Electronic Supplementary Information for:

# Quinoidal Diindenothienoacenes: Synthesis and Properties of New Functional Organic Materials 

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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. $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ 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. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}$ using a Varian Inova $500\left({ }^{1} \mathrm{H}: 500.11 \mathrm{MHz},{ }^{13} \mathrm{C}: 125.75 \mathrm{MHz}\right)$ or Bruker Avance-III-HD $600\left({ }^{1} \mathrm{H}: 599.98 \mathrm{MHz},{ }^{13} \mathrm{C}: 150.87 \mathrm{MHz}\right)$ NMR spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm relative to the residual chloroform ( ${ }^{1} \mathrm{H}: 7.26 \mathrm{ppm},{ }^{13} \mathrm{C}: 77.16 \mathrm{ppm}$ ) 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 ( $6.0 \mathrm{~g}, 31 \mathrm{mmol}$ ), $\mathrm{Pd}_{2} \mathrm{dba}_{3}(120 \mathrm{mg}, 0.124 \mathrm{mmol})$, SPhos $(100 \mathrm{mg}, 0.248 \mathrm{mmol})$, anhydrous $\mathrm{K}_{3} \mathrm{PO}_{4}(10.5 \mathrm{~g}, 49.6 \mathrm{mmol})$ and toluene $(35 \mathrm{~mL})$ 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 $100^{\circ} \mathrm{C}$ for 16 h . Upon cooling to rt , the reaction was diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ then filtered. The organics were washed with brine then dried over $\mathrm{MgSO}_{4}$. 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 ( $20 \% \mathrm{EtOAc} /$ hexanes) (v/v). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.70$ (dd, $J=7.7$, $1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{td}, J=7.5,1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{td}, J=7.6,1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.26(\mathrm{dd}, J=7.5,1.4$ $\mathrm{Hz}, 2 \mathrm{H}), 7.20(\mathrm{~s}, 2 \mathrm{H}), 4.08(\mathrm{q}, J=7.2 \mathrm{~Hz}, 4 \mathrm{H}), 1.12(\mathrm{t}, J=7.1 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 126 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 167.92,141.38,136.60,131.98,131.74,130.87,129.40,127.11,122.62,60.84,13.84$. HRMS (ES+) calcd for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{O}_{4} \mathrm{~S}(\mathrm{M}+\mathrm{H})^{+} 381.1161$, found 381.1168.


Diindeno[2,1-b:1', $\left.\mathbf{2}^{\prime}-\boldsymbol{d}\right]$ thiophene-5,7-dione (9). To a solution of the crude diester $\mathbf{8}$ (4.4 g) in ethanol ( 100 mL ) was added aqueous $\mathrm{KOH}(115 \mathrm{mmol}, 5 \mathrm{M})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ was added 5 drops DMF. Oxalyl chloride ( $4.0 \mathrm{~mL}, 46 \mathrm{mmol}$ ) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed in vacuo. $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ was added and the flask was cooled to $0^{\circ} \mathrm{C} . \mathrm{AlCl}_{3}(9.25 \mathrm{~g}, 69 \mathrm{mmol})$ was added and the reaction was stirred at $0{ }^{\circ} \mathrm{C}$ for 16 h . The dark solution was poured onto ice and the precipitate was collected by filtration then washed with water. Recrystallization from $\mathrm{CHCl}_{3}(1.5 \mathrm{~L})$ provided the title compound as orange needles $(1.71 \mathrm{~g}, 46 \%$ from 3,4dibromothiophene). ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.64(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.54(\mathrm{t}, J=7.5 \mathrm{~Hz}$, $2 \mathrm{H}), 7.46(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H})$; limited solubility of the title compound hindered acquisition of ${ }^{13} \mathrm{C}$ NMR spectra; UV-Vis $\left(\mathrm{CHCl}_{3}\right) \lambda_{\max }: 313,440$ (br) nm; HRMS (EI+) calcd for $\mathrm{C}_{18} \mathrm{H}_{8} \mathrm{O}_{2} \mathrm{~S}\left(\mathrm{M}^{+}\right)$289.0245, found 288.0240 .


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DI1T-TIPSE. In a dry two-neck flask, (triisopropylsilyl)acetylene ( $0.8 \mathrm{~mL}, 3.45 \mathrm{mmol}$ ) was added to THF ( 5 mL ) and cooled to $0^{\circ} \mathrm{C}$. A solution of $n$-butyllithium ( $3.1 \mathrm{mmol}, 1.6 \mathrm{M}$ ) was added dropwise then stirred for 5 min . In a second flask, dione 9 ( $200 \mathrm{mg}, 0.69 \mathrm{mmol}$ ) was suspended in THF ( 25 mL ) at $0^{\circ} \mathrm{C}$. The (triisopropylsilyl)ethynyllithium solution was transferred via syringe to the dione suspension and stirred for 30 min . The reaction was quenched with
saturated $\mathrm{NH}_{4} \mathrm{Cl}$ soln ( 50 mL ). The organics were extracted with EtOAc ( $2 \times 50 \mathrm{~mL}$ ), washed with brine and dried over $\mathrm{MgSO}_{4}$. 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 $\mathrm{SnCl}_{2}(400 \mathrm{mg}, 10.4$ 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 $1: 1 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ /hexanes. Removal of the volatiles under reduced pressure provided the title compound ( $270 \mathrm{mg}, 63 \%$ ) as a green solid. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.51(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.20(\mathrm{td}, J=7.5,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.13(\mathrm{~d}, J=7.3 \mathrm{~Hz}$, $2 \mathrm{H}), 7.07(\mathrm{td}, J=7.5,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.17(\mathrm{~s}, 42 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 153.77,148.89$, 144.03, 130.77, 130.19, 125.78, 124.37, 120.68, 116.32, 105.90, 99.70, 18.73, 11.28; UV-Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) \lambda_{\max }(\varepsilon): 266$ (36000), 303 (30000), 311 (30300), 416 (31600), 443 (38400), 655 (br, 6400), 765 (sh, 6000) nm; HRMS (ES+) calcd for $\mathrm{C}_{40} \mathrm{H}_{51} \mathrm{SSi}_{2}(\mathrm{M}+\mathrm{H})^{+}$619.3250, found 619.3243.


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DI1T-TESE

DI1T-TESE. The procedure for DI1T-TIPSE was adapted with (triethylsilyl)acetylene ( $521 \mathrm{mg}, 3.71 \mathrm{mmol}$ ), n-butyllithium ( $3.34 \mathrm{mmol}, 1.6 \mathrm{M}$ ) and $9(214 \mathrm{mg}, 0.74 \mathrm{mmol})$ to provide the title compound ( $147 \mathrm{mg}, 37 \%$ ) as a green solid. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47(\mathrm{~d}, J=$ $7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{td}, J=7.5,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.06(\mathrm{td}, J=7.5,1.1 \mathrm{~Hz}$, $2 \mathrm{H}), 1.14(\mathrm{t}, J=7.9 \mathrm{~Hz}, 18 \mathrm{H}), 0.77(\mathrm{q}, J=7.9 \mathrm{~Hz}, 12 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 153.79$, $148.73,144.01,130.66,130.11,125.80,124.35,120.62,116.17,106.53,99.06,7.63,4.48$; HRMS (ES+) calcd for $\mathrm{C}_{34} \mathrm{H}_{38} \mathrm{SSi}_{2}\left(\mathrm{M}^{+}\right) 534.2233$, found 534.2208.


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2-Benzoyl-3,4-dibromothiophene (10). $\mathrm{AlCl}_{3}(15 \mathrm{~g}, 125 \mathrm{mmol})$ was added in three portions to a stirred solution of 3,4-dibromothiophene ( $10.0 \mathrm{~g}, 41.3 \mathrm{mmol}$ ) and benzoyl chloride $(8.7 \mathrm{~g}, 62 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$. The cooling bath was removed and the reaction was stirred for 16 h . The dark solution was poured onto ice, diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 100 mL ) and washed successively with aqueous $\mathrm{NaOH}(1 \mathrm{M})$ and brine. The organic phases were combined and dried over $\mathrm{MgSO}_{4}$. Removal of volatiles by reduced pressure provided the title compound (13.13 g, 92\%) as a yellow solid. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.88-7.84(\mathrm{~m}, 2 \mathrm{H}), 7.67(\mathrm{~s}, 1 \mathrm{H})$, $7.67-7.63(\mathrm{~m}, 1 \mathrm{H}), 7.52(\mathrm{dd}, \mathrm{J}=8.5,7.1 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 187.38$, 136.87, 136.82, 133.42, 129.86, 128.56, 128.08, 118.19, 116.67; HRMS (ES+) calcd for $\mathrm{C}_{11} \mathrm{H}_{6} \mathrm{SBr}_{2}\left(\mathrm{M}^{+}\right), 343.8506$ found 343.8521 .


Ethyl 6-bromo-3-phenylthieno[3,2-b]thiophene-2-carboxylate (11). To a solution of $\mathbf{1 0}$ $(13.13 \mathrm{~g}, 37.9 \mathrm{mmol})$ in DMF ( 50 mL ) was added $\mathrm{K}_{2} \mathrm{CO}_{3}(15.7 \mathrm{~g}, 113.8 \mathrm{mmol})$ and the reaction was rigorously degassed under dynamic vacuum. With stirring, ethyl thioglycolate ( $4.79 \mathrm{~g}, 39.8$ mmol ) was added dropwise via syringe and then the reaction was heated at $60^{\circ} \mathrm{C}$ for 1 d . After cooling, the mixture was poured into water $(100 \mathrm{~mL})$. The solids were collected and washed with water. Recrystallization from ethanol ( 500 mL ) provided $\mathbf{1 1}(11.2 \mathrm{~g}, 80 \%)$ as tan needles. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.60-7.55(\mathrm{~m}, 2 \mathrm{H}), 7.53-7.45(\mathrm{~m}, 4 \mathrm{H}), 4.30(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.29$ $(\mathrm{t}, J=7.1,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 162.08,141.75,141.14,140.77,133.72,129.21$, $129.05,128.82,128.30,128.17,103.14,61.36,14.08$; HRMS (ES+) calcd for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{~S}_{2} \mathrm{O}_{2} \mathrm{Br}$ $(\mathrm{M}+\mathrm{H})^{+} 366.9462$, found 366.9454 .


Diester 12. In a dry glass pressure vessel, 2-ethoxycarbonylbenzeneboronic acid ( 581 mg , $2.99 \mathrm{mmol}), \mathrm{Pd}_{2} \mathrm{dba}_{3}(25 \mathrm{mg}, 0.027 \mathrm{mmol})$, SPhos ( $22 \mathrm{mg}, 0.054 \mathrm{mmol}$ ), anhydrous $\mathrm{K}_{3} \mathrm{PO}_{4}(1.15$ $\mathrm{g}, 5.44 \mathrm{mmol}), \mathbf{1 1}(1.00 \mathrm{~g}, 2.72 \mathrm{mmol})$ and toluene $(10 \mathrm{~mL})$ were combined. The mixture was sparged with nitrogen ( 10 min ). The vessel was sealed and brought to $100^{\circ} \mathrm{C}$ for 16 h . Upon cooling to rt the reaction was diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ then filtered. The organics were washed with brine and dried over $\mathrm{MgSO}_{4}$. 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 ( $20 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) (v/v) to give a yellow solid. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) $\delta 8.01(\mathrm{dd}, J=7.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.63(\mathrm{~m}, 2 \mathrm{H}), 7.61(\mathrm{dd}, J=7.4,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.57(\mathrm{dd}, J=$ $7.6,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.47(\mathrm{~m}, 4 \mathrm{H}), 7.45(\mathrm{~s}, 1 \mathrm{H}), 4.26(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.18(\mathrm{q}, J=7.1 \mathrm{~Hz}$, $2 \mathrm{H}), 1.25(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}), 1.06(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.58$, $162.35,141.73,141.01,140.94,134.82,134.78,134.28,131.91,131.07,130.61,130.55,129.17$, 128.61, 128.44, 128.21, 127.88, 127.84, 61.23, 61.09, 14.10, 13.71; HRMS (ES+) calcd for $\mathrm{C}_{24} \mathrm{H}_{21} \mathrm{~S}_{2} \mathrm{O}_{4}(\mathrm{M}+\mathrm{H})^{+} 437.0881$, 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 $(0.98 \mathrm{~g}, 2.25 \mathrm{mmol})$ in ethanol ( 100 mL ) was added aqueous $\mathrm{KOH}(12 \mathrm{mmol}, 1.5 \mathrm{M})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ was added DMF ( 5 drops). Oxalyl chloride (1.0
$\mathrm{mL}, 11.2 \mathrm{mmol}$ ) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed in vacuo. $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL})$ was added and the flask was cooled to $0{ }^{\circ} \mathrm{C}$. $\mathrm{AlCl}_{3}(3.0 \mathrm{~g}, 22.3 \mathrm{mmol})$ 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 ( $630 \mathrm{mg}, 79 \%$ ) as a magenta solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }}: 370,490$, 522 (sh) nm; HRMS (EI+) calcd for $\mathrm{C}_{20} \mathrm{H}_{8} \mathrm{O}_{2} \mathrm{~S}_{2}\left(\mathrm{M}^{+}\right) 343.9966$, found 343.9959.


DI2T-TIPSE. To a solution of (triisopropylsilyl)acetylene ( $527 \mathrm{mg}, 2.9 \mathrm{mmol}$ ) in THF (5 mL ) at $0{ }^{\circ} \mathrm{C}$ was added $n$-butyllithium ( $2.6 \mathrm{mmol}, 1.6 \mathrm{M}$ in hexanes) dropwise. In a separate flask, $13(200 \mathrm{mg}, 0.58 \mathrm{mmol})$ was suspended in THF $(25 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$. The (triisopropylsilyl)ethynyllithium solution was transferred to the dione suspension via syringe then sonicated for 10 min . After quenching with a saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution, the organics were extracted with $\mathrm{Et}_{2} \mathrm{O}$ and dried over $\mathrm{MgSO}_{4}$. 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 $\mathrm{SnCl}_{2}(250 \mathrm{mg}, 1.25 \mathrm{mmol})$ was added and the reaction was stirred for 3 h. The mixture was passed through a plug of silica $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ hexanes $)$. Evaporation of the volatiles provided the title compound ( $260 \mathrm{mg}, 66 \%$ ) as a dark blue solid. ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.36(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.28-7.24(\mathrm{~m}, 2 \mathrm{H}), 7.22(\mathrm{dd}, J=7.5,1.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.12(\mathrm{td}, J$ $=7.3,1.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.21(\mathrm{~s}, 42 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 150.07,147.30,146.98$, 139.43, 129.62, 128.82, 125.51, 122.65, 120.76, 114.77, 105.47, 99.95, 18.76, 11.30; UV-Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) \lambda_{\text {max }}(\varepsilon): 267$ (22100), 444 (13100), 477 (11800), 652 (br, 15100) nm; HRMS (ES+) calcd for $\mathrm{C}_{42} \mathrm{H}_{50} \mathrm{~S}_{2} \mathrm{Si}_{2}\left(\mathrm{M}^{+}\right)$674.2893, found 674.2892.


3,5-Dibromodithieno[3,2-b:2',3'-d]thiophene. In a 3-neck flask, tetrabromodithieno[3,2$\left.b: 2^{\prime}, 3^{\prime}-d\right]$ thiophene ${ }^{1}(2.7 \mathrm{~g}, 5.3 \mathrm{mmol})$ in glacial $\mathrm{AcOH}(150 \mathrm{~mL})$ was brought to reflux. Zn powder ( $3.44 \mathrm{~g}, 53 \mathrm{mmol}$ ) 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 ( $450 \mathrm{mg}, 24 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3} / \mathrm{CS}_{2}$ ) $\delta 7.31$ (s); ${ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3} / \mathrm{CS}_{2}$ ) $\delta$ $142.74,130.84,123.16,103.90$. These spectroscopic data correspond to previously reported data. ${ }^{2}$


Diester 14. In a dry glass pressure vessel, 3,5 -dibromodithieno $\left[3,2-b: 2^{\prime}, 3^{\prime}-d\right]$ thiophene (450 $\mathrm{mg}, 1.27 \mathrm{mmol}$ ), 2-ethoxycarbonylbenzeneboronic acid ( $754 \mathrm{mg}, 3.18 \mathrm{mmol}$ ), $\mathrm{Pd}_{2} \mathrm{dba}_{3}(12 \mathrm{mg}$, 0.013 mmol ), SPhos ( $24 \mathrm{mg}, 0.05 \mathrm{mmol}$ ), anhydrous $\mathrm{K}_{3} \mathrm{PO}_{4}(1.0 \mathrm{~g}, 5.1 \mathrm{mmol})$ and toluene ( 15 mL ) were combined and sparged with nitrogen ( 10 min ). The vessel was sealed and brought to $100{ }^{\circ} \mathrm{C}$ for 24 h . Upon cooling to rt the reaction was diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ then filtered. The organics were washed with brine and dried over $\mathrm{MgSO}_{4}$. 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. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.94(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.58-7.54 (m, 4H), 7.50-7.42 (m, 2H), 7.23 $(\mathrm{s}, 2 \mathrm{H}), 4.12(\mathrm{q}, J=7.2 \mathrm{~Hz}, 4 \mathrm{H}), 1.01(\mathrm{t}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 167.76$, $142.24,135.53,135.00,131.73,131.27,130.42,130.40,130.18,128.25,122.45,61.13,13.75$; HRMS (ES+) calcd for $\mathrm{C}_{26} \mathrm{H}_{21} \mathrm{~S}_{3} \mathrm{O}_{4}(\mathrm{M}+\mathrm{H})^{+} 493.0602$, found 493.0601 .


Diindenodithieno[3,2-b:2',3'-d]thiophene-3,13-dione (15). To a solution of 14 ( 0.50 g , $2.25 \mathrm{mmol})$ in ethanol $(100 \mathrm{~mL})$ was added aqueous $\mathrm{KOH}(14.3 \mathrm{mmol}, 1.4 \mathrm{M})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ was added DMF ( 5 drops). Oxalyl chloride ( 0.35 $\mathrm{mL}, 11.2 \mathrm{mmol}$ ) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed in vacuo. $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL})$ was added and the flask was cooled to $0{ }^{\circ} \mathrm{C}$. $\mathrm{AlCl}_{3}(1.0 \mathrm{~g}, 22.3 \mathrm{mmol})$ 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 ( $328 \mathrm{mg}, 81 \%$ ) as a red solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis $\left(\mathrm{CHCl}_{3}\right) \lambda_{\max }: 296,481,514 \mathrm{~nm}$; HRMS (EI+) calcd for $\mathrm{C}_{22} \mathrm{H}_{8} \mathrm{O}_{2} \mathrm{~S}_{3}\left(\mathrm{M}^{+}\right) 399.9686$, found 399.9700 .


DI3T-TIPSE. To a solution of (triisopropylsilyl)acetylene ( $227 \mathrm{mg}, 1.25 \mathrm{mmol}$ ) in THF (5 mL ) at $0{ }^{\circ} \mathrm{C}$ was added $n$-butyllithium ( $1.12 \mathrm{mmol}, 1.5 \mathrm{M}$ in hexanes) dropwise. In a separate flask, 15 ( $100 \mathrm{mg}, 0.25 \mathrm{mmol}$ ) was suspended in THF ( 25 mL ) and cooled to $0{ }^{\circ} \mathrm{C}$. The (triisopropylsilyl)ethynyllithium solution was transferred to the dione suspension via syringe then sonicated for 10 min . After quenching with a saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution, the organics were extracted with $\mathrm{Et}_{2} \mathrm{O}$ and dried over $\mathrm{MgSO}_{4}$. 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 $\mathrm{SnCl}_{2}(250 \mathrm{mg}, 1.25 \mathrm{mmol})$ was added and the reaction was stirred for 10
min. The mixture was passed through a plug of silica $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ hexanes $)$. Evaporation of the volatiles provided the title compound ( $131 \mathrm{mg}, 72 \%$ ) as a deep purple solid. ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.31(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.25(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.07(\mathrm{t}, J=$ $7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.21(\mathrm{~s}, 42 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 148.91,146.56,143.92,142.96$, $138.51,129.20,128.52,125.08,122.04,120.72,113.17,105.36,100.45,18.78,11.34$; UV-Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) \lambda_{\max }(\varepsilon): 256$ (32300), 320 (8000), 513 (27600), 553 (39400), 683 (19600), 740 (sh, $16600) \mathrm{nm} ;$ HRMS (ES+) calcd for $\mathrm{C}_{44} \mathrm{H}_{51} \mathrm{~S}_{3} \mathrm{Si}_{2}(\mathrm{M}+\mathrm{H})^{+} 731.2691$, 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 Apex 2 CCD diffractometer with a micro-focus $I \mu S$ source using $\mathrm{CuK} \alpha$ radiation $\lambda=1.54178 \AA$ or a sealed X-ray tube with a triumph monochromator, $\mathrm{MoK} \alpha$ radiation $\lambda=0.71073 \AA$ ( 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 $-i-\mathrm{Pr}$ 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 $I \mu S \mathrm{Cu}$ source we could collected data only up to $2 \theta_{\max }=114.98^{\circ}, 120.0^{\circ}$ and $132.0^{\circ}$, 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and anhydrous $\mathrm{Bu}_{4} \mathrm{NBF}_{4}$, 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 ( $\mathrm{Fc} / \mathrm{Fc}^{+}$) 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 $\mathrm{Fc} / \mathrm{Fc}^{+}$couple in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. When necessary, potentials were re-referenced to NHE using SCE $=-0.24$ (V vs. NHE). LUMO and HOMO levels were approximated using SCE $=-4.68 \mathrm{eV}$ vs. vacuum. ${ }^{5}$ Cyclic voltammetry experiments were conducted at sweep rates of 50 (reported), 75,100 and $125 \mathrm{mV} \mathrm{s}^{-1}$. All scan rates show quasi-reversible kinetics with no alteration of peak splitting with scan rate. $\mathrm{E}_{1 / 2}$ values were calculated assuming $\mathrm{E}_{1 / 2} \approx \mathrm{E}^{0}=\left(\mathrm{E}_{\text {anodic }}\right.$ $\left.+\mathrm{E}_{\text {cathodic }}\right) / 2$ based on these observations for reversible couples; for irreversible couples the $\mathrm{E}^{0}$ value is estimated as the potential at peak current. The $\mathrm{E}_{\mathrm{a}, \mathrm{c}}$ peak splitting of the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple was similar to that of the analyte ( $\sim 100 \mathrm{mV}$ ). The anodic peak current increases linearly with the square root of the scan rate in the range 50 to $125 \mathrm{mV} \mathrm{s}^{-1}$, 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 $100^{\circ} \mathrm{C}$ 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 $\mathrm{DI}[\mathrm{n}] \mathrm{T}$ 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 EasySpin ${ }^{6}$ package utilizing MATLAB code. ${ }^{7}$ DFT calculations were performed for the gas phase molecules using Gaussian09 Revision C. $01^{8}$ 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 ${ }^{-}$.


Table S1 Hyperfine Coupling Constants and
Carbon spin densities ( $\rho_{\mathrm{c}}$ ).

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

$\qquad$

Fig. S9 EPR spectrum of DI3T ${ }^{-}$.

## 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 <br> 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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=
0.444806 (Hartree/Particle)
0.478102
0.479046
0.375054
-2058.828161
-2058.794866

NIMAG $=0$

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| :--- | :--- | :--- | :--- |
| 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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies=
0.442213 (Hartree/Particle)
0.475713
0.476657
0.372411
-2058.797119

Sum of electronic and thermal Free Energies=
-2058.763620

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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=
0.463062 (Hartree/Particle)
0.498623
0.499567
0.389852
-2533.040684
-2533.005123

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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= 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 |

相
0.459072 (Hartree/Particle)
0.494818
0.495763
0.385295
-2533.175198
-2533.139451
-2533.138507
-2533.248975

| 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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= 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 |

0.456790 (Hartree/Particle)
0.492717
0.493661
0.383872
-2533.159282
-2533.123355
-2533.122411
-2533.232201

| 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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=
0.476970 (Hartree/Particle)
0.515018
0.515962
0.400435
-3007.373585
-3007.335538
-3007.334594

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= Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= 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 |
|  |  |  |  |

0.473045 (Hartree/Particle)
0.511285
0.512229
0.396153
-3007.518003
-3007.479764
-3007.478820
-3007.594896

| 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=
Thermal correction to Energy=
Thermal correction to Enthalpy=
Thermal correction to Gibbs Free Energy=
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= 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 |
|  |  |  |  |

0.471050 (Hartree/Particle)
0.509493
0.510437
0.394727
-3007.516246
-3007.477803
-3007.476858
-3007.592569

| 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 ( $\AA$ ) 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, $\mathrm{R}=$ TMSE.

Table S3 Bond distances ( $\AA$ ) 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.


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

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##  <br>  <br> DI1T-TIPSE






## 





## GER-2-171-2_H





GER-2-171-2_C



## GER-2-089-3_H



11



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|  |  | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 30 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 |  | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | ( |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |



$12$



12


| ; |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 148 | 146 | 144 | 142 | 140 | 138 | 136 | 134 | 132 | 130 | 128 | 126 | 124 | 122 | 12 |
|  |  |  |  |  |  |  |  | m) |  |  |  |  |  |  |  |





##  <br> DI2T-TIPSE <br> 




## GER-2-119-3_C $\underset{\sim}{\text { Non }}$ <br> $n$ $\cdots$ $\vdots$ $i$ <br>  <br> 14 <br> 



$M$




## 




