.00523
C	2.62682	0.51601	-0.00248
C	0.70015	1.82703	-0.00023
C	1.23578	0.50367	-0.00224
C	3.50917	-0.57731	-0.00251
S	0.00000	-0.74381	-0.00407
C	-1.23578	0.50367	-0.00223
C	-0.70015	1.82703	-0.00023
C	-1.83308	2.73021	0.00101
C	-2.62682	0.51601	-0.00246
C	-3.01300	1.92490	-0.00043
C	-1.94799	4.11942	0.00311
C	-4.27088	2.52067	-0.00015
C	-3.21241	4.70462	0.00363
C	-4.36507	3.91079	0.00201
H	-1.06232	4.74584	0.00428
H	-3.30306	5.78711	0.00525
H	-5.16532	1.90406	-0.00196
H	-5.34345	4.38340	0.00224

C	-3.50917	-0.57731	-0.00250
C	4.28847	-1.52013	-0.00336
Si	5.42442	-2.93673	0.00093
C	-4.28847	-1.52012	-0.00335
Si	-5.42442	-2.93673	0.00093
C	-5.70944	-3.54927	1.76173
C	-4.69630	-4.34160	-1.02205
C	-7.08060	-2.42031	-0.73782
C	4.69622	-4.34167	-1.02191
C	5.70953	-3.54918	1.76176
C	7.08056	-2.42037	-0.73794
H	-3.72561	-4.65081	-0.62244
H	-4.54105	-4.02936	-2.05921
H	-5.35811	-5.21507	-1.02284
H	-4.76626	-3.85770	2.22313
H	-6.39345	-4.40553	1.77888
H	-6.13788	-2.75819	2.38493
H	3.72557	-4.65085	-0.62221
H	5.35804	-5.21514	-1.02270
H	4.54089	-4.02948	-2.05908
H	4.76637	-3.85757	2.22323
H	6.13802	-2.75806	2.38489
H	6.39354	-4.40544	1.77892
H	6.95664	-2.07507	-1.76888
H	7.78968	-3.25584	-0.74047
H	7.52492	-1.60041	-0.16514
H	-7.52495	-1.60041	-0.16493
H	-7.78971	-3.25579	-0.74040
H	-6.95674	-2.07492	-1.76874

DI1T Dianion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.442213 (Hartree/Particle)

Thermal correction to Energy= 0.475713

Thermal correction to Enthalpy= 0.476657

Thermal correction to Gibbs Free Energy= 0.372411

Sum of electronic and zero-point Energies= -2058.797119

Sum of electronic and thermal Energies= -2058.763620

Sum of electronic and thermal Enthalpies= -2058.762676

Sum of electronic and thermal Free Energies= -2058.866921

NIMAG = 0

C	-1.96138	4.10054	0.01211
C	-1.84371	2.70439	0.00652
C	-3.21726	4.69851	0.01847
C	-3.04402	1.90052	0.00746
C	-4.29859	2.52313	0.01394
C	-4.38387	3.91054	0.01938
H	-5.20058	1.91486	0.01461
H	-5.36013	4.39176	0.02441
H	-1.06942	4.72052	0.01145
H	-3.29776	5.78361	0.02274
C	-2.67242	0.50957	0.00102
C	-0.72161	1.80756	-0.00055
C	-1.24168	0.51219	-0.00370
C	-3.54520	-0.57112	-0.00026
S	0.00252	-0.72847	-0.01276
C	1.24609	0.51285	-0.01205
C	0.72540	1.80793	-0.00535
C	1.84709	2.70530	-0.00535
C	2.67682	0.51087	-0.01663
C	3.04781	1.90205	-0.01225
C	1.96399	4.10152	-0.00014
C	4.30196	2.52549	-0.01386
C	3.21951	4.70024	-0.00180
C	4.38655	3.91291	-0.00865
H	1.07167	4.72096	0.00517
H	3.29943	5.78537	0.00220
H	5.20432	1.91777	-0.01967
H	5.36254	4.39469	-0.01005

C	3.54968	-0.56971	-0.02105
C	-4.33915	-1.51613	-0.00131
Si	-5.47090	-2.89818	-0.00313
C	4.34126	-1.51671	-0.02839
Si	5.46945	-2.90140	0.00762
C	6.97412	-2.59983	-1.10675
C	4.61708	-4.48486	-0.58232
C	6.15385	-3.25367	1.74296
C	-5.25356	-4.01577	1.51347
C	-5.25297	-4.01171	-1.52255
C	-7.26553	-2.28942	-0.00239
H	4.26668	-4.37379	-1.61323
H	3.74198	-4.70303	0.03801
H	5.29410	-5.34677	-0.53729
H	6.66070	-2.46141	-2.14636
H	7.68083	-3.43812	-1.06633
H	7.50346	-1.69155	-0.80001
H	-4.22906	-4.39879	1.56319
H	-5.93945	-4.87200	1.48701
H	-5.43698	-3.45376	2.43487
H	-4.22832	-4.39419	-1.57322
H	-5.43653	-3.44738	-2.44250
H	-5.93853	-4.86825	-1.49835
H	-7.46419	-1.67427	0.88113
H	-7.97161	-3.12884	-0.00306
H	-7.46436	-1.67267	-0.88475
H	6.68105	-2.37674	2.13321
H	6.85063	-4.10176	1.74123
H	5.33797	-3.47963	2.43715

DI2T Neutral

UCAM-B3LYP/6-31G(d,p)

Zero-point correction= 0.463062 (Hartree/Particle)

Thermal correction to Energy= 0.498623

Thermal correction to Enthalpy= 0.499567

Thermal correction to Gibbs Free Energy= 0.389852

Sum of electronic and zero-point Energies= -2533.040684

Sum of electronic and thermal Energies= -2533.005123

Sum of electronic and thermal Enthalpies= -2533.004179

Sum of electronic and thermal Free Energies= -2533.113894

NIMAG = 0

C	4.07561	3.49564	-0.11229
C	3.20184	2.42553	-0.07788
C	1.80398	2.63860	-0.08716
C	1.28393	3.92068	-0.13100
C	1.18186	1.32102	-0.04381
C	2.17037	4.99840	-0.16571
H	0.21176	4.08979	-0.13835
C	3.54523	4.78691	-0.15638
H	1.78196	6.01058	-0.20021
H	4.21720	5.63849	-0.18375
H	5.14807	3.33146	-0.10499
C	3.47382	0.96806	-0.02864
C	2.26383	0.34784	-0.00955
C	4.75780	0.38065	-0.00730
S	1.69141	-1.31324	0.04584
C	0.03465	-0.72812	0.02395
C	-0.03348	0.73074	-0.02549
S	-1.69023	1.31584	-0.04716
C	-2.26267	-0.34524	0.00830
C	-1.18069	-1.31841	0.04249
C	-1.80276	-2.63600	0.08627
C	-3.20062	-2.42295	0.07732
C	-1.28270	-3.91807	0.13045
C	-3.47262	-0.96550	0.02768
C	-4.07444	-3.49300	0.11253
C	-4.75682	-0.37858	0.00620
C	-2.16916	-4.99576	0.16585
H	-0.21054	-4.08720	0.13761

C	-3.54403	-4.78425	0.15694
H	-5.14691	-3.32878	0.10588
H	-1.78075	-6.00792	0.20066
H	-4.21599	-5.63582	0.18502
C	5.86787	-0.11460	0.01072
Si	7.54086	-0.88138	0.03869
C	7.35853	-2.68171	0.53848
C	8.59984	0.04180	1.28481
C	8.28952	-0.75030	-1.67858
H	7.67699	-1.27178	-2.41887
H	9.29024	-1.19324	-1.69931
H	8.37893	0.29253	-1.99449
H	8.16859	-0.01122	2.28800
H	8.69798	1.09772	1.01872
H	9.60609	-0.38647	1.32941
H	6.90672	-2.77443	1.52967
H	8.33457	-3.17600	0.56758
H	6.72821	-3.22759	-0.16863
C	-5.86751	0.11525	-0.01154
Si	-7.54251	0.87760	-0.03825
C	-7.47622	2.49142	0.91892
C	-8.75046	-0.31375	0.76682
C	-8.02979	1.19393	-1.82393
H	-7.17916	2.32397	1.95761
H	-8.45629	2.97862	0.92488
H	-6.75957	3.18732	0.47460
H	-7.32683	1.87389	-2.31248
H	-9.02566	1.64477	-1.87897
H	-8.05049	0.26505	-2.40012
H	-8.46854	-0.52677	1.80141
H	-8.78962	-1.26437	0.22808
H	-9.76070	0.10721	0.77492

DI2T Radical Anion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.459072 (Hartree/Particle)

Thermal correction to Energy= 0.494818

Thermal correction to Enthalpy= 0.495763

Thermal correction to Gibbs Free Energy= 0.385295

Sum of electronic and zero-point Energies= -2533.175198

Sum of electronic and thermal Energies= -2533.139451

Sum of electronic and thermal Enthalpies= -2533.138507

Sum of electronic and thermal Free Energies= -2533.248975

NIMAG = 0

C	-4.21159	-3.38926	-0.00394
C	-3.31638	-2.32209	-0.00479
C	-1.91111	-2.57068	-0.00592
C	-1.42996	-3.87850	-0.00620
C	-1.25784	-1.28240	-0.00644
C	-2.33681	-4.93529	-0.00538
H	-0.36109	-4.07301	-0.00706
C	-3.71594	-4.69068	-0.00424
H	-1.97135	-5.95801	-0.00561
H	-4.40836	-5.52791	-0.00363
H	-5.28185	-3.20355	-0.00314
C	-3.54674	-0.87917	-0.00471
C	-2.28392	-0.29342	-0.00581
C	-4.80016	-0.24338	-0.00226
S	-1.64880	1.34103	-0.00591
C	-0.00921	0.70770	-0.00633
C	0.00920	-0.70771	-0.00660
S	1.64880	-1.34104	-0.00635
C	2.28391	0.29341	-0.00559
C	1.25784	1.28239	-0.00590
C	1.91111	2.57067	-0.00485
C	3.31637	2.32209	-0.00376
C	1.42996	3.87849	-0.00465
C	3.54674	0.87917	-0.00422
C	4.21158	3.38925	-0.00246
C	4.80016	0.24338	-0.00195
C	2.33681	4.93528	-0.00339
H	0.36108	4.07300	-0.00549

C	3.71593	4.69067	-0.00229
H	5.28184	3.20354	-0.00169
H	1.97134	5.95800	-0.00325
H	4.40835	5.52790	-0.00132
C	-5.89532	0.30046	0.00009
Si	-7.51188	1.13178	0.00846
C	-7.25687	2.99101	-0.14876
C	-8.42389	0.76311	1.61691
C	-8.55965	0.52167	-1.43529
H	-8.06651	0.73011	-2.38961
H	-9.54154	1.00827	-1.44483
H	-8.71772	-0.55963	-1.37436
H	-7.84865	1.11356	2.47929
H	-8.57984	-0.31324	1.73958
H	-9.40395	1.25313	1.63854
H	-6.65148	3.37340	0.67866
H	-8.21506	3.52251	-0.14385
H	-6.73625	3.23630	-1.07939
C	5.89532	-0.30046	0.00024
Si	7.51189	-1.13177	0.00841
C	7.25690	-2.99096	-0.14934
C	8.42385	-0.76353	1.61699
C	8.55969	-0.52124	-1.43514
H	6.65151	-3.37359	0.67796
H	8.21510	-3.52244	-0.14457
H	6.73630	-3.23599	-1.08004
H	8.06659	-0.72942	-2.38953
H	9.54159	-1.00782	-1.44479
H	8.71774	0.56005	-1.37391
H	7.84860	-1.11425	2.47925
H	8.57977	0.31278	1.73998
H	9.40393	-1.25353	1.63850

DI2T Dianion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.456790 (Hartree/Particle)

Thermal correction to Energy= 0.492717

Thermal correction to Enthalpy= 0.493661

Thermal correction to Gibbs Free Energy= 0.383872

Sum of electronic and zero-point Energies= -2533.159282

Sum of electronic and thermal Energies= -2533.123355

Sum of electronic and thermal Enthalpies= -2533.122411

Sum of electronic and thermal Free Energies= -2533.232201

NIMAG = 0

C	4.26785	3.38184	-0.01673
C	3.37813	2.29933	-0.01833
C	1.95863	2.55021	-0.02045
C	1.48655	3.86803	-0.02107
C	1.30352	1.27556	-0.02133
C	2.38848	4.92602	-0.01961
H	0.41642	4.06204	-0.02268
C	3.77505	4.68087	-0.01742
H	2.02113	5.94968	-0.02012
H	4.46863	5.51933	-0.01630
H	5.33993	3.19867	-0.01518
C	3.60419	0.87589	-0.01804
C	2.29996	0.29414	-0.02008
C	4.84110	0.23817	-0.01184
S	1.64345	-1.33004	-0.02079
C	0.00295	-0.68926	-0.02210
C	-0.00294	0.68926	-0.02217
S	-1.64345	1.33004	-0.02095
C	-2.29996	-0.29414	-0.02011
C	-1.30351	-1.27556	-0.02123
C	-1.95863	-2.55021	-0.02025
C	-3.37813	-2.29933	-0.01817
C	-1.48654	-3.86802	-0.02073
C	-3.60418	-0.87588	-0.01803
C	-4.26785	-3.38184	-0.01648
C	-4.84110	-0.23817	-0.01190
C	-2.38847	-4.92601	-0.01917
H	-0.41641	-4.06203	-0.02230

C	-3.77505	-4.68087	-0.01703
H	-5.33993	-3.19866	-0.01496
H	-2.02113	-5.94967	-0.01958
H	-4.46863	-5.51933	-0.01583
C	5.94404	-0.31148	-0.00690
Si	7.53776	-1.12707	0.03143
C	7.33030	-2.99939	-0.12974
C	8.47601	-0.78915	1.64397
C	8.66210	-0.54360	-1.37868
H	8.20645	-0.76314	-2.34944
H	9.64427	-1.03093	-1.33945
H	8.81583	0.53934	-1.32618
H	7.90266	-1.14967	2.50394
H	8.63034	0.28624	1.78130
H	9.45725	-1.28012	1.65278
H	6.70855	-3.39030	0.68175
H	8.29894	-3.51276	-0.09911
H	6.83564	-3.25378	-1.07230
C	-5.94404	0.31148	-0.00703
Si	-7.53776	1.12706	0.03139
C	-7.33050	2.99918	-0.13247
C	-8.47485	0.79134	1.64505
C	-8.66307	0.54160	-1.37712
H	-6.70809	3.39120	0.67798
H	-8.29912	3.51256	-0.10172
H	-6.83662	3.25232	-1.07578
H	-8.20817	0.75989	-2.34851
H	-9.64526	1.02889	-1.33780
H	-8.81666	-0.54128	-1.32306
H	-7.90087	1.15302	2.50412
H	-8.62909	-0.28386	1.78395
H	-9.45608	1.28234	1.65392

DI3T Neutral

UCAM-B3LYP/6-31G(d,p)

Zero-point correction= 0.476970 (Hartree/Particle)

Thermal correction to Energy= 0.515018

Thermal correction to Enthalpy= 0.515962

Thermal correction to Gibbs Free Energy= 0.400435

Sum of electronic and zero-point Energies= -3007.373585

Sum of electronic and thermal Energies= -3007.335538

Sum of electronic and thermal Enthalpies= -3007.334594

Sum of electronic and thermal Free Energies= -3007.450121

NIMAG = 0

C	-6.14426	-2.29908	0.00174
C	-4.89363	-1.70945	0.00162
C	-6.22368	-3.69286	0.00177
C	-5.07472	-4.47804	0.00164
C	-3.72473	-2.50607	0.00140
C	-3.81027	-3.88826	0.00143
C	-4.51073	-0.27776	0.00156
C	-2.59609	-1.58565	0.00107
C	-3.15007	-0.24067	0.00119
C	-5.41514	0.80620	0.00162
S	-1.91719	1.01190	0.00067
C	-1.24379	-1.57253	0.00053
C	-0.67621	-0.23443	0.00028
C	0.67622	-0.23443	-0.00029
C	1.24379	-1.57254	-0.00054
S	0.00000	-2.81411	-0.00001
C	2.59609	-1.58565	-0.00107
C	3.15007	-0.24068	-0.00120
S	1.91720	1.01190	-0.00068
C	3.72473	-2.50607	-0.00140
C	4.89364	-1.70946	-0.00161
C	4.51073	-0.27776	-0.00155
C	5.41514	0.80619	-0.00161
H	-2.91685	-4.50493	0.00128
H	-5.16182	-5.55922	0.00167
H	-7.04067	-1.68783	0.00168
H	-7.19764	-4.17128	0.00184
C	3.81027	-3.88826	-0.00143

C	5.07472	-4.47804	-0.00164
C	6.22368	-3.69287	-0.00175
C	6.14426	-2.29909	-0.00172
H	2.91685	-4.50494	-0.00128
H	5.16182	-5.55922	-0.00166
H	7.19764	-4.17128	-0.00182
H	7.04067	-1.68784	-0.00166
C	6.20350	1.73175	-0.00134
Si	7.38808	3.13985	0.00115
C	-6.20350	1.73175	0.00136
Si	-7.38810	3.13984	-0.00115
C	6.82671	4.39115	1.28349
C	7.40236	3.91793	-1.70792
C	9.09226	2.47852	0.43185
C	-7.40305	3.91739	1.70815
C	-9.09209	2.47863	-0.43275
C	-6.82621	4.39155	-1.28286
H	9.09687	2.00532	1.41742
H	9.82886	3.28788	0.44578
H	9.42627	1.73598	-0.29790
H	5.82513	4.76729	1.05846
H	7.50744	5.24775	1.31167
H	6.80089	3.95047	2.28363
H	8.09990	4.76071	-1.74261
H	6.41219	4.29148	-1.98226
H	7.70993	3.19690	-2.46996
H	-5.82470	4.76758	-1.05732
H	-7.50689	5.24820	-1.31099
H	-6.80003	3.95123	-2.28315
H	-7.71084	3.19612	2.46988
H	-8.10064	4.76013	1.74286
H	-6.41299	4.29091	1.98296
H	-9.42642	1.73590	0.29667
H	-9.09626	2.00567	-1.41844
H	-9.82868	3.28799	-0.44680

DI3T Radical Anion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.473045 (Hartree/Particle)

Thermal correction to Energy= 0.511285

Thermal correction to Enthalpy= 0.512229

Thermal correction to Gibbs Free Energy= 0.396153

Sum of electronic and zero-point Energies= -3007.518003

Sum of electronic and thermal Energies= -3007.479764

Sum of electronic and thermal Enthalpies= -3007.478820

Sum of electronic and thermal Free Energies= -3007.594896

NIMAG = 0

C	6.18998	-2.32068	0.00125
C	4.93936	-1.70687	0.00111
C	6.26311	-3.71100	0.00113
C	5.10098	-4.49305	0.00088
C	3.75533	-2.50307	0.00084
C	3.84434	-3.89396	0.00074
C	4.56729	-0.29403	0.00106
C	2.63834	-1.58870	0.00071
C	3.17681	-0.26837	0.00089
C	5.45642	0.79531	0.00115
S	1.93882	0.97404	0.00072
C	1.24775	-1.57160	0.00044
C	0.69588	-0.26928	0.00049
C	-0.69229	-0.26898	0.00021
C	-1.24477	-1.57104	-0.00018
S	0.00121	-2.80299	-0.00006
C	-2.63538	-1.58750	-0.00052
C	-3.17328	-0.26694	-0.00026
S	-1.93469	0.97487	0.00027
C	-3.75276	-2.50143	-0.00104
C	-4.93643	-1.70473	-0.00104
C	-4.56377	-0.29204	-0.00052
C	-5.45289	0.79728	-0.00016
H	2.94626	-4.50545	0.00053
H	5.18084	-5.57607	0.00078
H	7.09342	-1.71772	0.00131
H	7.23494	-4.19651	0.00120
C	-3.84241	-3.89226	-0.00154

C	-5.09936	-4.49073	-0.00204
C	-6.26113	-3.70815	-0.00203
C	-6.18740	-2.31784	-0.00153
H	-2.94463	-4.50419	-0.00156
H	-5.17972	-5.57372	-0.00244
H	-7.23318	-4.19321	-0.00243
H	-7.09058	-1.71446	-0.00153
C	-6.23505	1.73653	0.00022
Si	-7.38483	3.14656	0.00125
C	6.23663	1.73618	0.00086
Si	7.38182	3.15018	-0.00096
C	-7.10643	4.20854	-1.52998
C	-7.11081	4.20277	1.53725
C	-9.15536	2.50131	-0.00245
C	8.59216	2.99190	-1.43703
C	8.35441	3.19731	1.61291
C	6.39797	4.74511	-0.18300
H	-9.34573	1.88620	-0.88730
H	-9.87491	3.32761	-0.00199
H	-9.34825	1.88303	0.87963
H	-6.07977	4.58606	-1.56149
H	-7.78528	5.06869	-1.54290
H	-7.27297	3.62882	-2.44297
H	-6.08427	4.58025	1.57305
H	-7.27980	3.61954	2.44756
H	-7.78979	5.06278	1.55160
H	5.82900	4.74885	-1.11761
H	7.05952	5.61851	-0.18338
H	5.68434	4.85983	0.63850
H	9.17031	2.06575	-1.36058
H	9.29665	3.83109	-1.45523
H	8.06123	2.97196	-2.39359
H	8.92847	2.27570	1.75039
H	7.68187	3.29827	2.47015
H	9.05536	4.03957	1.62828

DI3T Dianion

UCAM-B3LYP/6-31++G(d,p)

Zero-point correction= 0.471050 (Hartree/Particle)

Thermal correction to Energy= 0.509493

Thermal correction to Enthalpy= 0.510437

Thermal correction to Gibbs Free Energy= 0.394727

Sum of electronic and zero-point Energies= -3007.516246

Sum of electronic and thermal Energies= -3007.477803

Sum of electronic and thermal Enthalpies= -3007.476858

Sum of electronic and thermal Free Energies= -3007.592569

NIMAG = 0

C	6.23630	2.32246	-0.00002
C	4.98782	1.68616	-0.00002
C	6.30279	3.70966	-0.00001
C	5.12980	4.48844	-0.00001
C	3.78808	2.48293	-0.00002
C	3.88060	3.87977	-0.00001
C	4.62741	0.29019	-0.00003
C	2.68036	1.57474	-0.00002
C	3.20379	0.27583	-0.00003
C	5.50715	-0.79130	-0.00002
S	1.95893	-0.95867	-0.00003
C	1.25122	1.55585	-0.00002
C	0.71212	0.28281	-0.00003
C	-0.71215	0.28281	-0.00002
C	-1.25125	1.55585	-0.00001
S	-0.00001	2.78121	-0.00001
C	-2.68039	1.57475	-0.00001
C	-3.20383	0.27585	-0.00002
S	-1.95897	-0.95866	-0.00003
C	-3.78810	2.48295	0.00002
C	-4.98785	1.68618	0.00002
C	-4.62745	0.29021	-0.00000
C	-5.50719	-0.79127	-0.00001
H	2.97771	4.48603	-0.00001
H	5.20237	5.57337	-0.00001
H	7.14565	1.72614	-0.00002
H	7.27315	4.20151	-0.00001
C	-3.88062	3.87979	0.00003

C	-5.12982	4.48847	0.00005
C	-6.30281	3.70969	0.00005
C	-6.23632	2.32249	0.00004
H	-2.97773	4.48604	0.00003
H	-5.20238	5.57339	0.00006
H	-7.27316	4.20154	0.00007
H	-7.14568	1.72617	0.00004
C	-6.29781	-1.73430	-0.00001
Si	-7.43862	-3.11928	-0.00000
C	6.29778	-1.73432	-0.00002
Si	7.43866	-3.11923	0.00003
C	-7.21031	-4.22179	1.52162
C	-7.21154	-4.22085	-1.52249
C	-9.22451	-2.49378	0.00088
C	7.21083	-4.22142	1.52195
C	9.22451	-2.49359	0.00035
C	7.21131	-4.22115	-1.52216
H	-9.41826	-1.87689	0.88414
H	-9.93767	-3.32673	0.00097
H	-9.41899	-1.87645	-0.88191
H	-6.18709	-4.60834	1.56708
H	-7.89854	-5.07579	1.50656
H	-7.38621	-3.65321	2.44028
H	-7.89976	-5.07487	-1.50742
H	-6.18836	-4.60736	-1.56903
H	-7.38819	-3.65170	-2.44065
H	6.18813	-4.60771	-1.56841
H	7.89956	-5.07514	-1.50703
H	7.38775	-3.65221	-2.44050
H	7.38699	-3.65264	2.44044
H	7.89908	-5.07541	1.50688
H	6.18764	-4.60799	1.56781
H	9.41844	-1.87654	0.88345
H	9.41871	-1.87640	-0.88259
H	9.93774	-3.32649	0.00040

Table S2 Bond distances (Å) for **DI1T-TMSE**

bond #	neutral	radical anion	dianion
1	1.357	1.391	1.431
2	1.456	1.428	1.396
3	1.353	1.400	1.447

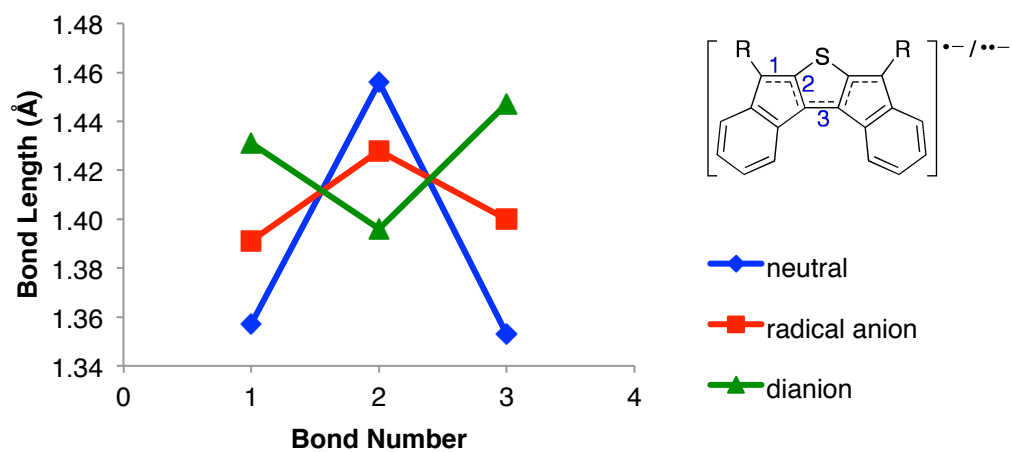


Fig. S10 Calculated bond distances upon reduction of **DI1T**, R = TMSE.

Table S3 Bond distances (Å) for **DI2T-TMSE**

bond #	neutral	radical anion	dianion
1	1.382	1.393	1.401
2	1.397	1.393	1.389
3	1.391	1.401	1.408
4	1.396	1.393	1.390
5	1.384	1.394	1.400
6	1.414	1.427	1.442
7	1.483	1.461	1.441
8	1.360	1.392	1.428
9	1.456	1.425	1.399
10	1.458	1.444	1.433
11	1.351	1.391	1.432
12	1.461	1.416	1.379

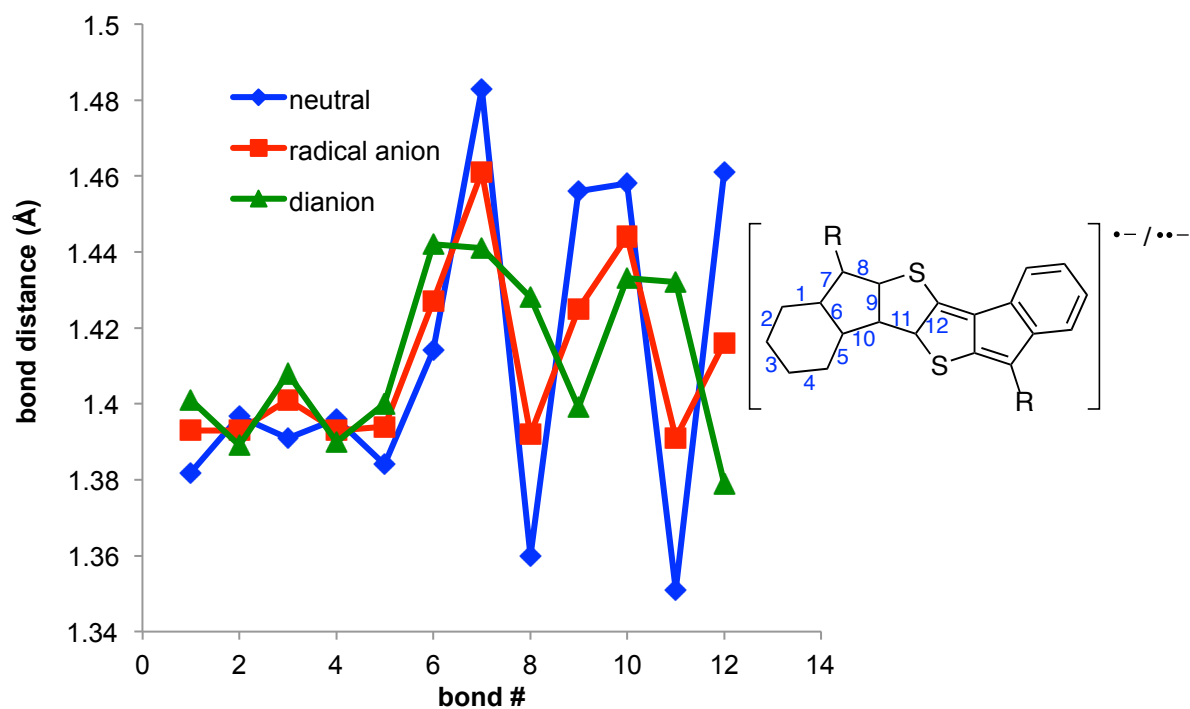
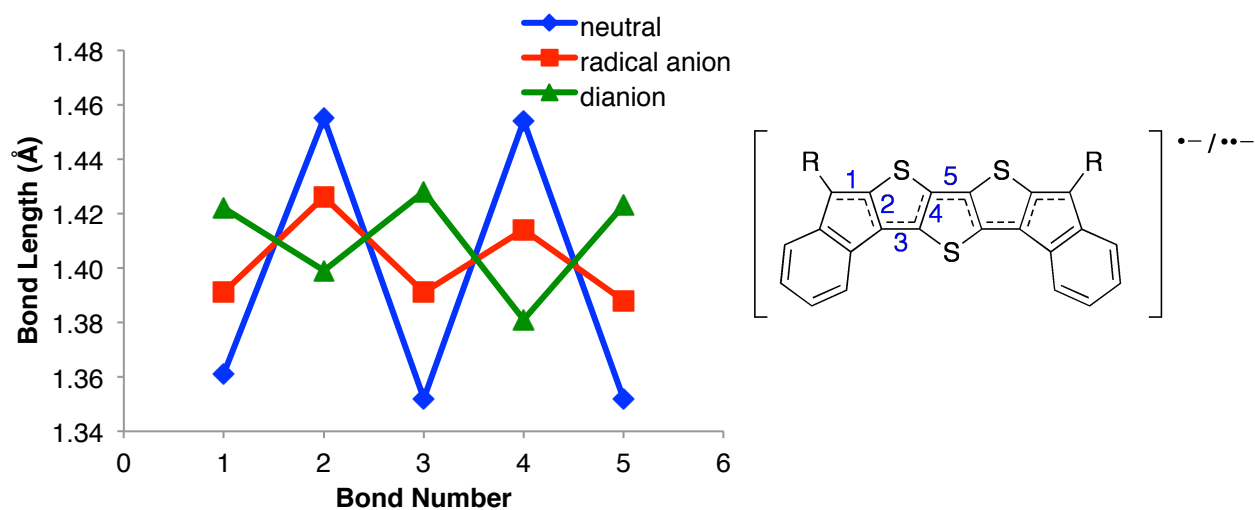
**Fig. S11** Calculated bond distances upon reduction of **DI2T**, R = TMSE.

Table S4 Bond distances (Å) for **DI3T-TMSE**

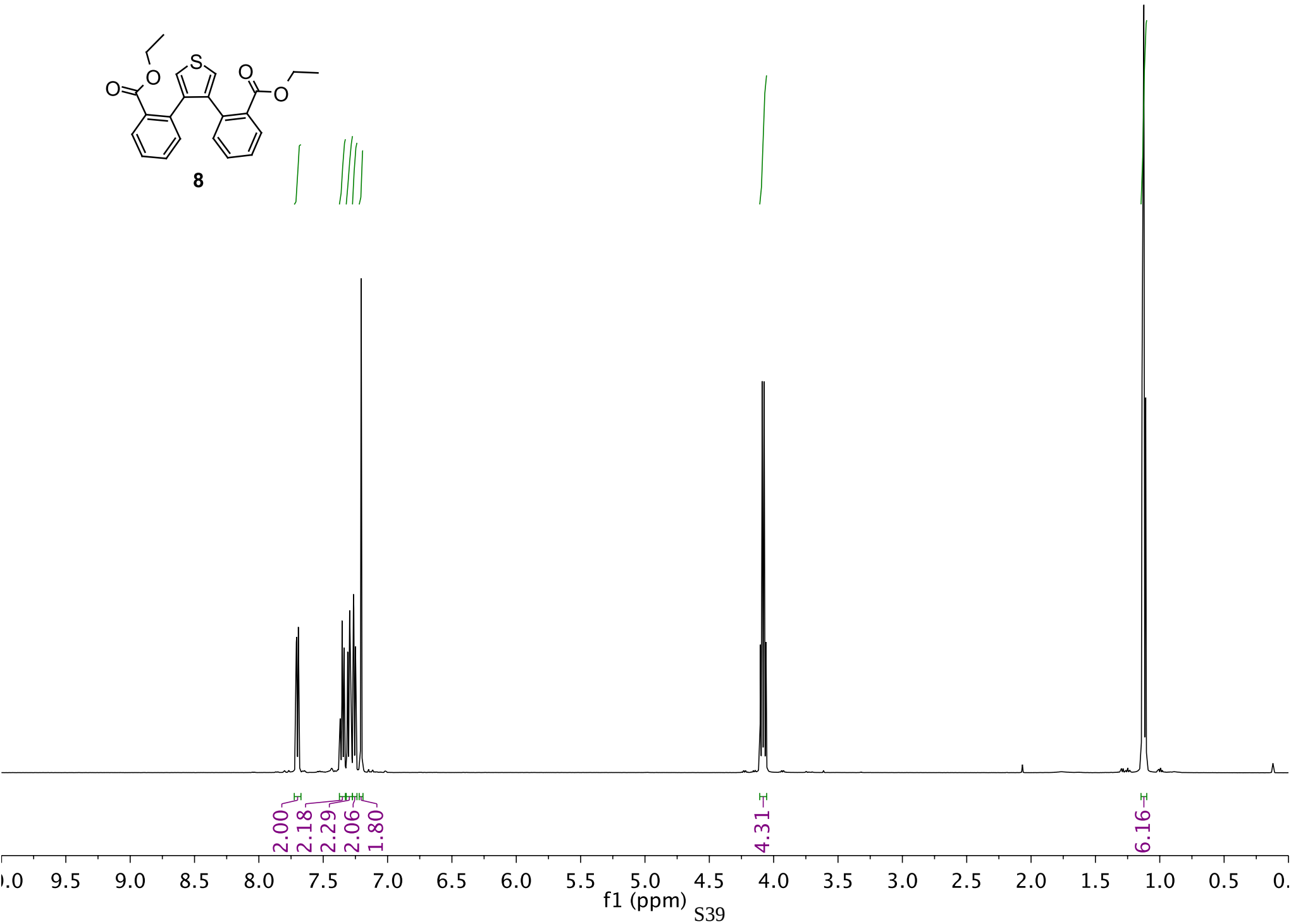
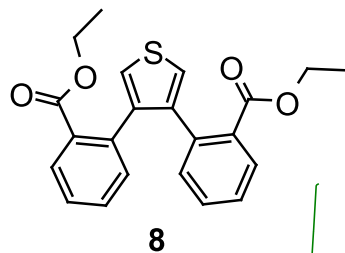
bond #	neutral	radical anion	dianion
1	1.361	1.391	1.424
2	1.455	1.426	1.400
3	1.352	1.391	1.429
4	1.454	1.414	1.382
5	1.352	1.388	1.424

**Fig. S12** Calculated bond distances upon reduction of **DI3T**, R = TMSE.

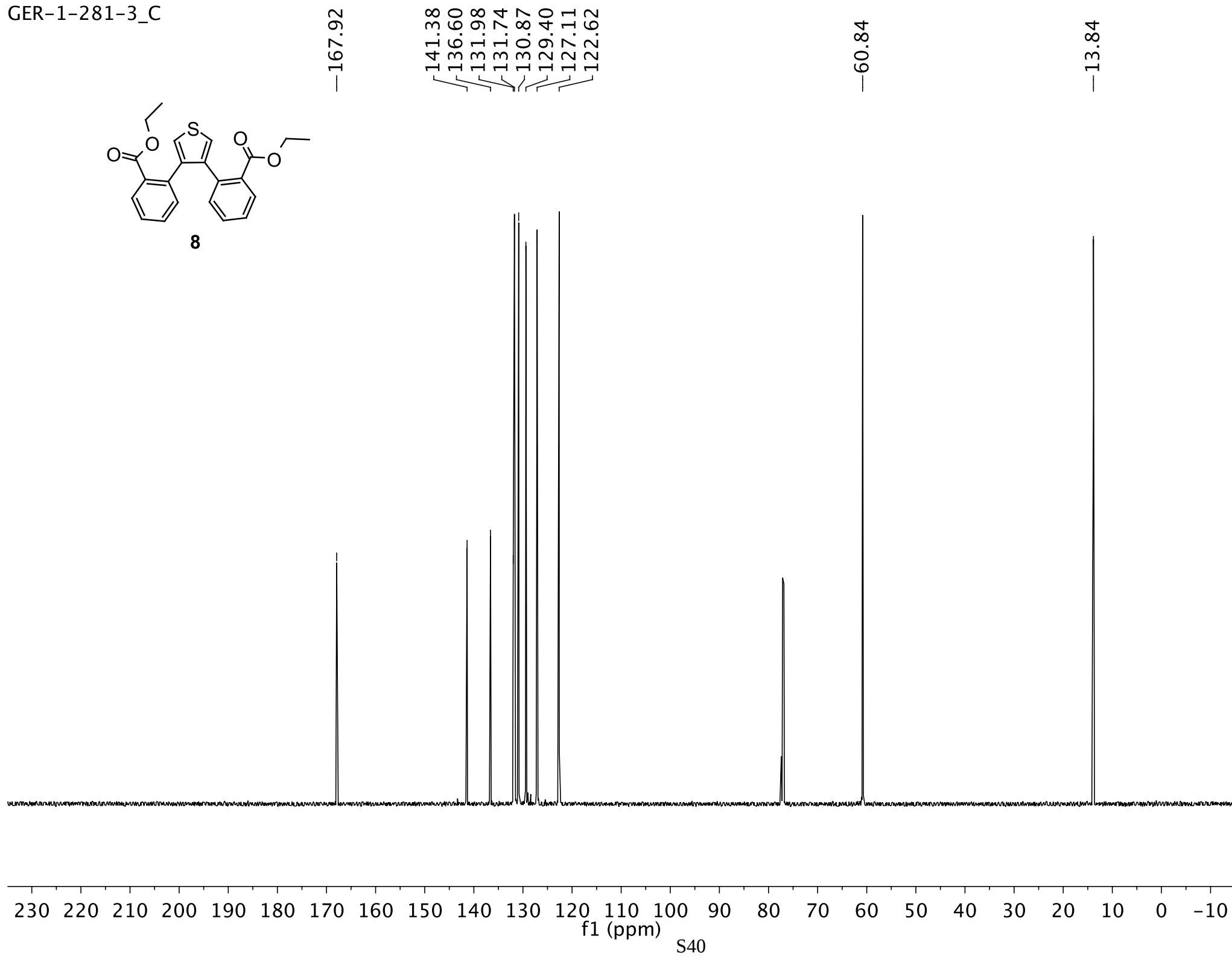
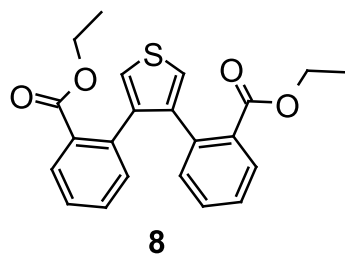
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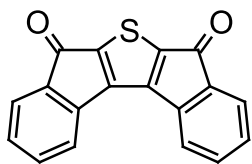
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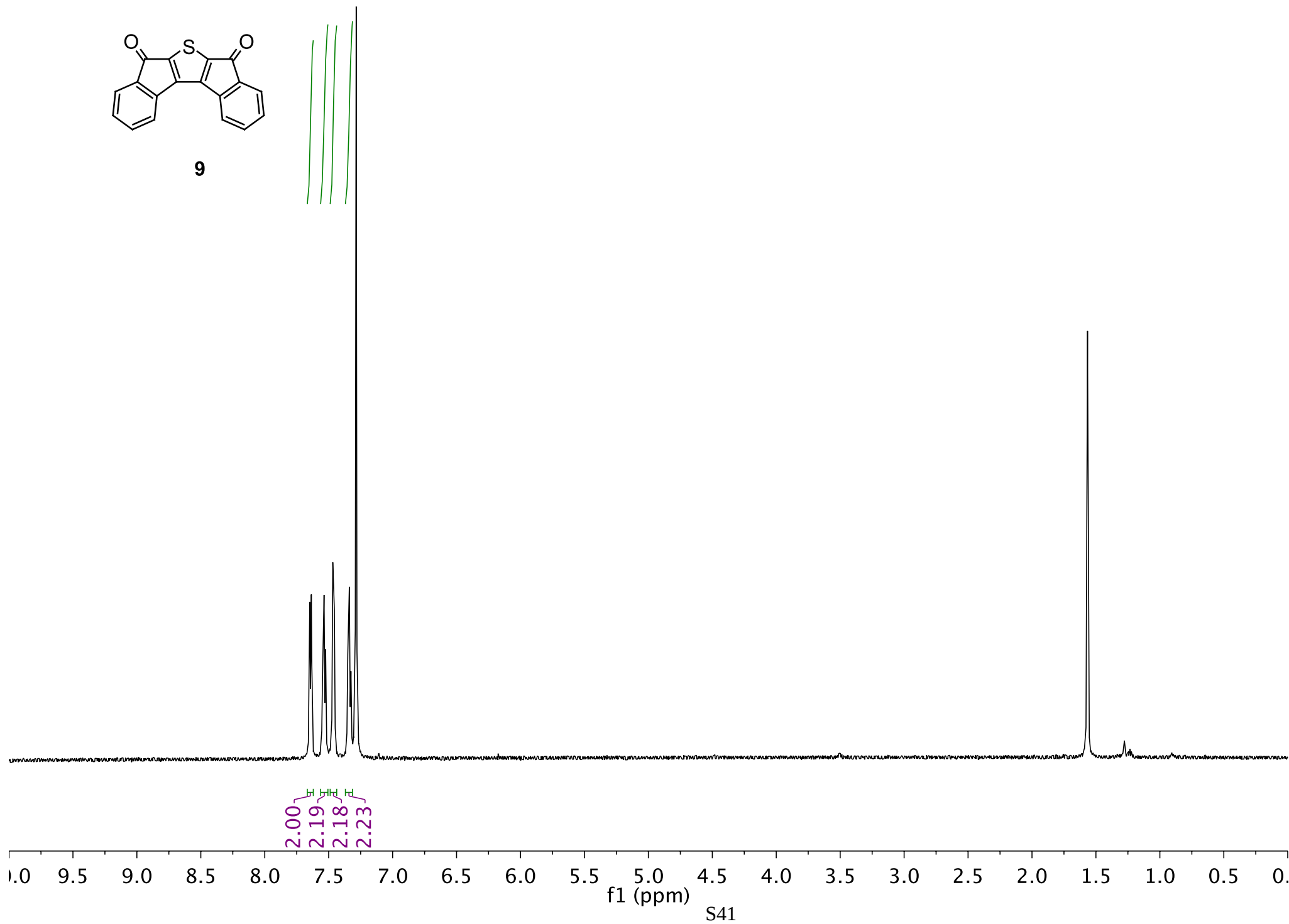
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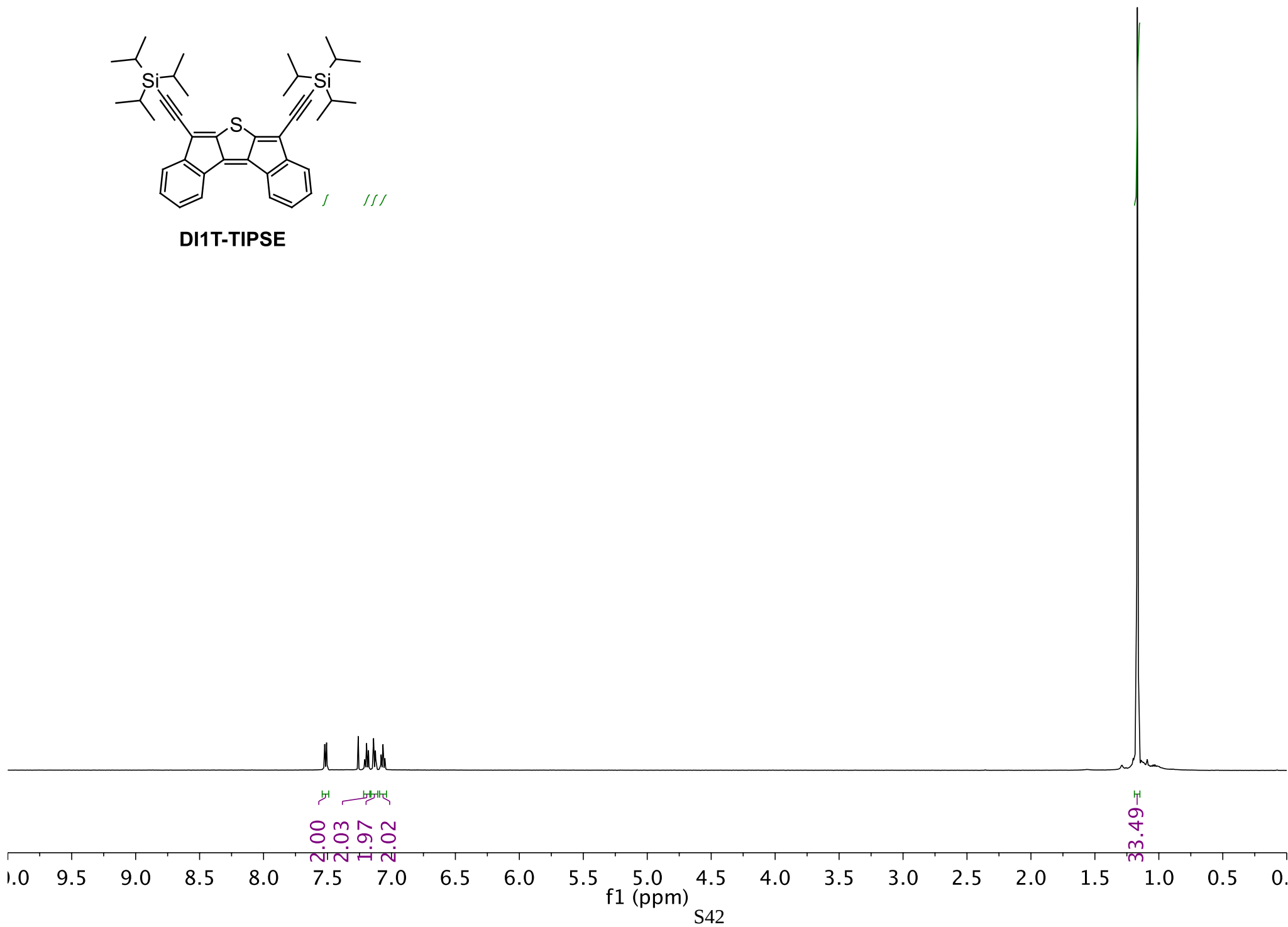


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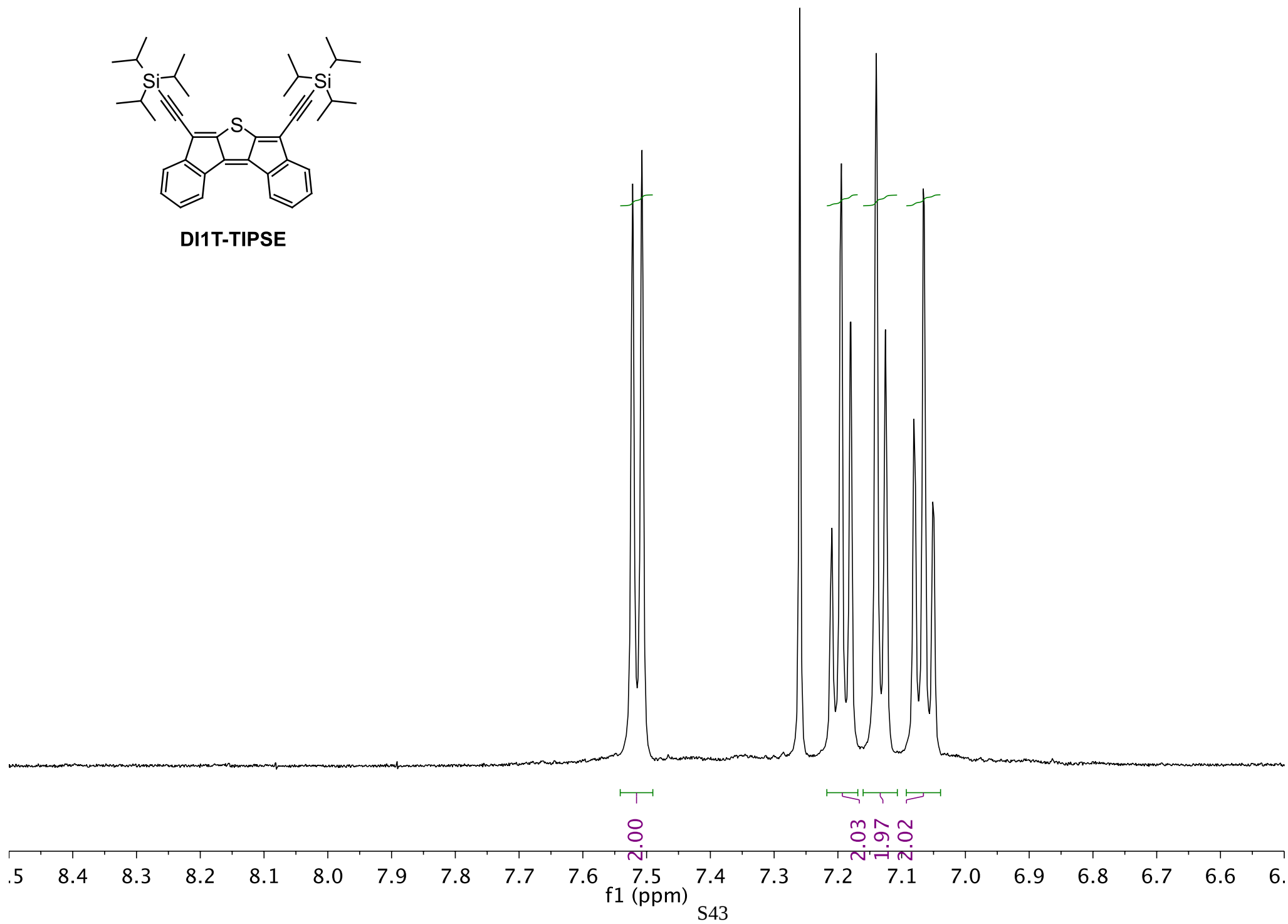


9





DI1T-TIPSE



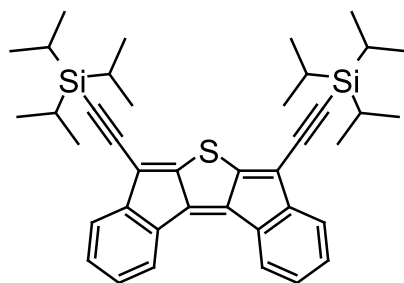
GER-1-271-1_C

153.77
148.89
144.03

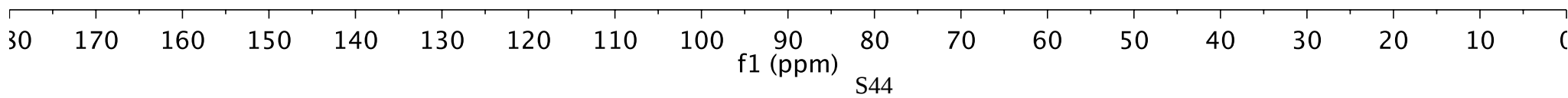
130.77
130.19
125.78
124.37
120.68
116.32

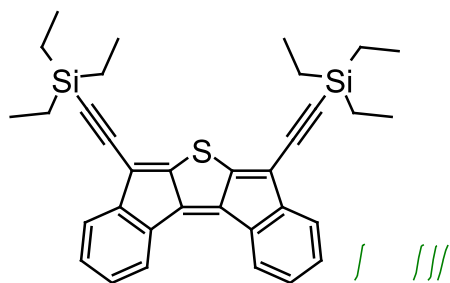
105.90
99.70

18.73
11.28

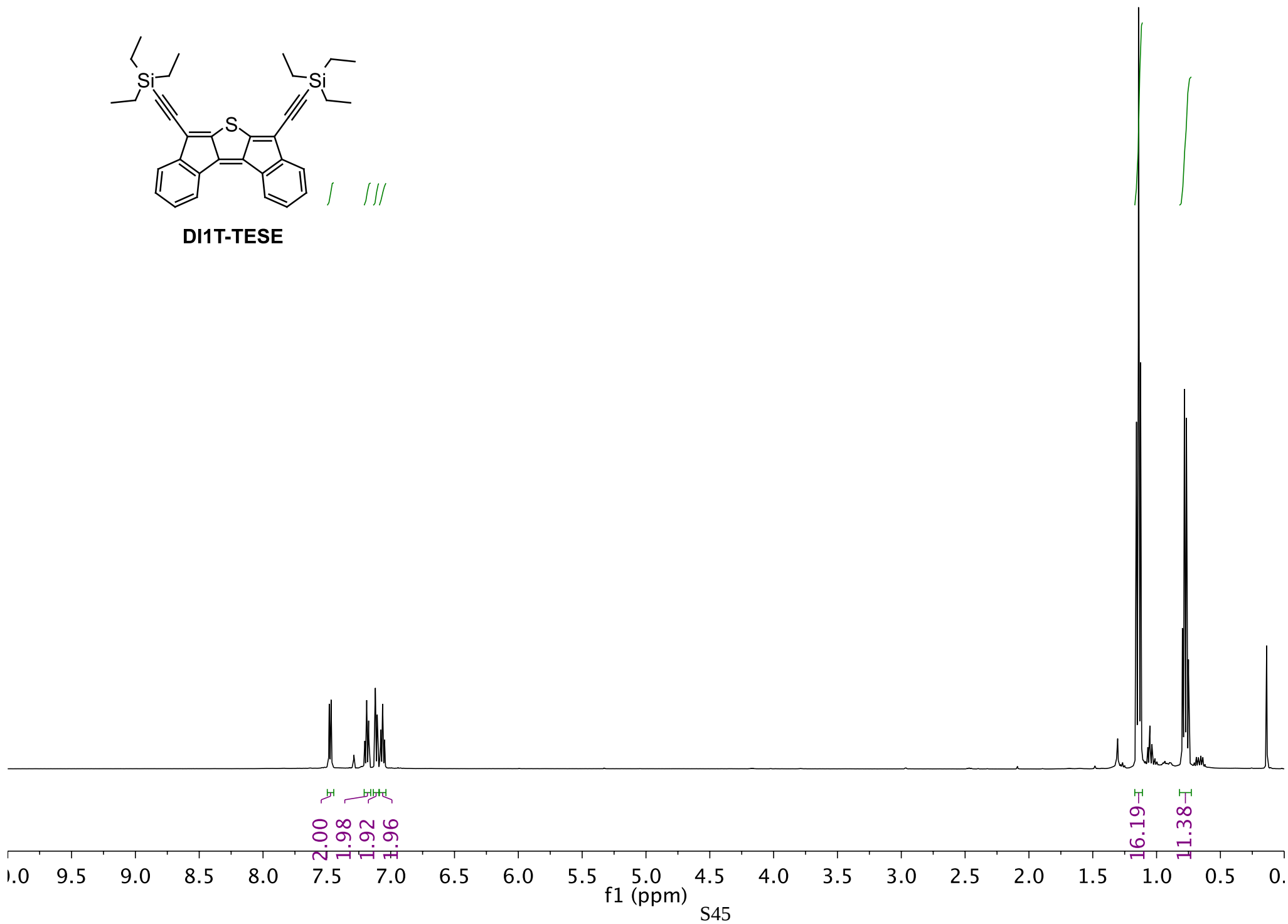


DI1T-TIPSE





DI1T-TESE



GER-1-251-2_C

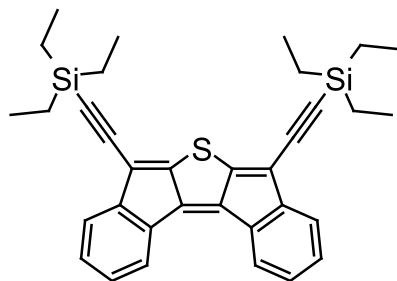
153.79
148.73
144.01

130.66
130.11
125.80
124.35
120.62
116.17

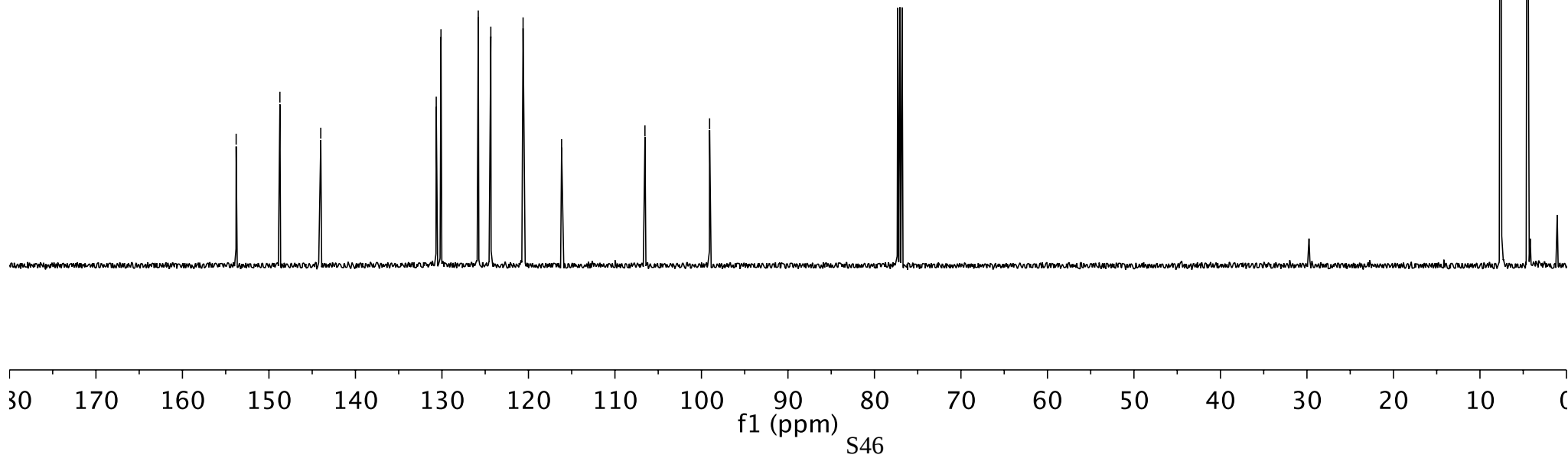
106.53

99.06

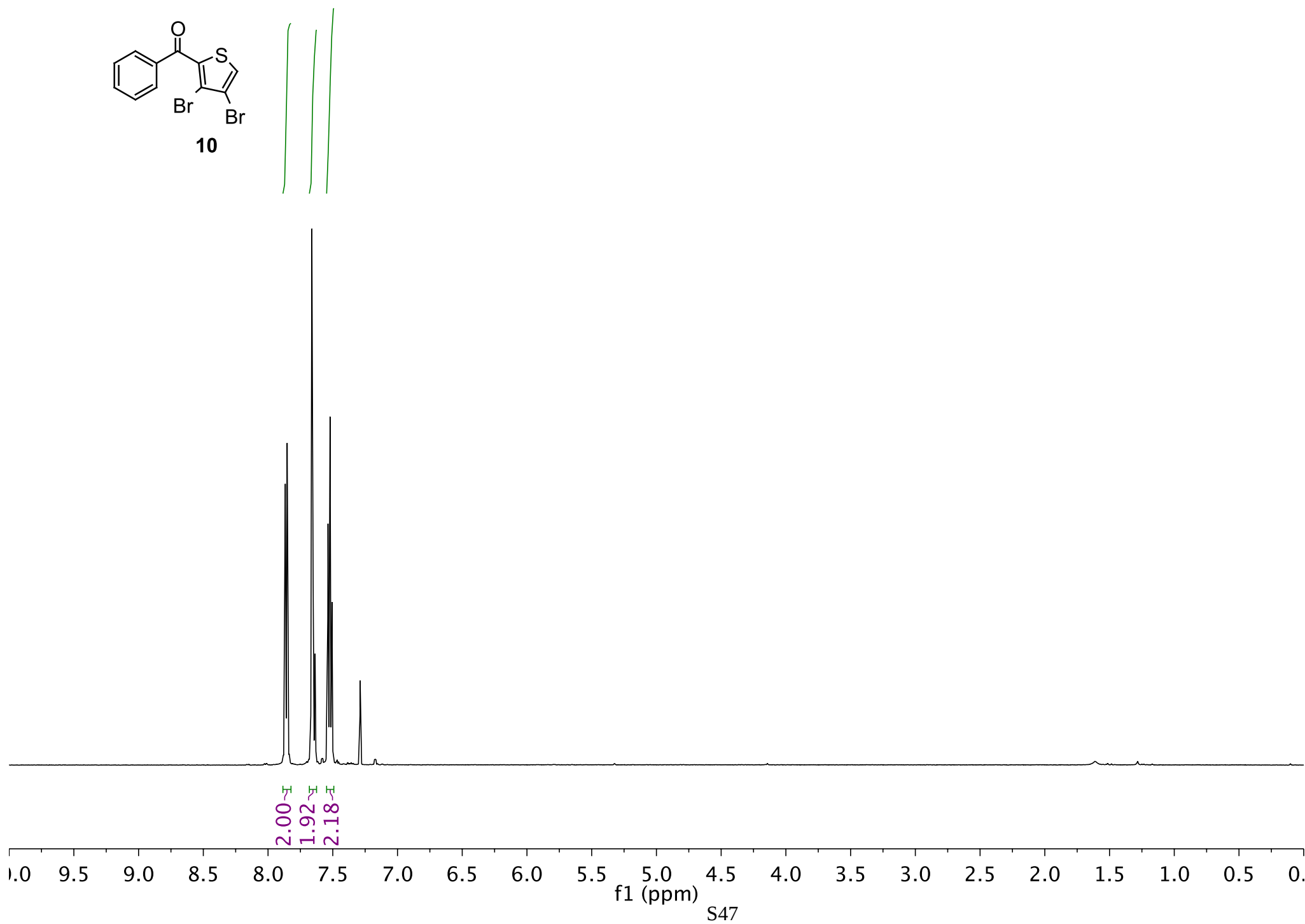
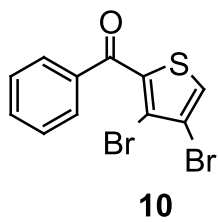
7.63
4.48



DI1T-TESE

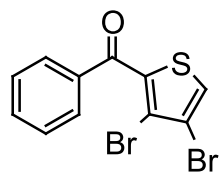


GER-2-171-2_H



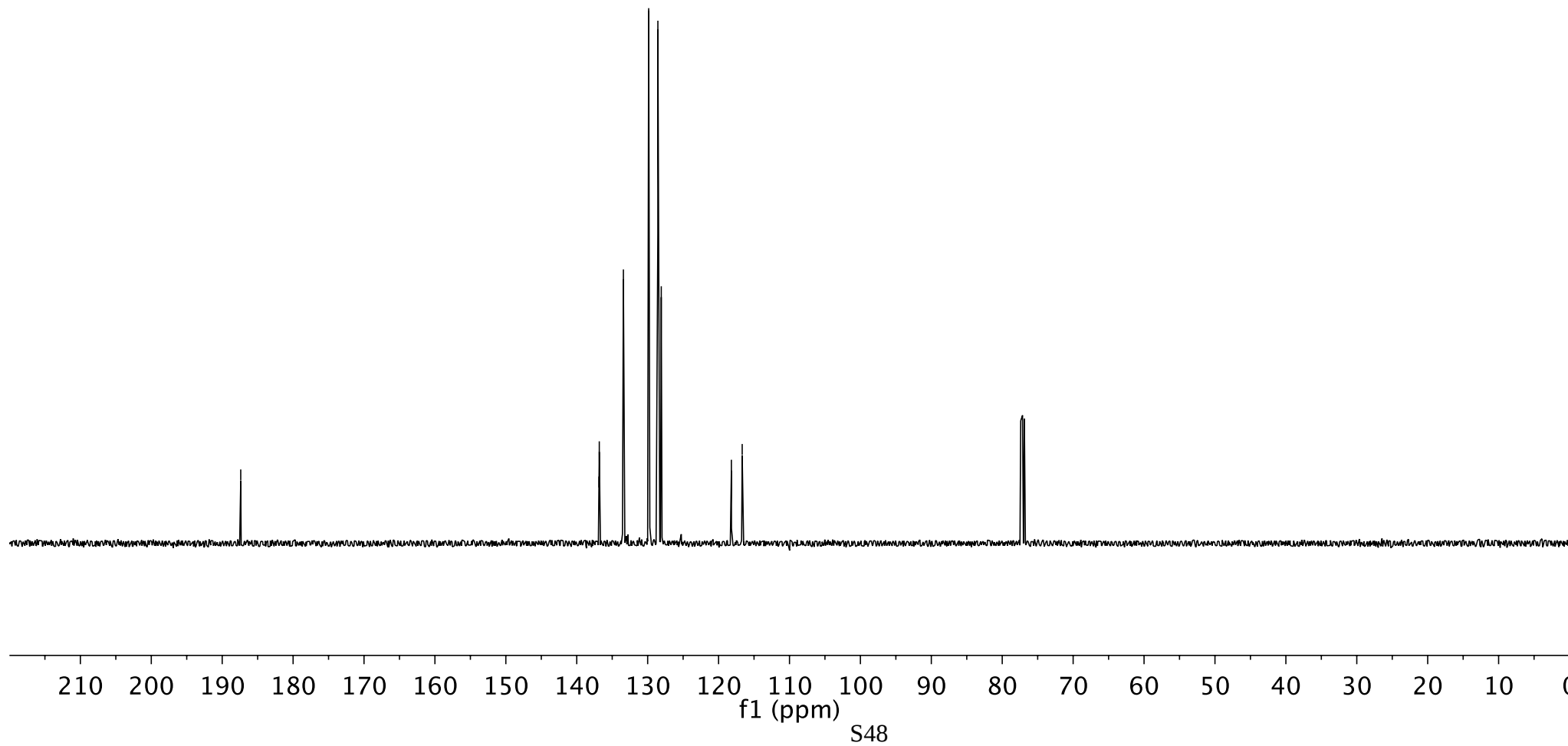
GER-2-171-2_C

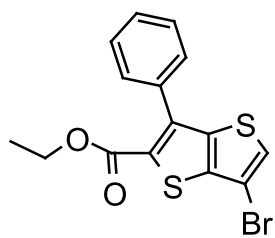
—187.38



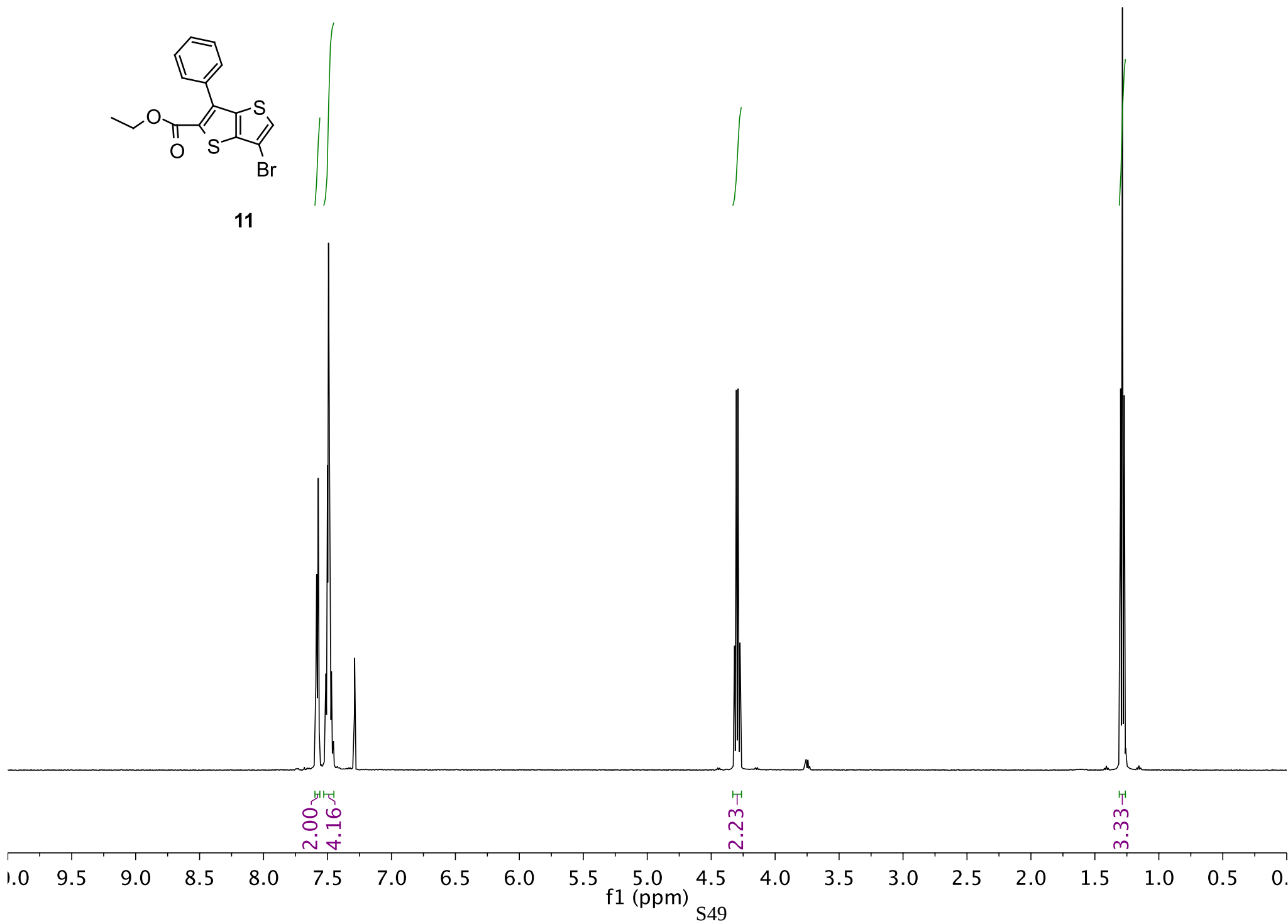
10

136.87
136.82
133.42
129.86
128.56
128.08
118.19
116.67

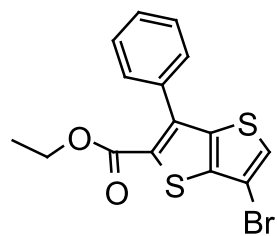




11



GER-2-089-3_C



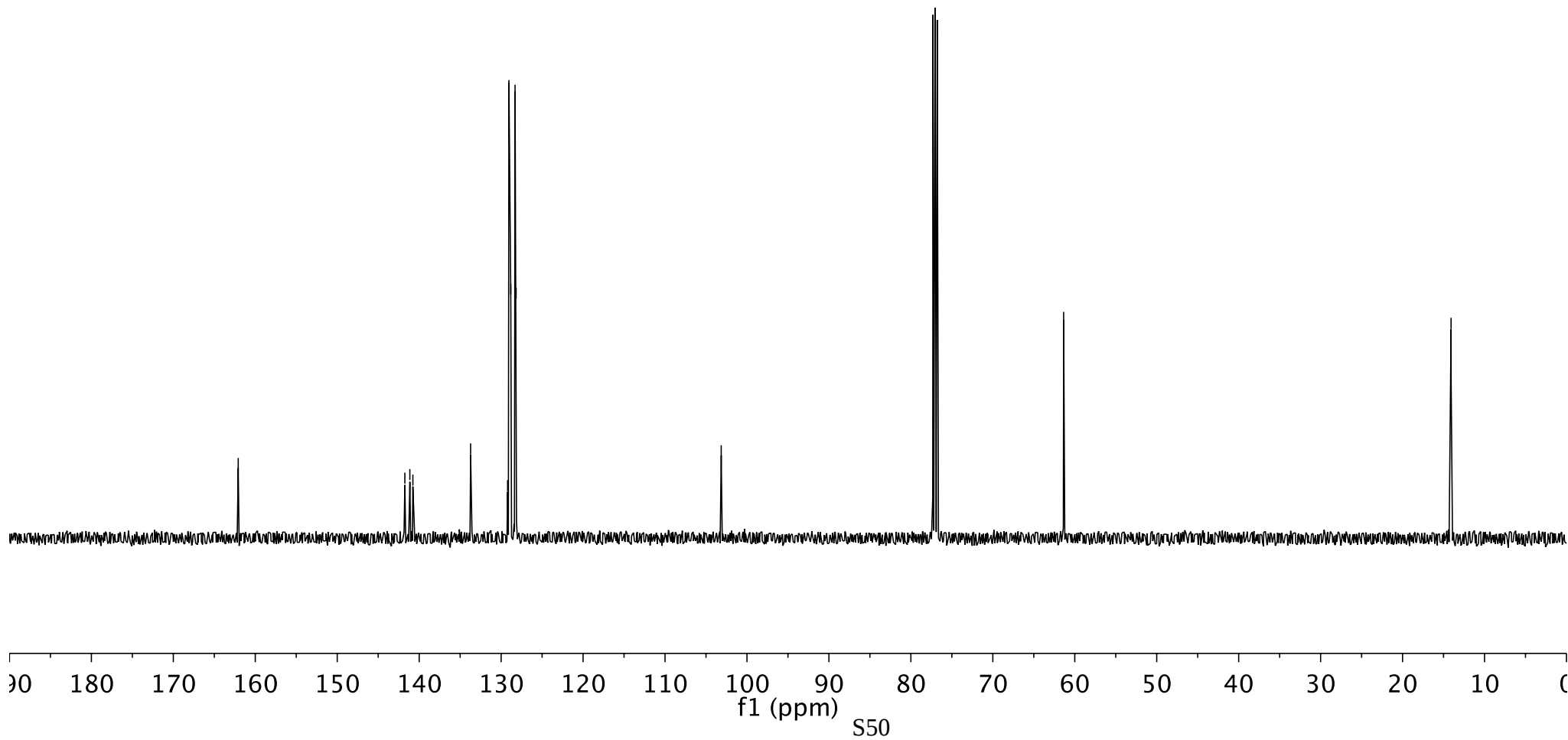
11

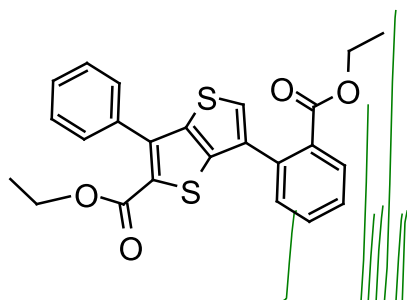
162.08
141.75
141.14
140.77
133.72
129.21
129.05
128.82
128.30
128.17

103.14

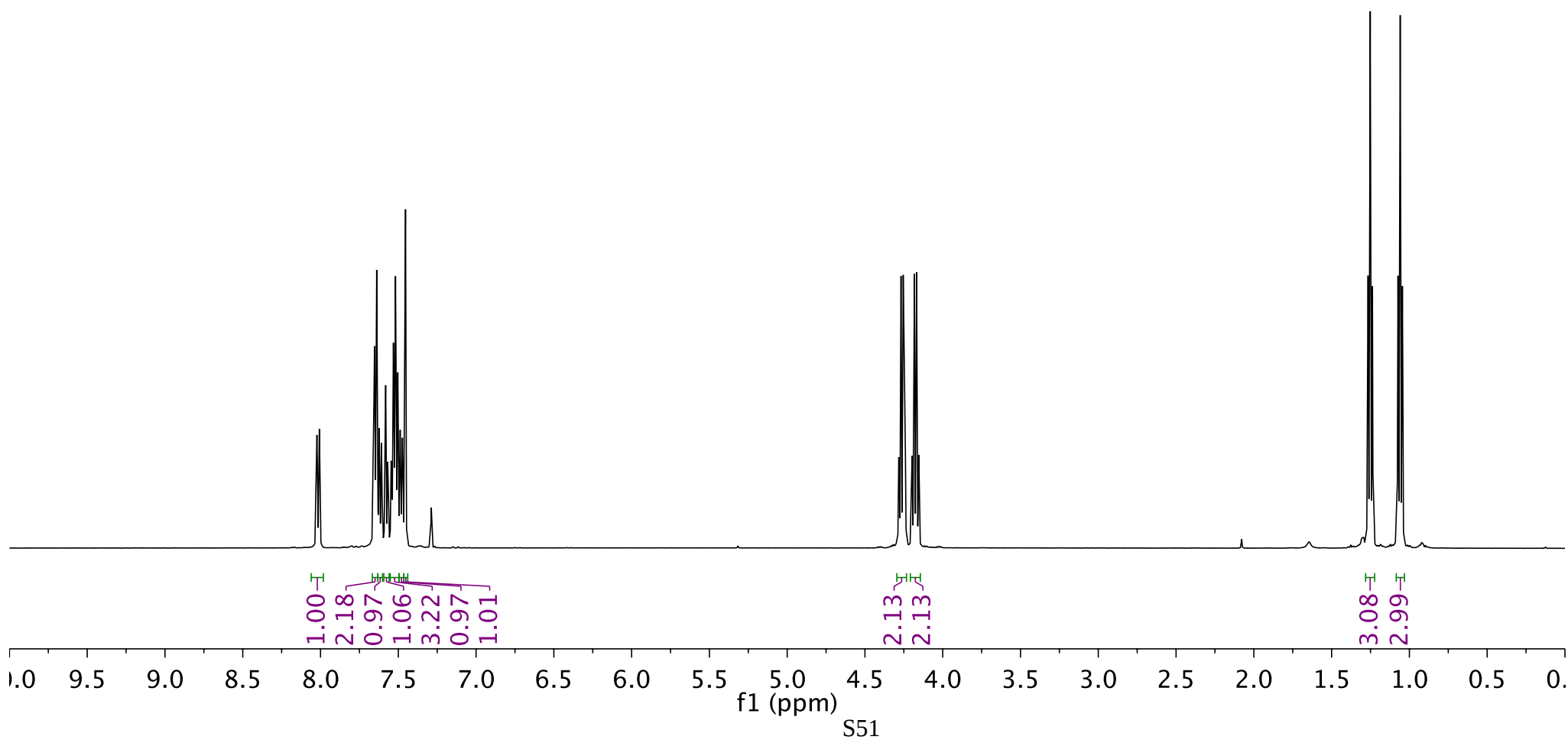
61.36

14.08

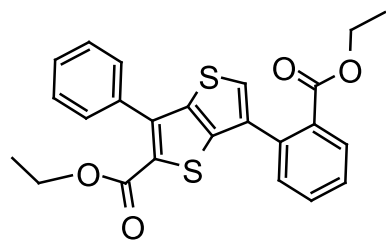




12



GER-2-181-2_C

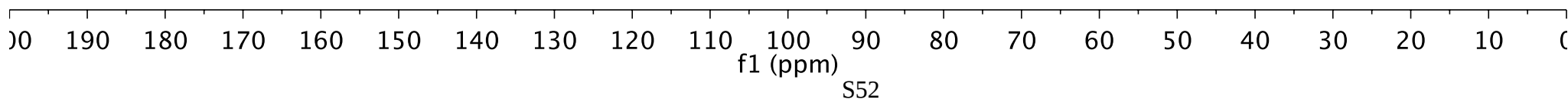


12

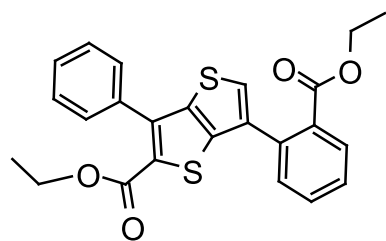
167.58
162.35
141.73
141.01
140.94
134.82
134.78
134.28
131.91
131.07
130.61
130.55
129.17
128.61
128.44
128.21
127.88
127.84

61.23
61.09

14.10
13.71



GER-2-181-2_C

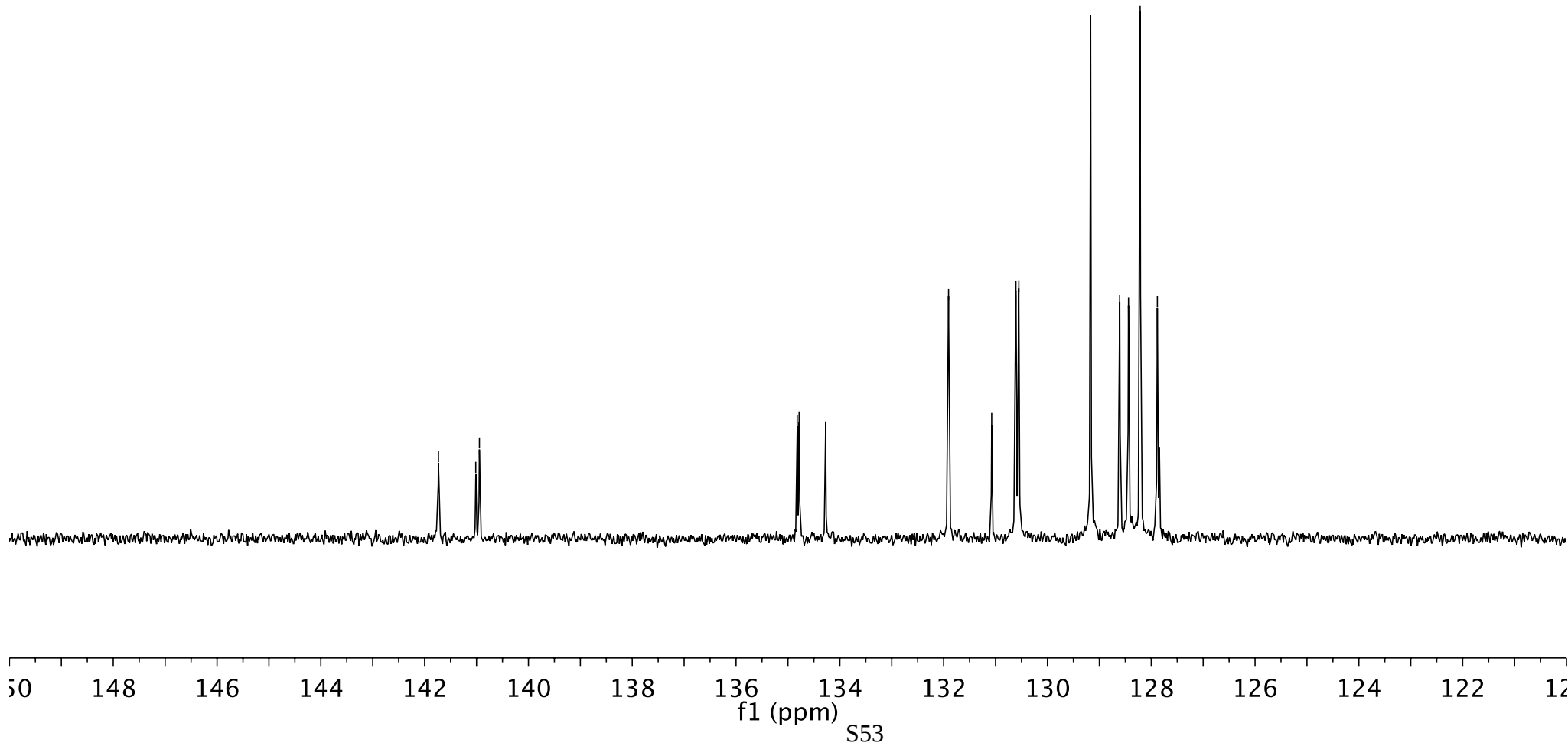


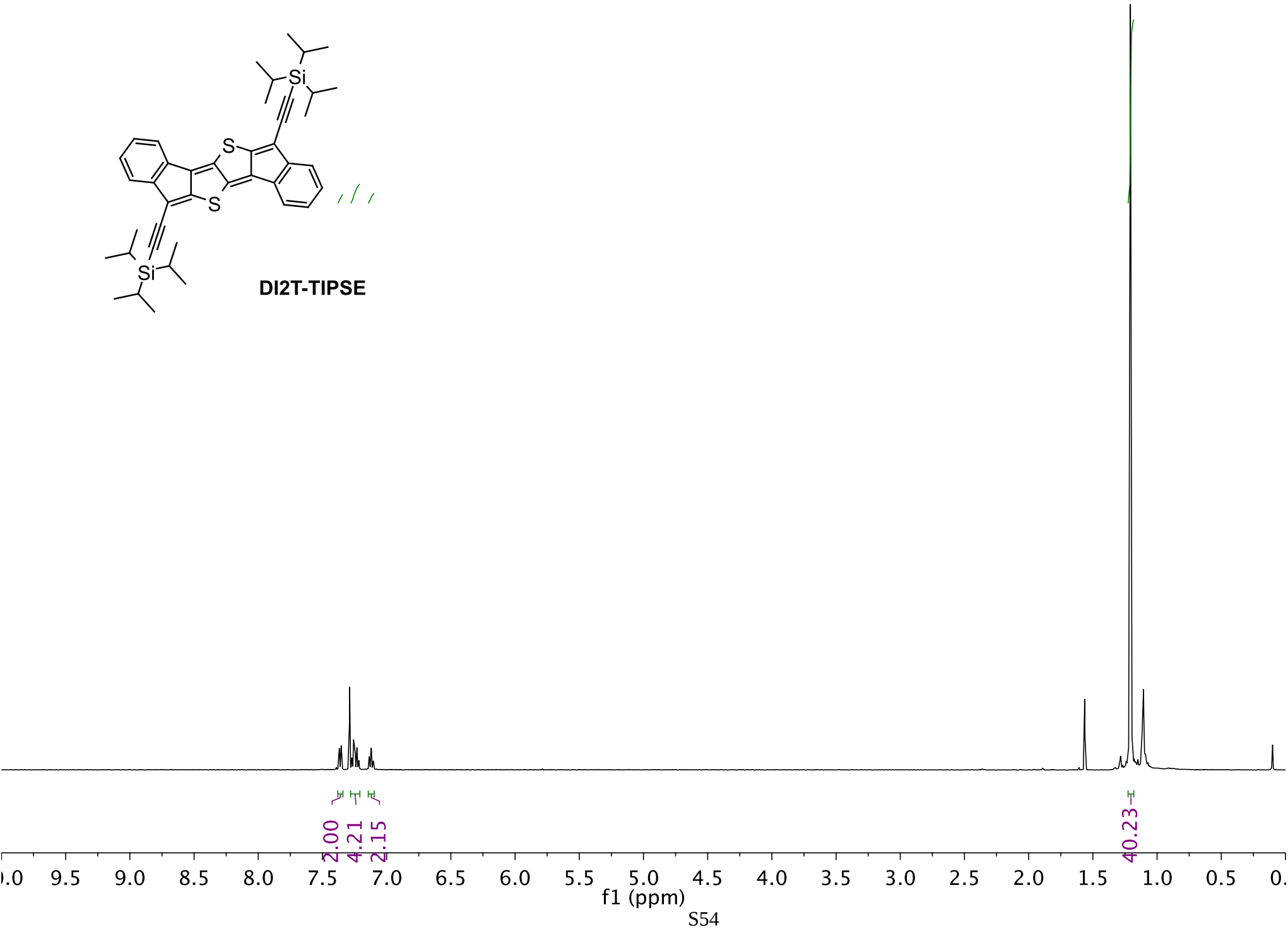
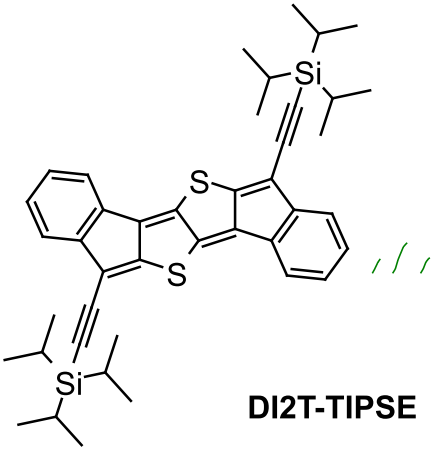
12

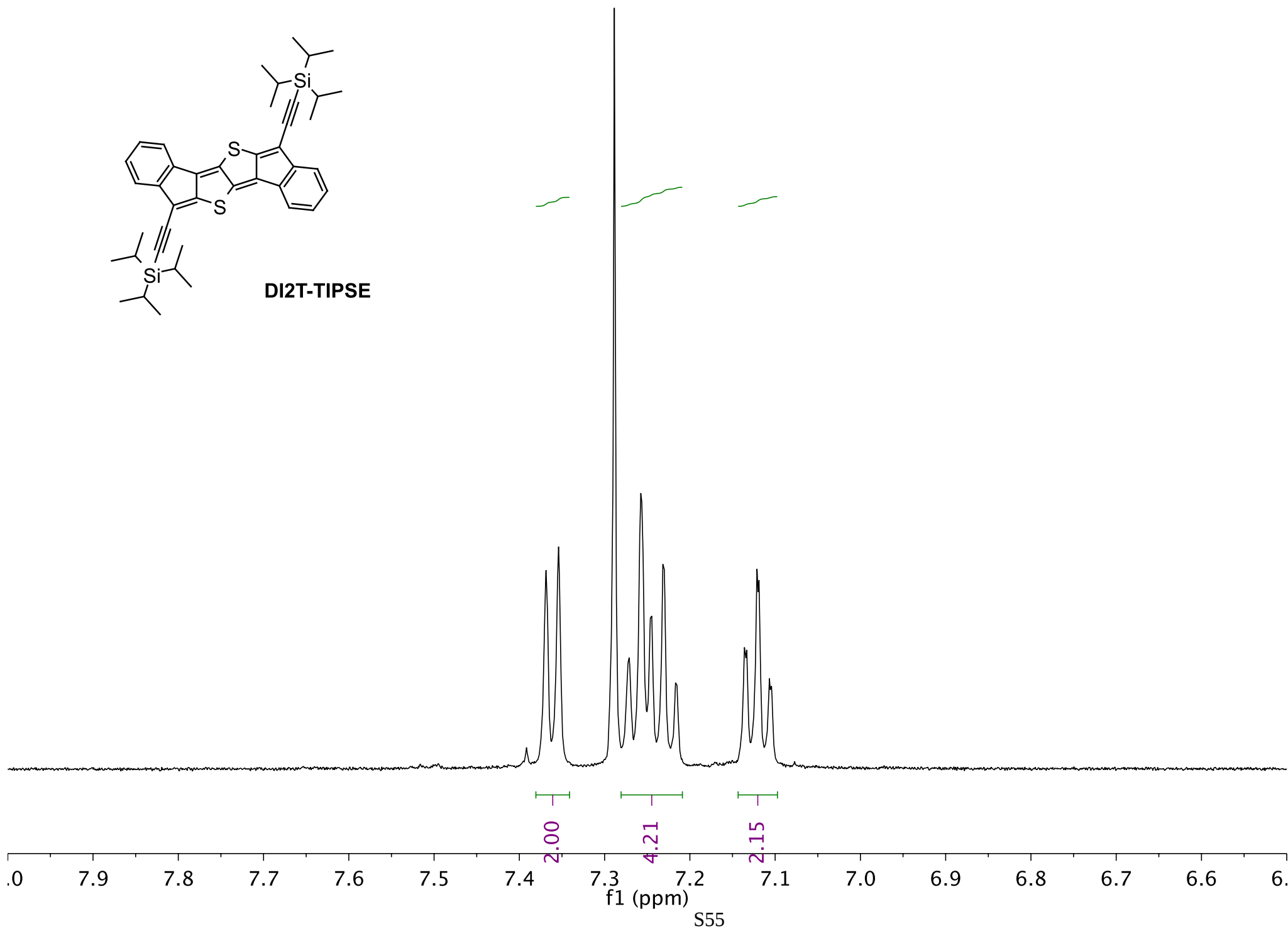
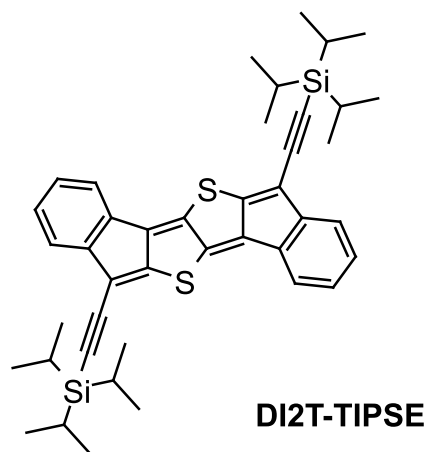
141.73
141.01
140.94

134.82
134.78
134.28

131.91
131.07
130.61
130.55
129.17
128.61
128.44
128.21
127.88
127.84







GER-2-049-2_C

150.07

147.30

146.98

139.43

129.62

128.82

125.51

122.65

120.76

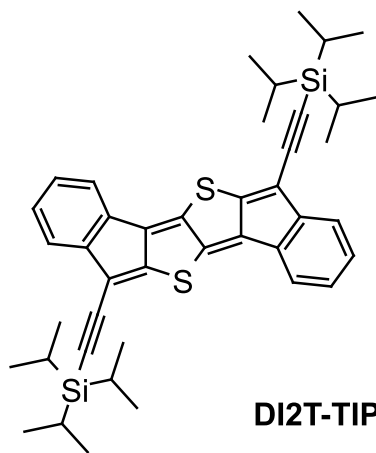
114.77

105.47

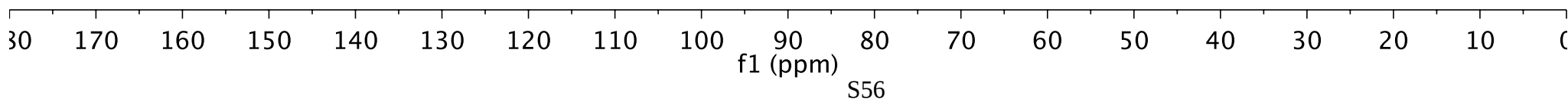
99.95

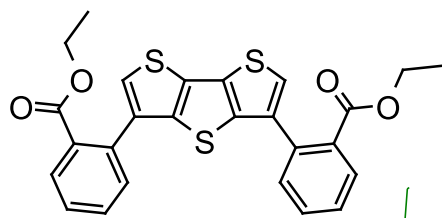
18.76

11.30

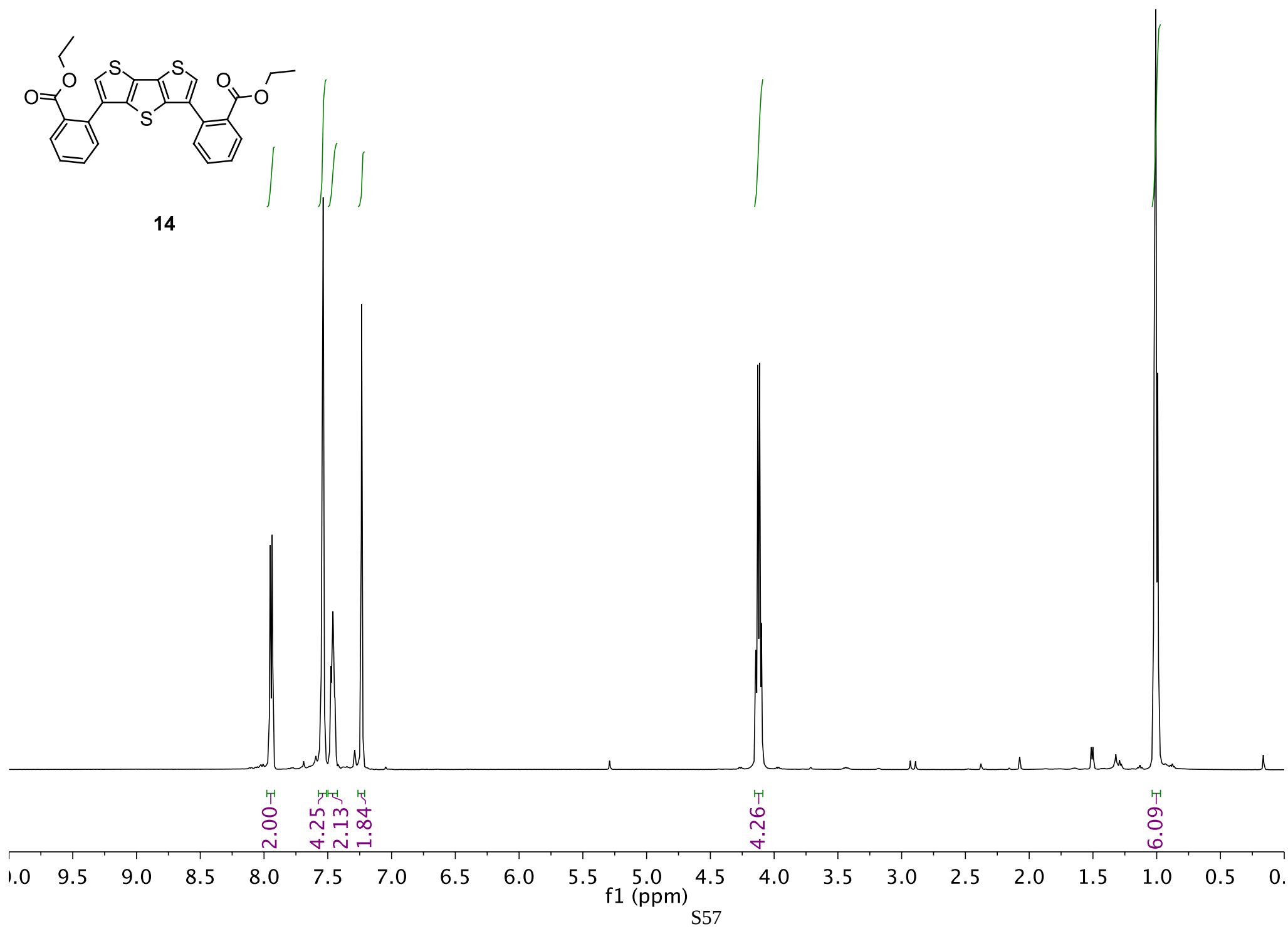


DI2T-TIPSE

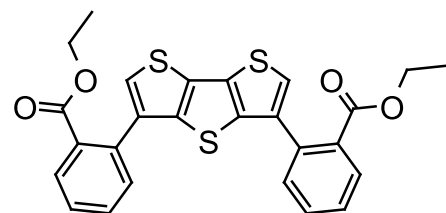




14



GER-2-119-3_C

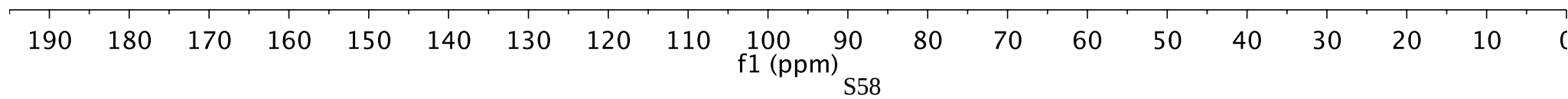


14

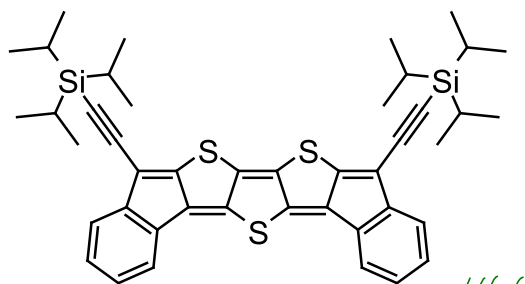
167.76
142.24
135.53
135.00
131.73
131.27
130.42
130.40
130.18
128.25
122.45

61.13

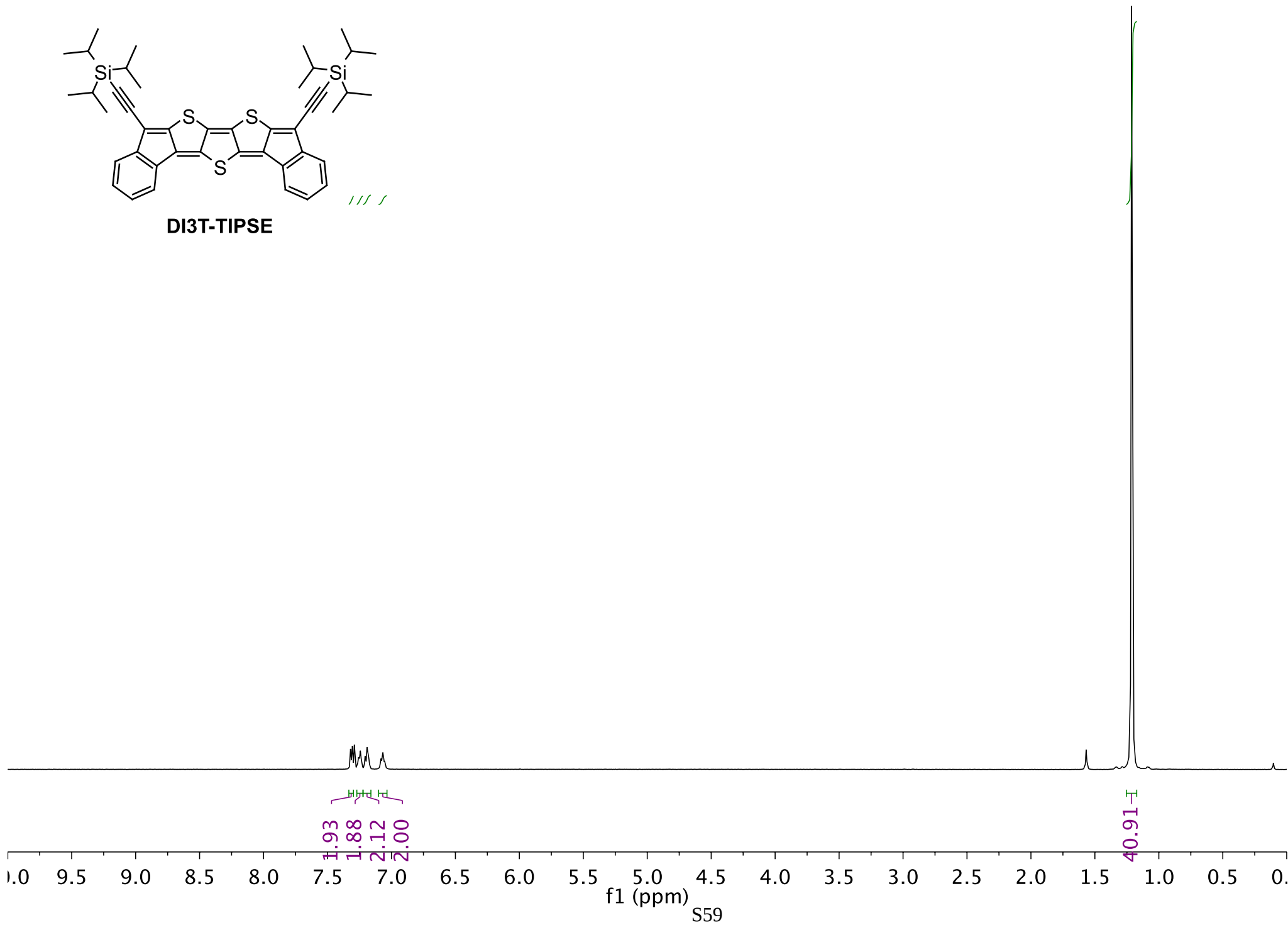
13.75



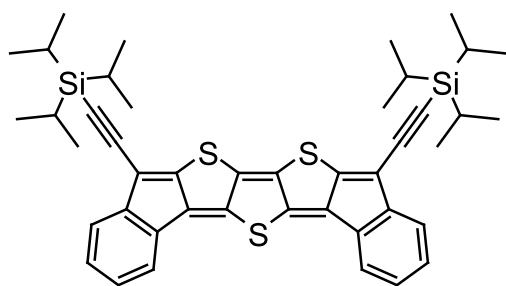
GER-2-125-3_H



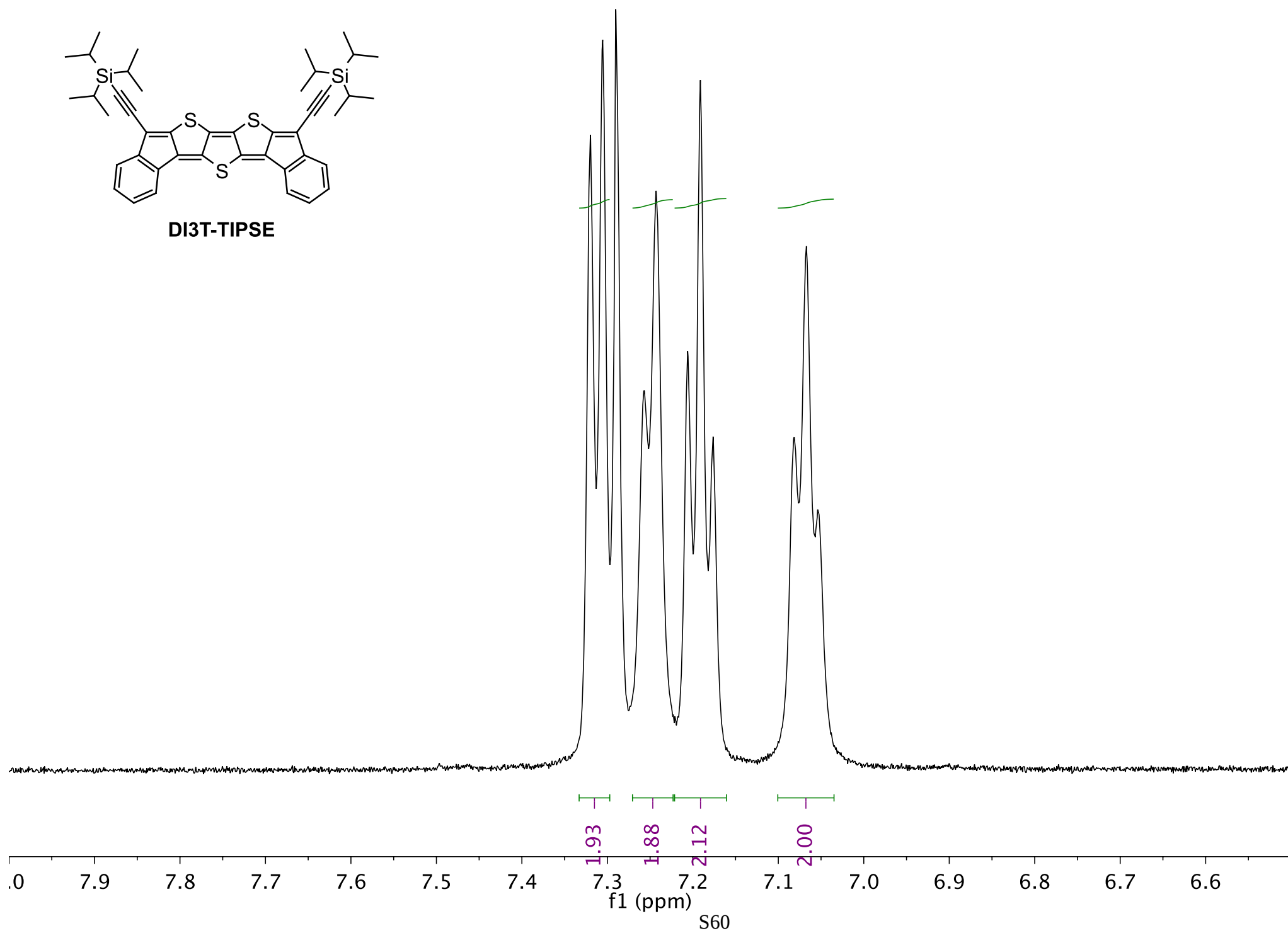
DI3T-TIPSE



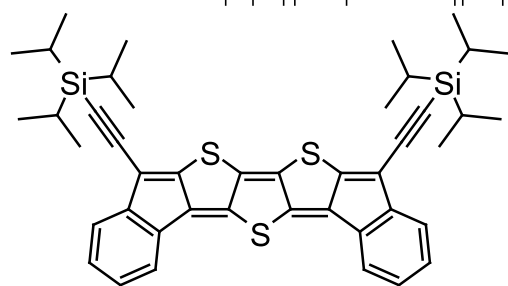
GER-2-125-3_H



DI3T-TIPSE



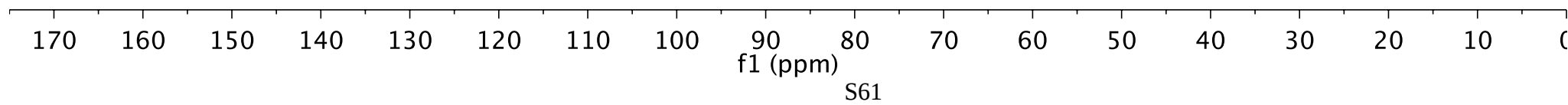
GER-2-125-3_C



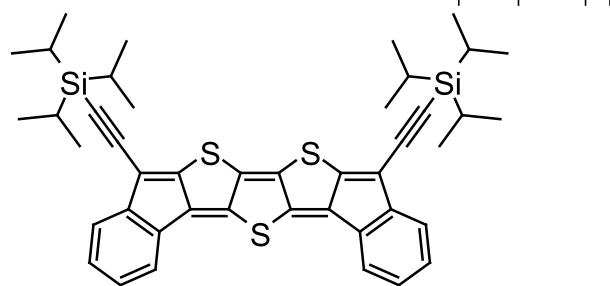
DI3T-TIPSE

148.91
146.56
143.92
142.96
138.51
129.20
128.52
125.08
122.04
120.72
113.17
105.36
100.45

18.78
11.34



GER-2-125-3_C



DI3T-TIPSE

